Designing SNS and NNO Donor Ni and Co Complexes Toward (De)hydrogenative Alcohol Activation: A Sustainable Approach to C-C and C-N Bond Construction

By

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Dedicated

To

My Family

&

Teachers

INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

Department of Chemistry

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STATEMENT

I, hereby declared that the work comprised in this thesis entitled "***Designing SNS and NNO Donor Ni and Co Complexes Toward (De)hydrogenative Alcohol Activation: A Sustainable Approach to C-C and C-N Bond Construction***" is the outcome of the research work carried out by me under the supervision of **Prof. Dipankar Srimani, Department of Chemistry, Indian Institute of Technology Guwahati, India**, for the award of the degree of Doctor of Philosophy. In harmony with the general practice of reporting scientific observations, due acknowledgments have been made if the work is established on the findings of other investigators.

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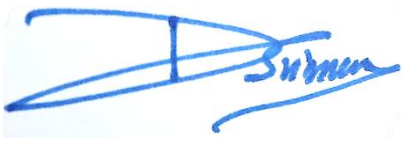
CERTIFICATE

This is to certify that the work incorporated in the thesis entitled "***Designing SNS and NNO Donor Ni and Co Complexes Toward (De)hydrogenative Alcohol Activation: A Sustainable Approach to C-C and C-N Bond Construction***" which is being submitted to the Indian Institute of Technology Guwahati for the award of Doctor of Philosophy in Chemistry by **Mr. Rahul Sharma** (Roll No: **186122107**) was carried out by him under my supervision at this institute. The work presented in his thesis is original and has not been submitted elsewhere for a degree.



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Prof. Dipankar Srimani

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~Acknowledgements~

Embarking on a PhD journey is both demanding and deeply enriching. The path is often marked by intense effort, stress, and moments of uncertainty, yet it leads to a rewarding culmination that offers far more than academic achievements. This journey fosters patience, resilience, and a commitment to learning, imparting life lessons that extend well beyond the bounds of research. The challenges encountered and overcome throughout this process are integral to personal growth and leave an enduring impact.

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the countless discussions and shared laughter, that made this journey memorable. To my juniors, ***Mithu Roy****,* ***Arup Samanta****,* ***Kailash Mohar****,* ***Hirok Jyoti Phukan****,* ***Rajashri Sarmah****,* ***Itu Mallick****,* ***Krishna Majhi****,* ***Rinku Dihingia*** *and* ***Rohit Baran Bera****, it's been a joy watching you bring fresh perspectives and energy to the lab. Also, I am thankful to the summer intern and project students,* ***Suman Maji****,* ***Saurabh kumar****,* ***Elinda Basumatary****,* ***Kanabeni Rajkumar*** *and others. Thank you for your enthusiasm, curiosity, and willingness to assist whenever needed.*

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I regret that I cannot individually name everyone who has supported me along this journey, but please know that each of you holds a special place in my heart.

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Sincerely,

Rahul Sharma

CONTENT

Abbreviation

Ac	Acetyl
α	Alpha
Å	Angstrom
Ar	Argon
ACN	Acetonitrile
AD	Acceptorless dehydrogenation
ADC	Acceptorless dehydrogenative coupling
br.	Broad
bi pyridine	2,2′-bipyridine
β	Beta
Bn	Benzyl
Bu	Butyl
BH	Borrowing hydrogen
CCDC	Cambridge crystallographic data centre
COD	1,5-Cyclooctadiene
$CDCl_3$	Chloroform-d
Cy	Cyclohexyl
Cat	Catalyst
°C	Degree Celsius
d	Doublet or day
dd	Doublet of doublet
δ	Chemical shift or delta
DA	Donor-acceptor
DCE	Dichloroethane
DCM	Dichloromethane
DFT	Density functional theory
DMSO	Dimethylsulfoxide
DMF	Dimethylformamide
DMA	Dimethylacetamide
dppe	1,2-Bis(diphenylphosphino)ethane
dppf	1,1′-Bis(diphenylphosphino)ferrocene
dppp	1,3-Bis(diphenylphosphino)propane
EtOAc	Ethyl acetate
equiv.	Equivalent
ESI	Electrospray ionization
Et	Ethyl
EWG	Electron withdrawing group
EDG	Electron donating group
g	Grams
γ	Gamma
HA	Hydrogen-autotransfer
h	Hours

HRMS	High resolution mass spectrometry
Hz	Hertz
MHz	Mega Hertz
i	Iso
FT-IR	Fourier transform infrared spectroscopy
J	Coupling constant
m	Multiplet
m	*Meta*
Me	Methyl
mg	Milligram
mL	Millilitre
mmol	Millimole
Mp	Melting point
MS	Molecular seive
MLC	Metal-ligand cooperation
NMR	Nuclear magnetic resonance
Ts	Tosylate
o	*Ortho*
ω	Omega
ORTEP	Oak ridge thermal ellipsoid plot program
p	*Para*
Ph	Phenyl
Py	Pyridine
Pr	propyl
PNP	2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine
ppm	Parts per million
q	Quartet
rt	Room temperature
s	Singlet
THF	Tetrahydrofuran
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
t	*Tert*
TMS	Tetramethylsilane
TS	Transition state
XRD	X-ray diffraction

~Abstract~

The present thesis entitled "**Designing SNS and NNO Donor Ni and Co Complexes Toward (De)hydrogenative Alcohol Activation: A Sustainable Approach to C-N and C-N Bond Construction**" is divided into five chapters. The first chapter primarily focused on a brief discussion of the concept outline such as Acceptorless Dehydrogenation, Borrowing Hydrogen approach, Metal-Ligand Cooperation, etc. The Chapter 2 to 5 discuss on development of Nickel and Cobalt complexes and its catalytic application toward various alcohol activation reaction.

Chapter 1: Alcohols: A Sustainable Application in Organic Synthesis

This chapter provides a comprehensive overview of the necessity of biomass feedstock-based starting materials for various chemical syntheses. Alcohol is one of the important components of renewable resources i.e., lignocellulosic biomass. Concerning on the diverse advantages of alcohol, chemists explored alcohol in organic synthesis in various manners which is discussed comprehensively. The chapter focus on the reactivity of alcohol for various C-C and C-N bond construction via "Acceptorless Dehydrogenation" and "Borrowing Hydrogen" approach. Moreover, the importance of Cobalt and Nickel based catalysis most importantly with respect to the activation of alcohol is discussed in details.

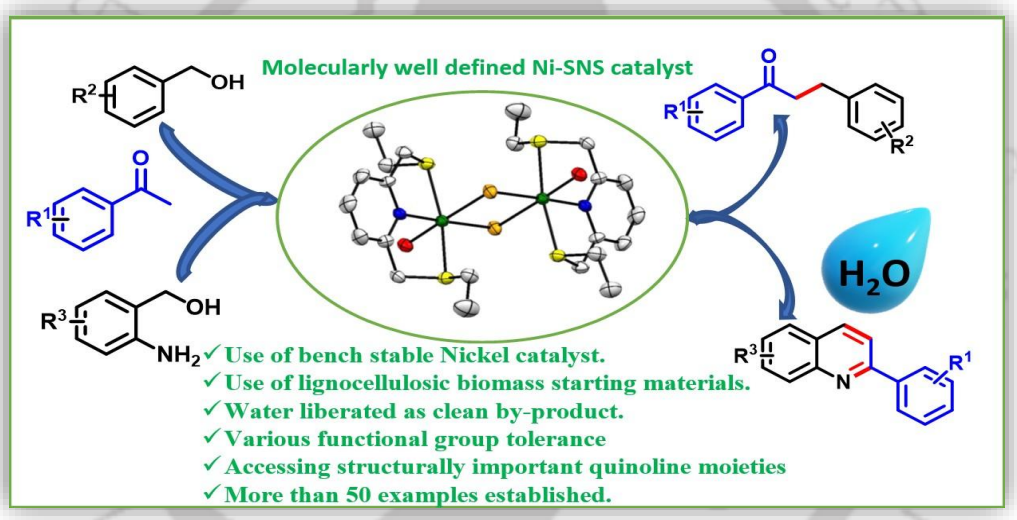
Aim of the Thesis:

The present objective of the thesis is designing a non-phosphine based ligand system, synthesizing from cheap and readily available starting materials. The synthesized ligand is then reacted with 3d Nickel and Cobalt metal precursors. The synthesized nickel and cobalt complexes are characterized using single crystal XRD and mass spectrometry. Further, these complexes are applied for alcohol activation followed by the construction of various C-C and C-N bonds.

Chapter 2: **Well-defined Ni-SNS Complex Catalysed Borrowing Hydrogenative α-Alkylation of Ketones and Dehydrogenative Synthesis of Quinolines**

The "Borrowing Hydrogen" (BH) method for C-alkylation reactions using alcohol as alkylating agents is an important synthetic transformation. In this respect, designing cheap and

bench-stable earth-abundant metal catalysts for borrowing hydrogen transformation is a key challenge to be witnessed. This chapter presents the synthesis, and characterisation of non-phosphine and bench-stable SNS-Ni complexes and successfully applied for C-alkylation of ketone enolates to α-alkylated ketones. Primary alcohol with different functional groups and various heteroaromatic alcohols are well tolerated. Moreover, the presence of both isolated and conjugated unsaturation in the substrates was well tolerated in the present catalytic protocols. The present catalyst system was efficiently applied to gram scale synthesis along with the calculating green chemistry metrics. The present protocol was also extended successfully for the synthesis of biologically important quinoline moieties. Finally, various control experiments and deuterium-labelled experiments suggest that the reaction proceeds via a non-radical borrowing hydrogen pathway.

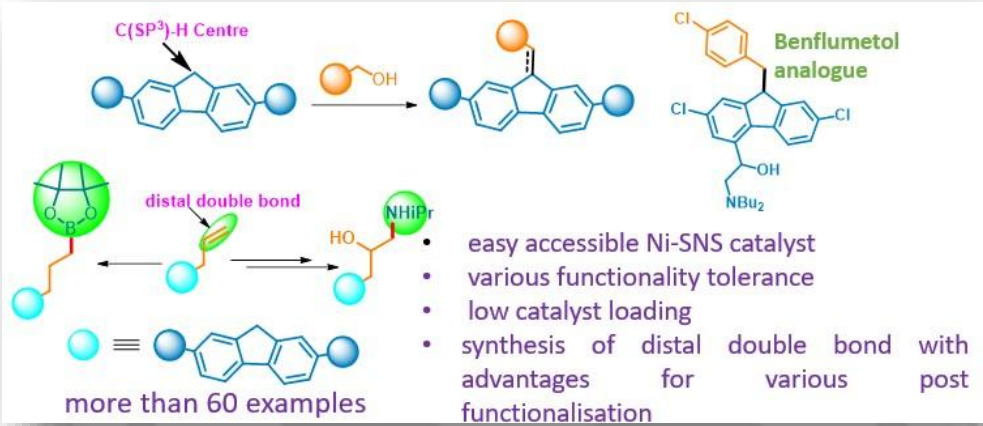


R. Sharma, A. Mondal, A. Samanta, N. Biswas, B. Das and D. Srimani *Adv. Synth. Catal.* **2022**, *364*, 2429–2437.

Chapter 3: A strategic approach for Csp3–H functionalization of 9H-fluorene: an acceptorless dehydrogenation and borrowing hydrogen approach

9H-Fluorene constitutes an important class in chemistry, featuring its significance both in material chemistry, showcasing the properties of optical devices, and in medicinal chemistry. Moreover, the alkylation in 9th position of 9H-fluorene is very important and from the context of borrowing hydrogen chemistry, it was much less explored. This chapter describes the selective synthesis of both alkylated and alkenylated fluorenes using a single SNS ligand-derived nickel complex. The protocol was employed for a wide range of substrates, including

substituted fluorenes and various alcohols including aliphatic alcohols with a distal double bond. To expand the synthetic utility, an antimalarial drug analogue, benflumetol, was synthesized, and various post-modifications of alkylated fluorene to its corresponding epoxides, amino alcohol, and boronate ester were demonstrated. Control experiments and kinetic profile diagram depict that the reaction works via an unsaturated intermediate and prove the involvement of borrowing hydrogen approach.



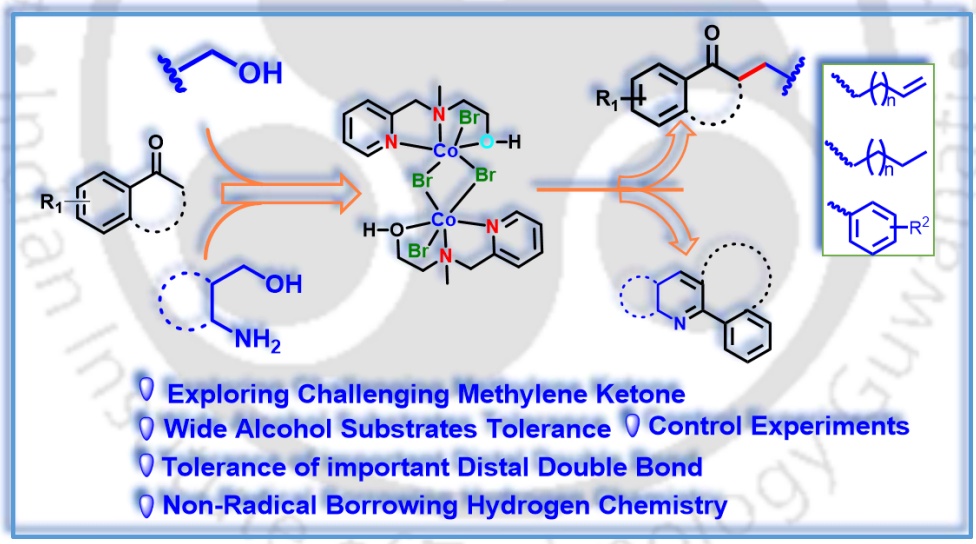
R. Sharma, A. Mondal, A. Samanta and D. Srimani, *Catal. Sci. Technol.*, **2023**, *13*, 611.

Chapter 4: Unveiling the Potential of SNS-Ni Complex for Establishing C-N Bonds: An Approach Toward Chemoselectivity

Recent research has focused a lot on using the Borrowing Hydrogen (BH) approach to react amines with alcohols to convert a C-O bond into a C-N bond. However, the notion of chemoselectivity in BH-mediated N-alkylation of amines, has rarely been studied. This chapter demonstrates the application of synthesized SNS-Ni complex toward constructing various C-N bonds via the coupling of diverse amines with varieties of alcohols. Delightfully, the catalytic protocol also activates challenging C4-C16 aliphatic alcohols. Aryl amino alcohols are selectively N-alkylated with different alcohols while keeping the OH group intact in the amino alcohol portion. Furthermore, without reducing the distal unsaturation, the catalytic technique was also successfully employed for chemoselective N-alkylation of different fatty alcohols. The preliminary mechanistic investigation suggests alkylation occurs via a non-radical "Borrowing Hydrogen" pathway.

R. Sharma, A. Mondal, S. Maji and D. Srimani, *Organometallics,* **2024**, *43,* 2697–2702.

Chapter 5: Exploring the Potential of Non-Phosphine Cobalt System for the Alcohol Activation: Expedition of C-C and C-N Bond Formation



Publication: Manuscript Submited

Non-phosphine Cobalt complexes are much less explored in "Acceptorless Dehydrogenation" and "Borrowing Hydrogen" chemistry. Most importantly the cobalt chemistry is not explored exclusively for C-alkylation of methylene ketones. This chapter focused on the development of NNO-Co complexes. The potential of the synthesized complexes was explored for the C-alkylation of challenging methylene ketones. The protocol displays a wide range of functional group tolerance. Important substrates including aliphatic alcohols bearing distal double bonds couples with ketones effectively. In addition, the protocol is also efficient toward multi-

substituted quinoline synthesis. Moreover, the catalyst was also applied for the C-alkylation of N-heteroarenes. The control experiments discard the involvement of radical pathways and the complex acts as a homogeneous catalyst. Deuterium scrambling experiments prove the involvement of Borrowing Hydrogen chemistry.

Chapter 1

Biomass Feedstock: Chemistry for Sustainable Future

1.1. Introduction

Famous Swedish chemist "**Jöns Jacob Berzelius"** first coined the term "**Catalysis**" in the year 1835. In the 21st century, it is needless to say the fact that the importance of catalysts lies in the core of scientific innovation in the field of chemistry which is fascinating and perennially new. The essential principle of a catalyst of providing an alternative and feasible pathway for chemical transformations has been widely admired since the 19th century.[1] This also supports the green chemistry principle by taking part in a chemical event without consumption and can work in just a small amount (catalytic amount).[2] Also, the catalyst plays a prominent role in improving environmental issues, one important example to address is the discovery of catalytic converters that prevent the exposure of harmful gases from vehicle exhaust.[3] It is the beauty of a catalyst that can activate the most inert chemical bond and thus participate in an extensive range of significant chemical transformations. The importance of catalysis was even more realized when such tremendous discoveries in catalysis were/are recognized by prestigious novel prizes.[4] By broadly categorizing catalysis into three types such as metal, enzyme, and organocatalysis; all classes of catalysis significantly contributed toward some of the important chemical transformations involving C-H bond activation,[5] photo-induced reactions,[6] small molecule activations (such as CO_2, MeOH, NH_3), etc.[7]

Fossil fuels have been the foundation of industrial chemical synthesis for decades. However, the rapid industrialization of the global economy and ever-increasing demand for energy-intensive products have accelerated the consumption of fossil fuel-derived feedstocks.[8] The rapid and unsustainable consumption of fossil fuels not only depletes finite reserves but also poses significant environmental challenges. As inherently limited resources, their ongoing exploitation accelerates global resource exhaustion. Additionally, the processes involved in extracting and utilizing fossil fuels have severe ecological impacts, including increased carbon emissions, air and water pollution, and the worsening of global climate change.[9] In response to the rapid consumption of fossil fuels and the adverse environmental impacts, there is an urgent need to identify and adopt sustainable alternatives. Ideal alternatives should reduce reliance on finite fossil reserves and promote ecological sustainability by minimizing carbon footprints and waste generation. In this regard, lignocellulosic biomass is considered a reliable alternative of fossil fuel where alcohol serves as a primary component of lignocellulosic biomass.

1.2. Alcohol: a significant biomass derived starting material

The primary source of chemicals used in industry and academia are mostly derived from fossil fuels. Due to their limited availability, excessive fossil fuel consumption can rapidly deplete these finite resources. Thus, addressing the problem, extensive research is engrossed on investigating the replacements to fossil fuels. Biomass-derived feedstocks, such as alcohols and sugars, have emerged as promising sustainable alternatives of fossil fuel-based starting materials (**figure 1.1**). These renewable resources are abundant, biodegradable, and Sustainable alternatives to fossil-based feedstocks in chemical synthesis and are favoured due to their potential to mitigate fossil fuel depletion and enhance environmental sustainability by reducing CO_2 emissions and other waste products. Additionally, integrating carbon dioxide as a feedstock and utilizing industrial waste further aligns with circular economy principles, thus developing a more sustainable chemical industry. Further optimization is necessary to ensure the economic feasibility and scalability of biomass conversion processes, especially in the development of effective catalytic systems. [10]

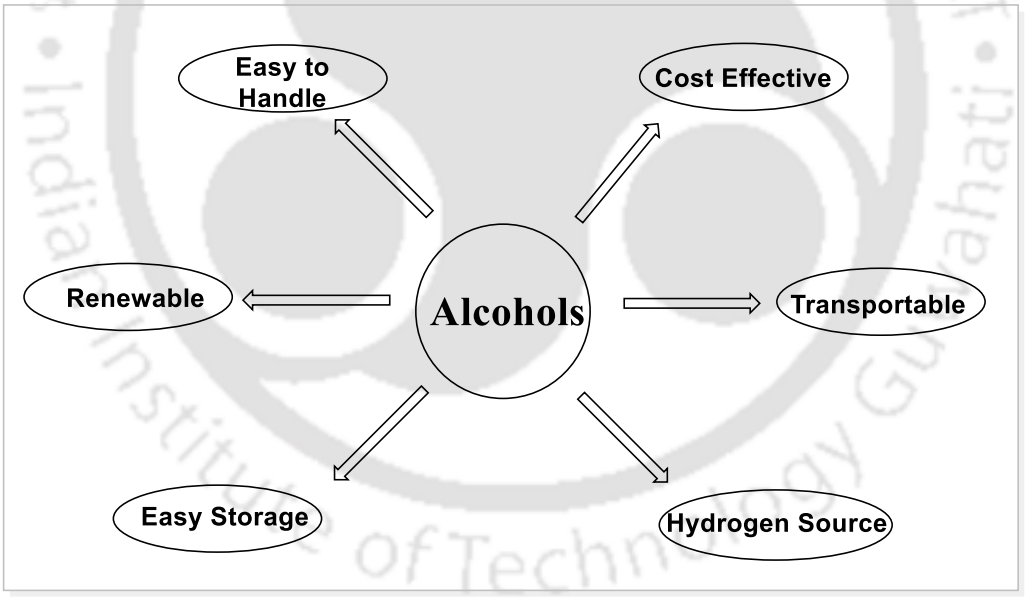


Figure 1.1: Advantages of alcohol.

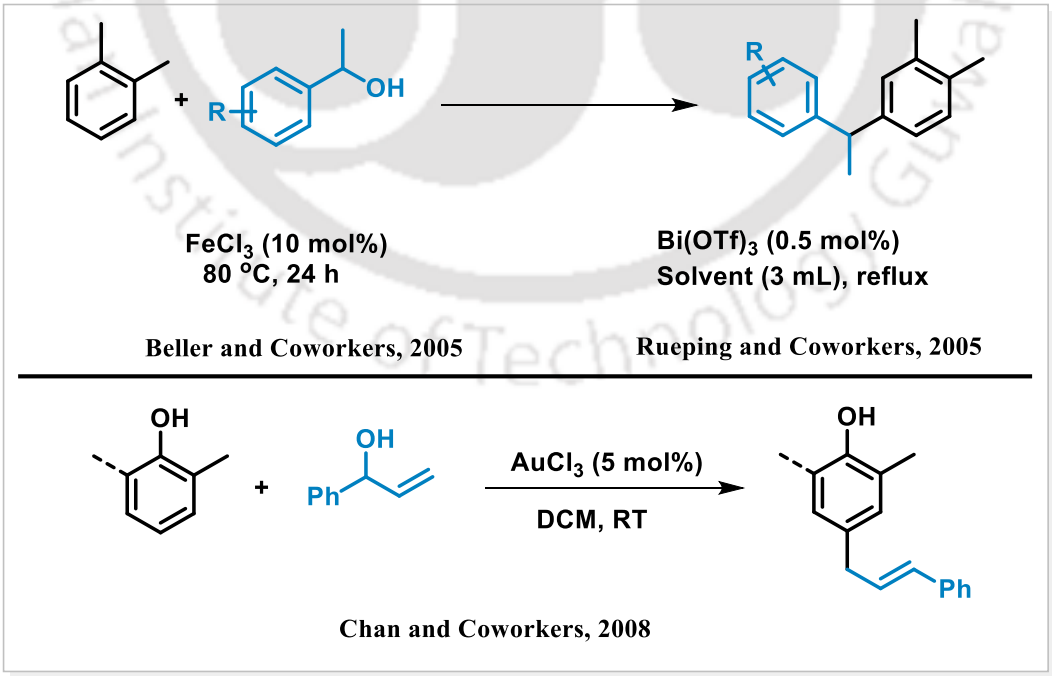
However, without prefunctionalization, alcohols are challenging to employ in organic synthesis due to their relative lack of reactivity. The hydroxyl group of alcohol act as a poor leaving group. To increase the electrophilicity of the carbon center in alcohols, they must undergo either protonation or conversion into suitable leaving groups, such as halides and tosylates.[11] Research in this area focuses on designing catalysts that can efficiently facilitate key

transformations, such as C-C and C-N bond formation, using sustainable feedstocks such as alcohols. The depletion of fossil fuels and the demanding environmental concerns associated with their use emphasize the urgency of transitioning to sustainable feedstocks with the potential to revolutionize the chemical industry and mitigate its environmental impact.

1.3. Alcohols in organic synthesis

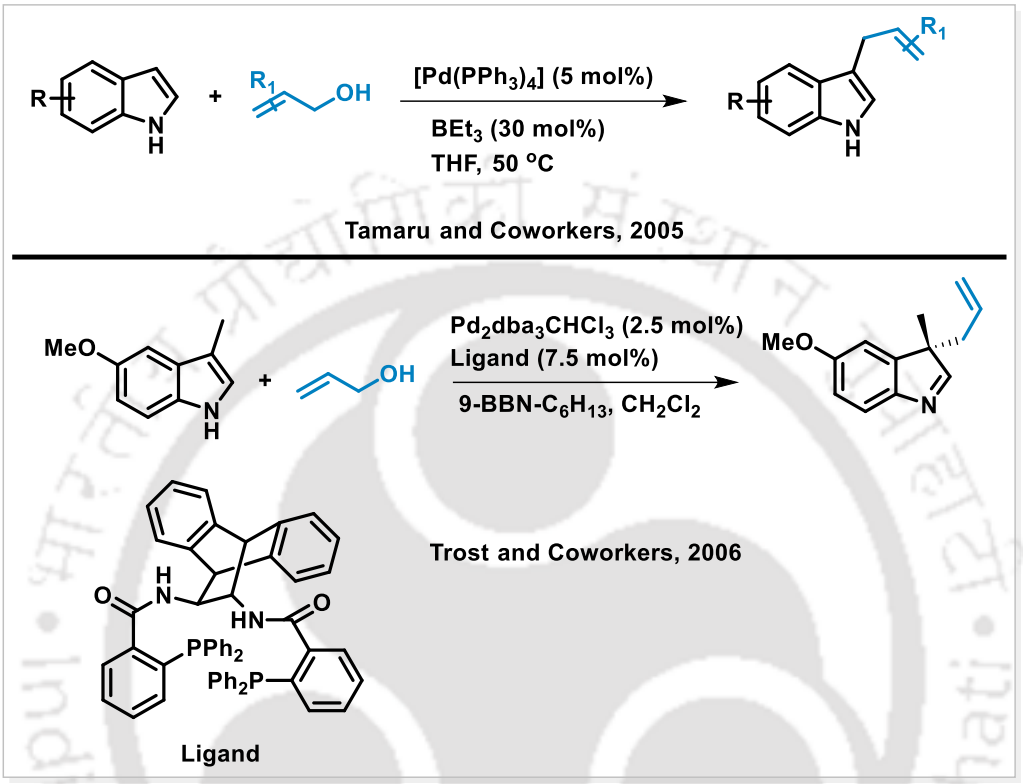
Despite the low reactivity of alcohol due to the poor leaving nature of the hydroxy group, various strategies have been developed to activate them, enabling their use as important starting materials for different C-C, C-O, and C-N bond fabrication reactions. Hence in recent years, chemical catalysis has evolved as an emerging tool to diversify alcohols. This section highlights some remarkable achievements in constructing various C-C, C-O and C-N bonds and further diversifying the alcohols.

Using the concept of π-activated alcohol [12] Beller and coworker [13] reported $FeCl_3$ (10 mol%) catalysed Friedel-Craft type C-alkylation of arenes using benzylic alcohol. Later on Rueping and coworkers, [14] in 2006 reported 0.5 mol% of $Bi(OTf)_3$ catalysed C-C bond formation involving coupling between benzylic alcohols and arenes. Moreover, Chan and coworkers [15] reported the C-C alkylation of the aromatic and heteroaromatic systems with allylic alcohol catalysed by $AuCl_3$ (5 mol%) (**Scheme 1.1**).



Scheme 1.1: Friedel-Craft type coupling of arenes with alcohols

Tamaru and coworkers [16] have developed C-3 alkylation of indole employing allylic alcohols in presence of palladium catalyst and borane as an additive. Soon after, Trost and coworkers [17] demonstrated the incorporation of an asymmetric centre in the C-3 position of 3-methyl indole using chiral phosphine ligand in presence of borane additives (**scheme 1.2**).

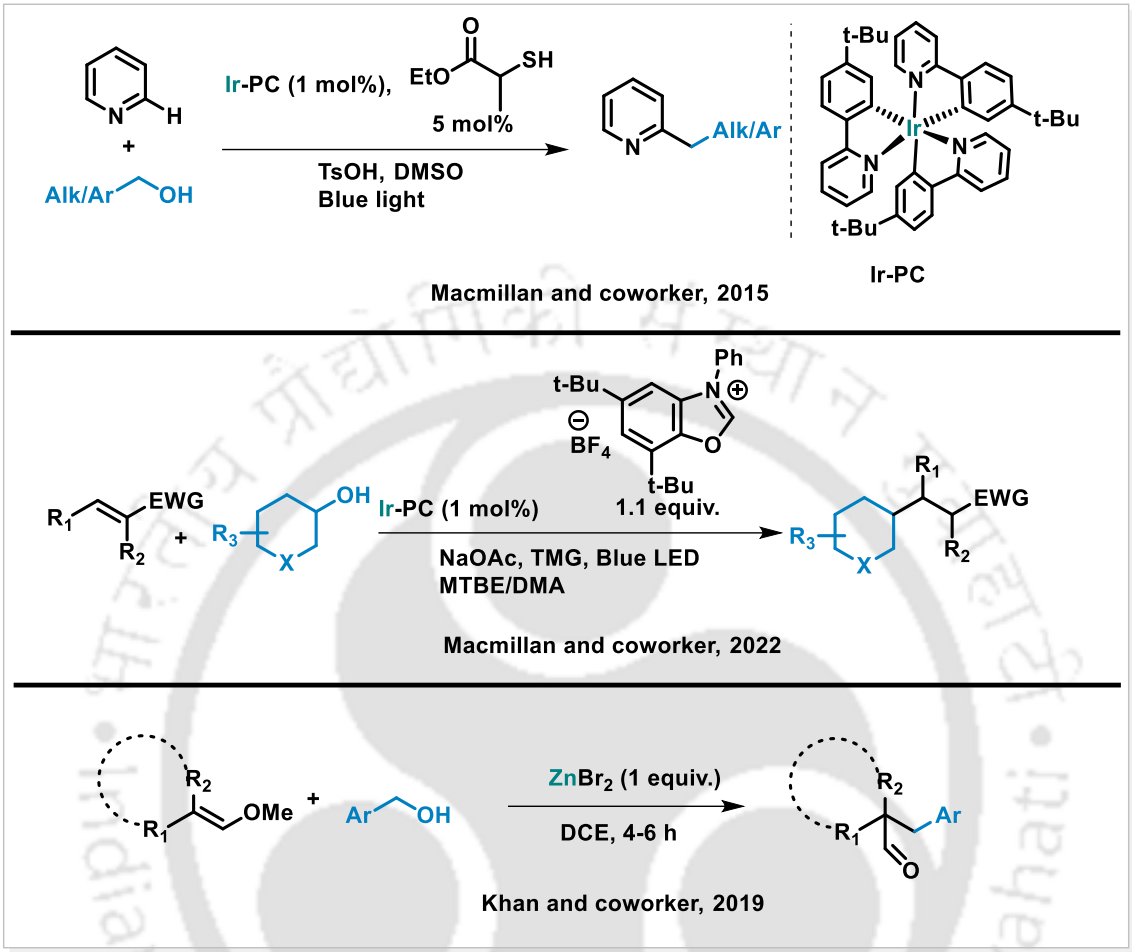


Scheme 1.2: Representative example of coupling between indole and allylic alcohol

The use of alcohol as alkylating agent under visible light photoredox catalysis was demonstrated by Macmillan and coworkers [18] in 2015. They demonstrated Ir-based photocatalyst in a combination with a thiol based organocatalyst for coupling of N-heteroarene using alcohol as carbon radical source Later, the same group [19] also successfully demonstrated the C-alkylation of alkene using alcohol precursor using combination of Ir-based photocatalyst and NHC as organocatalyst. Very recently Khan and coworkers [20], illustrates the use of $ZnBr_2$ mediated C-alkylation of enol ether using various benzylic alcohols (**scheme 1.3**).

