SINGLE ELECTRON TRANSFER REACTIONS AND THE SYNTHESIS OF CHIRAL BODIPYs

by

Reinner Ishaq Lerrick

A thesis submitted in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

May 2014

Declaration

I hereby declare that this thesis is written based on my own work. Any results or data from another person within Dr Michael J. Hall's group who contributed to this thesis have been stated clearly.

Acknowledgements

I would first like thank to my supervisor Dr Michael J. Hall for his outstanding supervision during the Ph.D project completion till the thesis write up.

I would also like to thank Dr Corrine Wills and Dr Ross Harrington for their assistance in NMR spectroscopy and X-ray crystallography analysis respectively.

I would like to thank Indonesian Ministry of National Education for the funding over Ph.D scholarship program.

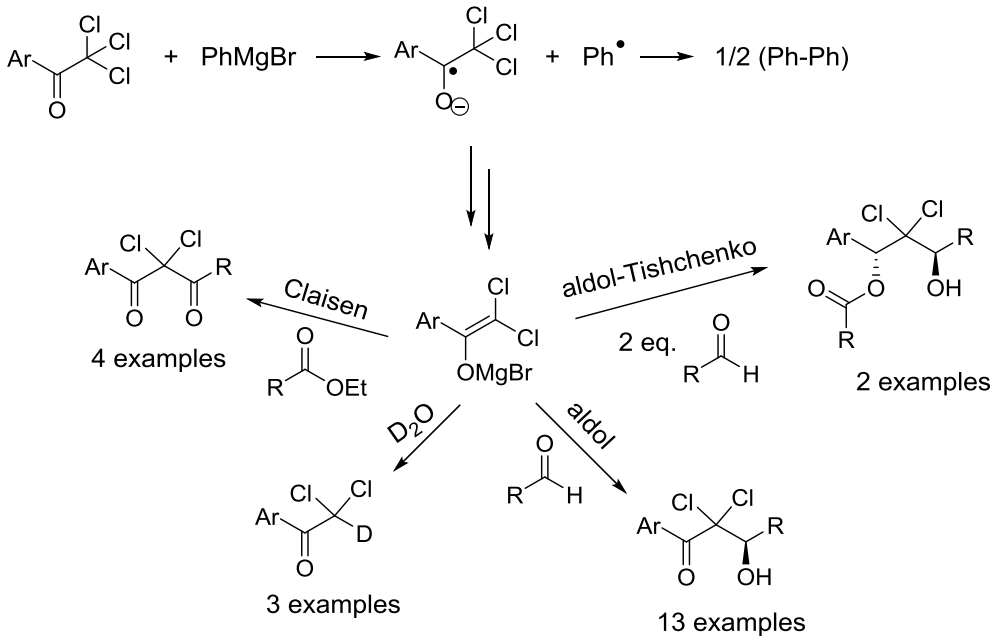
Finally I would like to thank my family especially my wife and son for their love, pray and support.

Abstract

This thesis is divided into two parts. Part one covers single electron transfer reactions of electron deficient carbonyls and Grignard reagents whilst part two discusses our progress towards the synthesis of axially chiral BODIPYs.

Part 1:

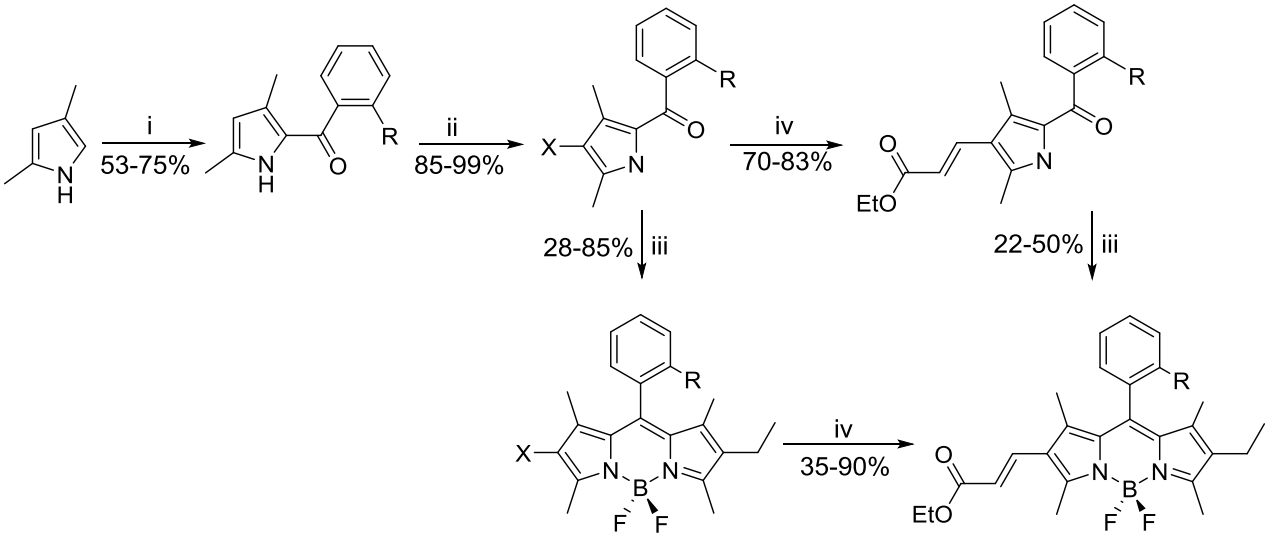
Reaction of 2,2,2-trichloro-1-arylethanones with PhMgBr resulted in a reduction to give 2,2-dichloro-1-arylethanones. We have shown through by-product analysis and EPR measurement that this reaction proceeds through a Single Electron Transfer (SET) mechanism with PhMgBr acting as the electron donor. Addition of electrophiles to the intermediate magnesium enolates, formed in the reaction, gave aldol, Claisen and aldol/Tishchenko products.



Scheme 1 Reaction of PhMgBr with 2,2,2-trichloro-1-arylethanones followed by addition of an electrophile

Part 2:

A number of BODIPYs have been synthesised which demonstrated axial chirality, based on the restricted rotation of *ortho*-aryl *meso* substituents

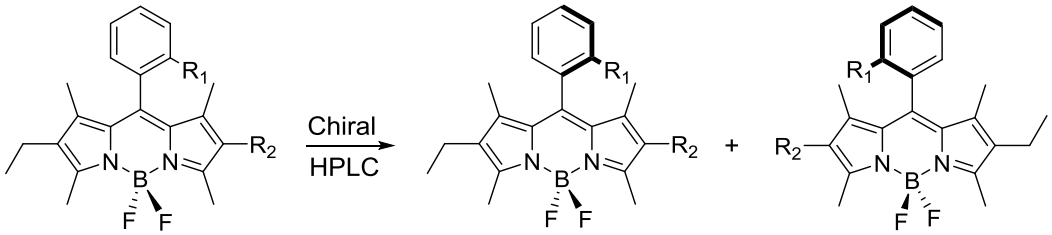


R = OMe, OAc
X = Br, I

i) *o*-substituted benzoylchloride, EtMgBr, THF, r.t., 24 h; ii) X_2, $EtNH_2$, DCM, r.t., 24 h; iii) (a) 3-ethyl-2,4-dimethyl-1*H*-pyrrole, TFA, DCM, r.t., 24 h (b) $^{i}PrNEt_2$, $BF_3.OEt_2$, DCM, 0 ^{o}C, 3 h ; iv) Ethylacrylate, $Pd(OAc)_2$ (cat.), PPh_3, DMF, Et_3N, 100 ^{o}C, 24 h

Scheme 2 General route for the synthesis of axially chiral BODIPYs

Resolution of a racemic axially chiral BODIPY was performed by preparative chiral HPLC.



Scheme 3 Resolution of racemic-BODIPYs using HPLC

Electronic Circular Dichroism (ECD) spectroscopy and α_D^{20} measurements showed that the separated BODIPYs were enantiomeric. Comparison of measured and computational ECD spectra allowed assignment of the absolute stereochemistry.

Publications from this work

Chapter 2

Reduction of 2,2,2-trichloro-1-arylethanones by RMgX: mechanistic investigation and the synthesis of substituted α,α-dichloroketones; Ali H. Essa, **Reinner I. Lerrick**, Floriana Tuna, Ross W. Harrington, William Clegg, Michael J., Hall, *Chem. Commun*. **2013**, *49*, 2756-2758 (Appendix 1)

Chapter 6

Axially Chiral BODIPYs; **Reinner I. Lerrick**, Thomas P. L. Winstanley, Karen Haggerty, Corinne Wills, William Clegg, Ross W. Harrington, Patrick Bultinck, Wouter Herrebout, Andrew C. Bennistona and Michael J. Hall, *Chem. Commun*. **2014** (accepted) (Appendix 2)

List of Abbreviations

Å	Angstrom
Ac_2O	Acetic acid anhydride
$AlCl_3$	Aluminium(III)chloride
Cat.	Catalitic amount
$CHCl_3$	Chloroform
CuI	Copper(I)iodide
^{11}B	Boron-11
BBr_3	Boron tribromide
BCl_2	Boron dichloride
BCl_3	Boron trichloride
$BF_3.OEt_2$	Boron trifluoride etherated
BINOL	1,1'-Bi-2-naphthol
BOC	Di-*t*-butyl dicarbonate
$B(OMe)_3$	Boron trimethoxy
Br_2	Bromine
^oC	Centigrade
d	Day(s)
DCC	*N*,*N*'-Dicyclohexylcarbodiimide
DCM	Dichloromethane
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DMAP	4-Dimethylaminopyridine
DMF	Dimethyl fomamide
dq	Doublet quartet
E^+	Electrophile(s)
EDCI	1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide
EPR	Electron Paramagnetic Resonance
EtMgBr	Ethylmagnesium bromide
Et_2O	Ether
eq.	Equivalent
^{19}F	Fluorine-19
^1H	Proton
h	Hour
HBr	Bromide acid
$h\nu$	Photon

HOAc	Acetic acid
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometer
Hz	Hertz
I	Iodo
I_2	Diiodo
I_3^+	Triiodo cation
IPA	Isopropylamine
$^iPr_2NEt$	Diisopropyl ethylamine (Hünig Base)
^{i}PrOH	Isopropyl alcohol
IR	Infra-red
J	Coupling constant
K	Kelvin degree
KOMe	Potassium methoxide
M	Molar
MeI	Methyl iodide
MeMgBr	Methylmagnesium bromide
m.p.	Melting point
Min	Minute(s)
Na_2CO_3	Sodium carbonate
NaHDMS	Sodium hexamethyldisilazide
NaOH	Sodium hydroxide
NaOMe	Sodium methoxide
NBS	*N*-bromo succinimide
NCS	*N*-chloro succinimide
NH_4OAc	Ammonium acetate
NIS	*N*-Iodo succinimide
nm	Nanometer
NMR	Nuclear Magnetic Resonance
OAc	Acethoxy
OMe	Methoxy
OR	Alkoxy
PEA	1-Phenylethylamine
rac.	Racemic
Rf	Retention factor
TCAC	Trichloro acetylchloride

TD-DFT	Time-Dependent Density Functional Theory
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
UV	Ultra-violet

Table of Contents

Chapter 1 Introduction

1.1 Single Electron Transfer (SET) Reactions

1.1.1 Introduction

Single electron transfer (SET) reactions are processes including the transfer of an electron from a donor to acceptor, forming reactive neutral or anionic radical species. These intermediates then undergo further reactions such as transfer of a second electron, radical coupling, rearrangements etc.. Electron donors which facilitate SET reactions are commonly alkali and alkali earth metals or transition metals such as iron, cobalt, copper, titanium, indium and samarium. Meanwhile, the acceptor is usually alkyl or aryl halides or π-conjugated organic molecules.[1]

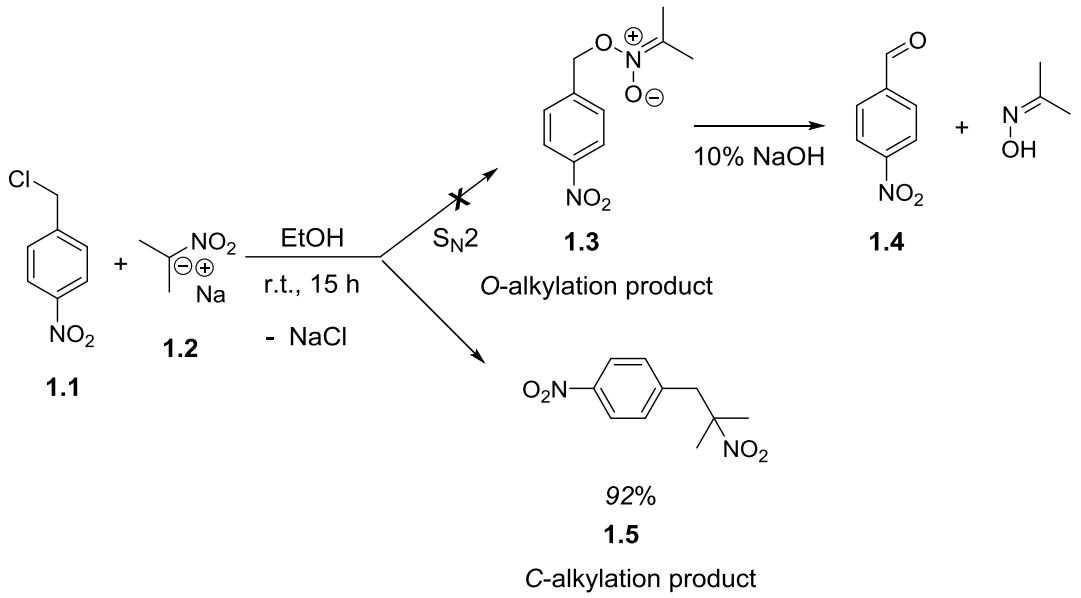
SET processes are found in many reactions in nature, for example in photosynthesis. In photosynthesis, the magnesium protein complex in chlorophyll harvests sunlight energy to initiate single electron transfer through metal reduction-oxidation processes. This is then followed by electron transfer to the protein reaction centre where the electrons are used to power the synthesis of primary metabolites. Other metal protein complexes such as cytochromes[2-5], ferredoxins[6] and rubredoxin[7] proteins are important in human metabolism by producing energy through SET processes.

Exploitation of electron transfer phenomena is also very important in allowing the development of modern semiconductors[8], polymers[9] and solar energy conversion.[10]

1.1.2 SET in Organic Chemistry

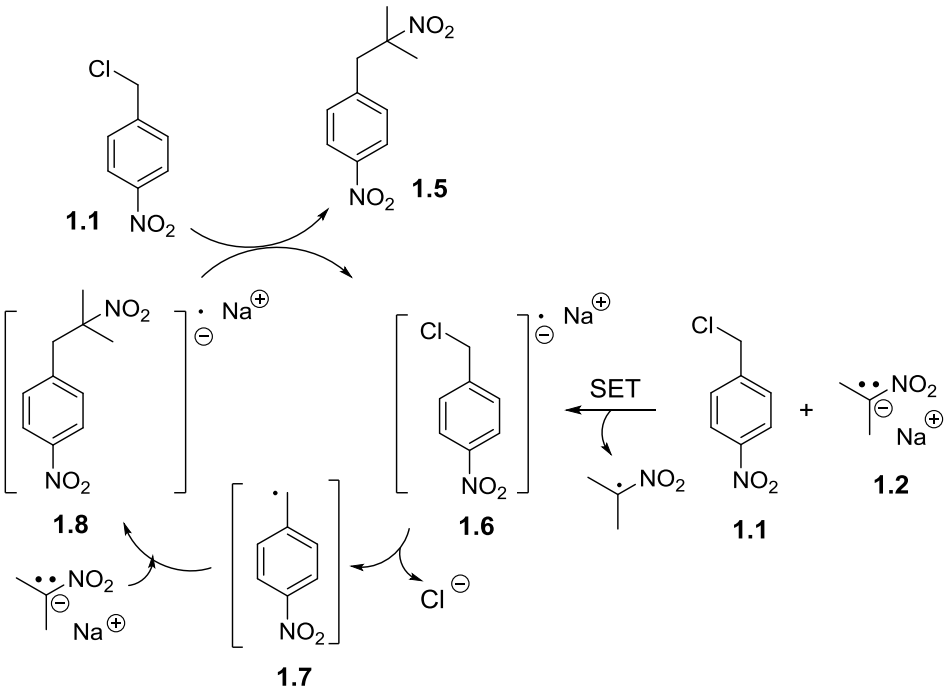
1.1.2.1 Unimolecular radical nucleophilic substitution ($S_{RN}1$) reactions

Early indications of SET in chemical reactions was observed by Hass in the oxidation of benzyl halides using 2-nitropropane salts.[11-12] Oxidation of benzyl halides to benzaldehydes was possible (through an S_N2 pathway) except in the case of 1-(chloromethyl)-4-nitrobenzene **1.1**. Reaction of **1.1** with the sodium salt of 2-nitropropane only resulted in C-alkylation to give **1.5** (Scheme 1.1).



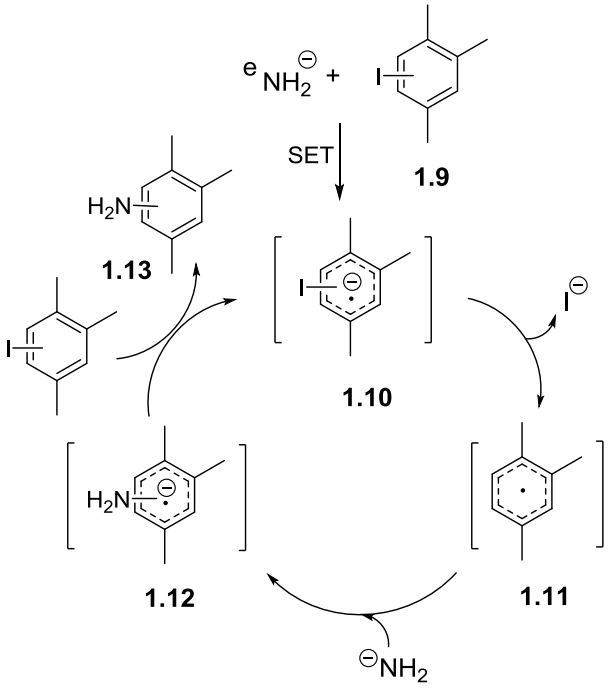
Scheme 1.1 Reaction of 4-nitrobenzyl chloride with 2-nitropropane sodium

Based on this result, a reaction mechanism was suggested by Kornblum and Russel[13], in which they proposed that the reaction of **1.1** with sodium 2-nitropropane involves radical intermediates. The reaction is initiated by the formation of a 1-(chloromethyl)-4-nitrobenze radical anion **1.6** through a SET process. Loss of chloride gives **1.7**, which reacts with further sodium 2-nitropropane to form **1.8**. This radical anion then donates one electron to a further molecule of 1-(chloromethyl)-4-nitrobenze **1.1** to give the product **1.5** (Scheme 1.2).



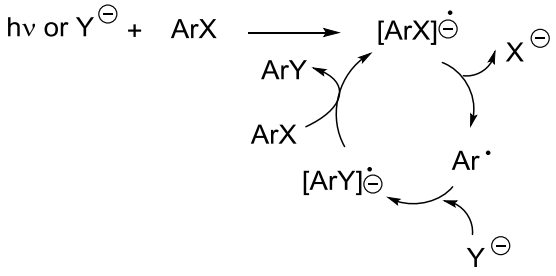
Scheme 1.2 C-alkylation of **1.1** to **1.5** via a proposed SET mechanism

In another experiment by Bunnett and Kim, evidence was seen for a SET mechanism in nucleophilic aromatic substitution reactions (S_NAr).[14-15] In the reaction of 5- and 6-iodo-1,2,4-trimethylbenzene (Scheme 1.3) with KHN_2 in liquid ammonia, Bunnet suggested that 5- and 6-iodo-1,2,4-trimethylbenzene **1.9** underwent a SET mediated S_NAr reaction leading to the product **1.13**.



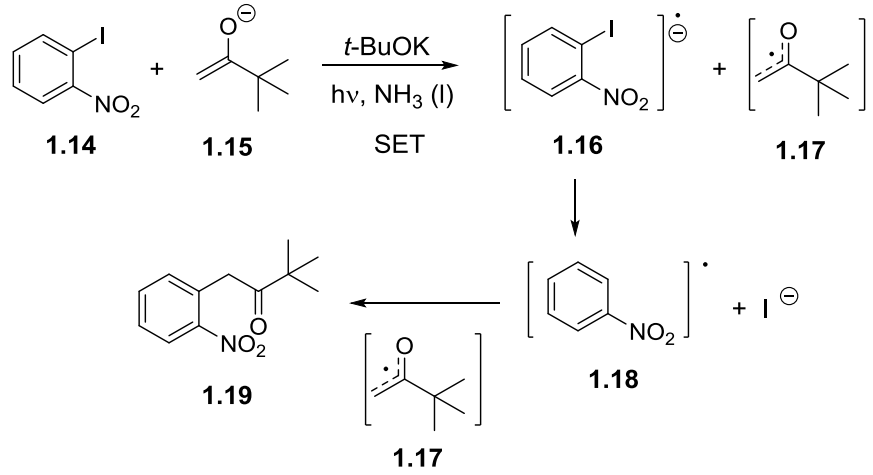
Scheme 1.3 Nucleophilic aromatic substitution of **1.9** *via* SET mechanism

Reactions such as those shown in Scheme 1.2 and Scheme 1.3 are called chain unimolecular radical nucleophilic substitution reactions ($S_{RN}1$), in which the reactive intermediate at the end of the reaction reacts with further starting material to continue the chain. The $S_{RN}1$ reaction involves SET initiated substrate radical anion formation, carbon-halogen bond fragmentation (propagation) and SET termination reaction steps (Scheme 1.4). This class of reaction mechanism has been shown in aromatic[16] and aliphatic halides.[17]



Scheme 1.4 $S_{RN}1$ chain reaction

Non-chain SET $S_{RN}1$ reactions were proposed by Galli in 1988, based on the light mediated reaction of 2-iodonitrobenzene **1.14** with pinacolone enolate in liquid ammonia (Scheme 1.5). The reaction was not quenched by the addition of free radical scavenger di-*t*-butylnitroxide (Table 1.1 entry 2 and 3) in contrary to what usually happens in chain $S_{RN}1$ reactions. Therefore Galli stated that the light mediated reaction of **1.14** is not a chain process $S_{RN}1$.[18]



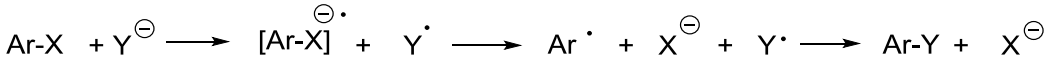
Scheme 1.5 $S_{RN}1$ reaction of **1.14**

Table 1.1 Reaction condition of synthesis **1.19**

Entry	Time (min)	Conditions	Yield (%)[a]	
			$PhNO_2$	**1.19**
1	1.5	hν	18	61
2	1.5	hν, 12% inhibitor[c]	nd[b]	39
3	1.5	hν, 33% inhibitor[c]	16	32

[a] determined by GLC, [b] not detected, [c] di-*t*-butylnitroxide

The non-chain $S_{RN}1$ reaction mechanism is shown in Scheme 1.6. The reaction starts by one electron transfer from an electron rich species (Y^-) to the substrate (ArX) yielding anionic radical $[Ar\text{-}X]^{-\bullet}$. Elimination of a halide ion produces radical Ar which can react with another radical to generate the product.

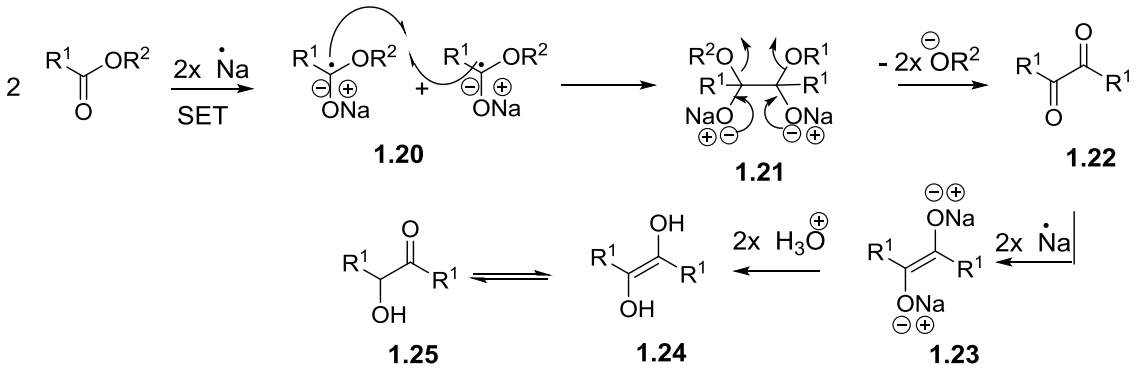


Scheme 1.6 Non-chain SET $S_{RN}1$ reaction mechanism

1.1.2.2 Na/K/Li mediated SET reactions

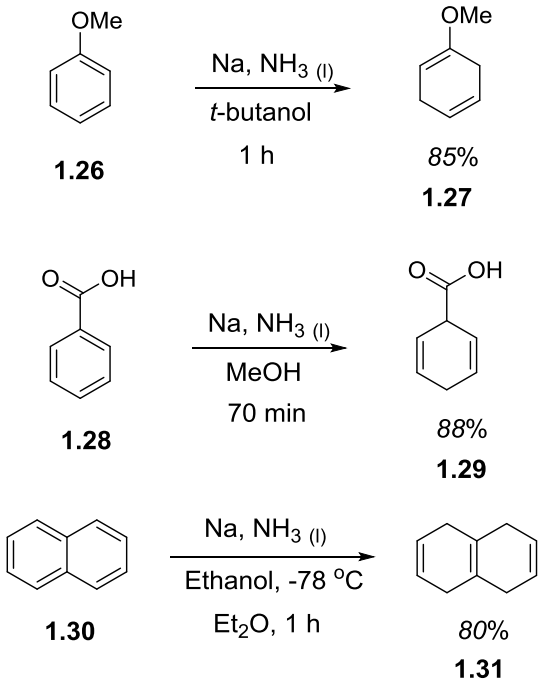
Other reactions are also known which involve single electron transfer steps. These include reactions involving alkali metals such as the acyloin condensation and the Birch reduction.[19]

The acyloin condensation has been proposed to occur *via* a SET reaction pathway, from the reaction between 2 equivalents of a ketone with 2 equivalents of sodium metal.[20-25] SET from Na to a ketone gives a radical anion **1.20**. Dimerization of 2 equivalents of **1.20** results in the formation of a 1,2-diol which then undergoes further sodium reduction to form acyloin products.



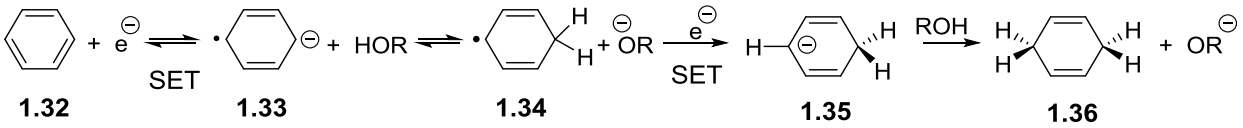
Scheme 1.7 Acyloin reaction mechanism

In 1944, Arthur J. Birch published his work on the reduction of substituted benzenes using sodium metal in liquid ammonia to give the corresponding unconjugated cyclohexadienes.[26] Many aromatic, heteroaromatic, alkene and alkyne contain molecules have since been reduced using sodium, lithium or potassium metal in alcoholic liquid ammonia.[27-32]



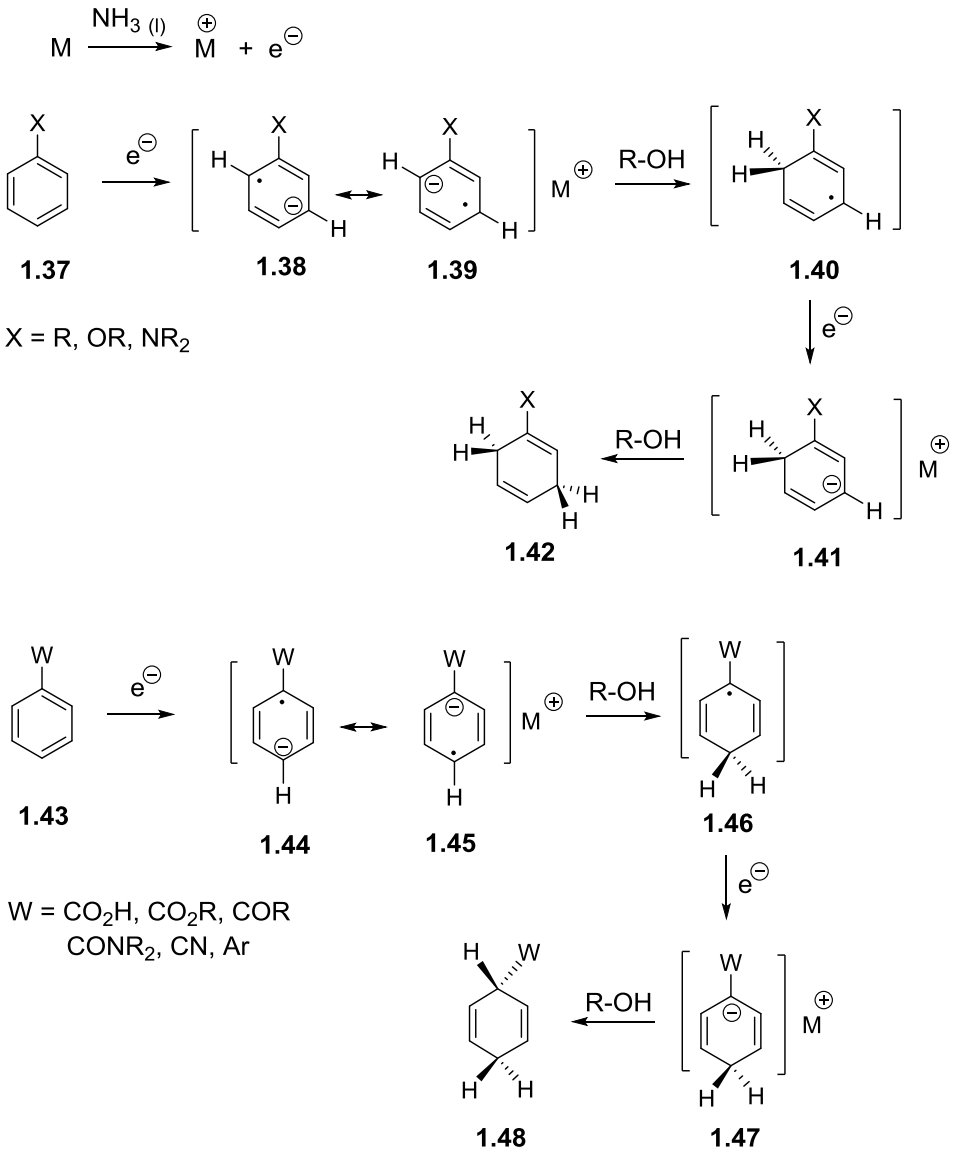
Scheme 1.8 The Birch reduction of anisole, benzoic acid and naphthalene

The Birch reduction is thought to occur *via* the initial formation of solvated electrons, when sodium or lithium metal is dissolved in liquid ammonia. Aromatic substrates then undergo a SET reaction where one electron is added to the ring to form a radical anion. The radical anion intermediate is then protonated by the alcohol, becoming a radical. This radical then readily undergoes the second SET reaction and further protonation leading to the reduced product (Scheme 1.9).[33]



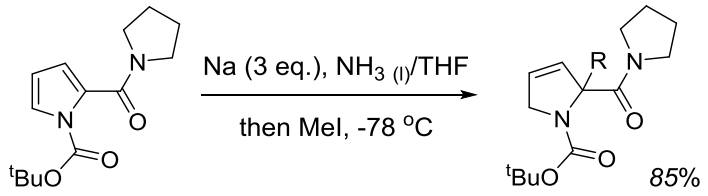
Scheme 1.9 General mechanism of Birch reaction

The Birch reduction is regioselective. Aromatic compounds containing electron donor groups are reduced at *ortho* and *meta* positions. Whilst the electron withdrawing group will direct the reduction to *ipso* and *para* position (Scheme 1.10).[34-39]



Scheme 1.10 Birch reduction of substituted aromatic compounds

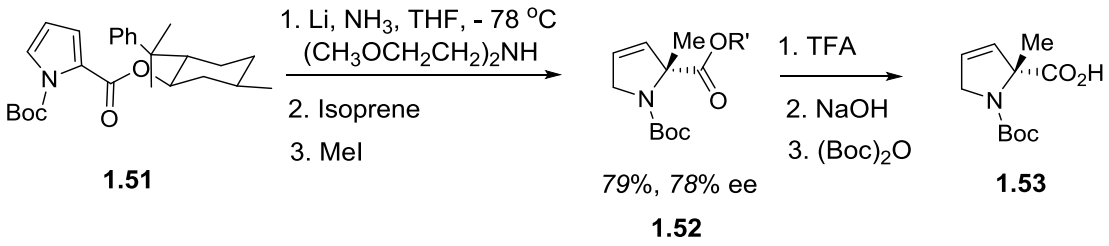
Reduction of electron rich heteroaromatic compounds such as pyrrole, furan and thiophene using Birch conditions only occurs if at least one electron withdrawing group is present, as these heterocyclic compounds are too electron rich to accept an electron and so be reduced.[40] Donohoe has shown that introduction of an electron withdrawing group onto the N of a pyrrole ring, allowed reduction of pyrrole followed by trapping of the intermediate anion with electrophiles to give the corresponding 3-pyrroline **1.50** (Scheme 1.11).[41]



1.49 **1.50**

Scheme 1.11 Birch reduction of *N*-Boc substituted pyrrole

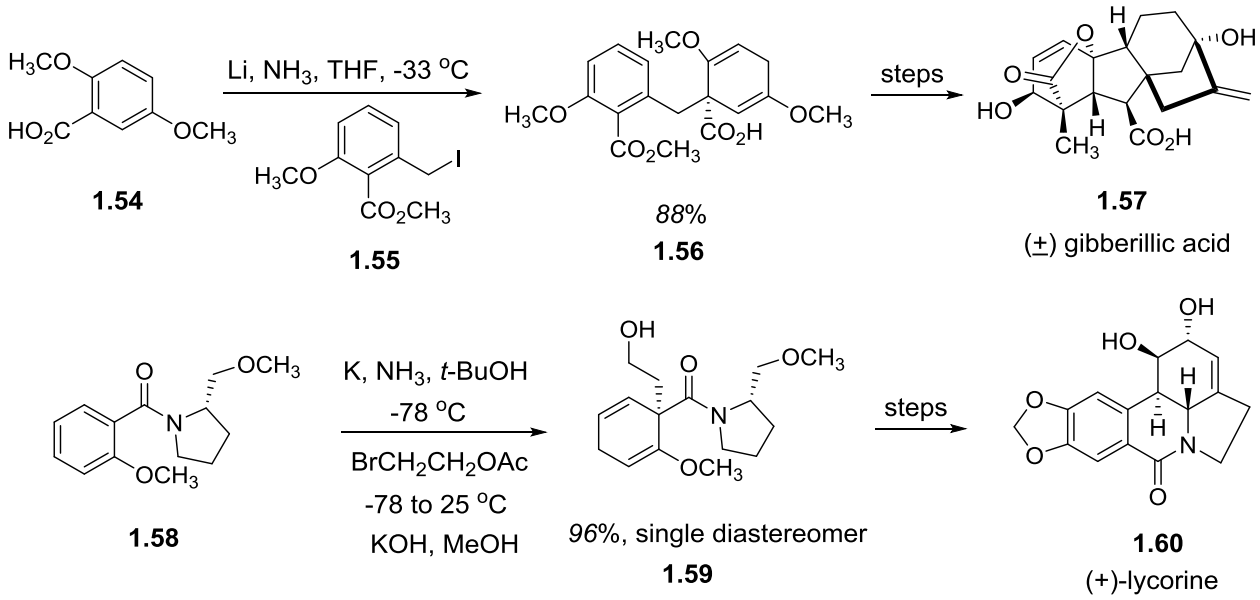
Many electron rich heteroaromatic compounds such as thiophene, furan and indole have been successfully reduced under SET condition through the introduction of an electron withdrawing group as a chiral auxiliary, before submission to Birch conditions.[42-43] A recent example of an enantioselective pyrroline synthesis under Birch conditions has been demonstrated by Halliwell, in which the intermediate anion trapped an electrophile to give chiral pyrolines such as **1.52**.[44]



1.51 **1.52** **1.53**

Scheme 1.12 Chiral auxillary directed Birch reduction of pyrrole **1.51**

Moreover, the Birch reaction has also been used widely in natural product synthesis, including examples such as the synthesis of racemic Gibberellic acid and (+)-Lycorine.[45-46]

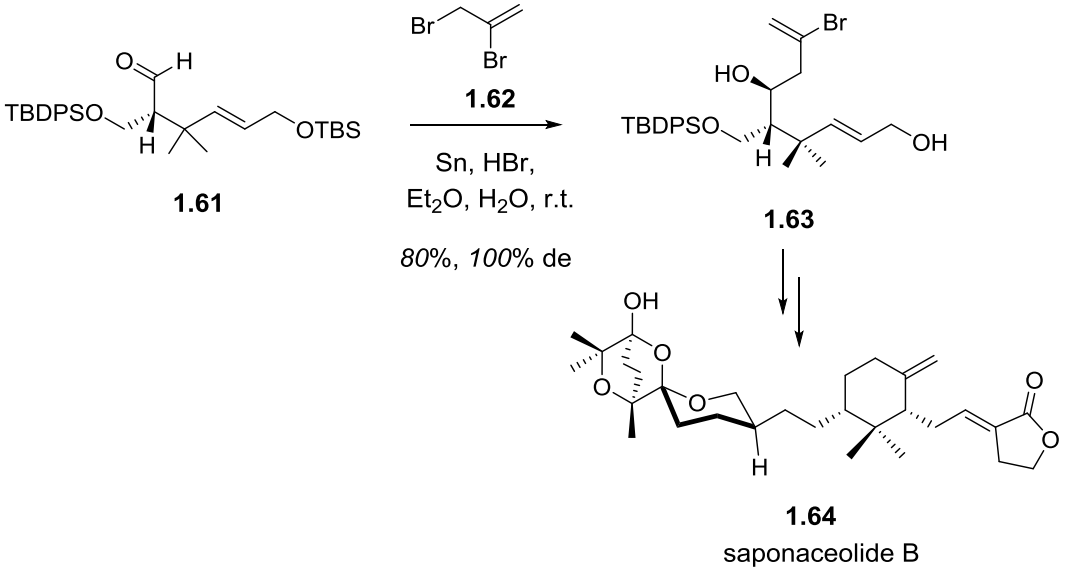


Scheme 1.13 Synthesis of gibberillic acid and (+)-lycorine via Birch reductions

1.1.2.3 Organomagnesium SET reactions

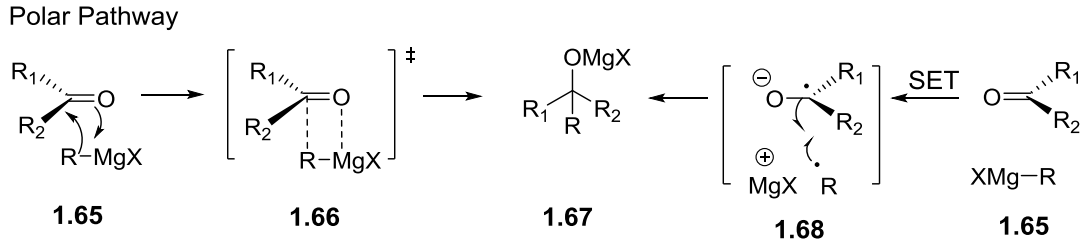
Barbier (1899) in his effort to convert a carbonyl to the corresponding substituted alcohol generated organomagnesium halides in the presence of a ketone.[47] The organomagenesium halides were later successfully isolated by Grignard leading to the development of Grignard reactions.

Several alternative metals such as Al, Zn, Sn, In and Zn have been used under Barbier conditions.[48-49] Barbier reactions have been used in the synthesis of natural products such as the indole alkaloids[50-52] or the synthesis of saponaceolide (Scheme 1.14).[53]



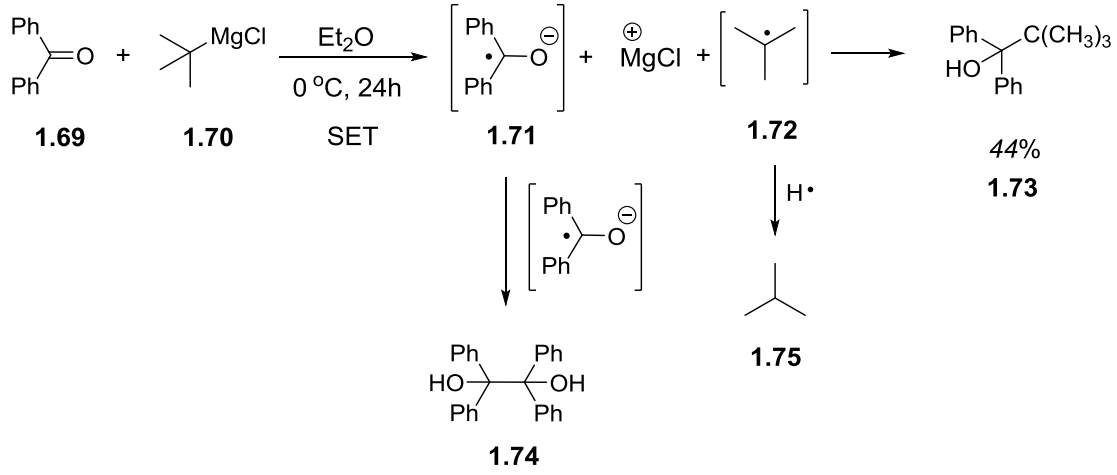
Scheme 1.14 Sn mediated Barbier reaction in the synthesis of saponacelide B

Organomagnesium reagents (RMgX) have become important reagents in organic synthesis mainly through their use in selective C-C bond formation through addition reactions to carbonyls. Grignard reactions can occur via two limiting mechanisms, either polar (2 electron) or stepwise single electron transfer (Scheme 1.15).



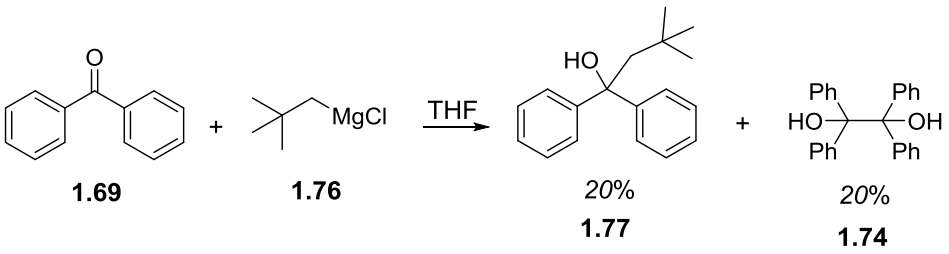
Scheme 1.15 SET vs two electron mechanism

A SET mechanism for Grignard reaction was initially postulated by Blicke and Powers after observing the reaction of benzophenone with series of alkylmagnesium halides.[54-55] They suggested that the formation of **1.74** occurs via a radical-radical coupling mechanism instead of a nucleophilic addition to benzophenone. A SET mechanism was postulated in order to account for the formation of the observed by-products benzopinacol **1.74** and *t*-butane **1.75** (Scheme 1.16).



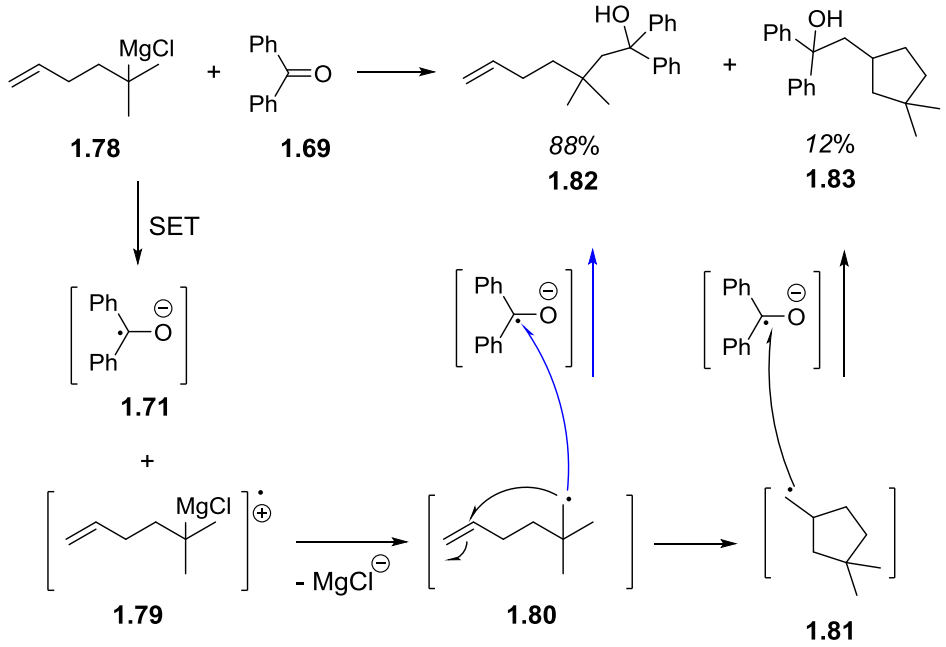
Scheme 1.16 SET reaction of benzophenone and *iso*-propyl magnesium chloride

Benzopinacol **1.74** was observed in Grignard reactions by Gilman[56], Bachmann[57] and Arbuzov[58] while reacting the benzophenone with Grignard reagents. Blomberg undertook EPR experiments that showed that reaction of neopentylmagnesium chloride with benzophenone goes via a radical mechanism giving the corresponding alcohol **1.77** and benzopinacol **1.74**.[59]



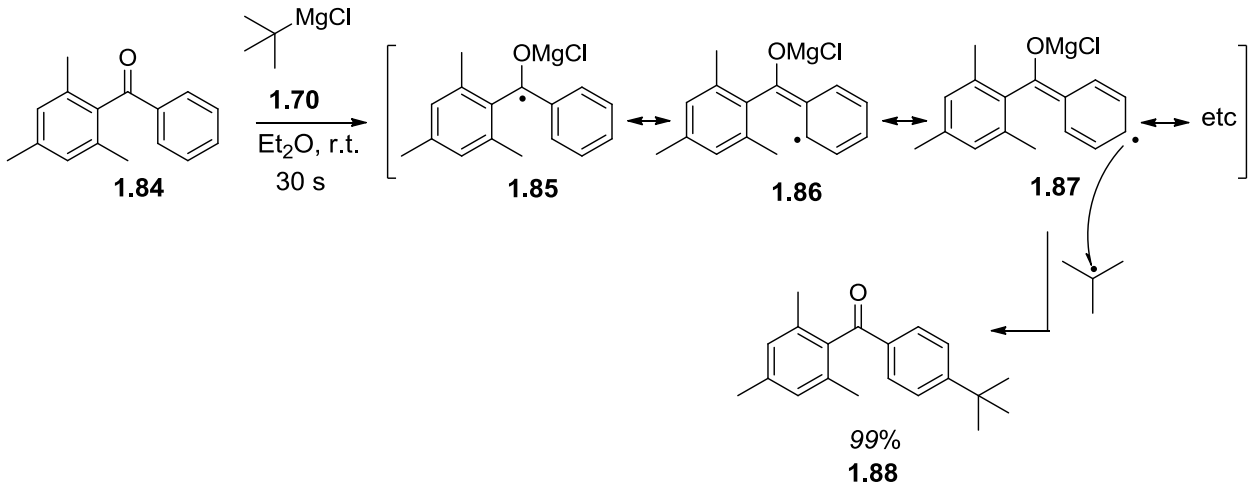
Scheme 1.17 SET reaction of neopentylmagnesium chloride with benzophenone

Further investigation of Grignard SET mechanisms was done by Ashaby.[60-61] Using Grignard derivative **1.78** in a reaction with benzophenone, Ashaby observed the formation of **1.83** which must be derived *via* a radical 5-exo-trig cyclisation to give **1.81**, followed by radical-radical coupling (Scheme 1.18).[62]



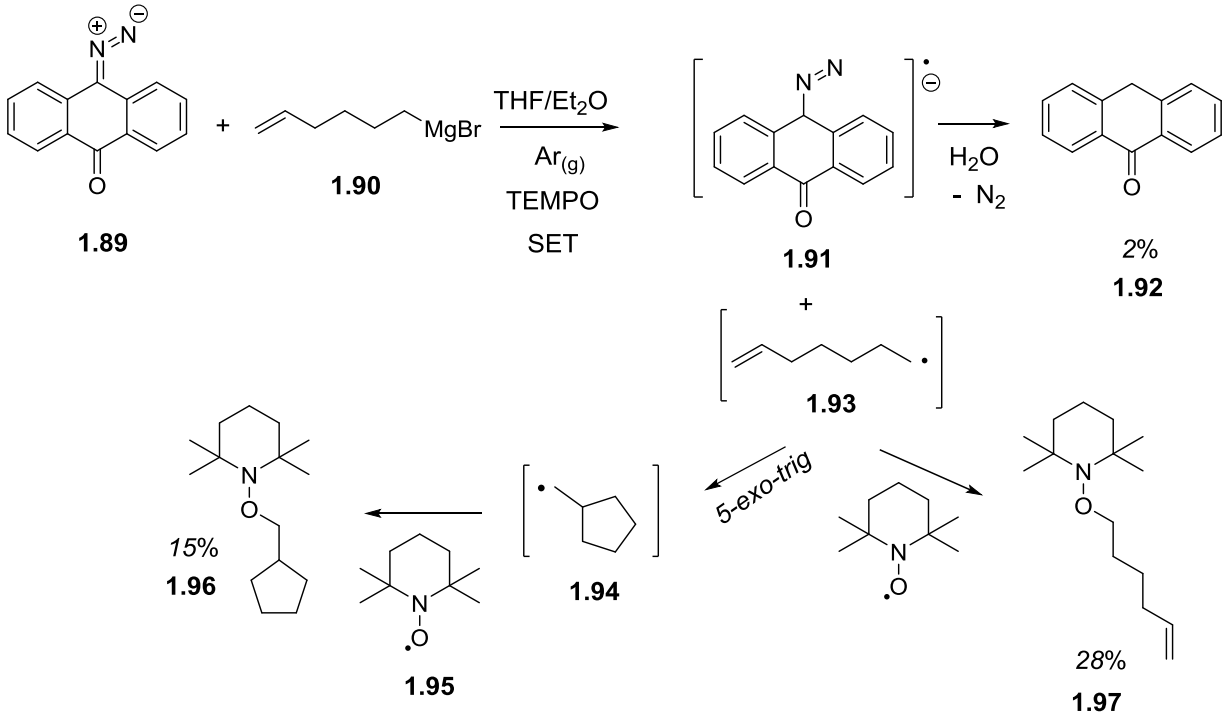
Scheme 1.18 Trapping intermediate radicals in Grignard reactions

In 1985, Zhang together with Ashaby gained further evidence for a Grignard SET mechanism by EPR. In that experiment they reacted a substituted benzophenone **1.84** with methyl, phenyl and *t*-butyl Grignard reagents. The ketyl radical could be detected in high concentration, especially in the reaction of ketones with bulky Grignard reagents (Scheme 1.19).[63]



Scheme 1.19 SET reaction of *t*-butyl magnesium chloride with substituted benzophenone **1.84**

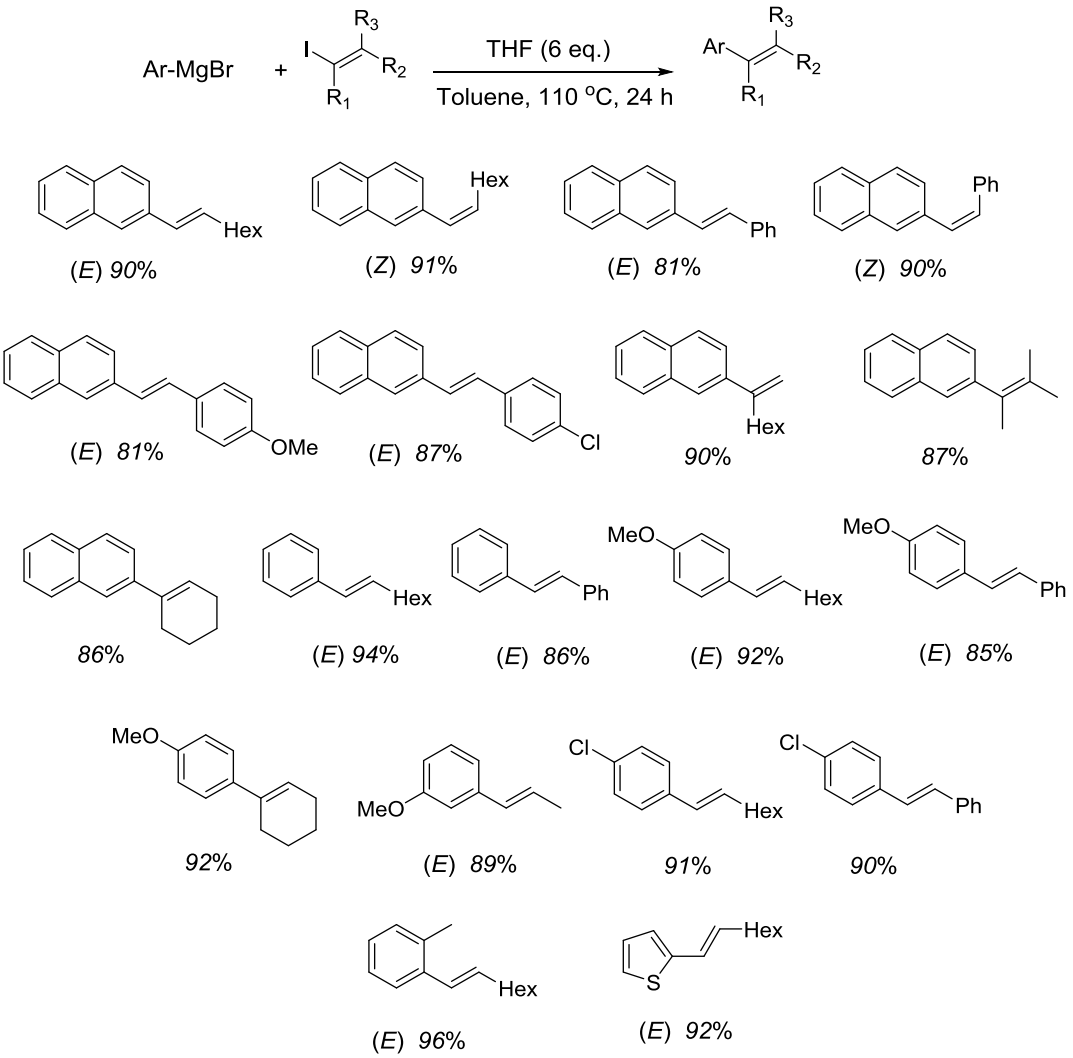
In order to show SET processes in the Grignard reaction, radical traps have been used such as alkenes[64], ketones[65] and 5,5-dimethyl-1-pyrroline *N*-oxide (DEMPO).[66-71] Bruni examined radical trapping in the reaction of 1-hexenyl magnesium bromide with azo-aromatic **1.89**. At the end of the reaction, two radical trapping products **1.96** and **1.97** were isolated in a 1 : 2 ratio.[72]



Scheme 1.20 TEMPO trapping of the SET reaction of arylazo **1.89** and 1-hexenyl magnesium bromide

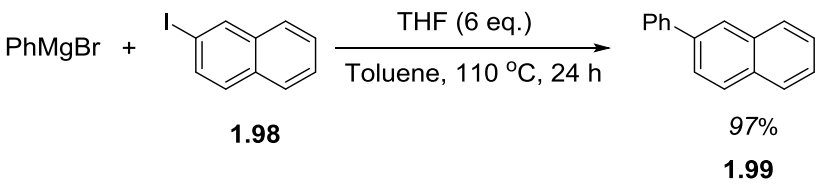
1.1.3 Grignard mediated Ar-Ar coupling

Recent work by Shirakawa and others has shown that Grignard reagents can be used in cross-coupling reactions with alkenyl halides, without the need for transition metal catalysts.[73]



Scheme 1.21 Cross-coupling reaction of aryl Grignard reagents and alkenyl iodides

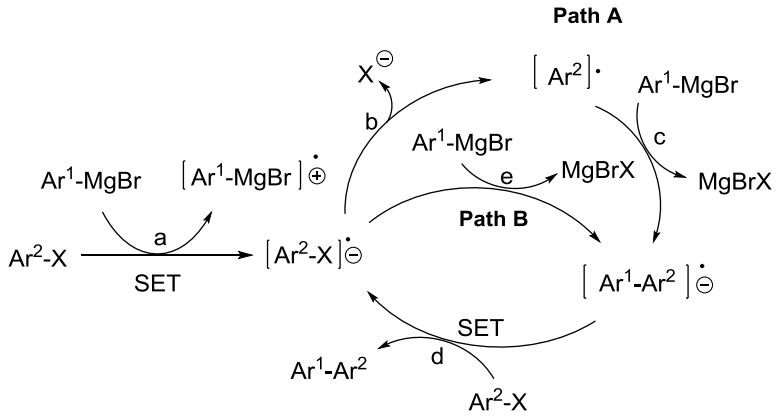
Grignard cross coupling reactions can also be used to form biaryl products.[74]



1.98 **1.99**

Scheme 1.22 Cross-coupling reactions of PhMgBr and aryl iodides

The mechanism of the aryl-aryl Grignard cross-coupling reaction has been postulated to occur through a SET step followed by an $S_{RN}1$ pathway (Scheme 1.23). The proposed mechanism could follow Path A in which the anion radical of [Ar^2-X] formed by abstraction of one electron from an aromatic Grignard reagent (step a), eliminates halide (X^-) (step b) to give radical [Ar^2]$^\bullet$. This is then attacked by Ar^1MgBr (step c) via an $S_{RN}1$ reaction mechanism leading to radical anion [Ar^2-Ar^1]$^{\bullet-}$. This reactive intermediate then donates an electron to another molecule of [Ar^2-X] to give radical anion [Ar^2-X]$^{\bullet-}$ (step d), and the product Ar^1-Ar^2.



Scheme 1.23 Suggested mechanism for the Ar-Ar cross-coupling of Ar^1MgBr and Ar^2X

Or in path B, the radical anion [Ar^2-X]$^{\bullet-}$ reacts with the nucleophile Ar^1MgBr affording the radical anion [Ar^1-Ar^2]$^{\bullet-}$ (step e). Donation of one electron from the radical anion [Ar^1-Ar^2]$^{\bullet-}$ to Ar^2-X gives the product [Ar^1-Ar^2] and regenerates the radical anion [Ar^2-X]$^{\bullet-}$.

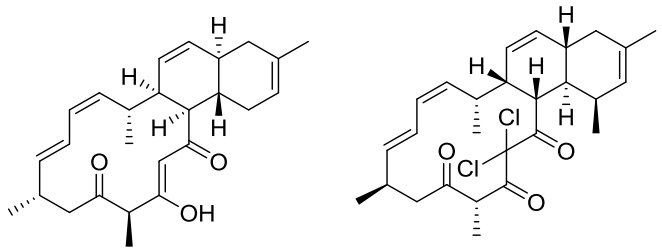
1.1.4 Conclusions

Single Electron Transfer (SET) processes can be observed in many organic reactions, typically those SET reactions involving reducing metals such as sodium (e.g. Pinacol reaction and Birch reduction). However there are only limited direct applications of Grignard mediated SET chemistry in organic synthesis.

1.2 2,2-Dichloroketones

1.2.1 Introduction

Bioactive natural products have been found which contain a 2,2-dichloroketone moiety in their structure. One of them is chlorotonil A which is a *gem*-dichloro-1,3-diketone macrolide analogue similar to anthracimycin.[75-78]



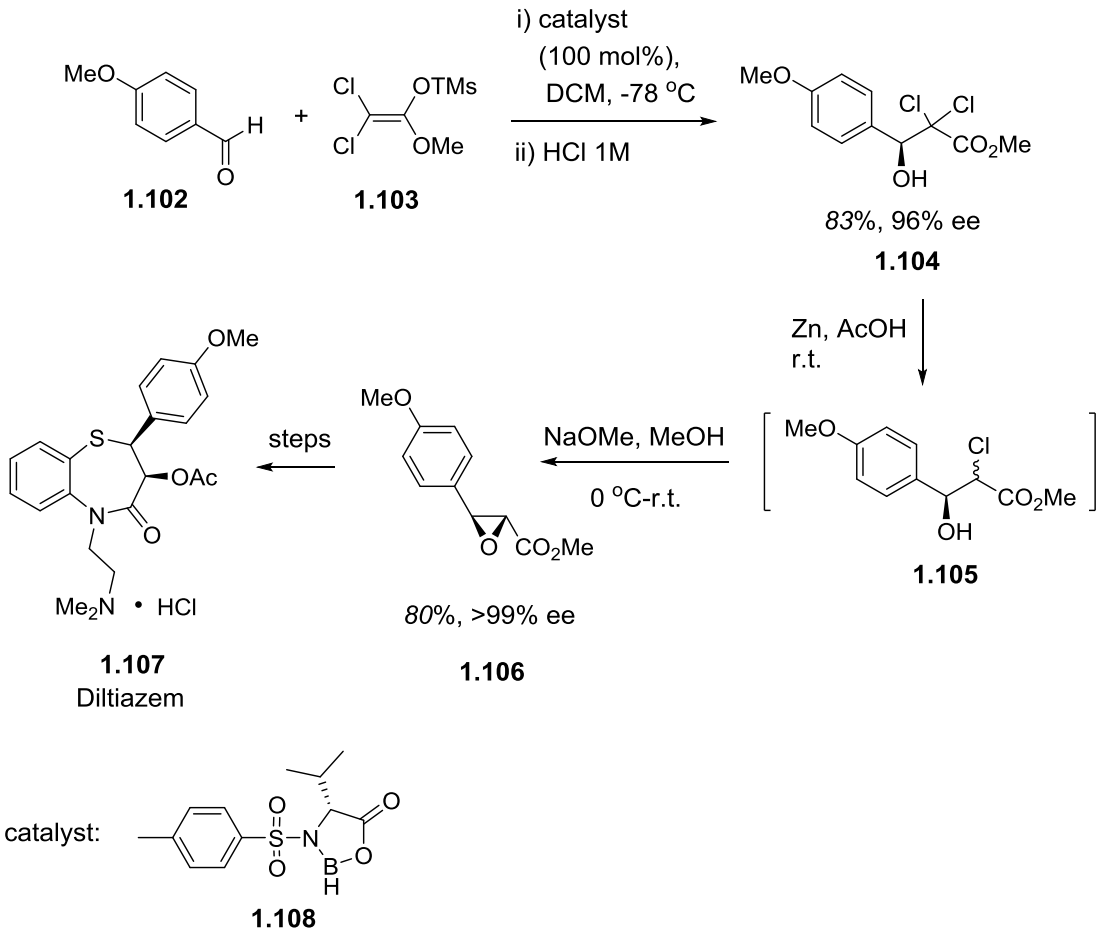
1.100
anthracimycin

1.101
chlorotonil A

Scheme 1.24 Structure of anthracimycin and chlorotonil A

2,2-Dichloro carbonyls have also been shown to be a useful reagent in the synthesis of chiral epoxides. Imashiro in his attempt to synthesise chiral epoxide **1.106** used a 2,2-chloroketone **1.104** as the starting material.[79] Epoxide **1.106** is an important intermediate in the synthesis of diltiazem, a drug for the treatment of hypertension.

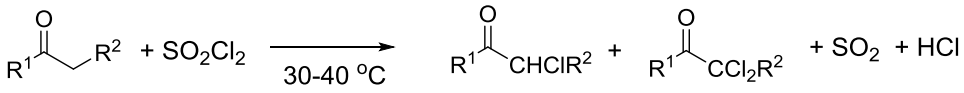
Imashiro employed a substituted benzaldehyde **1.102** in reaction with dichloro silyl enolate in a Mukaiyama aldol condensation allowing a one step synthesis of **1.106**.



Scheme 1.25 Synthesis of diltiazem from **1.106**

1.2.2 Synthesis of 2,2-dichloroketones

Synthesis of 2,2-dihalo ketones is mostly based electrophilic halogenation of ketones with halides source such as sulfuryl chloride, *N*-chlorosuccinimide (NCS), CF_3SO_2Cl and Lewis acidic metal halides.[80-82] Wyman demonstrated this approach through the reaction of a series of ketones, aldehydes and esters with SO_2Cl_2 affording the corresponding 2,2-dichloro carbonyl products.[83-84]



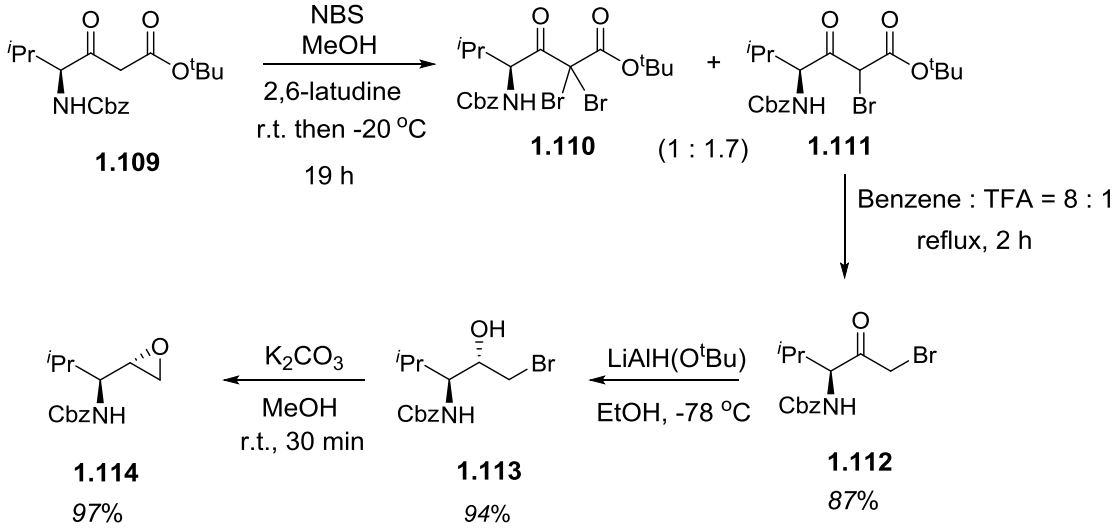
Scheme 1.26 Synthesis of 2,2-dichloro ketones with $SOCl_2$

Table 1.2 Yield of mono and di-chlorinated carbonyl compounds

entry	R_1	R_2	Monochlorinated (%)[a]	Dichlorinated (%)[a]
1	Me	Me	38-41	58-72
2	Me	Et	19	48
3	OEt	CH_2CN	21	67
4	OEt	CH_2CO_2Et	35-71	20-57

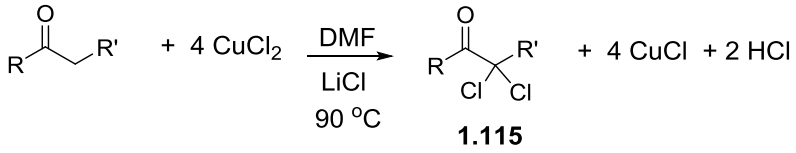
[a]: analysis by GC

Hoffman in his attempt to synthesise of amino epoxide **1.114** enantioselectively used NBS to afford *α*-monobromo-1,3-diketone **1.111** along with dibrominated species **1.110**. Decarboxylation of mono-brominated β-ketoester **1.111** followed by $LiAlH_4$ reduction and treatment with base gave epoxide **1.114**.[85]



Scheme 1.27 NBS bromination of β-ketoester

Another method of preparation 2,2-dichloro ketones is the reaction of ketones with Cu(II) chloride. Nobrega showed that this method is efficient for the selective preparation of 2,2-dichloroketones for enolisable aryl and alkyl ketones.[86-87]

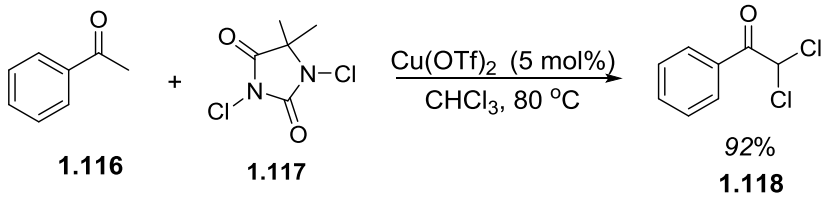


Scheme 1.28 Synthesis of 2,2-dichloroketones using $CuCl_2$

Table 1.3 Yield of **1.115**

entry	R	R'	Time (h)	Yield (%)
1	Ph	H	4	76
2	4-CH_3Ph	H	5	70
3	Me	Ph	2	65
4	EtO	$COCH_3$	2	94

A Lewis acid catalysed preparation of 2,2-dichloroketones was demonstrated by Jagdale. For the dichloronation of benzophenone, Jagdale used $Cu(OTf)_2$ as a catalyst and 1,3-dichloro-5,5-dimethylimidazolidine-2,4-dione **1.117** as the electrophilic chlorine source.[88]



Scheme 1.29 Synthesis of 2,2-dichloro-1-phenylethanone **1.118**

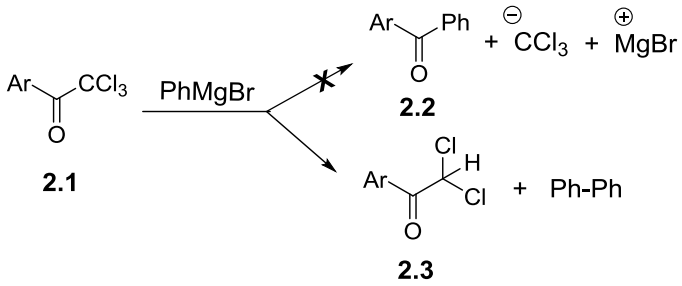
1.2.3 Conclusions

2,2-dichloro carbonyls are of interest due to their presence in bioactive molecules as well as their use as reactive intermediates in synthesis. Methods of synthesis of 2,2-dichloro carbonyls which are mostly over Michael addition and metal catalysed redox reactions are still non-regioselective.

Chapter 2 Grignard Mediated Reduction of 2,2,2-Trichloro-1-arylethanones

2.1 Introduction

During efforts in our group to synthesise diaryl ketones, we observed that treatment of 2,2,2-trichloro-1-arylethanones with PhMgBr gave not the desired diarylketones but 2,2-dichloro-1-arylethanones along with biphenyl (scheme 2.1).



Scheme 2.1 Reaction of 2,2,2-trichloro-1-arylethanone with PhMgBr

Sterically encumbered electron deficient ketones, such as 2,2,2-trichloro-1-arylethanones, show a preference for SET mechanisms with Grignard reagents.[89-90] Therefore, 2,2,2-trichloro-1-arylethanones could abstract one electron from PhMgBr becoming a ketyl radical. In a normal reaction of PhMgBr with a ketone this is then followed by phenyl radical coupling with ketyl anion leading to the diaryl alcohols. However, no such products were isolated in the aforementioned experiment.

The only by-product isolated during the reaction of 2,2,2-trichloro-1-arylethanones with PhMgBr was biphenyl.[91] The formation of biphenyl is typically for the dimerisation reaction of phenyl radicals, therefore any proposed mechanism must account for the formation of phenyl radicals.

Interested in that intriguing result, we further scrutinised the possible SET reaction mechanism of Grignard reagents with 2,2,2-trichloro-1-arylethanones. In order to further understand this reaction, we decided on the following approach:

- Step 1 investigation of the mechanism of PhMgBr SET reactions with 2,2,2-trichloro-1-arylethanones
- Step 2 examine a range of aromatic and heteroaromatic 2,2,2-trichloroethanones as reaction substrates
- Step 3 trap proposed intermediates with a range of substrates

In step one, investigation of the involvement of SET mechanism in the reaction of 2,2,2-trichloro-1-arylethanones with PhMgBr would be done through EPR measurement and the trapping of radical intermediates. Through this, the reaction mechanism then could be

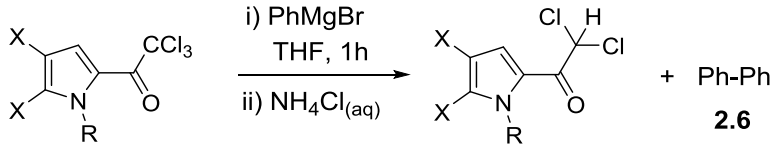
proposed. Following this, variation of the 2,2,2-trichloroethanones would inform the scope of the substrates which will undergo PhMgBr single electron transfer reactions (step 2).

As the results also indicated the involvement of a electrophilic intermediate, employing various electrophilic quenching agents would lead to understanding of the electrophile selectivity in the reactions of 2,2,2-trichloro-1-arylethanones with PhMgBr (Step 3).

With the success of these experiment, a new pathway for the preparation of functionalised 2,2-dichloroketones would be generated.

2.2 Further Investigation of Grignard SET Reactions

Mr Ali H. Essa (Newcastle) found that reaction of substituted 2,2,2-trichloro-1-(1*H*-pyrrole-2-yl)ethan-1-ones with PhMgBr resulted the formation of 2,2-dichloroketones (Scheme 2.2 and Table 2.1).[92]

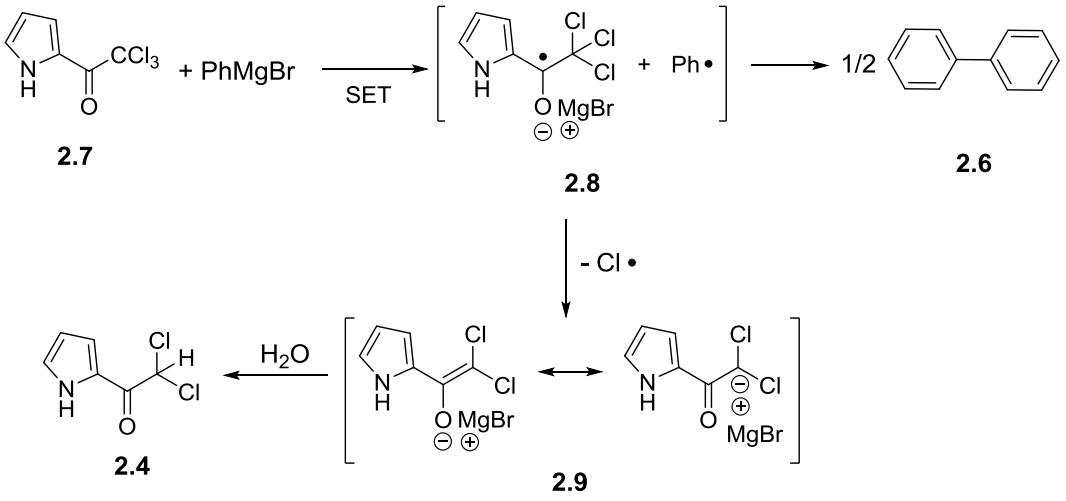


Scheme 2.2 PhMgBr reduction of substituted 2,2,2-trichloro-1-(1*H*-pyrrole-2-yl)ethan-1-ones

Table 2.1 Reaction of PhMgBr with substituted 2,2,2-trichloro-1-(1*H*-pyrrol-2-yl)ethan-1-ones

Entry	R	X	PhMgBr	Temp.	Product	Yield (%)
1	H	H	1.1 eq	0 °C	**2.4**	50
2	H	H	1.1 eq	r.t.	**2.4**	55
3	H	H	2.2 eq	r.t.	**2.4**	90
4	CH_3	H	1.0 eq	r.t.	**2.5**	94

Following these interesting results, a possible reaction mechanism was suggested. Driven by the consistency of the isolation of the radical-radical coupling product, biphenyl, which was found throughout reactions of PhMgBr with 2,2,2-trichloro-1-(1*H*-pyrrole-2-yl)ethan-1-ones, we postulate that the reaction of PhMgBr with 2,2,2-trichloro-1-(1*H*-pyrrole-2-yl)ethan-1-ones proceed by a single electron transfer reactions mechanism (Scheme 2.3).



Scheme 2.3 Proposed SET reaction mechanism of the reaction 2,2,2-trichloro-1-(1*H*-pyrrole-2-yl)ethan-1-one with PhMgBr

Donation of one electron from PhMgBr to the substrate produces radical anion **2.8**. The **2.8** then loses a chlorine atom in order to becoming an enolate **2.9**, followed by electrophile quenching leading to products such as **2.4**. Whilst the phenyl radical dimerises forming biphenyl **2.6**.

According to the postulated SET mechanism above (Scheme 2.3), several experiments were carried out in order to further investigate the Grignard mediated SET reduction of 2,2,2-trichloroaromatic or heteroaromatic ethanones. The proposed enolate intermediate could be trapped with electrophiles. Meanwhile evidence of the presence of either the radical **2.8** or the phenyl radical could be detected by spin trap Electron Paramagnetic Resonance (EPR) measurement.

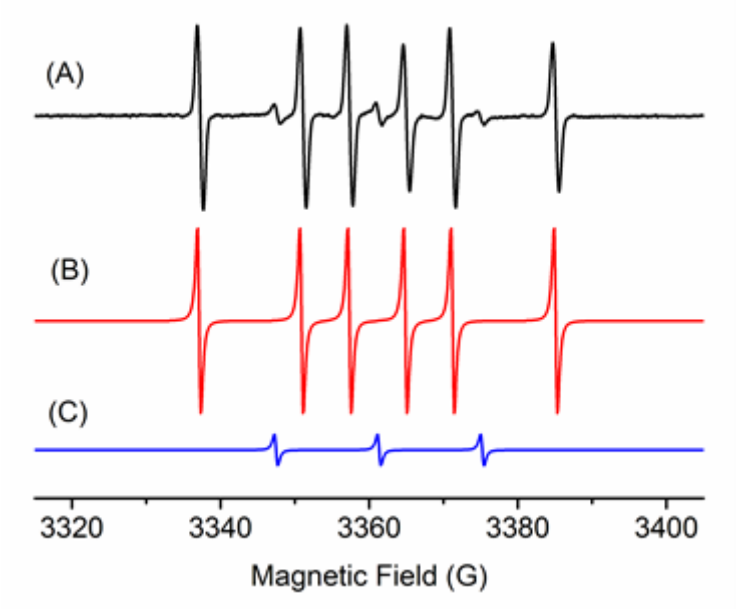
2.2.1 EPR experiments

Electron Paramagnetic Resonance (EPR) is a spectroscopic method for determining paramagnetic species such as radicals. In principle EPR works based on the resonant absorption of microwave radiation by the electron in the presence of an applied magnetic field.[93]

Only long lived radicals can be easily detected by the EPR. In case of unstable radicals, they have to be trapped by spin trapping reagent to produce a persistent radical adduct before submitting it to the EPR machine. 5,5-dimethyl-*N*-pyrroline-1-oxide (DMPO) **2.12** is the most common spin trapping reagent used for this application.[94]

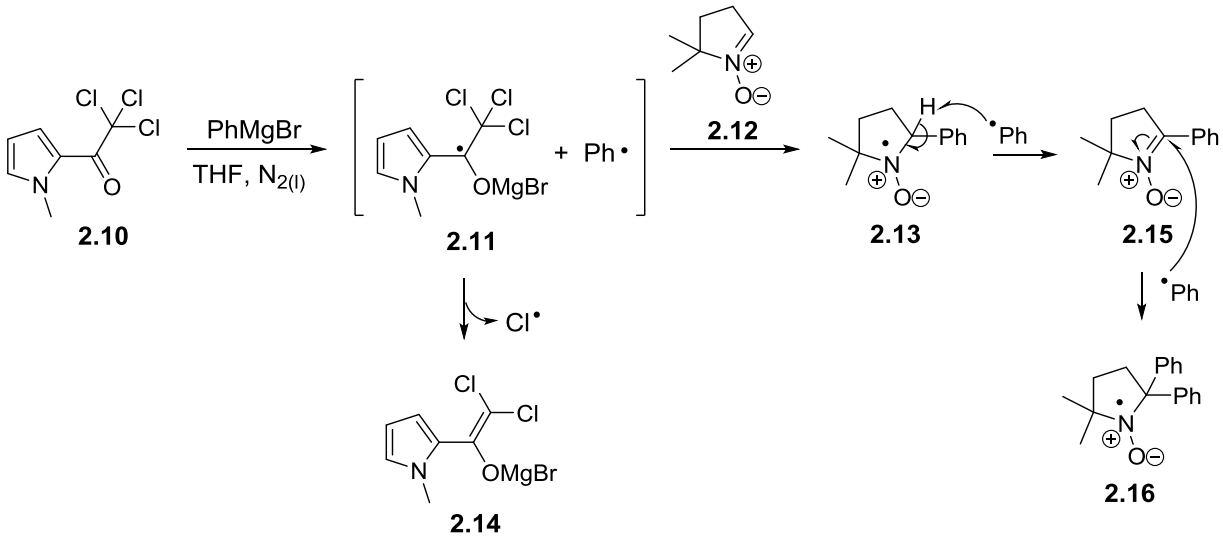
To look for radical intermediates in the reactions, PhMgBr and 2,2,2-trichloro-1-(*N*-methylpyrrol-2-yl)ethan-1-one were added in THF to an EPR tube and frozen in liquid N_2. The radical trap DMPO was added and the mixture allow to warm in the EPR spectrometer.

This experiment has been performed by Mr Ali H Essa (Newcastle) and Dr. Floriana Tuna (Manchester).



Scheme 2.4 EPR spectrum of DMPO spin trapped of PhMgBr and 2,2,2-trichloro-1-(*N*-methylpyrrol-2-yl)ethan-1-one (A), Simulated spectrum of Ph-DMPO adduct (B) and Simulated spectrum of Ph_2-DMPO adduct (C)

Scheme 2.4 shows the EPR spectrum showing 2 radical products. The six high intensity peaks corresponds to a Ph-DMPO adduct **2.13**. Meanwhile, the three low intensity peaks belongs to a Ph_2-DMPO adduct **2.16**. In the absence of 2,2,2-trichloro-1-(*N*-methylpyrrol-2-yl)ethan-1-one, PhMgBr in THF afforded no EPR signals. This indicates that the phenyl radical is generated under the reaction conditions.

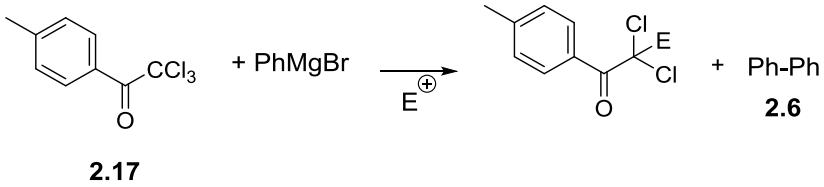


Scheme 2.5 DMPO trapped products

2.2.2 Enolate trapping

Following the success of the EPR investigation of the reaction of 2,2,2-trichloro-1-(1-methylpyrrol-2-yl)ethan-1-one with PhMgBr, we then continued examine the reaction of 2,2,2-trichloro-1-arylethanones with PhMgBr by trapping the intermediate enolates, shown in Scheme 2.3.

Therefore we planned to react 2,2,2-trichloro-1-(4-tolyl)ethan-1-one **2.17** with PhMgBr and subsequently quench with electrophiles to afford new products.

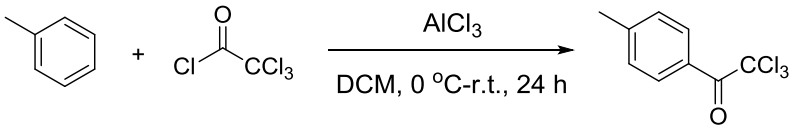


2.17

Scheme 2.6 Planned enolate trapping experiments

2.2.2.1 Synthesis of 2,2,2-trichloro-1-(4-tolyl)ethan-1-one

2,2,2-Trichloro-1-(4-tolyl)ethan-1-one (**2.17**) was first synthesised by the Friedel-Craft acylation of toluene with trichloroacylchloride (TCAC).[95] The reaction was done at 0 ^{o}C for 60 minutes before leaving it to warm to r.t. for 24 h. Following aqueous work-up and distillation under reduced pressure 2,2,2-trichloro-1-(4-tolyl)ethan-1-one was obtained in 65% yield.



65%

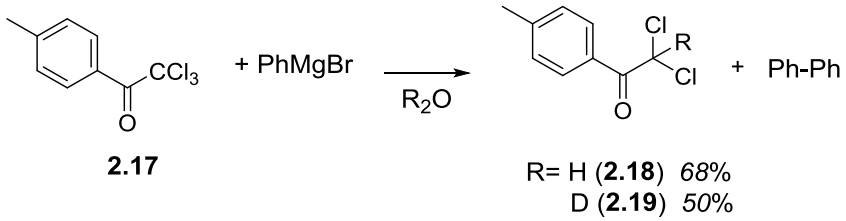
2.17

Scheme 2.7 The synthesis of 2,2,2-trichloro-1-(4-tolyl)ethan-1-one (**2.17**)

Proton NMR showed two aromatic doublets at 7.32 and 8.19 ppm suggesting that the desired *para*-substituted product had been obtained.

2.2.2.2 Reaction of 2.17, PhMgBr and electrophiles

With the 2,2,2-trichloro-1-(4-tolyl)ethan-1-one (**2.17**) in hand, trapping of the enolate formed by the reaction between **2.17** and PhMgBr was carried out. Reaction of **2.17** with PhMgBr followed by quenching using water afforded 68% of dichloroketone **2.18** along with biphenyl (38%).

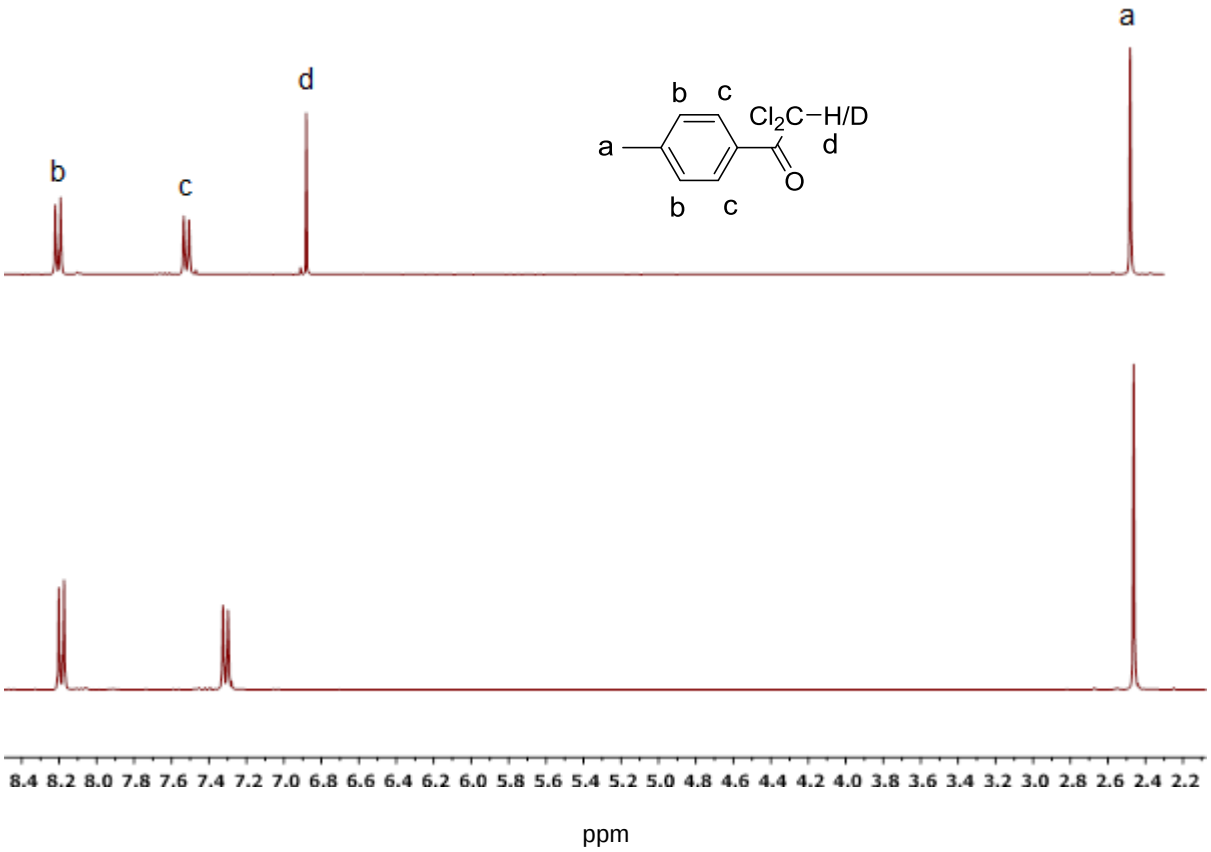


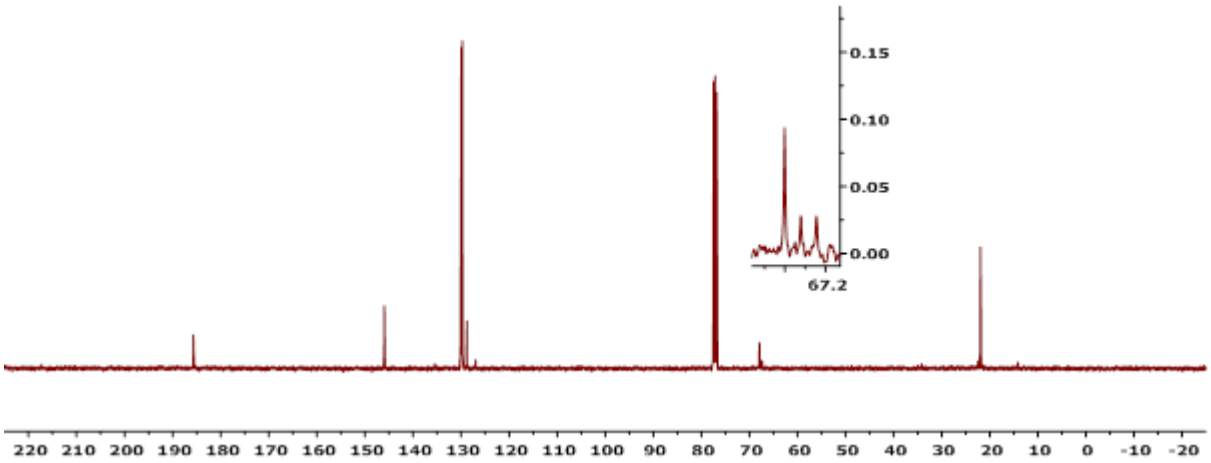
2.17

R= H (**2.18**) *68%*
D (**2.19**) *50%*

Scheme 2.8 Water and D_2O quenching reaction of **2.17** and PhMgBr

In order confirm the source of "H", the reaction of **2.17** with PhMgBr was repeated under the same conditions followed by D_2O quenching. The ^{1}H and ^{13}C NMR of **2.18** and **2.19** are shown in Scheme 2.9.

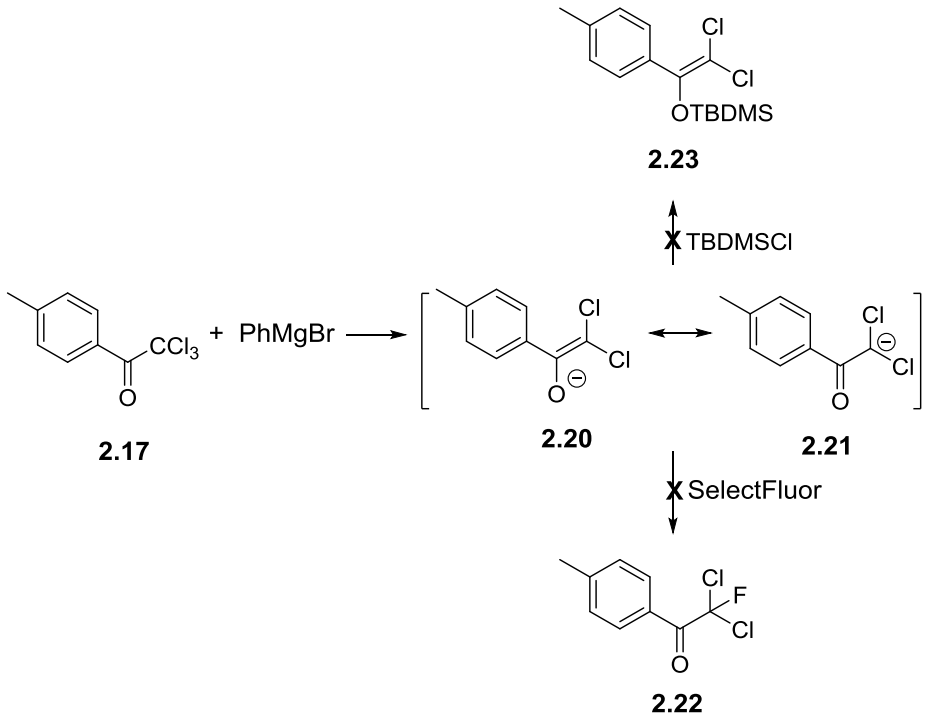




Scheme 2.9 ^{1}H and ^{13}C NMR of non-deutereted and deuterated **2.18**

The ^{1}H NMR spectra of deuterated product **2.19** showed disappearance of the singlet proton peak at 6.61 ppm due to the CCl_2**H** group. This shows a high % deuteration of the CCl_2H position. Moreover in the ^{13}C NMR spectra of **2.19**, a triplet peak resulting from carbon to deuterium coupling appeared at 67.6 ppm, $J_{C\text{-}D}$ = 27.1 Hz (Scheme 2.9) again suggesting a high % deuterium incorporation into the CCl_2H group.

Further enolate intermediate trapping was done by quenching of the reaction of 2,2,2-trichloro-1-(4-tolyl)ethan-1-one and PhMgBr with TBDMSCl[96-99] or SelectFluor.[100-101]



Scheme 2.10 TBDMSCl quenching of PhMgBr SET reaction of 2,2,2-trichloro-1-(4-tolyl)ethan-1-one

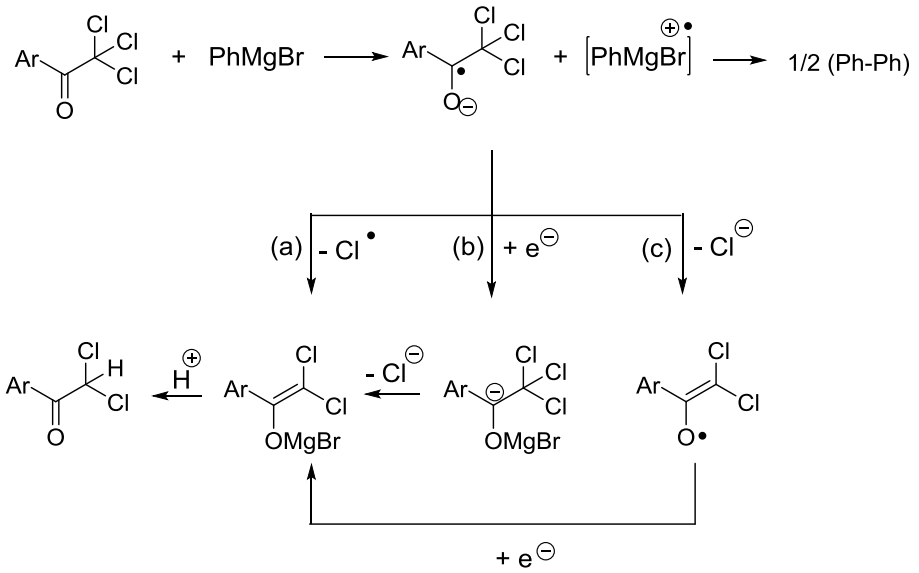
Table 2.2 TBDMS and SelectFluor quenching of PhMgBr reaction with **2.17**

Entry	E	Solvent	Temp (°C)	Time (h)	Yield (%)
1	TBDMSCl	THF	r.t.	24	No reaction
2	SelectFluor	THF	r.t.	24	No reaction

However, even after leaving the reaction for 24 h, mono-dechlorination product **2.18** and biphenyl were the only isolated products.

2.3 Proposed Mechanisms

We therefore propose that the Grignard mediated SET reduction of 2,2,2-trichloroarylethanones goes *via* the following possible mechanisms (Scheme 2.11).



Scheme 2.11 Proposed Grignard SET of 2,2,2-trichloroarylethanones reaction pathways

Initially the 2,2,2-trichloroarylketone accepts an electron from PhMgBr to form a radical anion. Meanwhile the phenyl radical dimerises to biphenyl. The radical anion then either: (a) loses a chlorine atom[102], (b) accepts a second electron and subsequently eliminates chloride or (c) loses chloride followed by addition of a second electron, to give the corresponding enolate. The enolates are then trapped by added electrophiles.

Imanishi proposed a similar SET reaction mechanism for the Pt/C catalysed H_2 reduction of 2,2,2-trichloro ketones derivatives. Imanishi found that SET Pt/C catalysed H_2 reduction of 2,2,2-trichloro aromatic or aliphatic ketones preferentially proceed *via* loss of a chlorine radical (route a).[103]

The presence of chlorine radical in the reaction was however unconfirmed despite EPR studies and GCMS to look for products arising (eq. PhCl).

2.4 Conclusions

The reaction mechanism for Grignard mediated SET reduction of 2,2,2-trichloroaromatic and heteroaromatic ethanones has been postulated mostly based on EPR measurements and trapping experiments which confirmed the presence of phenyl radicals. Trapping experiments also showed the presence of intermediate enolates.

Chapter 3 Synthesis of Substituted 2,2-Dichloroketones

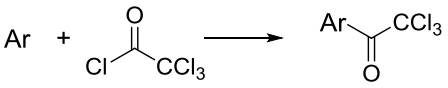
3.1 Introduction

The previous chapter has provided interesting results concerning the reaction of 2,2,2-trichloro-1-arylethanones with Grignard reagents. These reactions resulted in enolate intermediates, quenching of which with water or D_2O gave 2,2-dichloroketones in modest to good yield. Therefore we thought that by employing different electrophiles to probe the reaction of 2,2,2-trichloro-1-arylethanones with PhMgBr, a new synthetic route for the synthesis of substituted 2,2-dichloroarylketones could be developed.

In order to do that, several 2,2,2-trichloro-1-arylethanones and 2,2,2-trichloro-1-heteroaryl-ethanones have to be synthesised. Several different electrophiles will be tested in the reaction of 2,2,2-trichloro-1-(4-tolyl)ethan-1-one with PhMgBr. This then will give information on the selectivity of the electrophile as well as the scope of the substrates undertaking Grignard SET reactions. Successful electrophiles will then be used in the preparation of new 2,2-dichloro aryl and heteroarylethanones.

3.2 Synthesis of 2,2,2-Trichloroaryl and Heteroarylethanones

A series of 2,2,2-trichloro aromatic and heteroaromatic ethanones were needed to test reactions with various electrophiles (Scheme 3.1). Synthesis of compound **3.1**, **3.3** and **3.4** was done by Miss Ece Cifti (Erasmus student) supervised by Reinner I Lerrick. 2,2,2-trichloroaryl and heteroarylketones (**3.1** to **3.4**) would then be submitted to reaction with PhMgBr followed by water or D_2O quenching in order to confirm that the substrates undergo Grignard SET reactions to give enolates. Successful substrates will then be used as starting materials in order to test different electrophiles in their reaction with the enolates genarated.

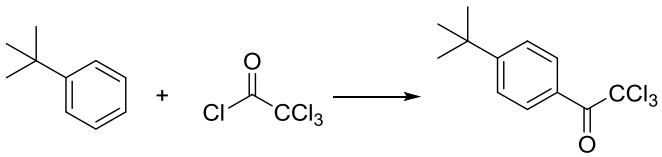


Ar = *4-t*-butylphenyl (**3.1**)
2-methylfuran (**3.2**)
1-*H*-Indole (**3.3**)
1-methylindole (**3.4**)

Scheme 3.1 Target 2,2,2-trichloroaryl and heteroarylethanones

3.2.1 Synthesis of 1-(4-*t*-butylphenyl)-2,2,2-trichloroethan-1-one

In the synthesis 1-(4-*t*-butylphenyl)-2,2,2-trichloroethan-1-one, reaction of *t*-butyl benzene **3.5** with trichloroacetyl chloride (TCAC) was done initially in the absence of a Lewis catalyst. However, *t*-butylbenzene showed no reaction with TCAC in DCM even at reflux.



3.5 **3.1**

Scheme 3.2 Synthesis of 1-(4-*t*-butylphenyl)-2,2,2-trichloroethan-1-one

Use of $AlCl_3$ as a Lewis acid catalyst resulted in decomposition of the starting material (Table 3.1 entry 2 and 3). $BF_3.OEt_2$ was then used however, only *t*-butylbenzene was isolated after 4 days at room temperature (entry 4). We then turned to using $AlCl_3$ at low temperatures. Reaction of **3.5** and TCAC at -30 ^oC gave the desired product **3.1** after 2 days (entry 5) in 45% yield after distillation. Meanwhile cooling the reaction to -78 ^oC (entry 6) gave no observable product after 8 hours.

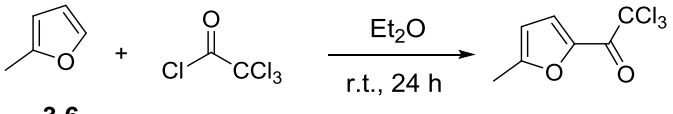
Table 3.1 The synthesis condition of 1-(4-*t*-butylphenyl)-2,2,2-trichloroethanone preparation

No	Catalyst	Conditions	Time (h)	Solvent	Yield (%)
1	no catalyst	r.t. then reflux	48	DCM	no reaction
2	$AlCl_3$	0 ^oC to r.t.	3	DCM	decomposition
3	$AlCl_3$	0 ^oC to 4 ^oC	4	DCM	decomposition
4	BF_3. OEt_2	0 ^oC to r.t.	50	DCM	no reaction
5	$AlCl_3$	-30 ^oC	48	DCM	45
6	$AlCl_3$	-78 ^oC	8	DCM	no reaction

3.2.2 Synthesis of 2,2,2-trichloro-1-(5-methylfuran-2-yl)ethan-1-one

When considering the synthesis of 2,2,2-trichloro-1-(5-methylfuran-2-yl)ethan-1-one, we were concerned that strong Lewis acids would lead to ring opening and other side reactions with electron rich furans.[104] We therefore decided to include a methyl group at the C2 position of the furan order to prevent possible double addition of TCAC.

2-Methylfuran (**3.6**) was therefore reacted with TCAC at r.t. for 2 days in Et_2O without any Lewis acid catalysis (Scheme 3.3). After purification 2,2,2-trichloro-1-(5-methylfuran-2-yl)ethan-1-one (**3.2**) was obtained in 65% yield.



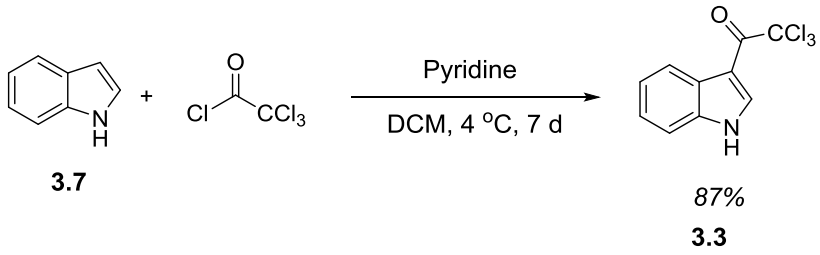
3.6 *65%* **3.2**

Scheme 3.3 The synthesis of 2,2,2-trichloro-1-(5-methylfuran-2-yl)ethan-1-one

3.2.3 Synthesis of 2,2,2-trichloro-1-(1*H*-indol-3-yl)ethan-1-one

The synthesis of 2,2,2-trichloro-1-(1*H*-indol-3-yl)ethan-1-one **3.3** was performed based on a literature approach.[4-6] Being an electron rich heteroaromatic, no Lewis acid was required for the Friedel-Craft acylation of **3.7**. Instead we employed pyridine as a nucleophilic catalyst. Therefore indole **3.7** and TCAC in DCM were stirred at 4 ^{o}C for a week with catalytic pyridine.

The desired product 2,2,2-trichloro-1-(1*H*-indol-3-yl)ethan-1-one (**3.3**) was obtained in 87% yield following recrystallization.



Scheme 3.4 Synthesis of 2,2,2-trichloro-1-(1*H*-indole-3-yl)ethan-1-one

In order to confirm the regiochemistry of **3.3**, crystals were grown through slow evaporation from DCM/Petrol (Figure 3.1). Single crystal X-ray analysis confirmed C3 substitution.

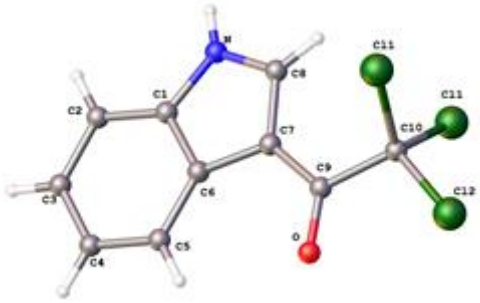
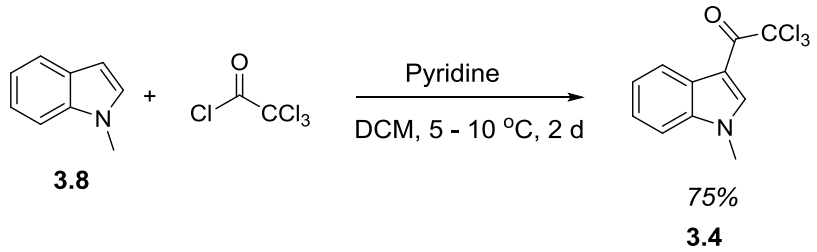


Figure 3.1 X-ray crystal structure of 2,2,2-trichloro-1-(1*H*-indol-3-yl)ethan-1-one

3.2.4 Synthesis of 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one

Since we were concerned that the acidic N-H of **3.3** might be deprotonated by PhMgBr in our subsequent investigations, we decided to synthesis *N*-methyl protected indole **3.8**. Analogous to the synthesis of 2,2,2-trichloro-1-(1*H*-indol-3-yl)ethan-1-one, 1-methylindole was reacted with TCAC at 5-10 ^{o}C for 2 days in the presence of pyridine to give 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one **3.4** in good yield.



3.8

75%

3.4

Scheme 3.5 The synthesis of 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one

The correct regiochemistry of the product was confirmed by single crystal X-ray analysis, after crystals of **3.4** were grown from DCM/Petrol (Figure 3.2).

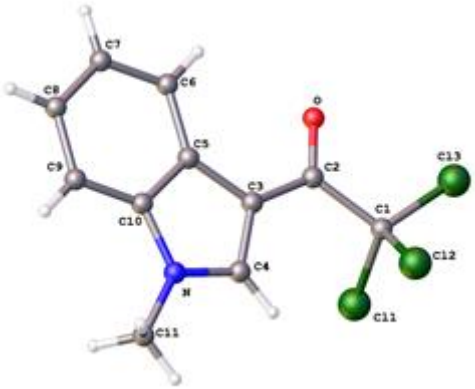


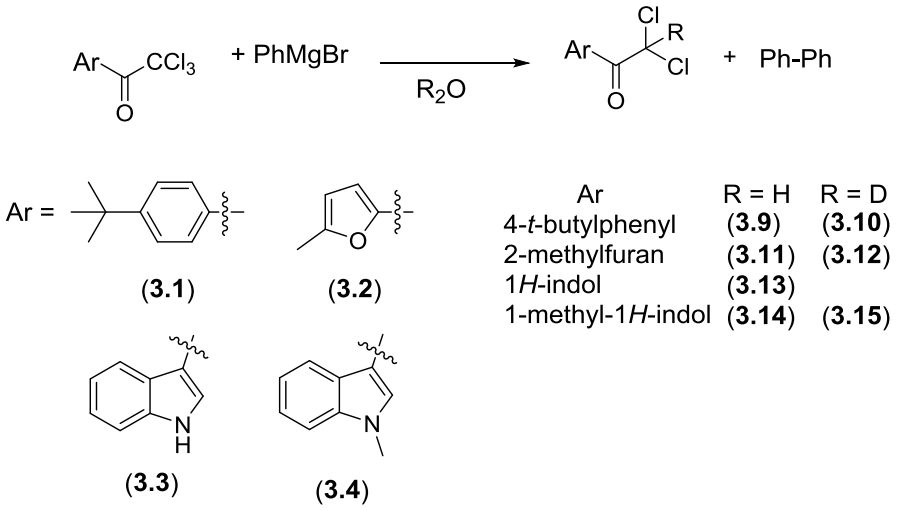
Figure 3.2 X-ray crystal structure of 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one

3.2.5 Conclusions

Several aromatic and heteroaromatic substituted 2,2,2-trichloroethanones have been synthesised in moderate to good yield through a mixture of Lewis acid catalysed, nucleophile catalysed and uncatalysed acylation reactions.

3.3 Reaction of 2,2,2-Trichloroaryl and Heteroaroarylethanones with PhMgBr

With several aromatic and heteroaromatic substituted 2,2,2-trichloroethanones in hand, we examined their reactions with PhMgBr. Compounds **3.1** to **3.4** were reacted with PhMgBr followed by water or D_2O quenching as previously. Synthesis of **3.13** was done by Miss Ece Cifti.



Scheme 3.6 Reduction of 2,2,2-trichloroaryl and heteroarylethanones, quenching with H_2O or D_2O

Table 3.2 Yield of reduction of 2,2,2-trichloroaryl and heteroethanones, quenching with H_2O or D_2O

Entry	Compound	Yield (%)	Compound	Yield (%)
1	**3.9**	71	**3.10**	96 (96)*
2	**3.11**	58	**3.12**	68 (94)*
3	**3.13**	33		
4	**3.14**	75	**3.15**	65 (98)*

* : % D incorporation according to H-NMR

Reaction of **3.1** to **3.4** with PhMgBr followed by quenching using water afforded 2,2-dichloroaryl or heteroarylethanone products in 30-90% yield along with biphenyl. Repeating these reactions but quenching with D_2O produced the corresponding deuterated 2,2-dichloroaryl or heteroarylethanones in almost quantitative yield (Table 3.2).

Low yield of **3.13** (entry 3) might be caused by a side reaction (deprotonation of acidic indole proton in **3.3**) of the Grignard. This then affected the generation of enolate **3.3** in the SET process. Overcoming this effect by protection the indole to *N*-methyl indole **3.4** proved significantly yield increasing (entry 4).

In case of **3.9** and **3.11**, electronic effect seems to contribute to the result obtained. In **3.11** quite electropositive furan ring could slightly reduce the nucleophilicity of the corresponding enolate formed. This then gave moderate yield in the electrophilic quenching process (entry 2). Meanwhile the more electron donor of aryl ring in **3.1** significantly contributes to give quite high yield (entry 1).

The structure of **3.12** was confirmed by single crystal X-ray analysis, showing a dechlorinated product (Figure 3.3).

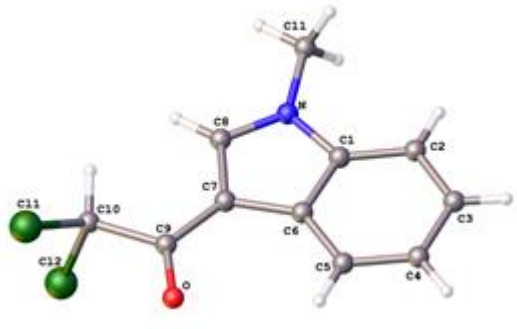


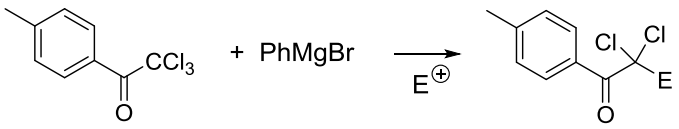
Figure 3.3 X-ray crystal structure of 2,2-dichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one

3.3.1 Conclusions

A series of aromatic and heteroaromatic substituted 2,2,2-trichloroethanones have been synthesised in quite high yield especially for 2,2,2-trichloro-1-(1*H*-indol-3-yl)ethan-1-one and 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one. The 2,2,2-trichloroaryl and heteroarylethanones underwent SET reactions with PhMgBr similar to those of 2,2,2-trichloro-1-(4-tolyl)ethan-1-one. Quenching with water or D_2O produced good to excellent yields of the corresponding reduced products.

3.4 Trapping with Alternative Electrophiles

As the aromatic and heteroaromatic substituted 2,2,2-trichloroethanones synthesised previously have been found to proceed *via* a Grignard mediated SET reaction, then these compounds could be used as a starting point for reaction with other electrophiles. Compound **2.17** was chosen as a model to screen the reaction of the enolates, generated by PhMgBr reduction, with more complex electrophiles. Following the same procedure for PhMgBr reduction of **2.17**, a range of electrophiles were added to the enolate.

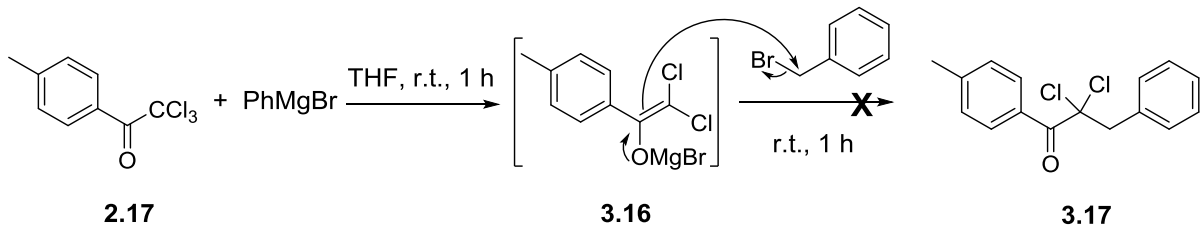


2.17 **3.7**

Scheme 3.7 Reaction of 2,2,2-trichloro-1-(4-tolyl)ethan-1-one with PhMgBr followed by electrophile addition

Commercially available benzyl bromide, arylaldehydes, acid chlorides and ketones were chosen as a representative set of reactive electrophiles.[105-106]

Solution of benzylbromide in THF was added into the reaction mixture of **2.17** with PhMgBr. After 24 hours no new product spots were detected, only reduced product **2.18** was isolated along with biphenyl.

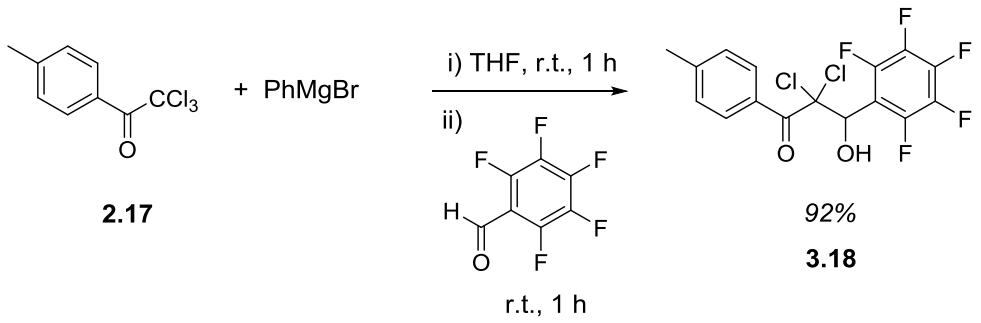


2.17 **3.16** **3.17**

Scheme 3.8 Attempted reaction of benzyl bromide with enolate **3.16**

To improve the reactivity of the benzylbromide, we generated benzyliodide *in situ* through addition of catalytic NaI, however no desired product was observed. Changing the benzylbromide to 4-nitrobenzylchloride was also unsuccessful.

Next we examined reaction with arylaldehydes. It was envisaged that enol **3.16** will undergo an aldol reaction with non-enolisable reactive aldehydes.[4] We selected perfluorobenzaldehyde as a reactive arylaldehyde. Therefore reaction of **2.17** with PhMgBr in THF was then followed by addition of perfluorobenzaldehyde (Scheme 3.9).



2.17 *92%* **3.18**

Scheme 3.9 Reaction of 2,2,2-trichloro-1-(4-tolyl)ethan-1-one, PhMgBr and perfluorobenzaldehyde

After 1 hour, TLC of the mixture indicated a new compound which was then isolated in near quantitative yield (92%). Crystalisation of the product was achieved through slow evaporation of a solution of 2,2-dichloro-3-hydroxy-3-(perfluorophenyl)-1-(*p*-tolyl)propane-1-one in petrol-ether. The structure of 2,2-dichloro-3-hydroxy-3-(perfluorophenyl)-1-(*p*-tolyl)propane-1-one (**3.18**) was confirmed by single crystal X-ray analysis (Figure 3.4).

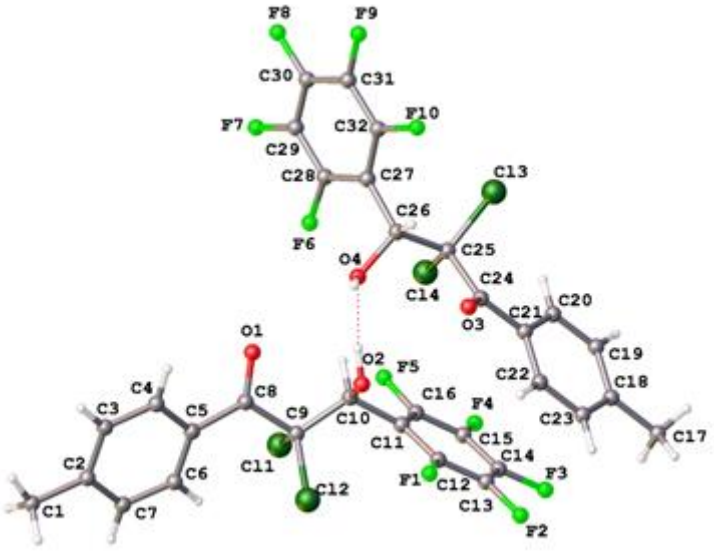
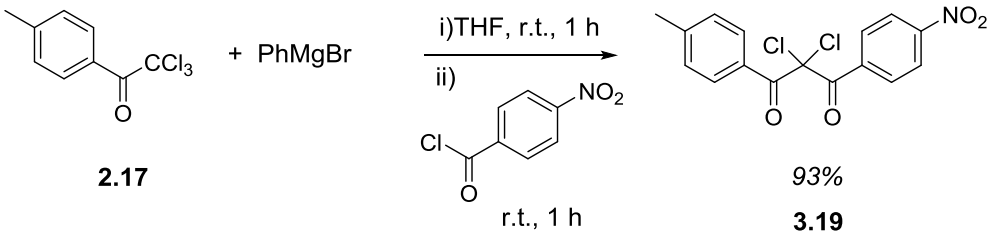


Figure 3.4 X-ray crystal of 2,2-dichloro-3-hydroxy-3-(perfluorophenyl)-1-(*p*-tolyl)propane-1-one

The crystal structure showed hydrogen bonding between the OH groups of the two different enantiomers within the cell unit (O(2)-H(2)…O(4) = 1.92 Å). In addition π-stacking of the electron rich *p*-tolyl and the electron poor perfluorophenyl groups can be seen.

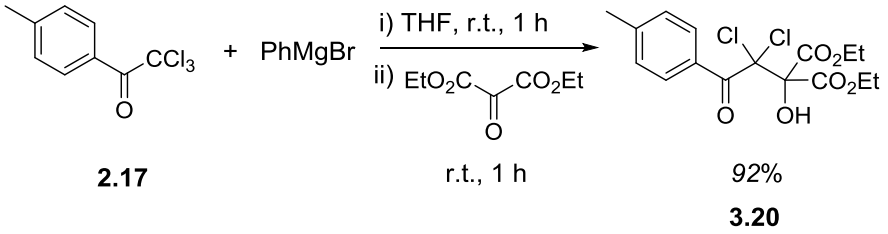
Following the success of reacting aldehydes with enolate **3.16**, we then decided to investigate acid chlorides as the electrophile. 4-Nitrobenzoylchloride was used in the reaction of 2,2,2-trichloro-1-(4-tolyl)ethan-1-one with PhMgBr in THF to give the Claisen product diketone **3.19** as a colourless oil in high yield.



2.17 *93%* **3.19**

Scheme 3.10 Reaction of 4-nitrobenzoylchloride with 2,2,2-trichloro-1-(4-tolyl)ethan-1-one and PhMgBr

We then turned to reactive ketones, commercially available diethylketomalonate was used to give the resulting diethyl 2-(1,1-dichloro-2-oxo-2-(*p*-tolyl)ethyl)-2-hydroxymalonate, **3.20** in high yield (Scheme 3.11) arising from an aldol type reaction.



2.17 r.t., 1 h *92%* **3.20**

Scheme 3.11 Reaction of diethylketomalonate with 2,2,2-trichloro-1-(4-tolyl)ethan-1-one and PhMgBr

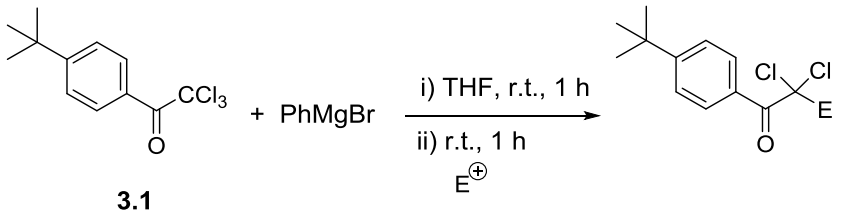
3.4.1 Conclusions

Reacting the electrophiles derived from the reaction of 2,2,2-trichloro-1-(4-tolyl)ethanone with PhMgBr with a range of electrophiles gave a number of aldol and Claisen condensation products in good yield with aldehydes, ketones and acid chlorides.

The high yields observed suggests this route is a promising pathway for the synthesis of functionalised 2,2-dichloroketones.

3.5 Reaction of 1-(4-(*t*-butyl)phenyl)-2,2,2-trichloroethan-1-one

Following the success of the synthesis of 2,2-dichloro-1-(4-tolyl)ketones through Grignard mediated SET reaction, we decided to extend the reaction to the fuctionalisation of 2,2-dichloroaryl and heteroarylethanones. Firstly we carried out electrophilic quenching of PhMgBr SET of 1-(4-(*t*-butyl)phenyl)-2,2,2-trichloroethan-1-one using carbonyl compounds (Scheme 3.12).



3.1

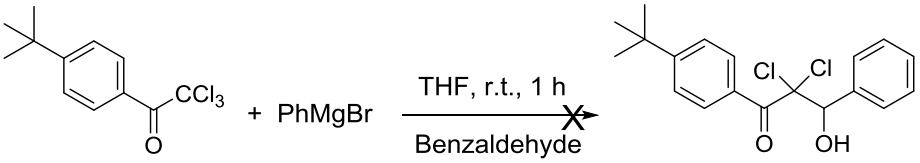
Scheme 3.12 Electrophile quenching of Grignard SET reaction of 1-(4-(*t*-butyl)phenyl)-2,2,2-trichloroethan-1-one

Analogues to the previous reaction the enolate of **3.1** was quenched with a range of electrophiles.

Table 3.3 Reaction of 1-(4-(*t*-butyl)phenyl)-2,2,2-trichloroethan-1-one, PhMgBr and electrophiles

Entry	Electrophile	Product (E)	Compound	Yield (%)
1	perfluorobenzaldehyde	$C(OH)(C_6F_5)$	**3.21**	53
2	benzaldehyde	$C(OH)(C_6H_5)$	**3.22**	No reaction
3	4-nitrobenzoylchloride	$CO(C_6H_4NO_2)$	**3.23**	38
4	diethylketomalonate	$C(OH)(CO_2Et)_2$	**3.24**	57

Table 3.3 showed the yield of the quenching products. Benzaldehyde was found to be unreactive towards the enolate of **3.1** (entry 2). However the reaction was successful with more electron poor aldehydes (entry 3-4).

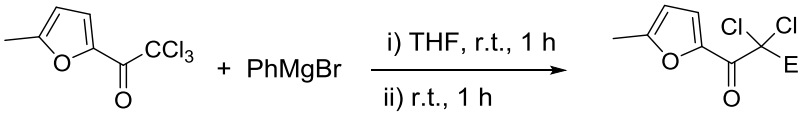


3.1 **3.22**

Scheme 3.13 Attempted reaction of **3.1** with PhMgBr and benzaldehyde

3.6 Reaction of 2,2,2-trichloro-1-(5-methylfuran-2-yl)ethan-1-one

We then examined the reaction of 2,2,2-trichlo-1-(5-methylfuran-2-yl)ethanone **3.2** with PhMgBr using the same protocol as before.



3.2

Scheme 3.14 Electrophile quenched 2,2,2-trichloro-1-(5-methylfuran-2-yl)ethan-1-one

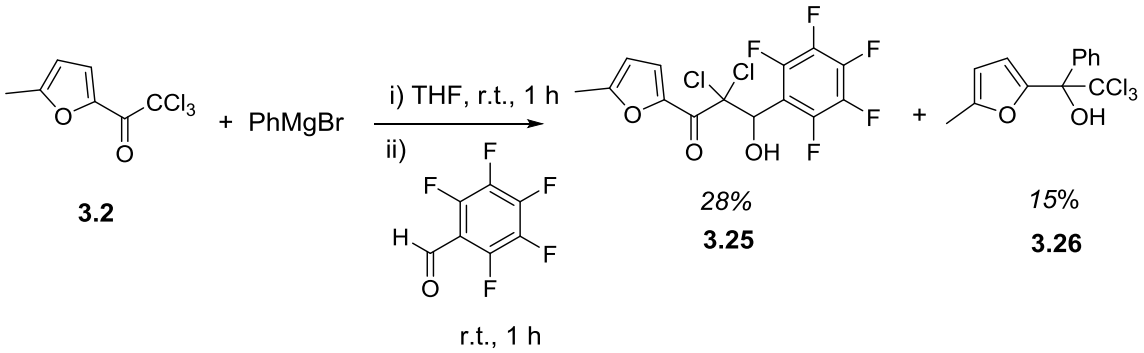
Quenching the reaction of **3.2** and PhMgBr with acid chlorides or aldehydes gave moderate yield of 2,2-dichloroketones (Table 3.4, entry 1).

Table 3.4 Yield of reaction of 2,2,2-trichloro-1-(5-methylfuran-2-yl)ethan-1-one, PhMgBr and electrophiles

Entry	Electrophile	Product (E)	Compound	Yield (%)
1	perfluorobenzaldehyde	$C(OH)(C_6F_5)$	**3.25**	28
2	4-nitrobenzoylchloride	$CO(C_6H_4NO_2)$	**3.27**	65
3	diethylketomalonate	$C(OH)(CO_2Et)_2$	**3.28**	69
4	4-nitrobenzaldehyde	$C(OH)(C_6H_4NO_2)$	**3.29**	64

Quenching the corresponding enolate of **3.2** with perfluorobenzaldehyde afforded not only the desired 2,2-dichloro-3-hydroxy-1-(5-methylfuran-2-yl)-3-(perfluorophenyl)propan-1-one

3.25 but also Grignard addition product **3.26**. This 2,2-dichloro-3-hydroxy-1-(5-methylfuran-2-yl)-3-(perfluorophenyl)propan-1-one was isolated in a 15% yield (Scheme 3.15).

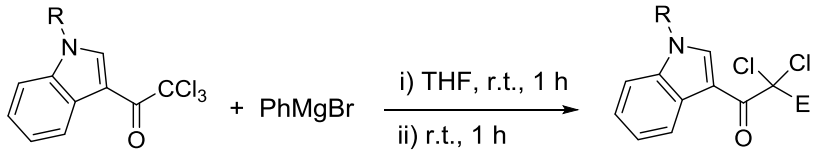


3.2 — *28%* **3.25** — *15%* **3.26**

Scheme 3.15 Reaction of 2,2,2-trichlo-1-(5-methylfuran-2-yl)ethan-1-one with PhMgBr and perfluorobenzaldehyde

3.7 Reaction of 2,2,2-trichloro-1-(1*H*-indol-3-yl)ethan-1-one and 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one

2,2,2-trichloro-1-(1*H*-indol-3-yl)ethan-1-one **3.3** and 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one **3.4** have been subjected to the PhMgBr SET reaction as before followed by the addition of various electrophiles.



R = H (**3.3**)
CH_3 (**3.4**)

Scheme 3.Reaction of 2,2,2-trichloro-1-(1*H*-indol-3-yl)ethan-1-one **3.3** and 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one **3.4** with PhMgBr followed by addition of electrophiles

Table 3.5 Reaction of **3.3** or **3.4**, PhMgBr and electrophiles

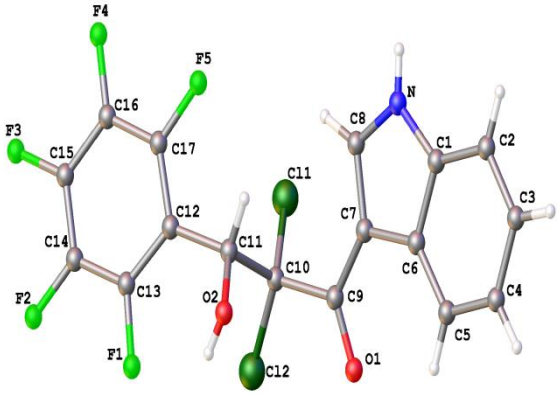
Entry	R	Electrophile	Product (E)	Compound	Yield (%)
1	H	perfluorobenzaldehyde	$C(OH)(C_6F_5)$	**3.30**	57
2	CH_3	perfluorobenzaldehyde	$C(OH)(C_6F_5)$	**3.31**	62
3	CH_3	4-nitrobenzoylchloride	$CO(C_6H_4NO_2)$	**3.32**	65
4	CH_3	diethylketomalonate	$C(OH)(CO_2Et)_2$	**3.33**	32
5	CH_3	4-nitrobenzaldehyde	$C(OH)(C_6H_4NO_2)$	**3.34**	64

Reaction of enolate of **3.3** and **3.4** with benzaldehydes and acid chloride gave moderate yields, although poor yield s were observed with diethyl ketomalonate (entry 4).

The structure of 2,2-dichloro-1-(1*H*-indol-3-yl)-2-(perfluorophenyl)ethan-1-one **3.30** and 2,2-dichloro-1-(1-methyl-1*H*-indol-3-yl)-2-(perfluorophenyl)ethan-1-one **3.31** were

confirmed through the X-ray single crystal analysis. Crystals of **3.30** and **3.31** were grown through very slow evaporation of the solution of the product in DCM/petrol.

A)



B)

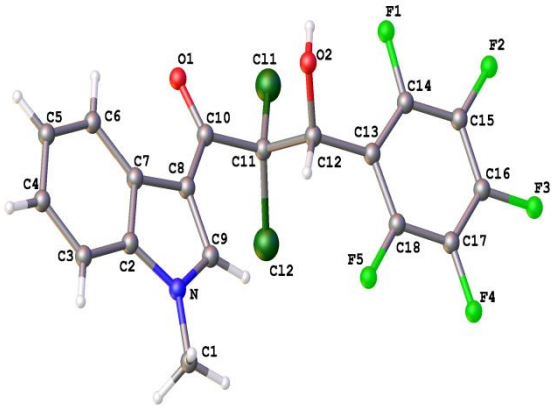


Figure 3.5 X-ray crystal structure of **3.30** (A) and **3.31** (B)

Diethyl 2-(1,1-dichloro-2-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-2-hydroxymalonate **3.33** was also identified by X-ray crystallography (Figure 3.6).

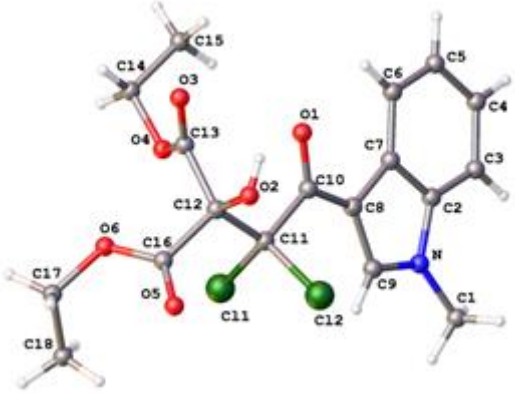


Figure 3.6 X-ray crystal structure of diethyl 2-(1,1-dichloro-2-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-2-hydroxymalonate

3.8 Conclusions

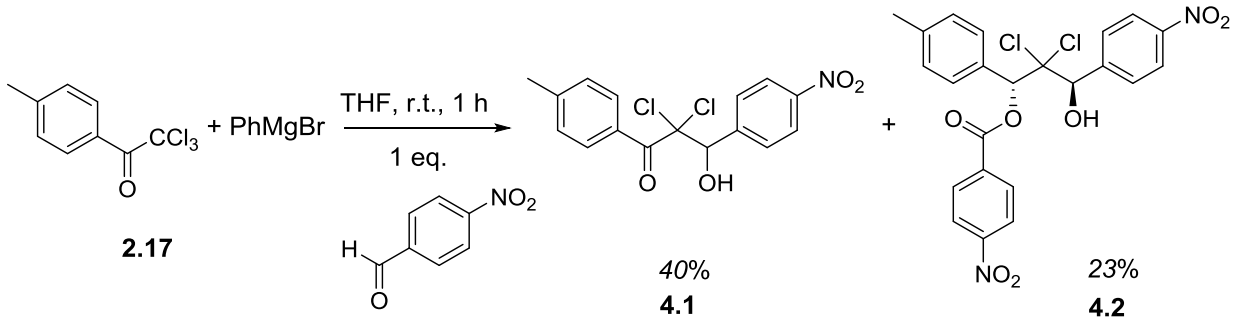
Enolates generated by SET reaction of 2,2,2-trichloroaryl and heteroarylethanones with PhMgBr have been reacted with carbonyl electrophiles to give functionalised 2,2-dichloroketones. 2,2-dichloroheteroaromatic ketones found to be low to moderate yield whilst the 2,2-dichloroarylketones isolated in excellent yield.

Electronic effect was found to affect the generation of aryl and furan enolates over the Grignard mediated SET process. In the case of 2,2,2-trichloroindole ethanones, the indole enolates formation was controlled by the indole type used.

Chapter 4 Grignard SET Initiated Aldol-Tishchenko Reactions

4.1 Introduction

Whilst examining the reaction of **2.17** with PhMgBr and aromatic aldehydes, as described in Chapter 3, we observed that addition of one equivalent of 4-nitrobenzaldehyde at room temperature to the enolate of **2.17** gave a new product not previously observed. Purification of the reaction products by column chromatography gave not only the expected β-hydroxy ketone **4.1**, but also a minor compound **4.2**. Compound **4.2** was identified through ^{1}H NMR spectroscopy and mass spectrometry, showing the incorporation of two *para*-nitro substituted aromatic rings.



Scheme 4.1 Reaction of **2.17** with PhMgBr and 4-nitrobenzaldehyde

The structure of the **4.2** was confirmed through X-ray single crystal diffraction (Figure 4.1). Crystals of **4.2** were grown by slow evaporation from petrol (done by Mr. Ali H. Essa). Solution of the crystal structure showed that **4.2** was produced as a single regio- and diastereoisomer, the 1,3-diol having an *anti* configuration.

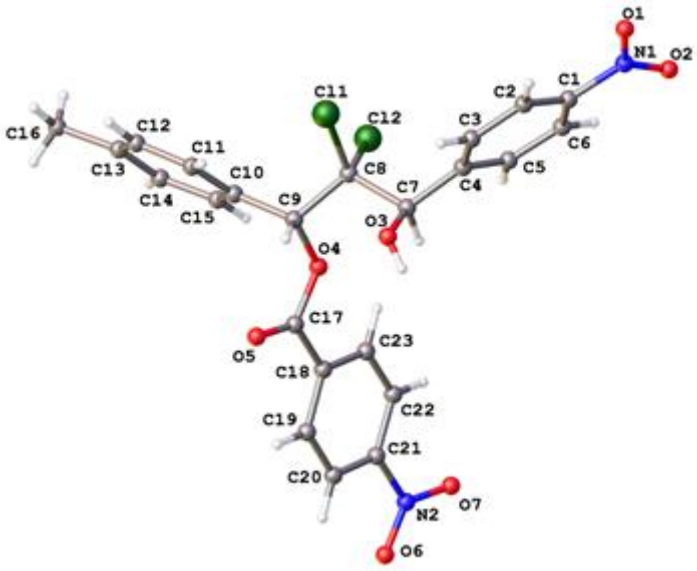
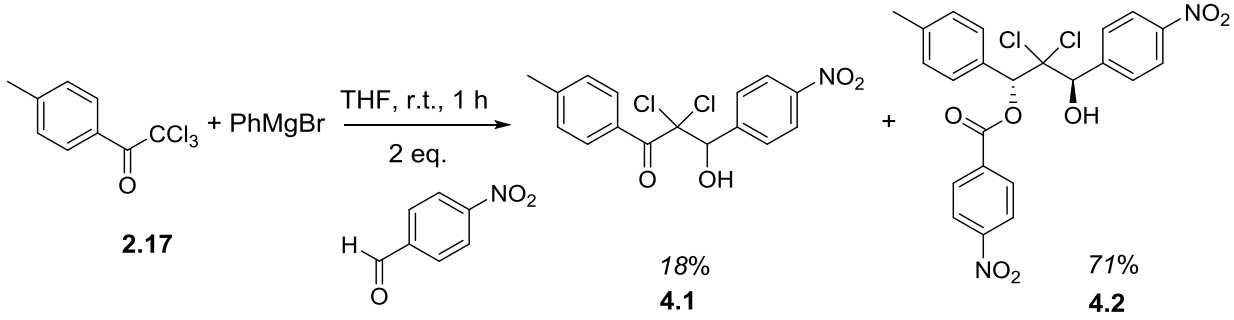


Figure 4.1 X-ray crystal structure of 2,2,-dichloro-3-hydroxy-3-(4-nitrophenyl)-1-(4-tolyl)propyl 4-nitrobenzoate **4.2**

Being interested by this result, we decided to further investigate this reaction. Since the structure of 1,3-diol **4.2** incorporates two molecules of aryladehyde, we postulated that the yield could be increased by doubling the equivalents of 4-nitrobenzaldehyde.

