Novel Applications of Triarylfluoroboranes in Organic Synthesis

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I Acknowledgments

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II Abstract

The work described in this thesis is concerned with the utilisation of bulky boron-based Lewis acids as catalysts in organic synthesis. Chapter one provides a general introduction towards the bulky boron-based Lewis acids and diazo compounds, wherein their general synthesis, reactivity, and utilisation in the organic synthesis will be discussed in more detail. Furthermore, the introductory part of this thesis will cover frustrated Lewis pairs, including how they can activate small molecules *via* two different pathways and how such divergent activation was later utilised in the organic synthesis. Chapter two and three will cover the use of tris(pentafluorophenyl)borane as a catalyst for alkenylation and cyclopropenation of diazo esters, wherein the optimisation reactions, substrate scope, and reaction mechanism will be discussed. Lastly, frustrated Lewis pairs mediated cross-coupling reactions of arylacetylenes and aryl esters will be covered together with conducted studies for a determination of the reaction mechanism.

III List of publications

1. **K. Stefkova**, L. Gierlichs, D. Willcox, R. L. Melen (2020). Borocation in Catalysis. In Encyclopedia of Inorganic and Bioinorganic Chemistry.

2. A. Dasgupta[*], **K. Stefkova**[*], R. Babbahmadi, L. Gierlichs, A. Ariafard, R. L. Melen, *Angew. Chem. Int. Ed.* **2020**, *59*, 15492–15496.
3. **K. Stefkova**, J. L. Carden. R. L. Melen (2021). Frustrated Lewis pairs in catalysis. In Comprehensive Inorganic Chemistry III (3rd Ed.).

4. M. J. Heard, **K. Stefkova,** Y. van Ingen, R. L. Melen (2021). Frustrated Lewis Pairs in Organic Synthesis. In Comprehensive Organometallic Chemistry IV (4th Ed.).
5. A. Dasgupta, **K. Stefkova**, R. Babaahmadi, B. F. Yates, N. J. Buurma, A. Ariafard, E. Richards, R. L. Melen, *J. Am. Chem. Soc.* **2021**, *143*, 4451−4464.

6. **K. Stefkova**, M. J. Heard, A. Dasgupta, R. L. Melen, *Chem. Commun.* **2021**, *57*, 6736–6739.
7. **K. Stefkova**[*], M. G. Guerzoni[*], Y. van Ingen, E. Richards, R. L. Melen, *Org. Lett.* **2023**, *25*, 500–505.

[∗] Equal contribution

IV List of Abbreviations

AN	Acceptor number
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
1,2-DCE	1,2-dichloroethene
DDQ	2,3-dichloro5,6-dicyanoquinone
DFT	Density functional theory
EI	Electron ionization
EDA	Electron donor-acceptor
EPR	Electron paramagnetic resonance
ESR	Electron spin resonance
FDA	U.S Food and Drug Administration
FIA	Fluoride ion affinity
FLP	Frustrated Lewis pair
FRP	Frustrated radical pair
GEI	Global electrophilicity index
HIA	Hydride ion affinity
HOMO	Highest occupied molecular orbital
HRMS	high-resolution mass spectroscopy
LA	Lewis acid
LB	Lewis base
LD_{50}	Lethal dose at 50%
LUMO	Lowest unoccupied molecular orbital
Mes	mesityl
Ms	mesyl

NMR	Nuclear magnetic resonance
ppm	parts per million
TBAF	tetrabutylammonium fluoride
TFT	trifluorotoluene
THF	tetrahydrofuran
TMP	2,2,6,6-tetramethylpiperidine
TMS	trimethylsilyl
Ts	tosyl

V List of Contents

1.0 General introduction

1.1.0 Importance of catalysis

Over the past several decades, catalysis has become a central focus of modern synthetic chemistry. It is estimated that around 90% of all commercially available chemicals have been prepared with at least one catalytic step their production.[1] Such observed increase of interest in catalysis can be attributed to the catalyst's ability to not only significantly improve the efficiency of well-established reactions but also allow novel chemical transformations, such cross-coupling or metathesis, to become permittable.[2,3] Thus, industries highly benefit from the usage of catalysts as the production costs, reaction times, or the formation of unwanted waste can be drastically reduced.

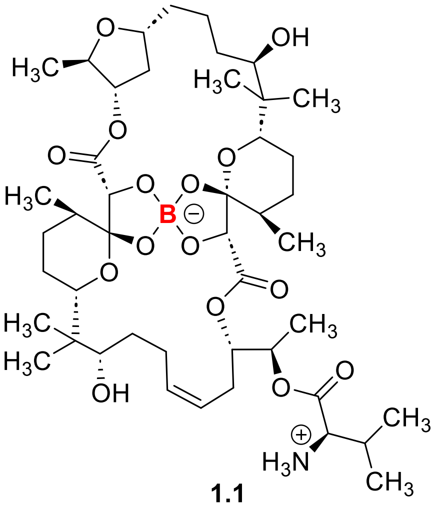
In the pharmaceutical industry, as a result of their readily accessible *d*-orbitals and an ability to easily undergo redox processes, precious transition metals have been extensively utilised to mediate such catalytic transformations. However, the use of precious transition metals comes with its own disadvantages. Due to their limited and low abundancy on Earth, precious transition metals are expensive commodities, and they are often susceptible to fluctuation in the supply. Apart from these economic issues, simultaneous concerns have been raised about their negative environmental impact as their mining and refinement often requires the use of fossil fuels which results in the increased production of greenhouse gases. Moreover, these metals are relatively toxic, which is particularly detrimental for the pharmaceutical industry as only up to ten ppm (parts per million) of the residual metal is allowed in the final pharmaceutical product.[4] This often leads to the requirement of additional purification, which then results in increased costs as well as the production of unwanted waste. Therefore, over the past two decades there has been a tremendous focus for a development of more sustainable catalytic alternatives. To amplify the importance of such catalytic alternatives, a recent Nobel

Prize in Chemistry 2021 has been awarded for the development of asymmetric catalysis utilising chiral organic molecules rather than the precious transition metals.[5]

1.1.1 Main-group catalysis as a plausible alternative

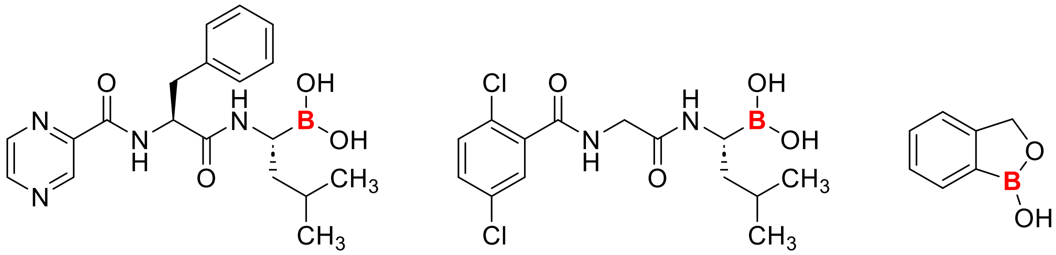
Apart from small organic molecules, main-group based catalysts have also become of an emerging interest for the development of more sustainable catalysis as they are generally less toxic and usually found in larger quantities on Earth.[6] More precisely, the fifth element, boron, has showed to be promising alternative towards transition metals. It has been estimated that boron's prevalence in Earth's crust is 10 ppm. This is roughly 600−10,000 more than most of precious transition metals, such as palladium, gold, or rhodium.[7] However, in nature, boron in its elemental form is not present and rather it is found in its borate anionic form $(B_xO_x)^-$ as a mineral. Overall, around 100 different borate minerals have been identified, from which the most widely prevalent and commercialised is borax $Na_2B_4O_5(OH)_4{\cdot}3H_2O$, usually used in household cleaning products.[8]

Boron has been also found in natural products, such as Boromycin **1.1**, which is secreted from bacteria *Streptomyces antibioticus*, and since it has shown to be a potential antibacterial and anti-HIV agent.[9] This has later started a new research interest in the boron-containing therapeutics and so far, there have been five boronic acid-derived pharmaceuticals approved by the FDA (U.S. Food and Drug Administration), including anticancer medications Bortezomib **1.2** and Izaxomib **1.3**, or antifungal Tavaborole **1.4**. Moreover, in general, boron containing compounds exhibit low toxicity towards mammals. For instance, in rats, oral LD_{50} of sodium chloride, a common table salt is 3,000 mg/kg, whereas LD_{50} of boric acid is 4,000 mg/kg.[10,11] Thus, their general low toxicities and higher abundance make boron containing catalysts perfect alternatives towards precious transition metals, especially in the pharmaceutical industry.



1.1

Figure 1.1*:* Natural product Boromycin **1.1**



1.2 **1.3** **1.4**

Figure 1.2: FDA approved boronic acid-derived therapeutics

1.2.0 Boron-based Lewis acids

Being a group 13 element with the electronic configuration of $1s^2\ 2s^2\ 2p^1$, boron is trivalent, whilst having one vacant *p*-orbital. Such characteristics make the neutral uncoordinated boron compounds, such as boron trihalides highly electrophilic species, known as Lewis acids (LAs). Furthermore, the reactivity and stability of Lewis acids can be tuned by a judicious choice of a functional group attached to the boron centre. Apart for the steric aspects, there are two crucial electronic factors to consider when predicting the Lewis acidity of boranes. First, the electronegativity plays an important role, as more electronegative the ligand is, the more electron density is pulled from the boron centre *via* σ-bonding, making the empty *p*-orbital more electron-deficient. The other factor is the ability of the ligand to participate in the π-backbonding, in which the electron density is donated into the empty *p*-orbital of boron centre from a lone pair of the ligand, thus making the boron's *p*-orbital less electron deficient. This factor is dependent on the efficiency of the orbital overlap which is decreasing as the size of the ligand's orbital is increasing. Hence in the case of boron trihalides, boron trifluoride is less acidic than boron tribromide, which is subsequently weaker Lewis acid than boron tribromide **(Figure 1.3)**.

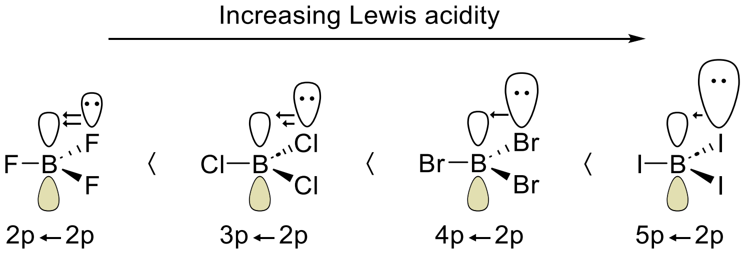
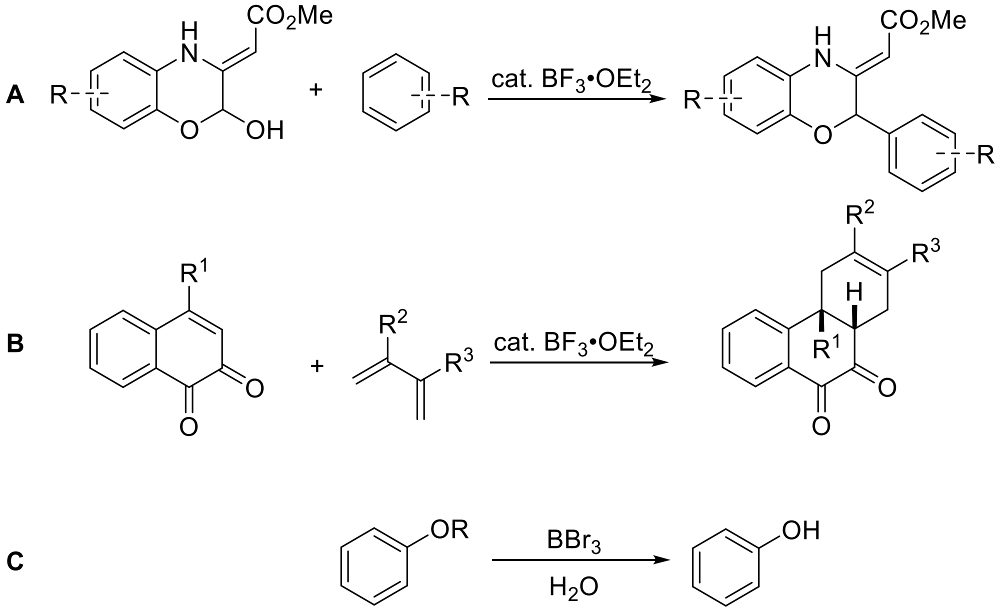


Figure 1.3: Representation of π-backbonding in boron trihalides and their relative Lewis acidity

Due to their high reactivity, boron trihalides have found numerous applications as catalysts in organic synthesis. Friedel–Crafts **(Scheme 1.1, A)**, Diels–Alder **(Scheme 1.1, B)**, or dealkylation of alkyl ethers **(Scheme 1.1, C)**, are just a few examples, which have been shown to be catalysed by the boron trihalides.[12,13,14] Moreover, boron trihalides are commercially available, mostly as the acid-base adducts, making them quite convenient catalysts. Although, it is worth mentioning that they are highly unstable and sensitive towards moisture. Even more reactive BCl_3, BBr_3, and BI_3 react vigorously with water and an explosion can occur if they are not handled with extra care and under inert conditions.[15]

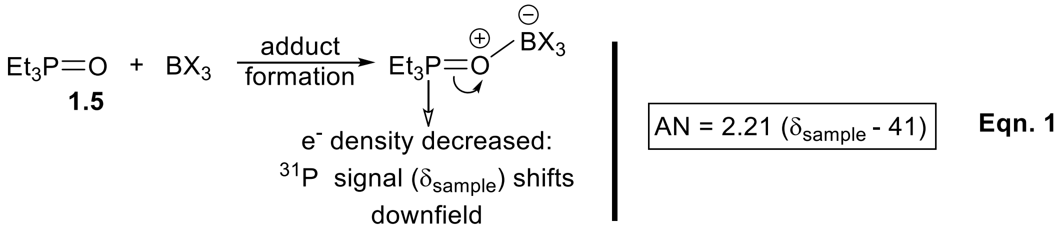


Scheme 1.1: Well established reactions catalysed by boron trihalides

1.2.1 Determination of Lewis acidity: experimental and computational methodologies

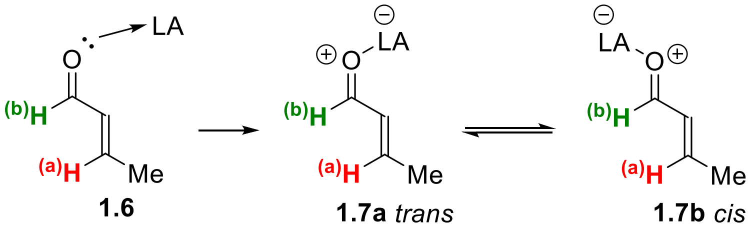
There are various experimental and computational methods on how to quantitively measure the acidity of the boron-based Lewis acids. The Gutmann-Beckett is one of the most convenient experimental procedures used for the determination of Lewis acidity. It is based on the original Gutmann methodology, which quantified the Lewis acidity of solvents by their Acceptor Number (AN).[16] The simplified experiment consists of mixing a Lewis acid with the excess of triethylphosphine oxide (Et_3PO) **1.5**, used as a Lewis base (LB) probe, in order to form an acid-base adduct. Due to the oxygen atom donating the electron density to the empty *p*-orbital of the Lewis acid, a decrease in electron density on the P atom occurs, causing a deshielding, which results in a downfield chemical shift observed in ^{31}P nuclear magnetic resonance (NMR) **(Scheme 1.2)**. Then, from the observed ^{31}P chemical shift, AN is calculated by using an equation 1 **(Scheme 1.2, Eqn. 1)**, in which 41.0 value represents the ^{31}P chemical shift of the free, uncoordinated Et_3PO in hexane (AN=0).[17] As such, higher AN value indicates a higher

Lewis acidity. This methodology has been widely used to quantify a Lewis acidity of boron trihalides, fluoroarylboranes as well as borenium cations.[18] The drawback of Gutmann-Beckett is that it cannot be used for more sterically hindered Lewis acids, such as the aluminium superacids $Al(OCAr_3^F)_3$.[19] In this case, aluminium atom is greatly shielded by the adjacent bulky $(OCAr_3^F)_3$ group, and hence it cannot form an adduct with the phosphine oxide, thus the calculation of AN is not accurate.



Scheme 1.2: Deshielding at P centre during Lewis adduct formation and **Eqn. 1**

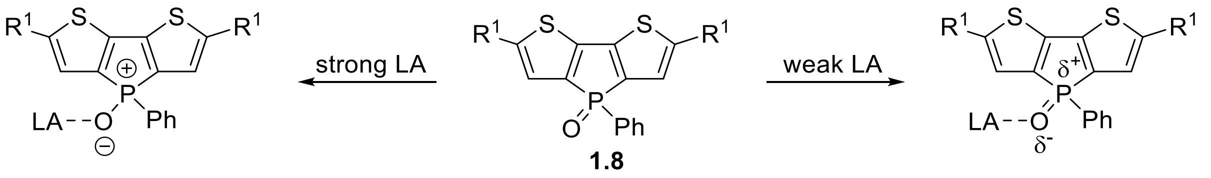
The Childs method is another useful experimental measurement of a Lewis acidity.[20] Again, it is an NMR-based methodology, in which the Lewis acid of interest is reacted with the crotonaldehyde **1.6**. Upon the coordination of the Lewis acid to the carbonyl, and a subsequent formation of the acid-base adduct **1.7**, an induced chemical shift of the protons is observed in the ^1H NMR. The relative acidity of the studied Lewis acid is then calculated by **equation 2**, in which the magnitude of induced chemical shift of $\mathbf{H^{(a)}}$ is compared to that of BBr_3, whose value is assigned to 1.00 on the acidity scale **(Scheme 1.3, Eqn. 2)**. The acidity is not determined from the signal belonging to the more adjacent $\mathbf{H^{(b)}}$ because this aldehydic proton is highly influenced by the local anisotropy. This is because the acid can bind to the carbonyl in *trans* **1.7a** or *cis* **1.7b** fashion relative the proton $\mathbf{H^{(b)}}$. This causes the complexation-induced shift of $\mathbf{H^{(b)}}$ to vary randomly, which further results in the calculation errors.[20]



$$\boxed{\text{Relative acidity [LA]} = \frac{\Delta\delta\ ^{(a)}\text{H of LA adduct}}{\Delta\delta\ ^{(a)}\text{H of BBr}_3\text{ adduct}}}$$ **Eqn. 2**

Scheme 1.3: Coordination and complexation of Lewis acid towards crotonaldehyde **1.6** and **Eqn. 2**

More recently, Baumgartner and Caputo introduced a fluorescence-based methodology in order to determine a Lewis acidity.[21] It utilises a fluorescent dithienophosphole oxide scaffold **1.8** as a Lewis base, which upon the Lewis acid coordination, a fluorescent adduct is formed. Depending on a strength of the Lewis acid, a polarity of the P=O bond will change upon the complexation **(Scheme 1.4)**. As such, a stronger Lewis acid will polarise the P=O bond by a higher magnitude, resulting in an increased σ^*–π^* interaction and lowering of the lowest unoccupied molecular orbital (LUMO) energy, which essentially translates into red-shifted emission. Overall, this methodology was shown to be highly reliable acidity quantification for a wide range of boron-based Lewis acids ranging from BPh_3 to $[Ph_3C]^+[B(C_6F_5)_4)]^-$.



Scheme 1.4: Complexation of a Lewis acid with a fluorescent dithienophosphole **1.8**

Despite the aforementioned experimental methodologies being readily accessible and easy to run, their drawbacks include calculation errors in the obtained values due to physical factors such as sterical shielding, hardness of the Lewis base, or the polarity of the solvent in which the experiments are carried out.[22] To overcome these shortcomings and to obtain more reliable intrinsic values of Lewis acidities, computational calculations, such as fluoride ion affinity (FIA), hydride ion affinity (HIA), or global electrophilicity index (GEI) have been also extensively utilised for the acidity determination.[23,24] The FIA methodology, first reported by Barlett in 1984, consisted of calculating negative enthalpy of the reaction between a naked fluoride ion and a Lewis acid in a gas phase **(Eqn. 3)**.[25] However, the calculation of the electron affinity of F^- showed to be quite difficult, thus Christe *et al.* later simplified the calculations by rather using density functional theory (DFT) calculation of ionisation of COF_2 as a reference, whose value was also experimentally determined to be -209 kJ/mol **(Eqn. 4)**. Moreover, the HIA can be calculated through the isodesmic reaction between a Lewis acid and $[HBEt_3^-]$ **(Eqn. 5)**.[26]

$$\mathrm{LA} + \mathrm{F}^- \longrightarrow [\mathrm{LA{-}F}]^- \qquad \textbf{Eqn. 3}$$

$$\mathrm{LA} + \mathrm{COF_3}^- \longrightarrow [\mathrm{LA{-}F}]^- + \mathrm{COF_2} \qquad \textbf{Eqn. 4}$$

$$\mathrm{COF_2} + \mathrm{F}^- \longrightarrow \mathrm{COF_3}^- \qquad \textbf{-209 kJ/mol}$$

$$\mathrm{LA} + [\mathrm{HBEt_3}^-] \longrightarrow [\mathrm{LA{-}H}]^- + \mathrm{BEt_3} \qquad \textbf{Eqn. 5}$$

On the other hand, GEI describes the ability of Lewis acid to accept electrons, which is based on the derivation of index (ω) (**Eqn. 6)**, in which μ represents the chemical potential and η relates to chemical hardness, obtained from the energy level difference between the highest occupied molecular orbital (HOMO) and LUMO of the studied Lewis acid.[25] The advantage of GEI over FIA or HIA is its accessibility as the needed values are readily calculated and do not require extensive computational calculations as FIA or HIA methodologies do. This both saves time and cost needed for the computer equipment. Moreover, GEI completely removes the dependency on a Lewis base, which again results in less time needed to carry out the calculations.

$$\omega = \mu^2 / 2\eta \qquad \textbf{Eqn. 6}$$

$$\eta = E_{LUMO} - E_{HOMO}$$

1.3.0 Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$)

1.3.1 Introduction

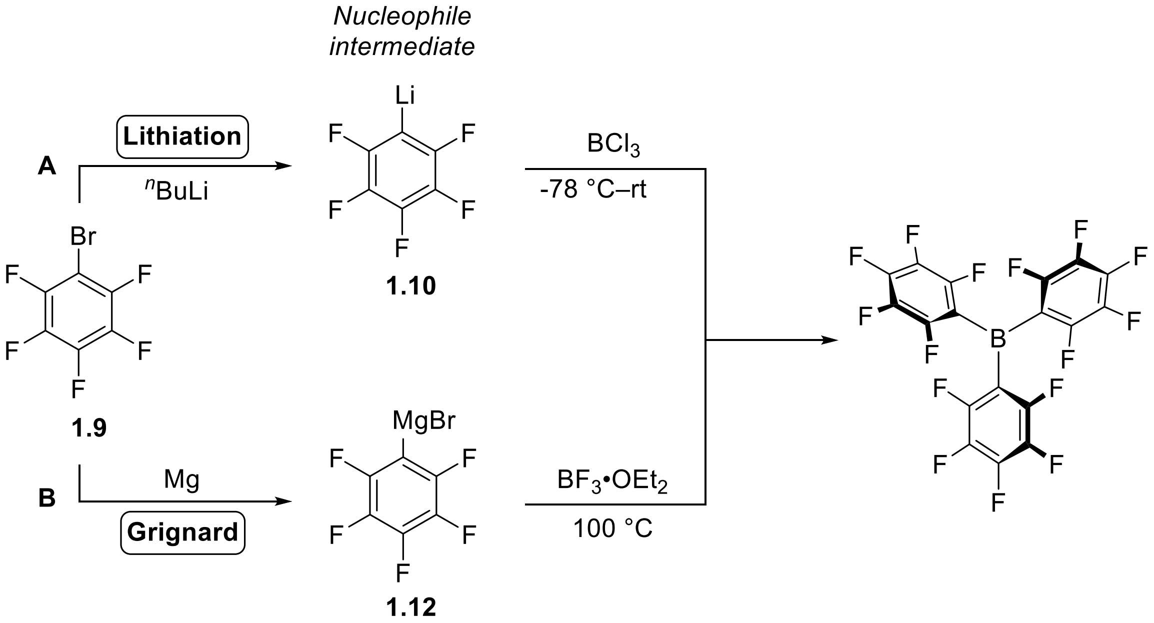
Boron trihalides represent a quintessential class of Lewis acids and to this date they have been extensively utilised in both organic and inorganic transformations. Nevertheless, their high moisture sensitivity, volatility and a production of highly toxic hydrogen halide by-products make these reagents quite difficult to work with.[27] Furthermore, for an easier handling, boron trihalides are usually obtained in adduct form with weaker Lewis bases, which also results in their decreased Lewis acidity. Therefore, there has been a tremendous interest in a plausible alternative towards the boron trihalides. First, a synthesis of perfluorinated alkyl boranes $B(R^f)_3$ was attempted in 1950s.[28] A strong inductive effect of the electron withdrawing CF_3 group near the boron centre should have rendered a stronger acidic boron centre, whilst the covalent B–C bond should have improved the stability of the acid, as the CF_3 group would be less prone towards the nucleophilic substitution when compared to B–X bond (X=halide). However, it was shown that the uncoordinated $B(CF_3)_3$ undergoes thermal decomposition **(Eqn. 7)**, in which the fluorine from CF_3 group readily migrates towards the boron, whilst the CF_2 group is eliminated in the form of a polymer and simultaneously BF_3 is released. Thus, the perfluorinated alkyl boranes have only been isolated as adducts, most prevalently with nitrogen-based π-donor ligands, such as B $(C_nF_{2n+1})_3 \cdot NH_3$ or $B(C_nF_{2n+1})_3 \cdot NHMe_2$.[29,30]

$$B(CF_3)_3 \longrightarrow BF_3 + (CF_2)_n \qquad \textbf{Eqn. 7}$$

Subsequently in 1960s, Massey *et al.* reported a formation of tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, which showed to have remarkable properties when compared to the commercially available boron trihalides.[31,32] Whilst the Lewis acidity of $B(C_6F_5)_3$ is comparable to that of $BF_3{\cdot}OEt_2$, its thermal stability is significantly improved.[33] In fact, it was demonstrated that the bulkier fluorinated borane does not decompose even at temperatures of up to 150 °C.[27,32] $B(C_6F_5)_3$ also shows to be inert towards molecular oxygen and it is more tolerant towards the moisture. This can be attributed to the less reactive B–C bond, which does hydrolyse into HC_6F_5 and a non-toxic boric acid [$B(OH)_3$] but at a much slower rate than its halogenated substitute. Furthermore, the less reactive B–C bonds enable $B(C_6F_5)_3$ to be more substrate tolerant, and thus could be suitable for catalytic transformations, which are normally constrained to the more reactive boron trihalides. Lastly, $B(C_6F_5)_3$ is isolated as a white solid, which makes it a lot easier to handle than gaseous boron trihalides, or their pyrophoric adduct derivatives. Despite these advantages, the catalytic potential of $B(C_6F_5)_3$ had not been investigated for almost 30 years, until the early 1990s, when Marks *et al.* showed its applicability as a co-catalyst in olefin polymerisation in the presence of Group 4 metallocene alkyls.[34,35] Since then, the popularity of $B(C_6F_5)_3$ as a Lewis acid catalyst has sky rocketed, which has also led to the design and synthesis of other triarylflurophenyl borane derivatives.

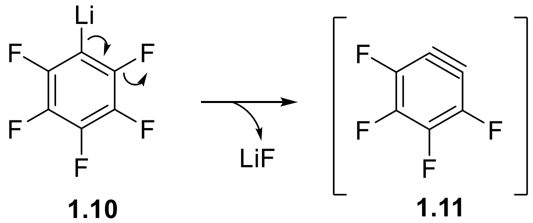
1.3.2 Synthesis of $B(C_6F_5)_3$ and other triarylfluoroboranes

In general, there are two main synthetic strategies to prepare tris(pentalfluorophenyl)borane, mainly differing in the choice of a nucleophilic intermediate **(Scheme 1.5)**. In the first report of $B(C_6F_5)_3$ synthesis, a lithiation route was applied **(Scheme 1.5, A)**.[31] In this procedure, pentafluorophenyl bromide **1.9** is lithiated with *n*Buli in hexane. The lithiation must be carried out at -78 °C as a pentafluorophenyllithium intermediate **1.10** is not stable at ambient temperature.[36] Subsequently, the generated intermediate **1.10** is reacted with BCl_3, which is suspended in cold pentane. A precipitation of lithium chloride by-product is then observed when the reaction mixture is warmed to a room temperature. Further filtration and sublimation of the crude under vacuum at 80 °C affords $B(C_6F_5)_3$ as a white solid. Although, this methodology is relatively safe, its scalability is questionable, as it is known that fluorophenyllithium intermediates undergo thermally induced β-elimination of lithium fluoride even at lower temperatures, resulting in the formation highly unstable and explosive benzyne **1.11 (Scheme 1.6)**.[37] Thus, it is not recommended to use the lithiation route for the synthesis of $B(C_6F_5)_3$ or other triarylfluoroboranes, which possess any *ortho*-fluorines, especially if their synthesis is carried at a larger scale.



Scheme 1.5: General synthesis of $B(C_6F_5)_3$

As such, a Grignard route is used as an alternative, **(Scheme 1.5, B)**, in which the transmetallation step is carried out with the Grignard reagent, pentafluorophenylmagnesium bromide **1.12**.[38] Subsequently, to the Grignard intermediate **1.12**, a solution of $BF_3{\cdot}OEt_2$ in toluene is added, and then the reaction is refluxed for approximately one hour. This further suggests that the intermediate **1.12** is thermally more stable and thus a safer alternative towards the boranes at a larger scale.


1.10 1.11

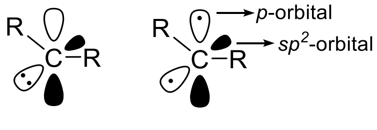
Scheme 1.6: Benzyne formation *via* lithium fluoride elimination

The syntheses of other homoleptic triarylfluoroboranes boranes are carried out in similar fashion to the aforementioned lithiation or Grignard formation routes, with some modifications in the reaction conditions or purification steps in order to maximise their purity and the obtained yields. These different strategies have been extensively reviewed and thus they will not be discussed in further detail.[39]

Surprisingly, despite $B(C_6F_5)_3$ being first synthesised in 1960s, its catalytic potential was discovered more than 30 years later by Piers *et al.* in the hydrosilylation of carbonyls.[40] Since then, $B(C_6F_5)_3$ has found to be an effective catalyst in a broad scope of chemical transformations, which have been extensively reviewed.[27,41,42] More recently, it has been also demonstrated that $B(C_6F_5)_3$ is a capable substitute to transition metals in the activation of diazo compounds, which can be further utilised for C–H, X–H activation as well as cyclisation reactions.

1.4.0.0 Diazo compounds

Diazo compounds are defined as neutrally charged organic molecules bearing two nitrogen atoms. They are well-known reactive carbene precursors, which makes them useful as versatile building blocks in organic synthesis. Carbenes are highly unstable and short-lived, whose instability can be contributed to their electronic configuration structure **(Figure 1.4)**. They are neutral, divalent carbon species with six valent electrons, which possess two non-bonding electrons. Depending on where these non-bonding electrons are located, carbenes can be further classified as singlet **(Figure 1.4**, **I)** or triplet **(Figure 1.4**, **II)**. In the singlet carbene, both electrons are in the same sp^2 orbital, leaving the *p*-orbital empty, whereas the triplet carbene has one unpaired electron in each of the sp^2 and *p*-orbitals. Hence, carbene's instability can be contributed to their coordinative unsaturation as well as the electron deficiency.[43]



I **II**

Figure 1.4: Electronic configuration structures of carbenes

1.4.1.0 Stability of diazo compounds

Diazo compounds, the carbene precursors, are highly reactive and in general they tend to undergo thermal and light-mediated decomposition with release of N_2. However, the stability of diazo reagents is highly tuneable by their substitution pattern. The electronic resonance structure of the diazo compound shows a positive charge on the central nitrogen atom, whereas the negative charge is distributed between the carbon and the terminal nitrogen **(Figure 1.5)**.

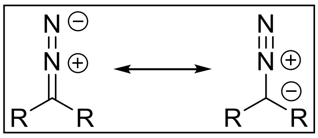
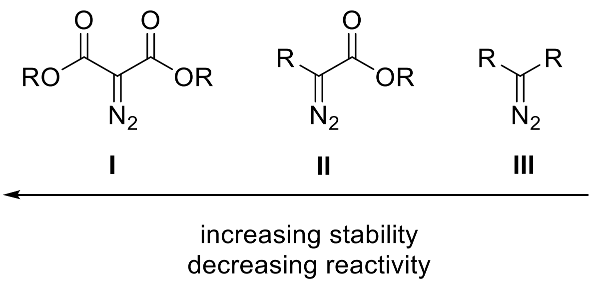


Figure 1.5: Electronic structure of diazo compounds

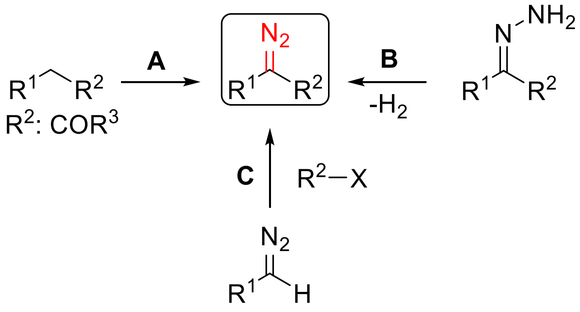
The more the negative charge is delocalised, the more stable the resulting diazo species is. As such, diazo malonates **(Scheme 1.7, I)**, containing two acceptor carbonyl groups exhibit better stability than α-diazo carbonyls **(Scheme 1.7, II)**, which are more stable in comparison to the simple diazo alkanes **(Scheme 1.7, III)**, such as diazomethane, which is a highly explosive gas.[44,45] As such, special caution should be taken when handling diazo reagents.



Scheme 1.7: Stability of diazo compounds

1.4.2.0 Synthesis of diazo compounds

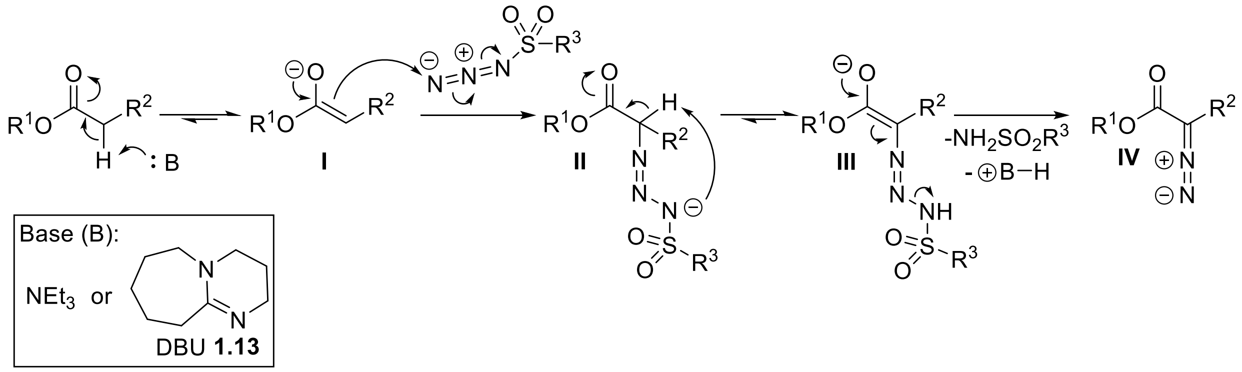
As a result of diazo compounds being such useful building blocks in organic synthesis, there has been a continuous development on their most efficient and safest preparation. Depending on the diazo substitution and stabilisation pattern, several synthetic routes have been developed, including *via* diazo-group transfer reactions **(Scheme 1.8**, **A)**, dehydrogenation of hydrazones **(Scheme 1.8**, **B)**, or *via* an electrophilic substitution of diazomethyl compounds **(Scheme 1.8**, **C)**.



Scheme 1.8: Synthetic routes towards diazo compounds

1.4.2.1 Synthesis of diazo compounds *via* a diazo-group transfer reagent

A base-assisted diazo transfer reaction, also known as Regitz diazo transfer, is used for functionalising activated methylene compounds utilising sulfonyl azide diazo group transfer reagents, and it is the most popular synthetic route towards α-carbonyl substituted diazo compounds.[46] The general reaction mechanism of the diazo transfer first involves the deprotonation at the α-position on the carbonyl substituent by generally using weaker organic bases, such as triethylamine (NEt_3) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) **1.13**. This leads to the formation of the enolate intermediate **(Scheme 1.9**, **I)**, serving as a nucleophile, which attacks the azide, resulting in the intermediate **(Scheme 1.9**, **II)** with the negative charge present on the nitrogen atom adjacent to the sulfonyl functionality. The subsequent proton transfer **(Scheme 1.9**, **III)** results in the expulsion of an amide byproduct, whilst the diazo functionality remains **(Scheme 1.9**, **IV)**.



Scheme 1.9: Reaction mechanism of base-assisted diazo transfer reaction

For many years, *p*-tosyl azide **1.14** has been a go to azide reagent for the base-assisted diazo-transfer reactions. However, **1.14** has shown to be highly impact-sensitive and the formed *p*-tosyl amide by-product has caused the purification step to be challenging, due to its difficult separation from the final diazo compound.[47] As such, several sulfonyl azide reagent alternatives have been developed to try to overcome the safety and purification shortcomings. *P*-acetamidobenzenesulfonyl azide (*p*-ABSA) **1.15** and methanesulfonyl azide **1.16** have both shown to resolve the safety risks, though the purification issues have remained.[47] On the other hand, the polystyrene-supported benzenesulfonyl azide **1.17** has resolved the purification problems, as the amide by-product is not soluble in the organic solvents and thus can be simply filtered out.[48] Nevertheless, the higher cost of the polymer azide reagent makes it quite restrictive in its use.[47] Furthermore, the hydrochloride salt of imidazole-1-sulfonyl azide **1.18** has been shown to be an initially safe azide reagent with improved shelf-life, however later it was reported that **1.18** exhibits the impact-sensitivity comparable to cyclotrimethylenetrinitramine **(Figure 1.6)**, a nitroamine commonly used as an explosive.[49, 50]

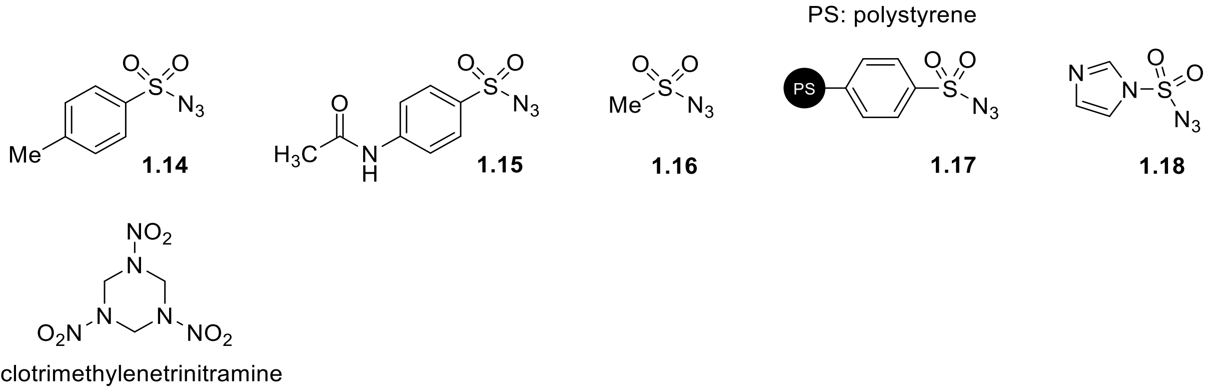
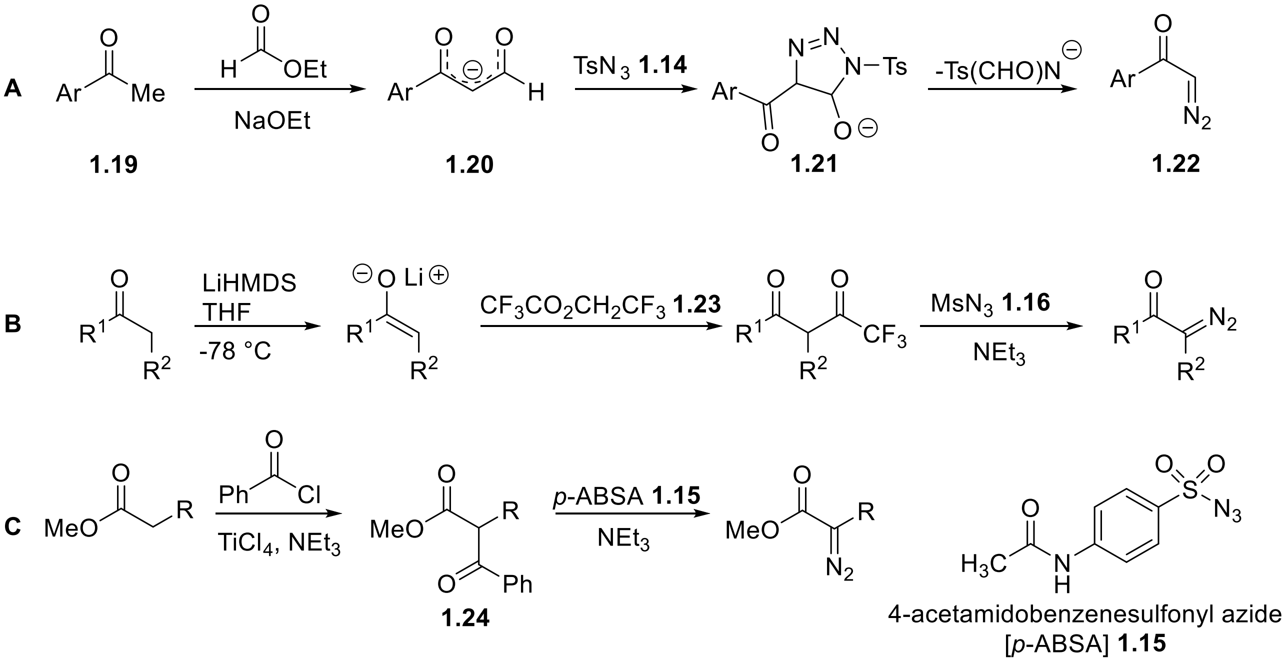


Figure 1.6: Cyclotrimethylenetrinitramine; sulfonyl azide reagents utilised for diazo transfer reactions

However, when installing a diazo functionality on simple carbonyl substrates, such as methyl ketone **1.19**, a direct diazo transfer cannot be utilised, as the methylene group is not sufficiently activated. Regitz *et al.* solved this obstacle by introducing an additional carbonyl functionality to the substrate *via* a Claisen condensation of a ketone with ethyl formate in the presence of sodium ethoxide (NaOEt). The formed 1,3-dicarbonyl intermediate **1.20** then undergoes a diazo-transfer reaction in the presence of tosyl azide (TsN_3) **1.14** to form the triazolinic intermediate **1.21**, which subsequently undergoes fragmentation, in this case deformylation, to obtain an α-diazocarbonyl **1.22 (Scheme 1.10, A)**.[51] Nevertheless, such methodology afforded the corresponding α-diazo carbonyls in quite moderate yields due to the harsh conditions, which are needed for the condensation to occur. Furthermore, the unsaturated diazo carbonyls were limited by the presented methodology due to poor regioselectivity when forming the enolate intermediate. As such, Dansenhier *et al.* have modified the 'deformylating diazo-group-transfer' methodology by generating the enolate intermediate *via* kinetic conditions, using a lithium base, such lithium bis(trimethylsilyl)amide (LiHMDS), a low temperature of -78 °C, and a very reactive acetylation agent, trifluoroethyl trifluoroacetate **1.23 (Scheme 1.10, B)**.[52]

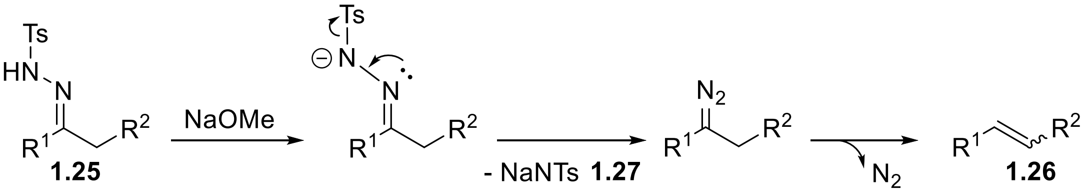
With this methodology, the previously problematic unsaturated diazo carbonyls, could be prepared in very good yields. A simpler and more cost-effective approach was later also reported by Taber *et al.*, in which the carbonyl substrate was initially activated by benzoylation using readily available benzoyl chloride in the presence of $TiCl_4$ and NEt_3 to form the benzoylated ester intermediate **1.24**, which subsequently readily underwent diazo transfer reaction under mild conditions **(Scheme 1.10**, **C).**[53]



Scheme 1.10: Deformylating diazo group transfer reactions and other alternatives

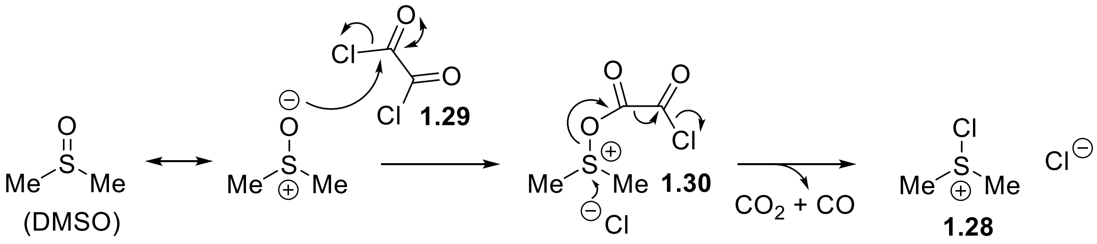
1.4.2.2 Synthesis of diazo compounds *via* the dehydrogenation of hydrazones

Another popular approach for accessing diazo compounds is the oxidation of hydrazones. Simple hydrazones are readily available as stable diazo precursors, which can undergo dehydrogenation under milder reaction conditions in both batch and flow.[54] This makes the oxidation of hydrazones a preferred strategy for the synthesis of less stabilised, electron-rich mono-alkyl and disubstituted diazo compounds when compared to other methodologies, such as Bamford-Stevens reaction **(Scheme 1.11).**[55] In this approach, harsh conditions, such elevated temperatures or a stronger base need to be applied for the sulfonylhydrazone **1.25** to undergo the fragmentation. This makes the Bambord-Stevens reaction less compatible with the less stabilised diazo compounds, which then usually undergo N_2 release, resulting in the alkene **1.26** formation instead. Additionally, the stoichiometric formation of the sulfinate by-product **1.27** makes this protocol less desirable for the larger scale synthesis.



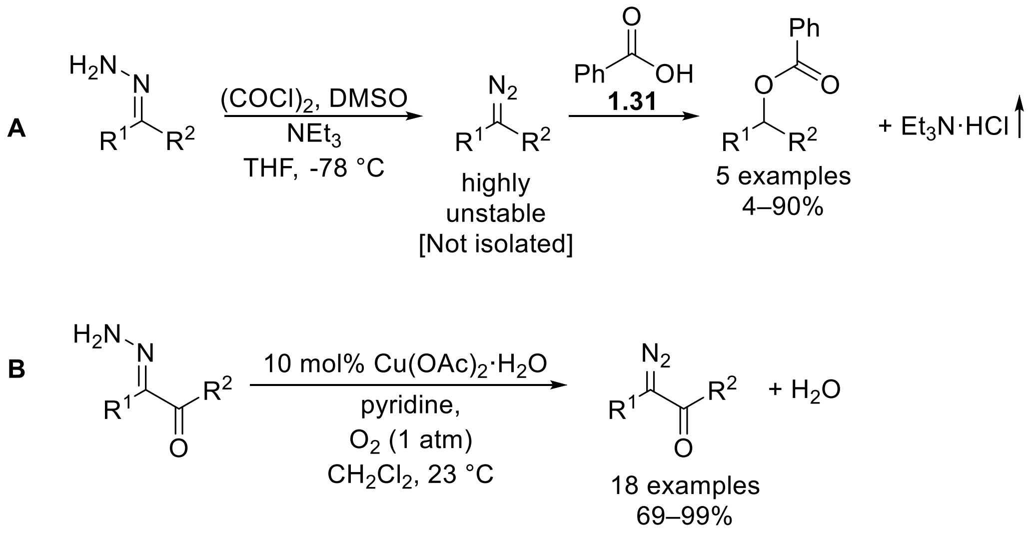
Scheme 1.11: Bamford-Stevens reaction

Typically, the oxidation of hydrazones is carried out in the presence of stoichiometric amounts of metal-based oxidants, including Ag_2O, HgO, MnO_2.[56,57,58] However, lately there has been a continuous development to substitute these toxic and environment unfriendly heavy metal-based oxidants. One of such first metal-free oxidants includes chlorodimethylsulfonium chloride **1.28**, also known as the Swern reagent. This oxidant is generated *in situ* from the initial nucleophilic attack of dimethyl sulfoxide (DMSO) on oxalyl chloride **1.29**, which results in the formation of highly unstable intermediate **1.30**, which immediately undergoes further decomposition, resulting in the formation of the Swern reagent **1.28**, whilst simultaneously CO and CO_2 are being released **(Scheme 1.12)**.

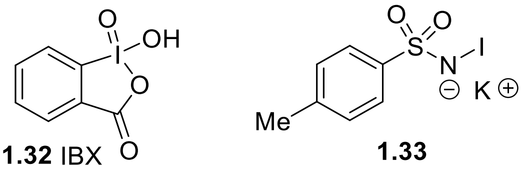


Scheme 1.12: *In-situ* formation of the Swern reagent **1.28**

Brewer *et al*. showed that various aryl- and alkyl-substituted diazo compounds can be obtained by the Swern oxidation. Nevertheless, the high instability of the formed diazo compounds made them difficult to be directly isolated. Therefore, the formed unstable diazo compounds were directly utilised in an esterification reaction, wherein an excess of benzoic acid **1.31** was added into the solution. The resulting ester products were formed in up to 90% of isolated yield, and they showed to be easily separated from triethylamine hydrochloride byproduct precipitate *via* a simple filtration **(Scheme 1.13, A)**.[59] Iodine-based oxidants, including hypervalent iodine reagent 2-Iodoxybenzoic acid **1.32** (IBX) and *N*-Iodo potassium *p*-toluenesulfonamide salt **1.33**, which is readily prepared from iodine and *p*-toluenesulfonamide in aqueous KOH, have also been explored for the transformation of hydrazones.[60,61] The corresponding diazo compounds have been obtained in up to quantitative yields under mild reaction conditions. Nevertheless, stoichiometric amounts of the iodine-based oxidant had to be used for the reaction to occur. More recently, there has been a report of the catalytic oxidation of hydrazones, in the presence of 10 mol% $Cu(OAc)_2{\cdot}H_2O$, pyridine, and ambient air, which was utilised as an oxidant. With this methodology, various α-diazo esters, diaryl diazo compounds, as well as diazo amides were obtained in good to excellent yields and the only by-product from the reaction was water **(Scheme 1.13, B)**.[62]



Scheme 1.13: Synthesis of diazo compounds from hydrazones *via* the Swern Oxidation

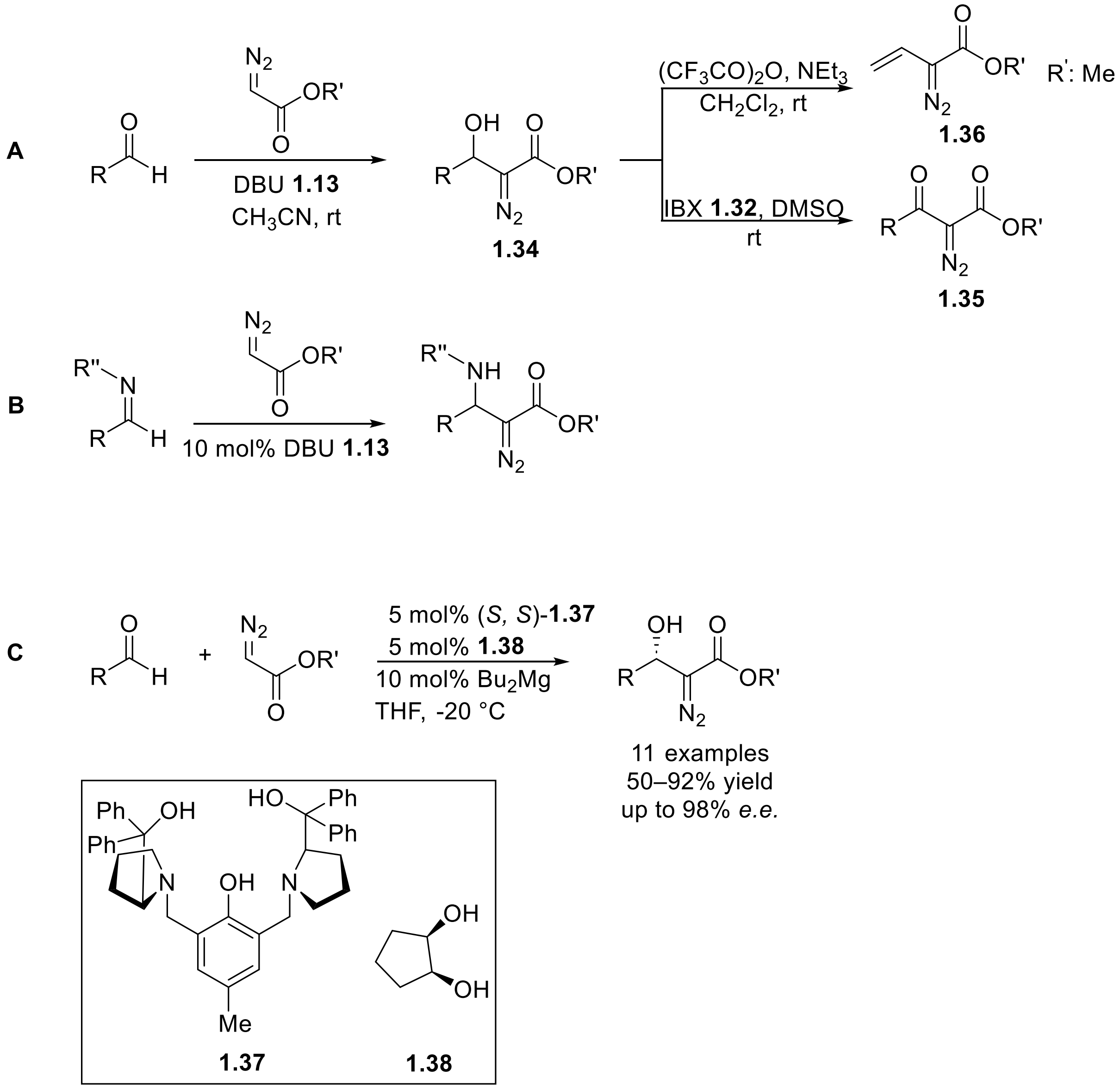


1.32 IBX **1.33**

Figure 1.7: Iodine-based oxidants utilised for the synthesis of diazo compounds from hydrazones

1.4.2.3 Synthesis of diazo compounds via electrophilic substitution of diazomethyl compounds

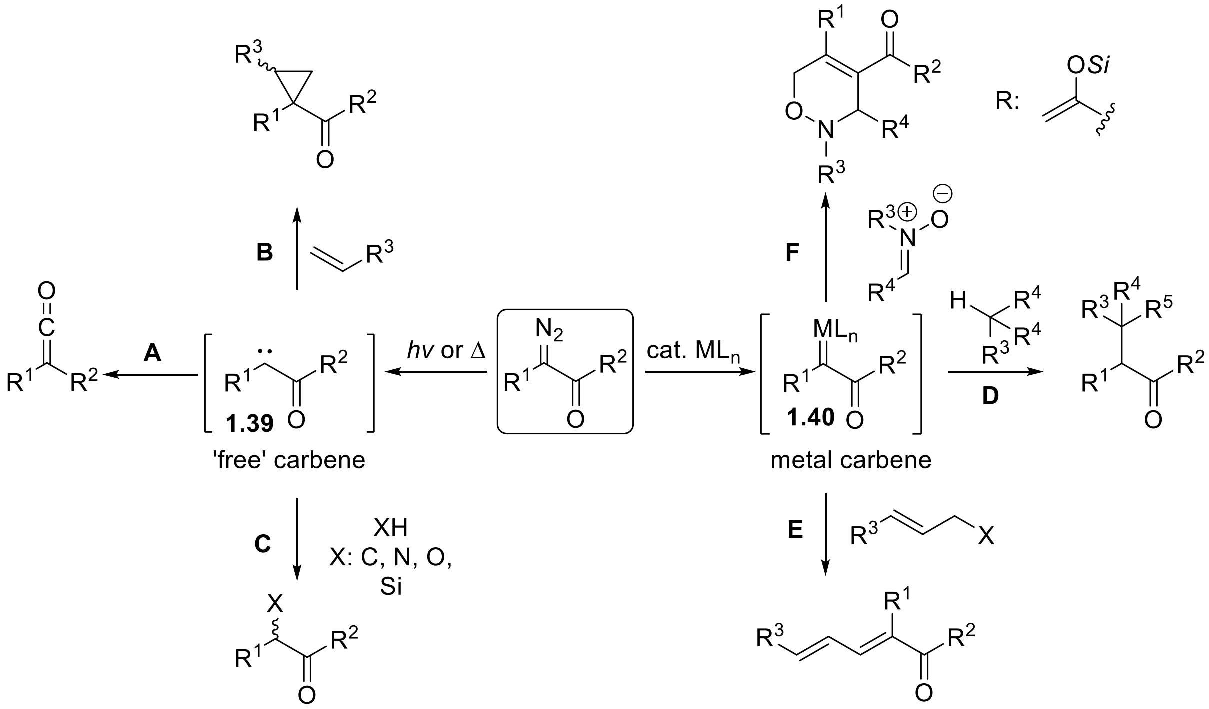
The aldol-type condensation of diazo carbonyls with aldehydes, ketones, and imines is another widely used methodology to access diazo compounds. It is a particularly useful approach when introducing a hydroxyl or amino group into the diazo compound. Initially, the condensation of ethyl diazoesters with carbonyls have been carried out exclusively in the presence of strong inorganic bases, including ^{n}BuLi, KOH, NaH, and LDA (lithium diisopropylamide).[63] However, later there have been reports of utilising stoichiometric or catalytic amounts (10 mol%) of an organic base, such DBU **1.13**, to deprotonate the ethyl diazoacetate under milder reaction conditions. Nevertheless, the catalytic protocol showed to be useful for the condensation of ethyl diazoacetate with alcohols and imines **(Scheme 1.14**, **B)**, but it was too slow for the condensation with ketones.[64] Furthermore, it was demonstrated the α-diazo-β-hydroxy carbonyls **1.34**, obtained *via* the initial aldol condensation, can be further transformed into the corresponding diazo dicarbonyl **1.35** upon oxidation with IBX **1.32** or into vinyldiazo compound **1.36** in the presence of trifluoroacetic acid and NEt_3 at room temperature **(Scheme 1.14**, **A)**.[65,66] There have also been reports of asymmetric catalytic aldol-type condensation of ethyldiazo carbonyls **(Scheme 14, C)**. The most efficient asymmetric protocol was reported by Trost *et al.* by utilising 5 mol% of chiral bidentate ProPhenol ligand **1.37** together with 10 mol% of di-*n*-butylmagnesium (Bu_2Mg) catalyst. However, initially, the formation of the corresponding alcohol was with a rather poor *e.e.* of 27%. This was attributed to the possibility of the magnesium catalyst to remain coordinatively unsaturated in the complex. As such, various chelating agents were screened in order to improve enantioselectivities, from which *cis*-1,2-cyclopentadiol **1.38** gave the best *e.e.* result of 82% at -20 °C in THF. Variously substituted chiral aliphatic and aromatic α-diazo-β-hydroxy carbonyls were obtained in good to excellent (50–92%) and with excellent *e.e.*s of up to 98%.[67]



Scheme 1.14: Aldol addition of carbonyls and imines with ethyl diazoacetates

1.4.3.0 Activation of diazo compounds

As mentioned in the section **1.4.2.0**, diazo compounds are useful building blocks in organic synthesis as they are carbene precursors. As such, several strategies have been developed for their activation, which is mainly categorised into thermally, photochemically, and catalytically mediated activation **(Scheme 1.15)**. Initially, diazo compounds have been exclusively activated thermally or photochemically however this has led to the formation of highly unstable and hard to control free-carbene intermediates **1.39** and thus the generation of unwanted by-products is inevitable.[68] Nevertheless, over the past decades there has been a tremendous effort for a better control of the formed carbenes *via* thermal and photochemical approaches in various chemical transformations, including Wolff rearrangement **(Scheme 15**, **A)**, cyclopropanation **(Scheme 15, B)** or C–H insertion reactions **(Scheme 15**, **C)**. Such recent developments have been extensively reviewed and will not be discussed here in any more details.[65, 69, 70]



Scheme 1.15: General activation and utilisation of diazo compounds in organic synthesis

Nowadays, more focus is in the area for the diazo activation involving a catalyst, more commonly a transition metal (including Rh, Cu, Pd), forming the metal carbenoid intermediate **1.40**. The metal carbenoid is a tetravalent species, wherein the carbene carbon is stabilised by a metal *via* a strong σ C–M bond, which is originating from the lone electron pair in the C sp^2 orbital of the carbene donating to the metal centre, whilst the electrons in *d*-orbitals of the metal participate in a weak π-backbonding with the vacant *p*-orbital of the carbene **(Figure 1.8)**. This results in an additional stabilisation of the carbene, whilst allowing it to still exhibit electrophilic character and a similar reactivity of the free singlet carbene. Furthermore, the reactivity of the metal carbenoid can be influenced by the incorporation of the electron-withdrawing ligands into the metal complex, which reduces the π-backbonding, resulting in the higher activity of the carbene. On the other hand, if electron-donating ligand is incorporated instead, the reactivity of the carbene is decreased, though the stability and the selectivity is improved. As such, throughout the last couple of decades, there has been a tremendous progress in a development of the metal complex catalysts for the activation of the diazo compounds, which can be furtherly utilised for C–C bond forming reactions, such as C–H insertion (Scheme **1.15**, **D)**, C–C cross-coupling reactions **(Scheme 1.15, E)** or cycloaddition reactions **(Scheme 1.15, F)** in the presence of vinyldiazo compounds.[71, 72]

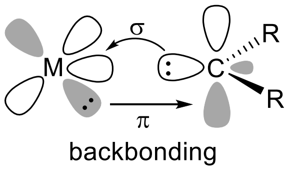
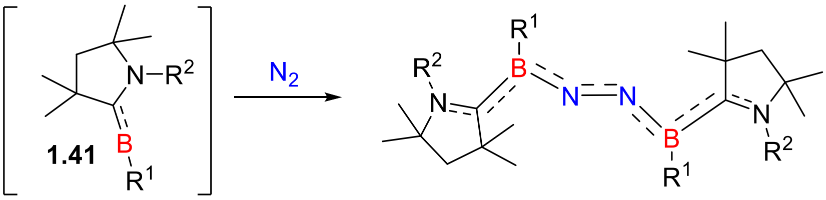


Figure 1.8: Carbene stabilisation by metal centres

1.4.3.1 Activation of diazo compounds by triarylboranes

Despite transition metal catalysts being highly efficient and tuneable, their disadvantages, as discussed in the section **1.1.0**, have caused to shift an attention from using toxic and environment-unfriendly precious transition metals towards developing main group-based alternatives. In 2019, Braunschweig *et al.* have reported a first metal-free activation of dinitrogen by employing a transient dicoordinate-borylene **1.41 (Scheme 1.16)**, and such exciting discovery has facilitated a shift towards utilising boron-based Lewis acids for diazo compounds activation.[73]

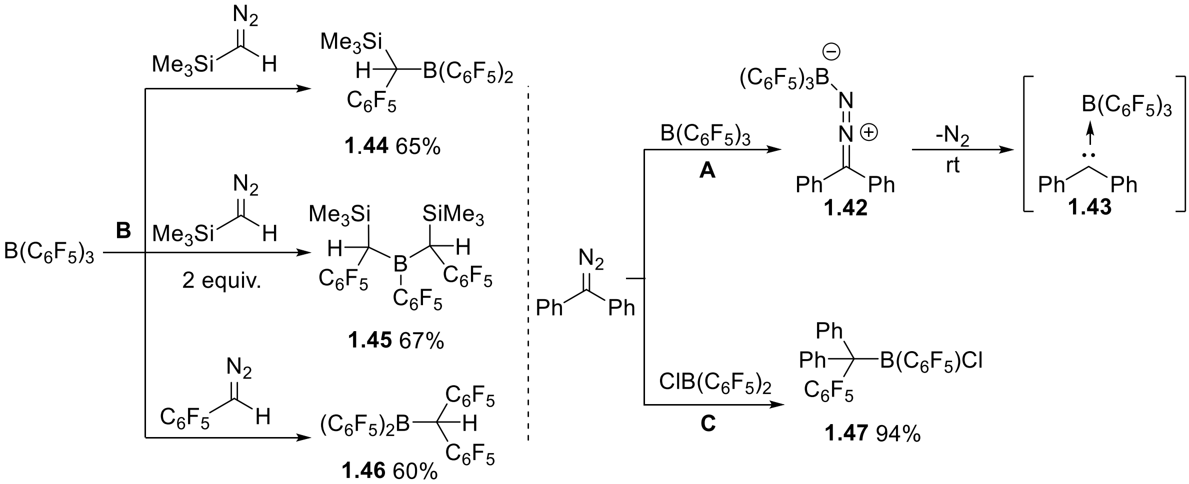


Scheme 1.16: The first metal-free activation of dinitrogen

1.4.3.2 Stoichiometric activation of diazo compounds by triarylboranes

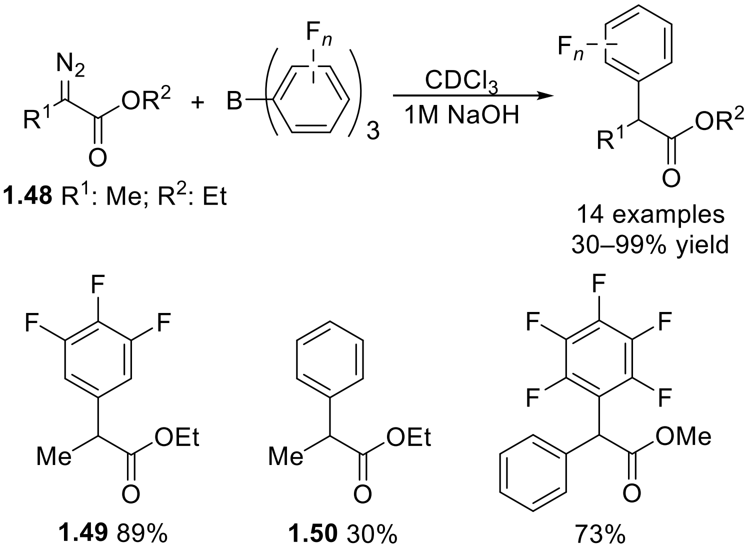
One of the first demonstrations that aryl boranes undergo diazo activation was reported by Stephan *et al.* in which the sterically hindered diazomethane $Ph_2C(N_2)$ formed a diazo-borane adduct **1.42** when reacted with stoichiometric amounts of $B(C_6F_5)_3$.[74] The crystals of the adduct **1.42** were shown to be highly sensitive, as the rapid evolution of N_2 gas was observed even at room temperature, wherein the formation of $Ph_2C \rightarrow B(C_6F_5)_3$ **1.43** was proposed. Such instability was later attributed to the weak N–B donation and was also investigated computationally, wherein the loss of N_2 and the carbene-borane adduct **1.43** formation was calculated to be exergonic by about 53 kcal mol^{-1} (**Scheme 1.17, A**).

When less sterically hindered diazomethanes, such as $Me_3SiCH(N_2)$ and $(C_6F_5)CH(N_2)$ were employed with the stoichiometric amounts of various perfluoroarylboranes, different reactivities have been observed.[75] $Me_3SiCH(N_2)$ and $(C_6F_5)CH(N_2)$ were shown to undergo the insertion reactions, which proceeded smoothly even at –78 °C in a presence of stoichiometric $B(C_6F_5)_3$ **(Scheme 1.17, B)**. This resulted in the formation of new boranes **1.44** and **1.46** in good yields of 65% and 60%, respectively. Furthermore, when 2 equiv. of $Me_3SiCH(N_2)$ was used, a double insertion reaction was observed, wherein the borane product **1.45** was isolated in 67% yield. The borane **1.45** showed to be sterically highly congested around the boron centre as when the higher excess of the diazomethane was used, no further insertion reaction was observed. Similar reactivities were also observed with $PhB(C_6F_5)_2$, however in this case the single and double insertion products could not be separated. Lastly, when $Me_3SiCH(N_2)$ was reacted with $ClB(C_6F_5)_2$, only a complex mixture of products was observed. Interestingly, when the more sterically hindered $Ph_2C(N_2)$ was reacted with $ClB(C_6F_5)_2$, the insertion reaction was observed, and it proceeded rapidly at −78 °C, wherein the new borane product **1.47** was isolated in an excellent yield of 94% **(Scheme 1.17**, **C)**. Surprisingly, no double insertion product was formed when 2 equiv. of $Ph_2C(N_2)$ was utilised. Similar aryl group migration reactions were also later observed with $(C_6F_5)_2B(OC_6F_5)_2$ and BPh_3 in the presence of $Me_3SiCH(N_2)$.[76]



Scheme 1.17: Stoichiometric reactions of triarylboranes with diazo compounds

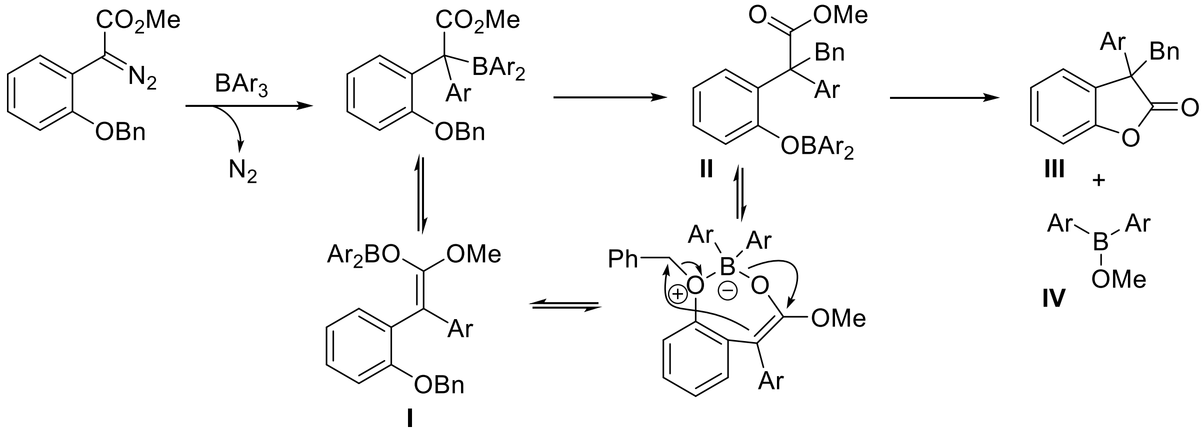
Aryl group migration was also observed with α-diazocarbonyl compounds, wherein the aryl group of the triarylborane was transferred onto the carbene carbon atom, forming the corresponding products in 30–99% of isolated yields **(Scheme 1.18)**.[77] Generally, the reactions were more efficient with the less sterically hindered ethyl 2-diazopropanoate **1.48**, which underwent the high yielding insertion reactions even with substoichiometric amounts (0.5 equiv.) of the triaryl borane. Whereas, when the α-aryl-α-diazoacetates were employed, 1 equivalent of triaryl borane had to be used. Moreover, the reaction showed to be more facile with the more electron deficient boranes, and as such, the aryl migration proceeded more efficiently with $B(3,4,5\text{-}F_3C_6H_2)_3$, yielding the product **1.49** in 89% when compared to BPh_3, which resulted in the corresponding product **1.50** in 30% of isolated yield. The more sterically demanding α-aryl-α-diazoacetates failed to react with the less acidic BPh_3, $B(4\text{-}FC_6H_4)_3$, and $B(2,6\text{-}F_2C_6H_3)_3$ completely, even at elevated temperatures.



Scheme 1.18: Aryl group migration observed from the reaction of triarylboranes with diazo carbonyls

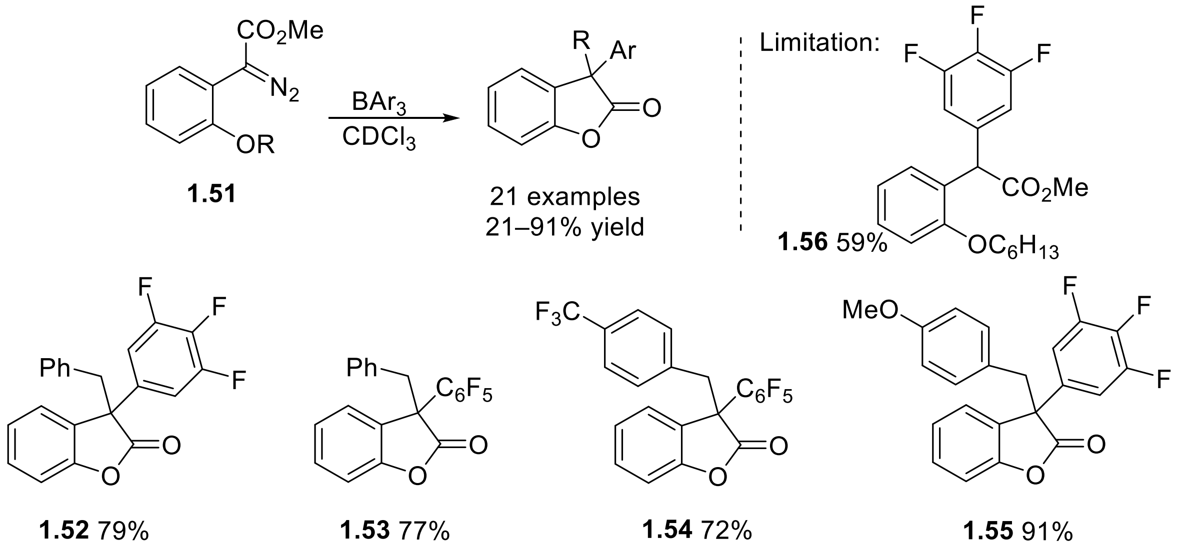
Interestingly, when 2-benzyloxy-substituted diazo derivative **1.51** was reacted with stoichiometric $B(3,4,5\text{-}F_3C_6H_2)_3$ or $B(C_6F_5)_3$, an unprecedented benzyl group rearrangement was observed. As such, instead of the expected aryl transfer product, a 3,3-disubstituted benzofuran-2-(3*H*)-ones **1.52** (79%) and **1.53** (77%) were formed at room temperature.

Thorough kinetic and mechanistic studies revealed that such lactone formation proceeded initially *via* 1,2-aryl shift from the borane on the diazo substrate, wherein the formation of enolate **I** was accompanied by the loss of N_2. A subsequent rearrangement of the unstable boron enolate **I** into a phenol derivative **II** occurs rapidly within 1 hour at room temperature. Finally, the intermediate **II** undergoes a cyclisation, which results in the formation of lactone product **III** and diarylboronic ether **IV (Scheme 1.19)**.



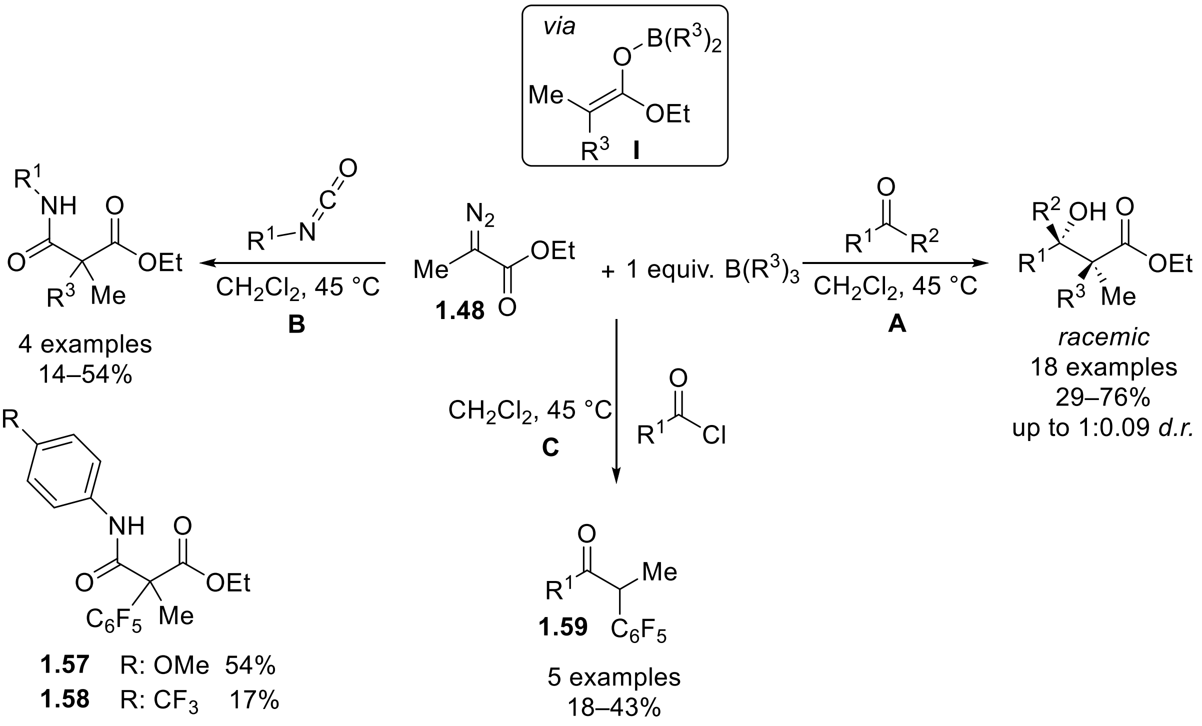
Scheme 1.19: Proposed mechanism for lactone formation

A further substrate scope of such tandem rearrangement/ lactonisation was explored **(Scheme 1.20)**. In general, aryl diazo esters with an electron-withdrawing substituent on the migrating group, such CF_3 **1.54**, required higher temperatures of up to 50 °C in order to proceed and wherein the products were obtained in up to 72% of isolated yields. On the other hand, diazo esters bearing an electron-donating substituent on the migrating aryl group, such OMe **1.55**, underwent the reaction smoothly and afforded the corresponding lactone products in good to excellent isolated yields of up to 91%. Apart the benzylic functionality, an allylic and cinnamic functionalities were explored as well, and the corresponding products were obtained in moderate to good yields of up to 60%. A limitation of such methodology included the alkyl substituent, *n*-hexyl, wherein the rearrangement step is prevented due to the alkyl migrating group to be less able to stabilise the carbocation intermediate. As such, only the formation of the functionalised ester **1.56** was observed in 59% of isolated yield.[77]



Scheme 1.20: Presented substrate scope of the tandem rearrangement/lactonisation reaction

It has been also demonstrated that the stoichiometric amounts of perfluoroarylboranes undergoes the aryl transfer with α-diazoesters, after which the formed boron enolate intermediate **(Scheme 1.21, I)** further reacts with electrophiles in three-component reactions.[78] Variously substituted aldehydes were explored in a reaction with diazo ester **1.48** and 1 equiv. $B(C_6F_5)_3$ for 24 hours at 45 °C in dichloromethane (CH_2Cl_2. As expected, the β-hydroxy ester products were obtained as a mixture of diastereomers in good yields of up to 76%. The major diastereomer was later identified by the single crystal X-ray diffraction to be the racemic 2*S*, 3*S*-alcohol. Ketones were explored in such tandem reaction as well, wherein the β-hydroxy esters were formed in good yields of up to 67% **(Scheme 1.21, A)**. This methodology was also used to obtain amino functionalised β-keto esters by utilising isocyanates as electrophiles **(Scheme 1.21, B)**. The best yield of 54% was observed with the more electron-rich *p*-OMe substituted aryl isocyanate **1.57** and the worst yield of 17% was obtained with *p*-CF_3 substituted aryl isocyanate **1.58**. Interestingly, when acyl chlorides were reacted with 1 equiv. $B(C_6F_5)_3$, the formation of ketones **1.59** was observed instead, which was attributed to the additional decarboxylation step occurring right after the boron enolate attacks the highly reactive acyl chloride electrophile **(Scheme 1.21, C)**.