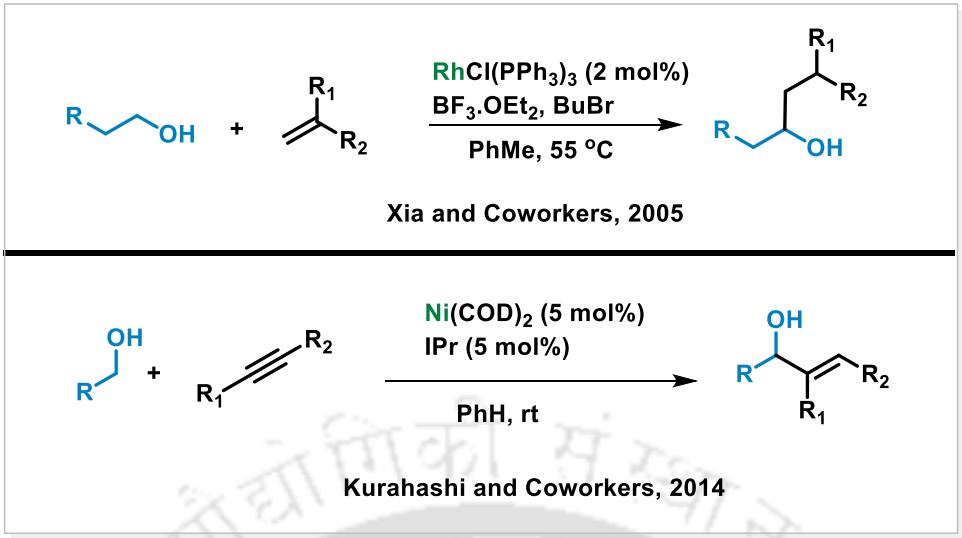
α-functionalisation of alcohol is one of the efficient strategies to post-modify the alcohols into an α-alkylated valuable product. In this respect, Xia and coworkers [21] in 2005 disclosed the α-alkylation of unprotected alcohols with alkenes via rhodium catalyst alongside $BF_3.Et_2O$. In

2014, Kurahashi and coworkers [22] demonstrated α-vinylation of alcohols catalysed by Nickel in the presence of NHC based ligand (**scheme 1.4**).

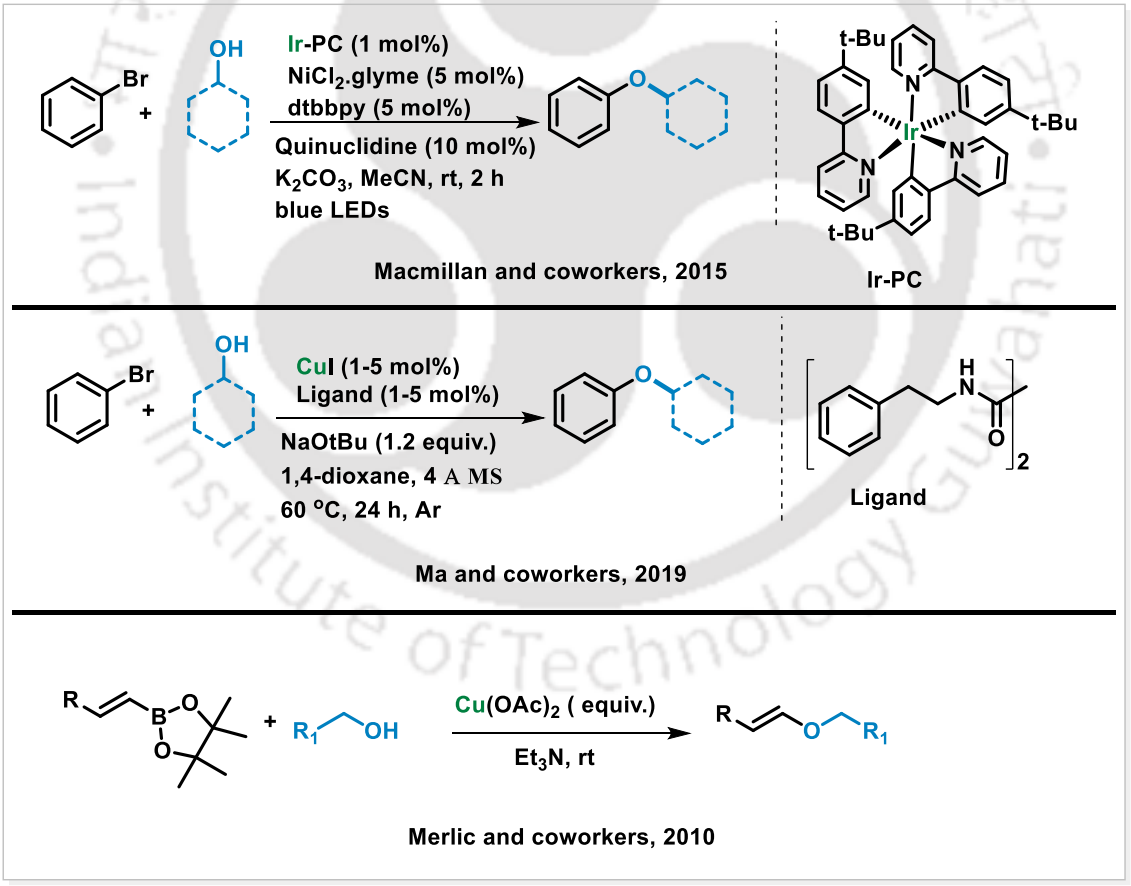


Scheme 1.3: Representative example of C-alkylation on various π-systems with alcohols as coupling partner

Alcohols are also used in the making of C-O bonds applying sustainable strategies. Macmillan and coworkers [23] illustrated the fabrication of C-O bonds by coupling secondary alcohols and alkyl halide by merging photoredox catalysis with Ni complex. Very recently Ma and coworkers [24] demonstrated Cu-based catalysis with N,N-Diphenethyloxalamide ligand for the synthesis of O-alkylation of alkyl halide in a thermal condition. C-O bond construction can also be achieved by applying Chan-Lam type coupling reactions [25] involving coupling between boronic acids and alcohols catalysed by copper acetate (**scheme 1.5**).

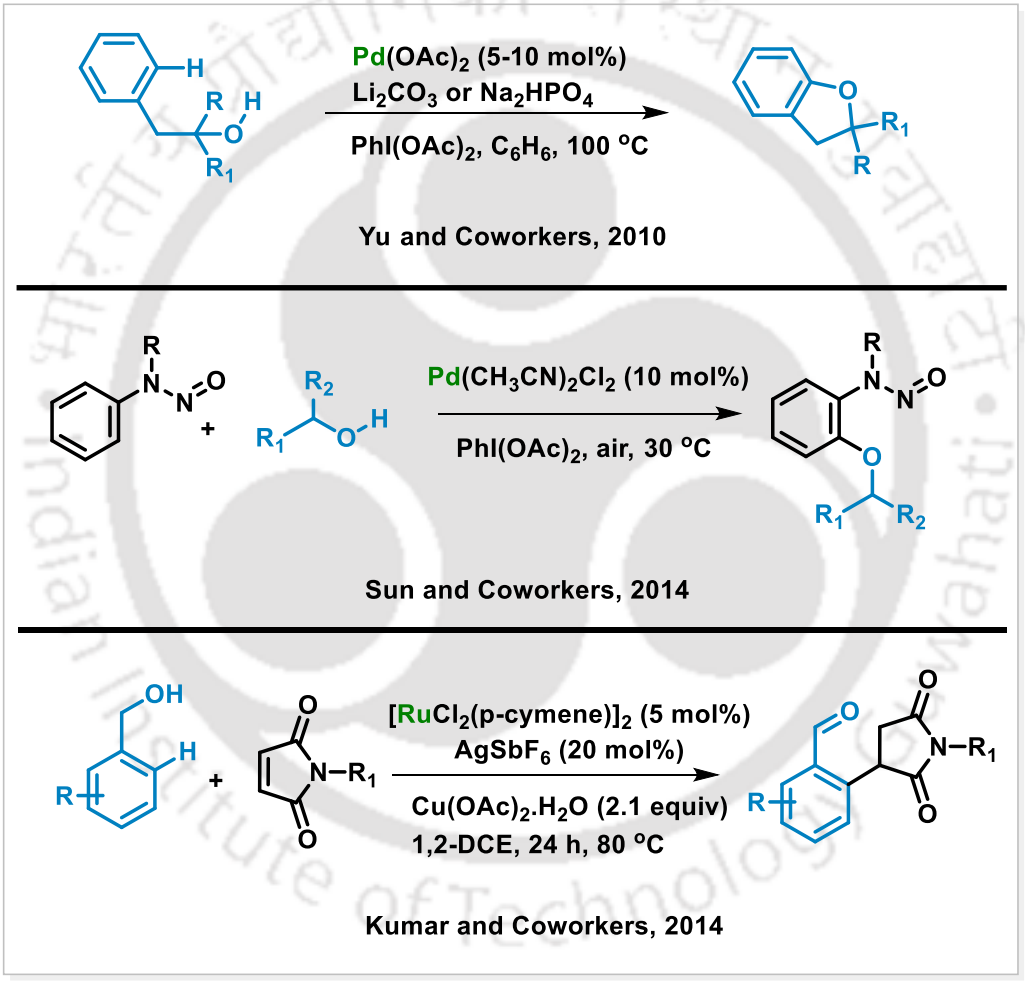


Scheme 1.4: Representative example demonstrates α-functionalisation of alcohol with alkene and alkynes



Scheme 1.5: Representative example demonstrates the use of alcohol for various C-O bond constructions using aryl halides and boronates

With time, the development of C-H activation also led to the construction of C-O bonds. In this respect, Yu and coworkers reported intramolecular O-arylation of alcohol to benzo fused cyclic ether via palladium catalysed C-H activation.[26] Later on, nitroso as a directing group in nitrosoaryl amine, Sun and coworkers [27] successfully constructed the C-O bond via Pd catalysed C-H activation in presence of hypervalent iodine compound. Similar works were reported by various groups just changing the directing groups. Interestingly, benzyl alcohols have also been employed as directing groups to activate the ortho C-H bond [28] and construction of C-C bonds employing alkenes or various other coupling partners (**scheme 1.6**).



Scheme 1.6: Representative example of C-O and C-C bond construction via the concept of C-H activation reaction

In the late 2000's, alcohols were also highly applied in organic synthesis, providing a waste-free method, use of renewable earth resources, liberation of benign byproducts and also use of *insitu* generated dihydrogen. These remarkable achievements are also named as "Acceptorless

dehydrogenation (AD)" and "Borrowing hydrogen (BH)" approach and its background is discussed briefly in the next section.

1.4. Overview of Acceptorless Dehydrogenation (AD) and Borrowing Hydrogen (BH)

The sustainable utilization of the Earth's natural resources is invariably advantageous for the well-being of humanity. Majority of chemicals used in academia and industry for various chemical transformations are predominantly derived from fossil fuels.[29] However, given that fossil fuels are finite resources, their excessive consumption accelerates their depletion. The overuse of fossil fuels further contributes to significant health risks, environmental degradation, and the escalation of climate change. [30] In context to the above problems, "Acceptorless Dehydrogenation" is a welcoming area of research as it fulfils various green chemistry principles.[10] Alcohols and alkanes are the most established and investigated substrates that undergo dehydrogenations with a suitable catalyst.[31] However, in the context of the present thesis, alcohols are considered as a substrate for the discussion on AD and BH path. Removal of hydrogens from adjacent atoms of organic substrates is always a thermodynamically uphill process. Hence in doing so, copious amounts of oxidant are required, or else a sacrificial amount of hydrogen acceptor is necessary as a result of which a sacrificial amount of waste is generated. However, the phenomenon can also proceed in an atom-economical way by designing such a catalyst that enables the release of molecular hydrogen as a green by-product without the need for a hydrogen acceptor, and hence the name "**Acceptorless Dehydrogenation** (**AD**)" comes into existence (**figure 1.2**). This concept is believed to be revolutionized in the area of organic chemistry as it opens up the building of different C-C and C-N bonds and hence structurally important heterocycle units.

Another perspective of the above catalytic system involves parking the hydrogens (obtained in the dehydrogenation step) in the catalyst in the form of hydride without liberating it. This further opens up the utilization of hydrogen *in situ* for the hydrogenation of unsaturated species without the use of hydrogen gas. This reshuffling of hydrogens from one species to another in situ is the basis of "**Borrowing Hydrogen** (**BH**) or **Hydrogen Autotransfer** (**HA**)" and the term was first coined by Williams and coworkers back in 2004 (**figure 1.3**).[32] The whole phenomenon is primarily dependent on transition metals with appropriate ligand systems, making the Hydrogen dissociation and recombination in comparatively mild reaction conditions. The concept demonstrates the involvement of mild reaction conditions followed by

the release of water as a condensation byproduct. This attracts the scientific community tremendously and leads to the development of the area in the context of organic synthesis in the present time.

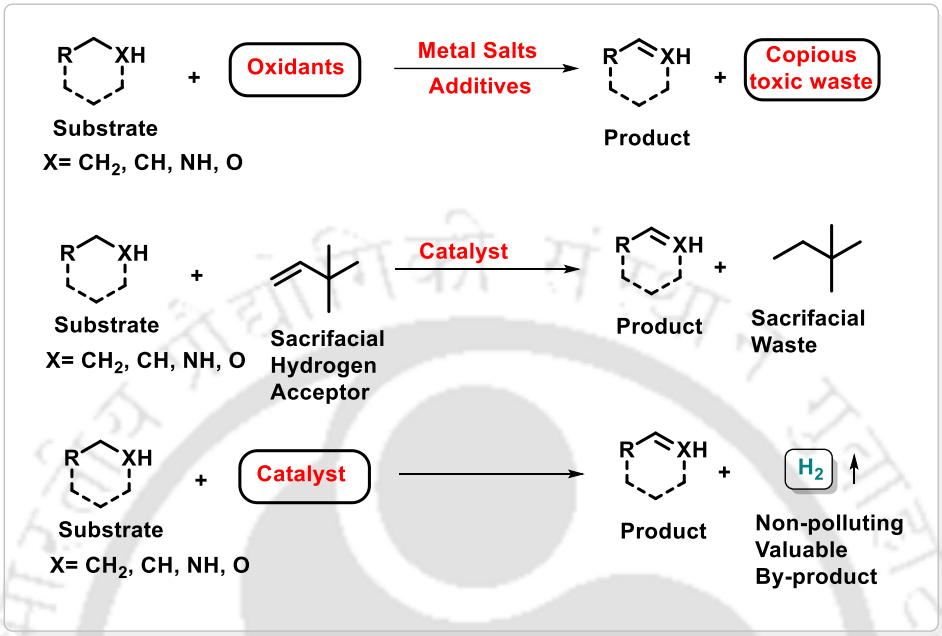


Figure 1.2: Depicts the development of the concept of Acceptorless Dehydrogenation

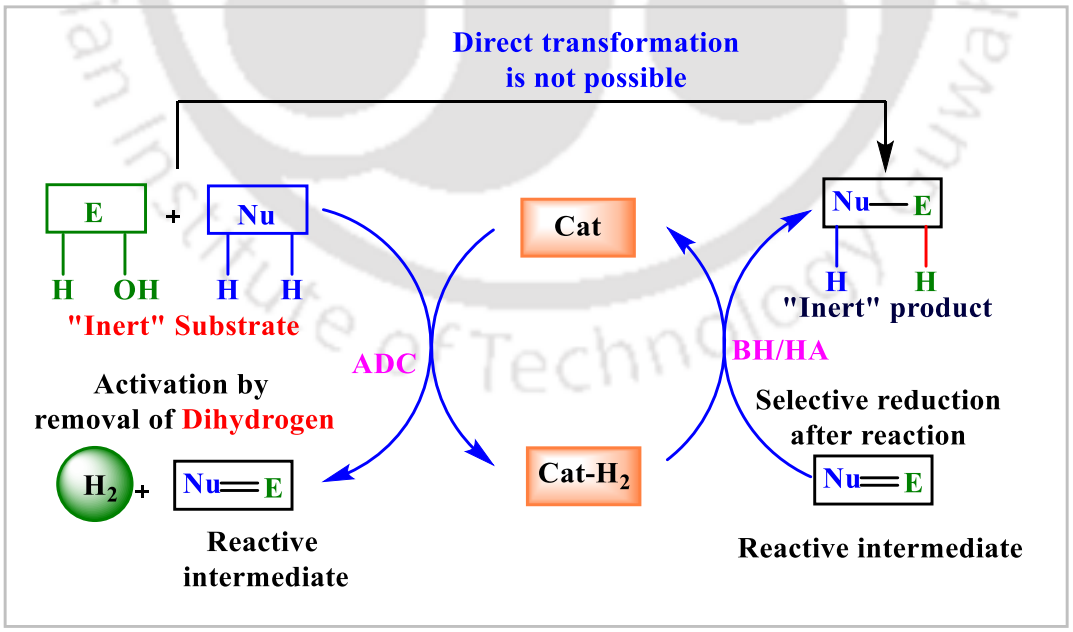


Figure 1.3: Depicts the concept of Borrowing Hydrogen

1.5. The beauty of catalyst design and the overview of the mechanistic pathway that supports the AD and BH approach

Transition metals have a unique ability to carry out such chemical transformations that conventional non-transition metals can't achieve. This is the beauty of transition metals that can activate the most inert bond around an organic substrate making the chemical event more facile. Nature itself realizes the beauty of transition metals and therefore has been found to use them in a variety of ways to activate an inert chemical bond or to drive unprecedented chemical events, devoid of which nature can't work in an organized way.

In conventional organometallic chemistry, transition metals were realized to participate in a reaction via oxidative addition, reductive elimination, β-hydride elimination, migratory insertion, etc.[33] In all such classical events, ligands act as a spectator and control electronic or steric properties around the metal centre (**figure 1.4**).

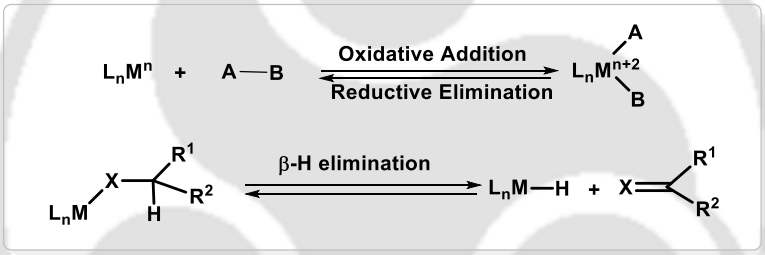


Figure 1.4: Conventional mechanistic pathway of an organometallic catalysis

On the contrary, a different pathway was realized where the ligand framework along with the metal centre also participates in bond activation. Some significant examples that occur in nature include hydrogen activation using various metalloenzymes such as [**FeFe**], [**NiFe**], and [**Fe**] hydrogenase (**figure 1.5**).[34] This inspires chemists to design catalytic system capable of activating a bond via cooperation between both metal and ligand and hence the term **Metal Ligand Cooperation** (**MLC**) comes into existence.

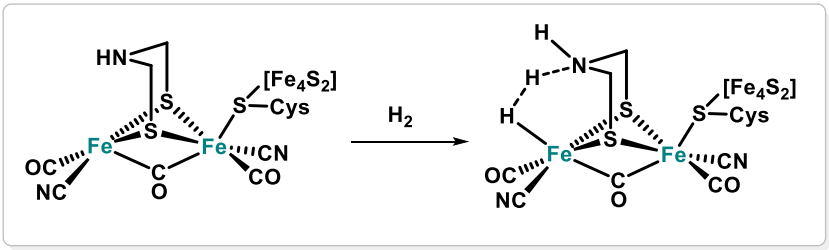


Figure 1.5: H_2 activation catalysed by [FeFe] hydrogenase via Metal-Ligand cooperation

Synthetically, different approaches were employed to activate certain inert bond via metal-ligand cooperation mode: a) metal-bound ligand functions as a Lewis base, synergistically facilitating the cleavage of the E-H bond.; b) pendant ligand acting as Lewis acid to accept electron from substrate donor and metal act as Lewis base; c) Metal bound redox non-innocent ligand act as electron reservoir and engage in substrate's bond activation (**figure 1.6**). [35]

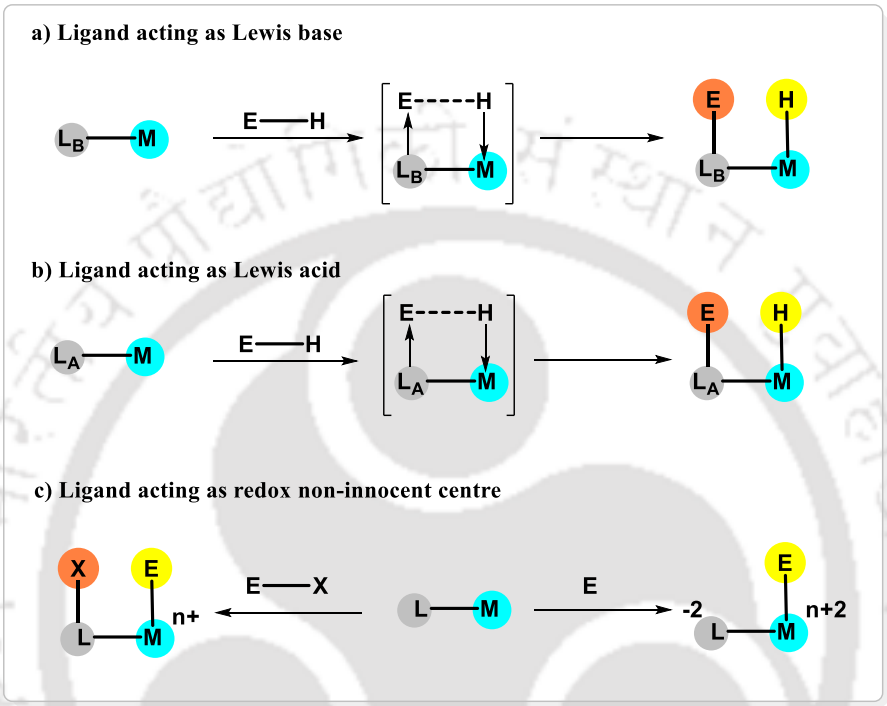


Figure 1.6: Various modes of Metal-Ligand cooperative approach

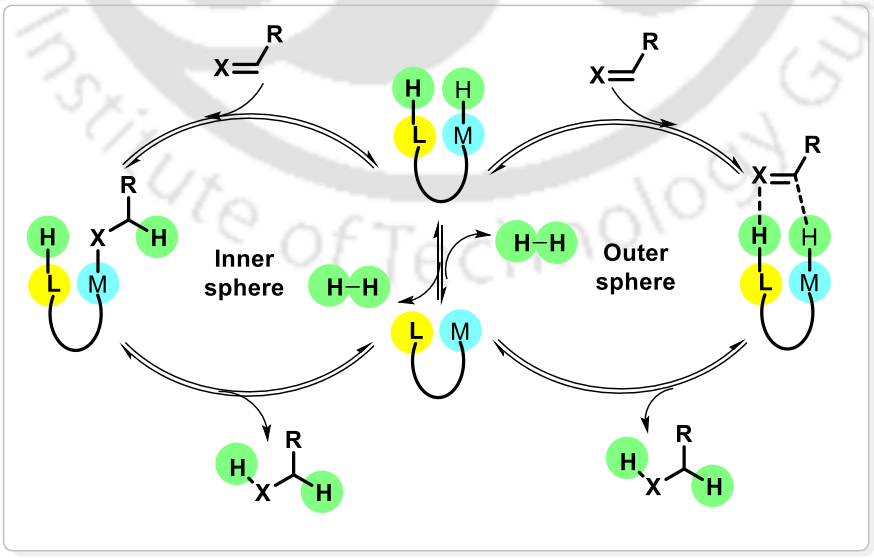


Figure 1.7: Different mechanistic pathway for substrate activation via MLC

Cooperative mechanism in substrate activation takes place via either of the two-mechanism a) stepwise inner sphere mechanism occurs via β-hydride elimination, b) concerted step outer sphere mechanism. In inner sphere mechanism, transfer of both proton and hydride from the metal complex to the unsaturated intermediate in two step process. In case of outer sphere mechanism, transfer of proton and hydride from metal complex to the unsaturated intermediate takes place in one step concerted manner (**figure 1.7**).

1.6. Chemistry of Nickel and Cobalt based metal complexes in catalysis

The area of catalysis and further development of synthetic organic chemistry was mostly dominated by precious noble metal such as Pd, Ru, Rh, Ir, Os, etc.[36] because these metals show exceptionally strong catalytic activity responsible to activate some of the most important and inert chemical bonds. However, the quest to search for something new allowed chemist to discover the potential of 3d base metals such as Mn, Co, Ni, Fe to take part in catalytic reaction with equal efficiency as that possess by noble metals.[37]

The thesis's main research work involves applying Nickel and Cobalt based catalysis. Hence this section deals with the evolution of the Ni and Co complexes in catalysis. In recent times, transition metal catalysis has revolutionized tremendously in organic synthesis. In particular, Cobalt and Nickel have been springing up as an efficient catalyst that facilitate diverse chemical transformations under mild reaction conditions. This 3d metals serves as one of the most important alternatives to the noble metals such as Pd, Rh, Pt, Ir, Ru, etc.

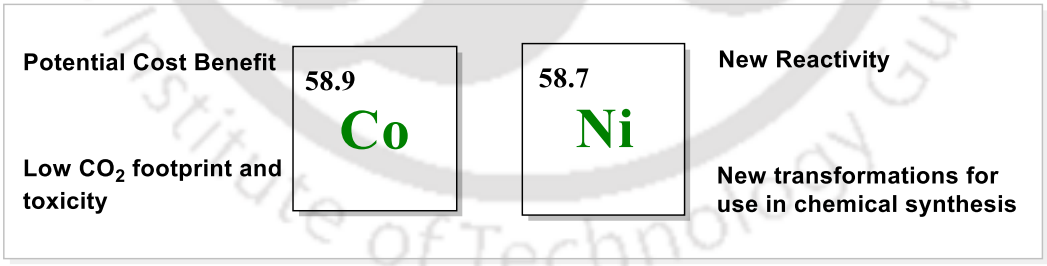
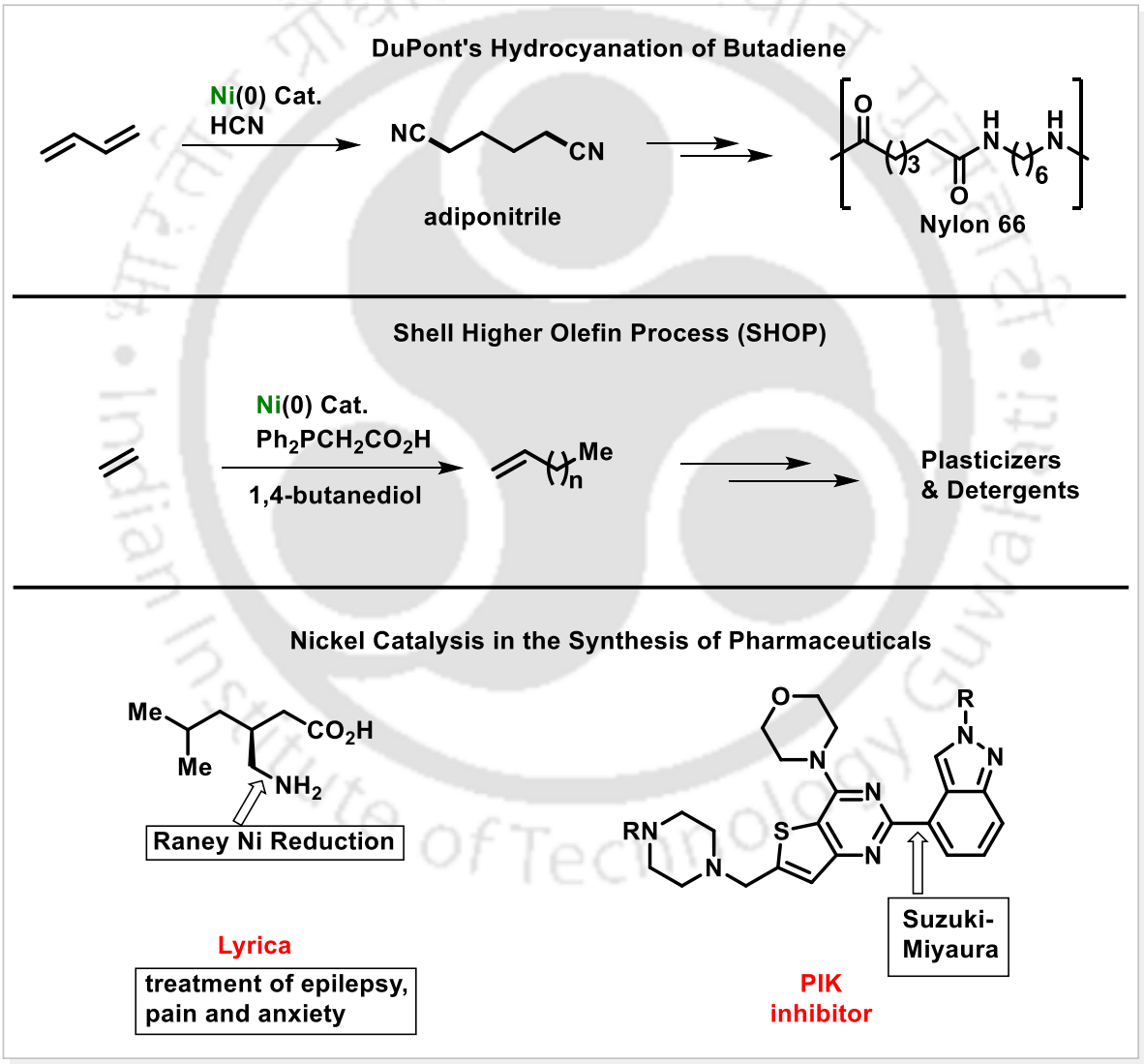


Figure 1.8: Advantages of Cobalt and Nickel chemistry

Nickel has been known as one of the most significant transition metals as a catalyst in both homogeneous and heterogeneous reactions and is also sometimes known as a spirited horse.[38] Nickel exists just above the palladium in the periodic table and considered as one of the potential catalyst candidates for the various cross-coupling reactions despite the longer prevalence of palladium catalysis.[39] Research groups are interested in the use of nickel

because of following reasons: natural abundance & low cost, favourable toxicological profiles for orally administered drugs, prospects in green chemistry, and potential to advance new chemical transformations based on alternate reactivity profiles. Industrially, Nickels were used for some notable chemical transformations, including DuPont's hydrocyanation of butadiene, Shell Higher Olefin Process (SHOP) and nickel catalysts used in the synthesis of pharmaceuticals (**scheme 1.7**). Moreover, recent advances both in industrial and academic research include C-C coupling reactions, amination, reductive coupling reactions, C-H activation reactions, C-F bond activation, amide C-N bond activation and photoredox catalysis (**figure 1.9**).[40]



Scheme 1.7: Importance of Nickel in chemical industry and toward synthesis of pharmaceuticals

On the other hand, Cobalt also serves as an important position in catalysis because of high natural abundance, low cost, variable oxidation states and taking part in important bond activation.

