Synthetic and Mechanistic Prospects of Homogeneous Gold Catalysis

Von der Fakultät Chemie der Universität Stuttgart
zur Erlangung der Würde eines Doktors der
Naturwissenschaften
-Dr. rer. nat.-
genehmigte Abhandlung

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Tag der mündlichen Prüfung:	02/09/09

Institut für Organische Chemie
der Universität Stuttgart
2009

To my dear parents.....

Most of what I knew was left untold,
Most of what I spoke was hardly worthy,
While you hate me with half your heart,
Forgive me with the other half;
This is my flesh and blood,
and this is all I have left to offer.

Balachandran Chullikkad

അറിഞ്ഞതിൽ പാതി പറയാതെ പോയി
പറഞ്ഞതിൽ പാതി പതിരായും പോയി
പകുതി ഹൃത്തിനാൽ വെറുക്കുമ്പോഴെന്നെ
പകുതി ഹൃത്തിനാൽ പൊറുത്തുകൊള്ളുക
ഇതെന്റെ രക്തമാണിതെന്റെമാംസമാണെടുത്തുകൊള്ളുക

ബാലചന്ദ്രൻ ചുള്ളിക്കാട്

(This thesis work was done during August 2006-June 2009, at the Institute of Organic Chemistry, University of Stuttgart, under the supervision of Prof. Dr. A. Stephen. K. Hashmi)

Acknowledgements

Let me convey my 'vote of thanks' to all those who helped me to materialize this manuscript.

First and foremost, I am obliged to Prof. Dr. A. Stephen K. Hashmi, for offering me a doctoral position in his workgroup and for the motivation and encouragement he provided during my tenure as a PhD student. I am hugely benefited from the 'freedom of thought' and independence that he conveys to his co-workers.

I am grateful to Prof. Dr. S. Laschat, for being a benevolent presence in my stay at the University of Stuttgart, and for her willingness to be one of my examiners. I am thankful to Prof. Dr. W. Kaim, for being my examiner.

My sincere thanks to Frau Kraschewski, Frau Henn, Frau Luginsland, Frau Baro and Frau Schwarzkopf for helping me out in administrative matters. Frau Panicker-Otto deserves special mention for her immense support and care that made my academic and personal life at ease.

I am grateful to all those who provided the technical and analytical support to complete this thesis work (Dr. P. Fischer, Frau N. Böres, Herrn E. Ehrlich, Frau A. Pikulski, Frau U. Twiehaus, and Herrn J. Rebell for NMR, Dr. J. Opitz, Herrn J. Trinkner and Frau K. Wohlbold for mass spectroscopy, Frau D. Göhringer, Frau C. Lauxmann, Frau L. Müller, Frau M. Ragaly and Frau M. Richter for elemental analysis, Dr. W. Frey, Dr. F. Rominger and Dr. T. Oeser for X-ray measurements). Dr. B. Miehlich is gratefully appreciated for his prompt assistance on software/hardware problems.

Many thanks to Herrn H.-J. Bräuner and Herrn P. Schüle for assisting me in ordering the chemicals and other required things and Herrn R. A. Linderer for providing the laboratory requirements.

Thanks a ton to all my colleagues in Stuttgart and in Heidelberg for their support and intimacy on and off the academia. Special thanks to Matthias, Michel, Tobi, Sacha, Filiz, Melissa,

Tanuja, Miriam, Ralph and Christoph for the productive discussions and helps at various stages of my PhD. Tom (visiting student from U.S.A) is much appreciated for his experimental contribution and for the nice company he was in the lab.

I am hugely indebted to my previous research mentors, Prof. Curt Wentrup and Prof. Dr. C. Schneider for their guidance, inspiration and the expertise I gained from their laboratories. I also owe a lot to all my teachers-especially Joseph sir (7^{th} standard), Jony sir (higher-secondary), Prasad sir (bachelors), and Asokan sir (masters)- from schooling to graduation who influenced me to the core and played such an important role in shaping up my career and self.

My very special thanks to all my dear friends, Biju, Pratheesh, Girish and Rajesh in my hometown for their support and love that enabled me to endure the difficult times. Sreeraj, Gopan, Sreenivasan, Sajeev, Krishnamohan, Sudheendran, Thomachayan, Ramesh and Rajesh- friends from my home university- deserve a lot for what they are always; selfless, motivating and funny that entertained and enriched my life a lot. Nandakumar and Lisa are appreciated for their guidance and inspiration. Thanks a lot to my friends here in and out of Stuttgart- Kamal, Sankaran, Lijo, George, Samith, Sony, Arun, Rajagopal, Jimmy, Sajid, Atanu, Nithin, Prasanth,…- for the lively social circle and entertainment. Chara, Thanks a lot for the wonderful company, discussions, and contributions to the thesis. Fathima has been a jovial customer to my lab and thanks to her for the routine chit-chats in my broken German that cheered up most of my days.

Last but never the least, I express my sincere gratitude to my parents, sisters and brothers-in-law for their life-long love, support and intimacy. I bow to the almighty for strengthening me to follow the destiny.

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List of abbreviations

BuLi	Butyllithium
Bs	4-bromobenzenesulfonyl
Calcd	Calculated
d	day(s)
DCM	Dichlormethane
DFT	Density functional theory
DMAP	4-*N*,*N*-Dimethylaminopyridine
DMF	*N*,*N*-Dimethylformamid
DQF-COSY	Double-quantum filtered COSY
dr	*diastereomeric ratio*
eq	equivalent
EtOAc	Ethyl acetate
EI	*electron impact*
ESI	*Electrospray ionisation*
Et	Ethyl-
Et_2O	Diethylether
h	hour(s)
HMBC	Heteronucelar multiple bond correlation
HSQC	Heteronucelar single quantum coherence
IR	Infrared spectrum
J	coupling constant
$LiAlH_4$	Lithium aluminiumhydride
m	Multiplet
M	molar
M^+	Molecular ion
min	Minute(n)
Me	Methyl-
MeOH	Methanol
MHz	Megahertz (10^6 Hz)
MS	Mass spectroscopy
m/z	mass/charge
Bs	para-Bromo
NEt_3	Triethylamine
NMR	*nuclear magnetic resonance*
PE	Petrolether
Ph	Phenyl-
PMP	*para*-Methoxybenzyl-
q	quartet
quin	quintet
R_f	*ratio of fronts*
rt	Room temperature
s	singlet
t	triplet
TBAF	*Tetra-n*-butylammoniumfluoride
THF	Tetrahydrofuran
Ts	*para*-toluenesulfonyl

Specific projects in this thesis have been presented/appeared in:

Publications

1. Gold Catalysis: Anellated Heterocycles and Control of the Chemoselectivity by Tether Length, A. S. K. Hashmi, **S. Pankajakshan**, M. Rudolph, F. Rominger. (Submitted to *Chem. Eur. J*)
2. Gold Catalysis of Furyl-Alkynes: Proof for the cationic nature of the 'carbene' intermediate, A. S. K. Hashmi, S. W. Schäfer, **S. Pankajakshan**, T. Hengst, W. Frey. (Manuscript in preparation for *Angewandte Chemie*)

Posters

1. 'Synthesis of Organogold Complexes for Gold-loaded Zeolite systems', **S.Pankajakshan**, A. S. K. Hashmi, SFB-706 Postgraduate Workshop, October 6-8, 2008, Hirschegg, Austria.

2. 'Catalytic Aerobic Alcohol oxidation by Gold/n-Butyl Lithium', **S. Pankajakshan**, A. S. K. Hashmi, International Symposium on Selective Oxidation Catalysis: C-H activation via molecular oxygen, October 29-31, 2007, Hohenheim, Germany.

3. 'Gold catalysis-Interesting formation of *N*,*O*-Acetals', **S. Pankajakshan**, A. S. K. Hashmi, GDCh-Wissenschaftsforum Chemie, September 16-19, 2007, Ulm, Germany.

Oral presentations

1. 'Catalytic Aerobic Alcohol oxidation by Gold/*n*-Butyl Lithium' SFB-706 Postgraduate Workshop, September 25-27, 2007, Kloster Banz, Germany.

Zusammenfassung

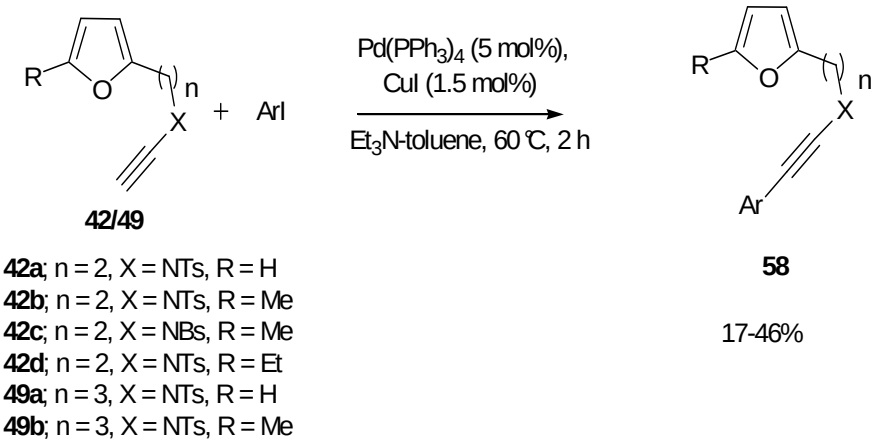
a) Das erste Kapitel dieser Doktorarbeit befasst sich mit der homogenen goldkatalysierten Umsetzung von furylsubstituierten Arylinamiden und Arylinolethern. Enine gehören wohl zu den am besten erforschten Substratstrukturen auf dem Gebiet der homogenen Goldkatalyse, wohingegen die Reaktivität von Eninamiden oder Eninolethern bisher kaum untersucht wurde.[34,35] Erst kürzlich berichteten Hashmi et al. von der homogenen goldkatalysierten Synthese von Phenolen aus furansubstituierten Inamiden/Inolethern.[45e] Diese Substrate zeigten eine exzellente Reaktivität und Selektivität, die offensichtlich auf die Heteroatome zurückzuführen sind, welche direkt an die Alkineinheit angeknüpft sind. Beeindruckt von der Reaktivität und der hohen Selektivität dieser Systeme, entschieden wir uns, die Eigenschaften der arylsubstituierten Derivate in der katalysierten Umsetzung dieser Stoffe zu untersuchen.

Synthese von Inamiden und Inolethern

Für die Untersuchungen wurden Substrate mit zwei bzw. drei verbrückenden Kohlenstoffatomen zwischen Furyl- und Alkineinheit dargestellt. Zunächst wurden die terminal unsubstituierten Furaninamide und Inolether synthetisiert.[10k-m,45e] Eine anschließende Sonogashira[51]- oder Negishiarylierung des endständigen Alkins lieferten dann die gewünschten Arylinamid beziehungsweise Arylinolether.

Sonogashira-Kupplung: Synthese von Arylinamiden

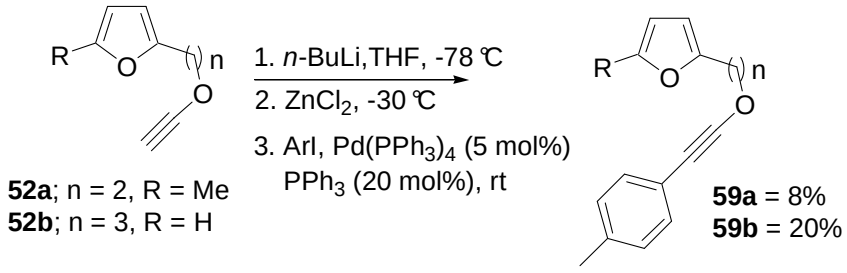
Die Arylsubstitution der terminalen Inamide **42/49** wurde mit der Sonogashira-Kupplung durchgeführt (Schema A).[51] Die Reaktion konnte nur für Aryliodide ausgeführt werden. Sterisch anspruchsvolle Gruppen in *ortho*-Position des Arensubstituenten wurden nicht toleriert.



Schema A: Sonogashira-Kupplung mit Furlyinamiden

Negishi-Kupplung: Synthese von Arylinolether

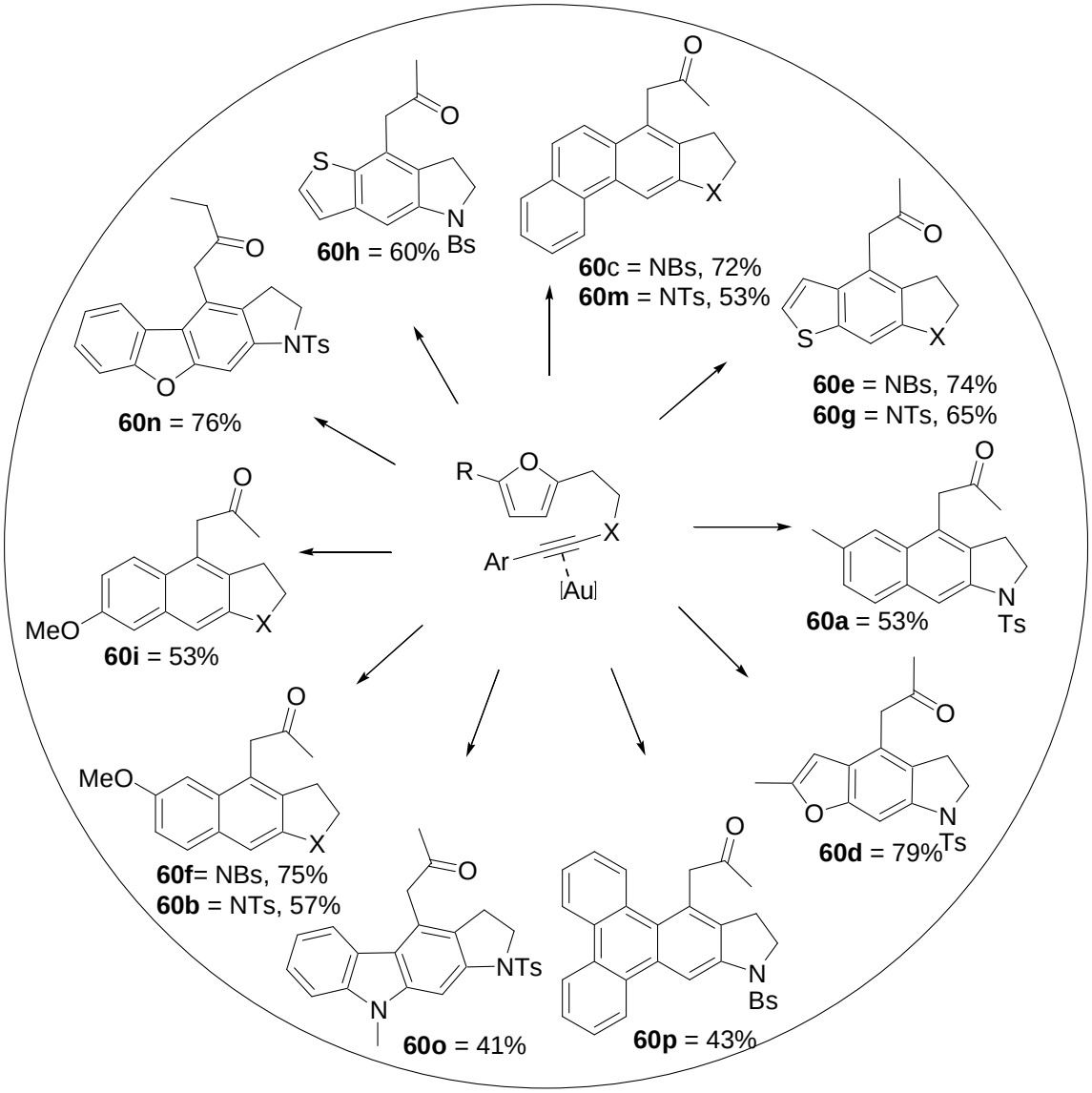
Da eine Arylierung der Inolether über die Sonogashira-Kupplung nicht erfolgreich war wurde daher das Protokoll von Negishi zur Darstellung von Arylinolethern **59** (Schema B) angewendet. Die Reaktion lieferte die Produkte **59** nur mit geringen Ausbeuten.



Schema B: Negishi-Kupplung mit Inolethern **52**

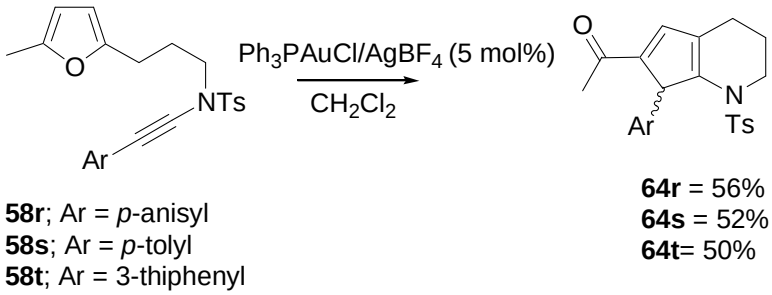
Goldkatalysierte Umsetzung von Arylinamiden

Die Arylinamid-Substrate stellten sich als interessante Kandidaten für die Goldkatalyse heraus, da die Art der Reaktivität von der Kettenlänge abhing. Die Substrate mit zwei Kohlenstoffeinheiten in der Kette vollzogen eine Friedel-Crafts-artigen Reaktion und lieferten benzannelierte Arene in hervorragenden bis moderaten Ausbeuten (Schema C). Eine Kombination aus $Ph_3PAuCl/AgBF_4$ (5 mol%, 1:1) in CH_2Cl_2 oder $CHCl_3$ stellte sich als die geeignetste Katalysatorwahl heraus. Daduch konnte ein breites Spektrum an Polyarenen und Polyheteroarenen synthetisiert werden. Substrate, die ein nicht-aktiviertes Aren besitzen, reagierten selbst bei höheren Temperaturen und verlängerten Reaktionszeiten nicht.



Schema C: Produktspektrum der goldkatalysierten Benzannelierung von Arylinamiden **58**

Die Goldkatalyse der Substrate **58r-58t** mit einer C_3- Kette zwischen Furan und Inamideinheit ergab eine komplett andere Reaktivität und führte zu Cyclopentadien-Strukturen (Schema D). Wie bei den kürzerkettigen Substraten wurden elektronenziehende Gruppen am Aren nicht toleriert.



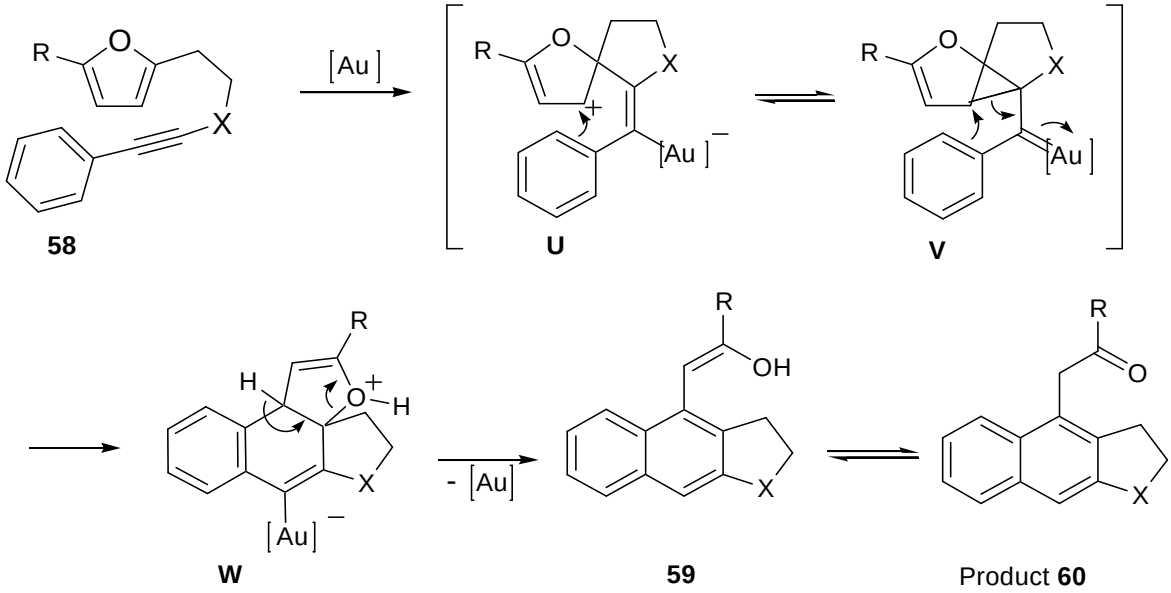
58r; Ar = *p*-anisyl
58s; Ar = *p*-tolyl
58t; Ar = 3-thiphenyl

64r = 56%
64s = 52%
64t= 50%

Schema D: Goldkatalysierte Umsetzung von Arylinamiden **58** mit einer C_3-Kette

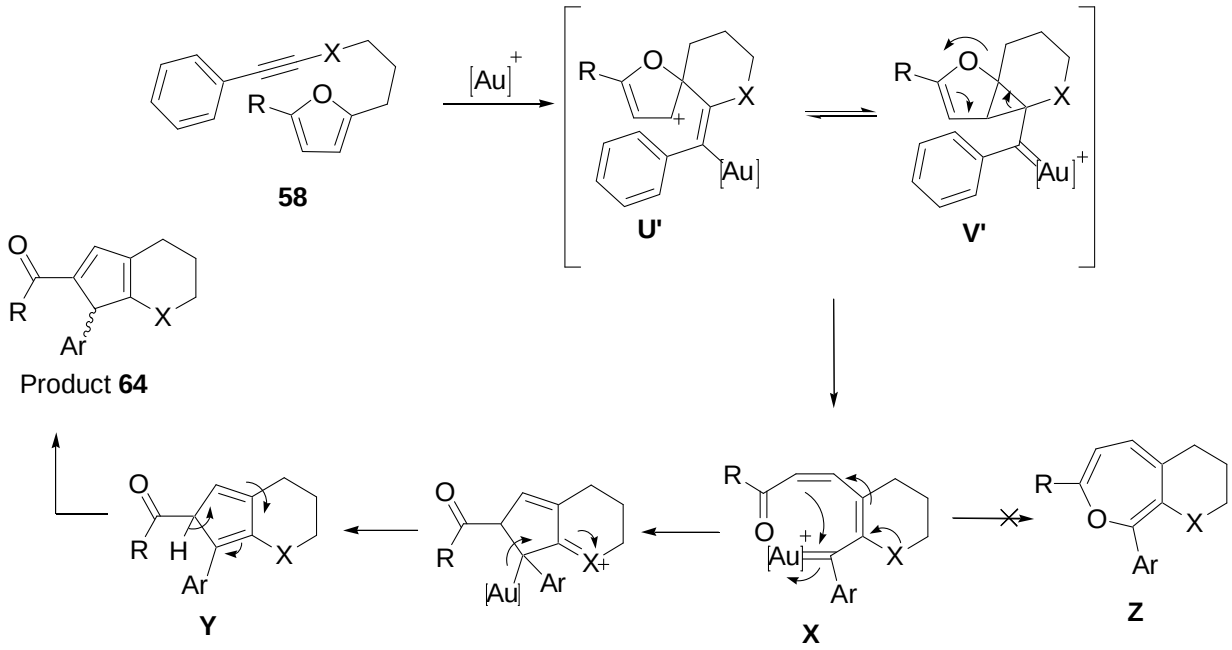
Mechanistischer Vorschlag

Die Formierung der benzannelierten Produkten aus C_2-verbrückten Furylinamiden **58a-58p** verläuft im ersten Schritt über eine *5-exo-dig*-Cyclisierung des Alkins mit dem Furylsybstituenten gefolgt von einer Friedel-Crafts-artigen Arylierung (Schema E).



Schema E: Vorgeschlagener Mechanismus zur goldkatalysierten Benzannelierung von C_2-verbrückten Arylinamiden.

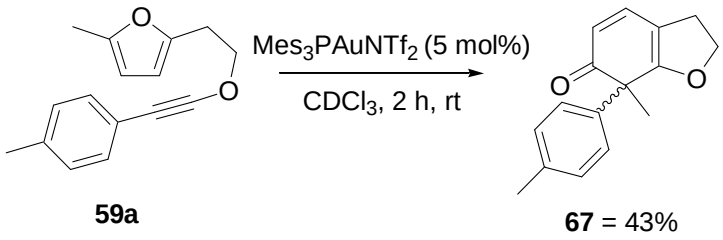
Der mechanistische Vorschlag zur Bildung der Cyclopentadienstrukturen **64** aus Arylinamiden mit verlängerter Kette (1,7-Enin) sieht vor, dass dieser zunächst über einen Reaktionspfad analog der goldkatalysierten Phenolbildung verläuft. Dies führt zur Entstehung des monocyclischen Carbenzwischenproduktes **X**. Durch eine Isomerisierung der C-C π-Bindungen des Intermediates bildet sich schließlich das Endprodukt **64** (ein Ringschluss des nucleophilen Carbonylsauerstoffs mit dem Carbenkohlenstoff würde zum Benzooxipin führen **Z**, eine Zwischenstufe des Phenolprodukt[11b]) (Schema F).



Schema F: Vorgeschlagener Mechanismus zur goldkatalysierten Bildung von Cyclopentanonen aus C_3-verbrückten Furylinamiden **58**

Goldkatalysierte Umsetzung von Arylinolethern

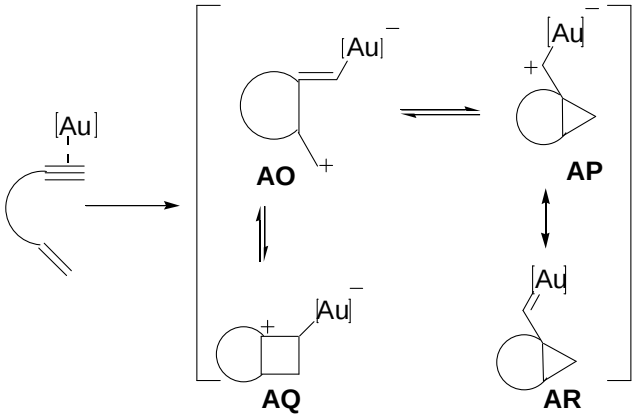
Die goldkatalysierte Umsetzung der Inoletherverbindungen **59a** führte zum cyclisch konjugierten Keton **67** (Schema G). Bei Substraten mit verlängerter Alkinyl-Kette erfolgte jedoch eine Addition von Wasser an das Alkin.



Schema G: Goldkatalyse des Arylinolethers **59a**

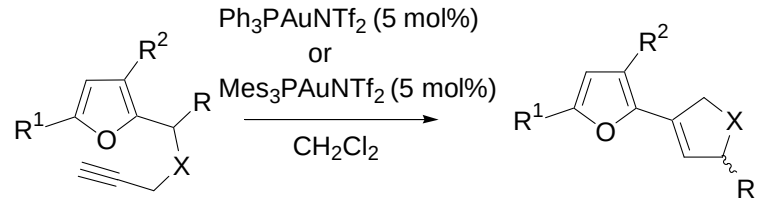
b) Das zweite Kapitel dieser Arbeit behandelt die goldkatalysierte Umsetzung von Alkinylfuranen, die ein mögliches kationischen Intermediats im Reaktionverlauf nachweisen sollen. Hintergrund sind die neusten wissenschaftlichen Diskussionen um die elektronische Natur des Zwischenprodukts in der goldkatalysierten Enin-Cycloisomerisierung.[20] Von der Mehrzahl der Autoren wird für den Reaktionsmechanismus hierzu ein Cyclopropyl-Carben–Intermediat postuliert. Bisher konnte jedoch eine solche Spezies nicht isoliert oder spektroskopisch analysiert werden. Kürzlich schlug Fürstner et al. einen experimentellen

Beweis für die Beteiligung einer kationischen Form dieses Zwischenprodukts in goldkatalysierten Cyclisierungen vor.[20] Dieses Szenario verlangt die Betrachtung des Zwischenprodukts als eine mesomere und tautomere Kombination von verschiedenen kanonischen Formen (Schema H).



Schema H: Tautomere/mesomere Zwischenstufen der goldkatalysierten Enin-Cyclisierungen

Die Untersuchungen ergaben, dass Alkinylfurane mit Donorsubstituenten R in α-Position der Alkinylkette in der Goldkatalyse unerwartete Fünfringstrukturen, statt der erwarteten Phenole bildeten (Schema I).



112/105

116/118; 20-78%

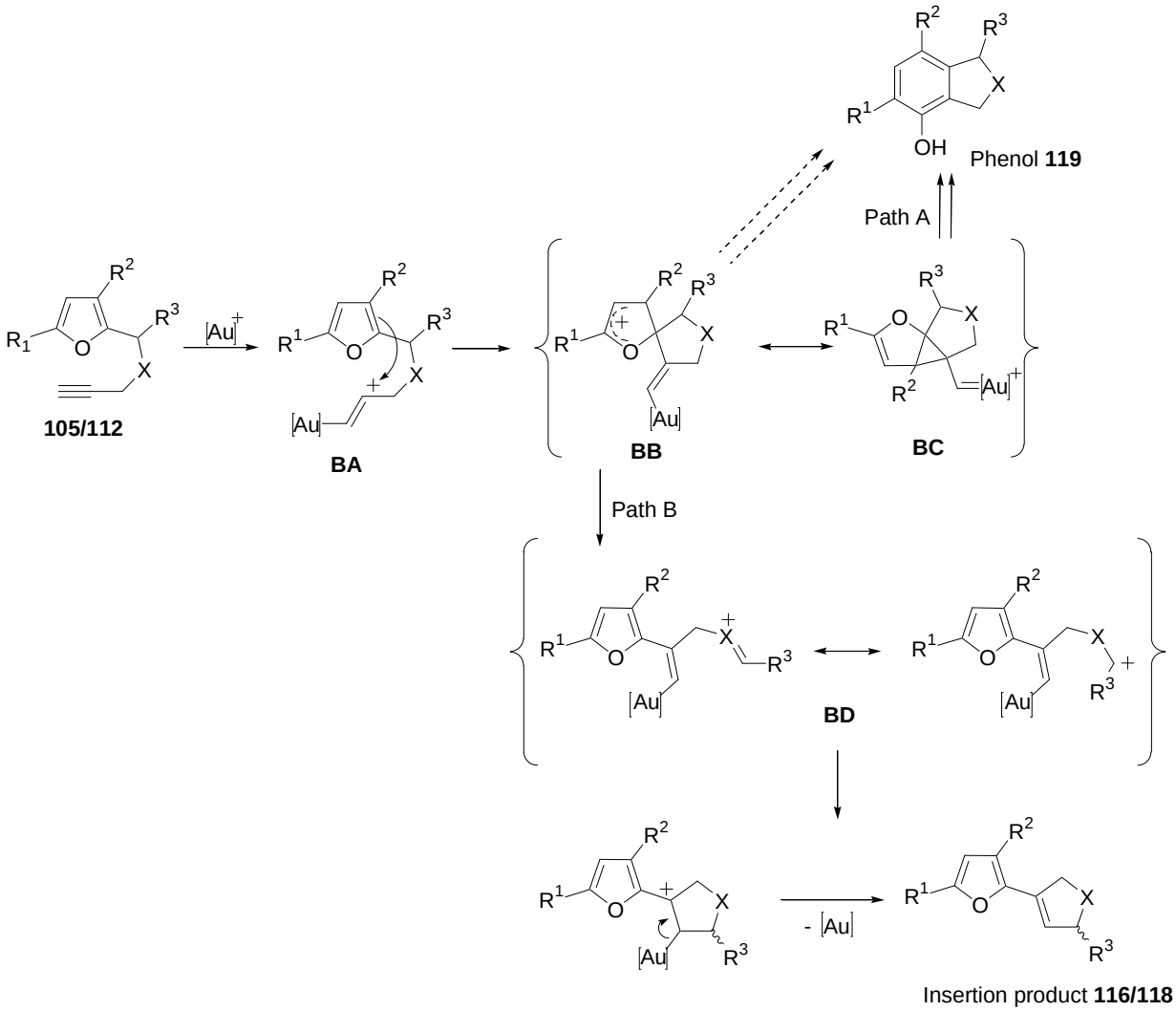
$R^1 = R^2 = H, Me$

R = Alkyl, Aryl, Vinyl

X = NTs, O, NSO_2tBu

Schema I: Goldkatalysierte Bildung von Fünfringstrukturen **116/118**

Aus dem Reaktionsmuster der Substrate **116/118** erschloss sich, dass eine kationische Form des Intermediats **BB** im mesomeren/tautomeren Gleichgewicht auftreten muss, wie in Schema H gezeigt wird. Der mechanistische Vorschlag hierzu basiert auf dem Zwischenprodukt für diese bislang unbekannte Umformung in der Goldkatalyse von Furylalkinen (Schema J).



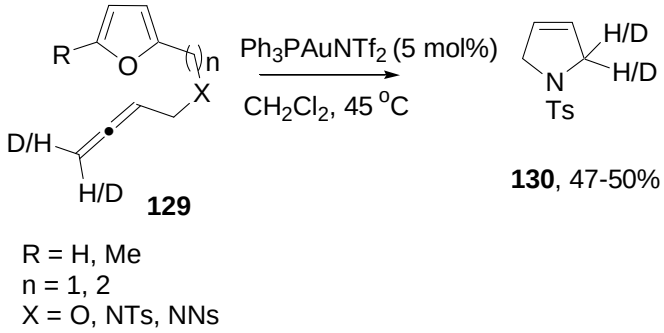
Schema J: Vorgeschlagener Mechanismus für die Bildung des Insertionproduktes

Nach diesem Mechanismus wird in Anwesenheit eines Donorsubstituenten R^3 am α-Kohlenstoffatom der Kette der Ring des Intermediates **BA** geöffnet. Über den Reaktionspfad B wird die kationische Form des Zwischenprodukts **BB** gebildet. Die Bildung des fünfgliedrigen Insertionsprodukts **116/118** durch die kationische Form des Intermediats **BB** erscheint plausibel, wenn die Tatsache in Betracht gezogen wird, dass die Substrate Kation-stabilisierende Substitutenten am C-3 des Furans besitzen (Lokalisierung der positiven Ladung im Kation **BB**).

Nach diesem Mechanismus bildet sich zunächst die kationische Form des Zwischenprodukts **BB**. Die Cyclisierung wird durch Kation-stabilisierende Substitutenten am C-3 des Furans begünstigt. In Anwesenheit eines Donorsubstituenten R^3 an dem □-Kohlenstoffatom der Kette kann sich über den Reaktionspfad B der Fünfring zu dem kationischen Intermediat **BD** öffnen. Die Reaktivität der Substrate korreliert hierbei mit der Fähigkeit der Substituenten das

offenkettige Kation zu stabilisieren und es ergibt sich die Reihenfolge p-Anisyl > Cyclopropyl > Phenyl > Furyl > Ethyl. Die □-Positionierung des Heteroatoms X am kationischen Kohlenstoff von **BD** war auschlaggebend für die Stabilisierung des Intermediats. Bei einer Verschiebung des Heteroatoms um eine Position vom kationischen Zentrum weg, war das Substrat nicht mehr in der Lage, ein Insertionsprodukt zu liefern.

Die homogen goldkatalysierten Umsätze von Furylallenen wurden als eine Fortsetzung zu dem oben erwähnten Projekt untersucht. Doch die Substrate unterliefen keiner typischen Allencycloisomerisierung, formten stattdessen jedoch das formale Metatheseprodukt Dihydrotosylpyrrol (Schema K).



Schema K: Goldkatalyse des Furylallenen

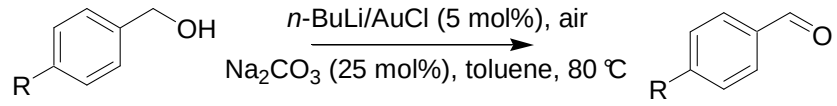
c) Das dritte Kapitel der Arbeit befasst sich mit der unerwartete Formierung von *N*,*O*-Acetalen aus Oxanorbornadienen, einem Diels-Alder-Produkt aus Alkinylfuranen ,die sich unter der Einwirkung von Gold und anderen Lewissäuren bildeten (Schema L). AuCl hat sich unter den gegebenen Bedingungen als die beste Lewissäure erwiesen, wobei $Yb(CF_3SO_3)_3$ ebenfalls eine bemerkenswerte Reaktivität aufzeigte. Die Untersuchungen zeigten, dass die Reaktion einem einfachen säurekatalysierten Mechanismus unterliegt. Da aber im Produkt eine Umlagerung des annelierten Heterocyclus stattfindet, deutet dies auf einen komplexen Reaktionsmechanismus hin.

137
R = H, Me, Ph
R^1 = Me, Et

138, 77-87%

Schema L: Goldkatalysierte Formierung von *N*,*O*-acetalen aus Oxanorbornadienen

d) Das vierte Kapitel dieser Doktorarbeit untersucht goldkatalysierte aerobe Oxidationsreaktionen. Das hierzu entwickelte homogene Katalysatorsystem, bestehend aus Gold(I)-chlorid, *n*-Butyllithium und Natriumcarbonat war in der Lage primäre aromatische Alkohole zu Aldehyden mit Luftsauerstoff in guten bis sehr guten Ausbeuten zu oxidierten (Schema M). Dieses System zeigte jedoch kaum Aktivität bezüglich aliphatischen und sekundären Alkoholen.



R = H,OMe, CH_3

85-95% (GC)
8-16 h

Schema M: Gold/*n*-BuLi-Katalysatorsystem für die Oxidation von primären aromatischen Alkoholen mit Luftsauerstoff

1. General Introduction

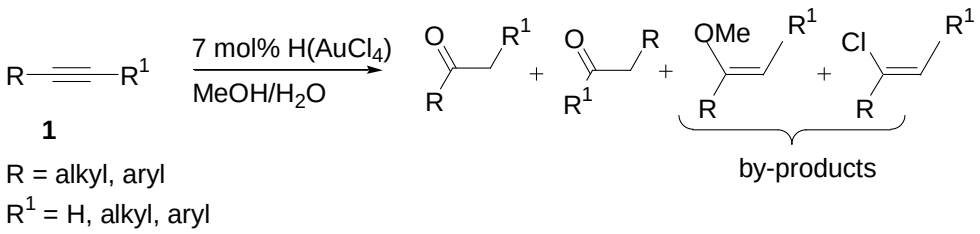
1.1 Gold as a homogeneous catalyst; Reactivity and special features

1.1.1 Introduction

Gold is considered to be the first metal used by humans and its history dates back to antiquity. This element which falls in the 'coinage' group 11 of the periodic table has been and still one of the most sought-after metals owing to its preciousness, durability and inertness. The very same features made people sceptical about its chemical reactivity thereby detaining it's destiny as a useful element rather as a catalyst in chemical transformations. The role of gold in organic/organo-metallic chemistry had long been confined to its stoichiometirc usage. It took as late as mid-1900s to have reports on the authentic potential of gold catalysts. Since then gold has been of profound application in heterogeneous catalysis. But homogeneous catalysis using gold pretty much remained in the cold until the last two decades when and where it started to blossom.[1] The introductory part of this thesis could only offer a brief overview of the key discoveries that revealed the pertinence of gold in the field of homogeneous catalysis. A few sections are devoted to the qualitative theoretical understanding of the catalytic reactivity of gold which is often unique compared to its transition metal counterparts.

1.1.2 Early stages (1976-1999)

The roots of homogenous gold catalysis could be traced back to 1930s and there were scattered reports in the succeeding four decades.[1k] The first remarkable report on gold catalysis came in 1976 when Thomas et al. found out the addition of methoxy and hydroxyl nucleophiles on alkynes **1**, when treated with catalytic amounts of hydrogen tetrachloroaurate[2] (Scheme 1). This work identified the side products of this reaction too, which later became important in gold catalysis. Later on, Utimoto and co-workers developed similar and related nucleophilic additions on alkynes using sodium tetrachloroaurate as catalyst.[3]



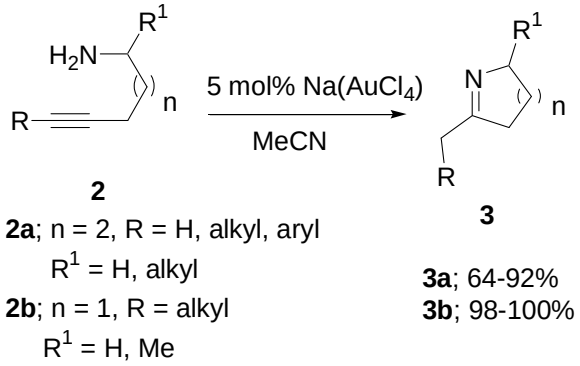
1

R = alkyl, aryl

R^1 = H, alkyl, aryl

Scheme1: Gold catalyzed nucleophilic addition to alkynes

Another key discovery on the Lewis acid catalysis of gold was made by Utimoto et al., in 1986.[4] They described the intramolecular hydroamination of alkynes **2a** catalyzed by sodium tetrachloroaurate (Scheme 2). The reaction surpassed the then existed palladium catalyzed methodologies to synthesize N-hydroheterocycles in terms of selectivity and milder conditions. It was also possible to produce dihydropyrrole units **3b** from 4-alkynyl amines **2b**. Later on an improved methodology on related substrates was introduced by Müller et al.[5]



Scheme 2: Gold catalyzed hydroamination of alkynes

Ito-Hayashi Aldol reaction based on ferrocene ligands and $(Au(c\text{-}C_6H_{11}\text{-}NC)_2)BF_4$ as the gold source was a significant report in the area of asymmetric gold catalysis.[6] In 1998 Teles et al. proposed the first application of phosphine-gold complexes in homogeneous catalysis[7]. They have shown that bis-hydroalkoxylations of alkynes can be done much effectively and selectively using the in situ generated catalyst from a combination of $Ph_3PAu(I)Me$ and methanesulfonic acid. This discovery was a major breakthrough in gold catalysis as evident from the incredible popularity these catalytic systems attained in the following years.

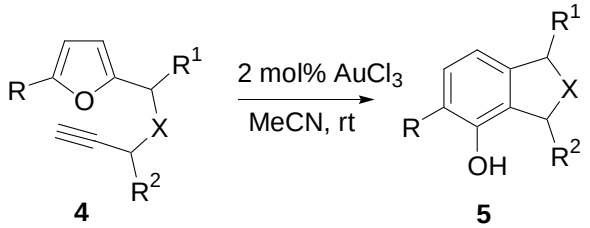
1.1.3 The 'Gold rush' in homogeneous catalysis

The last decade witnessed an exponential raise in activity in the area of gold catalysis and is still counting. The substrate scope for these mild and selective catalytic systems has significantly been broadened and new catalytic systems were developed. The typical π and σ electrophilicities of gold has made several transformations feasible such as additions of carbon and heteroatom nucleophiles to unsaturated bonds, Friedel-Crafts reactions, cycloisomerization of enynes, carbonyl and imine activations and so on.[1, 8] The mere multitude of publications and reviews that came out in this period testimony these facts. As Stephen Hashmi wrote in his review, "A change in paradigm has taken place. While the

ancient alchemists investigated the question of how to make gold, now the question is what to make with gold."[1i]

The impetus for extensive research in this field was provided by a report from Hashmi et.al in 2000 where they described the gold catalyzed C-C and C-O bond formation.[9] The reaction of furans (in situ formed) with allenyl ketones produced α, β-unsaturated ketones. The proposed mechanism involved a nucleophilic addition of the heteroaryl species on to the double bond and the subsequent protodeauration furnished the molecule. The formation of furans from propargyl ketones and enynols were also mentioned in the same report.

Another remarkable transformation was reported by Hashmi and co-workers in the same year.[10a] The treatment of furyl-alkynes **4** with $AuCl_3$ in acetonitrile furnished the phenol product **5** in excellent yield and selectivity (Scheme 3).



4 **5**

X = CH_2, O, NTs, NNs, $C(CO_2Me_2)_2$, $NTsCH_2$

R^1 = H, Me

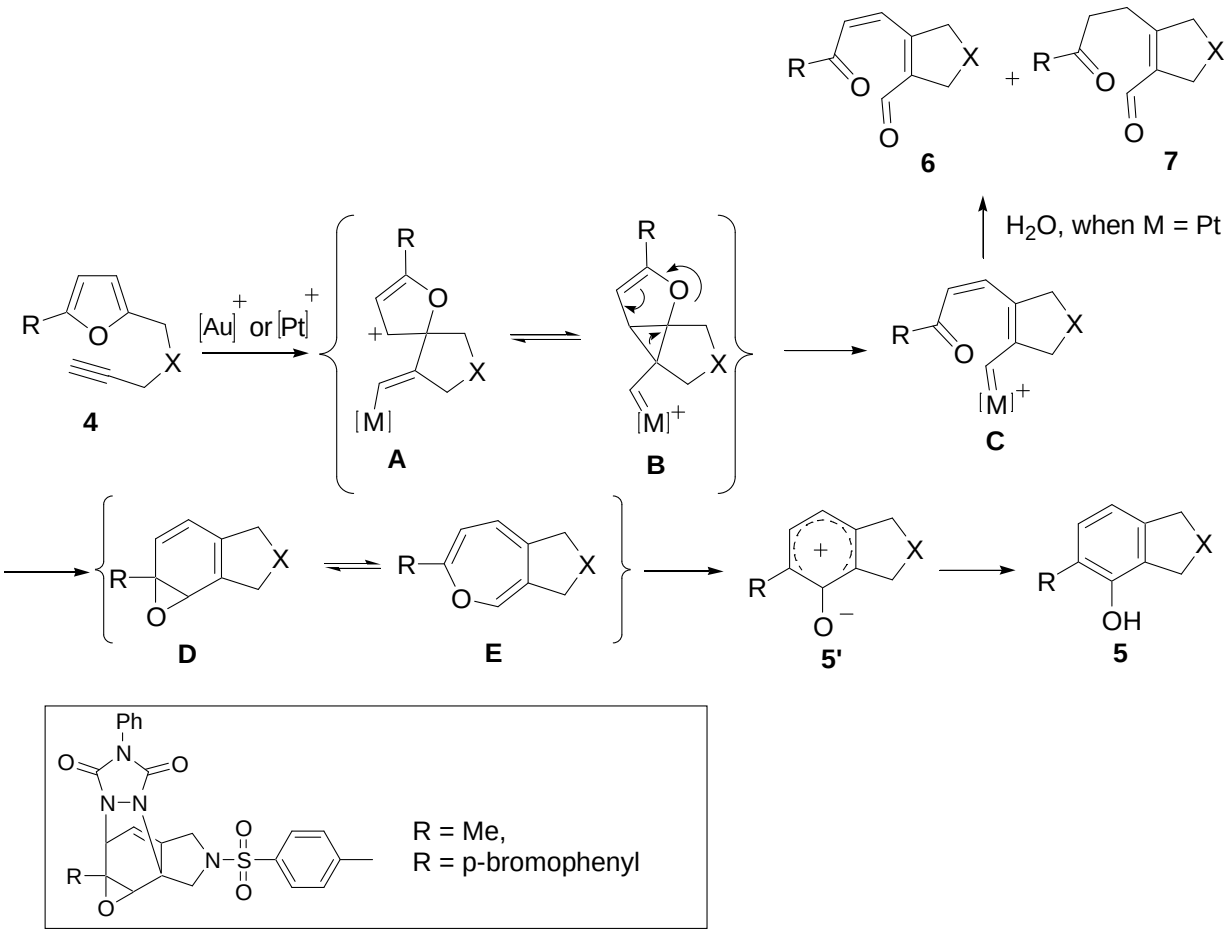
R^2 = H, Me

31-96%

Scheme 3: Gold catalyzed phenol synthesis

This methodology was quite remarkable for it served an excellent protocol for the synthesis of highly functionalized aromatics from commercially available cheap furfurals.[10] The suggested mechanistic pathway for this transformation was debatable for a while. The initially proposed pathway was based on an intramolecular Diels-Alder reaction between the furan and the alkyne. Later on Echavarren et.al found out that $PtCl_2$ also catalyzed this reaction.[11] They have isolated conjugated carbonyl by-products **6** and **7,** when the reactions were carried out in aqueous solvents. A Diels-Alder type mechanism cannot explain the formation of these by-products, although it could be argued that such compounds are formed as a result of a competing side reaction and not necessarily from a common intermediate. Echavarren introduced a carbene mechanism for the proposed reaction which account for the formation of carbonyl by-products also[11b] (Scheme 4). According to this proposal the gold activated alkyne

undergo nucleophilic attack from the furan double bond to form the intermediate cyclopropyl 'carbene' **B** (The authenticity of such an intermediate is yet to be proved experimentally/spectroscopically. So the rendition of the intermediate as purely 'carbene' wouldn't be accurate. The mesomeric/tautomeric cationic form **A** should also be considered as a potential candidate for intermediacy). The ring opening of this intermediate led to the formation of the conjugated monocyclic carbene **C** which in the presence of external nucleophiles like water produced the carbonyl by-products **6** and **7**. In the absence of water, **C** rearranged to the arene oxide **D** or its tautomer oxepin **E**. The cyclopentadienyl cation **5′** is formed in the next step (the direction of the ring opening of the arene oxide intermediate **D** depends on the intrinsic stability of the resulting cation) which upon aromatisation produced the final phenol **5**. The DFT calculations performed on this system supported the carbene pathway.[11b]



D isolated as cycloadduct **8**

Scheme 4: Proposed mechanism for the gold catalyzed phenol synthesis

Later on, Hashmi and co-workers managed to isolate the arene oxide intermediate **D**, by trapping it as a Diels-Alder cycloadduct **8**, thereby unambiguously establishing the

intermediacy of these species.[12] Deuterium labelling experiments revealed further information about the observed regioselectivity in the reaction.[13] The methodology didn't work for terminally substituted alkynes.

The gold catalyzed phenol synthesis encouraged the chemists around the world to verify the activity of similar substrate skeletons (1,n-enynes) towards gold catalysts, and a plethora of catalytic transformations were developed consequently.[1, 8] Although enynes hold the impressive heritage of the most widely studied systems in transition metal catalysis, a new door to chemical discovery was opened on the introduction of gold and to certain extent platinum catalysts.

1.1.4 What makes gold a special Lewis acid?

Cationic gold complexes especially, gold(I) compounds are superior Lewis acids compared to other metal cations for many transformations. Their unique 'alkynophilicity' coupled with reluctance to switch between oxidation states[14] ensued the development of novel modes of catalytic cycles other than the classical oxidative addition/reductive elimination pathways prevalent in late transition metal catalysis. Also tolerance towards air and moisture and the nontoxicity render these catalysts much user friendly and a premier choice for green chemistry. A brief mention of the parameters accounting for the observed reactivity of gold catalysts/ reactivity difference to its close relatives are described below.

1.1.4.1 'π acidity' of gold

The molecular orbital picture of the bonding between a metal (M) and a π ligand (L) (alkyne, alkene, allene, or carbonyl moieties) consists of four components of which only two make significant contribution towards the total bond energy. The in-plane π orbitals make a σ-symmetric L→M donation as well as a π symmetric M→L back donation. The high level computations for the parent gold-acetylene [(Au(C_2H_2)] and gold-ethylene [(Au(C_2H_4)] complexes revealed that the σ interaction (L→M) accounted for 65% of the total bonding situation and the π interaction (M→L) accounted for only 27% of the same.[15] Analogous copper complexes were found to have a higher percentage of back bonding towards the total bonding energy.[16] Spectroscopic studies on gold-carbonyl complexes showed that the stretching frequency of the carbon-oxygen bond (υ_{CO}) is actually greater than that of the free CO, suggesting that the back bonding from the metal to the ligand is minimal.[17] These observations are relevant to the higher reactivity of gold-π ligand systems where the lack of back bonding makes the unsaturated ligand electron deficient, thereby enhancing the

possibility of an intramolecular or intermolecular nucleophilic attack. The notably higher 'alkynophilicity' over 'alkeneophilicity' of gold catalysts could be rationalized on the fact that an Au-alkyne complex has an energetically lower LUMO compared to an Au-alkene complex.[18]

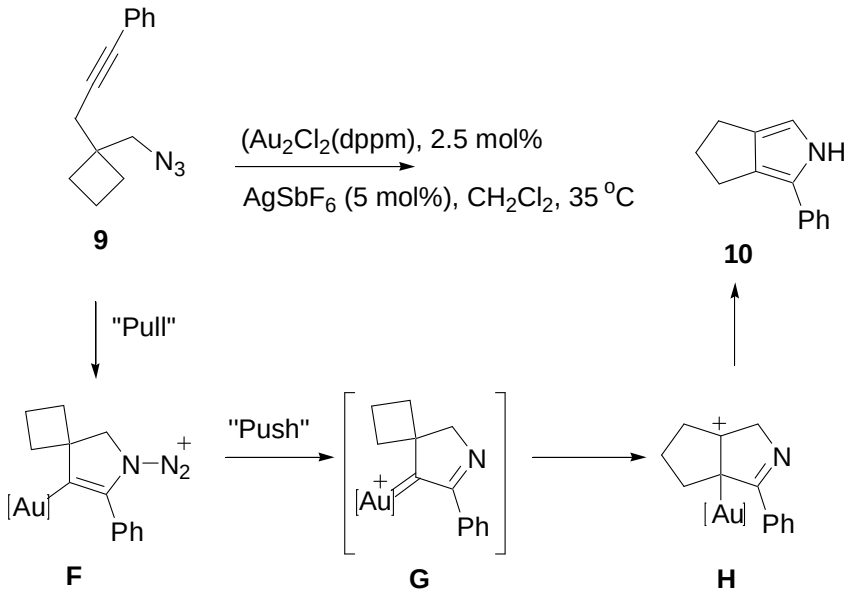
1.1.4.2 Pull-Push reactivity of gold

The gold cation falls under the category of 'π acids' with its ability to coordinate to a multiple bond and deplete its electron density ('pull' effect). This coordination normally accompanies ligand activation and leads to further nucleophilic attack. But this property is exhibited by a number of late transition metal cations (Mercury, Platinum, Copper, Silver, Iridium, Rhodium, Gallium etc.) and this alone (notwithstanding the extra-activation caused by a lack of back bonding in the case of gold) won't be sufficient enough to sense the remarkable success of gold complexes in the realm of enyne cyclization.

Advanced computational calculations carried out on Au-CH_2^+ fragment showed that the bond energy of these species is surprisingly higher compared to other late transition metal analogues.[19] These findings considerable multiple bond character between the gold and the carbon atom. In other words gold can engage in electron back-donation from the metal atom to the carbene ligand (*The usage of the term 'carbene' for gold-carbon complexes is a debatable issue*[20a-c] *as such a compound is yet to be isolated and the observed Au-C bond lengths in many of the known Fischer type 'gold carbene,*[20d] *and NHC complexes*[20e] *fall in the range of a single bond. The experimental evidence available so far support rather the existence of a metal-stabilized cation than a typical metal-carbene*). Later on, Barysz and Pyykkö proposed that the species AuC^+ should have some triple-bond character[21] and mass spectroscopic evidence for such a species has been gained.[22] The thermodynamic stability of gold 'carbene' is evident from the fact that Fischer-carbene complexes of chromium, tungsten, and molybdenum readily undergo carbene transfer reactions with gold complexes.[23] These findings are in sharp contrast to the absence of backing bonding in gold-alkyne/alkene/carbonyl complexes. Thus, gold cationic species is able to drag the multiple bonded ligand towards nucleophilic attack by making it electron deficient yet are capable of stabilizing the developing positive charge on the vicinal 'carbene' carbon (when the nucleophile is a double bond) by back-donation ('push' effect) of electrons.

This 'pull-push' effect whereby the gold simultaneously initiates and stabilizes the incipient cationic (or 'carbene') centres could be regarded as the key feature behind the unique success

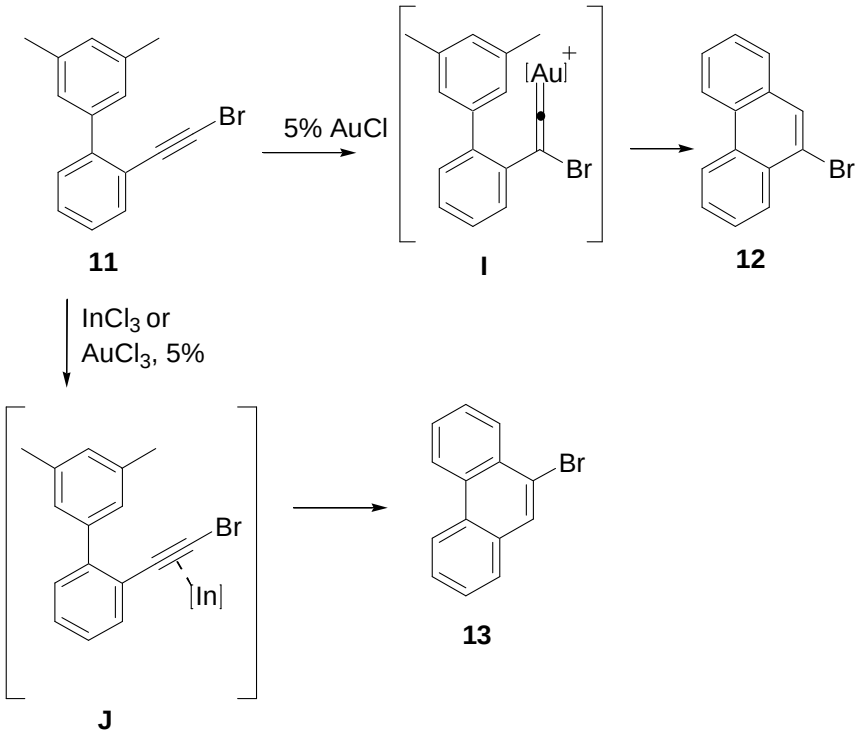
of gold catalysts as carbophilic catalysts. A typical reaction where this effect is apparent is the acetylenic-Schmidt reaction[24] (Scheme 5). Initial gold-activation of the alkyne leads to the nucleophilic attack by the azide in 5-*endo-dig* fashion followed by the liberation of N_2 and stabilization of the resulting 'carbene' **G** by gold.



Scheme 5: Acetylenic Schmidt reaction. Typical 'pull-push' chemistry of gold.

1.1.4.2.1 Au (I)-A 'carbene' friendly gold

The ability to back-donate and thereby lowering the energy profile of the reaction pathway is more pronounced for Au (I) catalysts. Other metal cations like, Indium[25a], Gallium[25b] and in some cases Gold(III)[25c] show traditional Lewis acidic reactivity. A typical example for the delicate 'modus operandi' of gold(I) catalysts is evident from the metal-catalyzed synthesis of halophenanthrenes [26] (Scheme 6). The 'halide walk'[27] observed in the reaction with AuCl could be explained by the formation of a metal-vinylidene intermediate **I**. The less electron rich $InCl_3$ or $AuCl_3$ drive the activated alkyne **J** towards a normal Friedel-Crafts hydroarylation to form **13**.



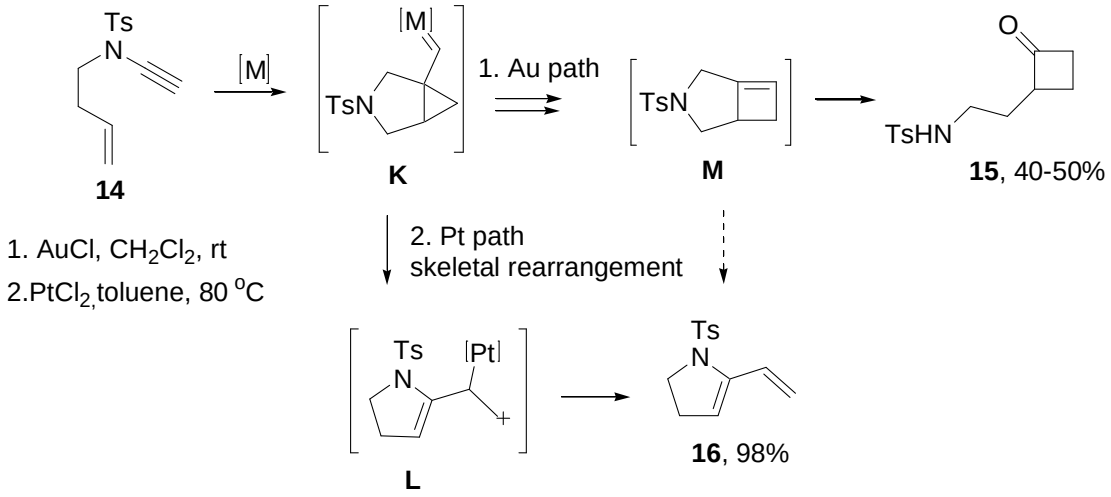
Scheme 6: Dichotomy in the catalytic pathways of Au^{+} and In^{3+}/Au^{3+}

1.1.4.3 Relativistic effects in Gold catalysis

It was known for three decades that relativistic effects play a crucial place in the reactivity and observed physical features of elements.[28] Particularly for heavier transition metals having a highly positive nucleus the electrons tend to be heavier resulting in contraction of the orbitals closer to the nucleus (mainly 's' electrons). The effect is most pronounced for gold where the outer 6s shell contracts and shields the penultimate 5d shell from the electrostatic attraction from the nucleus, causing it to expand. The relativistically expanded 5d orbitals of gold explain its 'soft' Lewis acidic nature (one of the consequences of HSAB[29] concept is that the bigger a charged species is, the higher its 'softness' will be) and also the lower nucleophilicity (in other words lower affinity for oxidative addition) of organoaurate (I) species compared to organocopper complexes.[30] The relativistic contraction (of course together with lanthanide contraction) reduces the size of the metal resulting in greatly strengthened metal-ligand bonding.[31] Computational calculations carried out on the phosphine complexes of gold and silver found out a greater amount of covalent character (greater stability) in the former.[32,33] The higher electronegativity of gold compared to other members of the group also originates from the relativistic effects (The electronegativity of atomic gold is comparable to that of iodine).

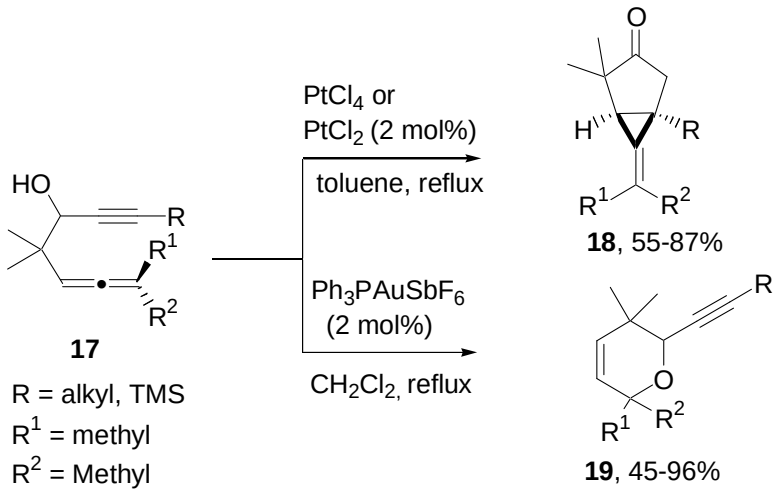
1.1.5 Gold vs Platinum: Divergent reactivities

Platinum (II) salts exhibit similar reactivity to gold(I) complexes in many transformations.[1h] Apart from the operational simplicity and chemoselectivity, they do share some of the features that are seen in the reaction profile for gold(I) catalysts; e.g. ability to stabilize cationic centres, reluctance towards oxidative addition etc. Platinum catalysis normally proceeds with simple salts or in the presence of carbon monoxide to enhance the electrophilicity of platinum. The crucial advantage of gold catalysts is the tuneable reactivity using differently substituted ligands (mainly organophosphines). The metal catalyzed cycloisomerization of ene-ynamides **14** is a noteworthy reaction where platinum(II) and gold (I) engendered different reactivities[34] (Scheme 7). Whereas platinum afforded the "classical metathesis product" **16**, cyclobutanone product **15** was formed under gold catalysis. The milder reaction conditions for the gold catalyzed reaction was assumed to be freezing the skeletal rearrangements[30] of the intermediate 'carbene' **K**, thereby driving the reaction to the observed product **15** via the cyclobutene intermediate **M**.



Scheme 7: Ene-ynamide cycloisomerization. Different pathways of gold and platinum

Malacria & Fensterbank reported an interesting case showing the different chemospecificities of gold and platinum[36] (Scheme 8). Whereas platinum activated the alkyne towards nucleophilic attack from the allene fragment, gold(I) catalyst selectively activated the allene moiety to form the ether product **19** by subsequent hydroxylation.



Scheme 8: Allene vs Alkyne activation in gold and platinum catalyzed cycloisomerization

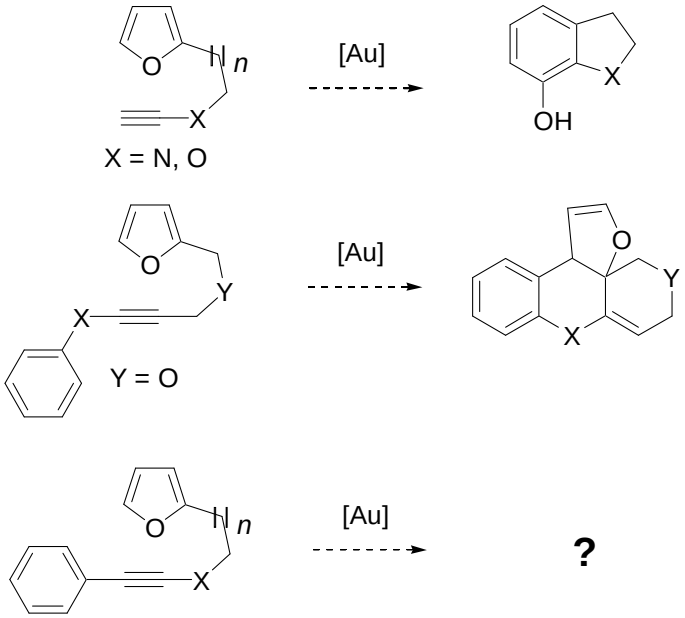
1.1.6 Conclusion

There is growing body of evidence that gold catalysis would remain in the hot spot of scientific interest for a good number of years to come. The focus may shift from classical π activation isomerizations to the development of asymmetric methodologies[37], cluster catalysis, and industrial applications of gold mediated transformations. Theoretical investigations that would enable finer mechanistic perceptions would also add more insight into the already thriving field of homogeneous gold catalysis.

1.2 Setting the goal

The last decade witnessed the reincarnation of gold as an effective homogeneous catalyst shedding the demons of inertness and preciousness. The aura owes much to the renounced 'alkynophilicity' of gold cations and a great deal of research has been focussed on exploring the synthetic utilities of enyne type substrates. An appreciable extent of mechanistic understanding of these transformations has also been unveiled. This thesis pursues the line and attempts to explore the synthetic and mechanistic prospects of homogeneous gold catalysis further.

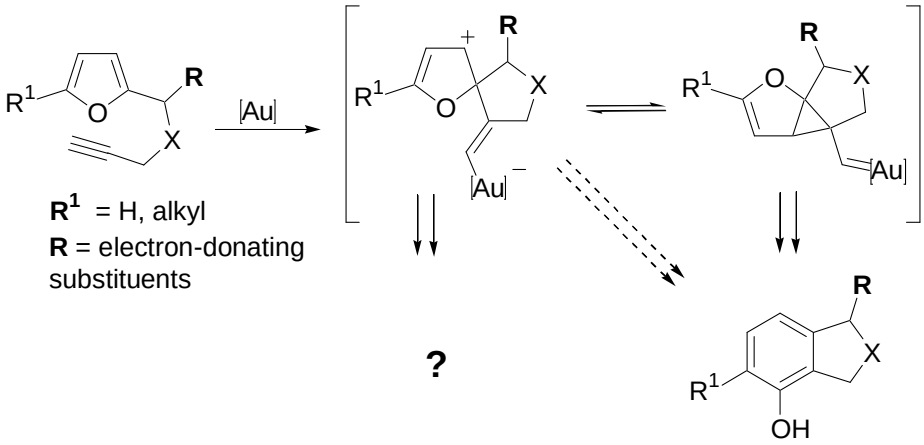
The first project addresses the exploration of homogeneous gold catalyzed cycloisomerizations of aryl substituted furyl-ynamides and ynol ethers. The preparative advantages of having a heteroatom directly attached to the alkyne moiety are magnificently demonstrated in the precedence available,[45f] but the substrate-scope of donor-substituted alkynes remain less-explored. It was assumed that the reactivity of aryl-ynamides and ynol ethers would be interesting in this context (Scheme I)



Scheme I: Different types of alkynyl furans with heteroatom attached on the alkyne

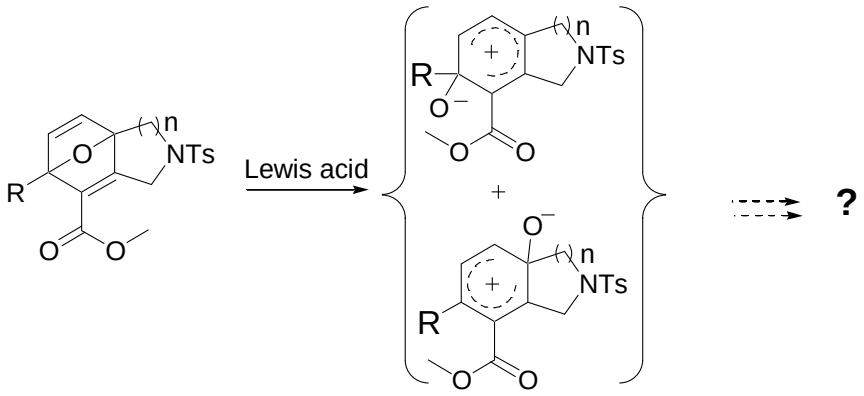
The second project focuses on the development of gold catalyzed cycloisomerization reactions that could provide experimental testaments for unfolding the 'identity crisis', which the intermediates in these transformations have long been suffering from[1g, 20a-c]. Although, majority of the chemical community has embraced a 'carbenic' form of the intermediate,

spectroscopic or conclusive experimental evidence for such a species is yet to obtain. Recent investigative arguments raised by Fürstner[20a,20c] pose a mighty conundrum that demands careful interpretation of the nature of the intermediates involved. We envisage that suitable α-substitutions on the tether of furan containing alkynes (which are precursors for the gold catalyzed phenol synthesis[10]) would initiate a divergent pathway typical for the cationic form of the intermediate, thereby providing telling support for its significance in the mesomeric/tautomeric pool (Scheme II).



Scheme II: Enrichment of a cationic pathway in gold catalyzed cycloisomerization of furyl-alkynes by increasing the electronic bulk on the tether

The third project of this thesis address the gold and other Lewis acid catalyzed ring-opening reactions of norbornadienes. These molecules resemble the oxabicylic intermediates proposed in the first edition of gold catalyzed phenol synthesis.[10a-b] The direction of the ring opening finds a compromise between the resonance versus the ring strain energies of the conceivable intermediates (Scheme III). The regioselectivity of the ring opening and the reaction fate of these intermediates are subjects of investigation.



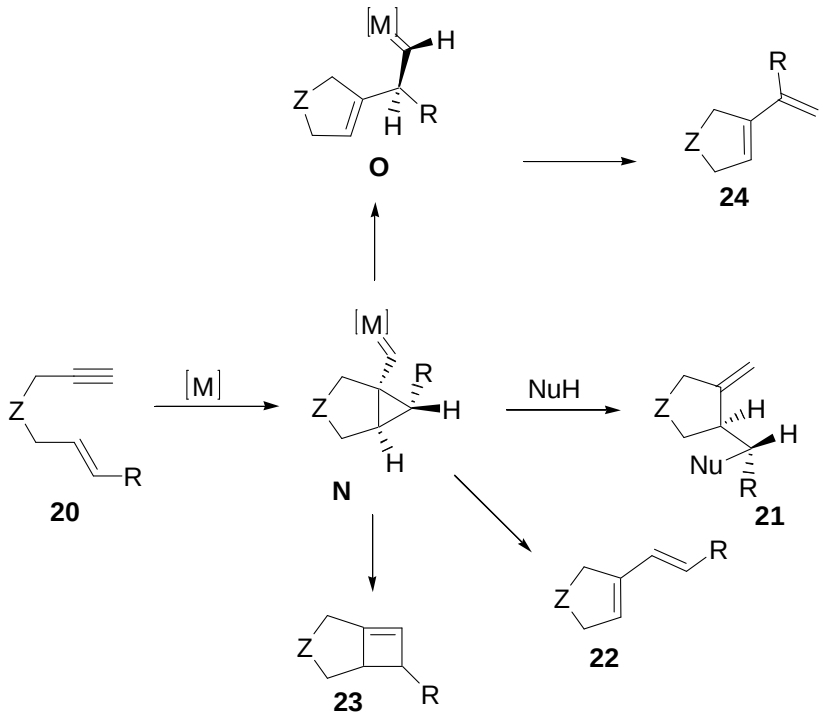
Scheme III: Lewis acid catalysis of oxanorbornadienes

The final chapter focus on the development of gold catalysts for the homogeneous aerobic oxidations of arenes and alcohols. The synthesis of suitable organogold complexes for the development of gold-loaded zeolite systems (which are potential catalytic systems for the oxidation of hydrocarbons, CO etc.) is also attempted as a part of these investigations.

1.3 Gold-catalyzed conversions of Furan containing Aryl-Ynamides and Aryl-Ynol Ethers

1.3.1 Background – Gold catalyzed conversions of aryl substituted 1,6-enynes

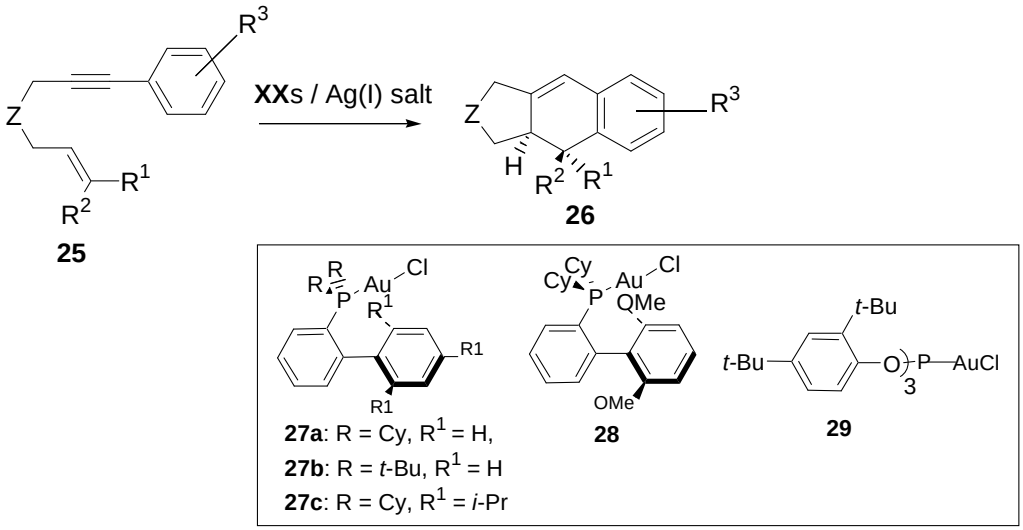
The 5-*exo-dig* mode cycloisomerization of enynes when subjected to noble metal catalysts is thought to proceed via an cyclopropyl 'carbene' intermediate[38] **N,** which further reacts through a variety of ways furnishing different kinds of products, e.g., olefins of type **21**[38], dienes of type **22** when a nucleophile is absent,[39] or less commonly, cyclobutenes of type **23.**[39d-e, 40] Alternatively, the carbene **N** can rearrange to form a new open chain carbene **O** which gives double cleavage rearrangement diene **24** after α-hydrogen elimination (Scheme 9).[39d-e]



Scheme 9: Possible products from the noble metal catalyzed 5-*exo-dig* cyclization of 1,6-enynes

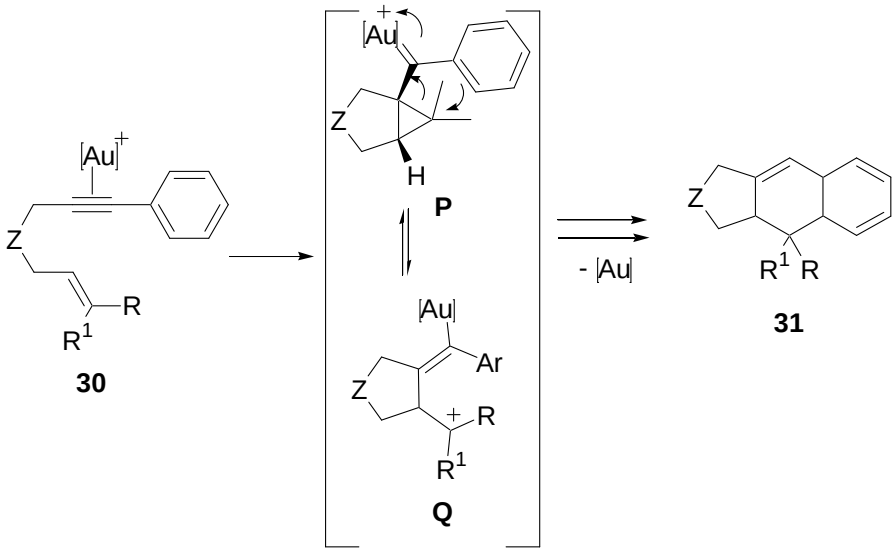
Most of these transformations were effectively done by gold complexes generated by the abstraction of the chloride ion from Ph_3PAuCl. However enynes bearing an aryl group on the alkyne carbon were found to be quite reluctant towards catalytic transformations.[38d, 41] Echavarren et al., developed biphenyl-based phosphine gold complexes (**27**, **28**), and another bulky ligand (2,6-di-*tert*-butylphenyl)phosphite carrying gold complex (**29**) which upon

mixing with Ag(I) salts turned out to be excellent catalyts for the formal [4+2] cycloaddition of aryl-alkynes (Scheme 10).[42]



Scheme 10: Gold catalyzed [4+2] cycloaddition of aryl-alkynes

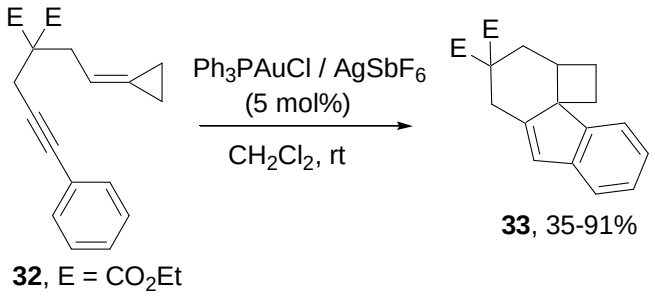
These cycloaddition reactions that provide bi- or tricyclic ring systems are suggested to proceed through the following mechanism. The activation of the triple bond by the gold catalyst leads to the formation of the 'carbene' intermediate **P** (The involvement of a canonical carbocation **Q** cannot be ruled out as DFT calculations done one these systems showed minimal energy difference between **P** and **Q**.[42] Also the reactions of some of the substrates in methanol yielded methoxylated side products which are telling support for the significant mesomeric contribution of the cationic form of the intermediate) which undergoes a Friedel-Crafts-type reaction with the aryl ring. Rearomatisation followed by protodemetallation furnished the final product (Scheme 11). [42]



Scheme 11: Proposed mechanism for the gold catalyzed [4+2] cycloaddition of aryl-alkynes

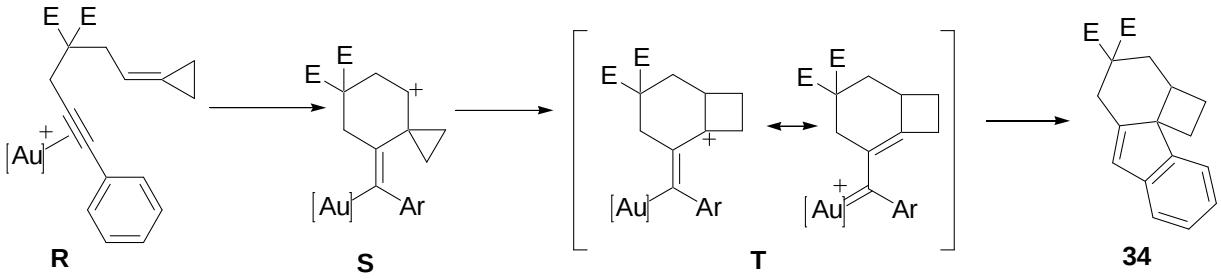
Similar transformations were reported by Yeh et al. where they replaced the open chain olefin in the substrate with cyclic hexa and hepta dienes.[43] The reactions afforded polycycles in a diasteroselective fashion.