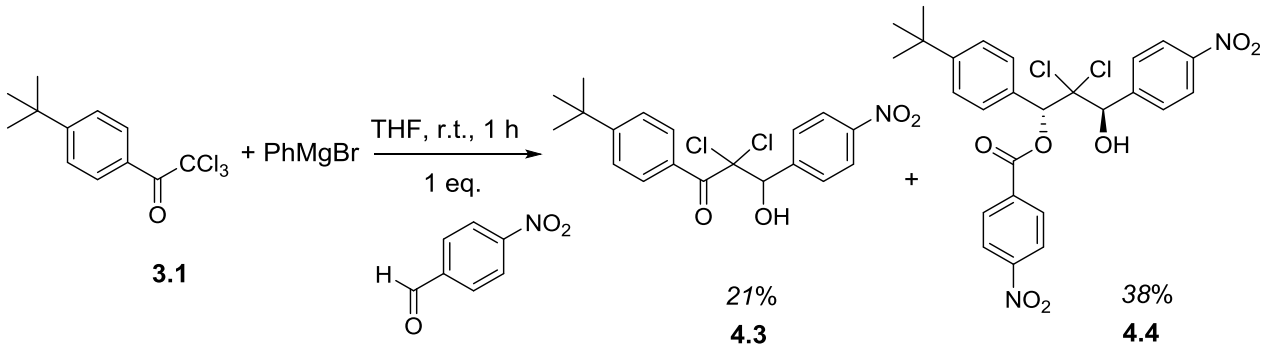
Quenching the enolate of **2.16** with two equivalents of 4-nitrobenzaldehyde afforded 71% of the 1,3-diol **4.2** whilst the expected β-hydroxy ketone **4.1** was isolated in an 18% yield.



Scheme 4.2 Reaction of **2.17** with PhMgBr and 2 eq. of 4-nitrobenzaldehyde

According to this result, it is likely that **4.1** is an intermediate in the formation of 1,3-diol monoester **4.2**. We then decided to examine other substrates in this reaction.

Therefore analogous to the previous reaction procedures given, quenching of the reaction mixture of 1-(4-*t*-butylphenyl)-2,2,2-trichloroethan-1-one **3.1** and PhMgBr with 4-nitrobenzaldehyde afforded 1-(4-*t*-butyl)-2,2-dichloro-3-hydroxy-3-(4-nitrophenyl)propan-1-one **4.4** as the major product in the ratio of 2 : 1 to the corresponding β-hydroxy ketone **4.3**.



Scheme 4.3 Reaction of **3.1** with PhMgBr and 4-nitrobenzaldehyde to give **4.3** and **4.4**

Examination of the ^{13}C NMR spectrum of **4.4** showed that the product is a single regioisomer. Single crystals were grown through very slow evaporation of the solution of **4.4** in petrol-DCM where the X-ray crystallography confirmed that **4.4** is a single diastereoisomer as the *anti*-1,3-diol.

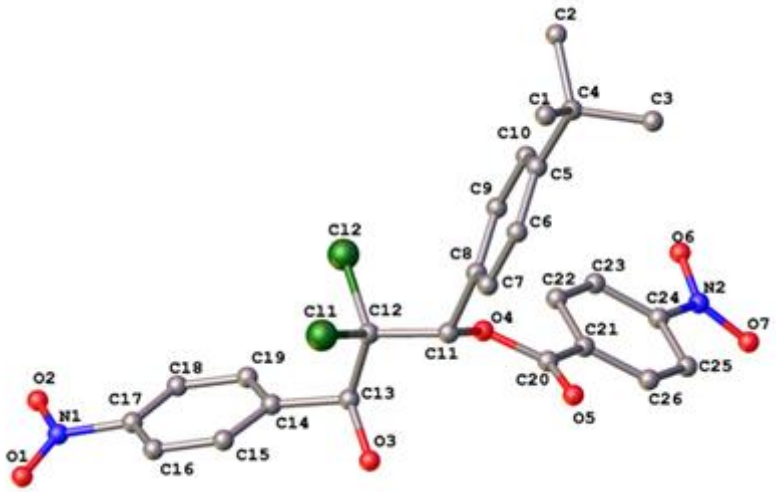
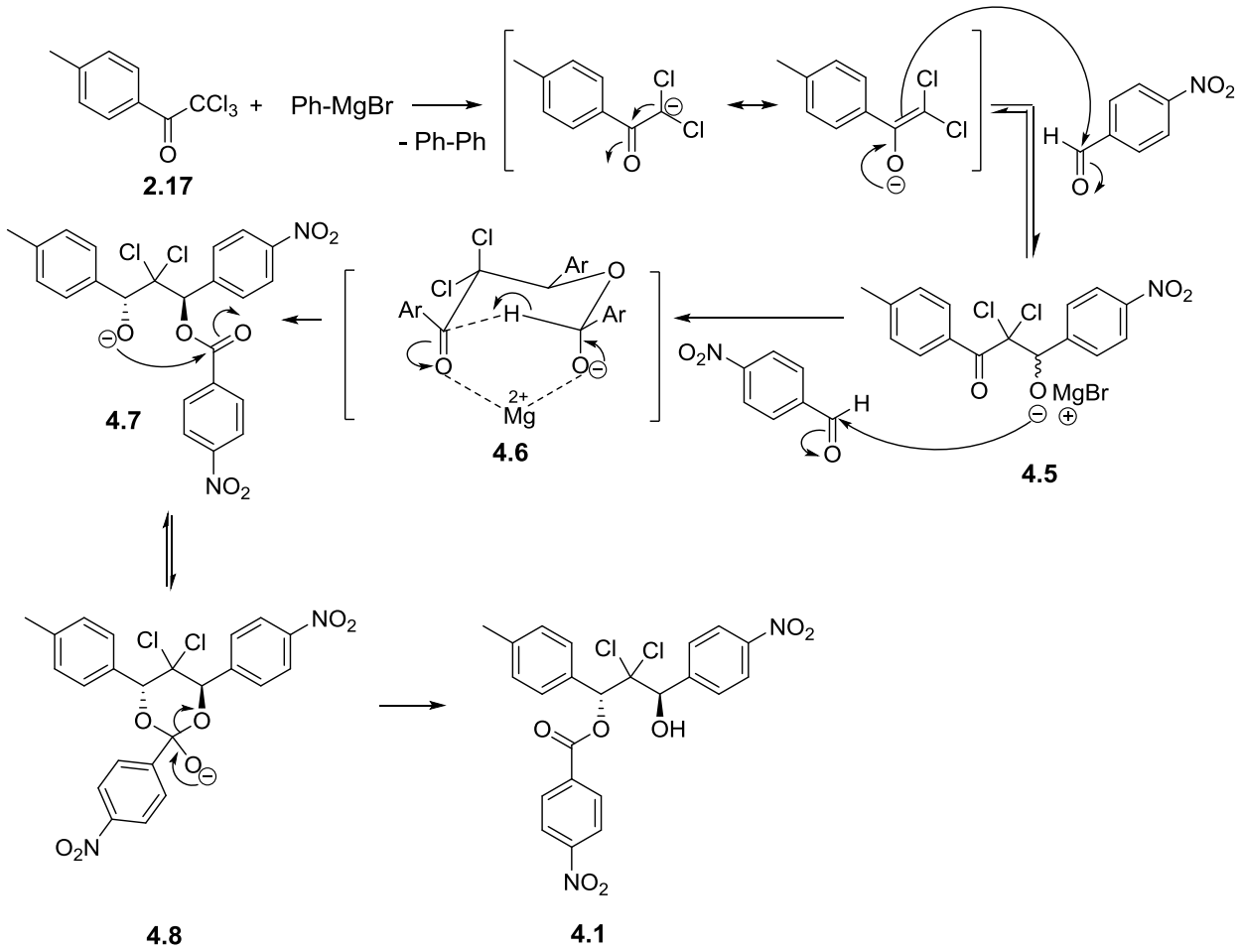


Figure 4.2 X-ray crystal structure of 1-(4-*t*-butyl)-2,2,-dichloro-3-(4-nitrophenyl)-1,3-diol monoester **4.4**

Repeating the reaction whilst increasing the added 4-nitrobenzaldehyde to two equivalents gave only **4.4** in 88% yield, with no **4.3** observed.

4.2 Reaction Mechanism

We propose that the enolates initially formed by the reaction of 2,2,2-trichloroarylethanones with PhMgBr react with one molecule of aryl aldehyde to give a β-hydroxy ketone. This step is proposed to be reversible[185] due to the fact that 1 : 1 ratio of quenching of enolate **3.16** with 4-nitrobenzaldehyde gave Aldol-Tishchenko product. The β-hydroxy ketone then reacts with a second aryl aldehyde to give a hemiacetal which then undergoes a magnesium chelated diastereoselective hydride transfer *via* six membered transition state producing **4.6**. Rearrangement of *anti*-1,3-diol monester, **4.7** to **4.1** then occurs through an ester migration. Overall this process is very similar to an Aldol-Tischenko reaction.[107-113]

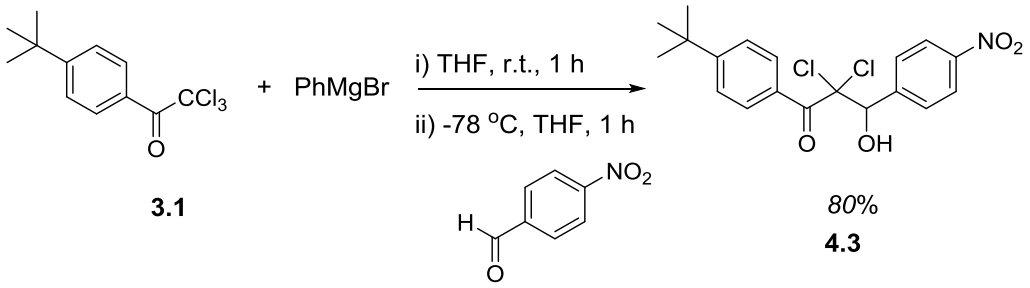


Scheme 4.4 Aldol-Tishchenko mechanism for the synthesis of **4.1**

To further examine this process we performed the Grignard mediated reduction of **3.1** and addition of 4-nitrobenzaldehyde under a range of temperature conditions.

We envisaged that at low temperatures, addition of 4-nitrobenzaldehyde to the enolate formed from **3.1** would produce only the β-hydroxyketones. Then at higher temperatures, the β-hydroxy ketones would react more 4-nitrobenzaldehyde to give Aldol-Tishchenko products.

In order to test this idea, we first tried to prepare β-hydroxy ketones selectively. Addition of one equivalent 4-nitrobenzaldehyde to the enolate of **3.1** at -78 ^{o}C, followed by subsequent aqueous work up, yielded a white solid in 80% yield which was identified as the corresponding β-hydroxy ketone **4.3** by ^{1}H NMR spectroscopy. There were no Aldol-Tishchenko products observed under these conditions.



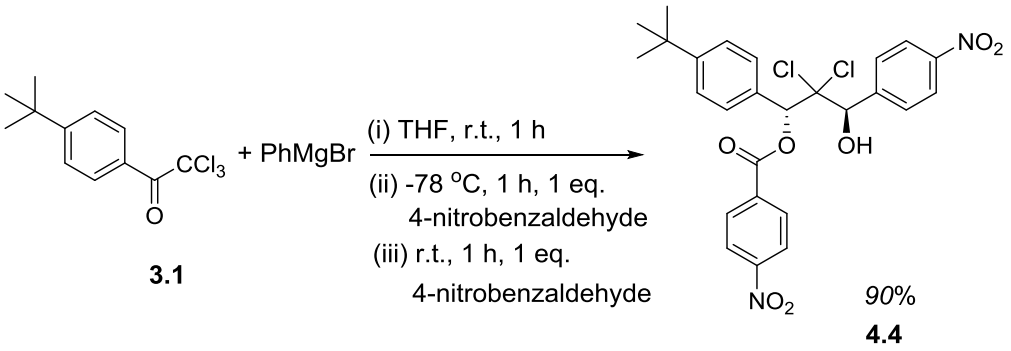
3.1

80%

4.3

Scheme 4.5 Synthesis of 1-(4-*t*-butylphenyl)-2,2-dichloro-2-hydroxy-2-(4-nitrophenyl)ethan-1-one **4.3**

To get a high yield of the **4.4**, two equivalents of 4-nitrobenzaldehyde were used to react with the enolate formed from **3.1**. The reaction was done as before with the addition of one equivalent of 4-nitrobenzaldehyde at -78 °C. This was followed by leaving the mixture to warm to r.t. before further adding a second equivalent of 4-nitrobenzaldehydeto give the aldol-Tishchenko product **4.4** in 90% yield.



3.1

90%

4.4

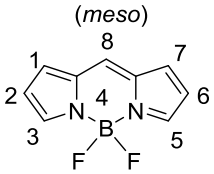
Scheme 4.6 Reaction of **3.1** with PhMgBr and 2 eq. 4-nitrobenzaldehyde under different temperature

4.3 Conclusions

The formation of β-hydroxy ketones or *anti* 1,3-diol monoesters was shown to be controllable. Grignard mediated reduction of aromatic 2,2,2-trichloroethanones at -78 °C gave exclusively β-hydroxy ketones whilst low temperature generation of a β-hydroxy ketone followed by room temperature addition of an additional equivalent of 4-nitrobenzaldehyde gave very good yields of *anti* 1,3-diols.

Chapter 5 Introduction

4,4-Difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacenes (BODIPYs) are well known organic fluorophores and have found considerable application in spectroscopically demanding situations. This is because BOIDPYs have high extinction coefficients in the visible range and emit relatively sharp fluorescence bands with high quantum yield.[114] Furthermore, the photophysical properties of BODIPY can easily be tuned to that required by the specific application by modification of the dipyrromethene core (Scheme 5.1).



5.1

Scheme 5.1 Core structure of a BODIPY

BODIPY dyes have been used in a wide range of applications. Some examples include:

1. Use as anion or cation selective chemosensors[115-117] through the introduction of chelating groups capable of binding analytes such as metal ions. This application is based on the ‘’off-on’’ switching of fluorescence emission of the BODIPYs because of a PET (Photoinduced Electron Transfer) process. In the presence of metal cations, non-fluorescent BODIPYs (off condition) will emit light (on condition), as the electron transfer from the chelating agent to the BODIPYs (PET process) is blocked through metal-ligand complex formation.

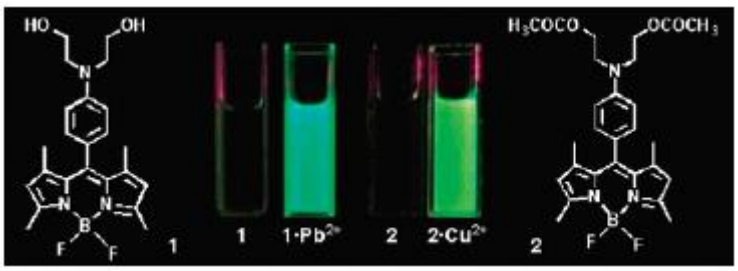
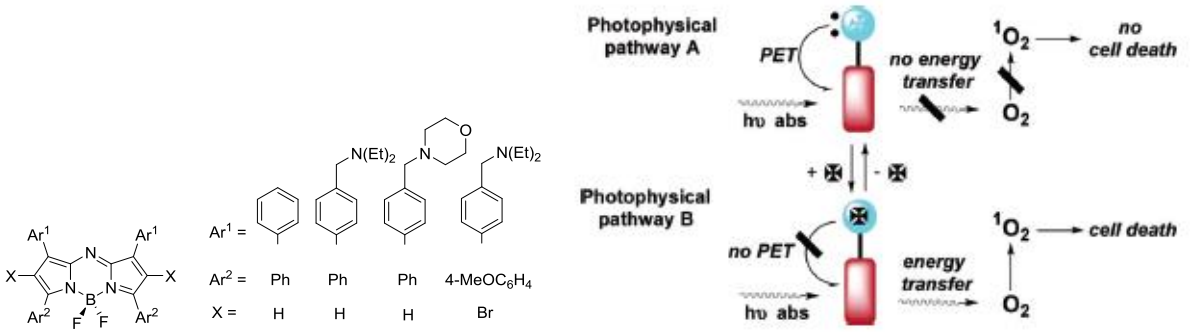


Figure 5.1 BODIPYs for Pb(II) and Cu(II) selective chemosensor
(Adapted from Qi, X., Jun, E. J., Xu, L., Kim, S. J., Hong, J. S. J., Yoon, Y. J., Yoon, J. *J. Org. Chem*. **2006**, *71*, 2881-2884)

2. Photodynamic therapy.[118-121]

BODIPYs have been used as a photosensitizer in a non-invasive technique for cancer tumor treatment. O'Shea demonstrated generation of singlet oxygen (cell killer) by blocking the PET process of halogenated BODIPYs, which exhibited light within the body's therapeutic window (650-900 nm).



Red rectangle: Photosensitizer, Blue circle: substrate-specific receptor

Figure 5.2 Aza-BODIPYs for PDT
(Adapted from McDonnell, S. O., Hall, M. J., Allen, L. T., Byrne, A., Gallagher, W. M., O'Shea, D. F. *J. Am. Chem. Soc*. **2005**, *127*, 16360-16361)

3. Use in biological labelling of proteins or biomolecules[122-124]

BODIPYs have also been developed as a selective protein dyes. Due to their easily structural modification properties, incorporation of BODIPY with selective amino acid functionality groups such as succinimidyl ester or isothiocyanate, turns these dyes to probe lysines specifically. Changing the reactive site to iodoacetamide, malemaide or thiosulfate/thiosulfonate produces cysteine specific dyes.

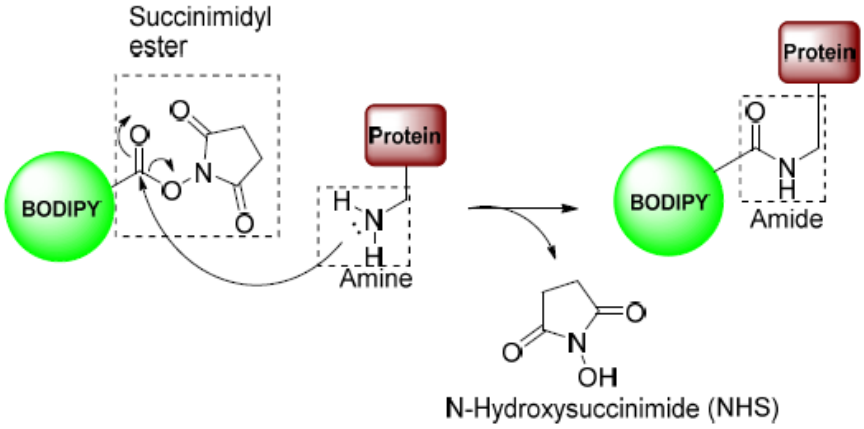


Figure 5.3 Protein labelling by succinimidyl ester BODIPY dyes
(Adapted from Rezende, L. C. D., Emery, F. S. *Orbital Elec. J. Chem*. **2013**, *5*, 62-83)

4. Photovoltaic system[125-126]

   Development of BODIPYs as a dye-sensitized solar cell (DSSC) is still on going. One example of a DSSC was produced by Kolemen and co-workers. Using a long conjugated BODIPY containing *meso* substituted electron acceptor groups, Kolemen demonstrated charge transfer within the BODIPY. This process was used to facilitate the generation of electricity.

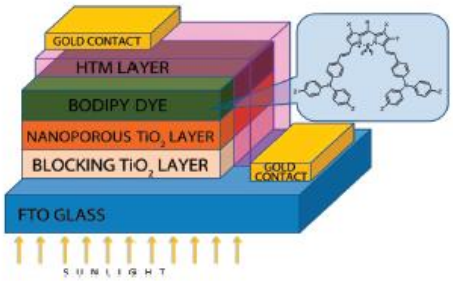
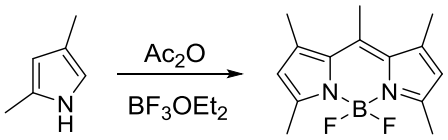


Figure 5.4 BODIPY for solar cells
(Adapted from Kolemen, S., Cakmak, Y., Ela, S. E., Altay, Y., Brendel, J., Thelakkat, M., Akkaya, E. U. *Org. Lett*. **2010**, *12*, 3812-3815)

5.1 Synthetic Approaches to BODIPYs

BODIPYs were first synthesised by Treibs and Kreuzer (1968).[128] Reaction of 2,4-dimethyl pyrrole with acetic anhydride and of $BF_3.OEt_2$ afforded a highly fluorescent molecule 4,4-difluoro-4-bora-3*a*,4*a*-diaza-1,3,5,7,8-pentamethyl-*s*-indacene **5.3**, as the product.



5.2 **5.3**

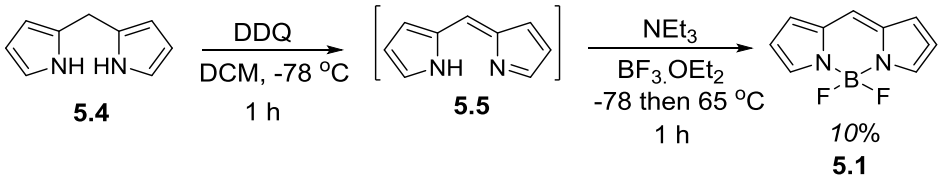
Scheme 5.2 Treibs and Kreuzer BODIPY synthesis

5.1.1 Modern synthetic route to BODIPYs

A. Oxidative routes to BODIPY

BODIPY synthetic methodologies involve the chelation of dipyrromethenes with BF_2. Dipyrromethenes can be accessed by condensation of pyrroles with aldehydes under Lewis acid catalysis, followed by oxidation using a benzoquione oxidant.[129] During most BODIPY syntheses the dipyrromethenes are not isolated, as they are unstable, especially for *meso* unsubstituted dipyrromethenes.[130]

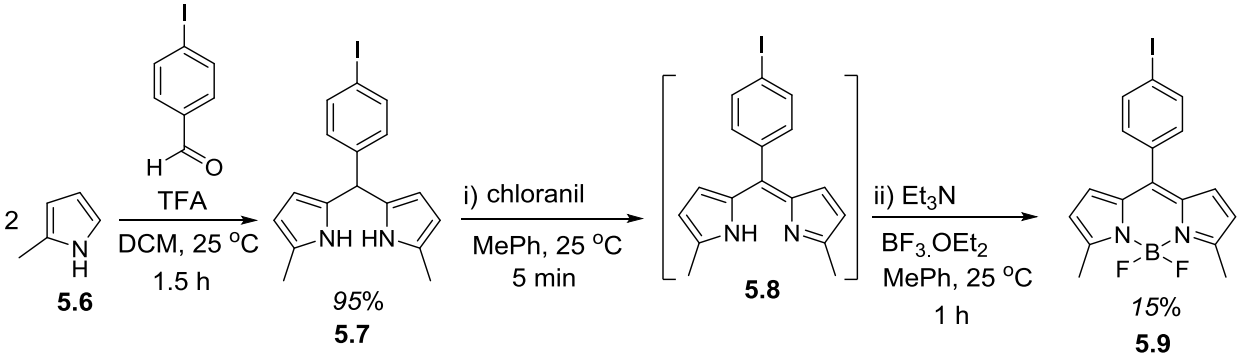
Tram and co-workers demonstrated the synthesis of unsubstituted BODIPY **5.1** *via* dipyrromethane **5.4**. Low temperature oxidation of **5.4** by DDQ, gave intermediate **5.5**. This was then subsequently chelated with $BF_3.OEt_2$ at low temperature to afford 10% of the unsubstituted BODIPY **5.1**.[128]



5.4 **5.5** **5.1**

Scheme 5.3 Synthesis of unsubstituted BODIPY

Meso-substituted BODIPYs can also be synthesised *via* condensation of pyrroles with benzaldehydes followed by oxidation and BF_2 chelation (Scheme 5.4).[114]

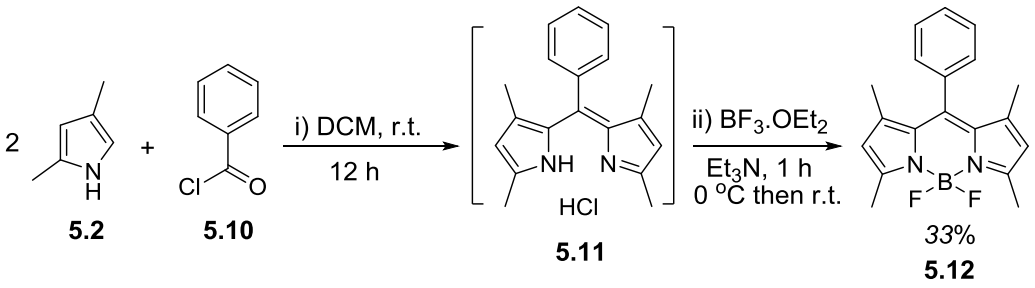


5.6 **5.7** **5.8** **5.9**

Scheme 5.4 Synthesis of **5.9** via condensation/oxidation route

B. Non-oxidative routes to BODIPY

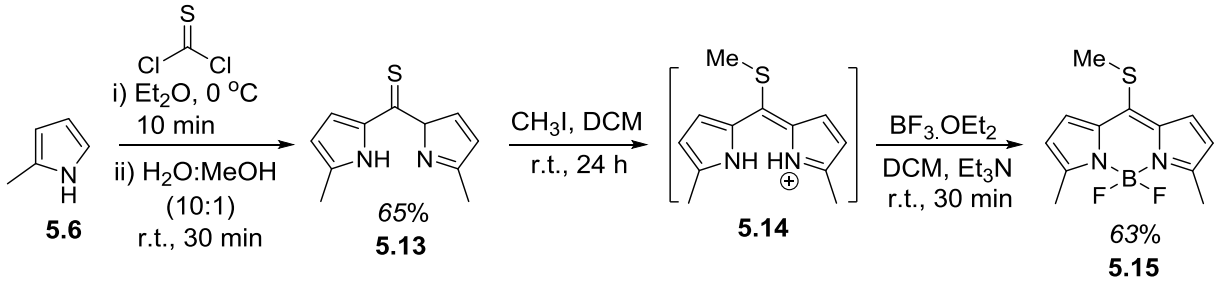
Another approach of synthesising BODIPYs is *via* condensation of pyrroles with acid chlorides. This approach is advantageous as no oxidation steps are needed.[114] In this method, BODIPYs are prepared in one-pot with no isolation of the dipyrromethanes. Dipyrromethenes are chelated with $BF_3.OEt_2$ leading to the desired BODIPY. An example is the synthesis of **5.12** from 2,4-dimethylpyrrole **5.2** and benzoyl chloride **5.10** (Scheme 5.5).[131]



5.2 **5.10** **5.11** **5.12**

Scheme 5.5 Synthesis of BODIPY **5.12** *via* condensation with acid chlorides

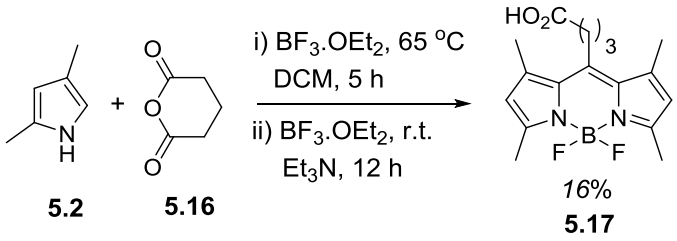
Goud has also synthesised *meso*-thiomethyl substituted BODIPY **5.15**, from 2-methyl pyrrole with thiophosgene ($CSCl_2$) followed by thiol methylation and chelation by $BF_3.OEt_2$.[132]



Scheme 5.6 Synthesis of *meso*-thiomethyl BODIPY

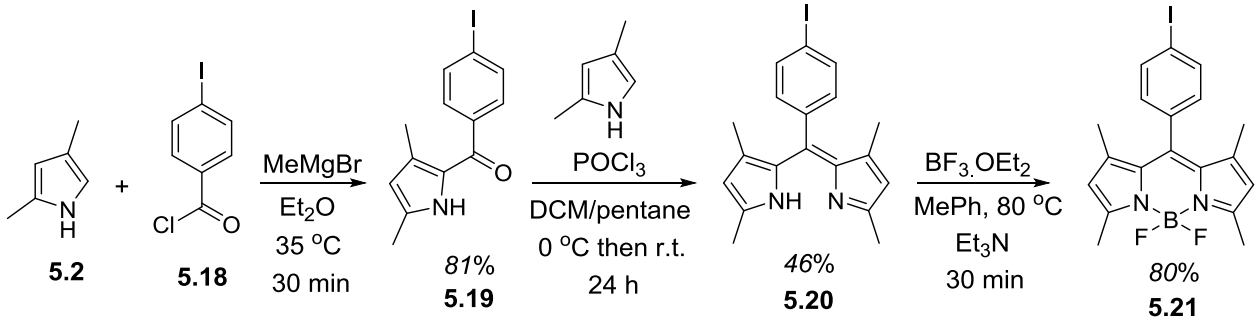
BODIPYs such as **5.15** can then be used as starting materials in the synthesis of more complex *meso*-substituted BODIPYs by exchange of the SMe group with other substituents.[133]

Meso-substituted BODIPYs have also been accessed *via* condensation of pyrrole with acid anhydrides. Bittman and co-workers prepared *meso* substituted BODIPY **5.17**, from 2,4-dimethylpyrrole **5.2** with glutaric acid **5.16**. This **5.17** offered useful features as the free carboxylic acid could be used for further functionalisation.[134]



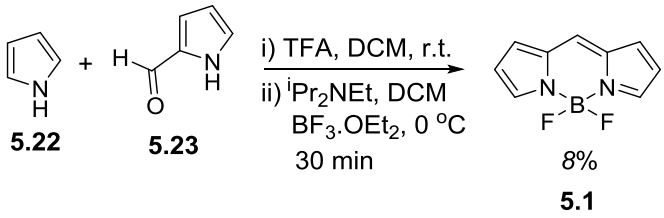
Scheme 5.7 Synthesis of BODIPY **5.17** from 2,4-dimethylpyrrole and **5.16**

Another non-oxidative route of accessing BODIPYs is through stepwise approach. Tahtaoui has demonstrated this in the synthesis of 1,3,5,7-tetramethyl-8-(4-iodophenyl)BODIPY **5.21** (Scheme 5.8). The diaryl ketone **5.19** was produced by reaction of 2,4-dimethylpyrrole **5.2** with acid chloride **5.18** in the presence of MeMgBr. Condensation between **5.19** with another molecule of 2,4-dimethylpyrrole **5.2** catalysed by $POCl_3$ leading to dipyrromethene **5.20**. Chelation the **5.20** with $BF_3.OEt_2$ then gave **5.21**.[135]



Scheme 5.8 Synthesis of **5.21** via ketopyrroles modular step

A similar approach was used by Schmitt in order to synthesise unsubstituted BODIPY **5.1**. In this case, he used 2-formylpyrrole **5.22** in a condensation reaction with pyrrole **5.23** catalysed by TFA, followed by BF_2 chelation leading to BODIPY **5.1**.[136]

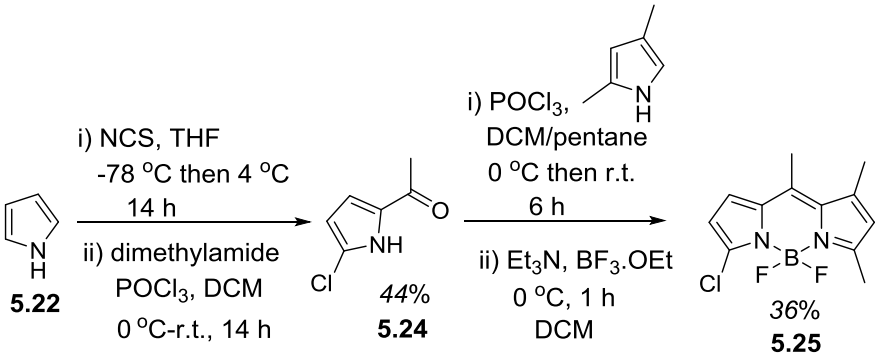


Scheme 5.9 Synthesis of BODIPY **5.1**

5.1.2 Stepwise synthesis of unsymmetrial BODIPYs

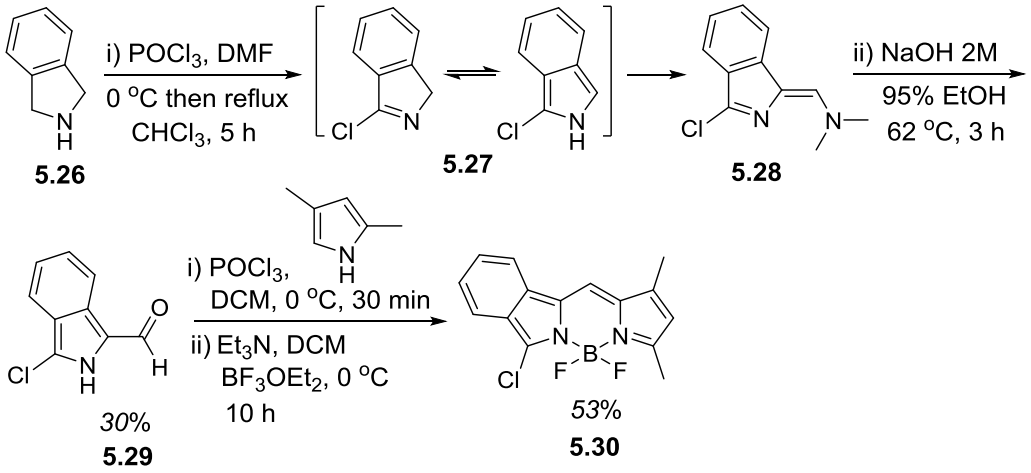
Most of the routes to BODIPY's discussed allow to access to symmetrical systems (i.e. both pyrroles are the same). In order to construct unsymmetrical BODIPYs an alternative route is required.

Leen has demonstrated the synthesis of unsymmetric BODIPY **5.25** through a stepwise approach. 2-Chloro substituted keto pyrrole **5.24** was formed by chlorination of 1-*H*-pyrrole **5.22** with *N*-chlorosuccinimide (NCS), which was subsequently followed by a Vilsmeier acylation. Keto pyrrole **5.24** then reacted with 2,4-dimethylpyrrole followed by BF_2 chelation gave the corresponding unsymmetrical BODIPY **5.25** in 36% yield (Scheme 5.10).[137]



Scheme 5.10 Synthesis of unsymmetrical BODIPY **5.25** via ketopyrroles stepwise approach

Another example of unsymmetrical BODIPY synthesis is the synthesis of benzo-fused BODIPY **5.30** from 3-chloro-1-formylisoindole **5.29** with 2,4-dimethylpyrrole under $POCl_3$ catalysis (Scheme 5.11).[138]



Scheme 5.11 Synthesis of benzo-fused unsymmetric BODIPY **5.30**

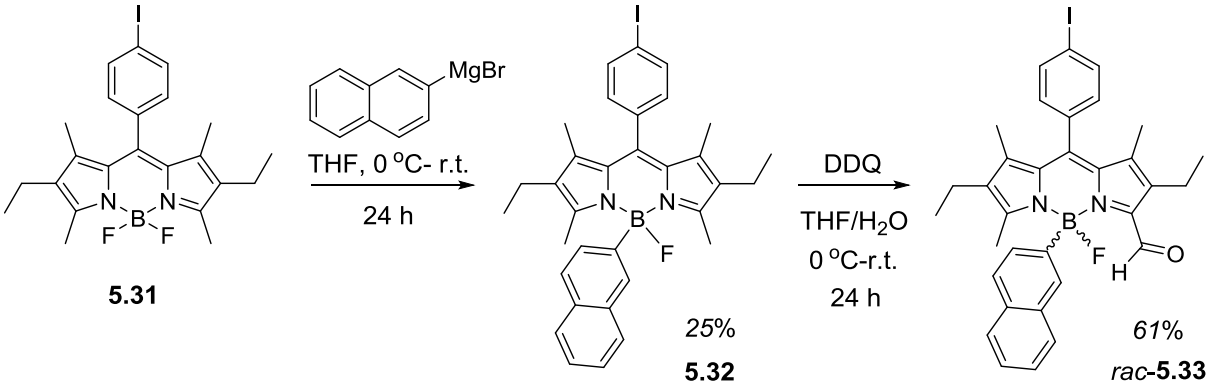
5.2 Chiral BODIPYs

Chiral fluorophores are interesting for their intrinsic chiro-optical properties as well as for use as potent optical sensors of chirality. Chiral BODIPYs are rare, with most of the enatiomerically pure BODIPYs known consisting of a dipyrromethene core decorated with chiral substitutents.[139-141] Very few examples are known involving chirality within the core of the BODIPY. Examples of chiral BODIPYs developed so far include boron centred and helical chirality.

5.2.1 Boron centred chiral BODIPYs

The first example of a boron centred chiral BODIPY was **5.33** developed by Ziessel.[139] In his work, Ziessel reacted iodo-BODIPY **5.31** with napthylmagnesium bromide resulting in a mono-substitution of the BF_2 unit producing BODIPY **5.32**. Through selective

oxidation of the 3-methyl substituent of BODIPY **5.32** with DDQ, chiral BODIPY **5.33** was formed (Scheme 5.12). Conversion to the aldehyde results in desymmetrisation of the BODIPY molecule and the introduction of a stabilising H bond to fluorine.



Scheme 5.12 Ziessel synthesis of *rac*-**5.33**

Chiral **5.33** then separated into its enantiomers through chiral HPLC. Investigation using Circular Dichroism (CD) spectroscopy showed that each of the enantiomers gave mirror image CD spectra (Figure 5.5) demonstrating the chiral nature of **5.33**.

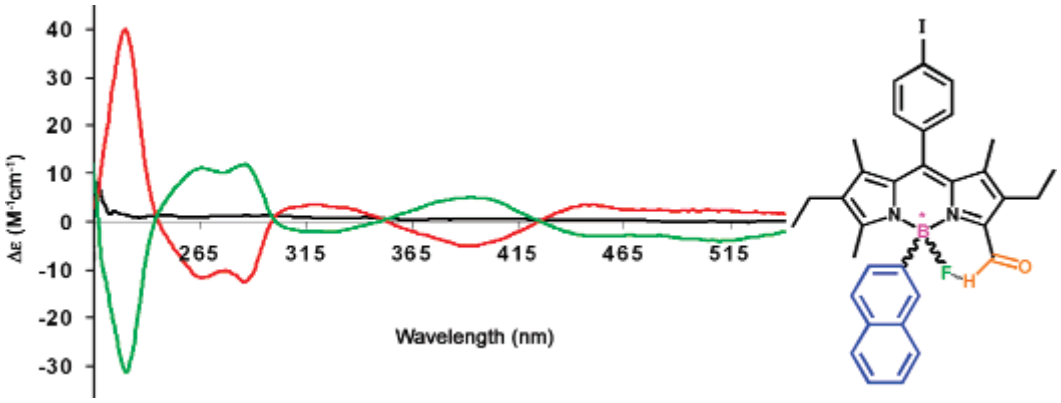
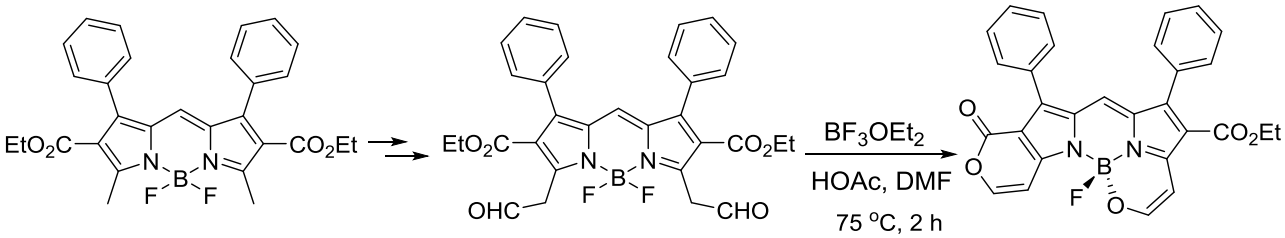


Figure 5.5 CD spectra of both enantiomers of **5.33** (black line is for racemic **5.33**) (adapted from Haefele, A., Zedde, C., Retailleau, P., Ulrich, G., Ziessel, R. *Org. Lett*. **2010**, *12*, 1672-1675)

Shandura in his study of 3,5-dimethyl functionalisation of BODIPY **5.34** has prepared BODIPY **5.35**. Heating BODIPY **5.35** in the presence of Lewis acid ($BF_3.OEt_2$) produced cyclic BODIPY **5.36** which shows boron centred chirality. However, Shandura did not report resolution of BODIPY **5.36** or any investigation into its chiro-optical properties.[142]



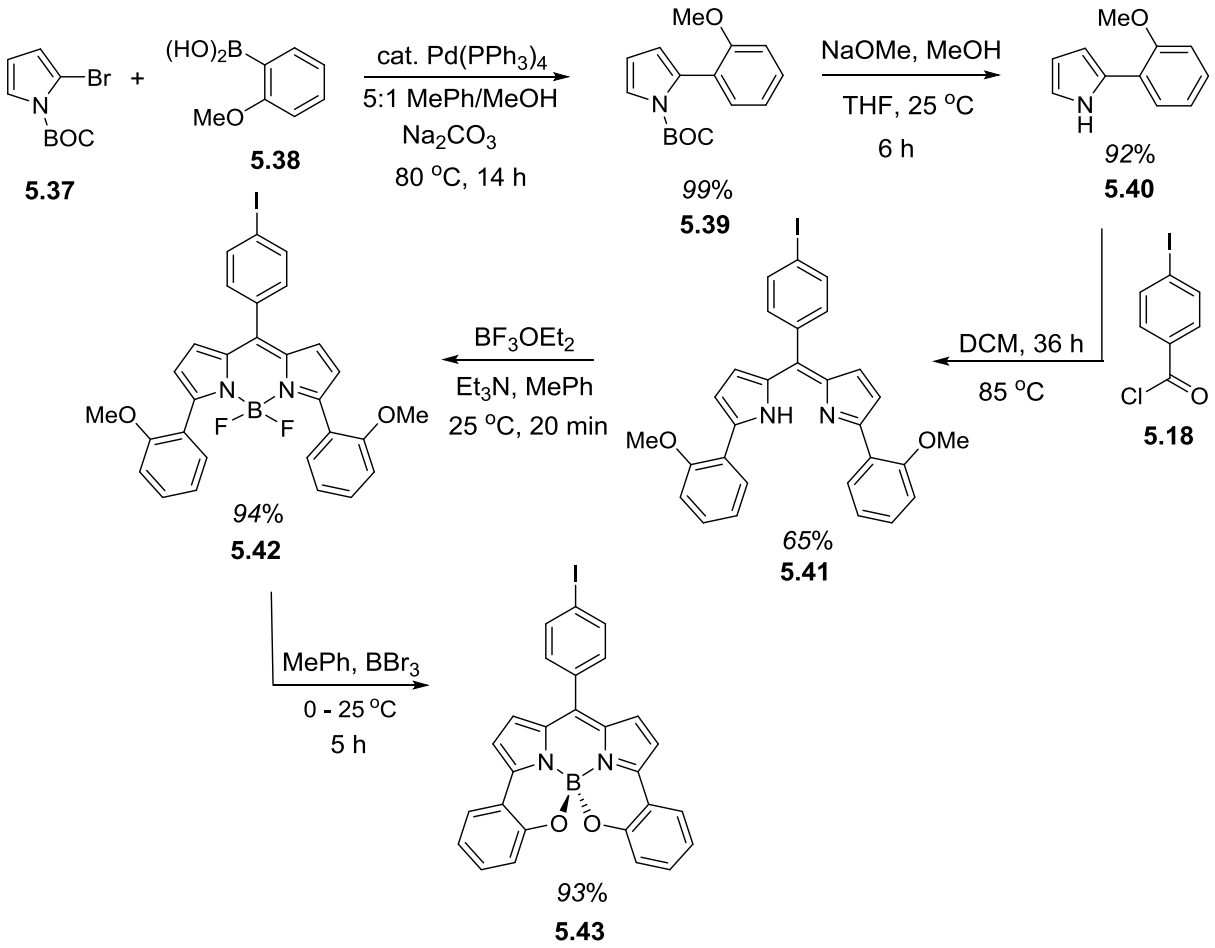
5.34 **5.35** *40%* **5.36**

Scheme 5.13 Synthesis of **5.36**

5.2.2 Helically chiral BODIPYs

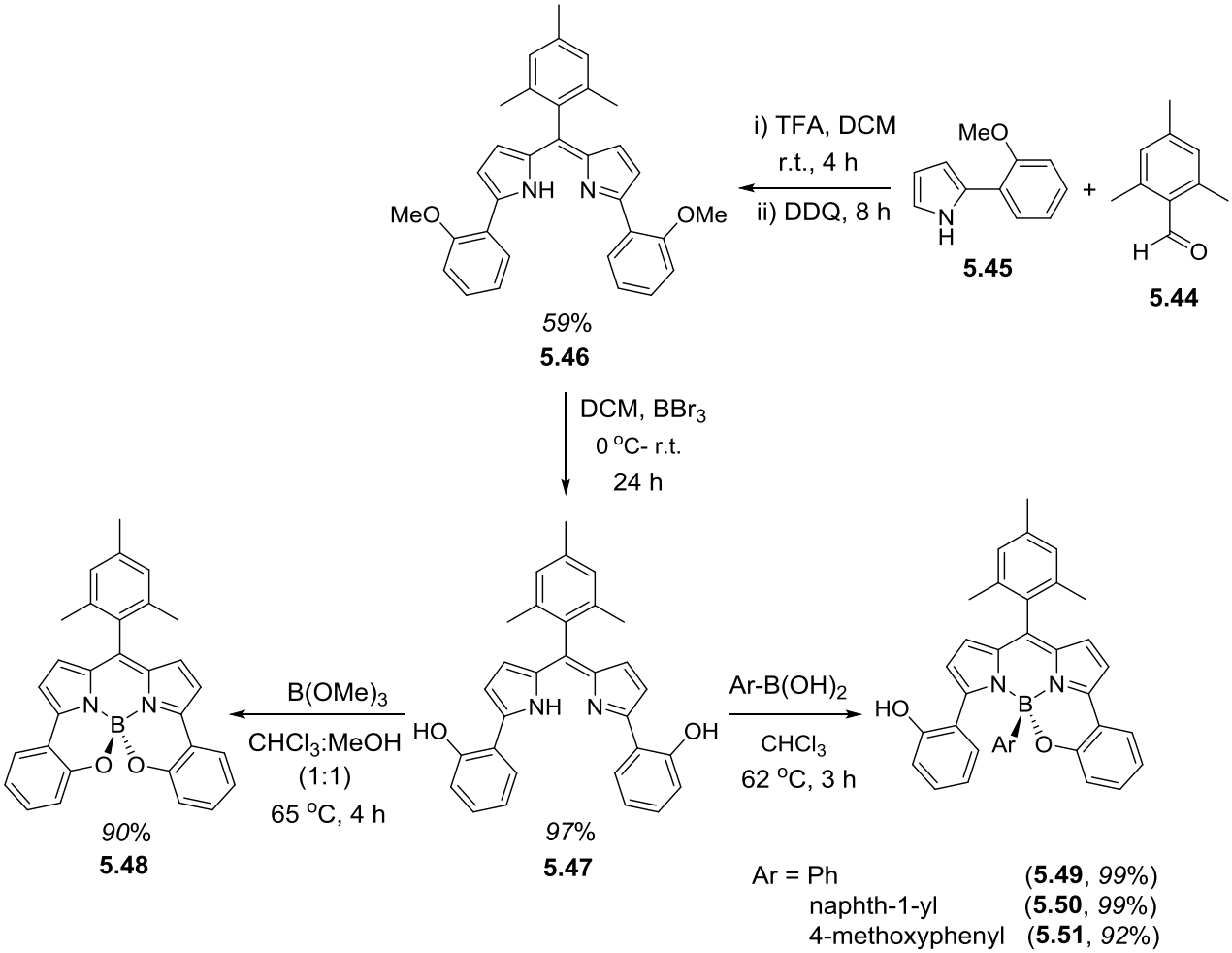
Burgess in his effort to red shift the emission maxima of the BODIPY fluorophore examined a number of approaches to increase the conjugation. BODIPY **5.43** was synthesised by a Suzuki coupling reaction between 2-bromo-*N*-BOC pyrrole **5.37** and 2-methoxy phenyl boronic acid **5.38** followed by Boc de-protection and condensation of pyrrole **5.40** with aryl chloride **5.18**. However the introduction of a free rotatable aryl groups onto the 3,5 positions of the BODIPY diminished the fluorescence quantum yield (φ_F) of **5.42**.[143]

Demethylation of **5.42** with BBr_3 resulted in the replacement of the B-F bonds with B-O bonds. This locked the two aryl groups by making a B-O chelated system. This C2 symmetrical BODIPY (**5.43**) shows helical chirality.[144] The chelation of the bottom aryl rings also rigidifies the system and extends conjugation resulting in an increase in φ_F and a red shift of the absorption and emission maxima.



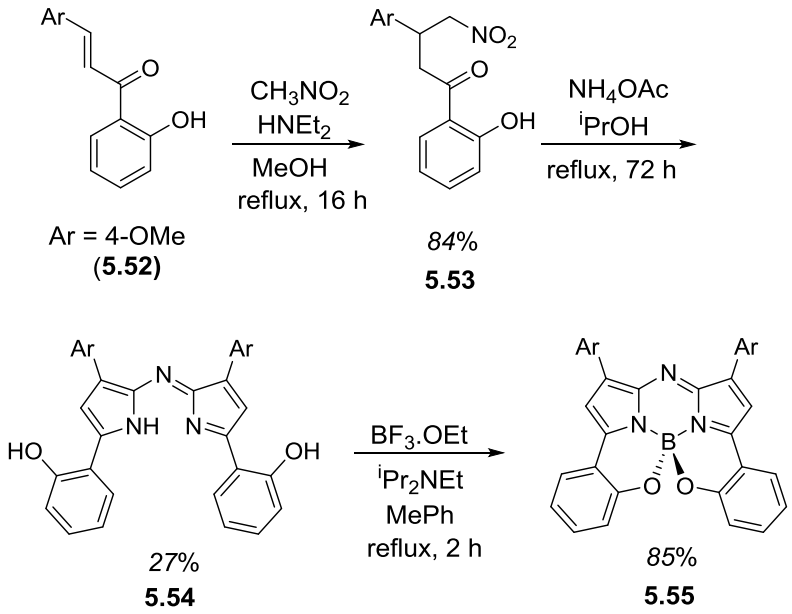
Scheme 5.14 Synthesis of helically chiral BODIPY **5.43**

Similar to this was the system studied by Ikeda.[145] Following demethylation of dipyrrin **5.46** using BBr_3, Ikeda reacted dipyrrin **5.47** directly with $B(OMe)_3$ leading to BODIPY **5.48**.[146] Alternatively the use of arylboronic acid gave the *N,N,O,C*-boron chelated chiral BODIPYs **5.49**-**5.51**, incorporating an R group on the central boron atom (Scheme 5.15). These racemic BODIPYs were not separated to study their chiral properties.



Scheme 5.15 Boron centred chiral BODIPYs

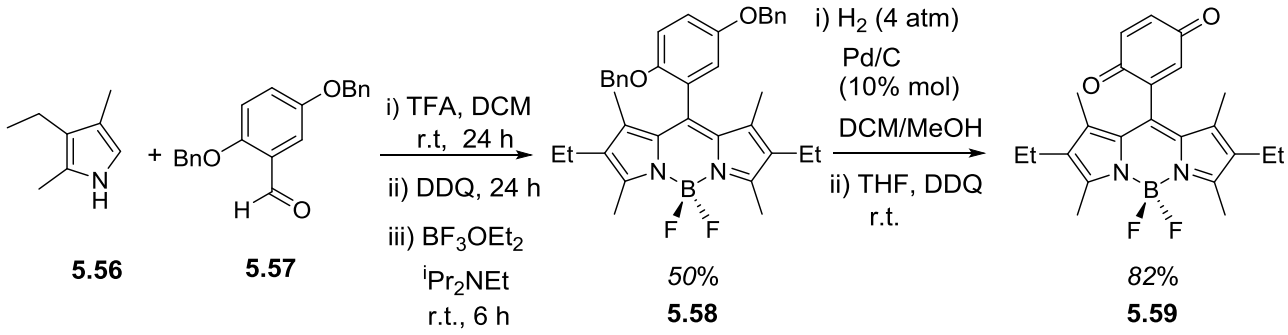
A similar *N,N,O,O*-boron chelated aza-BODIPY was synthesised by O'Shea and Burgess. After the synthesis of the azadipyromethene core (**5.54**) followed by chelation with $BF_3.OEt_2$ resulted a helically chiral aza-BODIPY **5.55**.[141]



Scheme 5.16 Synthesis of helically chiral aza-BODIPY **5.55**

5.2.3 Axially chiral BODIPYs

Benniston and co-workers in their attempt to develop re-usable redox-responsive fluorescence probes have synthesised the symmetric quinone substituted BODIPY **5.59**.[147]



Scheme 5.17 Synthesis of quinone substituted BODIPY

The ^{19}F NMR spectrum of a typical BODIPY appears as a quartet with *J* (^{19}F-^{11}B) = 32 Hz. In BODIPY **5.59**, the ^{19}F NMR spectra appeared as doublet of quartets splitting pattern with *J* (^{11}B-$^{19}F_a$) = 33.5 Hz, *J* (^{11}B-$^{19}F_b$) = 31.0 Hz and *J* (^{19}F-^{19}F) = 108.7 Hz (Figure 5.6), indicating that the fluorines are diastereotopic.

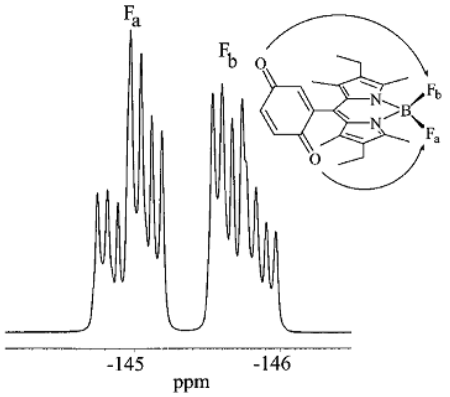
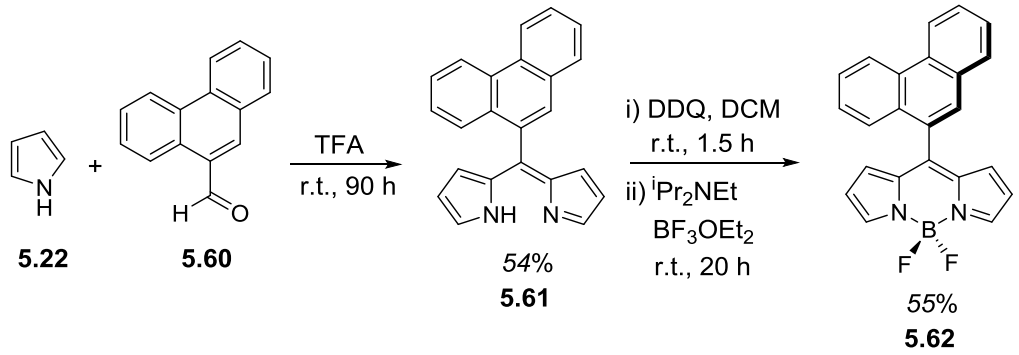


Figure 5.6 ^{19}F NMR spectrum of **5.59**

Further investigation to the ^{19}F NMR spectrum of BODIPY **5.59** through variable temperature (VT) ^{19}F NMR experiments (from 303 to 378 K) showed no sign of broadening or coalescence of the peaks. This indicated that restricted rotation of the benzoquinone/BODIPY bond, even at high temperature results in the fluorine atoms being magnetically inequivalent.

A similar phenomenon was also observed in BODIPY **5.62**. Although BODIPY **5.62** did not contain methyl substituents at the 1 and 7 positions, the *meso*-phenanthrene substituent showed no free rotation which could be seen by the double quartet in the ^{19}F NMR spectrum of BODIPY **5.62** (Figure 5.7).[148]



5.22 **5.60** *54%* **5.61** *55%* **5.62**

Scheme 5.18 Synthesis of BODIPY **5.62**

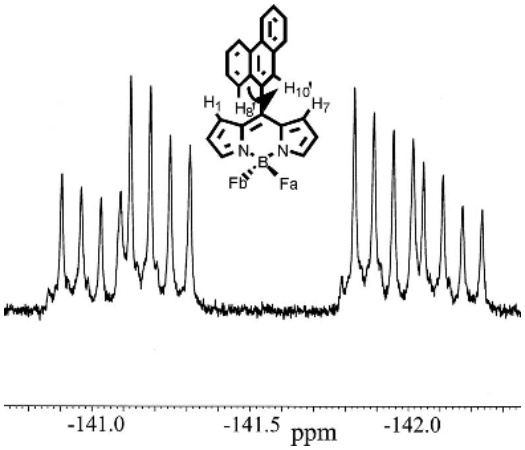
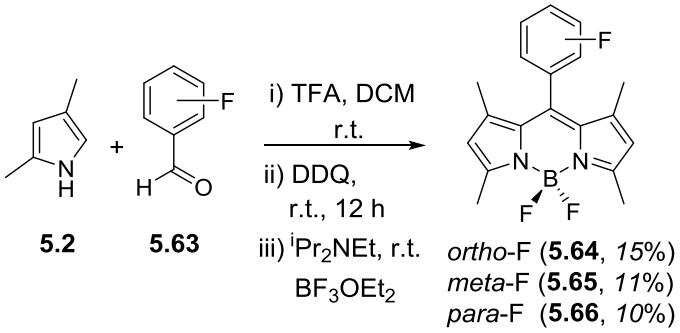


Figure 5.7 ^{19}F NMR spectrum of BODIPY **5.62**

Another BODIPY showing restricted rotation was found by Benniston *et al*. when studying BODIPYs with *meso*-aromatic substituents. In his study into the effect of fluorine substitution of the *meso*-aryl ring of BODIPYs, Benniston found that BODIPY **5.64** showed restricted rotation through steric clash of the *ortho*-fluorophenyl and the 1,7-dimethylated dipyrromethene core. The ^{19}F NMR spectra of BODIPY **5.64** appeared as double quartet consistent to that of diastereotopic fluorines, therefore indicating restricted rotation. *Meta* and *para*-substituted aryl groups did not show any diastereotopicity in the ^{19}F NMR.[149]

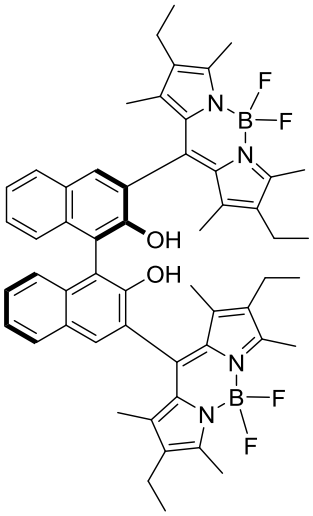


Scheme 5.19 Synthesis of *meso*-aryl substituted BODIPYs **5.64**-**5.66**

5.3 BODIPY as a Chiral Sensing Agent

BODIPYs have been used in chiral sensing.[150] This has mainly been done by decorating the BODIPY core with chiral BINOL ligands capable of chelating to a chiral analyte.

Beer employed BODIPY **5.67** to differentiate between (*R*)- and (*S*)-1-phenylethyl amine (PEA).[151] By measuring the fluorescence as a function of the concentration of the chiral analyte, it was possible to determine the %ee of a solution of PEA by fluorescence.



5.67

Scheme 5.20 (*R*)-BINOL substituted BODIPY **5.67**

Interaction of BODIPY **5.67** with the chiral amine most probably involves hydrogen bonding (R-OH….NR_3) or the formation of tight ion pairs (RO^-…HNR_3^+) between the BINOL and the amine.

Beer found that the interaction between BODIPY **5.67** with (*S*)-PEA gave higher sensitivity than that of (*R*)-PEA (Figure 5.8). This therefore indicated the suitability of BODIPY **5.67** as a potential sensor of percent enantiomeric excess (%ee).

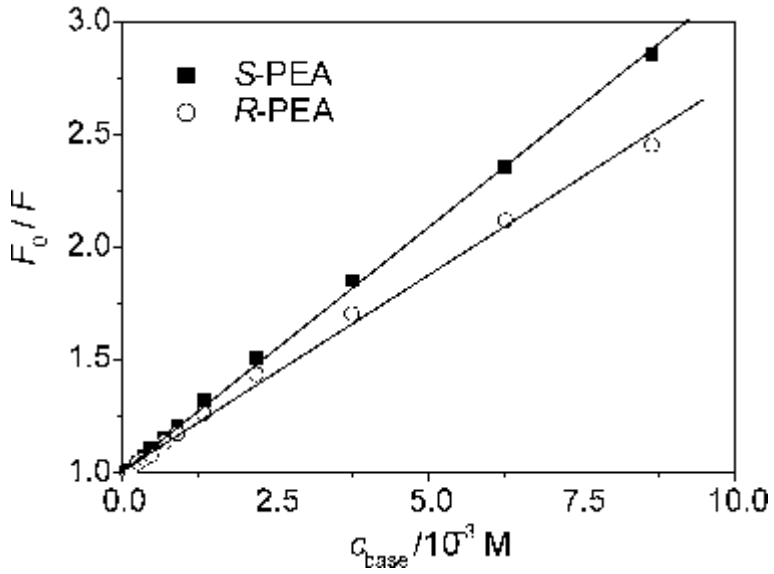


Figure 5.8 Quenching of BODIPY **5.68** with (*S*)-PEA and (*R*)-PEA in acetonitrile (Adapted from Beer, G., Rurack, K., Daub, J. *Chem. Commun*. **2001**, 1138-1139)

5.4 Conclusions

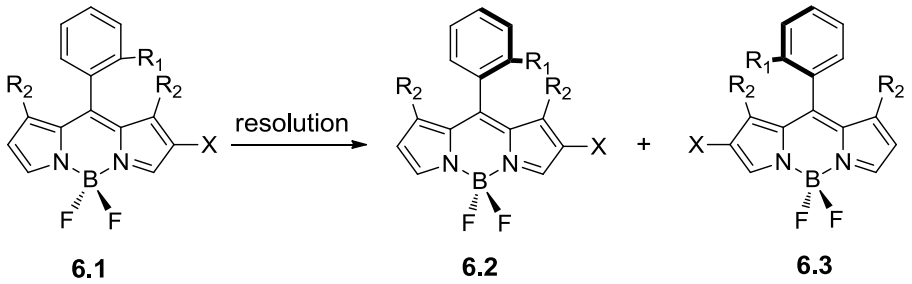
Although 4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacenes (BODIPYs) have been widely used for fluorescence applications, the use of BODIPYs as sensor of enantiomeric excess is very rare. Meanwhile synthesis of chiral BODIPYs is also very limited, with a small number of chiral BODIPYs developed hitherto based around boron centred or helical chirality.

Chapter 6 Synthesis of Axially Chiral BODIPYs

6.1 Introduction

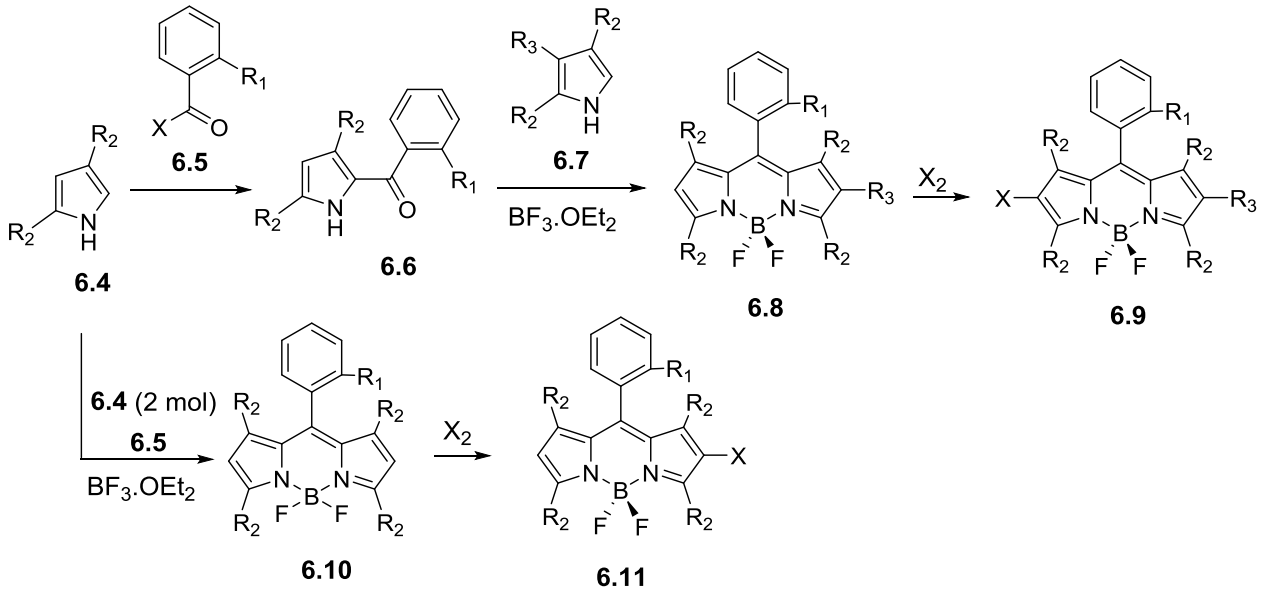
Chapter 5 overviewed the evidence for axial chirality in BODIPYs involving a 1,7-methylated core with a *ortho*-substituted aromatic at the *meso* position. These BODIPY systems have restricted rotation of the *meso* group as indicated by the diastereotopic fluorine atoms. Therefore, we decided to focus on axially chiral BODIPYs in order to investigate routes to novel chiral BODIPY systems, since no axially chiral BODIPY syntheses had been described.

Our design of an axially chiral BODIPY is shown in Scheme 6.1. Restricted rotation of the *meso*-aryl group combined with a desymmetrisation of the dipyrromethene core will afford two enantiomeric BODIPYs.



Scheme 6.1 Our design for an axially chiral BODIPY

Therefore we have designed a synthetic route for BODIPYs of this type approach. This will involve the synthesis of a series of BODIPYs such as **6.1** followed by resolution of racemic axially chiral BODIPY to give single enantiomers.

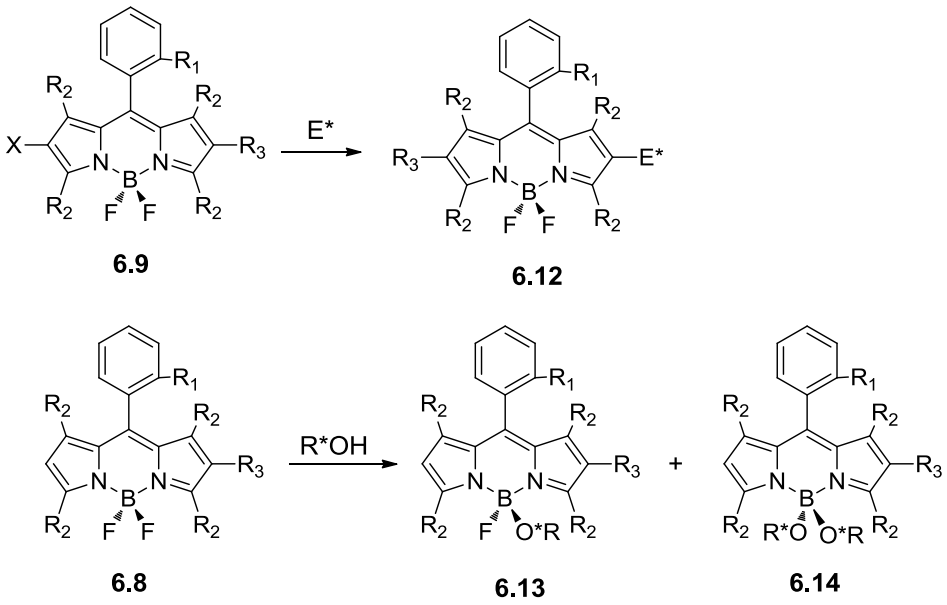


Scheme 6.2 General scheme for the synthesis of axially chiral BODIPYs

Our first approach toward the synthesis of axially chiral BODIPYs involved the synthesis of diaryl ketone **6.6**. **6.6** can be prepared from pyrrole **6.4** by condensation with acid chloride **6.5**. Condensation of **6.6** with different pyrroles **6.7** followed by *in situ* BF_2 chelation would give racemic axially chiral BODIPYs **6.8**.

Meanwhile symmetrical BODIPY **6.10** could also be accessed from diaryl ketone **6.6**. Mono-halogenation onto the dipyrrromethene core would generate halogenated axially chiral BODIPYs **6.11**. These halogenated BODIPYs (**6.9** and **6.11**) would then provide versatile starting materials for doing further functionalization of the BODIPYs.

Resolution of racemic chiral BODIPYs could then be done by converting enantiomeric BODIPYs into diastereomers. Substitution of the halogen BODIPY **6.9** or **6.11** with an enantiopure functional group could generate diastereomeric BODIPY **6.12**. Alternatively the fluorine(s) of **6.8** could be replaced by OR* or $(OR^*)_2$ with chiral alcohols or diols (Scheme 6.3). The diastereomeric BODIPYs then be separated through column chromatography.

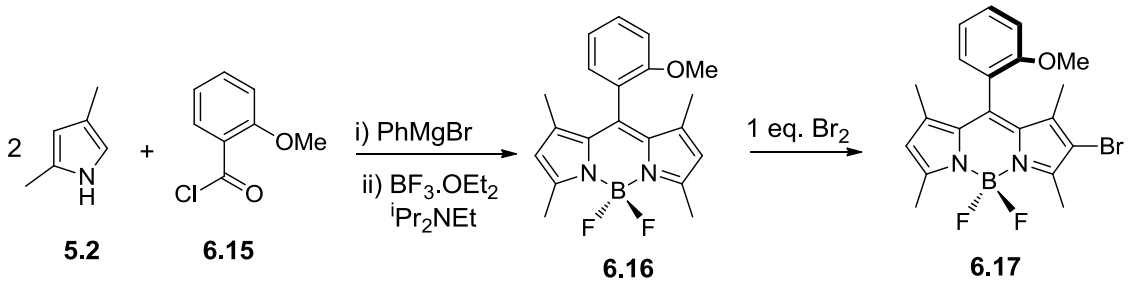


6.9 **6.12** **6.8** **6.13** **6.14**

Scheme 6.3 Proposed resolution of axially chiral BODIPYs

6.2 First Generation of Synthesis of Axially Chiral BODIPYs

Our first approach was to desymmetrise a BODIPY such as **6.16** by mono-bromination (Scheme 6.4).

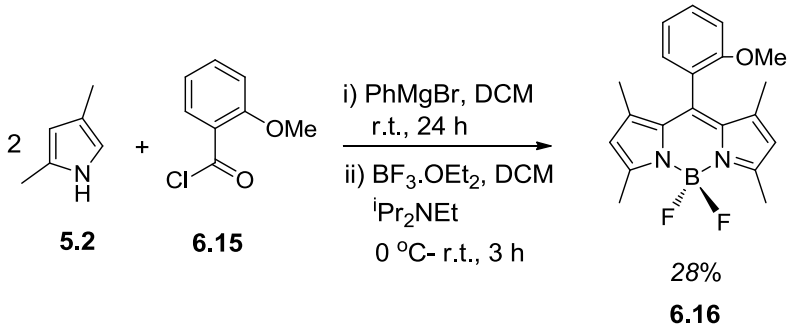


Scheme 6.4 Synthesis of axially chiral BODIPY **6.17**

6.2.1 BODIPY 6.16

Synthesis of BODIPY **6.16** was performed using PhMgBr as a base in order to N-protect pyrrole **5.2** followed by reaction with 2-methoxy benzoylchloride (**6.15**) and then BF_2 chelation.[131]

Overnight reaction of 2,4-dimethylpyrrole, PhMgBr and 2-methoxybenzoyl chloride, followed by addition of $BF_3.OEt_2$ and Hünig's base gave BODIPY **6.16**.



Scheme 6.5 Synthesis of BODIPY **6.16**

Purification through column chromatography afforded BODIPY **6.16** in 28% yield.[152] Single crystal X-ray diffraction of **6.16**, after crystal growth through slow evaporation of a solution of **6.16** in DCM/Petrol, confirmed the structure as the desired BODIPY product. Compound **6.16** crystalised to give a monoclinic $P12_1/c1$ system. In the crystal structure the steric clash of the *ortho*-methoxy group of the *meso*-aryl substituent and the 1,7-dimethyl groups forces the *meso*-aryl group orthogonal to the BODIPY core.

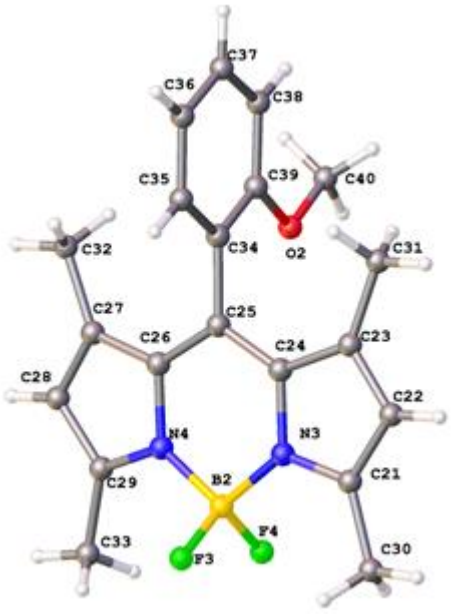


Figure 6.1 X-ray crystal structure of **6.16**

The ^{19}F NMR spectrum of **6.16** showed 16 lines suggesting that the two fluorine atoms are diastereotopic. This is consistent with restricted rotation of the *meso*-aryl group.[147-149]

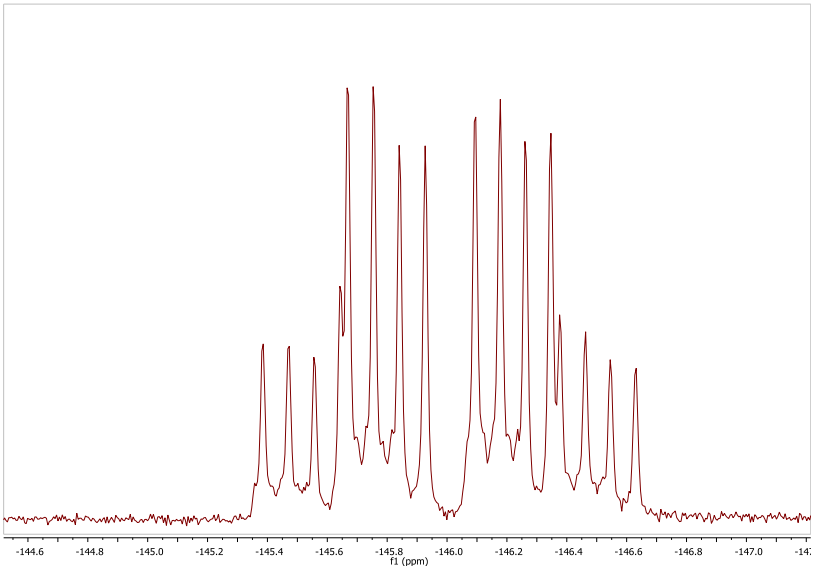
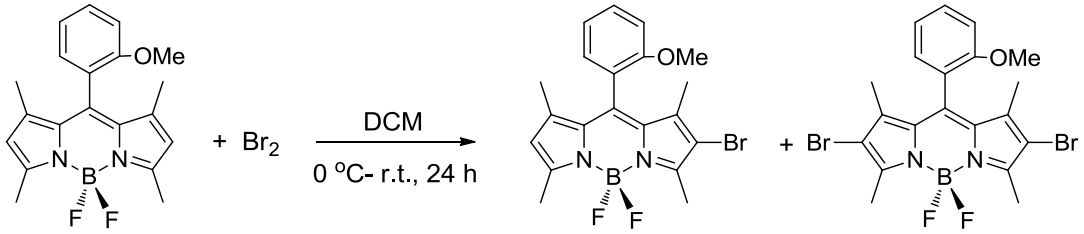


Figure 6.2 ^{19}F-NMR spectrum of **6.16** in $CDCl_3$

As shown in Figure 6.2, the fluorine spectrum showed a splitting pattern of two double quartets. As the two fluorine atoms are non-equivalent, the coupling of the two fluorine atoms (I= 1/2) resulted doublet splitting pattern with the $J(^{19}F\text{-}^{19}F)$ = 110.8 Hz. Further coupling of each ^{19}F to ^{11}B (I = 3/2) then gave quartets $J(^{19}F\text{-}^{11}B)$ = 33.7 Hz and $J(^{19}F\text{-}^{11}B)$ = 32.8 Hz.

6.2.2 Mono-halogenation of BODIPYs

Desymmetrisation of the BODIPY **6.16** should lead to an axially chiral system. We therefore decided to employ a halogenation reaction, such as bromination, to desymmetrise **6.16** by differentiating the two pyrrole units of the BODIPY. This will also allow further functionalization as bromo-BODIPYs have shown to be reactive as coupling partners in Heck and Suzuki reactions.[153]



Scheme 6.6 Bromination of BODIPY **6.16**

Our initial attempts at mono-bromination of **6.16**, following literature approaches, gave the dibrominated BODIPY **6.18** as the major product.[154-157] To optimise the reaction for the desired mono-bromo BODIPY **6.17**, we therefore decreased the quantity of Br_2 to 1.1 equivalents.[158] However this also yielded a 1:1 mixture of mono- to dibromo BODIPYs (entry 2). The optimal conditions were found to be a ratio of 1:1 starting BODIPY **6.16** to Br_2 giving a 2:2:1 ratio of BODIPYs **6.16**: **6.17**: **6.18** (entry 3). This allowed starting material to be recovered and re-submitted into further the bromination reaction. Whilst simplifying the difficult separation of the mono- and dibromo BODIPYs **6.17** and **6.18**.

Extending the reaction time to 2 days increased the formation of dibromo, so this approach was not continued (entry 4).

Table 6.1 Ratio of non-brominated, mono and di brominated **6.18**

Entry	Ratio of 6.17 to Br_2	Time (h)	Ratio*		
			Recovered **6.16**	**6.17**	**6.18**
1	1:2	24	0	1	4
2	1:1.1	48	1	4	4
3	1:1	24	2	2	1
4	1:1	48	1	5	4

* based on % yield

The ^{1}H-NMR spectrum of BODIPY **6.17** shows 4 signals at 1.44, 1.45, 2.58 and 2.61 ppm corresponded to the four dipyrromethene CH_3 groups. In comparison to that of **6.16** which only showed 2 singlet peaks (1.45 and 2.57 ppm).

Further confirmation of the structure of monobrominated product, **6.17** was achieved by X-ray crystallography. A monoclinic crystal with $P12_1/c1$ symmetry of **6.17** was grown by slow evaporation of solution of **6.17** from DCM/petrol (Figure 6.3). Interestingly, four molecules were present per asymmetric unit cell which were two in each of the (*R*)- and (*S*)-axially chiral configurations.

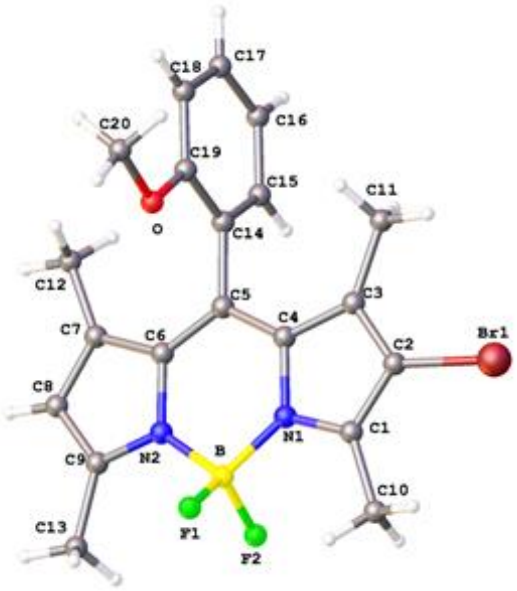


Figure 6.3 X-ray crystal structure of **6.17**

The crystal structure shows the *meso*-aryl group orthogonal to the plane of the BODIPY, indicating steric hindrance between the *meso*-aryl and the two flanking methyl groups.

The ^{19}F NMR spectra of **6.17** showed that expected set of two double quartets arising from the diastereotopic fluorines showing both ^{19}F-^{19}F coupling and ^{19}F-^{11}B coupling.[147-149] The observed ^{19}F NMR spectra complements the ^{1}H NMR and the X-ray crystallography results, showing the chirality of **6.17**.

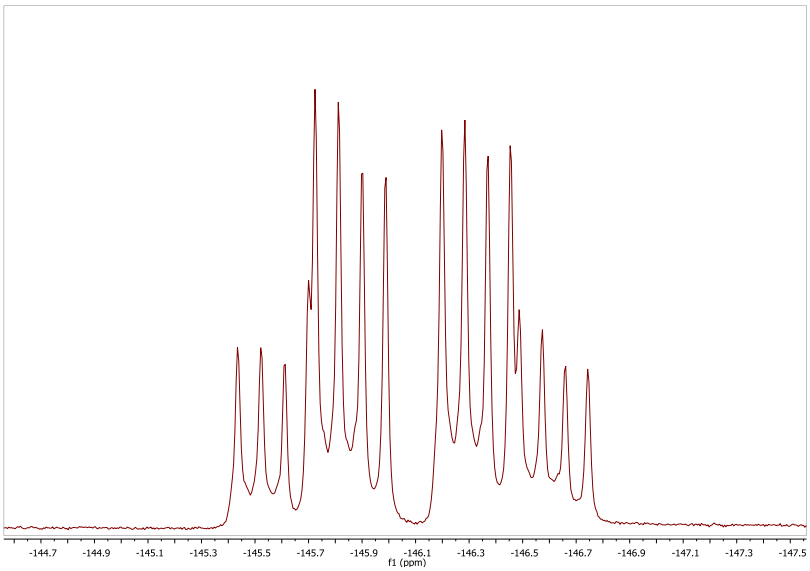


Figure 6.4 ^{19}F NMR spectrum of **6.17**

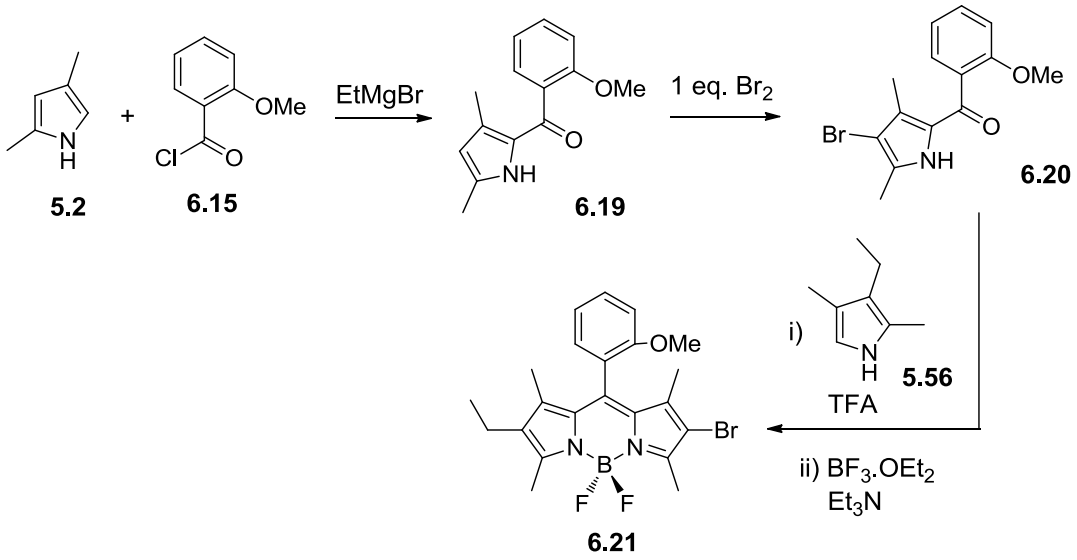
6.2.3 Conclusions

The concept of axially chiral BODIPYs has been successfully demonstrated by the synthesis bromo-BODIPY **6.17** through the regioselective mono-bromination of BODIPY **6.17**.

BODIPY **6.17** has the potential for the synthesis of further axially chiral BODIPY systems through metal catalysed coupling of the aryl halide. However the difficulties in synthesising mono-bromo BODIPY **6.17** suggested that an alternative synthetic approach was needed.

6.3 Modular Synthesis of Axially Chiral BODIPYs

In order to increase the overall yield in the synthesis of the axially chiral BODIPYs, a modular synthesis was planned. This new approach involve the synthesis of ketopyrrole **6.19** followed by bromination reaction to give **6.20**. The axially chiral **6.21** could then be accessed by reaction of **6.20** with 2,4-dimethyl-3-ethyl-1*H*-pyrrole **5.56**.



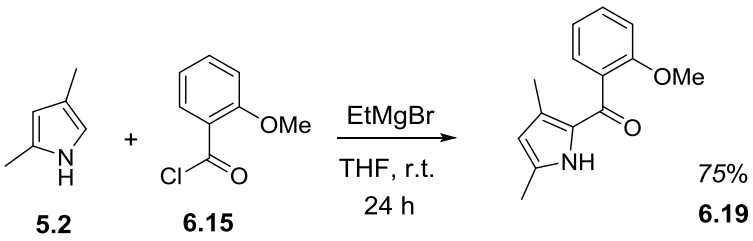
Scheme 6.7 Planned modular synthesis step of preparation **6.21**

This modular approach avoids the low yielding direct bromination reaction shown previously, therefore it should provide a more flexible and higher yielding approach to target BODIPYs.

Bromination of **6.19** would be anticipated to be selective as just one reactive site is available to be brominated. Furthermore through a modular approach, employing different substituted pyrroles in reaction with **6.20** would lead to a range of different chiral BODIPYs.

6.3.1 Synthesis of 1-(2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-methoxyphenyl)methane-1-one 6.19

The synthesis of **6.19** was adapted from the work of Burgess et al.[135] By using EtMgBr as a base, the deprotonated pyrrole **5.2** reacts with 2-methoxybenzoyl chloride **6.15** resulting in a selective C-2 acylation (Scheme 6.8). Pyrrole **6.19** was isolated in high yield from the reaction.



Scheme 6.8 Synthesis of **6.19**

X-ray crystallography analysis of **6.19** confirmed that the substitution of pyrrole **5.2** had taken place at desired C-2 position. Solution of the X-ray crystal structure showed that the **6.19** crystal system and space unit were monoclinic, $P12_1/n1$ respectively. Interestingly

H-bonding between the carbonyl oxygen and the pyrrole N-H was observed with bond lengths of 1.97 Å and 1.92 Å respectively for N(1)-H(1)…O(3) and N(2)-H(2)….O(1).

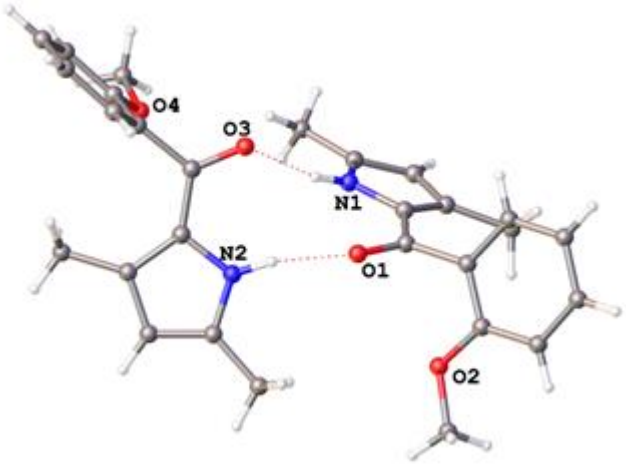
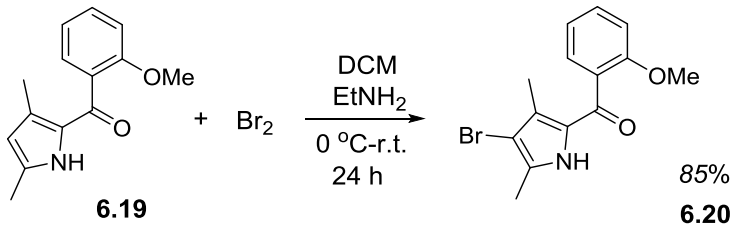


Figure 6.5 X-ray crystal structure of **6.19**

6.3.2 Synthesis of 1-(4-bromo-2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-methoxyphenyl) methane-1-one 6.20

The next step was the bromination of **6.19**. Addition of Br_2 in DCM to solution of **6.19** under the similar **6.16** bromination procedure only resulted in recovered starting material. The addition of diethylamine to the reaction to remove the HBr produced 1-(4-bromo-2,4-dimethyl-1H-pyrrol-5-yl)-1-(2-methoxyphenyl)methane-1-one **6.20** in good yield (85%).



Scheme 6.9 Synthesis of **6.20**

Monoclinic crystals of **6.20** in the Pc space group were grown by slow evaporation of solution of **6.20** from petrol/DCM. Four molecules were observed in each unit cell joined by H-bonding (2.60 Å and 2.61 Å for N(2)-H(2)…O(1) and N(1)-H(1)….O(3) respectively). The X-ray crystal structure showed that the bromination had occurred on the pyrrole ring as desired.

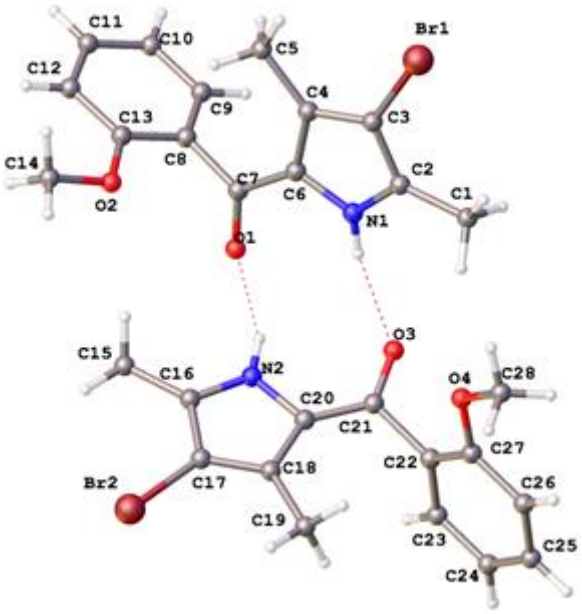
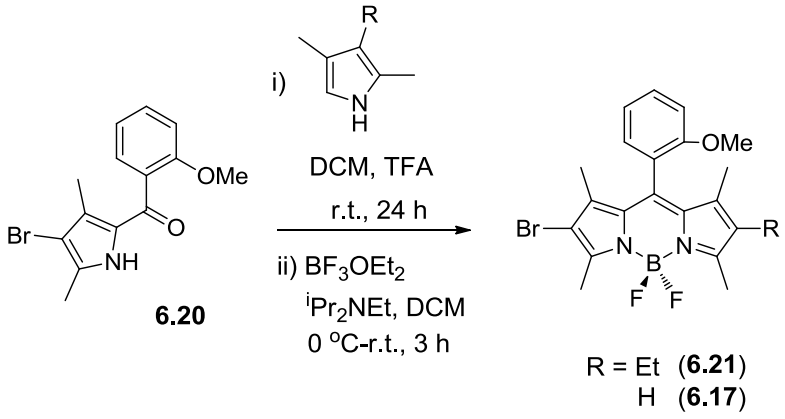


Figure 6.6 X-ray crystal structure of **6.20**

6.3.3 Synthesis of BODIPY 6.21

After completing the synthesis of 1-(4-bromo-2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-methoxyphenyl)methane-1-one **6.20**, the next task was the assembly of the dipyrromethene scaffold. This involved the condensation of **6.20** with pyrrole followed by chelation with BF_3 which will then lead to the desired BODIPY.



Scheme 6.10 Synthesis of **6.21**

Table 6.2 Yield of **6.21** and **6.17**

Entry	R	Yield (%)
1	H	10
2	Et	85

Reaction of **6.20** with either di- or tri-substituted pyrroles was done under standard BODIPY synthesis conditions.[159-160] The corresponding dipyrromethenes are formed *in situ* by TFA catalysed pyrrole condensation with **6.20**. Subsequent addition of BF_3 to the dipyrromethene gave the corresponding BODIPYs.

X-ray crystallography of a crystal of **6.21**, grown by slow evaporation of the solution of petrol/DCM, confirmed the desired structure. The crystals of **6.21** were found to be triclinic with a $P\bar{1}$ space group. Interestingly, two molecules of **6.21**, each in (*R*)- or (*S*)- axially chiral configuration were found in the unit cell.

The axially chiral properties of **6.21** have been confirmed through ^{1}H and ^{19}F NMR spectroscopy. The ^{1}H NMR spectrum showed the four magnetically different methyl groups (1.38, 1.41, 2.58 and 2.59 ppm) whilst the ^{19}F NMR spectrum of **6.21** showed a dq splitting pattern typical of this class of BODIPY (eg. two diastereotopic fluorine atoms).

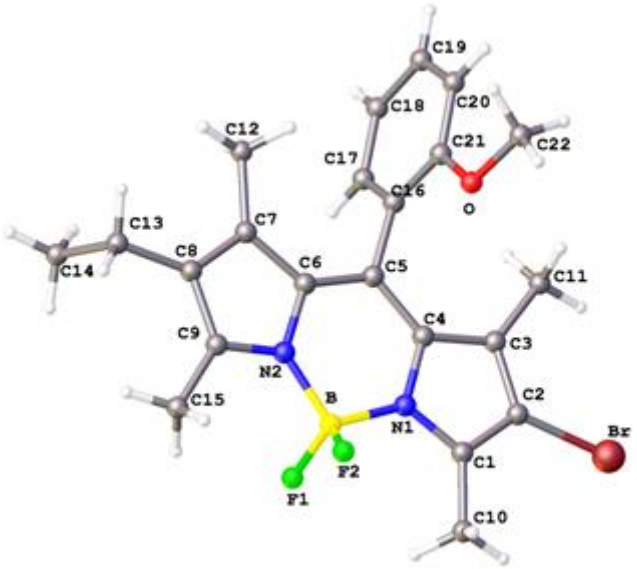


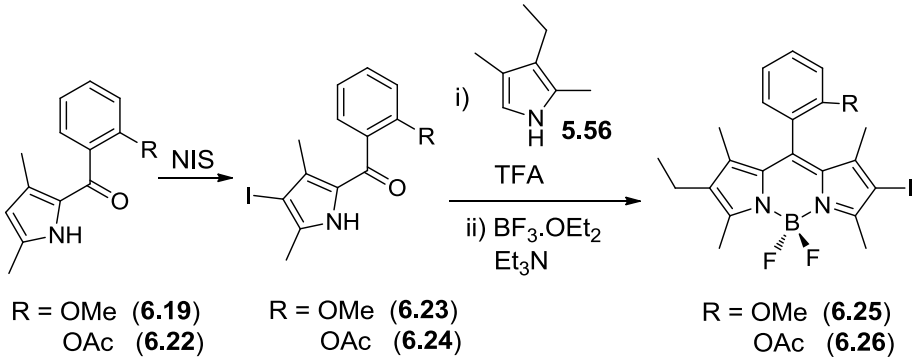
Figure 6.7 X-ray crystal structure of **6.21**

Synthesis of **6.21** was found to be higher yielding than that of **6.17** (Table 6.2). This may be due to the reactivity of the 3-ethyl-2,4-dimethylpyrrole **5.56** verses 2,4-dimethylpyrrole **5.2** with the more electron rich pyrrole being more reactive.

Moreover, comparing the overall yield of **6.21** between this modular synthesis and our original approach, it is clear that a modular approach is synthetically more useful. The modular approach also allowed a controlled bromination reaction with high yield, due to only one possible reaction site on the pyrrole, thus simplifying the purification of intermediates. Furthermore, employing different substituted pyrroles to react with **6.20** would then produce different functionalisable chiral axial BODIPYs.

6.4 Synthesis of Iodo-substituted Axially Chiral BODIPYs

Following the success in preparing axially chiral BODIPY **6.21** and **6.17** through a modular synthetic route, we decided to apply a similar approach to form iodo-substituted systems.



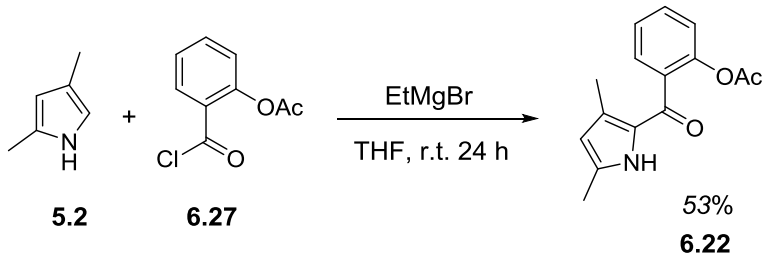
Scheme 6.11 Modular steps of synthesis of **6.25** and **6.26**

Synthesis of iodo-BODIPYs **6.25** and **6.26** was intended to produce BODIPYs for further functionalization. Due to the better leaving group properties of iodide to that of bromide, the iodo-BODIPYs would be expected to be easily functionalised through metal catalysed coupling reactions.

We also wished to include an *ortho*-acetate group in **6.26**, at a later stage this could be used for a trans-esterification reaction with enantiopure acids to form diastereomeric BODIPYs. Accordingly, the racemic axially chiral BODIPY could then be resolved by column chromatography and hydrolysis back of the enantiopure axial BODIPYs.

6.4.1 Synthesis of 1-(2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-acethoxyphenyl)methane-1-one 6.22

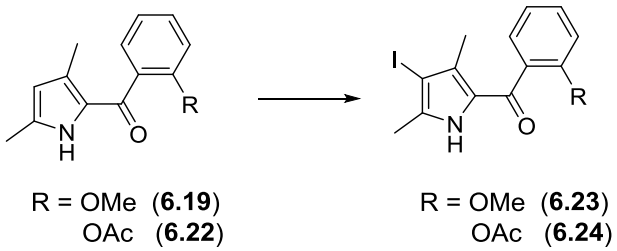
In order to synthesis an 2-acetoxyphenyl *meso*-substituted BODIPY, **6.26**, we first had to prepare pyrrole **6.22**. Reaction of 2,4-dimethylpyrrole with 2-acetoxybenzoyl chloride **6.27** was done by an analogous procedure to previously. Following column chromatography purification, **6.22** was isolated in 53% yield.



Scheme 6.12 Synthesis of **6.22**

6.4.2 Synthesis of 1-(4-iodo-2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-methoxyphenyl) methane-1-one 6.23 and 1-(4-iodo-2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-acetoxy phenyl)methane-1-one 6.24

Iodination of **6.19** and **6.22** was attempted using a similar procedure to the corresponding bromination reaction. However none of the desired products were observed. Literature suggested the use of iodic acid (HIO_3) or $PhI(OAc)_2$ along with I_2 to generate I_3^+ which is a potent electrophilic iodinating agent.[161-164]



R = OMe (**6.19**) R = OMe (**6.23**)
OAc (**6.22**) OAc (**6.24**)

Scheme 6.13 Synthesis of **6.23** and **6.24**

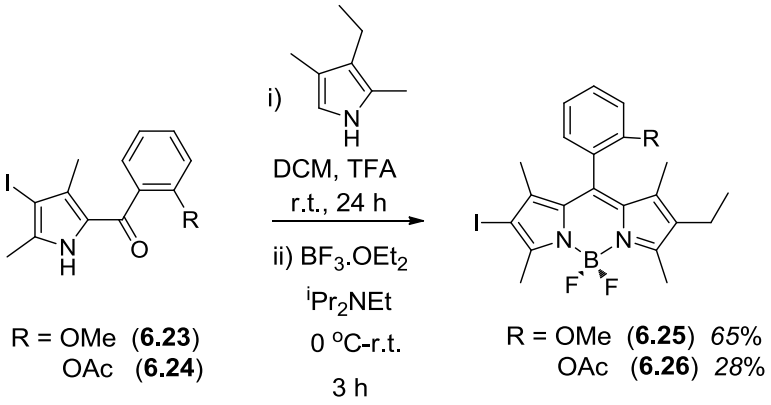
Table 6.3 Condition of iodification of **6.19** and **6.22**

Entry	Compound	Reagent	Solvent	Temperature (°C)	Time (h)	Yield (%)
1	**6.23**	I_2/HIO_3	EtOH	60	6	81
2	**6.23**	NIS	DCM	10-15	2	99
3	**6.24**	NIS	DCM	10-15	2	99

Carrying out iodination of **6.19** in the presence of iodic acid and I_2 resulted the formation of **6.23** in good yield (entry 1). An alternative approach involved reaction of **6.19** with NIS,[165] after 2 hours at room temperature **6.23** was isolated in excellent yield (entry 2). The same conditions were applied to iodination of 2-acetoxyphenyl pyrrole ketone, **6.22** with NIS to give a 99% yield of **6.24** (entry 3).

6.4.3 Synthesis of iodo-substituted chiral BODIPY 6.25 and 6.26

The synthesis of the corresponding iodo-substituted axially chiral BODIPYs was then attempted as before.



Scheme 6.14 Synthesis of **6.25** and **6.26**

Condensation and chelation of **6.23** gave BODIPY **6.25** in moderate yield. The reduced yield in comparison to the corresponding bromo-BODIPY **6.21**, indicates a difference in reactivity of pyrrole **6.23** compared to the bromo equivalent. In the case of **6.24**, BODIPY **6.26** only gave a 28% yield due to partial hydrolysis of the acetate, however this was sufficient for further work.

Slow evaporation of a solution of **6.25** in petrol/ether gave suitable crystals for X-ray analysis. Similar to that of the bromo-BODIPY **6.17** crystals, four molecules of **6.25** were found in the unit cell, two in each of the (*R*)- and (*S*)- axially chiral configurations. Examination of the crystal structure shows that the *meso*-aryl group is still orthogonal to the BODIPY resulting in axial chirality.

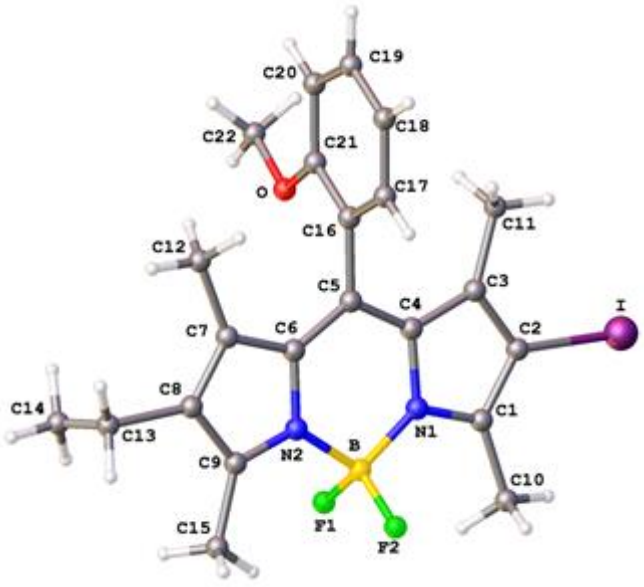


Figure 6.8 X-ray crystal structure of **6.25**

6.5 Conclusions

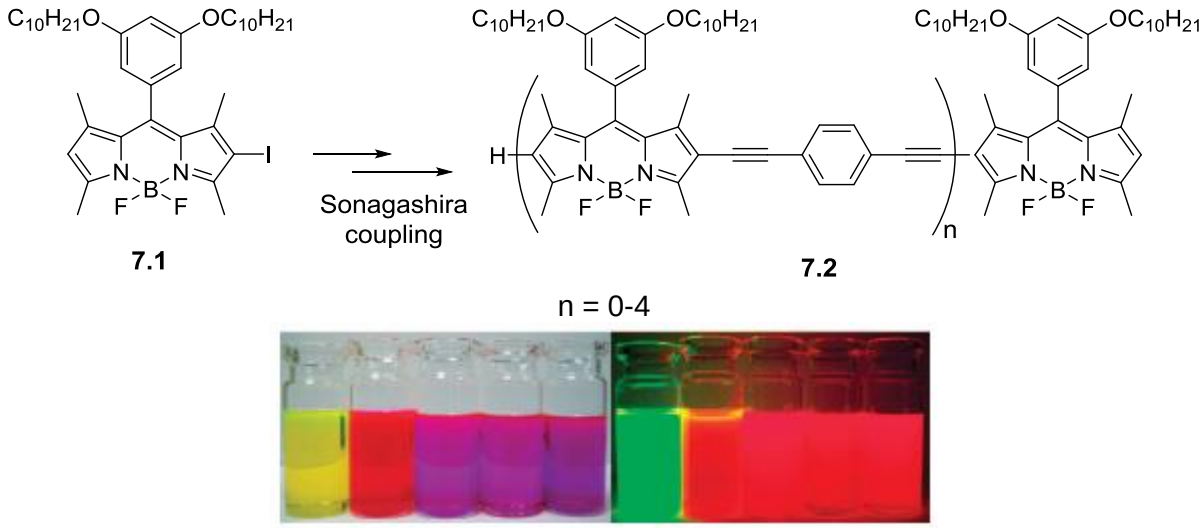
Axially chiral BODIPYs have been successfully synthesised through the use of *ortho* substituted *meso*-aryl groups in combination with different pyrrole ring substitutions within the dipyrromethene scaffold.

Regioselective monobromination approaches were low yielding. Optimisation of the synthesis of axially chiral BODIPYs was improved through the use of a modular approach. Although increasing the number of steps, this method gave good yields. This approach also allows versatility in the synthesis of axially chiral BODIPYs. Simply by introducing different pyrroles in the condensation step, a range of axially chiral BODIPYs could be produced.

Chapter 7 Synthesis of π Extended BODIPYs

7.1 Introduction

There is interest in developing BODIPY dyes as red-emitting fluorophores (650-750 nm), in particular in biological applications which are red light can penetrate biological tissue. Accordingly the parent green emitting BODIPY dye is usually structurally modified to extend the π-conjugation so that the absorption and emission wavelengths are moved to the red or even near infra-red region.



Scheme 7.1 Example of red-emitting fluorophore with extended π-conjugation (adapted from: Cakmak, Y., Akkaya, E. U. *Org. Lett*. **2009**, *11*, 85-88)

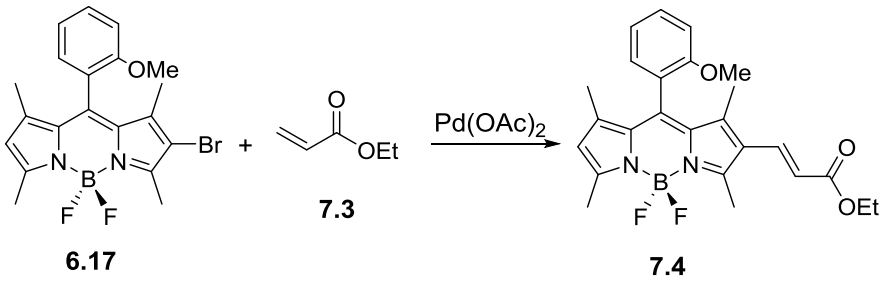
Palladium coupling reactions are one method to extend the BODIPY π-system from the pyrrole rings. The dipyrromethene core can be substituted with halides allowing alkenes, aromatics or alkynes to be attached.

Hence bromo and iodo-substituted axially chiral BODIPYs which have been synthesised previously could be submitted to palladium coupling reactions to extend the π-system. Furthermore by employing alkenes or alkynes bearing chiral groups, the BODIPYs will then become diastereomeric, this would allow racemic BODIPYs to be resolved.

Therefore we decided to investigate the palladium coupling reactions of axially chiral BODIPYs (**6.17**, **6.21**, **6.25** and **6.26**) with alkenes, alkynes and aromatics to shift the absorption and the emission wavelength towards the red region and also to produce diastereomeric BODIPYs to allow chiral resolution.

7.2 Heck Reaction of Halogenated Axially Chiral BODIPYs

In order to add an exocyclic double bond to the axially chiral BODIPYs, we decided to examine the halogenated BODIPY **6.17** in a Heck reaction with commercially available ethyl acrylate.

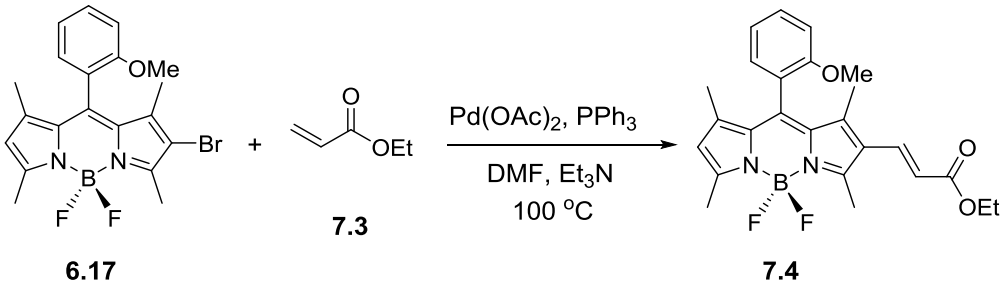


6.17 **7.3** **7.4**

Scheme 7.2 Heck reaction of BODIPY **6.17**

7.2.1 Synthesis of BODIPY 7.4

Heck reaction of **6.17** with ethyl acrylate **7.3** was performed using $Pd(OAc)_2$ and PPh_3 in DMF. TLC monitoring indicated a new red fluorescence spot (Rf = 0.35) and suggested the formation of a new BODIPY. After 12 h, 43% of a red solid was isolated and confirmed as **7.4** by ^{1}H NMR spectroscopy (Table 3.1 entry 1). Recovered starting material (10%) was also observed which suggested that the reaction yield could be improved with longer reaction times. Reaction optimisation through increasing the reaction time to 24 h gave **7.4** in an improved yield of 65% (entry 2).[166]



6.17 **7.3** **7.4**

Scheme 7.3 Synthesis of **7.4**

Table 7.1 Conditions for the synthesis of **7.4**

Entry	Time (h)	Yield (%)
1	12	43
2	24	65

Analysis of the ^{1}H NMR spectrum of **7.4** showed two new doublet peaks at 6.05 and 7.63 ppm (J = 16.2 Hz) which corresponded to a *trans*-alkene. The new ethoxy group was also observed as a triplet and a quartet at 1.32 and 4.24 ppm, respectively.

Further structural confirmation of **7.4** was performed through X-ray crystallography. A crystal of **7.4** was grown by slow evaporation of the solution of petrol/ether. The crystal structure confirmed the *trans* orientation of the alkene and the regioselective introduction of a new group.

Looking of the crystal packing, two molecules which are a pair of (*R*)- and (*S*)- axially chiral **7.4** are present per unit cell. The *meso*-aryl group was also shown to be orthogonal to the BODIPY core with the torsion angel of C(6)-C(5)-C(14)-C(19) of 109.4°.

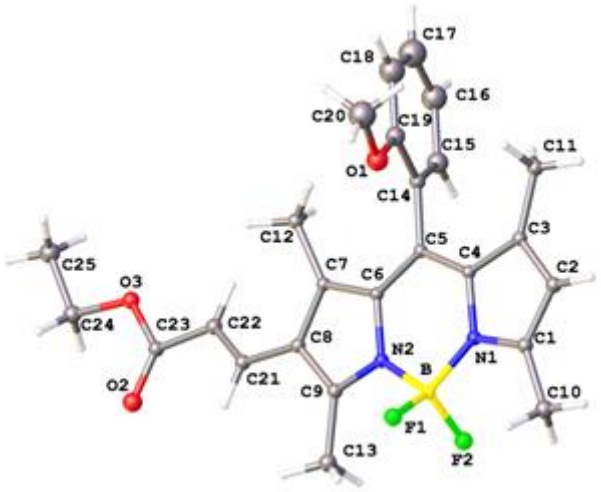
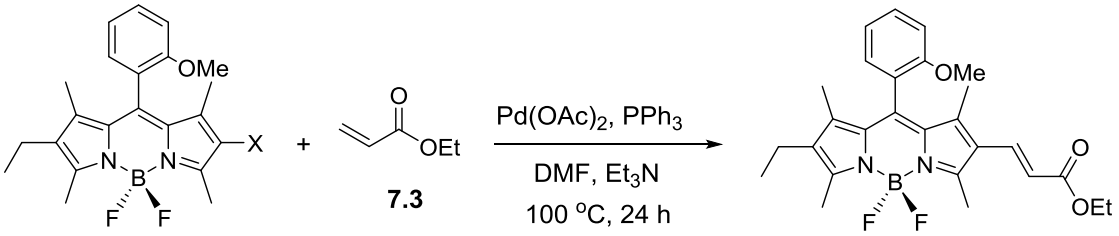


Figure 7.1 X-ray crystal structure of **7.4**

7.2.2 Synthesis of BODIPY 7.5

Following the successful Heck reaction to make **7.4**, we examined **6.21** under similar Heck conditions with ethylacrylate. From the reaction 35% of a pale red solid was isolated and confirmed by ^{1}H NMR spectroscopy as **7.5** (Table 7.2 entry 1), along with 15% recovered starting material.



X = Br (**6.21**)
I (**6.25**)

Scheme 7.4 Synthesis of **7.5**

Table 7.2 Yield of **7.5**

Entry	X	Yield (%)
1	Br	35
2	I	90

The low yield for this Heck reaction may be due to the steric encumbrance of the two methyl groups adjacent to the bromine. To improve the yield, the same Heck conditions were applied to iodo-substituted BODIPY **6.25**. In this case a 90% yield of **7.5** was achieved through the use of a better leaving group.

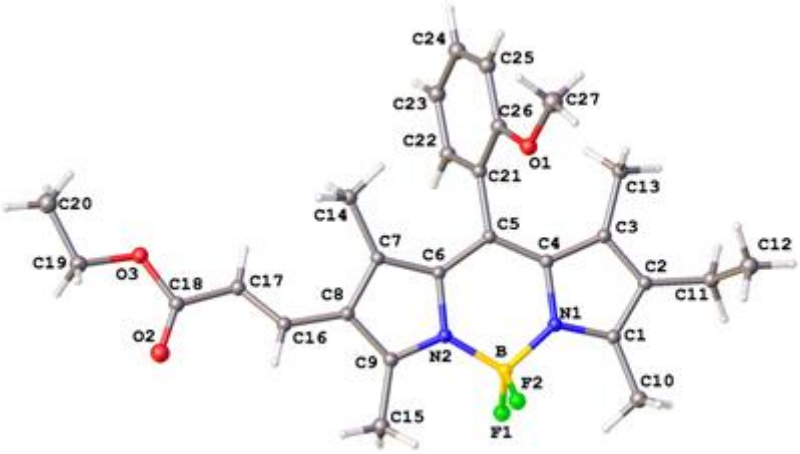
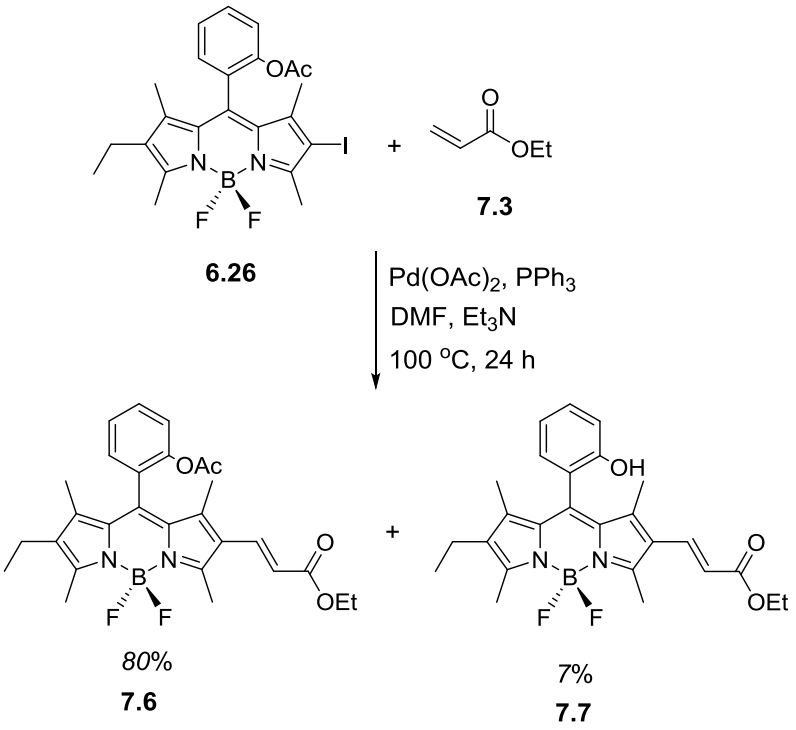


Figure 7.2 X-ray crystal structure of **7.5**

X-ray crystallography analysis of the crystal of **7.5** revealed the desired Heck BODIPY product. The crystals grown through slow evaporation of solution of **7.5** from petrol/ether, belonged to $P\bar{1}$ space group. Similar to that of crystal **7.4**, two molecules, each is in (*R*)- or (*S*)- axially chiral configurations were present in the unit cell. The *meso*-aryl group was still found orthogonal (torsion angle of C(6)-C(5)-C(21)-C(26) is 110.5^{o}) to the BODIPY core indicating steric hindrance between the meso-aryl and the flanking 1,7-dimethyl groups.

7.2.3 Synthesis of BODIPY 7.6

Based on these results, we decided to carry out further Heck reactions on iodo-BODIPY **6.26**. Submission of BODIPY **6.26** to a Heck coupling with ethyl acrylate **7.3** was performed under the same conditions as before. This gave two isolated red solids in moderate yield following column chromatography purification. ^{1}H NMR analysis of these two products confirmed the structures to be BODIPY **7.6** and BODIPY **7.7** in which the acetate has been lost. This suggests that the acetate was cleaved under the basic Heck reaction conditions.

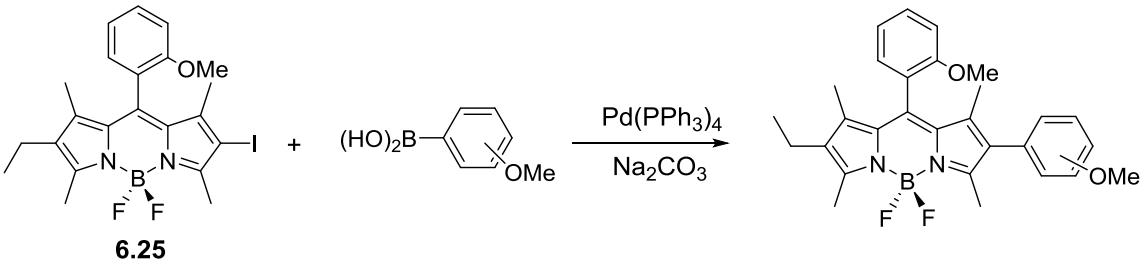


Scheme 7.5 Heck coupling reaction of **6.26**

We have shown that axially chiral BODIPYs can be further functionalised through Heck reactions, especially in the case of iodo-substituted BODIPYs. We then decided to examine other metal catalysed cross coupling reactions.

7.3 Suzuki Coupling Reactions of Halogenated Axially Chiral BODIPYs

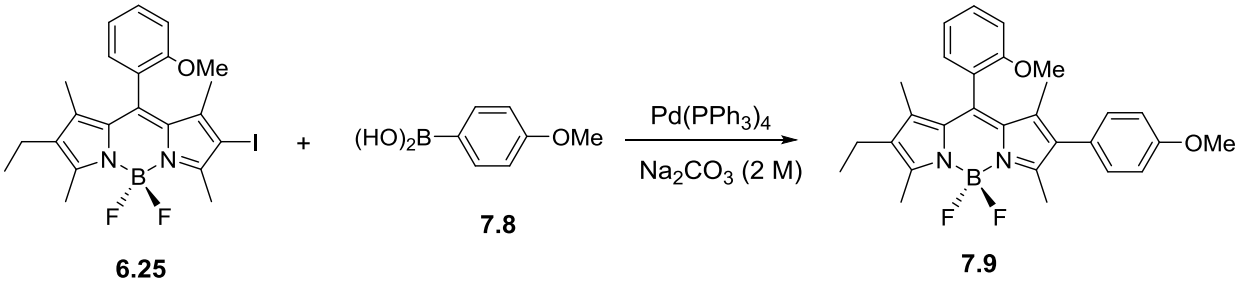
Following the success of Heck coupling reactions of the iodo-substituted axially chiral BODIPYs, we decided to introduce aromatic substituents to the BODIPYs through Suzuki coupling. We were interested in introducing a 2-methoxy phenyl substituent as this would potentially introduce an additional axial chiral centre thus producing diastereomeric BODIPYs.



Scheme 7.6 Aromatic Suzuki coupling reaction of BODIPY **6.25**

7.3.1 Synthesis of BODIPY 7.9

Iodo-substituted BODIPY **6.25**, which performed well in Heck reactions, was chosen for Suzuki coupling using 4-methoxyphenyl boronic acid **7.8**. Reaction of **6.25** with 4-methoxyphenyl boronic acid under Pd catalysis[143] gave predominantly starting material after 24 h at 80 ^{o}C, giving a 10% yield of **7.9** (Table 3.3 entry 1).



Scheme 7.7 Synthesis of BODIPY **7.9**

Table 7.3 Synthesis of BODIPY **7.9**

Entry	Boronic acid	Solvent	Temp (^{o}C)	Time (h)	Yield (%)
1	4-OMe	Toluene : MeOH (5 : 1)	80	24	10
2	4-OMe	Toluene	111	24	50
3	4-OMe	DMF	100	2	51

The yield was improved through the use of high boiling solvents (entry 2 and 3). In both toluene and DMF similar yields of **7.9** (50 and 51%) were obtained however reaction times were reduced in DMF.

A crystal of **7.9** was grown through slow evaporation of the solution from DCM/petrol gave material suitable for X-ray analysis. These monoclinic crystals contained four molecules per cell unit in a P12$_1$/n1 space group, two in each of the (*R*)- and (*S*)- axially chiral configurations.

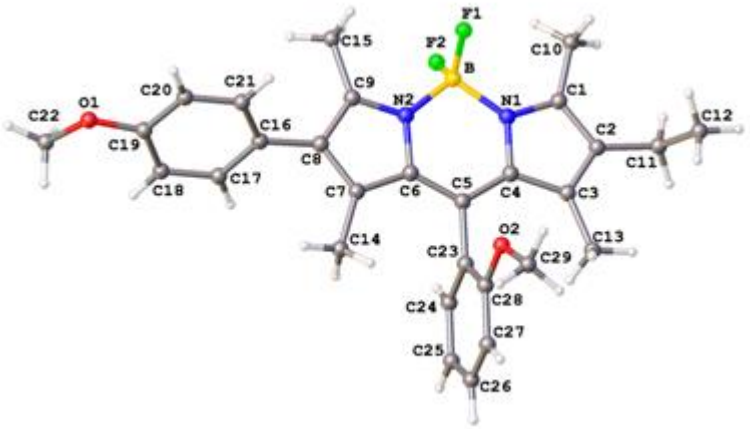
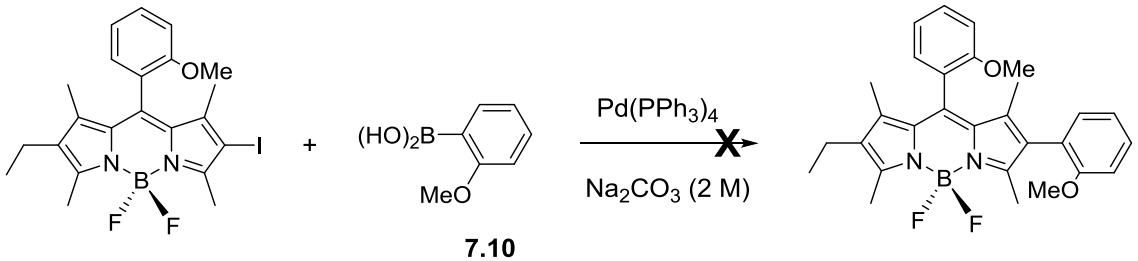


Figure 7.3 X-ray crystal structure of BODIPY **7.9**

7.3.2 Synthesis of iodo-BODIPY 7.11

Following the successful synthesis of **7.9**, we employed the same conditions in order to prepare the regiomeric BODIPY **7.11**. However attempted Suzuki coupling of 2-methoxyphenyl boronic acid **7.10** with BODIPY **6.25** gave only recovered starting material (Table 7.4 entry 1) [Even after extensive reaction time over several days or in different solvents (entry 2 and 3)]. The lack of reaction is likely due to the high steric repulsion between the hindered BODIPY **6.25** and the 2-methoxyphenyl boronic acid.



6.25 **7.10** **7.11**

Scheme 7.8 Synthesis of **7.11**

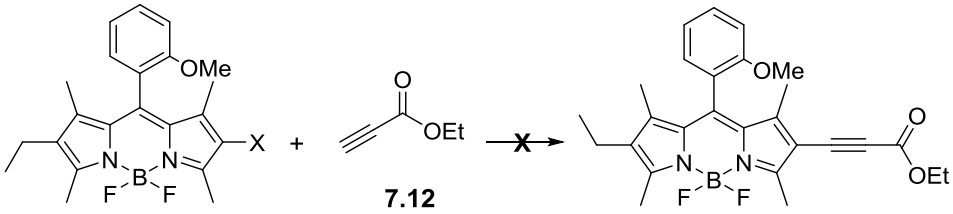
Table 7.4 Attempted synthesis of BODIPY **7.11**

Entry	Solvent	Temp. (°C)	Time (day)	Yield (%)
1	DMF	100	1	No reaction
2	DMF	100	3	No reaction
2	Toluene	111	1	No reaction

Successful Suzuki couplings with *para*-substituted aryl boronic acids have been demonstrated, however coupling with *ortho*-substituted aryl boronic acids were unsuccessful.

7.4 Sonogashira Coupling Reactions of Halogenated Axially Chiral BODIPYs

Following on from our Heck and Suzuki reactions, we decided to examine Sonogashira couplings. **6.21** was reacted with ethyl propiolate **7.12** under $Pd(OAc)_2$ and CuI catalysis,[166] however only starting material was isolated (Table 7.5 entry 1). Changing the reaction conditions to $Pd(PPh_3)_4$ and CuI in refluxing benzene, in accordance to Ziessel[167] still did not provide any of the desired product (entry 2). Addition of Hünig's base was attempted in order to improve the reaction[137], however no improvement was observed.



X = Br (**6.21**)
I (**6.25**)

7.13

Scheme 7.9 Synthesis of **7.13**

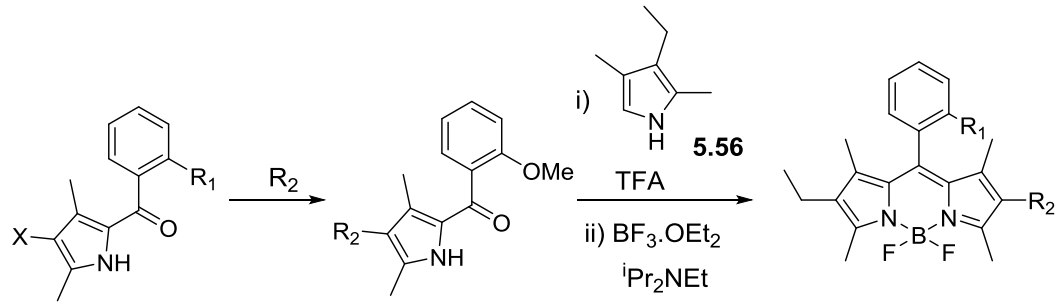
Table 7.5 Attempted synthesis of **7.13**

Entry	X	catalyst	solvent	Base	Temp (°C)	Time (h)	Yield (%)
1	Br	$Pd(OAc)_2/PPh_3/CuI$	DMF	Et_3N	80	24	Recovered starting material
2	Br	$Pd(PPh_3)_4/CuI$	C_6H_6	Et_3N	60	24	Recovered starting material
3	Br	$Pd(PPh_3)_4/CuI$	DMF	$^iPr_2NEt$	100	24	Recovered starting material
4	I	$Pd(OAc)_2/PPh_3/CuI$	DMF	Et_3N	80	24	Recovered starting material
5	I	$Pd(PPh_3)_4/CuI$	MePh	Et_3N	60	24	Recovered starting material
6	I	$Pd(PPh_3)_2Cl_2/CuI$	THF	$^iPr_2NEt$	60	24	Recovered starting material

Since bromide is poorer leaving group than iodide, iodo-BODIPY **6.25** was examined in the Sonogashira reaction. However iodo-BODIPY **6.25** was also not reactive under these conditions, even with the more reactive $Pd(PPh_3)_2Cl_2$.[168]

7.5 Modular Synthesis of Pd Coupled BODIPYs

Attempts to introduce groups by metal catalysed coupling reactions to BODIPYs were partially successful. However yields were sometimes low. Therefore, we decided to change the order of synthetic steps to allow coupling reactions on pyrrole precursors, in an attempt to increase yields.



R_1= OMe X = Br (**6.20**)
OMe I (**6.23**)
OAc I (**6.24**)

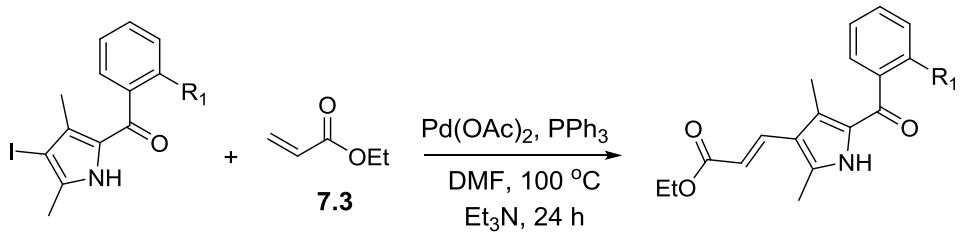
R_2 = Alkenes, alkynes or aromatics

Scheme 7.10 Proposed modular cross-coupling approach to chiral BODIPYs

Therefore we decided to attempt cross-coupling on halo-pyrroles followed by BODIPY formation.

7.5.1 Heck coupling of halo-pyrroles

3-Iodo ketopyrroles (**6.23** and **6.24**) were chosen in order to examine Heck couplings with ethyl acrylate **7.3**. We chose the iodo-pyrroles as they were expected to give higher yields than bromo derivatives.



R_1 = OMe (**6.26**)
OAc (**6.27**)

R_1 = OMe (**7.14**)
OAc (**7.15**)

Scheme 7.11 Synthesis of **7.14** and **7.15**

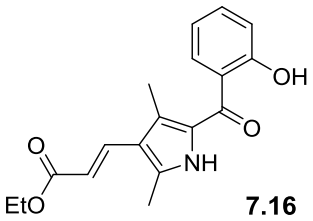
Table 7.6 Yield of **7.14** and **7.15**

Entry	R_1	X	Yield (%)
1	OMe	I	83
2	OAc	I	71

Iodo-pyrrole **6.23** was reacted with ethyl acrylate, Et_3N and $Pd(OAc)_2/PPh_3$ in DMF at 100 °C.[166] Pyrrole **7.14** was isolated in excellent yield as a colourless solid. ^{1}H NMR

analysis showed two doublets at 5.94 and 7.59 ppm (J = 16.1 Hz) corresponding to a *trans* alkene.

Submission of iodo-pyrrole **6.24** to the Heck reaction conditions produced a 72% yield of **7.15** (entry 2) along with 10% of the hydrolysed product, **7.16**. Hydrolysis of the acetate occurred under the basic conditions of the Heck reaction.

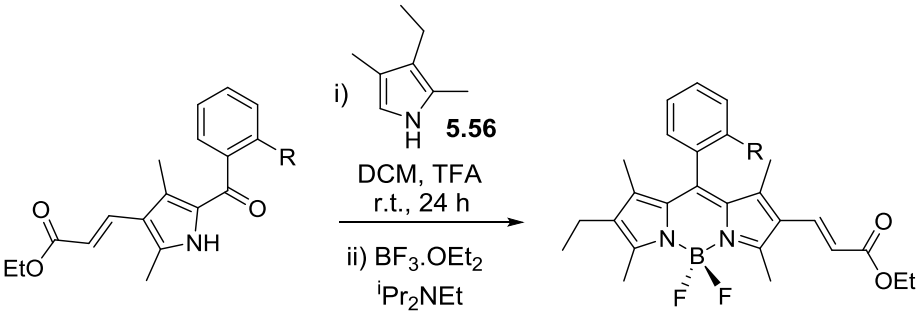


7.16

Scheme 7.12 Compound **7.16**

7.5.2 Synthesis of BODIPYs 7.5, 7.6 and 7.7

With the Heck products, **7.14**, **7.15** and **7.16** in hand, they were submitted to condensation with 3-ethyl-2,4-dimethyl pyrrole **5.56** followed by BF_2 chelation leading to the corresponding BODIPY **7.5**, **7.6**, **7.7**.



R= OMe (**7.14**)
OAc (**7.15**)
OH (**7.16**)

R= OMe (**7.5**) *22%*
OAc (**7.6**) *28%*
OH (**7.7**) *50%*

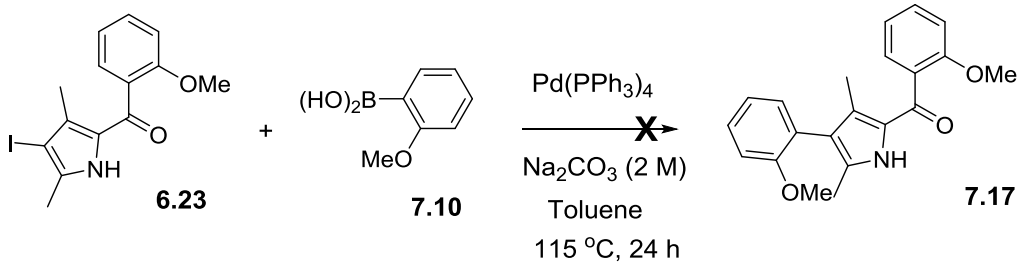
Scheme 7.13 Modular synthesis of **7.5**, **7.6** and **7.7**

Low yields were obtained for BODIPY **7.5** and **7.6**, whereas BODIPY synthesis with **7.16** gave the BODIPY **7.7** in moderate yield. In the synthesis of **7.6** a 15% of the hydrolysed BODIPY **7.7** was also isolated.

7.5.3 Suzuki coupling of iodo-pyrrole 6.23

After success of a modular synthetic approach to functionalised BODIPYs, we decided to examine **6.23** under Suzuki coupling conditions in order to make **7.17**. Through

this route, the diastreomeric BODIPYs containing an *ortho*-methoxyphenyl group such as **7.11** could be prepared.



Scheme 7.14 Synthesis of **7.17**

However attempts to form Suzuki product **7.17** was not successful, possibly due to the steric demands of the reaction.

7.6 Conclusions

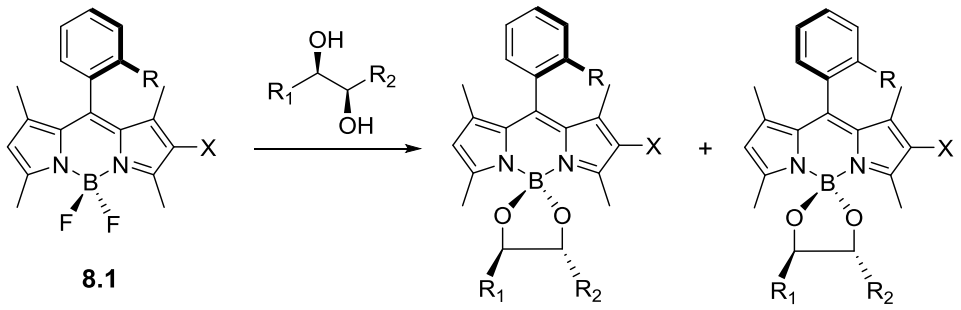
Axially chiral BODIPYs (**7.4**, **7.5**, **7.6**, **7.7** and **7.9**) were synthesised through metal catalysed cross-coupling reactions. Attempts to introduce the metal catalysed cross-coupling step early or late in the synthesis gave mixed results. Heck couplings of iodo-substrates proving to be the most successful.

Chapter 8 Axially Chiral BODIPY Resolution

8.1 Introduction

In the preceding chapters, we have described the synthesis of a number of axially chiral racemic BODIPYs. The next step was to examine the resolution of these compounds. In order to achieve this, we decided to convert the racemic BODIPYs into diastereosiomers by conjugating them with another chiral molecule. This would then allow column chromatography or other methods to be used to separate the products.

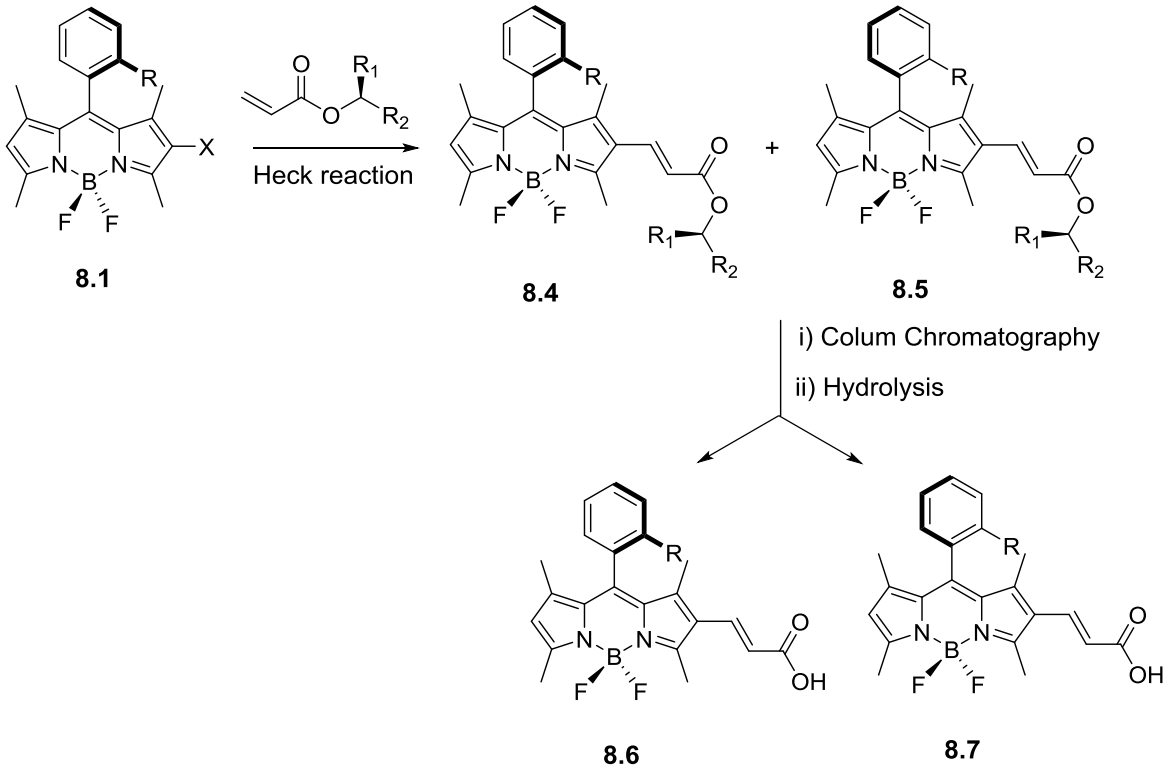
We thought that axially chiral BODIPYs could be converted into resolvable diastereosiomers by introducing another chiral centre onto the molecules. Literature showed that the fluorine atom in a BODIPY could be substituted with other groups including alcohols.[169-170] Therefore we proposed that the use of commercially available chiral diols, to replace the fluorine atoms could give diastereomeric BODIPY such as **8.2**/**8.3** (Scheme 8.1). Compound **8.2** and **8.3** could then be separated by column chromatography to give single diatereomeric BODIPYs.



