The First Anionic Thia-Fries Rearrangement at Arene Tricarbonylchromium Complexes and Reactions of Phthalimide Tricarbonylchromium Complexes

Der Naturwissenschaftlichen Fakultät der Gottfried Wilhelm Leibniz Universität Hannover
zur Erlangung des Grades einer

Doktorin der Naturwissenschaften
Dr. rer. nat.

genehmigte Dissertation

von

M. Sc.
Zhirong Zhao-Karger

geboren am 01.11.1970 in Damaolianhe Banner, China

2006

Referent: Prof. Dr. Holger Butenschön
Koreferent: Prof. Dr. Helmut Duddeck
Tag der Promotion: 15.12.2006

Abstract

The First Anionic Thia-Fries Rearrangement at Arene Tricarbonylchromium Complexes and Reactions of Phthalimide Tricarbonylchromium Complexes

Two topics concerning the chemistry of arene tricarbonylchromium complexes with functionalized anellated ring are involved *i.e.* generation of an η^6-aryne tricarbonylchromium(0) complex and the exploration of the anion accelerated reactions of *N*-substituted phthalimide complex.

Some moderately air-stable aryl triflate tricarbonylchromium complexes have been prepared from the corresponding phenols and attempted to generate aryne tricarbonylchromium complexes by triflic acid elimination. Unanticipated *ortho* sulfone substituted phenol complexes were obtained in high yield as a result of an anionic thia-Fries rearrangement of the arene chromium tricarbonyl triflate complexes upon treatment with LDA or BuLi at –78 °C. Double anionic thia-Fries rearrangement of tricarbonyl(1,4-dihydroxylbenzene)chromium(0) bis(triflate) has been achieved by using LDA as base. Asymmetric deprotonation using an enantiomerically pure chiral lithium amide base has been applied to the anionic thia-Fries rearrangement of the tricarbonylchromium phenyl triflate complex to afford the corresponding enantiomerically enriched planar chiral 2-sulfonylphenol complex. The new anionic thia-Fries rearrangement of tricarbonyl(phenyltriflate)chromium complexes has been applied to the tricarbonylchromium complex of estrone, providing a new 2-trifluoromethylsulfonyl substituted steroid.

An unusual *endo*-adduct obtained in the nucleophilic adddition of 1-propynyllithium to *N*-vinylphthalimide tricarbonylchromium complex provides evidence for the intermadiacy of a planar chiral acylimium ion. The synthetic application of planar chiral tricarbonylchromium complex of *N*-acyliminium ion has been preliminarily investigated.

(η^6-Arene)tricarbonylchromium(0) Complex · Anionic Thia-Fries Rearrangement · Asymmetric Deprotonation · Planar Chiral *N*-Acyliminium Ion

Kurzfassung

Die erste anionische Thia-Fries Umlagerung an (Aren)tricarbonylchrom(0)-Komplexen und Reaktionen der (Phthalimid)tricarbonylchrom(0)-Komplexe

Zwei Themen in Bezug auf die Chemie der (Aren)tricarbonylchrom(0)-Komplexen mit funktionalisiertem anelliertem Ring wurden behandelt, nämlich die Erzeugung von (Arin)tricarbonylchrom(0)-Komplexen und die Untersuchung anionisch beschleunigte Reaktionen von *N*-substituierte (Phthalimid)tricarbonylchrom(0)-Komplexe.

Im Rahmen dieser Arbeit wurden zahlreiche mässig luftstabile (Aryltriflat)tricarbonylchrom(0)-Komplexe erstmals aus den entsprechenden Phenolen dargestellt, um durch die Eliminierung von Trifluoromethansulfonsäure (Arin)tricarbonylchrom(0)-Komplexe darzustellen. Unerwarted entstanden *ortho* Sulfone substituierte Phenol-Komplexe in guter Ausbeute aus einer anionischen thia-Fries-Umlagerung der (Aryltriflat)tricarbonylchrom(0)-Komplexe nach Umsetzung mit LDA oder BuLi bei –78 °C. Die doppelte anionische thia-Fries Umlagerung des Tricarbonyl(1,4-dihydroxylbenzene)-bis(triflate)chrom(0)-Komplexes gelang mit LDA als Base. Zur Synthese von einem enantiomerenreichem planar chiralen 2-sulfonylphenol-Komplexes wurde eine asymmetrische Deprotonierung mit einer chiralen Lithiumamid-Base durchgeführt. Die neue anionische thia-Fries-Umlagerung wurde zur Synthese eines neuen 2-Trifluoromethylsulfonyl substituierten Steroids aus einem Tricarbonylchrom(0)-Komplex der Estrone angewendet.

Die Bildung eines ungewöhnlischen *endo*-Adduktes nach der nucleophilen Addition von 1-Propynyllithium zum *N*-vinylphthalimid Komplex liefert einen Hinweis ein intermediäre planar chirales Acylimium Ion. Die synthetische Anwendung des planar chiralen Tricarbonylchrom(0)-Komplexes des Acylimium Ions wurde untersucht.

(η^6-Aren)tricarbonylchrom(0)-Komplex · anionische thia-Fries Umlargung · asymmetrische Deprotonierung · planar chirale *N*-acyliminium Ion

Meinen Eltern

Yining und Stephan

Die experimentellen Ergebnisse dieser Dissertation wurden in der Zeit von November 2002 bis März 2006 am Institut für Organische Chemie der Universität Hannover unter der Leitung von Herrn Prof. Dr. H. Butenschön durchgeführt.

Mein besonderer Dank gilt Herrn Prof. Dr. H. Butenschön für die Überlassung des interessanten Themas, die stets freundliche Unterstützung, sowie die gute Betreuung und die vielfältigen Anregungen.
Meinen ehemaligen und jetzigen Kollegen Herrn Dr. Markus Schwarz, Herrn Dr. Ingo Weidner, Herrn Dr. Mazhar Hussain, Herrn M. Sc. Nikolai Vinokurov, Frau Dipl.-Chem. Bianka Muschalek, Frau Dipl.-Chem. Karin Kirleis, Herrn Dipl.-Chem. Marc Vollmann, Herrn Dipl.-Chem. Ingma Baumgart gilt mein Dank für die gute Zusammenarbeit, die ständige Hilfsbereitschaft und die interessanten Diskussionen, die zum Gelingen dieser Arbeit beigetragen haben.
Herrn Stephan Karger danke ich für das unermüdliche Korrekturlesen dieser Arbeit.
Frau A. Kandil danke ich für die Hilfe bei organisatorischen Problemen.
Aus der instrumentalanalytischen Abteilung gilt mein Dank Frau D. Körtje, Frau M. Rettstadt, Herrn R. Nöthel und Herrn M. Astratov für die wertvolle Diskussionen und die schnelle Aufnahme der NMR- und Massenspektren.
Besonderer Dank gilt Herrn Dr. Wartchow und Herrn Dr. M. Wiebcke vom Instiut für Anorganische Chemie der Universität Hannover für die Anfertigung aller Kristallstrukturanalysen.
Bedanken möchte ich mich bei Herrn Prof. Dr. H. Menzel (TU Brauschweig) für die DSC Messung.
Nicht vergessen möchte ich, allen Mitgliedern der Arbeitskreise Duddeck, Hoffmann, Winterfeldt, Dräger, Kirschning und Kalesse für ihre Unterstützung zu danken.
Der Deutschen Forschungsgemeinschaft (DFG) gilt mein besonderer Dank für die Vergabe einer Stelle als wissenschaftlicher Mitarbeiterin in Rahmen eines DFG-Projekts.

Meiner Familie danke ich dafür, dass sie mich immer liebevoll unterstützt hat.

Abbreviations

$[\alpha]^{D}_{rt}$	Specific Rotation
Å	Angstrom(s)
aq.	Aqueous
APT	Attached Proton Test
Ar	Aryl
ATR	Attenuated Total Reflection
Bn	Benzyl
br	Broad (spectral)
Bu	Butyl
i-Bu	*iso*-Butyl
t-Bu	*tert*-Butyl
c	Concentration
°C	Degrees Celsius
calcd	Calculated
cat.	Catalyst
cm^{-1}	Wavenumber(s)
^{13}C NMR	^{13}C Nuclear Magnetic Resonance
δ	Chemical Shift
*m*CPBA	*meta*-Chloroperbenzoic acid
d	Day(s)
d	Doublet (spectral)
dd	Doublet of Doublets (spectral)
dr	Diastereomeric Ratio
de	Diastereomeric Excess
decomp.	Decomposition
DEE	Diethyl Ether
DCM	Dichlormethan
DME	Dimethoxymethan
DMF	dimethylformamide
DIPA	*N,N*-diisopropylamine
DSC	Differential scanning calorimetry

ee	Enantiomeric Excess
EI	Electronic Impact (in mass spectrometry)
equiv.	Equivalent(s)
Et	Ethyl
FAB	Fast Atom Bombardament (in mass spectrometry)
FT-ICR	Fourier-Transform Ion Cyclotron Resonance
FT-IR	Fourier-Transform-Infrarot
g	Gramm
GC	Gas Chromatography
GP	General procedure
h	hour(s)
^{1}H NMR	^{1}H Nuclear Magnetic Resonance
HPLC	High performance Liquid Chromatography
HRMS	High resolution Mass Spectrometry
Hz	Hertz
IR	Infrarot
ISQ	*In situ* quenching
J	Coupling Constant in NMR Spectrometry
L	Ligand
LDA	Lithium diisopropylamide
m	Multiplet (spectral)
M	Molar (moles per liter)
M^+	Parent Molecular Cation (in mass spectrometry)
Me	Methyl
MHz	Megahertz
mL	Milliliter(s)
min	Minute(s)
mmol	Millimol
MOMCl	Methoxyethoxymethyl chloride
m.p.	Melting Point
Me_3SiCl	trimethylsilylchloride
MS	Mass Spectrometry
MTPA	α-Methoxy-α-(trifluoromethyl)-phenylacetic acid
MTPA-Cl	α-Methoxy-α-(trifluoromethyl)-phenylacetate chloride

m / z	Mass-to-charge Ratio (in mass spectrometry)
MW	Microwave
NMR	Nuclear Magnetic Resonance
Nu	Nucleophile
PE	Petroleum Ether
PG	Protecting Group
Ph	Phenyl
ppm	Part(s) per Million
i-Pr	Isopropyl
p-TsOH	*para*-Toluene sulfonyl acid
q	Quartet (spectral)
rac	Racemic
s	Singlet (spectral)
TBAF	Tetrabutylammoniumflouoride
TBME	*tert*-Butylmethyl Ether
THF	Tetrahydrofuran
LiTMP	Lithium 2,2,6,6-tetramethylpiperidide
TMEDA	*N,N,N′,N′*-Tetramethylethane-1,2-diamine
t	Triplet (spectral)
TLC.	Thin-layer Chromatography
TMS	Tetramethylsilane
TPB	1,3,5-Triphenylbenzene

Contents

A. Introduction

(η^6-Arene)tricarbonylchromium complexes have received much attention as key building blocks for organic synthesis.[1] The reactivity changes that arise upon the complexation of an arene to the tricarbonylchromium(0) unit allow a variety of transformations that can otherwise not be achieved by free arenes.[2] The ease of preparation and handling and the ease with which the fragment can be readily removed at the end of a synthetic sequence complement the characteristic versatility of (arene)$Cr(CO)_3$ complexes.

The $Cr(CO)_3$ group modifies chemical properties of the arene ring in several distinct characteristic fashions (Fig. 1). The η^6-coordinated arene ring is more susceptible to nucleophilic attack due to the electron withdrawing properties of the $Cr(CO)_3$ unit. The kinetic acidity of the hydrogen atoms at the aromatic ring is increased. Benzylic anions are readily formed by deprotonation, but despite the predominantly electrophilic character of the $Cr(CO)_3$ unit, benzylic carbocations are also readily stabilized. In addition to this, the $Cr(CO)_3$ moiety has found widespread use as a "stereodirecting" group in reactions at side chains attached to the arene ring by sterically hindering the reagent approach to the same face of the arene.

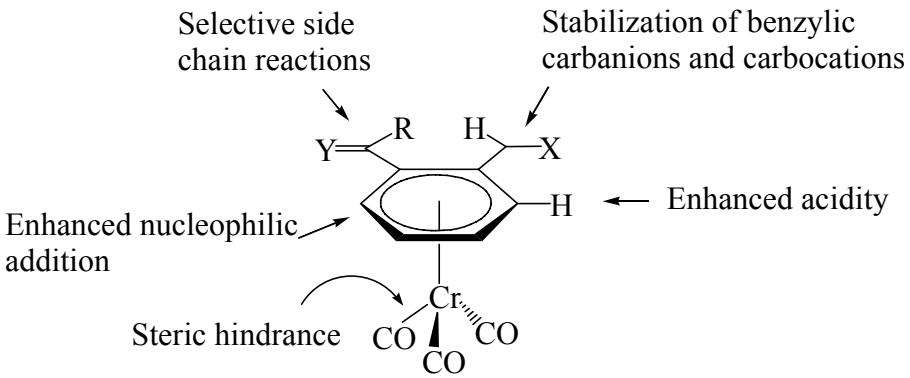
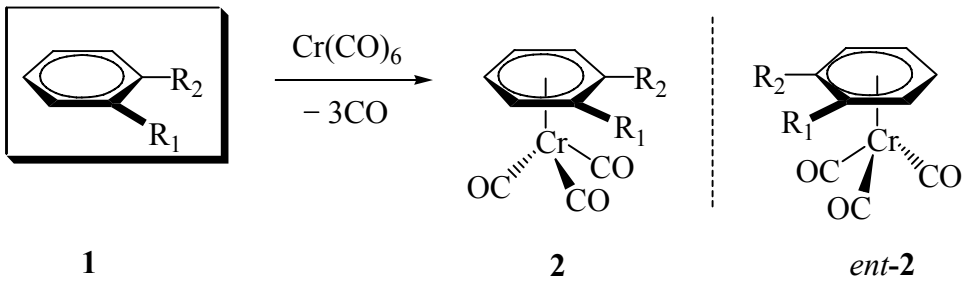


Fig. 1 Changes in arene reactivity after complexation with tricarbonyl chromium[3]

Another stereochemical feature of (arene)tricarbonylchromium complexes is the transformation of achiral disubstituted *ortho* or *meta* unsymmetrically arene ligands into chiral complexes. The only symmetry element present in a unsymmetrically 1,2- or 1,3-disubstituted achiral arene is a plane of symmetry, which lies in the plane of the arene ring and can be eliminated through the complexation at a $Cr(CO)_3$ moiety. As a consequence complex **2** cannot be superimposed on its mirror image *ent*-**2**; complexes such as **2** and *ent*-**2** are planar chiral. (Fig. 2)



1 **2** *ent*-**2**

Fig. 2 Planar chirality of arene tricarbonylchromium complex

The stereochemical assignment of such complexes in this report is in accord with the Cahn-Ingold-Prelog (CIP) rules [4] and will be explained by means of complex **3.** All the carbon atoms of the complexed arene ring are considered to be pseudo-tetrahedral with the chromium atom occupying the fourth corner of the tetrahedron. The priorities are assigned according to the CIP rules. As illustrated that the tetrahedron is rotated so that the position with the lowest priority is furthest from the observer; in the case illustrated, this results in a clockwise screw and therefore a (1*R*) centre. In most cases it is sufficient to classify only the stereogenic centre with the highest priority substituent. To further specify the element of planar chirality, a (*p*) is put in front, complex **3** is described as (1*pR*)-**3** (Fig. 3).

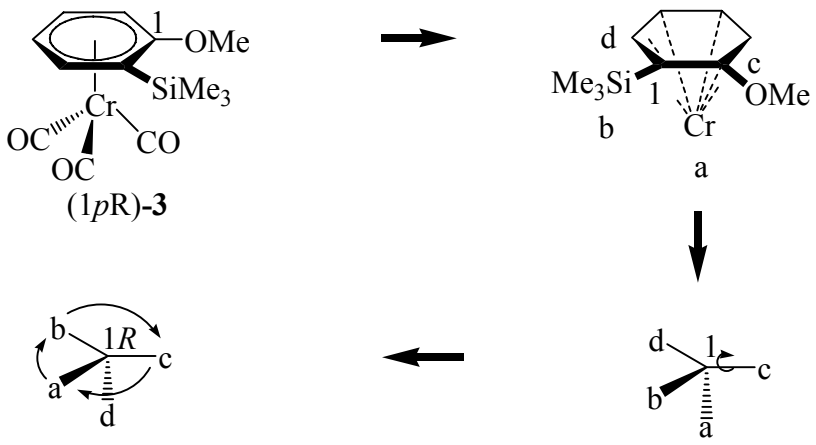


Fig. 3 Stereochemical assignment in (arene)tricarbonylchromium complex

The effect of acidification of the ring protons by coordination of an arene to the highly electrophilic $Cr(CO)_3$ group allows direct proton abstraction with base from the arene ligand.[5] Deprotonation of substituted (arene)$Cr(CO)_3$ complexes with base can occur at three different ring H positions as well as at the benzylic position.[6] Selective proton abstraction requires a base with high kinetic basicity and low nucleophilic reactivity. Commonly used bases include alkyllithium, among which butyllithium is the most widely used, and hindered amides such as LDA and LiTMP.

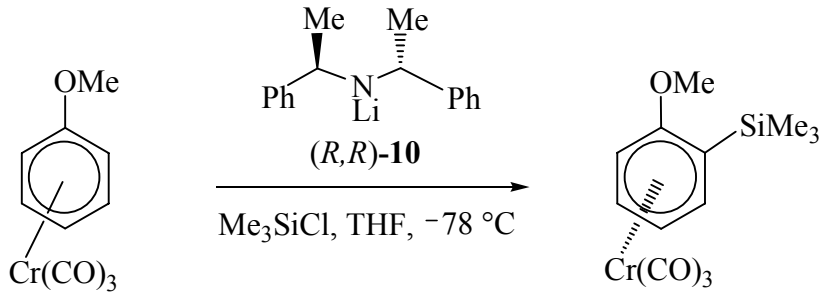
Some heteroatom containing substituents show an *ortho* directing effect in metalation of (arene)$Cr(CO)_3$ complexes, which is presumably because the *ortho* position is favoured by chelation to the heteroatom.[7] In addition, because of the lone electron pairs the heteroatoms of the substituents have been proven to be very efficient for precoordinating and selectively directing the incoming base. Most suitable *ortho*-directing groups consist of oxygen or nitrogen functionalities such as tertiary amines, ether or acetal groups.[7]

The steric effect of the tricarbonyl chromium group at one face of the arene ring can be exploited in the induction of asymmetric reactions. Planar chiral (η^6-arene)tricarbonylchromium complexes have been extensively applied as stoichiometric auxiliaries and suitable starting materials for the diastereo- and enantioselective synthesis of natural products and biologically active compounds.[8]

Recently they emerge as a valuable and versatile class of ligands for asymmetric catalysis as well.[9]

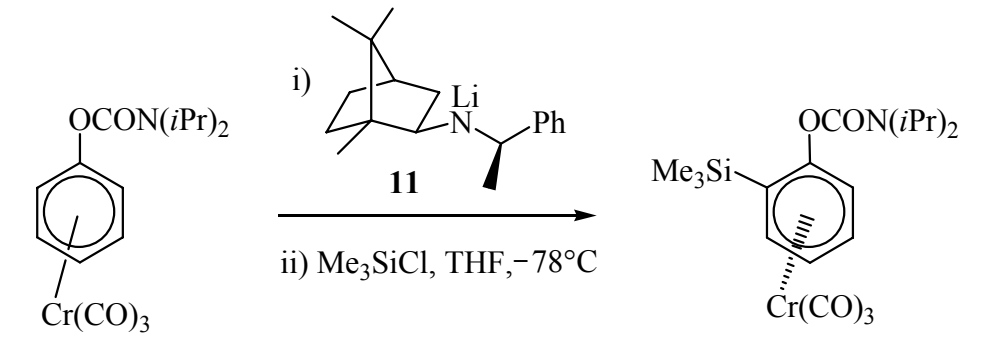
Stimulated by these successful applications, much attention has been directed to an efficient access to enantiomerically pure or enantiomerically enriched complexes. Several methods have been successfully applied to the asymmetric synthesis of enantiomerically enriched planar chiral (arene)tricarbarbonylchromium complexes, which include distereoselective complexation of chiral arenes,[10] diastereoselective or enantioselective nucleophilic addition / hydride abstraction,[11] and enantioselective *ortho*-lithiation/electrophile addition reactions.[12]

The last procedure has successfully been applied to the synthesis of a wide range of enantiomerically enriched planar chiral (arene)tricarbonylchromium(0) complexes. Because of the increased acidity of ring H-atoms in the complexes, deprotonation readily occurs with lithium amide or alkyllithium. The enantiomerically pure chiral lithium amide base or alkyllithium in combination with chiral ligands can differentiate the deprotonation of enantiotropic hydrogen atoms of a monosubstituted (arene)tricarbonylchromium complex. The Simpkins group has successfully desymmetrised (anisole)$Cr(CO)_3$ **4** using chiral base (*R,R*)-**10**, in the presence of Me_3SiCl [*in situ* quench (ISQ) conditions] to give the planar chiral *ortho*-silylated complex **3** with high enantiomeric excess in very good yield, where the MeO group of complex **4** acts as an *ortho*-directing group.[13]



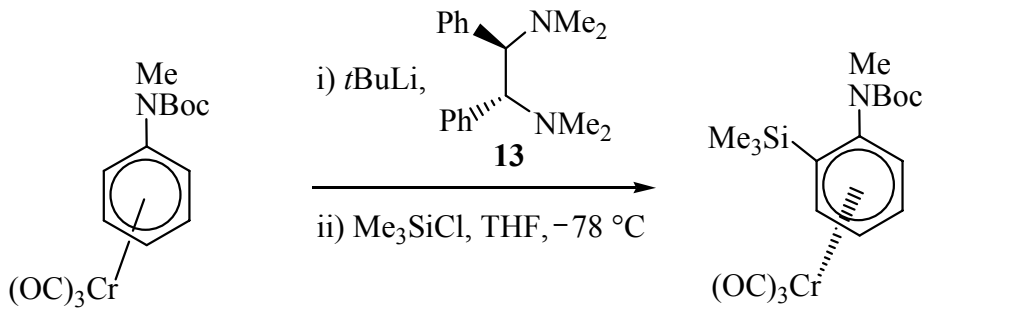
4 (+)-**3** 83 %, 84 % *ee*

The Kündig group has desymmetrised the prochiral carbomate complex **5** using the chiral base **11** to give the enantiomerically enriched trimethylsilyl derivative **12**.[14]



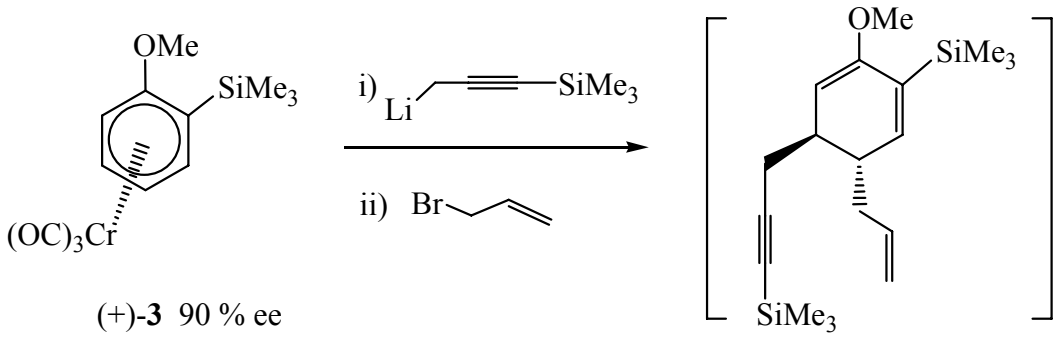
5 **12** 86%, 67% *ee*

The Uemura group has desymmetrised the Boc-protected amine complex **6** using chiral diamine **13** in conjunction with *t*-BuLi to yield **14**.[15]



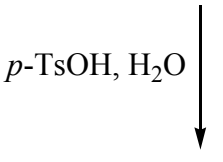
6 **14** 50 %, 57 % *ee*

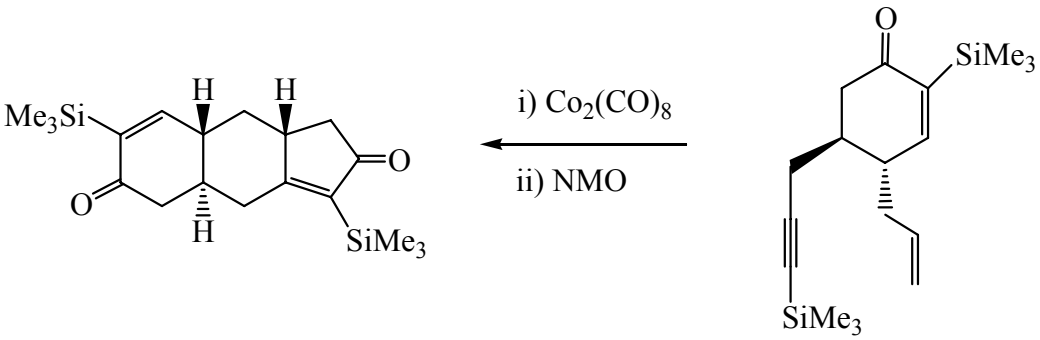
Simpkin's protocol has been applied to some synthetic studies. Kündig has used a nucleophilic addition to (+)-**3** followed by an electrophilic quench and *in situ* hydrolysis to form the substituted cyclohexenone **16.** A subsequent Pauson-Khand reaction gave a diastereomerically pure tricycle **17** in enantiomeric excess equal to that of (+)-**3**.[16]



(+)-**3** 90 % ee

15

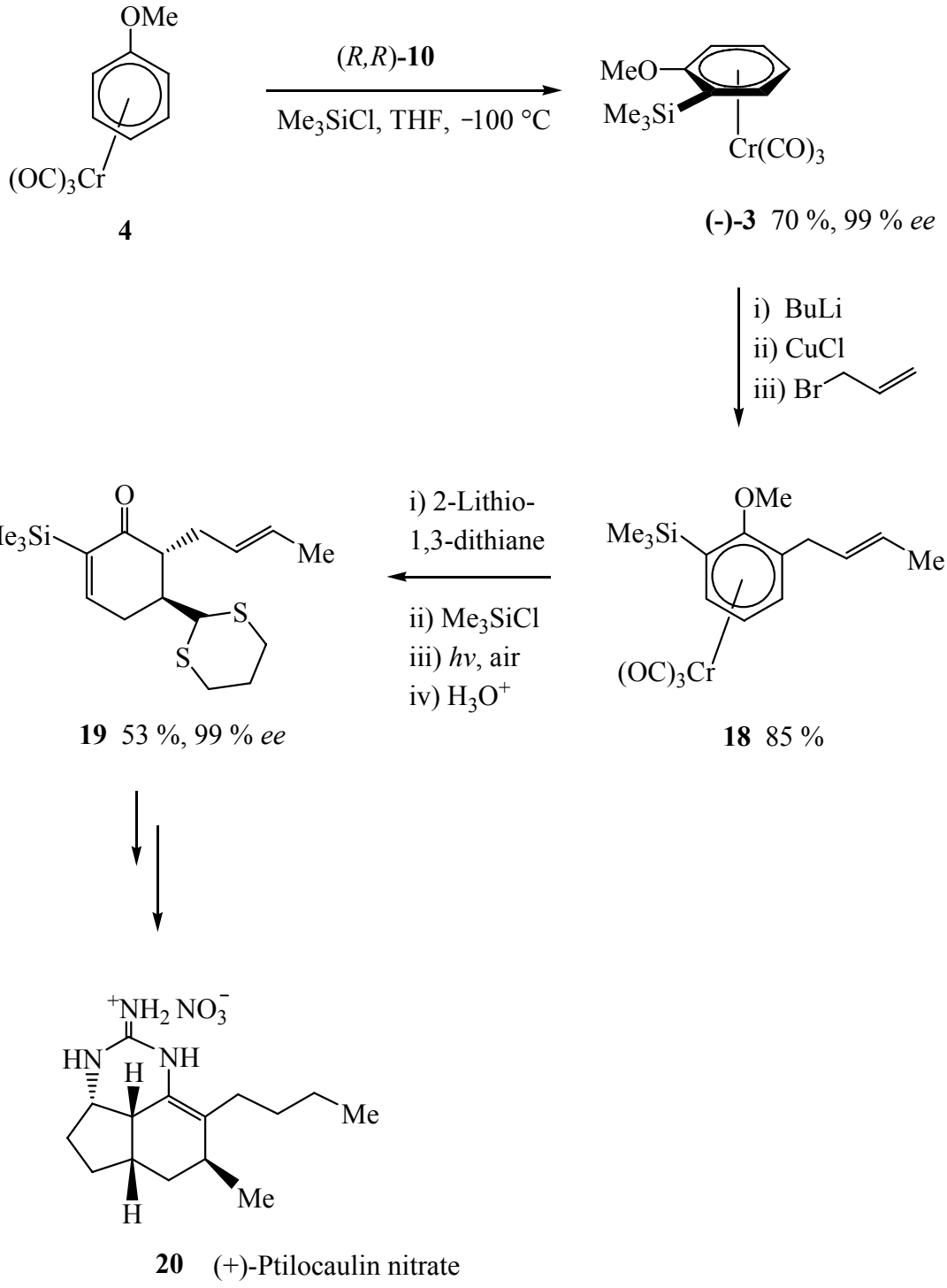




16 40 %

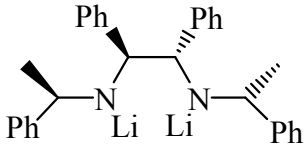
17 88 %, 90 % *ee*

Schmalz has described the synthesis of (+)-ptilocaulin, a marine natural product which shows high antimicrobial and cytotoxic activity. Cu-mediated *ortho* substitution of enantiomerically enriched complex (–)-**3** prepared following Simpkin's procedure afforded complex **18**. A highly diatereoselective nucleophilic addition of 2-lithio-1,3-dithiane, treatment with acid-free chlorotrimethylsilane and subsequent acidic work up provided substituted cyclohexenone **19** in good yield and excellent enantiomeric excess (99 % *ee*).[17] This can subsequently be converted into (+)-ptilocaulin nitrate (**20**).



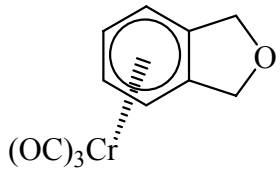
The ability of the $Cr(CO)_3$ fragment to stabilize a negative charge in the benzylic position and the strong steric effect make the *exo* deprotonation of benzylic hydrogen possible. The methodology using chiral amide bases to asymmetrically functionalize the benzylic position has been successfully extended to the prochiral complexes bearing enantiotropic benzylic methylene and methyl groups.[18]

The group of Gibson has discovered that the enantioselective benzylic funtionalisation of (benzyloxyalkane)tricarbonylchromium(0) complexes could be achieved in high enantiomeric excess (>99 % *ee*) using C_2-symmetric vicinal chiral diamide base (*R,S,S,R*)-**21**.[19] A straightforward two-step synthesis of this base had been reported in 1994.[20]



(*R*,*S*,*S*,*R*)-**21**

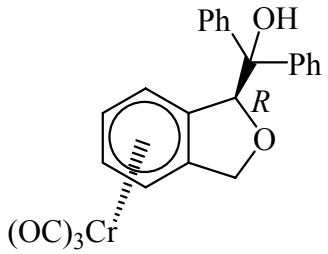
The reactions of the cyclic ether complex **22** with monoamide base (*R, R*)-**10** and the diamide base (*R,S,S,R*)-**21** followed by a benzophenone quench have been reported by Simpkins [13c] Interestingly, changing from monoamide base to diamide base raised the enantioselectivity of this reaction from 75 to 99 %. Moreover, the absolute configuration of the product **23** changed from *R* to *S* with the change of the base.



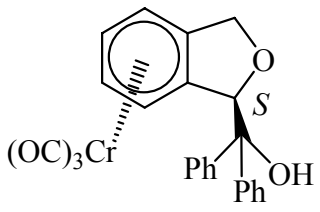
22

1. (*R,R*)-**10**
2. PhC(O)Ph

1. (*R,S,S,R*)-**22**
2. PhC(O)Ph

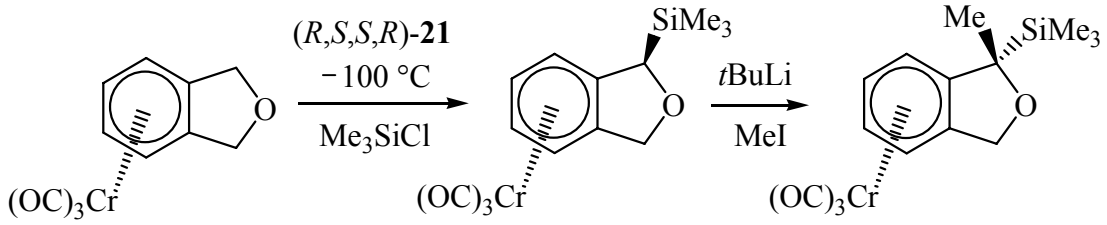


(+)-**23** 72 %, 75 % *ee*



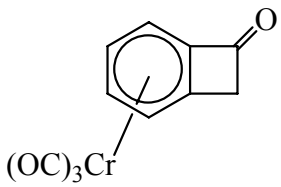
(-)-**23** 70 %, 99 % *ee*

This valuable methodology of high enantioselectively benzylic deprotonation has been applied in the diastereo- and enantioselectively synthesis of *trans*-1,3-disubstituted phthalan complexes by Schmalz.[21] The prochiral complex **22** was treated with chiral amide base **21** in the presence of Me_3SiCl (ISQ conditions) at –100 °C and the intermediate **24** (formed *in situ*) was directly converted by deprotonation with *t*-BuLi and electrophilic quench (MeI) into complex **25** with >99 % *ee* in 75 % yield.

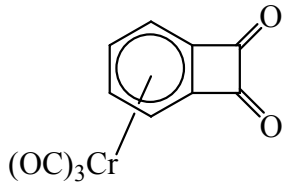


22 **24** **25** 75 %, >99 % *ee*

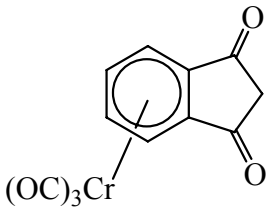
Based on the various chemical and stereochemical effects of the tricarbonylchromium unit on arene rings, the chemistry of arene tricarbonylchromium has been exploited in a wide range of applications. The group of Butenschön has contributed to this development with the investigation of (arene)tricarbonylchromium complexes with functionalized anellated rings for some time.[22, 23, 25] Two features of such type of chromium complexes have attracted the interests of organic synthesis. Firstly, the electron withdrawal of tricarbonylchromium groups renders the anellated ring electron poor, which supports the efficient nucleophilic attack at keto groups at anellated ring. Secondly, facial differentiation caused by complexation at only one side of the aromatic system decreases symmetry and as a consequence can induce changes to the seteroselectivity of chemical reaction at the anellated ring. Usually attack of reagents takes place from the face opposite to the tricarbonylchromium group. Key compounds in this research are the complexes **26**-**30** of benzocyclobutenone,[22] benzocyclobutendione, [27, 29, 31, 33-39] 1,3-indandione,[40] 1,2,3-indantrione,[40] 1,2-indandione.[41]



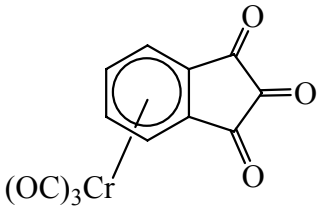
26



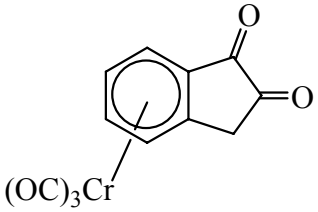
27



28

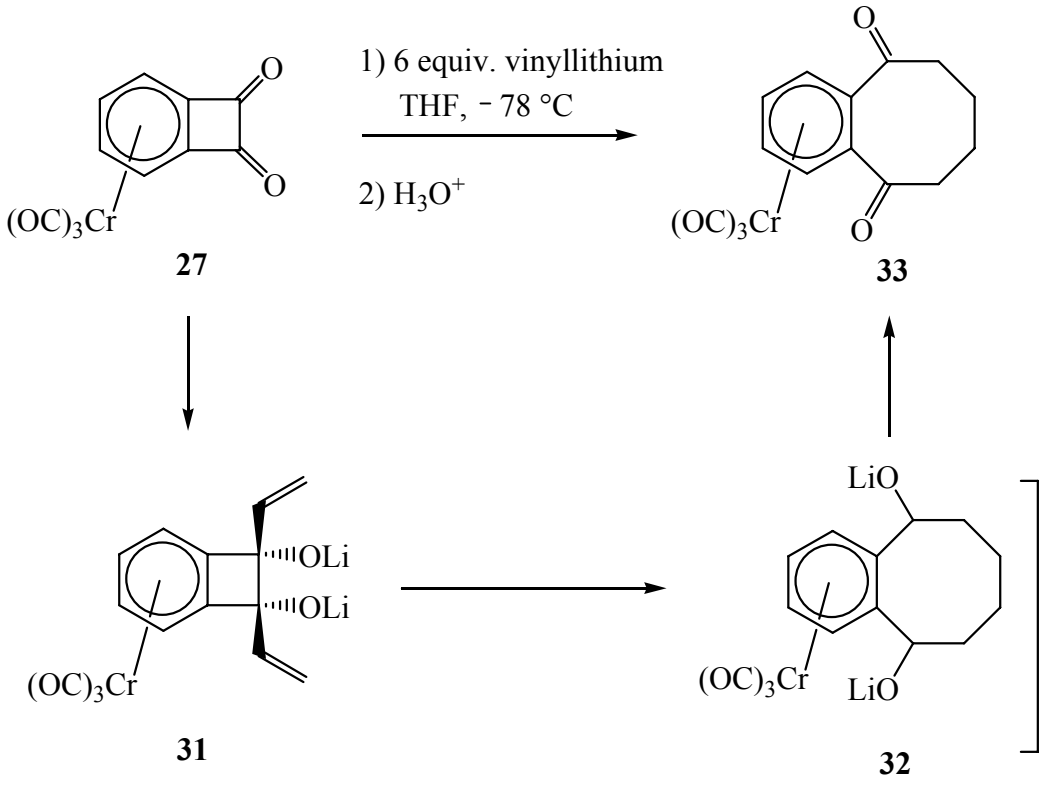


29



30

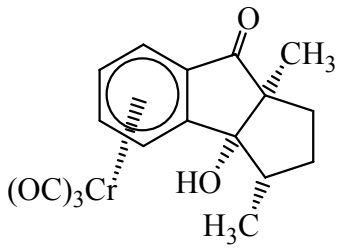
Much attention has been paid to the additions of carbon nucleophile to the keto groups of complexes of benzocyclobutenone **26** and benzocyclobutendione **27** for formation of naphthoquinone or indanone derivatives by an oxy anion-accelerated ring expansion reactions.[32] Double addition of an excess of vinyllithium to bezocyclobutendione chromium complex **27** at –78 °C facilitated an important dianionic oxy Cope rearrangement, resulting in the formation of benzocyclooctenedione complex **33** in high yield.[34]



27 **33**

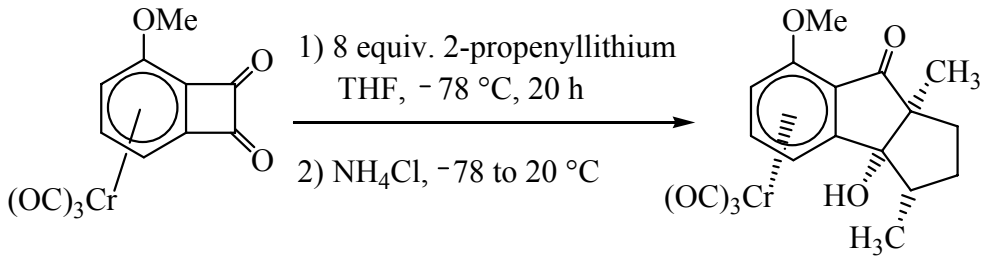
31 **32**

The dianionic oxy-Cope rearrangements staring from **27** are possible with a number of alkenylmetal reagents. In most of the cases a subsequent intramolecular aldol addition results in the formation of a highly functionalized benz-anellated diquinane, *e*. *g*. **34** from **30** and 2-propyllithium.[38]



34

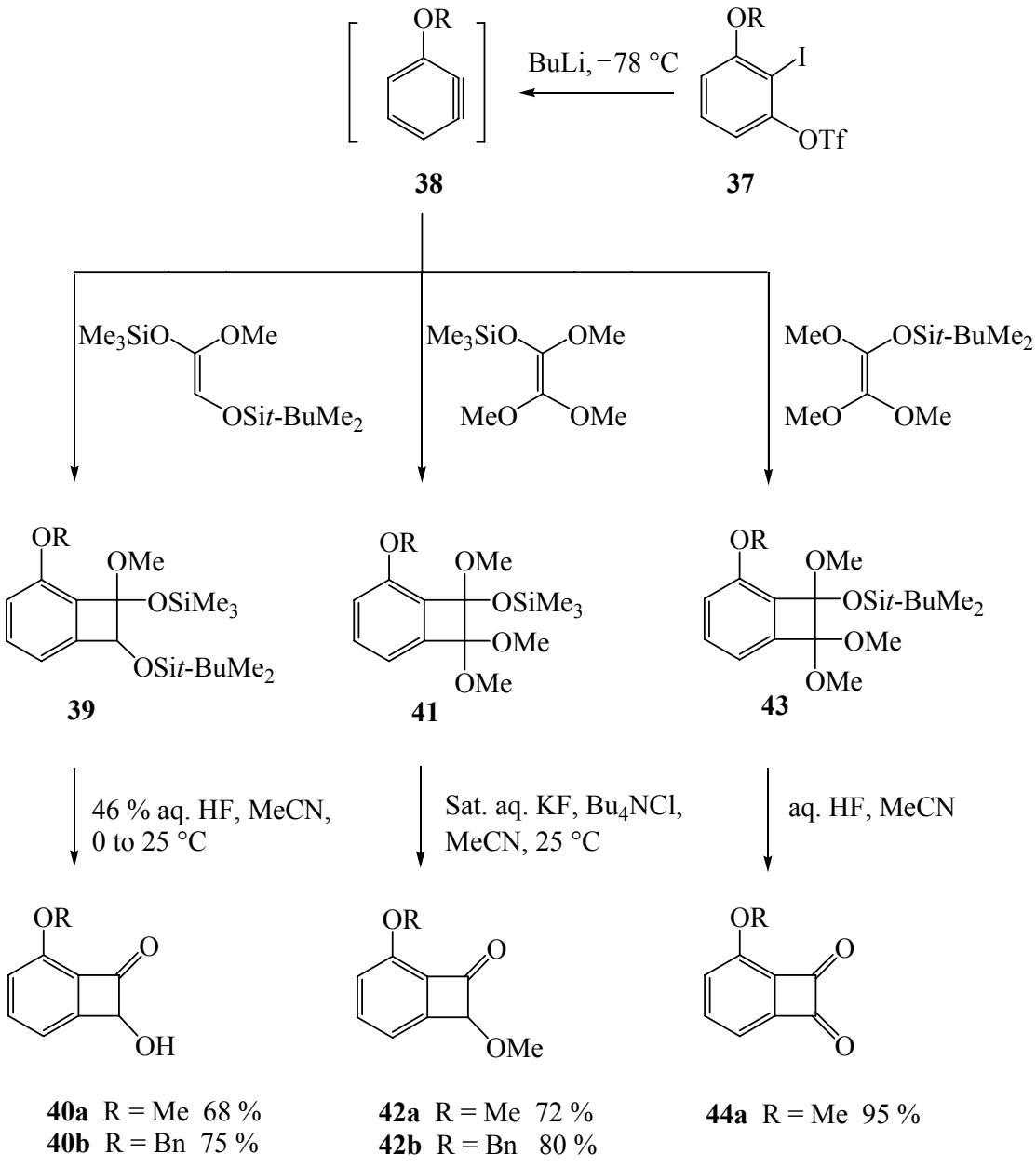
Dianionic oxy-Cope rearrangement followed by an intramolecular aldol addition occurs with remarkable regioselectivity on nucleophilic additions at substituted bezocyclobutendione *rac*-**35**.[39] For example, upon treatment of *rac*-**35** with 2-propenyllithium *rac*-**39** was obtained in 74 % yield as only one intramolecular aldol adduct instead of a mixture of isomers.



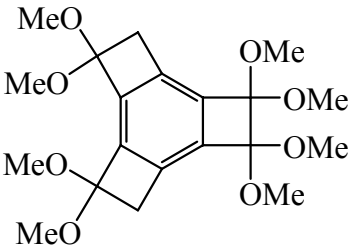
35 **36** 74 %

Encouraged by the exciting results obtained in the past years, our group continually exploits both the chemical and stereochemical potential of tricarbonylchromium complexes of benzencyclobutenone and benzencyclobutendione derivatives. In order to meet the need for the flexible and efficient accesses of complexes of benzencyclobutenone and benzencyclobutendione derivatives, we keep attention upon the progress in the related area. Recently the group was intrigued by the report from the group of Suzuki, where arynes are generated cleanly and rapidly by halogen-lithium exchange of *ortho*-haloaryl triflates with BuLi at –78 °C, followed by a [2+2] cycloaddition of arynes and ketene silyl acetals resulting highly oxygenated

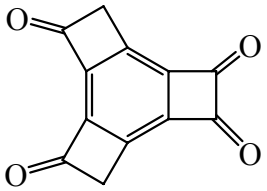
benzocyclobutene derivatives.[42] The cycloadducts can be converted to selectively protected alkoxybenzocyclobutenediones.[43]



This method has been shown to be a facile and efficient method. Most recently they reported the synthesis of poly-oxygenated tricyclobutabenzene derivatives **45** and **46** via repeated [2+2] cycloaddtion of benzyne and ketene silyl acetal.[44]



45



46

The same methodology is envisaged for synthesis of complexes of tricarbonylchromium bezencyclobuteneone, bezencyclobutenedione and the related complexes as the uncomplexed case [42, 43] by [2+2] cycloaddition between an aryne complex and a keten acetal followed by hydrolysis. Furthermore, in contrast to the wide range of applications of the highly reactive uncomplexed free arynes in organic synthesis, the utility of complexes of tricarbonylchromium aryne is surprisingly still unknown. Generation of tricarbonylchromium arynes using suitable reaction precursors is though to be of both theoretical and applicable meaning to the chemistry of arene tricarbonylchromium complex.

In addition, we currently consider to exploit the reaction potential of the (arene)tricarbonylchromium complexes with functionalized anellated nitrogen containing heterocycles affording nitrogen containing medium-and large-size ring and polycyclic system. Some complexes of isatin have been prepared and attempts towards dianionic oxy-Cope rearrangement upon diaddition of alkenyllithium reagents are underway in our group.[45] As the readily available imides, phthalimide derivatives have provided convenient routes for the construction of nitrogen containing heterocycles.[46] However, the reactivity and synthetic utility of tricarbonylchromium complexes of phthalimide derivatives remained unexplored. In parallel to the study of tricarbonylchromium isatin complexes, complexes of *N*-substituted phthalimide are considered to be used as reaction precursors for possible anion driven reactions in this work.

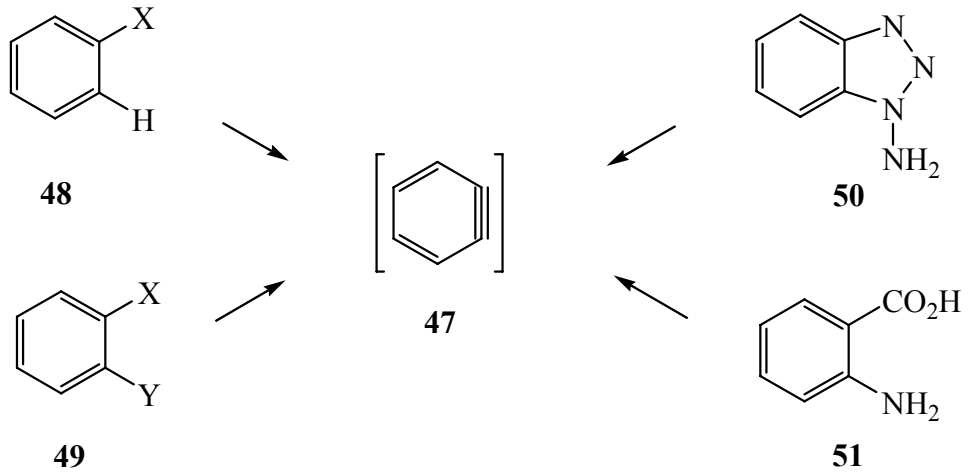
Two topics are involved in this work: one is generation of (aryne)tricarbonylchromium complexes towards synthesis of complexes of tricarbonylchromium benzencyclobutendione derivatives; the other is the study of the chemistry of phthalimide tricarbonylchromium complexes with the aim of carrying out anion driving reactions such as anionic oxy-Cope rearrangements.

B. Results and Discussion

1. (Aryltriflate)tricarbonylchromium Complexes

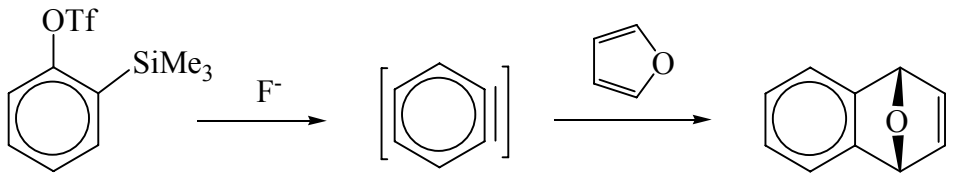
1.1 Attempted Gerneration of Tricarbonylchromium Aryne Complexes

Since the benzyne molecule has proposed by Wittig in 1942,[47] the chemistry of this reactive intermediate and its derivatives (*i. e.* arynes) has been recognized as a potential tool in organic synthesis. Arynes are not only intriguing and theoretically interesting reactive species,[48] but key intermediates for the synthesis of a large number of natural and unnatural organic products.[49] Some metal-aryne complexes have been studied, where the carbon-carbon triple bond is coordinated at the metal.[50] η^6-Aryne tricarbonylchromium(0) complexes are still unknown, although the benzyne chromium cation has been identified in a mass spectrometric FT-ICR investigation.[51] Arynes **47** have been generated by the base-mediated elimination of hydrogen halide from halobenzenes **48**[52] or metal–halogen exchange of *ortho* dihalogen substituted benzenes **49**[53] or by the oxidation of aminobenzotriazoles **50**[54] or by the decomposition of diazocarboxylate salts **51**.[55]



X, Y = halogen

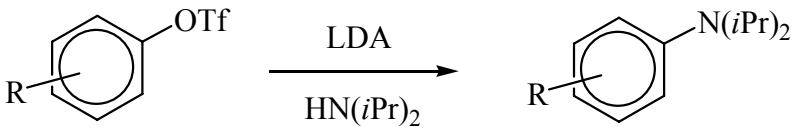
Due to the importance of arynes as reactive intermediates, many studies on new methods of their generation have been undertaken. The ability to use phenols for aryne generation would greatly expand the choice of possible starting materials and would accordingly greatly enhance the synthetic utility of the aryne intermediates. *O*-haloaryl tosylates have proven quite useful in this respect.[56] In 1983, Kobayashi described a convenient route to benzyne (**47)** under mild reaction conditions through fluoride ion displacement of the trimethylsilyl group of *o*-trimethylsilylphenyl triflate (**52)** followed by elimination of the triflate group at moderate temperature.[57] Benzyne intermediate **47** has been trapped with furan giving cycloadduct **53**.



52 **47** **53**

This mild method has revived the interest in employing arynes as substrates in organic synthesis, especially in the past 5 years, this mild method has led to the extension of aryne chemistry to multicomponent assembling reactions,[58] element-element σ-bond addition[59] and transition-metal-catalyzed muticomponent[60] and cyclotrimerization reactions.[61]

Aryl triflates **54** have also been used to generate arynes.[62] Employing LDA with an excess of *N,N*-diisopropylamine (DIPA) as *in situ* traps in THF or DME as solvent, aryl triflates underwent elimination and gave anilines **55** in good yields.



54 **55**

Suzuki and coworkers have reported the generation of arynes from *ortho*-haloaryl triflates by halogen-lithium exchange followed by metal triflate elimination[63] and applied this method to a total synthesis of the gilvocarcins through a regioselective [4+2] cycloaddition of a sugar-bearing benzyne species with 2-methyoxyfuran.[64] The

methodology has been successfully utilized for an efficient, divergent access to benzocyclobutenedione derivatives through [2+2] cycloaddition of an aryne thus generated and a ketene silyl acetal.[42, 43]

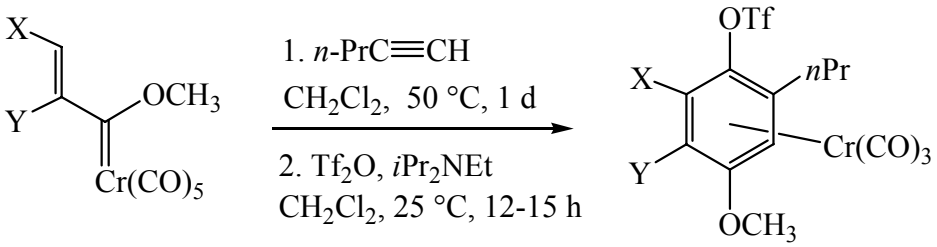
In the context of our interest in benzocyclobutenone tricarbonylchromium(0) complexes and related compounds, we were intrigued by the possibility to prepare derivatives of such complexes flexibly just as in the uncomplexed case by a [2+2] cycloaddition between an aryne complex and a ketene acetal followed by hydrolysis.

Much attention has initially been centred to the generation of aryne chromium complexes using suitable precursors. The direct complexation of *ortho*-iodo triflate with complexation reagents, *e.g.* $Cr(CO)_6$, $Cr(NH_3)_3(CO)_3$ and so on, failed because of the incompatibility of chromium complexes with Br or I atom at arene.

In order to provide the suitable precursors for the generation of aryne complexes, attention was focused on other newly developed methods for the generation of aryne without the process of metal-halogen exchange. We speculated that using pseudohalide complexes such as tricarbonylchromium aryl triflate complexes might be simple and feasible to generate aryne complexes as in the uncomplexed cases. It was anticipated that the electron withdrawal of the tricarbonylchromium group would facilate the *ortho*-metallation and subsequent metal triflate elimination of tricarbonylchromium aryl triflate complexes, providing the intermediates of tricarbonylchromium aryne complexes for the desired [2+2] cycloaddition.

1.2 Synthesis of (Aryltriflate)tricarbonylchromium Complexes

Some highly substituted arene-$Cr(CO)_3$ triflate complexes have been synthesized by Wulff and coworkers. Tetrasubsituted triflate complexes **57a-c** were prepared in moderate to good yields, respectively, from carbene complexes **56a-c** and 1-pentyne using one-pot sequential benzannulation/triflation sequence using triflic anhydride and Hünig base.(Table 1)[65]



56a-c **57a-c**

Table 1. Aryltriflate complexes prepared by benzannulation and triflation[64]

Carbene complex	X	Y	Aryltriflate complex (% Yield)
56a	H	$SiMe_3$	**57a** (81 %)
56b	H	CH_3	**57b** (66 %)
56c	--$(CH_2)_4$--		**57c** (43 %)

We attempted to develop a common and general method using commercially available hexacarbonylchromium and phenols to prepare phenyl triflate chromium complexes for our investigation. The direct complexation of phenyl triflates **66** with hexacarbonylchromium by heating gave no access to the complex of the phenyl triflate. This is presumably due to the electron deficiency of the sulfonyl group on arene. However, phenyl triflate chromium complexes could be obtained by using a different route, *i.e.* treatment of the corresponding tricarbonylchromium phenol complexes **58-65** with triflic anhydride in THF/pyridine (3:1). Tricarbonylchromium phenol complexes **67-74** were prepared in up to 94 % yield by treatment of the phenol derivatives with hexacarbonylchromium in dibutyl ether / THF (10:1) at reflux for 2-3

days. The new differently substituted phenyl triflate tricarbonylchromium complexes **75-82** were synthesized in good yield as moderately air stable to air stable yellow solids or oils. (Table 2)

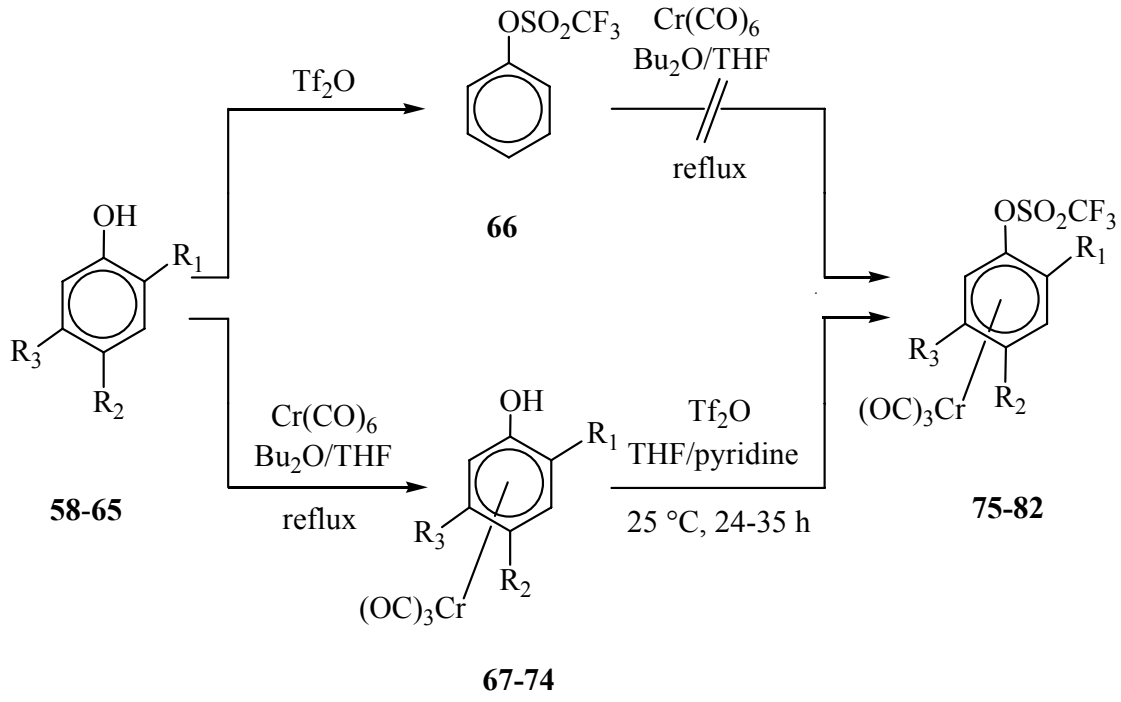


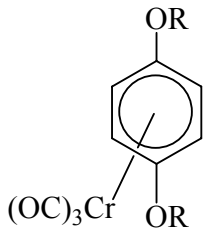
Table 2. Phenol and phenyl triflate tricarbonylchromium complexes

Entry	R_1	R_2	R_3	Product (yield)	Product (yield)
1	H	H	H	**67** (90 %)[66-68]	**75** (69 %)
2	H	OMe	H	**68** (73 %)	**76** (75 %)
3	H	Me	H	**69** (65 %)[69]	**77** (72 %)
4	$SiMe_3$	H	H	**70** (48 %)	**78** (39 %)
5	OMe	allyl	H	**71** (88 %)	**79** (88 %)
6	*i*Pr	H	Me	**72** (81 %)	**80** (74 %)
7	Me	H	*i*Pr	**73** (74 %)	**81** (48 %)
8	F	H	H	**74** (78 %)	**82** (53 %)

All the tricarbonylchromium complexes of aryl triflate are readily identified by inspection of their spectral data. The IR spectra of complex **75-82** show the typical absorption of carbonyl groups of $Cr(CO)_3$ from 1980 to 1870 cm^{-1} and the signals for the C-F vibration are found around 1420 cm^{-1}. In the ^{13}C NMR spectra, signals for Ar-OSO_2CF_3 group appear around δ = 118 ppm as a quartet with $^1J_{C\text{-}F}$ = 320 Hz. In entry 8, a doublet at δ = 141 ppm with $^1J_{C\text{-}F}$ = 269 Hz is characteristic signal for Ar-F. The chemical shifts of the *o*-arene hydrogen atoms shift from 5.13 ppm in phenol complexes to 5.50 ppm in the corresponding arene triflate tricarbonylchromium complexes. This trend agrees with the poorer π-donor ability of the triflate group as compared with the OH group.

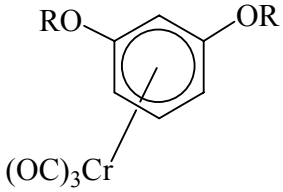
This procedure provides a flexible and convenient pathway to the phenyl triflate tricarbonylchromium complexes from the corresponding phenols with triflic anhydride as a common triflating agent Pyridine is commonly employed as a solvent for the triflation of phenols.[70] The triflation reactions presented herein proceeded smoothly under elaborated conditions using the mixture of THF and pyridine as solvent and the best ratio is found to be 3:1.

To extend the scope of the reaction, the tricarbonylchromium complexes **83-85** of hydroquinone[71,72] resorcinol and of phloroglucinol were prepared by direct complexation with $Cr(CO)_6$ in good yield. The complexes are rather sensitive to air and light, thus should be used directly after purification for the triflation. After triflation of **83-85**, double and triple triflate groups substituted complexes **86-88** were obtained respectively in moderate to good yield as air stable solids.