Another interesting case of gold catalyzed cyclization of aryl-enynes was reported by Toste et al.[44] They designed aryl ynylidenecyclopropanes **32** and subjected them to gold(I) catalysts. The basic idea was to explore the potential ring expansion chemistry of cyclopropyl methyl cation. The reactions yielded tetracycles **33** in moderate to excellent yields (Scheme 12).



Scheme 12: Cyclization of aryl ynylidenecyclopropanes

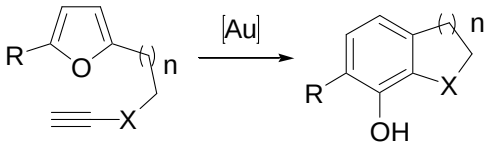
The reaction mechanism was proposed to proceed through the following way. The activation of the triple bond by the gold initiates a 6-*exo-dig* cyclization leading to the formation of a cyclopropylcarbinyl cation **S** which opened up to form the cation or carbene intermediate **T**. A Nazarov-type electrocyclization followed by rearomatisation and protodemetallation furnished the final tetracylic product **34** (Scheme 13).



Scheme 13: Proposed mechanism for the cyloisomerization of aryl ynylidenecyclopropanes

1.3.2 Motivation for the present work

Ene-ynamides form an interesting class of enynes with a donor atom directly attached to the alkynyl moiety. Although, Gold(I) complexes are emerging as the premier choice of catalytic systems for enyne cyclizations, the scope of catalyzing ene-ynamide substrates using them are much less explored till date.[34, 45] Last year Hashmi et al. reported the gold catalyzed synthesis of hydroheterocycles starting from furan containing ynamides and ynol ethers.[45e] The methodology which was essentially a modification of the classical gold catalyzed phenol synthesis, was proven to be an excellent tool to produce different types of heterocycles such as chromans, dihydrobenzofurans, dihydroindoles, and tetrahydroquinolines (Scheme 14).



35

n = 1, 2
R = H, Me
X = NTs, O

36, 29-88%

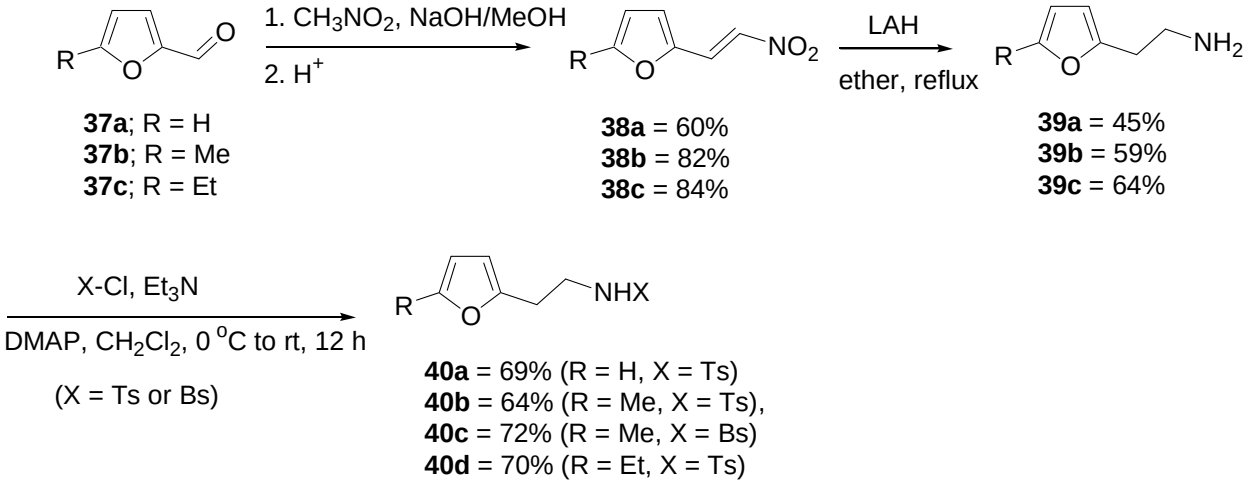
Scheme 14: Gold catalyzed synthesis of hydroheterocycles from ynamides and ynol ethers

These substrates exihibited remarkable reactivity and excellent selectivity compared to the normal furyl alkynes. The presence of the heteroatom closer to the ring ensured that the intermediate arene oxides in the catalytic cycle underwent selective opening to form single isomers of phenols. Impressed with the reactivity and high selectivity of these systems, we decided to explore the catalytic activity of the aryl substituted variants of these compounds.

1.3.3 Synthesis of the Substrates

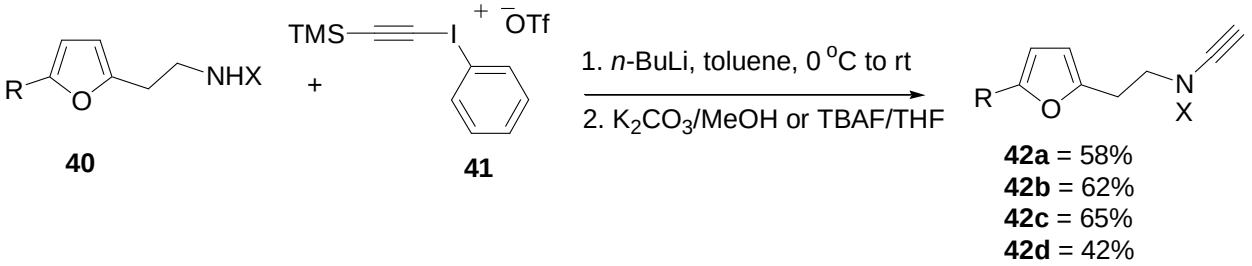
1.3.3.1 Synthesis of the ynamides

The starting materials for the synthesis of ynamides with a two-carbon chain were the toluene sulfonamides **40** which were prepared by literature procedures.[10k-m] The reaction sequence starts from the Henry reaction (nitro-Aldol reaction) of furfurals with nitromethane in alkaline medium to furnish α,β-unsaturated nitrofurans **38**. Reduction with lithium aluminium hydride produced the corresponding amines **39,** which upon tosylation/brosylation furnished the required toluene sulfonamides **40** (Scheme 15).



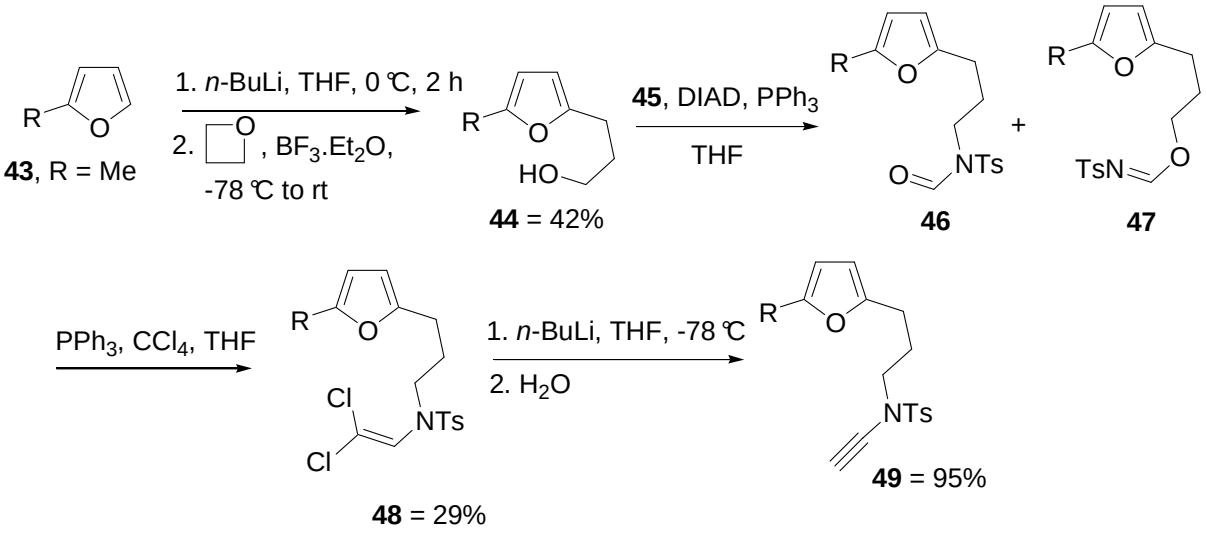
Scheme 15: Synthesis route to furan containing toluene sulfonamides

The toluene sulfonamides **40** thus obtained were alkynylated using Witulski's procedure.[46] Accordingly, deprotonation of **40** using *n*-butyl lithium in toluene followed by treatment with trimethylsilylethynylphenyliodonium triflate[47] **41** delivered the TMS-protected ynamides which were deprotected using TBAF in THF or pottassium carbonate in methanol to form the terminal ynamides **42** (Scheme 16)



Scheme 16: Synthesis of ynamides by Witulski's procedure

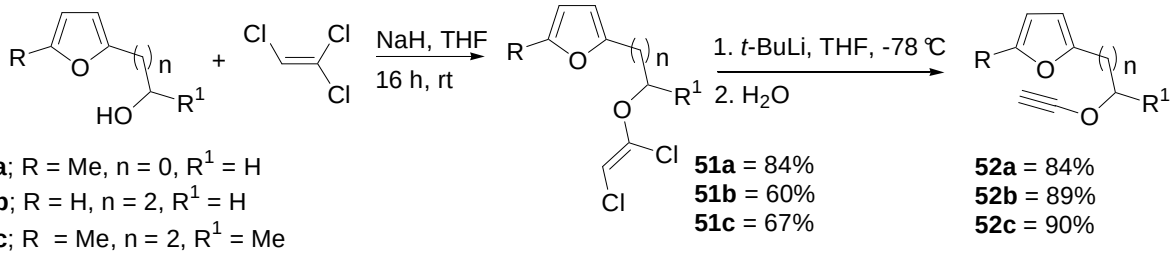
For the synthesis of ynamides with three carbon tether a different protocol was adopted. The alcohol precursor **44** was synthesized by the ring opening of oxirane with furan **43**.[48] A Mitsunobu reaction[49] of this alcohol with *N*-formyl toluene sulfonamide **45** furnished a mixture of *N*- and *O*-alkylated products **46** & **47** which -without purification- were directley converted to the dichlorovinyl amide **48**. Chloride elimination from **48** led to ynamide **49** in excellent yield (Scheme 17). The final product wwas isolated pure and no further purification was required.



Scheme 17: Synthesis of ynamides **49** with longer tether

1.3.3.2 Synthesis of ynol ethers

The synthesis of ynol ethers were initiated from the furyl alcohols **50** which were produced by known procedures.[10l, 48] In the first step, the alcohols were converted to dichlorovinyl ethers **51** by following a protocol of Greene et al.[50] The addition of the alcohols to trichloroethene in THF provided acess to to dichlorovinyl ethers which were subjected to elimination by *t*-BuLi in THF at –78 °C. The elimination delivered pure ynol ethers **52** which were used without further purification (Scheme 18).



50a; R = Me, n = 0, R^1 = H
50b; R = H, n = 2, R^1 = H
50c; R = Me, n = 2, R^1 = Me

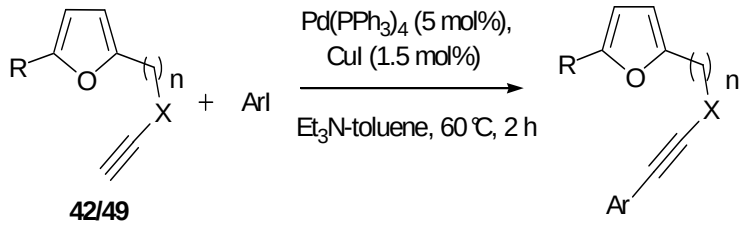
51a = 84%
51b = 60%
51c = 67%

52a = 84%
52b = 89%
52c = 90%

Scheme 18: Synthetic protocol for furan containing ynol ethers

1.3.3.3 Sonogashira coupling: Synthesis of aryl-ynamides

Having synthesized the ynamide precrusors, the terminal aryl substitution was accomplished by Sonogashira coupling.[51] The reaction was done by heating a degassed mixture of the ynamide and the aryl iodide with a catalytic combination of $Pd(PPh_3)_4$ (5 mol%) and cuprous iodide (1.5 mol %) in a solvent combination of triethylamine and toluene (Scheme 19). The reaction worked only with iodoarenes and sterically demanding substituents on the *ortho*-carbon of the arene partner were not tolerated. The sequence of addition of the catalysts had a crucial effect on the yield of the coupling product 58.[51]



42/49

42a; n = 2, X = NTs, R = H
42b; n = 2, X = NTs, R = Me
42c; n = 2, X = NBs, R = Me
42d; n = 2, X = NTs, R = Et
49a; n = 3, X = NTs, R = H
49b; n = 3, X = NTs, R = Me

58

17-46%

Scheme 19: Sonogashira coupling of furyl-ynamides

The different aryl-ynamides synthesized by Sonogashira coupling are given below (Table 1)

Table 1: Aryl-Ynamides synthesized by Sonogashira coupling

Entry	Alkyne	ArI	Product **58**	Yield [%]
1	**42b**	p-iodo toluene	**58a**	33
2	**42b**	p-iodo anisole	**58b**	31
3	**42b**	1-iodo napthalene	**58c**	29
4	**42b**	5-methyl iodofuran	**58d**	20
5	**42b**	2-iodo thiophene	**58e**	41
6	**42c**	p-iodo anisole	**58f**	17
7	**42c**	2-iodo thiophene	**58g**	36
8	**42c**	3-iodo thiophene	**58h**	27
9	**42b**	3-iodo anisole	**58i**	40
10	**42b**	p-nitro iodobenzene	**58j**	43
11	**42b**	4-iodo pyridine	**58k**	34
12	**42c**	p-chloro iodobenzene	**58l**	25
13	**42c**	1-iodo napthalene	**58m**	27
14	**42d**	2-iodo benzofuran	**58n**	20
15	**42c**	2-iodo N-methyl pyrrole	**58o**	30
16	**42c**	9-iodo anthracene	**58p**	31
17	**42a**	p-iodo toluene	**58q**	41
18	**49b**	p-iodo anisole	**58r**	37
19	**49b**	p-iodo toluene	**58s**	24
20	**49b**	3-iodo thiophene	**58t**	39
21	**49b**	4-iodo pyridine	**58u**	46
22	**49b**	1-iodo napthalene	**58v**	35
23	**42b**	2-isopropyl iodobenzene	**58w**	0

The X-ray crystallographic structure of one of the aryl-ynamides (**58l**) is shown in the figure 1.

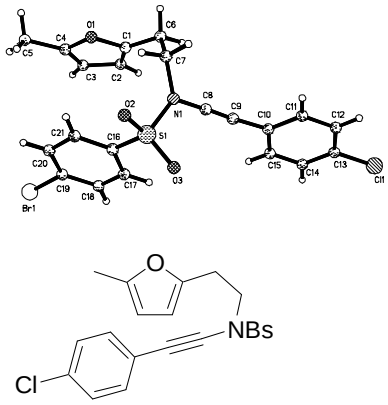
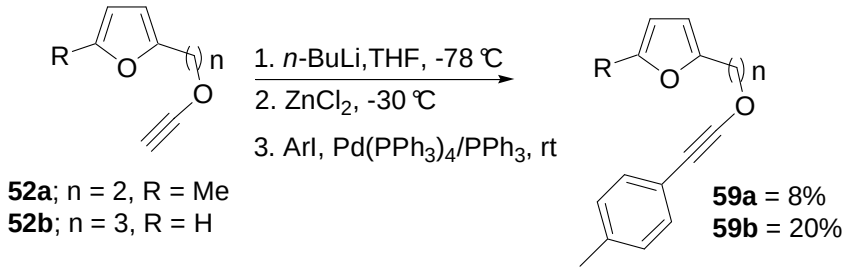


Figure 1: X-ray crystal structure of the aryl-ynamide **58l**

1.3.3.4 Negishi coupling: Synthesis of aryl-ynol ethers

Sonogashira coupling was unfortunately not suitable for the aryl substitution of terminal ynol ethers **52**. The reaction was tried at various temperatures, solvents, and by changing the palladium source. The results were either decomposition of the substrate or no reaction.

Hence Negishi coupling was attempted for the effective coupling of terminal ynol ethers and aryl halides. The required alkynylzinc species was generated by deprotonation of the terminal alkyne carbon using *n*-BuLi and subsequent addition of zinc chloride. The reaction mixture was then canulated to a suspension of $Pd(PPh_3)_4$ and PPh_3 (additive) in THF. The aryl iodide was then added (Scheme 20).



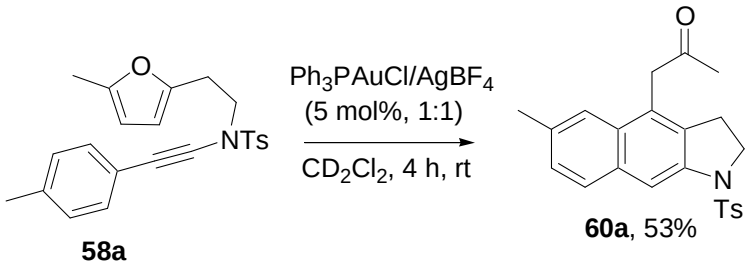
Scheme 20: Negishi coupling of ynol ethers **52**

The Negishi strategy also was not quite successful and the arylated products **59a** and **59b** were isolated in poor yields. The optimisation efforts didn't improve the outcomes any significantly.

1.3.4 Gold catalysis of aryl-ynamides

58a was chosen as a model substrate and subjected to catalysis with 5 mol% PPh_3AuNTf_2 in CD_2Cl_2 in an NMR tube and the reaction was monitored by ^{1}H-NMR. The conversion was slow and in 16 h at 45 ºC, the peaks corresponding to the starting material disappeared and new peaks appeared. $Mes_3PAuNTf_2$ showed similar activity and with $AuCl_3$ decomposition of the substrate was observed. Finally, a combination of Ph_3PAuCl and $AgBF_4$ (5 mol%, 1:1) was found to catalyze the reaction much faster (complete conversion in 4 h at rt in CD_2Cl_2).

Characterization of the purified product showed it to be the benzannulated hydroindole derivative **60a** with an isolation yield of 53% (Scheme 21). Particularly pleasing was the observation that the enol ether part of the furan moiety opened up in one stretch establishing the synthetically important polyarene unit.



58a **60a**, 53%

Scheme 21: Gold catalyzed benzannulation of the model substrate **58a**

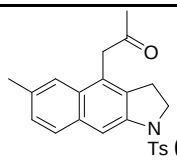
1.3.4.1 Results and discussion

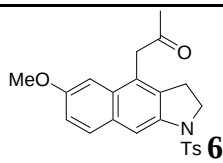
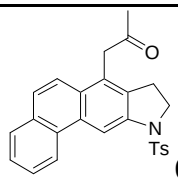
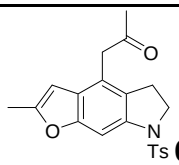
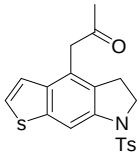
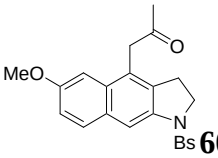
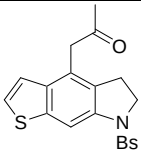
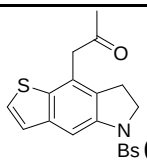
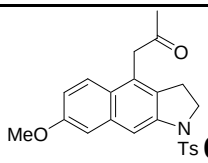
The methodology was extended to other aryl-ynamides and the results are summarized in the table 2.

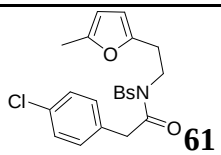
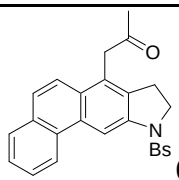
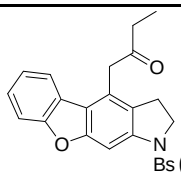
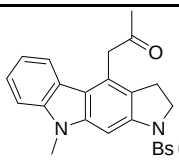
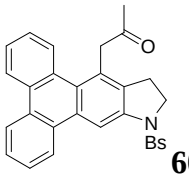
The substrate **58b** with a more electron donating methoxy group reacted in 1h to furnish the product **60b** in 57% yield (table 2, entry 2). The naphthyl substituted **58c** furnished the tetracyclic compound **60c** in 53% yield with a reaction time of 7h at rt (table 2, entry 3). The substrate **58d** with a heteroaryl group attached to the alkyne has responded nicely and the benzofuran derivative **60d** was isolated in an excellent yield of 79% in 6h at rt (table 2, entry 4).The thiophene variant **58e** also fit to the plot and the benzothiophene product **60e** was obtained in 65% yield (table 2, entry 5).We then switched to **58f**, a brosyl (Bs) substituted ynamide,and the product **60f** was isolated with a significantly improved yield of 75% (table 2,

entry 6).On a similar note, **58g** gave the benzothiophene product **60g** with an enhanced yield of 74% (table 2, entry 7). X-ray crystallographic analysis of **60g** proved the structure unambiguously and gave conclusive support for the benzannulation chemistry (Figure 1). The substrate **58h**, where the thiophene moiety is connected to the alkyne at the third carbon reacted selectively at 0 °C (2h) to furnish **60h**-the constitutional isomer of **60g**-in 60% yield (table 2, entry 8). The substrate **58i** having two potential nuclophilic attacking centres on the arene reacted regioselectively to give the product **60i** in 53% yield (table 2, entry 9) The regioselectivity is particularly noteworthy when compared to the aryl-alkyne substrates Echavarren et al. reported where meta substitution of the arene produced regioisomeric products.[42] Deactivated substrate **58j** with *p*-nitro group on the arene failed to react and decomposed when exposed to prolonged reaction conditions (table 2, entry 10). **58k** with a pyridine substitution at the alkyne had a similar fate (table 2, entry 11). The substrate **58l** underwent prior water addition, and the expected annulated product could not be isolated pure. Instead the amide **61** was isolated in 18% yield (table 2, entry 12). The superior performance of brosyl (Bs) systems over the tosyl ones was evident again as naphthyl substituted **58m**, gave the phenanthrene derivative **60m** in 72% yield (table 2, entry 13). The substrate **58n**, with a benzofuran end group on the alkyne and an ethyl group on the 5-C of the furan reacted beautifully to give the dibenzofuran derivative **60n** in 76% yield (table 2, entry 14). So did the substrate **58o** with an *N*-methyl indole moiety and the benzoindole product **60o** was isolated in 41% yield (table 2, entry 15). A bulky substituent like anthracene on the alkyne **(58p)** was also reactive –albeit slower- and the Triphenylene derivative **60p** was isolated in 43% yield (table 2, entry 16). We also examined the reactivity of unsubstituted furan substrate **58q**, but the system was too passive to react (table 2, entry 17). The incompetence of Sonogashira coupling towards steric bulk and the failure to couple bromo and chloro arenes were constraints to synthesize those kinds of substrates.

Table 2: Gold catalysis of aryl-ynamides **58a-58q** (with two carbon tether)

Entry	**58**	Time [h]	Temp [°C]	Product **60**	Yield [%]
1[a]	**58a**	4	rt	 **60a**	53

2[b]	**58b**	1	45	 **60b**	57
3[a]	**58c**	7	rt	 **60c**	53
4[a]	**58d**	6	rt	 **60d**	79
5[a]	**58e**	1	rt	 **60e**	65
6[a]	**58f**	4	rt	 **60f**	75
7[a]	**58g**	3	rt	 **60g**	74
8[a]	**58h**	2	0	 **60h**	60
9[a]	**58i**	1	50	 **60i**	53
10[b]	**58j**	24	50	substrate decompose	-
11[b]	**58k**	20	65	no reaction	-

12[a]	**58l**	1	rt	 **61**	18
13[a]	**58m**	8	rt	 **60m**	72
14[a]	**58n**	3	rt	 **60n**	76
15[a]	**58o**	12	rt	 **60o**	41
16[a]	**58p**	20	45	 **60p**	43
17[a]	**58q**	48	45	No reaction	-

[a] in CH_2Cl_2. [b] in $CHCl_3$

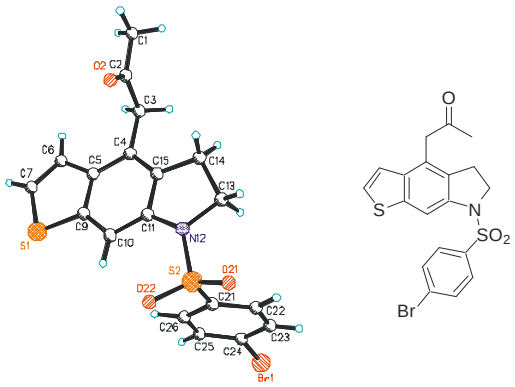
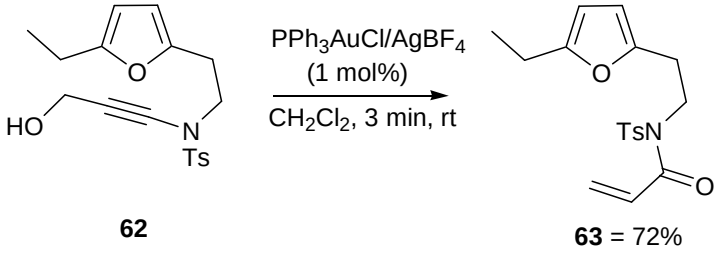


Figure 2: X-ray crystal structure of the benzannulated product **60g**

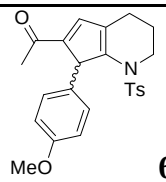
Having established the generality of arene nucleophiles, the substrate **62** with a hydroxyl group on the terminal alkyne was subjected to catalysis. The Meyer-Schuster type rearrangement[52] product **63** was formed instead of cyclization (Scheme 22).

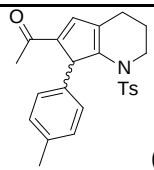
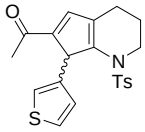


Scheme 22: Gold catalysis of **62**

The catalysis of aryl-ynamides with three carbon tether had a completely different thing to offer. They were expected to follow suit with the shorter tethered variants but the test trial of the substrate **58r** witnessed the exclusive formation of an unknown compound. The examination of 1-D and 2-D NMR spectra combined with mass spectroscopic data led to the assumption that the product would be **64r**, a cyclic, unsaturated ketone with a stereogenic centre (Table 3, entry 1). The reaction was much faster (finished in 45 min at rt) and no trace of the benzannulated product was isolated from the reaction. This points to a completely different mechanistic choice the system is taking. The substrate **58s** with a *p*-tolyl substitution on the alkyne was followed and a similar reaction product **64s** was isolated in 52% yield (Table 3, entry 2). An X-ray crystallographic structure of this compound was obtained thereby unambiguously proving the product identity (Figure 3). A heteroaryl ynamide substrate **58t** also furnished the cyclopentenone derivative **64t** in 50% yield (Table 3, entry 3). An electron withdrawing group on the alkyne was not tolerated and hence the pyridine substituted **58u**, remained unreactive (Table 3, entry 4). The substrate **58v** yielded a complicated mixture of products (Table 3, entry 5). The NMR spectra of the crude reaction mixture showed the presence of both cyclopentadiene and benzannulated products. But none could be isolated pure.

Table 3: Gold catalysis of aryl-ynamides **58r-58v** (with three carbon tether)

Entry [a]	Alkyne	Time [h]	Temp [°C]	Product **64**	Yield [%]
1	**58r**	0.7	rt	 **64r**	56

2	**58s**	1	rt	 **64s**	52
3	**58t**	4	rt	 **64t**	50
4	**58u**	20	50	No reaction	-
5	**58v**	1.5	rt	Complex mixture	-

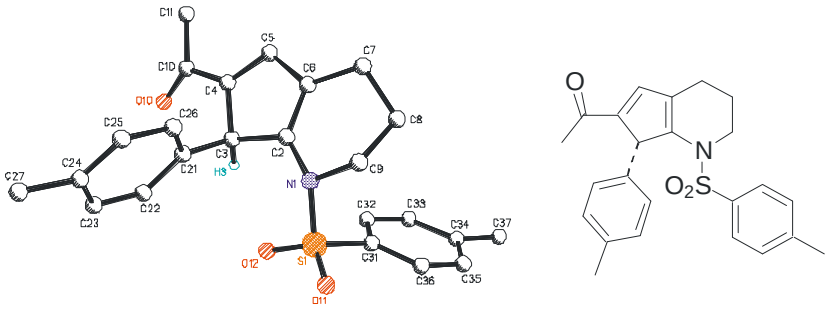
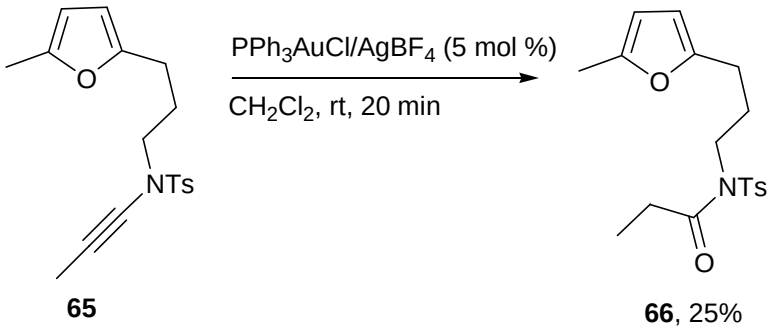


Figure 3: X-ray crystal structure of the cyclopentadiene product **64s**

It was also examined whether an alkyl group attached to the alkyne would lead to similar transformations. But the substrate **65** underwent water addition to form the amide **66**, in 25% yield (Scheme 23).

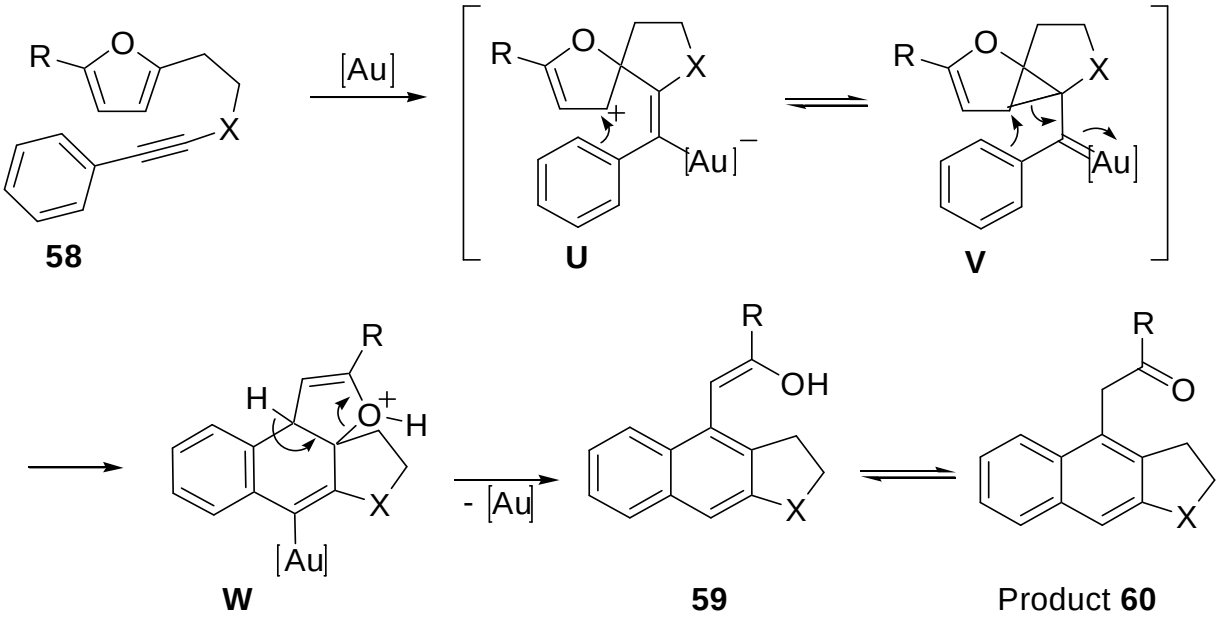


65 **66**, 25%

Scheme 23: Gold catalysis of the methyl-ynamide **65**

1.3.5 Mechanistic Discussion

The mechanistic pathways for the formation of benzannulated products from aryl-ynamides **58a-58p** are fairly straightforward and proceeds through the classical *exo*-1,6-enyne cyclization mode (Scheme 24).

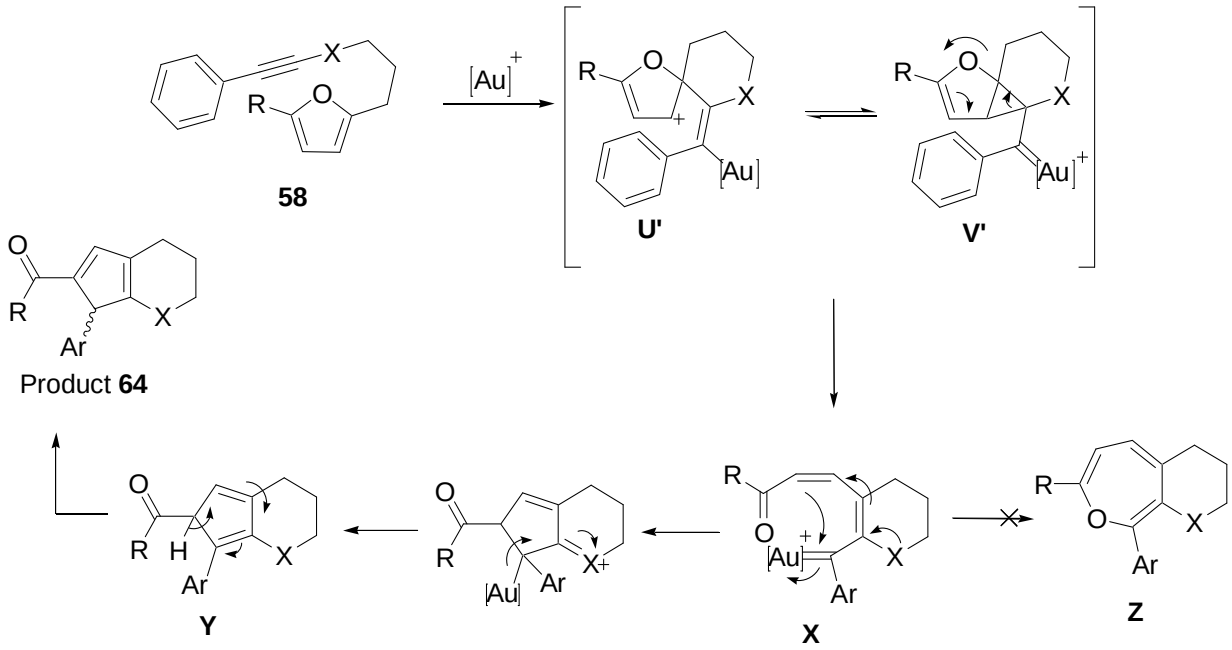


Scheme 24: Proposed mechanism for the gold catalysed benzannulation of aryl-ynamides

The activation of the alkyne by gold leads to the formation of intermediates **U** or **V** having a cationic or carbene identity respectively. A Friedel-Crafts arylation[53,42] followed by rearomatisation of the arene unit leads to the cyclized intermediate **W**. This semi-aromatic species undergoes the crucial second aromatisation process by opening up of the furyl enol ether bridge and the following protodemetallation to form the enol precursor **59** which tautomerizes to the more stable ketone form **60**

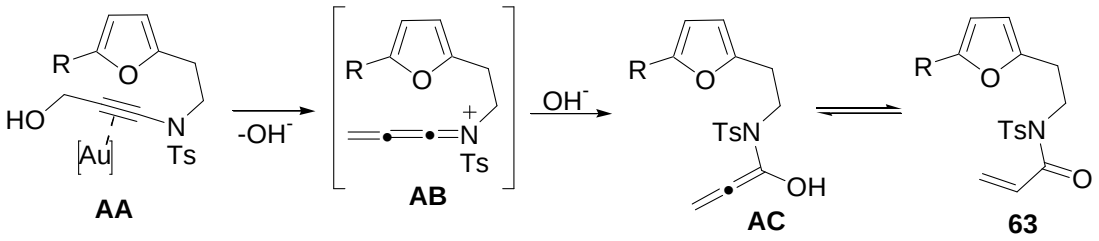
The mechanistic routes for the cyclopentadiene structures from aryl-ynamides having longer tether (1,7 enynes) are somewhat enigmatic but provide equally exciting prospects (Scheme 25). The reaction initiates by *exo*-1,7 attack to give the cation **U′** or carbene **V′** intermediate. Concerted cleavage of the cyclopropane bond and the dihydrofuran forms the conjugated monocyclic carbene intermediate **X**. This species resembles the crucial carbene intermediate in gold and platinum catalyzed phenol synthesis from furyl alkynes.[11b] Such an intermediate was reported to be incapable (or too stable owing to the presence of the arene moiety on the carbene carbon) for further reaction, and this unreactivity was reasoned for the failure of gold/platinum catalyzed phenol synthesis from terminally substituted furyl alkynes. But the

proposed intermediate **X** is found to be active enough (if not to form the benzooxepin **Z**) and undergoes electrocyclization (Nazarov-type cyclization) followed by reductive elimination of gold to form the cyclopentadiene compound **Y**, which eventually transforms to the final product **64** by a possible 1,5-H shift. The activity of the intermediate **X**, compared to its analogue in phenol synthesis is attributed to the presence of the heteroatom (nitrogen here) which would stabilize the formation of charges in the conjugated fragment. The absence of benzannulation pathway could be because of the fact that the longer tether reduces the proximity of the arene moiety towards the electron deficient 3-C of the furan thereby making the intermediates **U'** or **V'** to undergo the concerted ring opening. The assumption makes sense considering the fact that the substrate **58v** with naphthyl moiety (with a better 'reach' towards the 3-C of furan than monoarenes) was found to give both types of products (**60** and **64).**



Scheme 25: Plausible mechanism for the formation of cyclopentenones from gold catalysis of aryl-ynamides **58** with three carbon tether.

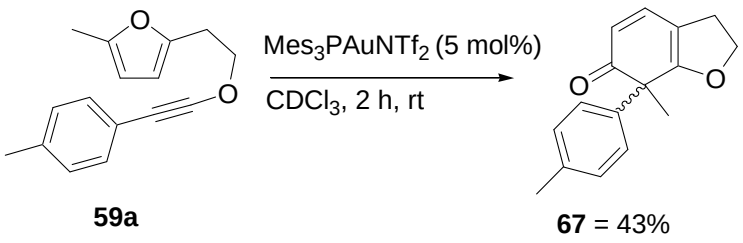
The formation of the α,β-unsaturated amide **63** by the Meyer-Schuster type rearrangement is speculated to proceed through a cumulene intermediate **AB** (Scheme 26). The reaction is interesting since primary propargyl alcohols are hitherto known to be poor substrates for Meyer-Schuster rearrangement.[54] The very low catalyst loading and fast reaction time also point towards a rate enhancing involvement of the nitrogen atom in the catalytic pathway.



Scheme 26: Proposed mechanism for the formation of **63**

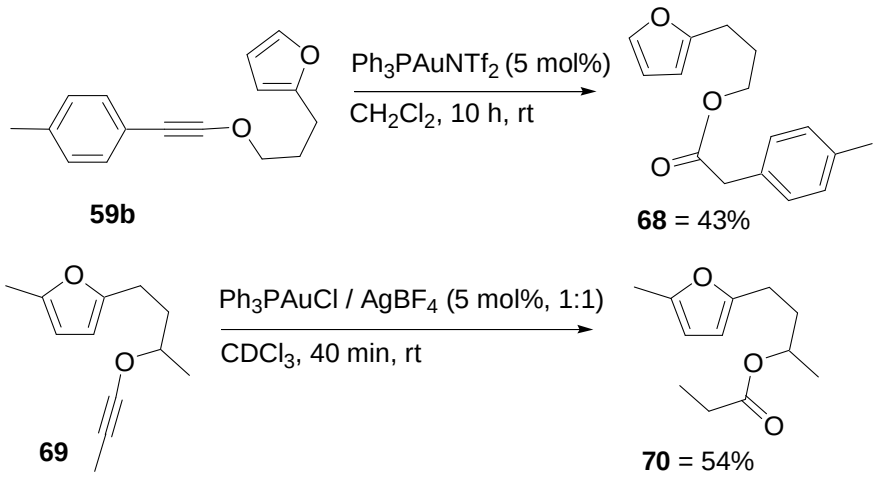
1.3.6 Gold catalysis of aryl-ynol ethers

The aryl-ynol ethers synthesized were subjected to gold catalysis. The substrate **59a** with a two carbon chain reacted in 2h at rt with 5 mol% $Mes_3PAuNTf_2$ in $CDCl_3$. The product was isolated and examination of 1D and 2D NMR spectroscopic data led to the conclusion that the product could be **67**, a cyclic conjugated ketone (Scheme 27). Th product was isolated with an yield of 43%. Unfortunately the compound was unstable and the mass spectroscopic data could not be obtained.



Scheme 27: Gold catalysis of the aryl-ynol ether **59a**

The formation of the cyclic ketone compound **67** prompted to test a substrate having no substitution on the 5-C of furan, as it could well lead to the formation of the phenolic product. But unfortunately the substrate **59b** underwent prior water addition and the ester product **68** was isolated in 43% yield. The substrate **69** with a methyl substituted alkyne also had a similar fate (Scheme 28).



Scheme 28: Gold catalysis of aryl-ynol ether **59b** and methyl-ynol ether **69**

1.3.7 Conclusion and outlook

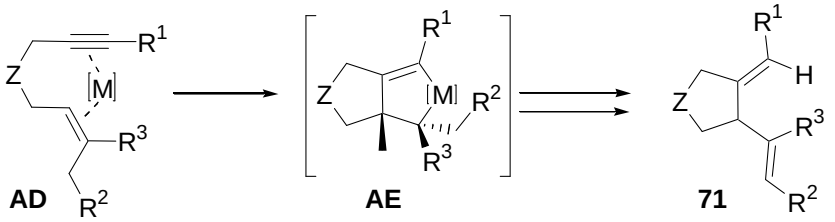
The gold catalyzed conversions of aryl-ynamides and aryl-ynol ethers were explored for the first time. Among the former category, the shorter tethered substrates constitute excellent precursors for the synthesis of important polyarenes and polyheteroarenes under very mild reaction conditions. The keto group present at the beta carbon atom of these products promises room for wide spectra of further functionalisation. The longer tethered substrates seem to be having interesting and unique reactivity .The initial results are encouraging and hopefully further tuning up of this substrates would provide intermediates similar to **X** but are inclined to react towards the phenol direction (formation of benzooxepines **Z**). The catalytic scope of aryl-ynol ethers could not be investigated thoroughly as the synthesis of these substrates were found to be difficult and the isolated yields were poor. But the experiments done with a few of these substrates indicate that there are interesting prospects to explore. The formation of the cyclic conjugated ketone **67** is exciting considering its structural closeness to the related phenol system. The development of a better coupling method could initiate in-depth investigations. Furan containing aryl-ynamides/aryl-ynol ethers seem to be the answer for gold catalyzed phenol synthesis from disubstituted alkynes.

1.4 Gold catalyzed Cycloisomerization of Furyl-Alkynes: Proof for the Cationic nature of the 'Carbene' Intermediate

1.4.1 Background

In the past decade there has been tremendous growth in the application of gold catalysts in organic synthesis. These Lewis acids are well known for their carbophilic nature and have a high affinity for triple bonds in carbon fragments. The enyne systems have been and still are the favourite substrates for homogeneous gold catalysis.[1] The preparative advantages of gold catalyzed transformations are quite well explored but the mechanistic picture is often left wanting for authentic and definite experimental and spectroscopic confirmations; particularly the electronic nature of the intermediates involved.

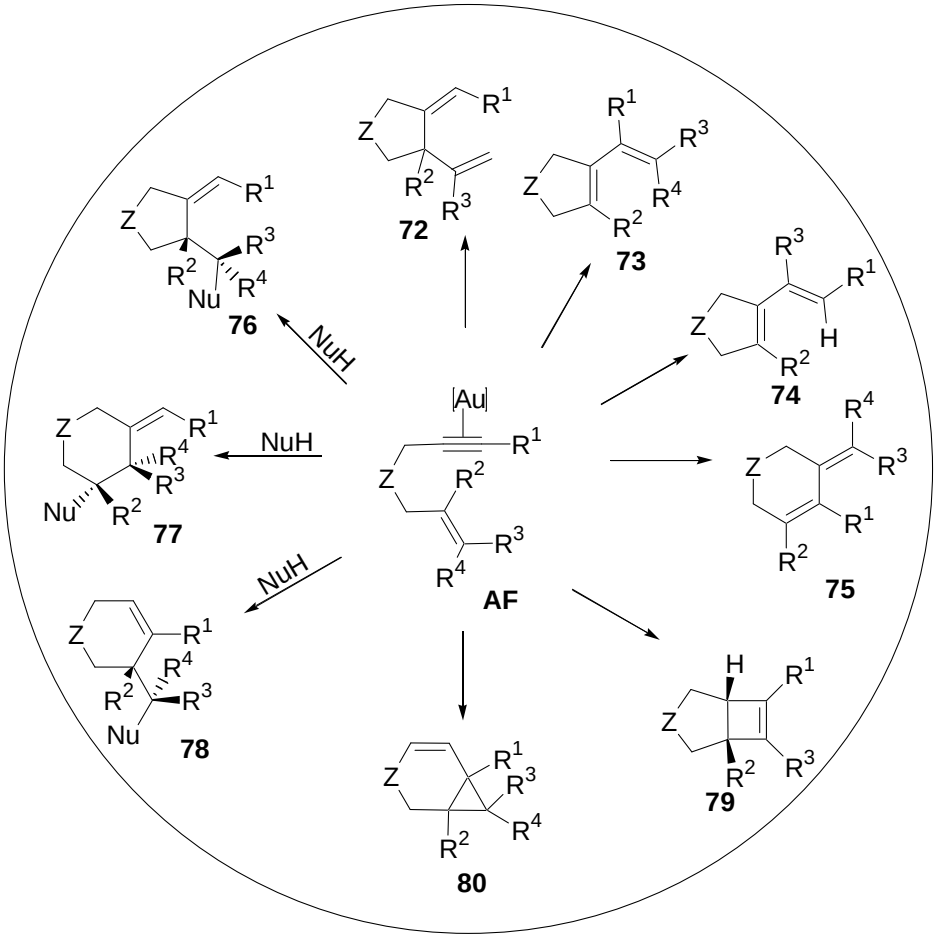
In the reaction of enynes with palladium catalysts, the Alder-ene cycloisomerization[38a,55] is assumed to happen where the metal is coordinated simultaneously to the alkyne and the olefin to form the cyclometalated intermediate **AD** (Scheme 29). The metallacycle **AE** evolves by β-elimination and reductive elimination of the metal to form the final product **71**. A formal enyne metathesis reaction was also reported for palladium complexes.[56]



Scheme 29: Alder-ene pathway for the transition metal catalyzed cycloisomerization of enynes

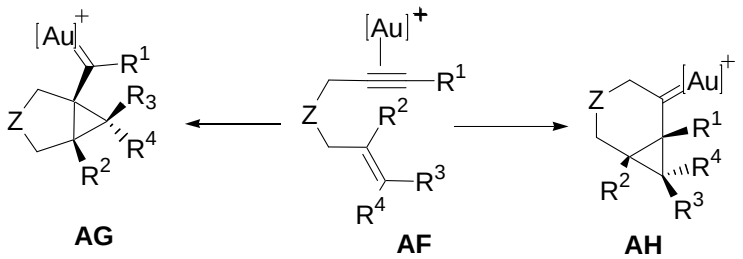
But other late transition metals like platinum, ruthenium, rhodium and typically gold, don't follow this particular reaction pattern. This is attributed to the inertness of gold cations towards oxidative addition. Also the $(AuL)^+$ fragment adopts a linear combination and binds to either the alkyne or the alkene. Most gold-catalyzed cycloisomerizations of enynes proceed by the initial attack of the cationic gold to the alkyne to form complexes of type **AF** which reacts further with the alkene by either the *exo-dig* or *endo-dig* pathway to form a wide variety of products (Scheme 30). Among this **73** and **74** are products of *exo*-cyclization, **75** originated from *endo*-rearrangement, **76-78** are products formed in the presence of

nucleophiles, **79** is the less common cyclobutene product, and **80** originated from an intramolecular cyclopropanation were observed.[38-40] Complex transformations are possible for more-functionalized enynes.



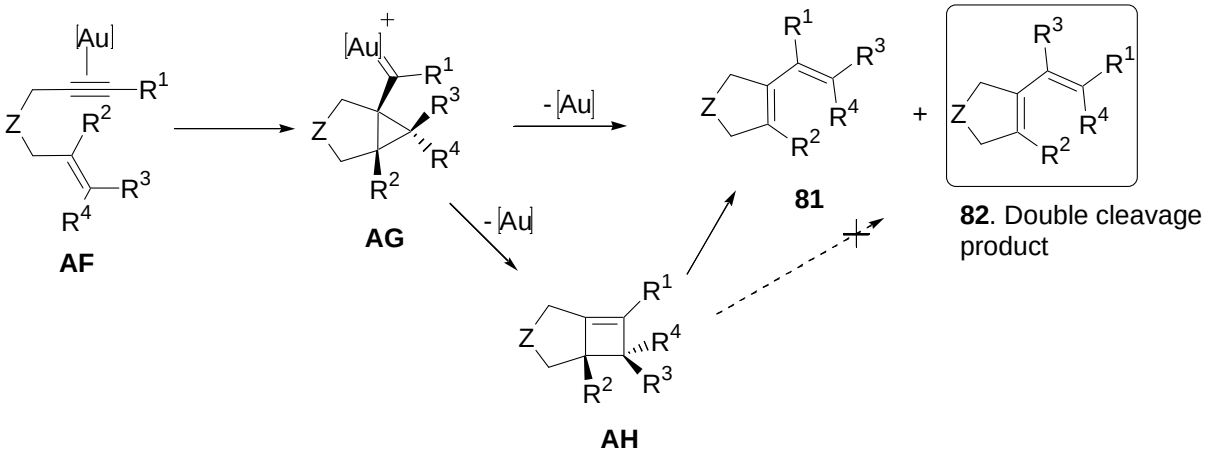
Scheme 30: Product spectra for gold catalyzed cycloisomerization of enynes

The cyclopropyl gold carbenes **AG** and **AH** were generally proposed as the key intermediates in these reactions (Scheme 31) as is common for the other carbophilic metals like platinum, rhodium, and ruthenium for this type of reactions.[57]



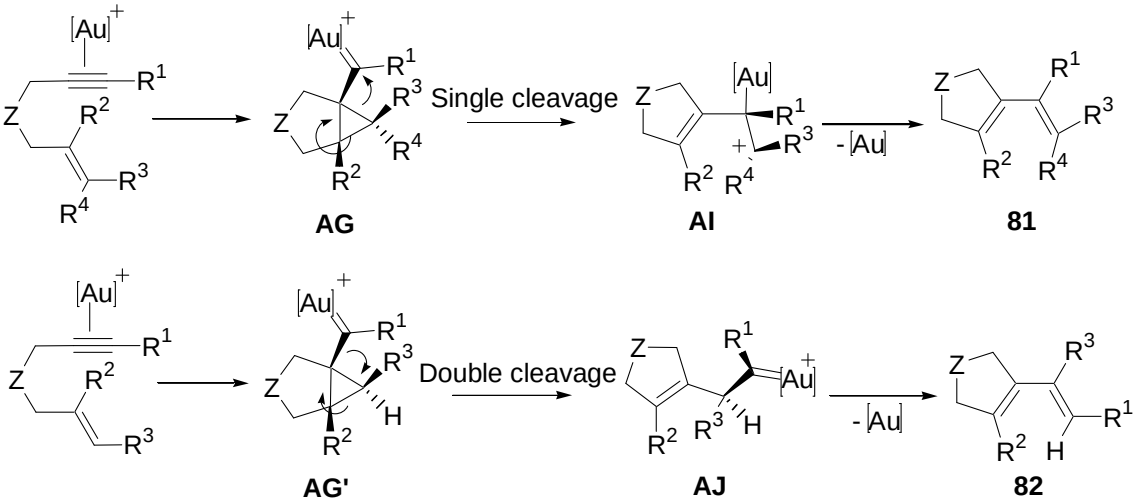
Scheme 31: Proposed carbene intermediates for *exo-dig* and *endo-dig* cycloisomerization of 1,6-enynes

These carbenes could react with nucleophiles like water and alcohols (if present) to give products of alkoxy or hydroxycyclization and in the absence of nucleophiles skeletal rearrangement form diene products. A pathway for the formation of single cleavage product **81** was generally speculated to involve the conrotatory ring opening of a cyclobutene intermediate **AH** which was formed from the cyclopropyl carbene intermediate **AG**.[58,59] But this rational could not explain the formation of skeletal rearrangement products of type **82** which are found to have a double cleavaged structure (Scheme 32).[39d]



Scheme 32: Proposed cyclobutene intermediate **AH** for the enyne cycloisomerization

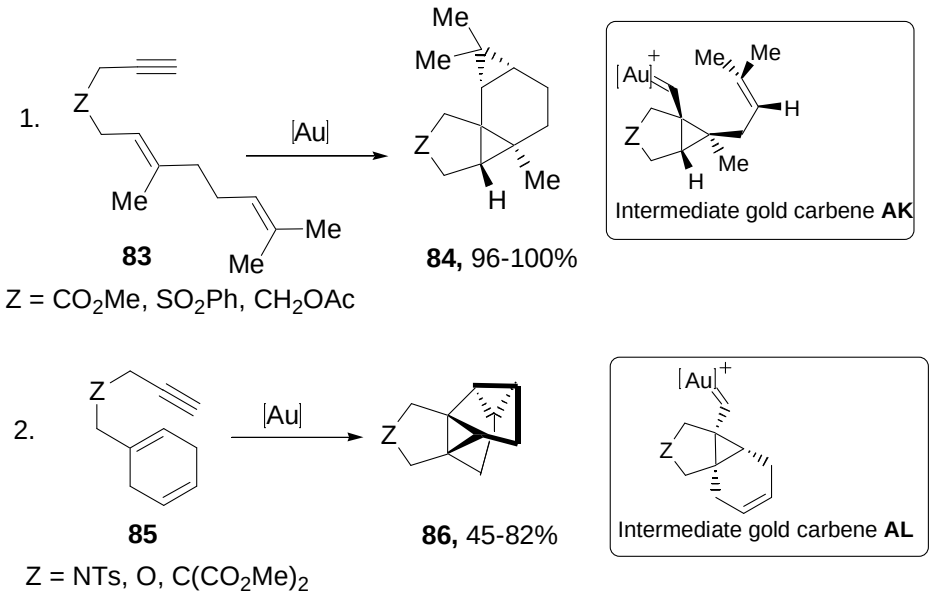
It was the pioneering work by Echavarren et al. that threw light to this saga. They have proposed a direct pathway for the formation of single cleavage and double cleavage products from the cyclopropyl gold carbene **AG/AG′** (Scheme 33).[39d]



Scheme 33: Proposed pathways for the formation of single cleavage and double cleavage products

Based on DFT calculations and supporting experimental evidence they established that the hypothetical conrotatory ring opening of the cyclobutene intermediate **AH** should be a fast process even at temperatures as low as -63 °C which is not consistent with theoretical data for ring opening of related cyclobutenes.[39d] According to their proposal, the initially formed cyclopropyl carbene **AG** opened up to form the cation **AI** which then undergo metal elimination to form the single cleavage product **81**. For the double cleavage, a diotropic rearrangement[60] of the carbene **AG′** was suggested which led to a new open chain carbene **AJ**. Proton loss and protodeauration delivered the product **82**.

Echavarren et al., had also succeeded in securing experimental evidence for the involvement of gold carbenes in the catalytic cycles of gold catalyzed enyne cycloisomerization, by trapping them intramolecularly with an alkene fragment (Scheme 34, **1**).[41]

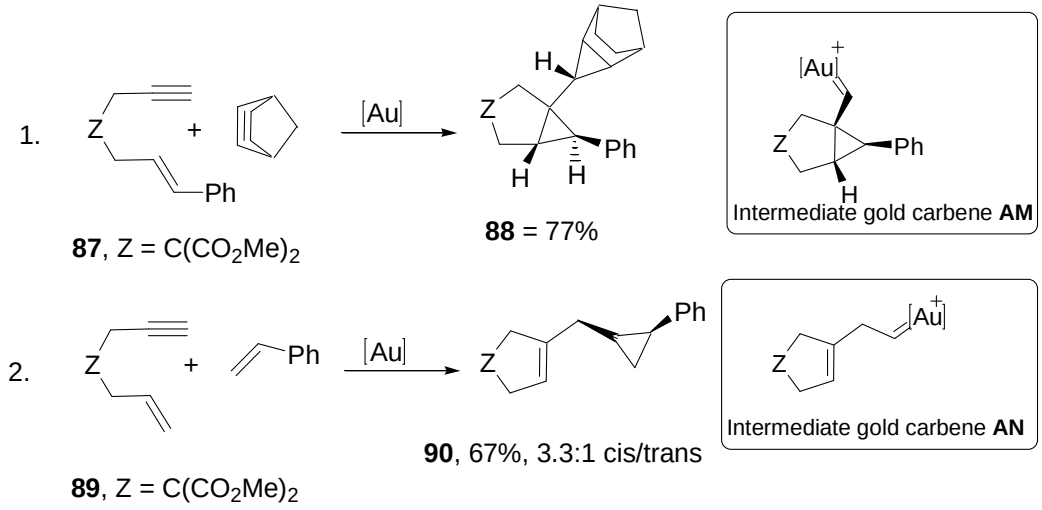


Scheme 34: Intramolecular trapping of Gold carbene intermediate

These kind of biscyclopropanation was also reported from gold carbenes formed in other reactions.[62] A remarkable transformation of this type was achieved under mild conditions through the use of dienynes **85** to form pentacyclic derivatives **86** (Scheme 34, **2**).[61] In both these reactions the initially formed carbene intermediate reacted with the second olefin to undergo cyclopropanation.

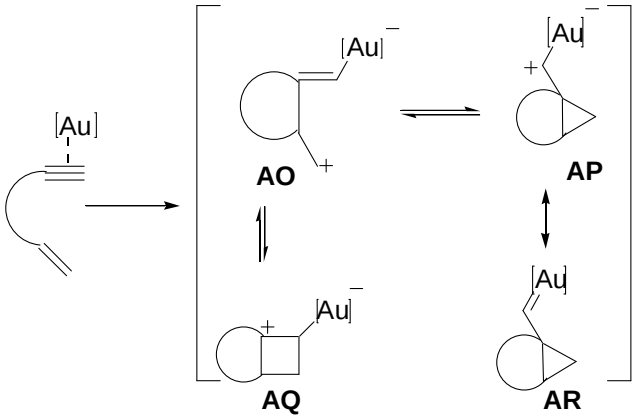
Similarly intermolecular trapping of intermediate carbenes by various alkenes has also been reported.[63] The products **88** and **90** represent trapping of the classical anti-cyclopropyl gold

carbene **AM** and the open chain gold carbene (which lead to skeletal rearrangement products) **AN** respectively (Scheme 35).



Scheme 35: Intermolecular trapping of cyclopropyl gold carbenes

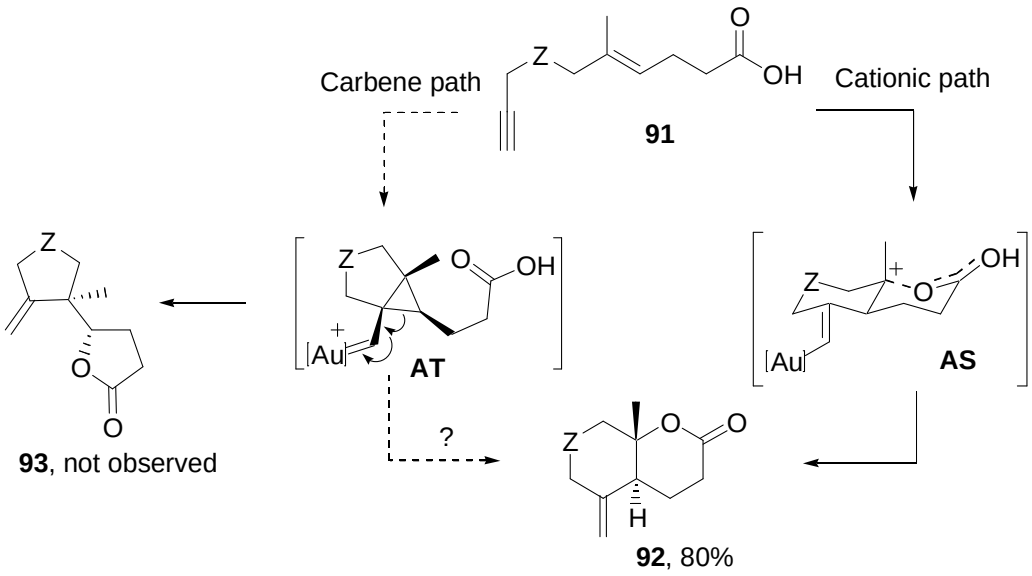
Although the projected examples support the intermediacy of a gold-carbenoid in enyne cycloisomerizations, it is important to recall that such an intermediate is yet to be characterized spectroscopically. Also the DFT calculations revealed the possible intermediate in gold catalyzed cycloisomerizations as a highly delocalized entity.[39d,39f] In fact the actual electronic nature of the intermediate involved should not be portrayed as a single structure, but a mesomeric/tautomeric package of different canonical forms (Scheme 36).[20b]



Scheme 36: Tautomeric/Mesomeric forms of the intermediates in gold catalyzed enyne cyclization

Although the true electronic state of the intermediate is yet to be established with conviction, the carbene form **AR** has been the favourite choice for most publications and the catalytic

cycles were discussed mostly based on this single mesomeric form. Recently Fürstner et al., authentically postulated the need to appreciate other mesomeric forms of this intermediate particularly the cationic form **AO**.[20a] They have examined a series of cycloisomerization experiments of substituted enynes with a pendant carboxylate trap. The results were interesting and highly instructive. The substrate **91**, upon subjected to gold catalyst, converted exclusively to the annulated bicycle **92** (Scheme 37).

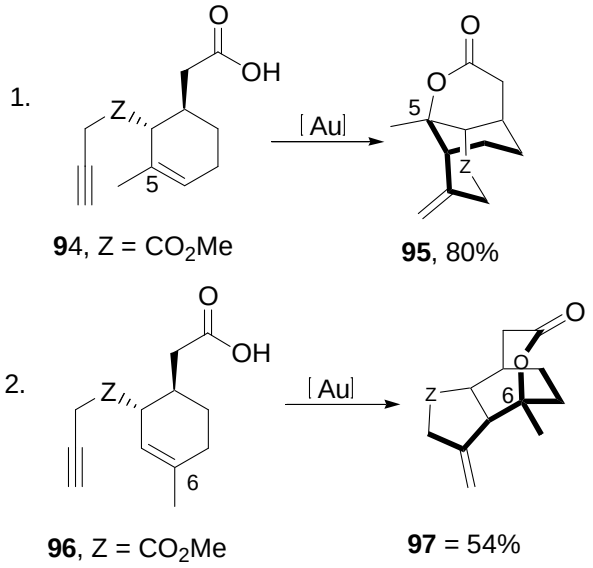


Scheme 37: Gold catalyzed cycloisomerization of **91**; A possible cation way

If the intermediate were an ordinary cyclopropyl carbene **AT** as often depicted, it would be hard to understand the formation of this product **92** because it is highly unlikely that the nucleophilic attack of the carboxylate would occur to the then more substituted (sterically shielded) carbon atom of the cyclopropyl ring forming the observed product. Instead it should have attacked the less crowded carbon to form the five-membered product **93** which was not observed at all. On the other hand a carbocation like intermediate (transition state) **AS** would easily explain the chemo and stereo selectivities associated with the product. An ordered chair like charge-delocalized species **AS** ensured the net anti addition of the alkyne and carboxylate to the alkene.

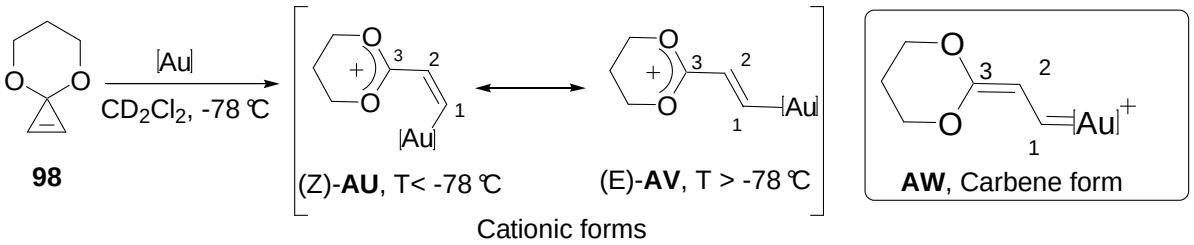
Other substrates also were shown to follow a conceivable 'cation way' (Scheme 38).[20a] The cyclohexenyl derivative **94** delivered **95**, where the nucleophilic attack occurred at the more substituted (more stabilized cation) C-5. Even in the case of substrate **96**, the nucleophile attacked the site where a cationic intermediate is more stabilized (C-6), compromising the

larger conformational strain. A set of reactions repeated with alcohol substrates also exhibited similar trend and cemented the involvement of a cationic intermediate.



Scheme 38: Gold catalyzed cycloisomerization of cyclohexenynes; Evidence for cationic cyclization.

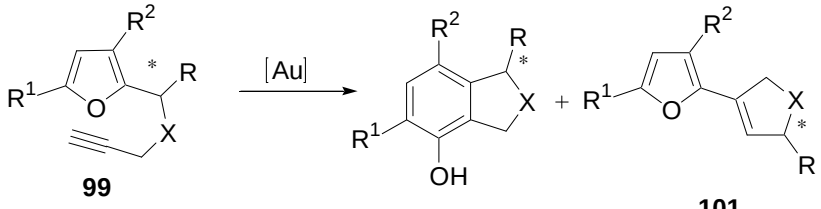
Fürstner et al., also succeeded in deriving spectroscopic information about the bonding situation in an organogold species that was generated from 3,3′-disubstituted cyclopropenes.[20c] Adding the gold catalyst to these substrates in CD_2Cl_2 at -78 °C afforded the product with very characteristic spectroscopic properties (Scheme 39). The two -OCH_2- groups of the generated species gave rise to a single signal in both ^1H and the ^{13}C NMR which is indicative of the free and rapid rotation about the C2-C3 bond. Such a rotation is possible only for a cationic structure. Also the conversion of the initially formed Z isomer to the E isomer took several hours, a fact which is informative about the high barrier to rotation in other words the high double bond character of C1-C2 bond. These observations led to the conclusion that the ground-state structure of the organogold species generated was mostly cationic and the contribution of the carbene form **AW** is only marginal.



Scheme 39: Generation of the cationic Organogold species from Cyclopropenone Ketal

1.4.2 Motivation for the Present Work

An extension of the gold catalyzed phenol synthesis by Hashmi et al. was reported last year in which enantiomerically pure furyl-alkyne systems were subjected to gold catalysts, thereby synthesizing a wide variety of enantiopure dihydroheterocycles.[67] Most of the substrates delivered the expected phenols but a few of them led to the formation of an unexpected five-membered ring products **101** (Scheme 40).

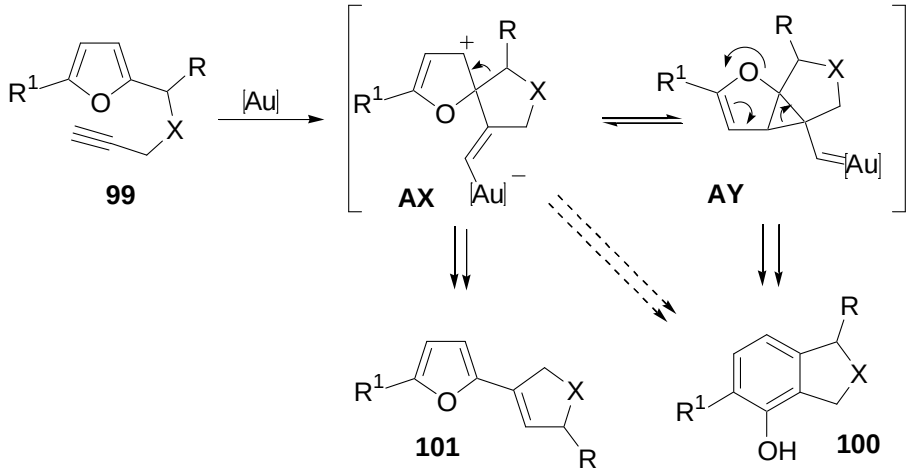


$R^1 = R^2 = H$, Me
R = alkyl, cycloalkyl, aryl, propargyl,

R^1 = Me, R^2 = Me, X = NSO_2tBu, R = cyclopropyl; 75%
R^1 = H, R^2 = Me, X = NSO_2tBu, R = Ph; 85%
R^1 = Me, R^2 = H, X = NTs, R = cyclopropyl; 35%

Scheme 40: Formation of five-membered ring structures during phenol synthesis

This observation was interesting as the formation of this five-membered compound required a cationic mechanism that operates in/parallel to the classical phenol formation pathway. The mechanism for the gold catalyzed phenol synthesis is considered to be a thoroughly explored one and was suggested to follow through the intermediacy of the cyclopropyl gold carbene **AY**. The formation of the above mentioned cyclic compounds is highly instructive of the significant cationic behaviour of this intermediate (Scheme 41).



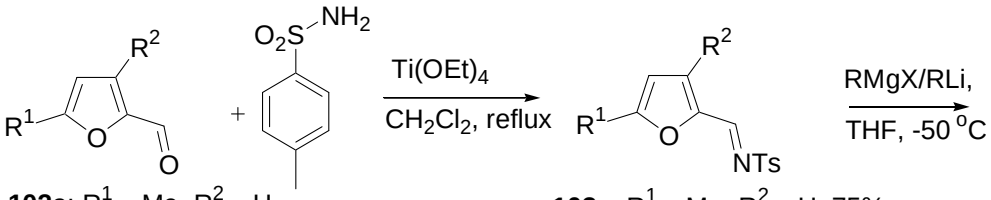
Scheme 41: Speculated source of formation of **101**; The cationic Intermediate **AX**

The transformation offered highly interesting and crucial mechanistic prospects regarding gold catalyzed enyne cyclization and was taken for further exploration.

1.4.3 Synthesis of the Substrates

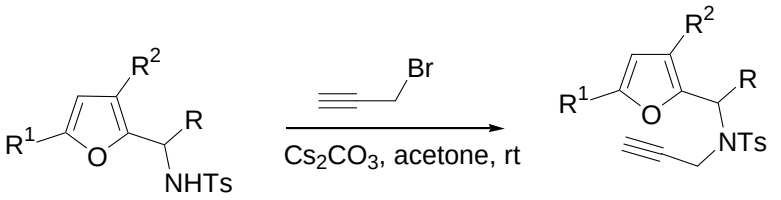
1.4.3.1 Synthesis of Nitrogen-tethered substrates

The substrates with nitrogen tether were prepared based on the literature protocols.[68] In the first step, substituted furfurals were converted to corresponding tosyl imines **103** by reaction with tosyl amine and titanium tetraethoxide $Ti(OEt)_4$ in dichloromethane. The imines thus obtained were subjected to nucleophilic addition by different organolithiums or Grignard reagents. The resulting α-substituted tosyl amines **104** were propargylated using propargyl bromide and caesium carbonate in acetone to furnish the required substrates **105** (Scheme 42).



102a; R^1 = Me, R^2 = H
102b; R^1 = H , R^2 = Me

103a; R^1 = Me, R^2 = H, 75%
103b; R^1 = H, R^2 = Me, 91%



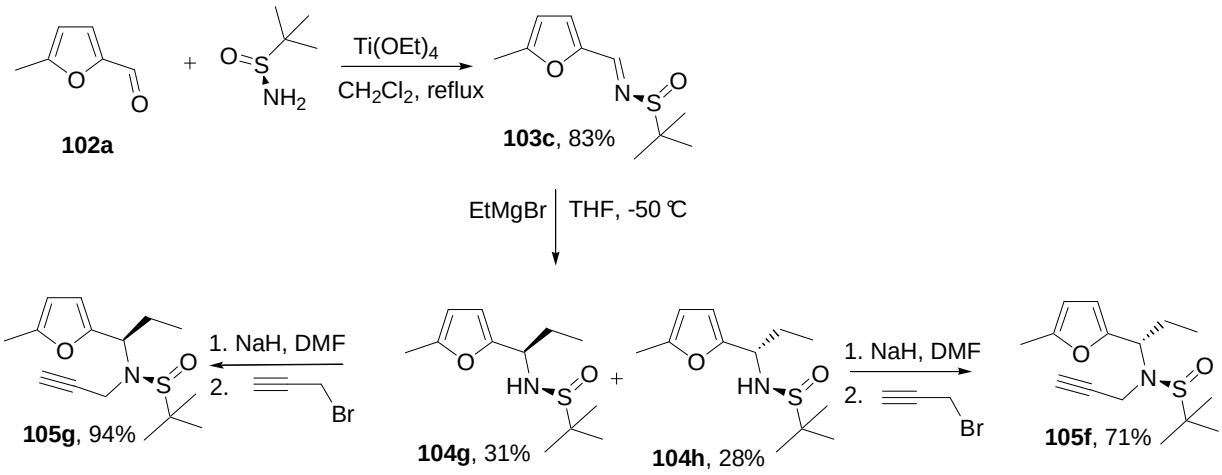
104a; R = 5-methyl furyl, 51%
104b; R = *p*-anisyl, 30%
104c; R = *p*-anisyl, 84%
104d; R = allyl, 72%
104e; R = vinyl, 66%
104f; R = *N*-tosyl pyrrole, 0%

105a; R^1 = Me, R^2 = H, R = 5-methyl furyl, 83%
105b; R^1 = Me , R^2 = H, R = *p*-anisyl, 75%
105c; R^1= H, R^2 = Me, R = *p*-anisyl, 81%
105d; R^1 = H, R^2 = Me, R = allyl, 92%
105e; R^1 = H, R^2 = Me, R = vinyl, 74%

Scheme 42: Synthetic route towards nitrogen tethered substrates

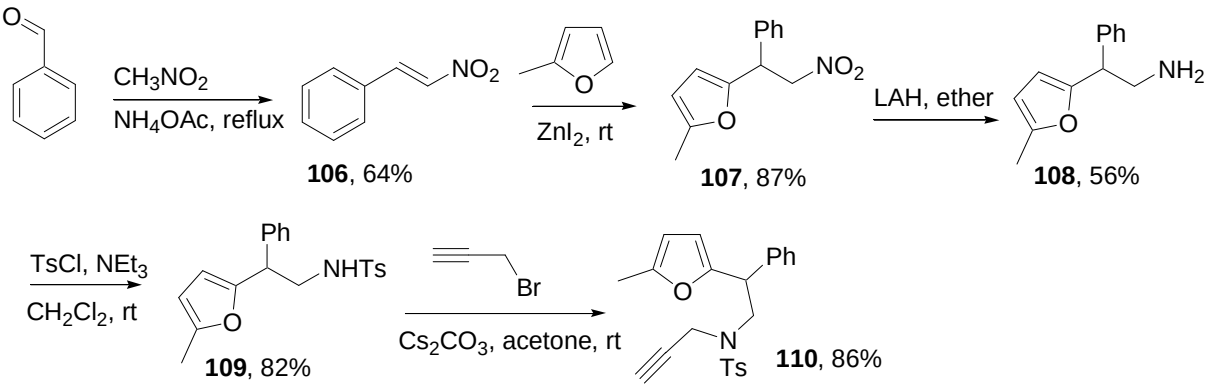
An enantiomerically pure, nitrogen tethered substrate was attempted to be prepared based on Ellman's protocol for diasteroselective addition of Grignard reagents to enantiopure tert-butanesulfinimines.[68b] The enantiopure imine **103c** was synthesized by condensation of furfural **102c** with (R)-(+)-2-methyl-2-propan-sufinamide. But the addition of ethyl Grignard to this imine didn't proceed diasteroselectively and delivered diasteromeric amine products **104g** and **104h** in almost 1:1 ratio. These isomers were separated using a long column of

silica gel and propargylation of each isomer delivered the diasteromeric enantiopure substrates **105f** and **105g** (Scheme 43).



Scheme 43: Synthesis of enantiopure substrates **105f** and **105g**

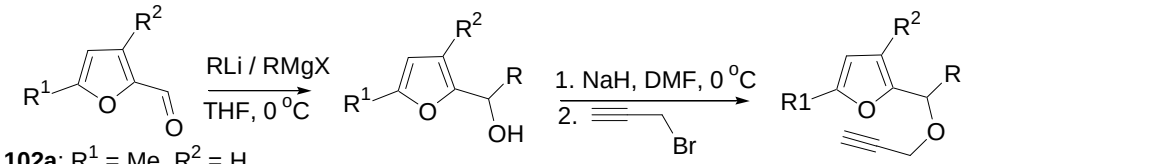
A substrate with two carbon tether was also synthesized. The synthesis for this molecule started from 1-nitro styrene which was prepared by the Henry reaction of benzaldehyde and nitromethane. The nitro compound **106** was treated with zinc iodide and methyl furan to form the addition product **107**.[69] Reduction followed by tosylation of **107** delivered the tosylated amine **109**. Propargylation of **109**delivered the required substrate **110** (Scheme 44).