8.1 **8.2** **8.3**

Scheme 8.1 Diastereoisomeric BODIPYs through fluorine substitution with chiral diols

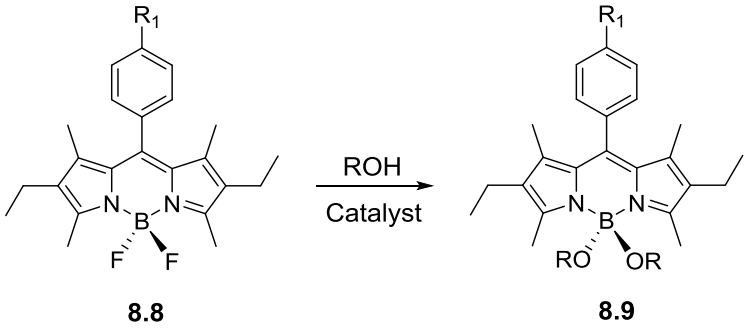
Another approach to make diastereosiomeric BODIPYs would be through a Heck coupling of a bromo-BODIPY (see Chapter 7) with an enantiopure acrylate. Racemic halogenated BODIPYs, especially iodo-BODIPYs, could be converted to diastereomers by the route depicted in Scheme 8.2. Separation of the diastereomers by column chromatography followed by ester hydrolysis would then afford enantiopure axially chiral BODIPYs.



Scheme 8.2 Resolution of chiral BODIPYs by Heck/Hydrolysis approach

8.2 Fluorine Substitution by Chiral Alcohols

In order to examine the fluorine substitution reactions of BODIPY **8.8** with alcohols, we started with replacement of F with simple OR groups. This was to provide a model reaction to develop a suitable approach to fluorine substitution before using chiral diols.

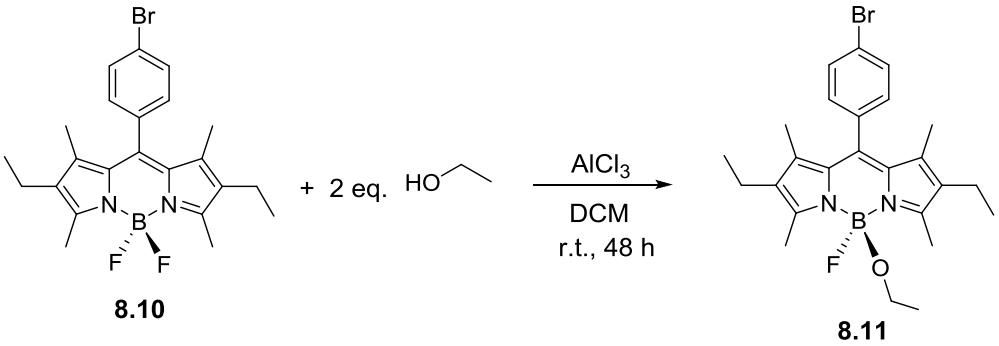


Scheme 8.3 Fluorine substitution with a simple alcohol

8.2.1 Fluorine substitution with ethanol

BODIPY **8.10** was submitted to a Lewis catalysed B-F substitution reaction with ethanol.[169] After 2 days, the starting material had not been consumed. Following work up and column chromatography, a product was isolated and confirmed by ^{1}H NMR spectrum

examination as the mono fluoro substituted **8.11**. However there was no desired disubstitution product was observed (Table 8.1 Entry 1).



Scheme 8.4 F substitution by EtOH

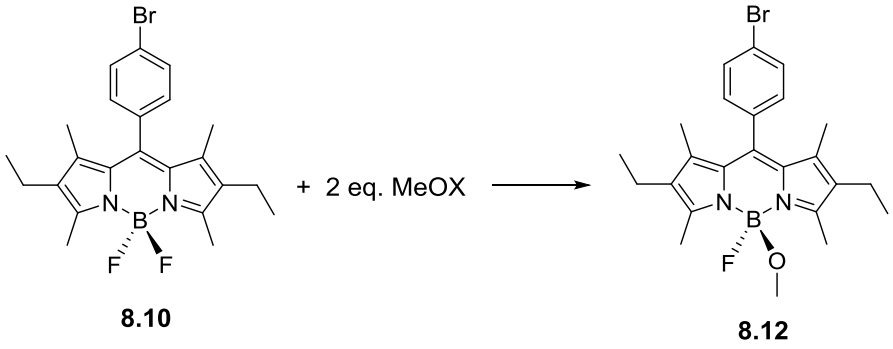
Table 8.1 Fluorine substitution by ethanol

Entry	Solvent	Temp (^{o}C)	Time (h)	Yield (%)
1	DCM	r.t.	48	54
2	THF	r.t.	48	50
3	DCM	reflux	48	57

Optimisation of the reaction was attempted through changing the solvent to THF, in accordance with Brizet.[171] However, the **8.11** was still isolated in a similar yield (entry 2). Reforming the reaction under reflux also showed no effect on the yield of the reaction (entry 3). There was still no disubstituted products isolated under different conditions.

8.2.2 Fluorine substitution by methanol

We postulated that ethanol is might be too sterically bulky to allow two substitutions of F to occur easily. Therefore methanol was examined under similar Lewis acid catalysed reaction conditions to see if a double substitution was possible. However, only starting material was recovered from reaction in DCM or THF (Table 8.2 entry 1-3).



Scheme 8.5 Fluorine substitution by MeOH

Table 8.2 Fluorine substitution by methanol

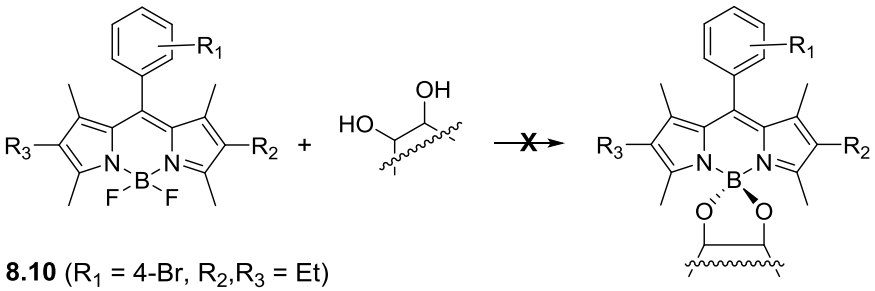
Entry	X	Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)
1	H	$AlCl_3$	DCM	r.t.	48	no reaction
2	H	$AlCl_3$	THF	r.t.	48	no reaction
3	H	$AlCl_3$	DCM	reflux	48	no reaction
4	K	-	DCM	reflux	24	decomposition
5	K	-	THF	reflux	24	decomposition
6	Na	-	DCM	reflux	24	25

In order to increase the reactivity of the methanol, potassium methoxide was employed.[172] Adding MeOK into a solution of **8.10** in DCM at reflux gave many spots on TLC but no formation of **8.12** was observed by ^{1}H NMR spectroscopy (entry 4). Repeating the reaction in THF also produced similar results (entry 5).

Using sodium methoxide in DCM at reflux gave predominantly recovered starting material but also a mono substituted product **8.12** in 25% yield (entry 6).

8.2.3 Fluorine substitution by diols

Next we attempted to substitute the fluorines with a chiral diol. Diols should be better than simple alcohols due to their bidentate nature. Initially displacement of the fluorines by diols was done under $AlCl_3$ catalysed conditions as in the synthesis of **8.11** (Table 8.3, entry 1 and 2). However, no disubstitution products were observed with tartrates or BINOL. Using $AlCl_3$ and a diol but under reflux also gave only recovered starting material (entry 3).



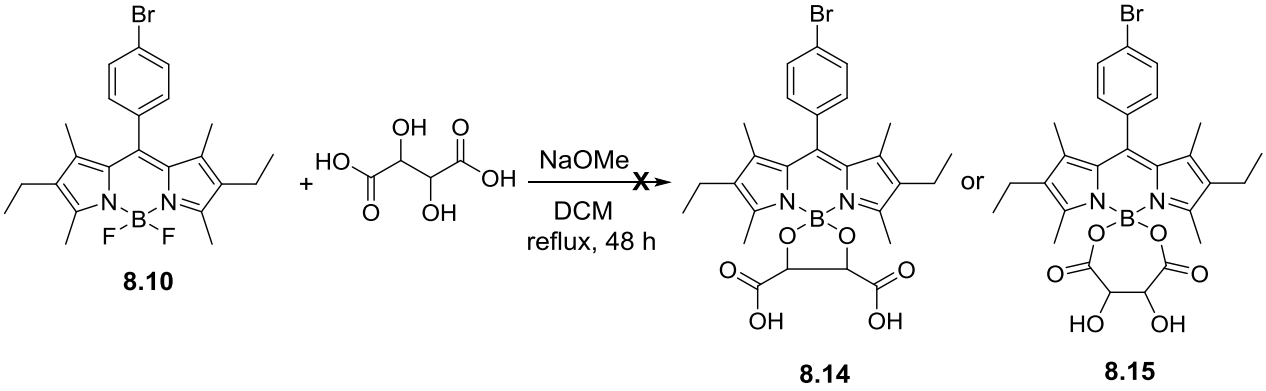
8.10 (R_1 = 4-Br, R_2,R_3 = Et)
8.13 (R_1 = 4-NO_2, R_2, R_3 = Et)
6.17 (R_1 = 2-OMe, R_2 = Br, R_3 = H)

Scheme 8.6 Fluorine substitution by diols

Table 8.3 Fluorine substitution by diols

Entry	Compound	Diol	Conditions	Yield (%)
1	**8.13**	*rac*-diethyltartrate	$AlCl_3$, DCM, r.t., 48 h	no reaction
2	**8.10**	*rac*-dimethyltartrate	$AlCl_3$, DCM, r.t., 48 h	no reaction
3	**8.10**	*rac*-dimethyltartrate	$AlCl_3$, DCM, reflux, 48 h	no reaction
4	**8.10**	*rac*-dimethyltartrate	NaOMe, DCM, reflux, 48 h	no reaction
5	**8.10**	*rac*-dimethyltartrate	KOMe, THF, r.t., 48 h	no reaction
6	**8.10**	*rac*-dimethyltartrate	KOMe, THF, reflux, 48 h	no reaction
7	**8.10**	*rac*-tartaric acid	NaOMe, DCM, reflux, 48 h	no reaction
8	**6.17**	*rac*-dimethyltartrate	KOMe, THF, reflux, 48 h	no reaction
9	**6.17**	*S*-BINOL	$AlCl_3$, DCM, r.t., 48 h	no reaction

Following the same idea as in the synthesis of **8.12**, racemic dimethyltartrate was reacted first with a base (NaOMe or KOMe) before addition to a solution of **8.10** in DCM or THF at different temperatures. However, again only recovered the starting material was isolated (entry 4-6). Since diethyl and dimethyl tartrate may be undergoing ester hydrolysis under the reaction conditions, we did a comparison reaction using tartaric acid. This reaction could give **8.14** or **8.15**. However, no incorporation of tartaric was observed by HRMS.



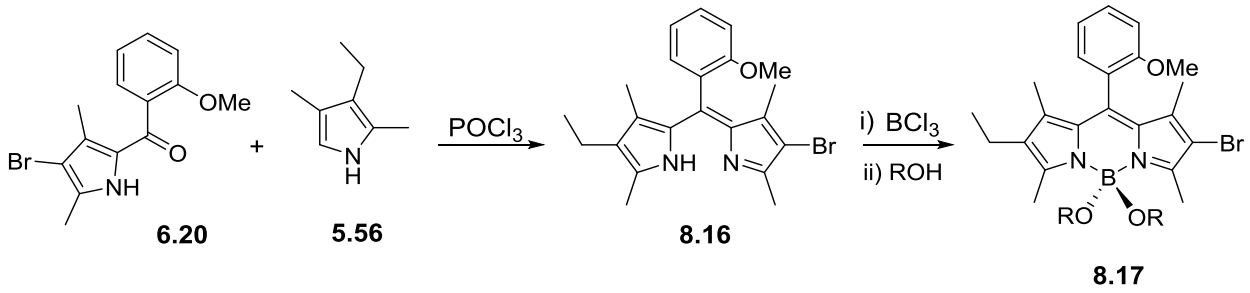
Scheme 8.7 Attempted Fluorine substitution with L-tartaric acid in the presence of NaOMe

Despite the successful incorporation of simple alcohols, preparation of diastereoisomeric BODIPYs by the addition of chiral diols was shown to be unsuccessfully under our conditions. We then decided to examine other routes to diol incorporation.

8.3 BCl_2 Chelated BODIPYs

In order to improve the addition of chiral diols to BODIPYs, we decided to use BODIPYs where the BF_2 is replaced by a BCl_2 unit. A BCl_2 chelated BODIPY may be a more feasible starting material for alcohol substitution reactions due to the more labile B-Cl bond.[173]

Literature suggested that BCl_2 chelated BODIPYs could be synthesised by adding BCl_3 to a solution of dipyrromethene under air and moisture free conditions.[173] Therefore we initially synthesised a dipyrromethene which could be transformed into an axially chiral molecule.

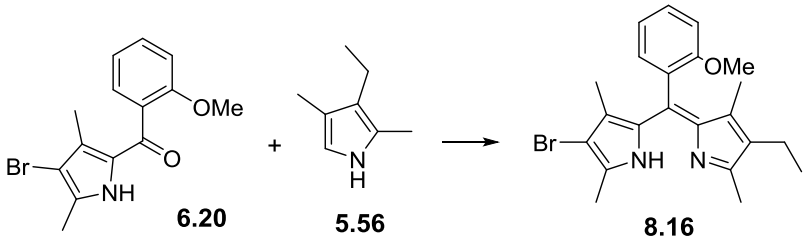


Scheme 8.8 Planned route to BCl_2 chelated BODIPYs and subsequent substitution by alcohols

8.3.1 Synthesis of chiral BODIPY precursors, unsymmetrical dipyrromethenes

In order to access diastereomeric BODIPYs directly, we chose the modular synthetic route to get to the corresponding dipyrromethenes (see Chapter 6). To do this, we will react ketopyrroles with another pyrrole to give dipyrromethenes. These will then be reacted with BCl_3 to give the corresponding BCl_2 chelated BODIPYs. The chlorines will then be substituted with a chiral diol.

Initially **6.20** was submitted to a condensation reaction with 3-ethyl-2,4-dimethyl-1*H*-pyrrole **5.56** following similar conditions to our previous modular BODIPY synthesis (see Chapter 6). However, none of the desired products were observed (Table 8.4, entry 1).



Scheme 8.9 Synthesis of **8.16**

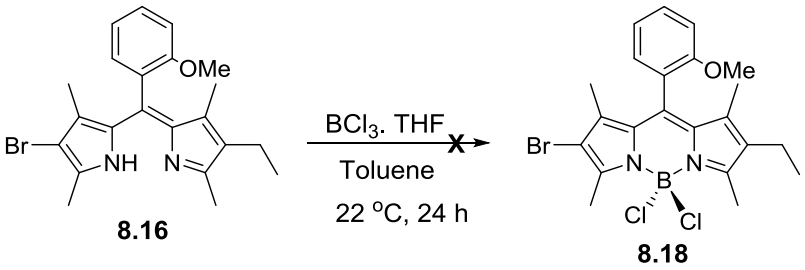
Table 8.4 Synthesis **8.16**

Entry	Conditions	Yield (%)
1	DCM, TFA, r.t., 24 h	No reaction
2	$POCl_3$, DCM, Et_3N, 0 then 27 ^oC, 24 h	70

Changing the conditions to the use of $POCl_3$ to activate the ketone, in accordance with the literature,[174] gave a 70% yield of a red solid product which was confirmed as **8.16** by ^1H NMR spectroscopy.

8.3.2 BCl_2 chelated BODIPYs

With dipyrromethene **8.16** in hand, the synthesis of BCl_2 chelated BODIPYs could be attempted according to Lundrigan's procedure.[173] Addition of BCl_3 into the solution of **8.16** in THF under nitrogen produced a change in the colour of the solution. However, after filtering the mixture over celite, none of the desired compound was isolated.

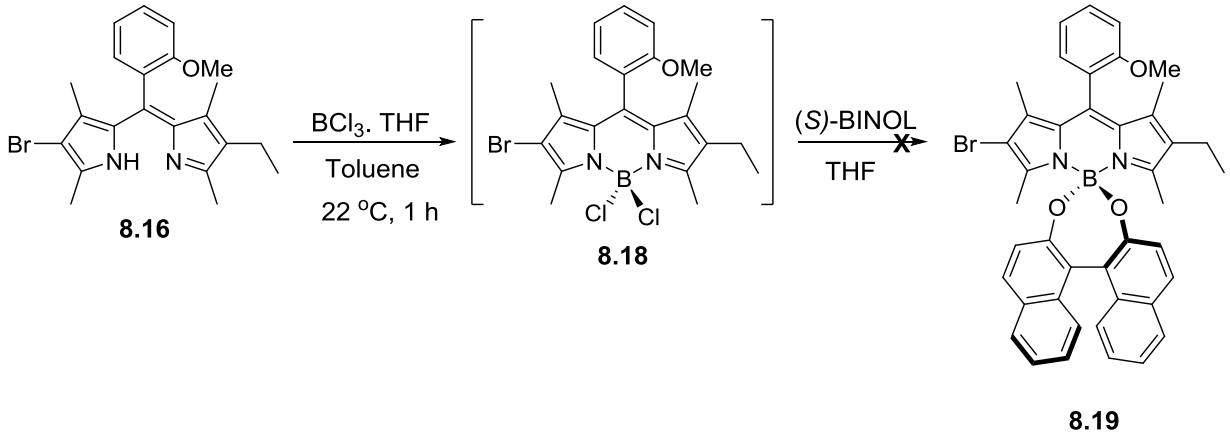


Scheme 8.10 Synthesis of **8.18**

Repeating the reaction under the same conditions followed by ^{1}H NMR of the crude reaction mixture indicated that **8.18** had been formed. However, the BCl_2 chelated BODIPY could not be isolated.

8.3.3 Approaches to chiral diol substituted BODIPYs

Since BCl_2 chelated BODIPY **8.18** had proved difficult to isolate, we decided to attempt to quench directly with (*S*)-BINOL, in an attempt to go directly to the diastereomeric BODIPY **8.19**.

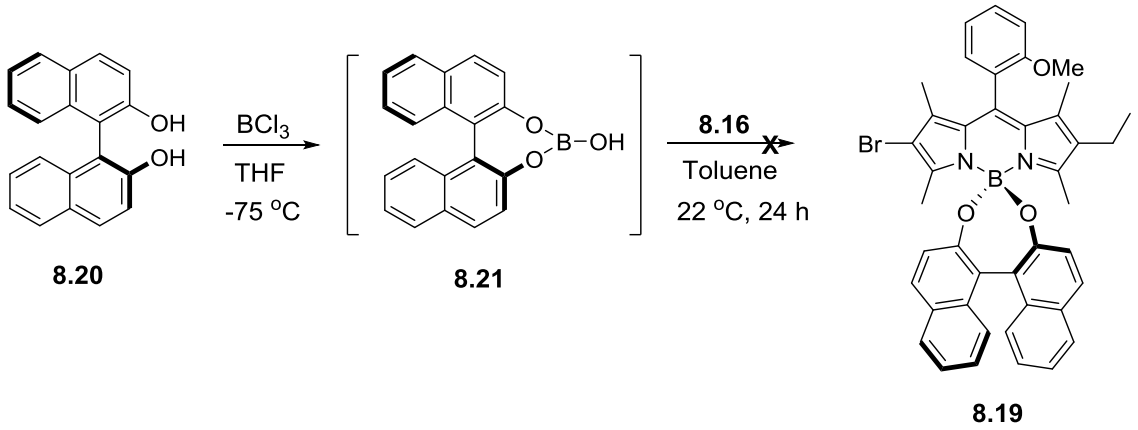


Scheme 8.11 Quenching BCl_2 chelated BODIPY **8.18** with (*S*)-BINOL

Dipyrromethene **8.16** was reacted with BCl_3 in a Schlenk tube under nitrogen and solution of (*S*)-BINOL in THF was then added to the reaction mixture. Monitoring of the

reaction by TLC showed that a new red compound appeared after 24 h. However, after aqueous work up, the crude ^{1}H NMR spectrum indicated no desired product.

We then changed our approach to **8.21**. First we added (*S*)-BINOL to BCl_3 in THF at -78 ^{o}C.[175] This solution was added to **8.16** in attempt to chelate with boronic acid **8.21** to give BODIPY **8.19**. However, none of the desired diol chelated BODIPY was isolated.



8.20 **8.21** **8.19**

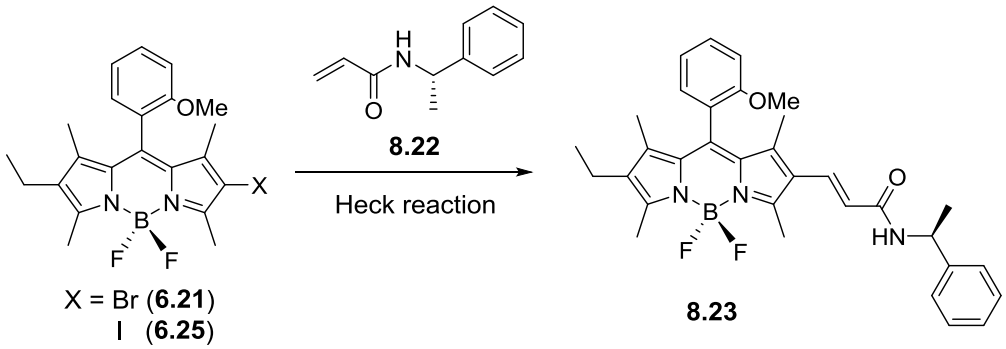
Scheme 8.12 Chelation of dipyrromethene **8.16** with pre-prepared boronic acids

8.3.4 Conclusions

Unfortunately the synthesis of diastereomeric BODIPYs through the addition of chiral diols did not prove successful under our conditions. Therefore we decided to pursue alternative approaches to resolution of chiral BODIPY systems.

8.4 Diatereomeric BODIPYs through Heck Coupling Reactions

Our next approach to prepare diastereoisomer BODIPYs is through a palladium catalysed Heck reaction with chiral acrylates or acrylamides. Previously we have described Heck reactions of acrylates with halogenated axially chiral BODIPYs (see Chapter 7). Through the use of chiral acrylates or acrylamides, diastereomeric BODIPYs can be formed. Resolution by chromatography followed by hydrolysis of the chiral ester or amide should give enantiopure axially chiral BODIPYs.



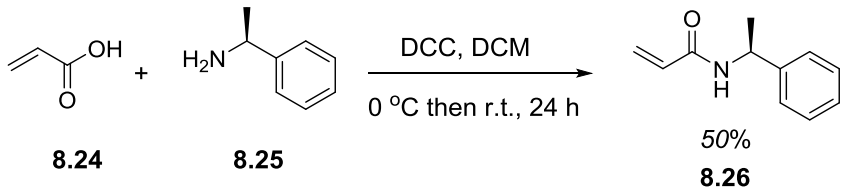
X = Br (**6.21**)
I (**6.25**)

8.23

Scheme 8.13 Diastereomeric with a chiral BODIPYs from acrylamide Heck reaction

8.4.1 Synthesis of (*S*)-ethylbenzylacrylamide

In order to perform a Heck reaction with a chiral acrylamide, we first need to prepare **8.26** from a DCC coupling of acrylic acid with (*S*)-methylbenzylamine.



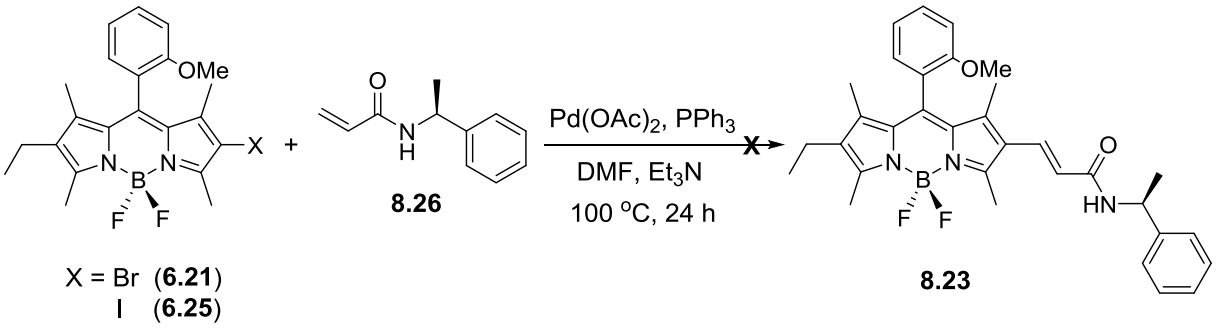
8.24 **8.25** **8.26**

Scheme 8.14 Synthesis of **8.26**

Addition of acrylic acid to a mixture of DCC and (*S*)-methylbenzylamine in DCM[176] gave, after aqueous work up and column chromatography, a 50% yield of **8.26**.

8.4.2 Heck coupling of chiral BODIPYs with chiral acrylamide

With chiral acrylamide **8.26** in hand, a Heck reaction of BODIPY **6.21** and **6.25** was carried out in accordance to our previous conditions (Chapter 3). However, coupling of **8.26** to **6.21** with $Pd(OAc)_2/PPh_3$ in DMF resulted only recovered starting material (Table 8.5, entry 1). Changing the bromo-BODIPY **6.21** to iodo BODIPY **6.25** also only gave recovered starting material (entry 2).



X = Br (**6.21**)
I (**6.25**)

8.26 **8.23**

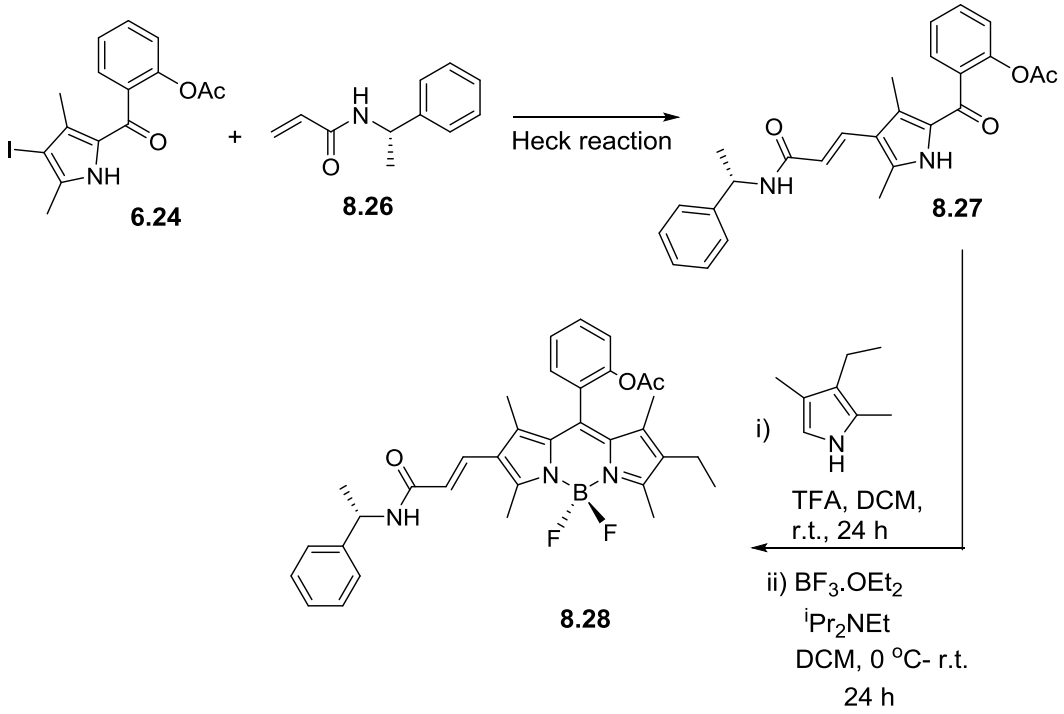
Scheme 8.15 Attempted Heck coupling of **8.26** with BODIPY **6.21** or **6.25**

Table 8.5 Attempted synthesis of **8.23**

Entry	X	Yield (%)
1	Br	no reaction
2	I	no reaction

8.5 Modular Diastereomeric BODIPY Synthesis with Early Stage Heck Reaction

Since Heck reactions on halogenated axially chiral BODIPYs with a chiral acrylamide had proven unseccessful, we decided to introduce a chiral acrylamide earlier in the synthetic route.

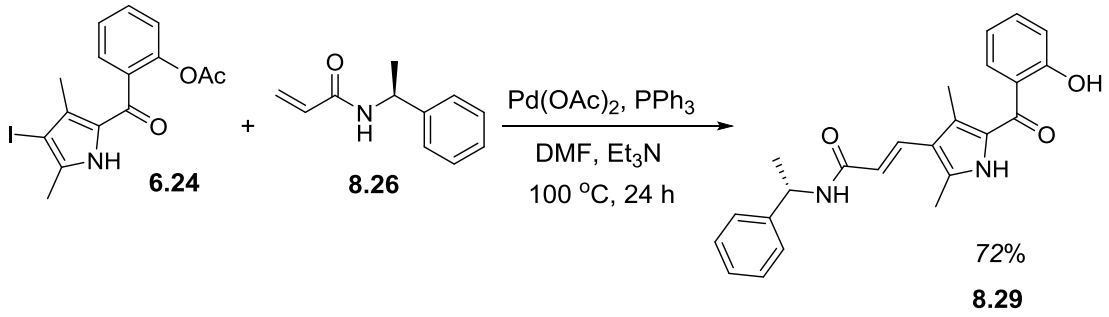


Scheme 8.16 Early stage Heck reaction

We expected that submission of pyrrole **6.24** to a palladium catalysed Heck reaction with acrylamide **8.26** would allow access to **8.27**. This would then provide pyrrole **8.27** for condensation with 3-ethyl-2,4-dimethylpyrrole to give the diastereomeric BODIPY **8.28**.

8.5.1 Heck reaction with pyrrole 6.24

Reaction of acrylamide **8.26** with pyrrole **6.24** using $Pd(OAc)_2/PPh_3$ in DMF gave functionalised pyrrole **8.29**. The ^{1}H and the ^{13}C NMR showed the disappearance of the acetoxy group from the phenol. This was confirmed by HRMS analysis giving a molecular formula of $C_{24}H_{24}N_2O_3$ for **8.29** (parent ion m/z = 389.1861).

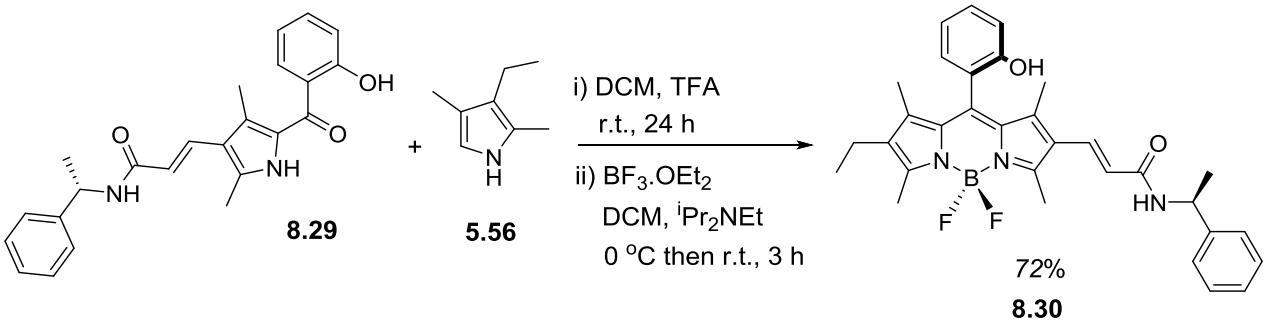


Scheme 8.17 Heck reaction of **6.24**

This suggested that the basic conditions of the Heck reaction have caused hydrolysis of the acetate group.

8.5.2 Condensation of pyrrole 8.29 with 3-ethyl-2,4-dimethylpyrrole 5.56

Following the successful preparation of pyrrole **8.29**, it was submitted to a Lewis acid catalysed condensation reaction with 3-ethyl-2,4-dimethylpyrrole **5.56** followed by addition of $BF_3.Et_2O$ and Hünig's base.



Scheme 8.18 Synthesis of diastereomeric BODIPY **8.30**

Analysis of product through HRMS gave a parent ion m/z = 542.2791 corresponding to $C_{32}H_{35}BF_2N_3O_2$ confirming the structure as **8.30** in combination with ^{1}H NMR spectroscopy.

Analysis of the ^{1}H NMR of **8.30** showed that two diastereomers had been formed in a ratio of 1 : 1. However, we could not separate the two diastereomers of **8.30** by column chromatography.

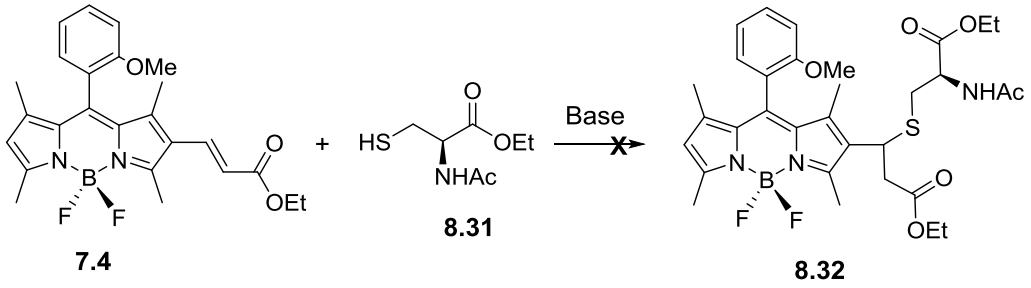
8.5.3 Conclusions

Diastereomeric BODIPYs have been successfully prepared through a modular approach involving a Heck coupling reaction between a halo-pyrrole and a chiral acrylamide. This approach gave a diastereomeric BODIPY in 52% (2 steps) from 1-(2,4-dimethyl-3-iodo-5-yl-pyrrole)-1-(2-acethoxyphenyl)ethan-1-one **6.24**.

Attempts to separate the diastereomeric BODIPYs are still on going.

8.6 Diastereomer Formation by Michael Addition of Chiral Thiols

In order to add an alternative stereocentre, we decided to employ the axially chiral BODIPY **7.4** in a conjugate Michael addition with a chiral thiol **8.31**.[177-178] This should allow production of a distereomeric BODIPY (**8.32**) for separation by column chromatography.



7.4 **8.31** **8.32**

Scheme 8.19 Attempted synthesis of diastereomeric BODIPY **8.32**

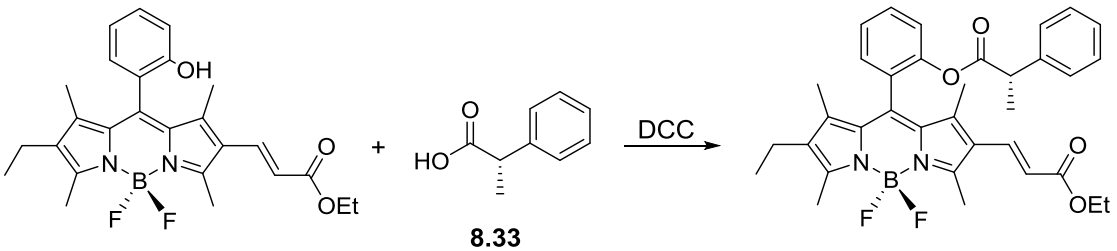
Table 8.6 Reaction condition of synthesising **8.32**

Entry	Solvent	Base	Temp. (°C)	Time (h)	Yield (%)
1	DCM	Et_3N	r.t.	48	no reaction
2	DCM	$^{i}Pr_2NEt$	r.t.	48	no reaction
3	DCM	NaHDMS	r.t.	48	no reaction

Attempts to form a diastereomeric BODIPY by Michael addition of a chiral thiol with different bases proved unsuccessful. Therefore we attempted an alternative approach.

8.7 Synthesis of Diastereomeric BODIPYs by Formation of Chiral Esters

Another approach to add a stereocentre to axially chiral BODIPYs was attempted through a DCC coupling of **7.7** with (*R*)-2-phenylpropionic acid **8.33** to introduce a new stereocentre to the *meso* aryl group of the BODIPYs. Following similar conditions as previously, only recovered starting material was isolated (Table 8.15, entry 1). Extension of the reaction time to 3 days also gave no reaction.



7.7 **8.33** **8.34**

Scheme 8.20 Synthesis of **8.34**

Table 8.7 DCC coupling of **7.7** with **8.33**

Entry	Solvent	Coupling agent	Base	Temp (°C)	Time (h)	Yield (%)
1	DCM	DCC	-	0 then r.t.	24	no reaction
2	MeOH:H_2O = 2:1	DCC	1 eq. Na_2CO_3	reflux	24	5
3	MeOH:H_2O = 2:1	DCC	3 eq. Na_2CO_3	reflux	24	10
4	DCM	EDCI	DMAP	0 then r.t.	24	25

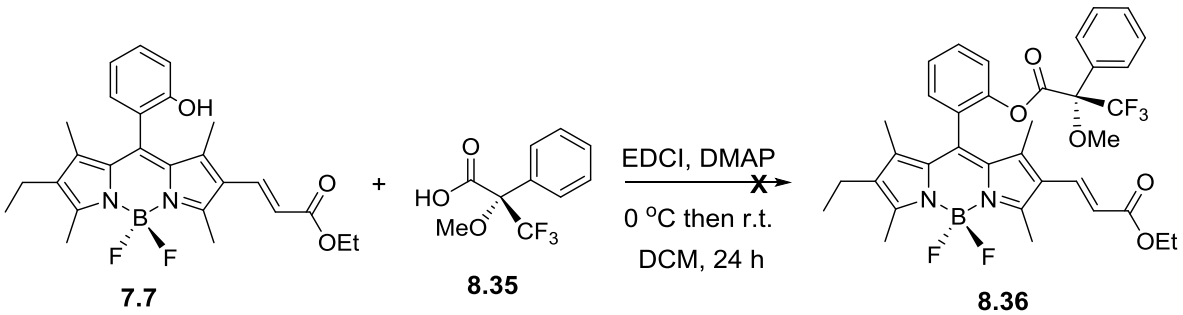
In order to deprotonate **7.7**, we added sodium carbonate to the reaction. We also changed the solvent to methanol : water (2:1) in order to dissolve the base. This gave a 5% yield of BODIPY **8.34** (entry 2). Increasing the base to 3 equivalents raised the yield to 10% (entry 3).

Due to the low solubility of **7.7** in methanol, we used DCM to increase the product yield. We also changed the base to the organic soluble base and nucleophilic catalyst, DMAP. Under these conditions, 25% of **8.34** was isolated (entry 4).

As the ^{1}H and ^{13}C NMR spectra showed that **8.34** was a mixture of diastereomers, we attempted to separate the two diastereoisomer by column chromatography and preparative TLC. However no separation was observed. Further approaches for separation are on going.

8.7.1 Alternative diastereomeric esters

Following success of the preparation of **8.34**, similar conditions were employed in order to synthesise the alternative ester **8.36**. In this case the use of Mosher chiral acid could directly give a simple method for of determining the diastereomeric ratio by ^{19}F NMR spectroscopy.[179-180] However attempts to synthesise **8.36** by coupling **7.7** and acid **8.35** under similar conditions as previously, only gave recovered starting material.



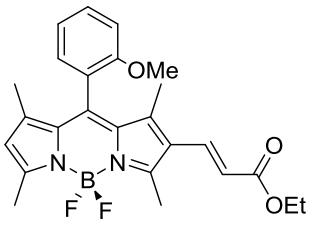
Scheme 8.21 Attempted synthesis of **8.36**

8.7.2 Conclusions

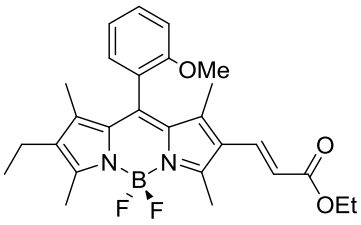
Coupling of axially chiral BODIPYs with chiral (*R*)-2-phenylpropionic acid was successful with EDCI. However the diastereomeric BODIPYs synthesised were still not separable by column chromatography.

8.8 Chiral HPLC Separation

With difficulties in separation of diastereomeric BODIPYs, we decided to examine chiral HPLC as a method for separation of axially chiral BODIPYs. Separation of **7.4** by chiral HPLC using a Chiralpak AD-H column and Heptane : IPA = 95 : 5 as the eluent gave two peaks confirming that **7.4** was racemic (Figure 8.1).

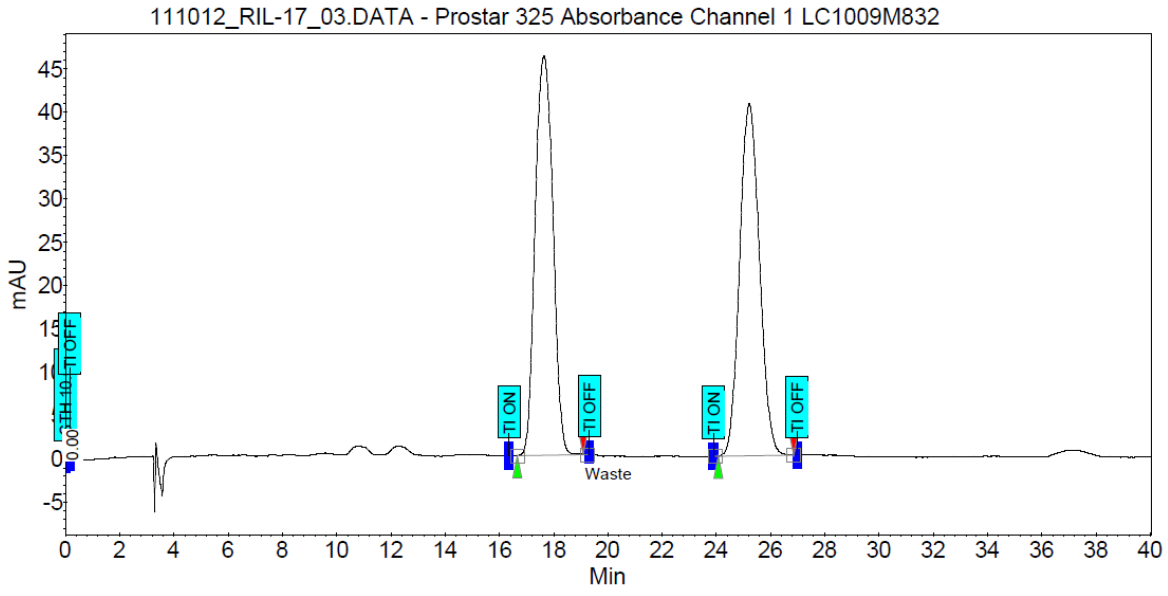


7.4



7.5

Analysis of the other axially chiral BODIPYs gave similar HPLC traces. Racemic BODIPY **7.5** and racemic BODIPY **8.38** were separated using Chiralcel OD-H column and Heptane : IPA = 95 : 5 and Chiralpak IA column and Heptane : IPA = 95 : 5 as the eluent, respectively (Figure 8.2). This showed that the axially chiral BODIPYs were separable by chiral HPLC.

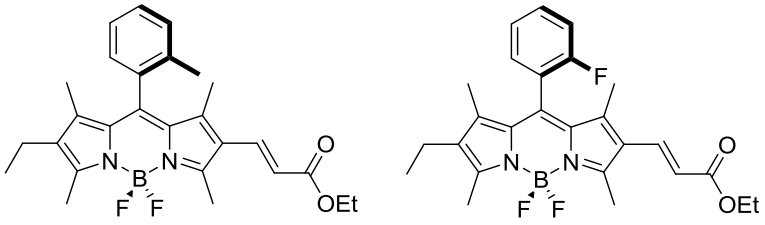


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	17.64	50.39	46.1	35.0	50.387
2	UNKNOWN	25.21	49.61	40.6	34.4	49.613
Total			100.00	86.7	69.4	100.000

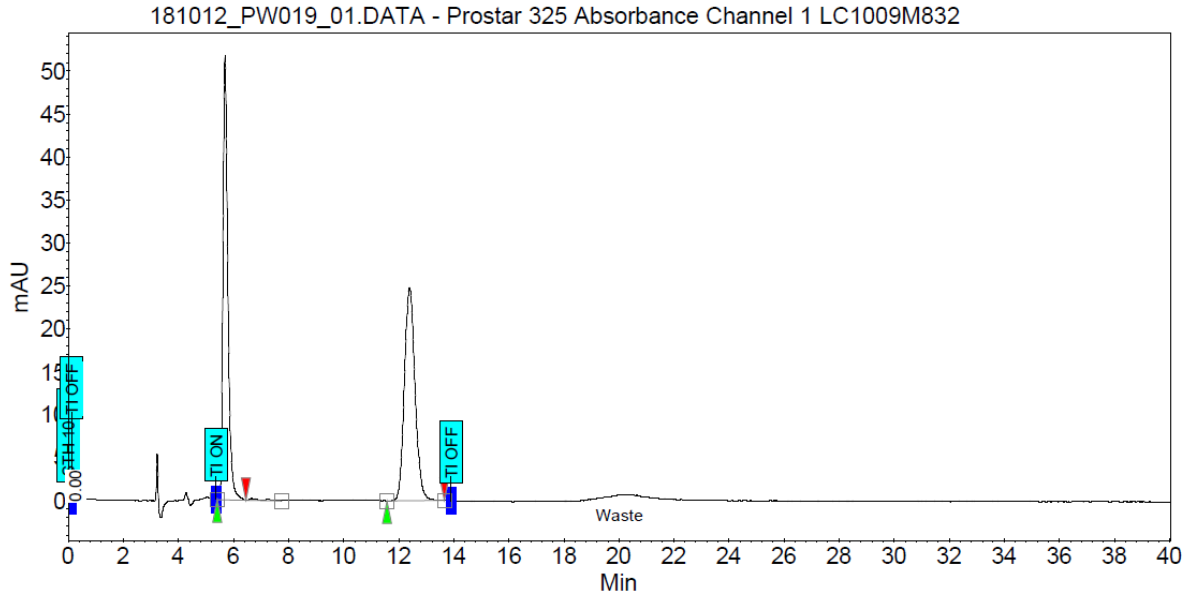
Figure 8.1 Chiral HPLC trace of **7.4**

Submission BODIPY **8.37** and **8.38** (synthesised by Mr Thomas Winstanley) to preparative chiral HPLC (column: Chiralpak AD-H, eluent: Heptane/IPA = 85/15 and Chiralpak IA, eluent Heptane/IPA= 95/5, respectively) successfully separated each BODIPY into two fractions. α_D^{20} measurement using a polarimeter revealed that these two fractions were enantiomeric.



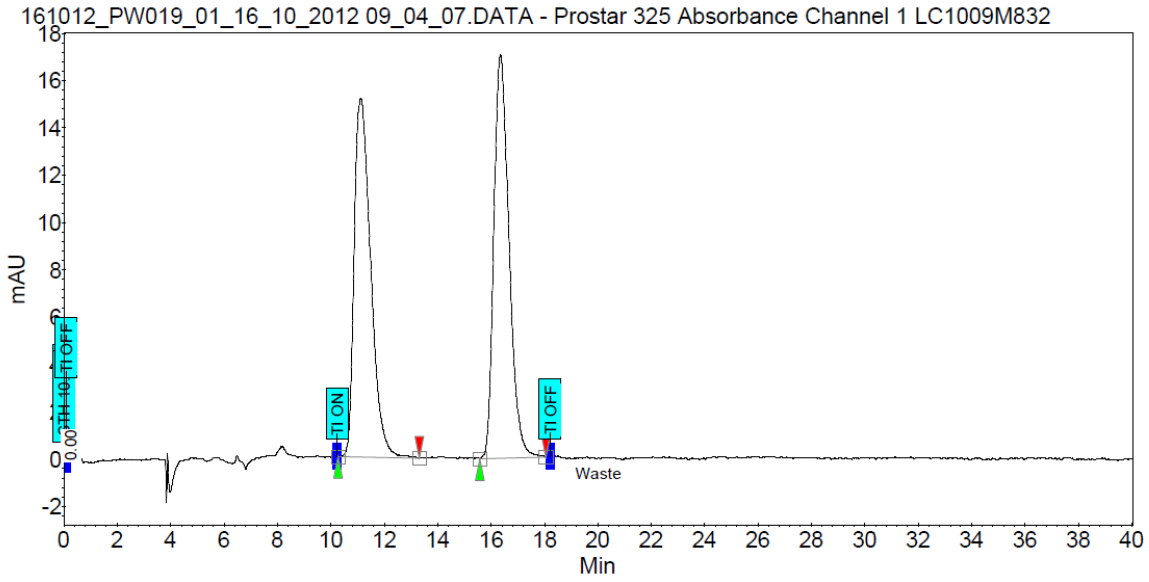
8.37 **8.38**

Scheme 8.22 α_D^{20} of **8.37** (fraction 1 = +13.0°, fraction 2 = -13.0°) and α_D^{20} of **8.38** (fraction 1 = +32.5°, fraction 2 = -32.5°)



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.69	49.27	51.7	10.8	49.266
2	UNKNOWN	12.39	50.73	24.9	11.2	50.734
Total			100.00	76.6	22.0	100.000



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.11	49.24	15.2	10.9	49.238
2	UNKNOWN	16.35	50.76	17.1	11.2	50.762
Total			100.00	32.2	22.1	100.000

Figure 8.2 Chiral HPLC trace of **8.37** (up) and **8.38** (bottom)

8.9 Conclusions

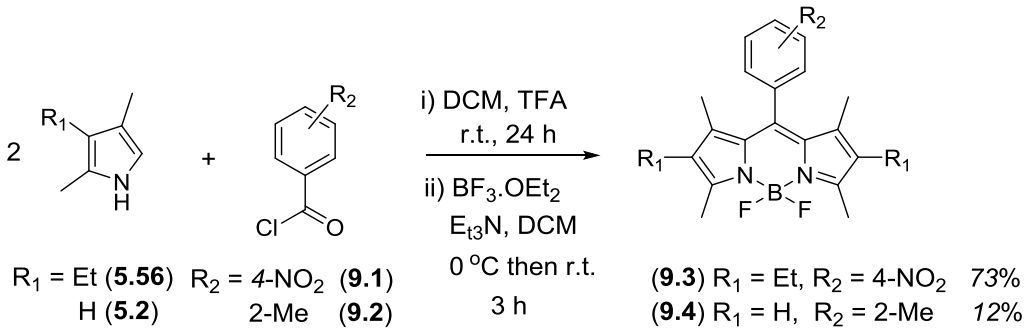
Preparation of diastereomeric BODIPYs was successful through Heck coupling of chiral acrylamides and esterification with chiral acids. However separation of the diastereomeric BODIPYs by standard chromatography was not successful.

The axially chiral BOIDPYs could be seen to be enatiomeric by chiral HPLC analysis. Separation of BODIPY **8.37** was successful by preparative chiral HPLC and gave sufficient material for further analysis.

Chapter 9 Photophysical Properties of Axially Chiral BODIPYs

9.1 UV and Fluorescence

The UV and fluorescence spectra of our synthesised BODIPYs were measured. Firstly we measured the UV/Vis and fluorescence spectra of BODIPY **9.3** and **9.4**. These are known compounds allowing data to be compared to the literature.



R$_1$ = Et (**5.56**) R$_2$ = *4*-NO$_2$ (**9.1**)
H (**5.2**) 2-Me (**9.2**)

(**9.3**) R$_1$ = Et, R$_2$ = 4-NO$_2$ *73%*
(**9.4**) R$_1$ = H, R$_2$ = 2-Me *12%*

Scheme 9.1 Synthesis of **9.3** and **9.4**

Fluorescence measurements were performed by excitation of the sample and the standard (BODIPY **6.16**) at 485 nm. The area under the fluorescence peak (F) was measured and the fluorescence quantum yield calculated based on equation below:

$$\varphi_F^{sample} = \varphi^{standard} x \left({F^{sample}}/{F^{standard}}\right) x \left({n^{sample}}/{n^{standard}}\right)^2 x \left({Abs^{standard}}/{Abs^{sample}}\right)$$

The UV/Vis spectra was measured versus an appropriate standard (BODIPY 2.4) to give Abs(standard) and Abs(sample).

UV and fluorescence data of **9.3** and **9.4** are shown in Table 9.1. The measured data were in agreement with the literature.

Table 9.1 UV and Fluorescence properties of **9.3** and **9.4**

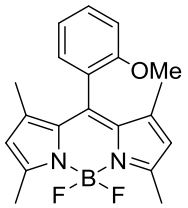
Compound	λ_{Abs} (nm)[a]	λ_{Em} (nm)[a]	ε (M^{-1} cm^{-1})[a]	φ_F[a]
9.3	532 (533)[b]	540 (540)[b]	60300 (70000)[b]	0.02 (0.02)[b]
9.4	503 (503)[c]	514 (514)[c]	73500[c]	0.82 (0.86)[c]

a: **6.16** was the standard in $CHCl_3$ (φ_F = 0.89, λ_{ex} = 485 nm) b: literature[181] (in DCM using Rhodamine 6G as the standard, λ_{ex} = 488 nm) c: literature[152] (in $CHCl_3$ using fluorescein as the standard, λ_{ex} = 490 nm)

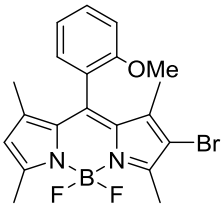
9.1.1 Heavy atom effect

As mentioned in Chapter 6, BODIPY **6.16** was used as a synthetic intermediate in the preparation of axially chiral BODIPYs. As part of this approach, **6.16** was then mono-brominated to give **6.17** whilst over bromination gave dibromo BODIPY **6.18**.

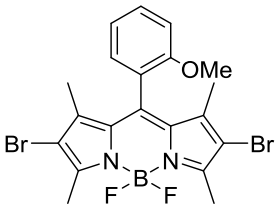
BODIPY **6.16** is known in the literature, therefore **6.16** was used as a standard for measuring the fluorescence quantum yields (φ_F) of our other BODIPYs. Rhodamine B was used as a standard for any BODIPYs for which the S_0-S_1 excitation wavelength was over 500 nm. Photophysical data for **6.16** and mono- and dibromo BODIPY **6.17** and **6.18** are shown below (Table 9.2).



6.16



6.17



6.18

Table 9.2 UV and Fluorescence properties of **6.16**, **6.17** and **6.18**

Entry	Compound	λ_{Abs} (nm)	λ_{Em} (nm)	Stokes Shift (nm)	ε (M^{-1} cm^{-1})	φ_F
1	**6.16**	505 (505)[a]	515 (515)[a]	10	-	0.89
2	**6.17**	517	528	11	170,900	0.17[b]
3	**6.18**	532	544	12	72,000	0.05[b]

a: literature[152] b: **6.16** was the standard in $CHCl_3$ (φ_F = 0.89, λ_{ex} = 485 nm)

UV-Visible spectroscopy measurement of solution of **6.16** in $CHCl_3$ gave an absorption spectra that matched the literature. Excitation of a solution 3.3 x10^{-6} M of **6.16** at 485 nm gave a fluorescence spectra which also matched the literature (λ_{Em} = 515 nm) (Table 8.1, entry 1).

Mono-brominated BODIPY **6.17** gave a high extinction coefficient (ε = 170,900 M^{-1} cm^{-1}), however the φ_F was lower than **6.16**, due to the heavy atom effect. The λ_{Abs} of **6.17** exhibited a red shift compared to the parent (**6.16**) due to the electronic donating Br group.

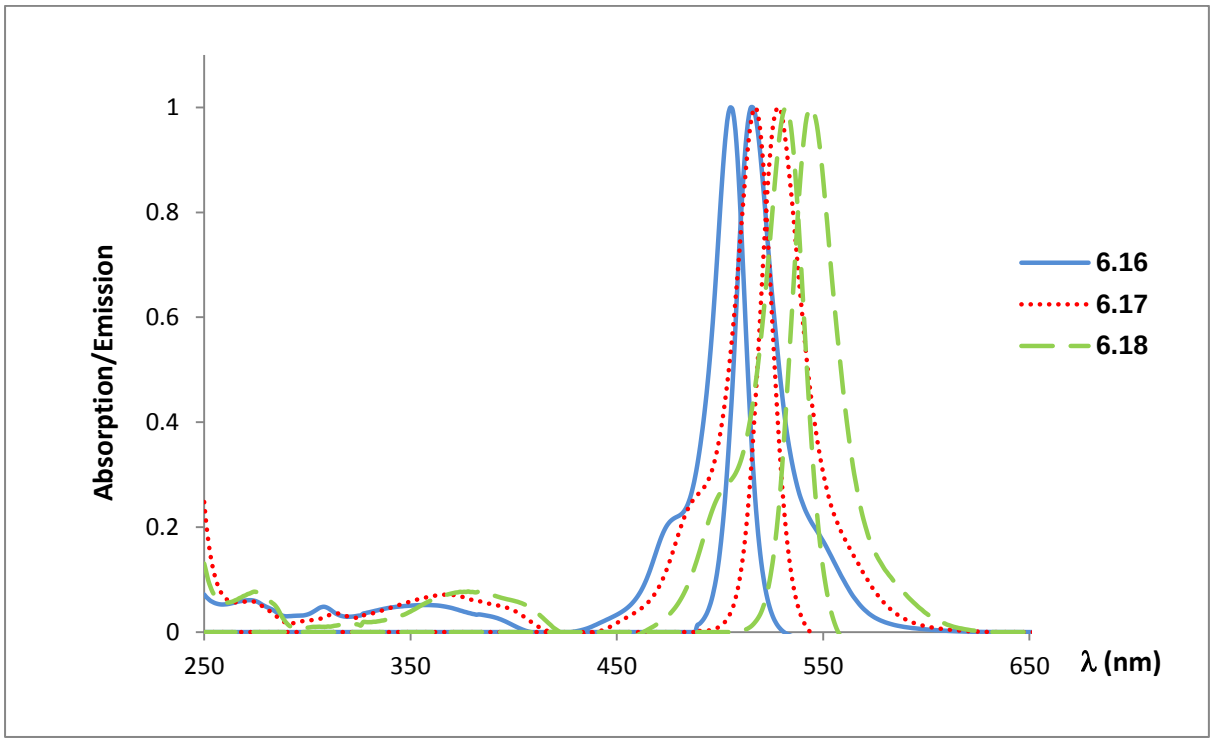
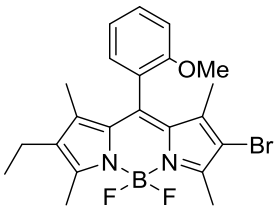


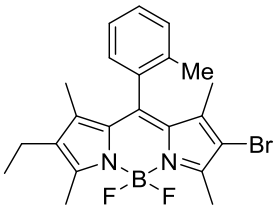
Figure 9.1 Absorption and emission spectra of **6.16**, **6.17** and **6.18** (in $CHCl_3$)

Di-brominated BODIPY **6.18** showed a further red shift in both absorption and emission, as well as a very low φ_F, due to heavy atom promoted intersystem crossing to the triplet (T_1) state.

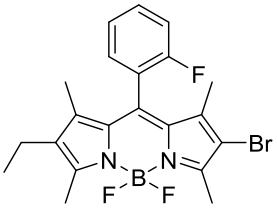
We also examined other BODIPY **6.21**, **6.25**, **6.26** (synthesised previously) and BODIPY **9.5** and **9.6** (synthesised by Mr. Thomas Winstanley).



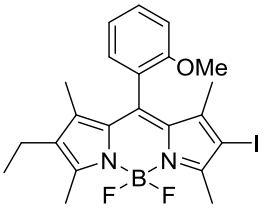
6.21



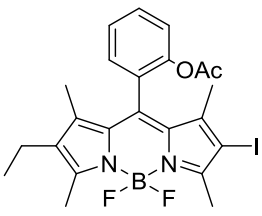
9.5



9.6



6.25



6.26

The Uv/Vis and fluorescence spectra are shown in Figure 8.2, λ_{max} (Abs), λ_{max} (Em), Stokes shift, ε and φ_F are shown in Table 9.3.

Table 9.3 UV/Vis and Fluorescence properties of **6.21**, **9.5**, **9.6**, **6.25** and **6.26**

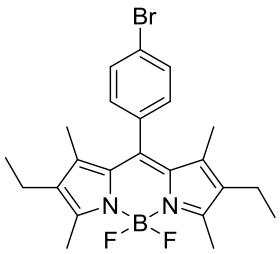
Entry	Compound	λ_{Abs} (nm)	λ_{Em} (nm)	Stokes Shift (nm)	ε (M^{-1} cm^{-1})	φ_F
1	**6.21**	528	541	13	64,900	0.19[a]
2	**9.5**	526	540	14	98,800	0.15[b]
3	**9.6**	532	545	13	63,200	0.14[b]
4	**6.25**	529	542	13	67,100	0.04[a]
5	**6.26**	532	546	14	47,400	0.07[b]

a: **6.16** as the standard in $CHCl_3$ (φ_F = 0.89, λ_{ex} = 485 nm), b: Rhodamine B as the standard in MeOH (φ_F = 0.70, λ_{ex} = 512 nm)

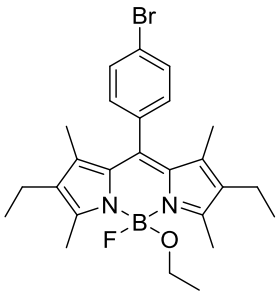
BODIPY **6.21**, **9.5** and **9.6**, all showed low φ_F due to the influence of the bromine atom. The introduction of an iodide to **6.25**/**6.26** caused the φ_F to decrease still further. λ_{Abs} of these BODIPYs showed a red shift of 11 nm, in comparison to **6.17**, due to the electron donating nature of the ethyl group.[182]

9.1.2 UV/Vis and fluorescence of *N,N,O,F* chelated BODIPYs

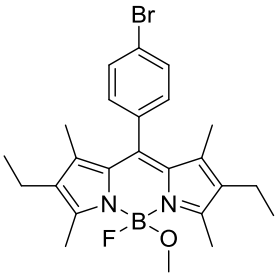
The UV/Vis and fluorescence spectra of *N,N,O,F* chelated BODIPYs have been measured. Mono ethoxy BODIPY **8.11** and mono methoxy BODIPY **8.12**, have been synthesised through Lewis acid ($AlCl_3$) mediated F replacement with ethanol or methanol starting from BODIPY **8.10**.



8.10



8.11



8.12

Rhodamine B in methanol was used as the standard for measuring φ_F and ε. BODIPY **8.11** and **8.12** showed ε over 60,000 M^{-1} cm^{-1} and φ_F consistent with smilar literature compounds.[169]

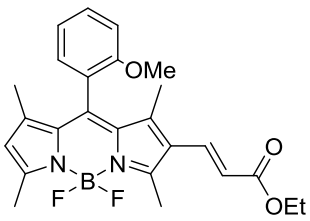
Table 9.4 UV and Fluorescence properties of **8.10**, **8.11** and **8.12**

Entry	Compound	λ_{Abs} (nm)	λ_{Em} (nm)	Stokes Shift (nm)	ε (M^{-1} cm^{-1})	φ_F[a]
1	**8.10**	529	542	13	62,100	0.37
2	**8.11**	527	540	13	65,900	0.51
3	**8.12**	528	541	13	96,000	0.49

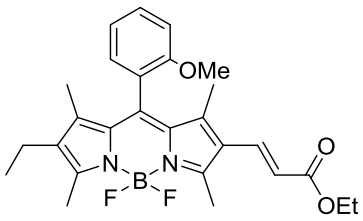
a: Rhodamine B as the standard in MeOH (φ_F = 0.70, λ_{ex} = 512 nm)

9.1.3 Substituent effect

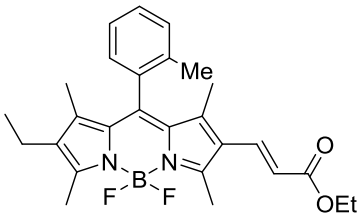
The Heck and Suzuki π-extended BODIPYs have also being analysed by UV-Vis and fluorescence spectrometry. Additional conjugation of the chromophore altered the photophysical properties in comparison to the Br or I substituted precursors (Appendix 1).



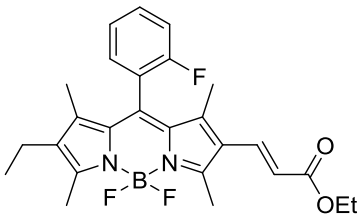
7.4



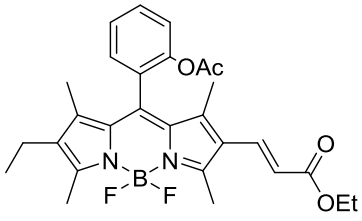
7.5



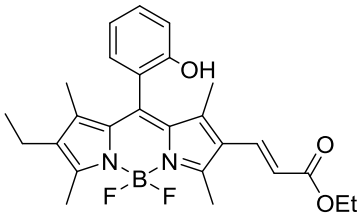
8.37



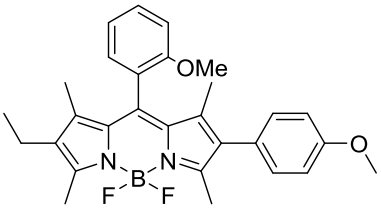
8.38



7.6



7.7



7.9

BODIPY **7.4**, **7.5**, **4.31**, **8.38**, **7.6**, **7.7** and **7.9**, all gave ε between 60,000 and 78,000 M^{-1} cm^{-1} (Table 9.5). The extended conjugation gave a small red shift in comparison to Br or I substituted systems.

Table 9.5 UV and Fluorescence properties of **7.4**, **7.5**, **8.37**, **8.38**, **7.6**, **7.7** and **7.9**

Entry	Compound	λ_{Abs} (nm)	λ_{Em} (nm)	Stokes Shift (nm)	ε (M^{-1} cm^{-1})	φ_F [a]
1	**7.4**	530	548	18	60,000	0.22
2	**7.5**	539	556	17	81,800	0.23
3	**8.37**	538	555	17	71,500	0.24
4	**8.38**	544	562	18	78,200	0.59
5	**7.6**	542	559	17	61,600	0.17
6	**7.7**	540	560	18	46,500	0.28
7	**7.9**	532	558	26	47,800	0.30

a: Rhodamine B as the standard in MeOH (φ_F = 0.70, λ_{ex} = 512 nm)

8.38 gave a very high φ_F. This has been attributed to the *ortho*-fluoro substituent and this effect has been observed for other BODIPYs with similar *ortho*-fluorophenyl groups at the *meso* position.[149]

9.2 Axial Chiral Demonstration and Absolute Stereochemistry Determination

After the resolution of **8.37** by chiral HPLC (Chapter 8), enantiopure of **8.37** was then submitted to Electronic Circular Dichroism (ECD). ECD spectroscopy is a valuable technique for observing chiral molecules.[183-184]

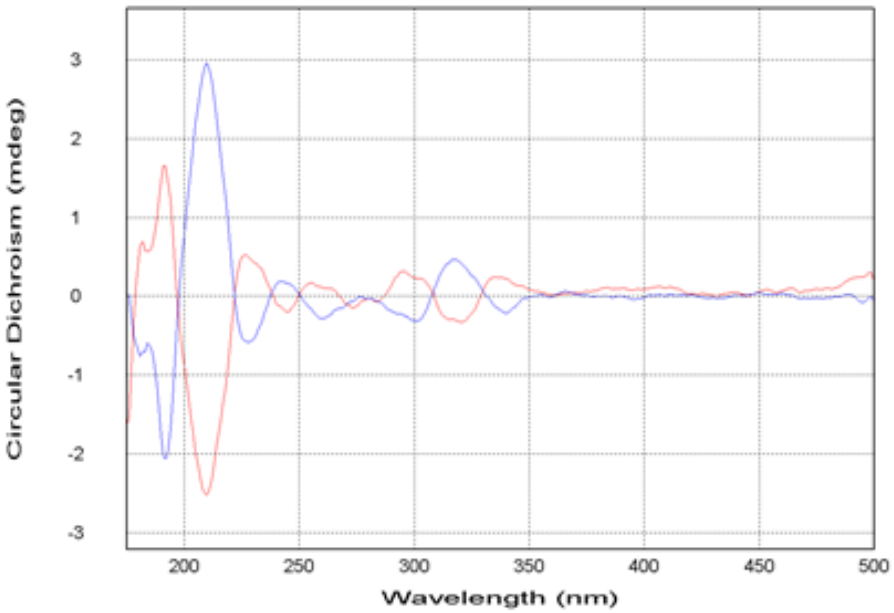


Figure 9.2 CD spectra for **8.37** (red= fraction 1, α_D^{20} = +13.0°, blue = fraction 2, α_D^{20} = -13.0°)

Measurement of the ECD spectra of both (+) and (-)-**8.37**, in methanol, produced mirror image spectra of the two compounds (Figure 9.2). The mirror image spectra showed that (+)-**8.37** and (-)-**8.37** are enantiomers.

TD-DFT computational calculation for (*R*)-**8.37** produced a calculated ECD spectrum. The calculated spectrum then was compared to the experimental spectra of both (+) and (-)-**8.37**. In this case, the calculated spectrum matched to the (+)-**8.37** spectrum in the region of 175-275 nm. This allowed determining the absolute stereochemistry of (+)-BODIPY **8.37** as (*R*)-**8.37**. Therefore the absolute stereochemistry of the (-)-**8.37** should be (*S*)-**8.37**.

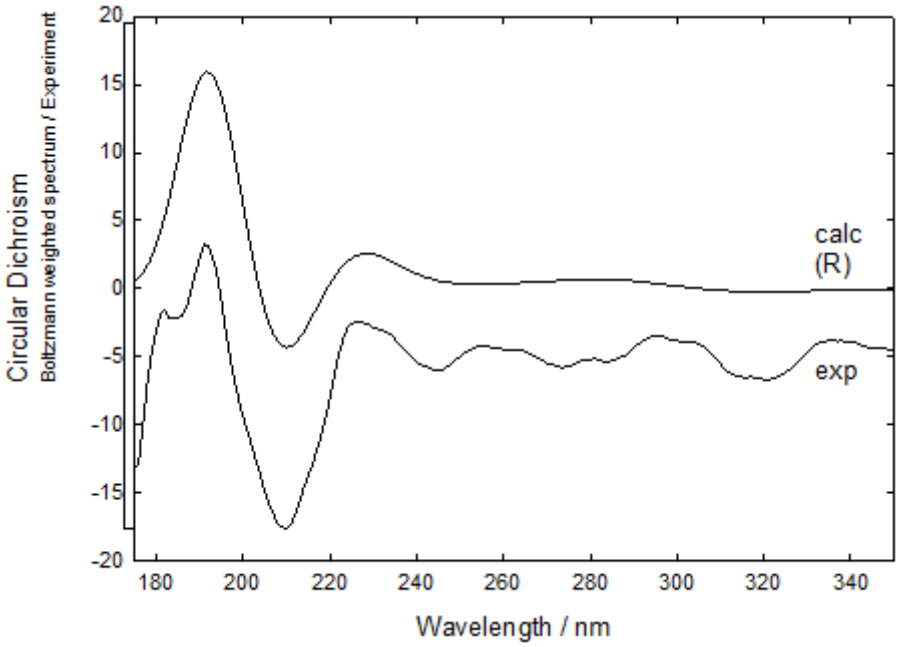


Figure 9.3 Calculation and experimental ECD spectra of (*R*)-**8.37** and (+)-**8.37**

9.3 Conclusions

We have successfully measured the Abs, Em, φ_F, ε and Stokes shift of our synthesised BODIPYs. Halogen substituents of the BODIPYs gave decreased φ_F through the heavy atom effect. The introduction of ortho-fluorophenyl groups at the meso position gave unusually increased φ_F.

ECD and VCD, in combination with computational modelling allowed the R/S assignment of axially chiral BODIPY **8.37**.

Chapter 10 Experimental

10.1 General Procedures

All chemicals were purchased from Sigma Aldrich, TCI and Alfa Aesar. All reaction solvents used were dried. DCM and toluene were dried over CaH_2, THF was dried over sodium wire in the presence of benzophenone whilst DMF was dried through reduced pressure distillation.

Purification was done through silica gel column chromatography (flash, Kieselgel 60). TLC were visualized with UV light (λ = 235 nm).

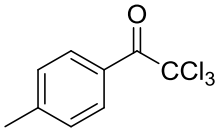
^{1}H and ^{13}C NMR spectra were analysed using 300.13 MHz and 75.47 MHz, respectively on Bruker Avance BVT3200 spectrometer, or 399.78 MHz and 100.53 MHz, respectively using Jeol JNM ECS400 spectrometer. ^{19}F NMR spectra were recorded at 376.17 MHz on Jeol JNM ECS400 spectrometer. Proton NMR spectra were expressed as chemical shift (in part per million, ppm) relative to tetramethylsilane (TMS). Proton coupling constants (*J*) are stated in Hz and proton multiplicities such as s (singlet), d (doublet), t (triplet), dd (doublet of doublet) and m (multiplet).

Infra-red analysis used Varian 800 FT-IR Scimitar Series spectrometer scanning from 4000-600 cm^{-1}. Mass spectrometry analysis was done using Micromass LCT Premier Mass Spectrometer in Electron Spray (ES) mode or by the NMSCC Swansea.

Samples analysed in solution were dissolved in spectroscopic grade of chloroform or methanol. Optical polarity measurement (α_D^{20}) of the chiral samples was done using POLAAR 2001 at 589 nm of sodium lamp source and 0.5 dcm cell length. UV-Vis and fluorescence spectra were recorded on PerkinElmer Lamda 35 and DIGILAB HITACHI F-2500 FL spectrophotometer, respectively. The slit width was 2.5 nm for both excitation and emission. Electronic Circular Dichroism (ECD) spectroscopy measurement used JASCO J-810 spectropolarimeter with the light source is Xe polarised light.

10.2 Compound Experimental

10.2.1 2,2,2-Trichloro-1-(4-tolyl)ethan-1-one



2.17

To a round bottom flask was added sequentially $AlCl_3$ (8.82 g, 66 mmol) and DCM (30 mL). While cooling to 0^oC, 6.4 mL (60 mmol) of toluene and 7.4 mL (66 mmol) of TCAC were added. The solution was stirred for 1 hour under nitrogen atmosphere. The solution

was quenched with 30 mL of saturated Na_2CO_3 solution. The organic layer was washed with 30 mL of brine then dried using $MgSO_4$. Solvent was removed under reduce pressure to give a black oil. The crude product then distilled by reduced pressure distillation (0.02 torr, b.p. = 115-116 ^oC) to give a yellow oil (**2.16**), 9.23 g (65%).

R_f : 0.46 (UV active, petrol 40/60 : ether = 90: 1)

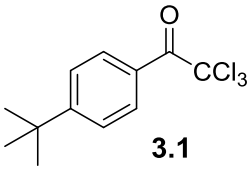
^1H NMR (300 MHz, $CDCl_3$) : δ_H 2.47 (s, 3H, C**H**$_3$), 7.29-7.35 (m, 2H, Ar**H**), 8.16-8.22 (m, 2H, Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 21.8 (**C**H_3), 95.8 (**C**Cl_3), 126.2 (Ar**C**-CH_3), 129.2 (2 Ar**C**H), 131.7 (2 Ar**C**H), 145.6 (Ar**C**-CO), 180.6 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 1704.5 (C=O), 1604.9, 842.3, 744.6, and 656.6

HRMS : calcd for $C_9H_8OCl_3$ $(M+H)^+$: 236.9635, found 236.9637

10.2.2 2,2,2-Trichloro-1-(4-*t*-butyl)ethan-1-one



3.1

To a round bottom flask under nitrogen was added sequentially $AlCl_3$ (6.68 g, 50.1 mmol), DCM (10 mL) and *t*-butylbenzene (7.74 g, 50 mmol). While cooling to -30^{o}C, a solution 5.58 mL (50.1 mmol) of TCAC in 10 mL DCM was added over 30 min. The solution was stirred for a further 4 days. The solution was quenched with 50 g ice followed by additional 50 mL DCM. The organic layer was washed with 5x50 mL of NaOH 2M and 50 mL of brine then dried using MgSO4. The solvent was removed under reduce pressure to give a black oil. The crude product then distilled through reduced pressure distillation (0.02 torr, b.p. = 76-77 ^{o}C) to give a colourless oil (**3.1**), 4.00 g (45%).

R_f : 0.32 (UV active, petrol 40/60 : ether = 7: 3)

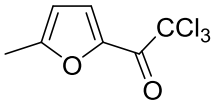
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.38 (s, 9H), 7.53 (dd, *J* = 6.9, 1.8 Hz, 2H), 8.24 (dd, *J* = 6.9, 1.8 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 31.1 (**C**H_3), 35.4 (**C**), 95.8 (**C**Cl_3), 125.6 (Ar**C**-CH_3), 126.2 (2 Ar**C**H), 131.8 (2 Ar**C**H), 158.5 (Ar**C**-CO), 187.0 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 2971.2, 1709.9 (C=O), 1602.9, 1231.3, 853.9, 783.9, 700.3

HRMS : calcd for $C_{12}H_{14}OCl_3$ $(M+H)^+$: 279.0105, found 279.0104

10.2.3 2,2,2-Trichloro-1-(5-methylfuran-2-yl)ethan-1-one



3.2

To a round bottom flask was added sequentially DCM (60 mL), 3.7 mL of TCAC (33 mmol) and 2.463 g (30 mmol) of 2-methylfuran. The solution was stirred for 24 hour under a nitrogen atmosphere. The solution was quenched with a solution of 1.38 g of K_2CO_3 in 50 mL of water. The organic layer was washed with 3x100 mL of water and followed by 100 mL of brine then dried using $MgSO_4$. Solvent was removed under reduce pressure to give a brown oil. The crude was purified through column chromatography using petrol : ether = 4 : 1 to give a brown oil (**3.2**), 4.43 g (65%).

R_f : 0.50 (UV active, petrol 40/60 : ether = 4: 1)

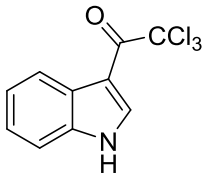
^{1}H NMR (400 MHz, $CDCl_3$) : δ_H 2.47 (s, 3H, C**H**$_3$), 6.29 (dd, *J* = 3.6, 0.8 Hz, 1H, Furan **H**), 7.57 (dd, *J* = 3.6, 0.8 Hz, 1H, Furan **H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 14.2 (**C**H$_3$), 94.4 (**C**Cl$_3$), 109.7 (Furan-**C**H), 125.9 (Furan-**C**H), 143.5 (Furan-**C**CH$_3$), 160.7 (Furan-**C**CO), 170.0 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 1685.9 (C=O), 1500.3, 1211.1, 1031.1, 811.0, 742.2, and 666.0

HRMS : calcd for $C_7H_6O_2Cl_3$ $(M+H)^+$: 226.9428, found 226.9426

10.2.4 2,2,2-Trichloro-1-(1*H*-indol-3-yl)ethan-1-one



3.3

To a round bottom flask under ice bath was added sequentially DCM (40 mL), 1.17 g (10 mmol) of indol and 1.2 mL pyridine (11 mmol). A 1.96 g of TCAC (11 mmol) was added into the solution for over 15 min. The solution was kept in fridge (5 ^{o}C) for 7 days. A solid was filtered out and washed with 50 mL methanol and 50 mL water respectively. The solid was dried under vacuum to give brown solid (**3.3**), 2.28 g (87%).

m.p. = 235-237 ^{o}C

R_f : 0.35 (UV active, petrol 40/60 : EtOAc = 7: 3)

^{1}H NMR (400 MHz, d_6-DMSO) : δ_H 7.30-7.33 (m, 2H, 2 ArC**H**), 7.57-7.60 (m, 1H, ArC**H**), 8.18-8.22 (m, 1H, ArC**H**), 8.60 (s, 1H, indole C**H**), 12.54 (s, 1H, N**H**)

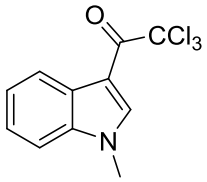
^{13}C NMR (100 MHz, d_6-MDSO) : δ_C 96.5 (**C**Cl_3), 104.7 (Ar**C**H), 112.9 (indole **C**-CO), 121.2 (Ar**C**H), 123.1 (Ar**C**H), 123.8 (Ar**C**H), 127.1 (Ar**C**-indole C), 136.1 (indole **C**H), 136.7 (Ar**C**NH), 176.7 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3250.5 (NH), 2981.3, 1638.9 (C=O)

HRMS : calcd for $C_{10}H_7NOCl_3$ $(M+H)^+$: 261.9438, found 261.9436

Crystal Growth: slow evaporation from DCM : Petrol 40/60 = 1 : 2

10.2.5 2,2,2-Trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one



3.4

To a round bottom flask under ice bath was added sequentially DCM (20 mL), 0.655 g (5 mmol) of methylindol and 0.4 mL pyridine (5.1 mmol). A 0.899 g of TCAC (5.1 mmol) was added into the solution for over 15 min. The solution was kept in fridge (5 ^{o}C) for 3 days. A solid was filtered out and diluted in 25 mL DCM. The solution was washed with 5x50 mL HCl 1M and dried the organic solvent to give a colourless solid (**3.4**), 1.03 g (75%).

m.p. = 118-120 ^{o}C

R_f : 0.52 (UV active, petrol 40/60 : ether = 7: 3)

^{1}H NMR (400 MHz, $CDCl_3$) : δ_H 3.89 (s, 3H, C**H**$_3$), 7.36-7.39 (m, 2H, 2 ArC**H**), 7.41-7.44 (m, 1H, ArC**H**), 8.19-8.23 (m, 1H, ArC**H**), 8.44 (s, 1H, indole C**H**)

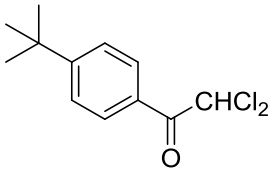
^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 96.7 (**C**Cl_3), 105.3 (Ar**C**H), 110.0 (indole **C**-CO), 122.6 (Ar**C**H), 123.6 (Ar**C**H), 124.0 (Ar**C**H), 128.2 (Ar**C**-indole C), 133.9 (**C**H_3), 136.8 (indole **C**H), 138.0 (Ar**C**NH), 176.7 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 2980.3, 1651.7 (C=O)

HRMS : calcd for $C_{11}H_9NOCl_3$ $(M+H)^+$: 275.9743, found 275.9741

Crystal Growth: slow evaporation from DCM : Petrol 40/60 = 1 : 2

10.2.6 1-(4-(*t*-Butyl)phenyl)-2,2-dichloroethan-1-one



3.9

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.279 g (1 mmol) of 2,2,2-trichloro-1-(4-(*t*-butyl)phenyl)ethen-1-one (**3.1**) in 1 mL THF and stirred for 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 50 : 1 to give a colourless oil (**3.9**), 0.175 g (71%).

R_f : 0.43 (UV active, petrol 40/60 : ether = 50: 1)

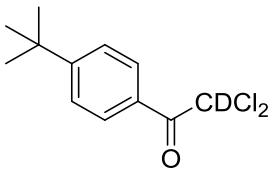
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.37 (s, 9H, 3 C**H**$_3$), 6.70 (s, 1H, C**H**), 7.55 (d, *J* = 8.6 Hz, 2H, Ar**H**), 8.04 (d, *J* = 8.6 Hz, 2H, Ar**H**)

^{13}C NMR (75 MHz, $CDCl_3$) : δ_C 30.9 (3 **C**H$_3$), 35.3 (**C**-CH$_3$), 67.8 (**C**HCl$_2$), 125.8 (2 Ar**C**H), 128.8 (Ar**C-C**O), 129.7 (2 Ar**C**H), 158.6 (Ar**C**), 185.5 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 2964.6, 2869.9 (C-H), 1703.6 (C=O), 852.9 and 701.3

HRMS : calcd for $C_{12}H_{15}OCl_2$ $(M+H)^+$: 245.0494, found 245.0493

10.2.7 1-(4-(*t*-Butyl)phenyl)-2,2-dichloroethan-1-one-2-*d*



3.10

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.279 g (1 mmol) of 2,2,2-trichloro-1-(4-(*t*-butyl)phenyl)ethen-1-one (**3.1**) in 1 mL THF and stirred for 1 hour. The reaction quenched with 0.02 mL of D_2O and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 70 : 1 to give a colourless oil (**3.10**), 0.238 g (96%).

R_f : 0.33 (UV active, petrol 40/60 : ether = 70: 1)

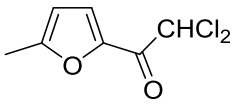
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.37 (s, 9H, 3 C**H**$_3$), 7.53(d, *J* = 8.8 Hz, 2H, Ar**H**), 8.05 (d, *J* = 8.8 Hz, 2H, Ar**H**)

^{13}C NMR (75 MHz, $CDCl_3$) : δ_C 30.9 (3 **C**H$_3$), 35.3 (**C**-CH$_3$), 67.6 (**C**DCl_2, $J_{C\text{-}D}$ = 26.8 Hz), 125.8 (2 Ar**C**H), 128.7 (Ar**C**-CO), 129.7 (2Ar**C**H), 158.6 (Ar**C**) , 185.5 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 2964.8, 2870.1 (C-H), 1699.3 (C=O), 1603.5, 1256.3, 916.8, 767.5 and 695.8

HRMS : calcd for $C_{12}H_{14}DOCl_2$ $(M+H)^+$:246.0558, found 246.0557

10.2.8 2,2-Dichloro-1-(5-methylfuran-2-yl)ethan-1-one



3.11

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.180 g (0.79 mmol) of 2,2,2-trichloro-1-(2-methylfuran-5-yl)ethen-1-one (**3.2**) in 1 mL THF and stirred for 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 7 : 3 to give a brown oil (**3.11**), 0.088 g (58%).

R_f : 0.54 (UV active, petrol 40/60 : ether = 7: 3)

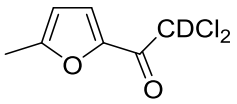
^{1}H NMR (400 MHz, $CDCl_3$) : δ_H 2.46 (s, 3H, C**H**$_3$), 6.30 (dd, *J* = 3.6, 0.8 Hz, 1H, Furan **H**), 6.50 (s, 1H, C**H**Cl_2), 7.45 (dd, *J* = 3.6, 0.8 Hz, 1H, Furan **H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 14.1 (**C**H_3), 66.6 (**C**HCl_2), 110.1 (Furan **C**H), 123.4 (Furan **C**H), 146.1 (Furan**C**CH_3), 160.2 (Furan **C**CO), 174.5 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3123.0, 1678.7 (C=O), 1504.9, 1203.4, 1022.3, 802.7 and 741.9

HRMS : calcd for $C_7H_7O_2Cl_2$ $(M+H)^+$: 192.9818, found 192.9819

10.2.9 2,2-Dichloro-1-(5-methylfuran-2-yl)ethan-1-one-2-*d*



3.12

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.180 g (0.79 mmol) of 2,2,2-trichloro-1-(2-methylfuran-5-yl)ethen-1-one (**3.2**) in 1 mL THF and stirred for 1 hour. The reaction quenched with 0.02 mL of D_2O and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 8 : 2 to give a yellow oil (**3.12**), 0.132 g (68%).

R_f : 0.41 (UV active, petrol 40/60 : ether = 7: 3)

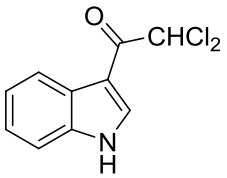
^{1}H NMR (400 MHz, $CDCl_3$) : δ_H 2.42 (s, 3H, C**H**$_3$), 6.26 (dd, *J* = 3.6, 0.9 Hz, 1H, Furan C**H**), 7.41 (dd, *J* = 3.6, 0.9 Hz, 1H, Furan C**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 14.1 (**C**H$_3$), 66.7 (**C**DCl_2, $J_{C\text{-}D}$ = 27.1 Hz), 110.2 (Furan **C**H), 123.4 (Furan **C**H), 146.1 (Furan**C**CH_3), 160.2 (Furan **C**CO), 174.5 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3123.1, 1674.4 (C=O), 1505.0, 1211.3, 1032.7, 914.3 and 761.0

HRMS : $C_7H_6DO_2Cl_2$ ($M+H^+$) :193.9880, found 193.9877

10.2.10 2,2-dichloro-1-(1*H*-indol-3-yl)ethan-1-one



3.13

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 1.1 mL, 2.1 mmol). Into that flask was added 0.262 g (1 mmol) of 2,2,2-trichloro-1-(1*H*-indol-3-yl)ethanone (**3.3**) in 1 mL THF and stirred for 1 hour. The reaction was quenched with 10 mL of NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : EtOAc = 3 : 2 to give a colourless solid (**3.13**), 0.108 g (33%).

R_f : 0.15 (UV active, petrol 40/60 : EtOAc = 7 : 3)

m.p. = 235-237 ^oC

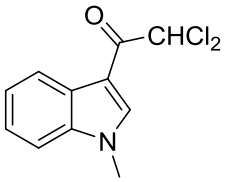
^1H NMR (300 MHz, d_6-DMSO) : δ_H 7.23-7.33 (m, 2H, 2 Ar**H**), 7.51-7.56 (m, 1H, Ar**H**), 7.61 (2, 1H, C**H**Cl_2), 8.11-8.21 (m, 1H, ArC**H**), 8.61 (s, 1H, indole **C**H), 12.42 (s, 1H, N**H**)

^{13}C NMR (100 MHz, d_6-DMSO) : 68.7 (**C**HCl_2), 109.7 (Ar**C**H), 112.7 (indole **C**H), 121.2 (indole **C**CO), 122.8 (3 Ar**C**H), 123.8 (indole Ar**C**), 127.9 (Ar**C**NH), 135.9 (Ar **C**), 181.4 (**C**=O)

IR (ν_{max} /cm^{-1}) : 3216.1 (NH), 2980.9, 1640.4 (C=O), 1424.5, 1235.9, 1148.3, 739.6 and 626.5

HRMS : calcd for $C_{10}H_8Cl_2NO$ ($M+H^+$) : 227.9977, found 227.9979

10.2.11 2,2-dichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one



3.14

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 1.1 mL, 2.2 mmol). Into that flask was added 0.274 g (1 mmol) of 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethanone (**3.4**) in 1 mL THF and stirred for 1 hour. The reaction was quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : EtOAc = 9 : 1 to give a yellow solid (**3.14**), 0.180 g (75%).

R_f : 0.49 (UV active, petrol 40/60 : EtOAc = 7: 3)

m.p. = 206-208 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 3.93 (s, 3H, C**H**$_3$), 6.41 (s, 1H, C**H**Cl_2), 7.36-7.46 (m, 3H, 3 ArC**H**), 8.09 (s, 1H, indole C**H**), 8.38-8.40 (m, 1H, ArC**H**)

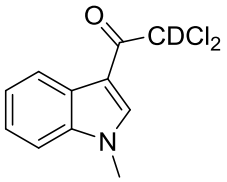
^{13}C NMR (100 MHz, $CDCl_3$) : 33.9 (**C**H_3), 69.2 (**C**HCl_2), 109.9 (Ar**C**H), 122.7 (**C**CO), 123.5 (indole Ar**C**), 124.1(2 Ar**C**H), 127.2 (Ar**C**H), 136.8 (Ar**C**NCH_3), 137.4 (Ar**C**), 181.8 (**C**=O)

IR (ν_{max} /cm^{-1}) : 3100.3, 1636.1 (C=O), 1531.4, 1087.1, 741.3, 710.1 and 699.1

HRMS : calcd for $C_{11}H_{10}Cl_2NO$ ($M+H^+$) : 242.0134, found 242.0134

Crystal Growth: slow evaporation of Petrol 40/60 : DCM = 2 : 1

10.2.12 2,2-dichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one-2-d



3.15

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 1.1 mL, 2.2 mmol). Into that flask was added 0.274 g (1 mmol) of 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethanone (**3.4**) in 1 mL THF and stirred for 1 hour. The reaction was quenched with 0.02 mL of D_2O and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : EtOAc = 9 : 1 to give a colourless solid (**3.15**), 0.158 g (65%).

R_f : 0.14 (UV active, petrol 40/60 : EtOAc = 9: 1)

m.p. = 211-213 ^oC

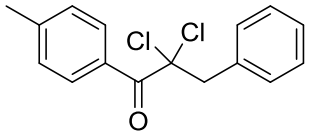
^1H NMR (300 MHz, $CDCl_3$) : δ_H 3.93 (s, 3H, CH_3), 7.34-7.44 (m, 3H, 3 Ar**H**), 8.09 (s, 1H, indole C**H**), 8.40 (m, 1H, ArC**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : 34.0 (**C**H_3), 110.1 (**C**DCl_2), 122.8 (**C**CO), 123.6 (indole Ar**C**), 124.2 (2Ar**C**H), 127.2 (Ar**C**H), 136.9 (Ar**C**NCH_3), 137.4 (Ar**C**), 181.8 (**C**=O)

IR (ν_{max}/cm^{-1}) : 3099.5, 2980.7, 1631.7 (C=O), 1530.0, 1371.8, 1238.9, 739.8, 698.2 and 660.6

HRMS : calcd for $C_{11}H_9DCl_2NO$ ($M+H^+$) : 243.0197, found 243.0200

10.2.13 2,2-dichloro-3-phenyl-1-(4-tolyl)propan-1-one



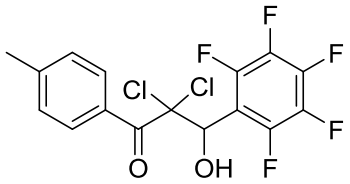
3.17

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.237 g (1 mmol) of 2,2,2-trichloro-1-(*p*-tolyl)ethenone (**2.17**) in 1 mL THF and stirred for 1 hour. A solution of 0.171 g (1 mmol) of benzylbromide in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction was quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 7 : 3 but no of **3.17** was isolated.

Another procedure

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.237 g (1 mmol) of 2,2,2-trichloro-1-(*p*-tolyl)ethenone (**2.17**) in 1 mL THF and stirred for 1 hour. A solution of 0.171 g (1 mmol) of benzylbromide and sodium iodide (10%) (0.015 g, 0.1 mmol) in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction was quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 7 : 3 but no of **3.17** was isolated.

10.2.14 2,2-Dichloro-3-hydroxy-3-(perfluorophenyl)-1-(*p*-tolyl)propan-1-one



3.18

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.237 g (1 mmol) of 2,2,2-trichloro-1-(*p*-tolyl)ethenone (**2.17**) in 1 mL THF and stirred for 1 hour. A solution of 0.196 g (1 mmol) of *per*-fluorobenzaldehyde in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction was quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 7 : 3 to give a colourless solid (**3.18**), 0.367 g (92%).

R_f : 0.48 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 119-120 ^oC

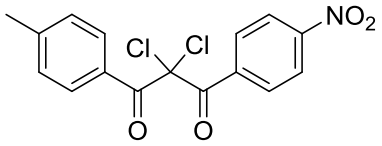
^1H NMR (300 MHz, $CDCl_3$) : δ_H 2.47 (s, 3H, C**H**$_3$), 3.98 (d, *J* = 6.5 Hz, 1H, O**H**), 6.11 (d, *J* = 6.5 Hz, 1H, C**H**), 7.32 (d, *J* = 8.7 Hz, 2H, Ar**H**), 8.23 (d, *J* = 8.7 Hz, 2H, Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 21.7 (**C**H$_3$), 72.9 (**C**H-OH), 85.3 (**C**Cl$_3$), 128.3 (Ar**C**-CH$_3$), 129.0 (2 Ar**C**H), 131.3 (2 Ar**C**H), 145.7 (5 Ar**C**F), 188.7 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3333.6 (OH), 1689.2 (C=O), 1606.1, 1524.0, 1496.2, 994.0 and 858.8

HRMS : calcd for $C_{16}H_{10}O_2Cl_2F_5$ $(M+H)^+$: 398.9973 found 398.9968

10.2.15 2,2-Dichloro-1-(4-nitrophenyl)-3-(4-tolyl)propane-1,3-dione



3.19

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.237 g (1 mmol) of 2,2,2-trichloro-1-(4-tolyl)ethen-1-one (**2.17**) in 1 mL THF and stirred for 1 hour. A solution of 0.185 g (1 mmol) of 4-nitrobenzoylchloride in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 9 : 1 to give a colourless oil (**3.19**), 0.326 g (93%).

R_f : 0.35 (UV active, petrol 40/60 : ether = 9: 1)

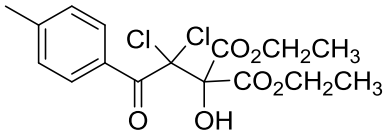
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 2.42 (s, 3H, C**H**$_3$), 7.27 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.95 (d, *J* = 8.4 Hz, 2H, Ar**H**), 8.12 (d, *J* = 8.4 Hz, 2H, Ar**H**), 8.25 (d, *J* = 8.1 Hz, 2H, Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 21.9 (**C**H_3), 83.3 (**C**Cl_2), 123.7 (2 Ar**C**H), 128.2 (Ar**C**), 129.6 (2 Ar**C**H), 130.7 (2 Ar**C**H), 131.4 (2 Ar**C**H), 136.4 (Ar**C**), 146.3 (Ar**C-**CH_3), 150.5 (Ar**C**-NO_2), 184.1 and 185.1 (2 **C**=O)

IR(neat): ν_{max}/cm^{-1} 3111.0, 3054.7 (C-H), 1703.4 and 1689.8 (2 C=O), 1601.1, 1526.4, 693.8

HRMS : calcd for $C_{16}H_{12}NO_4Cl_2$ $(M+H)^+$: 352.0138, found 352.0134

10.2.16 Diethyl 2-(1,1-dichloro-2-oxo-2-(*p*-tolyl)ethyl)-2-hydroxymalonate



3.20

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.237 g (1 mmol) of 2,2,2-trichloro-1-(4-tolyl)ethen-1-one (**2.17**) in 1 mL THF and stirred for 1 hour. A solution of 0.160 g (1 mmol) of diethyl ketomalonate in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 9 : 1 to give a yellow oil (**3.20**), 0.345 g (92%).

R_f : 0.21 (UV active, petrol 40/60 : ether = 9: 1)

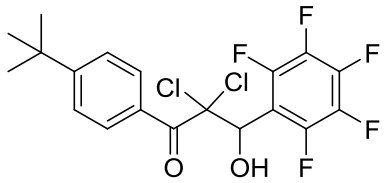
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.25 (t, *J* = 7.1 Hz, 6H, C**H**$_3$), 2.36 (s, 3H, C**H**$_3$), 4.29 (q, *J* = 7.1 Hz, 4H, C**H**$_2$), 4.56 (s, 1H, O**H**), 7.21 (d, *J* = 7.5 Hz, 2H, Ar**H**), 8.05 (d, *J* = 8.3 Hz, 2H, Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 13.8 (2 **C**H$_3$), 21.7 (**C**H$_3$), 63.3 (2 **C**H$_2$), 82.6 (**C**Cl$_2$), 85.3 (**C**OH), 150.7 (Ar**C**), 128.8 (2 Ar**C**H), 130.8 (2 Ar**C**H), 144.9 (Ar**C**-CH$_3$), 166.5 (2 C=O) , 187.6 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3454.5, 2984.1, 1737.7 (C=O), 1690.3, 1235.6, 1133.8 and 858.2

HRMS : calcd for $C_{16}H_{19}O_6Cl_2$ $(M+H)^+$:377.0559, found 377.0553

10.2.17 1-(4-(*t*-Butyl)phenyl)-2,2-dichloro-3-hydroxy-3-(perfluorophenyl) propan-1-one



3.21

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.279 g (1 mmol) of 2,2,2-trichloro-1-(4-(*t*-butyl)phenyl)ethen-1-one (**3.1**) in 1 mL THF and stirred for 1 hour. A solution of 0.196 g (1 mmol) of perfluorobenzaldehyde in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 9 : 1 to give a colourless oil (**3.21**), 0.234 g (53%).

R_f : 0.15 (UV active, petrol 40/60 : ether = 90: 1)

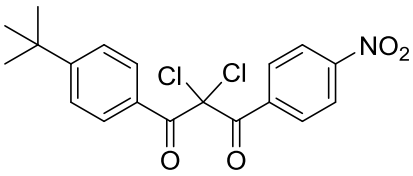
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.38 (s, 9H, 3 C**H**$_3$), 3.93 (d, *J* = 6.6 Hz, 1H, O**H**), 6.11 (d, *J* = 6.6 Hz, 1H, C**H**-OH), 7.54 (d, *J* = 8.4 Hz, 2H, 2 Ar**H**), 8.28 (d, *J* = 8.4 Hz, 2H, 2 Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 31.0 (3 **C**H$_3$), 35.4 (**C**H-OH), 73.1 (**C**Cl$_2$), 125.5 (2 Ar**C**H), 125.7 (Ar**C-**CF), 128.3 (Ar**C**-CH$_3$) , 128.4 (Ar**C**-CO), 131.4 (2 Ar**C**H), 158.7 (5 Ar**C**F), 188.8 (CO)

IR(neat): ν_{max}/cm^{-1} 3519.0, 2968.0, 1682.5 (C=O), 1603.6, 1524.5, 1499.4 and 997.2

HRMS : calcd for $C_{19}H_{19}NCl_2F_5O_2$ $(M+NH_4)^+$:458.0707, found 458.0708

10.2.18 1-(4-(*t*-Butyl)phenyl)-2,2-dichloro-3-(4-nitrophenyl)propane-1,3-dione



3.23

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.279 g (1 mmol) of 2,2,2-trichloro-1-(4-(*t*-butyl)phenyl)ethen-1-one (**3.1**) in 1 mL THF and stirred for 1 hour. A solution of 0.185 g (1 mmol) of 4-nitrobenzoylchloride in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 40 : 1 to give a colourless oil (**3.23**), 0.150 g (38%).

R_f : 0.28 (UV active, petrol 40/60 : ether = 30: 1)

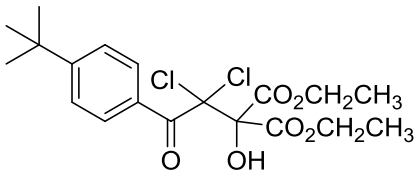
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.25 (s, 9H, 3 C**H**$_3$), 7.40 (dd, *J* = 8.7, 2.1 Hz, 2H, 2ArC**H**), 7.93 (dd, *J* = 8.7, 2.1 Hz, 2H, 2 Ar**H**), 8.05 (dd, *J* = 9.3, 2.3 Hz, 2H, 2 Ar**H**), 8.17 (dd, *J* = 9.3, 2.3 Hz, 2H, 2 Ar**H**)

^{13}C NMR (75 MHz, $CDCl_3$) : δ_C 30.8 (3 **C**H$_3$), 35.3 (**C**-CH$_3$), 86.4 (**C**Cl$_2$), 123.5 (2 Ar**C**H), 125.8 (2 ArCH), 129.7 (Ar**C**), 130.0 (2 Ar**C**H), 131.4 (2 Ar**C**H), 136.9 (Ar**C-**CO), 150.5 (Ar**C**-CO), 159.0 (Ar**C**-NO$_2$), 184.2 (**C**O), 185.2 (**C**O)

IR(neat): ν_{max}/cm^{-1} 2964.8, 2869.5, 1695.2 (C=O), 1602.4, 1528.4, 1346.9, 849.0 and 692.1

HRMS : calcd for $C_{19}H_{18}NO_4Cl_2$ $(M+H)^+$:394.0607, found 394.0604

10.2.19 Diethyl 2-(2-(4-(*t*-butyl)phenyl)-1,1-dichloro-2-oxoethyl)-2-hydroxymalonate



3.24

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.279 g (1 mmol) of 2,2,2-trichloro-1-(4-(*t*-butyl)phenyl)ethen-1-one (**3.1**) in 1 mL THF and stirred for 1 hour. A solution of 0.171 g (1 mmol) of diethyl ketomalonate in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 40 : 1 to give a yellow oil (**3.24**), 0.240 g (57%).

R_f : 0.05 (UV active, petrol 40/60 : ether = 40: 1)

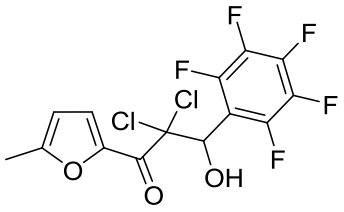
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.28 (t, *J* = 7.0 Hz, 6H, 2 C**H**$_3$), 1.31 (s, 9H, 3 C**H**$_3$), 2.00 (s, 1H, O**H**), 4.19-4.50 (m, 4H, 2 C**H**$_2$), 7.45 (dd, *J* = 8.8,1.7 Hz, 2H, 2 Ar**H**), 8.14 (dd, *J* = 8.8, 1.7 Hz, 2H, 2 Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 13.9 (2 **C**H$_3$), 31.0 (3 **C**H$_3$), 35.3 (**C**-CH$_3$), 63.4 (2 **C**H$_2$), 82.8 (**C**Cl$_2$), 125.3 (2 Ar**C**H), 128.9 (Ar**C**-CO), 125.9 (**C**-OH), 130.9 (2 Ar**C**H), 157.9 (Ar**C**), 166.7 (2 C=O) , 187.5 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3457.2, 2965.1, 1736.9 (C=O), 1690.8 (C=O), 1603.8, 1224.5 and 863.3

HRMS : calcd for $C_{19}H_{25}O_6Cl_2$ $(M+H)^+$: 419.1023, found 419.1024

10.2.20 2,2-Dichloro-3-hydroxy-1-(5-methylfuran-2-yl)-3-(perfluorophenyl) propan-1-one



3.25

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.234 g (1 mmol) of 2,2,2-trichloro-1-(2-methylfuran-5-yl)ethen-1-one (**3.2**) in 1 mL THF and stirred for 1 hour. A solution of 0.196 g (1 mmol) of perfluorobenzaldehyde in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 9 : 1 to give a yellow oil (**3.25**), 0.108 g (28%).

R_f : 0.35 (UV active, petrol 40/60 : ether = 6: 4)

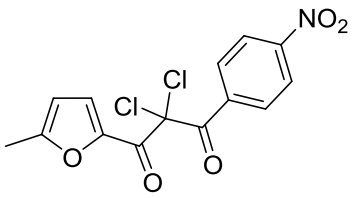
^{1}H NMR (400 MHz, $CDCl_3$) : δ_H 2.48 (s, 3H, C**H**$_3$), 3.97 (d, *J* = 7.2 Hz, 1H, O**H**), 6.11 (d, *J* = 7.2 Hz, 1H, C**H**), 6.31 (dd, *J* = 3.6, 0.9 Hz, 1H, furan C**H**), 7.66 (dd, *J* = 3.6, 0.9 Hz, 1H, furan C**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 14.3 (**C**H$_3$), 72.8 (**C**OH), 85.3 (**C**Cl$_2$), 110.1 (2 furan **C**H), 110.3 (Ar**C**), 126.3 (furan **C**CO), 145.7 (5Ar**C**F), 160.9 (furan **C**), 177.0 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3390.0 (OH), 1656.0 (C=O), 1498.7, 1292.2, 1148.1, 996.2 and 800.8

HRMS : calcd for $C_{14}H_8Cl_2F_5O_3$ $(M+H)^+$: 388.9765, found 388.9758

10.2.21 2,2-Dichloro-1-(5-methylfuran-2-yl)-3-(4-nitrophenyl)propane-1,3-dione



3.27

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.234 g (1 mmol) of 2,2,2-trichloro-1-(2-methylfuran-5-yl)ethen-1-one (**3.2**) in 1 mL THF and stirred for 1 hour. A solution of 0.185 g (1 mmol) of 4-nitrobenzoylchloride in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of NH_4Cl and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 8 : 2 to give a yellow oil (**3.27**), 0.221 g (65%).

R_f : 0.45 (UV active, petrol 40/60 : ether = 7: 3)

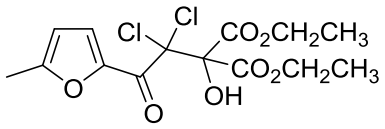
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 2.35 (s, 3H, C**H**$_3$), 6.21 (d, *J* = 3.5 Hz, 1H, Ar**H** furan), 7.42 (d, *J* = 3.6 Hz, 1H, Ar**H** furan), 8.16 (d, *J* = 9.0 Hz, 2H, Ar**H**), 8.28 (d, *J* = 9.0 Hz, 2H, Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 14.3 (**C**H$_3$), 99.6 (**C**Cl$_2$), 110.5 (furan **C**H), 123.8 (Ar**C**H), 125.2 (furan **C**H), 131.2 (Ar**C**H), 136.8 (Ar**C**), 145.9 (furan **C**-CO), 150.5 (Ar**C-**NO_2), 160.6 (furan **C**-CH_3), 172.7 (**C**=O), 183.7 (C=O)

IR(neat): ν_{max}/cm^{-1} 3119.3, 1713.0 (C=O), 1681.5 (C=O), 1530.9, 1503.6, 813.1, 787.0 and 694.9

HRMS : $C_{14}H_{10}Cl_2NO_5$ (M+H$^+$) : 341.9931, found 341.9927

10.2.22 Diethyl 2-(1,1-dichloro-2-(5-methylfuran-2-yl)-2-oxoethyl)-2-hydroxymalonate



3.28

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.234 g (1 mmol) of 2,2,2-trichloro-1-(2-methylfuran-5-yl)ethen-1-one (**3.2**) in 1 mL THF and stirred for 1 hour. A solution of 0.174 g (1 mmol) of diethyl ketomalonate in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 40 : 1 to give a yellow oil (**3.28**), 0.255 g (69%).

R_f : 0.13 (UV active, petrol 40/60 : ether = 4: 1)

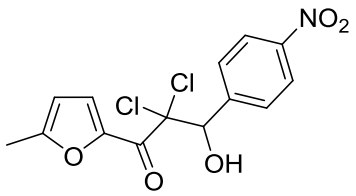
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.30 (s, 6H, 2 C**H**$_3$), 2.42 (s, 3H, C**H**$_3$), 4.37 (q, *J* = 7.1 Hz, 4H, 2 C**H**$_2$), 4.58 (d, *J* = 6.0 Hz, 1H, C**H**), 6.24 (dd, *J* = 3.6, 0.4 Hz, 1H, furan C**H**), 7.65 (dd, *J* = 3.6, 0.4 Hz, 1H, furan C**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 13.9 (2 **C**H$_3$), 14.3 (**C**H$_3$), 63.5 (2 C**H**$_2$), 82.3 (**C**OH), 109.7 (**C**Cl$_2$), 125.7 (2 furan **C**H), 145.4 (furan **C**CO), 160.5 (furan **C**), 166.4 (**C=**O), 175.8 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3345.9 (OH), 2995.5, 1726.1 (C=O), 1235.9, 1152.2, 1082.9, 719.4 and 618.4

HRMS : calcd for $C_{14}H_{17}Cl_2O_7$ $(M+H)^+$: 367.0346, found 367.0352

10.2.23 2,2-Dichloro-3-hydroxy-1-(5-methylfuran-2-yl)-3-(4-nitrophenyl) propan-1-one



3.29

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.234 g (1 mmol) of 2,2,2-trichloro-1-(2-methylfuran-5-yl)ethen-1-one (**3.2**) in 1 mL THF and stirred for 1 hour. A solution of 0.151 g (1 mmol) of 4-nitrobenzaldehyde in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of NH_4Cl and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 15 : 1 to give a yellow oil (**3.29**), 0.218 g (64%).

R_f : 0.40 (UV active, petrol 40/60 : ether = 8: 2)

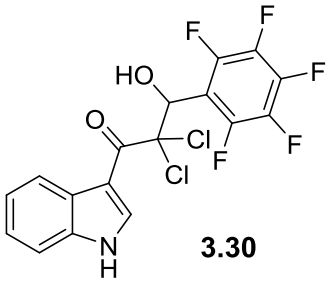
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 2.32 (s, 3H, C**H**$_3$), 3.82 (s, 1H, C**H**OH), 6.04 (d, *J* = 3.2 Hz, 1H, Ar**H** furan), 6.68 (d, *J* = 3.2 Hz, 1H, Ar**H** furan), 7.36-7.43 (m, 2H, Ar**H**), 7.80-7.88 (m, 2H, Ar**H**)

^{13}C NMR (75 MHz, $CDCl_3$) : δ_C 13.4 (**C**H$_3$), 84.4 (**C**OH), 105.6 (**C**Cl$_2$), 106.5 (furan **C**H), 111.8 (furan **C**H), 127.2 (2 Ar**C**H), 128.7 (Ar**C**-COH), 128.9 (2 Ar**C**H), 136.6 (Ar**C-**NO$_2$), 150.0 (furan **C**-CO), 152.8 (furan **C**), 174.5 (C=O)

IR(neat): ν_{max}/cm^{-1} 3557.9 (OH), 2980.9, 1689.8 (C=O), 1604.8, 1449.2, 1026.8, 762.9 and 720.2

HRMS : calcd for $C_{14}H_{12}Cl_2NO_5$ $(M+H)^+$: 343.9941, found 343.9939

10.2.24 2,2-Dichloro-3-hydroxy-1-(1*H*-indol-3-yl)-3-(perfluorophenyl)propan-1-one



3.30

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 1.1 mL, 2.2 mmol). Into that flask was added 0.262 g (1 mmol) of 2,2,2-trichloro-1-(1*H*-indol-3-yl)ethan-1-one (**3.1**) in 1 mL THF and stirred for 1 hour. A solution of 0.196 g (1 mmol) of *per*fluorobenzaldehyde in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 3 : 2 to give a colourless solid (**3.30**), 0.242 g (57%).

R_f : 0.14 (UV active, petrol 40/60 : ether = 3: 2)

m.p. = 229-231 ^oC

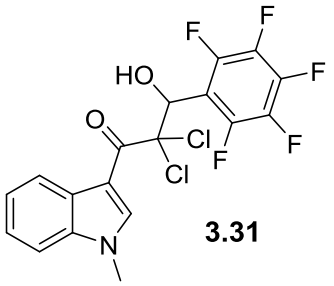
^1H NMR (300 MHz, d_6-DMSO) : δ_H 6.08 (d, *J* = 6.6 Hz, 1H, O**H**), 7.20 (d, *J* = 6.6 Hz, 1H, C**H**), 7.23-7.33 (m, 2H, 2 ArC**H**), 7.51-7.62 (m, 1H, ArC**H**), 8.23 (dd, *J* = 6.3, 3.3 Hz, 1H, ArC**H**), 8.57 (d, *J* = 3.3 Hz, 1H, indole C**H**), 10.14 (s, 1H, N**H**)

^{13}C NMR (100 MHz, d_6-DMSO) : δ_C 72.2 (**C**H-OH), 90.3 (**C**Cl_2), 109.4 (Ar**C**H), 113.1 (indole **C**H), 121.9 (indole **C**CO), 123.2 (3 Ar**C**H), 124.0 (Ar **C**CO), 127.8 (Ar**C**), 136.2 (Ar **C**NH), 136.4 (5 Ar**C**F), 182.7 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3572.2 (NH), 3254.3 (OH), 1641.8 (C=O), 1500.9, 1433.4, 1240.4 and 998.7

HRMS : calcd for $C_{17}H_9Cl_2F_5NO_2$ $(M+H)^+$: 423.9925, found 423.9922

10.2.25 2,2-Dichloro-3-hydroxy-1-(1-methyl-1*H*-indol-3-yl)-3-(perfluorophenyl) propan-1-one



3.31

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 1.1 mL, 2.2 mmol). Into that flask was added 0.274 g (1 mmol) of 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one (**3.4**) in 1 mL THF and stirred for 1 hour. A solution of 0.196 g (1 mmol) of perfluorobenzaldehyde in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : EtOAc = 9: 1 to give a colourless solid (**3.31**), 0.271 g (62%).

R_f : 0.25 (UV active, petrol 40/60 : EtOAc = 9: 1)

m.p. = 209-210 ^oC

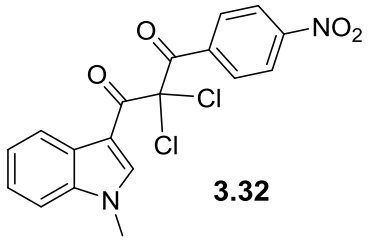
^1H NMR (400 MHz, $CDCl_3$) : δ_H 3.92 (s, 3H, C**H**$_3$), 4.38(d, *J* = 5.2 Hz, 1H, O**H**), 6.12 (d, *J* = 5.2 Hz, 1H, C**H**), 7.33-7.42 (m, 3H, ArC**H**), 8.35 (s, 1H, indole C**H**), 8.35-8.40 (m, 1H, Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 34.1 (**C**H_3), 73.2 (**C**-OH), 85.9 (**C**Cl_2), 108.2 (2 Ar**C**H), 110.2 (Ar**C**CO), 122.8 (2 Ar**C**H), 123.9 (Ar**C**), 124.2 (indole Ar**C**), 128.1 (Ar**C**-NCH_3), 136.9 (indole **C**H), 138.9 (5 Ar**C**F), 185.4 (C=O)

IR(neat): ν_{max}/cm^{-1} 3467.0 (OH), 1645.7 (C=O), 1524.1, 1503.7, 1229.5, 998.2 and 748.0

HRMS: calcd for $C_{18}H_{11}Cl_2F_5NO_2$ $(M+H)^+$:438.0082, found 438.0080

10.2.26 2,2-Dichloro-1-(1-methyl-1*H*-indol-3-yl)-3-(4-nitrophenyl)propane-1,3-dione



3.32

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 1.1 mL, 2.2 mmol). Into that flask was added 0.274 g (1 mmol) of 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one (**3.4**) in 1 mL THF and stirred for 1 hour. A solution of 0.185 g (1 mmol) of *p*-nitrobenzoylchloride in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of NH_4Cl and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : EtOAc = 4 : 1 to give a yellow solid (**3.32**), 0.253 g (65%).

R_f : 0.26 (UV active, petrol 40/60 : EtOAc = 4: 1)

m.p. = 74-75 ^oC

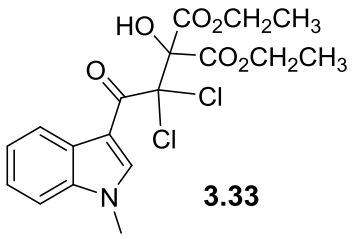
^1H NMR (300 MHz, $CDCl_3$) : δ_H 3.89 (s, 3H, C**H**$_3$), 7.39 (m, 3H, ArC**H**), 8.04 (s, 1H, indole C**H**), 8.13-8.25 (m, 4H, ArC**H** indole), 8.36-8.42 (m, 1H, ArC**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 34.2 (**C**H$_3$), 109.3 (**C**Cl$_2$), 110.2 (indole Ar**C**H), 122.8 (2 Ar**C**H), 123.6 (indole Ar**C**CO), 124.2 (indole Ar**C**H), 124.7 (2 indole Ar**C**H), 127.8 (indole Ar**C**), 131.6 (2 Ar**C**H), 137.0 (indole **C**H), 138.0 (indole Ar**C**-NCH$_3$), 150.4 (Ar**C**), 158.2 (Ar**C**-NO$_2$), 179.9 (C=O), 184.8 (C=O)

IR(neat): ν_{max}/cm^{-1} 2981.1, 1710.6 (C=O), 1659.3 (C=O), 1627.6, 1521.1, 1346.6, 1225.9, 746.1 and 692.9

HRMS: calcd for $C_{18}H_{13}Cl_2N_2O_4$ $(M+H)^+$: 391.0247, found 391.0247

10.2.27 Diethyl 2-(1,1-dichloro-2-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-2-hydroxymalonate



3.33

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 1.1 mL, 2.2 mmol). Into that flask was added 0.274 g (1 mmol) of 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one (**3.4**) in 1 mL THF and stirred for 1 hour. A solution of 0.174 g (1 mmol) of diethyl ketomalonate in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : EtOAc = 40 : 1 to give a brown solid (**3.33**), 0.135 g (32%).

R_f : 0.07 (UV active, petrol 40/60 : EtOAc = 40: 1)

m.p. = 218-219 ^oC

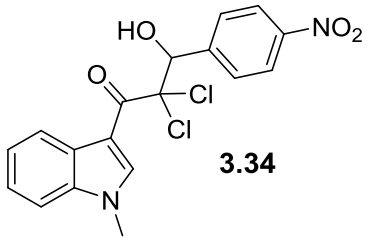
^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.34 (t, *J* = 7.1 Hz, 6H, 2 C**H**$_3$), 3.91 (s, 3H, C**H**$_3$), 4.45-4.31 (m, 4H, 2 C**H**$_2$), 4.77 (s, 1H, C**H**), 7.36 (m, 3H, indole ArC**H**), 8.36-8.31 (m, 1H, indole ArC**H**),8.42 (s, 1H, indole C**H**)

^{13}C NMR (75 MHz, $CDCl_3$) : δ_C 13.8 (2 **C**H$_3$), 33.7 (**C**H$_3$), 62.9 (2 **C**H$_2$), 82.9 (**C**-OH), 85.9 (**C**Cl$_2$), 108.2 (indole Ar**C**H), 109.7 (indole Ar**C**H), 122.8 (indole Ar**C**H), 123.3 (indole Ar**C**H), 123.8 (indole Ar**C**CO), 128.3 (indole Ar**C**), 136.8 (indole **C**H), 138.0 (indole Ar**C**-NCH_3), 166.6 (C=O), 183.1 (C=O)

IR(neat): ν_{max}/cm^{-1} 3516.9 (OH), 2984.4, 1753.5 (C=O), 1736.1(C=O), 1635.3, 1519.1, 1223.0, 1126.6, 1093.5, 755.5 and 626.7

HRMS: calcd for $C_{18}H_{20}Cl_2NO_6$ $(M+H)^+$: 416.0662, found 416.0666

10.2.28 2,2-Dichloro-3-hydroxy-1-(1-methyl-1*H*-indol-3-yl)-3-(4-nitrophenyl) propan-1-one



3.34

To a 25 mL of round bottom flask under nitrogen was added PhMgBr (2M, 1.1 mL, 2.2 mmol). Into that flask was added 0.274 g (1 mmol) of 2,2,2-trichloro-1-(1-methyl-1*H*-indol-3-yl)ethan-1-one (**3.4**) in 1 mL THF and stirred for 1 hour. A solution of 0.151 g (1 mmol) of 4-nitrobenzaldehyde in 1 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 1 hour. The reaction quenched with 10 mL of NH_4Cl and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : EtOAc = 4 : 1 to give a colourless solid (**3.34**), 0.250 g (64%).

R_f : 0.15 (UV active, petrol 40/60 : EtOAc = 4: 1)

m.p. = 216-218 ^oC

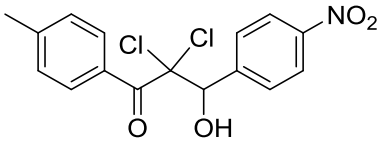
^1H NMR (300 MHz, $CDCl_3$) : δ_H 3.94 (s, 3H, C**H**$_3$), 4.57(d, *J* = 3.3 Hz, 1H, O**H**), 5.72 (d, *J* = 3.0 Hz, 1H, O**H**), 7.36-7.48 (m, 3H, ArC**H**), 7.86 (dd, *J* = 8.8, 2.1 Hz, 2H, 2 ArC**H**), 8.28 (dd, *J* = 8.8, 2.1 Hz, 2H, 2 ArC**H**), 8.36 (s, 1H, indole C**H**), 8.38-8.48 (m, 1H, indole ArC**H**)

^{13}C NMR (75 MHz, $CDCl_3$) : δ_C 33.8 (**C**H$_3$), 86.4 (**C**-OH), 108.8 (**C**Cl$_2$), 109.9 (indole Ar**C**H), 122.3 (2 Ar**C**H), 122.8 (indole Ar**C**CO), 123.8 (indole Ar**C**H), 124.1 (2 indole Ar**C**H), 128.1 (indole Ar**C**), 130.8 (2 Ar**C**H), 136.9 (indole **C**H), 138.8 (indole Ar**C**), 143.1 (Ar**C**), 148.3 (Ar**C**-NO_2), 186.1 (C=O)

IR(neat): ν_{max}/cm^{-1} 3524.4 (OH), 1631.3 (C=O), 1519.8, 1349.4, 751.4, 710.9 and 710.9

HRMS : calcd for $C_{18}H_{15}Cl_2N_2O_4$ $(M+H)^+$: 393.0403 found 393.0399

10.2.29 2,2-dichloro-3-hydroxy-3-(4-nitrophenyl)-1-(4-tolyl)propan-1-one



4.1

To a 25 mL round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.237 g (1 mmol) of 2,2,2-trichloro-1-(4-tolyl)ethen-1-one (**2.17**) in 1 mL THF and stirred for 1 hour. A solution of 0.151 g (1 mmol) of 4-nitrobenzaldehyde in 1 mL of THF was then added drop wise into the mixture and the mixture stirred for a further 1 hour. The reaction was quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 7 : 3 to give a colourless solid (**4.1**), 0.143 g (40%).

R_f : 0.51 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 236-238 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 2.47 (s, 3H, C**H**$_3$), 4.02 (d, *J* = 3.8 Hz, 1H, O**H**), 5.68 (d, *J* = 3.7 Hz, 1H, C**H**-OH), 7.32 (dd, *J* = 8.7, 0.8 Hz, 2H, 2Ar**H**), 7.78-7.88 (m, 2H, 2Ar**H**), 8.21-8.32 (m, 4H, 4Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 21.9 (**C**H$_3$), 77.1 (**C**-OH), 85.4 (**C**Cl$_2$), 122.6 (Ar**C**), 128.5 (2 Ar**C**H), 129.4 (2 Ar**C**H), 130.9 (2 Ar**C**H), 131.7 (2 Ar**C**H), 142,6 (Ar**C**-CO), 146.0 (Ar**C**-CH$_3$), 148.3 (Ar**C**-NO$_2$), 190.0 (**C**=O)

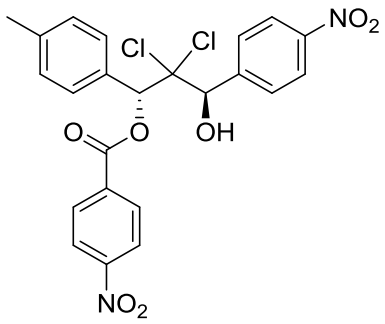
IR(neat): ν_{max}/cm^{-1} 3537.1, 2921.9, 1664.1 (C=O)

HRMS: calcd for $C_{16}H_{13}Cl_2NO_4$ $[M+Na]^+$: 378.0084; found: 378.0086

Second procedure:

To a 25 mL round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.237 g (1 mmol) of 2,2,2-trichloro-1-(4-tolyl)ethen-1-one (**2.17**) in 1 mL THF and stirred for 1 hour. A solution of 0.151 g (1 mmol) of 4-nitrobenzaldehyde in 1 mL of THF was then added drop wise into the mixture at -78 ^{o}C and stirred for a further 1 hour. The reaction was quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 7 : 3 to give a colourless solid (**4.1**), 0.219 g (62%).

10.2.30 (1*R*,3*R*)-1-(4-tolyl-2,2-dichloro-3-hydroxy-3-(4-nitrophenyl) propyl 4-nitrobenzoate



4.2

To a 25 mL round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.237 g (1 mmol) of 2,2,2-trichloro-1-(4-tolyl)ethen-1-one (**2.17**) in 1 mL THF and stirred for 1 hour. A solution of 0.151 g (1 mmol) of 4-nitrobenzaldehyde in 1 mL of THF was then added drop wise into the mixture and the mixture stirred for a further 1 hour. The reaction was quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 7 : 3 to give a colourless solid (**4.2**), 0.116 g (23%).

R_f : 0.16 (UV active, petrol 40/60 : ether = 8: 2)

m.p. = 148-150 ^oC

^1H NMR (300 MHz, d_6-DMSO) : δ_H 2.28 (s, 3H, C**H**$_3$), 5.48 (d, *J* = 5.6 Hz, 1H, O**H**), 5.27 (d, *J* = 5.4 Hz, 1H, C**H**-OH), 6.50 (s, 1H,C**H**-CCl_2), 7.25-7.13 (m, 3H, 3Ar**H**), 7.42-7.54 (m, 2H, 2Ar**H**), 7.87-7.96 (m, 2H, 2Ar**H**), 8.30-8.37 (m, 2H, 2Ar**H**), 8.38-8.46 (m, 3H, 3Ar**H**)

^{13}C NMR (100 MHz, d_6-DMSO) : δ_C 21.3 (3 **C**H_3), 78.1 (**C**-OH), 94.5 (**C**Cl_2), 122.7 (**C**-OC=O), 124.6 (2 Ar**C**H), 128.9 (2 Ar**C**H), 129.7 (2 Ar**C**H), 131.5 (2 Ar**C**H), 131.7 (2 Ar**C**H), 131.9 (2 Ar**C**H), 134.9 (Ar**C**), 139.1 (Ar**C**), 146,7 (Ar**C**-COH), 147.8 (Ar**C**-CH_3), 151.1 (Ar**C**-NO_2), 152.9 (Ar**C**-NO_2), 162.7 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3497.3, 2960.1, 1727.1 (C=O)

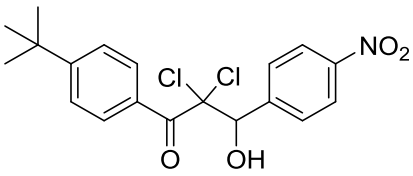
HRMS: calcd for $C_{23}H_{18}Cl_2N_2O_7$ $(M+NH_4)^+$: 522.0825; found: 522.0829

Crystal Growth: slow evaporation of Petrol 40/60 : ether = 2 : 1

Optimisation procedure:

To a 25 mL round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.237 g (1 mmol) of 2,2,2-trichloro-1-(4-tolyl)ethen-1-one (**2.17**) in 1 mL THF and stirred for 1 hour. A solution of 0.302 g (2 mmol) of 4-nitrobenzaldehyde in 1 mL of THF was then added drop wise into the mixture and the mixture stirred for a further 1 hour. The reaction was quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 7 : 3 to give a colourless solid (**4.2**), 0.367 g (71%).

10.2.31 1-(4-(*t*-Butyl)phenyl)-2,2-dichloro-3-hydroxy-3-(4-nitrophenyl)propan-1-one



4.3

To a 25 mL round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.279 g (1 mmol) of 2,2,2-trichloro-1-(4-(*t*-butylphenyl)ethen-1-one (**3.1**) in 1 mL THF and stirred for 1 hour. A solution of 0.151 g (1 mmol) of 4-nitrobenzaldehyde in 1 mL of THF was then added drop wise into the mixture at -78 ^{o}C and the mixture stirred for a further 1 hour. The reaction was quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 50 : 1 to give a colourless solid (**4.3**), 0.318 g (80%).

R_f : 0.15 (UV active, petrol 40/60 : ether = 10: 1)

m.p. = 182-184 ^{o}C

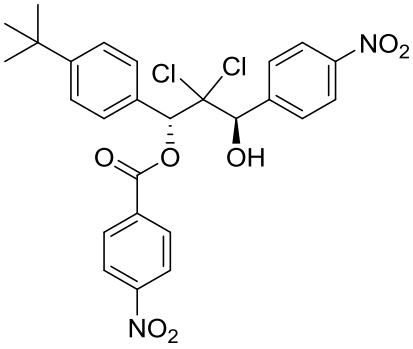
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.38 (s, 9H, 3 C**H**$_3$), 4.04 (d, *J* = 3.9 Hz, 1H, O**H**), 5.68 (d, *J* = 3.6 Hz, 1H, C**H**-OH), 7.50-7.56 (m, 2H, 2 Ar**H**), 7.81-7.86 (m, 2H, 2 Ar**H**), 8.25-8.32 (m, 4H, 4 Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 30.9 (3 **C**H$_3$), 35.3 (**C**-CH$_3$), 85.2 (**C**-OH), 122.5 (2 Ar**C**H), 125.3 (2 Ar**C**H), 128.2 (**C**Cl$_2$), 130.8 (2 Ar**C**H), 131.5 (2 Ar**C**H), 142.5 (Ar**C-**CO), 148.1 (2 Ar**C**) , 158.7 (Ar**C**-CCH$_3$), 189.8 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3554.2, 2965.2, 1670.9 (C=O), 1599.3, 1512.2, 1344.5, 1254.8, 869.8, 706.4 and 612.9

HRMS: calcd for $C_{19}H_{23}N_2O_4Cl_2$ $(M+NH_4)^+$: 413.1029, found 413.1027

10.2.32 (1*R*,3*R*)-1-(4-(*t*-Butyl)phenyl)-2,2-dichloro-3-hydroxy-3-(4-nitrophenyl) propyl 4-nitrobenzoate



4.4

To a 25 mL round bottom flask under nitrogen was added PhMgBr (2M, 0.55 mL, 1.1 mmol). Into that flask was added 0.279 g (1 mmol) of 2,2,2-trichloro-1-(4-(*t*-butylphenyl)ethen-1-one in 1 mL THF and stirred for 1 hour. A solution of 0.151 g (1 mmol) of 4-nitrobenzaldehyde in 1 mL of THF was then added drop wise into the mixture and the mixture stirred for a further 1 hour. The reaction was quenched with 10 mL of saturated NH_4Cl solution and extracted with 3x15 mL of ethylacetate. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 9 : 1 to give a colourless solid (**4.4**), 0.247 g (90%).

R_f : 0.25 (UV active, petrol 40/60 : ether = 9: 1)

m.p. = 147-149 ^oC

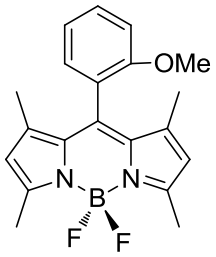
^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.34 (s, 9H, 3 C**H**$_3$), 3.75 (d, *J* = 5.4 Hz, 1H, O**H**), 5.24 (d, *J* = 5.4 Hz, 1H, C**H**-OH), 6.74 (s, 1H,C**H**-CCl_2), 7.46 (dd, *J* = 8.7, 1.8 Hz, 2H, 2Ar**H**), 7.65 (dd, *J* = 8.4, 1.8 Hz, 2H, 2Ar**H**), 7.80 (dd, *J* = 8.7, 1.8 Hz, 2H, 2Ar**H**), 8.24 (dd, *J* = 8.7, 1.9 Hz, 2H, 2Ar**H**), 8.33-8.41 (m, 4H, 4Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 31.3 (3 **C**H_3), 34.8 (**C**-CH_3), 78.4 (**C**-OH), 93.0 (**C**Cl_2), 122.7 (**C**-OC=O), 124.0 (2 Ar**C**H), 125.2 (2 Ar**C**H), 129.5 (2 Ar**C**H), 130.3 (2 Ar**C**H), 130.5 (2 Ar**C**H), 131.3 (2 Ar**C**H), 134.4 (2 Ar**C**), 143,6 (Ar**C**-COH), 148.2 (Ar**C**-CH_3), 151.2 (Ar**C**-NO_2), 152.9 (Ar**C**-NO_2), 164.0 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3495.4, 2964.2, 1726.9 (C=O), 1513.8

HRMS: calcd for $C_{26}H_{28}N_3O_7Cl_2$ $(M+NH_4)^+$: 564.1299, found 564.1294

10.2.33 5,5-Difluoro-10-(2-methoxyphenyl)-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo [1,2-*c*:2',1'-*f*][1,3,2]diazaborinine



6.16

To a round bottom flask was added sequentially 2-methoxybenzoylchloride (0.179 g, 1 mmol), DCM (25 mL) and 2,4-dimethylpyrrole (0.190 g, 2 mmol). The solution was stirred for overnight at room temperature under nitrogen atmosphere. The solution was treated with 1 mL of *N*,*N*-diisopropyl-*N*-ethylamine over 5 minutes and followed by addition of 1 mL of $BF_3.Et_2O$ at 0 ^oC. The solution was stirred for 3 hours. The solution was washed with 2x25 mL of water then dried using $MgSO_4$. Solvent was removed under reduce pressure to give dark brown solid residue. The crude product then purified through column chromatography (petrol 40/60 : ether = 15 : 1) to give an orange solid (**6.16**), 0.088 g (25%).

R_f : 0.33 (UV active, petrol 40/60 : ether = 1: 1)

m.p. = 242-243 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.45 (s, 6H, 2 Pyrrole C**H**$_3$), 2.57 (s, 6H, 2 Pyrrole C**H**$_3$), 3.79 (s, 3H, C**H**$_3$), 5.98 (s, 2H, 2 Pyrrole **H**), 7.00 (dd, *J* = 8.4, 0.9 Hz, 1H, Ar**H**), 7.09 (dd, *J* = 7.4, 2.1 Hz, 1H, Ar**H**), 7.15 (dd, *J* = 7.4, 2.1 Hz, 1H, Ar**H**), 7.46 (dd, *J* = 8.4, 0.9 Hz, 1H, Ar**H**)

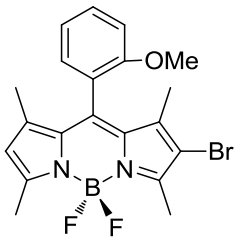
^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 13.8 (2 Pyrrole **C**H$_3$), 14.6 (2 Pyrrole **C**H$_3$), 55.6 (O**C**H$_3$), 111.1 (2 Pyrrole **C**H), 120.8 (Ar**C**H), 121.4 (Ar**C**H), 123.9 (2 Pyrrole **C**), 129.5 (Ar**C**H), 130.6 (Ar**C**H), 131.6 (Ar**C**), 139.0 (2 Pyrrole **C**-CH$_3$), 142.6 (2 Pyrrole **C**-CH$_3$), 154.9 (**C**meso), 156.4 (Ar**C**-OCH$_3$)

^{19}F NMR (376 MHz, $CDCl_3$) : $J(^{19}F_A\text{-}^{11}B)$ = 33.7 Hz, $J(^{19}F_B\text{-}^{11}B)$ = 32.8 Hz, $J(^{19}F_A\text{-}^{19}F_B)$ = 110.7 Hz

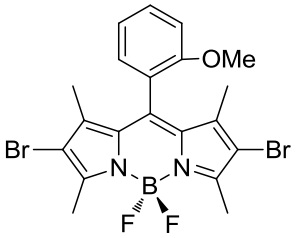
IR(neat): ν_{max}/cm^{-1} 2980.9, 1540.0, 1505.3, 1463.0, 1307.0, 1187.6, 1156.6, 971.2

HRMS : calcd for $C_{20}H_{22}BF_2N_2O$ $(M+H)^+$: 355.1788, found 355.1792

10.2.34 2-Bromo-5,5-difluoro-10-(2-methoxyphenyl)-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine 6.17 and 2,8-dibromo-5,5-difluoro-10-(2-methoxyphenyl)-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine 6.18



6.17



6.18

To a round bottom flask was added sequentially 4,4-difluoro-8-(2-methoxyphenyl)-1,3,5,7-tetramethyl-4-bora-3*a*,4*a*-diaza-*s*-indacene (**6.16**) (0.285 g, 0.8 mmol), DCM (300 mL) and bromine (16.35 µL, 0.8 mmol). The solution was stirred for 48 hours at room temperature under nitrogen atmosphere. The solution was washed with 2x25 mL of water then dried using $MgSO_4$. Solvent was removed under reduce pressure to give brown solid residue. The crude product then purified through column chromatography (petrol 40/60 : ether = 15 : 1) to give a red solid (**6.17**), 0.190 g (55%) and (**6.18**). 0.190 g (46%).