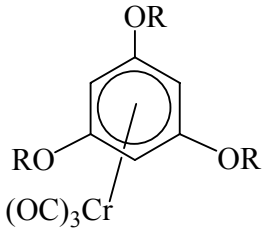
83: R = H (78 %)

86: R = SO_2CF_3 (67 %)



84: R = H (70 %)

87: R = SO_2CF_3 (63 %)



85: R = H (58 %)

88: R = SO_2CF_3 (35 %)

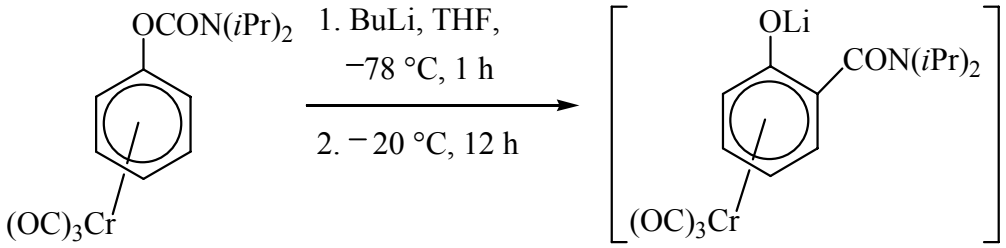
1.3 Anionic thia-Fries Rearrangement of Tricarbonylchromium Arene Triflate Complexes

The catalytic conversion of phenolic esters to hydroxyaryl ketones in the presence of Lewis acids is commonly referred to Fries rearrangement, which is a useful synthetic method for the preparation of acylphenols from phenols.[73] The reaction is facilated by Brønsted or Lewis acids such as HF, $AlCl_3$, BF_3, $TiCl_4$ or $SnCl_4$. The acids are used in excess of the stoichiometric amount, especially the Lewis acids, since they form complexes with both the starting materials and products. The complex can dissociate to form an acylium ion, which undergoes normal electrophilic aromatic substitution.[74] The thia-Fries rearrangement promoted by Brønsted, Lewis acid[75] and dry support ($AlCl_3$/$ZnCl_2$/silica-gel)[76] is an analogous reaction to the Fries rearrangement.[77]

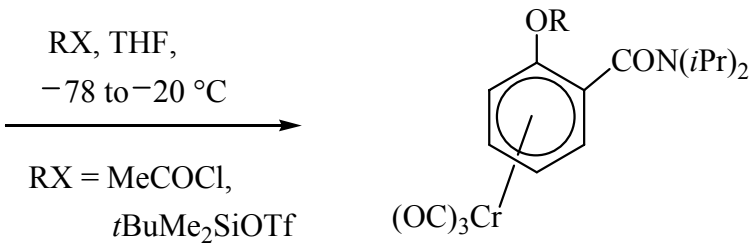
The anionic rearrangement proceeds via a directed *ortho*-metalation to form a metaleted complex intermediate at low temperature and a 1,3 transposition of the related functional group.[78] It is found that the anionic rearrangement occurs mostly on the arenes with a subsitituent bearing a heteroatom, such as O[78-80], N,[81, 82] which are responsible for the directed regioselective lithiation at the *ortho*-position by intramolecular coordination.

Compared to the normal Fries rearrangement, the anionic Fries rearrangement takes place under different conditions (low temperature and basic medium) via a different mechanism involving *ortho*-directed metalation and affords the regio-specifically *o*-substituted aromatics.[72] Based on these advantages, the anionic Fries rearrangement has been applied in regio- and stereoselective synthesis.[77, 78, 83]

The first example of an anionic Fries rearrangement was reported by Sibi and Snieckus. It was found that *o*-arylcarbamates could be *ortho*-metalated with *s*-BuLi/TMEDA at –78 °C and that 1,3-carbamoyl migration occurs upon warming to 25 °C to provide salicylamides in good yield.[79] Kündig reported an anionic oxa-Fries rearrangement of a phenylcarbamate tricarbonylchromium complex (**5**).[80] Raising the temperature to –20 °C after the lithiation of complex **5** gave access to the 1,3-transposition of carbamoyl group. The formed intermediate anionic phenolate **89** was treated directly with the electrophiles acetyl chloride or (*tert*-butyl)dimethylsilyl triflate to give complexes **90a** and **90b**, respectively.



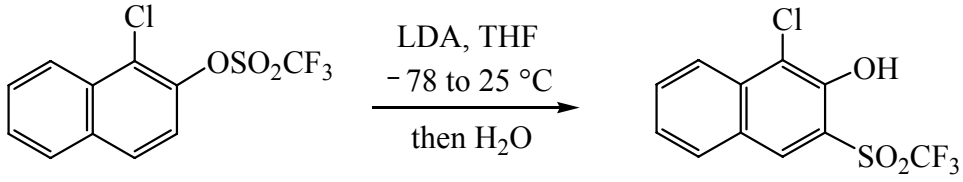
5 **89**



90a R = MeC(O) 65 %

90b R = *t*BuMe$_2$Si 65 %

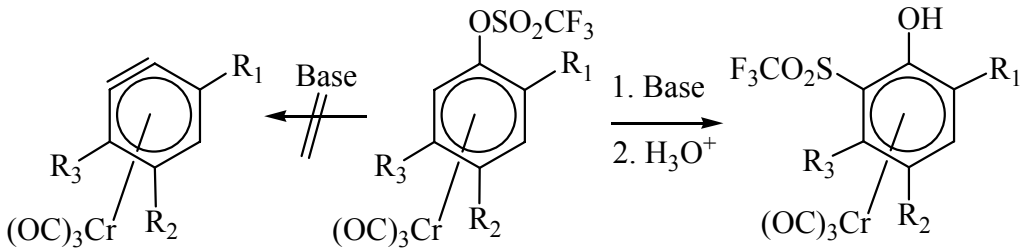
The first anionic thia-Fries rearrangement has recently been reported by Lloyd-Jones.[81] For example, 1-chloro-2-naphthyltriflate (**91**) was treated with LDA at –78 °C to room temperature, giving a product of a thia-Fries rearrangement, identified as **92**.



91 **92** 64 %

By testing various aryl triflates under analogous reaction conditions, it was revealed that the rearrangement occurred as a competing reaction with the formation of arynes. A clear differentiation was found between aryl trilaftes bearing an electron withdrawing group, especially *ortho* to the triflate group, which readily underwent anionic thia-Fries rearrangement and those with an electron donating group which exclusively underwent benzyne generation.

An *ortho* deprotonation of the tricarbonylchromium complexes of aryl triflate with lithium diisopropylamide (LDA) or with butyllithium was envisaged in order to induce triflate elimination with formation of the respective aryne chromium complexes. Several reaction conditions including *in situ* quenching with a diene to trap aryne intermediates were tested. However, in contrast to our anticipation, no evidence for aryne complex formation was observed. Instead, the anionic thia-Fries rearrangement took place and high yields of *ortho*-trifluoromethylsulfonylphenol complexes **93-99** were delivered under very mild conditions (Table 3).



A **75-77**, **79-82** **93-99**

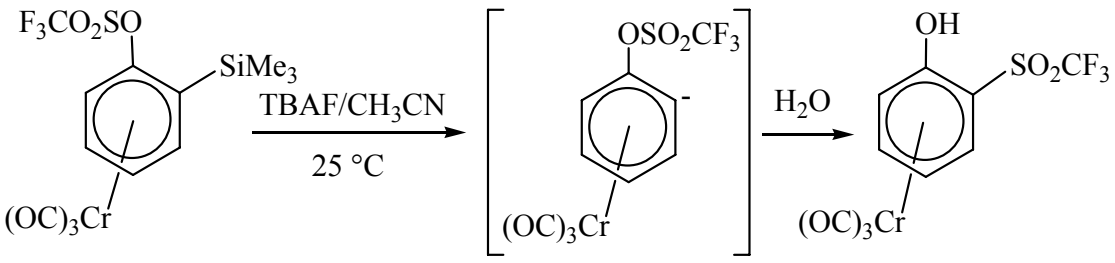
Table3. *ortho*-Trifluoromethylsulfonylphenol complexes from phenyl triflate complexes.

Entry	R_1	R_2	R_3	Triflate complex	Product (yield)
1	H	H	H	**75**	**93** (90 %)
2	H	OMe	H	**76**	**94** (82 %)
3	H	Me	H	**77**	**95** (94 %)
4	OMe	allyl	H	**79**	**96** (88 %)
5	*i*Pr	H	Me	**80**	**97** (80 %)
6	Me	H	*i*Pr	**81**	**98** (47 %)
7	F	H	H	**82**	**99** (92 %)

Tricarbonylchromium arene triflate complexes bearing either electron donating or electron withdrawing substituents at the arene ring were examined for the anionic thia Fries rearrangement giving the corresponding complexes of *ortho*-sulfonyl substituted phenols in good yields. Entry 6 shows a comparatively poor yield under the standard conditions, which is most likely due to the steric congestion in **73** with the trifluoromethylsulfonyl group being located next to the isopropyl substituent. However, the yield of the product **98** was significantly improved from 12 % to 47 % by increasing the temperature to 0 °C and stirring for another 2 hour after the addition of butyllithium at –78 °C.

Complexes **93-99** were characterized spectroscopically; the signals for aromatic ring protons adjacent to OH groups and SO_3CF_3 are found around δ = 4.70 and 5.90 ppm, respectively. This significant change exhibits the effects of the π- donor OH group and the electron withdrawing SO_2CF_3 group on the chemical shifts of the arene tricarbonylchromium complexes. In ^{13}C NMR spectra, the carbon atoms of the triflate substituents appear around δ = 122 ppm as quartets with $^1J_{C\text{-}F}$ = 326 to 328 Hz, in which the coupling constants between carbon atom and the adjacent flourine atoms are around 7 Hz higher than those of in aryl triflate complexes described above.

In an alternative approach, *o*-trimethylsilylphenyl triflate chromium complex **78** was treated with tetrabutylammonium fluoride in acetonitrile at 25 °C. Again, an anionic thia-Fries rearrangement occurred via **100** instead of a benzyne complex formation giving *ortho*-trifluoromethylsulfonylphenol complex (**93**) in 86 % yield after aqueous work up, where an anionic aryl tricarbonylchromium intermediate was generated by fluoride-induced desilylation under neutral condition and the triflouoromethsulfonyl group migrated to the *ortho* position of phenol simultaneously.



78 **100** **93**

After recrystallization of **93** from hexanes/THF (3:1), crystals of its THF monoadduct were obtained, which were suitable for an X-ray crystal structure analysis (Fig.4), confirming the assigned constitution.

Presumably due to its push pull substitution C2-C3 is obviously shorter than the other C,C bonds of the aromatic ring. Cr-C8 is significantly shorter than Cr-C9 and Cr-C10 indicating substantial back bonding, which most likely is due to a *trans* effect involving the substituted C1-C2 bond of the aromatic ring. C1-O1 bond is much shorter than C2-S, which indicates the stronger π-donor ability of OH group than that of SO_3CF_3 group.

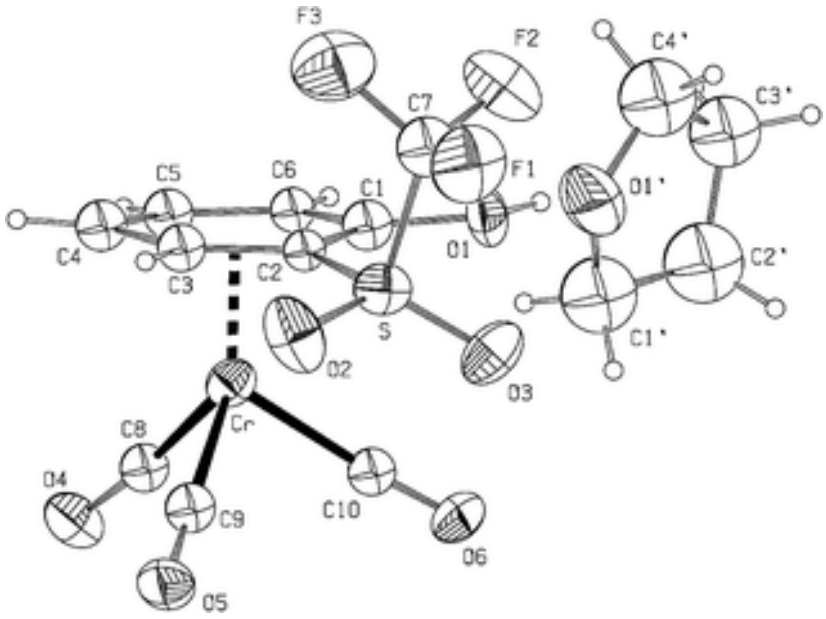


Fig. 4 Structure of **93**•THF in the crystal

Selected bond lengths [Å] and angles [°]:

C1-O1 1.37(2), C1-C2 1.41(2), C1-C6 1.40(2), C2-C3 1.37(2), C3-C4 1.43(2), C4-C5 1.45(2), C5-C6 1.39(2), C2-S 1.770(12), S-C7 1.83(2), Cr-C1 2.25(2), Cr-C2 2.207(13), Cr-C8 1.74(2), Cr-C9 1.84(2), Cr-C10 1.86(2); O1-C1-C2 116.4(12), C1-C2-S 124.9(11).

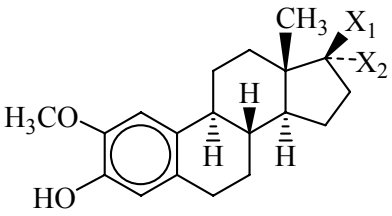
In contrast to the uncomplexed ligands of aryl triflates, in which the title rearrangement was observed only from some electron poor naphthyl and few chlorinated phenyl systems, the aryl triflate complexes readily undergo a base-mediated anionic thia- Fries rearrangement. The sulfonyl groups demonstrate an *ortho* directing effect for lithiation of arene triflate tricarbonylchromium complexes, which might be attributed to the occurrence of the rearrangement. The preference of the rearrangement of aryl triflate tricarbonylchromium complexes is presumably caused by the powerful electron withdrawal of the tricarbonylchromium fragment, which increases the acidity of the hydrogen atoms of the complexed arene and facilitates the deprotonation and the migration better satisfied by the formation of the rearranged phenolate in contrast to the alternative formation of an aryne.

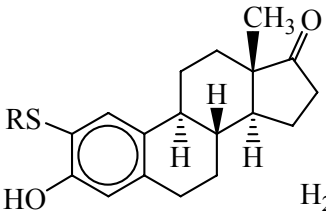
The result of the anionic thia Fries rearrangement of tricarbonylchromium triflate complexes is the formation of *ortho* trifluoromethylsulfonyl phenol complexes. Removal of the tricarbonyl chromium group by established method [84] in the reaction reported here provides an easy access to a wide range of respective *ortho*-trifluoromethylsulfonyl substituted phenol ligands.

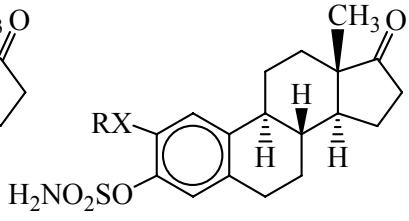
Some of the obtained examples are derivatives of natural products, *e.g.* entries 4-6, which could conveniently afford *ortho*-sulfonyl subsitituted eugenol, thymol and carvacrol derivatives respectively. Eugenol is extracted from certain essential oils especially from clove oil and cinnamon. It is used in perfumeries, flavorings, essential oils and in medicine as a local antiseptic and anesthetic. When mixed with zinc oxide, eugenol forms cement used in dentistry. Thymol is a component of the oil of thyme, ethereal oils of oregano and the bean herb and used in perfume or preserving biological specimens or in embalming or medically as a fungicide or antiseptic. The natural antimicrobial compound carvacrol is a constituent of the ethereal oil of *Origanum hirtum*, oil of thyme, oil obtained from pepperwort and wild bergamot, of strong bactericidal and fungicidal properties.

1.4 Application of Anionic thia-Fries Rearrangement in Synthesis of 2-Trifluoromethylsulfonyl Estrone (114)

The discovery that 2-methoxyestradiol (**101)** could inhibit cancer cell proliferation and angiogenesis[85] has stimulated considerable interest in the investigation of novel 2-substituted estrone and estradiols as potential therapeutic agents.[86] Most recently Potter et al. have reported the syntheses of some 2-substituted estrones, estradiol and their 3-*O*-sulfamate (EMATE) derivatives and proved the antiproliferative activity against a range of human cancer cell lines of EMATEs,[87] such as 2-methoxy (**104**), 2-alkylsulfanyl EMATEs (**105a** and **105b**). The transformation of the 2-methoxy (**102**) and 2-alkylsulfanyl (**103a** and **103b**) estrones into their respective sulfamates have been achieved with sulfanyl chloride in high yields.







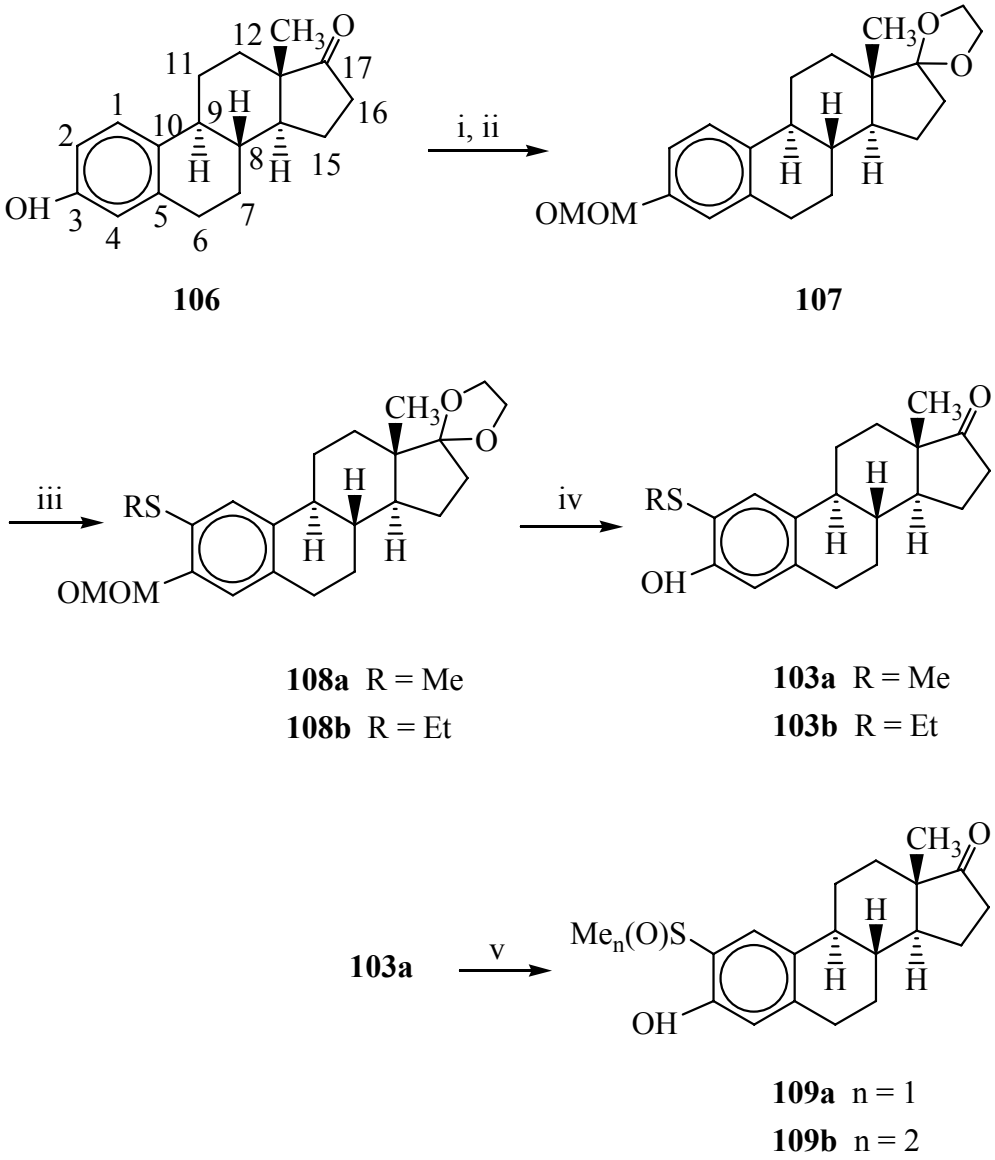
101 X_1 = OH, X_2 = H
102 X_1 = X_2 = O

103a R = Me
103b R = Et

104 R = Me, X = O
105a R = Me, X = S
105b R = Et, X = S

2-methoxy estradiol (**101**) has been recently synthesized using a Fries rearrangement to introduce the 2-acyl group in a selective and high yielding manner.[88]

The recent syntheses of 2-alkylsulfanyl and 2-alkylsolfonyl estrone from estrone **106** have been reported as most efficient entries presently available.[87] The approaches towards 2-alkylsulfanyl estrones **103a** and **103b** involved a MOM group directed *ortho*-lithation of **107** followed by quenching with disulfides, in which a protecting group for the 17-keto group was required because of the conditions for lithiation. Subsequent acidic deprotonation at the 3- and 17-positions afforded 2-alkylsulfonyl estrones **103a** and **103b**. The oxidation of **103a** to the corresponding sulfoxide **109a** and sulfone **109b** was achieved by use of the appropriate quantity of *m*CPBA in dichloromethane.



Reagents and conditions: i. ethylene glycol, *p*-TsOH, Dean-Stark, PhMe, quant; ii. NaH, MOMCl, DMF, 95 %; iii. *s*-BuLi, THF, –78 °C, 1 h then RSSR, –78 to 25 °C; iv. 4 M HCl /MeOH; v. *m*CPBA, DCM, $CHCl_3$.[87]

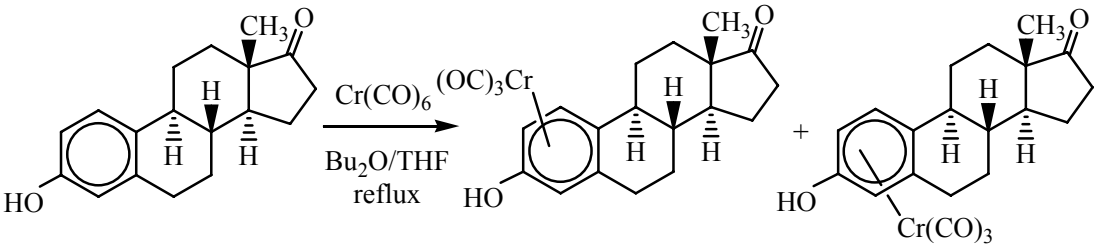
Since an *ortho* sulfonyl substituted phenol can be efficiently and conveniently prepared through an anionic thia-Fries rearrangement of $Cr(CO)_3$ facilated arene triflate, our interest was directed to apply this methodology in possible synthesis of a new *ortho* sufonyl substituted estrone from estrone **106**. It was expected that 2-sulfonyl substituted estrone could be synthesized by exploiting the opportunities of the anionic thia-Fries rearrangement of its corresponding tricarbonylchromium triflate complexes.

The reaction of $Cr(CO)_6$ with the natural derivatives estradiol and estrone has been known for a long time.[89] The well known enhanced acidity of aromatic and benzylic positions in such compounds has been exploited in regio- and stereospecific functionalization including selective functionalization of the A-ring[90, 91] and the benzylic position (C-6)[92] in the B-ring. Moreover, tricarbonylchromium derivatives of suitable steroids have been utilized advantageously in the field of analytical medicinal chemistry as new types of markers for the detection of hormone receptors by FT-IR spectroscopy, which is based on the characteristic strong absorption of terminal CO groups in the tricarbonylchromium moiety.[93] In addition, the ability of the hormones to recognize their specific receptor site is significantly dependent on their configuration (α- or β-forms).

The complexation of steroids is diastereogenic, leading to both α- or β-isomeric tricarbonylchromium complexes in similar quantities in the reaction reported earlier.[91, 92] Jaouen *et al*. have studied both the α- or β-diastereoisomers of estradiol derivatives by using high resolution one- and two-dimensional NMR spectroscopy.[94]

In early 1963, tricarbonylchromium estrone complexes have been prepared by direct complexation of estrone with hexacarbonylchromium using the mixture of dibutyl ether and hexane as solvents.[95] The stereochemical problem of α- or β-isomers was not settled.

Estrone **106** undergoes easy complexation with $Cr(CO)_6$ by heating at reflux in Bu_2O/THF (10:1). The complexation of estron is diastereoselective, leading to the mixture of both α- and β-isomeric tricarbonylchromium complex **110** of estron in a ratio of 5:3 (NMR). The separation of diastereoisomers **110** has not been carried out.

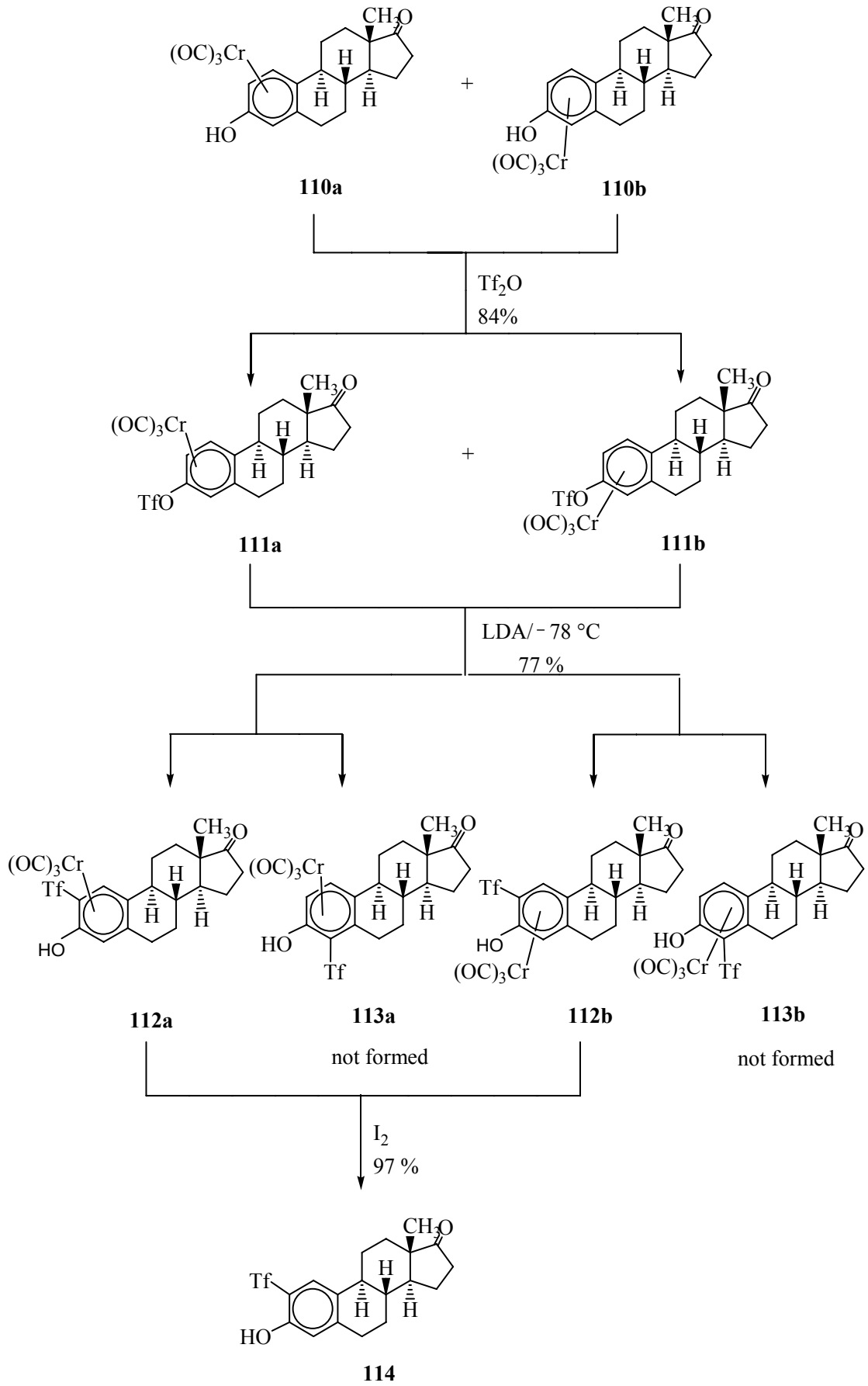


106 **110a** **110b**

Triflation of complex **110** using triflic acid anhydride under elaborated reaction conditions (described in chapter B 1.2) afforded moderately air stable complexes **111a** and **111b** in 84 % yield. The ratio of diastereoisomers deduced by NMR spectroscopy resembles that of complex **110.** Subsequently, the anionic thia-Fries rearrangement was carried out by treatment of complex **111** with LDA at –78 °C for 1 h and allowing the mixture to be warmed to 25 °C for another 30 minutes, after hydrolysis with aqueous NH_4Cl gave the product **112** in 77 % yield.

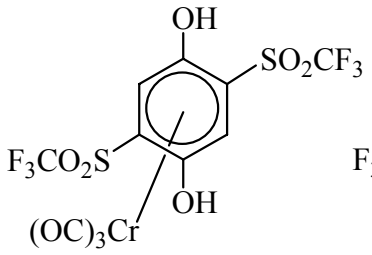
We were aware that the stereochemical outcome of the rearrangement could be two regioisomers as **112** and **113** due to two non equivalent *ortho*-protons to triflate group in aromatic ring of complexes **111a** and **111b**. Interestingly, the NMR spectra indicated that only one set of diastereoisomers **112a** and **112b** was formed in the reaction. The ratio (2:1) of diastereoisomers of **112a** and **112b** is kept from α- or β-diastereoisomers of estrone complex **110a**, **110b** and **111a**, **111b**. This indicates that the anionic thia-Fries rearrangement has occurred with complete regioselectity. Two singlets at δ = 4.62 ppm and 5.83 ppm in ^{1}H NMR spectrum of the major isomer of the product are assigned for two aromatic protons 4-H and 1-H respectively, and the constitution of the product is assigned as **112**. It is assumed that the steric reasons attributed to the regioselectivity. Subsequent oxidative decomplexation with I_2 in THF at ambient temperature for 4 hours afforded **114** in 97 % yield.

Thus an efficient and straightforward synthesis of a 2-trifluoromethsulfonyl substituted estrone has been elaborated with intrinsically fewer steps starting from estrone since no protection is required.

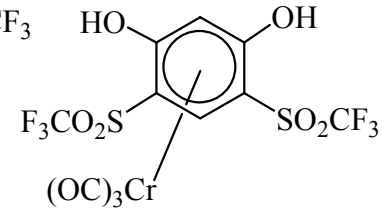

(OC)3Cr
CH3O
H
HO
110a
110b
Tf2O
84%
TfO
111a
111b
LDA/ – 78 °C
77 %
Tf
112a
113a
112b
113b
not formed
not formed
I2
97 %
114

1.5 Attempts Towards Double and Triple Anionic Thia-Fries Rearrangemnents

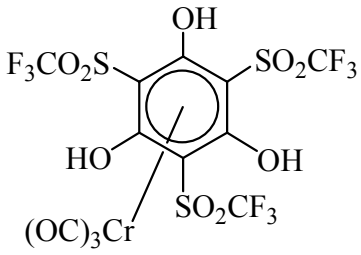
Having successfully performed the anionic thia-Fries rearrangement on various substituted aryl triflate complexes, we intended to extend the scope of the reaction. Double and triple rearrangements were envisaged by treatment of triflate chromium complexes **86-88** with butyllithium to form double or triple sulfonyl group substituted phenol derivatives **115a-117**.



115a



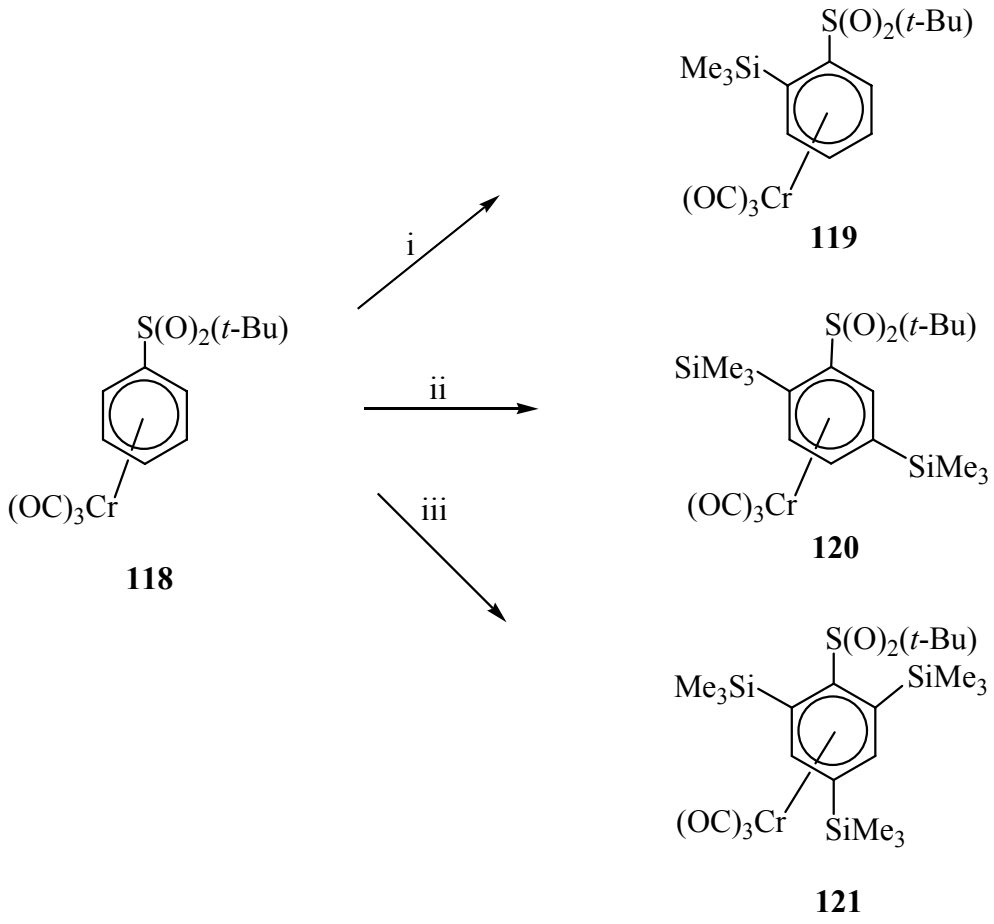
116



117

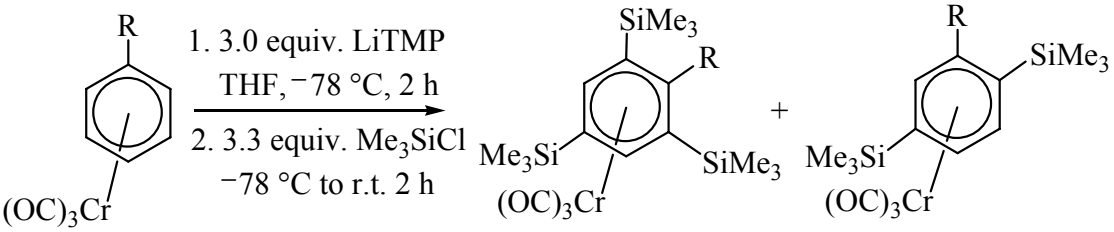
The anticipated uncommon multiply substituted arene tricarbonylchromium complexes would not only have a C_{2v}- or C_{3v} element of symmetry, but could due to their push pull substitution pattern also be envisaged as precursors for a variety of molecules having interesting material properties.[96] To achieve such type of compounds in one-pot through multiple anionic thia Fries rearrangements should involve the generation of di- and tri-anions (multiply metallated species) according to the accepted mechanism. There are very few reports detailing the generation of di- and tri-metallated aromatics, and its subsequent functionalization is severely limited due to the need to use extremely harsh conditions(lithium vapour).[97] In parallel, the characteristic, enhanced kinetic acidity of (η^6-arene)tricarbonylchromium(0) complexes has been utilized regularly for the introduction of a single function via a deprotonation-electrophilic quench sequence and has been the subject of numerous synthetic and mechanistic studies.[98] As in the case of uncomplexed aromatic substrates, reports regarding double functionalization employing a similar sequence are relatively few although di-lithiation has been observed in studies on the enantioselective deprotonation of monosubstituted arene tricarbonylchromium complexes by a chiral amine lithium base.[13a] Widdowson *et al*. have achieved

enantiomerically enriched planar chiral chromium complexes in up to 95 % *ee* via enantioselective dilithiation of arenetricarbonylchromium complexes with butyllithium and (–)-sparteine followed by electrophilic quench.[99] A 2,5-disubstituted product has been obtained from the reaction of (anisole)tricarbonylchromium(0) with one equivalent of LDA followed by a Me_3SiCl quench[100] Gibson has also observed and systematically investigated di- and tri-metallation in the course of study of deprotonation-electrophilic quench to tricarbonylchromium complex of (*tert*-butylsulfonyl)benzene (**118**). Addition of complex **118** to the cooled solution of 1.0, 2.0 or 3.5 equivalents of LiTMP (lithium 2,2,6,6-tetramethylpiperidide) followed by a Me_3SiCl quench gave the *ortho* silylated product **119**, *ortho, meta* disilylated product **120** and the *ortho, ortho, para* trisilylated product **121**, respectively.[101]



Reagents and conditions: i. LiTMP (1 equiv.), then Me_3SiCl, 51 %; ii. LiTMP (2 equiv.), then Me_3SiCl, 59 %; iii. LiTMP (3.5 equiv.), then Me_3SiCl, 50 %.[101]

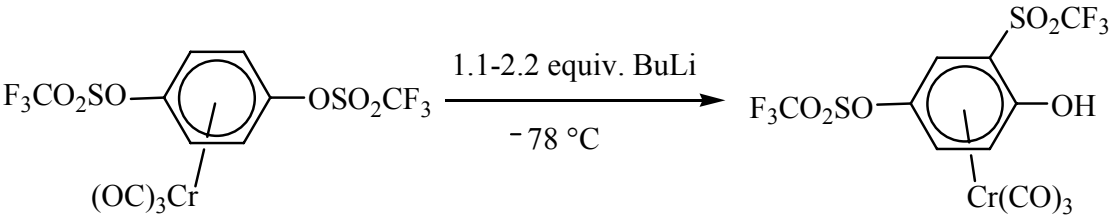
Trisubstitution on electron-poor, neutral, electron-rich substituted and unsubsituted (η^6-benzene)tricarbonylchromium(0) complexes **122** were performed by treatment of the reaction precursors with 3 equivalents of 2,2,6,6-tetramethylpiperidinyllithium (LiTMP) or LDA followed by an electrophilic quench with Me_3SiCl, Me_3SnCl and Ph_2PCl, wherein it was assumed that the di- and trianion were generated under very mild conditions.[102]



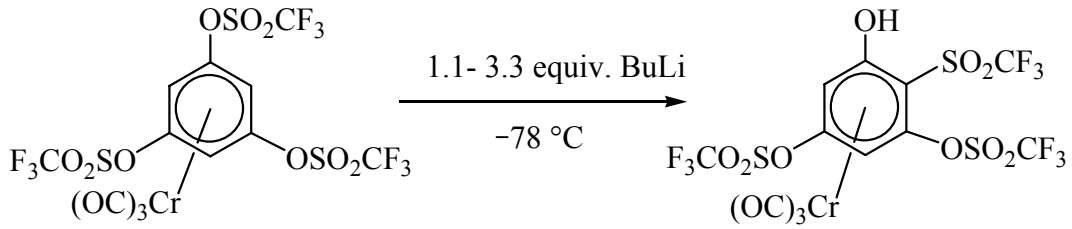
122a R = $SO_2(t\text{Bu})$
122b R = OMe
122c R = CH_2NMe_2
122d R = H

123a-d **123b-d**

In order to generate double and triple anionic thia-Fries rearrangements, **86** and **88** were respectively subjected to an excess of butyllithium at –78 °C. The colour of the reaction mixture changed from yellow to orange in the case of less than 3 equivalents of butyllithium being used. The isolated products **124** and **125** resulted from a single anionic thia-Fries rearrangement, respectively. In the cases in which more than 3 equivalents of base were used, decomposition was observed. Changing reaction time from 0.5 h to 12 h and reaction temperature from –78 to –30 °C did not show any significant change in the distribution of the desired products. Carrying out the reaction at temperature higher than –30 °C resulted in extensive decomposition.

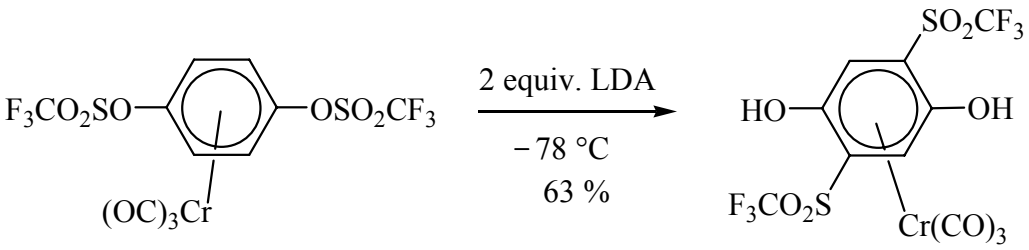


86 **124**



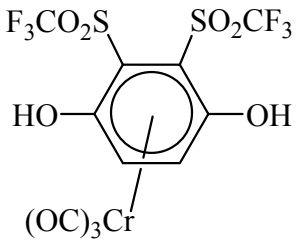
88 **125**

To our delight, treatment of **86** with 2 equivalents of the sterically hindered amide base lithiumdiisopropylamide (LDA) at –78 °C led to a deep red solution after few minutes, indicating the generation of the dianion and consequently afforded the desired symmetrically doubly rearranged complex **115a** in good yield.



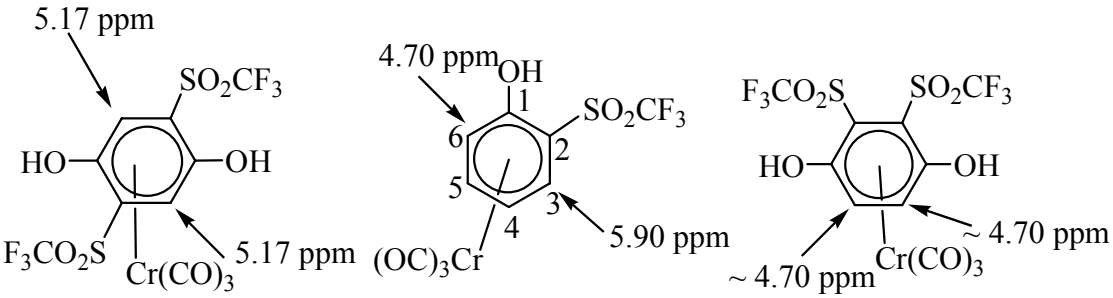
86 **115a**

The constitution of the product **115** is based on its spectra data. A singlet at δ = 5.17 ppm in ^{1}H NMR spectrum is assigned to the symmetric aromatic ring protons. Only one quartet at 121.9 ppm with $^{1}J_{C\text{-}F}$ = 327.4 Hz is observed in the ^{13}C NMR spectrum, which is fitting with the two *para* symmetric SO_2CF_3 groups for the product. However, to assign the structure of the product the argument about two possibilities, *i.e*. **115a** and **115b** emerges.



115b

The significant difference of the chemical shifts between aromatic ring protons adjacent to OH groups and SO_3CF_3 of the products from the single rearrangement has been discussed in chapter 1.3, which may support the assumption of structure as **115a**. For example, in complex **93**, the effects of the π-donor OH group and the electron withdrawing SO_2CF_3 group exhibits significant difference of the chemical shifs between H-6 and H-3.



115a **93** **115b**

(Estimated values)

In the case of complex **115b**, the NMR signal of both symmetric aromatic ring protons might at least be similar with H-6 in complex **93** because they are in similar electron-rich chemical environments leading to high field absorption. The singlet in NMR spectrum for the aromatic ring protons of the product obtained in the double rearrangement appears at δ = 5.17 ppm, in a lower field than the comparable H-6 in complex **93**. This is likely the average result of the influence of both neighbor groups, *i.e*. the electron-donating OH group and the electron-withdrawing SO_2CF_3 group as in **115a**. In addition, the case in which both SO_3CF_3 groups rearrange each other to *para* position leading to **115a** is less sterically congested than that of to *ortho*-position leading to **115b**.

The symmetric regiochemical outcome of the reaction may be predicted by assuming that the double anions are generated and that the charges arrange themselves to be as far apart as possible to achieve minimum electronic repulsion. Thus it appears that the *para* symmetric dianions of least energy is more stable than the *ortho* symmetric dianions.

This double anionic this-Fries rearrangement of tricarbonlychromium aryl triflate **86** is consistent with the results of some symmetrically 2,5-disustituted (η^6-benzene)tricarbonylchromium(0) complexes obtained from those described in the

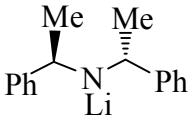
Gibson's study above.[101, 102] It appears that the combination of a steric hindered amide base provides access to dianion generation presumably by facilitating anion equilibration and promoting the migration of trifluoromethylsulfonyl group at a relatively unhindered site.

To the best of our knowledge, the direct generation of multiple anions on one arene ring is rather rare.[102] The multiple lithiation on (arene)tricarbonylchromium(0) complexes demonstrates again the powerful eletronwithdrawing effect of $Cr(CO)_3$ leading to the enhanced kinetic acidity of arene ring. The efficient difunctionalisation of benzene ring in one step is of importance to explore its synthetic utility.

Encouraged by the accomplishment of the double rearrangement, we next attempted to generate triple rearrangement using the now established protocol. Complex **88** was treated with 3-8 equivalents of LDA at –78 °C, the colour of the reaction mixture was rapidly changed from yellow to deep red, indicating the formation of the di or trianion. However, no anticipated product **117** of a triple rearrangement was isolated after the reaction sequences. Increasing the reaction temperature from –78 to 25 °C for a period of 30 minutes gave no desired product at all. The reason for the failure of the triple rearrangement is possibly that the aryl ring is too crowded to contain three triflouoromethylsulfonyl groups.

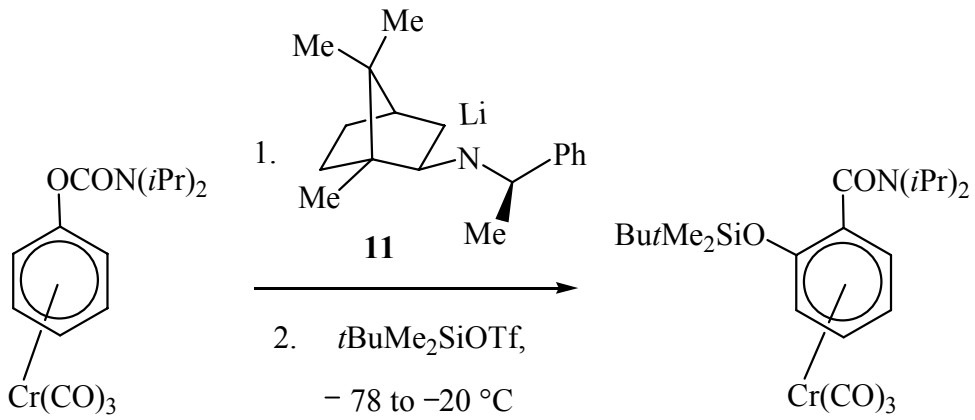
1.6 Enantioselective *ortho*-Deprotonation of Tricarbonyl(phenyltriflate) chromium(0) (93)

The desymmetrization of prochiral (arene)$Cr(CO)_3$ complexes by directed enantioselective *ortho*-metalation and subsequent quench with an electrophile remains one of the most efficient methods to access of enantiomerically pure and enantionmerically enriched planar chiral chromium complexes.[9] The two *ortho* protons in a monosubstituted (arene)$Cr(CO)_3$ complexes are enantiotropic and can be distinguished by a chiral base. Application of this strategy has so far been dominated by enantiomerically pure amides lithium bases **10** and **11**. The chiral base **10** has been used by Simpkins for the enantioselective *ortho* deprotonation of (anisole)tricarbonylchromium followed by *in situ* quenching (ISQ) with electrophile of Me_3SiCl, which resulted in the formation of *ortho*-silylated complex of more than 97 % *ee* after a single recrystallization.[13]



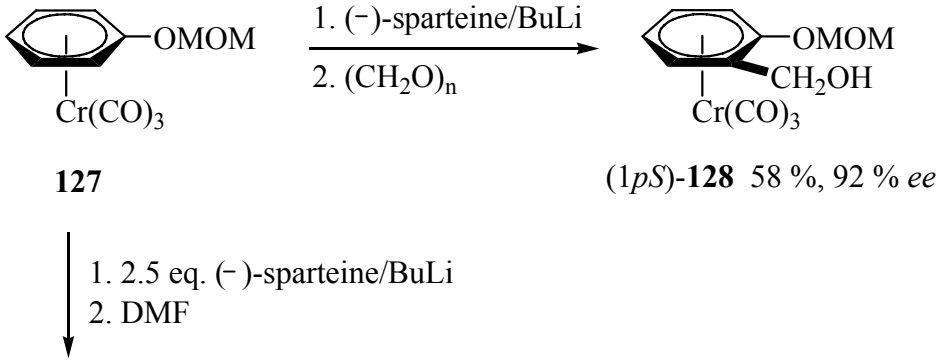
(*R,R*)**-10**

Lithium amide **11** has been used to initiate an anionic *ortho*-Fries rearrangement. Warming the anion generated to –20 °C and stirring for 12 h induced the rearrangement; after quenching, product **126** was isolated and shown to be enantiomerially enriched.[80]

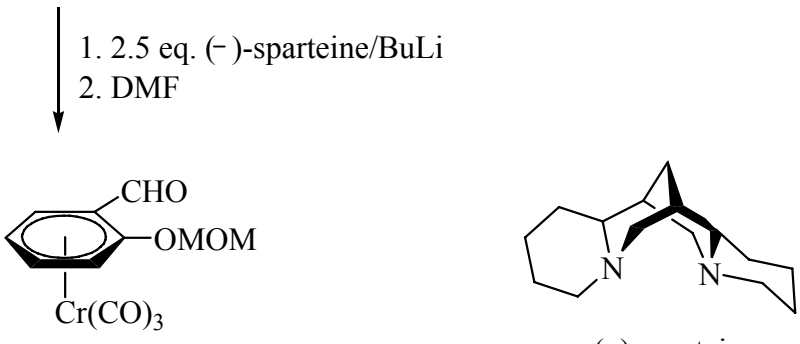


5 (1*R*)-**126** 42 %, 54 % *ee*

Widdowson and co-workers reported the successful application of (–)-spartein/butyllithium in the enantioselective *ortho*-lithiation of complex **127** bearing an OCH_2OMe (OMOM) group as an *ortho*-directing group. Complex **127** could be selectively deprotonated using (–)-sparteine and BuLi to give after electrophilic quench with $(CH_2O)_n$ the planar chiral complex (1*pS*)-**128** in 58 % yield and 92 % *ee*.[103] In a subsequent study the same complex showed that the opposite stereochemistry was also accessible *via* a dilithiation approach using 2.5 equivalents of (–)-sparteine/BuLi, thus avoiding the use of non-commercially available (+)-sparteine. Using this strategy, complex (1*pR*)-**129** was obtained in 95 % *ee* and 30 % yield.[104]



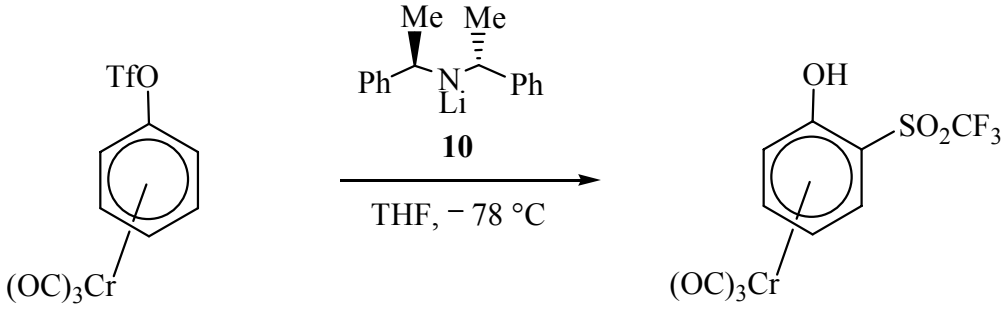
127 (1*pS*)-**128** 58 %, 92 % *ee*



(1*pR*)-**129** 30 %, 95 % *ee* (−)-sparteine

Since the anionic thia-Fries rearrangement of phenyltriflate chromium complexes involves an exclusively *ortho* selective deprotonation with base giving 1,2 disubstituted arene tricarbonyl complexes, we anticipated that a direct approach to enantiomerically enriched tricarbonyl(*ortho*-trifluoromethylsulfonylphenol)chromium complexes would be possible by treatment of a prochiral complex, namely a symmetric arene triflate complex with an enantiomerically pure chiral lithium amide base, which could discriminate the two enantiotropic *ortho*-hydrogen atoms, leading directly to a non-racemic product of the anionic Fries rearrangement.

To avoid an increase of the reaction temperature, the solid phenyl triflate complex **67** was directly added in one portion to the cooled (–78 °C) solution of chiral lithium amide base **10,** which was prepared *in situ*.[105] The mixture was stirred at –78 °C for 1.5 h, hydrolyzed and purified by column chromatography. Tricarbonyl(*ortho*-trifluoromethylsulfonylphenol)chromium complex (+)-**93** resulted in 70 % yield and 30 % *ee* (The determination of enantiomeric excess using Mosher ester is described in chapter 1.7).



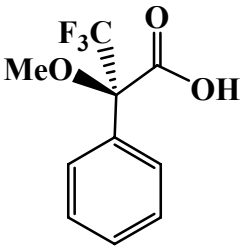
75 **(+)-93** 70 %, 30 % *ee*

Several reaction conditions were tested, including changing reaction time from 0.5 to 2 hours, the sequence of addition of chiral base and complex. (–)-Sparteine/BuLi has also been used for the enantioselective deprotonation. However, there was no significant improvement of enantioselectivity. The low enantiomeric excess of the product is presumably caused by the pre-coordination of chiral base at Lewis basic oxygen atoms of the triflate group or occurrence of dilithiation at both enantiotropic positions of the phenyl ring,[13, 99] leading to kinetically non-selective migration of the triflate group.

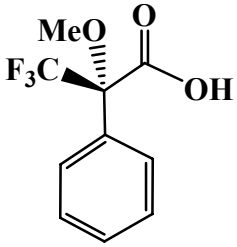
1.7 Determination of Enantiomeric Excess of (+)-93 Using Mosher's reagent

1.7.1 Introduction

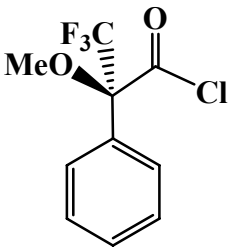
In early 1969 Mosher *et al*. established their method for the determination of enantiomeric composition and absolute configuration of alcohol and amines.[106, 107] This method includes preparation of diastereomeric esters and amides from enantiomerically pure Mosher reagents, such as α-methoxy-α-(trifluoromethyl)-phenylacetic acid (*R*)-MTPA (**130**) and (*S*)-MTPA (**131**) or α-methoxy-α-(trifluoromethyl)phenylacetate chloride (*S*)-MTPA-Cl (**132**) and (*S*)-MTPA-Cl (**133**). By measuring the intensities of the significantly different NMR signals of the diastereometrically substituted groups of ester and amides the enantiomeric excess of alcohols and amines can be determined.



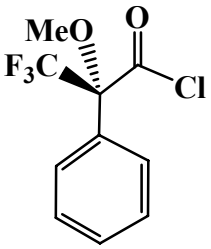
130 (*R*)-MTPA



131 (*S*)-MTPA



132 (*S*)-MTPA-Cl



133 (*R*)-MTPA-Cl

Mosher proposed that, in solution, the carbinyl proton and ester carbonyl and trifluoromethyl groups of the MTPA moiety preferentially lie in the same plane (Fig 5 A).[107] When the MTPA group is in the hypothesized conformation, Mosher pointed

out that the ^{1}H NMR signal of L^2 of the (*R*)-MTPA ester will appear upfield relative to that of the (*S*)-MTPA ester due to the diamagnetic effect of the benzene ring. The basic concept of the modified method is essentially the same as Mosher proposed: The idealized conformation is depicted in Fig. 5B.

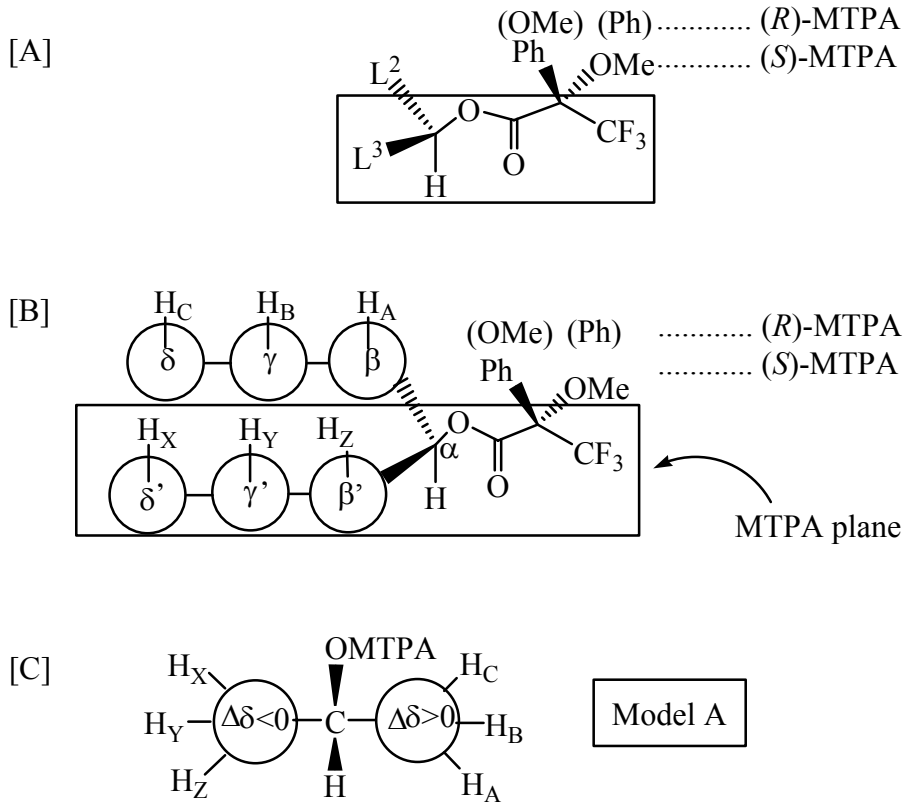


Fig. 5 [A] Configuration correlation model for the (*R*)-MTPA derivatives and the (*S*)-MTPA derivatives proposed by Mosher. [B] MTPA plane of an MTPA ester. [C] Model A to determine the absolute configurations of the secondary alcohols.

Due to the diamagnetic effect of the benzene ring the ^{1}H NMR signal of $H_{A,B,C...}$ of the (*R*)–MTPA ester will appear upfield relative to those of the (*S*)–MTPA ester. The reverse should hold true for $H_{X,Y,Z...}$. Therefore, if it is definded $\Delta\delta = \delta_S - \delta_R$, when the protons $H_{A,B,C}$… on the right side of the plane, $\Delta\delta$ is positive ($\Delta\delta > 0$), when the proton $H_{X,Y,Z}$… on the left side of the plan, $\Delta\delta$ is negative ($\Delta\delta < 0$). Put the protons with positive $\Delta\delta$ on the right side and those with negative $\Delta\delta$ on the left side of the model A as illustrated in Fig 5C.

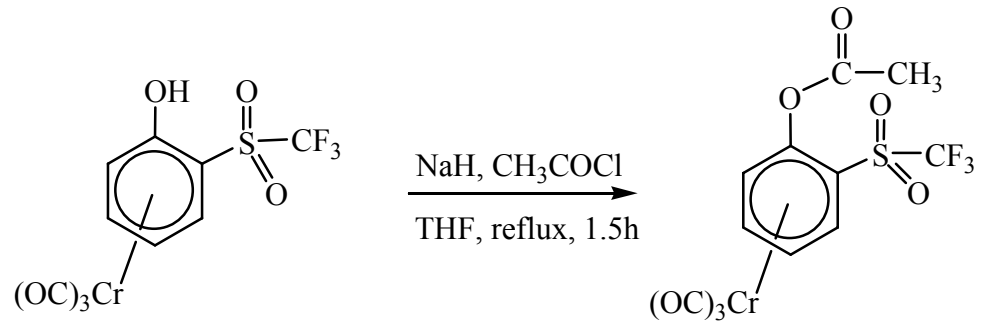
Mosher's method has been most frequently used for determination of enantiomeric excess and the absolute configuration of organic compounds[108] including tricarbonylchromium complexes.[13a]

Because the complete assignment of protons of complex organic molecules was practically impossible, modifications have been used upon the basic concept as Mosher proposed.[107b] The most important factor of the modified methods is the difference in steric bulkiness of the substituents on the β- and β'-carbons (Fig. 5B); the steric repulsion between the phenyl group of the MTPA moiety and the β-substituents is essential to bring out the chemical shift difference of the CF_3 (^{19}F) or OMe (^{1}H) group. The application of Mosher's method by use of high-field FT-NMR spectroscopy has been reported.[108] This method enables one to examine the chemical shift differences of as many protons as can be assigned by means of up to date NMR techniques. It is more reliable for the prediction of the absolute configurations of complex molecules, especially natural products.

1.7.2 Synthesis of Tricarbonyl[(2-trifluoromethanesulfonyl)phenylacetate]-chromium(0) (134)

The aim of this experiment was to probe the optimised conditions for the esteration of complex (+)-**93** with Mosher's reagent (*R*)-MTPA-Cl (**133**).