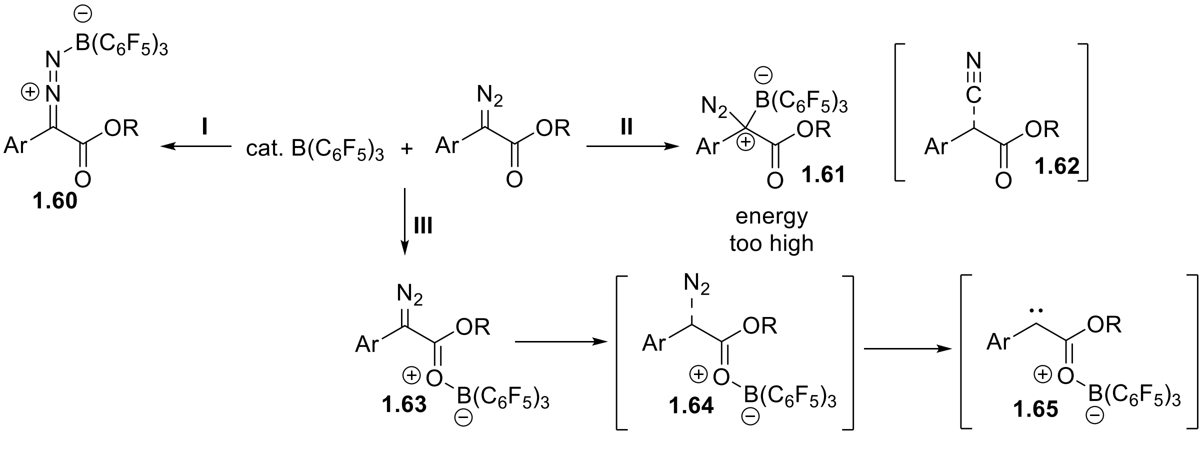


Scheme 1.21: Three-component reactions with diazo esters, triarylboranes and various electrophiles

1.4.3.3 Catalytic activation of diazo compounds-computational studies

In addition to the stoichiometric activation of diazo compounds by bulky boranes, it has been demonstrated that such activation can proceed *via* catalytic manner. Extensive DFT studies have been undertaken by Zhang *et al.* to better understand how such carbene transfer reactions of α-aryl-α-diazoesters are accomplished with catalytic $B(C_6F_5)_3$.[79]

Three possible binding sites on the diazo ester have been considered for $B(C_6F_5)_3$ to coordinate to and to form an adduct, upon which N_2 release is initiated **(Scheme 1.22)**. In the first scenario, $B(C_6F_5)_3$ coordinates towards the terminal N_2 functionality to form the B–N adduct **1.60** **(Scheme 1.22, I)**, a pathway which has been also proposed earlier by Stephan *et al.* when activating the diazomethane **(Scheme 1.17)**.[74] The DFT calculations showed that the adduct intermediate **1.60** is formed with the increased free energy of 7.1 kcal/mol and the N–N bond is slightly stretched from 1.14 Å to 1.16 Å.[79]

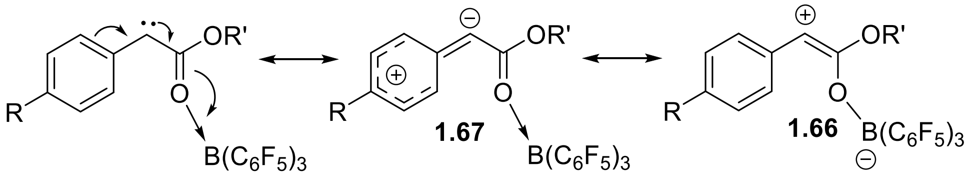


Scheme 1.22: Three possible binding sites of diazo esters

In the second scenario, $B(C_6F_5)_3$ coordinates directly towards the carbene carbon **(Scheme 1.22, II)**. However, in this case, the quaternary carbon adduct intermediate **1.61** was shown to undergo an immediate B−C bond breakage due to the high steric hindrance between the borane and the diazo ester. Thus, the free energy for the adduct **1.61** could not be even calculated. To reduce the steric hindrance, a successive dissociation of N_2 and $B(C_6F_5)_3$ bonding towards the carbene carbon was calculated instead, in which the C−N cleavage transition state **1.62** showed to have highly unfavourable free energy of 30.0 kcal/mol.

The third possibility is for $B(C_6F_5)_3$ to coordinate towards the carbonyl functionality to form O−B adduct **(Scheme 1.22, III)**. Such coordination showed to be the most favourable as the adduct **1.63** has decreased free energy of -2.9 kcal/mol. This could be possibly justified by a slight stretching of C−N bond from 1.32 Å to 1.33 Å upon the adduct formation, resulting in a reduction of the steric hindrance around the carbene carbon. Subsequently, it was calculated that N_2 release proceeds *via* a transition state **1.64** with the free energy of 21.5 kcal/mol, upon which the intermediate **1.65** is obtained with free energy of 0.1 kcal/mol. The lower energy observed in the borane-carbene intermediate **1.65** was attributed to the formed conjugated system between the carbene carbon and the carbonyl group, through which the LUMO orbital energy is decreased by the highly Lewis acidic $B(C_6F_5)_3$, which pulls the electron density away from the carbene centre.[79]

Further DFT studies, conducted by Ariafard *et al.*, explored an effect of the substituents present on both the aryl ring and at the carbonyl functionality of the α-aryl-α-diazoesters on the ease of N_2 release **(Scheme 1.23)**.[80] First, without any presence of the borane catalyst, the substituents on the aryl ring at the *para* position with the electron-donating effect, such NMe_2 or OMe, showed to reduce the activation energy needed for the N_2 release to form the carbene. On the other hand, the substituents with the electron-withdrawing effect, such NO_2 or CF_3, have little to no influence on the activation energy for the N_2 release, essentially justifying why stronger Lewis acid catalyst is required for activating such substrates. These observations have been attributed to the π-donation towards the carbene centre, wherein in the case of electron-donating substituents, the electron density is pushed from the aromatic ring towards the empty *p*-orbital of the carbene carbon. This results in a better stabilisation of the carbene intermediate, thus rendering the carbene formation to be more thermodynamically favourable.



Scheme 1.23: Influence of aryl and ester substituents on the borane’s catalytic efficiency

In a presence of $B(C_6F_5)_3$, it was shown that the borane’s efficiency as a catalyst directly relies on a strength of the B−O bond in the borane carbene adduct **1.66**. The bond strength is influenced by the substituent on the aryl and ester moiety. The calculations revealed that the diazo compounds bearing strong electron donating substituent on the aryl ring form stronger B−O bond. This is due to the increased electron-density on the carbene carbon, which is then subsequently pulled by the bonded Lewis acid in the adduct **1.67**. It was also suggested that the substitution on the carbonyl moiety lacking an electron lone pair, such Me, H, or Ph (i.e an aldehyde or ketone), results in a stronger B−O bond, when compared to the substituent bearing a lone pair such, F or OMe. This was attributed to the lone pair on the ester substitution to significantly reduce the effective interaction of carbene lone pair and the carbonyl functional group, which then leads to a smaller stabilisation by the bonded borane catalyst, and thus resulting in a weaker B−O bond.

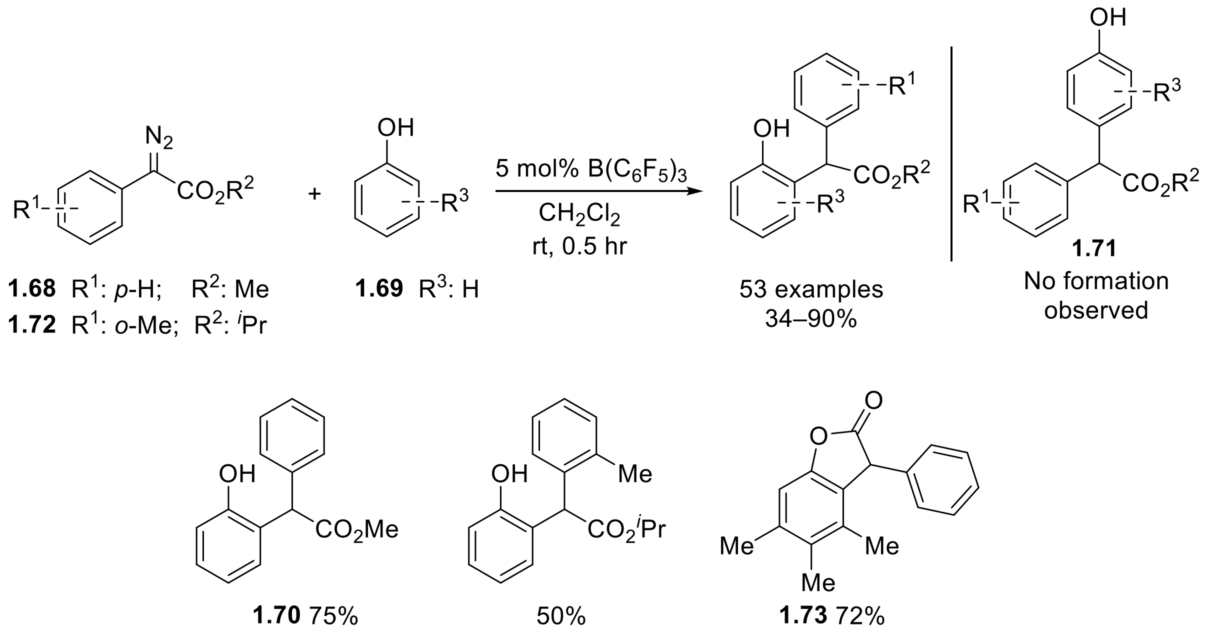
1.5.0 $B(C_6F_5)_3$-catalysed transfer carbene reactions

The computational and experimental stoichiometric studies have encouraged the development of synthetic methodologies for carbene transfer reactions in a presence of catalytic amounts of perfluroarylboranes, which since have been extensively reviewed.[39, 81] In the following section, only a few examples, wherein the highly electrophilic boron enolate **1.66** undergoes X−H insertion and/or C−C bond forming reactions will be discussed in more detail.

1.5.1 $B(C_6F_5)_3$-catalysed X−H insertion reactions of aryl diazoesters

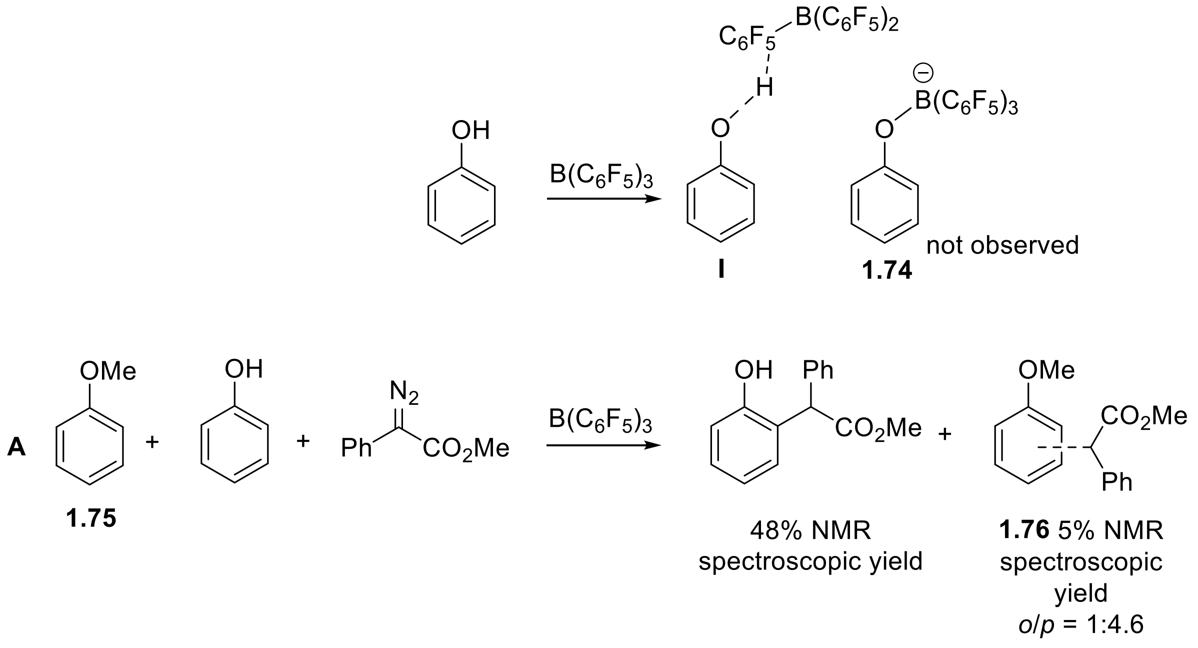
One of the first examples of $B(C_6F_5)_3$-catalysed insertion of aryl esters was reported by Zhang *et al.* in 2016 **(Scheme 1.24)**. [82] An initial screening reaction revealed that 10 mol% $B(C_6F_5)_3$ is sufficient to promote the C−H insertion of α-phenyl α-diazoacetate **1.68** onto phenol **1.69** at the *ortho*-position, wherein the product **1.70** was obtained in a yield of 57%. Interestingly, the formation of the *para*-substituted product **1.71** was not observed, which is usually obtained by using an Au-based catalyst.[83,84] Furthermore, the reaction was observed to be highly chemoselective, as the O−H insertion product was obtained in a mere 9% of yield. Further optimisation revealed that the most optimal solvent was CH_2Cl_2 and the loading of $B(C_6F_5)_3$ could be decreased to 5 mol% if the amount of diazo ester was increased to 1.5 equiv.

Subsequently, a broad scope of 53 examples for the highly chemo- and *ortho*-selective methodology was demonstrated, wherein different substitutions on both phenol and the aryl diazoacetate were explored. In general, regarding the substitutions present on aryl diazoacetate, electron-withdrawing and electron-donating substituents at *meta*- and *para*-positions on the phenyl ring were tolerated and the corresponding products were obtained in good to very good yields of up to 86% and in high chemoselectivity of up to 28:1. Nevertheless, 2 equiv. of more sterically hindered diazo ester **1.72** (*o*-Me) was required to improve the obtained yield of 50%. Furthermore, methyl α-aryl α-diazoacetates reacted as well, though with lower chemoselectivities when compared to isopropyl α-aryl α-diazoacetates. Most substitutions on the phenol were well tolerated either. Interestingly, the *ortho*-substituted phenols were incompatible with the present methodology, which was attributed to the steric hindrance at the reaction centre. Furthermore, lactone product **1.73** was obtained in 72% with the sterically congested 3,4,5-trimethylphenol.



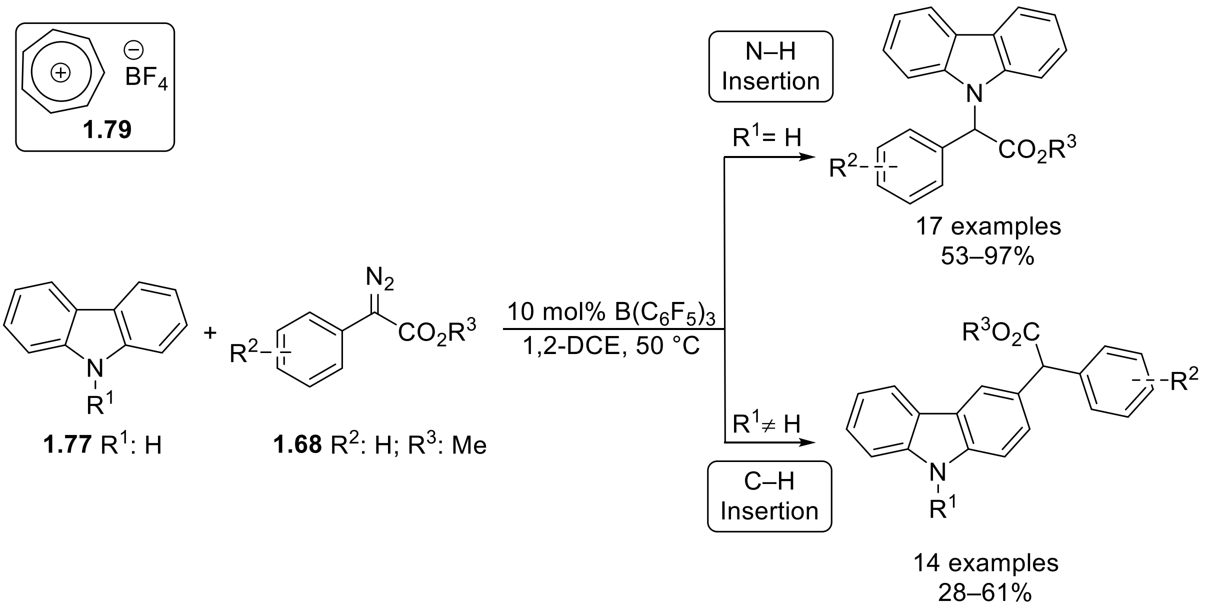
Scheme 1.24: $B(C_6F_5)_3$-catalysed C–H insertion reactions of aryl esters with phenols

Mechanistic studies were undertaken to justify the observed regioselectivity. NMR titrations studies revealed a downfield shift in the ^{19}F-NMR spectrum when phenol was mixed with $B(C_6F_5)_3$, whereas there was no shift in the ^{1}B-NMR spectrum. Such observations suggested that there was no coordination of the borane with the hydroxy group of the phenol to form a four-coordinate boron intermediate **1.74**. As such, the *ortho*-selectivity was attributed to the hydrogen bonding between a fluorine atom of $B(C_6F_5)_3$ and the hydroxy group of the phenol **(Scheme 1.25, I)**. This hypothesis was further supported by the competition experiment between phenol and anisole **1.75 (Scheme 1.25, A)**. The anisole substituted compound **1.76** was obtained as a minor product, wherein the *para*-substituted product **1.76** was formed as a major regioisomer. Additional deuterium labelling studies also supported this hypothesis, as it was shown that the hydroxy group served as a proton source during the reaction.



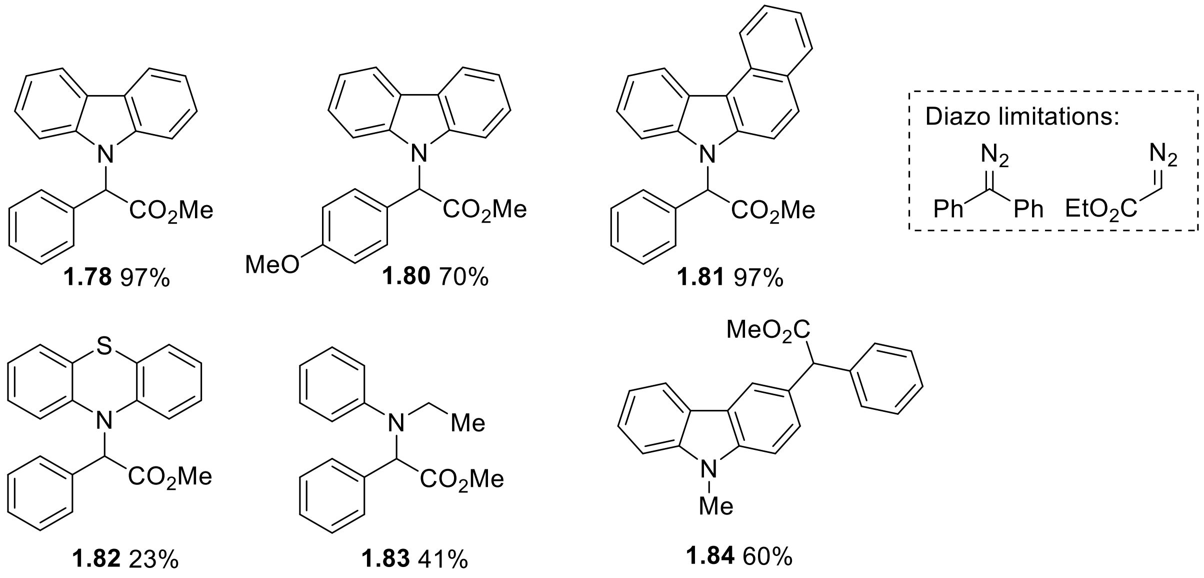
Scheme 1.25: Control studies for justifying *ortho*-selectivity

Another example of a $B(C_6F_5)_3$-catalysed insertion reaction was reported by Koenigs *et al.*, wherein carbazole heterocycles were showed to undergo selective C–H or N–H insertion reaction with aryl diazoesters.[85] The initial screening reaction was carried out at 50 °C in THF and in a presence of 10 mol% of $B(C_6F_5)_3$, wherein unprotected carbazole **1.77** and methyl phenyldiazoacetate **1.68** were utilised as model substrates **(Scheme 1.26)**. Initially, no reactivity was observed, which was presumed to be due to the coordination of $B(C_6F_5)_3$ to THF solvent, resulting in the poisoning of the catalyst. This was confirmed by exchanging THF for non-coordinating solvents, such CH_2Cl_2 or $CHCl_3$, wherein the formation of N–H functionalised product was observed, though in very low isolated yields of 14% and 20%, respectively. Surprisingly, 1,2-dichloethene (1,2-DCE) showed to be the most optimal solvent, wherein the desired product **1.78** was obtained in an improved isolated yield of 79%. An increase in reaction concentration to 0.05 M improved the obtained yield to 97%. Furthermore, when $BF_3{\cdot}OEt_2$ and tropylium tetrafluoroborate **1.79** were used to catalyse the reaction, a decreased isolated yield of 53% was observed, confirming the superiority of $B(C_6F_5)_3$ for this transformation.



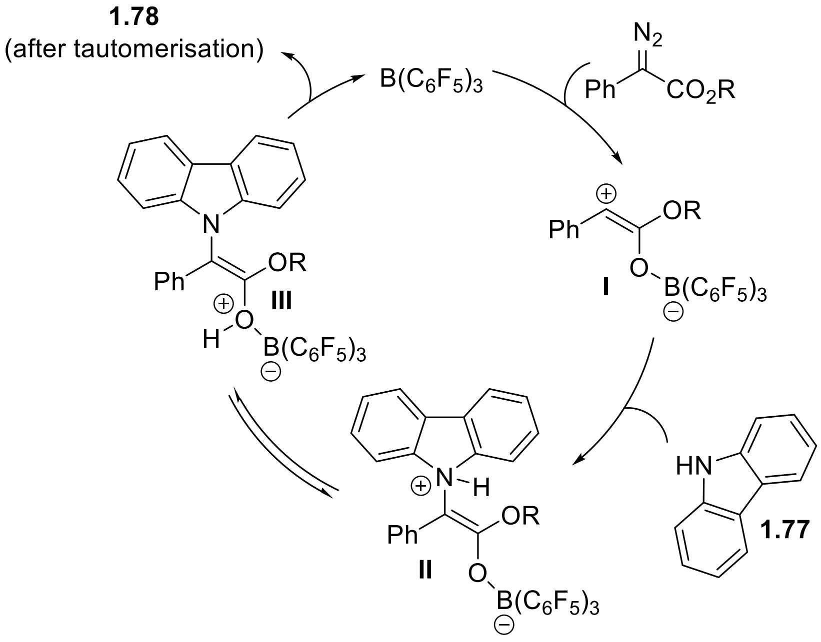
Scheme 1.26: $B(C_6F_5)_3$ catalysed C–H and N–H insertions of aryl diazoesters on unprotected and protected carbazoles

A broad substrate scope of 25 examples of N–H functionalised carbazoles was demonstrated, wherein different diazoacetates and *N*-heterocycles were explored **(Scheme 1.27)**. Generally, the substitutions on aryl diazoesters, including halogen or alkyl substituents on the aryl ring, or different ester substitutions were well tolerated. A slight decrease in yield of 70% was observed with the product **1.80** obtained from diazo ester bearing a *p*-OMe group. On the other hand, the more reactive diazo alkanes, such diphenyl diazomethane or ethyl 2-diazo propanoate were not compatible with the present methodology. Carbazoles with halogen substituents at the *meta*- or *para*-position were also well tolerated. Furthermore, excellent reactivity was also observed with a carbazole bearing additional benzene ring, wherein the corresponding product **1.81** was obtained in 97% of isolated yield. However, carbazoles substituted at the *ortho*-position failed to react, presumably due to increased sterics. Other unprotected *N*-heterocycles, such phenothiazine or the secondary aromatic amine also reacted, albeit less efficiently, as the corresponding products **1.82** and **1.83** were obtained in 23% and 41%, respectively. Furthermore, when *N*-methyl carbazole was reacted with aryl diazoacetate under the optimised reaction conditions, a selective C–H insertion was observed at C_3-position and the product **1.84** was obtained in 60%. As such, nine examples of C_3-functionalised *N*-methyl carbazoles were presented, though the obtained yields of up to 60% were quite moderate.



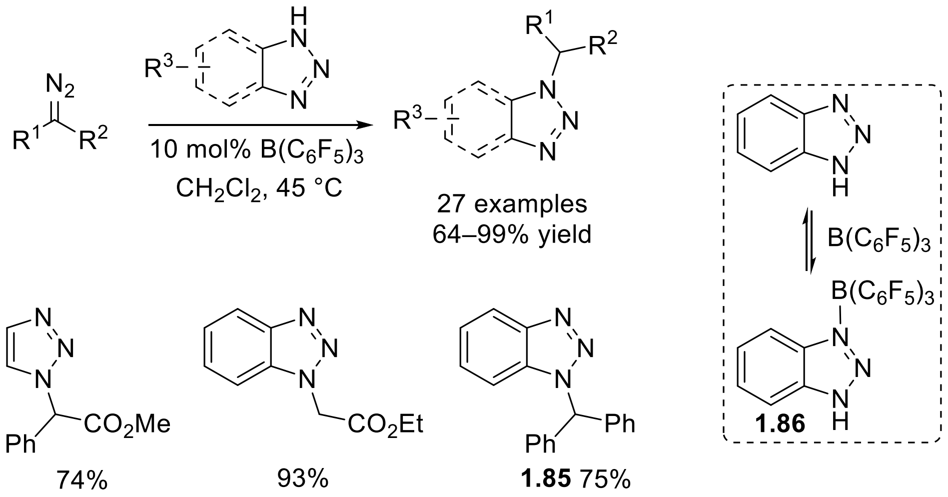
Scheme 1.27: Substrate scope and limitation for the $B(C_6F_5)_3$ catalysed X–H insertions of aryl diazoesters onto carbazoles

The catalytic cycle for the selective N–H insertion reaction of aryl diazoester with unprotected carbazoles was proposed as well **(Scheme 1.28)**. As discussed in the section **1.4.3.3**, the first step is comprised of $B(C_6F_5)_3$ coordinating towards the carbonyl moiety of the aryl diazoester, forming the boron-stabilised activated carbene **I** upon N_2 release, which is then attacked by the nucleophilic carbazole. The unprotected carbazole **1.77** contains two possible binding sites, a soft carbon-based or hard nitrogen-based nucleophilic binding sites. As the activated carbene **I** is a hard electrophile, **I** binds preferably towards the hard *N*-based nucleophile, forming intermediate **II**. Subsequently, a proton migration onto a carbonyl functionality occurs **III**, which is followed by proton transfer, resulting in the final product **1.78**.



Scheme 1.28: Proposed catalytic cycle for the $B(C_6F_5)_3$ catalysed N–H insertions of aryl diazoesters onto carbazoles

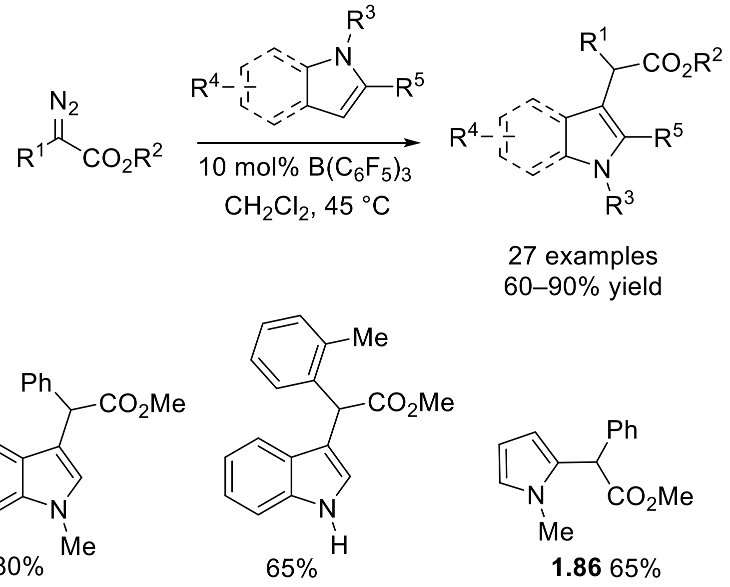
Stephan *et al.* demonstrated that similar reaction conditions of 10 mol% $B(C_6F_5)_3$, heating at 45 °C, and using chlorinated solvent such as CH_2Cl_2, were also applicable towards the site selective N_1-alkylation of benzotriazoles with aryl diazoesters **(Scheme 1.29)**.[86] Overall, 27 examples of N_1-functionliased substituted benzotriazoles were obtained in a very good to excellent yields of up to 99%. Furthermore, the methodology was also scalable to a gram-scale synthesis, wherein the alkylated triazole **1.85**, known for exhibiting antimicrobial properties, was obtained in 75% yield. The site selectivity of $B(C_6F_5)_3$ catalysed N_1-alkylation of triazoles was attributed to the Lewis basicity of N_1 atom and the reversible formation of triazole-borane adduct **1.86**.



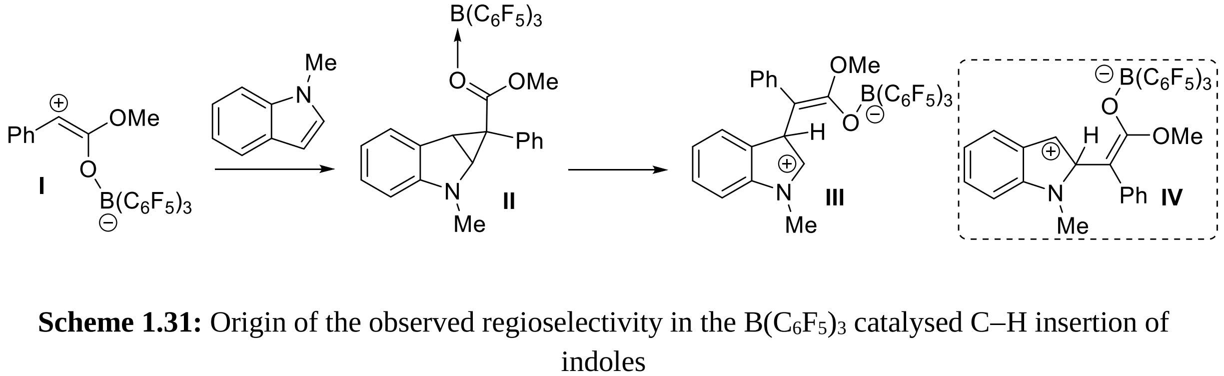
Scheme 1.29: $B(C_6F_5)_3$ catalysed N_1-alkylation of triazoles

Identical reactions conditions were also applied by Melen *et al.*, in a presence of indoles with aryl diazoesters **(Scheme 1.30)**.[87] 20 examples of C_3-substituted *N*-methyl indoles, (obtained in up to 90% of isolated yields) were obtained as one regioisomer, and various substitutions, including halogens and alkyl groups were well-tolerated on both indole and diazo substrates. The methodology was also chemoselective, as when unprotected indoles were reacted, there was no observation of *N*-functionalisation, and rather the formation of C_3-substitituted products were observed in up to 72% of isolated yields. Moreover, when pyrroles were reacted under the optimised reaction conditions, the expected C_2-substituted products were obtained in 65% (**1.86**) and 68% of isolated yields.

Extensive mechanistic studies were undertaken to justify the observed regioselectivity in the case of protected indoles **(Scheme 1.31)**. The expected electrophilic carbene-borate intermediate **I** is first formed, serving as an electrophile, which initially undergoes a cyclopropanation reaction with indole to form the cyclopropanated intermediate **II**, which is formed with a free energy of -38.8 kcal/mol. The cyclised intermediate is highly unstable, due to the nature of the indole and consequently, a rapid ring opening is initiated. This results in the formation of the carbocation intermediate **III**, wherein the carbocation is preferably present on C_2-position, as it is readily stabilised *via* π-donation from the nitrogen atom. Formation of the carbocation intermediate at the C_3-position **IV** was also calculated, which showed to have higher free energy 11.7 kcal/mol, thus justifying the observed regioselectivity.



Scheme 1.30: $B(C_6F_5)_3$ catalysed C–H insertion of indoles

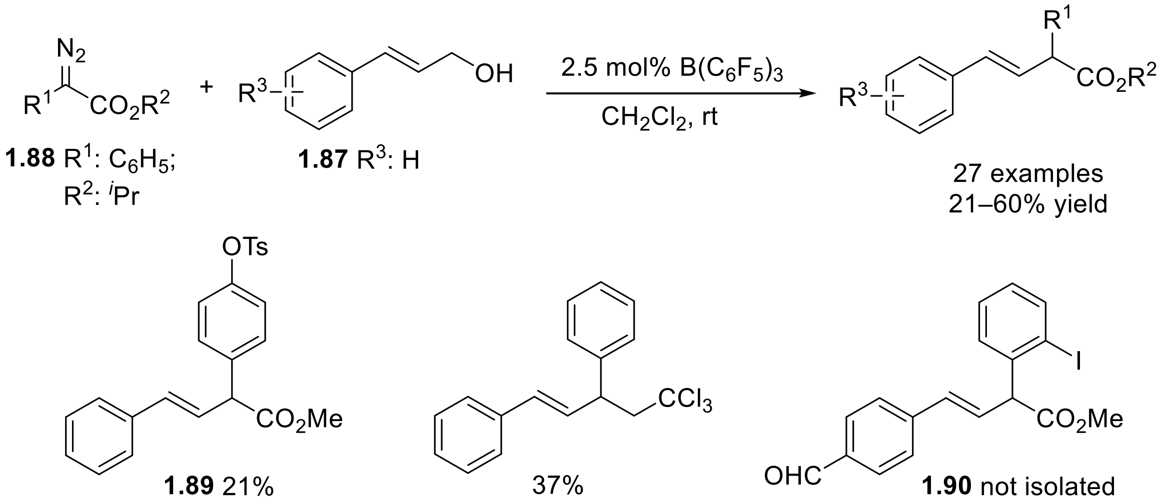


Scheme 1.31: Origin of the observed regioselectivity in the $B(C_6F_5)_3$ catalysed C–H insertion of indoles

1.5.2 $B(C_6F_5)_3$-catalysed C–C functionalisation of aryl diazoesters

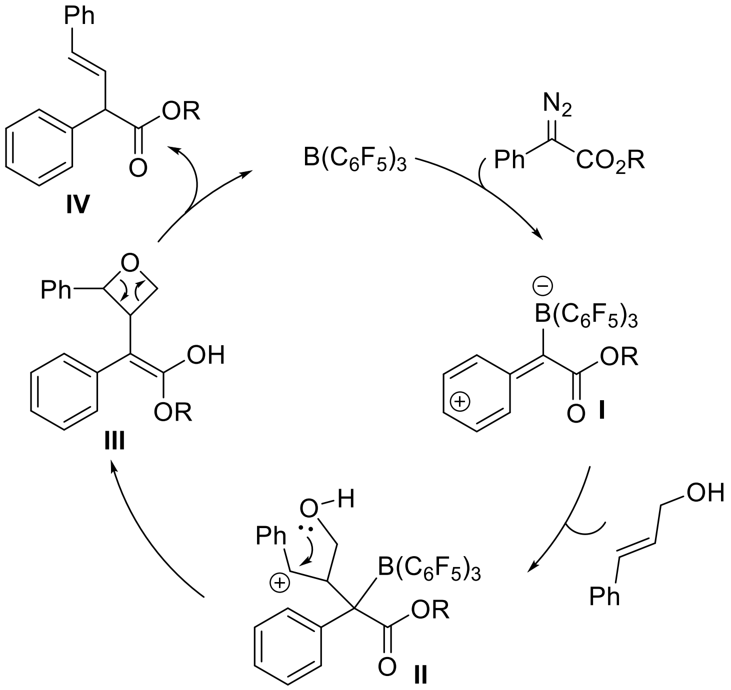
In addition to the C–H functionalisation reactions, $B(C_6F_5)_3$ has also been found to be also an effective catalyst towards the C–C functionalisation of allyl alcohols.[88] During a thorough optimisation it was revealed that a low loading of 2.5 mol% of $B(C_6F_5)_3$ promoted the reaction between the cinnamyl alcohol **1.87** and isopropyl phenyldiazoacetate **1.88** most efficiently, as the functionalised product was obtained in the highest observed yield of 52%. The improved yield was observed due to the minimisation of the formation of the O–H insertion byproduct, which was attributed to the lower amounts of the catalyst and carrying out the reactions in higher dilution. Moreover, when other Lewis acids such, $BF_3{\cdot}OEt_2$ or TMSOTf were screened, no products were observed. A potential hydrolysed product of $B(C_6F_5)(OH)_2$ also failed to catalyse the reaction, indicating that the bulkier strong Lewis acid is indeed required for the chemical transformation.

A wide substrate scope of 27 examples was presented, wherein different substitutions on the aryl ring of both cinnamyl alcohol and aryl diazoacetate substrates were explored **(Scheme 1.32)**. With regards to aryl diazoacetates, alkyl, halide, as well as methoxy group substitutions were all well tolerated, with the observed isolated yields of up to 60%. A slight decrease in yield was observed with a *para*-tosyl substitution, wherein the product **1.89** was obtained in a poor yield of 21%. Furthermore, different substitutions on the carbonyl moiety of the diazo ester were investigated, wherein methyl, 2-butyl, benzyl, and trichloroethyl groups were all tolerated. Similarly, in terms of the substitutions present on the aryl ring of cinnamyl alcohols, alkyl, ether, as well as halide substitutions were well tolerated as the corresponding compounds were obtained in moderate to good yields of 36–55 % isolated yield. Interestingly, electron-withdrawing groups (such *p*-NO_2 and *p*-CF_3) resulted in a decrease of the obtained yields as the isolation of the corresponding products was difficult due to their instability during purification by silica column chromatography. Furthermore, it was also shown that the formaldehyde functionality on the aryl ring was tolerated, thought the isolation of the corresponding product **1.90** was unsuccessful due to the similar R_f with the O–H by-product.



Scheme 1.32: $B(C_6F_5)_3$ catalysed C–C functionalisation of cinammyl alcohols

Furthermore, based on the undertaken mechanistic studies, a catalytic cycle for the $B(C_6F_5)_3$ mediated C–C functionalisation of allylic alcohols was proposed **(Scheme 1.33)**. In the initial step, $B(C_6F_5)_3$ activates the diazo ester at the N_2 functionality, forming a carbene intermediate **I**, which is then susceptible towards the nucleophilic attack at the β-*sp*^{2}-carbon present on the cinnamyl alcohol to form the quaternary carbon centre intermediate **II** with a benzylic carbocation. The carbocation is subsequently additionally stabilised by the adjacent oxygen atom, forming an oxetane ring **III**, which then undergoes ring opening, resulting in a formation of the final product **IV** whilst simultaneously the catalyst is regenerated.



Scheme 1.33: Proposed catalytic cycle for the $B(C_6F_5)_3$-catalysed C–C functionalisation of vinyl alcohols

1.6.0 Frustrated Lewis Pairs

As discussed in the previous sections, $B(C_6F_5)_3$ is a strong bulky Lewis acid, capable of mediating diazo compound activation, which can be further utilised for various organic transformations. As such, this makes $B(C_6F_5)_3$ a plausible alternative towards the precious transition metal catalysts, whose drawbacks often include high toxicity as well as higher costs.

In 2007, it has been demonstrated that in a presence of bulky Lewis base (LB), including ^{t}Bu$_3$P or Mes$_3$P, $B(C_6F_5)_3$ does not undergo a typical formation of Lewis acid-base adduct **(Figure 1.9)** and the combination showed to rather activate dihydrogen at room temperature instead **(Scheme 1.34)**.[89] The observed reactivity was shown to be due to the unquenched Lewis acidity and basicity **(Figure 1.9, B)**. The Lewis pair is still able to accept an electron density from the filled σ-orbital of H_2 into the empty *p*-orbital of the LA and simultaneously the Lewis pair donates an electron density from the filled *p*-orbital of the LB into the σ^*-orbital of H_2, thus facilitating the heterolytic cleavage of H_2 (**Figure 1.10, A**). This activation is similar to the H_2

activation by the transition metals, wherein the *d*-orbitals of transition metal accept and donate the electron density instead **(Figure 1.10, B)**.

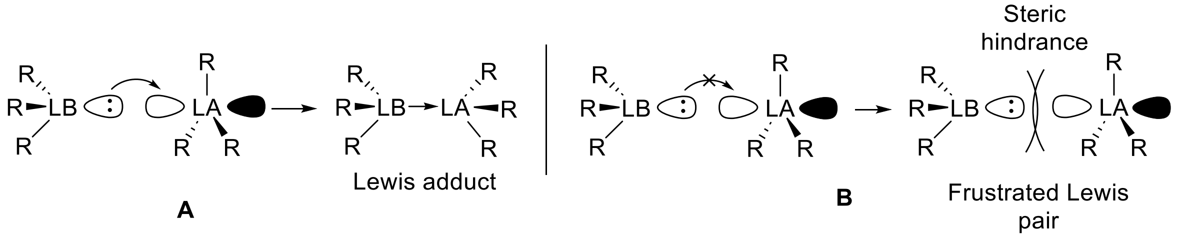
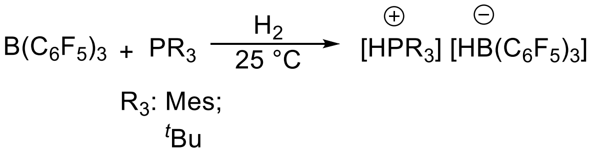


Figure 1.9: Conventional formation of Lewis adducts *vs* formation of frustrated Lewis pairs



$$B(C_6F_5)_3 + PR_3 \xrightarrow[25\ °C]{H_2} \overset{\oplus}{[HPR_3]}\ \overset{\ominus}{[HB(C_6F_5)_3]}$$

R_3: Mes; ${}^tBu$

Scheme 1.34: Activation of dihydrogen by FLPs

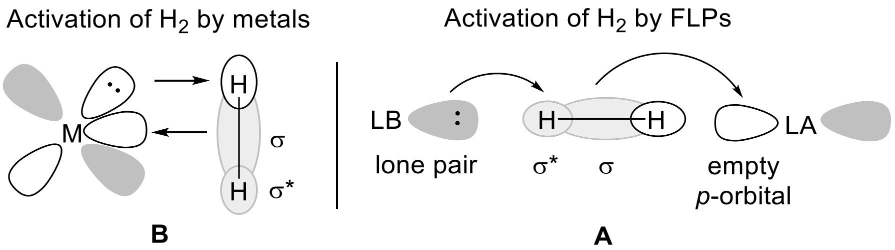
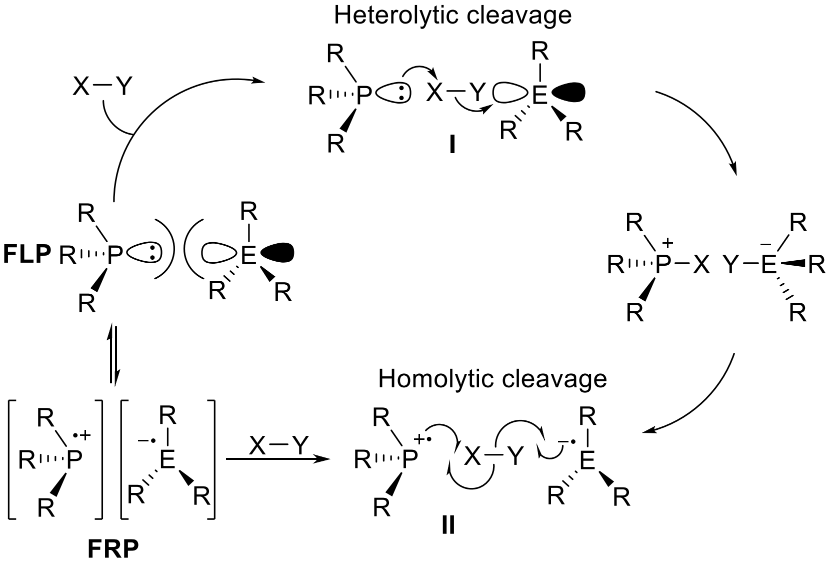


Figure 1.10: Activation of H_2 by metals *vs* FLPs

The unquenched Lewis acidity and basicity has been later coined with the term 'frustrated Lewis pairs (FLPs)'. Since their discovery, FLPs' utilisation has been expanded towards the activation of other small molecules, including CO_2, NO_2, or SO_2.[90,91]

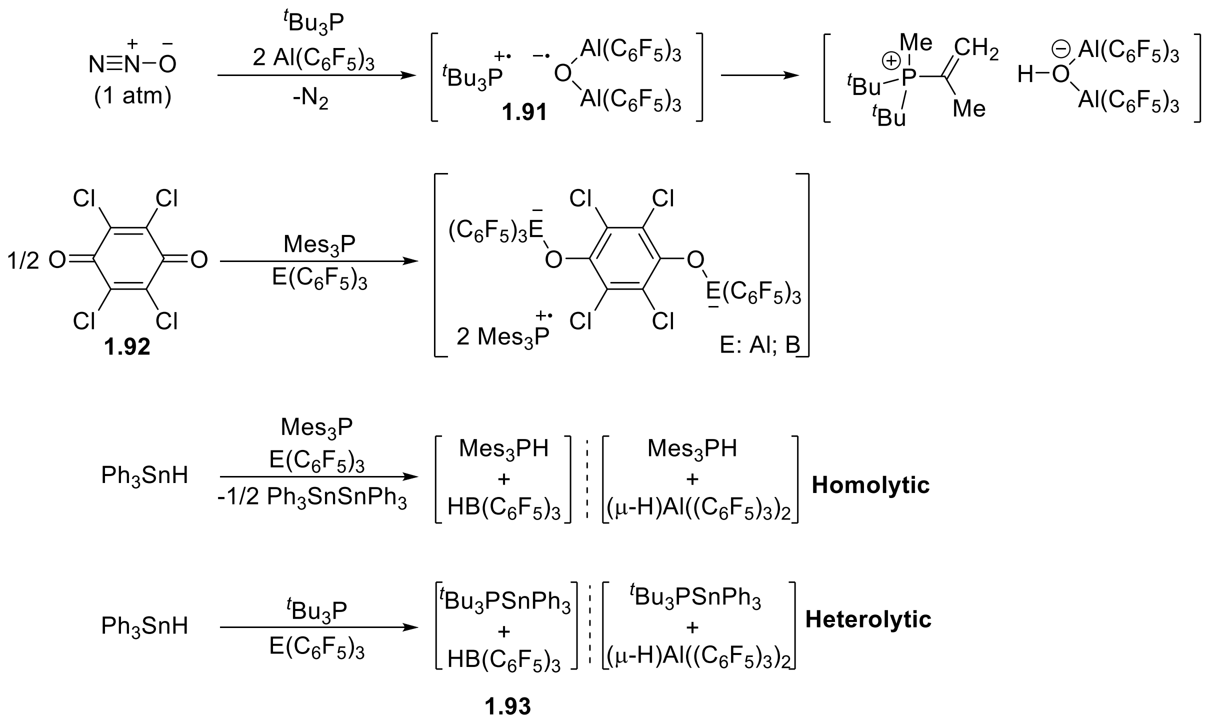
1.6.1 Divergent activation of small molecules by FLPs

Since the initial discovery of FLPs, it has been postulated that the small molecule activation proceeds solely *via* a two-electron pathway, wherein the heterolytic bond cleavage takes place **(Scheme 1.35, I)**. However, more recent studies suggest that certain combinations of Lewis acids and bases, under certain reaction conditions, promote the formation of frustrated radical pairs (FRPs) instead, which subsequently mediate the homolytic bond cleave of the substrate **(Scheme 1.35, II)**.



Scheme 1.35: Modes of activation of small molecules by FLPs *vs* FRPs

One of the earliest examples of FRPs was reported by Stephan *et al.*, wherein a 1:2 mixture of ^{t}Bu$_3$P/Al(C$_6$F$_5$)$_3$ and nitrous oxide formed a transient FRP species **1.91**, which was subsequently utilised for alkyl- and aryl C–H bond activation **(Scheme 1.36)**.[92] Another FLP system, composed of Mes$_3$P/E(C$_6$F$_5$)$_3$ (E: B; Al) underwent FRP formation in the presence of tetrachloro-1,4-benzoquinone **1.92**.[93] The same FRP system promoted the homolytic cleavage of an Si–H bond, when in a presence of Ph$_3$SnH. Interestingly, when ^{t}Bu$_3$P was used instead, [^{t}Bu$_3$P-SnPh$_3$]$^+$[HB(C$_6$F$_5$)$_3$]$^-$ **1.93**, the product of heterolytic cleavage was obtained.[93] Further examples of FRP-mediated single-electron transfer reactions were also reported in a presence of dihydrogen, nitric oxide, or peroxide [(PhCOO)$_2$] substrates, whose electron paramagnetic resonance (EPR) studies have been recently extensively reviewed.[94, 95, 96, 97] As such, in the following sections, only selected examples of FLP and FRPmediated C−X bond-forming reactions will be covered in more details.



Scheme 1.36: FLP systems reported to also form FRPs

1.6.2 FLP-mediated C–X bond forming reactions

The most prevalent utilisation of frustrated Lewis pairs in organic synthesis has been demonstrated in catalytic hydrogenation reactions of unsaturated substrates, including carbonyls, imines, alkenes, or alkynes. The reported hydrogenation reactions have been performed in a presence of molecular hydrogen (H_2), or in a presence of a surrogate H_2 source, such as NH_3BH_3, diisopropylamine, cyclohexa-1-4-diene, or a Hantzsch ester **1.94**. More recently, FLPs have been also utilised in the asymmetric hydrogenations, wherein the chirality has been introduced into the final product *via* using a chiral ligand, chiral borane, or a chiral Lewis base.[98, 99]

Further utilisation of FLPs have been demonstrated in cyclisation reactions, in both stoichiometric and catalytic fashion **(Scheme 1.37)**. The stoichiometric FLP-mediated cyclisation reactions include intramolecular cyclisations in a presence of 1 equiv. of $B(C_6F_5)_3$ and aliphatic unsaturated phospines **(Scheme 1.37, A)**, unsaturated amines **(Scheme 1.37, B)**, or propargyl amides **(Scheme 1.37, C)**, wherein the basic functionality of the substrate represented a Lewis base component of the FLP system.[100,101,102]

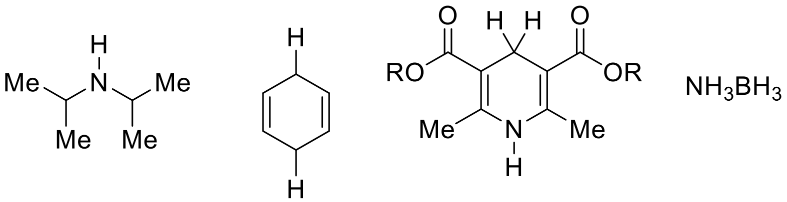
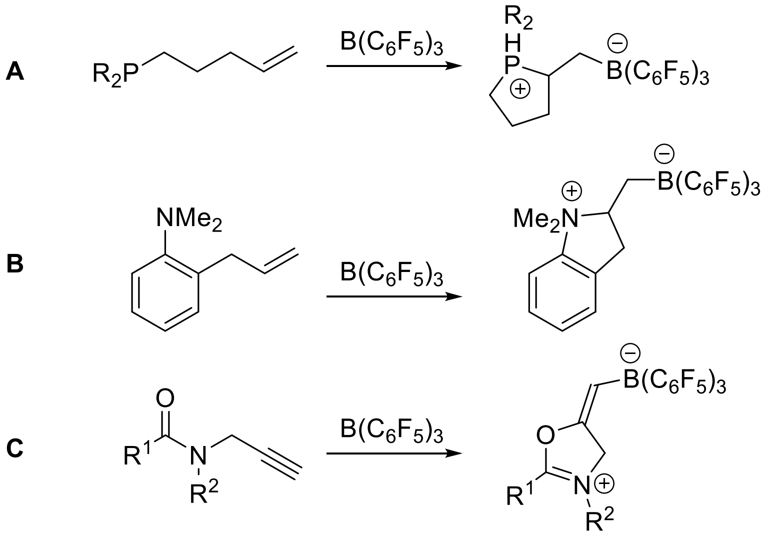


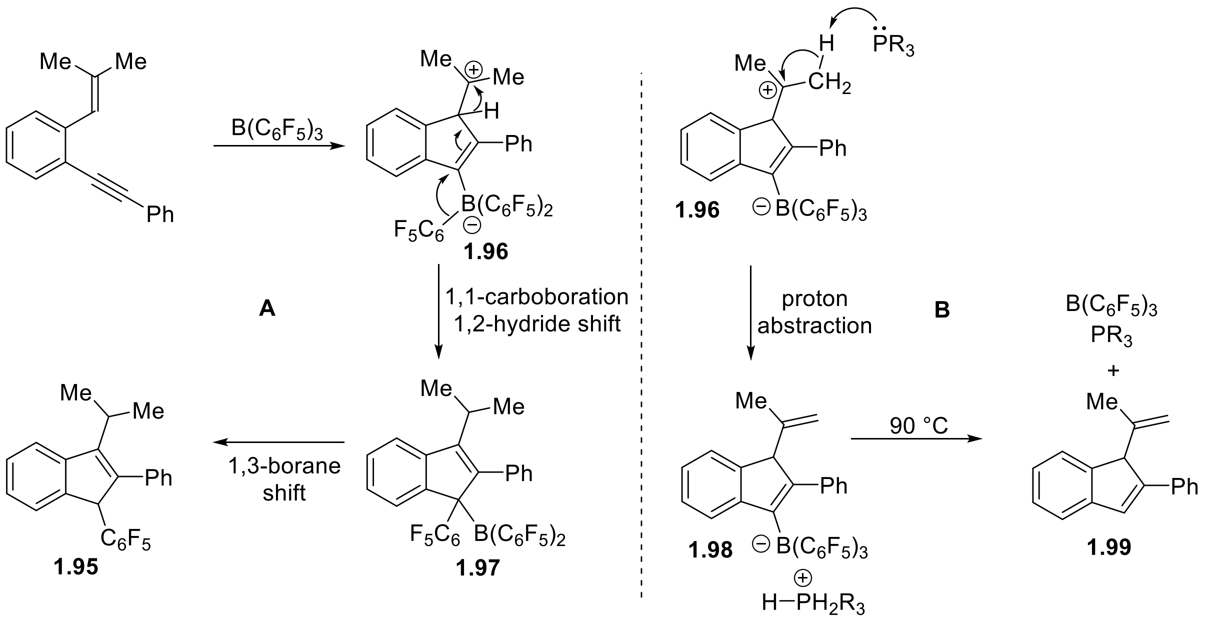
Figure 1.11: Alternative: H_2 source for FLP mediated transfer hydrogenation reactions



Scheme 1.37: FLP mediated cyclisation reactions with stoichiometric $B(C_6F_5)_3$

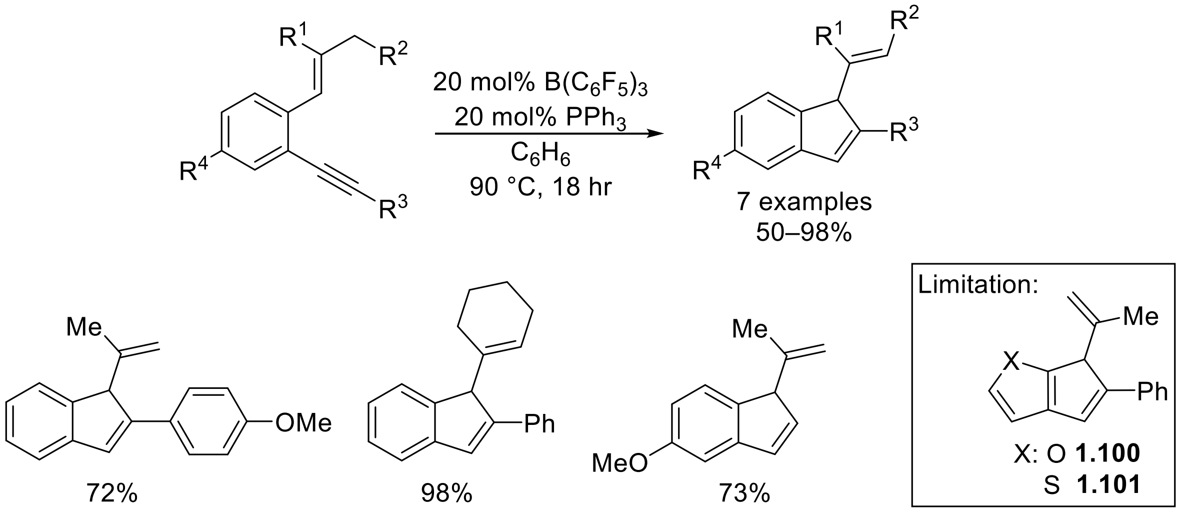
Subsequently, the first catalytic FLP mediated cycloisomerisation of 1,5-enynes was reported by Paradies *et al.*[103] Initially, the reaction was carried out solely in a presence of a stoichiometric amount of $B(C_6F_5)_3$, wherein *5-endo*-dig product **1.95** was isolated in 54% yield. Conducted DFT studies revealed that the cyclised product **1.95** was formed *via* initial Lewis acid activation of the alkyne moiety, upon which the intramolecular addition of the alkene into the vinylic carbocation occurred, resulting in formation of the zwitterionic intermediate **1.96** **(Scheme 1.38)**. In the absence of Lewis base, the formed reactive carbocation intermediate **1.96** is not quenched properly, and therefore a rearrangement sequence proceeds, involving a

1,2-hydride shift and 1,1-carboboration to form intermediate **1.97**. Lastly, a subsequent 1,3-borane shift results in a formation of the *5-endo*-dig product **1.95 (Scheme 1.38, A)**. Nevertheless, in a presence of stoichiometric phosphine-based Lewis base, such PPh_3, intermediate **1.96** undergoes a proton abstraction, resulting in the formation of a stable onium borate intermediate **1.98** was observed instead. Subsequent heating of the intermediate **1.98** at 90 °C caused protodeborylation to occur, resulting in the formation of the final cycloisomerised product **1.99** as well as the regeneration of the FLP system **(Scheme 1.38, B)**.



Scheme 1.38: Formation of cyclised products in the presence of stoichiometric $B(C_6F_5)_3$ *versus* in the presence of stoichiometric FLP

The regeneration of both Lewis acid and base indicated that the reaction could also be carried out in a catalytic fashion. Indeed, 20 mol% and 10 mol% of $B(C_6F_5)_3/PPh_3$ afforded the corresponding cyclised product in 69% and 57% yield, respectively. Reducing the catalytic loading even more to 5 mol% resulted in a poor yield of 24%. As such, reaction conditions of 20 mol% of $B(C_6F_5)_3/PPh_3$ in benzene and heating to 90 °C resulted in a cycloisomerisation of seven variously substituted enynes in up to 98% yield. Notably, a limitation of this methodology included substrates bearing furanyl **1.100** or thiopentyl **1.101** rings in a central aromatic moiety **(Scheme 1.39)**.

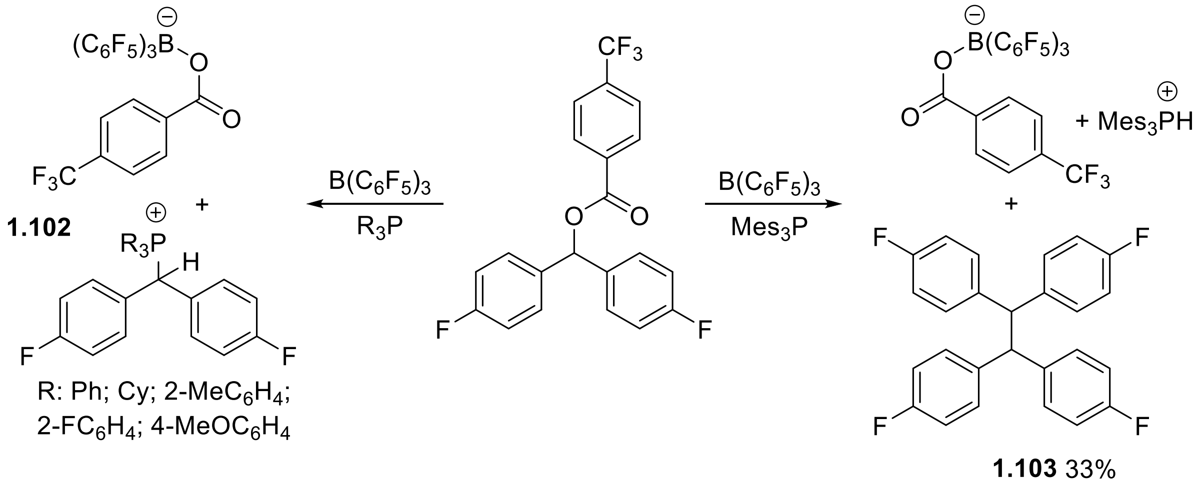


Scheme 1.39: FLP-catalysed cycloisomerisation of 1,5-enynes

1.6.3 FRP mediated C–C bond forming reactions

As described in the **section 1.6.1**, under certain conditions, the formation of a frustrated radical pair is observed before the activation of small molecules. Several reports have been already made, wherein such FRP systems have been utilized in C–C bond forming reactions.

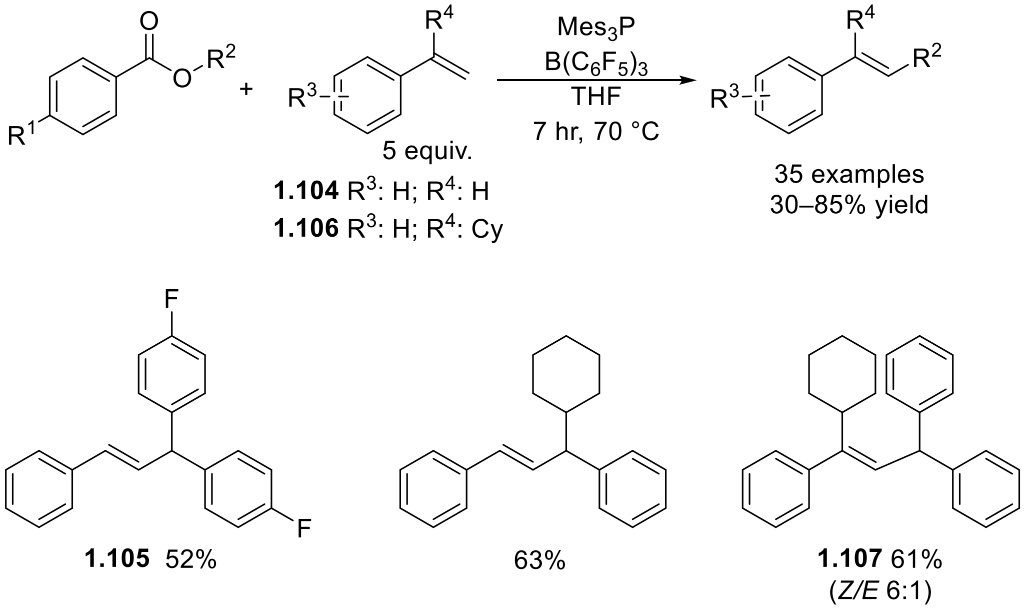
One of the first examples of the utilisation of FRPs in the organic synthesis has been reported by Melen *et al.*[104] In this study, various FLP systems containing $B(C_6F_5)_3$ and phosphine-based Lewis bases were utilized for the activation of the $C(sp^3)$–O bond of diaryl esters. In a presence of most screened Lewis bases, including PCy_3, PPh_3, $P(o\text{-}MeC_6H_4)_3$, the formation of expected phosphonium borate **1.102**, a product of the heterolytic cleavage, was obtained. However, upon mixing of $PMes_3$ with $B(C_6F_5)_3$ and the diaryl ester in $CDCl_3$, the formation of a purple-coloured solution was observed. Such a colour change was thought to be indicative of the formation of $[PMes_3]^{+\cdot}$, as previously described in a study conducted by Stephan *et al.*[105] Furthermore, an unprecedented formation of the homocoupled benzyhydryl **1.103** was observed, which was isolated in 33% yield **(Scheme 1.40)**. Subsequent EPR studies indeed revealed a doublet signal in the EPR spectrum upon mixing $B(C_6F_5)_3$, $PMes_3$ and ester, which again was attributed to the generation of $[PMes_3]^{+\cdot}$.



Scheme 1.40: Observed divergent reactivities in the presence of various frustrated Lewis pairs and diaryl esters

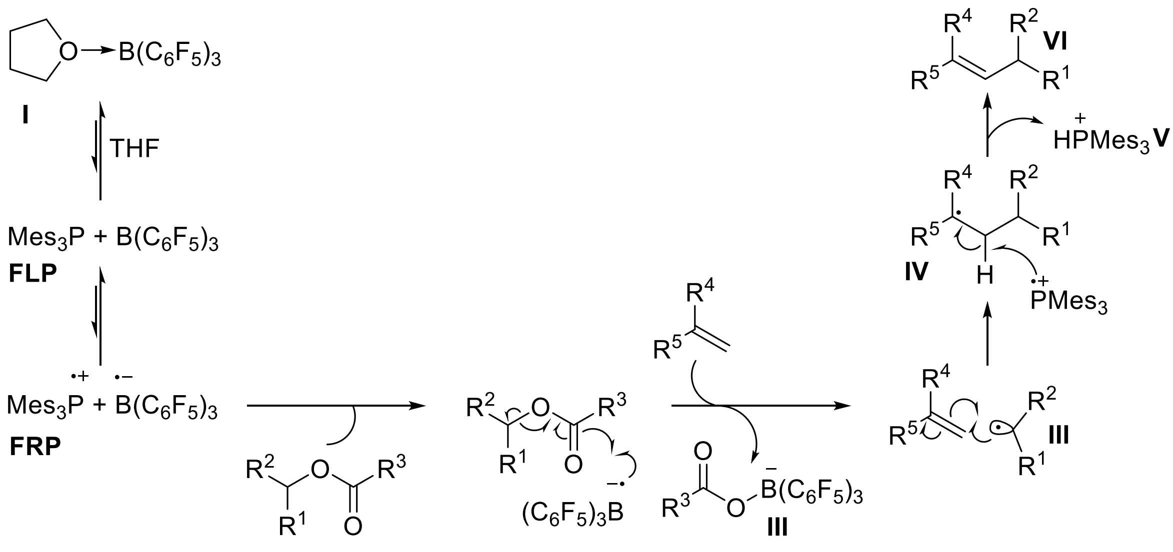
Subsequently, the observed radical reactivity was further utilised in the organic synthesis, wherein the FRPs promoted a C–H bond activation of commercially available styrene **1.104**, resulting in the formation of (*E*)-isomer of $C_{sp}{}^3$–$C_{sp}{}^2$ coupled product **1.105** in 11% yield. Further optimisations revealed that in order to maximise the obtained yield, the excess (of up to 5 equiv.) of styrene substrate is necessary. Moreover, the use of a coordinating solvent, such THF, improved the yield of the desired β-functionalised product **1.105** to 52%. This was presumably due to the coordination of THF to $B(C_6F_5)_3$, which resulted in lower concentration of $[PMes_3]^{+\cdot}$, essentially resulting in better observed yield and purity of the final product.

A broad substrate scope was presented as well, wherein 35 variously substituted β-functionalised styrenes were presented in good to excellent isolated yields of up to 85% **(Scheme 1.41)**. In general, better yields were obtained with diaryl esters bearing electron-donating groups (*p*-OMe) when compared to electron poor diaryl esters (*p*-F), presumably due to the better stabilisation of the benzylic radical species. Esters bearing an alkyl moiety, such cyclohexyl or methyl, were compatible with the present methodology, though generally poorer yields were observed when compared to the diaryl esters. Interestingly, when di-substituted styrene such **1.106** was reacted, a mixture of isomeric products **1.107** was obtained in up to 6:1 ratio.



Scheme 1.41: FRP mediated C–C bond coupling of styrenes with diaryl esters

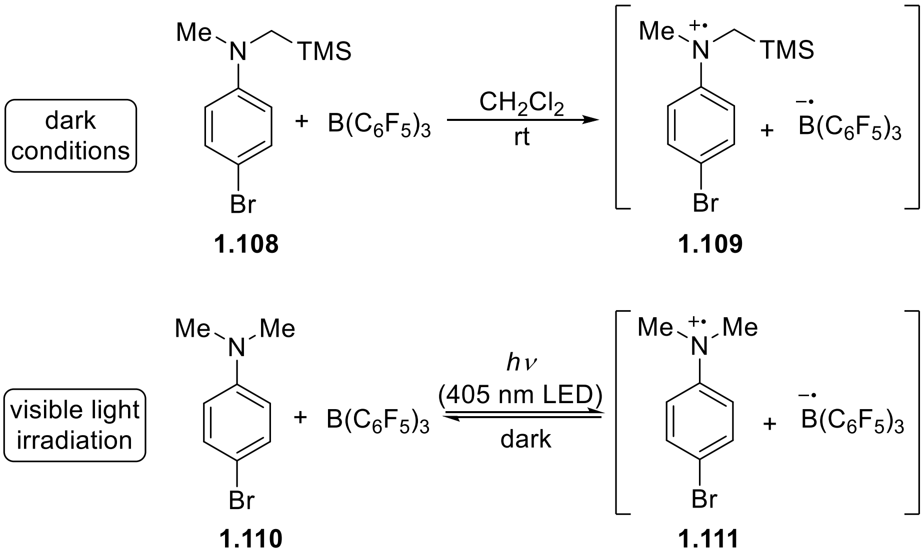
Based on the conducted DFT and EPR studies, and the observed reactivity, a mechanism for FRP-mediated C−H bond functionalisation was proposed **(Scheme 1.42)**. Initial formation of FRPs is promoted by the dissociation of $B(C_6F_5)_3{\cdot}THF$ adduct **I**, which is also in equilibrium with both FLP and FRP system. A subsequent homolytic activation of C−O bond in the aryl ester by $B(C_6F_5)_3^-$ results in the formation of benzylic radical **II** and borate adduct **III**. The benzylic radical **III** then undergoes an addition towards the styrene, forming a tertiary carbon-based radical species **IV**, which subsequently undergoes a hydrogen atom abstraction by $[PMes_3]^{+\cdot}$, forming phosphonium cation **V** and the final β-functionalised product **VI**.



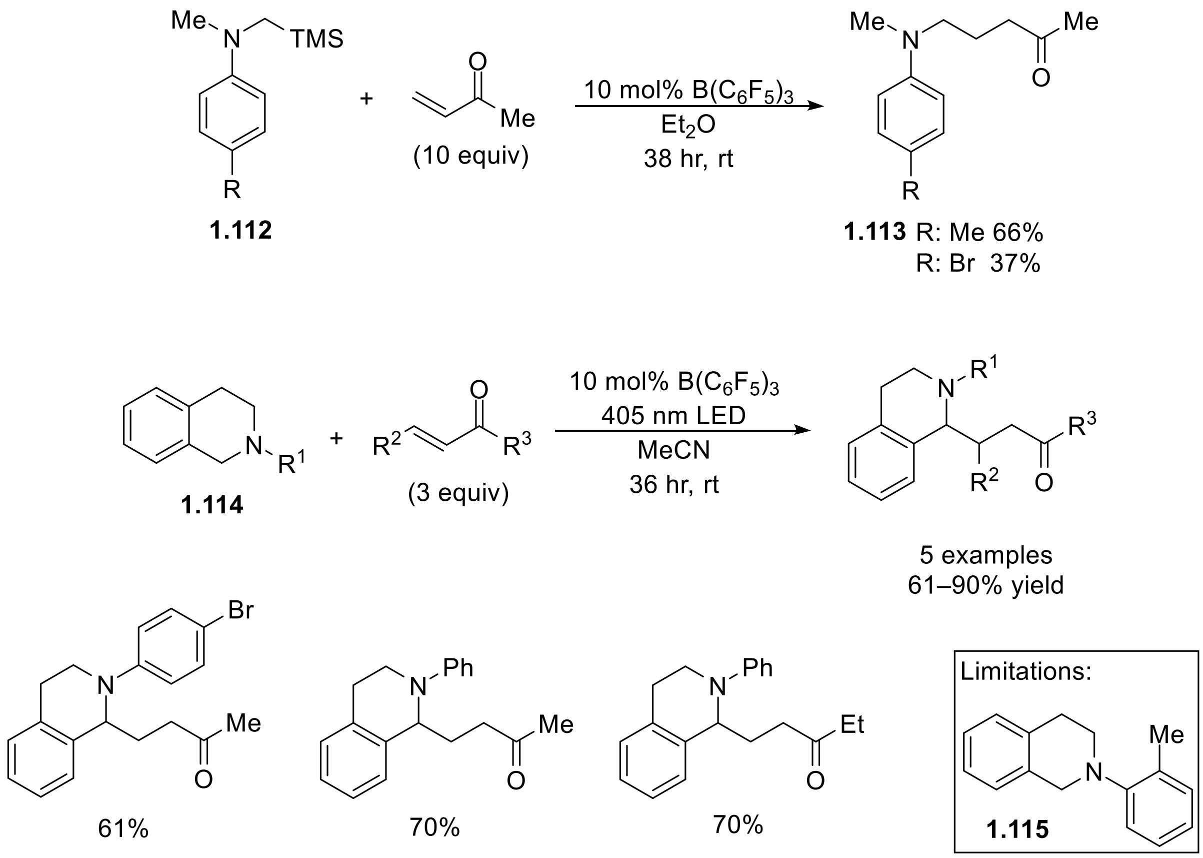
Scheme 1.42: Proposed mechanism for FRP-mediated C–C coupling reactions

Other FRP system have been reported by Ooi *et al.*, wherein a single-electron transfer was observed between $B(C_6F_5)_3$ and *N,N*-dialkyl aniline.[106] It was later identified that the FRPs were generated *via* the formation of an electron donor-acceptor (EDA) complexes, wherein $B(C_6F_5)_3$ served as π-acceptor and aniline as the π-donor, which could be generated under both dark or visible-light irradiation conditions, depending on the substitution present on the aniline **(Scheme 1.43)**. In case of a trimethylsilyl derivative **1.108**, the formation of α-aminoalkyl radical cation **1.109** was observed even under dark conditions. However, when the *para*-bromo-*N,N*-dimethylaniline **1.110** was mixed with $B(C_6F_5)_3$, no signal in the electron spin resonance (ESR) was observed. Nevertheless, upon the irradiation of the solution with 405 nm light emitting diode (LED) light, a formation of aminoalkyl radical cation **1.111** was detected.

Such reactivity was subsequently employed for the redox catalysis, wherein 10 mol% of $B(C_6F_5)_3$ was shown to mediate C–C bond forming reaction of trimethylsilyl derivatives of *N,N*-dialkyl aniline **1.112** with an excess (10 equiv) of electron-deficient methyl vinyl ketone **(Scheme 1.44)**. The observed yields of the radical addition product **1.113** were initially rather poor (up to 66%), which was attributed to the formation of the enolate ion, a side product of desilylation of the cationic radical species, followed by one electron reduction by $B(C_6F_5)_3^{-\bullet}$. As such, MeOH, serving both as a proton source and trimethylsilyl (TMS) trapping agent, was used in a solvent system together with Et_2O in 1:10 ratio, which improved the yield of the desired product to 92%. Additionally, variously substituted *N*-aryltetrahydroisoquinolines **1.114** were reacted with α,β-unsaturated ketones, under UV-visible light and in a presence of 10 mol% $B(C_6F_5)_3$. Both electron-withdrawing and -donating substituents on the aryl ring attached to the nitrogen were tolerated, however better yields were generally obtained with *p*-OMe group when compared to *p*-Br substitution. However, the limitation included a tolyl group substitution at *ortho*-position **1.115**, wherein no product formation was observed, which was attributed to the lack of EDA complexes formation due to the increased sterics.



Scheme 1.43: Generating α-amino alkyl radicals under dark and visible light irradiation conditions



Scheme 1.44: C–C bond coupling of *N*,*N*-dialkyl anilines and *N*-aryltetrahydroisoquinolines with unsaturated ketones

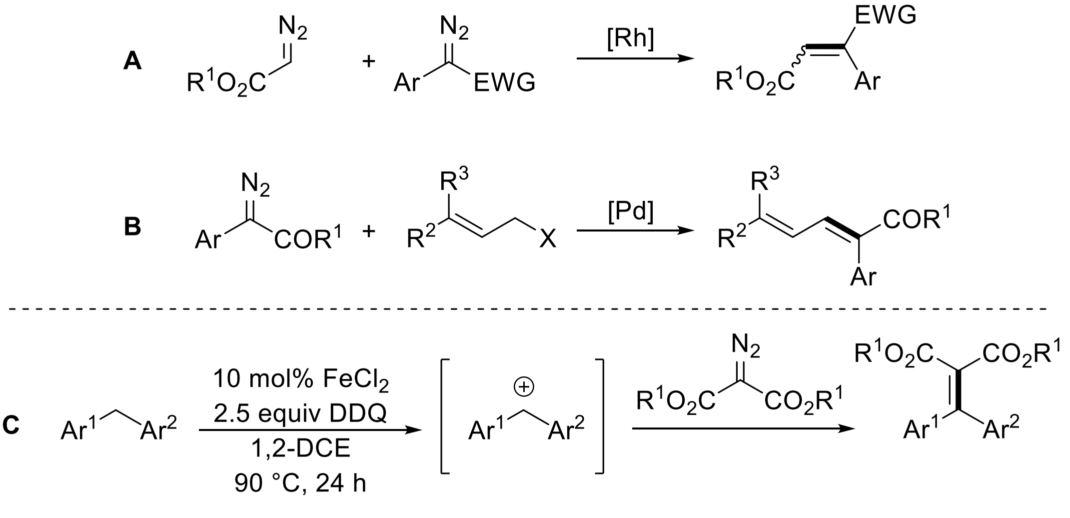
1.7 Summary

In the introductory part of this thesis, I have reviewed boron-based Lewis acids, mainly $B(C_6F_5)_3$, as plausible alternatives towards transition metal-based catalysts. I have justified boranes' exhibited reactivity, their most common synthesis, as well as their utilisation in organic synthesis when in a presence of diazo ester substrates. Furthermore, I have introduced the diazo esters, wherein I have discussed nature of these carbene precursors, their synthesis, and how these can be activated either *via* transition metals, heat, light, or by the boranes. I have included a discussion of some more relevant reports, wherein the diazo activation by borane catalyst was utilised in organic synthesis. Lastly, I have introduced frustrated Lewis pairs and their discovery, and how their divergent reactivities led to their utilisation in various chemical transformations.