(**6.17**)

R_f : 0.40 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 204-206 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.44 (s, 3H, Pyrrole C**H**$_3$), 1.45 (s, 3H, Pyrrole C**H**$_3$), 2.58 (s, 3H, Pyrrole C**H**$_3$), 2.61 (s, 3H, Pyrrole C**H**$_3$), 3.79 (s, 3H, OC**H**$_3$), 6.03 (s, 1H, Pyrrole C**H**), 7.02 (d, *J* = 8.4 Hz, 1H, Ar**H**), 7.06-7.14 (m, 2H, 2 Ar**H**), 7.48 (ddd, *J* = 8.3, 6.3, 2.9 Hz, 1H, Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 12.8 (Pyrrole **C**H$_3$), 13.5 (Pyrrole **C**H$_3$), 13.9 (Pyrrole **C**H$_3$), 14.7 (Pyrrole **C**H$_3$), 55.6 (O**C**H$_3$), 110.3 (Pyrrole **C**-Br), 111.2 (Pyrrole **C**H), 121.6 (Ar**C**H), 121.7 (Pyrrole **C**-CH$_3$), 123.4 (Unbrominated pyrrole **C**-Cmeso), 129.3 (Ar**C**H), 129.9 (Pyrrole **C**-CH$_3$), 130.9 (Ar**C**H), 132.2 (Ar**C**), 138.1 (Ar**C**H), 139.2 (Pyrrole **C**-CH$_3$), 144.6 (Pyrrole **C**-CH$_3$), 150.8 (Brominated pyrrole **C**-Cmeso), 156.2 (**C**meso), 157.4 (Ar**C**-OCH$_3$)

^{19}F NMR (376 MHz, $CDCl_3$) : $J(^{19}F_A$-$^{11}B)$ = 32.5 Hz, $J(^{19}F_B$-$^{11}B)$ = 31.8 Hz, $J(^{19}F_A$-$^{19}F_B)$ = 107.2 Hz

IR(neat): ν_{max}/cm^{-1} 2980.8, 1538.2, 1497.3, 1463.3, 1304.5, 1176.0, 1157.2, 975.8, 707.5

HRMS : calcd for $C_{20}H_{21}BBrF_2N_2O$ $(M+H)^+$: 433.0893, found 433.0895

Crystal Growth: slow evaporation of petrol 40/60 : DCM = 2 : 1

(**6.18**)

R_f : 0.54 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 231-233 ^oC

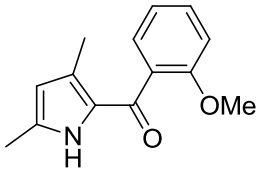
^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.44 (s, 6H, 2 Pyrrole C**H**$_3$), 2.62 (s, 6H, 2 Pyrrole C**H**$_3$), 3.79 (s, 3H, OC**H**$_3$), 7.03 (d, *J* = 8.3 Hz, 1H, Ar**H**), 7.10-7.14 (m, 2H, 2 Ar**H**), 7.51 (ddd, *J* = 8.3, 5.8, 3.4 Hz, 1H, Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 13.0 (2 Pyrrole **C**H$_3$), 13.7 (2 Pyrrole **C**H$_3$), 55.7 (O**C**H$_3$), 100.0 (2 Pyrrole **C**-Br), 111.3 (Ar**C**H), 121.7 (Ar**C**H), 123.3 (2 Pyrrole **C**-CH$_3$), 129.2 (Ar**C**H), 130.6 (2 Pyrrole **C**-CH$_3$), 131.2 (Ar**C**H), 139.7 (Ar**C**), 140.2 (Pyrrole **C**-Cmeso), 153.5 (**C**meso), 156.4 (Ar**C**-OCH$_3$)

IR(neat): ν_{max}/cm^{-1} 2924.5, 1541.3, 1460.6, 1401.2, 1350.0, 1178.5, 991.8, 756.5

HRMS : calcd for $C_{20}H_{20}BBr_2F_2N_2O$ $(M+H)^+$: 512.9982, found 512.9977

10.2.35 (3,5-Dimethyl-1*H*-pyrrol-2-yl)(2-methoxyphenyl)methane-1-one



6.19

To a 25 mL of round bottom flask under nitrogen was added EtMgBr (2M, 7.4 mL, 51.8 mmol). Into that flask was added 5.0 g (52.6 mmol) of 2,4-dimethylpyrrole in 150 mL THF and stirred for 30 minutes. A solution of 8.9 g (52. 6 mmol) of 2-methoxybenzoylchloride in 50 mL of THF then added drop wise into the mixture and the mixture was keep stirred for further 24 hour. The reaction quenched with 5 mL of saturated NH_4Cl solution and extracted with 3x150 mL of DCM. The organic solvent was dried using $MgSO_4$ and evaporated to give an oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 7 : 3 to give a brown solid (**6.19**), 9.126 g (75%).

R_f : 0.22 (UV active, Petrol 40/60 : Ether = 1: 1)

m.p. = 140-141 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.75 (s, 3H, Pyrrole C**H**$_3$), 2.29 (s, 3H, Pyrrole C**H**$_3$), 3.82 (s, 3H, OC**H**$_3$), 5.83 (d, *J* = 3 Hz, 1H, Pyrrole C**H**), 6.97-7.06 (m, 2H, Ar**H**), 7.27 (dd, *J* = 7.2, 1.8 Hz, 1H, Ar**H**), 7.41 (ddd, *J* = 8.3, 7.2, 1.8 Hz, 1H, Ar**H**), 9.22 (s, 1H, Pyrrole N**H**)

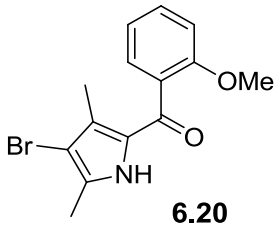
^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 12.8 (Pyrrole **C**H$_3$), 13.1 (Pyrrole **C**H$_3$), 55.7 (O**C**H$_3$), 111.2 (Pyrrole **C**H), 112.8 (Ar**C**H), 120.6 (Ar**C**H), 128.0 (Ar**C**H), 130.3 (Ar**C**H), 130.7 (Pyrrole **C**-CO), 131.3 (Pyrrole **C**-CH$_3$), 135.7 (Pyrrole **C**-CH$_3$), 156.2 (Ar**C**-OCH$_3$), 183.9 (Ketone **C**=O)

IR(neat): ν_{max}/cm^{-1} 3272.0, 2954.2, 1701.7, 1566.0, 1432.6, 1290. 4, 1244.3, 1082.7, 927.4, 761.0

HRMS : calcd for $C_{14}H_{16}NO_2$ $(M+H)^+$: 230.1176, found 230.1178

Crystal Growth: slow evaporation of petrol 40/60 : ether = 2 : 1

10.2.36 (4-Bromo-3,5-dimethyl-1*H*-pyrrol-2-yl)(2-methoxyphenyl)methane-1-one



6.20

To a 500 mL of round bottom flask under nitrogen was added 0.114 g (0.5 mmol) of (2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-methoxyphenyl)methane-1-one (**6.19**) in 50 mL DCM. Into that flask was added 0.3 mL of Ethylamine and stirred for 30 minutes. Solution of 25.8 µL (1.0 mmol) of bromine in 20 mL of DCM then added drop wise into the mixture and the mixture was keep stirred for further 24 hour. The reaction washed with 3x10 mL of water. The organic solvent was dried using $MgSO_4$ and evaporated to give a colourless solid (**6.20**), 0.131 g (85%).

R_f : 0.31 (UV active, petrol 40/60 : ether = 1: 1)

m.p. = 119-120 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.72 (s, 3H, Pyrrole C**H**$_3$), 2.32 (s, 3H, Pyrrole C**H**$_3$), 3.81 (s, 3H, OC**H**$_3$), 6.97-7.08 (m, 2H, Ar**H**), 7.25-7.30 (m, 1H, Ar**H**), 7.45 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H, Ar**H**), 10.39 (s, 1H, Pyrrole N**H**)

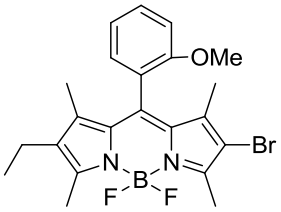
^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.8 (Pyrrole **C**H$_3$), 12.2 (Pyrrole **C**H$_3$), 55.6 (O**C**H$_3$), 102.2 (Pyrrole **C**-Br), 111.2 (Ar**C**-C=O), 120.7 (Ar**C**H), 127.6 (Ar**C**H), 128.2 (Ar**C**H), 129.3 (Pyrrole **C**-C=O), 129.7 (Pyrrole **C**-CH$_3$), 131.1 (Ar**C**H), 134.6 (Pyrrole **C**-CH$_3$), 156.3 (Ar**C**-OCH$_3$), 183.9 (Ketone **C**=O)

IR(neat): ν_{max}/cm^{-1} 3264.2, 2981.2, 1701.5, 1567.4, 1431.8, 1372.0, 1244.8, 927.9, 750.4

HRMS : calcd for $C_{14}H_{15}BrNO_2$ $(M+H)^+$: 308.0281, found 308.0281

Crystal Growth: slow evaporation of petrol 40/60 : ether = 2 : 1

10.2.37 2-Bromo-8-ethyl-5,5-difluoro-10-(2-methoxyphenyl)-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine



6.21

To a 500 mL of round bottom flask was added 5.00 g (16.2 mmol) of (3-bromo-2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-methoxyphenyl)methanone (**6.20**), 2.40 g of 3-ehtyl-2,4-dimethyl-1*H*-pyrrole (19.5 mmol), 200 mL DCM and 1.80 mL of trifluoroacetic acid and stirred for overnight. The reaction washed with 3x100 mL of water. The organic solvent was dried using $MgSO_4$ and evaporated to give a black oil. The residue was dissolved in 200 mL DCM and added 32.4 mL *N*,*N*-diisopropyl-*N*-ethylamine at room temperature. The mixture was stirred for 30 minutes and followed by the addition of 32.4 mL $BF_3.Et_2O$ at 0 ^oC. The mixture then continued to stir for further 3 hours. The reaction washed with 3x100 mL of water. The organic solvent was dried using $MgSO_4$ and evaporated to give a dark brown solid residue. The crude product then purified through column chromatography (petrol 40/60 ; ether = 15 : 1) to give a red solid (**6.21**), 6.350 g (85%).

R_f : 0.52 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 202-203 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.02 (t, *J* = 7.6 Hz, 3H, C**H**$_3$), 1.38 (s, 3H, Pyrrole C**H**$_3$), 1.41 (s, 3H, Pyrrole C**H**$_3$), 2.33 (q, *J* = 7.5 Hz, 2H, C**H**$_2$), 2.58 (s, 3H, Pyrrole C**H**$_3$), 2.59 (s, 3H, Pyrrole C**H**$_3$), 3.78 (s, 3H, OC**H**$_3$), 7.01 (d, *J* = 8.3 Hz, 1H, Ar**H**), 7.09-7.14 (m, 2H, 2 Ar**H**), 7.48 (ddd, *J* = 8.7, 6.5, 2.8 Hz, 1H, Ar**H**)

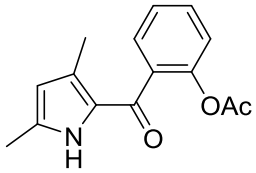
^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.2 (Brominated pyrrole **C**H$_3$), 12.6 (Brominated pyrrole **C**H$_3$), 12.9 (Pyrrole **C**H$_3$), 13.4 (Pyrrole CH$_2$**C**H$_3$), 14.4 (Pyrrole **C**H$_3$), 17.0 (Pyrrole **C**H$_2$CH$_3$), 109.5 (Pyrrole **C**-Br), 111.2 (Ar**C**H), 121.5 (Ar**C**H), 123.8 (Brominated pyrrole **C**-Cmeso), 129.4 (Brominated pyrrole **C**-CH$_3$), 129.5 (Ar**C**H), 130.8 (Ar**C**H), 132.2 (Pyrrole **C**-CH$_2$CH$_3$), 134.1 (Brominated pyrrole **C**-CH$_3$), 136.8 (Ar**C**), 138.1 (**C**meso), 140.5 (Pyrrole **C**), 149.1 (Pyrrole **C**-CH$_3$), 156.4 (Pyrrole **C**-CH$_3$), 157.7 (Ar**C**-OCH$_3$)

IR(neat): ν_{max}/cm^{-1} 2960.6, 2927.4, 1532.2, 1458.9, 1401.6, 1369.4, 1312.9, 1179.7, 1074.5, 710.2

HRMS : calcd for $C_{22}H_{25}BBrF_2N_2O$ $(M+H)^+$: 461.1207, found 461.1208

Crystal Growth: slow evaporation of petrol 40/60 : DCM = 2 : 1

10.2.38 2-(3,5-Dimethyl-1*H*-pyrrole-2-carbonyl)phenyl acetate



6.22

To a 25 mL of round bottom flask under nitrogen was added EtMgBr (2M, 3.04 mL, 23.12 mmol). Into that flask was added 2.0 g (21.02 mmol) of 2,4-dimethylpyrrole in 150 mL THF and stirred for 30 minutes. A solution of 4.2 g (21. 02 mmol) of 2-acetoxybenzoylchloride in 50 mL of THF was added drop wise into the mixture and the mixture was keep stirred for a further 24 hour. The reaction quenched with 5 mL of saturated NH_4Cl solution and extracted with 3x150 mL of DCM. The organic solvent was dried using $MgSO_4$ and evaporated to give a black oil. The crude product was purified through column chromatography using petrol 40/60 : ether = 6 : 4 to give a brown solid (**6.22**), 2.57 g (53%).

R_f : 0.14 (UV active, Petrol 40/60 : Ether = 7: 3)

m.p. = 120-121 ^oC

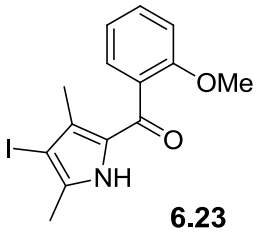
^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.88 (s, 3H, C**H**$_3$), 2.18 (s, 3H, Pyrrole C**H**$_3$), 2.29 (s, 3H, Pyrrole C**H**$_3$), 5.86 (d, *J* = 2.8 Hz, 1H, Pyrrole C**H**), 7.20 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar**H**), 7.27-7.36 (m, 1H, Ar**H**), 7.44-7.53 (m, 2H, Ar**H**), 9.27 (s, 1H, Pyrrole N**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 13.1 (Pyrrole **C**H$_3$), 13.2 (Pyrrole **C**H$_3$), 20.7 (Acetyl **C**H$_3$), 113.1 (Pyrrole **C**H), 123.1 (Ar**C**H), 125.8 (Ar**C**H), 127.8 (Ar**C**CO), 128.9 (Ar**C**H), 130.9 (Ar**C**H), 132.0 (Pyrrole **C**-CH$_3$), 133.3 (Pyrrole **C**-CH$_3$), 136.5 (Ar**C-**O), 147.5 (Pyrrole **C**-CO), 169.3 (**C**=O), 182.0 (Acetyl **C**=O)

IR(neat): ν_{max}/cm^{-1} 3261.9, 2954.2, 1762.9, 1682.4, 1571.9, 1435.5, 1370.7, 1183.8, 939.6, 759.6

HRMS : calcd for $C_{15}H_{16}NO_3$ $(M+H)^+$: 258.1125, found 258.1126

10.2.39 (4-Iodo-3,5-dimethyl-1*H*-pyrrol-2-yl)(2-methoxyphenyl)methane-1-one



6.23

To a 500 mL of round bottom flask under nitrogen was added 2.0 g (8.72 mmol) of (2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-methoxyphenyl)methane-1-one (**6.19**) in 50 mL DCM. Into that flask was added a solution of 1.96 g (8.71 mmol) of NIS in 50 mL of DCM over 1 minute and the mixture was keep stirred for further 2 hours. The reaction washed with 3x15 mL of water. The organic solvent was dried using $MgSO_4$ and evaporated to give a brown solid. The crude product purified through column chromatography using petrol 40/60 : ether = 1 : 1 to give a slight brown solid (**6.23**), 3.0672 g (99%).

R_f : 0.33 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 129-130 ^oC

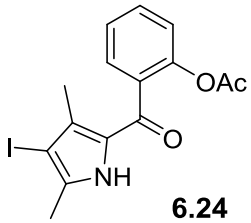
^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.74 (s, 3H, Pyrrole C**H**$_3$), 2.34(s, 3H, Pyrrole C**H**$_3$), 3.81 (s, 3H, OC**H**$_3$), 6.96-7.08 (m, 2H, Ar**H**), 7.25-7.29 (m, 1H, Ar**H**), 7.44 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H, Ar**H**), 9.90 (s, 1H, Pyrrole N**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 14.4 (Pyrrole **C**H$_3$), 14.7 (Pyrrole **C**H$_3$), 55.6 (O**C**H$_3$), 74.3 (Pyrrole **C**-I), 111.2 (ArC-C=O), 120.7 (Ar**C**H), 128.2 (Ar**C**H), 128.8 (Ar**C**H), 129.6 (Pyrrole **C**-CH$_3$), 131.2 (Ar**C**H), 132.8 (Pyrrole **C**-C=O), 137.5 (Pyrrole **C**-CH$_3$), 156.4 (Ar**C**-OCH$_3$), 183.7 (Ketone **C**=O)

IR(neat): ν_{max}/cm^{-1} 3215.2, 2837.8, 1704.6, 1585.8, 1545.2, 1486.6, 1462.0, 1372.4, 1247.0, 753.6

HRMS : calcd for $C_{14}H_{15}INO_2$ $(M+H)^+$: 355.0019, found 355.0019

10.2.40 2-(4-Iodo-3,5-dimethyl-1*H*-pyrrole-2-carbonyl)phenyl acetate



6.24

To a 500 mL of round bottom flask under nitrogen was added 2.27 g (9.90 mmol) of (2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-acetoxyphenyl)methane-1-one (**6.22**) in 50 mL DCM. Into that flask was added a solution of 2.23 g (9.90 mmol) of NIS in 50 mL of DCM over 1 minute and the mixture was keep stirred for further 2 hours. The reaction washed with 3x15 mL of water. The organic solvent was dried using $MgSO_4$ and evaporated to give a brown solid residue. The crude product was purified through column chromatography using petrol 40/60 : ether = 1 : 1 to give a slight brown solid (**6.24**), 3.930 g (99%).

R_f : 0.45 (UV active, petrol 40/60 : EtOAc = 7: 3)

m.p. = 156-158 ^oC

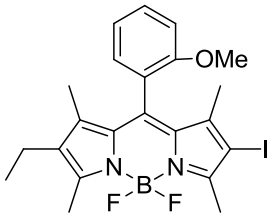
^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.86 (s, 3H, C**H**$_3$), 2.14 (s, 3H, Pyrrole C**H**$_3$), 2.32 (s, 3H, Pyrrole C**H**$_3$), 7.21 (dd, *J* = 8.1, 1.1 Hz, 1H, Ar**H**), 7.27-7.36 (m, 1H, Ar**H**), 7.42-7.55 (m, 2H, Ar**H**), 10.06 (s, 1H, Pyrrole N**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 14.4 (Pyrrole **C**H$_3$), 15.3 (Pyrrole **C**H$_3$), 20.7 (Acetyl **C**H$_3$), 74.5 (Pyrrole **C**-I), 123.1 (Ar**C**H), 125.8 (Ar**C**H), 128.0 (Ar**C-**CO), 129.0 (Ar**C**H), 131.2 (Ar**C**H), 132.7 (Pyrrole **C**-CH$_3$), 133.4 (Pyrrole **C**-CH$_3$), 138.3 (Ar**C**-O), 147.6 (Pyrrole **C**-CO), 169.2 (**C**=O), 181.9 (Acetyl **C**=O)

IR(neat): ν_{max}/cm^{-1} 3262.5, 2981.1, 1770.2, 1595.6, 1420.9, 1367.2, 1203.3, 1182.8, 939.0, 746.5

HRMS : calcd for $C_{15}H_{15}INO_3$ $(M+H)^+$: 384.0091, found 384.0091

10.2.41 2-Ethyl-5,5-difluoro-8-iodo-10-(2-methoxyphenyl)-1,3,7,9-tetramethyl-5*H*-5λ^4,6λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine



6.25

To a 500 mL of round bottom flask was added 600 mg (1.69 mmol) of (3-iodo-2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-methoxyphenyl)methane-1-one (**6.23**), 250 mg of 3-ehtyl-2,4-dimethyl-1*H*-pyrrole (2.17 mmol), 50 mL DCM and 0.13 mL of trifluoroacetic acid and stirred for overnight. The reaction washed with 3x15 mL of water. The organic solvent was dried using $MgSO_4$ and evaporated to give a black red oil. The residue was then dissolved in 50 mL DCM and added 4 mL *N*,*N*-diisopropyl-*N*-ethylamine at room temperature. The mixture was stirred for 30 minutes and followed by the addition of 4 mL $BF_3.Et_2O$ at 0 ^oC. The mixture then continued to stir for further 1 hour. The reaction washed with 3x15 mL of water. The organic solvent was dried using $MgSO_4$ and evaporated to give a dark red solid. The crude product was purified through column chromatography (petrol 40/60 ; ether = 20 : 1) to give a dark pink solid (**6.25**), 0.859 g (65%).

R_f : 0.37 (UV active, petrol 40/60 : ether = 1: 1)

m.p. = 220-221 ^oC

^{1}H NMR (400 MHz, $CDCl_3$) : δ_H 0.99 (t, *J* = 7.6 Hz, 3H, C**H**$_3$), 1.37 (s, 3H, Pyrrole C**H**$_3$), 1.433 (s, 3H, Pyrrole C**H**$_3$), 2.30 (q, *J* = 7.6 Hz, 2H, C**H**$_2$), 2.57 (s, 3H, Pyrrole C**H**$_3$), 2.62 (s, 3H, Pyrrole C**H**$_3$), 3.75 (s, 3H, OC**H**$_3$), 6.98 (d, *J* = 8.3 Hz, 1H, Ar**H**), 7.03-7.14 (m, 2H, 2 Ar**H**), 7.45 (ddd, *J* = 8.4, 6.7, 2.5 Hz, 1H, Ar**H**)

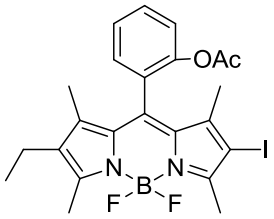
^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.2 (Iodinated pyrrole **C**H$_3$), 12.9 (Iodinated pyrrole **C**H$_3$), 14.4 (Pyrrole **C**H$_3$), 15.7 (Pyrrole CH$_2$**C**H$_3$), 15.8 (Pyrrole **C**H$_3$), 17.1 (Pyrrole **C**H$_2$CH$_3$), 55.6 (O**C**H$_3$), 83.2 (Pyrrole **C**-I), 111.1 (Ar**C**H), 121.5 (Ar**C**H), 123.9 (Iodinated pyrrole **C**-Cmeso), 129.5 (Ar**C**H), 130.6 (Iodinated pyrrole **C**-CH$_3$), 130.8 (Ar**C**H), 132.1 (Pyrrole **C**-CH$_2$CH$_3$), 134.2 (Iodinated pyrrole **C**-CH$_3$), 137.8(Ar**C**), 140.5 (**C**meso), 141.2 (Pyrrole **C**-Cmeso), 152.2 (Pyrrole **C**-CH$_3$), 156.4 (Pyrrole **C**-CH$_3$), 157.6 (Ar**C**-OCH$_3$)

IR(neat): ν_{max}/cm^{-1} 3025.4, 1539.2, 1458.2, 1458.8, 1352.6, 1182.0, 974.9, 708.9

HRMS : calcd for $C_{22}H_{25}BF_2IN_2O$ $(M+H)^+$: 508.1104, found 508.1096

Crystal Growth: slow evaporation of petrol 40/60 : DCM = 2 : 1

10.2.42 2-(2-Ethyl-5,5-difluoro-8-iodo-1,3,7,9-tetramethyl-5*H*-5λ^4,6λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)phenyl acetate



6.26

To a 500 mL of round bottom flask was added 671 mg (1.69 mmol) of (3-iodo-2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-acethoxyphenyl)methane-1-one (**6.24**), 250 mg of 3-ethyl-2,4-dimethyl-1*H*-pyrrole (2.02 mmol), 50 mL DCM and 0.13 mL of trifluoroacetic acid and stirred for overnight. The reaction washed with 3x15 mL of water. The organic solvent was dried using $MgSO_4$ and evaporated to give a black red oil. The residue then dissolved in 50 mL DCM and added 4 mL *N*,*N*-diisopropyl-*N*-ethylamine at room temperature. The mixture was stirred for 30 minutes and followed by the addition of 4 mL $BF_3.Et_2O$ at 0 ^oC. The mixture then continued to stir for further 1 hour. The reaction washed with 3x15 mL of water. The organic solvent was dried using $MgSO_4$ and evaporated to give a dark red solid. The crude product was purified through column chromatography (petrol 40/60 : ether = 20 : 1) to give a red solid (**6.26**), 0.240 g (28%).

R_f : 0.55 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 170-172 ^oC

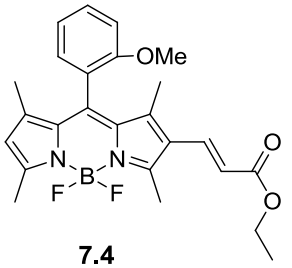
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.00 (t, *J* = 7.6 Hz, 3H, C**H**$_3$), 1.41 (s, 3H, Pyrrole C**H**$_3$), 1.46 (s, 3H, Pyrrole CH_3), 2.09 (s, 3H, Acetyl C**H**$_3$), 2.33 (q, *J* = 7.5 Hz, 2H, C**H**$_2$), 2.57 (s, 3H, Pyrrole C**H**$_3$) 2.63 (s, 3H, Pyrrole C**H**$_3$), 7.29 (ddd, *J* = 7.5, 5.5, 1.4 Hz, 2H, Ar**H**), 7.38 (td, *J* = 7.5, 1.1 Hz, 1H, Ar**H**), 7.53 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H, Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.5 (Pyrrole **C**H$_3$), 13.0 (Pyrrole **C**H$_3$), 14.4 (Pyrrole CH_2**C**H$_3$), 15.9 (Pyrrole **C**H$_3$), 16.0 (Pyrrole **C**H$_3$), 17.1 (Pyrrole **C**H$_2$CH$_3$), 20.9 (Acetyl **C**H$_3$), 83.6 (Pyrrole **C**-I), 123.9 (Ar**C**H), 126.6 (Ar**C**H), 127.7 (Ar**C** and Pyrrole **C**-CH$_3$), 129.9 (Ar**C**H), 130.5 (Ar**C**H), 131.8 (Pyrrole **C**), 134.9 (Pyrrole **C**-CH$_3$), 135.3 (Pyrrole **C**-CH$_2$CH$_3$), 141.1 (**C**), 141.8 (Pyrrole **C**-CH$_3$), 148.1 (Pyrrole **C**), 153.1 (Pyrrole C-**C**H$_3$), 158.6 (Ar**C**-OAc), 168.9 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 2969.2, 1765.0, 1539.4, 1456.7, 1311.3, 1175.8, 975.9, 708.3

HRMS : calcd for $C_{23}H_{25}BF_2IN_2O_2$ $(M+H)^+$: 537.1020, found 537.1006

10.2.43 Ethyl (*E*)-3-(5,5-difluoro-10-(2-methoxyphenyl)-1,3,7,9-tetramethyl-5*H*-4λ^4, 5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl)acrylate



7.4

To a Schlenk tube was added 4,4-difluoro-8-(2-methoxyphenyl)-1,3,5,7-tetramethyl-6-bromo-4-bora-3*a*,4*a*-diaza-*s*-indacene (**6.17**) (175 mg g, 0.400 mmol) , Pd (II) acetate (12 mg, 0.052 mmol), triphenylphosphine (14 mg, 0.052 mmol) and 5 mL DMF. The mixture was stirred for 10 minutes and followed by addition of ethyl acrylate (92 mg, 0.922 mmol), triethylamine (185 mg, 1.832 mmol) in DMF (7 mL). The solution then warmed for 24 hours. The solution was added 50 mL DCM and washed with 2 x 200 mL of water. The organic phase dried using $MgSO_4$ and removed the solvent under reduce pressure to a red solid. The crude product then purified through column chromatography (petrol 40/60 ; ether = 10 : 1) to give a red solid (**7.4**), 0.117 g (65%).

R_f : 0.35 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 209-211 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.32 (t, *J* = 7.1 Hz, 3H, C**H**$_3$), 1.46 (s, 3H, Pyrrole C**H**$_3$), 1.54 (s, 3H, Pyrrole C**H**$_3$), 2.59 (s, 3H, Pyrrole C**H**$_3$), 2.72 (s, 3H, Pyrrole C**H**$_3$), 3.79 (s, 3H, OC**H**$_3$), 4.24 (q, *J* = 7.1 Hz, 2H, C**H**$_2$), 6.05 (d, *J* = 16.2 Hz, 1H, C**H**), 6.06 (s, 1H, Pyrrole**H**), 7.02(d, *J* = 8.3 Hz, 1H, Ar**H**), 7.08-7.21 (m, 2H, 2 Ar**H**), 7.49 (ddd, *J* = 8.4, 6.4, 2.8 Hz, 1H, Ar**H**), 7.63 (d, *J* = 16.2 Hz, 1H, C**H**)

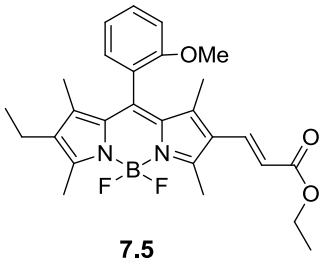
^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.9 (Substituted pyrrole **C**H$_3$), 14.2 (usnubstituted pyrrole **C**H$_3$ and Acrylic CH$_2$**C**H$_3$), 14.4 (Substituted pyrrole **C**H$_3$), 14.9 (Unsubstituted pyrrole **C**H$_3$), 55.6 (O**C**H$_3$), 60.2 (Acrylic **C**H$_2$CH$_3$), 100.0 (Unsubstituted pyrrole **C**H), 111.2 (Ar**C**H), 117.1 (=**C**HCO), 121.6 (Ar**C**H), 122.4 (Substituted pyrrole **C**-CH), 123.6 (Unsubtituted pyrrole **C**-CH$_3$), 129.4 (Ar**C**H), 130.7 (**C**meso), 130.9 (Ar**C**), 132.9 (Unsubstituted pyrrole **C**-CH$_3$), 135.9 (Ar**C**H), 139.8 (Unsubstitued pyrrole **C**-Cmeso), 140.0 (Unsubstituted pyrrole **C**-Cmeso), 144.9(=**C**H), 153.9 (Substituted pyrrole **C**-CH$_3$), 156.4 (Substituted pyrrole **C**-CH$_3$), 158.0 (Ar**C**-OCH$_3$), 167.7 (Acrylic **C**=O)

IR(neat): ν_{max}/cm^{-1} 2926.0, 1716.4, 1536.4, 1511.3, 1464.4, 1407.9, 1314.2, 1158.2, 973.2, 809.1

HRMS : calcd for $C_{25}H_{28}BF_2N_2O_3$ $(M+H)^+$: 452.2192, found 452.2190

Crystal Growth: slow evaporation of petrol 40/60 : DCM = 2 : 1

10.2.44 Ethyl (*E*)-3-(8-ethyl-5,5-difluoro-10-(2-methoxyphenyl)-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl)acrylate



7.5

To a Schlenk tube was added 4,4-difluoro-8-(2-methoxyphenyl)-1,3,5,7-tetramethyl-2-ethyl-6-iodo-4-bora-3*a*,4*a*-diaza-*s*-indacene (**6.25**) (59 mg g, 0.116 mmol) , Pd (II) acetate (3 mg, 0.012 mmol), triphenylphosphine (3 mg, 0.012 mmol) and 2.5 mL DMF. The mixture was stirred for 10 minutes and followed by addition of ethyl acrylate (23 mg, 0.232 mmol), triethylamine (54 mg, 0.534 mmol) in DMF (2.5 mL). The solution then warmed for 24 hours. The solution was added 15 mL DCM and washed with 3 x 25 mL of water. The organic phase dried using $MgSO_4$ and removed the solvent under reduce pressure to a red solid. The crude product then purified through column chromatography (petrol 40/60 ; ether = 15 : 1) to give a red solid (**7.5**), 0.050 g (90%).

R_f : 0.28 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 167-169 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.02 (t, *J* = 7.6 Hz, 3H, C**H**$_3$), 1.37 (t, *J* = 7.2 Hz, 3H, OCH$_2$C**H**$_3$), 1.38 (s, 3H, Pyrrole C**H**$_3$), 1.52 (s, 3H, Pyrrole C**H**$_3$), 2.34 (q, *J* = 7.6 Hz, 2H, C**H**$_2$), 2.59 (s, 3H, Pyrrole C**H**$_3$), 2.71 (s, 3H, Pyrolle C**H**$_3$), 3.79 (s, 3H, OC**H**$_3$), 4.24 (q, *J* = 7.1 Hz, 2H, OC**H**$_2$CH$_3$), 6.03 (d, *J* = 16.2 Hz, 1H, C**H**), 7.02(d, *J* = 8.4 Hz, 1H, Ar**H**), 7.07-7.18 (m, 2H, 2 Ar**H**), 7.49 (ddd, *J* = 8.3, 6.6, 2.7 Hz, 1H, Ar**H**), 7.64 (d, *J* = 16.2 Hz, 1H, C**H**)

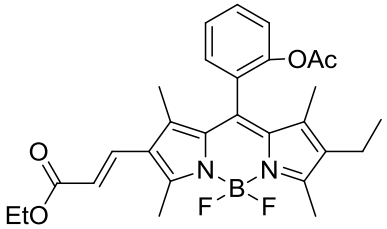
^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.4 (Ethyl pyrrole **C**H$_3$), 11.8 (Ethyl pyrrole **C**H$_3$), 13.0 (Acrylic CH$_2$**C**H$_3$), 14.1 (Ethyl pyrrole CH$_2$**C**H$_3$), 14.4 (Acrylic pyrrole **C**H$_3$), 14.5 (Acrylic pyrrole **C**H$_3$), 17.2 (Ethyl pyrrole **C**H$_2$CH$_3$), 55.6 (O**C**H$_3$), 60.2 (Acrylic **C**H$_2$CH$_3$), 111.2 (Ar**C**H), 116.5 (=**C**HCO), 121.6 (Ar**C**H), 123.8 (Acrylic pyrrole **C**-CH$_3$), 124.1 (Ethyl pyrrole **C**-CH$_2$CH$_3$), 129.6 (Ar**C**H), 130.4 (**C**meso), 130.8 (Ar**C**H), 132.6 (Pyrrole **C**-CH$_3$), 134.6 (Ethyl pyrrole **C**-CH$_3$), 136.2 (=**C**H), 138.6 (Ar**C**), 140.8 (Acrylic pyrrole **C**-CH), 152.6 (Arylic pyrrole **C**-CH$_3$), 156.4 (2 Pyrrole **C**-Cmeso), 158.8 (Ar**C**-OCH$_3$), 167.8 (Acrylic **C**=O)

IR(neat): ν_{max}/cm^{-1} 2980.6, 1719.2, 1537.1, 1471.2, 1384.0, 1170.9, 971.8, 713.4

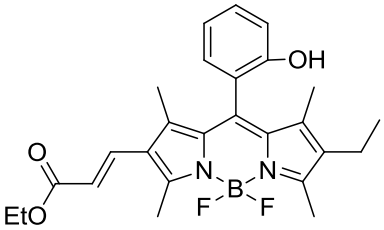
HRMS : calcd for $C_{27}H_{32}BF_2N_2O_3$ $(M+H)^+$: 481.2473, found 481.2468

Crystal Growth: slow evaporation of petrol 40/60 : DCM = 2 : 1

10.2.45 Ethyl (*E*)-3-(10-(2-acetoxyphenyl)-8-ethyl-5,5-difluoro-1,3,7,9-tetramethyl-5*H*-5λ^4,6λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl)acrylate 7.6 and ethyl (*E*)-3-(8-ethyl-5,5-difluoro-10-(2-hydroxyphenyl)-1,3,7,9-tetramethyl-5*H*-5λ^4,6λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl)acrylate 7.7



7.6



7.7

To a Schlenk tube was added 4,4-difluoro-8-(2-acethoxyphenyl)-1,3,5,7-tetramethyl-2-ethyl-6-iodo-4-bora-3*a*,4*a*-diaza-*s*-indacene (**6.26**) (135 mg g, 0.25 mmol) , Pd (II) acetate (6 mg, 0.025 mmol), triphenylphosphine (7 mg, 0.025 mmol) and 1 mL DMF. The mixture was stirred for 10 minutes and followed by addition of ethyl acrylate (50 mg, 0.50 mmol), triethylamine (110 mg, 1.08 mmol) in DMF (1.5 mL). The solution then warmed for 24 hours. The solution was added 15 mL DCM and washed with 3 x 125 mL of water. The organic phase dried using $MgSO_4$ and removed the solvent under reduce pressure to a red solid. The crude product then purified through column chromatography (petrol 40/60 ; ether = 10 : 1) to give a brown solid (**7.6**), 0.100 g (80%) for the acetate protected product and a red solid (**7.7**), 0.080 g (70%) of deprotected one.

(**7.6**)

R_f : 0.35 (UV active, petrol 40/60 : ether = 8: 4)

m.p. = 204-206 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.01 (t, *J* = 7.5 Hz, 3H, Pyrrole $CH_2C\mathbf{H}_3$), 1.32 (t, *J* = 7.1 Hz, 3H, $OCH_2C\mathbf{H}_3$), 1.42 (s, 3H, Pyrrole $C\mathbf{H}_3$), 1.54 (s, 3H, Pyrrole $C\mathbf{H}_3$), 2.08 (s, 3H, acetic $C\mathbf{H}_3$), 2.34 (q, *J* = 7.1 Hz, 2H, Pyrrole $C\mathbf{H}_2CH_3$), 2.59 (s, 3H, Pyrrole $C\mathbf{H}_3$), 2.70 (s, 3H, Pyrolle $C\mathbf{H}_3$), 4.23 (q, *J* = 7.1 Hz, 2H, $OC\mathbf{H}_2CH_3$), 6.04 (d, *J* = 16.2 Hz, 1H, C**H**), 7.27-7.33(m, 2H, 2 Ar**H**), 7.37 (d, *J* = 1.1 Hz, 1H, Ar**H**), 7.55 (td, *J* = 7.7, 1.7 Hz, 1H, Ar**H**), 7.63 (d, *J* = 16.2 Hz, 1H, C**H**)

^{13}C NMR(100 MHz, $CDCl_3$) : δ_C 11.5 (Pyrrole **C**H_3), 12.1 (Pyrrole **C**H_3), 13.1 (Pyrrole **C**H_3), 14.2 (Pyrrole **C**H_3), 14.3 (Pyrrole CH_2**C**H_3), 14.5 (Acrylic **C**H_3), 17.1 (Pyrrole **C**H_2CH_3), 20.8 (Acetyl **C**H_3), 60.2 (Acrylic **C**H_2CH_3), 116.9 (=**C**H-CO), 123.9 (Ar**C**H), 124.4 (Pyrrole **C**), 126.6 (Ar**C**H), 127.7 (Ar**C**), 129.8 (Pyrrole **C**-CH_2CH_3), 129.9 (Ar**C**H), 130.5 (Ar**C**H), 132.6 (Pyrrole **C**-CH), 135.2 (Pyrrole **C**-CH_3), 135.9 (Pyrrole **C**-CH_3), 136.0 (=**C**H), 139.2 (**C**), 141.1 (Pyrrole **C**), 148.1 (Pyrrole **C**-CH_3), 153.1 (Pyrrole **C**-CH_3), 159.2 (Ar**C**-OAc), 167.6 (Acrylic **C**=O), 168.8 (Acetyl **C**=O)

IR(neat): ν_{max}/cm^{-1} 2975.4, 1764.5, 1699.9, 1541.1, 1470.2, 1284.2, 1181.6, 974.0, 713.4

HRMS : calcd for $C_{28}H_{32}BF_2N_2O_4$ $(M+H)^+$: 509.2423, found 509.2409

(**7.7**)

R_f : 0.15 (UV active, petrol 40/60 : ether = 8: 4)

m.p. = 226-228 ^oC

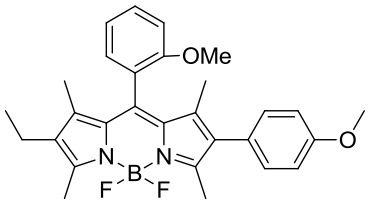
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.01 (t, *J* = 7.5 Hz, 3H, Pyrrole CH_2C**H**$_3$), 1.30 (t, *J* = 7.1 Hz, 3H, OCH_2C**H**$_3$), 1.47 (s, 3H, Pyrrole C**H**$_3$), 1.58 (s, 3H, Pyrrole C**H**$_3$), 2.34 (q, *J* = 7.6 Hz, 2H, Pyrrole C**H**$_2CH_3$), 2.56 (s, 3H, Pyrrole C**H**$_3$), 2.66 (s, 3H, Pyrolle C**H**$_3$), 4.17 (q, *J* = 7.1 Hz, 2H, OC**H**$_2CH_3$), 5.99 (d, *J* = 16.2 Hz, 1H, C**H**), 7.02-7.11(m, 3H, 3 Ar**H**), 7.38-7.44 (m, 1H, Ar**H**), 7.55 (d, *J* = 16.2 Hz, 1H, C**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.3 (Pyrrole **C**H_3), 11.8 (Pyrrole **C**H_3), 13.1 (Pyrrole **C**H_3), 14.2 (Pyrrole **C**H_3), 14.4 (Pyrrole CH_2**C**H_3), 14.5 (Acrylic **C**H_3), 17.2 (Pyrrole **C**H_2CH_3), 60.4 (Acrylic **C**H_2CH_3), 116.7 (=**C**H-CO), 117.1 (Ar**C**H), 121.2 (Pyrrole **C**), 121.7 (Ar**C**H), 124.6 (Ar**C**), 129.2 (Ar**C**H), 130.5 (Pyrrole C-CH2CH3), 131.3 (Ar**C**H), 132.9 (Pyrrole **C**-CH), 135.5 (Pyrrole **C**-CH_3), 135.6 (Pyrrole **C**-CH_3), 135.8 (=**C**H), 139.3 (**C**), 141.1 (Pyrrole **C**), 152.7 (Pyrrole **C**-CH_3), 153.7 (Pyrrole **C**-CH_3), 159.7 (Ar**C**-OH), 167.9 (Acrylic **C**=O)

IR(neat): ν_{max}/cm^{-1} 3182.5, 2965.6, 1769.2, 1706.2, 1618.4, 1533.1, 1470.9, 1186.7, 1170.9, 712.9

HRMS : calcd for $C_{26}H_{30}BF_2N_2O_3$ $(M+H)^+$: 467.2313, found 467.2310

10.2.46 2-Ethyl-5,5-difluoro-10-(2-methoxyphenyl)-8-(4-methoxyphenyl)-1,3,7,9-tetramethyl-5*H*-5λ^4,6λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine



7.9

To a round bottom flask was added 4,4-difluoro-8-(2-methoxyphenyl)-1,3,5,7-tetramethyl-2-ethyl-6-iodo-4-bora-3*a*,4*a*-diaza-*s*-indacene (**6.25**) (40 mg g, 0.078 mmol) , Tetrakis (0.6 mg, 0.004 mmol), 4-methoxyphenyl boronic acid (28 mg, 0.185 mmol), 2M Na_2CO_3 solution (0.4 mL, 0.394 mmol) and toluene (5 mL). The solution then refluxed at 111 ^oC for 24 hours. The solution was added 15 mL DCM and washed with 3 x 25 mL of water. The organic phase dried using $MgSO_4$ and removed the solvent under reduce pressure to a red solid. The crude product then purified through column chromatography (petrol 40/60 ; ether = 10 : 1) to give a red solid (**7.9**), 0.019 g (50%).

R_f : 0.36 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 210-212 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.03 (t, *J* = 7.6 Hz, 3H, C**H**$_3$), 1.34 (s, 3H, Pyrrole C**H**$_3$), 1.38 (s, 3H, Pyrrole C**H**$_3$), 2.34 (q, *J* = 7.5 Hz, 2H, C**H**$_2$), 2.51 (s, 3H, Pyrrole C**H**$_3$), 2.58 (s, 3H, Pyrrole C**H**$_3$), 3.80 (s, 3H, OC**H**$_3$), 3.84 (s, 3H, OC**H**$_3$), 6.90-6.96 (m, 2H, Ar**H**), 7.00 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar**H**), 7.06-7.13 (m, 3H, 3 Ar**H**), 7.18 (dd, *J* = 7.5, 1.9 Hz, 1H, Ar**H**), 7.45 (ddd, *J* = 8.3, 7.4, 1.9, 1H, Ar**H**)

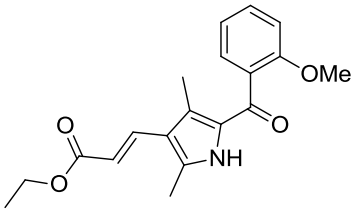
^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.2 (Aromatic substituted pyrrole **C**H_3), 12.0 (Aromatic substituted pyrrole **C**H_3), 12.8 (Ethyl pyrrole **C**H_3), 13.3 (Ethyl pyrrole **C**H_3), 14.6 (Ethyl pyrrole CH_2**C**H_3), 17.2 (Ethyl pyrrole **C**H_2CH_3), 55.3 (O**C**H_3), 55.7 (O**C**H_3), 111.2 (Ar**C**H), 113.6 (2 Ar**C**H), 121.6 (Ar**C**H), 124.5 (Pyrrole **C**-Cmeso), 126.4 (2 Ar**C**), 129.8 (Ar**C**H), 130.6 (Ar**C**H), 131.4 (2 Ar**C**H), 132.3 (**C**meso), 133.1 (Ethyl pyrrole **C**-CH_2CH_3), 137.7 (2 Pyrrole **C**), 138.2 (Pyrrole **C**-Ar), 138.9 (Aromatic substituted pyrrole **C**-CH_3), 150.4 (Ethyl pyrrole **C**-CH_3) 152.2 (Aromatic substituted pyrrole **C**-CH_3), 154.9 (Ethyl pyrrole **C**-CH_3), 156.6 (Ar**C**-OCH_3), 158.5 (Ar**C**-OCH_3)

IR(neat): ν_{max}/cm^{-1} 3136.9, 1462.4, 1394.1, 1316.6, 1188.0, 1057.8, 976.1

HRMS : calcd for $C_{29}H_{32}BF_2N_2O_2$ $(M+H)^+$: 488.2446, found 488.2437

Crystal Growth: slow evaporation of petrol 40/60 : DCM = 2 : 1

10.2.47 Ethyl (*E*)-3-(5-(2-methoxybenzoyl)-2,4-dimethyl-1*H*-pyrrol-3-yl)acrylate



7.14

To a Schlenk tube was added (3-iodo-2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-methoxyphenyl)methanone (**6.23**) (133 mg g, 0.37 mmol) , Pd (II) acetate (8 mg, 0.03 mmol), triphenylphosphine (10 mg, 0.03 mmol) and 2.5 mL DMF. The mixture was stirred for 10 minutes and followed by addition of ethyl acrylate (75 mg, 0.75 mmol), triethylamine (162 mg, 1.60 mmol) in DMF (2.5 mL). The solution then warmed for 24 hours. The solution was added 15 mL DCM and washed with 3 x 25 mL of water. The organic phase dried using $MgSO_4$ and removed the solvent under reduce pressure to a brown solid. The crude product then purified through column chromatography (petrol 40/60 : EtOAc = 10 : 1) to give a brown solid (**7.14**), 0.100 g (83%).

R_f : 0.25 (UV active, petrol 40/60 : EtOAc = 6: 4)

m.p. = 181-183 ^oC

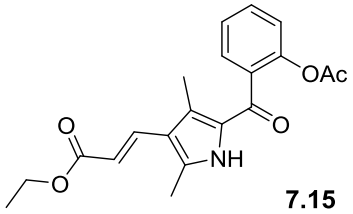
^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.23 (t, *J* = 7.0 Hz, 3H, C**H**$_3$), 1.78 (s, 3H, pyrrole C**H**$_3$), 2.37 (s, 3H, pyrrole C**H**$_3$), 3.71 (s, 3H, OC**H**$_3$), 4.15 (q, *J* = 7.1 Hz, 2H, OC**H**$_2$CH$_3$), 5.94 (d, *J* = 16.1 Hz, 1H, C**H**), 6.84-7.08 (m, 2H, 2 Ar**H**), 7.15-7.27 (m, 1H, Ar**H**), 7.30-7.44 (m, 1H, Ar**H**), 7.59 (d, *J* = 16.1 Hz, 1H, C**H**), 10.52 (s, 1H, N**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.4 (Acrylic CH$_2$**C**H$_3$), 13.2 (Pyrrole **C**H$_3$), 14.3 (Pyrrole **C**H$_3$), 55.5 (O**C**H$_3$), 60.1 (Acrylic **C**H$_2$CH$_3$), 111.2 (Ar**C**H), 114.5 (=**C**H$_2$), 118.5 (Pyrrole **C**-CH Acrylate), 120.7 (Ar**C**H), 128.4 (Ar**C**H), 128.8 (Ar**C**), 129.8 (Pyrrole **C**-CH$_3$), 130.3 (Pyrrole **C**-CO), 131.3 (Ar**C**H), 137.2 (=**C**H), 138.4 (Pyrrole **C**-CH$_3$), 156.4 (Ar**C**-OCH$_3$), 167.9 (Ester **C**=O), 184.7 (Ketone **C**=O)

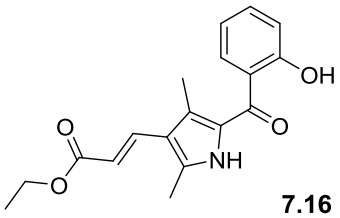
IR(neat): ν_{max}/cm^{-1} 3254.3, 2986.4, 1699.1, 1589.5, 1549.8, 1239.3, 1170.9, 1048.8, 761.1

HRMS : calcd for $C_{19}H_{22}NO_4$ $(M+H)^+$: 328.1543, found 328.1545

10.2.48 Ethyl (*E*)-3-(5-(2-acetoxybenzoyl)-2,4-dimethyl-1*H*-pyrrol-3-yl)acrylate 7.15 and ethyl (*E*)-3-(5-(2-hydroxybenzoyl)-2,4-dimethyl-1*H*-pyrrol-3-yl)acrylate 7.16



7.15



7.16

To a Schlenk tube was added (3-iodo-2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-acethoxyphenyl)methane-1-one (**6.24**) (780 mg, 1.96 mmol) , Pd (II) acetate (44 mg, 0.19 mmol), triphenylphosphine (52 mg, 0.19 mmol) and 1.5 mL DMF. The mixture was stirred for 10 minutes and followed by addition of ethylacrylate (393 mg, 3.92 mmol), triethylamine (950 mg, 9.39 mmol) in DMF (1.0 mL). The solution then warmed for 24 hours. The solution was added 15 mL DCM and washed with 3 x 25 mL of water. The organic phase dried using $MgSO_4$ and removed the solvent under reduce pressure to a brown solid. The crude product then purified through column chromatography (petrol 40/60 : EtOAc = 10 : 1) to give a yellow solid (**7.15**), 0.500 g (72%) and a yellow solid of deprotected product (**7.16**), 0.060 g (10%).

(**7.15**)

R_f : 0.26 (UV active, petrol 40/60 : EtOAc = 7: 3)

m.p. = 162-163 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.25 (t, *J* = 7.1 Hz, 3H, C**H**$_3$), 1.91 (s, 3H, Pyrrole C**H**$_3$), 2.04 (s, 3H, Pyrrole C**H**$_3$), 2.36 (s, 3H, COC**H**$_3$), 4.17 (q, *J* = 7.1 Hz, 2H, C**H**$_2$), 5.98 (d, *J* = 16.1 Hz, 1H, =C**H**), 7.13 (dd, *J* = 7.9 Hz, 1H, Ar**H**), 7.26 (d, *J* = 7.7 Hz, 1H, Ar**H**), 7.35-7.53 (m, 2H, 2 Ar**H**), 7.62 (d, *J* = 16.1 Hz, 1H, =C**H**), 10.57 (s, 1H, N**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.9 (Pyrrole **C**H$_3$), 13.1 (Pyrrole **C**H$_3$), 14.2 (Acetyl **C**H$_3$), 20.6 (Acrylic CH$_2$**C**H$_3$), 60.1 (Acrylic **C**H$_2$CH$_3$), 114.9 (=**C**H-CO), 118.8 (Ar**C**), 123.1 (Ar**C**H), 125.8 (Ar**C**H), 127.9 (Pyrrole **C**), 129.1 (Ar**C**H), 130.5 (Pyrrole **C**-CO), 131.4 (Ar**C**H), 132.9 (Pyrrole **C**-CH$_3$), 136.8 (=**C**H), 138.7 (Pyrrole **C**-CH$_3$), 147.6 (Ar**C**-OAc), 167.8 (Acrylic **C**=O), 169.1 (Acetyl **C**=O), 183.1 (Ketone **C**=O)

IR(neat): ν_{max}/cm^{-1} 3262.9, 2980.7, 1760.4, 1704.2, 1693.9, 1594.9, 1548.6, 1171.5

HRMS : calcd for $C_{20}H_{22}NO_5$ $(M+H)^+$: 356.1492, found 356.1495

(**7.16**)

R_f : 0.50 (UV active, petrol 40/60 : EtOAc = 7: 3)

m.p. = 156-158 ^oC

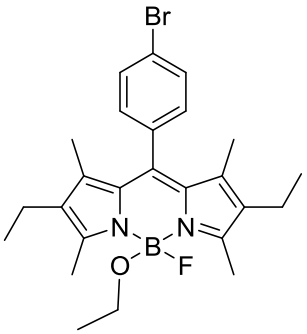
^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.25 (t, *J* = 7.1 Hz, 3H, C**H**$_3$), 2.16 (s, 3H, Pyrrole C**H**$_3$), 2.36 (s, 3H, Pyrrole C**H**$_3$), 4.17 (q, *J* = 7.1 Hz, 2H, C**H**$_2$), 6.01 (d, *J* = 16.2 Hz, 1H, =C**H**), 6.83 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H, Ar**H**), 6.94 (dd, *J* = 8.4, 1.1 Hz, 1H, Ar**H**), 7.38 (ddd, *J* = 8.8, 7.2, 1.7 Hz, 1H, Ar**H**), 7.54 (dd, *J* = 7.9, 1.7 Hz, 1H, Ar**H**), 7.62 (d, *J* = 16.2 Hz, 1H, =C**H**), 9.61 (s, 1H, N**H**), 11.19 (s, 1H, O**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 13.0 (Pyrrole **C**H_3), 13.7 (Acrylic CH_2**C**H_3), 14.3 (Pyrrole **C**H_3), 60.3 (Acrylic **C**H_2CH_3), 115.2 (=**C**H-CO), 117.8 (Ar**C**H), 118.8 (Ar**C**H), 119.0 (Pyrrole **C**), 120.3 (Ar**C**), 127.2 (Pyrrole **C**-CO), 128.8 (Pyrrole **C**-CH_3), 132.3 (Ar**C**H), 135.4 (Ar**C**H), 136.8 (=**C**H), 137.6 (Pyrrole **C**-CH_3), 161.3 (Ar**C**-OH), 167.9 (Acrylic **C**=O), 188.4 (Ketone **C**=O)

IR(neat): ν_{max}/cm^{-1} 3315.6, 2980.6, 1712.8, 1619.1, 1552.5, 1145.9, 761.3

HRMS : calcd for $C_{18}H_{20}NO_4$ $(M+H)^+$: 314.1387, found 314.1390

10.2.49 10-(4-Bromophenyl)-5-ethoxy-2,8-diethyl-5-fluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine



8.11

To a round bottom flask was added solution of 4,4-difluoro-8-(4-bromophenyl)-1,3,5,7-tetramethyl-4-bora-3*a*,4*a*-diaza-*s*-indacene (0.23 g, 0.5 mmol) in 10 mL DCM and aluminium chloride (0.10 g, 0.75 mmol). The solution was refluxed for 5 minutes under nitrogen atmosphere. After cooling at room temperature, 0.04 g (1 mmol) ethanol in 5 mL DCM was added into the solution and stirred for 48 h. The solution was washed with 2x25 mL of water then dried using $MgSO_4$. Solvent was removed under reduce pressure to give a black solid. The crude product then purified through column chromatography (petrol 40/60 ; ether = 15 : 1) to give a red solid (**8.11**), 0.130 g (54%).

R_f : 0.33 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 172-174 ^oC

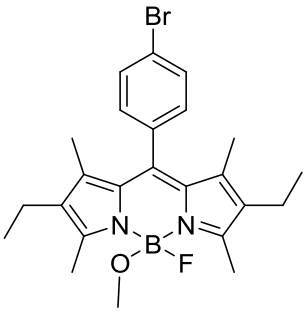
^1H NMR (300 MHz, $CDCl_3$) : δ_H 0.99 (t, *J* = 7.6 Hz, 6H, 2 C**H**$_3$), 1.07 (t, *J* = 7.0 Hz, 3H, $OCH_2C\mathbf{H}_3$), 1.33 (s, 6H, 2 C**H**$_3$), 2.32 (q, *J* = 7.6 Hz, 4H, C**H**$_2$), 2.56 (s, 6H, 2 C**H**$_3$), 3.10 (q, *J* = 7.0 Hz, 2H, $OC\mathbf{H}_2CH_3$), 7.17-7.24 (m, 2H, 2 Ar**H**), 7.62-7.67 (m, 2H, 2Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.9 (2 Pyrrole $CH_2\mathbf{C}H_3$), 12.5 (2 Pyrrole **C**H$_3$), 14.8 (2 Pyrrole **C**H$_3$), 17.1 (2 Pyrrole **C**H_2CH_3), 17.8 ($O\mathbf{C}H_2CH_3$), 56.4 ($OCH_2\mathbf{C}H_3$), 122.8 (2 Pyrrole **C**-CH_2CH_3), 130.5 (2 Ar**C**H), 131.8 (Ar**C**-Br), 132.2 (2 Ar**C**H), 132.7 (2 Pyrrole **C**-Cmeso), 135.6 (2 Pyrrole **C**-CH_3), 136.2 (Ar**C**), 138.2 (**C**meso), 154.6 (2 Pyrrole **C**-CH_3)

IR(neat): ν_{max}/cm^{-1} 3112.1, 1474.3, 1307.6, 1173.6, 972.8

HRMS : calcd for $C_{23}H_{29}BBrFN_2O$ $(M\text{-}C_2H_3)^+$: 457.1280, found 457.1278

10.2.50 10-(4-Bromophenyl)-2,8-diethyl-5-fluoro-5-methoxy-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine



8.12

To a round bottom flask was added 4,4-difluoro-8-(4-bromophenyl)-1,3,5,7-tetramethyl-4-bora-3*a*,4*a*-diaza-*s*-indacene (0.23 g, 0.5 mmol), DCM (20 mL) and sodium methoxide (0.05 g, 1 mmol). The solution was refluxed for 24 minutes under nitrogen atmosphere. The solution was washed with 3 x 15 mL of water then dried using $MgSO_4$. Solvent was removed under reduce pressure to give a black solid. The crude product then purified through column chromatography (petrol 40/60 ; ether = 15 : 1) to give an orange solid (**8.12**), 0.060 g (25%).

R_f : 0.29 (UV active, petrol 40/60 : ether = 7: 3)

m.p. = 121-123 ^oC

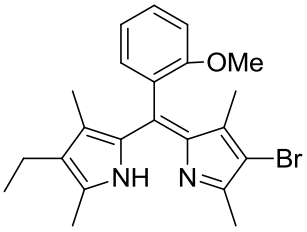
^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.00 (t, *J* = 7.5 Hz, 6H, 2 C**H**$_3$), 1.34 (s, 6H, 2 C**H**$_3$), 2.33 (q, *J* = 7.4 Hz, 4H, 2 C**H**$_2$), 2.54 (s, 6H, 2 C**H**$_3$), 2.97 (s, 3H, OC**H**$_3$), 7.17-7.25 (m, 2H, 2 Ar**H**), 7.50 (dt, *J* = 7.5, 1.5 Hz, 2H, 2 Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.9 (2 Pyrrole CH_2**C**H_3), 12.4 (2 Pyrrole **C**H_3), 14.7 (2 Pyrrole **C**H_3), 17.1 (2 Pyrrole **C**H_2CH_3), 49.2 (O**C**H_3), 122.9 (2 Pyrrole **C**-CH_2CH_3), 130.2 (2 Ar**C**H), 131.3 (Ar**C**-Br), 132.4 (2 Ar**C**H), 132.9 (2 Pyrrole **C**-Cmeso), 135.2 (2 Pyrrole **C**-CH_3), 137.3 (Ar**C**), 138.5 (**C**meso), 154.3 (2 Pyrrole **C**-CH_3)

IR(neat): ν_{max}/cm^{-1} 3146.5, 3010.6, 1473.7, 1312.2, 1178.9, 962.4

HRMS : calcd for $C_{24}H_{30}BBrFN_2O$ $(M+H)^+$: 471.1617, found 471.1613

10.2.51 (*Z*)-2-((4-Bromo-3,5-dimethyl-2*H*-pyrrol-2-ylidene)(2-methoxyphenyl) methyl)-4-ethyl-3,5-dimethyl-1*H*-pyrrole



8.16

To 50 mL of round bottom flask was added solution of 0.853 g (2.70 mmol) of 1-(3-bromo-2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-methoxyphenyl)methane-1-one (**6.20**) in 50 mL DCM. The solution then cooled to 0 ^{o}C and added 0.400 g 3-ethyl-2,4-dimethyl-1*H*-pyrrole, 50 mL DCM and 0.415 g $POCl_3$ into the flask respectively. The mixture was stirred for 30 minutes then warmed at 27 ^{o}C and stirred for 24 hours. The reaction quenched with 0.2 mL Et_3N then washed with 3x100 mL of water. The organic solvent then dried using $MgSO_4$ and evaporated to give a red solid. The crude product then purified through column chromatography (petrol 40/60 ; ether = 1 : 1 then turn to ether: MeOH = 7:3) to give a red solid (**8.16**), 0.560 g (70%).

R_f : 0.33 (UV active, petrol 40/60 : ether = 1: 1)

m.p. = 166-168 ^{o}C

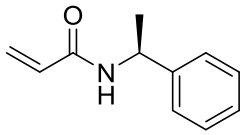
^{1}H NMR (400 MHz, $CDCl_3$) : δ_H 0.97 (t, *J* = 7.5 Hz, 3H, C**H**$_3$), 1.27 (s, 3H, Pyrrole C**H**$_3$), 1.33 (s, 3H, Pyrrole C**H**$_3$), 2.27 (q, *J* = 7.5 Hz, 2H, C**H**$_2$), 2.32 (s, 3H, Pyrrole C**H**$_3$), 2.36 (s, 3H, Pyrrole C**H**$_3$), 3.75 (s, 3H, OC**H**$_3$), 6.95 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar**H**), 7.03 (dd, *J* = 7.4, 1.0 Hz, 1H, Ar**H**), 7.13 (dd, *J* = 7.4, 1.8 Hz, 1H, Ar**H**), 7.41 (ddd, *J* = 8.3, 7.4, 1.8, 1H, Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 10.9 (Brominated pyrrole **C**H_3), 12.9 (Brominated pyrrole **C**H_3), 13.7 (Pyrrole **C**H_3), 14.7 (Pyrrole CH_2**C**H_3), 15.3 (Pyrrole **C**H_3), 17.4 (Pyrrole **C**H_2CH_3), 55.6 (O**C**H_3), 110.3 (Pyrrole **C**-Br), 111.3 (Ar**C**H), 121.2 (Ar**C**H), 127.1 (Pyrrole **C**-CH_2CH_3), 128.9 (Ar**C**H), 130.2 (Brominated pyrrole **C**-CH_3), 130.8 (Ar**C**), 133.9 (Brominated pyrrole **C**-CH_3), 134.7 (**C**meso), 135.2 (Ar**C**H), 136.9 (Brominated pyrrole **C**-CH_3), 137.4 (Pyrrole **C**-Cmeso), 147.1 (Pyrrole **C**-CH_3), 151.0 (Ar**C**-OCH3), 157.4 (Pyrrole **C**-CH_3)

IR(neat): ν_{max}/cm^{-1} 2959.2, 2923.4, 1562.2, 131.4, 1461.8, 1369.5, 1290.7, 1114.2, 957.1, 700.8

HRMS : calcd for $C_{22}H_{26}BrN_2O$ $(M+H)^+$: 413.1223, found 413.1223

10.2.52 (*S*)-*N*-(1-Phenylethyl)acrylamide



8.26

To a round bottom flask was added DCC (573 mg g, 2.78 mmol) and DCM (2.5 mL). The solution then cooled to 0 ^{o}C before adding (*S*)-ethylbenzylamine (336 mg, 2.78 mmol). Into the solution was added acrylic acid (200 mg, 2.78 mmol) in 5 mL DCM which was then stirred for 24 h at room temperature. Ethyl acetate (25 mL) was added into the mixture and washed with 3 x 25 mL of water. The organic phase dried using $MgSO_4$ and removed the solvent under reduce pressure to a white solid. The crude product then purified through column chromatography (petrol 40/60 : EtOAc = 10 : 1) to give a colourless solid (**8.26**), 0.226 g (50%).

R_f : 0.20 (UV active, petrol 40/60 : ethylacetate = 7: 3)

m.p. = 98-100 ^{o}C

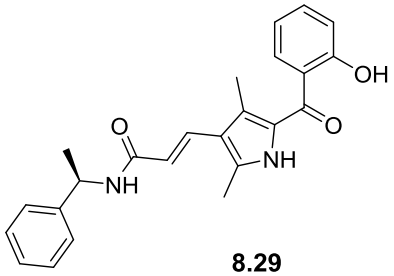
^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 1.53 (d, *J* = 6.9 Hz, 3H, C**H**$_3$), 5.15-5.29 (m, 1H, C**H**), 5.64 (dd, *J* = 10.1, 1.6 Hz, 1H, =C**H**$_2$), 6.06 (s, 1H, N**H**), 6.06-6.17 (m, 1H, =C**H**), 6.30 (dd, *J* = 17.0, 1.6 Hz, 1H, =C**H**), 7.28 (td, *J* = 5.7, 5.1, 1.4 Hz, 1H, Ar**H**), 7.35 (d, *J* = 4.0, 4H, Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 21.6 (**C**H$_3$), 48.8 (**C**HCH$_3$), 126.2 (2 Ar**C**H), 126.6 (Ar**C**H), 127.4 (=**C**H$_2$), 128.6 (2 Ar**C**H), 130.8 (=**C**H), 142.9 (Ar**C**), 164.6 (**C**=O)

IR(neat): ν_{max}/cm^{-1} 3286.9, 1655.2, 1537.7, 1449.7, 1238.7, 969.9, 701.6

HRMS : calcd for $C_{11}H_{14}NO$ $(M+H)^+$: 176.1070, found 176.1069

10.2.53 (*S*,*E*)-3-(5-(2-Hydroxybenzoyl)-2,4-dimethyl-1*H*-pyrrol-3-yl)-*N*-(1-phenyl ethyl)acrylamide



8.29

To a Schlenk tube was added 1-(3-iodo-2,4-dimethyl-1*H*-pyrrol-5-yl)-1-(2-acethoxyphenyl)methane-1-one (**6.24**) (216 mg, 0.54 mmol) , Pd (II) acetate (12 mg, 0.05 mmol), triphenylphosphine (14 mg, 0.05 mmol) and 2.5 mL DMF. The mixture was stirred for 10 minutes and followed by addition of (*S*)-N-methylbenzylacrylamide (191 mg, 1.08 mmol), triethylamine (270 mg, 2.67 mmol) in DMF (2.5 mL). The solution then warmed for 24 hours. The solution was added 15 mL DCM and washed with 3 x 25 mL of water. The organic phase dried using $MgSO_4$ and removed the solvent under reduce pressure to a brown solid. The crude product then purified through column chromatography (petrol 40/60 : EtOAc = 10 : 1) to give a colourless solid (**8.29**), 0.150 g (72%).

R_f : 0.15 (UV active, petrol 40/60 : EtOAc = 8: 2)

m.p. = 210-211 ^oC

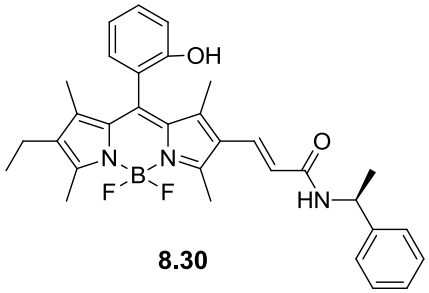
^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.59 (d, *J* = 6.9 Hz, 3H, C**H**$_3$), 1.68 (s, 1H, O**H**), 2.27 (s, 3H, Pyrrole C**H**$_3$), 2.44 (s, 3H, Pyrrole C**H**$_3$), 5.30 (p, *J* = 7.0 Hz, 1H, C**H**CH_3), 5.78 (d, *J* = 7.9 Hz, 1H, Phenyl C**H**), 6.06 (d, *J* = 15.8 Hz, 1H, =C**H**), 6.89-6.96 (m, 1H, Ar**H**), 7.05 (dd, *J* = 8.4, 1.1 Hz, 1H, Ar**H**), 7.26-7.36 (m, 2H, 2 ArC**H**), 7.36-7.43 (m, 3H, 3 ArC**H**), 7.48 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H, ArC**H**), 7.69 (d, *J* = 15.7 Hz, 1H, =C**H**), 9.05 (s, 1H, N**H**), 11.25 (s, 1H, N**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 13.2 (Pyrrole **C**H_3), 13.9 (Pyrrole **C**H_3), 21.8 (Amide **C**H_3), 49.1 (Amide **C**H), 117.9 (Pyrrole **C**), 118.9 (Phenolic **C**H), 119.2(Phenolic **C**H), 120.4 (Phenolic **C**H), 126.4 (2 Ar**C**H), 127.2 (Ar**C**H), 128.5 (Phenolic **C**)128.6 (=**C**H-CO), 128.8 (2 Ar**C**H), 132.2 (Phenolic **C**H), 133.7 (Pyrrole **C**-CO), 135.4 (Pyrrole **C**-CH_3), 136.9 (Pyrrole **C**-CH_3), 143.3 (=**C**H), 161.5 (Ar**C**), 165.8 (Phenolic **C**-OH), 188.5 (Ketone **C**=O), 189.8 (Amide **C**=O)

IR(neat): ν_{max}/cm^{-1} 3276.6, 3061.3, 1647.6, 1586.6, 1543.1, 1282.9, 760.9, 694.7

HRMS : calcd for $C_{24}H_{25}N_2O_3$ $(M+H)^+$: 389.1860, found 389.1861

10.2.54 (*S*,*E*)-3-(8-Ethyl-5,5-difluoro-10-(2-hydroxyphenyl)-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl)-*N*-(1- phenyl ethyl)acrylamide



8.30

To 50 mL of round bottom flask was added 52 mg (0.14 mmol) of (*S,Z*)-3-(5-(2-hydroxybenzoyl)-2,4-dimethyl-1*H*-pyrrol-3-yl)-*N*-(1-phenylethyl)acrylamide (**8.29**), 20 mg of 3-ethyl-2,4-dimethyl-1*H*-pyrrole (0.16 mmol), 5 mL DCM and 0.02 mL of trifluoroacetic acid and stirred for overnight. The reaction washed with 3x5 mL of water. The organic solvent then dried using $MgSO_4$ and evaporated to give black red oil residue. The residue then dissolved in 5 mL DCM and added 0.1 mL N,N-diisopropyl-N-ethylamine at room temperature. The mixture was stirred for 30 minutes and followed by the addition of 0.1 mL $BF_3.Et_2O$ at 0 ^oC. The mixture then continued to stir at room temperature for further 1 hour. The reaction washed with 3x5 mL of water. The organic solvent then dried using $MgSO_4$ and evaporated to give a dark red solid. The crude product then purified through column chromatography (petrol 40/60 : EtOAc = 20 : 1) to give a red solid (**8.30**), 0.052 g (72%).

R_f : 0.29 (UV active, petrol 40/60 : EtOAc = 6: 4)

m.p. = 163-165 ^oC

^{1}H NMR (500 MHz, $CDCl_3$) : δ_H 0.87 (t, *J* = 7.8 Hz, 3H, Pyrrole $CH_2C\mathbf{H}_3$), 0.96 (d, *J* = 7.5 Hz, 3H, Acrylic C$\mathbf{H}_3$), 1.44 (s, 3H, Pyrrole C$\mathbf{H}_3$), 1.51 (s, 3H, Pyrrole C$\mathbf{H}_3$), 2.52 (s, 3H, Pyrrole C$\mathbf{H}_3$), 2.58 (s, 3H, Pyrrole **C**H_3), 2.31 (q, *J* = 7.4 Hz, 2H, Pyrrole C$\mathbf{H}_2CH_3$), 5.16 (q, *J* = 7.1 Hz, 1H, Acrylic C**H**), 5.86 (d, *J* = 15.8 Hz, 1H, =C**H**), 7.21-7.35 (m, 7H, 5 ArC**H**), 6.95-7.06 (m, 4H, 2 ArC**H**), 5.86 (d, *J* = 15.8 Hz, 1H, =C**H**), 7.35 (d, *J* = 15.6 Hz, 1H, =C**H**)

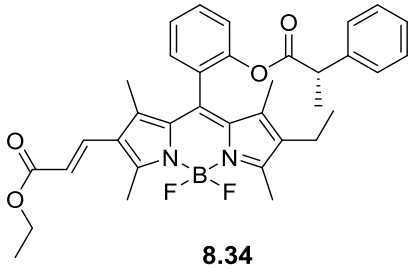
^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.4 (Pyrrole **C**H_3), 13.0 (Pyrrole **C**H_3), 14.5 (Pyrrole CH_2**C**H_3), 17.2 (Pyrrole **C**H_3), 21.8 (Amide **C**H_3), 23.9 (**C**H_3), 40.9 (Pyrrole **C**H_2CH_3), 49.2 (Amide **C**H), 117.2 (Phenolic **C**H), 119.5 (Phenolic **C**H), 121.2 (Phenolic **C**H), 121.5 (Pyrrole **C**), 124.8 (Ar**C**H), 126.3 (2 Ar**C**H), 127.4 (=**C**H-CO), 128.8 (2 Ar**C**H), 129.4 (Phenolic **C**), 130.4 (Pyrrole **C**-CH_2CH_3), 131.4 (Pyrrole **C**-CH), 133.1 (Phenolic **C**H), 134.8 (Pyrrole **C**-

CH_3), 137.0 (Pyrrole **C**-CH_3), 139.3 (**C**), 140.9 (Pyrrole **C**), 143.2 (=**C**H), 153.2 (Pyrrole **C**-CH_3), 153.4 (Pyrrole **C**-CH_3), 158.2 (Ar**C**), 158.7 (Phenolic **C**-OH), 165.9 (Amide **C**=O)

IR(neat): ν_{max}/cm^{-1} 3277.6, 2969.5, 2929.4, 1701.6, 1686.6, 1608.5, 1535.4, 1188.1, 977.0

HRMS : calcd for $C_{32}H_{35}BF_2N_3O_2$ $(M+H)^+$: 542.2785, found 542.2791

10.2.55 Ethyl (*S*,*E*)-3-(8-ethyl-5,5-difluoro-1,3,7,9-tetramethyl-10-(2-((2-phenylpropanoyl)oxy)phenyl)-5*H*-5λ^4,6λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl)acrylate



8.34

To a round bottom flask was added EDCI (0.04 mL g, 0.19 mmol) and DCM (2.5 mL). The solution then cooled to 0 ^{o}C before adding (*R*)-2-phenylpropionic acid (16 mg, 0.11 mmol). Into the solution was added 1,3,5,7-dimethyl-2-ethyl-8-(2-hydroxyphenyl)-6-(acrylacetate-3-yl)BODIPY (**7.7**) (45 mg, 0.10 mmol) in 2.5 mL DCM and followed by DMAP (25 mg, 0.20 mmol). The mixture was then stirred for 24 h at room temperature. DCM (10 mL) was added into the mixture and washed with 3 x 10 mL of water. The organic phase dried using $MgSO_4$ and removed the solvent under reduce pressure to a red solid. The crude product then purified through column chromatography (petrol 40/60 ; ether = 10 : 1) to give a red solid (**8.34**), 0.009 g (16%).

R_f : 0.32 (UV active, petrol 40/60 : Ether = 7: 3)

m.p. = 346-348 ^{o}C

^{1}H NMR (300 MHz, $CDCl_3$) : δ_H 0.98 (t, *J* = 7.7 Hz, 3H, Pyrrole $CH_2C\mathbf{H}_3$), 1.00 (t, *J* = 7.7 Hz, 3H, Acrylic C**H**$_3$), 1.35 (d, *J* = 7.5, 3H, Ester CH_3), 1.39 (s, 3H, Pyrrole C**H**$_3$), 1.45 (s, 3H, Pyrrole C**H**$_3$), 2.28 (q, *J* = 7.7 Hz, 2H, Pyrrole $CH_2C\mathbf{H}_3$), 2.60 (s, 3H, Pyrrole C**H**$_3$), 2.71 (s, 3H, Pyrrole C**H**$_3$), 3.74 (q, *J* = 7.3 Hz, 1H, Ester C**H**), 4.25 (q, *J* = 7.3 Hz, 2H, Acrylic C**H**$_2$), 6.01 (d, *J* = 16.3 Hz, 1H, =C**H**), 7.06-7.21 (m, 4H, 4 Ar**H**), 7.25-7.39 (m, 4H, 4 Ar**H**), 7.50-7.56 (m, 1H, Ar**H**), 7.58 (d, *J* = 16.3, Hz, 1H, =C**H**)

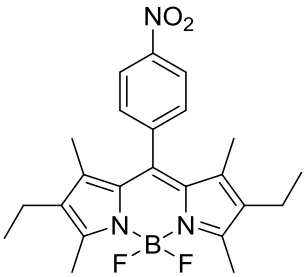
^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.6 (Ester **C**H$_3$), 12.1 (Acrylic $CH_2\mathbf{C}H_3$), 13.1 (Pyrrole **C**H$_3$), 14.2 (Pyrrole $CH_2\mathbf{C}H_3$), 14.5 (Pyrrole **C**H$_3$), 17.2 (Pyrrole **C**H$_3$), 17.8 (Pyrrole **C**H$_3$), 30.4 (Pyrrole **C**H$_2$CH$_3$), 45.5 (Ester **C**H), 60.4 (Acrylic **C**H$_2$CH$_3$), 116.9 (Ar**C**H), 123.6 (Ar**C**H), 124.4 (Acrylic =**C**H-CO), 125.6 (Ar**C**), 126.7 (Ar**C**H), 127.1 (Ar**C**H), 127.3 (2 Ar**C**H), 127.7 (Pyrrole **C**-CH$_3$), 128.6 (2 Ar**C**H), 129.8 (Pyrrole **C**-CH), 130.0 (Ar**C**H), 130.5 (**C**), 132.5 (Pyrrole **C**), 135.2 (Pyrrole **C**-CH$_3$), 135.8 (Pyrrole **C**-CH$_2$CH$_3$), 136.2 (Pyrrole **C**), 139.2

(Pyrrole **C**-CH_3), 141.0 (Acrylic =**C**H), 148.1 (Ar**C**), 153.2 (Pyrrole **C**-CH_3), 158.9 (Ar**C**-OC=O), 167.8 (Acrylic **C**=O), 172.4 (Ester **C**=O)

IR(neat): ν_{max}/cm^{-1} 2915.9, 2850.7, 1735.8, 1701.7, 1538.8, 1452.5, 1177.8, 699.0

HRMS : calcd for $C_{24}H_{24}N_2O_3$ $(M+H)^+$: 599.2890, found 599.2887

10.2.56 2,8-Diethyl-5,5-difluoro-1,3,7,9-tetramethyl-10-(4-nitrophenyl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine



9.3

To a round bottom flask was added sequentially 3-ethyl-2,4-dimethylpyrrole (0.617 g, 2 mmol), DCM (25 mL) and 4-nitrobenzoylchloride (0.185 g, 1 mmol). The solution was stirred for 5 hours at room temperature under nitrogen atmosphere. The solution was added 1 mL of triethylamine over 5 minutes and followed by addition of 1 mL of $BF_3.Et_2O$ at 0 ^oC. The solution was stirred for 2 hours. The solution was washed with 2x25 mL of water then dried using $MgSO_4$. Solvent was removed under reduce pressure to give a red solid. The crude product then purified through column chromatography to give a red solid (**9.3**), 0.310 g (73%).

R_f : 0.42 (UV active, petrol 40/60 : DCM = 1: 1)

m.p. = 170-172 ^oC

^1H NMR (300 MHz, $CDCl_3$) : δ_H 1.00 (t, *J* = 7.6 Hz, 6H, 2 C**H**$_3$), 1.27 (s, 6H, 2 Pyrrole C**H**$_3$), 2.32 (q, *J* = 7.5 Hz, 4H, 2 C**H**$_2$), 2.56 (s, 6H, 2 Pyrrole C**H**$_3$), 7.56 (dt, *J* = 8.9, 2.4 Hz, 2H, 2 Ar**H**), 8.40 (dt, *J* = 8.9, 2.4 Hz, 2H, 2 Ar**H**)

^{13}C NMR (100 MHz, $CDCl_3$) : δ_C 11.9 (2 Pyrrole CH_2**C**H_3), 12.6 (2 Pyrrole **C**H_3), 14.6 (2 Pyrrole **C**H_3), 17.0 (2 Pyrrole **C**H_2CH_3), 123.6 (2 Pyrrole **C**-CH_2CH_3), 124.2 (2 Ar**C**H), 129.9 (2 Ar**C**H), 133.6 (**C**), 136.9 (2 Pyrrole **C**-Cmeso), 137.8 (2 Pyrrole **C**-CH_3), 142.9 (2 Pyrrole **C**-CH_3), 148.3 (Ar**C**), 155.0 (Ar **C**-NO2)

IR(neat): ν_{max}/cm^{-1} 2966.2, 1523.7, 1474.8, 1346.1, 1319.9, 1186.8, 976.5, 724.8

HRMS : calcd for $C_{23}H_{27}BF_2N_3O_2$ $(M+H)^+$: 425.2195, found 425.2037

References

1. Rowlands, G. J. *Tetrahedron* **2009**, *65*, 8603-8655
2. Salemme, F. R. *Ann. Rev. Biochem*. **1977**, *46*, 299-329
3. Trumpower, B. L. *Biochemica et Biophysica Acta*. **1981**, *639*, 129-155
4. Whitmarsh, J., Cramer, W. A. *Biophys. J*. **1979**, *26*, 223-234
5. Zhang, Z., Huang, L., Shulmeister, V. M., Chi, Y. I., Kim, K. K., Hung, L. W., Crofts, A. R., Berry, E. A., Kim, S. H. *Nature*. **1998**, *392*, 677-684
6. Peterson, J. A., Kusunose, M., Kusunose, E., Coon, M. J. *J. Biol. Chem*. **1967**, *242*, 4334-4340
7. Lovenberg, W., Sobel, B. *Biochem*. **1965**, *54*, 193-199
8. Xiang, X., Fielden, J., Cordoba, W. R., Huang, Z., Zhang, N., Luo, Z., Musaev, D. G., Lian, T., Hill, C. L. *J. Phys. Chem*. **2013**, *117*, 918-926
9. Rosen, B. M., Percec, V. *Chem. Rev*. **2009**, *109*, 5069-5119
10. Halls, J. E., Wadhawan, J. D. *Phys. Chem. Chem. Phys*. **2013**, *15*, 3218-3226
11. Hass, H. B., Bender, M. L. *J. Am. Chem. Soc*. **1949**, *71*, 1767-1769
12. Hass, H. B., Bender, M. L. *J. Am. Chem. Soc*. **1949**, *71*, 3482-3485
13. Kornblum, N. Angew. Chem. Int. Ed. 1975, 14, 734-745
14. Kim, J. K., Bunnett, J. F. *J.Am. Chem. Soc*. **1970**, *92*, 7463-7464
15. Kim, J. K., Bunnett, J. F. *J. Am. Chem. Soc*. **1970**, *92*, 7464-7465
16. Rossi, R. A. *Acc. Chem. Res*. **1982**, *15*, 164-170
17. Galli, C., Gentili, P., Rappoport, Z. *J. Org. Chem*. **1994**, *59*, 6786-6795
18. Galli, C. *Tetrahedron* **1988**, *44*, 5205-5208
19. Schmittel, M., Burghart, A. *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2550-2589
20. Finley, K. T. *Chem. Rev*. **1964**, *64*, 573-589
21. Jin, M. Y., Kim, S. M., Han, H., Ryu, D. H., Yang, J. W. *Org. Lett*. **2011**, *13*, 880-883
22. Kekaya, H., Morishita, M.,Koshino, H., Morita, T., Kobayashi, K., Osada, H. *J. Org. Chem*. **1999**, *64*, 1052-1053
23. McElvain, S. M. *Org. React*. **1948**, *4*, 256-268
24. Bloomfiled, J. J., Owsley, D. C., Ainsworth, C., Robertson, R. E. *J. Org. Chem*. **1975**, *40*, 393-402
25. Blanchard, A. N., Burnell, D. J. *Tetrahedron Lett*. **2001**, *42*, 4779-4781
26. Birch, A. J. *J. Chem. Soc*. **1944**, 430-436
27. Birch, A. J. *J. Chem. Soc*. **1945**, 593-597
28. Birch, A. J. *J. Chem. Soc*. **1945**, 809-813
29. Birch, A. J. *J. Chem. Soc*. **1946**, 102-105
30. Birch, A. J. *J. Chem. Soc*. **1947**, 1642-1648

31. Birch, A. J. *J. Chem. Soc*. **1949**, 2531-2536
32. Kaiser, E. M. *Synt*. **1971**, 391-415
33. Birch, A. J., Smith, H. *Quart. Rev*. **1958**, *12*, 17-33
34. Ziemmerman, H. E., Wang, P. A. *J. Am. Chem. Soc*. **1993**, *115*, 2205-2216
35. Ziemmerman, H. E. *Tetrahedron* **1961**, *16*, 169-176
36. Burnham, D. R. *Tetrahedron* **1969**, *25*, 897-904
37. Birch, A. J., Nasipuri, D. *Tetrahedron* **1959**, 148-153
38. Krapcho, A. P., Bothner-By, A. A. *J. Am. Chem. Soc*. **1959**, *81*, 3658-3666
39. Birch, A. J., Hinde, A. L., Random, L. *J Am. Chem. Soc*. **1981**, *103*, 284-289
40. Birch, A. J., Slobbe, J. *Heterocycles* **1976**, *5*, 905
41. Donohoe, T. J., Guyo, P. M. *J. Org. Chem*. **1996**, *61*, 7664-7665
42. Blenderman, W. G., Joullie, M. M. *Tetrahedron Lett*. **1979**, *52*, 4985-4988
43. Donohoe, T. J., Guyo, P. M., Harji, R. R., Halliwell, M. *Tetrahedron Lett*. 1**998**, *39*, 3075-3078
44. Donohoe, T. J., Helliwell, M., Stevenson, C. A. *Tetrahedron Lett*. **1998**, *39*, 3071-3074
45. Hook, J.M., Mander, L. N., Urech, R. *J. Org. Chem*. **1984**, *49*, 3250-3260
46. Schultz, A. G., Holoboski, M. A., Smyth, M. S. *J. Am. Chem. Soc*. **1996**, *118*, 6210-6219
47. Breton, G. W., Shugart, J. H., Hughey, C. A., Conrad, B. P., Perala, S. M. *Molecules* **2001**, *6*, 655-662
48. Li, C. J. *Tetrahedron* **1996**, *52*, 5643-5668
49. Jogi, A., Maerog, U. *Molecules* **2001**, *6*, 964-968
50. Yu, P., Wang, T., Li, J., Cook, J. M. *J. Org. Chem*. **2000**, *65*, 3173-3191
51. Yanagisawa, A., Habaue, S., Yamamoto, H. *J. Am. Chem. Soc*. **1991**, *113*, 8955-8956
52. Abad, A., Agullo, C., Arno, M., Cunat, A. C., Meseguer, B., Zaragoza, R. J. *J. Org. Chem*. **1998**, *63*, 5100-5106
53. Trost, B. M., Corte, J. R. *Angew. Chem. Int. Ed. Engl*. **1999**, *38*, 3664-3666
54. Blicke, F. F., Powers, L. D. *J. Am.Chem. Soc*. **1929**, *51*,3378-3383
55. Holm, T. Crossland, I. *Act. Chem. Scand*. **1971**, *25*, 59-69
56. Gilman, H., Fothergill, R. E. *J. Am. Chem. Soc*. **1929**, *51*, 3149
57. Bachmann, W. E. *J. Am. Chem. Soc*. **1931**, *53*, 2758
58. Arbuzov, A. E., Arbuzova, I. A. *J. Gen. Chem*. **1932**, *2*, 388
59. Blomberg, C., Mosher, H. S. *J. Organometal. Chem*. **1968**, *13*, 519-522
60. Ashaby, E. C., DePriest, R. N., Goel, A. B. *Tetrahedron Letters*. **1981**, *22*, 1763-1766
61. Ashaby, E. C. *Acc. Chem. Res*. **1988**, *21*, 414-421

62. Ashaby, E. C., Bowers, J., Depriest, R. *Tetrahedron Letters*. **1980**, *21*, 3541-3542
63. Zhang, Y., Wenderoth, B., Su, W. Y., Ashaby, E. C. *J. Organometal. Chem*. **1985**, *292*, 29-37
64. Galli, C., Gentili, P., Rappoport, Z. *J. Org. Chem*. **1994**, *59*, 6786-6795
65. Liotta, D., Saindane, M., Waykole, L. *J. Am. Chem. Soc*. **1983**, *105*, 2922-2923
66. Soroka, M., Shine, H. J. *Tetrahedron*. **1986**, *42*, 6111-6121
67. Haberfield, P. *J. Am. Chem. Soc*. **1995**, *117*, 3314-3315
68. Carloni, P., Greci, L., Stipa, P. *J. Org. Chem*. **1991**, *56*, 4733-4737
69. Padwa, A., Goldstein, S. I., Rosenthal, R. J. *J. Org. Chem*. **1987**, *52*, 3278-3285
70. McKinley, J., Aponick, A., Raber, J. C., Fritz, C., Montgomery, D., Wigal, C. T. *J. Org. Chem*. **1997**, *62*, 4874-4876
71. McKinley, J., Aponick, A., Raber, J. C., Fritz, C., Montgomery, D., Wigal, C. T. *J. Org. Chem.* **1997**, *62*, 4874-4876
72. Bruni, P., Carloni, P., Conti, C., Giogini, E., Greci, G., Iacussi, M., Stipa, P., Tosi, G. *Tetrahedron*. **1996**, *52*, 6795-6802
73. Shirakawa, E., Watabe, R., Murakami, T., Hayashi, T. *Chem. Commun*. **2013**, *49*, 5219-5221
74. Uchiyama, N., Shirakawa, E., Hayashi, T. *Chem. Commun*. **2013**, *49*, 364-366
75. Johnson, R. *Nature Chem*. **2013**, *5*, 728
76. Jang, K. H. W., Nam, S. J., Locke, J. B., Kauffman, C. A., Beatty, D. S., Paul, L. A., Fenical, W. *Angew. Chem. Int. Ed*. **2013**, *52*, 7822-7824
77. Gerth, K., Steinmetz, H., Hofle, G., Jansen, R. *Angew. Chem. Int. Ed*. **2008**, *47*, 600-602
78. Rahn, N., Kalesse, M. *Angew. Chem. Int. Ed*. **2008**, *47*, 597-599
79. Imashiro, R., Kuroda, T. *J. Org. Chem*. **2003**, *68*, 974-979
80. Zhang, Y., Shibatomi, K., Yamamoto, H. *J. Am. Chem. Soc*. **2004**, *126*, 15038-15039
81. Reed, S. F. *J. Org. Chem*. **1965**, *30*, 2195-2198
82. Akula, R., Galligan, M., Ibrahim, H. *Chem. Commun*. **2009**, 6991-6993
83. Wyman, D. P., Kaufman, P. R. *J. Org. Chem*. **1964**, *29*, 1956-1960
84. Wyman, D. P., Kaufman, P. R., Freeman, W. P. *J. Org. Chem*. **1964**, *29*, 2706-2710
85. Hoffman, R. V., Weiner, W. S., Maslouh, N. *J. Org. Chem*. **2001**, *66*, 5790-5795
86. Nobrega, A., J., Goncalves, S. M., Peppe, C. *Syn. Commun*. **2002**, *32*, 3711-3717
87. Kosower, E. M., Cole, W. J., Wu, G. S., Cardy, D. E., Meisters, G. *J. Org. Chem*. **1963**, *28*, 630-633
88. Jagdale, A. R., Chouthaiwale, P. V., Sudalai, A. *Indian J. Chem*. **2009**, *488*, 1424-1430
89. Pross, A. *Acc. Chem. Res*. **1985**, *18*, 212-219

90. Yamazaki, S., Yamabe, S. *J. Org. Chem*. **2002**, *67*, 9346-9353
91. Tsierkezos, N. G. *J. Sol. Chem*. **2007**, *36*, 1301-1310
92. Essa, A. H.; Lerrick, R. I.; Tuna, F.; Harrington, R. W.; Clegg, W.; Hall, M. J. *Chem. Comm.*, **2013**, *49*, 2756-2758
93. Lund, A.; Shiotani, M.; Shimada, S. Principles and Application of ESR Spectroscopy, **2011**, Springer, New York
94. Eberson, L. *J. Chem. Soc. Perkin Trans*. **1994**, 2, 171-176
95. Morliere, C. M. M.; Aitken, D. J.; Bull, S. D.; Davies, S. G.; Husson, H. P. *Tetrahedron Assym*. **2001**, *12*, 149-155
96. Stork, G.; Hudrlik, P. F. *J. Am. Chem. Soc*. **1968**, *90*, 4462-4464
97. Stork, G.; Hudrlik, P. F. *J. Am. Chem. Soc*. **1968**, *90*, 4464-4465
98. Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. Organic Chemistry, **2006**, Oxford University Press
99. Orban, J.; Turner, J. V.; Twitchin, B. *Tetrahedron Lett*., **1984**, *25*, 5099-5102
100. Differding, E.; Ruegg, G. M; Lang, R. W. *Tetrahedron Lett*. **1991**, *32*, 1779-1782
101. Nyffeler, P. T.; Duron,S. G.; Burkat, M. D.; Vincent, S P.; Wong, C. H. *Angew.Chem. Int. Ed*. **2005**, *44*, 192-212
102. Tsuruta, T.; Haruda, T.; Nishino, H.; Kurosawa, K. *Bull. Chem. Soc. Jpn*. **1985**, *58*, 142-145
103. Imanishi, T.; Fujiwara, Y.; Sawama, Y.; Monguchi, Y.; Sajiki, H. *Adv. Synt. Cat*. **2012**, *354*, 771-776
104. Ellis, W. W., Odenkirik, W., Bosnich, B. *Chem. Commun*. **1998**, 1311-1312
105. Davies, H. J., Ruda, A. M., Tomkinson, N. C. O. *Tetrahedron Letters*. **2007**, *48*, 1461-1464
106. Denmark, S. E., Bui, T. *J Org. Chem*. **2005**, *70*, 10190-10193
107. Yamaguchi, A., Matsunaga, S., Shibasaki, M. *J. Am. Chem. Soc*. **2009**, *131*, 10842-10843
108. Gnanadesikan, V., Horiuchi, Y., Ohshima, T., Shibasaki, M. *J. Am. Chem. Soc*. **2004**, *126*, 7782-7783
109. Jakob, F., Schneider, C. *Eur. J. Org. Chem*. **2007**, 2958-2963
110. Reutrakul, V., Jaratjaroonphong, J., Tuchinda, P., Kuhakarn, C., Kongsaeree, P., Prabpai, S., Pohmakort, M. *Tetrahedron Letters*. **2006**, *47*, 4753-4757
111. Kurti, L., Czako, B. *Strategic Applications of Named Reactions in Organic Synthesis*, **2005**, Elsevier Inc., London
112. Tormakangas, O. P., Saarenketo, P., Koskinen, A. M. P. *Organic Process Research & Development*. **2002**, *6*, 125-131

113. Fu, Y., Yang, Y., Hugel, H. M., Du, Z., Wang, K., Huang D., Hu, Y. *Org. Biomol. Chem*. **2013**, *11*, 4429-4432
114. Loudet, A., Burgess, K. *Chem. Rev*. **2007**, *107*, 4891-4932
115. Golovkova, T. A., Kozlov, D. V., Neckers, D. C. J. Org. Chem. 2005, 70, 5545-5549
116. Qi, X., Jun, E. J., Xu, L., Kim, S. J., Hong, J. S.J., Yoon, Y. J., Yoon, J. *J. Org. Chem*. **2006**, *71*, 2881-2884
117. Guliyev, R., Ozturk, S., Shani, E., Akkaya, E. U. *Org. Lett*. **2012**, *14*, 1528-1531
118. Bellier, Q., Pegaz, S., Aronica, C., Guennic, B. L., Andraud, C., Maury, O. *Org. Lett*. **2011**, *13*, 22-25
119. Davila, J., Harriman, A., Gulliya, K. S. *Photochem. Photobiol*. **1991**, *53*, 1-
120. Buyukcakir, O., Bozdemir, A., Kolemen, S., Erbas, S., Akkaya, E. U. *Org. Lett*. **2009**, *11*, 4644-4647
121. McDonnel, S. O., Hall, M. J., Allen, L. T., Byrne, A., Gallagher, W. M., O'Shea, D. F. *J. Am. Chem. Soc*. **2005**, *127*, 16360-16361
122. Karolin, J., Johansson, L. B. A., Strandberg, L., Ny, T. *J. Am. Chem. Soc*. **1994**, *116*, 7801-7806
123. McCusker, C., Carrol, J. B., Rotello, V. M. *Chem. Commun*. **2005**, 996-998
124. Rezende, L. C. D., Emery, F. S. *Orbital Elec. J. Chem*. **2013**, *5*, 62-83
125. Rousseau, T., Cravino, A., Bura, T., Ulrich, G., Ziessel, R., Roncali, J. *Chem. Commun*. **2009**, 1673-1675
126. Kolemen, S., Cakmak, Y., Ela, S. E., Altay, Y., Brendel, J., Thelakkat, M., Akkaya, E. U. *Org. Lett*. **2010**, *12*, 3812-3815
127. Arbeloa, T. L., Arbeloa, F. L., Gracia, M. I., Costela, A., Sastre, R., Amat, G. F. *Chem. Phys. Lett*. **1999**, *299*, 315-
128. Tram, K., Yan, H., Jemkims, H. A., Vassiliev, S., Bruce, D. *Dyes and Pigments* **2009**, *82*, 392-395
129. Rohand, T., Dolusic, E., Ngo, T. H., Maes, W., Dehaen, W. *Arkivoc* **2007**,*10*, 307-324
130. Arroyo, I. J., Hu, R., Merino, G., Tang, B. Z., Cabrera, E. P. *J. Org. Chem*. **2009**, *74*, 5719-5722
131. Hu W., Guo, H., Wu, W., Ji, S., Zhao, J. *J. Org. Chem*. **2011**, *76*, 7056-7064
132. Goud, T. V., Tutar, A., Biellmann, J. F. *Tetrahedron* **2006**, *62*, 5084-5091
133. Lager, E., Liu, J., Augilar, A. A., Tang, B. Z., Cabrera, E. P. *J. Org. Chem*. **2009**, *74*, 2053-2058
134. Li, Z., Mintzer, E., Bittman, R. J. Org. Chem. 2006, 71, 1718-1721
135. Wu, L., Burgess, K. *Chem. Commun*. **2008**, 4933-4935
136. Schmitt, A., Hinkeldey, B., Wild, M. *J. Fluoresc*. **2009**, *19*, 755-758

137. Leen, V., Breaken, E., Luckermans, K., Jackers, C., Auweraer, M. V., Boens, N., Dehaen, W. *Chem. Commun*. **2009**, 4515-4517
138. Jiao, L., Yu, C., Liu, M., Wu, Y., Cong, K., Meng, T., Wang, Y., Hao, E. *J. Org. Chem*. **2010**, *75*, 6035-6038
139. Haefele, A., Zedde, C., Retailleau, P., Ulrich, G., Ziessel, R. *Org. Lett*. **2010**, *12*, 1672-1675
140. Beer, G., Niederalt, C., Grimme, S., Daub, J. *Angew. Chem. Int. Ed*. **2000**, *39*, 3252-3255
141. Loudet, A., Bandichhor, R., Burgess, K., Palma, A., McDonnell, S. O., Hall, M. J., O'Shea, D. F. *Org. Lett*. **2008**, *10*, 4771-4774
142. Shandura, M. P., Yakubovskyi, V. P., Kovtun, Y. P. *Org. Biomol. Chem*. **2013**, *11*, 835-841
143. Burghart, A., Kim, H., Welch, M. B., Thoresen, L. H., Reinbenspies, J., Burgess, K. *J. Org. Chem*. **1999**, *64*, 7813-7819
144. Kim, H., Burghart, A., Welch, M. B., Reibenspies, J., Burgess, K. *Chem. Commun*. **1999**, 1889-1890
145. Ikeda, C., Maruyama, T., Nabeshima, T. *Tetrahedron Lett*. **2009**, *50*, 3349-3351
146. Ikeda, C., Ueda, S., Nabeshima, T. *Chem. Commun*. **2009**, 2544-2546
147. Benniston, A. C., Copley, G., Elliot, K. J., Harrington, R. W., Clegg, W. *Eur. J. Org. Chem*. **2008**, 2705-2713
148. Benniston, A. C., Harriman, A., Whittle, V. L., Zelzer, M. *Eur. J. Org. Chem*. **2010**, 523-530
149. Alamiry, M. A.H., Benniston, A. C., Hagon, J., Winstanley, T. P. L., Lemmetyinen, H., Tkachenko, N. V. *RSC Adv*. **2012**, *2*, 4944-4950
150. Pu, L. *Chem. Rev*. **2004**, *104*, 1687-1716
151. Beer, G., Rurack, K., Jorg, D. *Chem. Commun*. **2001**, 1138-1139
152. Sunahara, H., Urano, Y., Kojima, H., Nagano, T. *J. Am. Chem. Soc*. **2007**, *129*, 5597-5604
153. Hayashi, Y, Yamaguchi, S., Cha, W. Y., Kim, D., Shinokubo, H. *Org. Lett*. **2011**, *13*, 2992-2995
154. Chen, W., Cave, M. P. *Tetrahedron Lett*. **1987**, *28*, 6025-6026
155. Ye, J. H., Wang, G., Huang, C., Hu, Z., Zhang, W., Zhang, Y. *Synthesis* **2012**, *44*, 104-110
156. Lee, P. H. *Bull. Korean Chem. Soc*. **2008**, *29*, 261-264
157. Deniz, E., Isbasar, G. C., Bozdemir, O. A., Yildirim, L. T., Siemiarczuk, A., Akkaya, E. U. *Org. Lett*. **2008**, *10*, 3401-3403

158. Jiao, L., Pang, W., Zhou, J., Wei, Y., Mu, X., Bai, G., Hao, E. *J. Org. Chem*. **2011**, *76*, 9988-9996
159. Guo, H., Jing, Y., Yuan, X., Ji, S., Zhao, J., Li, X., Kan, Y. *Org. Biomol. Chem*. **2011**, *9*, 3844-3853
160. Guzow, K., Kornowska, K., Wiczk, W. *Tetrahedron Lett*. **2009**, *50*, 2908-2910
161. Yogo, T., Urano, Y., Ishitsuka, Y., Maniwa, F., Nagano, T. *J. Am. Chem. Soc*. **2005**, *127*, 12162-12163
162. Wang. J., Hou, Y., Lei, W., Zhou, Q., Li, C., Zhang, B., Wang, X. *Chem. Phys. Chem*. **2012**, *13*, 2739-2747
163. Kolemen, S., Bozdemir, A., Cakmak, Y., Barin, G., Ela, S.E., Marszalek, M., Yum, J. H., Zakeeruddin, S. M., Nazeeruddin, M., K., Gratzel, M., Akkaya, E. U. *Chem. Sci*. **2011**, *2*, 949-954
164. Ye, J. H., Hu, Z., Wang, Y., Zhang, W., Zhang, Y. *Tetrahedron Lett*. **2012**, *53*, 6858-6860
165. Fu, G. L., Pan, H., Zhao, Y. H., Zhao, C. H. *Org. Biomol. Chem*. **2011**, *9*, 8141
166. Rohand, T., Qin, W., Boens, N., Dehaen, W. *Eur. J. Org. Chem*. **2006**, 4658-4663
167. Olliver, J. H., Haefele, A., Retailleau, P., Ziessel, R. *Org. Lett*. **2010**, *12*, 408-411
168. Cakmak, Y., Akkaya, E. U. *Org. Lett*. **2009**, *11*, 85-88
169. Tahtaoui, C., Thomas, C., Rohmer, F., Klotz, P., Duportail, G., Mely, Y., Bonnet, D., Hibert, M. *J. Org. Chem*. **2007**, *72*, 269-272
170. Bonnier, C., Piers, W. E., Parvez, M., Sorensen, T. S. *Chem. Commun*. **2008**, 4593-4595
171. Brizet, B., Eggenspiller, A., Gross, C. P., Barbe, J. M., Goze, C., Denat, F., Harvey, P. D. *J. Org. Chem*. **2012**, *77*, 3646-3650
172. Smithen, D. A., Baker, A. E. G., Offman, M., Crawford, S. M., Cameron, T. S., Thompson, A. *J. Org. Chem*. **2012**, *77*, 3439-3453
173. Lundrigan, T., Crawford, S. M., Cameron, S., Thompson, A. *Chem. Commun*. **2012**, *48*, 1003-1005
174. Emrullahoglu, M., Ucuncu, M., Karakus, E. *Chem. Commun*. **2013**, *49*, 7836-7838
175. Gerrard, W., Lappert, M. F. *J. Chem. Soc*. **1955**, 3084-3088
176. Neises, B., Steglich, W. *Org. Syn*. **1990**, *7*, 93-95
177. Isik, M., Ozdemir, T., Turan, I. S., Kolemen, S., Akkaya, E. U. *Org. Lett*. **2013**, *15*, 216-219
178. Rosenker, C. J., Krenske, E. H., Houk, K. N., Wipf, P. *Org. Lett*. **2013**, *15*, 1076-1079
179. Dale, J. A., Mosher, H. S. *J. Am. Chem. Soc*. **1973**, *95*, 512-519
180. Dale, J. A., Dull, D. L., Mosher, H. S. *J. Org. Chem*. **1969**, *34*, 2543-2549
181. Ziessel, R., Bonardi, L., Retailleau, P., Ulrich, G. *J. Org. Chem*. **2006**, *71*, 3093-3102

182. Hedley, G., J., Ruseckas, A., Harriman, A., Samuel, I. D. W. *Angew. Chem. Int. Ed*. **2011**, *50*, 6634-6637

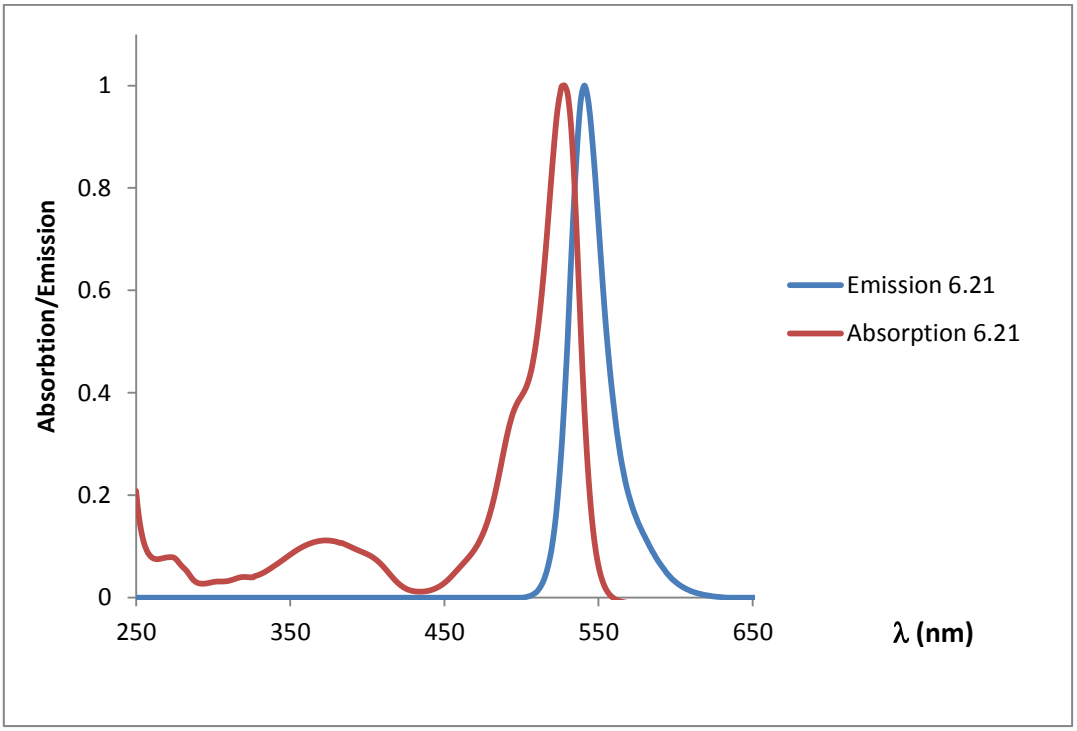
183. Kelly, S. M., Jess, T. J., Price, N. C. *Biochimica et Biophysica Acta* **2005**, *1751*, 119-139

184. Wolf, C., Bentley, K. W. *Chem. Soc. Rev*. **2013**, *42*, 5408-5424

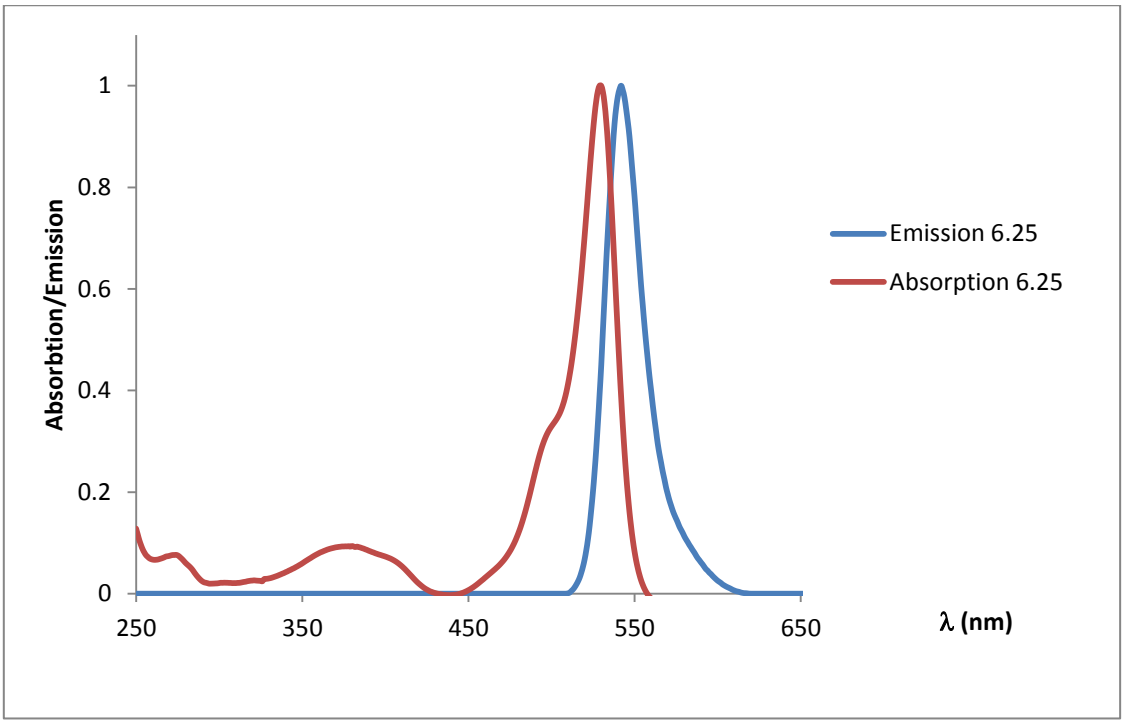
185. Gnanadesikan, V., Horiuchi, Y., Ohshima, T., Shibasaki, M. *J. Am. Chem. Soc*. **2004**,*126*, 7782-7783

Appendix 3 UV/Vis and Fluorescence Spectra

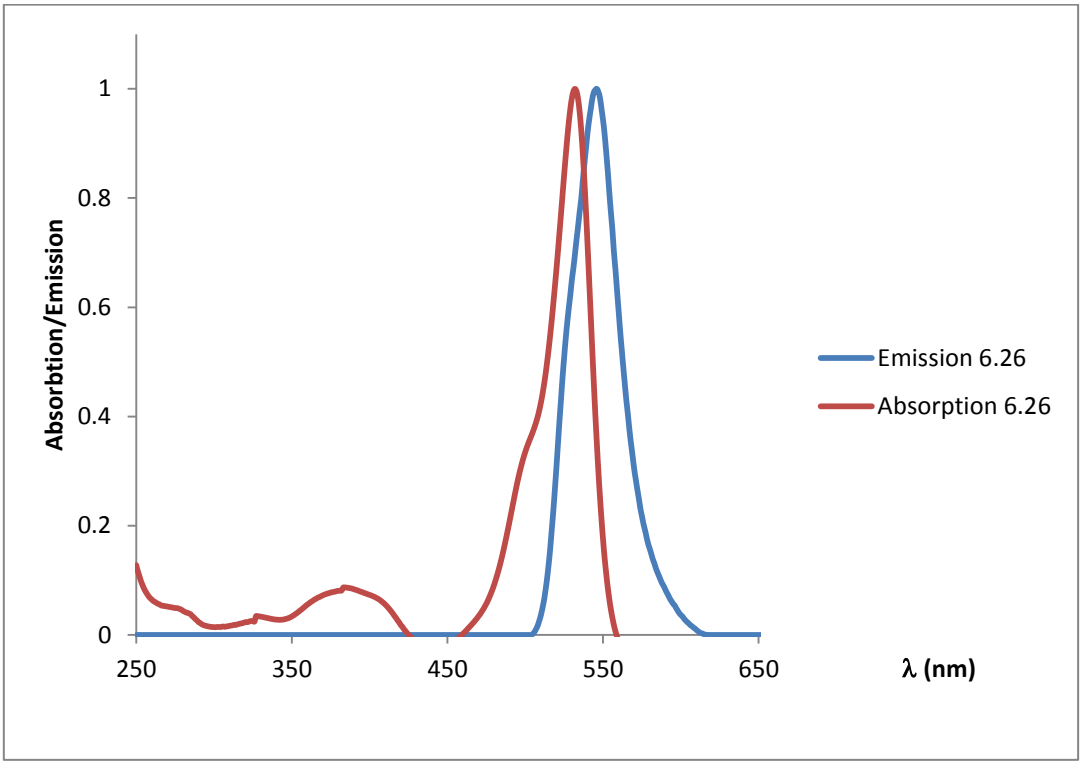
Compound **6.21**



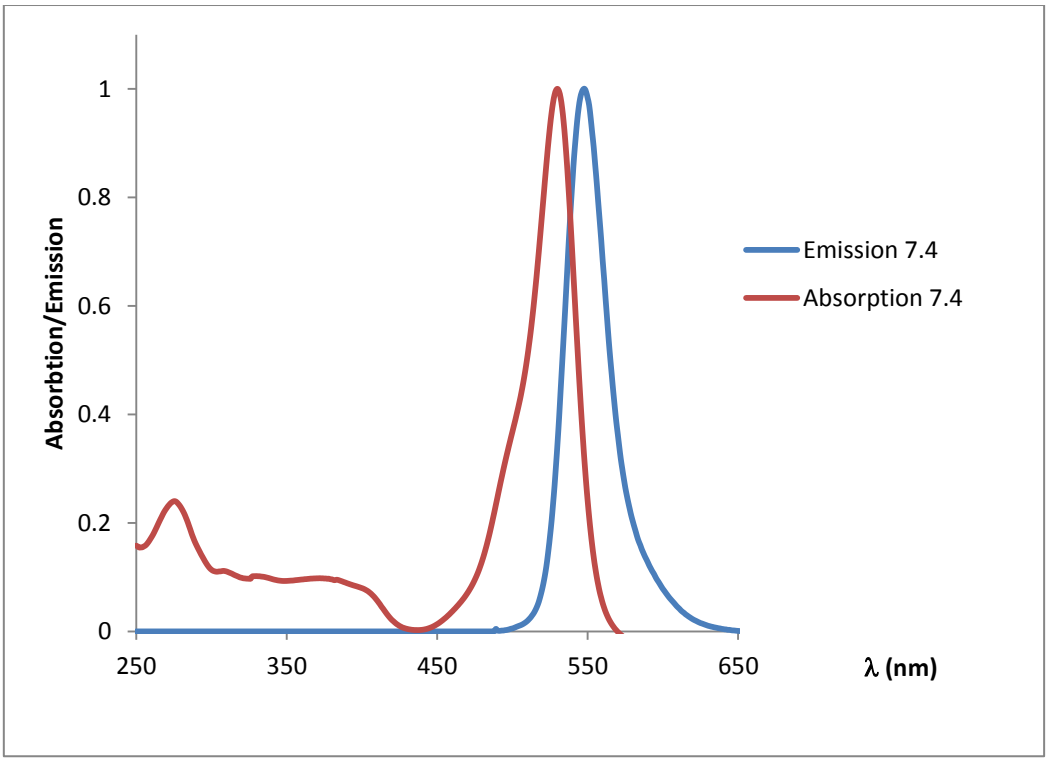
Compound **6.25**



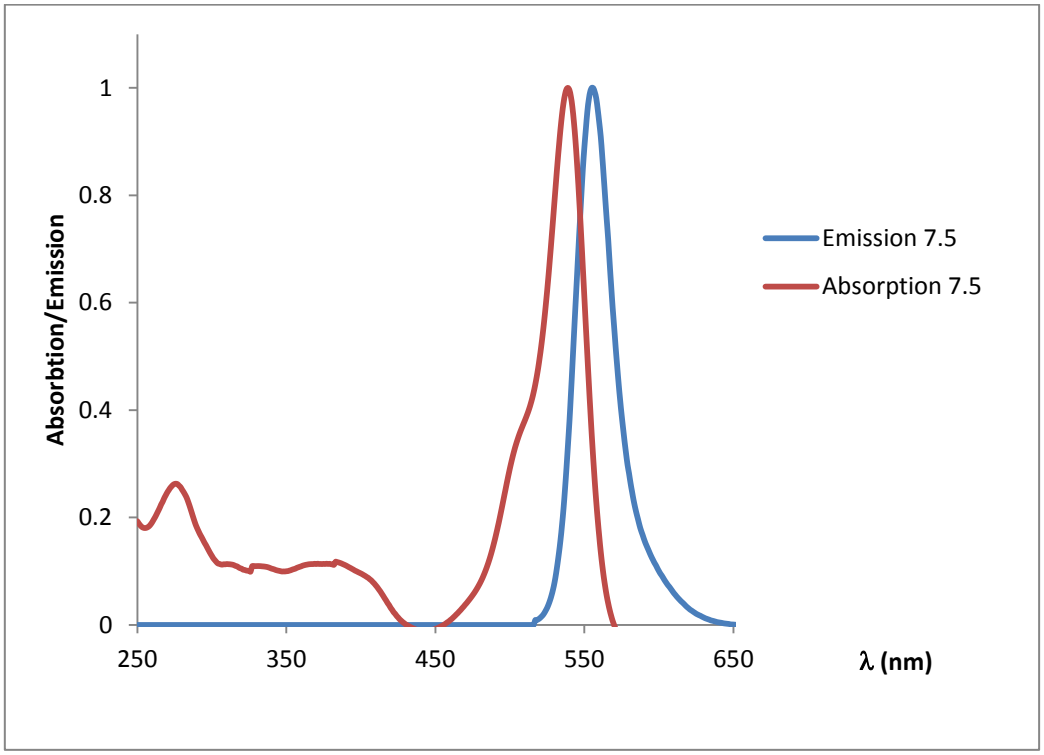
Compound **6.26**



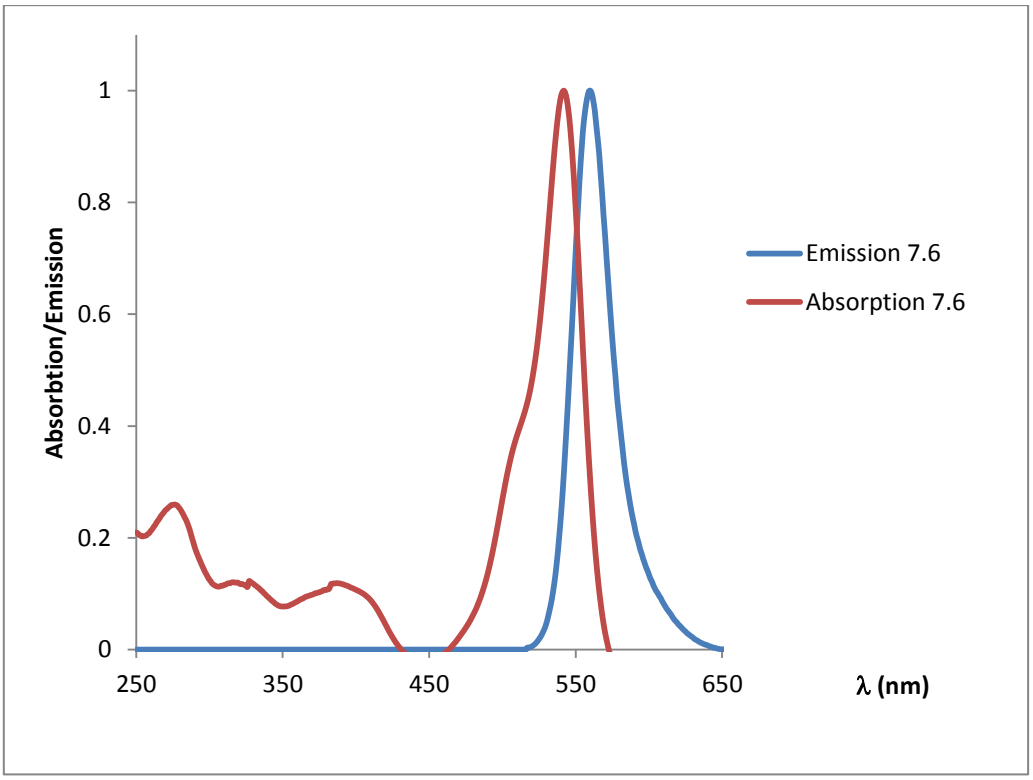
Compound **7.4**



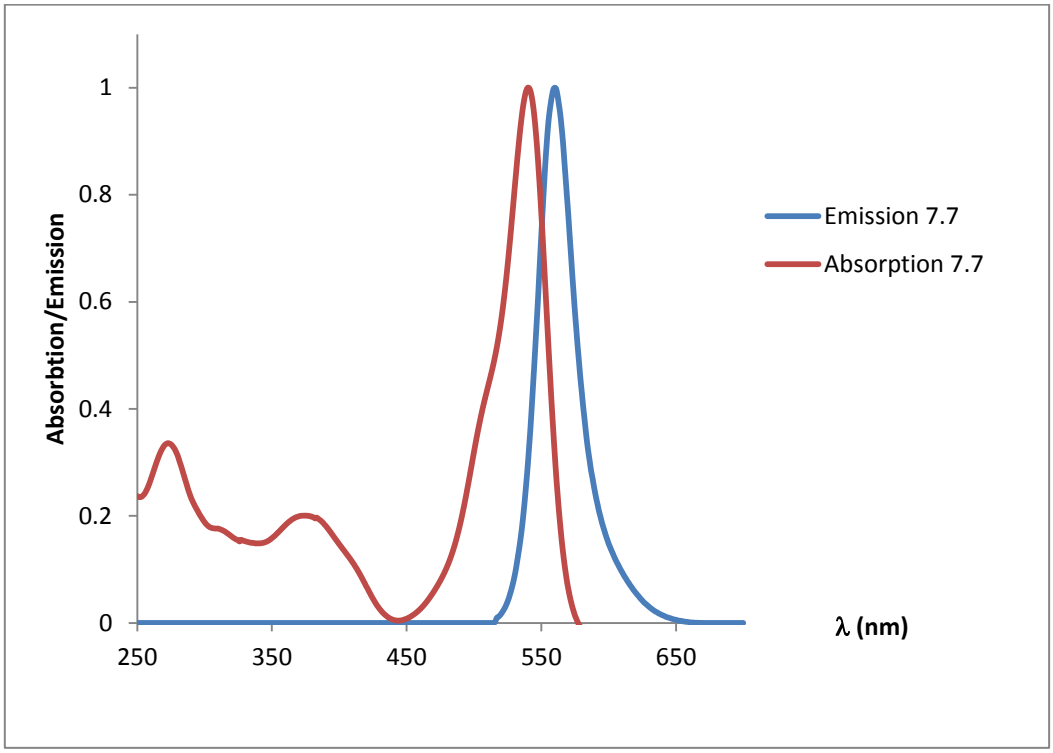
Compound **7.5**



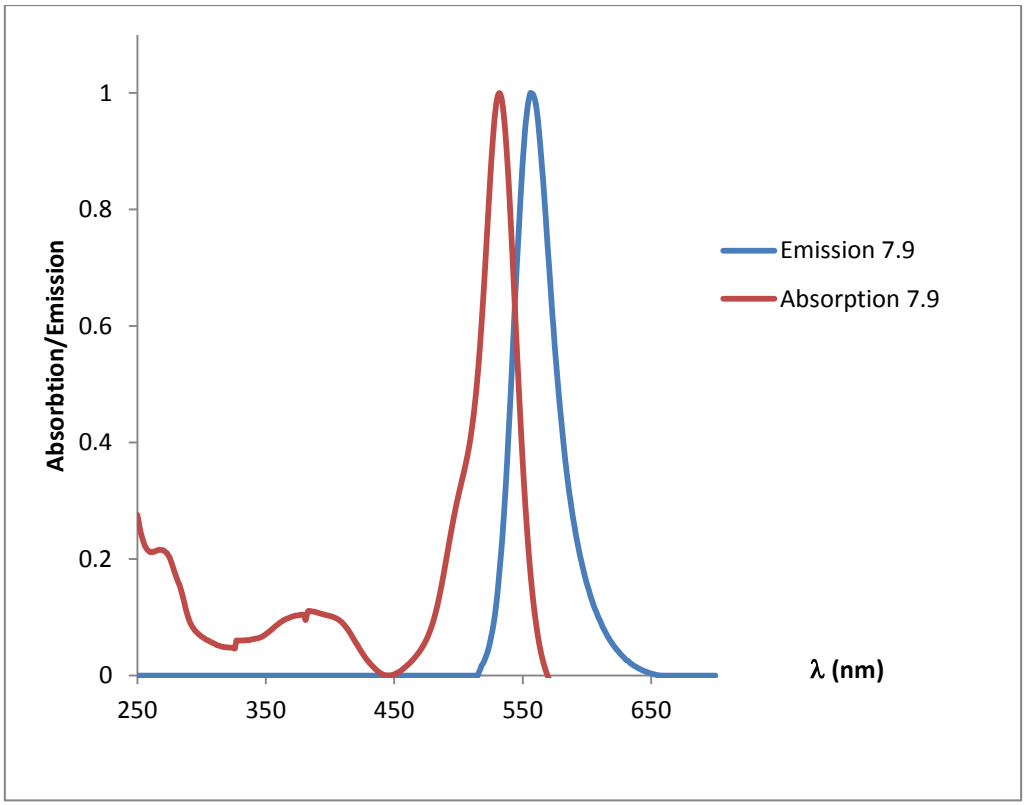
Compound **7.6**



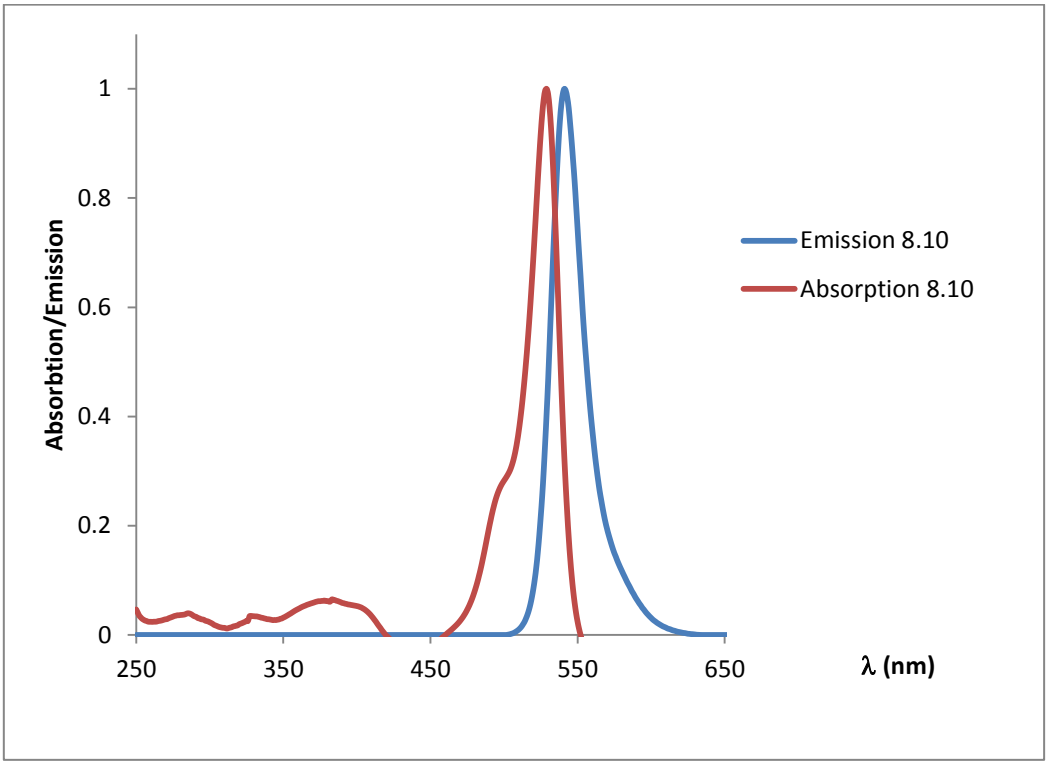
Compound **7.7**



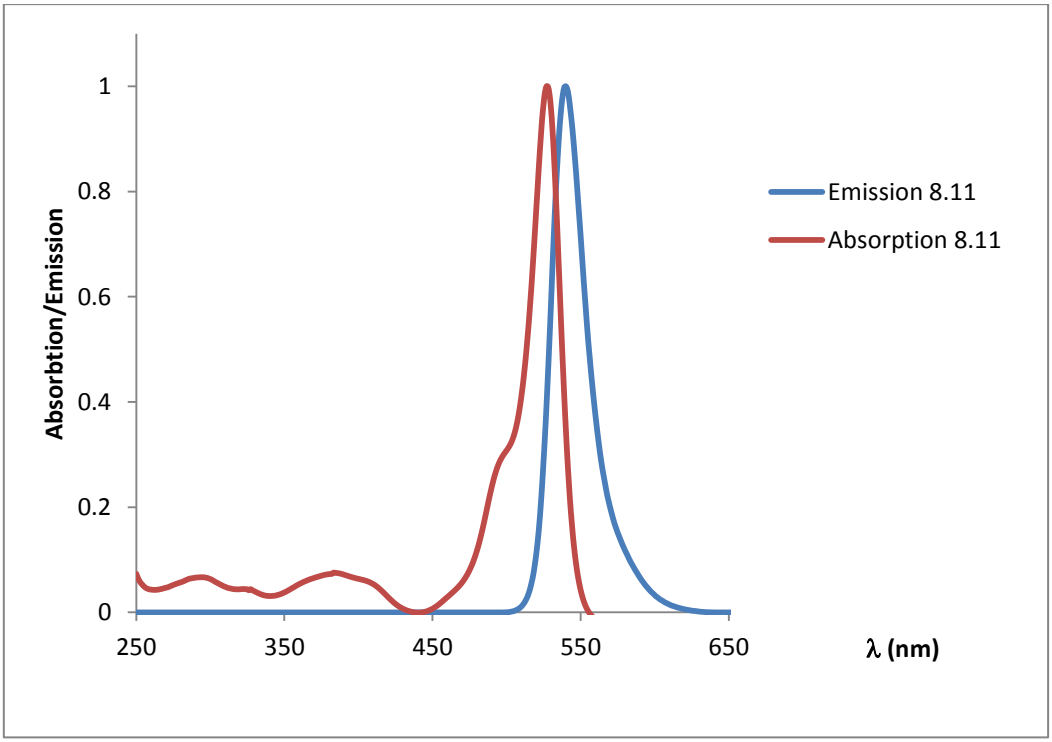
Compound **7.9**



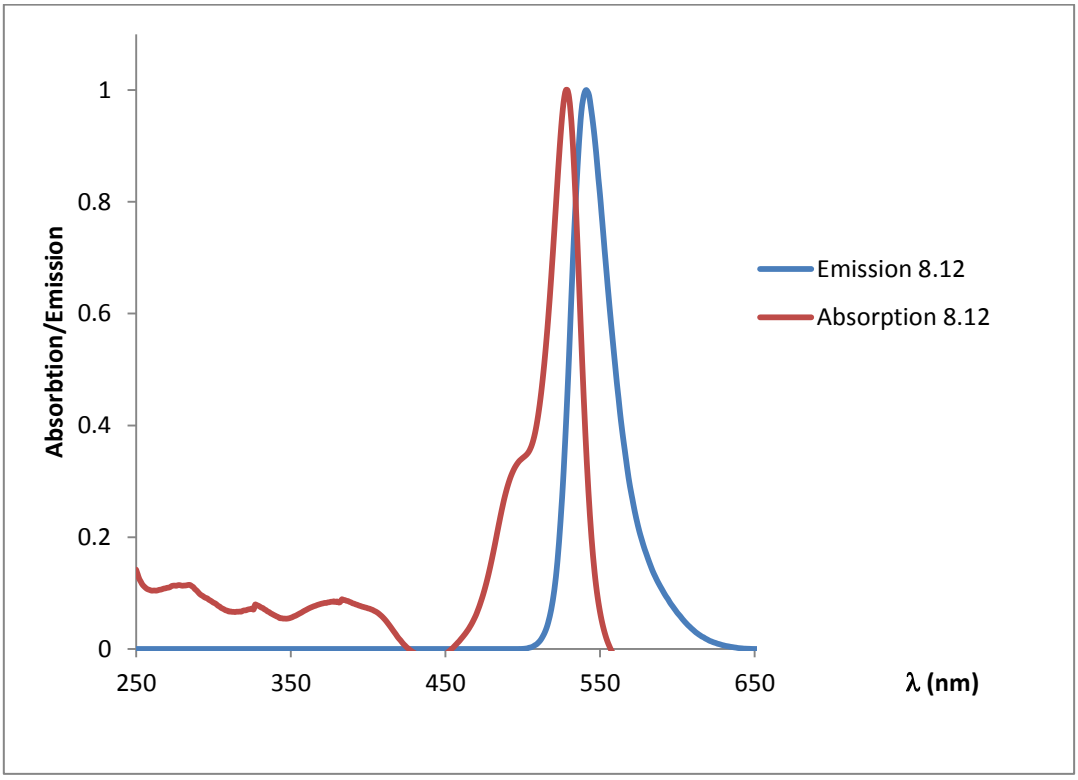
Compound **8.10**



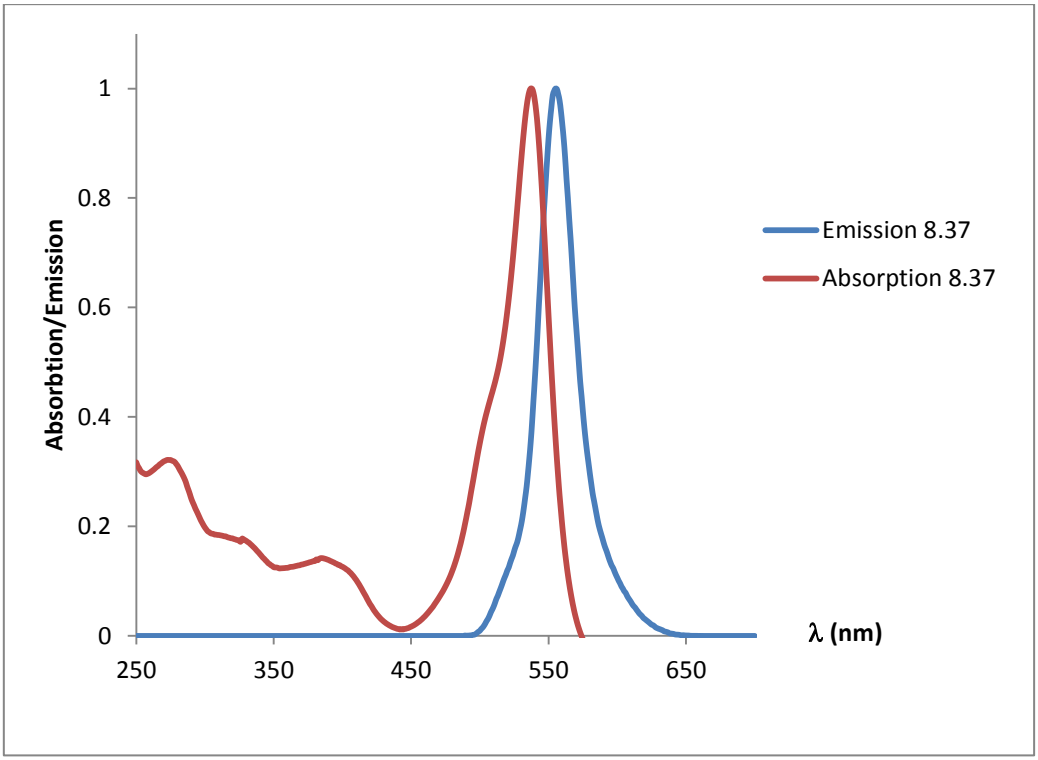
Compound **8.11**



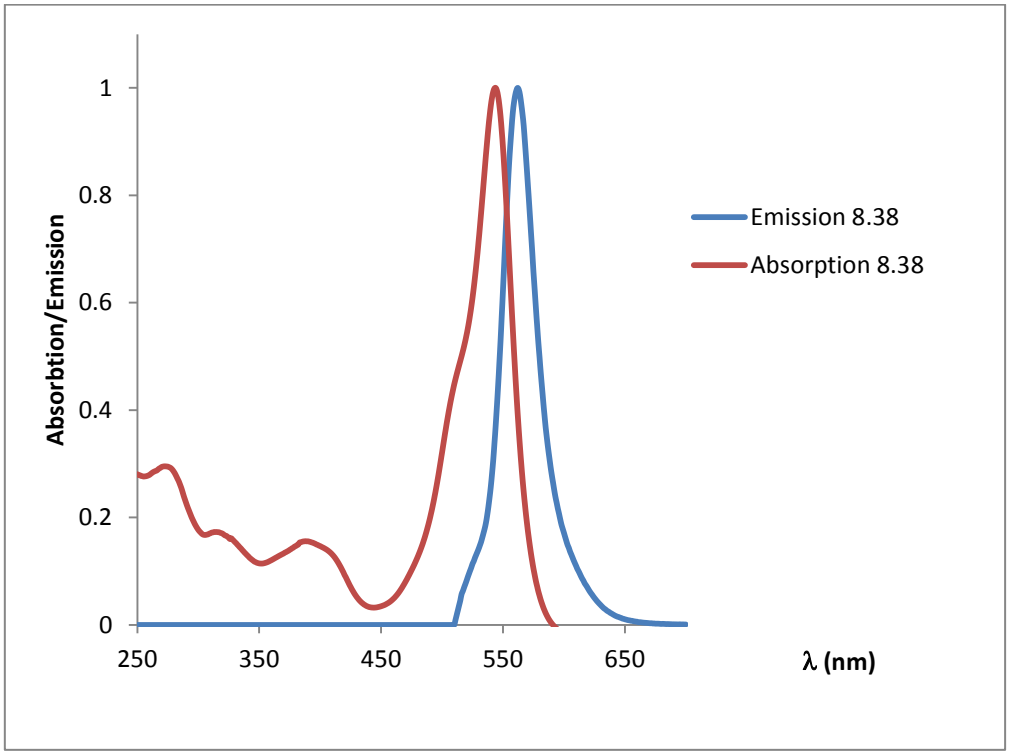
Compound **8.12**



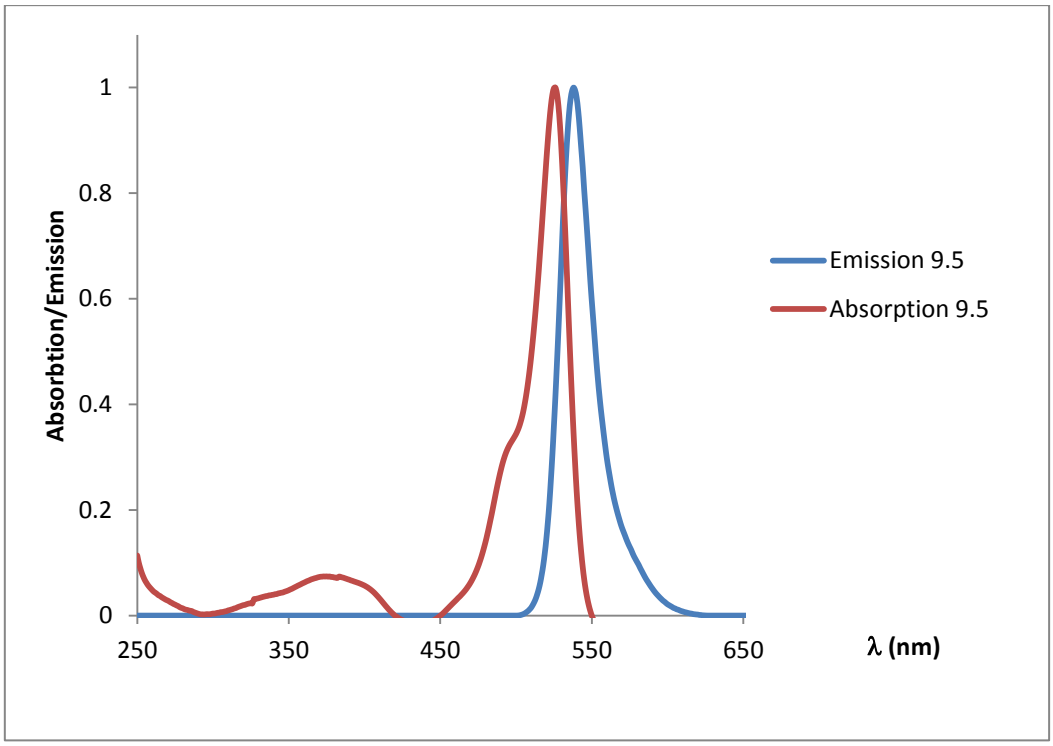
Compound **8.37**



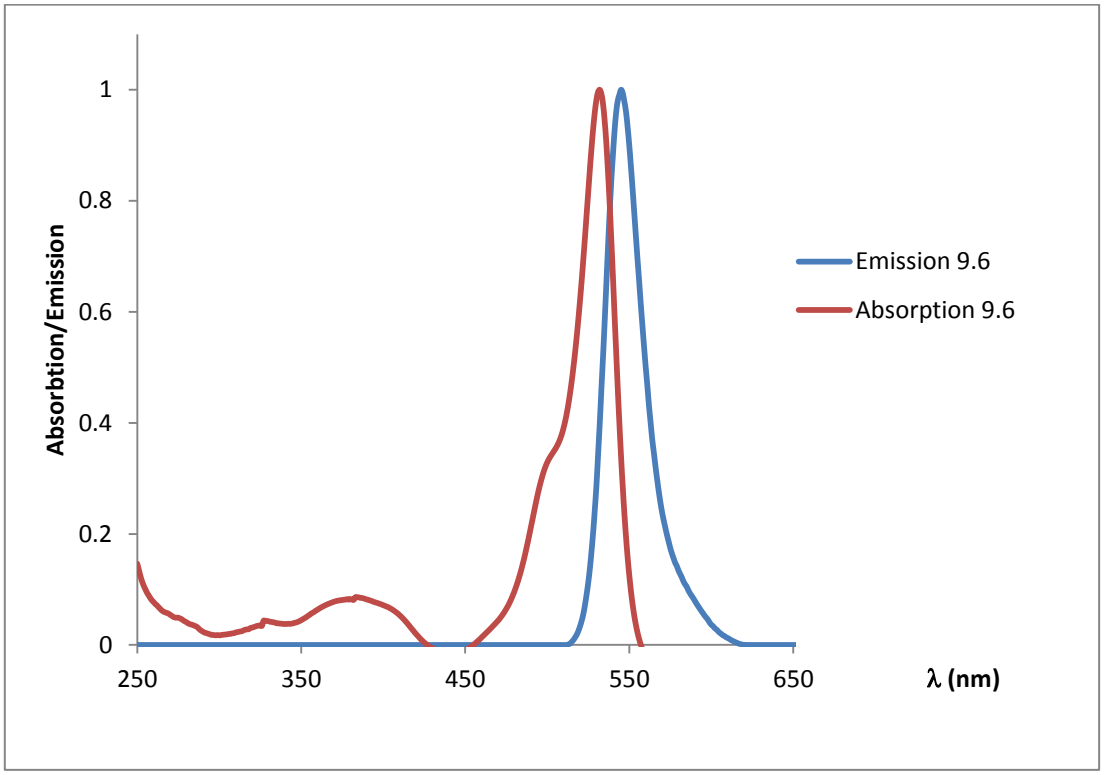
Compound **8.38**



Compound **9.5**



Compound **9.6**


Absorbtion/Emission
1
0.8
0.6
0.4
0.2
0
250
350
450
550
650
λ (nm)
Emission 9.6
Absorption 9.6

Appendix 4 X-ray Crystallography Data

Compound **3.3**

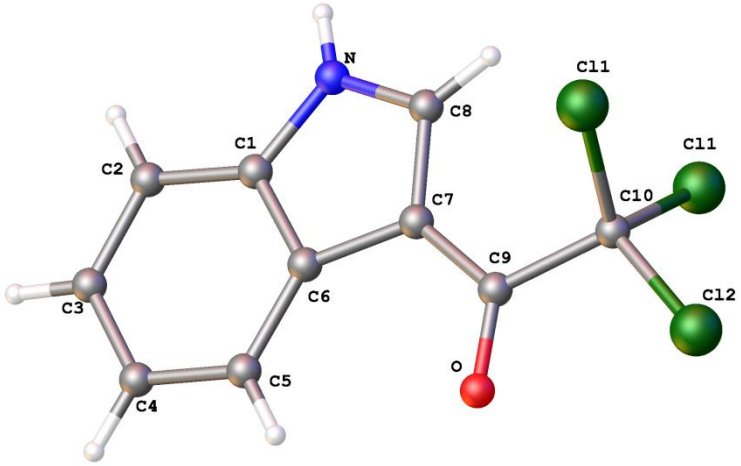


Table 1. Crystal data and structure refinement for mjh85.