One strong effect of the coordination of tricarbonylchromium to an arene ligand is the acidification of the ring protons. The acidity of phenol group of *ortho* trifluoromethylsulfone substituted phenol tricarbonylchromium complexes should be much more increased than the normal phenol as well. Treatment of complex **93** with sodium hydride in THF for few minutes followed by addition of acetyl chloride and refluxing for 1-2 hours afforded the acetate **134** in 60 % yield.

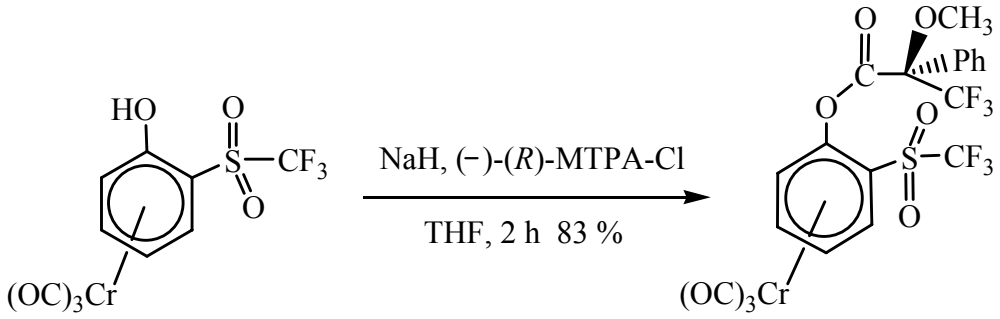


93 **134** 60 %

Complex **134** is readily characterized spectroscopically. In the IR spetrum, the absorptions at 1790 and 1774 cm^{-1} correspond to the stretching absorptions of the keto group; the appearance of the singlet at δ = 2.3 ppm in the ^{1}H NMR spectrum accounts for the methyl group and the signal at δ = 169.6 ppm for carbonyl group in the ^{13}C NMR spectrum, confirm the acetate moiety.

1.7.3 (*R*)-MTPA Ester of Tricarbonyl(2-trifluoromethanesulfonylphenyl)-chromium(0) (135)

By the same procedure as for the preparation of complex **134** described above, Mosher ester complex **135** is accessible in good yield for the determination of enantiomeric excess of complex (+)**-93**.



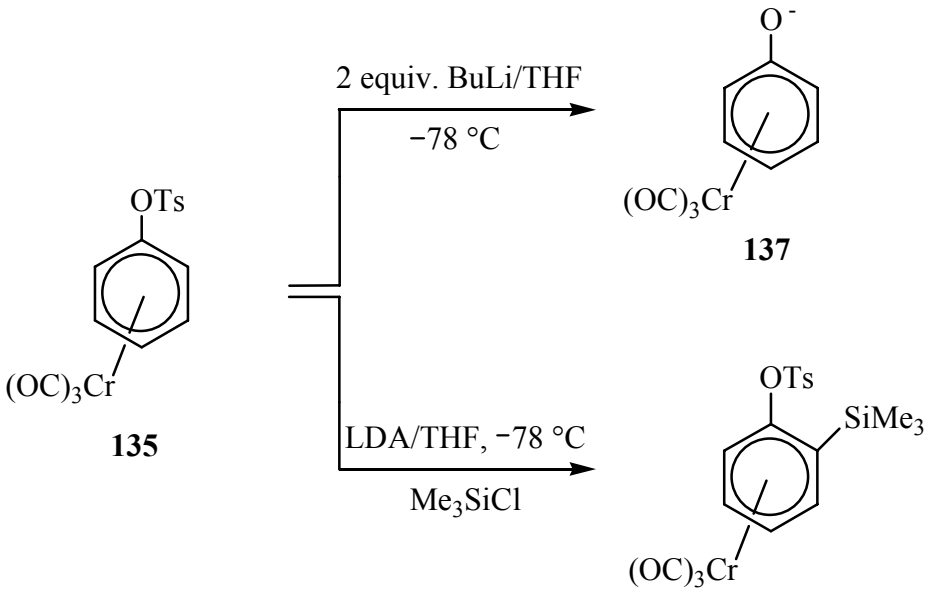
(+)**-93** **135**

The isomeric products were not separable under the conditions of column chromatography and the diastereomeric ratio was deduced from the intergration of peaks in ^{1}H NMR spectrum. The complexed aromatic ring proton peaks are almost overlapping, thus the intergration of two singlets at δ = 3.68 and δ = 3.72 ppm for OCH_3 groups of two diastereoisomers were used for calculation of the enantiomeric excess and revealed that complex **(+)-93** was obtained in about 30 % *ee*.

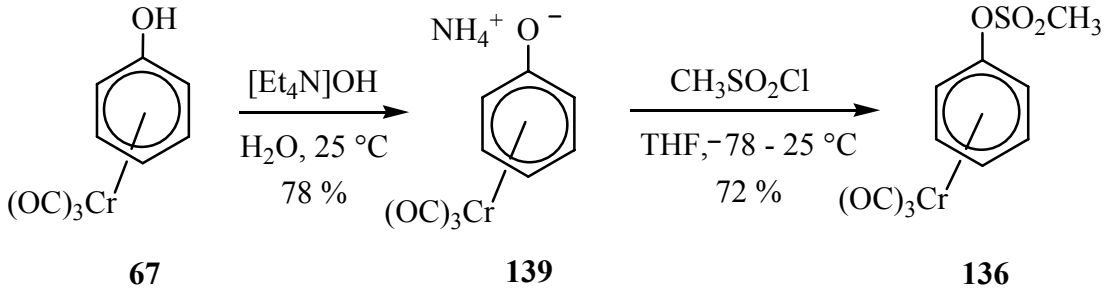
1.8 Tricarbonyl(phenyl mesylate)chromium(0) (136)

Since the tricarbonylchromium arene triflate complexes show a stronger preference to anionic thia Fries rearrangement upon treatment with base than the formation of aryne, we speculated that this type of rearrangement could be extended to other complexed sulfonate arene analogues, such as phenyl tosylate tricarbonylchromium(0) (**135**) and mesylate tricarbonylchromium complex (**136**).

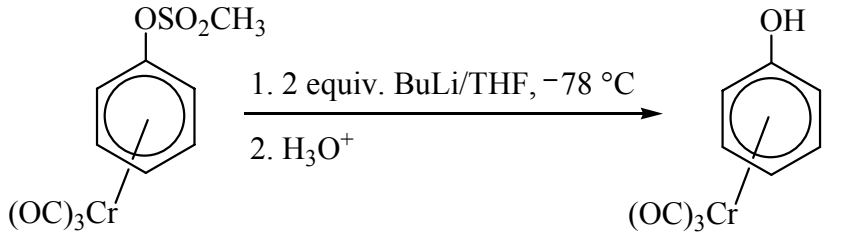
Phenyl tosylate complex **135** has firstly been synthesized and investigated by Heppert's group in early 1989.[109] They reported that the tosylate complex **135** cleaved into (phenoxide)$Cr(CO)_3$ and sulfenium anions under treatment with BuLi at low temperature. Upon treatment of **135** with LDA followed by addition of Me_3SiCl, however, a small mount of *o*-Me_3Si substituted tosylate complex **138** was obtained as the results of an *ortho*-lithiation reaction without anionic thia-Fries rearrangement.



Following the procedures of preparation of tosylate tricarbonylchromium complex (**135**) described by Heppert, we prepared phenylmesylate tricarbonylchromium(0) (**136**) as below: the phenoxide chromium anion is conveniently prepared as the crystalline Et_4N^+ salts **139** by reaction of phenol chromium complex **67** with aqueous tetraethylammounium hydroxide. The chromium phenoxide anion reacts readily with methanesulfonyl chloride to form (phenylmesylate)$Cr(CO)_3$ complex **136** in 3 hours at room temperature**.**



The subsequent attempt to the anionic thia Fries rearrangement by treatment **146** with BuLi followed by work-up using aqueous NH_4Cl exclusively phenol complex **67** as reported case of tosylate complex **135**.



136 **67** 77 %

In contrast to the triflate chromium complexes, the result of mesylate chromium complex not undergoing anionic Fries rearrangement exhibits the difference between the SO_2CH_3 and SO_2CF_3 group. Obviously the strong electron withdrawal of the trifluoromethyl substituent accounts for the strong migration aptitude of the trifluoromethylsulfone moiety.

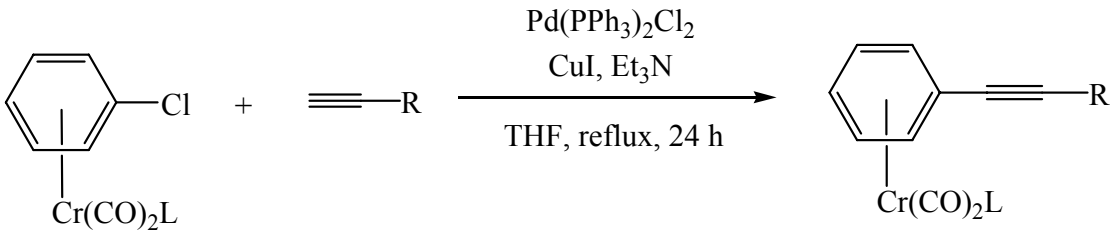
2. Palladium(0)-Catalyzed Cross-Coupling of Aryl Triflate Tricarbonyl-chromium Complexes

The palladium(0)-catalyzed coupling of aryl halides and aryl triflates with main group organometallics has been well known as a straightforward and powerful method for the formation of carbon-carbon bonds.[110] The combination of palladium catalysis and arene tricarbonylchromium complex chemistry not only greatly expanded the scope of the arene chemistry, but also implemented the versatility of the cross coupling reaction.

It has been found that the coordination of an electron-withdrawing tricarbonylchromium fragment to the aryl halides dramatically accelerates the oxidative addition of the arene-halogen bond to the palladium(0) due to the decrease of the π-electron density on an arene ring, and even the oxidation of chlorobenzene chromium complex to palladium(0) species takes place at ambient temperature.[111] Due to the presence of the $Cr(CO)_3$ fragment, the aryl chlorides, hitherto regarded as rather inert to the cross coupling reaction, have been shown to react about 15-fold faster than the free iodoarenes in palladium catalyzed carbon-carbon bond formation reactions under very mild experimental conditions.[112] Thus the palladium(0)

catalyzed cross-coupling reaction using aryl halides chromium complexes have been easily achieved.[113]

Alkynylated (η^6-arene)$Cr(CO)_3$ complexes have received much attention in recent years due to their beneficial introduction into building blocks with potential application in material science.[114] The palladium catalyzed Sonogashira coupling appeared to be the most appropriate approach to the preparation of alkynylated complexes. Müller reported the first Sonogashia coupling reaction of chlorobenzene chromium complexes **140** giving the alkynylated complexes **141**.[115] Although replacing the CO residue by a phosphane ligand reduced the electron-withdrawing ability of the metallic fragment, the (η^6-chlorobenzene)$Cr(CO)_2PPh_3$ complexes were found to be efficient coupling partners.

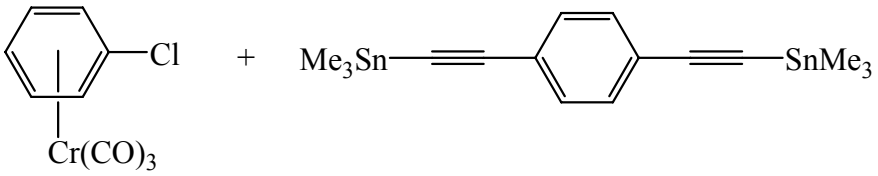


140 **141** (41-89 %)

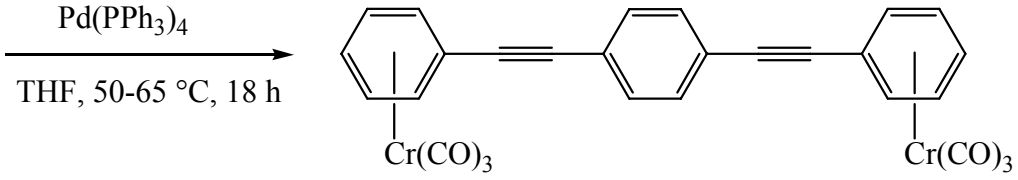
L = CO, PPh_3
R = $SiMe_3$, Ph-4-NO_2, $C(OH)Me_2$, $C(OH)Ph_2$

Complementary to the Sonogashira methodology, Stille couplings between trimethylstannylacetalenes and (η^6-chlorobenzene)$Cr(CO)_3$ have been used to prepare organometallic-substituted acetylenes.

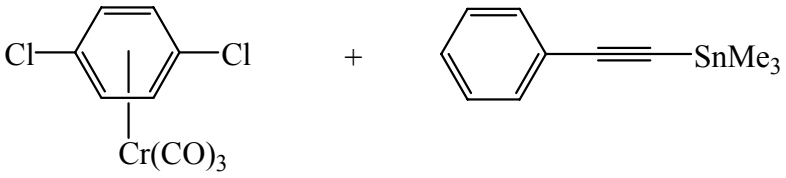
In one example, two molar equivalents of (η^6-chlorobenzene)$Cr(CO)_3$ **140** were treated with 1,4-di-(trimethylstannylethynyl)benzene **142**, affording the corresponding dichromium complex **143** in excellent yield.[116] Similar coupling using complexed 1,4-dichlorobenzene **144** and trimethylethnylphenylstannane **145** gave corresponding monochromium complex **146** in 84 % yield.[117]



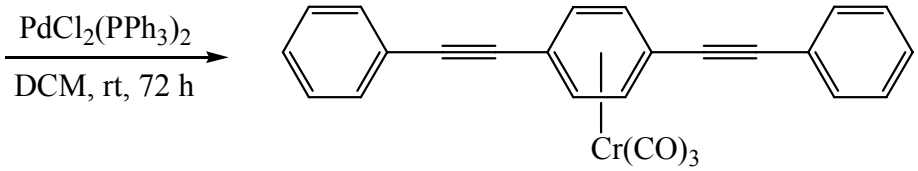
140 **142**



143 93 %

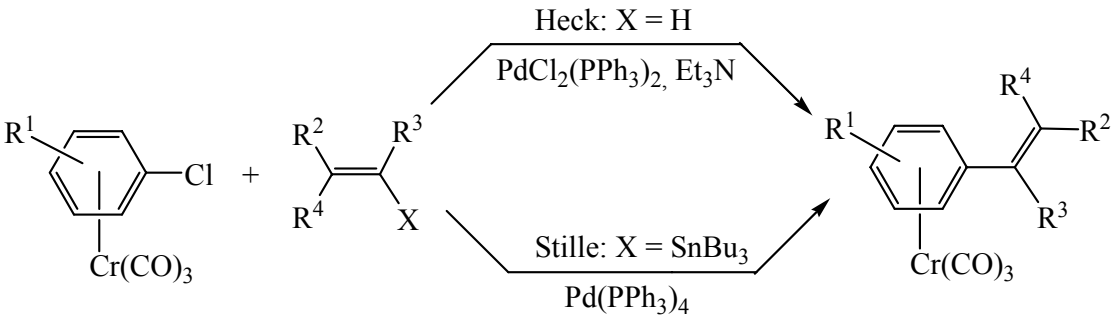


144 **145**



146 84 %

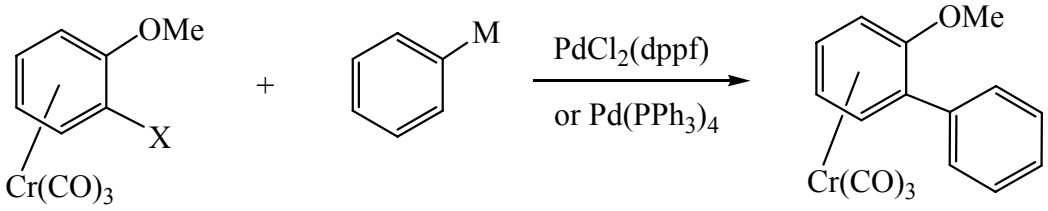
Stille reaction and Heck olefination have been applied to arene tricarbonylchromium complexes to introduce vinyl substitutents using vinylstannanes and alkenes, respectively. Variously substituted styrene complexes **148** could be prepared in high yield by reacting with (η^6-chlorobenzene)$Cr(CO)_3$ complexes **147** in the presence of Pd(0).[118]



147 **148** 58-72 %

R^1 = *p*-Me, *p*-MeO
R^2 = H, $COCH_3$
R^3 = H, Ph, CH_2OMe, CH(OH)Me, $C(OH)Me_2$
R^4 = H

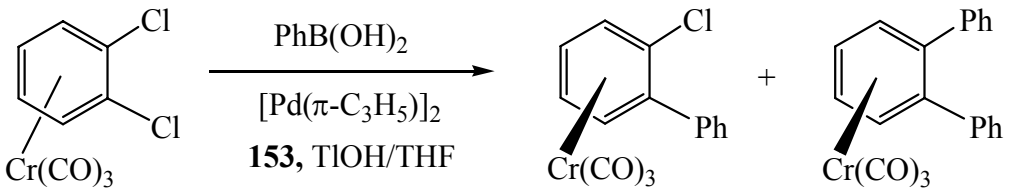
The selective tricarbonylchromium complexation of biphenyl compounds remains elusive and leads to complex mixture.[119] However, direct coupling reactions between an arene chromium complex and another arene provide an elegant route to biphenyl complexes. Uemura et al. have first reported this approach. The palladium-catalysed coupling between a haloarene complex **149** and a metallated species **150** afforded the expected monochromium biphenyl complex **151** in poor to excellent yields. The best result was obtained by coupling the phenylboronic acid with the *o*-bromoanisole chromium complex using $Pd(PPh_3)_4$ as catalyst in the presence of Na_2CO_3.[120]



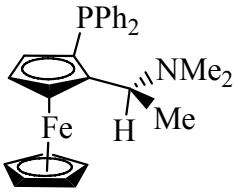
149 X = Cl, Br **150** M = ZnCl, $B(OH)_2$, $SnBu_3$, MgBr **151** (0-86 %)

As described earlier, *ortho*- and *meta*-disubstituted arene chromium complexes exist in two enantiomeric forms and can give rise to biaryl complexes with both planar and axial chiralities. The catalytic desymmetrization of prochiral 1,2-dichlorobenzene chromium complex **152** was achieved by a mono Suzuki coupling under the combination of a palladium catalyst with a chiral ligand **153**. The expected biaryl **154**

was isolated in moderate to good yields with enantiomeric excesses up to 69 % together with a small amount of the achiral bis-coupling product **155**.[121]



152 **154** 69 % *ee* **155**

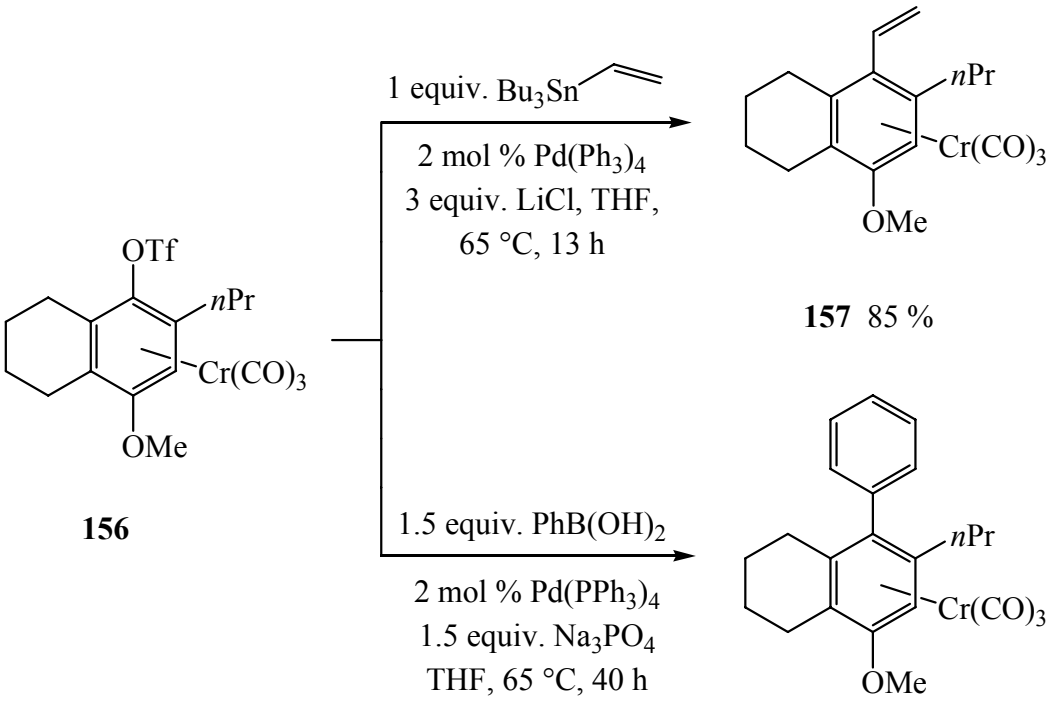


(*S*)-(*R*)-PPFA(**153**)

To the best of our knowledge, very few examples of cross coupling reaction involving arene chromium complexes bearing non-halogenated leaving groups have been reported up to date. It is known that the incompatibility of tricarbonylchromium group with halogen atomes at the arene ring, especially brom and iod atoms, leads to insufficient complexation and the instable haloarene tricarbonylchromium complexes often occur decomposition under the required reaction conditions. It is noteworthy that triflates were found to be good alternative partner for the coupling reaction.[122] Conversion of phenols into triflates renders the Ar-O bond sufficiently electron deficient to permit insertion of transition metals such as Pd(0). The catalytic process required for cross coupling relies on Pd(0) insertion into the Ar-O bond. Successful reactions require this bond to be weakened by electron withdrawing groups on the arene. Therefore it is considerable meaning to build in a tricarbonylchromium fragment on an arene ring to activate the coupling reaction which can not be achieved otherwise.

In 1994, Wulff *et al*[65] first reported that the Stille couplings between tricarbonylchromium complexed electron-rich arene triflates and organostannes proceeded rather smoothly and efficiently while such type of couplings of uncomplexed free electron rich aryl triflates failed. Highly substituted

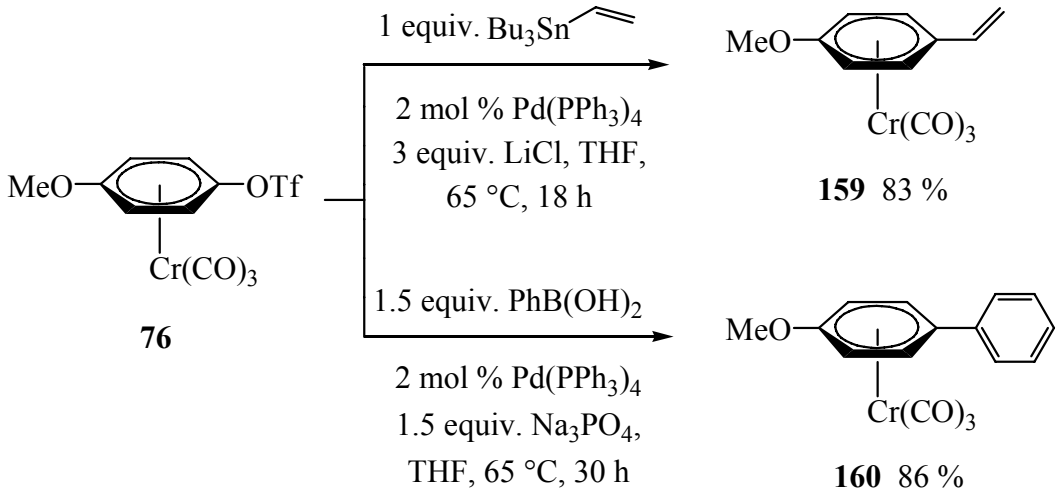
arenetricarbonylchromium triflate complex **156** could undergo both Stille and Suzuki couplings giving product **157** and **158** in good yields respectively. The results obtained by Wulff demonstrated the efficacy of tricarbonylchromium group in promoting cross-coupling with electron-rich aryl triflate.



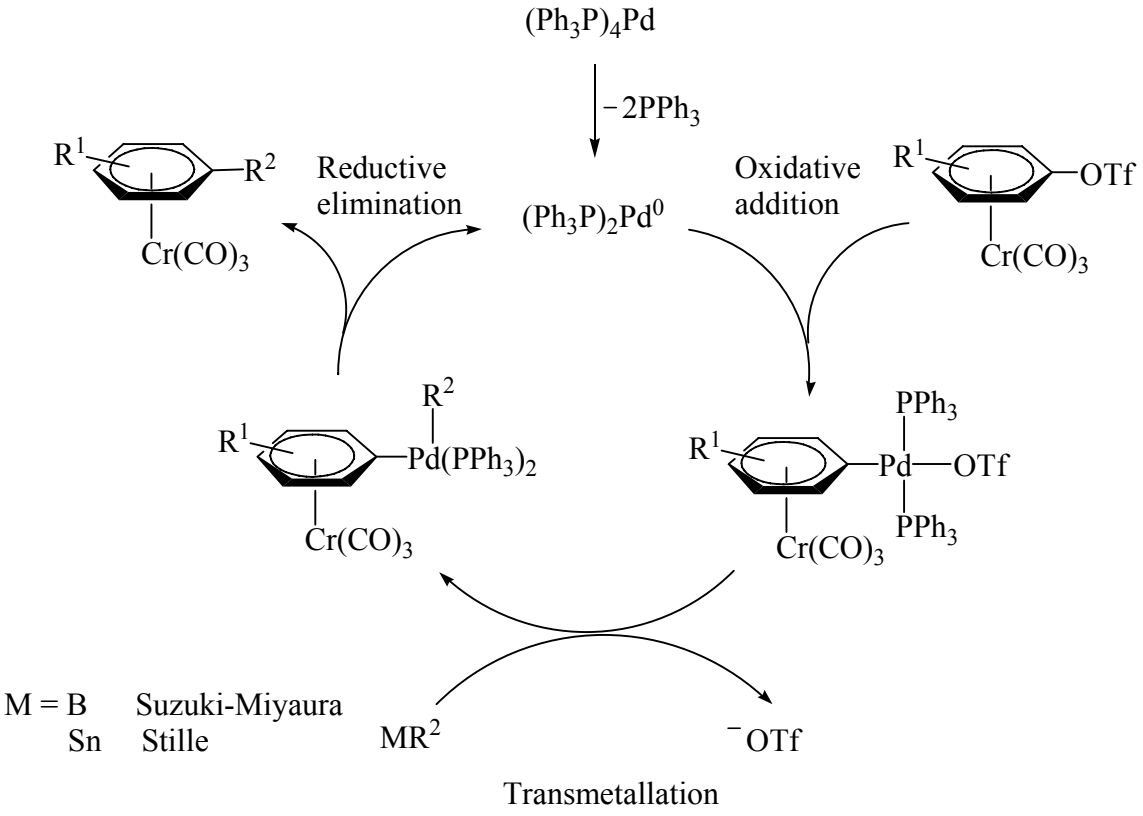
The aryl triflate chromium complexes used for these successful palladium-catalyzed cross-couplings were prepared by benzannulation between chromium carbene complexes and 1-pentyne followed by triflation[65] as described before (see chapter B 2.1). It has been established in this work that moderately air stable to air stable aryl triflate tricarbonylchromium complexes could be flexibly and generally prepared from the corresponding phenols. These compounds were thought to be valuable starting material for C-C bond formation because of the stability and great availability from phenols. In light of the results of Wulff *et al*[65] we wished to broaden and generalize the scope of utilities of aryl triflate chromium complexes towards carbon-carbon bond formation. Several palladium catalyzed cross-coupling reactions with aryl triflate tricarbonylchromium complexes have been examined in this work.

In the presence of 2 mol % of $Pd(PPh_3)_4$, tricarboylchromium anisole triflate complex (**76**) underwent efficient cross-coupling reaction with vinyltributyltin (Stille coupling)

and phenylboronic acid (Suzuki coupling) under standard conditions giving the coupling product **159**and **160** in excellent yields, respectively.



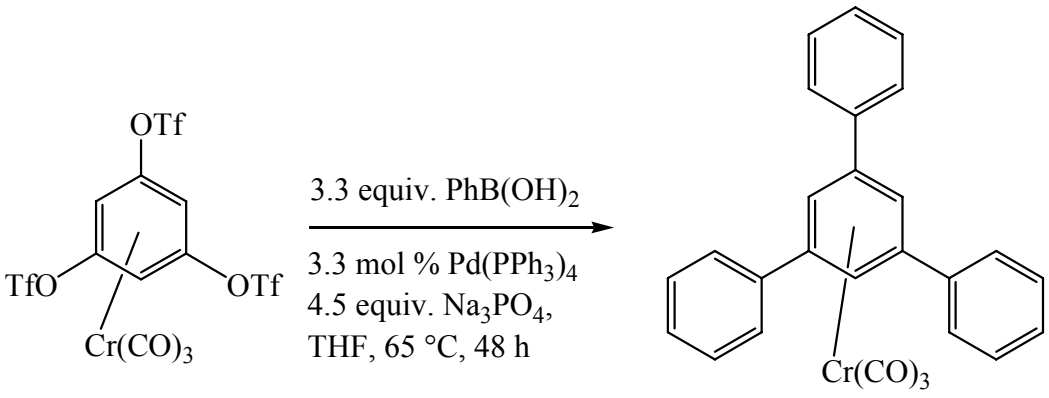
The process of the cross-coupling of aryl triflate chromium complexes is assumed to be the classic addition-elimination sequence via an *exo*-oxidative addition of palladium to Ar-OTf bond of the complex followed by metal triflate loss to produce the coupling product.



The high reactivity of aryl triflate chromium complexes for cross coupling is presumably because the C-OTf bond would be activated for oxidative addition to palladium(0) by the coordination of the an electron-withdrawing $Cr(CO)_3$ moiety to the arene.

The same cross coupling reactions with [η^6-(4-methoxyfluorobenzene)-tricarbonylchromium(0) have been reported by Widdowson *et al*, where the Stille reaction was optimal with 5 mol % $Pd_2(dba)_3$ in the presence of PMe_3 and CsF in DME at reflux giving **159** in 40 % yield; the Suzuki reaction was optimal with 5 mol % $Pd_2(dba)_3$ in the presences of PMe_3 and Cs_2CO_3 in DME at reflux giving **160** in 76 % yield.[123] Compared with the Suzuki and Stille couplings with chromium complexes of chlorobenzene and bromobenzen, aryl triflate chromium complexes have the advantages of higher reactivity and stability.

Furthermore, Suzuki cross coupling with air stable tricarbonyl(1,3,5-trihydroxylbenzene)chromium tris(triflate) (**88**) has been carried out. In the presence of 3.3 mol % of $Pd(PPh_3)_4$, the cross couplings of three triflate groups at the arene ring of the complex **88** with phenlyboronic acid proceeded completely giving tricarbonylchromium complex of 1,3,5-triphenylbenzene [(TPB)$Cr(CO)_3$] **161** in excellent yield.



88

161 87 %

The direct complexation of 1,3,5-triphenylbenzene (TPB) with chromium hexacarbonyl has been reported earlier, in which a set of chromium complexes containing one, two and three metal fragments were formed with tiny quantities for each, including complex **161** in 4 % yield.[124]

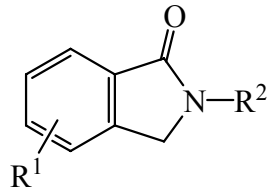
These preliminary results in palladium cross coupling reactions in this work represents the great potential of arene triflate tricarbonylchromium complexes as coupling partners because of the possible preparation from phenol derivatives, the high reactivity and stability. Moreover, the phenolic group can be used as a means to introduce the desired functionality in the aromatic ring and then be converted into a carbon-carbon bond via the corresponding triflate. Furthermore, the easy accesses to arene bis-triflate chromium chromium complex, such as complex **87**, would render this methodology more attractive for the versatile asymmetric cross couplings.

3. Chemistry of Tricarbonylchromium Complexes of *N*-substituted Phthalimides

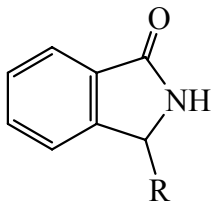
3.1 Introduction

Investigations in the chemistry of arene tricarbonylchromium complexes with functionalized anellated rings have disclosed a number of oxy-anion accelerated reactions.[22-25] Nucleophilic additions at the keto groups of complexes of benzocyclobutenone and benzocyclobutenedione were the key steps of highly selective, anion driven reactions, such as the distal ring opening to *ortho*-quinodimethane intermediates followed by cycloaddition,[27, 29] an anionic ring expansion to indanone systems upon acyl anion addition to benzocyclobutenone complexes,[30] and the dianionic oxy-Cope rearrangement followed by intramolecular aldol addition upon alkenyllithium to benzocyclobutenone complexes.[31, 35-36, 38] The electron withdrawing property of the tricarbonylchromium group is thought to support a nucleophilic attack at the keto groups. In most cases such reactions occurred at low temperature (–78 °C), and the facial differentiation due to the tricarbonylchromium moiety caused them to take place with high degrees of diastereoselectivity. Among the reactions mentioned the dianionic oxy-Cope rearrangement of (arene)tricarbonylchromium complexes with anellated cyclobutendione have been investigated for some time and still deserves special interest, because starting from rather simple substrates the reaction sequence yields a remarkable amount of structural complexity with complete diastereoselectivity. The efforts are being undertaken to broaden the reaction scope to arene tricarbonylchromium complexes with functionalized anellated five member ring. Tricarbonylchromium indanone[41] and isatin[45] complexes have recently been prepared and the accomplishment of respective dianionic oxy-Cope rearrangement is underway. In the continuous investigation, *N*-substituted phthalimide complexes are considered as interesting substrates for possible anion driven reactions.

The class of isoindolin-1-one (**162**) and 3-substituted 2,3-dihydro-1*H*-isoindolin-1-ones (**163**) called phthalimidines are of importance in organic chemistry, particularly in the field of medicinal applications.[125]

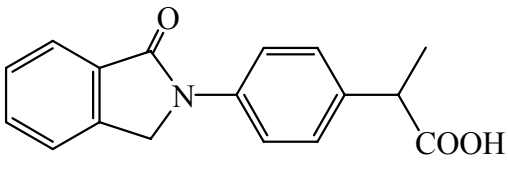


162

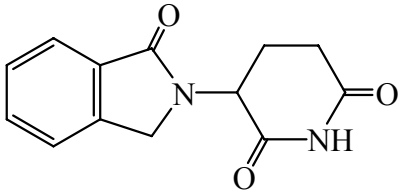


163

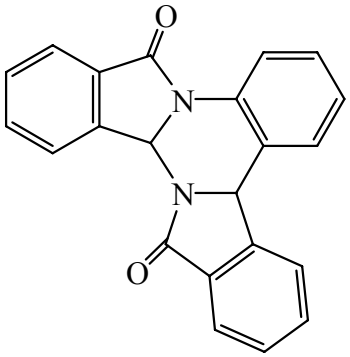
The considerable interest in these heterobicyclic compounds stems mainly from their diverse biological activities[126] and their availability as reactive intermediates in synthesis.[127] A wide range of naturally occurring and bioactive substances are linked to the potential compounds comprising the phthalimidine unit as synthetic building blocks.[128] For example, indoprofen (**164**, anti-inflammatory agent),[129] deoxythalidomide (**165**, reducer of tumor necrosis factor production),[130] batracyclin (**166**, neoplasm inhibitor),[131] lennoxamine[132] (**167**, isolated from various barberries species), pazinaclone (**168** anxiolytic drug candidate)[133] 3-piperazinylethyl isoindolinone derivative (**169** dopamine D4 receptor antagonist).[134] In addition, (*R*)- and (*S*)-3-methyl-isoindolin-1-ones have been shown to be valuable chiral auxiliaries.[135]



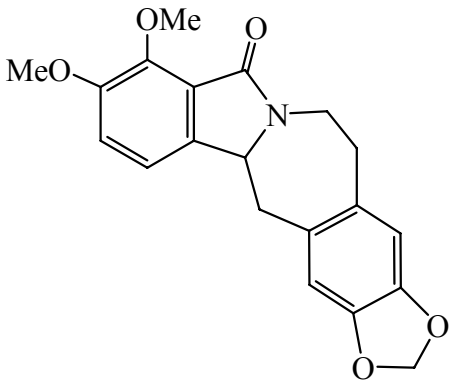
164



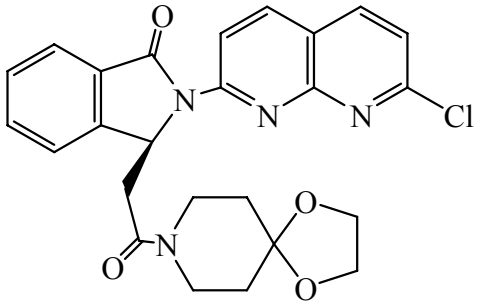
165



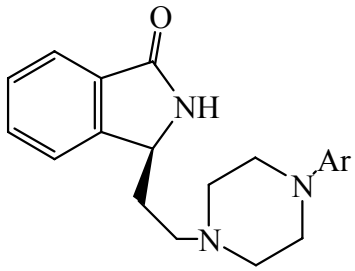
166



167



168



169

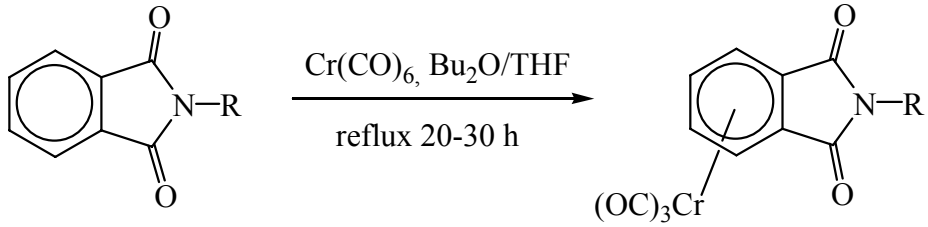
Accordingly, many efforts have been devoted to the asymmetric synthese of the simple chiral 3-substituted isoindolinones **163**.[136-138] Among the number of synthetic routes to 3-substituted isoindolin-1-ones (**163**), the straightforward and efficient asymmetric synthetic approaches are based on the nucleophilic addition of an organometallic reagent to a phthalimide precursor attached to a chiral auxiliary at the nitrogen atom.[137]

It is well established that planar-chiral arene tricarbonylchromium complexes represent highly valuable building blocks for the diastereo- and enantioselective synthesis of complex compounds. In principle, the powerful electron withdrawing effect of the $Cr(CO)_3$ group might dramatically facilitate the nucleophilic attack at the amide group of the phthalimide. Moreover, it is possible to induce stereoselectivity of chemical reactions of tricarbonylchromium phthalimide complexes with respect to the "stereodirecting" effect of the $Cr(CO)_3$ group. With this background, it is of considerable interest to exploit the chemical and stereochemical reaction potential of tricarbonylchromium phthalimide complexes for the synthesis of nitrogen containing heterocycles.

3.2 Synthesis of Phthalimide Tricarbonylchromium Complexes

N-alkyl phthalimide Tricarbonylchromium complexes can be prepared by direct complexation. By heating *N*-methyl phthalimide **170**[139] with hexacarbonyl chromium in Bu_2O/THF at reflux complex **171** was obtained in 58 % yield after purification by column chromatography. The direct complexation of *N*-vinylphthalimide **172**[140] with

hexacarbonyl chromium could not be completed because of the decomposition giving product **173** in only 20 – 48 % yield. Uncomplexed *N*-vinylphthalimide could be recovered in about 40 % by column chromatography, however. Complexation of *N*-vinylphthalimide through arene exchange using Kündig's complexation reagent (tricarbonylchromium naphthalene complex) did not significantly improve the yield of the complex. Other methods of complexation including heating with $Cr(CO)_3(NH)_3$ in dioxane and $Cr(CO)_3(pyridine)_3/BF_3{\cdot}Et_2O$ failed due to decomposition. The insufficient electron density on the aromatic ring caused by the two carbonyl groups most likely is responsible for the insufficient complexation of the ligand.

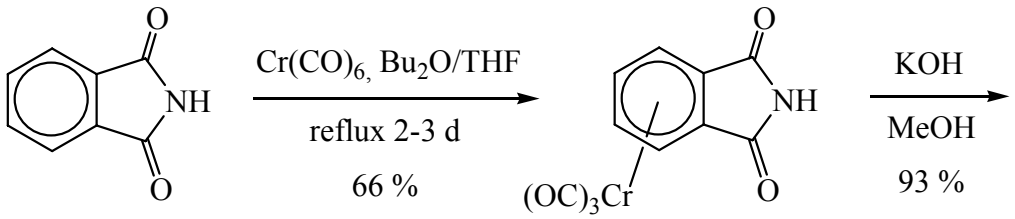


170 (R = Me)
172 (R = vinyl)

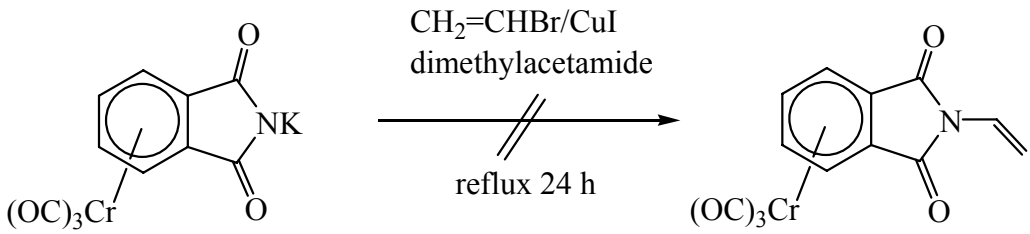
171 (R = Me) 58 %
173 (R = vinyl) 20-48 %

The ^1H and ^{13}C NMR spectra of complexes **171** and **173** show the usual upfield shift of the proton and carbon resonances of the aromatic system with respect to the corresponding free ligands. The vinyl group in complex **173** is easily recognized by the typical signal pattern of the terminal olefinic proton resonances at δ = 5.07 ppm ($^2J_{cis}$ = 9.8 Hz) and at δ = 6.03 ppm overlapping with two protons of the aromatic ring; one highly deshielded internal alkenyl proton resonance is observed at δ = 6.75 ppm.
In order to improve the yield of *N*-vinylphthalimide complex, another synthetic pathway has been designed: that is, starting from tricarbonylchromium phthalimide complex **175** to synthesize *N*-substituted phthalimide complex using the methods for preparing *N*-substituted phthalimide ligand. The direct complexation proceeded smoothly by heating phthalimide (**174**) with hexacarbonylchromium in Bu_2O/THF at reflux for 2-3 days. Complex **175** was obtained in 66 % yield as an air stable red solid, which could conveniently and efficiently be converted into its potassium salt **176** as an air stable orange solid by treatment with KOH. Unfortunately, the next step using the procedure for the uncomplexed ligand to prepare the complex of *N*-

vinylphthalimide **173** failed presumably because of the high reaction temperature and the long reaction time.[140]



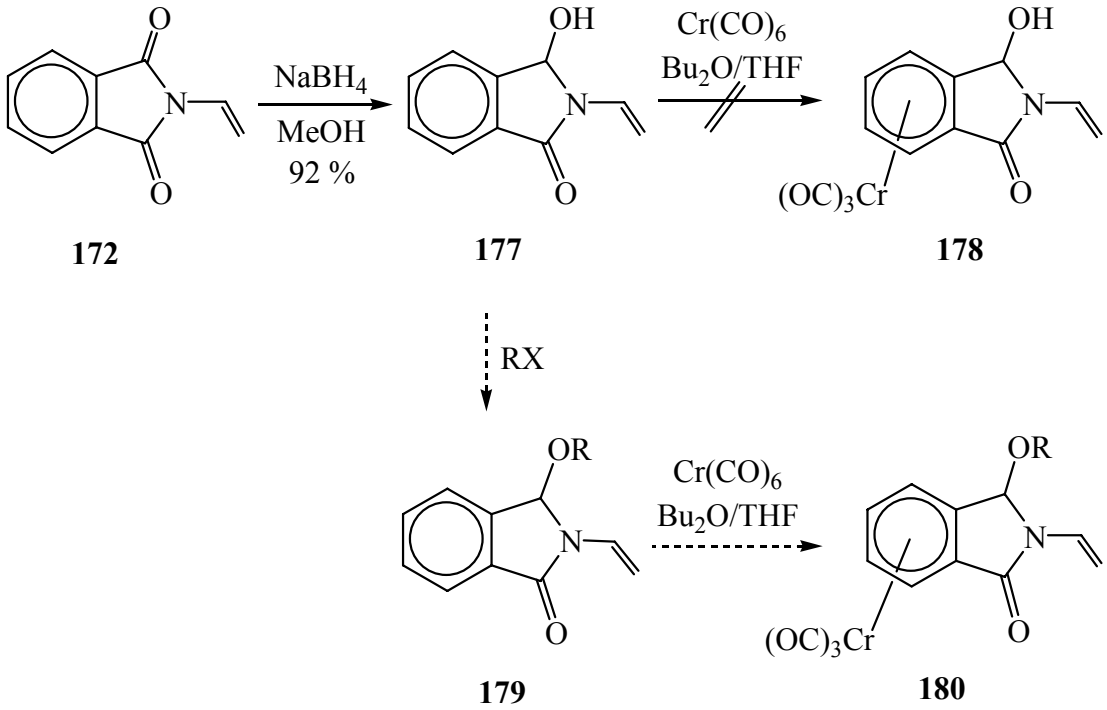
174 **175**



176 **173**

Some simple, relatively mild, efficient synthetic methods for preparation of *N*-substituted phthalimide derivatives have been developed in recent years. For example, the coupling of arylboronic acids with phthalimide gives *N*-arylphthalimides in excellent yield[141] and *N*-alkylation of phthalimide in ionic liquids has been reported as a convenient, efficient, environmentally benign method.[142] Therefore, the stability and the ease to prepare and handle of both complexes of phthalimide and its potassium salt are still of interest for exploration of its synthetic applicability to afford complexes of *N*-substituted phthalimides directly.

In addition, to increase the electron density of the aromatic ring of *N*-vinyl phthalimide (**172**), one carbonyl group was reduced using $NaBH_4$ which afforded 2-vinyl-3-hydroxyisoindol-1-one (**177**) in 93 % yield.[143] The subsequent complexation of **176** with hexacarbonylchromium in Bu_2O / THF (10:1) by heating at refluxing was unsuccessful to aford complex **178**. This is possibly due to the low solubility of **176** in the reaction solvents to inhibit in the complexation. Another possible solution to modify the *N*-vinylphthalimide for improving its capability of complexation with $Cr(CO)_6$ is to convert the hydroxy group in **176** into a methoxy or ethoxy group or to protect it with Me_3SiCl prior to the complexation.

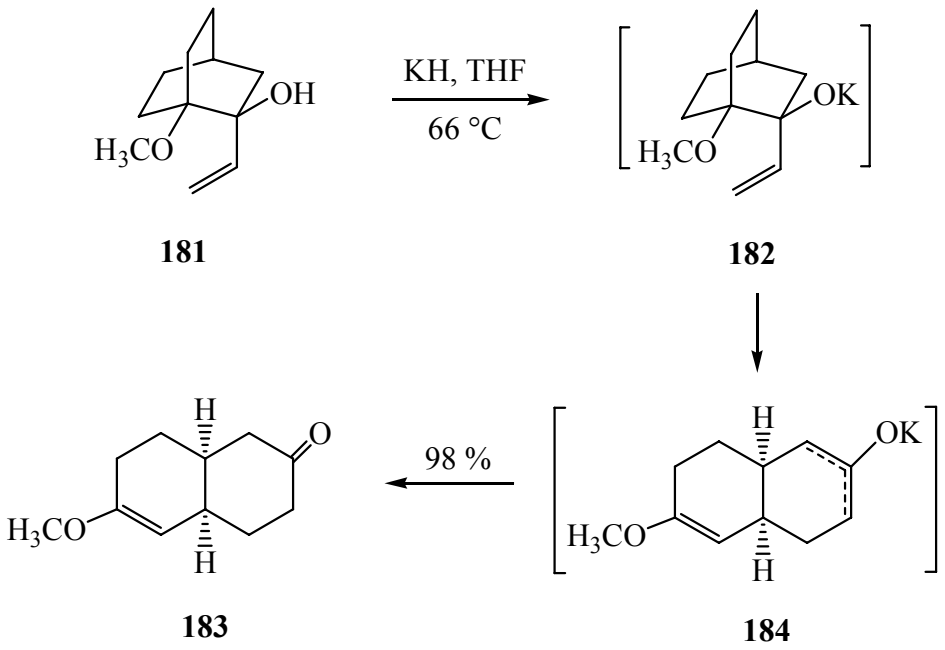


172 **177** **178**

179 **180**

3.3 Attempts Towards an Anionic Oxy-Cope Rearrangement

Berson and Jones[144] were the first to recognize that the thermal isomerization of 1,5-dienes carrying a hydroxyl group at C-3 constitutes a viable extension of the classical Cope rearrangement.[145] The subsequent important discovery by Evas and Golob, who used the potassium alkoxide instead of the traditional alcohol facilitates the reaction at a 10^{10}-10^{17} fold rate and offers a new anionic version of the oxy-Cope rearrangement.[146] Potassium hydride and potassium hexamethyldisilazide are the most commonly used bases to generate the alkoxide. The reaction precursor **181** was heated with KH at 66 °C, forming an alkoxide **182** by deprotonation firstly, and subsequent anionic oxy-Cope rearrangement giving the enolate **183** and the final product **184** in 98 % yield after hydrolysis. This reaction was completed in only 1 minute under such reaction conditions.[146]

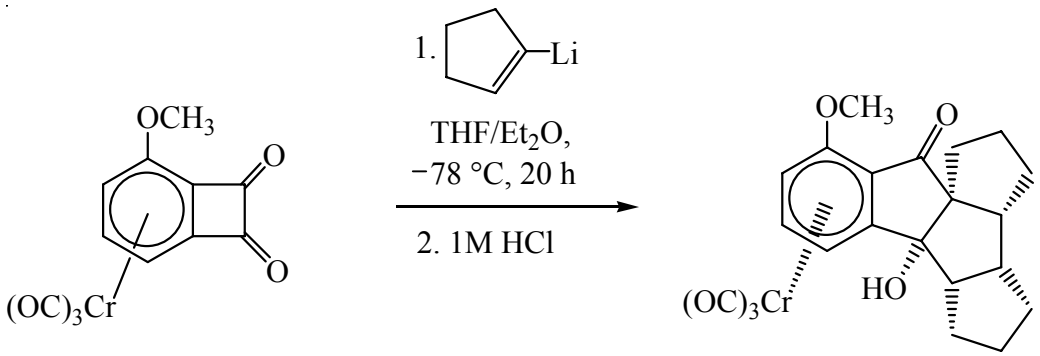


181 **182** **183** **184**

The most remarkable feature of this anionic version of oxy-Cope rearrangement is the immense rate acceleration relative to that of the neutral version. This leads to reactions being carried out at reduced temperature, making the methodology more versatile and minimising the competing thermal retro-ene side reaction. This also renders the reaction irreversible. Due to its remarkable advantages the anionic oxy-Cope reaction has been used in many ring-closure reactions and ring expansions to form medium sized rings, polycyclic networks and natural products.[146, 147] In addition, with the dramatic development of the catalysis of the transition metallic complexes, such as palladium catalysts, the desired precursors for anionic oxy-Cope rearrangement are more easily accessible. As a result, the anionic oxy-Cope rearrangement attracts more attention of synthetic chemists to date.

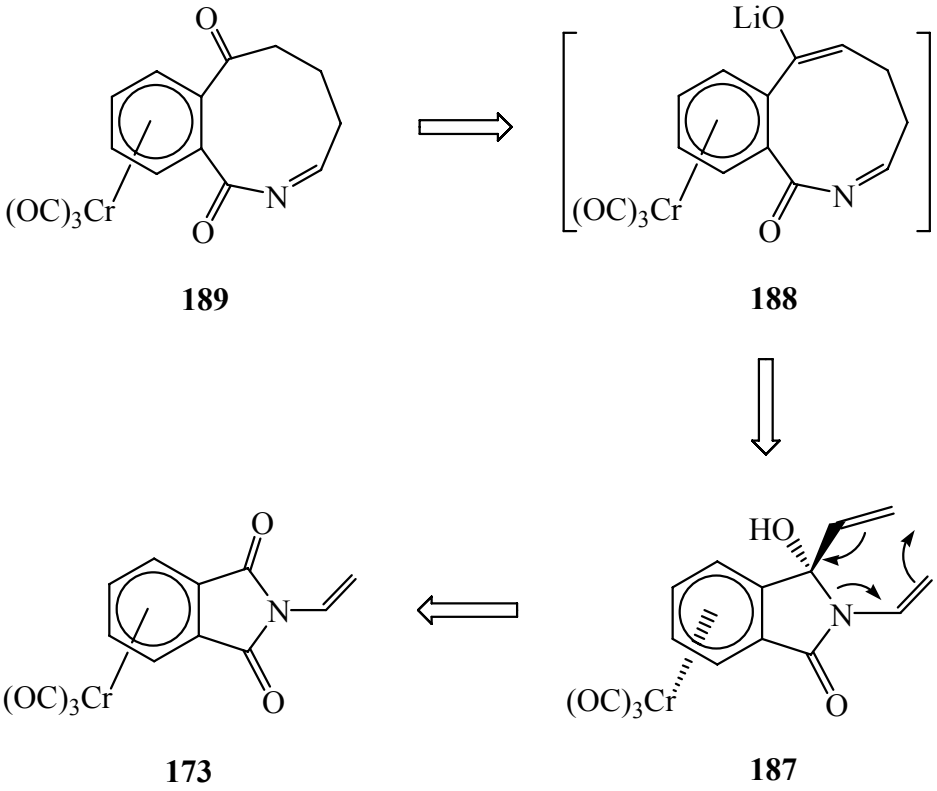
The Butenschön group has independently found the occurrence of dianionic oxy-Cope rearrangement by the double addition of vinyl metal reagents to tricarbonylchromium benzocyclobutenedione complexes at very low temperature (–78 °C).[35, 38, 39] The double addition of alkenyllithium reagents to tricarbonylchromium bezocyclobutendione complexes occurs anti-face to the $Cr(CO)_3$ group, causing a dianionic oxy-Cope rearrangement, resulting in benzocyclooctenedione complexes, most of which subsequently underwent an intramolecular aldol addition delivering the complex polycyclic products in good yields and with complete diastereoselectivity. For instance, the dianionic oxy-Cope rearrangement of benzocyclobutendione chromium complex **185** through a *syn* diaddition of 1-cyclopentenyllithium, followed

by an intramolecular aldol addition furnished the final products **186** with complete diastereoselectivity.[39]



185 (R = OCH_3) **186** 89 %

In connection with the investigation in the chemistry of an arene tricarbonylchromium complex with functionalized anellated five member ring, complex **187** is next envisioned as a suitable precursor for an anionic oxy-Cope rearrangement leading to complex **189** or related compounds through an intermediate like **188**. Complex **187** could easily be prepared by a nucleophilic addition of an alkenyllithium to one carbonyl function of tricarbonylchromium *N*-vinylphthalimide complex (**173**).



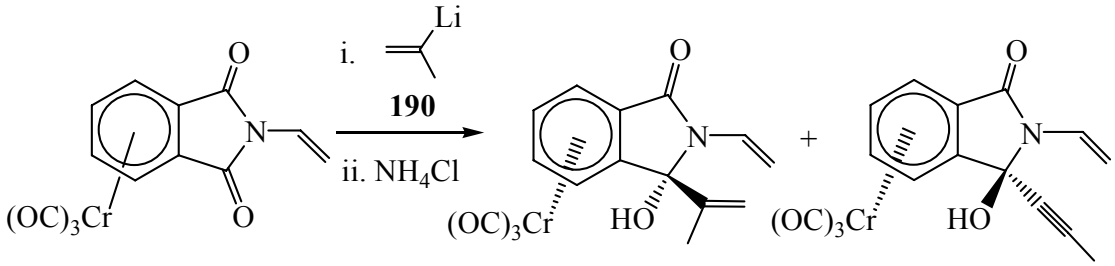
189 **188**

173 **187**

3.3.1 Addition of 2-Propenyllithium and 1-Propynyllithium to Tricarbonyl(*N*-vinylphthalimide)chromium(0) (173)

Nucleophilic additions to one or both of the carbonyl group of *N*-substituted phthalimide chromium complexes are the basis for the exploration of anionic oxy-Cope rearrangement and other reactions in this investigation. Two features of such chromium complexes are expected to facilitate the reactions: Firstly, the electron withdrawing nature of $Cr(CO)_3$ is thought to support nucleophilic attack at both.

Double nucleophilic additions of 2-propenyllithium (**190**) to benzocyclobutenedione complexes cause an dianionic oxy-Cope rearrangements, followed by intramolecular aldol addition.[38, 39] Addition of 2-propenyllithium (**190**) to *N*-vinyl phthalimide complex **173** was firstly carried out with the intention of an anionic oxy-Cope rearrangement. 2-propenyllithium (**190**) was prepared by heating the 2-brompropene with an excess lithium sand in Et_2O at reflux for 2 h.[150] The solution of complex **173** in THF was added to the cooled 2-propenyllithium solution at –78 °C dropwise and stirred for 2 h followed by hydrolysis with 1 M HCl or aq. NH_4Cl. After purification by carbonyl groups; secondly, additions to the carbonyl groups normally should take place from the *anti* face of the organic ligands with respect to the steric bulk of the $Cr(CO)_3$ fragment. This renders the transformation diastereoselective and helps to avoid the formation of complicated product mixtures column chromatography two products were isolated: the first fraction was eluted with PE/TBME (1:1 to 1:2) to give, after removal the solvents, a yellow solid **191** in 40 % yield; another product was eluted with pure ethyl acetate and a red solid **192** was obtained in 48 % yield.



173 **191** 40 % **192** 48 %

Both products were characterized spectroscopically. Inspection of the NMR spectra of both complexes indicates one stereoisomer respectively. The ^{13}C NMR spectrum of

191 shows the characteristic absorptions for 2-propenyl substituent with δ = 18.6 ppm assigned for CH_3, δ = 117.1 ppm and δ = 144.3 ppm for two carbon atoms of C,C double bond. In the ^{1}H NMR spectrum of complex **191** a singlet for methyl group appears at δ = 1.47 ppm, the terminal olefinic protons of *N*-vinyl group are assigned as δ = 4.58 ppm with J_{cis} = 9.8 Hz, and δ = 5.20 ppm with J_{trans} = 16.4 Hz, the deshielded internal alkenyl proton resonance at δ = 6.70 ppm; two terminal olefinic protons of 2-propyl group resonate at δ = 5.33 ppm and in the region of δ = 5.79-5.82 ppm overlapping with two protons of aromatic ring. The signal of OH group of complex **191** appears at δ = 5.16 ppm. It is thought that the chemical shift of *exo* and *endo* OH in the complexes should be different due to the shielding of the $Cr(CO)_3$. The *exo*-OH should be less shielded by $Cr(CO)_3$ than the *endo*-OH. Therefore the value of chemical shift for OH is used to ascertain the configuration of the complex **191** and other adducts discussed later.

The chemical shift of the OH group in complex **191** is similar to that of tricarbonylchromium hydroxyalkenylindanone complexes **193** and **194**, hydroxyvinylindolone and hydroxymethylindolone chromium complexes **195** and **196** and hydroxymethylisoindolinone complex **197**, which was prepared from similar nucleophilic addition of lithium reagents to the corresponding isatin, indan and *N*-methylphthalimide chromium complexes (Fig. 6). The configurations of complexes **193**-**197** have been spectroscopically assigned as *exo*-adducts and the structure of complexes **193** and **197** have been unambiguously proven by X-ray crystallography.[45] Based on the well established rule that the nucleophilic reagents attack arene $Cr(CO)_3$ complexes from the *exo* face of the ligands and comparison of the spectroscopy data of the known related complexes the configuration of complex **191** is assigned as an *exo* adduct.

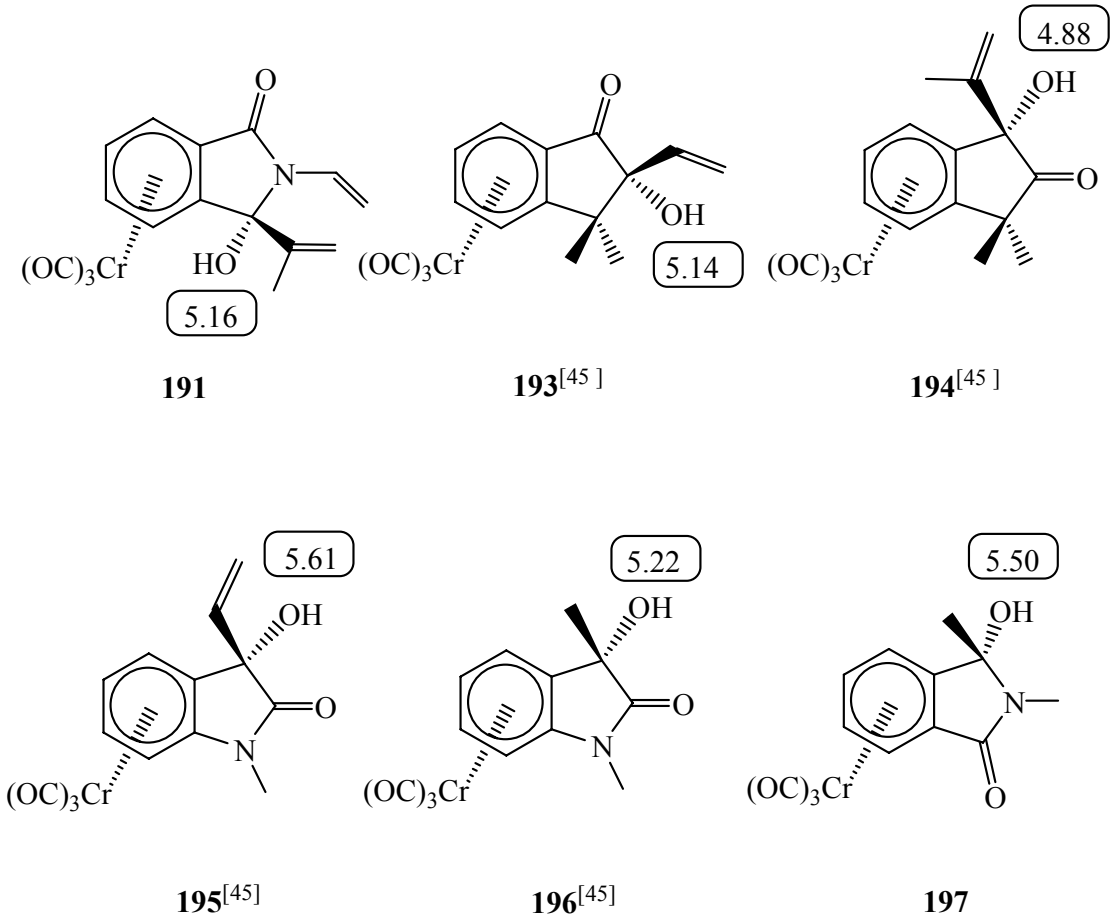


Fig. 6 ^{1}H NMR chemical shifts in ppm assigned for OH group

Compared with complex **191**, the apparent changes in NMR spectra of product **192** are the appearance of a signal for OH at δ = 6.60 ppm and the disappearance of one of olefinic mutiplets. The ^{13}C NMR spectrum of **192** exhibits the absorptions of two quaternary carbon atoms of C,C triple bond at δ = 83.7 and 87.6 ppm, respectively. The chemical shift at δ = 4.02 ppm is assigned for the CH_3 group attached to the C≡C bond, which is significantly distinguished from the signal for CH_3 group connected to C=C in complex **191** at δ = 18.6 ppm.