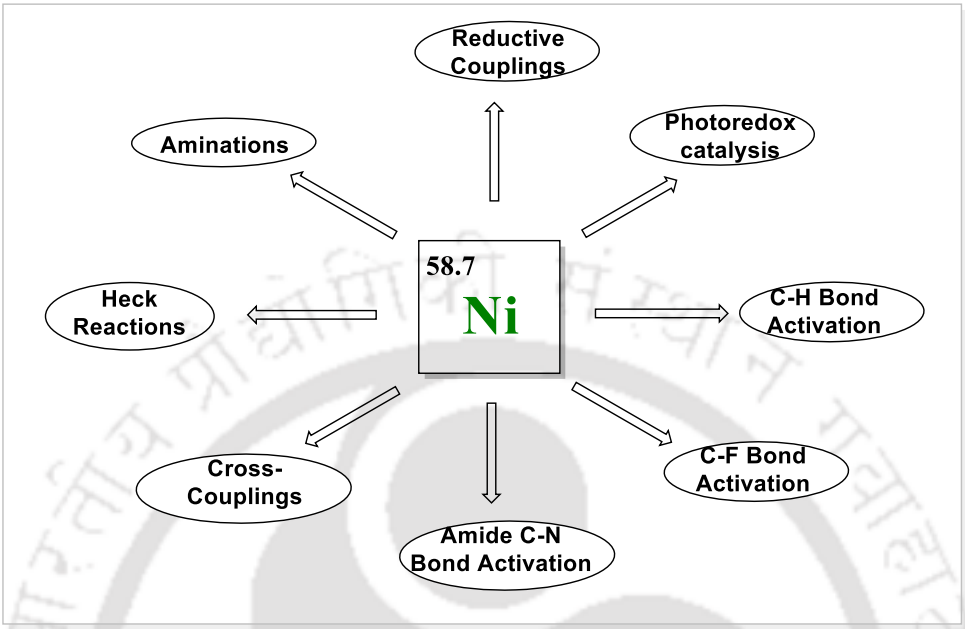


Figure 1.9: Application of Nickel in organic synthesis

Cobalt is found in nature in the form of vitamin B12 which plays a vital role in the regeneration of erythrocytes. Even in synthetic world, cobalt is known for its notable important chemical transformations such as Pauson-Khand reaction, Nicholas reaction, hydroformylation, coupling reactions, cyclisation reaction, C-H bond activations, etc (**figure 1.10)**.[41]

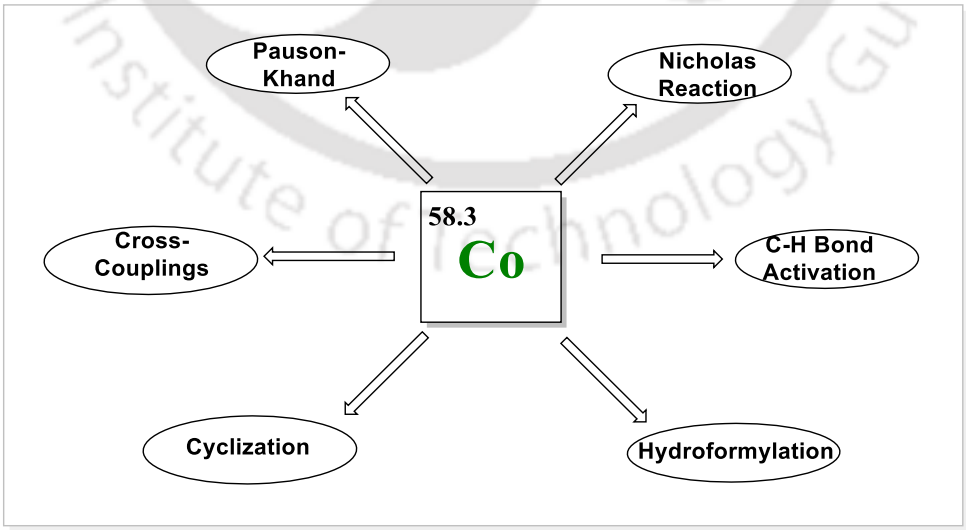


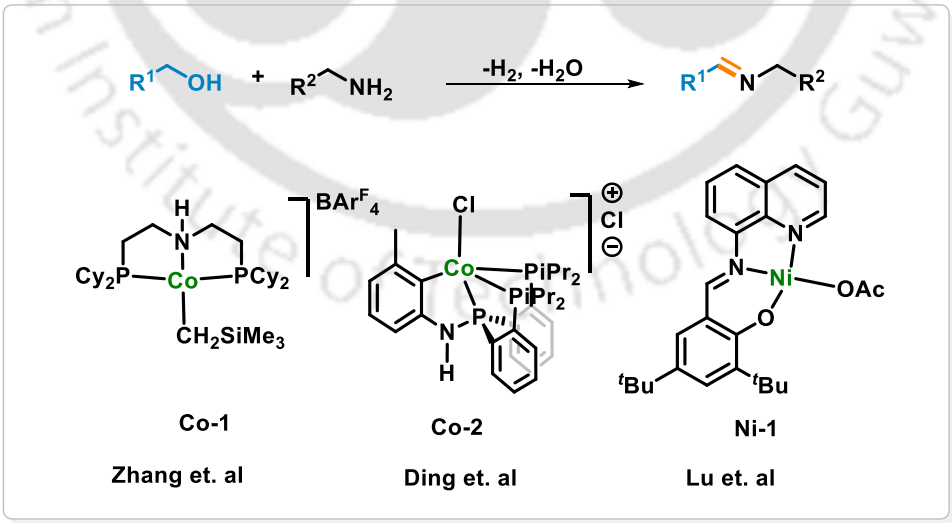
Figure 1.10: Application of Cobalt in organic synthesis

Expanding the scope of cobalt and nickel catalysis, recent research has been devoted to exploring potential applications toward more advanced and sustainable catalytic processes, including acceptorless dehydrogenation (AD) and the borrowing hydrogen (BH) methodology. The development of nickel and cobalt catalysts for these methodologies not only boosts their significance in synthetic chemistry but also aligns with the mounting demand for greener and sustainable chemical processes. By optimizing these catalytic systems, researchers aim to create more scalable and economically viable pathways for the production of valuable chemicals and fuels.

1.7. Representative examples of application of Nickel and Cobalt catalyst to activate alcohols in organic synthesis via AD approach

1.7.1. Formation of imines

One of the most extensively studied applications of alcohols in acceptorless dehydrogenation (AD) chemistry is the synthesis of imines through the coupling of amines and alcohol. Mechanistically the reaction involves the release of molecular hydrogen and water as a clean byproduct. The group of Milstein was the first to report the synthesis of imines using a lutidine-based dearomatized PNP-Mn complex.[42] After the first discovery, various groups contributed extensively to the development of chemistry with manganese catalysts.[43] However, in this race, people were also very much interested in exploring the potential of neighboring 3d metals such as nickel and cobalt (**scheme 1.8**).

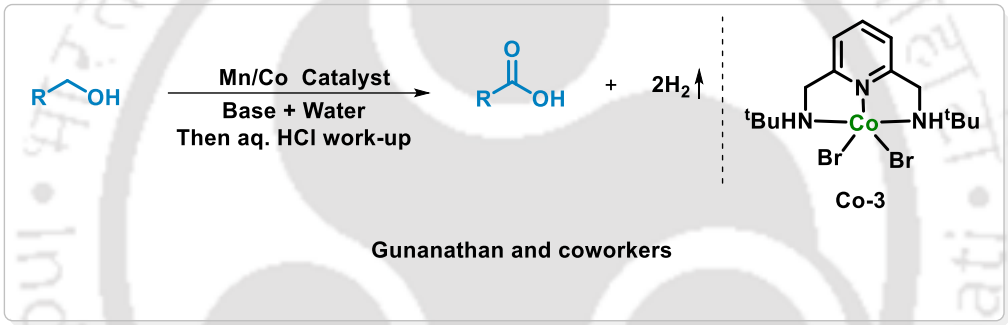


Scheme 1.8: Representative example of coupling between amines and alcohols resulting in imine formation

In this context, Zhang and coworkers [44] developed first base-free PNP-cobalt catalyzed imine synthesis using **Co-1** (1 mol%) with 1:1.1 ratio of alcohols and amines. Later on, Ding and coworkers [45] also reported a tetradentate NPPP donor cobalt complex (**Co-2** 2.5 mol%) in very low base loading of 7.5 mol% and low temperature (105 °C). Similarly, Lu and coworkers [46] reported ONN-Ni complex (**Ni-1**) in association with 1 equivalent of NaOH base at reflux condition in toluene medium to afford the desired imine product (**scheme 1.8**).

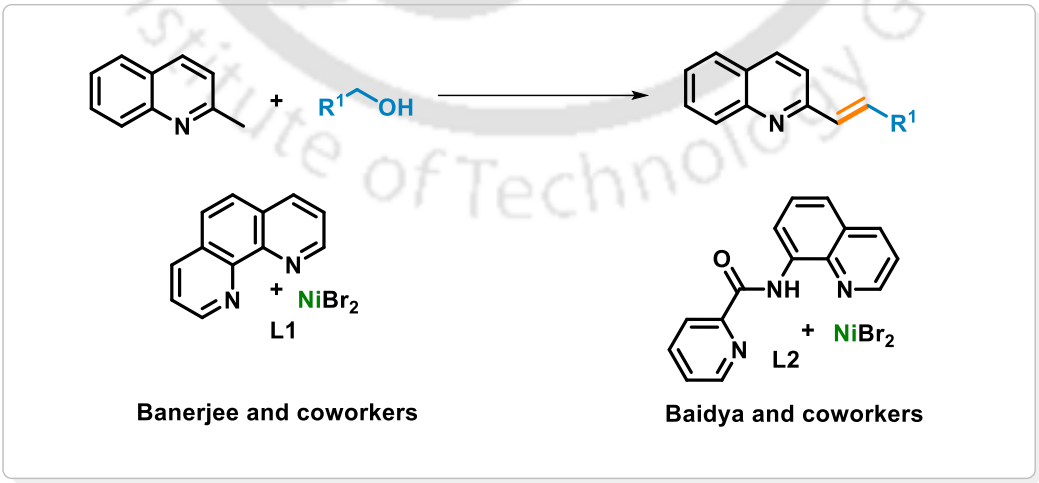
1.7.2. Alcohol to carboxylic acid

The ADC chemistry also helps direct the synthesis of carboxylic acid from alcohol. In 2020 Gunanathan and coworkers [47] reported the NNN-Co (**Co-3**) pincer complex catalysed conversion of alcohol to carboxylate using 1.5 equiv. of KOH in a toluene medium (**scheme 1.9**).



Scheme 1.9: Conversion of alcohol to acid via dehydrogenation.

1.7.3. Coupling of N-Heteroarenes with alcohol



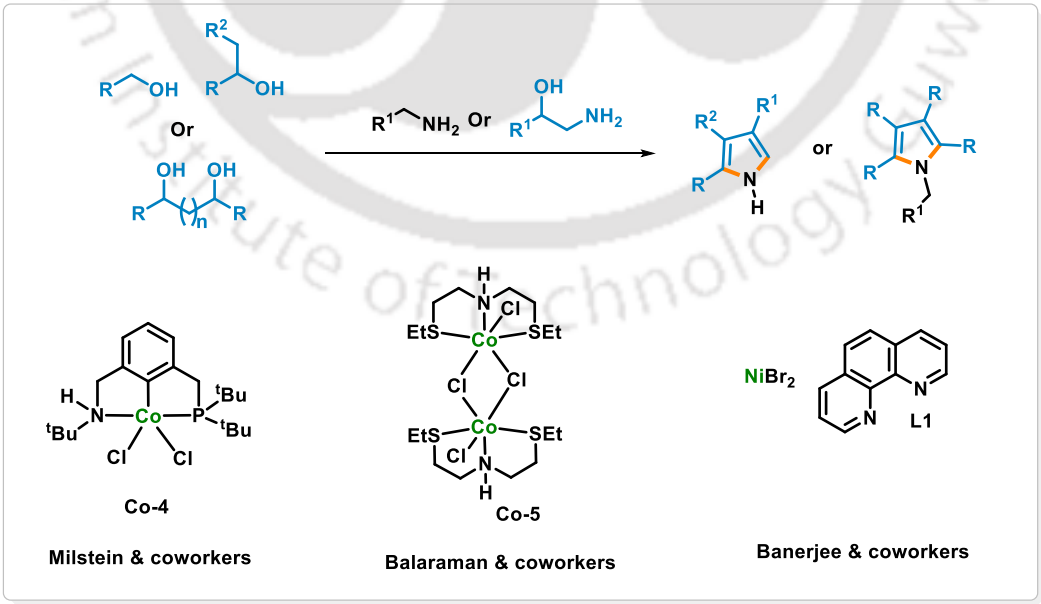
Scheme 1.10: Coupling of N-heteroarene and alcohols via acceptorless dehydrogenation.

Functionalising N-heteroarenes is an important strategy in organic synthesis as N-heteroarenes constitute an important class of pharmacologically active compounds. Although noble metal-catalyzed olefination of N-heteroarenes [48] is reported, however, with time base metal catalysis was systematically developed (**scheme 1.10**). Banerjee and coworkers also demonstrated the role of *insitu* derived Nickel [49] for smooth functioning in the olefination reaction. Baidya and his coworkers [50] also parallelly demonstrated the efficacy of NNN pincer ligand decorated Ni complex for the olefination of N-heteroarenes.

1.7.4. Synthesis of various heterocyclic compounds

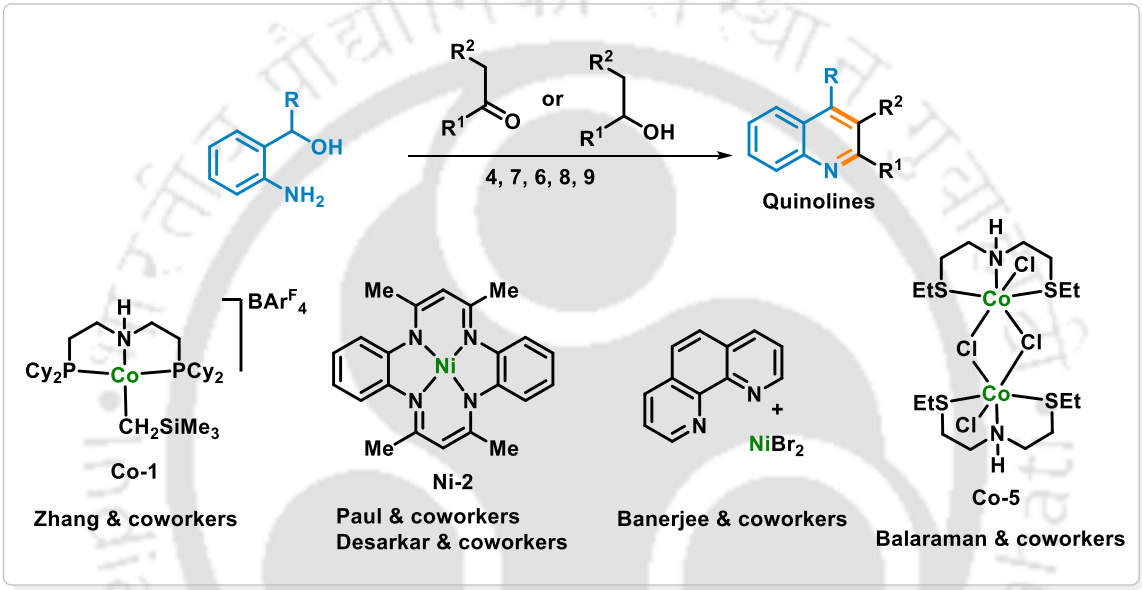
The ADC chemistry also allows access to synthesize five and six-membered heterocyclic units by liberating molecular hydrogen and water as byproducts. Several groups have made significant contributions to developing the methodology for heterocyclic synthesis and here in this section representative examples are chosen for discussion.

Milstein and coworkers[51] described the synthesis of N-substituted pyrrole from diol and primary amines using **Co-4** and low-loading of additives such as $NaEt_3BH$ and KOtBu. Balaraman and coworkers[52] illustrated the synthesis of NH-pyrrole employing alcohol derivatives and various amino alcohols using **Co-5** catalysts. Moreover, Banerjee and coworkers [53], described the role of insitu derived Ni-complex ($NiBr_2$ and phenanthroline) for the following transformation (**scheme 1.11**).



Scheme 1.11: Synthesis of pyrrole via dehydrogenative coupling.

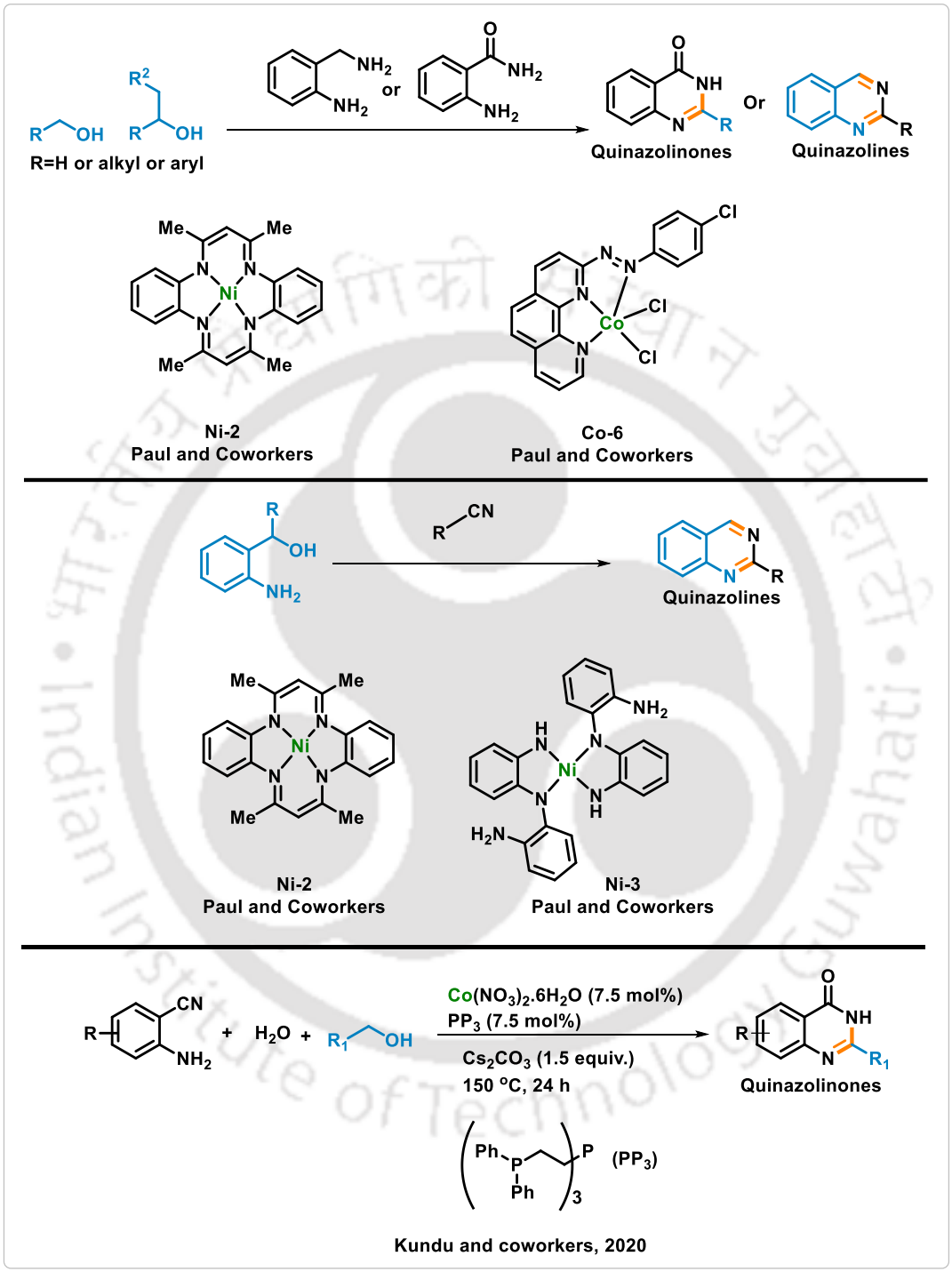
Quinolines also constitute an important class of heterocyclic moiety and several groups have contributed to the development of the methodology. Zhang and his coworkers [54] describe the use of PNP-Co (**Co-1**) complex as a catalyst and catalytic amount of base. Further, both Paul and De Sarkar groups [55] have demonstrated the use of tetradentate Ni-complex (**Ni-2**) efficiently in product formation. The methodology was further developed by using secondary alcohol as one of the substrates. The groups of Balaraman,[52] Paul,[55] and several other groups have made a notable development employing Co, and Ni complexes respectively (**scheme 1.12)**. [56]



Scheme 1.12: Synthesis of quinolines via dehydrogenative coupling.

Quinazolines and quinazolinones are also important heterocyclic units present in nature. With time, the AD approach also allows access to synthesize the heterocyclic unit with various combinations of both amines or amides and alcohol substrates (**scheme 1.13**). Paul and coworkers[57] demonstrated the tetradentate Ni-complex (**Ni-2**) for the coupling of 2-aminobenzyl amine and alcohols to quinazoline for the preparation of quinazoline derivatives. Paul and coworkers[57,58] further extended the work using 2-aminobenzyl alcohol and benzonitrile derivatives using **Ni-2** and **Ni-3** complexes. Further, the same group has also employed non-innocent ligand derived Ni-complex for the similar chemical transformation. However, when the starting substrate was changed to 2-amino benzamide and benzyl alcohols, a new heterocyclic unit i.e., quinazolinones was introduced and reported by the same groups [59] by employing **Ni-2** complex. In 2020, the same research group [60] reported a similar

reaction using the same set of substrates, facilitated by a Co(II) complex (Co-6) incorporating a redox-active arylazo ligand.

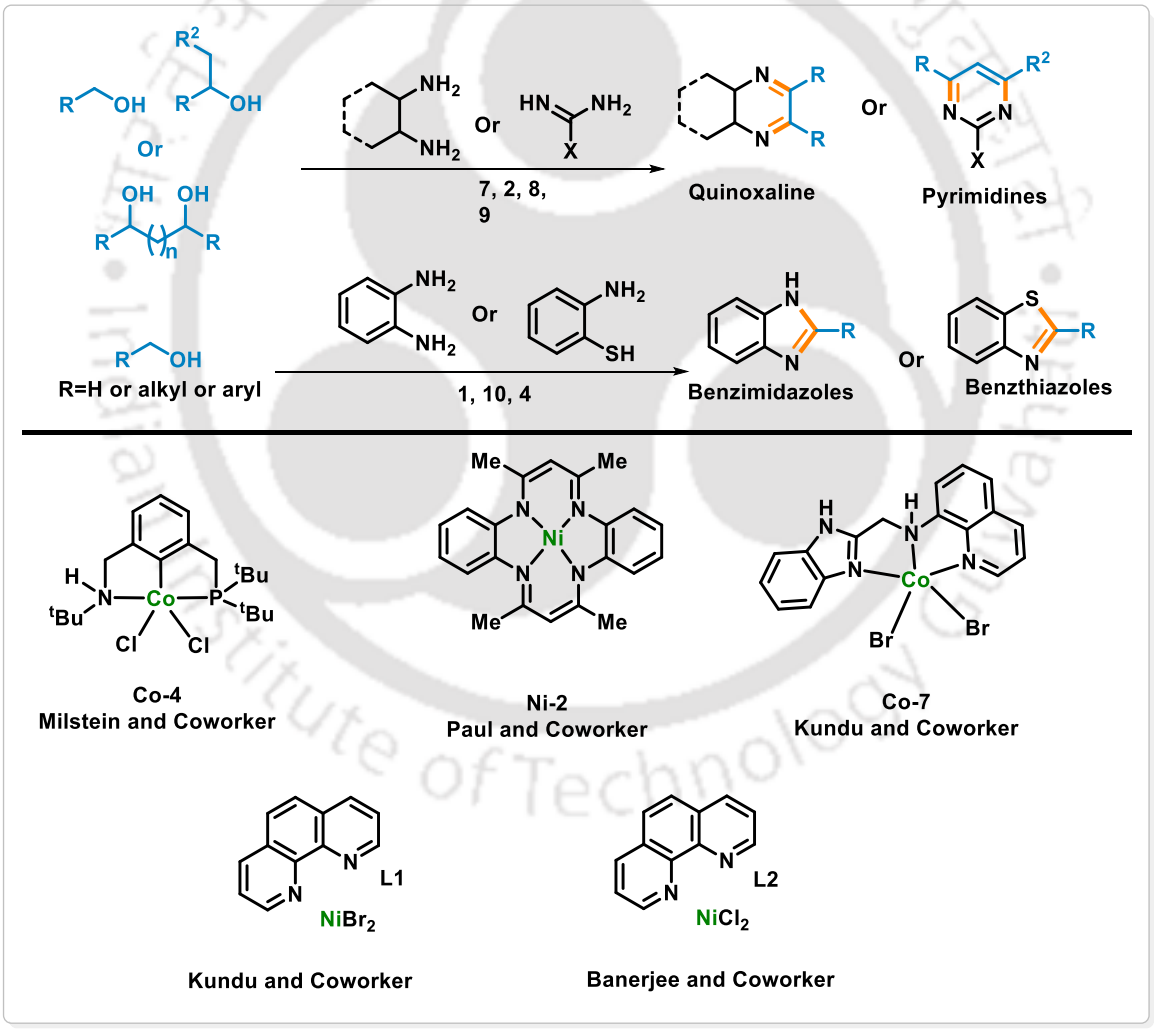


Scheme 1.13: Synthesis of quinazolines and quinazolinones via dehydrogenative coupling.

Kundu and co-workers have introduced a cost-effective and widely accessible Co-catalyzed method for quinazolinones synthesis.[61] 2-aminobenzonitrile reacted efficiently with different

aliphatic alcohols (Scheme 32) to afford the desired product. An in situ formed catalytic system by reacting 7.5 mol% of $Co(NO_3)_2.6H_2O$ with 7.5 mol% of tris[2-(diphenylphosphino)ethyl]phosphine, (PP_3) was found to catalyze the reaction effectively (**scheme 1.13**).

When 1,2-diaminobenzene reacts with diol, it results in quinoxaline [62, 56] however, when instead of diol, simple benzyl alcohol or aliphatic primary alcohol is used, a five-membered N-heterocycle i.e., benzimidazole is formed. [63] Similarly using amidine starting material such as benzamidine or guanidine, and combining it with primary and secondary alcohol, leads to the formation of pyrimidine. Various Co and Ni catalysts are employed to carry out the desired transformations via AD approach (**scheme 1.14**).

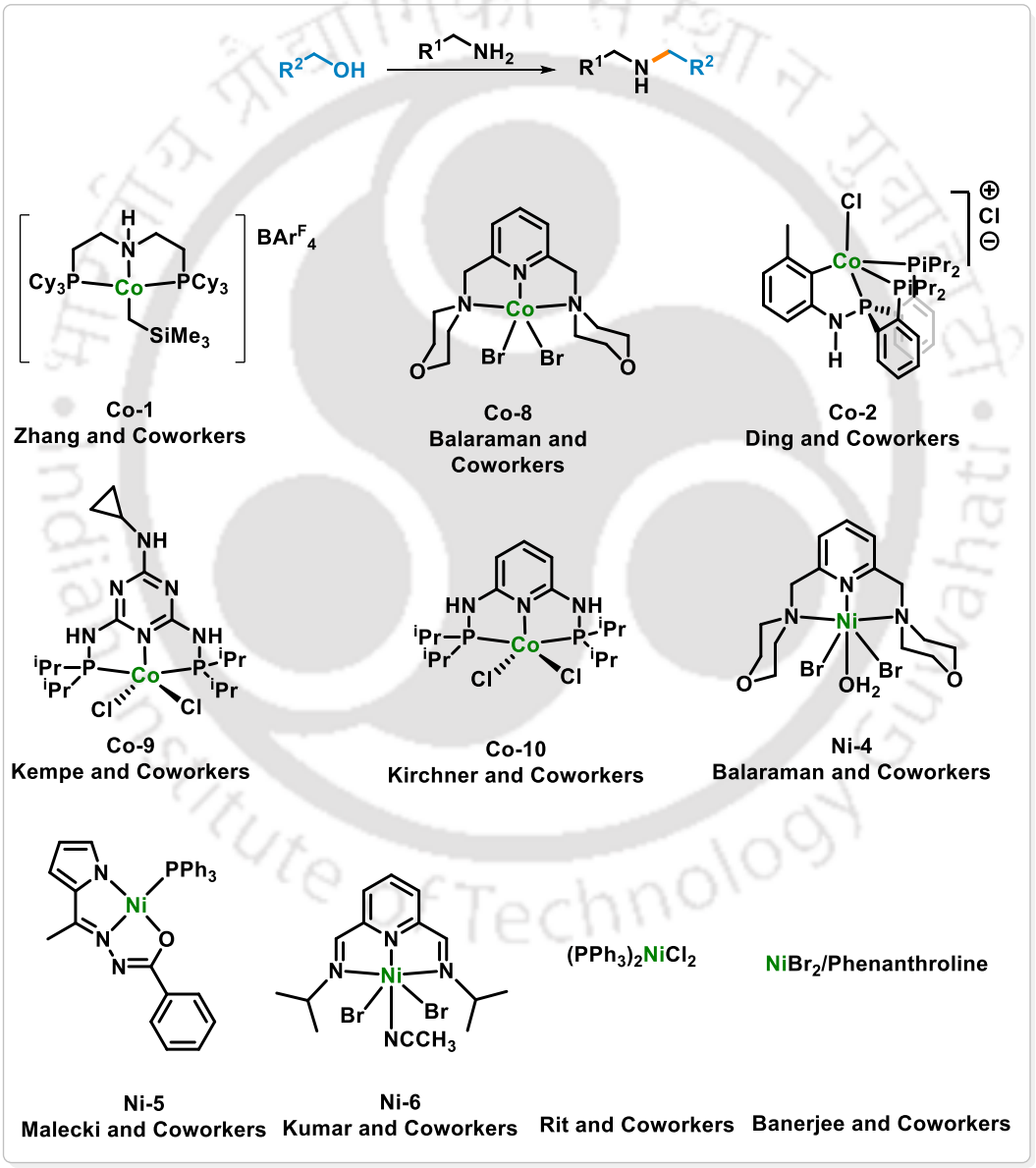


Scheme 1.14: Coupling of diamines and alcohols to produce various heterocycles via double dehydrogenative coupling.