2.0 Triarylborane-catalysed alkenylation reaction of aryl esters

2.1 Introduction

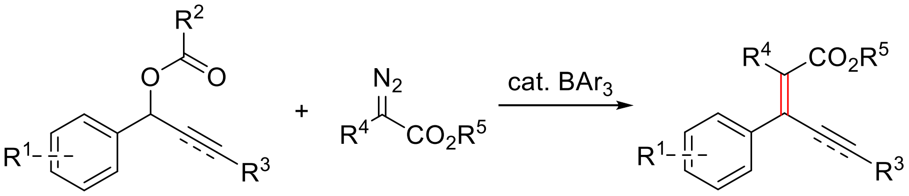
As covered in the introductory part of the thesis, bulky triarylboranes have been shown to catalyse various C–C bond forming reactions, mainly C–X insertion reactions, in the presence of diazo compounds as reactive carbene precursors. However, it has been also demonstrated that diazo compounds in the presence of precious transition metals can also undergo C=C bond forming reactions, whether in the presence of another diazo compounds or in the presence of allyl halides **(Scheme 2.1**, **A** and **B)**.[107, 108] More recently, such alkenylation reactions were also reported to be mediated by more abundant firstrow transition metals, such as iron, wherein the diazo esters were reacted with variously substituted diphenylmethanes **(Scheme 2.1, C)**.[109] Such reactions were shown to proceed *via* initial benzylic carbocation formation, wherein the carbocation was generated by using an excess amount of oxidant, in this case 2,3-dichloro5,6-dicyanoquinone (DDQ).



Scheme 2.1: Transition-metal-catalysed alkenylation reactions

2.2 Aims of this work

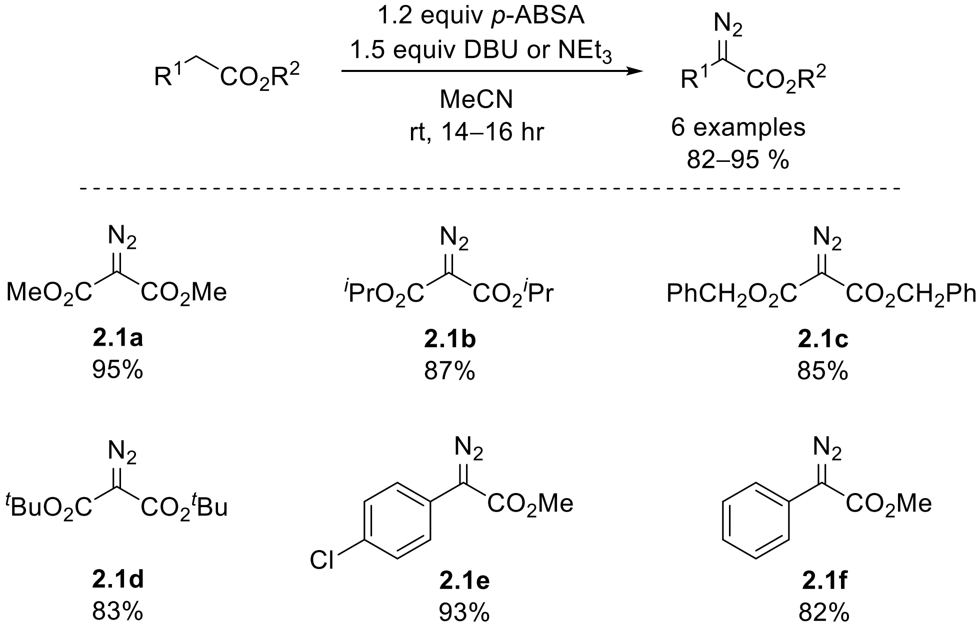
Previously, it was demonstrated that triarylboranes also promote $C_{(sp^3)}$–O bond cleavage of diaryl esters, which results in the formation of a benzylic carbocation.[104] As such, it was questioned whether we could utilise such activation, wherein the formed carbocation intermediate would react with diazo esters without need for an additional oxidant, contrary to Wang *et al.*[109] Furthermore, the reported substrate scope was mainly limited to diphenylmethanes and benzyl sulfides and two equivalents of the carbocation precursor had to be used to achieve satisfactory yields. Therefore, I wanted to develop a more efficient alkenylation methodology and to expand the substrate scope towards substrates bearing both alkyne and alkene functionalities **(Scheme 2.2)**. The resulting ester products with enyne and diene framework would be useful building blocks for the synthesis of various heterocycles, including biologically active lactones.[110]



Scheme 2.2: Aims of this work

2.3 Synthesis of starting materials

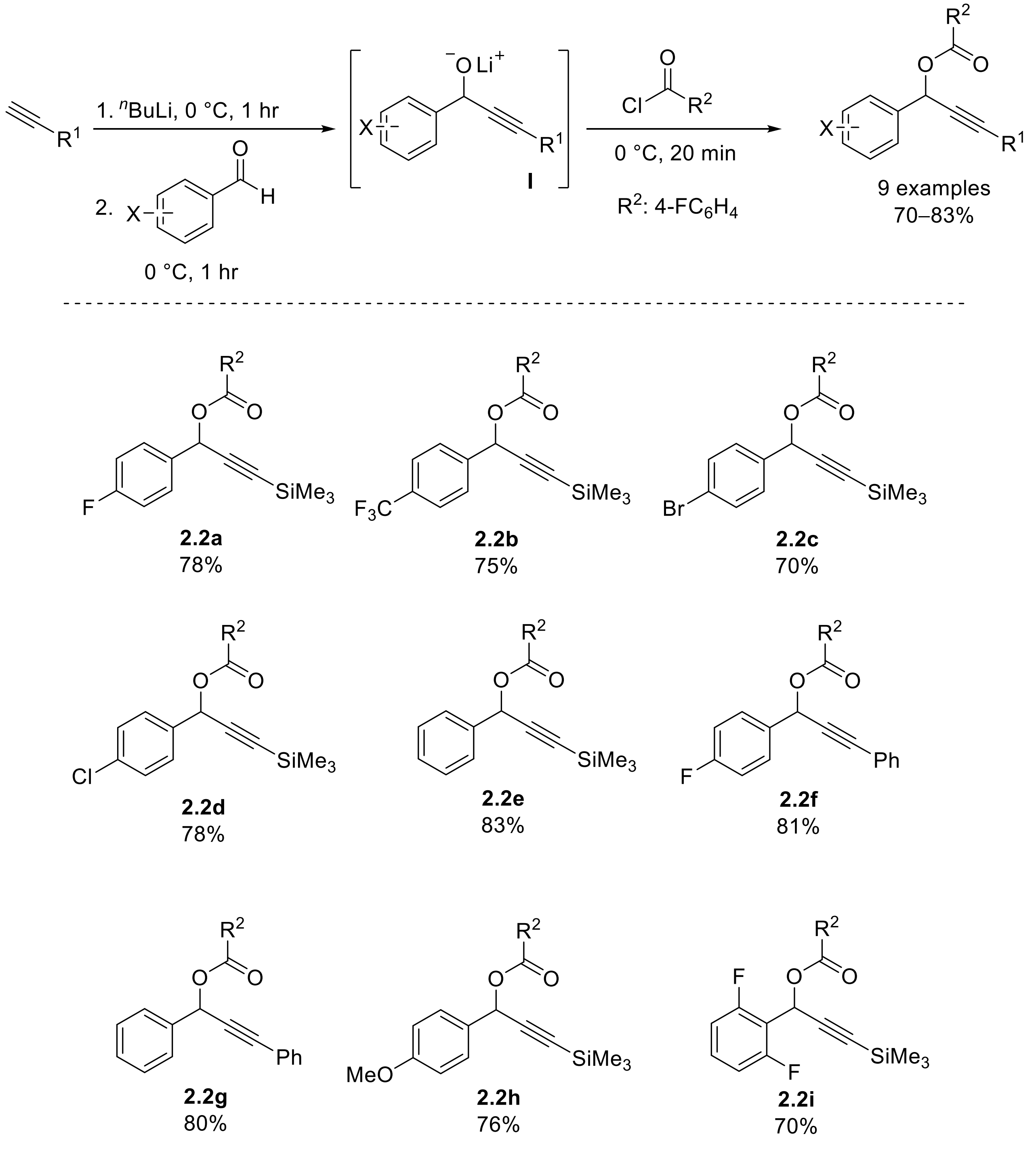
For this study, various diazo esters and aryl esters were synthetised. The diazo esters were prepared with well-known diazo-group transfer reactions (as already discussed in the section **1.4.2.1**), wherein *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) was used as the sulfonyl azide reagent and bases such triethylamine (NEt_3) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were used for the initial deprotonation. In overall, eight different diazo esters (**2.1a**–**2.1f**) were prepared in good to excellent yields of up to 95% **(Scheme 2.3)**. Symmetrical diazo esters, such diazomalonates **2.1a–2.1d,** were chosen as main diazo substrates because they exhibit better overall stability. Moreover, by employing symmetrical diazo esters, a possible formation of diastereoisomers is eliminated, unlike in a presence of unsymmetrical diazo esters **2.1e** and **2.1f**



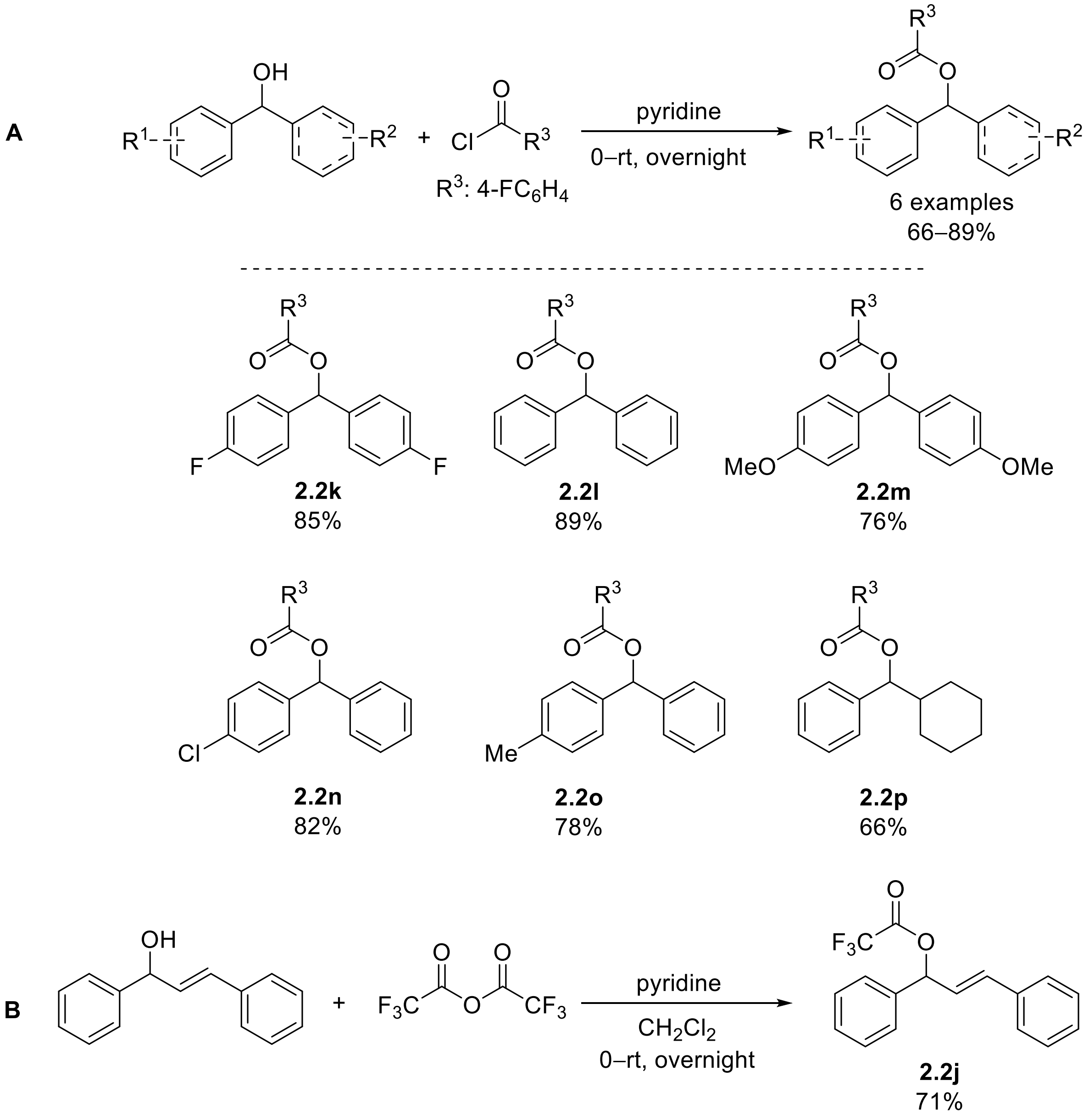
Scheme 2.3: Synthetised diazo esters **2.1a–2.1f**

Various propargyl esters were prepared by the procedure as depicted in **Scheme 2.4**. An initial deprotonation of a terminal alkyne was carried out using ^{n}BuLi at 0 °C, resulting in the formation of an acetylide ion. A subsequent addition of benzaldehyde at 0 °C led to a formation of a reactive alkoxy anion intermediate **(Scheme 2.4**, **I)**, which can be readily trapped with an acyl chloride, thus forming propargyl ester products. With such methodology, nine propargyl esters **2.2a–2.2i** were obtained in good to very good isolated yields of up to 83%.

Diaryl esters were prepared by a similar synthesis, wherein the alcohols were directly reacted with the acyl chloride in pyridine **(Scheme 2.5, A)**. Such ester formation starts with the nucleophilic addition of alcohol on the acyl chloride, resulting in the alkoxy intermediate, which undergoes deprotonation by pyridine as well as an expulsion of the chloride ion, forming the ester product and the pyridinium chloride salt as a by-product. In case of the synthesis of vinyl ester **2.2j (Scheme 2.5, B)**, trifluoroacetic anhydride was used instead of 4-fluorobenzoyl chloride. Overall, seven variously substituted esters **2.2j–2.2p** were prepared with such methodology in up to 89% isolated yield.



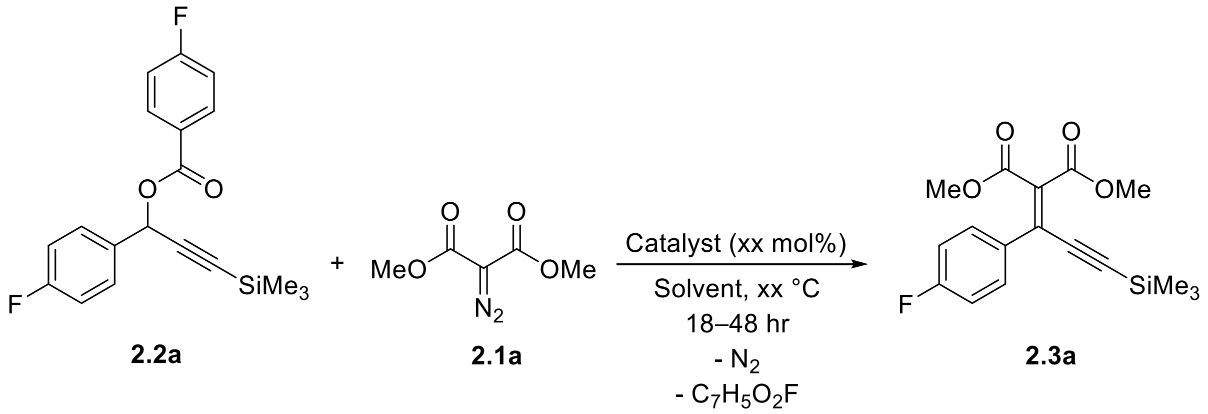
Scheme 2.4: Synthesised propargyl esters **2.2a–2.2i**



Scheme 2.5: Synthesis of vinyl **2.2j** and diaryl esters **2.2k–2.2p**

2.4 Optimisation reactions

The initial optimisation reactions were carried out with 1 equivalent of 1-(4-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-yl-4-fluoro-benzoate **2.2a** and 1.1 equivalent of diazo malonate **2.1a** as model substrates **(Table 2.1)**. It is worth to note that a slight excess of diazo malonate was chosen due to its potential instability even at a room temperature, whereas *para*-F substituted propargyl ester **2.2a** was chosen for an easier monitoring of the completion of reactions *via* ^{19}F-NMR spectroscopy. Moreover, the initial reactions were carried out in α,α,α-trifluorotoluene (TFT) as a solvent, due to its higher boiling point when compared to CH_2Cl_2, hence the reaction could be run at a wider temperature range. On top of that, TFT exhibits slightly higher polarity when compared to toluene, which aided with the better solubilisation of the catalysts, mainly $B(C_6F_5)_3$.



Entry	Catalyst	Catalytic loading [mol%]	Solvent	Temperature [°C]	Time [hr]	Isolated Yield [%]
1	-	-	TFT	65	22	-
2	$B(C_6F_5)_3$	20	TFT	65	18	78
3	$B(C_6F_5)_3$	20	TFT	rt	48	30
4	$B(2,4,6\text{-}F_3C_6H_2)_3$	20	TFT	65	18	41
5	$B(3,4,5\text{-}F_3C_6H_2)_3$	20	TFT	65	18	25
6	$BF_3 \cdot OEt_2$	20	TFT	65	18	-
7	PTSA	10	TFT	65	22	-
8	**$B(C_6F_5)_3$**	**10**	**TFT**	**65**	**18**	**81**
9	$B(C_6F_5)_3$	5	TFT	65	18	42
10	$B(C_6F_5)_3$	10	TFT	100	22	48
11	$B(C_6F_5)_3$	5	TFT	100	22	30
12	$B(C_6F_5)_3$	10	THF	65	22	-
13	$B(C_6F_5)_3$	10	hexane	65	22	45

14	$B(C_6F_5)_3$	10	toluene	65	22	68
15	$B(C_6F_5)_3$	10	CH_2Cl_2	65	22	52

Table 2.1: Optimisation reaction of borane-catalysed alkenylation of propargyl ester

Firstly, a control reaction was carried out to ensure that no reaction takes place in absence of any catalyst. Indeed, after heating the reaction mixture at 65 °C for 22 hours, no formation of a product was observed. However, when 20 mol% of $B(C_6F_5)_3$ was added into the solution of propargyl ester, there was an immediate colour change observed, wherein the colourless solution turned into deep purple. And upon the addition of the diazo malonate, vigorous bubbling was observed from N_2 release from the diazo starting material. After heating the reaction mixture for 18 hours at 65 °C, a major compound, obtained as a yellow solid, was isolated in 78%. ^{1}H-NMR spectroscopy showed two peaks at $\delta = 3.61$ ppm and 3.85 ppm, both having integration of three **(Figure 2.1)**. Such downfield shifted methyl groups were indicating that the product contained both ester moieties from the diazo malonate. A very intense singlet peak at $\delta = 0.23$ ppm with the integration of nine indicated the presence of $SiMe_3$ group from the propargyl ester. In the ^{13}C-NMR spectrum, two distinctive peaks were observed at $\delta = 111.9$ ppm and 102 ppm, which were assigned to the alkyne (C≡C) functionality, even though the alkyne carbons are usually in a region of $\delta = 70\text{–}100$ ppm **(Figure 2.2)**. As a comparison, C≡C peaks of propargyl ester **2.2a** are at $\delta = 101.0$ ppm and 93.2 ppm. Such downfield shift indicated a proximity of electron withdrawing moiety towards the alkyne functionality. Moreover, two signals at $\delta = 165.6$ ppm and 164.1 ppm confirmed a presence of the carbonyl carbons, in this case esters. Lastly, ^{19}F-NMR spectroscopy confirmed a presence of one *para*-substituted phenyl ring, as a single peak at $\delta = -110.80$ ppm was shown. Based on these observations, we elucidated that the alkenylated product **2.3a** was indeed formed. This was later confirmed by a high-resolution mass spectroscopy (HRMS), which identified a compound with a molecular weight of 334.1031, which agreed with the predicted alkenylated product **2.3a**. In addition to the alkenylated product, a white solid was also isolated, which was later identified to be 4-fluorobenzoic acid, which is an expected by-product from this alkenylation reaction.

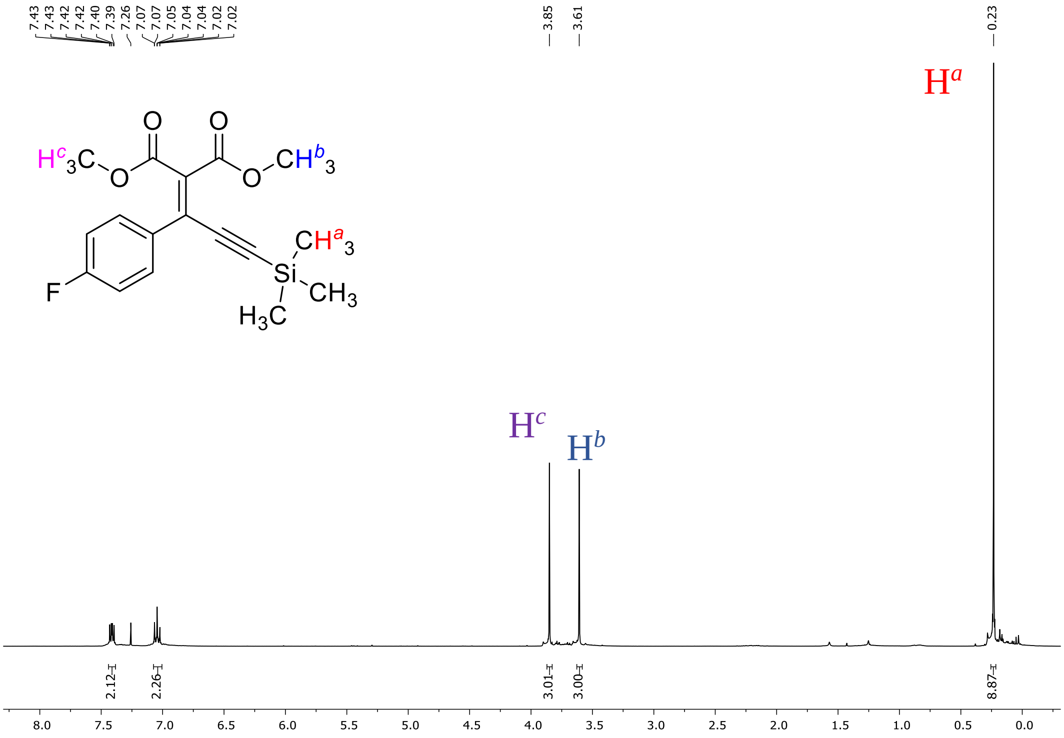


Figure 2.1: ^{1}H-NMR spectrum of the isolated compound **2.3a**

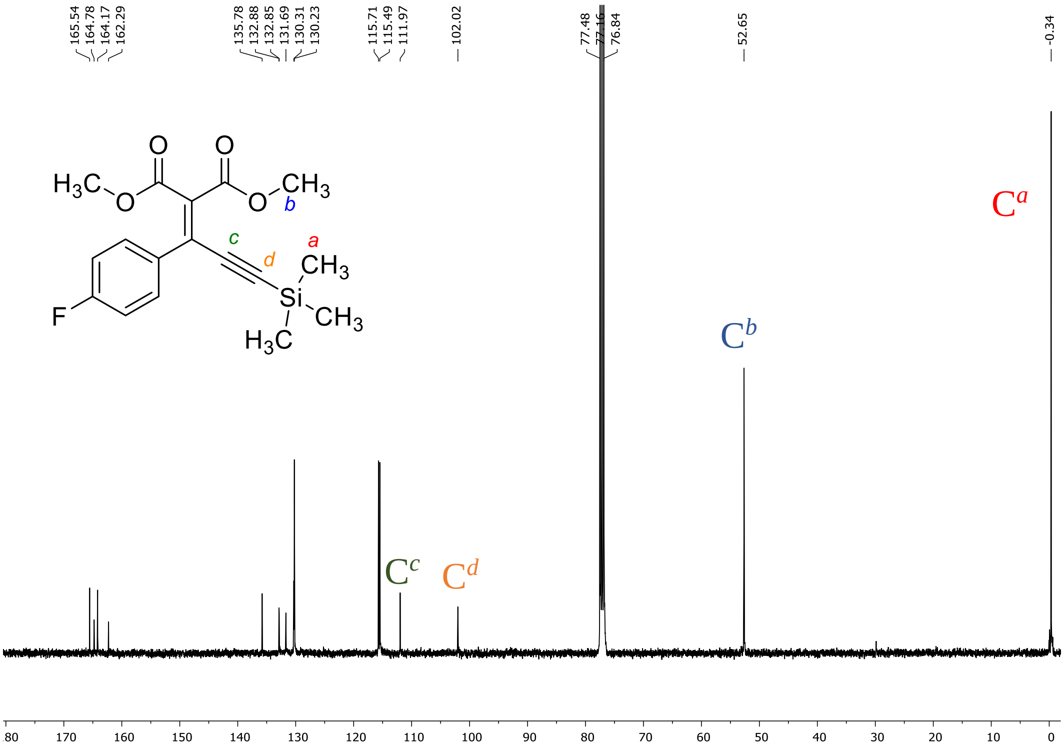


Figure 2.2: ^{13}C-NMR spectrum of isolated compound **2.3a**

With the confirmed formation of the desired alkenylated product, further optimisation of the reaction was undertaken **(Table 2.1)**. First, when the identical reaction was carried out at a room temperature, the formation of a product was barely observed after 18 hours. Hence, we carried the reaction for another 30 hours, after which the product was obtained in a poor isolated yield of 30%, possibly indicating that the deactivation of the catalyst has taken place. Nevertheless, I was delighted to see that the reaction indeed worked, and next I have proceeded to screen different catalysts. Other bulky fluorinated Lewis acids such $B(2,4,6\text{-}F_3C_6H_2)_3$ and $B(3,4,5\text{-}F_3C_6H_2)_3$ catalysed the reaction in a less efficient manner, as the resulted alkenylated product was obtained in poorer isolated yields of 41% and 24%, respectively. Furthermore, the commercially available Lewis acid ($BF_3{\cdot}OEt_2$) or Brønsted acid [*p*-toluenesulfonic acid (PTSA)] failed to catalyse the reaction completely. Hence, the most efficient catalyst for such alkenylation protocol was shown to be $B(C_6F_5)_3$. Interestingly, when the catalytic loading was reduced from 20 to 10 mol%, the product **2.3a** was obtained in a slightly better yield of 81%. Nevertheless, further reduction of the catalytic loading to 5 mol% resulted in a worse yield of 42%. A higher temperature of 100 °C was investigated next, which resulted in lower obtained yields of 48% and 30%, indicating that higher temperatures promote side reactions, such as diazo decomposition and dimerization, which was to be expected with such an unstable substrate. Lastly, we explored different solvent systems. When the reaction was carried out in a coordinating solvent, such as THF, the product formation was not observed. This was to be expected, as $B(C_6F_5)_3$ coordinates with the lone pair present on the oxygen atom of THF, thus reducing its Lewis acidity. Non-polar solvent, such hexane, was found to be poorer solvent choice as the catalyst was poorly soluble in the solvent, though the solubility issues disappeared once the catalyst solution was mixed with the propargyl ester and diazo malonate. Nevertheless, hexane was not a suitable solvent, as the product was obtained in a poor yield of 45%. Toluene gave better results, wherein the alkenylated product was obtained in 68%. Lastly, the reaction was carried out in dichloromethane (CH_2Cl_2) at 65 °C, which resulted in a yield of 52%, confirming that TFT is indeed the best solvent for this alkenylation protocol.

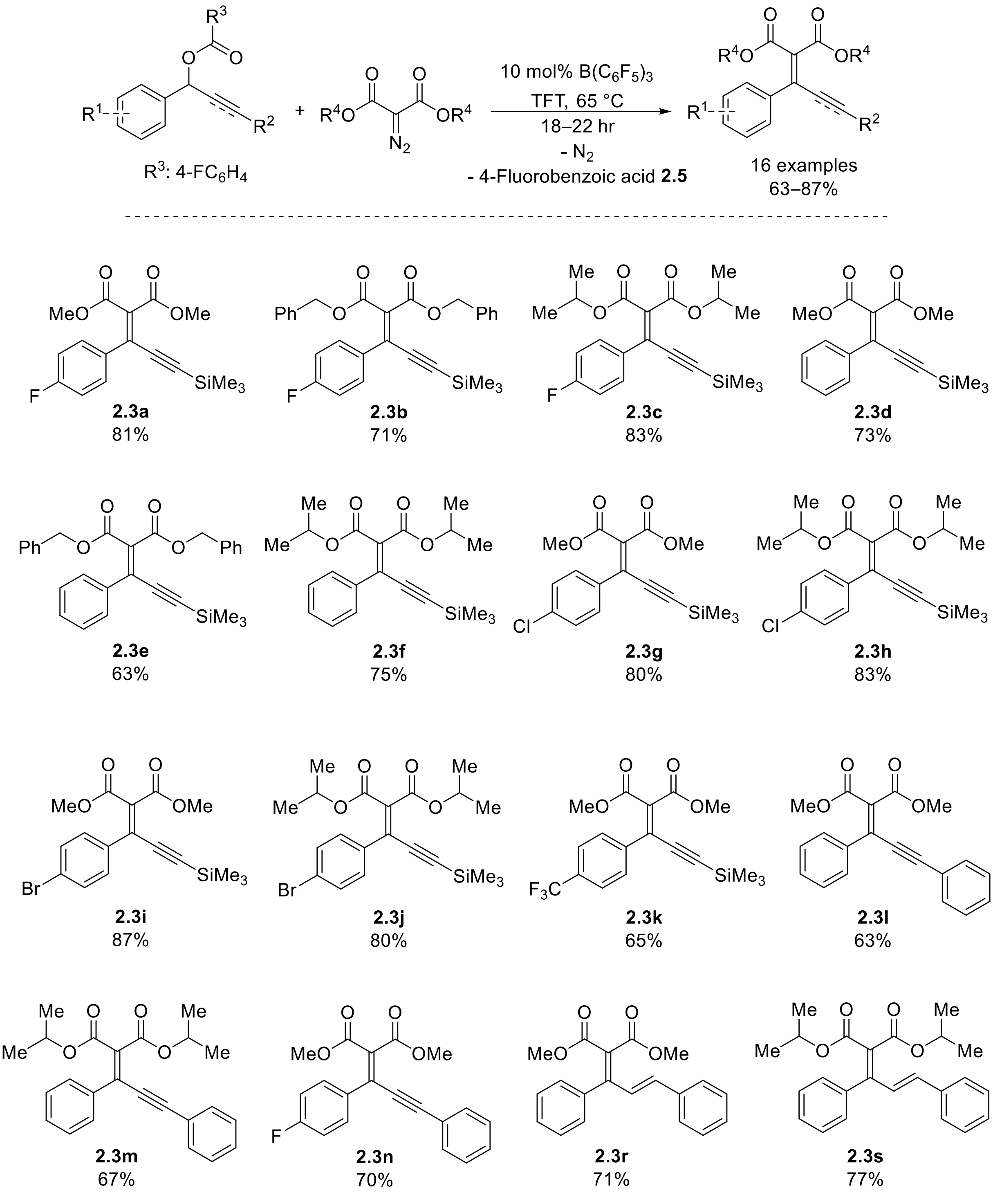
2.5 Substrate scope

With the optimised reaction conditions in hand **(Table 1, entry 8)**, I proceeded to screen the applicability of such alkenylation protocol with a range of substrates **(Schemes 2.6–2.8)**. Firstly, variously substituted propargyl esters were reacted with diazo malonate **2.1a (Scheme 2.6)**. In general, halogens, such F, Cl, Br at the *para*-position of the aryl ring (Ar^1) ester were well tolerated, wherein the best yield of 87% was obtained with *p*-Br (**2.3i**), followed by *p*-F (**2.3a**) substitution with a yield of 81%, and then *p*-Cl (**2.3g**) which was obtained in 80% isolated yield. The unsubstituted aryl ring (i.e. Ar^1 = Ph) resulted in the formation of the alkenylated product in 73%. Worse yields of 63% were observed with an electron-withdrawing *p*-CF_3 (**2.3k**) substituted aryl ring. Interestingly, propargyl esters with either an electron-donating group at the *para* position, such *p*-OMe (**2.2h**) or with highly electron-withdrawing substitution, such 2,6-F_2 (**2.2i**) underwent the reaction though the products could not be isolated due to the formation of multiple inseparable side-products. Next, I investigated substrates with a phenyl ring (**2.2f**, **2.2g**) instead $SiMe_3$ group on the alkyne functionality. To our delight, such substitution was well tolerated and the corresponding products were obtained in yield of 63% (**2.3l**) and 70% (**2.3n**), respectively. Diazomalonates with different ester moieties, such ^{i}Pr (**2.1b**), CH_2Ph (**2.1c**), and ^{t}Bu (**2.1d**) were investigated as well. Both ^{i}Pr and CH_2Ph substituted diazomalonates were well tolerated, wherein the corresponding products were obtained in 63–83%. However, di-*tert*-butyl diazomalonate **2.1d** failed to react with the propargyl ester completely and instead underwent a decomposition reaction, wherein ^{t}Bu group was lost.

Next, unsymmetrical α-aryl α-diazoacetates were investigated **(Scheme 2.7)**. Interestingly, when α-aryl α-diazoacetate **2.1e** was reacted with the unsubstituted propargyl ester **2.2e**, the alkenylated product **2.3q** was formed in a lower yield of 43% and isolated as a mixture of

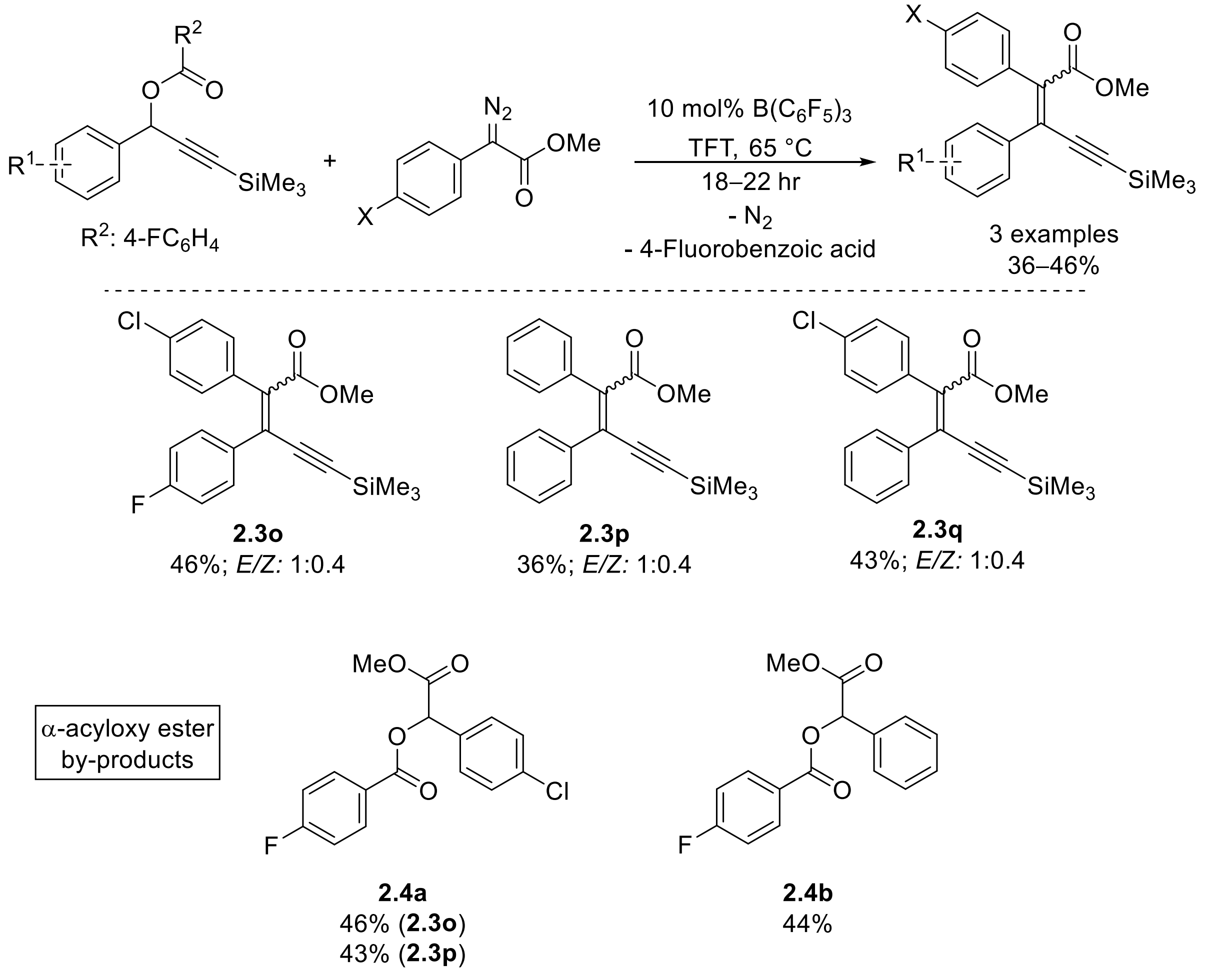
(*E*)/(*Z*) diastereoisomers in a ratio of 1:0.4 (determined by the crude ^{1}H-NMR spectrum analysis). Subsequent isolation of the diastereosiomers by a preparative thin layer chromatography helped to identify (*E*)-diastereoisomer as the major product. The overall lower yield of the alkenylated product was also observed due to the formation of α-acyloxy ester **2.4a** in 43%. **2.4a** is a by-product of the reaction between the α-aryl α-diazoacetate and 4-fluorobenzoic acid **2.5** (the side product generated by the alkenylation reaction). Such formation of the α-acyloxy ester was unexpected but could be rationalised by the nature of the carbene. As mentioned in the introductory part of the thesis, the reactivity and selectivity of diazo compounds is strongly influenced by the stabilisation of to the carbene centre. While the carbonyl groups such esters or ketones make the carbene centre less nucleophilic, aryl or alkyl groups donates the electron density towards the carbene, making it more reactive towards the electrophiles.

The more reactive α-aryl α-diazoacetate undergoes the side reactions more easily. Nonetheless, the formation of α-acyloxy ester **2.4a** was an interesting observation as such compounds together with α-acyloxy ketones are widely used as the essential building blocks of natural products and pharmaceuticals.[111] Moreover the α-acyloxy esters could be selectively reduced to the corresponding α-hydroxy esters, which are widely used in the food, pharmaceutical, and cosmetic industry.[112] Similar results were also observed with the α-aryl α-diazoacetate **2.1f**, wherein the corresponding alkenylated product **2.3p** was isolated in 36% yield as a mixture of diastereomers in a comparable (*E*)/(*Z*) ratio of 1:0.4, and the α-acyloxy ester **2.4b** was isolated in 44% **(Scheme 2.7)**. Hence, the use of unsymmetric and more reactive α-aryl α-diazoacetates for such alkenylated protocol was found to be less tolerated and thus their use was not investigated in any further alkenylated reactions.



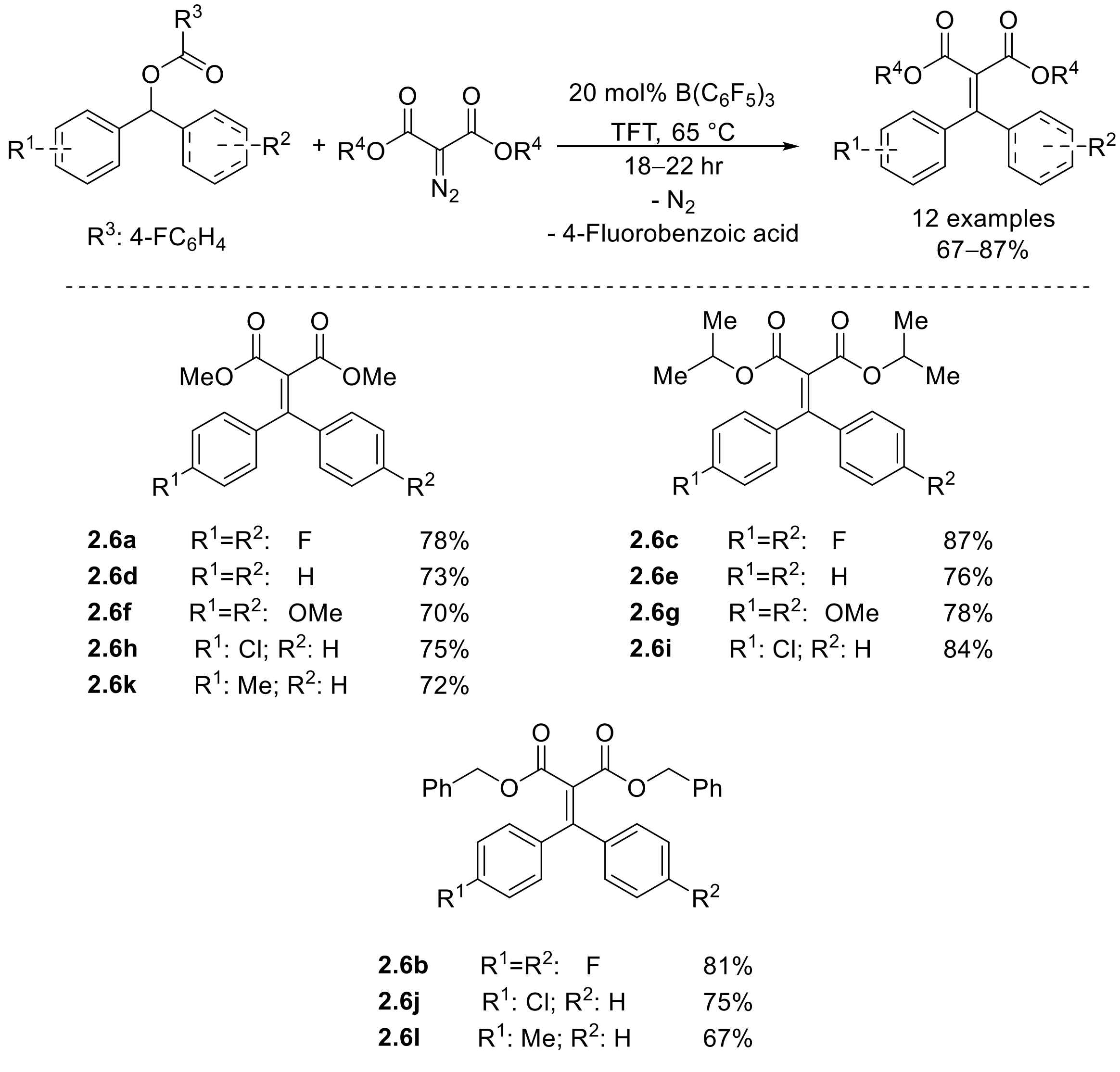
Scheme 2.6: Substrate scope of the $B(C_6F_5)_3$-catalysed alkenylation reactions at propargylic and allylic positions with diazo malonates

Next, the alkenylation reactions at the allylic position with the aryl alkenyl ester **2.2j** were investigated **(Scheme 2.6)**. The reactions proceeded smoothly with diazomalonates **2.1a** and **2.1b**, wherein the corresponding diene products **2.3r** and **2.3s** were isolated in very good yields of 71% and 77%, respectively. The alkenylation reaction at the allylic position was also carried out with dibenzyl diazomalonate **2.1c**. The formation of the expected diene product was observed, though the pure product could not be isolated due to the inseparable mixture of impurities.



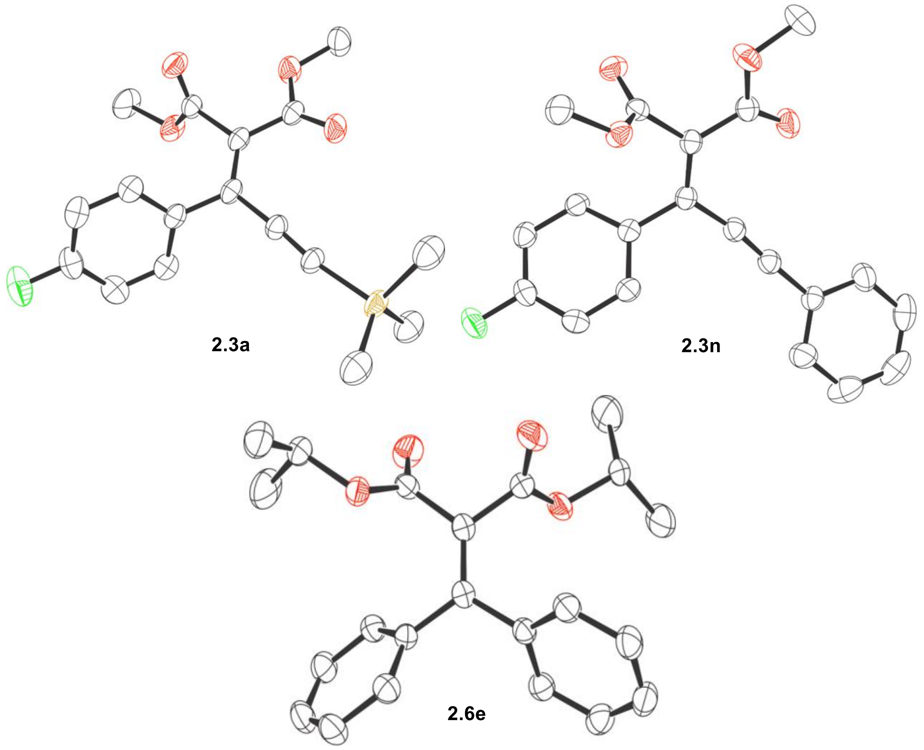
Scheme 2.7: Substrate scope of the $B(C_6F_5)_3$-catalysed alkenylation reactions at propargylic position with unsymmetrical diazo esters

Lastly, I have investigated alkenylation reactions at a benzylic position with diaryl esters and diazomalonates **(Scheme 2.8)**. Generally, non-substituted and *p*-F substituted symmetrical diaryl esters (**2.2k**, **2.1l**) were found to be compatible with this protocol, wherein the corresponding alkenylated products (**2.6a–2.6e**) were obtained in up to 87% yield. Interestingly, unlike in the case of propargyl esters, an electron-donating substitution (OMe) at the *para* position (**2.2m**) was also tolerated, wherein the corresponding products **2.6f** and **2.6g** were obtained in 70% and 78% yields, respectively. Unsymmetrical diaryl esters with *p*-Cl (**2.2n**) and *p*-Me (**2.2o**) substitutions were also tolerated, though **2.2o** generally reacted in lower yields of up to 72% (**2.6k**) when compared to **2.2n**, whose corresponding products could be obtained in up to 84% (**2.6i**). Unfortunately, when unsymmetrical cyclohexyl(phenyl)methyl-4-fluorobenzoate **2.2p** was reacted with diazomalonate under the optimised reaction conditions, no product formation was observed.



Scheme 2.8: Substrate scope of the $B(C_6F_5)_3$ catalysed alkenylation reactions at benzylic position with diazo malonates

Single crystals of **2.3a**, **2.3n** and **2.6e** were grown by a slow evaporation from a saturated solution of the compounds in CH_2Cl_2. These crystals were suitable for a single crystal X-ray diffraction analysis, which was run by Lukas Gierlichs, a colleague from the research group. The solid-state structures are shown in **(Figure 2.3)** and are unambiguously confirming the formation of alkenylated products.



2.3a **2.3n** **2.6e**

Figure 2.3: Solid-state structures of compounds **2.3a**, **2.3n**, and **2.6e**; thermal ellipsoids drawn at 50% probability; carbon: black; oxygen: red; fluorine: green; silicone: yellow

2.6 Catalytic cycle and DFT studies

After a broad substrate scope was demonstrated, attention was turned towards elucidating the mechanism for $B(C_6F_5)_3$-catalysed alkenylations. As such, I have collaborated with Prof. A. Ariafard from University of Tasmania, who together with his PhD student Dr. R. Babaahmadi, conducted DFT calculations at the SMD/M06-2X-D3/def2-TZVP//CPCM/B3LYP/6-31G(d) level of theory using toluene as the solvent, which helped to elucidate the most probable catalytic cycle for the reported alkenylation protocol.

First, two possible initial substrate activations were considered, wherein $B(C_6F_5)_3$ first activates a diazomalonate, by coordinating towards one of the carbonyl groups, which results in the intermediate **2.7** formation, after the expulsion of a diazo group **(Figure 2.4)**. The other possibility is for $B(C_6F_5)_3$ to activate first a propargyl ester *via* coordination towards the pendant oxygen of the carboxylate group **(Figure 2.5)**. The undertaken DFT analysis revealed that $B(C_6F_5)_3$ is in fact initially coordinating towards the carbonyl's pendant oxygen of the propargyl ester, wherein an adduct intermediate **I1 (Figure 2.5)** is obtained *via* low-energy transition state **TS$_1$ (Figure 2.5)** with a low activation barrier of 3.6 kcal/mol. In comparison, the diazomalonate-borane adduct showed to be formed *via* a higher energy transition state **TS$_{2.1a-7}$ (Figure 2.4)** with an activation barrier energy of 13.6 kcal/mol.

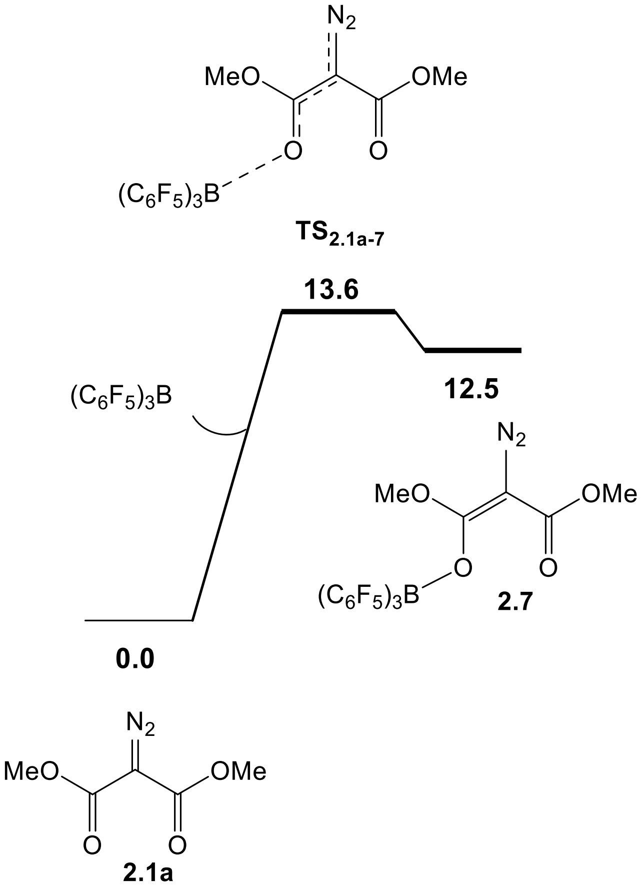


Figure 2.4: DFT-calculated free energy profile for a coordination of the borane to the diazo compound; the relative free energies are given in kcal/mol

Moreover, it has been shown that adduct **I1 (Figure 2.5)** exhibits a slightly elongated C–O bond (1.502 Å **I1 (Figure 2.5)** vs 1.469 Å (**2.2a**)), which subsequently undergoes a C_{sp}^3–O bond cleavage *via* **TS**$_2$ **(Figure 2.5,)** resulting in the formation of electrophilic propargyl carbocation and a borate adduct as a salt **I2 (Figure 2.5,)**, with a free energy of 10.4 kcal/mol.

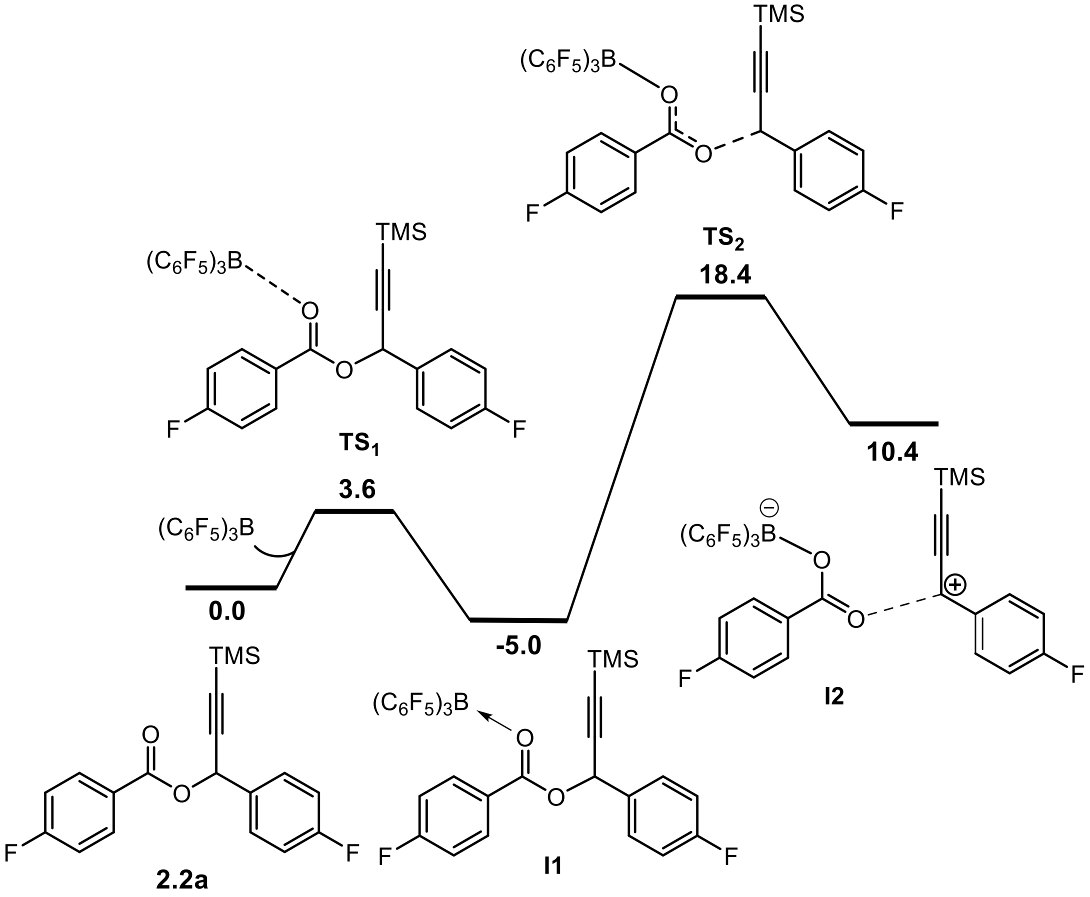


Figure 2.5: DFT-calculated free energy profile for a coordination of the borane to the propargyl ester starting material; the relative free energies are given in kcal/mol

Once the starting material has been activated by the catalyst, the carbocation intermediate then undergoes a nucleophilic attack by the diazomalonate *via* **TS3 (Figure 2.6)**, which results in the formation of a quaternary carbon intermediate **I3 (Figure 2.6)**, whilst simultaneously π C–N bond of the diazo functionality is being disrupted, which is showed by the elongated bond of 1.440 Å. Lastly, **I3 (Figure 2.6)** undergoes an E_2-type elimination *via* a low energy **TS**$_4$ **(Figure 2.6)**, which results in the formation of the final alkenylated product, release of N_2 as well as the by-product 4-fluorobenzoic acid **2.5**, with $B(C_6F_5)_3$ being regenerated. Based on these calculations the elucidated catalytic cycle is depicted in **Scheme 2.9**.

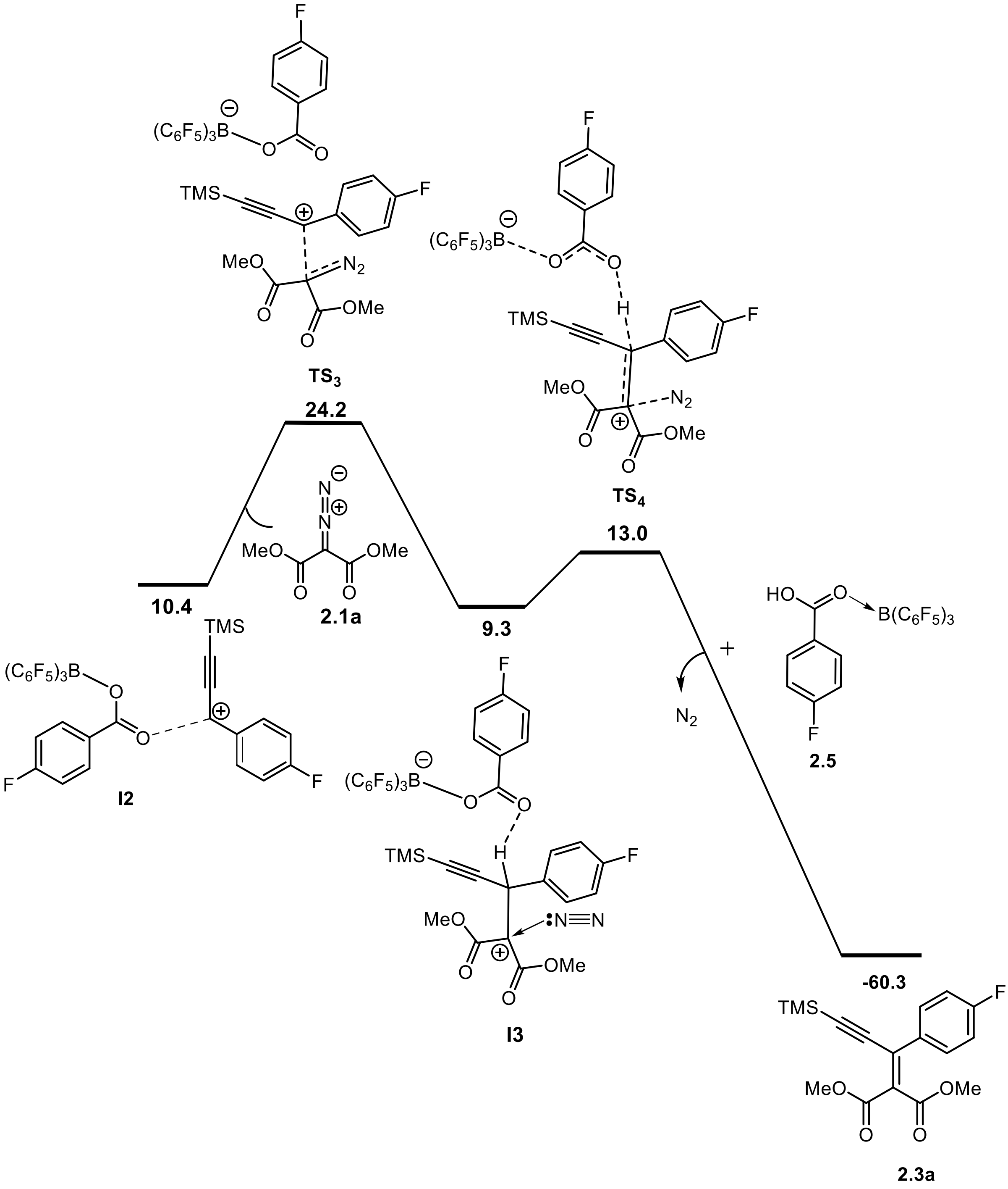
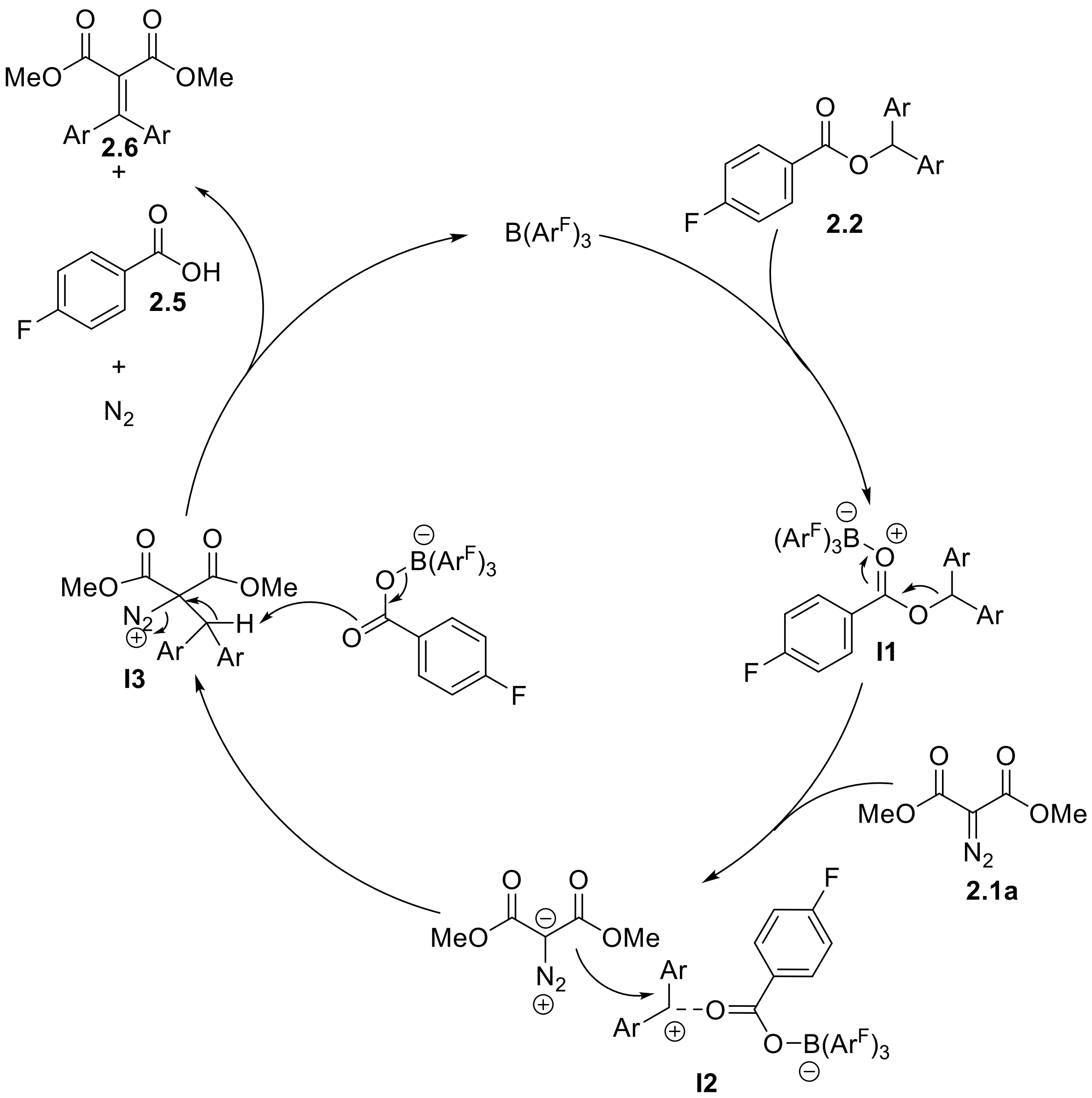


Figure 2.6: DFT calculated free energy profile for the reaction; the relative free energies are given in kcal.mol^{-1}



Scheme 2.9: Catalytic cycle proposed by DFT calculations

2.7 Summary and outlook

To conclude, a mild, facile, and transition metal-free alkenylation reaction of aryl esters with diazomalonates was demonstrated, wherein 31 examples of alkenylated products, obtained in good to excellent yields of up to 87% were presented. This protocol employed as low as 10 mol% of the borane catalyst and has omitted the use of an external oxidant needed for the crucial carbocation formation. I have also demonstrated that such alkenylation reaction can proceed at a propargylic, allylic, and benzylic position. Lastly, a catalytic cycle was proposed, which was based on DFT studies. However, a current protocol is quite limited towards symmetrical diazo malonates, as a formation of diastereomers and a formation of α-acyloxy ester side products was observed when α-aryl α-diazoacetates were reacted. As such, future work in this alkenylation protocol should focus on modifying the reaction conditions, which would lead to expanding the substrate scope for more reactive α-aryl α-diazoacetates. But for now, the discussed alkenylation methodology was successfully published in *Angew. Chem. Int. Ed.* **2020**, *59*, 15492–15496.[113]

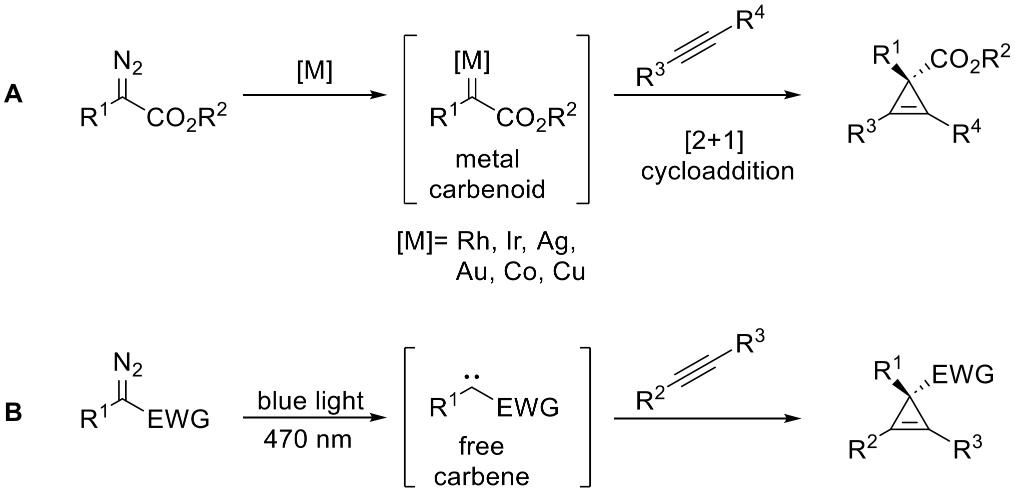
2.8 Work contribution

My contribution majorly involved carrying the initial optimisation reactions, synthetising starting materials, as well as exploring the substrate scope of benzylic and allylic alkenylation reactions. A substrate scope for propargylic alkenylation reactions was majorly carried out by Dr. Ayan Dasgupta.

3.0 Borane-catalysed cyclopropenation of arylacetylenes

3.1 Introduction

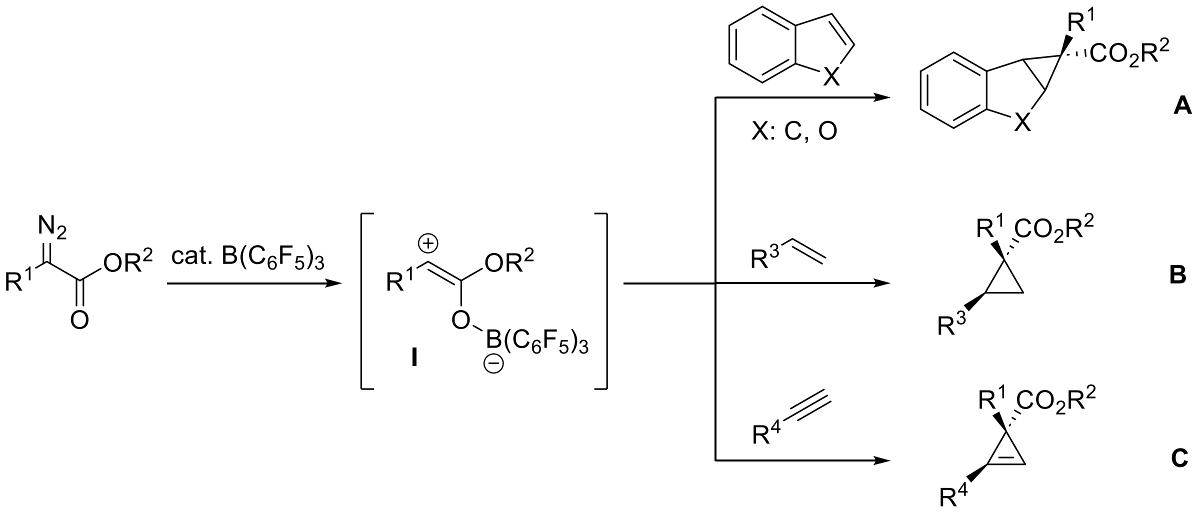
Cyclopropenes are the smallest unsaturated 3-membered cyclic molecules, which exhibit a high strain energy, making them highly reactive and useful building blocks in the organic synthesis.[114] Furthermore, it has been discovered that cyclopropenes are also prevalent in natural products, making their efficient synthesis even more desirable.[115] These unsaturated carbocycles are typically synthetised from arylacetylenes and diazo compounds, wherein the carbene precursors are activated by transition metals to form a metal carbenoid species, which then readily undergoes [2+1] cycloaddition reaction with arylacetylenes **(Scheme 3.1, A)**. Mostly, precious transition metals, including Rh, Ir, Ag, and Au, have been utilised to catalyse such cyclopropenation reactions.[116,117,118,119] There have been also reports of using more abundant first row transition metals, including Cu or Co.[120,121] More recently, Koenings *et al.* has reported a transition metal-free cyclopropenation in both batch and continuous flow, wherein the carbene intermediate has been generated using a visible-light **(Scheme 3.1, B)**.[122]



Scheme 3.1: Reported transition metal- and light-catalysed cyclopropenation of arylacetylynes

3.2 Aims of this work

As already covered in the introductory part of the thesis, boron-based bulky Lewis acids have been reported to catalyse numerous chemical transformations, including cyclisation reactions. More recently, our group has demonstrated that a catalytic amount of $B(C_6F_5)_3$ mediates a diastereoselective cyclopropanation of unsaturated substrates, including indenes and benzofurans with α-aryl α-diazoacetates **(Scheme 3.2, A)**.[123] Similar observations have also been reported by Wilkerso—Hill *et al.*, wherein 10 mol% of the $B(C_6F_5)_3$ catalysed cyclopropanation of styrenes in good to excellent yields of up to 88% **(Scheme 3.2, B)**.[124] Conducted computational studies revealed that such reactions proceed *via* a $B(C_6F_5)_3$ activated carbene **(Scheme 3.2, I)**, which then undergoes a cycloaddition reaction with the unsaturated substrates. As such, there was a hypothesis whether the Lewis acid activated carbene would undergo similar reactivity with alkynes in order to obtain cyclopropenated compounds **(Scheme 3.2, C)**.



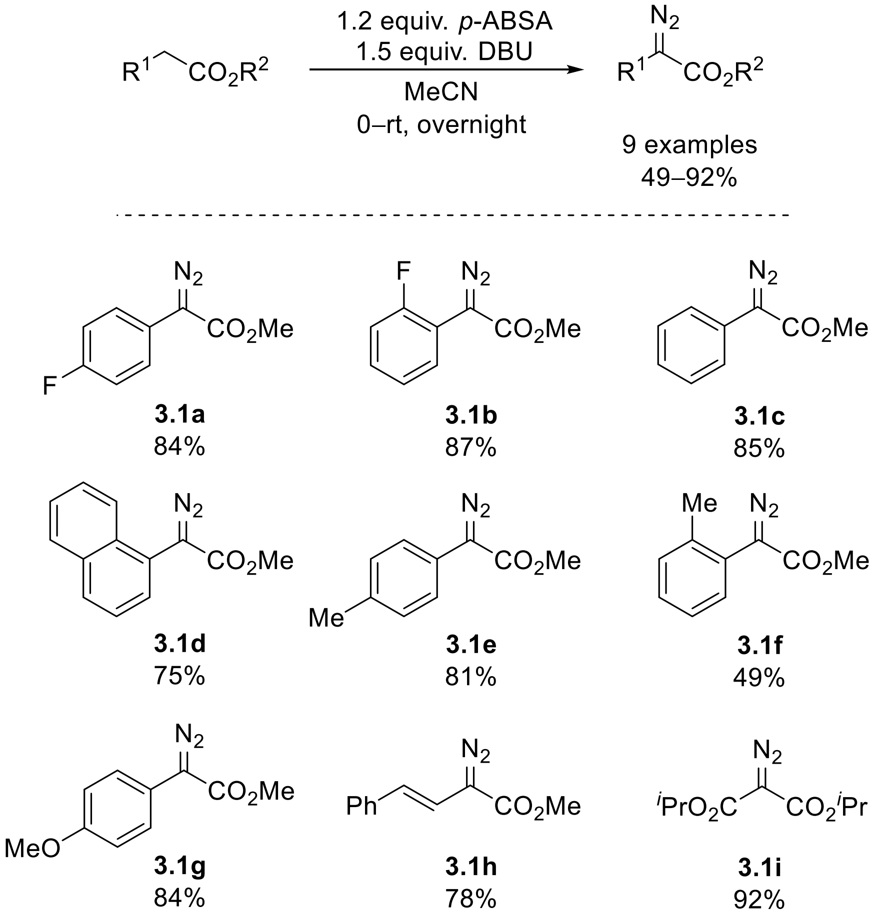
Scheme 3.2: Previously reported $B(C_6F_5)_3$-catalysed cyclopropanation reactions (**A, B**) and aims of this work (**C**)

3.3 Work contribution

This work was mostly undertaken by me, wherein I have synthetised diazo esters and enyne starting materials, conducted optimisation reactions, as well as provided a substrate scope for the borane-catalysed cyclopropenation of terminal arylacetylenes. My colleague Matthew J. Heard assisted me with the synthesis of internal alkynes, conducted reactions of borane-catalysed cyclopropenation of these internal alkynes, as well as he had undertaken reactions with carbonyl substrates in an attempt to promote epoxidation reactions.

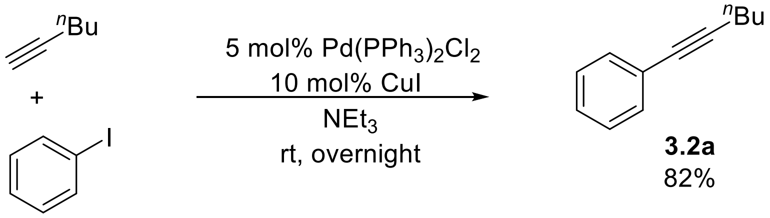
3.4 Synthesis of starting materials

First, variously substituted α-aryl α-diazoesters **3.1a–3.1g**, vinyldiazo acetate **3.1h**, and symmetrical diisopropyl 2-diazomalonate **3.1i** have been synthetised *via* the conventional diazotransfer reactions, using DBU as a base and *p*-ABSA as the sulfonyl azide reagent. In total, nine different diazo compounds were prepared and obtained in good to excellent yields of up to 92% **(Scheme 3.3)**.



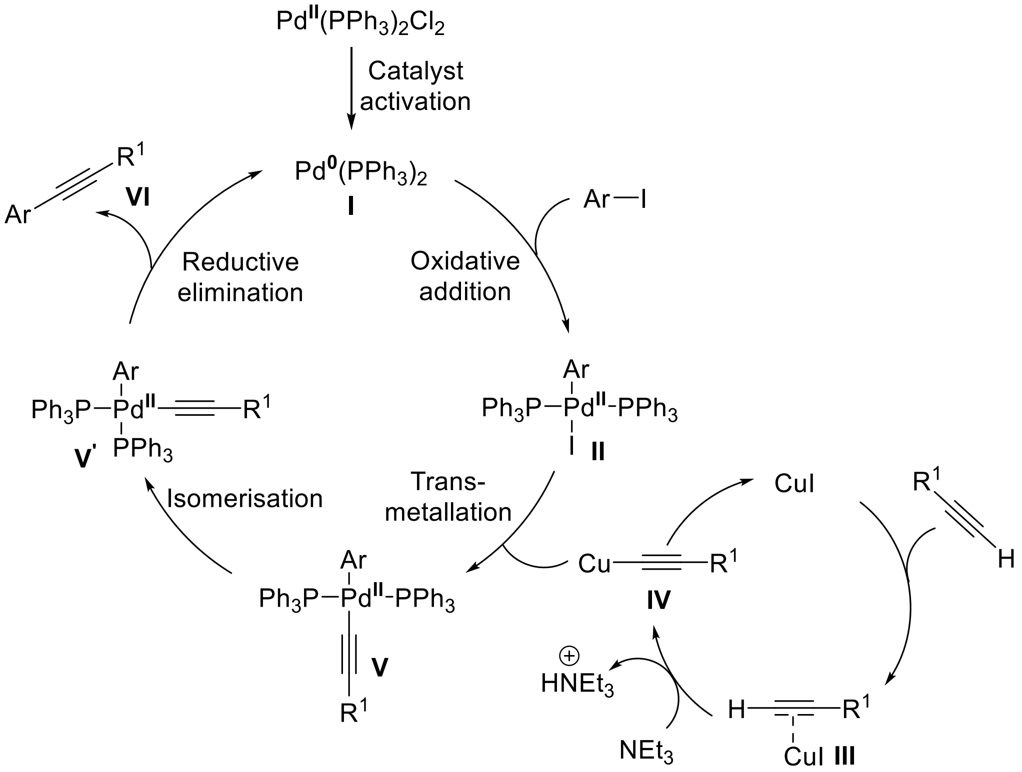
Scheme 3.3: Synthetised diazo esters **3.1a–3.1i** for cyclopropenation reactions

Most of the aryl- and alkyl acetylenes used were commercially available, and thus no synthesis was required to obtain these. Nevertheless, internal aryl acetylene **3.2a** was obtained *via* a Sonogashira cross-coupling reaction, wherein iodobenzene was coupled with a terminal alkyne, in this case 1-hexyne, in a presence of NEt_3 and the catalytic system comprised of 5 mol% of $Pd(PPh_3)Cl_2$ and 10 mol% of CuI co-catalyst **(Scheme 3.4)**.