Complex **192** could be recrystallized from CH_2Cl_2 at –18 °C affording suitable crystals for an X-ray crystal structure analysis (Fig. 7).

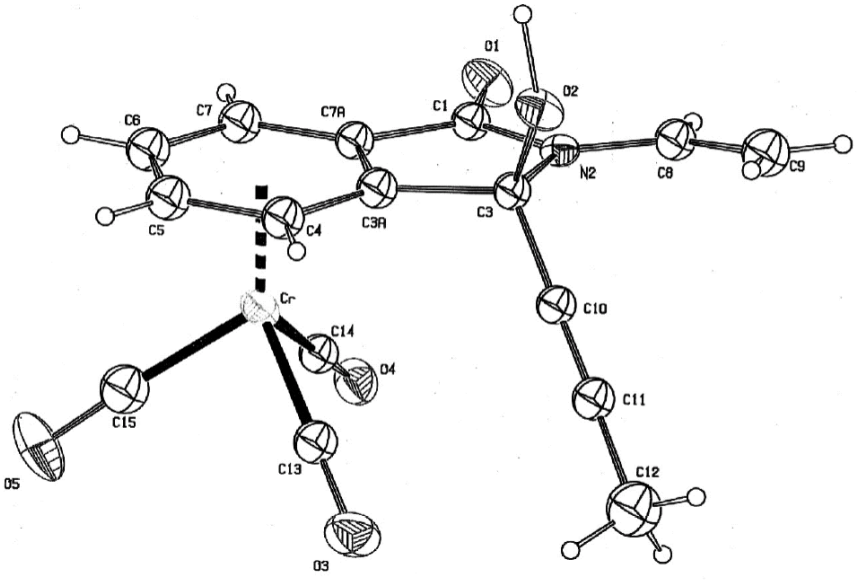


Fig. 7 X-ray Structure of *endo*-**192**

Selected bond lengths [Å]and angles [°]

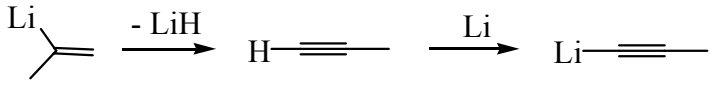
Cr-C13 1.813(6), Cr-C15 1.837(7), Cr-C14 1.840(7), Cr-C3a 2.197(5), Cr-C4 2.222(6), Cr-C5 2.196(7), Cr-C6 2.182(6), Cr-C7 2.206(5), Cr-C7a 2.170(5), N2-C1 1.374(6), N2-C8 1.410(7), N2-C3 1.482(7), O1-C1 1.221(6), O2-C3 1.435(6), C1-C7a 1.492(8), C3-C10 1.447(7), C3-C3a 1.534(7), C3a-C7a 1.375(7), C3a-C4 1.385(8), C4-C5 1.395(7), C5-C6 1.384(7), C6-C7 1.388(8), C7-C7a 1.409(7), C8-C9 1.317(7), C10-C11 1.143(6), C11-C12 1.502(8), C1-N2-C3 113.1(5), N2-C1-C7a 106.45, N2-C3-C3a 101.4(4), C7a-C3a-C4 121.5(5), C7a-C3a-C3 109.6(6), C4-C3a-C3 128.9(5), C9-C8-N2 126.6(6).

The X-ray structure analysis data of **192** shows that the Cr-C7a bond length [2.170(5) Å] is shorter and Cr-C4 bond length [2.222(6) Å] is longer than that of the other carbon atoms to the chromium atom, which indicates that the coordination of the aromatic ring is slightly off-centre with the Cr atom closest to C7a and far from C4. C7a is the carbon atom in the aromatic ring with the lower electron density due to the electron withdrawal by the attached carbonyl group. Therefore the shorter Cr-C7a bond shows higher backbonding character as compared to the others. Presumably for

steric reasons, *endo*-**192** adopts a conformation with no CO ligand below the anellated five-membered ring. The arene C,C bond lengths alternate slightly as a result of the *trans* effect of the opposite CO ligands. Presumably due to the electron withdrawal of the carbonyl group at C1 along with the electron donating substitution at C2, the bond length of N2-C1 [1.374(6) Å] is shorter than N2-C3 [1.482(7) Å] and C1-C7a [1.492(8) Å] is shorter than C3-C3a [1.534(7) Å], respectively. The short C10-C11 bond length with 1.143(6) Å shows the typical value of the triple bond (C≡C).

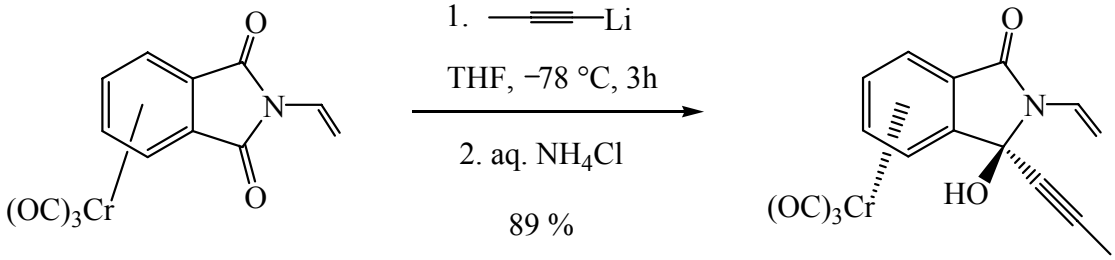
To our surprise, the crystal structure unambiguously revealed that the complex **192** is an *endo*-propynyl monoadduct of *N*-vinylphthalimide complex **173**. At the first glance this means that 1-propynyllithium (**199**) was transformed during the reaction and attacked at the amide group of *N*-vinylphthalimide chromium from the *endo* face and not, as usually expected, from the *exo* face of the ligand ring.

The conversion of 2-propenyllithium (**190**) into 1-propynyllithium (**199**) may be explained by elimination of LiH giving propyne (**198**), which might be lithiated directly during the preparation of 2-propenyllithium (**190**) by heating the 2-bromopropene with lithium sand in diethyl ether.



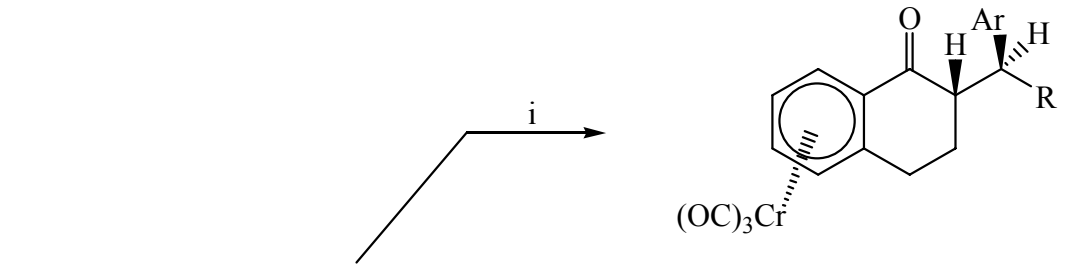
190 **198** **199**

However, we were puzzled about the phenomenon of the observed *endo* selectivity of the 1-propynyllithium (**199**) addition to the carbonyl group of *N*-vinylphthalimide complex. In order to look into whether 1-propynyllithium (**199**) really attacks the carbonyl group of *N*-vinylphthalimide from the *endo* face of the complex in a general fashion in such type of nucleophilic reaction, the reaction of *N*-vinylphthalimide complex **173** with 1-propynyllithium (**199**) was performed. 1-propynyllithium (**199**) has been prepared *in situ* from 1-bromopropene and butyllithium at –78 °C.[151] The solution of complex **173** in THF was added dropwise to the cooled (–78 °C) solution of 1-propynyllithium, followed by hydrolysis with saturated aqueous NH_4Cl. The product was obtained in high yield after column chromatography. The spectroscopic data of the product are identical with those of the *endo*-adduct **192** described above. Obviously the *endo*-adduct **192** was again obtained.

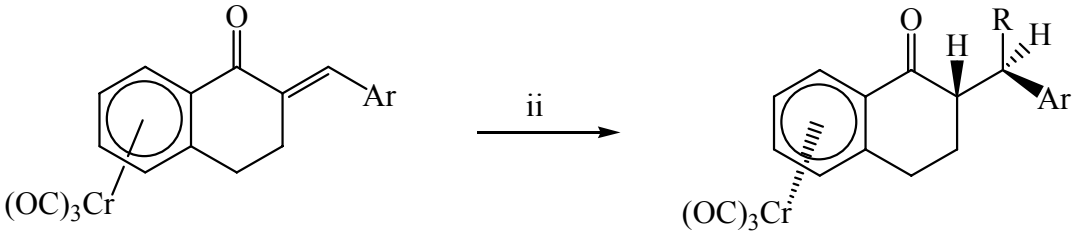


173 **192**

This unusual nucleophilic *endo* addition of the reaction deserves special recognition because it contradicts one of the basic paradigms in arene-$Cr(CO)_3$ chemistry, *i. e.* the rule that nucleophiles usually attack the ligand from the face opposite to the $Cr(CO)_3$ fragment. Literature precedence of *endo*-addition of nucleophiles at (arene)tricarbonylchromium complexes is rare to date. Sarkar *et al.* have studied the *endo*-mode of nucleophilic attack at 2-arylidene-tetralone tricarbonylchromium complexes **200a-c**.[152] It was found that the presence of a Lewis acid, such as $TiCl_4$, could predictably and efficiently reverse the normal *exo*-selectivity trend in these additions to afford 1,4-addition products **201a-h** with *endo*-selectivity; the corresponding *exo*-adducts **201a-h** were obtained by the addition of cuprates in the absence of Lewis acid; the reactions with simple alkyl and aryllithium in the absence of $TiCl_4$ provided predominantly 1,2-adducts **202a-h**.

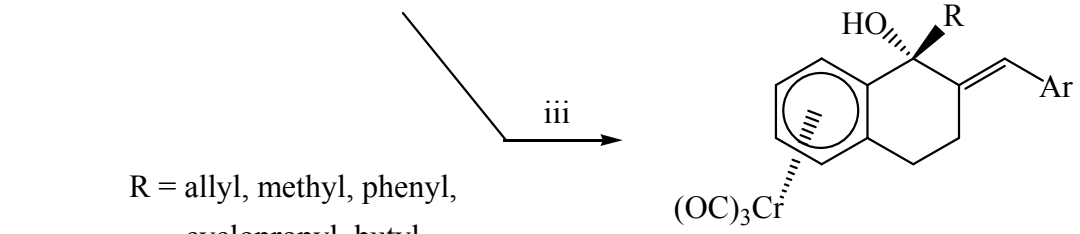


201a-h (80-95 %)



200a (Ar = C_6H_5)
200b (Ar = 4-Me-C_6H_4)
200c (Ar = 2-Me-C_6H_4)

201a-h (80-96 %)



R = allyl, methyl, phenyl, cyclopropyl, butyl

202a-h (83-95 %)

Reagent and conditions: i. $TiCl_4$, –90 °C, 15 min; RLi or RMgX, –90 °C, 15 min; ii. $Li_2[CuR_2(CN)]$; iii. RLi, –90 °C, 15 min.[152]

The observed *endo*-selectivity of nucleophiles would presuppose that the titanium cation coordinates to the carbonyl oxygen from the *exo* face of the substrate since $Cr(CO)_3$ unit blocks the *endo*-face of the carbonyl function, thereby forcing the nucleophiles to react from the less favored, but more accessible *endo* face (Fig.8).

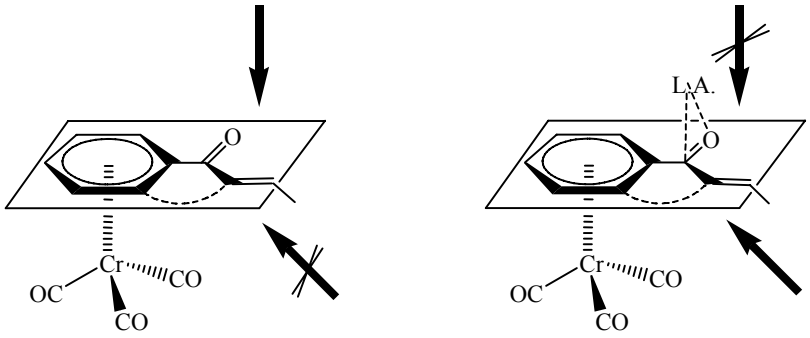
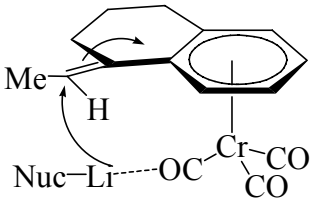


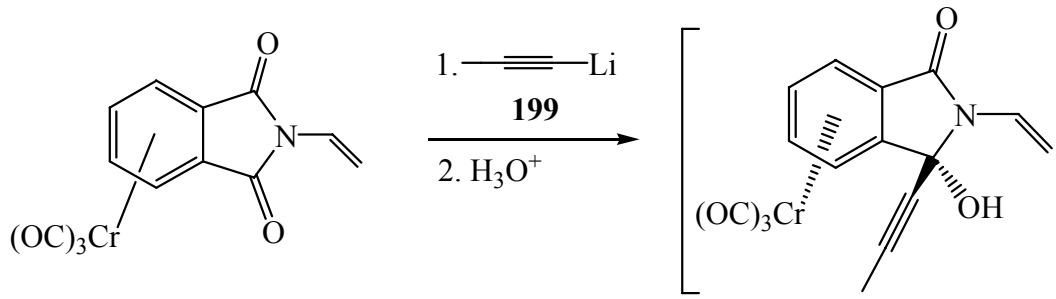
Fig. 8 Stereochemistry of nucleophilic attack at **200**

Schmalz *et al* have also discovered an unexpected *endo* selectivity of conjugated nucleophilic addition of 2-lithioacetonitrile to an 1-ethylidene-tetralin-$Cr(CO)_3$ derivative **203** in the course of the synthesis of diterpene 11-*epi*-helioporin B.[153a] For the *endo*-selectivity, it is assumed that the nucleophiles are guided to the *endo* face of the double bond through coordination of the lithium atom to a carbonyl ligand.[153b]

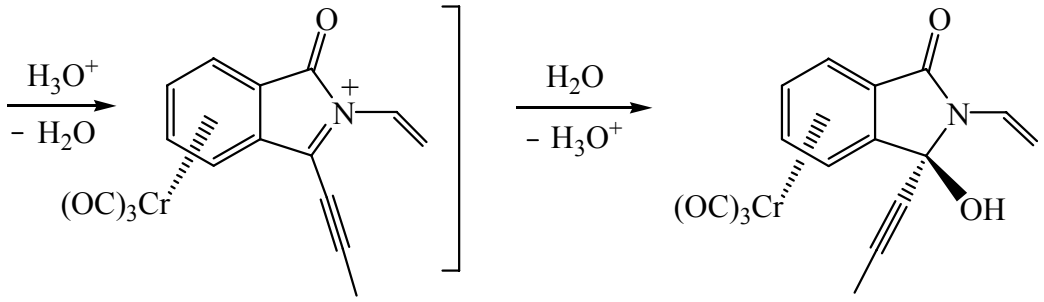


203

To understand the formation of *endo* adducts **192** of *N*-vinylphthalimide chromium complex **173**, more attention was paid on the nature of the precursor of the reaction. It was thought that properties of phthalimide or imides might attribute to the formation of the product with unusual configuration. A possible mechanism for this reaction was proposed as follows.



173 **204**



205 **192**

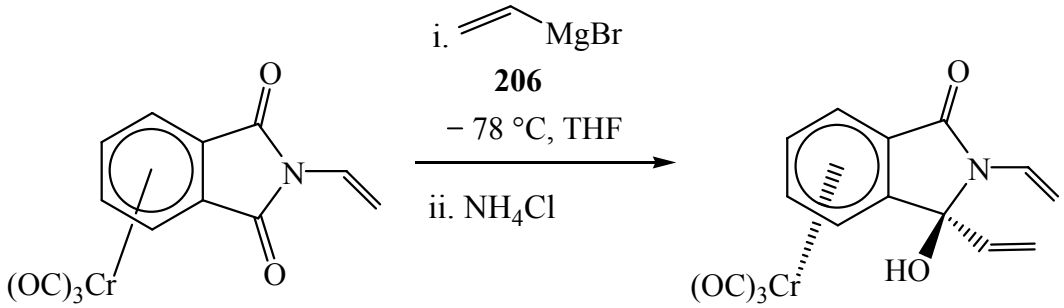
Firstly, 1-propynyllithium (**199**) attacks at one of the carbonyl groups of *N*-vinylphthalimide complex **173** from the *exo* face of the ligand as the normal nucleophilic addition to an (arene)$Cr(CO)_3$ complex giving complex of adduct **204**. Complex **204** could be subsequently transformed into a tricarbonylchromium *N*-acyliminium intermediate **205**, which would be stabilized through conjungation with the propynyl substituent, the *N*-vinyl group, the carbonyl group and even the benzene ring. In the last step, H_2O as a nucleophile attacks at the reactive tricarbonylchromium *N*-acyliminium intermediate from the face opposite to the $Cr(CO)_3$ unit resulting the final product **192** with an "abnormal" *endo* configuration.

This mechanism is thought to be plausible because it is consistent with the well established rule that the nucleophilic addition of the arene tricarbonylchromium complexes from the *exo* face with respect to the steric hindrance of $Cr(CO)_3$ fragment. The unexpected stereochemical outcome of the key reaction in the course of our preliminary study of tricarbonylchromium phthalimide complexes implicates the existence of the tricarbonylchromium *N*-acyliminium cation under the reaction conditions. According to the well known reactivity and applications of the uncomplexed *N*-acyliminium species,[154] the electrophilic tricarbonylchromium *N*-acyliminium might show interesting reactivity. The discovery of the first planar chiral

tricarbonylchromium *N*-acyliminium species offers the opportunity to impart the chemical and stereochemical aspects of $Cr(CO)_3$ unit into the reactions of *N*-acyliminium intermediate. We are intrigued to explore the applications of tricarbonylchromium *N*-acyliminium ions in the synthesis of nitrogen containing compounds.

3.3.2 Addition of Vinyl Metal Reagents to Tricarbonylchromium *N*-vinylphthalimide Complex (173)

Another vinyl group could be introduced into the *N*-vinyl phthalimide chromium complex **173** by nucleophilic addition to the carbonyl function for the desired anionic oxy-Cope rearrangement. Vinylmagnisiumbromide (**206**) (1.0 M in THF) was added to the solution of complex **173** in THF at –78 °C and stirred for 2 h followed by hydrolysis with saturated aqueous NH_4Cl, after chromatography affording the product **207** in 70 % yield as an orange-yellow solid.



173 **207** 70 %

The adduct **207** is obtained as a single isomer as evident from the NMR spectra. The constitution of **207** can be readily confirmed spectroscopically. In the ^1H NMR, the terminal olefinic protons of *N*-vinyl group are assigned as δ = 4.65 ppm with J_{cis} = 10.0 Hz, and δ = 5.27 ppm with J_{trans} = 16.4 Hz, the double dublets at δ = 6.71 ppm are assigned for deshielded internal alkenyl proton of *N*-vinyl group; two terminal olefinic protons of vinyl substituent resonate at δ = 5.59 ppm and δ = 5.69 ppm as mutiplets respectively, the deshielded internal alkenyl proton resonance is found at δ

= 6.08 ppm. The configuration of complex **207** is tentatively assigned as *endo* based on the appearance of the peak for OH at δ = 6.31 ppm in ^{1}H NMR spetrum, which is in relatively downfield compared to some previously confirmed *exo*-adducts in our group and in this work (Fig. 4), which is probably because the *exo*-OH is apart from $Cr(CO)_3$ and has less influence of $Cr(CO)_3$ than the *endo*-OH.

In order to trigger the occurrence of an anionic oxy-Cope rearrangement, complex **207** was treated then with 6 equivalents of BuLi in THF at –78 °C for 16 h till TLC indicating no starting material left. Hydrolysis with saturated aqueous NH_4Cl and extraction with ethyl acetate gave a red residue, which could not be separated under the column chromatography conditions. The mass spectrum of the crude mixture indicates the decomposed unidentified compounds. Some attempts have been done by the treatment *N*-vinylphthalimide complex **173** with 8 equivalents of vinyllithium[155] in THF/Et_2O (1:1) at –78 °C for 15-20 h, followed by hydrolysis. Again some unidentifiable decomposed compounds were obtained.

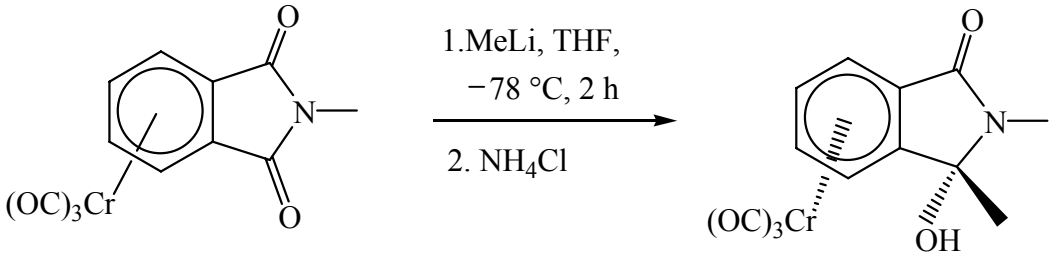
It is noteworthy that the experiments towards an anionic oxy Cope rearrangement have only been made following the procedure previously elaborated in our group for the dianionic oxy-Cope rearrangements of benzocyclobutendione complexes. The substrates derived from vinylphthalimide chromium complex **173** such as **192** and **207** are still of interests for anionic oxy-Cope rearrangement according to the suggestion using potassium hydride as metal source to generate the alkoxide.

3.4 Addition of Carbon Nucleophiles to *N*-methylphthalimide Tricarbonyl Chromium Complex (171)

3.4.1 Addition of Methyllithium

Although a reasonable mechanism has been proposed for the formation of the *endo*-products of the nucleophilic addition to *N*-vinylphthalimide chromium complex **173**, it is still not clear whether the formation of tricarbonylchromium *N*-acyliminium intermediate is a general reaction under the reaction conditions of nucleophilic

addition to the tricarbonylchromium phthalimide complexes. In the continuation of the study, we performed the addition of methyllithium to tricarbonylchromium *N*-methylphthalimide complex **171**. An excess of MeLi solution (1.6 M in cyclohexane) was added to the cooled (–78 °C) solution of complex **171**, the color of the mixture changing from red to orange indicating the nucleophilic attack took place. After stirring for 2 h till TLC indicated no starting complex, hydrolysis with saturated aqueous NH_4Cl and subsequent column chromatography, product **197** was obtained in 81 % yield as a yellow solid.



171 *exo*-**197** 81 %

The spectroscopic data are in agreement with the confirmed structure. In the ^1H NMR spectrum, the chemical shifts at δ = 1.77 ppm and δ = 2.91 ppm are assigned to CH_3 and *N*-CH_3 group respectively; the peak of *endo*-OH appears at δ = 5.50 ppm, which corresponds to those of other related *exo*-adducts (Fig. 9).

Single crystals were obtained by recrystallization from CH_2Cl_2/hexane (1:3) at –18 °C, and the configuration of complex **197** was revealed as an *exo*-adduct by X-ray crystallography (Fig. 9).

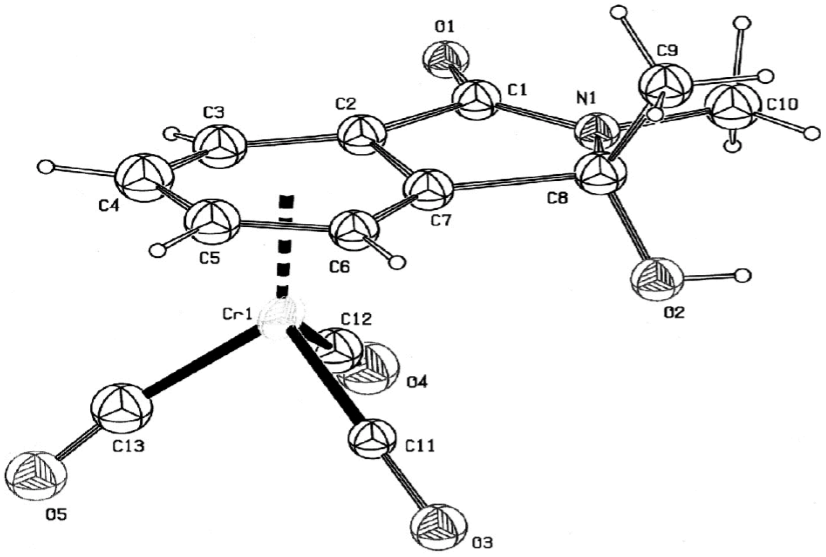


Fig. 9 Structure of **197** in the crystal

Selected bond lengths [Å]and angles [°]

Cr1-C11 1.74(2), Cr1-C12 1.89(3), Cr1-C13 1.86(3), Cr1-C2 2.24(2), Cr1-C3 2.07(2), Cr1-C4 2.19(2), Cr1-C5 2.16(2), Cr1-C6 2.23(2), Cr1-C7 2.16(2), O1-C1 1.21(2), O2-C8 1.33(2), N1-C1 1.32(2), N1-C8 1.41(2), N1-C10 1.49(2), C1-C2 1.56(2), C2-C3 1.33(2), C2-C7 1.45(2), C3-C4 1.38(2), C4-C5 1.28(2), C5-C6 1.34(2), C6-C7 1.36(2), C7-C8 1.65(2), C8-C9 1.51(2), C1-N1-C8 122(2), O1-C1-C2 123(2), N1-C1-C2 103(2), C3-C2-C1 134(2), C3-C2-C7 114(2), C7-C2-C1 110(2), N1-C8-C7 101(2).

The X-ray structure analysis data show that the Cr-C3 bond length [2.07 (2) Å] is shorter and Cr-C2 bond length [2.24(2) Å] is longer than that of the other carbon atoms to the chromium atom, which indicates that the coordination of the aromatic ring is slightly off-centre with the Cr atom closest to C3 and far from C2. The comparablely long bond Cr-C2 contrasts the corresponding bond in *endo*-**192**. While the bond is short in *endo*-**192**, it is rather long in **197**. The difference reflects the different steric and electronic situation of the *endo*-alkynyl and *exo*-methyl substituted derivatives. Presumably for steric reasons, *exo*-**197** adopts a conformation with no CO ligand below the anellated five-membered ring. The arene C,C bond lengths alternate slightly as a result of the *trans* effect of the opposite CO ligands. Due to the electron withdrawal of the carbonyl group at C1 and along with the electron donating

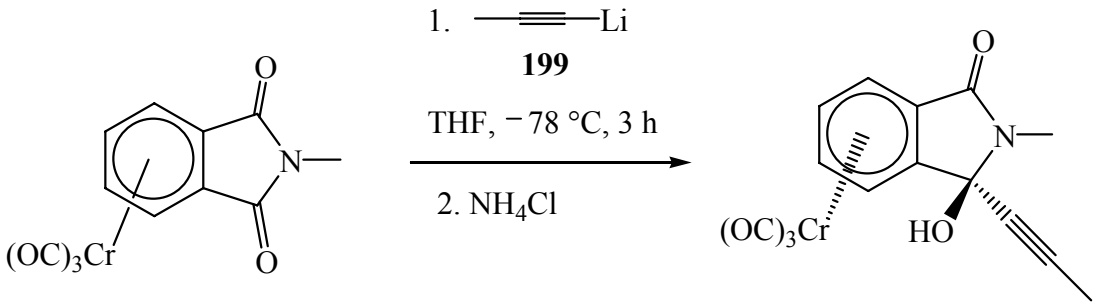
substitution at C2, the bond length of N1-C1 [1.32(2) Å] is shorter than N1-C8 [1.41(2) Å] and C1-C2 [1.56(2) Å] is shorter than C7-C8 [1.65(2) Å], respectively. Presumably due to the interaction of the *endo*-OH group with the $Cr(CO)_3$ unit the bond length of Cr-C11 [1.74(2) Å] is obviously shorter than that of Cr-C12 [1.89(3) Å] and Cr-C13 [1.86(3) Å]. The bond length of O2-C8 [1.33(2) Å] is comparably shorter than that of the corresponding O2-C3 [1.435(6)] in complex **192** with an *exo* OH group, which reflects the different interaction of $Cr(CO)_3$ moiety with *endo* and *exo* OH group.

The *exo*-configuration of the complex **197** indicates that the addition of methyllithium to *N*-methylphthalimide complex is a normal nucleophilic addition from *exo*-face of the ligand with respect to the bulk of the $Cr(CO)_3$ group. It is assumed that both the *N*-methyl substituent and the nucleophile methyllithium are not prone to form an *N*-acyliminium ion and that the product **197** is furnished by one nucleophilic addition of methyllithium from the *exo*-face of $Cr(CO)_3$ as usually expected.

3.4.2 Addition of 1-Propynyllithium (199)

It is of interest to take insight into the formation *N*-acyliminium intermediate in the nucleophilic addition to phthalimide chromium complexes. We speculated whether the suitable nucleophile could govern the formation of *N*-acyliminium intermediate.

Since the *endo*-adduct was discovered in the reaction of 1-propynyllithium (**199**) with tricarbonylchromium *N*-vinylphthalimide **173**, the addition of 1-propynyllithium (**199**) to *N*-methylphthalimide complex (**171**) was examined following the same procedure.



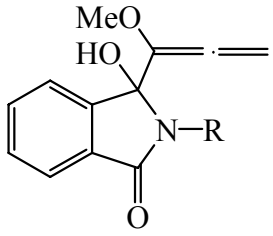
171 **208** 90 %

The product **208** is identified by inspection of the spectroscopic data. All the characteristic signals show no significant difference from the complex *endo*-**192**. It is worth to point out that the chemical shift of *endo*-OH appears at δ = 6.82 ppm, which is also similar to that of other related *endo*-adducts. Thus the configuration of complex **208** is assigned as the *endo*-adduct, which implicates the formation of an *N*-acyliminium intermediate in the nucleophilic addition of 1-propynyllithium (**199**) to *N*-methylphthalimide complex (**171**). In ^{13}C NMR spectrum, the characteristic chemical shifts for 1-propynyl group are assigned as δ = 3.82 ppm for CH_3, δ = 82.5 and 84.6 ppm for two carbon atoms of C≡C.

Compared with methyl adduct *exo* **197**, the 1-propynyl substituent may be attributed to stabilize the iminium cation in the reaction and to the formation of the *endo*-adduct **208** based on the mechanism proposed for the formation of complex *endo* **192**. Obviously the formation of the acyliminium cation is a result of the conjugation to the alkynyl substituent rather than to the alkenyl group in **191**.

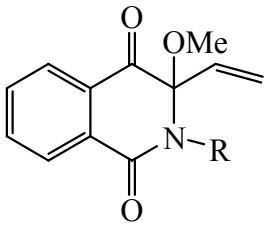
3.5 Palladium(0)-Catalyzed Ring Expansion Reactions

Ring expansion reactions have provided efficient tactics for the construction of various biologically active natural products and drugs.[156] Palladium(0)-catalyzed one-atom ring expansions of various hydroxy methoxyallenyl compounds have been achieved in excellent yields without the use of aryl halides. Hydroxy methoxyallenylisoindolinones **209a**,**c-e**, -indanones **210a**,**b**,**e**, and -phthalans **211a**,**b** have been readily converted to the corresponding isoquinolones **212a**,**c-e**, naphthoquinones **213a**,**b**,**e**, and isochromanones **214a**,**b** in the presence of P(*o*-tolyl)$_3$.[158]

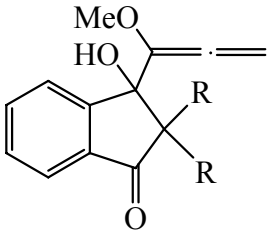


209a, **c-e**

5 mol % $Pd(PPh_3)_4$
additive
THF, reflux

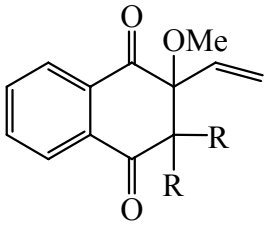


210a, **c-e** (63-93 %)

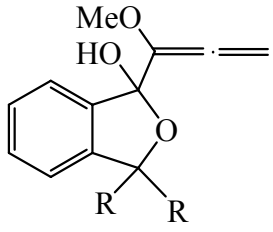


211a, **b**, **e**

5 mol % $Pd(PPh_3)_4$
additive
THF, reflux

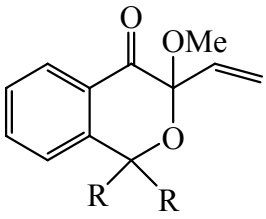


212a, **b**, **e** (90-98 %)



213a, **b**

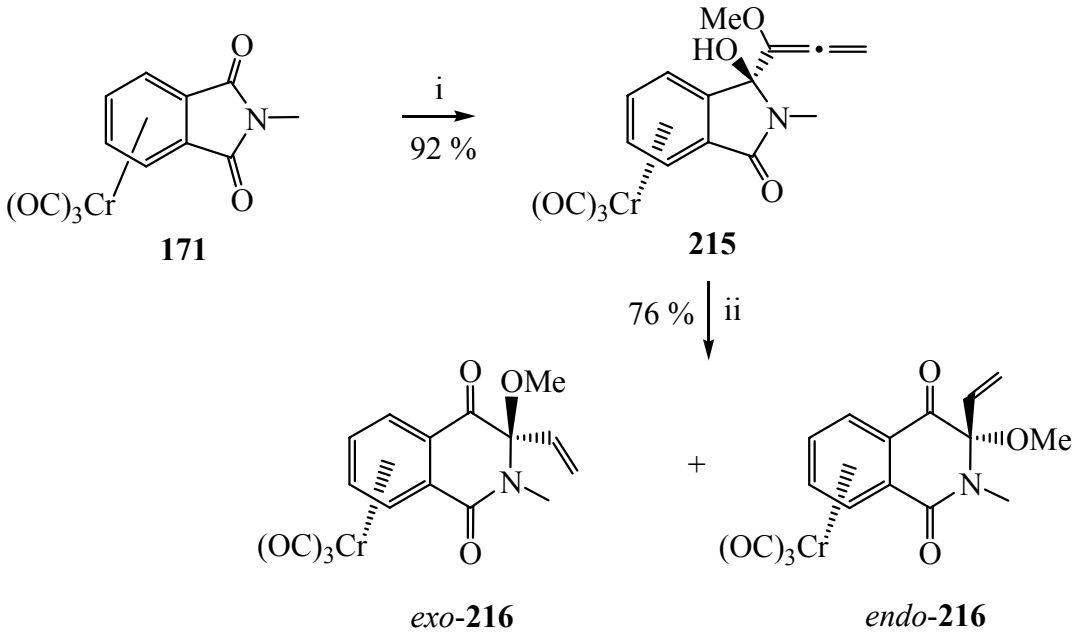
5 mol % $Pd(PPh_3)_4$
additive
THF, reflux



214a, **b** (63-91 %)

a: R = Me, **b**: R = Et, **c**: R = *n*Bu, **d**: R = *i*Bu, **e**: R = Bn

Compared with the uncomplexed case, it is of interests to examine the stereoselectivity of the reaction with complexed 1-isoindolinone with respect to the steric bulk of $Cr(CO)_3$ group. The addition of lithiated methoxyallene to *N*-methylphthalimide complex was carried out and the palladium catalyzed ring expansion reaction was envisaged. Complex of hydroxylmethoxyallenylisoindolinone **215** was prepared by treatment of *N*-methylphthalimide complex **171** with 2.0 equivalents of 1-lithiomethoxyallene[159] in THF at –78 °C for 2 h. The constitution of **215** was confirmed by inspection of the characteristic spectroscopic data. In the ^1H NMR spectrum, the singlet at 3.38 ppm is readily assigned for OMe, two doublets at δ = 5.76 ppm and 5.84 ppm with ^2J = 8.9 Hz belong to the allenyl protons, respectively. The higher chemical shift value (δ = 6.09 ppm) of OH group is used to ascertain the *endo* configuration of **215**. The ring expansion was performed as following. Complex **215** was heated at refluxing in the presence of 5 mol % of $Pd(PPh_3)_4$ and 3 equivalents of K_2CO_3 for 12 h to give the mixture of two isomers of the corresponding *N*-methylisoquinoline-1,4-dione *exo*-**216** and *endo*-**216** in 76 % yield. The products were not separable under the conditions of column chromatography.



exo-**216**: *endo*-**216** 4:1 (NMR)

Reagents and conditions: i. methoxyallene (2.0 equiv.), BuLi (2.0 mol equiv.), THF, –78 °C. ii. $Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (3 mol equiv.), THF, reflux.

Both diastereoisomers were indentified by means of detection of NMR spectra. Considering the different shielding effect of the $Cr(CO)_3$ group on the chemical shifts of the corresponding methoxy protons and olefin protons in two isomers, in the ^1H NMR spectra: the chemical shifts of OCH_3 at δ = 3.27 ppm, of terminal olefinic protons at δ = 5.45 and 5.46 ppm are assigned for *rac-exo*-**216**; the resonance at δ = 3.21 ppm corresponds to OCH_3, δ = 5.52 and 5.56 ppm are assigned for two terminal olefinic protons in *rac-endo*-**216**. The ratio of the *exo*- and *endo*-racemate (4:1) is deduced from the integration of peaks in NMR spectra.

The isomeric mixture **216** could be recrystallized in solution of CH_2Cl_2/hexane (3:1) at –18 °C affording deep red crystals for X-ray crystallography. Interestingly, the structure analysis indicates that the single crystal contains 8 molecules of both isomers with ratio1:1, which allows the explicit determination of the structures of both *endo* and *exo* isomers, as separately illustrated in Fig. 10 and Fig. 11.

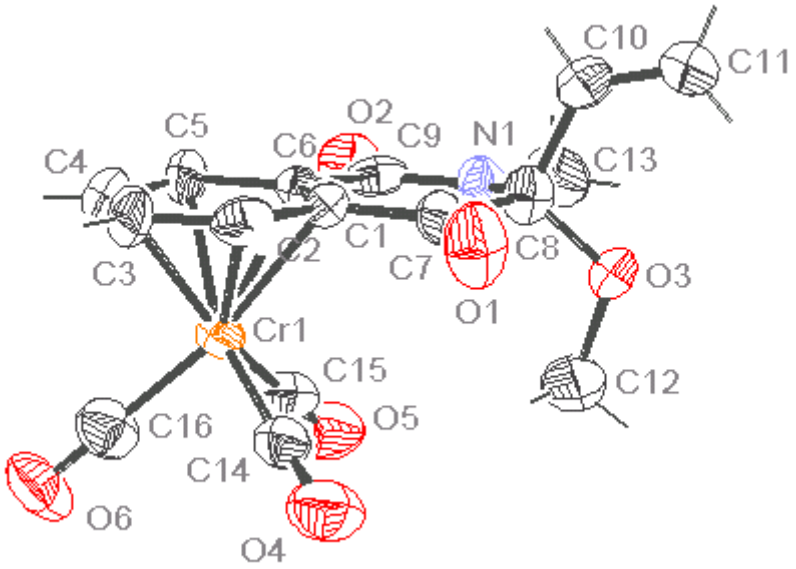


Fig. 10 X-ray structure of *endo*-**216**

Selected bond lengths [Å]and angles [°]

Cr1-C14 1.848(14), Cr1-C15 1.879(17), Cr1-C16 1.848(15), Cr1-C1 2.170(11), Cr1-C2 2.194(13), Cr1-C3 2.228(13), Cr1-C4 2.210(13), Cr1-C5 2.266(13), Cr1-C6 2.185(11), C1-C2 1.417(17), C1-C7 1.441(16), C1-C6 1.443(16), C2-C3 1.410(18)

C3-C4 1.41(2), C4-C5 1.42(2), C5-C6 1.429(15), C6-C9 1.482(18), C7-O1 1.226(15),C7-C8 1.542(18), C8-O3 1.420(15), C8-C10 1.562(18), C9-O2 1.197(14), C10-C11 1.294(18), C12-O3 1.457(16), C1-C6-C9 121.9(9), O1-C7-C8 118.5(11), C1-C7-C8 120.1(10), O3-C8-C7 110.7(10), O3-C8-C10 105.7(9), C7-C8-C10 106.8(11), C8-O3-C12 113.2(10), C11-C10-C8 125.3(12).

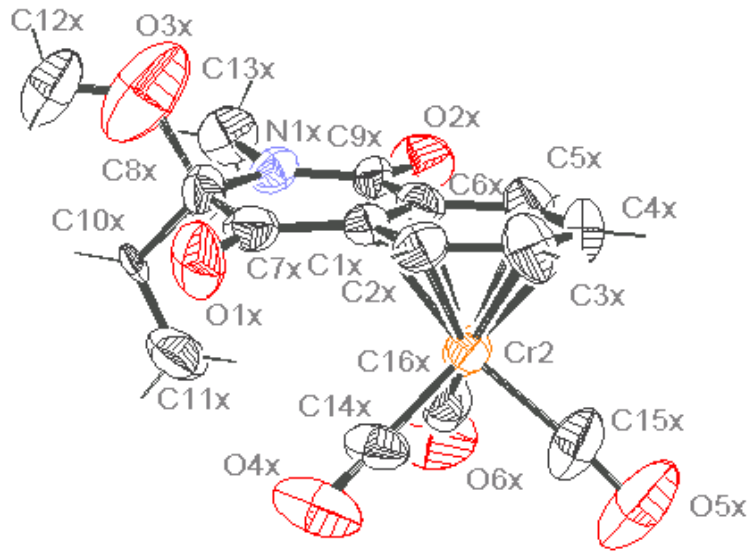


Fig. 11 X-ray structure of *exo*-**216**

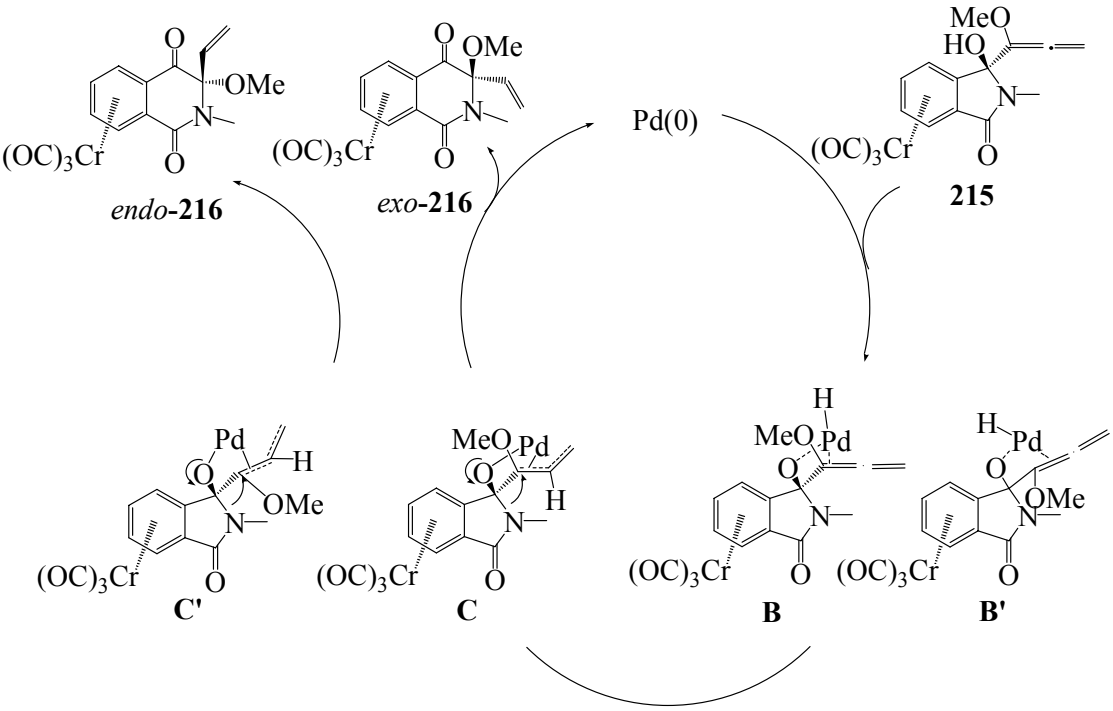
Selected bond lengths [Å]and angles [°]

Cr2-C14x 1.836(14), Cr2-C15x 1.876(15), Cr2-C16x 1.842(19), Cr2-C1x 2.159(11), Cr2-C2x 2.179(12), Cr2-C6x 2.191(12), Cr2-C5x 2.206(14), Cr2-C4x 2.217(14), Cr2-C3x 2.248(14), C6x-C1x 1.401(17), C6x-C5x 1.441(18), C6x-C9x 1.484(18), C4x-C3x 1.40(2), C3x-C2x 1.412(18), C2x-C1x 1.409(17), C1x-C7x 1.497(17), C7x-O1x 1.189(16), C7x-C8x 1.542(18), C8x-C10x 1.411(16), C8x-O3x 1.58(2), O3x-C12x 1.23(2), C9x-O2x 1.242(15), C10x-C11x 1.401(19), C6x-C1x-C2x 119.9(11), C6x-C1x-C7x 118.5(11), C1x-C7x-C8x 117.9(11), C10x-C8x-O3x 109.2(11), C11x-C10x-C8x 114.3(10). C12x-O3x-C8x 122.8(19).

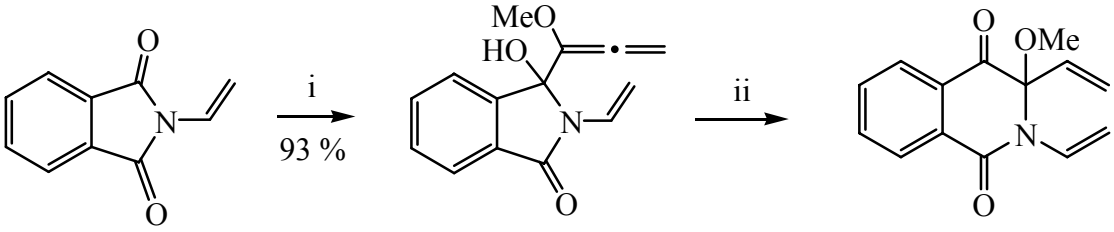
In *endo*-**216**, the Cr1-C1 bond length [2.170(11) Å] and the Cr1-C6 bond length [Cr1-C6 2.185(11)] are shorter and Cr1-C5 bond length [2.266(13) Å] is longer than that of the other carbon atoms to the chromium atom, which indicates that the coordination of the aromatic ring is distinctly off-centre with the Cr atom closest to C1 and far from C5. Similarly, the significantly different bond lengths of Cr-C bond in *exo*-**216** implicate the comparably stronger coordination of $Cr(CO)_3$ to C1x and C6x atoms than to other carbon atoms. The fact that the distance of the electron poor atoms C1 and C6 to Cr atom are shorter than the other distances is presumably due to an increased back bonding character because of the electron withdrawal of the carbonyl groups. Presumably for steric reasons, both isomers *endo*-**216** and *exo*-**216** adopt a conformation with no CO ligand below the anellated six-membered ring. The arene C,C bond lengths alternate slightly as a result of the *trans* effect of the opposite CO ligands. Comparing the X-ray analysis data of both isomers, it can be readily observed that the C-O bond length of methoxy group at C8 in *endo*-**216** (C12-O3 = 1.457 Å) is longer than that in *exo*-**216** (O3x-C12x = 1.23 Å) by 0.23 Å. This might be attributed to the power of the electron withdrawal $Cr(CO)_3$ fragment, which decreases the electron density of C-O bond of *endo*-OCH_3 group since it shares the same side with $Cr(CO)_3$ group. In contrast to the case of *endo*-**216**, the OCH_3 group in *exo*-**216** suffers less influence of $Cr(CO)_3$ unit possessing a shorter bond length. The same effect of $Cr(CO)_3$ unit is reflected on the bond lengths of vinyl group in both isomers *i.e*. C=C bond (C10-C11 = 1.294 Å) directed to the *exo*-face in *endo*-**224** is shorter than that (C10x-C11x = 1.401 Å) in *exo*-**216** by 0.11 Å. Presumably due to the electronic effect of $Cr(CO)_3$ the C-O bond [C8-O3-C12 113.2°(10)] of OCH_3 group in *endo*-**216** is bent to the $Cr(CO)_3$ moiety while it has larger bond angel [C12x-O3x-C8x 122.8°(19)] in *exo*-**216**. Similarly, C=C bond [C11x-C10x-C8x 114.3°(10)] of vinyl group is more strongly bent to the $Cr(CO)_3$ moiety in *exo*-**216** than that [C(11)-C(10)-C(8) 125.3°(12)] in *endo*-**216**.

A plausible mechanism for the Pd(0)-catalyzed ring expansion can be represented on the basis of the earlier reports of Nagao et al.[158] In the first step of the catalytic cycle, oxidative addition of the hydroxy group of the hydroxy methoxyallenyl cyclic complexe **215** is presumed to occur onto the Pd(0) catalyst to form complex **B** and **B'**. In the second step, a π-allylpalladium complex **C** and **C'** can be generated by hydropalladation, in which the release of the Pd(0) and rearrangement of the N-C bond in the π-allylpalladium complex may concertedly proceed to give the one-atom

ring expanded product **216**. In the last step of the catalytic cycle, it is hypothesized that the electron-rich OMe group prefers the opposite face of the *N*-methyl-3-isoquinoline-1,4-diones with respect to the steric hindrance of the $Cr(CO)_3$ moiety, leading to an excess of *exo*-product **216**.



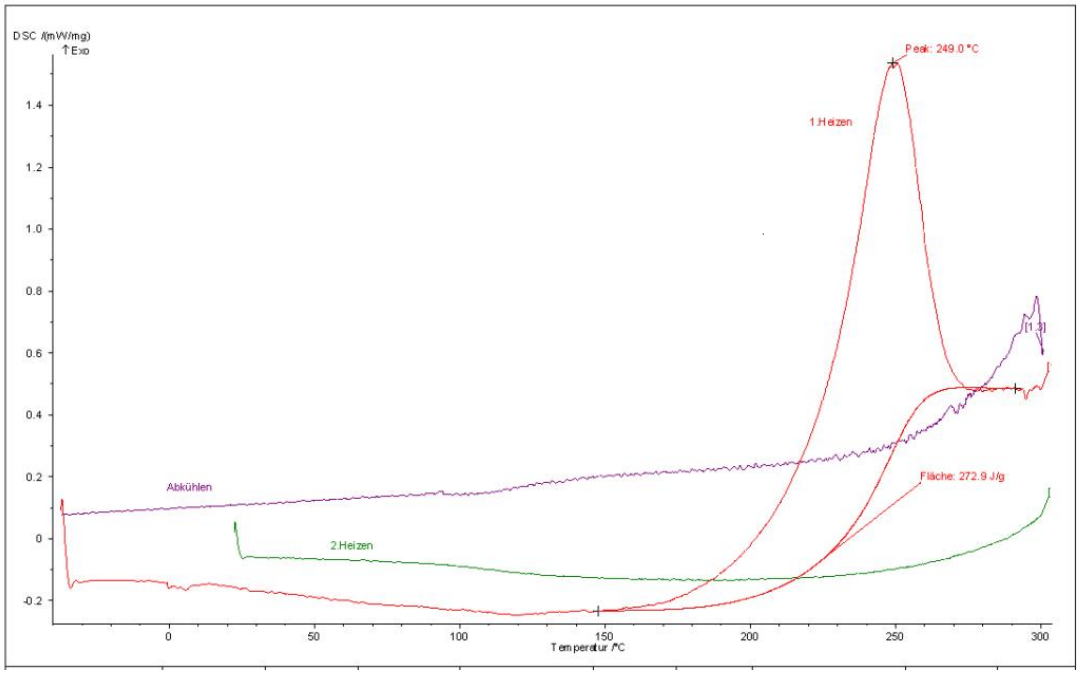
Microwave heating has emerged as a powerful technique to assist a variety of chemical transformations such as additions, cycloadditions, substitutions, eliminations *etc*. Many examples of the benefits of microwave irradiation in palladium catalyzed cross-coupling reactions have been reported.[160] The palladium-catalyzed ring expansion reaction of hydroxy methoxyallenylisoindolinone **217** prepared from the corresponding *N*-vinylphthalimide (**172**) with 1-lithio-1-methoxyallene was employed for the palladium-catalyzed ring expansion in the presence of 5 mol % of $Pd(PPh_3)_4$ and 3 equivalents of K_2CO_3 under microwave irradiation for 0.5 h, giving the desired ring expansion product **218** in 76 % yield. The reference reaction was performed by heating at reflux in THF for 24 h without changing other reaction conditions, giving the same product **218** in 74 % yield.



171 **217** **218** 74[a]-76 %[b]

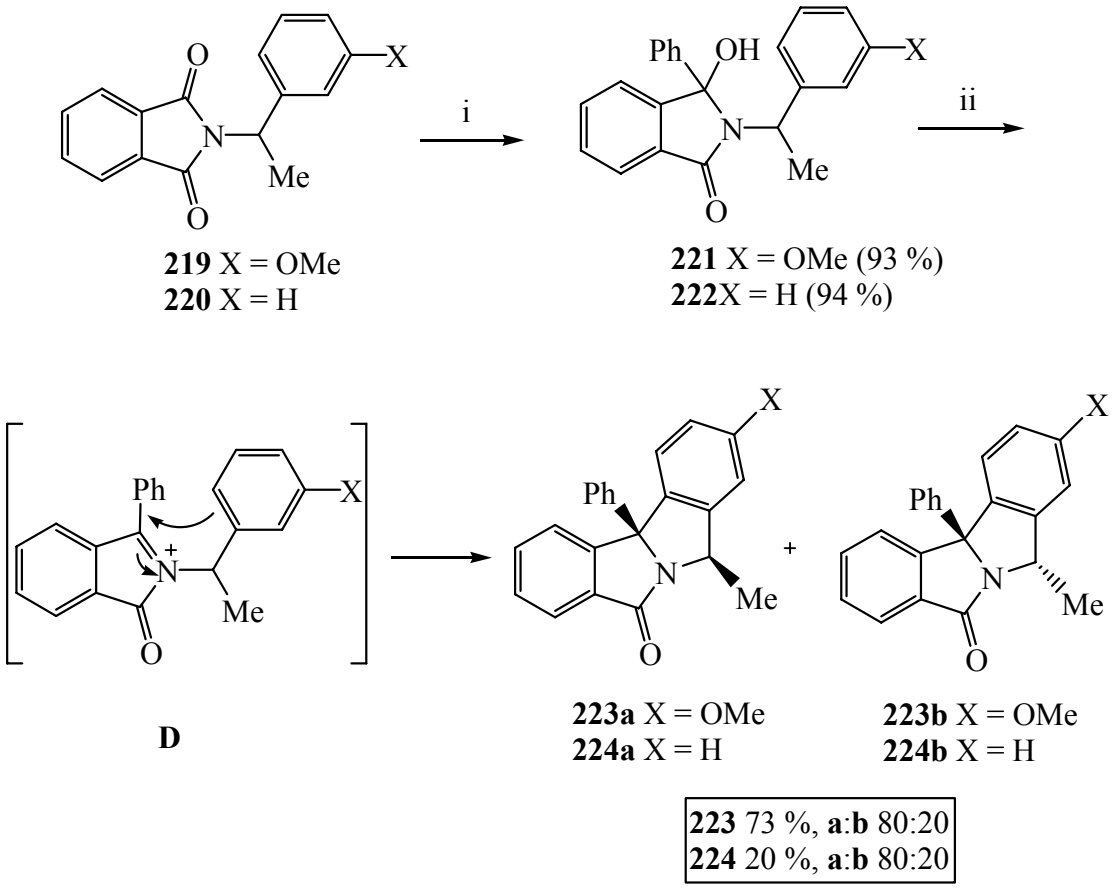
Reagents and conditions: i. methoxyallene (2.0 equiv.), BuLi (2.0 mol equiv.), THF, –78 °C. ii. (a) $Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (3 mol equiv.), THF, reflux, 24 h; (b) $Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (3 mol equiv.), THF, 140 °C, 250 W under microwave irradiation for 0.5 h.

Compound **218** containing two adjacent vinyl groups might undergo an aza-Cope rearrangement under thermal conditions. In order to learn more about the thermal properties of **218**, a differential scanning calorimetric (DSC) measurement has been carried out in cooperation with Prof. Dr. H. Menzel (TU Brauschweig). As illustrated below, the DSC chart revealed that a clear exothermic peak appeared at about 249 °C implicating an occurrence of an exothermic reaction. Moreover, it was an irreversible chemical reaction because another baseline was observed after cooling down the temperature and no thermal flat was recognized neither on the cooling curve nor the reheating curve.



3.6 Planar Chiral Tricarbonylchromium *N*-acyliminium Ion

The reaction of *N*-acyliminium intermediates with various nucleophiles has been widely used a key step in the synthesis of many nitrogen-containing compounds.[154] Cyclisations via *N*-acyliminium ions provide access to many fused heterocyclic systems. Intramolecular *N*-acyliminium ion cyclization of α-hydroxy lactams has been reported as a useful approach for the construction of fused heterocyclic systems and has widely been applied in the synthesis of alkaloid natural products.[154, 161] Analogous cyclisations are also achievable in the phthalimide series. Hydroxy lactam precusors **221**, **222** originating from phthalimides **219**, **220** undergo cyclisation *via N*-acyliminium ion intermediates **C** on heating in polyphosphoric acid (PPA) to give the fused tetracyclic products **223** and **224**, respectively. The mixture of diastereoisomeric products **223** and **224** were inseparable by chromatography, and the major component was the *cis*-isomer **223a**.[162]



219 X = OMe
220 X = H

221 X = OMe (93 %)
222X = H (94 %)

D

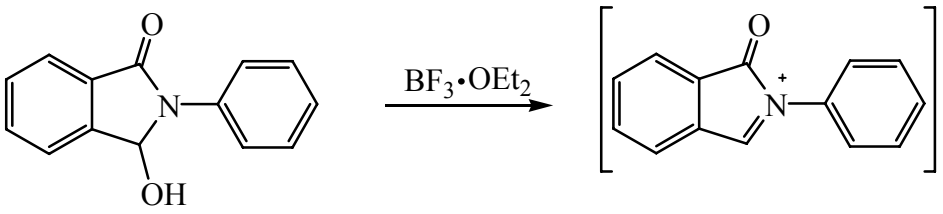
223a X = OMe
224a X = H

223b X = OMe
224b X = H

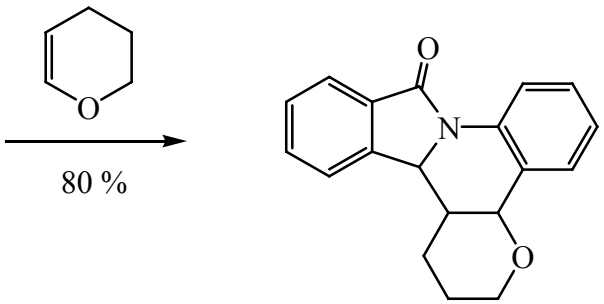
223 73 %, **a**:**b** 80:20
224 20 %, **a**:**b** 80:20

Reagents and conditions: i. PhMgBr; ii. PPA, 100 °C or $AlCl_3$, DCE, –7 °C.[161]

A facile and efficient synthesis of isoindolo[2,1-α]quinolinones by means of intermolecular [4+2] reaction of *N*-acyliminium cation with olefins has been reported recently.[163] *N*-acyliminium cation **226** was generated by dehydroxylation of 2,3-dihydro-3-hydroxy-2-arylisoindol-1-one **225** obtained by simple reduction of the corresponding *N*-aryl phthalimide with borohydride. The reaction has been successfully performed with a variety olefins leading to isoindolo[2,1-α]quinolin-11-ones as mixtures of *cis* and *trans* stereoisomeres, including the 2,3-dihydropyran illustrated below as the dienophile affording product **227**.