Scheme 44: Synthesis of longer tethered substrate **110**

1.4.3.2 Synthesis of Oxygen tethered substrates

The synthesis of substrates with oxygen tether was fairly simple and consisted of only two steps. The substituted furfurals **102** were treated with different organolithiums or Grignard reagents and the resulting secondary alcohols upon deprotonation with sodium hydride and subsequent propargylation delivered the substrates of choice (Scheme 45).



102a; R^1 = Me, R^2 = H
102b; R^1 = H, R^2 = Me

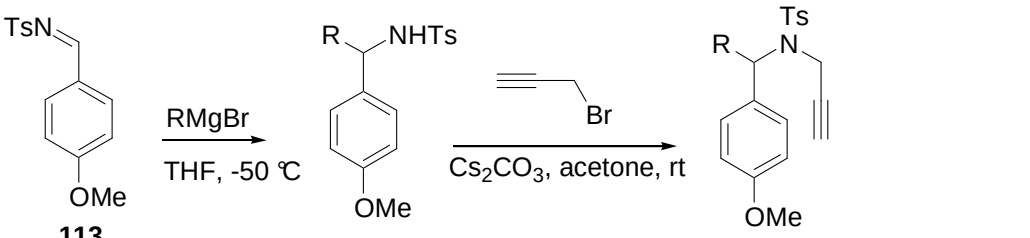
111a; R = *p*-anisyl, 80%
111b; R = Ph, 78%
111c: R = vinyl,
111d: R = 5-methyl furyl, 95%
111e: R = Ph, 75%

112a; R^1 = Me, R^2 = H, R = p-anisyl, 54%
112b; R^1 = Me, R^2 = H, R = Ph, 83%
112c; R^1 = Me, R^2 = H, R = vinyl, 70%
112d; R^1 = Me, R^2 = H, R = 5-methyl furryl, 68%
112e; R^1 = H, R^2 = Me, R = Ph, 65%

Scheme 45: Synthetic route towards oxygen tethered substrates

1.4.3.3 Synthesis of aryl-alkyne Substrates

Finally another class of substrates where the furan group was replaced by a *p*-anisyl group were synthesized. The starting imine **113** was treated with Grignard reagents and the resulting amines were propargylated (Scheme 46).



113

114a; R = cyclopropyl, 72%
114b; R = Ph, 66%

115a; R = cyclopropyl, 78%
115b; R = Ph, 98%

Scheme 46: Synthesis of aryl-alkyne substrates **115**

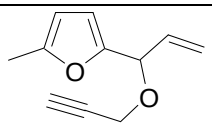
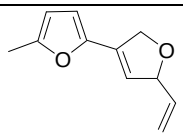
1.4.4 Results and discussion

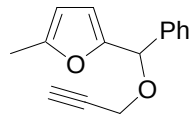
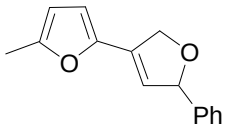
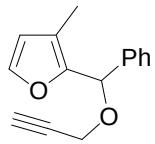
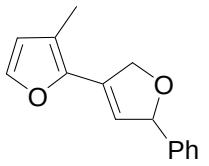
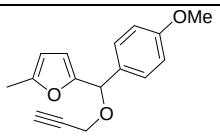
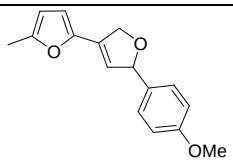
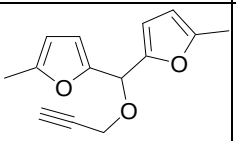
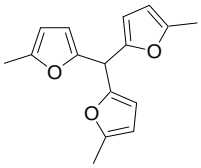
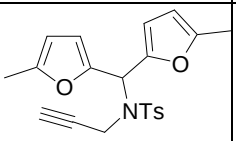
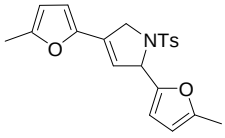
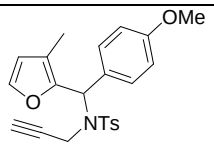
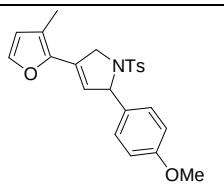
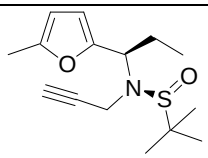
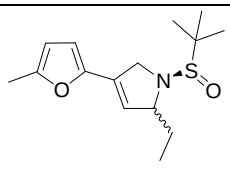
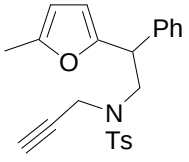
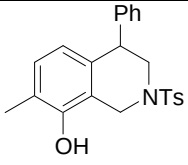
The synthesized substrates were then subjected to catalysis. Out of the various catalysts screened $Ph_3PAuNTf_2$ (A, here onwards) and $Mes_3PAuNTf_2$ (B, here onwards) were found to be the optimum catalysts in terms of reactivity and selectivity. The outcomes of catalysis are shown in Table 4.

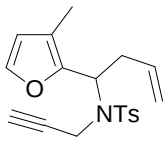
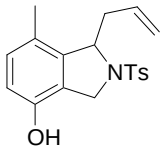
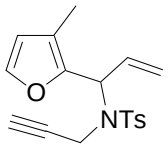
The substrate **112c** with a vinyl substituted oxygen tether was found to be slow-reacting and highly unselective. The reaction was completed in 7h at rt and the five-membered ring product **116c** was isolated in a lame yield of 20% (table 4, entry 1). The substrate **112b** with a phenyl substitution on the tether was very reactive. The reaction was finished in 5 min at rt but again the yield of the expected product **116b** was low (30%) (table 4, entry 2). The crude NMR spectra showed peaks of liberated benzaldehyde with significant intensity. This hinted

at the decomposition of any of the intermediates involved in the catalytic cycle, which accounts for the lower yield. The phenyl substituted substrate **112e** with methyl group on 3-C of the furan was tested next. As expected, the reaction was finished in 4 min at rt, and the product **116e** was isolated with a comparatively better yield of 44% (table 4; entry 3). The formation of *p*-anisaldehyde was observed in this case also. The substrate **112a**, with a *p*-anisyl substitution reacted in 15 min at rt to furnish the product **116a** in 43% isolation yield (table 4, entry 4). The substrate **112d** with a 5-methyl furyl substitution didn't react in the expected way, instead led to the formation of an interesting trifuran compound **117** in 60% isolated yield in 2h at 60 °C (table 4, entry 5). The nitrogen tethered variant **105a** had reacted in 4 min and delivered the five-membered ring product **118a** with an isolation yield of 42% (table 4, entry 6). The substrate **105c** with a *p*-anisyl substitution on the tether and methyl group on the 3-C of furan was quite reactive and highly selective. The product **118c** was isolated with an excellent yield of 78% (table 4, entry 7). The enantiomerically pure substrate **105g** was comparatively slower and delivered the product **118g** in 8h at 45 °C with an isolation yield of 50% (table 4, entry 8). The interesting substrate **110** with a longer tether (consisting of two carbon atoms) didn't give the possible six membered product but reacted in the conventional fashion to form the phenol **119a**, in 65% isolated yield (table 4, entry 9). Surprisingly the substrate **105d** with an allyl substitution on the tether also furnished phenol product **119d**. The reaction provided a complex product mixture and **119d** was isolated in 32% (table 4, entry 10). Finally the substrate **105e** with vinyl substituted nitrogen tether was tested. Similar to the oxygen analogue **112c**, this reaction gave a complicated mixture of products and none could be isolated pure (table 4, entry 11).

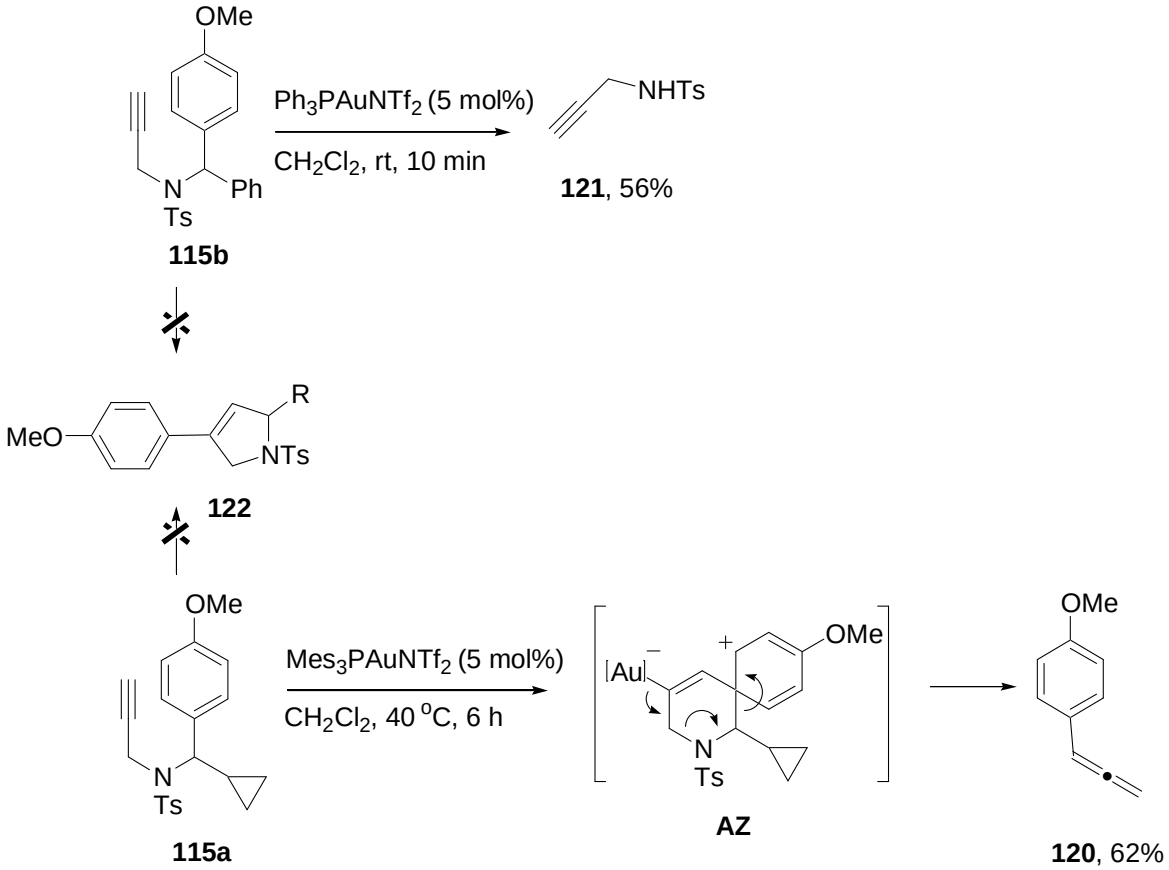
Table 4: Gold catalysis of α-substituted furyl-alkynes

Entry	Substrate	Cata	Time & Temp	Insertion Product	Yield	Phenol **119**	Yield **119**
1	 **112c**	B	7h, (rt)	 **116c**	20	-	-

2	 **112b**	B	5 min, (rt)	 **116b**	30	-	-
3	 **112e**	B	4 min, (rt)	 **116e**	44	-	-
4	 **112a**	B	15 min, (rt)	 **116a**	43	-	-
5	 **112d**	B	2h, (rt)	 **117**	60	-	-
6	 **105a**	A	4 min, (rt)	 **118a**	42	-	-
7	 **105c**	A	4 min, (rt)	 **118c**	78	-	-
8	 **105g**	A	8h, (45 °C)	 **118g**	50	-	-
9	 **110**	A	10 min, (rt)	-	-	 **119a**	65

10	 **105d**	B	5 min, (rt)	-	-	 **119d**	32
11	 **105e**	A	2h, (rt)	Complex mixture	-	-	-

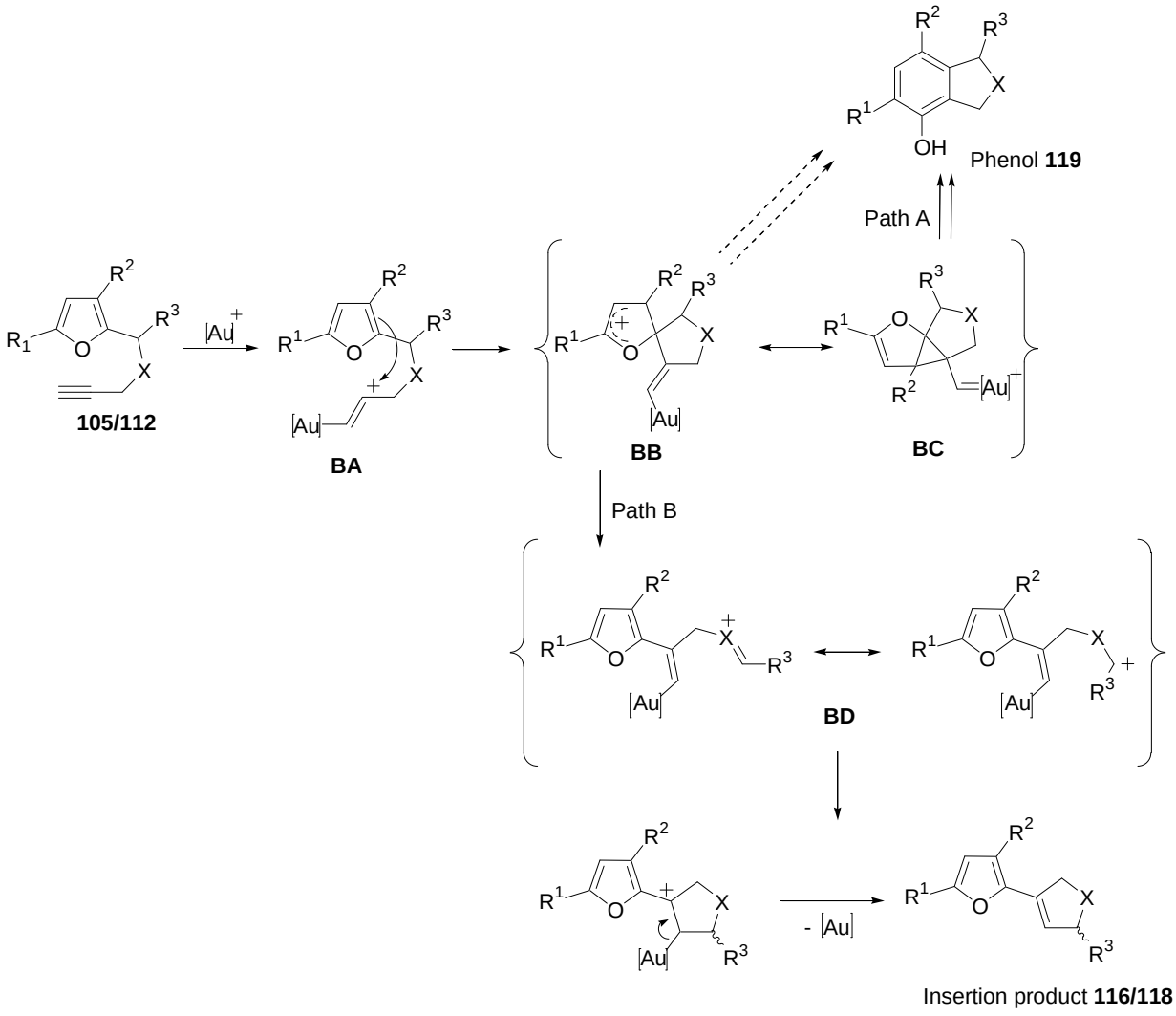
The substrates **115a** and **115b** with an anisyl group replacing the furyl didn't follow the expected pathway to furnish the insertion product **122**. Instead, **115b** underwent detosylation under the reaction conditions and **115a** produced the allene product **120**. The formation of **120** could be conceived to proceed through the initial *endo*-dig cyclization to form the spiro-intermediate **AZ** which undergoes concerted detosylation and deauration to form the allene product (Scheme 47).



Scheme 47: Gold catalysis of α-substituted *p*-anisyl-alkynes **115a** and **115b**

1.4.5 Mechanistic discussion

The observed reactivity pattern for the substrates **105/112** was highly informative and served as an experimental evidence for the significant contribution of the cationic form of the intermediate **BB** in the mesomeric/tautomeric equilibria shown in the scheme 47. A mechanistic proposal based on this intermediate was suggested for this hitherto unknown transformation in the gold catalysis of furyl-alkynes (Scheme 48).

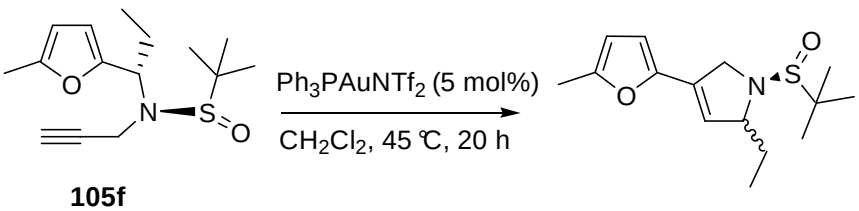


Scheme 48: Plausible mechanism for the formation of the insertion product **116/118**

According to the proposed mechanism, the activation of the alkyne by the gold catalyst led to the formation of cyclic intermediates **BB** and **BC**. On a normal note, these intermediates (rather the 'carbene' form **BC**) would have followed the classical phenol formation path (path A).[11b, 12] But the presence of an electron rich group on the α-carbon atom opened up another reaction pathway (path B) where the cationic form **BB** of the intermediate opened up to form a second cationic intermediate **BD** thereby regaining the aromatic furan moiety. This

intermediate **BD** was stabilized by the heteroatom present next to the cationic centre. A nucleophilic attack by the double bond followed by deauration established the final product structure **116/118**. The assumption that the five-membered insertion products were formed from the cationic form **BB** of the intermediate made sense considering the fact that the substrates having a cation stabilizing methyl substitution on the 3-C of the furan (where there is a higher accumulation of positive charge in the cation **BB**) showed increased propensity and higher reactivity to form these products. Also the reactivity showed more or less satisfactory correlation with the stabilization of the ring-opened cation **BD** brought about by the substituents on the tether (p-anisyl > cyclopropyl > phenyl > furyl > ethyl). The α-positioning of the heteroatom with the cationic carbon of **BD** was crucial for the stabilization or even existence of this species, as was exemplified in the case of substrate **110** where the heteroatom placed one carbon away from the cationic centre failed to deliver any insertion product.

An authentic confirmation for the proposed cationic mechanism was secured from the catalytic transformation of the enantiopure substrate **105f**. Should the mechanism be correct, there would be a racemization of the sterocentre on the tether when the SN_1 type cationic cyclization led to ring closure in the final step. As expected, the substrate **105f** delivered a 1:1 mixture of diastereomers upon subjected to catalytic isomerization (Scheme 49). The diasteromeric ratio was determined from ^{1}H-NMR and HPLC data.



105f

118f, 41%, dr 1:1

Scheme 49: Proof for the proposed cationic mechanism operating in the formation of the insertion products **116/118**

1.4.6 Conclusion

The investigations on the gold catalysis of α-substituted furyl-alkynes served as a solid experimental support to the remarkable argument that Fürstner et al. raised.[20a,20c] The formalism that the 'cationic' and 'carbenoid' rendition of the putative intermediates -in the catalytic cycle of gold catalyzed enyne cyclizations- are mere canonical extremes of the same intermediate/transition state can no longer be sustained. The formation of the insertion

products **116/118** from the potential phenol precursors add to the mere handful of experimental precedence so far available to show that the reaction fate of the 'cationic' and 'carbene' intermediates generated from a given substrate need not be identical. The cationic polycyclization mechanism that Fürstner found to be operating in the gold catalyzed enyne cycloisomerizations suffered from the need to have a methyl group on the would be cationic carbon for remarkable regioselectivity. It could be argued that these methyl groups are not 'innocent' and support a cationic intermediate rather than a competing carbene form. But in the above discussed project, substrates were found to be following a cationic mechanism even when there was no direct stabilization for the cationic intermediate **BB**. The α-substitution on the tether with electron-rich groups offered a parallel reaction route (other than the phenol formation) through which only a cationic species can proceed to. It is hard to imagine that a 'carbene' intermediate **BC** would also ensue similar transformation. The fact that majority of the substrates exclusively delivered the insertion products **116/118** indicated that the canonical contribution of the 'carbene' form of the intermediate is negligibly marginal in these cases. In fact, it should be noticed that the formation of the cyclopropyl gold carbene **BC** could be accounted by a step-wise process featuring the cationic form **BB**. Over all, the 'high noon' in gold catalysis throw serious but interesting questions about the core mechanistic details of gold catalysis.

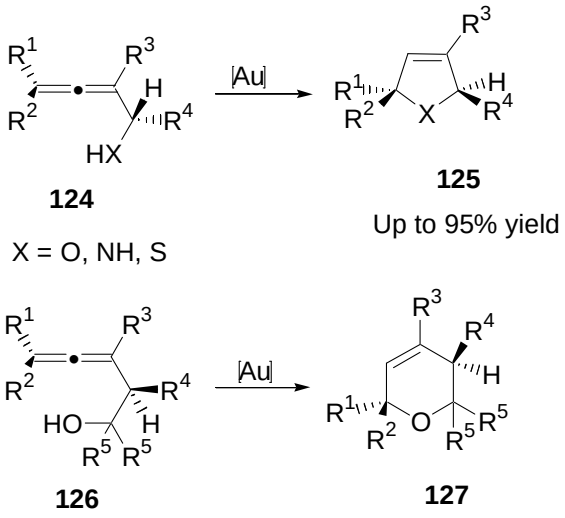
1.4.7 Gold catalysis of Furyl-Allenes

1.4.7.1 Background - Gold catalyzed transformations of hydroxy and amino allenes

The substrate arena of homogeneous gold catalysis owe mostly to enynes. The copious structural 'creations' the alkynophilicity of gold offers, often shadowed the prospects of other unsaturated fragments in gold catalysis.

The activation of allenes by gold is promising and there have been notable reports on the cycloisomerizations of allenenes, allenynes etc.[64,70] But in general heteroatoms were proved to be more effective intramolecular nucleophiles for activated allenes. The first such example was reported by Hashmi et al., for the gold catalyzed synthesis of furans from allenyl ketones.[9] The inherent axial chirality of allenes make them particularly attractive precursors for the synthesis of chiral heterocycles. For example, the Au(I)- or Au(III)-catalyzed *endo*-cycloisomerization of α- and β-hydroxyallenes to the corresponding heterocycles occurs with complete transfer of chirality in most cases (Scheme 50).[65,71] The method was extended to unprotected aminoallene substrates as well.[66,72] Another prominent report came from Zhang and Widenhoefer where they developed highly enantioselective exo-hydroalkoxylation of γ-

and δ-hydroxy allenes with a cationic gold(I) catalyst generated from Au-biphep-complex and silver tosylate.[73] The chiral counter ion strategy employed by Toste et al., also used hydroxyallene substrates.[37]

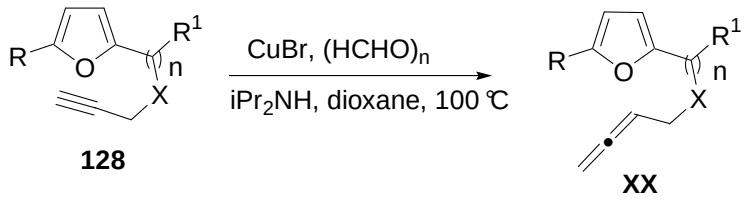


Scheme 50: Gold catalyzed cycloisomerization of heterosubstituted allenes

Although the gold catalysis of furyl-alkynes is a thoroughly investigated area, the same cannot be said about furyl-allene systems. The reactivity of furyl-allenes towards gold-catalysts was verified as a follow up to the preceding project.

1.4.7.2 Synthesis of Substrates

The model substrates required were easily synthesized by the Crabbe reaction[74] of the respective alkynes (Scheme 51).



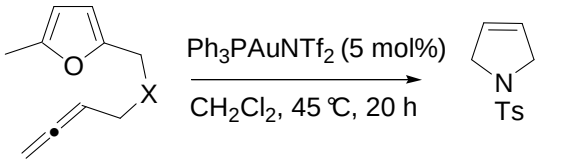
R = H, Me
n = 1, 2
X = NTs, NNs, O
R^1 = H, Ph

129a; R = Me, R^1 = H, n = 1, X = NTs, 39%
129b; R = Me, R^1 = Ph, n = 1, X = O, 49%
129c; R = Me, R^1 = H, n = 2, X = NTs, 58%
129d; R = Me, R^1 = H, n = 1, X = NNs, 58%
129e; R = Me, R^1 = H, n = 1, X = O, 54%
129f; R = H, R^1 = H, n = 1, X = NTs,14%

Scheme 51: Synthesis of furyl-allene substrates

1.4.7.3 Results and discussion

The screening of different gold complexes was done with **129a** as a model substrate. The reactions were generally slower and $Ph_3PAuNTf_2$ was found to be the best catalyst among $Mes_3PAuNTf_2$, $Ph_3PAuCl/AgBF_4$ and $AuCl_3$. The starting material reacted in 20h at 45 °C in the presence of 5 mol% of $Ph_3PAuNTf_2$ in CH_2Cl_2. Characterisation of the product formed showed it to be the dihydrotosylpyrrole **130** with an isolation yield of 47% (Scheme 52).

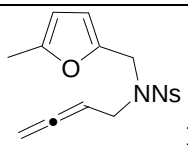


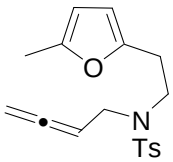
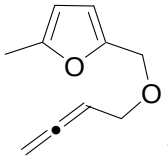
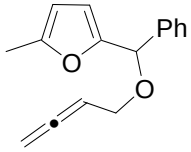
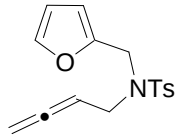
129 **130**, 47%

Scheme 52: Gold-catalysis of furyl-allene **129a**

The formation of this product indicated that there was no involvement of the olefinic bond of the furan moiety in the cyclization; instead the nitrogen atom of the tether acted as a nucleophile towards the gold-activated allene to form the five-membered ring product **130**. This assumption was supported when the substrate **129d** carrying p-nitro benzenesulfonyl (NNs) tether failed to react owing to the lower nucleophilicity of the nitrogen atom. The substrate **129c** with a longer tether also failed to react under the catalytic conditions because the removal of the furan unit as a localized primary cationic species was a hindered process. The substrates **129b** and **129e** with an oxygen tether were found to be decomposing upon catalyst addition. The substrate **129f** with a mono-substituted furan reacted in 10h at 45 °C to form the product **130** in 62% yield (based on ^{1}H-NMR). The results are summarised in table 5.

Table 5: Gold catalysis of furyl-allenes **129b-129f**

Entry	Substrate	Time & temp	Product	Yield
1	 **129d**	2d, 45 °C	No reaction	-

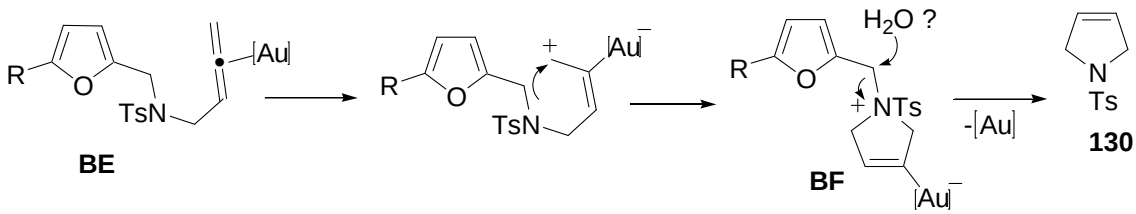
2	 **129c**	1d, 45 °C	No reaction	-
3	 **129e**	40 min, rt	decomposition	-
4 [a]	 **129b**	10 min, rt	decomposition	-
5[b]	 **129f**	10h, 45 °C	 **130**	62

[a] with 5 mol%, 1:1 $Ph_3PAuCl/AgBF_4$. No reaction with $Ph_3PAuNTf_2$

[b] yield based on ^{1}H-NMR

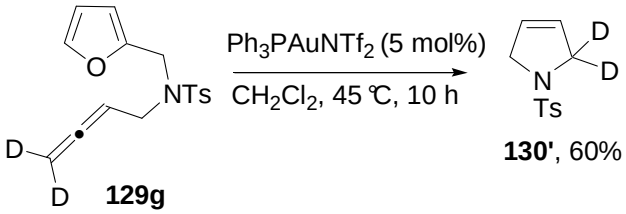
1.4.7.4 Mechanistic Proposal

The proposed mechanism for the formation of the dihydropyrrole **130** was depicted in Scheme 53.



Scheme 53: Proposed mechanism for the formation of **130**

The mode of liberation of the pyrrole moiety in the final step was not quite clear. Presumably the water present in the reaction medium would be facilitating the nucleophilic displacement process. But no furyl alcohol was isolated from the reaction mixture! But a highly polar material was detected at the baseline of the TLC plate indicative of a possible polymerization/decomposition that the liberated furan compound could have undergone. The catalytic transformation of the deuterated substrate **129g** delivered the product **130′** with the deuterium atoms intact thereby providing experimental support for the proposed mechanism (Scheme 54).



Scheme 54: Gold catalysis of the deuterated substrate **129g**.

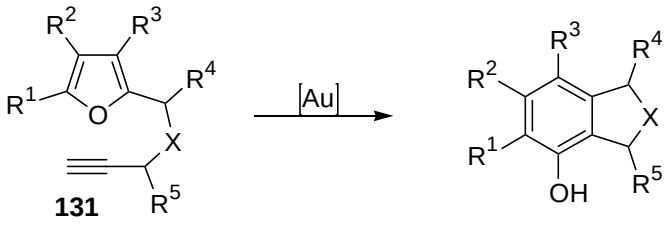
1.4.7.5 Conclusion

The furyl-allene substrates were not inclined towards the typical metal catalyzed cycloisomerizations of allenenes. Instead the substrates carrying an electron-rich nitrogen atom in the tether gave rise to the 'formal metathesis product' **130** provided the liberation of the furan unit is an energetically favoured process. The reactions testament the higher 'allenophilicity' of heteroatoms over 'π' nucleophiles. It is worth noticing that; lately similar substrates with a terminally substituted allene were shown to undergo [4+3] cycloaddition upon treatment with an NHC gold catalyst.[75]

1.5 Gold catalysis of Oxanorbornadienes; Novel formation of *N,O*-Acetals

1.5.1 Back ground - Mechanistic investigations of gold catalyzed phenol synthesis

The synthesis of highly substituted phenols from furan containing alkynes could be termed as a break-through in gold catalysis.[10] The discovery paved the way for a highly selective and robust synthesis of multiple functionalized aromatic compounds, rather phenols (Scheme 55). Following this report, there has been an exponential rise in the activity in the arena of gold catalyzed homogeneous transformations of enyne systems.[1]



131 **132**

X = O, OCR_2, NR, CR_2NR, CR_2...

R^1 = H, alkyl, aryl, alkynyl

R^2 = H, alkyl, Br, CO_2R

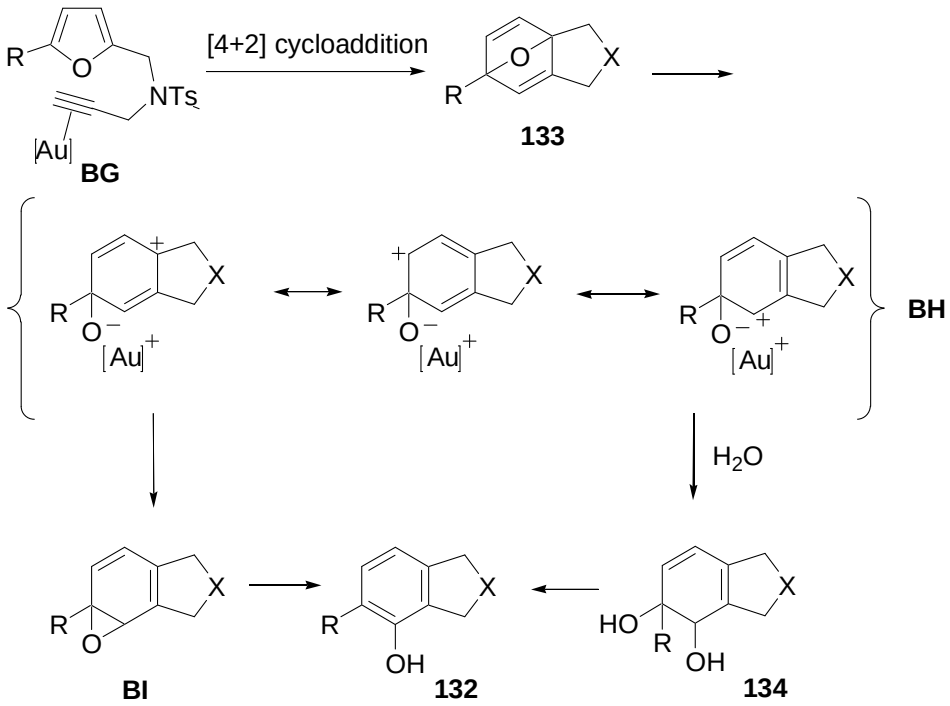
R^3 = H, alkyl

R^4, R^5 = H, alkyl, aryl

Scheme 55: Gold catalyzed synthesis of phenols from furyl-alkynes

The first mechanism suggested for this remarkable transformation propagated through an intramolecular Diels-Alder reaction between the furan and the gold activated alkyne to form the oxanorbornadiene **133**.[10a-b] Usually furans are passive towards Diels-Alder reactions and react only if the dienophile is activated by either a Lewis acid or an electron withdrawing group or under high pressure.[76] In the next step it was assumed that the oxygen bridge was broken by the Lewis acid activation of the gold cation and the resulting resonance stabilized cationic species **BH**, formed the arene oxide **BI**. The possibility of a dihydroxy intermediate **134** formed via an external nucleophilic attack of water was also conceived. The ring opening of **BI** or water elimination from **134**, delivered the final phenol product **132** (Scheme 56).

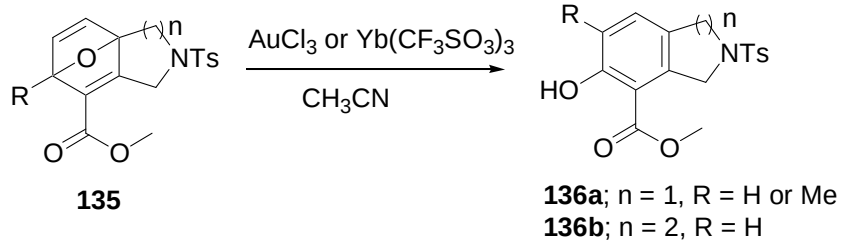
Although this mechanistic proposal was reasonable it could not explain the remarkably high regioselectivity exhibited by the reaction. The regioselective formation of the arene oxide could not be explained solely based on it's formation from the cyclopentadienyl cation **BH**. The reaction carried out in the presence of excess of $H_2{}^{18}O$[5] and usage of methanol as the solvent revealed that the oxygen transfer is mainly intramolecular, thus ruling out the possibility of an external water addition pathway.[10b]



Scheme 56: The Diels-Alder pathway proposed for the gold catalyzed phenol synthesis

While probing the mechanistic details of the gold catalyzed formation of phenols from furyl-alkynes, synthesis of oxanorbornadienes and examining their reactivity towards gold and other Lewis acids was proposed to be worth investigating. These reactions should be valuable source of information regarding the key mechanistic steps in the phenol synthesis. The generation of the cyclopentadienyl cationic species by Lewis acid activation of oxanorbornadiene systems and investigating the further transformations they undergo should help to envisage the odds of similar transformations proposed to take place in the phenol synthesis.

The oxanorbornadienes with five-membered tether and the systems with a hydrogen substituted epoxy carbon were found to deliver the expected phenol products on treatment with $AuCl_3$ or $Yb(CF_3SO_3)_3$ (Scheme 57).[77]

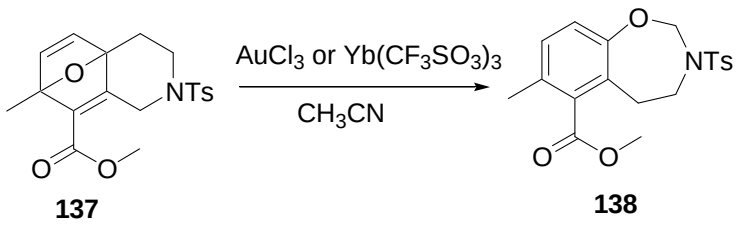


Scheme 57: Lewis acid catalyzed conversions of oxanorbornadienes to phenols

The outcomes of these reactions were partially in disagreement with some of the important features of the phenol synthesis, e.g., there was no transposition of the oxygen atom as was found in the phenol synthesis. The phenol formation from the furyl-alkynes did not show any NIH shift[78] of alkyl groups but the transformation of oxanorbornadienes to phenols was accompanied by the migration of the methyl group. Later on, Echavarren et al., discovered that platinum salts also induced phenol synthesis from furyl alkynes.[11b] They proposed a carbene pathway for such transformations which later on was acclaimed as the blueprint for such transformations.[12, 13]

1.5.2 Motivation for the present work

The oxanorbornadiene systems **137** with a six membered tether and a methyl substitution at the epoxy carbon didn't furnish the expected phenols when subjected to Lewis acids, instead underwent a curious rearrangement to form seven membered *N,O*-acetals (Scheme 58).



137 **138**

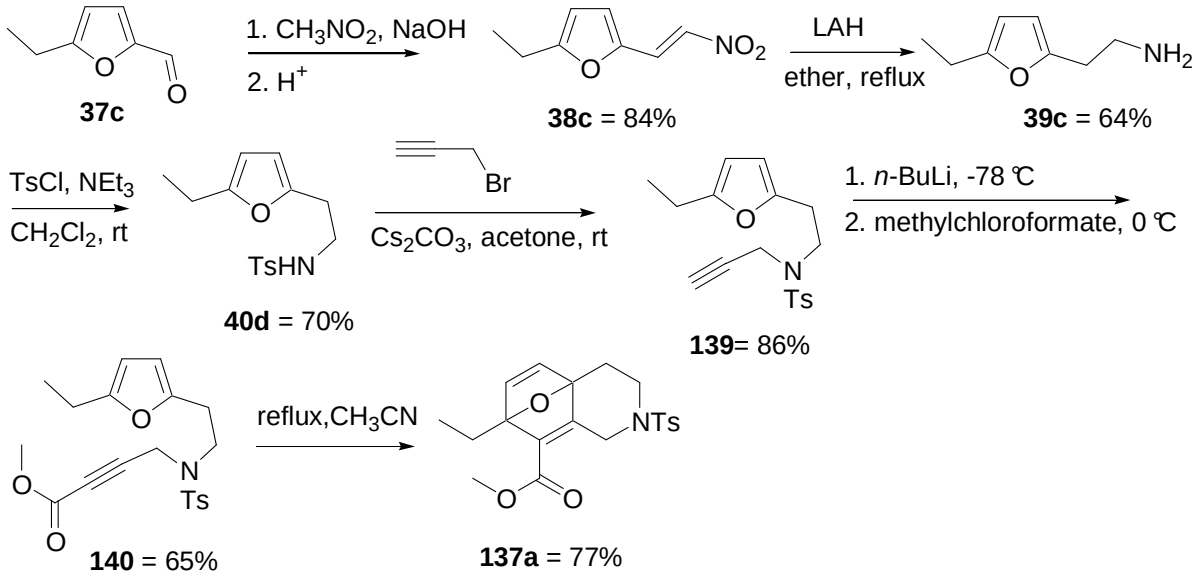
Scheme 58: Formation of *N,O*-acetals from oxanorbornadienes

This transformation was quite interesting considering its novelty. The formation of acetal ring would require the opening up of the oxygen bridge in the opposite direction to that leading to the form the phenol **132**. But the observation that there is a net reversal in the connectivity of the tether in the product hinted at a complex mechanism operating in the process. The reactions were taken for further structural explorations and screening of various Lewis acids.

1.5.3 Synthesis of the substrates

The substrate **137a** with an ethyl substituted epoxy carbon was synthesized by the same procedure adopted for the preparation of the other systems (Scheme 59).[77] The reaction sequence started from 5-ethyl furfural. Henry reaction of this compound led to the unsaturated nitro compound **38c** which upon reduction with lithium aluminium hydride and following tosylation delivered the amine **39c**. Propargylation and methoxycarbonylation furnished **140**,

the precursor for Diels-Alder reaction. **140** was refluxed in acetonitrile for 36 h to form the oxanorbornadiene **137a** as a crystalline solid. The X-ray crystal structure of this compound was obtained (Figure 4).



Scheme 59: Synthetic route towards the norbornadiene **137a**

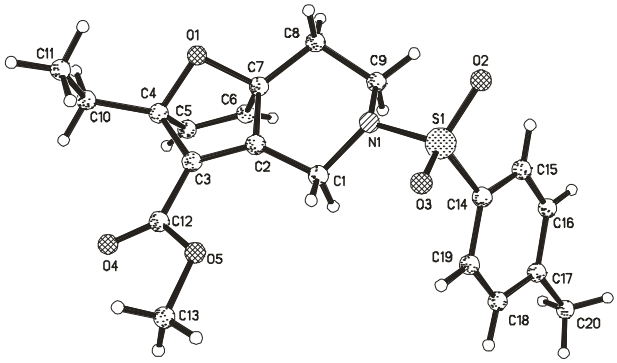
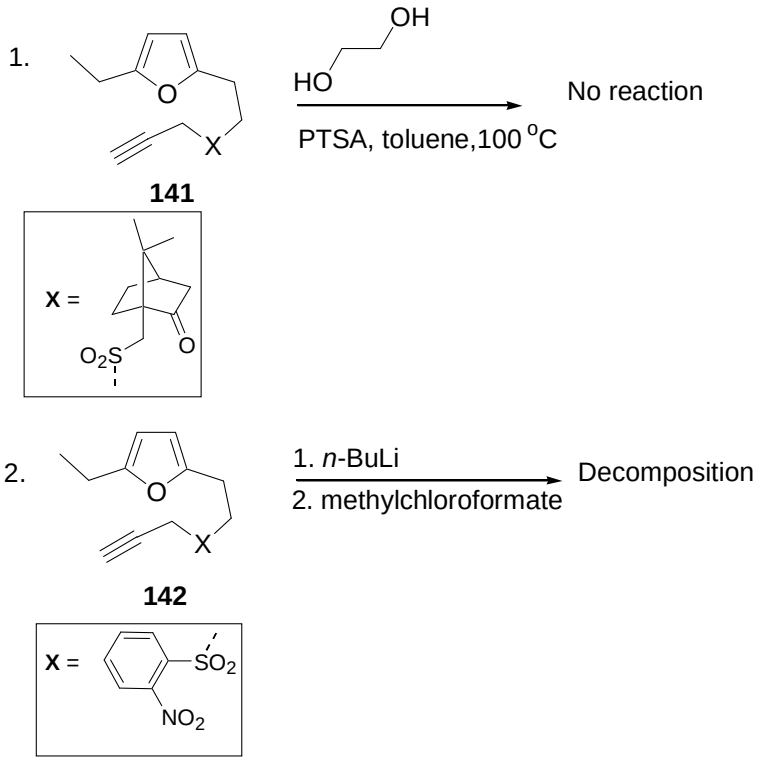


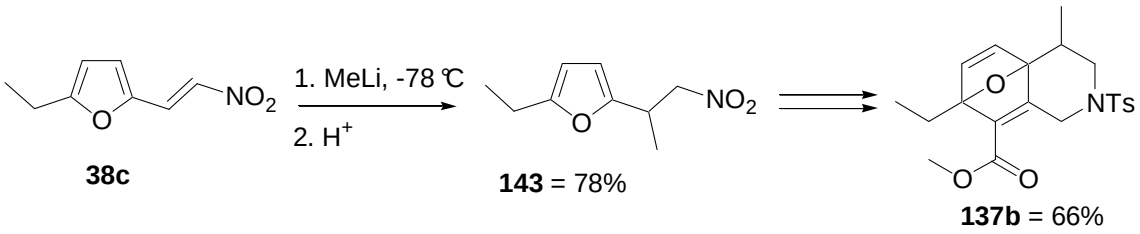
Figure 4: X-ray crystal structure of the substrate **137a**

The attempts to synthesize the camphorsulfonyl and 2-nitro-benzenesulfonyl protected variants of **137a** were failed (equations 1 & 2). The acetal-protection of the keto function of the camphor group before proceeding to the methoxycarbonylation didn't succeed. The compound **142** carrying an -NNs tether was found to decompose on addition of *n*-butyl lithium.



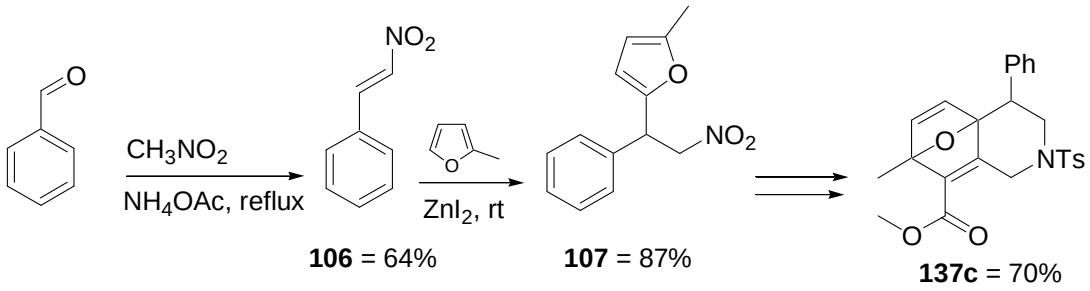
Equations 1 and 2: Failure of camphor sulfonyl and 2-nitro benzenesulfonyl tethers.

The substrate **137b** with a methyl substitution on the α-carbon of the tether was prepared. The methylation[79] was done on the Henry product **38c** and further conversions of the resulting nitro compound **143** furnished the required substrate **137b** (Scheme 60).



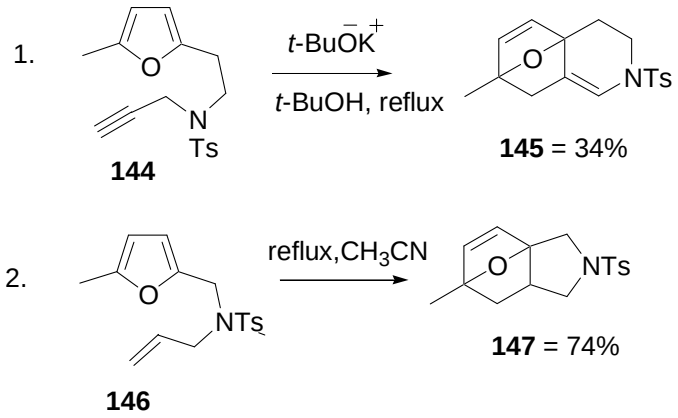
Scheme 60: Synthesis of substrate **137b** with an α-methyl substitution on the tether

The substrate **137c** with an α-phenyl substitution on the tether was prepared next. The synthesis started from nitrosyrene **106** which was treated with 5-methyl furan in presence of zinc (II) iodide.[69] The resulting addition product **107** was taken through subsequent steps to deliver the phenyl substituted substrate **137c** (Scheme 61).



Scheme 61: Synthesis of the phenyl substituted substrate **137c**

The substrates **145** and **147** having an oxanorbornene substructure were also prepared. Treatment of the alkyne **144** with potassium *tert*-butoxide in *tert*-butyl alcohol under reflux conditions[80] furnished **145**, while refluxion of the furyl-alkene **146** in acetonitrile produced the shorter, saturated tethered **147** (Scheme 62).

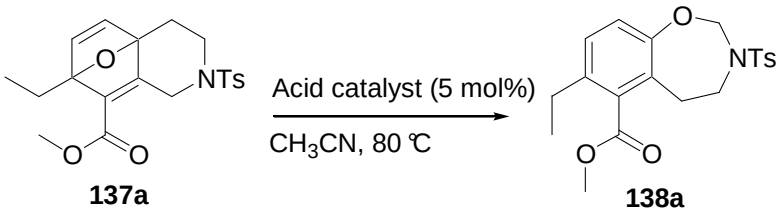


Scheme 62: Synthesis of oxanorbornene substrates **152** and **154**

1.5.4 Results and discussion

The substrate **137a** was subjected to various Lewis acid catalysts (5 mol%) and it was found that a range of metal salts delivered the *N*,*O*-acetal **138a** (table 5). AuCl was found to be the best Lewis acid catalyst under the given conditions (table 5, entry 2), and $Yb(CF_3SO_3)_3$ also showed remarkable reactivity (table 5, entry 3). The conversion also worked well with the Bronsted acid PTSA. The generality and the absence of any other products/side products confirmed that the reaction followed general acid catalysis. The X-ray crystal structure of the product **138a** was obtained thereby unambiguously proving the structural identity (Figure 5).

Table 5: Screening of various acid catalysts for the model substrate **137a**



137a **138a**

Entry	Acid catalyst	Time (h)	Yield of **138a** (%)
1	$AuCl_3$	2h	68
2	AuCl	1.5	87
3	$Yb(CF_3SO_3)_3$	8	74
4	PTSA	7	77
5	$AgBF_4$	10	-
6	ZnI_2	24h	30
7	$BF_3.Et_2O$	3	63
8	Cu(OTf)	3.5	60
9	$Cu(OTf)_2$	2.5	67

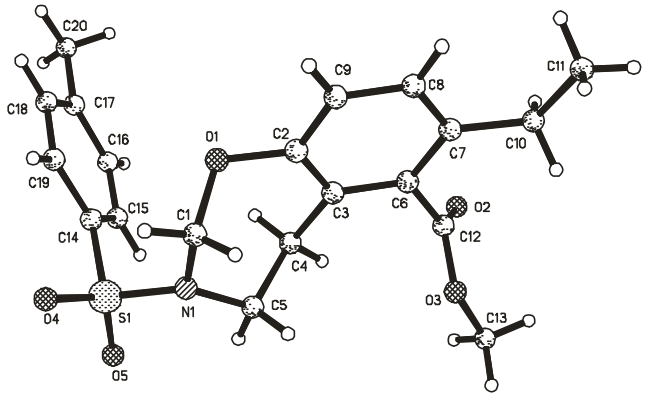
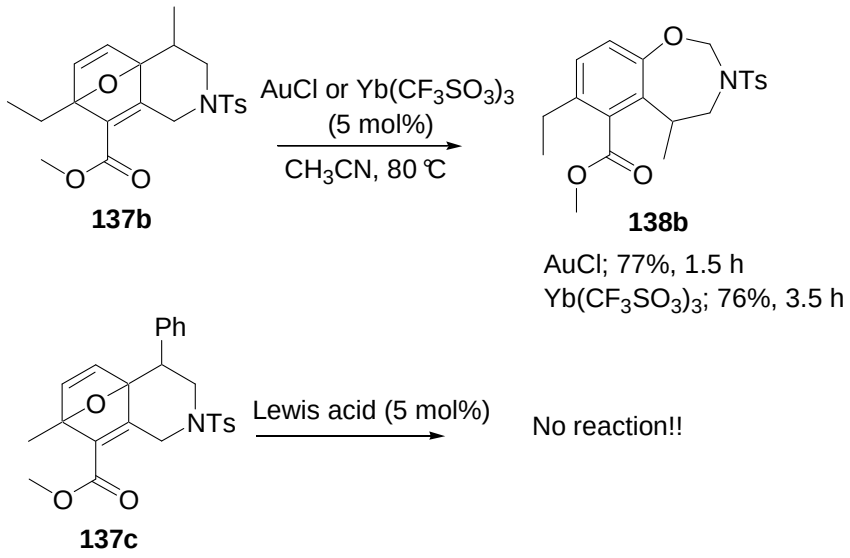


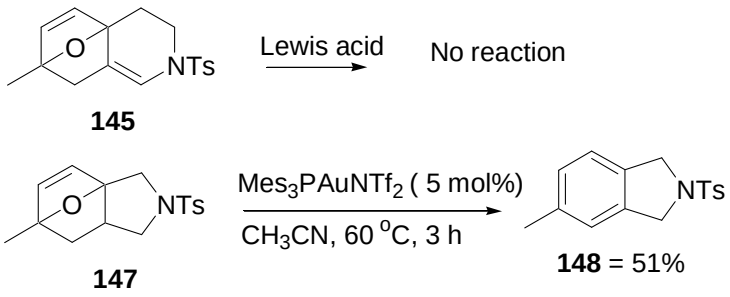
Figure 5: X-ray crystal structure of the *N*,*O*-acetal **138a**

The oxanorbornadiene substrates **137b** and **137c** were followed (Scheme 63). The methyl substituted **137b** delivered the acetal product **138b** in very good yields. But the phenyl substituted **137c** was surprisingly inert under the reaction conditions. There was no reaction even with a powerful Lewis acid like $AlCl_3$. Slow decomposition was observed with PTSA as the catalyst at high temperature.



Scheme 63: Lewis acid catalysis of **137b** and **137c**

The oxabicyclic-ene systems **145** and **147** were subjected to Lewis acids. **145** didn't give any reaction with $Yb(CF_3SO_3)_3$, and with AuCl decomposition was observed at higher temperature. The substrate **147** was found to be inert towards AuCl and $Yb(CF_3SO_3)_3$ even at elevated temperature. But on treatment with 5 mol% $Mes_3PAuNTf_2$ in CH_3CN at 60 °C, the deoxygenated product **148** was formed (Scheme 64).

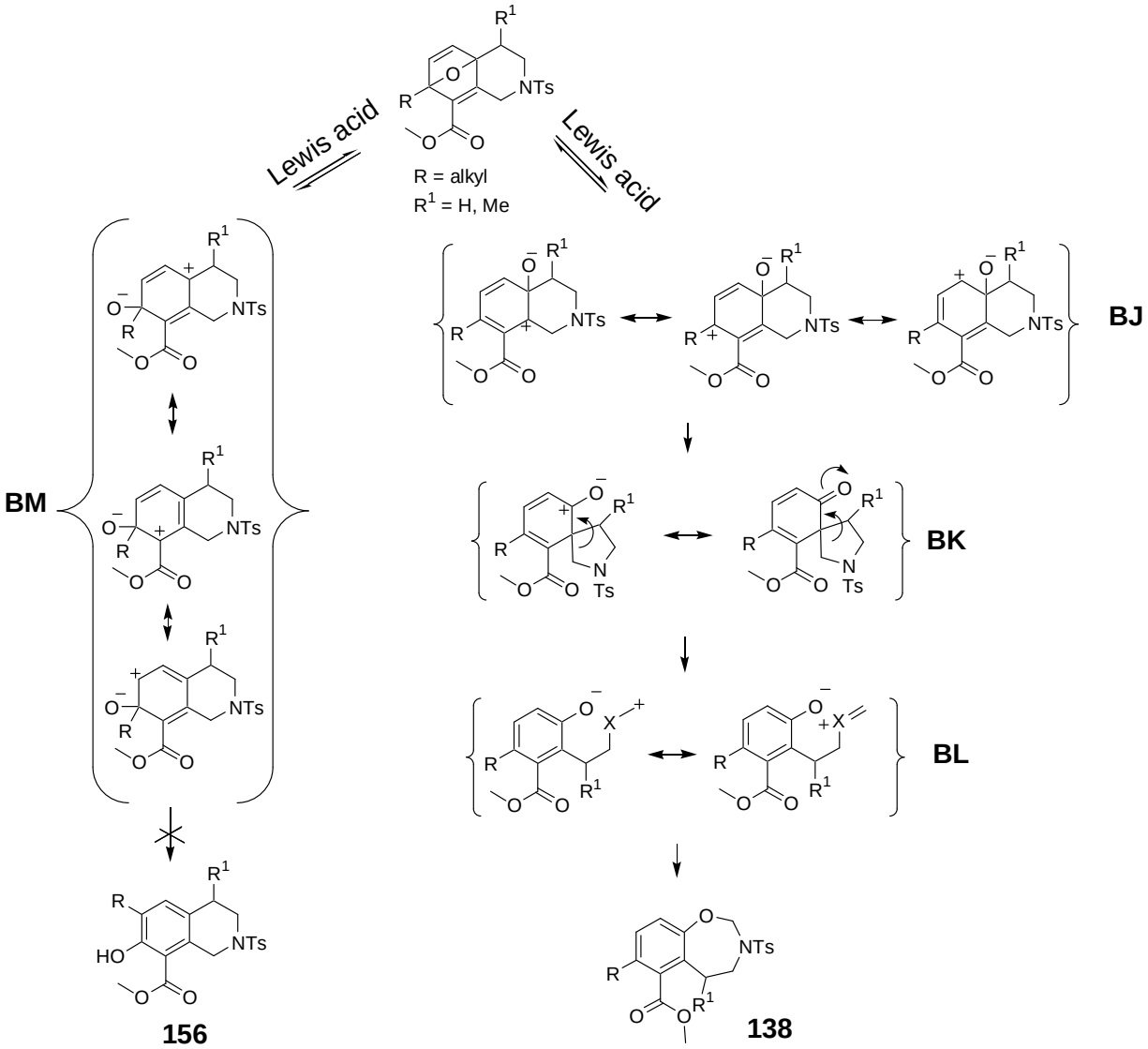


Scheme 64: Lewis acid catalysis of oxanorbornenes **145** and **147**

1.5.5 Mechanistic discussion

The Lewis acid activation of the oxygen in the oxanorbornadiene systems could possibly open up the bridge to either direction. The opening up of the bridge towards the ring carbon led to the formation of phenols in accordance with the mechanism that Prinzbach and Vogel proposed.[81] The oxanorbornadiene substrates with a shorter tether or those with hydrogen substituted epoxy carbon tend to react this way and delivered the phenol products. The *N*,*O*-acetal formation would require the hitherto unobserved opening up of the bridge towards the

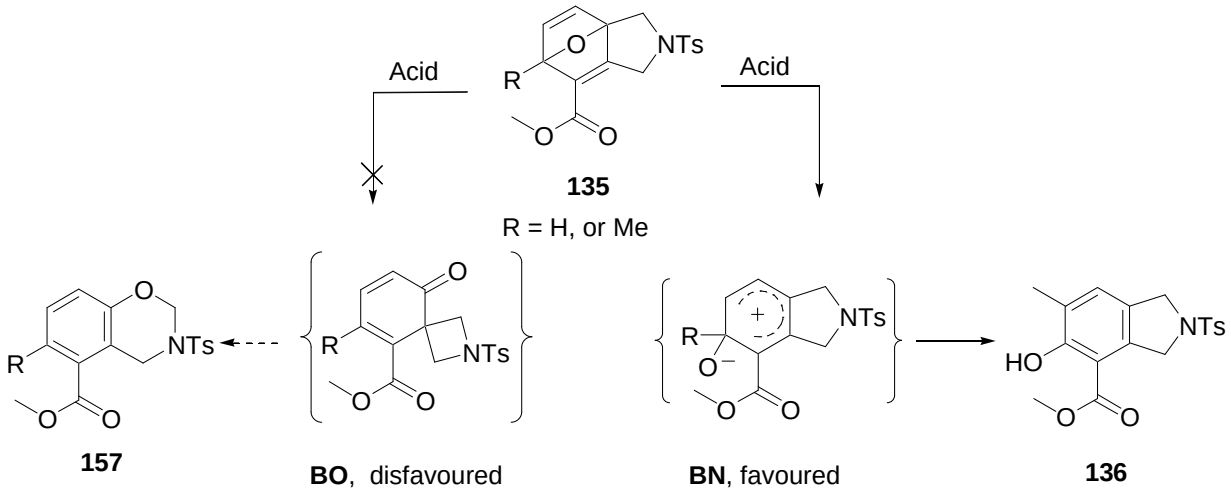
bridge-head carbon. The formation of *N*,*O*-acetals over the normally expected phenols in the case of substrates with a longer tether and an alkyl substitution on the epoxy ring carbon could be explained on the basis of two competing parameters; the stability of the cyclopentadienyl cation **BM** that leads to the phenol versus the stability of the spiro intermediate **BK** that leads to the *N*,*O*-acetal (Scheme 65).



Scheme 65: Plausible mechanism for the formation of *N*,*O*-acetals

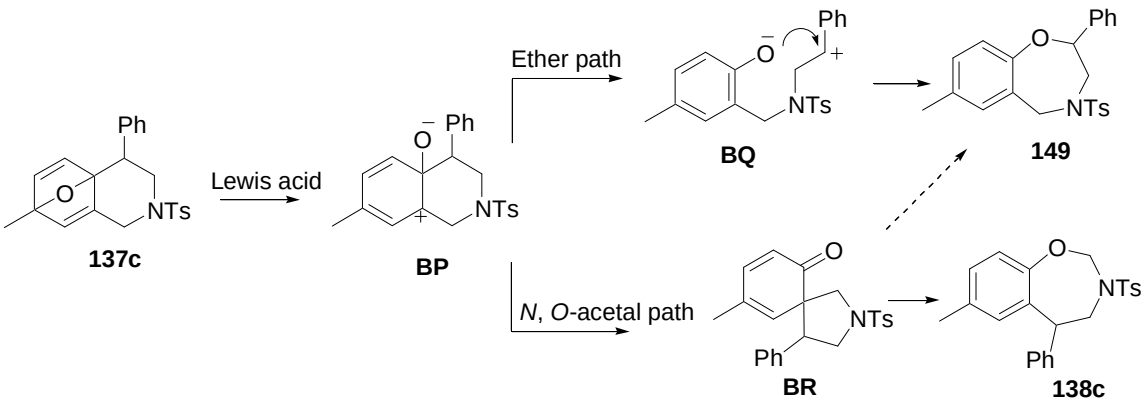
The cationic precursor **BM** for the phenol formation is destabilized by the mesomeric contribution of one of the canonical forms where the positive charge is located on the electron deficient carbon attached with the methoxycarbonyl moiety. Such a scenario would prompt the oxygen bridge to open to the other direction forming the mesomerically more stable cyclohexadienyl cation **BJ**. The migration of the tether to the cationic centre would form the spiro-ketone intermediate **BK**. The feasibility of this transformation would depend upon the

stability (in other words Baeyer and ring strain) of the spiro-ketone that is formed. A two carbon tethered cation like **BJ** would form five-membered spiro ring that is relatively free of ring strain and hence stable. The aromaticity was established by the 'switch over' ring opening (driven by the higher stabilization of the carbenium ion **BL**, when bonded to nitrogen atom) of **BK** forming the resonance stabilized cationic species **BL**, which underwent ring closure to form the final *N*,*O*-acetal product **138**. The consequence of the 'switch over' ring opening is that there occurred an 'inverse transposition' of the tether in the final product. The formation of such a product won't be favourable for a shorter tethered substrate as the generated four membered spiro ketone would be highly strained and hence unstable. The formation of phenols via the cyclohexadienyl cation of type **BM** is an energetically favoured process for such substrates (Scheme 66).



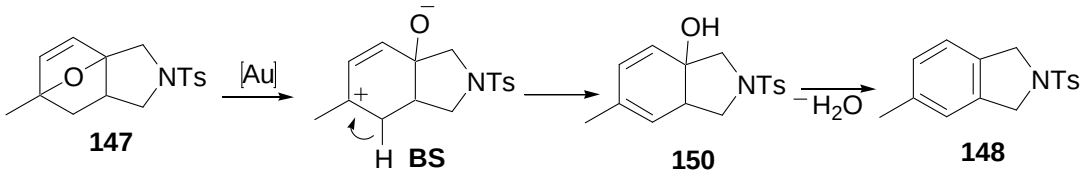
Scheme 66: Phenol formation prevails in the case of shorter tethered substrates

The total inertness of the phenyl substituted oxanorbornadiene **137c** towards acid catalysts was surprising, considering the fact that the stability and migratory aptitude of the benzyl carbanion is higher than that of methyl (applies to the substrate **137a**) or isopropyl (applies to the substrate **137b**) analogues. Also the introduction of the phenyl substitution was supposed to open up a competing ether formation pathway owing to the higher stability of the benzyl cation (Scheme 67). The higher steric bulk presented by the phenyl substituent could be reasoned for the untypically high tolerance of **137c** towards acid catalysts.



Scheme 67: Possible pathways assigned for the phenyl substituted substrate **137c**

The deoxygenated arene **148** could be formed from the oxabicyclic-ene **147**, by the following pathway (Scheme 68).



Scheme 68: Deoxygenation pathway of the oxanorbornaene **147**

1.5.6 Conclusion

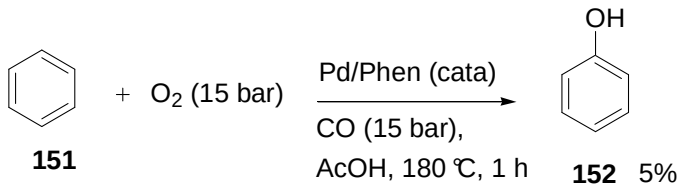
The unanticipated formation of *N*,*O*-acetals from oxanorbornadienes-the potential phenol precursors- upon exposure to Lewis acids, is an interesting transformation. The reaction followed general acid catalysis and gold(I) chloride was found to be the most efficient catalyst for this cycloisomerization. The salient feature of this reaction lies in the conceived mechanism, where the intermediacy of the spiro compound **BK**, induced a net reversal in the connectivity of the carbon chain from the substrate to the product. The introduction of a sterocentre on the pro-cationic carbon atom of the tether-where the cation forms in course of the reaction- would provide conclusive support for the speculated spiro-intermediate pathway, and is underway.

1.6 Investigations on Catalytic Aerobic Oxidations by Gold

1.6.1 Back ground: Catalytic aerobic oxidations of arenes, alkanes and alcohols

The catalytic aerobic oxidation of arenes, alkanes, and alcohols is of considerable interest to contemporary chemistry. The oxidation products (phenols, alcohols and carbonyl compounds respectively) found immense importance in industry as well as in academic sector. The development of catalytic systems for the selective oxidation of the former two class of substrates is quite challenging owing to the high bond energy of their C-H bonds (e.g., methane 105kcol/mol, benzene, 110 kcal/mol). Still the endeavour presents fascinating advantages such as lower cost, abundance of the stoichiometirc oxidant, and cleanness of the methodology.

Direct phenol synthesis from benzene has been extensively studied as it offers a very efficient alternative to cumene process; the classical route to phenol synthesis which suffers from low yields, high energy consumption, and the treatment of by-products.[82] O_2[83], H_2O_2[84], N_2O[85], NO [86] and (H_2+O_2)[82] as stoichiometirc oxidants have been reported to effect this conversion. Most of these systems rely on heterogeneous conditions. There are very few reports on successful homogeneous aerobic catalytic oxidations of benzene to phenol.[83a] Homogeneous variants bear the advantage of milder reaction conditions, and provide a better conviction about the reaction mechanism. Fujiwara et. al developed a phenol synthesis from benzene and O_2 using $Pd(OAc)_2$/phenanthroline catalytic system and CO as reductant (Scheme 69).[83a] The reaction showed remarkable selectivity but the yield of the phenol formed was minimal.

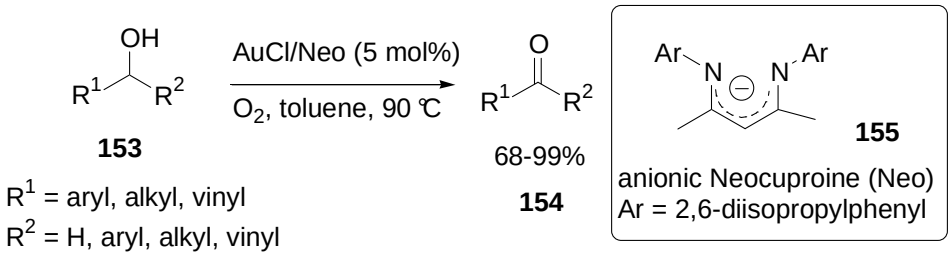


Scheme 69: Phenol synthesis reported by Fujiwara

Although the area of aerobic catalytic C-H oxidation of unactivated hydrocarbons is yet to embrace a highly selective and practical methodology to fulfil the demands of the industry, the same can't be said about the aerobic oxidation of alcohols.[87] Several noticeable heterogeneous catalysts such as the hydroxyapatite (HAP) bound RuHAP or PdHAP[88, 89], Ru/Al_2O_3 [90] were developed for the aerobic oxidation of alcohols. Recently several supported gold catalysts were reported to be potential oxidation systems both in cluster and in nano

forms.[91] Rossi, Prati and co-workers in their seminal studies have shown that supported gold nanoparticles can be very effective catalysts for the oxidation of alcohols, including diols.[92] Rossi et. al. also discovered the catalytic activity of 'naked' gold colloidal particles (3.6nm diameter) on the aerobic oxidation of glucose.[93] Under similar conditions, Cu, Ag, Pd, and Pt colloidal particles of similar dimension were found be devoid of any catalytic activity.

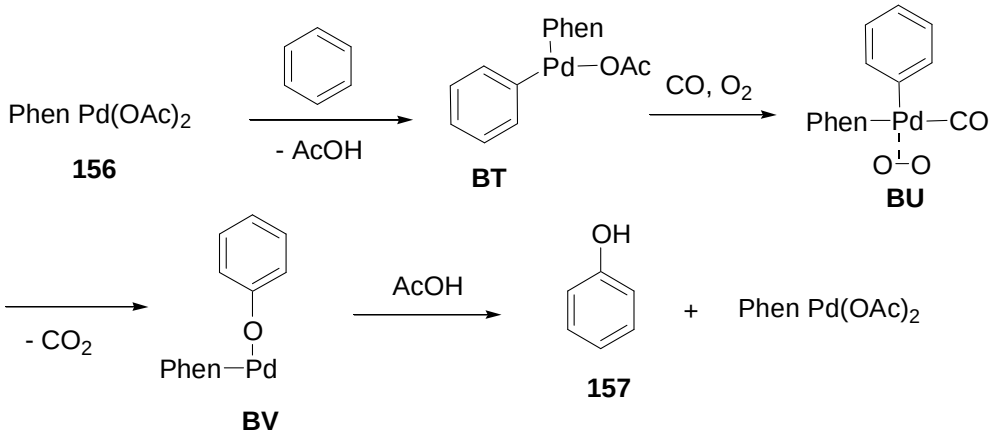
Shi et. al reported a remarkable aerobic oxidation system that works under typical homogeneous conditions using neocuproine/AuCl catalyt (Scheme 70).[94] They also extended these studies to report the catalytic oxidation of benzylic and allylic alcohols in water.[94b]



Scheme 70: Homogeneous aerobic gold catalyzed oxidation of alcohols

1.6. 2 Motivation for the present work

Fujiwara's phenol synthesis boast the only homogeneous methodology reported so far for this purpose.[83a] The speculated mechanism for this reaction involved the incorporation of benzene and CO to the Pd/Phen complex to form a Pd-Ph complex **BT**. Molecular oxygen activated by coordination to the metal centre underwent reduction by CO and subsequently inserted between Pd-C bond to form a Pd-OPh complex **BV**. The liberation of the phenol in the presence of acetic acid regenerates the catalyst (Scheme 71).



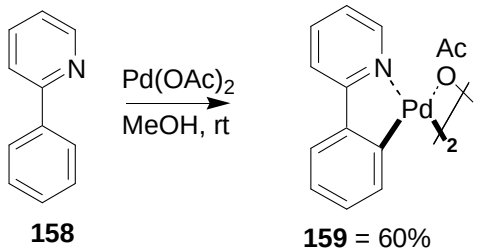
Scheme 71: Proposed mechanism for aerobic oxidation of benzene by Pd/Phen complex

Fujiwara's mechanistic proposal was taken as a starting point to initiate the efforts to develop an catalytic oxidation system for arenes. Different palladium (II) complexes having a Pd-arene substructure could be synthesized and exposed to high pressure oxygen atmosphere to investigate the oxygen insertion to the Pd-C bond.(such palladacycles are known to undergo arylation of the ligand by a Pd(II)/Pd(IV) pathway).[95] The system should mimic the in situ formed Pd-Ph complex in Fujiwara's reaction and was expected to provide crucial information about the 'susceptibility' of the Pd-C bond towards oxygen insertion; the key step in the catalytic aerobic phenol synthesis.

Gold clusters dispersed in the cavities of zeolites are found to be potentially active systems towards alkanes, CO and alcohol oxidations. The stability of these clusters is often a matter of concern as the pronounced aurophilicity of gold lead to agglomerization, thereby destroying the catalytically optimum particle size and homogeneity of the system. Stabilization of gold clusters with suitable ligands should hinder aggolomerization and generate catalytic systems with enhanced activity. The presence of suitably poised ligands around the cluster should also improve the selectivity of the oxidation process. Some of the organogold complexes/ligands were synthesized and handed over to collaborators in heterogeneous wing for further studies.

1.6.3 Synthesis of substrates

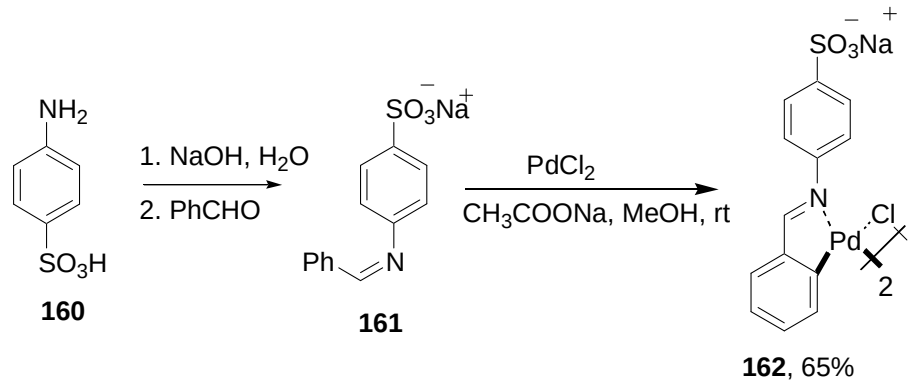
The palladacycle required was synthesized by known methods. The complexe **159** was obtained by stirring a suspension of 2-phenyl pyridine and palladium acetate in methanol at room temperature (Scheme 72)



158 **159** = 60%

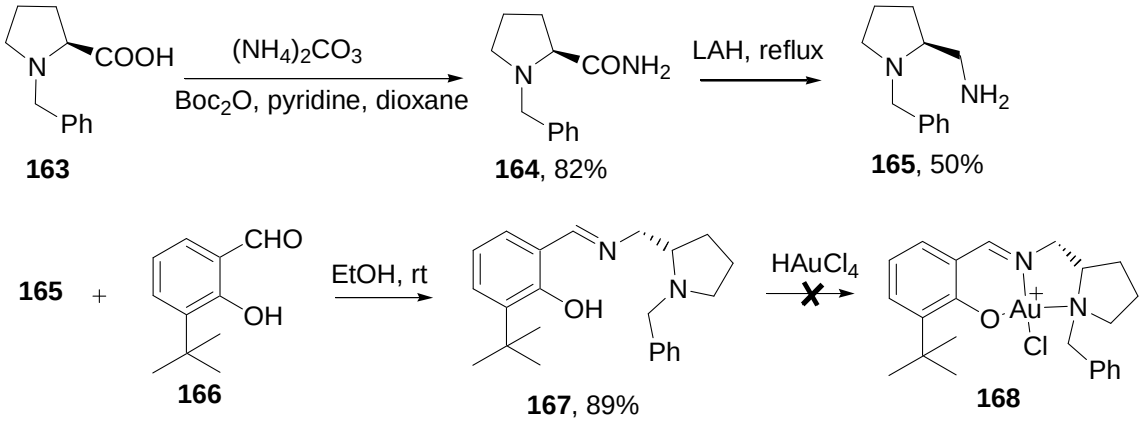
Scheme 72: Synthesis of palladacycle **159**

Another water soluble palladium complex **162** was prepared by stirring a mixture of the Schiff base ligand **161** with $PdCl_2$ and sodium acetate in methanol at room temperature (Scheme 73).[96]



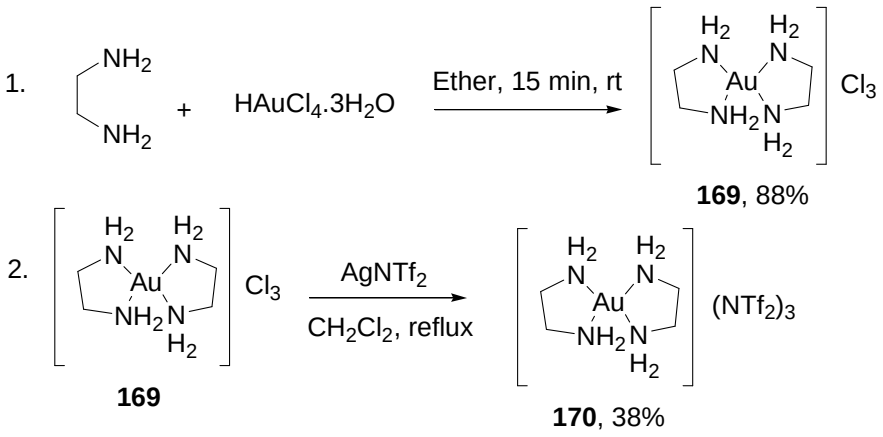
Scheme 73: Synthesis of the water soluble palladacycle **162**

The semi-salen ligand **167** was prepared by a related procedure (Scheme 74).[97] The efforts to complexate this ligand with gold did not work.



Scheme 74: Synthesis of semi-salen ligand **167**

A gold(III) complex based on ethylenediamine ligand was also prepared.[98] The counter ion exchange of this complex with silver triflate was also done (Scheme 75).