Scheme 3.4: Synthesis of internal arylacetylene starting material **3.2a**

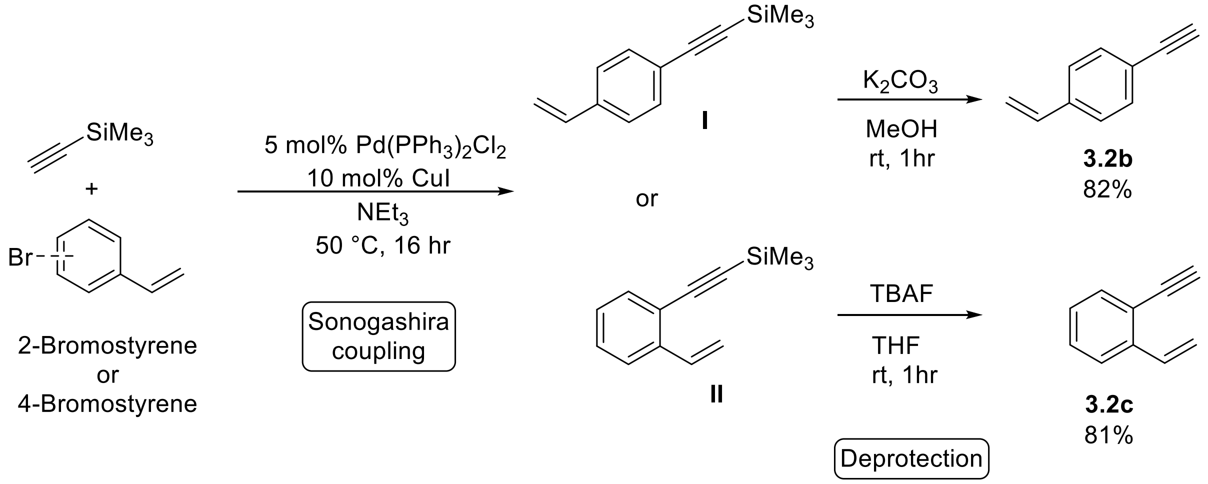
The catalytic cycle of the Pd-catalysed Sonogashira coupling is depicted in **Scheme 3.5**, which starts with the initial activation of the palladium pre-catalyst $Pd(PPh_3)_2Cl_2$, whose oxidation state is reduced from Pd(II) to Pd(0) **I**. Once active, the palladium catalyst then undergoes a rate-limiting step, comprised of an oxidative addition with iodobenzene, forming an electrophilic Pd(II) complex **II**. In a meantime, the second cycle is comprised of Cu(I) co-catalyst initially forming a π-alkyne complex **III**, which increases the acidity of terminal proton, which is then readily deprotonated by NEt_3 base, forming a copper acetylide **IV**. The copper acetylide **IV** then undergoes a transmetallation step with the electrophilic Pd(II) intermediate **II**, resulting in the formation of complex **V** as well as in regenerating the copper catalyst. The last step is comprised of a reductive elimination, which proceeds when the substrate groups are in proximity to each other, more precisely in a *cis*-orientation. Thus, *trans-cis* isomerisation might take place before the reductive elimination, which then results in the internal alkyne product **VI**, as well as the regeneration of active Pd(0) catalyst.



Scheme 3.5: Catalytic cycle of CuI co-catalysed Sonogashira coupling

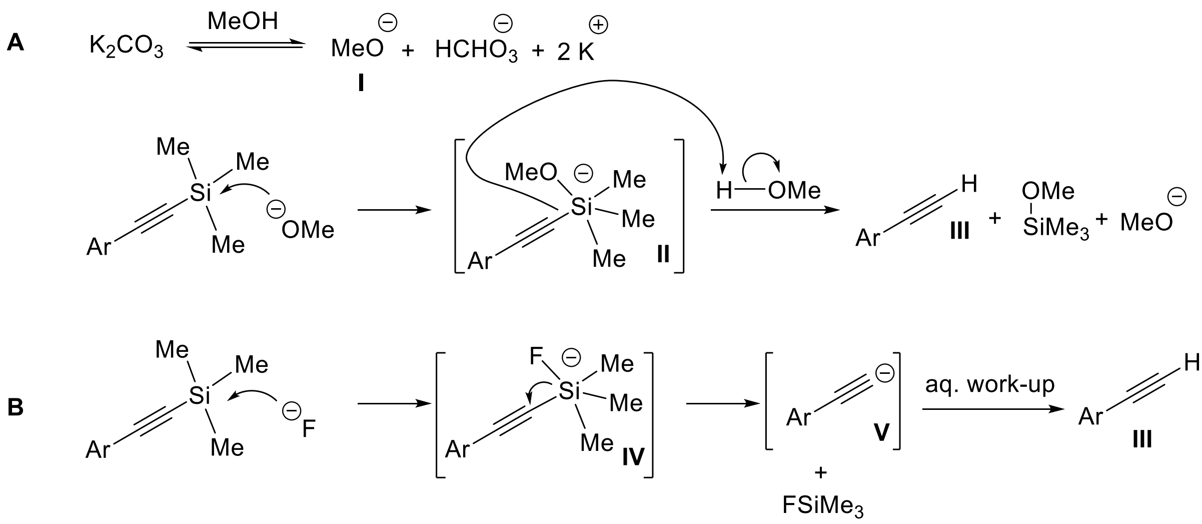
Both enyne substrates **3.2b** and **3.2c** were synthetised from the corresponding bromostyrene and obtained in 82% and 81% respectively, according to literature procedures **(Scheme 3.6)**.[125,126] The first step was comprised of Sonogashira coupling of the corresponding bromostyrere with trimethylsilylacetylene, forming 4-(trimethylsilyl)ethynylstyrene **(Scheme 3.6, I)** or trimethyl((2-vinylphenyl)ethynyl)silane **(Scheme 3.6, II)** intermediates, which were then deprotected either by K_2CO_3 in MeOH in case of **3.2a** or by tetra-*n*-butyl ammonium fluoride in THF, also known as TBAF, in case of **3.2b**.

Regarding the mechanism of potassium carbonate-mediated deprotection, an initial solvation of potassium carbonate in methanol takes place, which results in the formation of methoxide anion **I (Scheme 3.7, A)**. The methoxide **I** then attacks silicon in TMS group, as silicon has a higher affinity towards oxygen than towards carbon, thus forming pentavalent intermediate **II**, which subsequently undergoes Si–C bond cleavage, and simultaneously abstracts a proton from methanol, resulting in the deprotected alkyne **III (Scheme 3.7)**.



Scheme 3.6: Synthesis of enyne starting materials **3.2b** and **3.2c**

Similarly, deprotection of TMS group using a fluoride source **(Scheme 3.7, B)**, such as tetrabutylammonium fluoride (TBAF), proceeds with the formation of stronger Si–F bond, forming pentavalent intermediate **IV**, which then undergoes Si–C bond cleavage, resulting in a formation of acetylidine anion **V**. Lastly, the alkyne **V** is protonated during aqueous work up, resulting in the deprotected alkyne **III (Scheme 3.7)**.



Scheme 3.7: Mechanism of K_2CO_3/MeOH (**A**) and TBAF (**B**) mediated deprotection of silyl acetylenes

3.5 Optimisation reactions

Once the starting materials were synthesised, I proceeded with the optimisation reactions next, wherein unsubstituted phenylacetylene and *para*-F substituted phenyldiazo acetate **3.1a** were chosen as model substrates **(Table 3.1)**. At first, a control reaction was carried out with 1.3 equiv. of phenylacetylene and 1 equiv. of diazo ester in CH_2Cl_2, with no catalyst employed at a room temperature and even after 24 hours, no product formation was observed. Furthermore, the identical reaction was carried out at reflux conditions at 45 °C, and again no formation of cyclopropenated product was observed after 24 hours but rather the decomposition of diazo compound took place. Next, I used 20 mol% of commercially available Lewis acid, $BF_3{\cdot}OEt_2$, which resulted in the unwanted decomposition of diazo ester into the homocoupled product. Similarly, 40 mol% of commercially available Brønsted acid, triflic acid (TfOH), failed to catalyse the reaction. Next, I screened 20 mol% of $B(C_6F_5)_3$ for promoting the reaction. At first, there was no formation of a new product observed at a room temperature. Nevertheless, when an identical reaction was carried out at reflux conditions, after 24 hours, TLC analysis showed a presence of new spot apart from the already observed homocoupled isomeric products, resulting from the thermal diazo decomposition. After a purification of crude reaction mixture by a column chromatography, a new compound was isolated in 48% yield. ^{1}H-NMR spectroscopy revealed a singlet peak at δ = 7.19 ppm with an integration of one, suggesting a proton attached to C_{sp}^{2} carbon, which is in no proximity to any neighbouring protons. Further presence of eight aromatic peaks in a range of δ = 7.61–6.95 ppm confirmed a presence of both aryl rings in the isolated compound. Lastly, a characteristic singlet at δ= 3.71 ppm with integration of three suggested the OMe functionality present in the isolated compound **(Figure 3.1)**. In the ^{13}C-NMR spectrum, a signal at δ = 100.2 ppm suggested the presence of a non-aromatic alkene carbon and a signal at δ = 32.9 ppm showing the presence of an C_{sp}^{3} carbon **(Figure 3.2)**.

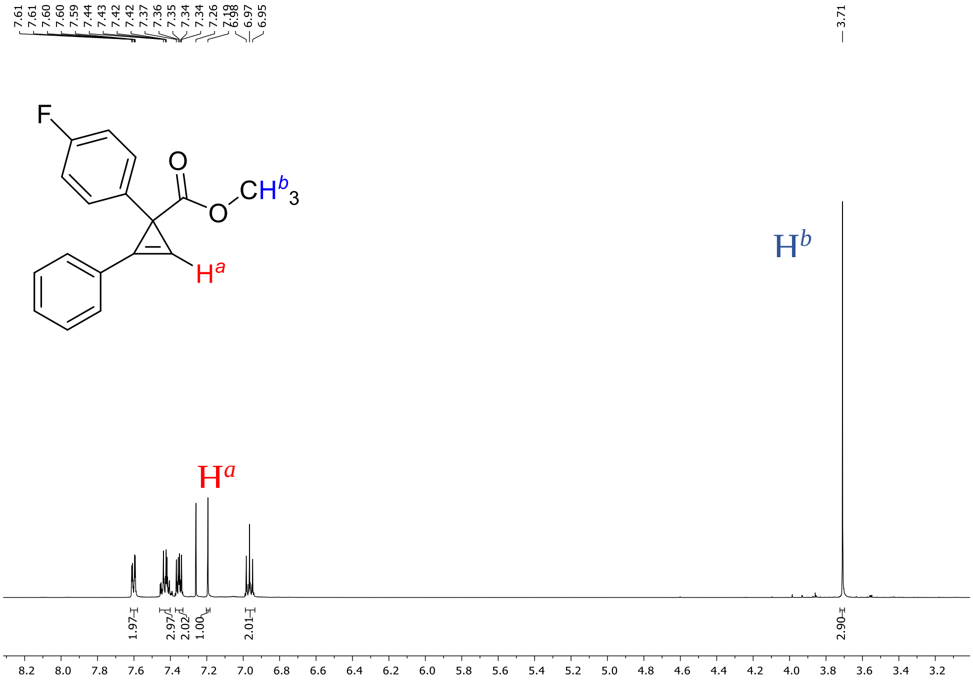


Figure 3.1: ^{1}H-NMR spectrum of the isolated compound **3.3i**

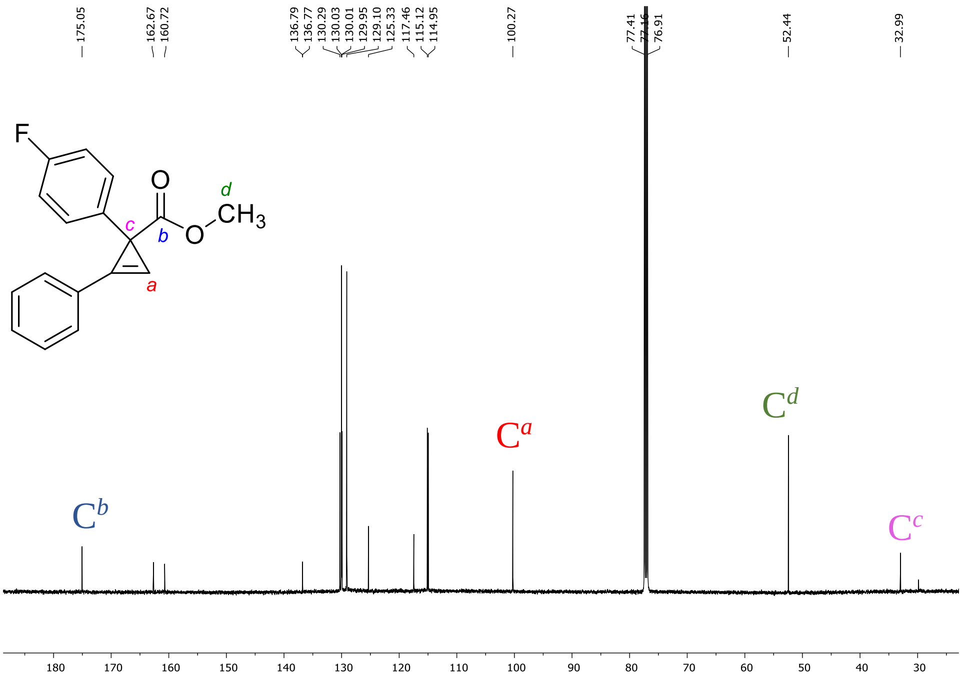


Figure 3.2: ^{13}C-NMR spectrum of the isolated compound **3.3i**

Lastly, a signal at δ= -116.31 ppm in ^{19}F-NMR spectrum confirmed the presence of a single fluorine environment in the resulting compound **(Figure 3.3)**. Such NMR analysis suggested that a cyclopropenated product **3.3i** was indeed formed. Furthermore, the cyclopropene **3.3i** is known and the obtained NMR data matched with the literature.[122]

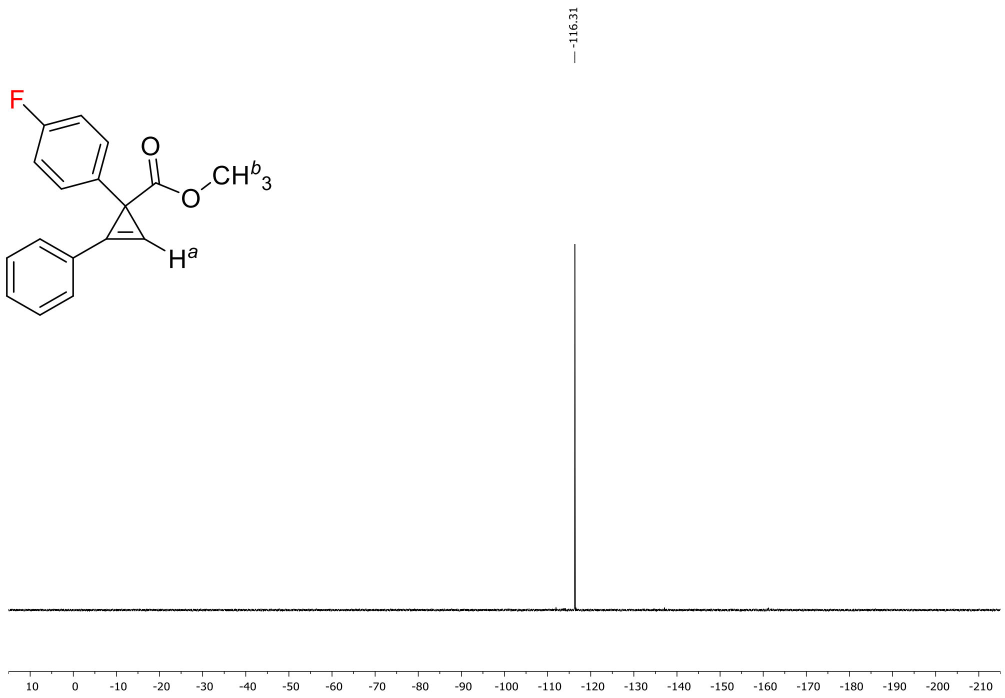
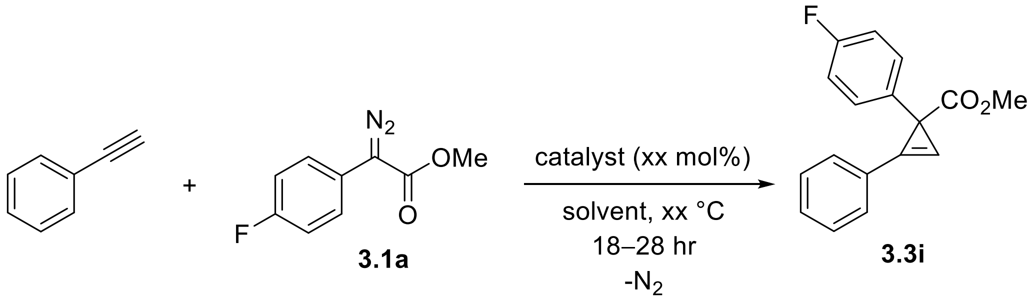


Figure 3.3: ^{19}F-NMR spectrum of the isolated compound **3.3i**

Delighted with these results, the solvent system was then switched from CH_2Cl_2 to $C_2H_4Cl_2$ in order to be able to screen broader range of temperatures. As such, next we carried a reaction at 50 °C, which afforded the cyclised product with an improved yield of 57%. However, increasing the reaction temperature further to 70 °C led to the promotion of side reactions, as the isolation of desired cyclised product was not possible due to the complicated crude reaction mixture. The improvement of the yield was further observed with decreasing of the catalytic loading from 20 mol% to 10 mol%, wherein the cyclopropene **3.3i** was obtained in 65%. Further decrease in a catalytic loading to 5 mol% however resulted in decrease yield of 32%. Less acidic boron-based Lewis acid, such $B(2,4,5\text{-}F_3C_6H_2)_3$ promoted the cyclopropenation of phenylacetylene, though in a less efficient manner, as the cyclopropenated products was obtained in an isolated yield of 28%. Interestingly, 10 mol% of other fluorinated boranes such $B\ (3,4,5\text{-}F_3C_6H_2)_3$ or $B\ (3,5\text{-}CF_3C_6H_3)_3$ failed to catalyse the reaction.



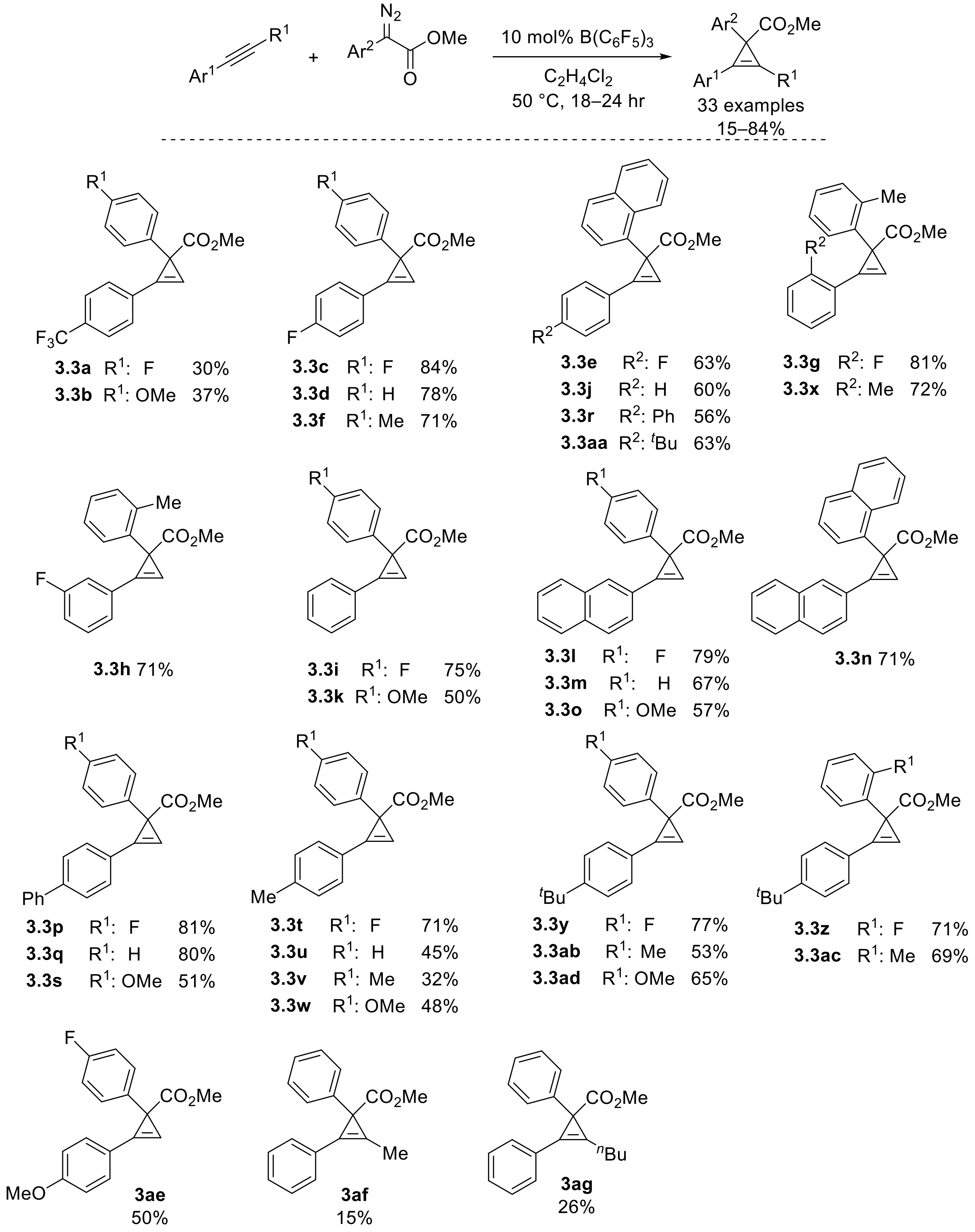
Entry	Catalyst	Catalytic loading [mol%]	Solvent	Temperature [°C]	Time [hr]	Isolated Yield [%]
1	-	-	CH_2Cl_2	rt	24	-
2	-	-	CH_2Cl_2	45	24	-
3	$BF_3{\cdot}OEt_2$	20	CH_2Cl_2	45	24	-
4	TfOH	40	CH_2Cl_2	45	24	-
5	$B(C_6F_5)_3$	20	CH_2Cl_2	rt	24	-
6	$B(C_6F_5)_3$	20	CH_2Cl_2	45	24	48
7	$B(C_6F_5)_3$	20	$C_2H_4Cl_2$	50	22	57
8	$B(C_6F_5)_3$	20	$C_2H_4Cl_2$	70	18	-
9	$B(C_6F_5)_3$	10	$C_2H_4Cl_2$	50	24	65
10	$B(C_6F_5)_3$	5	$C_2H_4Cl_2$	50	28	32
11	$B(2,4,6\text{-}F_3C_6H_2)_3$	10	$C_2H_4Cl_2$	50	24	28
12	$B(3,4,5\text{-}F_3C_6H_2)_3$	10	$C_2H_4Cl_2$	50	24	-
13	$B(3,5\text{-}CF_3C_6H_3)_3$	10	$C_2H_4Cl_2$	50	24	-
14	**$B(C_6F_5)_3$[a]**	**10**	**$C_2H_4Cl_2$**	**50**	**24**	**75**

Table 3.1: Optimisation reactions of borane catalysed cyclopropenation of arylacetylene; all reactions were carried out on 0.1 mmol scale. **3.1a** (1 equiv.), phenylacetylene (1.3. equiv.) and 1.5 mL solvent; [a] phenylacetylene (1 equiv.), **3.1a** (1.3 equiv.), and 1.5 mL of solvent

Throughout most of these reactions, we have noticed that the diazo ester would not only react with the phenylacetylene but it also underwent decomposition reaction wherein two homocoupled products would be observed. As such, to maximise the efficiency of the reaction, the ratios of starting materials was switched, wherein 1.3 equiv. of diazo ester was reacted with 1 equivalent of phenylacetylene. The switch in stoichiometry indeed led to an improvement, wherein the desired cyclopropenated product **3.3i** was obtained in 75 % **(Table 3.1, entry 14)**.

3.6 Substrate Scope

With the optimised reactions in hand, I proceeded with exploring a substrate scope for the borane-catalysed cyclopropenation protocol, starting first with terminal arylacetylenes and α-aryl α-diazoacetates **(Scheme 3.8)**. In terms of different substitutions on arylacetylenes, a strongly electron-withdrawing CF_3 group at the *para* position was tolerated, though the corresponding cyclopropenated products **3.3a** and **3.3b** were isolated in lower yields of 30% and 37%, respectively. On the other hand, fluorine-substitution at the *ortho, meta,* and *para* positions were all well tolerated and the corresponding products **3.3c**–**3.3h** were obtained in 71–84% yields. Unsubstituted phenylacetylene also showed good reactivity, wherein the best yield of 75% (**3.3i**) was observed with the stabilised aryl diazo ester **3.1a**, whereas the worst yield of 50% (**3.3k**) was obtained with the more reactive *p*-OMe substituted diazoester **3.1g**. 2-ethynyl-naphtalene and arylacetylene with another phenyl ring at *para*-position also reacted with variously substituted α-aryl α-diazoacetates in good to very good yields of up to 81% (**3.3l–3.3s**). Lower yields of 32–72% (**3.3t–3.3x**) were observed with an electron-donating Me group at both the *para* and *meta* position of arylacetylenes, whereas *p*-^{t}Bu substituted arylacetylene resulted in the corresponding cyclopropenes (**3.3y–3.3ad**) in better yields of up to 81%. Lastly, the strongly electron-donating OMe group at the *para* position was only tolerated when reacted with a more stable diazoester **3.1a**, though the corresponding cyclopropenated product **3.3ae** was obtained in a lower yield of 50%. Aliphatic terminal alkynes, such as trimethylsilylacetylene, hex-1-yne, as well as *tert*-butylacetylene, all failed to react with diazo esters to give cyclopropenated compounds.



Scheme 3.8: Substrate scope of the $B(C_6F_5)_3$-catalysed cyclopropenation of arylacetylenes

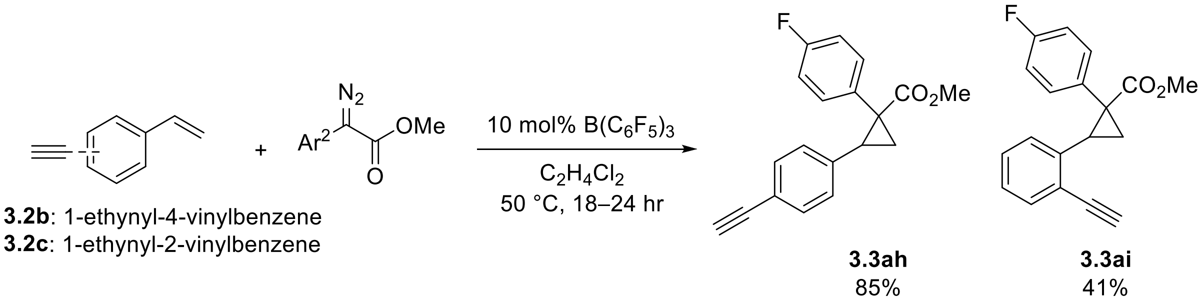
Next, internal alkynes were screened for the $B(C_6F_5)_3$-catalysed cyclopropenation reactions, which showed to be quite limiting, presumably due to the increased steric hindrance around the reaction centre. As such, bulkier internal alkynes such 1,2-diphenylacetylene, 1-(prop-1-

yn-1-yl)-4-(trifluoromethyl)benzene, and trimethyl(phenylethynyl)silane failed to react with α-aryl α-diazoacetates. On the other hand, smaller internal alkynes such 1-phenyl-1-propyne and hex-1-ynyl-benzene **3.2a** reacted with diazo esters, though in poor yields of 15% (**3.3af**) and 26% (**3.3ag**), respectively.

Regarding different substitutions on the α-aryl α-diazoacetates, a general trend was observed, wherein the best yields were obtained with fluorine substitutions (**3.1a**, **3.1b**), followed by 1-naphtyl **3.1d**, then the non-substituted **3.1c** diazo ester. On the other hand, worst yields were observed with the more reactive, less stabilised diazo esters with *p*-OMe (**3.1g**), *o*-Me (**3.1f**), or *p*-Me (**3.1e**) substitutions on the aryl ring, presumably as they are more prone towards the decomposition at elevated temperatures. Unexpectedly, methyl 2-diazo-2-(3-fluorophenyl)acetate failed to react with phenylacetylene completely. Furthermore, more stabilised symmetrical diisopropyl 2-diazomalonate **3.1i** or more sterically hindered diazo dimedone also failed to react with phenylacetylene. Other diazo compounds which were limitations for this protocol, include commercially available ethyl 2-diazoacetate and vinyl diazo acetate **3.1h**.

Furthermore, the regioselectivity of the cyclisation reaction was investigated with substrates bearing both alkene and alkyne functionalities, such as 1-ethynyl-4-vinylbenzene (**3.2b**) and 1-ethynyl-2vinylbenzene (**3.2c**). In both cases, cyclopropanation was favoured over cyclopropenation, wherein the cyclopropanated products **3.3ah** and **3.3ai** were obtained as single diastereomers in isolated yields of 85% and 41%, respectively **(Scheme 3.9)**.

Most of the obtained cyclopropenes were obtained as colourless oils at room temperature. However, certain cyclopropenes containing naphthyl rings, such **3.3n** or **3.3o**, were obtained as solids and this led me to attempt for their recrystallisation by slow vapour diffusion from a solution of CH_2Cl_2/pentane. The formed single crystals were suitable for X-ray diffraction and they were measured by Lukas Gierlichs, a fellow PhD student in the group. The elucidated structures are depicted in **Figure 3.4**. Here it can be seen that the formed cyclopropenes have the aryl rings *trans* to each other, which could be expected due to better sterics.



Scheme 3.9: Selective cyclopropanation of enynes (**3.2b, 3.2c**) catalysed by B(C_6F_5)$_3$

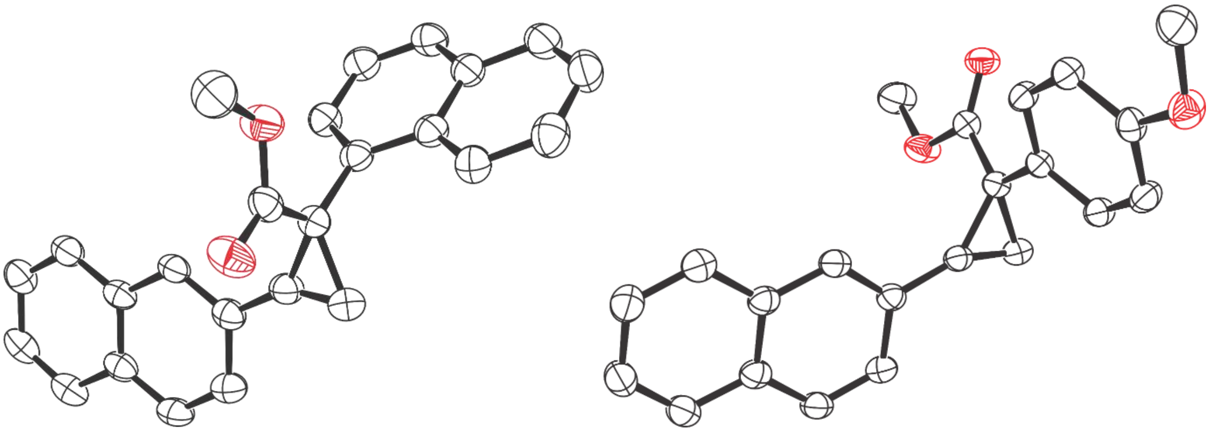
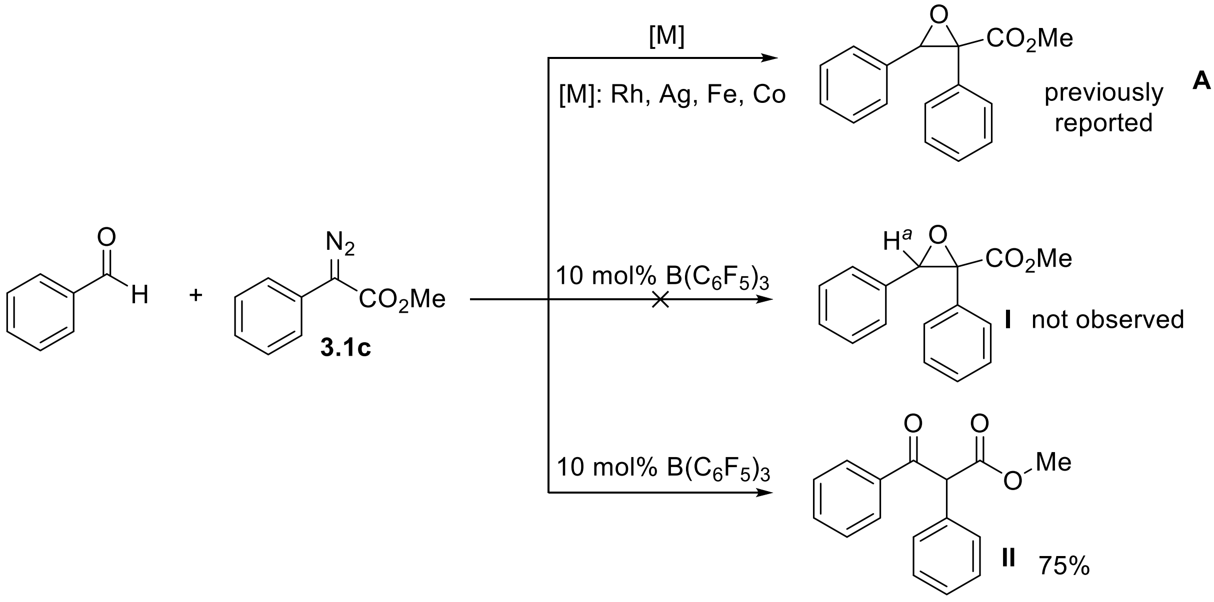


Figure 3.4: Solid-state structures of compound **3.3n** (left) and **3.3o** (right); thermal ellipsoids drawn at 50% probability; carbon: black; oxygen: red; H atoms omitted for clarity

3.7 Attempted epoxidation reaction

Lastly, a synthesis of three membered heterocycles, more precisely epoxides, from benzaldehyde and unsubstituted α-aryl α-diazoacetate **3.1c** was attempted. Similar epoxidation reactions were previously reported using transitions metals, including Rh, Ag, Fe, and more recently a cobalt catalyst **(Scheme 3.10, A).**[127,128,129,130] Such high interest in synthetising epoxides in an efficient catalytic manner with high selectivities rises from the epoxide's usefulness as building blocks in the organic synthesis, as well as their high prevalence in natural products.[131]



Scheme 3.10: Reported and attempted epoxidation of benzaldehyde with aryl diazoester **3.1c**

When the optimised conditions were applied, the two substrates reacted, and a new compound was formed and isolated in a very good yield of 75%. Excitingly, the ^{1}H-NMR spectrum **(Figure 3.5)** showed expected signals for the epoxide **(Scheme 3.10, I)**, including OCH_3 signal at δ= 3.76 ppm as well as a singlet at δ= 5.63 ppm, which would be within a range for H_a proton. However, the ^{13}C-NMR spectrum did not agree with the formation of the **(Scheme 3.10, I)**. First, there was a peak at δ= 193.3 ppm, indicating that a ketone or aldehyde carbon is present. Furthermore, there were only two peaks at δ= 60.5 and δ= 52.9 ppm, which is in the C_{sp^3} region, therefore three signals would be expected within this region **(Figure 3.6)**. As such it was clear that the epoxide was not formed. After a closer analysis, we have concluded that α-aryl-β-keto ester **(Scheme 3.10, II)** was formed *via* well-known Roskamp reaction, which is a reaction between α-diazoesters and aldehydes in a presence of various Lewis acids, including $BF_3 \cdot OEt_2$.[132,133]

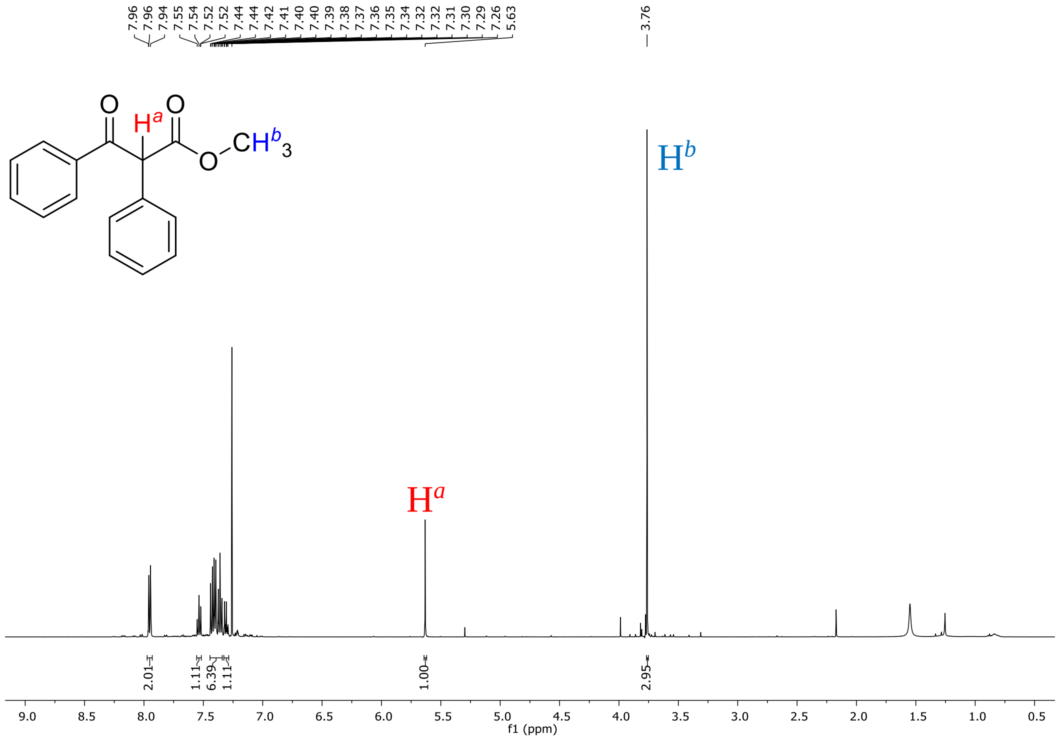


Figure 3.5: ^{1}H-NMR spectrum of methyl 3-oxo-2,3-diphenylpropanoate

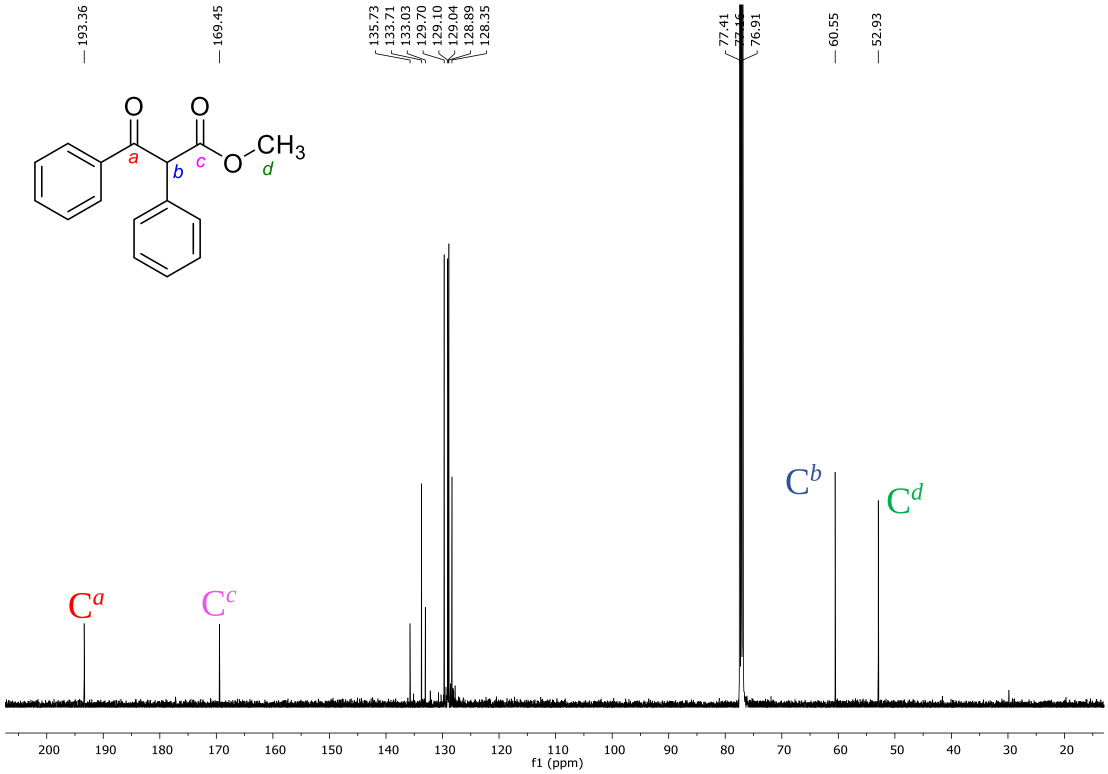
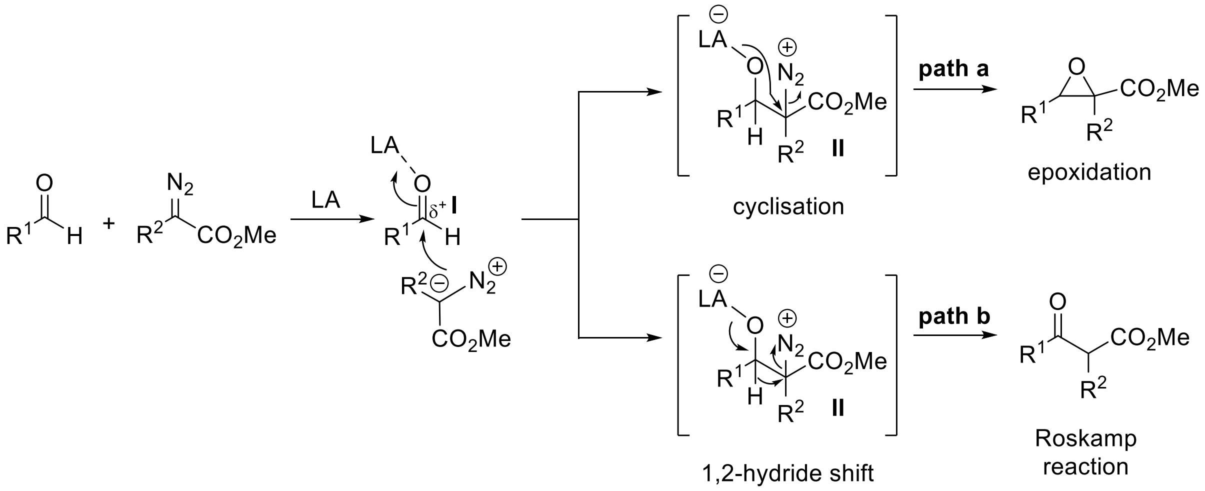


Figure 3.6: ^{13}C-NMR spectrum of methyl 3-oxo-2,3-diphenylpropanoate

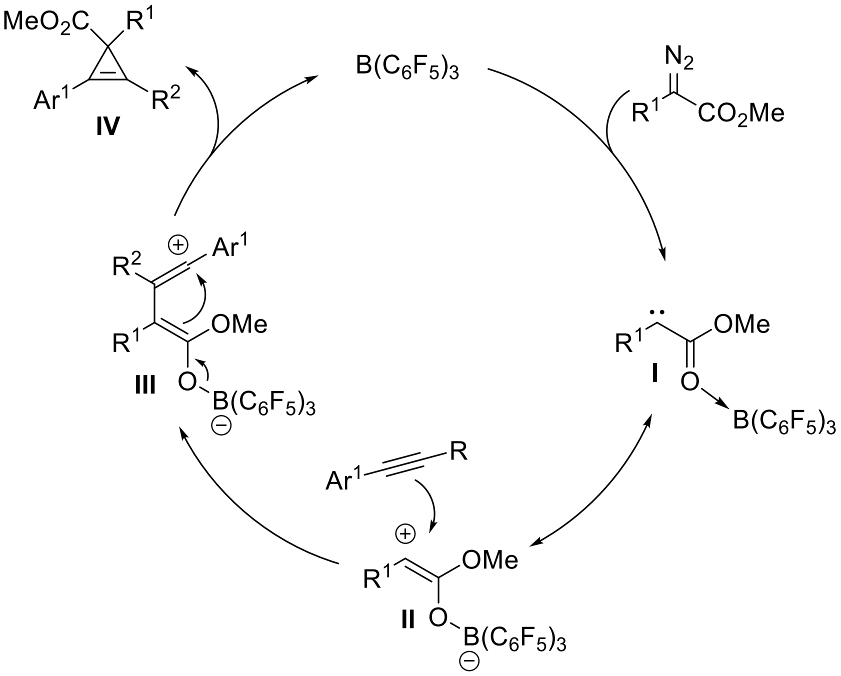
The mechanism of Roskamp reaction is also well-known, wherein a Lewis acid coordinates and activates the carbonyl group of the benzaldehyde, which makes the carbonyl's carbon more electrophilic **(Scheme 3.11, I)**. In this case, the carbon adjacent to the diazo functionality acts as a nucleophile and readily attacks the activated aldehyde, which results in a diazonium intermediate **II**. There are two possible rearrangement pathways, which could subsequently occur, whilst diazo functionality is released, and the catalyst is regenerated. Either the intermediate **II** undergoes cyclisation to form an epoxide **(Scheme 3.11, path a)** or as preferred in the observed case, the intermediate undergoes a hydride transfer, thus forming the β-keto ester **(Scheme 3.11, path b)**.[134]



Scheme 3.11: Reaction mechanism of Lewis acid-catalysed Roskamp reaction or epoxidation reaction

3.8 Proposed catalytic cycle for the borane-catalysed cyclopropenation reaction

Based on the previous cyclopropanation studies as well as observations made on the tolerability of the substrates, a catalytic cycle for the $B(C_6F_5)_3$-catalysed cyclopropenation of arylacetylenes was proposed as depicted in **Scheme 3.12**. First, $B(C_6F_5)_3$ coordinates to the carbonyl's oxygen of the diazo ester, resulting in substrate activation and a subsequent N_2 release, forming a carbene intermediate **I**, which is in a resonance with electrophilic borane carbene adduct **II**. Adduct **II** is then attacked by the nucleophilic arylacetylene, forming intermediate **III**, bearing a vinylic carbocation. As such, substrates unable to sufficiently stabilise this carbocation centre would not form such intermediate and thus would not result in the cyclopropene product, justifying why terminal alkylacetylenes did not react. Lastly, the carbocation is attacked by the boron enolate, forming the cyclopropenated product **IV** and regenerating the catalyst.



Scheme 3.12: Proposed catalytic cycle for the $B(C_6F_5)_3$ mediated cyclopropenation of arylacetylenes

3.9 Summary and outlook

To conclude, I have developed a mild, transition metal free methodology towards a cyclopropenation of arylacetylenes. I have presented a wide substrate scope of 33 examples, including terminal and internal alkynes. Furthermore, I have performed intramolecular competition reactions with 1,2- and 1,4-enyne substrates, demonstrating that the cyclopropanation is favoured over cyclopropenation. Lastly, an attempt to apply the optimised reaction conditions towards a synthesis of epoxides was conducted, however a formation of α-aryl-β-keto ester was observed instead. Limitation of the current protocol includes the incompatibility of more sterically hindered internal aryl- and alkyl- alkynes, terminal alkyl alkynes. As well as less reactive diazo esters. As such, future work could be comprised of extending the current substrate scope towards the more difficult substrates. The presented cyclopropenation protocol was published in *Chem. Commun.* **2021**, *57*, 6736–6739.[135]

4.0 Site-selective $C_{sp}{}^3$–C_{sp}/$C_{sp}{}^3$–$C_{sp}{}^2$ cross-coupling reactions using frustrated Lewis pairs

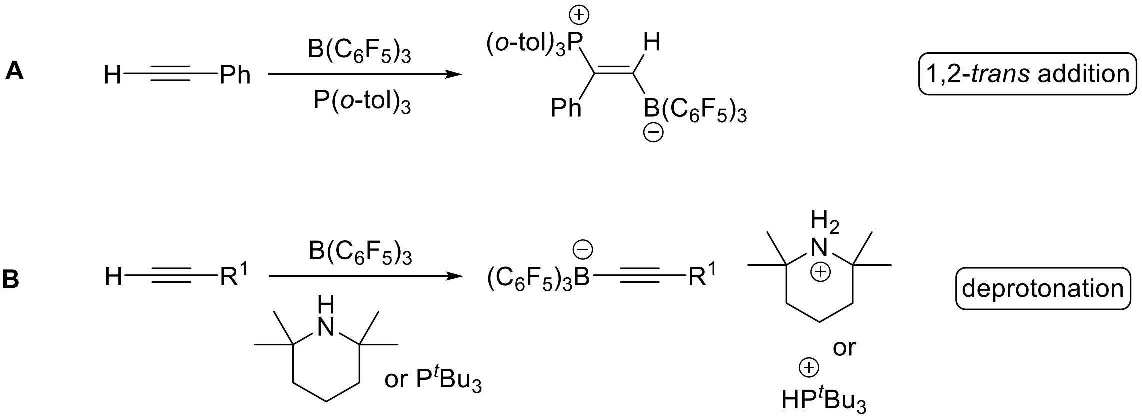
4.1 Introduction

In the last 50 years, C–C cross-coupling reactions have become one of the most utilised methodologies in the organic synthesis for preparation of a wide variety of organic molecules, including pharmaceutically active compounds or natural products.[136] In fact, the high importance of metal catalysed cross-coupling reactions have been recognised in 2010, wherein Heck, Negishi, and Suzuki were jointly awarded a prestigious Nobel prize. However, the most common catalysts utilised for such reactions are based on transition metals, including Pd, Cu, Ni, or Fe.[137]

There has been a continuous development of new catalytic systems, which could substitute such use of precious transition metals in carbon–carbon bond forming reactions, due to their high cost, toxicity, and low abundancy. In 2006, a crucial discovery has been made, wherein the catalytic system comprised of a bulky Lewis acid and Lewis base could reversibly activate H_2 at a room temperature, which had been demonstrated before only in a presence of transition metals, due to the availability of *d*-orbitals.[138] Such transition metal-free catalytic system has been later named as frustrated Lewis pairs (FLPs).[139] and since their discovery, FLPs have been utilised for various chemical transformations in the organic synthesis, as well as for the activation of small molecules, which both have been reviewed1 in the introductory part of this thesis (see sections **1.6.1–1.6.3**).[140]

FLP-mediated alkyne activation has been demonstrated, wherein 1,2-*trans* addition is usually observed, which has been later utilised also for catalytic reductions **(Scheme 4.1, A)**.[141,142] However, in a presence of stronger Lewis bases, such P^tBu_3 or 2,2,6,6-tetramethylpiperidine (TMP), a deprotonation of acetylenic proton was observed instead, as acetylide-based salt

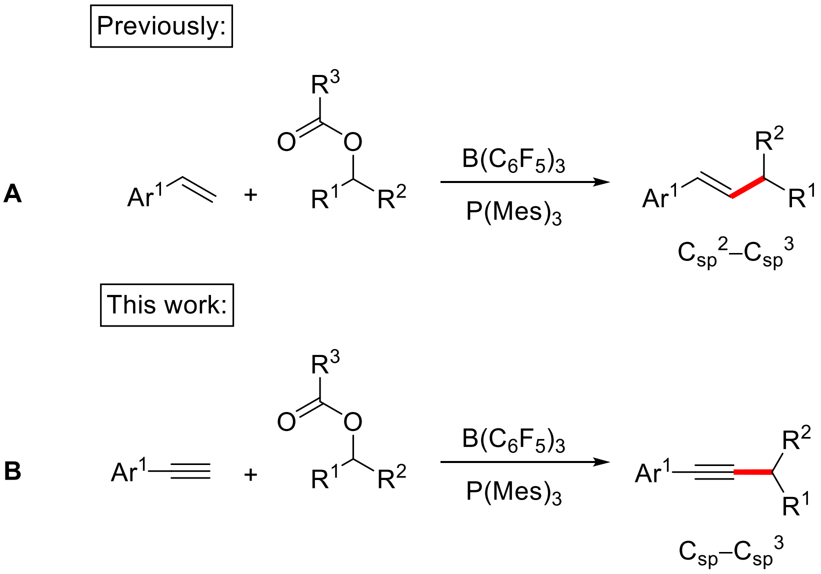
[LBH] [PhC≡CB(C_6F_5)$_3$] was obtained **(Scheme 4.1, B)**.[143] Such deprotonation of terminal alkynes is commonly observed in a Pd and/or Cu-catalysed $C_{sp}{}^2$–C_{sp} cross-coupling reactions, also known as Sonogashira reaction.[144]



Scheme 4.1: Previously reported activation of acetylenes by FLPs

4.2 Aims of this work

As mentioned in the introductory part of this thesis, our group has demonstrated a transition metal-free $C_{sp}{}^2$–$C_{sp}{}^3$ cross-coupling of commercially available styrenes and diaryl substituted esters in a presence of stoichiometric amounts of B(C_6F_5)$_3$ and P(Mes)$_3$ **(Scheme 4.2, A)**.[104] Such discovery has prompted our curiosity towards expanding the scope of FLP-catalysed cross-coupling reactions even further. As such, the aims of this chapter include developing a methodology towards FLP-mediated cross-coupling reactions of arylacetylenes and diaryl esters in order to obtain $C_{sp}{}^3$–C_{sp} coupled products **(Scheme 4.2, B)**. These reactions are typically reported in a presence of transition metals, including Pd, Fe, or Cu and more recently with Brønsted acid, such as $HBF_4 \cdot OEt_2$.[145,146,147, 148] Furthermore, a selectivity of intramolecular and intermolecular $C_{sp}{}^3$–C_{sp} versus $C_{sp}{}^3$–$C_{sp}{}^2$ reactions have been investigated. Lastly, extensive DFT and EPR studies have been conducted to elucidate a reaction mechanism for the developed methodology.



Scheme 4.2: Previously reported FLP-mediated C–C coupling reactions (**A**) and the aims of this work (**B**)

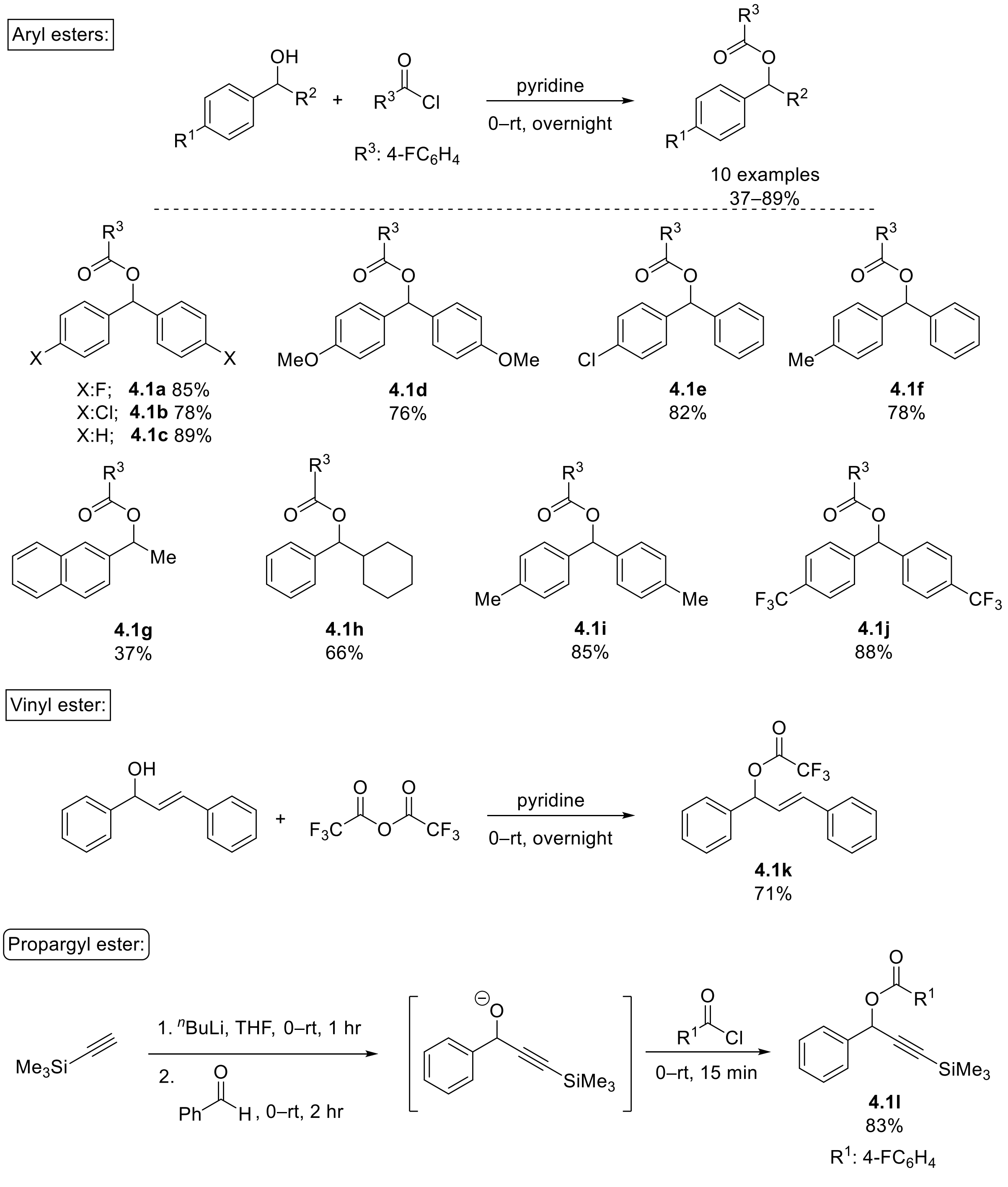
4.3 Work contribution

The optimisation reactions and a substrate scope of $C_{sp}{}^3$–C_{sp} coupled products have been majorly performed by Dr. Ayan Dasgupta. EPR studies have been performed in a collaboration with Dr. Emma Richards, kinetic studies have been performed in a collaboration with Dr. Niklaas J. Buurma, and DFT calculations have been conducted in a collaboration with Dr. Alireza Ariafard and Dr. Rassol Babaahmadi. My contribution majorly involved conducting synthetic reactions, wherein chemoselectivities were studied as well as assisting in exploring a substrate scope for $C_{sp}{}^3$–C_{sp} coupling reactions, and interpretation of data (including that from kinetic, EPR and DFT studies).

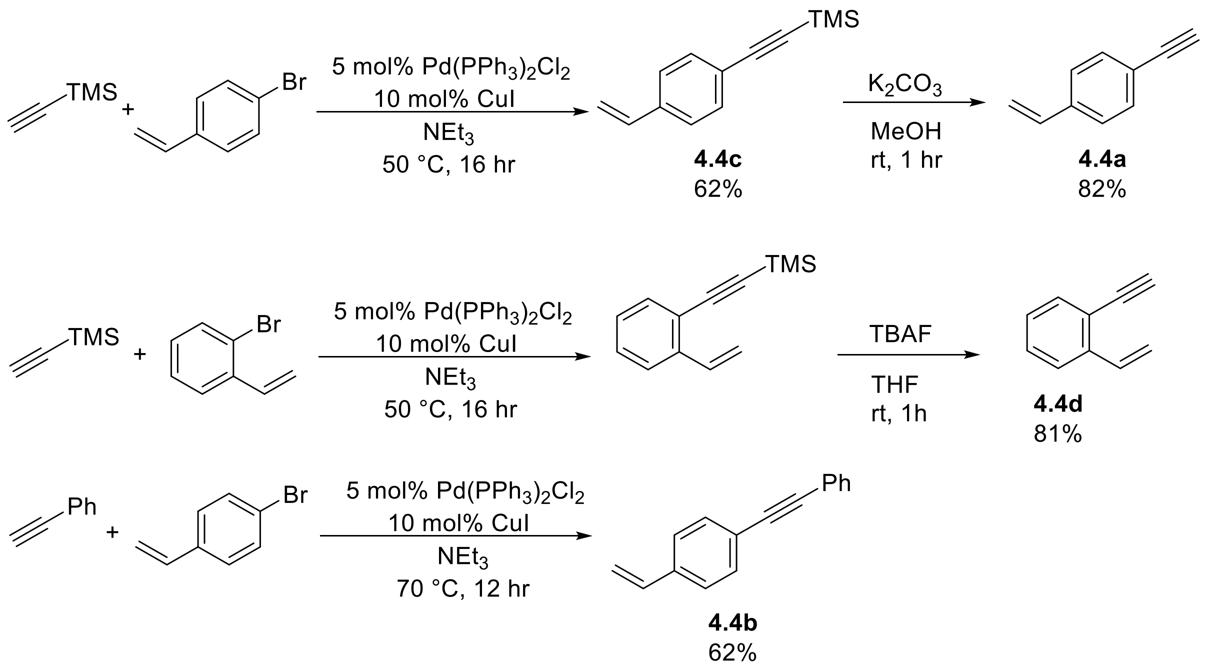
4.4 Synthesis of starting materials

Diaryl, allyl, and propargyl esters **4.1a–4.1l (Scheme 4.3)** have been synthetised according to procedures already disclosed in the sections **2.3** and **3.4** of this thesis. Similarly, syntheses of enyne substrates **4.4a–4.4d (Scheme 4.4)** have been followed as outlined in the section **3.4**.

Lastly, the utilised aryl acetylenes are all commercially available and hence were not synthetised for the purpose of this work.



Scheme 4.3: Synthetised aryl, vinyl, and propargyl esters **4.1a–4.1l**



Scheme 4.4: Synthesis of enynes **4.4a**–**4.4d**

4.5 Optimisation reactions

Initial optimisation reactions **(Table 4.1)** were conducted with bis(4-fluorophenyl)methyl-4-fluorobenzoate **4.1a** and phenylacetylene as model substrates. First, a control reaction was performed, wherein no catalyst was included. As expected, no reactivity was observed between the ester and alkyne whilst heating the reaction at 70 °C in toluene for about 20 hours. However, when the reaction was repeated in a presence of stoichiometric amounts of $PMes_3$ and $B(C_6F_5)_3$ **(Table 4.1, entry 4)**, a consumption of starting materials was observed, and a new compound was isolated in 54% yield.

The ^{1}H-NMR spectrum showed that a characteristic signal for terminal alkyne proton at around $\delta = 3$ ppm is indeed missing in the isolated compound and a singlet at $\delta = 5.18$ ppm suggested a presence of proton H_a **(Figure 4.1)**. The ^{13}C-NMR spectrum confirmed a presence of the alkyne moiety, as signals at $\delta = 89.7$ ppm and $\delta = 85.4$ were observed and a missing signal at $\delta = 164.6$ ppm confirmed that the ester functionality is no longer present in the isolated compound **(Figure 4.2)**. Furthermore, an observed J_{C-F} coupling confirmed a presence of fluorine in the isolated compound as well as a presence of a single peak at δ = -115.81 ppm in the ^{19}F-NMR spectrum **(Figure 4.3)**. Based on these observations, it was suggested that the $C_{sp}{}^{3}$–C_{sp} coupled product **4.2c** was indeed formed. This was subsequently confirmed by HRMS, wherein the compound with a mass of 304.1058 was detected with an electron ionisation (EI+) method, which is matching with the proposed product **4.2c**.

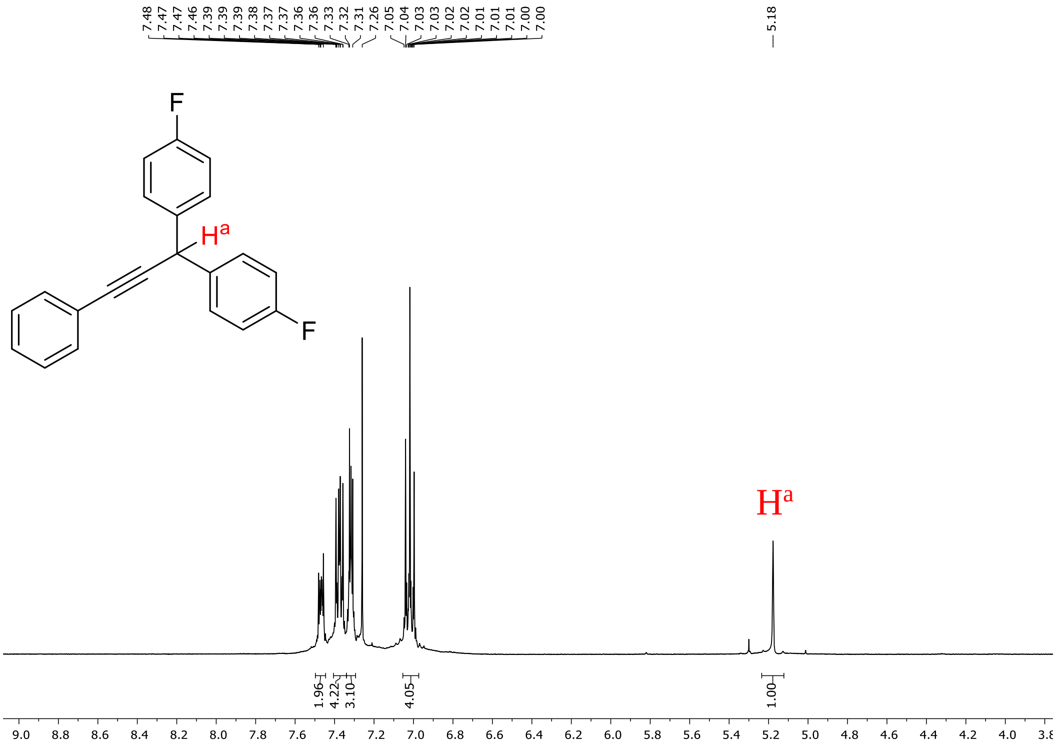


Figure 4.1: ^{1}H-NMR spectrum of the isolated compound **4.2c**

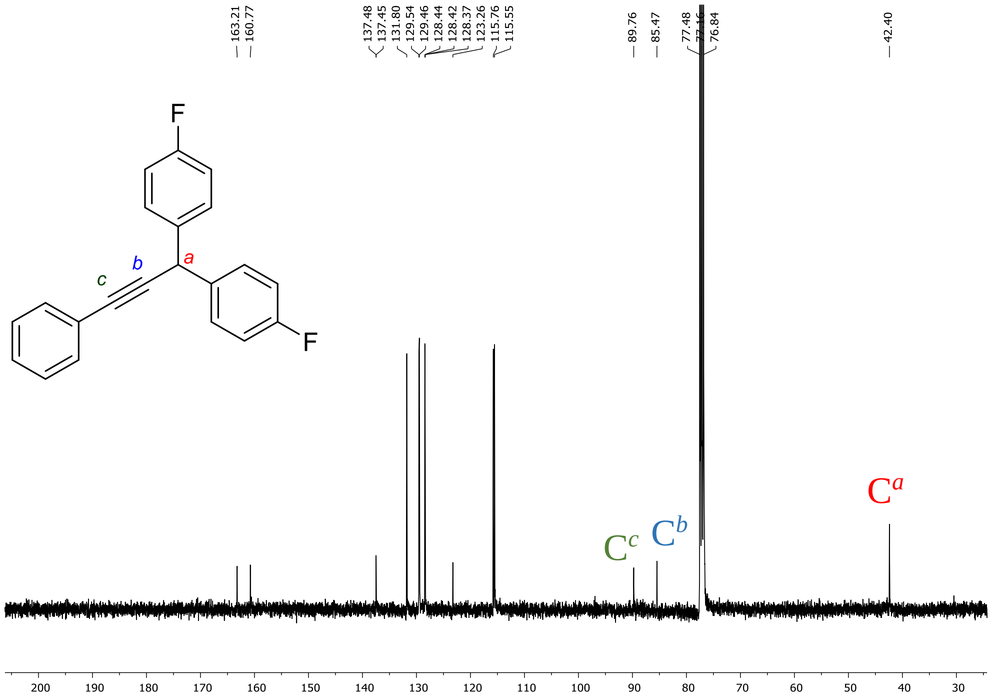


Figure 4.2: ^{13}C-NMR spectrum of isolated compound **4.2c**

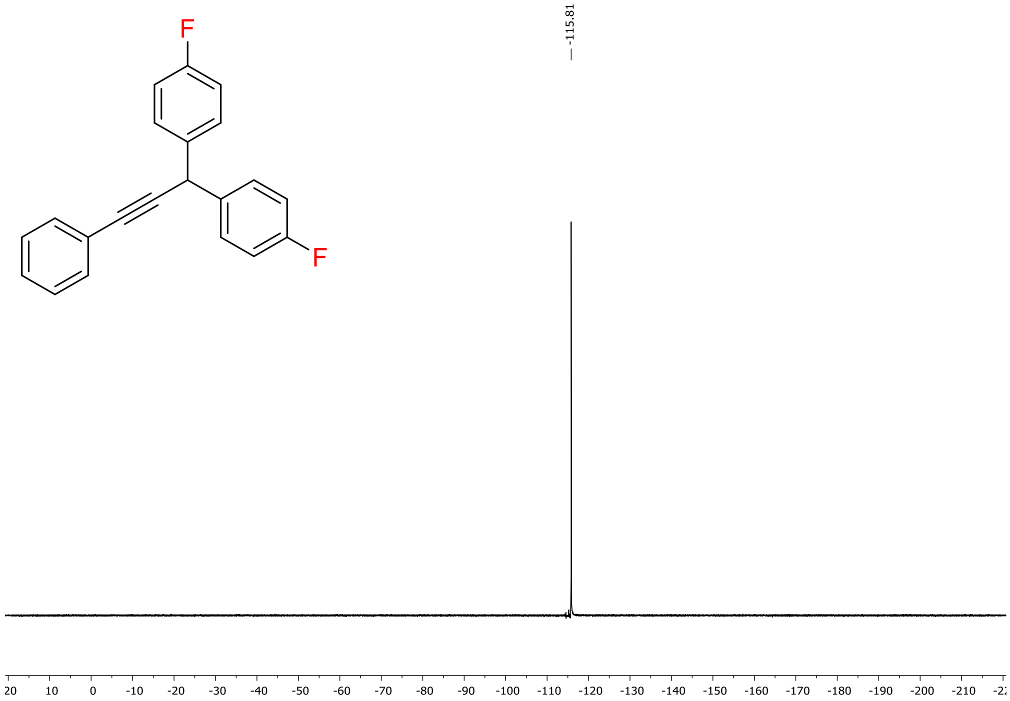
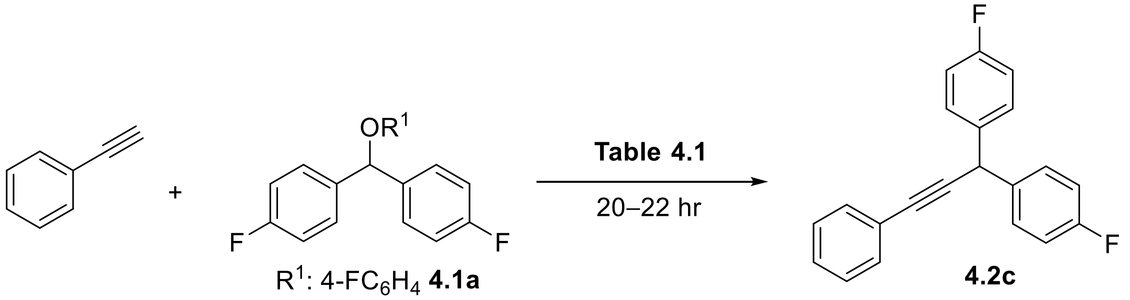


Figure 4.3: ^{19}F-NMR spectrum of isolated compound **4.2c**

Delighted by these results, further optimisation was conducted. First, it was investigated whether the reaction works in a sole presence of Lewis acid or base. When the reaction was carried in a presence of PMes$_3$, no production formation was observed. Interestingly, both stoichiometric and catalytic amounts (10 mol%) of $B(C_6F_5)_3$ did promote the reaction, though the product was formed in poor yields of 22% and 5%, respectively. Next different temperatures were investigated, wherein both reflux and ambient temperatures resulted in the product formation, though the obtained yields were decreased to 45% and 18%, respectively. Different solvent systems were also screened, wherein the improved yields of 83% and 71% were observed with THF and trifluorotoluene (TFT) respectively. On the other hand, a decreased yield of 38% was observed when the reaction was carried out in dichloromethane (CH_2Cl_2), presumably due to the decreased temperature used. Lastly, no product was formed in hexane, presumably due to the poor solubility of $B(C_6F_5)_3$. Finally, different catalytic systems were investigated. As expect, in a presence of $BF_3{\cdot}OEt_2$ or triflic acid, no product formation was observed, presumably due to the failure of forming frustrated Lewis pairs. Furthermore, less acidic borane BPh_3 also failed to catalyse the reaction. Different phosphine and nitrogen-based Lewis bases were screened next, wherein only P^tBu_3 managed to catalyse the reaction together with $B(C_6F_5)_3$, though in decreased yield of 45%. Other bases, such PPh_3, tri(*o*-tolyl)phosphine (P(*o*-tol)$_3$), TMP, 4-bromo dimethyl aniline (DMA) or 1,4-diazabicyclo(2,2,2)octane (DABCO) all failed to mediate $C_{sp}{}^3$–C_{sp} cross coupling reaction. As such, the best results were observed with using stoichiometric amounts of $B(C_6F_5)_3$ and $PMes_3$ and heating the reaction at 70 °C in THF for around 22 hours **(Table 4.1, entry 8)**.

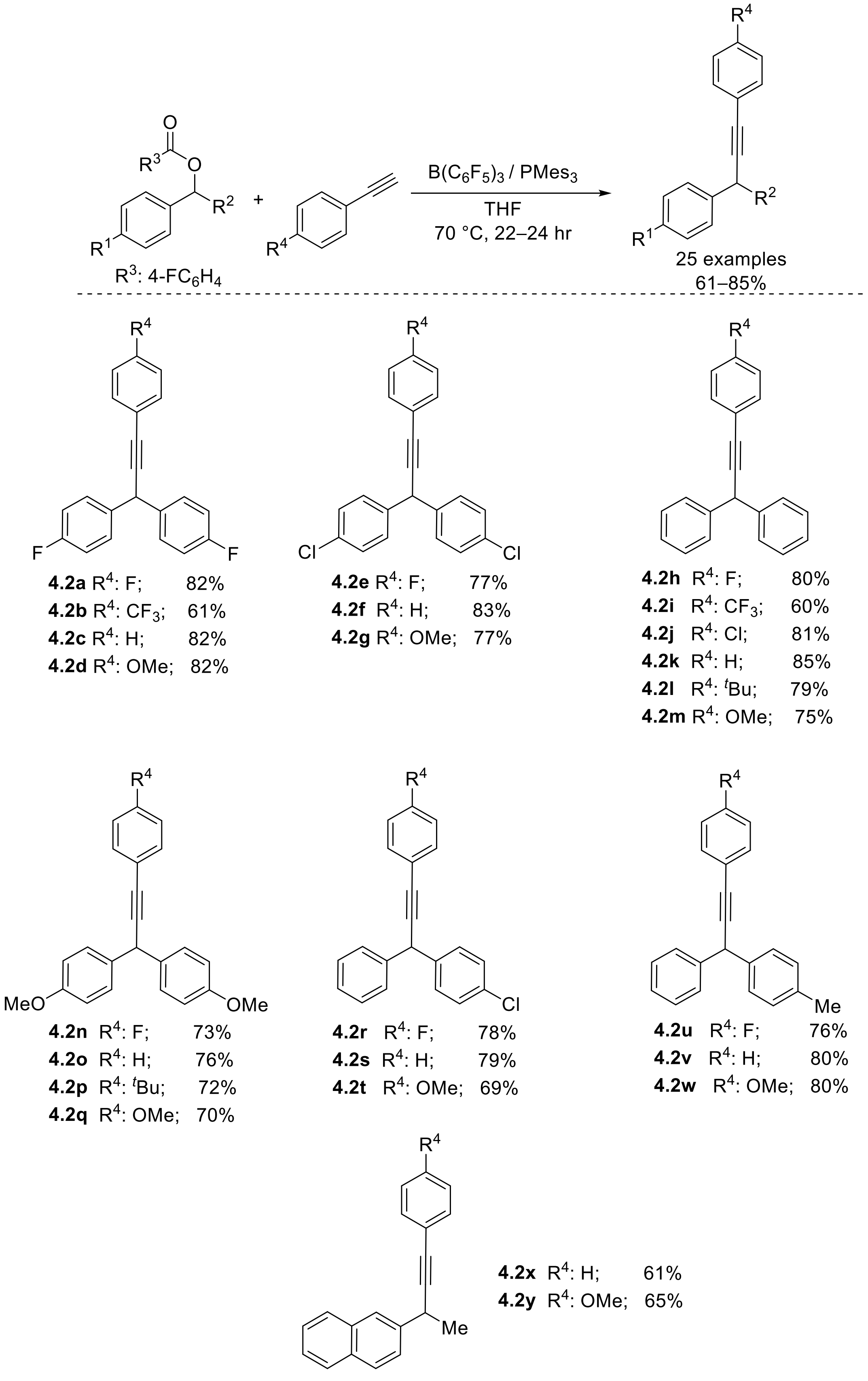


Entry	**Lewis acid**	**Lewis base**	**Solvent**	**Temperature [°C]**	**Yield [%]**
1	-	-	toluene	70	0
2	$B(C_6F_5)_3$	$PMes_3$	toluene	70	54
3	-	$PMes_3$	toluene	70	-
4	$B(C_6F_5)_3$	-	toluene	70	22
5	10mol% $B(C_6F_5)_3$	-	toluene	70	5
6	$B(C_6F_5)_3$	$PMes_3$	toluene	21	18
7	$B(C_6F_5)_3$	$PMes_3$	toluene	110	45
8	**$B(C_6F_5)_3$**	**$PMes_3$**	**THF**	**70**	**83**
9	$B(C_6F_5)_3$	$PMes_3$	TFT	70	71
10	$B(C_6F_5)_3$	$PMes_3$	CH_2Cl_2	45	38
11	$B(C_6F_5)_3$	$PMes_3$	hexane	70	0
12	$BF_3·Oet_2$	$PMes_3$	toluene	70	0
13	BPh_3	$PMes_3$	toluene	70	0
14	CF_3SO_3H	$PMes_3$	THF	70	0
15	$B(C_6F_5)_3$	P^tBu_3	toluene	70	45
16	$B(C_6F_5)_3$	PPh_3	THF	70	0
17	$B(C_6F_5)_3$	P*o*-tol$_3$	THF	70	0
18	$B(C_6F_5)_3$	TMP	THF	70	0
19	$B(C_6F_5)_3$	DABCO	THF	70	0
20	$B(C_6F_5)_3$	DMA	THF	70	0

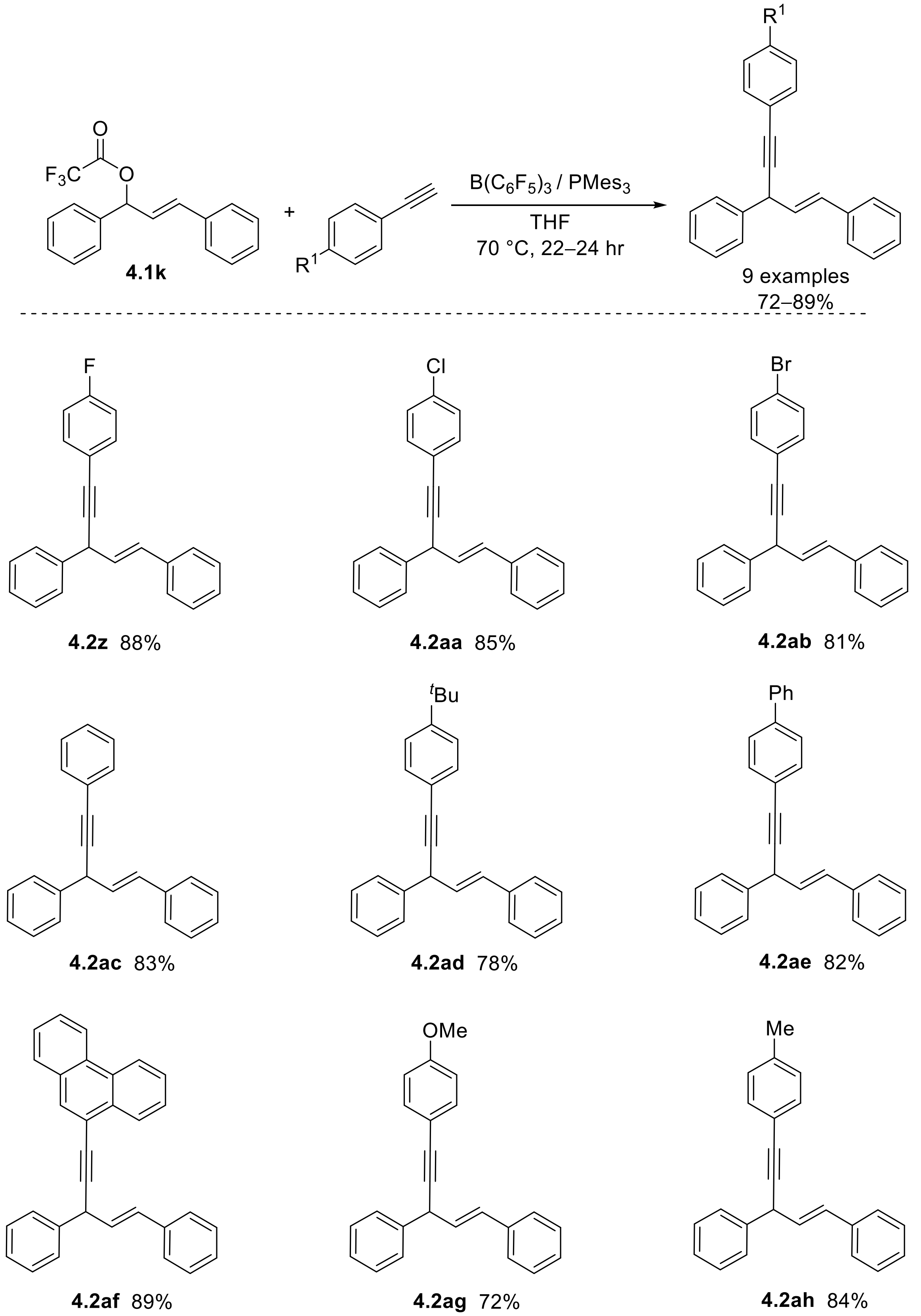
Table 4.1: Optimisation reactions for FLP catalysed C_{sp}–$C_{sp}{}^3$ coupling of diaryl ester **4.1a** and phenyl acetylene

4.6 Substrate scope for $C_{sp}{}^3$–C_{sp} coupled reactions

With the identified optimal reaction conditions, a substrate scope for FLP-mediated $C_{sp}{}^3$–C_{sp} cross-coupling was investigated next, wherein substituted symmetrical and unsymmetrical aryl or alkyl esters **4.1a–4.1g** were reacted with variously substituted aryl acetylenes **(Scheme 4.5)**. Generally, symmetrical diaryl esters with halogen (*p*-F, *p*-Cl), neutral (*p*-H), and electron-donating (*p*-OMe) substitutions reacted with *p*-CF_3, *p*-F, *p*-Cl, *p*-H, *p*-^{t}Bu, or *p*-OMe substituted phenylacetylenes in good to very good yields of up to 85% (see **4.2a–4.2q**). Similar results were observed with unsymmetrical diaryl esters bearing *p*-Cl and *p*-Me moieties, wherein the corresponding products **4.2r–4.2w** were obtained in 69–80%. Pleasingly, an ester bearing an alkyl moiety **4.1g** was also tolerated, though the corresponding products **4.2x** and **4.2y** were obtained in lower yields of 61% and 65%, respectively. However, an ester with a cyclohexyl group **4.1h** or a strongly electron-withdrawing *p*-CF_3 group **4.1j** failed to react under the optimised reaction conditions, presumably due to the insufficient stabilisation of the carbocation intermediate, which will be discussed later in more details. Furthermore, an allylic ester **4.1k** also showed to be compatible with the reaction protocol, as the corresponding products **4.2z–4.2ah** were obtained in 72–89% **(Scheme 4.6)**. Lastly, I have also investigated C–C cross coupling with a propargyl ester **4.1l**, however no product could be isolated from such reaction, presumably due to the decomposition of the propargyl ester in a presence.