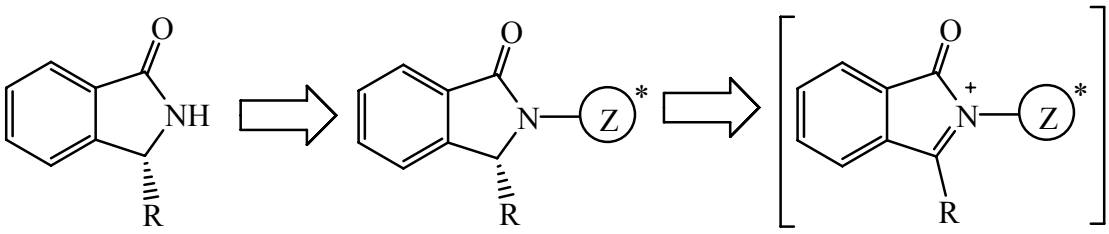


225 **226**

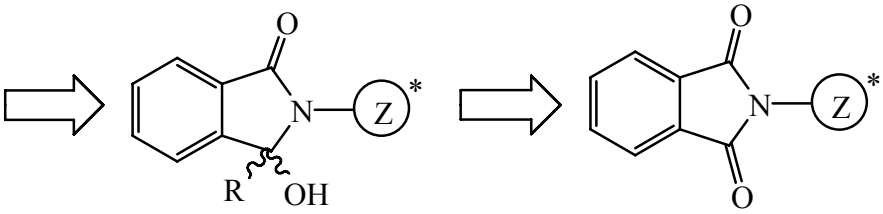


227

The synthetic utility of *N*-acylimiunium ion has been recently extended in chiral applications.[154b].As already mentioned in the foregoing section, the concise and efficient syntheses of enantiomerically enriched 3-substuitued isoindol-1-ones **228** via a *N*-acylimiunium ion equipped with a chiral auxiliary (Z^*) as the retrosynthetic route depicted below have been reported.[137]



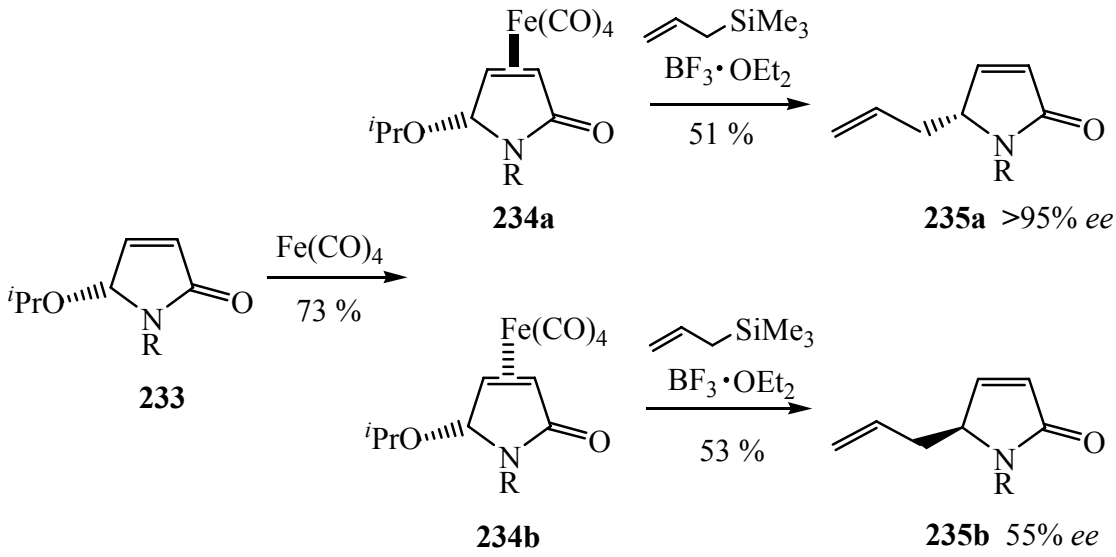
228 **229** **230**



231 **232**

The key step of this method relies on the diastereoselective reduction of 3-hydroxy isoindolinone derivatives **231** via *N*-acylimium **230** leading to enantiomerically enriched **228**. **231** can be obtained by reacting phthalimide **232** with a chiral auxiliary attached to the nitrogen atom with appropriate organometallic reagents. Crucial for the success of this strategy is to identify an easily incorporated stereocontrolling agent, which would be sufficiently robust to survive the projected addition reaction and which would be also labile enough to be removed in the final step without racemization. (*R*)-phenylglycinol[164] and (*S*)-1-amino-2-methoxymethylpyrrolidine (SAMP)[137] have been successfully used as the chiral auxiliary for this strategy.

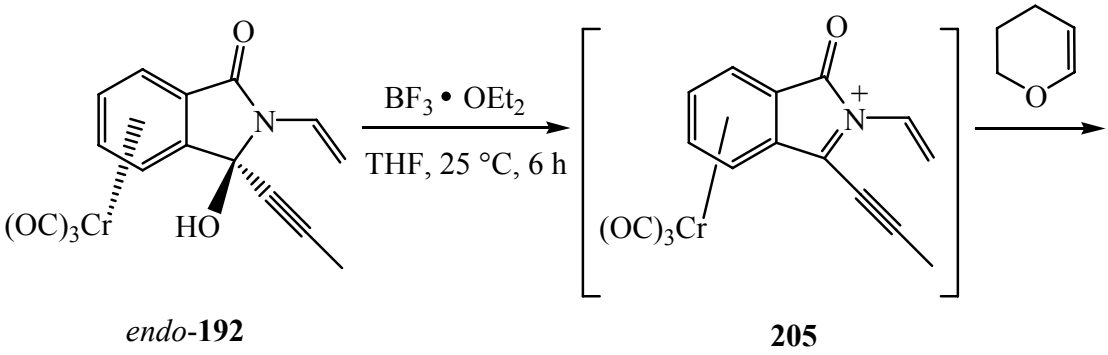
The $Fe(CO)_4$ moiety as a non-chiral-auxiliary has been attached to enelactam **233**, such type of *N*-acyl-oxylactam iron complexes **234a-b** undergo substitution with a variety of nucleophiles including allylTMS / $BF_3{\cdot}OEt_2$. After oxidative removal of the $Fe(CO)_4$ group, compound **235a** was obtained (via a planar chiral *N*-acylimium intermediate) with retention at C-5 (*ee* >95 %); **235b** was obtained on the contrary with inversion because of the steric hindrance of $Fe(CO)_4$.[165]



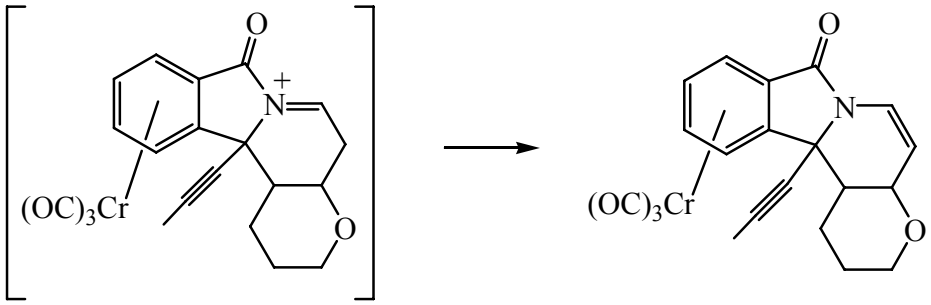
As discussed in chapter B 3.3.1, the unusual *endo*-**192** obtained by the normal nucleophilic addition with 1-propynyllithium (**199**) implicates the formation of the interesting chiral *N*-acyliminium complex **205** during the reaction procedure. To our best knowledge, such type of planar chiral *N*-acyliminium ion is so far unknown. This discovery prompted us to explore the synthetic and asymmetric synthetic potential of planar chiral tricarbonylchromium complex of *N*-acyliminium ion with respect to the classic characteristics of tricarbonylchromium group. Owing to the electron-withdrawing properties of $Cr(CO)_3$ group, the iminium carbon atom is now more electron-deficient, which may cause such *N*-acyliminium ions to be much more reactive electrophile than simple *N*-acyliminium ions. It is expected that the introduction of the nucleophile would take place under stereocontrol of the $Cr(CO)_3$ moiety, thus effectively promoting the approach from the less hindered side.

It was envisaged to perform the intermolecular [4+2] reaction between an *N*-acyliminium ion precursor 3-hydroxyisoindolin-1-one complex derived from *N*-vinylphthalimide complex **173** and an appropriate dienophile. The first attempt was carried out as follows: complex **192** and an excess of 2,3-dihydropyran were dissolved in THF at 25 °C, 1.05 equivalents of $BF_3{\cdot}OEt_2$ was added in one portion. After stirring for 6 hours, TLC indicated no starting material left. The reaction was then quenched with an aqueous solution of sodium carbonate. After the extraction with ethyl acetate, the residue was purified by column chromatography. Two products were obtained: eluting with PE/TBME (2:1) gave the first product **236** in 11 % yield as yellow oil; eluting with TBME gave the second product **237** in 40 % yield as a red

solid. There was still unseparatable compound left. The constitution of the outcome of the reaction are tentatively assumed as **236** and **237** supported by the mass spectra, respectively.

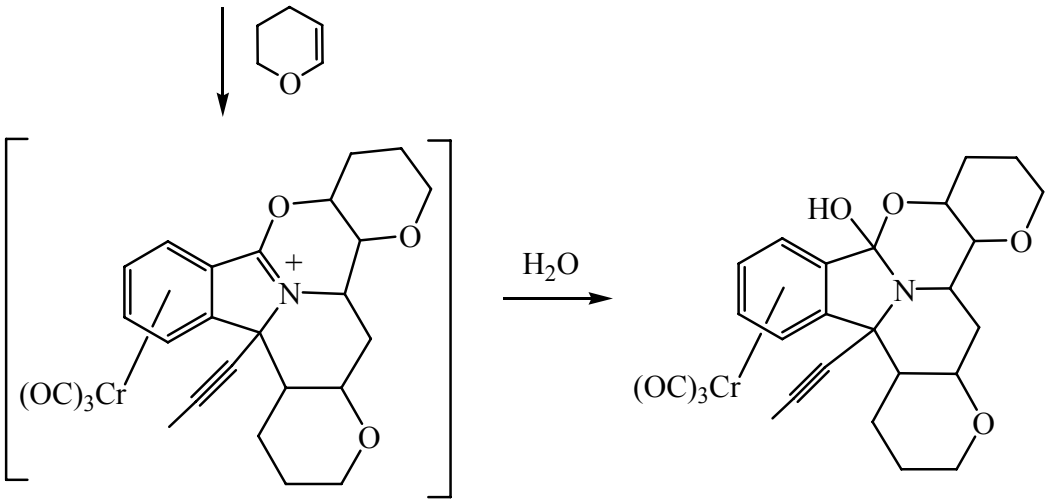


endo-**192** **205**



E **236**

m/z 415



F **237**

m/z 517

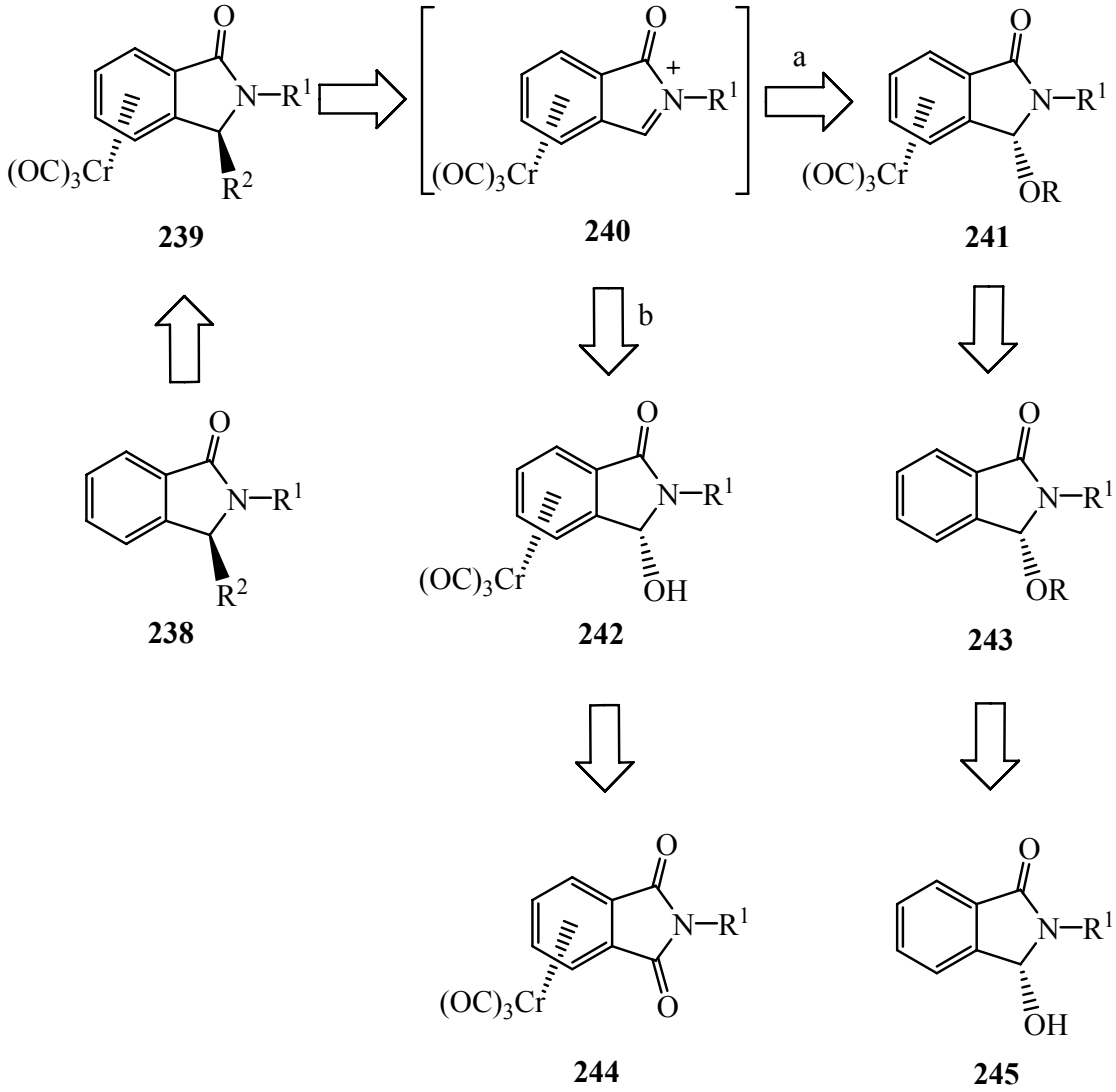
It is hypothesized that the *N*-acyliminium ion **205** is formed from complex **192** in the presence of Lewis acid. With the aid of the π-participation of vinyl group attaching to the nitrogen atom, intermediate **205** then reacts with the dienophile 2,3-dihydropyran

in a hetero Diels-Alder reaction,[166] leading to a new cation **E**, furnishing **236** after hydrolysis. Interestingly, the molecule ion peak in mass spectrum of the separated major product fits with the case of the addition of *N*-acyliminium ion **205** with 2 molecules of 2,3-dihydropyran and one molecule of H_2O. This could be understood by the new cation **E** formed by the first addition of 2,3-dihydropyran, which might be an analogue of reactive *N*-acyliminium ion, which reacts with the second molecule 2,3-dihydropyran in a hetero Diels-Alder reaction giving an iminium ion intermediate **F**, which is attacked by nucleophile H_2O affording the product **237**.

These outlined preliminary results offer an attractive target towards novel applications of chiral *N*-acyliminium ions. We are highly motivated to gain a better insight into the transformations and stereochemistry in the reaction involving the chiral tricarbonylchromium complex *N*-acyliminium intermediate.

Concerning the importance for synthesis of valuable optically active 3-substuitued isoindol-1-ones **238**, asymmetric synthetic methodology using planar chiral tricarbonylchromium complex *N*-acyliminium ion is of interests to be developed, in which $Cr(CO)_3$ group could act as an non-chiral auxiliary building block for the diastereoselective synthesis.

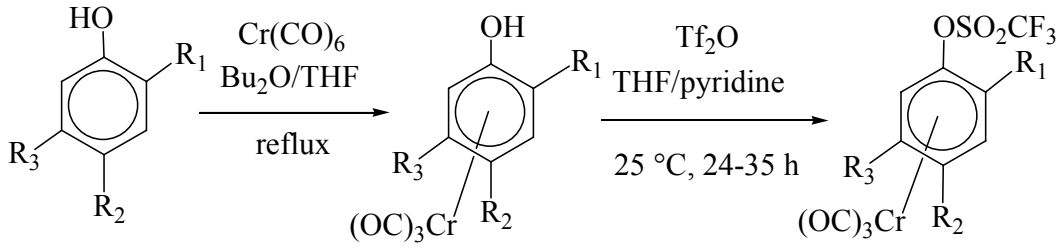
Two possible retrosynthetic routes are depicted below. Both routes rely on an enantioselective reduction strategy to provide the complex of α-alkoxylactam **241** or the complex of α-hydroxylactam **242** as the precursor for chiral tricarbonylchromium *N*-acyliminium ion **240**. In route a, the conversion of α-hydroxylactam **245** into alkoxylactam **243** is necessary. Because of the unsuccessful experience of direct complexation between α-hydroxylactam **177** and $Cr(CO)_3$ (in section B 3.2.). Enantiomerically pure α-hydroxylactam **245** might be obtained by means of an enantioselective borane reduction (CBS reduction).[167, 168] In route b, the enantiomerically pure α-hydroxylactam **242** could also be obtained by an enantioselective reduction of **244** by CBS[167] or an alternative asymmetric transfer hydrogenation of ketones catalyzed by enantiomerically pure chiral ruthenium or rhodium complexes.[168] The latter asymmetric synthetic method has been used by Noyori to catalyze the reduction of indan-1-one in >99 % yield and 99 % *ee*.[169b] Subsequently, the diastereoselective addition of a suitable nucleophile to tricarbonylchromium *N*-acyliminium ion **240** would give rise to product type **239** with respect to the steric bulk of $Cr(CO)_3$ unit. The final removal of $Cr(CO)_3$ group would afford the desired enantiomerically enriched 3-substituted isoindol-1-ones **238**.


O
N–R1
(OC)3Cr
R2
239
240
a
OR
241
b
238
OH
242
243
244
245

C. Summary

Investigations in the chemistry of arene tricarbonylchromium complexes with functionalized anellated rings have disclosed a number of oxy-anion accelerated reactions such as a dianionic oxy-Cope rearrangement.[22-25] As these reactions in most cases started from benzocyclcobutene derivatives, which had been obtained by [2+2] cycloaddition reactions of benzyne derivatives with alkenes, we were intrigued by the possibility to prepare these complexes just as in the uncomplexed case[42] by a [2+2] cycloaddition between an aryne complex and a ketene acetal followed by hydrolysis. As an extension of the chemistry arene tricarbonylchromium complexes with functionalized anellated ring, *N*-substituted phthalimide complexes were aimed at anion accelerated reactions. Thus two topics initiated from the chemistry of arene tricarbonylchromium complexes with functionalized anellated ring are involved in this work *i. e.* generation of benzyne tricarbonylchromium complex and exploration of the anion accelerated reactions of *N*-vinylphthalimide complex such as an anionic oxy-Cope reaction.

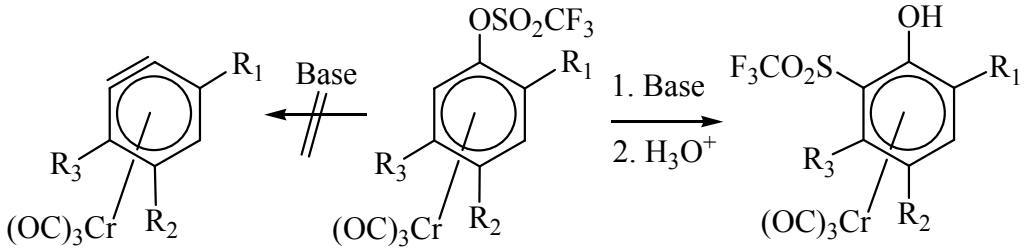
η^6-Aryne tricarbonylchromium(0) complexes are still unknown. We undertook an effort to prepare them by a triflic acid elimination process, which should, in contrast to most other methods, be compatible with the tricarbonylchromium group. It has been established in this work that moderately air stable or air stable aryl triflate tricarbonylchromium complexes could be flexibly and generally prepared from the corresponding phenols. Tricarbonylchromium phenol complexes **75**-**82** were prepared in up to 94 % yield by treatment of the ligands with hexacarbonylchromium in dibutyl ether / THF (10:1) at reflux for 2-3 days. Subsequent treatment with triflic anhydride afforded phenyl triflate complexes **58**-**65** in up to 88 % yield as moderately air stable yellow solids.



58-65 **67-74** **75-82**

R_1, R_2, R_3 = H. Me, allyl, *i*Pr, OMe, $SiMe_3$, F

Next, an *ortho* deprotonation of the aryl triflate with lithium diisopropylamide or with butyllithium was envisaged to induce triflate metal elimination with formation of the respective aryne complexes **A**. However, in contrast to our anticipation, no evidence for the formation of aryne complex **A** was obtained. Instead, high yields of *ortho*-trifluoromethyl sulfonyl phenol complexes **93-99** were achieved.



A **75-77**, **79-82** **93-99**

R_1, R_2, R_3 = H, Me, allyl, *i*Pr, OMe, F

In an alternative approach, triflate complex **78** (R_1 = $SiMe_3$, R_2, R_3 = H) was treated with tetrabutylammonium fluoride in acetonitrile at 25 °C. Again, an anionic thia-Fries rearrangement occurred instead of a benzyne complex formation giving *ortho*-trifluoromethyl sulfonyl phenol (**93**) in 86 % yield after aqueous work up.

The X-ray structure of complex **93•THF** (R_1, R_2, R_3 = H) proved the formation *ortho*-trifluoromethylsulfonylphenol complex, which is the result of an anionic thia-Fries rearrangement.

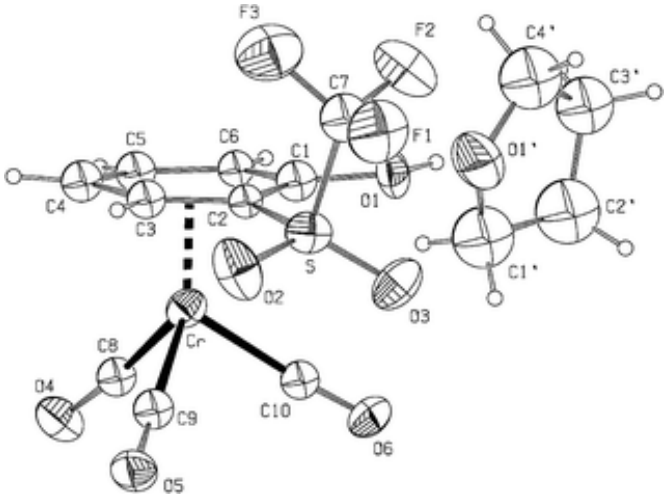
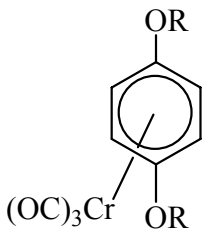
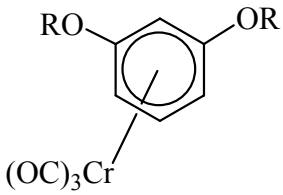


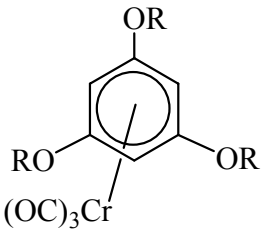
Fig. 4 Structure of **93•THF** in the crystal

The preference of this anionic thia-Fries rearrangement mode is presumably caused by the electron withdrawal of the tricarbonylchromium fragment, which is better satisfied by the formation of the rearranged phenolate than by the alternative formation of an aryne, which is observed with the uncomplexed ligands.[57, 62]

To extend the scope of the reaction, the tricarbonylchromium complexes **83**-**85** of hydroquinone[84, 85] resorcinol and of phloroglucinol were prepared by direct complexation with $Cr(CO)_6$ in good yield. After triflation of **83**-**85**, double and triple triflate groups substituted complexes **86**-**88** were obtained in moderate to good yield as air stable solids, respectively.





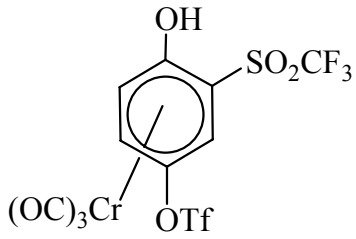


83: R = H (78 %)
86: R = SO_2CF_3 (67 %)

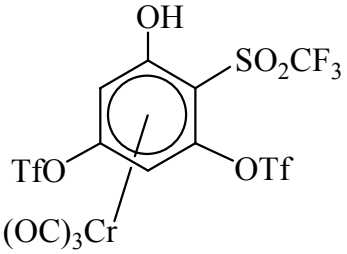
84: R = H (78 %)
87: R = SO_2CF_3 (63 %)

85: R = H (58 %)
88: R = SO_2CF_3 (35 %)

Treatment of complex **86** and **88** with butyllithium gave products **133** (78 %) and **134** (66 %) resulting from single anionic thia-Fries rearrangements.

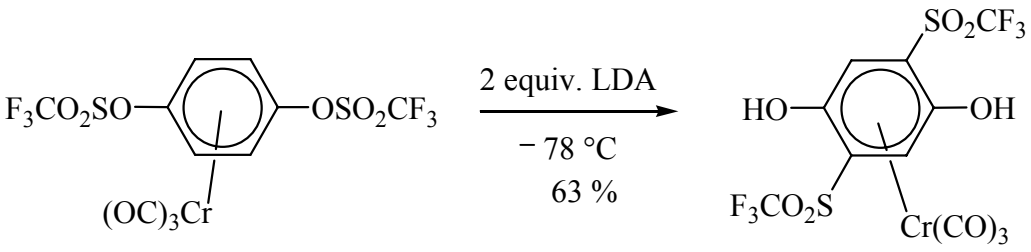


133 (78 %)



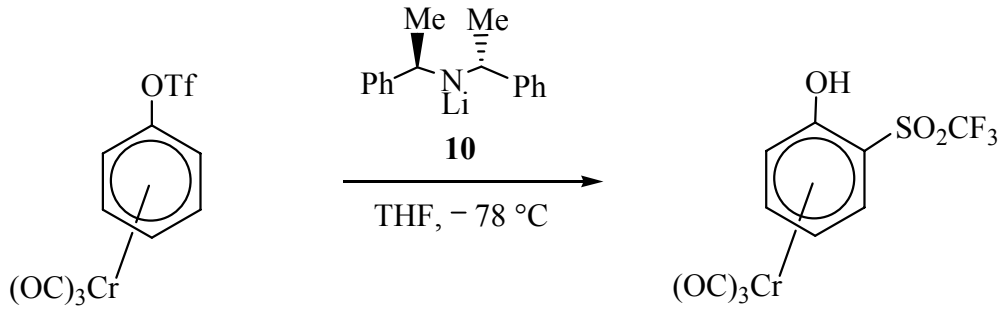
134 (66 %)

However, treatment of **86** with 2 equivalents of the sterically hindered amide base lithiumdiisopropylamide (LDA) at –78 °C led to the desired symmetrically doubly rearranged complex **115a** in good yield.



86 **115a**

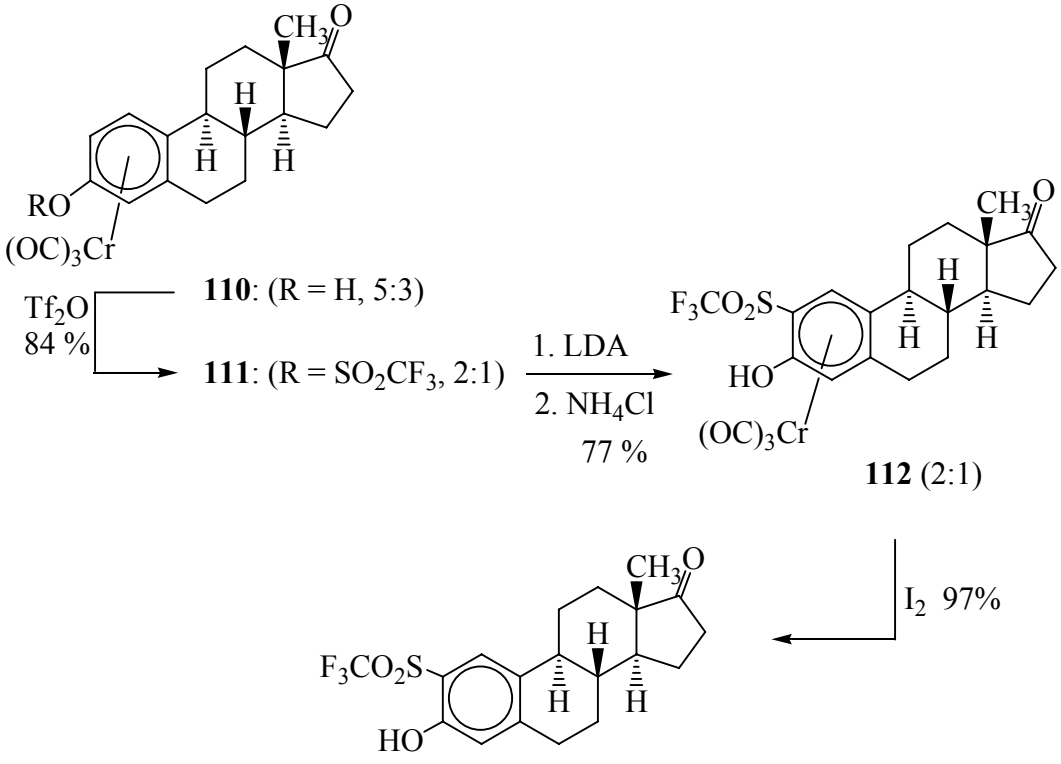
The bases used so far (LDA, BuLi) cannot differentiate the enantiotropic *ortho* hydrogen atoms in the phenyl triflate complex **75** (R_1, R_2, R_3 = H). In order to achieve a desymmetrization resulting in non-racemic **93**, **75** was treated with (*R,R*)-di(1-phenylethylamine), which has been used by Simpkins for the enantioselective *ortho*-deprotonation of (anisole)tricarbonylchromium.[13] Inspection of the NMR spectra (^{1}H, ^{13}C) of the respective Mosher esters revealed that phenol complex (+)-**93** had been obtained in only 30 % *ee*. This might be due to a pre-coordination of the chiral base at the Lewis basic oxygen atoms of the triflate group.



75

(+)-93 70 %, 30 % *ee*

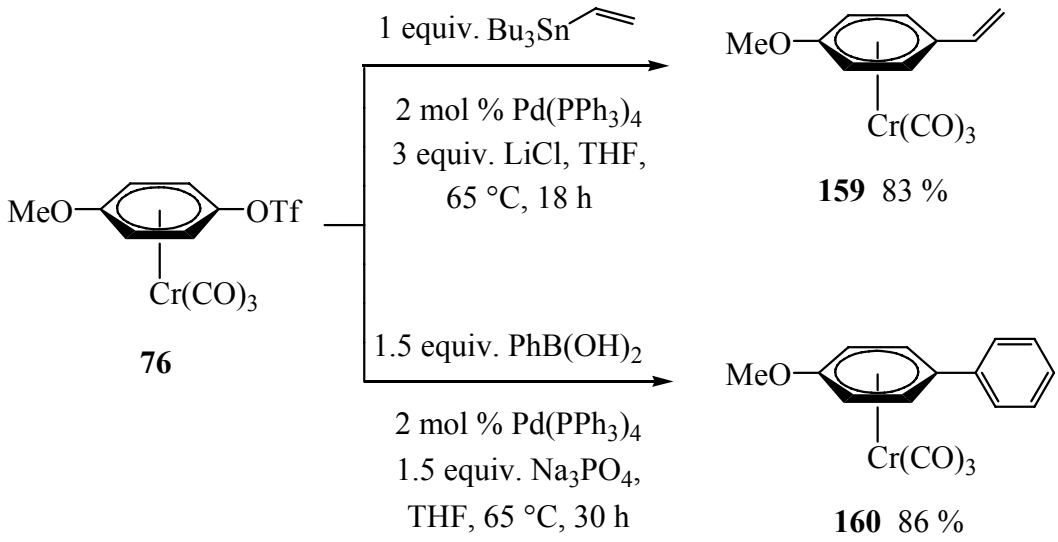
The new anionic thia-Fries rearrangement of tricarbonyl(phenyltriflate)chromium complexes has been applied to the tricarbonylchromium complex of estrone **110**, which was obtained as a 5:3 (NMR) mixture of diastereomers. Triflation under standard reaction conditions afforded **111** (2:1) in 84 % yield. Subsequent treatment with LDA at –78 °C caused a regioselective rearrangement exclusively to **112** (2:1), which was isolated in 77 % yield. Subsequent decomplexation afforded the new steroid **114** in 97 % yield.



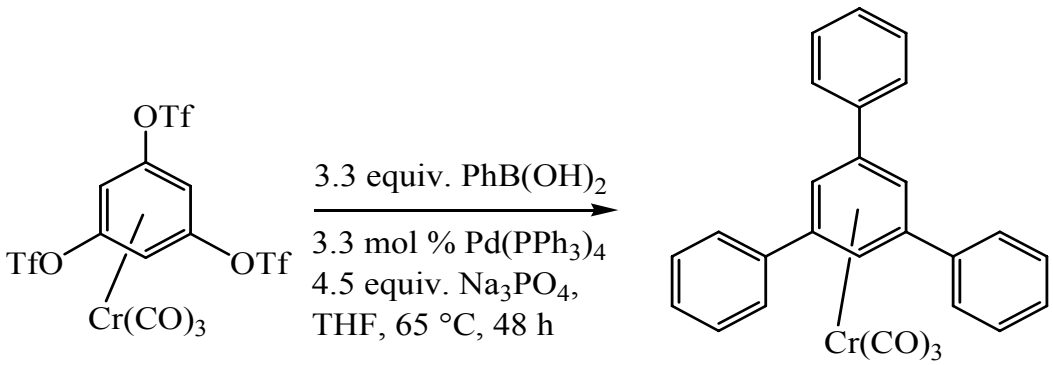
In conclusion we have demonstrated the impressing propensity of phenyl triflate tricarbonylchromium complexes to an anionic thia-Fries rearrangement, which takes place at –78 °C in high yield. This pathway contrasts the chemistry of the uncomplexed ligand systems, which usually react with benzyne formation.[81] Thus, the desired benzynetricarbonylchromium still remains a highly attractive target of our investigations.

The combination of palladium catalysis and arene tricarbonylchromium complex chemistry not only greatly expanded the scope of the arene chemistry, but also implemented the versatility of the cross coupling reaction. To the best of our knowledge, very few examples of cross coupling reaction involving arene chromium complexes bearing non-halogenated leaving groups have been reported up to date. It is noteworthy that triflates were found to be good alternative partner for the coupling reaction.[122] Conversion of phenols into triflates renders the Ar-O bond sufficiently electron deficient to permit insertion of transition metals such as Pd(0). Successful reactions require this bond to be weakened by electron withdrawing groups on the arene.

Aryl triflate tricarbonylchromium complexes were thought to be valuable starting material for C-C bond formation because of the stability and great availability from phenols. In light of the results of Wulff *et al*[65] we wished to broaden and generalize the scope of utilities of aryl triflate chromium complexes towards carbon-carbon bond formation. Palladium catalyzed Suzuki and Stille cross-coupling reactions with aryl triflate tricarbonylchromium complexes **76** have been investigated in this work.



Furthermore, Suzuki cross coupling with air stable tricarbonyl(1,3,5-trihydroxylbenzene)chromium(0) tris(triflate) (**88**) has been carried out. In the presence of 3.3 mol % of $Pd(PPh_3)_4$, the cross couplings of three triflate groups at the arene ring of the complex **88** with phenlyboronic acid proceeded completely giving tricarbonylchromium complex of 1,3,5-triphenylbenzene [(TPB)$Cr(CO)_3$] **161** in excellent yield.

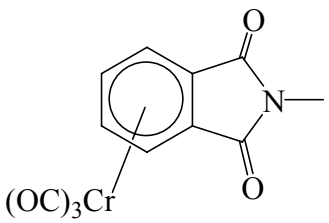


88 **161** 87 %

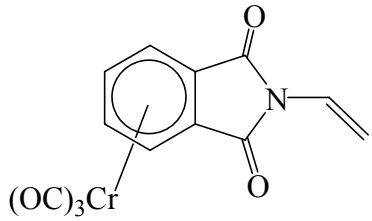
These preliminary results in palladium cross coupling reactions in this work represents the great potential of arene triflate tricarbonylchromium complexes as coupling partners because of the possible preparation from phenol derivatives, the high reactivity and stability. Moreover, the easy accesses to aryl bis-triflate chromium chromium complexes, such as complex **87**, would render this methodology more attractive for the versatile asymmetric cross couplings.

In the continual investigation of arene tricarbonylchromium complexes with functionalized anellated rings, *N*-vinylphthalimide complex **173** was aimed at anion accelerated reactions based on a number of results disclosed in our group in past years such as an anionic oxy-Cope rearrangement. In addition, phthalimide has provided convenient routes for the construction of nitrogen containing heterocycles.[46] However, the reactivity and synthetic utility of tricarbonylchromium complexes of phthalimide remain unexplored.

N-methyl and *N*-vinyl phthalimide tricarbonylchromium complexes **171** and **173** have been prepared by direct complexation with $Cr(CO)_6$ in Bu_2O/THF.

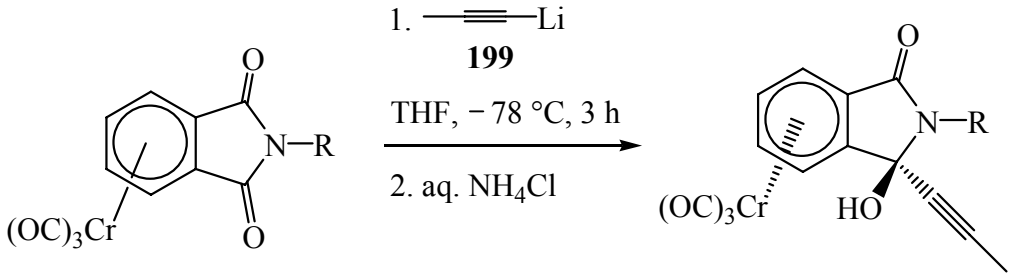


171 58 %



173 20 - 48 %

Nucleophilic additions to one or both of the carbonyl group of *N*-substituted phthalimide chromium complexes are the basis for exploration of anionic oxy-Cope reactions and other reactions in this work. Unusual adducts *endo*-**192** and *endo*-**208** obtained upon the nucleophilic addditions of 1-propynyllithium provides evidence for the intermediate of the planar chiral acylimium ion.



171 (R = CH_3)
173 (R = vinyl)

192 (R = vinyl) 89 %
208 (R = CH_3) 90 %

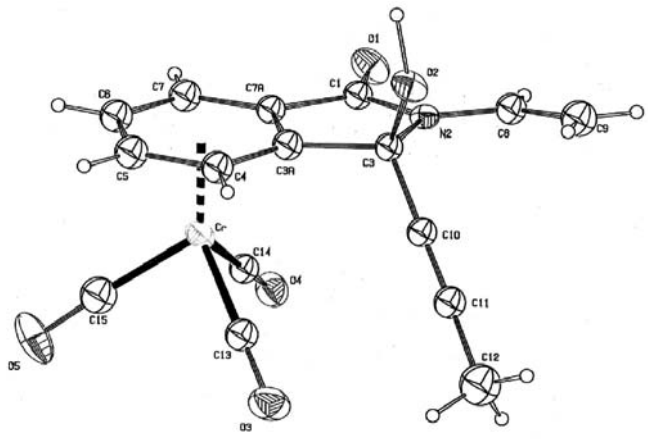
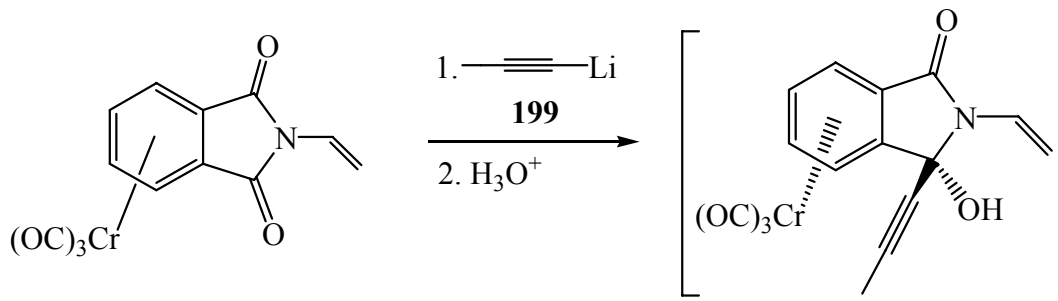
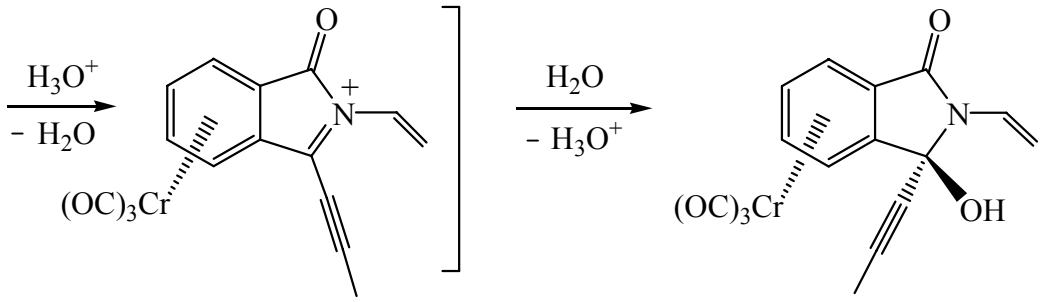


Fig. 8 X-ray Structure of *endo*-**192**

A possible mechanism for such type of reaction was proposed as follows.



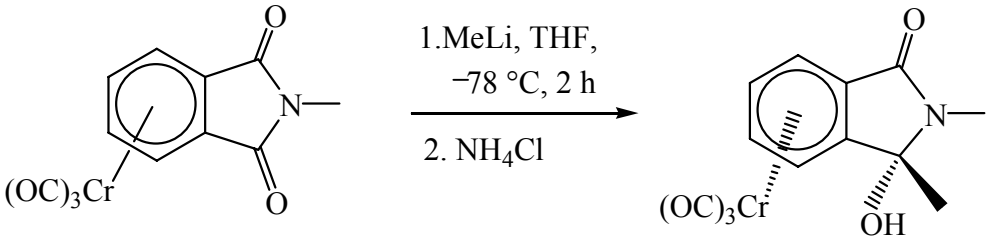
173 **204**



205 **192**

Firstly, 1-propynyllithium (**199**) attacks at one of the carbonyl groups of *N*-vinylphthalimide complex **173** from the *exo* face of the ligand as the normal nucleophilic addition to an (arene)$Cr(CO)_3$ complex giving complex of adduct **204**. Complex **204** could be subsequently transformed into a tricarbonylchromium *N*-acyliminium intermediate **205**. In the last step, H_2O as a nucleophile attacks at the reactive tricarbonylchromium *N*-acyliminium intermediate from the face opposite to the $Cr(CO)_3$ unit resulting the final product **192** with an "abnormal" *endo* configuration.

In order to learn whether the formation tricarbonylchromium *N*-acyliminium intermediate is a general reaction under the reaction conditions of nucleophilic addition to the tricarbonylchromium phthalimide complexes, the addition of methyllithium to tricarbonylchromium *N*-methylphthalimide complex **171** was performed.



171 *exo*-**207** 81%

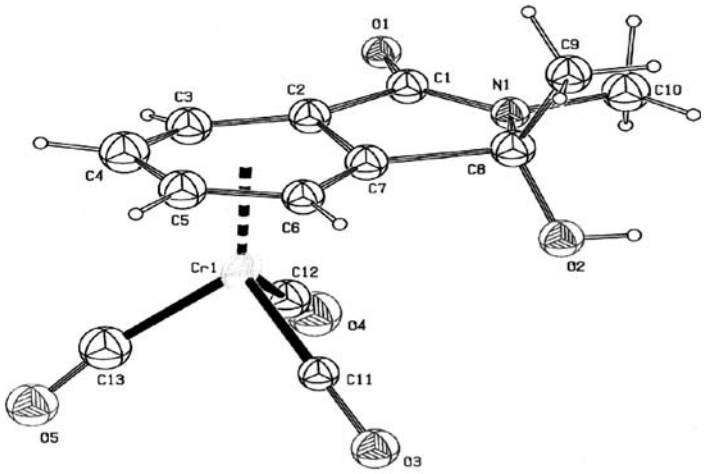
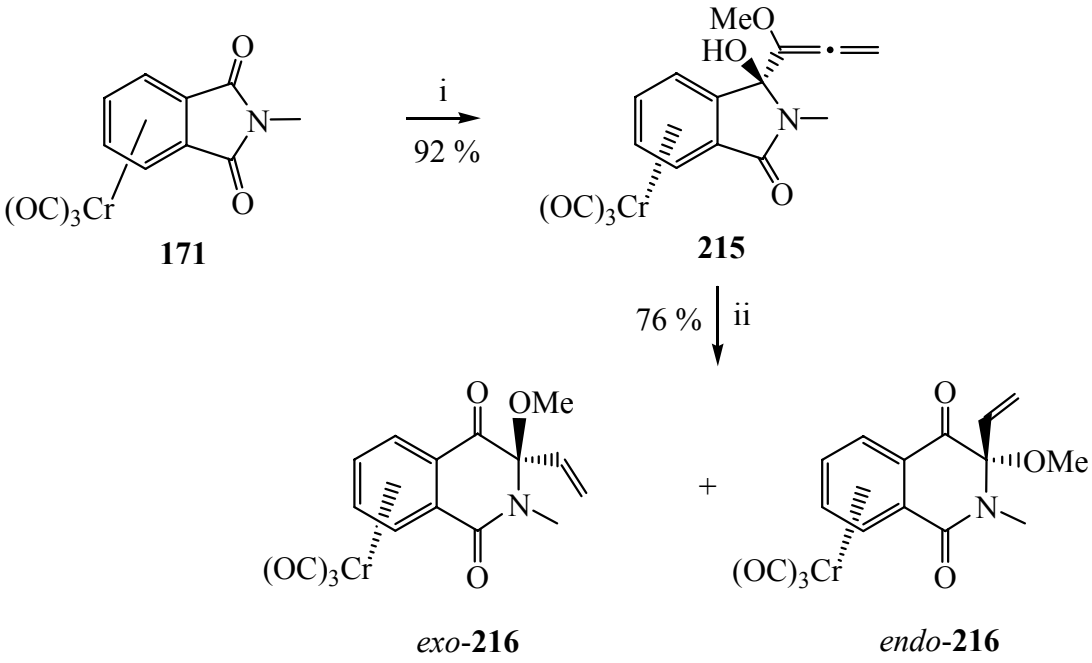


Fig. 9 Structure of **207** in the crystal

The *exo*-configuration of the complex **207** indicates that the addition of methyllithium to *N*-methylphthalimide complex is a normal nucleophilic addition from *exo*-face of the ligand with respect to the bulk of the $Cr(CO)_3$ group. It is assumed that both the *N*-methyl substituent and the nucleophile methyllithium are not prone to form an *N*-acyliminium ion and that the product **207** is furnished by one nucleophilic addition of methyllithium from the *exo*-face of $Cr(CO)_3$ as usually expected. Compared with 1-propynyl adduct *endo*-**208**, it is hypothesized that the 1-propynyl substituent may be attributed to stabilize the iminium cation in the reaction by means of the conjugation and lead to the formation of the *endo*-adduct **208** based on the mechanism proposed for the formation of complex *endo* **192**.

The addition of lithiated methoxyallene to *N*-methylphthalimide complex **171** and the subsequent palladium catalyzed ring expansion reaction have been carried out. The mixture of two isomers of the corresponding *N*-methylisoquinoline-1,4-dione *exo*-**216** and *endo*-**216** (4:1) was obtained in 76 % yield.



exo-**216**: *endo*-**216** 4:1 (NMR)

Reagents and conditions: i. methoxyallene (2.0 equiv.), BuLi (2.0 mol equiv.), THF, –78 °C. ii. $Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (3 mol equiv.), THF, reflux.

Both diastereoisomers of complex **216** were indentified by means of X-ray crystallography.

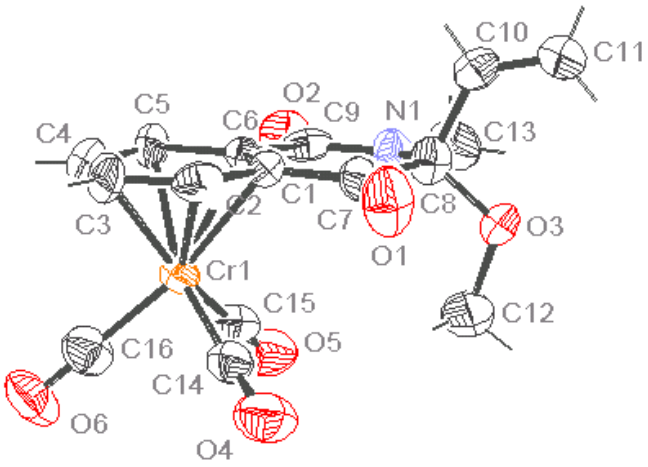


Fig. 10 X-ray structure of *endo*-**216**

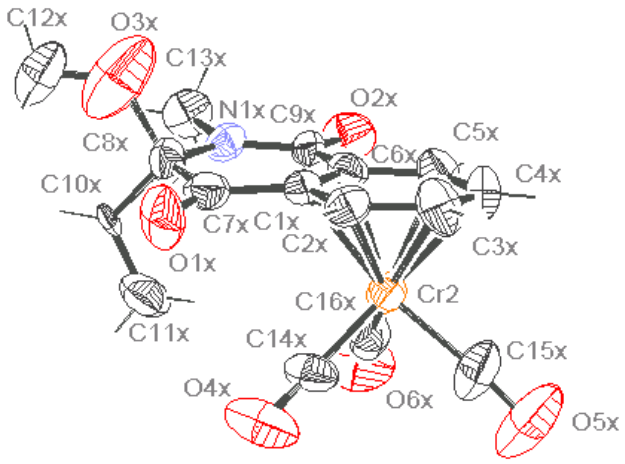
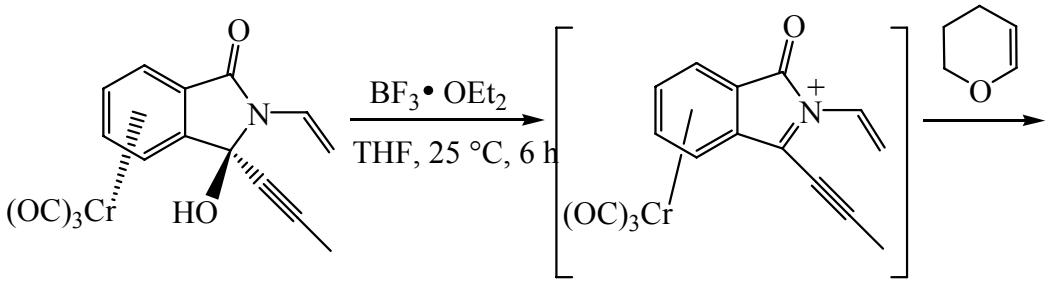


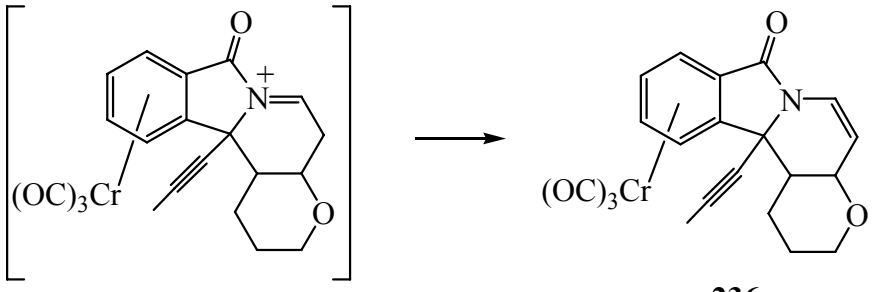
Fig. 11 X-ray structure of *exo*-**216**

To our best knowledge, planar chiral tricarbonylchromium complexes of *N*-acyliminium ion are so far unknown. This discovery prompted us is to explore its synthetic and asymmetric synthetic potential with respect to the classic characteristics of tricarbonylchromium group.

The intermolecular [4+2] reaction between an *N*-acyliminium ion precursor 3-hydroxy isoindolin-1-one complex *endo*-**192** derivatived from *N*-vinyl phthalimide complex **173** and 2,3-dihydropyran as an dienophile has been carried out. The structures of the outcome of the reaction are tentatively assumed as **236** and **237** supported by the mass spectra, respectively.

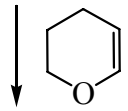


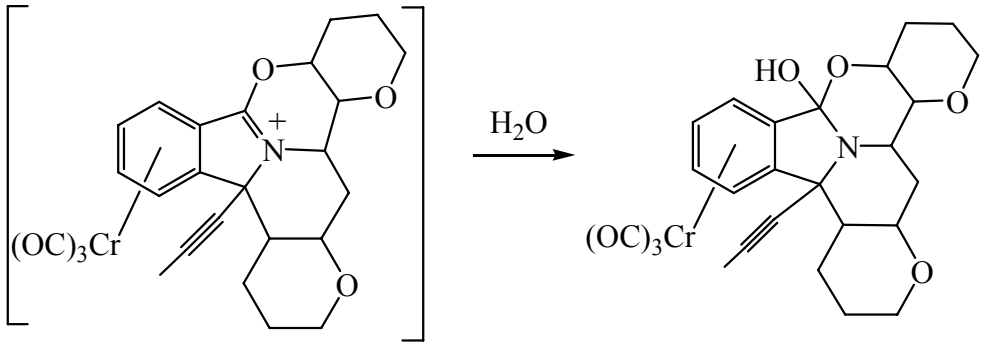
endo-**192** **205**



E **236**

m/z 415





F **237**

m/z 517

D. Experimental Section

1. General Remark

All operations were performed in an argon atmosphere using the Schlenk technique. Reaction vessels were heated at reduced pressure with a heat gun and flushed with argon or nitrogen. This procedure was repeated three times.

Solvents were dried and argonated before use. Diethyl ether and THF were distilled from sodium wire/benzophenone under nitrogen; petroleum ether (PE), *tert*-butylmethyl ether (TBME) and ethyl acetate were dried with calcium chloride. Hexane, dibutyl ether, methylene chloride and acetonitrile were dried with calcium hydride.

Preparative column chromatography was carried out using flash chromatography.[170] Silica gel (J. T. Baker, ∅ 40 μm) was degassed by heating it with a heat gun at reduce pressure followed by setting it under normal pressure with argon. All the solvents used for column chromatography were distilled over drying agents e.g. calcium chloride, calcium hydride, and then argonated for about 20 min by flowing with a constant argon stream.

Thin layer chromatography (TLC) was carried out using aluminum TLC plates coated with the silica gel $60F_{254}$ from Merck (Polygram®). The detection of changed substances over the TLC was done with the help of the UV-lamp (λ = 254 nm) or developed with Ce (IV) sulfate reagent.

Infrared Spectra (IR) were obtained using the spectrometer Perkin-Elmer FT 1710 with Golden Gate ATR. The following abbreviations were used to indicate the intensity of the absorption bands: s = strong, m = middle, w = weak, br = broad.

Mass spectrometry (MS) was carried out using a Finnegan AM 400 mass spectrometer (ionization potential 70 eV). FAB-MS spectra were carried out using a VG-Autospec spectrometer in a low resolution measurement with a nitrobenzyl alcohol matrix (NBA-Matrix). LC-MS (ESI) mass spectra were recorded on a Micromass LCT with Lock-Spray-unit (ESI). The injection was done in the Loop-Modus in a HPLC-Alliance 2695 column (Waters). All values are given in atomic units of mass per elemental charge (*m / z*). The intensity is given as a percentage of the base peak.

High resolution mass spectra (**HRMS)** were recorded with the peak-matching method using perfluorkerosen (PFK) as the internal standard using a VG-Autospec spectrometer (the NBA-Matrix was used) or with the Peak-Matching method in a Micromass LCT spectrometer with Lock-Spray-unit (ESI).

^{1}H NMR spectra were measured using the instruments Bruker WP 200 (200.1 MHz) and AVS 400 (400.1 MHz) at 25 °C. In the case no tetramethylsilane (TMS, $\delta = 0.00$ ppm) was used as a reference, residual solvent signals (acetone $\delta = 2.05$ ppm, chloroform $\delta = 7.26$ ppm) as internal standards. The multiplicity of the peaks were abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).

^{13}C NMR spectra were measured using the instrument Bruker AVS 200 (50.3 MHz) and AVS 400 (100.6 MHz). . In the case no tetramethylsilane (TMS, $\delta = 0.00$ ppm) was used as a reference, residual solvent signals (acetone $\delta = 30.5$ ppm, chloroform $\delta = 77.0$ ppm) as internal standards. The multiplicity of the signals was determined with ATP and DEPT techniques. Signals (peaks) with negative phase for CH and CH_3 were labeled with "–", and those with positive phase for C and CH_2 were labeled with "+". Air sensitive samples prepared under argon using the Schlenk technique. The deuterated solvents were stored under argon.

Melting points were measured by using a Büchi apparatus according to Dr. Tottoli without any correction.

Elemental analyses were carried out for CHN with element Vario EL instrument, with acetanilide as the standard. All values are given as mass percentages.

Optical rotation were measured using Polarimeter Perkin-Elmer 341 at 25 °C Optical rotations The degree of rotation was determined with the yellow sodium D line near 589 nm wavelength, concentration (c) is given in g / 100 mL.

Microwave Oven (µW) Microwave heating was carried out with a Discover® LabMate™ single-mode microwave cavity operating at 250 W from CEM Corporation. The reactions were conducted in a 10 mL sealed Pyrex vessel, with a maximum operating temperature of 150 °C and a maximum operating pressure of 8 bar.

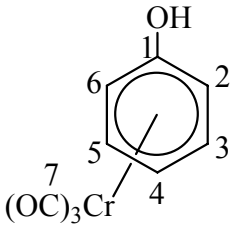
Preparation of different reagents were carried out using the following references: isopropenyllithium,[150] 1-propynyllithium,[151] vinyllithium,[155] methoxyallenyllithium,[159] 2-(trimethylsilyl)phenol,[171] diisopropylaminelithium,[172] vinyltributylstannane[173] Methoxyallen.[174]
Unless otherwise specified, all reagents were purchased from commercial suppliers (Across, Aldrich, Fluka, Lancaster, Merck) and used without further purification.

2. Tricarbonylchromium Phenol Complexes

2.1 General Procedure for the Synthesis of Phenol Tricarbonylchromium Complexes (GP1)

The phenol and 1.1 equiv. of hexacarbonylchromium in dibutyl ether and THF (10:1) are heated at reflux for 2 to 3 days. After cooling to 25 °C, the reaction mixture is carefully filtered through a P4 frit covered with a 2 cm thick layer of silica gel. The solvents are removed at reduced pressure, and the crude product is purified by flash chromatography at SiO_2, eluting with TBME/PE (1:1 to 4:1). The tricarbonylchromium phenol complexes are very sensitive to air and light and decompose quickly in air.

2.1.1 Tricarbonyl(phenol)chromium(0) (67)



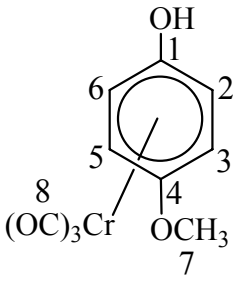
67

GP1, 1.13 g (12.0 mmol) of phenol (**58**), 2.90 g (13.2 mmol) of hexacarbonylchromium in 40 mL of dibutyl ether and 4 mL of THF, 2 d. 2.48 g (10.8 mmol, 90 %) of **67** was obtained as a yellow solid, m. p. 43 °C (dec.)

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.85 (t, *J* = 6.0 Hz, 1H, 4-H), 5.13 [d, *J* = 6.5 Hz, 2H, 2(6)-H], 5.58[t, *J* = 6.3 Hz, 2H, 3(5)-H], 6.89 (s, 1H, OH) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 79.8 [–, C-2(6)], 85.1 (–, C-4), 95.9 [–, C-3(5)], 140.6 (+,

C-1), 233.7 (+, C-7) ppm. – MS (70 eV): *m/z* (%) = 230 (82) [M^+], 202 (17) [M^+ – CO], 174 (8) [M^+ – 2CO], 146 (72) [M^+ – 3CO], 94 (100) [M^+ – $Cr(CO)_3$], 80 (31), 66 (65), 52 (92) [^{52}Cr].

2.1.2 Tricarbonyl(4-methoxyphenol)chromium(0) (68)

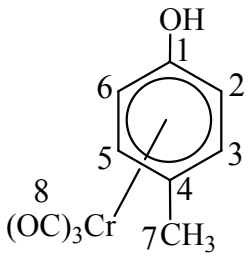


68

GP1, 2.10 g (16.9 mmol) of 4-methoxyphenol(**59**), 4.09 g (18.6 mmol) of hexacarbonylchromium, in 60 mL of dibutyl ether and 6 mL of THF, 60 h. 3.21 g (12.3 mmol, 73 %) of **68** was obtained as a yellow solid, m. p. 52 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 3095 (br) cm^{-1}, 2977 (w), 1946 (s, CO), 1839 (s, CO), 1556 (w), 1535 (m), 1491 (m), 1235 (m), 1181 (m), 1145 (w), 1081 (w), 1018 (m), 916 (w), 880 (w), 825 (w), 737 (m), 668 (s), 620 (s). – ^1H NMR (400.1 MHz, $CDCl_3$): δ = 3.60 (s, 3H, 7-H), 5.25 [d, *J* = 7.0 Hz, 2H, 3(5)-H], 5.32 [d, *J* = 6.9 Hz, 2H, 2(6)-H], 7.12 (s, 1H, OH) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 56.3 (–, C-7), 80.9 [–, C-2(6)], 81.0 [–, C-3(5)], 134.1 (+, C-1), 135.9 (+, C-4), 234.3 (+, C-8) ppm. – MS (70 eV): *m/z* (%) = 260 (66) [M^+], 204 (45) [M^+ – 2CO], 176 (73) [M^+ – 3CO], 124 (72) [M^+ – $Cr(CO)_3$], 109 (75) [M^+ – $Cr(CO)_3$ – CH_3], 93 (8), 81 (67), 72 (24). – HRMS ($C_{10}H_8O_5Cr$) calcd. 259.9777, found. 259.9776.