1.8. Representative examples of application of alcohols in organic synthesis via BH Approach

The "Borrowing Hydrogen" or "Hydrogen Autotransfer" approach allows the transfer of hydrogens insitu to give a saturated compound. This approach allows the construction of various C-N, C-C bonds. The sub-section includes some important representative developments in the "Borrowing Hydrogen" approach.

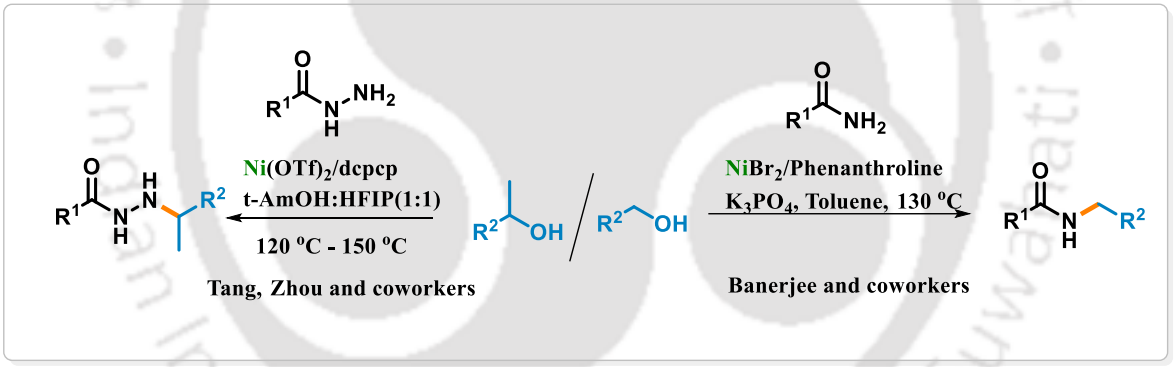
1.8.1. N-alkylations of amines and amides



Scheme 1.15: Conversion of alcohol to N-alkylated amine via borrowing hydrogen approach.

The BH approach provides easy access to the conversion of primary amines to secondary amines or amides to their corresponding N-alkylated amides. The groups of Zhang, Kirchner, Ding, and Balaraman [64] have developed several Co-pincer complexes (**Co-1**, **Co-2**, **Co-8**, **Co-9** & **Co-10**) that include phosphine and non-phosphine-based ligand systems to achieve N-alkylation smoothly. Parallelly, various groups had also contributed in developing Nickel based catalysis for N-alkylation reaction. Several homogeneous pincers and non-pincer based Ni-catalyst were explored and interestingly, nickel catalyst also shows similar potential like that of several other 3d metal based catalyst reported (**scheme 1.15**). [65]

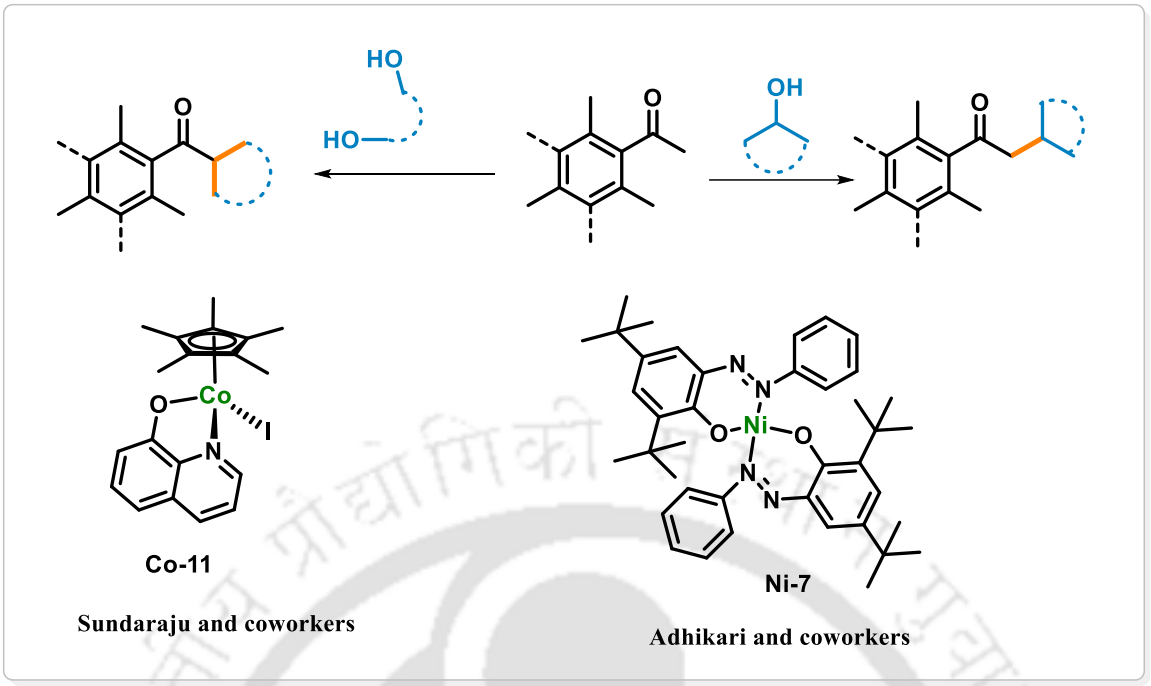
In contrast to the N-alkylation of amines, the N-alkylation of various amides are relatively very challenging (**scheme 1.16**). In this development, Banerjee and a coworkers [66] recently reported a work on the Ni-catalysed N-alkylation of amides. Many other groups have also contributed extensively toward Ni-catalysed N-alkylation of amide. In addition, the group of Tang and Zhou [67] reported the $Ni(OTf)_2$ and 1,3-bis (di-cyclohexyl phosphine)propane (dcpp) to mono-alkylate hydrazide.



Scheme 1.16: Coupling of Various amides with alcohols.

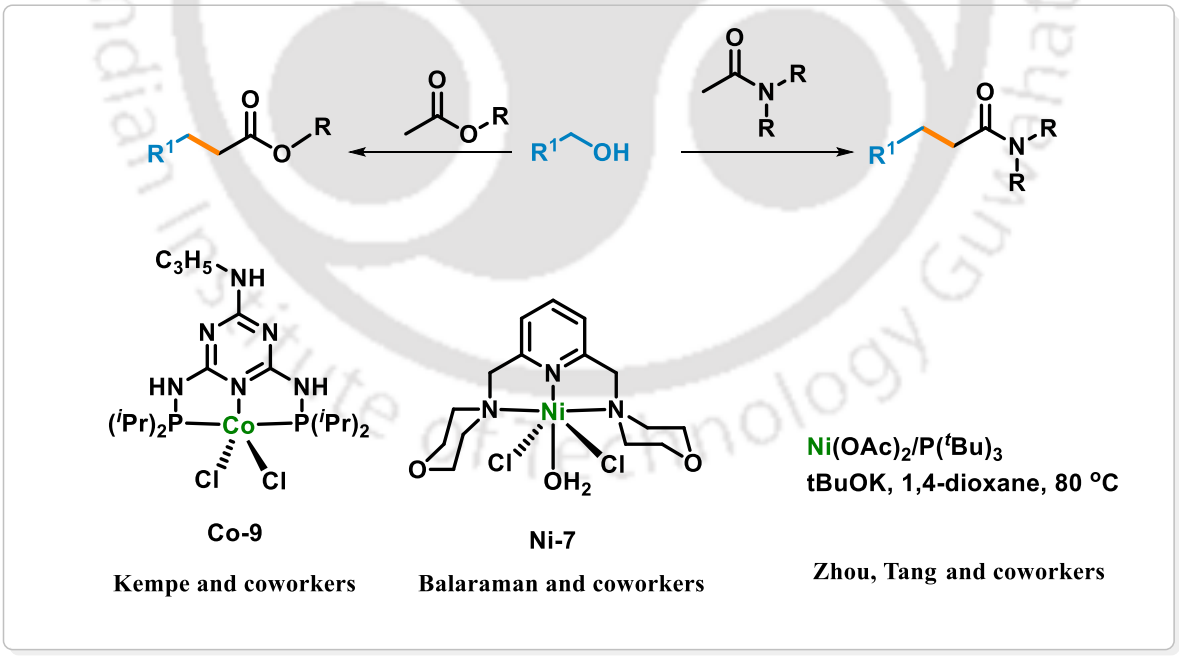
1.8.2. C-alkylation of Hindered ketones

C-alkylation of ketones with secondary alcohols is one of the most challenging works that has been witnessed. However, modifying the simple ketones to methyl-substituted ketones either in 2,4,6 or 2,3,4,5,6 positions is crucial to carry out the reactions (**scheme 1.17**). In this context, Sundaraju and coworkers[68] have introduced the derivative of Cp^*Co-complex (**Co-11**) in the super stoichiometric loading of the base to accomplish the reaction. Interestingly, Adhikari and coworkers [69] has developed the Ni-catalyzed (**Ni-7)** coupling of multi-substituted ketones with diols, the reaction results in the formation of stereoselective (1+n)-membered cycloalkane.



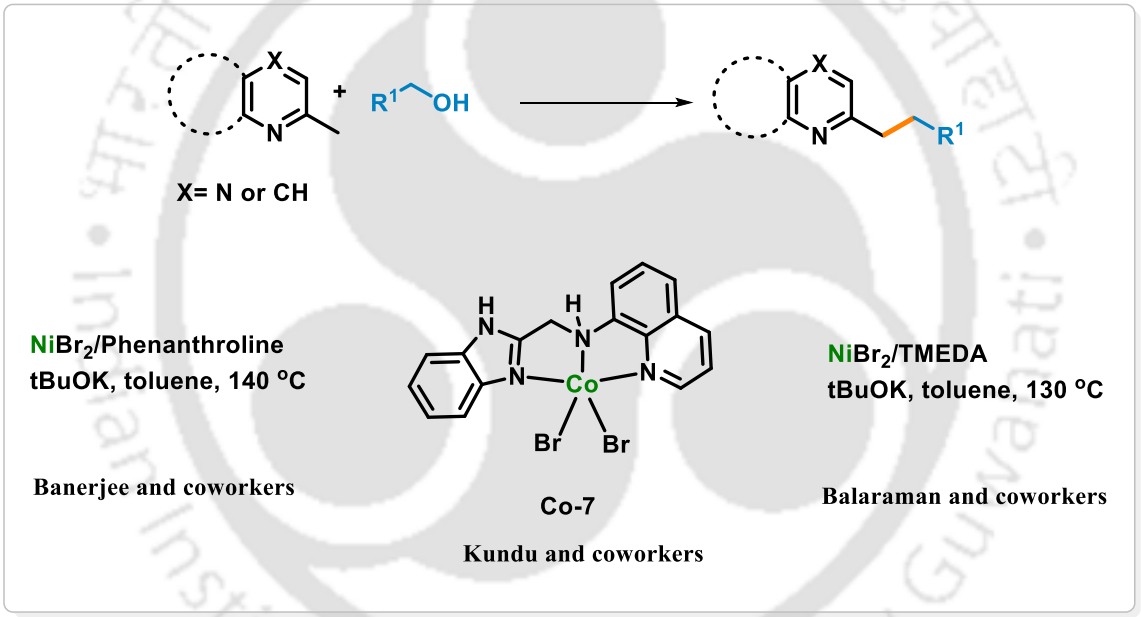
Scheme 1.17: Coupling of hindered ketones with primary diols and secondary alcohol via Borrowing Hydrogen pathway.

1.8.3. C-alkylation of amides, esters and 2-methyl N-heteroarenes



Scheme 1.18: Coupling of amides and esters with alcohols to give C-alkylated esters and amides via Borrowing Hydrogen pathway.

The C-C bond construction of esters and amides using alcohol as an alkylating agent is extremely challenging because of the low acidic α-CH bond due to resonance stabilized carbonyl groups of esters and amides (**scheme 1.18**). Initially, the C-alkylation of unactivated amides or esters was accomplished by Ir or Ru catalyst [70]. However, Kempe and coworkers[71] demonstrated the first base metal-catalyzed C-alkylation of unactivated amides and esters. They employed the PNP-Co complex (**Co-9**) in association with a stoichiometric amount of base to accomplish the C-alkylation of diverse N-substituted amides and esters. Further, the group of Balaraman [72] demonstrated the potential of phosphine-free NNN-Ni (**Ni-7**) complex for C-alkylation of amides and esters & Zhou, Tang and coworkers[73] demonstrated $Ni(OAc)_2$ in association with $P(^tBu)_3$ as an efficient catalytic system that under low temperature (80 °C).



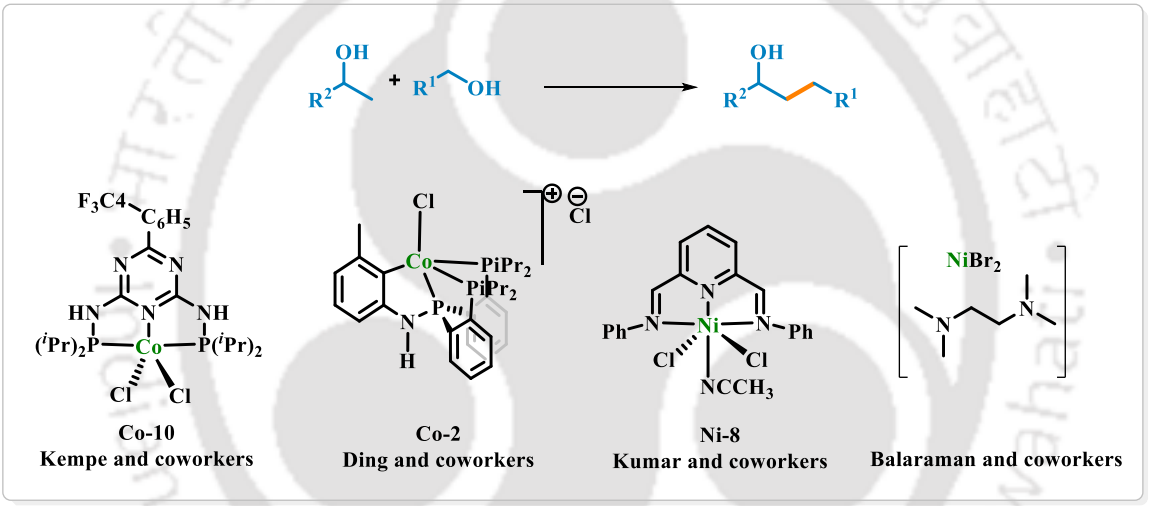
Scheme 1.19: Coupling of hindered ketones with primary diols and secondary alcohol via Borrowing Hydrogen pathway.

C-alkenylation of methyl-substituted N-heteroarenes is already discussed in section **1.4.4**. It was further observed that under certain catalytic systems and under certain catalytic conditions the 2-methyl N-heteroarenes can also be alkylated (**scheme 1.19**). In 2018 Balaraman and coworkers [74] illustrated the use of Nickel catalyst in association with TMEDA ligand for the C-alkylation of N-heteroarenes. Kundu and coworkers [75] in 2020 demonstrated the use of non-phosphine NNN-Co (**Co-7**) complexes for the chemical transformations. In addition, Banerjee and coworkers [76] illustrated the use of $NiBr_2$/Phenanthroline system for the same

chemical transformations. In all the cases, the catalytic protocol requires stoichiometric amount of base.

1.8.4. C-alkylation of secondary alcohols (Guerbet reaction)

Converting secondary alcohol to long-chain secondary alcohols via borrowing hydrogen strategy is an important area to explore and also challenging (**scheme 1.20**). The reaction was widely explored using various Ru and Ir-based catalytic systems. Kempe and coworkers [77] developed the C-alkylation of secondary alcohols using PNP-Co (**Co-10**) complex and KHMDS base at 80 °C. Later on, Ding and coworkers [78] employed NPPP-Co (**Co-2**) complex and KO*t*Bu in a stoichiometric amount and the protocol worked for various aliphatic and benzylic alcohols.



Scheme 1.20: Coupling of primary and secondary alcohols to give guerbet alcohol

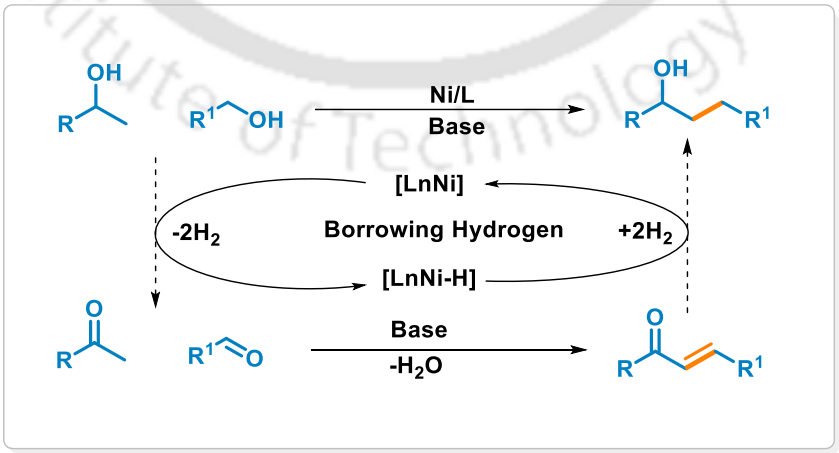


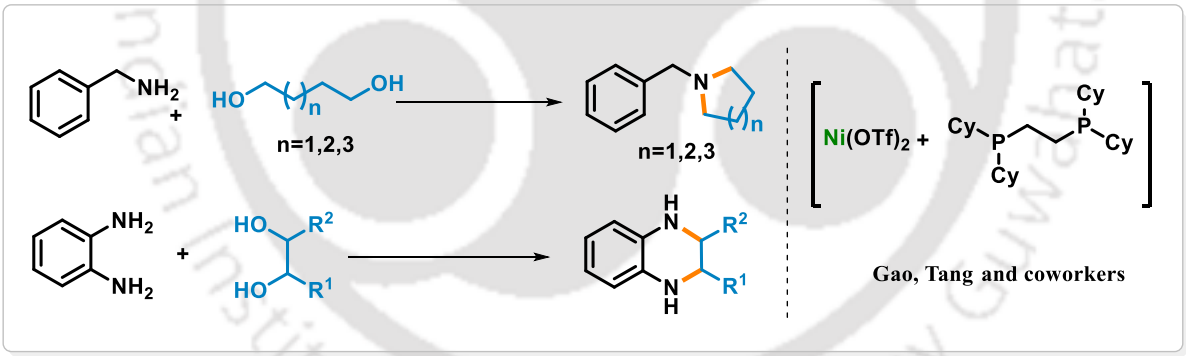
Figure 1.11: Mechanistic pathway for Guerbet reaction.

Balaraman and coworkers [79] reported an *insitu* generated Ni-complex from $NiBr_2$/TMEDA to alkylate 1-phenylethanol derivatives and cyclopentanols with various aliphatic alcohols. In addition, Kumar and coworkers [80] demonstrated the applicability of NNN-Ni pincer toward C-alkylation of secondary alcohols.

The mechanistic pathway describes the dehydrogenative conversion of both the alcohols to the corresponding carbonyl compounds. In the presence of base, condensation of carbonyls to give α,β-unsaturated carbonyl compound which upon borrowing hydrogenation leads to the formation of Guerbet alcohol (**figure 1.11**).

1.8.5. Synthesis of saturated heterocycles via BH approach

Zhao and coworkers [81] demonstrated the cyclization between aniline and diols to give various saturated N-heterocycles using Fe-knolker complex. However, Tang and coworkers [82] in 2019 described synthesis of N-heterocycles via nickel-catalyzed borrowing hydrogen strategy. They further expanded their approach to the synthesis of tetrahydroquinoxalines through the double alkylation of o-phenylenediamines, utilizing a range of symmetrical and unsymmetrical vicinal diols. (**scheme 1.21**).



Scheme 1.21: Synthesis of N-heterocycles via Borrowing Hydrogen pathway.

1.9. Concluding Remarks

This chapter discusses very briefly on the importance of alcohol in organic synthesis describing some of the most important organic transformations by various groups. However, in the recent times, alcohols are discovered to take part in sustainable reaction that liberate either molecular hydrogen and water or only water which are clean byproducts. This area of catalysis is known as Acceptorless Dehydrogenation and Borrowing Hydrogen approach. Moreover, this catalysis is widely explored using noble transition metals including Ru, Ir and Pd. It was later discovered

that 3d-transition metals have the potential to activate alcohols and participate in the AD and BH approaches While reviewing literature it was observed that manganese is one such 3d metal that was explored extensively, however, the investigation using Co and Ni-based complexes is comparatively less. Moreover, mostly metal complexes were decorated with expensive, toxic and sensitive phosphine ligands was explored. Hence, the potential scope toward development of Nickel or Cobalt based catalytic system is still present and can be explored by changing ligand with cheap and readily available donor atoms that has to some extent the electronic properties similar to that of phosphorous. And in this respect, along with nitrogen donor ligand, oxygen and sulphur donor atoms was thought as a suitable candidate and was found to have very few investigations and tremendous scope in AD and BH chemistry. Hence, following this, the thesis work describes the activity of non-phosphine derived Ni and Co complexes toward various important C-C and C-N bond constructions.

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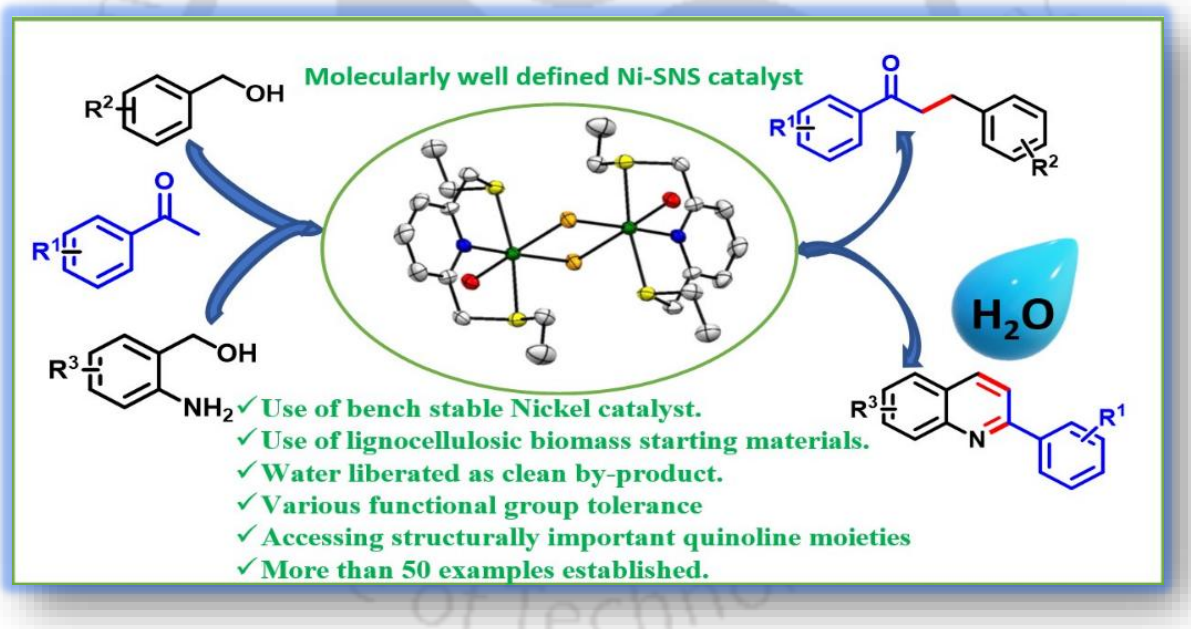
Chapter 2

Well-defined Ni-SNS Complex Catalysed Borrowing Hydrogenative α-Alkylation of Ketones and Dehydrogenative Synthesis of Quinolines



2.1. Introduction:

This chapter discusses the sustainable synthesis of phosphine free nickel complexes. The primary aim is to apply the synthesized catalyst for sustainable organic transformation. Hence, the synthesized complexes are utilized to investigate their applicability toward "Acceptorless Dehydrogenation" and "Borrowing Hydrogen" chemistry. The coupling of methyl ketone derivatives with alcohol derivatives is chosen for the investigation. The details of the work will be discussed in the upcoming sections.

C-C bond construction is among the most important chemical transformations in organic synthesis.[1] In this regard, α-alkylation of ketones is one of the fundamentally significant transformations frequently used in a wide range of chemical synthesis and biological processes.[2] Conventionally, α-alkylation of ketones was performed by using alkyl halides as an alkylating agent in the presence of a stoichiometric amount of base.[3] However, the method suffers from generating stoichiometric amounts of toxic byproducts, making the entire methodology environmentally unfriendly and low in atom economy. A significant achievement of the scientific community's efforts was the introduction of the concept of "Hydrogen Autotransfer (HA)" or "Borrowing Hydrogen (BH)" strategy, which allows the reactions to proceed in a waste-free and environmentally benign manner. Thus, this concept has received a lot of attention and appreciation in the catalysis community during the last decade.[4] The use of alcohol as an alkylating agent has attracted a lot of interest in recent years. Because alcohols can be easily obtained from cheap and abundantly available lignocellulosic biomasses which clearly appear as an attractive alternative to fossil fuel derived starting materials.[5] In a typical BH methodology, first alcohol is dehydrogenated to its corresponding carbonyl group. The formed carbonyl compound is then coupled with the enolate to result in α, β-unsaturated ketone upon elimination of H_2O. The α, β-unsaturated ketone upon borrowing hydrogen (released in the first step) furnish α-alkylated ketones. Interestingly, the metal catalyst has a tremendous role in the key step of hydrogen shuttling. Moreover, alcohol dehydrogenation is a thermodynamically uphill process, and transition metals also play a significant role in this process.[6]

2.2. Literature Survey:

Early contribution in homogeneous catalysis for the α-alkylation of ketones involves the use of various precious metals such as Ru,[7] Ir,[8] Pd,[9] Os[10] based catalytic systems which clearly

shows that this type of synthetic modification is still an intriguing chapter in the area of research.[11] The replacement of noble metals with non-precious, earth-abundant 3d metals is always desirable from a sustainability standpoint. Base metal promoted AD and BH transformations are still remain in their infancy. In this context, Darcel, and coworkers in 2015 reported Fe-Knölker type complex catalysed BH alkylation of ketones with alcohols. [12] The applicability of Mn and Co complexes towards this transformation was also demonstrated by the group of Beller, Zheng, Ke, and Milstein (figure **2.1**).[13]

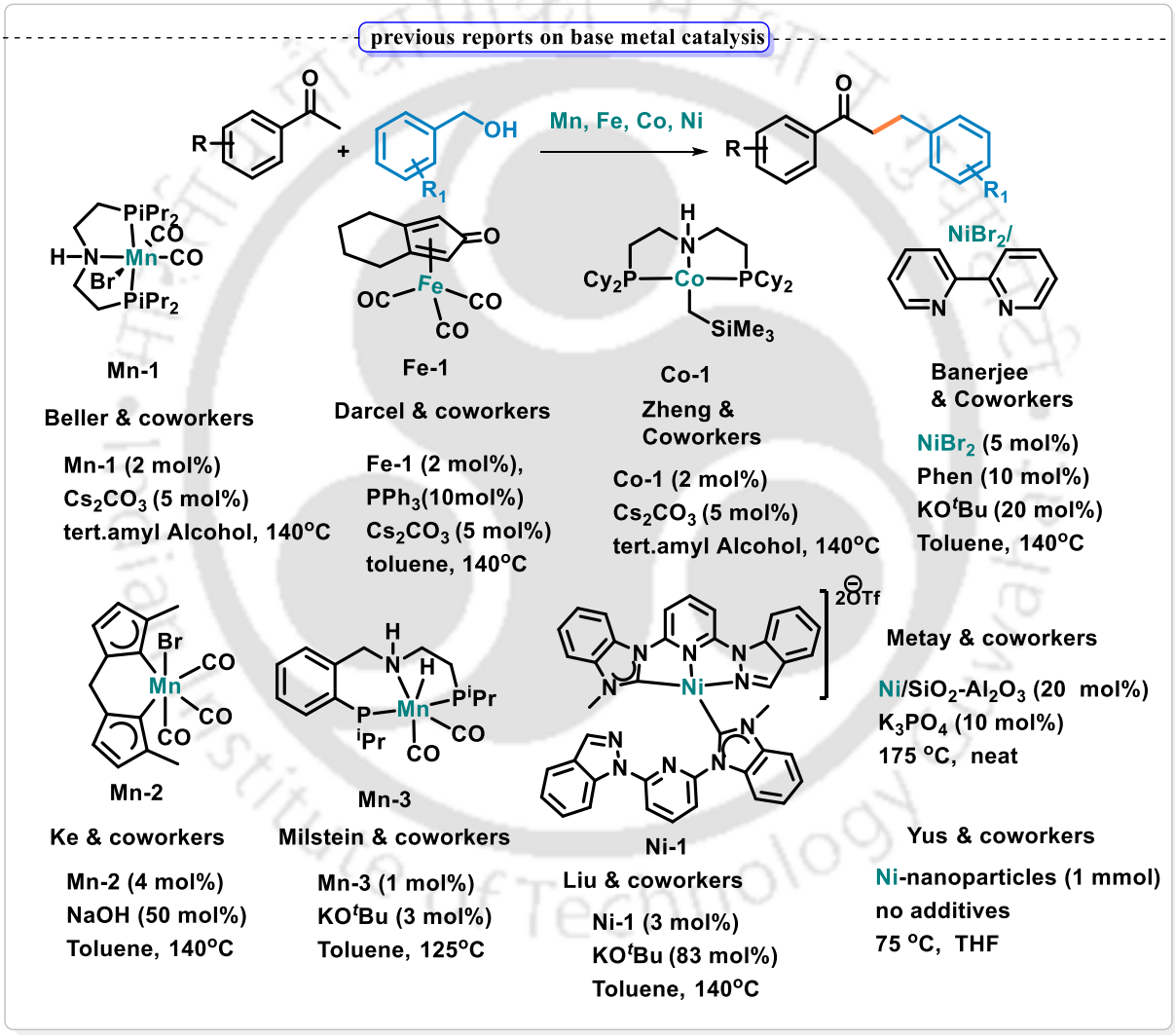


Figure 2.1: Previous reports on C-alkylation of ketones using various Mn, Co, Fe & Ni catalysts

The reported complexes mostly possess either air sensitive phosphine-based ligands or sophisticated ligand frameworks which needs tedious synthetic procedures/sophisticated storage and handling techniques.[14] Recently, the applicability of nickel for AD and BH transformations

has been perceived because of its low cost and high natural abundance.[15] In this regard, only a handful of reports is published to date in nickel-catalysed C-alkylation of ketones using BH tool. Yus *et. al*.[16] in 2007 reported the use of stoichiometric amount of nickel nanoparticles (from nickel chloride) for this process with low substrate scope. Metay and coworkers[17] in 2018 reported high loading of heterogeneous Ni/SiO_2-Al_2O_3 (20 mol%) catalysed α-alkylation of ketones at very high temperature (175 ºC). In 2019, Banerjee and coworkers [18] reported homogeneous $NiBr_2$/phenanthroline (5 mol%/6 mol%) and KO^{t}Bu (20 mol%) catalysed C-alkylation of ketones. Very recently, Liu and coworkers [19] reported Ni-NHC catalysed C-alkylation of ketones. However, the method suffers from using very high base loading (LiO^{t}Bu 83 mol%) and tedious synthetic procedure of ligands. Moreover, an important challenge witnessed in alkylation is the competitive side reaction to double borrowing hydrogen.[20] Hence, the development of a well-defined catalyst that can overcome the following challenges is always encouraged by the scientific community.