Identification code	temp	
Chemical formula (moiety)	$C_{10}H_6Cl_3NO$	
Chemical formula (total)	$C_{10}H_6Cl_3NO$	
Formula weight	262.51	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	orthorhombic, Pnma	
Unit cell parameters	a = 20.5153(14) Å	α = 90°
	b = 6.7406(4) Å	β = 90°
	c = 7.4148(5) Å	γ = 90°
Cell volume	1025.36(12) $Å^3$	
Z	4	
Calculated density	1.700 g/cm^3	
Absorption coefficient μ	0.860 mm^{-1}	
F(000)	528	
Reflections for cell refinement	2265 (θ range 2.9 to 28.5°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	2.9 to 28.5°	
Index ranges	h –27 to 26, k –6 to 9, l –9 to 7	
Completeness to θ = 25.0°	99.9 %	
Reflections collected	5188	
Independent reflections	1240 (R_{int} = 0.0272)	
Reflections with $F^2>2\sigma$	1121	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.79138 and 1.00000	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0271, 0.4418	
Data / restraints / parameters	1240 / 0 / 91	
Final R indices [$F^2>2\sigma$]	R1 = 0.0282, wR2 = 0.0662	
R indices (all data)	R1 = 0.0321, wR2 = 0.0694	
Goodness-of-fit on F^2	1.111	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.46 and –0.25 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh85. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	0.19434(2)	0.03543(7)	0.14280(6)	0.02613(15)
Cl(2)	0.18075(3)	0.2500	–0.18813(7)	0.02060(16)
O	0.05058(8)	0.2500	–0.0692(2)	0.0208(4)
N	0.04694(10)	0.2500	0.5452(3)	0.0173(4)
C(1)	–0.01594(11)	0.2500	0.4771(3)	0.0159(5)
C(2)	–0.07483(12)	0.2500	0.5683(3)	0.0199(5)
C(3)	–0.13055(12)	0.2500	0.4647(3)	0.0211(5)
C(4)	–0.12765(11)	0.2500	0.2762(3)	0.0205(5)
C(5)	–0.06857(11)	0.2500	0.1862(3)	0.0179(5)
C(6)	–0.01141(11)	0.2500	0.2882(3)	0.0149(5)
C(7)	0.05778(10)	0.2500	0.2457(3)	0.0156(5)
C(8)	0.08982(11)	0.2500	0.4103(3)	0.0178(5)
C(9)	0.08372(10)	0.2500	0.0670(3)	0.0148(5)
C(10)	0.15978(11)	0.2500	0.0421(3)	0.0165(5)

Table 3. Bond lengths [Å] and angles [°] for mjh85.

Cl(1)–C(10)	1.7754(13)	Cl(2)–C(10)	1.761(2)
O–C(9)	1.217(3)	N–C(1)	1.385(3)
N–C(8)	1.332(3)	N–H(1)	0.81(3)
C(1)–C(2)	1.384(3)	C(1)–C(6)	1.404(3)
C(2)–H(2A)	0.950	C(2)–C(3)	1.377(3)
C(3)–H(3A)	0.950	C(3)–C(4)	1.399(3)
C(4)–H(4A)	0.950	C(4)–C(5)	1.383(3)
C(5)–H(5A)	0.950	C(5)–C(6)	1.395(3)
C(6)–C(7)	1.454(3)	C(7)–C(8)	1.386(3)
C(7)–C(9)	1.428(3)	C(8)–H(8A)	0.950
C(9)–C(10)	1.571(3)	C(10)–Cl(1A)	1.7754(13)

C(1)–N–C(8)	109.97(19)	C(1)–N–H(1)	126(2)
C(8)–N–H(1)	124(2)	N–C(1)–C(2)	129.4(2)
N–C(1)–C(6)	107.58(19)	C(2)–C(1)–C(6)	123.0(2)
C(1)–C(2)–H(2A)	121.6	C(1)–C(2)–C(3)	116.9(2)
H(2A)–C(2)–C(3)	121.6	C(2)–C(3)–H(3A)	119.3
C(2)–C(3)–C(4)	121.5(2)	H(3A)–C(3)–C(4)	119.3
C(3)–C(4)–H(4A)	119.4	C(3)–C(4)–C(5)	121.3(2)
H(4A)–C(4)–C(5)	119.4	C(4)–C(5)–H(5A)	120.8
C(4)–C(5)–C(6)	118.4(2)	H(5A)–C(5)–C(6)	120.8
C(1)–C(6)–C(5)	119.0(2)	C(1)–C(6)–C(7)	106.31(19)
C(5)–C(6)–C(7)	134.7(2)	C(6)–C(7)–C(8)	105.78(19)
C(6)–C(7)–C(9)	124.4(2)	C(8)–C(7)–C(9)	129.8(2)
N–C(8)–C(7)	110.4(2)	N–C(8)–H(8A)	124.8
C(7)–C(8)–H(8A)	124.8	O–C(9)–C(7)	124.2(2)
O–C(9)–C(10)	117.22(19)	C(7)–C(9)–C(10)	118.62(19)
Cl(1)–C(10)–Cl(1A)	109.10(12)	Cl(1)–C(10)–Cl(2)	108.07(9)
Cl(1A)–C(10)–Cl(2)	108.07(9)	Cl(1)–C(10)–C(9)	110.32(10)
Cl(1A)–C(10)–C(9)	110.32(10)	Cl(2)–C(10)–C(9)	110.88(15)

Symmetry operations for equivalent atoms
A x,–y+1/2,z

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh85. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	0.0252(2)	0.0276(3)	0.0256(3)	0.00874(18)	0.00205(17)	0.00888(18)
Cl(2)	0.0197(3)	0.0279(3)	0.0141(3)	0.000	0.0039(2)	0.000
O	0.0188(8)	0.0327(9)	0.0110(8)	0.000	–0.0001(7)	0.000
N	0.0207(10)	0.0219(10)	0.0092(9)	0.000	–0.0016(8)	0.000
C(1)	0.0199(11)	0.0133(10)	0.0144(11)	0.000	0.0000(9)	0.000
C(2)	0.0248(12)	0.0192(11)	0.0157(11)	0.000	0.0048(10)	0.000
C(3)	0.0194(12)	0.0213(12)	0.0226(13)	0.000	0.0061(10)	0.000
C(4)	0.0184(11)	0.0208(11)	0.0224(12)	0.000	–0.0031(10)	0.000
C(5)	0.0210(11)	0.0182(11)	0.0145(11)	0.000	–0.0006(9)	0.000
C(6)	0.0184(11)	0.0127(10)	0.0135(11)	0.000	0.0006(9)	0.000
C(7)	0.0168(11)	0.0185(11)	0.0114(11)	0.000	–0.0001(9)	0.000
C(8)	0.0186(11)	0.0213(11)	0.0134(11)	0.000	0.0001(9)	0.000
C(9)	0.0165(11)	0.0133(10)	0.0147(11)	0.000	–0.0006(9)	0.000
C(10)	0.0196(11)	0.0175(11)	0.0124(11)	0.000	–0.0003(9)	0.000

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh85.

	x	y	z	U
H(2A)	–0.0767	0.2500	0.6963	0.024
H(3A)	–0.1719	0.2500	0.5225	0.025
H(4A)	–0.1670	0.2500	0.2086	0.025
H(5A)	–0.0670	0.2500	0.0582	0.022
H(8A)	0.1358	0.2500	0.4248	0.021
H(1)	0.0568(14)	0.2500	0.651(4)	0.029(8)

Table 6. Torsion angles [°] for mjh85.

C(8)–N–C(1)–C(2)	180.0	C(8)–N–C(1)–C(6)	0.0
N–C(1)–C(2)–C(3)	180.0	C(6)–C(1)–C(2)–C(3)	0.0
C(1)–C(2)–C(3)–C(4)	0.0	C(2)–C(3)–C(4)–C(5)	0.0
C(3)–C(4)–C(5)–C(6)	0.0	C(4)–C(5)–C(6)–C(1)	0.0
C(4)–C(5)–C(6)–C(7)	180.0	N–C(1)–C(6)–C(5)	180.0
N–C(1)–C(6)–C(7)	0.0	C(2)–C(1)–C(6)–C(5)	0.0
C(2)–C(1)–C(6)–C(7)	180.0	C(1)–C(6)–C(7)–C(8)	0.0
C(1)–C(6)–C(7)–C(9)	180.0	C(5)–C(6)–C(7)–C(8)	180.0
C(5)–C(6)–C(7)–C(9)	0.0	C(1)–N–C(8)–C(7)	0.0
C(6)–C(7)–C(8)–N	0.0	C(9)–C(7)–C(8)–N	180.0
C(6)–C(7)–C(9)–O	0.0	C(6)–C(7)–C(9)–C(10)	180.0
C(8)–C(7)–C(9)–O	180.0	C(8)–C(7)–C(9)–C(10)	0.0
O–C(9)–C(10)–Cl(1)	–119.69(10)	O–C(9)–C(10)–Cl(1A)	119.69(10)
O–C(9)–C(10)–Cl(2)	0.0	C(7)–C(9)–C(10)–Cl(1)	60.31(10)
C(7)–C(9)–C(10)–Cl(1A)	–60.31(10)	C(7)–C(9)–C(10)–Cl(2)	180.0

Symmetry operations for equivalent atoms
A x,–y+1/2,z

Table 7. Hydrogen bonds for mjh85 [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N–H(1)...OB	0.81(3)	2.08(3)	2.861(2)	162(3)
N–H(1)...Cl(2B)	0.81(3)	2.81(3)	3.383(2)	130(2)

Symmetry operations for equivalent atoms
B x,y,z+1

Compound **3.4**

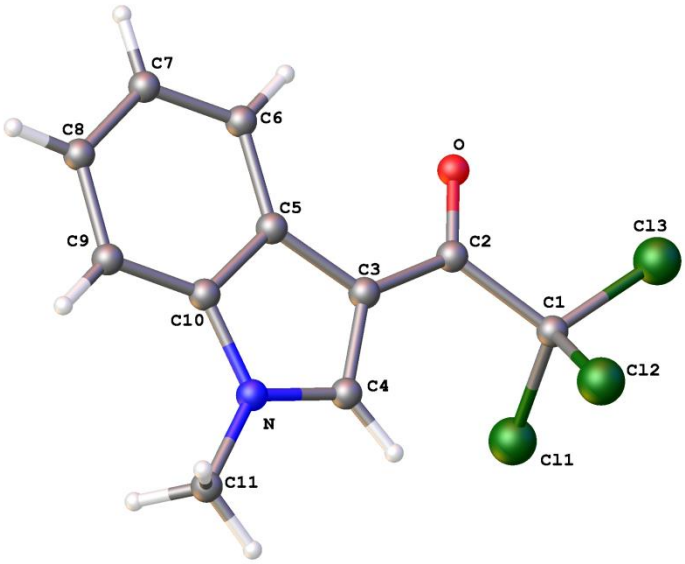


Table 1. Crystal data and structure refinement for mjh88.

Identification code	mjh88	
Chemical formula (moiety)	$C_{11}H_8Cl_3NO$	
Chemical formula (total)	$C_{11}H_8Cl_3NO$	
Formula weight	276.53	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	monoclinic, $P12_1/c1$	
Unit cell parameters	a = 9.8736(5) Å	α = 90°
	b = 11.2992(4) Å	β = 98.358(5)°
	c = 10.6096(5) Å	γ = 90°
Cell volume	1171.08(9) $Å^3$	
Z	4	
Calculated density	1.568 g/cm^3	
Absorption coefficient μ	0.757 mm^{-1}	
F(000)	560	
Crystal colour and size	colourless, 0.40 × 0.40 × 0.20 mm^3	
Reflections for cell refinement	3708 (θ range 3.2 to 28.6°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	3.2 to 28.6°	
Index ranges	h −12 to 13, k −15 to 15, l −14 to 13	
Completeness to θ = 25.0°	99.9 %	
Reflections collected	9535	
Independent reflections	2573 (R_{int} = 0.0277)	
Reflections with $F^2>2\sigma$	2165	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.7515 and 0.8633	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0280, 0.5291	
Data / restraints / parameters	2573 / 0 / 147	
Final R indices [$F^2>2\sigma$]	R1 = 0.0301, wR2 = 0.0650	
R indices (all data)	R1 = 0.0411, wR2 = 0.0715	
Goodness-of-fit on F^2	1.051	
Extinction coefficient	0.0022(8)	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.33 and −0.23 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh88. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	0.07438(5)	0.16419(4)	0.15589(4)	0.02814(13)
Cl(2)	–0.00613(5)	0.35121(4)	0.31666(5)	0.03025(13)
Cl(3)	–0.02966(5)	0.10937(4)	0.38923(5)	0.03419(14)
O	0.25314(13)	0.13279(10)	0.46509(11)	0.0294(3)
N	0.41174(15)	0.44632(12)	0.25823(13)	0.0228(3)
C(1)	0.07055(17)	0.20977(14)	0.31626(16)	0.0215(4)
C(2)	0.22147(17)	0.21035(14)	0.38700(15)	0.0195(3)
C(3)	0.31446(17)	0.29921(14)	0.35501(15)	0.0193(3)
C(4)	0.29745(18)	0.38214(14)	0.25734(15)	0.0203(3)
C(5)	0.45227(17)	0.31606(14)	0.42082(16)	0.0211(4)
C(6)	0.53117(18)	0.26375(16)	0.52664(16)	0.0273(4)
C(7)	0.6625(2)	0.30605(19)	0.56363(19)	0.0368(5)
C(8)	0.7157(2)	0.39880(19)	0.4996(2)	0.0390(5)
C(9)	0.64039(19)	0.45236(18)	0.39616(19)	0.0330(4)
C(10)	0.50861(17)	0.40908(15)	0.35816(16)	0.0234(4)
C(11)	0.4315(2)	0.54210(16)	0.17047(17)	0.0311(4)

Table 3. Bond lengths [Å] and angles [°] for mjh88.

Cl(1)–C(1)	1.7834(17)	Cl(2)–C(1)	1.7686(17)
Cl(3)–C(1)	1.7572(17)	O–C(2)	1.2153(19)
N–C(4)	1.340(2)	N–C(10)	1.386(2)
N–C(11)	1.459(2)	C(1)–C(2)	1.568(2)
C(2)–C(3)	1.434(2)	C(3)–C(4)	1.389(2)
C(3)–C(5)	1.449(2)	C(4)–H(4A)	0.950
C(5)–C(6)	1.401(2)	C(5)–C(10)	1.401(2)
C(6)–H(6A)	0.950	C(6)–C(7)	1.384(3)
C(7)–H(7A)	0.950	C(7)–C(8)	1.393(3)
C(8)–H(8A)	0.950	C(8)–C(9)	1.374(3)
C(9)–H(9A)	0.950	C(9)–C(10)	1.394(2)
C(11)–H(11A)	0.980	C(11)–H(11B)	0.980
C(11)–H(11C)	0.980		

C(4)–N–C(10)	109.14(14)	C(4)–N–C(11)	125.97(15)
C(10)–N–C(11)	124.88(15)	Cl(1)–C(1)–Cl(2)	109.37(9)
Cl(1)–C(1)–Cl(3)	108.98(9)	Cl(1)–C(1)–C(2)	107.90(11)
Cl(2)–C(1)–Cl(3)	108.28(9)	Cl(2)–C(1)–C(2)	111.87(11)
Cl(3)–C(1)–C(2)	110.40(11)	O–C(2)–C(1)	117.11(14)
O–C(2)–C(3)	123.78(15)	C(1)–C(2)–C(3)	119.09(13)
C(2)–C(3)–C(4)	129.54(15)	C(2)–C(3)–C(5)	124.52(15)
C(4)–C(3)–C(5)	105.91(14)	N–C(4)–C(3)	110.45(15)
N–C(4)–H(4A)	124.8	C(3)–C(4)–H(4A)	124.8
C(3)–C(5)–C(6)	134.81(17)	C(3)–C(5)–C(10)	106.24(14)
C(6)–C(5)–C(10)	118.94(16)	C(5)–C(6)–H(6A)	121.0
C(5)–C(6)–C(7)	118.07(18)	H(6A)–C(6)–C(7)	121.0
C(6)–C(7)–H(7A)	119.1	C(6)–C(7)–C(8)	121.75(18)
H(7A)–C(7)–C(8)	119.1	C(7)–C(8)–H(8A)	119.3
C(7)–C(8)–C(9)	121.47(18)	H(8A)–C(8)–C(9)	119.3
C(8)–C(9)–H(9A)	121.6	C(8)–C(9)–C(10)	116.81(19)
H(9A)–C(9)–C(10)	121.6	N–C(10)–C(5)	108.25(14)
N–C(10)–C(9)	128.77(17)	C(5)–C(10)–C(9)	122.97(17)
N–C(11)–H(11A)	109.5	N–C(11)–H(11B)	109.5
N–C(11)–H(11C)	109.5	H(11A)–C(11)–H(11B)	109.5
H(11A)–C(11)–H(11C)	109.5	H(11B)–C(11)–H(11C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh88. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	0.0293(2)	0.0336(2)	0.0204(2)	–0.00387(18)	–0.00010(17)	–0.00517(18)
Cl(2)	0.0241(2)	0.0262(2)	0.0414(3)	0.00194(19)	0.00804(19)	0.00525(18)
Cl(3)	0.0349(3)	0.0327(2)	0.0365(3)	0.0033(2)	0.0103(2)	–0.0151(2)
O	0.0366(8)	0.0261(6)	0.0245(7)	0.0089(5)	0.0010(6)	–0.0010(5)
N	0.0252(8)	0.0233(7)	0.0209(7)	–0.0026(6)	0.0065(6)	–0.0055(6)
C(1)	0.0233(9)	0.0198(7)	0.0219(8)	–0.0002(7)	0.0049(7)	–0.0032(7)
C(2)	0.0244(9)	0.0187(7)	0.0154(8)	–0.0027(7)	0.0027(6)	0.0006(7)
C(3)	0.0204(8)	0.0188(7)	0.0183(8)	–0.0026(6)	0.0017(6)	0.0005(7)
C(4)	0.0216(9)	0.0211(8)	0.0185(8)	–0.0025(7)	0.0036(6)	–0.0021(7)
C(5)	0.0196(8)	0.0225(8)	0.0211(8)	–0.0081(7)	0.0029(7)	0.0019(7)
C(6)	0.0280(10)	0.0298(9)	0.0231(9)	–0.0074(8)	0.0001(7)	0.0080(8)
C(7)	0.0266(10)	0.0470(12)	0.0333(11)	–0.0132(9)	–0.0075(8)	0.0135(9)
C(8)	0.0186(9)	0.0531(12)	0.0440(12)	–0.0227(10)	0.0005(8)	–0.0001(9)
C(9)	0.0229(10)	0.0398(10)	0.0380(11)	–0.0155(9)	0.0107(8)	–0.0074(8)
C(10)	0.0201(9)	0.0259(8)	0.0252(9)	–0.0102(7)	0.0068(7)	–0.0012(7)
C(11)	0.0415(11)	0.0274(9)	0.0270(10)	–0.0001(8)	0.0131(8)	–0.0119(8)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh88.

	x	y	z	U
H(4A)	0.2162	0.3920	0.1982	0.024
H(6A)	0.4956	0.2011	0.5717	0.033
H(7A)	0.7177	0.2709	0.6346	0.044
H(8A)	0.8062	0.4256	0.5282	0.047
H(9A)	0.6764	0.5158	0.3526	0.040
H(11A)	0.3511	0.5477	0.1046	0.047
H(11B)	0.5130	0.5260	0.1304	0.047
H(11C)	0.4437	0.6169	0.2174	0.047

Table 6. Torsion angles [°] for mjh88.

Cl(1)–C(1)–C(2)–O	−108.09(15)	Cl(1)–C(1)–C(2)–C(3)	70.61(16)
Cl(2)–C(1)–C(2)–O	131.56(14)	Cl(2)–C(1)–C(2)–C(3)	−49.74(18)
Cl(3)–C(1)–C(2)–O	10.91(18)	Cl(3)–C(1)–C(2)–C(3)	−170.39(12)
O–C(2)–C(3)–C(4)	170.56(17)	O–C(2)–C(3)–C(5)	−7.2(3)
C(1)–C(2)–C(3)–C(4)	−8.0(3)	C(1)–C(2)–C(3)–C(5)	174.20(14)
C(10)–N–C(4)–C(3)	−0.78(19)	C(11)–N–C(4)–C(3)	−179.52(15)
C(2)–C(3)–C(4)–N	−177.82(16)	C(5)–C(3)–C(4)–N	0.26(18)
C(2)–C(3)–C(5)–C(6)	−3.0(3)	C(2)–C(3)–C(5)–C(10)	178.55(15)
C(4)–C(3)–C(5)–C(6)	178.83(18)	C(4)–C(3)–C(5)–C(10)	0.35(18)
C(3)–C(5)–C(6)–C(7)	−178.97(18)	C(10)–C(5)–C(6)–C(7)	−0.6(2)
C(5)–C(6)–C(7)–C(8)	0.8(3)	C(6)–C(7)–C(8)–C(9)	−0.3(3)
C(7)–C(8)–C(9)–C(10)	−0.3(3)	C(4)–N–C(10)–C(5)	1.00(18)
C(4)–N–C(10)–C(9)	−178.63(17)	C(11)–N–C(10)–C(5)	179.75(15)
C(11)–N–C(10)–C(9)	0.1(3)	C(8)–C(9)–C(10)–N	179.96(17)
C(8)–C(9)–C(10)–C(5)	0.4(3)	C(3)–C(5)–C(10)–N	−0.82(18)
C(3)–C(5)–C(10)–C(9)	178.84(15)	C(6)–C(5)–C(10)–N	−179.58(14)
C(6)–C(5)–C(10)–C(9)	0.1(3)		

Compound **3.14**

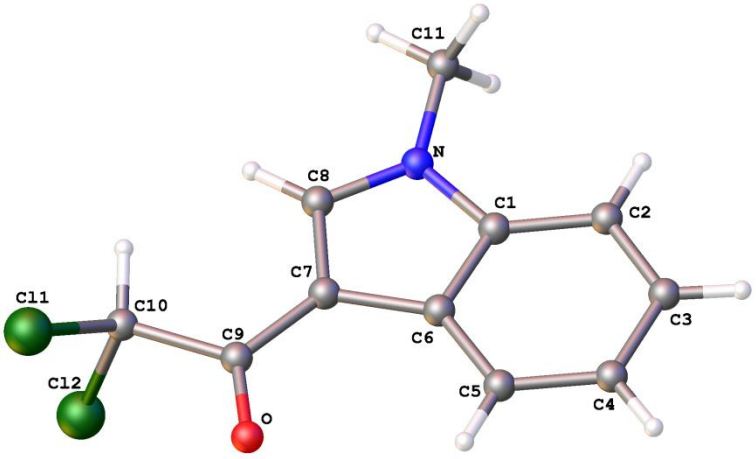


Table 1. Crystal data and structure refinement for mjh92.

Identification code	mjh92	
Chemical formula (moiety)	$C_{11}H_9Cl_2NO$	
Chemical formula (total)	$C_{11}H_9Cl_2NO$	
Formula weight	242.09	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	monoclinic, $P2_1/c$	
Unit cell parameters	a = 6.9827(4) Å	α = 90°
	b = 11.0753(6) Å	β = 111.091(5)°
	c = 14.6118(11) Å	γ = 90°
Cell volume	1054.31(11) $Å^3$	
Z	4	
Calculated density	1.525 g/cm^3	
Absorption coefficient μ	0.584 mm^{-1}	
F(000)	496	
Crystal colour and size	colourless, 0.40 × 0.30 × 0.30 mm^3	
Reflections for cell refinement	3367 (θ range 2.9 to 28.5°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	3.1 to 28.5°	
Index ranges	h –9 to 9, k –14 to 14, l –19 to 8	
Completeness to θ = 25.0°	99.9 %	
Reflections collected	4275	
Independent reflections	4305 (R_{int} = 0.0000)	
Reflections with $F^2>2\sigma$	3703	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.7999 and 0.8442	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0386, 0.4774	
Data / restraints / parameters	4305 / 0 / 139	
Final R indices [$F^2>2\sigma$]	R1 = 0.0402, wR2 = 0.0899	
R indices (all data)	R1 = 0.0503, wR2 = 0.0980	
Goodness-of-fit on F^2	1.054	
Extinction coefficient	0.0024(9)	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	0.32 and –0.36 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh92. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	0.82885(7)	0.49134(4)	0.87623(3)	0.04128(15)
Cl(2)	0.40881(8)	0.51663(4)	0.86472(4)	0.04168(15)
O	0.5334(2)	0.32864(10)	0.72864(9)	0.0409(3)
N	0.2331(2)	0.61946(11)	0.49893(9)	0.0223(3)
C(1)	0.1989(2)	0.50594(14)	0.45511(12)	0.0222(3)
C(2)	0.0923(2)	0.47671(15)	0.35794(12)	0.0294(4)
C(3)	0.0826(3)	0.35600(17)	0.33355(14)	0.0369(4)
C(4)	0.1764(3)	0.26849(16)	0.40420(14)	0.0368(4)
C(5)	0.2826(3)	0.29871(14)	0.50094(13)	0.0294(4)
C(6)	0.2936(2)	0.42021(13)	0.52767(11)	0.0222(3)
C(7)	0.3866(2)	0.48612(13)	0.61814(11)	0.0204(3)
C(8)	0.3439(2)	0.60728(13)	0.59461(11)	0.0218(3)
C(9)	0.4990(3)	0.43601(14)	0.71239(12)	0.0263(3)
C(10)	0.5759(3)	0.52565(14)	0.79789(12)	0.0270(4)
C(11)	0.1701(3)	0.73248(14)	0.44583(13)	0.0326(4)

Table 3. Bond lengths [Å] and angles [°] for mjh92.

Cl(1)–C(10)	1.7660(17)	Cl(2)–C(10)	1.7735(18)
O–C(9)	1.2195(18)	N–C(1)	1.3920(19)
N–C(8)	1.339(2)	N–C(11)	1.4549(19)
C(1)–C(2)	1.384(2)	C(1)–C(6)	1.399(2)
C(2)–H(2A)	0.950	C(2)–C(3)	1.379(2)
C(3)–H(3A)	0.950	C(3)–C(4)	1.396(3)
C(4)–H(4A)	0.950	C(4)–C(5)	1.380(3)
C(5)–H(5A)	0.950	C(5)–C(6)	1.396(2)
C(6)–C(7)	1.444(2)	C(7)–C(8)	1.391(2)
C(7)–C(9)	1.429(2)	C(8)–H(8A)	0.950
C(9)–C(10)	1.534(2)	C(10)–H(10A)	1.000
C(11)–H(11A)	0.980	C(11)–H(11B)	0.980
C(11)–H(11C)	0.980		

C(1)–N–C(8)	109.17(12)	C(1)–N–C(11)	124.25(13)
C(8)–N–C(11)	126.43(13)	N–C(1)–C(2)	128.56(15)
N–C(1)–C(6)	107.95(13)	C(2)–C(1)–C(6)	123.48(14)
C(1)–C(2)–H(2A)	121.6	C(1)–C(2)–C(3)	116.77(16)
H(2A)–C(2)–C(3)	121.6	C(2)–C(3)–H(3A)	119.5
C(2)–C(3)–C(4)	121.05(16)	H(3A)–C(3)–C(4)	119.5
C(3)–C(4)–H(4A)	119.2	C(3)–C(4)–C(5)	121.69(16)
H(4A)–C(4)–C(5)	119.2	C(4)–C(5)–H(5A)	120.8
C(4)–C(5)–C(6)	118.40(16)	H(5A)–C(5)–C(6)	120.8
C(1)–C(6)–C(5)	118.61(14)	C(1)–C(6)–C(7)	106.55(13)
C(5)–C(6)–C(7)	134.84(15)	C(6)–C(7)–C(8)	106.01(13)
C(6)–C(7)–C(9)	126.59(14)	C(8)–C(7)–C(9)	127.40(14)
N–C(8)–C(7)	110.32(13)	N–C(8)–H(8A)	124.8
C(7)–C(8)–H(8A)	124.8	O–C(9)–C(7)	124.59(15)
O–C(9)–C(10)	119.07(14)	C(7)–C(9)–C(10)	116.33(13)
Cl(1)–C(10)–Cl(2)	109.49(9)	Cl(1)–C(10)–C(9)	111.35(11)
Cl(1)–C(10)–H(10A)	109.4	Cl(2)–C(10)–C(9)	107.77(12)
Cl(2)–C(10)–H(10A)	109.4	C(9)–C(10)–H(10A)	109.4
N–C(11)–H(11A)	109.5	N–C(11)–H(11B)	109.5
N–C(11)–H(11C)	109.5	H(11A)–C(11)–H(11B)	109.5
H(11A)–C(11)–H(11C)	109.5	H(11B)–C(11)–H(11C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh92. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	0.0327(3)	0.0467(3)	0.0340(3)	0.0034(2)	–0.0007(2)	0.0037(2)
Cl(2)	0.0449(3)	0.0451(3)	0.0400(3)	–0.0126(2)	0.0213(2)	–0.0076(2)
O	0.0630(9)	0.0186(6)	0.0323(7)	0.0025(5)	0.0066(6)	0.0071(6)
N	0.0248(7)	0.0193(6)	0.0216(7)	0.0029(5)	0.0069(5)	0.0024(6)
C(1)	0.0176(7)	0.0252(7)	0.0250(8)	–0.0041(6)	0.0091(6)	–0.0023(7)
C(2)	0.0229(8)	0.0389(9)	0.0249(9)	–0.0024(7)	0.0065(7)	–0.0001(7)
C(3)	0.0292(9)	0.0487(11)	0.0292(10)	–0.0168(8)	0.0064(8)	–0.0075(9)
C(4)	0.0344(10)	0.0303(9)	0.0463(11)	–0.0172(8)	0.0152(9)	–0.0076(8)
C(5)	0.0281(9)	0.0215(8)	0.0379(10)	–0.0044(7)	0.0112(8)	–0.0018(7)
C(6)	0.0206(7)	0.0221(7)	0.0252(8)	–0.0020(6)	0.0098(6)	–0.0013(7)
C(7)	0.0224(8)	0.0185(7)	0.0211(8)	–0.0001(6)	0.0085(6)	–0.0003(6)
C(8)	0.0229(8)	0.0212(7)	0.0210(8)	–0.0012(6)	0.0075(6)	–0.0004(6)
C(9)	0.0315(9)	0.0207(7)	0.0261(9)	0.0019(6)	0.0096(7)	0.0020(7)
C(10)	0.0308(9)	0.0259(8)	0.0203(8)	0.0030(6)	0.0043(7)	0.0014(7)
C(11)	0.0397(10)	0.0258(8)	0.0302(10)	0.0087(7)	0.0103(8)	0.0041(8)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh92.

	x	y	z	U
H(2A)	0.0289	0.5369	0.3103	0.035
H(3A)	0.0109	0.3320	0.2676	0.044
H(4A)	0.1670	0.1860	0.3852	0.044
H(5A)	0.3466	0.2383	0.5482	0.035
H(8A)	0.3872	0.6721	0.6400	0.026
H(10A)	0.5719	0.6093	0.7715	0.032
H(11A)	0.2125	0.8002	0.4919	0.049
H(11B)	0.0205	0.7333	0.4131	0.049
H(11C)	0.2348	0.7400	0.3967	0.049

Table 6. Torsion angles [°] for mjh92.

C(8)–N–C(1)–C(2)	−179.93(16)	C(8)–N–C(1)–C(6)	−0.03(17)
C(11)–N–C(1)–C(2)	−4.2(3)	C(11)–N–C(1)–C(6)	175.70(15)
N–C(1)–C(2)–C(3)	179.54(16)	C(6)–C(1)–C(2)–C(3)	−0.4(3)
C(1)–C(2)–C(3)–C(4)	0.0(3)	C(2)–C(3)–C(4)–C(5)	−0.1(3)
C(3)–C(4)–C(5)–C(6)	0.5(3)	C(4)–C(5)–C(6)–C(1)	−0.8(2)
C(4)–C(5)–C(6)–C(7)	179.93(18)	N–C(1)–C(6)–C(5)	−179.14(15)
N–C(1)–C(6)–C(7)	0.31(17)	C(2)–C(1)–C(6)–C(5)	0.8(2)
C(2)–C(1)–C(6)–C(7)	−179.78(15)	C(1)–C(6)–C(7)–C(8)	−0.47(17)
C(1)–C(6)–C(7)–C(9)	179.43(15)	C(5)–C(6)–C(7)–C(8)	178.86(18)
C(5)–C(6)–C(7)–C(9)	−1.2(3)	C(1)–N–C(8)–C(7)	−0.28(18)
C(11)–N–C(8)–C(7)	−175.90(15)	C(6)–C(7)–C(8)–N	0.47(18)
C(9)–C(7)–C(8)–N	−179.43(15)	C(6)–C(7)–C(9)–O	0.8(3)
C(6)–C(7)–C(9)–C(10)	−177.89(15)	C(8)–C(7)–C(9)–O	−179.31(17)
C(8)–C(7)–C(9)–C(10)	2.0(2)	O–C(9)–C(10)–Cl(1)	43.1(2)
O–C(9)–C(10)–Cl(2)	−76.96(18)	C(7)–C(9)–C(10)–Cl(1)	−138.08(13)
C(7)–C(9)–C(10)–Cl(2)	101.83(15)		

Compound **3.16**

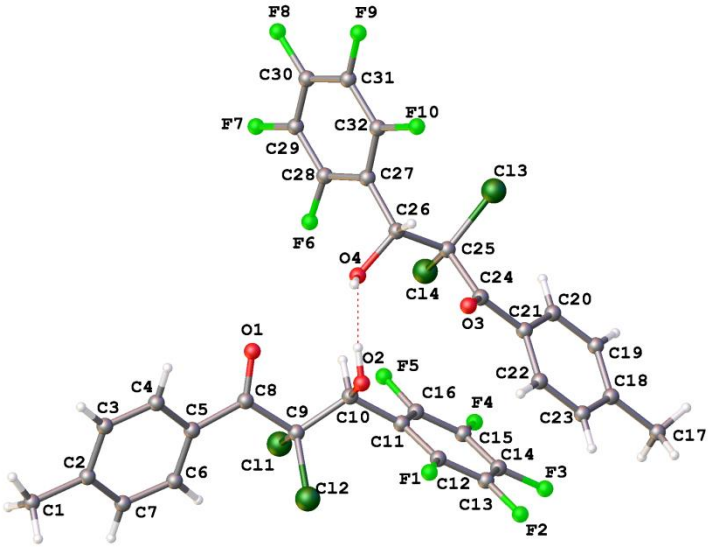


Table 1. Crystal data and structure refinement for mjh82.

Identification code	mjh82	
Chemical formula (moiety)	$C_{16}H_9Cl_2F_5O_2$	
Chemical formula (total)	$C_{16}H_9Cl_2F_5O_2$	
Formula weight	399.13	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	orthorhombic, Pccn	
Unit cell parameters	a = 14.3029(5) Å	α = 90°
	b = 20.8740(9) Å	β = 90°
	c = 20.9090(8) Å	γ = 90°
Cell volume	6242.6(4) $Å^3$	
Z	16	
Calculated density	1.699 g/cm^3	
Absorption coefficient μ	0.479 mm^{-1}	
F(000)	3200	
Crystal colour and size	block, 0.30 × 0.10 × 0.10 mm^3	
Reflections for cell refinement	9619 (θ range 2.9 to 28.6°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	3.1 to 28.6°	
Index ranges	h −14 to 18, k −22 to 27, l −27 to 26	
Completeness to θ = 25.0°	99.8 %	
Reflections collected	33189	
Independent reflections	7084 (R_{int} = 0.0431)	
Reflections with $F^2>2\sigma$	5560	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.8697 and 0.9537	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0493, 4.0256	
Data / restraints / parameters	7084 / 0 / 461	
Final R indices [$F^2>2\sigma$]	R1 = 0.0387, wR2 = 0.0921	
R indices (all data)	R1 = 0.0563, wR2 = 0.1043	
Goodness-of-fit on F^2	1.040	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	0.45 and −0.27 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh82. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	0.43943(3)	0.11709(3)	0.49016(2)	0.02748(13)
Cl(2)	0.59588(3)	0.06686(2)	0.41769(2)	0.02572(12)
F(1)	0.59128(8)	0.12641(6)	0.28581(6)	0.0302(3)
F(2)	0.47414(10)	0.09977(6)	0.19146(6)	0.0357(3)
F(3)	0.29052(10)	0.13002(7)	0.20077(7)	0.0416(3)
F(4)	0.22367(8)	0.18494(7)	0.30905(7)	0.0401(3)
F(5)	0.34124(8)	0.21591(6)	0.40425(6)	0.0319(3)
O(1)	0.62710(11)	0.21773(7)	0.51216(7)	0.0312(3)
O(2)	0.62217(9)	0.20945(7)	0.38006(7)	0.0243(3)
C(1)	0.79178(16)	–0.00118(12)	0.69927(10)	0.0336(5)
C(2)	0.74382(14)	0.03990(10)	0.65000(9)	0.0255(4)
C(3)	0.77561(14)	0.10123(11)	0.63706(9)	0.0265(4)
C(4)	0.73313(14)	0.13895(10)	0.59118(9)	0.0249(4)
C(5)	0.65679(14)	0.11570(10)	0.55672(9)	0.0233(4)
C(6)	0.62409(15)	0.05434(11)	0.56975(10)	0.0293(5)
C(7)	0.66705(15)	0.01724(11)	0.61602(10)	0.0295(5)
C(8)	0.61427(14)	0.16067(10)	0.50990(9)	0.0235(4)
C(9)	0.54962(13)	0.13647(9)	0.45493(9)	0.0218(4)
C(10)	0.53477(13)	0.18995(9)	0.40493(9)	0.0206(4)
C(11)	0.47042(14)	0.17088(9)	0.35027(9)	0.0212(4)
C(12)	0.50127(14)	0.14173(10)	0.29448(9)	0.0227(4)
C(13)	0.44140(15)	0.12809(10)	0.24468(10)	0.0261(4)
C(14)	0.34851(16)	0.14293(10)	0.24919(10)	0.0298(5)
C(15)	0.31480(14)	0.17131(10)	0.30389(11)	0.0279(5)
C(16)	0.37575(14)	0.18534(10)	0.35298(9)	0.0242(4)
Cl(3)	0.56730(4)	0.45476(2)	0.28573(2)	0.02913(13)
Cl(4)	0.49345(3)	0.34655(3)	0.35687(2)	0.02773(13)
F(6)	0.56772(9)	0.37456(7)	0.48860(6)	0.0403(3)
F(7)	0.55575(10)	0.46675(9)	0.57564(6)	0.0544(5)
F(8)	0.64774(12)	0.57975(9)	0.55867(7)	0.0620(5)
F(9)	0.74545(11)	0.60051(6)	0.44934(7)	0.0466(4)
F(10)	0.75034(9)	0.51133(6)	0.35858(6)	0.0297(3)
O(3)	0.71158(10)	0.32416(8)	0.26186(7)	0.0311(3)
O(4)	0.69506(11)	0.32951(7)	0.39866(7)	0.0264(3)
C(17)	0.39260(17)	0.22326(13)	0.06876(11)	0.0389(6)
C(18)	0.45181(15)	0.25271(11)	0.12059(10)	0.0285(5)
C(19)	0.41977(15)	0.30465(12)	0.15600(11)	0.0338(5)
C(20)	0.47356(15)	0.33138(11)	0.20397(11)	0.0324(5)
C(21)	0.56244(14)	0.30715(10)	0.21707(9)	0.0243(4)
C(22)	0.59481(14)	0.25527(10)	0.18171(9)	0.0254(4)
C(23)	0.53973(15)	0.22843(10)	0.13430(10)	0.0275(4)
C(24)	0.62862(14)	0.33452(10)	0.26422(10)	0.0231(4)
C(25)	0.59468(13)	0.37862(10)	0.31980(9)	0.0220(4)
C(26)	0.67421(13)	0.38849(9)	0.36860(9)	0.0212(4)
C(27)	0.65717(14)	0.43977(10)	0.41851(9)	0.0227(4)
C(28)	0.60957(14)	0.43022(11)	0.47570(10)	0.0288(5)
C(29)	0.60494(16)	0.47763(14)	0.52192(10)	0.0394(6)
C(30)	0.64987(17)	0.53462(13)	0.51328(11)	0.0393(6)
C(31)	0.69845(16)	0.54552(11)	0.45769(11)	0.0329(5)
C(32)	0.70024(14)	0.49871(10)	0.41155(9)	0.0252(4)

Table 3. Bond lengths [Å] and angles [°] for mjh82.

Cl(1)–C(9)	1.7860(19)	Cl(2)–C(9)	1.776(2)
F(1)–C(12)	1.339(2)	F(2)–C(13)	1.344(2)
F(3)–C(14)	1.336(2)	F(4)–C(15)	1.338(2)
F(5)–C(16)	1.342(2)	O(1)–C(8)	1.206(2)
O(2)–C(10)	1.414(2)	O(2)–H(2)	0.86(3)
C(1)–H(1A)	0.980	C(1)–H(1B)	0.980
C(1)–H(1C)	0.980	C(1)–C(2)	1.506(3)
C(2)–C(3)	1.385(3)	C(2)–C(7)	1.391(3)
C(3)–H(3A)	0.950	C(3)–C(4)	1.382(3)
C(4)–H(4A)	0.950	C(4)–C(5)	1.395(3)
C(5)–C(6)	1.391(3)	C(5)–C(8)	1.486(3)
C(6)–H(6A)	0.950	C(6)–C(7)	1.383(3)
C(7)–H(7A)	0.950	C(8)–C(9)	1.559(3)
C(9)–C(10)	1.544(3)	C(10)–H(10A)	1.00
C(10)–C(11)	1.520(3)	C(11)–C(12)	1.388(3)
C(11)–C(16)	1.388(3)	C(12)–C(13)	1.378(3)
C(13)–C(14)	1.367(3)	C(14)–C(15)	1.375(3)
C(15)–C(16)	1.378(3)	Cl(3)–C(25)	1.785(2)
Cl(4)–C(25)	1.773(2)	F(6)–C(28)	1.334(3)
F(7)–C(29)	1.345(3)	F(8)–C(30)	1.338(3)
F(9)–C(31)	1.342(3)	F(10)–C(32)	1.345(2)
O(3)–C(24)	1.207(2)	O(4)–C(26)	1.414(2)
O(4)–H(4)	0.81(3)	C(17)–H(17A)	0.980
C(17)–H(17B)	0.980	C(17)–H(17C)	0.980
C(17)–C(18)	1.507(3)	C(18)–C(19)	1.390(3)
C(18)–C(23)	1.386(3)	C(19)–H(19A)	0.950
C(19)–C(20)	1.382(3)	C(20)–H(20A)	0.950
C(20)–C(21)	1.395(3)	C(21)–C(22)	1.391(3)
C(21)–C(24)	1.481(3)	C(22)–H(22A)	0.950
C(22)–C(23)	1.385(3)	C(23)–H(23A)	0.950
C(24)–C(25)	1.560(3)	C(25)–C(26)	1.542(3)
C(26)–H(26A)	1.00	C(26)–C(27)	1.515(3)
C(27)–C(28)	1.390(3)	C(27)–C(32)	1.384(3)
C(28)–C(29)	1.385(3)	C(29)–C(30)	1.364(4)
C(30)–C(31)	1.373(4)	C(31)–C(32)	1.373(3)

C(10)–O(2)–H(2)	110(2)	H(1A)–C(1)–H(1B)	109.5
H(1A)–C(1)–H(1C)	109.5	H(1A)–C(1)–C(2)	109.5
H(1B)–C(1)–H(1C)	109.5	H(1B)–C(1)–C(2)	109.5
H(1C)–C(1)–C(2)	109.5	C(1)–C(2)–C(3)	120.70(19)
C(1)–C(2)–C(7)	121.0(2)	C(3)–C(2)–C(7)	118.27(19)
C(2)–C(3)–H(3A)	119.4	C(2)–C(3)–C(4)	121.19(19)
H(3A)–C(3)–C(4)	119.4	C(3)–C(4)–H(4A)	119.9
C(3)–C(4)–C(5)	120.3(2)	H(4A)–C(4)–C(5)	119.9
C(4)–C(5)–C(6)	118.85(19)	C(4)–C(5)–C(8)	116.14(18)
C(6)–C(5)–C(8)	124.97(18)	C(5)–C(6)–H(6A)	119.9
C(5)–C(6)–C(7)	120.22(19)	H(6A)–C(6)–C(7)	119.9
C(2)–C(7)–C(6)	121.2(2)	C(2)–C(7)–H(7A)	119.4
C(6)–C(7)–H(7A)	119.4	O(1)–C(8)–C(5)	122.39(18)
O(1)–C(8)–C(9)	116.05(18)	C(5)–C(8)–C(9)	121.56(17)
Cl(1)–C(9)–Cl(2)	108.92(10)	Cl(1)–C(9)–C(8)	107.02(13)
Cl(1)–C(9)–C(10)	108.76(13)	Cl(2)–C(9)–C(8)	111.55(13)
Cl(2)–C(9)–C(10)	110.23(13)	C(8)–C(9)–C(10)	110.26(16)

O(2)–C(10)–C(9)	109.61(15)	O(2)–C(10)–H(10A)	107.9
O(2)–C(10)–C(11)	109.52(15)	C(9)–C(10)–H(10A)	107.9
C(9)–C(10)–C(11)	113.76(16)	H(10A)–C(10)–C(11)	107.9
C(10)–C(11)–C(12)	123.65(17)	C(10)–C(11)–C(16)	120.18(17)
C(12)–C(11)–C(16)	116.09(18)	F(1)–C(12)–C(11)	121.62(18)
F(1)–C(12)–C(13)	116.49(17)	C(11)–C(12)–C(13)	121.88(18)
F(2)–C(13)–C(12)	120.00(19)	F(2)–C(13)–C(14)	119.68(19)
C(12)–C(13)–C(14)	120.33(19)	F(3)–C(14)–C(13)	120.3(2)
F(3)–C(14)–C(15)	119.9(2)	C(13)–C(14)–C(15)	119.71(19)
F(4)–C(15)–C(14)	120.00(19)	F(4)–C(15)–C(16)	120.71(19)
C(14)–C(15)–C(16)	119.29(19)	F(5)–C(16)–C(11)	119.66(17)
F(5)–C(16)–C(15)	117.62(18)	C(11)–C(16)–C(15)	122.70(19)
C(26)–O(4)–H(4)	108.6(18)	H(17A)–C(17)–H(17B)	109.5
H(17A)–C(17)–H(17C)	109.5	H(17A)–C(17)–C(18)	109.5
H(17B)–C(17)–H(17C)	109.5	H(17B)–C(17)–C(18)	109.5
H(17C)–C(17)–C(18)	109.5	C(17)–C(18)–C(19)	121.1(2)
C(17)–C(18)–C(23)	120.6(2)	C(19)–C(18)–C(23)	118.31(19)
C(18)–C(19)–H(19A)	119.4	C(18)–C(19)–C(20)	121.2(2)
H(19A)–C(19)–C(20)	119.4	C(19)–C(20)–H(20A)	119.9
C(19)–C(20)–C(21)	120.2(2)	H(20A)–C(20)–C(21)	119.9
C(20)–C(21)–C(22)	118.76(19)	C(20)–C(21)–C(24)	124.96(19)
C(22)–C(21)–C(24)	116.20(18)	C(21)–C(22)–H(22A)	119.8
C(21)–C(22)–C(23)	120.4(2)	H(22A)–C(22)–C(23)	119.8
C(18)–C(23)–C(22)	121.1(2)	C(18)–C(23)–H(23A)	119.5
C(22)–C(23)–H(23A)	119.5	O(3)–C(24)–C(21)	122.13(18)
O(3)–C(24)–C(25)	116.23(18)	C(21)–C(24)–C(25)	121.64(16)
Cl(3)–C(25)–Cl(4)	109.35(10)	Cl(3)–C(25)–C(24)	107.23(13)
Cl(3)–C(25)–C(26)	107.88(13)	Cl(4)–C(25)–C(24)	110.91(14)
Cl(4)–C(25)–C(26)	111.32(13)	C(24)–C(25)–C(26)	110.01(15)
O(4)–C(26)–C(25)	109.47(16)	O(4)–C(26)–H(26A)	107.1
O(4)–C(26)–C(27)	110.06(16)	C(25)–C(26)–H(26A)	107.1
C(25)–C(26)–C(27)	115.57(16)	H(26A)–C(26)–C(27)	107.1
C(26)–C(27)–C(28)	124.75(19)	C(26)–C(27)–C(32)	118.96(17)
C(28)–C(27)–C(32)	115.85(19)	F(6)–C(28)–C(27)	121.21(19)
F(6)–C(28)–C(29)	117.4(2)	C(27)–C(28)–C(29)	121.4(2)
F(7)–C(29)–C(28)	119.2(3)	F(7)–C(29)–C(30)	120.3(2)
C(28)–C(29)–C(30)	120.6(2)	F(8)–C(30)–C(29)	120.6(2)
F(8)–C(30)–C(31)	119.7(3)	C(29)–C(30)–C(31)	119.7(2)
F(9)–C(31)–C(30)	120.4(2)	F(9)–C(31)–C(32)	120.5(2)
C(30)–C(31)–C(32)	119.1(2)	F(10)–C(32)–C(27)	119.86(18)
F(10)–C(32)–C(31)	116.7(2)	C(27)–C(32)–C(31)	123.4(2)

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh82. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	0.0223(2)	0.0330(3)	0.0271(2)	0.0025(2)	0.00358(19)	–0.0032(2)
Cl(2)	0.0279(2)	0.0224(2)	0.0269(2)	–0.0029(2)	–0.0016(2)	0.0040(2)
F(1)	0.0252(6)	0.0367(7)	0.0286(6)	–0.0053(5)	0.0057(5)	0.0031(5)
F(2)	0.0532(8)	0.0312(7)	0.0228(6)	–0.0064(5)	0.0028(6)	–0.0028(6)
F(3)	0.0467(8)	0.0392(8)	0.0390(7)	–0.0044(6)	–0.0211(6)	–0.0044(6)
F(4)	0.0210(6)	0.0453(8)	0.0538(8)	–0.0039(7)	–0.0093(6)	0.0028(6)
F(5)	0.0230(6)	0.0425(7)	0.0300(7)	–0.0060(6)	0.0016(5)	0.0096(5)
O(1)	0.0382(8)	0.0256(8)	0.0298(8)	–0.0026(6)	–0.0040(7)	–0.0009(7)
O(2)	0.0195(7)	0.0250(8)	0.0285(8)	–0.0016(6)	0.0032(6)	–0.0033(6)
C(1)	0.0349(12)	0.0398(13)	0.0262(11)	0.0039(10)	–0.0045(9)	–0.0003(10)
C(2)	0.0263(10)	0.0336(11)	0.0166(9)	–0.0007(9)	0.0020(8)	0.0026(9)
C(3)	0.0251(10)	0.0334(11)	0.0210(10)	–0.0046(9)	–0.0027(8)	–0.0016(9)
C(4)	0.0265(10)	0.0251(10)	0.0231(10)	–0.0039(8)	0.0005(8)	–0.0013(9)
C(5)	0.0233(9)	0.0267(10)	0.0197(9)	–0.0028(8)	0.0013(8)	–0.0003(8)
C(6)	0.0283(10)	0.0333(12)	0.0262(11)	0.0013(9)	–0.0065(9)	–0.0072(9)
C(7)	0.0319(11)	0.0306(11)	0.0261(11)	0.0051(9)	–0.0027(9)	–0.0059(9)
C(8)	0.0221(9)	0.0266(11)	0.0217(9)	–0.0017(8)	0.0013(8)	0.0001(8)
C(9)	0.0191(9)	0.0227(10)	0.0234(10)	–0.0021(8)	0.0022(8)	–0.0011(8)
C(10)	0.0169(9)	0.0219(10)	0.0230(9)	–0.0016(8)	0.0011(7)	0.0002(8)
C(11)	0.0230(9)	0.0202(10)	0.0203(9)	0.0016(8)	–0.0001(8)	–0.0008(8)
C(12)	0.0224(9)	0.0227(10)	0.0229(10)	0.0025(8)	0.0020(8)	0.0019(8)
C(13)	0.0377(11)	0.0207(10)	0.0199(10)	0.0006(8)	0.0012(9)	–0.0014(9)
C(14)	0.0380(12)	0.0231(10)	0.0282(11)	0.0023(9)	–0.0122(9)	–0.0061(9)
C(15)	0.0208(9)	0.0270(11)	0.0360(12)	0.0020(10)	–0.0049(9)	0.0008(9)
C(16)	0.0235(10)	0.0246(10)	0.0246(10)	–0.0005(8)	0.0019(8)	0.0018(8)
Cl(3)	0.0344(3)	0.0245(3)	0.0284(3)	0.0028(2)	–0.0049(2)	0.0051(2)
Cl(4)	0.0190(2)	0.0351(3)	0.0290(3)	0.0011(2)	0.00364(19)	0.0009(2)
F(6)	0.0328(7)	0.0606(9)	0.0275(7)	0.0127(6)	0.0040(5)	–0.0051(7)
F(7)	0.0375(8)	0.1077(14)	0.0181(6)	–0.0019(7)	0.0040(6)	0.0250(8)
F(8)	0.0693(11)	0.0766(12)	0.0402(8)	–0.0362(8)	–0.0173(8)	0.0370(9)
F(9)	0.0576(9)	0.0265(7)	0.0556(9)	–0.0126(7)	–0.0223(8)	0.0070(7)
F(10)	0.0375(7)	0.0255(6)	0.0262(6)	0.0040(5)	–0.0008(5)	–0.0023(5)
O(3)	0.0199(7)	0.0406(9)	0.0329(8)	–0.0099(7)	0.0008(6)	0.0029(6)
O(4)	0.0218(7)	0.0233(7)	0.0341(8)	0.0062(6)	–0.0008(6)	0.0035(6)
C(17)	0.0379(13)	0.0433(14)	0.0355(12)	–0.0047(11)	–0.0053(10)	–0.0074(11)
C(18)	0.0278(10)	0.0335(12)	0.0242(10)	0.0010(9)	–0.0007(9)	–0.0080(9)
C(19)	0.0241(10)	0.0440(13)	0.0334(12)	–0.0042(11)	–0.0055(9)	0.0047(10)
C(20)	0.0270(11)	0.0379(13)	0.0322(12)	–0.0072(10)	0.0000(9)	0.0055(10)
C(21)	0.0219(9)	0.0284(11)	0.0225(10)	0.0003(8)	0.0031(8)	0.0000(8)
C(22)	0.0246(10)	0.0264(11)	0.0253(10)	0.0019(9)	0.0024(8)	0.0007(9)
C(23)	0.0323(11)	0.0253(11)	0.0249(10)	–0.0020(9)	0.0036(9)	–0.0030(9)
C(24)	0.0229(9)	0.0225(10)	0.0238(10)	0.0006(8)	0.0029(8)	0.0026(8)
C(25)	0.0210(9)	0.0226(10)	0.0225(9)	0.0019(8)	0.0017(8)	0.0033(8)
C(26)	0.0210(9)	0.0198(9)	0.0227(9)	0.0019(8)	0.0014(8)	0.0024(8)
C(27)	0.0211(9)	0.0285(11)	0.0186(9)	0.0009(8)	–0.0018(8)	0.0066(8)
C(28)	0.0236(10)	0.0429(13)	0.0198(10)	0.0039(9)	–0.0018(8)	0.0076(9)
C(29)	0.0284(11)	0.0737(19)	0.0161(10)	–0.0030(11)	–0.0018(8)	0.0216(12)

C(30)	0.0384(13)	0.0499(15)	0.0296(12)	–0.0171(11)	–0.0130(10)	0.0230(12)
C(31)	0.0357(12)	0.0288(12)	0.0343(12)	–0.0076(10)	–0.0146(10)	0.0126(10)
C(32)	0.0269(10)	0.0283(11)	0.0205(9)	–0.0002(9)	–0.0041(8)	0.0088(9)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh82.

	x	y	z	U
H(1A)	0.8431	0.0230	0.7188	0.050
H(1B)	0.8167	–0.0398	0.6787	0.050
H(1C)	0.7467	–0.0135	0.7324	0.050
H(3A)	0.8276	0.1177	0.6601	0.032
H(4A)	0.7560	0.1809	0.5831	0.030
H(6A)	0.5721	0.0378	0.5468	0.035
H(7A)	0.6437	–0.0245	0.6247	0.035
H(10A)	0.5061	0.2275	0.4272	0.025
H(17A)	0.3550	0.2567	0.0482	0.058
H(17B)	0.3512	0.1909	0.0875	0.058
H(17C)	0.4331	0.2030	0.0368	0.058
H(19A)	0.3598	0.3221	0.1471	0.041
H(20A)	0.4500	0.3664	0.2281	0.039
H(22A)	0.6551	0.2381	0.1901	0.031
H(23A)	0.5626	0.1928	0.1108	0.033
H(26A)	0.7310	0.4015	0.3439	0.025
H(4)	0.749(2)	0.3204(12)	0.3913(12)	0.034(7)
H(2)	0.633(2)	0.2481(15)	0.3912(13)	0.050(8)

Table 6. Torsion angles [°] for mjh82.

C(1)–C(2)–C(3)–C(4)	178.89(19)	C(7)–C(2)–C(3)–C(4)	–0.7(3)
C(2)–C(3)–C(4)–C(5)	0.0(3)	C(3)–C(4)–C(5)–C(6)	0.5(3)
C(3)–C(4)–C(5)–C(8)	178.19(18)	C(4)–C(5)–C(6)–C(7)	–0.2(3)
C(8)–C(5)–C(6)–C(7)	–177.7(2)	C(5)–C(6)–C(7)–C(2)	–0.6(3)
C(1)–C(2)–C(7)–C(6)	–178.6(2)	C(3)–C(2)–C(7)–C(6)	1.0(3)
C(4)–C(5)–C(8)–O(1)	–18.5(3)	C(4)–C(5)–C(8)–C(9)	161.84(18)
C(6)–C(5)–C(8)–O(1)	159.0(2)	C(6)–C(5)–C(8)–C(9)	–20.6(3)
O(1)–C(8)–C(9)–Cl(1)	–104.36(18)	O(1)–C(8)–C(9)–Cl(2)	136.60(17)
O(1)–C(8)–C(9)–C(10)	13.8(2)	C(5)–C(8)–C(9)–Cl(1)	75.3(2)
C(5)–C(8)–C(9)–Cl(2)	–43.7(2)	C(5)–C(8)–C(9)–C(10)	–166.57(17)
Cl(1)–C(9)–C(10)–O(2)	175.48(13)	Cl(1)–C(9)–C(10)–C(11)	–61.54(18)
Cl(2)–C(9)–C(10)–O(2)	–65.17(17)	Cl(2)–C(9)–C(10)–C(11)	57.81(18)
C(8)–C(9)–C(10)–O(2)	58.4(2)	C(8)–C(9)–C(10)–C(11)	–178.60(15)
O(2)–C(10)–C(11)–C(12)	34.2(3)	O(2)–C(10)–C(11)–C(16)	–142.54(18)
C(9)–C(10)–C(11)–C(12)	–88.9(2)	C(9)–C(10)–C(11)–C(16)	94.4(2)
C(10)–C(11)–C(12)–F(1)	2.1(3)	C(10)–C(11)–C(12)–C(13)	–176.69(19)
C(16)–C(11)–C(12)–F(1)	178.92(18)	C(16)–C(11)–C(12)–C(13)	0.1(3)
F(1)–C(12)–C(13)–F(2)	1.2(3)	F(1)–C(12)–C(13)–C(14)	–179.13(18)
C(11)–C(12)–C(13)–F(2)	–179.97(18)	C(11)–C(12)–C(13)–C(14)	–0.3(3)
F(2)–C(13)–C(14)–F(3)	–0.7(3)	F(2)–C(13)–C(14)–C(15)	179.34(18)
C(12)–C(13)–C(14)–F(3)	179.64(18)	C(12)–C(13)–C(14)–C(15)	–0.3(3)
F(3)–C(14)–C(15)–F(4)	1.2(3)	F(3)–C(14)–C(15)–C(16)	–178.88(19)
C(13)–C(14)–C(15)–F(4)	–178.84(19)	C(13)–C(14)–C(15)–C(16)	1.1(3)
F(4)–C(15)–C(16)–F(5)	–3.3(3)	F(4)–C(15)–C(16)–C(11)	178.65(19)
C(14)–C(15)–C(16)–F(5)	176.72(19)	C(14)–C(15)–C(16)–C(11)	–1.3(3)
C(10)–C(11)–C(16)–F(5)	–0.4(3)	C(10)–C(11)–C(16)–C(15)	177.60(19)
C(12)–C(11)–C(16)–F(5)	–177.32(18)	C(12)–C(11)–C(16)–C(15)	0.7(3)
C(17)–C(18)–C(19)–C(20)	179.4(2)	C(23)–C(18)–C(19)–C(20)	–0.4(3)
C(18)–C(19)–C(20)–C(21)	1.1(4)	C(19)–C(20)–C(21)–C(22)	–1.0(3)
C(19)–C(20)–C(21)–C(24)	175.7(2)	C(20)–C(21)–C(22)–C(23)	0.2(3)
C(24)–C(21)–C(22)–C(23)	–176.83(18)	C(21)–C(22)–C(23)–C(18)	0.5(3)
C(17)–C(18)–C(23)–C(22)	179.8(2)	C(19)–C(18)–C(23)–C(22)	–0.4(3)
C(20)–C(21)–C(24)–O(3)	–158.9(2)	C(20)–C(21)–C(24)–C(25)	20.9(3)
C(22)–C(21)–C(24)–O(3)	17.8(3)	C(22)–C(21)–C(24)–C(25)	–162.28(18)
O(3)–C(24)–C(25)–Cl(3)	105.43(19)	O(3)–C(24)–C(25)–Cl(4)	–135.24(17)
O(3)–C(24)–C(25)–C(26)	–11.6(3)	C(21)–C(24)–C(25)–Cl(3)	–74.5(2)
C(21)–C(24)–C(25)–Cl(4)	44.9(2)	C(21)–C(24)–C(25)–C(26)	168.47(17)
Cl(3)–C(25)–C(26)–O(4)	177.47(13)	Cl(3)–C(25)–C(26)–C(27)	52.55(19)
Cl(4)–C(25)–C(26)–O(4)	57.50(18)	Cl(4)–C(25)–C(26)–C(27)	–67.42(19)
C(24)–C(25)–C(26)–O(4)	–65.9(2)	C(24)–C(25)–C(26)–C(27)	169.22(16)
O(4)–C(26)–C(27)–C(28)	–39.1(3)	O(4)–C(26)–C(27)–C(32)	133.04(18)
C(25)–C(26)–C(27)–C(28)	85.6(2)	C(25)–C(26)–C(27)–C(32)	–102.3(2)
C(26)–C(27)–C(28)–F(6)	–5.6(3)	C(26)–C(27)–C(28)–C(29)	173.31(19)
C(32)–C(27)–C(28)–F(6)	–177.96(18)	C(32)–C(27)–C(28)–C(29)	1.0(3)
F(6)–C(28)–C(29)–F(7)	–2.9(3)	F(6)–C(28)–C(29)–C(30)	176.88(19)
C(27)–C(28)–C(29)–F(7)	178.07(18)	C(27)–C(28)–C(29)–C(30)	–2.1(3)
F(7)–C(29)–C(30)–F(8)	1.8(3)	F(7)–C(29)–C(30)–C(31)	–178.83(19)
C(28)–C(29)–C(30)–F(8)	–178.04(19)	C(28)–C(29)–C(30)–C(31)	1.4(3)
F(8)–C(30)–C(31)–F(9)	1.5(3)	F(8)–C(30)–C(31)–C(32)	179.84(19)
C(29)–C(30)–C(31)–F(9)	–177.87(19)	C(29)–C(30)–C(31)–C(32)	0.4(3)

F(9)–C(31)–C(32)–F(10)	–0.4(3)	F(9)–C(31)–C(32)–C(27)	176.72(18)
C(30)–C(31)–C(32)–F(10)	–178.73(18)	C(30)–C(31)–C(32)–C(27)	–1.6(3)
C(26)–C(27)–C(32)–F(10)	5.1(3)	C(26)–C(27)–C(32)–C(31)	–171.93(18)
C(28)–C(27)–C(32)–F(10)	177.91(17)	C(28)–C(27)–C(32)–C(31)	0.9(3)

Table 7. Hydrogen bonds for mjh82 [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(4)–H(4)...O(2A)	0.81(3)	1.95(3)	2.765(2)	174(3)
O(2)–H(2)...O(4)	0.86(3)	1.92(3)	2.742(2)	161(3)
O(2)–H(2)...Cl(4)	0.86(3)	2.96(3)	3.4373(16)	117(2)

Symmetry operations for equivalent atoms
A –x+3/2,–y+1/2,z

Compound **3.27**

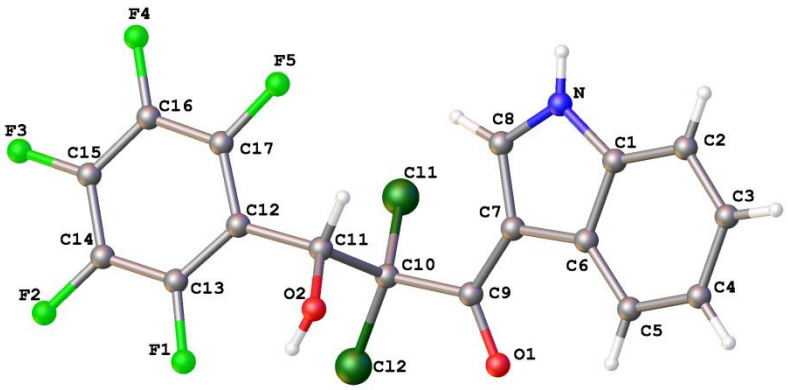


Table 1. Crystal data and structure refinement for mjh90.

Identification code	mjh90	
Chemical formula (moiety)	$C_{17}H_8Cl_2F_5NO_2$	
Chemical formula (total)	$C_{17}H_8Cl_2F_5NO_2$	
Formula weight	424.14	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 7.3186(3) Å	α = 83.481(5)°
	b = 9.4938(6) Å	β = 89.534(4)°
	c = 11.7970(7) Å	γ = 76.102(4)°
Cell volume	790.38(8) $Å^3$	
Z	2	
Calculated density	1.782 g/cm^3	
Absorption coefficient μ	0.480 mm^{-1}	
F(000)	424	
Crystal colour and size	colourless, 0.24 × 0.20 × 0.20 mm^3	
Reflections for cell refinement	2048 (θ range 3.0 to 28.6°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	3.0 to 28.6°	
Index ranges	h −9 to 8, k −10 to 12, l −15 to 15	
Completeness to θ = 25.0°	99.7 %	
Reflections collected	6097	
Independent reflections	3273 (R_{int} = 0.0246)	
Reflections with $F^2>2\sigma$	2691	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.8934 and 0.9100	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0340, 0.3892	
Data / restraints / parameters	3273 / 1 / 252	
Final R indices [$F^2>2\sigma$]	R1 = 0.0385, wR2 = 0.0808	
R indices (all data)	R1 = 0.0524, wR2 = 0.0895	
Goodness-of-fit on F^2	1.036	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	0.40 and −0.37 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh90. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	0.75041(7)	0.62450(6)	0.36769(5)	0.02434(15)
Cl(2)	1.07506(7)	0.73297(6)	0.40410(5)	0.02601(15)
O(1)	0.89955(19)	0.94353(18)	0.22677(13)	0.0272(4)
O(2)	0.7850(3)	0.98526(18)	0.50051(14)	0.0320(4)
N	0.2765(2)	0.9647(2)	0.20593(15)	0.0219(4)
F(1)	1.05815(18)	0.79892(16)	0.64885(11)	0.0324(3)
F(2)	1.10620(17)	0.60619(16)	0.83326(11)	0.0321(3)
F(3)	0.84552(19)	0.45086(16)	0.89011(11)	0.0356(4)
F(4)	0.5270(2)	0.50048(18)	0.76067(12)	0.0447(4)
F(5)	0.47414(17)	0.69373(18)	0.57381(11)	0.0387(4)
C(1)	0.3237(3)	1.0706(2)	0.12773(18)	0.0202(5)
C(2)	0.2147(3)	1.1657(3)	0.04283(19)	0.0259(5)
C(3)	0.2989(3)	1.2611(3)	–0.02128(19)	0.0311(6)
C(4)	0.4865(3)	1.2618(3)	–0.0016(2)	0.0306(6)
C(5)	0.5954(3)	1.1649(3)	0.08136(19)	0.0249(5)
C(6)	0.5150(3)	1.0652(2)	0.14728(17)	0.0183(4)
C(7)	0.5808(3)	0.9497(2)	0.23945(17)	0.0180(4)
C(8)	0.4261(3)	0.8947(2)	0.27081(18)	0.0202(5)
C(9)	0.7743(3)	0.8984(2)	0.27636(17)	0.0185(4)
C(10)	0.8265(3)	0.7852(2)	0.38521(18)	0.0190(4)
C(11)	0.7336(3)	0.8538(2)	0.49118(17)	0.0192(4)
C(12)	0.7673(3)	0.7502(2)	0.60032(17)	0.0196(5)
C(13)	0.9245(3)	0.7259(2)	0.67101(18)	0.0214(5)
C(14)	0.9511(3)	0.6269(2)	0.76798(18)	0.0223(5)
C(15)	0.8187(3)	0.5497(3)	0.79806(18)	0.0244(5)
C(16)	0.6581(3)	0.5740(3)	0.73198(19)	0.0255(5)
C(17)	0.6351(3)	0.6730(3)	0.63541(18)	0.0242(5)

Table 3. Bond lengths [Å] and angles [°] for mjh90.

Cl(1)–C(10)	1.778(2)	Cl(2)–C(10)	1.776(2)
O(1)–C(9)	1.220(2)	O(2)–H(2)	0.795(19)
O(2)–C(11)	1.403(3)	N–H	0.84(3)
N–C(1)	1.390(3)	N–C(8)	1.332(3)
F(1)–C(13)	1.337(2)	F(2)–C(14)	1.339(2)
F(3)–C(15)	1.335(2)	F(4)–C(16)	1.336(2)
F(5)–C(17)	1.351(2)	C(1)–C(2)	1.384(3)
C(1)–C(6)	1.409(3)	C(2)–H(2A)	0.950
C(2)–C(3)	1.370(3)	C(3)–H(3A)	0.950
C(3)–C(4)	1.396(3)	C(4)–H(4A)	0.950
C(4)–C(5)	1.377(3)	C(5)–H(5A)	0.950
C(5)–C(6)	1.393(3)	C(6)–C(7)	1.449(3)
C(7)–C(8)	1.388(3)	C(7)–C(9)	1.437(3)
C(8)–H(8A)	0.950	C(9)–C(10)	1.564(3)
C(10)–C(11)	1.552(3)	C(11)–H(11A)	1.000
C(11)–C(12)	1.512(3)	C(12)–C(13)	1.384(3)
C(12)–C(17)	1.382(3)	C(13)–C(14)	1.379(3)
C(14)–C(15)	1.370(3)	C(15)–C(16)	1.373(3)
C(16)–C(17)	1.376(3)		

H(2)–O(2)–C(11)	108(3)	H–N–C(1)	126.8(18)
H–N–C(8)	123.1(18)	C(1)–N–C(8)	110.10(17)
N–C(1)–C(2)	129.85(19)	N–C(1)–C(6)	107.08(18)
C(2)–C(1)–C(6)	123.06(19)	C(1)–C(2)–H(2A)	121.5
C(1)–C(2)–C(3)	117.1(2)	H(2A)–C(2)–C(3)	121.5
C(2)–C(3)–H(3A)	119.4	C(2)–C(3)–C(4)	121.3(2)
H(3A)–C(3)–C(4)	119.4	C(3)–C(4)–H(4A)	119.3
C(3)–C(4)–C(5)	121.4(2)	H(4A)–C(4)–C(5)	119.3
C(4)–C(5)–H(5A)	120.6	C(4)–C(5)–C(6)	118.9(2)
H(5A)–C(5)–C(6)	120.6	C(1)–C(6)–C(5)	118.2(2)
C(1)–C(6)–C(7)	106.62(17)	C(5)–C(6)–C(7)	135.12(19)
C(6)–C(7)–C(8)	105.85(17)	C(6)–C(7)–C(9)	123.87(17)
C(8)–C(7)–C(9)	129.91(19)	N–C(8)–C(7)	110.34(19)
N–C(8)–H(8A)	124.8	C(7)–C(8)–H(8A)	124.8
O(1)–C(9)–C(7)	121.76(19)	O(1)–C(9)–C(10)	118.74(17)
C(7)–C(9)–C(10)	119.47(16)	Cl(1)–C(10)–Cl(2)	107.21(12)
Cl(1)–C(10)–C(9)	110.22(14)	Cl(1)–C(10)–C(11)	110.08(14)
Cl(2)–C(10)–C(9)	109.31(13)	Cl(2)–C(10)–C(11)	110.22(14)
C(9)–C(10)–C(11)	109.76(17)	O(2)–C(11)–C(10)	109.81(16)
O(2)–C(11)–H(11A)	106.5	O(2)–C(11)–C(12)	113.12(17)
C(10)–C(11)–H(11A)	106.5	C(10)–C(11)–C(12)	113.92(18)
H(11A)–C(11)–C(12)	106.5	C(11)–C(12)–C(13)	124.52(19)
C(11)–C(12)–C(17)	119.74(18)	C(13)–C(12)–C(17)	115.74(19)
F(1)–C(13)–C(12)	121.30(19)	F(1)–C(13)–C(14)	116.50(18)
C(12)–C(13)–C(14)	122.20(19)	F(2)–C(14)–C(13)	120.05(19)
F(2)–C(14)–C(15)	119.79(19)	C(13)–C(14)–C(15)	120.16(19)
F(3)–C(15)–C(14)	120.57(19)	F(3)–C(15)–C(16)	120.1(2)
C(14)–C(15)–C(16)	119.4(2)	F(4)–C(16)–C(15)	120.1(2)
F(4)–C(16)–C(17)	120.50(19)	C(15)–C(16)–C(17)	119.39(19)
F(5)–C(17)–C(12)	119.82(19)	F(5)–C(17)–C(16)	117.08(19)
C(12)–C(17)–C(16)	123.09(19)		

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh90. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	0.0267(3)	0.0191(3)	0.0286(3)	–0.0053(2)	0.0010(2)	–0.0071(2)
Cl(2)	0.0143(2)	0.0310(3)	0.0300(3)	0.0000(2)	–0.0009(2)	–0.0016(2)
O(1)	0.0148(7)	0.0378(10)	0.0293(9)	0.0049(7)	0.0015(6)	–0.0110(7)
O(2)	0.0529(12)	0.0177(9)	0.0273(9)	–0.0046(7)	0.0009(8)	–0.0109(8)
N	0.0122(8)	0.0308(11)	0.0240(10)	–0.0025(8)	0.0012(7)	–0.0079(8)
F(1)	0.0321(7)	0.0389(9)	0.0317(7)	0.0009(6)	–0.0065(6)	–0.0216(6)
F(2)	0.0262(7)	0.0388(9)	0.0289(7)	0.0014(6)	–0.0111(6)	–0.0052(6)
F(3)	0.0423(8)	0.0324(9)	0.0288(7)	0.0107(6)	–0.0044(6)	–0.0091(7)
F(4)	0.0414(8)	0.0638(12)	0.0359(8)	0.0115(8)	–0.0022(7)	–0.0343(8)
F(5)	0.0203(6)	0.0669(11)	0.0299(8)	0.0082(7)	–0.0042(6)	–0.0182(7)
C(1)	0.0179(10)	0.0240(12)	0.0184(10)	–0.0051(9)	0.0032(8)	–0.0031(9)
C(2)	0.0207(10)	0.0297(14)	0.0236(12)	–0.0069(10)	–0.0021(9)	0.0030(9)
C(3)	0.0374(13)	0.0292(14)	0.0185(11)	0.0028(10)	–0.0035(10)	0.0058(11)
C(4)	0.0389(13)	0.0257(14)	0.0249(12)	0.0025(10)	0.0081(10)	–0.0059(11)
C(5)	0.0248(11)	0.0253(13)	0.0243(12)	0.0001(10)	0.0057(9)	–0.0072(10)
C(6)	0.0176(9)	0.0210(12)	0.0159(10)	–0.0041(9)	0.0031(8)	–0.0033(8)
C(7)	0.0153(9)	0.0227(12)	0.0159(10)	–0.0009(9)	0.0025(8)	–0.0050(8)
C(8)	0.0173(10)	0.0250(12)	0.0187(11)	–0.0012(9)	0.0015(8)	–0.0064(9)
C(9)	0.0168(10)	0.0213(12)	0.0191(11)	–0.0043(9)	0.0030(8)	–0.0068(9)
C(10)	0.0145(9)	0.0204(12)	0.0228(11)	–0.0032(9)	–0.0012(8)	–0.0053(8)
C(11)	0.0193(10)	0.0177(12)	0.0198(11)	–0.0039(9)	0.0018(8)	–0.0023(8)
C(12)	0.0205(10)	0.0197(12)	0.0166(10)	–0.0041(9)	0.0019(9)	–0.0003(9)
C(13)	0.0199(10)	0.0210(12)	0.0244(11)	–0.0052(9)	0.0017(9)	–0.0061(9)
C(14)	0.0192(10)	0.0227(12)	0.0234(11)	–0.0052(9)	–0.0043(9)	–0.0005(9)
C(15)	0.0297(12)	0.0212(12)	0.0190(11)	0.0009(9)	0.0009(9)	–0.0012(10)
C(16)	0.0239(11)	0.0293(13)	0.0257(12)	–0.0006(10)	0.0041(10)	–0.0123(10)
C(17)	0.0166(10)	0.0347(14)	0.0208(11)	–0.0039(10)	–0.0019(9)	–0.0047(9)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh90.

	x	y	z	U
H(2)	0.893(3)	0.966(5)	0.519(4)	0.117(19)
H	0.170(4)	0.946(3)	0.214(2)	0.035(7)
H(2A)	0.0871	1.1648	0.0296	0.031
H(3A)	0.2283	1.3281	–0.0802	0.037
H(4A)	0.5402	1.3307	–0.0465	0.037
H(5A)	0.7232	1.1661	0.0935	0.030
H(8A)	0.4268	0.8180	0.3301	0.024
H(11A)	0.5947	0.8800	0.4758	0.023

Table 6. Torsion angles [°] for mjh90.

C(8)–N–C(1)–C(2)	178.3(2)	C(8)–N–C(1)–C(6)	–0.5(2)
N–C(1)–C(2)–C(3)	179.1(2)	C(6)–C(1)–C(2)–C(3)	–2.3(3)
C(1)–C(2)–C(3)–C(4)	0.1(3)	C(2)–C(3)–C(4)–C(5)	1.3(4)
C(3)–C(4)–C(5)–C(6)	–0.5(4)	C(4)–C(5)–C(6)–C(1)	–1.5(3)
C(4)–C(5)–C(6)–C(7)	179.9(2)	N–C(1)–C(6)–C(5)	–178.0(2)
N–C(1)–C(6)–C(7)	0.9(2)	C(2)–C(1)–C(6)–C(5)	3.0(3)
C(2)–C(1)–C(6)–C(7)	–178.0(2)	C(1)–C(6)–C(7)–C(8)	–0.9(2)
C(1)–C(6)–C(7)–C(9)	172.6(2)	C(5)–C(6)–C(7)–C(8)	177.7(2)
C(5)–C(6)–C(7)–C(9)	–8.7(4)	C(1)–N–C(8)–C(7)	–0.1(3)
C(6)–C(7)–C(8)–N	0.6(2)	C(9)–C(7)–C(8)–N	–172.4(2)
C(6)–C(7)–C(9)–O(1)	–4.7(3)	C(6)–C(7)–C(9)–C(10)	173.34(19)
C(8)–C(7)–C(9)–O(1)	167.2(2)	C(8)–C(7)–C(9)–C(10)	–14.7(3)
O(1)–C(9)–C(10)–Cl(1)	–123.44(18)	O(1)–C(9)–C(10)–Cl(2)	–5.9(2)
O(1)–C(9)–C(10)–C(11)	115.2(2)	C(7)–C(9)–C(10)–Cl(1)	58.5(2)
C(7)–C(9)–C(10)–Cl(2)	176.06(16)	C(7)–C(9)–C(10)–C(11)	–62.9(2)
Cl(1)–C(10)–C(11)–O(2)	–176.39(14)	Cl(1)–C(10)–C(11)–C(12)	55.5(2)
Cl(2)–C(10)–C(11)–O(2)	65.6(2)	Cl(2)–C(10)–C(11)–C(12)	–62.5(2)
C(9)–C(10)–C(11)–O(2)	–54.9(2)	C(9)–C(10)–C(11)–C(12)	177.04(16)
O(2)–C(11)–C(12)–C(13)	–40.9(3)	O(2)–C(11)–C(12)–C(17)	138.6(2)
C(10)–C(11)–C(12)–C(13)	85.4(3)	C(10)–C(11)–C(12)–C(17)	–95.1(2)
C(11)–C(12)–C(13)–F(1)	2.6(3)	C(11)–C(12)–C(13)–C(14)	–178.0(2)
C(17)–C(12)–C(13)–F(1)	–176.99(19)	C(17)–C(12)–C(13)–C(14)	2.4(3)
F(1)–C(13)–C(14)–F(2)	–1.1(3)	F(1)–C(13)–C(14)–C(15)	178.7(2)
C(12)–C(13)–C(14)–F(2)	179.4(2)	C(12)–C(13)–C(14)–C(15)	–0.8(3)
F(2)–C(14)–C(15)–F(3)	–2.0(3)	F(2)–C(14)–C(15)–C(16)	178.6(2)
C(13)–C(14)–C(15)–F(3)	178.2(2)	C(13)–C(14)–C(15)–C(16)	–1.2(3)
F(3)–C(15)–C(16)–F(4)	1.1(4)	F(3)–C(15)–C(16)–C(17)	–178.1(2)
C(14)–C(15)–C(16)–F(4)	–179.4(2)	C(14)–C(15)–C(16)–C(17)	1.4(4)
F(4)–C(16)–C(17)–F(5)	1.3(3)	F(4)–C(16)–C(17)–C(12)	–178.8(2)
C(15)–C(16)–C(17)–F(5)	–179.5(2)	C(15)–C(16)–C(17)–C(12)	0.4(4)
C(11)–C(12)–C(17)–F(5)	–1.9(3)	C(11)–C(12)–C(17)–C(16)	178.2(2)
C(13)–C(12)–C(17)–F(5)	177.7(2)	C(13)–C(12)–C(17)–C(16)	–2.2(3)

Table 7. Hydrogen bonds for mjh90 [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(2)–H(2)...F(1)	0.795(19)	2.21(4)	2.800(2)	131(4)
O(2)–H(2)...Cl(2)	0.795(19)	2.78(5)	3.1102(19)	107(4)
N–H...O(1A)	0.84(3)	1.99(3)	2.821(2)	169(3)

Symmetry operations for equivalent atoms
A x–1,y,z

Compound **3.28**

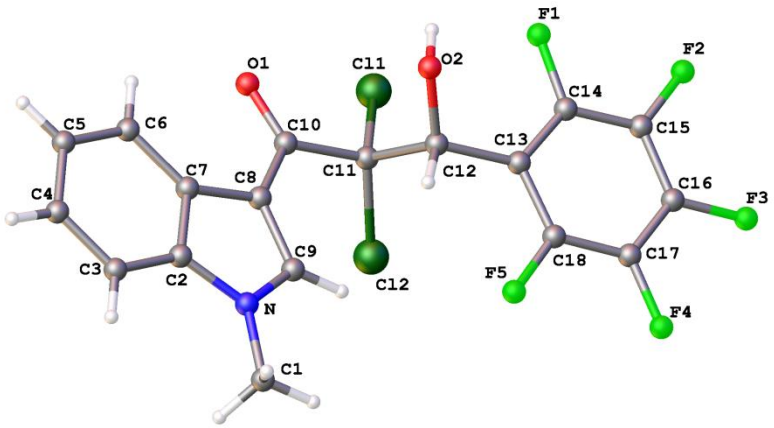


Table 1. Crystal data and structure refinement for mjh94.

Identification code	mjh94	
Chemical formula (moiety)	$C_{18}H_{10}Cl_2F_5NO_2$	
Chemical formula (total)	$C_{18}H_{10}Cl_2F_5NO_2$	
Formula weight	438.17	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 7.7970(6) Å	α = 91.836(7)°
	b = 9.7342(7) Å	β = 97.659(6)°
	c = 12.0220(10) Å	γ = 109.698(7)°
Cell volume	848.48(11) Å^3	
Z	2	
Calculated density	1.715 g/cm^3	
Absorption coefficient μ	0.451 mm^{-1}	
F(000)	440	
Crystal colour and size	colourless, 0.20 × 0.10 × 0.10 mm^3	
Reflections for cell refinement	1889 (θ range 2.8 to 28.5°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	2.8 to 28.5°	
Index ranges	h −8 to 10, k −10 to 12, l −14 to 15	
Completeness to θ = 25.0°	99.9 %	
Reflections collected	7559	
Independent reflections	3605 (R_{int} = 0.0415)	
Reflections with $F^2>2\sigma$	2523	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.9153 and 0.9563	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0274, 0.3237	
Data / restraints / parameters	3605 / 0 / 258	
Final R indices [$F^2>2\sigma$]	R1 = 0.0482, wR2 = 0.0812	
R indices (all data)	R1 = 0.0837, wR2 = 0.0953	
Goodness-of-fit on F^2	1.035	
Extinction coefficient	0.0005(7)	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.32 and −0.30 e Å^{-3}	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh94. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	0.41389(9)	0.24919(7)	0.01275(6)	0.02401(19)
Cl(2)	0.67525(9)	0.13184(7)	0.12467(6)	0.02378(19)
O(1)	0.5925(2)	0.4824(2)	0.17541(16)	0.0253(5)
O(2)	0.7587(3)	0.47672(19)	–0.05878(16)	0.0207(4)
N	1.1516(3)	0.4659(3)	0.3287(2)	0.0240(6)
F(1)	0.5032(2)	0.27640(18)	–0.22619(13)	0.0294(4)
F(2)	0.4724(2)	0.07516(18)	–0.38793(14)	0.0347(4)
F(3)	0.7018(3)	–0.08321(19)	–0.37186(15)	0.0437(5)
F(4)	0.9667(3)	–0.0311(2)	–0.18965(16)	0.0479(6)
F(5)	0.9976(2)	0.17056(19)	–0.02309(14)	0.0327(4)
C(1)	1.3164(4)	0.4286(3)	0.3599(3)	0.0327(7)
C(2)	1.1101(4)	0.5768(3)	0.3827(2)	0.0234(6)
C(3)	1.2086(4)	0.6704(3)	0.4770(2)	0.0297(7)
C(4)	1.1359(4)	0.7713(3)	0.5133(3)	0.0341(8)
C(5)	0.9707(4)	0.7789(3)	0.4577(3)	0.0318(7)
C(6)	0.8719(4)	0.6838(3)	0.3649(2)	0.0262(7)
C(7)	0.9414(4)	0.5786(3)	0.3271(2)	0.0199(6)
C(8)	0.8775(4)	0.4606(3)	0.2386(2)	0.0195(6)
C(9)	1.0135(4)	0.3977(3)	0.2444(2)	0.0224(6)
C(10)	0.7019(4)	0.4199(3)	0.1663(2)	0.0180(6)
C(11)	0.6499(3)	0.2939(3)	0.0705(2)	0.0175(6)
C(12)	0.7728(4)	0.3448(3)	–0.0215(2)	0.0176(6)
C(13)	0.7476(3)	0.2287(3)	–0.1156(2)	0.0173(6)
C(14)	0.6187(4)	0.2004(3)	–0.2117(2)	0.0201(6)
C(15)	0.6019(4)	0.0979(3)	–0.2972(2)	0.0232(6)
C(16)	0.7179(4)	0.0193(3)	–0.2894(3)	0.0280(7)
C(17)	0.8496(4)	0.0437(3)	–0.1967(3)	0.0295(7)
C(18)	0.8643(4)	0.1477(3)	–0.1119(2)	0.0232(6)

Table 3. Bond lengths [Å] and angles [°] for mjh94.

Cl(1)–C(11)	1.777(3)	Cl(2)–C(11)	1.787(3)
O(1)–C(10)	1.217(3)	O(2)–C(12)	1.407(3)
O(2)–H(2)	0.87(3)	N–C(1)	1.456(3)
N–C(2)	1.392(3)	N–C(9)	1.345(3)
F(1)–C(14)	1.343(3)	F(2)–C(15)	1.341(3)
F(3)–C(16)	1.347(3)	F(4)–C(17)	1.343(3)
F(5)–C(18)	1.343(3)	C(1)–H(1A)	0.980
C(1)–H(1B)	0.980	C(1)–H(1C)	0.980
C(2)–C(3)	1.391(4)	C(2)–C(7)	1.401(4)
C(3)–H(3A)	0.950	C(3)–C(4)	1.376(4)
C(4)–H(4A)	0.950	C(4)–C(5)	1.396(4)
C(5)–H(5A)	0.950	C(5)–C(6)	1.385(4)
C(6)–H(6A)	0.950	C(6)–C(7)	1.399(4)
C(7)–C(8)	1.447(4)	C(8)–C(9)	1.387(4)
C(8)–C(10)	1.443(4)	C(9)–H(9A)	0.950
C(10)–C(11)	1.564(4)	C(11)–C(12)	1.545(4)
C(12)–H(12A)	1.000	C(12)–C(13)	1.518(3)
C(13)–C(14)	1.380(4)	C(13)–C(18)	1.388(4)
C(14)–C(15)	1.372(4)	C(15)–C(16)	1.363(4)
C(16)–C(17)	1.365(4)	C(17)–C(18)	1.379(4)

C(12)–O(2)–H(2)	111(2)	C(1)–N–C(2)	125.3(2)
C(1)–N–C(9)	125.7(2)	C(2)–N–C(9)	109.0(2)
N–C(1)–H(1A)	109.5	N–C(1)–H(1B)	109.5
N–C(1)–H(1C)	109.5	H(1A)–C(1)–H(1B)	109.5
H(1A)–C(1)–H(1C)	109.5	H(1B)–C(1)–H(1C)	109.5
N–C(2)–C(3)	128.9(3)	N–C(2)–C(7)	107.9(2)
C(3)–C(2)–C(7)	123.2(3)	C(2)–C(3)–H(3A)	121.5
C(2)–C(3)–C(4)	116.9(3)	H(3A)–C(3)–C(4)	121.5
C(3)–C(4)–H(4A)	119.4	C(3)–C(4)–C(5)	121.2(3)
H(4A)–C(4)–C(5)	119.4	C(4)–C(5)–H(5A)	119.3
C(4)–C(5)–C(6)	121.5(3)	H(5A)–C(5)–C(6)	119.3
C(5)–C(6)–H(6A)	120.8	C(5)–C(6)–C(7)	118.5(3)
H(6A)–C(6)–C(7)	120.8	C(2)–C(7)–C(6)	118.6(2)
C(2)–C(7)–C(8)	106.8(2)	C(6)–C(7)–C(8)	134.7(3)
C(7)–C(8)–C(9)	105.8(2)	C(7)–C(8)–C(10)	124.0(2)
C(9)–C(8)–C(10)	130.2(2)	N–C(9)–C(8)	110.6(2)
N–C(9)–H(9A)	124.7	C(8)–C(9)–H(9A)	124.7
O(1)–C(10)–C(8)	122.3(2)	O(1)–C(10)–C(11)	118.0(2)
C(8)–C(10)–C(11)	119.7(2)	Cl(1)–C(11)–Cl(2)	106.98(14)
Cl(1)–C(11)–C(10)	108.82(16)	Cl(1)–C(11)–C(12)	110.24(19)
Cl(2)–C(11)–C(10)	111.02(18)	Cl(2)–C(11)–C(12)	110.30(16)
C(10)–C(11)–C(12)	109.4(2)	O(2)–C(12)–C(11)	109.48(19)
O(2)–C(12)–H(12A)	105.7	O(2)–C(12)–C(13)	114.3(2)
C(11)–C(12)–H(12A)	105.7	C(11)–C(12)–C(13)	115.1(2)
H(12A)–C(12)–C(13)	105.7	C(12)–C(13)–C(14)	124.3(2)
C(12)–C(13)–C(18)	120.5(2)	C(14)–C(13)–C(18)	115.2(2)
F(1)–C(14)–C(13)	120.3(2)	F(1)–C(14)–C(15)	116.4(2)
C(13)–C(14)–C(15)	123.3(2)	F(2)–C(15)–C(14)	120.2(2)
F(2)–C(15)–C(16)	120.3(2)	C(14)–C(15)–C(16)	119.5(3)
F(3)–C(16)–C(15)	120.3(3)	F(3)–C(16)–C(17)	119.9(2)
C(15)–C(16)–C(17)	119.7(2)	F(4)–C(17)–C(16)	120.0(2)
F(4)–C(17)–C(18)	120.2(3)	C(16)–C(17)–C(18)	119.7(2)

F(5)–C(18)–C(13)	119.5(2)	F(5)–C(18)–C(17)	118.0(2)
C(13)–C(18)–C(17)	122.5(3)		

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh94. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	0.0161(3)	0.0247(4)	0.0287(4)	–0.0019(3)	0.0021(3)	0.0045(3)
Cl(2)	0.0288(4)	0.0171(3)	0.0265(4)	0.0058(3)	0.0067(3)	0.0080(3)
O(1)	0.0251(11)	0.0280(11)	0.0258(12)	–0.0047(9)	0.0023(9)	0.0141(9)
O(2)	0.0232(11)	0.0153(10)	0.0244(12)	0.0050(8)	0.0054(9)	0.0067(8)
N	0.0188(12)	0.0284(14)	0.0233(14)	0.0035(11)	0.0005(11)	0.0070(11)
F(1)	0.0315(9)	0.0358(10)	0.0254(10)	–0.0005(8)	–0.0034(8)	0.0206(8)
F(2)	0.0364(10)	0.0350(10)	0.0230(10)	–0.0051(8)	–0.0038(8)	0.0034(8)
F(3)	0.0750(14)	0.0293(10)	0.0306(11)	–0.0082(9)	0.0145(10)	0.0215(10)
F(4)	0.0706(14)	0.0571(13)	0.0410(12)	0.0049(10)	0.0149(10)	0.0520(12)
F(5)	0.0273(9)	0.0481(11)	0.0289(10)	0.0008(8)	–0.0006(8)	0.0230(9)
C(1)	0.0216(16)	0.0414(19)	0.036(2)	0.0120(15)	0.0036(14)	0.0110(14)
C(2)	0.0251(16)	0.0231(15)	0.0168(16)	0.0043(13)	0.0064(12)	0.0000(12)
C(3)	0.0256(16)	0.0347(18)	0.0206(17)	0.0067(14)	0.0031(13)	–0.0007(14)
C(4)	0.0365(19)	0.0302(18)	0.0205(18)	–0.0025(14)	0.0042(14)	–0.0075(14)
C(5)	0.0377(19)	0.0216(16)	0.0297(19)	–0.0039(14)	0.0135(15)	–0.0006(14)
C(6)	0.0280(16)	0.0248(16)	0.0233(18)	–0.0012(13)	0.0080(13)	0.0047(13)
C(7)	0.0190(15)	0.0200(14)	0.0175(16)	0.0048(12)	0.0062(12)	0.0008(11)
C(8)	0.0187(14)	0.0228(15)	0.0158(15)	0.0012(12)	0.0030(11)	0.0054(12)
C(9)	0.0253(16)	0.0236(15)	0.0192(16)	0.0049(13)	0.0062(13)	0.0082(13)
C(10)	0.0211(15)	0.0178(14)	0.0154(15)	0.0035(11)	0.0058(11)	0.0058(12)
C(11)	0.0155(14)	0.0168(14)	0.0197(15)	0.0034(11)	0.0013(11)	0.0054(11)
C(12)	0.0181(14)	0.0163(14)	0.0184(15)	0.0016(11)	0.0018(11)	0.0063(11)
C(13)	0.0174(14)	0.0159(14)	0.0170(15)	0.0026(11)	0.0052(11)	0.0026(11)
C(14)	0.0222(15)	0.0168(14)	0.0230(17)	0.0044(12)	0.0050(12)	0.0083(12)
C(15)	0.0272(16)	0.0230(16)	0.0146(16)	0.0014(12)	0.0024(12)	0.0029(13)
C(16)	0.0435(19)	0.0201(16)	0.0217(17)	–0.0019(13)	0.0139(15)	0.0096(14)
C(17)	0.0402(19)	0.0285(17)	0.0324(19)	0.0077(15)	0.0159(15)	0.0238(15)
C(18)	0.0223(15)	0.0285(16)	0.0209(16)	0.0039(13)	0.0037(12)	0.0112(13)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh94.

	x	y	z	U
H(1A)	1.3129	0.3467	0.3090	0.049
H(1B)	1.3213	0.4004	0.4375	0.049
H(1C)	1.4259	0.5135	0.3543	0.049
H(3A)	1.3210	0.6648	0.5146	0.036
H(4A)	1.1993	0.8372	0.5775	0.041
H(5A)	0.9250	0.8508	0.4841	0.038
H(6A)	0.7596	0.6899	0.3278	0.031
H(9A)	1.0097	0.3176	0.1957	0.027
H(12A)	0.9025	0.3701	0.0172	0.021
H(2)	0.646(4)	0.466(3)	–0.088(3)	0.040(10)

Table 6. Torsion angles [°] for mjh94.

C(1)–N–C(2)–C(3)	−2.2(5)	C(1)–N–C(2)–C(7)	179.5(3)
C(9)–N–C(2)–C(3)	176.7(3)	C(9)–N–C(2)–C(7)	−1.6(3)
N–C(2)–C(3)–C(4)	179.9(3)	C(7)–C(2)–C(3)–C(4)	−2.0(4)
C(2)–C(3)–C(4)–C(5)	0.0(4)	C(3)–C(4)–C(5)–C(6)	1.0(5)
C(4)–C(5)–C(6)–C(7)	−0.1(5)	C(5)–C(6)–C(7)–C(2)	−1.8(4)
C(5)–C(6)–C(7)–C(8)	177.4(3)	N–C(2)–C(7)–C(6)	−178.7(3)
N–C(2)–C(7)–C(8)	1.9(3)	C(3)–C(2)–C(7)–C(6)	2.9(4)
C(3)–C(2)–C(7)–C(8)	−176.5(3)	C(2)–C(7)–C(8)–C(9)	−1.6(3)
C(2)–C(7)–C(8)–C(10)	175.9(3)	C(6)–C(7)–C(8)–C(9)	179.2(3)
C(6)–C(7)–C(8)–C(10)	−3.4(5)	C(1)–N–C(9)–C(8)	179.5(3)
C(2)–N–C(9)–C(8)	0.6(3)	C(7)–C(8)–C(9)–N	0.6(3)
C(10)–C(8)–C(9)–N	−176.6(3)	C(7)–C(8)–C(10)–O(1)	−0.6(4)
C(7)–C(8)–C(10)–C(11)	177.8(3)	C(9)–C(8)–C(10)–O(1)	176.2(3)
C(9)–C(8)–C(10)–C(11)	−5.4(4)	O(1)–C(10)–C(11)–Cl(1)	−11.3(3)
O(1)–C(10)–C(11)–Cl(2)	−128.8(2)	O(1)–C(10)–C(11)–C(12)	109.3(3)
C(8)–C(10)–C(11)–Cl(1)	170.3(2)	C(8)–C(10)–C(11)–Cl(2)	52.8(3)
C(8)–C(10)–C(11)–C(12)	−69.2(3)	Cl(1)–C(11)–C(12)–O(2)	65.3(2)
Cl(1)–C(11)–C(12)–C(13)	−65.1(2)	Cl(2)–C(11)–C(12)–O(2)	−176.80(17)
Cl(2)–C(11)–C(12)–C(13)	52.8(3)	C(10)–C(11)–C(12)–O(2)	−54.4(3)
C(10)–C(11)–C(12)–C(13)	175.3(2)	O(2)–C(12)–C(13)–C(14)	−40.3(4)
O(2)–C(12)–C(13)–C(18)	136.1(3)	C(11)–C(12)–C(13)–C(14)	87.7(3)
C(11)–C(12)–C(13)–C(18)	−95.9(3)	C(12)–C(13)–C(14)–F(1)	−0.9(4)
C(12)–C(13)–C(14)–C(15)	178.0(3)	C(18)–C(13)–C(14)–F(1)	−177.5(2)
C(18)–C(13)–C(14)–C(15)	1.4(4)	F(1)–C(14)–C(15)–F(2)	−1.6(4)
F(1)–C(14)–C(15)–C(16)	178.4(3)	C(13)–C(14)–C(15)–F(2)	179.4(2)
C(13)–C(14)–C(15)–C(16)	−0.6(4)	F(2)–C(15)–C(16)–F(3)	−0.9(4)
F(2)–C(15)–C(16)–C(17)	179.8(3)	C(14)–C(15)–C(16)–F(3)	179.1(3)
C(14)–C(15)–C(16)–C(17)	−0.2(5)	F(3)–C(16)–C(17)–F(4)	2.2(5)
F(3)–C(16)–C(17)–C(18)	−179.3(3)	C(15)–C(16)–C(17)–F(4)	−178.6(3)
C(15)–C(16)–C(17)–C(18)	−0.1(5)	F(4)–C(17)–C(18)–F(5)	−0.3(4)
F(4)–C(17)–C(18)–C(13)	179.5(3)	C(16)–C(17)–C(18)–F(5)	−178.8(3)
C(16)–C(17)–C(18)–C(13)	1.0(5)	C(12)–C(13)–C(18)–F(5)	1.4(4)
C(12)–C(13)–C(18)–C(17)	−178.3(3)	C(14)–C(13)–C(18)–F(5)	178.2(2)
C(14)–C(13)–C(18)–C(17)	−1.6(4)		

Table 7. Hydrogen bonds for mjh94 [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(2)–H(2)...O(1A)	0.87(3)	2.23(3)	3.061(3)	160(3)
O(2)–H(2)...F(1)	0.87(3)	2.31(3)	2.808(3)	117(2)

Symmetry operations for equivalent atoms
A –x+1,–y+1,–z

Compound **3.30**

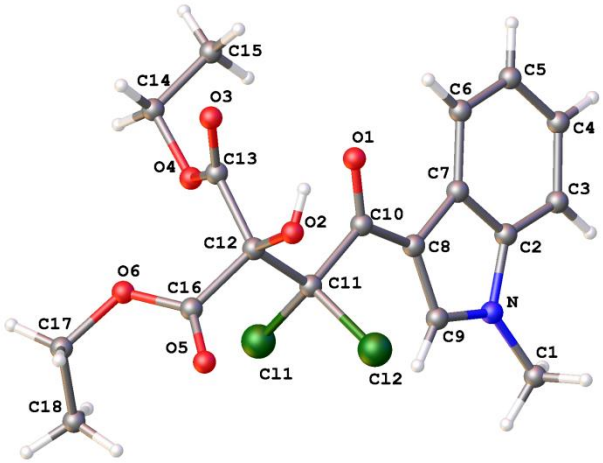


Table 1. Crystal data and structure refinement for mjh95.

Identification code	mjh95	
Chemical formula (moiety)	$C_{18}H_{19}Cl_2NO_6$	
Chemical formula (total)	$C_{18}H_{19}Cl_2NO_6$	
Formula weight	416.24	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 8.6111(5) Å	α = 87.574(5)°
	b = 10.1757(6) Å	β = 70.982(6)°
	c = 11.1365(7) Å	γ = 75.760(5)°
Cell volume	893.45(9) $Å^3$	
Z	2	
Calculated density	1.547 g/cm^3	
Absorption coefficient μ	0.401 mm^{-1}	
F(000)	432	
Crystal colour and size	colourless, 0.40 × 0.30 × 0.15 mm^3	
Reflections for cell refinement	2555 (θ range 2.9 to 28.5°)	
Data collection method	Oxford Diffraction Gemini A Ultra diffractometer thick-slice ω scans	
θ range for data collection	2.9 to 28.6°	
Index ranges	h −9 to 10, k −12 to 9, l −13 to 14	
Completeness to θ = 25.0°	99.8 %	
Reflections collected	7004	
Independent reflections	3683 (R_{int} = 0.0285)	
Reflections with $F^2>2\sigma$	3089	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.8562 and 0.9424	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0301, 0.3809	
Data / restraints / parameters	3683 / 0 / 252	
Final R indices [$F^2>2\sigma$]	R1 = 0.0364, wR2 = 0.0790	
R indices (all data)	R1 = 0.0481, wR2 = 0.0876	
Goodness-of-fit on F^2	1.068	
Extinction coefficient	0.0018(14)	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	0.43 and −0.31 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh95. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	0.50094(6)	0.50603(5)	0.84032(4)	0.01848(14)
Cl(2)	0.66226(6)	0.46173(5)	0.56865(4)	0.02092(14)
O(1)	0.78599(18)	0.72465(14)	0.68290(14)	0.0247(3)
O(2)	0.97596(18)	0.42969(16)	0.61137(12)	0.0212(3)
O(3)	1.04565(18)	0.54757(14)	0.78678(13)	0.0241(3)
O(4)	0.77593(17)	0.59304(13)	0.91890(12)	0.0196(3)
O(5)	0.83660(17)	0.22309(13)	0.71801(12)	0.0205(3)
O(6)	0.82262(18)	0.31054(13)	0.90388(12)	0.0198(3)
N	0.2574(2)	0.85777(16)	0.64801(15)	0.0175(4)
C(1)	0.1036(3)	0.8636(2)	0.6175(2)	0.0247(5)
C(2)	0.3233(2)	0.96913(19)	0.65228(17)	0.0159(4)
C(3)	0.2541(3)	1.1054(2)	0.63979(18)	0.0202(4)
C(4)	0.3453(3)	1.1957(2)	0.65067(18)	0.0219(5)
C(5)	0.5010(3)	1.1503(2)	0.67214(18)	0.0215(4)
C(6)	0.5698(3)	1.0148(2)	0.68230(17)	0.0188(4)
C(7)	0.4801(2)	0.92083(19)	0.67200(17)	0.0154(4)
C(8)	0.5078(2)	0.77541(19)	0.67930(17)	0.0157(4)
C(9)	0.3665(2)	0.7442(2)	0.66455(17)	0.0168(4)
C(10)	0.6600(2)	0.68595(19)	0.68950(17)	0.0160(4)
C(11)	0.6749(2)	0.53186(19)	0.70914(17)	0.0154(4)
C(12)	0.8469(2)	0.45706(19)	0.72858(17)	0.0160(4)
C(13)	0.9007(3)	0.53995(19)	0.81490(17)	0.0173(4)
C(14)	0.8193(3)	0.6694(2)	1.00651(19)	0.0257(5)
C(15)	0.8197(3)	0.8115(2)	0.9655(2)	0.0307(5)
C(16)	0.8331(2)	0.31574(19)	0.78211(17)	0.0161(4)
C(17)	0.7986(3)	0.1838(2)	0.96548(19)	0.0231(5)
C(18)	0.6238(3)	0.1660(2)	0.98562(19)	0.0233(5)

Table 3. Bond lengths [Å] and angles [°] for mjh95.

Cl(1)–C(11)	1.7839(18)	Cl(2)–C(11)	1.7923(19)
O(1)–C(10)	1.222(2)	O(2)–C(12)	1.396(2)
O(2)–H(2)	0.77(3)	O(3)–C(13)	1.205(2)
O(4)–C(13)	1.321(2)	O(4)–C(14)	1.463(2)
O(5)–C(16)	1.195(2)	O(6)–C(16)	1.329(2)
O(6)–C(17)	1.463(2)	N–C(1)	1.459(3)
N–C(2)	1.395(2)	N–C(9)	1.346(3)
C(1)–H(1A)	0.980	C(1)–H(1B)	0.980
C(1)–H(1C)	0.980	C(2)–C(3)	1.389(3)
C(2)–C(7)	1.404(3)	C(3)–H(3A)	0.950
C(3)–C(4)	1.379(3)	C(4)–H(4A)	0.950
C(4)–C(5)	1.401(3)	C(5)–H(5A)	0.950
C(5)–C(6)	1.376(3)	C(6)–H(6A)	0.950
C(6)–C(7)	1.398(3)	C(7)–C(8)	1.443(3)
C(8)–C(9)	1.390(3)	C(8)–C(10)	1.436(3)
C(9)–H(9A)	0.950	C(10)–C(11)	1.554(3)
C(11)–C(12)	1.569(3)	C(12)–C(13)	1.550(3)
C(12)–C(16)	1.550(3)	C(14)–H(14A)	0.990
C(14)–H(14B)	0.990	C(14)–C(15)	1.498(3)
C(15)–H(15A)	0.980	C(15)–H(15B)	0.980
C(15)–H(15C)	0.980	C(17)–H(17A)	0.990
C(17)–H(17B)	0.990	C(17)–C(18)	1.504(3)
C(18)–H(18A)	0.980	C(18)–H(18B)	0.980
C(18)–H(18C)	0.980		

C(12)–O(2)–H(2)	108(2)	C(13)–O(4)–C(14)	116.17(16)
C(16)–O(6)–C(17)	116.31(15)	C(1)–N–C(2)	124.80(17)
C(1)–N–C(9)	125.91(17)	C(2)–N–C(9)	109.02(16)
N–C(1)–H(1A)	109.5	N–C(1)–H(1B)	109.5
N–C(1)–H(1C)	109.5	H(1A)–C(1)–H(1B)	109.5
H(1A)–C(1)–H(1C)	109.5	H(1B)–C(1)–H(1C)	109.5
N–C(2)–C(3)	128.87(18)	N–C(2)–C(7)	107.78(16)
C(3)–C(2)–C(7)	123.34(18)	C(2)–C(3)–H(3A)	121.6
C(2)–C(3)–C(4)	116.87(19)	H(3A)–C(3)–C(4)	121.6
C(3)–C(4)–H(4A)	119.5	C(3)–C(4)–C(5)	120.92(19)
H(4A)–C(4)–C(5)	119.5	C(4)–C(5)–H(5A)	119.1
C(4)–C(5)–C(6)	121.76(19)	H(5A)–C(5)–C(6)	119.1
C(5)–C(6)–H(6A)	120.7	C(5)–C(6)–C(7)	118.67(19)
H(6A)–C(6)–C(7)	120.7	C(2)–C(7)–C(6)	118.42(18)
C(2)–C(7)–C(8)	106.74(16)	C(6)–C(7)–C(8)	134.82(19)
C(7)–C(8)–C(9)	106.07(17)	C(7)–C(8)–C(10)	124.42(17)
C(9)–C(8)–C(10)	129.34(17)	N–C(9)–C(8)	110.38(17)
N–C(9)–H(9A)	124.8	C(8)–C(9)–H(9A)	124.8
O(1)–C(10)–C(8)	122.90(18)	O(1)–C(10)–C(11)	115.53(17)
C(8)–C(10)–C(11)	121.57(16)	Cl(1)–C(11)–Cl(2)	107.85(10)
Cl(1)–C(11)–C(10)	110.36(13)	Cl(1)–C(11)–C(12)	110.23(12)
Cl(2)–C(11)–C(10)	106.84(12)	Cl(2)–C(11)–C(12)	109.00(12)
C(10)–C(11)–C(12)	112.39(15)	O(2)–C(12)–C(11)	110.12(15)
O(2)–C(12)–C(13)	108.41(15)	O(2)–C(12)–C(16)	104.88(15)
C(11)–C(12)–C(13)	112.92(15)	C(11)–C(12)–C(16)	109.02(15)
C(13)–C(12)–C(16)	111.19(15)	O(3)–C(13)–O(4)	126.17(18)
O(3)–C(13)–C(12)	120.43(17)	O(4)–C(13)–C(12)	113.35(16)
O(4)–C(14)–H(14A)	109.3	O(4)–C(14)–H(14B)	109.3

O(4)–C(14)–C(15)	111.49(17)	H(14A)–C(14)–H(14B)	108.0
H(14A)–C(14)–C(15)	109.3	H(14B)–C(14)–C(15)	109.3
C(14)–C(15)–H(15A)	109.5	C(14)–C(15)–H(15B)	109.5
C(14)–C(15)–H(15C)	109.5	H(15A)–C(15)–H(15B)	109.5
H(15A)–C(15)–H(15C)	109.5	H(15B)–C(15)–H(15C)	109.5
O(5)–C(16)–O(6)	125.32(18)	O(5)–C(16)–C(12)	122.55(17)
O(6)–C(16)–C(12)	112.09(15)	O(6)–C(17)–H(17A)	109.3
O(6)–C(17)–H(17B)	109.3	O(6)–C(17)–C(18)	111.80(17)
H(17A)–C(17)–H(17B)	107.9	H(17A)–C(17)–C(18)	109.3
H(17B)–C(17)–C(18)	109.3	C(17)–C(18)–H(18A)	109.5
C(17)–C(18)–H(18B)	109.5	C(17)–C(18)–H(18C)	109.5
H(18A)–C(18)–H(18B)	109.5	H(18A)–C(18)–H(18C)	109.5
H(18B)–C(18)–H(18C)	109.5		

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh95. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	0.0151(2)	0.0182(3)	0.0224(3)	0.00448(18)	–0.00466(19)	–0.00715(19)
Cl(2)	0.0253(3)	0.0203(3)	0.0218(3)	–0.00096(18)	–0.0130(2)	–0.0063(2)
O(1)	0.0206(8)	0.0200(8)	0.0410(9)	0.0116(6)	–0.0171(7)	–0.0106(6)
O(2)	0.0178(8)	0.0255(8)	0.0181(7)	0.0017(6)	–0.0018(6)	–0.0074(6)
O(3)	0.0170(8)	0.0255(8)	0.0343(8)	0.0034(6)	–0.0131(6)	–0.0074(6)
O(4)	0.0221(8)	0.0187(7)	0.0206(7)	–0.0015(5)	–0.0076(6)	–0.0085(6)
O(5)	0.0219(8)	0.0168(7)	0.0226(7)	–0.0022(5)	–0.0065(6)	–0.0047(6)
O(6)	0.0259(8)	0.0166(7)	0.0218(7)	0.0055(5)	–0.0118(6)	–0.0096(6)
N	0.0129(8)	0.0186(9)	0.0239(9)	0.0016(6)	–0.0092(7)	–0.0050(7)
C(1)	0.0154(10)	0.0291(12)	0.0337(12)	0.0011(9)	–0.0126(9)	–0.0066(9)
C(2)	0.0153(10)	0.0165(10)	0.0162(9)	0.0000(7)	–0.0047(8)	–0.0050(8)
C(3)	0.0180(10)	0.0197(11)	0.0218(10)	–0.0007(8)	–0.0070(8)	–0.0020(8)
C(4)	0.0263(11)	0.0145(10)	0.0233(11)	0.0003(8)	–0.0076(9)	–0.0030(8)
C(5)	0.0260(11)	0.0173(10)	0.0248(11)	–0.0007(8)	–0.0094(9)	–0.0098(9)
C(6)	0.0199(10)	0.0216(11)	0.0174(10)	0.0008(7)	–0.0070(8)	–0.0082(8)
C(7)	0.0149(10)	0.0178(10)	0.0145(9)	0.0007(7)	–0.0051(8)	–0.0053(8)
C(8)	0.0153(10)	0.0165(10)	0.0171(9)	0.0019(7)	–0.0065(8)	–0.0058(8)
C(9)	0.0171(10)	0.0159(10)	0.0181(10)	0.0005(7)	–0.0057(8)	–0.0055(8)
C(10)	0.0178(10)	0.0185(10)	0.0146(9)	0.0028(7)	–0.0070(8)	–0.0080(8)
C(11)	0.0151(10)	0.0171(10)	0.0172(9)	0.0009(7)	–0.0068(8)	–0.0074(8)
C(12)	0.0136(10)	0.0179(10)	0.0175(10)	0.0025(7)	–0.0059(8)	–0.0049(8)
C(13)	0.0208(11)	0.0140(10)	0.0215(10)	0.0073(7)	–0.0119(8)	–0.0063(8)
C(14)	0.0355(13)	0.0254(12)	0.0223(11)	–0.0034(8)	–0.0134(10)	–0.0126(10)
C(15)	0.0318(13)	0.0213(12)	0.0455(14)	–0.0019(9)	–0.0196(11)	–0.0086(10)
C(16)	0.0110(9)	0.0172(10)	0.0190(10)	0.0009(7)	–0.0038(8)	–0.0027(8)
C(17)	0.0287(12)	0.0182(11)	0.0262(11)	0.0088(8)	–0.0127(9)	–0.0089(9)
C(18)	0.0277(12)	0.0184(11)	0.0237(11)	0.0012(8)	–0.0063(9)	–0.0082(9)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh95.

	x	y	z	U
H(1A)	0.0669	0.7797	0.6423	0.037
H(1B)	0.1263	0.8737	0.5259	0.037
H(1C)	0.0140	0.9412	0.6638	0.037
H(3A)	0.1489	1.1350	0.6245	0.024
H(4A)	0.3020	1.2899	0.6435	0.026
H(5A)	0.5607	1.2148	0.6799	0.026
H(6A)	0.6760	0.9857	0.6960	0.023
H(9A)	0.3494	0.6554	0.6659	0.020
H(14A)	0.9328	0.6227	1.0105	0.031
H(14B)	0.7363	0.6721	1.0928	0.031
H(15A)	0.8290	0.8645	1.0332	0.046
H(15B)	0.7141	0.8531	0.9482	0.046
H(15C)	0.9163	0.8098	0.8882	0.046
H(17A)	0.8174	0.1835	1.0486	0.028
H(17B)	0.8836	0.1065	0.9122	0.028
H(18A)	0.6036	0.0918	1.0431	0.035
H(18B)	0.6142	0.1443	0.9038	0.035
H(18C)	0.5397	0.2501	1.0231	0.035
H(2)	1.025(4)	0.486(3)	0.601(3)	0.063(11)

Table 6. Torsion angles [°] for mjh95.

C(1)–N–C(2)–C(3)	5.7(3)	C(1)–N–C(2)–C(7)	−174.12(16)
C(9)–N–C(2)–C(3)	−179.98(18)	C(9)–N–C(2)–C(7)	0.2(2)
N–C(2)–C(3)–C(4)	178.65(18)	C(7)–C(2)–C(3)–C(4)	−1.5(3)
C(2)–C(3)–C(4)–C(5)	0.6(3)	C(3)–C(4)–C(5)–C(6)	0.5(3)
C(4)–C(5)–C(6)–C(7)	−0.6(3)	C(5)–C(6)–C(7)–C(2)	−0.3(3)
C(5)–C(6)–C(7)–C(8)	−178.78(19)	N–C(2)–C(7)–C(6)	−178.74(15)
N–C(2)–C(7)–C(8)	0.14(19)	C(3)–C(2)–C(7)–C(6)	1.4(3)
C(3)–C(2)–C(7)–C(8)	−179.71(17)	C(2)–C(7)–C(8)–C(9)	−0.39(19)
C(2)–C(7)–C(8)–C(10)	175.15(17)	C(6)–C(7)–C(8)–C(9)	178.2(2)
C(6)–C(7)–C(8)–C(10)	−6.2(3)	C(1)–N–C(9)–C(8)	173.78(17)
C(2)–N–C(9)–C(8)	−0.4(2)	C(7)–C(8)–C(9)–N	0.5(2)
C(10)–C(8)–C(9)–N	−174.73(18)	C(7)–C(8)–C(10)–O(1)	−5.9(3)
C(7)–C(8)–C(10)–C(11)	174.42(16)	C(9)–C(8)–C(10)–O(1)	168.54(18)
C(9)–C(8)–C(10)–C(11)	−11.1(3)	O(1)–C(10)–C(11)–Cl(1)	128.45(15)
O(1)–C(10)–C(11)–Cl(2)	−114.55(16)	O(1)–C(10)–C(11)–C(12)	5.0(2)
C(8)–C(10)–C(11)–Cl(1)	−51.9(2)	C(8)–C(10)–C(11)–Cl(2)	65.13(19)
C(8)–C(10)–C(11)–C(12)	−175.35(16)	Cl(1)–C(11)–C(12)–O(2)	156.20(13)
Cl(1)–C(11)–C(12)–C(13)	−82.47(16)	Cl(1)–C(11)–C(12)–C(16)	41.64(17)
Cl(2)–C(11)–C(12)–O(2)	38.00(18)	Cl(2)–C(11)–C(12)–C(13)	159.34(12)
Cl(2)–C(11)–C(12)–C(16)	−76.55(15)	C(10)–C(11)–C(12)–O(2)	−80.24(18)
C(10)–C(11)–C(12)–C(13)	41.1(2)	C(10)–C(11)–C(12)–C(16)	165.20(14)
C(14)–O(4)–C(13)–O(3)	0.8(3)	C(14)–O(4)–C(13)–C(12)	178.31(16)
O(2)–C(12)–C(13)–O(3)	−14.3(2)	O(2)–C(12)–C(13)–O(4)	168.02(15)
C(11)–C(12)–C(13)–O(3)	−136.62(18)	C(11)–C(12)–C(13)–O(4)	45.7(2)
C(16)–C(12)–C(13)–O(3)	100.5(2)	C(16)–C(12)–C(13)–O(4)	−77.2(2)
C(13)–O(4)–C(14)–C(15)	82.0(2)	C(17)–O(6)–C(16)–O(5)	−5.6(3)
C(17)–O(6)–C(16)–C(12)	176.38(15)	O(2)–C(12)–C(16)–O(5)	−43.4(2)
O(2)–C(12)–C(16)–O(6)	134.68(16)	C(11)–C(12)–C(16)–O(5)	74.5(2)
C(11)–C(12)–C(16)–O(6)	−107.40(17)	C(13)–C(12)–C(16)–O(5)	−160.35(18)
C(13)–C(12)–C(16)–O(6)	17.7(2)	C(16)–O(6)–C(17)–C(18)	−71.1(2)

Table 7. Hydrogen bonds for mjh95 [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(2)–H(2)...O(3)	0.77(3)	2.26(3)	2.633(2)	110(3)
O(2)–H(2)...Cl(2A)	0.77(3)	2.90(3)	3.5186(16)	139(3)

Symmetry operations for equivalent atoms
A –x+2,–y+1,–z+1

Compound **4.2**

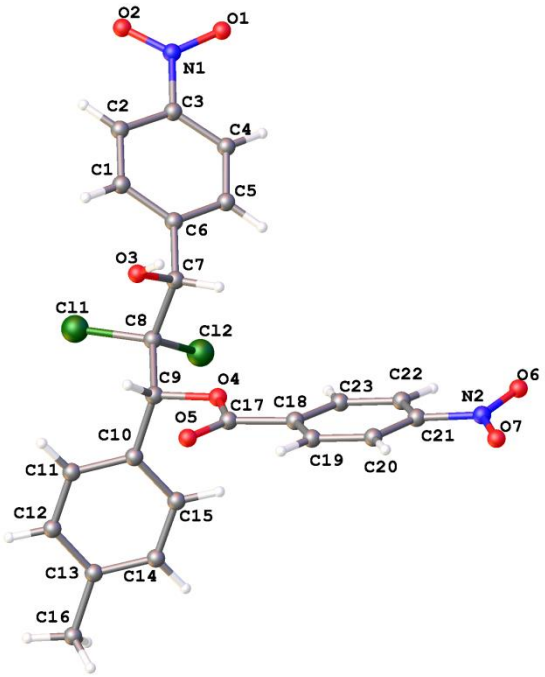

O2
O1
N1
C3
C2
C4
C1
C5
C6
O3
C7
C11
C8
C12
C9
O4
C17
C18
C23
C22
N2
O6
O5
C10
C21
O7
C19
C20
C11
C12
C15
C13
C14
C16

Table 1. Crystal data and structure refinement for mjh12.

Identification code	mjh120015	
Chemical formula (moiety)	$C_{23}H_{18}Cl_2N_2O_7$	
Chemical formula (total)	$C_{23}H_{18}Cl_2N_2O_7$	
Formula weight	505.29	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	orthorhombic, $P2_12_12_1$	
Unit cell parameters	a = 8.4714(4) Å	α = 90°
	b = 15.4385(7) Å	β = 90°
	c = 17.2354(9) Å	γ = 90°
Cell volume	2254.14(19) $Å^3$	
Z	4	
Calculated density	1.489 g/cm^3	
Absorption coefficient μ	0.337 mm^{-1}	
F(000)	1040	
Crystal colour and size	colourless, 0.32 × 0.15 × 0.15 mm^3	
Reflections for cell refinement	2938 (θ range 2.9 to 28.4°)	
Data collection method	Oxford Diffraction Gemini A Ultra diffractometer thick-slice ω scans	
θ range for data collection	2.9 to 28.5°	
Index ranges	h −9 to 10, k −18 to 20, l −16 to 22	
Completeness to θ = 25.0°	99.7 %	
Reflections collected	10456	
Independent reflections	4733 (R_{int} = 0.0491)	
Reflections with $F^2>2\sigma$	3658	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.8999 and 0.9512	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0351, 0.0162	
Data / restraints / parameters	4733 / 0 / 311	
Final R indices [$F^2>2\sigma$]	R1 = 0.0507, wR2 = 0.0880	
R indices (all data)	R1 = 0.0783, wR2 = 0.1025	
Goodness-of-fit on F^2	1.059	
Absolute structure parameter	0.00(7)	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	0.32 and −0.27 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh12. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	0.55330(9)	0.74026(5)	0.86640(5)	0.0320(2)
Cl(2)	0.31313(10)	0.68327(5)	0.97402(5)	0.0307(2)
O(1)	–0.1937(3)	0.97807(16)	0.78331(15)	0.0423(6)
O(2)	0.0149(3)	1.03545(16)	0.73322(15)	0.0441(7)
O(3)	0.3649(3)	0.63678(16)	0.75037(14)	0.0296(6)
O(4)	0.3628(2)	0.51000(13)	0.89868(13)	0.0245(5)
O(5)	0.5009(3)	0.40815(15)	0.83616(16)	0.0474(7)
O(6)	–0.2700(4)	0.2423(2)	0.93735(18)	0.0593(8)
O(7)	–0.1372(3)	0.13434(17)	0.89131(18)	0.0558(8)
N(1)	–0.0538(4)	0.97504(18)	0.76429(16)	0.0314(7)
N(2)	–0.1489(4)	0.2105(2)	0.91169(18)	0.0420(8)
C(1)	0.2567(4)	0.8068(2)	0.75733(19)	0.0258(8)
C(2)	0.1769(4)	0.8828(2)	0.74335(19)	0.0257(7)
C(3)	0.0328(4)	0.8952(2)	0.78035(19)	0.0245(7)
C(4)	–0.0310(4)	0.8351(2)	0.83041(19)	0.0286(8)
C(5)	0.0528(4)	0.7600(2)	0.84405(18)	0.0267(8)
C(6)	0.1967(4)	0.7451(2)	0.80759(17)	0.0216(7)
C(7)	0.2829(4)	0.66019(19)	0.81908(17)	0.0220(7)
C(8)	0.4084(4)	0.65917(19)	0.88463(18)	0.0230(7)
C(9)	0.4912(4)	0.57041(19)	0.88808(19)	0.0224(7)
C(10)	0.6158(4)	0.55806(19)	0.94932(19)	0.0247(8)
C(11)	0.7699(4)	0.5848(2)	0.9347(2)	0.0300(8)
C(12)	0.8860(4)	0.5731(2)	0.9897(2)	0.0343(9)
C(13)	0.8561(4)	0.5317(2)	1.0590(2)	0.0346(9)
C(14)	0.7040(5)	0.5033(2)	1.0724(2)	0.0359(9)
C(15)	0.5840(4)	0.5171(2)	1.0196(2)	0.0316(8)
C(16)	0.9848(5)	0.5159(3)	1.1180(2)	0.0511(11)
C(17)	0.3837(4)	0.4294(2)	0.8702(2)	0.0279(8)
C(18)	0.2458(4)	0.3723(2)	0.8839(2)	0.0271(8)
C(19)	0.2460(4)	0.2897(2)	0.8512(2)	0.0348(9)
C(20)	0.1177(5)	0.2362(2)	0.8610(2)	0.0397(9)
C(21)	–0.0101(4)	0.2668(2)	0.9026(2)	0.0311(8)
C(22)	–0.0129(4)	0.3471(2)	0.9362(2)	0.0334(9)
C(23)	0.1168(4)	0.4005(2)	0.9265(2)	0.0306(8)

Table 3. Bond lengths [Å] and angles [°] for mjh12.