2.1.3 Tricarbonyl(4-methylphenol)chromium(0) (69)

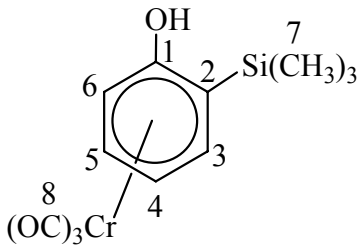


69

GP1, 2.00 g (18.5 mmol) of 4-methylphenol (**60**), 4.48 g (20.3 mmol) of hexacarbonylchromium in 70 mL of dibutyl ether and 7 mL of THF, 54 h. 2.94 g (12.0 mmol, 65 %) of **69** was obtained as yellow oil.

IR (ATR): $\tilde{\nu}$ = 3463 (br) cm^{-1}, 1941 (s, CO), 1885 (s, CO), 1793 (s, CO), 1557 (m), 1475 (m), 1449 (m), 1398 (w), 1383 (w), 1309 (m), 1263 (m), 1201 (m), 1152 (m), 1088 (w), 1039 (w), 879 (w), 828 (w), 740 (w), 768 (m), 669 (m), 628 (m). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.06 (s, 3H, 7-H), 4.87 (s, 1H, OH), 5.15 [d, *J* = 6.0 Hz, 2H, 2(6)-H], 5.46 [d, *J* = 6.0 Hz, 2H, 3(5)-H] ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.8 (–, C-7), 80.4 [–, C-2(6)], 96.0 [–, C-3 (5)], 101.7 (+, C-4), 137.5 (+, C-1), 233.9 (+, C-8) ppm. – MS (70 eV): *m/z* (%) = 244 (35) [M^+], 188 (13) [M^+ – 2CO], 160 (65) [M^+ – 3CO], 107 (70) [M^+ – $Cr(CO)_3$], 90 (9), 77 (23), 69 (8), 52 (100) [^{52}Cr]. – HRMS ($C_{10}H_8O_4Cr$) calcd. 243.9828, found. 243.9826.

2.1.4 Tricarbonyl(2-trimethylsilylphenol)chromium(0) (70)

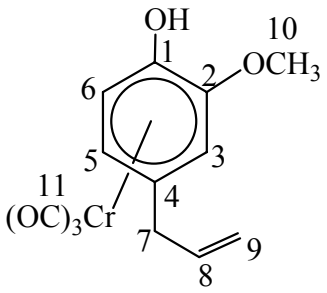


70

GP1, 2.53 g (15.2 mmol) of 2-(trimethylsilyl)phenol (**61**), 3.68 g (16.7 mmol) of hexacarbonylchromium, 30 h; 2.21 g (7.3 mmol, 48 %) of **70** was obtained as yellow solid, m. p. 41 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 3513 (w) cm^{-1}, 2959 (w), 1943 (s, CO), 1876 (s, CO), 1822 (s, CO), 1523 (w), 1512 (w), 1465 (m), 1373 (m), 1280 (m), 1257 (m), 1246 (w), 1177 (w), 1154 (m), 1108 (w), 1068 (m), 1022 (w), 949 (w), 871 (s), 845 (m), 820 (w), 763 (w), 756 (w), 691 (w), 668 (m), 631(s). – ^{1}H NMR (400.1 MHz, [D6]acetone): δ = 0.35 (s, 9H, 7-H), 4.99 (m, ^{3}J = 5.5 Hz, ^{5}J = 0.62 Hz, 1H, 6-H,), 5.29 (dd, J = 0.64, 6.2 Hz, 1H, 4-H), 5.77 (dd, J = 1.4, 4.8 Hz, 1H, 5-H), 5.91 (m, ^{3}J = 5.5 Hz, ^{4}J = 1.5 Hz, 1H, 3-H) ppm. – ^{13}C NMR (100.6 MHz, [D_6]acetone): δ = 0.11 (–, C-7), 80.9 (–, C-6), 86.9 (–, C-4), 88.8 (+, C-2), 99.6 (–, C-5), 104.1 (–, C-3), 148.2 (+, C-1), 236.2 (+, C-8) ppm. – MS (70 eV): *m/z* (%) = 302 (43) [M^+], 246 (21) [M^+ – 2CO], 218 (95) [M^+ – 3CO], 202 (28) [M^+ – 3CO – CH_3], 187 (100) [M^+ – 3CO – 2CH_3], 166 (26) [M^+ – $Cr(CO)_3$], 151 (92) [M^+– $Cr(CO)_3$ – 3CH_3], 133 (45), 123 (51) [M^+ – Cr $(CO)_3$ – $Si(CH_3)_3$], 91 (46), 75 (28), 65 (12), 52 (82) [^{52}Cr]. – HRMS ($C_{12}H_{14}O_4CrSi$) calcd. 302.0066, found. 302.0067.

2.1.5 (2-Allyl-4-methoxyphenol)tricarbonylchromium(0) (71)

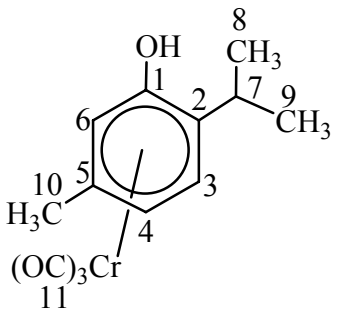


71

GP1, 0.82 g (5.0 mmol) of 2-allyl-4-methoxyphenol (**62**), 1.21 g (5.5 mmol) of hexacarbonyl- chromium in 40 mL of dibutyl ether and 4 mL of THF, 48 h. 1.32 g (4.4 mmol, 88 %) of **71** was obtained as yellow oil.

IR (ATR): $\tilde{\nu}$ = 3450 (br) cm^{-1}, 3087 (w), 2978 (w), 1939 (s, CO), 1828 (s, CO), 1640 (w), 1560 (w), 1540 (w), 1488 (w), 1462 (m), 1408 (m), 1396 (w), 1322 (w), 1272 (m), 1241 (m), 1195 (m), 1142 (m) 1099 (m), 1052 (w), 1021 (w), 993 (m), 955 (w), 923 (m), 853 (w), 794 (m), 751 (w), 671 (s), 651 (w), 629 (s). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.21 (m, 2H, 7-H), 3.86 (s, 3H, 10-H), 4.97 (d, *J* = 6.5 Hz, 1H, 6-H), 5.12 (d, *J* = 1.5 Hz, 1H, 9-H), 5.16-5.19 (m, 1H, 5-H), 5.26 (d, *J* = 1.5 Hz, 1H, 9-H), 5.32 (s, 1H, OH), 5.47 (d, *J* = 6.5 Hz, 1H, 3-H), 5.81-5.91 (m, 1H, 8-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 38.5 (+, C-7), 57.4 (–, C-10), 78.8 (–, C-3), 81.1 (–, C-6), 88.5 (–, C-5), 104.4 (+, C-4), 118.6 (+, C-9), 129.7 (+, C-1), 129.3 (+, C-2), 135.1 (–, C-8), 234.1 (+, C-11) ppm. – MS (70 eV): *m/z* (%) = 300 (59) [M^+], 244 (22) [M^+ – 2CO], 216 (94) [M^+ – 3CO], 164 (100) [M^+ – $Cr(CO)_3$], 149 (72) [M^+ – $Cr(CO)_3$ – CH_3], 137 (78), 121 (54), 103 (67), 91 (62), 77 (74), 65 (43), 52 (80) [^{52}Cr]. – HRMS ($C_{13}H_{12}O_5Cr$) calcd. 300.0090, found. 300.0090.

2.1.6 Tricarbonyl(5-methyl-2-isopropylphenol)chromium(0) (72)

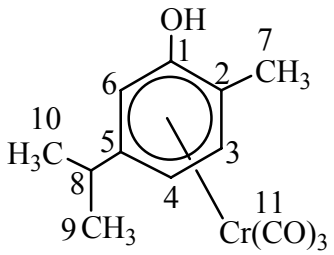


72

GP1, 1.50 g (10.0 mmol) 5-methyl-2-isopropylphenol (**63**), 2.42 g (11.0 mmol) hexacarbonylchromium in 40 mL of dibutyl ether and 4 mL of THF, 2 d. 2.32 g (8.1 mmol, 81 %) of **72** were obtained as yellow oil.

IR (ATR): $\tilde{\nu}$ = 3498 (br) cm^{-1}, 2970 (w), 1937 (s, CO), 1861 (s, CO), 1821 (s, CO), 1550 (w), 1528 (w), 1489 (w), 1449 (w), 1397 (m), 1378 (m), 1351 (w), 1283 (m), 1222 (w), 1181 (w), 1158 (m), 1112 (w), 1084 (w), 949 (w), 883 (w), 842 (w), 743 (w), 709 (w), 672 (m), 631 (s). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.4 Hz, 3H, 8-H or 9-H), 1.29 (d, *J* = 6.4 Hz, 3H, 8H or 9-H), 2.21 (s, 3H, 10-H), 2.98 (m, 1H, 7-H), 4.57 (s, 1H, 6-H), 4.73 (d, *J* = 6.2 Hz, 1H, 4-H), 4.94 (s, 1H, OH), 5.58 (d, *J* = 6.2 Hz, 1H, 3-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 20.3 (–, C-10), 21.6 (–, C-8 or C-9), 24.1 (–, C-8 or C-9), 26.7 (–, C-7), 80.8 (–, C-6), 86.3 (–, C-4), 93.5 (–, C-3), 104.7 (+, C-5), 110.0 (+, C-2), 137.9 (+, C-1), 234.2 (+, C-12) ppm. – MS (70 eV): *m/z* (%) = 286 (43) [M^+], 230 (25) [M^+ – 2CO], 202 (85) [M^+ – 3CO], 150 (75) [M^+ – $Cr(CO)_3$], 135 (100) [M^+ – $Cr(CO)_3$ – CH_3], 115 (50), 107 (33), 201 (96), 91 (60), 77 (35), 65 (21), 52 (68) [^{52}Cr]. – LC-MS (ESI) ($C_{13}H_{14}O_4Cr$) [– H] calcd. 285.0219, found. 285.0232.

2.1.7 Tricarbonyl(2-methyl-5-isopropylphenol)chromium(0) (73)

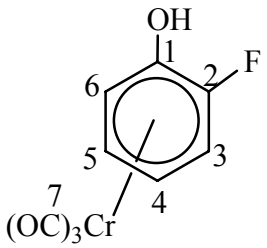


73

GP1, 1.50 g (10.0 mmol) of 2-methyl-5-isopropylphenol (**64**) reacted with 2.42 g (11.0 mmol) hexacarbonylchromium in 40 mL of dibutyl ether and 4 mL of THF, 2 d. 2.12 g (7.4 mmol, 74 %) of **73** was obtained as yellow oil.

IR (ATR): $\tilde{\nu}$ = 3486 (br) cm^{-1}, 2965 (w), 1945 (s, CO), 1853 (s, CO), 1693 (w), 1536 (w), 1461 (w), 1449 (w), 1402 (w), 1381(w), 1366 (w), 1282 (w), 1260 (w), 1167 (w), 1095 (w), 996 (w), 934 (w), 850 (w), 816 (w), 753 (w), 669 (m), 630 (m). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.21-1.24 [dd, *J* = 6.4 Hz, 6H, 9(10)-H], 2.17 (s, 3H, 7-H), 2.63 (m, 1H, 8-H), 4.85 (d, *J* = 6.4 Hz, 1H, 3-H), 5.15 (s, 1H, 6-H), 5.55 (d, *J* = 6.4 Hz, 1H, 4-H), 6.26 (s, 1H, OH) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.3 (–, C-7), 22.8 (–, C-9 or C-10), 23.1 (–, C-9 or C-10), 32.3 (–, C-8), 80.1 (–, C-6), 85.3 (–, C-4), 94.6 (+, C-2), 97.5 (–, C-3), 121.2 (+, C-5), 138.5 (+, C-1), 235.0 (+, C-11) ppm. – MS (70 eV): *m/z* (%) = 286 (43) [M^+], 230 (25) [M^+ – 2CO], 202 (85) [M^+–3CO], 150 (75) [M^+– $Cr(CO)_3$], 135 (100) [M^+ – $Cr(CO)_3$ – CH_3], 115 (50), 107 (33), 201 (96), 91 (60), 77 (35), 65 (21), 52 (46) [^{52}Cr] . – HRMS ($C_{13}H_{14}O_4Cr$) calcd. 286.0297, found. 286.0296.

2.1.8 Tricarbonyl(2-fluorophenol)chromium(0) (74)

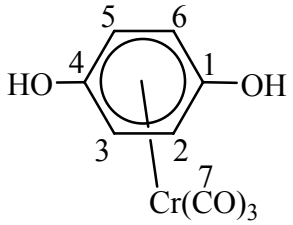


74

GP1, 0.74 g (6.6 mmol) of 2-fluorophenol (**65**) reacted with 1.60 g (7.3 mmol) of hexacarbonylchromium in 40 mL of dibutyl ether and 4 mL of THF, 40 h. 1.28 g (5.2 mmol, 78 %) of **74** was obtained as yellow oil.

IR (ATR): $\tilde{\nu}$ = 3091 (w) cm^{-1}, 2978 (w), 1956 (s, CO), 1848 (s, CO), 1706 (w), 1616 (w), 1531 (w), 1502 (w), 1474 (m), 1428 (w), 1391 (w), 1247 (m), 1169 (w), 1077 (w), 1043 (w), 881 (w), 858 (w), 818 (w), 754 (m), 730 (w), 661 (s), 622 (s). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 5.23 (m, 1H, 6-H), 5.48 (m, 1H, 3-H), 5.66 (m, 1H, 4-H), 6.12 (m, 1H, 5-H), 9.71 (br, 1-H, OH) ppm. – ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 83.7 (–, C-6), 86.5 (–, C-3), 87.3 (–, C-4), 93.9 (–, C-5), 132.6 (+, C-1), 135.8 (+, d, $^{1}J_{C\text{-}F}$ = 258.6 Hz, C-2), 235.0 (+, C-7) ppm. – MS (70 eV): *m/z* (%) = 248 (30) [M^+], 220 (6) [M^+ – CO], 192 (7) [M^+ – 2CO], 164 (36) [M^+ – 3CO], 112 (100) [M^+ – Cr(CO)$_3$], 92 (32), 83 (16), 71 (13), 64 (57), 52 (95) [^{52}Cr]. – HRMS ($C_9H_5O_4CrF$) calcd. 247.9577, found. 247.9576.

2.1.9 Tricarbonyl(1,4-dihydroxybenzene)chromium(0) (83)

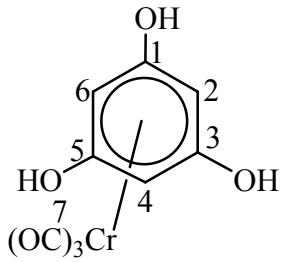


83

GP1, 1.40 g (12.7 mmol) of 1,4-dihydroxybenzene (hydroquinone), 3.07 g (14.0 mmol) of hexacarbonylchromium in 40 mL of dibutyl ether and 4 mL of THF, 60 h. 2.44 g (9.9 mmol, 78 %) of **83** was obtained as a yellow solid, m. p. 35 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 3143 (br) cm^{-1}, 1953 (s, CO), 1855 (s, CO), 1653 (w), 1560 (w), 1516 (m), 1516 (m), 1472 (s), 1365 (w), 1246 (m), 1215 (m), 1195 (s), 1097 (w), 1077 (w), 1042 (w), 1011 (w), 877 (w), 833 (s), 760 (s), 675 (s), 631 (s). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.47 [s, 4H, 2(3, 5, 6)-H], 8.65 (br, 2H, 2OH) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 84.0 [-, C-2(3, 5, 6)], 136.2 [+, C-1(4)], 237.1 (+, C-7) ppm. – MS (70 eV): *m/z* (%) = 246 (34) [M^+], 190 (12) [M^+ – 2CO], 162 (51) [M^+ – 3CO], 110 (100) [M^+ – $Cr(CO)_3$], 94 (14), 81 (74), 63 (28), 52 (83) [^{52}Cr]. – HRMS ($C_9H_6O_5Cr$) calcd. 245.9620, found. 245.9621.

2.1.10 Tricarbonyl(1,3,5-trihydroxybenzene)chromium(0) (85)



85

GP1, 2.00 g (15.9 mmol) of 1,3,5-trihydroxybenzene (phloroglucinol), 3.84 g (17.5 mmol) of hexacarbonylchromium in 60 mL of dibutyl ether and 6 mL of THF, 2 d. 2.42 g (9.17 mmol, 58 %) of was obtained as a yellow solid, m. p. 30 °C (dec.).

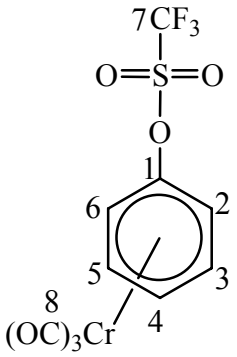
IR (ATR): $\tilde{\nu}$ = 3092 (br) cm^{-1}, 2976 (w), 1945 (s, CO), 1850 (s, CO), 1614 (w), 1548 (w), 1477 (w), 1388 (w), 1369 (w), 1265 (w), 1240 (w), 1196 (w), 1154 (m), 1061 (m) 1044 (w), 1019 (w), 990 (m), 916 (w), 880 (w), 838 (m), 719 (m), 681(s), 632 (s). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.02 [s, 3H, 2(4,6)-H]), 9.01 (br, 3H, 3OH) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 69.1 [–, C-2 (4, 6)], 143.5 [+, C-1 (3, 5)], 237.7 (+, C-7) ppm. – MS (70 eV): *m/z* (%) = 262 (41) [M^+], 234 (12) [M^+ – CO], 206 (15) [M^+ – 2CO], 178 (60) [M^+ –3CO], 126 (73) [M^+ – $Cr(CO)_3$], 110 (19), 97 (33), 80 (51), 69 (63), 52 (100) [^{52}Cr]. – HRMS ($C_9H_6O_6Cr$) calcd. 261.9569, found. 261.9570.

3. Tricarbonylchromium Arene Triflate Complexes

3.1 General Procedure for the Triflation of Tricarbonyl(phenol)chromium(0) Complexes (GP2)

To a stirred solution of the phenol tricarbonylchromium complex in anhydrous THF and pyridine (3:1) 1.2 equiv. of trifluoromethanesulfonic anhydride is added dropwise at –78 °C. The reaction is allowed to return to 25 °C over 1 h and is then stirred for 24 to 60 h. The color of the solution changes from yellow to dark orange. The reaction mixture is quenched with 30 mL of water and extracted with 3 x 30 mL of ethyl acetate. The collected organic layers are washed with water till the aqueous layer remains colorless, dried over anhydrous $MgSO_4$ and filtered through a P4 frit. After solvent removal at reduced pressure, the crude product is purified by flash chromatography at SiO_2, eluting with TBME / PE (1:4 to 1:1).

3.1.1 Tricarbonyl(phenyl)chromium(0) Triflate (75)



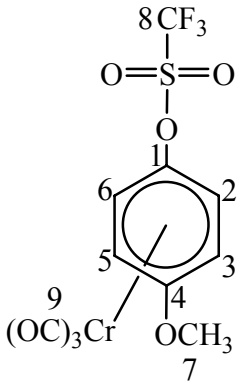
75

GP2, 1.15 g (5.0 mmol) of **67**, 20 mL of THF, 7 mL of pyridine, 1.69 g (6.0 mmol) trifluoromethanesulfonic anhydride, 24 h, flash chromatography with TBME / PE (1:3). 1.25 g (3.5 mmol, 69 %) of product **75** was obtained as yellow solid, m. p. 72

°C.

IR (ATR): $\tilde{\nu}$ = 3099 (w) cm^{-1}, 1971 (s, CO), 1880 (s, CO), 1500 (w), 1430 (s), 1250 (m), 1029 (s), 1129 (s), 992 (w), 891 (w), 863 (m), 814 (m), 741 (m), 683 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.03 (t, *J* = 3.3 Hz, 1H, 4-H), 5.46 [d, *J* = 3.1 Hz, 4H, 2(6)-H, 3(5)-H] ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 84.3 [–, C-2(6)], 88.4 (–, C-4), 91.3 [–, C-3(5)], 118.6 (+, q, $^{1}J_{C\text{-}F}$ = 321.0 Hz, C-7), 130.9 (+, C-1), 230.2 (+, C-8) ppm. – MS (70 eV): *m/z* (%) = 363 (17) [M^+], 306 (11) [M^+ – 2CO], 278 (8) [M^+ – 3CO], 226 (16) [M^+ – $Cr(CO)_3$], 209 (10),164 (8),145 (100), 93 (13) [M^+ – $Cr(CO)_3$ – OH – (SO_2CF_3)], 77 (17), 69 (24). – LC-MS (ESI) $C_{10}H_5O_6F_3SCr$ [–H]: calcd. 360.9086, found. 360.9095.

3.1.2 Tricarbonyl(4-methoxyphenyl)chromium(0) Triflate (76)



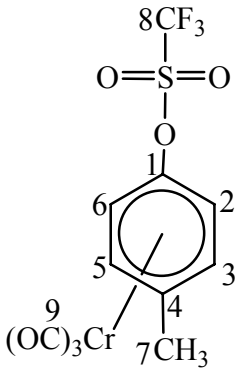
76

GP2, 2.10 g (8.1 mmol) of **68**, 30 mL of THF, 10 mL of pyridine, 2.73 g (9.7 mmol) of trifluoromethanesulfonic anhydride, 20 h. Flash chromatography, eluting with TBME / PE (1:2). 2.37 g (6.1 mmol, 75 %) of **76** was obtained as a yellow solid, m. p. 44 °C.

IR (ATR): $\tilde{\nu}$ = 3379 (w) cm^{-1}, 2951 (w), 1974 (s, CO), 1886 (s, CO), 1531 (w), 1509 (m), 1472 (m), 1429 (s), 1369 (w), 1212 (s), 1134 (s), 1101 (m), 865 (m), 822 (s), 770 (w), 731 (m), 665 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.68 (s, 3H, 7-H), 5.10 [d, *J* = 4.8 Hz, 2H, 3(5)-H], 5.72 [d, *J* = 4.6 Hz, 2H, 2(6)-H] ppm. – ^{13}C NMR (100.6

MHz, $CDCl_3$, DEPT): δ = 56.2 (–, C-7), 74.8 [–, C-3(5)], 87.4 [–, C-2(6)], 118.5 (+, q, $^1J_{C\text{-}F}$ = 321.2 Hz, C-8), 122.3 (+, C-1), 140.7 (+, C-4), 230.2 (+, C-9) ppm. – MS (70 eV): *m/z* (%) = 392 (45) [M^+], 335 (17) [M^+ – 2CO], 307 (36) [M^+ – 3CO], 239 (16) [M^+ – $Cr(CO)_3$ – CH_3], 194 (76),175 (100), 124 (32), 95 (13) [M^+ – $Cr(CO)_3$ – OCH_3 – (SO_2CF_3)], 81 (15). – LC-MS (ESI) $C_{11}H_7O_7F_3SCr$ [–H]: calcd. 390.9191, found. 390.9185.

3.1.3 Tricarbonyl(4-methylphenyl)chromium(0) Triflate (77)



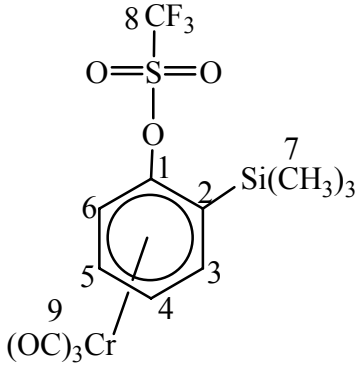
77

GP2, 1.30 g (5.3 mmol) of **69**, 20 mL of THF, 7 mL of pyridine, 1.80 g (6.4 mmol) of trifluoromethanesulfonic anhydride, 24 h, flash chromatography eluting with *tert*-butyl methyl ether/petroleum ether (1:1). 1.44 g (3.8 mmol, 72 %) of **77** was obtained as yellow oil.

IR (ATR): $\tilde{\nu}$ = 3098 (w) cm^{-1}, 2917 (w), 1972 (s, CO), 1878 (s, CO), 1524 (w), 1465 (w), 1426 (m), 1386 (s), 1249 (w), 1209 (s), 1132 (s), 1096 (w), 1035 (w), 862 (s), 802 (w), 770 (w), 719 (m), 653 (m), 608 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.11 (s, 3H, 7-H), 5.27 [s, 2H, 2(6)-H], 5.56 [s, 2H, 3(5)-H] ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 19.5 (–, C-7), 86.0 [–, C-2(6)], 91.2 [–, C-3(5)], 106.8 (+, C-1), 118.4 (+, q, $^1J_{C\text{-}F}$ = 321.1 Hz, C-8), 128.1 (+, C-4), 230.6 (+, C-9) ppm. – MS (70 eV): *m/z* (%) = 376 (42) [M^+], 320 (16) [M^+ – 2CO], 292 (25) [M^+ – 3CO], 223

(13) [M^+ – $Cr(CO)_3$ – CH_3], 187 (10), 178 (70), 159 (100), 107 (7), 91 (11), 77 (29), 69 (10), 52 (85) [^{52}Cr]. –HRMS ($C_{11}H_6O_6F_3SCr$): calcd. 375.9321, found. 375.9322.

3.1.4 Tricarbonyl(2-trimethylsilylphenyl)chromium(0) Triflate (78)

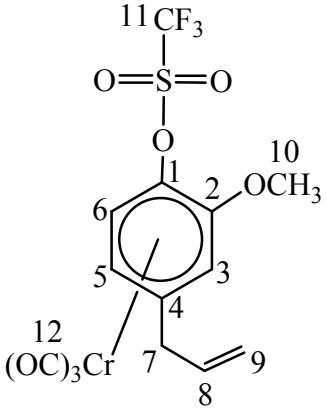


78

GP2, 1.80 g (6.0 mmol) of **70**, 30 mL of THF, 10 mL of pyridine, 2.02 g (7.2 mmol) of trifluoromethanesulfonic anhydride, 24 h, flash chromatography, eluting with TBME / PE (1:1). 1.01 g (2.3 mmol, 39 %) of **78** was obtained as yellow oil.

IR (ATR): $\tilde{\nu}$ = 2960 (w) cm^{-1}, 1975 (s, CO), 1891 (s, CO), 1504 (w), 1421 (m), 1356 (w), 1251 (m), 1211(s), 1130 (s), 1101(w), 1061 (m), 880 (s), 839 (s), 814 (m), 744 (m), 695 (w). –^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.43 (s, 9H, 7-H), 4.90 (t, *J* = 6.0 Hz, 1H, 6-H), 5.51 [t, *J* = 5.0 Hz, 2H, 4(5)-H], 5.64 (t, 1H, 3-H, *J* = 6.4 Hz) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –0.66 (–, C-7), 82.6 (–, C-6), 87.4 (–, C-4), 91.0 (+, C-2), 93.8 (–, C-5), 98.2 (–, C-3), 118.3 (+, q, $^1J_{C\text{-}F}$ = 320.2 Hz, C-8), 137.4 (+, C-1), 231.1 (+, C-9) ppm. – MS (70 eV): *m/z* (%) = 434 (49) [M^+], 378 (8) [M^+ –2CO], 350 (62) [M^+ – 3CO], 283 (10) [M^+ – $Cr(CO)_3$ – CH_3], 236 (26), 217 (89), 201 (80), 187 (70), 150 (18), 135 (23),126 (35), 96 (26), 73 (25), 52 (100) [^{52}Cr]. – HRMC $C_{13}H_{13}O_6F_3SSiCr$ [−H]: calcd. 433.9559, found. 433.9561.

3.1.5 (2-Allyl-4-methoxyphenyl)tricarbonylchromium(0) Triflate (79)

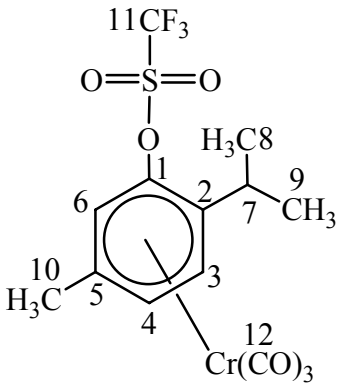


79

GP2, 1.68 g (5.6 mmol) of **71**, 30 mL of THF, 10 mL of pyridine, 1.89 g (6.7 mmol) of trifluoromethanesulfonic anhydride, 30 h, flash chromatography, eluting with TBME / PE (1:1). 2.13 g (4.9 mmol, 88 %) of **79** was obtained as yellow oil.

IR (ATR): $\tilde{\nu}$ = 2962 (w) cm^{-1}, 1969 (s, CO), 1882 (s, CO), 1641 (w), 1606 (w), 1532 (w), 1504 (w), 1466 (m), 1259 (s), 1209 (m), 1172 (m), 1134 (m) 1096 (s), 1018 (s), 927 (w), 857 (m), 796 (s), 735 (w), 663 (w), 616 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.07 (m, 2H, 7-H), 3.87 (s, 3H, 10-H), 4.75 (d, *J* = 6.4 Hz, 1H, 6-H), 5.05 (s, 1H, 3-H), 5.19-5.26 (m, 2H, 9-H), 5.77 (d, *J* = 6.5 Hz, 1H, 5-H), 5.86-5.95 (m, 1H, 8-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT, HMQC): δ = 38.5 (+, C-7), 56.7 (–, C-10), 74.1 (–, C-3), 82.7 (–, C-6), 88.5 (–, C-5), 110.3 (+, C-4), 116.8 (+, C-1), 119.4 (+, C-9), 133.7 (–, C-8), 136.7 (+, C-2), 115.2 (+, q, $^{1}J_{C\text{-}F}$ = 320.7 Hz, C-11), 230.5 (+, C-12) ppm. – MS (70 eV): m/z (%) = 432 (47) [M^+], 376 (10) [M^+ – 2CO], 348 (40) [M^+ – 3CO], 296 (67) [M^+ – $Cr(CO)_3$], 234 (95), 219 (73), 200 (84), 173 (36), 163 (100) [M^+ – $Cr(CO)_3$ – SO_2CF_3], 135 (41), 103 (76), 91 (78), 77 (65), 69 (79), 52 (59) [^{52}Cr]. – HRMS ($C_{14}H_{11}O_7F_3SCr$) calcd. 431.9583, found. 431.9581.

3.1.6 Tricarbonyl(5-methyl-2-isopropylphenyl)chromium(0) Triflate (80)

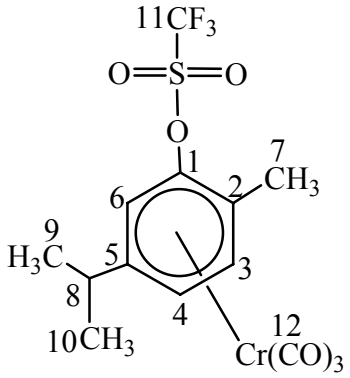


80

GP2, 1.00 g (3.5 mmol) of **72**, 20 mL of THF, 7 mL of pyridine, 1.18 g (4.2 mmol) of trifluoromethanesulfonic anhydride, 30 h, flash chromatography, eluting with TBME / PE (1:2). 1.08 g (2.6 mmol, 74 %) of **80** was obtained as yellow oil.

IR (ATR): $\tilde{\nu}$ = 2978 (w) cm^{-1}, 1974 (s, CO), 1879 (s, CO), 1432 (m), 1366 (w), 1218 (s), 1132 (m), 1069 (w), 953 (w), 843 (w), 818 (m), 730 (w), 666 (m), 618 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.8 Hz, 3H, 8-H or 9-H), 1.33 (d, *J* = 6.8 Hz, 3H, 8-H or 9-H), 2.27 (s, 3H, 10-H), 2.96 (m, 1H, 7-H), 4.86 (d, *J* = 6.2 Hz, 1H, 4-H), 5.30 (s, 1H, 6-H), 5.51 (d, *J* = 6.3 Hz, 1H, 3-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT, HMQC): δ = 20.2 (–, C-10), 23.1 (–, C-8 or C-9), 24.7 (–, C-8 or C-9), 26.7 (–, C-7), 84.0 (–, C-6), 88.8 (–, C-4), 90.6 (–, C-3), 108.0 (+, C-5), 109.3 (+, C-2), 119.8 (+, q, $^{1}J_{C\text{-}F}$ = 320.3 Hz, C-11), 131.8 (–, C-1), 231.5 (+, C-12) ppm. – MS (70 eV): *m/z* (%) = 418 (18) [M^+], 362 (11) [M^+ – 2CO], 334 (41) [M^+ – 3CO], 282 (10) [M^+ – $Cr(CO)_3$], 267 (18) [M^+ – $Cr(CO)_3$ – CH_3], 250 (12), 220 (88), 201 (96), 185 (100), 159 (22), 105 (36), 91 (32) [M^+ – $Cr(CO)_3$ – OH – (SO_2CF_3)], 77 (17), 69 (24). – HRMS ($C_{14}H_{13}O_6F_3SCr$) calcd. 417.9790, found. 417.9787.

3.1.7 Tricarbonyl(2-methyl-5-isopropylphenyl)chromium(0) Triflate (81)

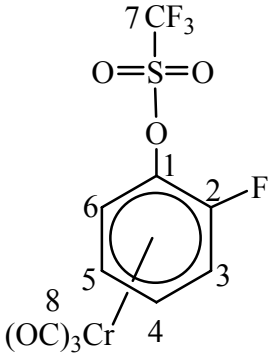


81

GP2, 1.20 g (4.2 mmol) of **73**, 30 mL of THF, 10 mL of pyridine, 1.42 g (5.0 mmol) of trifluoromethanesulfonic anhydride, 30 h. Flash chromatography eluting with *tert*-butyl methyl ether/petroleum ether (1:2). 0.84 g (2.0 mmol, 48 %) of **81** was obtained as yellow oil.

IR (ATR): $\tilde{\nu}$ = 2962 (w) cm^{-1}, 1970 (s, CO), 1885 (s, CO), 1623 (w), 1501 (w), 1464 (w), 1423 (m), 1249 (w), 1214 (s), 1135 (s), 1061 (m), 1036 (w), 997 (w), 929 (m), 878 (m), 812 (s), 768 (w), 738 (w), 709 (w), 683 (w), 655 (m), 605 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.28 [m, 6H, 9(10)-H], 2.33 (s, 3H, 7-H), 2.71 (m, 1H, 8-H), 5.11 (d, *J* = 6.1 Hz, 1H, 4-H), 5.35 (d, *J* = 6.2 Hz, 1H, 3-H), 5.56 (s, 1H, 6-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 15.9 (–, C-7), 23.0 (–, C-9 or C-10), 23.9 (–, C-9 or C-10), 32.2 (–, C-8), 85.1 (–, C-6), 90.0 (–, C-4), 92.1 (–, C-3), 100.2 (+, C-5), 118.6 (+, q, $^{1}J_{C\text{-}F}$ = 320.0 Hz, C-11), 129.2 (+, C-2), 148.4 (+, C-1), 231.5 (+, C-12) ppm. – MS (70 eV): *m/z* (%) = 418 (24) [M^+], 362 (6) [M^+ – 2CO], 334 (15) [M^+ – 3CO], 265 (9) [M – $Cr(CO)_3$ – CH_3], 220 (68), 201(100), 185 (15), 135 (21), 91 (12) [M^+ – $Cr(CO)_3$ – OH – (SO_2CF_3)], 77 (7), 69 (6), 52 (49) [^{52}Cr]. –HRMS ($C_{14}H_{13}O_6F_3SCr$) calcd. 417.9790, found. 417.9791.

3.1.8 Tricarbonyl(2-fluorophenyl)chromium(0) Triflate (82)

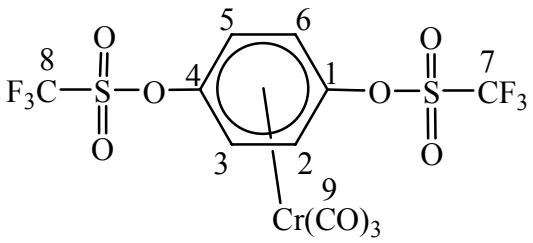


82

GP2, 0.50 g (2.0 mmol) of **74**, 20 mL of THF, 7 mL of pyridine, 0.62 g (2.2 mmol) of trifluoromethanesulfonic anhydride, 30 h, flash chromatography, eluting with TBME / PE (1:1). 0.40 g (1.1 mmol, 53 %) of **82** was obtained as yellow oil.

IR (ATR): $\tilde{\nu}$ = 3101 (w) cm^{-1}, 2363 (w), 1984 (s, CO), 1891 (s, CO), 1610 (w), 1517 (w), 1460 (m), 1429 (m), 1212 (s), 1129 (s), 1084 (w), 1005 (w), 877 (s), 800 (s), 770 (m), 724 (m), 650 (m), 613 (w). – ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 5.43 (s, 1H, 3-H), 5.82 (s, 1H, 5-H), 6.08 (s, 1H, 6-H), 6.42 (s, 1H, 4-H) ppm. – ^{13}C NMR (100.6 MHz, [D_6]acetone, DEPT): δ = 80.9 (–, C-3), 88.1 (–, C-6), 90.0 (–, C-4), 94.4 (–, C-5), 119.3 (+, C-1), 141.2 (+, d, $^{1}J_{C\text{-}F}$ = 269.0 Hz, C-2), 120.1 (+, q, $^{1}J_{C\text{-}F}$ = 320.3 Hz, C-7), 231.2 (+, C-8) ppm. – MS (70 eV): *m/z* (%) = 380 (18) [M^+], 324 (8) [M^+ –2CO], 296 (62) [M^+ – 3CO], 227 (6) [M^+ – $Cr(CO)_3$ – F], 182 (36), 163 (100) [M^+ – $Cr(CO)_3$ – F – SO_2CF_3], 135 (73), 92 (47), 80 (12), 71 (34), 52 (75) [^{52}Cr]. – HRMC $C_{10}H_4O_6F_4SCr$: calcd. 379.9070, found. 379.9069.

3.1.9 Tricarbonyl(1,4-dihydroxylbenzene)chromium(0) Bis(triflate) (86)

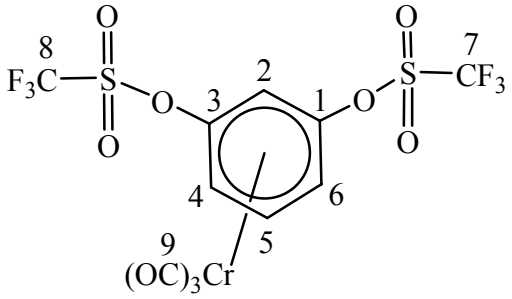


86

GP2, 1.40 g (5.7 mmol) of **83**, 40 mL of THF, 13 mL of pyridine, 3.85 g (13.6 mmol) of trifluoromethanesulfonic anhydride, 48 h. Flash chromatography eluting with TBME / PE (1:2). 1.93 g (3.8 mmol, 67 %) of **86** was obtained as yellow solid, m. p. 69 °C.

IR (ATR): $\tilde{\nu}$ = 3085 (w) cm^{-1}, 2963 (w), 1975 (s, CO), 1871 (s, CO), 1715 (w), 1623 (m), 1540 (m), 1489 (m), 1428 (m), 1250 (m), 1194 (s), 1159 (m), 1118 (s), 1098 (m), 903 (s), 850 (s), 799 (m), 766 (w), 744 (w), 692 (w), 666 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.58 [s, 4H, 2(3, 5, 6)-H] ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 82.7 [–, C-2(3, 5, 6)], 118.4 [+, q, $^{1}J_{C\text{-}F}$ = 321.1 Hz, C-7(8)], 125.5 [+, C-1(4)], 227.1 (+, C-9) ppm. – MS (70 eV): m/z (%) = 510 (30) [M^+], 426 (48) [M^+ – 3CO], 374 (16) [M^+ – $Cr(CO)_3$], 357 (48), 312 (38), 293 (88), 229 (10), 179 (100), 160 (58), 135 (19), 116 (12), 80 (33), 69 (52), 52 (89) [^{52}Cr]. – HRMS $C_{11}H_4O_9F_6S_2Cr$: calcd. 509.8606, found. 509.8606.

3.1.10 Tricarbonyl(1,3-dihydroxylbenzene)chromium(0) Bis(triflate) (87)

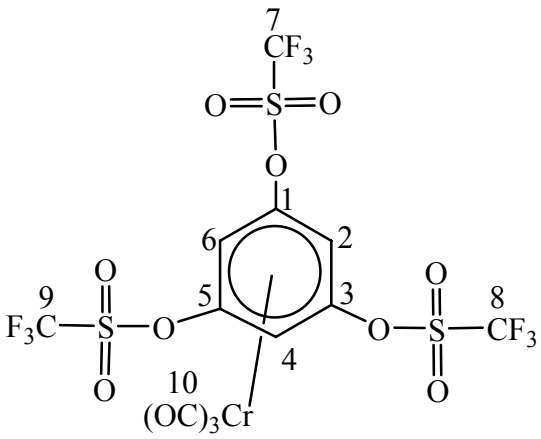


87

GP2, 1.68 g (6.8 mmol) of 84, 40 mL of THF, 13 mL of pyridine, 4.62 g (16.3 mmol) of trifluoromethanesulfonic anhydride, 48 h. Flash chromatography eluting with TBME / PE (1:2). 2.18 g (4.3 mmol, 63 %) of 87 was obtained as yellow solid, m. p. 86 °C.

IR (ATR): $\tilde{\nu}$ = 3094 (w) cm^{-1}, 2004 (m), 1948 (m, CO), 1915 (s, CO), 1502 (w), 1432 (s), 1400 (w), 1213 (s), 1185 (m), 1092 (s), 1003 (m), 933 (m), 868 (m), 1098 (m), 903 (s), 850 (s), 830 (m), 793 (m), 755 (w), 723 (m), 648 (w), 610 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.26 [d, *J* = 6.0 Hz, 2H, 4(6)-H], 5.58 [t, *J* = 6.3 Hz, 1H, 5-H], 5.70 [s, 1H, 2-H] ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 81.0 (–, C-2), 82.1 [–, C-4(6),], 88.2 (–, C-5), 118.5 [+, q, $^{1}J_{C\text{-}F}$ = 321.3 Hz, C-7(8)], 131.5 [+, C-1(3)], 227.8 (+, C-9) ppm. – MS (70 eV): m/z (%) = 510 (10) [M^+], 454 (23) [M^+ – 2CO], 426 (58) [M^+ – 3CO], 374 (18) [M^+ – $Cr(CO)_3$], 342 (27), 312 (68), 293 (89), 215 (56), 201 (44), 196 (54), 160 (40), 151 (71), 132 (71), 116 (23), 92 (61), 81 (57), 77 (40), 69 (78), 52 (100) [^{52}Cr]. – HRMS $C_{11}H_4O_9F_6S_2Cr$: calcd. 509.8606, found. 509.8605.

3.1.11 Tricarbonyl(1,3,5-trihydroxylbenzene)chromium(0) Tris(triflate) (88)



88

GP2, 1.32 g (5.0 mmol) of **85**, 40 mL of THF, 13 mL of pyridine, 4.69 g (16.6 mmol) of trifluoromethanesulfonic anhydride, 60 h. Flash chromatography eluting with TBME / PE (1:3). 1.16 g (1.8 mmol, 35 %) of **88** was obtained as a yellow solid, m. p. 67 °C

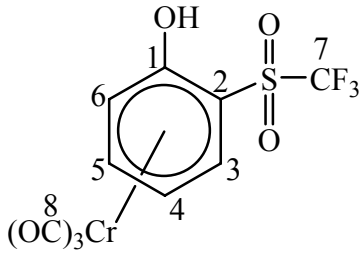
IR (ATR): $\tilde{\nu}$ = 3103 (w) cm^{-1}, 2962 (w), 2019 (s, CO), 1947 (s, CO), 1496 (w), 1438 (s), 1400 (m), 1207 (s), 1128 (s), 1091(s), 949 (m), 850 (m), 792 (m), 752 (m), 703 (m), 668 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.59 [s, 3H, 2(4, 6)-H] ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 75.2 [–, C-2(4, 6)], 118.5 [+, q, $^{1}J_{C\text{-}F}$ = 321.5 Hz, C-7(8, 9)], 126.8 [+, C-1(3, 5)], 225.6 (+, C-10) ppm. – MS (70 eV): *m/z* (%) = 602 (20) [M^{+} – 2CO], 574 (53) [M^{+} – 3CO], 522 (48) [M^{+} – Cr(CO)$_3$], 460 (33), 441 (68), 373 (33), 330 (49), 308 (46), 240 (43), 195 (22), 178 (52), 164 (37), 147 (43), 123 (52), 107 (29), 91 (57), 69 (100), 52 (50) [^{52}Cr]. – HRMS $C_9H_3O_9F_9S_3$ calcd. 521.8796, found. 521.8796.

4. Anionic Thia-Fries Rearrangement of Aryltriflate Tricarbonylchromium Complexes

4.1 General Procedure for the Anionic Thia-Fries Rearrangement of Aryltriflate Tricarbonylchromium Complexes (GP3)

All operations are carried out under exclusion of air using standard Schlenk technique with argon as the inert gas. At –78 °C 1.5 equiv. of butyl lithium in hexane or LDA (Lithium diisopropylamide) is added dropwise to the solution of the aryltriflate tricarbonylchromium complex in THF. The mixture is stirred for 2 h at –78 °C, the color changing from yellow to orange. The mixture is warmed to 0 °C and is stirred for 2 h. The reaction is quenched by addition of 10 mL of saturated aqueous ammonium chloride and then extracted three times with the same volume of with ethyl acetate. The collected organic layers are washed three times with 30 mL of water, filtered through a P4 frit covered with a 2 cm thick layer of silica gel, and dried over anhydrous $MgSO_4$. After solvent removal at reduced pressure, the crude product is purified by column chromatography at SiO_2, eluting with ethyl acetate, and recrystallized from hexane / THF.

4.1.1 Tricarbonyl(2-trifluoromethylsulfonylphenol)chromium(0) (93)



93

a) GP3, 500 mg (1.38 mmol) of **75**, 1.04 mL (2.1 mmol) of LDA (2 M solution in

THF/ heptane/ethylbenzene). 450 mg (1.2 mmol, 90 %) of **93** was obtained as orange-red oil. Orange-red crystals were obtained by recrystallization from hexane/THF (3:1), m. p. 160 °C (dec.).

b) At 25 °C a suspension of 5.33 g (0.8 mmol) of tetrabutylammonium fluoride on silica gel (1.5 mmol F^-/g) in 10 mL of acetonenitrile was added dropwise 0.35 g (0.8 mmol) of tricarbonyl(2-trimethylsilylphenyltriflate)chromium(0) (**70**) in 10 mL of acetonitrile. After stirring the mixture at 25 °C for 2 h the reaction was quenched by addition of 15 mL of water. The mixture was extracted three times with 15 mL of ethyl acetate each. The collected organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed at reduced pressure. The crude product was purified by column chromatography at SiO_2, eluting with ethyl acetate. The product was recrystallized from hexane/THF (3:1) to yield 0.249 g (0.7 mmol, 86 %) of **93**.

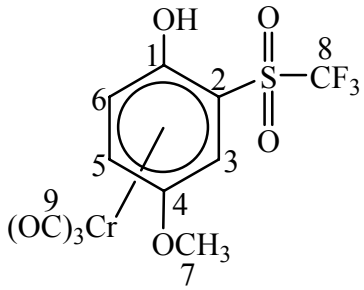
IR (ATR): $\tilde{\nu}$ = 2984 (w) cm-1, 1955 (s, CO), 1856 (s, CO), 17 03 (w), 1524 (s), 1469 (s), 1398 (w), 1352 (w), 1261 (w), 1193 (s), 1132 (m), 1097 (m), 1046 (m), 852 (w), 818 (w), 764 (w), 709 (m), 681 (w), 666 (w). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 4.70 (d, *J* = 7.3 Hz, 1H, 6-H), 4.93 (t, *J* = 6.4 Hz, 1H, 4-H), 5.90-5.97 [m, 2H, 3(5)-H], 7.34 (br, 1H, OH) ppm. – ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 80.4 (–, C-6), 83.8 (–, C-4), 85.1 (+, C-2), 99.6 (–, C-5), 103.2 (–, C-3), 122.2 (+, q, $^1J_{C\text{-}F}$ = 325.3 Hz, C-7), 161.7 (+, C-1), 235.4 (+, C-8) ppm. – MS (70 eV): m/z (%) = 363 (57) [M^+], 306 (36) [M^+ – 2CO], 278 (100) [M^+–3CO], 226 (8) [M^+– Cr(CO)$_3$], 209 (98) [M^+– Cr(CO)$_3$ – OH], 191 (14), 163 (16), 145 (59), 116 (11), 91 (21) [M^+ – Cr(CO)$_3$ – OH – (SO_2CF_3)], 69 (11), 52 (53) [^{52}Cr]. – HRMS ($C_{10}H_5O_6F_3SCr$) calcd. 361.9164, found. 361.9166.

X-Ray Structure Analysis of **93•THF**

$C_{14}H_{13}CrF_3O_7S$, molecular weight 434.30, crystal system monoclinic, space group P 21/c, a = 6.519(3) Å α = 90°, *b* = 17.392(7) Å, β = 101.43(5)°, *c* = 16.169(8) Å γ = 90°, *V* = 1796.9(14) Å^3, *Z* = 4, $d_{calcd.}$ = 1.605 g/cm^3, F(000) = 880e, μ = 0.815 mm^{-1}, crystal color yellow, crystal size 0.44 x 0.41 x 0.26 mm, Stoe IPDS (Area Detector) diffractometer, *T* = 307(2) K, λ ($Mo_{K\alpha}$) = 0.71073 Å, θ_{min} = 2.34°, θ_{max} = 26.29°, -8≤ h≤8, -21≤ k≤21, -20≤ l≤19, no absorption correction, no extinction correction, 24868 collected, 3537 unique reflections, [*R*(int) = 0.2789], refinement program: SHELXL-93, refinement by full-matrix least squares method (F^2), *S* = 1.065, *R*-Indices: [I>2

σ(I)] R_1 = 0.1202, wR_2 = 0.2342, *R*-Indices (all data): R_1 = 0.2793 , wR_2 = 0.2585, min., max. residual electron density: – 0.592, 0.387 $Å^{-3}$, completeness of data 100 %.

4.1.2 Tricarbonyl(4-methoxy-2-trifluoromethylsulfonylphenol)chromium(0) (94)

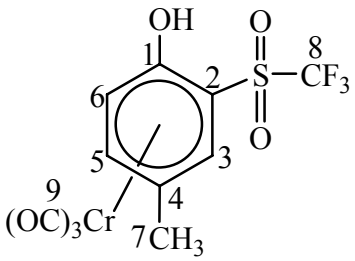


94

GP3, 150 mg (0.4 mmol) of **76** 0.29 mL (0.57 mmol) of LDA (2M solution in THF/ heptane/ethylbenzene), 123 mg (0.3 mmol, 82 %) of **94** was obtained as an orange-red oil. Orange-red crystals were obtained by recrystallization in the solution of hexane/THF (3:1), m. p. 173 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 2189 (w) cm^{-1}, 1976 (w, CO), 1957 (m, CO), 1854 (s, CO), 1547 (w), 1509 (m), 1439 (w), 1323 (w), 1255 (w), 1194 (m), 1041 (m), 1025 (w), 895 (w), 799 (w), 705 (m), 673 (s). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.60 (s, 3H, 7-H), 4.54 (d, *J* = 7.8 Hz, 1H, 6-H), 5.68 (d, *J* = 2.8 Hz, 1H, 3-H), 5.99 (dd, *J* = 2.8, 5.0 Hz, 1H, 5-H) ppm, – ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 58.3 (–, C-7), 80.7 (–, C-6), 80.0 (+, C-2), 83.6 (–, C-3), 94.0 (–, C-5), 122.3 (+, q, $^1J_{C\text{-}F}$ = 325.9 Hz, C-8), 129.1 (+, C-4), 160.2 (+, C-1), 235.9 (+, C-9) ppm. – MS (70 eV): m/z (%) = 392 (23) [M^+], 336 (15) [M^+ – 2CO], 308 (19) [M^+ – 3CO], 256 (91) [M^+ – Cr(CO)$_3$], 240 (13) [M^+– Cr(CO)$_3$ – OH], 220 (58), 185 (88), 139 (91), 108 (66), 91 (100) [M^+ – Cr(CO)$_3$ – SO_2CF_3 – OCH_3], 80 (66), 69 (69), 52 (63) [^{52}Cr]. – HRMS ($C_{11}H_7O_7F_3SCr$) calcd. 391.9270, found. 391.9275.

4.1.3 Tricarbonyl(4-methyl-2-trifluoromethylsulfonylphenol)chromium(0) (95)

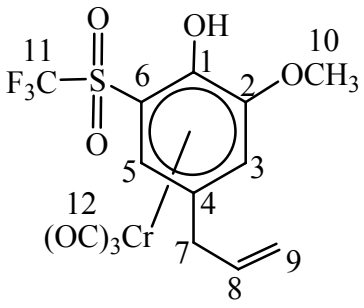


95

GP3, 200 mg (0.5 mmol) of **77**, 0.50 mL (0.80 mmol) of BuLi (1.6 M solution in hexane). 188 mg (0.5 mmol, 94 %) of **95** was obtained as an orange-red solid, m. p. 120 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 2988 (w) cm^{-1}, 1957 (s, CO), 1856 (s, CO), 1538 (w), 1493 (m), 1378 (w), 1349 (w), 1195 (s), 1125 (m), 1097 (m), 1050 (w), 891 (w), 841 (w), 791 (w), 708 (m), 666 (w). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.08 (s, 3H, 7-H), 4.73 (d, *J* = 6.9 Hz, 1H, 6-H), 5.92-5.94 [m, 2H, 3(5)-H], 8.34 (br, 1H, OH) ppm. – ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 49.1 (–, C-7) 82.6 (–, C-6), 84.3 (+, C-2), 99.5 (–, C-3), 104.6 (–, C-5), 121.5 (+, q, $^{1}J_{C\text{-}F}$ = 327.0 Hz, C-8), 159.8 (+, C-1), 171.6 (+, C-4), 235.3 (+, C-9) ppm. – MS (70 eV): *m/z* (%) = 376 (39) [M^+], 320 (15) [M^+ – 2CO], 292 (94) [M^+ – 3CO], 240 (28) [M^+ – Cr(CO)$_3$], 223 (55) [M^+ – Cr(CO)$_3$ – OH], 190 (17), 159 (55), 123 (40), 107 (35), 86 (100) [M^+ – Cr(CO)$_3$ – OH – (SO$_2$CF$_3$)], 77 (41), 69 (32), 52 (63) [^{52}Cr]. – HRMS ($C_{11}H_7O_6F_3SCr$) calcd. 375.9321, found. 375.9321.

4.1.4 (2-Allyl-4-methoxy-6-trifluoromethylsulfonylphenol)tricarbonyl Chromium Complex (96)

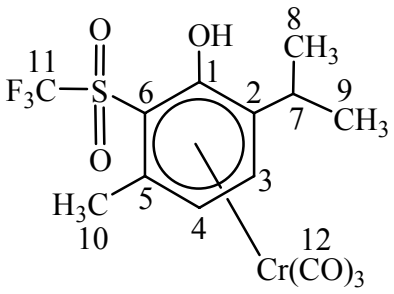


96

GP3, 244 mg (0.6 mmol) of **79**, 0.39 mL (0.6 mmol) of BuLi (1.6 M solution in hexane). 215 mg (0.5 mmol, 88 %) of **96** was obtained as an orange-yellow solid, m.p. 130 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 2359 (w) cm^{-1}, 2221 (w), 2055 (w), 1948 (s, CO), 1836 (s, CO), 1735 (w), 1517 (m), 1437 (w), 1338 (m), 1257 (m), 1196 (m), 1138 (m), 1106 (m), 1039 (m), 797 (w), 709 (m), 683 (w), 670 (w). – ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 3.10 (m, 2H, 7-H), 3.82 (s, 3H, 10-H), 4.75 (d, *J* = 6.4Hz, 1H, 3-H), 5.09–5.20 (m, 2H, 9-H), 5.55 (s, 1H, 5-H), 5.85–5.91 (m, 1H, 8-H), 6.01 (s, 1H, OH) ppm. – ^{13}C NMR (100.6 MHz, [D_6]acetone, DEPT): δ = 68.7 (+, C-7), 58.3 (–, C-10), 83.1 (+, C-6), 89.4 (–, C-3), 94.1 (–, C-5), 112.6 (+, C-4), 118.2 (+, C-9), 122.1 (+, q, $^1J_{C\text{-}F}$ = 327.5 Hz, C-11), 137.6 (–, C-8), 148.8 (+, C-2), 155.9 (+, C-1), 235.3 (+, C-12) ppm. – MS (70 eV): m/z (%) = 432 (8) [M^+], 348 (34) [M^+ – 3CO], 296 (89) [M^+ – $Cr(CO)_3$], 277 (62), 220 (24), 210 (49), 171 (42),163 (59), 148 (25), 131 (26), 120 (31),105 (100), 91 (52), 77 (57), 69 (32), 52 (70) [^{52}Cr]. – HRMS ($C_{14}H_{11}O_7F_3SCr$) calcd. 431.9583, found. 431.9586.

4.1.5 Tricarbonyl(5-methyl-2-isopropyl-6-trifluoromethylsulfonylphenol)-chromium(0) (97)

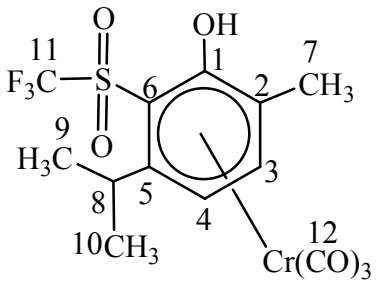


97

GP3, 230 mg (0.6 mmol) of **80,** 0.52 mL (0.82 mmol) of BuLi (1.6 M solution in hexane). 184 mg (0.4 mmol, 80 %) of **97** was obtained as orange-yellow oil.

IR (ATR): $\tilde{\nu}$ = 2971 (w) cm^{-1}, 1948 (s, CO), 1830 (s, CO), 1748 (w), 1480 (m), 1343 (w), 1206 (m), 1131 (w), 1086 (w), 1049 (w), 895 (w), 805 (w), 734 (w), 676 (w). – ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 1.09 (d, *J* = 6.1 Hz, 3H, 8-H or 9-H), 1.11 (d, *J* = 6.5 Hz, 3H, 8-H or 9-H), 2.39 (s, 3H, 10-H), 3.02 (m, 1H, 7-H), 4.80 (d, *J* = 6.3 Hz, 1H, 3-H), 5.94 (d, *J* = 6.2 Hz, 1H, 4-H) ppm. – ^{13}C NMR (100.6 MHz, [D_6]acetone, DEPT): δ = 21.6 (–, C-10), 24.8 (–, C-8 or C-9), 25.3 (–, C-8 or C-9), 27.4 (–, C-7), 83.9 (–, C-4), 85.1 (+, C-6); 98.8 (–, C-3), 106.9 (+, C-2); 112.5 (+, C-5), 122.4 (+, q, $^{1}J_{C\text{-}F}$ = 327.5 Hz, C-11), 161.2 (+, C-1), 235.6 (+, C-12). – MS (70 eV): *m/z* (%) = 418 (42) [M^+], 362 (19) [M^+ – 2CO], 334 (100) [M^+ – 3CO], 282 (32) [M^+ – $Cr(CO)_3$], 267 (88) [M^+ – $Cr(CO)_3$ – CH_3], 250 (32), 201 (45), 150 (25), 135 (78), 105 (26), 91 (50) [M^+ – $Cr(CO)_3$ – OH – (SO_2CF_3)], 73 (71), 61 (78), 52 (60) [^{52}Cr]. – HRMS ($C_{14}H_{13}O_6F_3SCr$) calcd. 417.9790, found. 417.9792.

4.1.6 Tricarbonyl(2-methyl-5-isopropyl-6-trifluoromethylsulfonylphenol) chromium(0) (98)

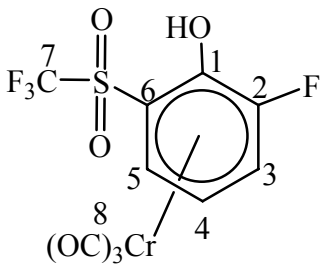


98

GP3, 260 mg (0.6 mmol) of **81** 0.58 mL (0.9 mmol) of BuLi (1.6 M solution in hexane).122 mg (0.3 mmol, 47 %) of **98** was obtained as an orange-yellow solid, m. p. 227 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 2961 (w) cm^{-1}, 1950 (s, CO), 1847 (s, CO), 1527 (w), 1506 (w), 1481 (m), 1389 (w), 1378 (w), 1330 (w), 1205 (m), 1138 (w), 1106 (m), 1007 (w), 957 (w), 841 (w), 763 (w), 719 (m), 675 (m), 631 (m), 610 (m). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.16 (d, *J* = 7.3 Hz, , 3H, 9-H or 10-H), 1.20 (d, *J* = 6.9 Hz, , 3H, 9-H or 10-H), 1.88 (s, 3H, 7-H), 3.62 (m, 1H, 8-H), 4.84 (d, *J* = 6.4 Hz, 1H, 3-H), 5.96 (d, *J* = 6.4 Hz, 1H, 4-H). – ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 17.4 (–, C-7), 22.5 (–, C-9 or C-10), 22.8 (–, C-9 or C-10), 28.8 (–, C-8), 78.1 (–, C-4), 85.8 (+, C-6), 102.7 (–, C-3), 96.1 (+, C-2), 112.5 (+, C-5), 122.6 (+, q, $^{1}J_{C\text{-}F}$ = 328.5 Hz, C-11), 164.2 (+, C-1), 236.3 (+, C-12) ppm. – MS (70 eV): m/z (%) = 418 (18) [M^+], 362 (10) [M^+ – 2CO], 334 (53) [M^+ – 3CO], 282 (26) [M^+ – Cr(CO)$_3$], 267 (16) [M^+ – Cr(CO)$_3$ – CH$_3$], 213 (13), 201 (33), 167 (13), 150 (35), 135 (100) [M^+ – Cr(CO)$_3$ – CH$_3$ – (SO$_2$CF$_3$)], 123 (27), 107 (28), 91 (38), 81 (57), 71 (98), 55 (87), 52 (43) [^{52}Cr]. – HRMS (C$_{14}$H$_{13}$O$_6$F$_3$SCr) calcd. 417.9790, found. 417.9789.