Scheme 4.5: A substrate scope for $B(C_6F_5)_3$/$PMes_3$ mediated C–C coupling reactions of aryl/alkyl esters with aryl acetylenes

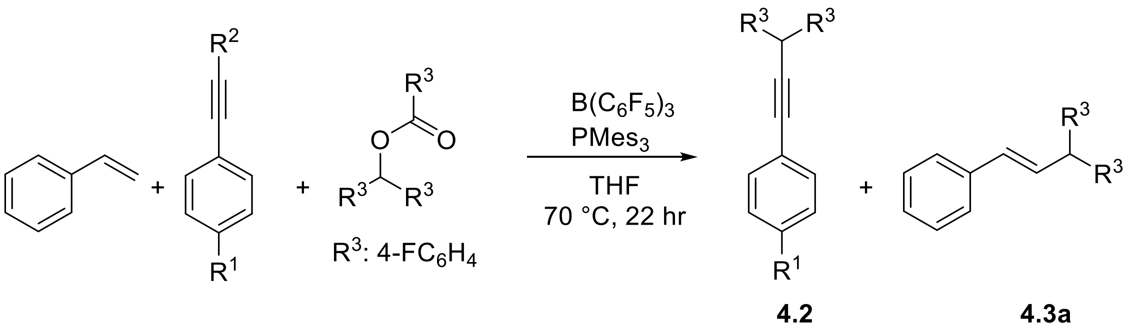


Scheme 4.6: A substrate scope for the $B(C_6F_5)_3$/$PMes_3$ mediated C–C coupling reactions of allyl ester **4.1k** with aryl acetylenes

4.7 Site selectivity investigations

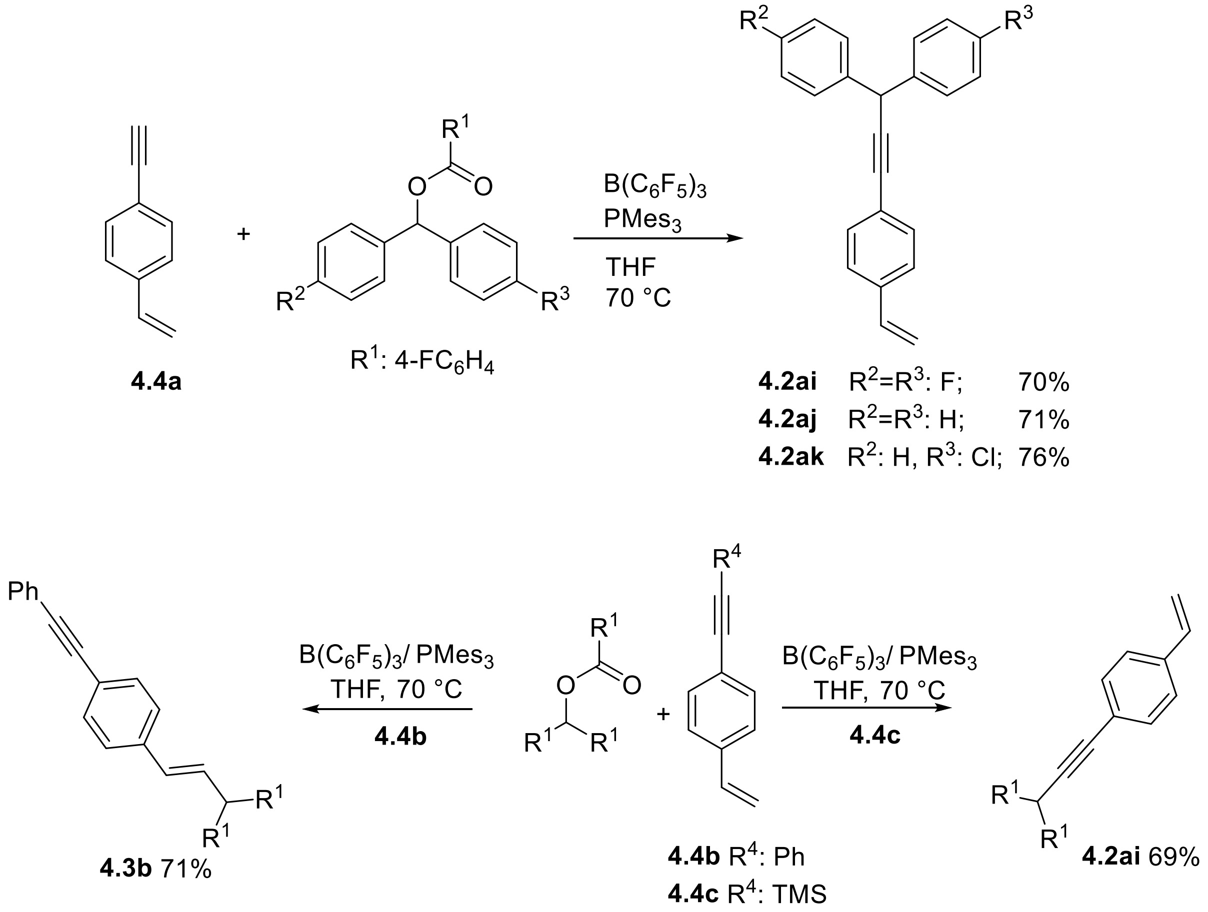
After the broad substrate scope of C_{sp}^3–C_{sp} coupled products was demonstrated, intermolecular competition reactions were investigated next **(Table 4.2)**. For such reactions, an equimolar mixture of 4-fluorophenylacetylene and 4-fluorostyrene was reacted with ester **4.1a** using the optimised reaction conditions. A crude ^{1}H-NMR spectrum showed a formation of a singlet at $\delta = 5.09$ ppm, which is distinctive of C_{sp}^3–C_{sp} coupled product and no doublet at $\delta = 4.98$ ppm was seen, which would belong to C_{sp}^3–C_{sp}^2 coupled product.[104] Indeed, after a purification of a reaction mixture, **4.2a** was obtained in 78% as the sole product. When the reaction was repeated with the internal diphenylacetylene, the reactivity was pushed towards the alkene functionality instead, as only C_{sp}^3–C_{sp}^2 coupled product **4.3a** was formed and obtained in 63%. This was to be expected as there is the internal alkyne sterically hindered and thus possibly inert towards the 1,2-*trans*-addition. Interestingly, when the reaction was carried out in a presence of a protected alkyne, such trimethyl(phenylethynyl)silane, a deprotection was observed and a formation of both C_{sp}^3–C_{sp} (**4.2c**) and C_{sp}^3–C_{sp}^2 (**4.3a**) coupled products in 1:0.4 ratio (determined by crude ^{1}H-NMR spectroscopy) was shown, wherein **4.2c** was isolated in 58%.

Next, intramolecular reactions were investigated, wherein 1-ethynyl-4-vinylbenzene **4.4a** was reacted with esters **4.1a**, **4.1c**, and **4.1e** under the optimised reaction conditions **(Scheme 4.7)**. Agreeing with the observations made in the previous intermolecular competition reactions, the alkyne was found to be more reactive than alkene, as the corresponding C_{sp}^3–C_{sp} coupled products **4.2ai**, **4.2aj**, **2.2ak** were formed in up to 76%. Internal enynes, such 1-(phenylethynyl)-4-vinylbenzene **4.4b** and trimethyl{(4-vinylphenyl)ethynyl}silane **4c** showed similar reactivities as well. In the case of **4.4b**, the reaction was pushed towards the alkene functionality, affording the corresponding product in 71%, whereas in case of **4.4c**, *in situ* deprotection of TMS group occurred and the C_{sp}^3–C_{sp} product was formed and isolated in 69%.



Entry	R^1	R^2	Yield of 4.2	Yield of 4.3a
1	F	H	78% (**4.2a**)	-
2	H	Ph	-	63%
3	H	TMS	58% (**4.2c**)	18%

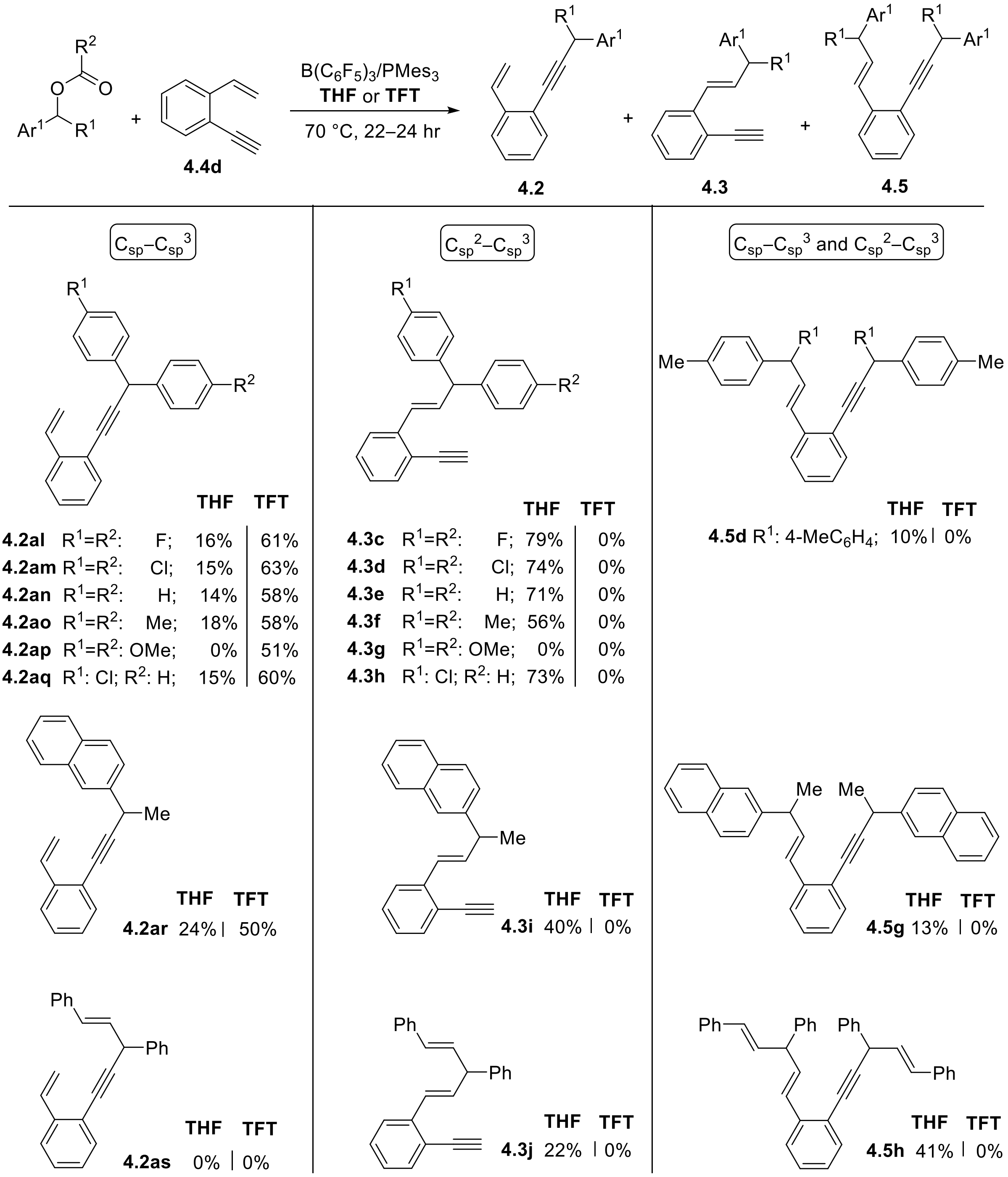
Table 4.2: Intermolecular competition reactions between 4-fluorostyrene and terminal/internal alkynes



Scheme 4.7: Intramolecular reactions of enynes **4.4a**–**4.4c** with diaryl esters

Lastly, it was investigated whether such chemoselectivity would be observed with a substrate, bearing the alkene and alkyne moiety closer together **(Scheme 4.8)**. For such purpose, 1-ethynyl-2-vinylbenzene **4.4d** was synthetised and reacted with ester **4.1a** using the optimised reaction conditions. An analysis of the crude ^{1}H-NMR spectrum suggested that both C_{sp}^2–C_{sp}^3 **4.3c** and C_{sp}^3–C_{sp} **4.2al** coupled products were indeed formed, and contrary to the previous observations, the chemoselectivity was switched, wherein **4.3c** showed to be the major product formed in 1:0.2 ratio, which was subsequently isolated in 79%, whereas **4.2al** was isolated in a low yield of 16%. Wondering whether the observed chemoselectivity could be improved, additional reaction optimisation was undertaken, more precisely wherein different solvent systems were screened. When carrying the reactions in dichloromethane no product formation was observed, whereas the reaction in toluene resulted in a complicated reaction mixture. Interestingly, when the reaction was carried out in trifluorotoluene (TFT), only the formation of the C_{sp}^3–C_{sp} coupled product **4.2al** was observed and later isolated in 61%.

To identify whether such observations were only isolated incidents, a substrate scope was investigated, wherein 1-ethynyl-2-vinylbenzene **4.4d** was reacted with variously substituted esters in both THF and TFT solvent systems **(Scheme 4.8)**. Following the previously observed trend, the reactions carried out in THF showed a clear preference for the alkene functionality, as when *p*-Cl and *p*-H symmetrical esters were reacted, the corresponding C_{sp}^2–C_{sp}^3 products **4.3d** and **4.3e** showed to be formed in 1:0.2 ratio and were isolated in 74% and 71%, respectively. Similarly, unsymmetrical ester with *p*-Cl substitution resulted in the product **4.3h** as major which was again formed in 1:0.2 ratio and was isolated in 73%. *p*-OMe substituted ester **4.1d**, showed no product formation in THF, whereas *p*-Me substituted ester **4.1i** and alkyl/aryl ester **4.1g** both formed C_{sp}^2–C_{sp}^3(**4.3f** and **4.3i**) and C_{sp}–C_{sp}^3 (**4.2ao** and **4.2ar**) products, and furthermore a formation of double substituted products **4.5d** and **4.5g** was observed as well, though in very low yields of 10% and 13%, respectively. Surprisingly, when allylic ester **4.1k** was reacted a clear preference for the double coupled product was observed, as **4.5h** was isolated in 41% and the C_{sp}^2–C_{sp}^3 product **4.3j** was obtained in 22%, whereas no C_{sp}–C_{sp}^3 product **4.2as** was formed.



		THF	TFT
4.2al	R^1=R^2: F;	16%	61%
4.2am	R^1=R^2: Cl;	15%	63%
4.2an	R^1=R^2: H;	14%	58%
4.2ao	R^1=R^2: Me;	18%	58%
4.2ap	R^1=R^2: OMe;	0%	51%
4.2aq	R^1: Cl; R^2: H;	15%	60%
4.2ar		24%	50%
4.2as		0%	0%

		THF	TFT
4.3c	R^1=R^2: F;	79%	0%
4.3d	R^1=R^2: Cl;	74%	0%
4.3e	R^1=R^2: H;	71%	0%
4.3f	R^1=R^2: Me;	56%	0%
4.3g	R^1=R^2: OMe;	0%	0%
4.3h	R^1: Cl; R^2: H;	73%	0%
4.3i		40%	0%
4.3j		22%	0%

		THF	TFT
4.5d	R^1: 4-MeC_6H_4;	10%	0%
4.5g		13%	0%
4.5h		41%	0%

Scheme 4.8: Substrate scope for solvent-dependent site selectivity of C–C coupling reactions of enyne **4.4d** and aryl esters

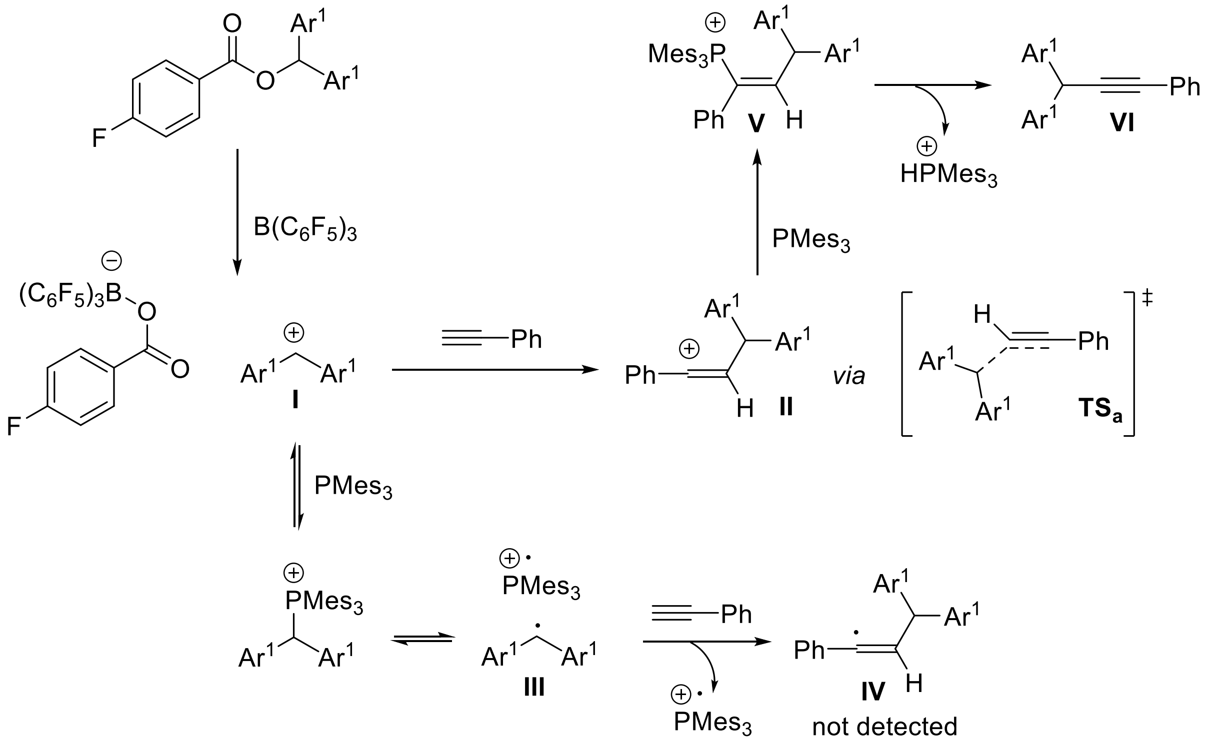
When carrying parallel reactions in TFT, only the formation of C_{sp}–$C_{sp}{}^3$ coupled products was observed, though the obtained yields were generally lower **(Scheme 4.8)**. As such, products **4.2ai–4.2ar** were obtained in up to 63%, with the best yield observed with symmetrical *p*-Cl ester **4.1b** and the worst yield of 50% was obtained with alkyl aryl ester **4.1g**. Interestingly, whereas *p*-OMe substituted ester **4.1d** showed no reactivity in THF, in TFT, the corresponding C_{sp}–$C_{sp}{}^3$ product **4.2ap** was obtained in 51%. Lastly, no formation of desired C–C coupled product could be identified with allylic ester **4.1k** in TFT.

4.8 Proposed reaction mechanism

As highlighted in the **section 1.5.1** of the introductory part of this thesis, FLPs activate small molecules *via* either classical diamagnetic pathway or as demonstrated by our previous study, through the possible formation of frustrated radical pairs, which then mediate the cross-coupling reaction.[104] Based on the extensive EPR, kinetic, and DFT studies, undertaken with the collaborators described above, we have proposed that indeed most likely the diamagnetic pathway takes place. For the purpose of this thesis, these studies will not be discussed in much detail and only the key findings will be outlined whilst discussing the proposed reaction mechanism **(Scheme 4.9)**.

Using the data from these studies, it is proposed that the activation of the diaryl ester, such **4.1a** by $B(C_6F_5)_3$ first takes place, wherein the $C_{sp}{}^3$–O bond is cleaved and diaryl methylene carbocation intermediate **I (Scheme 4.9)** is formed together with a borate anion. These intermediates showed to be formed *via* initial activation energy of 10.7 kcal/mol, whereas the initial frustrated radical pair formation showed to be unfavourable by 35.7 kcal/mol in comparison. DFT calculations at the SMD/B3LYP-D3/def2-TZVP//SMD/B3LYP-D3/6-31G(d) level of theory using THF as the solvent also showed that the energy for the diaryl ester activation by $B(C_6F_5)_3$ is highly influenced by the substitutions present on the aryl rings of the ester. As such, the activation of *p*-OMe substituted ester **4.1d** showed be slightly favoured when compared to *p*-F ester **4.1a** by 0.8 kcal/mol, and as expected the resulting carbocation of *p*-OMe ester **4.1d** showed to be more thermodynamically favourable by −11.7 kcal/mol when compared with *p*-F ester **4.1a**. On the other hand, the activation of *p*-CF_3 substituted ester **4.1j** showed to be both kinetically and thermodynamically less favourable, as the activation energy was calculated to be 10.9 kcal/mol more and the resulting carbocation intermediate was calculated to have a higher free energy by 11.2 kcal/mol when compared to *p*-F substituted intermediate. Such calculations would justify why **4.1j** failed to react with phenyl acetylene in our optimised reaction conditions.

In the next step, it was determined that the carbocation intermediate **I (Scheme 4.9)** undergoes an addition to an alkyne *via* a transition state **TS$_a$** with an activation energy of 16.3 kcal/mol, resulting in a vinylic carbocation intermediate **II** with a free energy of 4.8 kcal/mol. As for the comparison, it was calculated that if the diaryl carbocation **I** underwent a single electron transfer with $PMes_3$, and thus forming a carbon-based radical intermediate **III**, the radical addition towards the alkyne would require a higher activation energy by 7.7 kcal/mol and the formed vinyl radical intermediate **IV** would be less thermodynamically favourable only by 0.6 kcal/mol. As such, there might be a possibility that the radical pathway is indeed simultaneously taking place, however the formation of carbon-based radical under the optimised reaction conditions could not be confirmed by the EPR studies. Lastly, the highly reactive vinylic carbocation **II** is then trapped by $PMes_3$, forming stabilised phosphine-based cation intermediate **V**, which then undergoes elimination of $[HPMes_3]^+$, thus resulting in the final product **VI**. During the optimisation reactions, we have shown that the C_{sp}–$C_{sp}{}^3$ coupled product could be obtained in a presence of $B(C_6F_5)_3$ only, though the obtained yields were significantly lower. This was also justified by DFT calculations, which showed that if the previously formed borate anion accepts the proton from vinylic intermediate **II** instead of $PMes_3$, such reaction is thermodynamically less favourable by more than 20 kcal/mol.



Scheme 4.9: Proposed reaction mechanism for the $B(C_6F_5)_3$/$PMes_3$-mediated cross-coupling reaction based on the mechanistic studies

With an aid of further DFT calculations at SMD/B3LYP-D3/def2-TZVP//SMD/B3LYP-D3/6-31G(d) level in THF and toluene, the observed regioselectivity of the reactions with 1-ethynyl-4-vinylbenzene **4.4a** was explained as well. It was calculated that although the addition of the diaryl carbocation towards the alkyne functionality requires only 0.1 kcal/mol more than the addition towards the alkene functionality, a free energy of the corresponding intermediates differed significantly more, wherein the $C_{sp}{}^3$–C_{sp} coupled product showed to be more thermodynamically stable by about 7 kcal/mol, thus justifying why the reactions showed to be chemoselective.

Similarly, the switching site-selectivity observed with 1-ethynyl-2-vinylbenzene **4.4d** was explained by the DFT calculations **(Figure 4.4)**. It was shown that when the reaction is carried out in THF, the free energy of the alkene-addition **TS1** showed to be only slightly favourable by 0.5 kcal/mol when compared to alkyne-addition **TS$_2$**. However, when the reaction was calculated in toluene (or TFT), the alkene-addition showed to be now less favourable and with a higher energy difference of 3.7 kcal/mol. These findings indeed helped to justify why only $C_{sp}{}^3$–C_{sp} coupled product **4.2** was observed in TFT whereas in THF, a mixture of C–C coupled products was always obtained.

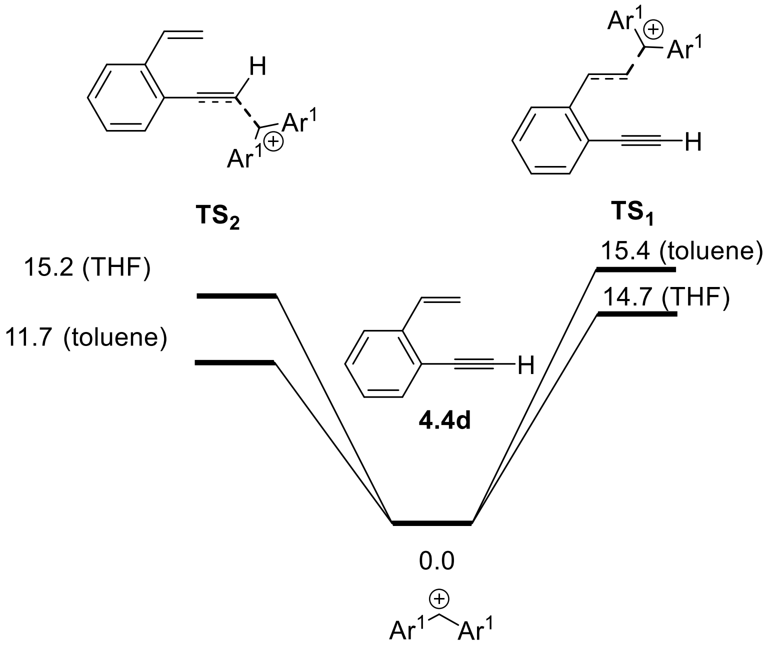


Figure 4.4: DFT calculations for site selectivity of diaryl methylene carbocation with **4.4d**; the relative free energies are given in kcal/mol

4.9 Summary and outlook

To conclude, the FLP-mediated functionalisation of terminal arylacetylenes has been developed, wherein a broad substrate scope of 34 examples has been demonstrated in up to 89% yields. Moreover, it was shown that such reactions are highly chemoselective towards alkyne rather than alkene functionality in intermolecular competitive reactions and identical selectivity was observed in a presence of 1-ethynyl-4-vinylbenzene **4.4a**. However, when the reactions were carried out with 1-ethynyl-2-vinylbenzene **4.4d**, the selectivity was highly influenced by the solvent system used. As such, the alkene functionalisation was preferred in

THF whereas TFT solely promoted the C−C coupling at the alkyne moiety. Lastly, based on the extensive mechanistic studies, which were undertaken by our collaborators, it was concluded that although the formation of frustrated radical pairs is observed in solution, they do not seem to participate in mediating of the coupling reactions. Instead, it is more plausible that the diamagnetic pathway takes place in the demonstrated $B(C_6F_5)_3$/$PMes_3$ catalysed alkyne functionalisation reactions. The deeper mechanistic studies could be used as a tool for a further development of frustrated radical or Lewis pair-mediated C−C bond forming reactions. Moreover, such catalytic system could be potentially employed in future for a metal-free synthesis of novel natural products. The presented methodology was successfully published in *J. Am. Chem. Soc.* **2021**, *143*, 4451−4464.[149]

5.0 Experimental

5.1.0 General experimental

Except for the starting materials, all reactions and manipulations were carried out under an atmosphere of dry, O_2-free nitrogen using standard double-manifold techniques with a rotary oil pump. A nitrogen-filled glove box (MBraun) was used to manipulate solids including the storage of starting materials, ambient temperature reactions, product recovery and sample preparation for analysis. The solvents dichloromethane, hexane, and acetonitrile were dried by employing a Grubbs-type column system (Innovative Technology) or a solvent purification system MB SPS-800 and stored under a nitrogen atmosphere. Anhydrous (with Sure/Seal) 1,2-dichloroethane (1,2-DCE) and α,α,α-trifluorotoluene (TFT) were purchased from Merck and dried over molecular sieves before use. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. All the triarylfluoroboranes were prepared as per the standard literature reports.[77] Thin-layer chromatography (TLC) was performed on pre-coated aluminum sheets of Merck silica gel 60 F254 (0.20 mm) and visualised by UV radiation (254 nm) also a solution of $KmnO_4$ (1.5 g $KmnO_4$, 10 g K_2CO_3, and 1.25 mL 10% NaOH in 200 mL water) were used to develop the stain on TLC plates.^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance II 400 or Bruker Avance 500 spectrometers. All coupling constants are absolute values and are expressed in Hertz (Hz). ^{13}C NMR was measured as ^1H decoupled. Yields are given as isolated yields. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to $CHCl_3$ (7.26/77.16 ppm) as internal standard. NMR spectra were referenced to $CFCl_3$ (^{19}F).[150] The description of signals includes s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet, br. = broad. All coupling constants are absolute values and are expressed in Hertz (Hz). ^{13}C NMR was measured as ^1H decoupled. All spectra were analysed assuming a first order approximation. IR-Spectra were measured on a Shimadzu IRAffinity-1 photo-spectrometer. Mass spectra were measured on a Waters LCT Premier/XE or a Waters GCT Premier spectrometer. Ions were generated by the Atmospheric Solids, Analysis Probe (ASAP), GC analysis, Electrospray (ES) or Electron Ionisation (EI). The molecular ion peaks values quoted for either molecular ion (M^+), molecular ion plus or minus hydrogen ($M+H^+$, $M–H^-$), molecular ion minus hydride ($M–H^+$), molecular ion plus sodium ($M+Na^+$).

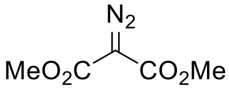
5.2.0.0 Synthesis of starting materials

5.2.1.0 General procedure for a synthesis of diazo compounds

General procedure a: 1,8-Diazabicyclo[5.4.0]undec-7-ene (1.5 equiv) (until otherwise mentioned) was added to a solution of corresponding ester (1 equiv) and 4-acetamidobenzenesulfonyl azide (1.2 equiv) in anhydrous CH_3CN (30 mL). The reaction mixture was stirring at room temperature for (14–16) hrs under the nitrogen atmosphere. The organic compounds were extracted with diethyl ether (3 × 25 mL), the combined organic fractions were washed with brine solution (1 × 30 mL), dried over $MgSO_4$ and concentrated using vacuum. The crude compound was purified *via* column chromatography using silica gel (Merck, 60 Å, 230 – 400 mesh particle size) and hexane-ethyl acetate as eluent.

5.2.1.1 Synthesis and spectral characterisation of diazo compounds

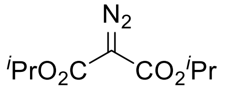
*Synthesis of dimethyl 2-diazomalonate (**2.1a**)*[151]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (6.3 mL, 42.0 mmol), 4-acetamidobenzenesulfonyl azide (8.65 g, 36.0 mmol) and dimethyl malonate (3.4 mL, 30.0 mmol). The crude compound was purified *via* column chromatography using hexane-ethyl acetate (80:20 v/v) as eluent. The desired product (**2.1a**) was obtained as a yellow liquid. Yield: 4.50 g, 95%, 28.5 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 3.81 (s, 6H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 161.5 (C=O), 52.6 (OMe).

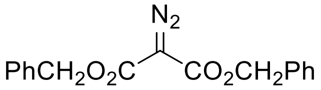
*Synthesis of diisopropyl 2-diazomalonate (**2.1b** or **3.1i**)*



Synthesised in accordance with *General procedure a* using triethylamine (4.40 mL, 31.9 mmol, 2 equiv.), 4-acetamidobenzenesulfonyl azide (4.60 g, 19.1 mmol) and diisopropyl malonate (3.00 mL, 15.9 mmol). The crude compound was purified *via* column chromatography using hexane-ethyl acetate (80:20 v/v) as eluent. The desired product (**2.1b** or **3.1i**) was obtained as a yellow liquid. Yield: 2.96 g, 87%, 13.8 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 5.15 (hept, J = 6.2 Hz, 2H, OCH), 1.29 (d, J = 6.3 Hz, 12H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 160.8 (C=O), 69.5 (OCH), 22.0 (Me); HRMS (ES+) $[M+Na]^+$ $[C_9H_{14}N_2O_4Na]^+$: calculated 237.0851, found 237.0854.

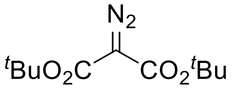
*Synthesis of dibenzyl 2-diazomalonate (**2.1c**)*[152]



Synthesised in accordance with *General procedure a* using triethylamine (2.90 mL, 21.1 mmol, 2 equiv.), 4-acetamidobenzenesulfonyl azide (3.04 g, 12.6 mmol) and dibenzyl malonate (2.60 mL, 10.5 mmol). The crude compound was purified *via* column chromatography using hexane-ethyl acetate (80:20 v/v) as eluent. The desired product (**2.1c**) was obtained as a white solid. Yield: 2.8 g, 85%, 9.02 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.42–7.31 (m, 10H, Ar–H), 5.28 (s, 4H, OCH_2); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 161.0 (C=O), 135.4, 128.8, 128.6, 128.4, 67.2 (OCH_2).

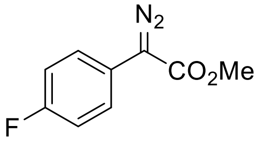
*Synthesis of di-tert-butyl 2-diazomalonate (**2.1d**)*[153]



Synthesised in accordance with *General procedure a* using triethylamine (2.90 mL, 21.1 mmol, 2 equiv.), 4-acetamidobenzenesulfonyl azide (3.04 g, 12.6 mmol) and di-tert-butyl malonate (2.3 mL, 10.5 mmol). The crude compound was purified *via* column chromatography using hexane-ethyl acetate (80:20 v/v) as eluent. The desired product (**2.1d**) was obtained as a colourless oil. Yield: 2.1g, 83%, 8.67 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 1.48 (s, 18H, Me); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 160.4 (C=O), 82.8, (OC), 28.3 (Me).

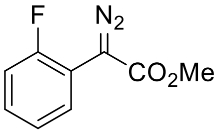
*Synthesis of methyl 2-diazo-2-(4-fluorophenyl)acetate (**3.1a**)*[154]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (4 mL, 26.7 mmol), 4-acetamidobenzenesulfonyl azide (5.14 g, 21.4 mmol), and methyl 2-(4-fluorophenyl)acetate (3.00 g, 17.8 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**3.1a**) was obtained as a yellow solid. Yield: 2.90 g, 84%, 14.9 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.46–7.42 (m, 2H, Ar–H), 7.11–7.07 (m, 2H, Ar–H), 3.86 (s, 3H, OMe); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 165.8 (C=O), 161.2 (d, J_{C-F} = 246.3 Hz), 126.0 (d, J_{C-F} = 8.0 Hz), 121.3 (d, J_{C-F} = 3.2 Hz), 116.1 (d, J_{C-F} = 22.0 Hz), 52.2 (OMe); ^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ: -116.23 (Ar–F).

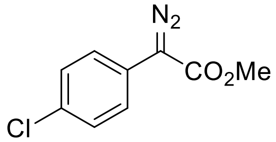
*Synthesis of methyl 2-diazo-2-(2-fluorophenyl)acetate (**3.1b**)*[154]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (2.8 mL, 17.8 mmol), 4-acetamidobenzenesulfonyl azide (4.30 g, 17.8 mmol), and methyl 2-(2-fluorophenyl)acetate (2.00 g, 11.9 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.1b**) was obtained as a yellow solid. Yield: 2.00 g, 87%, 10.4 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.69 (td, J = 7.8, 1.9 Hz, 1H, Ar–H), 7.26–7.21 (m, 1H, Ar–H), 7.20–7.17 (m, 1H, Ar–H), 7.10–7.06 (m, 1H, Ar–H), 3.86 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.8 (C=O), 159.5 (d, $J_{C–F}$ = 247.4 Hz), 129.5, 128.8 (d, $J_{C–F}$ = 8.3 Hz), 124.7 (d, $J_{C–F}$ = 3.5 Hz), 115.9 (d, $J_{C–F}$ = 21.2 Hz), 113.9 (d, $J_{C–F}$ = 11.9 Hz), 52.3 (OMe); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -114.15 (Ar–F).

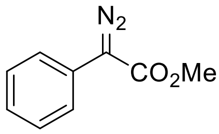
*Synthesis of methyl 2-(4-chlorophenyl)-2-diazoacetate (**2.1e**)*[155]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (2.4 mL, 16.2 mmol), 4-acetamidobenzenesulfonyl azide (3.12 g, 13.0 mmol) and methyl 2-(4-chlorophenyl)acetate (2 g, 10.8 mmol). The crude compound was purified *via* column chromatography using hexane-ethyl acetate (20:1 v/v) as eluent. The desired product (**2.1e**) was obtained as an orange solid. Yield: 2.12 g, 93%, 10.1 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.43–7.40 (m, 2H, Ar–H), 7.36–7.33 (m, 2H, Ar–H), 3.87 (s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 165.4 (C=O), 131.6, 129.2, 125.1, 124.2, 52.2 (OMe).

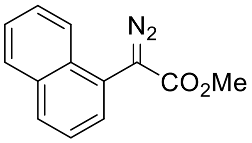
*Synthesis of methyl 2-diazo-2-phenylacetate (**2.1f** or **3.1c**)*[155]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (2.9 mL, 20.0 mmol), 4-acetamidobenzenesulfonyl azide (3.84 g, 16.0 mmol) and methyl 2-phenylacetate (2 g, 13.3 mmol). The crude compound was purified *via* column chromatography using hexane-ethyl acetate (20:1 v/v) as eluent. The desired product (**2.1f** or **3.1c**) was obtained as a yellow solid. Yield: 1.92 g. 82%, 10.9 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.49–7.47 (m, 2H, Ar–H), 7.40–7.37 (m, 1H, Ar–H), 7.21–7.17 (m, 2H, Ar–H), 3.87 (s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 165.7 (C=O), 129.0, 125.9, 125.6, 124.1, 52.1 (OMe).

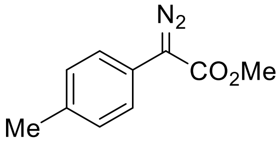
*Synthesis of methyl 2-diazo-2-(naphthalen-1-yl)acetate (**3.1d**)*[156]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (2.2 mL, 14.9 mmol), 4-acetamidobenzenesulfonyl azide (2.88 g, 11.9 mmol), and methyl 2-(naphthalen-1-yl)acetate (2.00 g, 9.9 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.1d**) was obtained as yellow oil. Yield: 1.70 g, 75%, 7.5 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.02 (s, 1H, Ar–H), 7.86 (d, *J* = 8.8 Hz, 1H, Ar–H), 7.80 (d, *J* = 8.8 Hz, 2H, Ar–H), 7.54 (dd, *J* = 8.7, 2.0 Hz, 1H, Ar–H), 7.50–7.43 (m, 2H, Ar–H), 3.91 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.9 (C=O), 133.7, 131.5, 128.8, 127.7 (d, *J* = 3.2 Hz), 126.7, 125.9, 122.7, 122.6, 121.9, 52.2 (OMe).

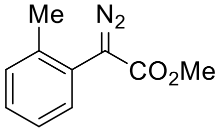
Synthesis of methyl 2-diazo-2-(p-tolyl)acetate (***3.1e***)[154]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (4.1 mL, 27.4 mmol), 4-acetamidobenzenesulfonyl azide (5.27 g, 21.9 mmol), and methyl 2-(*p*-tolyl)acetate (3.00 g, 18.2 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**3.1e**) was obtained as a red oil. Yield: 2.8 g, 81%, 14.7 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.28–7.25 (m, 2H, Ar–H), 7.11–7.09 (m, 2H, Ar–H), 3.75 (s, 3H, OMe), 2.24 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 165.9 (C=O), 135.8, 129.7, 124.2, 122.2, 51.9 (OMe), 21.0 (Me).

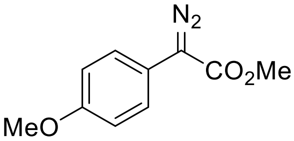
Synthesis of methyl 2-diazo-2-(o-tolyl)acetate (***3.1f***)[154]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (0.8 mL, 5.3 mmol), 4-acetamidobenzenesulfonyl azide (1.3 g, 5.3 mmol), and methyl 2-(*o*-tolyl)acetate (0.60 g, 3.5 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.1f**) was obtained as an orange oil. Yield: 0.32 g, 49 %, 1.7 mmol.

^{1}H NMR (300 MHz, CDCl$_3$, 298 K) δ: 7.41–7.36 (m, 1H, Ar–H), 7.29–7.26 (m, 2H, Ar–H), 7.20–7.16 (m, 1H, Ar–H), 3.83 (s, 3H, OMe), 2.31 (s, 3H, Me); ^{13}C NMR (75 MHz, CDCl$_3$, 298 K) δ: 137.8, 131.0, 130.9, 129.0, 126.57, 124.2, 52.3 (OMe), 20.0 (Me).

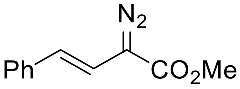
Synthesis of methyl 2-diazo-2-(4-methoxyphenyl)acetate (***3.1g***)[154]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (3.7 mL, 24.9 mmol), 4-acetamidobenzenesulfonyl azide (4.80 g, 19.9 mmol), and methyl 2-(4-methoxyphenyl)acetate (3.00 g, 16.6 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3.1g**) was obtained as a red solid. Yield: 2.9 g, 84%, 14.0 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.39–7.37 (m, 2H, Ar–H), 6.96–6.93 (m, 2H, Ar–H), 3.85 (s, 3H, COOMe), 3.81 (s, 3H, OMe); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 158.2 (C=O), 126.1, 117.0, 114.7, 55.5 (OMe), 52.1 (COOMe).

Synthesis of methyl €-2-diazo-4-phenylbut-3-enoate (***3.1h***)[157]



Synthesised in accordance with *General procedure a* using 1,8-diazabicyclo[5.4.0]undec-7-ene (2.5 mL, 17.0 mmol), 4-acetamidobenzenesulfonyl azide (4.09 g, 17.0 mmol), and methyl €-4-phenylbut-3-enoate

(2.00 g, 11.3 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**3.1h**) was obtained as a red oil. Yield: 1.8 g, 78%, 8.9 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.25–7.17 (m, 4H, Ar–H), 7.10–7.06 (m, 1H, Ar–H), 6.37 (d, J = 16.3 Hz, 1H, CH_2), 6.08 (d, J = 16.3 Hz, 1H, CH_2), 3.72 (s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 165.5 (C=O), 136.8, 128.9, 127.1, 125.8, 123.1, 111.2, 52.3 (OMe).

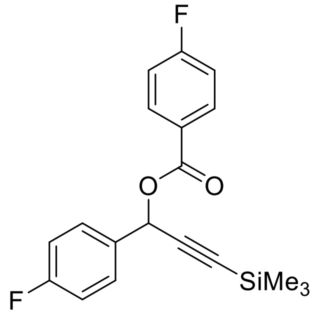
5.2.2.0 General procedure for a synthesis of propargyl, allyl, and diaryl esters

General procedure b: Corresponding alkyne (1.2 equiv) was dissolved in dry tetrahydrofuran (25 mL) and the reaction mixture was cooled to 0 °C. *n*-BuLi (2.5 M in hexanes, 1.2 equiv) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for 1 hr at ambient temperature. The mixture was cooled down to 0 °C and the aldehyde (1 equiv) was added dropwise, allowed the reaction mixture to warm to room temperature and stirred for additional 2 hrs at ambient temperature. 4-Fluorobenzoyl chloride (1.2 equiv) was added to the reaction mixture dropwise at 0 °C. The reaction was stirred at ambient temperature for 15 min. Saturated aqueous NH_4Cl solution was used to quench the reaction. The organic layer was extracted with ethyl acetate (3 × 25 mL). The combined organic fractions were washed with brine solution and dried over $MgSO_4$ and concentrated using vacuum. The crude compound was purified *via* column chromatography using silica gel (Merck, 60 Å, 230 – 400 mesh particle size) and hexane-ethyl acetate as eluent.

General procedure c: Diaryl alcohol (1 equiv) was dissolved in pyridine at 0 °C. Acyl chloride (1.2 equiv) was added to the reaction mixture drop wise at 0 °C The mixture was allowed to stir at ambient temperature overnight. The reaction was quenched with water and extracted with ethyl acetate (3 × 25 ml). The combined organic fractions were washed with saturated brine solution (1 × 25 ml) and dried over $MgSO_4$. All volatiles were removed *in vacuo* and the crude compound was purified *via* column chromatography using silica gel (Merck, 60 Å, 230 – 400 mesh particle size) and hexane-ethyl acetate as eluent.

5.2.2.1 Synthesis and spectral characterisation of propargyl, allyl, and diaryl esters

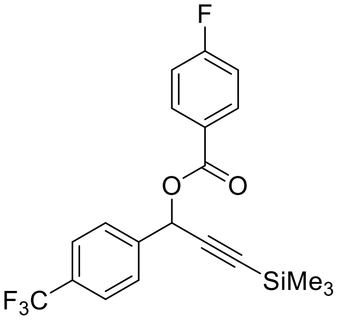
*Synthesis of 1-(4-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-yl 4-fluorobenzoate (**2.2a**)*



Synthesised in accordance with *General procedure b* using trimethylsilylacetylene (2.80 mL, 19.3 mmol), *n*-BuLi (7.70 mL, 19.3 mmol), 4-fluorobenzaldehyde (2.00 g, 16.1 mmol), and 4-fluorobenzoyl chloride (2.30 mL, 19.3 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**2.2a**) was obtained as a yellow oil. Yield: 4.33 g, 78%, 12.6 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.10–8.07 (m, 2H, Ar–H), 7.61–7.58 (m, 2H, Ar–H), 7.13–7.06 (m, 4H, Ar–H), 6.70 (s, 1H, CH), 0.22 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 166.1 (d, $J_{C\text{–}F}$ = 254.5 Hz), 164.4 (C=O), 163.1 (d, $J_{C\text{–}F}$ = 248.2 Hz), 133.0 (d, $J_{C\text{–}F}$ = 3.2 Hz), 132.6 (d, $J_{C\text{–}F}$ = 9.4 Hz), 129.9 (d, $J_{C\text{–}F}$ = 8.5 Hz), 126.0 (d, $J_{C\text{–}F}$ = 3.1 Hz), 115.7 (dd, $J_{C\text{–}F}$ = 21.9, 3.7 Hz), 101.0 (C≡C), 93.2 (C≡C), 65.9 (CH), -0.1 (Si(Me)$_3$); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -104.93 (Ar–F), -112.45 (Ar–F); IR ν_{max} (cm^{-1}): 3076, 2964, 2179 (C≡C), 1724 (C=O), 1602, 1506, 1413, 1367, 1251, 1230, 1101, 1083; HRMS (EI+) $[M]^+$ $[C_{19}H_{18}F_2O_2Si]^+$: calculated 344.1044, found 344.1039.

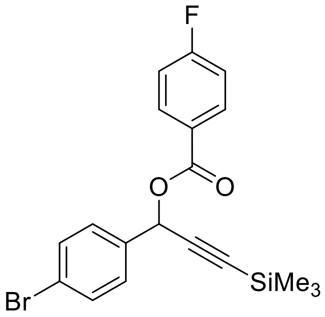
Synthesis of 1-(4-(trifluoromethyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-yl 4-fluorobenzoate ***(2.2b)***



Synthesised in accordance with *General procedure b* using trimethylsilylacetylene (2 mL, 13.8 mmol), *n*-BuLi (5.5 mL, 13.8 mmol), 4-(trifluoromethyl)benzaldehyde (2 g, 11.5 mmol), and 4-fluorobenzoyl chloride (1.6 mL, 13.8 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**2.2b**) was obtained as off–white solid. Yield: 3.40 g, 75%, 8.61 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 8.11–8.08 (m, 2H, Ar–H), 7.73–7.65 (m, 4H, Ar–H), 7.14–7.10 (m, 2H, Ar–H), 6.75 (s, 1H, CH), 0.21 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 166.2 (d, $J_{C–F}$ = 254.9 Hz), 164.3 (C=O), 140.9, 132.7 (d, $J_{C–F}$ = 9.4 Hz), 131.2 (q, $J_{C–F}$ = 32.5 Hz), 128.2, 125.9 (d, $J_{C–F}$ = 3.8 Hz), 125.88, 125.84, 122.6, 115.8 (d, $J_{C–F}$ = 22.1 Hz), 100.3 (C≡C), 93.9 (C≡C), 65.9 (CH), -0.1 (Si(Me)$_3$); ^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ: -62.71 (3F, Ar–CF$_3$), -104.59 (1F, Ar–F); IR ν_{max} (cm^{-1}): 3026, 2986, 2123 (C≡C), 1724 (C=O), 1604, 1506, 1413, 1163, 1045; HRMS (EI+) [M]$^+$ [C$_{20}$H$_{18}$F$_4$O$_2$Si]$^+$: calculated 394.1012, found 394.1008.

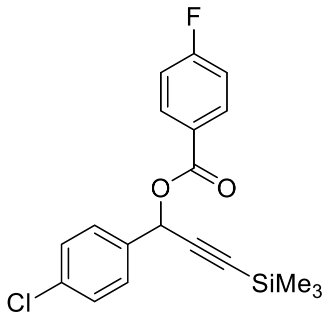
Synthesis of 1-(4-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-yl 4-fluorobenzoate ***(2.2c)***



Synthesised in accordance with *General procedure b* using trimethylsilylacetylene (1.9 mL, 13.0 mmol), *n*-BuLi (5.2 mL, 12.97 mmol), 4-bromobenzaldehyde (2 g, 10.8 mmol), and 4-fluorobenzoyl chloride (1.5 mL, 13.0 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**2.2c**) was obtained as a yellow liquid. Yield: 3.07 g, 70 %, 7.57 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 8.10–8.06 (m, 2H, Ar–H), 7.54–7.47 (m, 4H, Ar–H), 7.13–7.08 (m, 2H, Ar–H), 6.67 (s, 1H, CH), 0.21 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 166.1 (d, $J_{C–F}$ = 254.7 Hz), 164.4 (C=O), 136.1, 132.6 (d, $J_{C–F}$ = 9.4 Hz), 131.9, 129.6, 125.9 (d, $J_{C–F}$ = 3.0 Hz), 123.3, 115.7 (d, $J_{C–F}$ = 22.0 Hz), 100.7 (C≡C), 93.4 (C≡C), 65.9 (CH), -0.1 (Si(Me)$_3$); ^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ: -104.77 (Ar–F); IR ν_{max} (cm^{-1}): 3053, 2960, 2141 (C≡C), 1722 (C=O), 1602, 1506, 1487, 1315, 1290, 1153, 1153, 1058; HRMS (EI+) [M]$^+$ [$C_{19}H_{18}BrFO_2Si$]$^+$: calculated 404.0243, found 404.0238.

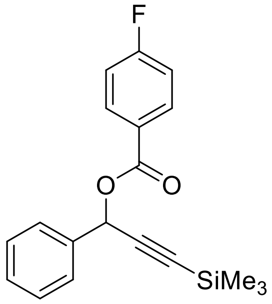
*Synthesis of 1-(4-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-yl 4-fluorobenzoate (**2.2d**)*



Synthesised in accordance with *General procedure b* using trimethylsilylacetylene (2.4 mL, 17.1 mmol), *n*-BuLi (6.8 mL, 17.1 mmol), 4-chlorobenzaldehyde (2 g, 14.2 mmol), and 4-fluorobenzoyl chloride (2 mL, 17.1 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**2.2d**) was obtained as a yellow liquid. Yield: 4.01 g, 78%, 11.1 mmol).

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 8.09–8.07 (m, 2H, Ar–H), 7.55–7.53 (m, 2H, Ar–H), 7.38–7.36 (m, 2H, Ar–H), 7.12–7.09 (m, 2H, Ar–H), 6.68 (s, 1H, CH), 0.21 (s, 9H, Si(Me)$_3$); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 166.1 (d, $J_{C–F}$ = 254.6 Hz), 164.4 (C=O), 135.6, 135.0, 132.6 (d, $J_{C–F}$ = 9.4 Hz), 129.3, 129.0, 125.9 (d, $J_{C–F}$ = 3.0 Hz), 115.7 (d, $J_{C–F}$ = 22.1 Hz), 100.7 (C≡C), 93.4 (C≡C), 65.9 (CH), -0.1 (Si(Me)$_3$); ^{19}F NMR (471 MHz, CDCl$_3$, 298 K) δ: -104.84 (Ar–F); IR ν_{max} (cm^{-1}): 3053, 2960, 2150 (C≡C), 1724 (C=O), 1602, 1506, 1490, 1411, 1315, 1290, 1153, 1043; HRMS (EI+) [M]$^+$ [$C_{19}H_{18}ClFO_2Si$]$^+$: calculated 360.0749, found 360.0743.

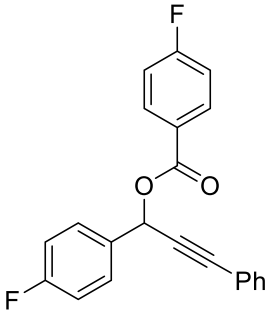
*Synthesis of 1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl 4-fluorobenzoate (**2.2e** or **4.1l**)*



Synthesised in accordance with *General procedure b* using trimethylsilylacetylene (3.2 mL, 22.6 mmol), *n*-BuLi (9.1 mL, 22.8 mmol), benzaldehyde (2 g, 18.8 mmol), and 4-fluorobenzoyl chloride (2.7 mL, 22.6 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**2.2e** or **4.1l**) was obtained as a yellow liquid. Yield: 5.11 g, 83%, 15.6 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.11–8.08 (m, 2H, Ar–H), 7.61–7.59 (m, 2H, Ar–H), 7.42–7.37 (m, 3H, Ar–H), 7.12–7.08 (m, 2H, Ar–H), 6.72 (s, 1H, CH), 0.20 (s, 9H, $Si(Me)_3$); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.0 (d, $J_{C–F}$ = 254.3 Hz), 164.5 (C=O), 137.0, 132.6 (d, $J_{C–F}$ = 9.4 Hz), 129.1, 128.8, 127.9, 126.2 (d, $J_{C–F}$ = 3.0 Hz), 115.6 (d, $J_{C–F}$ = 22.0 Hz), 101.2 (C≡C), 93.0 (C≡C), 66.6 (CH), -0.1 (s, 9H, $Si(Me)_3$); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -105.17 (Ar–F); IR ν_{max} (cm^{-1}): 3062, 2960, 2177 (C≡C), 1720 (C=O), 1602, 1506, 1454, 1411, 1345, 1256, 1125, 1054; HRMS (EI+) $[M]^+$ $[C_{19}H_{19}FO_2Si]^+$: calculated 326.1138, found 326.1133.

*Synthesis of 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl 4-fluorobenzoate (**2.2f**)*

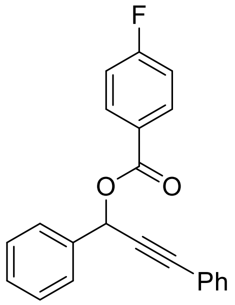


Synthesised in accordance with *General procedure b* using phenylacetylene (2.1 mL, 19.3 mmol), *n*-BuLi (7.8 mL, 19.3 mmol), 4-fluorobenzaldehyde (2 g, 16.1 mmol), and 4-fluorobenzoyl chloride (2.3 mL, 19.3 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**2.2f**) was obtained as a white solid. Yield: 4.55 g, 81%, 13.1 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.13–8.10 (m, 2H, Ar–H), 7.69–7.66 (m, 2H, Ar–H), 7.50 (dt, J = 7.7, 1.5 Hz, 2H, Ar–H), 7.38–7.31 (m, 3H, Ar–H), 7.12 (t, J = 8.7 Hz, 4H, Ar–H), 6.92 (s, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 166.1 (d, $J_{C–F}$ = 254.6 Hz), 164.6

(C=O), 163.1 (d, $J_{C–F}$ = 248.2 Hz), 133.2 (d, $J_{C–F}$ = 3.2 Hz), 132.6 (d, $J_{C–F}$ = 9.4 Hz), 132.0, 129.9 (d, $J_{C–F}$ = 8.5 Hz), 129.1, 128.4, 126.0 (d, $J_{C–F}$ = 3.0 Hz), 122.0, 87.7 (C≡C), 85.3 (C≡C), 66.2 (CH); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -104.85 (Ar–F), -112.34 (Ar–F); IR ν_{max} (cm^{-1}): 3076, 2964, 2179 (C≡C), 1724 (C=O), 1651, 1523, 1454, 1413, 1367, 1251, 1153, 1083; HRMS (EI+) $[M]^+$ $[C_{22}H_{14}F_2O_2]^+$: calculated 348.0962, found 348.0954.

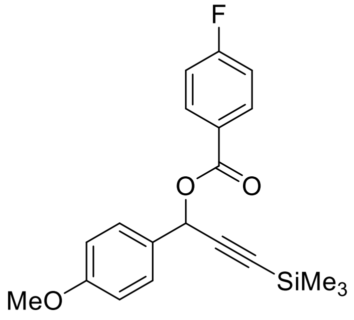
*Synthesis of 1,3-diphenylprop-2-yn-1-yl 4-fluorobenzoate (**2.2g**)*



Synthesised in accordance with *General procedure b* using phenylacetylene (2.5 mL, 22.6 mmol), *n*-BuLi (9.1 mL, 22.6 mmol), benzaldehyde (2 g, 18.8 mmol), and 4-fluorobenzoyl chloride (2.7 mL, 22.6 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**2.2g**) was obtained as a yellow solid. Yield: 4.98 g, 80%, 15.1 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.16–8.11 (m, 2H, Ar–H), 7.69 (dt, J = 6.1, 1.7 Hz, 2H, Ar–H), 7.51 (dt, J = 6.1, 2.2 Hz, 2H, Ar–H), 7.47–7.40 (m, 3H, Ar–H), 7.35–7.30 (m, 3H, Ar–H), 7.12 (td, J = 8.6, 1.6 Hz, 2H, Ar–H), 6.95 (s, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 166.0 (d, $J_{C–F}$ = 254.4 Hz), 164.6 (C=O), 137.2, 132.6 (d, $J_{C–F}$ = 9.4 Hz), 132.0, 129.1, 129.0, 128.8, 128.4, 127.9, 126.2 (d, $J_{C–F}$ = 3.0 Hz), 122.2, 115.7 (d, $J_{C–F}$ = 22.0 Hz), 87.5 (C≡C), 85.6 (C≡C), 66.9 (CH); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -105.03 (Ar–F); IR ν_{max} (cm^{-1}): 3053, 2983, 2156 (C≡C), 1720 (carbonyl C=O stretching), 1602, 1508, 1490, 1442, 1321, 1232, 1153, 1062; HRMS (EI+) $[M]^+$ calculated for $[C_{22}H_{15}FO_2]^+$: calculated 330.1056, found 330.1050.

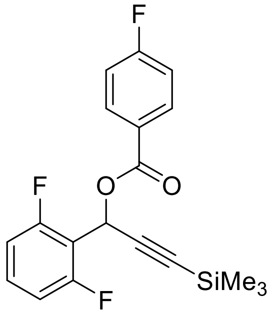
*Synthesis of 1-(4-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-yl 4-fluorobenzoate (**2.2h**)*



Synthesised in accordance with *General procedure b* using trimethylsilylacetylene (2.5 mL, 17.6 mmol), *n*-BuLi (7.0 mL, 17.6 mmol), 4-methoxybenzaldehyde (2 g, 14.7 mmol), and 4-fluorobenzoyl chloride (2.8 mL, 17.6 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**2.2h**) was obtained as a yellow liquid. Yield: 4.0 g, 76%, 11.2 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 8.10–8.06 (m, 2H, Ar–H), 7.56–7.53 (m, 2H, Ar–H), 7.11–7.07 (m, 2H, Ar–H), 6.93–6.91 (m, 2H, Ar–H), 6.69 (s, 1H, CH), 3.82 (s, 3H, OMe), 0.21 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 166.0 (d, $J_{\text{C–F}}$ = 254.2 Hz), 164.5 (C=O), 160.2, 132.6 (d, $J_{\text{C–F}}$ = 9.3 Hz), 129.5, 129.3, 126.3 (d, $J_{\text{C–F}}$ = 3.0 Hz), 115.6 (d, $J_{\text{C–F}}$ = 22.1 Hz), 114.1, 101.5 (C≡C), 92.6 (C≡C), 66.4 (OMe), 55.4 (CH), −0.1 (Si(Me)$_3$); ^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ: -105.31 (Ar–F); IR ν_{max} (cm^{-1}): 3062, 2960, 2177 (C≡C), 1720 (C=O), 1602, 1506, 1454, 1411, 1345, 1256, 1125, 1054; HRMS (ES+) [M]$^+$ [$C_{20}H_{21}O_3FNaSi$]$^+$: calculated 379.1142, found 379.1155.

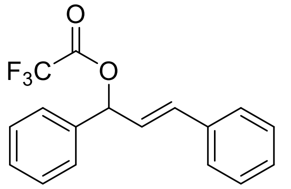
*Synthesis of 1-(2,6-difluorophenyl)-3-phenylprop-2-yn-1-yl 4-fluorobenzoate (**2.2i**)*



Synthesised in accordance with *General procedure b* using trimethylsilylacetylene (2.4 mL, 16.9 mmol), *n*-BuLi (6.8 mL, 16.9 mmol), 2,6-difluorobenzaldehyde (2 g, 14.1 mmol), and 4-fluorobenzoyl chloride (2.7 mL, 16.9 mmol). The crude compound was purified *via* column chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**2.2i**) was obtained as a yellow solid. Yield: 3.6 g, 70%, 9.8 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.10 (dd, *J* = 8.3, 5.6 Hz, 2H, Ar–H), 7.36–7.29 (m, 1H, Ar–H), 7.10 (t, *J* = 8.6 Hz, 2H, Ar–H), 7.01–7.00 (m, 1H, Ar–H), 6.94 (t, *J* = 8.2 Hz, 2H, Ar–H), 0.18 (s, 9H, $Si(Me)_3$); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 166.1 (d, $J_{C–F}$ = 254.5 Hz), 164.1 (C=O), 161.1 (dd, $J_{C–F}$ = 253.8, 6.8 Hz), 132.7 (d, $J_{C–F}$ = 9.5 Hz), 131.0 (t, $J_{C–F}$ = 10.3 Hz), 125.9 (d, $J_{C–F}$ = 3.0 Hz), 115.7 (d, $J_{C–F}$ = 21.9 Hz), 114.1 (t, $J_{C–F}$ = 16.5 Hz), 112.0 (d, $J_{C–F}$ = 25.3 Hz), 99.3 (C≡C), 92.1 (C≡C), 56.9 (CH), −0.2 ($Si(Me)_3$); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -104.91 (1F, Ar–F), -112.30 (2F, Ar–F); IR ν_{max} (cm^{-1}): 3062, 2960, 2177 (C≡C), 1720 (C=O), 1602, 1506, 1454, 1411, 1345, 1256, 1125, 1054; HRMS (ES+) $[M+Na]^+$ $[C_{20}H_{17}O_2F_3NaSi]^+$: calculated 385.0839, found 385.0848.

*Synthesis of (E)-1,3-diphenylallyl 2,2,2-trifluoroacetate (**2.2j** or **4.1k**)*

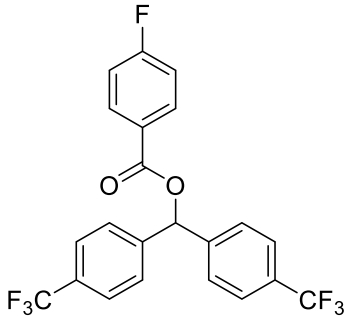


Pyridine (1.4 mL, 14.3 mmol, 1.5 equiv.) was added to a stirred CH_2Cl_2 (25 mL) solution of (*E*)-1,3-diphenylprop-2-en-1-ol (2 g) at 0 °C. The reaction mixture was allowed to stir for 15 min under nitrogen at same temperature. Trifluoroacetic anhydride (2 mL, 14.3 mmol, 1.5 equiv.) was added to the reaction mixture dropwise at 0 °C. The reaction mixture was allowed to stir over night at ambient temperature and quenched the reaction with saturated aq. $NaHCO_3$ solution (1 × 30 mL). The organic compounds were extracted with ethyl acetate (3 × 25 mL), the combined organic fractions were washed with brine solution (1 × 30 mL), dried over $MgSO_4$ and concentrated using vacuum. The crude compound was purified *via* column chromatography using silica gel (Merck, 60 Å, 230–400 mesh particle size) and hexane/ethyl acetate as eluent. The desired compound (**2.2j** or **4.1k**) was obtained as thick liquid which was recrystallized using pentane at −30 °C. White solid was obtained as pure compound. Yield: 2 g, 71%, 6.7 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.46–7.43 (m, 2H, Ar–H), 7.41–7.36 (m, 4H, Ar–H), 7.33–7.29 (m, 3H, Ar–H), 7.26–7.23 (m, 1H, Ar–H), 6.61 (dd, *J* = 15.8, 5.0 Hz, 1H, CH), 6.36

(ddd, $J = 26.2, 15.9, 7.1$ Hz, 1H, CH), 5.11 (dd, $J = 9.6, 7.2$ Hz, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 141.39, 141.31, 136.7 (d, $J_{C–F} = 2.1$ Hz), 131.6 (d, $J_{C–F} = 22.7$ Hz), 130.5 (d, $J_{C–F} = 21.1$ Hz), 128.69, 128.67, 127.87 (d, $J_{C–F} = 1.9$ Hz), 127.82, 127.2, 126.7 (d, $J_{C–F} = 2.3$ Hz), 79.3, 79.2; ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -75.15 (CF_3); IR ν_{max} (cm^{-1}): 3061, 3026, 1651, 1598, 1492, 1448, 1296, 1093, 1068, 1024.

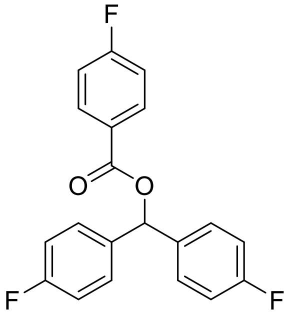
*Synthesis of bis(4-(trifluoromethyl)phenyl)methyl 4-fluorobenzoate (**4.1j**)*



Synthesised in accordance with *General procedure c* using 4-fluorobenzoyl chloride (1.4 mL, 13.1 mmol.), bis(4-(trifluoromethyl)phenyl)methanol (3.5 g, 10.9 mmol), and pyridine (20 mL). The crude compound was purified *via* column chromatography using silica gel and hexane/ethyl acetate (20:1 v/v) as eluent: The desired product (**4.1j**) was obtained as a white solid. Yield: 4.24 g, 88%, 9.6 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.15 (dd, $J = 8.8, 5.4$ Hz, 2H, Ar–H), 7.65 (d, $J = 8.2$ Hz, 4H, Ar–H), 7.54 (d, $J = 8.0$ Hz, 4H, Ar–H), 7.18–7.14 (m, 3H, Ar–H and CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.2 (d, $J_{C–F} = 255.3$ Hz), 164.4 (C=O), 143.2, 132.5 (d, $J_{C–F} = 9.4$ Hz), 130.7 (q, $J_{C–F} = 32.7$ Hz), 127.5, 126.0 (q, $J_{C–F} = 3.7$ Hz), 125.7 (d, $J_{C–F} = 3.0$ Hz), 123.9 (q, $J_{C–F} = 272.3$ Hz), 116.0 (d, $J_{C–F} = 22.0$ Hz), 76.3 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -62.73 (Ar–CF_3), -104.17 (Ar–F); IR ν_{max} (cm^{-1}): 3109, 2978, 1724 (C=O), 1620, 1605, 1508, 1413, 1323, 1259, 1239, 1168, 1154, 1128, 1112, 1089, 1066, 1018; HRMS (ASAP-) [M–H]$^-$ calculated for $[C_{22}H_{12}O_2F_7]^-$: 441.0726, found: 441.0724.

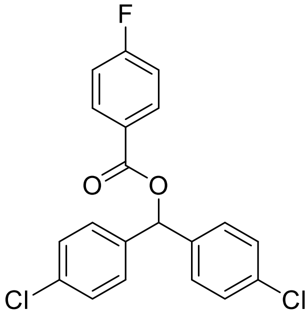
*Synthesis of bis(4-fluorophenyl)methyl 4-fluorobenzoate (**2.2k** or **4.1a**)*



Synthesised in accordance with *General procedure c* using 4-fluorobenzoyl chloride (2.7 mL, 23.2 mmol.), bis(4-fluorophenyl)methanol (4.4 g, 20.0 mmol), and pyridine (25 mL). The crude compound was purified *via* column chromatography using silica gel and hexane/ethyl acetate (20:1 v/v) as eluent: The desired product (**2.2k** or **4.1a**) was obtained as a white solid. Yield: 5.81 g, 85%, 17.0 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.15–8.12 (m, 2H, Ar–H), 7.39–7.36 (m, 4H, Ar–H), 7.16–7.12 (m, 2H, Ar–H), 7.08–7.04 (m, 5H, Ar–H and CH, not able to detect distinct singlet peak for CH); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 166.1 (d, J_{C-F} = 254.7 Hz), 164.8 (C=O), 162.6 (d, J_{C-F} = 247.3 Hz), 135.8 (d, J_{C-F} = 3.3 Hz), 132.4 (d, J_{C-F} = 9.4 Hz), 129.0 (d, J_{C-F} = 8.3 Hz), 126.2 (d, J_{C-F} = 3.0 Hz), 115.8 (d, J_{C-F} = 22.2 Hz), 115.7 (d, J_{C-F} = 21.6 Hz), 76.4 (CH); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -104.80 (1F, Ar–F), -113.67 (2F, Ar–F); IR ν_{max} (cm^{-1}): 3116, 3074, 1724 (C=O), 1602, 1504, 1413, 1340, 1301, 1265, 1186, 1099; HRMS (EI+) $[M]^+$ $[C_{20}H_{13}O_2F_3]^+$: calculated 342.0868, found 342.0871.

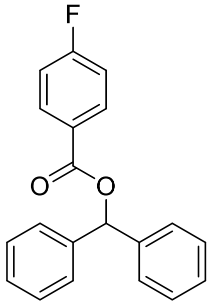
*Synthesis of bis(4-chlorophenyl)methyl 4-fluorobenzoate (**4.1b**)*



Synthesised in accordance with *General procedure c* using 4-fluorobenzoyl chloride (2.7 mL, 23.2 mmol.), bis(4-chlorophenyl)methanol (3 g, 11.8 mmol), and pyridine (20 mL). The crude compound was purified *via* column chromatography using silica gel and hexane/ethyl acetate (20:1 v/v) as eluent: The desired product (**4.1b**) was obtained as a white solid. Yield: 3.5 g, 78%, 9.3 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.12 (dd, J = 8.9, 5.4 Hz, 2H, Ar–H), 7.35–7.31 (m, 8H, Ar–H), 7.16–7.12 (m, 2H, Ar–H), 7.02 (s, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.1 (d, J_{C-F} = 254.9 Hz), 164.5 (C=O), 138.2, 134.3, 132.4 (d, J_{C-F} = 9.4 Hz), 129.0, 128.6, 126.0 (d, $J_{C–F}$ = 3.0 Hz), 115.9 (d, J = 22.0 Hz), 76.3 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -104.64 (Ar–F);); IR ν_{max} (cm^{-1}): 3023, 2994, 1723 (C=O), 1602, 1507, 1492, 1412, 1340, 1302, 1260, 1238, 1153, 1108, 1087, 1014; HRMS (EI+) $[M]^+$ calculated for $[C_{20}H_{13}O_2Cl_2F]^+$: 374.0271, found: 274.0271.

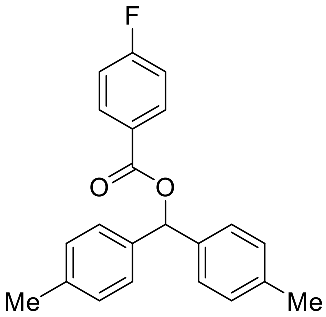
*Synthesis of benzhydryl 4-fluorobenzoate (**2.2l** or **4.1c**)*[158]



Synthesized in accordance with *General procedure c* using 4-fluorobenzoyl chloride (2.7 ml, 23.2 mmol), diphenylmethanol (3.68 g, 20.0 mmol), and pyridine (25 ml). The crude product was purified *via* column chromatography using silica gel and hexane/ethyl acetate (20:1 v/v) as eluent. The desired product (**2.2l** or **4.1c**) was obtained as a white solid. Yield: 5.49 g, 89%, 17.8 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.18–8.15 (m, 2H, Ar–H), 7.44–7.42 (m, 4H, Ar–H), 7.38–7.35 (m, 4H, Ar–H), 7.32–7.30 (m, 2H, Ar–H), 7.15–7.11 (m, 3H, Ar–H and CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.0 (d, $J_{C–F}$ = 254.3 Hz), 164.7 (C=O), 143.9, 140.2, 132.49 (d, $J_{C–F}$ = 9.3 Hz), 128.7, 128.6, 127.7, 127.2, 126.68, 126.61, 126.5, 115.7 (d, $J_{C–F}$ = 22.0 Hz), 77.7 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: −105.19 (Ar–F); IR ν_{max} (cm^{-1}): 3026, 3030, 1716 (C=O), 1598, 1504, 1454, 1411, 1361, 1294, 1184, 1105, 1089, 1014; HRMS (EI+) $[M]^+$ $[C_{20}H_{15}O_2F]^+$: calculated 306.1056, found: 306.1056.

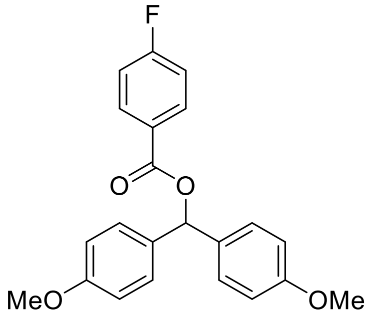
*Synthesis of di-p-tolylmethyl 4-fluorobenzoate (**4.1i**)*



Synthesised in accordance with *General procedure c* using 4-fluorobenzoyl chloride (2.7 mL, 23.2 mmol), di-*p*-tolylmethanol (4.24 g, 20.0 mmol), and pyridine (25 mL). The crude product was purified *via* column chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**4.1i**) was obtained as a colourless oil. Yield: 5.68 g, 85%, 17.0 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 8.04 (ddd, *J* = 8.9, 5.3, 2.5 Hz, 2H, Ar–H), 7.22 (m, 4H, Ar–H), 7.06 (m, 4H, Ar–H), 7.04–6.95 (m, 3H, Ar–H and CH), 2.22 (s, 6H, Me); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 166.0 (d, $J_{C–F}$ = 254.1 Hz), 164.8 (C=O), 137.8, 137.5, 132.4 (d, $J_{C–F}$ = 9.3 Hz), 129.4, 128.4, 128.0, 127.2, 126.8, 125.9, 115.7 (d, $J_{C–F}$ = 22.0 Hz), 77.6 (CH), 21.3 (Me); ^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ: -105.39 (Ar–F); IR ν_{max} (cm^{-1}): 3026, 2965, 2922, 1721 (C=O), 1604, 1506, 1311, 1259, 1237, 1180, 1152, 1102, 1088, 1014.