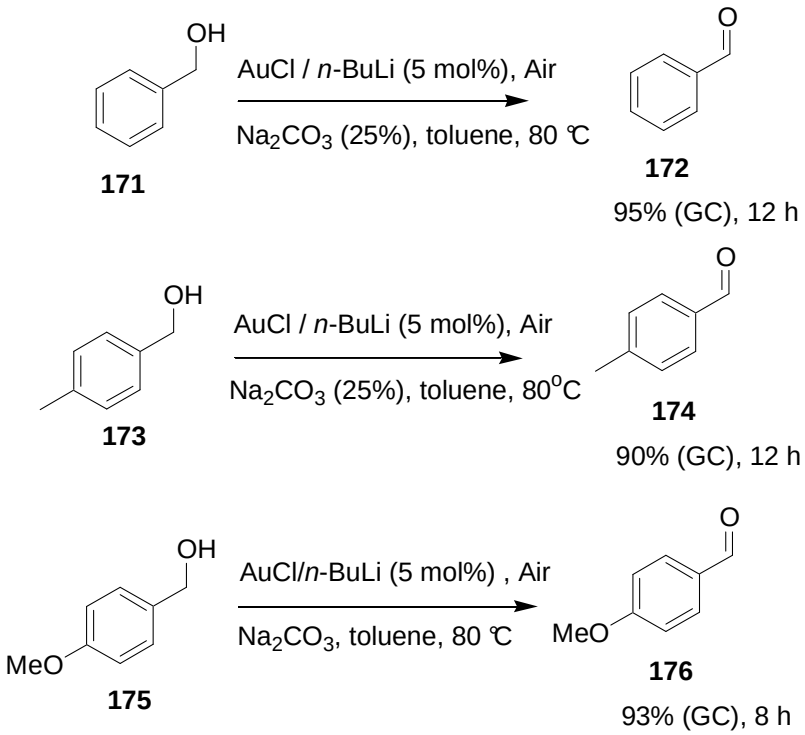


Scheme 75: Preparation of ethylenediamine gold complexes

1.6.4 Results and Discussion

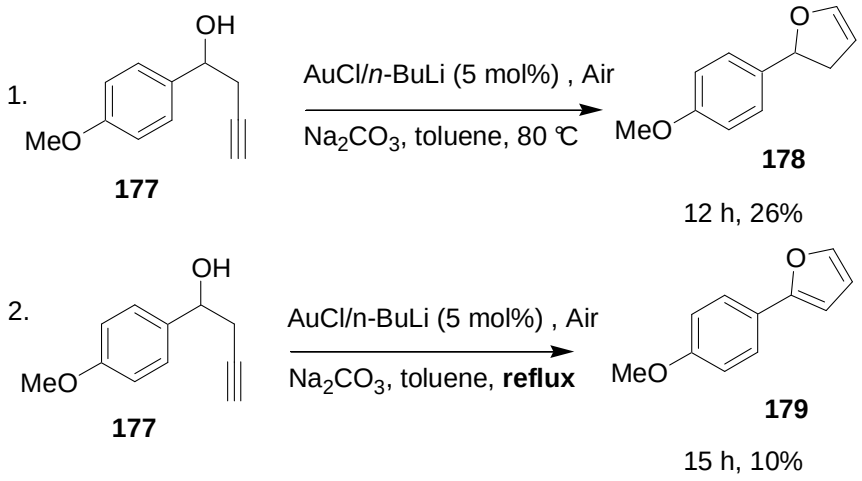
The synthesized palladium complexes were subjected to oxygenation conditions (the reactions were carried out in heated acetic acid under an oxygen pressure of 7 bar) to see if there is any oxidation occurs for the metal-carbon bond. Unfortunately all these complexes were either inert under the reaction conditions or decomposed with the formation of palladium black. The use of reducing agents like ascorbic acid or sodium formate also couldn't alter the outcome of these reactions.

The failure of these systems -which probably goes back to the inertness of the palladium-carbon bond or the need to have harsher conditions-, prompted to go after the oxidation chemistry of more reactive families. Alcohols possess a reactive carbon-oxygen bond and the development of environmentally benign aerobic oxidation protocols for alcohols is much attractive. Several transition-metal-ligand combinations were screened for the aerobic catalytic oxidation of the model substrate benzyl alcohol and it was found that a combination of AuCl (5 mol%) and n-butyl lithium (5 mol%) in the presence of sodium carbonate (25 mol%) in toluene at 80 °C constitute a reactive catalytic system for the oxidation of the model substrate benzyl alcohol to benzaldehyde. 95% conversion was obtained on GC scale and only a trace of benzoic acid (over oxidation product) was detected (Scheme 76).



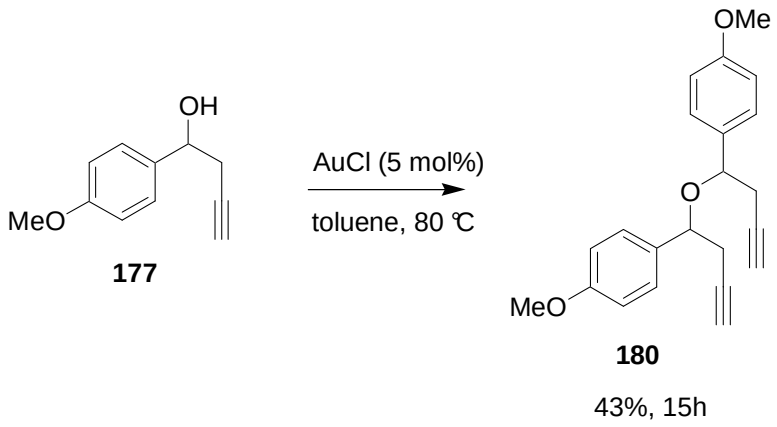
Scheme 76: Oxidation of primary aromatic alcohols using AuCl/*n*-BuLi

No significant oxidation was observed in the absence of *n*-butyl lithium. The catalyst was effective for other primary aromatic alcohols but couldn't oxidize aliphatic, secondary or deactivated alcohols. The propargyl alcohol **177** has undergone cyclization when treated with this catalytic system to furnish dihydrofuran compound **178**. On reflux conditions further oxidation occurred and the furan compound **179** was obtained (Scheme 77).



Scheme 77: Gold catalysis of propargyl alcohol **177**

An intermolecular SN reaction took place when the substrate **180** was treated with AuCl in the absence of *n*-butyl lithium and sodium carbonate (Scheme 78).



Scheme 78: Intermolecular SN reaction of the substrate **180** catalyzed by AuCl

The gold-ethylenediamine complexes **169** and **170** were used as the cationic gold sources for the ion-exchange/impregnation with various Zeolite systems to develop stable gold-zeolite systems. The activity of these systems in hydrocarbon, CO and other oxidations are investigated.

1.6.5 Mechanistic discussion

The oxidation of the alcohols by the AuCl/*n*-BuLi system is thought to proceed by the activity of zerovalent gold particles[93] and hence cannot be speculated to follow a typical homogeneous mechanism. The formation of these species is conceived by the reduction of gold(I) chloride by *n*-BuLi. The wine red colouration characteristic for the formation of gold(0) particles was observed at this step. It was also found that the catalytic activity of the system reduces with time hinting the possible decomposition/aggolomerization of the gold particles. A coating of metallic gold was observed on the walls of the reaction flask.

The formation of the dihydrofuran compound **178 a**nd the nucleophilic substitution product **180** could easily be envisaged. The former ensue the 1,5-*endo* nucleophilic attack of the oxygen atom on the gold-activated triple bond and the subsequent protodeauration to furnish **178**. The latter product represents a simple case of metal assisted nucleophilic substitution.

1.6.6 Conclusion

A catalytic system for the aerobic oxidation of primary aromatic alcohols was developed. The catalytically active species is supposed to be zero valent gold particles. The in situ formed catalyst was not reactive/living enough to oxidize aliphatic, secondary and deactivated alcohols. The ‘nakedness’ of these particles could be attributed for the observed aggolomerization. The possible stabilization of the ‘naked’ particles by suitable additives (Kobayashi’s report on the stabilization of gold nanoparticles by polystyrene additives is noteworthy in this scenario).[99] is underway and would increase the life time of gold(0) particles thereby enhancing their reactivity.

1.7 Summary

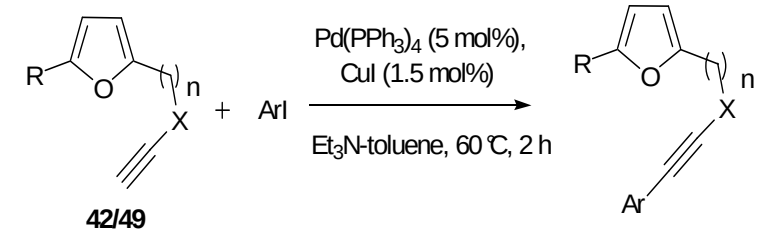
a) The first chapter of this thesis manifests the exploration of homogeneous gold-catalyzed conversions of furan containing aryl-ynamides and ynol ethers. Enynes boast to be the most explored substrate structures in the realm of homogeneous gold catalysis, whereas the reactivity of ene-ynamides and ene-ynol ethers are much less explored till date.[34, 45] Hashmi and co-workers recently reported the homogeneous gold-catalyzed synthesis of phenols from furan containing ynamides/ynol ethers.[45e] These substrates showed excellent reactivity and selectivity apparently owing to the heteroatom directly attached to the alkyne unit. Impressed with the reactivity and high selectivity of these systems, we decided to explore the catalytic activity of the aryl substituted variants of these compounds.

Synthesis of ynamide and ynol substrates

Both two and three carbon tethered substrates were synthesized for the investigations. The terminally unsubstituted furan-ynamides and ynol ethers were synthesized[10k-m, 45e] first and a subsequent Sonogashira[51] or Negishi arylation of the terminal alkyne furnished the required aryl-ynamides and aryl-ynol ethers respectively.

Sonogashira coupling: Synthesis of aryl-ynamides

The terminal aryl substitution of the ynamides **42/49** was done by Sonogashira coupling (Scheme A).[51] The reaction worked only for aryl iodides and sterically demanding groups on the *ortho*-carbon of the arene partner were not tolerated.



42/49

42a; n = 2, X = NTs, R = H
42b; n = 2, X = NTs, R = Me
42c; n = 2, X = NBs, R = Me
42d; n = 2, X = NTs, R = Et
49a; n = 3, X = NTs, R = H
49b; n = 3, X = NTs, R = Me

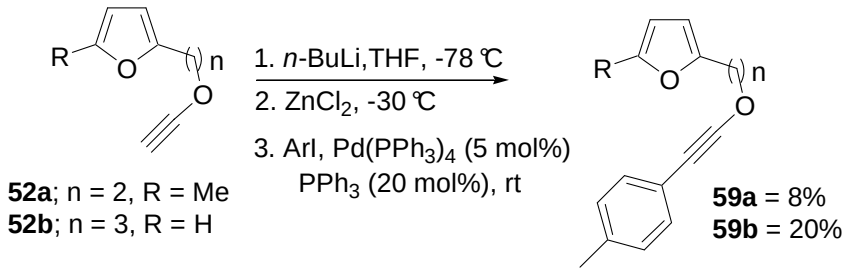
58

17-46%

Scheme A: Sonogashira coupling of furyl-ynamides

Negishi coupling: Synthesis of aryl-ynol ethers

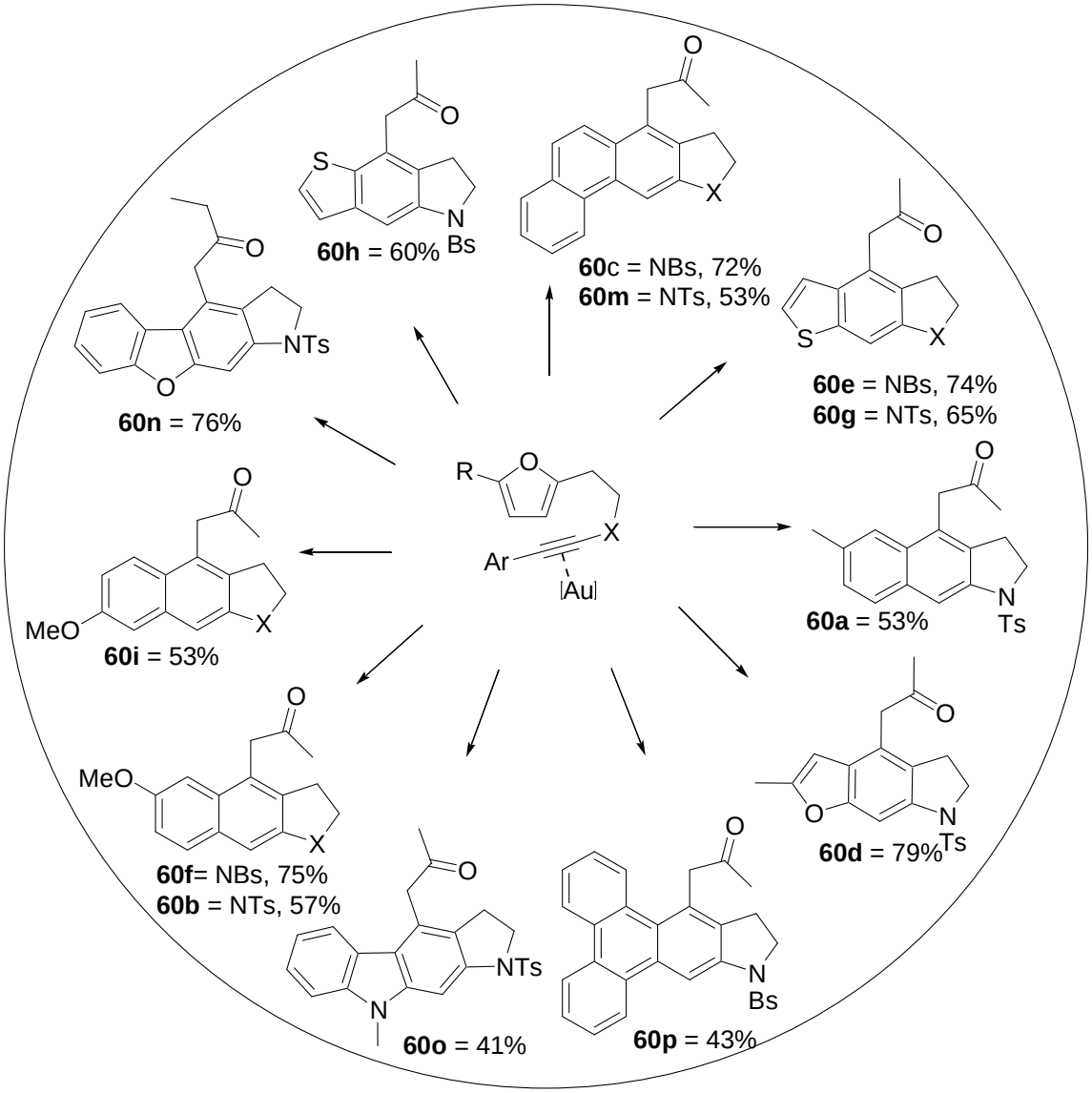
The Sonogashira coupling was not effective to arylate ynol ethers and hence Negishi protocol was attempted for the synthesis of aryl-ynol ethers **59** (Scheme B). The reaction furnished the products in poor yields.



Scheme B: Negishi coupling of Ynol ethers **52**

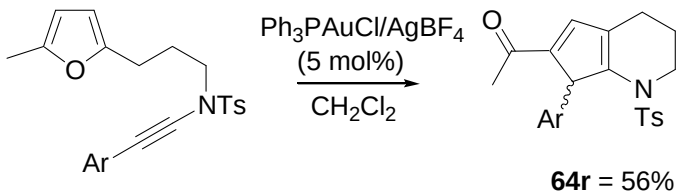
Gold catalysis of aryl-ynamides

The aryl-ynamide substrates turned out to be interesting candidates for gold catalysis. The mode of reactivity depended on the tether length. The substrates with two carbon tether underwent a Friedel-Crafts type reaction upon subjected to gold catalysts and furnished benzannulated arenes in moderate to excellent yields (Scheme C). A combination of Ph_3PAuCl /$AgBF_4$ (5 mol%, 1:1) in CH_2Cl_2 or $CHCl_3$ was found to be the best choice of catalyst. The reaction conditions were mild and a broad spectrum of polyarenes and polyheteroarenes were synthesized. The substrates carrying an unactivated arene failed to react even under higher temperature and prolonged reaction time.



Scheme C: Product spectra of gold-catalyzed benzannulation of aryl-ynamides **58**

The gold catalysis of substrates **58r**-**58t** with a longer tether took a completely different pathway and gave rise to cyclopentadiene structures (Scheme D). Similar to shorter tethered substrates, electron withdrawing groups on the arene were not tolerated.



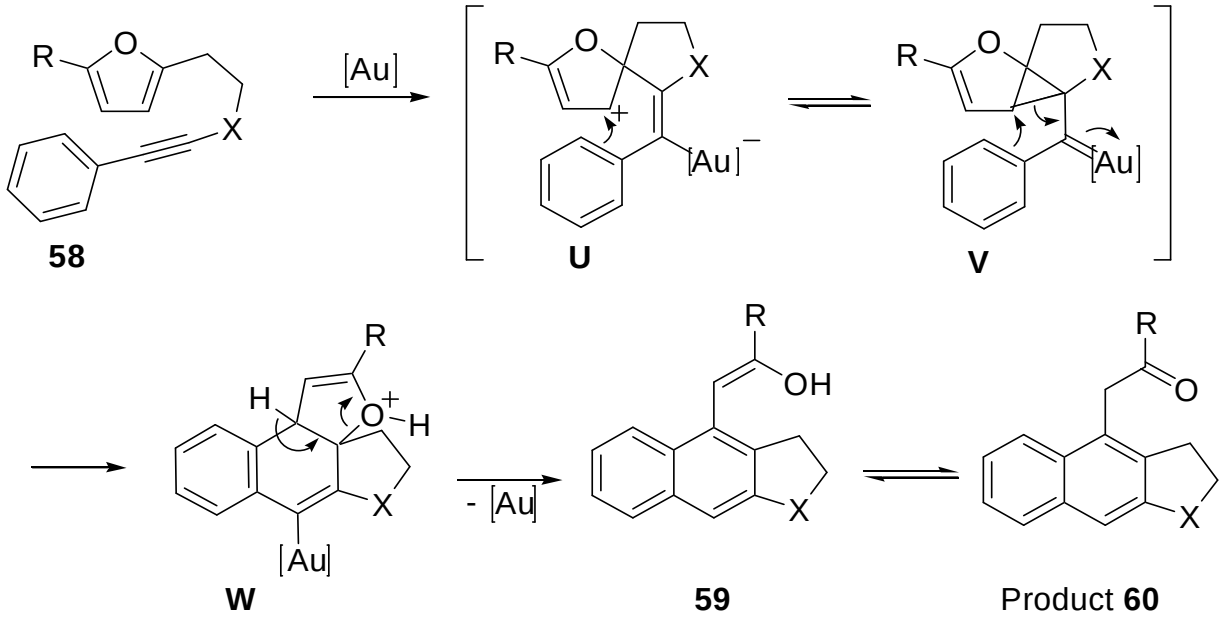
58r; Ar = *p*-anisyl
58s; Ar = *p*-tolyl
58t; Ar = 3-thiphenyl

64r = 56%
64s = 52%
64t= 50%

Scheme D: Gold catalysis of aryl-ynamides **58** (with three carbon tether)

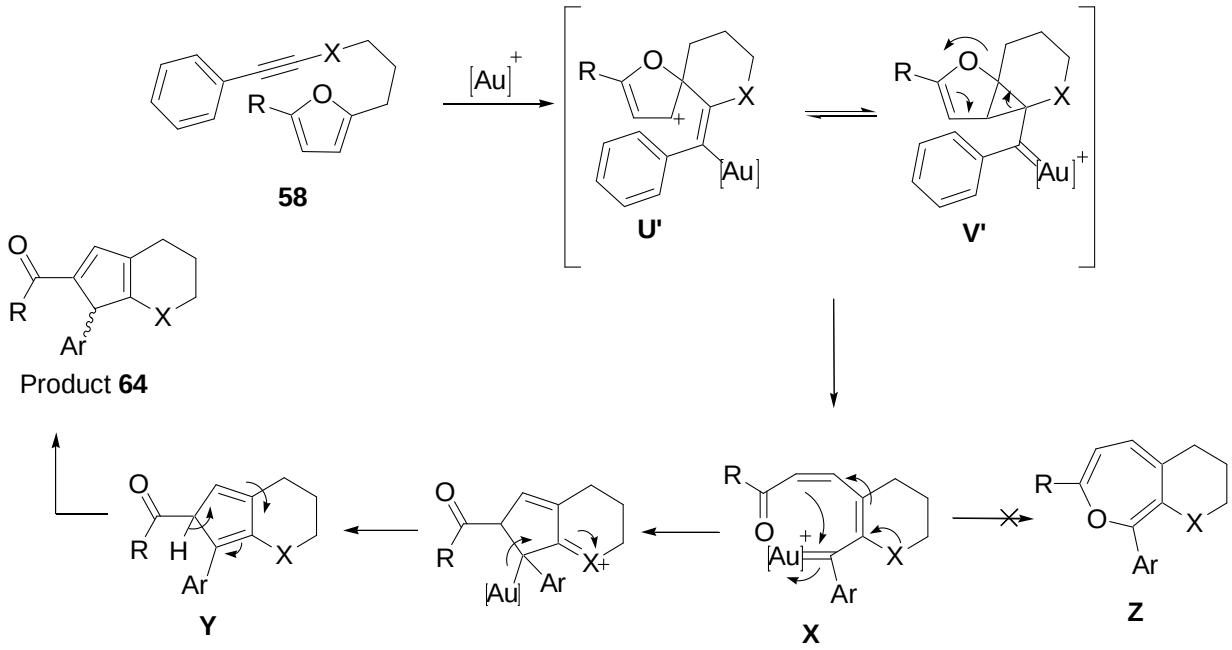
Mechanistic proposal

The mechanistic pathways for the formation of benzannulated products from aryl-ynamides **58a-58p** are fairly straightforward and proceeds through the classical *exo*-1,6-enyne cyclization mode involving a Friedel-Crafts arylation (Scheme E).



Scheme E: Proposed mechanism of the gold-catalysed benzannulation of aryl-ynamides

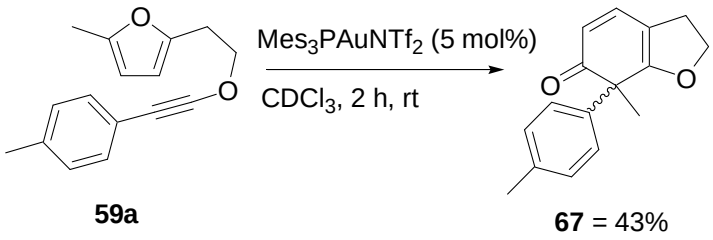
The mechanistic routes for the cyclopentadiene structures from aryl-ynamides having longer tether (1, 7-enyne) are somewhat enigmatic and is assumed to proceed through the phenol formation pathway, leading to the formation of the conjugated monocyclic carbene intermediate **X.** This intermediate undergoes electrocyclization of the C-C π bonds (an electrocyclization involving the C-O π bond would lead to the benzooxepine **Z**; the intermediate precursor for the phenol product[11b]) and eventually transforms to the final product **64** (Scheme F).



Scheme F: Plausible mechanism for the formation of cyclopentadienes in the gold-catalysed conversion of aryl-ynamides **58** with three carbon tether.

Gold catalysis with aryl-ynol ethers

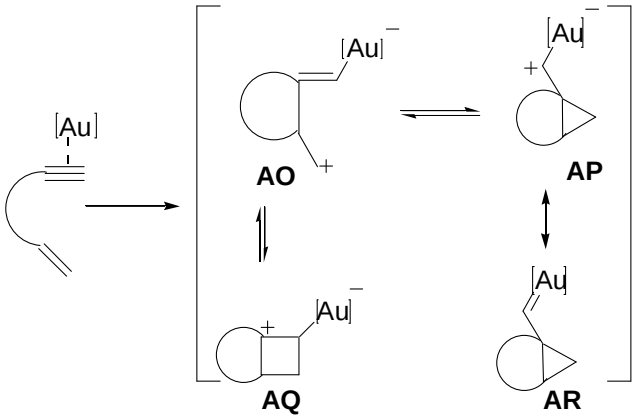
The ynol ether substrate **59a** gave rise to the cyclic conjugated ketone **67** when subjected to gold catalyst (Scheme G). But the substrates with longer tether failed to undergo any kind of cyclization and underwent water addition instead.



Scheme G: Gold catalysis of the aryl-ynol ether **59a**

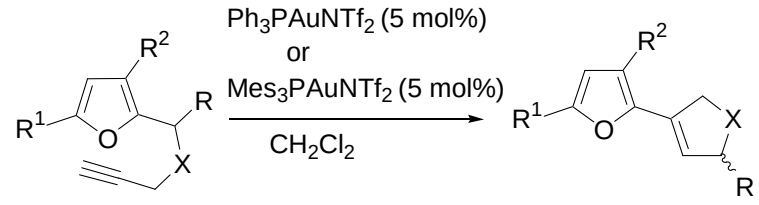
b) The second chapter of this thesis deals with the development of gold-catalyzed transformations of furan containing alkynes that prove the potential intermediacy of a cationic intermediate in these types of reactions. The actual electronic state of the intermediate in gold-catalyzed enyne cycloisomerizations is a hot spot in recent scientific reports.[20a-c] A cyclopropyl 'carbene' form of the intermediate has been used by most of the authors. But it is important to note that such a species is yet to be isolated or characterized spectroscopically. Recently Fürstner et al., proposed remarkable experimental evidence for the involvement of

the cationic form of this intermediate in gold-catalyzed cyclizations.[20a,20c] The scenario demands the consideration of the actual electronic state of the intermediate as a mesomeric/tautomeric package of different canonical forms (Scheme H).



Scheme H: Tautomeric/Mesomeric intermediates in gold-catalyzed enyne cyclization

In the context of this thesis it was found that furyl-alkynes carrying electron donating substituents in the α-position of the tether led to the formation of unexpected five-membered structures (instead of the expected phenols) when subjected to gold catalysts (Scheme I).



112/105

116/118; 20-78%

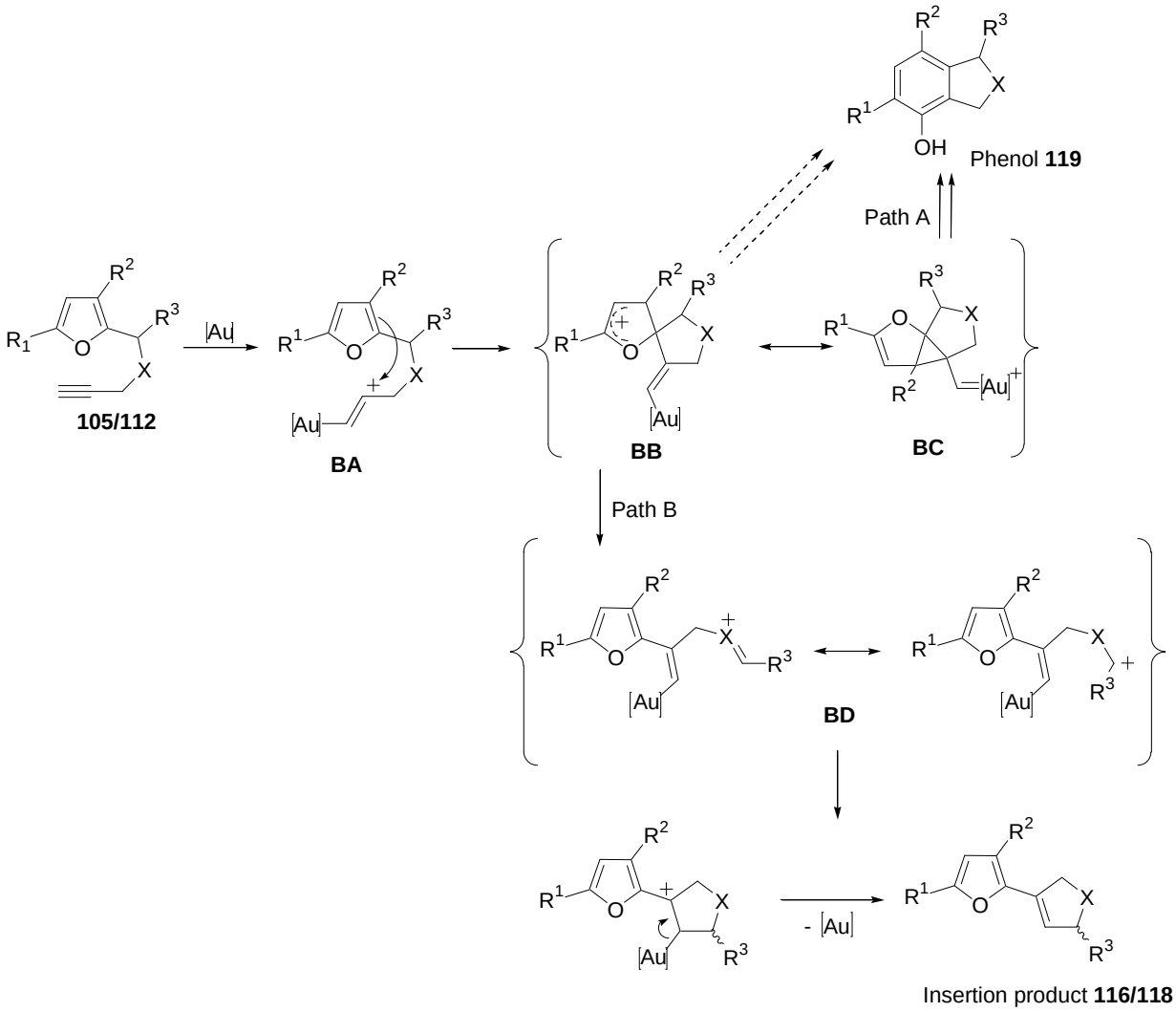
$R^1 = R^2$ = H, Me

R = alkyl, aryl, vinyl

X = NTs, O, NSO_2tBu

Scheme I: Formation of five-membered ring structures as a competing process in the phenol synthesis

The observed reactivity pattern for the substrates **116/118** was highly informative and served as an experimental evidence for the significant contribution of the cationic form of the intermediate **AO** in the mesomeric/tautomeric equilibria shown in the scheme H**.** A mechanistic proposal based on this intermediate was suggested for this hitherto unknown transformation in the gold catalysis of furyl-alkynes (Scheme J).

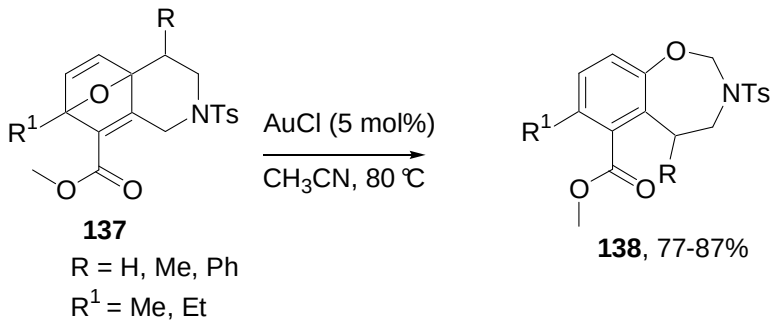


Scheme J: Proposed mechanism for the formation of the insertion product

According to this mechanism, the presence of the electron-donating substituent on the α-carbon atom of the tether opened up a new reaction path (path B) through which only the cationic form of the intermediate **BB** can proceed to. The assumption that the five-membered insertion products **116/118** were formed from the cationic form **BB** of the intermediate made sense considering the fact that the substrates having a cation stabilizing methyl substitution on the 3-C of the furan (where there is a higher accumulation of positive charge in the cation **BB**) showed increased propensity and higher reactivity to form these products. Also the reactivity showed more or less satisfactory correlation with the stabilization of the ring-opened cation **BD** brought about by the substituents on the tether (p-anisyl > cyclopropyl > phenyl > furyl > ethyl). The α-positioning of the heteroatom with the cationic carbon of **BD** was crucial for the stabilization or even existence this species as was exemplified in the case of substrate **110** where the heteroatom placed one carbon away from the cationic centre failed to deliver any insertion product.

The homogeneous gold-catalyzed conversions of furyl-allenes were investigated as a follow up to the above project. But the substrates didn't undergo any typical allenene cycloisomerization, instead formed the formal metathesis product dihydrotosylpyrrole.

c) The third chapter of this thesis elaborates the unexpected formation of *N*,*O*-acetals from oxanorbornadienes-the potential precursors for phenols- upon exposure to gold and other Lewis acids (Scheme K). AuCl was found to be the best Lewis acid catalyst under the given conditions, and $Yb(CF_3SO_3)_3$ also showed remarkable reactivity. The generality and the absence of any other products/side products confirmed that the reactions followed general acid catalysis. The observation that there is a net reversal in the connectivity of the tether in the product hinted at a complex mechanism operating in the process.

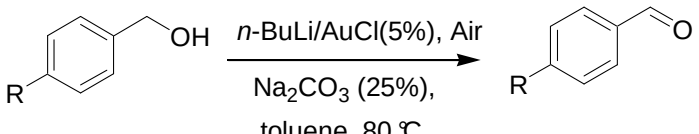


137
R = H, Me, Ph
R^1 = Me, Et

138, 77-87%

Scheme K: Gold-catalyzed formation of *N*,*O*-acetals from oxanorbornadienes

d) The fourth chapter of this thesis describes the investigations carried out on the aerobic oxidation reactions catalyzed by gold. A homogeneous catalytic system comprising of gold(I) chloride, *n*-butyl lithium and sodium carbonate was developed and was found to oxidize primary aromatic alcohols to aldehydes. The system was poor in activity towards aliphatic and secondary alcohols (Scheme L).



R = H,OMe, CH_3

85-95% (GC)
8-16 h

Scheme L: Gold/*n*-BuLi system for the oxidation of primary aromatic alcohols

2. Experimental and Spectroscopic data

2.1 General

2.1.1 Chemicals and Solvents

The chemicals were purchased from Aldrich, Fluka, Acros, Strem, Lancaster and used without further purification. The solvents for column chromatography were distilled before use. Air and moisture free solvents for reactions were obtained by refluxion in suitable drying agents and handling under inert atmosphere.

2.1.2 Chromatography

2.1.2.1 Thin-layer chromatography

Thin-layer aluminium foils from Merck (Silica gel 60 F_{254}) were used. UV lamp and different staining agents based on anisaldehyde, cerium, potassium permanganate, and vanillin were used for detection.

2.1.2.2 Preparative column chromatography

For preparative column chromatography silica gel -Macherey-Nagel Gmbh & Co. KG (MN silica gel 60M: 0.040-0.063 particle size, 230-400 mesh ASTM) was used as the stationary phase. Solvents like ethyl acetate, petether, dichloromethane, and methanol were used as the mobile phase.

2.1.3 Analysis

2.1.3.1 Melting point determination

The melting points were determined using a melting point apparatus from Büchi (SMP-20) and were given uncorrected

2.1.3.2 Infrared spectroscopy

Infrared spectra were recorded in a Bruker machine as pure substance in solution or on a diamond surface. The absorptions were given in cm^{-1}

2.1.3.3 Nuclear magnetic resonance spectroscopy (NMR)

NMR spectra were measured in Bruker devices at different frequencies (250/62.9 MHz, 300/75.5 MHz, and 500/126 MHz) and in suitable solvents with TMS calibration. The chemical shifts (δ) are given in ppm, and coupling constants (*J*) in Hertz (Hz). The signal multiplicity is given as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin) and multiplet (m) etc. The ^{13}C-signals are abbreviated as, s ($C_{quart)}$, d (CH), t (CH_2), and q (CH_3). These multiplicities were based on DEPT-90 and DEPT-135 spectra. 2-D NMR techniques used were DQF-COSY, HMQC and HSBC.

2.1.3.4 Mass spectroscopy

The mass spectra were taken in Finnigan MAT (MAT95) and Bruker Daltonics (MicroTOFQ) machines. The different methods are given and the intensity of the signals are given in percentage (%) based on the base peak.

2.1.3.5 Elemental analysis

Elemental analysis was done in a Carlo Erba elemental analyzer (1106).

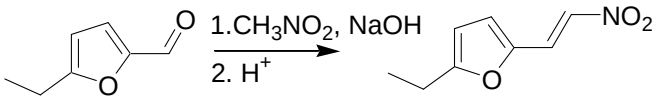
2.1.3.6 X-ray crystallography

Crystal data were derived using a SIEMENS P4 or a NICOLET P3 (Uni Stuttgart) and a Bruker APEX (Uni Heidelberg). The programmes used were Sadabs, Shelxs, Shelxl-97, x-scans, SHELXTL and P3/PC data collection system.

2.2 Gold catalyzed conversions of Furan containing Aryl-Ynamides and Aryl-Ynol Ethers

A. Preparation of the substrates

1. **2-Ethyl-5-(2-nitro-vinyl)-furan**[100] (**38c**/SP123)



124 mg (1 mmol, 1 eq) of 5-ethyl furfural was added to an ice-cold solution of 1ml methyl alcohol and 0.13 ml of nitro methane (2 mmol, 2 eq). Aqueous 1M NaOH (2.5 eq) was added followed by 4 ml of ice water. The reaction mixture was stirred for 20 min at 0 °C and then slowly added to 8 M HCl (1.6 eq) and was stirred for 1.5 h at room temperature. The organic part was extracted with dichloromethane and then dried over $MgSO_4$. Column chromatography (PE:EtOAc) furnished 144 mg (84 %) of the nitroalkene product as yellow crystals.

R_f (PE:EtOAc, 1:1) = 0.44

IR (neat): $\tilde{\nu}$ = 3129, 2992, 2919, 1670, 1552, 1520, 1498, 1070, 970, 826, 821, 725, 558 cm^{-1}

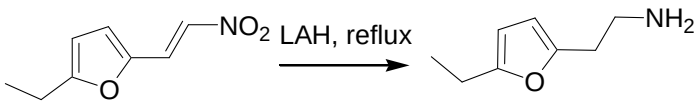
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.28 (t, J = 7.6 Hz, 3H), 2.65 (q, J = 7.6 Hz, 2H), 6.24 (d, J = 3.5 Hz, 1H), 6.82 (d, J = 3.5 Hz, 1H), 7.44 (d, J = 13.2 Hz, 1H), 7.72 (d, J = 13.2 Hz, 1H)

^{13}C-NMR (62.89 MHz, $CDCl_3$): δ = 11.74 (q), 21.81 (t), 108.7 (d), 122.0 (d), 125.6 (d), 133.3 (d), 145.1 (s), 163.8 (s)

MS (EI): m/z (%) = 167 (100) (M^+), 138 (35), 124 (60), 105 (76), 83 (60), 77 (40), 55 (30).

Anal. Calcd. For $C_8H_9NO_3$: C 57.48, H 5.43, N 8.38; found: C 57.70, H 5.49, N 8.27.

2. **2-(5-Ethyl-furan-2-yl)-ethylamine** (**39c**/SP126)



3g (18 mmol, 1 eq) of **38c** was dissolved in 50ml of anhy.ether. The solution was slowly added to 2g (54 mmol, 3 eq) of $LiAlH_4$ taken in 150ml of anhy.ether under nitrogen at 0 °C. The reaction mixture was stirred for 1h at rt and then refluxed for 18h. Cooled to 0 °C and the reaction was quenched with 10ml of NH_4Cl. The solid was filtered out and the organic layer was extracted with ether. Dried over $MgSO_4$ and column chromatography (PE:EtOAc, 1% NEt_3) furnished 1.52g (64 %) of the pure amine as a light brown oil

R_f (PE:EtOAc, 1:1) = 0.05

IR (film): $\tilde{\nu}$ = 2970, 2937, 1566, 1464, 1325, 1211, 1011, 934, 777 cm^{-1}

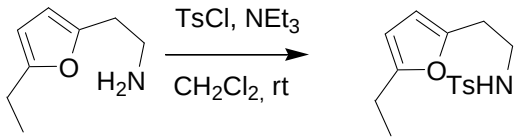
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, J = 8.0 Hz, 3H) 1.43 (bs, 1H), 2.60 (q, J = 8.0 Hz, 2H), 2.72 (t, J = 6.8 Hz, 2H), 2.94 (t, J = 7.24 Hz, 2H), 5.86 (d, J = 3.2 Hz, 1H), 5.93 (d, J= 3.2 Hz, 1H)

^{13}C-NMR (75.46 MHz, $CDCl_3$): δ = 12.13 (q), 21.34 (t), 32.50 (t), 40.83 (t), 104.2 (t), 106.3 (t), 151.9 (s), 156.5 (s)

MS (EI): m/z (%) = 140 (10) (M+1), 123 (100)

HRMS (ESI): $C_8H_{13}NO$: Calcd: 140.1079; found: 140.1070

3. **2-(5-ethylfuran-2-yl)-N-tosylethanamine** (**40d**/SP127)



1.3 g (9.4 mmol, 1 eq) of the amine **39c** was dissolved in 20ml of dichloromethane. 1.4ml

(10.4 mmol, 1.1 eq) of triethyl amine and 1.8g (9.4 mmol, 1 eq) of tosyl chloride were added to this solution. The reaction mixture was stirred at rt for 24h.The reaction was quenched with 10ml of water, and the organic layer was extracted with dichloromethane. Dried over $MgSO_4$. Column chromatography (PE:EtOAc) furnished 1.87g (70%) of the product as yellow oil.

R_f (PE:EtOAc, 4:1) = 0.30

IR (film): $\tilde{\nu}$ = 3282, 2971, 2937, 1566, 1420, 1322, 1153, 1092, 1009, 795, 660, 549 cm^{-1}

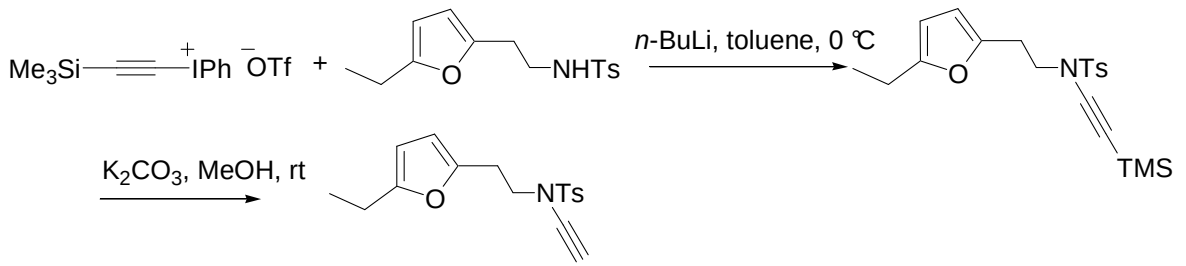
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, J = 7.3 Hz, 3H), 2.41 (s, 3H), 2.53 (q, J = 8.0 Hz, 2H), 2.71 (t, J = 7.0 Hz, 2H), 3.20 (q, J = 6.8 Hz, 2H), 4.71 (t, J = 6.9 Hz , 1H), 5.82 (d, J = 3.2 Hz, 1H), 5.88 (d, J = 3.2 Hz, 1H), 7.30 (d, J = 8.1Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H)

^{13}C-NMR (75.46 MHz, $CDCl_3$): δ = 12.09 (q), 21.30 (t), 21.54 (q), 28.31(t), 41.77 (t), 104.4 (d), 107.4 (d), 127.1 (d, 2C), 129.7 (d, 2C), 136.9 (s), 143.4(s), 149.7 (s), 157.1 (s)

MS (EI): m/z (%) = 293 (40) (M^+), 184 (30), 155 (95), 122 (70), 109 (100), 91 (60)

Anal. Calcd. For $C_{15}H_{19}NSO_3$: C 61.41; H 6.53; N 4.77; found: C 61.35; H 6.55; N 4.92

4. **N-[2-(5-Ethyl-furan-2-yl)-ethyl]-N-ethynyl-4-methyl-benzenesulfonamide**[46] (**42d**/SP620A)



2.65g (9 mmol, 1 eq) of the amine **40d** was dissolved in 70ml of dry toluene under nitrogen.The solution was cooled to 0 °C and 4ml (10 mmol, 1.1 eq) *n*-Butyl lithium (2.5M solution in hexane) was added drop by drop. The reaction mixture was stirred for 1h at the same temperature. 4.9g (10.8 mmol, 1.2 eq) of trimethylsilylethynyliodonium triflate was added in portions and the reaction mixture was warmed to room temperature for 36h. The

solvent was removed by vacuum and the crude product was passed through a pad of silica gel to remove all residual impurities. The crude TMS protected alkyne obtained as brownish-yellow oil (2.8g, 7.2 mmol) was dissolved in 20ml of methanol and 1.26g (9 mmol, 1.2 eq) of K_2CO_3 was added in portions. The suspension was stirred at room temperature for 1h after which the solvent was removed and column chromatography done (PE:EtOAc). 1.2 (42%, overall yield) of the pure product was isolated as an yellow oil.

R_f (PE:EtOAc, 4:1) = 0.50

IR (film): $\tilde{\nu}$ = 3296, 2972, 2936, 2135, 1698, 1596, 1566, 1453, 1362, 1166, 1090, 950, 683 cm^{-1}

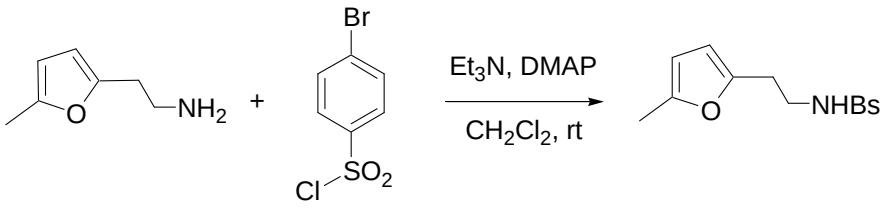
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.19 (t, J = 7.6Hz, 3H), 2.44 (s, 3H), 2.57 (q, J = 7.6Hz, 2H), 2.75 (s, 1H), 2.92 (t, J = 7.5Hz, 2H), 3.58 (t, J = 7.6Hz, 2H), 5.81-5.84 (m, 1H), 5.92 (d, J = 3.1Hz, 1H), 7.33 (d, J = 8.3Hz, 2H), 7.78 (d, J = 8.3Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 12.14 (q), 21.29 (t), 21.67 (q), 26.99 (t), 49.78 (t), 59.48 (d), 75.66 (s), 104.4 (d), 107.3 (d), 127.6 (d, 2C), 129.8 (d, 2C), 134.5 (s), 144.7 (s), 149.0 (s), 156.9 (s)

MS (APCI): *m/z* (%): 318 (100) $(M+1)^+$, 123 (24)

HRMS (APCI): $C_{17}H_{19}NO_3S$: Calcd: 317.1086 found: 317.1079

5. **4-Bromo-N-[2-(5-methyl-furan-2-yl)-ethyl]-benzenesulfonamide** (**40c**/SP605)



1.3 g (9.4 mmol, 1 eq) of 2-(5-Methyl-furan-2-yl)-ethylamine[10m] was dissolved in 20ml of dichloromethane. Cooled to 0 °C and 1.4ml (10.4 mmol, 1.1 eq) of triethyl amine, a pinch of DMAP and 2.6g (10.34 mmol, 1.1 eq) of brosyl chloride were added to this solution. The

reaction mixture was stirred at rt for 12h.The reaction was quenched with 10ml of water, and the organic layer was extracted with dichloromethane. Dried over $MgSO_4$. Column chromatography (PE:EtOAc) gave 2.6g (72%) of the product as a pale-yellow solid.

M.P: 56-58 °C

R_f (PE:EtOAc, 1:1) = 0.45

IR (film): $\tilde{\nu}$ = 3275, 2918, 1573, 1471, 1388, 1320, 1155, 1065, 1009, 927, 821, 783, 738, 655, 602 cm^{-1}

^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 2.20 (s, 3H), 2.73 (t, J = 6.5Hz, 2H), 3.23 (q, J = 6.4Hz, 2H), 4.61 (t, J = 6.3Hz, 1H), 5.80-5.84 (m, 1H), 5.88 (d, J = 3.0Hz, 1H), 7.59-7.72 (m, 4H)

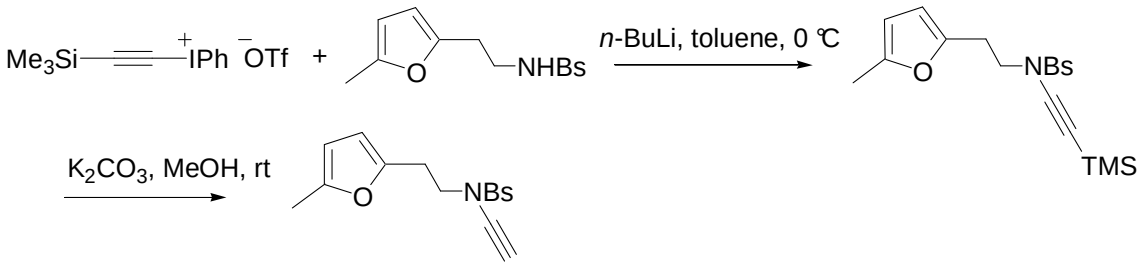
^{13}C-NMR ($CDCl_3$, 62.89 MHz): 13.49 (q), 28.30 (t), 41.79 (t), 106.1 (d), 107.9 (d), 127.6 (s), 128.6 (d, 2C), 132.3 (d, 2C), 139.0 (s), 149.5 (s), 151.5 (s)

MS (APCI): *m/z* (%): 344 (7) (M+1), 109 (100)

HRMS (APCI): $C_{13}H_{14}BrNO_3S$: Calcd: 342.9878; found: 342.9876

Anal. Calcd. For $C_{13}H_{14}BrNO_3S$: C 45.36, H 4.10, N 4.07; found: C 45.49, H 4.13, N 4.04

6. **4-Bromo-N-ethynyl-N-[2-(5-methyl-furan-2-yl)-ethyl]-benzenesulfonamide** (**42c**/SP648)



4g (11.6 mmol, 1 eq) of amine **40c** was dissolved in 100ml of dry toluene under nitrogen. The solution was cooled to 0 °C and *n*-Butyl lithium was added drop by drop. The reaction

mixture was stirred for 1h at the same temperature.6.2g (13.76mol, 1.2 eq) of the trimethylsilylethynyl iodonium triflate was added in portions and the reaction mixture was warmed to room temperature for 36h. The solvent was removed by vacuum and the product was passed through a short pad of silica gel. The crude TMS protected alkyne thus obtained (4g, 9 mmol) was dissolved in 20ml of methanol and 1.5g (10.8 mmol, 1.2 eq) of K_2CO_3 was added in portions. The suspension was stirred at room temperature for 1h after which the solvent was removed and column chromatography done (PE:EtOAc). 2.8g (65%, overall yield) of the pure product was isolated as a colourless solid.

M.P: 70-72 °C

R_f (PE:EtOAc, 4:1) = 0.53

IR (film): $\tilde{\nu}$ = 3296, 2137, 1573, 1367, 1169, 1068, 965, 785, 744, 664 cm^{-1}

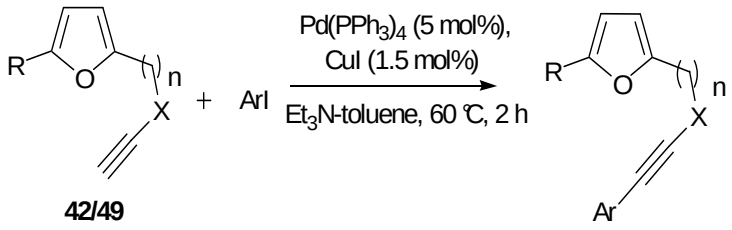
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.78 (s, 1H), 2.92 (t, J = 7.5Hz, 2H), 3.60 (t, J = 7.5Hz, 2H), 5.79-5.82 (m, 1H), 5.90 (d, J = 3.1Hz, 1H), 7.64-7.76 (m, 4H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.59 (q), 26.97 (t), 49.96 (t), 60.00 (d), 75.02 (s), 106.1 (d), 107.7 (d), 128.9 (d, 2C), 132.5 (d, 2C), 136.4 (s), 148.8 (s), 151.2 (s), 161.1 (s)

MS (ESI (+)): *m/z* (%): 390 (100) $(M+Na)^+$, 368 $(M+1)^+$, 186 (16)

HRMS (ESI (+)): $C_{15}H_{14}BrNO_3S$: Calcd: 366.9878; found: 366.9885

A1. General procedure for the Sonogashira couplings



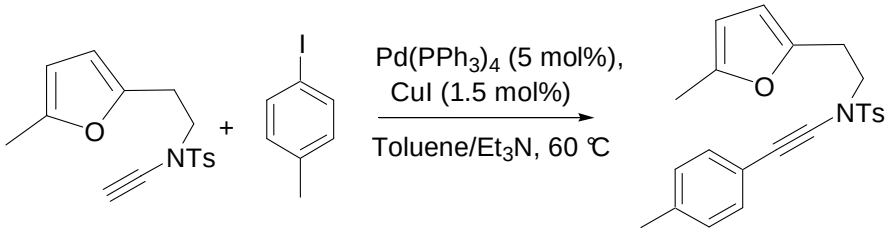
42/49

n = 2, 3
R = H, Me, Et
X = NTs, NBs

58

1 mmol (1 eq) of the ynamide[45e] and 1.1 mmol of the aryl iodide was added to a mixture of 2ml dry toluene and 2ml triethyl amine. 5 mol% of tetrakistriphenylphosphine palladium (0) was added and the mixture was degassed. Stirred for 10 minutes at room temperature and 1.5 mol% copper (I) iodide was added. The reaction mixture was heated at 60 °C for 2h. The solvent was removed under vacuum and the crude product was purified over flash column chromatography (PE:EtOAc).

7. **4-Methyl-N-[2-(5-methyl-furan-2-yl)-ethyl]-N-p-tolylethynyl-benzenesulfonamide** (**58a**/SP562/SP635, 31%, pale brown oil)



R_f (PE:EtOAc, 4:1) = 0.44

IR (film): $\tilde{\nu}$ = 2922, 2235, 1365, 1168, 903, 722, 649 cm^{-1}

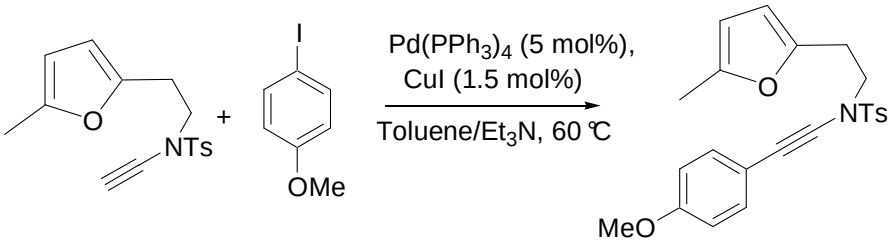
^{1}H-NMR (CD_2Cl_2, 250 MHz): δ = 2.20 (s, 3H), 2.34 (s, 3H), 2.44 (s, 3H), 2.96 (t, J = 7.6Hz, 2H), 3.65 (t, J = 7.6Hz, 2H), 5.83-5.85 (m, 1H), 5.94 (d, J = 3.2Hz, 1H), 7.10 (dd, J = 8.6, 0.7Hz, 2H), 7.27 (d, J = 8.2Hz, 2H), 7.33 (dd, J = 8.6, 0.7Hz, 2H), 7.81 (d, J = 8.3Hz, 2H)

^{13}C-NMR ($CDCl_3$, 62.89 MHz): 13.47 (q), 21.45 (q), 21.65 (q), 27.18 (t), 50.22 (t), 70.94 (s), 81.18 (s), 106.1 (d), 107.5 (d), 119.6 (s), 127.6 (d, 2C), 127.8 (d, 2C), 129.7 (d, 2C), 131.5 (d, 2C), 134.6 (s), 138.0 (s), 144.5 (s), 149.3 (s), 151.2 (s)

MS (EI (+)): *m/z* (%): 394 $(M+1)^+$ (14), 393 (M^+) (41), 246 (55), 214 (57), 108 (96), 91 (100)

HRMS (ESI (+)): $C_{23}H_{23}NO_3S$: Calcd: 393.1399; found: 394.1395

8. **N-(4-Methoxy-phenylethynyl)-4-methyl-N-[2-(5-methyl-furan-2-yl)-ethyl]-benzenesulfonamide** (**58b**/SP590A**,** 31%, brown oil)



R_f (PE:EtOAc, 4:1) = 0.42

IR (film): $\tilde{\nu}$ = 2923, 2235, 1605, 1511, 1363, 1247, 1167, 904, 721 cm^{-1}

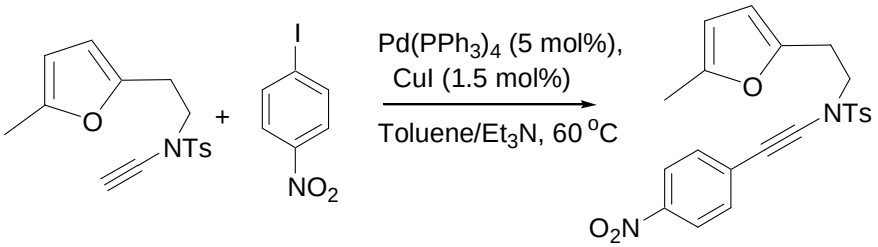
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.45 (s, 3H), 2.96 (t, J = 7.8Hz, 2H), 3.65 (t, J = 7.8Hz, 2H), 3.81 (s, 3H), 5.81-5.83 (m, 1H), 5.92 (d, J = 3.2Hz, 1H), 6.8 (d, J = 8.8Hz, 2H), 7.29-7.35 (m, 4H), 7.81 (d, J = 8.4Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.59 (q), 21.71 (q), 27.28 (t), 29.48 (q); 50.40 (t), 55.35 (q), 70.71 (s), 80.5 (s), 106.1 (d), 107.5 (d), 113.8 (d, 2C), 114.7 (s), 127.6 (d, 2C), 129.6 (d, 2C), 133.4 (d, 2C), 144.5 (s), 149.4 (s), 151.1 (s), 159.6 (s)

MS (ESI (+)): *m/z* (%): 432 (100) $(M+Na)^+$

HRMS (EI (+)): $C_{23}H_{23}NO_4S$: Calcd: 409.1348; found: 409.1349

9. **4-Methyl-N-[2-(5-methyl-furan-2-yl)-ethyl]-N-(4-nitro-phenylethynyl)-benzenesulfonamide** (**58j/** SP590B, 43%, brown oil)



R_f (PE:EtOAc, 4:1) = 0.41

IR (film): $\tilde{\nu}$ = 2923, 2225, 1593, 1514, 1368, 1337, 1167, 1090, 852, 748, 685 cm^{-1}

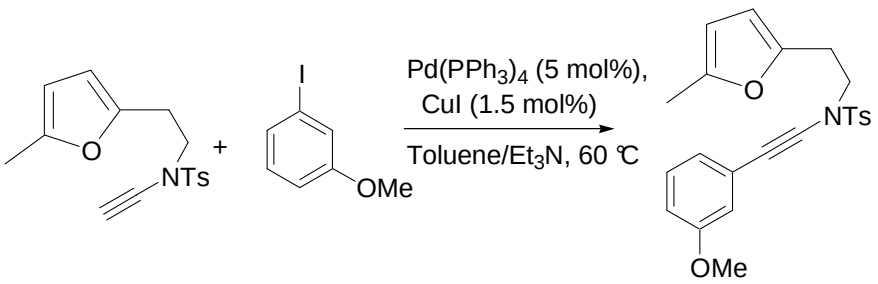
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.42 (s, 3H), 2.97 (t, J = 7.5Hz, 2H), 3.72 (t, J = 7.5Hz, 2H), 5.82-5.85 (m, 1H), 5.92 (d, J = 3.2Hz, 1H), 7.36 (d, J = 8.4Hz, 2H), 7.43 (d, J = 8.8Hz, 2H), 7.81 (d, J = 8.3Hz, 2H), 8.16 (d, J = 8.8Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.53 (q), 21.75 (q), 27.41 (t), 50.27 (t), 70.79 (s), 88.60 (s), 106.2 (d), 107.8 (d), 123.6 (d, 2C), 127.7 (d, 2C), 129.9 (d, 2C), 130.2 (s), 130.9 (d, 2C), 134.5 (s), 145.1 (s), 146.2 (s), 148.9 (s), 151.2 (s)

MS (ESI (+)): *m/z* (%): 425 (100) $(M+H)^+$, 155 (25)

HRMS (EI (+)):$C_{22}H_{20}N_2O_5S$: Calcd: 425.1179; found: 425.1183

10. **N-(3-Methoxy-phenylethynyl)-4-methyl-N-[2-(5-methyl-furan-2-yl)-ethyl]-benzenesulfonamide** (**58i/**SP590C, 40%, brown oil)



R_f (PE:EtOAc, 4:1) = 0.43

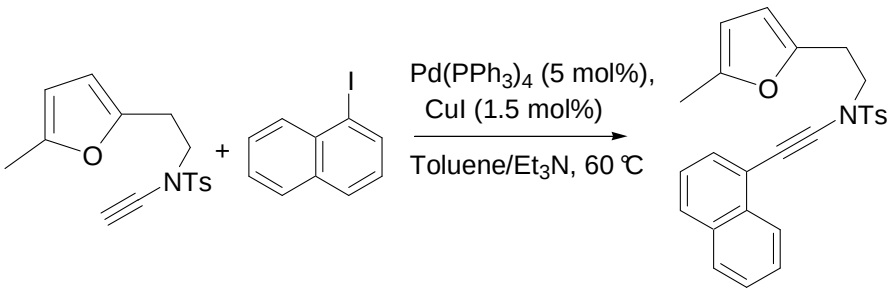
IR (film): $\tilde{\nu}$ = 2921, 2549, 2236, 1365, 1168, 873, 785 cm^{-1}

^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.21 (s, 3H), 2.43 (s, 3H), 2.99 (t, J = 7.5Hz, 2H), 3.67 (t, J = 7.6Hz, 2H), 3.81 (s, 3H), 5.81-5.83 (m, 1H), 5.93 (d, J = 3.2H, 1H), 76.81-6.95 (m, 3H), 7.19 (t, J = 8.1Hz, 1H), 7.35 (d, J = 8.4Hz, 2H), 7.82 (d, J = 8.3Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.55 (q), 21.76 (q), 27.35 (t), 50.21 (t), 55.29 (q), 106.1 (d), 107.6 (d), 114.1 (d), 116.3 (d), 123.9 (d), 127.7 (d, 2C), 129.3 (d), 129.8 (d, 2C), 134.6 (s), 144.7 (s), 149.2 (s), 151.1 (s), 159.3 (s)

MS (ESI (+)): *m/z* (%):432 (100) $(M+Na)^+$
HRMS (EI (+)): $C_{23}H_{23}NO_4S$: Calcd: 409.1345; found: 409.1348

11. **4-Methyl-N-[2-(5-methyl-furan-2-yl)-ethyl]-N-naphthalen-1-ylethynyl-benzenesulfonamide** (**58c**/SP596A, 29%, yellow oil)



R_f (PE:EtOAc, 4:1) = 0.33

IR (film): $\tilde{\nu}$ = 3057, 2921, 2230, 1364, 1167, 1090 cm^{-1}

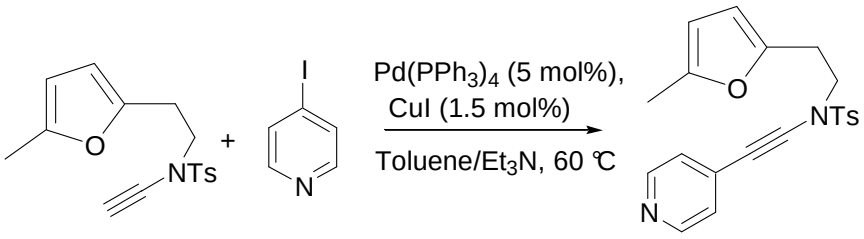
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.44 (s, 3H), 3.06 (t, J = 7.6Hz, 2H), 3.78 (t, J = 7.6Hz, 2H), 5.82-5.85 (m, 1H), 5.96 (d, J = 3.1Hz, 1H), 7.33 (d, J = 8.3Hz, 2H), 7.38-7.42 (m, 1H), 7.50-7.58 (m, 3H), 7.79 (d, J = 8.3Hz, 2H), 7.86 (d, J = 8.4Hz, 2H), 8.18-8.22 (m, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.54 (q), 21.74 (q), 27.31 (t), 50.37 (t), 69.5 (s), 86.6 (s), 106.2 (d), 107.6 (d), 120.5 (s), 125.1 (d), 126.2 (d), 126.3 (d), 126.7 (d), 127.7 (d, 2C), 128.2 (d), 129.7 (d), 129.8 (d, 2C), 130.9 (d), 133.1 (s), 133.2 (s), 134.7 (s), 144.7 (s), 149.2 (s), 151.2 (s)

MS (ESI (+)): *m/z* (%): 452 (100) $(M+Na)^+$

HRMS (ESI (+)): $C_{26}H_{23}NO_3S$: Calcd: 430.1469; found: 430.1479

12. **4-Methyl-N-[2-(5-methyl-furan-2-yl)-ethyl]-N-pyridin-4-ylethynyl-benzenesulfonamide** (**58k**/SP596B, 34%, dark oil)



R_f (PE:EtOAc, 4:1) = 0.11

IR (film): $\tilde{\nu}$ = 2922, 2229, 1592, 1365, 1166, 1088, 815, 779, 676 cm^{-1}

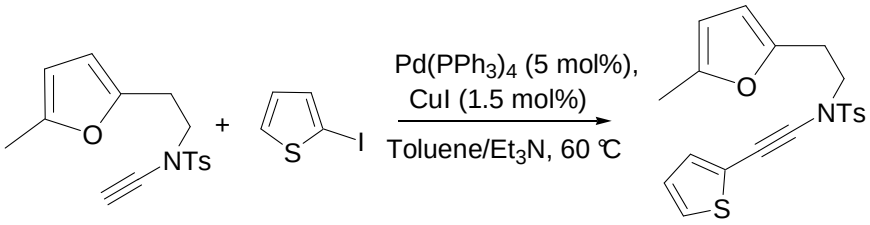
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.45 (s, 3H), 2.98 (t, J = 7.6Hz, 2H), 3.70 (t, J = 7.6Hz, 2H), 5.81-5.83 (m, 1H), 5.93 (d, J = 3.1Hz, 1H), 7.18 (dd, J = 6.1, 1.4Hz, 2H), 7.35 (d, J = 8.3Hz, 2H), 7.81 (d, J = 8.3Hz, 2H), 8.51 (dd, J = 6.1, 1.5Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.49 (q), 21.75 (q), 27.47 (t), 50.26 (t), 70.82 (s), 88.03 (s), 106.3 (d), 107.8 (d), 123.6 (d, 2C), 127.6 (d, 2C), 129.9 (d, 2C), 130.3 (s), 130.9 (d, 2C), 134.5 (s), 145.2 (s), 146.3 (s), 148.8 (s), 151.3 (s)

MS (EI (+)): *m/z* (%): 380 (15) (M^+), 225 (35), 109 (50), 95 (100)

HRMS (ESI (+)): $C_{21}H_{20}N_2O_3S$: Calcd: 380.1195; found: 380.1195

13. **4-Methyl-N-[2-(5-methyl-furan-2-yl)-ethyl]-N-thiophen-2-ylethynyl-benzenesulfonamide** (**58e**/SP596C, 41%, yellow oil)



R_f (PE:EtOAc, 4:1) = 0.26

IR (film): $\tilde{\nu}$ = 2922, 2227, 1366, 1167, 1090, 709, 662, 547 cm^{-1}

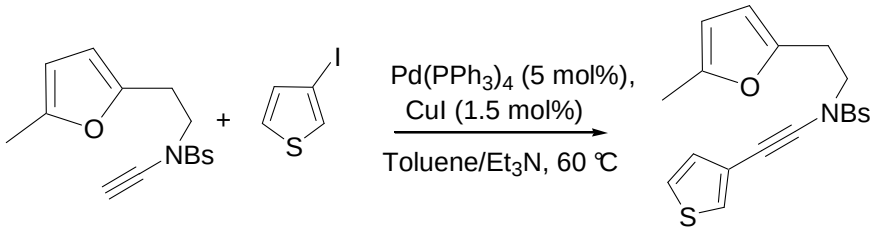
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.45 (s, 3H), 2.94 (t, J = 7.6Hz, 2H), 3.67 (t, J = 7.6Hz, 2H), 5.81-5.83 (m, 1H), 5.92 (d, J = 3.2Hz, 1H), 6.95-6.98 (m, 1H), 7.17 (dd, J = 3.7, 1.1Hz, 1H), 7.26-7.28 (m, 1H), 7.35 (d, J = 8.3Hz, 2H), 7.80 (d, J = 8.4Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.47 (q), 21.69 (q), 27.26 (t), 50.35 (t), 64.24 (s), 85.46 (s), 106.1 (d), 107.6 (d), 122.8 (s), 127.0 (d), 127.6 (d, 2C), 127.8 (d), 129.8 (d, 2C), 133.1 (d), 134.5 (s), 144.7 (s), 149.2 (s), 151.1(s)

MS (EI (+)): *m/z* (%): 386 (52) $(M+H)^+$, 231 (100)

HRMS (ESI (+)): $C_{20}H_{19}NO_3S_2$: Calcd: 386.0886; found: 386.0879

14. **4-Bromo-N-[2-(5-methyl-furan-2-yl)-ethyl]-N-thiophen-2-ylethynyl-benzenesulfonamide** (**58h**/SP611, 27%, brown oil)



R_f (PE:EtOAc, 4:1) = 0.62

IR (film): $\tilde{\nu}$ = 3106, 2920, 2238, 1572, 1367, 1169, 1068, 901, 863, 782, 744, 592, 569 cm^{-1}

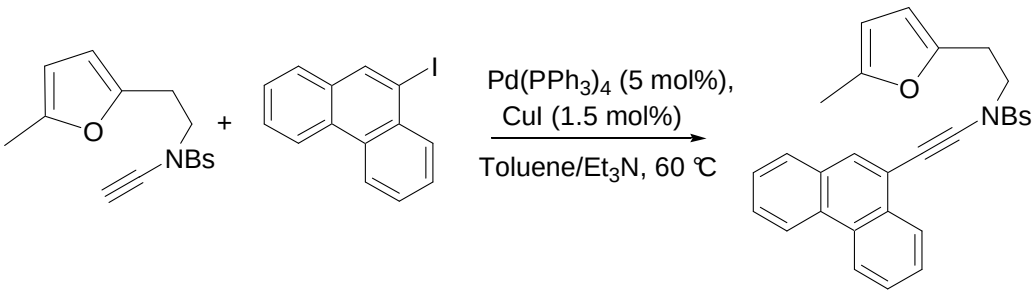
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.98 (t, J = 7.4Hz, 2H), 3.68 (t, J = 7.4Hz, 2H), 5.81-5.83 (m, 1H), 5.92 (d, J = 3.1Hz, 1H), 7.05 (dd, J = 5.0, 1.0Hz, 1H), 7.25-7.29 (m, 1H), 7.41 (dd, J = 3.0, 1.1Hz, 1H), 7.68 (d, J = 8.7Hz, 2H), 7.76 (d, J = 8.7Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.54 (q), 27.17 (t), 50.38 (t), 66.30 (s), 80.58 (s), 106.1 (d), 107.7 (d), 121.1 (s), 125.3(d), 128.8 (s), 129.0 (d, 2C), 129.3 (d), 130.3 (d), 132.5 (d, 2C), 136.6 (s), 149.0 (s), 151.3 (s)

MS (APCI): *m/z* (%): 451 (100) $(M+H)^+$, 450 (98) (M^+), 231 (99)

HRMS (APCI): $C_{19}H_{16}BrNO_3S_2$: Calcd: 448.9879; found: 449.9845

15. **4-Bromo-N-[2-(5-methyl-furan-2-yl)-ethyl]-N-phenanthren-9-ylethynyl-benzenesulfonamide** (**58p**/SP612, 31%, sticky brown oil)



R_f (PE:EtOAc, 4:1) = 0.42

IR (film): $\tilde{\nu}$ = 3061, 2921, 2230, 1572, 1365, 1168, 1067, 906, 742, 724, 567 cm^{-1}

^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.22 (s, 3H), 7.40 (t, J = 7.4Hz, 2H), 3.83 (t, J = 7.4Hz, 2H), 5.81-5.83 (m, 1H), 5.98 (d, J = 3.1Hz, 1H), 7.56-7.73 (m, 6H), 7.80-7.85 (m, 3H), 7.88 (s, 1H), 8.24-8.28 (m, 1H), 8.62-8.71 (m, 2H)

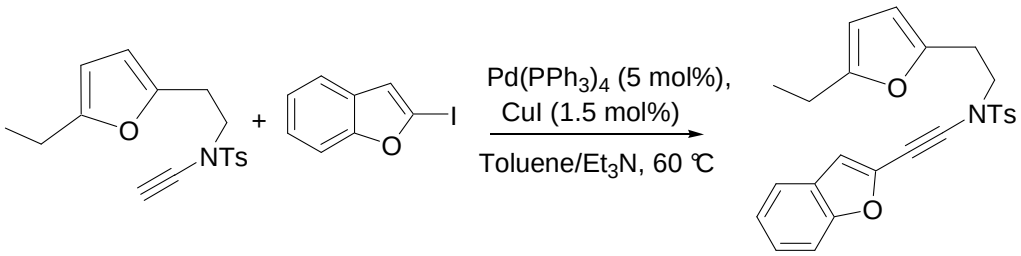
^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.61 (q), 27.36 (t), 50.54 (t), 70.02 (s), 85.37 (s), 106.2 (d), 107.9 (d), 118.9 (s), 122.6 (d), 122.9 (d), 126.7 (d), 127.0 (d), 127.1 (d), 127.2 (d), 127.4 (d),

128.3 (d), 128.9 (s), 129.1 (d, 2C), 130.0 (s), 131.1 (s), 131.3 (d), 132.5 (d, 2C), 136.5 (s), 149.0 (s), 151.3 (s)

MS (APCI): *m/z* (%): 544 (8) (M^+), 325 (100), 282 (42)

HRMS (APCI): $C_{29}H_{22}BrNO_3S$: Calcd: 544.0579; found: 544.0573

16. **N-Benzofuran-2-ylethynyl-N-[2-(5-ethyl-furan-2-yl)-ethyl]-4-methyl-benzenesulfonamide** (**58n**/SP624, 20%, brown oil)



R_f (PE:EtOAc, 4:1) = 0.32

IR (film): $\tilde{\nu}$ = 2253, 1368, 1168, 1090, 902, 723, 649 cm^{-1}

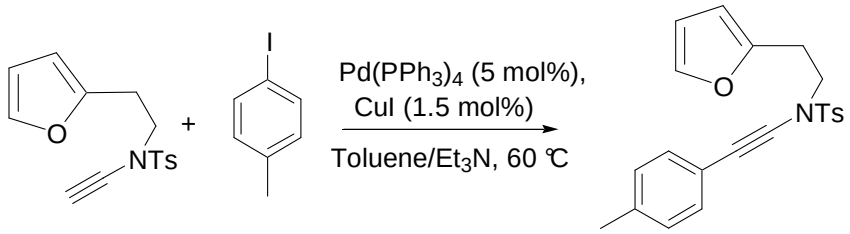
^{1}H-NMR (CD_2Cl_2, 300 MHz): δ = 1.16 (t, J = 7.6Hz, 3H), 2.46 (s, 3H), 2.55 (q, J = 7.6Hz, 2H), 2.96 (t, J = 7.4Hz, 2H), 3.70 (t, J = 7.4Hz, 2H), 5.84-5.86 (m, 1H), 5.96 (d, J = 3.1Hz, 1H), 6.96 (d, J = 1.1Hz, 1H), 7.22-7.47 (m, 5H), 7.56 (d, J = 7.7Hz, 1H), 7.80 (d, J = 8.3Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 12.09 (q), 21.33 (t), 21.78 (q), 27.27 (t), 50.41 (t), 62.17 (s), 87.5 (s), 104.5 (d), 107.3 (s), 107.6 (d), 111.1 (d), 113.1 (d), 121.1 (d), 123.2 (d), 125.6 (d), 127.7 (d, 2C), 129.7 (s), 130.0 (d, 2C), 134.5 (s), 135.3 (s), 145.0 (s), 148.8 (s), 157.1 (s)

MS (APCI): *m/z* (%): 434 $(M+1)^+$ (34), 279 (100), 222 (31)

HRMS (APCI): $C_{24}H_{23}NO_4S$: Calcd: 434.1428; found: 434.1422

17. **N-(2-Furan-2-yl-ethyl)-4-methyl-N-p-tolylethynyl-benzenesulfonamide** (**58q**/SP580, 41%, brown oil)



R_f (PE:EtOAc, 8:1) = 0.34

IR (film): $\tilde{\nu}$ = 2922, 2235, 1597, 1363, 1167, 1090, 814, 735, 664 cm^{-1}

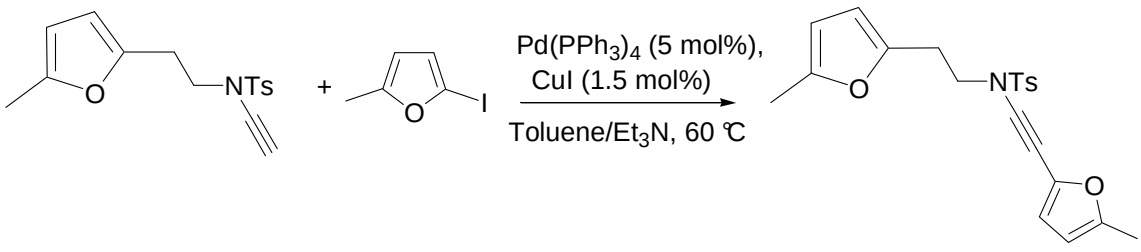
^{1}H-NMR (CD_2Cl_2, 300 MHz): δ = 2.34 (s, 3H), 2.44 (s, 3H), 3.01 (t, J = 7.4Hz, 2H), 3.66 (t, J = 7.4Hz, 2H), 6.08-6.10 (m, 1H), 6.27-6.30 (m, 1H), 7.12 (d, J = 8.4Hz, 2H), 7.25 (d, J = 8.2Hz, 2H), 7.31 (dd, J = 1.9, 0.7Hz, 1H), 7.37 (d, J = 8.4Hz, 2H), 7.78 (d, J = 8.4Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 21.47 (q), 21.73 (q), 27.15 (t), 50.06 (t), 71.01 (s), 81.13 (s), 106.9 (d), 109.3 (d), 127.7 (d, 2C), 129.0 (d, 2C), 129.8 (d, 2C), 131.5 (d, 2C), 134.5 (s), 138.1 (s), 141.6 (d), 144.6 (d), 151.3 (d)

MS (ESI (+)): *m/z* (%): 375 (7), 360 (6), 304 (100)

HRMS (APCI): $C_{22}H_{21}NO_3S$: Calcd: 402.1639; found: 402.1635

18. **4-Methyl-N-[2-(5-methyl-furan-2-yl)-ethyl]-N-(5-methyl-furan-2-ylethynyl)-benzenesulfonamide** (**58d**/SP634C, 20%, yellow oil)



R_f (PE:EtOAc, 8:1) = 0.25

IR (film): $\tilde{\nu}$ = 2922, 2220, 1543, 1436, 1365, 1264, 1167, 1090, 1019, 920, 786, 712 cm^{-1}

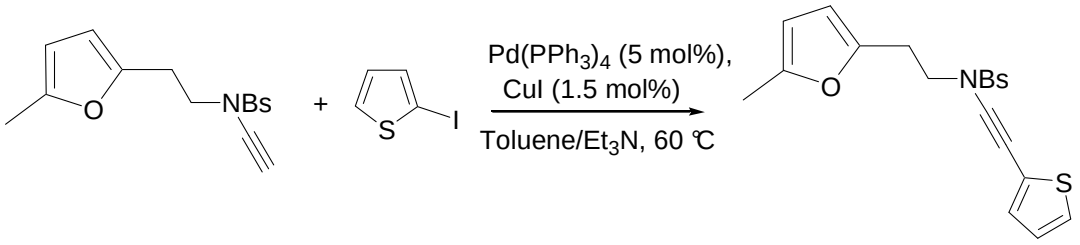
^{1}H-NMR (CD_2Cl_2, 300 MHz): δ = 2.20 (s, 3H), 2.29 (s, 3H), 2.44 (s, 3H), 2.94 (t, J = 7.8Hz, 2H), 3.65 (t, J = 7.9Hz, 2H), 5.79-5.82 (m, 1H), 5.91 (d, J = 5.9Hz, 1H), 5.96-5.99 (m, 1H), 6.51 (d, J = 3.2Hz, 1H), 7.33 (d, J = 8.2Hz, 2H), 7.79 (d, J = 8.2Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.46 (q), 13.95 (q), 21.70 (q), 27.18 (t), 50.36 (t), 62.41 (s), 85.78 (s), 106.1 (d), 107.3 (d), 107.6 (d), 118.8 (d), 127.6 (d, 2C), 129.8 (d, 2C), 134.8 (s), 134.9 (s), 144.7 (s), 149.2 (s), 151.2 (s), 154.2 (s)