2.3. Present Work:

This Chapter focus on the synthesis, characterisation, and application of newly synthesized SNS donor containing Ni-complexes. The potential of SNS-Ni complex toward Borrowing Hydrogenation Chemistry was proved by conducting experiments for C-C bond forming reactions using acetophenone derivative and alcohol derivatives. Moreover, structurally important quinoline moieties are also explored using present protocol.

2.3.1. Synthesis of SNS-Ni complexes and its characterisation:

Ni-sulfur complexes always pull special attention because sulfur chemistry manifests an imperative contribution in biological and metalloenzyme based catalytic systems.[22] Inspired by nature's catalytic phenomenon, several groups unfold great accomplishments in sulfur ligand-based catalysts for the enhancement of the catalytic activity in various areas, including AD and BH catalysis.[23] Sulfur-based ligand systems in Ni metal are although explored in coupling reactions[24] however, underexplored in AD, BH catalysis or in hydrogenation reactions. This observation necessitates an investigation into the catalytic properties of the SNS-Ni catalyst in the context above. The synthesis of non-phosphine based, easily accessible, and bench-stable SNS Ni catalysts has been achieved. Lutidine-based SNS ligands varying alkyl substituents on the sulfur atoms were chosen. The ligand was synthesized following the literature procedures

(synthetic procedure are described in **experimental section**). Interestingly, a less bulky substituent in sulfur (C_2H_5) results in μ2-bromobridged dinuclear nickel complex with two distorted octahedral nickel centers (synthetic procedure in **experimental section**).

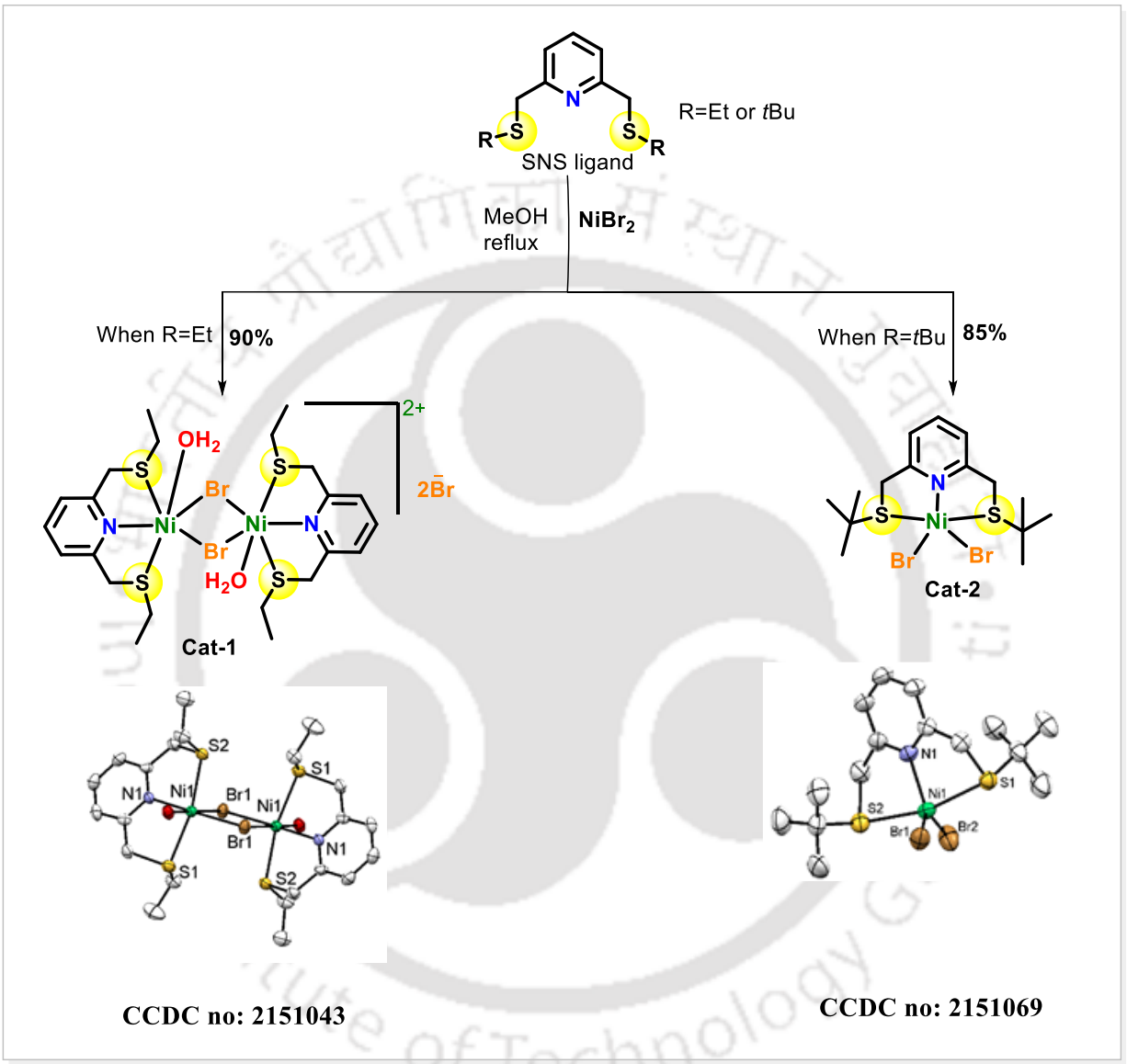


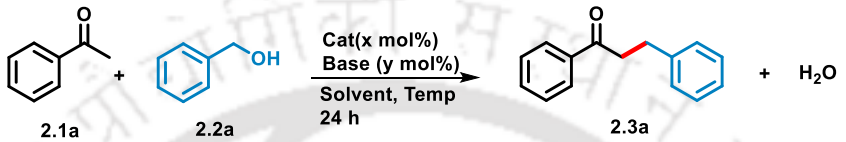
Figure 2.2: Synthetic representation of SNS-Ni catalysts

However, incorporating bulky substituent (-tBu) in sulfur results in a mononuclear nickel bromide complex which adopts a distorted trigonal bipyramidal structure. This steric feature regulates the complex's nuclearity and its effect can be seen in the catalytic properties of the two complexes to some extent. The bond length of Ni-S bond length ranges from approx. 2.4 to 2.5 Å and Ni-N bond length is approx. 2.00 Å respectively. In contrast, similar Ni-complexes bearing

PNP reported by Julia and coworkers, and Mukherjee *et. al.*, have Ni-P bond length lies approx. around 2.0 Å Ni-N bond length around 1.9 to 2.0 Å. [25]

2.3.2. Application of Synthesised Ni-complexes toward C-alkylation of ketones via alcohol activation

Table 2.**1.** Optimization of C-alkylation of Acetophenone[a]



Entry	2.1a (mmol)	2.2a (mmol)	Ni(SNS) (mol%)	Base (equiv.)	Solvent	Yield[b] 3a
1	0.5	0.6	Cat 1 (3)	KO^{t}Bu (0.5)	tol	62%
2	0.5	0.75	Cat 1 (3)	KO^{t}Bu (0.5)	tol	73%
3	0.5	0.75	Cat 1 (3)	NaO^{t}Bu (0.5)	tol	82%
4	0.5	0.6	Cat 1 (3)	NaO^{t}Bu (0.5)	tol	65%
5	0.5	0.75	Cat 1 (3)	KOH (0.5)	tol	70%
6	0.5	0.75	Cat 1 (3)	NaOH, K_2CO_3, Cs_2CO_3	tol	<20%
7	0.5	0.75	Cat 1 (3)	NaO^{t}Bu (0.4)	tol	83%
8	0.5	0.75	Cat 1 (3)	NaO^{t}Bu (0.3)	tol	70%
9[c]	0.5	0.75	Cat 1 (3)	NaO^{t}Bu (0.4)	tol	68%
10	0.5	0.75	Cat 1 (3)	NaO^{t}Bu (0.4)	Xylene,(THF, Dioxane)	62%,(<20%)
11	0.5	0.75	Cat 1 (3)	NaO^{t}Bu (0.4)	H_2O	NR
12	0.5	0.75	Cat 1 (1)	NaO^{t}Bu(0.4)	tol	65%
13	0.5	0.75	$NiBr_2$ (3)	NaO^{t}Bu (0.5)	tol	<25%
14	0.5	0.75	Cat 2 (6)	NaO^{t}Bu (0.5)	tol	71%
15	0.5	0.75	-	NaO^{t}Bu (0.4)	tol	trace
16	0.5	0.75	Cat 1 (3)	-	tol	NR

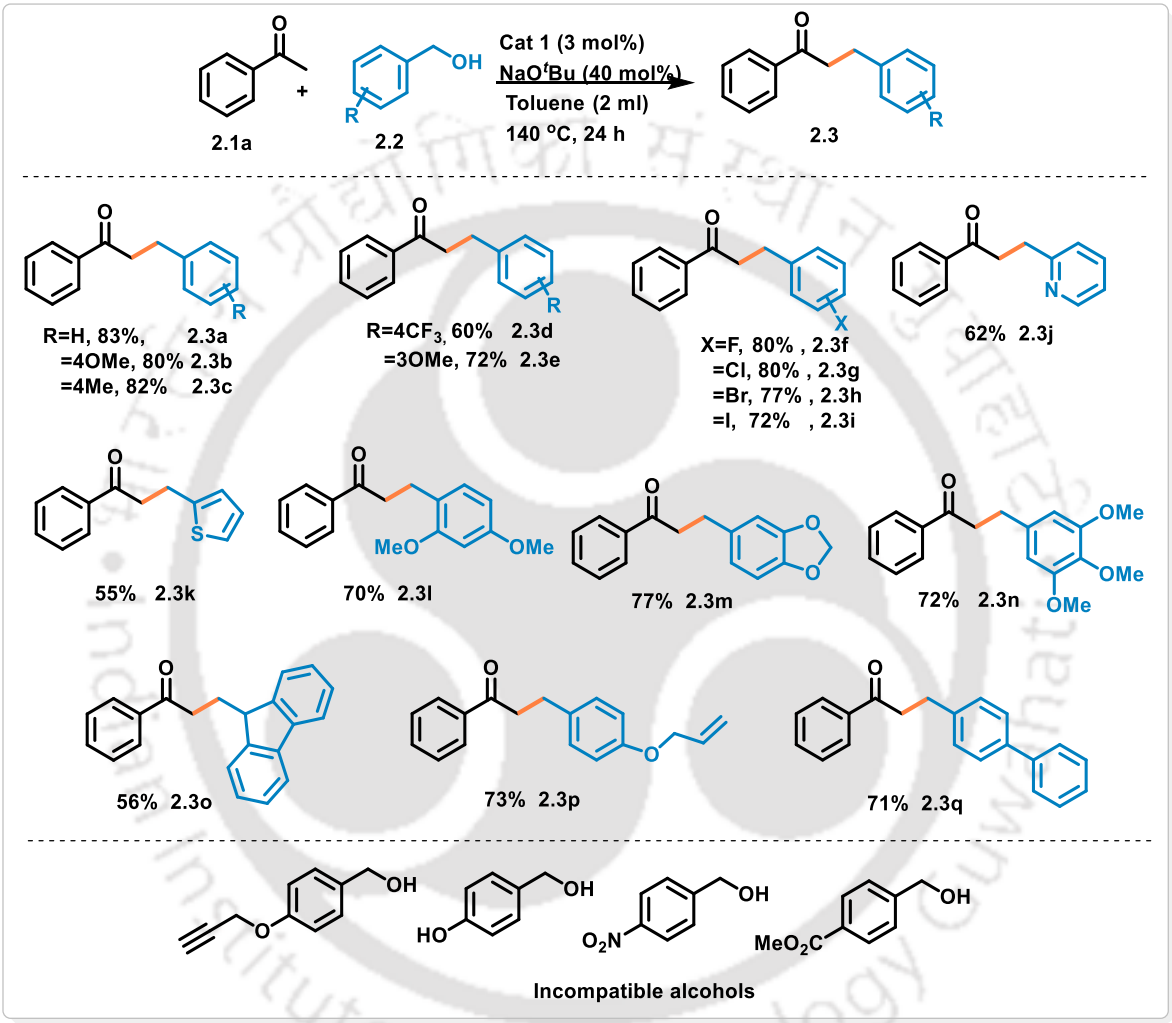
[a]**Reaction Condition**: **1a** (0.5 mmol), **2a** (0.6 – 0.75 mmol), Cat (1 – 3 mol%), Base (0.15 - 0.25 mmol), Solvent (2 mL) Temperature 140 ºC, [b]Isolated yield, [c]120 ºC

The optimization reactions were initiated by choosing acetophenone and benzyl alcohol as a model system. Initially, acetophenone (1 equiv.) and benzyl alcohol (1.2 equiv.) were reacted in the presence of Cat **1** (3 mol%), 50 mol% of KO^{t}Bu and 2 mL toluene at 140 ºC. After 24 h, 62% of the desired product **2a** (table **2.1** entry **1**) was isolated. However, on increasing the amount of the alcohol to 1.5 equiv. **2a** was obtained in 73% of the isolated yield (table **2.1** entry **2**). Next, the nature of bases (KOH, K_2CO_3, NaO^{t}Bu, NaOH and Cs_2CO_3) were changed to observe their influence on the reaction (table **2.1** entries **3**-**6**). NaO^{t}Bu was found to be the optimal candidate that furnished **2a** in 82% of the isolated yield (Table **1** entry **3**). Notably, lowering the base loading to 40 mol% does not have any detrimental effect on the yield of the reaction (table **2.1** entry **7**). However, the further decrease in the amount of NaO^{t}Bu (30 mol%), diminished the yield of the desired product (table **2.1** entry **8**). Furthermore, the solvent screening suggests toluene to be the suitable solvent in our catalytic system (table **2.1** entries **10** & **11**). Also, decreasing catalyst loading hamper the progress of the reaction (table **2.1** entry **12**). **Cat. B** was found to be less reactive compared to **Cat. A** whereas $NiBr_2$ (in the absence of any external ligand) gave only 25% of C-alkylated product **2a** (table **2.1** entries **13** & **14**). Finally, the reaction failed to proceed in the absence of either catalyst or base, which clearly indicates the crucial role of both catalyst and base in driving the reaction (table **2.1** entries **15** & **16**).

Next, the applicability of the developed reaction conditions was investigated toward a diverse range of benzyl alcohols and acetophenone derivatives (table **2.2**). Benzyl alcohols bearing electron donating group (like -OMe, -Me) at para position confer excellent yield of the desired α-alkylated products (table **2.2**, **2.3b** & **c**). Under similar conditions, the halide substituted benzyl alcohols (like F, Cl, Br, I) also reacted smoothly furnishing good yield of the desired product which provides an excellent scope for post-functionalization (table **2.2**, **2.3f - i**). Further, benzyl alcohols containing electron withdrawing group (-CF_3) proceeded well, thus delivering the desired product in good yield (table **2.2**, **2.3d**). Pleasingly, alcohols bearing heteroaromatic moieties such as pyridine, thiophene are also amenable to C-alkylation reaction (table **2.2**, **2.3j - k**). Sterically demanding groups like 2-OMe in benzyl alcohol delivered the desired product with good yield (table **2.2**, **2.3l**). Piperonyl alcohol and 3,4,5-trimethoxybenzyl alcohols are also responsive toward C-alkylation (table **2.2**, **2.3m - n**). Delightfully, structurally demanding fluorenyl alcohol was also found compatible with acetophenone to furnish the desired C-alkylated product (table **2.2**, **2.3o**). In addition, isolated double bond containing benzyl alcohol

also tolerates the present protocol (table **2.2**, **2.3p**). However, benzyl alcohols having terminal alkyne groups and phenolic -OH group were found incompatible in the present protocol (table **2.2**).

Table 2.2. Scope of Various Alcohols[a]

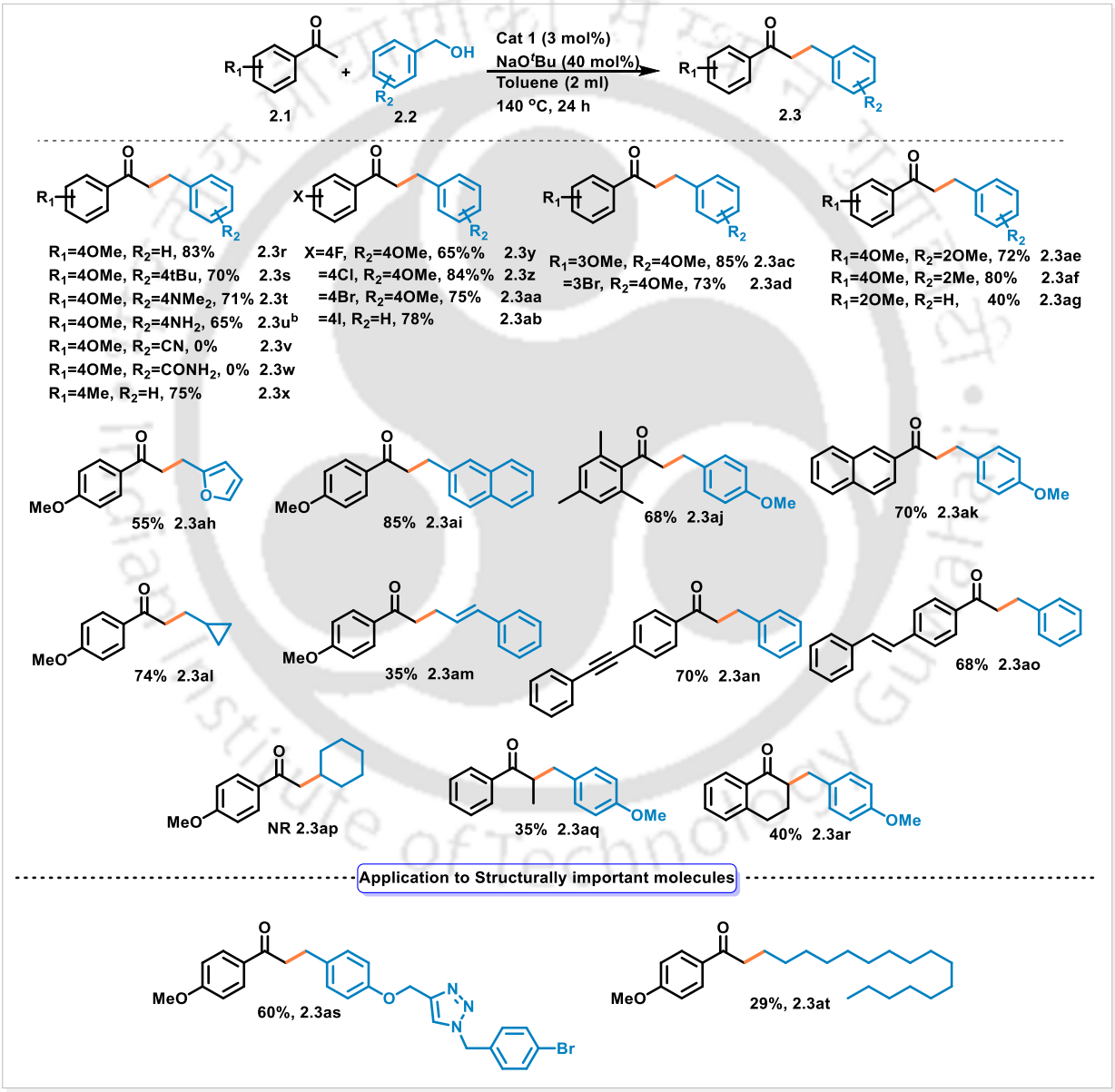


[a]**Reaction Condition**: **2.1a** (0.5 mmol), **2.2** (0.75 mmol), Cat **1** (3 mol%), NaO^{t}Bu (40 mol%), Toluene (2 mL), 140 °C, 24 h, Under argon.

Subsequently, the scope of acetophenone derivatives with various benzyl alcohols were also explored as discussed below. Electron donating group containing acetophenone (4-OMe, 4-Me) furnished good to an excellent yield of the desired product with various benzyl alcohols including 4-phenyl benzyl alcohol (table **2.3**, **2.3r** – **2.3x**). Interestingly, 4-aminobenzyl alcohol chemoselectively undergoes C-alkylation reaction to give desired product (table **2.3**, **2.3u**).

Acetophenone with halide substituents (F, Cl, Br, I) in both para and meta position showed smooth reactivity toward C-alkylation reaction (table **2.3**, **2.3y** – **2.3ab**). When 4-methoxyacetophenone was subjected to react with sterically hindered alcohol, good yield of the product was observed. However, 2-methoxy acetophenone gave moderate yield of the desired product (table **2.3**, **2.3ae** – **2.3ag**).

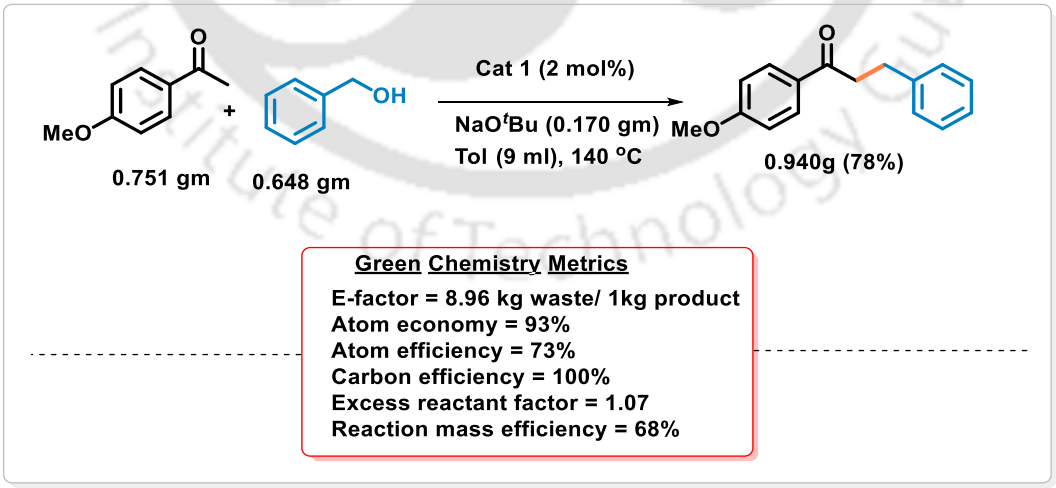
Table 2.3. Scope of Various Acetophenones[a]



[a]**Reaction Condition**: **2.1** (0.5 mmol), **2.2** (0.75 mmol), Cat **1** (3 mol%), NaO^{t}Bu (40 mol%), Toluene (2 mL), 140 °C, 24 h, Under argon. [b]1 equiv. alcohol

Under similar conditions, the reaction of acetophenone containing 3-OMe and 3-Br group proceeded smoothly with 4-methoxybenzyl alcohol thus furnishing 85% and 73% of the desired product (table **2.3**, **2.3ac** & **2.3ad**). Also, substituted acetophenone reacted well with heteroaromatic alcohol delivering moderate conversion (table **2.3**, **2.3ah**). Ring strain containing alcohols also converted efficiently thus ruling out the possibility of reaction driven by radical pathway (table **2.3**, **2.3al**). Furthermore, considering the borrowing hydrogen mechanism, the study also aimed to explore the involvement of other unsaturated functionalities in the transfer hydrogenation step. Pleasingly, both isolated as well as conjugated double bond and triple bond sustain in the present protocol to deliver C-alkylated product in good yield (table **2.3**, **2.3am** – **2.3ao**). Apart from arylmethyl acetophenone, propiophenone and α-tetralone also successfully couple with benzyl alcohols to furnish desired product (table **2.3**, **2.3aq** & **2.3ar**). To study the tolerability of alcohols containing biologically and structurally significant motifs, triazole containing alcohols were examined which operate up to the mark (table **2.3**, **2.3as**). In addition, long chain aliphatic alcohol such as cetyl alcohol also couples with acetophenone derivative to furnish 29% of **2.3at** (table **2.3**).

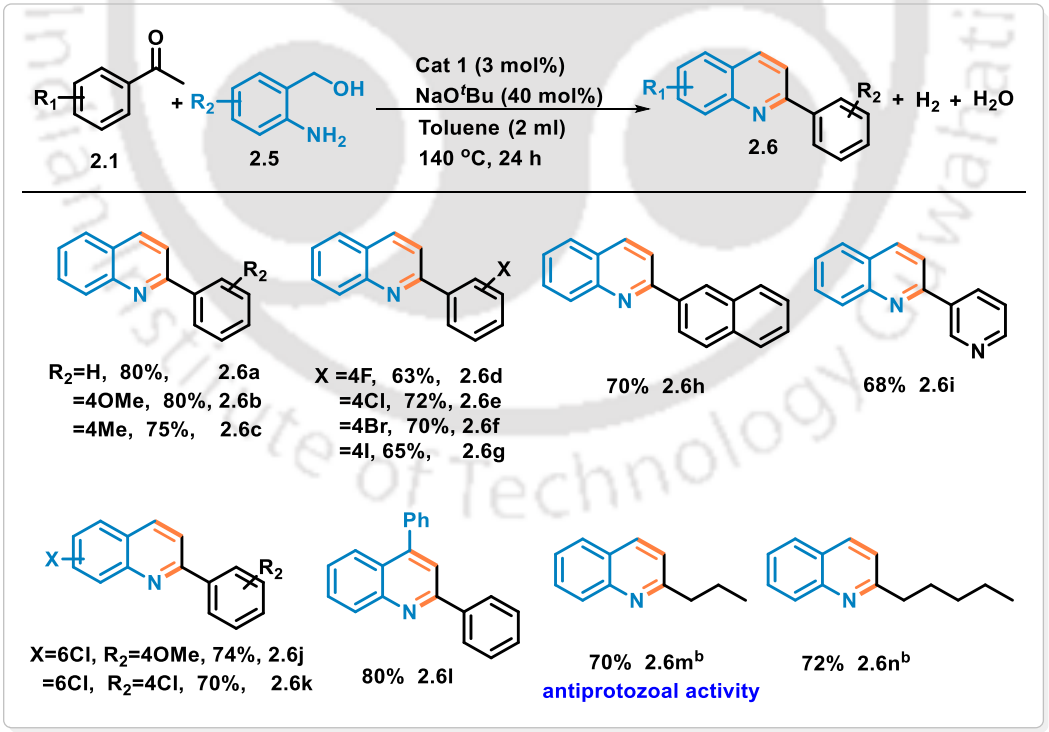
In addition, a gram scale synthesis was also conducted in order to find the efficiency of the present protocol. Delightfully, the reaction afforded excellent yield (78%) of the desired product in 5 mmol scale (83% in 0.5 mmol scale), thereby displaying excellent results in the form of green chemistry metrics making the overall system affordable and benign (Scheme **2.1**).



Scheme 2.1. Gram Scale Synthesis and Calculating Green Chemistry Metrics

Further, keeping the optimized conditions in hand, the coupling of 2-aminobenzyl alcohol and various acetophenones was then investigated. The reaction was observed to end up with the formation of the quinoline moiety, which displays itself as one of the most important heterocyclic moieties in organic chemistry.[26] During the reaction the hydrogen molecule liberation take place which was detected by Gas Chromatography. Various electron donating acetophenones and halogen substituted acetophenones were reacted with 2-aminobenzyl alcohols which afforded good to excellent yield of the desired products (table **2.4**, **2.6a - g**). In addition, napthophenone and 3-acetyl pyridine also worked well to afford good yields of the products (table **2.4**, **2.6h** & **i**). Moreover, chloro substituted 2-aminobenzyl alcohol and 2-aminobenzophenone were also found reacting smoothly with various acetophenone derivatives (table **2.4**, **2.6j** & **k**). Interestingly, 2-aminobenzyl alcohol reacts efficiently with aliphatic ketones (pentanone and heptanone) out of which **4m** serves as important medicinal activity (antiprotozoal activity) which proves the efficiency of the present catalytic protocol (table **2.4**, **2.6m** & **n**).

Table 2.4. Scope of Quinoline Synthesis[a]



[a]**Reaction Condition**: **1** (0.5 mmol), **5** (0.75 mmol), Cat **A** (3 mol%), NaO^{t}Bu (40 mol%), Toluene (2 mL), 140 °C, 24 h, Under argon. [b] 1 (aliphatic ketone 1 mmol)

Finally, particular emphasis was placed on examining the mechanistic insight for the C-alkylation of ketones. Time dependent kinetic experiments was also conducted for C-alkylation of ketone enolate which shows that the product formation was slow initially, however, after 12 h product formation increases rapidly (figure **2.3**). The reaction starts with initial dehydrogenation of alcohol to form the aldehyde (which was confirmed from the nmr). Only in the presence of base, **2.1b** was found to react with aldehyde to form α, β -unsaturated species. However, in the absence of base the reaction did not proceed which indicates that base plays an important role in the condensation step (table **2.5**, **5a**). When the reaction between **2.1b** and **2.2a** was stopped at 9 h and subjected to GC analysis, the α, β -unsaturated species was clearly detected in the reaction medium (table 2.5, **5b**).