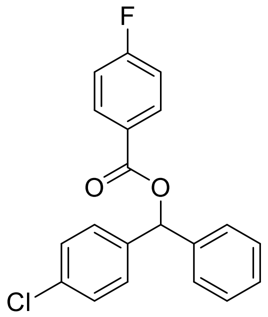
*Synthesis of bis(4-methoxyphenyl)methyl 4-fluorobenzoate (**2.2m** or **4.1d**)*



Synthesised in accordance with *General procedure c* using 4-fluorobenzoyl chloride (2.74 mL, 23.2 mmol), bis(4-methoxyphenyl)methanol (4.86 g, 20.0 mmol), and pyridine (25 ml). The crude product was purified *via* column chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**2.2m** or **4.1d**) was obtained as a colourless oil. Yield: 5.46 g, 76%, 14.9 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 8.13 (ddd, *J* = 8.9, 5.4, 1.4 Hz, 2H, Ar–H), 7.34–7.32 (m, 4H, Ar–H), 7.12 (td, *J* = 8.5, 1.4 Hz, 2H, Ar–H), 7.04 (s, 1H, CH), 6.90–6.87 (m, 4H, Ar–H), 3.80 (s, 6H, OMe); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 165.9 (d, $J_{C–F}$ = 254.0 Hz), 164.8 (C=O), 159.4, 132.6, 132.4 (d, $J_{C–F}$ = 9.3 Hz), 128.6, 126.7 (d, $J_{C–F}$ = 3.0 Hz), 115.6 (d, $J_{C–F}$ = 22.0 Hz), 114.0, 77.1 (CH), 55.4 (OMe); ^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ: -105.46 (Ar–F); IR ν_{max} (cm^{-1}): 3116, 3074, 1724 (C=O), 1002, 1413, 1340, 1301, 1263, 1186, 1099, 1014; HRMS (EI+) [M+Na]$^+$ [$C_{22}H_{19}O_4FNa$]$^+$: calculated 389.1165, found 389.1166.

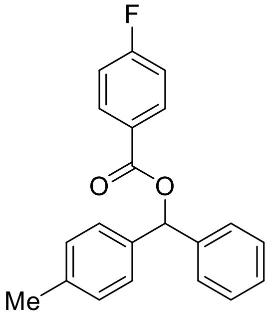
*Synthesis of (4-chlorophenyl)(phenyl)methyl 4-fluorobenzoate (**2.2n** or **4.1e**):*



Synthetised in accordance with *General procedure c* using 4-fluorobenzoyl chloride (2.7 mL, 23.2 mmol), 4-chlorobenzohydrol (4.37 g, 20.0 mmol), and pyridine (25 ml). The crude product was purified *via* column chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**2.2n** or **4.1e**) was obtained as a white solid. Yield 5.59 g, 82%, 16.4 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.17–8.11 (m, 2H, Ar–H), 7.42–7.30 (m, 9H, Ar–H), 7.16–7.11 (m, 2H, Ar–H), 7.07 (s, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.1 (d, $J_{C–F}$ = 254.6 Hz), 164.6 (C=O), 139.7, 138.8, 134.1, 132.4 (d, $J_{C–F}$ = 9.4 Hz), 128.9, 128.8, 128.6, 128.4, 127.2, 126.3 (d, $J_{C–F}$ = 3.0 Hz), 115.8 (d, $J_{C–F}$ = 22.1 Hz), 77.0 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -104.96 (Ar–F); IR ν_{max} (cm^{-1}): 3053, 2970, 1722 (C=O), 1602, 1506, 1490, 1415, 1367, 1263, 1232, 1151, 1105, 1087, 1012; HRMS (EI+) $[M]^+$ $[C_{20}H_{14}ClFO_2]^+$: calculated 340.0666, found 340.0661.

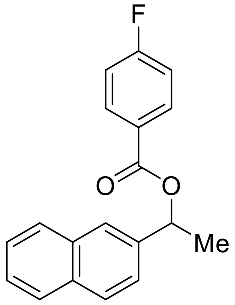
*Synthesis of phenyl(p-tolyl)methyl 4-fluorobenzoate (**2.2o** or **4.1f**)*



Synthetised in accordance with *General procedure c* using 4-fluorobenzoyl chloride (2.7 mL, 23.2 mmol), (4-methylphenyl)(phenyl)methanol (3.97 g, 20 mmol), and pyridine (25 ml). The crude product was purified *via* column chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**2.2o** or **4.1f**) was obtained as a white solid. Yield: 4.99 g. 78%, 15.6 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.18–8.13 (m, 2H, Ar–H), 7.42 (d, J = 7.1 Hz, 2H, Ar–H), 7.36 (t, J = 7.5 Hz, 2H, Ar–H), 7.31 (t, J = 6.8 Hz, 3H, Ar–H), 7.17 (d, J = 7.7 Hz, 2H, Ar–H), 7.13 (t, J = 8.7 Hz, 2H, Ar–H), 7.08 (s, 1H, CH), 2.34 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.0 (d, $J_{C–F}$ = 254.1 Hz), 164.8 (C=O), 140.4, 138.0, 137.3, 132.5 (d, $J_{C–F}$ = 9.3 Hz), 129.4, 128.7, 128.1, 127.3, 127.1, 126.7 (d, $J_{C–F}$ = 3.0 Hz), 115.7 (d, $J_{C–F}$ = 22.0 Hz), 77.7 (CH), 21.3 (Me); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -105.39 (Ar–F); IR ν_{max} (cm^{-1}): 3053, 1718 (C=O), 1602, 1506, 1450, 1411, 1309, 1261, 1236, 1151, 1107, 1087, 1014; HRMS (EI+) $[M]^+$ $[C_{21}H_{17}FO_2]^+$: calculated 320.1213, found 320.1207.

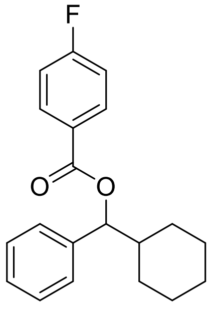
*Synthesis of 1-(naphthalen-2-yl)ethyl 4-fluorobenzoate (**4.1g**)*



Synthesised in accordance with *General procedure c* using 4-fluorobenzoyl chloride (2.3 mL, 20.2 mmol), 1-(naphthalen-2-yl)ethan-1-ol (3.17 g, 18.4 mmol), and pyridine (15 mL). The crude compound was purified *via* column chromatography using silica gel and hexane/ ethyl acetate (9:1 v/v) as eluent. The desired product (**4.1g**) was obtained as a while solid. Yield: 2 g, 37%, 6.8 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.16–8.10 (m, 2H, Ar–H), 7.92–7.81 (m, 4H, Ar–H), 7.58 (dd, *J* = 8.5, 1.8 Hz, 1H, Ar–H), 7.53–7.46 (m, 2H, Ar–H), 7.16–7.09 (m, 2H, Ar–H), 6.30 (q, *J* = 6.6 Hz, 1H, Ar–H), 1.77 (d, *J* = 6.6 Hz, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.9 (d, *J* = 254.5 Hz), 165.0, 139.0, 133.2 (d, *J* = 13.8 Hz), 132.3 (d, *J* = 8.8 Hz), 128.6, 128.1, 127.8, 126.3 (d, *J* = 18.9 Hz), 125.2, 124.1, 115.6 (d, *J* = 22.0 Hz), 73.4 (CH), 22.4 (Me); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -105.69 (Ar–F); HRMS (EI$^+$) $[M^+]$ $[C_{19}H_{15}O_2F]^+$: calculated 294.1056, found: 294.1061.

*Synthesis of cyclohexyl(phenyl)methyl 4-fluorobenzoate (**2.2p** or **4.1h**)*

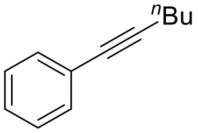


Synthetised in accordance with *General procedure c* using 4-fluorobenzoyl chloride (3.4 mL, 28.9 mmol), cyclohexyl(phenyl)methanol (5 g, 26.3 mmol), and pyridine (18 mL). The crude compound was purified *via* column chromatography using silica gel and hexane/ethyl acetate (95:5 v/v) as eluent. The desired product (**2.2p** or **4.1h**) was obtained as a white solid. Yield: 5.4 g, 66%, 17.4 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.12–8.08 (m, 2H, Ar–H), 7.37–7.32 (m, 4H, Ar–H), 7.29–7.26 (m, 1H, Ar–H), 7.13–7.10 (m, 2H, Ar–H), 5.73 (d, J = 7.5 Hz, 1H, CH), 1.95–1.88 (m, 2H, CH_2), 1.78–1.65 (m, 3H, CH_2), 1.50–1.48 (m, 1H, CH), 1.29–1.12 (m, 4H, CH_2), 1.02 (qd, J = 12.3, 3.8 Hz, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.8 (d, $J_{C–F}$ = 254.5 Hz), 165.0, 139.7, 132.2 (d, $J_{C–F}$ = 10.0 Hz), 128.3, 127.9, 127.1, 126.9 (d, $J_{C–F}$ = 3.0 Hz), 115.6 (d, $J_{C–F}$ = 22.6 Hz), 81.1, 43.3, 29.2, 29.1, 26.4, 26.05, 26.00; ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -105.88 (Ar–F); IR ν_{max} (cm^{-1}): 2939, 2848, 1720 (C=O), 1600, 1504, 1448, 1292, 1253, 1238, 1219, 1153, 1107, 1087, 1053, 1012; HRMS (EI+) $[M]^+$ $[C_{20}H_{21}O_2F]^+$: calculated 312.1526, found 312.1519.

5.2.3.0 Synthesis and spectral characterisation of aryl acetylenes

Synthesis of hex-1-ynylbenzene (**3.2a**)[159]

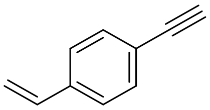


An oven-dried Schlenk flask was charged with iodobenzene (1.6 mL, 14.7 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (516 mg, 0.73 mmol, 5 mol%), and CuI (280 mg, 1.47 mmol, 10 mol%) and placed under a nitrogen atmosphere. Subsequently, NEt_3 (30 mL) and 1-hexyne (2.0 mL, 17.6 mmol, 1.2 equiv) were added into the reaction flask. The reaction mixture was stirred at room temperature until all iodobenzene was consumed. The reaction mixture was then diluted with diethyl ether (*ca.* 50 mL), washed with brine (1 × 30 mL), dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo* and the resulting residue purified *via* flash column chromatography using hexane as eluent. The desired product (**3.2a**) was obtained as yellow liquid. Yield: 1.9 g, 82%, 12.0 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.39 (d, J = 7.9 Hz, 2H, Ar–H), 7.29–7.25 (m, 3H, Ar–H), 2.41 (t, J = 7.1 Hz, 2H), 1.62–1.55 (m, 2H), 1.51–1.44 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 131.6, 128.3, 127.5, 124.1, 90.5 (C≡C), 80.6 (C≡C), 30.9, 22.1, 19.2, 13.8.

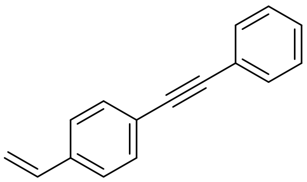
*Synthesis of 1-ethynyl-4-vinylbenzene (**3.2b** or **4.4a**)*[160]



To a solution of trimethyl((4-vinylphenyl)ethynyl)silane (1.5 g, 7.4 mmol, 1.0 equiv) in dry THF (8 mL), 1.0 M THF solution of tetra-*n*-butyl ammonium fluoride (12 mL, 12 mmol, 1.6 equiv) was added dropwise and the reaction was stirred at ambient temperature for 1 hr under nitrogen atmosphere. After completion, the reaction mixture was quenched with water (10 mL), and the organic layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with saturated brine solution (1 × 15 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography using hexane as eluent. The desired product (**3.2b** or **4.4a**) was obtained as a colourless liquid. Yield: 790 mg, 82%, 7.5 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.45 (d, J = 8.3 Hz, 2H, Ar–H), 7.36 (d, J = 8.3 Hz, 2H, Ar–H), 6.70 (dd, J = 17.6, 10.9 Hz, 1H, CH_2), 5.78 (d, J = 17.5 Hz, 1H, CH_2), 5.31 (d, J = 10.9 Hz, 1H, Me), 3.11 (s, 1H, C≡CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 138.1, 136.2, 132.4, 126.2, 121.4, 115.2, 83.7 (C≡C), 77.8 (C≡C).

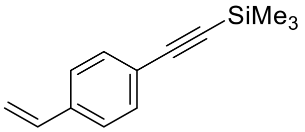
*Synthesis of 1-ethenyl-4-(2-phenylethynyl)benzene (**4.4b**)*[161]



In an oven dried Schlenk flask, 1-bromo-4-vinylbenzene (3 mL, 22.9 mmol, 1 equiv), CuI (436 mg, 2.3 mmol, 10 mol%) and $PdCl_2(PPh_3)_2$ (805 mg, 1.1 mmol, 5 mol%.) were all dissolved in NEt_3 (40 mL) and the resulting solution was stirred for 10 minutes at room temperature under a nitrogen atmosphere. Phenylacetylene (3 mL, 27.5 mmol, 1.2 equiv) was added dropwise to vigorously stirred reaction mixture. The reaction mixture was then heated at 70 °C for next 12 hr and subsequently quenched with water. The organic layer was extracted with diethyl ether (3 × 20 mL) and the combined organic layers were washed with brine solution (1 × 20 mL) and dried over $MgSO_4$. All volatiles were removed *in vacuo* and the crude compound was purified by flash column chromatography using hexane as eluent. The desired product (**4.4b**) was obtained as a white solid. Yield: 2.63 g, 56%, 12.8 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.55–7.53 (m, 2H, Ar–H), 7.51–7.49 (m, 2H, Ar–H), 7.40–7.39 (m, 2H, Ar–H), 7.36–7.34 (m, 3H, Ar–H), 6.72 (dd, J = 17.6, 10.9 Hz, 1H, CH_2), 5.79 (d, J = 17.6 Hz, 1H, CH_2), 5.30 (d, J = 10.9 Hz, 1H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 137.5, 136.4, 131.9, 131.7, 128.5, 128.4, 126.3, 123.4, 122.7, 114.9, 90.2 (C≡C), 89.5 (C≡C).

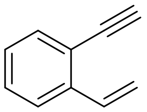
Synthesis of 4-(trimethylsilyl)ethynylstyrene (***4.4c***)[160]



In an oven dried Schlenk flask, 1-bromo-4-vinylbenzene (2 mL, 15.3 mmol, 1 equiv), CuI (291 mg, 1.5 mmol, 10 mol%) and $PdCl_2(PPh_3)_2$ (536 mg, 0.76 mmol, 5 mol%.) were all dissolved in NEt_3 (30 mL) and the resulting solution was stirred for 10 minutes at room temperature under a nitrogen atmosphere. Ethynyltrimethylsilane (2.5 mL, 18.3 mmol, 1.2 equiv) was added dropwise to the vigorously stirred reaction mixture. The reaction mixture was then heated at 60 °C for next 16 hr and subsequently quenched with water. The organic layer was extracted with diethyl ether (3 × 20 mL), and the combined organic layers were washed with brine solution (1 × 20 mL) and dried over $MgSO_4$. All volatiles were removed *in vacuo* and the crude compound was purified by flash column chromatography using hexane as eluent. The desired product (**4.4c**) was obtained as a yellow liquid. Yield: 1.9 g, 62%, 9.4 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.44–7.41 (m, 2H, Ar–H), 7.35–7.32 (m, 2H, Ar–H), 6.69 (dd, J = 17.7, 10.8 Hz, 1H, CH_2), 5.76 (dd, J = 17.6, 0.8 Hz, 1H, CH_2), 5.29 (dd, J = 10.9, 0.8 Hz, 1H, CH_2), 0.26 (s, 9H, $Si(Me)_3$); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 137.7, 136.3, 132.2, 126.1, 122.5, 114.9, 105.2 (C≡C), 94.9 (C≡C), 0.1 ($Si(Me)_3$).

*Synthesis of 1-ethynyl-2-vinylbenzene (**3.2c** or **4.4d**)*[162]



To a solution of trimethyl((2-vinylphenyl)ethynyl)silane (1 g, 5.0 mmol, 1.0 equiv) in MeOH (10 mL), K_2CO_3 (827 mg , 6.0 mmol, 1.2 equiv) was added in one portion and the reaction was stirred at ambient temperature for 30 minutes under nitrogen atmosphere. The reaction mixture was quenched with water (15 mL), and the organic layer was extracted with hexane (3 × 15 mL). The combined organic layers were washed with saturated brine solution (1 × 15 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography using hexane as eluent. The desired product (**3.2c** or **4.4d**) was obtained as a colourless liquid. Yield: 520 mg, 81%, 4.0 mmol,

^1H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.59–7.57 (m, 1H, Ar–H), 7.49–7.48 (m, 1H, Ar–H), 7.33–7.30 (m, 1H, Ar–H), 7.26–7.19 (m, 2H, Ar–H), 5.81 (d, J = 17.6 Hz, 1H, CH_2), 5.36 (d, J = 11.0 Hz, 1H, CH_2), 3.30 (s, 1H, C≡CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 139.8, 134.8, 133.2, 129.0, 127.5, 124.7, 120.9, 115.9, 82.0 (C≡C), 81.8 (C≡C).

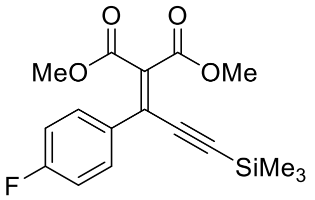
5.3.0.0 Product characterisation

5.3.1.0 General procedure for the $B(C_6F_5)_3$ catalysed alkenylation reactions of aryl esters

General procedure d: Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (10–20 mol%) was dissolved in TFT (0.5 mL) and added to a TFT solution (0.5 mL) of the α-diazoester (1 equiv). The aryl ester (0.2 mmol, 1.1 equiv.) was also dissolved in TFT (0.5 mL) and then added to the reaction mixture dropwise. The reaction tube was sealed in the glove box under nitrogen atmosphere and heated at 65 °C for 18–24 hr. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent.

5.3.1.1 Synthesis and spectral characterisation of alkenylated products

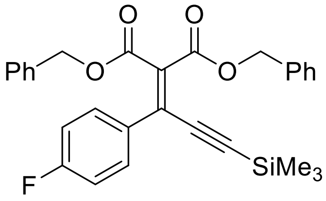
*Synthesis of dimethyl 2-(1-(4-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ylidene)malonate **(2.3a)***



Synthesised in accordance with *General procedure d* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), diazoester **2.1a** (16 mg, 0.10 mmol) and alkynyl aryl ester **2.2a** (38 mg, 0.11 mmol) in TFT to afford **2.3a**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3a**) was obtained as pale-yellow solid. Yield: 27 mg. 81%, 0.08 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.43–7.39 (m, 2H, Ar–H), 7.07–7.02 (m, 2H, Ar–H), 3.85 (s, 3H, OMe), 3.61 (s, 3H, OMe), 0.23 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 165.5 (C=O), 164.1 (C=O), 163.5 (d, $J_{C\text{–}F}$ = 251.4 Hz), 135.7, 132.8 (d, $J_{C\text{–}F}$ = 3.4 Hz), 131.6, 130.2 (d, $J_{C\text{–}F}$ = 8.6 Hz), 115.6 (d, $J_{C\text{–}F}$ = 21.9 Hz), 111.9 (C≡C), 102.0 (C≡C), 52.6 (OMe), -0.3 (Si(Me)$_3$); ^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ: -110.80 (Ar–F); IR ν_{max} (cm^{-1}): 3027, 2954, 2232 (C≡C), 1724 (carbonyl C=O stretching), 1600, 1575, 1508, 1436, 1313, 1301, 1249, 1217, 1161, 1056; HRMS (EI+) [M]$^+$ [$C_{17}H_{19}FO_4Si$]$^+$: calculated 334.1037, found: 334.1031.

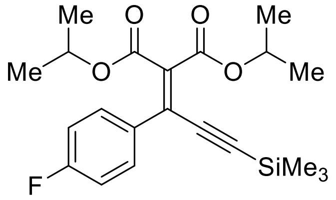
*Synthesis of dibenzyl 2-(1-(4-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ylidene)malonate **(2.3b)***



Synthesised in accordance with *General procedure d* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), diazoester **2.1c** (31 mg, 0.10 mmol) and alkynyl aryl ester **2.2a** (38 mg, 0.11 mmol) in TFT to afford **2.3b**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3b**) was obtained as pale-yellow liquid. Yield: 34 mg, 71%, 0.07 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.16–7.14 (m, 6H, Ar–H), 7.08–7.06 (m, 4H, Ar–H), 6.89–6.86 (m, 2H, Ar–H), 6.72–6.69 (m, 2H, Ar–H), 5.10 (s, 2H, CH_2), 4.83 (s, 2H, CH_2), 0.00 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 164.9 (C=O), 163.5 (d, $J_{C\text{–}F}$ = 251.4 Hz), 163.3 (C=O), 136.0, 135.5, 134.8, 132.8 (d, $J_{C\text{–}F}$ = 3.4 Hz), 131.7, 130.3 (d, $J_{C\text{–}F}$ = 8.6 Hz), 128.6, 128.6, 128.5, 128.5, 128.3, 128.1, 115.5 (d, $J_{C\text{–}F}$ = 22.0 Hz), 112.4 (C≡C), 102.1 (C≡C), 67.4 (CH_2), 67.2 (CH_2), -0.4 (Si(Me)$_3$); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -110.81 (Ar–F); IR ν_{max} (cm^{-1}): 3016, 2933, 2210 (C≡C), 1721 (carbonyl C=O stretching), 1603, 1565, 1525, 1416, 1353, 1310, 1275, 1235, 1155, 1035; HRMS (ES+) [M+Na]$^+$ [$C_{29}H_{27}FO_4SiNa$]$^+$: calculated 509.1560, found: 509.1562.

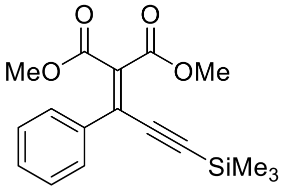
Synthesis of diisopropyl 2-(1-(4-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ylidene)malonate (2.3c)



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1b** (22 mg, 0.10 mmol) and alkynyl aryl ester **2.2a** (38 mg, 0.11 mmol) in TFT to afford **2.3c**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3c**) was obtained as pale-yellow liquid. Yield: 32 mg, 83%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.44–7.40 (m, 2H, Ar–H), 7.04–7.01 (m, 2H, Ar–H), 5.18 (hept, J = 6.3 Hz, 1H), 4.94 (hept, J = 6.3 Hz, 1H), 1.33 (d, J = 6.3 Hz, 6H, Me), 1.08 (d, J = 6.3 Hz, 6H, Me), 0.22 (s, 9H, Si(Me)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.5 (C=O), 163.4 (d, $J_{C\text{–}F}$ = 249.4 Hz), 163.3 (C=O), 134.1, 133.2 (d, $J_{C\text{–}F}$ = 3.3 Hz), 130.3 (d, $J_{C\text{–}F}$ = 8.4 Hz), 115.4 (d, $J_{C\text{–}F}$ = 21.8 Hz), 110.9 (C≡C), 102.2 (C≡C), 69.48 (CH), 69.41 (CH), 21.8 (Me), 21.4 (Me), -0.3 (Si(Me)$_3$); ^{19}F NMR (471 MHz, CDCl$_3$, 298 K) δ: -111.47 (Ar–F); IR ν_{max} (cm^{-1}): 2981, 2897, 2254 (C≡C), 1720 (carbonyl C=O stretching), 1610, 1541, 1456, 1412, 1325, 1247, 1217, 1135, 1051; HRMS (ES+) [M+Na]$^+$ [$C_{21}H_{27}FO_4SiNa$]$^+$: calculated 413.1560, found: 413.1560.

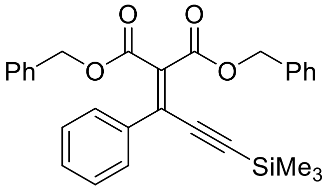
*Synthesis of dimethyl 2-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-ylidene)malonate (**2.3d**)*



Synthesised in accordance with *General procedure d* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), diazoester **2.1a** (16 mg, 0.10 mmol) and alkynyl aryl ester **2.2e** (36 mg, 0.11 mmol) in TFT to afford **2.3d**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3d**) was obtained as pale yellow solid, Yield: 23 mg, 73%, 0.07 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.43–7.41 (m, 2H, Ar–H), 7.38–7.35 (m, 3H, Ar–H), 3.86 (s, 3H, OMe), 3.58 (s, 3H, OMe), 0.23 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 165.7 (C=O), 164.2 (C=O), 136.9, 131.6, 129.7, 128.4, 128.1, 111.8 (C≡C), 102.1 (C≡C), 52.6 (OMe), 52.5 (OMe), -0.3 (Si(Me)$_3$); IR ν_{max} (cm^{-1}): 3010, 2958, 2254 (C≡C), 1732 (carbonyl C=O stretching), 1651, 1558, 1516, 1433, 1410, 1372, 1321, 1247, 1150, 1052; HRMS (ES+) [M+Na]$^+$ [$C_{17}H_{20}O_4SiNa$]$^+$: calculated 339.1029, found: 339.1032.

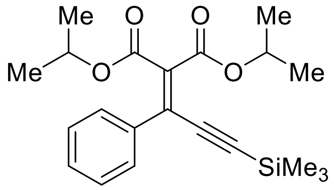
*Synthesis of dibenzyl 2-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-ylidene)malonate (**2.3e**)*



Synthesised in accordance with *General procedure d* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), diazoester **2.1c** (31 mg, 0.10 mmol) and alkynyl aryl ester **2.2e** (36 mg, 0.11 mmol) in TFT to afford **2.3e**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3e**) was obtained as pale yellow solid. Yield: 32 mg, 68%, 0.07 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.22–7.12 (m, 7H, Ar–H), 7.10–7.01 (m, 6H, Ar–H), 6.83–6.81 (m, 2H, Ar–H), 5.10 (s, 2H, CH$_2$), 4.80 (s, 2H, CH$_2$), 0.00 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 165.1 (C=O), 163.4 (C=O), 137.2, 137.0, 135.6, 134.9, 131.6, 129.7, 128.6, 128.5, 128.46, 128.45, 128.35, 128.32, 128.2, 128.1, 112.3 (C≡C), 102.3 (C≡C), 67.4 (CH$_2$), 67.2 (CH$_2$), -0.3 (Si(Me)$_3$); IR ν_{max} (cm^{-1}): 2981, 2925, 2254 (C≡C), 1740 (carbonyl C=O stretching), 1651, 1532, 1512, 1492, 1456, 1417, 1355, 1249, 1201, 1162, 1048; HRMS (ES+) [M+Na]$^+$ [$C_{29}H_{28}O_4SiNa$]$^+$: calculated 491.1655, found: 491.1660.

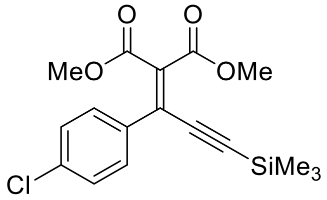
*Synthesis of diisopropyl 2-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-ylidene)malonate (**2.3f**)*



Synthesised in accordance with *General procedure d* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), diazoester **2.1b** (22 mg, 0.10 mmol) and alkynyl aryl ester **2.2e** (36 mg, 0.11 mmol) in TFT to afford **2.3f**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3f**) was obtained as pale colorless liquid. Yield: 28 mg, 75%, 0.07 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.44–7.41 (m, 2H, Ar–H), 7.34 (dt, J = 3.7, 1.4 Hz, 3H, Ar–H), 5.19 (hept, J = 6.5 Hz, 1H), 4.92 (hept, J = 6.5 Hz, 1H), 1.33 (d, J = 6.3 Hz, 6H, Me), 1.04 (d, J = 6.3 Hz, 6H, Me), 0.22 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 164.7 (C=O), 163.4 (C=O), 137.3, 135.2, 133.2, 129.3, 128.3, 110.7 (C≡C), 102.3 (C≡C), 69.3 (CH), 69.2 (CH), 21.8 (Me), 21.3 (Me), -0.2 (Si(Me)$_3$; IR ν_{max} (cm^{-1}): 3030, 2981, 2250 (C≡C), 1714 (carbonyl C=O stretching), 1651, 1541, 1512, 1492, 1391, 1303, 1246, 1180, 1145, 1049; HRMS (ES+) [M+Na]$^+$ [$C_{21}H_{28}O_4SiNa$]$^+$: calculated 395.1655, found: 395.1667.

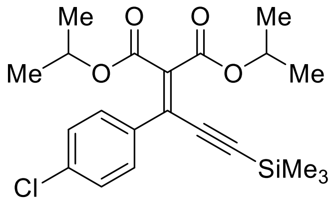
*Synthesis of dimethyl 2-(1-(4-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ylidene)malonate **(2.3g)***



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1a** (16 mg, 0.10 mmol) and alkynyl aryl ester **2.2d** (40 mg, 0.11 mmol) in TFT to afford **2.3g** The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3g**) was obtained as pale yellow solid. Yield: 28 mg, 80%, 0.08 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.37 – 7.31 (m, 4H, Ar–H), 3.85 (s, 3H, OMe), 3.61 (s, 3H, OMe), 0.2 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 165.3 (C=O), 164.1 (C=O), 135.8, 135.6, 135.3, 131.9, 129.5, 128.7, 112.1 (C≡C), 101.81 (C≡C), 52.7 (OMe), 52.6 (OMe), -0.3 (Si(Me)$_3$); IR ν_{max} (cm^{-1}): 3033, 2915, 2215 (C≡C), 1722(carbonyl C=O stretching), 1640, 1530, 1525, 1465, 1409, 1376, 1314, 1255, 1221, 1162, 1039; HRMS (EI+) $[M]^+$ $[C_{17}H_{19}O_4ClSi]^+$: calculated 350.0741, found: 350.0738.

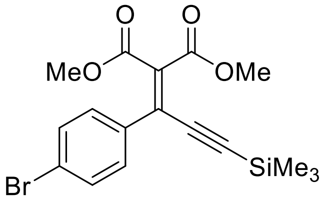
*Synthesis of diisopropyl 2-(1-(4-chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ylidene)malonate **(2.3h)***



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1b** (22 mg, 0.10 mmol) and alkynyl aryl ester **2.2d** (40 mg, 0.11 mmol) in TFT to afford **2.3h**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3h**) was obtained as pale yellow solid. Yield: 34 mg, 83%, 0.07 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.38–7.35 (m, 2H, Ar–H), 7.33–7.30 (m, 2H, Ar–H), 5.18 (hept, *J* = 6.4 Hz, 1H), 4.94 (hept, *J* = 6.4 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 6H, Me), 1.09 (d, *J* = 6.3 Hz, 6H, Me), 0.21 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 164.3 (C=O), 163.2 (C=O), 135.6, 135.5, 134.0, 133.4, 129.7, 128.5, 111.0 (C≡C), 101.9 (C≡C), 69.54 (CH) 69.50 (CH), 21.8 (Me), 21.4 (Me), -0.3 (Si(Me)$_3$); IR ν$_{max}$ (cm^{-1}): 3010, 2915, 2230 (C≡C), 1720 (carbonyl C=O stretching), 1643, 1560, 1526, 1461, 1423, 1350, 1322, 1241, 1221, 1152, 1065; HRMS (ES+) [M+Na]$^+$ [$C_{21}H_{27}ClO_4SiNa$]$^+$: calculated 429.1265, found: 429.1265.

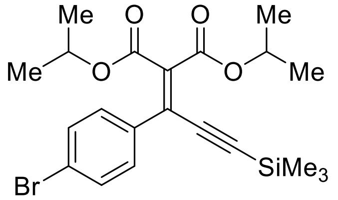
*Synthesis of dimethyl 2-(1-(4-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ylidene)malonate **(2.3i)***



Synthesised in accordance with *General procedure d* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), diazoester **2.1a** (16 mg, 0.10 mmol) and alkynyl aryl ester **2.2c** (45 mg, 0.11 mmol) in TFT to afford **2.3i**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3i**) was obtained as pale yellow solid. Yield: 34 mg, 87%, 0.08 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.53–7.50 (m, 2H, Ar–H), 7.33–7.28 (m, 2H, Ar–H), 3.88 (s, 3H, OMe), 3.64 (s, 3H, OMe), 0.25 (s, 9H, Si(Me)$_3$); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 165.3 (C=O), 164.1 (C=O), 135.79, 135.70, 131.9, 131.7, 129.8, 124.1, 112.2, 101.7, 52.73 (Me), 52.70 (Me), -0.3 (Si(Me)$_3$); IR ν$_{max}$ (cm^{-1}): 3025, 2920, 2210 (C≡C), 1725 (carbonyl C=O stretching), 1650, 1545, 1512, 1478, 1412, 1382, 1325, 1245, 1201, 1182, 1047; HRMS (ES+) [M+Na]$^+$ [$C_{17}H_{19}BrO_4SiNa$]$^+$: calculated 417.0134, found: 417.0139.

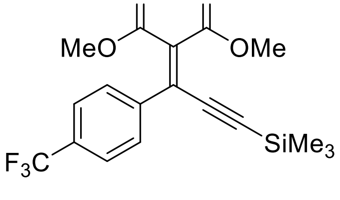
*Synthesis of diisopropyl 2-(1-(4-bromophenyl)-3-(trimethylsilyl)prop-2-yn-1-ylidene)malonate (**2.3j**)*



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1b** (22 mg, 0.10 mmol) and alkynyl aryl ester **2.2c** (45 mg, 0.11 mmol) in TFT to afford **2.3j**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3j**) was obtained as pale yellow solid. Yield: 36 mg, 80%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.49–7.46 (m, 2H, Ar–H), 7.31–7.28 (m, 2H, Ar–H), 5.18 (hept, *J* = 6.3 Hz, 1H), 4.94 (hept, *J* = 6.3 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 6H, Me), 1.09 (d, *J* = 6.3 Hz, 6H, Me), 0.21 (s, 9H, $Si(Me)_3$); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 164.3 (C=O), 163.2 (C=O), 136.1, 134.0, 133.4, 131.5, 129.9, 123.7, 111.1 (C≡C), 101.9 (C≡C), 69.55 (CH), 69.51 (CH), 21.8 (Me), 21.4 (Me), -0.3 ($Si(Me)_3$); IR ν_{max} (cm^{-1}): 3030, 2970, 2252 (C≡C), 1722 (carbonyl C=O stretching), 1620, 1558, 1539, 1487, 1456, 1375, 1296, 1217, 1105, 1049; HRMS (ES+) $[M+Na]^+$ $[C_{21}H_{27}O_4BrSiNa]^+$: calculated 473.0760, found: 473.0759.

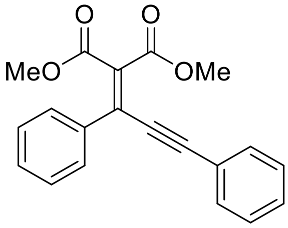
*Synthesis of dimethyl 2-(1-(4-(trifluoromethyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ylidene) malonate (**2.3k**)*



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1a** (16 mg, 0.10 mmol) and alkynyl aryl ester **2.2b** (43 mg, 0.11 mmol) in TFT to afford **2.3k**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound **2.3k** was obtained as pale-yellow liquid. Yield: 25 mg, 65%; 0.06 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.63–7.61 (m, 2H, Ar–H), 7.53–7.51 (m, 2H, Ar–H), 3.87 (s, 3H, OMe), 3.60 (s, 3H, OMe), 0.23 (s, 9H, Si(Me)$_3$); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 164.9 (C=O), 164.0 (C=O), 140.3, 135.4, 132.8, 129.0, 128.5, 125.4 (q, $J_{C\text{–}F}$ = 3.7 Hz), 112.7 (C≡C), 101.4 (C≡C), 52.8 (Me), 52.7 (Me), -0.3 (Si(Me)$_3$); ^{19}F NMR (471 MHz, CDCl$_3$, 298 K) δ: -62.83. (Ar–CF$_3$); IR ν_{max} (cm^{-1}): 3025, 2920, 2215 (C≡C), 1725 (carbonyl C=O stretching), 1650, 1545, 1512, 1478, 1412, 1382, 1325, 1245, 1201, 1182, 1047; HRMS (ES+) [M+Na]$^+$ [C$_{18}$H$_{19}$F$_3$O$_4$SiNa]$^+$: calculated 407.0902, found: 407.0901.

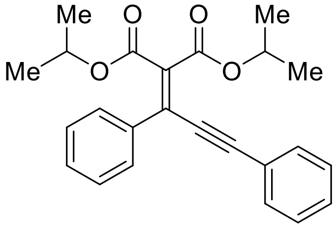
*Synthesis of dimethyl 2-(1,3-diphenylprop-2-yn-1-ylidene)malonate (**2.3l**)*



Synthesised in accordance with *General procedure d* using B(C$_6$F$_5$)$_3$ (5 mg, 0.01 mmol), diazoester **2.1a** (16 mg, 0.10 mmol) and alkynyl aryl ester **2.2h** (36 mg, 0.11 mmol) in TFT to afford **2.3l**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3l**) was obtained as pale yellow solid. Yield: 20 mg, 63%, 0.07 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.54–7.50 (m, 4H, Ar–H), 7.41–7.35 (m, 6H, Ar–H), 3.89 (s, 3H, OMe), 3.60 (s, 3H, OMe); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 166.1 (C=O), 164.1 (C=O), 137.7, 137.3, 132.3, 130.4, 129.8, 129.7, 128.59, 128.57, 128.0, 122.3, 105.0 (C≡C), 88.1 (C≡C), 52.65 (Me), 52.61 (Me); IR ν_{max} (cm^{-1}):3014, 2970, 2252 (C≡C), 1734 (carbonyl C=O stretching), 1633, 1558, 1489, 1435, 1365, 1234, 1205, 1095, 1043; HRMS (EI+) [M]$^+$ [C$_{20}$H$_{16}$O$_4$]$^+$: calculated 320.1049, found: 320.1040.

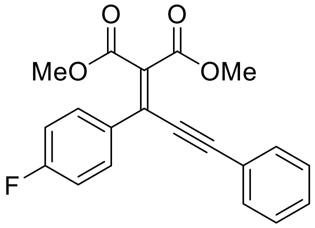
*Synthesis of diisopropyl 2-(1,3-diphenylprop-2-yn-1-ylidene)malonate (**2.3m**)*



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1b** (22 mg, 0.10 mmol) and alkynyl aryl ester **2.2h** (36 mg, 0.11 mmol) in TFT to afford **2.3m**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3m**) was obtained as pale yellow solid, Yield: 25 mg, 67%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.52–7.49 (m, 4H, Ar–H), 7.39–7.32 (m, 6H, Ar–H), 5.22 (hept, *J* = 6.4 Hz, 1H, CH), 4.95 (hept, *J* = 6.4 Hz, 1H, CH), 1.34 (d, *J* = 6.3 Hz, 6H, Me), 1.08 (d, *J* = 6.3 Hz, 6H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 165.0 (C=O), 163.3 (C=O), 137.6, 136.0, 132.2, 132.1, 129.5, 129.4, 128.5, 128.4, 128.2, 122.5, 103.9 (C≡C), 88.2 (C≡C), 69.28 (CH), 69.25 (CH), 21.9 (Me), 21.4 (Me); IR ν_{max} (cm^{-1}): 2981, 2920, 2200 (C≡C), 1720 (carbonyl C=O stretching), 1651, 1558, 1512, 1490, 1412, 1396, 1247, 1211, 1178, 1037; HRMS (ES+) [M+Na]$^+$ $[C_{24}H_{24}O_4Na]^+$: calculated 399.1572, found: 399.1581.

*Synthesis of dimethyl 2-(1-(4-fluorophenyl)-3-phenylprop-2-yn-1-ylidene)malonate (**2.3n**)*

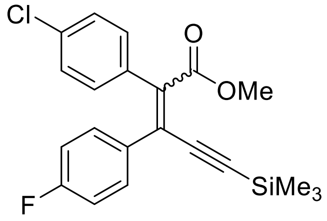


Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1a** (16 mg, 0.10 mmol) and alkynyl aryl ester **2.2i** (38 mg, 0.11 mmol) in TFT to afford **2.3n** The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane-ethyl acetate (90:10 v/v) as eluent. The desired compound (**2.3n**) was obtained as pale yellow solid. Yield: 24 mg, 70%, 0.07 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.53–7.48 (m, 4H, Ar–H), 7.39–7.33 (m, 3H, Ar–H), 7.10–7.05 (m, 2H, Ar–H), 3.89 (s, 3H, OMe), 3.63 (s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 165.8 (C=O), 164.1 (C=O), 163.6 (d, $J_{C\text{–}F}$ = 251.4 Hz), 136.3, 133.4 (d, $J_{C\text{–}F}$ = 3.5

Hz), 132.3, 130.8, 130.2 (d, J_{C-F} = 8.5 Hz), 129.9, 128.6, 122.4, 115.6 (d, J_{C-F} = 22.0 Hz), 104.9 (C≡C), 88.1 (C≡C), 52.57 (Me), 52.53 (Me); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -110.96 (Ar–F); IR ν_{max} (cm^{-1}): 3051, 2945, 2198 (C≡C), 1734 (carbonyl C=O stretching), 1637, 1598, 1541, 1506, 1489, 1408, 1375, 1332, 1278, 1203, 1190, 1089; HRMS (EI+) $[M]^+$ $[C_{20}H_{15}FO_4]^+$: calculated 338.0954, found: 338.0949.

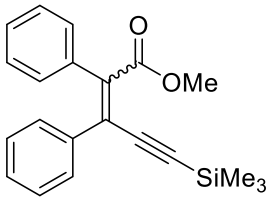
*Synthesis of methyl 2-(4-chlorophenyl)-3-(4-fluorophenyl)-5-(trimethylsilyl)pent-2-en-4-ynoate (**2.3o**)*



Synthetised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1e** (21 mg, 0.10 mmol), and alkynyl aryl ester **2.2a** (38 mg, 0.11 mmol) in TFT to afford **2.3o**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (92:8 v/v) as eluent. The desired compound (**2.3o**) was obtained as a mixture of isomers (1:0.4) which appeared as a yellow liquid. Yield: 18 mg, 46%, 0.46 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.62–7.59 (m, Ar–H), 7.46–7.42 (m, Ar–H), 7.37–7.34 (m, Ar–H), 7.19–7.16 (m, Ar–H), 7.08–7.01 (m, Ar–H), 6.91–6.86 (m, Ar–H), 3.85 (s, Me, minor isomer), 3.56 (s, 3H, Me, major isomer), 0.24 (s, $Si(Me)_3$, minor isomer), 0.12 (s, 9H, $Si(Me)_3$, major isomer); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 169.1 (C=O), 168.5 (C=O), 163.0 (d, J_{C-F} = 239.4 Hz), 162.5 (d, J_{C-F} = 252 Hz), 139.6, 139.4, 134.7, 134.4, 134.39, 134.38, 134.35, 133.4, 132.49, 132.46, 131.6 (d, J_{C-F} = 8.3 Hz), 131.0, 130.4, 129.9 (d, J_{C-F} = 8.3 Hz), 128.8, 128.4, 126.5, 126.3, 115.5 (d, J_{C-F} = 25.2 Hz), 115.4 (d, J_{C-F} = 25.2 Hz), 105.4, 104.3, 103.6, 103.5, 52.6 (OMe), 52.4 (OMe), -0.1 ($Si(Me)_3$, minor isomer), -0.4 ($Si(Me)_3$ major isomer); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -112.38 (Ar–F, minor isomer), -112.54 (Ar–F, major isomer); IR ν_{max} (cm^{-1}): 3053, 2954, 1742 (C=O), 1720 (C=O), 1598, 1504, 1431, 1319, 1263, 1215, 1157, 1089, 1068, 1012; HRMS (ES+) $[M+H]^+$ $[C_{21}H_{21}O_2FSiCl]^+$: calculated 387.0983, found 387.0985.

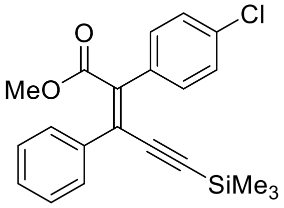
*Synthesis of methyl 2,3-diphenyl-5-(trimethylsilyl)pent-2-en-4-ynoate (**2.3p**)*



Synthetised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1f** (18 mg, 0.10 mmol), and alkynyl aryl ester **2.2e** (36 mg, 0.11 mmol) in TFT to afford **2.3p**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (92:8 v/v) as eluent. The desired compound (**2.3p**) was obtained as a mixture of isomers (1:0.4) which appeared as a yellow liquid. Yield: 12 mg, 36%, 0.12 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.67–7.64 (m, Ar–H), 7.48–7.44 (m, Ar–H), 7.40–7.33 (m, Ar–H), 7.21–7.16 (m, Ar–H), 7.11–7.08 (m, Ar–H), 7.07–7.03 (m, Ar–H), 6.88–6.83 (m, Ar–H), 3.86 (s, OMe, minor isomer), 3.57 (s, 3H, OMe, major isomer), 0.24 (s, $Si(Me)_3$, minor isomer), 0.10 (s, 9H, $Si(Me)_3$, major isomer); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 169.5 (C=O), 168.9 (C=O), 163.8, 163.4, 161.8, 161.4, 141.0, 140.9, 135.9, 134.9, 134.6, 131.66, 131.60, 129.5, 129.4, 129.0, 128.9, 128.5, 128.4, 128.9, 125.56, 125.50, 115.5, 115.2, 115.1, 104.4, 103.8, 103.7, 103.3, 52.5 (OMe, minor isomer), 52.3 (OMe, major isomer), -0.1 ($Si(CH_3)_3$, minor isomer)$_3$), -0.4 ($Si(Me)_3$, major isomer); IR ν_{max} (cm^{-1}): 3055, 2956, 1759 (C=O), 1720 (C=O), 1600, 1504, 1433, 1263, 1217, 1157, 1070, 1035, 1018.

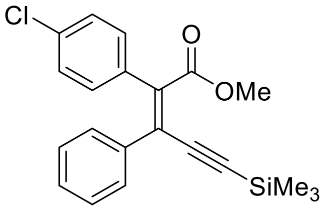
*Synthesis of methyl (E)-2-(4-chlorophenyl)-3-phenyl-5-(trimethylsilyl)pent-2-en-4-ynoate (**2.3q**)*



Synthetised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1e** (21 mg, 0.10 mmol), and alkynyl aryl ester **2.2e** (36 mg, 0.11 mmol) in TFT to afford **2.3q** as major isomer. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (92:8 v/v) as eluent. The desired compound (**2.3q**) (major isomer) was obtained as a yellow liquid. Yield: 11 mg, 30%, 0.30 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.64–7.61 (m, 2H, Ar–H), 7.47–7.44 (m, 2H, Ar–H), 7.39–7.33 (m, 5H, Ar–H), 3.53 (s, 3H, OMe), 0.12 (s, 9H, $Si(Me)_3$); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 169.3, 139.5, 138.3, 134.6, 134.5, 130.5, 128.7, 128.5, 128.3, 128.0, 127.4, 105.1, 103.6, 52.3 (OMe), -0.4 $Si(Me)_3$; IR ν_{max} (cm^{-1}): 2933, 2848, 1718 (C=O), 1656, 1492, 1444, 1433, 1323, 1263, 1249, 1213, 1091, 1068, 1029, 1012; HRMS (ES+) $[M+H]^+$ $[C_{21}H_{22}O_2SiCl]^+$: calculated 369.1078, found 369.1075.

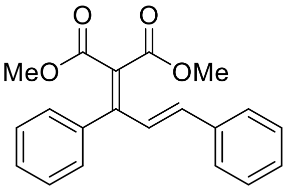
*Synthesis of methyl (Z)-2-(4-chlorophenyl)-3-phenyl-5-(trimethylsilyl)pent-2-en-4-ynoate **(2.3q')***



Synthetised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1e** (21 mg, 0.10 mmol), and alkynyl aryl ester **2.2e** (36 mg, 0.11 mmol) in TFT to afford **2.3q'** as minor isomer. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (92:8 v/v) as eluent. The desired compound (**2.3q'**) (minor isomer) was obtained as a yellow liquid. Yield: 5 mg, 13%, 0.13 mmol. Isomeric ratio: 1:0.4.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.22–7.18 (m, 5H, Ar–H), 7.16–7.13 (m, 2H, Ar–H), 7.03–7.00 (m, 2H, Ar–H), 3.86 (s, 3H, OMe), 0.23 (s, 9H, $Si(Me)_3$); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 168.7 (C=O), 139.4, 136.5, 134.3, 133.6, 131.0, 129.7, 128.6, 128.4, 128.3, 127.5, 104.0, 103.8, 52.6 (OMe), -0.1 ($Si(Me)_3$); IR ν_{max} (cm^{-1}): 2954, 2899, 1720 (C=O), 1489, 1433, 1263, 1249, 1209, 1091; HRMS (ES+) $[M+H]^+$ $[C_{21}H_{22}O_2SiCl]^+$: calculated 369.1078, found 369.1078.

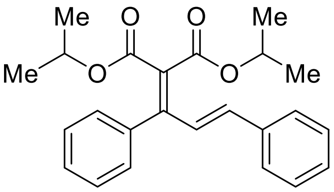
*Synthesis of dimethyl (E)-2-(1,3-diphenylallylidene)malonate (**2.3r**)*



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1a** (16 mg, 0.10 mmol), and alkene ester **2.2j** (34 mg, 0.11 mmol) in TFT to afford **2.3r**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (90:10 v/v) as eluent. The desired compound (**2.3r**) was obtained as a colorless oil. Yield: 23 mg, 71%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.14 (d, *J* = 15.9 Hz, 1H, CH), 7.44–7.39 (m, 5H, Ar–H), 7.33–7.29 (m, 4H, Ar–H), 7.25–7.24 (m, 1H, Ar–H), 6.45 (d, *J* = 15.9 Hz, 1H, CH), 3.87 (s, 3H, Me), 3.44 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.8 (C=O), 164.9 (C=O), 154.6, 142.8, 136.9, 136.2, 129.5, 128.9, 128.8, 128.6, 128.2, 127.8, 126.7, 124.0, 52.4 (Me), 52.1 (Me); IR ν_{max} (cm^{-1}): 3331, 2927, 1704 (C=O), 1604, 1558, 1485, 1394, 1342, 1263, 1232, 1184, 1101; HRMS (ES+) $[M+Na]^+$ $[C_{20}H_{18}O_4Na]^+$: calculated 345.1103, found 345.1107.

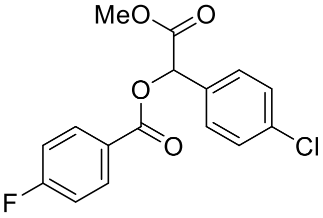
*Synthesis of diisopropyl (E)-2-(1,3-diphenylallylidene)malonate (**2.3s**)*



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), diazoester **2.1b** (21 mg, 0.10 mmol), and alkene ester **2.2j** (34 mg, 0.11 mmol) in TFT to afford **2.3s**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (90:10 v/v) as eluent. The desired compound (**2.3s**) was obtained as a colorless oil. Yield: 29 mg, 77%, 0.08 mmol.

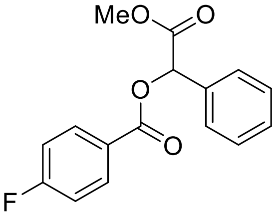
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.15 (d, *J* = 16.0 Hz, 1H, CH), 7.42–7.37 (m, 5H, Ar–H), 7.33–7.26 (m, 5H, Ar–H), 6.40 (d, *J* = 16.0 Hz, 1H, CH), 5.20 (hept, *J* = 6.3 Hz, 1H, CH), 4.80 (hept, *J* = 6.3 Hz, 1H, CH), 1.34 (d, *J* = 6.3 Hz, 6H, Me), 0.98 (d, *J* = 6.3 Hz, 6H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.7 (C=O), 164.1 (C=O), 152.9, 141.8, 137.0, 136.4, 129.28, 129.24, 128.8, 128.4, 128.1, 127.7, 127.0, 125.7, 69.0 (OCH), 68.5 (OCH), 21.9 (Me), 21.3 (Me); IR ν_{max} (cm^{-1}): 2981, 1703 (C=O), 1610, 1573, 1467, 1386, 1323, 1228, 1105, 1051; HRMS (ES+) [M+Na]$^+$ [$C_{24}H_{26}O_4Na$]$^+$: calculated 401.1729, found 401.1730.

*Synthesis of 1-(4-chlorophenyl)-2-methoxy-2-oxoethyl 4-fluorobenzoate (**2.4a**)*[163]



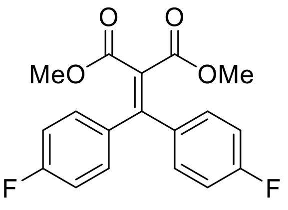
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.15–8.11 (m, 2H, Ar–H), 7.52–7.49 (m, 2H, Ar–H), 7.42–7.39 (m, 2H, Ar–H), 7.16–7.11 (m, 2H, Ar–H), 6.12 (s, 1H, CH), 3.76 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 169.0 (C=O), 166.3 (d, $J_{C–F}$ = 255.1 Hz), 164.9 (C=O), 135.6, 132.7 (d, $J_{C–F}$ = 9.5 Hz), 132.5, 129.3, 129.1, 125.4 (d, $J_{C–F}$ = 3.0 Hz), 115.9 (d, $J_{C–F}$ = 22.1 Hz), 74.3 (CH), 53.0 (OMe); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -104.28 (Ar–F).

*Synthesis of 2-methoxy-2-oxo-1-phenylethyl 4-fluorobenzoate (**2.4b**)*[163]



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.17–8.13 (m, 2H, Ar–H), 7.59–7.55 (m, 2H, Ar–H), 7.46–7.40 (m, 3H, Ar–H), 7.16–7.11 (m, 2H, Ar–H), 6.15 (s, 1H, CH), 3.76 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 169.4 (C=O), 166.3 (d, $J_{C–F}$ = 254.8 Hz), 165.0 (C=O), 134.0, 132.7 (d, $J_{C–F}$ = 9.5 Hz), 129.5, 129.0, 127.8, 125.6 (d, $J_{C–F}$ = 3.0 Hz), 115.8 (d, $J_{C–F}$ = 22.1 Hz), 75.1 (CH), 52.9 (OMe); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -104.58 (Ar–F).

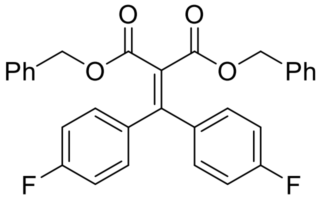
*Synthesis of dimethyl 2-(bis(4-fluorophenyl)methylene)malonate (**2.6a**)*[164]



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (10 mg, 0.02 mmol), diazoester **2.1a** (16 mg, 0.10 mmol), and diaryl ester **2.2k** (35 mg, 0.11 mmol) in TFT to afford **2.6a**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (87:13 v/v) as eluent. The desired compound (**2.6a)** was obtained as a pale-yellow solid. Yield: 26 mg, 78%, 0.08 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.17–7.13 (m, 4H, Ar–H), 7.05–7.01 (m, 4H, Ar–H), 3.63 (s, 6H, OMe); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 166.3 (C=O), 163.6 (d, $J_{C–F}$ = 250.5 Hz), 154.4, 135.8 (d, $J_{C–F}$ = 3.5 Hz), 131.3 (d, $J_{C–F}$ = 8.5 Hz), 125.7, 115.6 (d, $J_{C–F}$ = 21.9 Hz), 52.5 (OMe); ^{19}F NMR (471 MHz, CDCl$_3$, 298 K) δ: -110.81 (Ar–F).

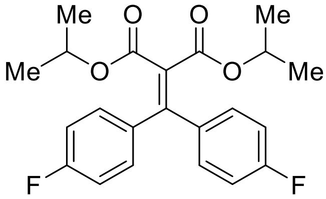
*Synthesis of dibenzyl 2-(bis(4-fluorophenyl)methylene)malonate (**2.6b**)*



Synthesised in accordance with *General procedure d* using B(C$_6$F$_5$)$_3$ (10 mg, 0.02 mmol), diazoester **2.1c** (31 mg, 0.10 mmol), and diaryl ester **2.2k** (35 mg, 0.11 mmol) in TFT to afford **2.6b**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (85:15 v/v) as eluent. The desired compound (**2.6b**) was obtained as a colorless oil. Yield: 39 mg, 81%, 0.08 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.34–7.27 (m, 6H, Ar–H), 7.13–7.11 (m, 4H, Ar–H), 7.07–7.03 (m, 4H, Ar–H), 6.90–6.85 (m, 4H, Ar–H), 5.07 (s, 4H, OCH$_2$); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 165.6 (C=O), 163.6 (d, $J_{C–F}$ = 250.5 Hz), 154.5, 135.7 (d, $J_{C–F}$ = 3.3 Hz), 135.1, 131.3 (d, $J_{C–F}$ = 8.5 Hz), 128.7, 128.6, 128.5, 115.5 (d, $J_{C–F}$ = 21.8 Hz), 67.3 (OCH$_2$); ^{19}F NMR (471 MHz, CDCl$_3$, 298 K) δ: -110.84 (Ar–F); IR ν_{max} (cm^{-1}): 3066, 3035, 1718 (C=O), 1600, 1504, 1454, 1408, 1375, 1319, 1259, 1220, 1157, 1066. HRMS (ES+) [M+Na]$^+$ [C$_{30}$H$_{22}$F$_2$ O$_4$Na]$^+$: calculated 507.1384, found 507.1385.

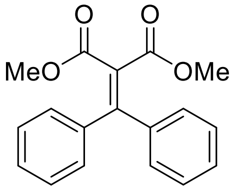
*Synthesis of diisopropyl 2-(bis(4-fluorophenyl)methylene) malonate (**2.6c**)*



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (10 mg, 0.02 mmol), diazoester **2.1b** (22 mg, 0.10 mmol), and diaryl ester **2.2k** (35 mg, 0.11 mmol) in TFT to afford **2.6c**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (87:13 v/v) as eluent. The desired compound (**2.6c**) was obtained as a while solid. Yield: 34 mg, 87%, 0.09 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.19–7.15 (m, 4H, Ar–H), 7.04–6.99 (m, 4H, Ar–H), 4.97 (hept, *J* = 6.3 Hz, 2H, OCH), 1.12 (d, *J* = 6.3 Hz, 12H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.3 (C=O), 163.4 (d, $J_{C\text{–}F}$ = 249.9 Hz), 152.5, 136.0 (d, $J_{C\text{–}F}$ = 3.3 Hz), 131.3 (d, $J_{C\text{–}F}$ = 8.4 Hz), 127.7, 115.5 (d, $J_{C\text{–}F}$ = 21.8 Hz), 69.2 (OCH), 21.5 (Me); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -111.51 (Ar–F); IR ν_{max} (cm^{-1}): 2983, 2937, 1720 (C=O), 1600, 1506, 1373, 1315, 1226, 1161, 1105, 1070; HRMS (ES+) $[M+Na]^+$ $[C_{22}H_{22}F_2O_4Na]^+$: calculated 411.1384, found 411.1385.

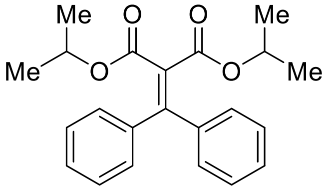
*Synthesis of dimethyl 2-(diphenylmethylene) malonate (**2.6d**)*[164]



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (10 mg, 0.02 mmol), diazoester **2.1a** (16 mg, 0.10 mmol), and diaryl ester **2.2l** (31 mg, 0.11 mmol) in TFT to afford **2.6d**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (87:13 v/v) as eluent. The desired compound (**2.6d**) was obtained as a pale-yellow oil. Yield: 21 mg, 73%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.38–7.31 (m, 6H, Ar–H), 7.19–7.17 (m, 4H, Ar–H), 3.61 (s, 6H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.5 (C=O), 156.7, 140.0, 129.5, 129.2, 128.3, 125.6, 52.4 (OMe).

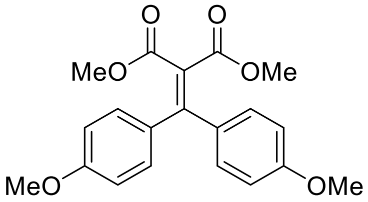
*Synthesis of diisopropyl 2-(diphenylmethylene) malonate (**2.6e**)*[164]



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (10 mg, 0.02 mmol), diazoester **2.1b** (22 mg, 0.10 mmol), and diaryl ester **2.2l** (31 mg, 0.11 mmol) in TFT to afford **2.6e**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (87:13 v/v) as eluent. The desired compound (**2.6e**) was obtained as a white solid. Yield: 27 mg, 76%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.36–7.29 (m, 6H, Ar–H), 7.21–7.19 (m, 4H, Ar–H), 4.94 (hept, J = 6.3 Hz, 2H, OCH), 1.08 (d, J = 6.3 Hz, 12H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.6 (C=O), 154.8, 140.3, 129.2, 129.1, 128.2, 127.4, 69.0 (OCH), 21.4 (Me).

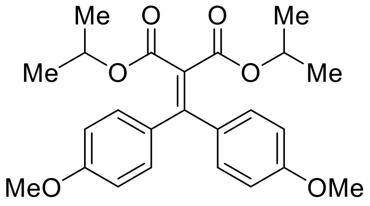
*Synthesis of dimethyl 2-(bis(4-methoxyphenyl)methylene) malonate (**2.6f**)*[164]



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (10 mg, 0.02 mmol), diazoester **2.1a** (16 mg, 0.10 mmol), and diaryl ester **2.2m** (37 mg, 0.11 mmol) in TFT to afford **2.6f**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (70:30 v/v) as eluent. The desired compound (**2.6f**)was obtained as a white solid. Yield: 25 mg, 70%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.12–7.09 (m, 4H, Ar–H), 6.86–6.83 (m, 4H, Ar–H), 3.82 (s, 6H, COOMe), 3.62 (s, 6H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 167.2 (C=O), 160.9 (C=O), 156.8, 132.6, 131.3, 123.0, 113.7, 55.4 (COOMe), 52.3 (OMe).

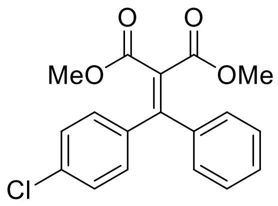
*Synthesis of diisopropyl 2-(bis(4-methoxyphenyl)methylene) malonate (**2.6g**)*



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (10 mg, 0.02 mmol), diazoester **2.1b** (22 mg, 0.10 mmol), and diaryl ester **2.2m** (37 mg, 0.11 mmol) in TFT to afford **2.6g**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (75:25 v/v) as eluent. The desired compound (**2.6g**) was obtained as a white solid. Yield: 32 mg, 78%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.13–7.11 (m, 4H, Ar–H), 6.84–6.81 (m, 4H, Ar–H), 4.97 (hept, *J* = 6.3 Hz, 2H, OCH), 3.81 (s, 6H, Ome), 1.13 (d, *J* = 6.3 Hz, 12H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.2 (C=O), 160.6 (C=O), 154.9, 132.9, 131.3, 125.1, 113.6, 68.7(OCH), 55.4 (Ome), 21.6 (Me); IR ν_{max} (cm^{-1}): 2981, 2935, 1705 (C=O), 1602, 1508, 1463, 1246, 1166, 1107, 1074, 1031; HRMS (ES+) $[M+Na]^+$ $[C_{24}H_{28}O_6Na]^+$: calculated 435. 1784, found 435.1785.

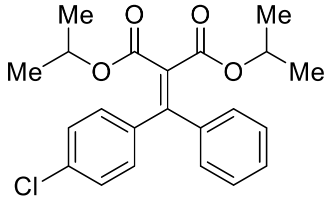
*Synthesis of dimethyl 2-((4-chlorophenyl)(phenyl)methylene) malonate (**2.6h**)*[164]



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (10 mg, 0.02 mmol), diazoester **2.1°** (16 mg, 0.10 mmol), and diaryl ester **2.2n** (34 mg, 0.11 mmol) in TFT to afford **2.6h**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (85:15 v/v) as eluent. The desired compound (**2.6h**) was obtained as a colourless oil. Yield: 25 mg, 75%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.40–7.29 (m, 5H, Ar–H), 7.17–7.15 (m, 2H, Ar–H), 7.13–7.10 (m, 2H, Ar–H), 3.64 (s, 3H, Ome), 3.60 (s, 3H, Ome); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.3 (C=O), 166.2 (C=O), 155.3, 139.6, 138.4, 135.7, 130.6, 129.7, 129.2, 128.7, 128.5, 125.9, 52.5 (Ome), 52.4 (Ome).

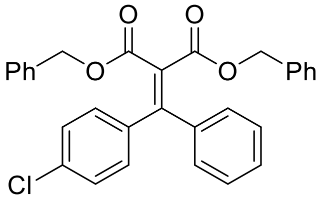
*Synthesis of diisopropyl 2-((4-chlorophenyl)(phenyl)methylene) malonate (**2.6i**)*



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (10 mg, 0.02 mmol), diazoester **2.1b** (22 mg, 0.10 mmol), and diaryl ester **2.2n** (34 mg, 0.11 mmol) in TFT to afford **2.6i**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (87:13 v/v) as eluent. The desired compound (**2.6i**) was obtained as a white solid. Yield: 32 mg, 84%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.37–7.28 (m, 5H, Ar–H), 7.19–7.16 (m, 2H, Ar–H), 7.15–7.12 (m, 2H, Ar–H), 5.01–4.90 (m, 2H, OCH), 1.12 (d, J = 6.3 Hz, 6H, Me), 1.08 (d, J = 6.3 Hz, 6H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.4 (C=O), 165.2 (C=O), 153.5, 139.8, 138.6, 135.3, 130.6, 129.4, 129.2, 128.5, 128.4, 127.8, 69.2 (OCH), 69.1 (OCH), 21.5 (Me), 21.4 (Me); IR ν_{max} (cm^{-1}): 2980, 2935, 1718 (C=O), 1598, 1506, 1487, 1448, 1371, 1355, 1315, 1236, 1166, 1105, 1070, 1014; HRMS (ES+) [M+Na]$^+$ $[C_{22}H_{23}ClO_4Na]^+$: calculated 409.1183, found 409.1184.

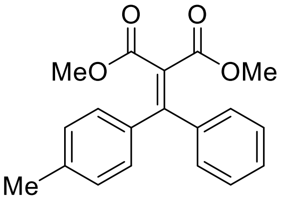
*Synthesis of dibenzyl 2-((4-chlorophenyl)(phenyl)methylene)malonate (**2.6j**)*



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (10 mg, 0.02 mmol), diazoester **2.1c** (31 mg, 0.10 mmol), and diaryl ester **2.2n** (34 mg, 0.11 mmol) in TFT to afford **2.6j**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (87:13 v/v) as eluent. The desired compound (**2.6j**) was obtained as a colourless oil. Yield: 36 mg, 75%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.30–7.18 (m, 9H, Ar–H), 7.12–7.09 (m, 2H, Ar–H), 7.07–7.04 (m, 4H, Ar–H), 7.02–7.00 (m, 2H, Ar–H), 6.98–6.96 (m, 2H, Ar–H), 5.02 (s, 2H, OCH_2), 4.99 (s, 2H, OCH_2); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 165.7 (C=O), 165.6 (C=O), 155.4, 139.6, 138.4, 135.6, 135.1, 135.0, 130.6, 129.7, 129.3, 128.7, 128.59, 128.57, 128.53, 128.50, 128.4, 128.3, 67.35 (OCH_2), 67.34 (OCH_2); IR ν_{max} (cm^{-1}): 3034, 1718 (C=O), 1591, 1489, 1452, 1375, 1323, 1261, 1224, 1161, 1066, 1014; HRMS (ES+) $[M+Na]^+$ $[C_{30}H_{23}ClO_4Na]^+$: calculated 505.1183, found 505.1183.

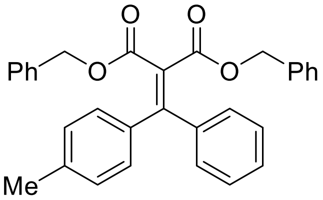
*Synthesis of dimethyl 2-(phenyl(p-tolyl)methylene) malonate (**2.6k**)*[164]



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (10 mg, 0.02 mmol), diazoester **2.1°** (16 mg, 0.10 mmol), and diaryl ester **2.2°** (32 mg, 0.11 mmol) in TFT to afford **2.6k**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (87:13 v/v) as eluent. The desired compound (**2.6k**) was obtained as a colourless liquid. Yield: 22 mg, 72%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.38–7.31 (m, 3H, Ar–H), 7.19–7.16 (m, 2H, Ar–H), 7.14–7.12 (m, 2H, Ar–H), 7.07–7.05 (m, 2H, Ar–H), 3.64 (s, 3H, Ome), 3.59 (s, 3H, Ome), 2.36 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 166.7 (C=O), 166.6 (C=O), 140.3, 139.8, 137.1, 129.4, 129.3, 129.2, 129.1, 128.3, 125.0, 52.4 (Ome), 52.3 (Ome), 21.5 (Me).

*Synthesis of dibenzyl 2-(phenyl(p-tolyl)methylene)malonate (**2.6l**)*



Synthesised in accordance with *General procedure d* using $B(C_6F_5)_3$ (10 mg, 0.02 mmol), diazoester **2.1c** (31 mg, 0.10 mmol), and diaryl ester **2.2°** (32 mg, 0.11 mmol) in TFT to afford **2.6l**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/diethyl ether (87:13 v/v) as eluent. The desired compound (**2.6l**) was obtained as a colorless oil. Yield: 31 mg, 67%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.29–7.18 (m, 9H, Ar–H), 7.10–7.08 (m, 2H, Ar–H), 7.03–6.95 (m, 8H, Ar–H), 5.02 (s, 2H, OCH_2), 4.98 (s, 2H, OCH_2), 2.28 (s, 3H, Me); ^{13}C NMR

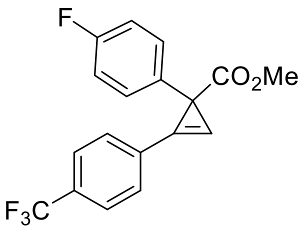
(126 MHz, $CDCl_3$, 298 K) δ: 166.1 (C=O), 166.0 (C=O), 157.1, 140.3, 139.7, 137.2, 135.3, 135.2, 129.4, 129.0, 128.5, 128.47, 128.46, 128.43, 128.3, 128.24, 128.23, 125.1, 67.16 (OCH_2), 67.14 (OCH_2), 21.5 (Me); IR ν_{max} (cm^{-1}): 2976, 2872, 1718 (C=O), 1450, 1379, 1325, 1303, 1259, 1224, 1159, 1109, 1070; HRMS (ES+) $[M+Na]^+$ $[C_{31}H_{26}O_4Na]^+$: calculated 485.1729, found 485.1729.

5.3.2.0 General procedure for the $B(C_6F_5)_3$ catalysed cyclopropenation reactions

General procedure e: In the glove box under nitrogen atmosphere, tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] (10 mol%), arylacetylene (1 equiv) and α-aryl α-diazoester **3.1** (1.3 equiv) were all dissolved separately in 1,2-DCE (0.5 mL). Subsequently, the $B(C_6F_5)_3$ and arylacetylene solutions were combined and stirred for 30 seconds before α-aryl α-diazoester solution was added dropwise into the reaction mixture. The reaction tube was sealed and heated outside at 50 °C for 18–24 hr. Afterwards, all volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent. Note: Some of the carbocycles were found to be unstable at room temperature and decomposed quickly.

5.3.2.1 Synthesis and spectral characterization of cyclopropenated products

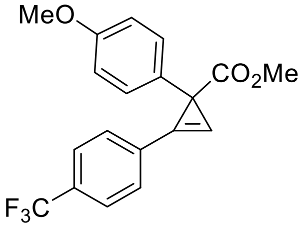
*Synthesis of methyl 1-(4-fluorophenyl)-2-(4-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (**3.3a**)*



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1a** (25 mg, 0.13 mmol), and 1-ethynyl-4-(trifluoromethyl)benzene (17 mg, 0.1 mmol) in 1,2-DCE to afford **3.3a**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3a**) was obtained as a yellow oil. Yield: 10 mg, 30%, 0.03 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.72–7.68 (m, 4H, Ar–H), 7.37 (s, 1H, C=CH), 7.33 (dd, *J* = 8.8, 5.3 Hz, 2H, Ar–H), 6.98 (t, *J* = 8.7 Hz, 2H, Ar–H), 3.72 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 174.5 (C=O), 161.8 (d, $J_{C–F}$ = 245.6 Hz), 136.0 (d, $J_{C–F}$ = 3.2 Hz), 132.0, 131.7, 130.1, 129.8 (d, $J_{C–F}$ = 8.0 Hz), 128.7, 126.1 (q, $J_{C–F}$ = 3.7 Hz), 124.9, 122.7, 116.7, 115.2 (d, $J_{C–F}$ = 21.4 Hz), 103.3, 52.6 (OMe), 33.2 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -62.93 (s, 3F, Ar–CF_3), -115.76 (s, 1F, Ar–F); IR ν_{max} (cm^{-1}): 3056, 2957, 2923, 1718 (C=O), 1509, 1324, 1265, 1224, 1168, 1128, 1065, 1017. HRMS could not be obtained.

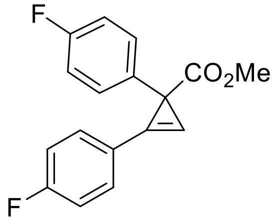
*Synthesis of methyl 1-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (**3.3b**)*



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1g** (26 mg, 0.13 mmol), and 1-ethynyl-4-(trifluoromethyl)benzene (17 mg, 0.1 mmol) in 1,2-DCE to afford **3.3b**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3.3b**) was obtained as a yellow oil. Yield: 13 mg, 37%, 0.03 mmol

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.70 (q, *J* = 8.2 Hz, 4H, Ar–H), 7.38 (s, 1H, C=CH), 7.29–7.27 (m, 2H, Ar–H), 6.84 (d, *J* = 8.8 Hz, 2H, Ar–H), 3.78 (s, 3H, OMe), 3.72 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 174.9 (C=O), 158.5, 132.5, 131.8, 131.5, 130.1, 129.3, 129.1, 126.0 (q, $J_{C–F}$ = 3.8 Hz), 124.9, 122.8, 117.0, 113.8, 103.8, 55.4 (COOMe), 52.5 (OMe), 31.3 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -62.89 (Ar–F); IR ν_{max} (cm^{-1}): 3058, 2954, 2841, 1718 (C=O), 1607, 1513, 1323, 1248, 1166, 1124, 1064; HRMS (ES+) $[M+H]^+$ calculated for $[C_{19}H_{16}O_3F_3]^+$: 349.1052; found 349.1050.

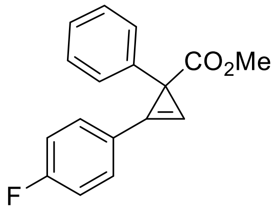
Synthesis of methyl 1,2-bis(4-fluorophenyl)cycloprop-2-ene-1-carboxylate (***3.3c***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1a** (25 mg, 0.13 mmol), and 1-ethynyl-4-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3c**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.3c**) was obtained as a yellow oil. Yield: 24 mg, 84%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.61–7.57 (m, 2H, Ar–H), 7.35–7.31 (m, 2H, Ar–H), 7.16 (s, 1H, C=CH), 7.13 (t, J = 8.7 Hz, 2H, Ar–H), 6.97 (t, J = 8.8 Hz, 2H, Ar–H), 3.71 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 174.8 (C=O), 163.8 (d, $J_{C–F}$ = 251.8 Hz), 161.7 (d, $J_{C–F}$ = 245.3 Hz), 136.5 (d, $J_{C–F}$ = 3.3 Hz), 132.0 (d, $J_{C–F}$ = 8.6 Hz), 129.8 (d, $J_{C–F}$ = 8.1 Hz), 121.6 (d, $J_{C–F}$ = 3.4 Hz), 116.6, 116.4 (d, $J_{C–F}$ = 22.3 Hz), 115.1 (d, $J_{C–F}$ = 21.4 Hz), 99.72 (d, J = 2.7 Hz), 52.4 (OMe), 33.0 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -108.87 (s, 1F, Ar–F), -116.13 (s, 1F, Ar–F); IR ν_{max} (cm^{-1}): 2953, 1716 (C=O), 1600, 1508, 1224, 1157, 1097, 1014; HRMS (ES+) $[M+H]^+$ calculated for $[C_{17}H_{13}O_2F_2]^+$: 287.0884, found: 287.0880.

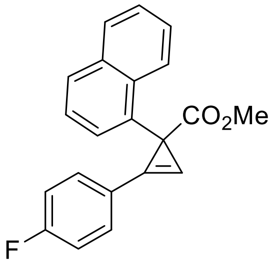
Synthesis of methyl 2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxylate (***3.3d***)[122]



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1c** (23 mg, 0.13 mmol), and 1-ethynyl-4-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3d**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.3d**) was obtained as a yellow oil. Yield: 21 mg, 78%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.60 (dd, *J* = 8.8, 5.4 Hz, 2H, Ar–H), 7.37–7.35 (m, 2H, Ar–H), 7.31–7.28 (m, 2H, Ar–H), 7.23–7.20 (m, 1H, Ar–H), 7.18 (s, 1H, C=CH), 7.14–7.09 (m, 2H, Ar–H), 3.72 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.0 (C=O), 163.7 (d, $J_{C–F}$ = 251.5 Hz), 140.7, 132.0 (d, $J_{C–F}$ = 8.7 Hz), 128.28, 128.25, 126.7, 121.8 (d, $J_{C–F}$ = 3.4 Hz), 116.6, 116.3 (d, $J_{C–F}$ = 22.2 Hz), 99.8 (d, $J_{C–F}$ = 2.7 Hz), 52.4 (OMe), 33.7 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -109.17 (Ar–F).

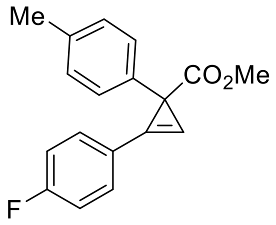
Synthesis of methyl 2-(4-fluorophenyl)-1-(naphthalen-1-yl)cycloprop-2-ene-1-carboxylate (***3.3e***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1d** (29 mg, 0.13 mmol), and 1-ethynyl-4-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3e**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3e**) was obtained as a white solid. Yield: 20 mg, 63%, 0.06 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.13 (d, *J* = 8.9 Hz, 1H, Ar–H), 7.87 (d, *J* = 8.1 Hz, 1H, Ar–H), 7.77 (d, *J* = 8.3 Hz, 1H, Ar–H), 7.73 (dd, *J* = 8.8, 5.4 Hz, 2H, Ar–H), 7.57–7.54 (m, 1H, Ar–H), 7.52–7.49 (m, 1H, Ar–H), 7.47 (s, 1H, C=CH), 7.43 (dd, *J* = 7.1, 1.3 Hz, 1H, Ar–H), 7.35 (dd, *J* = 8.2, 7.0 Hz, 1H, Ar–H), 7.18–7.15 (m, 2H, Ar–H), 3.66 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 176.0 (C=O), 163.7 (d, $J_{C–F}$ = 251.5 Hz), 138.7, 133.9, 132.4, 131.9 (d, $J_{C–F}$ = 8.6 Hz), 128.9, 128.1, 126.3, 125.8, 125.77, 125.70, 124.5, 122.6 (d, $J_{C–F}$ = 3.3 Hz), 117.8, 116.4 (d, $J_{C–F}$ = 22.2 Hz), 103.0 (d, $J_{C–F}$ = 2.6 Hz), 52.7 (OMe), 32.9 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -109.20 (Ar–F); IR ν_{max} (cm^{-1}): 3061, 2952, 1718 (C=O), 1599, 1502, 1434, 1265, 1221, 1155; HRMS (ES+) $[M+H]^+$ calculated for $[C_{21}H_{16}O_2F]^+$: 319.1134; found 319.1136.