MS (ESI (+)): *m/z* (%): 406 (72) $(M+Na)^+$, 301 (100)

HRMS (ESI): $C_{21}H_{21}NO_4S$: Calcd: 406.1088; found: 406.1078

19. **4-Bromo-N-[2-(5-methyl-furan-2-yl)-ethyl]-N-thiophen-2-ylethynyl-benzenesulfonamide** (**58g**/SP640, 36%, yellow oil)



R_f (PE:EtOAc, 8:1) = 0.50

IR (film): $\tilde{\nu}$ = 3102, 2920, 2226, 1572, 1368, 1168, 1088, 1067, 783, 742, 703, 592, 565 cm^{-1}

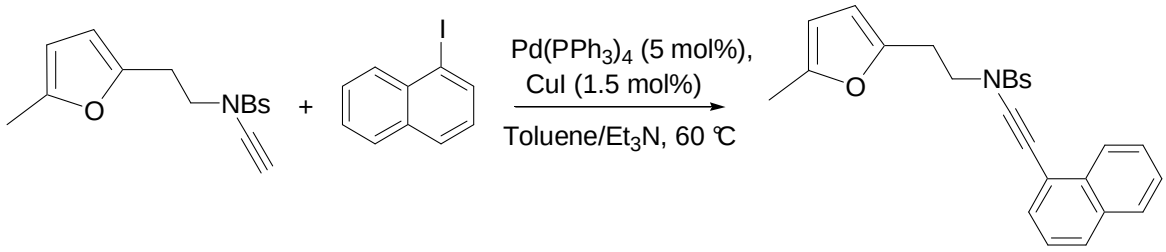
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.95 (t, J = 7.4Hz, 2H), 3.69 (t, J = 7.4Hz, 2H), 5.80-5.83 (m, 1H), 5.91 (d, J = 3.2Hz, 1H), 6.96-7.00 (m, 1H), 7.18 (dd, J = 3.8, 1.3Hz, 1H), 7.29 (dd, J = 5.2, 1.2Hz, 1H), 7.65-7-78 (m, 4H)

^{13}C NMR ($CDCl_3$, 75.46 MHz): 13.49 (q), 27.16 (t), 50.51 (t), 64.68 (s), 84.82 (s), 106.1 (d), 106.8 (d), 122.4 (s), 127.0 (d), 128.1 (d), 128.9 (s), 129.0 (d, 2C), 132.4 (d, 2C), 133.4 (d), 136.4 (s), 148.9 (s), 151.2 (s)

MS (ESI (+)): *m/z* (%): 471 (100) (M+Na)+, 231 (59)

HRMS (ESI): $C_{19}H_{16}BrNO_3S_2$: Calcd: 448.9750; found: 448.9746

20. **4-Bromo-N-[2-(5-methyl-furan-2-yl)-ethyl]-N-naphthalen-1-ylethynyl-benzenesulfonamide** (**58m/** SP648A, 27%, yellow oil)



R_f (PE:EtOAc, 4:1) = 0.60

IR (film): $\tilde{\nu}$ = 3058, 2920, 2231, 1572, 1366, 1168, 1067, 1010, 932, 743, 706 cm^{-1}

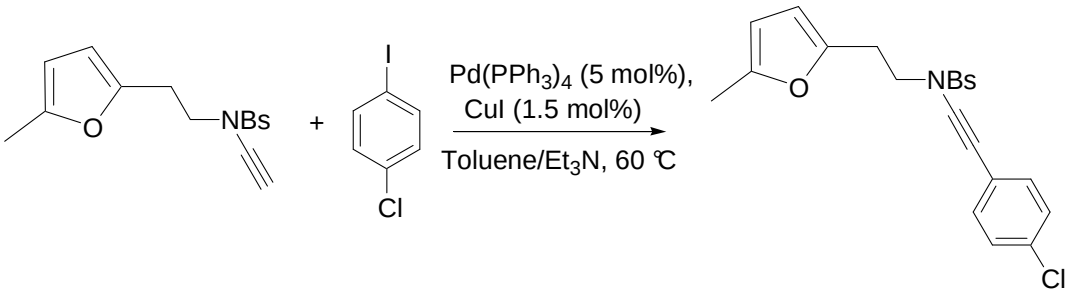
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.21 (s, 3H), 3.07 (t, J = 7.3Hz, 2H), 3.80 (t, J = 7.3Hz, 2H), 5.81-5.83 (m, 1H), 5.96 (d, J = 3.2Hz, 1H), 7.38-7.44 (m, 1H), 7.50-7.59 (m, 3H), 7.66 (d, J = 8.6Hz, 2H), 7.77-7.86 (m, 4H) , 8.13-8.16 (m, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.50 (q), 27.29 (t), 50.46 (t), 106.2 (d), 107.9 (d), 120.1 (s), 125.1 (s), 126.0 (d), 126.4 (d), 126.8 (d), 128.3 (d), 128.5 (d), 128.9 (s), 129.1 (d, 2C), 130.0 (d), 132.5 (d, 2C), 133.1 (s), 133.2 (s), 136.5 (s), 149.0 (s), 151.0 (s)

MS (ESI (+)): *m/z* (%): 495 (18) (M+2)+, 274 (100), 155 (46), 109 (44), 95 (52)

HRMS (ESI): $C_{25}H_{20}BrNO_3S$: Calcd: 493.0338; found: 493.0347

21. **4-Bromo-N-(4-chloro-phenylethynyl)-N-[2-(5-methyl-furan-2-yl)-ethyl]-benzenesulfonamide** (**58l/** SP648B, 25%, yellow solid)



M.P: 64-66 °C

R_f (PE:EtOAc, 4:1) = 0.60

IR (film): $\tilde{\nu}$ = 2920, 2236, 1573, 1370, 1170, 1088, 1011, 825, 743, 600 cm^{-1}

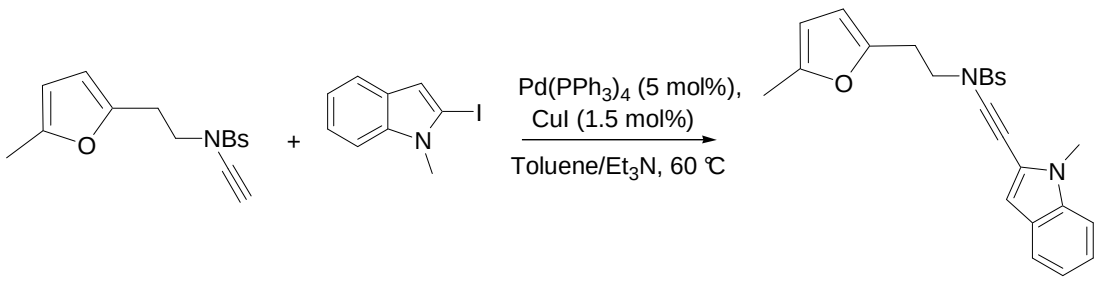
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 2.96 (t, J = 7.5Hz, 2H), 3.69 (t, J = 7.5Hz, 2H), 5.80-5.83 (m, 1H), 5.92 (d, J = 3.2Hz, 1H), 7.28 (s, 4H), 7.66-7.77 (m, 4H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.50 (q), 27.24 (t), 50.40 (t), 70.42 (s), 82.14 (s), 106.2 (d), 107.9 (d), 120.9 (s), 128.6 (d, 2C), 129.0 (d, 2C), 132.5 (d, 2C), 132.7 (d, 2C), 134.1 (s), 136.5 (s), 148.9 (s), 151.3 (s)

MS (ESI (+)): *m/z* (%): 479 (6) (M+2), 258 (30), 139 (58), 109 (46), 95 (100)

Anal. Calcd. for $C_{21}H_{17}BrClNO_3S$: C 52.68, H 3.58, N 2.93; found: C 52.50, H 3.66, N 2.93

22. **4-Bromo-N-[2-(5-methyl-furan-2-yl)-ethyl]-N-(1-methyl-1H-indol-2-ylethynyl)-benzenesulfonamide** (**58o/** SP652, 30%, off-white solid)



M.P: 122-124 °C

R_f (PE:EtOAc, 4:1) = 0.52

IR (film): $\tilde{\nu}$ = 2218, 1572, 1365, 1169, 966 cm^{-1}

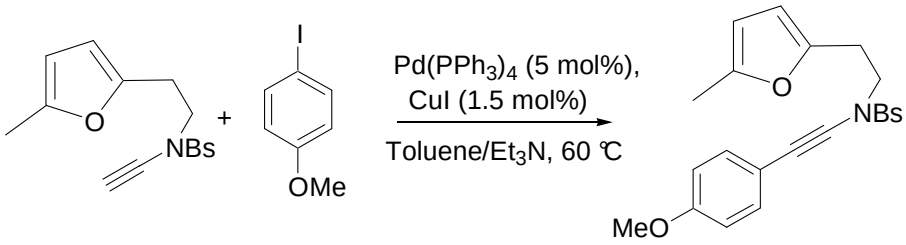
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3H), 3.00 (t, J = 7.1Hz, 2H), 3.72 (s, 3H), 3.76 (t, J = 7.2Hz, 2H), 5.81-5.84 (m, 1H), 5.94 (d, J = 3.0Hz, 1H), 6.73 (s, 1H), 7.08-7.14 (m, 1H), 7.27 (dd, J = 4.9, 1.0 Hz, 2H), 7.57 (td, J = 7.7, 0.8Hz, 1H), 7.68 (d, J = 8.8Hz, 2H9, 7.76 (d, J = 8.7Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.50 (q), 27.24 (t), 30.45 (q), 50.45 (t), 63.46 (s), 86.68 (s), 106.2 (d), 107.9 (d), 108.7 (d), 109.5 (d), 120.1 (d), 121.0 (d), 123.2 (d), 126.9 (s), 129.1 (d, 2C), 132.5 (d, 2C), 136.5 (s), 137.3 (s), 148.9 (s), 151.3 (s)

MS (APCI): *m/z* (%): 499 (100) $(M+1)^+$, 278 (46)

HRMS (APCI): $C_{24}H_{21}BrN_2O_3S$: Calcd: 496.0456; found: 496.0480

23. **4-Bromo-N-(4-methoxy-phenylethynyl)-N-[2-(5-methyl-furan-2-yl)-ethyl]-benzenesulfonamide** (**58f**/ SP677, 17%, yellow oil)



R_f (PE:EtOAc, 4:1) = 0.35

IR (film): $\tilde{\nu}$ = 2925, 1605, 1573, 1367, 1248, 1170, 902, 725, 649 cm^{-1}

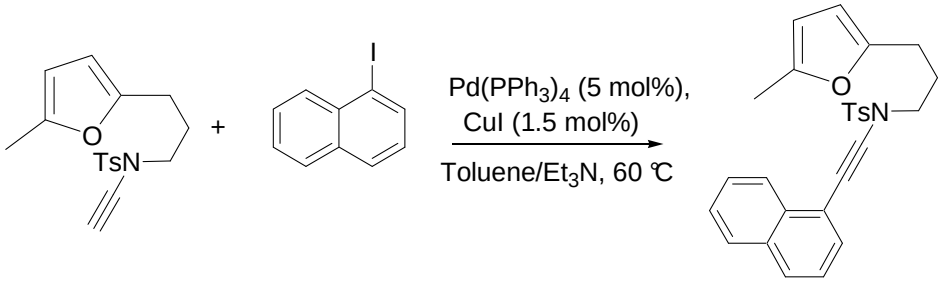
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.21 (s, 3H), 2.96 (t, J = 7.4Hz, 2H), 3.67 (t, J = 7.5Hz, 2H), 3.81 (s, 3H), 5.80-5.83 (m, 1H), 5.92 (d, J = 3.1Hz, 1H), 6.83 (d, J = 8.8Hz, 2H), 7.31 (d, J = 8.9Hz, 2H), 7.67 (d, J = 8.6Hz, 2H), 7.76 (d, J = 8.6Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.57 (q), 27.15 (t), 50.46 (t), 55.40 (q), 71.03 (s), 79.78 (s), 106.1 (d), 107.7 (d), 114.0 (d, 2C), 114.3 (s), 128.7 (s), 129.0 (d, 2C), 132.3 (d, 2C), 133.6 (d, 2C), 136.6 (s), 149.2 (s), 151.3 (s), 159.7 (s)

MS (ESI): *m/z* (%): 473 (3) (M^+), 255 (100), 212 (42)

HRMS (ESI): $C_{22}H_{20}BrNO_4S$: Calcd: 474.0371; found: 474.0375

24. **4-Methyl-N-[3-(5-methyl-furan-2-yl)-propyl]-N-naphthalen-1-ylethynyl-benzenesulfonamide (58v**/ SP643A, 35%, brown oil**)**



R_f (PE:EtOAc, 4:1) = 0.54

IR (film): $\tilde{\nu}$ = 3058, 2922, 2230, 1596, 1569, 1448, 1363, 1167, 1090, 1018, 951, 774, 669 cm^{-1}

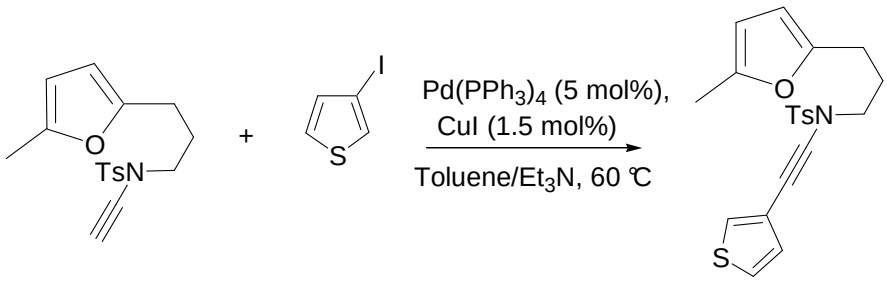
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.03-2.15 (m, 2H), 2.22 (s, 3H), 2.44 (s, 3H), 2.70 (t, J = 7.6Hz, 2H), 3.54 (t, J = 7.2Hz, 2H), 5.83-5.87 (m, 1H), 5.91 (d, J = 3.1Hz, 1H), 7.38 (d, J = 7.8Hz, 2H), 7.43 (d, J = 7.8Hz, 1H), 7.50-7.59 (m, 3H), 7.81 (d, J = 8.6Hz, 2H), 7.87 (d, J = 8.3Hz, 2H), 8.15-8.20 (m, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.62 (q), 21.74 (q), 24.92 (t), 26.70 (t), 50.99 (t), 69.26 (s), 86.82 (s), 105.8 (d), 106.2 (d), 120.5 (s), 125.2 (d), 126.2 (d), 126.3 (d), 126.7 (d), 127.0 (s), 127.7 (d, 2C), 128.1 (d), 128.2 (d), 129.6 (d), 129.8 (d, 2C), 133.1 (s), 134.5 (s), 144.7 (s), 150.6 (s), 152.5 (s)

MS (ESI): *m/z* (%): 466 (26) $(M+Na)^+$, 444 (100) $(M+1)^+$

HRMS (ESI): $C_{27}H_{25}NO_3S$: Calcd: 443.1555; found: 443.1550

25. **4-Methyl-N-[3-(5-methyl-furan-2-yl)-propyl]-N-thiophen-3-ylethynyl-benzenesulfonamide** (**58t/** SP643B, 39%, yellow oil)



R_f (PE:EtOAc, 4:1) = 0.55

IR (film): $\tilde{\nu}$ = 3106, 2921, 2236, 1597, 1569, 1363, 1167, 1091, 781 658, 579 cm^{-1}

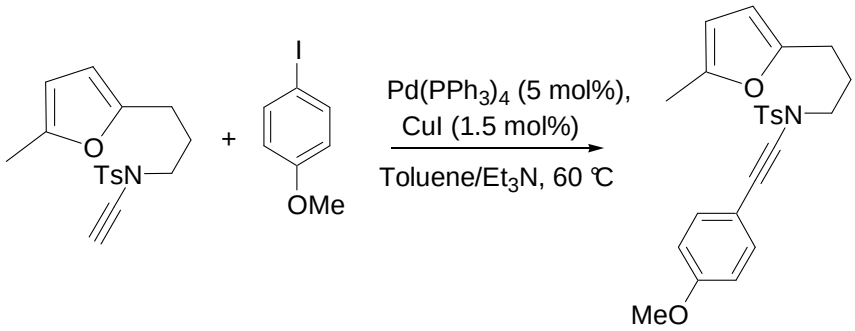
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.97 (quin, J = 7.21Hz, 2H), 2.21 (s, 3H), 2.45 (s, 3H), 2.62 (t, J = 7.4Hz, 2H), 3.41 (t, J = 7.2Hz, 2H), 5.82-5.85 (m, 1H), 5.87 (d, J = 3.0Hz, 1H), 7.06 (dd, J = 5.06, 1.1HZ, 1H), 7.27-7.31 (m, 1H), 7.35-7.41 (m,3H), 7.79 (d, J = 8.8Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.49 (q), 21.65 (q), 24.83 (t), 26.57 (t), 50.98 (t), 65.74 (s), 81.59 (s), 105.8 (d), 106.1 (d), 121.5 (s), 125.1 (d), 127.7 (d, 2C), 128.7 (d), 129.7 (d, 2C), 130.2 (d), 134.5 (s), 144.5 (s), 150.5 (s), 152.5 (s)

MS (ESI): *m/z* (%): 422 (100) $(M+Na)^+$, 400 (23)

HRMS (ESI): $C_{21}H_{21}NO_3S_2$: Calcd: 399.0963; found: 399.0958

26. **N-(4-Methoxy-phenylethynyl)-4-methyl-N-[3-(5-methyl-furan-2-yl)-propyl]-benzenesulfonamide** (**58r/** SP658, 37%, brown oil)



R_f (PE:EtOAc, 4:1) = 0.47

IR (film): $\tilde{\nu}$ = 2922, 2235, 1604, 1511, 1361, 1287, 1246, 1166, 1090, 1020, 831, 722, 663, 577 cm^{-1}

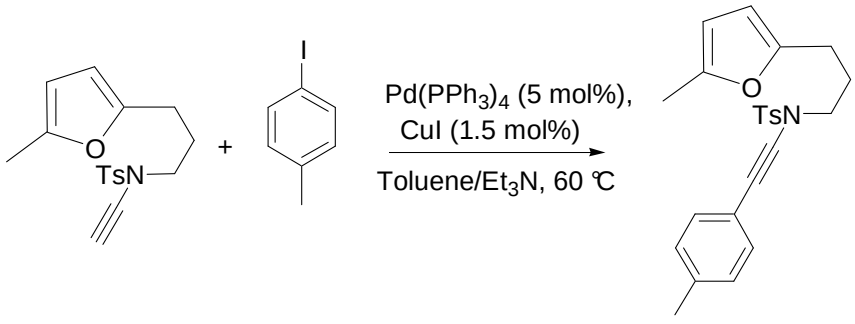
^{1}H-NMR (CD_2Cl_2, 250 MHz): δ = 2.01 (quin, J = 7.2Hz, 2H), 2.23 (s, 3H), 2.45 (s, 3H), 2.65 (t, J = 7.3Hz, 2H), 3.42 (t, J = 7.1Hz, 2H), 3.80 (s, 3H), 5.81-5.85 (m, 1H), 5.88 (d, J = 3.0Hz, 1H), 6.82 (d, J = 8.8Hz, 2H), 7.28-7.38 (m, 4H), 7.82 (d, J = 8.6Hz, 2H)

^{13}C-NMR ($CDCl_3$, 62.89 MHz): 13.56 (q), 21.74 (q), 24.92 (t), 26.61 (t), 51.07 (t), 55.35 (q), 70.41 (s), 80.92 (s), 105.8 (d), 106.1 (d), 113.9 (d, 2C), 114.7 (s), 127.7 (d, 2C), 129.7 (d, 2C), 133.4 (d, 2C), 134.5 (s), 144.5 (s), 150.5 (s), 152.6 (s), 159.5 (s)

MS (APCI): *m/z* (%): 424 (100) $(M+1)^+$

HRMS (ESI): $C_{24}H_{25}NO_4S$: Calcd: 423.1504; found: 423.1499

27. **4-Methyl-N-[3-(5-methyl-furan-2-yl)-propyl]-N-p-tolylethynyl-benzenesulfonamide** (**58s/** SP666, 24%, yellow oil)



R_f (PE:EtOAc, 4:1) = 0.55

IR (film): $\tilde{\nu}$ = 2924, 2235, 1448, 1363, 1166, 1090, 907, 814, 727, 662, 576 cm^{-1}

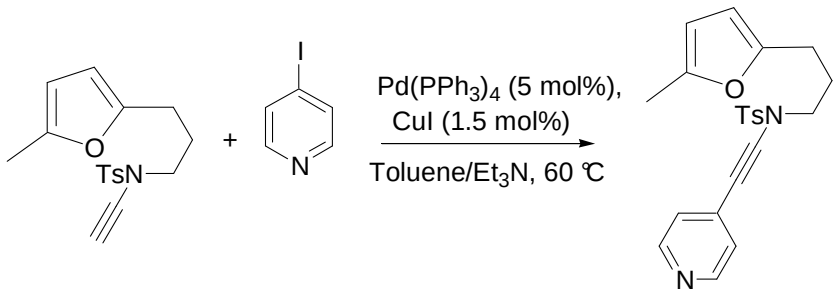
^{1}H-NMR (CD_2Cl_2, 250 MHz): δ = 1.99 (quin, J = 7.3Hz, 2H), 2.21 (s, 3H), 2.33 (s, 3H), 2.44 (s, 3H), 2.63 (t, J = 7.3Hz, 2H), 3.41 (t, J = 7.3Hz, 2H), 5.82-5.85 (m, 1H), 5.87 (d, J = 3.1Hz, 1H), 7.11 (d, J = 8.4Hz, 2H), 7.25 (d, J = 8.3Hz, 2H), 7.37 (d, J = 8.4Hz, 2H), 7.80 (d, J = 8.3Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.47 (q), 21.43 (q), 21.67 (q), 24.87 (t), 26.60 (t), 50.99 (t), 70.72 (s), 81.61 (s), 105.8 (d), 106.1 (d), 119.7 (s), 127.7 (d, 2C), 129.0 (d, 2C), 129.7 (d, 2C), 131.5 (d, 2C), 134.5 (s), 138.0 (s), 144.5 (s), 150.5 (s), 152.6 (s)

MS (ESI): m/z (%): 430 $(M+Na)^+$, 408 (18)

HRMS (ESI): $C_{24}H_{25}NO_3S$: Calcd: 407.1555; found: 407.1550

28. **4-Methyl-N-[3-(5-methyl-furan-2-yl)-propyl]-N-pyridin-4-ylethynyl-benzenesulfonamide** (**58u/** SP664, 46%, dark brown oil)



R_f (PE:EtOAc, 4:1) = 0.10

IR (film): $\tilde{\nu}$ = 2922, 2229, 1592, 1366, 1167, 1089, 815, 675, 579, 545 cm^{-1}

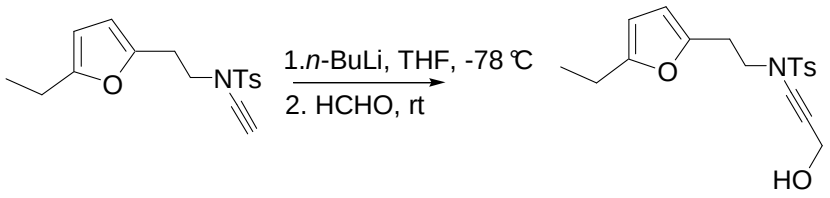
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.95-2.06 (m, 2H), 2.22 (s, 3H), 2.45 (s, 3H), 2.63 (t, J = 7.4Hz, 2H), 3.47 (t, J = 7.4Hz, 2H), 5.83-5.86 (m, 1H), 5.88 (d, J = 3.1Hz, 1H), 7.17-7.20 (m, 2H), 7.39 (d, J = 8.4Hz, 2H), 7.80 (d, J = 8.5Hz, 2H), 8.47-8.50 (m, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.57 (q), 21.75 (q), 24.80 (t), 26.71 (t), 50.81 (t), 69.80 (s), 87.80 (s), 106.0 (d), 106.4 (d), 124.3 (d, 2C), 127.6 (d, 2C), 130.0 (d, 2C), 131.7 (s), 134.4 (s), 145.3 (s), 149.6 (d, 2C), 150.8 (s), 152.5 (s)

MS (ESI): *m/z* (%): 417 (90) $(M+Na)^+$, 395 (100) $(M+1)^+$, 240 (62)

HRMS (ESI): $C_{22}H_{22}N_2O_3S$: Calcd: 394.1351; found: 394.1349

29. **N-[2-(5-Ethyl-furan-2-yl)-ethyl]-N-(3-hydroxy-prop-1-ynyl)-4-methyl-benzenesulfonamide** (**62**/SP626)



210 mg (0.66 mmol, 1 eq) of the alkyne **42d** was dissolved in 10ml dry THF taken in a flame dried round bottom flask under nitrogen. The solution was cooled to –78 °C and 0.29ml (0.73 mmol, 1.1 eq) *n*-butyl lithium (2.5M solution in hexane) was added drop wise. The solution was stirred for 45 min at the same temperature and then 40 mg (1.2 mmol, 2 eq) of paraformaldehyde was added in portions. The reaction mixture was warmed to room temperature and stirred for overnight. Quenched with ammonium chloride solution and extracted with ether. Dried over magnesium sulphate and the solvent was removed under vacuum. Column chromatography (PE:EtOAc) furnished 110 mg (48%) of the pure product as a light brown oil.

R_f (PE:EtOAc, 2:1) = 0.23

IR (film): $\tilde{\nu}$ = 3523, 2972, 2241, 1360, 1165, 998, 847, 813, 677, 573 cm^{-1}

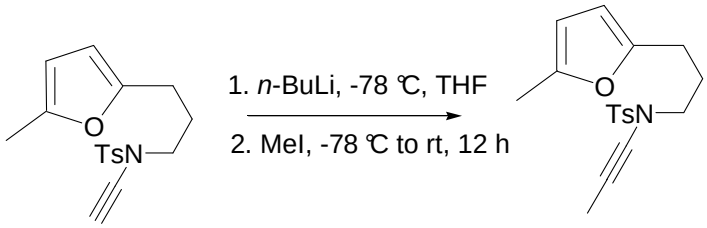
^{1}H-NMR (CD_2Cl_2, 250 MHz): δ = 1.18 (t, J = 7.6Hz, 3H), 2.43 (s, 3H), 2.56 (q, J = 7.6Hz, 2H), 2.88 (t, J = 7.2Hz, 2H), 3.57 (t, J = 7.3Hz, 2H), 4.33 (d, J = 5.5Hz, 2H), 5.83-5.86 (m, 1H), 5.91 (d, J = 3.1Hz, 1H), 7.35 (d, J = 8.6Hz, 2H), 7.75 (d, J = 8.5Hz, 2H)

^{13}C-NMR ($CDCl_3$, 62.89 MHz): 12.12 (q), 21.32 (t), 21.65 (q), 27.26 (t), 50.09 (t), 51.22 (t), 69.95 (s), 78.87 (s), 104.4 (d), 107.4 (d), 127.5 (d, 2C), 129.9 (d, 2C), 134.6 (s), 144.7 (s), 149.1 (s), 157.0 (s)

MS (APCI): *m/z* (%): 348 (6) $(M+1)^+$, 330 (100)

HRMS (ESI): $C_{18}H_{21}NO_4S$: Calcd: 347.1191; found: 330.1145 (water molecule lost)

30. **4-Methyl-N-[3-(5-methyl-furan-2-yl)-propyl]-N-prop-1-ynyl-benzenesulfonamide** (**65**/SP660)



300 mg (0.95 mmol, 1 eq) of the ynamide was dissolved in 10ml of dry THF under nitrogen. The system was cooled to –78 °C and 0.44ml (1.1 mmol, 1.1 eq) of n-Butyl lithium was added slowly. The reaction mixture was stirred for 45 min at the same temperature and then 0.31ml (5 mmol, 5 eq) of methyl iodide was added. The reaction mixture was warmed to room temperature in 12h, and then quenched with saturated aqueous ammonium chloride. The organic layer was extracted with ether, dried over magnesium sulphate. The solvent was removed under vacuum leaving 307 mg (98%) of the product as an yellow oil which was directly used without further purification.

R_f (PE:EtOAc, 8:1) = 0.54

IR (film): $\tilde{\nu}$ = 2253, 1968, 1360, 1169, 902, 723, 649 cm^{-1}

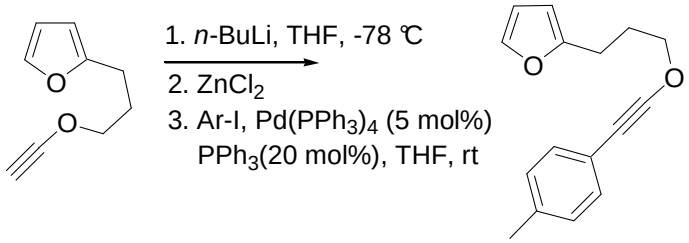
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.89 (s, 3H), 1.93 (quin, J = 7.4Hz, 2H), 2.24 (s, 3H), 2.44 (s, 3H), 2.60 (t, J = 7.4Hz, 2H), 3.29 (t, J = 7.4Hz, 2H), 5.81-5.84 (m, 1H), 5.87 (d, J = 3.1Hz, 1H), 7.33 (d, J = 8.4Hz, 2H), 7.76 (d, J = 8.4Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 3.31 (q), 13.51 (q), 21.62 (q), 24.82 (t), 26.42 (t), 50.81 (t), 65.78 (s), 71.84 (s), 105.8 (d), 106.0 (d), 127.5 (d, 2C), 129.6 (d, 2C), 134.6 (s), 144.3 (s), 150.5 (s), 152.8 (s)

MS (APCI): *m/z* (%): 332 (100) $(M+1)^+$, 177 (25)

HRMS (ESI): $C_{18}H_{21}NO_3S$: Calcd: 331.1241; found: 331.1239

31. **2-(3-p-Tolylethynyloxy-propyl)-furan** (**59b**/SP521)



350 mg (2.33 mmol, 1 eq) of the alkynyl ether was dissolved in 8 ml dry THF under nitrogen. Cooled to -78 ^{o}C, and 1 ml (2.5 mmol, 1.1 eq) of *n*-BuLi was added. The reaction mixture was stirred for 30 min at the same temperature and then 2.5 ml (2.5 mmol, 1.1 eq) of zinc chloride was added and stirred at 0^{o}C for 5 min. The reaction mixture was then canulated to another flask containing 558 mg (2.5 mmol, 1.1 eq) of iodotoluene, 148 mg (5 mol%) $Pd(PPh_3)_4$, and 134 mg (20 mol%) of PPh_3 in 5 ml of dry THF. The reaction mixture was stirred at rt for 12 h. Filtered through celite and column chromatography (PE) furnished 100 mg (20%) of the coupled product as an yellow oil. Traces of PPh_3 was present as impurity in the isolated product.

R_f (PE:EtOAc, 10:1) = 0.53

IR (film): $\tilde{\nu}$ = 3053, 2257, 1590, 1438, 1315, 1188, 1118, 1054, 997, 815, 762, 719, 695, 538 cm^{-1}

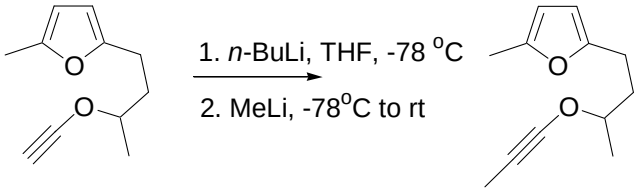
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.07-2.17 (m, 2H), 2.30 (s, 3H), 2.78 (t, J = 7.3Hz, 2H), 4.16 (t, J = 6.5Hz, 2H), 6.05-6.07 (m, 1H), 6.28-6.31 (m, 1H), 7.06 (d, J = 8.2Hz, 2H), 7.20 (d, J = 8.2Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 21.43 (q), 24.32 (t), 27.77 (t), 78.64 (t), 105.8 (d), 110.6 (d), 129.4 (d, 2C), 131.6 (d, 2C), 134.9 (s), 137.1 (s), 138.7 (s), 141.6 (d)

MS (EI): *m/z* (%): 240 (46) (M+), 109 (32), 81 (100)

HRMS (EI): $C_{16}H_{16}O_2$: Calcd: 240.1150; found: 240.1152

32. **2-Methyl-5-(3-prop-1-ynyloxy-butyl)-furan** (**69**/SP569)



178 mg (1 mmol, 1 eq) of the alkynyl ether was dissolved in 10 ml of dry THF under nitrogen. The system was cooled to -78 °C and 0.44 ml (1.1 mmol, 1.1 eq) *n*-BuLi was added. Stirred for 45 min at the same temperature and 0.31 ml (5 mmol, 5 eq) of methyl lithium was added slowly. The reaction mixture was warmed to rt for 1 h. 10 ml of saturated aqueous ammonium chloride was added. Extracted with ether, dried over magnesium sulphate and the solvent was removed under vacuum. 170 mg (98%) of the product was obtained and no further purification required.

R_f (PE:EtOAc, 10:1) = 0.66

IR (film): $\tilde{\nu}$ = 2921, 2275, 1570, 1447, 1378, 1245, 1219, 1058, 1020, 779 cm^{-1}

^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.35 (d, J = 6.4Hz, 3H), 1.74 (s, 3H), 1.76-2.00 (m, 2H), 2.24 (s, 3H), 2.62-2.73 (m, 2H), 3.98-4.10 (m, 1H), 5.81-5.89 (m, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 11.78 (t), 17.36 (q), 22.11 (t), 32.13 (t), 81.20 (d), 84.70 (s), 104.1 (d), 148.7 (s), 151.3 (s)

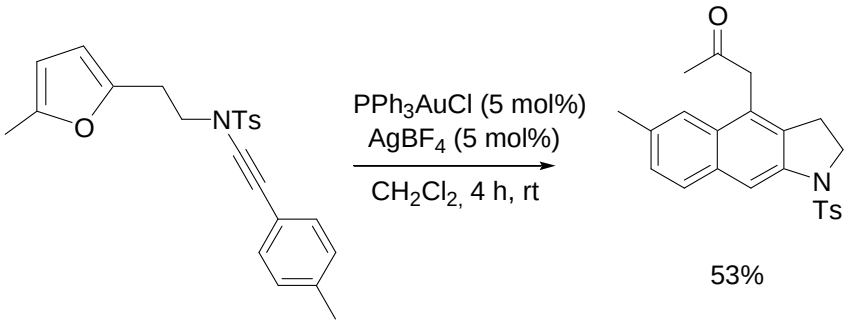
MS (EI): *m/z* (%): 192 (M+) (2), 95 (100)

HRMS (ESI): $C_{12}H_{16}O_2$: Calcd: 192.1150; found: 192.1144

B. Catalysis: General procedure

1 mmol (1 eq) of the substrate was dissolved in CH_2Cl_2 or $CHCl_3$ and 0.05 mmol (5mol %) of PPh_3AuCl was added, followed by 0.05 mmol (5mol %) of $AgBF_4$. The reaction mixture was stirred at room temperature or as mentioned till the starting material is consumed. The solvent was removed under vacuum and the product was purified over flash column chromatography (PE:EtOAc).

33. **1-[6-Methyl-1-(toluene-4-sulfonyl)-2,3-dihydro-1H-benzo[f]indol-4-yl]-propan-2-one** (**60a**/ SP637, off white solid)



M.P: 158-160 °C

R_f (PE:EtOAc, 2:1) = 0.18

IR (film): $\tilde{\nu}$ = 2923, 1717, 1351, 1163, 1091, 914, 814, 664, 596 cm^{-1}

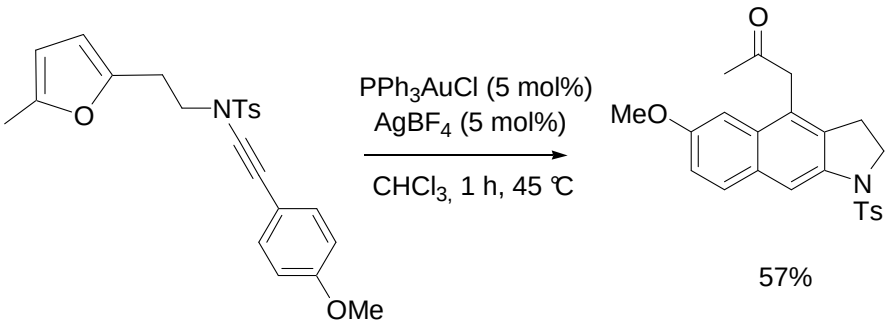
^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.02 (s, 3H), 2.33 (s, 3H), 2.48 (s, 3H), 2.98 (t, J = 8.24, 2H), 3.91 (s, 2H), 4.00 (t, J = 8.2Hz, 2H), 7.19 (d, J = 8.3Hz, 2H), 7.29 (d, J = 8.3Hz, 2H), 7.47 (s, 1H), 7.69-7.77 (m, 3H), 7.91 (s, 1H)

^{13}C-NMR ($CDCl_3$, 125 MHz): 21.54 (q), 21.99 (q), 27.19 (t), 29.24 (q), 45.01 (t), 47.02 (t), 110.8 (d), 122.2 (d), 126.2 (s), 127.3 (d, 2C), 128.2 (d), 128.5 (d), 129.7 (d, 2C), 132.2 (s), 132.4 (s), 133.9 (s), 135.0 (s), 138.9 (s), 144.2 (s), 205.5 (s)

MS (ESI (+)): *m/z* (%): 416 $(M+Na)^+$(100), 394 (7)

HRMS (ESI (+)): $C_{23}H_{23}NO_3S$: Calcd: 416.1296; found: 416.1298

34. **1-[6-Methoxy-1-(toluene-4-sulfonyl)-2,3-dihydro-1H-benzo[f]indol-4-yl]-propan-2-one** (**60b/** SP592A, yellow solid)



57%

M.P: 122-124 °C

R_f (PE:EtOAc, 2:1) = 0.17

IR (film): $\tilde{\nu}$ = 2922, 1706, 1613, 1413, 1347, 1233, 1160, 1088, 812, 662, 593, 543 cm^{-1}

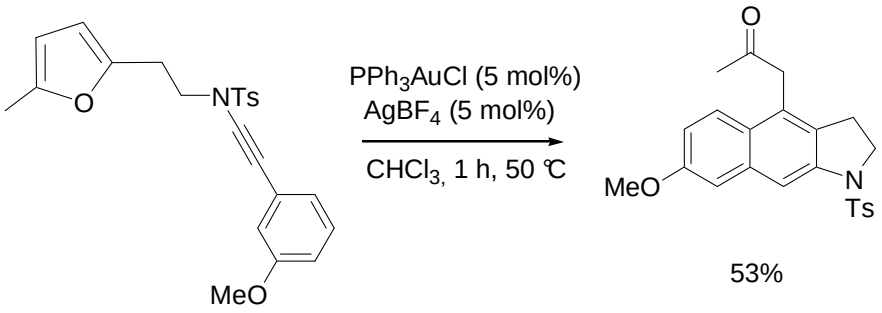
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.98 (s, 3H), 2.34 (s, 3H), 2.99 (t, J = 8.1Hz, 2H), 3.88 (s, 5H), 4.01 (t, J = 8.1Hz, 2H), 7.03 (d, J = 2.4Hz, 1H), 7.14 (dd, J = 8.9, 2.5Hz, 1H), 7.20 (d, J = 8.2Hz, 2H), 7.70 (d, J = 8.3Hz, 2H), 7.75 (d, J = 8.9Hz, 1H), 7.91 (s, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 21.51 (q), 27.40 (t), 29.08 (q), 45.56 (t), 49.67 (t), 55.39 (q), 102.6 (d), 111.3 (d), 118.0 (d), 125.6 (s), 127.3 (d, 2C), 129.3 (s), 129.7 (d, 2C), 130.1 (d), 130.6 (s), 132.7 (s), 133.9 (s), 137.9 (s), 144.2 (s), 157.5 (s), 205.5 (s)

MS (ESI (+)): *m/z* (%): 432 $(M+Na)^+$ (100), 276 (39), 254 (41)

HRMS (ESI (+)): $C_{23}H_{23}NO_4S$: Calcd: 432.1245; found: 432.1240

35. **1-[7-Methoxy-1-(toluene-4-sulfonyl)-2,3-dihydro-1H-benzo[f]indol-4-yl]-propan-2-one** (**60i/** SP592C, yellow solid)



M.P: 116-118 °C

R_f (PE:EtOAc, 2:1) = 0.16

IR (film): $\tilde{\nu}$ = 2924, 1707, 1625, 1418, 1350, 1156, 1089, 813, 663, 596, 545 cm^{-1}

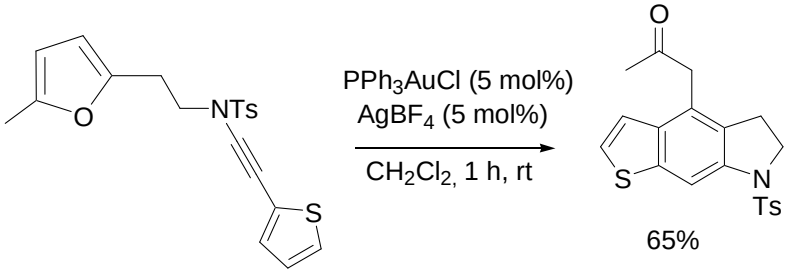
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.01 (s, 3H), 2.35 (s, 3H), 2.98 (t, J = 8.2Hz, 2H), 3.90 (s, 2H), 3.93 (s, 3H), 4.00 (t, J = 8.2Hz, 2H), 7.06 (dd, J = 8.9, 2.6Hz, 1H), 7.17 (d, J = 2.7Hz, 1H), 7.22 (d, J = 8.2Hz, 2H), 7.63 (d, J = 8.9Hz, 1H), 7.74 (d, J = 8.3Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 21.53 (q), 26.86 (t), 29.24 (q), 45.19 (t), 49.83 (t), 55.34 (q), 107.1 (d), 109.8 (d), 117.6 (d), 124.5 (d), 124.6 (s), 126.) (s), 127.3 (d, 2C), 129.7 (d, 2C), 134.0 (s), 135.8 (s), 140.4 (s), 144.3 (s), 157.8 (s), 205.3 (s)

MS (ESI (+)): *m/z* (%): 410 (M^+) (12), 255 (100)

HRMS (ESI (+)): $C_{23}H_{23}NO_4S$: Calcd: 432.1245; found: 432.1243

36. **1-[7-(Toluene-4-sulfonyl)-6,7-dihydro-5H-1-thia-7-aza-s-indacen-4-yl]-propan-2-one** (**60e/** SP597C, yellow oil)



R_f (PE:EtOAc, 2:1) = 0.19

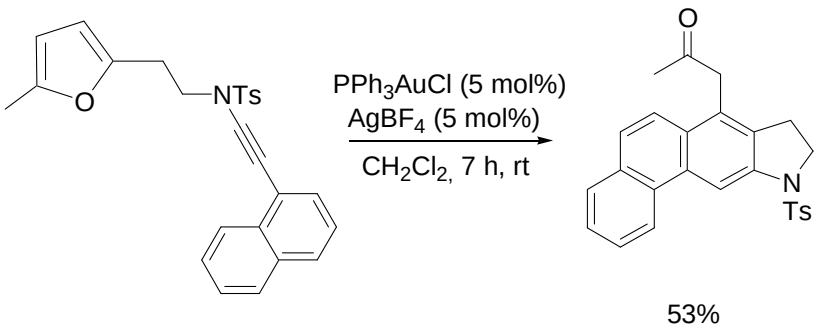
IR (film): $\tilde{\nu}$ = 2924, 1710, 1597, 1430, 1353, 1253, 1161, 1091, 1065, 905, 729, 662 cm^{-1}

^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.03 (s, 3H), 2.35 (s, 3H), 2.89 (t, J = 8.2Hz, 2H), 3.82 (s, 2H), 4.01 (t, J = 8.2Hz, 2H), 7.19-7.24 (m, 3H), 7.38 (d, J = 5.6Hz, 1H), 7.69 (d, J = 8.3Hz, 2H), 8.07 (s, 1H)
^{13}C-NMR ($CDCl_3$, 75.46 MHz): 21.56 (q), 26.60 (t), 29.28 (q), 46.39 (t), 50.39 (t), 107.4 (d), 120.8 (d), 125.0 (s), 125.9 (d), 127.3 (d, 2C), 129.5 (s), 129.7 (d, 2C), 133.9 (s), 135.7 (s), 139.7 (s), 140.5 (s), 144.3 (s)204.6 (s)

MS (ESI (+)): *m/z* (%): 408 $(M+Na)^+$ (27), 253 (50), 230 (71), 188 (100)

HRMS (ESI (+)): $C_{20}H_{19}NO_3S_2$: Calcd: 386.0886; found: 386.0879

37. **1-[10-(Toluene-4-sulfonyl)-9,10-dihydro-8H-10-aza-cyclopenta[b]phenanthren-7-yl]-propan-2-one** (**60c**/ SP604, pale white solid)



53%

M.P: 202-205 °C

R_f (PE:EtOAc, 2:1) = 0.11

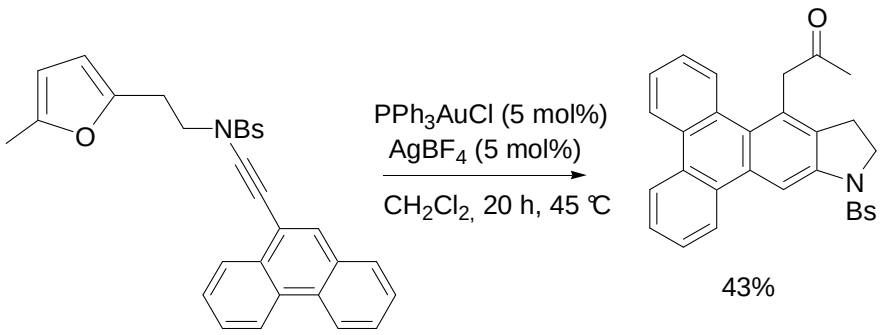
IR (film): $\tilde{\nu}$ = 2923, 2253, 1711, 1454, 1352, 1162, 1090, 905, 670 cm^{-1}

^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.04 (s, 3H), 2.31 (s, 3H), 3.04 (t, J = 8.2Hz, 2H), 3.99 (s, 2H), 4.07 (t, J = 8.2Hz, 2H), 7.18 (d, J = 8.2Hz, 2H), 7.58-7.73 (m, 4H), 7.76 (d, J = 8.3Hz, 2H), 7.88 (dd, J = 7.8, 1.3Hz, 1H), 8.77 (d, J = 8.4Hz, 1H), 8.91 (s, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 21.52 (q), 27.30 (t), 29.31 (q), 45.48 (t), 49.92 (t), 106.8 (d), 121.5 (d), 123.2 (d), 126.4 (d), 126.8 (d), 127.3 (d, 2C), 127.4 (s), 127.8 (s), 128.4 (d), 129.7 (d, 2C), 130.4 (s), 131.4 (s), 131.7 (s), 132.0 (s), 133.9 (s), 140.7 (s), 144.3 (s), 205.2 (s)

MS (ESI (+)): *m/z* (%): 430 $(M+1)^+$ (29), 429 (M^+) (100), 217 (45)
HRMS (ESI (+)): $C_{26}H_{23}NO_3S$: Calcd: 430.1469; found: 430.1479

38. **1-[10-(4-Bromo-benzenesulfonyl)-11,12-dihydro-10H-10-aza-cyclopenta[b]triphenylen-13-yl]-propan-2-one** (**60p/** SP614, , pale yellow solid)



43%

M.P: 108-110 °C

R_f (PE:EtOAc, 2:1) = 0.13

IR (film): $\tilde{\nu}$ = 3056, 2923, 1716, 1573, 1356, 1263, 1164, 733, 702, 568 cm^{-1}

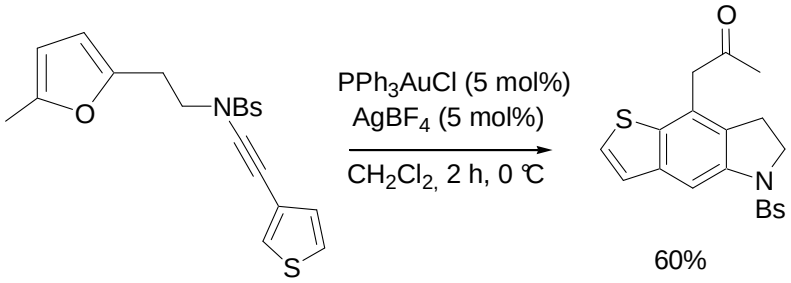
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.29 (s, 3H), 2.93 (t, J = 8.3Hz, 2H), 4.02 (t, J = 8.3Hz, 2H), 4.23 (s, 2H), 7.41-7.49 (m, 1H), 7.52-7.59 (m, 8H), 8.54-8.66 (m, 3H), 8.81 (s, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 27.46 (t), 29.80 (q), 49.86 (t), 106.7 (d), 123.0 (d), 123.7 (d), 125.7 (d), 126.3 (s), 126.7 (d), 126.9 (d), 127.5 (d), 127.6 (d), 128.6 (s), 128.7 (d, 2C), 129.1 (s), 129.9 (s), 130.0 (s), 130.6 (s), 132.1 (s), 132.5 (d, 2C), 133.5 (s), 135.7 (s), 140.6 (s), 165.2 (s), 205.6 (s)

MS (APCI): *m/z* (%): 545 (62) $(M+1)^+$, 306 (100), 280 (54)

HRMS (APCI): $C_{29}H_{22}BrNO_3S$: Calcd: 544.0579; found: 544.0573

39. **1-[5-(4-Bromo-benzenesulfonyl)-6,7-dihydro-5H-1-thia-5-aza-s-indacen-8-yl]-propan-2-one** (**60h/** SP615, yellow oil)



60%

R_f (PE:EtOAc, 2:1) = 0.17

IR (film): $\tilde{\nu}$ = 3086, 1873, 1716, 1573, 1357, 1253, 1168, 1093, 1067, 909, 826, 738, 612 cm^{-1}

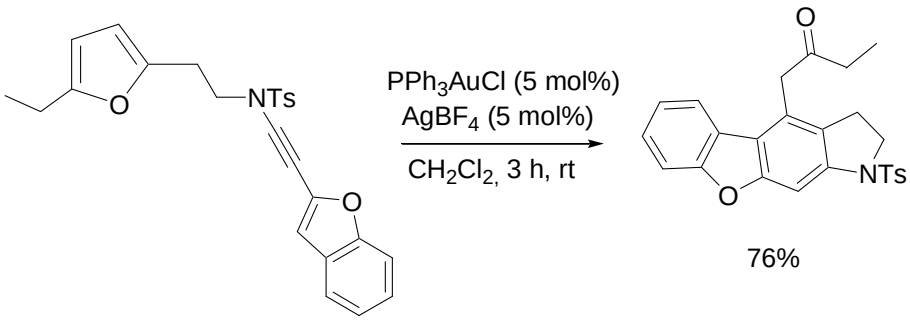
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.12 (s,3H), 2.89 (t, J = 8.2Hz; 2H), 3.79 (s, 2H), 4.00 (t, J = 8.2Hz, 2H), 7.34 (d, J = 5.5Hz, 1H), 7.43 (d, J = 5.5Hz, 1H), 7.56 (d, J = 8.6Hz, 2H), 7.66 (d, J = 8.7Hz, 2H), 7.98 (s, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 26.58 (t), 29.67 (q), 47.41 (t), 50.41 (t), 108.5 (d), 124.8 (s), 125.0 (d), 126.4 (d), 128.4 (s), 128.6 (d, 2C), 129.5 (s), 132.4 (d, 2C), 135.9 (s), 136.6 (s), 139.8 (s), 139.9 (s), 203.9 (s)

MS (APCI): *m/z* (%):452 (27) $(M+1)^+$, 246 (22), 231 (100)

HRMS (APCI): $C_{19}H_{16}BrNO_3S_2$: Calcd: 449.9834; found: 449.9829

40. **1-[1-(Toluene-4-sulfonyl)-2,3-dihydro-1H-9-oxa-1-aza-cyclopenta[b]fluoren-4-yl]-butan-2-one** (**60n/** SP625, yellow solid)



76%

M.P: 134-137 °C

R_f (PE:EtOAc, 2:1) = 0.25

IR (film): $\tilde{\nu}$ = 2924, 1712, 1598, 1449, 1353, 1332, 1162, 1090,904, 727 cm^{-1}

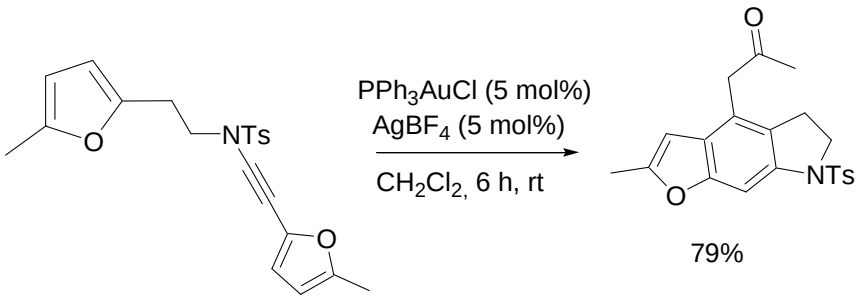
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.95 (t, J = 7.2Hz, 3H), 2.33-2.39 (m, 5H), 2.94 (t, J = 8.5Hz, 2H), 4.00 (s, 2H), 4.05 (t, J = 8.5Hz, 2H), 7.22 (d, J = 8.4Hz, 2H), 7.29 (dt, J = 7.6, 1.1Hz, 1H), 7.40 (dt, J = 7.8, 1.2Hz, 1H), 7.56 (d, J = 8.4Hz, 1H), 7.72 (d, J = 8.3Hz, 2H), 7.79 (d, J = 8.1Hz, 1H), 7.82 (s, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 7.65 (q), 21.53 (q), 26.41 (t), 35.23 (t), 45.23 (t), 50.54 (t), 98.29 (d), 111.7 (d), 119.2 (s), 121.1 (d), 123.0 (d), 123.7 (s), 125.6 (s), 126.2 (d), 126.9 (s), 127.3 (d, 2C), 129.8 (d, 2C), 133.9 (s), 141.7 (s), 144.3 (s), 156.6 (s), 156.7 (s), 206.9 (s)

MS (ESI (+)): *m/z* (%): 456 (100) $(M+Na)^+$, 300 (54), 278 (34), 222 (46), 179 (54)

HRMS (ESI): $C_{24}H_{23}NO_4S$: Calcd: 456.1245; found: 456.1250

41. **1-[2-Methyl-7-(toluene-4-sulfonyl)-6,7-dihydro-5H-1-oxa-7-aza-s-indacen-4-yl]-propan-2-one** (**60d**/ SP636, yellow oil)



R_f (PE:EtOAc, 2:1) = 0.11

IR (film): $\tilde{\nu}$ = 2923, 2253, 1978, 1711, 1355, 1163, 1093, 902, 723, 649 cm^{-1}

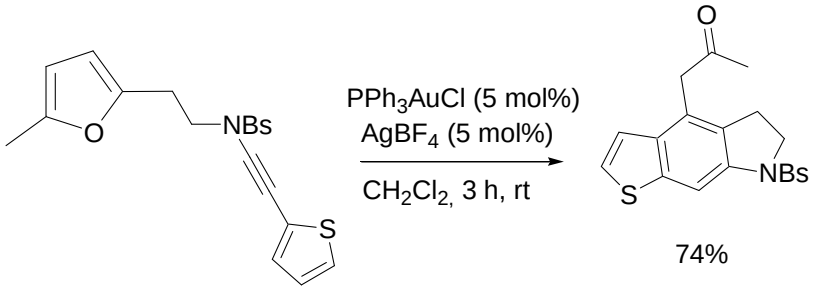
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.99 (s, 3H), 2.35 (s, 3H), 2.43 (s, 3H), 2.79 (t, J = 8.3Hz, 2H), 3.63 (s, 2H), 3.98 (t, J = 8.3Hz, 2H), 6.24 (s,1H), 7.19 (d, J = 8.2Hz, 2H), 7.63-7.68 (m, 3H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 14.23 (q), 21.50 (q), 26.40 (t), 29.14 (q), 46.11 (t), 5058 (t), 98.29 (d), 100.7 (d), 121.4 (s), 125.6 (s), 126.5 (s), 127.3 (d, 2C), 129.6 (d, 2C), 134.0 (s), 138.8 (s), 144.1 (s), 154.6 (s), 155.9 (s), 204.7 (s)

MS (ESI (+)): *m/z* (%): 406 (89) $(M+Na)^+$, 250 (85), 228 (100)

HRMS (ESI): $C_{21}H_{21}NO_4S$: Calcd: 406.1088; found: 406.1091

42. **1-[7-(4-Bromo-benzenesulfonyl)-6,7-dihydro-5H-1-thia-7-aza-s-indacen-4-yl]-propan-2-one** (**60g/** SP641, yellow solid)



M.P: 182-185 °C

R_f (PE:EtOAc, 2:1) = 0.20

IR (film): $\tilde{\nu}$ = 2922, 2851, 1710, 1574, 1430, 1353, 1164, 1067 cm^{-1}

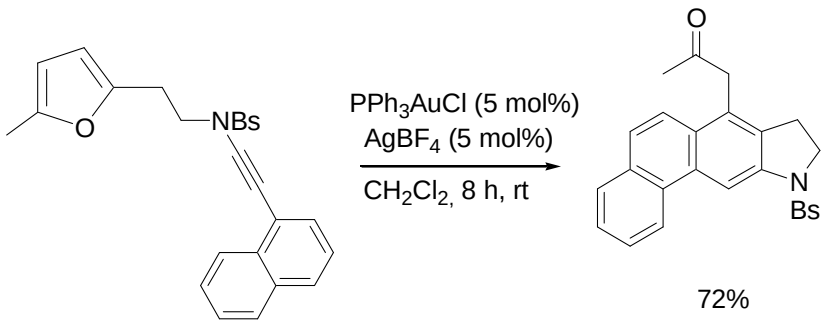
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.06 (s, 3H), 2.92 (t, J = 8.4Hz, 2H), 3.84 (s, 2H), 4.01 (t, J = 8.4Hz, 2H), 7.22 (d, J = 5.5Hz, 1H), 7.40 (d, J = 5.6Hz, 1H), 7.56 (d, J = 8.6Hz, 2H), 7.66 (d, J = 8.6Hz, 2H), 8.05 (s, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 26.54 (t), 29.33 (q), 46.33 (t), 50.43 (t), 107.4 (d), 120.8 (d), 125.2 (s), 126.2 (d), 128.5 (s), 128.6 (d, 2C), 129.4 (s), 132.4 (d, 2C), 135.9 (s), 136.0 (s), 139.2 (s), 140.5 (s), 204.5 (s)

MS (ESI (+)): *m/z* (%): 471 (100) $(M+Na)^+$, 231 (78)

HRMS (ESI): $C_{19}H_{16}BrNO_3S_2$: Calcd: 448.9750; found: 448.9752

43. **1-[10-(4-Bromo-benzenesulfonyl)-9,10-dihydro-8H-10-aza-cyclopenta[b]phenanthren-7-yl]-propan-2-one** (**60m/** SP649A, off white solid)



M.P: 186-188 °C

R_f (PE:EtOAc, 2:1) = 0.16

IR (film): $\tilde{\nu}$ = 2924, 1713, 1359, 1164, 1066, 821, 748, 615 cm^{-1}

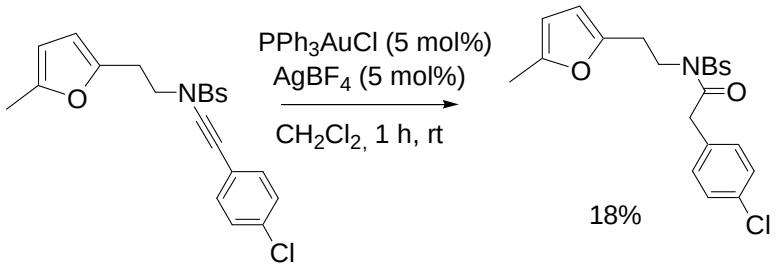
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.07 (s, 3H), 3.06 (t, J = 8.2Hz, 2H), 4.01 (s, 2H), 4.06 (t, J = 8.2Hz, 2H), 7.53 (d, J = 8.6Hz, 2H), 7.59-7.75 (m, 6H), 7.88 (dd, J = 7.8, 1.1Hz, 1H), 8.75 (d, J = 8.3Hz, 1H), 8.90 (s, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 27.25 (t), 29.44 (q), 45.37 (t), 49.93 (t), 106.9 (d), 121.5 (d), 123.1 (d), 126.6 (d), 126.9 (d), 127.0 (d), 127.6 (s), 128.0 (s), 128.5 (d), 128.6 (d, 2C), 130.3 (s), 131.3 (s), 131.7 (s), 131.8 (s), 132.4 (d, 2C), 135.8 (s), 140.1 (s), 205.1 (s)

MS (APCI): *m/z* (%): 494 (11) (M^+), 275 (100)

HRMS (ESI): $C_{25}H_{20}BrNO_3S$: Calcd: 493.0347; found: 493.0352

44. **4-Bromo-N-[2-(4-chloro-phenyl)-acetyl]-N-[2-(5-methyl-furan-2-yl)-ethyl]-benzenesulfonamide** (**61/** SP649B, yellow oil)



R_f (PE:EtOAc, 2:1) = 0.38

IR (film): $\tilde{\nu}$ = 2365, 2253, 1974, 1698, 1360, 1089, 902 cm^{-1}

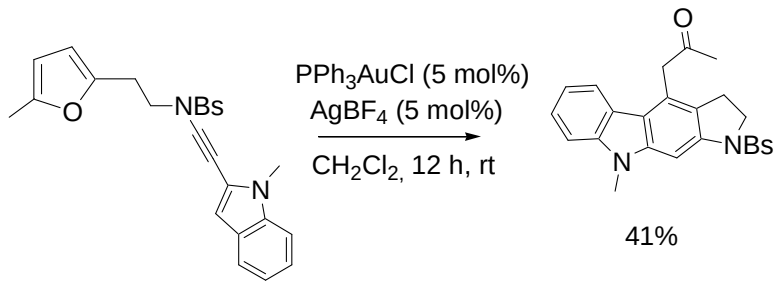
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.21 (s, 3H), 3.00 (t, J = 7.1Hz, 2H), 3.63 (s, 2H), 4.01 (t, J = 7.1Hz, 2H), 5.86-5.89 (m, 1H), 5.94 (d, J = 3.0Hz, 1H), 6.96 (d, J = 8.5Hz, 2H), 7.24 (d, J = 8.5Hz, 2H), 7.64 (d, J = 8.6Hz, 2H), 7.75 (d, J = 8.6Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.51 (q), 28.76 (t), 41.70 (t), 46.21 (t), 106.4 (d), 108.3 (d), 128.8 (d, 2C), 129.1 (s), 129.6 (d, 2C), 130.7 (d, 2C), 131.3 (s), 132.3 (d, 2C), 133.3 (s), 138.2 (s), 149.2 (s), 151.5 (s), 170.5 (s)

MS (APCI): *m/z* (%): 498 (9) $(M+2)^+$, 479 (20), 109 (100)

HRMS (APCI): $C_{21}H_{19}BrClNO_4S$: Calcd: 494.9907; found: 494.9900

45. **1-[1-(4-Bromo-benzenesulfonyl)-9-methyl-1,2,3,9-tetrahydro-pyrrolo[2,3-b]carbazol-4-yl]-propan-2-one** (**60o/** SP653, pale yellow solid)



41%

M.P: 186-188 °C

R_f (PE:EtOAc, 2:1) = 0.23

IR (film): $\tilde{\nu}$ = 2925, 1722, 1599, 1570, 1469, 1440, 1354, 1318, 1160, 1065, 840, 816, 746 cm^{-1}

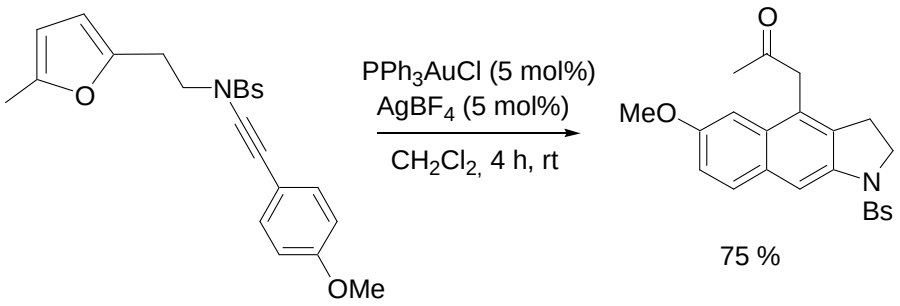
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.03 (s, 3H), 2.93 (t, J = 8.2Hz, 2H), 3.88 (s, 3H), 4.05 (t, J = 8.2Hz, 2H), 4.10 (s, 2H), 7.18-7.24 (m, 1H), 7.39-7.48 (m, 2H), 7.53 (d, J = 8.6Hz, 2H), 7.65 (d, J = 8.7Hz, 2H), 7.95 (d, J = 7.9Hz, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 26.44 (t), 29.14 (q), 29.49 (q), 46.58 (t), 50.65 (t), 95.25 (d), 108.6 (d), 119.5 (d), 121.3 (d), 121.9 (s), 123.7 (s), 125.1 (d), 125.7 (s), 126.3 (s), 128.6 (d, 2C), 132.4 (d, 2C), 136.1 (s), 140.1 (s), 141.5 (s), 141.8 (s), 160.2 (s), 205.2 (s)

MS (APCI): *m/z* (%): 497 (90) (M^+), 278 (100)

HRMS (APCI): $C_{24}H_{21}BrN_2O_3S$: Calcd: 496.0456; found: 496.0449

46. **1-[1-(4-Bromo-benzenesulfonyl)-6-methoxy-2,3-dihydro-1H-benzo[f]indol-4-yl]-propan-2-one** (**60f/** SP678, pale yellow solid)



M.P: 110-114 °C

R_f (PE:EtOAc, 2:1) = 0.14

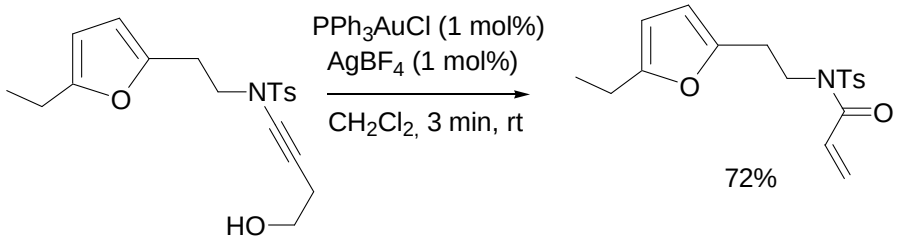
IR (film): $\tilde{\nu}$ = 2935, 1707, 1614, 1573, 1355, 1235, 1168, 1091, 738 cm^{-1}

^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.01 (s, 3H), 2.99 (t, J = 8.1Hz, 2H), 3.89 (s, 5H), 4.01 (t, J = 8.1Hz, 2H), 7.03-7.05 (m, 1H), 7.15 (dd, J = 8.6, 2.4Hz, 1H), 7.55 (d, J = 8.6Hz, 2H), 7.68 (d, J = 8.6Hz, 2H), 7.75 (d, J = 8.7Hz, 1H), 7.89 (s, 1H)
^{13}C-NMR ($CDCl_3$, 75.46 MHz): 27.36 (t), 29.18 (q), 45.53 (t), 49.86 (t), 55.47 (q), 102.6 (d), 111.3 (d), 118.2 (d), 125.9 (s), 128.4 (s), 128.7 (d, 2C), 129.3 (s), 130.1 (d), 130.8 (s), 132.4 (d, 2C), 135.9 (s), 137.5 (s), 157.9 (s), 205.1 (s)

MS (ESI): *m/z* (%):473 (5) (M^+), 255 (100)

HRMS (ESI): $C_{22}H_{20}BrNO_4S$: Calcd: 496.0189; found: 496.0189

47. **N-Acryloyl-N-[2-(5-ethyl-furan-2-yl)-ethyl]-4-methyl-benzenesulfonamide** (**63/** SP627, colourless oil)



R_f (PE:EtOAc, 2:1) = 0.35

IR (film): $\tilde{\nu}$ = 2970, 2934, 1684, 1346, 1159, 1087, 812, 709, 662 cm^{-1}

^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.19 (t, J = 7.8Hz, 3H), 2.43 (s, 3H), 2.58 (q, J = 7.8Hz, 2H), 2.97-3.05 (m, 2H), 4.02-4.07 (m, 2H), 5.72 (dd, J = 10.4, 1.8Hz, 1H), 5.83-5.86 (m, 1H), 5.96 (d, J = 3.1Hz, 1H), 6.37 (dd, J = 16.7Hz, 1.8HZ, 1H), 6.72-6.82 (m, 1H), 7.32 (d, J = 8.4Hz, 2H), 7.79 (d, J = 8.4Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 12.40 (q), 21.70 (q), 29.17 (t), 46.00 (t), 104.9 (d), 107.7 (d), 128.0 (d, 2C), 128.7 (d), 130.1 (d, 2C), 131.1 (t), 137.1 (s), 145.6 (s), 150.0 (s), 157.5 (s), 165.6 (s)

MS (APCI): *m/z* (%): 348 (15) $(M+1)^+$, 177 (22), 123 (100)

HRMS (APCI): $C_{18}H_{21}NO_4S$: Calcd: 347.1191; found: 347.1172

48. **1-[7-Thiophen-3-yl-1-(toluene-4-sulfonyl)-2,3,4,7-tetrahydro-1H-[1]pyrindin-6-yl]-ethanone** (**64t/** SP645, yellow solid)

M.P: 180-183 °C

R_f (PE:EtOAc, 2:1) = 0.08

IR (film): $\tilde{\nu}$ = 2926, 1647, 1520, 1361, 1169, 1088, 1049, 831, 784, 731, 671 cm^{-1}

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 1.22-1.30 (m, 1H), 1.66-1.72 (m, 1H), 2.23 (s, 3H), 2.25-2.36 (m, 2H), 2.40 (s, 3H), 2.97-3.03 (m, 1H), 3.88 (td, J = 13.6, 3.6Hz, 1H), 5.50 (s, 1H),

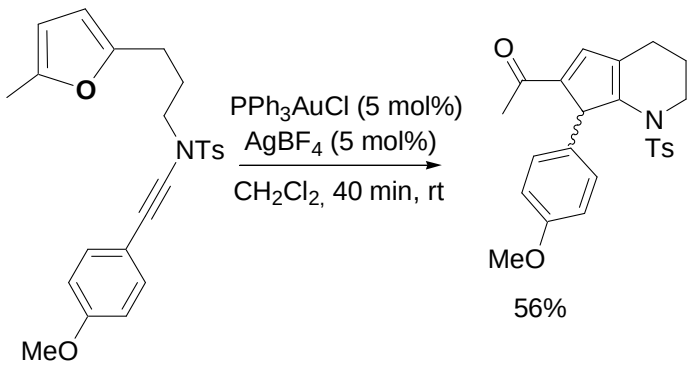
6.77 (dd, J = 5.03, 1.3Hz, 1H), 7.12 (d, J = 1.3Hz, 1H), 7.13-7.15 (m, 1H), 7.17-7.18 (m, 1H), 7.21 (d, J = 8.5Hz, 2H), 7.38 (d, J = 8.5Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 20.29 (t), 21.55 (q), 21.90 (t), 26.41 (q), 46.85 (t), 52.87 (d), 122.9 (d), 124.7 (d), 126.4 (s), 126.7 (d), 127.3 (d, 2C), 129.7 (d, 2C), 135.6 (s), 136.5 (s), 142.2 (d), 143.9 (s), 144.9 (s), 149.3 (s), 192.3 (s)

MS (ESI): *m/z* (%): 422 (100) $(M+Na^+)^+$, 400 (35) $(M+1)^+$, 245 (12)

HRMS (ESI): $C_{21}H_{21}NO_3S_2$: Calcd: 399.0963; found: 399.0958

49. **1-[7-(4-Methoxy-phenyl)-1-(toluene-4-sulfonyl)-2,3,4,7-tetrahydro-1H-[1]pyrindin-6-yl]-ethanone** (**64r**/SP659, yellow solid)



M.P: 188-193 °C

R_f (PE:EtOAc, 2:1) = 0.23

IR (film): $\tilde{\nu}$ = 2932, 1646, 1509, 1362, 1299, 1247, 1168, 907, 820, 729, 672 cm^{-1}

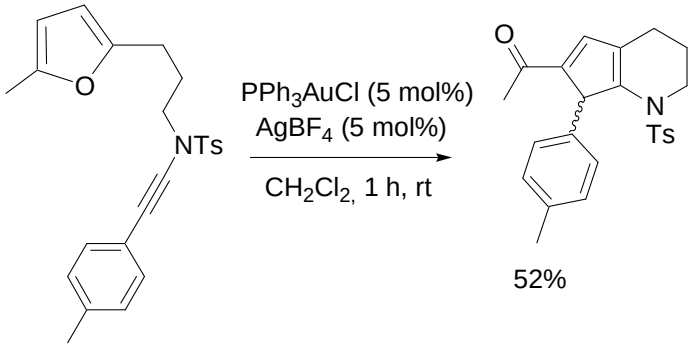
^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 1.21-1.31 (m, 1H), 1.66-1.72 (m, 1H), 2.2.0 (s, 3H), 2.24-2.37 (m, 2H), 2.38 (s, 3H), 2.96-3-02 (m, 1H), 3.77 (s, 3H), 3.87 (td, J = 13.6Hz, 1H), 5.27 (s, 1H), 6.76 (d, J = 8.7Hz, 2H), 7.05 (d, J = 8.6Hz, 2H), 7.11 (d, J = 1.3Hz, 1H), 7.17 (d, J = 8.4Hz, 2H), 7.34 (d, J = 8.4Hz, 2H)

^{13}C-NMR ($CDCl_3$, 125 MHz): 20.33 (t), 21.59 (q), 22.01 (q), 26.46 (q), 46.87 (t), 55.18 (q), 56.86 (d), 113.8 (d, 2C), 126.5 (s), 127.3 (d, 2C), 128.8 (s), 129.3 (d, 2C), 129.6 (d, 2C), 135.7 (s), 142.1 (d), 143.8 (s), 146.3 (s), 150.3 (s), 158.4 (s), 192.8 (s)

MS (ESI): *m/z* (%): 424 (23) (M+1)+, 268 (100)

HRMS (ESI): $C_{24}H_{25}NO_4S$: Calcd: 446.1401; found: 446.1407

50. **1-[1-(Toluene-4-sulfonyl)-7-p-tolyl-2,3,4,7-tetrahydro-1H-[1]pyrindin-6-yl]-ethanone** (**64s/** SP667, off-white solid)



M.P: 165-168 °C

R_f (PE:EtOAc, 2:1) = 0.13

IR (film): $\tilde{\nu}$ = 2922, 2549, 2190, 1974, 1643, 1521, 1167, 809, 672, 552 cm^{-1}

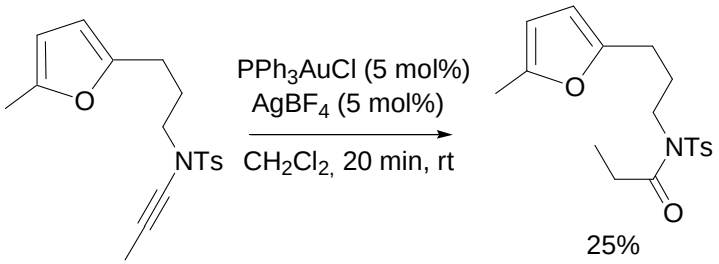
^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 1.22-1.31 (m, 1H), 1.66-1.73 (m, 1H), 2.19 (s, 3H), 2.30 (s, 3H), 2.38 (s, 3H), 2.31-2.37 (m, 2H), 2.95-3.02 (m, 1H), 3.86 (td, J = 13.4, 3.7Hz, 1H), 5.29 (s, 1H), 7.11 (d, J = 1.5Hz, 1H), 7.16 (d, J = 8.3Hz, 2H), 7.33 (d, J = 8.3Hz, 2H)

^{13}C-NMR ($CDCl_3$, 125 MHz): 20.34 (t), 21.16 (q), 21.55 (q), 21.92 (t), 26.46 (q), 46.99 (t), 126.7 (s), 127.4 (d, 2C), 128.2 (d, 2C), 129.1 (d, 2C), 129.6 (d, 2C), 133.8 (s), 135.7 (s), 136.1 (s), 142.2 (d), 143.8 (s), 146.2 (s), 150.3 (s), 192.3 (s)

MS (ESI): *m/z* (%): 430 $(M+Na)^+$, 275 (28)

HRMS (ESI): $C_{24}H_{25}NO_3S$: Calcd: 407.1555; found: 407.1550

51. **4-Methyl-N-[3-(5-methyl-furan-2-yl)-propyl]-N-propionyl-benzenesulfonamide**(**66/** SP661, colourless oil)



R_f (PE:EtOAc, 8:1) = 0.62

IR (film): $\tilde{\nu}$ = 2923, 1700, 1350, 1159, 903, 724 cm^{-1}

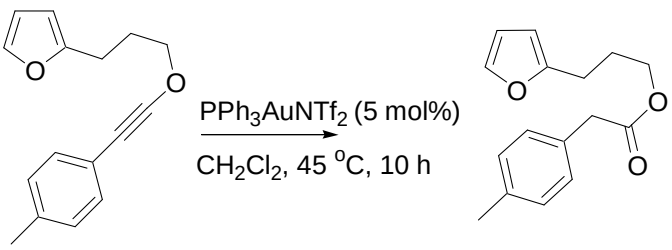
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.04 (t, J = 7.2Hz, 3H), 1.99-2.12 (m, 2H), 2.25 (s, 3H), 2.44 (s, 3H), 2.56 (q, J = 7.3Hz, 2H), 2.64 (t, J = 7.4Hz, 2H), 3.83 (t, J = 7.8Hz, 2H), 7.32 (d, J = 8.2Hz, 2H), 7.76 (d, J = 8.3Hz, 2H)

^{13}C-NMR ($CDCl_3$, 125 MHz): 8.840 (q), 13.52 (q), 21.59 (q), 23.45 (t), 28.27 (t), 29.68 (t), 59.04 (t), 105.3 (d), 105.9 (d), 127.5 (d, 2C), 129.8 (d, 2C), 133.7 (s); 143.2 (s), 151.7 (s), 157.8 (s), 180.0 (s)

MS (ESI): *m/z* (%): 350 (24) $(M+1)^+$, 332 (92), 294 (100)

HRMS (APCI): $C_{18}H_{23}NO_4S$: Calcd: 349.1438; found: 349.1334

52. **Carbonic acid 3-furan-2-yl-propyl ester p-tolyl ester** (**68/** SP522, colourless oil, 43%)



R_f (PE:EtOAc, 8:1) = 0.42

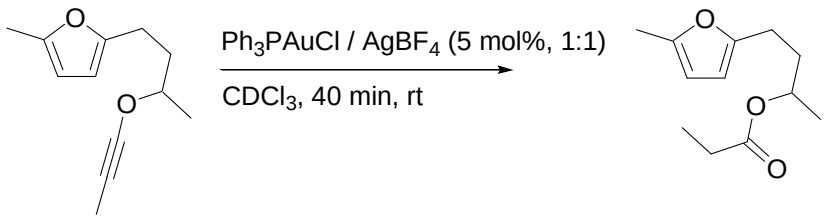
IR (film): $\tilde{\nu}$ = 2924, 1731, 1263, 1144, 1004, 729 cm^{-1}

^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.92-1.99 (m, 2H), 2.33 (s, 3H), 2.66 (t, J = 7.6Hz, 2H), 3.57 (s, 2H), 4.11 (t, J = 6.6Hz, 2H), 5.94-5.96 (m, 1H), 6.25-6.27 (m, 2H), 7.13 (d, J = 8.1HZ, 2H), 7.17 (d, J = 8.1Hz, 2H), 7.28-7.29 (m, 1H)

^{13}C-NMR ($CDCl_3$, 125 MHz): 21.11 (t), 24.48 (q), 27.18 (t), 40.96 (t), 63.90 (t), 105.2 (d), 110.0 (d), 129.1 (d, 2C), 129.3 (d, 2C), 131.0 (s), 136.7 (s), 141.1 (d), 154.9 (s), 171.7 (s)
MS (ESI): *m/z* (%): 281 (100) $(M+Na)^+$

HRMS (ESI): $C_{16}H_{18}O_3$: Calcd: 258.1256; found: 258.1235

53. **Propionic acid 1-methyl-3-(5-methyl-furan-2-yl)-propyl ester** (**70**/ SP570, pale yellow oil, 54%)



R_f (PE:EtOAc, 8:1) = 0.52

IR (film): $\tilde{\nu}$ = 2924, 1736, 1461, 1377, 1191 cm^{-1}

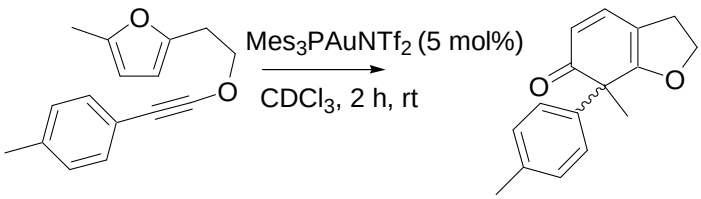
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.13 (t, J = 7.6HZ, 3H), 1.23 (d, J = 6.3Hz, 3H), 1.80-1.94 (m, 2H), 2.24 (s, 3H), 2.30 (q, J = 7.7HZ, 2H), 2.56-2.64 (m, 2H), 4.88-5.00 (m, 1H), 5.80-5.86 (m, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 9.170 (q), 13.47 (q), 19.99 (q), 24.21 (t), 27.94 (t), 34.32 (t), 70.07 (d), 105.4 (d), 105.9 (d), 150.4 (s), 153.3 (s), 174.2 (s)

MS (EI): *m/z* (%): 210 (35) (M+), 136 (96), 121 (100), 95 (38)

HRMS (ESI): $C_{12}H_{18}O_3$: Calcd: 210.1256; found: 210.1343

54. **7-Methyl-7-p-tolyl-3,7-dihydro-2H-benzofuran-6-one** (**67**/ SP506, yellow liquid, 43%)



R_f (PE:EtOAc, 8:1) = 0.38

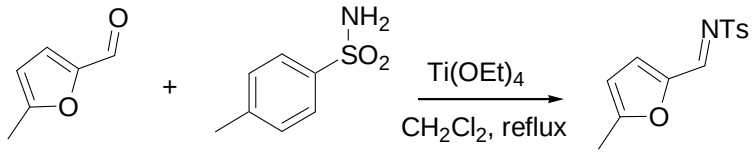
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.74 (s, 3H), 2.31 (s, 3H), 2.61-2.67 (m, 2H), 3.82-3.88 (m, 1H), 4.12-4.18 (m, 1H), 6.07-6.11 (m, 1H), 6.65-6.68 (m, 1H), 7.13 (d, J = 8.1Hz, 2H), 7.46 (d, J = 8.1Hz, 2H)

^{13}C-NMR ($CDCl_3$, 125 MHz): 15.13 (q), 21.30 (q), 30.07 (t), 66.11 (t), 89.50 (s), 115.7 (d), 125.9 (d, 2C), 129.6 (d, 2C), 131.3 (s), 132.4 (s), 137.4 (d), 138.5 (s), 151.7 (s), 201.6 (s)

2.3 Gold catalyzed Cycloisomerization of Furyl-Alkynes: Proof for the Cationic nature of the 'Carbene' Intermediate

A. Preparation of the substrates

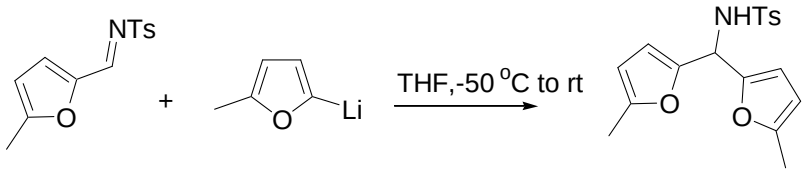
1. **(5-methylfuran-2-yl)-N-tosylmethanimine**[10k] (**103a**/SP288)



0.646ml (6.47 mmol, 1 eq) of 5-methyl furfural was taken in 30ml dry DCM in a two necked round bottom flask connected with a reflux condenser, under nitrogen. 1.32g (7.76 mmol, 1.2 eq) of p-toluene sulfonamide was added. The system was cooled to 0 ^{o}C and 8ml (32 mmol, 5 eq) of titanium tetraethoxide was added. The reaction mixture was refluxed for 4h cooled to 0 ^{o}C and 20ml water was added. The solid was filtered off and the product was extracted with DCM, dried over magnesium sulfate. The solvent was evaporated and the pale white solid (1.26g, 75%) obtained was used without further purification.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.40 (s, 6H), 6.25 (d, J=3.5Hz, 1H), 7.24 (d, J=3.5Hz, 1Hz), 7.30-7.36 (m, 2H), 7.80-7.88 (m, 2H), 8.65(s, 1H)

2. **bis(5-methylfuran-2-yl)-N-tosylmethanamine** (**104a**/SP290)



0.50ml (5 mmol, 2 eq) of 5-methyl furan was taken in a flame dried round bottom flask under nitrogen. 10ml of dry THF was added and the system was cooled to 0 ^{o}C. 2.5ml (5 mmol, 2 eq) of n-butyl lithium was added and the reaction mixture was stirred at 0 ^{o}C for 2h. This solution was then canulated to a 10ml THF solution of the iminosulfonamide **103a** (600 mg,

2.47 mmol, 1 eq) kept at -50 ^{o}C under nitrogen. The reaction mixture was stirred for 4h at the same temperature and then warmed to rt. The reaction was quenched with aqueous .ammonium chloride and then extracted with DCM. Dried over magnesium sulfate and the solvent was evaporated. Column chromatography (PE/EtOAc) furnished 400 mg (51%) of the product as a pale yellow solid.