4.1.7 Tricarbonyl(2-fluoro-6-trifluoromethylsulfonylphenol)chromium(0) (99)



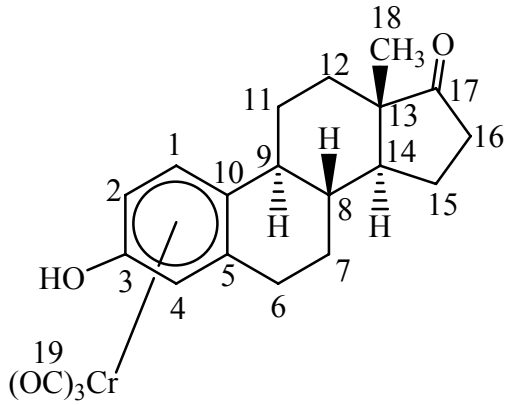
99

GP3, 250 mg (0.66 mmol) of **82**, 0.49 mL (0.79 mmol) of BuLi (1.6 M solution in hexane). 230 mg (0.5 mmol, 92 %) of **99** was obtained as orange-red oil.

IR (ATR): $\tilde{\nu}$ = 2979 (w) cm^{-1}, 2878 (w), 2336 (w), 1963 (s, CO), 1857 (s, CO), 1539 (s), 1506 (m), 1477 (w), 1353 (m), 1288 (w), 1191 (s), 1159 (m), 1133 (w), 1098 (s), 1050 (m), 967 (s), 891 (m), 847 (m), 763 (w), 700 (w), 670 (m), 658 (m), 619 (s). – ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 4.84 (t, *J* = 5.9 Hz, 1H, 3-H), 5.73 (d, *J* = 6.2 Hz, 1H, 4-H), 6.26 (t, *J* = 6.6Hz, 1H, 5-H), 7.34 (br, 1H, OH) ppm. – ^{13}C NMR (100.6 MHz, [D_6]acetone, DEPT, HMQC): δ = 75.1 (–, C-3), 85.0 (+, C-6), 91.3 (–, C-4), 97.5 (–, C-5), 122.1 (+, q, $^{1}J_{C\text{-}F}$ = 326.4 Hz, C-7), 134.2 (+, d, $^{1}J_{C\text{-}F}$ = 253.8 Hz, C-2), 154.6 (+, C-1), 234.4 (+, C-8) ppm. – MS (70 eV): *m/z (%)* = 244 (18) [M^+ – $Cr(CO)_3$], 185 (24), 175 (10), 159 (20), 121 (14), 112 (24), 95 (28) [M^+ – $Cr(CO)_3$ – OH – F – (SO_2CF_3)], 83 (20), 75 (24), 69 (53), 64 (100). – HRMS ($C_7H_4O_3F_4S$) calcd. 243.9817, found. 243.9818.

5. Application of the Anionic thia-Fries Rearrangement in Synthesis of 2-trifluoromethanelsulfonylestrone

5.1 Tricarbonyl(estrone)chromium(0) (110)



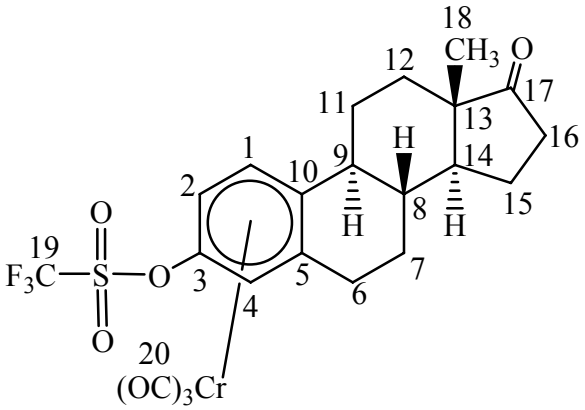
110

1017 mg (4.6 mmol) of $Cr(CO)_6$ and 1027 mg (3.8 mmol) of estrone (**106**) in 44 mL of dibutyl ether / THF (10:1) was heated at 117 °C for 40 h. A yellow precipitate formed. After filtration and dissolution of the precipitate in THF the mixture was subjected to column chromatography [300 x 30 mm, PE, PE / TBME (6:1), PE / TMBE (2:1), ethyl acetate]. 1437 mg (3.5 mmol, 93 %) of **110** was obtained as a yellow solid, mixture of diastereomers (3:5, NMR). Signals assigned to the minor diastereomer are marked with b.

IR (ATR) $\tilde{\nu}$ = 3089 (w) cm^{-1}, 2933 (w), 2858 (w), 1946 (s, CO), 1845 (s, CO), 1728 (s, C=O), 1543 (m, aryl-C=C), 1470 (m, aryl-C=C), 1260 (m), 1042 (m). – ^{1}H NMR (400.1 MHz, [D_6]acetone) δ = 0.89 (s, 3 H, 18b-H), 0.90 (s, 3 H, 18-H), 1.37-1.67 (m, 7-H, 7b-H, 9-H, 9b-H, 11-H, 11b-H, 16b-H), 1.81 (t, *J* = 11.7 Hz, 2 H, 16-H), 1.96-2.08 (m, 15-H), 2.17–2.27 (m, 13-H, 13b-H), 2.41-2.48 (m, 6-H), 2.77-3.01 (m, 8-H, 8b-H, 12-H), 5.14 (dd, *J* = 7.0, 2.0 Hz, 1 H, 2-H), 5.21 (d, *J* = 1.9 Hz, 1 H, 4b-H), 5.23 (d, *J* = 1.8 Hz, 1 H, 4-H), 5.30 (dd, *J* = 7.0, 2.0 Hz, 1 H, 2b-H,), 5.93 (d, *J* = 7.03

Hz, 1 H, 1-H), 6.09 (d, *J* = 7.0 Hz, 1 H, 1b-H) ppm; – ^{13}C NMR (100.6 MHz, BB, DEPT, HMQC [D6]acetone) δ = 13.8 (C-18), 14.1 (C-18b), 21.9 (C-15b), 22.1 (C-15), 25.9 (C-7b), 26.2 (C-11), 26.3 (C-7), 26.7 (C-11b), 28.2 (C-12), 32.1 (C-16), 32.2 (C-16b), 36.0 (C-6), 38.4 (C-9), 39.0 (C-9b), 43.2 (C-13), 44.2 (C-13b), 50.2 (C-14b), 50.5 (C-14) 78.9 (C-2), 80.0 (C-4b), 81.4 (C-2b), 81.8 (C-4), 95.3 (C-1), 96.1 (C-1b), 105.1 (C-10b), 107.6 (C-10), 113.8 (C-5b), 114.1 (C-5), 142.5 (C-3b), 143.0 (C-3), 219.0 (C-17b), 219.1 (C-17), 235.7 (C-19b), 236.3 (C-19) ppm; – MS (70 eV) m/z (%) = 406 (58) [M^+], 350 (54) [M^+ – 2CO], 322 (100) [M^+ – 3CO], 270 (76) [M^+ – $Cr(CO)_3$], 213 (48), 199 (23), 173 (40), 159 (49), 146 (56), 133 (45), 115 (40), 91 (40). – LC-MS (ESI) $C_{21}H_{22}CrO_5$ [M – H]: calcd. 405.0805, found 405.0794.

5.2 Tricarbonyl(3-trifluoromethylsulfonylestrone)chromium(0) (111)



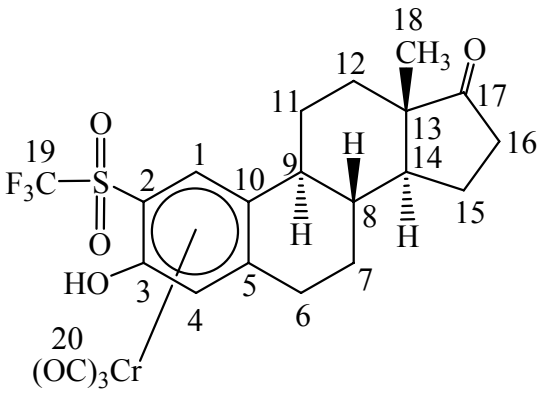
111

To a stirred solution of 1.1 g (2.7 mmol) tricarbonyl(estron)chromium(0) (**110**) in 30 mL anhydrous THF and 15 mL pyridine was added 1.2 eq. Trifluoromathanesulfonic anhydride dropwise under Argon at –78 °C. The reaction was allowed to return to room temperature in one hour and stirred for 48h. The colour of solution changed from yellow to dark orange. The reaction mixture was quenched with water and extracted in ethyl acetate. The collected organic layers were washed with water till the aqueous phase colourless, dried over anhydrous magnesium sulfate and filtered through a P4 frit. After solvents removal *in vacuo*, the crude product was purified by flash chromatography, eluting with TBME, 1200 mg (2.2 mmol, 84 %) of **111** was

obtained as a yellow solid as a mixture of diastereomers (2:1, NMR). Signals assigned to the minor diasteromer are marked with b.

IR (ATR): $\tilde{\nu}$ = 2939 (w) cm^{-1}, 2866 (w), 1969 (s, CO), 1888 (s, CO), 1732 (m, C=O), 1543 (m), 1457 (m), 1342 (w), 1248 (m), 1214 (m), 1137 (w), 1090 (m), 912 (m), 824 (w), 783 (w), 725 (w), 663 (w), 622 (w). – ^{1}H NMR (400 MHz, [D_6]acetone): δ = 0.91 (s, 18b-H), 0.93 (s, 3 H, 18-H), 1.39-1.57 (m, 7-H, 7b-H, 11-H, 11b-H,), 1.64-1.73 (m, 15-H, 15b-H, 9-H, 9b-H), 1.81-1.89 (m, 16-H, 16b-H), 2.08-2.12 (m, 14-H, 14b-H), 2.26-2.39 (m, 8-H, 8b-H), 2.43-2.49 (m, 6-H, 6b-H), 2.91-3.03 (m, 12-H, 12b-H), 5.85 (dd, *J* = 2.3, 2.3 Hz, 1 H, 2-H), 5.95 (d, *J* = 2.2 Hz, 1 H, 4-H), 5.98 (d, 4b-H, *J* = 2.3 Hz), 6.01 (dd, J = 2.2, 2.2 Hz, 2b-H), 6.09 (d, *J* = 7.0 Hz, 1 H,1-H), 6.18 (d, *J* = 7.04 Hz, 1b-H) ppm. – ^{13}C NMR (100.6 MHz, DEPT, HMQC [D_6]acetone): δ = 14.5 (–, C-18), 14.7 (–, C-18b), 22.6 (+, C-15b), 22.7 (+, C-15), 38.9 (–, C-9), 39.2 (–, C-9b), 26.3 (+, C-7b), 26.6 (+, C-11), 26.7 (+, C-7), 27.0 (+, C-11b), 28.6 (+, C-12), 30.6 (+, C-12b), 32.7 (+, C-16), 32.9 (+, C-16b), 36.6 (+, C-6), 36.7 (+, C-6b), 38.9 (–, C-9), 39.2 (–, C-9b), 43.9 (–, C-8), 45.0 (–, C-8b), 48.8 (+, C-13), 48.9 (+, C-13b), 50.9 (–, C-14b), 51.2 (–, C-14), 85.1 (–, C-2), 86.1 (–, C-2b), 87.0 (–, C-4b), 87.4 (–, C-4), 93.3 (–, C-1), 93.7 (–, C-1b), 111.5 (+, C-10b), 112.0 (+, C-5b), 112.7 (+, C-10), 113.8 (+, C-5), 120.4 (+, q, $^{1}J_{C,F}$ = 319.9 Hz, C-19), 120.6 (+, q, $^{1}J_{C,F}$ = 319.9 Hz, C-19b),133.1 (+, C-3b), 134.1 (+, C-3), 219.4 (+, C-17), 219.6 (+, C-17b), 233.6 (+, C-19b), 234.3 (+, C-19) ppm. – MS (EI): m/z (%) = 538 (58) [M^+], 482 (10) [M^+ – 2CO], 454 (67) [M^+ – 3CO], 402 (100) [M^+ – $Cr(CO)_3$], 385 (29), 370 (38), 358 (65), 340 (86), 321 (82), 305 (8), 292 (33), 269 (20), 251 (55), 241 (9), 225 (45), 213 (80), 195 (23), 185 (28), 171 (26), 157 (40), 145 (31), 52 (37). – LC-MS (ESI): $C_{22}H_{21}O_7F_3SCr$ [M − H]: calcd. 537.0287, found. 537.0292.

5.3 Tricarbonyl-[2-(trifluoromethylsulfonyl)estrone]chromium(0) (112)



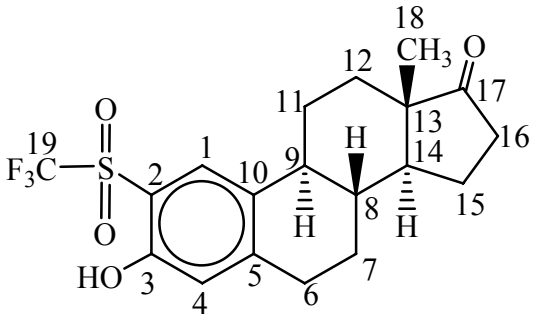
112

1.7 eq. Lithium-diisopropylamide (LDA) (2 M solution in THF/heptane/ethylbenzene) was added dropweise to the solution of 155 mg (0.29 mol) of Tricarbonyl(3 trifluoromethylsulfonylestrone)chromium(0) **(111)** in 10 mL THF under argon at –78 ˚C. The reaction was stirred at –78 °C for 2 h and for another 0.5 h after being warmed to room temperature. The colour of the reaction changed from yellow to orange. The reaction mixture was quenched with saturated ammonium chloride and extracted with ethyl acetate. The collected organic layers were washed for three times, filtered through a P4 frit, over 2 cm layer of silica gel, and dried over anhydrous magnesium sulfate. After solvent removal at reduced pressure, the crude product was purified by column chromatography, eluting with ethyl acetate. 115 mg (0.2 mmol, 77 %) of **112** was obtained as an orange-yellow solid, mixture of diastereomers (2:1, NMR). Signals assigned to the minor diasteromer are marked with b.

IR (ATR): $\tilde{\nu}$ = 2937 (w) cm^{-1}, 2864 (w), 1948 (s, CO), 1846 (s, CO), 1736 (m, C=O), 1617 (w), 1542 (m), 1485 (m), 1454 (w), 1376 (w), 1290 (w), 1265 (m), 1192 (s), 1118 (m), 1085 (m), 1043 (w), 956 (w), 925 (w), 894 (w), 863 (w), 832 (w), 783 (w), 725 (w), 705 (w), 672 (w), 630 (m), 611 (m). – ^{1}H NMR (400 MHz, [D_6]acetone): δ = 0.91 (s, 18b-H), 0.93 (s, 3 H, 18-H), 1.34-1.53 (m, 7-H, 7b-H, 11-H, 11b-H,), 1.61-1.74 (m, 15-H, 15b-H, 9-H, 9b-H), 1.81-1.86 (m, 16-H, 16b-H), 2.06-2.11 (m, 14-H, 14b-H), 2.27-2.36 (m, 8-H, 8b-H), 2.39-2.47 (m, 6-H, 6b-H), 2.86-3.02 (m, 12-H, 12b-H), 4.57 (s, 4b-H), 4.62 (s, 1H, 4-H), 5.93 (s, 1H, 1-H), 6.12 (s, 1b-H) ppm. – ^{13}C

NMR (100.6 MHz, [D_6]acetone, DEPT, HMQC): δ = 14.6 (–, C-18), 14.8 (–, C-18b), 22.6 (+, C-15b), 22.8 (+, C-15), 26.7 (+, C-7b), 26.8 (+, C-11), 27.0 (+, C-7), 27.2 (+, C-11b), 29.4 (+, C-12), 30.7 (+, C-12b), 32.7 (+, C-16), 32.9 (+, C-16b), 36.7 (+, C-6), 36.8 (+, C-6b), 39.1 (–, C-9), 39.3 (–, C-9b), 44.0 (–, C-8), 45.0 (–, C-8b), 48.9 (+, C-13), 49.0 (+, C-13b), 51.0 (–, C-14b), 51.2 (–, C-14), 80.7 (+, C-2), 81.0 (+, C-2b), 83.5 (–, C-4b), 85.2 (–, C-4), 95.3 (–, C-1), 96.9 (–, C-1b), 99.0 (+, C-10b), 101.2 (+, C-10), 119.3 (+, C-5), 119.4 (+, C-5b), 122.1 (+, q, $^1J_{C\text{-}F}$ = 326.9 Hz, C-19), 122.2 (+, q, $^1J_{C\text{-}F}$ = 326.9 Hz, C-19b), 160.8 (+, C-3b), 160.9 (+, C-3), 219.7 (+, C-17), 219.8 (+, C-17b), 235.9 (+, C-20b), 236.5 (+, C-20) ppm. – MS (EI): m/z (%) = 538 (38) [M^+], 482 (10) 402 (12) [M^+ – $Cr(CO)_3$], 358 (7), 279 (23), 190 (25), 167 (42), 149 (100), 140 (29), 113 (15), 104 (21), 86 (26), 69 (77), 52 (93) [^{52}Cr]. – HRMS: $C_{22}H_{21}O_7F_3SCr$: calcd. 537.0325, found. 537.0329

5.4 2-(Trifluoromethylsulfonyl)estrone (114)



114

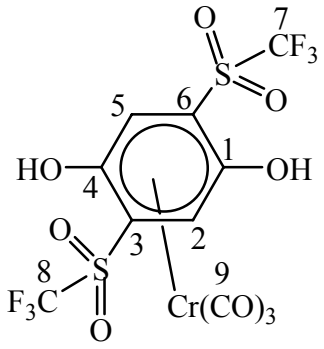
To the solution of tricarbonyl-[2-(trifluoromethylsulfonyl)estrone]chromium(0) **(112)** (162 mg, 0.30 mmol) in 5 mL THF a solution of 4 eq. I_2 (307 mg, 1.2 mmol) in 5 mL THF was added in one portion at 0 °C. The mixture was stirred for 1h at 0 °C and then 5 h at room temperature, then poured into 10 % aqueous sodium bisulfite solution (30 mL), and extracted with two 20 mL–portions of ethyl acetate. The combined ether solution was washed with saturated sodium bicarbonate solution and water and dried over $MgSO_4$. After filtration and removal of solvent, the crud product

was purified by column chromatography (THF / PE 3:1) to give 118 mg (0.29 mmol, 97 %) of **114** as light yellow solid.

IR (ATR): $\tilde{\nu}$ = 3285 (br) cm^{-1}, 2962 (m), 2926 (m), 2857 (w), 2116 (br), 1721 (m, C=O), 1619 (w), 1581 (w), 1496 (w), 1454 (w), 1418 (m), 1374 (w), 1355 (w), 1287 (w), 1259 (s), 1208 (m), 1140 (m), 1086 (s), 1014 (s), 919 (m), 897 (w), 877 (w), 796 (s), 701 (w), 661 (w), 610 (w). – ^{1}H NMR (400 MHz, [D_6]acetone): δ = 0.90 (s, 3 H, 18-H), 1.41-1.69 (m, 6H, 7-H, 11-H, 15-H), 1.78-1.99 (m, 2H, 16-H), 2.08-2.12 (m, 1H, 14-H), 2.16-2.28 (m, 2H, 8-H, 9-H), 2.33-2.48 (m, 2H, 6-H), 2.76-2.99 (m, 2H, 12-H), 6.54 (s, 1H, 4-H), 7.10 (d, *J* = 8.4 Hz, 1H, 1-H), 7.97 (br, 1H, OH) ppm. – ^{13}C NMR (100.6 MHz, [D_6]acetone, DEPT, HMQC): δ = 14.8 (–, C-18), 22.8 (+, C-11), 27.4 (+, C-7), 28.0 (+, C-15), 29.9 (+, C-12), 33.3 (+, C-16), 36.7 (+, C-6), 40.0 (–, C-9), 45.6 (–, C-8), 49.1 (+, C-13), 51.8 (–, C-14), 116.5 (–, C-4), 122.2 (+, q, $^{1}J_{C\text{-}F}$ = 319.1 Hz, C-19), 127.8 (–, C-1), 132.2 (+, C-10), 139.0 (+, C-5), 149.2 (C-2), 156.7 (+, C-3), 220.2 (+, C-17) ppm. – MS (EI): m/z (%) = 402 (100) [M^{+}], 358 (86), 345 (76), 304 (29), 292 (43), 270 (56), 251 (52), 225 (34), 213 (82), 185 (33), 171 (21), 157 (37), 145 (29), 128 (28), 115 (40), 107 (23), 97 (56), 81(21), 69 (35), 55 (46). – HRMS: $C_{19}H_{21}O_7F_3S$: calcd. 402.1112, found. 402.1110.

6. Attempts Towards Double and Triple Anionic Thia-Fries Rearrangemnents

6.1 Tricarbonyl(2,5-bis-trifluoromethanesulfonyl-benzene-1,4-diol)-chromium(0) (115a)



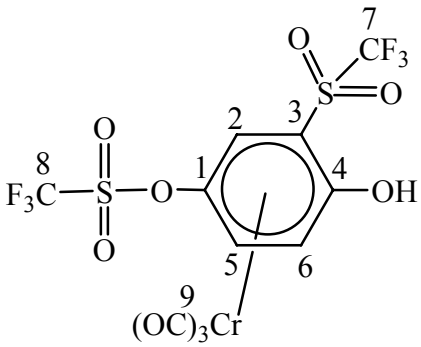
115a

To a stirred solution of diisopropylamine (0.08 mL, 0.6 mmol) in THF (3 mL) cooled to –78 °C, MeLi (0.38 mL of a 1.6 M solution in Hexane, 0.6 mmol) was added dropwise. Then the temperature of the solution was raised to 0 °C and stirred for 0.5 h and cooled back to –78 °C. A solution of 153 mg (0.3 mmol) of complex **86** in THF 6 mL was then added and the reaction mixture was stirred for 2 h at –78 °C. 5 mL of saturated NH_4Cl solution was then added to the reaction and the mixture was allowed to reach room temperature. The solvent was evaporated under reduced pressure. Flash column chromatography (200 x 20 mm, TBME / ethyl acetate 5:1) 96 mg (0.19 mmol, 63 %) of complex **115a** as deep red solid, m. p. 103 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 3289 (w) cm^{-1}, 2962 (w), 2101 (w), 1994 (s, CO), 1921 (s, CO), 1702 (w), 1544 (m), 1500 (m), 1435 (m), 1377 (w), 1356 (m), 1260 (m), 1197 (s), 1118 (s), 1044 (s), 975 (s), 885 (m), 815 (m), 795 (s), 746 (w), 704 (w), 690 (w), 633 (m), 608 (w). – ^{1}H NMR (400.1 MHz, [D6]acetone): δ = 5.17 [s, 2H, 2(5)-H], – ^{13}C NMR (100.6 MHz, [D_6]acetone, DEPT): δ = 79.8 [–, C-2(5)], 83.8 [+, C-3(6)], 94.6 [+, C-1(4)], 121.9 [+, q, $^{1}J_{C\text{-}F}$ = 327.4 Hz, C-7(8)], 235.1 (+, C-9). – MS (70 eV): m/z (%) =

510 (23) (M^+), 426 (16) [M^+ – 2CO], 374 (5) [M^+ – $Cr(CO)_3$], 357 (20) [M^+ – $Cr(CO)_3$ – OH], 293 (65), 179 (100), 160 (25), 149 (10), 91 (14), 69 (20), 52 (61) [^{52}Cr]. – MS (ESI, ES^-): *m / z* = 508.8 [M^-], 480.8 [M^- – CO], 424.8 [M^- – 3CO]. – HRMS (EI) $C_{11}H_4O_9F_6S_2$: calcd. 509.8606, found. 509.8608. – HRMS (ESI) $C_{10}H_4O_9F_6S_2$ [M–H]: calcd. 508.8528, found. 508.8531.

6.2 Tricarbonyl(3-trifluoromethansulfonyl-4-hydroxy-phenyl)chromium(0) Triflate (124)

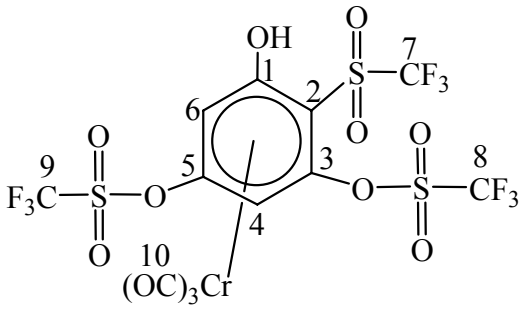


124

GP3, 400 mg (0.78 mmol) of **86**, 0.54 mL (0.86 mmol) of BuLi (1.6 M solution in hexane). 310 mg (0.61 mmol, 78 %) of **124** was obtained as an orange-red solid.

IR (ATR): $\tilde{\nu}$ = 3282 (w) cm^{-1}, 2961 (w), 2081 (w), 1981 (s, CO), 1896 (s, CO), 1714 (w), 1535 (m), 1485 (m), 1430 (m), 1378 (w), 1357 (w), 1259 (s), 1198 (s), 1119 (s), 1096 (s), 1040 (s), 904 (m), 852 (s), 795 (s), 746 (w), 703 (w), 664 (w), 632 (w). – ^1H NMR (400.1 MHz, [D6]acetone): δ = 4.53 (d, *J* = 7.8 Hz, 1H, 6-H), 5.30 (d, *J* = 6.0 Hz, 1H, 3-H), 6.02 (d, *J* = 6.1 Hz, 1H, 5-H), 7.34 (br. 1H, OH) – ^{13}C NMR (100.6 MHz, [D_6]acetone, DEPT, HMQC): δ = 73.8 (–, C-6), 79.8 (+, C-3), 96.6 (–, C-5), 100.8 (–, C-2) 102.8 (+, C-1), 120.6 (+, $^1J_{C\text{-}F}$ = 320.0 Hz, C-8), 122.3 (+, $^1J_{C\text{-}F}$ = 326.9 Hz, C-7), 137.3 (+, C-4), 234.4 (+, C-10). – MS (70 eV): m/z (%) = 374 (33) [M^+ – $Cr(CO)_3$], 355 (15) [M^+ – $Cr(CO)_3$ – OH], 293 (15), 255 (16), 242 (20), 220 (28), 193 (16), 149 (25), 109 (56), 97 (94), 75 (97), 64 (100), 52 (98) [^{52}Cr]. – HRMS $C_8H_4O_6F_6S_2$: calcd. 373.9354, found. 373.9353.

6.3 Tricarbonyl(3-trifluoromethansulfonyl-4-hydroxy-phenyl)chromium(0) Triflate (125)



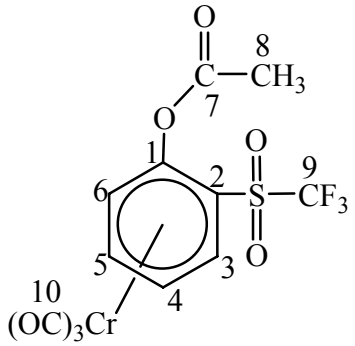
125

GP3, 900 mg (1.37 mmol) of **88**, 1.28 mL (2.05 mmol) of BuLi (1.6 M solution in hexane). 595 mg (0.90 mmol, 66 %) of **125** was obtained as a red solid, m. p. 132°C (decomp.).

IR (ATR): $\tilde{\nu}$ = 3282 (w) cm^{-1}, 2961 (w), 2124 (w), 1957 (s, CO), 1875 (s, CO), 1720 (w), 1598 (m), 1537 (m), 1510 (m), 1416 (w), 1378 (w), 1340 (w), 1262 (w), 1186 (s), 1120 (s), 1060 (m), 920 (m), 778 (w), 764 (w), 721 (w), 676 (w), 633 (w). – ^{1}H NMR (400.1 MHz, [D6]acetone): δ = 4.53 (d, *J* = 7.8 Hz, 1H, 6-H), 5.30 (d, *J* = 6.0 Hz, 1H, 6-H), 6.02 (d, *J* = 6.1 Hz, 1H, 4-H), 7.34 (br.1H, OH) – ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT, HMQC): δ = 73.8 (–, C-6), 79.8 (+, C-2), 96.6 (–, C-4), 102.6 (+, C-3), 102.9 (+, C-5), 120.6 (+, q, $^{1}J_{C\text{-}F}$ = 320.0 Hz, C-8), 120.9 (+, q, $^{1}J_{C\text{-}F}$ = 320.2 Hz, C-9), 122.3 (+, q, $^{1}J_{C\text{-}F}$ = 326.9 Hz, C-7), 137.3 (+, C-1), 234.4 (+, C-10). – MS (70 eV): *m/z* (%) = 430 (21), 418 (18), 387 (22), 361 (9), 334 (47), 298 (22), 282 (34), 255 (100), 239 (87), 122 (37), 108 (34), 80 (42), 69 (56), 52 (88) [^{52}Cr].

7. Enantioselective *ortho*-Deprotonation of Tricarbonyl(phenyltriflate) chromium(0) (93)

7.1.1 Tricarbonyl(2-trifluoromethansulfonylphenylacetate)chromium(0) (134)



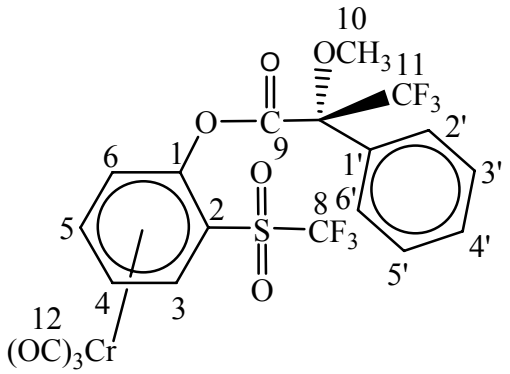
134

The mixture of 180 mg (0.50 mmol) of **93** and 14 mg (0.58 mmol) of NaH in 8 mL THF was stirred for 5 min. 393 mg (0.50 mmol) of acetyl chloride was added and refluxed for 2.5 h. After the reaction cooling down, the crude product was purified by Flash chromatography, eluting with *tert*-butylmethyl ether. 121 mg (0.30 mmol, 60 %) of **134** was obtained as an orange-yellow solid, m.p. 97 °C.

IR (ATR): $\tilde{\nu}$ = 3099 (w) cm^{-1}, 2963 (w), 2004 (m), 1989 (m), 1960 (m), 1936 (s, CO), 1923 (s, CO), 1790 (m), 1774 (m), 1589 (w), 1504 (w), 1473 (w), 1429 (w), 1409 (w), 1365 (s), 1261(w), 1218(s), 1196 (s), 1147 (s), 1133 (s), 1116 (s), 1091 (s), 1061 (s), 1004 (w), 911 (w), 887 (w), 873 (m), 835 (m), 823 (m), 801 (m), 734 (m), 715 (w), 698 (w), 674 (w), 653 (w), 636 (w), 609 (w). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.30 (s, 3H, 8-H), 5.48 (d, *J* = 6.5 Hz, 1H, 6-H), 5.85 (d, *J* = 6.5 Hz, 1H, 3-H), 6.38 (d, *J* = 6.5 Hz, 1H, 4-H), 6.43 (t, *J* = 6.2 Hz, 1H, 5-H). – ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT, HMQC): δ = 21.5 (–, C-8), 86.7 (–, C-6), 87.4 (–, C-3), 97.7 (–, C-4), 98.3 (–, C-5), 120.0 (+, q, $^{1}J_{C\text{-}F}$ = 325.5 Hz, C-9), 133.6 (+, C-2), 152.6 (+, C-1), 169.6 (+, C-7), 229.8 (+, C-10). – MS (70 eV): *m/z* (%) = 404 (57) [M^+], 348 (78) [M^+ – 2CO], 320 (63) [M^+ – 3CO], 277 (65) [M^+ – 3CO – $COCH_3$], 261 (12), 251 (52),

227 (11), 206 (53), 187 (100), 163 (52), 144 (51), 135 (34), 111 (58), 90 (37), 80 (28), 69 (38), 52 (69) [^{52}Cr]. – HRMS ($C_{12}H_7O_7F_3SCr$) calcd. 403.9270, found. 403.9268.

7.1.2 Tricarbonyl(2-trifluoromethansulfonylphenyl-α-methoxy-α-trifluoro-methylphenylacetate)chromium(0) (135)



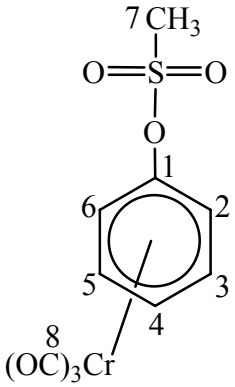
135

The mixture of 510 mg (0.14 mmol) of (+)-**93** and 3.7 mg (0.16 mmol) of NaH in 4 mL THF was stirred for 5 min. 35.1 mg (0.026 mL, 0.14 mmol) of Mosher's reagent (–) MTPA-Cl [R-(–)-α-methoxy-α-(trifluoromethyl)phenyacetatechloride] (**133**) was added and refluxed for 2h. After the reaction cooling down, the crude product was purified by flash chromatography, eluting with *tert*-butylmethyl ether. The ratio of diasteromere is 2:1 (30 % *ee*) calculated by the integration of NMR. The minor isomer is labelled with b. 0.67 mg (0.12 mmol, 83 %) of **135** was obtained as orange-yellow oil.

IR (ATR): $\tilde{\nu}$ = 3095 (br) cm^{-1}, 2963 (w), 2003 (s, CO), 1935 (s, CO), 1777 (m), 1640 (w), 1590 (w), 1499 (w), 1474 (w), 1451 (w), 1428 (w), 1374 (m), 1260 (s), 1202 (s), 1168 (s), 1096 (s), 1016 (s), 1116 (s), 964 (m), 949 (m), 920 (w), 799 (s), 764 (m), 729 (m), 696 (m), 641 (m), 605 (m). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 3.68 (s, 3H, 9-H), 3.72 (s, 9-Hb), 5.56 (t, *J* = 6.3 Hz, 4-Hb, 5-Hb), 5.79 (d, *J* = 6.6Hz, 3-Hb), 5.95 (d, *J* = 6.8 Hz, 6-Hb), 6.42-6.50 (m, 4H, 3-H, 4-H, 5-H, 6-H), 7.53-7.59 (m, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H). – ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 57.0 (–, C-

10b), 57.3 (–, C-10), 85.3 (–, C-6b), 85.5 (–, C-6), 87.8 (–, C-3), 87.9 (–, C-3b), 97.6 (–, C-4), 97.7 (–, C-4b), 98.0 (–, C-5), 98.1(–, C-5b), 121.2 (+, q, $^{1}J_{C\text{-}F}$ = 325.5 Hz, C-7), 121.4 (+, q, $^{1}J_{C\text{-}F}$ = 325.7 Hz, C-7b), 124.7(+, q, $^{1}J_{C\text{-}F}$ = 288.0 Hz, C-11), 124.6 (+, q, $^{1}J_{C\text{-}F}$ = 288.1 Hz, C-11b), 128.0 (–, C-4b´), 129.2 (–, C-4´), 130.2 (–, C-3´, C-5´), 130.3 (–, C-3b´, C-5b´), 131.7 (–, C-2´), 131.9 (–, C-2b´), 132.0 (+, C-1b´), 132.5 (+, C-1´), 133.3 (–, C-6´), 133.4 (–, C-6b´), 151.6 (+, C-1), 166.4 (+, C-8b), 166.5 (+, C-8), 229.1 (+, C-12b), 229.3 (+, C-12) . – MS (70 eV): m/z (%) = 522 (18) [M^{+} – 2CO], 494 (98) [M^{+} – 3CO], 466 (90), 446 (15), 425 (16), 361 (25), 308 (13), 296 (95), 277 (45), 189 (100), 170 (83), 139 (68), 119 (64), 105 (70), 92 (62), 77 (63), 52 (69) [^{52}Cr]. – HRMS ($C_{17}H_{12}O_5F_6SCr$) calcd. 493.9715, found. 493.9710.

7.1.3 Tricarbonyl(phenylmesylate)chromium(0) (136):



136

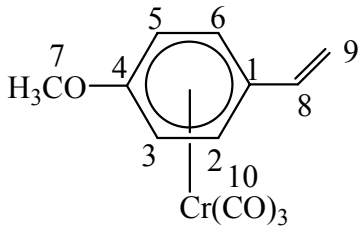
In a Schlenk flask, tetraethylammonium (phenolato)tricarbonylchromate (**139**)[109] (3.0 g, 8.32 mmol) was dissolved in THF (50 mL) and methanesulfonyl chloride (0.95 g, 8.32 mmol) was added dropwise under argon at –78 °C. Then the reaction mixture was warmed to room temperature and stirred for 3 h. After the solvents removal in *vacuo*, the crude product was purified by column chromatography (200 x 20 mm, TBME). 1.85 g (5.99 mmol, 72 %) of **136** was obtained as yellow solid, m. p. 78 °C.

IR (ATR): $\tilde{\nu}$ = 3098 (w) cm^{-1}, 3016 (w), 1960 (s, CO), 1863 (s, CO), 1507 (w), 1453 (w), 1420 (w), 1370 (m), 1357 (m), 1328 (m), 1197 (w), 1160 (m), 1151 (m), 1011

(w), 997 (m), 878 (w), 851 (m), 814 (m), 782 (m), 718 (m), 679 (w), 653 (m), 622 (m). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.45 (s, 3H, 7-H), 5.41 (m, 1H, 4-H), 5.85 [s, 2H, 2(6)-H], 5.88 [s, 2H, 3(5)-H] ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 38.8 (–, C-7), 89.0 [–, C-2(6)], 92.1 (–, C-4), 95.7 [–, C-3(5)], 132.6 (+, C-1), 233.8 (+, C-8) ppm. – MS (70 eV): *m/z* (%) = 308 (22) [M^+], 252 (28) [M^+ – 2CO], 224 (21) [M^+ – 3CO], 176 (26), 160 (45), 145 (100), 96 (24), 73 (27), 52 (79) [^{52}Cr]. – HRMS $C_{10}H_8O_6SCr$: calcd. 307.9447, found. 307.9448.

8. Cross-coupling Reactions of Arene Triflate Tricarbonylchromium Complexes

8.1 Tricarbonyl[(4-methoxy)vinylbenzene]chromium(0) (159)

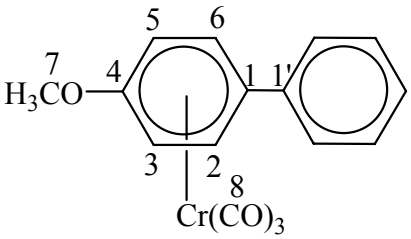


159

A solution of the tricarbonyl(4-methoxyphenyl)chromium(0) triflate**76** (196 mg, 0.50 mmol), 1 equivalent of vinyltributylstannane (159 mg, 0.50 mmol), 3 equivalents of LiCl (63.6 mg, 1.5 mmol), 2 mol % of $Pd(Ph_3P)_4$ (11.4 mg, 0.01 mmol) in THF (20 mL) was stirred under reflux for 18 h. Ether (20 mL) was added and the solution was washed with 10 % NaOH (10 mL), water (10 mL). Concentration in *vacuo* followed by column chromatography (200 x 20 mm, PE / TBME 2:1), 82.6 mg (0.23 mmol, 83 %) of η^6-(1-Phenyl-4-methoxybenzene)tricarbonylchromium(0) was obtained as yellow solid.

IR (ATR): $\tilde{\nu}$ = 3287 (w) cm^{-1}, 2362 (w), 2340 (w), 1951 (s, CO), 1849 (s, CO), 1703 (w), 1558 (w), 1565 (m), 1538 (m), 1485 (s), 1434 (s), 1367 (s), 1176 (m), 1009 (s), 922 (s), 816 (m), 790 (m), 708 (m), 670 (s), 624 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.70 (s, 3H, 7-H), 5.15 [d, *J* = 6.8 Hz, 2H, 3(5)-H], 5.18 (d, $^{3}J_{cis}$ = 10.9 Hz, 1H, *Z*-9-H), 5.55 (d, $^{3}J_{trans}$ = 17.3 Hz, 1H, *E*-9-H), 5.65 [d, *J* = 6.9 Hz, 2H, 2(6)-H], 6.18 [dd, $^{3}J_{cis}$ = 10.8 Hz, $^{3}J_{trans}$ = 17.4 Hz 1H, 8-H] ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 55.7 (–, C-7), 77.8 [–, C-3(5)], 92.5 [–, C-2(6)], 98.9 (+, C-1), 114.7 (+, C-9), 132.6 (–, C-8), 142.5(+, C-4), 232.8 (+, C-10) ppm. – MS (70 eV): *m/z* (%) = 270 (25) [M^+], 214 (11) [M^+ – 2CO], 186 (100) [M^+ – 3CO], 171 (22), 134 (18) [M^+ – 3CO – Cr], 119 (8), 91 (10), 57 (7), 52 (73) [^{52}Cr]. – HRMS $C_{10}H_8O_6SCr$: calcd. 269.9984, found. 269.9983.

8.2 Tricarbonyl(1-phenyl-4-methoxybenzene)chromium(0) (160)



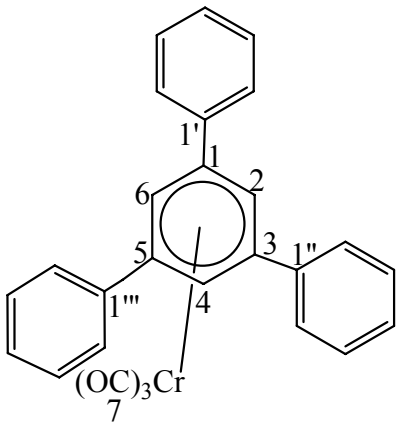
160

A solution of the tricarbonyl(4-methoxyphenyl)chromium(0) triflate **76** (118 mg, 0.30 mmol), benzeneboronic acid (36.6 mg, 0.30 mmol), 1.5 equivalents of Na_3PO_4 (70.0 mg, 0.45 mmol), 2 mol % of $Pd(Ph_3P)_4$ (6.9 mg, 0.006 mmol) in THF (15 mL) was stirred under reflux for 30 h. Ether (20 mL) was added and the solution was washed with 10 % NaOH (10 mL), water (10 mL). Concentration in *vacuo* followed by column chromatography (200 x 20 mm, PE / TBME 2:1), 82.6 mg (0.23 mmol, 86 %) of **160** was obtained as yellow solid.

IR (ATR): $\tilde{\nu}$ = 3382 (w) cm^{-1}, 3095 (w), 3033 (w), 2951 (w), 2835 (w), 2063 (w), 1954 (s, CO), 1867 (s, CO), 1659 (w), 1606 (w), 1532 (w), 1509 (s), 1465 (s), 1434

(s), 1360 (w), 1298 (w), 1223 (s), 1178 (w), 1110 (m), 1021 (s), 1002 (w), 867 (w), 823 (s), 766 (m), 733 (w), 693 (w), 666 (s), 625 (m). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.73 (s, 3H, 7-H), 5.24 [d, *J* = 6.2 Hz, 2H, 3(5)-H], 5.92 [d, *J* = 6.3 Hz, 2H, 2(6)-H], 7.36-7.47 (m, 5H, Ph-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 55.8 (–, C-7), 77.7 [–, C-3(5)], 94.6 [–, C-2(6)], 103.7 (+, C-1), 95.7 [–, C-3(5)], 126.9 [–, C-2'(5')], 128.6 (–, C-4'), 128.7 [–, C-3'(5')], 136.1 (+, C-1'), 142.6 (+, C-4), 233.0 (+, C-8) ppm. – MS (70 eV): *m/z* (%) = 320 (45) [M^+], 264 (23) [M^+ – 2CO], 236 (100) [M^+ – 3CO], 221 (20), 184 (23) [M^+ – $Cr(CO)_3$], 169 (11), 141 (13), 115 (18), 52 (81) [^{52}Cr]. – HRMS $C_{10}H_8O_6SCr$: calcd. 320.0141, found. 320.0139.

8.3 Tricarbonyl(1,3,5-triphenylbenzene)chromium(0) (161)



161

A solution of the tricarbonyl(1,3,5-trihydroxylbenzene)chromium(0) tris(triflate) (**88**) (200 mg, 0.30 mmol), 3.3 equivalents of benzeneboronic acid (120.7 mg, 0.99 mmol), 4.5 equivalents of Na_3PO_4 (210 mg, 1.35 mmol), 3.3 mol % of $Pd(Ph_3P)_4$ (11.4 mg, 0.01 mmol) in THF (20 mL) was stirred under reflux for 48 h. Ether (20 mL) was added and the solution was washed with 10 % NaOH (10 mL), water (10 mL). Concentration in *vacuo* followed by column chromatography (200 x 20 mm, PE / TBME 1:1), 117 mg (0.26 mmol, 87 %) of **161** was obtained as yellow solid.

IR (ATR): $\tilde{\nu}$ = 2963 (w) cm^{-1}, 2364 (w), 1939 (s, CO), 1880 (s, CO), 1658 (w), 1594 (w), 1534 (w), 1490 (w), 1410 (w), 1259 (s), 1159 (w), 1078 (s), 1012 (s), 867 (w),

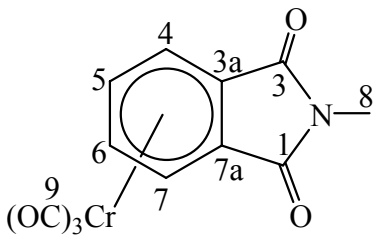
792 (s), 762 (s), 792 (m), 695 (m), 695 (m), 656 (w), 629 (w), 611 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 6.10 [s, 3H, 2(4,6)-H)], 7.46-7.495.41 (m, 15H, Ph-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 91.2 [–, C-2(4,6)], 110.3 [+, C-1(3,5)], 127.5 (–, C-Ph), 136.8 [+, C-1'(1'', 1''')], 132.6 (+, C-1), 232.6 (+, C-7) ppm. – MS (70 eV): *m/z* (%) = 442 (15) [M^+], 414 (23) [M^+ – CO], 386 (96) [M^+ – 2CO], 358 (100) [M^+ –3CO], 334 (43), 306 (100) [M^+ – 3CO – Cr], 282 (25), 228 (20), 105 (18), 77 (13), 52 (83) [^{52}Cr].

9. *N*-substituted phthalimide Tricarbonylchromium Complexes

9.1 General Procedure for the Synthesis of *N*-substituted phthalimide Tricarbonylchromium Complexes (GP4)

The phthalimide and 1.1 equiv. of hexacarbonylchromium in dibutyl ether and THF (10:1) are heated at reflux for 20 h to 40 h. After cooling to 25 °C, the reaction mixture is carefully filtered through a P4 frit covered with a 2 cm thick layer of silica gel. The solvents are removed at reduced pressure, and the crude product is purified by flash chromatography at SiO_2, eluting with TBME / PE (1:1 to 4:1). The tricarbonylchromium phthalimide complexes are obtained as red solids, which are moderate air stable.

9.1.1 Tricarbonyl(*N*-methylphthalimide)chromium(0) (171)

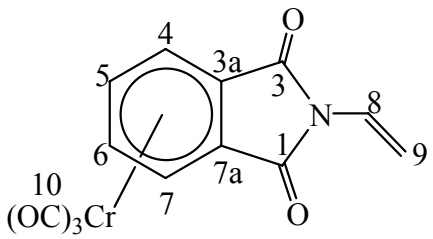


171

GP4. 1.18 g (7.3 mmol) methylphthalimide (**170**)[139] and 1.77g (8.1 mmol) hexacarbonylchromium in 60 mL of Bu_2O and 6 mL of THF were heated under Argon at reflux for 35 h. After filtration and solvent removal at reduced pressure, the reaction mixture was separated by column chromatography (200 x 20 mm, PE / TBME 1:3) to yield 1.25 g (4.25 mmol, 58 %) of **171** as a deep red solid, m. p. 196 °C (decomp).

IR (ATR): $\tilde{\nu}$ = 3082 (w) cm^{-1}, 2961 (w), 1974 (s, CO), 1894 (s, CO), 1761 (m), 1698 (s), 1432 (m), 1371 (m), 1249 (w), 1203 (w), 1141 (w), 1080 (w), 1005 (m), 954 (w), 846 (w), 799 (w), 751 (w), 703 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.13 (s, 3H, 8-H), 5.52 [s, 2H, 5(6)-H], 6.05 [s, 2H, 4(7)-H] ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 24.5 (–, C-8), 87.3 [–, C-5(6)], 90.6 [–, C-4(7)], 90.8 [+, C-3a(7a)], 167.2 [+, C-1(3)], 228.9 (+, C-9) ppm. – MS (70 eV): *m/z* (%) = 297 (53) [M^+], 241 (20) [M^+ – 2CO], 213 (97) [M^+ –3CO], 161 (25) [M^+ – $Cr(CO)_3$], 117 (10), 104 (12), 76 (19), 52 (100) [^{52}Cr]. – HRMS $C_{12}H_7NO_5Cr$: calcd. 296.9729, found. 296.9727.

9.1.2 Tricarbonyl(*N*-vinylphthalimide)chromium(0) (173)

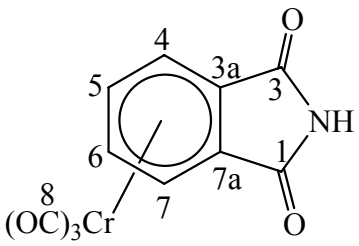


173

GP4. 320 mg (1.9 mmol) vinylphthalimide (**172**)[140] and 450 mg (2.0 mmol) hexacarbonylchromium in 40 mL of Bu_2O and 4 mL of THF were heated under Argon at reflux for 24 h. After filtration and solvent removal at reduced pressure, the reaction mixture was purified by column chromatography (200 x 20 mm, PE / TBME 1:2) to yield product **173** 278 mg (0.85 mmol, 45 %) as a deep red solid, m. p. 204 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 3088 (w) cm^{-1}, 1980 (s, CO), 1894 (s, CO), 1771 (m), 1711 (s), 1635 (w), 1526 (w), 1425 (w), 1401 (w), 1367 (s), 1306 (m), 1225 (m), 1167 (m), 1139 (m), 1079 (w), 1016 (m), 984 (w), 899 (w), 873 (m), 831 (m), 757 (w), 718 (m), 698 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.07 (d, $^2J_{cis}$ = 9.8 Hz, 1H, 9-H), 5.46 [dd, *J* = 2.5 Hz, 2H, 5(6)-H], 6.03 [m, 3H, 4(7)-H, 9-H], 6.75 (m, 1H, 8-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 87.2 [–, C-5(6)], 89.6 [+, C-3a(7a)], 90.8 [–, C-4 (7)], 105.9 (+, C-9), 123.3 (–, C-8), 165.6 [+, C-1(3)], 228.5 (+, C-10) ppm. – MS (70 eV): *m/z* (%) = 309 (45) [M^+], 253 (32) [M^+ – 2CO], 225 (83) [M^+ – 3CO], 209 (46), 173 (33) [M^+ – $Cr(CO)_3$], 154 (13), 129 (8), 108 (10), 97 (35), 80 (28), 69 (63), 52 (100) [^{52}Cr]. – HRMS $C_{13}H_7NO_5Cr$: calcd. 308.9729, found. 308.9729.

9.1.3 Tricarbonyl(phthalimide)chromium(0) Complexe (175)

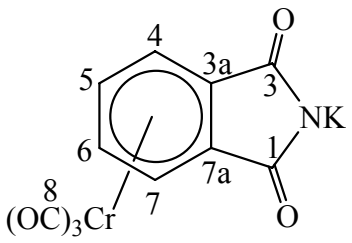


175

GP4. 1.00 g (6.80 mmol) of phthalimide (**174**) and 1.65 g (7.48 mmol) of hexacarbonylchromium in 60 ml Dibuthylether und 6 ml THF were heated at reflux for 40 h. Purificationby flash chromatography (200 x 20 mm, PE / TBME 1:3, then TBME) to yield product 1.27 g (4.5 mmol, 66 %) as a red solid, m.p. 204 °C (decomp.).

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.19 (s, 1H, N-H); 5.54 [s, 2H, 5(6)-H], 6.03 [s, 2H, 4(7)] – LC-MS (ESI): *m/z* = 282 [M^-], 254 [M^- – CO], 226 [M^- – 2CO], 198 [M^- – 3CO], 146 [M^- – $Cr(CO)_3$], 113, 97. HRMS (ESI) $C_{11}H_5NO_5Cr$ [– H]: calcd. 281.9495, found. 281.9498.

9.1.4 Tricarbonyl(potassiumphthalimide)chromium(0) Complexe (176)



176

0.50 g (1.8 mmol) of tricarbonyl(phthalimide)chromium complex (**175**) was dissolved in 5.2 ml ethanol at 50 °C. The solution of 0.10 g (1.8 mmol) of potassiumhydroxid in 5.6 ml ethanol was added dropwise and stirred for 2 h at 50 °C, the colour of the solution changing from red to orange. The mixture was cooled to 25 °C and the orange solid precipitated in the solution. After filtration, 0.54 g (1.7 mmol, 93 %) of **176** was obtained as orange air stable solids.

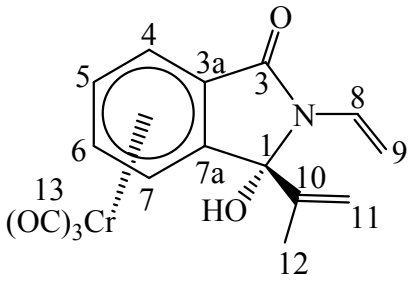
LC-MS (ESI): ($C_{11}H_4NO_5CrK$) [+H]: calcd.321.9130, found. 321.9133

9.2 General Procedure for the Nucleophilic Addition to *N*-substituted Phthalimide Tricarbonylchromium Complexes (GP5)

A solution of the complex in THF / Et_2O was added dropwise at –78 °C to a cooled the solution (–78 °C) of the nucleophile in THF or Et_2O. After the mixture was stirred for 2 to 16 h at –78 °C till TLC indicated no starting material, the reaction was hydrolyzed by addition of either saturated aqueous NH_4Cl or 1 M HCl at –78 °C. The color of the reaction mixture was changed from red to yellow or orange. The reaction was allowed to warm up to 20 °C, and extracted with portions of ethyl acetate (15 mL) till the aqueous layer remained colorless. The collected organic layers were washed with water and dried over $MgSO_4$, filtered through P4-frit cover with 2 cm thick layer

of silica gel. After the solvent removal of at reduced pressure, the crude product was purified by flash chromatography (200 x 20 mm, TBME / PE or ethyl acetate).

9.2.1 Tricarbonyl[1-hydroxy-1-(1-methylethenyl)-*N*-vinylphthalimide]-chromium(0) (191)



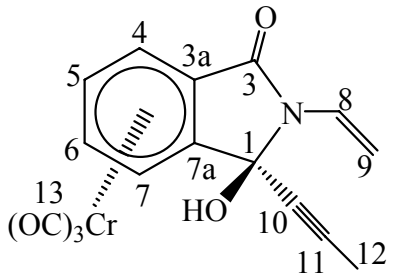
191

GP5, In the mixture of 25 mg (3.58 mmol) of lithium sand in 10 mL of diethyl ether was added 279 mg (2.31 mmol) of 2-bromopropene dropwise and heated at reflux for 2 h. Then the solution of 2-lithiopropene was cooled at – 78 °C, 143 mg (0.46 mmol) of complex **173** in 10 mL of THF was added dropwise, stirring for 2 h at –78 °C. After hydrolysis with 10 mL of 1 M hydrochloric acid, the mixture was extracted three times with ethyl acetate. The crude products were purified by column chromatography (200 x 20 mm), eluted with PE/TBME, 1:1 to 1:2), 65 mg (0.18 mmol, 40 %) of **191** was obtained as a yellow solid, m.p. 113 °C (dec.); eluted with ethyl acetate, 79 mg (0.22 mmol, 48 %) of **192** was obtained as red solid, single crystals for X-ray analysis were obtained by recrystallization in CH_2Cl_2 / hexane (5:1), m. p. 182 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 3368 (w, OH) cm^{-1}, 3249 (w), 2951 (w), 1960 (s, CO), 1884 (s, CO), 1721 (w), 1675 (m), 1638 (m), 1586 (w), 1571 (w), 1538 (w), 1511 (w), 1445 (w), 1408 (w), 1317 (m), 1260 (w), 1215 (w), 1175 (m), 1117 (m), 1022 (m), 996 (m), 914 (w), 865 (w), 831 (w), 831 (w), 797 (w), 770 (w), 737 (w), 713 (w), 682 (w). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.47 (s, 3H, 12-H), 4.58 (d, $^3J_{cis}$ = 9.8 Hz, 1H, *Z*-9-H), 5.20 (d, $^3J_{trans}$ = 16.4 Hz, 1H, *E*-9-H), 5.33 (m, 1H, *E*-11-H or *Z*-11-H), 5.16 (s,

1H, OH), 5.79-5.82 (m, 3H, 5-H, 6-H, *E*-11-H or *Z*-11-H), 5.97-6.01 (m, 2H, 4-H, 7-H), 6.70 (m, 1H, 8-H) ppm. – ^{13}C NMR (100.6 MHz, [D$_6$]acetone, HMQC): δ = 18.6 (–, C-12), 86.7 (–, C-4 or C-7), 89.5 (–, C-4 or C-7), 91.6 (+, C-1), 93.3 (–, C-5 or C-6), 95.2 (–, C-5 or C-6), 97.0 (+, C-3a), 99.3 (+, C-9), 117.1 (+, C-11), 119.4 (+, C-7a), 127.2 (–, C-8), 144.3 (+, C-10), 165.7 (+, C-3), 233.1 (+, C-13) ppm. – MS (70 eV, 115 °C): *m/z* (%) = 351 (34) [M$^+$], 295 (43) [M$^+$ – 2CO], 267 (87) [M$^+$ – 3CO], 249 (71), 239 (20), 221 (43), 208 (11), 198 (91), 182 (30), 173 (14), 154 (18), 128 (18), 115 (22), 91 (13), 77 (22), 69 (29), 52 (100) [^{52}Cr]. – HRMS $C_{16}H_{13}NO_5Cr$: calcd. 351.0199, found. 351.0199.

9.2.2 Tricarbonyl[1-*exo*-hydroxy-1-*endo*-(1-propyl)-*N*-vinylphthalimide]-chromium(0) (192)



192

b)GP5, To the solution of 130 mg (1.1 mmol) of 1-bromo-1-propene in 8 mL THF was added 1.03 mL (0.64 mmol) of butyllithium (1.6 M in hexane) at –78 °C, stirring at –78 °C for 2 h. 83 mg (0.27 mmol) of **173** in 10 mL of THF was added at – 78 °C, stirred for 18 h at –78 °C, hydrolysis with 5 mL 1 M hydrochloric acid, extracted three times with ethyl acetate, purified by column chromatography (200 x 20 mm, PE / TBME, 1:3, then ethyl acetate). 84 mg (0.23 mmol, 89 %) of **192** was obtained as red-orange solid, single crystals for X-ray were obtained by recrystallization in CH_2Cl_2 / hexane (5 : 1), m.p. 182 °C (decomp.).

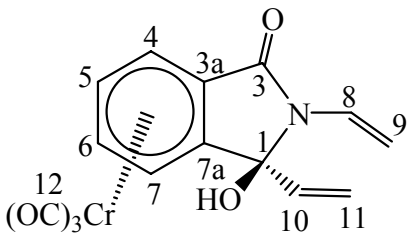
IR (ATR): $\tilde{\nu}$ = 3320 (w, OH) cm^{-1}, 2960 (w), 2926 (w), 2856 (w), 1975 (s, CO), 1907 (s, CO), 1702 (s), 1610 (w), 1468 (w), 1379 (w), 1260 (m), 1191 (w), 1096 (m),

1017 (m), 798 (m), 762 (w), 740 (w), 696 (w). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.94 (s, 3H, 12-H), 4.76 (d, $^{3}J_{cis}$ = 9.8 Hz, 1H, *Z*-9-H), 5.49 (d, $^{3}J_{trans}$ = 16.4 Hz, 1H, *E*-9-H), 5.78 (m, 2H, 5-H, 6-H), 5.97 (m, 1H, 4-H or 7-H), 6.28 (m, 1H, 4-H or 7-H), 6.60 (s, 1H, OH), 6.70 (dd, $^{3}J_{cis}$ = 9.8 Hz, $^{3}J_{trans}$ = 16.9 Hz, 1H, 8-H) ppm. – ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 4.02 (–, C-12), 76.5 (+, C-1), 83.7 (+, C-10), 86.4 (+, C-11), 87.1 (–, C-4), 90.5 (–, C-7), 93.8 (–, C-5), 95.2 (–, C-6), 95.5 (+, C-3a), 100.6 (+, C-9), 117.7 (+, C-7a), 126.9 (–, C-8), 164.8 (+, C-3), 232.8 (+, C-13) ppm. – MS (70 eV): *m/z* (%) = 349 (28) [M$^+$], 309 (38), 293 (24) [M$^+$ – 2CO], 265 (54) [M$^+$ –3CO], 247 (55), 237 (35), 225 (62), 213 (19) [M$^+$ – Cr(CO)$_3$], 196 (61), 167 (77), 149 (58), 130 (25), 115 (59), 104 (50), 89 (24), 76 (55), 52 (100) [^{52}Cr]. – HRMS $C_{16}H_{11}NO_5Cr$: calcd. 349.0042, found. 349.0042.