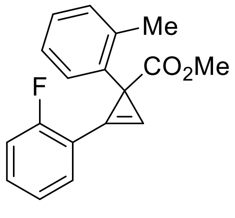
Synthesis of methyl 2-(4-fluorophenyl)-1-(p-tolyl)cycloprop-2-ene-1-carboxylate (***3.3f***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1e** (25 mg, 0.13 mmol), and 1-ethynyl-4-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3f**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3f**) was obtained as a yellow oil. Yield: 20 mg, 71%, 0.07 mmol

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.69 (dd, J = 8.6, 5.5 Hz, 2H, Ar–H), 7.35–7.33 (m, 3H, Ar–H), 7.22–7.18 (m, 4H), 3.80 (s, 3H, OMe), 2.40 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.2 (C=O), 163.7 (d, $J_{C\text{–}F}$ = 251.5 Hz), 137.7, 136.4, 132.0 (d, $J_{C\text{–}F}$ = 8.7 Hz), 129.0, 128.1, 121.9 (d, $J_{C\text{–}F}$ = 3.5 Hz), 116.8, 116.3 (d, $J_{C\text{–}F}$ = 22.2 Hz), 100.00 (d, J = 2.7 Hz), 52.3 (OMe), 33.5 (quaternary C_{sp^3}), 21.2 (Me); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -109.30 (Ar–F); IR ν_{max} (cm^{-1}): 3134, 2951, 2922, 1716 (C=O), 1598, 1500, 1435, 1220, 1153, 1091, 1029, 1016, 1001; HRMS (ES+) $[M+H]^+$ calculated for $[C_{18}H_{16}O_2F]^+$: 283.1134; found: 283.1136.

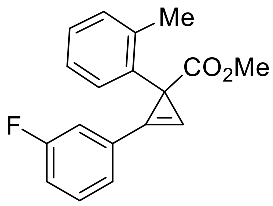
Synthesis of methyl 2-(2-fluorophenyl)-1-(o-tolyl)cycloprop-2-ene-1-carboxylate (***3.3g***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1f** (25 mg, 0.13 mmol), and 1-ethynyl-2-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3g**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3g**) was obtained as a colourless oil. Yield: 23 mg, 81%, 0.08 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.65 (td, J = 7.3, 1.8 Hz, 1H, Ar–H), 7.49 (s, 1H, C=CH), 7.45–7.39 (m, 1H, Ar–H), 7.25–7.15 (m, 5H, Ar–H), 7.10–7.07 (m, 1H, Ar–H), 3.71 (s, 3H, OMe), 2.40 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 175.5 (C=O), 161.6 (d, $J_{C–F}$ = 255.0 Hz), 140.3, 137.5, 131.9 (d, $J_{C–F}$ = 8.2 Hz,), 131.0, 130.9, 130.4, 128.5, 127.4, 126.1, 124.5 (d, $J_{C–F}$ = 3.8 Hz), 116.2 (d, $J_{C–F}$ = 20.3 Hz), 115.0, 114.9, 113.0, 106.3 (d, J = 4.6 Hz), 52.6 (OMe), 32.4 (quaternary C_{sp^3}), 19.7 (Me); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -111.5 (Ar–F); IR ν_{max} (cm^{-1}): 3138, 2951, 1716 (C=O), 1608, 1577, 1485, 1450, 1433, 1265, 1219, 1022, 1001; HRMS (ES+) $[M+H]^+$ calculated for $[C_{18}H_{16}O_2F]^+$: 283.1134; found 283.1139.

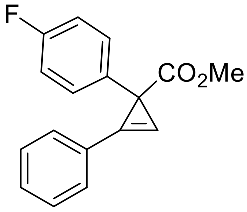
Synthesis of methyl 2-(3-fluorophenyl)-1-(o-tolyl)cycloprop-2-ene-1-carboxylate (***3.3h***)



Synthetised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1f** (25 mg, 0.13 mmol), and 1-ethynyl-3-fluorobenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3h**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3h**) was obtained as a colourless oil. Yield: 20 mg, 71%, 0.07 mmol,

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.48–7.40 (m, 3H, C=CH and Ar–H), 7.38–7.35 (m, 1H, Ar–H), 7.21–7.06 (m, 5H, Ar–H), 3.71 (s, 3H, OMe), 2.39 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 175.3 (C=O), 162.9 (d, $J_{C–F}$ = 247.5 Hz), 140.1, 137.4, 130.6 (d, $J_{C–F}$ = 8.5 Hz), 128.5, 128.3, 127.5, 126.2, 125.5 (d, $J_{C–F}$ = 3.1 Hz), 117.2, 117.0, 116.4 (d, $J_{C–F}$ = 22.4 Hz), 104.9, 52.6 (COOMe), 33.8 (quaternary C_{sp^3}), 19.8 (Me). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -112.09 (Ar–F); IR ν_{max} (cm^{-1}): 3145, 2953, 1716 (C=O), 1583, 1483, 1433, 1222, 1022; HRMS (ES+) $[M+H]^+$ calculated for $[C_{18}H_{16}O_2F]^+$: 283.1134; found 283.1125.

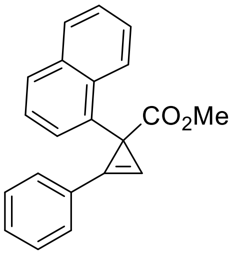
Synthesis of methyl 1-(4-fluorophenyl)-2-phenylcycloprop-2-ene-1-carboxylate (***3.3i***)[122]



Synthesised in accordance with *General procedure e* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), **3.1a** (25 mg, 0.13 mmol), and phenylacetylene (10 mg, 0.1 mmol) in 1,2-DCE to afford **3.3i**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.3i**) was obtained as a yellow oil. Yield: 20 mg, 75%, 0.07 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.61–7.59 (m, 2H, Ar–H), 7.46–7.40 (m, 3H, Ar–H), 7.37–7.34 (m, 2H, Ar–H), 7.19 (s, 1H, C=CH), 6.97 (t, J = 8.8 Hz, 2H, Ar–H), 3.71 (s, 3H, OMe); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 175.0 (C=O), 161.7 (d, $J_{C–F}$ = 245.0 Hz), 136.7 (d, $J_{C–F}$ = 3.2 Hz), 130.2, 130.03, 130.01, 129.9, 129.1, 125.3, 117.4, 115.0 (d, $J_{C–F}$ = 21.4 Hz), 100.2, 52.4 (OMe), 32.9 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, CDCl$_3$, 298 K) δ: -116.31 (Ar–F).

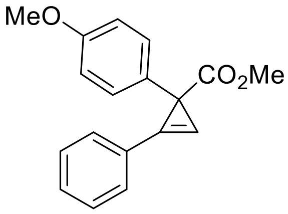
Synthesis of methyl 1-(naphthalen-1-yl)-2-phenylcycloprop-2-ene-1-carboxylate (***3.3j***)[122]



Synthesised in accordance with *General procedure e* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), **3.1d** (29 mg, 0.13 mmol), and phenylacetylene (10 mg, 0.1 mmol) in 1,2-DCE to afford **3.3j**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3j**) was obtained as a yellow oil. Yield: 18 mg, 60%, 0.06 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 8.15 (d, J = 8.4 Hz, 1H, Ar–H), 7.88–7.86 (m, 1H, Ar–H), 7.77–7.74 (m, 3H, Ar–H), 7.57–7.54 (m, 1H, Ar–H), 7.51–7.45 (m, 5H), 7.48–7.42 (m, 1H, Ar–H), 7.34 (dd, J = 8.2, 7.0 Hz, 1H, Ar–H), 3.66 (s, 3H, OMe); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 176.1 (C=O), 138.9, 133.9, 132.4, 130.1, 129.1, 128.9, 128.0, 126.3, 126.2, 125.9, 125.77, 125.74, 124.6, 118.6, 103.6, 52.6 (OMe), 32.8 (quaternary C_{sp}^3).

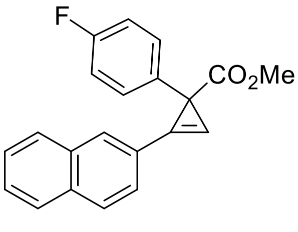
Synthesis of methyl 1-(4-methoxyphenyl)-2-phenylcycloprop-2-ene-1-carboxylate (***3.3k***)[122]



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1g** (27 mg, 0.13 mmol), and phenylacetylene (10 mg, 0.1 mmol) in 1,2-DCE to afford **3.3k**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3.3k**) was obtained as a colourless oil. Yield: 14 mg, 50%, 0.05 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.61 (dd, *J* = 8.1, 1.6 Hz, 2H, Ar–H), 7.44–7.37 (m, 3H, Ar–H), 7.32–7.29 (m, 2H, Ar–H), 7.20 (s, 1H, C=CH), 6.82 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H, OMe), 3.71 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.4 (C=O), 158.3, 133.2, 130.0, 129.4, 129.0, 125.6, 117.7, 113.6, 100.7, 55.3 (OMe), 52.3 (COOMe), 33.0 (quaternary C_{sp}^3).

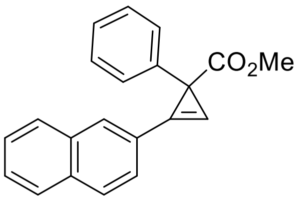
Synthesis of methyl 1-(4-fluorophenyl)-2-(naphthalen-2-yl)cycloprop-2-ene-1-carboxylate (***3.3l***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1a** (25 mg, 0.13 mmol), and 2-ethynylnaphthalene (15 mg, 0.1 mmol) in 1,2-DCE to afford **3.3l**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3l**) was obtained as a white solid. Yield: 25 mg, 79%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.04 (s, 1H, Ar–H), 7.91–7.84 (m, 3H, Ar–H), 7.70 (dd, *J* = 8.4, 1.6 Hz, 1H, Ar–H), 7.56–7.51 (m, 2H, Ar–H), 7.43–7.40 (m, 2H, Ar–H), 7.28 (s, 1H, C=CH), 6.98 (t, *J* = 8.8 Hz, 2H, Ar–H), 3.73 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.0 (C=O), 161.7 (d, $J_{C–F}$ = 245.0 Hz), 148.7, 136.8 (d, $J_{C–F}$ = 3.2 Hz), 134.0, 133.2, 130.9, 130.1, 129.9 (d, *J* = 8.0 Hz), 129.0, 128.6, 128.0, 127.6, 127.5, 126.9, 126.5, 122.1, 117.3, 115.0 (d, $J_{C–F}$ = 21.3 Hz), 101.1, 52.4 (OMe), 32.1 (quaternary C_{sp^3}); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.25 (Ar–F); IR ν_{max} (cm^{-1}): 3056, 2960, 1718 (C=O), 1508, 1434, 1264, 1222, 1159; HRMS (ASAP+) $[M+H]^+$ calculated for $[C_{21}H_{16}O_2F]^+$: 319.1134; found 319.1128.

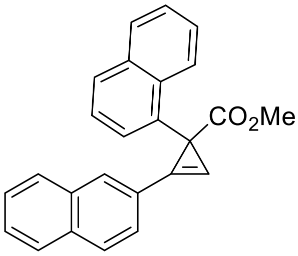
Synthesis of methyl 2-(naphthalen-2-yl)-1-phenylcycloprop-2-ene-1-carboxylate (***3.3m***)[122]



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1c** (23 mg, 0.13 mmol), and 2-ethynylnaphthalene (15 mg, 0.1 mmol) in 1,2-DCE to afford **3.3m**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3m**) was obtained as a white solid. Yield: 20 mg, 67%, 0.06 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.07 (s, 1H, Ar–H), 7.90–7.83 (m, 3H, Ar–H), 7.72 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar–H), 7.55–7.50 (m, 2H, Ar–H), 7.46–7.44 (m, 2H, Ar–H), 7.31–7.30 (m, 3H), 7.24–7.20 (m, 1H, Ar–H), 3.74 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.1 (C=O), 141.0, 134.0, 133.2, 130.1, 128.9, 128.6, 128.3, 128.2, 128.0, 127.5, 126.9, 126.7, 126.6, 122.9, 117.2, 101.3, 52.4 (OMe), 33.8 (quaternary C_{sp^3}).

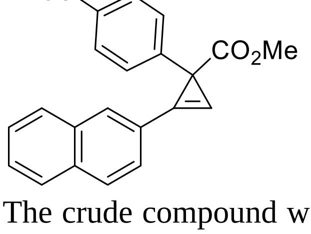
Synthesis of methyl 1-(naphthalen-1-yl)-2-(naphthalen-2-yl)cycloprop-2-ene-1-carboxylate (***3.3n***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1d** (29 mg, 0.13 mmol), and 2-ethynylnaphthalene (15 mg, 0.1 mmol) in 1,2-DCE to afford **3.3n**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3n**) was obtained as a white solid. Yield: 25 mg, 71%, 0.07 mmol. Single crystals of **3.3n** could be obtained from vapour diffusion using CH_2Cl_2/pentane.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.26 (s, 1H, Ar–H), 8.21 (d, *J* = 7.4 Hz, 1H, Ar–H), 7.94–7.87 (m, 4H, Ar–H), 7.80 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar–H), 7.77 (d, *J* = 8.2 Hz, 1H, Ar–H), 7.60–7.50 (m, 6H, C=CH and Ar–H), 7.34 (dd, *J* = 8.2, 7.1 Hz, 1H, Ar–H), 3.70 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 176.1 (C=O), 138.9, 134.0, 133.9, 133.3, 132.4, 129.9, 128.98, 128.95, 128.6, 128.06, 128.04, 127.5, 126.9, 126.7, 126.2, 125.9, 125.8, 125.7, 124.6, 123.6, 118.6, 104.2, 52.7 (OMe), 33.0 (quaternary C_{sp^3}); IR ν_{max} (cm^{-1}): 3117, 3062, 2949, 2916, 2848, 1713 (C=O), 1506, 1431, 1226; HRMS (ES+) $[M+H]^+$ calculated for $[C_{25}H_{19}O_2]^+$: 351.1385; found 351.1374.

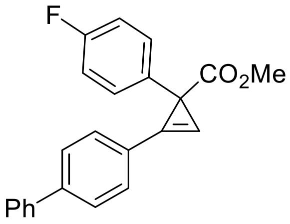
Synthesis of methyl 1-(4-methoxyphenyl)-2-(naphthalen-2-yl)cycloprop-2-ene-1-carboxylate (**3.3*o***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1g** (26 mg, 0.13 mmol), and 2-ethynylnaphthalene (15 mg, 0.1 mmol) in 1,2-DCE to afford **3.3o**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3.3o**) was obtained as a white solid. Yield: 19 mg, 57%, 0.05 mmol. Single crystals of **3.3o** could be obtained from vapour diffusion using CH_2Cl_2/pentane.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.06 (s, 1H, Ar–H), 7.89–7.83 (m, 3H, Ar–H), 7.71 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar–H), 7.53–7.51 (m, 2H, Ar–H), 7.38–7.36 (m, 2H, Ar–H), 7.30 (s, 1H, C=CH), 6.84 (d, *J* = 8.9 Hz, 2H, Ar–H), 3.77 (s, 3H, COOMe), 3.73 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.4 (C=O), 158.4, 134.0, 133.2, 130.0, 129.4, 128.8, 128.6, 128.0, 127.4, 126.8, 126.6, 123.0, 117.5, 113.7, 101.5, 55.4 (OMe), 52.4 (COOMe), 33.2 (quaternary $C_{sp}{}^3$); IR ν_{max} (cm^{-1}): 3056, 2955, 2919, 2839, 1718 (C=O); 1510, 1264, 1249, 1176, 1031; HRMS (ES+) $[M+H]^+$ calculated for $[C_{22}H_{19}O_3]^+$: 331.1134; found 331.1332.

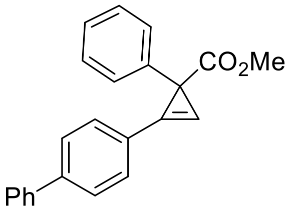
*Synthesis of methyl 2-([1,1'-biphenyl]-4-yl)-1-(4-fluorophenyl)cycloprop-2-ene-1-carboxylate (**3.3p**)*



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1a** (25 mg, 0.13 mmol), and 4-ethynyl-1,1'-biphenyl (18 mg, 0.1 mmol) in 1,2-DCE to afford **3.3p**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3p**) was obtained as a white solid. Yield: 28 mg, 81%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.67 (s, 4H, Ar–H), 7.60 (d, *J* = 7.7 Hz, 2H, Ar–H), 7.46 (t, *J* = 7.7 Hz, 2H, Ar–H), 7.39–7.37 (m, 3H, Ar–H), 7.22 (s, 1H, C=CH), 6.98 (t, *J* = 8.5 Hz, 2H, Ar–H), 3.73 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.0 (C=O), 161.7 (d, $J_{C–F}$ = 245.0 Hz), 143.1, 140.3, 136.8 (d, $J_{C–F}$ = 3.2 Hz), 130.4, 129.9 (d, $J_{C–F}$ = 8.0 Hz), 129.0, 128.0, 127.8, 127.2, 124.2, 117.1, 115.0 (d, $J_{C–F}$ = 21.4 Hz), 100.3, 52.4 (OMe), 33.0 (quaternary $C_{sp}{}^3$); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.28 (Ar–F); IR ν_{max} (cm^{-1}): 3057, 3030, 2951, 1718 (C=O), 1600, 1508, 1486, 1448, 1264, 1221, 1158, 1007; HRMS (ES+) $[M+H]^+$ calculated for $[C_{23}H_{18}O_2F]^+$: 345.1291; found: 345.1285.

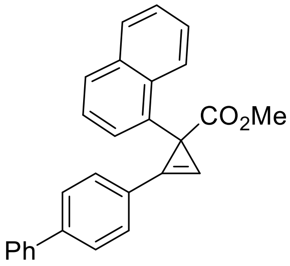
Synthesis of methyl 2-([1,1'-biphenyl]-4-yl)-1-phenylcycloprop-2-ene-1-carboxylate (***3.3q***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1c** (23 mg, 0.13 mmol), and 4-ethynyl-1,1'-biphenyl (18 mg, 0.1 mmol) in 1,2-DCE to afford **3.3q**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3q**) was obtained as a white solid. Yield: 26 mg, 80%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.71–7.65 (m, 4H, Ar–H), 7.61–7.59 (m, 2H, Ar–H), 7.46 (t, *J* = 7.6 Hz, 2H, Ar–H), 7.43–7.36 (m, 3H, Ar–H), 7.30 (t, *J* = 7.6 Hz, 2H, Ar–H), 7.24–7.20 (m, 2H), 3.74 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.1 (C=O), 143.0, 141.0, 140.3, 130.5, 129.0, 128.3, 128.2, 128.0, 127.7, 127.2, 126.6, 124.4, 117.0, 100.5, 52.3 (OMe), 33.7 (quaternary C_{sp^3}); IR ν_{max} (cm^{-1}): 3057, 3029, 2950, 1718 (C=O), 1696, 1485, 1264, 1207, 1007; HRMS (ASAP+) $[M+H]^+$ calculated for $[C_{23}H_{19}O_2]^+$: 327.1385; found 327.1388.

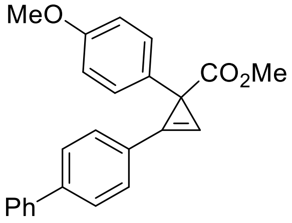
Synthesis of methyl 2-([1,1'-biphenyl]-4-yl)-1-(naphthalen-1-yl)cycloprop-2-ene-1-carboxylate (***3.3r***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1d** (29 mg, 0.13 mmol), and 4-ethynyl-1,1'-biphenyl (18 mg, 0.1 mmol) in 1,2-DCE to afford **3.3r**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3r**) was obtained as a white solid. Yield: 21 mg, 56%, 0.05 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.18 (d, *J* = 7.4 Hz, 1H, Ar–H), 7.88 (d, *J* = 8.1 Hz, 1H, Ar–H), 7.83–7.82 (m, 2H, Ar–H), 7.78–7.76 (m, 1H, Ar–H), 7.72–7.70 (m, 2H, Ar–H), 7.63 (dd, *J* = 8.4, 1.3 Hz, 2H, Ar–H), 7.58–7.55 (m, 1H, Ar–H), 7.53–7.46 (m, 5H), 7.41–7.35 (m, 2H, Ar–H), 3.68 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 176.1 (C=O), 142.9, 140.3, 138.9, 133.9, 132.4, 130.4, 129.0, 128.9, 128.0, 127.8, 127.3, 126.2, 125.9, 125.79, 125.76, 125.1, 124.6, 118.3, 103.6, 52.6 (OMe), 32.8 (quaternary C_{sp^3}); IR ν_{max} (cm^{-1}): 3125, 3063, 2955, 2917, 2848, 1714 (C=O), 1264, 1234; HRMS (ES+) $[M+H]^+$ calculated for $[C_{27}H_{21}O_2]^+$: 377.1542; found 377.1527.

Synthesis of methyl 2-([1,1'-biphenyl]-4-yl)-1-(4-methoxyphenyl)cycloprop-2-ene-1-carboxylate (***3.3s***)

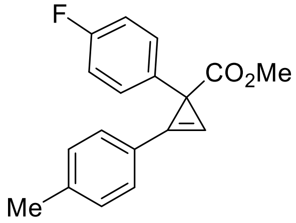


Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1g** (26 mg, 0.13 mmol), and 4-ethynyl-1,1'-biphenyl (18 mg, 0.1 mmol) in 1,2-DCE to afford **3.3s**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3.3s**) was obtained as a yellow solid. Yield: 18 mg, 51%, 0.05 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.67 (q, *J* = 8.6 Hz, 4H, Ar–H), 7.61–7.59 (m, 2H, Ar–H), 7.46 (t, *J* = 7.6 Hz, 2H, Ar–H), 7.39–7.38 (m, 1H, Ar–H), 7.34–7.33 (m, 2H, Ar–H), 7.23 (s, 1H, C=CH), 6.84 (d, *J* = 8.8 Hz, 2H, Ar–H), 3.78 (s, 3H, COOMe), 3.73 (s, 3H, COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.4 (C=O), 158.4, 142.9, 140.4, 133.2, 130.4, 129.4, 129.0, 128.0, 127.7, 127.2, 124.5, 117.4, 113.7, 100.8, 55.4 (OMe), 52.3 (COOMe), 33.0

(quaternary C_{sp^3}); IR ν_{max} (cm^{-1}): 3054, 2955, 2839, 1715 (C=O), 1605, 1511, 1264, 1248, 1176, 1031; HRMS (ES+) $[M+H]^+$ calculated for $[C_{24}H_{21}O_3]^+$: 357.1491; found 357.1485.

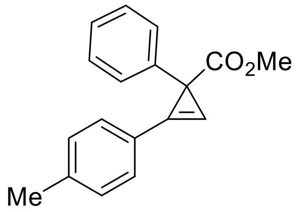
Synthesis of methyl 1-(4-fluorophenyl)-2-(p-tolyl)cycloprop-2-ene-1-carboxylate (***3.3t***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1a** (25 mg, 0.13 mmol), and 1-ethynyl-4-methylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3t**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3t**) was obtained as a yellow oil. Yield: 20 mg, 71%, 0.07 mmol.

^1H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.49 (d, *J* = 8.1 Hz, 2H, Ar–H), 7.35 (dd, *J* = 8.8, 5.3 Hz, 2H, Ar–H), 7.24 (d, *J* = 7.7 Hz, 2H, Ar–H), 7.11 (s, 1H, C=CH), 6.95 (t, *J* = 8.7 Hz, 2H, Ar–H), 3.70 (s, 3H, OMe), 2.39 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.1 (C=O), 161.6 (d, $J_{C–F}$ = 244.8 Hz), 140.7, 136.9 (d, $J_{C–F}$ = 3.2 Hz), 130.0, 129.9, 129.8, 122.5, 117.1, 114.9 (d, $J_{C–F}$ = 21.3 Hz), 99.0, 52.3 (OMe), 32.8 (quaternary C_{sp^3}), 21.7 (Me); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.48 (Ar–F); IR ν_{max} (cm^{-1}): 2951, 2922, 1716 (C=O), 1602, 1508, 1435, 1222, 1159, 1014; HRMS (ES+) $[M+H]^+$ calculated for $[C_{18}H_{16}O_2F]^+$: 283.1134, found: 283.1127.

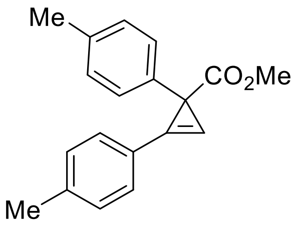
Synthesis of methyl 1-phenyl-2-(p-tolyl)cycloprop-2-ene-1-carboxylate (***3.3u***)[122]



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1c** (23 mg, 0.13 mmol), and 1-ethynyl-4-methylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3u**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3u**) was obtained as a colourless oil. Yield: 12 mg, 45%, 0.04 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.51 (d, *J* = 8.3 Hz, 2H, Ar–H), 7.40–7.37 (m, 3H, Ar–H), 7.28 (d, *J* = 7.4 Hz, 1H, Ar–H), 7.24–7.20 (m, 3H, Ar–H), 7.13 (s, 1H, C=CH), 3.71 (s, 3H, OMe), 2.38 (s, 3H, Me); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 175.3 (C=O), 141.2, 140.5, 130.0, 129.7, 128.3, 128.1, 126.5, 122.7, 117.1, 99.2, 52.3 (COOMe), 33.5 (quaternary $C_{sp}{}^3$), 21.7 (Me).

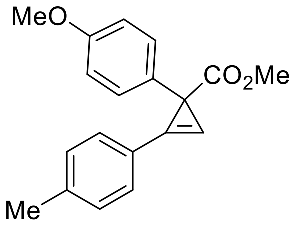
Synthesis of methyl 1,2-di-p-tolylcycloprop-2-ene-1-carboxylate (***3.3v***)



Synthesised in accordance with *General procedure e* using B(C$_6$F$_5$)$_3$ (5 mg, 0.01 mmol), **3.1e** (25 mg, 0.13 mmol), and 1-ethynyl-4-methylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3v**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3v**) was obtained as a colourless oil. Yield: 9 mg, 32%, 0.03 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.51 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.27 (s, 1H, Ar–H), 7.23–7.19 (m, 3H, Ar–H), 7.12 (s, 1H, C=CH), 7.09 (d, *J* = 8.2 Hz, 2H, Ar–H), 3.70 (s, 3H, OMe), 2.38 (s, 3H, Me), 2.30 (s, 3H, Me); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 175.5 (C=O), 140.4, 138.2, 136.1, 130.0, 129.7, 128.9, 128.2, 122.8, 117.3, 99.4, 52.3 (OMe), 33.2 (quaternary $C_{sp}{}^3$), 21.7 (Me), 21.2 (Me); IR ν_{max} (cm^{-1}): 2951, 2924, 1717 (C=O), 1606, 1512, 1435, 1219, 1207, 1031, 1018, 1002; HRMS (ES+) [M+H]$^+$ calculated for [C$_{19}$H$_{19}$O$_2$]$^+$: 279.1385; found 279.1384.

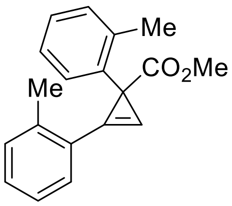
Synthesis of methyl 1-(4-methoxyphenyl)-2-(p-tolyl)cycloprop-2-ene-1-carboxylate (***3.3w***)



Synthesised in accordance with *General procedure e* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), **3.1g** (26 mg, 0.13 mmol), and 1-ethynyl-4-methylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3w**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3.3w**) was obtained as a colourless oil. Yield: 14 mg, 48%, 0.04 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.50 (d, *J* = 7.8 Hz, 2H, Ar–H), 7.30 (d, *J* = 9.0 Hz, 2H, Ar–H), 7.23 (d, *J* = 7.7 Hz, 2H, Ar–H), 7.12 (s, 1H, C=CH), 6.82 (d, *J* = 8.9 Hz, 2H, Ar–H), 3.77 (s, 3H, OMe), 3.70 (s, 3H, COOMe), 2.38 (s, 3H, Me); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 175.5 (C=O), 158.3, 140.4, 133.4, 130.0, 129.7, 129.4, 122.8, 117.4, 113.6, 99.4, 55.4 (OMe), 52.3 (COOMe), 32.9 (quaternary $C_{sp}{}^3$), 21.7 (CH$_3$); IR ν_{max} (cm^{-1}): 3132, 2951, 2837, 1716 (C=O), 1608, 1510, 1435, 1246, 1174, 1026; HRMS (ES+) [M+H]$^+$ calculated for [$C_{19}H_{19}O_3$]$^+$: 295.1334, found: 295.1331.

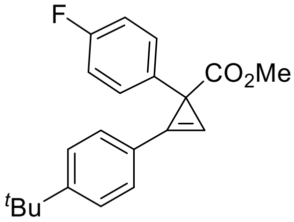
Synthesis of methyl 1,2-di-o-tolylcycloprop-2-ene-1-carboxylate (***3.3x***)



Synthetised in accordance with *General procedure e* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), **3.1f** (25 mg, 0.13 mmol), and 1-ethynyl-2-methylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3x**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3x**) was obtained as a yellow oil. Yield: 20 mg, 72%, 0.07 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.66–7.64 (m, 1H, Ar–H), 7.39 (s, 1H, C=CH), 7.34–7.29 (m, 3H, Ar–H), 7.26–7.24 (m, 1H, Ar–H), 7.18–7.14 (m, 2H, Ar–H), 7.07–7.04 (m, 1H, Ar–H), 3.71 (s, 3H, OMe), 2.49 (s, 3H, Me), 2.41 (s, 3H, Me); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 175.8 (C=O), 140.8, 140.4, 137.5, 130.5, 130.3, 130.2, 130.0, 128.4, 127.3, 126.3, 126.1, 125.0, 116.9, 105.8, 52.6 (OMe), 31.9 (quaternary $C_{sp}{}^3$), 20.3 (Me), 19.7 (Me); IR ν_{max} (cm^{-1}): 2951, 1714 (C=O), 1483, 1458, 1435, 1226, 1022, 1002; HRMS (ES+) $[M+H]^+$ calculated for $[C_{19}H_{19}O_2]^+$: 279.1385; found 279.1377.

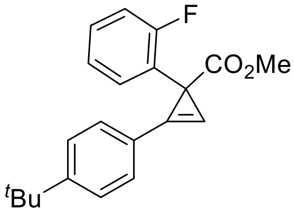
Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(4-fluorophenyl)cycloprop-2-ene-1-carboxylate (***3.3y***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1a** (25 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3.3y**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.3y**) was obtained as a colourless oil. Yield: 25 mg, 77%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.54 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.45 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.37–7.34 (m, 2H, Ar–H), 7.12 (s, 1H, C=CH), 6.96 (t, *J* = 8.7 Hz, 2H, Ar–H), 3.70 (s, 3H, OMe), 1.33 (s, 9H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.1 (C=O), 161.6 (d, $J_{C–F}$ = 244.8 Hz), 153.7, 136.9 (d, $J_{C–F}$ = 3.3 Hz), 130.0 (d, $J_{C–F}$ = 8.0 Hz), 129.8, 126.1, 122.4, 117.2, 114.9 (d, $J_{C–F}$ = 21.4 Hz), 99.1, 52.3 (OMe), 35.1 (quaternary $C_{sp}{}^3$), 31.3 (Me); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.50 (Ar–F); IR ν_{max} (cm^{-1}): 3138, 2962, 2868, 1716 (C=O), 1602, 1508, 1435, 1408, 1363, 1220, 1159, 1105, 1014; HRMS (ES+) $[M+H]^+$ calculated for $[C_{21}H_{22}O_2F]^+$: 325.1604; found 325.1603.

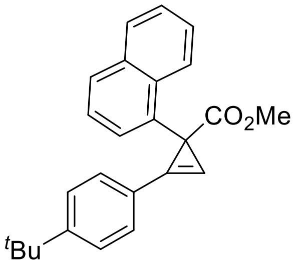
Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(2-fluorophenyl)cycloprop-2-ene-1-carboxylate (***3.3z***)



Synthesised in accordance with *General procedure e* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), **3.1b** (25 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3.3z**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.3z**) was obtained as a colourless oil. Yield: 23 mg, 71%, 0.07 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.63 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.46 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.24–7.17 (m, 3H, C=CH and Ar–H), 7.06–7.01 (m, 2H, Ar–H), 3.70 (s, 3H, OMe), 1.32 (s, 9H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 174.9 (C=O), 161.9 (d, $J_{C–F}$ = 245.8 Hz), 153.7, 130.06, 130.01, 129.92, 129.90, 128.8 (d, $J_{C–F}$ = 8.0 Hz), 126.0, 124.1 (d, $J_{C–F}$ = 3.5 Hz), 122.4, 118.8, 115.4 (d, $J_{C–F}$ = 22.3 Hz), 98.5, 52.5 (OMe), 35.1 (quaternary C_{sp^3}), 31.3 (Me); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -114.50 (Ar–F); IR ν_{max} (cm^{-1}): 3142, 2958, 1722 (C=O), 1608, 1489, 1435, 1259, 1228, 1205, 1105, 1091, 1020; HRMS (ES+) [M+H]$^+$ calculated for [$C_{21}H_{22}O_2F$]$^+$: 325.1604; found 325.1606.

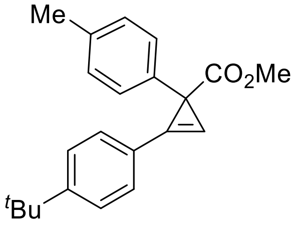
Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(naphthalen-1-yl)cycloprop-2-ene-1-carboxylate (***3.3aa***)



Synthesised in accordance with *General procedure e*using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), **3.1d** (29 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3.3aa**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3aa**) was obtained as a colourless oil. Yield: 29 mg, 81%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.16 (d, *J* = 9.0 Hz, 1H, Ar–H), 7.87 (d, *J* = 8.1 Hz, 1H, Ar–H), 7.75 (d, *J* = 8.4 Hz, 1H, Ar–H), 7.70–7.68 (m, 2H, Ar–H), 7.57–7.54 (m, 1H, Ar–H), 7.51–7.48 (m, 4H, Ar–H), 7.43 (s, 1H, C=CH), 7.34 (dd, *J* = 8.2, 7.1 Hz, 1H, Ar–H), 3.66 (s, 3H, OMe), 1.35 (s, 9H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 176.2 (C=O), 153.6, 139.1, 133.9, 132.5, 129.7, 128.9, 127.9, 126.18, 126.10, 125.9, 125.75, 125.72, 124.7, 123.3, 118.3, 102.4, 52.6 (OMe), 35.1 (quaternary C_{sp^3}), 31.3 (Me); IR ν_{max} (cm^{-1}): 3121, 2960, 1716 (C=O), 1264, 1230; HRMS (ES+) $[M+H]^+$ calculated for $[C_{25}H_{25}O_2]^+$: 357.1855; found 357.1862.

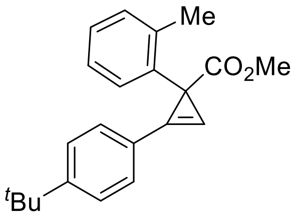
Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(p-tolyl)cycloprop-2-ene-1-carboxylate (***3.3ab***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1e** (25 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3.3ab**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.3ab**) was obtained as a colourless oil. Yield: 17 mg, 53%, 0.05 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.55 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.44 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.28 (d, *J* = 8.1 Hz, 2H, Ar–H), 7.13 (s, 1H, C=CH), 7.09 (d, *J* = 7.8 Hz, 2H, Ar–H), 3.70 (s, 3H, OMe), 2.30 (s, 3H, Me), 1.32 (s, 9H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.5 (C=O), 153.5, 138.2, 136.1, 129.8, 128.9, 128.2, 126.0, 122.7, 117.3, 99.4, 52.3 (OMe), 35.0 (quaternary C_{sp^3}), 31.3 (CH_3), 21.2 (Me); IR ν_{max} (cm^{-1}): 2962, 2868, 1716 (C=O), 1606, 1514, 1435, 1363, 1220, 1205, 1105, 1016, 1002; HRMS (ES+) $[M+H]^+$calculated for $[C_{22}H_{25}O_2]^+$: 321.1855; found 321.1850.

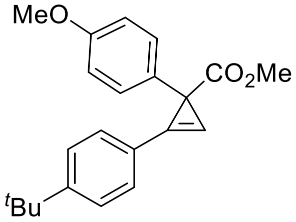
Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(o-tolyl)cycloprop-2-ene-1-carboxylate (***3.3ac***)



Synthesised in accordance with *General procedure e* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), **3.1f** (25 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3.3ac**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.3ac**) was obtained as a yellow oil. Yield: 22 mg, 69%, 0.06 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.62 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.48 (d, *J* = 8.3 Hz, 2H, Ar–H), 7.27–7.25 (m, 2H, C=CH and Ar–H), 7.16–7.13 (m, 2H, Ar–H), 7.08–7.04 (m, 1H, Ar–H), 3.70 (s, 3H, OMe), 2.40 (s, 3H, Me), 1.35 (s, 9H, Me); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 175.8 (C=O), 153.5, 140.8, 137.5, 130.3, 129.6, 128.6, 127.3, 126.1, 126.0, 123.4, 118.3, 102.2, 52.5 (OMe), 35.1 (quaternary $C_{sp}{}^3$), 31.3 (Me), 19.8 (Me); IR ν_{max} (cm^{-1}): 2964, 1712 (C=O), 1458, 1433, 1265, 1226, 1105, 1022, 1001; HRMS (ES+) [M+H]$^+$ calculated for [$C_{22}H_{25}O_2$]$^+$: 321.1855; found 321.1851.

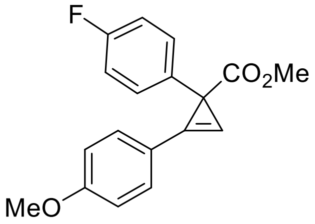
Synthesis of methyl 2-(4-(tert-butyl)phenyl)-1-(4-methoxyphenyl)cycloprop-2-ene-1-carboxylate (***3.3ad***)



Synthesised in accordance with *General procedure e* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), **3.1g** (27 mg, 0.13 mmol), and 1-(*tert*-butyl)-4-ethynylbenzene (16 mg, 0.1 mmol) in 1,2-DCE to afford **3.3ad**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (85:15 v/v) as eluent. The desired product (**3.3ad**) was obtained as a colourless oil. Yield: 22 mg, 65%, 0.06 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.55 (d, *J* = 8.6 Hz, 2H, Ar–H), 7.44 (d, *J* = 8.7 Hz, 2H, Ar–H), 7.31 (d, *J* = 8.9 Hz, 2H, Ar–H), 7.13 (s, 1H, C=CH), 6.82 (d, *J* = 8.9 Hz, 2H, Ar–H), 3.77 (s, 3H, OMe), 3.70 (s, 3H, COOMe), 1.32 (s, 9H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.6 (C=O), 158.3, 153.5, 133.4, 129.8, 129.4, 126.0, 122.7, 117.5, 113.6, 99.5, 55.3 (OMe), 52.3 (COOMe), 35.0 (quaternary $C_{sp}{}^3$), 31.3 (Me); IR ν_{max} (cm^{-1}): 2960, 2904, 1714 (C=O), 1608, 1510, 1463, 1246, 1176, 1105, 1026; HRMS (ES+) $[M+H]^+$ calculated for $[C_{22}H_{25}O_3]^+$: 337.1804; found 337.1814.

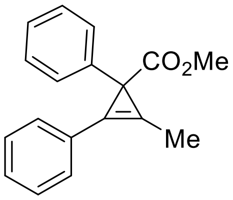
Synthesis of methyl 1-(4-fluorophenyl)-2-(4-methoxyphenyl)cycloprop-2-ene-1-carboxylate (***3.3ae***)



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1a** (25 mg, 0.13 mmol), and 1-ethynyl-4-methoxybenzene (13 mg, 0.1 mmol) in 1,2-DCE to afford **3.3ae**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.3ae**) was obtained as a colourless oil. Yield: 15 mg, 50%, 0.05 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.54 (d, J = 8.7 Hz, 2H, Ar–H), 7.34 (dd, J = 8.8, 5.4 Hz, 2H, Ar–H), 7.03 (s, 1H, C=CH), 6.97–6.94 (m, 4H, Ar–H), 3.84 (s, 3H, COOMe), 3.70 (s, 3H, OMe); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.2 (C=O), 161.6 (d, $J_{C–F}$ = 244.8 Hz), 161.2, 137.0 (d, $J_{C–F}$ = 3.3 Hz), 131.6, 129.9 (d, $J_{C–F}$ = 8.0 Hz), 117.8, 116.7, 114.9 (d, $J_{C–F}$ = 21.3 Hz), 114.6, 97.4, 55.5 (OMe), 52.3 (COOMe), 32.8 (quaternary $C_{sp}{}^3$); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.53 (Ar–F); IR ν_{max} (cm^{-1}): 2953, 2839, 1716 (C=O), 1602, 1506, 1249, 1222, 1166, 1095, 1029; HRMS (ES+) $[M+H]^+$ calculated for $[C_{18}H_{16}O_3F]^+$: 299.1083; found 299.1078.

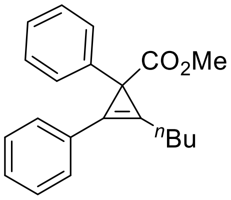
Synthesis of methyl 2-methyl-1,3-diphenylcycloprop-2-ene-1-carboxylate (***3.3af***)[122]



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1c** (23 mg, 0.13 mmol), and prop-1-ynylbenzene (12 mg, 0.1 mmol) in 1,2-DCE to afford **3.3af**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.3af**) was obtained as a yellow oil. Yield: 4 mg, 15%, 0.01 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.55–7.54 (m, 2H, Ar–H), 7.40 (t, *J* = 7.5 Hz, 2H, Ar–H), 7.39–7.33 (m, 3H, Ar–H), 7.28–7.26 (m, 2H, Ar–H), 7.21–7.18 (m, 1H, Ar–H), 3.70 (s, 3H, OMe), 2.39 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.3 (C=O), 141.2, 129.4, 128.9, 128.3, 128.2, 126.7, 126.4, 111.4, 108.6, 52.1 (OMe), 35.4 (quaternary $C_{sp}{}^3$), 9.8 (Me).

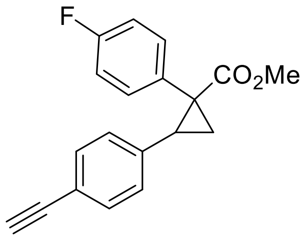
Synthesis of methyl 2-butyl-1,3-diphenylcycloprop-2-ene-1-carboxylate (***3.3ag***)[165]



Synthesised in accordance with *General procedure e* using $B(C_6F_5)_3$ (5 mg, 0.01 mmol), **3.1c** (23 mg, 0.13 mmol), and **3.2a** (16 mg, 0.1 mmol) in 1,2-DCE to afford **3.3ag**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The desired product (**3.3ag**) was obtained as a yellow oil. Yield: 8 mg, 26%, 0.02 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.54 (d, *J* = 7.0 Hz, 2H, Ar–H), 7.42–7.39 (m, 2H, Ar–H), 7.36–7.34 (m, 3H, Ar–H), 7.27–7.24 (m, 2H, Ar–H), 7.20–7.17 (m, 1H, Ar–H), 3.69 (s, 3H, OMe), 2.74 (t, *J* = 7.4 Hz, 2H, CH_2), 1.77–1.71 (m, 2H, CH_2), 1.45–1.40 (m, 2H, CH_2), 0.93 (t, *J* = 7.4 Hz, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 175.4 (C=O), 141.4, 129.4, 128.9, 128.8, 128.3, 128.1, 126.7, 126.2, 115.7, 107.8, 52.0 (COOMe), 35.4 (quaternary $C_{sp}{}^3$), 29.7, 24.7, 22.6, 13.8.

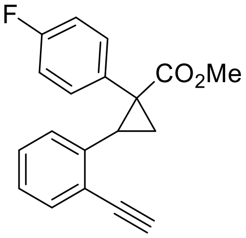
Synthesis of methyl 2-(4-ethynylphenyl)-1-(4-fluorophenyl)cyclopropane-1-carboxylate (***3.3ah***)



Synthesised in accordance with *General procedure e* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), **3.1a** (45 mg, 0.23 mmol), and 1-ethynyl-4-vinylbenzene (13 mg, 0.1 mmol) in 1,2-DCE to afford **3.3ah**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3ah**) was obtained as a colourless oil. Yield: 25 mg, 85%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.21 (d, *J* = 8.3 Hz, 2H, Ar–H), 6.98–6.95 (m, 2H, Ar–H), 6.83 (t, *J* = 8.8 Hz, 2H, Ar–H), 6.71 (d, *J* = 8.1 Hz, 2H, Ar–H), 3.67 (s, 3H, OMe), 3.08 (dd, *J* = 9.3, 7.2 Hz, 1H, CH), 3.02 (s, 1H, C≡CH), 2.16 (dd, *J* = 9.3, 5.0 Hz, 1H, CH), 1.83 (dd, *J* = 7.3, 5.0 Hz, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 173.9 (C=O), 161.9 (d, $J_{C–F}$ = 246.4 Hz), 137.3, 133.5 (d, $J_{C–F}$ = 8.2 Hz), 131.7, 130.3 (d, $J_{C–F}$ = 3.3 Hz), 128.0, 120.2, 115.0 (d, $J_{C–F}$ = 21.5 Hz), 83.5 (C≡C), 77.4 (C≡C) 52.8 (OMe), 37.1 (CH), 33.0 (CH), 20.8 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -114.62 (Ar–F); IR ν_{max} (cm^{-1}): 3300 (C≡CH), 2953, 1714 (C=O), 1512, 1257; HRMS (GC) [M] calculated for [$C_{19}H_{15}O_2F$]: 294.1050; found 294.1050.

Synthesis of methyl 2-(2-ethynylphenyl)-1-(4-fluorophenyl)cyclopropane-1-carboxylate (***3.3ai***)

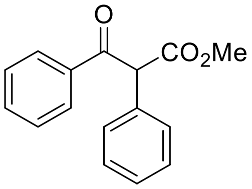


Synthesised in accordance with *General procedure e* using B(C_6F_5)$_3$ (5 mg, 0.01 mmol), **3.1a** (45 mg, 0.23 mmol), and 1-ethynyl-2-vinylbenzene (13 mg, 0.1 mmol) in 1,2-DCE to afford **3.3ai**. The crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (92:8 v/v) as eluent. The desired product (**3.3ai**) was obtained as a colourless oil. Yield: 12 mg, 41%, 0.04 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.44 (dd, *J* = 7.7, 1.5 Hz, 1H, Ar–H), 7.09–7.03 (m, 3H, Ar–H), 6.96 (t, *J* = 7.7 Hz, 1H, Ar–H), 6.77 (t, *J* = 8.7 Hz, 2H, Ar–H), 6.42 (d, *J* = 7.4 Hz, 1H, Ar–H), 3.69 (s, 3H, OMe), 3.52 (dd, *J* = 9.2, 7.5 Hz, 1H, CH), 3.40 (s, 1H, C≡CH), 2.13 (dd, *J* = 9.1, 5.1 Hz, 1H, CH), 1.97 (dd, *J* = 7.5, 5.0 Hz, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 174.1 (C=O), 161.8 (d, $J_{C–F}$ = 245.9 Hz), 139.0, 133.2 (d, $J_{C–F}$ = 8.1 Hz), 132.6, 130.8 (d, $J_{C–F}$ = 3.2 Hz), 128.5, 126.5, 125.9, 123.9, 114.7 (d, $J_{C–F}$ = 21.5 Hz), 82.48 (C≡C), 82.44 (C≡C), 52.7 (OMe), 36.1 (CH), 32.3 (CH), 19.0 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -115.15 (Ar–F); IR ν_{max} (cm^{-1}): 3298 (C≡CH), 2953, 2926, 1718 (C=O), 1513, 1260, 1221, 1160; HRMS (ES+) $[M+H]^+$ calculated for $[C_{19}H_{16}O_2F]^+$: 295.1134; found 295.1136.

5.3.2.2 Attempted epoxidation reaction and characterisation of the product

Synthesis of methyl 3-oxo-2,3-diphenylpropanoate[166]



In the glove box under nitrogen atmosphere, tris(pentafluorophenyl)borane $B(C_6F_5)_3$ (5 mg, 0.01 mmol), benzaldehyde (11 mg, 0.1 mmol, 1 equiv), and **3.1c** (23 mg, 0.13 mmol, 1.3 equiv) were all dissolved separately in 1,2-DCE (0.5 mL). The $B(C_6F_5)_3$ solution was mixed with the aldehyde solution, and then the **3.1c** solution was added dropwise into the reaction mixture. The reaction tube was sealed and was left to stir at room temperature for 3 hr. Afterwards, all volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using silica gel and hexane/ethyl acetate (90:10 v/v) as eluent. The product was obtained as yellow oil. Yield: 19 mg, 75%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.96–7.94 (m, 2H, Ar–H), 7.55–7.52 (m, 1H, Ar–H), 7.44–7.34 (m, 6H, Ar–H), 7.32–7.29 (m, 1H, Ar–H), 5.63 (s, 1H, CH), 3.76 (s, 3H, OMe); ^{13}C

NMR (126 MHz, $CDCl_3$, 298 K) δ: 193.3 (C=O), 169.4 (C=O), 135.7, 133.7, 133.0, 129.7, 129.1, 129.0, 128.8, 128.3, 60.5 (CH), 52.9 (OMe).

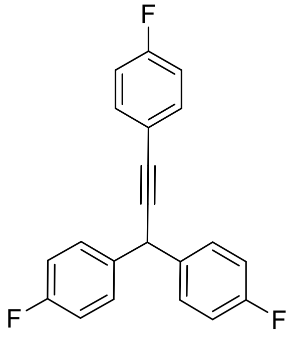
5.3.3.0 General procedure for the FLP-mediated C−C cross coupling reactions

General procedure f: Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] (51 mg, 0.1 mmol, 1 equiv) and trimesitylphosphine [Mes_3P] (39 mg, 0.1 mmol, 1 equiv) were dissolved separately in THF (0.3 mL) and added to the reaction tube. Aryl esters (1 equiv) and aryl acetylene (1.2 equiv) were dissolved separately in THF/TFT (0.3 mL) and added together same time dropwise to the reaction tube at ambient temperature. The reaction tube was sealed in the glove box under nitrogen atmosphere and heated at 80 ºC for 22–24 hr in fume cupboard. All volatiles were removed *in vacuo* and the crude compound was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent.

[when TFT was used as solvent for C–C cross coupling reaction, 0.6 mL of TFT was taken to dissolve each reactant]

5.3.3.1 Synthesis and spectral characterisation of C−C cross coupled products

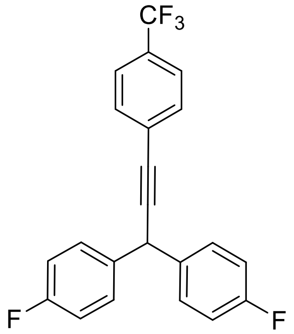
Synthesis of 4,4',4"-(prop-2-yne-1,1,3-triyl)tris(fluorobenzene) (***4.2a***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-fluorobenzene (15 mg, 0.12 mmol) and aryl ester **4.1a** (34 mg, 0.1 mmol) in THF to afford **4.2a**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2a**) was obtained as pale-yellow liquid. Yield: 26 mg, 82%, 0.08 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.39–7.30 (m, 3H, Ar–H), 7.29–7.22 (m, 5H, Ar–H), 7.21–7.16 (m, 2H, Ar–H), 6.93 (ddt, *J* = 9.9, 8.7, 1.5 Hz, 2H, Ar–H), 5.09 (s, 1H, CH); ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 162.6 (d, $J_{C\text{–}F}$ = 249.2 Hz), 141.3, 140.3, 133.7 (d, $J_{C\text{–}F}$ = 8.3 Hz), 132.9, 129.4, 128.9, 127.9, 127.3, 119.4 (d, $J_{C\text{–}F}$ = 3.6 Hz), 115.7 (d, $J_{C\text{–}F}$ = 22.0 Hz), 89.4 (C≡C), 84.3 (C≡C), 43.2 (CH); ^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ: -111.08 (s, 1F, Ar–F), -115.69 (s, 2F, Ar–F); IR ν_{max} (cm^{-1}): 3033, 2902, 2184 (C≡C), 1633, 1556, 1502, 1477, 1423, 1333, 1302, 1256, 1221, 1165, 1031; HRMS (ES+) [M+H]$^+$ [$C_{21}H_{14}F_3$]$^+$: calculated 323.1048, found 323.1045.

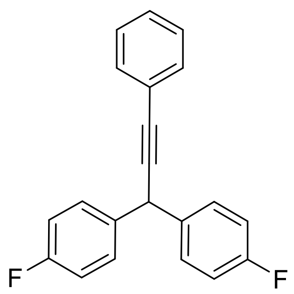
Synthesis of 4,4',4''-(prop-2-yne-1,1,3-triyl)tris(fluorobenzene) (***4.2b***)



Synthesised in accordance with *General procedure f* using B(C$_6$F$_5$)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), 1-ethynyl-4-(trifluoromethyl)benzene (21 mg, 0.12 mmol) and aryl ester **4.1a** (34 mg, 0.1 mmol) in THF to afford **4.2b**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:02 v/v) as eluent. The desired compound (**4.2b**) was obtained as colourless liquid. Yield: 23 mg, 61%, 0.06 mmol,

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.57 (s, 4H, Ar–H), 7.42–7.32 (m, 4H, Ar–H), 7.02 (q, J = 8.2 Hz, 4H, Ar–H), 5.20 (s, 1H, CH); ^{13}C NMR (125 MHz, CDCl$_3$, 298 K) δ: 162.1 (d, $J_{C\text{–}F}$ = 245.7 Hz), 136.9 (d, $J_{C\text{–}F}$ = 3.3 Hz), 132.1, 129.5 (d, $J_{C\text{–}F}$ = 8.7 Hz), 128.9 (d, $J_{C\text{–}F}$ = 8.7 Hz), 127.0, 125.4, 115.8 (d, $J_{C\text{–}F}$ = 21.2 Hz), 92.4 (C≡C), 84.1 (C≡C), 42.4 (CH); ^{19}F NMR (471 MHz, CDCl$_3$, 298 K) δ -62.82 (s, 3F, Ar–CF$_3$), -115.42 (s, 2F, Ar–F); IR ν_{max} (cm^{-1}): 3015, 2923, 2180 (C≡C), 1685, 1536, 1498, 1431, 1401, 1384, 1325, 1212, 1130, 1022; HRMS (ES+) [M+H]$^+$ [$C_{22}H_{14}F_5$]$^+$: calculated 373.1016, found 373.1019.

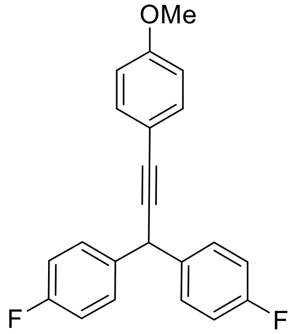
Synthesis of 4,4'-(3-phenylprop-2-yne-1,1-diyl)bis(fluorobenzene) (***4.2c***)[167]



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), phenylacetylene (12 mg, 0.12 mmol) and aryl ester **4.1a** (34 mg, 0.1 mmol) in THF to afford **4.2c**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2c**) was obtained as a white solid. Yield: 26 mg, 0.08 mmol, 84%.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.48–7.46 (m, 2H, Ar–H), 7.39–7.36 (m, 4H, Ar–H), 7.33–7.31 (m, 3H, Ar–H), 7.05–7.00 (m, 4H, Ar–H), 5.18 (s, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 162.0 (d, $J_{C–F}$ = 245.7 Hz), 137.5 (d, $J_{C–F}$ = 3.0 Hz), 131.8, 129.5 (d, $J_{C–F}$ = 8.1 Hz), 128.4, 128.4, 123.3, 115.6 (d, $J_{C–F}$ = 21.5 Hz), 89.8 (C≡C), 85.5 (C≡C), 42.4 (CH); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -115.81 (Ar–F); IR ν_{max} (cm^{-1}): 3002, 2921, 2188 (C≡C), 1602, 1522, 1454, 1435, 1321, 1311, 1254, 1218, 1152, 1028; HRMS (EI+) $[M]^+$ $[C_{21}H_{14}F_2]^+$: calculated 304.1064, found 304.1058.

Synthesis of 4,4'-(3-(4-methoxyphenyl)prop-2-yne-1,1-diyl)bis(fluorobenzene) (***4.2d***)[168]

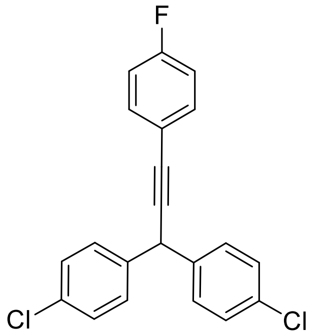


Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), 1-ethynyl-4-methoxybenzene (16 mg, 0.12 mmol) and aryl ester **4.1a** (34 mg, 0.1 mmol) in THF to afford **4.2d**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (92:08 v/v) as eluent. The desired compound (**4.2d**) was obtained as yellow liquid. Yield: 24 mg, 72%, 0.07 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.33–7.27 (m, 6H, Ar–H), 6.92 (d, *J* = 8.4 Hz, 4H, Ar–H), 6.76 (d, *J* = 8.4 Hz, 2H, Ar–H), 5.07 (s, 1H, CH), 3.72 (s, 3H, Ome);^{13}C NMR (101 MHz,

$CDCl_3$, 298 K) δ: 162.0 (d, $J_{C\text{–}F}$ = 245.6 Hz), 159.7, 137.7 (d, $J_{C\text{–}F}$ = 3.2 Hz), 133.2, 129.5 (d, $J_{C\text{–}F}$ = 8.0 Hz), 115.7, 115.5, 115.4, 114.0, 88.3 (C≡C), 85.3 (C≡C), 55.4 (Ome), 42.4 (CH); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -115.90 (Ar–F); IR ν_{max} (cm^{-1}): 3012, 2954, 2182 (C≡C), 1621, 1535, 1444, 1425, 1333, 1316, 1241, 1208, 1135, 1033; HRMS (ES+) $[M+H]^+$ $[C_{22}H_{17}F_2O]^+$: calculated 335.1247, found 335.1246.

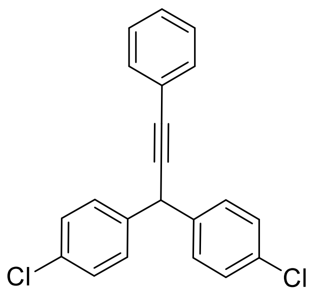
Synthesis of 4,4'-(3-(4-fluorophenyl)prop-2-yne-1,1-diyl)bis(chlorobenzene) (***4.2e***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-fluorobenzene (15 mg, 0.12 mmol) and aryl ester **4.1b** (37 mg, 0.1 mmol) in THF to afford **4.2e**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2e**) was obtained as colourless liquid. Yield: 27 mg, 77%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.44 (dd, J = 8.4, 5.4 Hz, 2H, Ar–H), 7.31 (q, J = 8.5 Hz, 8H, Ar–H), 7.01 (t, J = 8.5 Hz, 2H, Ar–H), 5.14 (s, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 162.6 (d, $J_{C\text{–}F}$ = 249.8 Hz), 139.8, 133.7 (d, $J_{C\text{–}F}$ = 8.7 Hz), 133.2, 129.2 (d, $J_{C\text{–}F}$ = 41.8 Hz), 115.7, 88.8 (C≡C), 84.6 (C≡C), 42.6 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -110.92 (Ar–F); IR ν_{max} (cm^{-1}): 3023, 2966, 2172 (C≡C), 1685, 1610, 1542, 1425, 1401, 1346, 1361, 1223, 1211, 1154, 1021; HRMS (ES+) $[M+H]^+$ $[C_{21}H_{14}Cl_2F]^+$: calculated 355.0457, found 355.0459.

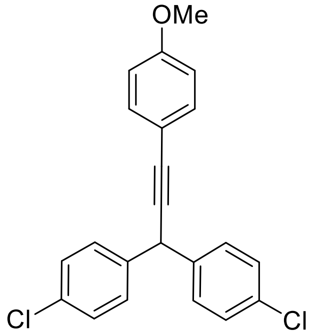
Synthesis of 4,4'-(3-phenylprop-2-yne-1,1-diyl)bis(chlorobenzene) (***4.2f***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), phenylacetylene (12 mg, 0.12 mmol) and aryl ester **4.1b** (37 mg, 0.1 mmol) in THF to afford **4.2f**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2f**) was obtained as yellow liquid. Yield: 28 mg, 83%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.48–7.44 (m, 2H, Ar–H), 7.37–7.29 (m, 11H, Ar– H), 5.15 (s, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ: 139.9, 133.1, 131.8, 129.3, 129.0, 128.5, 123.1, 89.1 (C≡C), 85.7 (C≡C), 42.7 (CH); IR ν_{max} (cm^{-1}): 3021, 2978, 2172 (C≡C), 1654, 1602, 1544, 1441, 1405, 1364, 1302, 1287, 1232, 1174, 1031; HRMS (EI+) [M]+ [$C_{21}H_{14}Cl_2$]: calculated 336.0473, found 336.0465.

Synthesis of 4,4'-(3-(4-methoxyphenyl)prop-2-yne-1,1-diyl)bis(chlorobenzene) (***4.2g***)

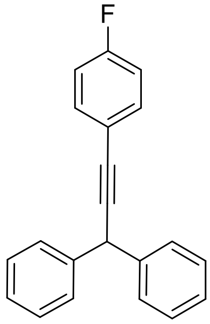


Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-methoxybenzene (16 mg, 0.12 mmol) and aryl ester **4.1b** (37 mg, 0.1 mmol) in THF to afford **4.2g**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2g**) was obtained as pale-yellow liquid. Yield: 27 mg, 77%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.81–7.58 (m, 4H, Ar–H), 7.55–7.45 (m, 4H, Ar–H), 7.41–7.38 (m, 1H, Ar–H), 7.30–7.29 (m, 1H, Ar–H), 7.03–6.77 (m, 2H, Ar–H), 5.13 (s, 1H, CH), 3.81 (s, 3H, OMe); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ: 159.7, 140.1, 139.3, 135.6, 133.2, 133.1, 131.5, 129.3, 128.9, 115.2, 114.1, 87.6 (C≡C), 85.6 (C≡C), 55.5 (OMe), 42.7

(CH); IR ν_{max} (cm^{-1}): 3023, 2987, 2174 (C≡C), 1654, 1578, 1456, 1433, 1378, 1305, 1256, 1215, 1147, 1032; HRMS (ES-) $[M-H]^-$ $[C_{22}H_{15}Cl_2O]^-$: calculated 365.0500, found 365.0493.

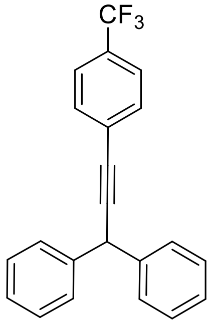
Synthesis of (3-(4-fluorophenyl)prop-2-yne-1,1-diyl)dibenzene (***4.2h***)[169]



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-fluorobenzene (15 mg, 0.12 mmol) and aryl ester **4.1c** (31 mg, 0.1 mmol) in THF to afford **4.2h**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (92:08 v/v) as eluent. The desired compound (**4.2h**) was obtained as a yellow oil. Yield: 23 mg, 80%, 0.08 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.39–7.35 (m, 5H, Ar–H), 7.25 (t, J = 7.7 Hz, 4H, Ar–H), 7.19–7.14 (m, 3H, Ar–H), 6.94–6.90 (m, 2H, Ar–H), 5.13 (s, 1H, CH);^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 162.5 (d, $J_{C–F}$ = 248.8 Hz), 141.8, 133.7 (d, $J_{C–F}$ = 8.4 Hz), 128.8, 128.0, 127.1, 119.7 (d, $J_{C–F}$ = 3.6 Hz), 115.6 (d, $J_{C–F}$ = 21.9 Hz), 90.0 (C≡C), 83.9 (C≡C), 43.8 (CH); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -111.55 (Ar–F); IR ν_{max} (cm^{-1}): 3030, 2969, 2180 (C≡C), 1630, 1545, 1465, 1402, 1329, 1332, 1245, 1221, 1144, 1028; HRMS (EI+) $[M]^+$ $[C_{21}H_{15}F]^+$: calculated 286.1158, found 286.1158.

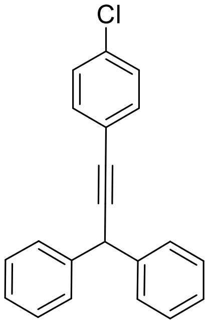
Synthesis of (3-(4-(trifluoromethyl)phenyl)prop-2-yne-1,1-diyl)dibenzene (***4.2i***)[170]



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-(trifluoromethyl)benzene (21 mg, 0.12 mmol) and aryl ester **4.1c** (31 mg, 0.1 mmol) in THF to afford **4.2i**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2i**) was obtained as an yellow oil. Yield: 20 mg, 60%, 0.06 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.57 (d, *J* = 1.1 Hz, 2H, Ar–H), 7.53–7.51 (m, 2H, Ar–H), 7.44–7.52 (m, 2H, Ar–H), 7.36–7.29 (m, 7H, Ar–H), 7.27 (td, *J* = 1.3, 0.3 Hz, 1H, Ar–H), 5.24 (s, 1H, CH);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 141.4, 134.1, 132.1, 129.7, 128.9, 128.7, 128.5, 128.0, 128.0, 127.9, 127.4, 127.2, 127.1, 125.3 (q, $J_{C\text{–}F}$ = 3.9 Hz), 93.1 (C≡C), 83.7 (C≡C), 43.9 (CH); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -62.78. (Ar–CF_3); IR ν_{max} (cm^{-1}): 3020, 2969, 2185 (C≡C), 1670, 1566, 1430, 1410, 1334, 1318, 1230, 1202, 1132, 1033; HRMS (EI+) $[M]^+$ $[C_{22}H_{15}F_3]^+$: calculated 336.1126, found 336.1119.

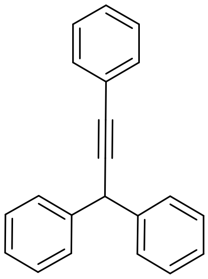
Synthesis of (3-(4-chlorophenyl)prop-2-yne-1,1-diyl)dibenzene (***4.2j***)[169]



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-chloro-4-ethynylbenzene (16 mg, 0.12 mmol) and aryl ester **4.1c** (31 mg, 0.1 mmol) in THF to afford **4.2j**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2j**) was obtained as a white solid. Yield: 24 mg, 81%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.38–7.30 (m, 6H, Ar–H), 7.28–7.22 (m, 4H, Ar–H), 7.21–7.14 (m, 4H, Ar–H), 5.13 (s, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 141.6, 134.1, 133.07, 128.8, 128.7, 128.0, 127.1, 122.1, 91.4 (C≡C), 83.9 (C≡C), 43.9 (CH); IR ν_{max} (cm^{-1}): 3022, 2945, 2178 (C≡C), 1655, 1578, 1502, 1444, 1361, 1341, 1277, 1145, 1102, 1031; HRMS (EI+) $[M]^+$ $[C_{21}H_{15}Cl]$: calculated 302.0862, found 302.0861.

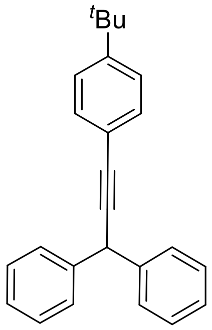
Synthesis of prop-2-yne-1,1,3-triyltribenzene (***4.2k***)[169]



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), phenyl acetylene (12 mg, 0.12 mmol) and aryl ester **4.1c** (31 mg, 0.1 mmol) in THF to afford **4.2k**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2k**) was obtained as white solid. Yield: 23 mg, 85%, 0.08 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.50–7.44 (m, 6H, Ar–H), 7.35–7.30 (m, 7H, Ar–H), 7.25–7.22 (m, 2H, Ar–H), 5.22 (s, 1H, CH);^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 141.9, 131.3, 128.8, 128.4, 128.1, 128.0, 127.04, 123.6, 90.3 (C≡C), 85.0 (C≡C), 43.9 (CH); IR ν_{max} (cm^{-1}): 3010, 2915, 2181 (C≡C), 1645, 1528, 1415, 1364, 1328, 1254, 1189, 1142, 1082, 1025; HRMS (EI+) [M]$^+$ [C$_{21}$H$_{16}$]$^+$: calculated 268.1252, found 268.1247.

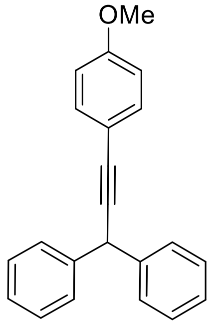
Synthesis of (3-(4-(tert-butyl)phenyl)prop-2-yne-1,1-diyl)dibenzene (***4.2l***)[171]



Synthesised in accordance with *General procedure f* using B(C$_6$F$_5$)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), 1-(*tert*-butyl)-4-ethynylbenzene (19 mg, 0.12 mmol) and aryl ester **4.1c** (31 mg, 0.1 mmol) in THF to afford **4.2l**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2l**) was obtained as white solid. Yield: 26 mg, 79%, 0.08 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.46–7.42 (m, 6H, Ar–H), 7.34–7.31 (m, 6H, Ar–H), 7.25–7.22 (m, 2H, Ar–H), 5.21 (s, 1H, CH), 1.31 (s, 9H, Me);^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 151.3, 142.0, 137.7, 134.1, 132.6, 131.5, 130.2, 129.7, 128.7, 128.4, 128.0, 127.9, 127.0, 125.4, 120.6, 89.6(C≡C), 85.1(C≡C), 43.9 (CH), 34.9 (quaternary C), 31.3 (Me); IR ν_{max} (cm^{-1}): 3025, 2975, 2182 (C≡C), 1603, 1565, 1455, 1332, 1302, 1278, 1220, 1177, 1132, 1025; HRMS (EI+) [M]$^+$ [C$_{25}$H$_{24}$]$^+$: calculated 324.1878, found 324.1872.

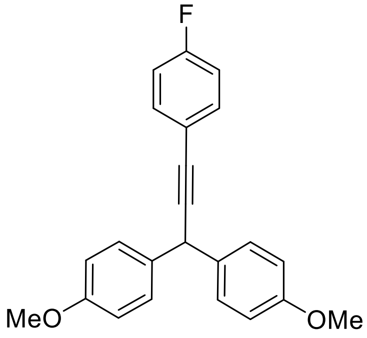
Synthesis of (3-(4-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (***4.2m***)[170]



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-methoxybenzene (16 mg, 0.12 mmol) and aryl ester **4.1c** (31 mg, 0.1 mmol) in THF to afford **4.2m**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:02 v/v) as eluent. The desired compound (**4.2m**) was obtained as yellow liquid. Yield: 22 mg, 75%, 0.07 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.38–7.32 (m, 6H, Ar–H), 7.27–7.22 (m, 4H, Ar–H), 7.17–7.13 (m, 2H, Ar–H), 6.77–6.74 (m, 2H, Ar–H), 5.12 (s, 1H, CH), 3.72 (s, 3H, OMe);^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 159.5, 142.1, 133.2, 128.7, 128.0, 127.0, 115.8, 114.0, 88.8 (C≡C), 84.8 (C≡C), 55.4 (OMe), 43.9 (CH); IR ν_{max} (cm^{-1}): 3017, 2181 (C≡C), 1668, 1525, 1421, 1367, 1255, 1235, 1165, 1118, 1033; HRMS (EI+) $[M]^+$ $[C_{22}H_{18}O]^+$: calculated 298.1358, found 298.1353.

Synthesis of 4,4'-(3-(4-fluorophenyl)prop-2-yne-1,1-diyl)bis(methoxybenzene) (***4.2n***)

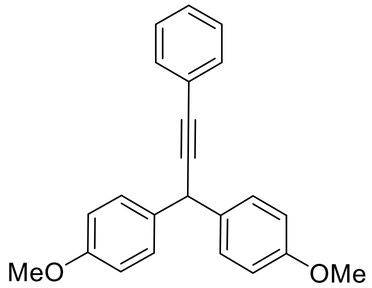


Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-fluorobenzene (15 mg, 0.12 mmol) and aryl ester **4.1d** (37 mg, 0.1 mmol) in THF to afford **4.2n**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:02 v/v) as eluent. The desired compound (**4.2n**) was obtained as yellow liquid. Yield: 25 mg, 73%, 0.07 mmol,

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.45–7.40 (m, 2H, Ar–H), 7.33–7.30 (m, 4H, Ar–H), 7.01–6.97 (m, 2H, Ar–H), 6.87–6.84 (m, 4H, Ar–H), 5.11 (s, 1H, CH), 3.79 (s, 6H, OMe);^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 162.4 (d, $J_{C–F}$ = 248.7 Hz), 158.6, 134.3, 133.6 (d, $J_{C–F}$ = 8.3 Hz), 128.9, 115.6 (d, $J_{C–F}$ = 21.9 Hz), 114.1, 90.6 (C≡C), 83.6 (C≡C), 55.4 (OMe), 42.1

(CH); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -111.71 (Ar–F); IR ν_{max} (cm^{-1}): 3003, 2927, 2186 (C≡C), 1635, 1546, 1454, 1387, 1324, 1232, 1222, 1131, 1165, 1043; HRMS (EI+) $[M]^+$ $[C_{23}H_{20}FO_2]^+$: calculated 347.1447, found 347.1443.

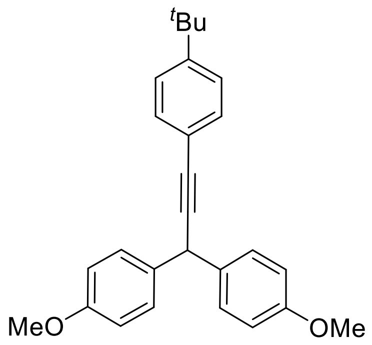
Synthesis of 4,4'-(3-phenylprop-2-yne-1,1-diyl)bis(methoxybenzene) (***4.2o***)[172]



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), phenyl acetylene (12 mg, 0.12 mmol) and aryl ester **4.1d** (37 mg, 0.1 mmol) in THF to afford **4.2o**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:02 v/v) as eluent. The desired compound (**4.2o**) was obtained as yellow oil. Yield: 25 mg, 76%, 0.08 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.48–7.43 (m, 3H, Ar–H), 7.35–7.29 (m, 7H, Ar–H), 6.86 (d, *J* = 8.3 Hz, 1H, Ar–H), 5.13 (s, 1H, CH), 3.79 (s, 6H, OMe);^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 158.6, 134.4, 131.8, 131.8, 129.9, 128.9, 128.3, 128.2, 128.0, 123.7, 114.1, 90.9 (C≡C), 84.7 (C≡C), 55.4 (OMe), 42.2 (CH); IR ν_{max} (cm^{-1}): 3022, 2956, 2185 (C≡C), 1647, 1510, 1433, 1325, 1287, 1215, 1130, 1156, 1033; HRMS (EI+) $[M]^+$ $[C_{23}H_{21}O_2]^+$: calculated 329.1542, found 329.1537.

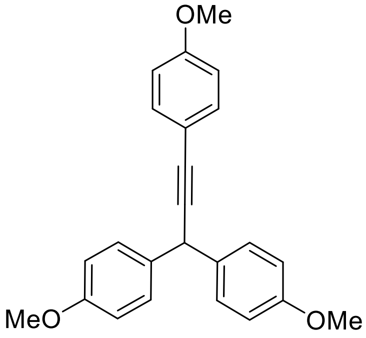
Synthesis of 4,4'-(3-(4-(tert-butyl)phenyl)prop-2-yne-1,1-diyl)bis(methoxybenzene) (***4.2p***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-(*tert*-butyl)-4-ethynylbenzene (19 mg, 0.12 mmol) and aryl ester **4.1d** (37 mg, 0.1 mmol) in THF to afford **4.2p**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:02 v/v) as eluent. The desired compound (**4.2p**) was obtained as yellow oil. Yield: 28 mg, 72%, 0.07 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.41–7.40 (m, 2H, Ar–H), 7.34–7.31 (m, 6H, Ar–H), 6.87–6.84 (m, 4H, Ar–H), 5.11 (s, 1H. CH), 3.79 (s, 6H, OMe), 1.31 (s, 9H, Me);^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 158.5, 151.3, 134.6, 131.5, 129.0, 125.3, 120.7, 114.1, 90.2 (C≡C), 84.7 (C≡C), 55.4 (OMe), 42.2 (CH), 34.9 (quaternary C), 31.3 (Me); IR ν_{max} (cm^{-1}): 3003, 2933, 2180 (C≡C), 1623, 1545, 1453, 1378, 1322, 1244, 1231, 1178, 1105, 1031; HRMS (EI+) [M]$^+$ [$C_{27}H_{28}O_2$]$^+$: calculated 384.2089, found 384.2084.

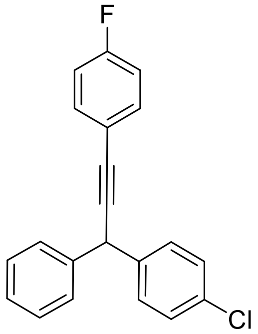
Synthesis of 4,4',4''-(prop-2-yne-1,1,3-triyl)tris(methoxybenzene) (***4.2q***)



Synthesised in accordance with *General procedure f* using B(C$_6$F$_5$)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), 1-ethynyl-4-methoxybenzene (16 mg, 0.12 mmol) and aryl ester **4.1d** (37 mg, 0.1 mmol) in THF to afford **4.2q**. The crude reaction mixture was purified via preparative thin layer chromatography using hexane/ethyl acetate (92:08 v/v) as eluent. The desired compound (**4.2q**) was obtained as pale-yellow oil. Yield: 25 mg, 70%, 0.07 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.42–7.39 (m, 2H, Ar–H), 7.36–7.32 (m, 4H, Ar–H), 6.88– 6.82 (m, 3H, Ar–H), 5.12 (s, 1H, Ar–H), 3.81 (s, 3H, OMe), 3.79 (s, 6H, OMe);^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 159.4, 158.5, 134.6, 133.1, 128.9, 115.9, 114.1, 89.4 (C≡C), 84.4 (C≡C), 55.4 (OMe), 42.2 (CH); IR ν_{max} (cm^{-1}): 3010, 2954, 2184 (C≡C), 1645, 1514, 1465, 1366, 1330, 1265, 1210, 1134, 1110, 1033; HRMS (ES+) [M+H]$^+$ [$C_{24}H_{23}O_3$]$^+$: calculated 359.1647, found 359.1652.