Cl(1)–C(8)	1.781(3)	Cl(2)–C(8)	1.779(3)
O(1)–N(1)	1.231(4)	O(2)–N(1)	1.223(3)
O(3)–C(7)	1.420(4)	O(3)–H(3)	0.75(4)
O(4)–C(9)	1.444(3)	O(4)–C(17)	1.349(4)
O(5)–C(17)	1.199(4)	O(6)–N(2)	1.220(4)
O(7)–N(2)	1.231(4)	N(1)–C(3)	1.461(4)
N(2)–C(21)	1.471(4)	C(1)–H(1A)	0.950
C(1)–C(2)	1.375(4)	C(1)–C(6)	1.385(4)
C(2)–H(2A)	0.950	C(2)–C(3)	1.391(5)
C(3)–C(4)	1.377(5)	C(4)–H(4A)	0.950
C(4)–C(5)	1.379(4)	C(5)–H(5A)	0.950
C(5)–C(6)	1.390(4)	C(6)–C(7)	1.513(4)
C(7)–H(7A)	1.000	C(7)–C(8)	1.551(4)
C(8)–C(9)	1.541(4)	C(9)–H(9A)	1.000
C(9)–C(10)	1.505(5)	C(10)–C(11)	1.392(5)
C(10)–C(15)	1.392(5)	C(11)–H(11A)	0.950
C(11)–C(12)	1.378(5)	C(12)–H(12A)	0.950
C(12)–C(13)	1.379(5)	C(13)–C(14)	1.380(5)
C(13)–C(16)	1.510(5)	C(14)–H(14A)	0.950
C(14)–C(15)	1.382(5)	C(15)–H(15A)	0.950
C(16)–H(16A)	0.980	C(16)–H(16B)	0.980
C(16)–H(16C)	0.980	C(17)–C(18)	1.483(5)
C(18)–C(19)	1.394(5)	C(18)–C(23)	1.387(5)
C(19)–H(19A)	0.950	C(19)–C(20)	1.376(5)
C(20)–H(20A)	0.950	C(20)–C(21)	1.381(5)
C(21)–C(22)	1.370(5)	C(22)–H(22A)	0.950
C(22)–C(23)	1.383(5)	C(23)–H(23A)	0.950

C(7)–O(3)–H(3)	105(3)	C(9)–O(4)–C(17)	116.8(2)
O(1)–N(1)–O(2)	123.1(3)	O(1)–N(1)–C(3)	117.7(3)
O(2)–N(1)–C(3)	119.2(3)	O(6)–N(2)–O(7)	123.8(3)
O(6)–N(2)–C(21)	118.2(3)	O(7)–N(2)–C(21)	118.0(4)
H(1A)–C(1)–C(2)	119.5	H(1A)–C(1)–C(6)	119.5
C(2)–C(1)–C(6)	121.1(3)	C(1)–C(2)–H(2A)	121.0
C(1)–C(2)–C(3)	118.0(3)	H(2A)–C(2)–C(3)	121.0
N(1)–C(3)–C(2)	118.0(3)	N(1)–C(3)–C(4)	119.4(3)
C(2)–C(3)–C(4)	122.6(3)	C(3)–C(4)–H(4A)	120.9
C(3)–C(4)–C(5)	118.1(3)	H(4A)–C(4)–C(5)	120.9
C(4)–C(5)–H(5A)	119.5	C(4)–C(5)–C(6)	120.9(3)
H(5A)–C(5)–C(6)	119.5	C(1)–C(6)–C(5)	119.3(3)
C(1)–C(6)–C(7)	120.1(3)	C(5)–C(6)–C(7)	120.5(3)
O(3)–C(7)–C(6)	110.3(2)	O(3)–C(7)–H(7A)	108.3
O(3)–C(7)–C(8)	105.6(2)	C(6)–C(7)–H(7A)	108.3
C(6)–C(7)–C(8)	115.8(2)	H(7A)–C(7)–C(8)	108.3
Cl(1)–C(8)–Cl(2)	108.57(16)	Cl(1)–C(8)–C(7)	109.7(2)
Cl(1)–C(8)–C(9)	108.5(2)	Cl(2)–C(8)–C(7)	108.5(2)
Cl(2)–C(8)–C(9)	111.0(2)	C(7)–C(8)–C(9)	110.4(2)
O(4)–C(9)–C(8)	103.7(2)	O(4)–C(9)–H(9A)	108.2
O(4)–C(9)–C(10)	111.0(2)	C(8)–C(9)–H(9A)	108.2
C(8)–C(9)–C(10)	117.3(3)	H(9A)–C(9)–C(10)	108.2
C(9)–C(10)–C(11)	119.5(3)	C(9)–C(10)–C(15)	122.1(3)
C(11)–C(10)–C(15)	118.3(3)	C(10)–C(11)–H(11A)	119.8
C(10)–C(11)–C(12)	120.4(3)	H(11A)–C(11)–C(12)	119.8

C(11)–C(12)–H(12A)	119.1	C(11)–C(12)–C(13)	121.8(3)
H(12A)–C(12)–C(13)	119.1	C(12)–C(13)–C(14)	117.6(3)
C(12)–C(13)–C(16)	121.6(4)	C(14)–C(13)–C(16)	120.7(4)
C(13)–C(14)–H(14A)	119.1	C(13)–C(14)–C(15)	121.8(3)
H(14A)–C(14)–C(15)	119.1	C(10)–C(15)–C(14)	120.1(3)
C(10)–C(15)–H(15A)	120.0	C(14)–C(15)–H(15A)	120.0
C(13)–C(16)–H(16A)	109.5	C(13)–C(16)–H(16B)	109.5
C(13)–C(16)–H(16C)	109.5	H(16A)–C(16)–H(16B)	109.5
H(16A)–C(16)–H(16C)	109.5	H(16B)–C(16)–H(16C)	109.5
O(4)–C(17)–O(5)	122.6(3)	O(4)–C(17)–C(18)	112.8(3)
O(5)–C(17)–C(18)	124.6(3)	C(17)–C(18)–C(19)	118.6(3)
C(17)–C(18)–C(23)	121.3(3)	C(19)–C(18)–C(23)	120.1(3)
C(18)–C(19)–H(19A)	120.0	C(18)–C(19)–C(20)	119.9(3)
H(19A)–C(19)–C(20)	120.0	C(19)–C(20)–H(20A)	120.7
C(19)–C(20)–C(21)	118.5(3)	H(20A)–C(20)–C(21)	120.7
N(2)–C(21)–C(20)	118.7(3)	N(2)–C(21)–C(22)	118.4(3)
C(20)–C(21)–C(22)	122.9(3)	C(21)–C(22)–H(22A)	120.8
C(21)–C(22)–C(23)	118.3(3)	H(22A)–C(22)–C(23)	120.8
C(18)–C(23)–C(22)	120.2(3)	C(18)–C(23)–H(23A)	119.9
C(22)–C(23)–H(23A)	119.9		

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	0.0238(5)	0.0260(4)	0.0463(5)	0.0044(4)	–0.0071(4)	–0.0067(3)
Cl(2)	0.0313(5)	0.0328(5)	0.0280(4)	–0.0041(4)	0.0001(4)	0.0069(4)
O(1)	0.0267(15)	0.0430(15)	0.0573(17)	0.0030(13)	0.0078(13)	0.0090(12)
O(2)	0.0410(16)	0.0352(14)	0.0561(18)	0.0179(13)	0.0059(14)	0.0039(13)
O(3)	0.0291(15)	0.0314(14)	0.0282(14)	–0.0060(12)	–0.0002(12)	0.0036(12)
O(4)	0.0193(12)	0.0182(11)	0.0360(13)	–0.0021(10)	0.0016(10)	–0.0012(9)
O(5)	0.0352(16)	0.0316(14)	0.075(2)	–0.0158(13)	0.0194(14)	–0.0008(12)
O(6)	0.0467(19)	0.065(2)	0.066(2)	0.0042(16)	0.0132(16)	–0.0248(17)
O(7)	0.0564(19)	0.0383(17)	0.073(2)	0.0085(15)	–0.0150(16)	–0.0206(15)
N(1)	0.0266(18)	0.0318(16)	0.0360(17)	–0.0003(14)	–0.0005(15)	0.0040(14)
N(2)	0.047(2)	0.042(2)	0.0373(19)	0.0117(16)	–0.0085(17)	–0.0180(17)
C(1)	0.0203(18)	0.0288(18)	0.0284(18)	–0.0005(16)	–0.0007(14)	0.0005(15)
C(2)	0.0232(19)	0.0257(17)	0.0282(17)	0.0026(14)	–0.0003(16)	–0.0017(15)
C(3)	0.0204(19)	0.0245(17)	0.0286(17)	–0.0019(14)	–0.0030(15)	0.0024(15)
C(4)	0.0211(19)	0.035(2)	0.0297(18)	0.0007(15)	0.0049(15)	0.0017(16)
C(5)	0.0215(18)	0.0292(18)	0.0294(18)	0.0045(15)	0.0001(15)	–0.0028(16)
C(6)	0.0162(17)	0.0257(17)	0.0229(16)	–0.0029(14)	–0.0033(14)	0.0025(14)
C(7)	0.0215(18)	0.0199(16)	0.0247(17)	0.0000(14)	0.0010(14)	–0.0017(13)
C(8)	0.0196(18)	0.0216(16)	0.0279(18)	–0.0003(14)	0.0027(14)	–0.0024(13)
C(9)	0.0164(17)	0.0215(16)	0.0292(18)	–0.0015(13)	0.0020(14)	–0.0052(13)
C(10)	0.0209(18)	0.0193(17)	0.0339(19)	0.0000(15)	0.0020(15)	0.0032(14)
C(11)	0.023(2)	0.0300(19)	0.037(2)	0.0064(16)	0.0014(16)	–0.0019(15)
C(12)	0.0228(19)	0.0280(18)	0.052(2)	0.0022(18)	–0.0044(18)	0.0047(15)
C(13)	0.032(2)	0.030(2)	0.042(2)	–0.0085(17)	–0.0116(18)	0.0106(17)
C(14)	0.041(2)	0.038(2)	0.029(2)	0.0038(16)	–0.0019(18)	0.0094(19)
C(15)	0.027(2)	0.0326(19)	0.035(2)	0.0037(16)	0.0055(18)	0.0038(15)
C(16)	0.047(3)	0.046(2)	0.061(3)	–0.005(2)	–0.022(2)	0.015(2)
C(17)	0.0229(19)	0.0235(17)	0.037(2)	–0.0038(16)	0.0042(17)	–0.0001(14)
C(18)	0.027(2)	0.0223(17)	0.032(2)	0.0006(14)	–0.0036(15)	–0.0007(15)
C(19)	0.034(2)	0.0237(18)	0.046(2)	–0.0075(17)	0.0079(17)	–0.0003(16)
C(20)	0.049(2)	0.0262(18)	0.044(2)	–0.0006(18)	–0.004(2)	–0.0051(18)
C(21)	0.034(2)	0.0300(19)	0.0291(18)	0.0082(15)	–0.0048(17)	–0.0112(17)
C(22)	0.031(2)	0.035(2)	0.035(2)	–0.0017(16)	0.0036(16)	–0.0046(17)
C(23)	0.030(2)	0.0272(19)	0.035(2)	–0.0048(16)	0.0021(16)	–0.0027(16)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh12.

	x	y	z	U
H(1A)	0.3546	0.7966	0.7321	0.031
H(2A)	0.2189	0.9255	0.7095	0.031
H(4A)	–0.1298	0.8450	0.8548	0.034
H(5A)	0.0117	0.7180	0.8788	0.032
H(7A)	0.2030	0.6142	0.8305	0.026
H(9A)	0.5403	0.5590	0.8363	0.027
H(11A)	0.7952	0.6112	0.8865	0.036
H(12A)	0.9893	0.5941	0.9796	0.041
H(14A)	0.6811	0.4735	1.1193	0.043
H(15A)	0.4797	0.4987	1.0312	0.038
H(16A)	1.0843	0.5404	1.0989	0.077
H(16B)	0.9974	0.4535	1.1261	0.077
H(16C)	0.9564	0.5438	1.1671	0.077
H(19A)	0.3346	0.2705	0.8221	0.042
H(20A)	0.1169	0.1795	0.8396	0.048
H(22A)	–0.1017	0.3658	0.9655	0.040
H(23A)	0.1175	0.4566	0.9491	0.037
H(3)	0.310(5)	0.606(3)	0.730(2)	0.044(14)

Table 6. Torsion angles [°] for mjh12.

C(6)–C(1)–C(2)–C(3)	−0.9(5)	C(1)–C(2)–C(3)–N(1)	−178.7(3)
C(1)–C(2)–C(3)–C(4)	0.6(5)	O(1)–N(1)–C(3)–C(2)	164.9(3)
O(1)–N(1)–C(3)–C(4)	−14.5(5)	O(2)–N(1)–C(3)–C(2)	−15.4(4)
O(2)–N(1)–C(3)–C(4)	165.2(3)	N(1)–C(3)–C(4)–C(5)	179.5(3)
C(2)–C(3)–C(4)–C(5)	0.2(5)	C(3)–C(4)–C(5)–C(6)	−0.7(5)
C(2)–C(1)–C(6)–C(5)	0.4(5)	C(2)–C(1)–C(6)–C(7)	177.1(3)
C(4)–C(5)–C(6)–C(1)	0.4(5)	C(4)–C(5)–C(6)–C(7)	−176.2(3)
C(1)–C(6)–C(7)–O(3)	−30.4(4)	C(1)–C(6)–C(7)–C(8)	89.5(3)
C(5)–C(6)–C(7)–O(3)	146.3(3)	C(5)–C(6)–C(7)–C(8)	−93.9(3)
O(3)–C(7)–C(8)–Cl(1)	64.1(3)	O(3)–C(7)–C(8)–Cl(2)	−177.4(2)
O(3)–C(7)–C(8)–C(9)	−55.5(3)	C(6)–C(7)–C(8)–Cl(1)	−58.3(3)
C(6)–C(7)–C(8)–Cl(2)	60.2(3)	C(6)–C(7)–C(8)–C(9)	−177.9(3)
C(17)–O(4)–C(9)–C(8)	151.1(3)	C(17)–O(4)–C(9)–C(10)	−82.1(3)
Cl(1)–C(8)–C(9)–O(4)	−177.0(2)	Cl(1)–C(8)–C(9)–C(10)	60.3(3)
Cl(2)–C(8)–C(9)–O(4)	63.8(3)	Cl(2)–C(8)–C(9)–C(10)	−58.9(3)
C(7)–C(8)–C(9)–O(4)	−56.7(3)	C(7)–C(8)–C(9)–C(10)	−179.4(3)
O(4)–C(9)–C(10)–C(11)	156.3(3)	O(4)–C(9)–C(10)–C(15)	−20.9(4)
C(8)–C(9)–C(10)–C(11)	−84.8(4)	C(8)–C(9)–C(10)–C(15)	98.0(4)
C(9)–C(10)–C(11)–C(12)	−179.2(3)	C(15)–C(10)–C(11)–C(12)	−2.0(5)
C(10)–C(11)–C(12)–C(13)	2.8(5)	C(11)–C(12)–C(13)–C(14)	−1.2(5)
C(11)–C(12)–C(13)–C(16)	177.7(3)	C(12)–C(13)–C(14)–C(15)	−1.4(5)
C(16)–C(13)–C(14)–C(15)	179.8(3)	C(13)–C(14)–C(15)–C(10)	2.2(5)
C(9)–C(10)–C(15)–C(14)	176.7(3)	C(11)–C(10)–C(15)–C(14)	−0.5(5)
C(9)–O(4)–C(17)–O(5)	−1.5(5)	C(9)–O(4)–C(17)–C(18)	180.0(3)
O(4)–C(17)–C(18)–C(19)	174.1(3)	O(4)–C(17)–C(18)–C(23)	−4.1(5)
O(5)–C(17)–C(18)–C(19)	−4.3(5)	O(5)–C(17)–C(18)–C(23)	177.4(4)
C(17)–C(18)–C(19)–C(20)	−178.1(3)	C(23)–C(18)–C(19)–C(20)	0.2(5)
C(18)–C(19)–C(20)–C(21)	0.9(5)	C(19)–C(20)–C(21)–N(2)	178.7(3)
C(19)–C(20)–C(21)–C(22)	−1.8(5)	O(6)–N(2)–C(21)–C(20)	−168.4(3)
O(6)–N(2)–C(21)–C(22)	12.0(5)	O(7)–N(2)–C(21)–C(20)	10.0(5)
O(7)–N(2)–C(21)–C(22)	−169.6(3)	N(2)–C(21)–C(22)–C(23)	−179.0(3)
C(20)–C(21)–C(22)–C(23)	1.4(5)	C(21)–C(22)–C(23)–C(18)	−0.3(5)
C(17)–C(18)–C(23)–C(22)	177.7(3)	C(19)–C(18)–C(23)–C(22)	−0.5(5)

Table 7. Hydrogen bonds for mjh12 [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(3)–H(3)...O(1A)	0.75(4)	2.22(4)	2.906(4)	152(4)
O(3)–H(3)...O(7B)	0.75(4)	2.59(4)	3.112(4)	129(4)

Symmetry operations for equivalent atoms
A –x,y–1/2,–z+3/2 B –x,y+1/2,–z+3/2

Compound **4.4**

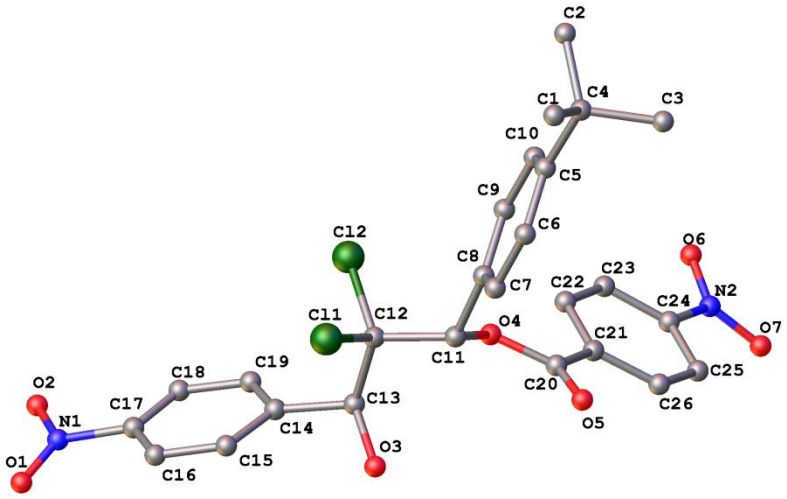

C2
C1
C4
C3
C10
C5
C9
C6
C12
C8
C7
O6
C23
C22
N2
C24
C11
C12
O4
C21
O7
C11
C25
O2
C18
C19
C20
C26
C17
C13
N1
C14
O5
O3
O1
C16
C15

Table 1. Crystal data and structure refinement for mjh83.

Identification code	mjh83	
Chemical formula (moiety)	$C_{27}H_{24}Cl_5N_2O_7$	
Chemical formula (total)	$C_{27}H_{24}Cl_5N_2O_7$	
Formula weight	665.73	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	monoclinic, P1n1	
Unit cell parameters	a = 6.7051(3) Å	α = 90°
	b = 14.1443(6) Å	β = 101.326(4)°
	c = 15.7774(6) Å	γ = 90°
Cell volume	1467.17(11) $Å^3$	
Z	2	
Calculated density	1.507 g/cm^3	
Absorption coefficient μ	0.543 mm^{-1}	
F(000)	682	
Crystal colour and size	colourless, 0.40 × 0.40 × 0.30 mm^3	
Reflections for cell refinement	5996 (θ range 3.0 to 28.6°)	
Data collection method	Oxford Diffraction Gemini A Ultra diffractometer thick-slice ω scans	
θ range for data collection	3.0 to 28.6°	
Index ranges	h −8 to 8, k −18 to 15, l −19 to 20	
Completeness to θ = 25.0°	99.8 %	
Reflections collected	9761	
Independent reflections	4882 (R_{int} = 0.0205)	
Reflections with $F^2>2\sigma$	4731	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.8121 and 0.8541	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0407, 1.3392	
Data / restraints / parameters	4882 / 2 / 372	
Final R indices [$F^2>2\sigma$]	R1 = 0.0385, wR2 = 0.0904	
R indices (all data)	R1 = 0.0399, wR2 = 0.0916	
Goodness-of-fit on F^2	1.043	
Absolute structure parameter	−0.03(5)	
Extinction coefficient	0.0059(9)	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	0.45 and −0.47 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh83. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	0.78729(10)	0.80622(5)	0.57580(5)	0.02659(17)
Cl(2)	0.36290(10)	0.79970(5)	0.49409(5)	0.02614(16)
N(1)	0.3827(9)	0.4951(3)	0.8053(3)	0.0765(16)
N(2)	–0.0554(3)	0.60918(16)	–0.01094(14)	0.0196(5)
O(1)	0.5158(9)	0.4677(4)	0.8626(2)	0.130(3)
O(2)	0.1972(8)	0.4875(2)	0.8051(3)	0.1043(18)
O(4)	0.5221(3)	0.73821(13)	0.33865(11)	0.0168(4)
O(5)	0.7596(3)	0.71804(17)	0.25826(14)	0.0313(5)
O(6)	–0.2284(3)	0.63294(17)	–0.00802(14)	0.0320(5)
O(7)	–0.0090(3)	0.56471(15)	–0.07045(13)	0.0277(5)
C(1)	0.9371(7)	1.2277(3)	0.3744(3)	0.0516(11)
C(2)	0.5662(7)	1.2376(2)	0.3147(3)	0.0477(10)
C(3)	0.7989(7)	1.1803(3)	0.2217(2)	0.0445(9)
C(4)	0.7582(5)	1.1797(2)	0.3139(2)	0.0286(7)
C(5)	0.7349(5)	1.0772(2)	0.34120(18)	0.0235(6)
C(6)	0.8991(5)	1.0237(2)	0.3800(2)	0.0300(7)
C(7)	0.8789(4)	0.9295(2)	0.4019(2)	0.0269(6)
C(8)	0.6897(4)	0.88579(19)	0.38570(17)	0.0193(5)
C(9)	0.5238(4)	0.9389(2)	0.3461(2)	0.0296(7)
C(10)	0.5469(5)	1.0318(2)	0.3244(2)	0.0343(8)
C(11)	0.6732(4)	0.78188(19)	0.40511(16)	0.0169(5)
C(12)	0.6093(4)	0.75430(19)	0.48991(16)	0.0173(5)
C(13)	0.6064(4)	0.64543(19)	0.50038(16)	0.0181(5)
C(14)	0.5463(4)	0.61169(18)	0.58265(17)	0.0184(5)
C(15)	0.6916(5)	0.5981(2)	0.65772(19)	0.0254(6)
C(16)	0.6390(6)	0.5611(2)	0.7308(2)	0.0378(8)
C(17)	0.4397(7)	0.5381(2)	0.7281(2)	0.0395(9)
C(18)	0.2906(5)	0.5516(2)	0.6562(3)	0.0378(8)
C(19)	0.3457(4)	0.5884(2)	0.5831(2)	0.0265(7)
C(20)	0.5848(4)	0.71398(19)	0.26586(17)	0.0195(5)
C(21)	0.4145(4)	0.6845(2)	0.19650(17)	0.0187(5)
C(22)	0.2129(4)	0.69436(19)	0.20504(17)	0.0185(5)
C(23)	0.0573(4)	0.6707(2)	0.13600(17)	0.0193(5)
C(24)	0.1093(4)	0.63587(19)	0.06183(16)	0.0176(5)
C(25)	0.3074(4)	0.6242(2)	0.05197(18)	0.0225(6)
C(26)	0.4594(4)	0.6499(2)	0.12039(19)	0.0233(6)
Cl(3)	1.8030(2)	0.08708(9)	0.59193(9)	0.0716(4)
Cl(4)	1.50012(19)	0.05793(10)	0.69446(8)	0.0680(4)
Cl(5)	1.3833(2)	0.12433(10)	0.51973(8)	0.0815(4)
C(27)	1.5523(8)	0.0519(3)	0.5905(3)	0.0574(12)
O(3)	0.8033(3)	0.61167(14)	0.49711(13)	0.0256(5)

Table 3. Bond lengths [Å] and angles [°] for mjh83.

Cl(1)–C(12)	1.779(2)	Cl(2)–C(12)	1.786(3)
N(1)–O(1)	1.202(7)	N(1)–O(2)	1.248(7)
N(1)–C(17)	1.477(5)	N(2)–O(6)	1.217(3)
N(2)–O(7)	1.220(3)	N(2)–C(24)	1.477(3)
O(4)–C(11)	1.446(3)	O(4)–C(20)	1.343(3)
O(5)–C(20)	1.203(3)	C(1)–H(1A)	0.980
C(1)–H(1B)	0.980	C(1)–H(1C)	0.980
C(1)–C(4)	1.537(4)	C(2)–H(2A)	0.980
C(2)–H(2B)	0.980	C(2)–H(2C)	0.980
C(2)–C(4)	1.528(5)	C(3)–H(3A)	0.980
C(3)–H(3B)	0.980	C(3)–H(3C)	0.980
C(3)–C(4)	1.533(5)	C(4)–C(5)	1.529(4)
C(5)–C(6)	1.377(4)	C(5)–C(10)	1.393(4)
C(6)–H(6A)	0.950	C(6)–C(7)	1.389(4)
C(7)–H(7A)	0.950	C(7)–C(8)	1.389(4)
C(8)–C(9)	1.385(4)	C(8)–C(11)	1.510(4)
C(9)–H(9A)	0.950	C(9)–C(10)	1.375(4)
C(10)–H(10A)	0.950	C(11)–H(11A)	1.000
C(11)–C(12)	1.533(4)	C(12)–C(13)	1.549(4)
C(13)–H(13A)	1.000	C(13)–C(14)	1.510(4)
C(13)–O(3)	1.414(3)	C(14)–C(15)	1.391(4)
C(14)–C(19)	1.386(4)	C(15)–H(15A)	0.950
C(15)–C(16)	1.374(5)	C(16)–H(16A)	0.950
C(16)–C(17)	1.368(6)	C(17)–C(18)	1.370(6)
C(18)–H(18A)	0.950	C(18)–C(19)	1.380(5)
C(19)–H(19A)	0.950	C(20)–C(21)	1.478(3)
C(21)–C(22)	1.391(4)	C(21)–C(26)	1.384(4)
C(22)–H(22A)	0.950	C(22)–C(23)	1.393(4)
C(23)–H(23A)	0.950	C(23)–C(24)	1.376(4)
C(24)–C(25)	1.377(4)	C(25)–H(25A)	0.950
C(25)–C(26)	1.380(4)	C(26)–H(26A)	0.950
Cl(3)–C(27)	1.749(5)	Cl(4)–C(27)	1.745(5)
Cl(5)–C(27)	1.756(5)	C(27)–H(27)	1.000

O(1)–N(1)–O(2)	124.5(4)	O(1)–N(1)–C(17)	118.6(5)
O(2)–N(1)–C(17)	116.9(5)	O(6)–N(2)–O(7)	124.1(2)
O(6)–N(2)–C(24)	118.2(2)	O(7)–N(2)–C(24)	117.7(2)
C(11)–O(4)–C(20)	115.9(2)	H(1A)–C(1)–H(1B)	109.5
H(1A)–C(1)–H(1C)	109.5	H(1A)–C(1)–C(4)	109.5
H(1B)–C(1)–H(1C)	109.5	H(1B)–C(1)–C(4)	109.5
H(1C)–C(1)–C(4)	109.5	H(2A)–C(2)–H(2B)	109.5
H(2A)–C(2)–H(2C)	109.5	H(2A)–C(2)–C(4)	109.5
H(2B)–C(2)–H(2C)	109.5	H(2B)–C(2)–C(4)	109.5
H(2C)–C(2)–C(4)	109.5	H(3A)–C(3)–H(3B)	109.5
H(3A)–C(3)–H(3C)	109.5	H(3A)–C(3)–C(4)	109.5
H(3B)–C(3)–H(3C)	109.5	H(3B)–C(3)–C(4)	109.5
H(3C)–C(3)–C(4)	109.5	C(1)–C(4)–C(2)	108.3(3)
C(1)–C(4)–C(3)	109.0(3)	C(1)–C(4)–C(5)	110.8(3)
C(2)–C(4)–C(3)	108.2(3)	C(2)–C(4)–C(5)	111.9(3)
C(3)–C(4)–C(5)	108.6(3)	C(4)–C(5)–C(6)	122.0(3)
C(4)–C(5)–C(10)	121.5(3)	C(6)–C(5)–C(10)	116.5(3)
C(5)–C(6)–H(6A)	119.0	C(5)–C(6)–C(7)	121.9(3)
H(6A)–C(6)–C(7)	119.0	C(6)–C(7)–H(7A)	119.6

C(6)–C(7)–C(8)	120.8(3)	H(7A)–C(7)–C(8)	119.6
C(7)–C(8)–C(9)	117.7(3)	C(7)–C(8)–C(11)	119.8(2)
C(9)–C(8)–C(11)	122.3(2)	C(8)–C(9)–H(9A)	119.6
C(8)–C(9)–C(10)	120.7(3)	H(9A)–C(9)–C(10)	119.6
C(5)–C(10)–C(9)	122.4(3)	C(5)–C(10)–H(10A)	118.8
C(9)–C(10)–H(10A)	118.8	O(4)–C(11)–C(8)	109.7(2)
O(4)–C(11)–H(11A)	108.1	O(4)–C(11)–C(12)	104.4(2)
C(8)–C(11)–H(11A)	108.1	C(8)–C(11)–C(12)	118.0(2)
H(11A)–C(11)–C(12)	108.1	Cl(1)–C(12)–Cl(2)	108.09(14)
Cl(1)–C(12)–C(11)	107.40(18)	Cl(1)–C(12)–C(13)	110.47(16)
Cl(2)–C(12)–C(11)	111.09(17)	Cl(2)–C(12)–C(13)	108.81(18)
C(11)–C(12)–C(13)	110.9(2)	C(12)–C(13)–H(13A)	108.4
C(12)–C(13)–C(14)	114.6(2)	C(12)–C(13)–O(3)	107.5(2)
H(13A)–C(13)–C(14)	108.4	H(13A)–C(13)–O(3)	108.4
C(14)–C(13)–O(3)	109.5(2)	C(13)–C(14)–C(15)	121.0(2)
C(13)–C(14)–C(19)	120.2(2)	C(15)–C(14)–C(19)	118.7(3)
C(14)–C(15)–H(15A)	119.5	C(14)–C(15)–C(16)	121.0(3)
H(15A)–C(15)–C(16)	119.5	C(15)–C(16)–H(16A)	120.8
C(15)–C(16)–C(17)	118.4(3)	H(16A)–C(16)–C(17)	120.8
N(1)–C(17)–C(16)	118.8(4)	N(1)–C(17)–C(18)	118.4(4)
C(16)–C(17)–C(18)	122.8(3)	C(17)–C(18)–H(18A)	120.9
C(17)–C(18)–C(19)	118.2(3)	H(18A)–C(18)–C(19)	120.9
C(14)–C(19)–C(18)	120.9(3)	C(14)–C(19)–H(19A)	119.5
C(18)–C(19)–H(19A)	119.5	O(4)–C(20)–O(5)	123.2(2)
O(4)–C(20)–C(21)	112.3(2)	O(5)–C(20)–C(21)	124.5(3)
C(20)–C(21)–C(22)	121.6(2)	C(20)–C(21)–C(26)	118.3(2)
C(22)–C(21)–C(26)	120.0(2)	C(21)–C(22)–H(22A)	120.2
C(21)–C(22)–C(23)	119.5(3)	H(22A)–C(22)–C(23)	120.2
C(22)–C(23)–H(23A)	120.8	C(22)–C(23)–C(24)	118.4(2)
H(23A)–C(23)–C(24)	120.8	N(2)–C(24)–C(23)	118.5(2)
N(2)–C(24)–C(25)	118.2(2)	C(23)–C(24)–C(25)	123.4(2)
C(24)–C(25)–H(25A)	121.3	C(24)–C(25)–C(26)	117.4(2)
H(25A)–C(25)–C(26)	121.3	C(21)–C(26)–C(25)	121.3(3)
C(21)–C(26)–H(26A)	119.4	C(25)–C(26)–H(26A)	119.4
Cl(3)–C(27)–Cl(4)	110.1(2)	Cl(3)–C(27)–Cl(5)	109.9(3)
Cl(3)–C(27)–H(27)	108.8	Cl(4)–C(27)–Cl(5)	110.2(3)
Cl(4)–C(27)–H(27)	108.8	Cl(5)–C(27)–H(27)	108.8

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh83. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	0.0373(4)	0.0226(3)	0.0163(3)	–0.0033(3)	–0.0036(3)	–0.0048(3)
Cl(2)	0.0270(3)	0.0268(4)	0.0263(3)	0.0038(3)	0.0093(3)	0.0108(3)
N(1)	0.170(5)	0.0288(18)	0.051(3)	–0.0171(17)	0.072(3)	–0.043(3)
N(2)	0.0251(11)	0.0187(11)	0.0143(10)	–0.0009(9)	0.0020(9)	–0.0007(9)
O(1)	0.240(6)	0.127(4)	0.0207(17)	0.0083(19)	0.017(3)	–0.129(4)
O(2)	0.181(4)	0.0366(18)	0.142(4)	0.003(2)	0.145(4)	–0.004(2)
O(4)	0.0178(8)	0.0209(10)	0.0114(8)	–0.0032(7)	0.0019(7)	–0.0036(7)
O(5)	0.0176(9)	0.0497(14)	0.0273(11)	–0.0125(10)	0.0059(8)	–0.0046(9)
O(6)	0.0201(10)	0.0475(14)	0.0263(11)	–0.0082(10)	–0.0007(9)	0.0034(9)
O(7)	0.0339(11)	0.0323(12)	0.0159(10)	–0.0064(9)	0.0027(8)	0.0008(9)
C(1)	0.073(3)	0.0246(17)	0.047(2)	0.0057(16)	–0.012(2)	–0.0181(18)
C(2)	0.066(2)	0.0210(17)	0.061(3)	0.0056(17)	0.023(2)	0.0087(17)
C(3)	0.081(3)	0.0263(17)	0.0306(18)	0.0086(14)	0.0209(18)	–0.0006(17)
C(4)	0.0426(17)	0.0178(14)	0.0245(15)	0.0028(12)	0.0042(13)	–0.0026(12)
C(5)	0.0368(15)	0.0178(14)	0.0158(13)	0.0001(11)	0.0052(11)	–0.0019(11)
C(6)	0.0304(15)	0.0216(15)	0.0372(17)	0.0015(13)	0.0047(13)	–0.0067(12)
C(7)	0.0219(13)	0.0201(14)	0.0363(16)	0.0013(13)	–0.0005(12)	–0.0012(11)
C(8)	0.0243(13)	0.0168(13)	0.0160(12)	–0.0009(10)	0.0021(10)	–0.0003(10)
C(9)	0.0232(14)	0.0240(15)	0.0377(17)	0.0081(13)	–0.0035(13)	–0.0025(11)
C(10)	0.0308(16)	0.0259(15)	0.0398(18)	0.0102(14)	–0.0091(14)	0.0003(13)
C(11)	0.0174(11)	0.0176(13)	0.0139(12)	–0.0023(10)	–0.0010(10)	–0.0009(10)
C(12)	0.0179(12)	0.0168(13)	0.0152(12)	–0.0031(10)	–0.0012(10)	0.0013(9)
C(13)	0.0228(12)	0.0174(13)	0.0143(12)	–0.0017(10)	0.0038(10)	0.0023(10)
C(14)	0.0251(13)	0.0128(12)	0.0185(13)	–0.0026(10)	0.0069(11)	0.0015(10)
C(15)	0.0318(15)	0.0217(14)	0.0210(14)	–0.0019(12)	0.0011(11)	–0.0057(12)
C(16)	0.072(3)	0.0237(16)	0.0159(14)	–0.0021(12)	0.0041(15)	–0.0126(16)
C(17)	0.081(3)	0.0168(15)	0.0310(18)	–0.0089(13)	0.0353(18)	–0.0139(16)
C(18)	0.0461(19)	0.0182(15)	0.058(2)	–0.0066(15)	0.0332(18)	–0.0060(13)
C(19)	0.0248(14)	0.0154(13)	0.0410(18)	–0.0039(13)	0.0103(13)	–0.0005(11)
C(20)	0.0209(12)	0.0201(13)	0.0177(13)	–0.0002(11)	0.0044(10)	–0.0004(10)
C(21)	0.0216(12)	0.0184(13)	0.0167(13)	–0.0016(10)	0.0051(10)	–0.0014(10)
C(22)	0.0197(12)	0.0212(14)	0.0148(12)	–0.0024(11)	0.0041(10)	–0.0012(10)
C(23)	0.0175(11)	0.0231(13)	0.0179(13)	–0.0009(11)	0.0050(10)	–0.0002(10)
C(24)	0.0203(12)	0.0171(13)	0.0144(12)	0.0004(10)	0.0008(10)	–0.0018(10)
C(25)	0.0264(13)	0.0249(14)	0.0184(13)	–0.0059(11)	0.0096(11)	0.0009(11)
C(26)	0.0180(12)	0.0292(16)	0.0240(14)	–0.0065(12)	0.0070(11)	–0.0020(11)
Cl(3)	0.0897(8)	0.0640(7)	0.0696(8)	–0.0188(6)	0.0361(7)	–0.0028(7)
Cl(4)	0.0738(7)	0.0779(8)	0.0512(6)	0.0196(6)	0.0093(5)	–0.0223(6)
Cl(5)	0.1167(11)	0.0659(8)	0.0457(6)	0.0028(6)	–0.0234(7)	–0.0019(7)
C(27)	0.087(3)	0.033(2)	0.047(2)	–0.0077(18)	–0.001(2)	–0.006(2)
O(3)	0.0312(10)	0.0242(11)	0.0250(10)	0.0021(9)	0.0144(8)	0.0105(8)

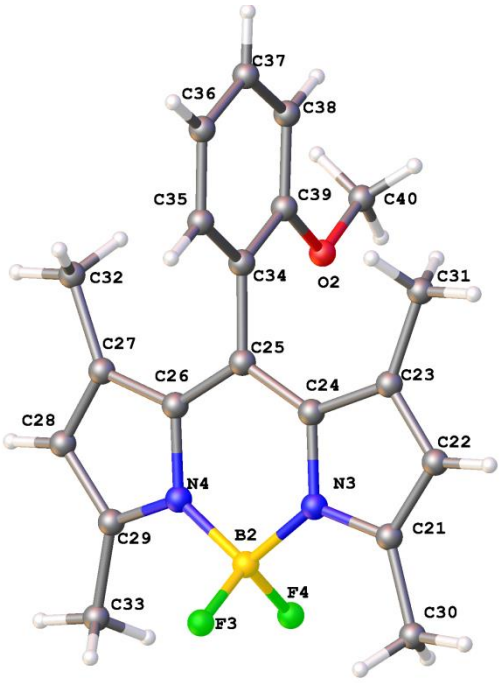
Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh83.

	x	y	z	U
H(1A)	0.9124	1.2274	0.4336	0.077
H(1B)	0.9499	1.2931	0.3557	0.077
H(1C)	1.0630	1.1933	0.3726	0.077
H(2A)	0.5373	1.2379	0.3732	0.072
H(2B)	0.4514	1.2094	0.2747	0.072
H(2C)	0.5869	1.3026	0.2967	0.072
H(3A)	0.6859	1.1495	0.1827	0.067
H(3B)	0.9254	1.1461	0.2204	0.067
H(3C)	0.8116	1.2457	0.2029	0.067
H(6A)	1.0302	1.0520	0.3921	0.036
H(7A)	0.9958	0.8946	0.4282	0.032
H(9A)	0.3927	0.9107	0.3338	0.035
H(10A)	0.4305	1.0663	0.2971	0.041
H(11A)	0.8075	0.7516	0.4041	0.020
H(13A)	0.5084	0.6184	0.4502	0.022
H(15A)	0.8292	0.6147	0.6585	0.031
H(16A)	0.7386	0.5516	0.7819	0.045
H(18A)	0.1529	0.5361	0.6567	0.045
H(19A)	0.2448	0.5978	0.5324	0.032
H(22A)	0.1816	0.7171	0.2576	0.022
H(23A)	–0.0813	0.6784	0.1400	0.023
H(25A)	0.3382	0.5994	0.0001	0.027
H(26A)	0.5975	0.6437	0.1151	0.028
H(27)	1.5349	–0.0149	0.5697	0.069

Table 6. Torsion angles [°] for mjh83.

C(1)–C(4)–C(5)–C(6)	−31.1(4)	C(1)–C(4)–C(5)–C(10)	151.9(4)
C(2)–C(4)–C(5)–C(6)	−152.1(3)	C(2)–C(4)–C(5)–C(10)	30.9(4)
C(3)–C(4)–C(5)–C(6)	88.5(4)	C(3)–C(4)–C(5)–C(10)	−88.5(4)
C(4)–C(5)–C(6)–C(7)	−177.6(3)	C(10)–C(5)–C(6)–C(7)	−0.4(5)
C(5)–C(6)–C(7)–C(8)	−0.4(5)	C(6)–C(7)–C(8)–C(9)	0.9(5)
C(6)–C(7)–C(8)–C(11)	176.3(3)	C(7)–C(8)–C(9)–C(10)	−0.5(5)
C(11)–C(8)–C(9)–C(10)	−175.8(3)	C(8)–C(9)–C(10)–C(5)	−0.3(5)
C(4)–C(5)–C(10)–C(9)	178.0(3)	C(6)–C(5)–C(10)–C(9)	0.8(5)
C(20)–O(4)–C(11)–C(8)	81.8(3)	C(20)–O(4)–C(11)–C(12)	−150.9(2)
C(7)–C(8)–C(11)–O(4)	−141.6(3)	C(7)–C(8)–C(11)–C(12)	99.1(3)
C(9)–C(8)–C(11)–O(4)	33.6(4)	C(9)–C(8)–C(11)–C(12)	−85.7(3)
O(4)–C(11)–C(12)–Cl(1)	−179.56(16)	O(4)–C(11)–C(12)–Cl(2)	−61.6(2)
O(4)–C(11)–C(12)–C(13)	59.6(2)	C(8)–C(11)–C(12)–Cl(1)	−57.5(3)
C(8)–C(11)–C(12)–Cl(2)	60.5(3)	C(8)–C(11)–C(12)–C(13)	−178.3(2)
Cl(1)–C(12)–C(13)–C(14)	60.6(3)	Cl(1)–C(12)–C(13)–O(3)	−61.3(2)
Cl(2)–C(12)–C(13)–C(14)	−57.9(2)	Cl(2)–C(12)–C(13)–O(3)	−179.80(17)
C(11)–C(12)–C(13)–C(14)	179.6(2)	C(11)–C(12)–C(13)–O(3)	57.7(2)
C(12)–C(13)–C(14)–C(15)	−89.4(3)	C(12)–C(13)–C(14)–C(19)	94.4(3)
O(3)–C(13)–C(14)–C(15)	31.4(3)	O(3)–C(13)–C(14)–C(19)	−144.8(2)
C(13)–C(14)–C(15)–C(16)	−175.3(3)	C(19)–C(14)–C(15)–C(16)	0.9(4)
C(14)–C(15)–C(16)–C(17)	−0.3(5)	C(15)–C(16)–C(17)–N(1)	177.9(3)
C(15)–C(16)–C(17)–C(18)	−0.8(5)	O(1)–N(1)–C(17)–C(16)	−11.8(5)
O(1)–N(1)–C(17)–C(18)	166.9(4)	O(2)–N(1)–C(17)–C(16)	170.2(3)
O(2)–N(1)–C(17)–C(18)	−11.1(5)	N(1)–C(17)–C(18)–C(19)	−177.5(3)
C(16)–C(17)–C(18)–C(19)	1.2(5)	C(17)–C(18)–C(19)–C(14)	−0.5(4)
C(13)–C(14)–C(19)–C(18)	175.7(3)	C(15)–C(14)–C(19)–C(18)	−0.6(4)
C(11)–O(4)–C(20)–O(5)	7.9(4)	C(11)–O(4)–C(20)–C(21)	−170.7(2)
O(4)–C(20)–C(21)–C(22)	8.1(4)	O(4)–C(20)–C(21)–C(26)	−174.5(3)
O(5)–C(20)–C(21)–C(22)	−170.5(3)	O(5)–C(20)–C(21)–C(26)	6.9(4)
C(20)–C(21)–C(22)–C(23)	176.3(2)	C(26)–C(21)–C(22)–C(23)	−1.1(4)
C(21)–C(22)–C(23)–C(24)	1.6(4)	C(22)–C(23)–C(24)–N(2)	179.0(2)
C(22)–C(23)–C(24)–C(25)	−0.8(4)	O(6)–N(2)–C(24)–C(23)	11.6(4)
O(6)–N(2)–C(24)–C(25)	−168.6(3)	O(7)–N(2)–C(24)–C(23)	−168.5(3)
O(7)–N(2)–C(24)–C(25)	11.2(4)	N(2)–C(24)–C(25)–C(26)	179.7(3)
C(23)–C(24)–C(25)–C(26)	−0.6(4)	C(24)–C(25)–C(26)–C(21)	1.1(4)
C(20)–C(21)–C(26)–C(25)	−177.7(3)	C(22)–C(21)–C(26)–C(25)	−0.3(5)

Compound **6.16**



An example of a molecule from the crystal structure. There are 9 independent molecules in the asymmetric unit.

Table 1. Crystal data and structure refinement for mjh120048.

Identification code	mjh120048	
Chemical formula (moiety)	$C_{20}H_{21}BF_2N_2O$	
Chemical formula (total)	$C_{20}H_{21}BF_2N_2O$	
Formula weight	354.20	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	monoclinic, $P12_1/c1$	
Unit cell parameters	a = 32.5037(11) Å	α = 90°
	b = 13.1260(7) Å	β = 98.807(3)°
	c = 38.8961(12) Å	γ = 90°
Cell volume	16399.1(12) $Å^3$	
Z	36	
Calculated density	1.291 g/cm^3	
Absorption coefficient μ	0.093 mm^{-1}	
F(000)	6696	
Crystal colour and size	red, 0.34 × 0.20 × 0.20 mm^3	
Reflections for cell refinement	10197 (θ range 2.9 to 28.5°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	3.0 to 25.0°	
Index ranges	h −38 to 36, k −15 to 11, l −46 to 46	
Completeness to θ = 25.0°	99.7 %	
Reflections collected	118293	
Independent reflections	28828 (R_{int} = 0.0676)	
Reflections with $F^2>2\sigma$	8206	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.9690 and 0.9816	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0636, 3.7348	
Data / restraints / parameters	28828 / 0 / 2143	
Final R indices [$F^2>2\sigma$]	R1 = 0.0581, wR2 = 0.1397	
R indices (all data)	R1 = 0.1730, wR2 = 0.2050	
Goodness-of-fit on F^2	1.017	
Extinction coefficient	0.00030(3)	
Largest and mean shift/su	0.114 and 0.022	
Largest diff. peak and hole	0.58 and −0.25 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh12. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
C(1)	–0.04135(16)	–0.5594(5)	0.57382(14)	0.0316(15)
B(1)	–0.03890(18)	–0.6783(6)	0.52159(18)	0.0305(17)
B(2)	–0.29389(17)	–0.3215(6)	0.47836(17)	0.0299(17)
B(3)	0.48298(16)	0.6013(6)	0.14402(15)	0.0229(16)
B(4)	0.24224(17)	0.0739(6)	0.22133(15)	0.0236(16)
B(5)	0.18433(17)	0.1011(6)	0.35628(17)	0.0273(17)
B(6)	0.09144(18)	0.5723(6)	0.27862(18)	0.0319(18)
B(7)	0.37294(18)	0.6800(6)	0.47864(16)	0.0284(17)
B(8)	0.42500(17)	0.5718(5)	0.27886(15)	0.0214(15)
B(9)	0.14975(17)	0.5997(6)	0.14387(16)	0.0270(17)
O(1)	–0.19063(10)	–0.6061(4)	0.51604(11)	0.0447(12)
O(2)	–0.14290(10)	–0.3947(4)	0.48406(11)	0.0443(12)
O(3)	0.63720(10)	0.5941(4)	0.16641(9)	0.0363(11)
O(4)	0.39982(9)	0.0633(4)	0.24479(9)	0.0344(11)
O(5)	0.02996(12)	0.0921(4)	0.33348(10)	0.0416(11)
O(6)	–0.06662(11)	0.5632(3)	0.25501(10)	0.0363(11)
O(7)	0.52419(10)	0.6056(4)	0.48408(11)	0.0423(12)
O(8)	0.26690(10)	0.5640(4)	0.25489(9)	0.0369(11)
O(9)	0.30363(10)	0.5924(4)	0.16647(10)	0.0408(12)
F(1)	–0.00394(9)	–0.7333(3)	0.53458(9)	0.0498(10)
F(2)	–0.02878(10)	–0.6037(3)	0.49935(9)	0.0475(10)
F(3)	–0.32934(8)	–0.2669(3)	0.46509(9)	0.0492(11)
F(4)	–0.30467(10)	–0.3962(3)	0.50055(8)	0.0449(9)
F(5)	0.44341(7)	0.5823(3)	0.12466(7)	0.0350(9)
F(6)	0.47777(9)	0.6454(3)	0.17525(8)	0.0396(9)
F(7)	0.23244(10)	0.0348(3)	0.25236(8)	0.0444(10)
F(8)	0.20545(8)	0.1013(3)	0.19999(8)	0.0393(9)
F(9)	0.22306(8)	0.0826(3)	0.37546(8)	0.0355(9)
F(10)	0.18901(9)	0.1452(3)	0.32450(8)	0.0425(9)
F(11)	0.12777(8)	0.6016(3)	0.29997(9)	0.0413(9)
F(12)	0.10093(10)	0.5348(3)	0.24761(9)	0.0474(10)
F(13)	0.33768(8)	0.7333(3)	0.46527(9)	0.0484(10)
F(14)	0.36197(10)	0.6034(3)	0.50068(8)	0.0476(10)
F(15)	0.46142(7)	0.6012(3)	0.29981(8)	0.0394(9)
F(16)	0.43437(9)	0.5347(3)	0.24766(8)	0.0426(10)
F(17)	0.11028(8)	0.5825(3)	0.12467(8)	0.0361(9)
F(18)	0.14472(9)	0.6448(3)	0.17539(8)	0.0390(9)
N(1)	–0.05923(12)	–0.6307(4)	0.55129(11)	0.0240(11)
N(2)	–0.07184(14)	–0.7490(4)	0.50172(12)	0.0338(13)
N(3)	–0.26112(13)	–0.2505(4)	0.49838(11)	0.0318(13)
N(4)	–0.27428(11)	–0.3690(4)	0.44877(10)	0.0242(11)
N(5)	0.50773(12)	0.6720(4)	0.12337(11)	0.0261(12)
N(6)	0.50695(11)	0.5006(4)	0.14964(10)	0.0208(11)
N(7)	0.26452(12)	–0.0090(4)	0.20279(10)	0.0252(12)
N(8)	0.27114(11)	0.1653(4)	0.22806(10)	0.0200(11)
N(9)	0.15978(12)	0.0008(4)	0.35022(10)	0.0229(11)
N(10)	0.15845(12)	0.1721(4)	0.37673(11)	0.0260(11)
N(11)	0.06187(12)	0.6647(4)	0.27186(11)	0.0258(12)
N(12)	0.06859(12)	0.4905(4)	0.29683(11)	0.0265(11)

N(13)	0.39211(11)	0.6294(4)	0.44890(10)	0.0236(12)
N(14)	0.40550(12)	0.7501(4)	0.49853(11)	0.0307(13)
N(15)	0.40192(11)	0.4920(4)	0.29731(10)	0.0223(11)
N(16)	0.39578(11)	0.6641(4)	0.27191(10)	0.0226(11)
N(17)	0.17465(12)	0.6729(4)	0.12328(11)	0.0256(12)
N(18)	0.17405(12)	0.4998(4)	0.14984(10)	0.0245(11)
C(2)	–0.06876(17)	–0.5368(5)	0.59690(14)	0.0322(15)
C(3)	–0.09751(15)	–0.6555(4)	0.55972(13)	0.0216(13)
C(4)	–0.10374(16)	–0.5969(5)	0.58954(13)	0.0259(14)
C(5)	–0.12388(14)	–0.7235(4)	0.53906(13)	0.0220(13)
C(6)	–0.11170(16)	–0.7701(5)	0.51015(14)	0.0262(14)
C(7)	–0.13247(18)	–0.8366(5)	0.48462(15)	0.0387(17)
C(8)	–0.1055(2)	–0.8541(6)	0.46112(16)	0.053(2)
C(10)	–0.00058(18)	–0.5122(6)	0.57050(16)	0.0482(19)
C(11)	–0.13981(17)	–0.5974(5)	0.60884(15)	0.0392(17)
C(12)	–0.17645(17)	–0.8743(6)	0.48105(16)	0.0453(18)
C(14)	–0.16586(15)	–0.7481(5)	0.54825(13)	0.0243(14)
C(15)	–0.17256(15)	–0.8326(5)	0.56809(13)	0.0257(14)
C(16)	–0.21157(15)	–0.8562(5)	0.57541(14)	0.0337(16)
C(17)	–0.24456(16)	–0.7952(6)	0.56200(15)	0.0375(17)
C(18)	–0.23891(16)	–0.7099(5)	0.54180(15)	0.0350(16)
C(19)	–0.20011(16)	–0.6868(5)	0.53480(14)	0.0297(14)
C(20)	–0.22387(18)	–0.5359(6)	0.5037(2)	0.067(3)
C(21)	–0.26459(19)	–0.1992(6)	0.52805(16)	0.0440(18)
C(22)	–0.2275(2)	–0.1451(6)	0.53858(16)	0.051(2)
C(23)	–0.20037(18)	–0.1645(5)	0.51552(15)	0.0395(17)
C(24)	–0.22195(15)	–0.2313(5)	0.48958(13)	0.0270(14)
C(25)	–0.20944(15)	–0.2748(5)	0.46043(13)	0.0235(13)
C(26)	–0.23569(13)	–0.3432(5)	0.43973(13)	0.0208(13)
C(27)	–0.22977(15)	–0.4027(5)	0.41043(13)	0.0262(14)
C(28)	–0.26461(16)	–0.4616(5)	0.40246(14)	0.0333(16)
C(29)	–0.29168(14)	–0.4411(5)	0.42653(13)	0.0256(14)
C(30)	–0.3033(2)	–0.2034(6)	0.54460(18)	0.067(2)
C(31)	–0.15696(18)	–0.1256(6)	0.51921(16)	0.0476(18)
C(32)	–0.19311(16)	–0.4040(5)	0.39169(14)	0.0350(16)
C(33)	–0.33299(15)	–0.4883(6)	0.42911(15)	0.0431(19)
C(34)	–0.16771(15)	–0.2517(5)	0.45204(13)	0.0230(13)
C(35)	–0.16107(16)	–0.1681(5)	0.43195(13)	0.0317(15)
C(36)	–0.12200(16)	–0.1447(5)	0.42483(14)	0.0335(16)
C(37)	–0.08851(16)	–0.2047(5)	0.43809(15)	0.0380(17)
C(38)	–0.09398(16)	–0.2888(5)	0.45795(15)	0.0361(16)
C(39)	–0.13389(15)	–0.3128(5)	0.46475(14)	0.0309(15)
C(40)	–0.10928(18)	–0.4630(6)	0.4957(2)	0.067(3)
C(41)	0.49720(15)	0.7670(6)	0.11174(15)	0.0342(16)
C(42)	0.52892(15)	0.8062(5)	0.09525(14)	0.0340(16)
C(43)	0.55977(14)	0.7360(5)	0.09678(13)	0.0275(15)
C(44)	0.54756(13)	0.6499(5)	0.11464(12)	0.0210(13)
C(45)	0.56514(13)	0.5561(5)	0.12253(12)	0.0201(13)
C(46)	0.54614(13)	0.4809(5)	0.13992(12)	0.0192(13)
C(47)	0.55830(13)	0.3811(5)	0.15018(12)	0.0234(14)
C(48)	0.52618(15)	0.3415(5)	0.16640(12)	0.0254(14)
C(49)	0.49540(15)	0.4163(5)	0.16588(12)	0.0268(15)

C(50)	0.45690(16)	0.8166(6)	0.11654(17)	0.0448(18)
C(51)	0.59981(15)	0.7517(5)	0.08227(15)	0.0343(16)
C(52)	0.59607(14)	0.3212(5)	0.14513(13)	0.0283(14)
C(53)	0.45515(15)	0.4086(5)	0.17966(14)	0.0344(16)
C(54)	0.60716(14)	0.5321(5)	0.11270(13)	0.0242(14)
C(55)	0.60968(16)	0.4873(6)	0.08085(15)	0.0380(17)
C(56)	0.64874(17)	0.4613(6)	0.07205(18)	0.0478(19)
C(57)	0.68383(17)	0.4822(6)	0.09556(17)	0.0474(19)
C(58)	0.68180(15)	0.5266(5)	0.12744(16)	0.0388(17)
C(59)	0.64252(14)	0.5509(5)	0.13585(14)	0.0266(14)
C(60)	0.67191(17)	0.6025(6)	0.19357(16)	0.0480(19)
C(61)	0.25012(15)	–0.1023(5)	0.19288(14)	0.0263(14)
C(62)	0.28012(16)	–0.1551(5)	0.17773(13)	0.0313(15)
C(63)	0.31444(15)	–0.0914(5)	0.17790(13)	0.0282(15)
C(64)	0.30461(14)	0.0016(5)	0.19371(12)	0.0210(13)
C(65)	0.32645(14)	0.0911(5)	0.20078(12)	0.0191(13)
C(66)	0.31058(13)	0.1724(4)	0.21757(11)	0.0163(12)
C(67)	0.32621(15)	0.2715(5)	0.22699(12)	0.0233(13)
C(68)	0.29660(15)	0.3197(5)	0.24274(12)	0.0263(14)
C(70)	0.20836(17)	–0.1375(6)	0.19917(15)	0.0419(17)
C(71)	0.35355(15)	–0.1206(5)	0.16507(13)	0.0316(15)
C(72)	0.36711(15)	0.3172(5)	0.22190(14)	0.0309(15)
C(73)	0.22449(15)	0.2714(5)	0.25879(14)	0.0350(16)
C(74)	0.36806(13)	0.1029(5)	0.18905(12)	0.0210(13)
C(75)	0.36998(16)	0.1324(5)	0.15505(13)	0.0311(15)
C(76)	0.40799(16)	0.1401(6)	0.14346(14)	0.046(2)
C(69)	0.26308(15)	0.2523(5)	0.24330(12)	0.0266(15)
C(77)	0.44418(17)	0.1217(6)	0.16622(16)	0.050(2)
C(78)	0.44280(14)	0.0948(5)	0.19990(16)	0.0380(18)
C(79)	0.40459(14)	0.0860(5)	0.21172(13)	0.0269(15)
C(80)	0.43651(15)	0.0613(6)	0.27073(14)	0.047(2)
C(81)	0.17148(15)	–0.0838(5)	0.33428(13)	0.0260(14)
C(82)	0.14017(16)	–0.1582(5)	0.33380(13)	0.0290(14)
C(83)	0.10884(17)	–0.1206(5)	0.34954(14)	0.0293(14)
C(84)	0.12095(15)	–0.0192(5)	0.36040(13)	0.0247(14)
C(85)	0.10057(14)	0.0552(5)	0.37734(13)	0.0219(13)
C(86)	0.11978(14)	0.1490(5)	0.38559(14)	0.0246(14)
C(87)	0.10607(16)	0.2364(5)	0.40330(14)	0.0295(15)
C(88)	0.13815(18)	0.3055(5)	0.40476(16)	0.0399(16)
C(89)	0.16988(16)	0.2646(5)	0.38827(15)	0.0331(15)
C(90)	0.21111(16)	–0.0923(5)	0.32044(16)	0.0412(17)
C(91)	0.07076(16)	–0.1778(5)	0.35490(15)	0.0344(15)
C(92)	0.06684(16)	0.2496(5)	0.41822(15)	0.0381(16)
C(93)	0.20964(17)	0.3151(6)	0.38285(19)	0.0510(19)
C(94)	0.05966(15)	0.0314(4)	0.38740(14)	0.0263(14)
C(95)	0.05670(18)	–0.0129(5)	0.41938(16)	0.0385(16)
C(96)	0.0176(2)	–0.0385(5)	0.42744(18)	0.0500(19)
C(97)	–0.0166(2)	–0.0188(6)	0.4044(2)	0.054(2)
C(98)	–0.01515(17)	0.0262(5)	0.37287(18)	0.0428(18)
C(99)	0.02388(17)	0.0505(5)	0.36390(15)	0.0334(15)
C(100)	–0.00555(18)	0.1015(6)	0.30641(17)	0.0493(19)
C(101)	0.07034(16)	0.7541(5)	0.25639(14)	0.0277(14)
C(102)	0.03689(16)	0.8194(5)	0.25711(14)	0.0340(15)
C(103)	0.00663(15)	0.7716(5)	0.27256(13)	0.0251(14)

C(104)	0.02327(14)	0.6727(5)	0.28237(13)	0.0236(14)
C(105)	0.00642(14)	0.5928(5)	0.29923(13)	0.0230(13)
C(106)	0.02913(16)	0.5010(5)	0.30615(13)	0.0266(14)
C(107)	0.01877(16)	0.4087(5)	0.32173(13)	0.0278(14)
C(108)	0.05324(17)	0.3467(5)	0.32196(14)	0.0354(16)
C(109)	0.08339(16)	0.3979(5)	0.30697(15)	0.0321(15)
C(110)	0.10909(17)	0.7695(5)	0.24182(15)	0.0393(17)
C(111)	–0.03391(15)	0.8171(5)	0.27789(14)	0.0309(14)
C(112)	–0.01979(16)	0.3787(5)	0.33570(15)	0.0374(16)
C(113)	0.12543(17)	0.3612(6)	0.30174(17)	0.0474(19)
C(114)	–0.03426(15)	0.6036(5)	0.31125(14)	0.0258(13)
C(115)	–0.03652(17)	0.6324(5)	0.34491(14)	0.0372(17)
C(116)	–0.07550(19)	0.6405(6)	0.35613(17)	0.0479(19)
C(117)	–0.11073(18)	0.6212(5)	0.33335(16)	0.0405(17)
C(118)	–0.10932(17)	0.5950(5)	0.29973(16)	0.0386(17)
C(119)	–0.07158(16)	0.5861(5)	0.28824(15)	0.0292(14)
C(120)	–0.10286(18)	0.5613(6)	0.22907(16)	0.051(2)
C(121)	0.37533(15)	0.5587(5)	0.42666(13)	0.0326(16)
C(122)	0.40179(15)	0.5380(5)	0.40243(13)	0.0321(16)
C(123)	0.43708(14)	0.5968(5)	0.41082(13)	0.0282(15)
C(124)	0.43167(13)	0.6566(5)	0.44006(12)	0.0209(14)
C(125)	0.45712(14)	0.7238(5)	0.46046(12)	0.0216(14)
C(126)	0.44485(15)	0.7708(5)	0.48983(13)	0.0278(15)
C(127)	0.46632(17)	0.8362(6)	0.51557(14)	0.0371(17)
C(128)	0.4388(2)	0.8551(6)	0.53817(17)	0.053(2)
C(129)	0.40221(19)	0.8027(7)	0.52789(16)	0.052(2)
C(130)	0.33418(15)	0.5116(6)	0.42942(15)	0.0401(17)
C(131)	0.47376(15)	0.5967(5)	0.39133(14)	0.0359(17)
C(132)	0.51006(16)	0.8748(6)	0.51943(16)	0.048(2)
C(133)	0.3639(2)	0.7957(8)	0.54457(19)	0.079(3)
C(134)	0.49927(13)	0.7490(5)	0.45199(13)	0.0228(14)
C(135)	0.50525(14)	0.8322(5)	0.43171(13)	0.0248(14)
C(136)	0.54468(15)	0.8561(5)	0.42499(14)	0.0323(16)
C(137)	0.57793(15)	0.7963(5)	0.43872(14)	0.0325(16)
C(138)	0.57251(14)	0.7123(5)	0.45862(14)	0.0338(17)
C(139)	0.53309(14)	0.6867(5)	0.46500(14)	0.0290(15)
C(140)	0.55674(17)	0.5374(6)	0.4965(2)	0.063(2)
C(141)	0.41634(16)	0.3976(5)	0.30685(13)	0.0302(15)
C(142)	0.38640(16)	0.3461(5)	0.32231(13)	0.0280(14)
C(143)	0.35250(15)	0.4069(5)	0.32190(13)	0.0243(13)
C(144)	0.36186(13)	0.5010(5)	0.30601(11)	0.0199(13)
C(145)	0.34027(14)	0.5918(5)	0.29904(12)	0.0196(13)
C(146)	0.35617(14)	0.6739(5)	0.28235(12)	0.0218(14)
C(147)	0.34048(15)	0.7713(5)	0.27322(13)	0.0255(14)
C(148)	0.37028(15)	0.8202(5)	0.25739(12)	0.0245(14)
C(149)	0.40346(15)	0.7536(5)	0.25692(12)	0.0235(14)
C(150)	0.45880(15)	0.3610(6)	0.30145(17)	0.0431(18)
C(151)	0.31299(16)	0.3787(6)	0.33504(14)	0.0357(16)
C(152)	0.29928(16)	0.8171(6)	0.27763(15)	0.0404(17)
C(154)	0.29902(14)	0.6041(5)	0.31136(14)	0.0269(14)
C(153)	0.44283(15)	0.7714(6)	0.24173(14)	0.0358(17)
C(155)	0.29679(16)	0.6324(5)	0.34498(13)	0.0315(16)
C(156)	0.25864(18)	0.6418(6)	0.35670(16)	0.0460(19)
C(157)	0.22282(17)	0.6214(6)	0.33399(16)	0.047(2)

C(158)	0.22402(16)	0.5948(5)	0.29959(15)	0.0357(16)
C(159)	0.26206(15)	0.5873(5)	0.28807(14)	0.0276(14)
C(160)	0.23031(16)	0.5599(6)	0.22916(15)	0.0451(18)
C(161)	0.16375(16)	0.7674(5)	0.11151(15)	0.0318(15)
C(162)	0.19554(16)	0.8082(5)	0.09512(15)	0.0350(15)
C(163)	0.22720(16)	0.7365(5)	0.09661(14)	0.0293(14)
C(164)	0.21412(15)	0.6512(5)	0.11429(13)	0.0233(13)
C(165)	0.23208(14)	0.5557(5)	0.12267(13)	0.0212(13)
C(166)	0.21281(14)	0.4810(5)	0.13969(12)	0.0210(13)
C(167)	0.22481(15)	0.3799(5)	0.15031(13)	0.0239(14)
C(168)	0.19276(16)	0.3425(5)	0.16623(13)	0.0301(15)
C(169)	0.16249(16)	0.4158(5)	0.16572(13)	0.0266(14)
C(170)	0.12391(17)	0.8153(5)	0.11671(18)	0.0473(18)
C(171)	0.26683(16)	0.7501(5)	0.08215(15)	0.0375(17)
C(172)	0.26286(15)	0.3217(5)	0.14522(14)	0.0342(15)
C(173)	0.12199(17)	0.4086(5)	0.17975(15)	0.0403(17)
C(174)	0.27369(14)	0.5316(5)	0.11267(14)	0.0258(14)
C(175)	0.27660(17)	0.4881(5)	0.08052(14)	0.0359(16)
C(176)	0.31580(17)	0.4606(6)	0.07254(17)	0.0476(19)
C(177)	0.35035(18)	0.4822(6)	0.09577(19)	0.0486(19)
C(178)	0.34858(16)	0.5265(6)	0.12740(19)	0.0459(19)
C(179)	0.31002(15)	0.5511(5)	0.13618(14)	0.0309(15)
C(180)	0.33861(17)	0.6019(6)	0.19359(15)	0.053(2)
C(9)	–0.06862(19)	–0.7993(6)	0.47239(17)	0.0489(18)
C(13)	–0.0304(2)	–0.7951(7)	0.45516(19)	0.073(2)

Table 3. Bond lengths [Å] and angles [°] for mjh12.

C(1)–N(1)	1.352(7)	C(1)–C(2)	1.390(7)
C(1)–C(10)	1.486(8)	B(1)–F(1)	1.376(7)
B(1)–F(2)	1.378(8)	B(1)–N(1)	1.547(8)
B(1)–N(2)	1.534(8)	B(2)–F(3)	1.387(7)
B(2)–F(4)	1.386(8)	B(2)–N(3)	1.535(9)
B(2)–N(4)	1.531(8)	B(3)–F(5)	1.410(6)
B(3)–F(6)	1.379(6)	B(3)–N(5)	1.533(8)
B(3)–N(6)	1.533(8)	B(4)–F(7)	1.393(6)
B(4)–F(8)	1.394(6)	B(4)–N(7)	1.546(8)
B(4)–N(8)	1.521(8)	B(5)–F(9)	1.383(7)
B(5)–F(10)	1.394(7)	B(5)–N(9)	1.539(8)
B(5)–N(10)	1.554(8)	B(6)–F(11)	1.390(7)
B(6)–F(12)	1.381(7)	B(6)–N(11)	1.545(9)
B(6)–N(12)	1.538(8)	B(7)–F(13)	1.375(7)
B(7)–F(14)	1.402(8)	B(7)–N(13)	1.545(7)
B(7)–N(14)	1.521(8)	B(8)–F(15)	1.386(6)
B(8)–F(16)	1.384(6)	B(8)–N(15)	1.530(8)
B(8)–N(16)	1.538(8)	B(9)–F(17)	1.400(6)
B(9)–F(18)	1.394(7)	B(9)–N(17)	1.555(8)
B(9)–N(18)	1.531(9)	O(1)–C(19)	1.348(7)
O(1)–C(20)	1.445(7)	O(2)–C(39)	1.369(7)
O(2)–C(40)	1.433(7)	O(3)–C(59)	1.352(6)
O(3)–C(60)	1.427(6)	O(4)–C(79)	1.352(6)
O(4)–C(80)	1.440(6)	O(5)–C(99)	1.345(7)
O(5)–C(10)	1.443(6)	O(6)–C(119)	1.360(6)
O(6)–C(120)	1.429(6)	O(7)–C(139)	1.354(7)
O(7)–C(140)	1.414(7)	O(8)–C(159)	1.359(6)
O(8)–C(160)	1.433(6)	O(9)–C(179)	1.342(6)
O(9)–C(180)	1.433(6)	N(1)–C(3)	1.374(6)
N(2)–C(6)	1.411(6)	N(2)–C(9)	1.336(8)
N(3)–C(21)	1.356(7)	N(3)–C(24)	1.391(6)
N(4)–C(26)	1.395(6)	N(4)–C(29)	1.348(7)
N(5)–C(41)	1.352(8)	N(5)–C(44)	1.418(6)
N(6)–C(46)	1.407(6)	N(6)–C(49)	1.355(7)
N(7)–C(61)	1.346(7)	N(7)–C(64)	1.408(6)
N(8)–C(66)	1.407(6)	N(8)–C(69)	1.330(7)
N(9)–C(81)	1.354(7)	N(9)–C(84)	1.404(6)
N(10)–C(86)	1.387(6)	N(10)–C(89)	1.328(7)
N(11)–C(101)	1.365(7)	N(11)–C(104)	1.382(6)
N(12)–C(106)	1.392(6)	N(12)–C(109)	1.345(7)
N(13)–C(121)	1.328(7)	N(13)–C(124)	1.426(6)
N(14)–C(126)	1.399(6)	N(14)–C(129)	1.353(7)
N(15)–C(141)	1.356(8)	N(15)–C(144)	1.399(6)
N(16)–C(146)	1.414(6)	N(16)–C(149)	1.351(7)
N(17)–C(161)	1.351(8)	N(17)–C(164)	1.409(6)
N(18)–C(166)	1.399(6)	N(18)–C(169)	1.345(7)
C(2)–H(2A)	0.950	C(2)–C(4)	1.377(8)
C(3)–C(4)	1.432(7)	C(3)–C(5)	1.402(7)
C(4)–C(11)	1.486(7)	C(5)–C(6)	1.390(7)
C(5)–C(14)	1.498(7)	C(6)–C(7)	1.414(8)
C(7)–C(8)	1.380(8)	C(7)–C(12)	1.498(8)
C(8)–H(8A)	0.950	C(8)–C(9)	1.408(9)
C(10)–H(10A)	0.980	C(10)–H(10B)	0.980

C(10)–H(10C)	0.980	C(11)–H(11A)	0.980
C(11)–H(11B)	0.980	C(11)–H(11C)	0.980
C(12)–H(12A)	0.980	C(12)–H(12B)	0.980
C(12)–H(12C)	0.980	C(14)–C(15)	1.387(8)
C(14)–C(19)	1.408(8)	C(15)–H(15A)	0.950
C(15)–C(16)	1.377(7)	C(16)–H(16A)	0.950
C(16)–C(17)	1.376(8)	C(17)–H(17A)	0.950
C(17)–C(18)	1.396(9)	C(18)–H(18A)	0.950
C(18)–C(19)	1.365(7)	C(20)–H(20A)	0.980
C(20)–H(20B)	0.980	C(20)–H(20C)	0.980
C(21)–C(22)	1.405(9)	C(21)–C(30)	1.500(8)
C(22)–H(22A)	0.950	C(22)–C(23)	1.374(8)
C(23)–C(24)	1.436(8)	C(23)–C(31)	1.487(8)
C(24)–C(25)	1.385(7)	C(25)–C(26)	1.405(8)
C(25)–C(34)	1.475(7)	C(26)–C(27)	1.419(8)
C(27)–C(28)	1.367(8)	C(27)–C(32)	1.489(7)
C(28)–H(28A)	0.950	C(28)–C(29)	1.405(7)
C(29)–C(33)	1.496(7)	C(30)–H(30A)	0.980
C(30)–H(30B)	0.980	C(30)–H(30C)	0.980
C(31)–H(31A)	0.980	C(31)–H(31B)	0.980
C(31)–H(31C)	0.980	C(32)–H(32A)	0.980
C(32)–H(32B)	0.980	C(32)–H(32C)	0.980
C(33)–H(33A)	0.980	C(33)–H(33B)	0.980
C(33)–H(33C)	0.980	C(34)–C(35)	1.383(8)
C(34)–C(39)	1.390(7)	C(35)–H(35A)	0.950
C(35)–C(36)	1.375(7)	C(36)–H(36A)	0.950
C(36)–C(37)	1.378(8)	C(37)–H(37A)	0.950
C(37)–C(38)	1.375(8)	C(38)–H(38A)	0.950
C(38)–C(39)	1.399(7)	C(40)–H(40A)	0.980
C(40)–H(40B)	0.980	C(40)–H(40C)	0.980
C(41)–C(42)	1.393(7)	C(41)–C(50)	1.500(7)
C(42)–H(42A)	0.950	C(42)–C(43)	1.356(8)
C(43)–C(44)	1.415(8)	C(43)–C(51)	1.510(7)
C(44)–C(45)	1.373(8)	C(45)–C(46)	1.393(7)
C(45)–C(54)	1.507(6)	C(46)–C(47)	1.408(8)
C(47)–C(48)	1.400(7)	C(47)–C(52)	1.496(7)
C(48)–H(48A)	0.950	C(48)–C(49)	1.400(8)
C(49)–C(53)	1.491(7)	C(50)–H(50A)	0.980
C(50)–H(50B)	0.980	C(50)–H(50C)	0.980
C(51)–H(51A)	0.980	C(51)–H(51B)	0.980
C(51)–H(51C)	0.980	C(52)–H(52A)	0.980
C(52)–H(52B)	0.980	C(52)–H(52C)	0.980
C(53)–H(53A)	0.980	C(53)–H(53B)	0.980
C(53)–H(53C)	0.980	C(54)–C(55)	1.386(8)
C(54)–C(59)	1.369(7)	C(55)–H(55A)	0.950
C(55)–C(56)	1.406(7)	C(56)–H(56A)	0.950
C(56)–C(57)	1.376(8)	C(57)–H(57A)	0.950
C(57)–C(58)	1.381(8)	C(58)–H(58A)	0.950
C(58)–C(59)	1.402(7)	C(60)–H(60A)	0.980
C(60)–H(60B)	0.980	C(60)–H(60C)	0.980
C(61)–C(62)	1.398(8)	C(61)–C(70)	1.489(7)
C(62)–H(62A)	0.950	C(62)–C(63)	1.392(8)
C(63)–C(64)	1.425(8)	C(63)–C(71)	1.485(7)
C(64)–C(65)	1.378(8)	C(65)–C(66)	1.391(7)
C(65)–C(74)	1.500(6)	C(66)–C(67)	1.424(8)

C(67)–C(68)	1.372(7)	C(67)–C(72)	1.499(7)
C(68)–H(68A)	0.950	C(68)–C(69)	1.406(8)
C(70)–H(70A)	0.980	C(70)–H(70B)	0.980
C(70)–H(70C)	0.980	C(71)–H(71A)	0.980
C(71)–H(71B)	0.980	C(71)–H(71C)	0.980
C(72)–H(72A)	0.980	C(72)–H(72B)	0.980
C(72)–H(72C)	0.980	C(73)–H(73A)	0.980
C(73)–H(73B)	0.980	C(73)–H(73C)	0.980
C(73)–C(69)	1.494(7)	C(74)–C(75)	1.388(7)
C(74)–C(79)	1.384(6)	C(75)–H(75A)	0.950
C(75)–C(76)	1.382(7)	C(76)–H(76A)	0.950
C(76)–C(77)	1.381(8)	C(77)–H(77A)	0.950
C(77)–C(78)	1.364(8)	C(78)–H(78A)	0.950
C(78)–C(79)	1.394(7)	C(80)–H(80A)	0.980
C(80)–H(80B)	0.980	C(80)–H(80C)	0.980
C(81)–C(82)	1.409(8)	C(81)–C(90)	1.474(7)
C(82)–H(82A)	0.950	C(82)–C(83)	1.359(7)
C(83)–C(84)	1.433(8)	C(83)–C(91)	1.490(8)
C(84)–C(85)	1.400(8)	C(85)–C(86)	1.395(8)
C(85)–C(94)	1.476(7)	C(86)–C(87)	1.443(8)
C(87)–C(88)	1.376(8)	C(87)–C(92)	1.490(7)
C(88)–H(88A)	0.950	C(88)–C(89)	1.402(8)
C(89)–C(93)	1.495(8)	C(90)–H(90A)	0.980
C(90)–H(90B)	0.980	C(90)–H(90C)	0.980
C(91)–H(91A)	0.980	C(91)–H(91B)	0.980
C(91)–H(91C)	0.980	C(92)–H(92A)	0.980
C(92)–H(92B)	0.980	C(92)–H(92C)	0.980
C(93)–H(93A)	0.980	C(93)–H(93B)	0.980
C(93)–H(93C)	0.980	C(94)–C(95)	1.390(8)
C(94)–C(99)	1.388(7)	C(95)–H(95A)	0.950
C(95)–C(96)	1.396(8)	C(96)–H(96A)	0.950
C(96)–C(97)	1.343(9)	C(97)–H(97A)	0.950
C(97)–C(98)	1.369(9)	C(98)–H(98A)	0.950
C(98)–C(99)	1.403(8)	C(10)–H(10D)	0.9800
C(10)–H(10E)	0.9800	C(10)–H(10F)	0.9800
C(101)–C(102)	1.388(8)	C(101)–C(110)	1.472(7)
C(102)–H(10G)	0.950	C(102)–C(103)	1.380(7)
C(103)–C(104)	1.436(8)	C(103)–C(111)	1.490(7)
C(104)–C(105)	1.392(8)	C(105)–C(106)	1.417(8)
C(105)–C(114)	1.475(7)	C(106)–C(107)	1.418(8)
C(107)–C(108)	1.384(8)	C(107)–C(112)	1.493(7)
C(108)–H(10H)	0.950	C(108)–C(109)	1.388(8)
C(109)–C(113)	1.492(7)	C(110)–H(11L)	0.980
C(110)–H(11M)	0.980	C(110)–H(11N)	0.980
C(111)–H(11G)	0.980	C(111)–H(11H)	0.980
C(111)–H(11I)	0.980	C(112)–H(11D)	0.980
C(112)–H(11E)	0.980	C(112)–H(11F)	0.980
C(113)–H(11Q)	0.980	C(113)–H(11R)	0.980
C(113)–H(11S)	0.980	C(114)–C(115)	1.376(7)
C(114)–C(119)	1.412(7)	C(115)–H(11J)	0.950
C(115)–C(116)	1.406(8)	C(116)–H(11O)	0.950
C(116)–C(117)	1.360(8)	C(117)–H(11P)	0.950
C(117)–C(118)	1.360(8)	C(118)–H(11K)	0.950
C(118)–C(119)	1.373(7)	C(120)–H(12D)	0.980
C(120)–H(12E)	0.980	C(120)–H(12F)	0.980

C(121)–C(122)	1.396(7)	C(121)–C(130)	1.492(7)
C(122)–H(12G)	0.950	C(122)–C(123)	1.380(7)
C(123)–C(124)	1.414(7)	C(123)–C(131)	1.508(7)
C(124)–C(125)	1.375(8)	C(125)–C(126)	1.408(7)
C(125)–C(134)	1.494(7)	C(126)–C(127)	1.419(8)
C(127)–C(128)	1.369(8)	C(127)–C(132)	1.495(8)
C(128)–H(12H)	0.950	C(128)–C(129)	1.380(9)
C(129)–C(133)	1.493(8)	C(130)–H(13H)	0.980
C(130)–H(13I)	0.980	C(130)–H(13J)	0.980
C(131)–H(13C)	0.980	C(131)–H(13D)	0.980
C(131)–H(13E)	0.980	C(132)–H(13K)	0.980
C(132)–H(13L)	0.980	C(132)–H(13M)	0.980
C(133)–H(13N)	0.980	C(133)–H(13O)	0.980
C(133)–H(13P)	0.980	C(134)–C(135)	1.378(8)
C(134)–C(139)	1.401(7)	C(135)–H(13A)	0.950
C(135)–C(136)	1.383(7)	C(136)–H(13F)	0.950
C(136)–C(137)	1.376(8)	C(137)–H(13B)	0.950
C(137)–C(138)	1.374(8)	C(138)–H(13G)	0.950
C(138)–C(139)	1.383(7)	C(140)–H(14A)	0.980
C(140)–H(14B)	0.980	C(140)–H(14C)	0.980
C(141)–C(142)	1.394(8)	C(141)–C(150)	1.506(7)
C(142)–H(14E)	0.950	C(142)–C(143)	1.358(7)
C(143)–C(144)	1.435(8)	C(143)–C(151)	1.500(7)
C(144)–C(145)	1.388(8)	C(145)–C(146)	1.397(8)
C(145)–C(154)	1.500(7)	C(146)–C(147)	1.402(8)
C(147)–C(148)	1.383(7)	C(147)–C(152)	1.502(7)
C(148)–H(14D)	0.950	C(148)–C(149)	1.391(7)
C(149)–C(153)	1.508(7)	C(150)–H(15N)	0.980
C(150)–H(15O)	0.980	C(150)–H(15P)	0.980
C(151)–H(15E)	0.980	C(151)–H(15F)	0.980
C(151)–H(15G)	0.980	C(152)–H(15B)	0.980
C(152)–H(15C)	0.980	C(152)–H(15D)	0.980
C(154)–C(155)	1.372(7)	C(154)–C(159)	1.407(7)
C(153)–H(15I)	0.980	C(153)–H(15J)	0.980
C(153)–H(15K)	0.980	C(155)–H(15H)	0.950
C(155)–C(156)	1.391(7)	C(156)–H(15L)	0.950
C(156)–C(157)	1.376(8)	C(157)–H(15Q)	0.950
C(157)–C(158)	1.389(8)	C(158)–H(15M)	0.950
C(158)–C(159)	1.382(7)	C(160)–H(16B)	0.980
C(160)–H(16C)	0.980	C(160)–H(16D)	0.980
C(161)–C(162)	1.401(8)	C(161)–C(170)	1.481(8)
C(162)–H(16F)	0.950	C(162)–C(163)	1.390(8)
C(163)–C(164)	1.413(8)	C(163)–C(171)	1.493(7)
C(164)–C(165)	1.400(8)	C(165)–C(166)	1.385(8)
C(165)–C(174)	1.497(7)	C(166)–C(167)	1.426(8)
C(167)–C(168)	1.381(7)	C(167)–C(172)	1.492(7)
C(168)–H(16E)	0.950	C(168)–C(169)	1.373(8)
C(169)–C(173)	1.503(7)	C(170)–H(17N)	0.980
C(170)–H(17O)	0.980	C(170)–H(17P)	0.980
C(171)–H(17I)	0.980	C(171)–H(17J)	0.980
C(171)–H(17K)	0.980	C(172)–H(17B)	0.980
C(172)–H(17C)	0.980	C(172)–H(17D)	0.980
C(173)–H(17F)	0.980	C(173)–H(17G)	0.980
C(173)–H(17H)	0.980	C(174)–C(175)	1.391(7)
C(174)–C(179)	1.402(7)	C(175)–H(17E)	0.950

C(175)–C(176)	1.404(7)	C(176)–H(17M)	0.950
C(176)–C(177)	1.359(9)	C(177)–H(17Q)	0.950
C(177)–C(178)	1.370(9)	C(178)–H(17L)	0.950
C(178)–C(179)	1.387(7)	C(180)–H(18B)	0.980
C(180)–H(18C)	0.980	C(180)–H(18D)	0.980
C(9)–C(13)	1.500(9)	C(13)–H(10I)	0.980
C(13)–H(10J)	0.980	C(13)–H(10K)	0.980

N(1)–C(1)–C(2)	108.2(5)	N(1)–C(1)–C(10)	122.2(5)
C(2)–C(1)–C(10)	129.5(6)	F(1)–B(1)–F(2)	109.9(4)
F(1)–B(1)–N(1)	111.1(5)	F(1)–B(1)–N(2)	109.9(6)
F(2)–B(1)–N(1)	110.6(6)	F(2)–B(1)–N(2)	109.2(5)
N(1)–B(1)–N(2)	106.0(4)	F(3)–B(2)–F(4)	108.8(4)
F(3)–B(2)–N(3)	110.3(6)	F(3)–B(2)–N(4)	110.4(5)
F(4)–B(2)–N(3)	109.6(5)	F(4)–B(2)–N(4)	110.8(6)
N(3)–B(2)–N(4)	107.0(4)	F(5)–B(3)–F(6)	108.6(4)
F(5)–B(3)–N(5)	109.7(4)	F(5)–B(3)–N(6)	109.0(5)
F(6)–B(3)–N(5)	110.7(5)	F(6)–B(3)–N(6)	111.4(4)
N(5)–B(3)–N(6)	107.5(4)	F(7)–B(4)–F(8)	108.8(4)
F(7)–B(4)–N(7)	109.3(5)	F(7)–B(4)–N(8)	111.0(5)
F(8)–B(4)–N(7)	108.9(5)	F(8)–B(4)–N(8)	110.5(5)
N(7)–B(4)–N(8)	108.3(4)	F(9)–B(5)–F(10)	109.7(4)
F(9)–B(5)–N(9)	109.9(5)	F(9)–B(5)–N(10)	110.4(5)
F(10)–B(5)–N(9)	110.1(5)	F(10)–B(5)–N(10)	110.3(5)
N(9)–B(5)–N(10)	106.4(4)	F(11)–B(6)–F(12)	109.7(4)
F(11)–B(6)–N(11)	109.5(6)	F(11)–B(6)–N(12)	110.1(5)
F(12)–B(6)–N(11)	110.3(5)	F(12)–B(6)–N(12)	110.0(6)
N(11)–B(6)–N(12)	107.2(4)	F(13)–B(7)–F(14)	108.7(4)
F(13)–B(7)–N(13)	110.1(5)	F(13)–B(7)–N(14)	111.1(6)
F(14)–B(7)–N(13)	108.6(6)	F(14)–B(7)–N(14)	110.2(5)
N(13)–B(7)–N(14)	108.2(4)	F(15)–B(8)–F(16)	109.3(4)
F(15)–B(8)–N(15)	110.6(4)	F(15)–B(8)–N(16)	109.4(5)
F(16)–B(8)–N(15)	111.1(5)	F(16)–B(8)–N(16)	109.6(4)
N(15)–B(8)–N(16)	106.7(4)	F(17)–B(9)–F(18)	108.4(4)
F(17)–B(9)–N(17)	109.3(5)	F(17)–B(9)–N(18)	110.6(5)
F(18)–B(9)–N(17)	109.3(5)	F(18)–B(9)–N(18)	111.0(5)
N(17)–B(9)–N(18)	108.1(4)	C(19)–O(1)–C(20)	117.3(4)
C(39)–O(2)–C(40)	116.7(4)	C(59)–O(3)–C(60)	119.4(4)
C(79)–O(4)–C(80)	117.9(4)	C(99)–O(5)–C(100)	117.9(5)
C(119)–O(6)–C(120)	118.0(4)	C(139)–O(7)–C(140)	118.3(4)
C(159)–O(8)–C(160)	117.8(4)	C(179)–O(9)–C(180)	118.0(4)
C(1)–N(1)–B(1)	125.0(4)	C(1)–N(1)–C(3)	108.9(4)
B(1)–N(1)–C(3)	126.1(5)	B(1)–N(2)–C(6)	126.6(4)
B(1)–N(2)–C(9)	126.1(5)	C(6)–N(2)–C(9)	107.2(5)
B(2)–N(3)–C(21)	126.3(5)	B(2)–N(3)–C(24)	125.1(5)
C(21)–N(3)–C(24)	108.6(5)	B(2)–N(4)–C(26)	125.8(5)
B(2)–N(4)–C(29)	125.9(4)	C(26)–N(4)–C(29)	108.3(4)
B(3)–N(5)–C(41)	127.4(4)	B(3)–N(5)–C(44)	125.0(5)
C(41)–N(5)–C(44)	107.6(5)	B(3)–N(6)–C(46)	125.6(5)
B(3)–N(6)–C(49)	126.8(4)	C(46)–N(6)–C(49)	107.5(5)
B(4)–N(7)–C(61)	127.4(4)	B(4)–N(7)–C(64)	124.4(5)
C(61)–N(7)–C(64)	108.2(5)	B(4)–N(8)–C(66)	124.6(5)
B(4)–N(8)–C(69)	126.5(4)	C(66)–N(8)–C(69)	108.8(5)
B(5)–N(9)–C(81)	126.6(4)	B(5)–N(9)–C(84)	125.7(5)
C(81)–N(9)–C(84)	107.7(5)	B(5)–N(10)–C(86)	125.3(5)

B(5)–N(10)–C(89)	125.2(4)	C(86)–N(10)–C(89)	109.5(5)
B(6)–N(11)–C(101)	126.0(4)	B(6)–N(11)–C(104)	125.3(5)
C(101)–N(11)–C(104)	108.6(5)	B(6)–N(12)–C(106)	125.4(5)
B(6)–N(12)–C(109)	126.1(5)	C(106)–N(12)–C(109)	108.4(5)
B(7)–N(13)–C(121)	128.0(4)	B(7)–N(13)–C(124)	123.7(5)
C(121)–N(13)–C(124)	108.3(4)	B(7)–N(14)–C(126)	125.8(4)
B(7)–N(14)–C(129)	126.8(5)	C(126)–N(14)–C(129)	107.4(5)
B(8)–N(15)–C(141)	125.4(4)	B(8)–N(15)–C(144)	126.6(5)
C(141)–N(15)–C(144)	107.9(5)	B(8)–N(16)–C(146)	125.9(5)
B(8)–N(16)–C(149)	127.6(4)	C(146)–N(16)–C(149)	106.4(5)
B(9)–N(17)–C(161)	127.7(4)	B(9)–N(17)–C(164)	124.6(5)
C(161)–N(17)–C(164)	107.7(5)	B(9)–N(18)–C(166)	125.1(5)
B(9)–N(18)–C(169)	126.7(4)	C(166)–N(18)–C(169)	108.2(5)
C(1)–C(2)–H(2A)	125.3	C(1)–C(2)–C(4)	109.5(5)
H(2A)–C(2)–C(4)	125.2	N(1)–C(3)–C(4)	108.2(5)
N(1)–C(3)–C(5)	120.7(4)	C(4)–C(3)–C(5)	131.0(5)
C(2)–C(4)–C(3)	105.2(5)	C(2)–C(4)–C(11)	126.0(5)
C(3)–C(4)–C(11)	128.8(5)	C(3)–C(5)–C(6)	121.3(5)
C(3)–C(5)–C(14)	120.0(5)	C(6)–C(5)–C(14)	118.7(5)
N(2)–C(6)–C(5)	119.1(5)	N(2)–C(6)–C(7)	108.3(5)
C(5)–C(6)–C(7)	132.5(5)	C(6)–C(7)–C(8)	106.5(5)
C(6)–C(7)–C(12)	127.9(5)	C(8)–C(7)–C(12)	125.3(6)
C(7)–C(8)–H(8A)	126.1	C(7)–C(8)–C(9)	107.8(6)
H(8A)–C(8)–C(9)	126.1	C(1)–C(10)–H(10A)	109.5
C(1)–C(10)–H(10B)	109.5	C(1)–C(10)–H(10C)	109.5
H(10A)–C(10)–H(10B)	109.5	H(10A)–C(10)–H(10C)	109.5
H(10B)–C(10)–H(10C)	109.5	C(4)–C(11)–H(11A)	109.5
C(4)–C(11)–H(11B)	109.5	C(4)–C(11)–H(11C)	109.5
H(11A)–C(11)–H(11B)	109.5	H(11A)–C(11)–H(11C)	109.5
H(11B)–C(11)–H(11C)	109.5	C(7)–C(12)–H(12A)	109.5
C(7)–C(12)–H(12B)	109.5	C(7)–C(12)–H(12C)	109.5
H(12A)–C(12)–H(12B)	109.5	H(12A)–C(12)–H(12C)	109.5
H(12B)–C(12)–H(12C)	109.5	C(5)–C(14)–C(15)	122.1(5)
C(5)–C(14)–C(19)	119.0(5)	C(15)–C(14)–C(19)	118.7(5)
C(14)–C(15)–H(15A)	119.2	C(14)–C(15)–C(16)	121.6(5)
H(15A)–C(15)–C(16)	119.2	C(15)–C(16)–H(16A)	120.7
C(15)–C(16)–C(17)	118.7(6)	H(16A)–C(16)–C(17)	120.7
C(16)–C(17)–H(17A)	119.4	C(16)–C(17)–C(18)	121.2(5)
H(17A)–C(17)–C(18)	119.4	C(17)–C(18)–H(18A)	120.1
C(17)–C(18)–C(19)	119.7(5)	H(18A)–C(18)–C(19)	120.1
O(1)–C(19)–C(14)	114.6(5)	O(1)–C(19)–C(18)	125.3(5)
C(14)–C(19)–C(18)	120.1(6)	O(1)–C(20)–H(20A)	109.5
O(1)–C(20)–H(20B)	109.5	O(1)–C(20)–H(20C)	109.5
H(20A)–C(20)–H(20B)	109.5	H(20A)–C(20)–H(20C)	109.5
H(20B)–C(20)–H(20C)	109.5	N(3)–C(21)–C(22)	108.6(5)
N(3)–C(21)–C(30)	122.1(6)	C(22)–C(21)–C(30)	129.3(6)
C(21)–C(22)–H(22A)	125.6	C(21)–C(22)–C(23)	108.9(5)
H(22A)–C(22)–C(23)	125.6	C(22)–C(23)–C(24)	106.2(5)
C(22)–C(23)–C(31)	124.6(6)	C(24)–C(23)–C(31)	129.2(5)
N(3)–C(24)–C(23)	107.7(5)	N(3)–C(24)–C(25)	121.4(5)
C(23)–C(24)–C(25)	130.8(5)	C(24)–C(25)–C(26)	120.3(5)
C(24)–C(25)–C(34)	119.5(5)	C(26)–C(25)–C(34)	120.2(5)
N(4)–C(26)–C(25)	120.1(5)	N(4)–C(26)–C(27)	107.9(5)
C(25)–C(26)–C(27)	131.9(4)	C(26)–C(27)–C(28)	106.5(4)
C(26)–C(27)–C(32)	128.1(5)	C(28)–C(27)–C(32)	125.4(5)

C(27)–C(28)–H(28A)	125.6	C(27)–C(28)–C(29)	108.8(5)
H(28A)–C(28)–C(29)	125.6	N(4)–C(29)–C(28)	108.5(4)
N(4)–C(29)–C(33)	122.8(5)	C(28)–C(29)–C(33)	128.7(6)
C(21)–C(30)–H(30A)	109.5	C(21)–C(30)–H(30B)	109.5
C(21)–C(30)–H(30C)	109.5	H(30A)–C(30)–H(30B)	109.5
H(30A)–C(30)–H(30C)	109.5	H(30B)–C(30)–H(30C)	109.5
C(23)–C(31)–H(31A)	109.5	C(23)–C(31)–H(31B)	109.5
C(23)–C(31)–H(31C)	109.5	H(31A)–C(31)–H(31B)	109.5
H(31A)–C(31)–H(31C)	109.5	H(31B)–C(31)–H(31C)	109.5
C(27)–C(32)–H(32A)	109.5	C(27)–C(32)–H(32B)	109.5
C(27)–C(32)–H(32C)	109.5	H(32A)–C(32)–H(32B)	109.5
H(32A)–C(32)–H(32C)	109.5	H(32B)–C(32)–H(32C)	109.5
C(29)–C(33)–H(33A)	109.5	C(29)–C(33)–H(33B)	109.5
C(29)–C(33)–H(33C)	109.5	H(33A)–C(33)–H(33B)	109.5
H(33A)–C(33)–H(33C)	109.5	H(33B)–C(33)–H(33C)	109.5
C(25)–C(34)–C(35)	121.1(5)	C(25)–C(34)–C(39)	120.4(5)
C(35)–C(34)–C(39)	118.4(5)	C(34)–C(35)–H(35A)	119.4
C(34)–C(35)–C(36)	121.3(5)	H(35A)–C(35)–C(36)	119.4
C(35)–C(36)–H(36A)	120.1	C(35)–C(36)–C(37)	119.9(6)
H(36A)–C(36)–C(37)	120.0	C(36)–C(37)–H(37A)	119.8
C(36)–C(37)–C(38)	120.4(5)	H(37A)–C(37)–C(38)	119.8
C(37)–C(38)–H(38A)	120.3	C(37)–C(38)–C(39)	119.4(5)
H(38A)–C(38)–C(39)	120.3	O(2)–C(39)–C(34)	115.1(4)
O(2)–C(39)–C(38)	124.3(5)	C(34)–C(39)–C(38)	120.6(5)
O(2)–C(40)–H(40A)	109.5	O(2)–C(40)–H(40B)	109.5
O(2)–C(40)–H(40C)	109.5	H(40A)–C(40)–H(40B)	109.5
H(40A)–C(40)–H(40C)	109.5	H(40B)–C(40)–H(40C)	109.5
N(5)–C(41)–C(42)	109.1(5)	N(5)–C(41)–C(50)	122.7(5)
C(42)–C(41)–C(50)	128.2(7)	C(41)–C(42)–H(42A)	125.6
C(41)–C(42)–C(43)	108.9(6)	H(42A)–C(42)–C(43)	125.6
C(42)–C(43)–C(44)	107.7(5)	C(42)–C(43)–C(51)	124.4(6)
C(44)–C(43)–C(51)	128.0(5)	N(5)–C(44)–C(43)	106.8(5)
N(5)–C(44)–C(45)	119.6(5)	C(43)–C(44)–C(45)	133.5(4)
C(44)–C(45)–C(46)	123.0(4)	C(44)–C(45)–C(54)	119.5(5)
C(46)–C(45)–C(54)	117.5(5)	N(6)–C(46)–C(45)	119.1(5)
N(6)–C(46)–C(47)	108.8(5)	C(45)–C(46)–C(47)	132.1(4)
C(46)–C(47)–C(48)	106.1(5)	C(46)–C(47)–C(52)	130.7(5)
C(48)–C(47)–C(52)	123.2(6)	C(47)–C(48)–H(48A)	125.9
C(47)–C(48)–C(49)	108.3(5)	H(48A)–C(48)–C(49)	125.9
N(6)–C(49)–C(48)	109.4(4)	N(6)–C(49)–C(53)	122.9(5)
C(48)–C(49)–C(53)	127.7(6)	C(41)–C(50)–H(50A)	109.5
C(41)–C(50)–H(50B)	109.5	C(41)–C(50)–H(50C)	109.5
H(50A)–C(50)–H(50B)	109.5	H(50A)–C(50)–H(50C)	109.5
H(50B)–C(50)–H(50C)	109.5	C(43)–C(51)–H(51A)	109.5
C(43)–C(51)–H(51B)	109.5	C(43)–C(51)–H(51C)	109.5
H(51A)–C(51)–H(51B)	109.5	H(51A)–C(51)–H(51C)	109.5
H(51B)–C(51)–H(51C)	109.5	C(47)–C(52)–H(52A)	109.5
C(47)–C(52)–H(52B)	109.5	C(47)–C(52)–H(52C)	109.5
H(52A)–C(52)–H(52B)	109.5	H(52A)–C(52)–H(52C)	109.5
H(52B)–C(52)–H(52C)	109.5	C(49)–C(53)–H(53A)	109.5
C(49)–C(53)–H(53B)	109.5	C(49)–C(53)–H(53C)	109.5
H(53A)–C(53)–H(53B)	109.5	H(53A)–C(53)–H(53C)	109.5
H(53B)–C(53)–H(53C)	109.5	C(45)–C(54)–C(55)	119.7(4)
C(45)–C(54)–C(59)	119.9(5)	C(55)–C(54)–C(59)	120.4(5)
C(54)–C(55)–H(55A)	120.0	C(54)–C(55)–C(56)	120.0(5)

H(55A)–C(55)–C(56)	120.0	C(55)–C(56)–H(56A)	120.8
C(55)–C(56)–C(57)	118.5(6)	H(56A)–C(56)–C(57)	120.7
C(56)–C(57)–H(57A)	118.9	C(56)–C(57)–C(58)	122.2(5)
H(57A)–C(57)–C(58)	118.9	C(57)–C(58)–H(58A)	120.8
C(57)–C(58)–C(59)	118.4(5)	H(58A)–C(58)–C(59)	120.8
O(3)–C(59)–C(54)	116.5(4)	O(3)–C(59)–C(58)	122.9(5)
C(54)–C(59)–C(58)	120.6(5)	O(3)–C(60)–H(60A)	109.4
O(3)–C(60)–H(60B)	109.5	O(3)–C(60)–H(60C)	109.5
H(60A)–C(60)–H(60B)	109.5	H(60A)–C(60)–H(60C)	109.5
H(60B)–C(60)–H(60C)	109.5	N(7)–C(61)–C(62)	109.7(5)
N(7)–C(61)–C(70)	121.4(5)	C(62)–C(61)–C(70)	128.9(6)
C(61)–C(62)–H(62A)	125.9	C(61)–C(62)–C(63)	108.1(6)
H(62A)–C(62)–C(63)	125.9	C(62)–C(63)–C(64)	106.5(5)
C(62)–C(63)–C(71)	124.7(6)	C(64)–C(63)–C(71)	128.7(5)
N(7)–C(64)–C(63)	107.5(5)	N(7)–C(64)–C(65)	120.1(5)
C(63)–C(64)–C(65)	132.4(5)	C(64)–C(65)–C(66)	122.1(4)
C(64)–C(65)–C(74)	119.2(5)	C(66)–C(65)–C(74)	118.7(5)
N(8)–C(66)–C(65)	120.4(5)	N(8)–C(66)–C(67)	106.9(5)
C(65)–C(66)–C(67)	132.7(4)	C(66)–C(67)–C(68)	106.8(5)
C(66)–C(67)–C(72)	128.3(5)	C(68)–C(67)–C(72)	124.9(6)
C(67)–C(68)–H(68A)	125.8	C(67)–C(68)–C(69)	108.4(6)
H(68A)–C(68)–C(69)	125.8	C(61)–C(70)–H(70A)	109.5
C(61)–C(70)–H(70B)	109.5	C(61)–C(70)–H(70C)	109.5
H(70A)–C(70)–H(70B)	109.5	H(70A)–C(70)–H(70C)	109.5
H(70B)–C(70)–H(70C)	109.5	C(63)–C(71)–H(71A)	109.5
C(63)–C(71)–H(71B)	109.5	C(63)–C(71)–H(71C)	109.5
H(71A)–C(71)–H(71B)	109.5	H(71A)–C(71)–H(71C)	109.5
H(71B)–C(71)–H(71C)	109.5	C(67)–C(72)–H(72A)	109.5
C(67)–C(72)–H(72B)	109.5	C(67)–C(72)–H(72C)	109.5
H(72A)–C(72)–H(72B)	109.5	H(72A)–C(72)–H(72C)	109.5
H(72B)–C(72)–H(72C)	109.5	H(73A)–C(73)–H(73B)	109.5
H(73A)–C(73)–H(73C)	109.5	H(73A)–C(73)–C(69)	109.5
H(73B)–C(73)–H(73C)	109.5	H(73B)–C(73)–C(69)	109.5
H(73C)–C(73)–C(69)	109.5	C(65)–C(74)–C(75)	119.5(4)
C(65)–C(74)–C(79)	121.0(4)	C(75)–C(74)–C(79)	119.5(4)
C(74)–C(75)–H(75A)	119.9	C(74)–C(75)–C(76)	120.3(5)
H(75A)–C(75)–C(76)	119.9	C(75)–C(76)–H(76A)	120.2
C(75)–C(76)–C(77)	119.6(5)	H(76A)–C(76)–C(77)	120.2
N(8)–C(69)–C(68)	109.1(4)	N(8)–C(69)–C(73)	124.0(5)
C(68)–C(69)–C(73)	126.9(6)	C(76)–C(77)–H(77A)	119.7
C(76)–C(77)–C(78)	120.7(5)	H(77A)–C(77)–C(78)	119.6
C(77)–C(78)–H(78A)	120.0	C(77)–C(78)–C(79)	120.0(5)
H(78A)–C(78)–C(79)	120.0	O(4)–C(79)–C(74)	115.4(4)
O(4)–C(79)–C(78)	124.8(5)	C(74)–C(79)–C(78)	119.8(5)
O(4)–C(80)–H(80A)	109.5	O(4)–C(80)–H(80B)	109.5
O(4)–C(80)–H(80C)	109.5	H(80A)–C(80)–H(80B)	109.5
H(80A)–C(80)–H(80C)	109.5	H(80B)–C(80)–H(80C)	109.5
N(9)–C(81)–C(82)	108.8(4)	N(9)–C(81)–C(90)	123.5(5)
C(82)–C(81)–C(90)	127.7(6)	C(81)–C(82)–H(82A)	125.3
C(81)–C(82)–C(83)	109.4(6)	H(82A)–C(82)–C(83)	125.3
C(82)–C(83)–C(84)	106.2(5)	C(82)–C(83)–C(91)	125.1(6)
C(84)–C(83)–C(91)	128.6(5)	N(9)–C(84)–C(83)	108.0(5)
N(9)–C(84)–C(85)	120.9(5)	C(83)–C(84)–C(85)	131.1(5)
C(84)–C(85)–C(86)	119.7(5)	C(84)–C(85)–C(94)	119.2(5)
C(86)–C(85)–C(94)	121.0(5)	N(10)–C(86)–C(85)	121.8(5)

N(10)–C(86)–C(87)	107.6(5)	C(85)–C(86)–C(87)	130.6(5)
C(86)–C(87)–C(88)	104.8(5)	C(86)–C(87)–C(92)	128.6(5)
C(88)–C(87)–C(92)	126.5(6)	C(87)–C(88)–H(88A)	125.2
C(87)–C(88)–C(89)	109.6(6)	H(88A)–C(88)–C(89)	125.2
N(10)–C(89)–C(88)	108.5(5)	N(10)–C(89)–C(93)	124.1(5)
C(88)–C(89)–C(93)	127.4(6)	C(81)–C(90)–H(90A)	109.5
C(81)–C(90)–H(90B)	109.5	C(81)–C(90)–H(90C)	109.5
H(90A)–C(90)–H(90B)	109.5	H(90A)–C(90)–H(90C)	109.5
H(90B)–C(90)–H(90C)	109.5	C(83)–C(91)–H(91A)	109.5
C(83)–C(91)–H(91B)	109.5	C(83)–C(91)–H(91C)	109.5
H(91A)–C(91)–H(91B)	109.5	H(91A)–C(91)–H(91C)	109.5
H(91B)–C(91)–H(91C)	109.5	C(87)–C(92)–H(92A)	109.5
C(87)–C(92)–H(92B)	109.5	C(87)–C(92)–H(92C)	109.5
H(92A)–C(92)–H(92B)	109.5	H(92A)–C(92)–H(92C)	109.5
H(92B)–C(92)–H(92C)	109.5	C(89)–C(93)–H(93A)	109.5
C(89)–C(93)–H(93B)	109.5	C(89)–C(93)–H(93C)	109.5
H(93A)–C(93)–H(93B)	109.5	H(93A)–C(93)–H(93C)	109.5
H(93B)–C(93)–H(93C)	109.5	C(85)–C(94)–C(95)	121.0(5)
C(85)–C(94)–C(99)	119.0(5)	C(95)–C(94)–C(99)	120.0(5)
C(94)–C(95)–H(95A)	120.3	C(94)–C(95)–C(96)	119.5(6)
H(95A)–C(95)–C(96)	120.3	C(95)–C(96)–H(96A)	120.2
C(95)–C(96)–C(97)	119.6(6)	H(96A)–C(96)–C(97)	120.2
C(96)–C(97)–H(97A)	118.6	C(96)–C(97)–C(98)	122.8(6)
H(97A)–C(97)–C(98)	118.6	C(97)–C(98)–H(98A)	120.7
C(97)–C(98)–C(99)	118.6(6)	H(98A)–C(98)–C(99)	120.7
O(5)–C(99)–C(94)	115.6(5)	O(5)–C(99)–C(98)	124.9(5)
C(94)–C(99)–C(98)	119.6(5)	O(5)–C(100)–H(10D)	109.5
O(5)–C(100)–H(10E)	109.5	O(5)–C(100)–H(10F)	109.5
H(10D)–C(100)–H(10E)	109.5	H(10D)–C(100)–H(10F)	109.5
H(10E)–C(100)–H(10F)	109.5	N(11)–C(101)–C(102)	108.1(5)
N(11)–C(101)–C(110)	122.0(5)	C(102)–C(101)–C(110)	129.9(6)
C(101)–C(102)–H(10G)	125.0	C(101)–C(102)–C(103)	110.0(6)
H(10G)–C(102)–C(103)	125.0	C(102)–C(103)–C(104)	105.2(5)
C(102)–C(103)–C(111)	125.7(6)	C(104)–C(103)–C(111)	129.1(5)
N(11)–C(104)–C(103)	108.2(5)	N(11)–C(104)–C(105)	121.5(5)
C(103)–C(104)–C(105)	130.3(5)	C(104)–C(105)–C(106)	119.9(5)
C(104)–C(105)–C(114)	120.9(5)	C(106)–C(105)–C(114)	119.2(5)
N(12)–C(106)–C(105)	120.6(5)	N(12)–C(106)–C(107)	108.4(5)
C(105)–C(106)–C(107)	131.1(5)	C(106)–C(107)–C(108)	105.1(5)
C(106)–C(107)–C(112)	130.4(5)	C(108)–C(107)–C(112)	124.5(6)
C(107)–C(108)–H(10H)	125.2	C(107)–C(108)–C(109)	109.6(6)
H(10H)–C(108)–C(109)	125.2	N(12)–C(109)–C(108)	108.5(5)
N(12)–C(109)–C(113)	123.1(6)	C(108)–C(109)–C(113)	128.4(6)
C(101)–C(110)–H(11L)	109.5	C(101)–C(110)–H(11M)	109.5
C(101)–C(110)–H(11N)	109.5	H(11L)–C(110)–H(11M)	109.5
H(11L)–C(110)–H(11N)	109.5	H(11M)–C(110)–H(11N)	109.5
C(103)–C(111)–H(11G)	109.5	C(103)–C(111)–H(11H)	109.5
C(103)–C(111)–H(11I)	109.5	H(11G)–C(111)–H(11H)	109.5
H(11G)–C(111)–H(11I)	109.5	H(11H)–C(111)–H(11I)	109.5
C(107)–C(112)–H(11D)	109.5	C(107)–C(112)–H(11E)	109.5
C(107)–C(112)–H(11F)	109.5	H(11D)–C(112)–H(11E)	109.5
H(11D)–C(112)–H(11F)	109.5	H(11E)–C(112)–H(11F)	109.5
C(109)–C(113)–H(11Q)	109.5	C(109)–C(113)–H(11R)	109.5
C(109)–C(113)–H(11S)	109.5	H(11Q)–C(113)–H(11R)	109.5
H(11Q)–C(113)–H(11S)	109.5	H(11R)–C(113)–H(11S)	109.5

C(105)–C(114)–C(115)	120.6(5)	C(105)–C(114)–C(119)	120.5(5)
C(115)–C(114)–C(119)	118.8(5)	C(114)–C(115)–H(11J)	120.1
C(114)–C(115)–C(116)	119.9(6)	H(11J)–C(115)–C(116)	120.1
C(115)–C(116)–H(11O)	120.2	C(115)–C(116)–C(117)	119.5(6)
H(11O)–C(116)–C(117)	120.2	C(116)–C(117)–H(11P)	119.2
C(116)–C(117)–C(118)	121.6(5)	H(11P)–C(117)–C(118)	119.2
C(117)–C(118)–H(11K)	120.1	C(117)–C(118)–C(119)	119.8(6)
H(11K)–C(118)–C(119)	120.1	O(6)–C(119)–C(114)	115.0(4)
O(6)–C(119)–C(118)	124.7(5)	C(114)–C(119)–C(118)	120.2(5)
O(6)–C(120)–H(12D)	109.5	O(6)–C(120)–H(12E)	109.5
O(6)–C(120)–H(12F)	109.5	H(12D)–C(120)–H(12E)	109.5
H(12D)–C(120)–H(12F)	109.5	H(12E)–C(120)–H(12F)	109.5
N(13)–C(121)–C(122)	110.0(5)	N(13)–C(121)–C(130)	121.7(5)
C(122)–C(121)–C(130)	128.3(6)	C(121)–C(122)–H(12G)	126.1
C(121)–C(122)–C(123)	107.9(5)	H(12G)–C(122)–C(123)	126.1
C(122)–C(123)–C(124)	107.4(4)	C(122)–C(123)–C(131)	125.0(5)
C(124)–C(123)–C(131)	127.6(5)	N(13)–C(124)–C(123)	106.4(5)
N(13)–C(124)–C(125)	120.4(4)	C(123)–C(124)–C(125)	133.0(4)
C(124)–C(125)–C(126)	121.9(4)	C(124)–C(125)–C(134)	120.4(4)
C(126)–C(125)–C(134)	117.7(5)	N(14)–C(126)–C(125)	119.6(5)
N(14)–C(126)–C(127)	108.4(4)	C(125)–C(126)–C(127)	131.9(5)
C(126)–C(127)–C(128)	105.3(5)	C(126)–C(127)–C(132)	129.3(5)
C(128)–C(127)–C(132)	125.3(6)	C(127)–C(128)–H(12H)	125.0
C(127)–C(128)–C(129)	110.0(6)	H(12H)–C(128)–C(129)	125.0
N(14)–C(129)–C(128)	108.8(5)	N(14)–C(129)–C(133)	121.0(6)
C(128)–C(129)–C(133)	130.2(6)	C(121)–C(130)–H(13H)	109.5
C(121)–C(130)–H(13I)	109.5	C(121)–C(130)–H(13J)	109.5
H(13H)–C(130)–H(13I)	109.5	H(13H)–C(130)–H(13J)	109.5
H(13I)–C(130)–H(13J)	109.5	C(123)–C(131)–H(13C)	109.5
C(123)–C(131)–H(13D)	109.5	C(123)–C(131)–H(13E)	109.5
H(13C)–C(131)–H(13D)	109.5	H(13C)–C(131)–H(13E)	109.5
H(13D)–C(131)–H(13E)	109.5	C(127)–C(132)–H(13K)	109.5
C(127)–C(132)–H(13L)	109.5	C(127)–C(132)–H(13M)	109.5
H(13K)–C(132)–H(13L)	109.5	H(13K)–C(132)–H(13M)	109.5
H(13L)–C(132)–H(13M)	109.5	C(129)–C(133)–H(13N)	109.5
C(129)–C(133)–H(13O)	109.5	C(129)–C(133)–H(13P)	109.5
H(13N)–C(133)–H(13O)	109.5	H(13N)–C(133)–H(13P)	109.5
H(13O)–C(133)–H(13P)	109.5	C(125)–C(134)–C(135)	121.0(5)
C(125)–C(134)–C(139)	119.1(5)	C(135)–C(134)–C(139)	119.9(4)
C(134)–C(135)–H(13A)	119.9	C(134)–C(135)–C(136)	120.2(5)
H(13A)–C(135)–C(136)	119.9	C(135)–C(136)–H(13F)	120.2
C(135)–C(136)–C(137)	119.5(6)	H(13F)–C(136)–C(137)	120.2
C(136)–C(137)–H(13B)	119.5	C(136)–C(137)–C(138)	121.1(5)
H(13B)–C(137)–C(138)	119.5	C(137)–C(138)–H(13G)	120.1
C(137)–C(138)–C(139)	119.9(5)	H(13G)–C(138)–C(139)	120.1
O(7)–C(139)–C(134)	115.8(4)	O(7)–C(139)–C(138)	124.8(5)
C(134)–C(139)–C(138)	119.4(6)	O(7)–C(140)–H(14A)	109.5
O(7)–C(140)–H(14B)	109.5	O(7)–C(140)–H(14C)	109.5
H(14A)–C(140)–H(14B)	109.5	H(14A)–C(140)–H(14C)	109.5
H(14B)–C(140)–H(14C)	109.5	N(15)–C(141)–C(142)	109.0(5)
N(15)–C(141)–C(150)	122.6(5)	C(142)–C(141)–C(150)	128.4(6)
C(141)–C(142)–H(14E)	125.4	C(141)–C(142)–C(143)	109.2(6)
H(14E)–C(142)–C(143)	125.4	C(142)–C(143)–C(144)	106.6(5)
C(142)–C(143)–C(151)	125.9(6)	C(144)–C(143)–C(151)	127.5(5)
N(15)–C(144)–C(143)	107.3(5)	N(15)–C(144)–C(145)	119.1(5)

C(143)–C(144)–C(145)	133.6(4)	C(144)–C(145)–C(146)	122.7(4)
C(144)–C(145)–C(154)	118.7(5)	C(146)–C(145)–C(154)	118.5(5)
N(16)–C(146)–C(145)	118.8(5)	N(16)–C(146)–C(147)	108.8(5)
C(145)–C(146)–C(147)	132.5(5)	C(146)–C(147)–C(148)	106.5(5)
C(146)–C(147)–C(152)	129.3(5)	C(148)–C(147)–C(152)	124.2(6)
C(147)–C(148)–H(14D)	125.9	C(147)–C(148)–C(149)	108.1(5)
H(14D)–C(148)–C(149)	125.9	N(16)–C(149)–C(148)	110.2(4)
N(16)–C(149)–C(153)	121.9(5)	C(148)–C(149)–C(153)	127.8(6)
C(141)–C(150)–H(15N)	109.5	C(141)–C(150)–H(15O)	109.5
C(141)–C(150)–H(15P)	109.5	H(15N)–C(150)–H(15O)	109.5
H(15N)–C(150)–H(15P)	109.5	H(15O)–C(150)–H(15P)	109.5
C(143)–C(151)–H(15E)	109.5	C(143)–C(151)–H(15F)	109.5
C(143)–C(151)–H(15G)	109.5	H(15E)–C(151)–H(15F)	109.5
H(15E)–C(151)–H(15G)	109.5	H(15F)–C(151)–H(15G)	109.5
C(147)–C(152)–H(15B)	109.5	C(147)–C(152)–H(15C)	109.5
C(147)–C(152)–H(15D)	109.5	H(15B)–C(152)–H(15C)	109.5
H(15B)–C(152)–H(15D)	109.5	H(15C)–C(152)–H(15D)	109.5
C(145)–C(154)–C(155)	120.9(5)	C(145)–C(154)–C(159)	119.6(5)
C(155)–C(154)–C(159)	119.4(5)	C(149)–C(153)–H(15I)	109.5
C(149)–C(153)–H(15J)	109.5	C(149)–C(153)–H(15K)	109.5
H(15I)–C(153)–H(15J)	109.5	H(15I)–C(153)–H(15K)	109.5
H(15J)–C(153)–H(15K)	109.5	C(154)–C(155)–H(15H)	119.5
C(154)–C(155)–C(156)	121.1(5)	H(15H)–C(155)–C(156)	119.5
C(155)–C(156)–H(15L)	120.6	C(155)–C(156)–C(157)	118.8(5)
H(15L)–C(156)–C(157)	120.6	C(156)–C(157)–H(15Q)	119.3
C(156)–C(157)–C(158)	121.4(5)	H(15Q)–C(157)–C(158)	119.3
C(157)–C(158)–H(15M)	120.4	C(157)–C(158)–C(159)	119.3(5)
H(15M)–C(158)–C(159)	120.4	O(8)–C(159)–C(154)	115.8(4)
O(8)–C(159)–C(158)	124.3(5)	C(154)–C(159)–C(158)	119.9(5)
O(8)–C(160)–H(16B)	109.5	O(8)–C(160)–H(16C)	109.5
O(8)–C(160)–H(16D)	109.5	H(16B)–C(160)–H(16C)	109.5
H(16B)–C(160)–H(16D)	109.5	H(16C)–C(160)–H(16D)	109.5
N(17)–C(161)–C(162)	109.4(5)	N(17)–C(161)–C(170)	122.2(5)
C(162)–C(161)–C(170)	128.4(6)	C(161)–C(162)–H(16F)	125.8
C(161)–C(162)–C(163)	108.4(6)	H(16F)–C(162)–C(163)	125.8
C(162)–C(163)–C(164)	106.3(5)	C(162)–C(163)–C(171)	125.4(6)
C(164)–C(163)–C(171)	128.3(6)	N(17)–C(164)–C(163)	108.3(5)
N(17)–C(164)–C(165)	119.1(5)	C(163)–C(164)–C(165)	132.6(5)
C(164)–C(165)–C(166)	122.8(4)	C(164)–C(165)–C(174)	119.3(5)
C(166)–C(165)–C(174)	117.9(5)	N(18)–C(166)–C(165)	120.2(5)
N(18)–C(166)–C(167)	107.5(5)	C(165)–C(166)–C(167)	132.3(5)
C(166)–C(167)–C(168)	105.6(5)	C(166)–C(167)–C(172)	129.3(5)
C(168)–C(167)–C(172)	125.1(6)	C(167)–C(168)–H(16E)	125.3
C(167)–C(168)–C(169)	109.4(6)	H(16E)–C(168)–C(169)	125.3
N(18)–C(169)–C(168)	109.3(5)	N(18)–C(169)–C(173)	122.7(5)
C(168)–C(169)–C(173)	128.0(6)	C(161)–C(170)–H(17N)	109.5
C(161)–C(170)–H(17O)	109.5	C(161)–C(170)–H(17P)	109.5
H(17N)–C(170)–H(17O)	109.5	H(17N)–C(170)–H(17P)	109.5
H(17O)–C(170)–H(17P)	109.5	C(163)–C(171)–H(17I)	109.5
C(163)–C(171)–H(17J)	109.5	C(163)–C(171)–H(17K)	109.5
H(17I)–C(171)–H(17J)	109.5	H(17I)–C(171)–H(17K)	109.5
H(17J)–C(171)–H(17K)	109.5	C(167)–C(172)–H(17B)	109.5
C(167)–C(172)–H(17C)	109.5	C(167)–C(172)–H(17D)	109.5
H(17B)–C(172)–H(17C)	109.5	H(17B)–C(172)–H(17D)	109.5
H(17C)–C(172)–H(17D)	109.5	C(169)–C(173)–H(17F)	109.5

C(169)–C(173)–H(17G)	109.5	C(169)–C(173)–H(17H)	109.5
H(17F)–C(173)–H(17G)	109.5	H(17F)–C(173)–H(17H)	109.5
H(17G)–C(173)–H(17H)	109.5	C(165)–C(174)–C(175)	120.6(5)
C(165)–C(174)–C(179)	119.7(5)	C(175)–C(174)–C(179)	119.7(5)
C(174)–C(175)–H(17E)	120.2	C(174)–C(175)–C(176)	119.5(5)
H(17E)–C(175)–C(176)	120.2	C(175)–C(176)–H(17M)	120.5
C(175)–C(176)–C(177)	119.0(6)	H(17M)–C(176)–C(177)	120.5
C(176)–C(177)–H(17Q)	118.6	C(176)–C(177)–C(178)	122.8(5)
H(17Q)–C(177)–C(178)	118.6	C(177)–C(178)–H(17L)	120.5
C(177)–C(178)–C(179)	118.9(6)	H(17L)–C(178)–C(179)	120.5
O(9)–C(179)–C(174)	114.7(4)	O(9)–C(179)–C(178)	125.3(5)
C(174)–C(179)–C(178)	120.0(6)	O(9)–C(180)–H(18B)	109.5
O(9)–C(180)–H(18C)	109.5	O(9)–C(180)–H(18D)	109.5
H(18B)–C(180)–H(18C)	109.5	H(18B)–C(180)–H(18D)	109.5
H(18C)–C(180)–H(18D)	109.5	N(2)–C(9)–C(8)	110.1(5)
N(2)–C(9)–C(13)	122.8(6)	C(8)–C(9)–C(13)	127.0(6)
C(9)–C(13)–H(10I)	109.5	C(9)–C(13)–H(10J)	109.5
C(9)–C(13)–H(10K)	109.5	H(10I)–C(13)–H(10J)	109.5
H(10I)–C(13)–H(10K)	109.5	H(10J)–C(13)–H(10K)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	0.030(3)	0.029(4)	0.032(3)	0.007(3)	−0.006(3)	−0.006(3)
B(1)	0.021(3)	0.028(5)	0.044(4)	0.003(4)	0.010(3)	0.001(3)
B(2)	0.021(3)	0.035(5)	0.035(4)	0.011(4)	0.008(3)	0.011(3)
B(3)	0.016(3)	0.032(5)	0.020(3)	−0.005(3)	−0.001(2)	0.002(3)
B(4)	0.022(3)	0.027(5)	0.022(3)	0.012(3)	0.002(3)	0.003(3)
B(5)	0.024(3)	0.022(5)	0.038(4)	0.003(3)	0.011(3)	0.001(3)
B(6)	0.021(3)	0.034(5)	0.044(4)	0.001(4)	0.015(3)	0.001(3)
B(7)	0.025(3)	0.034(5)	0.029(3)	0.003(4)	0.016(3)	0.004(3)
B(8)	0.020(3)	0.021(4)	0.023(3)	−0.003(3)	0.002(2)	0.004(3)
B(9)	0.023(3)	0.032(5)	0.028(3)	−0.005(3)	0.012(3)	−0.002(3)
O(1)	0.029(2)	0.043(3)	0.064(3)	0.032(3)	0.012(2)	0.006(2)
O(2)	0.0275(19)	0.041(3)	0.065(3)	0.034(3)	0.0074(19)	0.007(2)
O(3)	0.0212(18)	0.052(3)	0.033(2)	−0.008(2)	−0.0062(16)	−0.002(2)
O(4)	0.0172(17)	0.060(4)	0.023(2)	0.015(2)	−0.0061(15)	−0.001(2)
O(5)	0.049(2)	0.033(3)	0.038(2)	0.004(2)	−0.0048(19)	−0.006(2)
O(6)	0.040(2)	0.033(3)	0.033(2)	−0.010(2)	−0.0027(18)	0.002(2)
O(7)	0.0181(18)	0.045(3)	0.064(3)	0.039(3)	0.0076(18)	0.009(2)
O(8)	0.0281(19)	0.049(3)	0.031(2)	−0.007(2)	−0.0038(17)	0.002(2)
O(9)	0.0235(19)	0.061(4)	0.034(2)	−0.012(2)	−0.0070(17)	0.001(2)
F(1)	0.0336(17)	0.042(3)	0.075(3)	0.006(2)	0.0125(17)	0.0130(18)
F(2)	0.066(2)	0.035(3)	0.048(2)	0.0093(19)	0.0318(18)	−0.004(2)
F(3)	0.0208(15)	0.056(3)	0.072(2)	0.008(2)	0.0100(16)	0.0117(18)
F(4)	0.062(2)	0.034(3)	0.046(2)	−0.0023(19)	0.0311(17)	−0.0034(19)
F(5)	0.0072(12)	0.056(3)	0.0409(19)	0.0070(18)	0.0017(12)	−0.0011(15)
F(6)	0.0408(17)	0.050(3)	0.0305(18)	−0.0088(18)	0.0145(14)	0.0029(18)
F(7)	0.057(2)	0.043(3)	0.0386(19)	0.0121(18)	0.0260(16)	−0.0063(19)
F(8)	0.0205(14)	0.036(3)	0.058(2)	−0.0035(19)	−0.0030(14)	0.0020(16)
F(9)	0.0230(15)	0.034(2)	0.049(2)	−0.0043(18)	0.0042(14)	0.0001(16)
F(10)	0.0533(19)	0.038(3)	0.043(2)	0.0152(18)	0.0275(16)	0.0012(19)
F(11)	0.0255(15)	0.031(3)	0.066(2)	−0.0047(19)	0.0003(15)	−0.0012(16)
F(12)	0.068(2)	0.029(3)	0.052(2)	−0.0039(19)	0.0334(19)	0.0042(19)
F(13)	0.0176(15)	0.057(3)	0.072(2)	0.009(2)	0.0094(15)	0.0148(17)
F(14)	0.054(2)	0.056(3)	0.040(2)	0.009(2)	0.0299(17)	−0.004(2)
F(15)	0.0113(13)	0.047(3)	0.055(2)	−0.0035(19)	−0.0095(13)	−0.0007(15)
F(16)	0.0495(19)	0.048(3)	0.0354(19)	−0.0063(18)	0.0222(15)	0.0078(18)
F(17)	0.0277(15)	0.035(2)	0.047(2)	0.0023(18)	0.0077(14)	0.0011(16)
F(18)	0.0529(19)	0.029(2)	0.0395(19)	−0.0044(17)	0.0217(16)	0.0042(18)
N(1)	0.028(2)	0.019(3)	0.025(2)	0.005(2)	0.0029(19)	0.001(2)
N(2)	0.042(3)	0.028(3)	0.034(3)	−0.008(3)	0.016(2)	0.007(3)
N(3)	0.035(3)	0.032(4)	0.031(3)	−0.004(3)	0.012(2)	0.001(2)
N(4)	0.019(2)	0.030(3)	0.024(2)	0.009(2)	0.0034(18)	0.000(2)
N(5)	0.016(2)	0.038(4)	0.025(2)	−0.002(2)	0.0051(18)	0.002(2)
N(6)	0.019(2)	0.029(3)	0.016(2)	−0.003(2)	0.0044(17)	−0.002(2)
N(7)	0.020(2)	0.033(4)	0.022(2)	0.010(2)	0.0021(18)	0.001(2)
N(8)	0.021(2)	0.023(3)	0.016(2)	0.001(2)	0.0031(17)	0.001(2)
N(9)	0.026(2)	0.019(3)	0.024(2)	0.003(2)	0.0047(19)	0.008(2)
N(10)	0.026(2)	0.013(3)	0.038(3)	0.001(2)	0.002(2)	−0.002(2)
N(11)	0.024(2)	0.020(3)	0.033(3)	−0.008(2)	0.003(2)	−0.004(2)

N(12)	0.027(2)	0.015(3)	0.037(3)	–0.005(2)	0.004(2)	0.000(2)
N(13)	0.013(2)	0.035(3)	0.022(2)	–0.001(2)	0.0008(17)	–0.002(2)
N(14)	0.021(2)	0.045(4)	0.029(3)	–0.001(3)	0.0084(19)	0.002(2)
N(15)	0.016(2)	0.028(3)	0.020(2)	–0.001(2)	–0.0071(17)	0.007(2)
N(16)	0.017(2)	0.034(4)	0.017(2)	0.002(2)	0.0033(17)	0.001(2)
N(17)	0.021(2)	0.026(3)	0.032(3)	–0.002(2)	0.0095(19)	0.004(2)
N(18)	0.025(2)	0.028(3)	0.019(2)	0.001(2)	0.0003(18)	0.002(2)
C(2)	0.046(3)	0.022(4)	0.030(3)	–0.007(3)	0.009(3)	–0.006(3)
C(3)	0.030(3)	0.013(3)	0.023(3)	0.000(3)	0.007(2)	0.006(3)
C(4)	0.036(3)	0.022(4)	0.019(3)	0.006(3)	0.003(2)	0.004(3)
C(5)	0.020(3)	0.014(4)	0.031(3)	0.008(3)	0.000(2)	0.006(3)
C(6)	0.032(3)	0.016(4)	0.032(3)	0.005(3)	0.008(2)	0.004(3)
C(7)	0.049(3)	0.033(5)	0.034(3)	–0.012(3)	0.003(3)	0.001(3)
C(8)	0.074(5)	0.053(6)	0.033(4)	–0.018(4)	0.016(3)	0.004(4)
C(10)	0.053(4)	0.048(5)	0.043(4)	0.011(4)	0.006(3)	–0.019(4)
C(11)	0.055(4)	0.032(5)	0.034(3)	–0.008(3)	0.019(3)	0.000(3)
C(12)	0.050(4)	0.045(5)	0.037(4)	0.001(4)	–0.007(3)	–0.014(4)
C(14)	0.026(3)	0.025(4)	0.020(3)	0.002(3)	–0.003(2)	0.003(3)
C(15)	0.024(3)	0.024(4)	0.028(3)	0.006(3)	0.002(2)	0.005(3)
C(16)	0.026(3)	0.035(4)	0.039(3)	0.020(3)	0.001(3)	–0.007(3)
C(17)	0.028(3)	0.044(5)	0.041(4)	0.009(3)	0.006(3)	–0.006(3)
C(18)	0.024(3)	0.035(5)	0.045(4)	0.014(3)	0.003(3)	0.007(3)
C(19)	0.032(3)	0.027(4)	0.030(3)	0.009(3)	0.006(2)	–0.001(3)
C(20)	0.035(3)	0.053(6)	0.112(6)	0.056(5)	0.007(4)	0.015(4)
C(21)	0.058(4)	0.038(4)	0.042(3)	–0.020(3)	0.027(3)	0.010(3)
C(22)	0.070(4)	0.045(5)	0.040(4)	–0.028(4)	0.013(3)	–0.011(4)
C(23)	0.045(3)	0.033(5)	0.038(4)	–0.004(3)	–0.001(3)	0.000(3)
C(24)	0.025(3)	0.029(4)	0.027(3)	–0.001(3)	0.002(2)	–0.002(3)
C(25)	0.026(3)	0.020(4)	0.026(3)	0.005(3)	0.006(2)	0.005(3)
C(26)	0.014(2)	0.025(4)	0.022(3)	0.011(3)	0.001(2)	–0.002(3)
C(27)	0.032(3)	0.024(4)	0.024(3)	0.009(3)	0.005(2)	0.005(3)
C(28)	0.037(3)	0.041(5)	0.021(3)	0.000(3)	0.002(2)	–0.001(3)
C(29)	0.024(3)	0.026(4)	0.025(3)	0.013(3)	–0.002(2)	–0.004(3)
C(30)	0.081(5)	0.066(6)	0.068(5)	–0.034(4)	0.057(4)	0.001(4)
C(31)	0.056(4)	0.045(5)	0.037(4)	–0.004(4)	–0.007(3)	–0.011(4)
C(32)	0.048(3)	0.033(4)	0.027(3)	–0.001(3)	0.019(3)	–0.003(3)
C(33)	0.027(3)	0.064(6)	0.037(3)	0.010(4)	–0.002(3)	–0.015(3)
C(34)	0.027(3)	0.017(4)	0.025(3)	0.004(3)	0.004(2)	0.001(3)
C(35)	0.033(3)	0.034(5)	0.026(3)	0.007(3)	–0.004(2)	0.002(3)
C(36)	0.034(3)	0.034(4)	0.032(3)	0.013(3)	0.005(3)	–0.006(3)
C(37)	0.023(3)	0.043(5)	0.047(4)	0.019(4)	0.004(3)	–0.007(3)
C(38)	0.027(3)	0.034(5)	0.046(4)	0.013(3)	0.003(3)	0.000(3)
C(39)	0.027(3)	0.030(4)	0.035(3)	0.019(3)	0.000(2)	–0.002(3)
C(40)	0.043(4)	0.052(6)	0.106(6)	0.068(5)	0.015(4)	0.014(4)
C(41)	0.020(3)	0.040(5)	0.043(4)	–0.003(3)	0.006(3)	0.000(3)
C(42)	0.025(3)	0.035(4)	0.042(3)	0.005(3)	0.004(3)	–0.005(3)
C(43)	0.017(3)	0.042(5)	0.022(3)	–0.006(3)	–0.001(2)	–0.002(3)
C(44)	0.011(2)	0.032(4)	0.020(3)	0.003(3)	0.004(2)	0.002(3)
C(45)	0.015(2)	0.033(4)	0.012(2)	–0.008(3)	0.002(2)	–0.001(3)
C(46)	0.012(2)	0.030(4)	0.014(2)	0.001(3)	–0.001(2)	0.005(3)
C(47)	0.015(2)	0.043(5)	0.011(2)	–0.007(3)	–0.003(2)	–0.003(3)
C(48)	0.036(3)	0.025(4)	0.014(3)	0.003(3)	0.001(2)	–0.004(3)

C(49)	0.025(3)	0.039(5)	0.015(3)	–0.004(3)	–0.001(2)	–0.005(3)
C(50)	0.026(3)	0.044(5)	0.066(4)	0.004(4)	0.011(3)	0.014(3)
C(51)	0.029(3)	0.031(4)	0.046(4)	–0.004(3)	0.018(3)	–0.007(3)
C(52)	0.027(3)	0.034(4)	0.023(3)	–0.001(3)	0.001(2)	0.006(3)
C(53)	0.034(3)	0.045(5)	0.027(3)	–0.002(3)	0.012(2)	–0.012(3)
C(54)	0.015(2)	0.027(4)	0.031(3)	–0.001(3)	0.005(2)	0.004(3)
C(55)	0.030(3)	0.044(5)	0.044(4)	–0.002(3)	0.021(3)	0.004(3)
C(56)	0.043(4)	0.044(5)	0.061(4)	–0.007(4)	0.022(3)	–0.001(4)
C(57)	0.027(3)	0.055(6)	0.066(4)	–0.009(4)	0.025(3)	0.006(3)
C(58)	0.018(3)	0.040(5)	0.057(4)	–0.007(4)	0.000(3)	–0.005(3)
C(59)	0.016(3)	0.025(4)	0.040(3)	–0.004(3)	0.007(2)	0.000(3)
C(60)	0.038(3)	0.051(6)	0.048(4)	–0.008(4)	–0.016(3)	0.000(4)
C(61)	0.027(3)	0.021(4)	0.028(3)	0.008(3)	–0.005(2)	–0.007(3)
C(62)	0.042(3)	0.024(4)	0.026(3)	0.007(3)	–0.003(3)	–0.007(3)
C(63)	0.030(3)	0.035(4)	0.017(3)	0.004(3)	–0.004(2)	0.005(3)
C(64)	0.017(3)	0.025(4)	0.020(3)	0.007(3)	–0.002(2)	0.000(3)
C(65)	0.017(2)	0.027(4)	0.011(2)	0.006(3)	–0.003(2)	0.003(3)
C(66)	0.017(2)	0.021(4)	0.009(2)	0.006(2)	–0.0018(19)	–0.003(3)
C(67)	0.027(3)	0.026(4)	0.017(3)	0.005(3)	0.000(2)	0.002(3)
C(68)	0.040(3)	0.023(4)	0.016(3)	0.000(3)	0.004(2)	0.004(3)
C(70)	0.046(3)	0.036(5)	0.042(4)	0.001(3)	0.001(3)	–0.014(3)
C(71)	0.042(3)	0.028(4)	0.024(3)	0.001(3)	0.002(2)	0.008(3)
C(72)	0.029(3)	0.029(4)	0.034(3)	–0.004(3)	0.001(2)	–0.004(3)
C(73)	0.037(3)	0.038(5)	0.031(3)	–0.003(3)	0.006(3)	0.010(3)
C(74)	0.014(2)	0.031(4)	0.019(3)	0.003(3)	0.007(2)	0.003(3)
C(75)	0.033(3)	0.037(4)	0.024(3)	0.009(3)	0.004(2)	–0.010(3)
C(76)	0.034(3)	0.081(6)	0.025(3)	–0.010(4)	0.011(3)	–0.015(4)
C(69)	0.027(3)	0.036(5)	0.017(3)	0.010(3)	0.003(2)	0.003(3)
C(77)	0.026(3)	0.086(7)	0.045(4)	–0.014(4)	0.021(3)	–0.015(4)
C(78)	0.012(2)	0.053(5)	0.049(4)	–0.017(4)	0.003(2)	–0.001(3)
C(79)	0.013(2)	0.036(4)	0.031(3)	–0.009(3)	0.000(2)	0.002(3)
C(80)	0.027(3)	0.074(6)	0.034(3)	0.012(4)	–0.009(3)	0.003(3)
C(81)	0.029(3)	0.024(4)	0.026(3)	0.002(3)	0.006(2)	0.006(3)
C(82)	0.038(3)	0.019(4)	0.029(3)	0.000(3)	0.003(3)	0.007(3)
C(83)	0.040(3)	0.018(4)	0.028(3)	0.001(3)	–0.003(3)	–0.003(3)
C(84)	0.026(3)	0.019(4)	0.028(3)	0.010(3)	–0.001(2)	0.002(3)
C(85)	0.020(3)	0.021(4)	0.023(3)	0.000(3)	–0.002(2)	0.004(3)
C(86)	0.020(3)	0.020(4)	0.034(3)	0.004(3)	0.007(2)	0.002(3)
C(87)	0.032(3)	0.021(4)	0.037(3)	–0.002(3)	0.010(3)	0.000(3)
C(88)	0.049(4)	0.013(4)	0.057(4)	–0.010(3)	0.007(3)	–0.003(3)
C(89)	0.031(3)	0.017(4)	0.052(4)	–0.002(3)	0.008(3)	–0.006(3)
C(90)	0.041(3)	0.037(5)	0.049(4)	0.001(4)	0.018(3)	0.002(3)
C(91)	0.040(3)	0.019(4)	0.041(4)	–0.006(3)	–0.004(3)	–0.005(3)
C(92)	0.038(3)	0.029(4)	0.050(4)	–0.011(3)	0.014(3)	0.000(3)
C(93)	0.040(3)	0.029(5)	0.087(5)	–0.003(4)	0.021(3)	–0.013(3)
C(94)	0.030(3)	0.009(3)	0.042(3)	0.007(3)	0.013(3)	0.006(3)
C(95)	0.046(3)	0.024(4)	0.051(4)	0.003(3)	0.025(3)	–0.003(3)
C(96)	0.073(5)	0.029(5)	0.055(4)	0.021(4)	0.033(4)	–0.002(4)
C(97)	0.049(4)	0.035(5)	0.086(6)	0.012(4)	0.033(4)	–0.007(4)
C(98)	0.032(3)	0.018(4)	0.077(5)	–0.003(4)	0.002(3)	–0.006(3)
C(99)	0.043(3)	0.012(4)	0.046(4)	0.004(3)	0.009(3)	–0.005(3)
C(100)	0.054(4)	0.033(5)	0.053(4)	0.001(4)	–0.018(3)	0.002(4)