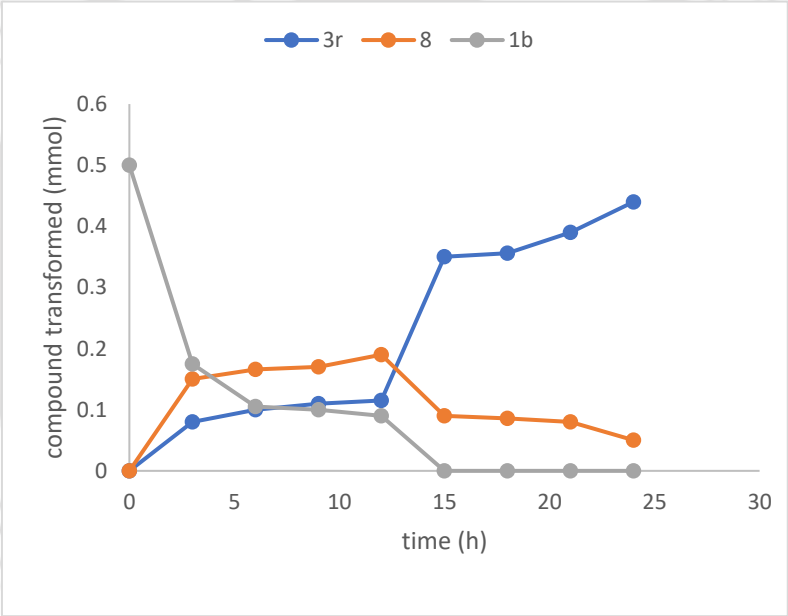
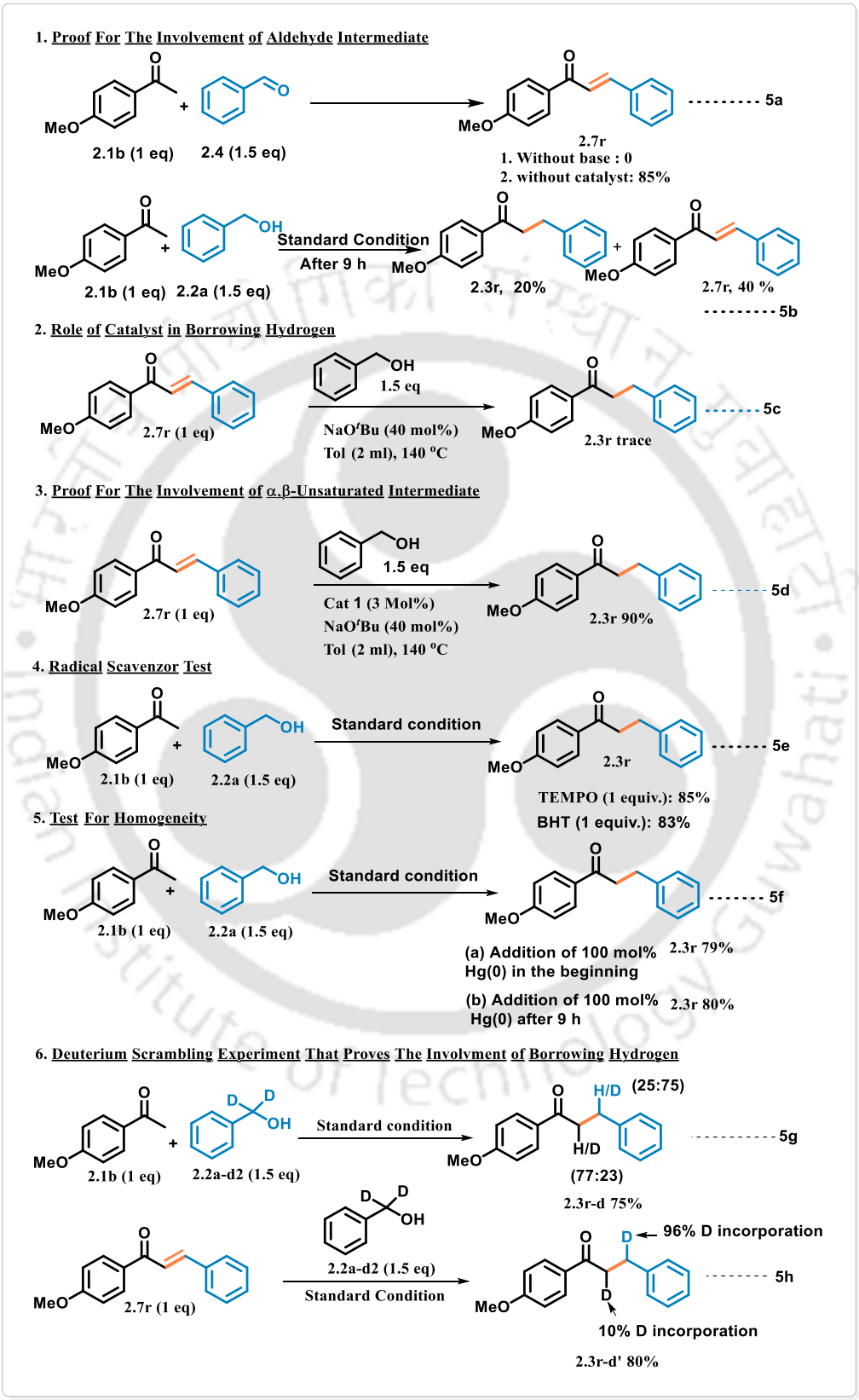


Figure 2.3. Kinetic Profile Diagram

Further, when the α, β -unsaturated species allowed to react with alcohol in the absence of catalyst and in the presence of base, trace amount of product was observed (table **2.5**, **5c**). However, in the presence of both catalyst and base, the α, β -unsaturated species do hydrogenate to give the saturated alkylated ketone which clears up the essential role of catalyst in hydrogen shuttling from dehydrogenation step to borrowing hydrogen step (table **2.5**, **5d**). Also, the involvement of the radical species in the reaction was ruled out after performing a reaction with a radical scavenger TEMPO furnishing 85% of the desired product (table **2.5**, **5e**). In addition, homogeneity test of the present catalytic system was also probed using Hg(0) poisoning test

Table 2.5. Table of Control Experiment



which has no detrimental effect in the yield of the product which conclude that no heterogeneous nature of the catalytic system was present (table **2.5**, **5f**). We also carried out deuterium labelled experiment to gain more insight on mechanism. Upon reaction of acetophenone with **2.2a-d2**, the incorporation of deuterium at α and β position is 23% and 75% respectively (table **2.5**, **5g**). Further, when α, β-unsaturated species is allowed to react with **2.2a-d2**, the deuterium incorporation in α and β position involves 10% and 96% respectively (table **2.5**, **5h**). It was observed that the deuterium incorporation in α-position is much higher than that in β position. From the literature reported earlier, depicts the involvement of borrowing hydrogen strategy, which may occur via monohydride mechanism in the present reaction system. [27] Finally, a reaction pathway is formulated as shown in **Figure 2.4** below according to which the alcohol upon conversion to corresponding aldehyde react with ketone enolate to give the α,β-unsaturated ketone. This upon borrowing hydrogenation results in the conversion to linear chain ketone.

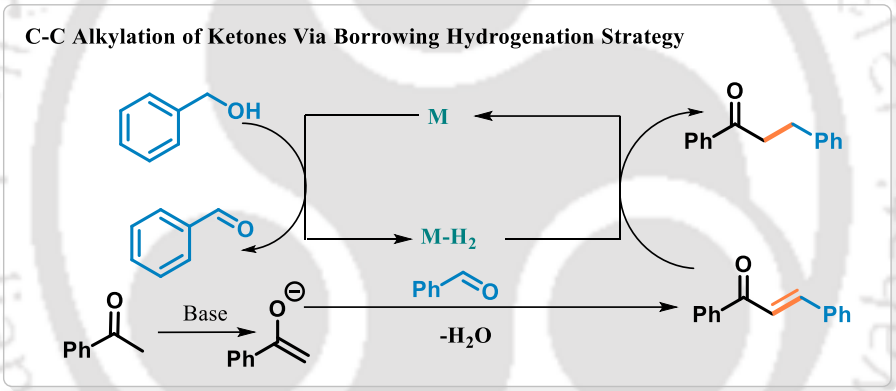


Figure 2.4: Reaction pathway for C-alkylation of methyl ketone

2.4. Conclusion:

In summary, the work presents the synthesis of sulphur based SNS-Ni complexes. Further, the catalysts were applied for the C-alkylation of ketone enolates via borrowing hydrogen strategy. The protocol demonstrates wide functional group tolerance in both ketone as well as benzyl alcohol counterparts. Structurally important triazole containing benzyl alcohol and direct lignocellulose derived cetyl alcohol also tolerates the present protocol. The catalytic system was further extended towards the synthesis of quinoline moieties. Various control experiments including deuterium labelled experiments were also conducted to support the BH pathway.

2.5. Experimental Section

2.5.1. General Considerations

Unless otherwise mentioned, all chemicals were purchased from common commercial sources and used as received. (4-(Allyloxy)phenyl)methanol,[28] 1-(4-(Phenylethynyl)phenyl)ethan-1-one[29] and (E)-1-(4-Styrylphenyl)ethan-1-one[30] were synthesised according to the literature reports. All solvents were dried by using standard procedure. All catalytic reactions were carried out under argon atmosphere using dried glassware and standard syringe/septa techniques. DRX-400 Varian spectrometer and Bruker Avance III 600, 500 and 400 spectrometers were used to record ^{1}H and ^{13}C NMR spectra using $CDCl_3$ as solvent and TMS as an internal standard. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (J) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dt = doublet of triplet, td = triplet of doublet and brs = broad singlet. X-ray crystallographic data were collected using BRUKER D8 VENTURE SC-XRD. Q-TOF ESI-MS instrument (model HAB 273) was used for recording mass spectra. SRL silica gel (100-200 mesh) was used for column chromatography.

2.5.2. Ligand Synthesis

Ligand [$(PyCH_2)HN(CH_2CH_2SR)$, R= Et, tBu] were synthesized according to the literature report.[31] The corresponding thiols (2.1 equiv.) was mixed with MeOH containing 2.2 equiv. of NaOH. Then 2,6-bis(bromomethyl)pyridine (1 equiv.) was added in one portion under stirring at room temperature. The mixture was then heated to reflux and stirred overnight. After evaporation of the solvent, the resulting slurry was taken in diethylether and washed twice with a saturated aqueous solution of $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent gave the ligands as colorless or slightly yellow oils in typical yields of about 90% and used without further purification.

2.5.3. Complex Preparation.

Ligand [$(Py(CH_2CH_2SR)2$, R= Et, tBu,] (1.2 mmol) was taken in 5 mL MeOH and was added dropwise to the orange suspension of [$NiBr_2$] (1.0 mmol) in 10 mL MeOH. Afterward, the suspension was refluxed for overnight under argon atmosphere. After the completion of the reaction, the reaction mixture was cooled down to the room temperature, then the solvent was

evaporated to obtain the residue, which was further washed with diethyl ether and dried under vacuum to get beautiful green solid of Ni-complexes.

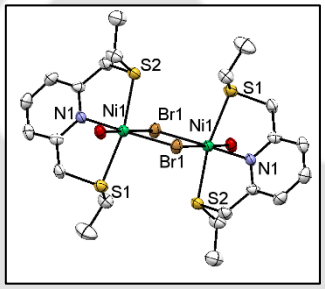
a) Yield=90%, HRMS data of Complex **A**: $C_{22}H_{38}Br_4N_2O_2S_4$:

HRMS (ESI) m/z: $[M - H_2O]^+$ $C_{11}H_{17}BrNNiS_2$: 363.9337; found 363.9369.

b) Yield=85%, HRMS data of Complex **B**:

$C_{15}H_{25}Br_2NNiS_2$: HRMS (ESI) m/z: $[M - Br]^+$ $C_{15}H_{25}BrNNiS_2$: 419.9963; found 419.9957.

2.5.4. Crystal Structure Data of Cat 1

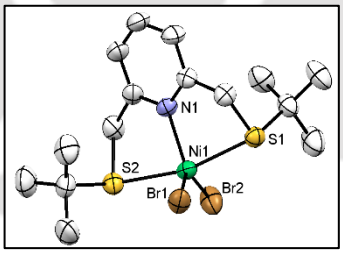


CCDC no: 2151043

Empirical formula	C22 H38 Br2 N2 Ni2 O2 S4, 2(Br)
Formula weight	463.92
Temperature, T	273 K
Crystal system	'Monoclinic'
Space group	C2/c
Unit cell dimensions	a=18.142(8)Å α=90° b=8.564(3)Å β=96.596(13)° c=20.690(7) Å γ=90°
Volume, V (Å3)	3193(2)
Density (calculated),	1.930
Absorption coefficient, μ (mm−1)	6.470
F(000)	1840.0
Theta range for data collection	2.77 to 24.67
Index ranges	-21 ≤ h ≤ 21, -10 ≤ k ≤ 10, -24 ≤ l ≤ 24
Reflections collected	3018
Independent reflections	2698
Completeness to theta	0.994
Absorption correction	Multi-scan
Max. and min. transmission	0.174 to 0.119
Refinement method	'SHELXL-97 (Sheldrick, 1997)'

Data / restraints / parameters	2698/0/166
Goodness-of-fit on F2	1.097
Final R indices [I>2sigma(I)]	R1= 0.0449 (1934), WR2 =0.0882 (2698)
R indices (all data)	R(reflections)= 0.0802, wR2(reflections)= 0.0768
Extinction coefficient	6.470
Largest diff. peak and hole	0.632 and -0.627 e·Å-3
Bond lengths [Å]	**Bond angles [°]**
Br1 Ni1 2.5209(12)	Ni1 Br1 Ni1 92.48(4)
Br1 Ni1 2.5831(13)	N1 Ni1 O1 91.39(19)
Ni1 N1 2.045(5)	N1 Ni1 S2 83.92(16)
Ni1 O1 2.100(4)	O1 Ni1 S2 95.02(13)
Ni1 S2 2.386(2)	N1 Ni1 S1 83.53(16)
Ni1 S1 2.446(2)	O1 Ni1 S1 84.26(13)
Ni1 Br1 2.5831(13)	S2 Ni1 S1 167.41(7)
S2 C9 1.792(7)	N1 Ni1 Br1 91.56(15)
S2 C10 1.811(7)	S2 Ni1 Br1 85.04(6)
S1 C3 1.803(7)	S1 Ni1 Br1 96.33(6)
S1 C2 1.806(7)	Br1 Ni1 Br1 87.52(4)

2.5.5. Crystal Data of Cat 2.

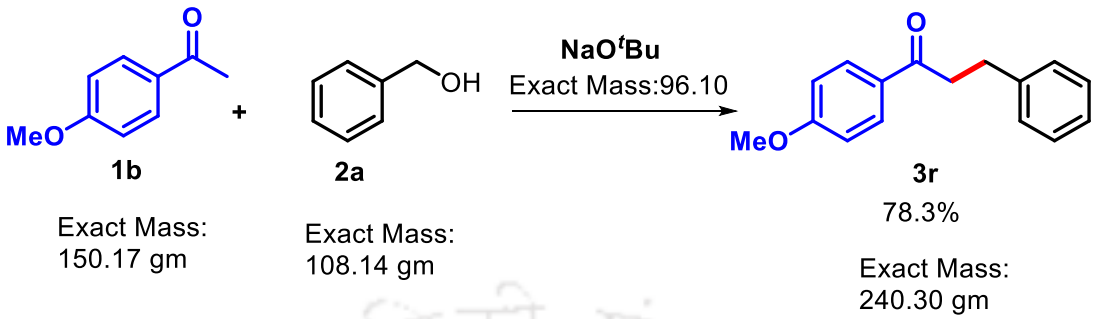


CCDC no: 2151069

Empirical formula	C16 H27 Br2 Cl2 N Ni S2
Formula weight	586.93
Temperature, T	273 K
Crystal system	'orthorhombic'
Space group	P b c n
Unit cell dimensions	a=17.457(6) Å α=90° b=16.532(6)Å β=90° c=16.352(6) Å γ=90°
Volume, V (Å3)	4719 (3)
Density (calculated)	1.652
Absorption coefficient, μ (mm−1)	4.613
F(000)	2352
Theta range for data collection	1.696 to 24.495
Index ranges	-20 ≤ h ≤ 20, -18 ≤ k ≤ 19, -19 ≤ l ≤ 19

Reflections collected	9310
Independent reflections	3919
Completeness to theta	0.999
Absorption correction	Multi-scan
Max. and min. transmission	0.174 to 0.119
Refinement method	'SHELXL-2018/3 (Sheldrick, 2018)'
Data / restraints / parameters	3919/0/223
Goodness-of-fit on F2	0.939
Final R indices [I>2sigma(I)]	R1= 0.0502(2940), WR2 = 0.1808(3919)
R indices (all data)	R(reflections)= 0.0817, wR2(reflections)= 0.1285
Extinction coefficient	4.613
Largest diff. peak and hole	0.923 and -0.762 e·Å-3
Bond lengths [Å]	**Bond angles [°]**
Br01 Ni1 2.4086(14)	N008 Ni1 Br02 120.49(18)
Br02 Ni1 2.4058(14)	N008 Ni1 Br01 106.55(18)
Ni1 N008 2.000(6)	Br02 Ni1 Br01 132.96(6)
Ni1 S004 2.479(2)	N008 Ni1 S004 82.89(19
Ni1 S005 2.504(2)	Br02 Ni1 S004 99.53(7)
S004 C00F 1.806(8)	Br01 Ni1 S004 86.09(6)
S004 C00A 1.855(9)	N008 Ni1 S005 83.01(19)
S005 C00C 1.801(9)	Br02 Ni1 S005 85.67(7)
S005 C00D 1.850(9)	Br01 Ni1 S005 100.17(7)
Cl2 C00O 1.719(19)	S004 Ni1 S005 165.71(8)

2.5.6. Calculation of Green Chemistry Metrics



Exact Mass: 150.17 gm

Exact Mass: 108.14 gm

Exact Mass: 240.30 gm

1b	2a	NaO^{t}Bu	Toluene	3r
0.751 gm	0.648 gm	0.170 gm	7.8 gm (9 mL)	0.940 gm

Total = 9.37 gm

E-factor: (9.37 - 0.940) ÷ 0.940 = 8.43 ÷ 0.940 = 8.96 kg waste/1kg product

Atom Economy: [240 ÷ (150.17+108.14)] × 100% = 93%

Atom Efficiency: 78.3 × (93 ÷ 100) = 72.8%

Carbon Efficiency: (16 ÷ 16) × 100% = 100%

Excess Reactant Factor: (Stoitiometric mass of reactant + exess mass of reactant) ÷ stoitiometric mass of reactant = [(0.751 + 0.540 +) 0.108)] ÷ 1.29 = 1.07

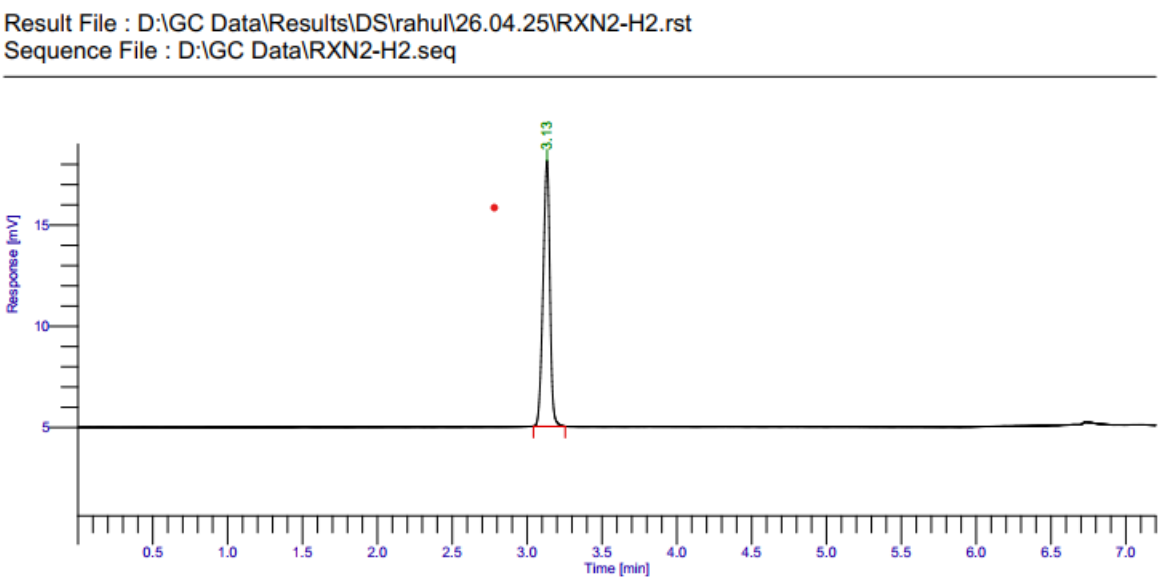
Reaction Mass Efficiency: [0.940 ÷ (0.751 + 0.648)] × 100 = 67.19%

2.5.7. General Experimental Procedure for the Synthesis of (4-((1-(4-Bromobenzyl)-1H-1,2,3-triazol-4yl)methoxy)phenyl)methanol (2.2am). (4-((1-(4-Bromobenzyl)-1H-1,2,3-triazol-4 yl)methoxy)phenyl)methanol was prepared according to the modified literature procedure.[32] To a mixture of CuI (5 mol%, 0.019 g) and CTAB (5 mol%, 0.036 g) was added (4-(prop-2-yn-1-yloxy)phenyl)methanol[33] (2.4 mmol, 0.389 g) and 1-(azidomethyl)-4-bromobenzene[34] (2 mmol, 0.424 g) in water (4 mL) and stirred at room temperature for 1 h. After completion of the reaction it was extracted with ethyl acetate and washed with brine, dried

over anhydrous sodium sulfate and concentrated under vacuum, which on column chromatography (ethyl acetate:hexanes) afforded the desired product in 70% yield. 1H NMR (600 MHz, Chloroform-d) δ 7.55 (s, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 5.49 (s, 2H), 5.19 (s, 2H), 4.63 (s, 2H). 13C{1H} NMR (150 MHz, CDCl3) δ 157.74, 144.82, 133.84, 133.45, 132.36, 129.74, 128.68, 123.04, 122.57, 114.84, 64.92, 62.09, 53.58. HRMS (ESI) m/z: $[M + H]^+$ C17H17BrN3O2 : 374.0504; found 375.0504.

2.5.8. General Experimental Procedure for the Alkylation of Acetophenone Derivatives. To an oven dried 100 mL Pressure tube, Acetophenones **2.1** (0.5 mmol), alcohols **2.2** (0.75 mmol), NaO^{t}Bu (40 mol%, 19 mg) and Cat **1** (3 mol%, 11.5 mg) were taken under argon atmosphere, after that 2 ml of toluene was added to the reaction mixture. The resulting mixture was heated in an oil bath at 140 °C for 24 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using hexane or 2%-10% ethyl acetate in hexane to get pure C-alkylated compound.

2.5.9. General Experimental Procedure for the Synthesis of Quinoline Moieties. To an oven dried 100 mL Pressure tube, Acetophenones **2.1** (0.5 mmol), 2-aminobenzyl alcohols **2.5** (0.75 mmol), NaO^{t}Bu (40 mol%, 19 mg) and Cat **1** (3 mol%, 11.5 mg) were taken under argon atmosphere, after that 2 mL of toluene was added to the reaction mixture. The resulting mixture was heated in an oil bath at 140 °C for 24 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using hexane or 2%-10% ethyl acetate in hexane to get pure quinoline. The reaction also involves the liberation of dehydrogenation molecule which was detected using GC.



2.5.10. Ni-Catalysed Hydrogenation of α, β -Unsaturated Ketone to Give Branched Ketone (2.3a). To an oven dried 100 mL Pressure tube, α, β -unsaturated ketone **2.7r** (0.5 mmol, 0.119 g), benzyl alcohol **2.2a** (0.75 mmol, 0.081 g), Cat **1** (3 mol%, 11.5 mg), NaO^{t}Bu (40 mol%, 19 mg) and 2 mL toluene were taken under argon atmosphere. Then the reaction mixture was kept for stirring at 130 °C in preheated oil bath. After 24 h, mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using 2-5% ethyl acetate in hexane as an eluting system to give the desired α-branched ketone product **2.3r** in 90% isolated yield. Later the same reaction was carried out in absence of catalyst, which delivered trace amount of the product.

2.5.11. Experiment Investigating Radical Possibility in the Reaction Mechanism. To an oven dried 100 mL Pressure tube, 4-methoxyacetophenone **2.1b** (0.5 mmol), benzyl alcohol **2.2a** (0.75 mmol, 0.081 g), Cat **1** (3 mol%, 11.5 mg) NaO^{t}Bu (40 mol%, 19 mg), TEMPO (1 equiv., 75 mg) or BHT (1 equiv., 110 mg) and 2 mL toluene were taken under argon atmosphere. Then the reaction mixture was kept for stirring at 130 °C in preheated oil bath. After 24 h, mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using 2-5% ethyl acetate in hexane as an eluting system to give the desired α-branched ketone product **2.3r** in 85% or 83% isolated yield.

2.5.12. Nickel Catalysed Alkylation of 4-Methoxy Acetophenone by Deuterated Alcohol (2.7r-d2). To an oven dried 100 mL pressure tube, 4-methoxy acetophenone **2.1b** (0.5 mmol), deuterated benzyl alcohol **2.2a-d2** (0.75 mmol, 0.082 g), NaO^{t}Bu (40 mol%, 19 mg) and Cat **1** (3 mol%, 11.5 mg) were taken, then 2 mL toluene was added under argon atmosphere. The resulting mixture was then placed into the preheated oil bath at 140 °C for 24 h under argon atmosphere. After completion the reaction cooled to room temperature, after that ethyl acetate was added to it and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture (0-2%) as eluent, % of **2.3r-d** was obtained with 75% deuterium incorporation in β position and 23% deuterium incorporation in α position. The percentage of deuterium incorporation was analysed using 1H NMR spectroscopy.

2.5.13. Nickel Catalysed Hydrogenation of Intermediate with Deuterated Alcohol (5a-d2). To an oven dried 100 mL pressure tube, α, β-unsaturated ketone **2.7r** (0.5 mmol, 0.119 g), deuterated benzyl alcohol **2.2a-d2** (0.75 mmol, 0.082 g), NaO^{t}Bu (40 mol%, 19 mg) and Cat **A** (3 mol%, 11.5 mg) were taken, then 2 mL toluene was added under argon atmosphere. The resulting mixture was then placed into the preheated oil bath at 140 °C for 24 h under argon atmosphere. After completion the reaction cooled to room temperature, after that ethyl acetate was added to it and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture (0-2%) as eluent, 80% of 3r-d' was obtained with 96% deuterium incorporation in β position and 10% deuterium incorporation in α position. The percentage of deuterium incorporation was analyzed using ^{1}HNMR spectroscopy.

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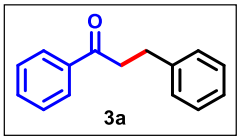
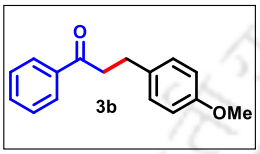
2.7. Characterization Data of Compounds:

1,3-Diphenylpropan-1-one (**2.3a**)



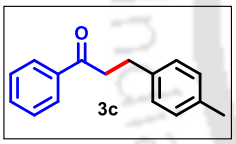
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 50:1). 83% Yield, 0.087 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.99 (d, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 3.7 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 3.37 – 3.30 (t, *J* = 7.7 Hz, 2H), 3.10 (t, *J* = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.2, 141.3, 136.9, 133.0, 128.6, 128.5, 128.4, 128.0, 126.1, 77.3, 77.0, 76.7, 40.4, 30.2.

3-(4-Methoxyphenyl)-1-phenylpropan-1-one (**2.3b**)



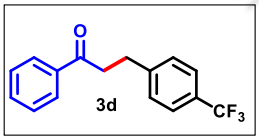
Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 25:1). 80% Yield, 0.096 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.98 (d, *J* = 7.0 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.81 (s, 1H), 3.30 (t, *J* = 7.7 Hz, 1H), 3.04 (t, *J* = 7.7 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 199.4, 158.0, 136.92, 133.3, 133.1, 129.4, 128.6, 128.1, 113.9, 55.3, 40.7, 29.3.

1-Phenyl-3-(p-tolyl)propan-1-one (**2.3c**)



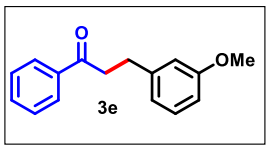
Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 40:1). 82% Yield, 0.091 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.00 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.16 (d, *J* = 7.3 Hz, 2H), 3.32 (t, *J* = 7.9 Hz, 2H), 3.08 (t, *J* = 7.9 Hz, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 199.38, 138.23, 136.92, 135.66, 133.07, 129.25, 128.63, 128.34, 128.08, 40.65, 29.75, 21.05.

1-Phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**2.3d**)



Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 40:1). 63% Yield, 0.087 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.53 – 7.57 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 3.32 (t, *J* = 7.5 Hz, 1H), 3.13 (t, *J* = 7.5 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 198.6, 145.5, 136.7, 133.3, 128.8, 128.7 128.5 (q, *J* = 32.41 Hz), 128.02, 125.4 (q, *J* = 3.76 Hz), 124.3 (q, *J* = 270.25 Hz), 39.84, 29.78.

3-(3-Methoxyphenyl)-1-phenylpropan-1-one (**2.3e**)

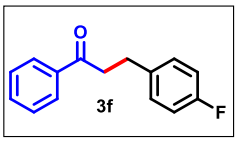


Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 30:1). 72% Yield, 0.086 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H),

6.83 (bs, 1H), 6.78 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.83 (s, 1H), 3.33 (t, *J* = 7.9 Hz, 2H), 3.08 (t, *J* = 7.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 199.2, 159.8, 142.9, 136. 9, 133.1, 129.5, 128.6, 128.0, 120. 8, 114.3, 111.4, 55.2, 40.4, 30.2.

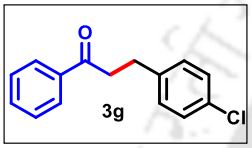
3-(4-Fluorophenyl)-1-phenylpropan-1-one (**2.3f**)

Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 50:1). 80% Yield, 0.091 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.98 (dt, *J* = 7.0, 1.4 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.22 (m, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 3.31 (t, *J* = 7.5 Hz, 2H), 3.07 (t, *J* = 7.5 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 199.01, 161.4 (d, J = 243 Hz), 136.9, 133.1, 129.8 (d, J = 7.5 Hz), 128.6, 128.0, 115.3, 115.2, 40.4, 29.3.



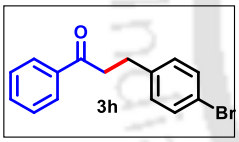
3-(4-Chlorophenyl)-1-phenylpropan-1-one (**2.3g**)

Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 50:1). 80% Yield, 0.096 g. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 1H), 3.04 (t, *J* = 7.5 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 198.84, 139.75, 136.81, 133.15, 131.90, 129.82, 128.64, 128.61, 128.01, 40.13, 29.40.