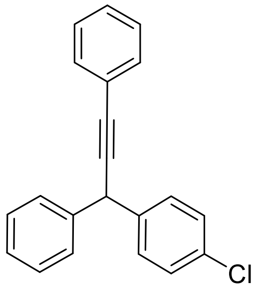
Synthesis of 1-chloro-4-(3-(4-fluorophenyl)-1-phenylprop-2-yn-1-yl)benzene (***4.2r***)



Synthesised in accordance with *General procedure f* using B(C_6F_5)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), 1-ethynyl-4-fluorobenzene (15 mg, 0.12 mmol) and aryl ester **4.1e** (34 mg, 0.1 mmol) in THF to afford **4.2r**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:02 v/v) as eluent. The desired compound (**4.2r**) was obtained as pale-yellow liquid. Yield: 25 mg, 78%, 0.08 mmol.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ: 7.46–7.39 (m, 3H, Ar–H), 7.37–7.28 (m, 8H, Ar–H), 7.03–6.98 (m, 2H, Ar–H), 5.17 (s, 1H, CH);^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ: 162.6 (d, $J_{C\text{–}F}$ = 249.1 Hz), 141.3, 140.3, 133.7 (d, $J_{C\text{–}F}$ = 8.4 Hz), 132.9, 129.4, 128.9, 128.8, 128.7, 128.7, 128.7, 128.6, 127.9, 127.3, 127.2, 119.4 (d, $J_{C\text{–}F}$ = 3.5 Hz), 115.7 (d, $J_{C\text{–}F}$ = 22.0 Hz), 89.4 (C≡C), 84.3 (C≡C), 43.2 (CH); ^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ: -111.24 (Ar–F); IR ν_{max} (cm^{-1}): 3005, 2984, 2180 (C≡C), 1622, 1542, 1431, 1321, 1298, 1232, 1254, 1127, 1103, 1031; HRMS (ES+) [M+H]$^+$ [$C_{21}H_{15}ClF$]$^+$: calculated 321.0846, found 321.0847.

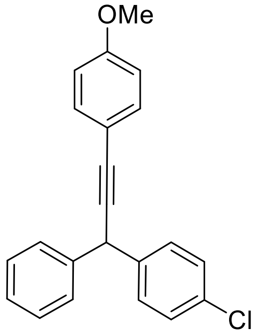
Synthesis of 3-(4-chlorophenyl)prop-1-yne-1,3-diyl dibenzene (***4.2s***)[169]



Synthesised in accordance with *General procedure f* using B(C_6F_5)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), phenyl acetylene (12 mg, 0.12 mmol) and aryl ester **4.1e** (34 mg, 0.1 mmol) in THF to afford **4.2s**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2s**) was obtained as yellow liquid. Yield: 24 mg, 79%, 0.08 mmol.

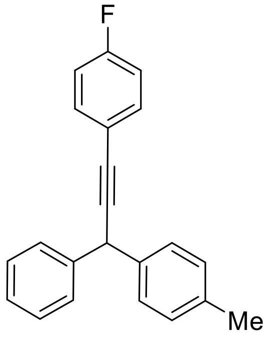
^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.41–7.38 (m, 2H, Ar–H), 7.35–7.32 (m, 2H, Ar–H), 7.31–7.2 8(m, 2H, Ar–H), 7.27–7.22 (m, 7H, Ar–H), 7.21–7.18 (m, 1H, Ar–H), 7.18–7.15 (m, 1H, Ar–H), 5.10 (s, 1H, CH);^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 141.4, 140.4, 132.9, 131.8, 129.4, 128.9, 128.4, 128.3, 128.0, 127.3, 125.9, 123.4, 89.7 (C≡C), 85.4 (C≡C), 43.3 (CH); IR ν_{max} (cm^{-1}): 3023, 2965, 2181 (C≡C), 1665, 1530, 1456, 1333, 1254, 1175, 1142, 1033; HRMS (EI+) [M]$^+$ [$C_{21}H_{15}Cl$]$^+$: calculated 302.0862, found 302.0860.

*Synthesis of 1-chloro-4-(3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-yl)benzene (**4.2t**)*



Synthesised in accordance with *General procedure f* using B(C_6F_5)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), 1-ethynyl-4-methoxybenzene (16 mg, 0.12 mmol) and aryl ester **4.1e** (34 mg, 0.1 mmol) in THF to afford **4.2t**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2t**) was obtained as yellow liquid. Yield: 23 mg, 69%, 0.07 mmol. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.42–7.38 (m, 4H, Ar–H), 7.36–7.31 (m, 4H, Ar–H), 7.30–7.27 (m, 2H, Ar–H), 7.25–7.24 (m, 1H, Ar–H), 6.86– 6.83 (m, 2H, Ar–H), 5.16 (s, 1H, CH), 3.81 (s, 3H, OMe);^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 159.6, 141.6, 140.7, 133.2, 132.8, 129.4, 128.8, 128.0, 127.2, 115.5, 114.0, 88.2 (C≡C), 85.2 (C≡C), 55.4 (OMe), 43.3 (CH); IR ν_{max} (cm^{-1}): 3030, 2947, 2182 (C≡C), 1644, 1556, 1430, 1341, 1277, 1195, 1114, 1025; HRMS (EI+) [M]$^+$ [$C_{22}H_{17}ClO$]$^+$: calculated 332.0968, found 332.0972.

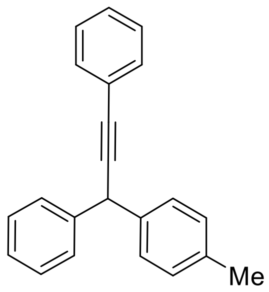
*Synthesis of 1-fluoro-4-(3-phenyl-3-(p-tolyl)prop-1-yn-1-yl)benzene (**4.2u**)*



Synthesised in accordance with *General procedure f* using B(C_6F_5)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), 1-ethynyl-4-fluorobenzene (15 mg, 0.12 mmol) and aryl ester **4.1f** (32 mg, 0.1 mmol) in THF to afford **4.2u**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2u**) was obtained as pale-yellow liquid. Yield: 23 mg, 76%, 0.08 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.46–7.41 (m, 4H, Ar–H), 7.32 (dd, *J* = 8.4, 7.3 Hz, 4H, Ar–H), 7.25–7.21 (m, 1H, Ar–H), 7.13 (d, *J* = 7.8 Hz, 2H, Ar–H), 7.02–6.97 (m, 2H, , Ar–H), 5.16 (s, 1H, CH), 2.32 (s, 3H, Me);^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 161.2 (d, $J_{C–F}$ = 249.1 Hz) 142.0, 138.9, 136.7, 133.6 (d, $J_{C–F}$ = 8.3 Hz), 129.5, 128.8, 127.9 (d, $J_{C–F}$ = 7.8 Hz), 127.0, 115.6 (d, $J_{C–F}$ = 22.0 Hz), 90.2 (C≡C), 83.7 (C≡C), 43.4 (CH), 21.2 (Me); ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ: -111.67 (Ar–F); IR ν_{max} (cm^{-1}): 3021, 2902, 2172 (C≡C), 1687, 1532, 1421, 1333, 1298, 1221, 1177, 1121, 1030; HRMS (ES+) $[M+H]^+$ $[C_{22}H_{18}F]^+$: calculated 301.1393, found 301.1397.

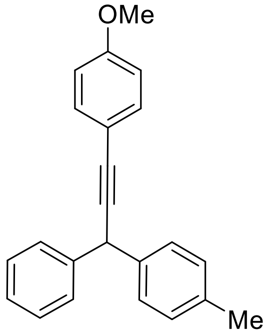
Synthesis of 3-(p-tolyl)prop-1-yne-1,3-diyl dibenzene (***4.2v***)[169]



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), phenyl acetylene (12 mg, 0.12 mmol) and aryl ester **4.1f** (32 mg, 0.1 mmol) in THF to afford **4.2v**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2v**) was obtained as yellow liquid. Yield: 23 mg, 80%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.49–7.47 (m, 2H, Ar–H), 7.45–7.43 (m, 2H, Ar–H), 7.34–7.29 (m, 7H, Ar–H), 7.25–7.21 (m, 1H, Ar–H), 7.14–7.13 (m, 2H, Ar–H), 5.18 (s, 1H, CH), 2.33 (s, 3H, Me);^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 142.1, 139.0, 136.6, 131.8, 129.4, 128.7, 128.3, 128.1, 128.0, 127.9, 127.0, 123.7, 90.5 (C≡C), 84.8 (C≡C), 43.5 (CH), 21.9 (Me); IR ν_{max} (cm^{-1}): 3001, 2932, 2173 (C≡C), 1656, 1534, 1471, 1341, 1287, 1235, 1165, 1033; HRMS (EI+) $[M]^+$ $[C_{22}H_{18}]^+$: calculated 282.1409, found 282.1404.

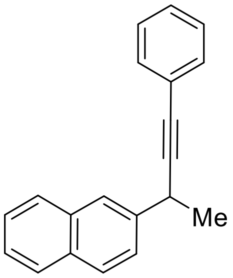
Synthesis of 1-methoxy-4-(3-phenyl-3-(p-tolyl)prop-1-yn-1-yl)benzene (***4.2w***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-methoxybenzene (16 mg, 0.12 mmol) and aryl ester **4.1f** (32 mg, 0.1 mmol) in THF to afford **4.2w**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (97:03 v/v) as eluent. The desired compound (**4.2w**) was obtained as a white solid. Yield: 23 mg, 80%, 0.08 mmol.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.38–7.32 (m, 4H, Ar–H), 7.27–7.22 (m, 4H, Ar–H), 7.19–7.14 (m, 1H, Ar–H), 7.07–7.04 (m, 2H, Ar–H), 6.77–6.74 (m, 2H, Ar–H), 5.09 (s, 1H, CH), 3.73 (s, 3H, OMe), 2.24 (s, 3H, Me);^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ: 159.5, 142.3, 139.2, 136.6, 133.2, 129.4, 128.7, 128.0, 127.9, 126.9, 115.9, 114.0, 89.0 (C≡C), 84.6 (C≡C), 55.4 (OMe), 43.5 (CH), 21.2 (Me); IR ν_{max} (cm^{-1}): 3001, 2912, 2177 (C≡C), 1588, 1465, 1333, 1256, 1201, 1134, 1030; HRMS (ES+) $[M+H]^+$ $[C_{23}H_{21}O]^+$: calculated 313.1592, found 313.1596.

Synthesis of 2-(4-phenylbut-3-yn-2-yl)naphthalene (***4.2x***)[173]

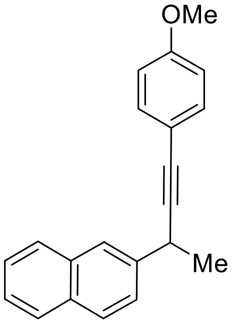


Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), phenyl acetylene (12 mg, 0.12 mmol) and aryl ester **4.1g** (30 mg, 0.1 mmol) in THF to afford **4.2x**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2x**) was obtained as colourless liquid. Yield: 16 mg, 61%, 0.06 mmol,

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.89 (dd, J = 1.7, 0.8 Hz, 1H, Ar–H), 7.85–7.81 (m, 3H, Ar–H), 7.58 (dd, J = 8.1 Hz, 4.2 Hz, 1H), 7.49–7.43 (m, 4H, Ar–H), 7.32–7.29 (m, 3H, Ar–H), 4.16 (q, J = 7.2 Hz, 1H), 1.67 (d, J = 7.1 Hz, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ:

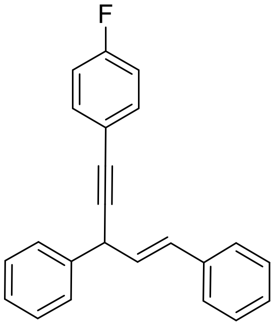
140.8, 133.7, 132.6, 131.8, 128.4, 128.4, 128.1, 127.9, 127.9, 127.8, 127.7, 126.2, 125.7, 125.7, 125.3, 123.9, 92.7 (C≡C), 82.8 (C≡C), 32.8 (CH), 24.5 (Me); IR ν_{max} (cm^{-1}): 3033, 2914, 2177 (C≡C), 1654, 1566, 1432, 1357, 1269, 1278, 1145, 1101, 1033; HRMS (ES+) $[M+H]^+$ $[C_{21}H_{19}O]^+$: calculated 287.1436, found 287.1439.

Synthesis of 2-(4-(4-methoxyphenyl)but-3-yn-2-yl)naphthalene (***4.2y***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-methoxybenzene (16 mg, 0.12 mmol) and aryl ester **4.1g** (30 mg, 0.1 mmol) in THF to afford **4.2y**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2y**) was obtained as colourless liquid. Yield: 19 mg, 0.06 mmol, 65%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.89 (s, 1H, Ar–H), 7.85–7.82 (m, 2H, Ar–H), 7.58 (dd, *J* = 8.6, 1.8 Hz, 1H, Ar–H), 7.50–7.38 (m, 5H, Ar–H), 6.85–6.83 (m, 2H, Ar–H), 4.14 (q, *J* = 7.1 Hz, 1H, CH), 3.81 (s, 1H, OCH_3), 1.66 (d, *J* = 7.1 Hz, 1H, CH_3);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 159.4, 141.1, 133.7, 133.1, 132.5, 129.4, 128.8, 128.4, 128.0, 127.9, 127.7, 126.2, 125.8, 125.7, 125.2, 116.0, 114.0, 91.1 (C≡C), 82.5 (C≡C), 55.4 (OMe), 32.8, (CH), 24.6 (Me); IR ν_{max} (cm^{-1}): 3021, 2902, 2175 (C≡C), 1687, 1532, 1421, 1333, 1298, 1221, 1177, 1121, 1030; HRMS (ES+) $[M+H]^+$ $[C_{21}H_{19}O]^+$: calculated 287.1436, found 287.1439.

Synthesis of (E)-(5-(4-fluorophenyl)pent-1-en-4-yne-1,3-diyl)dibenzene (***4.2z***)[174]

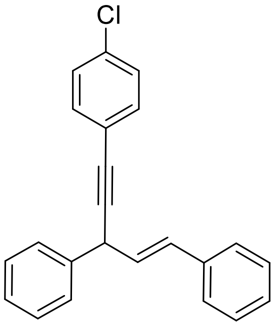


Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-fluorobenzene (15 mg, 0.12 mmol) and aryl ester **4.1k** (31 mg, 0.1 mmol) in THF to afford **4.2z**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate

(95:05 v/v) as eluent. The desired compound (**4.2z**) was obtained as colourless liquid. Yield: 27 mg, 88%, 0.09 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.49–7.45 (m, 4H, Ar–H), 7.41–7.35 (m, 4H, Ar–H), 7.32–7.27 (m, 3H, Ar–H), 7.24–7.21 (m, 1H, Ar–H), 7.03–6.99 (m, 2H, Ar–H), 6.76 (dd, *J* = 15.7, 1.5 Hz, 1H, CH_2), 6.33 (dd, *J* = 15.7, 6.6 Hz, 1H, CH_2), 4.74 (d, *J* = 6.6 Hz, 1H, CH);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 162.5 (d, $J_{C–F}$ = 248.9 Hz), 140.3, 136.9, 133.7 (d, $J_{C–F}$ = 8.3 Hz), 130.7, 129.6, 128.9, 128.7, 127.9, 127.7, 127.3, 126.7, 119.6 (d, $J_{C–F}$ = 3.5 Hz), 115.6 (d, $J_{C–F}$ = 22.0 Hz), 88.7 (C≡C), 84.4 (C≡C), 41.3 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -111.52 (Ar–F); IR ν_{max} (cm^{-1}): 2998, 2895, 2173 (C≡C), 1650 (C=C), 1521, 1487, 1378, 1305, 1277, 1205, 1165, 1031; HRMS (EI+) $[M]^+$ $[C_{23}H_{17}F]^+$: calculated 312.1314, found 312.1319.

Synthesis of (E)-(5-(4-chlorophenyl)pent-1-en-4-yne-1,3-diyl)dibenzene (***4.2aa***)

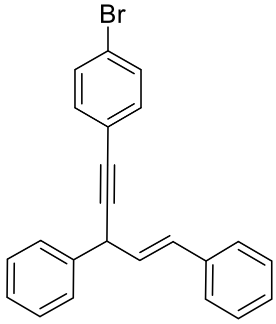


Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-chloro-4-ethynylbenzene (16 mg, 0.12 mmol) and aryl ester **4.1k** (31 mg, 0.1 mmol) in THF to afford **4.2aa**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2aa**) was obtained as pale-yellow liquid. Yield: 28 mg, 85%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.49–7.46 (m, 2H, Ar–H), 7.43–7.35 (m, 6H, Ar–H), 7.32–7.27 (m, 5H, Ar–H), 7.25–7.21 (m, 1H, Ar–H), 6.75 (dd, *J* = 15.7, 1.5 Hz, 1H, CH_2), 6.33 (dd, *J* = 15.7, 6.6 Hz, 1H, CH_2), 4.74 (d, *J* = 5.2 Hz, 1H, CH);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 140.2, 136.9, 134.2, 133.1, 130.7, 129.5, 128.9, 128.7, 128.7, 127.9, 127.8, 127.3, 126.7, 122.1, 90.1 (C≡C), 84.4 (C≡C), 41.4 (CH); IR ν_{max} (cm^{-1}): 3001, 2968, 2170 (C≡C), 1645

(C=C), 1578, 1467, 1357, 1341, 1265, 1212, 1137, 1030; HRMS (EI+) $[M]^+$ $[C_{23}H_{17}Cl]^+$: calculated 328.1019, found 328.1022.

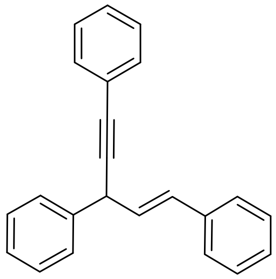
Synthesis of (E)-(5-(4-bromophenyl)pent-1-en-4-yne-1,3-diyl)dibenzene (***4.2ab***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-bromo-4-ethynylbenzene (22 mg, 0.12 mmol) and aryl ester **4.1k** (31 mg, 0.1 mmol) in THF to afford **4.2ab**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2ab**) was obtained as pale-yellow liquid. Yield: 30 mg, 81%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.48–7.44 (m, 4H, Ar–H), 7.40–7.34 (m, 6H, Ar–H), 7.32–7.27 (m, 3H, Ar–H), 7.25–7.21 (m, 1H, Ar–H), 6.74 (dd, *J* = 15.7, 1.5 Hz, 1H, CH_2), 6.33 (dd, *J* = 15.6, 6.6 Hz, 1H, CH_2), 4.73 (d, *J* = 5.4 Hz, 1H, CH);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 140.2, 136.9, 133.3, 131.6, 130.8, 129.4, 128.9, 128.7, 127.9, 127.8, 127.3, 126.7, 122.5, 122.3, 90.3 (C≡C), 84.5 (C≡C), 41.4 (CH); IR ν_{max} (cm^{-1}): 3011, 2981, 2171 (C≡C), 1655 (C=C), 1535, 1418, 1377, 1332, 1259, 1249, 1141, 1033; HRMS (EI+) $[M]^+$ $[C_{23}H_{17}Br]^+$: calculated 372.0514, found 372.0519.

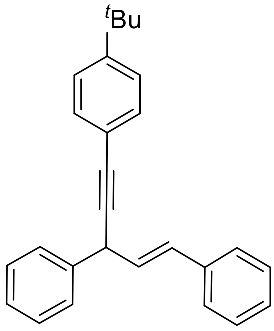
Synthesis of €-pent-1-en-4-yne-1,3,5-triyltribenzene (***4.2ac***)[174]



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), phenyl acetylene (22 mg, 0.12 mmol) and aryl ester **4.1k** (31 mg, 0.1 mmol) in THF to afford **4.2ac**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2ac**) was obtained as colourless liquid. Yield: 24 mg, 83%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.51–7.49 (m, 4H, Ar–H), 7.41–7.36 (m, 4H, Ar–H), 7.33–7.27 (m, 6H, Ar–H), 7.24–7.21 (m, 1H, Ar–H), 6.78 (dd, *J* = 15.7, 1.5 Hz, 1H, CH_2), 6.35 (dd, *J* = 15.6, 6.6 Hz, 1H, CH_2), 4.76 (d, *J* = 6.6 Hz, 1H, CH_2);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 140.4, 137.0, 131.8, 130.6, 129.8, 128.9, 128.7, 128.4, 128.2, 127.9, 127.7, 127.2, 126.7, 123.6, 89.0 (C≡C), 85.5 (C≡C), 41.4 (CH); IR ν_{max} (cm^{-1}): 3023, 2974, 2171 (C≡C), 1652 (C=C), 1532, 1425, 1364, 1314, 1251, 1222, 1140, 1028; HRMS (EI+) $[M]^+$ $[C_{23}H_{18}]^+$: calculated 294.1409, found 294.1412.

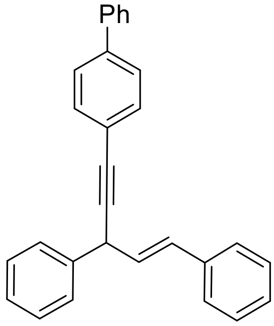
Synthesis of €-(5-(4-(tert-butyl)phenyl)pent-1-en-4-yne-1,3-diyl)dibenzene (***4.2ad***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-(*tert*-butyl)-4-ethynylbenzene (19 mg, 0.12 mmol) and aryl ester **4.1k** (31 mg, 0.1 mmol) in THF to afford **4.2ad**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2ad**) was obtained as white solid. Yield: 27 mg, 78%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.52–7.50 (m, 2H, Ar–H), 7.46–7.44 (m, 2H, Ar–H), 7.42–7.39 (m, 2H, Ar–H), 7.37–7.34 (m, 4H, Ar–H), 7.33–7.29 (m, 3H, Ar–H), 7.25–7.22 (m, 1H, Ar–H), 6.79 (d, *J* = 15.6 Hz, 1H, CH_2), 6.35 (dd, *J* = 15.6, 6.5 Hz, 1H, CH_2), 4.76 (d, *J* = 6.5 Hz, 1H, CH), 1.33 (s, 9H, Me);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 151.4, 140.6, 137.0, 131.5, 130.5, 123.0, 128.8, 128.7, 127.9, 127.6, 127.2, 126.7, 125.4, 120.6, 88.2 (C≡C), 85.6 (C≡C), 41.4 (CH), 34.9 (quaternary C), 31.3 (Me); IR ν_{max} (cm^{-1}): 3023, 2984, 2177 (C≡C), 1648 (C=C), 1498, 1461, 1351, 1314, 1237, 1202, 1177, 1028; HRMS (ES+) $[M+H]^+$ $[C_{27}H_{27}]^+$: calculated 351.2113, found 351.2111.

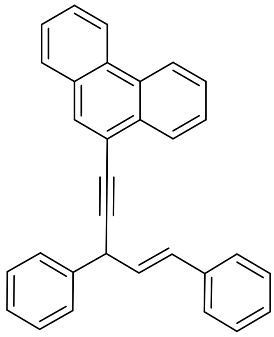
Synthesis of €-4-(3,5-diphenylpent-4-en-1-yn-1-yl)-1,1'-biphenyl (***4.2ae***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 4-ethynyl-1,1'-biphenyl (21 mg, 0.12 mmol) and aryl ester **4.1k** (31 mg, 0.1 mmol) in THF to afford **4.2ae**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2ae**) was obtained as colourless liquid. Yield: 30 mg, 82%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.62–7.60 (m, 2H, Ar–H), 7.58 (d, *J* = 0.7 Hz, 3H, Ar–H), 7.54–7.52 (m, 2H, Ar–H), 7.48–7.35 (m, 6H, Ar–H), 7.34– 7.27 (m, 4H, Ar–H), 7.25– 7.10 (m, 2H, Ar–H), 6.81 (dd, *J* = 15.7, 1.5 Hz, 1H, CH_2), 6.37 (dd, *J* = 15.6, 6.6 Hz, 1H, CH_2), 4.79 (dd, *J* = 6.6, 1.4 Hz, 1H, CH);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 140.9, 140.6, 140.4, 137.0, 132.3, 130.6, 129.8, 129.0, 128.8, 128.7, 127.9, 127.7, 127.6, 127.3, 127.2, 127.1, 126.7, 122.5, 89.7 (C≡C), 85.4 (C≡C), 41.5 (CH); IR ν_{max} (cm^{-1}): 3009, 2974, 2174 (C≡C), 1647 (C=C), 1503, 1477, 1337, 1323, 1237, 1242, 1156, 1038; HRMS (ES+) $[M+H]^+$ $[C_{29}H_{23}]^+$: calculated 371.1800, found 371.1803.

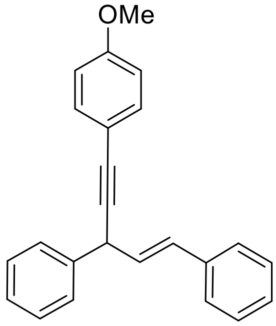
Synthesis of €-9-(3,5-diphenylpent-4-en-1-yn-1-yl)phenanthrene (***4.2af***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 9-ethynylphenanthrene (24 mg, 0.12 mmol) and aryl ester **4.1k** (31 mg, 0.1 mmol) in THF to afford **4.2af**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2af**) was obtained as a white solid. Yield: 35 mg, 89%, 0.09 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.58–8.52 (m, 2H, Ar–H), 8.40–8.39 (m, 1H, Ar–H), 7.94 (s, 1H, Ar–H), 7.73 (dt, *J* = 8.1, 3.8 Hz, 1H, Ar–H), 7.58–7.46 (m, 6H, Ar–H), 7.34–7.30 (m, 4H, Ar–H), 7.23–7.20 (m, 3H, Ar–H), 7.15–7.11 (m, 1H, Ar–H), 6.81 (dd, *J* = 15.7, 1.4 Hz, 1H, CH_2), 6.36 (dd, *J* = 15.6, 6.5 Hz, 1H, CH_2), 4.85 (dd, *J* = 6.6, 1.5 Hz, 1H, CH);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 140.5, 137.0, 131.9, 131.5, 131.4, 130.8, 130.3, 130.2, 129.8, 129.0, 128.7, 128.6, 128.0, 127.7, 127.4, 127.3 127.2, 127.1, 127.0, 126.72, 122.9, 122.7, 119.9, 93.6 (C≡C) 83.8 (C≡C), 41.8 (CH); IR ν_{max} (cm^{-1}): 3015, 2987, 2178 (C≡C), 1644 (C=C), 1533, 1481, 1351, 1333, 1245, 1230, 1151, 1033; HRMS (ES+) $[M+H]^+$ $[C_{31}H_{23}]^+$: calculated 395.1800, found 395.1805.

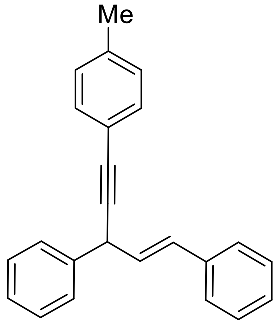
Synthesis of (E)-(5-(4-methoxyphenyl)pent-1-en-4-yne-1,3-diyl)dibenzene (***4.2ag***)[174]



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-methoxybenzene (16 mg, 0.12 mmol) and aryl ester **4.1k** (31 mg, 0.1 mmol) in THF to afford **4.2ag**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (92:08 v/v) as eluent. The desired compound (**4.2ag**) was obtained as colourless liquid. Yield: 23 mg, 72%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.52–7.50 (m, 2H, Ar–H), 7.46–7.44 (m, 2H, Ar–H), 7.42–7.37 (m, 4H, Ar–H), 7.33–7.29 (m, 3H, Ar–H), 7.25–7.22 (m, 1H, Ar–H), 6.88–6.85 (m, 2H, Ar–H), 6.79 (dd, *J* = 15.6, 1.5 Hz, 1H, CH_2), 6.36 (dd, *J* = 15.6, 6.6 Hz, 1H, CH_2), 4.76 (d, *J* = 6.2 Hz, 1H, CH), 3.82 (s, 3H, OMe);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 159.5, 140.6, 137.0, 133.2, 130.4, 130.0, 128.8, 128.6, 127.9, 127.6, 127.2, 126.6, 115.7, 114.0, 87.4 (C≡C), 85.3 (C≡C), 55.4 (OMe), 41.4 (CH); IR ν_{max} (cm^{-1}): 3009, 2978, 2171 (C≡C), 1655 (C=C), 1545, 1471, 1332, 1303, 1211, 1137, 1031; HRMS (ES+) $[M+H]^+$ $[C_{24}H_{21}O]^+$: calculated 325.1592, found 325.1595.

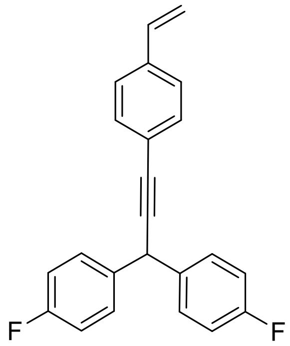
Synthesis of €-(5-(p-tolyl)pent-1-en-4-yne-1,3-diyl)dibenzene (***4.2ah***)[174]



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-ethynyl-4-methylbenzene (14 mg, 0.12 mmol) and aryl ester **4.1k** (31 mg, 0.1 mmol) in THF to afford **4.2ah**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. The desired compound (**4.2ah**) was obtained as colourless liquid. Yield: 26 mg, 84%, 0.08 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.52–7.49 (m, 2H, Ar–H), 7.41–7.36 (m, 6H, Ar–H), 7.33–7.28 (m, 3H, Ar–H), 7.25–7.21 (m, 1H, Ar–H), 7.13 (dt, *J* = 7.8, 0.7 Hz, 2H, Ar–H), 6.78 (dd, *J* = 15.7, 1.5 Hz, 1H, CH_2), 6.35 (dd, *J* = 15.7, 6.6 Hz, 1H, CH_2), 4.75 (d, *J* = 6.0 Hz, 1H, CH), 2.36 (s, 3H, Me);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 140.6, 138.2, 137.0, 131.7, 130.5, 129.9, 129.1, 128.8, 128.7, 127.9, 127.6, 127.2, 126.7, 120.5, 88.2 (C≡C), 85.6 (C≡C), 41.4 (CH), 21.6 (Me); IR ν_{max} (cm^{-1}): 3010, 2965, 2175 (C≡C), 1648 (C=C), 1563, 1474, 1322, 1347, 1257, 1232, 1165, 1030; HRMS (ES+) $[M+H]^+$ $[C_{24}H_{21}]^+$: calculated 309.1643, found 309.1647.

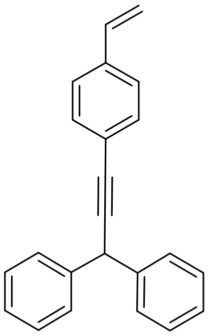
Synthesis of 4,4'-(3-(4-vinylphenyl)prop-2-yne-1,1-diyl)bis(fluorobenzene) (***4.2ai)***



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4a** (15 mg, 0.12 mmol) and aryl ester **4.1a** (34 mg, 0.1 mmol) in THF to afford **4.2ai**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:2 v/v) as eluent. The desired compound (**4.2ai**) was obtained as yellow liquid. Yield: 23 mg, 70%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.43–7.41 (m, 2H, Ar–H), 7.38–7.34 (m, 6H, Ar–H), 7.04–6.99 (m, 4H, Ar–H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1H, CH_2), 5.76 (dd, *J* = 17.6, 0.8 Hz, 1H, CH_2), 5.29 (dd, *J* = 10.9, 0.7 Hz, 1H, CH_2), 5.18 (s, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 162.0 (d, $J_{C\text{–}F}$ = 245.6 Hz), 137.6, 137.4 (d, $J_{C\text{–}F}$ = 3.1 Hz), 136.3, 132.0, 129.5 (d, $J_{C\text{–}F}$ = 8.0 Hz), 126.2, 122.5, 115.7 (d, $J_{C\text{–}F}$ = 21.5 Hz), 114.9, 90.4 (C≡C), 85.4 (C≡C), 42.5 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -115.77 (Ar–F); IR ν_{max} (cm^{-1}): 3066, 2998, 2180 (C≡C), 1602 (C=C), 1506, 1375, 1276, 1224, 1157; HRMS: (ASAP) [M] [$C_{23}H_{16}F_2$]: calculated 330.1220, found 330.1228.

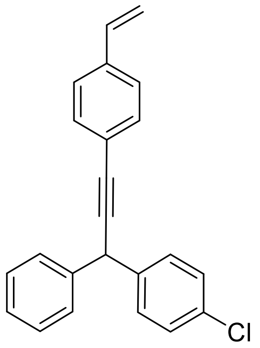
Synthesis of (3-(4-vinylphenyl)prop-2-yne-1,1-diyl)dibenzene (***4.2aj***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4a** (15 mg, 0.12 mmol) and aryl ester **4.1c** (31 mg, 0.1 mmol) in THF to afford **4.2aj**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (97:3 v/v) as eluent. The desired compound (**4.2aj**) was obtained as colourless liquid. Yield: 21 mg, 71%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.45–7.43 (m, 6H, Ar–H), 7.36–7.31 (m, 6H, Ar–H), 7.26–7.23 (m, 2H, Ar–H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1H, CH_2), 5.76 (dd, *J* = 17.6, 0.8 Hz, 1H, CH_2), 5.28 (dd, *J* = 10.9, 0.8 Hz, 1H, CH_2), 5.22 (s, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 141.9, 137.3, 136.4, 132.0, 128.8, 128.1, 127.1, 126.2, 122.1, 114.7, 91.0 (C≡C), 85.0 (C≡C), 44.0 (CH); IR ν_{max} (cm^{-1}): 3028, 2928, 2120 (C≡C), 1600 (C=C), 1506, 1492, 1276, 1111, 1029; HRMS: (ASAP+) [M] [$C_{23}H_{18}$]: calculated 294.1409, found 294.1406.

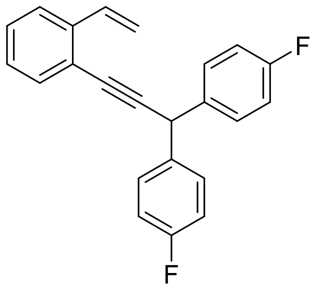
Synthesis of 1-chloro-4-(1-phenyl-3-(4-vinylphenyl)prop-2-yn-1-yl)benzene (***4.2ak***)



Synthesised in accordance with *General procedure f* using B(C_6F_5)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), enyne **4.4a** (15 mg, 0.12 mmol) and aryl ester **4.1e** (34 mg, 0.1 mmol) in THF to afford **4.2ak**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (97:3 v/v) as eluent. The desired compound (**4.2ak**) was obtained as colourless liquid. Yield: 25 mg, 75%, 0.07 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.37–7.32 (m, 4H, Ar–H), 7.31–7.24 (m, 6H, Ar–H), 7.24–7.19 (m, 3H, Ar–H), 6.62 (dd, *J* = 16.8, 10.5 Hz, 1H, CH$_2$), 5.69 (dd, *J* = 17.6, 0.8 Hz, 1H, CH$_2$), 5.21 (dd, *J* = 10.9, 0.8 Hz, 1H, CH$_2$), 5.12 (s, 1H, CH); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 141.3, 140.4, 137.5, 136.4, 132.9, 131.9, 129.4, 128.9, 127.9, 127.2, 126.2, 122.6, 114.8, 90.3(C≡C), 85.3(C≡C), 43.3(CH); IR ν_{max} (cm^{-1}): 3028, 2924, 2116 (C≡C), 1654, 1600 (C=C), 1489, 1450, 1402, 1271, 1176, 1014; HRMS: (ES+) [M+H] [$C_{23}H_{18}Cl$]: calculated 329.1097, found 328.1084.

Synthesis of 4,4'-(3-(2-vinylphenyl)prop-2-yne-1,1-diyl)bis(fluorobenzene) (***4.2al***)

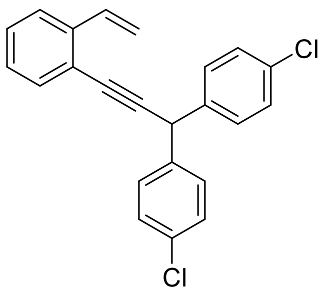


Synthesised in accordance with *General procedure f* using B(C_6F_5)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1a** (34 mg, 0.1 mmol) in TFT to afford **2al**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (97:3 v/v) as eluent. The desired compound (**4.2al**) was obtained as yellow liquid. Yield: 20 mg, 61%, 0.06 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.58–7.57 (m, 1H, Ar–H), 7.47–7.45 (m, 1H, Ar–H), 7.40–7.37 (m, 4H, Ar–H), 7.30–7.29 (m, 1H, Ar–H), 7.21 (td, *J* = 7.5, 1.3 Hz, 1H, Ar–H), 7.16 (dd, *J* = 17.6, 11.0 Hz, 1H, Ar–H), 7.04–7.01 (m, 4H, Ar–H), 5.79 (dd, *J* = 17.6, 1.1 Hz, 1H,

CH_2), 5.31 (dd, J = 11.0, 1.1 Hz, 1H, CH_2), 5.23 (s, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 162.0 (d, $J_{C–F}$ = 245.7 Hz), 139.3, 137.4 (d, $J_{C–F}$ = 3.3 Hz), 135.0, 132.7, 129.5 (d, $J_{C–F}$ = 8.1 Hz), 128.5, 127.6, 124.8, 121.9, 115.8, 115.6 (d, $J_{C–F}$ = 21.7 Hz), 94.4 (C≡C), 83.9 (C≡C), 42.6 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -115.75 (Ar–F); IR ν_{max} (cm^{-1}): 2958, 2928, 1701, 1654, 1620 (C=C), 1506, 1297, 1261, 1230, 1157, 1096, 1015; HRMS (GC-MS) [M] [$C_{23}H_{16}F_2$]: calculated 330.1220, found 330.1219.

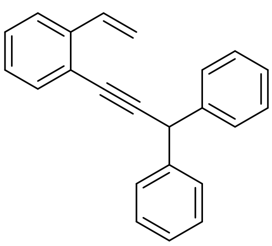
Synthesis of 4,4'-(3-(2-vinylphenyl)prop-2-yne-1,1-diyl)bis(chlorobenzene) (***4.2am***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1b** (37 mg, 0.1 mmol) in TFT to afford **4.2am**. The crude reaction mixture was purified via preparative thin layer chromatography using hexane/ethyl acetate (98:2 v/v) as eluent. The desired compound (**4.2am**) was obtained as a yellow liquid. Yield: 23 mg, 63%, 0.06 mmol.

^1H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.58–7.57 (m, 1H, Ar–CH), 7.45 (dd, J = 7.7, 0.8 Hz, 1H, Ar–CH), 7.36–7.34 (m, 4H, Ar–CH), 7.32–7.28 (m, 5H, Ar–CH), 7.21 (td, J = 7.5, 1.3 Hz, 1H, Ar–CH), 7.14 (dd, J = 17.6, 11.0 Hz, 1H, Ar–CH), 5.79 (dd, J = 17.6, 1.1 Hz, 1H,), 5.32 (dd, J = 11.0, 1.0 Hz, 1H), 5.21 (s, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 139.9, 139.3, 134.9, 133.1, 132.7, 129.3, 129.0, 128.6, 127.6, 124.8, 121.7, 115.9, 93.7 (C≡C), 84.1 (C≡C), 42.9 (CH); IR ν_{max} (cm^{-1}): 3065 (C=CH), 2922, 2850, 1771, 1683, 1653, 1590, 1558, 1539, 1520, 1506, 1489, 1447, 1400, 1090, 1014; HMRS (EI+) $[M-Cl]^+$ $[C_{23}H_{16}Cl]^+$: calculated 327.0935, found 327.0936.

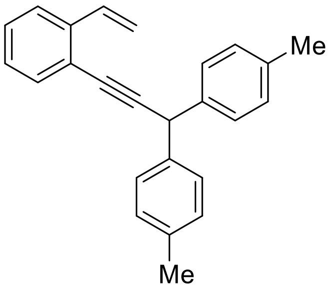
Synthesis of (3-(2-vinylphenyl)prop-2-yne-1,1-diyl)dibenzene (***4.2an***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1c** (31 mg, 0.1 mmol) in TFT to afford **4.2an**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (97:3 v/v) as eluent. The desired compound (**4.2an**) was obtained as colourless liquid. Yield: 17 mg, 58%, 0.06 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.58–7.56 (m, 1H, Ar–H), 7.48–7.44 (m, 5H, Ar–H), 7.35–7.31 (m, 4H, Ar–H), 7.30–7.28 (m, 1H, Ar–H), 7.25–7.18 (m, 4H, Ar–H), 5.79 (dd, *J* = 17.6, 1.1 Hz, 1H, CH_2), 5.31 (dd, *J* = 11.0, 1.1 Hz, 1H, CH_2), 5.27 (s, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 141.8, 139.3, 135.2, 132.7, 128.7, 128.3, 128.0, 127.5, 127.0, 124.6, 122.3, 115.5, 95.0 (C≡C), 83.4 (C≡C), 44.1 (CH); IR ν_{max} (cm^{-1}): 3086 (C=CH), 3062, 3028, 1625 (C=C stretch), 1597, 1558, 1541, 1519, 1492, 1477, 1452, 1076, 1029; HRMS (AP+) $[M+H]^+$ $[C_{23}H_{19}]^+$: calculated 295.1487, found 295.1495.

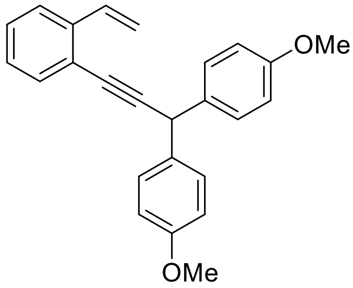
Synthesis of 4,4'-(3-(2-vinylphenyl)prop-2-yne-1,1-diyl)bis(methylbenzene)(***4.2ao***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol), and aryl ester **4.1i** (33 mg, 0.1 mmol) in TFT to afford **4.2ao**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:2 v/v) as eluent. The desired compound (**4.2ao**) was obtained as a colourless liquid. Yield: 19 mg, 58%, 0.06 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.58–7.56 (m, 1H, Ar–H), 7.46 (dd, *J* = 7.7, 0.9 Hz, 1H, Ar–H), 7.34–7.32 (m, 4H, Ar–H), 7.28 (dd, *J* = 6.9, 1.0 Hz, 1H, Ar–H), 7.23–7.17 (m, 2H, Ar–H), 7.14–7.12 (m, 4H, Ar–H), 5.78 (dd, *J* = 17.6, 1.2 Hz, 1H, CH_2), 5.30 (dd, *J* = 11.0, 1.1 Hz, 1H, CH_2), 5.20 (s, 1H, CH), 2.32 (s, 6H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 139.2, 139.1, 136.5, 135.3, 132.7, 129.4, 128.1, 127.8, 127.5, 124.6, 122.5, 115.4, 95.4 (C≡C), 83.0 (C≡C), 43.3 (CH), 21.1 (Me); IR ν_{max} (cm^{-1}): 3018 (C=CH), 2921, 2861, 1510, 1493, 1477, 1447, 1413, 1379, 1327, 1297, 1260, 1186, 1118, 1100, 1021; HRMS (ASAP+) $[M+H]^+$: calculated 323.1800, found: 323.1793.

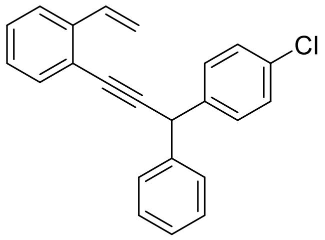
Synthesis of 4,4'-(3-(2-vinylphenyl)prop-2-yne-1,1-diyl)bis(methoxybenzene) (***4.2ap***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), aryl ester **4.1d** (37 mg, 0.1 mmol) and enyne **4.4d** (15 mg, 0.12 mmol) in TFT to afford **4.2ap**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (92:8 v/v) as eluent. The desired compound (**4.2ap**) was obtained as yellow liquid. Yield: 18 mg, 51%. 0.05 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.58–7.56 (m, 1H, Ar–H), 7.47–7.45 (m, 1H, Ar–H), 7.36–7.33 (m, 4H, Ar–H), 7.24–7.17 (m, 3H, Ar–H), 6.88–6.85 (m, 4H, Ar–H), 5.79 (dd, J = 17.6, 1.1 Hz, 1H, CH_2), 5.31 (dd, J = 11.0, 1.1 Hz, 1H, CH_2), 5.18 (s, 1H, CH), 3.79 (s, 6H, OCH_3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 158.5, 139.1, 138.9, 135.1, 134.3, 132.7, 130.9, 129.0, 128.9, 128.6, 128.2, 127.5, 124.6, 115.5, 114.1, 114.0, 113.9, 95.5 (C≡C), 83.0 (C≡C), 55.4 (OCH_3), 42.4 (CH); IR ν_{max} (cm^{-1}): 3036 (C=CH), 2957, 2935, 2836, 1700, 1683, 1653, 1608 (C=C), 1583, 1559, 1540, 1508, 1461, 1441, 1301, 1246, 1175, 1110, 1034; HRMS (ASAP+) $[M+H]^+$: calculated 355.1698, found 355.1702.

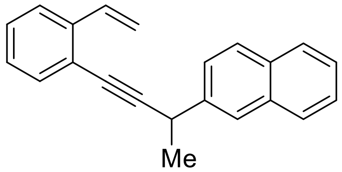
Synthesis of 1-(3-(4-chlorophenyl)-3-phenylprop-1-en-1-yl)-2-ethynylbenzene (***4.2aq***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1d** (34 mg, 0.1 mmol) in TFT to afford **4.2aq**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (97:3 v/v) as eluent. The desired compound (**4.2aq**) was obtained as yellow liquid. Yield: 21 mg, 60%, 0.06 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.58–7.56 (m, 1H, Ar–H), 7.46 (dd, *J* = 7.7, 0.9 Hz, 1H, Ar–H), 7.44–7.42 (m, 2H, Ar–H), 7.39–7.37 (m, 2H, Ar–H), 7.36–7.32 (m, 2H, Ar–H), 7.31–7.28 (m, 3H, Ar–H), 7.24–7.15 (m, 3H, Ar–H), 5.79 (dd, *J* = 17.6, 1.1 Hz, 1H, CH_2), 5.31 (dd, *J* = 11.0, 1.1 Hz, 1H, CH_2), 5.24 (s, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 141.3, 140.4, 139.3, 135.1, 132.9, 132.7, 129.4, 128.9, 128.4, 127.9, 127.5, 127.2, 124.7, 122.0, 115.7, 94.4 (C≡C), 83.8 (C≡C), 43.5 (CH); IR ν_{max} (cm^{-1}): 2959, 2924, 2853, 1558, 1539, 1490, 1477, 1449, 1261, 1091, 1015; HRMS (GC-MS) [M] [$C_{23}H_{17}Cl$]: calculated 328.1019, found 328.1014.

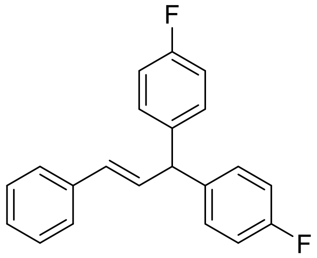
Synthesis of 2-(4-(2-vinylphenyl)but-3-yn-2-yl)naphthalene (***4.2ar***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1g** (29 mg, 0.1 mmol) in TFT to afford **4.2ar**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:2 v/v) as eluent. The desired compound (**4.2ar**) was obtained as white solid. Yield: 14 mg, 50%, 0.05 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.92 (s, 1H, Ar–H), 7.84 (dd, *J* = 8.0, 5.4 Hz, 3H, Ar–H), 7.60–7.58 (m, 2H, Ar–H), 7.50–7.44 (m, 3H, Ar–H), 7.30–7.19 (m, 3H, Ar–H), 5.82 (dd, *J* = 17.7, 1.2 Hz, 1H, CH_2), 5.34 (dd, *J* = 11.0, 1.1 Hz, 1H, CH_2), 4.21 (q, *J* = 7.1 Hz, 1H, CH), 1.70 (d, *J* = 7.2 Hz, 3H, Me); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 140.8, 139.1, 135.2, 133.6, 132.7, 132.5, 128.4, 128.1, 127.9, 127.7, 127.5, 126.2, 125.75, 125.74, 125.3, 124.7, 122.5, 115.4, 97.4 (C≡C), 81.2 (C≡C), 33.0 (CH), 24.5 (Me); IR ν_{max} (cm^{-1}): 3057 (C=CH), 2974, 2924, 1654, 1625, 1600 (C=C), 1559, 1507, 1476, 1447, 1374, 1363, 1302, 1260, 1198, 1126, 1100, 1073, 1054, 1019; HRMS (ASAP)+ [M+H]$^+$: calculated 283.1487, found 283.1487.

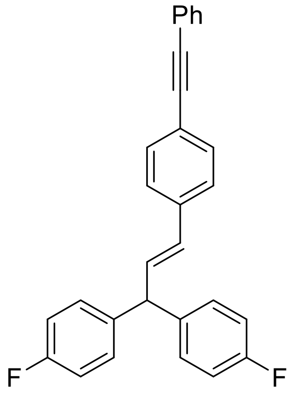
Synthesis of 4,4'-(3-phenylprop-2-ene-1,1-diyl)bis(fluorobenzene) (**4.3*a***)[104]



Synthesised in accordance with *General procedure f* using B(C$_6$F$_5$)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), ethenylbenzene (10 mg, 0.1 mmol), 1-phenyl-2-trimethylsilylacetylene (17 mg, 0.1 mmol) and aryl ester **4.1a** (34 mg, 0.1 mmol) in THF to afford **4.3a**. The crude reaction mixture was purified via preparative thin layer chromatography using hexane/ethyl acetate (97:3 v/v) as eluent. The desired compound (**4.3a**) was obtained as a yellow liquid. Yield: 19 mg, 63%, 0.06 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.38–7.36 (m, 2H, Ar–H), 7.32–7.29 (m, 2H, Ar–H), 7.24–7.23 (m, 1H, Ar–H), 7.19–7.16 (m, 4H, Ar–H), 7.03–6.99 (m, 4H, Ar–H), 6.59 (dd, *J* = 15.8, 7.4 Hz, 1H, CH$_2$), 6.31 (dd, *J* = 15.8, 1.3 Hz, 1H, CH$_2$), 4.87 (d, *J* = 7.4 Hz, 1H, CH); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 161.7 (d, $J_{C\text{–}F}$ = 245.1 Hz), 139.1 (d, $J_{C\text{–}F}$ = 3.3 Hz), 137.0, 132.2, 131.9, 130.1 (d, $J_{C\text{–}F}$ = 7.9 Hz), 128.7, 127.7, 126.4, 115.5 (d, $J_{C\text{–}F}$ = 21.3 Hz), 52.7 (CH); ^{19}F NMR (471 MHz, CDCl$_3$, 298 K) δ: -166.44 (Ar–F).

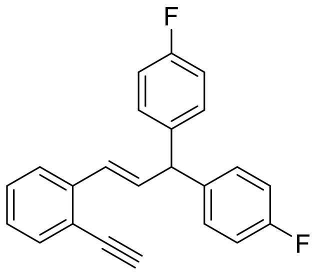
Synthesis of 4,4'-(3-(4-(phenylethynyl)phenyl)prop-2-ene-1,1-diyl)bis(fluorobenzene) (***4.3b***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), 1-(phenylethynyl)-4-vinylbenzene **4.4b** (24 mg, 0.12 mmol) and aryl ester **4.1a** (34 mg, 0.1 mmol) in THF to afford **4.3b**. The crude reaction mixture was purified via preparative thin layer chromatography using hexane/ethyl acetate (97:3 v/v) as eluent. The desired compound (**4.3b**) was obtained as a yellow liquid. Yield: 29 mg, 71%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.71–7.69 (m, 2H, Ar–H), 7.52–7.50 (m, 2H, Ar–H), 7.39–7.36 (m, 5H, Ar–H), 7.33–7.31 (m, 1H, Ar–H), 7.25–7.22 (m, 4H, Ar–H), 7.04–7.00 (m, 4H, Ar–CH), 6.76 (d, *J* = 9.9 Hz, 1H, CH_2), 5.56 (d, *J* = 9.9 Hz, 1H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 161.8 (d, $J_{C–F}$ = 245.2 Hz), 139.1 (d, $J_{C–F}$ = 3.3 Hz), 138.5, 137.6, 131.8, 129.9 (d, $J_{C–F}$ = 7.9 Hz), 128.7, 128.64, 128.60, 128.2, 126.4, 124.5, 123.1, 115.6 (d, $J_{C–F}$ = 21.3 Hz), 96.1 (C≡C), 86.4 (C≡C), 50.8 (CH); ^{19}F NMR (471 MHz, $CDCl_3$, 298 K) δ: -116.26; IR ν_{max} (cm^{-1}): 3047, 2984, 2172 (C≡C), 1640 (C=C), 1601, 1559, 1505, 1489, 1447, 1360, 1222, 1157, 1085, 1015; HRMS (ES+) [M+H]$^+$ [$C_{29}H_{21}F_2$]: calculated 407.1611, found 407.1607.

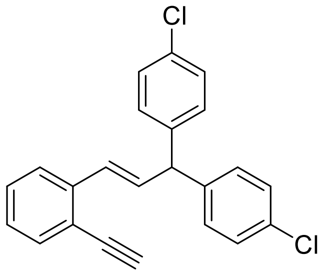
Synthesis of 4,4'-(3-(2-ethynylphenyl)prop-2-ene-1,1-diyl)bis(fluorobenzene) (***4.3c***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1a** (34 mg, 0.1 mmol) in THF to afford **4.3c**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (96:4 v/v) as eluent. The desired compound (**4.3c**) was obtained as yellow liquid. Yield: 26 mg, 79%, 0.07 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.57–7.55 (m, 1H, Ar–H), 7.47 (dd, *J* = 7.7, 0.9 Hz, 1H, Ar–H), 7.32–7.28 (m, 1H, Ar–H), 7.21–7.17 (m, 5H, Ar–H), 7.04–6.99 (m, 4H, Ar–H), 6.87–6.83 (m, 1H, Ar–H), 6.66 (dd, *J* = 15.8, 7.6 Hz, 1H, CH$_2$), 4.91 (d, *J* = 7.6 Hz, 1H, CH), 3.23 (s, 1H, C≡CH); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 161.7 (d, $J_{C–F}$ = 245.2 Hz), 139.2, 139.0 (d, $J_{C–F}$ = 3.1 Hz), 134.2, 133.3, 130.1 (d, $J_{C–F}$ = 7.9 Hz), 129.7, 129.0, 127.2, 125.0, 120.8, 115.5 (d, $J_{C–F}$ = 21.2 Hz), 82.0 (C≡C), 81.9 (C≡C), 52.9 (CH); ^{19}F NMR (471 MHz, CDCl$_3$, 298 K) δ: -116.41 (Ar–F); IR ν_{max} (cm^{-1}): 3300 (C≡CH), 2953, 2926, 2852, 2159 (C≡C), 1600 (C=C), 1505, 1474, 1445, 1259, 1221, 1157, 1096, 1015; HRMS (GC-MS) [M] [$C_{23}H_{16}F_2$]: calculated 330.1220, found 330.1219.

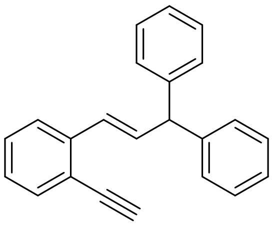
Synthesis of 4,4'-(3-(2-ethynylphenyl)prop-2-ene-1,1-diyl)bis(chlorobenzene) (***4.3d***)



Synthesised in accordance with *General procedure f* using B(C$_6$F$_5$)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1b** (37 mg, 0.1 mmol) in THF to afford **4.3d**. The crude reaction mixture was purified via preparative thin layer chromatography using hexane/ethyl acetate (98:2 v/v) as eluent. The desired compound (**4.3d**) was obtained as a yellow liquid. Yield: 27 mg, 74%, 0.07 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.54 (d, *J* = 7.9 Hz, 1H, Ar–H), 7.47 (dd, *J* = 7.8, 1.4 Hz, 1H, Ar–H), 7.32–7.28 (m, 5H, Ar–H), 7.21–7.14 (m, 5H, Ar–H), 6.88–6.85 (m, 1H, CH$_2$), 6.63 (dd, *J* = 15.9, 7.7 Hz, 1H, CH$_2$), 4.88 (d, *J* = 7.6 Hz, 1H, CH), 3.24 (s, 1H, C≡CH); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 141.5, 139.0, 133.5, 133.3, 132.7, 130.2, 130.0, 129.0, 128.8, 127.3, 125.1, 120.8, 82.0 (C≡C), 81.9 (C≡C), 53.2 (CH); IR ν_{max} (cm^{-1}): 3027, 2926, 2172 (C≡C), 1637 (C=C), 1488, 1408, 1260, 1089, 1089, 1014; HRMS (ES-) [M-H]$^-$ calculated for [$C_{23}H_{15}Cl_2$]$^-$: 361.0511, found: 361.0545.

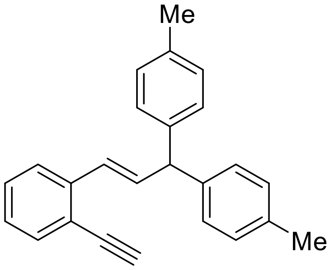
Synthesis of 3-(2-ethynylphenyl)prop-2-ene-1,1-diyl)dibenzene (***4.3e***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1c** (31 mg, 0.1 mmol) in THF to afford **4.3e**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (97:3 v/v) as eluent. The desired compound (**4.3e**) was obtained as colourless liquid. Yield: 21 mg, 71%, 0.07 mmol

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.58–7.56 (m, 1H, Ar–H), 7.45 (dd, *J* = 7.7, 0.9 Hz, 1H, Ar–H), 7.35–7.27 (m, 7H, Ar–H), 7.26–7.20 (m, 4H, Ar–H), 7.16 (td, *J* = 7.6, 1.3 Hz, 1H, Ar–H), 6.92–6.88 (m, 1H, CH_2), 6.74 (dd, *J* = 15.8, 7.8 Hz, 1H, CH_2), 4.94 (d, *J* = 7.8 Hz, 1H, CH), 3.22 (s, 1H, C≡CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 143.5, 139.5, 134.7, 133.2, 129.4, 129.0, 128.7, 128.6, 127.0, 126.6, 125.0, 120.7, 82.1 (C≡C), 81.8 (C≡C), 54.5 (CH); IR ν_{max} (cm^{-1}): 3302 (C≡CH), 3061, 3026 (C=CH), 2247 (C≡C), 1645 (C=C), 1595, 1492, 1475, 1446, 1029; HRMS (AP+) $[M+H]^+$ $[C_{23}H_{19}]^+$: calculated 295.1487, found 295.1495.

Synthesis of 4,4'-(3-(2-ethynylphenyl)prop-2-ene-1,1-diyl)bis(methylbenzene) (***4.3f***)

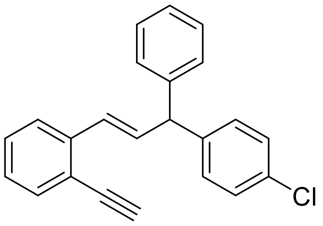


Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1i** (33 mg, 0.1 mmol) in THF to afford **4.3f**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:2 v/v) as eluent. The desired compound (**4.3f**) was obtained as colourless liquid. Yield: 18 mg, 56%, 0.06 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.57–7.55 (m, 1H, Ar–H), 7.45 (dd, *J* = 7.8, 1.0 Hz, 1H, Ar–H), 7.17–7.10 (m, 10H, Ar–H), 6.90 (d, *J* = 15.9 Hz, 1H, CH_2), 6.71 (dd, *J* = 15.8, 8.1 Hz, 1H, CH_2), 4.86 (d, *J* = 8.0 Hz, 1H, CH), 3.24 (s, 1H, C≡CH), 2.32 (s, 6H, Me); ^{13}C NMR (126

MHz, $CDCl_3$, 298 K) δ: 140.8, 139.7, 136.0, 135.1, 133.2, 129.3, 129.1, 128.98, 128.97, 128.5, 127.2, 126.9, 125.1, 120.6, 82.2 (C≡C), 81.7 (C≡C), 53.8 (CH), 21.1 (Me); IR ν_{max} (cm^{-1}): 3302 (C≡CH), 2964, 2923, 1654 (C=C), 1558, 1511, 1475, 1445, 1259, 1091, 1020; HRMS (AP+) $[M+H]^+$ $[C_{25}H_{23}]^+$: calculated 323.1800, found 323.1801.

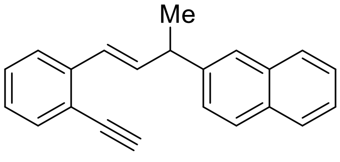
Synthesis of 1-(3-(4-chlorophenyl)-3-phenylprop-1-en-1-yl)-2-ethynylbenzene (***4.3h***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1e** (34 mg, 0.1 mmol) in THF to afford **4.3h**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (97:3 v/v) as eluent. The desired compound (**4.3h**) was obtained as yellow liquid. Yield: 24 mg, 73%, 0.07 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.57–7.55 (m, 1H, Ar–H), 7.47 (dd, J = 7.7, 0.9 Hz, 1H, Ar–H), 7.34–7.28 (m, 6H, Ar–H), 7.25–7.23 (m, 2H, Ar–H), 7.20–7.18 (m, 3H, Ar–H), 6.91–6.87 (m, 1H, Ar–H), 6.69 (dd, J = 15.8, 7.8 Hz, 1H, CH_2), 4.92 (d, J = 7.7 Hz, 1H, CH), 3.24 (s, 1H, C≡CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 143.0, 142.0, 139.3, 134.1, 133.3, 132.4, 130.1, 129.8, 129.0, 128.75, 128.73, 128.70, 127.2, 126.8, 125.0, 120.7, 82.0 (C≡C), 81.9 (C≡C), 53.8 (CH); IR ν_{max} (cm^{-1}): 3301 (C≡CH), 2963, 2928, 2855, 2187 (C≡C), 1653 (C=C), 1600, 1490, 1475, 1447, 1405, 1259, 1090, 1014; HRMS (GC-MS) [M] $[C_{23}H_{17}Cl]$: calculated 328.1019, found 328.1016.

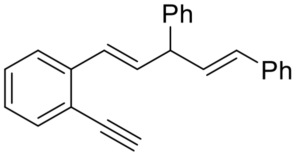
Synthesis of 2-(4-(2-ethynylphenyl)but-3-en-2-yl)naphthalene (***4.3i***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1g** (29 mg, 0.1 mmol) in THF to afford **4.3i**. The crude reaction mixture was purified via preparative thin layer chromatography using hexane/ethyl acetate (98:2 v/v) as eluent. The desired compound (**4.3i**) was obtained as a white solid. Yield: 11 mg, 40%, 0.04 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.82–7.80 (m, 3H, Ar–H), 7.72 (s, 1H, Ar–H), 7.54 (d, J = 8.0 Hz, 1H, Ar–H), 7.49–7.43 (m, 4 H, Ar–H), 7.28 (d, J = 7.5 Hz, 1H, Ar–H), 7.16 (t, J = 7.6 Hz, 1H, Ar–H), 7.03 (d, J = 15.9 Hz, 1H, CH_2), 6.53 (dd, J = 15.9, 7.0 Hz, 1H, CH_2), 3.87 (p, J = 7.0 Hz, 1H, CH), 3.31 (s, 1H, C≡CH), 1.59 (d, J = 7.0 Hz, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 143.0, 139.8, 137.3, 133.8, 133.2, 132.4, 129.0, 128.2, 127.8, 127.7, 126.8, 126.7, 126.4, 126.1, 125.5, 125.3, 124.8, 120.6, 82.3 (C≡C), 81.7 (C≡C), 43.0 (CH), 21.2 (Me); IR ν_{max} (cm^{-1}): 3289 (C≡CH), 3054 (C=CH), 2963, 2927, 2863, 1644 (C=C), 1559, 1549, 1506, 1474, 1446, 1373, 1362, 1270, 1260, 1160, 1018; HRMS (ASAP+) [M]$^+$ [$C_{22}H_{18}$]$^+$: calculated 282.1409, found 282.1408.

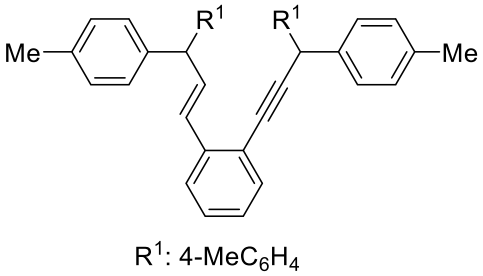
Synthesis of ((1E)-5-(2-ethynylphenyl)penta-1,4-diene-1,3-diyl)dibenzene (***4.3j***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1k** (31 mg, 0.1 mmol) in THF to afford **4.3j**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (96:4 v/v) as eluent. The desired compound (**4.3j**) was obtained as colourless liquid. Yield: 7 mg, 22%, 0.02 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.58–7.56 (m, 1H, Ar–H), 7.48 (dd, *J* = 7.7, 0.9 Hz, 1H, Ar–H), 7.41–7.39 (m, 2H, Ar–H), 7.35–7.34 (m, 4H, Ar–H), 7.32–7.27 (m, 4H, Ar–H) 7.25–7.20 (m, 2H, Ar–H), 7.18 (td, *J* = 7.6, 1.3 Hz, 1H, CH_2), 7.04–7.01 (m, 1H, CH_2), 6.55 (dd, *J* = 15.9, 7.4 Hz, 1H, CH_2), 6.51–6.50 (m, 1H, CH_2), 4.46–4.43 (m, 1H, CH), 3.27 (s, 1H, C≡CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 142.8, 139.5, 137.5, 134.0, 133.3, 131.9, 131.1, 129.0, 128.8, 128.6, 128.2, 127.4, 127.0, 126.8, 126.4, 125.0, 120.7, 82.2 (C≡C), 81.8 (C≡C), 52.0 (CH); IR ν_{max} (cm^{-1}): 3301 (C≡CH), 3025 (C=CH), 2960, 2921, 2853, 1653 (C=C), 1646, 1598, 1575, 1570, 1559, 1542, 1533, 1520, 1507, 1492, 1473, 1447, 1377, 1363, 1258, 1080, 1011; HRMS (ASAP +) [M+H]$^+$: $C_{25}H_{21}$ calculated 321.1643, found 321.1647.

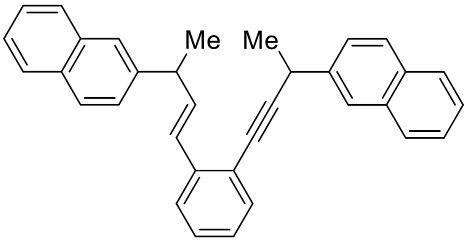
Synthesis of 4,4'-(3-(2-(3,3-di-p-tolylprop-1-en-1-yl)phenyl)prop-2-yne-1,1-diyl)bis (methylbenzene) (***4.5d***)



Synthesised in accordance with *General procedure f* using B(C_6F_5)$_3$ (51 mg, 0.1 mmol), Mes$_3$P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1i** (33 mg, 0.1 mmol) in THF to afford **4.5d**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:2 v/v) as eluent. The desired compound (**4.5d**) was obtained as colourless liquid. Yield: 5 mg, 10%, 0.01 mmol.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ: 7.50–7.49 (m, 1H, Ar–H), 7.38 (dd, *J* = 7.7, 1.0 Hz, 1H, Ar–H), 7.24–7.18 (m, 6H, Ar–H), 7.11–7.03 (m, 12H, Ar–H), 6.87 (d, *J* = 15.8 Hz, 1H, CH$_2$), 6.63 (dd, *J* = 15.8, 8.0 Hz, 1H, CH$_2$), 5.08 (s, 1H, CH), 4.72 (d, *J* = 8.0 Hz, 1H, CH), 2.27 (s, 6H, Me), 2.26 (s, 6H, Me); ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) δ: 140.9, 139.3, 139.1, 136.4, 135.9, 134.6, 132.5, 129.5, 129.3, 129.2, 128.5, 128.1, 127.8, 126.8, 125.1, 122.2, 95.4 (C≡C), 83.3 (C≡C), 53.9 (CH), 43.3 (CH), 21.18 (Me), 21.16 (Me); IR ν_{max} (cm^{-1}): 3020 (C≡CH), 2919, 2856, 1653 (C≡C), 1509, 1476, 1445, 1412, 1378, 1327, 1296, 1263, 1211, 1186, 1110, 1038, 1020; HRMS (ASAP +) [M+H]$^+$ [$C_{40}H_{37}$]$^+$: calculated 517.2895, found 517.2894.

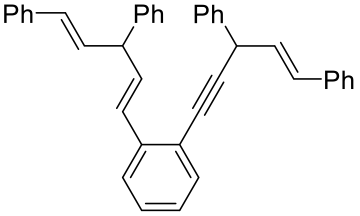
Synthesis of 2-(4-(2-(3-(naphthalen-2-yl)but-1-en-1-yl)phenyl)but-3-yn-2-yl)naphthalene (***4.5g***)



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1g** (29 mg, 0.1 mmol) in THF to afford **4.5g**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (98:2 v/v) as eluent. The desired compound **4.5g** was obtained as white solid. Yield: 6 mg, 13%, 0.01 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.87 (t, *J* = 1.9 Hz, 1H, Ar–H), 7.82–7.73 (m, 6H, Ar–H), 7.68–7.65 (m, 1H, Ar–H), 7.57–7.54 (m, 1H, Ar–H), 7.53 (d, *J* = 7.3 Hz, 1H, Ar–H), 7.46–7.36 (m, 6H, Ar–H), 7.23 (td, *J* = 8.2, 1.5 Hz, 1H, Ar–H), 7.15 (td, *J* = 7.4, 1.2 Hz, 1H, Ar–H), 7.00 (dd, *J* = 16.0, 1.5 Hz, 1H, CH_2), 6.53 (ddd, *J* = 16.0, 6.6, 2.5 Hz, 1H, CH_2), 4.12 (q, *J* = 7.0 Hz, 1H, CH), 3.79 (h, *J* = 6.1 Hz, 1H, CH), 1.59 (dd, *J* = 7.1, 4.7 Hz, 3H, Me), 1.51 (dd, *J* = 7.0, 5.6 Hz, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 143.0, 140.8, 139.2, 136.7, 133.7, 133.6, 132.58, 132.57, 132.3, 128.4, 128.1, 128.0, 127.9, 127.8, 127.77, 127.72, 127.3, 126.8, 126.5, 126.4, 126.2, 126.0, 125.7, 125.4, 125.27, 125.26, 124.8, 122.2, 97.4 (C≡C), 81.3 (C≡C), 42.9 (CH), 32.9 (CH), 24.3 (Me), 21.0 (Me); IR ν_{max} (cm^{-1}): 3059 (C≡CH), 2960, 2925, 1700, 1680, 1635 (C=C), 1600, 1559, 1507, 1476, 1457, 1448, 1374, 1363, 1270, 1126, 1019; HRMS (ASAP+) $[M+H]^+$: calculated 437.2269, found 437.2264.

*Synthesis of ((1E)-5-(2-((E)-3,5-diphenylpent-4-en-1-yn-1-yl)phenyl)penta-1,4-diene-1,3-diyl)dibenzene (**4.5h**)*



Synthesised in accordance with *General procedure f* using $B(C_6F_5)_3$ (51 mg, 0.1 mmol), Mes_3P (39 mg, 0.1 mmol), enyne **4.4d** (15 mg, 0.12 mmol) and aryl ester **4.1k** (31 mg, 0.1 mmol) in THF to afford **4.5h**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (96:4 v/v) as eluent. The desired compound (**4.5h**) was obtained as colourless liquid. Yield: 21 mg, 41%, 0.04 mmol.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.57 (dd, J = 8.0, 0.7 Hz, 1H, Ar–H), 7.49–7.45 (m, 3H, Ar–H), 7.37–7.27 (m, 14H, Ar–H), 7.26–7.17 (m, 6H, Ar–H), 7.06 (d, J = 15.9 Hz, 1H, CH_2), 6.76 (dd, J = 15.3, 1.2 Hz, 1H, CH_2), 6.56 (ddd, J = 15.9, 7.3, 1.5 Hz, 1H, CH_2), 6.46–6.45 (m, 2H, CH_2), 6.30 (ddd, J = 15.6, 6.5, 2.1 Hz, 1H, CH_2), 4.73 (dd, J = 6.5, 1.5 Hz, 1H, CH), 4.38–4.35 (m, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ: 142.8, 140.4, 139.0, 137.4, 136.9, 133.7, 132.7, 131.9, 131.0, 130.6, 129.6, 129.3, 128.8, 128.7, 128.67, 128.63, 128.3, 128.2, 127.9, 127.6, 127.4, 127.2, 127.0, 126.7, 126.6, 126.4, 125.1, 122.0, 93.7 (C≡C), 84.1 (C≡C), 52.0 (CH), 41.5 (CH); IR ν_{max} (cm^{-1}): 3058 (C≡CH), 3025 (C=CH), 2956, 2929, 1700, 1647 (C=C), 1598, 1491, 1476, 1447, 1309, 1264, 1203, 1156, 1074, 1029; HRMS (ASAP+) $[M+H]^+$ $[C_{40}H_{33}]^+$: calculated 513.2582, found: 513.2579.

5.4.0.0 Crystallographic data

5.4.1.0 Single crystal X-ray diffraction experimental

All the following crystals were measured and analysed by my colleague Lukas Gierlichs. Single crystals of **2.3a**, **2.3n**, **2.6e** were grown in a fume hood by slow evaporation or vapor diffusion. Single crystals of **3.3n** and **3.3o** were grown in a freezer (3 ˚C) by vapor diffusion. Crystallographic studies were undertaken on single crystal mounted in paratone and studied on an Agilent SuperNova Dual Atlas three-circle diffractometer using Mo- or Cu-Kα radiation and a CCD detector. Measurements were taken at 190.00(10) K (**2.3a**, **2.3n**), 200.01(10) K (**2.6e**) or 150 (2) K (**3.3n**, **3.3o**) with temperatures maintained using an Oxford cryostream. Data were collected and integrated and data corrected for absorption using a numerical absorption correction based on Gaussian integration over a multifaceted crystal model within CrysAlisPro.[175] The structures were solved by direct methods and refined against F2 within SHELXL-2013.[176]The structures have been deposited with the Cambridge Structural Database (CCDC deposition numbers **1976457**, **1976537**, **1977547**, **2072873**, **2072872**). These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

5.4.1.1 X-Ray refinement data for 2.3a

Crystal data and structure refinement for compound **2.3a**.

Empirical formula	$C_{17}H_{19}FO_4Si$	
Formula weight	334.42	
Temperature	190(10) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 5.9971(11) Å	α = 85.473(14)°.
	B = 10.4508(18) Å	β = 84.051(14)°.
	C = 14.670(2) Å	γ = 84.797(15)°.
Volume	908.4(3) Å^3	
Z	2	
Density (calculated)	1.223 Mg/m^3	
Absorption coefficient	0.154 mm^{-1}	
F(000)	352.0	
Crystal size	0.977 × 0.216 × 0.185 mm^3	
θ range for data collection	4.2060 to 28.3770°.	
Index ranges	$-6 \le h \le 8$, $-13 \le k \le 12$, $-14 \le l \le 19$	
Reflections collected	7611	
Independent reflections	4270 [R(int) = 0.0307]	
Completeness to θ = 29.659 °	83.0%	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.763	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4270 / 33 / 213	
Goodness-of-fit on F^2	0.875	
Final R indices [I>2σ(I)]	R1 = 0.0620, wR2 = 0.1615	
R indices (all data)	R1 = 0.0913, wR2 = 0.1975	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.441 and -0.378 e.Å^{-3}	

5.4.1.2 X- Ray refinement data for 2.3n

Crystal data and structure refinement for compound **2.3n**.

Empirical formula	$C_{20}H_{15}FO_4$	
Formula weight	338.32	
Temperature	190(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 18.3342(11) Å	α = 90°.
	B = 5.7085(5) Å	β = 93.557(6)°.
	C = 16.2664(11) Å	γ = 90°.
Volume	1699.2(2) Å^3	
Z	4	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	0.099 mm^{-1}	
F(000)	704	
Crystal size	0.535 × 0.186 × 0.053 mm^3	
θ range for data collection	4.2750 to 29.0220°.	
Index ranges	$-23 \leq h \leq 25$, $-7 \leq k \leq 6$, $-22 \leq l \leq 19$	
Reflections collected	9432	
Independent reflections	4101 [R(int) = 0.0251]	
Completeness to θ = 29.795 °	84.7%	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.654	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4095 / 0 / 227	
Goodness-of-fit on F^2	0.934	
Final R indices [I>2σ(I)]	R1 = 0.0490, wR2 = 0.1003	
R indices (all data)	R1 = 0.0743, wR2 = 0.1130	
Extinction coefficient	0.0043(6)	
Largest diff. peak and hole	0.248 and -0.184 e.Å^{-}	

5.4.1.3 X-Ray refinement data for 2.6e

Crystal data and structure refinement for compound **2.6e**.

Empirical formula	$C_{22}H_{24}O_4$	
Formula weight	352.41	
Temperature	200.01(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.6266(5) Å	$\alpha = 90°$.
	B = 10.1624(5) Å	$\beta = 93.715(4)°$.
	C = 18.5303(7) Å	$\gamma = 90°$.
Volume	1996.91(15) $Å^3$	
Z	4	
Density (calculated)	1.172 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	752.0	
Crystal size	0.249 × 0.226 × 0.209 mm^3	
θ range for data collection	3.8490 to 27.9840°.	
Index ranges	$-13 \leq h \leq 11$, $-12 \leq k \leq 12$, $-23 \leq l \leq 22$	
Reflections collected	10172	
Independent reflections	4337 [R(int) = 0.0250]	
Completeness to θ = 27.100 °	98.7%	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.779	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4337 / 114 / 270	
Goodness-of-fit on F^2	1.005	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0434, wR2 = 0.0821	
R indices (all data)	R1 = 0.0638, wR2 = 0.0917	
Extinction coefficient	0.0169(9)	
Largest diff. peak and hole	0.220 and -0.190 e.$Å^{-3}$	

5.4.1.4 X-Ray refinement data for 3.3n

Crystal data and structure refinement for compound **3.3n**.

Empirical formula	$C_{25}H_{18}O_2$
Formula weight	350.39
Temperature/K	150 (2)
Crystal system	Orthorhombic
Space group	Pca21
a/Å	26.0464 (11)
b/Å	18.2137 (8)
c/Å	7.6051 (4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3607.9 (3)
Z	8
Density (ρ_{calc}g/cm^3)	1.290
Absorption coefficient (μ/mm^{-1})	0.636
F(000)	1472.0
Crystal size/mm^3	0.199 × 0.063 × 0.040
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.260 to 151.604
Index ranges	$-25 \leq h \leq 32$, $-22 \leq k \leq 19$, $-9 \leq l \leq 9$
Reflections collected	34640
Independent reflections	7272 [R_{int} = 0.0785, R_{sigma} = 0.0584]
Data/restraints/parameters	7272/1/489
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.052, wR_2 = 0.117
Final R indexes [all data]	R_1 = 0.080, wR_2 = 0. 0.141
Largest diff. Peak/hole / e Å^{-3}	0.23/-0.21

5.4.1.5 X-Ray refinement data for 3.3o

Crystal data and structure refinement for compound **3.3o**.

Empirical formula	$C_{22}H_{18}O_3$
Formula weight	330.36
Temperature/K	150 (2)
Crystal system	Monoclinic
Space group	C2/c
a/Å	29.133 (2)
b/Å	5.3113 (3)
c/Å	22.5850 (13)
α/°	90
β/°	107.704 (8)
γ/°	90
Volume/Å^3	3329.1 (4)
Z	8
Density (ρ_{calc}g/cm^3)	1.318
Absorption coefficient (μ/mm^{-1})	0.697
F(000)	1392.0
Crystal size/mm^3	0.225 × 0.120 × 0.100
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.200 to 147.944
Index ranges	$-36 \le h \le 36$, $-6 \le k \le 6$, $-28 \le l \le 21$
Reflections collected	14074
Independent reflections	3476 [R_{int} = 0.0936, R_{sigma} = 0.0763]
Data/restraints/parameters	3476/0/228
Goodness-of-fit on F^2	0.868
Final R indexes [I>=2σ (I)]	R_1 = 0.047, wR_2 = 0.098
Final R indexes [all data]	R_1 = 0.0798, wR_2 = 0.107
Largest diff. Peak/hole / e Å^{-3}	0.21/-0.23

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