M.P: 118-120 °C

R_f (PE:EtOAc, 4:1) = 0.53

IR (neat): 3267, 1566, 1411, 1322, 1216, 1159, 1003, 906, 794, 665 cm^{-1}

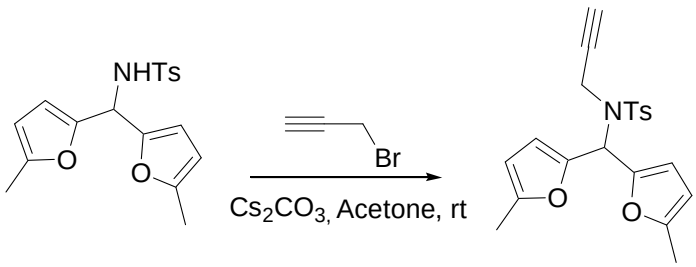
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.12 (s, 6H), 2.38 (s, 3H), 5.18 (d, J = 8.1Hz, 1H), 5.60 (d, J= 8.1Hz, 1H), 5.76-5.79 (m, 2H), 5.98 (d, J = 3.2Hz, 2H), 7.18 (d, J = 7.8Hz, 2H), 7.60 (d, J = 7.8Hz, 2H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 13.38 (q, 2C), 21.45 (q), 49.87 (d), 106.1 (d, 2C), 109.0 (d, 2C), 127.1 (d, 2C), 129.1 (d, 2C), 137.6 (s), 142.9 (s), 148.4 (s), 152.2 (s)

MS (EI): m/z (%) = 346 (2) (M+1), 345 (5) (M^{+}), 264 (7), 190 (71), 175 (100)

Anal. Calcd. For $C_{18}H_{19}NO_4S$: C 62.59, H 5.54, N 4.06; found: C 62.39, H 5.50, N 4.05.

3. **N-(bis(5-methylfuran-2-yl)methyl)-N-tosylprop-2-yn-1-amine** (**105a**/SP292)



345 mg (1 mmol, 1 eq) of the amine **104a** was dissolved in 10ml of dry acetone. 685 mg (2 mmol, 2 eq) of caesium carbonate was added followed by .33ml (3 mmol, 3 eq, 80% solution in toluene) of propargyl bromide. The reaction mixture was stirred for 12h. The solvent was

evaporated, 10ml of water was added and the product was extracted with ether. Dried over magnesium sulphate and the solvent was evaporated. Column chromatography (PE/EtOAc) furnished 320 mg (83%) of the product as an yellow oil.
R_f (PE:EtOAc, 4:1) = 0.63

IR (film): 3286, 2922, 1597, 1556, 1331, 1216, 1157, 1090, 885, 782, 663, 560, 538 cm^{-1}

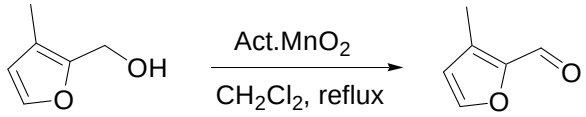
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.88 (t, J = 2.5Hz, 1H), 2.16 (s, 6H), 2.42 (s, 3H), 4.08 (d, J = 2.5Hz, 2H), 5.86-5.89 (m, 2H), 6.18 (d, J = 3.2Hz, 2H), 6.25 (s, 1H), 7.24 (d, J = 7.9Hz, 2H), 7.80 (d, J = 8.2Hz, 2H)

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 13.53 (q, 2C), 21.51 (q), 33.88 (t), 52.84 (d), 70.99 (d), 78.21 (s) 106.3 (d, 2C), 111.0 (d, 2C), 128.0 (d, 2C), 128.9 (d, 2C), 137.3 (s), 143.1 (s), 147.5 (s), 152.3 (s)

MS (EI): m/z (%) = 383 (19) (M^+), 302 (16), 228 (35), 227 (23), 175 (100)

HRMS (ESI): $C_{21}H_{21}NO_4S$: Calcd: 406.1088 $(M+Na)^+$; found: 406.10086 $(M+Na)^+$

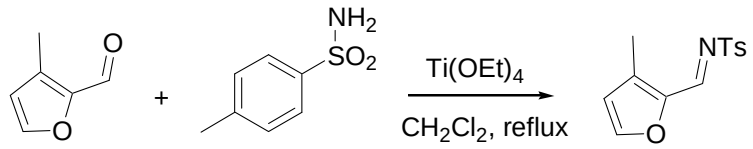
4. **3-methyl furfural**[101] (**102b**/SP316)



2.88g (25.7 mmol, 1 eq) of 3-methyl furfurol was dissolved in 50ml of DCM. 5.2g (60 mmol, 2.2 eq) of activated manganese dioxide was added in portion. The suspension was refluxed for 2 days and then filtered through celite. The solvent was evaporated and the residue was purified over column chromatography (PE/EtOAc) to furnish 2.05g (75%) of the aldehyde as a colorless liquid.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 6.43 (d, J = 1.7Hz, 1H), 7.56 (d, J = .18Hz, 1H), 9.77 (s, 1H)

5. **(3-methylfuran-2-yl)-N-tosylmethanimine** (**103b**/SP321)



The procedure for **103a** was repeated. The crude product was recrystallized over pet ether to give a pale white solid in 91% isolated yield.

M.P: 115-117 ^{o}C

R_f (PE:EtOAc, 2:1) = 0.06

IR (neat): 3125, 2923, 1604, 1547, 1314, 1286, 1151, 1085, 892, 830, 774, 673, 655 cm^{-1}

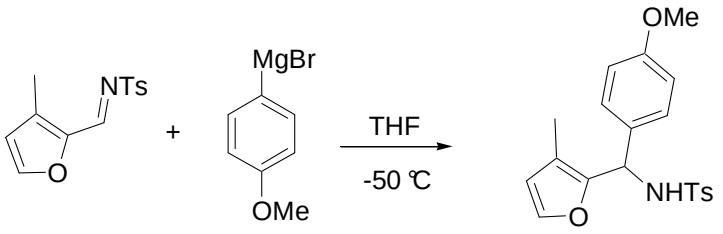
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 2.42 (s, 3H), 6.48 (d, J = 1.5Hz, 1H), 7.32 (d, J = 7.9Hz, 2H), 7.63 (d, J = 1.6Hz, 1H), 7.88 (d, J = 7.9Hz, 2H) 8.92 (s, 1H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 11.12 (q), 21.63 (q), 116.2 (d), 127.9 (d, 2C), 129.7 (d, 2C), 135.7 (s), 138.1 (s), 144.2 (s), 145.3 (s), 149.2 (s), 154.3 (d)

MS (EI): m/z (%) = 264 (39) (M+1), 155 (100), 91 (40)

Anal. Calcd. For $C_{13}H_{13}NO_3S$: C 59.30, H 4.98, N 5.32; found: C 59.27, H 4.97, N 5.35.

6. **(4-methoxyphenyl)(3-methylfuran-2-yl)-N-tosylmethanamine** (**104c**/SP405)



300 mg (1.14 mmol, 1 eq) of the iminosulfonxide **103b** was dissolved in 15ml of dry THF in a flame dried RB flask under nitrogen. The solution was cooled to -50 ^{o}C and then a THF solution of p-methoxy phenyl magnesium bromide (2.3 mmol, 2 eq) was added slowly. The

reaction mixture was stirred at the same temperature for 6h and then warmed to room temperature overnight. Quenched with aqueous ammonium chloride and extracted with ether. Dried over magnesium sulphate and the solvent was evaporated under vacuum. Column chromatography (PE/EtOAc) furnished 355 mg (84%) of the amine as a white solid.

M.P: 94-96 ^{o}C

R_f (PE:EtOAc, 4:1) = 0.29

IR (neat): 3233, 2926, 2841, 1609, 1508, 1429, 1321, 1244, 1156, 1088, 1053, 1025, 922, 812, 735, 662, 547 cm^{-1}

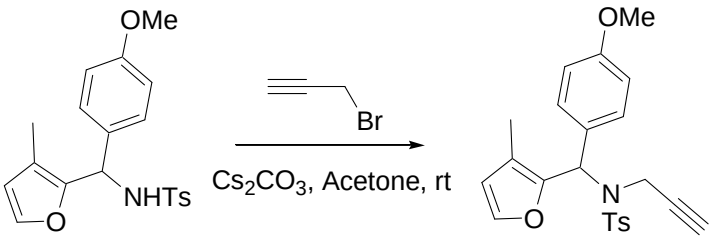
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.80 (s, 3H), 2.36 (s, 3H), 3.76 (s, 3H), 5.25 (d, J = 8.3Hz, 1H), 5.52 (d, J = 8.4Hz, 1H), 5.97 (d, J = 1.8Hz), 6.76-6.80 (m, 2H), 7.07 (d, J = 1.8 Hz, 1H), 7.10-7.16 (m, 4H), 7.51 (d, J = 8.3Hz, 2H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 9.53 (q), 21.45 (q), 52.44 (d), 52.28 (q), 112.6 (d), 113.8 (d, 2C), 116.9 (s), 126.8 (d, 2C), 128.2 (d, 2C), 129.2 (d), 130.6 (s), 137.3 (s), 141.3(d), 142.9 (s), 146.5 (s), 159.1 (s)

MS (EI): m/z (%) = 371 (4) (M^+), 290 (16), 216 (88), 91 (8)

HRMS (ESI): $C_{20}H_{21}NO_4S$: Calcd: 394.1088 $(M+Na)^+$; found: 394.1083 $(M+Na)^+$

7. N-**((4-methoxyphenyl)(3-methylfuran-2-yl)methyl)-N-tosylprop-2-yn-1-amine** (**105c**/SP408)



324 mg (0.87 mmol, 1 eq) of the amine **104c** was dissolved in 10ml of dry acetone. 605 mg (1.74 mmol, 2 eq) of cesium carbonate was added followed by 0.19ml (1.74 mmol, 2 eq) of

propargyl bromide (80% solution in toluene). The suspension was stirred overnight at room temperature. The solvent was removed and 10ml of water was added. The crude product was extracted with ether. Dried over magnesium sulfate and column chromatography over silica gel (PE/EtOAc) furnished 290 mg (81%) of the product as an yellow oil.

R_f (PE:EtOAc, 4:1) = 0.41

IR (film): 3287, 2928, 2837, 1734, 1609, 1509, 1332, 1247, 1156, 1089, 1031, 890, 803, 743, 655 cm^{-1}

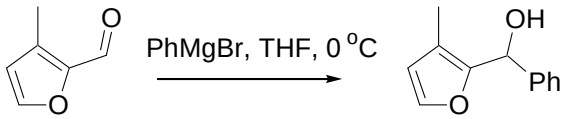
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.79 (s, 3H), 2.01 (s, 3H), 2.40 (s, 3H), 3.75 (s, 3H), 4.03 (dd, J = 19.2, 2.7Hz, 1H), 4.22 (dd, J = 18.5, 2.6Hz, 1H), 6.17 (d, J = 1.8Hz, 1H), 6.19 (s, 1H), 6.82 (d, J = 8.6Hz, 2H), 7.10 (d, J = 9.0Hz, 2H), 7.21-7.25 (m, 3H), 7.66 (d, J = 8.6Hz, 2H)

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 9.82 (q), 21.52 (q), 34.95 (t), 55.28 (d), 55.69 (q), 71.12 (d), 79.34 (s), 112.8 (d), 113.8 (d, 2C), 118.9 (s), 127.6 (d, 2C), 128.9 (d, 2C), 129.1 (d, 2C), 129.2 (s), 137.1 (s), 141.5 (s), 143.1 (d), 146.4 (s), 159.2 (s)

MS (EI): m/z (%) = 409 (28) (M^+), 254 (55), 201 (100)

HRMS (ESI): $C_{23}H_{23}NO_4S$: Calcd: 432.1245 $(M+Na)^+$; found: 432.1241 $(M+Na)^+$

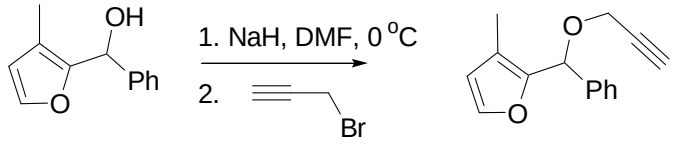
8. **(3-methylfuran-2-yl)(phenyl)methanol**[102] (**111e**/SP420)



1.25 ml (3.5 mmol, 1.3 eq) of phenyl magnesium bromide was taken in 10ml of dry THF under nitrogen. The system was cooled to 0 °C and a THF solution of 300 mg (2.7 mmol, 1 eq) 3-methyl furfural was slowly added. The reaction mixture was stirred at the same temperature for 1h and quenched with ammonium chloride. Extracted with ether and dried over magnesium sulfate. Column chromatography over silica gel (PE/EtOAc) furnished 380 mg (75%) of the alcohol as a white solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 3H), 2.30 (d, J = 4.8Hz, 1H), 5.87 (d, J = 4.7Hz, 1H), 6.20 (d, J = 1.8Hz, 1H), 7.25-7.44 (m, 6H)

9. **3-methyl-2-(phenyl(prop-2-ynyloxy)methyl)furan** (**112e**/SP421)



240 mg (1.27 mmol, 1 eq) of the alcohol **111e** was dissolved in 8ml of dry DMF under nitrogen. The system was cooled to 0 °C and 34 mg (1.4 mmol, 1.1 eq) of dry sodium hydride was added in portions. The reaction mixture was stirred at 0 °C for 30 minutes and then 0.18ml (1.6 mmol, 1.3 eq) of propargyl bromide (80% solution in toluene) was added. The reaction mixture was warmed to room temperature slowly and after 3h, 21 mg (0.9 mmol, 0.7 eq) more of the sodium hydride was added at 0 °C. The reaction mixture was warmed to room temperature overnight and quenched with ammonium chloride. The organic layer was extracted with plenty of water and ether. Dried over magnesium sulfate and column chromatography over silica gel (PE/EtOAc) furnished 185 mg (65%) of the product as a pale yellow oil.

R_f (PE: EtOAc, 5:1) = 0.60

IR (film): 3289, 2924, 2855, 1966, 1598, 1493, 1450, 1063, 1012, 949, 738, 694, 632 cm^{-1}

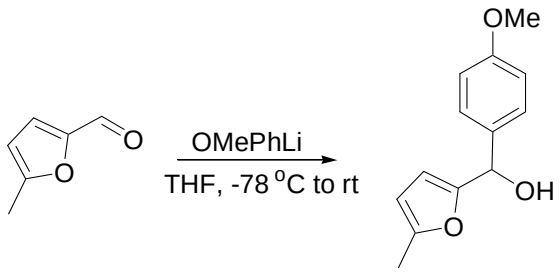
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.10 (s, 3H), 2.43 (t, J= 2.4Hz, 1H), 4.08 (dd, J = 16.1, 2.5Hz, 1H), 4.20 (dd, J = 15.9, 2.2Hz, 1H), 5.78 (s, 1H), 6.20 (d, J = 1.8Hz, 1H), 7.25-7.45 (m, 6H)

^{13}C-NMR (62.49 Mz, $CDCl_3$): δ = 9.180 (q), 53.14 (t), 70.71 (d), 72.49 (d), 77.41 (s), 110.75 (d), 112.6 (s), 124.8 (d, 2C), 126.0 (d), 126.1 (d, 2C), 136.5 (s), 139.9 (d), 144.8 (s)

MS (ESI): m/z (%) = 226 (0.5) (M^+), 171 (100), 128 (1)

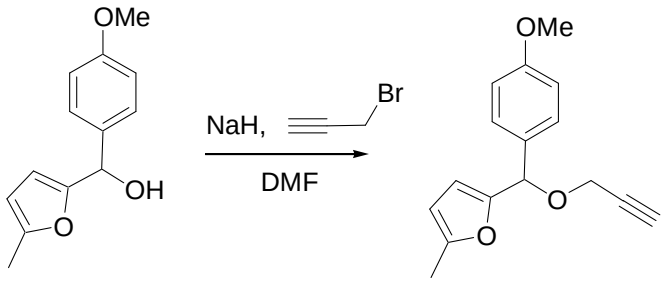
HRMS (ESI): $C_{15}H_{14}O_2$: Calcd: 227.0994 $(M+1)^+$; found: 227.1067 $(M+1)^+$

10. **(4-methoxyphenyl)(5-methylfuran-2-yl)methanol**[103] (**111a**/SP496)



1.25ml (10 mmol, 1.2 eq) of 4-bromo anisole was dissolved in 15ml of dry THF under nitrogen. The system was cooled to -78 ^{o}C and 4ml (10 mmol, 1.2 eq) of *n*-butyl lithium was added. The reaction mixture was stirred at the same temperature for 30 minutes and then 0.83ml (8.4 mmol, 1 eq) of 5-methyl furfural was added slowly. The reaction mixture was warmed to room temperature in one hour and then quenched with ammonium chloride. Extracted with ether and dried over magnesium sulfate. The solvent was removed in vacuum and the crude alcohol (1.6g, crude yield 80%, the product was a mixture of two non-separable alcohols out of which the required one was in major proportion) was used as such in the next step.

11. **2-((4-methoxyphenyl)(prop-2-ynyloxy)methyl)-5-methylfuran** (**112a**/SP497)



1.60g (7.20 mmol, 1 eq) of the crude alcohol **111a** was dissolved in 15ml of dry DMF under nitrogen. The system was cooled to 0 ^{o}C and 216 mg (9.0 mmol, 1.2 eq) of dry sodium hydride was added in portions. The reaction mixture was stirred at 0 ^{o}C for 30 minutes and then 0.99ml (9 mmol, 1.2 eq) of propargyl bromide (80% solution in toluene) was added. The reaction mixture was warmed to room temperature slowly and after 3h, 120 mg (5 mmol, 0.7 eq) more of the sodium hydride was added at 0 ^{o}C. The reaction mixture was warmed to room temperature overnight and quenched with ammonium chloride. The organic layer was

extracted with plenty of water and ether. Dried over magnesium sulfate and column chromatography over silica gel (PE:EtOAc) furnished 1.0g (54%) of the product as pale yellow oil.

R_f (PE: EtOAc, 4:1) = 0.46

IR (film): 3285, 2920, 2837, 1610, 1510, 1245, 1172, 1061, 1021, 836, 786, 634 cm^{-1}

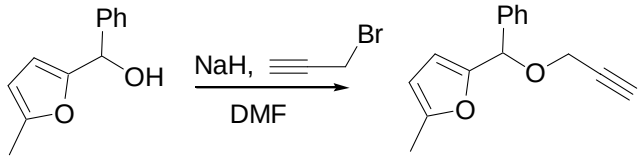
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 2.42 (t, J = 2.6Hz, 1H), 3.79 (s, 3H), 4.80 (dd, J = 15.9, 2.3Hz, 1H), 4.17 (dd, J = 15.8, 2.3Hz, 1H), 5.86-5.89 (m, 1H), 6.03 (d, J = 3.2Hz, 1H), 6.89 (d, J = 8.7Hz, 2H), 7.36 (d, J = 8.7Hz, 2H)

^{13}C-NMR (75.47 MHz, $CDCl_3$): δ = 13.65 (q), 50.76 (t), 55.24 (q), 73.76 (d), 79.59 (s), 106.0 (d), 110.1 (d), 113.7 (d, 2C), 128.8 (d, 2C), 130.4 (s), 151.7 (s), 152.7 (s), 159.4(s)

MS (EI): m/z (%) = 256 (26) (M^+), 228 (31), 135 (100)

HRMS (ESI): $C_{16}H_{16}O_3$: Calcd: 257. 1177$(M+1)^+$; found: 257.1172$(M+1)^+$

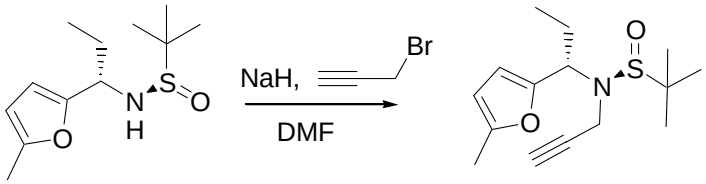
12. **2-methyl-5-(phenyl(prop-2-ynyloxy)methyl)furan**[104] (**112b**/SP351)



1.20g (6.40 mmol, 1 eq) of the alcohol was dissolved in 12ml of dry DMF under nitrogen. The system was cooled to 0 ^oC and 168 mg (7.0 mmol, 1.1 eq) of dry sodium hydride was added in portions. The reaction mixture was stirred at 0 ^oC for 30 minutes and then 0.78ml (7.0 mmol, 1.1 eq) of propargyl bromide (80% solution in toluene) was added. The reaction mixture was warmed to room temperature slowly and after 3h ,107 mg (4.40 mmol, 0.7 eq) more of the sodium hydride was added at 0 ^oC. The reaction mixture was warmed to room temperature overnight and quenched with ammonium chloride. The organic layer was extracted with plenty of water and ether. Dried over magnesium sulfate and column chromatography over silica gel (PE:EtOAc) furnished 1.2g (83%) of the product as pale yellow oil.

^{1}H-NMR 300 MHz, $CDCl_3$): δ = 2.32 (s, 3H), 2.56 (t, J = 2.5Hz, 1H), 4.17-4.19 (m, 2H), 5.62 (s, 1H), 5.95-5.97 (m, 1H), 6.12 (d, J = 3.0Hz, 1H), 7.36-7.48 (m, 5H)

13. **(*R*)-(+)-2-Methyl-*N*-[(5-methylfuran-2-yl)propyl]-*N*-prop-2-in-1-ylpropan-2-sulfoxamide** (**105f**/SP513B)



380 mg (1.56 mmol, 1 eq) of the sulfoxamide was dissolved in 10ml of dry DMF under nitrogen. Cooled to 0 ^{o}C and 125 mg (3.1 mmol, 2 eq, 60% in mineral oil) of sodium hydride was added in portions. The reaction mixture was stirred for 30 minutes and then 0.34ml (3.1 mmol, 2 eq) of propargyl bromide (80% solution in toluene) was added. The reaction mixture was stirred overnight, quenched with ammonium chloride. The organic layer was extracted with plenty of water and ether. Dried over magnesium sulfate, and column chromatography over silica gel (PE:EtOAc) furnished 380 mg (71%) the product as an yellow oil.

$[\alpha]_D^{20}$ = -54.1° (c 0.012, CH_2Cl_2)

R_f (PE: EtOAc, 4:1) = 0.32

IR (film): 3304, 3224, 2960, 2876, 1555, 1455, 1362, 1266, 1220, 1076, 1021, 920, 857, 788, 735, 703 cm^{-1}

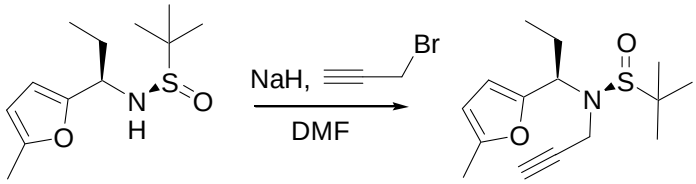
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.05 (t, J = 7.3Hz, 3H), 1.22 (s, 9H), 2.05 (q, J = 7.4Hz, 2H), 2.19 (t, J = 2.4Hz, 1H), 2.26 (s, 3H), 3.15 (dd, J = 18.9, 2.3Hz, 1H), 4.00 (dd, J = 18.9, 2.4Hz, 1H), 4.29 (t, J = 7.5Hz, 1H), 5.88 (d, J = 2.9Hz, 1H), 6.17 (d, J = 3.0Hz, 1H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 11.93 (q), 13.63 (q), 23.10 (q, 3C), 24.64 (t), 32.32 (t), 58.71 (d), 63.61 (s), 70.97 (d), 82.14 (s), 105.9 (d), 109.3 (d), 151.1 (s), 152.0 (s)

MS (ESI): m/z (%) = 281 (5) (M^+), 143 (10), 123 (100)

HRMS (ESI): $C_{15}H_{23}NO_2S$: Calcd: 304.1346 $(M+Na)^+$; found: 304.1343 $(M+Na)^+$

14. **(*s*)-(-)-2-Methyl-*N*-[(5-methylfuran-2-yl)propyl]-*N*-prop-2-in-1-ylpropan-2-sulfoxamide** (**105g**/SP513A)



460 mg (1.9 mmol, 1 eq) of the sulfoxamide was dissolved in 10ml of dry DMF under nitrogen. Cooled to 0 ^oC and 151 mg (3.8 mmol, 2 eq) of sodium hydride was added in portions. The reaction mixture was stirred for 30 minutes and then 0.42ml (3.8 mmol, 2 eq) of propargyl bromide (80% solution in toluene). The reaction mixture was stirred overnight, quenched with ammonium chloride. The organic layer was extracted with plenty of water and ether. Dried over magnesium sulfate, and column chromatography over silica gel (PE:EtOAc) furnished 500 mg (94%) the product as an yellowish soft solid.

$[\alpha]_D^{20}$ = +90.0° (c 0.015, CH_2Cl_2)

M.P: 38-40 ^oC

R_f (PE: EtOAc, 4:1) = 0.28

IR (film): 3048, 2965, 2859, 1593, 1531, 1457, 1264, 1073, 1020, 781, 734, 702 cm^{-1}

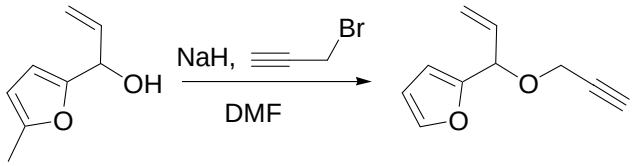
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.3Hz, 3H), 1.26 (s, 9H), 1.85-2.01 (m, 2H), 2.18 (t, J = 2.3Hz, 1H), 2.30 (s, 3H), 3.28 (d, J = 18.6, 2.3Hz, 1H), 4.02 (dd, J = 18.6, 2.6Hz, 1H), 4.19 (t, J = 7.7Hz, 1H), 5.94-5.97 (m, 1H), 6.21 (d, J = 3.2Hz, 1H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 10.84 (q), 13.83 (q), 23.13 (q, 3C), 24.20 (t), 32.30 (t), 58.77 (d), 63.61 (s), 70.96 (d) 82.17 (s), 105.2 (d), 109.3 (d), 151.1 (s), 152.1 (s)

MS (ESI): m/z (%) = 281 (5) (M^+), 143 (10), 123 (100)

HRMS (ESI): $C_{15}H_{23}NO_2S$: Calcd: 304.1346 $(M+Na)^+$; found: 304.1343 $(M+Na)^+$

15. **2-methyl-5-(1-(prop-2-ynyloxy)allyl)furan** (**112c**/SP385)



610 mg (4.4 mmol, 1 eq) of 1-(5-methylfuran-2-yl)prop-2-en-1-ol was dissolved in 10ml of dry DMF under nitrogen. The system was cooled to 0 ^oC and 117 mg (4.9 mmol, 1.1 eq) of dry sodium hydride was added in portions. Stirred for 30 minutes, and then 0.59ml (5.2 mmol, 1.2 eq) of propargyl bromide was added. The reaction mixture was stirred for overnight, quenched with ammonium chloride and extracted with plenty of water and ether. Dried over magnesium sulfate and column chromatography over silica gel (PE:EtOAc) furnished 544 mg (70%) of the product as an yellow oil.

R_f (PE: EtOAc, 5:1) = 0.63

IR (film): 3293, 2922, 2855, 1558, 1440, 1358, 1219, 1059, 1019, 925, 783, 661, 631 cm^{-1}

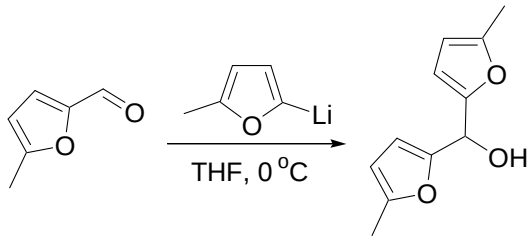
^{1}H-NMR 250 MHz, $CDCl_3$): δ = 2.28 (s, 3H), 2.43 (t, J = 2.2Hz, 1H), 4.12 (dd, J = 15.7, 2.3Hz, 1H), 4.18 (dd, J = 15.7, 2.3Hz, 1H), 5.02 (d, J = 7.0Hz, 1H), 5.30-5.44 (m, 2H), 5.90-5.93 (m, 1H), 5.97-6.10 (m, 1H), 6.21 (d, J = 3.2Hz, 1H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 13.63 (q), 55.05 (t), 74.20 (d), 74.56 (d), 79.58 (s), 106.1 (d), 109.7 (d), 118.4 (d), 134.4 (s), 150.5 (s), 152.7 (s)

MS (EI): m/z (%) = 176 (19) (M^+), 147 (22), 133 (30), 121 (100), 109 (38), 105 (32), 91 (30), 77 (29), 55(31), 43 (31)

HRMS (ESI): $C_{11}H_{12}O_2$: Calcd: 177.0913 $(M+1)^+$; found: 177.0916 $(M+1)^+$

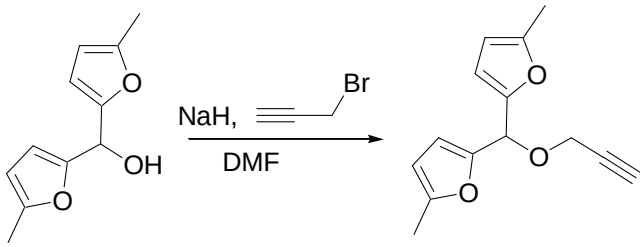
16. **bis(5-methylfuran-2-yl)methanol**[105] (**111d**/SP360)



0.45ml (5 mmol, 1.2 eq) of 5-methyl furfural was dissolved in dry THF under nitrogen. Cooled to 0 °C and 2ml (5mmo, 1.2eq) of *n*-butyl lithium was added. The reaction mixture was stirred for 2h at the same temperature and 0.42ml (4.2 mmol, 1 eq) of 5-methyl furfural was added slowly. The reaction mixture was stirred for 2more hours at 0 °C and then quenched with ammonium chloride. Extracted with ether and dried over magnesium sulfate. The solvent was removed in vacuum and column chromatography over silica gel (PE:EtOAc) furnished 770 mg (95%) of the alcohol as an yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 6H), 2.65 (bs, 1H), 5.70 (d, J = 4.7Hz, 1H), 5.90-5.94 (m, 2H), 6.17 (d, J = 3.0Hz, 2H)

17. **2-methyl-5-((5-methylfuran-2-yl)(prop-2-ynyloxy)methyl)furan** (**112d**/SP370)



750 mg (3.90 mmol, 1 eq) of the alcohol **111d** was dissolved in 10ml of dry DMF under nitrogen. The system was cooled to 0 °C and 103 mg (4.3 mmol, 1.1 eq) of dry sodium hydride was added in portions. The reaction mixture was stirred at 0 °C for 30 minutes and then 0.47ml (4.3 mmol, 1.2 eq) of propargyl bromide (80% solution in toluene) was added. The reaction mixture was warmed to room temperature and after 3h ,75 mg(3.1 mmol, 0.7 eq) more of the sodium hydride was added at 0 °C. The reaction mixture was warmed to room temperature overnight and quenched with ammonium chloride. The organic layer was extracted with plenty of water and ether. Dried over magnesium sulfate and column

chromatography over silica gel (PE:EtOAc) furnished 612 mg (68%) of the product as a pale yellow oil.

R_f (PE: EtOAc, 4:1) = 0.55

IR (film): 3288, 2921, 2854, 1557, 1442, 1354, 1298, 1218, 1056, 1018, 929, 774,633 cm^{-1}

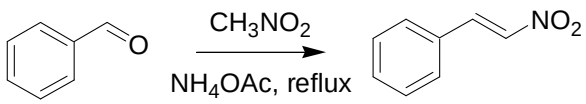
^{1}H-NMR 300 MHz, $CDCl_3$): δ = 2.30 (s, 6H), 2.46 (t, J = 2.4Hz, 1H), 4.14 (d, J = 2.4Hz, 2H), 5.62 (s, 1H), 5.92-5.95 (m, 2H), 6.29 (d, J = 3.0Hz, 2H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 13.67 (q, 2C), 55.27 (t), 68.90 (d), 74.88 (d), 79.33 (s), 106.3 (d), 110.5 (d), 149.0 (s), 152.7 (s)

MS (EI): m/z (%) = 206 (9), 149 (100), 109 (22)

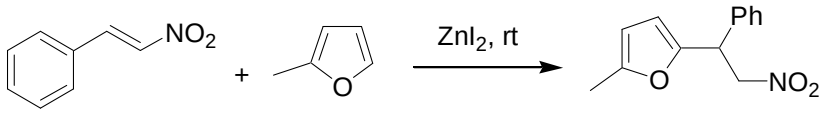
HRMS (ESI): $C_{14}H_{14}O_3$: Calcd: 230.0943 $(M)^+$; found: 230.0942 $(M)^+$

18. **(2-Nitro-vinyl)-benzene**[106] (**106**/SP172)



5ml (49.5 mmol, 1 eq) of benzaldehyde was added to a mixture of 25ml nitromethane and 950 mg (12.5 mmol, 25%) of ammonium acetate. The reaction mixture was refluxed for 5h. Cooled and poured to water and extracted with ether. Column chromatography (PE:EtOAc) furnished 4.5g (64 %) of the nitro styrene as yellow needles.

19. **2-Methyl-5-(2-nitro-1-phenyl-ethyl)-furan**[107] (**107**/SP186)



1g (6.7 mmol, 1 eq) of the nitro styrene **106** was mixed with 5ml of methyl furan. 600 mg of zinc iodide was added to the mixture under nitrogen and the reaction mixture was stirred at rt for 3 days under an inert atmosphere. 15ml of water was added and the product was extracted with ethyl acetate. Dried over $MgSO_4$ and column chromatography (PE:EtOAc) furnished 1.35g (87 %) of the product as a brown oil.

R_f (PE: EtOAc, 2:1) = 0.85

IR (film): 2921, 1552, 1376, 1216, 1022, 786, 703 cm^{-1}

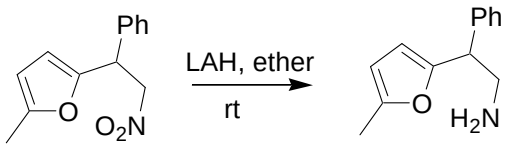
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.21 (s, 3H), 4.79 (dd, J = 12.1, 7.8 Hz, 1H), 4.86 (t, J = 7.8 Hz, 1H), 4.99 (dd, J = 12.8, 8.0 Hz , 1H), 5.88 (d, J = 2.9 Hz, 1H), 5.96 (d, J = 2.9 Hz, 1H), 7.27-7.36 (m, 5H)

^{13}C- NMR (125 Mz, $CDCl_3$): δ = 13.54 (q), 43.61 (d), 78.20 (t), 106.2 (d), 108.1 (d), 127.8 (d, 2C), 127.9 (d, 2C), 128.9 (s), 137.1 (s), 150.0 (s), 152.2 (s)

MS (ESI): m/z (%) = 254 (100) $(M+Na)^+$, 210 (8), 171 (8)

Anal. Calcd. For $C_{13}H_{13}NO_3$: C 67.52, H 5.67, N 6.06; found: C 67.58, H 5.79, N 5.53.

20. **2-(5-Methyl-furan-2-yl)-2-phenyl-ethylamine** (**108**/SP187)



1.30g (4.32 mmol, 1 eq) of the nitro compound **107** was dissolved in 50 ml of dry ether and added slowly to 330 mg (9 mmol, 2 eq.) of $LiAlH_4$ in 100ml of dry ether under nitrogen. The reaction mixture was stirred for 16h at rt. cooled to 0^{o}C, and 5ml of aqueous ammonium chloride was added. The residue was filtered off and the organic part was extracted with ether. Dried over $MgSO_4$, and column chromatography (PE:EtOAc, 1% NEt_3) furnished 650 mg (58%) of the pure amine product as an yellow oil.

R_f (PE: EtOAc, 2:1) = 0.45

IR (film): 3368, 3027, 2920, 1561, 1492, 1452, 1218, 1022, 782, 700 cm^{-1}

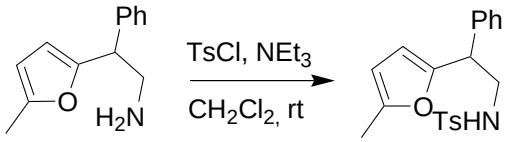
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.60 (bs, 2H), 2.24 (s, 3H), 3.15 (dd, J = 12.7, 7.0 Hz, 1H), 3.3 (dd, J = 12.9, 7.1 Hz, 1H), 3.9 (t, J = 7.8 Hz, 1H) , 5.88 (d, J = 3.2 Hz, 1H), 5.95 (d, J = 3.1 Hz, 1H), 7.22-7.33 (m, 5H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 13.58 (q), 46.54 (d), 49.53 (t), 105.1(d), 106.7 (d) 126.8 (d, 2C), 128.1 (d, 2C), 128.5 (d), 140.8 (s), 151.2 (s), 154.1 (s)

MS (ESI): m/z (%) = 202 (90) (M+1), 185 (100) 167 (10)

HRMS (ESI): $C_{13}H_{15}NO$: Calcd: 202.1274 $(M+1)^+$, found: 202.1226 $(M+1)^+$

21. **2-(5-methylfuran-2-yl)-2-phenyl-N-tosylethanamine** (**109**/SP189)



620 mg (3 mmol, 1 eq) of the amine **108** was dissolved in 20ml of dichloromethane. 600 mg (3 mmol, 1 eq) of tosyl chloride and 0.48ml (3 mmol, 1 eq) of NEt_3 were added and the mixture was stirred at rt for 36h. 20ml of water was added and the organic part was extracted with dichloromethane. Dried over $MgSO_4$ and column chromatography (PE:EtOAc) furnished 900 mg (82 %) of the pure product as an yellow oil.

R_f (PE: EtOAc, 3:1) = 0.58

IR (film): 3266, 2945, 1362, 1157, 1092, 785, 734, 699, 662 cm^{-1}

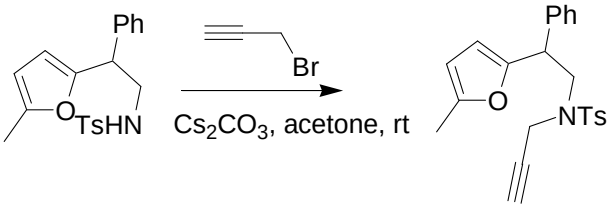
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.2 (s, 3H), 2.41 (s, 3H), 3.32-3.41 (m, 1H), 3.50-3.59 (m, 1H), 4.10 (t, J = 7.85 Hz, 1H), 4.43 (t, J = 6.9 Hz, 1H), 5.84-5.87 (m, 2H), 7.15 (d, J = 8.1 Hz, 2H), 7.23-7.30 (m, 5H), 7.70 (d, J = 8.1 Hz, 2H),

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 13.56 (q), 21.56 (q), 45.16 (d), 46.67 (t), 106.1 (d), 107.7 (d), 127.1 (d, 2C), 127.4 (d, 2C), 127.9 (d, 2C), 128.8 (d), 129.7 (d, 2C), 136.9 (s), 138.9 (s), 143.5 (s), 151.8 (s), 152.0 (s)

MS (ESI): m/z (%) = 378 (100) $(M+Na)^+$

Anal. Calcd. For $C_{20}H_{21}NO_3S$: C 67.58, H 5.95, N 3.94; found: C 67.39, H 5.97, N 3.93.

22. **N-(2-(5-methylfuran-2-yl)-2-phenylethyl)-N-tosylprop-2-yn-1-amine** (**110**/SP190)



815 mg (2.3 mmol, 1 eq), of the compound **109** was dissolved in 20ml of acetone. 1.5g (4.6 mmol, 2 eq) of cesium carbonate and 0.50ml (4.6 mmol, 2 eq) of propargyl bromide were added and the reaction mixture was stirred at rt for 24h. The solvent was removed in vacuum and 20 ml of water was added. The product was extracted with dichloromethane dried over $MgSO_4$. Column chromatography over $MgSO_4$ (PE:EtOAc) furnished 780 mg (86 %)of the product as a brown oil.

R_f (PE: EtOAc, 3:1) = 0.62

IR (film): 2186, 2157, 1453, 1349, 1160, 1094,900, 661 cm^{-1}

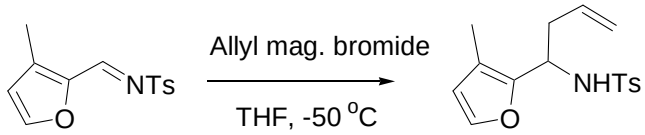
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.10 (t, J = 2.4 Hz, 1H), 2.21 (s, 3H),2.40 (s, 3H), 3.56 (dd, J = 14.0, 7.5 Hz, 1H), 3.74 (dd, J = 18.9, 2.0 Hz, 1H), 3.82 (dd, J = 13.9, 8.0 Hz ,1H), 3.89 (dd, J = 18.9, 7.9 Hz, 1H), 4.34 (t, J = 8.0 Hz, 1H), 5.89 (d, J = 3.1 Hz, 1H), 6.06 (d, J = 3.0 Hz, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.29-7.32 (m, 5H), 7.68 (d, J = 8.2 Hz, 2H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 13.58 q), 21.53 (q), 37.11 (t), 44.78 (d), 49.95 (t), 73.76 (d), 76.64 (s), 106.1 (d), 107.7 (d), 127.1 (d, 2C), 127.7 (d, 2C), 128.1 (d), 128.6 (d, 2C), 129.4 (d, 2C), 135.8 (s), 139.8 (s), 143.5 (s), 151.4 (s), 152.2 (s)

MS (ESI): m/z (%) = 416 (100) $(M+Na)^+$, 394 (5) (M+1)

Anal. Calcd. For $C_{23}H_{23}NO_3S$: C 70.20, H 5.89, N 3.56; found: C 70.23, H 6.03, N 3.53.

23. 1-**(3-methylfuran-2-yl)-N-tosylbut-3-en-1-amine** (**104d**/SP336)



658 mg (2.5 mmol, 1 eq) of the iminosulfonoxide **103b** was dissolved n 10ml of dry THF under nitrogen. The system was cooled to -50 °C and 0.65ml (7.5 mmol, 3 eq) of allyl magnesium bromide was added slowly. The reaction mixture was stirred for 6h at the same temperature, and then warmed to room temperature overnight. Quenched with ammonium chloride, and extracted with ether. Dried over magnesium sulfate, and column chromatography over silica gel (PE:EtOAc) furnished 550 mg (72%) of the product as a white solid.

M.P = 92-93 °C

R_f (PE: EtOAc, 4:1) = 0.33

IR (neat): 3262, 2982, 2923, 1642, 1596, 1495, 1440, 1405, 1313, 1142, 1052, 992, 910, 806, 749, 669 cm^{-1}

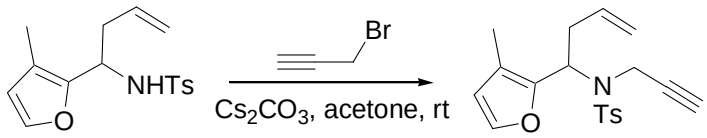
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.75 (s, 3H), 2.36 (s, 3H), 2.45-2.55 (m, 2H), 4.42-4.50 (m, 1H), 4.88-4.92 (m, 1H), 5.01-5.08 (m, 2H), 5.50-5.63 (m, 1H), 7.04 (d, J = 1.8Hz, 1H), 7.15 (d, J = 8.6H, 2H), 7.53 (d, J = 8.4Hz, 2H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 9.43 (q), 21.44 (q), 39.44 (t), 49.05 (d), 112.4 (d), 116.5 (s), 118.7 (t) , 126.7 (d, C), 129.2 (d, 2C), 132.9 (d), 137.5 (s), 140.9 (s), 142.8 (d), 147.0 (s)

MS (EI): m/z (%) = 305 (M^+), 264 (100), 155 (23), 91 (28)

Anal. Calcd. For $C_{16}H_{19}NO_3S$: C 62.93, H 6.27, N 4.59; found: C 62.90, H 6.26, N 4.48.

24. **1-(3-methylfuran-2-yl)-N-(prop-2-ynyl)-N-tosylbut-3-en-1-amine** (**105d**/SP340)



610 mg (2 mmol, 1 eq) of the amine **104d** was dissolved in 15ml of dry acetone. 1.3g (4 mmol, 2 eq) of caesium carbonate was added, followed by 0.44ml (4 mmol, 2 eq) of propargyl bromide (80% solution in toluene). The reaction mixture was stirred for overnight, and the solvent was then removed under vacum.10ml of water was added and the product was extracted with ether. Dried over magnesium sulphate, and column chromatography over silica gel (PE: EtOAc) furnished 553 mg (92%) of the product as a colourless liquid.

R_f (PE: EtOAc, 4:1) = 0.30

IR (film): 3298, 2925, 1597, 1335, 1159, 1091, 1054, 883, 813, 736, 657 cm^{-1}

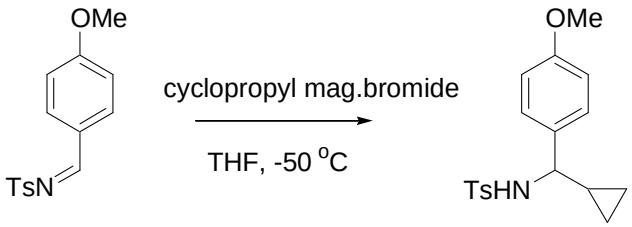
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.86 (s, 3H), 2.05 (t, J = 2.5Hz, 1H), 2.40 (s, 3H), 2.52-2.60 (m, 1H), 2.84-2.95 (m, 1H), 4.05 (dd, J = 11.6,2. 4Hz, 1H), 4.20 (dd, J = 18.6, 2.4Hz, 1H), 4.90-5.06 (m, 3H), 5.43-5.60 (m, 1H), 6.13 (d, J = 1.8Hz, 1H), 7.23-7.28 (m, 2H), 7.76 (d, J = 8.7Hz, 2H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 9.630 (q), 21.52 (q), 33.63 (t), 36.01 (t), 53.15 (d), 71.65 (d), 79.72 (s), 113.1 (d), 117.7 (s), 118.5 (t), 127.6 (d, 2C), 129.3 (d, C), 133.7 (d), 137.6 (s), 141.3 (s), 143.3 (d), 146.8 (s)

MS (EI): m/z (%) = 343 (11) (M^+), 302 (100), 262 (40), 135 (23)

Anal. Calcd. For $C_{19}H_{21}NO_3S$: C 66.45, H 6.16, N 4.08; found: C 66.35, H 6.22, N 4.09.

25. **Cyclopropyl(4-methoxyphenyl)-N-tosylmethanamine** (**114a**/SP352)



400 mg (1.38 mmol, 1 eq) of (4-methoxyphenyl)-N-tosylmethanimine was dissolved in 20ml of dry THF. Cooled to -50 ^{o}C and 5.53ml (2.8 mmol, 2 eq) of cyclopropyl magnesium bromide was added slowly and then stirred for 6h at the same temperature. The reaction mixture was then warmed to room temperature overnight, quenched with ammonium chloride, and extracted with ether. Dried over magnesium sulphate, and column chromatography over silica gel (PE:EtOAc) furnished 350 mg (72%) of the product as a white solid.

M.P = 92-94 ^{o}C

R_f (PE: EtOAc, 4:1) = 0.20

IR (neat): 3242, 3070, 1614, 1511, 1441, 1317, 1300, 1237, 1156, 1093, 1020, 941, 899, 802, 687 cm^{-1}

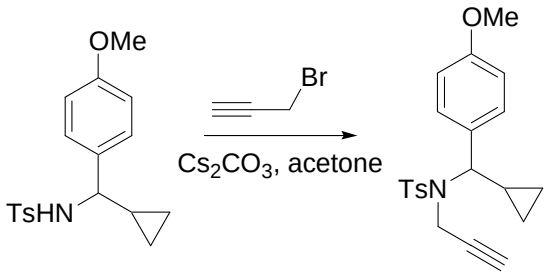
^{1}H-NMR 250 MHz, $CDCl_3$): δ = 0.20-0.26 (m, 2H), 043-0.49 (m, 2H), 1.02-1.12 (m, 1H), 2.37 (s, 3H), 3.63-3.67 (m, 1H), 3.75 (s, 3H), 5.04 (d, J = 5.8Hz, 1H), 6.70 (d, J = 8.7Hz, 2H), 7.03 (d, J = 8.7Hz, 2H), 7.14 (d, J = 8.4Hz 2H), 7.40 (d, J = 8.4Hz, 2H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 3.620 (t), 4.420 (t), 18.06 (d), 21.46 (q), 55.24 (q), 61.96 (d), 113.6 (d, 2C), 127.1 (d, 2C), 128.0 (d, 2C), 129.2 (d, 2C), 132.6 (s), 137.9 (s), 142.9 (s), 158.8 (s)

MS (ESI): m/z (%) = 354 (100) $(M+Na)^{+}$, 161 (61)

Anal. Calcd. For $C_{18}H_{21}NO_3S$: C 65.23, H 6.39, N 4.23; found: C 65.23, H 6.39, N 4.24.

26. **N-(cyclopropyl(4-methoxyphenyl)methyl)-N-tosylprop-2-yn-1-amine** (**115a**/SP359)



300 mg (0.90 mmol, 1 eq) of the amine **114a** was dissolved in 15ml of dry acetone. 585 mg (1.8 mmol, 2 eq) of caesium carbonate was added, followed by 0.19 ml (1.8 mmol, 2 eq) of propargyl bromide (80% solution in toluene). The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum, 10ml of water was added and the product was extracted with ether. Dried over magnesium sulphate, and column chromatography over silica gel (PE:EtOAc) furnished 260 mg (78%) of the product as a white solid.

M.P = 95-97 ^{o}C

R_f (PE: EtOAc, 4:1) = 0.21

IR (neat): 3283, 3003, 2836, 1609, 1510, 1329, 1245, 1150, 1090, 1052, 1029, 893, 813, 658 cm^{-1}

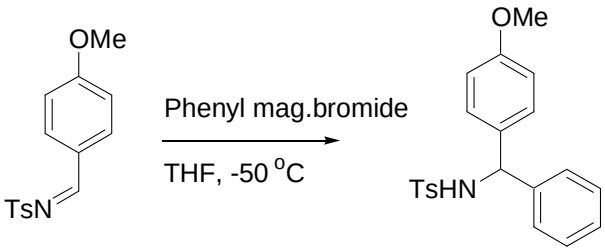
^{1}H-NMR (250 MHz, $CDCl_3$): δ = -0.04-0.03 (m, 1H), 0.07-0.13 (m, 1H), 0.28-0.38 (m, 1H), 0.56-0.65 (m, 1H), 1.34-1.41 (m, 1H), 2.08 (t, J = 2.5Hz, 1H), 2.31 (s, 3H), 3.63-3.71 (m, 4H), 3.94-4.01 (m, 1H), 4.11 (dd, J = 18.6, 2.3Hz, 1H), 6.70 (d, J = 8.7Hz, 2H), 7.17-7.24 (m, 4H), 7.64-768 (d, J = 8.4Hz, 2H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 5.790 (t), 6.41 (t), 13.82 (d), 21.55 (q), 33.47 (t), 55.27 (q), 66.04 (d), 72.26 (d), 80.12 (s), 113.6 (d, 2C), 127.6 (d, 2C), 129.2 (d, 2C), 129.3 (d, 2C), 131.2 (s), 138.4 (s), 143.1 (s), 159.0 (s)

MS (ESI): m/z (%) = 370 (22) $(M+1)^+$, 275 (25), 207 (23), 187 (100), 161 (68), 149 (41)

HRMS (ESI): $C_{21}H_{23}NO_3S$: Calcd: 392.1296 $(M+Na)^+$; found: 392.1294 $(M+Na)^+$

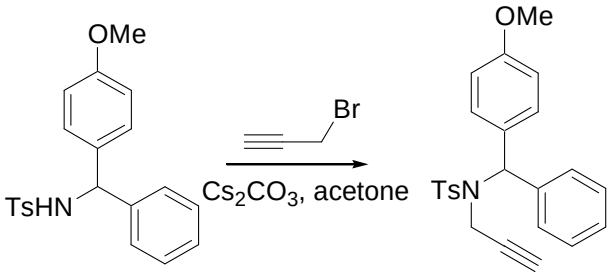
27. **(4-methoxyphenyl)(phenyl)-N-tosylmethanamine**[108] (**114b**/SP401)



300 mg (1.04 mmol, 1 eq) of (4-methoxyphenyl)-N-tosylmethanimine was dissolved in 20ml of dry THF. Cooled to -50 ^{o}C, and 0.75ml (2.08 mmol, 2 eq) phenyl magnesium bromide was added slowly and then stirred for 6h at the same temperature. The reaction mixture was then warmed to room temperature overnight, quenched with ammonium chloride, and extracted with ether. Dried over magnesium sulphate, and column chromatography over silica gel (PE:EtOAc) furnished 250 mg (66%) of the product as a white solid.

^{1}H-NMR 300 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 3.75 (s, 3H), 4.94 (d, J = 7.1Hz, 1H), 5.52 (d, J = 7.0Hz, 1H), 6.74 (d, J = 8.7Hz, 2H), 6.99 (d, J = 8.7Hz, 2H), 7.08-7.22 (m, 7H), 7.56 (d, J = 8.3Hz, 2H)

28. **N-((4-methoxyphenyl)(phenyl)methyl)-N-tosylprop-2-yn-1-amine** (**115b**/SP404)



250 mg (0.68 mmol, 1 eq) of the amine **114b** was dissolved in 15ml of dry acetone. 470 mg (1.40 mmol, 2 eq) of caesium carbonate was added, followed by 0.14 ml (1.40 mmol, 2 eq) of propargyl bromide (80% solution in toluene). The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum, 10ml of water was added and the product was extracted with ether. Dried over magnesium sulphate, and column chromatography over silica gel (PE:EtOAc) furnished 270 mg (98%) of the product as a colourless oil.

R_f (PE: EtOAc, 4:1) = 0.33

IR (film): 3286, 2933, 2837, 1733, 1608, 1509, 1333, 1304, 1248, 1156, 1090, 1030, 900, 812, 699, 662, 542 cm^{-1}

^{1}H-NMR 250 MHz, $CDCl_3$): δ = 1.94 (t, J = 2.5Hz, 1H), 2.41 (s, 3H), 3.78 (s, 3H), 4.05 (d, J = 2.5Hz, 2H), 6.29 (s, 1H), 6.76 (d, J = 8.7Hz 2H), 7.02 (d, J = 8.7Hz, 2H), 7.14-7.26 (m, 7H), 7.70 (d, J = 8.4Hz, 2H)

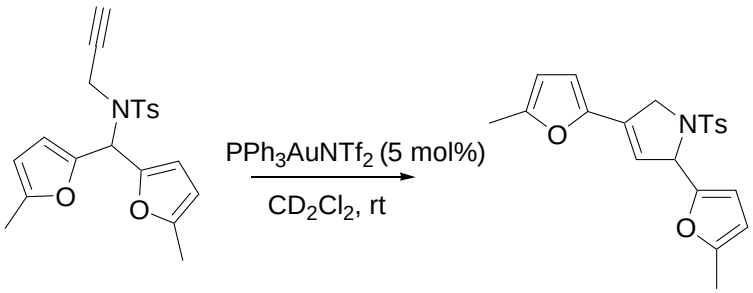
^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.55 (q), 34.94 (t), 55.26 (q), 64.67 (d), 72.24 (d), 79.12 (s), 113.6 (d, 2C), 125.5 (d, 2C), 127.6 (d, 2C), 128.2 (d, 2C), 128.7 (d, 2C), 129.2 (d), 130.1 (d, 2C), 130.5 (s), 137.6 (s), 138.6 (s), 143.2 (s), 159.1 (s)

MS (EI): m/z (%) = 405 (3) (M^+), 250 (100), 234 (23), 197 (84)

HRMS (ESI): $C_{24}H_{23}NO_3S$: Calcd: 428.1296 $(M+Na)^+$; found: 428.1296 $(M+Na)^+$

B. Gold catalysis of the furyl-alkyne substrates

29. **2,5-dihydro-2,4-bis(5-methylfuran-2-yl)-1-tosyl-1H-pyrrole** (**118a**/SP293/SP295)



20 mg (0.05 mmol) of the substrate **105a** was dissolved in 0.5ml of CD_2Cl_2 in an NMR tube. 1.85 mg (5 mol%) of the catalyst was added and the reaction was traced by ^{1}H-NMR. The starting material disappeared in 4 minutes giving rise to peaks characteristic for the rearranged product.

A preparative scale reaction is done in a small round bottom flask with 40 mg (0.10 mmol, 1 eq) of the substrate 3 and 3.7 mg (5 mol%) of the catalyst. The reaction is finished in five

minutes .The solvent was evaporated and column chromatography (PE:EtOAc) furnished 17 mg (42%) of the product as an yellow oil.

R_f (PE:EtOAc, 4:1) = 0.37

IR (film): 3121, 2920, 2870, 1734, 1595, 1448, 1342, 1161, 1093, 1019, 780, 668, 602, 547 cm^{-1}

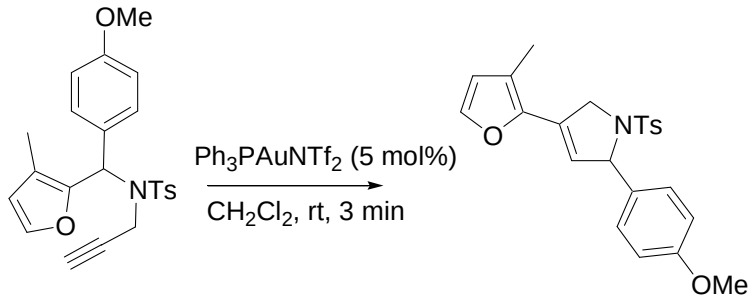
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.05 (s, 3H), 2.28 (s, 3H), 2.38 (s, 3H), 4.40-4.52 (m, 2H), 4.62-4.66 (m, 1H), 5.76-5.79 (m, 1H), 5.84 (dd, J = 3.1, 0.96Hz, 1H) 5.98 (dd, J = 3.1, 0.98Hz, 1H), 6.16 (d, J = 3.2Hz, 1H), 6.20 (d, J = 3.2Hz, 1H), 7.18 (d, J = 7.98Hz, 2H), 7.52 (d, J = 7.98Hz, 2H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 13.45 (q), 13.61 (q), 21.44 (q), 53.66 (t), 63.70 (d), 106.2 (d), 107.4 (d), 109.3 (s), 109.4 (s), 117.9 (d), 127.1 (d, 2C), 128.3 (s), 129.3 (d, 2C), 135.8 (s), 142.9 (s), 146.4 (s), 150.3 (s), 152.1 (s), 153.0 (s)

MS (EI): m/z (%) = 383 (9) (M^+), 229 (100), 228 (69), 213 (20), 186 (44)

HRMS (ESI): $C_{21}H_{21}NO_4S$: Calcd: 384.1191 $(M+1)^+$; found: 384.1264 $(M+1)^+$

30. **2,5-dihydro-2-(4-methoxyphenyl)-4-(3-methylfuran-2-yl)-1-tosyl-1H-pyrrole** (**118c**/SP410)



210g (0.51 mmol, 1 eq) of the substrate **105c** was dissolved in 5ml of DCM in an RB flask. 4 mg (1mol %) of the catalyst was added and the reaction was followed with TLC. The starting material disappeared in 5minutes and a new spot appeared. Filtered through celite and column

chromatography over silica gel (PE:EtOAc) furnished 165 mg (78%) of the product as an yellow oil

R_f (PE:EtOAc, 4:1) = 0.31

IR (film): 3286, 2925, 1610, 1510, 1346, 1249, 1162, 1094, 1063, 1033, 733, 704, 667 cm^{-1}

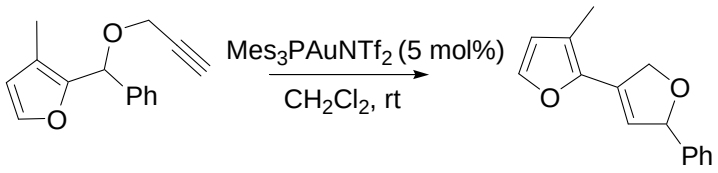
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.08 (s, 3H), 2.37 (s, 3H), 3.79 (s, 3H), 4.58-4.70 (m, 2H), 5.58-5.62 (m, 1H), 5.69-5.73 (m, 1H), 6.23 (d, J = 1.8Hz, 1H), 6.80 (d, 8.8Hz, 2H), 7.16-7.26 (m, 5H), 7.54 (d, J = 8.3Hz, 2H)

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 11.20 (q), 21.04 (q), 54.87 (t), 55.31 (q), 70.04 (d), 113.8 (d, 2C), 114.7 (d), 119.2 (s), 122.1 (d), 127.2 (d), 127.7 (s), 128.7 (d), 129.4 (d), 132.9 (s), 135.5 (s), 141.4 (d), 143.1 (s), 143.9 (s), 159.3 (s)

MS (EI): m/z (%) = 409 (27), 254 (100), 121 (12)

HRMS (ESI): $C_{23}H_{23}NO_4S$: Calcd: 410.1426 $(M+1)^+$; found: 410.1426 $(M+1)^+$

31. **2-(2,5-dihydro-5-phenylfuran-3-yl)-3-methylfuran** (**116e**/SP424)



90 mg (0.40 mmol, 1 eq) of the substrate **112e** was dissolved in DCM. 17 mg (5 mol %) of the catalyst was added. The reaction was followed by TLC. The starting material disappeared in 5 min. Filtered through celite and column chromatography over silica gel (PE:EtOAc) furnished 40 mg (44%) of the product as an pale yellow oil.

R_f (PE: EtOAc, 4:1) = 0.50

IR (film): 3029, 2847, 2359, 2340, 1650, 1492, 1454, 1352, 1301, 1091, 1069, 1026, 889, 843, 745, 697, 669 cm^{-1}

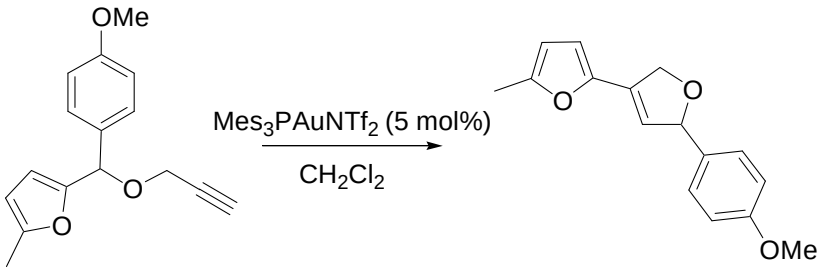
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.13 (s, 3H), 5.07-5.13 (m, 1H), 5.20-5.27 (m, 1H), 5.92-5.96 (m, 1H), 5.98-6.01 (m, 1H), 6.27 (d, J = 1.8Hz, 1H), 7.26-7.35 (m, 6H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 10.46 (q), 55.08 (t), 88.08 (d), 114.0 (d), 114.2 (s), 121.3 (d), 125.9 (d, 2C), 127.3 (s), 127.9 (d), 128.8 (d, 2C), 140.7 (s), 141.4 (d), 156.8 (s)

MS (ESI): m/z (%) = 225 (22) $(M-1)^+$, 209 (25), 181 (22), 145 (18), 131 (100), 117 (27), 109 (27), 105 (21)

HRMS (ESI): $C_{15}H_{14}O_2$: Calcd: 227.0994 $(M+1)^+$; found: 227.1060 $(M+1)^+$

32. **2-(2,5-dihydro-5-(4-methoxyphenyl)furan-3-yl)-5-methylfuran** (**116a**/SP383a)



70 mg (0.27 mmol, 1 eq) of the substrate **112a** was dissolved in DCM. 11.5 mg (5 mol %) of the catalyst was added, and the reaction was followed by TLC. The starting material was disappeared in 15 minutes. The solvent was evaporated and column chromatography over silica gel (PE:EtOAc) furnished 30 mg (43%) of the product an yellow oil.

R_f (PE: EtOAc, 4:1) = 0.42

IR (film): 2997, 2836, 1610, 1587, 1509, 1462, 1302, 1244, 1171, 1078, 1020, 827, 780 cm^{-1}

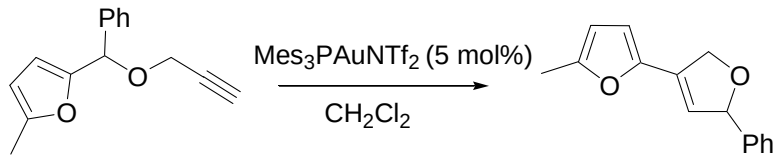
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3H), 3.79 (s, 3H), 4..91 (ddd, J = 11.7, 3.8, 2.2Hz, 1H), 5.05 (ddd, J = 11.7, 5.4, 2.2Hz, 1H), 5.86-5.90 (m, 1H), 5.98-6.04 (m, 2H), 6.14 (d, J = 3.2Hz, 1H), 6.87 (d, J = 8.7Hz, 2H), 7.26 (d, J = 8.7Hz, 1H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 12.79 (q), 52.25 (q), 73.68 (t), 88.04 (d), 106.4 (d), 108.1 (d, 2C), 120.3 (d), 125.6 (d, 2C), 127.0 (s), 128.7 (d, 2C), 129.4 (s), 141.0 (s), 145.3 (s), 151.9 (s)

MS (EI): m/z (%) = 256 (25 (M^+), 228 (30), 135 (100)

HRMS (ESI): $C_{16}H_{16}O_3$: Calcd: 257. 1177 $(M+1)^+$; found: 257.1175 $(M+1)^+$

33. **2-(2,5-dihydro-5-phenylfuran-3-yl)-5-methylfuran** (**116b**/SP354)



269 mg (1.19 mmol, 1 eq) of the substrate **112b** was dissolved in DCM. 50 mg (5 mol %) of the catalyst was added and the reaction was followed with TLC. The starting material disappeared in 5 minutes. Filtered through celite, and column chromatography over silica gel (PE:EtOAc) furnished 80 mg (30%) of the product as an yellowish oil.

R_f (PE: EtOAc, 4:1) = 0.53

IR (film): 3289, 3030, 2851, 1764, 1589, 1492, 1450, 1266, 1019, 912, 783, 734, 696 cm^{-1}

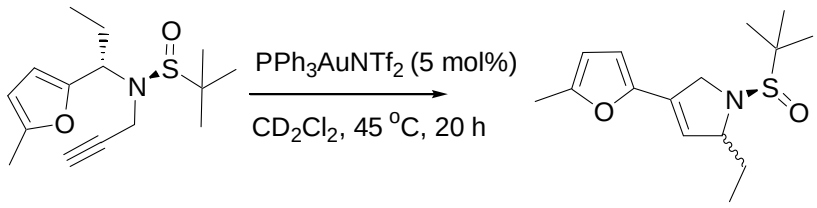
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 4.96 (ddd, J = 11.7, 3.9, 2.3Hz, 1H), 5.08 (ddd, J = 11.7, 5.4, 2.2Hz, 1H), 5.91-5.95 (m, 1H), 5.98-6.01 (m, 1H), 6.04-6.07 (m, 1H), 6.14 (d, J = 3.2Hz, 1H), 7.26-7.40 (m, 5H)

^{13}C-NMR (75.47 MHz, $CDCl_3$): δ = 12.79 (q), 73.68 (t), 88.04 (d), 106.4 (d), 108.1 (d), 120.3 (d), 125.6 (d, 2C), 127.0 (d, 2C), 127.6 (d), 128.7 (s), 141.0 (s), 145.3 (s), 159.1 (s)

MS (ESI): m/z (%) = 227 (0.5) $(M+1)^+$, 131 (100), 117 (26), 109 (53), 103 (48)

HRMS (ESI): $C_{15}H_{15}O_2$: Calcd: 225.0917 $(M-1)^+$; found: 225.0918$(M-1)^+$

34. **1-(tert-Butylsulfonyl)-2-ethyl-4-(5-methylfuran-2-yl)-2,5-dihydro-1H-pyrrole** (**118f**/SP514)



40 mg (0.14 mmol) of the substrate **105f** was dissolved in CD_2Cl_2 in an NMR tube. 5 mg (5 mol %) of the catalyst was added and heated at 45 ^oC. The reaction was traced by ^1H-NMR. The conversion was very slow, and the starting material was almost consumed in 20h. The solvent was evaporated and column chromatography over silica gel (PE:EtOAc) furnished 17 mg (41%) of the product as pale yellow oil. The NMR showed the product as a mixture of two diastereomers in equal ratio.

R_f (PE: EtOAc, 4:1) = 0.28

IR (film): 3048, 2965, 2859, 1593, 1531, 1457, 1264, 1073, 1020, 781, 734, 702 cm^{-1}

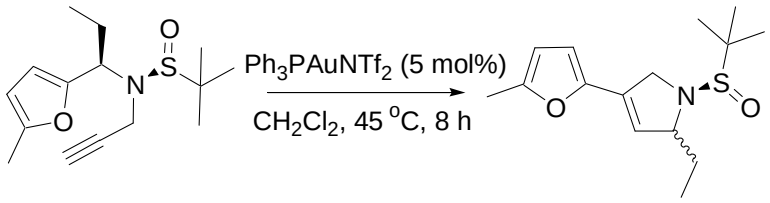
^1H-NMR (250 MHz, $CDCl_3$): δ = 0.86-0.98 (m, 6H), 1.28 (s, 18H), 1.54-1.91(m, 4H), 2.32 (s, 6H), 3.76 (ddd, J = 13.2, 5.2, 2.3Hz, 1H), 4.08-4.17 (m, 1H), 4.44-4.49 (m, 1H), 4.51-4.67 (m, 2H), 4.78 (ddd, J = 13.2, 4.4, 2.2Hz, 1H), 5.85-5.91 (m, 1H), 5.97-6.01 (m, 3H), 6.07-6.11 (m, 2H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 9.03 (q), 13.66 (q), 23.78 (q, 3C), 29.80 (t), 47.07 (t), 57.34 (s), 74.53 (d), 107.2 (d), 108.4 (d), 120.5 (d), 129.3 (s), 147.3 (s), 152.4 (s)

MS (ESI): m/z (%) = 304.1 (47) $(M+Na)^+$, 282.1 (42), 208 (20), 192 (14), 176 (100)

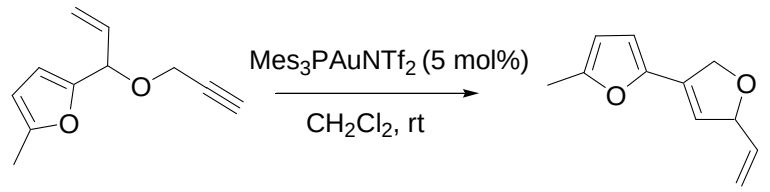
HRMS (ESI): $C_{15}H_{23}NO_2S$: Calcd: 282.1528 $(M+1)^+$; found: 282.1528 $(M+1)^+$

35. **1-(tert-Butylsulfonyl)-2-ethyl-4-(5-methylfuran-2-yl)-2,5-dihydro-1H-pyrrole** (**118g**/SP533)



36 mg (0.13 mmol) of the substrate **105g** was dissolved in CH_2Cl_2 in an RB flask. 4.7 mg (5 mol%) of the catalyst was added and heated at 45 ^oC. The reaction was traced by ^1H-NMR. The conversion was slow, and the starting material was consumed in 8h. The solvent was evaporated and column chromatography over silica gel (PE:EtOAc) furnished 18mg (50%) of the product as a pale yellow oil.