X-Ray Structure Analysis of **192**

C_{16} H_{11} Cr N O_5, molecular weight 349.26, crystal system triclinic, space group P–1, a = 6.970(1) Å α = 103.15(2)°, *b* = 9.211(3) Å, β = 105.27(2)°, *c* = 12.608(3) Å γ =91.74(2)°, *V* = 756.9(3) Å^3, *Z* = 2, $d_{calcd.}$ = 1.533 g/cm^3, F(000) = 356e, μ = 0.780 mm^{-1}, crystal color red, Stoe IPDS (Area Detector) diffractometer, *T* = 300(2) K, λ ($Mo_{K\alpha}$) = 0.71073 Å, θ_{min} = 2.28°, θ_{max} = 26.25°, -8≤ h≤8, -11≤ k≤11, -15≤ l≤15, no absorption correction, no extinction correction, 10788 collected, 2787 unique reflections, [*R*(int) = 0.1234], refinement program: SHELXL-93, refinement by full-matrix least squares method (F^2), *S* = 0.846, *R*-Indices: [I>2 σ(I)] R_1 = 0.0527, wR_2 = 0.0707, *R*-Indices (all data): R_1 = 0.1736 , wR_2 = 0.0870, min., max. residual electron density: –0.523, 0.365 Å^{-3}, completeness of data 93 %.

9.2.3 Tricarbonyl(1-hydroxy-1-vinyl-*N*-vinylphthalimide)chromium(0) (207)

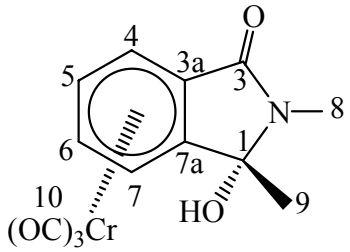


207

GP5, To the cooled solution of 210 mg (0.68 mmol) of **173** in 15 mL of THF was added 1.36 mL (1.36 mmol) of vinylmagnisiumbromide (1.0 M in THF) at –78 °C, stirring for 2 h, extracted three times with ethyl acetate, purified by column chromatography (200 x 20 mm, TBME). 161 mg (0.48 mmol, 70 %) of **207** as orange-yellow solid, m. p. 151 °C.

IR (ATR): $\tilde{\nu}$ = 3285 (w, OH) cm^{-1}, 2360 (w), 2118 (w), 1972 (s, CO), 1884 (s, CO), 1707 (w), 1673 (m), 1637 (w), 1521 (w), 1432 (w), 1400 (w), 1382 (w), 1347 (m), 1262 (w), 1188 (w), 1166 (m), 1068 (w), 1033 (w), 1012 (w), 984 (w), 942 (w), 865 (m), 825 (w), 775 (w), 722 (w), 650 (s), 624 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.65 (d, $^{3}J_{cis}$ = 9.9 Hz, 1H, *Z*-9-H), 5.27 (d, $^{3}J_{trans}$ = 16.4 Hz, 1H, *E*-9-H), 5.59 (m, 1H, *E*-11-H or *Z*-11-H), 5.69 (m, 1H, *E*-11-H or *Z*-11-H), 5.87-5.94 (m, ABCD-System, 4H, 4-H, 5-H, 6-H, 7-H), 6.08 (m, 1H, 10-H), 6.31 (s, 1H, OH), 6.71 (dd, $^{3}J_{trans}$ = 17.0 Hz, $^{3}J_{cis}$ = 9.8 Hz, 1H, 8-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, HMQC): δ = 86.5 (–, C-5 or C-6 or C-7), 91.6 (–, C-4), 93.4 (–, C-5 or C-6 or C-7), 93.5 (+, C-1), 96.7 (–, C-5 or C-6 or C-7), 97.1 (+, C-3a), 100.6 (+, C-9), 115.5 (+, C-7a), 119.7 (+, C-11), 127.2 (–, C-8), 138.6 (–, C-10), 165.5 (+, C-3), 233.2 (+, C-12) ppm. – MS (70 eV, 110°C): *m/z* (%) = 337 (46) [M^+], 281 (41) [M^+ – 2CO], 253 (82) [M^+ – 3CO], 235 (67), 225 (42), 207 (54), 207 (20) [M^+ – $Cr(CO)_3$], 184 (87), 159 (80), 130 (57), 115 (33), 103 (57), 91 (11), 77 (75), 52 (100) [^{52}Cr]. – HRMS $C_{15}H_{11}NO_5Cr$: calcd. 337.0042, found. 337.0043.

9.2.4 Tricarbonyl[1-*endo*-hydroxy-1-*exo*-methyl-*N*-methylphthalimide]-chromium(0) (197)



197

GP5, To the cooled solution of 436 mg (1.5 mmol) of **171** in 15 mL of THF was added 4.5 mL (6.3 mmol) of methyllithium (1.0 M in THF) at –78 °C, stirring for 2 h, extracted three times with ethyl acetate, purified by column chromatography (200 x 20 mm, TBME). 373 mg (1.2 mmol, 81 %) of **197** as yellow solid, single crystals for X-ray were obtained by recrystallization in CH_2Cl_2 / hexane (1: 3), m. p. 158 °C (decomp.).

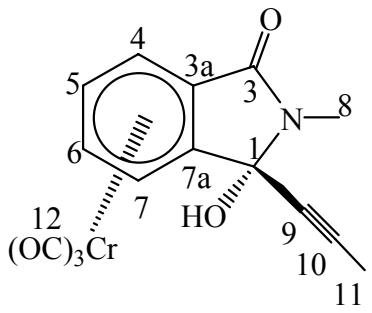
IR (ATR): $\tilde{\nu}$ = 3172 cm^{-1} (w, OH), 2982(w), 1952 (s, CO), 1869 (s, CO), 1669 (s), 1542 (w), 1482 (w), 1420 (m), 1373 (m), 1261 (w), 1225 (m), 1187 (w), 1151 (m), 1090 (m), 1074 (w), 1057 (w), 1027 (m), 949 (m), 806 (w), 774 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.77 (s, 3H, 9-H), 2.91 (s, 3H, 8-H), 5.50 (s, 1H, OH), 5.65-5.71 (m, 2H, 5-H, 6-H), 5.90 (d, *J* = 6.2 Hz, 1H, 4-H), 6.16 (d, *J* = 6.2 Hz, 1H, 7-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 24.7 (–, C-8), 26.7 (–, C-9), 87.7 (–, C-4), 88.4 (+, C-1), 90.2 (–, C-5), 93.5 (–, C-7), 95.4 (–, C-6), 99.5 (+, C-3a), 121.7 (+, C-7a), 166.2 (+, C-3), 234.0 (+, C-10) ppm. – MS (70 eV): *m/z* (%) = 313 (56) [M^+], 295 (10), 257 (23) [M^+ – 2CO], 230 (43) [M^+ –3CO], 211 (82), 201 (67), 213 (85), 201 (16) 171 (11), 160 (100), 146 (43), 130 (31), 117 (15), 103 (40), 91 (47), 77 (43), 52 (74) [^{52}Cr]. – HRMS $C_{13}H_{11}NO_5Cr$: calcd. 313.0042, found. 313.0042.

X-Ray Structure Analysis of **197**

C_{13} H_{11} Cr N O_5, molecular weight 313.25, crystal system monoclinic, space group P 21/c, a = 13.448(6) Å α = 90°, *b* = 6.432(2) Å, β = 105.29(6)°, *c* = 15.779(8) Å γ =90° *V* = 1316.5(10) $Å^3$, *Z* = 4, $d_{calcd.}$ = 1.580 g/cm^3, F(000) = 640e, μ = 0.887 mm^{-1},

crystal color red, crystal size 0.11 x 0.04 x 0.02 mm, Stoe IPDS (Area Detector) diffractometer, T = 300(2) K, λ ($Mo_{K\alpha}$) = 0.71073 Å, θ_{min} = 2.68°, θ_{max} = 24.53°, -15≤ h≤14, -7≤ k≤7, -17≤ l≤18, no absorption correction, no extinction correction, 6010 collected, 2117 unique reflections, [R(int) = 0.2967], refinement program: SHELXL-93, refinement by full-matrix least squares method (F^2), S = 0.839, R-Indices: [I>2 σ(I)] R_1 = 0.1055, wR_2 = 0.1488, R-Indices (all data): R_1 = 0.3936 , wR_2 = 0.2076, min., max. residual electron density: –0.331, 0.476 $Å^{-3}$, completeness of data 99.3 %.

9.2.5 Tricarbonyl[1-hydroxy-1-(1-propyl)-*N*-methylphthalimide]chromium(0) (208)



208

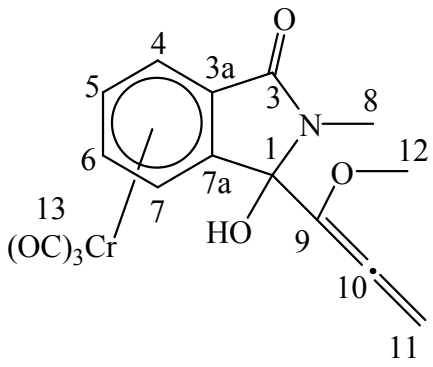
GP5, To the solution of 505 mg (4.2 mmol) of 1-bromo-1-propene in 10 mL THF was added 2.9 mL (1.8 mol) of butyllithium (1.6 M in hexane) at –78 °C, stirring at –78 °C for 2 h. 305 mg (1.03 mmol) of **171** in 15 mL of THF was added at – 78 °C, stirred for 2 h at –78 °C, hydrolysis with 20 mL methanol, extracted three times with ethyl acetate, purified by column chromatography (200 x 20 mm, PE / TBME, 1:4, then ethyl acetate). 306 mg (0.93 mmol, 90 %) of **208** was obtained as red-orange solid, m.p. 133 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 3435 cm^{-1} (w, OH), 2962 (w), 2253 (w), 2120 (w), 1969 (s, CO), 1881(s, CO), 1674 (m), 1544 (w), 1477 (w), 1415 (w), 1366 (w), 1259 (m), 1206 (s), 1165 (w), 1091 (m), 1015 (s), 943 (w), 908 (w), 874 (w), 796 (s), 764 (w), 698 (w), 670 (w), 652 (m), 619 (m). – ^{1}H NMR (400.1 MHz, [D_6]acetone): δ = 1.88 (s, 3H, 11-H), 2.95 (s, 3H, 8-H), 5.69-5.76 (m, 2H, 5-H, 6-H), 5.95 (m, 1H, 4-H or 7-H), 6.15 (m,

1H, 4-H or 7-H), 6.82 (s, 1H, OH) ppm. – ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 3.82 (–, C-11), 25.0 (–, C-8), 76.8 (+, C-1), 82.5 (+, C-9), 84.6 (+, C-10), 87.4 (–, C-4), 89.8 (–, C-7), 93.3 (–, C-5 or C-6), 94.4 (–, C-5 or C-6), 97.3 (+, C-3a), 119.1 (+, C-7a), 165.7 (+, C-3), 233.2 (+, C-8) ppm. – MS (70 eV): *m/z* (%) = 337 (45) [M^+], 297 (58) 281 (23) [M^+ – 2CO], 253 (63) [M^+ – 3CO], 235 (59), 225 (33), 213 (85), 201 (16) [M^+ – Cr(CO)$_3$], 184 (70), 161 (52), 128 (28), 117 (26), 104 (32), 91 (17), 77 (48), 52 (100) [^{52}Cr]. – HRMS $C_{15}H_{11}NO_5Cr$: calcd. 337.0042, found. 337.0042.

10. Palladium(0)-catalyzed Ring Expansion Reactions

10.1 Tricarbonyl[1-hydroxy-1-(1-methoxyallenyl)-*N*-methylphthalimide]-chromium(0) (215)

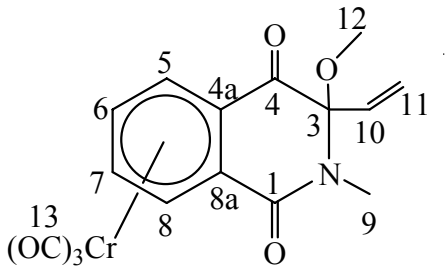


215

GP5, To a stirred solution of 127 mg (1.8 mmol) of methoxyallen in 5 mL diethyl ether under argon at –78 °C was added dropwise1.13 mL (1.8 mol) of butyllithium (1.6 M in hexanes), stirring at –78 °C for 2 h. 265 mg (0.89 mmol) of tricarbonylchromium methylphthalimde complex (**171**) in 10 mL of THF was added at –78 °C, stirring for 2 h, hydrolysis with 10 mL saturated aqueous NH_4Cl, extracted three times with ethyl acetate, purified by column chromatography (200 x 20 mm, PE / TBME, 1:2, then ethyl acetate). 301 mg (0.8 mmol, 92 %) of **215** was obtained as orange solid, m. p. 109 °C (decomp.).

IR (ATR): $\tilde{\nu}$ = 3421 cm^{-1} (w, OH), 2961 (w), 1974 (s, CO), 1881 (s, CO), 1678 (m), 1535 (w), 1392 (w), 1260 (w), 1096 (m), 1010 (m), 898 (w), 799 (m), 705 (w), 677 (w), 651 (m), 621 (m). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.84 (s, 3H, 8-H), 3.38 (s, 3H, 12-H), 5.62-5.70 [m, 2H, 5(6)-H], 5.76 (d, ^2J = 8.9 Hz, 1H, 11-H), 5.84 (d, ^2J = 8.9 Hz, 1H, 11-H), 5.95 (d, J = 6.1 Hz, 1H, 4-H), 6.06 (d, J = 6.2 Hz, 1H, 7-H), 6.09 (s, 1H, OH) ppm. – ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT): δ = 25.2 (–, C-8), 57.9 (–, C-12), 87.6 (–, C-7), 88.6 (+, C-1), 89.8 (–, C-4), 93.2 (–, C-6 or C-5), 94.5 (–, C-6 or C-5), 96.6 (+, C-11), 98.7 (+, C-3a), 118.9 (+, C-7a), 134.4 (+, C-9), 166.8 (+, C-3), 198.2 (+, C-10), 233.5 (+, C-13) ppm. – MS (70 eV, 130 °C): *m/z* (%) = 367 (24) [M^+], 311 (28) [M^+ – 2CO], 283 (94) [M^+ – 3CO], 265 (29), 251 (64), 235 (59), 214 (61), 199 (12), 182 (89), 162 (22), 143 (12), 127 (17), 115 (12), 77 (19), 52 (100) [^{52}Cr]. – HRMS $C_{13}H_{13}NO_3Cr$ calcd. 283.0300, found. 283.0301.

10.2 Tricarbonyl(*N*-methyl-3-methoxy-3-vinyl-2,3-dihydroisoquinoline-1,4-dione)chromium(0) (216)



216

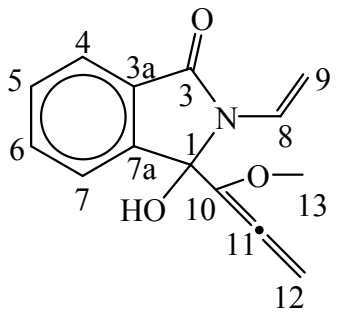
210 mg (0.6 mmol) of **215** were refluxed with 5 mol % of $Pd(PPh_3)_4$ (33 mg, 0.03 mmol), 3 equivalents of K_2CO_3 (236 mg, 1.71 mmol) in 15 ml of THF for 12 h, purified by column chromatography (200 x 20 mm, TBME, then ethyl acetate / PE, 2:1) to give160 mg (0.4 mmol, 76 %) of mixture of **216** in two isomers, *exo*-**216** : *endo*-**216** [methoxy group to $Cr(CO)_3$] is 4:1 (NMR). Red single crystals for X-ray were obtained by recrystallization in CH_2Cl_2 / hexane (3:1), m. p. 211 °C. Signals assigned to the minor isomer are marked with b

IR (ATR): $\tilde{\nu}$ = 3082 (w) cm^{-1}, 2962 (w), 2362 (w), 2120 (w), 1975 (s, CO), 1906 (s, CO), 1762 (w, C=O), 1681 (m, C=O), 1655 (m, C=O), 1432 (w), 1373 (w), 1258 (s), 1203 (w), 1071 (s), 1009 (s), 952 (w), 864 (w), 790 (s), 702 (w), 661 (w), 645 (m), 608 (w). – ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 2.97 (s, 3H, 9-H), 3.07 (s, 9-Hb), 3.21 (s, 12-Hb), 3.27 (s, 3H, 12-H), 5.45 (d, $^{3}J_{cis}$ = 10.4 Hz, 1H, *Z*-11-H), 5.46 (d, $^{3}J_{trans}$ = 17.3 Hz, 1H, *E*-11-H), 5.52 (d, $^{3}J_{cis}$ = 10.4 Hz, *Z*-11-Hb), 5.56 (d, $^{3}J_{trans}$ = 16.9 Hz, *E*-11-Hb), 5.85-5.92 (m, 6-H, 6-Hb, 10-H, 10-Hb), 5.98-5.60 (m, 5-Hb), 6.21-6.33 (m, 2H, 7-H or 8-H), 6.35-6.37 (m, 7b-Hb or 8b-Hb), 6.39-6.41 (m, 1H, 5-H) ppm. – ^{13}C NMR (100.6 MHz, [D$_6$]acetone, DEPT, HMQC): δ = 25.1 (–, C-9b), 29.3 (–, C-9), 52.5 (–, C-12b), 52.6 (–, C-12), 90.0 (+, C-3b), 90.3 (–, C-7b), 90.7 (–, C-7), 91.5 (+, C-3), 93.4 (–, C-6), 94.0 (+, C-4ab or C-8ab), 94.1 (–, C-5), 94.2 (+, C-4ab or C-8ab), 94.3 (–, C-5b), 94.8 (–, C-6b), 95.5 (+, C-4a or C-8a), 97.4 (+, C-4a or C-8a), 97.6 (–, C-8b), 98.5 (–, C-8), 120.8 (+, C-11b), 120.9 (+, C-11), 36.5 (–, C-10), 137.1(–, C-10b), 163.6 (+, C-1), 168.6 (+, C-1b),189.2 (+, C-4), 190.9 (+, C-4b), 231.6 (+, C-13), 231.9 (+, C-13b) ppm. – MS (70 eV): *m/z* (%) = 367 (34) [M^{+}], 283 (60) [M^{+} – 3CO], 253 (100), 238 (42), 225 (32), 200 (10), 77 (13), 68 (24), 128 (28), 52 (97) [^{52}Cr]. – HRMS $C_{16}H_{13}NO_6Cr$: calcd. 367.0148, found. 367.0148.

X-Ray Structure Analysis of **216a** and **216b**

$C_{128}H_{104}Cr8N8O_{48}$, molecular weight 2938.19, crystal system monoclinic, space group P 2 (1)/c, a = 16.020(3) Å α = 90°, b = 13.149(3) Å, β = 91.266(19)°, *c* = 14.835(2) Å γ =90° *V* = 3124.2(9) Å^3, *Z* = 1, $d_{calcd.}$ = 1.562 g/cm^3, F(000) = 1504e, μ = 0.765 mm^{-1}, crystal color red, diffractometer, *T* = 297K, λ ($Mo_{K\alpha}$) = 0.71073 Å, θ_{min} = 2°, θ_{max} = 24.24°, -18≤ h≤18, -15≤ k≤15, -16≤ l≤16, no absorption correction, no extinction correction, 35487 collected, 4954 unique reflections, [*R*(int) = 0.1144], refinement program: SHELXL-97, refinement by full-matrix least squares method (F^2), *S* = 1.052, *R*-Indices: [I>2 σ(I)] R_1 = 0.1058, wR_2 = 0.3326, *R*-Indices (all data): R_1 = 0.1584 , wR_2 = 0.3511, min., max. residual electron density: 1.159, –0.784Å^{-3}, completeness of data 98.2 %.

10.3 1-hydroxy-1-(1-methoxyallenyl)-*N*-vinylphthalimide (217)

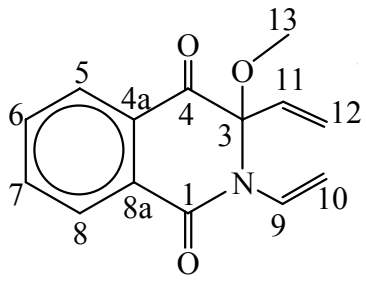


217

To a stirred solution of 250 mg (3.57 mmol) of methoxyallen in 7 mL diethyl ether was added dropwise 2.23 mL (3.57 mol) of butyllithium (1.6 M in hexanes) under argon at –78 °C, stirring at –78 °C for 2 h. 309 mg (1.78 mmol) of vinylphthalimde (**172**) in 12 mL of THF was added at –78 °C, stirring for another 3 h at –78 °C, hydrolysis with 10 mL saturated aqueous NH_4Cl, extracted three times with ethyl acetate, dried over $MgSO_4$, purified by column chromatography (200 x 20 mm, TBME, then ethyl acetate /PE, 2:1). 404 mg (1.66 mmol, 93 %) of **217** was obtained as colourless oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.30 (s, 3H, 13-H), 4.59 (d, $^3J_{cis}$ = 9.6 Hz, 1H, *Z*-9-H), 5.15 (d, $^3J_{trans}$ = 16.4 Hz, 1H, *E*-9-H), 5.80 (dd, *J* = 8.9, 8.6 Hz, 2H, 12-H), 6.68-6.77 (m, 1H, 8-H), 7.26 (s, 1H, OH), 7.42-7.62 (m, ABCD system , 4H, 4-H, 5-H, 6-H, 7-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT, HMQC): δ = 56.9 (–, C-13), 92.1 (+, C-1), 95.1 (+, C-11), 98.1 (+, C-9), 121.9 (–, C-4 or C-5 or C-6 or C-7), 123.7 (–, C-4 or C-5 or C-6 or C-7), 126.0 (–, C-8), 129.9 (–, C-4 or C-5 or C-6 or C-7), 132.9 (+, C-10), 133.0 (–, C-4 or C-5 or C-6 or C-7), 146.5 (+, C-3a or 7a), 147.1 (+, C-3a or 7a), 165.9 (+, C-3), 197.5 (+, C-11) ppm. – MS (70 eV): *m/z* (%) = 243 (8) [M^+], 228 (44), 212 (100), 198 (37), 184 (33), 174 (73), 163 (15), 155 (13), 147 (43), 130 (81), 115 (16), 102 (51), 91 (12), 76 (45), 63 (10).

10.4 *N*-vinyl-3-methoxy-3-vinyl-2,3-dihydroisoquinoline-1,4-dione (218)



218

a) The mixture of 650 mg (2.7 mmol) of hydroxy-(1-methoxyallenyl)-*N*-vinylphthalimide (**217**), 5 mol % of $Pd(PPh_3)_4$ (154.5 mg, 0.13 mmol) and 3 equivalents of K_2CO_3 (1.11 g, 8.0 mmol) in 20 mL of THF were heated at reflux for 24 h. After cooling down, the mixture was purified by column chromatography (200 x 20 mm, TBME / PE, 1.5:1) to give 480 mg (2.0 mmol, 74 %) of product as light yellow-brown oil.

b) A mixture of 210 mg (0.86 mmol) of hydroxy-(1-methoxyallenyl)-*N*-vinylphthalimide (**217**), 5 mol % of $Pd(PPh_3)_4$ (49.9 mg, 0.043 mmol) and 3 equivalents of K_2CO_3 (357 mg, 2.58 mmol) in 10 mL of THF were heated at 140 °C, 250W under Microwave irradation for 0.5 h. After cooling down, the mixture was purified by column chromatography (200 x 20 mm, TBME / PE, 1.5:1) to afford160 mg (0.7 mmol, 76 %) of **218** as light yellow-brown oil.

IR (ATR): $\tilde{\nu}$ = 2934 (w) cm^{-1}, 2863 (w), 2834 (w), 2359 (w), 2121 (w), 1703 (s, C=O), 1665 (s, C=O), 1634 (s, C=O), 1587 (m), 1467 (w), 1407 (w), 1343 (s), 1289 (s), 1228 (w), 1172 (w), 1136 (w), 1113 (w), 1072 (m), 1044 (w), 978 (m), 933 (m), 900 (m), 881 (m), 795 (w), 767 (w), 719 (s), 667 (w), 619 (w). – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.21 (s, 3H, 13-H), 4.85 (d, $^3J_{cis}$ = 10.0 Hz, 1H, *Z*-10-H), 5.33-5.42 [m, 3H, *E*-10-H, 12-H], 5.87 (dd, $^3J_{cis}$ = 10.5 Hz, $^3J_{trans}$ = 19.8 Hz, 1H, 11-H), 7.05 (dd, $^3J_{cis}$ = 10.2 Hz, $^3J_{trans}$ = 19.6 Hz,, 1H, 9-H), 7.68-7.79 (m, 1H, 6-H or 7-H), 7.80-7.84 (m, 1H, 6-H or 7-H), 8.03 (d, *J* = 7.0 Hz, 1H, 5-H or 8-H), 8.34 (d, *J* = 7.8 Hz, 1H, 5-H or 8-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 51.7 (–, C-13), 94.5 (+, C-3), 105.2 (+, C-10), 120.2 (+, C-12), 126.5 (–, C-5 or C-8), 127.9 (–, C-9),

129.3 (–, C-5 or C-8), 129.8 (+, C-8a), 131.3 (+, C-4a), 133.2 (–, C-6 or C-7), 134.4 (–, C-11), 135.6 (–, C-6 or C-7), 161.1 (+, C-1),189.4 (+, C-4) ppm. – MS (70 eV): *m/z* (%) = 243 (25) [M^+], 228 (24) 213 (32), 200 (17), 184 (13), 173 (37), 163 (11), 146 (11), 129 (19), 104 (100), 76 (68), 55 (66). – HRMS $C_{14}H_{13}NO_3Cr$: calcd. 243.0895, found. 243.0895.

E. References

[1] Review: A. R. Pape, K. P. Kaliappan, E. P. Kündig, *Chem. Rev.* **2000**, *100*, 2917-2940.

[2] M. F. Semmelhack, in: *Comprehensive Organometallic Chemistry II*, ed. E.W. Abel, F. G. A. Stone, G. Wilkinson, Pregamon, New York, **1995**, *12*, 979-1038.

[3] M. F. Semmelhack, *J. Organomet. Chem.* Lib. **1976**, *1*, 361-395.

[4] R. S. Cahn, C. Ingold, V. Prelog, *Angew. Chem.* **1966**, *78*, 413-447; *Angew. Chem.Int. Ed. Engl.* **1966**, *5*, 385-419.

[5] K. C. Nicolaou, W. E. Barnette, R. L. Magolda, *J. Am. Chem. Soc.* **1979**, *101*, 768-769.

[6] C. Merlic, J. C. Walsh, D. J. Tantillo, K. N. Houk, *J. Am. Chem. Soc.* **1999**, *121*, 3596-3606.

[7] V. Snieckus, *Chem. Rev.* **1990**, *90*, 879-933.

[8] H.-G. Schmalz, B. Gotov, A. Boettcher, *Top. Organomet.Chem.* **2004**, *7*, 157-179.

[9] Review: a) C. Bolm, K. Muniz, *Chem. Soc. Rev.* **1999**, *28*, 51-59; b) S. E. Gibson, H. Ibrahim *Chem. Comm.* **2002**, 2465-2473.

[10] a) E. P. Kündig, L.-H. Xu, P. Romanens, G. Bernardinelli, *Synlett.* **1996**, 270-272; b) A. Alexakis, P. Mangeney, I. Marek, F. Rose-Munch, E. Rose, A. Semra, F. Robert, *J. Am. Chem. Soc.* **1992**, *114*, 8288-8290; c) H. G. Schmalz, B. Milligan, J. W. Bats, G. Dürner, *Angew. Chem.* **1992**, *104*, 640-643; *Angew. Chem. Int. Ed. Engl.* **1992**, *21*, 631-634; d) M. Uemura, R. Miyake, K. Nakayama, M. Shiro, Y. Hayashi, *J. Org. Chem.* **1993**, *58*, 1238-1244.

[11] a) A. Fretzen, A. Ripa, R. Liu, G. Bernardinelli, E. P. Kündig, *Chem. Eur. J.* **1998**, *4*, 251-259; b) A. Fretzen, E. P. Kündig, *Helv. Chim. Acta* **1997**, *80*, 2023-2026; c) E. P. Kündig, R. Liu, A. Ripa, *Helv. Chim. Acta* **1992**, *75*, 2657-2660.

[12] Review: S. E. Gibson, E. G. Reddington, *Chem. Commun.* **2000**, 989-996.

[13] a) N. S. Simpkins, D. A. Price, A. M. MacLeod, A. P. Watt, *J. Org. Chem.* **1994**, *59*, 1961-1962; b) D. A. Price, N. S. Simpkins, A. M. MacLeod, A. P. Watt, *Tetrahedron Lett.* **1994**, *35*, 6159-6162; c) R. A. Ewin, A. M. MacLeod,

D. A. Price, N. S. Simpkins, A. P. Watt, *J. Chem. Soc. Perkin Trans.* **1997**, *1*, 401-415.

[14] P. Kündig, A. Quattropani, *Tetrahedron Lett.* **1994**, *35*, 3497-3500.

[15] M. Uemura, Y. Hayashi, Y. Hayashi, *Tetrahedron: Asymmetry* **1994**, *5*, 1427-1430.

[16] A. Quattropani, G. Anderson, G. Bernardinelli, E. P. Kündig, *J. Am. Chem. Soc.* **1997**, *119*, 4773-4774.

[17] a) H.-G. Schmalz, Schellhaas, K. *Angew. Chem.* **1996**, *108*, 2277-2280; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2146-2148; b) K. Schellhaas, H.-G. Schmalz, J. W. Bats, *Chem. Eur. J.* **1998**, *4*, 57-66.

[18] R. A. Ewin, N. S. Simpkins, *Synlett.* **1996**, 317-318.

[19] E. L. M. Cowton, S. E. Gibson, M. J. Schneide, M. H. Smith, *Chem. Commun.* **1996**, 839-840.

[20] N. S. Simpkins, K. Bambridge, M. J. Begley, *Tetrahedron Lett.* **1994**, *35*, 3391-3394.

[21] S. Zemolka, J. Lex , H. G. Schmalz, *Angew. Chem.* **2002**, *114*, 2635-2638; *Angew. Chem.Int. Ed. Engl.* **2002**, *41*, 2525-2528.

[22] H. Butenschön, *J. Chem. Soc. Pak.* **2004**, *26*, 322-327.

[23] H. Butenschön, *Synlett*. **1999**, 680-691.

[24] H. Butenschön, *Pure Appl. Chem.* **2002**, *74*, 57-62.

[25] H. Butenschön, *Ann. Polish Chem. Soc.* **2003**, *2/I,* 18-22.

[26] H. Butenschön, in: *The Chemistry of Cyclobutanes* (Eds.: Z. Rappoport, J. F. Liebman); John Wiley & Sons, Chichester, **2005**, *2*, 655-714.

[27] G. Wey, H. Butenschön, *Angew. Chem.* **1991**, *103*, 871-873; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 880-881.

[28] M. Brands, H. G. Wey, R. Goddard, H. Butenschön, *Inorg. Chim. Acta* **1994**, *220*, 175-186.

[29] M. Brands, H. G. Wey, R. Krömer, C. Krüger, H. Butenschön, *Liebigs Ann.* **1995**, 253-265.

[30] H. Ziehe, R. Wartchow, H. Butenschön, *Eur. J. Org. Chem.* **1999**, 823-835.

[31] G. Dongol, J. Krüger, M. Schnebel, B. Voigt, R. Wartchow, H. Butenschön, *Inorg. Chim. Acta* **1999**, *296*, 150-157.

[32] M. Brands, H. G. Wey, H. Butenschön, *J. Chem. Soc., Chem. Commun.* **1991**, 1541–1542.

[33] M. Schnebel, I. Weidner, R. Wartchow, H. Butenschön, *Eur. J. Org. Chem.* **2003**, 4363–4372.

[34] D. Wittneben, H.-F. Grützmacher, H. Butenschön, H. G. Wey, *Organometallics* **1992**, *11*, 3111–3116.

[35] M. Brands, R. Goddard, H. G. Wey, H. Butenschön, *Angew. Chem.* **1993**, *105*, 285–287; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 267–269.

[36] M. Brands, J. Bruckmann, C. Krüger, H. Butenschön, *J. Chem. Soc., Chem. Commun.* **1994**, 999–1000.

[37] M. Brands, H. G. Wey, J. Bruckmann, C. Krüger, H. Butenschön, *Chem. Eur. J.* **1996**, *2*, 182–190.

[38] B. Voigt, M. Brands, R. Goddard, R. Wartchow, H. Butenschön, *Eur. J. Org. Chem.* **1998**, 2719–2727.

[39] K. G. Dongol, R. Wartchow, H. Butenschön, *Eur. J. Org. Chem.* **2002**, 1972–1983.

[40] D. Leinweber, R. Wartchow, H. Butenschön, *Eur. J. Org. Chem.* **1999**, 167–179.

[41] D. Leinweber, I. Weidner R. Wilhelm, R. Wartchow, H. Butenschön, *Eur. J. Org. Chem.* **2005**, 5224-5235.

[42] T. Hosoya, T. Hasegawa, Y. Kuriyama, T. Matsumoto, K. Suzuki, *Synlett.* **1995**, 177-179.

[43] a) T. Hosoya, T. Hamura, Y. Kuriyama, M. Miyamoto, T. Matsumoto, K. Suzuki, *Synlett* **2000**, 520-522; b) T. Hamura, T. Hosoya, H. Yamaguchi, Y. Kuriyama, M. Tanabe, M. Miyamoto, Y. Yasui, T. Matsumoto, K. Suzuki, *Helv. Chim. Acta* **2002**, *85*, 3589-3604.

[44] T. Hamura, Y. Ibusuki, H. Uekusa, T. Matsumoto, K. Suzuki, *J. Am. Chem. Soc.* **2006**, *128*, 3534-3535.

[45] I. Weidner, Dissertation, Universität Hannover, **2004**.

[46] a) Y. Nagao, S. Tanaka, A. Ueki, I.-Y. Jeong, S. Sano, M. Shiro, *Synlett* **2002**, 480-482; b) S. Kaden, H.-U. Reissig, I. Brüdgam, H. Hart, *Synthesis* **2006**, 1351-1359.

[47] G. Wittig, *Naturwissenschaften* **1942**, *30*, 696.

[48] a) R. W. Hoffmann, *Dehydrobenzene and Cycloalkynes*, Academic Press, New York, 1967; b) H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem.*, **2003**, *115*, 518-546; *Angew. Chem.Int. Ed. Engl.* **2003**, *42*, 502-527; c) H. Hart, in *Chemistry of Functional Groups, Supplement C2*, ed. S. Patai, John Wiley & Sons Ltd, Chichester, United Kingdom, Editon edn., **1994**, pp. 1017-1134.

[49] a) S. V. Kessar, in: *Comprehensive Synthesis*; B. M. Trost, I. Flemming, Eds.; Pergamon Press: New York, **1991**, *4*, 483-515; b) H. Pellissier, M. Santelli, *Tetrahedron* **2003**, *59*, 701-730.

[50] a) M. A. Bennett, T. W. Hambley, N. K. Roberts, G. B. Robertson, *Organometallics* **1985**, *4*, 1992; b) M. A. Bennett, H. P. Schwemlein, *Angew. Chem.* **1989**, *101*, 1349-1373; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1296-1320; c) S. L. Buchwald, R. D. Broene, in: *Comprehansive Organometallic Chemistry II*; E. W. Able, F. G. A. Stone, G. Willkinson, Eds.; Pergamon: Oxford, **1995**, *12*, pp 771-784; d) W. M. Jones, J. Klosin, *Adv. Organomet. Chem.*, **1998**, *42*, 147-221.

[51] D. Wittneben, H.-F. Grützmacher, H. Butenschön, H. G. Wey, *Organometallics* **1992**, *11*, 3111-3116.

[52] a) L. Friedman, F. M. Logullo, *J. Am. Chem. Soc.* **1963**, *85*, 1549; b) F. M. Logullo, A.H. Seitz, L. Firedman, *Org. Synth.* **1968**, *48*, 12-17.

[53] C. D. Campbell, C. W. Rees, *J. Chem. Soc. C* **1969**, 742-747.

[54] J. D. Roberts, H. E. Simons, L. A. Carlsmith, C. W. Vaughn, *J. Am. Chem. Soc.* **1953**, *75*, 3290-3291.

[55] G. Wittig, *Org. Synth*. **1959**, *39*, 75-77.

[56] G. W. Gribble, R. B. Perni, K. D. Onan, *J. Org. Chem.* **1985**, *50*, 2934-2939.

[57] Y. Himeshima, T. Sonoda, H. Kobayashi, *Chem. Lett.* **1983**, 1211-1214.

[58] H. Yoshida, H. Fukushima, J. Ohshita, A. Kunai, *Angew. Chem.* **2003**, *1165*, 4025-4028; *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 3935-3938.

[59] a) Yoshida, M. Watanabe, J. Ohshita, A. Kunai, *Chem. Commun*. **2005**, 3292; b) U. K. Tambar, B. M. Stoltz, *J. Am. Chem. Soc.* **2005**, *127*, 5340-5344 and references therein.

[60] a) M. Jeganmohan, C.-H. Cheng, *Org. Lett*. **2004**, *6*, 2821-2824; b) M. Jeganmohan, C.-H. Cheng, *Synthesis* **2005**, *10*, 1693-1697.

[61] D. Peña, D. Pérez, E. Guitián, L. Castedo, *J. Org. Chem*. **2000**, *65*, 6944-6950; b) E. Yoshikawa, K. V. Radhakrishnan, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**,

122, 7280-7286; c) T. T. Jayanth, M. Jeganmohan, C.-H. Cheng, *J. Org. Chem.* **2004**, *69*, 8445-8450.

[62] P. P. Wickham, K. H. Hazen, H. Guo, G. Jones, K. H. Reuter, W. J. Scott, *J. Org. Chem.* **1991**, *56*, 2045-2050.

[63] T. Matsumoto, T. Hosoya, M. Katsuki, K. Suzuki, *Tetrahedron Letters*, **1991**, *32*, 6735-6736.

[64] T. Hosoya, E. Takashira, T. Matsumoto, K. Suzuki, *J. Am. Chem. Soc*. **1994**, *116*, 1004-1015.

[65] A. M.Gilbert, W. D.Wulff, *J. Am. Chem. Soc.* **1994**, *116*, 7449-7450.

[66] E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, W. Semmlinger, *Z. Naturforsch.*, **1958**, *13*b, 458.

[67] E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, W. Semmlinger, *Chem. Ber.* **1958**, *91*, 2763-2772.

[68] G. Natta, R. Ercoli, F. Calderazzo, E. Santambrogio, *Chim. Ind. (Milan)* **1958**, *40*, 1003-1007.

[69] A. Wu, E. R. Biehl, P. C. Reeves, *J. Chem*. *Soc., Perkin Trans*. *2* **1972**, 449-451.

[70] a) K. Ritter, *Synthesis* **1993**, 735-762. b) D. Gill, A. J. Hester, G. C. Lloyd-Jones, *Org. Biomol. Chem*. **2004**, *2*. 2547-2548.

[71] M. E. Wright, *J. Organomet. Chem.* **1989**, *376*, 353-358.

[72] H. Schumann, A. M. Arif , T. G. Richmond, *Polyhedron* **1990**, *9*, 1677-1681.

[73] Reviews a) R. Martin, *Org. Pre. Pro. Int.* **1992**, *24*, 369. b) H. Heaney, "The Biomolecular aromatic Friedel-Crafts Reaction" in *Comprehensive Organic Synthesis*, Trost, B .M., Ed.; Pergamon; Oxford, 991; *2*, Chapter 3.2, pp.733-775.

[74] V. Rozenberg, T. Danilova, E. Sergeeva, E. Vorontsov, Z. Starikova, K. Lysenkoand Y. Belokon *Eur. J. Org. Chem.* **2000**, 3295-3303.

[75] a) G. A. Benson, P. J. Maughan, D. P. Shelly, W. J. Spillane, *Tetrahedron Lett*. **2001**, *42*, 8729-8731; b) F. M. Moghaddam, M. G. Dekamin, M. Ghaffarzadeh, *Tetrahedron Lett*. **2001**, *42*, 8119-8121.

[76] F. M. Moghaddam, M.G. Dakamin, *Tetrahedron Lett.* **2000**, *41*, 3479-3481

[77] a) M. E. Jung , S. I. Lazerova, *Tetrahedron Lett.* **1996**, *37*, 7-8; b) A. Commarieu, W. Hoelderich, J. A. Laffitte, M. P. Dupont, *J. Mol. Cat. A.: Chemical* **2002**, *182-183*, 137-141.

[78] a) T. Focken, H. Hopf, V. Snieckus, I. Dix, P. G. Jones *Eur. J. Org. Chem.* **2001**, 2221-2228.

[79] M. P. Sibi, V. Snieckus, *J. Org. Chem.* **1983**, *48*, 1935-1937.

[80] A. Quattropani, G. Bernardinelli, E. P. Kündig, *Helv. Chim. Acta* **1999**, *82*, 90-104.

[81] J. P. H. Charmant, A. M. Dyke, G. C. Lloyd-Jones, *Chem. Commun.* **2003**, 380-381.

[82] J. W. Dankwardt *J. Org. Chem.* **1998,** *63,* 3753-3755.

[83] P. R. Blakemore, C. Kilner, and S. D. Milicevic *J. Org. Chem.* **2005**, *70*, 373-376.

[84] E. P. Kündig, *Top. Organomet. Chem.* **2004**, *7*, 3-20.

[85] T. Fotsis, Y. M. Zhang, M. S. Pepper, H. Adlercreutz, R. Montesano, P. P. Nawroth, L. Schweigerer, *Nature* **1994**, *368*, 237-239.

[86] a) C. J. Lovely, R. W. Brueggemeier, *Tetrahedron Lett.* **1994**, *35*, 8735-8738, b) M. Cushman, H. M. He, J. A. Katzenellenbogen, R. K. Varma, E. Hamel, C. M. Lin, S. Ram, Y. P. Sachdeva, *J. Med. Chem.* **1997**, *40*, 2323-2334. c) M. Cushman, A. K. Mohanakrishnan, M. Hollingshead, E. Hamel, *J. Med. Chem.* **2002**, *45*, 4748-4754. d) M. P. Leese, S. P. Newman, A. Purohit, M. J. Reed, B. V. L. Potter, *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3135-3138.

[87] M. P. Leese, A. M. H. Hejaz, M. F. Mahon, S. P. Newman, A. Purohit, M. J. Reed, B. V. L. Potter, *J. Med. Chem.* **2005,** *48,* 5243-5256.

[88] P. N. Rao, J. W. Cessac, *Steroids* **2002**, *67*, 1065-1070.

[89] A. J. Birch, P. E. Cross, D. T. Connor, G. S. R. Subbarao, *J. Chem. Soc. (C)* **1966**, 54.

[90] J. C. Gill, B. A. Marples, J. R. Traynor, *Tetrahedron Lett.* **1987**, *28*, 2643-2644.

[91] L. J. Diorazzo, D. A. Widdowson, J. M. Clough, *J. Chem. Soc., Perkin Trans. 1* **1992**, 421-425.

[92] a) S. Top, A. Vessieres, J. P. Abjeean, G. Jaouen, *J. Chem. Soc., Chem. Commun.* **1984**, 428; b) G. Jaouen, S. Top, A. Laconi, D. Couturier, J. Brochard, *J. Am. Chem. Soc.* **1984**, *106*, 2207-2208.

[93] a) G. Jaouen, A. Vessieres, S. Top, A. A. Ismail, I. S. Butler, *J. Am. Chem. Soc.* **1985**, *107*, 4778-4780; b) A. Vessieres, S. Top, A. A. Ismail, I. S. Butler, M. Louer, G. Jaouen, *Biochemistry* **1988**, *27*, 6659-6666.

[94] S. Top, G. Jaouen, A, Vassieres, J-P. Abjean, D. Davoust, C. A. Rodger, B. G. Sayer, M. J. McGlinchey, *Organometallics* **1985**, *4*, 2143-2150.

[95] A. Nakamura, M. Tsutsui, *Z. Naturforshung.* 18b, 1963, 666-666.

[96] J.Andraos,G.G.Barclay,D.R.Medeiros,M.V.Baldovi, J. C. Scaiano, R. Sinta, Chem. Mater., **1998**, 10, 1694–1699.

[97] L. A. Shimp, C. Chung, R. J. Lagow, *Inorg. Chim. Acta,* **1978**, *29*, 77-81.

[98] E. P. Kündig, *Top. Organomet. Chem.*, **2004**, *7*, 21-39.

[99] Y. L. Tan, A. J. P. White, D. A. Widdowson, R. Wilhelm, *J. Chem. Soc., Perkin Trans. 1* **2001**, 3269-3280.

[100] H. G. Schmalz, K. Schellhaas, *Tetrahedron Lett.* **1995**, *36*, 5515-5518.

[101] S. E. Gibson, N. Guillo, A. J. P. White, D. J. Williams, *J. Chem. Soc. Perkin Trans. 1,* **1996**, 2575-2581.

[102] S. E. Gibson, J. W. Steed and S. Sur, *J. Chem. Soc. Perkin, Trans. 1* **2001**, 636-641.

[103] R. Wilhelm, I. K. Sebbat, A. J. P. White, D. J. Williams, D. A. Widdowson, *Tetrahedron: Asymmetry* **2000**, *2*, 5003-5016.

[104] Y.-L. Tan, A. J. P. White, D. A. Widdowson, R. Wilhelm, D. J. Williams, *J. Chem. Soc. Perkin, Trans. 1* **2001**, 3269-3280.

[105] J. K. Whitesell, S. W. Felman, *J. Org. Chem.*, **1980**, *45*, 755-756.

[106] J. A. Dale, D. L. Dull and H. S. Mosher, *J. Org. Chem.*, **1969**, 34, 2543-2549.

[107] a) J. A. Dale, H. S. Mosher, *J. Am. Chem. Soc.* **1973**, *95*, 512-519. b) G. R. Sullivan, J. A. Dale, H. S. Mosher, *J. Org. Chem.* **1973**, *38*, 2143-2147 .

[108] I. Ohtani, T. Kusumi, Y. Kashman, H. Kakisawa, *J. Am. Chem. Soc.* **1991**, *113*, 4092-4096.

[109] J. A. Heppert, T. J. Boyle, F. Takusagawa, *Organometallics* **1989**, *8*, 461-467.

[110] a) A. Suzuki in: F. Diederich, P. J. Stang (eds), *Metal-Catalyzed Cross-Coupling Reactions*, chap 2. Wiley-VCH, Weinheim, **1998**; b) J. K. Still, *Angew. Chem.* **1986***, 98,* 504-520; *Angew. Chem. In. Ed Engl* **1986**, *25*, 508-524.

[111] a) J. M. Clough, I. S. Mann, D. A. Widdowson, *Tetrahedron Lett.*, **1987**, *28,* 2645-2648; b) R. Mutin, C. Lucas, J. Thivolle-Cazat, V. Dufaud, F. Dany, J. M. Basset, *J. Chem. Soc. Chem. Commun.* **1988**, 896; c) V. Dufand, J. Thivolle-Cazat, J. M. Basset, R. Mathieu, J. Jaud, J. Vaissermann, *Organometallics* **1991**, *10*, 4005-4015.

[112] M. Ansorge, T. J. J. Müller, *J. Organomet. Chem.* **1999**, *585*, 174-178.

[113] a) E. P. Kündig, *Top. Organomet. Chem.* **2004**, 144-156; b) D. Prim, B. Andriletti, F. Rose-Munch, E. Rose, F. Couty, *Tetrahedron*, **2004**, *60*, 3325-3347.

[114] J. P. Tranchier, R. Chavignon, D. Prim, A. Auffrant, J. Giner Planas, F. Rose-Munch, G. R. Stephenson, *Tetrahedron Lett.* **2001**, *42*, 3311-3313; T. J. J. Müller, M. Ansorge, H. J. Linder, *Chem. Ber.* **1996**, *129*, 1433-1440.; J. P. Tranchier, R. Chavignon, D. Prim, A. Auffrant, Z. F. Plyta, F. Rose-Munch, E. Rose, *Tetrahedron Lett.* **2000**, *41*, 3607-3610.

[115] M. Ansorg, T. J. J. Müller, *J. Organomet. Chem.* **1999**, *585*, 174-178.

[116] M. E. Wright *Macromolecules* **1989** *22*, 3256-3259.

[117] M. E. Wright, *J. Organomet. Chem.* **1989**, *376*, 353-358.

[118] a) J. F. Carpemtier, F. Petit, A. Motreux, V. Dufand, J. M. Basset, J. Thivolle-Cazat, *J. Mol. Catal.* **1993**, *81*, 1-15; b) W. J. J. Scott, *J. Chem. Soc. Chem. Commun*. **1987**, 1755-1756.

[119] M. Uemura, H. Nishimura, K. Kamikawa, M. Shira, *Inorg. Chim. Acta* **1994**, *222*, 63-70.

[120] M. Uemura, H. Nishimura, K. Kamikawa, K. Nakayama, *Tetrahedron Lett*. **1994**, *35*, 1909-1912.

[121] M. Uemura, H. Nishimura, T. Hayashi, *J. Organomet. Chem.* **1994**, *473*, 129-137.

[122] a) W. J. Scott, J. K. Stille, *J. Am. Chem. Soc*. **1986**, *108*, 3033-3040; b) A. M. Echavarren, J. K. Stille, *J. Am. Chem. Soc*. **1987**, *109*, 5478-5486.

[123] R. Wilhelm, A. A. Widdowson, *J. Chem. Soc., Perkin Trans.1* **2000**, 3808-3813.

[124] a) J. Deberitz, H. Nöth, *J. Organomet*. *Chem*. *55*, **1973**, 153-163; b) B. Mailvaganam,B. E. McCarry, B. G. Sayer, R. E. Perrier, R. Faggiani, M. J. McGlinchey, *J. Organomet*. *Chem*. **1987**, *55*, 213-227.

[125] a) F. A. Luzzio, D. Piatt Zacherl, *Tetrohedron Lett.* **1998**, *39*, 2285-2288; b) J. B. Campbell, R. F. Dedinas, S. A. Walsh *J. Org. Chem.* **1996**, *61*, 6205-6211; c) B. Decroix, P. Pigeon, M. Othman, *Tetrahedron* **1997**, *53*, 2495-2504; d) S. M. Allin, C. J. Northfield, M. I. Page, A. M. Z. Slawin, *Tetrahedron Lett.* **1997**, *38*, 3627-3630; e) M. S. Kitching, W. Clegg, M. R. J. Elsewood, R. J. Griffin, B. T. Golding *Synlett* **1999**, 997-999.

[126] a) V. Bailleux, L. Vallee, J. P. Nuyts, J. Vamecq, *J. Chem. Pharm. Bull.* **1994**, *42*, 1817; b) M. K. Hargreaves, J. G. Pritchard, H. R. Dave, *Chem. Rev*. **1970**, 439-469; c) Y. Shibata, K. Sasaki, Y. Hashimoto, S. Iwasaki, *Chem*. *Pharm*. *Bull*. **1996**, *44*, 156; d) S. Blicq, P.M. Danze, V. Dumur, P. Formstecher, M. Dautrevaux, *Biochem*. **1988**, *27*, 8436-8442.

[127] a) S. B. Mhaske, N. P. Argade, *Synthesis* **2003**, 863-870; b) L. M. Lima, P. Castro, A. L. Machado, C. A. M. Fraga, C. Lugnier, V. L. G. Moraes, E. J. Barreiro, *Bioorg. Med. Chem.* **2002**, *10*, 3067-3073; c) S. Chandrasekhar, M. B. Padmajy, A. Raza, *Synlett.* **1999**, 1597-1599.

[128] a) E. Valencia, I. Weiss, S. Firdous, A. J: Freyer, M. Shamma, A. Urzua, V. Fayardo, *Tetrahedron* **1984**, *40*, 3957-3962; b) P. Pigeon, B. Decroix, *Tetrahedron Lett.* **1996**, *37*, 7707-7710; c) A. Couture E. Deniau, P. Grandclaudon, *Tetrahedron* **1997**, *53*, 10313-10330; d) A. Couture, E. Deniau, P. Grandclaudon, C. Hoarau, *J. Org. Chem.* **1998**, *63*, 3128-3132; e) A. Couture, E. Deniau, P. Grandclaudon, C. Hoarau, *Tetrahedron* **2000**, *56*, 1491-1499; f) C. Hoarau, *Tetrahedron* **2000**, *56*, 1491-1499; g) C. Hoarau, A. Couture, E. Deniau, P. Grandclaudon, *Synthesis* **2000**, 655-660.

[129] G. Nannin, P. N. Griraldi, G. Molgora, G. Biasoli, F. Spinelli, L. Logggemann, E. Dradi, G. Zanni, A. Buttinoni, R. Tommasini *Arznei*. *Forsch*. **1973**, *23*, 1090.

[130] H.-J. Schmahl, L. Denker, C. Plum, I. Chahoud, H. Nau, *Arch. Toxicol.* **1996**, *11*, 749.

[131] J. Plowman, K. D. Paull, G. Atassi, S. Harrison, D. Dykes, N. Kabbe, V. L. Narayan, O. Yoder, *Invers. New. Drugs.* **1988**, *6*, 147.

[132] J. R. Fuchs, R. L. Funk, *Org. Lett.* **2001**, *3*, 3923-3925.

[133] a) Z. Hussein, D. J. Mulford, B. A. Bopp, G. R. Granneman, *Br. J. Clin. Pharmacol.* **1993**, *36*, 357-361; b) T. Kondo, K. Yoshida, M. Yamamoto, S. Tanayama, *Arzneim. Forsch.* **1996**, *46*, 11-14.

[134] T. R. Belliotti, W. A. Brink, S. R. Kesten, J. R. Rubin, D. J. Wustrow, K. T. Zoski, S. Z. Whetzel, A. E. Corbin, T. A. Pugsley, T. G. Heffner, L. D. Wise, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 1499-1502.

[135] H. McAlonan, J. P. Murphy, M. Nieuwenhuyzen, K. Reynolds, P. K. S. Sarma, P. J. Stevenson, N. J. Thompson, *J. Chem. Soc*. *Perkin Trans.* **2002**, *1*, 69-79.

[136] S. M. Allin, C. J. Northfield, M. I. Page, A. M. Z. Slawin, *J. Chem. Soc. Perkin Trans.* **2000**, *1*, 1715-1721.

[137] E. Deniau, D. Enders, A. Couture, P. Grandclaudon *Tetrahedron: Asymmetry* **2003**, *14*, 2253-2258.

[138] R. P. Kreher, H. Hennige, M. Konrad, J. Uhrig, A. Z. Clemens, *Naturforsch. B* **1991**, *46*, 809-828; b) E. Deniau, D. Enders *Tetrohedron Lett.* **2000**, *41*, 2347-2350.

[139] C. Graebe, A. Pictet. *Ber.* **1884**, *17*, 1173**.**

[140] R. G. R. Bacon, A. Karim, *J. Chem. Soc. Perkin Transactions 1* **1973,** 278-280.

[141] J. Lan, G. Zhang, X. Yu, J. You, L. Chen, M. Yan, R. Xie, *Synlett* **2004**, *6*, 1095-1097.

[142] Z.-G. Le, Z.-C. Chen, Y. Hu, Q.-G Zheng, *Synthesis* **2004**, *2*, 208-212.

[143] J. Matsuo, Y. Tani, Y. Hayakawa, *Chem. Lett.* **2004**, *33*, 464-465.

[144] J. A. Berson, M. Jones, *J. Am. Chem. Soc.* **1964**, *86*, 5019-5020.

[145] A. C. Cope, E. M. Hardy, *J. Am. Chem. Soc*. **1940**, *62*, 441-444.

[146] D. A. Evans, A. M. Golob, *J. Am. Chem. Soc*. **1975**, *97*, 4765-4766.

[147] Review: L. A. Paquette, *Tetrahedron* **1997**, *53*, 13971-14020.

[148] E. J. Corey, R. S. Kania, *Tetrahedron Lett.* **1998**, *39*, 741-744.

[149] M. L. Snapper, A. Meijere, M. Noltemeyer, K. Voigt, P. Zezschwitz, *Synthesis* **2000**, *9*, 1327-1340.

[150] R. Knorr *Tetrahedron* **1981**, *37*, 929-937.

[151] J. Suffert, D. Toussanint *J. Org. Chem*. **1995**, *60*, 3550-3553.

[152] A. Sarkar, S. Ganesh, S. Sur, S. K. Mandal, V. M. Swamy, B. C. Maity, T. S. Kumar, *J. Organomet. Chem*. **2001**, *624*, 18-25.

[153] F. Dehmel, H. G. Schmalz, *Org. Lett.* **2001**, *3*, 3579-3582. b) F. Dehmel, J. Lex, H. G. Schmalz, *Org. Lett.* **2002**, *4*, 3915-3918.

[154] Reviews, a) W. N. Speckamp, H. Hiemstra, *Tetrahedron*, **1985**, *41*, 4367.4416; b) W. N. Speckamp , M. J. Moolinaar, *Tetrahedron*, **2000**, *56*, 3817-3856; c) B. E. Maryanoff, H.-C. Zhang, J. H. Cohen, I. J. Turchi, C. A. Maryanoff, *Chem. Rev*. **2004,** *104,* 1431-1628.

[155] G. Majetich, S. Liu, J. Fang, D. Siesel, Y. Zhang *J. Org. Chem.* **1997**, *62*, 6928-6951.

[156] I-Y. Jeong, W. S. Lee, S. Goto, S. Sano, M. Shiro, Y. Nagao, *Tetrahedron* **1998**, *54*, 14437-14454.

[157] M. Hesse, *Ring Enlargement in Organic Chemistry*; VCH Publishers: New York, **1991**.

[158] Y. Nagao, A. Ueki, K. Asano, S. Tanaka, S. Sano, M. Shiro, *Org. Lett*. **2002**, *4*, 455-457.

[159] N. Miyaura, T. Yoshinari, M. Itoh, A. Suzuki, *Tetrahedron Letter* **1980**, *21*, 537-540.

[160] A. Loupy (Ed.) *Microwaves in Organic Synthesis*, WILEY-VCH Verlag GmbH & Co. KGaA **2002**.

[161] W. G. B. van Henegouwen, R. M. Fieseler, F. P. J. T. Rutjes, H. Hiemstra, *J. Org. Chem.* **2000**, *65*, 8317-8325.

[162] A. A. Bahajaj, J. M. Vernon, G. D. Wilson, *J. Chem. Soc.*, *Perkin Trans. 1*, **2001**, 1446–1451.

[163] W. Zhang, A. Zheng, Z. Liu, L, Yang, Z. Liu, *Tetrahedron Letter* **2005**, *46*, 5691-5694.

[164] P. Q. Huang, *Synlett* **2006**, *8*, 1133-1149.

[165] W. N. Speckamp, *Pure & Appl. Chem*. **1996**, *68*, 695-698.

[166] W. Carruthers, *Cycloaddition Reactions in Organic Synthesis*, Pergamon Press, Oxford **1990**.

[167] E. J. Corey, R. K. Bakshi, S. Shibata, *J. Am. Chem. Soc.* **1987**, *109*, 5551–5553. b) E. J. Corey, R. K. Bakshi, S. Shibata, C.-P. Chen, V. K. Singh, *J. Am. Chem. Soc.* **1987**, *109*, 7925–7926.

[168] H.-G. Schmalz, B. Millies, J. W. Bats, G. Dürner, *Angew. Chem.* **1992**, *104*, 640–643; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 631–633.

[169] a) A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 2521–2522; b) R. Noyori, M. Yamakawa, S. Hashiguchi, *J. Org. Chem.* **2001**, *66*, 7931–7944.

[170] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.

[171] J. E. V. Epp, Jr., D. R. Boyd, G. A. Berchtold, *J. Org. Chem.* **1981**, *46*, 1817-1820.

[172] P. G. Williard, J. M. Salvino, *J. Org.Chem.* 1993, *58*, 1-3.

[173] A. K. Flatt, S. M.Dirk, J. C. Henderson, D. E. Shen, J. Su, M. A. Reed, J. M. Tour, *Tetrahedron* 2003, *59*, 8555-8570.

[174] F. J. Weiberth, S. S. Hall, *J. Org. Chem.* **1985**, *50*, 5308-5314.

Curriculum Vitae

Personal Data

First Name: Zhirong **Family Name:** Zhao-Karger

Birthday: 1st. Nov. 1970 **Nationality:** Chinese

Education and experience

09/1986 – 07/1989	Middel school, Huhhot, China
09/1989 – 07/1993	Inner Mongolia University, China
	B. Sc. in Chemistry
09/1993 – 07/1996	Inner Mongolia University, China
	M. Sc. in Inorganic Chemistry
08/1996 – 03/2001	Faculty member in department of chemistry,
	Inner Mongolia University
04/2001 – 09/2001	Goethe-Institute Freiburg, Germany
	German language course University Trier, Germany
10/2001 –10/2002	Training study on Environmental Science
	Institute of Biogeography of University Trier, Germany
	supported by DAAD fellowship

Publication

"Unanticipated Formation of ortho Sulfone Substituted Phenols by Anionic Thia-Fries Rearrangement of Arene Triflate Tricarbonylchromium Complexes", *Chem. Commun.* **2006**, 3007-3009.