C(101)	0.034(3)	0.020(4)	0.031(3)	0.006(3)	0.010(3)	–0.002(3)
C(102)	0.040(3)	0.022(4)	0.040(4)	0.005(3)	0.007(3)	–0.001(3)
C(103)	0.029(3)	0.014(4)	0.030(3)	0.005(3)	–0.005(2)	0.003(3)
C(104)	0.020(3)	0.025(4)	0.026(3)	–0.004(3)	0.005(2)	0.001(3)
C(105)	0.022(3)	0.021(4)	0.025(3)	–0.004(3)	0.001(2)	–0.002(3)
C(106)	0.032(3)	0.021(4)	0.026(3)	–0.001(3)	0.004(2)	–0.003(3)
C(107)	0.035(3)	0.023(4)	0.025(3)	–0.005(3)	0.006(2)	0.000(3)
C(108)	0.045(3)	0.022(4)	0.037(4)	0.000(3)	0.000(3)	0.001(3)
C(109)	0.033(3)	0.022(4)	0.037(3)	–0.002(3)	–0.007(3)	0.007(3)
C(110)	0.046(3)	0.033(5)	0.042(4)	0.001(3)	0.016(3)	–0.006(3)
C(111)	0.038(3)	0.012(4)	0.042(3)	0.005(3)	0.005(3)	0.010(3)
C(112)	0.045(3)	0.025(4)	0.042(4)	–0.002(3)	0.009(3)	–0.009(3)
C(113)	0.040(3)	0.037(5)	0.064(4)	–0.005(4)	0.005(3)	0.009(3)
C(114)	0.032(3)	0.013(4)	0.033(3)	0.002(3)	0.005(2)	0.002(3)
C(115)	0.041(3)	0.040(5)	0.032(3)	0.006(3)	0.011(3)	0.011(3)
C(116)	0.060(4)	0.050(5)	0.038(4)	0.004(4)	0.023(3)	0.016(4)
C(117)	0.042(3)	0.033(4)	0.050(4)	0.012(3)	0.018(3)	0.012(3)
C(118)	0.033(3)	0.035(5)	0.048(4)	0.004(3)	0.010(3)	–0.002(3)
C(119)	0.035(3)	0.012(4)	0.041(4)	–0.006(3)	0.006(3)	0.000(3)
C(120)	0.053(4)	0.045(5)	0.048(4)	–0.014(4)	–0.012(3)	–0.005(4)
C(121)	0.030(3)	0.047(5)	0.018(3)	0.003(3)	–0.002(2)	–0.002(3)
C(122)	0.037(3)	0.043(5)	0.014(3)	0.001(3)	–0.003(2)	–0.007(3)
C(123)	0.017(2)	0.046(5)	0.021(3)	–0.001(3)	0.003(2)	–0.002(3)
C(124)	0.010(2)	0.035(4)	0.019(3)	0.007(3)	0.003(2)	0.002(3)
C(125)	0.019(2)	0.033(4)	0.012(2)	0.010(3)	0.000(2)	0.007(3)
C(126)	0.022(3)	0.040(5)	0.021(3)	0.003(3)	0.002(2)	0.005(3)
C(127)	0.040(3)	0.048(5)	0.024(3)	0.000(3)	0.005(3)	–0.004(3)
C(128)	0.059(4)	0.059(6)	0.041(4)	–0.016(4)	0.012(3)	–0.005(4)
C(129)	0.049(4)	0.074(6)	0.038(3)	–0.020(4)	0.023(3)	0.000(4)
C(130)	0.025(3)	0.052(5)	0.041(3)	–0.002(4)	–0.002(2)	–0.011(3)
C(131)	0.032(3)	0.048(5)	0.031(3)	0.006(3)	0.014(2)	0.001(3)
C(132)	0.042(3)	0.060(6)	0.036(4)	–0.008(4)	–0.008(3)	–0.011(4)
C(133)	0.077(5)	0.107(8)	0.070(5)	–0.040(5)	0.062(4)	–0.009(5)
C(134)	0.010(2)	0.034(4)	0.025(3)	0.000(3)	0.003(2)	–0.003(3)
C(135)	0.019(3)	0.027(4)	0.026(3)	0.012(3)	–0.004(2)	0.005(3)
C(136)	0.023(3)	0.039(5)	0.035(3)	0.010(3)	0.001(2)	–0.007(3)
C(137)	0.016(3)	0.043(5)	0.038(3)	0.001(3)	0.005(2)	–0.008(3)
C(138)	0.010(2)	0.050(5)	0.041(3)	0.020(3)	0.002(2)	0.003(3)
C(139)	0.012(2)	0.039(5)	0.036(3)	0.010(3)	0.002(2)	0.005(3)
C(140)	0.025(3)	0.061(6)	0.102(6)	0.036(5)	0.004(3)	0.015(4)
C(141)	0.030(3)	0.035(5)	0.023(3)	–0.003(3)	–0.004(2)	0.004(3)
C(142)	0.035(3)	0.022(4)	0.024(3)	0.008(3)	–0.005(2)	0.000(3)
C(143)	0.032(3)	0.021(4)	0.018(3)	0.003(3)	–0.002(2)	–0.003(3)
C(144)	0.013(2)	0.036(4)	0.010(2)	–0.004(3)	0.0002(19)	0.002(3)
C(145)	0.019(2)	0.027(4)	0.012(2)	–0.003(3)	0.000(2)	–0.003(3)
C(146)	0.016(2)	0.032(4)	0.016(3)	0.001(3)	–0.001(2)	–0.004(3)
C(147)	0.024(3)	0.033(4)	0.019(3)	–0.008(3)	–0.002(2)	0.003(3)
C(148)	0.028(3)	0.022(4)	0.021(3)	0.006(3)	–0.004(2)	0.001(3)
C(149)	0.028(3)	0.030(4)	0.011(2)	–0.004(3)	–0.003(2)	–0.009(3)
C(150)	0.027(3)	0.036(5)	0.065(4)	0.002(4)	0.003(3)	0.018(3)
C(151)	0.042(3)	0.040(5)	0.026(3)	0.010(3)	0.010(3)	0.000(3)
C(152)	0.031(3)	0.049(5)	0.040(4)	–0.002(3)	0.003(3)	0.008(3)

C(154)	0.022(3)	0.029(4)	0.029(3)	0.011(3)	0.001(2)	0.004(3)
C(153)	0.031(3)	0.052(5)	0.028(3)	–0.003(3)	0.017(2)	–0.007(3)
C(155)	0.030(3)	0.046(5)	0.019(3)	0.001(3)	0.006(2)	0.000(3)
C(156)	0.051(4)	0.058(6)	0.033(3)	–0.002(4)	0.019(3)	0.011(4)
C(157)	0.029(3)	0.068(6)	0.048(4)	0.012(4)	0.019(3)	0.010(4)
C(158)	0.024(3)	0.039(5)	0.042(4)	0.010(3)	0.000(3)	0.006(3)
C(159)	0.024(3)	0.029(4)	0.030(3)	0.002(3)	0.004(2)	0.001(3)
C(160)	0.034(3)	0.051(5)	0.044(4)	0.006(4)	–0.012(3)	0.001(3)
C(161)	0.030(3)	0.019(4)	0.046(4)	0.000(3)	0.005(3)	0.010(3)
C(162)	0.038(3)	0.020(4)	0.049(4)	0.004(3)	0.015(3)	0.006(3)
C(163)	0.030(3)	0.021(4)	0.037(3)	0.001(3)	0.007(3)	–0.006(3)
C(164)	0.023(3)	0.024(4)	0.023(3)	–0.005(3)	0.004(2)	0.002(3)
C(165)	0.015(2)	0.024(4)	0.023(3)	–0.005(3)	–0.001(2)	0.001(3)
C(166)	0.017(2)	0.027(4)	0.020(3)	0.001(3)	0.005(2)	0.001(3)
C(167)	0.027(3)	0.022(4)	0.020(3)	–0.001(3)	–0.006(2)	0.001(3)
C(168)	0.037(3)	0.031(4)	0.021(3)	0.003(3)	–0.001(2)	0.002(3)
C(169)	0.034(3)	0.025(4)	0.023(3)	0.001(3)	0.009(2)	–0.003(3)
C(170)	0.047(4)	0.022(4)	0.076(5)	0.003(4)	0.019(3)	0.006(3)
C(171)	0.032(3)	0.039(5)	0.043(4)	0.009(3)	0.011(3)	–0.003(3)
C(172)	0.031(3)	0.031(4)	0.038(3)	0.002(3)	–0.001(3)	0.005(3)
C(173)	0.049(3)	0.036(5)	0.042(4)	0.003(3)	0.025(3)	–0.008(3)
C(174)	0.020(3)	0.023(4)	0.033(3)	0.006(3)	0.003(2)	0.002(3)
C(175)	0.038(3)	0.037(5)	0.037(3)	–0.006(3)	0.018(3)	–0.004(3)
C(176)	0.034(3)	0.057(6)	0.058(4)	–0.002(4)	0.028(3)	0.005(4)
C(177)	0.032(3)	0.043(5)	0.076(5)	–0.006(4)	0.026(3)	0.005(3)
C(178)	0.014(3)	0.044(5)	0.077(5)	0.006(4)	0.001(3)	0.002(3)
C(179)	0.019(3)	0.036(5)	0.036(3)	0.001(3)	–0.003(2)	0.003(3)
C(180)	0.039(3)	0.075(7)	0.036(4)	–0.001(4)	–0.018(3)	–0.004(4)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh12.

	x	y	z	U
H(2A)	–0.0641	–0.4875	0.6150	0.039
H(8A)	–0.1108	–0.8958	0.4409	0.064
H(10A)	0.0195	–0.5657	0.5672	0.072
H(10B)	0.0096	–0.4738	0.5917	0.072
H(10C)	–0.0040	–0.4661	0.5505	0.072
H(11A)	–0.1343	–0.5511	0.6288	0.059
H(11B)	–0.1441	–0.6666	0.6171	0.059
H(11C)	–0.1648	–0.5749	0.5934	0.059
H(12A)	–0.1820	–0.9204	0.4611	0.068
H(12B)	–0.1956	–0.8163	0.4775	0.068
H(12C)	–0.1805	–0.9108	0.5023	0.068
H(15A)	–0.1497	–0.8751	0.5768	0.031
H(16A)	–0.2156	–0.9135	0.5894	0.040
H(17A)	–0.2717	–0.8114	0.5666	0.045
H(18A)	–0.2620	–0.6682	0.5330	0.042
H(20A)	–0.2126	–0.4778	0.4924	0.100
H(20B)	–0.2366	–0.5115	0.5235	0.100
H(20C)	–0.2449	–0.5705	0.4871	0.100
H(22A)	–0.2221	–0.1021	0.5584	0.062
H(28A)	–0.2697	–0.5087	0.3837	0.040
H(30A)	–0.3069	–0.2725	0.5532	0.100
H(30B)	–0.3274	–0.1854	0.5273	0.100
H(30C)	–0.3009	–0.1552	0.5640	0.100
H(31A)	–0.1521	–0.0774	0.5386	0.071
H(31B)	–0.1527	–0.0911	0.4977	0.071
H(31C)	–0.1374	–0.1827	0.5237	0.071
H(32A)	–0.1987	–0.4496	0.3716	0.052
H(32B)	–0.1686	–0.4282	0.4074	0.052
H(32C)	–0.1879	–0.3350	0.3838	0.052
H(33A)	–0.3310	–0.5276	0.4507	0.065
H(33B)	–0.3411	–0.5337	0.4092	0.065
H(33C)	–0.3540	–0.4347	0.4291	0.065
H(35A)	–0.1839	–0.1259	0.4229	0.038
H(36A)	–0.1181	–0.0874	0.4108	0.040
H(37A)	–0.0615	–0.1878	0.4335	0.046
H(38A)	–0.0709	–0.3303	0.4670	0.043
H(40A)	–0.1199	–0.5222	0.5070	0.100
H(40B)	–0.0884	–0.4279	0.5124	0.100
H(40C)	–0.0965	–0.4857	0.4758	0.100
H(42A)	0.5289	0.8714	0.0847	0.041
H(48A)	0.5254	0.2752	0.1761	0.030
H(50A)	0.4375	0.7647	0.1225	0.067
H(50B)	0.4448	0.8506	0.0949	0.067
H(50C)	0.4620	0.8669	0.1353	0.067
H(51A)	0.6019	0.8231	0.0754	0.052
H(51B)	0.6000	0.7078	0.0619	0.052
H(51C)	0.6235	0.7345	0.1001	0.052

H(52A)	0.5941	0.2524	0.1546	0.042
H(52B)	0.6210	0.3551	0.1573	0.042
H(52C)	0.5978	0.3168	0.1202	0.042
H(53A)	0.4502	0.4718	0.1918	0.052
H(53B)	0.4563	0.3512	0.1959	0.052
H(53C)	0.4324	0.3979	0.1603	0.052
H(55A)	0.5850	0.4741	0.0649	0.046
H(56A)	0.6508	0.4299	0.0504	0.057
H(57A)	0.7103	0.4656	0.0897	0.057
H(58A)	0.7064	0.5405	0.1433	0.047
H(60A)	0.6626	0.6299	0.2145	0.072
H(60B)	0.6927	0.6483	0.1862	0.072
H(60C)	0.6843	0.5350	0.1987	0.072
H(62A)	0.2776	–0.2226	0.1689	0.038
H(68A)	0.2984	0.3871	0.2517	0.032
H(70A)	0.1873	–0.0873	0.1898	0.063
H(70B)	0.2084	–0.1452	0.2242	0.063
H(70C)	0.2019	–0.2032	0.1876	0.063
H(71A)	0.3499	–0.1871	0.1536	0.047
H(71B)	0.3763	–0.1245	0.1847	0.047
H(71C)	0.3603	–0.0694	0.1484	0.047
H(72A)	0.3709	0.3825	0.2342	0.046
H(72B)	0.3675	0.3282	0.1970	0.046
H(72C)	0.3897	0.2708	0.2312	0.046
H(73A)	0.2004	0.2429	0.2436	0.052
H(73B)	0.2206	0.3450	0.2612	0.052
H(73C)	0.2271	0.2391	0.2817	0.052
H(75A)	0.3451	0.1474	0.1397	0.037
H(76A)	0.4092	0.1579	0.1200	0.055
H(77A)	0.4703	0.1279	0.1583	0.061
H(78A)	0.4679	0.0821	0.2153	0.046
H(80A)	0.4283	0.0548	0.2939	0.070
H(80B)	0.4522	0.1246	0.2696	0.070
H(80C)	0.4539	0.0031	0.2665	0.070
H(82A)	0.1409	–0.2244	0.3240	0.035
H(88A)	0.1387	0.3708	0.4153	0.048
H(90A)	0.2188	–0.0255	0.3122	0.062
H(90B)	0.2079	–0.1409	0.3011	0.062
H(90C)	0.2330	–0.1163	0.3389	0.062
H(91A)	0.0698	–0.2428	0.3424	0.052
H(91B)	0.0460	–0.1376	0.3460	0.052
H(91C)	0.0714	–0.1908	0.3798	0.052
H(92A)	0.0680	0.3137	0.4313	0.057
H(92B)	0.0635	0.1926	0.4338	0.057
H(92C)	0.0431	0.2513	0.3994	0.057
H(93A)	0.2114	0.3168	0.3579	0.076
H(93B)	0.2333	0.2766	0.3951	0.076
H(93C)	0.2103	0.3848	0.3919	0.076
H(95A)	0.0811	–0.0257	0.4356	0.046
H(96A)	0.0152	–0.0697	0.4491	0.060
H(97A)	–0.0430	–0.0369	0.4102	0.065
H(98A)	–0.0400	0.0407	0.3574	0.051
H(10D)	0.0035	0.1278	0.2852	0.074

H(10E)	–0.0258	0.1485	0.3140	0.074
H(10F)	–0.0185	0.0345	0.3016	0.074
H(10G)	0.0351	0.8869	0.2483	0.041
H(10H)	0.0559	0.2793	0.3310	0.042
H(11L)	0.1147	0.7092	0.2284	0.059
H(11M)	0.1322	0.7803	0.2608	0.059
H(11N)	0.1061	0.8293	0.2265	0.059
H(11G)	–0.0348	0.8888	0.2708	0.046
H(11H)	–0.0369	0.8125	0.3025	0.046
H(11I)	–0.0567	0.7800	0.2639	0.046
H(11D)	–0.0184	0.3063	0.3418	0.056
H(11E)	–0.0441	0.3909	0.3180	0.056
H(11F)	–0.0222	0.4193	0.3564	0.056
H(11Q)	0.1462	0.4141	0.3092	0.071
H(11R)	0.1253	0.3460	0.2771	0.071
H(11S)	0.1324	0.2994	0.3155	0.071
H(11J)	–0.0118	0.6469	0.3605	0.045
H(11O)	–0.0772	0.6592	0.3795	0.057
H(11P)	–0.1370	0.6263	0.3411	0.049
H(11K)	–0.1344	0.5827	0.2842	0.046
H(12D)	–0.0945	0.5558	0.2060	0.076
H(12E)	–0.1188	0.6242	0.2304	0.076
H(12F)	–0.1202	0.5026	0.2330	0.076
H(12G)	0.3964	0.4916	0.3835	0.039
H(12H)	0.4442	0.8980	0.5580	0.063
H(13H)	0.3325	0.4970	0.4539	0.060
H(13I)	0.3311	0.4480	0.4160	0.060
H(13J)	0.3118	0.5587	0.4201	0.060
H(13C)	0.4661	0.5616	0.3690	0.054
H(13D)	0.4972	0.5612	0.4052	0.054
H(13E)	0.4818	0.6670	0.3872	0.054
H(13K)	0.5158	0.9173	0.5403	0.072
H(13L)	0.5137	0.9154	0.4990	0.072
H(13M)	0.5294	0.8170	0.5215	0.072
H(13N)	0.3411	0.8322	0.5303	0.119
H(13O)	0.3692	0.8263	0.5678	0.119
H(13P)	0.3562	0.7240	0.5465	0.119
H(13A)	0.4822	0.8734	0.4223	0.030
H(13F)	0.5488	0.9134	0.4110	0.039
H(13B)	0.6051	0.8134	0.4344	0.039
H(13G)	0.5958	0.6718	0.4680	0.041
H(14A)	0.5468	0.4877	0.5122	0.095
H(14B)	0.5802	0.5755	0.5092	0.095
H(14C)	0.5658	0.5017	0.4769	0.095
H(14E)	0.3893	0.2792	0.3316	0.034
H(14D)	0.3684	0.8876	0.2484	0.029
H(15N)	0.4620	0.3697	0.2770	0.065
H(15O)	0.4619	0.2889	0.3077	0.065
H(15P)	0.4802	0.4008	0.3161	0.065
H(15E)	0.3175	0.3167	0.3491	0.054
H(15F)	0.2910	0.3667	0.3153	0.054
H(15G)	0.3047	0.4344	0.3493	0.054
H(15B)	0.2959	0.8828	0.2655	0.061
H(15C)	0.2983	0.8275	0.3024	0.061

H(15D)	0.2768	0.7711	0.2678	0.061
H(15I)	0.4669	0.7653	0.2601	0.054
H(15J)	0.4422	0.8399	0.2316	0.054
H(15K)	0.4449	0.7207	0.2236	0.054
H(15H)	0.3217	0.6458	0.3605	0.038
H(15L)	0.2573	0.6619	0.3800	0.055
H(15Q)	0.1967	0.6256	0.3420	0.056
H(15M)	0.1990	0.5819	0.2842	0.043
H(16B)	0.2378	0.5359	0.2071	0.068
H(16C)	0.2180	0.6280	0.2260	0.068
H(16D)	0.2101	0.5129	0.2369	0.068
H(16F)	0.1955	0.8738	0.0848	0.042
H(16E)	0.1918	0.2764	0.1760	0.036
H(17N)	0.1189	0.8028	0.1406	0.071
H(17O)	0.1011	0.7861	0.1003	0.071
H(17P)	0.1254	0.8889	0.1128	0.071
H(17I)	0.2667	0.8166	0.0707	0.056
H(17J)	0.2694	0.6961	0.0652	0.056
H(17K)	0.2905	0.7464	0.1011	0.056
H(17B)	0.2617	0.2535	0.1552	0.051
H(17C)	0.2876	0.3575	0.1568	0.051
H(17D)	0.2642	0.3160	0.1203	0.051
H(17F)	0.1221	0.4574	0.1988	0.060
H(17G)	0.1186	0.3394	0.1884	0.060
H(17H)	0.0989	0.4242	0.1612	0.060
H(17E)	0.2522	0.4770	0.0641	0.043
H(17M)	0.3181	0.4275	0.0512	0.057
H(17Q)	0.3769	0.4659	0.0898	0.058
H(17L)	0.3734	0.5402	0.1431	0.055
H(18B)	0.3295	0.6321	0.2142	0.079
H(18C)	0.3597	0.6457	0.1856	0.079
H(18D)	0.3505	0.5344	0.1995	0.079
H(10I)	–0.0238	–0.7240	0.4507	0.109
H(10J)	–0.0355	–0.8325	0.4331	0.109
H(10K)	–0.0070	–0.8263	0.4704	0.109

Table 6. Torsion angles [°] for mjh12.

C(2)–C(1)–N(1)–B(1)	−179.2(5)	C(2)–C(1)–N(1)–C(3)	−0.8(6)
C(10)–C(1)–N(1)–B(1)	5.0(9)	C(10)–C(1)–N(1)–C(3)	−176.6(5)
F(1)–B(1)–N(1)–C(1)	64.4(8)	F(1)–B(1)–N(1)–C(3)	−113.7(6)
F(2)–B(1)–N(1)–C(1)	−57.9(7)	F(2)–B(1)–N(1)–C(3)	123.9(6)
N(2)–B(1)–N(1)–C(1)	−176.2(5)	N(2)–B(1)–N(1)–C(3)	5.7(8)
F(1)–B(1)–N(2)–C(6)	117.1(6)	F(1)–B(1)–N(2)–C(9)	−65.5(8)
F(2)–B(1)–N(2)–C(6)	−122.2(6)	F(2)–B(1)–N(2)–C(9)	55.1(8)
N(1)–B(1)–N(2)–C(6)	−3.0(8)	N(1)–B(1)–N(2)–C(9)	174.3(6)
F(3)–B(2)–N(3)–C(21)	65.1(8)	F(3)–B(2)–N(3)–C(24)	−117.5(6)
F(4)–B(2)–N(3)–C(21)	−54.7(8)	F(4)–B(2)–N(3)–C(24)	122.7(6)
N(4)–B(2)–N(3)–C(21)	−174.8(6)	N(4)–B(2)–N(3)–C(24)	2.6(8)
F(3)–B(2)–N(4)–C(26)	113.7(6)	F(3)–B(2)–N(4)–C(29)	−64.8(8)
F(4)–B(2)–N(4)–C(26)	−125.8(5)	F(4)–B(2)–N(4)–C(29)	55.7(7)
N(3)–B(2)–N(4)–C(26)	−6.4(7)	N(3)–B(2)–N(4)–C(29)	175.1(5)
F(5)–B(3)–N(5)–C(41)	59.2(7)	F(5)–B(3)–N(5)–C(44)	−124.3(5)
F(6)–B(3)–N(5)–C(41)	−60.6(7)	F(6)–B(3)–N(5)–C(44)	115.9(5)
N(6)–B(3)–N(5)–C(41)	177.6(5)	N(6)–B(3)–N(5)–C(44)	−5.9(6)
F(5)–B(3)–N(6)–C(46)	123.4(5)	F(5)–B(3)–N(6)–C(49)	−59.3(6)
F(6)–B(3)–N(6)–C(46)	−116.7(5)	F(6)–B(3)–N(6)–C(49)	60.5(6)
N(5)–B(3)–N(6)–C(46)	4.7(6)	N(5)–B(3)–N(6)–C(49)	−178.1(4)
F(7)–B(4)–N(7)–C(61)	57.5(6)	F(7)–B(4)–N(7)–C(64)	−121.8(5)
F(8)–B(4)–N(7)–C(61)	−61.2(7)	F(8)–B(4)–N(7)–C(64)	119.5(5)
N(8)–B(4)–N(7)–C(61)	178.6(5)	N(8)–B(4)–N(7)–C(64)	−0.7(6)
F(7)–B(4)–N(8)–C(66)	122.4(5)	F(7)–B(4)–N(8)–C(69)	−60.5(7)
F(8)–B(4)–N(8)–C(66)	−116.8(5)	F(8)–B(4)–N(8)–C(69)	60.3(6)
N(7)–B(4)–N(8)–C(66)	2.4(6)	N(7)–B(4)–N(8)–C(69)	179.5(4)
F(9)–B(5)–N(9)–C(81)	−58.4(7)	F(9)–B(5)–N(9)–C(84)	121.6(5)
F(10)–B(5)–N(9)–C(81)	62.6(7)	F(10)–B(5)–N(9)–C(84)	−117.5(5)
N(10)–B(5)–N(9)–C(81)	−177.9(5)	N(10)–B(5)–N(9)–C(84)	2.0(7)
F(9)–B(5)–N(10)–C(86)	−122.5(5)	F(9)–B(5)–N(10)–C(89)	57.9(8)
F(10)–B(5)–N(10)–C(86)	116.1(6)	F(10)–B(5)–N(10)–C(89)	−63.5(7)
N(9)–B(5)–N(10)–C(86)	−3.3(7)	N(9)–B(5)–N(10)–C(89)	177.1(5)
F(11)–B(6)–N(11)–C(101)	60.1(7)	F(11)–B(6)–N(11)–C(104)	−115.9(5)
F(12)–B(6)–N(11)–C(101)	−60.8(7)	F(12)–B(6)–N(11)–C(104)	123.2(5)
N(12)–B(6)–N(11)–C(101)	179.5(5)	N(12)–B(6)–N(11)–C(104)	3.5(7)
F(11)–B(6)–N(12)–C(106)	117.2(5)	F(11)–B(6)–N(12)–C(109)	−61.6(8)
F(12)–B(6)–N(12)–C(106)	−121.7(5)	F(12)–B(6)–N(12)–C(109)	59.5(7)
N(11)–B(6)–N(12)–C(106)	−1.8(7)	N(11)–B(6)–N(12)–C(109)	179.4(5)
F(13)–B(7)–N(13)–C(121)	−62.8(8)	F(13)–B(7)–N(13)–C(124)	114.2(6)
F(14)–B(7)–N(13)–C(121)	56.1(7)	F(14)–B(7)–N(13)–C(124)	−126.9(5)
N(14)–B(7)–N(13)–C(121)	175.6(5)	N(14)–B(7)–N(13)–C(124)	−7.3(7)
F(13)–B(7)–N(14)–C(126)	−116.6(6)	F(13)–B(7)–N(14)–C(129)	64.2(8)
F(14)–B(7)–N(14)–C(126)	122.9(6)	F(14)–B(7)–N(14)–C(129)	−56.3(8)
N(13)–B(7)–N(14)–C(126)	4.3(8)	N(13)–B(7)–N(14)–C(129)	−174.9(6)
F(15)–B(8)–N(15)–C(141)	−63.7(7)	F(15)–B(8)–N(15)–C(144)	119.3(5)
F(16)–B(8)–N(15)–C(141)	57.9(6)	F(16)–B(8)–N(15)–C(144)	−119.1(5)
N(16)–B(8)–N(15)–C(141)	177.4(4)	N(16)–B(8)–N(15)–C(144)	0.3(6)
F(15)–B(8)–N(16)–C(146)	−116.8(5)	F(15)–B(8)–N(16)–C(149)	58.6(6)
F(16)–B(8)–N(16)–C(146)	123.3(5)	F(16)–B(8)–N(16)–C(149)	−61.3(7)
N(15)–B(8)–N(16)–C(146)	2.9(6)	N(15)–B(8)–N(16)–C(149)	178.2(4)

F(17)–B(9)–N(17)–C(161)	56.9(8)	F(17)–B(9)–N(17)–C(164)	–124.6(5)
F(18)–B(9)–N(17)–C(161)	–61.6(7)	F(18)–B(9)–N(17)–C(164)	116.8(5)
N(18)–B(9)–N(17)–C(161)	177.5(5)	N(18)–B(9)–N(17)–C(164)	–4.1(7)
F(17)–B(9)–N(18)–C(166)	122.4(5)	F(17)–B(9)–N(18)–C(169)	–58.2(7)
F(18)–B(9)–N(18)–C(166)	–117.2(5)	F(18)–B(9)–N(18)–C(169)	62.2(7)
N(17)–B(9)–N(18)–C(166)	2.7(7)	N(17)–B(9)–N(18)–C(169)	–177.9(5)
N(1)–C(1)–C(2)–C(4)	1.9(7)	C(10)–C(1)–C(2)–C(4)	177.3(6)
C(1)–N(1)–C(3)–C(4)	–0.6(6)	C(1)–N(1)–C(3)–C(5)	176.0(5)
B(1)–N(1)–C(3)–C(4)	177.8(5)	B(1)–N(1)–C(3)–C(5)	–5.6(8)
C(1)–C(2)–C(4)–C(3)	–2.2(7)	C(1)–C(2)–C(4)–C(11)	178.5(5)
N(1)–C(3)–C(4)–C(2)	1.8(6)	N(1)–C(3)–C(4)–C(11)	–179.0(5)
C(5)–C(3)–C(4)–C(2)	–174.4(6)	C(5)–C(3)–C(4)–C(11)	4.9(10)
N(1)–C(3)–C(5)–C(6)	2.0(8)	N(1)–C(3)–C(5)–C(14)	–178.8(5)
C(4)–C(3)–C(5)–C(6)	177.7(6)	C(4)–C(3)–C(5)–C(14)	–3.1(9)
C(3)–C(5)–C(6)–N(2)	0.5(8)	C(3)–C(5)–C(6)–C(7)	–176.9(6)
C(14)–C(5)–C(6)–N(2)	–178.7(5)	C(14)–C(5)–C(6)–C(7)	3.9(10)
B(1)–N(2)–C(6)–C(5)	0.3(9)	B(1)–N(2)–C(6)–C(7)	178.3(6)
C(9)–N(2)–C(6)–C(5)	–177.4(6)	C(9)–N(2)–C(6)–C(7)	0.6(7)
N(2)–C(6)–C(7)–C(8)	–0.6(7)	N(2)–C(6)–C(7)–C(12)	–175.3(6)
C(5)–C(6)–C(7)–C(8)	177.1(7)	C(5)–C(6)–C(7)–C(12)	2.4(12)
C(6)–C(7)–C(8)–C(9)	0.3(8)	C(12)–C(7)–C(8)–C(9)	175.2(7)
C(3)–C(5)–C(14)–C(15)	–94.5(7)	C(3)–C(5)–C(14)–C(19)	89.0(7)
C(6)–C(5)–C(14)–C(15)	84.7(7)	C(6)–C(5)–C(14)–C(19)	–91.8(7)
C(5)–C(14)–C(15)–C(16)	–177.9(5)	C(19)–C(14)–C(15)–C(16)	–1.3(9)
C(14)–C(15)–C(16)–C(17)	1.3(9)	C(15)–C(16)–C(17)–C(18)	–1.0(10)
C(16)–C(17)–C(18)–C(19)	0.7(10)	C(20)–O(1)–C(19)–C(14)	–175.4(6)
C(20)–O(1)–C(19)–C(18)	3.1(9)	C(17)–C(18)–C(19)–O(1)	–179.1(6)
C(17)–C(18)–C(19)–C(14)	–0.7(9)	C(5)–C(14)–C(19)–O(1)	–3.8(8)
C(5)–C(14)–C(19)–C(18)	177.7(5)	C(15)–C(14)–C(19)–O(1)	179.6(5)
C(15)–C(14)–C(19)–C(18)	1.0(9)	B(2)–N(3)–C(21)–C(22)	178.3(6)
B(2)–N(3)–C(21)–C(30)	–2.4(10)	C(24)–N(3)–C(21)–C(22)	0.6(8)
C(24)–N(3)–C(21)–C(30)	179.9(6)	N(3)–C(21)–C(22)–C(23)	–1.1(9)
C(30)–C(21)–C(22)–C(23)	179.7(7)	C(21)–C(22)–C(23)–C(24)	1.1(8)
C(21)–C(22)–C(23)–C(31)	–176.2(7)	B(2)–N(3)–C(24)–C(23)	–177.6(5)
B(2)–N(3)–C(24)–C(25)	1.6(9)	C(21)–N(3)–C(24)–C(23)	0.1(7)
C(21)–N(3)–C(24)–C(25)	179.3(6)	C(22)–C(23)–C(24)–N(3)	–0.8(7)
C(22)–C(23)–C(24)–C(25)	–179.9(7)	C(31)–C(23)–C(24)–N(3)	176.4(6)
C(31)–C(23)–C(24)–C(25)	–2.7(12)	N(3)–C(24)–C(25)–C(26)	–2.7(9)
N(3)–C(24)–C(25)–C(34)	179.6(5)	C(23)–C(24)–C(25)–C(26)	176.4(6)
C(23)–C(24)–C(25)–C(34)	–1.4(10)	B(2)–N(4)–C(26)–C(25)	6.1(8)
B(2)–N(4)–C(26)–C(27)	–178.4(5)	C(29)–N(4)–C(26)–C(25)	–175.2(5)
C(29)–N(4)–C(26)–C(27)	0.3(6)	C(24)–C(25)–C(26)–N(4)	–1.0(8)
C(24)–C(25)–C(26)–C(27)	–175.3(6)	C(34)–C(25)–C(26)–N(4)	176.7(5)
C(34)–C(25)–C(26)–C(27)	2.4(9)	N(4)–C(26)–C(27)–C(28)	0.4(6)
N(4)–C(26)–C(27)–C(32)	–178.8(5)	C(25)–C(26)–C(27)–C(28)	175.2(6)
C(25)–C(26)–C(27)–C(32)	–3.9(10)	C(26)–C(27)–C(28)–C(29)	–0.9(7)
C(32)–C(27)–C(28)–C(29)	178.3(5)	B(2)–N(4)–C(29)–C(28)	177.8(5)
B(2)–N(4)–C(29)–C(33)	–2.7(9)	C(26)–N(4)–C(29)–C(28)	–0.9(6)
C(26)–N(4)–C(29)–C(33)	178.6(5)	C(27)–C(28)–C(29)–N(4)	1.2(7)
C(27)–C(28)–C(29)–C(33)	–178.3(6)	C(24)–C(25)–C(34)–C(35)	–87.9(7)
C(24)–C(25)–C(34)–C(39)	91.0(7)	C(26)–C(25)–C(34)–C(35)	94.4(7)
C(26)–C(25)–C(34)–C(39)	–86.7(7)	C(25)–C(34)–C(35)–C(36)	178.3(5)

C(39)–C(34)–C(35)–C(36)	–0.6(9)	C(34)–C(35)–C(36)–C(37)	–0.6(9)
C(35)–C(36)–C(37)–C(38)	1.1(10)	C(36)–C(37)–C(38)–C(39)	–0.3(10)
C(40)–O(2)–C(39)–C(34)	176.2(6)	C(40)–O(2)–C(39)–C(38)	–4.5(9)
C(25)–C(34)–C(39)–O(2)	1.8(8)	C(25)–C(34)–C(39)–C(38)	–177.5(5)
C(35)–C(34)–C(39)–O(2)	–179.3(5)	C(35)–C(34)–C(39)–C(38)	1.4(9)
C(37)–C(38)–C(39)–O(2)	179.8(6)	C(37)–C(38)–C(39)–C(34)	–0.9(10)
B(3)–N(5)–C(41)–C(42)	177.9(5)	B(3)–N(5)–C(41)–C(50)	–2.7(9)
C(44)–N(5)–C(41)–C(42)	0.9(6)	C(44)–N(5)–C(41)–C(50)	–179.7(5)
N(5)–C(41)–C(42)–C(43)	–0.6(7)	C(50)–C(41)–C(42)–C(43)	–180.0(6)
C(41)–C(42)–C(43)–C(44)	0.0(6)	C(41)–C(42)–C(43)–C(51)	–178.8(5)
C(42)–C(43)–C(44)–N(5)	0.5(6)	C(42)–C(43)–C(44)–C(45)	176.9(6)
C(51)–C(43)–C(44)–N(5)	179.3(5)	C(51)–C(43)–C(44)–C(45)	–4.3(10)
B(3)–N(5)–C(44)–C(43)	–177.9(5)	B(3)–N(5)–C(44)–C(45)	5.1(7)
C(41)–N(5)–C(44)–C(43)	–0.9(6)	C(41)–N(5)–C(44)–C(45)	–177.8(5)
N(5)–C(44)–C(45)–C(46)	–2.0(7)	N(5)–C(44)–C(45)–C(54)	179.0(4)
C(43)–C(44)–C(45)–C(46)	–178.0(5)	C(43)–C(44)–C(45)–C(54)	3.0(9)
C(44)–C(45)–C(46)–N(6)	0.7(7)	C(44)–C(45)–C(46)–C(47)	179.5(5)
C(54)–C(45)–C(46)–N(6)	179.7(4)	C(54)–C(45)–C(46)–C(47)	–1.5(8)
B(3)–N(6)–C(46)–C(45)	–2.5(7)	B(3)–N(6)–C(46)–C(47)	178.5(4)
C(49)–N(6)–C(46)–C(45)	179.9(4)	C(49)–N(6)–C(46)–C(47)	0.9(5)
N(6)–C(46)–C(47)–C(48)	–0.5(5)	N(6)–C(46)–C(47)–C(52)	177.6(5)
C(45)–C(46)–C(47)–C(48)	–179.3(5)	C(45)–C(46)–C(47)–C(52)	–1.2(9)
C(46)–C(47)–C(48)–C(49)	–0.1(5)	C(52)–C(47)–C(48)–C(49)	–178.3(4)
B(3)–N(6)–C(49)–C(48)	–178.5(4)	B(3)–N(6)–C(49)–C(53)	2.9(8)
C(46)–N(6)–C(49)–C(48)	–0.9(5)	C(46)–N(6)–C(49)–C(53)	–179.5(4)
C(47)–C(48)–C(49)–N(6)	0.6(6)	C(47)–C(48)–C(49)–C(53)	179.1(5)
C(44)–C(45)–C(54)–C(55)	–91.3(7)	C(44)–C(45)–C(54)–C(59)	91.4(7)
C(46)–C(45)–C(54)–C(55)	89.7(7)	C(46)–C(45)–C(54)–C(59)	–87.6(7)
C(45)–C(54)–C(55)–C(56)	–177.7(6)	C(59)–C(54)–C(55)–C(56)	–0.4(10)
C(54)–C(55)–C(56)–C(57)	–0.6(10)	C(55)–C(56)–C(57)–C(58)	0.7(11)
C(56)–C(57)–C(58)–C(59)	0.0(11)	C(60)–O(3)–C(59)–C(54)	171.2(6)
C(60)–O(3)–C(59)–C(58)	–9.5(9)	C(45)–C(54)–C(59)–O(3)	–2.2(8)
C(45)–C(54)–C(59)–C(58)	178.4(6)	C(55)–C(54)–C(59)–O(3)	–179.5(6)
C(55)–C(54)–C(59)–C(58)	1.1(10)	C(57)–C(58)–C(59)–O(3)	179.7(6)
C(57)–C(58)–C(59)–C(54)	–0.9(10)	B(4)–N(7)–C(61)–C(62)	–178.5(4)
B(4)–N(7)–C(61)–C(70)	0.1(8)	C(64)–N(7)–C(61)–C(62)	0.8(6)
C(64)–N(7)–C(61)–C(70)	179.4(5)	N(7)–C(61)–C(62)–C(63)	–0.7(6)
C(70)–C(61)–C(62)–C(63)	–179.1(5)	C(61)–C(62)–C(63)–C(64)	0.2(6)
C(61)–C(62)–C(63)–C(71)	177.9(5)	B(4)–N(7)–C(64)–C(63)	178.7(4)
B(4)–N(7)–C(64)–C(65)	–1.1(7)	C(61)–N(7)–C(64)–C(63)	–0.7(5)
C(61)–N(7)–C(64)–C(65)	179.5(4)	C(62)–C(63)–C(64)–N(7)	0.3(6)
C(62)–C(63)–C(64)–C(65)	–180.0(5)	C(71)–C(63)–C(64)–N(7)	–177.3(5)
C(71)–C(63)–C(64)–C(65)	2.4(9)	N(7)–C(64)–C(65)–C(66)	1.4(7)
N(7)–C(64)–C(65)–C(74)	–176.5(4)	C(63)–C(64)–C(65)–C(66)	–178.3(5)
C(63)–C(64)–C(65)–C(74)	3.8(8)	C(64)–C(65)–C(66)–N(8)	0.2(7)
C(64)–C(65)–C(66)–C(67)	–178.4(5)	C(74)–C(65)–C(66)–N(8)	178.1(4)
C(74)–C(65)–C(66)–C(67)	–0.5(8)	B(4)–N(8)–C(66)–C(65)	–2.3(7)
B(4)–N(8)–C(66)–C(67)	176.6(4)	C(69)–N(8)–C(66)–C(65)	–179.9(4)
C(69)–N(8)–C(66)–C(67)	–0.9(5)	N(8)–C(66)–C(67)–C(68)	0.5(5)
N(8)–C(66)–C(67)–C(72)	179.4(5)	C(65)–C(66)–C(67)–C(68)	179.2(5)
C(65)–C(66)–C(67)–C(72)	–1.9(9)	C(66)–C(67)–C(68)–C(69)	0.2(5)
C(72)–C(67)–C(68)–C(69)	–178.8(5)	C(64)–C(65)–C(74)–C(75)	82.7(7)

C(64)–C(65)–C(74)–C(79)	–98.0(6)	C(66)–C(65)–C(74)–C(75)	–95.3(6)
C(66)–C(65)–C(74)–C(79)	84.0(7)	C(65)–C(74)–C(75)–C(76)	–177.7(6)
C(79)–C(74)–C(75)–C(76)	3.1(10)	C(74)–C(75)–C(76)–C(77)	–2.3(11)
B(4)–N(8)–C(69)–C(68)	–176.5(4)	B(4)–N(8)–C(69)–C(73)	4.5(8)
C(66)–N(8)–C(69)–C(68)	1.0(5)	C(66)–N(8)–C(69)–C(73)	–178.0(4)
C(67)–C(68)–C(69)–N(8)	–0.8(6)	C(67)–C(68)–C(69)–C(73)	178.3(5)
C(75)–C(76)–C(77)–C(78)	0.8(12)	C(76)–C(77)–C(78)–C(79)	–0.3(11)
C(80)–O(4)–C(79)–C(74)	–170.1(6)	C(80)–O(4)–C(79)–C(78)	8.6(9)
C(65)–C(74)–C(79)–O(4)	–3.0(9)	C(65)–C(74)–C(79)–C(78)	178.3(6)
C(75)–C(74)–C(79)–O(4)	176.3(6)	C(75)–C(74)–C(79)–C(78)	–2.5(9)
C(77)–C(78)–C(79)–O(4)	–177.6(7)	C(77)–C(78)–C(79)–C(74)	1.1(10)
B(5)–N(9)–C(81)–C(82)	–179.5(5)	B(5)–N(9)–C(81)–C(90)	0.9(8)
C(84)–N(9)–C(81)–C(82)	0.5(6)	C(84)–N(9)–C(81)–C(90)	–179.0(5)
N(9)–C(81)–C(82)–C(83)	–0.2(6)	C(90)–C(81)–C(82)–C(83)	179.3(5)
C(81)–C(82)–C(83)–C(84)	–0.2(6)	C(81)–C(82)–C(83)–C(91)	–178.3(5)
B(5)–N(9)–C(84)–C(83)	179.4(5)	B(5)–N(9)–C(84)–C(85)	0.7(7)
C(81)–N(9)–C(84)–C(83)	–0.7(6)	C(81)–N(9)–C(84)–C(85)	–179.3(5)
C(82)–C(83)–C(84)–N(9)	0.5(6)	C(82)–C(83)–C(84)–C(85)	179.0(5)
C(91)–C(83)–C(84)–N(9)	178.5(5)	C(91)–C(83)–C(84)–C(85)	–3.0(10)
N(9)–C(84)–C(85)–C(86)	–2.8(7)	N(9)–C(84)–C(85)–C(94)	179.6(4)
C(83)–C(84)–C(85)–C(86)	179.0(5)	C(83)–C(84)–C(85)–C(94)	1.4(8)
B(5)–N(10)–C(86)–C(85)	1.8(8)	B(5)–N(10)–C(86)–C(87)	–178.1(5)
C(89)–N(10)–C(86)–C(85)	–178.6(5)	C(89)–N(10)–C(86)–C(87)	1.6(6)
C(84)–C(85)–C(86)–N(10)	1.6(8)	C(84)–C(85)–C(86)–C(87)	–178.7(5)
C(94)–C(85)–C(86)–N(10)	179.1(5)	C(94)–C(85)–C(86)–C(87)	–1.1(9)
N(10)–C(86)–C(87)–C(88)	–1.7(6)	N(10)–C(86)–C(87)–C(92)	–179.5(5)
C(85)–C(86)–C(87)–C(88)	178.6(6)	C(85)–C(86)–C(87)–C(92)	0.7(10)
C(86)–C(87)–C(88)–C(89)	1.2(7)	C(92)–C(87)–C(88)–C(89)	179.0(6)
B(5)–N(10)–C(89)–C(88)	178.8(5)	B(5)–N(10)–C(89)–C(93)	0.7(9)
C(86)–N(10)–C(89)–C(88)	–0.9(7)	C(86)–N(10)–C(89)–C(93)	–179.0(6)
C(87)–C(88)–C(89)–N(10)	–0.2(7)	C(87)–C(88)–C(89)–C(93)	177.8(6)
C(84)–C(85)–C(94)–C(95)	88.5(7)	C(84)–C(85)–C(94)–C(99)	–89.2(7)
C(86)–C(85)–C(94)–C(95)	–89.0(7)	C(86)–C(85)–C(94)–C(99)	93.3(7)
C(85)–C(94)–C(95)–C(96)	–177.2(6)	C(99)–C(94)–C(95)–C(96)	0.5(10)
C(94)–C(95)–C(96)–C(97)	–0.9(10)	C(95)–C(96)–C(97)–C(98)	–0.2(12)
C(96)–C(97)–C(98)–C(99)	1.6(11)	C(100)–O(5)–C(99)–C(94)	172.2(5)
C(100)–O(5)–C(99)–C(98)	–7.9(9)	C(85)–C(94)–C(99)–O(5)	–1.3(8)
C(85)–C(94)–C(99)–C(98)	178.7(6)	C(95)–C(94)–C(99)–O(5)	–179.1(6)
C(95)–C(94)–C(99)–C(98)	0.9(9)	C(97)–C(98)–C(99)–O(5)	178.1(7)
C(97)–C(98)–C(99)–C(94)	–1.9(10)	B(6)–N(11)–C(101)–C(102)	–176.5(5)
B(6)–N(11)–C(101)–C(110)	4.4(8)	C(104)–N(11)–C(101)–C(102)	0.1(6)
C(104)–N(11)–C(101)–C(110)	–179.1(5)	N(11)–C(101)–C(102)–C(103)	–0.9(7)
C(110)–C(101)–C(102)–C(103)	178.2(6)	C(101)–C(102)–C(103)–C(104)	1.3(6)
C(101)–C(102)–C(103)–C(111)	–179.7(5)	B(6)–N(11)–C(104)–C(103)	177.3(5)
B(6)–N(11)–C(104)–C(105)	–3.1(8)	C(101)–N(11)–C(104)–C(103)	0.7(6)
C(101)–N(11)–C(104)–C(105)	–179.7(5)	C(102)–C(103)–C(104)–N(11)	–1.2(6)
C(102)–C(103)–C(104)–C(105)	179.2(5)	C(111)–C(103)–C(104)–N(11)	179.8(5)
C(111)–C(103)–C(104)–C(105)	0.2(10)	N(11)–C(104)–C(105)–C(106)	0.4(8)
N(11)–C(104)–C(105)–C(114)	178.1(5)	C(103)–C(104)–C(105)–C(106)	179.9(5)
C(103)–C(104)–C(105)–C(114)	–2.4(9)	B(6)–N(12)–C(106)–C(105)	–0.3(8)
B(6)–N(12)–C(106)–C(107)	179.0(5)	C(109)–N(12)–C(106)–C(105)	178.6(5)
C(109)–N(12)–C(106)–C(107)	–2.0(6)	C(104)–C(105)–C(106)–N(12)	1.2(8)

C(104)–C(105)–C(106)–C(107)	−177.9(5)
C(114)–C(105)–C(106)–C(107)	4.3(9)
N(12)–C(106)–C(107)–C(112)	−178.9(5)
C(105)–C(106)–C(107)–C(112)	0.4(10)
C(112)–C(107)–C(108)–C(109)	179.9(5)
B(6)–N(12)–C(109)–C(113)	0.1(9)
C(106)–N(12)–C(109)–C(113)	−178.9(5)
C(107)–C(108)–C(109)–C(113)	179.8(6)
C(104)–C(105)–C(114)–C(119)	84.2(7)
C(106)–C(105)–C(114)–C(119)	−98.1(7)
C(119)–C(114)–C(115)–C(116)	2.2(10)
C(115)–C(116)–C(117)–C(118)	−0.5(11)
C(120)–O(6)–C(119)–C(114)	−169.8(6)
C(117)–C(118)–C(119)–O(6)	−178.0(6)
C(105)–C(114)–C(119)–O(6)	−2.4(8)
C(115)–C(114)–C(119)–O(6)	176.6(6)
B(7)–N(13)–C(121)–C(122)	176.3(5)
C(124)–N(13)–C(121)–C(122)	−1.2(6)
N(13)–C(121)–C(122)–C(123)	1.8(7)
C(121)–C(122)–C(123)–C(124)	−1.6(7)
C(122)–C(123)–C(124)–N(13)	0.9(6)
C(131)–C(123)–C(124)–N(13)	179.9(5)
B(7)–N(13)–C(124)–C(123)	−177.4(5)
C(121)–N(13)–C(124)–C(123)	0.1(6)
N(13)–C(124)–C(125)–C(126)	−2.2(8)
C(123)–C(124)–C(125)–C(126)	−176.6(6)
B(7)–N(14)–C(126)–C(125)	−0.6(9)
C(129)–N(14)–C(126)–C(125)	178.7(6)
C(124)–C(125)–C(126)–N(14)	−0.9(8)
C(134)–C(125)–C(126)–N(14)	179.4(5)
N(14)–C(126)–C(127)–C(128)	−1.8(7)
C(125)–C(126)–C(127)–C(128)	−178.4(7)
C(126)–C(127)–C(128)–C(129)	1.4(8)
B(7)–N(14)–C(129)–C(128)	178.5(6)
C(126)–N(14)–C(129)–C(128)	−0.8(8)
C(127)–C(128)–C(129)–N(14)	−0.4(9)
C(124)–C(125)–C(134)–C(135)	93.3(7)
C(126)–C(125)–C(134)–C(135)	−86.9(6)
C(125)–C(134)–C(135)–C(136)	178.1(5)
C(134)–C(135)–C(136)–C(137)	−0.1(9)
C(136)–C(137)–C(138)–C(139)	0.2(9)
C(140)–O(7)–C(139)–C(138)	−4.7(9)
C(137)–C(138)–C(139)–C(134)	−2.1(9)
C(125)–C(134)–C(139)–C(138)	−177.0(5)
C(135)–C(134)–C(139)–C(138)	2.9(9)
B(8)–N(15)–C(141)–C(150)	2.6(8)
C(144)–N(15)–C(141)–C(150)	−179.9(5)
C(150)–C(141)–C(142)–C(143)	179.9(5)
C(141)–C(142)–C(143)–C(151)	178.0(5)
B(8)–N(15)–C(144)–C(145)	−2.9(7)
C(141)–N(15)–C(144)–C(145)	179.6(4)
C(142)–C(143)–C(144)–C(145)	−178.5(5)
C(114)–C(105)–C(106)–N(12)	−176.5(5)
N(12)–C(106)–C(107)–C(108)	1.5(6)
C(105)–C(106)–C(107)–C(108)	−179.3(6)
C(106)–C(107)–C(108)–C(109)	−0.5(6)
B(6)–N(12)–C(109)–C(108)	−179.3(5)
C(106)–N(12)–C(109)–C(108)	1.7(6)
C(107)–C(108)–C(109)–N(12)	−0.8(7)
C(104)–C(105)–C(114)–C(115)	−94.8(7)
C(106)–C(105)–C(114)–C(115)	82.9(7)
C(105)–C(114)–C(115)–C(116)	−178.8(6)
C(114)–C(115)–C(116)–C(117)	−1.1(10)
C(116)–C(117)–C(118)–C(119)	0.8(10)
C(120)–O(6)–C(119)–C(118)	8.7(9)
C(117)–C(118)–C(119)–C(114)	0.4(10)
C(105)–C(114)–C(119)–C(118)	179.1(6)
C(115)–C(114)–C(119)–C(118)	−1.9(9)
B(7)–N(13)–C(121)–C(130)	−4.3(9)
C(124)–N(13)–C(121)–C(130)	178.2(5)
C(130)–C(121)–C(122)–C(123)	−177.6(6)
C(121)–C(122)–C(123)–C(131)	179.3(5)
C(122)–C(123)–C(124)–C(125)	175.9(6)
C(131)–C(123)–C(124)–C(125)	−5.1(11)
B(7)–N(13)–C(124)–C(125)	6.8(8)
C(121)–N(13)–C(124)–C(125)	−175.6(5)
N(13)–C(124)–C(125)–C(134)	177.5(5)
C(123)–C(124)–C(125)–C(134)	3.1(10)
B(7)–N(14)–C(126)–C(127)	−177.6(6)
C(129)–N(14)–C(126)–C(127)	1.7(7)
C(124)–C(125)–C(126)–C(127)	175.4(6)
C(134)–C(125)–C(126)–C(127)	−4.4(10)
N(14)–C(126)–C(127)–C(132)	175.7(6)
C(125)–C(126)–C(127)–C(132)	−0.9(12)
C(132)–C(127)–C(128)–C(129)	−176.3(7)
B(7)–N(14)–C(129)–C(133)	0.4(11)
C(126)–N(14)–C(129)–C(133)	−178.9(7)
C(127)–C(128)–C(129)–C(133)	177.5(8)
C(124)–C(125)–C(134)–C(139)	−86.8(7)
C(126)–C(125)–C(134)–C(139)	92.9(7)
C(139)–C(134)–C(135)–C(136)	−1.8(9)
C(135)–C(136)–C(137)–C(138)	1.0(9)
C(140)–O(7)–C(139)–C(134)	177.1(6)
C(137)–C(138)–C(139)–O(7)	179.8(6)
C(125)–C(134)–C(139)–O(7)	1.3(8)
C(135)–C(134)–C(139)–O(7)	−178.8(5)
B(8)–N(15)–C(141)–C(142)	−178.8(4)
C(144)–N(15)–C(141)–C(142)	−1.2(6)
N(15)–C(141)–C(142)–C(143)	1.4(6)
C(141)–C(142)–C(143)–C(144)	−0.9(6)
B(8)–N(15)–C(144)–C(143)	178.1(4)
C(141)–N(15)–C(144)–C(143)	0.6(5)
C(142)–C(143)–C(144)–N(15)	0.2(6)
C(151)–C(143)–C(144)–N(15)	−178.8(5)

C(151)–C(143)–C(144)–C(145)	2.5(9)
N(15)–C(144)–C(145)–C(154)	−174.5(4)
C(143)–C(144)–C(145)–C(154)	4.0(8)
C(144)–C(145)–C(146)–C(147)	−179.0(5)
C(154)–C(145)–C(146)–C(147)	−1.9(8)
B(8)–N(16)–C(146)–C(147)	176.2(4)
C(149)–N(16)–C(146)–C(147)	0.0(5)
N(16)–C(146)–C(147)–C(152)	177.8(5)
C(145)–C(146)–C(147)–C(152)	−2.7(9)
C(152)–C(147)–C(148)–C(149)	−177.9(5)
B(8)–N(16)–C(149)–C(153)	5.2(8)
C(146)–N(16)–C(149)–C(153)	−178.7(4)
C(147)–C(148)–C(149)–C(153)	178.6(5)
C(144)–C(145)–C(154)–C(159)	−98.4(6)
C(146)–C(145)–C(154)–C(159)	84.4(7)
C(159)–C(154)–C(155)–C(156)	2.0(10)
C(155)–C(156)–C(157)–C(158)	−1.9(11)
C(160)–O(8)–C(159)–C(154)	−171.7(6)
C(157)–C(158)–C(159)–O(8)	−178.6(6)
C(145)–C(154)–C(159)–O(8)	−2.3(9)
C(155)–C(154)–C(159)–O(8)	177.1(6)
B(9)–N(17)–C(161)–C(162)	178.3(5)
C(164)–N(17)–C(161)–C(162)	−0.3(6)
N(17)–C(161)–C(162)–C(163)	0.3(7)
C(161)–C(162)–C(163)–C(164)	−0.1(7)
B(9)–N(17)–C(164)–C(163)	−178.4(5)
C(161)–N(17)–C(164)–C(163)	0.3(6)
C(162)–C(163)–C(164)–N(17)	−0.1(6)
C(171)–C(163)–C(164)–N(17)	179.7(5)
N(17)–C(164)–C(165)–C(166)	−0.3(8)
C(163)–C(164)–C(165)–C(166)	−178.1(6)
C(164)–C(165)–C(166)–N(18)	−1.1(8)
C(174)–C(165)–C(166)–N(18)	179.5(4)
B(9)–N(18)–C(166)–C(165)	−0.3(7)
C(169)–N(18)–C(166)–C(165)	−179.9(5)
N(18)–C(166)–C(167)–C(168)	0.1(5)
C(165)–C(166)–C(167)–C(168)	179.9(5)
C(166)–C(167)–C(168)–C(169)	−0.1(6)
B(9)–N(18)–C(169)–C(168)	−179.5(5)
C(166)–N(18)–C(169)–C(168)	0.1(6)
C(167)–C(168)–C(169)–N(18)	0.0(6)
C(164)–C(165)–C(174)–C(175)	−89.5(7)
C(166)–C(165)–C(174)–C(175)	89.9(7)
C(165)–C(174)–C(175)–C(176)	−176.2(6)
C(174)–C(175)–C(176)–C(177)	−3.4(10)
C(176)–C(177)–C(178)–C(179)	−0.4(11)
C(180)–O(9)–C(179)–C(178)	−7.4(10)
C(177)–C(178)–C(179)–C(174)	−0.7(10)
C(165)–C(174)–C(179)–C(178)	178.3(6)
C(175)–C(174)–C(179)–C(178)	−0.3(9)
B(1)–N(2)–C(9)–C(13)	2.0(11)
C(6)–N(2)–C(9)–C(13)	179.7(6)
N(15)–C(144)–C(145)–C(146)	2.6(7)
C(143)–C(144)–C(145)–C(146)	−178.8(5)
C(144)–C(145)–C(146)–N(16)	0.4(7)
C(154)–C(145)–C(146)–N(16)	177.5(4)
B(8)–N(16)–C(146)–C(145)	−3.4(7)
C(149)–N(16)–C(146)–C(145)	−179.6(4)
N(16)–C(146)–C(147)–C(148)	0.0(6)
C(145)–C(146)–C(147)–C(148)	179.4(5)
C(146)–C(147)–C(148)–C(149)	0.1(6)
B(8)–N(16)–C(149)–C(148)	−176.0(4)
C(146)–N(16)–C(149)–C(148)	0.0(5)
C(147)–C(148)–C(149)–N(16)	−0.1(6)
C(144)–C(145)–C(154)–C(155)	82.3(7)
C(146)–C(145)–C(154)–C(155)	−95.0(7)
C(145)–C(154)–C(155)–C(156)	−178.6(6)
C(154)–C(155)–C(156)–C(157)	0.4(11)
C(156)–C(157)–C(158)–C(159)	0.9(11)
C(160)–O(8)–C(159)–C(158)	8.5(9)
C(157)–C(158)–C(159)–C(154)	1.6(10)
C(145)–C(154)–C(159)–C(158)	177.6(6)
C(155)–C(154)–C(159)–C(158)	−3.0(9)
B(9)–N(17)–C(161)–C(170)	−0.9(9)
C(164)–N(17)–C(161)–C(170)	−179.5(5)
C(170)–C(161)–C(162)–C(163)	179.4(6)
C(161)–C(162)–C(163)–C(171)	−179.9(5)
B(9)–N(17)–C(164)–C(165)	3.3(7)
C(161)–N(17)–C(164)–C(165)	−178.1(5)
C(162)–C(163)–C(164)–C(165)	177.9(6)
C(171)–C(163)–C(164)–C(165)	−2.3(10)
N(17)–C(164)–C(165)–C(174)	179.0(4)
C(163)–C(164)–C(165)–C(174)	1.2(9)
C(164)–C(165)–C(166)–C(167)	179.2(5)
C(174)–C(165)–C(166)–C(167)	−0.1(8)
B(9)–N(18)–C(166)–C(167)	179.4(5)
C(169)–N(18)–C(166)–C(167)	−0.1(5)
N(18)–C(166)–C(167)–C(172)	178.6(5)
C(165)–C(166)–C(167)–C(172)	−1.6(10)
C(172)–C(167)–C(168)–C(169)	−178.7(5)
B(9)–N(18)–C(169)–C(173)	1.1(8)
C(166)–N(18)–C(169)–C(173)	−179.4(5)
C(167)–C(168)–C(169)–C(173)	179.5(5)
C(164)–C(165)–C(174)–C(179)	91.9(7)
C(166)–C(165)–C(174)–C(179)	−88.7(7)
C(179)–C(174)–C(175)–C(176)	2.4(10)
C(175)–C(176)–C(177)–C(178)	2.4(11)
C(180)–O(9)–C(179)–C(174)	171.8(6)
C(177)–C(178)–C(179)–O(9)	178.4(7)
C(165)–C(174)–C(179)–O(9)	−0.9(8)
C(175)–C(174)–C(179)–O(9)	−179.5(6)
B(1)–N(2)–C(9)–C(8)	−178.1(6)
C(6)–N(2)–C(9)–C(8)	−0.4(8)
C(7)–C(8)–C(9)–N(2)	0.0(9)

C(7)–C(8)–C(9)–C(13)	179.9(7)

Compound **6.17**

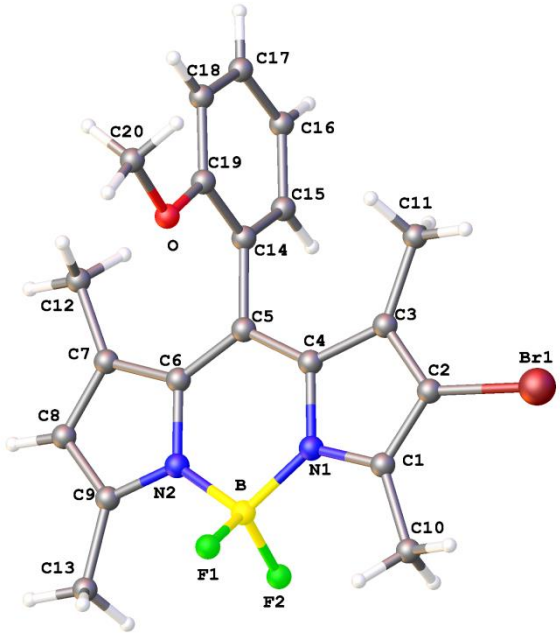


Figure showing the asymmetric unit. Minor disorder component is omitted.

Table 1. Crystal data and structure refinement for mjh109.

Identification code	mjh109	
Chemical formula (moiety)	$C_{20}H_{20}BBrF_2N_2O$	
Chemical formula (total)	$C_{20}H_{20}BBrF_2N_2O$	
Formula weight	433.10	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	monoclinic, $P12_1/c1$	
Unit cell parameters	a = 7.2298(3) Å	α = 90°
	b = 18.8888(10) Å	β = 98.276(4)°
	c = 14.1319(6) Å	γ = 90°
Cell volume	1909.79(15) $Å^3$	
Z	4	
Calculated density	1.506 g/cm^3	
Absorption coefficient μ	2.183 mm^{-1}	
F(000)	880	
Crystal colour and size	red, 0.30 × 0.30 × 0.20 mm^3	
Reflections for cell refinement	6614 (θ range 2.8 to 28.6°)	
Data collection method	Oxford Diffraction Gemini A Ultra diffractometer	
	thick-slice ω scans	
θ range for data collection	2.8 to 28.6°	
Index ranges	h −9 to 9, k −24 to 24, l −18 to 18	
Completeness to θ = 25.0°	99.9 %	
Reflections collected	19265	
Independent reflections	4263 (R_{int} = 0.0341)	
Reflections with $F^2>2\sigma$	3357	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.5604 and 0.6693	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0228, 3.1995	
Data / restraints / parameters	4263 / 0 / 260	
Final R indices [$F^2>2\sigma$]	R1 = 0.0522, wR2 = 0.1029	
R indices (all data)	R1 = 0.0712, wR2 = 0.1091	
Goodness-of-fit on F^2	1.144	
Extinction coefficient	0.0007(4)	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	0.54 and −0.56 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh109. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Br(1)	0.37026(5)	0.72838(3)	0.16953(3)	0.05424(18)
Br(1A)	–0.7095(7)	0.4514(3)	0.2922(4)	0.062(2)
O	–0.0297(3)	0.59005(11)	0.51419(14)	0.0371(5)
F(1)	–0.0861(4)	0.47099(11)	0.17056(15)	0.0666(7)
F(2)	–0.2655(4)	0.54830(12)	0.07468(13)	0.0614(7)
B	–0.1817(7)	0.5348(2)	0.1679(3)	0.0467(11)
N(1)	–0.0460(4)	0.59548(15)	0.20258(17)	0.0383(7)
C(1)	0.0937(5)	0.6182(2)	0.1591(2)	0.0440(9)
C(2)	0.1773(5)	0.6762(2)	0.2095(2)	0.0432(9)
C(3)	0.0883(5)	0.68978(18)	0.2881(2)	0.0347(7)
C(4)	–0.0550(5)	0.63870(16)	0.2827(2)	0.0322(7)
N(2)	–0.3311(4)	0.53306(14)	0.23536(18)	0.0402(7)
C(9)	–0.4777(6)	0.48892(19)	0.2300(3)	0.0506(10)
C(8)	–0.5808(6)	0.5040(2)	0.3030(3)	0.0519(10)
C(7)	–0.4955(5)	0.55868(18)	0.3573(2)	0.0395(8)
C(6)	–0.3360(5)	0.57731(16)	0.3145(2)	0.0336(7)
C(5)	–0.1983(4)	0.62846(16)	0.33765(19)	0.0296(7)
C(10)	0.1467(6)	0.5863(3)	0.0687(3)	0.0631(12)
C(11)	0.1378(5)	0.74832(19)	0.3590(2)	0.0406(8)
C(12)	–0.5609(5)	0.5887(2)	0.4434(3)	0.0448(9)
C(13)	–0.5153(7)	0.4330(2)	0.1540(3)	0.0705(14)
C(14)	–0.2059(4)	0.67523(16)	0.42262(19)	0.0265(6)
C(15)	–0.2990(4)	0.73935(16)	0.4134(2)	0.0329(7)
C(16)	–0.3088(5)	0.78151(18)	0.4929(2)	0.0367(7)
C(17)	–0.2231(4)	0.75869(17)	0.5808(2)	0.0342(7)
C(18)	–0.1284(4)	0.69551(17)	0.5922(2)	0.0314(7)
C(19)	–0.1189(4)	0.65329(16)	0.5122(2)	0.0279(6)
C(20)	0.0772(5)	0.5689(2)	0.6024(2)	0.0476(9)

Table 3. Bond lengths [Å] and angles [°] for mjh109.

Br(1)–C(2)	1.862(4)	Br(1A)–C(9)	2.124(7)
Br(1A)–C(8)	1.355(6)	O–C(19)	1.356(4)
O–C(20)	1.426(4)	F(1)–B	1.387(5)
F(2)–B	1.392(4)	B–N(1)	1.542(5)
B–N(2)	1.541(6)	N(1)–C(1)	1.327(5)
N(1)–C(4)	1.405(4)	C(1)–C(2)	1.395(5)
C(1)–C(10)	1.510(5)	C(2)–H(2)	0.950
C(2)–C(3)	1.385(4)	C(3)–C(4)	1.410(5)
C(3)–C(11)	1.501(5)	C(4)–C(5)	1.395(4)
N(2)–C(9)	1.342(5)	N(2)–C(6)	1.401(4)
C(9)–C(8)	1.387(6)	C(9)–C(13)	1.502(5)
C(8)–H(8)	0.950	C(8)–C(7)	1.379(5)
C(7)–C(6)	1.421(5)	C(7)–C(12)	1.481(5)
C(6)–C(5)	1.392(4)	C(5)–C(14)	1.498(4)
C(10)–H(10A)	0.980	C(10)–H(10B)	0.980
C(10)–H(10C)	0.980	C(11)–H(11A)	0.980
C(11)–H(11B)	0.980	C(11)–H(11C)	0.980
C(12)–H(12A)	0.980	C(12)–H(12B)	0.980
C(12)–H(12C)	0.980	C(13)–H(13A)	0.980
C(13)–H(13B)	0.980	C(13)–H(13C)	0.980
C(14)–C(15)	1.382(4)	C(14)–C(19)	1.394(4)
C(15)–H(15A)	0.950	C(15)–C(16)	1.387(4)
C(16)–H(16A)	0.950	C(16)–C(17)	1.376(4)
C(17)–H(17A)	0.950	C(17)–C(18)	1.374(4)
C(18)–H(18A)	0.950	C(18)–C(19)	1.392(4)
C(20)–H(20A)	0.980	C(20)–H(20B)	0.980
C(20)–H(20C)	0.980		

C(9)–Br(1A)–C(8)	39.8(3)	C(19)–O–C(20)	117.4(2)
F(1)–B–F(2)	109.4(3)	F(1)–B–N(1)	110.2(4)
F(1)–B–N(2)	110.8(3)	F(2)–B–N(1)	109.6(3)
F(2)–B–N(2)	110.0(4)	N(1)–B–N(2)	106.9(3)
B–N(1)–C(1)	125.8(3)	B–N(1)–C(4)	125.9(3)
C(1)–N(1)–C(4)	108.2(3)	N(1)–C(1)–C(2)	108.7(3)
N(1)–C(1)–C(10)	124.4(4)	C(2)–C(1)–C(10)	126.9(4)
Br(1)–C(2)–C(1)	123.3(3)	Br(1)–C(2)–H(2)	3.3
Br(1)–C(2)–C(3)	126.9(3)	C(1)–C(2)–H(2)	125.1
C(1)–C(2)–C(3)	109.8(3)	H(2)–C(2)–C(3)	125.1
C(2)–C(3)–C(4)	104.6(3)	C(2)–C(3)–C(11)	125.3(3)
C(4)–C(3)–C(11)	130.0(3)	N(1)–C(4)–C(3)	108.8(3)
N(1)–C(4)–C(5)	119.5(3)	C(3)–C(4)–C(5)	131.6(3)
B–N(2)–C(9)	126.6(3)	B–N(2)–C(6)	125.6(3)
C(9)–N(2)–C(6)	107.8(3)	Br(1A)–C(9)–N(2)	148.0(3)
Br(1A)–C(9)–C(8)	38.7(2)	Br(1A)–C(9)–C(13)	89.3(3)
N(2)–C(9)–C(8)	109.6(3)	N(2)–C(9)–C(13)	122.5(4)
C(8)–C(9)–C(13)	127.9(4)	Br(1A)–C(8)–C(9)	101.5(4)
Br(1A)–C(8)–H(8)	24.7	Br(1A)–C(8)–C(7)	149.0(5)
C(9)–C(8)–H(8)	125.6	C(9)–C(8)–C(7)	108.8(4)
H(8)–C(8)–C(7)	125.6	C(8)–C(7)–C(6)	105.9(3)
C(8)–C(7)–C(12)	125.1(4)	C(6)–C(7)–C(12)	129.0(3)
N(2)–C(6)–C(7)	107.9(3)	N(2)–C(6)–C(5)	120.2(3)
C(7)–C(6)–C(5)	132.0(3)	C(4)–C(5)–C(6)	121.9(3)
C(4)–C(5)–C(14)	118.7(3)	C(6)–C(5)–C(14)	119.3(3)

C(1)–C(10)–H(10A)	109.5	C(1)–C(10)–H(10B)	109.5
C(1)–C(10)–H(10C)	109.5	H(10A)–C(10)–H(10B)	109.5
H(10A)–C(10)–H(10C)	109.5	H(10B)–C(10)–H(10C)	109.5
C(3)–C(11)–H(11A)	109.5	C(3)–C(11)–H(11B)	109.5
C(3)–C(11)–H(11C)	109.5	H(11A)–C(11)–H(11B)	109.5
H(11A)–C(11)–H(11C)	109.5	H(11B)–C(11)–H(11C)	109.5
C(7)–C(12)–H(12A)	109.5	C(7)–C(12)–H(12B)	109.5
C(7)–C(12)–H(12C)	109.5	H(12A)–C(12)–H(12B)	109.5
H(12A)–C(12)–H(12C)	109.5	H(12B)–C(12)–H(12C)	109.5
C(9)–C(13)–H(13A)	109.5	C(9)–C(13)–H(13B)	109.5
C(9)–C(13)–H(13C)	109.5	H(13A)–C(13)–H(13B)	109.5
H(13A)–C(13)–H(13C)	109.5	H(13B)–C(13)–H(13C)	109.5
C(5)–C(14)–C(15)	121.0(3)	C(5)–C(14)–C(19)	119.3(3)
C(15)–C(14)–C(19)	119.7(3)	C(14)–C(15)–H(15A)	119.7
C(14)–C(15)–C(16)	120.5(3)	H(15A)–C(15)–C(16)	119.7
C(15)–C(16)–H(16A)	120.6	C(15)–C(16)–C(17)	118.9(3)
H(16A)–C(16)–C(17)	120.6	C(16)–C(17)–H(17A)	119.0
C(16)–C(17)–C(18)	122.0(3)	H(17A)–C(17)–C(18)	119.0
C(17)–C(18)–H(18A)	120.5	C(17)–C(18)–C(19)	119.0(3)
H(18A)–C(18)–C(19)	120.5	O–C(19)–C(14)	115.6(3)
O–C(19)–C(18)	124.6(3)	C(14)–C(19)–C(18)	119.9(3)
O–C(20)–H(20A)	109.5	O–C(20)–H(20B)	109.5
O–C(20)–H(20C)	109.5	H(20A)–C(20)–H(20B)	109.5
H(20A)–C(20)–H(20C)	109.5	H(20B)–C(20)–H(20C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh109. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	0.0309(2)	0.0977(4)	0.0351(2)	0.0087(2)	0.00789(15)	–0.0030(2)
Br(1A)	0.052(3)	0.080(4)	0.054(3)	0.001(3)	0.006(2)	–0.033(3)
O	0.0513(14)	0.0341(12)	0.0226(10)	0.0016(9)	–0.0058(10)	0.0166(11)
F(1)	0.124(2)	0.0379(12)	0.0383(12)	–0.0048(10)	0.0144(13)	0.0288(13)
F(2)	0.1095(19)	0.0492(13)	0.0197(9)	–0.0039(9)	–0.0107(11)	–0.0020(13)
B	0.086(3)	0.030(2)	0.0219(17)	–0.0045(16)	–0.0030(19)	0.012(2)
N(1)	0.0549(18)	0.0413(16)	0.0184(12)	–0.0007(12)	0.0048(12)	0.0167(14)
C(1)	0.053(2)	0.054(2)	0.0241(16)	–0.0012(16)	0.0008(15)	0.0241(18)
C(2)	0.0383(18)	0.064(2)	0.0280(16)	0.0112(17)	0.0063(14)	0.0118(17)
C(3)	0.0389(17)	0.0441(19)	0.0207(14)	0.0042(14)	0.0025(13)	0.0133(15)
C(4)	0.0462(18)	0.0304(17)	0.0176(13)	–0.0020(12)	–0.0029(13)	0.0101(14)
N(2)	0.0636(19)	0.0294(15)	0.0228(13)	–0.0018(11)	–0.0102(13)	0.0060(14)
C(9)	0.069(3)	0.0324(19)	0.042(2)	0.0027(16)	–0.0217(19)	–0.0057(18)
C(8)	0.057(2)	0.041(2)	0.052(2)	0.0029(18)	–0.0137(19)	–0.0104(18)
C(7)	0.0431(19)	0.0334(18)	0.0370(18)	0.0067(15)	–0.0109(15)	0.0016(15)
C(6)	0.049(2)	0.0244(16)	0.0224(15)	0.0001(12)	–0.0107(14)	0.0081(14)
C(5)	0.0421(17)	0.0278(16)	0.0163(13)	0.0027(12)	–0.0046(12)	0.0122(13)
C(10)	0.077(3)	0.082(3)	0.0327(19)	–0.008(2)	0.0161(19)	0.028(3)
C(11)	0.0407(18)	0.049(2)	0.0318(17)	0.0007(15)	0.0044(14)	–0.0027(16)
C(12)	0.0387(19)	0.044(2)	0.051(2)	0.0044(17)	0.0032(16)	–0.0004(16)
C(13)	0.106(4)	0.041(2)	0.054(3)	–0.013(2)	–0.024(2)	–0.011(2)
C(14)	0.0311(15)	0.0282(16)	0.0194(13)	–0.0006(12)	0.0010(11)	0.0029(12)
C(15)	0.0400(17)	0.0288(16)	0.0275(15)	–0.0019(13)	–0.0031(13)	0.0110(14)
C(16)	0.0404(18)	0.0321(17)	0.0372(17)	–0.0082(15)	0.0040(14)	0.0104(14)
C(17)	0.0356(17)	0.0372(18)	0.0299(16)	–0.0121(14)	0.0052(13)	–0.0008(14)
C(18)	0.0304(16)	0.0416(18)	0.0205(14)	–0.0030(13)	–0.0019(12)	–0.0002(14)
C(19)	0.0295(15)	0.0293(16)	0.0241(14)	–0.0013(12)	0.0013(12)	0.0040(13)
C(20)	0.060(2)	0.048(2)	0.0294(17)	0.0065(16)	–0.0114(16)	0.0208(19)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh109.

	x	y	z	U
H(2)	0.2798	0.7023	0.1926	0.052
H(8)	–0.6919	0.4804	0.3139	0.062
H(10A)	0.1292	0.5349	0.0698	0.095
H(10B)	0.2780	0.5970	0.0647	0.095
H(10C)	0.0674	0.6064	0.0131	0.095
H(11A)	0.2573	0.7694	0.3490	0.061
H(11B)	0.1483	0.7292	0.4240	0.061
H(11C)	0.0400	0.7846	0.3503	0.061
H(12A)	–0.6833	0.5688	0.4502	0.067
H(12B)	–0.5713	0.6403	0.4369	0.067
H(12C)	–0.4712	0.5771	0.5000	0.067
H(13A)	–0.4051	0.4027	0.1555	0.106
H(13B)	–0.5430	0.4556	0.0912	0.106
H(13C)	–0.6225	0.4043	0.1659	0.106
H(15A)	–0.3566	0.7547	0.3522	0.039
H(16A)	–0.3736	0.8254	0.4867	0.044
H(17A)	–0.2295	0.7875	0.6354	0.041
H(18A)	–0.0704	0.6808	0.6536	0.038
H(20A)	0.1335	0.5225	0.5945	0.071
H(20B)	–0.0045	0.5660	0.6519	0.071
H(20C)	0.1760	0.6038	0.6214	0.071

Table 6. Torsion angles [°] for mjh109.

F(1)–B–N(1)–C(1)	65.3(4)	F(1)–B–N(1)–C(4)	−118.4(3)
F(2)–B–N(1)–C(1)	−55.1(5)	F(2)–B–N(1)–C(4)	121.2(3)
N(2)–B–N(1)–C(1)	−174.2(3)	N(2)–B–N(1)–C(4)	2.1(4)
B–N(1)–C(1)–C(2)	176.8(3)	B–N(1)–C(1)–C(10)	−1.9(5)
C(4)–N(1)–C(1)–C(2)	−0.1(4)	C(4)–N(1)–C(1)–C(10)	−178.8(3)
N(1)–C(1)–C(2)–Br(1)	−176.1(2)	N(1)–C(1)–C(2)–C(3)	0.7(4)
C(10)–C(1)–C(2)–Br(1)	2.7(5)	C(10)–C(1)–C(2)–C(3)	179.4(3)
Br(1)–C(2)–C(3)–C(4)	175.6(2)	Br(1)–C(2)–C(3)–C(11)	−2.9(5)
C(1)–C(2)–C(3)–C(4)	−1.0(4)	C(1)–C(2)–C(3)–C(11)	−179.5(3)
B–N(1)–C(4)–C(3)	−177.4(3)	B–N(1)–C(4)–C(5)	−0.8(4)
C(1)–N(1)–C(4)–C(3)	−0.6(3)	C(1)–N(1)–C(4)–C(5)	176.1(3)
C(2)–C(3)–C(4)–N(1)	0.9(3)	C(2)–C(3)–C(4)–C(5)	−175.2(3)
C(11)–C(3)–C(4)–N(1)	179.4(3)	C(11)–C(3)–C(4)–C(5)	3.3(6)
F(1)–B–N(2)–C(9)	−60.9(5)	F(1)–B–N(2)–C(6)	118.2(3)
F(2)–B–N(2)–C(9)	60.1(4)	F(2)–B–N(2)–C(6)	−120.7(3)
N(1)–B–N(2)–C(9)	179.0(3)	N(1)–B–N(2)–C(6)	−1.9(4)
B–N(2)–C(9)–Br(1A)	173.9(5)	B–N(2)–C(9)–C(8)	−179.7(3)
B–N(2)–C(9)–C(13)	0.2(5)	C(6)–N(2)–C(9)–Br(1A)	−5.4(7)
C(6)–N(2)–C(9)–C(8)	1.0(4)	C(6)–N(2)–C(9)–C(13)	−179.1(3)
C(8)–Br(1A)–C(9)–N(2)	9.6(7)	C(8)–Br(1A)–C(9)–C(13)	−175.6(4)
C(9)–Br(1A)–C(8)–C(7)	−168.3(10)	Br(1A)–C(9)–C(8)–C(7)	173.7(5)
N(2)–C(9)–C(8)–Br(1A)	−174.6(4)	N(2)–C(9)–C(8)–C(7)	−0.9(4)
C(13)–C(9)–C(8)–Br(1A)	5.5(6)	C(13)–C(9)–C(8)–C(7)	179.2(4)
Br(1A)–C(8)–C(7)–C(6)	168.3(8)	Br(1A)–C(8)–C(7)–C(12)	−10.4(10)
C(9)–C(8)–C(7)–C(6)	0.4(4)	C(9)–C(8)–C(7)–C(12)	−178.4(3)
B–N(2)–C(6)–C(7)	180.0(3)	B–N(2)–C(6)–C(5)	0.3(4)
C(9)–N(2)–C(6)–C(7)	−0.7(3)	C(9)–N(2)–C(6)–C(5)	179.6(3)
C(8)–C(7)–C(6)–N(2)	0.2(3)	C(8)–C(7)–C(6)–C(5)	179.8(3)
C(12)–C(7)–C(6)–N(2)	178.9(3)	C(12)–C(7)–C(6)–C(5)	−1.5(6)
N(2)–C(6)–C(5)–C(4)	1.5(4)	N(2)–C(6)–C(5)–C(14)	−180.0(2)
C(7)–C(6)–C(5)–C(4)	−178.1(3)	C(7)–C(6)–C(5)–C(14)	0.4(5)
N(1)–C(4)–C(5)–C(6)	−1.3(4)	N(1)–C(4)–C(5)–C(14)	−179.8(2)
C(3)–C(4)–C(5)–C(6)	174.5(3)	C(3)–C(4)–C(5)–C(14)	−4.0(5)
C(4)–C(5)–C(14)–C(15)	87.6(4)	C(4)–C(5)–C(14)–C(19)	−92.8(4)
C(6)–C(5)–C(14)–C(15)	−90.9(4)	C(6)–C(5)–C(14)–C(19)	88.6(4)
C(5)–C(14)–C(15)–C(16)	178.5(3)	C(19)–C(14)–C(15)–C(16)	−1.0(5)
C(14)–C(15)–C(16)–C(17)	0.5(5)	C(15)–C(16)–C(17)–C(18)	−0.1(5)
C(16)–C(17)–C(18)–C(19)	0.0(5)	C(20)–O–C(19)–C(14)	173.7(3)
C(20)–O–C(19)–C(18)	−6.7(5)	C(17)–C(18)–C(19)–O	179.9(3)
C(17)–C(18)–C(19)–C(14)	−0.5(5)	C(5)–C(14)–C(19)–O	1.0(4)
C(5)–C(14)–C(19)–C(18)	−178.6(3)	C(15)–C(14)–C(19)–O	−179.4(3)
C(15)–C(14)–C(19)–C(18)	1.0(5)		

Compound **6.19**

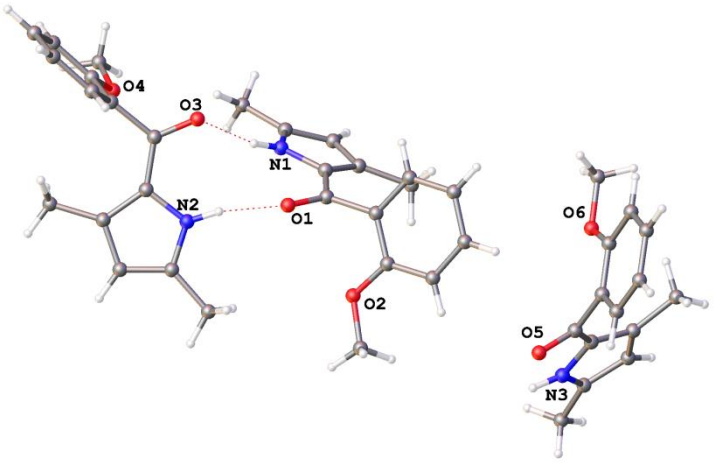


Table 1. Crystal data and structure refinement for mjh12.

Identification code	mjh120040	
Chemical formula (moiety)	$C_{14}H_{15}NO_2$	
Chemical formula (total)	$C_{14}H_{15}NO_2$	
Formula weight	229.27	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	monoclinic, $P12_1/n1$	
Unit cell parameters	a = 13.1933(5) Å	α = 90°
	b = 7.7391(2) Å	β = 93.752(3)°
	c = 37.0452(13) Å	γ = 90°
Cell volume	3774.4(2) $Å^3$	
Z	12	
Calculated density	1.210 g/cm^3	
Absorption coefficient μ	0.081 mm^{-1}	
F(000)	1464	
Crystal colour and size	colourless, 0.34 × 0.05 × 0.05 mm^3	
Reflections for cell refinement	9266 (θ range 2.8 to 28.6°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	2.8 to 28.6°	
Index ranges	h −17 to 17, k −10 to 10, l −43 to 47	
Completeness to θ = 25.0°	99.9 %	
Reflections collected	44740	
Independent reflections	8656 (R_{int} = 0.0386)	
Reflections with $F^2>2\sigma$	6602	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.9730 and 0.9960	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0555, 1.7805	
Data / restraints / parameters	8656 / 0 / 482	
Final R indices [$F^2>2\sigma$]	R1 = 0.0556, wR2 = 0.1268	
R indices (all data)	R1 = 0.0786, wR2 = 0.1382	
Goodness-of-fit on F^2	1.064	
Extinction coefficient	0.0024(4)	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.80 and −0.23 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh12. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	0.60905(10)	0.39467(15)	0.14529(3)	0.0323(3)
O(2)	0.80524(12)	0.4067(2)	0.10869(5)	0.0674(5)
N(1)	0.56270(10)	0.06437(17)	0.16607(4)	0.0238(3)
C(1)	0.52692(15)	–0.1798(2)	0.20641(5)	0.0357(4)
C(2)	0.56462(12)	–0.1068(2)	0.17267(5)	0.0277(4)
C(3)	0.60867(13)	–0.1858(2)	0.14417(5)	0.0333(4)
C(4)	0.63341(13)	–0.0594(2)	0.11933(5)	0.0323(4)
C(5)	0.68455(18)	–0.0931(3)	0.08511(6)	0.0502(6)
C(6)	0.60420(12)	0.0996(2)	0.13354(5)	0.0256(4)
C(7)	0.62035(13)	0.2753(2)	0.12374(5)	0.0270(4)
C(8)	0.64681(15)	0.3174(2)	0.08607(5)	0.0368(4)
C(9)	0.5751(2)	0.2943(3)	0.05750(6)	0.0565(6)
C(10)	0.5952(3)	0.3442(4)	0.02264(7)	0.0788(9)
C(11)	0.6876(3)	0.4147(4)	0.01666(8)	0.0769(9)
C(12)	0.7605(2)	0.4377(3)	0.04421(8)	0.0656(8)
C(13)	0.74000(17)	0.3910(3)	0.07945(6)	0.0474(5)
C(14)	0.8982(2)	0.4979(5)	0.10417(11)	0.0941(11)
O(3)	0.44575(9)	0.28295(16)	0.20874(3)	0.0293(3)
O(4)	0.43192(9)	0.07295(15)	0.28305(3)	0.0340(3)
N(2)	0.63531(10)	0.42574(17)	0.22101(4)	0.0255(3)
C(15)	0.80895(15)	0.5245(3)	0.21088(6)	0.0455(5)
C(17)	0.71455(14)	0.5273(2)	0.27083(5)	0.0355(4)
C(18)	0.61725(13)	0.4787(2)	0.27974(5)	0.0297(4)
C(20)	0.56744(12)	0.4157(2)	0.24776(4)	0.0239(3)
C(19)	0.57968(16)	0.4858(3)	0.31685(5)	0.0401(5)
C(21)	0.46922(12)	0.34581(19)	0.23897(4)	0.0224(3)
C(22)	0.38938(12)	0.3541(2)	0.26586(4)	0.0223(3)
C(23)	0.33024(13)	0.5011(2)	0.26806(5)	0.0292(4)
C(24)	0.25233(13)	0.5075(3)	0.29150(5)	0.0331(4)
O(5)	0.90288(11)	0.53501(18)	–0.03165(4)	0.0429(3)
O(6)	0.71339(10)	0.19472(19)	–0.06424(4)	0.0430(3)
N(3)	1.02141(11)	0.2492(2)	–0.02518(4)	0.0280(3)
C(25)	0.23440(13)	0.3661(3)	0.31248(5)	0.0317(4)
C(16)	0.72372(13)	0.4951(2)	0.23442(5)	0.0321(4)
C(26)	0.29202(13)	0.2171(2)	0.31059(4)	0.0291(4)
C(27)	0.36963(12)	0.2115(2)	0.28711(4)	0.0252(3)
C(28)	0.40724(18)	–0.0827(3)	0.30078(6)	0.0469(5)
C(29)	1.16474(15)	0.0609(3)	–0.00409(5)	0.0385(4)
C(30)	1.07732(13)	0.1072(2)	–0.02964(5)	0.0305(4)
C(31)	1.03797(14)	0.0253(2)	–0.06077(5)	0.0339(4)
C(32)	0.95551(14)	0.1214(2)	–0.07543(5)	0.0305(4)
C(33)	0.89383(16)	0.0762(3)	–0.10937(5)	0.0414(5)
C(34)	0.94520(13)	0.2638(2)	–0.05264(4)	0.0268(4)
C(35)	0.88342(13)	0.4157(2)	–0.05328(4)	0.0284(4)
C(36)	0.79745(13)	0.4463(2)	–0.08091(4)	0.0287(4)
C(37)	0.79864(15)	0.5996(2)	–0.10032(5)	0.0350(4)
C(38)	0.71996(16)	0.6435(3)	–0.12511(5)	0.0425(5)
C(39)	0.63756(16)	0.5358(3)	–0.12969(5)	0.0459(5)

C(40)	0.63247(14)	0.3847(3)	–0.10997(5)	0.0421(5)
C(41)	0.71254(14)	0.3385(3)	–0.08558(5)	0.0333(4)
C(42)	0.62815(19)	0.0809(4)	–0.06823(8)	0.0658(7)

Table 3. Bond lengths [Å] and angles [°] for mjh12.

O(1)–C(7)	1.236(2)	O(2)–C(13)	1.344(3)
O(2)–C(14)	1.434(3)	N(1)–H(1)	0.88(2)
N(1)–C(2)	1.347(2)	N(1)–C(6)	1.383(2)
C(1)–H(1A)	0.980	C(1)–H(1B)	0.980
C(1)–H(1C)	0.980	C(1)–C(2)	1.487(2)
C(2)–C(3)	1.381(3)	C(3)–H(3A)	0.950
C(3)–C(4)	1.396(3)	C(4)–C(5)	1.497(3)
C(4)–C(6)	1.402(2)	C(5)–H(5A)	0.980
C(5)–H(5B)	0.980	C(5)–H(5C)	0.980
C(6)–C(7)	1.427(2)	C(7)–C(8)	1.496(2)
C(8)–C(9)	1.384(3)	C(8)–C(13)	1.391(3)
C(9)–H(9A)	0.950	C(9)–C(10)	1.390(3)
C(10)–H(10A)	0.950	C(10)–C(11)	1.366(4)
C(11)–H(11A)	0.950	C(11)–C(12)	1.368(4)
C(12)–H(12A)	0.950	C(12)–C(13)	1.398(3)
C(14)–H(14A)	0.980	C(14)–H(14B)	0.980
C(14)–H(14C)	0.980	O(3)–C(21)	1.2416(19)
O(4)–C(27)	1.365(2)	O(4)–C(28)	1.420(2)
N(2)–H(2)	0.91(2)	N(2)–C(20)	1.380(2)
N(2)–C(16)	1.349(2)	C(15)–H(15A)	0.980
C(15)–H(15B)	0.980	C(15)–H(15C)	0.980
C(15)–C(16)	1.485(3)	C(17)–H(17A)	0.950
C(17)–C(18)	1.398(3)	C(17)–C(16)	1.384(3)
C(18)–C(20)	1.404(2)	C(18)–C(19)	1.493(3)
C(20)–C(21)	1.422(2)	C(19)–H(19A)	0.980
C(19)–H(19B)	0.980	C(19)–H(19C)	0.980
C(21)–C(22)	1.498(2)	C(22)–C(23)	1.385(2)
C(22)–C(27)	1.390(2)	C(23)–H(23A)	0.950
C(23)–C(24)	1.389(2)	C(24)–H(24A)	0.950
C(24)–C(25)	1.372(3)	O(5)–C(35)	1.239(2)
O(6)–C(41)	1.365(2)	O(6)–C(42)	1.429(2)
N(3)–H(3)	0.90(2)	N(3)–C(30)	1.340(2)
N(3)–C(34)	1.387(2)	C(25)–H(25A)	0.950
C(25)–C(26)	1.385(3)	C(26)–H(26A)	0.950
C(26)–C(27)	1.387(2)	C(28)–H(28A)	0.980
C(28)–H(28B)	0.980	C(28)–H(28C)	0.980
C(29)–H(29A)	0.980	C(29)–H(29B)	0.980
C(29)–H(29C)	0.980	C(29)–C(30)	1.487(3)
C(30)–C(31)	1.386(3)	C(31)–H(31A)	0.950
C(31)–C(32)	1.398(3)	C(32)–C(33)	1.494(3)
C(32)–C(34)	1.400(3)	C(33)–H(33A)	0.980
C(33)–H(33B)	0.980	C(33)–H(33C)	0.980
C(34)–C(35)	1.430(3)	C(35)–C(36)	1.496(2)
C(36)–C(37)	1.388(3)	C(36)–C(41)	1.398(3)
C(37)–H(37A)	0.950	C(37)–C(38)	1.383(3)
C(38)–H(38A)	0.950	C(38)–C(39)	1.371(3)
C(39)–H(39A)	0.950	C(39)–C(40)	1.383(3)
C(40)–H(40A)	0.950	C(40)–C(41)	1.391(3)
C(42)–H(42D)	0.980	C(42)–H(42A)	0.980
C(42)–H(42B)	0.980		

C(13)–O(2)–C(14)	117.3(2)	H(1)–N(1)–C(2)	122.9(13)
H(1)–N(1)–C(6)	126.7(13)	C(2)–N(1)–C(6)	110.36(14)

H(1A)–C(1)–H(1B)	109.5	H(1A)–C(1)–H(1C)	109.5
H(1A)–C(1)–C(2)	109.5	H(1B)–C(1)–H(1C)	109.5
H(1B)–C(1)–C(2)	109.5	H(1C)–C(1)–C(2)	109.5
N(1)–C(2)–C(1)	121.52(16)	N(1)–C(2)–C(3)	107.50(15)
C(1)–C(2)–C(3)	130.94(16)	C(2)–C(3)–H(3A)	125.6
C(2)–C(3)–C(4)	108.78(15)	H(3A)–C(3)–C(4)	125.6
C(3)–C(4)–C(5)	125.01(16)	C(3)–C(4)–C(6)	106.59(15)
C(5)–C(4)–C(6)	128.37(17)	C(4)–C(5)–H(5A)	109.5
C(4)–C(5)–H(5B)	109.5	C(4)–C(5)–H(5C)	109.5
H(5A)–C(5)–H(5B)	109.5	H(5A)–C(5)–H(5C)	109.5
H(5B)–C(5)–H(5C)	109.5	N(1)–C(6)–C(4)	106.77(14)
N(1)–C(6)–C(7)	118.92(14)	C(4)–C(6)–C(7)	133.74(15)
O(1)–C(7)–C(6)	121.43(15)	O(1)–C(7)–C(8)	119.00(15)
C(6)–C(7)–C(8)	119.51(15)	C(7)–C(8)–C(9)	119.70(18)
C(7)–C(8)–C(13)	121.09(19)	C(9)–C(8)–C(13)	119.06(19)
C(8)–C(9)–H(9A)	119.6	C(8)–C(9)–C(10)	120.8(3)
H(9A)–C(9)–C(10)	119.6	C(9)–C(10)–H(10A)	120.4
C(9)–C(10)–C(11)	119.2(3)	H(10A)–C(10)–C(11)	120.4
C(10)–C(11)–H(11A)	119.2	C(10)–C(11)–C(12)	121.5(2)
H(11A)–C(11)–C(12)	119.2	C(11)–C(12)–H(12A)	120.2
C(11)–C(12)–C(13)	119.5(2)	H(12A)–C(12)–C(13)	120.2
O(2)–C(13)–C(8)	114.96(18)	O(2)–C(13)–C(12)	125.2(2)
C(8)–C(13)–C(12)	119.9(2)	O(2)–C(14)–H(14A)	109.5
O(2)–C(14)–H(14B)	109.5	O(2)–C(14)–H(14C)	109.5
H(14A)–C(14)–H(14B)	109.5	H(14A)–C(14)–H(14C)	109.5
H(14B)–C(14)–H(14C)	109.5	C(27)–O(4)–C(28)	117.23(14)
H(2)–N(2)–C(20)	124.4(13)	H(2)–N(2)–C(16)	124.7(13)
C(20)–N(2)–C(16)	110.10(15)	H(15A)–C(15)–H(15B)	109.5
H(15A)–C(15)–H(15C)	109.5	H(15A)–C(15)–C(16)	109.5
H(15B)–C(15)–H(15C)	109.5	H(15B)–C(15)–C(16)	109.5
H(15C)–C(15)–C(16)	109.5	H(17A)–C(17)–C(18)	125.6
H(17A)–C(17)–C(16)	125.6	C(18)–C(17)–C(16)	108.76(16)
C(17)–C(18)–C(20)	106.30(16)	C(17)–C(18)–C(19)	124.96(16)
C(20)–C(18)–C(19)	128.66(16)	N(2)–C(20)–C(18)	107.25(14)
N(2)–C(20)–C(21)	118.76(15)	C(18)–C(20)–C(21)	133.97(15)
C(18)–C(19)–H(19A)	109.5	C(18)–C(19)–H(19B)	109.5
C(18)–C(19)–H(19C)	109.5	H(19A)–C(19)–H(19B)	109.5
H(19A)–C(19)–H(19C)	109.5	H(19B)–C(19)–H(19C)	109.5
O(3)–C(21)–C(20)	121.67(14)	O(3)–C(21)–C(22)	118.17(14)
C(20)–C(21)–C(22)	120.10(14)	C(21)–C(22)–C(23)	119.85(14)
C(21)–C(22)–C(27)	120.56(14)	C(23)–C(22)–C(27)	119.47(15)
C(22)–C(23)–H(23A)	119.7	C(22)–C(23)–C(24)	120.56(16)
H(23A)–C(23)–C(24)	119.7	C(23)–C(24)–H(24A)	120.4
C(23)–C(24)–C(25)	119.20(16)	H(24A)–C(24)–C(25)	120.4
C(41)–O(6)–C(42)	117.80(17)	H(3)–N(3)–C(30)	126.2(12)
H(3)–N(3)–C(34)	123.0(12)	C(30)–N(3)–C(34)	110.77(15)
C(24)–C(25)–H(25A)	119.3	C(24)–C(25)–C(26)	121.32(16)
H(25A)–C(25)–C(26)	119.3	N(2)–C(16)–C(15)	120.96(18)
N(2)–C(16)–C(17)	107.58(16)	C(15)–C(16)–C(17)	131.46(17)
C(25)–C(26)–H(26A)	120.4	C(25)–C(26)–C(27)	119.21(16)
H(26A)–C(26)–C(27)	120.4	O(4)–C(27)–C(22)	115.14(14)
O(4)–C(27)–C(26)	124.62(15)	C(22)–C(27)–C(26)	120.24(15)
O(4)–C(28)–H(28A)	109.5	O(4)–C(28)–H(28B)	109.5
O(4)–C(28)–H(28C)	109.5	H(28A)–C(28)–H(28B)	109.5
H(28A)–C(28)–H(28C)	109.5	H(28B)–C(28)–H(28C)	109.5

H(29A)–C(29)–H(29B)	109.5	H(29A)–C(29)–H(29C)	109.5
H(29A)–C(29)–C(30)	109.5	H(29B)–C(29)–H(29C)	109.5
H(29B)–C(29)–C(30)	109.5	H(29C)–C(29)–C(30)	109.5
N(3)–C(30)–C(29)	121.96(17)	N(3)–C(30)–C(31)	107.36(16)
C(29)–C(30)–C(31)	130.67(18)	C(30)–C(31)–H(31A)	125.7
C(30)–C(31)–C(32)	108.62(17)	H(31A)–C(31)–C(32)	125.7
C(31)–C(32)–C(33)	124.72(17)	C(31)–C(32)–C(34)	106.75(15)
C(33)–C(32)–C(34)	128.52(17)	C(32)–C(33)–H(33A)	109.5
C(32)–C(33)–H(33B)	109.5	C(32)–C(33)–H(33C)	109.5
H(33A)–C(33)–H(33B)	109.5	H(33A)–C(33)–H(33C)	109.5
H(33B)–C(33)–H(33C)	109.5	N(3)–C(34)–C(32)	106.50(15)
N(3)–C(34)–C(35)	117.64(15)	C(32)–C(34)–C(35)	135.62(16)
O(5)–C(35)–C(34)	120.57(15)	O(5)–C(35)–C(36)	116.12(16)
C(34)–C(35)–C(36)	123.19(15)	C(35)–C(36)–C(37)	117.12(16)
C(35)–C(36)–C(41)	123.74(16)	C(37)–C(36)–C(41)	118.82(17)
C(36)–C(37)–H(37A)	119.3	C(36)–C(37)–C(38)	121.35(19)
H(37A)–C(37)–C(38)	119.3	C(37)–C(38)–H(38A)	120.4
C(37)–C(38)–C(39)	119.2(2)	H(38A)–C(38)–C(39)	120.4
C(38)–C(39)–H(39A)	119.5	C(38)–C(39)–C(40)	120.92(18)
H(39A)–C(39)–C(40)	119.5	C(39)–C(40)–H(40A)	120.0
C(39)–C(40)–C(41)	119.95(19)	H(40A)–C(40)–C(41)	120.0
O(6)–C(41)–C(36)	116.02(16)	O(6)–C(41)–C(40)	124.25(18)
C(36)–C(41)–C(40)	119.70(19)	O(6)–C(42)–H(42D)	109.5
O(6)–C(42)–H(42A)	109.5	O(6)–C(42)–H(42B)	109.5
H(42D)–C(42)–H(42A)	109.5	H(42D)–C(42)–H(42B)	109.5
H(42A)–C(42)–H(42B)	109.5		

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	0.0417(7)	0.0181(6)	0.0380(7)	0.0001(5)	0.0107(6)	–0.0033(5)
O(2)	0.0409(9)	0.0818(13)	0.0811(12)	0.0199(10)	0.0158(9)	–0.0212(9)
N(1)	0.0228(7)	0.0171(7)	0.0319(7)	0.0007(6)	0.0037(6)	–0.0003(5)
C(1)	0.0347(10)	0.0268(9)	0.0454(11)	0.0120(8)	0.0002(8)	–0.0016(8)
C(2)	0.0220(8)	0.0193(8)	0.0410(10)	0.0037(7)	–0.0028(7)	–0.0025(6)
C(3)	0.0301(9)	0.0169(8)	0.0526(11)	–0.0015(8)	0.0005(8)	–0.0006(7)
C(4)	0.0265(9)	0.0236(9)	0.0473(11)	–0.0063(8)	0.0056(8)	–0.0013(7)
C(5)	0.0557(13)	0.0363(11)	0.0616(14)	–0.0127(10)	0.0256(11)	0.0018(10)
C(6)	0.0225(8)	0.0215(8)	0.0333(9)	–0.0002(7)	0.0058(7)	–0.0022(6)
C(7)	0.0238(8)	0.0228(8)	0.0351(9)	0.0000(7)	0.0073(7)	–0.0022(7)
C(8)	0.0480(11)	0.0232(9)	0.0410(10)	0.0009(8)	0.0175(9)	–0.0026(8)
C(9)	0.0789(17)	0.0554(14)	0.0354(11)	–0.0018(10)	0.0060(11)	–0.0070(13)
C(10)	0.117(3)	0.0784(19)	0.0418(14)	–0.0017(13)	0.0083(15)	–0.0101(19)
C(11)	0.124(3)	0.0634(17)	0.0471(15)	0.0001(13)	0.0345(17)	–0.0053(18)
C(12)	0.0848(19)	0.0440(13)	0.0738(18)	0.0071(13)	0.0494(16)	–0.0048(13)
C(13)	0.0508(13)	0.0374(11)	0.0566(13)	0.0045(10)	0.0243(11)	–0.0038(10)
C(14)	0.0445(15)	0.100(2)	0.140(3)	0.025(2)	0.0247(18)	–0.0250(16)
O(3)	0.0249(6)	0.0344(7)	0.0291(6)	–0.0056(5)	0.0055(5)	–0.0067(5)
O(4)	0.0348(7)	0.0233(6)	0.0450(7)	0.0082(5)	0.0119(6)	0.0044(5)
N(2)	0.0203(7)	0.0211(7)	0.0352(8)	0.0003(6)	0.0024(6)	–0.0018(5)
C(15)	0.0257(10)	0.0409(11)	0.0709(14)	–0.0006(10)	0.0105(10)	–0.0096(8)
C(17)	0.0255(9)	0.0303(9)	0.0491(11)	–0.0042(8)	–0.0109(8)	–0.0015(7)
C(18)	0.0295(9)	0.0230(8)	0.0355(9)	0.0010(7)	–0.0063(7)	0.0033(7)
C(20)	0.0227(8)	0.0181(8)	0.0307(8)	0.0029(6)	0.0010(7)	0.0018(6)
C(19)	0.0466(12)	0.0414(11)	0.0313(10)	–0.0024(8)	–0.0064(8)	0.0025(9)
C(21)	0.0224(8)	0.0159(7)	0.0291(8)	0.0037(6)	0.0014(6)	0.0010(6)
C(22)	0.0198(8)	0.0235(8)	0.0235(8)	–0.0011(6)	0.0003(6)	–0.0015(6)
C(23)	0.0317(9)	0.0276(9)	0.0281(8)	0.0017(7)	0.0012(7)	0.0049(7)
C(24)	0.0293(9)	0.0403(10)	0.0292(9)	–0.0036(8)	–0.0010(7)	0.0127(8)
O(5)	0.0461(8)	0.0380(7)	0.0421(7)	–0.0088(6)	–0.0168(6)	0.0015(6)
O(6)	0.0340(7)	0.0528(9)	0.0417(7)	0.0041(7)	–0.0015(6)	–0.0186(6)
N(3)	0.0266(8)	0.0318(8)	0.0251(7)	0.0022(6)	–0.0018(6)	–0.0052(6)
C(25)	0.0221(8)	0.0485(11)	0.0248(8)	–0.0038(8)	0.0025(7)	0.0019(8)
C(16)	0.0204(8)	0.0229(8)	0.0526(11)	–0.0009(8)	–0.0011(8)	–0.0015(7)
C(26)	0.0275(9)	0.0358(9)	0.0239(8)	0.0026(7)	0.0021(7)	–0.0050(7)
C(27)	0.0213(8)	0.0264(8)	0.0276(8)	–0.0015(7)	–0.0001(7)	–0.0003(6)
C(28)	0.0555(13)	0.0283(10)	0.0584(13)	0.0152(9)	0.0149(11)	0.0041(9)
C(29)	0.0333(10)	0.0465(11)	0.0354(10)	0.0090(9)	–0.0001(8)	0.0020(9)
C(30)	0.0278(9)	0.0351(9)	0.0290(9)	0.0089(7)	0.0044(7)	–0.0026(7)
C(31)	0.0355(10)	0.0346(10)	0.0318(9)	0.0024(8)	0.0037(8)	–0.0015(8)
C(32)	0.0324(9)	0.0343(9)	0.0251(8)	0.0036(7)	0.0034(7)	–0.0071(8)
C(33)	0.0480(12)	0.0443(11)	0.0311(10)	–0.0058(8)	–0.0044(9)	–0.0019(9)
C(34)	0.0250(8)	0.0323(9)	0.0226(8)	0.0047(7)	–0.0013(6)	–0.0083(7)
C(35)	0.0271(9)	0.0337(9)	0.0241(8)	0.0015(7)	–0.0006(7)	–0.0078(7)
C(36)	0.0263(9)	0.0365(10)	0.0230(8)	–0.0021(7)	0.0001(7)	0.0006(7)
C(37)	0.0380(10)	0.0365(10)	0.0303(9)	–0.0004(8)	0.0011(8)	0.0047(8)
C(38)	0.0490(12)	0.0465(12)	0.0315(10)	0.0016(9)	–0.0004(9)	0.0176(10)

C(39)	0.0384(11)	0.0695(15)	0.0286(10)	–0.0087(10)	–0.0060(8)	0.0244(11)
C(40)	0.0252(9)	0.0676(14)	0.0329(10)	–0.0146(10)	–0.0026(8)	0.0004(9)
C(41)	0.0285(9)	0.0443(11)	0.0269(9)	–0.0062(8)	0.0008(7)	–0.0022(8)
C(42)	0.0497(14)	0.0728(17)	0.0741(17)	0.0043(14)	–0.0023(12)	–0.0350(13)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh12.

	x	y	z	U
H(1)	0.5349(15)	0.139(3)	0.1803(5)	0.034(5)
H(1A)	0.4835	–0.0947	0.2175	0.054
H(1B)	0.5847	–0.2079	0.2233	0.054
H(1C)	0.4877	–0.2848	0.2006	0.054
H(3A)	0.6202	–0.3063	0.1418	0.040
H(5A)	0.6922	–0.2180	0.0818	0.075
H(5B)	0.7517	–0.0384	0.0866	0.075
H(5C)	0.6433	–0.0450	0.0646	0.075
H(9A)	0.5114	0.2437	0.0618	0.068
H(10A)	0.5454	0.3294	0.0032	0.095
H(11A)	0.7014	0.4487	–0.0072	0.092
H(12A)	0.8247	0.4850	0.0394	0.079
H(14A)	0.9368	0.5076	0.1276	0.141
H(14B)	0.8828	0.6137	0.0946	0.141
H(14C)	0.9385	0.4347	0.0872	0.141
H(2)	0.6189(15)	0.406(3)	0.1971(6)	0.034(5)
H(15A)	0.8289	0.4144	0.2004	0.068
H(15B)	0.8669	0.5737	0.2253	0.068
H(15C)	0.7873	0.6049	0.1914	0.068
H(17A)	0.7659	0.5747	0.2871	0.043
H(19A)	0.6285	0.5493	0.3329	0.060
H(19B)	0.5721	0.3680	0.3260	0.060
H(19C)	0.5138	0.5446	0.3160	0.060
H(23A)	0.3431	0.5985	0.2534	0.035
H(24A)	0.2120	0.6086	0.2930	0.040
H(3)	1.0298(14)	0.326(3)	–0.0069(5)	0.030(5)
H(25A)	0.1814	0.3703	0.3286	0.038
H(26A)	0.2785	0.1199	0.3252	0.035
H(28A)	0.4543	–0.1742	0.2944	0.070
H(28B)	0.3376	–0.1167	0.2931	0.070
H(28C)	0.4129	–0.0647	0.3270	0.070
H(29A)	1.1411	0.0467	0.0203	0.058
H(29B)	1.2157	0.1530	–0.0039	0.058
H(29C)	1.1949	–0.0476	–0.0118	0.058
H(31A)	1.0629	–0.0788	–0.0705	0.041
H(33A)	0.9307	–0.0087	–0.1231	0.062
H(33B)	0.8816	0.1806	–0.1240	0.062
H(33C)	0.8287	0.0271	–0.1032	0.062
H(37A)	0.8547	0.6760	–0.0965	0.042
H(38A)	0.7230	0.7469	–0.1388	0.051
H(39A)	0.5832	0.5655	–0.1467	0.055
H(40A)	0.5743	0.3124	–0.1131	0.051
H(42D)	0.6388	–0.0172	–0.0517	0.099
H(42A)	0.6207	0.0386	–0.0932	0.099
H(42B)	0.5665	0.1431	–0.0626	0.099

Table 6. Torsion angles [°] for mjh12.

C(6)–N(1)–C(2)–C(1)	178.42(15)	C(6)–N(1)–C(2)–C(3)	0.39(19)
N(1)–C(2)–C(3)–C(4)	−0.6(2)	C(1)–C(2)–C(3)–C(4)	−178.35(18)
C(2)–C(3)–C(4)–C(5)	178.64(19)	C(2)–C(3)–C(4)–C(6)	0.5(2)
C(2)–N(1)–C(6)–C(4)	−0.05(19)	C(2)–N(1)–C(6)–C(7)	−172.55(15)
C(3)–C(4)–C(6)–N(1)	−0.30(19)	C(3)–C(4)–C(6)–C(7)	170.60(19)
C(5)–C(4)–C(6)–N(1)	−178.31(19)	C(5)–C(4)–C(6)–C(7)	−7.4(3)
N(1)–C(6)–C(7)–O(1)	8.3(3)	N(1)–C(6)–C(7)–C(8)	−168.77(16)
C(4)–C(6)–C(7)–O(1)	−161.69(19)	C(4)–C(6)–C(7)–C(8)	21.2(3)
O(1)–C(7)–C(8)–C(9)	−108.8(2)	O(1)–C(7)–C(8)–C(13)	66.7(2)
C(6)–C(7)–C(8)–C(9)	68.4(2)	C(6)–C(7)–C(8)–C(13)	−116.2(2)
C(7)–C(8)–C(9)–C(10)	175.3(2)	C(13)–C(8)–C(9)–C(10)	−0.3(4)
C(8)–C(9)–C(10)–C(11)	0.8(4)	C(9)–C(10)–C(11)–C(12)	−0.1(5)
C(10)–C(11)–C(12)–C(13)	−1.2(4)	C(14)–O(2)–C(13)–C(8)	−173.7(2)
C(14)–O(2)–C(13)–C(12)	8.1(4)	C(7)–C(8)–C(13)–O(2)	5.2(3)
C(7)–C(8)–C(13)–C(12)	−176.51(19)	C(9)–C(8)–C(13)–O(2)	−179.3(2)
C(9)–C(8)–C(13)–C(12)	−1.0(3)	C(11)–C(12)–C(13)–O(2)	179.9(2)
C(11)–C(12)–C(13)–C(8)	1.7(4)	C(16)–C(17)–C(18)–C(20)	0.1(2)
C(16)–C(17)–C(18)–C(19)	176.99(17)	C(16)–N(2)–C(20)–C(18)	−1.40(18)
C(16)–N(2)–C(20)–C(21)	180.00(14)	C(17)–C(18)–C(20)–N(2)	0.80(18)
C(17)–C(18)–C(20)–C(21)	179.09(17)	C(19)–C(18)–C(20)–N(2)	−175.99(17)
C(19)–C(18)–C(20)–C(21)	2.3(3)	N(2)–C(20)–C(21)–O(3)	5.1(2)
N(2)–C(20)–C(21)–C(22)	−172.03(14)	C(18)–C(20)–C(21)–O(3)	−173.02(17)
C(18)–C(20)–C(21)–C(22)	9.8(3)	O(3)–C(21)–C(22)–C(23)	−92.38(19)
O(3)–C(21)–C(22)–C(27)	83.55(19)	C(20)–C(21)–C(22)–C(23)	84.9(2)
C(20)–C(21)–C(22)–C(27)	−99.21(18)	C(21)–C(22)–C(23)–C(24)	176.60(15)
C(27)–C(22)–C(23)–C(24)	0.6(3)	C(22)–C(23)–C(24)–C(25)	−0.1(3)
C(23)–C(24)–C(25)–C(26)	−0.3(3)	C(20)–N(2)–C(16)–C(15)	−178.37(16)
C(20)–N(2)–C(16)–C(17)	1.43(19)	C(18)–C(17)–C(16)–N(2)	−0.9(2)
C(18)–C(17)–C(16)–C(15)	178.87(19)	C(24)–C(25)–C(26)–C(27)	0.3(3)
C(28)–O(4)–C(27)–C(22)	−172.55(16)	C(28)–O(4)–C(27)–C(26)	8.1(3)
C(25)–C(26)–C(27)–O(4)	179.48(16)	C(25)–C(26)–C(27)–C(22)	0.2(2)
C(21)–C(22)–C(27)–O(4)	4.1(2)	C(21)–C(22)–C(27)–C(26)	−176.61(15)
C(23)–C(22)–C(27)–O(4)	180.00(15)	C(23)–C(22)–C(27)–C(26)	−0.7(2)
C(34)–N(3)–C(30)–C(29)	179.61(15)	C(34)–N(3)–C(30)–C(31)	0.20(19)
N(3)–C(30)–C(31)–C(32)	−0.1(2)	C(29)–C(30)–C(31)–C(32)	−179.45(18)
C(30)–C(31)–C(32)–C(33)	179.14(17)	C(30)–C(31)–C(32)–C(34)	0.0(2)
C(30)–N(3)–C(34)–C(32)	−0.21(18)	C(30)–N(3)–C(34)–C(35)	−175.45(14)
C(31)–C(32)–C(34)–N(3)	0.14(18)	C(31)–C(32)–C(34)–C(35)	174.10(18)
C(33)–C(32)–C(34)–N(3)	−178.98(17)	C(33)–C(32)–C(34)–C(35)	−5.0(3)
N(3)–C(34)–C(35)–O(5)	5.4(2)	N(3)–C(34)–C(35)–C(36)	−178.80(15)
C(32)–C(34)–C(35)–O(5)	−168.08(19)	C(32)–C(34)–C(35)–C(36)	7.7(3)
O(5)–C(35)–C(36)–C(37)	50.1(2)	O(5)–C(35)–C(36)–C(41)	−123.36(19)
C(34)–C(35)–C(36)–C(37)	−125.85(18)	C(34)–C(35)–C(36)–C(41)	60.7(2)
C(35)–C(36)–C(37)–C(38)	−176.69(16)	C(41)–C(36)–C(37)–C(38)	−2.9(3)
C(36)–C(37)–C(38)–C(39)	2.2(3)	C(37)–C(38)–C(39)–C(40)	−0.2(3)
C(38)–C(39)–C(40)–C(41)	−1.2(3)	C(42)–O(6)–C(41)–C(36)	−179.82(19)
C(42)–O(6)–C(41)–C(40)	2.5(3)	C(39)–C(40)–C(41)–O(6)	178.17(17)
C(39)–C(40)–C(41)–C(36)	0.6(3)	C(35)–C(36)–C(41)–O(6)	−3.0(3)
C(35)–C(36)–C(41)–C(40)	174.82(16)	C(37)–C(36)–C(41)–O(6)	−176.37(16)
C(37)–C(36)–C(41)–C(40)	1.4(3)		

Table 7. Hydrogen bonds for mjh12 [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N(1)–H(1)...O(3)	0.88(2)	1.97(2)	2.8389(18)	168(2)
N(2)–H(2)...O(1)	0.91(2)	1.92(2)	2.814(2)	168(2)
N(3)–H(3)...O(5A)	0.90(2)	1.96(2)	2.818(2)	160(2)

Symmetry operations for equivalent atoms
A –x+2,–y+1,–z

Compound **6.20**

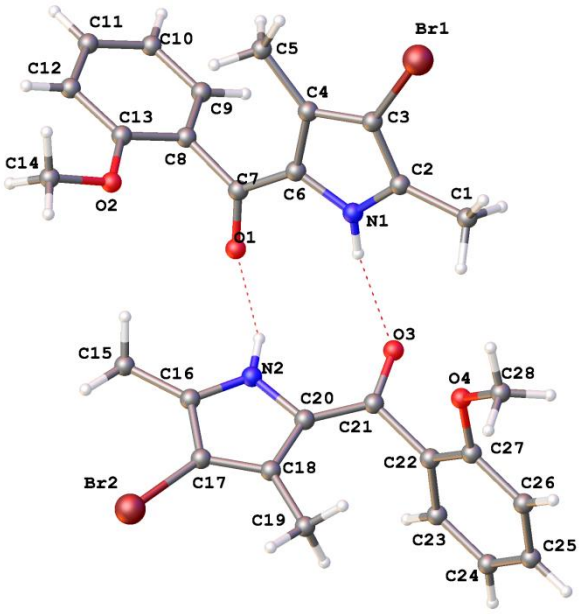


Table 1. Crystal data and structure refinement for mjh12.

Identification code	mjh120039	
Chemical formula (moiety)	$C_{14}H_{14}BrNO_2$	
Chemical formula (total)	$C_{14}H_{14}BrNO_2$	
Formula weight	308.17	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	monoclinic, Pc	
Unit cell parameters	a = 10.5320(9) Å	α = 90°
	b = 12.1959(8) Å	β = 104.670(7)°
	c = 10.5393(8) Å	γ = 90°
Cell volume	1309.61(17) $Å^3$	
Z	4	
Calculated density	1.563 g/cm^3	
Absorption coefficient μ	3.132 mm^{-1}	
F(000)	624	
Crystal colour and size	colourless, 0.24 × 0.10 × 0.10 mm^3	
Reflections for cell refinement	2189 (θ range 3.0 to 28.4°)	
Data collection method	Xcalibur, Atlas, Gemini ultra	
	thick-slice ω scans	
θ range for data collection	3.0 to 25.0°	
Index ranges	h −12 to 8, k −14 to 11, l −10 to 12	
Completeness to θ = 25.0°	99.5 %	
Reflections collected	6111	
Independent reflections	3506 (R_{int} = 0.0751)	
Reflections with $F^2>2\sigma$	2925	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.5202 and 0.7447	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0847, 0.0000	
Data / restraints / parameters	3506 / 2 / 332	
Final R indices [$F^2>2\sigma$]	R1 = 0.0666, wR2 = 0.1568	
R indices (all data)	R1 = 0.0792, wR2 = 0.1702	
Goodness-of-fit on F^2	1.044	
Absolute structure parameter	0.03(2)	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	1.36 and −0.72 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh12. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Br(1)	0.95542(11)	0.53830(9)	0.84872(9)	0.0490(4)
N(1)	0.7136(8)	0.3607(6)	0.5717(7)	0.0315(19)
O(1)	0.4567(8)	0.3703(5)	0.4117(7)	0.0421(18)
O(2)	0.3039(8)	0.4995(6)	0.5949(7)	0.0406(18)
C(8)	0.4287(11)	0.5573(8)	0.4527(9)	0.031(2)
C(1)	0.9369(12)	0.2946(8)	0.6858(11)	0.045(3)
C(2)	0.8277(10)	0.3755(7)	0.6598(8)	0.031(2)
C(3)	0.8194(11)	0.4767(8)	0.7164(9)	0.036(3)
C(4)	0.6990(12)	0.5245(6)	0.6618(9)	0.030(2)
C(5)	0.6525(12)	0.6345(8)	0.6981(9)	0.041(3)
C(6)	0.6309(11)	0.4482(7)	0.5680(9)	0.030(2)
C(7)	0.5020(13)	0.4518(8)	0.4794(9)	0.040(3)
C(9)	0.4581(13)	0.6321(7)	0.3634(10)	0.043(3)
C(10)	0.3854(12)	0.7273(8)	0.3361(10)	0.047(3)
C(11)	0.2856(13)	0.7481(8)	0.3918(11)	0.049(3)
C(12)	0.2521(13)	0.6750(9)	0.4833(11)	0.052(3)
C(13)	0.3268(11)	0.5780(7)	0.5105(8)	0.033(2)
C(14)	0.2104(17)	0.5223(8)	0.6640(14)	0.044(3)
Br(2)	0.19696(12)	–0.01993(9)	0.64559(10)	0.0496(4)
N(2)	0.4433(8)	0.1560(6)	0.4954(7)	0.0306(18)
O(3)	0.7020(8)	0.1443(5)	0.4713(6)	0.0393(17)
O(4)	0.8516(8)	0.0127(6)	0.7264(6)	0.0410(19)
C(15)	0.2217(12)	0.2234(8)	0.4897(11)	0.048(3)
C(16)	0.3287(11)	0.1423(7)	0.5204(8)	0.032(2)
C(17)	0.3331(12)	0.0383(7)	0.5819(9)	0.034(3)
C(18)	0.4528(11)	–0.0084(8)	0.5904(9)	0.030(2)
C(19)	0.5014(13)	–0.1163(8)	0.6562(9)	0.044(3)
C(20)	0.5244(10)	0.0644(7)	0.5311(9)	0.030(2)
C(21)	0.6507(13)	0.0648(8)	0.5124(10)	0.039(3)
C(22)	0.7277(13)	–0.0438(8)	0.5237(10)	0.042(3)
C(23)	0.6933(12)	–0.1216(8)	0.4223(10)	0.043(3)
C(24)	0.7628(12)	–0.2188(8)	0.4324(11)	0.047(3)
C(25)	0.8632(13)	–0.2388(8)	0.5384(12)	0.050(3)
C(26)	0.8964(12)	–0.1642(8)	0.6410(11)	0.044(3)
C(27)	0.8251(13)	–0.0648(8)	0.6307(10)	0.044(3)
C(28)	0.9478(17)	–0.0081(9)	0.8441(14)	0.046(3)

Table 3. Bond lengths [Å] and angles [°] for mjh12.

Br(1)–C(3)	1.884(10)	N(1)–H(1D)	0.880
N(1)–C(2)	1.331(12)	N(1)–C(6)	1.373(12)
O(1)–C(7)	1.246(12)	O(2)–C(13)	1.370(12)
O(2)–C(14)	1.393(19)	C(8)–C(7)	1.489(16)
C(8)–C(9)	1.401(14)	C(8)–C(13)	1.385(15)
C(1)–H(1A)	0.980	C(1)–H(1B)	0.980
C(1)–H(1C)	0.980	C(1)–C(2)	1.487(14)
C(2)–C(3)	1.384(13)	C(3)–C(4)	1.382(15)
C(4)–C(5)	1.511(12)	C(4)–C(6)	1.412(13)
C(5)–H(5A)	0.980	C(5)–H(5B)	0.980
C(5)–H(5C)	0.980	C(6)–C(7)	1.441(15)
C(9)–H(9A)	0.950	C(9)–C(10)	1.380(15)
C(10)–H(10A)	0.950	C(10)–C(11)	1.351(17)
C(11)–H(11A)	0.950	C(11)–C(12)	1.422(17)
C(12)–H(12A)	0.950	C(12)–C(13)	1.410(15)
C(14)–H(14A)	0.980	C(14)–H(14B)	0.980
C(14)–H(14C)	0.980	Br(2)–C(17)	1.871(12)
N(2)–H(2A)	0.880	N(2)–C(16)	1.310(13)
N(2)–C(20)	1.398(12)	O(3)–C(21)	1.240(13)
O(4)–C(27)	1.358(13)	O(4)–C(28)	1.412(16)
C(15)–H(15A)	0.980	C(15)–H(15B)	0.980
C(15)–H(15C)	0.980	C(15)–C(16)	1.472(14)
C(16)–C(17)	1.420(13)	C(17)–C(18)	1.365(16)
C(18)–C(19)	1.515(13)	C(18)–C(20)	1.409(14)
C(19)–H(19A)	0.980	C(19)–H(19B)	0.980
C(19)–H(19C)	0.980	C(20)–C(21)	1.393(16)
C(21)–C(22)	1.542(16)	C(22)–C(23)	1.407(14)
C(22)–C(27)	1.343(16)	C(23)–H(23A)	0.950
C(23)–C(24)	1.382(15)	C(24)–H(24A)	0.950
C(24)–C(25)	1.352(16)	C(25)–H(25A)	0.950
C(25)–C(26)	1.388(15)	C(26)–H(26A)	0.950
C(26)–C(27)	1.416(15)	C(28)–H(28D)	0.980
C(28)–H(28A)	0.980	C(28)–H(28B)	0.980

H(1D)–N(1)–C(2)	124.2	H(1D)–N(1)–C(6)	124.2
C(2)–N(1)–C(6)	111.6(8)	C(13)–O(2)–C(14)	117.7(8)
C(7)–C(8)–C(9)	119.8(10)	C(7)–C(8)–C(13)	119.8(9)
C(9)–C(8)–C(13)	120.3(10)	H(1A)–C(1)–H(1B)	109.5
H(1A)–C(1)–H(1C)	109.5	H(1A)–C(1)–C(2)	109.5
H(1B)–C(1)–H(1C)	109.5	H(1B)–C(1)–C(2)	109.5
H(1C)–C(1)–C(2)	109.5	N(1)–C(2)–C(1)	123.9(8)
N(1)–C(2)–C(3)	106.1(9)	C(1)–C(2)–C(3)	130.0(9)
Br(1)–C(3)–C(2)	123.8(8)	Br(1)–C(3)–C(4)	125.9(7)
C(2)–C(3)–C(4)	110.3(9)	C(3)–C(4)–C(5)	126.2(9)
C(3)–C(4)–C(6)	105.3(8)	C(5)–C(4)–C(6)	128.5(10)
C(4)–C(5)–H(5A)	109.5	C(4)–C(5)–H(5B)	109.5
C(4)–C(5)–H(5C)	109.5	H(5A)–C(5)–H(5B)	109.5
H(5A)–C(5)–H(5C)	109.5	H(5B)–C(5)–H(5C)	109.5
N(1)–C(6)–C(4)	106.6(9)	N(1)–C(6)–C(7)	122.0(8)
C(4)–C(6)–C(7)	131.4(9)	O(1)–C(7)–C(8)	118.4(10)
O(1)–C(7)–C(6)	120.6(10)	C(8)–C(7)–C(6)	120.5(9)
C(8)–C(9)–H(9A)	120.5	C(8)–C(9)–C(10)	118.9(12)
H(9A)–C(9)–C(10)	120.5	C(9)–C(10)–H(10A)	119.4

C(9)–C(10)–C(11)	121.2(11)	H(10A)–C(10)–C(11)	119.4
C(10)–C(11)–H(11A)	118.9	C(10)–C(11)–C(12)	122.1(11)
H(11A)–C(11)–C(12)	118.9	C(11)–C(12)–H(12A)	121.9
C(11)–C(12)–C(13)	116.2(12)	H(12A)–C(12)–C(13)	121.9
O(2)–C(13)–C(8)	116.2(9)	O(2)–C(13)–C(12)	122.5(10)
C(8)–C(13)–C(12)	121.3(10)	O(2)–C(14)–H(14A)	109.5
O(2)–C(14)–H(14B)	109.5	O(2)–C(14)–H(14C)	109.5
H(14A)–C(14)–H(14B)	109.5	H(14A)–C(14)–H(14C)	109.5
H(14B)–C(14)–H(14C)	109.5	H(2A)–N(2)–C(16)	124.0
H(2A)–N(2)–C(20)	124.0	C(16)–N(2)–C(20)	112.0(8)
C(27)–O(4)–C(28)	119.6(8)	H(15A)–C(15)–H(15B)	109.5
H(15A)–C(15)–H(15C)	109.5	H(15A)–C(15)–C(16)	109.5
H(15B)–C(15)–H(15C)	109.5	H(15B)–C(15)–C(16)	109.5
H(15C)–C(15)–C(16)	109.5	N(2)–C(16)–C(15)	124.3(9)
N(2)–C(16)–C(17)	106.3(9)	C(15)–C(16)–C(17)	129.4(10)
Br(2)–C(17)–C(16)	124.3(8)	Br(2)–C(17)–C(18)	126.7(7)
C(16)–C(17)–C(18)	109.0(10)	C(17)–C(18)–C(19)	126.2(10)
C(17)–C(18)–C(20)	107.3(8)	C(19)–C(18)–C(20)	126.4(10)
C(18)–C(19)–H(19A)	109.5	C(18)–C(19)–H(19B)	109.5
C(18)–C(19)–H(19C)	109.5	H(19A)–C(19)–H(19B)	109.5
H(19A)–C(19)–H(19C)	109.5	H(19B)–C(19)–H(19C)	109.5
N(2)–C(20)–C(18)	105.3(9)	N(2)–C(20)–C(21)	119.9(9)
C(18)–C(20)–C(21)	134.7(9)	O(3)–C(21)–C(20)	124.6(10)
O(3)–C(21)–C(22)	115.6(11)	C(20)–C(21)–C(22)	119.2(10)
C(21)–C(22)–C(23)	119.5(10)	C(21)–C(22)–C(27)	120.3(9)
C(23)–C(22)–C(27)	120.3(10)	C(22)–C(23)–H(23A)	120.3
C(22)–C(23)–C(24)	119.4(11)	H(23A)–C(23)–C(24)	120.3
C(23)–C(24)–H(24A)	119.8	C(23)–C(24)–C(25)	120.5(10)
H(24A)–C(24)–C(25)	119.8	C(24)–C(25)–H(25A)	119.5
C(24)–C(25)–C(26)	121.0(10)	H(25A)–C(25)–C(26)	119.5
C(25)–C(26)–H(26A)	120.7	C(25)–C(26)–C(27)	118.5(10)
H(26A)–C(26)–C(27)	120.7	O(4)–C(27)–C(22)	117.4(10)
O(4)–C(27)–C(26)	122.2(10)	C(22)–C(27)–C(26)	120.4(10)
O(4)–C(28)–H(28D)	109.5	O(4)–C(28)–H(28A)	109.5
O(4)–C(28)–H(28B)	109.5	H(28D)–C(28)–H(28A)	109.5
H(28D)–C(28)–H(28B)	109.5	H(28A)–C(28)–H(28B)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	0.0494(9)	0.0434(6)	0.0443(6)	–0.0070(5)	–0.0066(5)	0.0015(6)
N(1)	0.040(6)	0.017(4)	0.035(4)	0.004(3)	0.006(4)	0.001(4)
O(1)	0.039(5)	0.029(4)	0.049(4)	0.001(3)	–0.006(3)	–0.004(3)
O(2)	0.046(5)	0.032(4)	0.046(4)	0.011(3)	0.014(4)	0.008(4)
C(8)	0.026(7)	0.033(5)	0.031(5)	0.005(4)	0.004(4)	–0.014(5)
C(1)	0.044(8)	0.025(5)	0.064(7)	–0.001(5)	0.013(5)	0.006(5)
C(2)	0.039(7)	0.021(4)	0.025(4)	0.001(3)	–0.004(4)	0.001(4)
C(3)	0.032(7)	0.037(6)	0.033(5)	–0.006(4)	–0.006(5)	0.003(5)
C(4)	0.035(6)	0.024(4)	0.028(5)	0.007(4)	0.003(4)	0.003(5)
C(5)	0.052(8)	0.030(5)	0.035(5)	–0.002(4)	0.002(5)	0.015(5)
C(6)	0.030(7)	0.016(4)	0.039(5)	0.006(4)	0.000(4)	0.005(4)
C(7)	0.059(9)	0.028(5)	0.027(5)	0.004(4)	0.000(5)	–0.003(5)
C(9)	0.056(8)	0.015(4)	0.052(6)	0.000(4)	0.004(5)	–0.006(5)
C(10)	0.045(8)	0.022(5)	0.059(7)	0.014(4)	–0.017(6)	–0.007(5)
C(11)	0.050(8)	0.016(5)	0.071(7)	0.002(5)	–0.004(6)	–0.001(5)
C(12)	0.046(8)	0.034(6)	0.062(7)	–0.006(5)	–0.015(6)	0.008(5)
C(13)	0.038(7)	0.026(5)	0.034(5)	0.000(4)	0.004(4)	–0.007(5)
C(14)	0.040(9)	0.038(6)	0.051(8)	0.014(5)	0.007(6)	–0.012(6)
Br(2)	0.0474(9)	0.0454(6)	0.0585(7)	0.0049(6)	0.0181(6)	–0.0039(7)
N(2)	0.026(5)	0.018(4)	0.045(4)	0.000(3)	0.006(4)	–0.005(3)
O(3)	0.054(5)	0.016(3)	0.046(4)	0.002(3)	0.010(3)	0.000(3)
O(4)	0.042(5)	0.036(4)	0.035(4)	–0.006(3)	–0.008(3)	0.011(3)
C(15)	0.047(8)	0.016(4)	0.074(7)	–0.007(5)	0.004(6)	0.002(5)
C(16)	0.034(7)	0.024(5)	0.037(5)	–0.007(4)	0.005(4)	–0.007(4)
C(17)	0.047(8)	0.020(4)	0.031(5)	–0.001(4)	–0.001(4)	0.004(5)
C(18)	0.029(6)	0.025(4)	0.033(5)	0.004(4)	0.004(4)	–0.002(4)
C(19)	0.077(9)	0.018(5)	0.034(5)	0.007(4)	0.006(5)	0.004(5)
C(20)	0.024(6)	0.022(4)	0.036(5)	–0.005(4)	–0.005(4)	0.007(4)
C(21)	0.064(10)	0.018(5)	0.033(6)	–0.003(4)	0.010(5)	0.000(5)
C(22)	0.049(8)	0.034(6)	0.038(6)	0.009(4)	0.002(5)	–0.001(5)
C(23)	0.061(8)	0.022(5)	0.045(6)	–0.012(4)	0.013(5)	–0.005(5)
C(24)	0.047(9)	0.025(5)	0.073(7)	–0.021(5)	0.024(6)	–0.010(5)
C(25)	0.051(9)	0.016(5)	0.078(8)	0.003(5)	0.007(7)	0.006(5)
C(26)	0.052(8)	0.025(5)	0.059(6)	0.009(5)	0.022(6)	0.006(5)
C(27)	0.060(9)	0.028(5)	0.044(6)	0.005(4)	0.011(6)	0.004(5)
C(28)	0.045(9)	0.043(6)	0.045(6)	–0.008(6)	0.003(5)	0.015(7)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh12.

	x	y	z	U
H(1D)	0.6938	0.3020	0.5221	0.038
H(1A)	0.9008	0.2201	0.6759	0.067
H(1B)	0.9914	0.3045	0.7754	0.067
H(1C)	0.9906	0.3059	0.6233	0.067
H(5A)	0.7133	0.6614	0.7785	0.061
H(5B)	0.5646	0.6268	0.7126	0.061
H(5C)	0.6494	0.6868	0.6268	0.061
H(9A)	0.5269	0.6176	0.3223	0.051
H(10A)	0.4059	0.7792	0.2770	0.057
H(11A)	0.2363	0.8136	0.3690	0.059
H(12A)	0.1832	0.6907	0.5239	0.062
H(14A)	0.2026	0.4594	0.7194	0.066
H(14B)	0.1255	0.5364	0.6021	0.066
H(14C)	0.2375	0.5871	0.7193	0.066
H(2A)	0.4666	0.2158	0.4603	0.037
H(15A)	0.2533	0.2935	0.5314	0.072
H(15B)	0.1482	0.1973	0.5229	0.072
H(15C)	0.1924	0.2334	0.3945	0.072
H(19A)	0.4410	–0.1415	0.7071	0.066
H(19B)	0.5890	–0.1061	0.7147	0.066
H(19C)	0.5055	–0.1710	0.5892	0.066
H(23A)	0.6230	–0.1076	0.3476	0.051
H(24A)	0.7399	–0.2718	0.3644	0.056
H(25A)	0.9117	–0.3050	0.5428	0.060
H(26A)	0.9654	–0.1795	0.7164	0.053
H(28D)	0.9616	0.0582	0.8985	0.069
H(28A)	1.0303	–0.0290	0.8238	0.069
H(28B)	0.9182	–0.0679	0.8918	0.069

Table 6. Torsion angles [°] for mjh12.