36. **2-(2,5-dihydro-5-vinylfuran-3-yl)-5-methylfuran** (**116c**/SP387)



352 mg (2 mmol, 1 eq) of the substrate **112c** was dissolved in 5ml of DCM. 74 mg (5 mol %) of the catalyst was added, and the reaction was followed by TLC. The reaction was finished in 7h at room temperature. Filtered through celite, and column chromatography over silica gel (PE:EtOAc) furnished 70 mg (20%) of the product as an yellow oil.

R_f (PE: EtOAc, 5:1) = 0.40

IR (film): 3083, 2922, 2851, 1655, 1591, 1527, 1264, 1200, 1082, 1020, 926, 876, 779 cm^{-1}

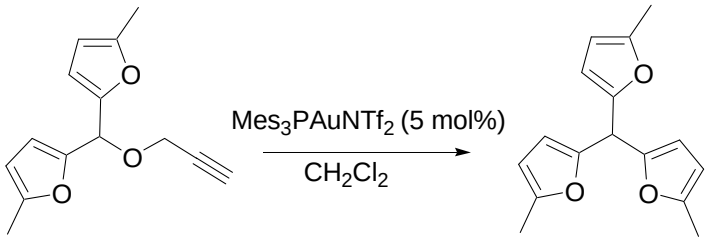
^1H-NMR (500 MHz, $CDCl_3$): δ = 2.32 (s, 3H), 4.81-4.85 (m, 1H), 4.92 (ddd, J = 11.52, 5.5, 2.4Hz, 1H), 5.12-5.14 (m, 1H), 5.29-5.36 (m, 2H), 5.82-5.89 (m, 1H), 5.91-5.93 (m, 1H), 5.97-5.99 (m, 1H), 6.09 (d, J = 3.2Hz, 1H)

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 13.64 (q), 74.00 (t), 88.14 (d), 107.28 (d), 108.8 (d), 115.8 (t), 119.9 (d), 129.8 (d), 137.8 (s), 146.2 (s), 152.7 (s)

MS (EI): m/z (%) = 176 (42) (M^+), 148 (100), 147 (30), 133 (35), 105 (45), 77 (16), 55 (20), 43 (18)

HRMS (ESI): $C_{11}H_{12}O_2$: Calcd: 177.0913 $(M+1)^+$; found: 177.0919 $(M+1)^+$

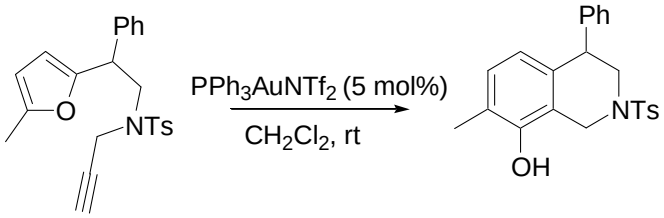
37. **(5-methylfuran-2-yl)methane**[109] (**117**/SP372)



200 mg (1 mmol, 1 eq) of the substrate **112d** was dissolved in DCM. 43 mg (5 mol%) of the catalyst was added and the reaction mixture was heated at 40 ^oC.The reaction progress was followed by TLC. The starting material was consumed in 2h. Filtered through celite, and column chromatography over silica gel (PE:EtOAc) furnished 150 mg (60%) of the product as an yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.20-2.28 (m, 9H), 5.40 (s, 1H), 5.88-5.90 (m, 3H), 5.96-5.97 (m, 3H)

38. **1,2,3,4-tetrahydro-7-methyl-4-phenyl-2-tosylisoquinolin-8-ol** (**119a**/SP305)



22 mg (0.055 mmol, 1 eq) of the substrate **110** was dissolved in 2ml DCM in an RB flask. 2 mg (5 mol%)of the catalyst was added and the reaction was followed by TLC. The starting material disappeared in 10minutes and a new spot appeared. Filtered through celite and column chromatography over silica gel (PE:EtOAc) furnished 14 mg (65%) of the phenol product as a white solid.

M.P: 146-148 ^{o}C

R_f (PE: EtOAc, 4:1) = 0.40

IR (neat): 3360, 22978, 2868, 1493, 1453, 1320, 1228, 1206, 1084, 983, 898, 802, 695 cm^{-1}

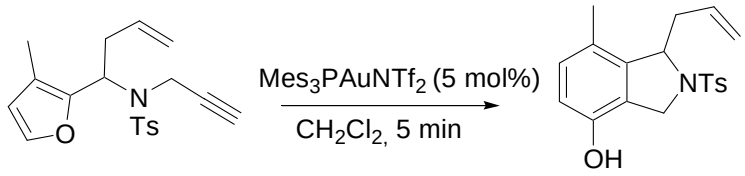
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.2 (s, 3H), 2.4 (s, 3H), 3.16 (dd, J = 11.5, 7.1Hz, 1H), 3.58 (dd, J = 11.7, 4.9Hz, 1H), 4.15-4.38 (m, 3H), 4.97 (s, 1H), 6.37 (d, J = 7.9Hz,1H), 6.88 (d, J = 7.9Hz, 1H), 7.08-7.13 (m, 2H), 7.21-7.35 (m, 5H), 7.66 (d, J = 8.2Hz, 2H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 15.46 (q), 21.63 (q), 44.27 (t), 45.33 (t), 50.90 (d), 119.8, (s) 120.4 (d), 121.6 (d), 127.2 (d), 128.0 (d, 2C), 128.7 (d), 129.1 (d, 2C), 129.2 (d, 2C), 130.0 (s), 133.6 (s), 136.0 (s), 143.4 (s), 144.2 (s), 150.4 (s)

MS (ESI): m/z (%) = 416 (32) $(M+Na)^+$, 394 (5) (M+1), 238 (100)

HRMS (ESI): $C_{23}H_{23}NO_3S$: Calcd: 394.1399 $(M+1)^+$; found: 394.1471 $(M+1)^+$

39. **1-allyl-5-methyl-2-tosylisoindolin-4-ol** (**119d**/SP344)



250 mg (0.73 mmol, 1 eq) of the substrate **105d** was dissolved in 5ml of DCM. 131 mg (5 mol %) of the catalyst was added, and the reaction was followed by TLC. The starting substrate was consumed in 5 minutes. Filtered through celite, and column chromatography over silica gel (PE:EtOAc) furnished 80 mg (32%) of the phenol product as a white solid.

M.P. = 146-148 ^{o}C

R_f (PE: EtOAc, 8:1) = 0.23

IR (neat): 3451, 2917, 2860, 1596, 1505, 1444, 1332, 1305, 1284, 1153, 1093, 1052, 920, 812, 658, 573 cm^{-1}

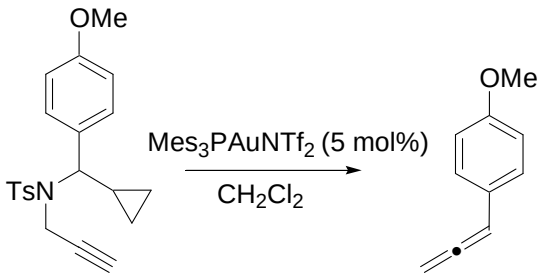
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.17 (s, 3H), 2.35 (s, 3H), 2.56-2.66 (m, 1H), 2.82-2.92 (m, 1H), 4.50-4.64 (m, 1H), 4.88-5.01 (m, 1H), 5.15-5.18 (m, 1H), 5.46-5.58 (m, 1H), 6.55 (d, J = 8.0Hz, 1H), 6.85 (d, J = 8.0Hz, 1H), 7.22 (d, J = 8.3Hz, 2H), 7.70 (d, J = 8.4Hz, 2H)

^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 15.79 (q), 19.06 (q), 36.63 (t), 49.51 (t), 63.56 (d), 111.9 (d), 116.1 (t), 120.4 (s) , 121.1 (d), 124.7 (s), 127.3 (d, 2C), 128.0 (d, 2C) , 130.1 (d), 133.0 (s), 137.0 (s), 141.0 (s), 146.3 (s)

MS (EI): m/z (%) = 366 (100) $(M+Na)^+$, 344 (72), 302 (50)

HRMS (ESI): $C_{19}H_{21}NO_3S$: Calcd: 344.1320 $(M+1)^+$; found: 344.1315$(M+1)^+$

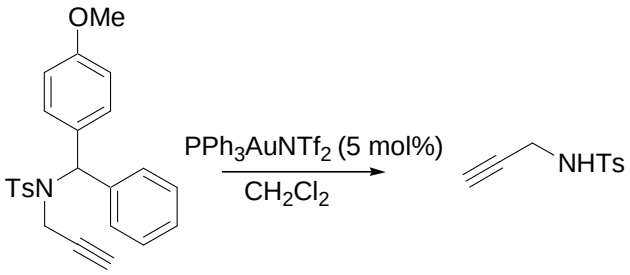
40. **1-methoxy-4-(propa-1,2-dienyl)benzene**[110] (**120**/SP392)



250 mg (0.67 mmol, 1 eq) of the substrate **115a**, was dissolved in 5ml of DCM. 29 mg (5mol %) of the catalyst was added, and the reaction mixture was heated at 40 ^{o}C. The starting material was consumed in 6h. Filtered through celite, and column chromatography over silica gel (PE:EtOAc) furnished 38g (62%) of the product allene as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 3H), 5.12 (d, J = 6.8Hz, 2H), 6.12 (t, J = 6.8Hz, 1H), 6.85 (d, J = 8.7Hz, 2H), 7.21 (d, J = 8.7Hz, 2H)

41. **N-tosylprop-2-yn-1-amine**[111] (**121**/SP406)

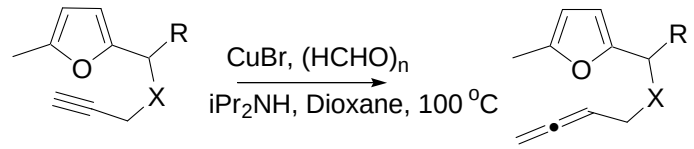


200 mg (0.51 mmol, 1 eq) of the substrate **115b** was dissolved in DCM. 22 mg (5 mol%) of the catalyst was added, and the reaction was followed by TLC. The starting material disappeared in 10 min, giving rise to numerous spots in TLC. Filtered through celite, and the solvent was removed under vacuum. Column chromatography over silica gel (PE:EtOAc) furnished 60 mg (56%) of the main product, as a white solid.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.10 (t, J = 2.5Hz, 1H), 2.43 (s, 3H), 2.82 (d, J = 6.0, 2.4Hz, 2H), 7.32 (d, J = 8.0Hz, 2H), 7.78 (d, J = 8.2Hz, 2H)

2.3.1 Gold catalysis of Furyl-Allenes

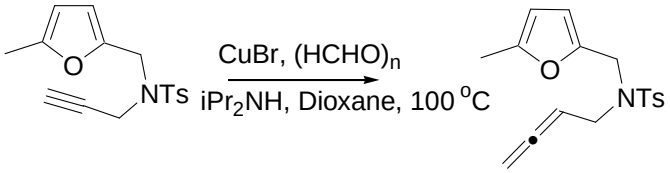
C. General procedure for the synthesis of furyl-allenes



R = H, Ph
X = O, NTs, NNs

1 mmol (1 eq) of the alkyne was added to 10ml of dioxane in a schlenk tube. 72 mg (0.5 mmol, 0.5 eq) of cuprous bromide, 76 mg (2.5 mmol, 2.5 eq) of paraformaldehyde and 0.23ml (1.5mmo, 1.5eq) of diisopropyl amine was added to the solution. The tube was sealed and degassed for 2 times. The reaction mixture was then heated at 100 ^{o}C till the starting material disappeared (2-3h). The solvent was removed under vaccum and column chromatography (PE:EtOAc) furnished the pure allenes as oily liquids.

42. **N-Buta-2,3-dienyl-4-methyl-N-(5-methyl-furan-2-ylmethyl)-benzenesulfonamide (129a**/SP523B, 39%, yellow oil)



R_f (PE:EtOAc, 4:1) = 0.43

IR (film): $\tilde{\nu}$ = 2902, 1953, 1597, 1562, 1439, 1337, 1155, 1091, 1019, 998, 891, 849, 758, 735, 660, 543 cm^{-1}

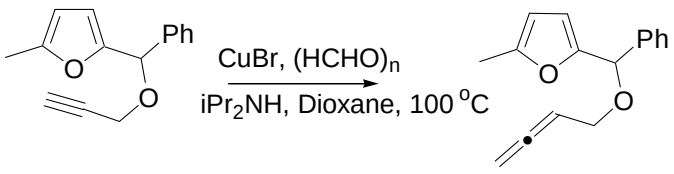
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 2.14 (s, 3H), 2.41 (s, 3H), 3.74-3.80 (m, 2H), 4.70-4.75 (m, 2H), 4.86-4.96 (m, 1H), 5.82-5.85 (m, 1H), 6.05 (d, J = 3.2Hz, 1H), 7.29 (d, J = 8.3Hz, 2H), 7.65 (d, J = 8.3Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.54 (q), 21.63 (q), 43.29 (t), 46.10 (t), 76.29 (t), 86.08 (d), 106.4 (d), 111.0 (d), 127.6 (d, 2C), 129.1 (d, 2C), 137.9 (s), 143.8 (s), 147.7 (s), 152.9 (s), 209.9 (s)

MS (APCI): *m/z* (%): 318 (15) $(M+1)^+$, 290 (47), 162 (100)

HRMS (ESI): $C_{17}H_{19}NO_3S$: Calcd: 317.1086; found: 317.1081

43. **2-(Buta-2,3-dienyloxy-phenyl-methyl)-5-methyl-furan(129b/**SP534, 49%,colourless oil)



R_f (PE:EtOAc, 4:1) = 0.55

IR (film): $\tilde{\nu}$ = 2921, 2865, 1955, 1702, 1452, 1086, 1021, 849, 787, 737, 700 cm^{-1}

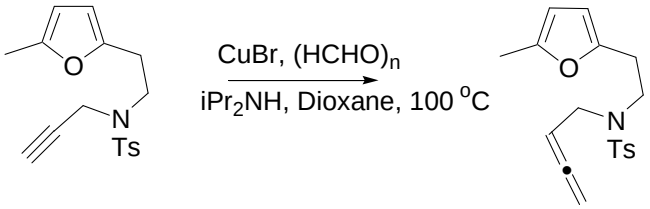
^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 2.26 (s, 3H), 4.03-4.08 (m, 2H), 4.73-4.78 (m, 2H), 5.25-5.31 (m, 1H), 5.44 (s, 1H), 5.84-5.88 (m, 1H), 5.97 (d, J = 3.0Hz, 1H), 7.26-7.46 (m, 5H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 13.70 (q), 66.45 (t), 75.62 (t), 75.94 (d), 87.63 (d), 106.1 (d), 109.9 (d), 127.3 (d, 2C), 127.8 (d), 128.3 (d, 2C), 139.2 (s), 209.4 (s)

MS (APCI): *m/z* (%): 263 (100) $(M+Na)^+$, 193 (28), 171 (19), 95 (14)

HRMS (APCI): $C_{16}H_{16}O_2$: Calcd: 240.1150; found: 240.1141

44. **N-Buta-2,3-dienyl-4-methyl-N-[2-(5-methyl-furan-2-yl)-ethyl]-benzenesulfonamide** (**129c**/SP535, 58%, colourless oil)



R_f (PE:EtOAc, 4:1) = 0.37

IR (film): $\tilde{\nu}$ = 2922, 2364, 1955, 1452, 1340, 1157, 1092, 851, 785, 730, 658 cm^{-1}

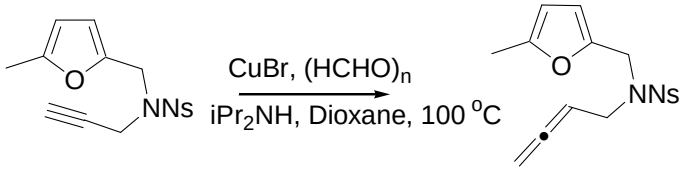
^{1}H-NMR ($CDCl_3$, 250 MHz): 2.22 (s, 3H), 2.41 (s, 3H), 2.84 (t, J = 7.8Hz, 2H), 3.42 (t, J = 7.5Hz, 2H), 3.77-3.83 (m, 2H), 4.69-4.76 (m, 2H), 4.82-4.95 (m, 1H), 5.91-5.94 (m, 1H), 5.89 (d, J = 3.1Hz, 1H), 7.28 (d, J = 8.2Hz, 2H), 7.69 (d, J = 8.2Hz, 2H)

^{13}C-NMR ($CDCl_3$, 62.90 MHz): 13.60 (q), 21.60 (q), 27.80 (t), 45.74 (t), 47.07 (t), 76.27 (t), 86.01 (d), 105.9 (d), 107.0 (d), 127.1 (d, 2C), 129.6 (d, 2C), 137.1 (s), 143.2 (s), 150.4 (s), 151.0 (s), 209.6 (s)

MS (APCI): *m/z* (%): 332 (6) $(M+1)^+$, 280 (50), 109 (100)

HRMS (APCI): $C_{18}H_{21}NO_3S$: Calcd: 331.1242; found: 331.1236

45. **N-Buta-2,3-dienyl-N-(5-methyl-furan-2-ylmethyl)-4-nitro-benzenesulfonamide** (**129d**/SP545, 58%, yellow oil)



R_f (PE:EtOAc, 4:1) = 0.38

IR (film): $\tilde{\nu}$ =3105, 2923, 1955, 1528, 1347, 1161, 1092, 854, 741, 605 cm^{-1}

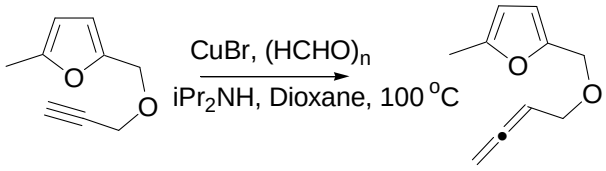
^{1}H-NMR ($CDCl_3$, 250 MHz): 2.06 (s, 3H), 3.82-3.89 (m, 2H), 4.46 (s, 2H), 4.75-4.83 (m, 2H), 4.98-5.09 (m, 1H), 5.78-5.82 (m, 1H), 6.07 (d, J = 3.1Hz, 1H), 7.95 (d, J = 8.8Hz, 2H), 8.29 (d, J = 8.8Hz, 2H)

^{13}C-NMR ($CDCl_3$, 62.90 MHz): 13.43 (q), 42.88 (t), 46.11 (t), 67.08 (t), 85.83 (d), 106.2 (d), 11.2 (d), 123.9 (d, 2C), 128.5 (d, 2C), 146.4 (s), 146.6 (s), 149.8 (s), 152.5 (s), 208.9 (s)

MS (APCI): *m/z* (%): 349 (56) $(M+1)^+$, 331 (100)162 (52)

HRMS (ESI): $C_{16}H_{16}N_2O_5S$: Calcd: 348.0780; found: 348.0783

46. **2-Buta-2,3-dienyloxymethyl-5-methyl-furan** (**129e**/SP456, 54%, colourless oil)



R_f (PE:EtOAc, 4:1) = 0.59

IR (film): $\tilde{\nu}$ = 2922, 2854, 1955, 1561, 1450, 1357, 1222, 1072, 1021, 843, 783 cm^{-1}

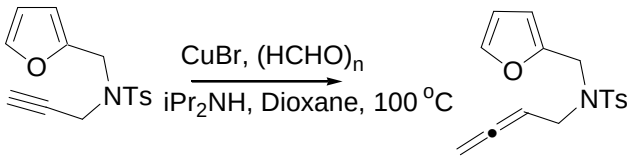
^{1}H-NMR ($CDCl_3$, 250 MHz): 2.29 (s, 3H), 4.01-4.10 (m, 2H), 4.41 (s, 2H), 4.75-4.85 (m, 2H), 5.18-5.30 (m, 1H), 5.87-5.92 (m, 1H), 6.19 (d, J = 3.0Hz, 1H)

^{13}C-NMR ($CDCl_3$, 62.90 MHz): 13.66 (q), 63.58 (t), 67.62 (t), 75.63 (t), 87.50 (d), 106.1 (d), 110.5 (d), 149.6 (s), 152.7 (s), 209.5 (s)

MS (APCI): *m/z* (%): 264 (100), 95 (41)

HRMS (APCI): $C_{10}H_{12}O_2$: Calcd: 164.0837; found: 164.084

47. **N-Buta-2,3-dienyl-N-furan-2-ylmethyl-4-methyl-benzenesulfonamide** (**129f**/SP559a, 14%, yellow oil)



R_f (PE:EtOAc, 4:1) = 0.50

IR (film): $\tilde{\nu}$ = 2925, 1957, 1341, 1159, 903, 727, 649 cm^{-1}

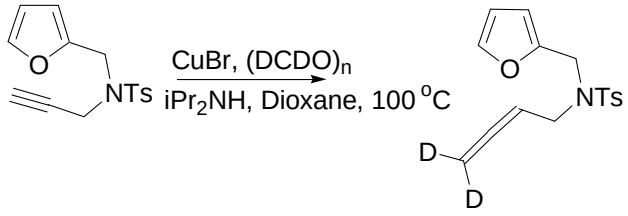
^{1}H-NMR ($CDCl_3$, 300 MHz): 2.41 (s, 3H), 3.78-3.83 (m, 2H), 4.44 (s, 2H), 4.68 –4.74 (m, 2H), 4.88-4.99 (m, 1H), 6.16-6.19 (m, 1H), 6.25-6.28 (m, 1H), 7.23-7.28 (m, 3H), 7.67 (d, J = 8.4Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 21.57 (q), 42.63 (t), 45.91 (t), 76.23 (t), 85.76 (d), 109.5 (d), 110.3 (d), 127.2 (d, 2C), 129.5 (d, 2C), 137.3 (s), 142.4 (d), 143.2 (s), 149.5 (s), 209.9 (s)

MS (APCI): *m/z* (%): 326 (100) $(M+Na)^+$

HRMS (ESI): $C_{16}H_{16}NO_3S$: Calcd: 303.0929; found: 303.0923

48. **N-Buta-2,3-dienyl-N-furan-2-ylmethyl-4-methyl-benzenesulfonamide** (**129g**/SP559B, 16%, yellow oil)



R_f (PE:EtOAc, 4:1) = 0.50

IR (film): $\tilde{\nu}$ = 2924, 1938, 1341, 1156, 1093, 1011, 904, 813, 728, 655, 548 cm^{-1}

^{1}H-NMR ($CDCl_3$, 300 MHz): 2.41 (s, 3H), 3.80 (d, J = 7.2Hz, 2H), 4.44 (s, 2H), 4.94 (t, J = 7.1Hz, 1H), 6.16-6.19 (m, 1H), 6.25-6.28 (m, 1H), 7.23-7.29 (m, 3H), 7.67 (d, J = 8.3Hz, 2H)

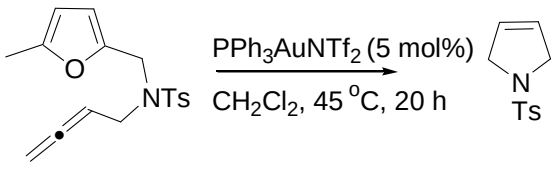
^{13}C-NMR ($CDCl_3$, 75.46 MHz): 21.50 (q), 42.80 (t), 46.00 (t), 67.20 (t), 86.00 (d), 109.5 (d), 110.3 (d), 127.2 (d, 2C), 129.5 (d, 2C), 137.3 (s), 142.5 (d), 143.1 (s), 149.5 (s), 209.7 (s)

MS (EI+): *m/z* (%): 305 (M^+) (4), 264 (38), 122 (42), 81 (100)

HRMS (ESI): $C_{16}H_{15}D_2NO_3S$: Calcd: 305.1053; found: 305.1051

D. Gold catalysis of furyl-allenes

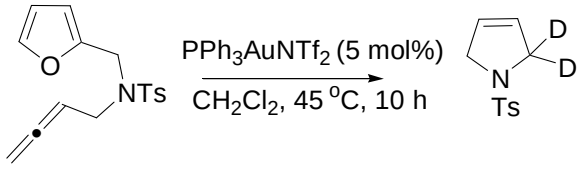
49. **1-(Toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole** (**130**/SP524)



30 mg (0.094 mmol, 1 eq) of the allene **129a** was dissolved in 1ml DCM.2 mg (5 mol%) of the catalyst was added and the reaction mixture was heated at 45 °C .The starting material disappeared in 20 h. The solvent was removed under vaccum and column chromatography (PE:EtOAc) furnished 10 mg (48%) of the product as an off-white solid.

^{1}H-NMR ($CDCl_3$, 300 MHz): 2.42 (s, 3H), 4.12 (s, 4H), 5.66 (s, 2H), 7.31 (d, 8.3Hz, 2H), 7.72 (d, J = 8.3Hz, 2H)

50. **1-(Toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole** (**130′**/SP561b)



16 mg (0.052 mmol, 1 eq) of the allene was dissolved in 0.5ml $CDCl_3$ in an NMR tube.1 mg (5 mol%) of the catalyst was added and the reaction mixture was heated at 45oC .The reaction was traced with ^{1}H-NMR. The starting material disappeared in 10h.The solvent was removed under vaccum and column chromatography (PE:EtOAc) furnished 7 mg (60%) of the product as an off-white solid.

R_f (PE:EtOAc, 4:1) = 0.19

IR (film): $\tilde{\nu}$ = 2921, 1339, 1161, 1099, 904, 727, 647, 596 cm^{-1}

^{1}H-NMR ($CDCl_3$, 300 MHz): 2.43 (s, 3H), 4.11 (s, 2H, deuterated), 5.65 (s, 2H), 7.31 (d, J = 8.3Hz, 2H), 7.72 (d, J = 8.3Hz, 2H)

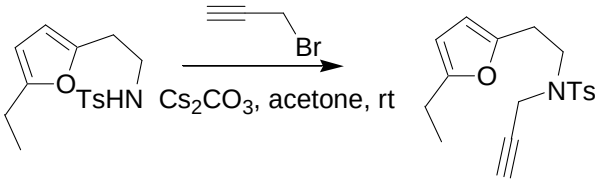
^{13}C-NMR ($CDCl_3$, 75.46 MHz): 21.62 (q), 54.96 (t, 2C), 125.3 (d), 125.6 (d), 127.4 (d, 2C), 129.7 (d, 2C), 134.3 (s), 143.4 (s)

MS (EI+): *m/z* (%): 225 (M+) (98), 155 (57), 91 (97), 70 (100)

HRMS (ESI): $C_{11}H_{11}D_2NO_2S$: Calcd: 225.0790; found: 225.0782

2.3 Gold catalysis of Oxanorbornadienes; Novel formation of *N,O*-Acetals

1. **N-(2-(5-ethylfuran-2-yl)ethyl)-N-tosylprop-2-yn-1-amine** (**139**/SP128)



1.64g (5.56 mmol, 1 eq) of the compound **40d** was dissolved in 20 ml acetone. Add 3.9g (12 mmol, 2 eq) of Cs_2CO_3 and 1.33 ml (12 mmol, 2 eq) propargyl bromide to this solution. The reaction mixture was allowed to stir at rt for 24h. The solvent was removed in vacuum, and 20 ml of water was added. The organic part was extracted with dichloromethane and dried over $MgSO_4$. Column chromatography (PE/EtOAc) gave 1.6g of the product as light brown oil (86 %).

R_f (PE: EtOAc, 4:1) = 0.51

IR (film): 3285, 2972, 2924, 1566, 1453, 1347, 1158, 1093, 870, 658 cm^{-1}

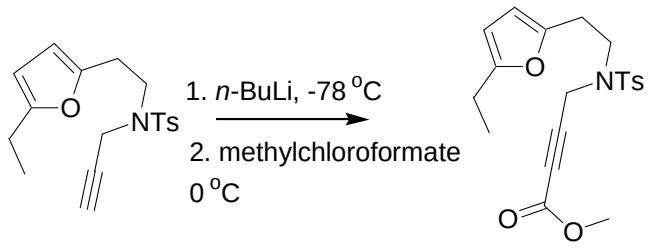
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.20 (t, J = 8.0 Hz, 3H), 2.05 (t, J = 2.6 Hz, 1H), 2.41 (s, 3H), 2.57 (q, J = 7.9 Hz, 2H), 2.89 (t, J = 7.0 Hz, 2H), 3.47 (t, J = 7.5 Hz, 2H), 4.06 (d, J = 2.4 Hz, 2H), 5.85 (d, J = 2.8 Hz, 1H), 5.96 (d, J = 2.8 Hz, 1H), 7.28 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H)

^{13}C- NMR (125 Mz, $CDCl_3$): δ = 12.18 (q), 21.32 (t), 21.53 (q), 27.49 (t), 36.82 (t), 45.24 (t), 73.70 (d), 76.75 (s) 104.4 (d), 106.9 (d), 127.6 (d, 2C), 129.4 (d, 2C), 135.9 (s), 143.5 (s), 150.0 (s), 156.8 (s)

MS (EI): m/z (%) = 331 (5) (M^+), 222 (100), 155 (65), 91(35)

Anal. Calcd. For $C_{18}H_{21}NSO_3$: C 65.23, H 6.39, N 4.23; found: C 65.24, H 6.43, N 4.18

2. **Methyl 4-(N-(2-(5-ethylfuran-2-yl)ethyl)-N-tosylamino)but-2-ynoate**[77] (**140**/SP129)



1.75 ml (4.38 mmol, 1 eq, 2.5M solution in hexane) of n-butyl lithium was added slowly under nitrogen to 1.45g (4.38 mmol, 1 eq) of the compound **139** in 40 ml of dry THF at -78 ^{o}C.The solution was stirred for 30 min at the same temperature. It was then added slowly to a solution of methyl chloroformate (1.7 ml, 22 mmol, 5 eq) in 5 ml dry THF kept at 0 ^{o}C. The reaction mixture was allowed to stir at 0 ^{o}C for 2h. Add 20 ml of water and extract with dichloromethane. Dried over $MgSO_4$ and purified over column chromatography (PE:EtOAc) to yield 1.10g (65%) of the product as an oil.

R_f (PE:EtOAc, 4:1) = 0.46

IR (film): 2973, 2240, 1717, 1566, 1434, 1349, 1255, 1161, 1092, 1060, 800, 723, 663 cm^{-1}

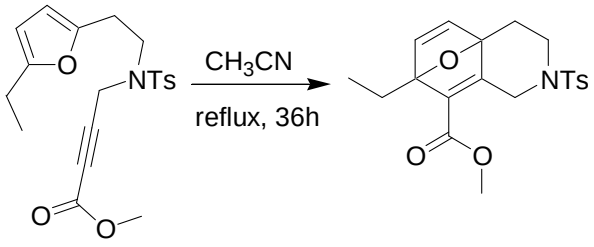
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.20 (t, J = 8.2 Hz, 3H), 2.41 (s, 3H), 2.59 (q, J = 7.7 Hz, 2H), 2.89 (t, J = 7.4 Hz, 2H), 3.43 (t, J = 7.4 Hz, 2H), 3.71 (s, 3H), 4.13 (s, 2H), 5.85 (d, J = 2.8 Hz, 1H), 5.98 (d, J = 2.8 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H)

^{13}C- NMR (125 Mz, $CDCl_3$): δ =11.17 (q), 21.32 (t), 21.55 (q), 27.62 (t), 36.93 (t), 45.77 (t), 52.74 (q), 80.80 (s), 104.5 (d), 107.3 (d), 127.6 (d, 2C), 129.7 (d, 2C), 135.4 (s), 143.9 (s), 149.6 (s), 153.0 (s), 156.9 (s)

MS (EI): m/z (%) = 389 (20) (M+), 280 (100), 155 (80), 109 (43), 91 (76)

Anal. Calcd. For $C_{20}H_{23}NO_3S$: C 61.68, H 5.95, N 3.60; found: C 61.65, H 5.98, N 3.64.

3.8 **Ethyl-4-(toluene-4-sulfonyl)-11-oxa-4-aza-tricyclo[6.2.1.01,6]undeca-6,9-diene-7-carboxylic acid methyl ester**[77] (**137a**/SP130)



0.920g (2.34 mmol) of the compound **140** was dissolved in 8 ml acetonitrile and refluxed for 36h. Cooled, removed the solvent in vacuum and purified over column chromatography (PE/EtOAc, 5:1) to give 710 mg (77%) of the cycloadduct as pale white crystals.

M.P: 125–127 ^{o}C

R_f (PE: EtOAc, 4:1) = 0.25

IR (neat): 2972, 171, 1437, 1345, 1161, 991, 916, 739 cm^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.8 Hz, 3H), 2.15-2.36 (m, 4H), 2.42 (s, 3H), 2.76 (tt, J = 13.7, 2.9 Hz, 1H), 3.35 (d, J = 17.9 Hz, 1H), 3.75 (s, 3H), 3.89-3.94 (m,

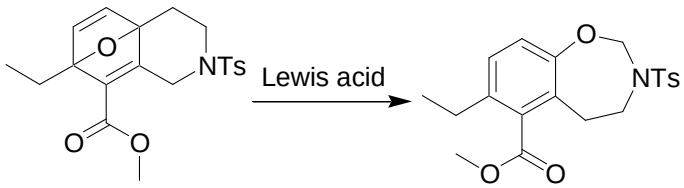
1H), 5.12 (dd, J = 17.7, 1.9 Hz, 1H), 6.79 (d, J = 5.2 Hz, 1H), 6.93 (d, J = 5.2 Hz, 1H), 7.34 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 9.310 (q), 21.58 (t), 22.68 (q), 28.19 (t) 43.26 (t), 47.29 (t), 51.57 (q), 88.47 (s), 96.04 (s), 127.6 (d, 2C), 129.9 (d, 2C), 133.8 (s), 139.9 s), 143.9 (s), 144.3 (d), 148.1 (d) , 164.0 (s), 164.2 (s)

MS(EI): m/z (%) = 389 (62) (M^+), 332 (100), 155 (30), 91(68)

Anal. Calcd. For $C_{20}H_{23}NO_3S$: C 61.68, H 5.95, N 3.60; found: C 61.67, H 5.92, N 3.68

4. **Methyl-7-ethyl-2,3,4,5-tetrahydro-3-tosylbenzo[f][1,3]oxazepine-6-carboxylate** (**138a**)



(a). 78 mg (0.2 mmol) of the cycloadduct was dissolved in 3 ml of acetonitrile and 3 mg (5%) of $AuCl_3$ was added. The flask was sealed and the reaction mixture was heated at 80^oC. The catalytic isomerization was completed in 2h. The solvent was removed in vacuum and purification over column chromatography (PE:EtOAc) to yield 54 mg (68%) of the *N, O*-acetal product as pale white crystals (SP140)

(b) 39 mg (0.1 mmol) of the cycloadduct was dissolved in 2 ml of acetonitrile and 1 mg (5%) of AuCl was added. The flask was sealed and the reaction mixture was heated at 80^oC. The catalytic isomerization was completed in 1.5h. The solvent was evaporated and purification over column chromatography gave 34 mg of the product in 87% yield (SP143)

(c) 117 mg (0.3 mmol) of the cycloadduct was dissolved in 3 ml of acetonitrile and 9 mg (5%) of ytterbium triflate was added. The flask was sealed and the reaction mixture was heated at 80^oC. The catalytic isomerization was completed in 8h. The solvent was evaporated and purification over column chromatography gave 86 mg of the product in 74% yield (SP138)

(d) 39 mg (0.1 mmol) of the cycloadduct was dissolved in 2 ml of acetonitrile and 1 mg (5%) of *p*-toluene sulfonic acid was added. The flask was sealed and the reaction mixture was heated at 80^oC. The reaction was finished in 7h. Purification of the crude mixture gave 30 mg (77%) of the product (SP167)

(e) 39 mg (0.1 mmol) of the cycloadduct was dissolved in 0.5 ml of deuterated acetonitrile in an NMR tube and a very tiny crystal of $AgBF_4$ was added. The tube was sealed and heated at 80^oC. No transformation was observed even after heating for 10h (SP173)

(f) 39 mg (0.1 mmol) of the cycloadduct was dissolved in 0.5 ml of deuterated acetonitrile in an NMR tube and 1.6 mg (5%) of zinc iodide was added. The tube was sealed and heated at 80^oC. The reaction was very slow and after 24h the reaction mixture was cooled and purification over column chromatography yielded 12 mg (30 %) of the *N,O*-acetal product

(SP237a)

(g) 39 mg (0.1 mmol) of the cycloadduct was dissolved in 2 ml of acetonitrile and 5% boron tirfluoride etherate was added. The flask was sealed and the reaction mixture was heated at 80^{o}C. The reaction was finished in 3h. Purification of the crude mixture gave 25 mg (63%) of the *N,O*-acetal product (SP237b)

(h) 39 mg (0.1 mmol) of the cycloadduct was dissolved in 2 ml of acetonitrile and small crystal of copper (I) triflate was added. The flask was sealed and the reaction mixture was heated at 80^{o}C. The reaction was finished in 3.5h. Purification of the crude mixture gave 24 mg (60%) of the *N,O*-acetal product (SP242).

(i) 39 mg (0.1 mmol) of the cycloadduct was dissolved in 2 ml of acetonitrile and small crystal of copper (II) triflate was added. The flask was sealed and the reaction mixture was heated at 80^{o}C. The reaction was finished in 2.5 h. Purification of the crude mixture gave 26 mg (67%) of the *N,O*-acetal product (SP243).

M.P: 110-112 ^{o}C

R_f (PE: EtOAc, 2:1) = 0.65
IR (neat): 2966, 2874, 1725, 1597, 1477, 1339, 1273, 1235, 1154, 1117, 995, 887, 731, 667 cm^{-1}

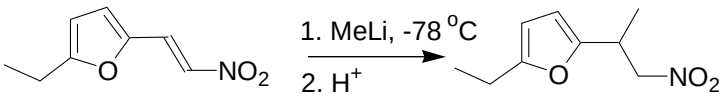
^{1}H-NMR (500 MHz, $CDCl_3$) : δ = 1.19 (t, J = 8.2Hz, 3H) 2.41 (s, 3H), 2.47 – 2.53 (m, 4H), 3.57-3.60 (m, 2H), 3.86 (s, 3H), 5.28 (s, 2H), 6.95 (d, J = 8.2 Hz, 1H), 7.1 (d, J = 8.2 Hz, 1H), 7.3 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 15.57 (q), 21.58 (q), 26.40 (t), 30.70 (t), 45.80 (t), 52.24 (q), 81.07 (t), 122.4 (d), 127.7 (d, 2C), 128.1 (s), 128.5 (d), 129.8 (d, 2C), 134.5 (s), 136.7 (s), 137.7 (s), 143.8 (s), 157.6 (s)

MS (EI): m/z (%) = 389 (54) (M^+), 206 (100), 42 (15)

Anal. Calcd. For $C_{20}H_{23}NO_3S$: C 61.68, H 5.95, N 3.60; found: C 61.87, H 6.04, N 3.64.

5. **2-Ethyl-5-(1-methyl-2-nitro-ethyl)-furan**[79] (**143**/SP148/SP154)



1.5 g (9 mmol 1 eq) of the compound **38c** was dissolved in 50 ml dry THF and added slowly under nitrogen to 27 ml (45 mmol, 5 eq, 1.6 M solution in ether) of methyl lithium in 10 ml dry THF at -78 ^{o}C. The reaction mixture was then transferred to 75 ml of aqueous HCl (15%) and stirred for 30 min, at rt. The organic layer was then extracted with DCM and dried over $MgSO_4$. 1.3g (78%) of the pure product was obtained as a colourless liquid by column chromatography (PE:EtOAc)

R_f (PE: EtOAc, 4:1) = 0.55

IR (film): 2975, 2938, 1549, 1375, 1314, 1184, 1014, 779 cm^{-1}

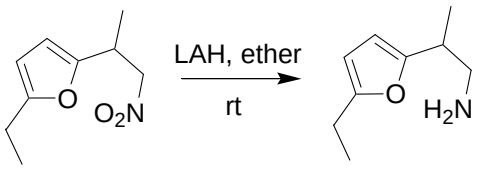
^{1}H-NMR (500 MHz, $CDCl_3$) : δ = 1.20 (t, J = 7.3 Hz, 3H), 1.35 (d, J = 7.7 Hz, 3H), 2.6 (q, J = 7.5 Hz, 2H), 3.65-3.72 (m, 1H), 4.40 (dd, J = 12.4 , 8.3 Hz, 1H), 4.65 (dd, J = 12.3 , 6.9 Hz, 1H), 5.89 (d, J = 3.2 Hz, 1H) 6.0 (d, J = 3.2 Hz, 1H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 12.01 (q), 16.11 q), 21.32 (t), 32.53 (d), 79.76 (t), 104.4 (d), 106.3 (d), 151.8 (s), 157.4 (s)

MS (EI): m/z (%) = 222 (100), 206 (4) $(M+Na)^{+}$, 175 (3), 123 (2)

Anal. Calcd. For $C_9H_{13}NO_3$: C 59.00; H 7.15; N 7.65; found: C 59.46; H 7.22; N 7.52

6. **2-(5-Ethyl-furan-2-yl)-propylamine** (SP156)



525 mg (13 mmol, 2 eq) of lithium aluminium hydride was dissolved in 50 ml of dry ether

under nitrogen. 1.2g (6.5 mmol, 1 eq) of the compound **143** was dissolved in 20 ml of dry ether and slowly added at 0 ^{o}C. Warm the reaction mixture to rt, and stirred overnight. Add 2 ml of aqeous ammonium chloride to quench the reaction. The solid was filtered out and the organic layer was extracted with dichloromethane. Dried over $MgSO_4$. Column chromatography (PE/EtOAc, 2:1, 1 % NEt_3) furnished 530 mg of the amine in 53 % yield as light brown oil.

R_f (PE: EtOAc, 1:1) = 0.05

IR (film): 2970, 2935, 2875, 1563, 1459, 1372, 1183, 1013, 950, 776 cm^{-1}

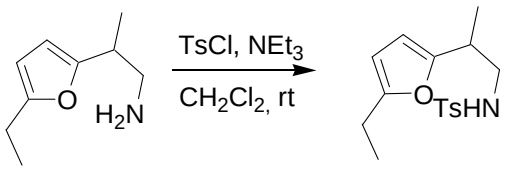
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.19-1.24 (m, 6H), 1.5 (bs, 2H), 2.60 (q, J = 7.5Hz, 2H), 2.80 – 2.87 (m, 3H), 5.89 (d, J = 3.3 Hz, 1H), 5.92 (d, J = 3.3 Hz, 1H)

^{13}C- NMR (125 MHz, $CDCl_3$): δ = 12.10 (q), 16.45 (q), 21.36 (q), 36.96 (d), 47.36 (t), 104.0 (d), 105.0 (d), 156.4 (s), 156.5 (s)

MS (EI): m/z (%) = 153 (10) (M^+), 124 (40), 123 (100)

HRMS (ESI): $C_8H_{13}NO$: Calcd: 154.1279 (M+1); found: 154.1230 (M+1)

7. **2-(5-ethylfuran-2-yl)-N-tosylpropan-1-amine** (SP158)



570 mg (3.7 mmol, 1 eq) of the amine was dissolved in 15 ml of DCM. 0.55 ml (4 mmol, 1.1 eq) of triethyl amine and 710 mg (3.7 mmol, 1 eq) of tosyl chloride were added and stirred at rt for 2 days. 15 ml of water was added and the organic layer was extracted with DCM and dried over $MgSO_4$. Column chromatography (PE:EtOAc) furnished 850 mg (75%) of the product as brown oil.

R_f (PE: EtOAc, 2:1) = 0.55

IR(film): 3283, 2971, 1563, 1323, 1156, 1091, 660, 549 cm^{-1}

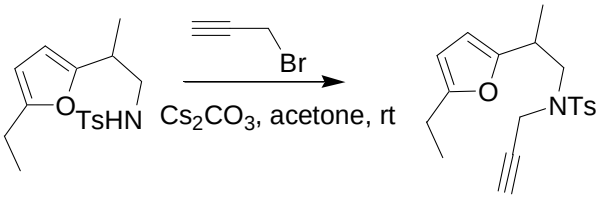
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.12-1.2 (m, 6H), 2.41 (s, 3H), 2.59 (q, J = 7.8 Hz, 2H), 2.81–3.20 (m, 3H), 4.59 (t, J = 6.4 Hz, 1H), 5.85 (d, J = 3.1 Hz, 1H), 5.88 (d, J = 3.1 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.7 (d, J = 8.2 Hz, 2H)

^{13}C- NMR (125 Mz, $CDCl_3$): δ = 12.02 (q), 16.43 (q), 21.29 (t), 21.52 (q), 33.32 (d), 47.68 (t), 104.2 (d), 106.0 (d), 127.0 (d, 2C), 129.6 (d, 2C), 137.0 (s), 143.3 (s), 154.3 (s), 156.9 (s)

MS(EI): m/z(%) = 307 (1) (M^+), 168 (100), 155 (40), 91 (60), 57 (30)

Anal. Calcd. For $C_{16}H_{21}NO_3S$: C 62.51, H 6.89, N 4.56; found: C 62.13, H 6.86, N 4.53.

8. **N-(2-(5-ethylfuran-2-yl)propyl)-N-tosylprop-2-yn-1-amine** (SP152)



370 mg (1.09 mmol, 1 eq) of the tosylamine was dissolved in 10 ml acetone. Add 715 mg (2.2 mmol, 2 eq) of Cs_2CO_3 and 0.24 ml (2.2 mmol, 2 eq) propargyl bromide to this solution. The reaction mixture was allowed to stir at rt for 24h. The solvent was removed in vacuum, and 10 ml of water was added. The organic part was extracted with dichloromethane and dried over $MgSO_4$. Column chromatography (PE/EtOAc) furnished the product as light brown oil (86%).

R_f (PE: EtOAc, 2:1) = 0.60

IR (film): 2969, 1710, 1456, 1436, 1346, 1162, 815, 656, 548 cm^{-1}

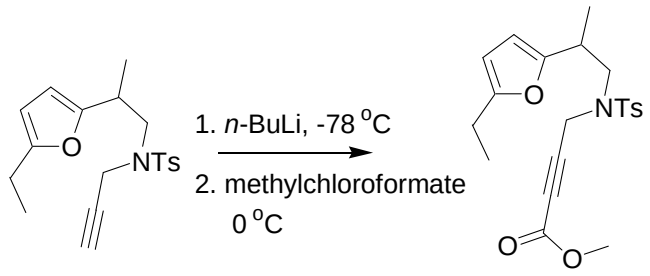
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.20 (t, J = 7.7 Hz, 3H), 1.29 (d, J = 6.8 Hz, 3H), 1.99 (t, J = 2.6 Hz, 1H), 2.41 (s, 3H), 2.59 (q, J = 7.6 Hz, 2H), 3.10-3.16 (m, 1H), 3.35 (d, J = 7.5 Hz, 2H), 3.8 (dd, J = 18.9, 2.7 Hz, 1H), 4.08 (dd, J = 18.8, 2.6 Hz), 5.86 (d, J = 3.1 Hz, 1H), 5.96 (d, J = 3.1 Hz, 1H), 7.27 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 12.17 (q), 16.63 (q), 21.35 (t), 21.54 (q), 32.49 (d), 37.02 (t), 50.98 (t), 73.65 (d), 76.71 (s), 104.3 (d), 105.6 (d), 127.7 (d, 2C), 129.4 (d, 2C), 136.0 (s), 143.4 (s), 154.8 (s), 156.5 (s)

MS(EI): m/z (%) = 345 (12) (M^+), 222 (100), 155 (30), 123 (72)

Anal. Calcd. For $C_{19}H_{23}NO_3S$: C 66.06, H 6.71, N 4.05; found: C 66.01, H 6.79, N 3.97.

9. **4methyl 4-(N-(2-(5-ethylfuran-2-yl)propyl)-N-tosylamino)but-2-ynoate** (SP160)



1.2 ml (3 mmol, 1 eq, 2.5M solution in hexane) of *n*-butyl lithium was added slowly under nitrogen to 1.05g (3 mmol, 1 eq) of the the alkyne in 40 ml of dry THF at -78 °C. The solution was stirred for 30 min at the same temperature. It was then added slowly to a solution of methyl chloroformate (1.2 ml, 15 mmol, 5 eq) in 5 ml dry THF kept at 0°C. The reaction mixture was allowed to stir at 0°C for 2h. Add 20ml of water and extract with dichloromethane. Dried over $MgSO_4$ and purified over column chromatography (PE:EtOAc) to yield 660g (54%) of the product as an oil.
R_f (PE: EtOAc, 2:1) = 0.58

IR (film): 2972, 2239, 1715, 1434, 1348, 1248, 1248, 1159, 1012, 749, 662, 544 cm^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$) : δ = 1.20 (t, J = 7.2 Hz, 3H), 1.29 (d, J = 7.3 Hz, 3H), 2.41 (s, 3H), 2.58 (q, J = 8.0 Hz, 2H), 3.06-3.10 (m, 1H), 3.29-3.39 (m, 2H), 3.69 (s, 3H), 3.86 (dd, J = 19.3, 1.8 Hz, 1H), 4.13 (dd, J = 19.4, 1.8 Hz, 1H), 5.86 (d, J = 3.1 Hz, 1H) , 5.96 (d, J = 3.1 Hz, 1H), 7.30 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H)

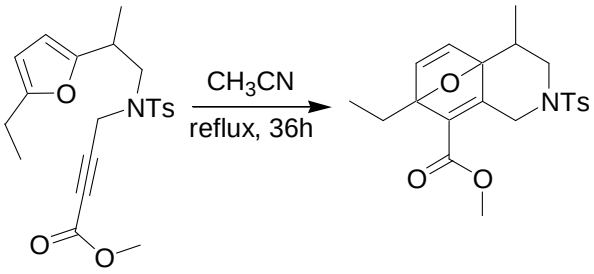
^{13}C-NMR (125 Mz, $CDCl_3$): δ = 12.15 (q), 16.56 (q), 21.32 (t), 21.54 (q), 32.74 (d) , 37.14 (t), 51.50 (t), 52.70 (q), 76.74 (s), 80.86 (s), 104.4 (d), 105.9 (d), 127.6 (d, 2C), 129.7 (d, 2C),

135.5 (s), 143.8 (s), 153.0 (s), 154.5 (s), 156.7 (s)

MS(ESI): m/z (%) = 426 (100) (M^+)

Anal. Calcd. For$C_{21}H_{25}NO_5S$: C 62.51, H 6.25, N 3.47; found: C 62.28, H 6.21, N 3.40.

10. **8-Ethyl-2-methyl-4-(toluene-4-sulfonyl)-11-oxa-4-aza-tricyclo[6.2.1.01,6]undeca-6,9-diene-7-carboxylic acid methyl ester** (**137b**/SP161)



580 mg (1.43 mmol) of the methoxycarbonylated alkyne was dissolved in 8 ml of the acetonitrile and the reaction mixture was refluxed for 36h. The solvent was removed in vacuum and purified over column chromatography (PE:EtOAc) to furnish 380 mg (66 %) of the pure cycloadduct as white crystals.

M.P: 158–160^oC

R_f(PE: EtOAc, 2:1) = 0.33
IR (neat): 2970, 1710, 1457, 1436, 1346, 1162, 1089, 914, 815, 777, 656, 548 cm^{-1}

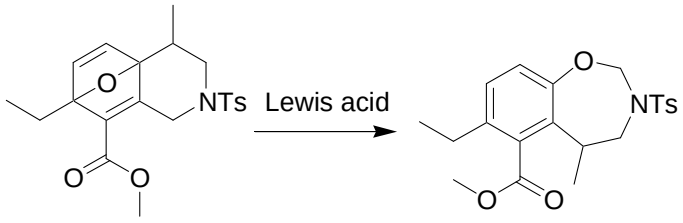
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.00 (t, j = 7.9 Hz, 3H), 1.1 (d, J = 7.2 Hz, 3H), .2.30-2.33 (m, 2H), 2.36–2.42 (m, 2H), 2.43 (s, 3H), 3.15 (d, J = 17.9 Hz, 1H), 3.79 (s, 3H), 3.95 (ddd, J = 12.6, 3.6, 1.8 Hz, 1H), 5.29 (dd, J = 18.3, 2.3 Hz, 1H), 6.84 (d, J = 5.7 Hz, 1H), 6.95 (d, J = 5.7 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 9.340 (q), 14.02 (q), 21.57 (q), 22.54 (t), 32.88 (d), 47.12 (t), 49.55 (t), 51.55 (q), 93.36 (s), 95.78 (s), 127.6 (d, 2C), 129.9 (d, 2C), 133.8 (s), 139.8 (s), 140.6 (s), 143.9 (d), 148.4 (d), 164.0 (s), 164.3 (s)

MS (EI): m/z (%) = 403 (28) (M^+), 346 (100), 314 (15), 123 (30), 91 (30)

Anal. Calcd. For $C_{21}H_{25}NO_5S$: C 62.51, H 6.25, N 3.47; found: C 62.20, H 6.25, N 3.45.

11. **Methyl-7-ethyl-2,3,4,5-tetrahydro-5-methyl-3-tosylbenzo[f][1,3]oxazepine-6carboxylate** (**138b**/SP165/SP166)



(a) 40.3 mg (0.1mmol, 1 eq), of the cycloadduct 13 was dissolved in 0.5 ml of CD_3CN in an NMR tube and 1.2 mg (5 %) of AuCl was added. The reaction mixture was heated at 80^{o}C. The reaction was finished in 1.5h according to NMR. Column chromatography (PE/EtOAc, 5:1) furnished 31 mg (77 %) of the product *N*, *O*-acetal as pale white crystals.

(b) 30 mg (0.075 mmol, 1 eq), of the cycloadduct 13 was dissolved in 0.5 ml of CD_3CN in an NMR tube and 2.4 mg (5 %) of ytterbium triflate was added . The reaction mixture was heated at 80^{o}C. The reaction was finished in 3.5h according to NMR. Column chromatography furnished 23 mg (76 %) of the product *N*, *O*-acetal .

M.P: 138 – 140 ^{o}C

R_f (PE: EtOAc, 2:1) = 0.47

IR (neat): 2969, 2874, 1726, 1477, 1339, 1269, 1242, 1158, 1133, 1100, 1022, 987, 908, 665, 547 cm^{-1}

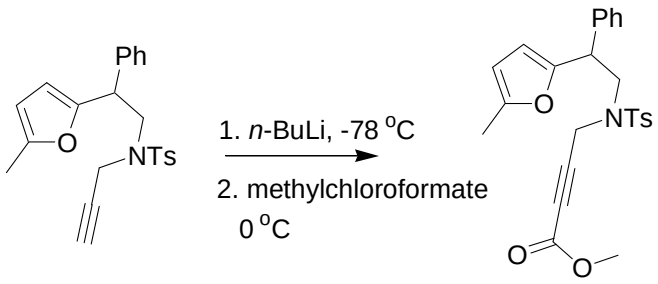
^{1}H-NMR (500 MHz, $CDCl_3$) : δ = 1.10 (t, J = 7.7 Hz, 3H), 1.18 (d, J = 7.5 Hz, 3H), 2.42 (s, 3H), 2.50 (q, J = 7.8 Hz, 2H), 2.92-2.95 (m, 1H), 3.10 (dd, J = 17.2, 2.5 Hz , 1H), 3.85 (s, 3H), 4.01-4.04 (m, 1H), 4.30 (dd, J = 15.6, 2.1 Hz , 1H), 5.80 (dd, J = 17.5, 2.5 Hz, 1H), 6.89 (d, J = 8.2 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H)

^{13}C- NMR (125 Mz, $CDCl_3$): δ = 15.42 (q), 17.76 (q), 21.49 (q), 26.33 (t), 38.31 (d), 51.16 (t), 52.70 (q), 81.47 (t), 123.0 (d), 126.9 (d, 2C), 127.9(d), 129.7 (d, 2C), 132.6 (s), 134.4 (s), 136.6 (s), 137.4 (s), 143.5 (s), 156.5 (s), 170.0 (s)

MS (EI): m/z (%) = 403 (25) (M^+), 220 (100), 205 (20), 91 (15)

Anal. Calcd. For $C_{21}H_{25}NO_5S$: C 62.51, H 6.25, N 3.47; found: C 62.84, H 6.39, N 3.40.

12. **Methyl-4-(N-(2-(5-methylfuran-2-yl)-2-phenylethyl)-N-tosylamino)but-2-ynoate** (SP191)



0.72 ml (1.8 mmol, 1 eq, 2.5M solution in hexane) of *n*-butyl lithium was added slowly under nitrogen to 700 mg (1.80 mmol, 1 eq) of the compound **110** in 40 ml of dry THF at -78^{o}C. The solution was stirred for 30 min at the same temperature. It was then added slowly to a solution of methyl chloroformate (0.75 ml, 9 mmol, 5 eq) in 5 ml dry THF kept at 0^{o}C. The reaction mixture was allowed to stir at 0^{o}C for 2h. Add 20 ml of water and extract with dichloromethane. Dried over $MgSO_4$ and purified over column chromatography (PE:EtOAc) to yield 460 mg (57%) of the product as an oil.

R_f (PE:EtOAc, 3:1) = 0.60

IR (film): 2953, 2239, 1717, 1434, 1351, 1257, 1161, 1092, 904, 750, 663 cm^{-1}

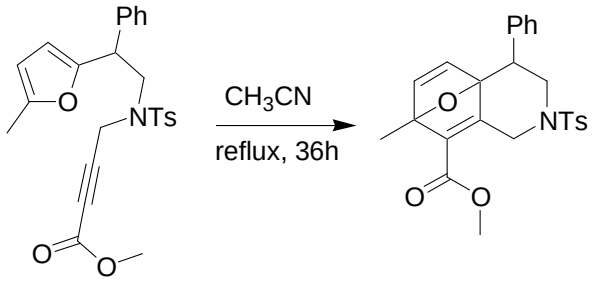
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 2.40 (s, 3H), 3.55 (dd, J = 14.4, 7.9 Hz, 1H), 3.69 (s, 3H), 3.77-3.81 (m, 2H), 3.90 (d, J = 19.1 Hz ,1H), 4.33 (t, J = 8.1 Hz, 1H), 5.89 (d, J = 3.1 Hz, 1H), 6.06 (d, J = 3.1 Hz, 1H), 7.27 (d, J = 8.3 Hz, 2H), 7.30-7.32 (m, 5H), 7.69 (d, J = 8.3 Hz, 2H).

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 13.58 (q), 21.53 (q), 37.40 (t), 45.21 (d), 50.75 (t), 52.71 (q), 76.74 (s), 80.80 (s), 106.2 (d), 107.9 (d), 127.2 (d), 127.6 (d, 2C), 128.1 (d, 2C), 128.7 (d, 2C), 129.7 (d, 2C), 135.3 (s), 139.6 (s), 143.9 (s), 151.5 (s), 151.9 (s), 152.9 (s)

MS (ESI): m/z (%) = 474 (100) $(M+ Na)^+$, 290 (3)

HRMS (ESI): $C_{25}H_{25}NO_5S$: Calcd: 474.1370 $(M+Na)^+$; found: 474.1346 $(M+Na)^+$

13. **8-Methyl-2-phenyl-4-(toluene-4-sulfonyl)-11-oxa-4-aza-tricyclo[6.2.1.01,6]undeca-6,9-diene-7-carboxylic acid methyl ester** (**137c**/SP192)



300 mg (0.67 mmol) of the methoxycarbonylated alkyne was dissolved in 10 ml of acetonitrile and refluxed for 36h. The solvent was removed in vacuum and recrystallization from DCM/PE furnished 210 mg (70%) of the cycloadduct as white crystals.

M.P: 174–176 ^oC

R_f (PE:EtOAc, 3:1) = 0.30

IR (neat): 2970, 1712, 1436, 1344, 1321, 1157, 1047, 980, 816, 770, 697, 656 cm^{-1}

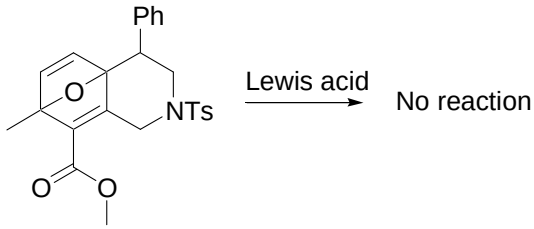
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.85 (s, 3H), 2.45 (s, 3H), 2.85 (t, J = 12.5 Hz, 1H), 3.25 (d, J = 17.6 Hz, 1H), 3.54 (dd, J = 12.5, 4.5 Hz, 1H), 3.79 (s, 3H), 4.28 (ddd, J = 12.9, 4.3, 1.9 Hz, 1H) 5.32 (dd, J = 17.6, 2.4 Hz, 1H), 6.65 (d, J = 5.1 Hz, 1H), 6.75 (d, J = 5.1 Hz, 1H), 7.22-7.31 (m, 7H), 7.75 (d,J = 8.2Hz, 2H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 16.13 (q), 21.61 (q), 42.91 (d), 46.98 (t), 47.11 (t), 51.61 (q), 91.33 (s), 93.29 (s), 127.4 (d), 127.6 (d, 2C), 127.7 (d, 2C), 128.5 (d, 2C), 130.0 (d, 2C), 133.7 (s), 137.5 (s), 141.1 (s), 141.2 (s), 144.0 (d), 148.5 (d), 163.2 (s), 164.0 (s)

MS(EI): m/z (%) = 452 (3) (M+1), 431 (25), 322 (18), 258 (18), 191 (100), 178 (15), 110 (18)

Anal. Calcd. For $C_{25}H_{25}NO_5S$: C, 66.50; H 5.58; N 3.10; found: C, 66.50; H 5.65; N 3.09

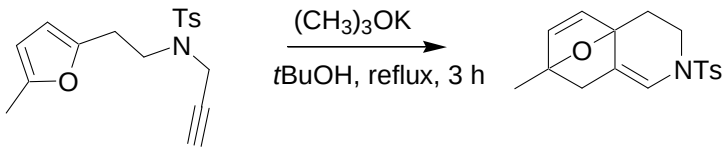
14.



22.5 mg (0.05mol, 1eq) of the cycloadduct was taken in 0.5 ml of CD_3CN (the compound was insoluble) and a tiny crystal of AuCl (approximately 5 mol%) was added. The reaction mixture was heated at 80 ^oC .On heating the mixture became homogeneous. The reaction was traced using NMR. No reaction even after 24h of heating.

The reaction was repeated with ytterbium triflate, aluminium chloride, and p-toluene sulphonic acid as catalysts. There was no reaction in these cases also.

15. **8Methyl-4-(toluene-4-sulfonyl)-11-oxa-4-aza-tricyclo[6.2.1.01,6]undeca-5,9-diene116**(**145**/SP226)



1.0 g (3.15 mmol ,1 eq) of the alkyne was dissolved in 20 ml of *tert*-butyl alcohol. 750 mg (6 mmol, 2 eq) of potassium *tert*-butoxide was added and the reaction mixture was refluxed for 3h. Cooled, 60 ml of water was added and the organic layer was extracted with ethyl acetate. Flash column chromatography (PE:EtOAc) furnished 340 mg (34%) of the cycloadduct[112] as a pale yellow liquid.

R_f (PE:EtOAc, 2:1) = 0.50

IR (film): 3063, 2973, 2929, 1692, 1348, 1273, 1160, 1105, 995, 960, 814, 733, 706, 672, 651, 579, 542 cm^{-1}

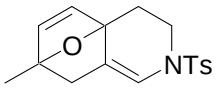
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.61 (s, 3H), 1.83 (dt, J = 13.7, 4.4 Hz , 1H), 2.03 (dd, J = 14.3, 1.8 Hz, 1H), 2.20-2.28 (m, 2H), 2.43 (s, 3H), 3.00 (dt, J = 13.6, 3.4 Hz, 1H), 3.99-4.03 (m, 1H), 6.05 (d, J = 5.6 Hz, 1H), 6.14 (d, J = 5.6 Hz, 1H), 6.56 (s, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 18.64 (q), 21.56 (q), 25.61 (t), 36.68 (t) , 41.77 (t), 82.74 (s), 86.10 (s), 117.0 (d), 122.8 (d), 127.0 (d, 2C), 129.8 (d, 2C), 134.9 (s), 135.4 (d), 138.8 (s), 143.7 (s)

MS(EI): m/z (%) = 317 (26) (M^+), 274 (100), 162 (20), 118 (16), 91 (30)

Anal. Calcd. For $C_{17}H_{19}NO_3S$: C, 64.33; H 6.03; N 4.41; found: C 64.17; H 6.24; N 4.32

16.



Lewis acid
CD_3CN, 80°C

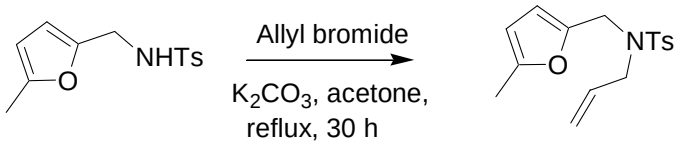
starting material decompsed.

(a).63 mg (0.2 mmol, 1 eq) of the cycloadduct **145** was dissolved in 0.5 ml of deuterated acetonitrile taken in an NMR tube.2.5 mg (5%) of AuCl was added and the reaction mixture was kept at rt. No reaction even after 24h. The mixture was then heated gradually to 80 °C and traced with ^{1}H-NMR. But the starting material decomposed completely at this temperature in 5h. TLC showed numerous spots and the main and isolable one was a solid whose NMR spectrum showed to be of polymeric structure.

(b). 63 mg (0.2mmol, 1 eq) of the cycloadduct 23 was dissolved in 0.5 ml of deuterated

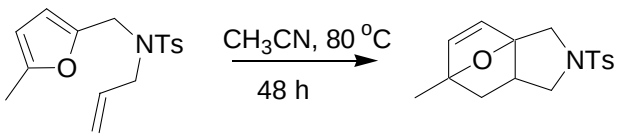
acetonitrile taken in an NMR tube. 3 mg (5%) of ytterbium trifalte was added and the reaction mixture was heated at 80^{o}C. No reaction was observed even after 24h.

17. **N-((5-methylfuran-2-yl)methyl)-N-tosylprop-2-en-1-amine** (**146**/SP254)



1.20 g (4.74 mmol, 1 eq) of the tosylamine was dissolved in 20 ml of acetone. 1.7g (12 mmol, 2.5 eq) of potassium carbonate and 0.87 ml (10 mmol, 2.1 eq) of allyl bromide were added and the suspension was refluxed for 30h. Cooled, and the solvent was removed in vacuum. 20 ml of water was added and the organic layer was extracted with DCM. Dried over $MgSO_4$, and column chromatography (PE/EtOAc, 8:1) furnished 1.1g (80 %) of the product as a pale yellow liquid.

18. **7-Methyl-3-(toluene-4-sulfonyl)-10-oxa-3-aza-tricyclo[5.2.1.01,5]dec-8-ene** (**147**/SP256)



1g (3.27 mmol) of the compound **146** was dissolved in 6 ml of acetonitrile and the mixture was refluxed for 48h. Cooled, the solvent was removed in vacuum, and column chromatography (PE:EtOAc) furnished 740 mg (74 %) of the cyloadduct as colourless solid.

M.P: 107–109 ^{o}C

R_f (PE:EtOAc, 4:1) = 0.14

IR (film): 2972, 2939, 2926, 1598, 1493, 1455, 1334, 1295, 1164, 1111, 1002, 958, 854, 816, 710, 658, 626, 570, 543 cm^{-1}

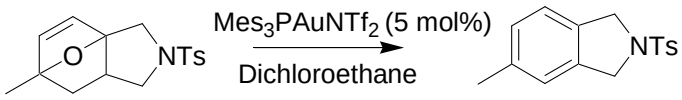
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.34 (dd, J = 11.7, 2.8 Hz, 1H), 1.47 (dt, J = 11.4, 4.4 Hz, 1H), 1.52 (s, 3H), 2.10-2.17 (m, 1H), 2.42 (s, 3H), 2.75 (t, J = 10.2 Hz, 1H), 3.47 (d, J = 12.2 Hz, 1H), 3.85-3.92 (m, 2H), 6.17 (d, J = 5.5 Hz, 1H), 6.32 (d, J = 5.5 Hz, 1H), 7.30 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 7.8 Hz, 2H)

^{13}C-NMR (125 Mz, $CDCl_3$): δ = 19.02 (q), 21.53 (q), 36.60 (t), 46.07 (d), 49.50 (t), 53.37 (t), 88.38 (s), 94.83 (s), 127.4 (d, 2C), 129.7 (d, 2C), 134.0 (s), 134.6 (d), 140.3 (d), 143.4 (s)

MS (EI): m/z (%) = 305 (7) (M^+), 150 (100), 149 (40), 122 (35), 122 (30), 95 (48), 91 (9)

HRMS (ESI): $C_{16}H_{19}NO_3S$: Calcd: 328.0970 $(M+Na)^+$; found: 328.0978 $(M+Na)^+$

19. **5-methyl-2-tosylisoindoline**[10g] (**148**/SP272)



30.5 mg (0.1 mmol, 1 eq) of the cycloadduct **147** was dissolved in 3 ml of dichloroethane in an RB flask. 4 mg (5%) of the catalyst $[Mes_3PAu]NTf_2$ was added and the reaction mixture was heated at 60 ^{o}C. The reaction was finished in 3h according to TLC. Column chromatography (PE:EtOAc) furnished 15 mg (51%) of the deoxygenated aromatic compound as a white solid.

M.P: 112–114^{o}C

R_f (PE:EtOAc, 1:1) = 0.50

IR (film): 2958, 2919, 2843, 1596, 1341, 1307, 1160, 1096, 1065, 810, 738, 708, 669, 624, 581, 547 cm^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.31 (s, 3H), 2.40 (s, 3H), 4.58 (s, 4H), 6.98 (s, 1H), 7.04 (s,

2H), 7.30 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H)

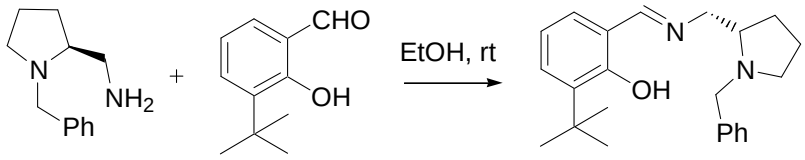
^{13}C-NMR (125 Mz, $CDCl_3$): δ = 21.24 (q), 21.49 (q), 53.52 (t), 53.64 (t), 122.3 (d), 123.1 (d), 127.5 (d, 2C), 128.5 (d), 129.7 (d, 2C), 133.0 (s), 133.7 (s), 136.2 (s), 137.6 (s), 143.6 (s)

MS (EI): m/z (%) = 287 (7) (M^+), 155 (5), 132 (100), 131 (30), 91 (28)

HRMS (ESI): $C_{16}H_{17}NO_2S$: Calcd: 310.0870 $(M+Na)^+$; found: 310.0872 $(M+Na)^+$

2.5 Investigations on Catalytic Aerobic Oxidations by Gold

1. **2-[(1-Benzyl-pyrrolidin-2-ylmethylimino)-methyl]-6-tert-butyl-phenol** (**165**/SP388)



930 mg (4.9 mmol, 1 eq) of the amine was dissolved in 5 ml of ethanol and slowly added to a solution of the aldehyde (915 mg, 5 mmol, 1 eq) in 10 ml ethanol for 30 min. Stirred for another 30 min at rt and then the solvent was evaporated and coloumn chromatography done (PE:EtOAc). 1.52g (89%) of the pure imine product was obtained as an yellow oil.

R_f (PE:EtOAc, 4:1) = 0.40

IR (film): 2955, 2910, 2872, 2791, 1632, 1604, 1437, 1267, 1199, 1144, 750, 698 cm^{-1}

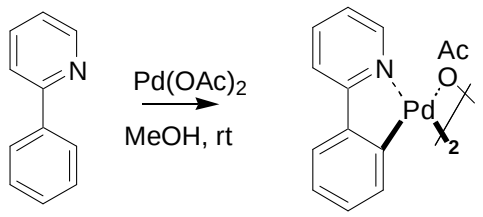
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.43 (s, 9H), 1.67-1.82 (m, 2H), 1.95-2.10 (m, 1H), 2.23-2.37 (m, 1H), 2.84-3.06 (m, 3H), 3.41-3.55 (m, 2H), 3.72-3.82 (m, 1H), 4.03 (d, J = 13.2Hz, 1H), 6.80 (t, J = 6.8HZ, 1H), 7.10 (dd, J = 7.5, 1.5Hz, 1H), 7.22-7.38 (m, 6H), 8.30 (s, 1H), 14.12 (s, 1H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 22.93 (t), 29.37 (q, 3C), 29.54 (t), 34.75 (s), 54.75 (t), 59.38 (t), 63.84 (t), 64.08 (d), 117.6 (d), 118.7 (s), 126.8 (d), 128.2 (d, 2C), 128.8 (d, 2C), 129.2 (d), 129.5 (d), 137.4 (s), 139.7 (s)

MS (APCI): m/z (%) = 351 (100) $(M+1)^+$

HRMS (ESI): $C_{23}H_{30}N_2O$: Calcd: 350.2358; found: 350.2347

2. **Palladacycle** (**159**/SP5)



163 mg (1.05 mmol, 1.eq) of 2-phenyl pyridine was added to a suspension of 168 mg (0.75 mmol, 1 eq) of palladium acetate in 10 ml of methanol. Stirred at rt for 12 h and the solvent was removed. The remaining yellow solid was washed with diethyl ether and dried to obtain 200 mg (60%) of the product.

M.P: 245-250 °C

IR (film): 3044, 1560, 1409, 1155, 1024, 752, 732 cm^{-1}

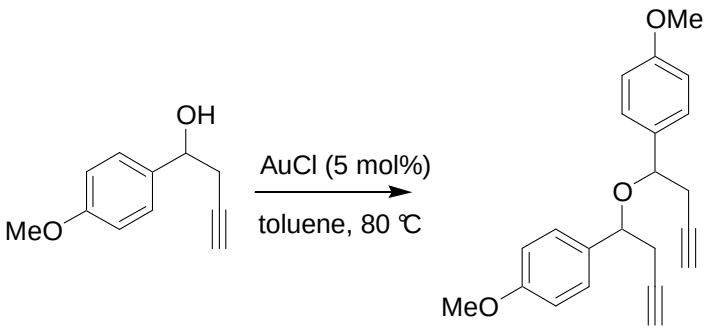
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 6H), 6.42-6.48 (dt, J = 8.0, 1.5Hz, 2H), 6.77-6.96 (m, 8H), 7.08 (d, J = 8.0Hz, 2H), 7.37 (dt, J = 8.1, 1.5Hz, 2H), 7.87 (dd, J = 5.5, 1.1Hz, 2H)

^{13}C-NMR ($CDCl_3$, 75.46 MHz): 24.60 (q, 2C), 117.0 (d), 120.9 (d), 122.3 (d), 123.9 (d), 128.3 (d), 131.8 (d), 137.6 (d), 144.4 (s), 150.1 (d), 164.1 (s), 181.6 (s)

MS (EI): m/z (%) = 581 (100) $(M\text{-}CH_3COO)^+$

HRMS (APCI): $C_{24}H_{19}N_2O_2Pd_2$ $(M\text{-}CH_3COO)^+$: Calcd: 578.9516; found: 578.9526

3. **[1-(1-(4-anisyl)-but-3-ynyloxy)-but-3-ynyl]-anisole** (**180**/SP80)



176 mg (1 mmol, 1 eq) of the alcohol was dissolved in 3 ml of toluene. 5 mol% AuCl was added and the reaction mixture was heated at 80 ^{o}C for 15 h. Filtered through celite and column chromatography (PE:CH_2Cl_2) furnished 30 mg (18%) of the dimeric compound **180** as a colourless oil. ^{1}H-NMR showed it to be a mixture of diastereomers in 3:2 ratio.

R_f (PE:Et_2O, 4:1) = 0.61

IR (film): 3289, 2835, 1610, 1509, 1301, 1243, 1172, 1072, 1029, 828, 645 cm^{-1}

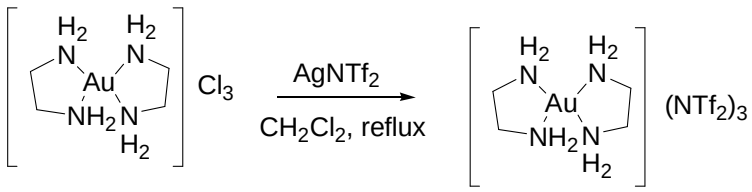
^{1}H-NMR (300 MHz, $CDCl_3$): δ (Major isomer) = 1.90 (t, J = 2.7Hz, 2H), 2.40-2.62 (m, 2H), 3.82 (s, 6H), 4.21 (t, J = 6.8Hz, 2H), 6.89 (d, J = 8.5Hz, 4H), 7.24 (d, J = 8.5Hz, 4H)

^{1}H-NMR (300 MHz, $CDCl_3$): δ (Minor isomer) = 1.95 (t, J = 2.7Hz, 2H), 2.63-2.81 (m, 4H), 3.77 (s, 6H), 4.55 (t, J = 6.5HZ, 2H), 6.80 (d, J = 8.6Hz, 4H), 7.17 (d, J = 8.6Hz, 4H)

MS (EI): m/z (%) = 357 (100) $(M+Na)^{+}$

HRMS (ESI): $C_{22}H_{22}O_3$: Calcd: 334.1569; found: 334.1557

4. **Ethylenediamine gold(III) N-triflate** (**170**/SP560)



100 mg (0.24 mmol, 1eq) of ethylenediamine gold(III) chloride[98] was taken in 10 ml of dichloromethane. 120 mg (0.30 mmol, 1.3 eq) of silver N-triflate was added and the reaction mixture refluxed for 4h in the dark. Cooled down to rt, and the precipitated silver chloride was filtered out. The solvent was then removed under vaccum and the residue was mixed with 5 ml of ethanol. The insoluble material was filtered off and the solvent was removed from the filterate to furnish the product as a pale yellow solid (100mg, 38%).