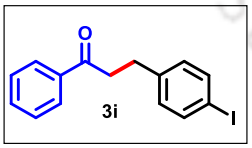
3-(4-Bromophenyl)-1-phenylpropan-1-one (**2.3h**)

Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 50:1). 77% Yield, 0.112 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 3.30 (t, *J* = 7.5 Hz, 2H), 3.06 (t, *J* = 7.5 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 198.8, 140.3, 136. 8, 133.2, 131.6, 131.5, 130.2, 128.6, 128.0, 119.9, 40.1, 29.4.



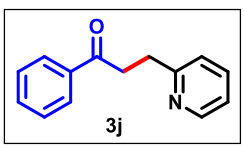
3-(4-Iodophenyl)-1-phenylpropan-1-one (**2.3i**)

Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 50:1). 72% Yield, 0.120 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.61 – 7.54 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 3.27 (t, *J* = 7.5 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 198. 8, 141.0 137. 6, 136.8, 133.2, 130.6, 128.6, 128.0, 91.2, 40.0, 29.5.

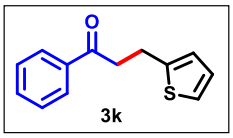


1-Phenyl-3-(pyridin-2-yl)propan-1-one (**2.3j**)

Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 10:1). 62% Yield, 0.066 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.54 (d, *J* = 4.3 Hz, 1H), 8.02 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.28 (m, 1H), 7.14 – 7.12 (m, 1H), 3.44 (t, *J* = 7.3 Hz, 2H), 3.17 (t, *J* = 7.3 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 199.3, 160.7, 149.2, 136.9, 136.4, 133.0, 128.5, 128.1, 123.4, 121.2, 37.8, 32.1.



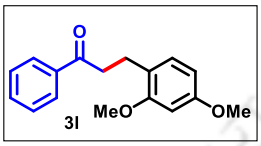
1-Phenyl-3-(thiophen-2-yl)propan-1-one (**2.3k**)



Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 30:1). 55% Yield, 0.059 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.00 (d, J = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 5.1 Hz, 1H), 6.94 – 6.94 (m, 1H), 6.90 – 6.89 (m, 1H), 3.39 (d, *J* = 7.1 Hz, 2H), 3.32 (d, J = 7.1 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 198.6, 143.9, 136.8, 133.2, 128.6, 128.0, 126.8, 124.7, 123.4, 40. 6, 24.2.

3-(2,4-Dimethoxyphenyl)-1-phenylpropan-1-one (**2.3l**)

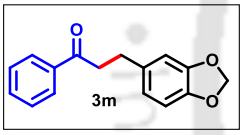
Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 10:1).



70% Yield, 0.094 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.00 (d, J = 7.3 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.48 (d, *J* = 2.5 Hz, 1H), 6.45 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.25 (t, *J* = 7.4 Hz, 2H), 3.01 (t, *J* = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 200.2, 159.5, 158.4, 137.0, 132.9, 130.3, 128.5, 128.1, 121.9, 103.9, 98.6, 55.4, 55.2, 39.2, 25.2.

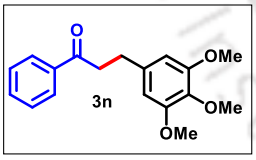
3-(Benzo[d][1,3]dioxol-5-yl)-1-phenylpropan-1-one (**2.3m**)

Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 10:1).



77% Yield, 0.097 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 6.77 – 6.71 (m, 3H), 5.94 (s, 2H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.02 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 199.2, 147.6, 145.9, 136.9, 135.1, 133.1, 128.6, 128.0, 121.2, 108.9, 108.3, 100.8, 40.7, 29.9.

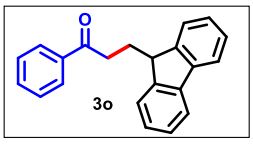
1-Phenyl-3-(3,4,5-trimethoxyphenyl)propan-1-one (**2.3n**)



Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 10:1). 72% Yield, 0.108 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 6.39 (s, 1H), 3.77 (s, 6H), 3.75 (s, 3H), 3.32 (t, *J* = 7.5 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 199.3, 153.3, 137.1, 136.9, 136.5, 133.1, 128.6, 128.6, 128.0, 105.5, 60.8, 56.1, 56.1, 40.6, 30.6.

3-(9H-fluoren-9-yl)-1-phenylpropan-1-one (**2.3o**)

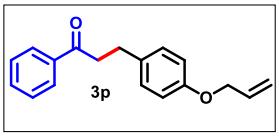
Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 50:1).



56% Yield, 0.083 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.20 (m, 4H), 4.07 (t, *J* = 4.9 Hz, 1H), 2.51– 2.48 (m, 2H), 2.44 – 2.41 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 200.2, 146.3, 141.4, 136.8, 132.9, 128.4, 127.9, 127.3, 127.1, 124.3, 119.9, 46.4, 33.3, 26.6.

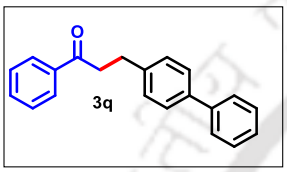
3-(4-(Allyloxy)phenyl)-1-phenylpropan-1-one (**2.3p**)

Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 50:1).



70% Yield, 0.093 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.10 – 5.99 (m, 1H), 5.40 (d, *J* = 17.3 Hz, 1H), 5.27 (d, *J* = 10.5 Hz, 1H), 4.51 (d, *J* = 5.3 Hz, 1H), 3.26 (t, *J* = 7.5 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.4, 157.1, 136.9, 133.5, 133.5, 133.0, 129.3, 128.6, 128.0, 117.5, 114.9, 68.9, 40. 7, 29.3.

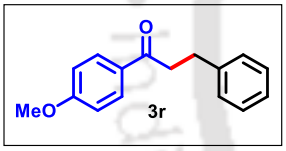
3-([1,1'-Biphenyl]-4-yl)-1-phenylpropan-1-one (**2.3q**)



Off white color oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 50:1). 71% Yield, 0.101 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.54 (m, 5H), 7.52 – 7.43 (m, 4H), 7.36 (m, 3H), 3.38 (t, *J* = 7.7 Hz, 2H), 3.15 (t, *J* = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 199.2, 141.0, 140.4, 139.2, 136.9, 133.1, 128.9, 128.7, 128.6, 128.1, 127.3, 127.1, 127.0, 40.4, 29.7.

1-(4-Methoxyphenyl)-3-phenylpropan-1-one (**2.3r**)

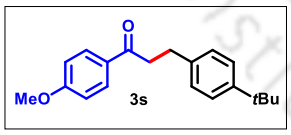
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 30:1).



83% Yield, 0.099 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.31 – 7.24 (m, 4H), 7.19 (t, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.25 (t, *J* = 7.5 Hz, 2H), 3.06 (t, *J* = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.8, 163.5, 141.5, 130.3, 130.1, 128.5, 128.4, 126.1, 113.7, 55.4, 40.1, 30.4.

3-(4-(Tert-butyl)phenyl)-1-(4-methoxyphenyl)propan-1-one (**2.3s**)

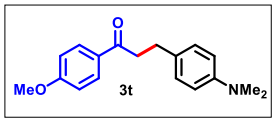
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 30:1).



70% Yield, 0.103 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 3H), 3.24 (t, *J* = 7.5 Hz, 2H), 3.02 (t, *J* = 7.5 Hz, 2H), 1.31 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.9, 163.5, 148.9, 138.4, 130.3, 130.1, 128.1, 125.4, 113.7, 55.4, 40.1, 34.4, 31.4, 29.8.

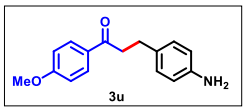
3-(4-(Dimethylamino)phenyl)-1-(4-methoxyphenyl)propan-1-one (**2.3t**)

Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



71% Yield, 0.100 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H), 3.23 (t, *J* = 7.5 Hz, 2H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.94 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 198.3, 163.4, 149.2, 130.3, 130.1, 129.5, 129.0, 113.7, 113.1, 55.5, 40.9, 40.6, 29.5.

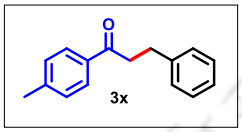
3-(4-aminophenyl)-1-(4-methoxyphenyl)propan-1-one (**2.3u**)



Brown oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 3:1). 65% Yield, 0.083 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 8.3 Hz, 2H), 3.85 (s, 3H), 3.58 (s, 2H), 3.18 (t, *J* = 7.4 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.3, 163.4, 144.5, 131.4, 130.3, 130.1, 129.2, 115.4, 113.7, 55.5, 40.5, 29.6. HRMS (ESI) m/z: $[M+H]^+$ $C_{16}H_{18}NO$: 256.1338; found 256.1350.

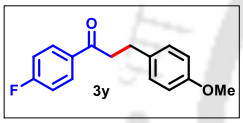
3-Phenyl-1-(p-tolyl)propan-1-one (**2.3x**)

Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 50:1).



75% Yield, 0.084 g. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.18 (m, 7H), 3.28 (t, *J* = 7.3 Hz, 2H), 3.06 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.9, 143.8, 141.4, 134.5, 129.3, 128.5, 128.4, 128.2, 126.1, 40.3, 30.2, 21.6.

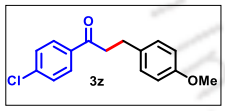
1-(4-Fluorophenyl)-3-(4-methoxyphenyl)propan-1-one (**2.3y**)



Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 30:1). 65% Yield, 0.084 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.98 – 7.95 (m, 2H), 7.16 – 7.09 (m, 4H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 3.23 (t, *J* = 7.7 Hz, 2H), 3.00 (t, *J* = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 197.81, 165.7 (d, *J* = 253.5 Hz), 158.04, 133.16, 130.7 (d, J = 9.3 Hz), 129.36, 115.7 (d, J = 21.9 Hz) 113.97, 55.29, 40.65, 29.27.

1-(4-Chlorophenyl)-3-(4-methoxyphenyl)propan-1-one (**2.3z**)

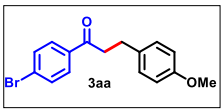
Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 30:1).



84% Yield, 0.115 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.23 (m, 3H), 3.30 (t, *J* = 7.7 Hz, 2H), 3.10 (t, *J* = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 198.0, 141.1, 139.5, 135.2, 129.49, 128.9, 128.6, 128.4, 126.3, 40.4, 30.1.

1-(4-Bromophenyl)-3-(4-methoxyphenyl)propan-1-one (**2.3aa**)

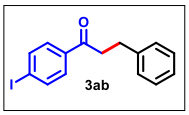
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 30:1).



75% Yield, 0.119 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 3.22 (t, *J* = 7.6 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.3, 158.1, 135.7, 133.1, 131.9, 129.5, 129.3, 128.1, 114.0, 55.3, 40.6, 29.2.

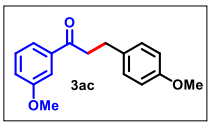
1-(4-Iodophenyl)-3-phenylpropan-1-one (**2.3ab**)

Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 50:1).



78% Yield, 0.126 g. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.19 (m, 5H), 3.25 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.5, 141.0, 137.9, 136.1, 129.5, 128.6, 128.4, 126.2, 100.9, 40.4, 30.0.

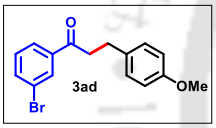
1-(3-Methoxyphenyl)-3-(4-methoxyphenyl)propan-1-one (**2.3ac**)



Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 10:1). 85% Yield, 0.114 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.47 (m, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.09 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 3.25 (t, *J* = 7.6 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.2, 159.9, 158.0, 138.3, 133.3, 129.6, 129.3, 120.7, 119.5, 113.9, 112.3, 55.4, 55.3, 40.8, 29.4.

1-(3-Bromophenyl)-3-(4-methoxyphenyl)propan-1-one (**2.3ad**)

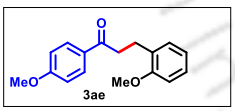
Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



73% Yield, 0.116 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.99 (s, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 6.78 – 6.63 (m, 3H), 3.71 (s, 3H), 3.18 (t, J = 7.6 Hz, 2H), 2.95 (t, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.8, 140.9, 138.6, 135.9, 131.2, 130.2, 128.7, 128.6, 128.4, 126.5, 126.3, 123.0, 40.5, 30.0.

3-(2-Methoxyphenyl)-1-(4-methoxyphenyl)propan-1-one (**2.3ae**)

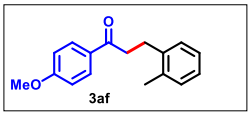
Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



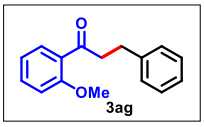
73% Yield, 0.116 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 2H), 6.95 – 6.88 (m, 4H), 3.89 (s, 3H), 3.86 (s, 3H), 3.23 (t, *J* = 7.4 Hz, 2H), 3.06 (t, *J* = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 198.7, 163.3, 157.5, 130.4, 130.2, 130.1, 129.7, 127.5, 120.5, 113.6, 110.2, 55.5, 55.2, 38.7, 25.9.

1-(4-Methoxyphenyl)-3-(o-tolyl)propan-1-one (**2.3af**)

Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).

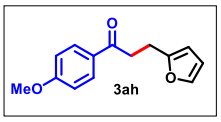


80% Yield, 0.101 g. ^{1}H NMR (500 MHz, Chloroform-D) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.19 – 7.11 (m, 4H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.19 (t, *J* = 7.3 Hz, 2H), 3.04 (t, *J* = 7.3 Hz, 2H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.0, 163.5, 139.6, 136.0, 130.4, 130.3, 130.1, 128.8, 126.3, 126.2, 113.8, 55.5, 38.8, 27.8, 19.4.

1-(2-Methoxyphenyl)-3-phenylpropan-1-one (**2.3ag**) Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 40% Yield, 0.050 g. 

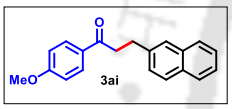
^{1}H NMR (600 MHz, Chloroform-d) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.21 (m, 5H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 3.33 (t, *J* = 7.7 Hz, 2H), 3.05 (t, *J* = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.8, 140.9, 138.6, 135.9, 131.2, 130.2, 128.7, 128.6, 128.4, 126.5, 126.3, 123.0, 55.5, 40.5, 29.9.

3-(Furan-2-yl)-1-(4-methoxyphenyl)propan-1-one (**2.3ah**)

Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 

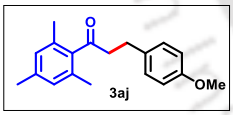
55% Yield, 0.063 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.98 (d, *J* = 8.8 Hz, 2H), 7.33 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.31 – 6.30 (m, 1H), 6.07 (d, *J* = 3.1 Hz, 1H), 3.89 (s, 3H), 3.31 (t, *J* = 7.6 Hz, 2H), 3.10 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 197.3, 163.5, 154.9, 141.1, 130.3, 129.9, 113.8, 110.2, 105.3, 55.5, 36.6, 22.7.

1-(4-Methoxyphenyl)-3-(naphthalen-2-yl)propan-1-one (**2.3ai**)

White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 

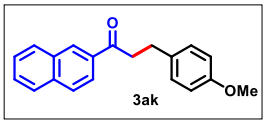
85% Yield, 0.123 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.80 – 7.69 (m, 2H), 7.68 (s, 1H), 7.46 – 7.38 (m, 3H), 6.92 (d, *J* = 8.5 Hz, 2H), 3.85 (s, 3H), 3.33 (t, *J* = 7.6 Hz, 2H), 3.22 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.0, 158.7, 134.2, 128.9, 127.4, 125.6, 125.3, 123.3, 122.9, 122.7, 122.5, 121.7, 121.2, 120.5, 109.0, 50.7, 35.3, 25.8.

1-Mesityl-3-(4-methoxyphenyl)propan-1-one (**2.3aj**)

Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 

85% Yield, 0.123 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.17 (d, *J* = 8.5 Hz, 2H), 6.85 – 6.83 (m, 4H), 3.81 (s, 3H), 3.00 (s, 4H), 2.29 (s, 3H), 2.14 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 209.9, 157.9, 139.5, 138.3, 133.0, 132.6, 129.4, 128.5, 113.9, 55.3, 46.6, 29.7, 28.6, 21.0, 19.0. HRMS (ESI) m/z: [M+Na]+ $C_{19}H_{22}NaO_2$: 305.1517; found 305.1513.

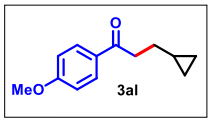
3-(4-Methoxyphenyl)-1-(naphthalen-2-yl)propan-1-one (**2.3ak**)

White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 

70% Yield, 0.101 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.48 (s, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.92 – 7.89 (m, 2H), 7.63 – 7.56 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 3.81 (s, 3H), 3.43 (t, *J* = 7.7 Hz, 2H), 3.10 (t, *J* = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 199.4, 158.0, 135.6, 134.2, 133.4, 132.5, 129.7, 129.6, 129.4, 128.5, 128.4, 127.8, 126. 8, 123.9, 113.9, 55.3, 40.9, 29.5.

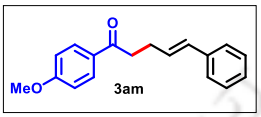
3-Cyclopropyl-1-(4-methoxyphenyl)propan-1-one (**2.3al**)

White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 74% Yield, 0.071 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.95 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 3H), 3.02 (t, *J* = 7.4 Hz, 2H), 1.65 – 1.60 (m, 2H), 0.80 – 0.73 (m, 1H), 0.43 (d, *J* = 7.8 Hz, 2H), 0.072 (d, *J* = 4.6 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.1, 163.3, 130.3, 113.7, 55.4, 38.3, 29.8, 10.8, 4.6. HRMS (ESI) m/z: [M+H]+ $C_{13}H_{18}O_2$: 205.1229; found 205.1237.



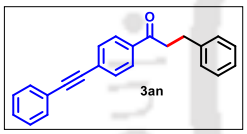
(E)-1-(4-Methoxyphenyl)-5-phenylpent-4-en-1-one (**2.3am**)

Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 35% Yield, 0.046 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.96 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.97 – 6.93 (m, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.29 (dt, *J* = 15.7, 6.9 Hz, 1H), 3.87 (d, *J* = 1.0 Hz, 2H), 3.10 (t, *J* = 7.4 Hz, 1H), 2.70 – 2.60 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.9, 163.5, 137.6, 130.7, 130.3, 130.1, 129.7, 128.5, 128.5, 128.4, 127.0, 126.0, 113.8, 55.5, 37.9, 27.7.



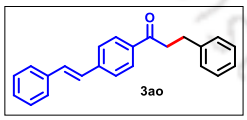
3-(4-Methoxyphenyl)-1-(4-(phenylethynyl)phenyl)propan-1-one (**2.3an**)

White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 70% Yield, 0.108 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.53 (m, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.35 (m, 3H), 7.31 – 7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 3.33 (t, *J* = 7.6 Hz, 2H), 3.10 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.4, 141.2, 135.9, 131.7, 131.7, 128.8, 128.6, 128.4, 128.4, 128.2, 128.0, 126.2, 122.7, 92.7, 88.6, 40.5, 30.1.



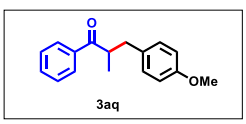
(E)-3-(4-Methoxyphenyl)-1-(4-styrylphenyl)propan-1-one (**2.3ao**)

White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 68% Yield, 0.106 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.24 (m, 6H), 7.15 (d, *J* = 16.3 Hz, 1H), 3.33 (t, *J* = 7.4 Hz, 2H), 3.11 (t, *J* = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 198.4, 141.2, 135.9, 131.7, 131.7, 128.8, 128. 6, 128.4, 128.4, 128.2, 128.0, 126.2, 122.7, 92.7, 88.6, 40.5, 30.1.



3-(4-methoxyphenyl)-2-methyl-1-phenylpropan-1-one (**2.3aq**)

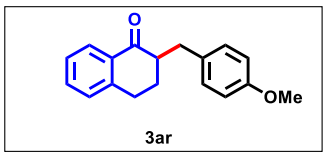
Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 35% Yield, 0.044 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.09 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 8.1 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 3.43 (dd, *J* = 13.9, 4.1 Hz, 1H), 3.01 – 2.9 (m, 2H), 2.75 – 2.70 (m, 1H), 2.67 – 2.63 (m, 1H), 2.16 – 2.11 (m, 1H), 1.84 – 1.77 (m, 1H). ^{13}C{^{1}H} NMR (125



MHz, $CDCl_3$) δ 199.5, 158.1, 144.0, 133.2, 132.5, 132.0, 130.2, 128.7, 127.5, 126.6, 113.8, 55.3, 49.6, 34. 8, 28.6, 27.6.

2-(4-methoxybenzyl)-3,4-dihydronaphthalen-1(2H)-one (**2.3ar**)

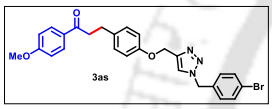
Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



40% Yield, 0.053 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.85 (d, J = 7.2 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.7 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 3.70 (s, 3H), 3.63 (p, J = 6.9 Hz, 1H), 3.03 (dd, J = 13.8, 6.4 Hz, 1H), 2.56 (dd, J = 13.8, 7.7 Hz, 1H), 1.12 (d, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 203.9, 158.0, 136.6, 132.9, 132.0, 130.0, 128.6, 128.3, 113.8, 55.2, 43.0, 38.5, 17.3.

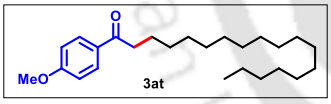
3-(4-((1-(4-Bromobenzyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)-1-(4-methoxyphenyl)propan-1-one (**2.3as**)

White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 60% Yield, 0.151 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.56 – 7.50 (m, 3H), 7.17 (dd, *J* = 8.16, 2.46 Hz, 4H), 6.95 – 6.90 (m, 4H), 5.50 (s, 2H), 5.18 (s, 2H), 3.88 (s, 3H), 3.23 (t, *J* = 7.6 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 197.9, 163.5, 156. 6, 145.0, 134.2, 133.5, 132.3, 130.3, 129.9, 129.7, 129.4, 123.0, 122.5, 114.8, 113.7, 62.2, 55.5, 53.5, 40.2, 29.4. HRMS (ESI) m/z: [M + K]+ C11H17BrNNiS2: 544.0638; found 544.0670.



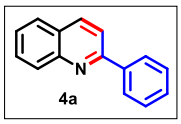
1-(4-methoxyphenyl)octadecan-1-one (**2.3at**)

White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 60:1). 29% Yield, 0.054 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.97 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 2.95 – 2.90 (m, 2H), 1.74 (p, *J* = 7.5 Hz, 2H), 1.28 (s, 27H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 199.32, 163.30, 130.33, 130.23, 113.67, 55.46, 38.35, 31.94, 29.71, 29.70, 29.68, 29.65, 29.54, 29.52, 29.47, 29.38, 24.68, 22.71, 14.14.



2-Phenylquinoline (**2.6a**)

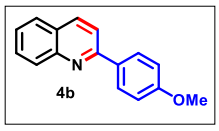
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



80% Yield, 0.082 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.25 (d, *J* = 8.6 Hz, 1H), 8.20 (t, *J* = 7.8 Hz, 3H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.1 Hz, 3H), 7.50 (t, *J* = 7.1 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 157.4, 148.3, 139.7, 136.8, 129.8, 129.7, 129.3, 128.9, 127.6, 127.5, 127.2, 126.3, 119.0.

2-(4-Methoxyphenyl)quinoline (**2.6b**)

White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).

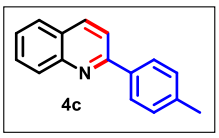


80% Yield, 0.094 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.18 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 3H), 7.84 – 7.79 (m, 2H), 7.72 – 7.69 (m, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR

(125 MHz, $CDCl_3$) δ 160.8, 156.9, 148.3, 136.6, 132.3, 129.6, 129.5, 128.9, 127.4, 126.9, 125.9, 118.6, 114.2, 55.4

2-(p-Tolyl)quinoline (**2.6c**)

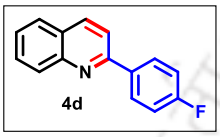
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



75% Yield, 0.082 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.20 – 8.15 (m, 2H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 2H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.4, 148.3, 139.4, 136.9, 136.6, 129.7, 129.6, 127.5, 127.4, 127.1, 126.1, 118.9, 21.3.

2-(4-Fluorophenyl)quinoline (**2.6d**)

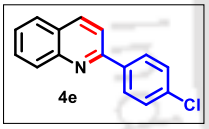
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



63% Yield, 0.070 g. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.22 (d, *J* = 8.6 Hz, 1H), 8.16 (m, 3H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.73 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 8.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.8 (d, *J* = 247.2 Hz), 156.26, 148.25, 136.92, 135.86, 129.80, 129.67, 129.4 (d, *J* = 8.5 Hz), 127.48, 127.10, 126.36, 118.63, 115.8 (d, *J* = 21.5 Hz).

2-(4-Chlorophenyl)quinoline (**2.6e**)

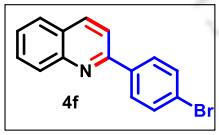
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



72% Yield, 0.082 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.22 (d, *J* = 8.6 Hz, 1H), 8.16 – 8.11 (m, 3H), 7.85 – 7.82 (m, 2H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.0, 148.3, 138.1, 136.9, 135.6, 129.8, 129.7, 129.0, 128.8, 127.5, 127.2, 126.5, 118.6.

2-(4-Bromophenyl)quinoline (**2.6f**)

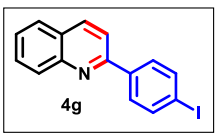
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



70% Yield, 0.099 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.25 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 2H), 7.86 (t, *J* = 8.04 Hz, 2H), 7.76 (t, *J* = 7.3 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 156.1, 148.3, 138.5, 137.0, 132.0, 129.9, 129.7, 129.1, 127.5, 127.3, 126.5, 123.9, 118.5.

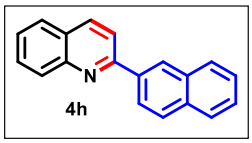
2-(4-Iodophenyl)quinoline (**2.6g**)

White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



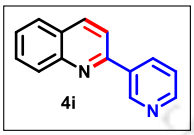
65% Yield, 0.104 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.22 (d, *J* = 8.6 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.93 – 7.82 (m, 6H), 7.73 (t, *J* = 8.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.2, 148.3, 139.1, 137.9, 136.9, 129.8, 129.7, 129.3, 127.5, 127.3, 126.5, 118.4, 95.8

2-(Naphthalen-2-yl)quinoline (**2.6h**)



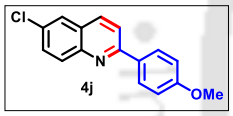
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 70% Yield, 0.089 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.64 (s, 1H), 8.40 (d, *J* = 8.5 Hz, 1H), 8.29 – 8.25 (m, 2H), 8.07 – 8.03 (m, 3H), 7.94 – 7.92 (m, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 7.1 Hz, 1H), 7.57 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 157.2, 148.3, 136.9, 136.9, 133.9, 133.5, 129.8, 129.7, 128.9, 128.6, 127.7, 127.5, 127.7, 127.2, 126.8, 126.4, 126.8, 125.1, 119.2.

2-(Pyridin-3-yl)quinoline (**2.6i**)



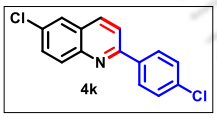
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 68% Yield, 0.070 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 9.36 (s, 1H), 8.70 (d, *J* = 4.6 Hz, 1H), 8.52 (d, *J* = 7.9 Hz, 1H), 8.27 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.76 (t, *J* = 8.3 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.46 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.6, 150.1, 148.7, 148.4, 137.2, 135.2, 135.1, 130.0, 129.8, 127.5, 127.4, 126.8, 123.7, 118.5.

6-Chloro-2-(4-methoxyphenyl)quinoline (**2.6j**)



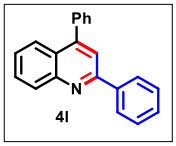
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 74% Yield, 0.097 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.12 (d, *J* = 8.8 Hz, 2H), 8.06 (t, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.62 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.1, 157.1, 146.7, 135.6, 131.8, 131.5, 131.1, 130.4, 128.9, 127.5, 126.1, 119.3, 114.3, 55.4.

6-Chloro-2-(4-chlorophenyl)quinoline (**2.6k**)



White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 70% Yield, 0.096 g ^{1}H NMR (600 MHz, Chloroform-d) δ 8.16 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.71 – 7.66 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 156.3, 146.6, 138.0, 136.1, 132.2, 132.1, 131.3, 130.8, 129.0, 127.8, 126.2, 124.2, 119.3.

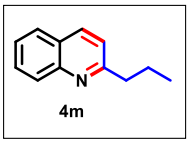
2,4-Diphenylquinoline (**2.6l**)



White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1). 80% Yield, 0.112 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.81 (s, 1H), 7.77 (t, *J* = 7.1 Hz, 1H), 7.59 – 7.50 (m, 8H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 155.6, 149.4, 148.8, 138.3, 138.1, 135.6, 130.1, 129.7, 129. 6, 129.0, 128.9, 128.7, 128.5, 126.6, 125.8, 125.7, 118.9.

2-Propylquinoline (**2.6m**)

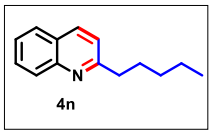
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



70% Yield, 0.060 g.^{1}H NMR (600 MHz, Chloroform-d) δ 8.08 (t, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 8.2, 1H), 7.70 (t, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 1.84 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.9, 147.9, 136.1, 129.3, 128.9, 127.5, 126.7, 125.6, 121.4, 41.3, 23.2, 13.9.

2-Pentylquinoline (**2.6n**)

Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 20:1).



72% Yield, 0.071 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.08 (t, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 2.99 (t, *J* = 7.8 Hz, 1H), 1.86 – 1.81 (m, 2H), 1.45 – 1.36 (m, 4H) 1.03 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 163.1, 147.9, 136.2, 129.3, 128.8, 127.5, 126.7, 125.6, 121.4, 39.4, 31.8, 29.8, 22.6, 14.0.