C(6)–N(1)–C(2)–C(1)	−179.9(9)	C(6)–N(1)–C(2)–C(3)	0.2(11)
N(1)–C(2)–C(3)–Br(1)	180.0(7)	N(1)–C(2)–C(3)–C(4)	−0.3(12)
C(1)–C(2)–C(3)–Br(1)	0.1(16)	C(1)–C(2)–C(3)–C(4)	179.8(10)
Br(1)–C(3)–C(4)–C(5)	−0.6(16)	Br(1)–C(3)–C(4)–C(6)	−180.0(8)
C(2)–C(3)–C(4)–C(5)	179.6(10)	C(2)–C(3)–C(4)–C(6)	0.3(12)
C(2)–N(1)–C(6)–C(4)	0.0(11)	C(2)–N(1)–C(6)–C(7)	179.4(9)
C(3)–C(4)–C(6)–N(1)	−0.2(11)	C(3)–C(4)–C(6)–C(7)	−179.5(11)
C(5)–C(4)–C(6)–N(1)	−179.5(10)	C(5)–C(4)–C(6)–C(7)	1.2(19)
N(1)–C(6)–C(7)–O(1)	6.9(16)	N(1)–C(6)–C(7)–C(8)	−164.2(9)
C(4)–C(6)–C(7)–O(1)	−173.9(11)	C(4)–C(6)–C(7)–C(8)	15.1(17)
C(9)–C(8)–C(7)–O(1)	−91.2(14)	C(9)–C(8)–C(7)–C(6)	80.1(13)
C(13)–C(8)–C(7)–O(1)	85.1(13)	C(13)–C(8)–C(7)–C(6)	−103.7(13)
C(7)–C(8)–C(9)–C(10)	177.4(9)	C(13)–C(8)–C(9)–C(10)	1.2(16)
C(8)–C(9)–C(10)–C(11)	−1.3(16)	C(9)–C(10)–C(11)–C(12)	1.5(17)
C(10)–C(11)–C(12)–C(13)	−1.5(16)	C(14)–O(2)–C(13)–C(8)	174.1(9)
C(14)–O(2)–C(13)–C(12)	−5.6(14)	C(7)–C(8)–C(13)–O(2)	2.8(14)
C(7)–C(8)–C(13)–C(12)	−177.5(9)	C(9)–C(8)–C(13)–O(2)	179.0(9)
C(9)–C(8)–C(13)–C(12)	−1.3(15)	C(11)–C(12)–C(13)–O(2)	−178.9(9)
C(11)–C(12)–C(13)–C(8)	1.4(14)	C(20)–N(2)–C(16)–C(15)	−178.1(8)
C(20)–N(2)–C(16)–C(17)	2.8(10)	N(2)–C(16)–C(17)–Br(2)	177.1(6)
N(2)–C(16)–C(17)–C(18)	−0.8(10)	C(15)–C(16)–C(17)–Br(2)	−1.9(14)
C(15)–C(16)–C(17)–C(18)	−179.8(10)	Br(2)–C(17)–C(18)–C(19)	−1.5(15)
Br(2)–C(17)–C(18)–C(20)	−179.3(6)	C(16)–C(17)–C(18)–C(19)	176.3(8)
C(16)–C(17)–C(18)–C(20)	−1.5(11)	C(16)–N(2)–C(20)–C(18)	−3.7(10)
C(16)–N(2)–C(20)–C(21)	−179.6(8)	C(17)–C(18)–C(20)–N(2)	3.0(10)
C(17)–C(18)–C(20)–C(21)	178.0(10)	C(19)–C(18)–C(20)–N(2)	−174.7(8)
C(19)–C(18)–C(20)–C(21)	0.2(17)	N(2)–C(20)–C(21)–O(3)	3.9(14)
N(2)–C(20)–C(21)–C(22)	−166.9(8)	C(18)–C(20)–C(21)–O(3)	−170.4(10)
C(18)–C(20)–C(21)–C(22)	18.7(16)	O(3)–C(21)–C(22)–C(23)	−97.4(13)
O(3)–C(21)–C(22)–C(27)	83.9(14)	C(20)–C(21)–C(22)–C(23)	74.3(14)
C(20)–C(21)–C(22)–C(27)	−104.5(14)	C(21)–C(22)–C(23)–C(24)	179.7(11)
C(27)–C(22)–C(23)–C(24)	−1.5(18)	C(22)–C(23)–C(24)–C(25)	−0.2(18)
C(23)–C(24)–C(25)–C(26)	1.9(19)	C(24)–C(25)–C(26)–C(27)	−1.8(18)
C(21)–C(22)–C(27)–O(4)	0.2(17)	C(21)–C(22)–C(27)–C(26)	−179.7(11)
C(23)–C(22)–C(27)–O(4)	−178.5(11)	C(23)–C(22)–C(27)–C(26)	1.6(18)
C(28)–O(4)–C(27)–C(22)	176.3(12)	C(28)–O(4)–C(27)–C(26)	−3.9(17)
C(25)–C(26)–C(27)–O(4)	−179.8(11)	C(25)–C(26)–C(27)–C(22)	0.0(18)

Table 7. Hydrogen bonds for mjh12 [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N(1)–H(1D)...O(1)	0.88	2.61	2.806(11)	94
N(2)–H(2A)...O(3)	0.88	2.60	2.802(11)	94

Compound **6.21**

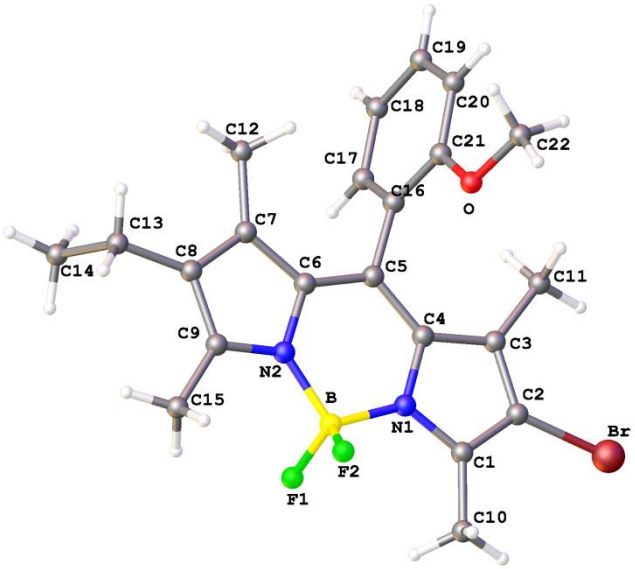


Table 1. Crystal data and structure refinement for mjh12.

Identification code	mjh120005	
Chemical formula (moiety)	$C_{22}H_{24}BBrF_2N_2O$	
Chemical formula (total)	$C_{22}H_{24}BBrF_2N_2O$	
Formula weight	461.15	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 8.2307(5) Å	α = 79.553(5)°
	b = 10.7497(6) Å	β = 85.581(5)°
	c = 12.6416(7) Å	γ = 70.255(5)°
Cell volume	1035.13(10) $Å^3$	
Z	2	
Calculated density	1.480 g/cm^3	
Absorption coefficient μ	2.019 mm^{-1}	
F(000)	472	
Crystal colour and size	red, 0.40 × 0.40 × 0.30 mm^3	
Reflections for cell refinement	3692 (θ range 3.1 to 28.4°)	
Data collection method	Xcalibur, Atlas, Gemini ultra	
	thick-slice ω scans	
θ range for data collection	3.1 to 28.5°	
Index ranges	h −10 to 8, k −14 to 13, l −15 to 16	
Completeness to θ = 25.0°	99.8 %	
Reflections collected	8613	
Independent reflections	4320 (R_{int} = 0.0252)	
Reflections with $F^2>2\sigma$	3727	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.4989 and 0.5826	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0220, 0.7791	
Data / restraints / parameters	4320 / 14 / 296	
Final R indices [$F^2>2\sigma$]	R1 = 0.0361, wR2 = 0.0732	
R indices (all data)	R1 = 0.0457, wR2 = 0.0769	
Goodness-of-fit on F^2	1.060	
Extinction coefficient	0.0026(7)	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	0.40 and −0.28 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh12. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Br	1.13629(3)	0.06831(3)	0.08570(2)	0.03322(12)
BrA	–0.1162(10)	0.2769(7)	0.4130(5)	0.0475(19)
C(14A)	1.148(5)	0.177(3)	0.048(3)	0.071(12)
C(13A)	1.098(3)	0.084(3)	0.143(3)	0.18(3)
C(13)	–0.0852(9)	0.2886(7)	0.3773(4)	0.0341(13)
C(14)	–0.0932(4)	0.3112(3)	0.4948(2)	0.0336(6)
O	0.5296(2)	–0.11982(15)	0.13047(11)	0.0264(4)
N(1)	0.6430(2)	0.22018(17)	0.18641(13)	0.0204(4)
N(2)	0.3426(2)	0.27315(16)	0.25915(14)	0.0205(4)
F(1)	0.51003(18)	0.41344(13)	0.27161(11)	0.0353(3)
F(2)	0.41609(19)	0.41524(14)	0.10726(11)	0.0397(4)
B	0.4771(3)	0.3357(2)	0.2046(2)	0.0240(5)
C(1)	0.7894(3)	0.2328(2)	0.13780(17)	0.0235(5)
C(2)	0.9106(3)	0.1042(2)	0.14233(17)	0.0235(5)
C(3)	0.8393(3)	0.0098(2)	0.19437(16)	0.0222(5)
C(4)	0.6685(3)	0.0840(2)	0.22204(16)	0.0187(4)
C(5)	0.5331(3)	0.0434(2)	0.27364(15)	0.0182(4)
C(6)	0.3729(3)	0.1357(2)	0.29200(16)	0.0190(4)
C(7)	0.2162(3)	0.1205(2)	0.34041(16)	0.0212(5)
C(8)	0.0970(3)	0.2483(2)	0.33616(17)	0.0236(5)
C(9)	0.1795(3)	0.3397(2)	0.28555(18)	0.0250(5)
C(10)	0.8096(3)	0.3633(2)	0.0889(2)	0.0342(6)
C(11)	0.9287(3)	–0.1387(2)	0.21308(19)	0.0277(5)
C(12)	0.1801(3)	–0.0061(2)	0.38634(18)	0.0272(5)
C(15)	0.1044(3)	0.4888(2)	0.2626(2)	0.0361(6)
C(16)	0.5600(3)	–0.1022(2)	0.30909(16)	0.0188(4)
C(17)	0.5878(3)	–0.1590(2)	0.41628(17)	0.0250(5)
C(18)	0.5995(3)	–0.2915(2)	0.45183(18)	0.0294(5)
C(19)	0.5809(3)	–0.3666(2)	0.37915(19)	0.0285(5)
C(20)	0.5568(3)	–0.3130(2)	0.27093(18)	0.0250(5)
C(21)	0.5486(3)	–0.1811(2)	0.23552(17)	0.0207(5)
C(22)	0.5188(4)	–0.1973(3)	0.05213(19)	0.0403(7)

Table 3. Bond lengths [Å] and angles [°] for mjh12.

Br–C(2)	1.877(2)	BrA–C(8)	1.897(7)
C(14A)–H(14A)	0.980	C(14A)–H(14B)	0.980
C(14A)–H(14C)	0.980	C(14A)–C(13A)	1.54(2)
C(13A)–H(13A)	0.990	C(13A)–H(13B)	0.990
C(13A)–C(2)	1.49(2)	C(13)–H(13A)	0.990
C(13)–H(13B)	0.990	C(13)–C(14)	1.542(6)
C(13)–C(8)	1.493(6)	C(14)–H(14A)	0.980
C(14)–H(14B)	0.980	C(14)–H(14C)	0.980
O–C(21)	1.366(2)	O–C(22)	1.430(3)
N(1)–B	1.539(3)	N(1)–C(1)	1.347(3)
N(1)–C(4)	1.399(3)	N(2)–B	1.540(3)
N(2)–C(6)	1.401(3)	N(2)–C(9)	1.340(3)
F(1)–B	1.391(3)	F(2)–B	1.386(3)
C(1)–C(2)	1.399(3)	C(1)–C(10)	1.485(3)
C(2)–C(3)	1.381(3)	C(3)–C(4)	1.415(3)
C(3)–C(11)	1.497(3)	C(4)–C(5)	1.404(3)
C(5)–C(6)	1.389(3)	C(5)–C(16)	1.492(3)
C(6)–C(7)	1.432(3)	C(7)–C(8)	1.387(3)
C(7)–C(12)	1.496(3)	C(8)–C(9)	1.411(3)
C(9)–C(15)	1.492(3)	C(10)–H(10A)	0.980
C(10)–H(10B)	0.980	C(10)–H(10C)	0.980
C(10)–H(10D)	0.980	C(10)–H(10E)	0.980
C(10)–H(10F)	0.980	C(11)–H(11A)	0.980
C(11)–H(11B)	0.980	C(11)–H(11C)	0.980
C(12)–H(12A)	0.980	C(12)–H(12B)	0.980
C(12)–H(12C)	0.980	C(15)–H(15A)	0.980
C(15)–H(15B)	0.980	C(15)–H(15C)	0.980
C(16)–C(17)	1.384(3)	C(16)–C(21)	1.395(3)
C(17)–H(17A)	0.950	C(17)–C(18)	1.387(3)
C(18)–H(18A)	0.950	C(18)–C(19)	1.376(3)
C(19)–H(19A)	0.950	C(19)–C(20)	1.386(3)
C(20)–H(20A)	0.950	C(20)–C(21)	1.388(3)
C(22)–H(22A)	0.980	C(22)–H(22B)	0.980
C(22)–H(22C)	0.980		

H(14A)–C(14A)–H(14B)	109.5	H(14A)–C(14A)–H(14C)	109.5
H(14A)–C(14A)–C(13A)	109.5	H(14B)–C(14A)–H(14C)	109.5
H(14B)–C(14A)–C(13A)	109.5	H(14C)–C(14A)–C(13A)	109.5
C(14A)–C(13A)–H(13A)	109.5	C(14A)–C(13A)–H(13B)	109.5
C(14A)–C(13A)–C(2)	111(3)	H(13A)–C(13A)–H(13B)	108.1
H(13A)–C(13A)–C(2)	109.5	H(13B)–C(13A)–C(2)	109.5
H(13A)–C(13)–H(13B)	108.1	H(13A)–C(13)–C(14)	109.5
H(13A)–C(13)–C(8)	109.5	H(13B)–C(13)–C(14)	109.5
H(13B)–C(13)–C(8)	109.5	C(14)–C(13)–C(8)	110.6(5)
C(21)–O–C(22)	117.68(17)	B–N(1)–C(1)	126.11(18)
B–N(1)–C(4)	125.20(18)	C(1)–N(1)–C(4)	108.64(18)
B–N(2)–C(6)	125.18(18)	B–N(2)–C(9)	126.35(18)
C(6)–N(2)–C(9)	108.45(18)	N(1)–B–N(2)	107.57(17)
N(1)–B–F(1)	109.99(19)	N(1)–B–F(2)	110.28(19)
N(2)–B–F(1)	109.29(18)	N(2)–B–F(2)	110.25(19)
F(1)–B–F(2)	109.43(18)	N(1)–C(1)–C(2)	107.77(19)
N(1)–C(1)–C(10)	123.8(2)	C(2)–C(1)–C(10)	128.5(2)
Br–C(2)–C(13A)	23.8(16)	Br–C(2)–C(1)	124.20(17)

Br–C(2)–C(3)	125.83(18)	C(13A)–C(2)–C(1)	120.2(14)
C(13A)–C(2)–C(3)	123.0(12)	C(1)–C(2)–C(3)	109.98(19)
C(2)–C(3)–C(4)	105.22(19)	C(2)–C(3)–C(11)	125.5(2)
C(4)–C(3)–C(11)	129.3(2)	N(1)–C(4)–C(3)	108.39(18)
N(1)–C(4)–C(5)	119.99(18)	C(3)–C(4)–C(5)	131.61(19)
C(4)–C(5)–C(6)	121.57(18)	C(4)–C(5)–C(16)	119.69(18)
C(6)–C(5)–C(16)	118.73(19)	N(2)–C(6)–C(5)	120.31(19)
N(2)–C(6)–C(7)	107.35(18)	C(5)–C(6)–C(7)	132.33(19)
C(6)–C(7)–C(8)	106.89(18)	C(6)–C(7)–C(12)	128.39(19)
C(8)–C(7)–C(12)	124.7(2)	BrA–C(8)–C(13)	11.1(4)
BrA–C(8)–C(7)	120.8(3)	BrA–C(8)–C(9)	130.8(3)
C(13)–C(8)–C(7)	128.6(3)	C(13)–C(8)–C(9)	124.1(3)
C(7)–C(8)–C(9)	107.36(19)	N(2)–C(9)–C(8)	109.94(18)
N(2)–C(9)–C(15)	122.6(2)	C(8)–C(9)–C(15)	127.5(2)
C(1)–C(10)–H(10A)	109.5	C(1)–C(10)–H(10B)	109.5
C(1)–C(10)–H(10C)	109.5	C(1)–C(10)–H(10D)	109.5
C(1)–C(10)–H(10E)	109.5	C(1)–C(10)–H(10F)	109.5
H(10A)–C(10)–H(10B)	109.5	H(10A)–C(10)–H(10C)	109.5
H(10A)–C(10)–H(10D)	141.1	H(10A)–C(10)–H(10E)	56.3
H(10A)–C(10)–H(10F)	56.3	H(10B)–C(10)–H(10C)	109.5
H(10B)–C(10)–H(10D)	56.3	H(10B)–C(10)–H(10E)	141.1
H(10B)–C(10)–H(10F)	56.3	H(10C)–C(10)–H(10D)	56.3
H(10C)–C(10)–H(10E)	56.3	H(10C)–C(10)–H(10F)	141.1
H(10D)–C(10)–H(10E)	109.5	H(10D)–C(10)–H(10F)	109.5
H(10E)–C(10)–H(10F)	109.5	C(3)–C(11)–H(11A)	109.5
C(3)–C(11)–H(11B)	109.5	C(3)–C(11)–H(11C)	109.5
H(11A)–C(11)–H(11B)	109.5	H(11A)–C(11)–H(11C)	109.5
H(11B)–C(11)–H(11C)	109.5	C(7)–C(12)–H(12A)	109.5
C(7)–C(12)–H(12B)	109.5	C(7)–C(12)–H(12C)	109.5
H(12A)–C(12)–H(12B)	109.5	H(12A)–C(12)–H(12C)	109.5
H(12B)–C(12)–H(12C)	109.5	C(9)–C(15)–H(15A)	109.5
C(9)–C(15)–H(15B)	109.5	C(9)–C(15)–H(15C)	109.5
H(15A)–C(15)–H(15B)	109.5	H(15A)–C(15)–H(15C)	109.5
H(15B)–C(15)–H(15C)	109.5	C(5)–C(16)–C(17)	120.36(18)
C(5)–C(16)–C(21)	120.34(18)	C(17)–C(16)–C(21)	119.21(19)
C(16)–C(17)–H(17A)	119.5	C(16)–C(17)–C(18)	121.0(2)
H(17A)–C(17)–C(18)	119.5	C(17)–C(18)–H(18A)	120.4
C(17)–C(18)–C(19)	119.1(2)	H(18A)–C(18)–C(19)	120.4
C(18)–C(19)–H(19A)	119.5	C(18)–C(19)–C(20)	120.9(2)
H(19A)–C(19)–C(20)	119.5	C(19)–C(20)–H(20A)	120.2
C(19)–C(20)–C(21)	119.6(2)	H(20A)–C(20)–C(21)	120.2
O–C(21)–C(16)	115.79(18)	O–C(21)–C(20)	124.22(19)
C(16)–C(21)–C(20)	119.98(19)	O–C(22)–H(22A)	109.5
O–C(22)–H(22B)	109.5	O–C(22)–H(22C)	109.5
H(22A)–C(22)–H(22B)	109.5	H(22A)–C(22)–H(22C)	109.5
H(22B)–C(22)–H(22C)	109.5		

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br	0.02442(16)	0.0488(2)	0.03002(18)	–0.01111(13)	0.00406(11)	–0.01541(12)
BrA	0.040(3)	0.031(2)	0.059(5)	0.003(3)	–0.002(3)	0.0003(18)
C(14A)	0.09(3)	0.029(18)	0.06(2)	–0.021(16)	0.03(2)	0.019(18)
C(13A)	0.40(7)	0.016(18)	0.04(2)	0.000(16)	0.10(4)	0.00(3)
C(13)	0.040(3)	0.033(2)	0.028(3)	–0.004(2)	–0.007(2)	–0.0093(19)
C(14)	0.0325(15)	0.0387(16)	0.0276(15)	–0.0084(12)	0.0033(12)	–0.0084(13)
O	0.0401(10)	0.0223(8)	0.0191(8)	–0.0041(6)	–0.0066(7)	–0.0116(7)
N(1)	0.0262(10)	0.0183(9)	0.0190(9)	–0.0015(7)	–0.0035(7)	–0.0105(8)
N(2)	0.0236(10)	0.0135(9)	0.0245(9)	–0.0040(7)	–0.0035(7)	–0.0051(7)
F(1)	0.0413(8)	0.0243(7)	0.0494(9)	–0.0168(6)	0.0033(7)	–0.0179(6)
F(2)	0.0413(9)	0.0309(8)	0.0337(8)	0.0130(6)	–0.0042(6)	–0.0033(7)
B	0.0287(14)	0.0182(12)	0.0261(13)	–0.0019(10)	–0.0037(10)	–0.0091(11)
C(1)	0.0273(12)	0.0280(12)	0.0187(11)	–0.0016(9)	–0.0038(9)	–0.0142(10)
C(2)	0.0198(11)	0.0358(13)	0.0182(11)	–0.0059(9)	0.0006(9)	–0.0131(10)
C(3)	0.0227(11)	0.0252(12)	0.0203(11)	–0.0063(9)	–0.0043(9)	–0.0077(9)
C(4)	0.0233(11)	0.0166(10)	0.0176(10)	–0.0031(8)	–0.0051(8)	–0.0071(9)
C(5)	0.0228(11)	0.0172(10)	0.0161(10)	–0.0042(8)	–0.0058(8)	–0.0066(9)
C(6)	0.0252(11)	0.0141(10)	0.0190(10)	–0.0025(8)	–0.0029(8)	–0.0077(9)
C(7)	0.0234(11)	0.0223(11)	0.0201(10)	–0.0058(8)	–0.0026(8)	–0.0086(9)
C(8)	0.0231(12)	0.0252(12)	0.0235(11)	–0.0070(9)	–0.0019(9)	–0.0076(9)
C(9)	0.0269(12)	0.0187(11)	0.0275(12)	–0.0066(9)	–0.0069(9)	–0.0024(9)
C(10)	0.0374(14)	0.0339(14)	0.0345(13)	0.0034(11)	–0.0010(11)	–0.0207(12)
C(11)	0.0248(12)	0.0246(12)	0.0311(12)	–0.0064(10)	–0.0024(10)	–0.0035(10)
C(12)	0.0272(13)	0.0264(12)	0.0305(12)	–0.0029(10)	0.0011(10)	–0.0133(10)
C(15)	0.0345(14)	0.0208(12)	0.0476(15)	–0.0064(11)	–0.0035(12)	–0.0010(11)
C(16)	0.0182(11)	0.0161(10)	0.0219(10)	–0.0035(8)	–0.0016(8)	–0.0050(8)
C(17)	0.0311(13)	0.0209(11)	0.0224(11)	–0.0049(9)	–0.0040(9)	–0.0063(10)
C(18)	0.0349(14)	0.0232(12)	0.0241(12)	0.0037(9)	–0.0041(10)	–0.0050(10)
C(19)	0.0319(13)	0.0159(11)	0.0353(13)	0.0008(9)	–0.0005(10)	–0.0074(10)
C(20)	0.0282(12)	0.0180(11)	0.0307(12)	–0.0083(9)	–0.0003(9)	–0.0079(9)
C(21)	0.0195(11)	0.0190(11)	0.0236(11)	–0.0048(8)	–0.0010(8)	–0.0054(9)
C(22)	0.0612(19)	0.0382(15)	0.0269(13)	–0.0127(11)	–0.0089(12)	–0.0179(13)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh12.

	x	y	z	U
H(14A)	1.2725	0.1616	0.0500	0.106
H(14B)	1.0839	0.2702	0.0539	0.106
H(14C)	1.1210	0.1566	–0.0195	0.106
H(13A)	1.1651	–0.0103	0.1382	0.213
H(13B)	1.1270	0.1038	0.2115	0.213
H(13A)	–0.1349	0.2177	0.3730	0.041
H(13B)	–0.1549	0.3721	0.3318	0.041
H(14A)	–0.0176	0.2307	0.5387	0.050
H(14B)	–0.2121	0.3299	0.5225	0.050
H(14C)	–0.0550	0.3875	0.4979	0.050
H(10A)	0.7601	0.4284	0.1377	0.051
H(10B)	0.7494	0.3960	0.0203	0.051
H(10C)	0.9325	0.3517	0.0766	0.051
H(10D)	0.8679	0.3557	0.0187	0.051
H(10E)	0.8786	0.3880	0.1361	0.051
H(10F)	0.6955	0.4324	0.0798	0.051
H(11A)	1.0535	–0.1578	0.2025	0.042
H(11B)	0.8866	–0.1790	0.1622	0.042
H(11C)	0.9046	–0.1763	0.2868	0.042
H(12A)	0.0550	0.0121	0.3919	0.041
H(12B)	0.2302	–0.0405	0.4580	0.041
H(12C)	0.2314	–0.0730	0.3392	0.041
H(15A)	0.1804	0.5280	0.2906	0.054
H(15B)	–0.0096	0.5176	0.2975	0.054
H(15C)	0.0930	0.5188	0.1848	0.054
H(17A)	0.5989	–0.1063	0.4663	0.030
H(18A)	0.6201	–0.3300	0.5254	0.035
H(19A)	0.5846	–0.4565	0.4035	0.034
H(20A)	0.5460	–0.3662	0.2213	0.030
H(22A)	0.5038	–0.1416	–0.0193	0.060
H(22B)	0.4200	–0.2292	0.0696	0.060
H(22C)	0.6251	–0.2743	0.0524	0.060

Table 6. Torsion angles [°] for mjh12.

C(1)–N(1)–B–N(2)	177.92(18)	C(1)–N(1)–B–F(1)	−63.1(3)
C(1)–N(1)–B–F(2)	57.7(3)	C(4)–N(1)–B–N(2)	−4.9(3)
C(4)–N(1)–B–F(1)	114.1(2)	C(4)–N(1)–B–F(2)	−125.2(2)
C(6)–N(2)–B–N(1)	3.8(3)	C(6)–N(2)–B–F(1)	−115.5(2)
C(6)–N(2)–B–F(2)	124.1(2)	C(9)–N(2)–B–N(1)	−177.80(18)
C(9)–N(2)–B–F(1)	62.8(3)	C(9)–N(2)–B–F(2)	−57.5(3)
B–N(1)–C(1)–C(2)	177.36(19)	B–N(1)–C(1)–C(10)	−3.0(3)
C(4)–N(1)–C(1)–C(2)	−0.2(2)	C(4)–N(1)–C(1)–C(10)	179.4(2)
N(1)–C(1)–C(2)–Br	−179.80(15)	N(1)–C(1)–C(2)–C(13A)	−152.0(17)
N(1)–C(1)–C(2)–C(3)	0.0(2)	C(10)–C(1)–C(2)–Br	0.6(3)
C(10)–C(1)–C(2)–C(13A)	28.5(17)	C(10)–C(1)–C(2)–C(3)	−179.6(2)
C(14A)–C(13A)–C(2)–Br	54(3)	C(14A)–C(13A)–C(2)–C(1)	−53(3)
C(14A)–C(13A)–C(2)–C(3)	158.9(19)	Br–C(2)–C(3)–C(4)	179.99(15)
Br–C(2)–C(3)–C(11)	−1.2(3)	C(13A)–C(2)–C(3)–C(4)	151(2)
C(13A)–C(2)–C(3)–C(11)	−30(2)	C(1)–C(2)–C(3)–C(4)	0.2(2)
C(1)–C(2)–C(3)–C(11)	179.0(2)	B–N(1)–C(4)–C(3)	−177.27(18)
B–N(1)–C(4)–C(5)	3.8(3)	C(1)–N(1)–C(4)–C(3)	0.3(2)
C(1)–N(1)–C(4)–C(5)	−178.57(18)	C(2)–C(3)–C(4)–N(1)	−0.3(2)
C(2)–C(3)–C(4)–C(5)	178.4(2)	C(11)–C(3)–C(4)–N(1)	−179.0(2)
C(11)–C(3)–C(4)–C(5)	−0.3(4)	N(1)–C(4)–C(5)–C(6)	−0.9(3)
N(1)–C(4)–C(5)–C(16)	178.56(17)	C(3)–C(4)–C(5)–C(6)	−179.5(2)
C(3)–C(4)–C(5)–C(16)	−0.1(3)	C(4)–C(5)–C(6)–N(2)	−0.1(3)
C(4)–C(5)–C(6)–C(7)	179.0(2)	C(16)–C(5)–C(6)–N(2)	−179.57(17)
C(16)–C(5)–C(6)–C(7)	−0.5(3)	B–N(2)–C(6)–C(5)	−1.7(3)
B–N(2)–C(6)–C(7)	179.00(18)	C(9)–N(2)–C(6)–C(5)	179.66(18)
C(9)–N(2)–C(6)–C(7)	0.4(2)	N(2)–C(6)–C(7)–C(8)	−0.4(2)
N(2)–C(6)–C(7)–C(12)	178.7(2)	C(5)–C(6)–C(7)–C(8)	−179.6(2)
C(5)–C(6)–C(7)–C(12)	−0.4(4)	C(6)–C(7)–C(8)–BrA	−169.2(3)
C(6)–C(7)–C(8)–C(13)	−178.9(4)	C(6)–C(7)–C(8)–C(9)	0.3(2)
C(12)–C(7)–C(8)–BrA	11.6(4)	C(12)–C(7)–C(8)–C(13)	1.9(5)
C(12)–C(7)–C(8)–C(9)	−178.9(2)	C(14)–C(13)–C(8)–BrA	41(2)
C(14)–C(13)–C(8)–C(7)	89.8(5)	C(14)–C(13)–C(8)–C(9)	−89.2(5)
B–N(2)–C(9)–C(8)	−178.81(19)	B–N(2)–C(9)–C(15)	1.0(3)
C(6)–N(2)–C(9)–C(8)	−0.2(2)	C(6)–N(2)–C(9)–C(15)	179.6(2)
BrA–C(8)–C(9)–N(2)	168.1(4)	BrA–C(8)–C(9)–C(15)	−11.8(5)
C(13)–C(8)–C(9)–N(2)	179.2(3)	C(13)–C(8)–C(9)–C(15)	−0.7(5)
C(7)–C(8)–C(9)–N(2)	0.0(2)	C(7)–C(8)–C(9)–C(15)	−179.9(2)
C(4)–C(5)–C(16)–C(17)	102.7(2)	C(4)–C(5)–C(16)–C(21)	−80.6(3)
C(6)–C(5)–C(16)–C(17)	−77.8(3)	C(6)–C(5)–C(16)–C(21)	98.9(2)
C(5)–C(16)–C(17)–C(18)	174.9(2)	C(21)–C(16)–C(17)–C(18)	−1.8(3)
C(16)–C(17)–C(18)–C(19)	−0.8(4)	C(17)–C(18)–C(19)–C(20)	2.3(4)
C(18)–C(19)–C(20)–C(21)	−1.0(4)	C(22)–O–C(21)–C(16)	179.5(2)
C(22)–O–C(21)–C(20)	−0.4(3)	C(19)–C(20)–C(21)–O	178.3(2)
C(19)–C(20)–C(21)–C(16)	−1.7(3)	C(5)–C(16)–C(21)–O	6.4(3)
C(5)–C(16)–C(21)–C(20)	−173.7(2)	C(17)–C(16)–C(21)–O	−176.87(19)
C(17)–C(16)–C(21)–C(20)	3.1(3)		

Compound **6.25**

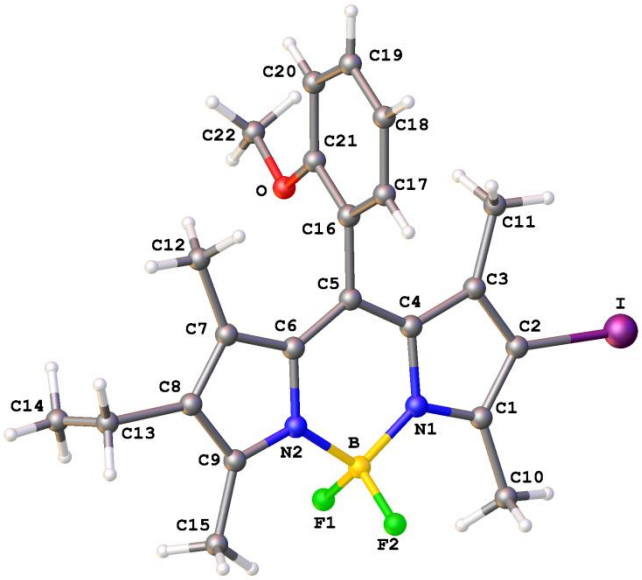


Table 1. Crystal data and structure refinement for mjh120044.

Identification code	mjh12	
Chemical formula (moiety)	$C_{22}H_{24}BF_2IN_2O$	
Chemical formula (total)	$C_{22}H_{24}BF_2IN_2O$	
Formula weight	508.14	
Temperature	150(2) K	
Radiation, wavelength	CuKα, 1.54178 Å	
Crystal system, space group	orthorhombic, $Pna2_1$	
Unit cell parameters	a = 13.6162(4) Å	α = 90°
	b = 19.6671(4) Å	β = 90°
	c = 8.1347(2) Å	γ = 90°
Cell volume	2178.40(9) $Å^3$	
Z	4	
Calculated density	1.549 g/cm^3	
Absorption coefficient μ	11.822 mm^{-1}	
F(000)	1016	
Crystal colour and size	red, 0.40 × 0.03 × 0.03 mm^3	
Reflections for cell refinement	6313 (θ range 2.2 to 66.5°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	4.0 to 66.6°	
Index ranges	h −16 to 15, k −23 to 22, l −9 to 8	
Completeness to θ = 66.6°	99.8 %	
Reflections collected	12925	
Independent reflections	3012 (R_{int} = 0.0378)	
Reflections with $F^2>2\sigma$	2906	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.0880 and 0.7181	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0945, 5.1874	
Data / restraints / parameters	3012 / 1 / 269	
Final R indices [$F^2>2\sigma$]	R1 = 0.0547, wR2 = 0.1465	
R indices (all data)	R1 = 0.0561, wR2 = 0.1483	
Goodness-of-fit on F^2	1.059	
Absolute structure parameter	0.043(12)	
Extinction coefficient	0.00120(16)	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.88 and −1.37 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh12. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
I	0.92974(4)	0.00405(2)	0.00513(18)	0.0516(2)
O	0.7794(4)	0.2592(2)	0.4459(8)	0.0466(14)
N(1)	0.7848(4)	0.0333(3)	0.4589(7)	0.0295(13)
N(2)	0.7195(4)	0.0678(3)	0.7319(8)	0.0336(13)
F(1)	0.6192(4)	0.0081(3)	0.5350(8)	0.0624(18)
F(2)	0.7429(5)	–0.0502(2)	0.6596(7)	0.0611(15)
B	0.7159(7)	0.0118(4)	0.5948(13)	0.038(2)
C(1)	0.8050(6)	–0.0022(3)	0.3219(12)	0.0370(19)
C(2)	0.8701(5)	0.0354(4)	0.2267(9)	0.0370(16)
C(3)	0.8927(5)	0.0965(3)	0.3061(9)	0.0306(14)
C(4)	0.8386(4)	0.0945(3)	0.4543(8)	0.0262(14)
C(5)	0.8340(4)	0.1396(3)	0.5872(8)	0.0245(13)
C(6)	0.7761(5)	0.1266(3)	0.7262(9)	0.0278(13)
C(7)	0.7582(5)	0.1640(4)	0.8735(10)	0.0326(15)
C(8)	0.6937(5)	0.1272(3)	0.9669(9)	0.0351(16)
C(9)	0.6700(5)	0.0676(3)	0.8755(10)	0.0356(16)
C(10)	0.7627(8)	–0.0717(5)	0.2923(14)	0.063(3)
C(11)	0.9618(6)	0.1495(4)	0.2472(11)	0.0435(18)
C(12)	0.8011(6)	0.2314(4)	0.9209(9)	0.0389(17)
C(13)	0.6400(7)	0.1486(4)	1.1425(11)	0.042(2)
C(14)	0.5704(17)	0.1756(8)	1.128(2)	0.145(10)
C(15)	0.6001(10)	0.0134(5)	0.9263(17)	0.074(4)
C(16)	0.8990(5)	0.2011(3)	0.5897(9)	0.0335(15)
C(17)	0.9919(5)	0.1962(4)	0.6633(11)	0.0439(19)
C(18)	1.0533(7)	0.2529(6)	0.6644(13)	0.063(3)
C(19)	1.0234(7)	0.3113(5)	0.5947(13)	0.063(3)
C(20)	0.9316(7)	0.3186(4)	0.5209(13)	0.055(2)
C(21)	0.8687(5)	0.2611(3)	0.5170(11)	0.0406(17)
C(22)	0.7471(8)	0.3184(4)	0.3552(13)	0.062(3)

Table 3. Bond lengths [Å] and angles [°] for mjh12.

I–C(2)	2.070(7)	O–C(21)	1.347(10)
O–C(22)	1.447(10)	N(1)–B	1.510(11)
N(1)–C(1)	1.343(10)	N(1)–C(4)	1.411(7)
N(2)–B	1.569(11)	N(2)–C(6)	1.390(8)
N(2)–C(9)	1.349(10)	F(1)–B	1.405(11)
F(2)–B	1.378(10)	C(1)–C(2)	1.390(12)
C(1)–C(10)	1.504(10)	C(2)–C(3)	1.399(10)
C(3)–C(4)	1.414(10)	C(3)–C(11)	1.484(10)
C(4)–C(5)	1.399(9)	C(5)–C(6)	1.402(9)
C(5)–C(16)	1.498(9)	C(6)–C(7)	1.427(10)
C(7)–C(8)	1.368(10)	C(7)–C(12)	1.500(10)
C(8)–C(9)	1.424(10)	C(8)–C(13)	1.660(12)
C(9)–C(15)	1.488(11)	C(10)–H(10A)	0.980
C(10)–H(10B)	0.980	C(10)–H(10C)	0.980
C(11)–H(11A)	0.980	C(11)–H(11B)	0.980
C(11)–H(11C)	0.980	C(12)–H(12A)	0.980
C(12)–H(12B)	0.980	C(12)–H(12C)	0.980
C(13)–H(13A)	0.990	C(13)–H(13B)	0.990
C(13)–C(14)	1.09(2)	C(14)–H(14A)	0.980
C(14)–H(14B)	0.980	C(14)–H(14C)	0.980
C(15)–H(15A)	0.980	C(15)–H(15B)	0.980
C(15)–H(15C)	0.980	C(16)–C(17)	1.403(10)
C(16)–C(21)	1.383(10)	C(17)–H(17A)	0.950
C(17)–C(18)	1.394(12)	C(18)–H(18A)	0.950
C(18)–C(19)	1.344(16)	C(19)–H(19A)	0.950
C(19)–C(20)	1.394(14)	C(20)–H(20A)	0.950
C(20)–C(21)	1.420(10)	C(22)–H(22A)	0.980
C(22)–H(22B)	0.980	C(22)–H(22C)	0.980

C(21)–O–C(22)	118.1(7)	B–N(1)–C(1)	126.1(6)
B–N(1)–C(4)	125.5(6)	C(1)–N(1)–C(4)	108.3(6)
B–N(2)–C(6)	125.3(6)	B–N(2)–C(9)	126.7(6)
C(6)–N(2)–C(9)	108.0(6)	N(1)–B–N(2)	107.7(6)
N(1)–B–F(1)	110.0(7)	N(1)–B–F(2)	111.2(7)
N(2)–B–F(1)	108.2(7)	N(2)–B–F(2)	109.9(7)
F(1)–B–F(2)	109.7(7)	N(1)–C(1)–C(2)	108.5(6)
N(1)–C(1)–C(10)	121.8(8)	C(2)–C(1)–C(10)	129.7(8)
I–C(2)–C(1)	125.3(6)	I–C(2)–C(3)	124.9(6)
C(1)–C(2)–C(3)	109.8(7)	C(2)–C(3)–C(4)	104.8(6)
C(2)–C(3)–C(11)	126.4(7)	C(4)–C(3)–C(11)	128.7(6)
N(1)–C(4)–C(3)	108.5(5)	N(1)–C(4)–C(5)	119.8(6)
C(3)–C(4)–C(5)	131.7(5)	C(4)–C(5)–C(6)	122.1(5)
C(4)–C(5)–C(16)	119.7(6)	C(6)–C(5)–C(16)	118.0(6)
N(2)–C(6)–C(5)	119.4(6)	N(2)–C(6)–C(7)	107.8(6)
C(5)–C(6)–C(7)	132.7(6)	C(6)–C(7)–C(8)	107.6(6)
C(6)–C(7)–C(12)	127.3(7)	C(8)–C(7)–C(12)	125.1(7)
C(7)–C(8)–C(9)	106.9(6)	C(7)–C(8)–C(13)	128.8(6)
C(9)–C(8)–C(13)	123.9(6)	N(2)–C(9)–C(8)	109.7(6)
N(2)–C(9)–C(15)	124.2(8)	C(8)–C(9)–C(15)	126.1(8)
C(1)–C(10)–H(10A)	109.5	C(1)–C(10)–H(10B)	109.5
C(1)–C(10)–H(10C)	109.5	H(10A)–C(10)–H(10B)	109.5
H(10A)–C(10)–H(10C)	109.5	H(10B)–C(10)–H(10C)	109.5
C(3)–C(11)–H(11A)	109.5	C(3)–C(11)–H(11B)	109.5

C(3)–C(11)–H(11C)	109.5	H(11A)–C(11)–H(11B)	109.5
H(11A)–C(11)–H(11C)	109.5	H(11B)–C(11)–H(11C)	109.5
C(7)–C(12)–H(12A)	109.5	C(7)–C(12)–H(12B)	109.5
C(7)–C(12)–H(12C)	109.5	H(12A)–C(12)–H(12B)	109.5
H(12A)–C(12)–H(12C)	109.5	H(12B)–C(12)–H(12C)	109.5
C(8)–C(13)–H(13A)	108.7	C(8)–C(13)–H(13B)	108.7
C(8)–C(13)–C(14)	114.3(11)	H(13A)–C(13)–H(13B)	107.6
H(13A)–C(13)–C(14)	108.7	H(13B)–C(13)–C(14)	108.7
C(13)–C(14)–H(14A)	109.5	C(13)–C(14)–H(14B)	109.5
C(13)–C(14)–H(14C)	109.5	H(14A)–C(14)–H(14B)	109.5
H(14A)–C(14)–H(14C)	109.5	H(14B)–C(14)–H(14C)	109.5
C(9)–C(15)–H(15A)	109.5	C(9)–C(15)–H(15B)	109.5
C(9)–C(15)–H(15C)	109.5	H(15A)–C(15)–H(15B)	109.5
H(15A)–C(15)–H(15C)	109.5	H(15B)–C(15)–H(15C)	109.5
C(5)–C(16)–C(17)	119.0(6)	C(5)–C(16)–C(21)	120.4(6)
C(17)–C(16)–C(21)	120.6(6)	C(16)–C(17)–H(17A)	120.3
C(16)–C(17)–C(18)	119.3(9)	H(17A)–C(17)–C(18)	120.3
C(17)–C(18)–H(18A)	120.0	C(17)–C(18)–C(19)	119.9(9)
H(18A)–C(18)–C(19)	120.0	C(18)–C(19)–H(19A)	118.6
C(18)–C(19)–C(20)	122.8(8)	H(19A)–C(19)–C(20)	118.6
C(19)–C(20)–H(20A)	121.0	C(19)–C(20)–C(21)	118.0(8)
H(20A)–C(20)–C(21)	121.0	O–C(21)–C(16)	115.4(6)
O–C(21)–C(20)	125.2(7)	C(16)–C(21)–C(20)	119.4(7)
O–C(22)–H(22A)	109.5	O–C(22)–H(22B)	109.5
O–C(22)–H(22C)	109.5	H(22A)–C(22)–H(22B)	109.5
H(22A)–C(22)–H(22C)	109.5	H(22B)–C(22)–H(22C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I	0.0606(4)	0.0538(3)	0.0405(4)	–0.0102(3)	0.0046(4)	0.0171(2)
O	0.048(3)	0.029(2)	0.063(4)	0.013(2)	0.001(3)	0.006(2)
N(1)	0.032(3)	0.023(2)	0.034(4)	0.002(2)	–0.002(2)	–0.004(2)
N(2)	0.035(3)	0.024(3)	0.043(4)	0.002(2)	0.001(3)	0.001(2)
F(1)	0.037(2)	0.086(3)	0.064(5)	–0.019(3)	–0.002(3)	–0.025(2)
F(2)	0.097(4)	0.023(2)	0.063(3)	0.004(2)	0.025(3)	–0.005(2)
B	0.040(4)	0.033(4)	0.041(6)	0.000(4)	–0.005(4)	–0.011(4)
C(1)	0.037(4)	0.023(3)	0.051(6)	–0.008(3)	–0.005(4)	0.001(2)
C(2)	0.036(3)	0.048(4)	0.026(4)	–0.006(3)	–0.001(3)	0.016(3)
C(3)	0.031(3)	0.030(3)	0.031(4)	–0.002(3)	0.000(3)	0.001(3)
C(4)	0.027(3)	0.019(3)	0.033(4)	0.004(2)	–0.006(3)	0.000(2)
C(5)	0.018(3)	0.023(3)	0.033(4)	0.003(2)	–0.006(3)	0.002(2)
C(6)	0.026(3)	0.025(3)	0.032(4)	0.004(3)	–0.001(3)	0.002(2)
C(7)	0.030(3)	0.034(3)	0.034(4)	0.000(3)	–0.006(3)	0.007(3)
C(8)	0.035(3)	0.038(3)	0.032(4)	0.004(3)	0.007(3)	0.008(3)
C(9)	0.029(3)	0.033(3)	0.044(4)	0.008(3)	0.012(3)	0.005(3)
C(10)	0.081(7)	0.047(5)	0.061(6)	–0.023(4)	0.012(5)	–0.024(5)
C(11)	0.041(4)	0.043(4)	0.047(5)	0.006(4)	0.013(4)	–0.006(3)
C(12)	0.040(4)	0.042(4)	0.035(4)	–0.013(3)	–0.002(3)	0.001(3)
C(13)	0.064(5)	0.039(4)	0.023(4)	0.022(3)	–0.018(4)	–0.010(4)
C(14)	0.26(3)	0.105(12)	0.065(10)	–0.043(9)	0.118(14)	–0.086(14)
C(15)	0.087(8)	0.050(5)	0.084(9)	–0.002(5)	0.055(7)	–0.025(5)
C(16)	0.042(4)	0.031(3)	0.027(4)	–0.010(3)	0.005(3)	–0.010(3)
C(17)	0.027(3)	0.060(5)	0.045(5)	–0.013(4)	–0.007(3)	–0.013(3)
C(18)	0.058(5)	0.077(7)	0.056(6)	–0.007(5)	–0.002(5)	–0.029(5)
C(19)	0.059(5)	0.060(6)	0.069(7)	–0.027(5)	0.014(5)	–0.032(5)
C(20)	0.087(6)	0.035(4)	0.042(6)	–0.005(4)	0.022(5)	–0.016(4)
C(21)	0.046(4)	0.028(3)	0.048(5)	–0.009(4)	0.010(4)	–0.004(3)
C(22)	0.093(7)	0.039(4)	0.052(6)	0.007(4)	0.007(5)	0.027(5)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh12.

	x	y	z	U
H(10A)	0.6920	–0.0710	0.3147	0.094
H(10B)	0.7946	–0.1046	0.3653	0.094
H(10C)	0.7738	–0.0849	0.1777	0.094
H(11A)	1.0076	0.1614	0.3357	0.065
H(11B)	0.9248	0.1900	0.2143	0.065
H(11C)	0.9988	0.1321	0.1528	0.065
H(12A)	0.7758	0.2449	1.0288	0.058
H(12B)	0.7827	0.2657	0.8390	0.058
H(12C)	0.8728	0.2278	0.9258	0.058
H(13A)	0.6282	0.1069	1.2075	0.050
H(13B)	0.6855	0.1778	1.2060	0.050
H(14A)	0.5415	0.1841	1.2362	0.218
H(14B)	0.5253	0.1478	1.0622	0.218
H(14C)	0.5820	0.2190	1.0719	0.218
H(15A)	0.5904	–0.0184	0.8349	0.111
H(15B)	0.5370	0.0339	0.9561	0.111
H(15C)	0.6268	–0.0111	1.0212	0.111
H(17A)	1.0127	0.1548	0.7119	0.053
H(18A)	1.1163	0.2503	0.7143	0.076
H(19A)	1.0666	0.3493	0.5959	0.075
H(20A)	0.9118	0.3608	0.4747	0.066
H(22A)	0.6808	0.3104	0.3122	0.092
H(22B)	0.7922	0.3269	0.2637	0.092
H(22C)	0.7462	0.3580	0.4284	0.092

Table 6. Torsion angles [°] for mjh12.

C(1)–N(1)–B–N(2)	177.6(7)	C(1)–N(1)–B–F(1)	–64.7(9)
C(1)–N(1)–B–F(2)	57.1(10)	C(4)–N(1)–B–N(2)	–2.8(10)
C(4)–N(1)–B–F(1)	114.9(7)	C(4)–N(1)–B–F(2)	–123.3(7)
C(6)–N(2)–B–N(1)	0.3(10)	C(6)–N(2)–B–F(1)	–118.6(7)
C(6)–N(2)–B–F(2)	121.7(7)	C(9)–N(2)–B–N(1)	–178.8(6)
C(9)–N(2)–B–F(1)	62.2(10)	C(9)–N(2)–B–F(2)	–57.5(10)
B–N(1)–C(1)–C(2)	178.9(7)	B–N(1)–C(1)–C(10)	–3.1(12)
C(4)–N(1)–C(1)–C(2)	–0.8(8)	C(4)–N(1)–C(1)–C(10)	177.2(8)
N(1)–C(1)–C(2)–I	178.0(5)	N(1)–C(1)–C(2)–C(3)	0.4(9)
C(10)–C(1)–C(2)–I	0.2(13)	C(10)–C(1)–C(2)–C(3)	–177.4(9)
I–C(2)–C(3)–C(4)	–177.5(5)	I–C(2)–C(3)–C(11)	0.4(11)
C(1)–C(2)–C(3)–C(4)	0.1(8)	C(1)–C(2)–C(3)–C(11)	178.0(7)
B–N(1)–C(4)–C(3)	–178.8(7)	B–N(1)–C(4)–C(5)	3.2(9)
C(1)–N(1)–C(4)–C(3)	0.9(7)	C(1)–N(1)–C(4)–C(5)	–177.1(6)
C(2)–C(3)–C(4)–N(1)	–0.6(7)	C(2)–C(3)–C(4)–C(5)	177.1(6)
C(11)–C(3)–C(4)–N(1)	–178.4(7)	C(11)–C(3)–C(4)–C(5)	–0.7(12)
N(1)–C(4)–C(5)–C(6)	–0.8(9)	N(1)–C(4)–C(5)–C(16)	173.7(6)
C(3)–C(4)–C(5)–C(6)	–178.3(6)	C(3)–C(4)–C(5)–C(16)	–3.7(10)
B–N(2)–C(6)–C(5)	1.6(10)	B–N(2)–C(6)–C(7)	179.7(7)
C(9)–N(2)–C(6)–C(5)	–179.0(6)	C(9)–N(2)–C(6)–C(7)	–0.9(7)
C(4)–C(5)–C(6)–N(2)	–1.5(9)	C(4)–C(5)–C(6)–C(7)	–179.0(6)
C(16)–C(5)–C(6)–N(2)	–176.1(6)	C(16)–C(5)–C(6)–C(7)	6.3(10)
N(2)–C(6)–C(7)–C(8)	1.4(7)	N(2)–C(6)–C(7)–C(12)	–178.6(6)
C(5)–C(6)–C(7)–C(8)	179.1(7)	C(5)–C(6)–C(7)–C(12)	–0.8(12)
C(6)–C(7)–C(8)–C(9)	–1.2(8)	C(6)–C(7)–C(8)–C(13)	–174.4(6)
C(12)–C(7)–C(8)–C(9)	178.7(6)	C(12)–C(7)–C(8)–C(13)	5.6(11)
B–N(2)–C(9)–C(8)	179.5(7)	B–N(2)–C(9)–C(15)	–1.7(13)
C(6)–N(2)–C(9)–C(8)	0.2(7)	C(6)–N(2)–C(9)–C(15)	179.0(9)
C(7)–C(8)–C(9)–N(2)	0.7(8)	C(7)–C(8)–C(9)–C(15)	–178.1(10)
C(13)–C(8)–C(9)–N(2)	174.3(6)	C(13)–C(8)–C(9)–C(15)	–4.5(13)
C(7)–C(8)–C(13)–C(14)	88.5(14)	C(9)–C(8)–C(13)–C(14)	–83.6(13)
C(4)–C(5)–C(16)–C(17)	–90.5(8)	C(4)–C(5)–C(16)–C(21)	87.9(8)
C(6)–C(5)–C(16)–C(17)	84.3(8)	C(6)–C(5)–C(16)–C(21)	–97.3(8)
C(5)–C(16)–C(17)–C(18)	179.2(8)	C(21)–C(16)–C(17)–C(18)	0.8(12)
C(16)–C(17)–C(18)–C(19)	–0.2(14)	C(17)–C(18)–C(19)–C(20)	0.6(16)
C(18)–C(19)–C(20)–C(21)	–1.4(14)	C(22)–O–C(21)–C(16)	–174.7(7)
C(22)–O–C(21)–C(20)	5.0(12)	C(5)–C(16)–C(21)–O	–0.3(11)
C(5)–C(16)–C(21)–C(20)	180.0(7)	C(17)–C(16)–C(21)–O	178.1(7)
C(17)–C(16)–C(21)–C(20)	–1.6(12)	C(19)–C(20)–C(21)–O	–177.8(8)
C(19)–C(20)–C(21)–C(16)	1.9(12)		

Compound **7.4**

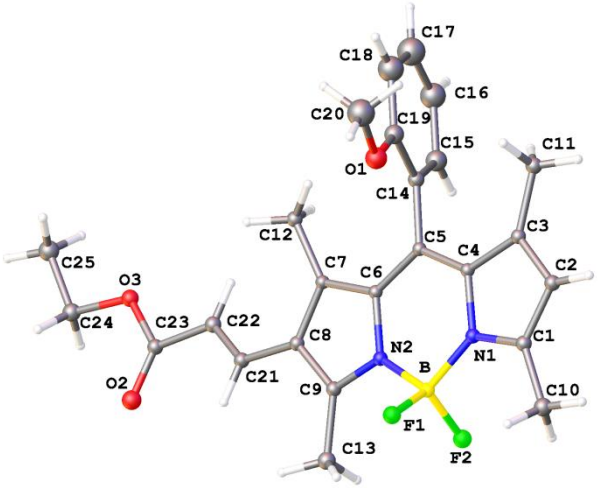

C17
C18
C16
C20
C19
C15
C11
O1
C14
C3
C12
C5
C4
C25
C7
C6
C2
O3
C24
C23
C22
C8
N2
N1
C1
O2
C21
B
C9
C10
F1
C13
F2

Table 1. Crystal data and structure refinement for mjh12.

Identification code	mjh12	
Chemical formula (moiety)	$C_{25}H_{27}BF_2N_2O_3$	
Chemical formula (total)	$C_{25}H_{27}BF_2N_2O_3$	
Formula weight	452.30	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 6.7704(5) Å	α = 91.415(5)°
	b = 10.8089(7) Å	β = 100.450(6)°
	c = 15.8433(11) Å	γ = 100.387(6)°
Cell volume	1119.53(13) $Å^3$	
Z	2	
Calculated density	1.342 g/cm^3	
Absorption coefficient μ	0.098 mm^{-1}	
F(000)	476	
Crystal colour and size	red, 0.20 × 0.20 × 0.15 mm^3	
Reflections for cell refinement	2597 (θ range 3.1 to 28.7°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	3.1 to 25.0°	
Index ranges	h −6 to 8, k −12 to 12, l −18 to 18	
Completeness to θ = 25.0°	99.8 %	
Reflections collected	8072	
Independent reflections	3926 (R_{int} = 0.0276)	
Reflections with $F^2>2\sigma$	3054	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.9806 and 0.9854	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0652, 0.9123	
Data / restraints / parameters	3926 / 0 / 305	
Final R indices [$F^2>2\sigma$]	R1 = 0.0555, wR2 = 0.1375	
R indices (all data)	R1 = 0.0739, wR2 = 0.1518	
Goodness-of-fit on F^2	1.052	
Extinction coefficient	0.007(3)	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.57 and −0.34 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh12. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
B	0.4546(4)	0.1175(3)	0.34864(18)	0.0254(6)
F(1)	0.3911(2)	0.08910(14)	0.42565(9)	0.0355(4)
F(2)	0.5095(2)	0.01306(13)	0.31442(10)	0.0373(4)
N(1)	0.6379(3)	0.22946(18)	0.36421(12)	0.0240(5)
N(2)	0.2798(3)	0.16036(18)	0.28562(12)	0.0233(5)
O(1)	0.4546(3)	0.5808(2)	0.38392(15)	0.0517(6)
O(2)	–0.6625(3)	0.01528(18)	0.08780(12)	0.0414(5)
O(3)	–0.6614(3)	0.19630(16)	0.02113(11)	0.0322(5)
C(1)	0.8263(4)	0.2294(2)	0.41079(15)	0.0277(6)
C(2)	0.9479(4)	0.3487(2)	0.41029(15)	0.0275(6)
C(3)	0.8333(4)	0.4258(2)	0.36319(15)	0.0246(5)
C(4)	0.6349(4)	0.3496(2)	0.33347(14)	0.0219(5)
C(5)	0.4591(3)	0.3754(2)	0.28239(14)	0.0215(5)
C(6)	0.2813(4)	0.2828(2)	0.25864(14)	0.0215(5)
C(7)	0.0857(3)	0.2869(2)	0.20955(14)	0.0216(5)
C(8)	–0.0301(4)	0.1649(2)	0.20624(15)	0.0245(5)
C(9)	0.0948(4)	0.0900(2)	0.25454(15)	0.0260(6)
C(10)	0.8836(4)	0.1174(3)	0.45478(18)	0.0371(7)
C(11)	0.9101(4)	0.5610(2)	0.34928(17)	0.0303(6)
C(12)	0.0074(4)	0.3995(2)	0.17321(16)	0.0277(6)
C(13)	0.0441(4)	–0.0467(2)	0.26902(18)	0.0356(7)
C(14)	0.4618(4)	0.5019(2)	0.24812(17)	0.0295(6)
C(15)	0.4669(4)	0.5146(3)	0.1598(2)	0.0498(9)
C(16)	0.4684(5)	0.6331(4)	0.1280(3)	0.0716(13)
C(17)	0.4668(5)	0.7338(4)	0.1807(4)	0.0861(18)
C(18)	0.4615(5)	0.7239(3)	0.2686(4)	0.0731(14)
C(19)	0.4603(4)	0.6049(3)	0.3016(2)	0.0418(8)
C(20)	0.4796(6)	0.6858(4)	0.4445(3)	0.0833(15)
C(21)	–0.2416(4)	0.1184(2)	0.16502(15)	0.0264(6)
C(22)	–0.3565(4)	0.1707(2)	0.10414(16)	0.0293(6)
C(23)	–0.5723(4)	0.1157(2)	0.07148(15)	0.0273(6)
C(24)	–0.8769(4)	0.1568(3)	–0.01434(17)	0.0362(7)
C(25)	–0.9486(4)	0.2637(3)	–0.0618(2)	0.0464(8)

Table 3. Bond lengths [Å] and angles [°] for mjh12.

B–F(1)	1.389(3)	B–F(2)	1.378(3)
B–N(1)	1.549(3)	B–N(2)	1.551(3)
N(1)–C(1)	1.353(3)	N(1)–C(4)	1.400(3)
N(2)–C(6)	1.400(3)	N(2)–C(9)	1.344(3)
O(1)–C(19)	1.341(4)	O(1)–C(20)	1.434(4)
O(2)–C(23)	1.204(3)	O(3)–C(23)	1.345(3)
O(3)–C(24)	1.446(3)	C(1)–C(2)	1.401(4)
C(1)–C(10)	1.487(3)	C(2)–H(2A)	0.950
C(2)–C(3)	1.380(3)	C(3)–C(4)	1.434(3)
C(3)–C(11)	1.496(3)	C(4)–C(5)	1.389(3)
C(5)–C(6)	1.405(3)	C(5)–C(14)	1.483(3)
C(6)–C(7)	1.417(3)	C(7)–C(8)	1.402(3)
C(7)–C(12)	1.500(3)	C(8)–C(9)	1.414(3)
C(8)–C(21)	1.454(3)	C(9)–C(13)	1.489(3)
C(10)–H(10A)	0.980	C(10)–H(10B)	0.980
C(10)–H(10C)	0.980	C(11)–H(11A)	0.980
C(11)–H(11B)	0.980	C(11)–H(11C)	0.980
C(12)–H(12A)	0.980	C(12)–H(12B)	0.980
C(12)–H(12C)	0.980	C(13)–H(13A)	0.980
C(13)–H(13B)	0.980	C(13)–H(13C)	0.980
C(14)–C(15)	1.415(4)	C(14)–C(19)	1.385(4)
C(15)–H(15A)	0.950	C(15)–C(16)	1.387(5)
C(16)–H(16A)	0.950	C(16)–C(17)	1.359(7)
C(17)–H(17A)	0.950	C(17)–C(18)	1.406(7)
C(18)–H(18A)	0.950	C(18)–C(19)	1.400(5)
C(20)–H(20A)	0.980	C(20)–H(20B)	0.980
C(20)–H(20C)	0.980	C(21)–H(21A)	0.950
C(21)–C(22)	1.329(3)	C(22)–H(22A)	0.950
C(22)–C(23)	1.468(3)	C(24)–H(24A)	0.990
C(24)–H(24B)	0.990	C(24)–C(25)	1.500(4)
C(25)–H(25A)	0.980	C(25)–H(25B)	0.980
C(25)–H(25C)	0.980		

F(1)–B–F(2)	109.4(2)	F(1)–B–N(1)	109.9(2)
F(1)–B–N(2)	109.5(2)	F(2)–B–N(1)	110.3(2)
F(2)–B–N(2)	110.9(2)	N(1)–B–N(2)	106.80(19)
B–N(1)–C(1)	126.3(2)	B–N(1)–C(4)	125.43(19)
C(1)–N(1)–C(4)	108.27(19)	B–N(2)–C(6)	125.42(19)
B–N(2)–C(9)	125.8(2)	C(6)–N(2)–C(9)	108.50(19)
C(19)–O(1)–C(20)	118.0(3)	C(23)–O(3)–C(24)	116.57(19)
N(1)–C(1)–C(2)	108.9(2)	N(1)–C(1)–C(10)	123.1(2)
C(2)–C(1)–C(10)	128.1(2)	C(1)–C(2)–H(2A)	125.4
C(1)–C(2)–C(3)	109.1(2)	H(2A)–C(2)–C(3)	125.4
C(2)–C(3)–C(4)	105.8(2)	C(2)–C(3)–C(11)	124.7(2)
C(4)–C(3)–C(11)	129.5(2)	N(1)–C(4)–C(3)	107.9(2)
N(1)–C(4)–C(5)	120.3(2)	C(3)–C(4)–C(5)	131.8(2)
C(4)–C(5)–C(6)	121.8(2)	C(4)–C(5)–C(14)	119.3(2)
C(6)–C(5)–C(14)	118.8(2)	N(2)–C(6)–C(5)	119.8(2)
N(2)–C(6)–C(7)	108.15(19)	C(5)–C(6)–C(7)	132.0(2)
C(6)–C(7)–C(8)	106.5(2)	C(6)–C(7)–C(12)	128.0(2)
C(8)–C(7)–C(12)	125.4(2)	C(7)–C(8)–C(9)	107.4(2)
C(7)–C(8)–C(21)	128.9(2)	C(9)–C(8)–C(21)	123.7(2)
N(2)–C(9)–C(8)	109.5(2)	N(2)–C(9)–C(13)	122.3(2)

C(8)–C(9)–C(13)	128.2(2)	C(1)–C(10)–H(10A)	109.5
C(1)–C(10)–H(10B)	109.5	C(1)–C(10)–H(10C)	109.5
H(10A)–C(10)–H(10B)	109.5	H(10A)–C(10)–H(10C)	109.5
H(10B)–C(10)–H(10C)	109.5	C(3)–C(11)–H(11A)	109.5
C(3)–C(11)–H(11B)	109.5	C(3)–C(11)–H(11C)	109.5
H(11A)–C(11)–H(11B)	109.5	H(11A)–C(11)–H(11C)	109.5
H(11B)–C(11)–H(11C)	109.5	C(7)–C(12)–H(12A)	109.5
C(7)–C(12)–H(12B)	109.5	C(7)–C(12)–H(12C)	109.5
H(12A)–C(12)–H(12B)	109.5	H(12A)–C(12)–H(12C)	109.5
H(12B)–C(12)–H(12C)	109.5	C(9)–C(13)–H(13A)	109.5
C(9)–C(13)–H(13B)	109.5	C(9)–C(13)–H(13C)	109.5
H(13A)–C(13)–H(13B)	109.5	H(13A)–C(13)–H(13C)	109.5
H(13B)–C(13)–H(13C)	109.5	C(5)–C(14)–C(15)	118.3(3)
C(5)–C(14)–C(19)	120.5(2)	C(15)–C(14)–C(19)	121.1(3)
C(14)–C(15)–H(15A)	121.0	C(14)–C(15)–C(16)	118.1(4)
H(15A)–C(15)–C(16)	121.0	C(15)–C(16)–H(16A)	119.7
C(15)–C(16)–C(17)	120.6(4)	H(16A)–C(16)–C(17)	119.7
C(16)–C(17)–H(17A)	118.7	C(16)–C(17)–C(18)	122.5(3)
H(17A)–C(17)–C(18)	118.7	C(17)–C(18)–H(18A)	121.2
C(17)–C(18)–C(19)	117.5(4)	H(18A)–C(18)–C(19)	121.2
O(1)–C(19)–C(14)	115.6(2)	O(1)–C(19)–C(18)	124.3(3)
C(14)–C(19)–C(18)	120.1(3)	O(1)–C(20)–H(20A)	109.5
O(1)–C(20)–H(20B)	109.5	O(1)–C(20)–H(20C)	109.5
H(20A)–C(20)–H(20B)	109.5	H(20A)–C(20)–H(20C)	109.5
H(20B)–C(20)–H(20C)	109.5	C(8)–C(21)–H(21A)	116.0
C(8)–C(21)–C(22)	128.0(2)	H(21A)–C(21)–C(22)	116.0
C(21)–C(22)–H(22A)	119.1	C(21)–C(22)–C(23)	121.9(2)
H(22A)–C(22)–C(23)	119.1	O(2)–C(23)–O(3)	123.5(2)
O(2)–C(23)–C(22)	126.6(2)	O(3)–C(23)–C(22)	110.0(2)
O(3)–C(24)–H(24A)	110.1	O(3)–C(24)–H(24B)	110.1
O(3)–C(24)–C(25)	107.8(2)	H(24A)–C(24)–H(24B)	108.5
H(24A)–C(24)–C(25)	110.1	H(24B)–C(24)–C(25)	110.1
C(24)–C(25)–H(25A)	109.5	C(24)–C(25)–H(25B)	109.5
C(24)–C(25)–H(25C)	109.5	H(25A)–C(25)–H(25B)	109.5
H(25A)–C(25)–H(25C)	109.5	H(25B)–C(25)–H(25C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B	0.0277(15)	0.0216(14)	0.0270(15)	0.0064(11)	0.0025(12)	0.0074(12)
F(1)	0.0308(8)	0.0411(9)	0.0321(8)	0.0167(7)	0.0022(6)	0.0023(7)
F(2)	0.0371(9)	0.0243(8)	0.0502(10)	0.0028(7)	0.0016(7)	0.0121(7)
N(1)	0.0228(11)	0.0243(11)	0.0257(11)	0.0066(8)	0.0020(8)	0.0086(9)
N(2)	0.0235(11)	0.0208(10)	0.0249(10)	0.0041(8)	0.0017(8)	0.0047(8)
O(1)	0.0368(12)	0.0509(13)	0.0642(15)	–0.0276(11)	0.0040(10)	0.0100(10)
O(2)	0.0302(10)	0.0371(11)	0.0477(12)	0.0113(9)	–0.0066(9)	–0.0056(9)
O(3)	0.0211(9)	0.0362(10)	0.0349(10)	0.0101(8)	–0.0039(7)	0.0016(8)
C(1)	0.0231(13)	0.0337(14)	0.0282(13)	0.0068(11)	0.0028(10)	0.0122(11)
C(2)	0.0182(12)	0.0341(14)	0.0296(13)	0.0043(11)	0.0005(10)	0.0069(11)
C(3)	0.0202(12)	0.0300(13)	0.0252(13)	0.0042(10)	0.0047(10)	0.0081(10)
C(4)	0.0221(12)	0.0237(12)	0.0214(12)	0.0041(9)	0.0053(9)	0.0069(10)
C(5)	0.0215(12)	0.0234(12)	0.0211(12)	0.0021(9)	0.0043(9)	0.0082(10)
C(6)	0.0230(12)	0.0204(12)	0.0219(12)	0.0031(9)	0.0038(9)	0.0061(10)
C(7)	0.0200(12)	0.0255(13)	0.0194(11)	0.0030(9)	0.0030(9)	0.0054(10)
C(8)	0.0233(13)	0.0264(13)	0.0231(12)	0.0037(10)	0.0020(10)	0.0053(10)
C(9)	0.0255(13)	0.0260(13)	0.0246(13)	0.0023(10)	0.0021(10)	0.0024(10)
C(10)	0.0292(14)	0.0393(16)	0.0427(16)	0.0144(13)	–0.0014(12)	0.0126(12)
C(11)	0.0196(13)	0.0286(14)	0.0403(15)	0.0034(11)	0.0023(11)	0.0019(10)
C(12)	0.0226(13)	0.0280(13)	0.0319(14)	0.0063(11)	0.0001(10)	0.0077(10)
C(13)	0.0349(15)	0.0249(14)	0.0416(16)	0.0067(11)	–0.0028(12)	0.0010(11)
C(14)	0.0137(12)	0.0233(13)	0.0495(16)	0.0123(12)	–0.0003(10)	0.0035(10)
C(15)	0.0162(13)	0.072(2)	0.062(2)	0.0531(18)	0.0022(12)	0.0082(13)
C(16)	0.0303(18)	0.077(3)	0.103(3)	0.065(3)	0.0004(18)	0.0011(18)
C(17)	0.0225(17)	0.060(3)	0.163(5)	0.074(3)	–0.013(2)	–0.0041(17)
C(18)	0.0206(16)	0.0249(16)	0.163(5)	–0.001(2)	–0.012(2)	0.0066(13)
C(19)	0.0179(13)	0.0276(15)	0.075(2)	0.0012(14)	–0.0041(13)	0.0034(11)
C(20)	0.043(2)	0.085(3)	0.113(3)	–0.068(3)	0.006(2)	0.0074(19)
C(21)	0.0249(13)	0.0257(13)	0.0273(13)	0.0008(10)	0.0033(10)	0.0025(10)
C(22)	0.0240(13)	0.0313(14)	0.0292(14)	0.0054(11)	0.0017(10)	–0.0006(11)
C(23)	0.0245(13)	0.0294(14)	0.0254(13)	0.0042(10)	0.0014(10)	0.0010(11)
C(24)	0.0202(13)	0.0504(17)	0.0350(15)	0.0066(13)	0.0000(11)	0.0033(12)
C(25)	0.0305(15)	0.065(2)	0.0432(17)	0.0059(15)	–0.0019(13)	0.0178(14)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh12.

	x	y	z	U
H(2A)	1.0869	0.3728	0.4379	0.033
H(10A)	0.8617	0.0463	0.4125	0.056
H(10B)	0.7989	0.0953	0.4982	0.056
H(10C)	1.0280	0.1369	0.4827	0.056
H(11A)	1.0599	0.5787	0.3627	0.045
H(11B)	0.8573	0.6151	0.3869	0.045
H(11C)	0.8633	0.5777	0.2892	0.045
H(12A)	0.0911	0.4764	0.2040	0.042
H(12B)	–0.1350	0.3940	0.1799	0.042
H(12C)	0.0149	0.4015	0.1121	0.042
H(13A)	0.1097	–0.0621	0.3272	0.053
H(13B)	0.0936	–0.0952	0.2269	0.053
H(13C)	–0.1045	–0.0728	0.2625	0.053
H(15A)	0.4692	0.4439	0.1234	0.060
H(16A)	0.4706	0.6440	0.0688	0.086
H(17A)	0.4695	0.8141	0.1573	0.103
H(18A)	0.4589	0.7953	0.3043	0.088
H(20A)	0.4770	0.6552	0.5021	0.125
H(20B)	0.3681	0.7322	0.4282	0.125
H(20C)	0.6108	0.7417	0.4446	0.125
H(21A)	–0.3055	0.0412	0.1839	0.032
H(22A)	–0.2971	0.2457	0.0811	0.035
H(24A)	–0.9542	0.1354	0.0323	0.043
H(24B)	–0.8988	0.0813	–0.0540	0.043
H(25A)	–1.0963	0.2414	–0.0834	0.070
H(25B)	–0.8777	0.2804	–0.1102	0.070
H(25C)	–0.9187	0.3393	–0.0227	0.070

Table 0. Torsion angles [°] for mjh12.

F(1)–B–N(1)–C(1)	65.9(3)	F(1)–B–N(1)–C(4)	−112.8(2)
F(2)–B–N(1)–C(1)	−54.8(3)	F(2)–B–N(1)–C(4)	126.5(2)
N(2)–B–N(1)–C(1)	−175.4(2)	N(2)–B–N(1)–C(4)	5.9(3)
F(1)–B–N(2)–C(6)	110.8(2)	F(1)–B–N(2)–C(9)	−62.2(3)
F(2)–B–N(2)–C(6)	−128.3(2)	F(2)–B–N(2)–C(9)	58.7(3)
N(1)–B–N(2)–C(6)	−8.1(3)	N(1)–B–N(2)–C(9)	178.9(2)
B–N(1)–C(1)–C(2)	−179.3(2)	B–N(1)–C(1)–C(10)	−0.1(4)
C(4)–N(1)–C(1)–C(2)	−0.4(3)	C(4)–N(1)–C(1)–C(10)	178.8(2)
N(1)–C(1)–C(2)–C(3)	0.6(3)	C(10)–C(1)–C(2)–C(3)	−178.6(3)
C(1)–C(2)–C(3)–C(4)	−0.4(3)	C(1)–C(2)–C(3)–C(11)	179.1(2)
B–N(1)–C(4)–C(3)	179.0(2)	B–N(1)–C(4)–C(5)	−1.9(3)
C(1)–N(1)–C(4)–C(3)	0.2(3)	C(1)–N(1)–C(4)–C(5)	179.2(2)
C(2)–C(3)–C(4)–N(1)	0.2(3)	C(2)–C(3)–C(4)–C(5)	−178.7(2)
C(11)–C(3)–C(4)–N(1)	−179.3(2)	C(11)–C(3)–C(4)–C(5)	1.8(4)
N(1)–C(4)–C(5)–C(6)	−1.1(3)	N(1)–C(4)–C(5)–C(14)	−177.9(2)
C(3)–C(4)–C(5)–C(6)	177.6(2)	C(3)–C(4)–C(5)–C(14)	0.9(4)
B–N(2)–C(6)–C(5)	6.3(3)	B–N(2)–C(6)–C(7)	−173.3(2)
C(9)–N(2)–C(6)–C(5)	−179.6(2)	C(9)–N(2)–C(6)–C(7)	0.8(3)
C(4)–C(5)–C(6)–N(2)	−1.0(3)	C(4)–C(5)–C(6)–C(7)	178.5(2)
C(14)–C(5)–C(6)–N(2)	175.8(2)	C(14)–C(5)–C(6)–C(7)	−4.7(4)
N(2)–C(6)–C(7)–C(8)	−1.2(3)	N(2)–C(6)–C(7)–C(12)	174.4(2)
C(5)–C(6)–C(7)–C(8)	179.3(2)	C(5)–C(6)–C(7)–C(12)	−5.1(4)
C(6)–C(7)–C(8)–C(9)	1.2(3)	C(6)–C(7)–C(8)–C(21)	179.0(2)
C(12)–C(7)–C(8)–C(9)	−174.6(2)	C(12)–C(7)–C(8)–C(21)	3.3(4)
B–N(2)–C(9)–C(8)	174.0(2)	B–N(2)–C(9)–C(13)	−8.0(4)
C(6)–N(2)–C(9)–C(8)	0.0(3)	C(6)–N(2)–C(9)–C(13)	177.9(2)
C(7)–C(8)–C(9)–N(2)	−0.8(3)	C(7)–C(8)–C(9)–C(13)	−178.5(2)
C(21)–C(8)–C(9)–N(2)	−178.7(2)	C(21)–C(8)–C(9)–C(13)	3.5(4)
C(4)–C(5)–C(14)–C(15)	106.0(3)	C(4)–C(5)–C(14)–C(19)	−73.8(3)
C(6)–C(5)–C(14)–C(15)	−70.8(3)	C(6)–C(5)–C(14)–C(19)	109.4(3)
C(5)–C(14)–C(15)–C(16)	179.7(2)	C(19)–C(14)–C(15)–C(16)	−0.6(4)
C(14)–C(15)–C(16)–C(17)	0.6(4)	C(15)–C(16)–C(17)–C(18)	−0.7(5)
C(16)–C(17)–C(18)–C(19)	0.8(5)	C(20)–O(1)–C(19)–C(14)	172.0(2)
C(20)–O(1)–C(19)–C(18)	−9.0(4)	C(5)–C(14)–C(19)–O(1)	−0.5(3)
C(5)–C(14)–C(19)–C(18)	−179.6(2)	C(15)–C(14)–C(19)–O(1)	179.7(2)
C(15)–C(14)–C(19)–C(18)	0.7(4)	C(17)–C(18)–C(19)–O(1)	−179.7(3)
C(17)–C(18)–C(19)–C(14)	−0.8(4)	C(7)–C(8)–C(21)–C(22)	18.5(4)
C(9)–C(8)–C(21)–C(22)	−164.0(3)	C(8)–C(21)–C(22)–C(23)	−176.9(2)
C(24)–O(3)–C(23)–O(2)	−0.2(4)	C(24)–O(3)–C(23)–C(22)	−178.5(2)
C(21)–C(22)–C(23)–O(2)	−8.1(4)	C(21)–C(22)–C(23)–O(3)	170.1(2)
C(23)–O(3)–C(24)–C(25)	175.4(2)		

Compound **7.5**

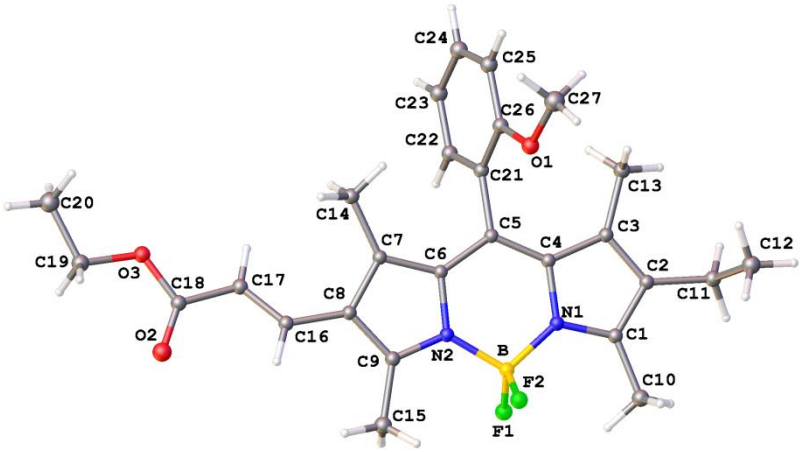

C24
C25
C23
C26
C27
C22
O1
C21
C13
C20
C14
C5
C3
C19
C7
C6
C4
C12
O3
C18
C17
C8
C2
C11
O2
C16
N1
C1
C9
N2
B
F2
C10
C15
F1

Table 1. Crystal data and structure refinement for mjh120043.

Identification code	mjh120043	
Chemical formula (moiety)	$C_{27}H_{31}BF_2N_2O_3$	
Chemical formula (total)	$C_{27}H_{31}BF_2N_2O_3$	
Formula weight	480.35	
Temperature	150(2) K	
Radiation, wavelength	CuKα, 1.54178 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 6.7998(5) Å	α = 83.236(7)°
	b = 10.6195(10) Å	β = 84.254(6)°
	c = 17.3332(13) Å	γ = 80.908(7)°
Cell volume	1223.06(17) $Å^3$	
Z	2	
Calculated density	1.304 g/cm^3	
Absorption coefficient μ	0.776 mm^{-1}	
F(000)	508	
Crystal colour and size	red, 0.10 × 0.10 × 0.01 mm^3	
Reflections for cell refinement	2069 (θ range 2.6 to 62.3°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	2.6 to 62.3°	
Index ranges	h −6 to 7, k −12 to 11, l −13 to 19	
Completeness to θ = 33.5°	100.0 %	
Reflections collected	6886	
Independent reflections	3772 (R_{int} = 0.0320)	
Reflections with $F^2>2\sigma$	2751	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.9265 and 0.9923	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0480, 0.2192	
Data / restraints / parameters	3772 / 0 / 324	
Final R indices [$F^2>2\sigma$]	R1 = 0.0476, wR2 = 0.1065	
R indices (all data)	R1 = 0.0731, wR2 = 0.1211	
Goodness-of-fit on F^2	1.050	
Extinction coefficient	0.0007(3)	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.23 and −0.19 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh12. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	0.3624(3)	–0.00852(17)	0.16490(10)	0.0382(5)
O(2)	–0.6882(3)	0.50907(19)	0.41867(11)	0.0453(5)
O(3)	–0.6685(3)	0.31105(17)	0.48287(10)	0.0344(5)
N(1)	0.5222(3)	0.37225(19)	0.16257(11)	0.0266(5)
N(2)	0.1891(3)	0.41792(19)	0.23558(11)	0.0266(5)
F(1)	0.4136(2)	0.57553(14)	0.21241(8)	0.0373(4)
F(2)	0.2632(2)	0.53164(14)	0.11011(8)	0.0389(4)
B	0.3466(4)	0.4793(3)	0.17928(16)	0.0286(7)
C(1)	0.6950(4)	0.3873(2)	0.11976(14)	0.0284(6)
C(2)	0.8240(4)	0.2691(2)	0.12138(14)	0.0281(6)
C(3)	0.7267(4)	0.1784(2)	0.16712(14)	0.0273(6)
C(4)	0.5340(4)	0.2428(2)	0.19427(14)	0.0262(6)
C(5)	0.3780(4)	0.2022(2)	0.24385(13)	0.0257(6)
C(6)	0.2036(4)	0.2876(2)	0.26364(13)	0.0251(6)
C(7)	0.0249(4)	0.2688(2)	0.30925(14)	0.0263(6)
C(8)	–0.0947(4)	0.3907(2)	0.30968(14)	0.0265(6)
C(9)	0.0127(4)	0.4790(2)	0.26335(14)	0.0292(6)
C(10)	0.7336(4)	0.5122(3)	0.07703(15)	0.0374(7)
C(11)	1.0289(4)	0.2492(3)	0.07925(15)	0.0332(6)
C(12)	1.0281(4)	0.2028(3)	–0.00046(16)	0.0432(7)
C(13)	0.8111(4)	0.0398(2)	0.18202(15)	0.0346(7)
C(14)	–0.0399(4)	0.1454(2)	0.34631(15)	0.0321(6)
C(15)	–0.0467(4)	0.6206(3)	0.24725(16)	0.0393(7)
C(16)	–0.2934(4)	0.4250(2)	0.34772(14)	0.0294(6)
C(17)	–0.3873(4)	0.3595(3)	0.40516(14)	0.0308(6)
C(18)	–0.5938(4)	0.4048(3)	0.43476(14)	0.0311(6)
C(19)	–0.8738(4)	0.3401(3)	0.51443(16)	0.0388(7)
C(21)	0.3969(4)	0.0682(2)	0.28236(15)	0.0298(6)
C(20)	–0.9304(4)	0.2194(3)	0.56030(17)	0.0496(8)
C(22)	0.4213(4)	0.0480(3)	0.36292(15)	0.0330(6)
C(23)	0.4381(4)	–0.0741(3)	0.40171(17)	0.0389(7)
C(24)	0.4294(4)	–0.1763(3)	0.36017(17)	0.0394(7)
C(25)	0.4033(4)	–0.1603(3)	0.28225(17)	0.0374(7)
C(26)	0.3874(4)	–0.0361(3)	0.24245(15)	0.0319(6)
C(27)	0.3640(5)	–0.1139(3)	0.12018(19)	0.0534(9)

Table 3. Bond lengths [Å] and angles [°] for mjh12.

O(1)–C(26)	1.364(3)	O(1)–C(27)	1.433(3)
O(2)–C(18)	1.206(3)	O(3)–C(18)	1.351(3)
O(3)–C(19)	1.447(3)	N(1)–B	1.543(4)
N(1)–C(1)	1.347(3)	N(1)–C(4)	1.412(3)
N(2)–B	1.545(3)	N(2)–C(6)	1.404(3)
N(2)–C(9)	1.343(3)	F(1)–B	1.385(3)
F(2)–B	1.395(3)	C(1)–C(2)	1.413(3)
C(1)–C(10)	1.488(3)	C(2)–C(3)	1.382(3)
C(2)–C(11)	1.503(3)	C(3)–C(4)	1.441(3)
C(3)–C(13)	1.495(3)	C(4)–C(5)	1.387(3)
C(5)–C(6)	1.413(3)	C(5)–C(21)	1.490(3)
C(6)–C(7)	1.410(3)	C(7)–C(8)	1.416(3)
C(7)–C(14)	1.501(3)	C(8)–C(9)	1.407(3)
C(8)–C(16)	1.455(3)	C(9)–C(15)	1.495(3)
C(10)–H(10A)	0.980	C(10)–H(10B)	0.980
C(10)–H(10C)	0.980	C(11)–H(11A)	0.990
C(11)–H(11B)	0.990	C(11)–C(12)	1.521(4)
C(12)–H(12A)	0.980	C(12)–H(12B)	0.980
C(12)–H(12C)	0.980	C(13)–H(13A)	0.980
C(13)–H(13B)	0.980	C(13)–H(13C)	0.980
C(14)–H(14A)	0.980	C(14)–H(14B)	0.980
C(14)–H(14C)	0.980	C(15)–H(15A)	0.980
C(15)–H(15B)	0.980	C(15)–H(15C)	0.980
C(16)–H(16A)	0.950	C(16)–C(17)	1.316(3)
C(17)–H(17A)	0.950	C(17)–C(18)	1.472(4)
C(19)–H(19A)	0.990	C(19)–H(19B)	0.990
C(19)–C(20)	1.510(4)	C(21)–C(22)	1.410(3)
C(21)–C(26)	1.387(3)	C(20)–H(20A)	0.980
C(20)–H(20B)	0.980	C(20)–H(20C)	0.980
C(22)–H(22A)	0.950	C(22)–C(23)	1.382(4)
C(23)–H(23A)	0.950	C(23)–C(24)	1.383(4)
C(24)–H(24A)	0.950	C(24)–C(25)	1.367(4)
C(25)–H(25A)	0.950	C(25)–C(26)	1.408(4)
C(27)–H(27A)	0.980	C(27)–H(27B)	0.980
C(27)–H(27C)	0.980		

C(26)–O(1)–C(27)	117.6(2)	C(18)–O(3)–C(19)	116.6(2)
B–N(1)–C(1)	126.1(2)	B–N(1)–C(4)	125.4(2)
C(1)–N(1)–C(4)	108.3(2)	B–N(2)–C(6)	125.4(2)
B–N(2)–C(9)	125.8(2)	C(6)–N(2)–C(9)	108.7(2)
N(1)–B–N(2)	107.4(2)	N(1)–B–F(1)	109.9(2)
N(1)–B–F(2)	110.1(2)	N(2)–B–F(1)	110.7(2)
N(2)–B–F(2)	109.9(2)	F(1)–B–F(2)	108.9(2)
N(1)–C(1)–C(2)	109.8(2)	N(1)–C(1)–C(10)	122.8(2)
C(2)–C(1)–C(10)	127.3(2)	C(1)–C(2)–C(3)	107.8(2)
C(1)–C(2)–C(11)	124.7(2)	C(3)–C(2)–C(11)	127.5(2)
C(2)–C(3)–C(4)	107.1(2)	C(2)–C(3)–C(13)	124.5(2)
C(4)–C(3)–C(13)	128.4(2)	N(1)–C(4)–C(3)	107.0(2)
N(1)–C(4)–C(5)	120.2(2)	C(3)–C(4)–C(5)	132.7(2)
C(4)–C(5)–C(6)	121.5(2)	C(4)–C(5)–C(21)	120.3(2)
C(6)–C(5)–C(21)	118.0(2)	N(2)–C(6)–C(5)	119.9(2)
N(2)–C(6)–C(7)	108.0(2)	C(5)–C(6)–C(7)	132.1(2)
C(6)–C(7)–C(8)	106.6(2)	C(6)–C(7)–C(14)	128.6(2)

C(8)–C(7)–C(14)	124.7(2)	C(7)–C(8)–C(9)	107.1(2)
C(7)–C(8)–C(16)	129.1(2)	C(9)–C(8)–C(16)	123.8(2)
N(2)–C(9)–C(8)	109.6(2)	N(2)–C(9)–C(15)	122.4(2)
C(8)–C(9)–C(15)	127.9(2)	C(1)–C(10)–H(10A)	109.5
C(1)–C(10)–H(10B)	109.5	C(1)–C(10)–H(10C)	109.5
H(10A)–C(10)–H(10B)	109.5	H(10A)–C(10)–H(10C)	109.5
H(10B)–C(10)–H(10C)	109.5	C(2)–C(11)–H(11A)	109.1
C(2)–C(11)–H(11B)	109.1	C(2)–C(11)–C(12)	112.7(2)
H(11A)–C(11)–H(11B)	107.8	H(11A)–C(11)–C(12)	109.1
H(11B)–C(11)–C(12)	109.1	C(11)–C(12)–H(12A)	109.5
C(11)–C(12)–H(12B)	109.5	C(11)–C(12)–H(12C)	109.5
H(12A)–C(12)–H(12B)	109.5	H(12A)–C(12)–H(12C)	109.5
H(12B)–C(12)–H(12C)	109.5	C(3)–C(13)–H(13A)	109.5
C(3)–C(13)–H(13B)	109.5	C(3)–C(13)–H(13C)	109.5
H(13A)–C(13)–H(13B)	109.5	H(13A)–C(13)–H(13C)	109.5
H(13B)–C(13)–H(13C)	109.5	C(7)–C(14)–H(14A)	109.5
C(7)–C(14)–H(14B)	109.5	C(7)–C(14)–H(14C)	109.5
H(14A)–C(14)–H(14B)	109.5	H(14A)–C(14)–H(14C)	109.5
H(14B)–C(14)–H(14C)	109.5	C(9)–C(15)–H(15A)	109.5
C(9)–C(15)–H(15B)	109.5	C(9)–C(15)–H(15C)	109.5
H(15A)–C(15)–H(15B)	109.5	H(15A)–C(15)–H(15C)	109.5
H(15B)–C(15)–H(15C)	109.5	C(8)–C(16)–H(16A)	115.8
C(8)–C(16)–C(17)	128.4(2)	H(16A)–C(16)–C(17)	115.8
C(16)–C(17)–H(17A)	119.1	C(16)–C(17)–C(18)	121.8(2)
H(17A)–C(17)–C(18)	119.1	O(2)–C(18)–O(3)	123.3(2)
O(2)–C(18)–C(17)	126.4(2)	O(3)–C(18)–C(17)	110.2(2)
O(3)–C(19)–H(19A)	110.2	O(3)–C(19)–H(19B)	110.2
O(3)–C(19)–C(20)	107.5(2)	H(19A)–C(19)–H(19B)	108.5
H(19A)–C(19)–C(20)	110.2	H(19B)–C(19)–C(20)	110.2
C(5)–C(21)–C(22)	118.3(2)	C(5)–C(21)–C(26)	122.6(2)
C(22)–C(21)–C(26)	119.1(2)	C(19)–C(20)–H(20A)	109.5
C(19)–C(20)–H(20B)	109.5	C(19)–C(20)–H(20C)	109.5
H(20A)–C(20)–H(20B)	109.5	H(20A)–C(20)–H(20C)	109.5
H(20B)–C(20)–H(20C)	109.5	C(21)–C(22)–H(22A)	119.6
C(21)–C(22)–C(23)	120.7(3)	H(22A)–C(22)–C(23)	119.6
C(22)–C(23)–H(23A)	120.6	C(22)–C(23)–C(24)	118.8(3)
H(23A)–C(23)–C(24)	120.6	C(23)–C(24)–H(24A)	118.9
C(23)–C(24)–C(25)	122.2(3)	H(24A)–C(24)–C(25)	118.9
C(24)–C(25)–H(25A)	120.4	C(24)–C(25)–C(26)	119.2(3)
H(25A)–C(25)–C(26)	120.4	O(1)–C(26)–C(21)	115.5(2)
O(1)–C(26)–C(25)	124.4(2)	C(21)–C(26)–C(25)	120.0(2)
O(1)–C(27)–H(27A)	109.5	O(1)–C(27)–H(27B)	109.5
O(1)–C(27)–H(27C)	109.5	H(27A)–C(27)–H(27B)	109.5
H(27A)–C(27)–H(27C)	109.5	H(27B)–C(27)–H(27C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	0.0404(11)	0.0276(11)	0.0488(12)	–0.0142(9)	–0.0040(9)	–0.0040(9)
O(2)	0.0397(12)	0.0314(12)	0.0564(13)	0.0028(10)	0.0107(10)	0.0059(10)
O(3)	0.0296(10)	0.0321(11)	0.0380(10)	0.0003(8)	0.0077(8)	–0.0030(8)
N(1)	0.0307(12)	0.0203(12)	0.0282(11)	–0.0022(9)	0.0024(9)	–0.0044(10)
N(2)	0.0293(12)	0.0179(12)	0.0309(11)	–0.0030(9)	0.0016(9)	–0.0004(9)
F(1)	0.0421(9)	0.0224(9)	0.0480(9)	–0.0085(7)	0.0048(7)	–0.0085(7)
F(2)	0.0409(9)	0.0364(10)	0.0344(8)	0.0069(7)	–0.0003(7)	–0.0003(7)
B	0.0330(17)	0.0210(17)	0.0305(16)	–0.0004(13)	0.0007(13)	–0.0038(14)
C(1)	0.0323(15)	0.0273(15)	0.0257(13)	–0.0024(11)	0.0026(12)	–0.0081(12)
C(2)	0.0274(14)	0.0277(15)	0.0294(14)	–0.0040(11)	0.0005(11)	–0.0056(12)
C(3)	0.0283(14)	0.0239(14)	0.0308(14)	–0.0067(11)	–0.0026(11)	–0.0039(12)
C(4)	0.0292(14)	0.0211(14)	0.0277(13)	–0.0024(10)	–0.0020(11)	–0.0028(11)
C(5)	0.0282(14)	0.0221(14)	0.0277(13)	–0.0036(11)	–0.0024(11)	–0.0060(11)
C(6)	0.0278(14)	0.0187(14)	0.0282(13)	–0.0020(10)	–0.0014(11)	–0.0023(11)
C(7)	0.0302(14)	0.0215(14)	0.0275(13)	–0.0018(11)	–0.0026(11)	–0.0047(11)
C(8)	0.0257(14)	0.0246(14)	0.0287(13)	–0.0018(11)	–0.0002(11)	–0.0038(11)
C(9)	0.0307(15)	0.0262(15)	0.0285(14)	–0.0018(11)	–0.0004(11)	0.0002(12)
C(10)	0.0422(17)	0.0307(17)	0.0376(16)	0.0007(12)	0.0064(13)	–0.0100(14)
C(11)	0.0293(15)	0.0324(16)	0.0384(15)	–0.0055(12)	0.0019(12)	–0.0074(12)
C(12)	0.0442(18)	0.0404(19)	0.0435(17)	–0.0090(14)	0.0070(14)	–0.0048(15)
C(13)	0.0258(14)	0.0298(16)	0.0461(16)	–0.0035(13)	0.0027(12)	–0.0013(12)
C(14)	0.0276(14)	0.0259(15)	0.0420(15)	–0.0031(12)	0.0034(12)	–0.0054(12)
C(15)	0.0401(17)	0.0249(16)	0.0469(17)	–0.0017(13)	0.0089(13)	0.0039(13)
C(16)	0.0342(15)	0.0225(15)	0.0309(14)	–0.0056(11)	–0.0028(12)	0.0005(12)
C(17)	0.0295(15)	0.0255(15)	0.0349(15)	–0.0031(12)	–0.0005(12)	0.0020(12)
C(18)	0.0327(15)	0.0303(16)	0.0296(14)	–0.0035(12)	0.0019(12)	–0.0049(13)
C(19)	0.0274(15)	0.0446(19)	0.0410(16)	–0.0021(13)	0.0052(12)	–0.0015(13)
C(21)	0.0203(13)	0.0218(15)	0.0464(16)	–0.0029(12)	0.0018(12)	–0.0035(11)
C(20)	0.0378(17)	0.056(2)	0.0535(19)	0.0000(16)	0.0091(15)	–0.0151(16)
C(22)	0.0250(14)	0.0292(16)	0.0414(16)	0.0036(12)	0.0024(12)	–0.0022(12)
C(23)	0.0365(16)	0.0330(17)	0.0439(16)	0.0054(13)	–0.0021(13)	–0.0027(13)
C(24)	0.0310(16)	0.0298(17)	0.0539(19)	0.0042(14)	–0.0003(13)	–0.0020(13)
C(25)	0.0261(15)	0.0250(16)	0.0610(19)	–0.0091(13)	0.0001(13)	–0.0027(12)
C(26)	0.0252(14)	0.0286(16)	0.0411(16)	–0.0054(12)	–0.0010(12)	–0.0010(12)
C(27)	0.060(2)	0.044(2)	0.060(2)	–0.0236(16)	–0.0048(17)	–0.0070(17)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh12.

	x	y	z	U
H(10A)	0.8729	0.5228	0.0805	0.056
H(10B)	0.6446	0.5822	0.1002	0.056
H(10C)	0.7088	0.5138	0.0222	0.056
H(11A)	1.1176	0.1856	0.1114	0.040
H(11B)	1.0841	0.3310	0.0728	0.040
H(12A)	1.1647	0.1912	–0.0254	0.065
H(12B)	0.9430	0.2664	–0.0330	0.065
H(12C)	0.9761	0.1209	0.0056	0.065
H(13A)	0.9570	0.0295	0.1723	0.052
H(13B)	0.7566	–0.0097	0.1472	0.052
H(13C)	0.7751	0.0088	0.2363	0.052
H(14A)	0.0351	0.0738	0.3199	0.048
H(14B)	–0.1831	0.1485	0.3418	0.048
H(14C)	–0.0140	0.1332	0.4015	0.048
H(15A)	–0.0083	0.6477	0.1925	0.059
H(15B)	0.0211	0.6648	0.2809	0.059
H(15C)	–0.1917	0.6422	0.2577	0.059
H(16A)	–0.3647	0.5050	0.3286	0.035
H(17A)	–0.3200	0.2808	0.4281	0.037
H(19A)	–0.9623	0.3683	0.4717	0.047
H(19B)	–0.8872	0.4097	0.5488	0.047
H(20A)	–1.0708	0.2349	0.5807	0.074
H(20B)	–0.8457	0.1945	0.6037	0.074
H(20C)	–0.9114	0.1503	0.5262	0.074
H(22A)	0.4262	0.1191	0.3908	0.040
H(23A)	0.4553	–0.0876	0.4559	0.047
H(24A)	0.4419	–0.2604	0.3867	0.047
H(25A)	0.3959	–0.2321	0.2553	0.045
H(27A)	0.3521	–0.0817	0.0652	0.080
H(27B)	0.2513	–0.1595	0.1395	0.080
H(27C)	0.4895	–0.1727	0.1252	0.080

Table 6. Torsion angles [°] for mjh12.

C(1)–N(1)–B–N(2)	−175.9(2)	C(1)–N(1)–B–F(1)	−55.3(3)
C(1)–N(1)–B–F(2)	64.6(3)	C(4)–N(1)–B–N(2)	−0.5(3)
C(4)–N(1)–B–F(1)	120.0(2)	C(4)–N(1)–B–F(2)	−120.1(2)
C(6)–N(2)–B–N(1)	−1.8(3)	C(6)–N(2)–B–F(1)	−121.9(2)
C(6)–N(2)–B–F(2)	117.9(2)	C(9)–N(2)–B–N(1)	−179.0(2)
C(9)–N(2)–B–F(1)	60.9(3)	C(9)–N(2)–B–F(2)	−59.3(3)
B–N(1)–C(1)–C(2)	176.5(2)	B–N(1)–C(1)–C(10)	−4.7(4)
C(4)–N(1)–C(1)–C(2)	0.5(3)	C(4)–N(1)–C(1)–C(10)	179.3(2)
N(1)–C(1)–C(2)–C(3)	−0.2(3)	N(1)–C(1)–C(2)–C(11)	179.2(2)
C(10)–C(1)–C(2)–C(3)	−179.0(2)	C(10)–C(1)–C(2)–C(11)	0.4(4)
C(1)–C(2)–C(3)–C(4)	−0.1(3)	C(1)–C(2)–C(3)–C(13)	178.5(2)
C(11)–C(2)–C(3)–C(4)	−179.5(2)	C(11)–C(2)–C(3)–C(13)	−0.9(4)
B–N(1)–C(4)–C(3)	−176.6(2)	B–N(1)–C(4)–C(5)	1.2(3)
C(1)–N(1)–C(4)–C(3)	−0.6(3)	C(1)–N(1)–C(4)–C(5)	177.2(2)
C(2)–C(3)–C(4)–N(1)	0.5(3)	C(2)–C(3)–C(4)–C(5)	−177.0(3)
C(13)–C(3)–C(4)–N(1)	−178.1(2)	C(13)–C(3)–C(4)–C(5)	4.4(4)
N(1)–C(4)–C(5)–C(6)	0.4(3)	N(1)–C(4)–C(5)–C(21)	−175.1(2)
C(3)–C(4)–C(5)–C(6)	177.7(2)	C(3)–C(4)–C(5)–C(21)	2.1(4)
B–N(2)–C(6)–C(5)	3.5(3)	B–N(2)–C(6)–C(7)	−176.3(2)
C(9)–N(2)–C(6)–C(5)	−178.9(2)	C(9)–N(2)–C(6)–C(7)	1.3(3)
C(4)–C(5)–C(6)–N(2)	−2.7(3)	C(4)–C(5)–C(6)–C(7)	177.0(2)
C(21)–C(5)–C(6)–N(2)	172.9(2)	C(21)–C(5)–C(6)–C(7)	−7.3(4)
N(2)–C(6)–C(7)–C(8)	−1.5(3)	N(2)–C(6)–C(7)–C(14)	174.3(2)
C(5)–C(6)–C(7)–C(8)	178.8(2)	C(5)–C(6)–C(7)–C(14)	−5.4(4)
C(6)–C(7)–C(8)–C(9)	1.1(3)	C(6)–C(7)–C(8)–C(16)	179.7(2)
C(14)–C(7)–C(8)–C(9)	−174.9(2)	C(14)–C(7)–C(8)–C(16)	3.7(4)
B–N(2)–C(9)–C(8)	177.0(2)	B–N(2)–C(9)–C(15)	−5.1(4)
C(6)–N(2)–C(9)–C(8)	−0.6(3)	C(6)–N(2)–C(9)–C(15)	177.3(2)
C(7)–C(8)–C(9)–N(2)	−0.3(3)	C(7)–C(8)–C(9)–C(15)	−178.1(2)
C(16)–C(8)–C(9)–N(2)	−179.0(2)	C(16)–C(8)–C(9)–C(15)	3.2(4)
C(1)–C(2)–C(11)–C(12)	−94.2(3)	C(3)–C(2)–C(11)–C(12)	85.1(3)
C(7)–C(8)–C(16)–C(17)	18.6(4)	C(9)–C(8)–C(16)–C(17)	−163.0(3)
C(8)–C(16)–C(17)–C(18)	−176.8(2)	C(19)–O(3)–C(18)–O(2)	1.1(4)
C(19)–O(3)–C(18)–C(17)	−177.8(2)	C(16)–C(17)–C(18)–O(2)	−10.2(4)
C(16)–C(17)–C(18)–O(3)	168.7(2)	C(18)–O(3)–C(19)–C(20)	175.2(2)
C(4)–C(5)–C(21)–C(22)	107.5(3)	C(4)–C(5)–C(21)–C(26)	−73.8(3)
C(6)–C(5)–C(21)–C(22)	−68.2(3)	C(6)–C(5)–C(21)–C(26)	110.5(3)
C(5)–C(21)–C(22)–C(23)	179.5(2)	C(26)–C(21)–C(22)–C(23)	0.8(4)
C(21)–C(22)–C(23)–C(24)	−0.4(4)	C(22)–C(23)–C(24)–C(25)	−0.5(4)
C(23)–C(24)–C(25)–C(26)	0.9(4)	C(27)–O(1)–C(26)–C(21)	176.3(2)
C(27)–O(1)–C(26)–C(25)	−3.8(4)	C(5)–C(21)–C(26)–O(1)	0.9(4)
C(5)–C(21)–C(26)–C(25)	−179.0(2)	C(22)–C(21)–C(26)–O(1)	179.6(2)
C(22)–C(21)–C(26)–C(25)	−0.4(4)	C(24)–C(25)–C(26)–O(1)	179.6(2)
C(24)–C(25)–C(26)–C(21)	−0.4(4)		

Compound **7.9**

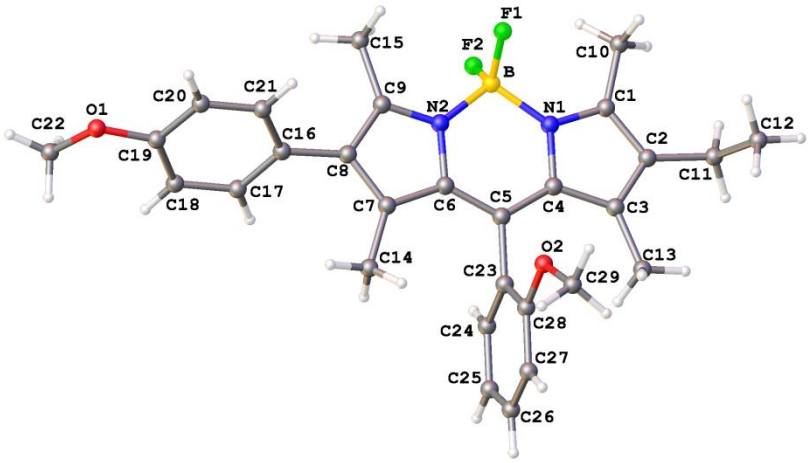

F1
F2
B
N2
N1
C15
C10
C9
C1
C20
C21
O1
C22
C16
C19
C8
C2
C12
C11
C18
C17
C7
C6
C5
C4
C3
C14
O2
C23
C29
C13
C24
C28
C27
C25
C26

Table 1. Crystal data and structure refinement for mjh12.

Identification code	mjh120047	
Chemical formula (moiety)	$C_{29}H_{31}BF_2N_2O_2$	
Chemical formula (total)	$C_{29}H_{31}BF_2N_2O_2$	
Formula weight	488.37	
Temperature	150(2) K	
Radiation, wavelength	CuKα, 1.54178 Å	
Crystal system, space group	monoclinic, $P12_1/n1$	
Unit cell parameters	a = 10.1087(2) Å	α = 90°
	b = 21.6288(4) Å	β = 101.057(2)°
	c = 12.1044(3) Å	γ = 90°
Cell volume	2597.37(10) $Å^3$	
Z	4	
Calculated density	1.249 g/cm^3	
Absorption coefficient μ	0.711 mm^{-1}	
F(000)	1032	
Crystal colour and size	red, 0.40 × 0.20 × 0.02 mm^3	
Reflections for cell refinement	4260 (θ range 2.0 to 66.2°)	
Data collection method	Xcalibur, Atlas, Gemini ultra	
	thick-slice ω scans	
θ range for data collection	4.1 to 66.2°	
Index ranges	h −11 to 11, k −16 to 25, l −14 to 13	
Completeness to θ = 66.2°	97.8 %	
Reflections collected	10142	
Independent reflections	4453 (R_{int} = 0.0238)	
Reflections with $F^2>2\sigma$	3780	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.7640 and 0.9859	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0928, 1.3708	
Data / restraints / parameters	4453 / 0 / 332	
Final R indices [$F^2>2\sigma$]	R1 = 0.0555, wR2 = 0.1536	
R indices (all data)	R1 = 0.0640, wR2 = 0.1629	
Goodness-of-fit on F^2	1.031	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.67 and −0.25 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for mjh12. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	0.72733(19)	0.34910(8)	0.03219(15)	0.0551(5)
O(2)	0.58015(16)	0.66842(9)	0.60537(14)	0.0503(4)
N(1)	0.99201(17)	0.71798(8)	0.55891(14)	0.0339(4)
N(2)	0.92908(17)	0.62971(8)	0.42794(14)	0.0331(4)
F(1)	0.98406(15)	0.72929(6)	0.35946(11)	0.0500(4)
F(2)	1.15333(12)	0.67236(7)	0.46025(12)	0.0489(4)
B	1.0179(2)	0.68831(11)	0.4485(2)	0.0363(5)
C(1)	1.0466(2)	0.77085(10)	0.60651(19)	0.0386(5)
C(2)	0.9997(2)	0.78247(10)	0.70689(18)	0.0384(5)
C(3)	0.9115(2)	0.73497(10)	0.72006(17)	0.0353(5)
C(4)	0.90825(19)	0.69388(9)	0.62739(17)	0.0317(4)
C(5)	0.84093(19)	0.63811(9)	0.59950(17)	0.0324(4)
C(6)	0.84990(19)	0.60616(9)	0.50097(17)	0.0315(4)
C(7)	0.7902(2)	0.55018(10)	0.45394(17)	0.0338(5)
C(8)	0.8342(2)	0.54112(10)	0.35261(18)	0.0354(5)
C(9)	0.9202(2)	0.59100(10)	0.33953(17)	0.0357(5)
C(10)	1.1407(3)	0.80955(12)	0.5547(2)	0.0551(7)
C(11)	1.0382(3)	0.83733(11)	0.7825(2)	0.0469(6)
C(12)	0.9426(4)	0.89127(15)	0.7564(3)	0.0838(11)
C(13)	0.8334(2)	0.73031(12)	0.81312(19)	0.0458(6)
C(14)	0.6945(2)	0.50830(11)	0.4986(2)	0.0455(6)
C(15)	0.9970(3)	0.60111(12)	0.2471(2)	0.0475(6)
C(16)	0.8003(2)	0.48936(10)	0.27208(18)	0.0371(5)
C(17)	0.8289(2)	0.42852(10)	0.30456(18)	0.0368(5)
C(18)	0.8063(2)	0.37987(10)	0.22809(19)	0.0400(5)
C(19)	0.7511(2)	0.39226(11)	0.11589(19)	0.0422(5)
C(20)	0.7149(3)	0.45237(12)	0.0830(2)	0.0501(6)
C(21)	0.7406(3)	0.50007(11)	0.1600(2)	0.0480(6)
C(22)	0.7912(3)	0.29120(13)	0.0547(3)	0.0624(7)
C(23)	0.7642(2)	0.60976(10)	0.68047(19)	0.0400(5)
C(24)	0.8331(3)	0.56664(12)	0.7614(2)	0.0534(7)
C(25)	0.7622(3)	0.53984(15)	0.8367(3)	0.0658(8)
C(26)	0.6306(3)	0.55711(13)	0.8339(2)	0.0581(7)
C(27)	0.5627(3)	0.59822(12)	0.7591(2)	0.0476(6)
C(28)	0.6327(2)	0.62567(11)	0.68224(19)	0.0414(5)
C(29)	0.4484(3)	0.69170(16)	0.6102(2)	0.0659(8)

Table 3. Bond lengths [Å] and angles [°] for mjh12.

O(1)–C(19)	1.365(3)	O(1)–C(22)	1.411(3)
O(2)–C(28)	1.347(3)	O(2)–C(29)	1.435(3)
N(1)–B	1.549(3)	N(1)–C(1)	1.350(3)
N(1)–C(4)	1.395(3)	N(2)–B	1.546(3)
N(2)–C(6)	1.397(3)	N(2)–C(9)	1.348(3)
F(1)–B	1.387(3)	F(2)–B	1.392(3)
C(1)–C(2)	1.409(3)	C(1)–C(10)	1.493(3)
C(2)–C(3)	1.390(3)	C(2)–C(11)	1.504(3)
C(3)–C(4)	1.427(3)	C(3)–C(13)	1.498(3)
C(4)–C(5)	1.394(3)	C(5)–C(6)	1.396(3)
C(5)–C(23)	1.493(3)	C(6)–C(7)	1.422(3)
C(7)–C(8)	1.396(3)	C(7)–C(14)	1.500(3)
C(8)–C(9)	1.413(3)	C(8)–C(16)	1.481(3)
C(9)–C(15)	1.495(3)	C(10)–H(10A)	0.980
C(10)–H(10B)	0.980	C(10)–H(10C)	0.980
C(11)–H(11A)	0.990	C(11)–H(11B)	0.990
C(11)–C(12)	1.509(4)	C(12)–H(12A)	0.980
C(12)–H(12B)	0.980	C(12)–H(12C)	0.980
C(13)–H(13A)	0.980	C(13)–H(13B)	0.980
C(13)–H(13C)	0.980	C(14)–H(14A)	0.980
C(14)–H(14B)	0.980	C(14)–H(14C)	0.980
C(15)–H(15A)	0.980	C(15)–H(15B)	0.980
C(15)–H(15C)	0.980	C(16)–C(17)	1.388(3)
C(16)–C(21)	1.395(3)	C(17)–H(17A)	0.950
C(17)–C(18)	1.391(3)	C(18)–H(18A)	0.950
C(18)–C(19)	1.392(3)	C(19)–C(20)	1.388(3)
C(20)–H(20A)	0.950	C(20)–C(21)	1.381(3)
C(21)–H(21A)	0.950	C(22)–H(22A)	0.980
C(22)–H(22B)	0.980	C(22)–H(22C)	0.980
C(23)–C(24)	1.432(3)	C(23)–C(28)	1.377(3)
C(24)–H(24A)	0.950	C(24)–C(25)	1.390(4)
C(25)–H(25A)	0.950	C(25)–C(26)	1.376(4)
C(26)–H(26A)	0.950	C(26)–C(27)	1.357(4)
C(27)–H(27A)	0.950	C(27)–C(28)	1.404(3)
C(29)–H(29A)	0.980	C(29)–H(29B)	0.980
C(29)–H(29C)	0.980		

C(19)–O(1)–C(22)	117.0(2)	C(28)–O(2)–C(29)	117.30(19)
B–N(1)–C(1)	126.60(17)	B–N(1)–C(4)	125.46(17)
C(1)–N(1)–C(4)	107.94(17)	B–N(2)–C(6)	125.63(17)
B–N(2)–C(9)	125.83(17)	C(6)–N(2)–C(9)	108.46(17)
N(1)–B–N(2)	106.83(16)	N(1)–B–F(1)	110.38(18)
N(1)–B–F(2)	109.88(18)	N(2)–B–F(1)	110.48(18)
N(2)–B–F(2)	110.04(18)	F(1)–B–F(2)	109.21(18)
N(1)–C(1)–C(2)	109.98(18)	N(1)–C(1)–C(10)	122.5(2)
C(2)–C(1)–C(10)	127.5(2)	C(1)–C(2)–C(3)	107.25(19)
C(1)–C(2)–C(11)	125.1(2)	C(3)–C(2)–C(11)	127.6(2)
C(2)–C(3)–C(4)	106.78(18)	C(2)–C(3)–C(13)	125.3(2)
C(4)–C(3)–C(13)	127.85(19)	N(1)–C(4)–C(3)	108.03(17)
N(1)–C(4)–C(5)	120.21(18)	C(3)–C(4)–C(5)	131.75(19)
C(4)–C(5)–C(6)	121.76(18)	C(4)–C(5)–C(23)	119.16(18)
C(6)–C(5)–C(23)	118.97(18)	N(2)–C(6)–C(5)	119.92(18)
N(2)–C(6)–C(7)	107.91(17)	C(5)–C(6)–C(7)	132.16(18)

C(6)–C(7)–C(8)	106.80(18)	C(6)–C(7)–C(14)	128.56(19)
C(8)–C(7)–C(14)	124.6(2)	C(7)–C(8)–C(9)	107.31(19)
C(7)–C(8)–C(16)	127.74(19)	C(9)–C(8)–C(16)	124.94(19)
N(2)–C(9)–C(8)	109.52(18)	N(2)–C(9)–C(15)	122.53(19)
C(8)–C(9)–C(15)	127.9(2)	C(1)–C(10)–H(10A)	109.5
C(1)–C(10)–H(10B)	109.5	C(1)–C(10)–H(10C)	109.5
H(10A)–C(10)–H(10B)	109.5	H(10A)–C(10)–H(10C)	109.5
H(10B)–C(10)–H(10C)	109.5	C(2)–C(11)–H(11A)	108.8
C(2)–C(11)–H(11B)	108.8	C(2)–C(11)–C(12)	113.7(2)
H(11A)–C(11)–H(11B)	107.7	H(11A)–C(11)–C(12)	108.8
H(11B)–C(11)–C(12)	108.8	C(11)–C(12)–H(12A)	109.5
C(11)–C(12)–H(12B)	109.5	C(11)–C(12)–H(12C)	109.5
H(12A)–C(12)–H(12B)	109.5	H(12A)–C(12)–H(12C)	109.5
H(12B)–C(12)–H(12C)	109.5	C(3)–C(13)–H(13A)	109.5
C(3)–C(13)–H(13B)	109.5	C(3)–C(13)–H(13C)	109.5
H(13A)–C(13)–H(13B)	109.5	H(13A)–C(13)–H(13C)	109.5
H(13B)–C(13)–H(13C)	109.5	C(7)–C(14)–H(14A)	109.5
C(7)–C(14)–H(14B)	109.5	C(7)–C(14)–H(14C)	109.5
H(14A)–C(14)–H(14B)	109.5	H(14A)–C(14)–H(14C)	109.5
H(14B)–C(14)–H(14C)	109.5	C(9)–C(15)–H(15A)	109.5
C(9)–C(15)–H(15B)	109.5	C(9)–C(15)–H(15C)	109.5
H(15A)–C(15)–H(15B)	109.5	H(15A)–C(15)–H(15C)	109.5
H(15B)–C(15)–H(15C)	109.5	C(8)–C(16)–C(17)	121.4(2)
C(8)–C(16)–C(21)	121.2(2)	C(17)–C(16)–C(21)	117.4(2)
C(16)–C(17)–H(17A)	119.0	C(16)–C(17)–C(18)	122.0(2)
H(17A)–C(17)–C(18)	119.0	C(17)–C(18)–H(18A)	120.4
C(17)–C(18)–C(19)	119.2(2)	H(18A)–C(18)–C(19)	120.4
O(1)–C(19)–C(18)	125.0(2)	O(1)–C(19)–C(20)	115.4(2)
C(18)–C(19)–C(20)	119.6(2)	C(19)–C(20)–H(20A)	120.0
C(19)–C(20)–C(21)	120.1(2)	H(20A)–C(20)–C(21)	120.0
C(16)–C(21)–C(20)	121.5(2)	C(16)–C(21)–H(21A)	119.2
C(20)–C(21)–H(21A)	119.2	O(1)–C(22)–H(22A)	109.5
O(1)–C(22)–H(22B)	109.5	O(1)–C(22)–H(22C)	109.5
H(22A)–C(22)–H(22B)	109.5	H(22A)–C(22)–H(22C)	109.5
H(22B)–C(22)–H(22C)	109.5	C(5)–C(23)–C(24)	118.0(2)
C(5)–C(23)–C(28)	122.1(2)	C(24)–C(23)–C(28)	119.8(2)
C(23)–C(24)–H(24A)	120.8	C(23)–C(24)–C(25)	118.4(2)
H(24A)–C(24)–C(25)	120.8	C(24)–C(25)–H(25A)	120.4
C(24)–C(25)–C(26)	119.2(3)	H(25A)–C(25)–C(26)	120.4
C(25)–C(26)–H(26A)	118.1	C(25)–C(26)–C(27)	123.9(3)
H(26A)–C(26)–C(27)	118.1	C(26)–C(27)–H(27A)	121.2
C(26)–C(27)–C(28)	117.7(2)	H(27A)–C(27)–C(28)	121.2
O(2)–C(28)–C(23)	114.5(2)	O(2)–C(28)–C(27)	124.5(2)
C(23)–C(28)–C(27)	121.0(2)	O(2)–C(29)–H(29A)	109.5
O(2)–C(29)–H(29B)	109.5	O(2)–C(29)–H(29C)	109.5
H(29A)–C(29)–H(29B)	109.5	H(29A)–C(29)–H(29C)	109.5
H(29B)–C(29)–H(29C)	109.5		

Table 4. Anisotropic displacement parameters ($Å^2$) for mjh12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	0.0600(11)	0.0515(10)	0.0504(10)	–0.0134(8)	0.0023(8)	–0.0005(8)
O(2)	0.0357(8)	0.0738(12)	0.0435(9)	0.0065(8)	0.0125(7)	0.0074(8)
N(1)	0.0335(9)	0.0347(9)	0.0354(9)	0.0038(7)	0.0116(7)	–0.0037(7)
N(2)	0.0315(9)	0.0360(9)	0.0342(9)	0.0028(7)	0.0125(7)	–0.0004(7)
F(1)	0.0723(9)	0.0422(7)	0.0394(7)	0.0076(6)	0.0203(6)	–0.0046(6)
F(2)	0.0356(7)	0.0585(8)	0.0577(8)	–0.0078(7)	0.0217(6)	–0.0080(6)
B	0.0363(12)	0.0376(13)	0.0386(13)	0.0011(10)	0.0163(10)	–0.0053(10)
C(1)	0.0384(11)	0.0369(11)	0.0421(12)	0.0023(9)	0.0117(9)	–0.0057(9)
C(2)	0.0380(11)	0.0379(11)	0.0393(11)	–0.0005(9)	0.0074(9)	–0.0017(9)
C(3)	0.0329(10)	0.0391(11)	0.0342(11)	0.0012(9)	0.0071(8)	–0.0006(8)
C(4)	0.0277(10)	0.0373(11)	0.0314(10)	0.0044(8)	0.0088(8)	0.0010(8)
C(5)	0.0272(9)	0.0366(11)	0.0346(10)	0.0042(9)	0.0089(8)	0.0010(8)
C(6)	0.0269(9)	0.0361(10)	0.0334(10)	0.0030(8)	0.0102(8)	–0.0001(8)
C(7)	0.0299(10)	0.0352(11)	0.0380(11)	0.0022(9)	0.0109(8)	0.0009(8)
C(8)	0.0337(11)	0.0358(11)	0.0377(11)	0.0016(9)	0.0097(8)	0.0027(8)
C(9)	0.0353(11)	0.0381(11)	0.0360(11)	0.0004(9)	0.0128(8)	0.0018(9)
C(10)	0.0630(16)	0.0492(14)	0.0591(16)	–0.0054(12)	0.0272(13)	–0.0197(12)
C(11)	0.0515(14)	0.0442(13)	0.0452(13)	–0.0060(10)	0.0095(10)	–0.0084(11)
C(12)	0.098(3)	0.0535(17)	0.088(2)	–0.0263(17)	–0.0116(19)	0.0169(17)
C(13)	0.0479(13)	0.0549(14)	0.0378(12)	–0.0080(10)	0.0165(10)	–0.0095(11)
C(14)	0.0450(13)	0.0440(13)	0.0523(13)	–0.0047(11)	0.0212(10)	–0.0129(10)
C(15)	0.0554(14)	0.0496(14)	0.0437(13)	–0.0032(11)	0.0251(11)	–0.0066(11)
C(16)	0.0343(11)	0.0389(11)	0.0407(11)	–0.0009(9)	0.0135(9)	0.0005(9)
C(17)	0.0286(10)	0.0434(12)	0.0387(11)	0.0001(9)	0.0072(8)	0.0025(9)
C(18)	0.0318(11)	0.0376(11)	0.0506(13)	–0.0016(10)	0.0082(9)	0.0032(9)
C(19)	0.0412(12)	0.0455(12)	0.0410(12)	–0.0076(10)	0.0111(9)	–0.0044(10)
C(20)	0.0612(15)	0.0520(14)	0.0359(12)	0.0031(11)	0.0066(11)	–0.0019(12)
C(21)	0.0638(16)	0.0388(12)	0.0410(13)	0.0040(10)	0.0093(11)	0.0004(11)
C(22)	0.0521(15)	0.0561(16)	0.0746(19)	–0.0223(14)	0.0012(13)	0.0032(12)
C(23)	0.0406(12)	0.0417(12)	0.0420(12)	–0.0041(10)	0.0188(9)	–0.0093(9)
C(24)	0.0590(15)	0.0484(14)	0.0616(16)	0.0200(12)	0.0332(12)	0.0122(11)
C(25)	0.0624(17)	0.0696(18)	0.0730(19)	0.0314(15)	0.0326(14)	0.0173(14)
C(26)	0.0511(14)	0.0635(16)	0.0669(17)	0.0089(14)	0.0291(13)	0.0037(12)
C(27)	0.0463(13)	0.0512(14)	0.0482(13)	–0.0008(11)	0.0163(10)	0.0006(11)
C(28)	0.0394(12)	0.0438(12)	0.0427(12)	–0.0026(10)	0.0123(9)	–0.0027(9)
C(29)	0.0496(15)	0.098(2)	0.0515(15)	0.0118(15)	0.0139(12)	0.0260(15)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for mjh12.

	x	y	z	U
H(10A)	1.1821	0.7841	0.5036	0.083
H(10B)	1.2112	0.8264	0.6140	0.083
H(10C)	1.0906	0.8436	0.5124	0.083
H(11A)	1.1297	0.8510	0.7758	0.056
H(11B)	1.0416	0.8244	0.8615	0.056
H(12A)	0.9753	0.9259	0.8065	0.126
H(12B)	0.8528	0.8789	0.7677	0.126
H(12C)	0.9375	0.9040	0.6780	0.126
H(13A)	0.8607	0.7637	0.8674	0.069
H(13B)	0.8515	0.6903	0.8510	0.069
H(13C)	0.7368	0.7339	0.7818	0.069
H(14A)	0.6250	0.5331	0.5241	0.068
H(14B)	0.7441	0.4843	0.5620	0.068
H(14C)	0.6519	0.4801	0.4390	0.068
H(15A)	1.0923	0.6080	0.2797	0.071
H(15B)	0.9608	0.6373	0.2028	0.071
H(15C)	0.9883	0.5646	0.1983	0.071
H(17A)	0.8649	0.4198	0.3814	0.044
H(18A)	0.8284	0.3387	0.2522	0.048
H(20A)	0.6724	0.4607	0.0075	0.060
H(21A)	0.7171	0.5411	0.1360	0.058
H(22A)	0.7815	0.2674	–0.0153	0.094
H(22B)	0.7494	0.2685	0.1091	0.094
H(22C)	0.8871	0.2975	0.0859	0.094
H(24A)	0.9250	0.5566	0.7634	0.064
H(25A)	0.8041	0.5100	0.8896	0.079
H(26A)	0.5845	0.5392	0.8874	0.070
H(27A)	0.4711	0.6081	0.7589	0.057
H(29A)	0.4277	0.7269	0.5588	0.099
H(29B)	0.4462	0.7051	0.6872	0.099
H(29C)	0.3814	0.6590	0.5880	0.099

Table 6. Torsion angles [°] for mjh12.

C(6)–N(2)–B–N(1)	−4.7(3)	C(6)–N(2)–B–F(1)	−124.8(2)
C(6)–N(2)–B–F(2)	114.5(2)	C(9)–N(2)–B–N(1)	178.86(18)
C(9)–N(2)–B–F(1)	58.8(3)	C(9)–N(2)–B–F(2)	−61.9(3)
C(1)–N(1)–B–N(2)	−178.25(19)	C(1)–N(1)–B–F(1)	−58.1(3)
C(1)–N(1)–B–F(2)	62.4(3)	C(4)–N(1)–B–N(2)	2.4(3)
C(4)–N(1)–B–F(1)	122.6(2)	C(4)–N(1)–B–F(2)	−116.9(2)
B–N(1)–C(1)–C(2)	−179.45(19)	B–N(1)–C(1)–C(10)	1.4(3)
C(4)–N(1)–C(1)–C(2)	0.0(2)	C(4)–N(1)–C(1)–C(10)	−179.2(2)
N(1)–C(1)–C(2)–C(3)	−0.8(3)	N(1)–C(1)–C(2)–C(11)	−179.7(2)
C(10)–C(1)–C(2)–C(3)	178.4(2)	C(10)–C(1)–C(2)–C(11)	−0.6(4)
C(1)–C(2)–C(3)–C(4)	1.2(2)	C(1)–C(2)–C(3)–C(13)	−177.2(2)
C(11)–C(2)–C(3)–C(4)	−179.9(2)	C(11)–C(2)–C(3)–C(13)	1.7(4)
B–N(1)–C(4)–C(3)	−179.77(18)	B–N(1)–C(4)–C(5)	1.0(3)
C(1)–N(1)–C(4)–C(3)	0.8(2)	C(1)–N(1)–C(4)–C(5)	−178.41(18)
C(2)–C(3)–C(4)–N(1)	−1.3(2)	C(2)–C(3)–C(4)–C(5)	177.8(2)
C(13)–C(3)–C(4)–N(1)	177.1(2)	C(13)–C(3)–C(4)–C(5)	−3.8(4)
N(1)–C(4)–C(5)–C(6)	−2.9(3)	N(1)–C(4)–C(5)–C(23)	173.25(19)
C(3)–C(4)–C(5)–C(6)	178.1(2)	C(3)–C(4)–C(5)–C(23)	−5.8(3)
C(4)–C(5)–C(6)–N(2)	0.7(3)	C(4)–C(5)–C(6)–C(7)	−178.8(2)
C(23)–C(5)–C(6)–N(2)	−175.46(18)	C(23)–C(5)–C(6)–C(7)	5.1(3)
B–N(2)–C(6)–C(5)	3.6(3)	B–N(2)–C(6)–C(7)	−176.86(18)
C(9)–N(2)–C(6)–C(5)	−179.50(18)	C(9)–N(2)–C(6)–C(7)	0.1(2)
N(2)–C(6)–C(7)–C(8)	−0.3(2)	N(2)–C(6)–C(7)–C(14)	−178.4(2)
C(5)–C(6)–C(7)–C(8)	179.2(2)	C(5)–C(6)–C(7)–C(14)	1.1(4)
C(6)–C(7)–C(8)–C(9)	0.4(2)	C(6)–C(7)–C(8)–C(16)	180.0(2)
C(14)–C(7)–C(8)–C(9)	178.6(2)	C(14)–C(7)–C(8)–C(16)	−1.8(4)
B–N(2)–C(9)–C(8)	177.11(19)	B–N(2)–C(9)–C(15)	−0.7(3)
C(6)–N(2)–C(9)–C(8)	0.2(2)	C(6)–N(2)–C(9)–C(15)	−177.6(2)
C(7)–C(8)–C(9)–N(2)	−0.4(2)	C(7)–C(8)–C(9)–C(15)	177.3(2)
C(16)–C(8)–C(9)–N(2)	−179.94(19)	C(16)–C(8)–C(9)–C(15)	−2.3(4)
C(1)–C(2)–C(11)–C(12)	92.6(3)	C(3)–C(2)–C(11)–C(12)	−86.1(3)
C(7)–C(8)–C(16)–C(17)	−58.7(3)	C(7)–C(8)–C(16)–C(21)	122.5(3)
C(9)–C(8)–C(16)–C(17)	120.8(2)	C(9)–C(8)–C(16)–C(21)	−58.0(3)
C(8)–C(16)–C(17)–C(18)	−175.40(19)	C(21)–C(16)–C(17)–C(18)	3.5(3)
C(16)–C(17)–C(18)–C(19)	−1.2(3)	C(22)–O(1)–C(19)–C(18)	−15.6(3)
C(22)–O(1)–C(19)–C(20)	165.0(2)	C(17)–C(18)–C(19)–O(1)	178.2(2)
C(17)–C(18)–C(19)–C(20)	−2.4(3)	O(1)–C(19)–C(20)–C(21)	−176.9(2)
C(18)–C(19)–C(20)–C(21)	3.7(4)	C(19)–C(20)–C(21)–C(16)	−1.4(4)
C(8)–C(16)–C(21)–C(20)	176.7(2)	C(17)–C(16)–C(21)–C(20)	−2.2(4)
C(4)–C(5)–C(23)–C(24)	−91.3(3)	C(4)–C(5)–C(23)–C(28)	86.0(3)
C(6)–C(5)–C(23)–C(24)	84.9(3)	C(6)–C(5)–C(23)–C(28)	−97.8(3)
C(5)–C(23)–C(24)–C(25)	−179.7(3)	C(28)–C(23)–C(24)–C(25)	2.9(4)
C(23)–C(24)–C(25)–C(26)	−2.3(5)	C(24)–C(25)–C(26)–C(27)	1.8(5)
C(25)–C(26)–C(27)–C(28)	−1.6(4)	C(29)–O(2)–C(28)–C(23)	−173.8(2)
C(29)–O(2)–C(28)–C(27)	6.4(4)	C(5)–C(23)–C(28)–O(2)	0.1(3)
C(5)–C(23)–C(28)–C(27)	179.9(2)	C(24)–C(23)–C(28)–O(2)	177.4(2)
C(24)–C(23)–C(28)–C(27)	−2.8(4)	C(26)–C(27)–C(28)–O(2)	−178.1(2)
C(26)–C(27)–C(28)–C(23)	2.1(4)		