M.P: 132-134 °C

Anal. Calcd. For $C_{10}H_{16}F_{18}N_7O_{12}S_6AuNO_3S$: C 10.37, H 1.38, N 8.47; found: C 11.00, H 1.92, N 9.05

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4. Curriculum Vitae

Sreekumar Pankajakshan

Date of birth: 20-05-1980

Nationality: Indian

Education

August 2006-June 2009: PhD (Organic Chemistry), Institute of Organic Chemistry, University of Stuttgart, Stuttgart, Germany

October 2000- March 2003: Masters in Organic Chemistry (72%), School of Chemical Sciences, Mahatma Gandhi University, Kerala, India

March 1997-March 2000: Bachelors in Chemistry (91%), Deva Matha College, Kuravilangadu, Mahatma Gandhi University, Kerala, India

Employment/positions

1. **Research Assistant** at Institute of Organic Chemistry, University of Leipzig, Leipzig, Germany / Research Advisor: **Prof. Dr. C. Schneider** / Research Topic: Zirconium-BINOLate catalyzed asymmetric aldol-Tishchenko reactions of aromatic ketone aldols. (May 2005-July 2006)

2. **Visiting Research Scholar** at Department of Chemistry, School of Molecular and Microbial Sciences, University of Queensland, Brisbane, Australia / Research Advisor: **Prof. Dr. Curt Wentrup** / Research Topic: Matrix isolation and spectroscopic investigation of neutral reactive intermediates like carbenes, nitrenes, azirines etc., produced by photolysis and thermolysis. (March 2004-February 2005)

Publications

1. Gold Catalysis: Anellated Heterocycles and Control of the Chemoselectivity by Tether Length, A. S. K. Hashmi, **S. Pankajakshan**, M. Rudolph, F. Rominger. (Submitted to *Angewandte Chemie*)

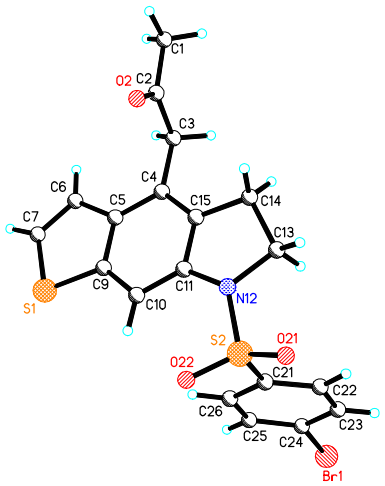
2. Gold Catalysis of Furyl-Alkynes: Proof for the cationic nature of the ‘carbene’ intermediate, A. S. K. Hashmi, S. W. Schäfer, **S. Pankajakshan**, T. Hengst, W. Frey. (Manuscript in preparation for *Angewandte Chemie*)
3. Zirconium-BINOLate-catalyzed, enantioselective, aldol-Tischenko reactions of aromatic ketone aldols, Schneider, C.; Hansch, M.; **Pankajakshan, S**. *Tetrahedron: Asymmetry*, **2006**, *17*, 2738-2742.
4. Kvaskoff, D.; Bednarek, P.; George, L.; **Pankajakshan, S**.; Wentrup, C. *J. Org. Chem*. **2005**, *70*, 7947-7955.

Academic achievements

- Qualified **Overseas Research Scholarship (ORS-2006)** for International Ph.D students from University of Warwick, Coventry, England.
- Qualified **Graduate Aptitude Test in Engineering (GATE-2003)**, conducted by Department of Education, Govt. of India, with a percentile of **93.6%**.
- Qualified **National Eligibility Test (NET-2003)** conducted by Council of Scientific & Industrial Research (CSIR), India.
- Awarded ‘**University Merit Scholarship**’ of Mahatma Gandhi University, Kerala, India, for the Masters programme.

5. X-Ray Crystallographic Data

1. Crystal data of 60g



Chemie : Sreekumar Pankajakshan (AK Hashmi)
Probe : SP641
Dateinamen : spa2.*
Operateur : F. Rominger (AK Hofmann)
Gerät : Bruker Smart CCD

Table 1: Crystal data and structure refinement for spa2.

Identification code	spa2
Empirical formula	$C_{19}H_{16}BrNO_3S_2$
Formula weight	450.36
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Pbca
Z	8
Unit cell dimensions	a =9.8384(1) Å □ =90 deg.
	b = 15.6493(2) Å □ =90 deg.
	c = 24.6489(1) Å □ =90 deg.
Volume	3795.05(6) $Å^3$
Density (calculated)	1.58 g/cm^3
Absorption coefficient	2.40 mm^{-1}
Crystal shape	polyhedron
Crystal size	0.22 x 0.22 x 0.14 mm^3
Crystal colour	brownish
Theta range for data collection	2.6 to 25.0 deg.
Index ranges	-11□h□11, -18□k□18, -29□l□29
Reflections collected	30269
Independent reflections	3353 (R(int) = 0.0723)

Observed reflections	2570 (I >2□(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.73 and 0.62
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3353 / 0 / 236
Goodness-of-fit on F^2	1.04
Final R indices (I>2□(I))	R1 = 0.044, wR2 = 0.105
Largest diff. peak and hole	0.68 and -0.59 eÅ^{-3}

Table 2: Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for spa2. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq}
S1	0.4544(1)	-0.0829(1)	0.3343(1)	0.0487(3)
C1	0.7862(7)	0.2137(5)	0.1608(2)	0.108(3)
O2	0.6043(4)	0.2196(2)	0.2226(1)	0.0619(9)
C2	0.7144(5)	0.1898(3)	0.2118(2)	0.0464(11)
C3	0.7876(4)	0.1302(3)	0.2489(2)	0.0419(10)
C4	0.7063(4)	0.1055(2)	0.2981(2)	0.0359(9)
C5	0.6257(4)	0.0307(2)	0.2981(2)	0.0383(9)
C6	0.6071(5)	-0.0328(3)	0.2563(2)	0.0502(11)
C7	0.5207(5)	-0.0949(3)	0.2701(2)	0.0543(12)
C9	0.5462(4)	0.0109(3)	0.3440(2)	0.0363(9)
C10	0.5419(4)	0.0626(2)	0.3899(2)	0.0344(9)
C11	0.6220(4)	0.1345(2)	0.3891(2)	0.0320(8)
N12	0.6349(3)	0.2002(2)	0.4292(1)	0.0338(7)
C13	0.7578(4)	0.2532(3)	0.4157(2)	0.0385(9)
C14	0.7718(4)	0.2410(3)	0.3540(2)	0.0413(10)
C15	0.7022(4)	0.1562(2)	0.3440(2)	0.0340(9)
S2	0.5986(1)	0.1860(1)	0.4936(1)	0.0337(2)
O21	0.6111(3)	0.2677(2)	0.5184(1)	0.0437(7)
O22	0.4723(3)	0.1410(2)	0.4958(1)	0.0399(7)
C21	0.7262(4)	0.1201(2)	0.5215(1)	0.0297(8)
C22	0.8328(4)	0.1578(2)	0.5484(2)	0.0383(9)
C23	0.9304(4)	0.1075(3)	0.5731(2)	0.0415(10)
C24	0.9185(4)	0.0198(3)	0.5699(2)	0.0403(10)
C25	0.8140(4)	-0.0190(2)	0.5412(2)	0.0368(9)
C26	0.7169(4)	0.0317(2)	0.5173(2)	0.0351(9)
Br1	1.0497(1)	-0.0471(1)	0.6067(1)	0.0617(2)

Table 3: Hydrogen coordinates and isotropic displacement parameters (Å^2) for spa2

Atom	x	y	z	U_{eq}
H1A	0.8697	0.2448	0.1697	0.163

H1B	0.7271	0.2502	0.1387	0.163
H1C	0.8091	0.1619	0.1404	0.163
H3A	0.8732	0.1576	0.2609	0.050
H3B	0.8119	0.0779	0.2285	0.050
H6	0.6520	-0.0307	0.2222	0.060
H7	0.4980	-0.1411	0.2468	0.065
H10	0.4864	0.0489	0.4202	0.041
H13A	0.8394	0.2322	0.4350	0.046
H13B	0.7430	0.3140	0.4250	0.046
H14A	0.7260	0.2877	0.3340	0.050
H14B	0.8685	0.2389	0.3431	0.050
H22	0.8394	0.2183	0.5501	0.046
H23	1.0045	0.1329	0.5918	0.050
H25	0.8097	-0.0795	0.5381	0.044
H26	0.6437	0.0064	0.4980	0.042

Table 4: Anisotrope Auslenkungsparameter ($Å^2$) für spa2. Der Exponent für den anisotropen Auslenkungsparameter hat die Form: $-2\ pi^2\ (h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12})$ (Anisotropic displacement parameters ($Å^2$) for spa2. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ (h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12})$

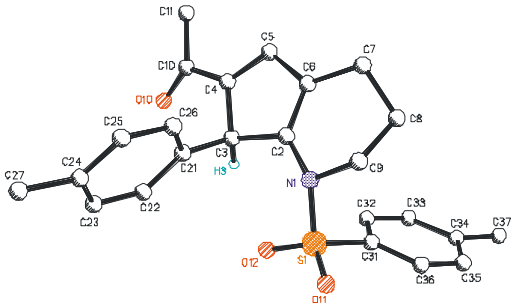
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0549(7)	0.0412(6)	0.0499(7)	0.0009(5)	-0.0071(5)	-0.0150(5)
C1	0.115(5)	0.131(6)	0.079(4)	0.062(4)	0.057(4)	0.063(5)
O2	0.056(2)	0.067(2)	0.062(2)	0.0220(17)	0.0113(17)	0.0243(18)
C2	0.051(3)	0.042(2)	0.046(2)	0.007(2)	0.011(2)	0.006(2)
C3	0.034(2)	0.049(2)	0.042(2)	0.006(2)	0.0044(18)	0.0013(19)
C4	0.028(2)	0.041(2)	0.039(2)	0.0104(18)	-0.0023(17)	0.0046(17)
C5	0.035(2)	0.042(2)	0.038(2)	0.0016(18)	-0.0053(18)	0.0055(18)
C6	0.058(3)	0.052(3)	0.040(2)	-0.006(2)	-0.001(2)	0.004(2)
C7	0.065(3)	0.043(3)	0.055(3)	-0.010(2)	-0.005(2)	-0.007(2)
C9	0.034(2)	0.035(2)	0.040(2)	0.0054(18)	-0.0073(18)	-0.0003(17)
C10	0.031(2)	0.037(2)	0.036(2)	0.0058(17)	0.0009(17)	-0.0019(17)
C11	0.0258(19)	0.0305(19)	0.040(2)	0.0062(16)	-0.0062(17)	0.0014(16)
N12	0.0339(18)	0.0276(16)	0.0401(18)	0.0025(14)	0.0006(14)	-0.0022(14)
C13	0.038(2)	0.032(2)	0.046(2)	0.0039(18)	-0.0034(19)	-0.0062(18)
C14	0.037(2)	0.037(2)	0.050(3)	0.0086(19)	0.0011(19)	-0.0037(18)
C15	0.0236(19)	0.035(2)	0.044(2)	0.0101(18)	-0.0024(17)	0.0010(16)
S2	0.0323(5)	0.0271(5)	0.0417(6)	-0.0014(4)	0.0018(4)	0.0032(4)
O21	0.0499(18)	0.0290(14)	0.0523(18)	-0.0072(13)	-0.0021(14)	0.0043(13)
O22	0.0327(15)	0.0394(15)	0.0476(17)	-0.0008(13)	0.0066(13)	0.0018(12)
C21	0.031(2)	0.0279(19)	0.0304(19)	0.0000(16)	0.0044(16)	0.0020(16)
C22	0.040(2)	0.030(2)	0.044(2)	-0.0025(18)	0.0023(19)	-0.0049(18)
C23	0.035(2)	0.042(2)	0.048(3)	-0.0008(19)	-0.0069(19)	-0.0073(19)
C24	0.038(2)	0.047(2)	0.035(2)	0.0052(18)	0.0027(18)	0.0117(19)
C25	0.043(2)	0.0274(19)	0.040(2)	0.0008(17)	0.0031(19)	0.0040(18)
C26	0.038(2)	0.031(2)	0.037(2)	-0.0004(17)	0.0006(18)	-0.0028(17)
Br1	0.0565(3)	0.0650(3)	0.0636(3)	0.0071(2)	-0.0114(2)	0.0246(3)

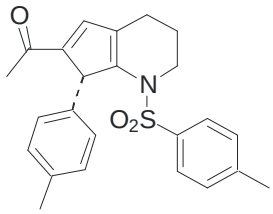
Table 5: Bond lengths (Å) and angles (deg) for spa2

S1-C7	1.721(5)
S1-C9	1.740(4)
C1-C2	1.489(6)
O2-C2	1.208(5)
C2-C3	1.492(6)
C3-C4	1.504(5)
C4-C15	1.383(6)
C4-C5	1.413(6)
C5-C9	1.409(6)
C5-C6	1.443(6)
C6-C7	1.334(7)
C9-C10	1.393(6)
C10-C11	1.374(5)
C11-C15	1.406(5)
C11-N12	1.431(5)
N12-C13	1.504(5)
N12-S2	1.643(3)
C13-C14	1.537(6)
C14-C15	1.513(5)
S2-O21	1.422(3)
S2-O22	1.429(3)
S2-C21	1.764(4)
C21-C22	1.375(5)
C21-C26	1.390(5)
C22-C23	1.382(6)
C23-C24	1.379(6)
C24-C25	1.389(6)
C24-Br1	1.893(4)
C25-C26	1.374(5)
C7-S1-C9	91.2(2)
O2-C2-C1	121.0(4)
O2-C2-C3	122.5(4)
C1-C2-C3	116.4(4)
C2-C3-C4	113.5(3)
C15-C4-C5	117.4(4)
C15-C4-C3	121.8(4)
C5-C4-C3	120.8(4)
C9-C5-C4	119.6(4)
C9-C5-C6	110.5(4)
C4-C5-C6	129.9(4)
C7-C6-C5	113.6(4)
C6-C7-S1	113.4(3)
C10-C9-C5	122.8(4)
C10-C9-S1	125.8(3)
C5-C9-S1	111.3(3)
C11-C10-C9	116.5(4)
C10-C11-C15	122.1(4)
C10-C11-N12	129.0(3)
C15-C11-N12	108.8(3)
C11-N12-C13	108.3(3)
C11-N12-S2	123.4(2)
C13-N12-S2	117.6(3)
N12-C13-C14	102.9(3)
C15-C14-C13	103.3(3)
C4-C15-C11	121.6(4)
C4-C15-C14	128.7(4)
C11-C15-C14	109.7(3)
O21-S2-O22	120.12(18)

O21-S2-N12	105.91(17)
O22-S2-N12	106.94(17)
O21-S2-C21	107.30(18)
O22-S2-C21	108.42(17)
N12-S2-C21	107.56(16)
C22-C21-C26	120.9(4)
C22-C21-S2	118.7(3)
C26-C21-S2	120.4(3)
C21-C22-C23	119.8(4)
C24-C23-C22	118.8(4)
C23-C24-C25	121.8(4)
C23-C24-Br1	117.7(3)
C25-C24-Br1	120.4(3)
C26-C25-C24	118.7(4)
C25-C26-C21	119.8(4)

2. Crystal data for 64s





Chemie : Sreekumar Pankajahshan (AK Hashmi)
Probe : SP667
Dateinamen : spa1.*
Operateur : F. Rominger (AK Hofmann)
Gerät : Bruker Smart CCD

Table 6: Crystal data and structure refinement for spa1

Identification code	spa1	
Empirical formula	$C_{24}H_{25}NO_3S$	
Formula weight	407.51	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Z	4	
Unit cell dimensions	a = 13.0319(8) Å	α = 90 deg.
	b =8.5404(5) Å	β =96.482(2) deg.
	c = 19.7383(11) Å	γ = 90 deg.
Volume	2182.8(2) $Å^3$	
Density (calculated)	1.24 g/cm^3	
Absorption coefficient	0.17 mm^{-1}	
Crystal shape	polyhedron	

Crystal size	0.16 x 0.09 x 0.06 mm^3
Crystal colour	colorless
Theta range for data collection	1.8 to 20.8 deg.
Index ranges	-13≤h≤13, -8≤k≤8, -19≤l≤19
Reflections collected	8280
Independent reflections	2291 (R(int) = 0.0824)
Observed reflections	1509 (I >2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.97
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2291 / 0 / 265
Goodness-of-fit on F^2	1.07
Final R indices (I>2σ(I))	R1 = 0.063, wR2 = 0.117
Largest diff. peak and hole	0.22 and -0.28 e$Å^{-3}$

Table 7: Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for spa1. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq}
N1	0.8668(3)	0.8271(5)	0.2139(2)	0.0344(11)
C2	0.8738(4)	0.9552(6)	0.1701(2)	0.0316(14)
C3	0.8537(4)	0.9484(6)	0.0934(2)	0.0344(14)
C4	0.8602(4)	1.1203(6)	0.0747(3)	0.0378(15)
C5	0.8753(4)	1.2058(6)	0.1318(3)	0.0360(15)
C6	0.8825(4)	1.1052(6)	0.1916(3)	0.0335(14)
C7	0.8986(4)	1.1538(6)	0.2649(2)	0.0402(15)
C8	0.9249(4)	1.0089(6)	0.3094(3)	0.0443(16)
C9	0.8553(4)	0.8731(6)	0.2854(3)	0.0395(15)
C10	0.8578(5)	1.1740(7)	0.0041(3)	0.0507(17)
O10	0.8761(5)	1.0809(5)	-0.0404(2)	0.108(2)
C11	0.8628(5)	1.3471(7)	-0.0085(3)	0.067(2)
C21	0.7489(5)	0.8790(6)	0.0685(3)	0.0350(15)
C22	0.7363(5)	0.7680(6)	0.0170(3)	0.0485(17)
C23	0.6394(6)	0.7124(7)	-0.0074(3)	0.0539(18)
C24	0.5521(5)	0.7638(7)	0.0186(3)	0.0485(17)
C25	0.5649(5)	0.8706(7)	0.0706(3)	0.0509(17)
C26	0.6615(5)	0.9271(6)	0.0954(3)	0.0455(16)
C27	0.4456(5)	0.7067(7)	-0.0091(3)	0.070(2)
S1	0.9283(1)	0.6618(2)	0.2030(1)	0.0406(5)
O11	0.8825(3)	0.5465(4)	0.2425(2)	0.0488(11)
O12	0.9280(3)	0.6394(4)	0.1311(2)	0.0507(11)
C31	1.0558(4)	0.6877(6)	0.2395(3)	0.0368(14)
C32	1.1251(5)	0.7700(7)	0.2055(3)	0.0507(17)
C33	1.2249(5)	0.7915(8)	0.2362(4)	0.066(2)
C34	1.2563(5)	0.7359(8)	0.3012(4)	0.0559(18)
C35	1.1852(5)	0.6542(7)	0.3334(3)	0.0551(17)
C36	1.0862(5)	0.6312(6)	0.3042(3)	0.0461(16)
C37	1.3651(5)	0.7639(9)	0.3337(4)	0.094(3)

Table 8: Hydrogen coordinates and isotropic displacement parameters Å^2) for spa1

Atom	x	y	z	U_{eq}
H3	0.9097	0.8880	0.0744	0.041
H5	0.8805	1.3168	0.1331	0.043
H7A	0.8351	1.2039	0.2779	0.048
H7B	0.9556	1.2307	0.2719	0.048
H8A	0.9979	0.9793	0.3072	0.053
H8B	0.9162	1.0336	0.3575	0.053
H9A	0.8720	0.7822	0.3157	0.047
H9B	0.7826	0.9027	0.2886	0.047
H11A	0.9332	1.3847	0.0052	0.101
H11B	0.8146	1.4013	0.0182	0.101
H11C	0.8439	1.3683	-0.0571	0.101
H22	0.7952	0.7294	-0.0019	0.058
H23	0.6332	0.6368	-0.0430	0.065
H25	0.5060	0.9069	0.0901	0.061
H26	0.6673	1.0007	0.1317	0.055
H27A	0.4116	0.6610	0.0281	0.105
H27B	0.4518	0.6271	-0.0442	0.105
H27C	0.4046	0.7949	-0.0290	0.105
H32	1.1046	0.8115	0.1613	0.061
H33	1.2730	0.8459	0.2121	0.079
H35	1.2055	0.6122	0.3774	0.066
H36	1.0383	0.5765	0.3284	0.055
H37A	1.3646	0.8445	0.3690	0.142
H37B	1.4080	0.7990	0.2990	0.142
H37C	1.3933	0.6665	0.3544	0.142

Table 9: Anisotropic displacement parameters (Å^2) for spa1. The anisotropic displacement factor exponent takes the form: -2 pi^2 (h^2 a^{*2} U_{11} + ... + 2 h k a* b* U_{12}

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	0.041(3)	0.026(3)	0.035(3)	0.006(2)	-0.003(2)	0.003(2)
C2	0.028(3)	0.032(4)	0.035(4)	-0.004(3)	0.000(3)	-0.003(3)
C3	0.039(4)	0.029(3)	0.035(4)	-0.001(3)	0.004(3)	0.004(3)
C4	0.047(4)	0.034(3)	0.030(4)	0.003(3)	-0.004(3)	0.001(3)
C5	0.034(4)	0.029(3)	0.044(4)	0.002(3)	-0.002(3)	-0.005(3)
C6	0.034(4)	0.036(4)	0.030(4)	0.003(3)	0.002(3)	-0.002(3)
C7	0.045(4)	0.039(3)	0.034(4)	-0.003(3)	-0.003(3)	-0.003(3)
C8	0.058(4)	0.041(4)	0.032(3)	-0.005(3)	-0.002(3)	0.003(3)
C9	0.047(4)	0.034(4)	0.038(4)	0.003(3)	0.006(3)	0.002(3)
C10	0.066(5)	0.044(4)	0.045(4)	0.003(4)	0.019(3)	0.007(4)
O10	0.229(7)	0.055(3)	0.051(3)	-0.001(3)	0.054(4)	-0.015(4)
C11	0.094(6)	0.049(4)	0.059(4)	0.008(3)	0.010(4)	-0.010(4)
C21	0.050(4)	0.025(3)	0.028(3)	0.003(3)	-0.002(3)	-0.001(3)
C22	0.066(5)	0.034(4)	0.047(4)	-0.014(3)	0.013(4)	-0.005(3)
C23	0.080(6)	0.042(4)	0.039(4)	-0.013(3)	0.001(4)	-0.016(4)
C24	0.058(5)	0.039(4)	0.044(4)	0.002(3)	-0.013(4)	-0.004(4)
C25	0.045(5)	0.056(4)	0.050(4)	-0.009(4)	-0.001(3)	0.007(3)

C26	0.044(4)	0.045(4)	0.044(4)	-0.014(3)	-0.010(4)	0.001(3)
C27	0.064(5)	0.063(5)	0.076(5)	0.000(4)	-0.025(4)	-0.011(4)
S1	0.0463(10)	0.0264(8)	0.0476(11)	0.0020(8)	-0.0011(8)	-0.0003(8)
O11	0.052(3)	0.027(2)	0.067(3)	0.010(2)	0.003(2)	-0.008(2)
O12	0.076(3)	0.034(2)	0.040(3)	-0.0080(19)	-0.003(2)	0.007(2)
C31	0.038(4)	0.029(3)	0.044(4)	0.003(3)	0.007(3)	0.011(3)
C32	0.050(5)	0.053(4)	0.050(4)	0.017(3)	0.010(4)	0.003(4)
C33	0.043(5)	0.076(5)	0.082(6)	0.015(4)	0.022(4)	-0.012(4)
C34	0.038(5)	0.060(4)	0.069(5)	-0.002(4)	-0.001(4)	0.007(4)
C35	0.050(5)	0.065(5)	0.049(4)	0.005(4)	0.002(4)	0.007(4)
C36	0.042(4)	0.055(4)	0.041(4)	0.011(3)	0.006(3)	0.004(3)
C37	0.045(5)	0.121(7)	0.114(6)	0.005(5)	-0.007(5)	-0.001(5)

Table 10: Bond lengths (Å) and angles (deg) for spa1

N1-C2	1.404(6)
N1-C9	1.487(6)
N1-S1	1.650(4)
C2-C6	1.351(7)
C2-C3	1.508(6)
C3-C4	1.518(7)
C3-C21	1.519(7)
C4-C5	1.338(7)
C4-C10	1.464(7)
C5-C6	1.454(7)
C6-C7	1.497(7)
C7-C8	1.534(7)
C8-C9	1.515(7)
C10-O10	1.228(6)
C10-C11	1.502(8)
C21-C26	1.373(7)
C21-C22	1.386(7)
C22-C23	1.384(8)
C23-C24	1.371(8)
C24-C25	1.369(7)
C24-C27	1.514(7)
C25-C26	1.384(7)
S1-O11	1.428(4)
S1-O12	1.430(4)
S1-C31	1.749(5)
C31-C32	1.378(7)
C31-C36	1.380(7)
C32-C33	1.384(8)
C33-C34	1.386(8)
C34-C35	1.371(8)
C34-C37	1.508(8)
C35-C36	1.367(8)
C2-N1-C9	113.5(4)
C2-N1-S1	121.3(4)
C9-N1-S1	116.9(3)
C6-C2-N1	123.7(5)
C6-C2-C3	110.5(4)
N1-C2-C3	125.0(4)
C2-C3-C4	101.4(4)
C2-C3-C21	112.8(4)
C4-C3-C21	111.8(4)

C5-C4-C10	128.0(5)
C5-C4-C3	109.3(4)
C10-C4-C3	122.5(5)
C4-C5-C6	110.5(5)
C2-C6-C5	108.1(4)
C2-C6-C7	124.4(5)
C5-C6-C7	127.5(5)
C6-C7-C8	109.1(4)
C9-C8-C7	110.5(4)
N1-C9-C8	112.3(4)
O10-C10-C4	119.6(5)
O10-C10-C11	120.2(5)
C4-C10-C11	118.0(5)
C26-C21-C22	116.9(5)
C26-C21-C3	120.9(5)
C22-C21-C3	122.1(6)
C23-C22-C21	121.2(6)
C24-C23-C22	121.5(6)
C25-C24-C23	117.3(6)
C25-C24-C27	120.9(6)
C23-C24-C27	121.8(6)
C24-C25-C26	121.8(6)
C21-C26-C25	121.3(5)
O11-S1-O12	119.7(2)
O11-S1-N1	106.2(2)
O12-S1-N1	107.3(2)
O11-S1-C31	107.3(3)
O12-S1-C31	108.8(3)
N1-S1-C31	106.9(2)
C32-C31-C36	119.6(5)
C32-C31-S1	120.5(5)
C36-C31-S1	119.8(5)
C31-C32-C33	119.3(6)
C32-C33-C34	121.7(6)
C35-C34-C33	117.3(6)
C35-C34-C37	122.3(6)
C33-C34-C37	120.4(7)
C36-C35-C34	122.2(6)
C35-C36-C31	119.9(6)

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3. Crystal data of 137a

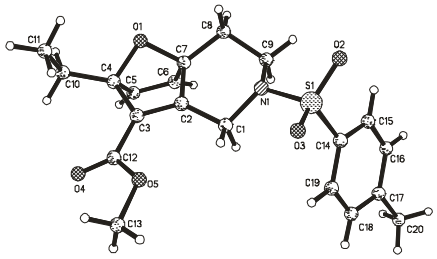


Table 11: Crystal data and structure refinement for s1460rc.

Identification code	s1460rc
Empirical formula	C20 H23 N O5 S
Formula weight	389.45
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 5.7400(9) A alpha = 65.085(9)° b = 13.134(3) A beta = 81.432(11)° c = 14.769(2) A gamma = 82.905(13)°
Volume	996.3(3) A^3
Z, Calculated density	2, 1.298 Mg/m^3
Absorption coefficient	1.702 mm^-1
F(000)	412
Crystal size	0.7 x 0.4 x 0.15 mm
Theta range for data collection	3.32 to 65.99 deg.
Limiting indices	-5<=h<=6, -14<=k<=14, -17<=l<=17
Reflections collected / unique	6166 / 3243 [R(int) = 0.0394]
Completeness to theta = 65.99	93.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3243 / 0 / 246
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma (I)]	R1 = 0.0597, wR2 = 0.1347
R indices (all data)	R1 = 0.1011, wR2 = 0.1791
Extinction coefficient	0.0129(10)
Largest diff. peak and hole	0.281 and -0.451 e.A^-3

Table 12: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s1460rc.U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	404(2)	6154(1)	7755(1)	60(1)
O(1)	3072(4)	8986(2)	9303(2)	61(1)
N(1)	1627(5)	6896(2)	8185(2)	49(1)
C(1)	2802(7)	7890(3)	7428(3)	57(1)
O(2)	-853(5)	5325(2)	8605(2)	75(1)
C(2)	3255(6)	8620(3)	7914(3)	54(1)
O(3)	-838(5)	6943(2)	6940(2)	72(1)
C(3)	3547(7)	9710(3)	7588(3)	63(1)
C(4)	4409(7)	9845(4)	8478(3)	67(1)
O(4)	4488(10)	11453(4)	6267(3)	145(2)
O(5)	2310(8)	10342(3)	6008(2)	108(1)
C(5)	6872(8)	9218(5)	8611(4)	90(2)
C(6)	6568(7)	8147(5)	8922(4)	83(1)
C(7)	3907(6)	8081(3)	9001(3)	56(1)
C(8)	2831(7)	6993(3)	9662(3)	61(1)
C(9)	2915(6)	6271(3)	9075(3)	57(1)
C(10)	4029(9)	10968(4)	8544(4)	87(1)
C(11)	1457(9)	11393(4)	8602(4)	97(2)
C(12)	3498(10)	10600(4)	6579(3)	85(1)
C(13)	2091(16)	11190(5)	4987(4)	155(3)
C(14)	2719(7)	5455(3)	7277(3)	57(1)
C(15)	3637(8)	4412(3)	7906(3)	70(1)
C(16)	5550(9)	3889(4)	7552(3)	77(1)
C(17)	6578(9)	4381(4)	6569(4)	80(1)
C(18)	5642(9)	5438(4)	5953(3)	85(1)
C(19)	3722(8)	5968(4)	6300(3)	72(1)
C(20)	8644(11)	3777(5)	6197(5)	125(2)

Table 13: Bond lengths [A] and angles [deg] for s1460rc.*

S(1)-O(3)	1.432(3)
S(1)-O(2)	1.434(3)
S(1)-N(1)	1.635(3)
S(1)-C(14)	1.753(4)
O(1)-C(7)	1.443(4)
O(1)-C(4)	1.457(5)
N(1)-C(1)	1.474(4)
N(1)-C(9)	1.476(4)
C(1)-C(2)	1.484(5)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-C(3)	1.327(5)
C(2)-C(7)	1.541(5)
C(3)-C(12)	1.457(6)
C(3)-C(4)	1.555(5)
C(4)-C(10)	1.506(6)

C(4)-C(5)	1.541(6)
O(4)-C(12)	1.198(5)
O(5)-C(12)	1.327(6)
O(5)-C(13)	1.461(6)
C(5)-C(6)	1.308(7)
C(5)-H(5)	0.9300
C(6)-C(7)	1.525(5)
C(6)-H(6)	0.9300
C(7)-C(8)	1.496(5)
C(8)-C(9)	1.525(5)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.516(7)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(19)	1.377(5)
C(14)-C(15)	1.383(5)
C(15)-C(16)	1.377(6)
C(15)-H(15)	0.9300
C(16)-C(17)	1.386(6)
C(16)-H(16)	0.9300
C(17)-C(18)	1.394(6)
C(17)-C(20)	1.510(7)
C(18)-C(19)	1.380(6)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600

O(3)-S(1)-O(2)	119.95(18)
O(3)-S(1)-N(1)	106.38(16)
O(2)-S(1)-N(1)	106.48(16)
O(3)-S(1)-C(14)	108.71(17)
O(2)-S(1)-C(14)	108.04(18)
N(1)-S(1)-C(14)	106.52(16)
C(7)-O(1)-C(4)	95.9(3)
C(1)-N(1)-C(9)	113.7(3)
C(1)-N(1)-S(1)	116.3(2)
C(9)-N(1)-S(1)	117.1(2)
N(1)-C(1)-C(2)	109.2(3)
N(1)-C(1)-H(1A)	109.8
C(2)-C(1)-H(1A)	109.8
N(1)-C(1)-H(1B)	109.8
C(2)-C(1)-H(1B)	109.8
H(1A)-C(1)-H(1B)	108.3
C(3)-C(2)-C(1)	134.2(3)
C(3)-C(2)-C(7)	105.6(3)
C(1)-C(2)-C(7)	119.6(3)
C(2)-C(3)-C(12)	129.7(4)
C(2)-C(3)-C(4)	105.4(3)
C(12)-C(3)-C(4)	124.2(4)
O(1)-C(4)-C(10)	112.2(3)
O(1)-C(4)-C(5)	98.1(3)
C(10)-C(4)-C(5)	119.0(4)

O(1)-C(4)-C(3)	98.7(3)
C(10)-C(4)-C(3)	119.6(4)
C(5)-C(4)-C(3)	105.5(3)
C(12)-O(5)-C(13)	117.0(4)
C(6)-C(5)-C(4)	107.1(4)
C(6)-C(5)-H(5)	126.5
C(4)-C(5)-H(5)	126.5
C(5)-C(6)-C(7)	105.0(4)
C(5)-C(6)-H(6)	127.5
C(7)-C(6)-H(6)	127.5
O(1)-C(7)-C(8)	113.6(3)
O(1)-C(7)-C(6)	100.3(3)
C(8)-C(7)-C(6)	119.3(4)
O(1)-C(7)-C(2)	99.6(3)
C(8)-C(7)-C(2)	115.3(3)
C(6)-C(7)-C(2)	106.0(3)
C(7)-C(8)-C(9)	109.5(3)
C(7)-C(8)-H(8A)	109.8
C(9)-C(8)-H(8A)	109.8
C(7)-C(8)-H(8B)	109.8
C(9)-C(8)-H(8B)	109.8
H(8A)-C(8)-H(8B)	108.2
N(1)-C(9)-C(8)	108.9(3)
N(1)-C(9)-H(9A)	109.9
C(8)-C(9)-H(9A)	109.9
N(1)-C(9)-H(9B)	109.9
C(8)-C(9)-H(9B)	109.9
H(9A)-C(9)-H(9B)	108.3
C(4)-C(10)-C(11)	113.8(4)
C(4)-C(10)-H(10A)	108.8
C(11)-C(10)-H(10A)	108.8
C(4)-C(10)-H(10B)	108.8
C(11)-C(10)-H(10B)	108.8
H(10A)-C(10)-H(10B)	107.7
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(4)-C(12)-O(5)	122.5(5)
O(4)-C(12)-C(3)	125.1(5)
O(5)-C(12)-C(3)	112.4(4)
O(5)-C(13)-H(13A)	109.5
O(5)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
O(5)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(19)-C(14)-C(15)	120.0(4)
C(19)-C(14)-S(1)	120.4(3)
C(15)-C(14)-S(1)	119.5(3)
C(16)-C(15)-C(14)	119.8(4)
C(16)-C(15)-H(15)	120.1
C(14)-C(15)-H(15)	120.1
C(15)-C(16)-C(17)	121.4(4)
C(15)-C(16)-H(16)	119.3
C(17)-C(16)-H(16)	119.3
C(16)-C(17)-C(18)	117.7(4)
C(16)-C(17)-C(20)	120.2(5)
C(18)-C(17)-C(20)	122.0(5)
C(19)-C(18)-C(17)	121.2(4)
C(19)-C(18)-H(18)	119.4

C(17)-C(18)-H(18)	119.4
C(14)-C(19)-C(18)	119.8(4)
C(14)-C(19)-H(19)	120.1
C(18)-C(19)-H(19)	120.1
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

*Symmetry transformations used to generate equivalent atoms

Table 14: Anisotropic displacement parameters (A^2 x 10^3) for s1460rc. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	52(1)	67(1)	62(1)	-23(1)	-11(1)	-13(1)
O(1)	51(2)	74(2)	66(2)	-35(1)	-7(1)	-8(1)
N(1)	47(2)	52(2)	48(1)	-17(1)	-12(1)	-6(1)
C(1)	63(2)	58(2)	51(2)	-19(2)	-6(2)	-16(2)
O(2)	63(2)	84(2)	69(2)	-19(1)	0(1)	-33(1)
C(2)	41(2)	62(2)	61(2)	-26(2)	-5(2)	-8(2)
O(3)	62(2)	82(2)	70(2)	-24(1)	-31(1)	-1(1)
C(3)	61(2)	66(2)	63(2)	-26(2)	1(2)	-19(2)
C(4)	54(2)	76(3)	83(3)	-42(2)	1(2)	-21(2)
O(4)	217(5)	104(3)	107(3)	-21(2)	2(3)	-88(3)
O(5)	162(4)	82(2)	68(2)	-3(2)	-32(2)	-43(2)
C(5)	42(2)	135(5)	118(4)	-75(4)	-4(2)	-19(3)
C(6)	44(2)	107(4)	119(4)	-66(3)	-24(2)	6(2)
C(7)	42(2)	68(2)	65(2)	-32(2)	-13(2)	0(2)
C(8)	60(2)	72(2)	53(2)	-23(2)	-20(2)	-1(2)
C(9)	52(2)	63(2)	52(2)	-17(2)	-15(2)	-3(2)
C(10)	91(4)	85(3)	98(3)	-51(3)	6(3)	-30(3)
C(11)	98(4)	70(3)	124(4)	-45(3)	-3(3)	-3(3)
C(12)	110(4)	72(3)	71(3)	-23(2)	4(3)	-38(3)
C(13)	254(10)	103(5)	75(4)	12(3)	-41(5)	-42(5)
C(14)	64(2)	50(2)	61(2)	-23(2)	-13(2)	-9(2)
C(15)	84(3)	59(2)	65(2)	-21(2)	-10(2)	-11(2)
C(16)	92(3)	60(2)	82(3)	-30(2)	-22(2)	2(2)
C(17)	83(3)	80(3)	81(3)	-37(2)	-9(2)	1(2)
C(18)	97(4)	81(3)	70(3)	-31(2)	5(2)	-3(3)
C(19)	83(3)	67(2)	61(2)	-23(2)	-9(2)	-4(2)
C(20)	124(5)	121(5)	123(5)	-61(4)	7(4)	32(4)

Table 15: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s1460rc.

	x	y	z	U(eq)
H(1A)	1805	8305	6894	69

H(1B)	4281	7654	7136	69
H(5)	8304	9539	8491	108
H(6)	7724	7555	9065	99
H(8A)	1207	7140	9895	74
H(8B)	3694	6597	10244	74
H(9A)	4541	6095	8867	69
H(9B)	2193	5570	9496	69
H(10A)	4883	11517	7960	104
H(10B)	4690	10908	9133	104
H(11A)	1344	12112	8636	145
H(11B)	606	10869	9191	145
H(11C)	793	11469	8016	145
H(13A)	1190	10914	4650	233
H(13B)	3634	11346	4628	233
H(13C)	1305	11868	5013	233
H(15)	2965	4065	8567	84
H(16)	6166	3191	7982	92
H(18)	6324	5793	5295	102
H(19)	3107	6669	5876	86
H(20A)	10047	3827	6453	187
H(20B)	8860	4119	5476	187
H(20C)	8340	3000	6423	187

Table 16: Torsion angles [deg] for s1460rc.*

O(3)-S(1)-N(1)-C(1)	-44.3(3)
O(2)-S(1)-N(1)-C(1)	-173.3(3)
C(14)-S(1)-N(1)-C(1)	71.6(3)
O(3)-S(1)-N(1)-C(9)	176.6(2)
O(2)-S(1)-N(1)-C(9)	47.6(3)
C(14)-S(1)-N(1)-C(9)	-67.5(3)
C(9)-N(1)-C(1)-C(2)	-54.1(4)
S(1)-N(1)-C(1)-C(2)	165.4(2)
N(1)-C(1)-C(2)-C(3)	-155.3(4)
N(1)-C(1)-C(2)-C(7)	35.5(4)
C(1)-C(2)-C(3)-C(12)	0.5(8)
C(7)-C(2)-C(3)-C(12)	170.8(4)
C(1)-C(2)-C(3)-C(4)	-169.9(4)
C(7)-C(2)-C(3)-C(4)	0.4(4)
C(7)-O(1)-C(4)-C(10)	-178.7(4)
C(7)-O(1)-C(4)-C(5)	-52.8(3)
C(7)-O(1)-C(4)-C(3)	54.3(3)
C(2)-C(3)-C(4)-O(1)	-34.5(4)
C(12)-C(3)-C(4)-O(1)	154.4(4)
C(2)-C(3)-C(4)-C(10)	-156.3(4)
C(12)-C(3)-C(4)-C(10)	32.6(6)
C(2)-C(3)-C(4)-C(5)	66.5(4)
C(12)-C(3)-C(4)-C(5)	-104.6(5)
O(1)-C(4)-C(5)-C(6)	34.1(5)
C(10)-C(4)-C(5)-C(6)	155.1(4)
C(3)-C(4)-C(5)-C(6)	-67.3(5)
C(4)-C(5)-C(6)-C(7)	-0.5(5)
C(4)-O(1)-C(7)-C(8)	-177.6(3)
C(4)-O(1)-C(7)-C(6)	53.8(3)
C(4)-O(1)-C(7)-C(2)	-54.5(3)
C(5)-C(6)-C(7)-O(1)	-33.9(5)
C(5)-C(6)-C(7)-C(8)	-158.5(4)
C(5)-C(6)-C(7)-C(2)	69.4(5)
C(3)-C(2)-C(7)-O(1)	34.3(4)

C(1)-C(2)-C(7)-O(1)	-153.7(3)
C(3)-C(2)-C(7)-C(8)	156.2(3)
C(1)-C(2)-C(7)-C(8)	-31.8(5)
C(3)-C(2)-C(7)-C(6)	-69.5(4)
C(1)-C(2)-C(7)-C(6)	102.5(4)
O(1)-C(7)-C(8)-C(9)	155.3(3)
C(6)-C(7)-C(8)-C(9)	-86.7(4)
C(2)-C(7)-C(8)-C(9)	41.2(4)
C(1)-N(1)-C(9)-C(8)	68.2(4)
S(1)-N(1)-C(9)-C(8)	-151.7(2)
C(7)-C(8)-C(9)-N(1)	-58.5(4)
O(1)-C(4)-C(10)-C(11)	-55.3(6)
C(5)-C(4)-C(10)-C(11)	-168.9(4)
C(3)-C(4)-C(10)-C(11)	59.5(6)
C(13)-O(5)-C(12)-O(4)	-4.7(9)
C(13)-O(5)-C(12)-C(3)	178.3(5)
C(2)-C(3)-C(12)-O(4)	-154.4(6)
C(4)-C(3)-C(12)-O(4)	14.4(8)
C(2)-C(3)-C(12)-O(5)	22.4(7)
C(4)-C(3)-C(12)-O(5)	-168.8(4)
O(3)-S(1)-C(14)-C(19)	26.9(4)
O(2)-S(1)-C(14)-C(19)	158.6(3)
N(1)-S(1)-C(14)-C(19)	-87.3(3)
O(3)-S(1)-C(14)-C(15)	-157.2(3)
O(2)-S(1)-C(14)-C(15)	-25.6(4)
N(1)-S(1)-C(14)-C(15)	88.5(3)
C(19)-C(14)-C(15)-C(16)	-0.2(6)
S(1)-C(14)-C(15)-C(16)	-176.0(3)
C(14)-C(15)-C(16)-C(17)	-0.5(7)
C(15)-C(16)-C(17)-C(18)	1.3(7)
C(15)-C(16)-C(17)-C(20)	-178.8(5)
C(16)-C(17)-C(18)-C(19)	-1.5(7)
C(20)-C(17)-C(18)-C(19)	178.7(5)
C(15)-C(14)-C(19)-C(18)	0.0(6)
S(1)-C(14)-C(19)-C(18)	175.8(3)
C(17)-C(18)-C(19)-C(14)	0.8(7)

Symmetry transformations used to generate equivalent atoms

4. Crystal data of 138a

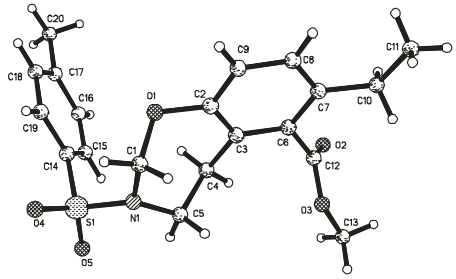


Table 17: Crystal data and structure refinement for s1456rc

Identification code	s1456rc
Empirical formula	C20 H23 N O5 S
Formula weight	389.45
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions	a = 23.8477(15) A alpha = 90 ° b = 12.5460(9) A beta = 27.279(4) ° c = 16.5366(9) A gamma = 90 °
Volume	3936.8(4) A^3
Z, Calculated density	8, 1.314 Mg/m^3
Absorption coefficient	1.722 mm^-1
F (000)	1648
Crystal size	0.5 x 0.4 x 0.25 mm (prism)
Theta range for data collection	4.22 to 67.99 deg.
Limiting indices	0<=h<=28, 0<=k<=15, -16<=l<=15
Reflections collected / unique	3241 / 3161 [R(int) = 0.0375]
Completeness to theta = 67.99	88.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3161 / 0 / 245
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0703, wR2 = 0.1666
R indices (all data)	R1 = 0.1124, wR2 = 0.2188
Extinction coefficient	0.0029(2)
Largest diff. peak and hole	.290 and -0.341 e.A^-3

Table 18: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s1456rc. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	2201(1)	8363(1)	2509(1)	73(1)
O(1)	1316(2)	8728(2)	-47(2)	75(1)
N(1)	2248(2)	8026(3)	1593(3)	67(1)
C(1)	2043(3)	8788(4)	807(4)	78(1)
C(2)	1182(2)	8007(3)	-792(4)	67(1)
O(2)	848(2)	4407(3)	-1381(3)	117(2)
O(3)	1958(2)	4875(2)	-568(3)	83(1)
C(3)	1280(2)	6918(3)	-580(3)	61(1)
O(4)	2466(2)	9427(3)	2800(3)	92(1)
C(4)	1511(2)	6521(3)	438(3)	64(1)
O(5)	2528(2)	7516(3)	3243(2)	85(1)
C(5)	2225(2)	6896(3)	1346(3)	70(1)
C(6)	1143(2)	6245(3)	-1350(3)	62(1)
C(7)	898(3)	6616(4)	-2308(4)	72(1)
C(8)	802(3)	7707(4)	-2475(4)	81(1)
C(9)	949(3)	8391(4)	-1724(4)	80(1)
C(10)	765(3)	5843(5)	-3119(4)	95(2)
C(11)	616(4)	6329(6)	-4053(5)	122(2)
C(12)	1276(2)	5079(3)	-1128(3)	67(1)
C(13)	2182(3)	3784(4)	-244(5)	98(2)
C(14)	1316(2)	8413(3)	2015(3)	61(1)
C(15)	977(2)	7504(3)	2003(3)	70(1)
C(16)	274(3)	7539(4)	1593(4)	76(1)
C(17)	-115(3)	8468(4)	1180(4)	73(1)
C(18)	229(3)	9374(4)	1198(4)	80(1)
C(19)	936(3)	9353(4)	1611(4)	78(1)
C(20)	-886(3)	8486(4)	726(5)	97(2)

Table 19: Bond lengths [A] and angles [deg] for s1456rc.*

S(1)-O(4)	1.431(3)
S(1)-O(5)	1.437(3)
S(1)-N(1)	1.641(4)
S(1)-C(14)	1.743(5)
O(1)-C(2)	1.401(5)
O(1)-C(1)	1.428(6)
N(1)-C(1)	1.440(6)
N(1)-C(5)	1.467(5)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-C(9)	1.369(6)
C(2)-C(3)	1.394(6)
O(2)-C(12)	1.187(5)
O(3)-C(12)	1.321(5)
O(3)-C(13)	1.448(5)
C(3)-C(6)	1.392(6)
C(3)-C(4)	1.504(6)
C(4)-C(5)	1.509(6)

C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-C(7)	1.396(6)
C(6)-C(12)	1.495(6)
C(7)-C(8)	1.388(6)
C(7)-C(10)	1.524(7)
C(8)-C(9)	1.369(7)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(10)-C(11)	1.490(8)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(19)	1.387(6)
C(14)-C(15)	1.390(6)
C(15)-C(16)	1.377(6)
C(15)-H(15)	0.9300
C(16)-C(17)	1.385(6)
C(16)-H(16)	0.9300
C(17)-C(18)	1.392(6)
C(17)-C(20)	1.507(7)
C(18)-C(19)	1.384(7)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600

O(4)-S(1)-O(5)	120.2(2)
O(4)-S(1)-N(1)	106.7(2)
O(5)-S(1)-N(1)	106.5(2)
O(4)-S(1)-C(14)	106.7(2)
O(5)-S(1)-C(14)	107.8(2)
N(1)-S(1)-C(14)	108.5(2)
C(2)-O(1)-C(1)	113.4(4)
C(1)-N(1)-C(5)	117.0(4)
C(1)-N(1)-S(1)	119.2(3)
C(5)-N(1)-S(1)	119.6(3)
O(1)-C(1)-N(1)	113.7(4)
O(1)-C(1)-H(1A)	108.8
N(1)-C(1)-H(1A)	108.8
O(1)-C(1)-H(1B)	108.8
N(1)-C(1)-H(1B)	108.8
H(1A)-C(1)-H(1B)	107.7
C(9)-C(2)-C(3)	121.3(4)
C(9)-C(2)-O(1)	118.9(4)
C(3)-C(2)-O(1)	119.8(4)
C(12)-O(3)-C(13)	117.6(4)
C(6)-C(3)-C(2)	117.0(4)
C(6)-C(3)-C(4)	123.1(4)
C(2)-C(3)-C(4)	119.9(4)
C(3)-C(4)-C(5)	116.0(4)
C(3)-C(4)-H(4A)	108.3
C(5)-C(4)-H(4A)	108.3
C(3)-C(4)-H(4B)	108.3
C(5)-C(4)-H(4B)	108.3

H(4A)-C(4)-H(4B)	107.4
N(1)-C(5)-C(4)	114.1(4)
N(1)-C(5)-H(5A)	108.7
C(4)-C(5)-H(5A)	108.7
N(1)-C(5)-H(5B)	108.7
C(4)-C(5)-H(5B)	108.7
H(5A)-C(5)-H(5B)	107.6
C(3)-C(6)-C(7)	122.7(4)
C(3)-C(6)-C(12)	118.2(4)
C(7)-C(6)-C(12)	119.1(4)
C(8)-C(7)-C(6)	117.4(4)
C(8)-C(7)-C(10)	122.1(5)
C(6)-C(7)-C(10)	120.5(4)
C(9)-C(8)-C(7)	121.1(5)
C(9)-C(8)-H(8)	119.5
C(7)-C(8)-H(8)	119.5
C(8)-C(9)-C(2)	120.5(4)
C(8)-C(9)-H(9)	119.8
C(2)-C(9)-H(9)	119.8
C(11)-C(10)-C(7)	116.4(5)
C(11)-C(10)-H(10A)	108.2
C(7)-C(10)-H(10A)	108.2
C(11)-C(10)-H(10B)	108.2
C(7)-C(10)-H(10B)	108.2
H(10A)-C(10)-H(10B)	107.4
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(2)-C(12)-O(3)	122.7(4)
O(2)-C(12)-C(6)	126.8(5)
O(3)-C(12)-C(6)	110.5(4)
O(3)-C(13)-H(13A)	109.5
O(3)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
O(3)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(19)-C(14)-C(15)	119.1(4)
C(19)-C(14)-S(1)	120.6(3)
C(15)-C(14)-S(1)	120.3(3)
C(16)-C(15)-C(14)	120.2(4)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(15)-C(16)-C(17)	121.6(4)
C(15)-C(16)-H(16)	119.2
C(17)-C(16)-H(16)	119.2
C(16)-C(17)-C(18)	117.7(5)
C(16)-C(17)-C(20)	120.7(4)
C(18)-C(17)-C(20)	121.6(5)
C(19)-C(18)-C(17)	121.4(5)
C(19)-C(18)-H(18)	119.3
C(17)-C(18)-H(18)	119.3
C(18)-C(19)-C(14)	119.9(4)
C(18)-C(19)-H(19)	120.0
C(14)-C(19)-H(19)	120.0
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5

H(20B)-C(20)-H(20C)	109.5	

*Symmetry transformations used to generate equivalent atoms

Table 20: Anisotropic displacement parameters (A^2 x 10^3) for s1456rc.The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	78(1)	70(1)	68(1)	-13(1)	43(1)	-11(1)
O(1)	94(2)	58(2)	77(2)	3(2)	54(2)	7(2)
N(1)	78(2)	59(2)	73(2)	-6(2)	50(2)	-6(2)
C(1)	102(4)	63(3)	86(3)	-4(3)	67(3)	-13(3)
C(2)	78(3)	55(2)	70(3)	4(2)	45(2)	7(2)
O(2)	95(3)	71(2)	141(4)	0(2)	49(3)	-22(2)
O(3)	87(2)	61(2)	114(3)	20(2)	67(2)	9(2)
C(3)	65(2)	57(2)	62(3)	5(2)	39(2)	1(2)
O(4)	101(3)	69(2)	103(3)	-36(2)	60(2)	-32(2)
C(4)	76(3)	54(2)	66(3)	0(2)	46(2)	-7(2)
O(5)	89(2)	85(2)	62(2)	8(2)	36(2)	6(2)
C(5)	73(3)	64(3)	67(3)	0(2)	40(2)	4(2)
C(6)	65(2)	57(2)	66(3)	4(2)	40(2)	0(2)
C(7)	78(3)	74(3)	65(3)	1(2)	45(2)	1(2)
C(8)	96(4)	79(3)	63(3)	14(3)	45(3)	7(3)
C(9)	99(4)	65(3)	77(3)	19(3)	53(3)	11(2)
C(10)	117(4)	89(4)	72(3)	-7(3)	53(3)	-13(3)
C(11)	126(5)	158(7)	80(4)	-6(4)	61(4)	-11(5)
C(12)	74(3)	59(2)	66(3)	-5(2)	42(2)	-10(2)
C(13)	121(5)	64(3)	116(5)	25(3)	76(4)	26(3)
C(14)	75(3)	54(2)	65(3)	-7(2)	48(2)	-6(2)
C(15)	79(3)	58(2)	73(3)	3(2)	47(2)	1(2)
C(16)	89(3)	62(3)	90(3)	0(2)	60(3)	-5(2)
C(17)	77(3)	68(3)	81(3)	-2(2)	51(3)	-3(2)
C(18)	94(4)	65(3)	98(4)	3(3)	67(3)	1(2)
C(19)	99(4)	57(3)	97(4)	1(2)	70(3)	-4(2)
C(20)	82(3)	92(4)	118(5)	11(3)	61(3)	2(3)

Table 21: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s1456rc.

	x	y	z	U(eq)
H(1A)	2143	9500	1092	94
H(1B)	2328	8674	575	94
H(4A)	1514	5748	428	76
H(4B)	1163	6738	529	76
H(5A)	2365	6471	1931	83
H(5B)	2565	6772	1216	83
H(8)	635	7979	-3108	97
H(9)	890	9120	-1847	96
H(10A)	1175	5387	-2814	114
H(10B)	370	5392	-3319	114

H(11A)	535	5775	-4513	183
H(11B)	1011	6753	-3874	183
H(11C)	205	6772	-4375	183
H(13A)	2686	3742	155	146
H(13B)	1971	3334	-830	146
H(13C)	2036	3554	157	146
H(15)	1227	6870	2272	84
H(16)	56	6925	1593	91
H(18)	-22	10007	927	96
H(19)	1156	9968	1619	93
H(20A)	-1071	9190	479	145
H(20B)	-942	8293	1235	145
H(20C)	-1137	7988	173	145

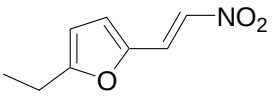
Table 22: Torsion angles [deg] for s1456rc.*

O(4)-S(1)-N(1)-C(1)	-42.5(4)
O(5)-S(1)-N(1)-C(1)	-172.0(3)
C(14)-S(1)-N(1)-C(1)	72.1(4)
O(4)-S(1)-N(1)-C(5)	161.2(3)
O(5)-S(1)-N(1)-C(5)	31.6(4)
C(14)-S(1)-N(1)-C(5)	-84.2(4)
C(2)-O(1)-C(1)-N(1)	-88.5(5)
C(5)-N(1)-C(1)-O(1)	66.3(5)
S(1)-N(1)-C(1)-O(1)	-90.6(4)
C(1)-O(1)-C(2)-C(9)	-113.8(5)
C(1)-O(1)-C(2)-C(3)	66.9(5)
C(9)-C(2)-C(3)-C(6)	1.2(7)
O(1)-C(2)-C(3)-C(6)	-179.6(4)
C(9)-C(2)-C(3)-C(4)	-177.7(4)
O(1)-C(2)-C(3)-C(4)	1.5(6)
C(6)-C(3)-C(4)-C(5)	118.5(5)
C(2)-C(3)-C(4)-C(5)	-62.7(6)
C(1)-N(1)-C(5)-C(4)	-57.4(5)
S(1)-N(1)-C(5)-C(4)	99.4(4)
C(3)-C(4)-C(5)-N(1)	71.5(5)
C(2)-C(3)-C(6)-C(7)	-1.8(6)
C(4)-C(3)-C(6)-C(7)	177.0(4)
C(2)-C(3)-C(6)-C(12)	177.1(4)
C(4)-C(3)-C(6)-C(12)	-4.1(6)
C(3)-C(6)-C(7)-C(8)	0.9(7)
C(12)-C(6)-C(7)-C(8)	-178.0(4)
C(3)-C(6)-C(7)-C(10)	179.2(4)
C(12)-C(6)-C(7)-C(10)	0.3(7)
C(6)-C(7)-C(8)-C(9)	0.7(8)
C(10)-C(7)-C(8)-C(9)	-177.6(5)
C(7)-C(8)-C(9)-C(2)	-1.3(8)
C(3)-C(2)-C(9)-C(8)	0.3(8)
O(1)-C(2)-C(9)-C(8)	-178.9(5)
C(8)-C(7)-C(10)-C(11)	7.6(8)
C(6)-C(7)-C(10)-C(11)	-170.6(5)
C(13)-O(3)-C(12)-O(2)	-1.1(7)
C(13)-O(3)-C(12)-C(6)	177.2(4)
C(3)-C(6)-C(12)-O(2)	102.1(6)
C(7)-C(6)-C(12)-O(2)	-79.0(7)
C(3)-C(6)-C(12)-O(3)	-76.2(5)
C(7)-C(6)-C(12)-O(3)	102.7(5)
O(4)-S(1)-C(14)-C(19)	24.4(5)

O(5)-S(1)-C(14)-C(19)	154.8(4)
N(1)-S(1)-C(14)-C(19)	-90.2(4)
O(4)-S(1)-C(14)-C(15)	-156.9(4)
O(5)-S(1)-C(14)-C(15)	-26.5(4)
N(1)-S(1)-C(14)-C(15)	88.5(4)
C(19)-C(14)-C(15)-C(16)	0.1(7)
S(1)-C(14)-C(15)-C(16)	-178.6(4)
C(14)-C(15)-C(16)-C(17)	0.3(7)
C(15)-C(16)-C(17)-C(18)	-0.4(8)
C(15)-C(16)-C(17)-C(20)	179.4(5)
C(16)-C(17)-C(18)-C(19)	0.1(8)
C(20)-C(17)-C(18)-C(19)	-179.7(5)
C(17)-C(18)-C(19)-C(14)	0.3(8)
C(15)-C(14)-C(19)-C(18)	-0.4(7)
S(1)-C(14)-C(19)-C(18)	178.3(4)

[*] *Symmetry transformations used to generate equivalent atoms*

6. Registry of new compounds



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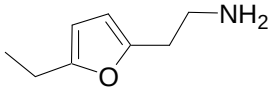

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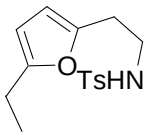

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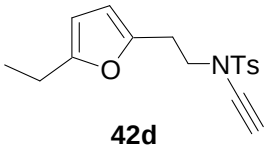

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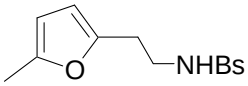

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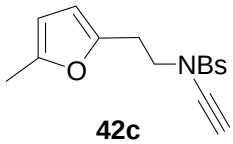

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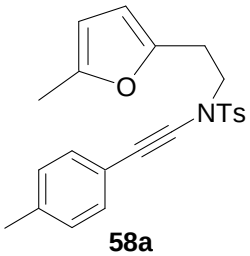

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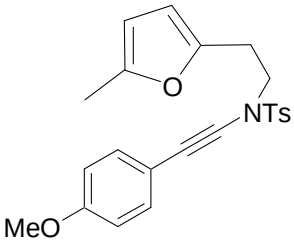

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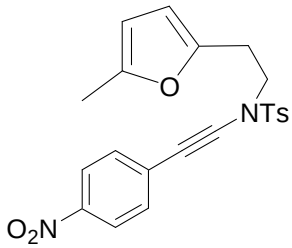

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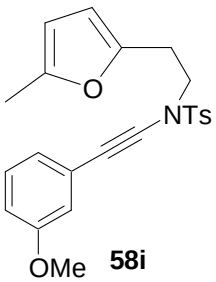

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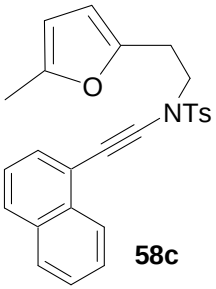

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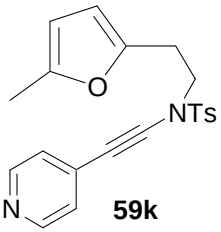

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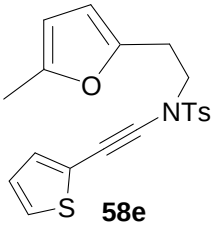

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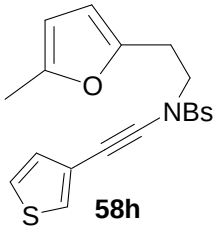

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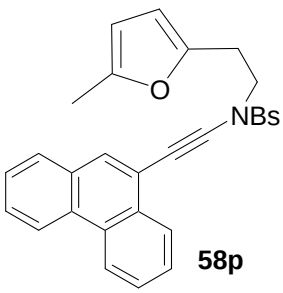

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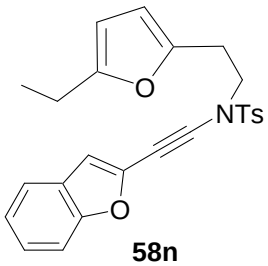

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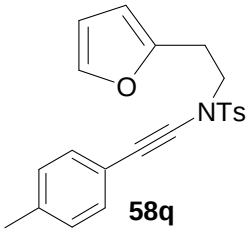

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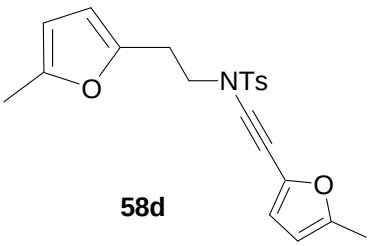

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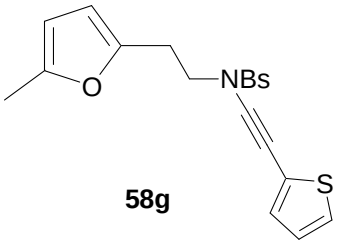

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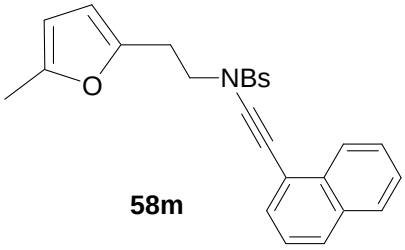

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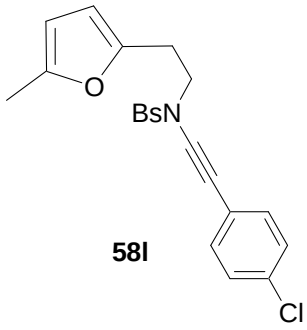

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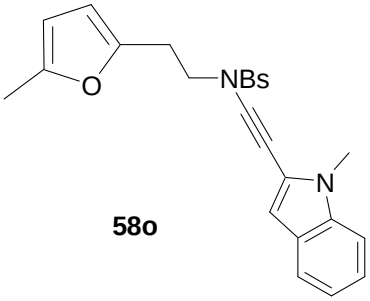

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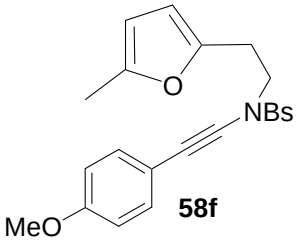

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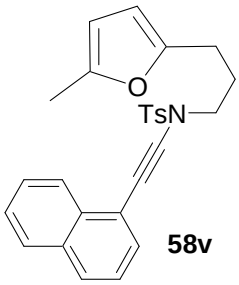

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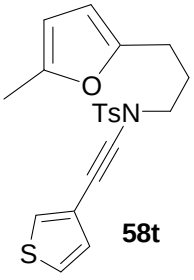

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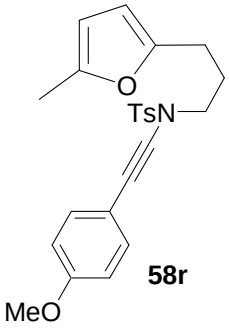

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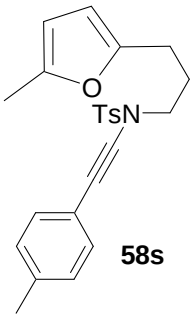

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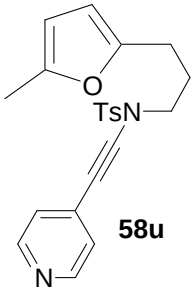

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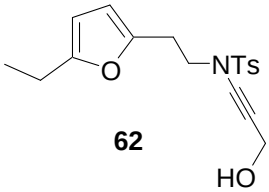

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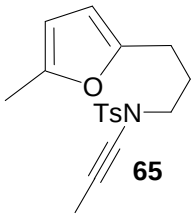

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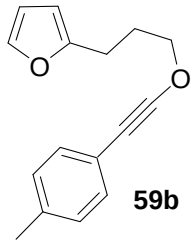

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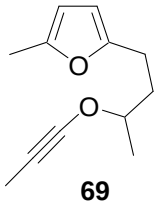

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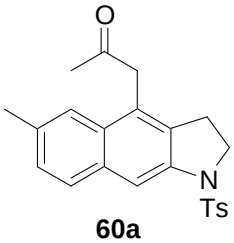

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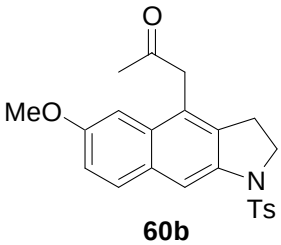

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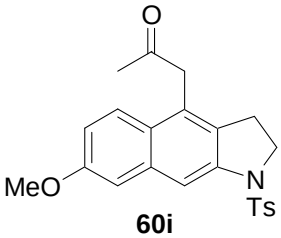

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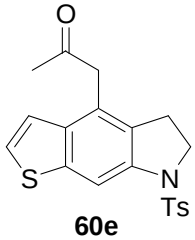

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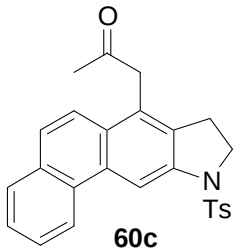

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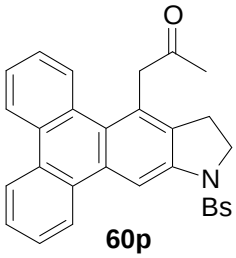

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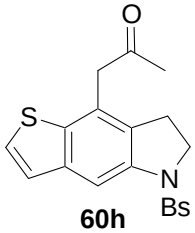

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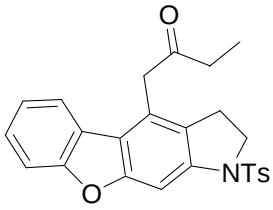

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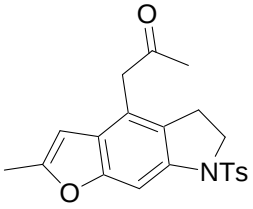

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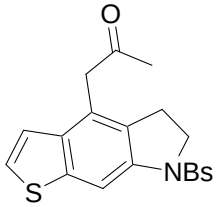

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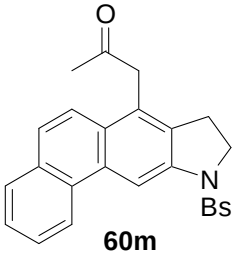

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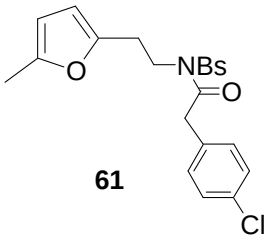

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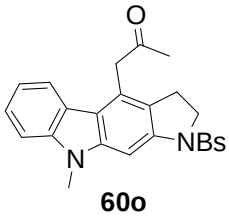

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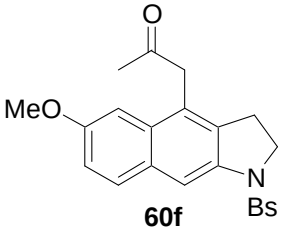

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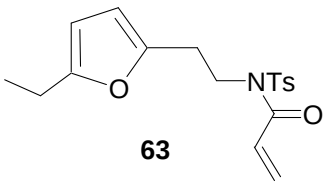

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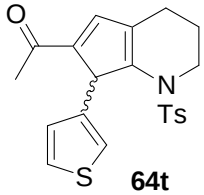

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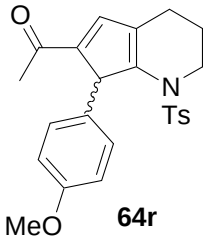

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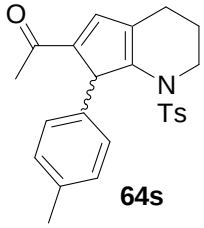

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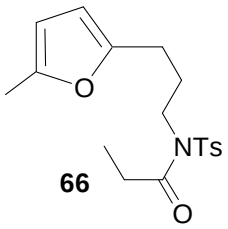

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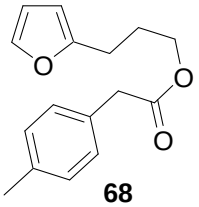

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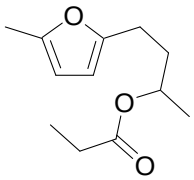

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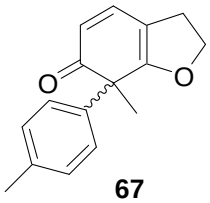

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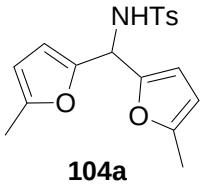

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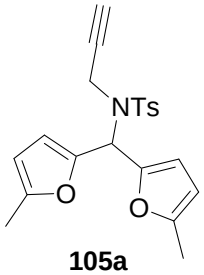

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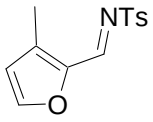

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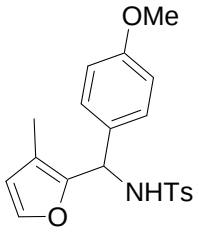

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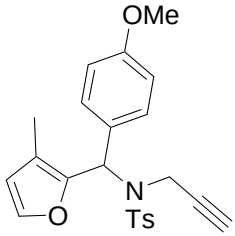

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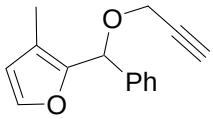

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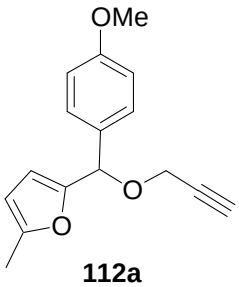

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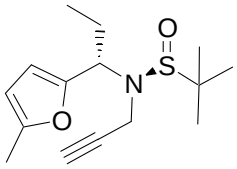

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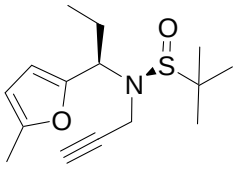

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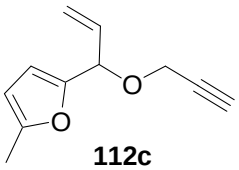

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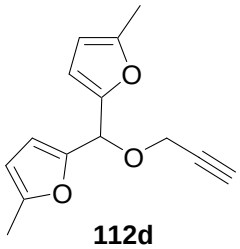

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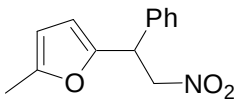

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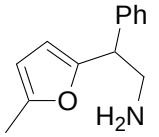

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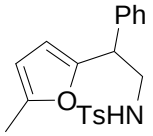

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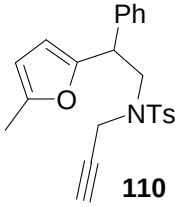

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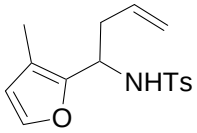

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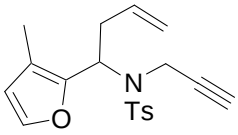

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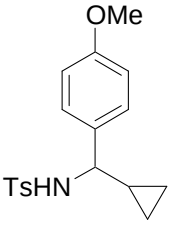

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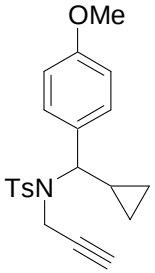

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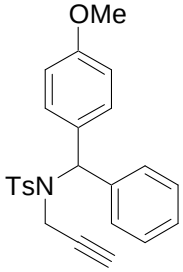

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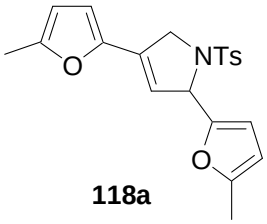

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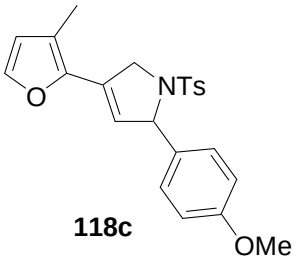

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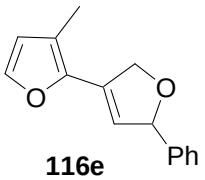

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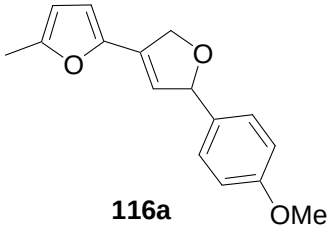

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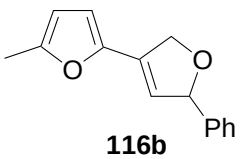

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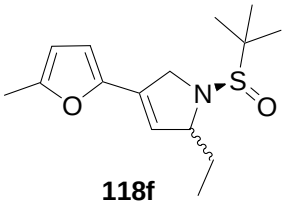

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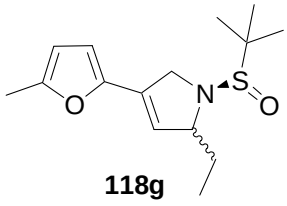

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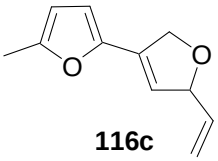

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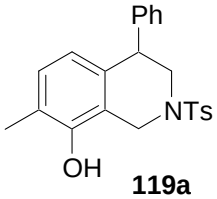

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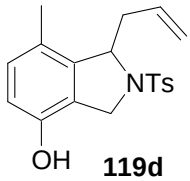

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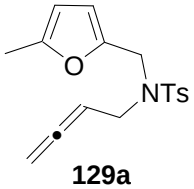

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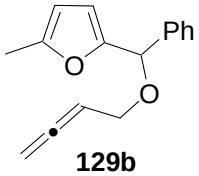

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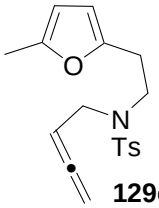

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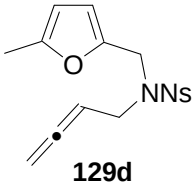

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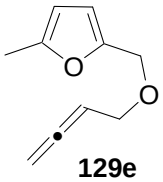

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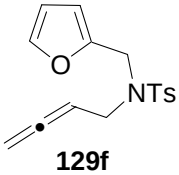

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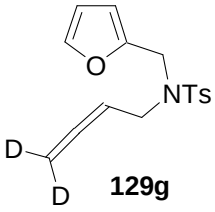

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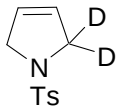

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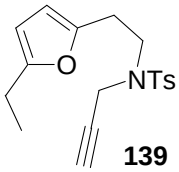

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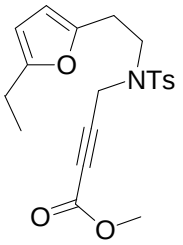

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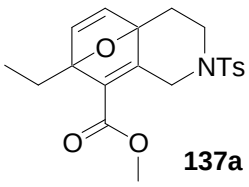

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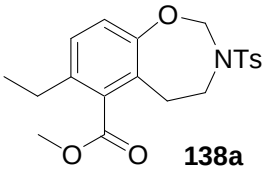

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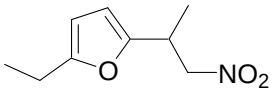

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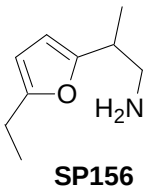

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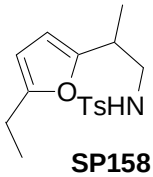

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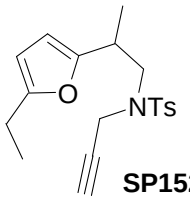

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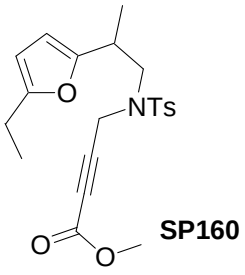

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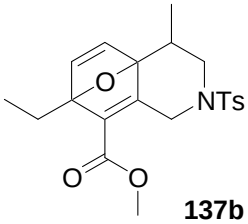
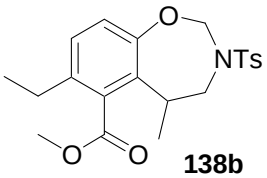


137b



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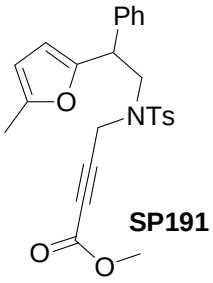

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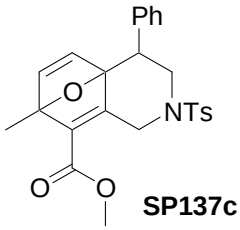

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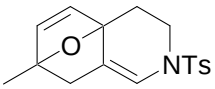

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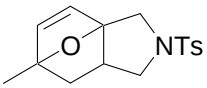

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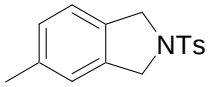

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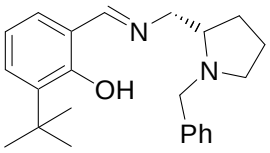

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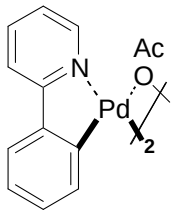

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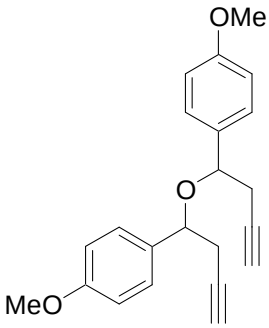

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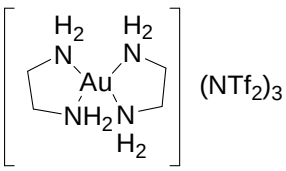

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