2.8. NMR Spectra of some representative compounds

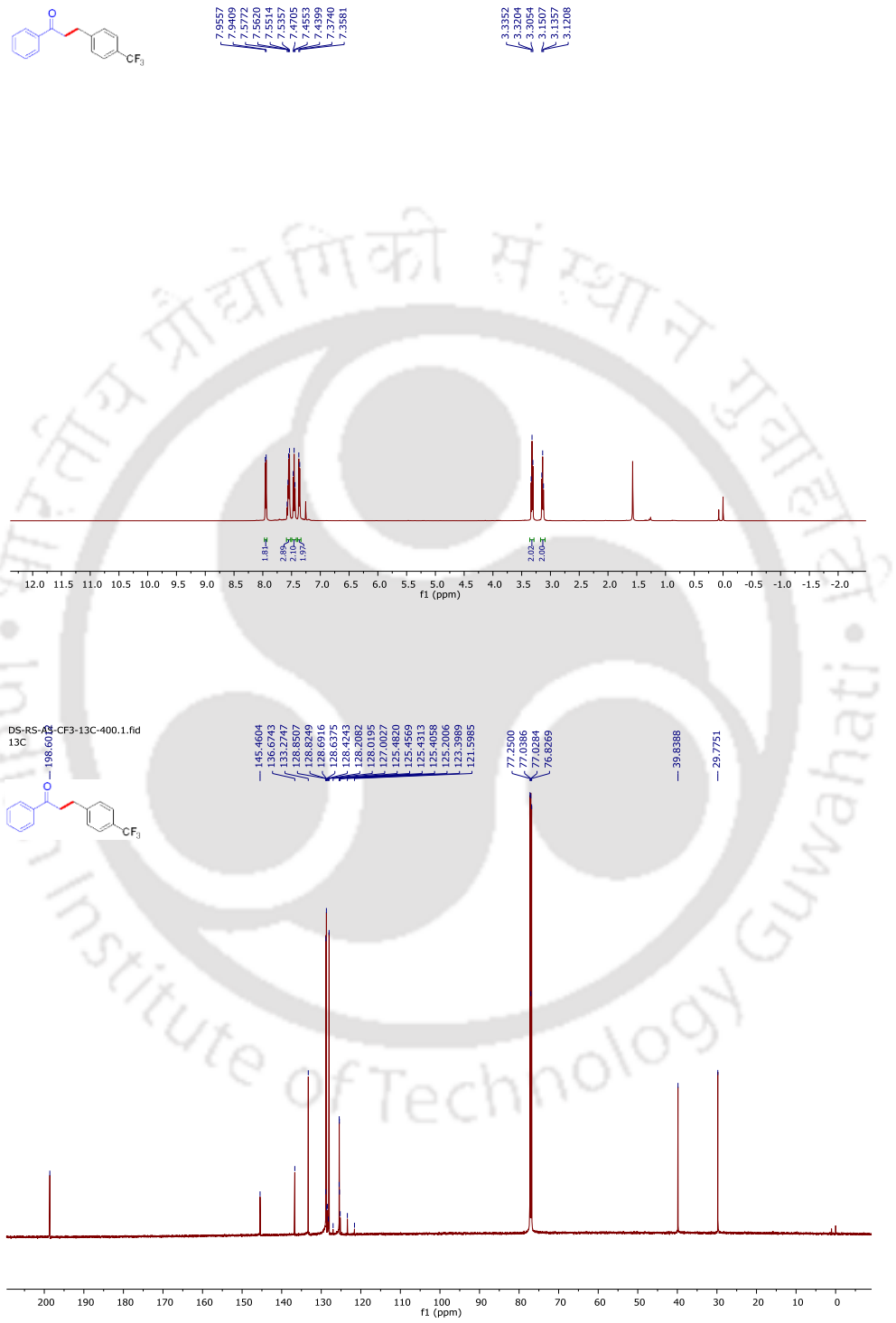


Fig S7: ^{1}H (500 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of 1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**3d**) in $CDCl_3$.

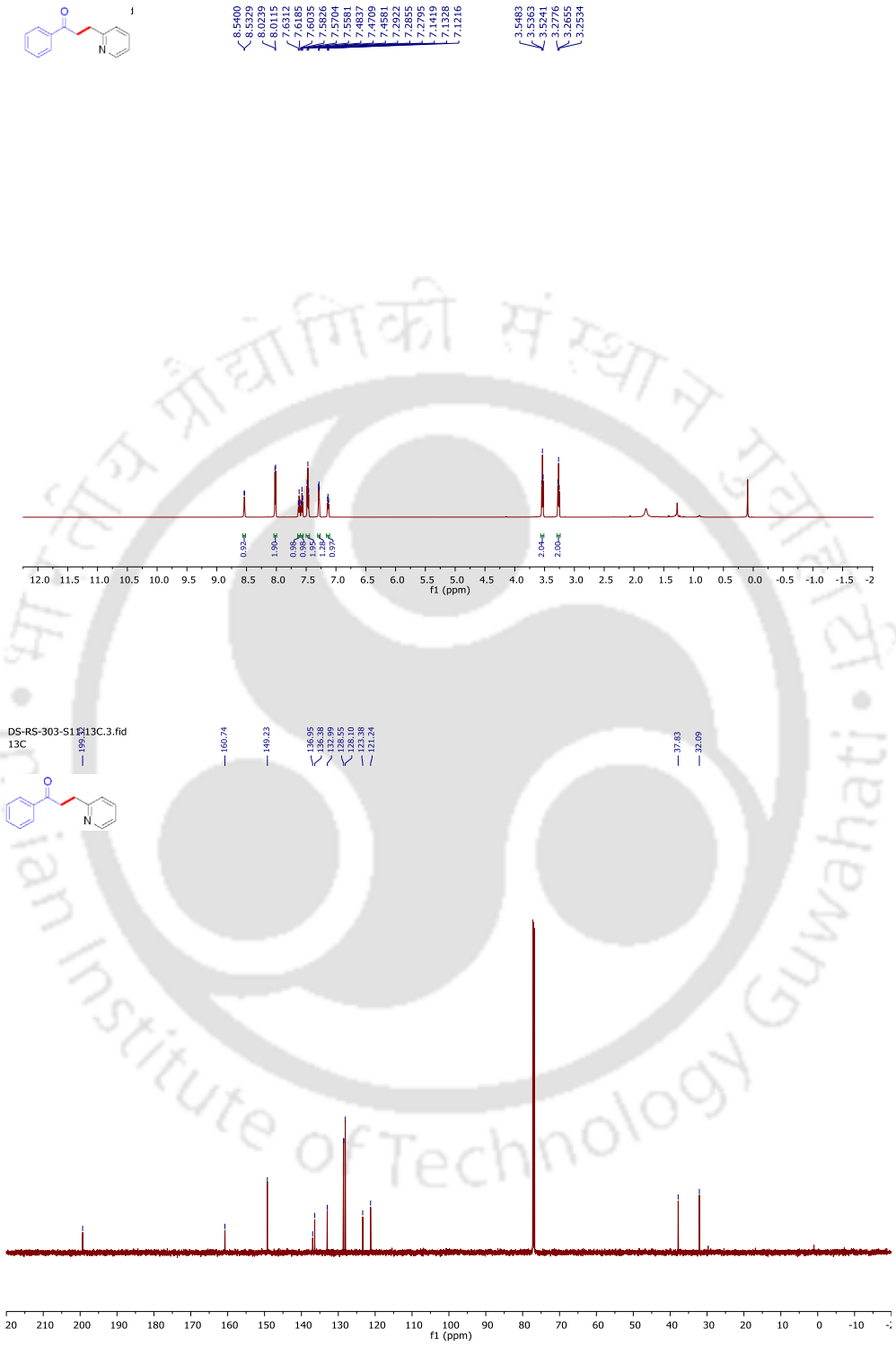


Fig S13: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of 1-phenyl-3-(pyridin-2-yl)propan-1-one (**3j**) in $CDCl_3$.

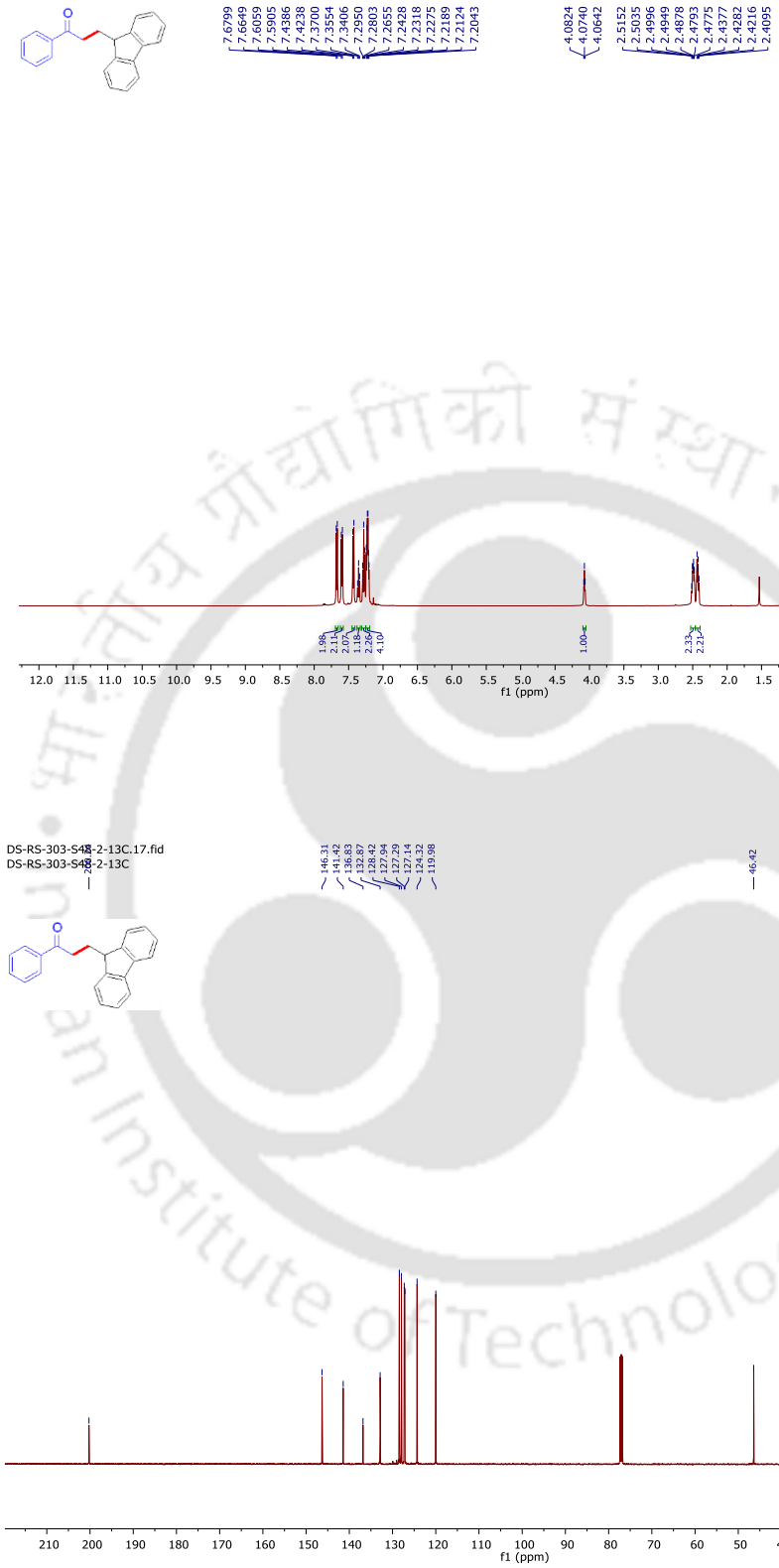


Fig S18: ^{1}H (500 MHz) & $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectra of 3-(9H-fluoren-9-yl)-1-phenylpropan-1-one (**3o**) in $CDCl_3$.

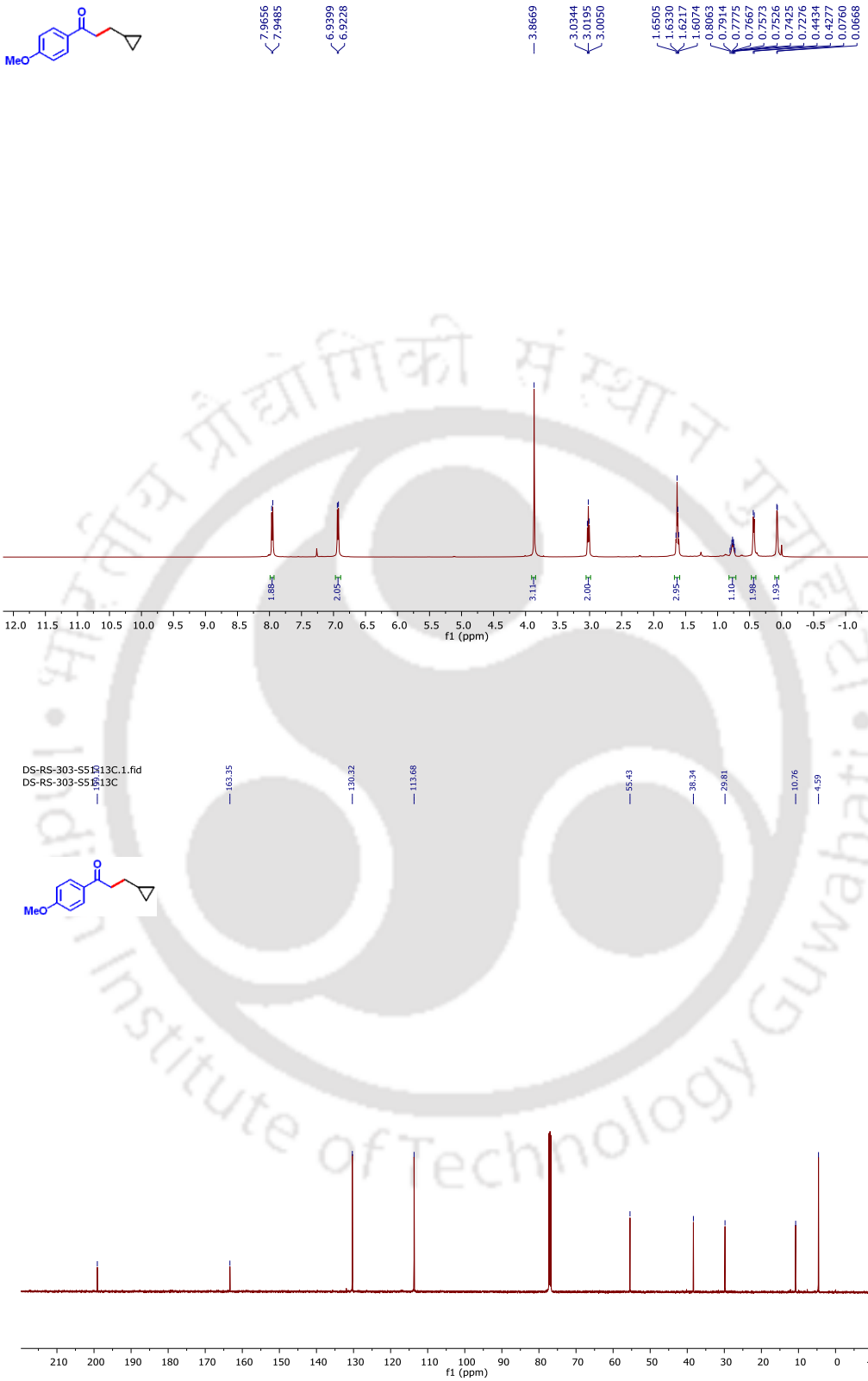


Fig S39: ^{1}H (500 MHz) & $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectra of 3-cyclopropyl-1-(4-methoxyphenyl)propan-1-one (**3al**) in $CDCl_3$.

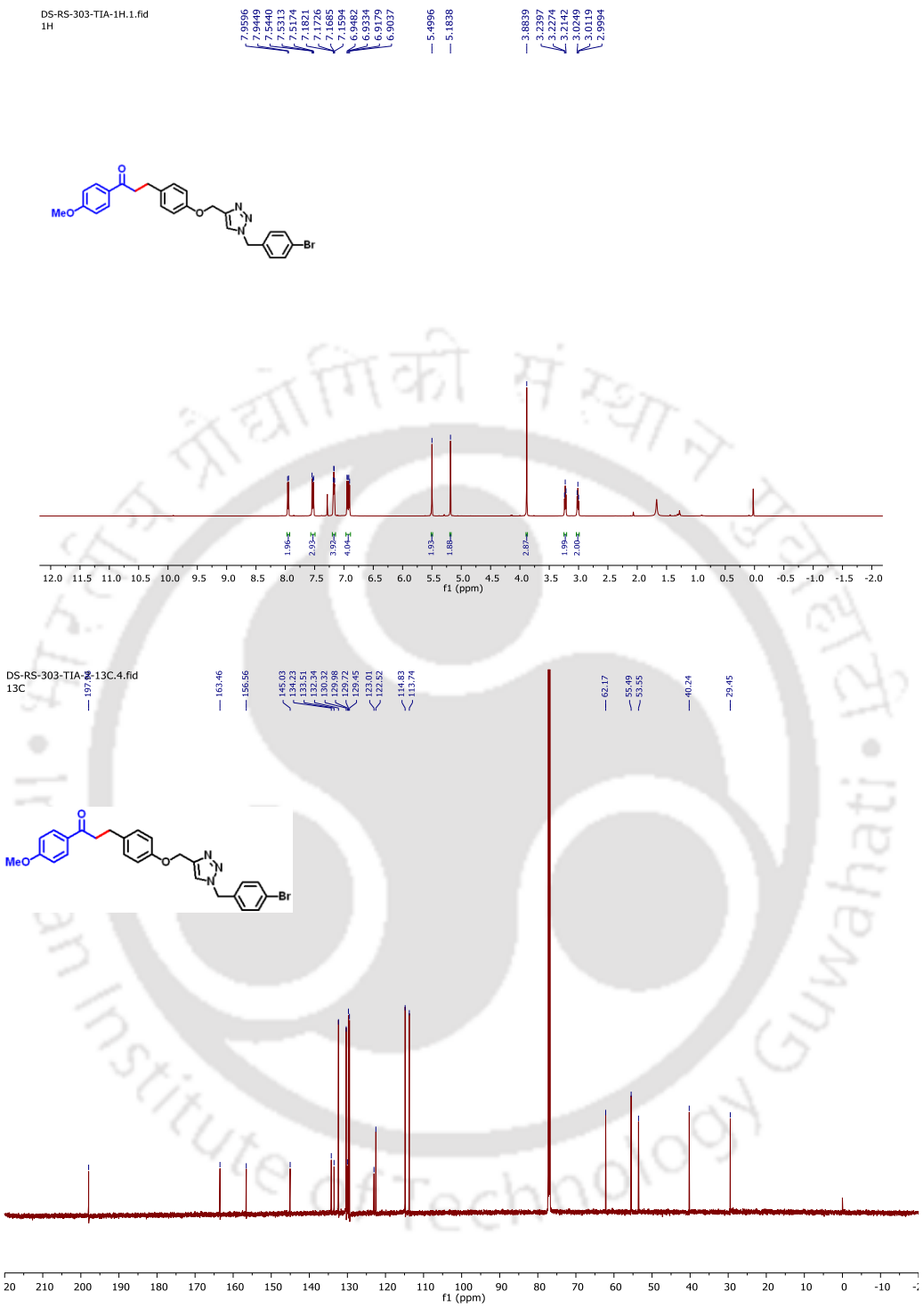


Fig S45: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of 3-(4-((1-(4-bromobenzyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)-1-(4-methoxyphenyl)propan-1-one (**3as**) in $CDCl_3$.

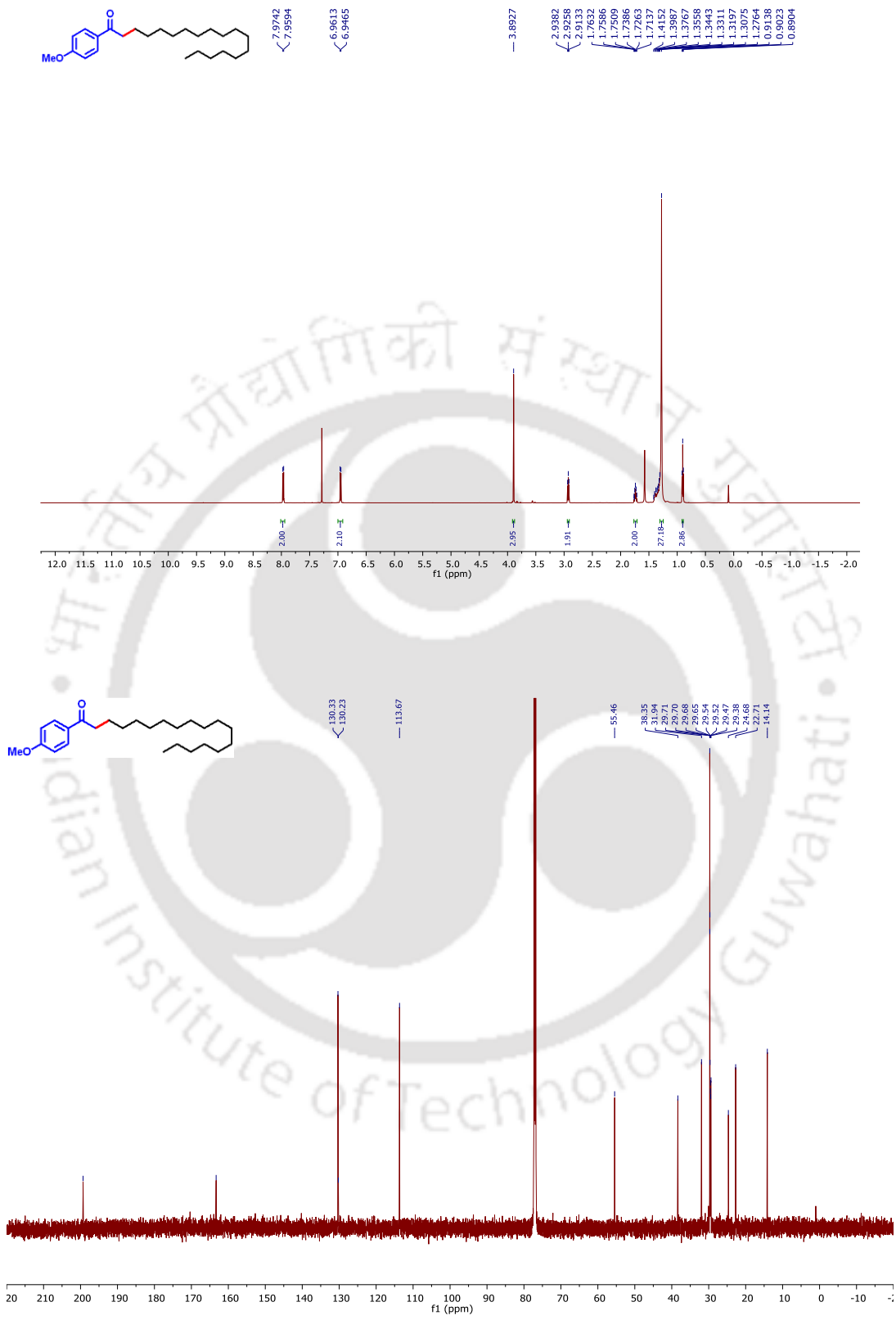
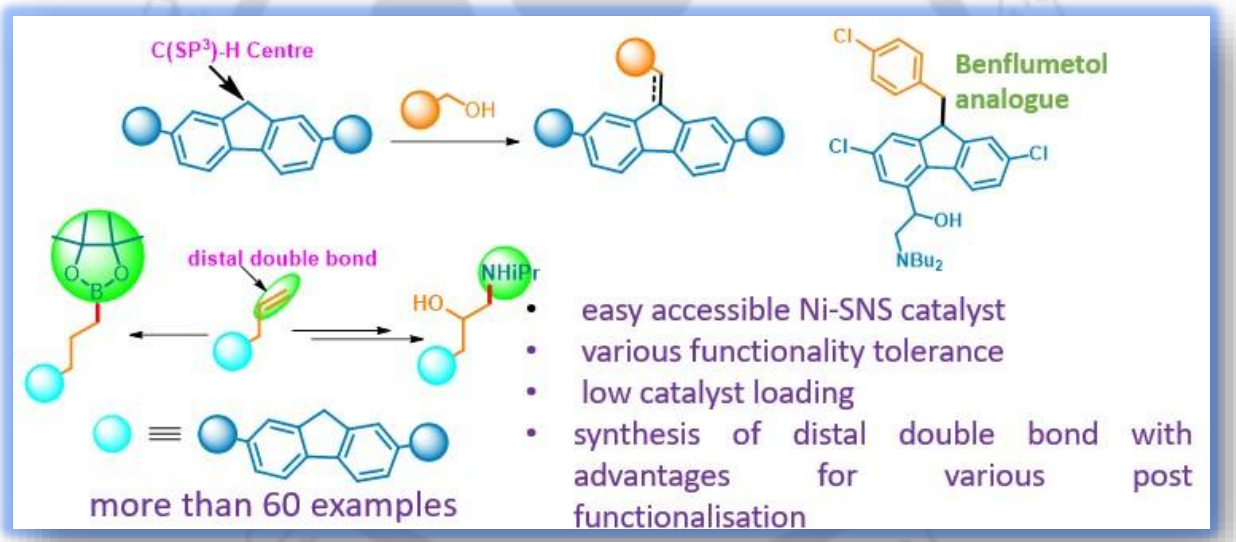


Fig S46: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of 1-(4-methoxyphenyl)octadecan-1-one (**3at**) in $CDCl_3$.

Chapter 3

A Strategic Approach for Csp3–H Functionalization of 9H-Fluorene: An Acceptorless Dehydrogenation and Borrowing Hydrogen Approach



3.1. Introduction:

This chapter discusses the application of SNS-Ni complex for the coupling of 9H-fluorene derivatives with alcohol derivatives. The protocol demonstrates high efficiency in the selective synthesis of alkylated and alkenylated in 9-position of fluorene derivatives. Moreover, the protocol also allows the installation of synthetically important unsaturated species. The details of the work will be discussed in the upcoming sections.

A major concern in the 21st century is the development of synthetic methods that can be implemented in a sustainable manner. The field of catalysis significantly contributed to resolving current scientific concerns.[1] One such prominent issue at the moment is the replacement of fossil fuel-based starting materials, which are widely used in organic synthesis for diverse chemical transformations.[2] Over the past few years, acceptorless dehydrogenation (AD) and the borrowing hydrogen (BH) approach have received tremendous attention[3] because of their ability to diversify the synthetic applicability of renewable alcohols derived from lignocellulosic biomass.[3] Moreover, the by-products of these processes are only H_2 and/or water, making the overall process green and sustainable. Early contributions involve the use of expensive and noble metals like Ru, Ir, Pd, and Os, which is still of tremendous interest to the scientific community for further development.[4] However, growing environmental concerns motivate chemists to develop a technology or methodology or catalytic systems which are eco-friendly and cost-effective. In this context, various earth-abundant non-toxic transition metal complexes were developed to catalyze AD or BH-mediated transformations in a similar or even more efficient manner.[5] Construction of carbon–carbon bonds are the core of organic synthesis. Thus, the development of AD or BH mediated carbon–carbon bond forming reactions is highly desirable. In this context, various groups explored the C-alkylation of carbonyl compounds, [6,7] heterocycles [8,9] nitriles,[10] etc. [11,12] However, the alkylation of carbocycles [13] such as 9H-fluorene has been explored insufficiently to date.[14]

Fluorene derived organic materials have potential applications in optoelectronics, semiconductors, and solar cells.[15] These compounds are also known to possess profound applications in pharmaceuticals (Figure **3.1**).[16] Thus, the strategic functionalization of fluorene at the 9-position is highly valuable and can have the opportunity to synthesise synthetically important alkylated and alkenylated fluorene moieties.

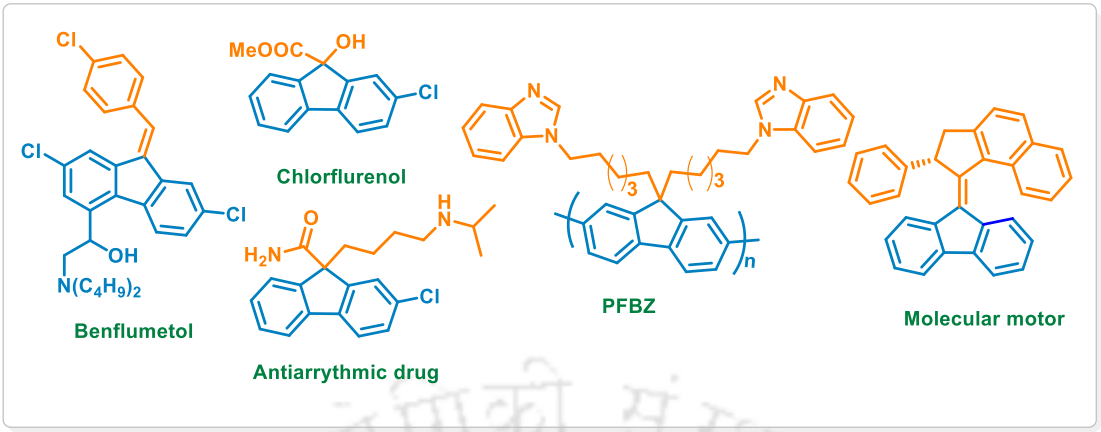


Figure 3.1: Various Structurally Important Derivative of Fluorene

3.2. Literature Survey:

The conventional way for alkylation of fluorene involves the use of a stoichiometric amount of a very strong base and organic halides which in turn results in the elimination of toxic waste.[17] Also, the control toward monoalkylation over dialkylation was found to be very poor. Gnanaprakasam and coworkers [14a] reported first time the application of Ru-catalysed alkylation of 9H-fluorene via borrowing hydrogen approach. Manganese catalysed alkylation of fluorenes with alcohols represents a single report on base-metal catalysed functionalization of carbocycles. [14b]

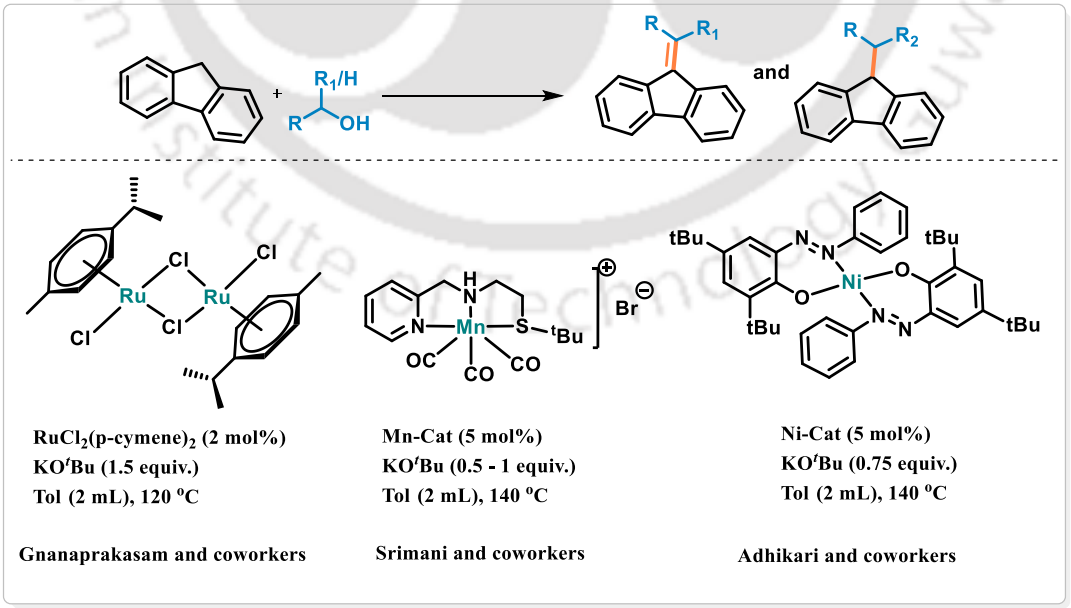


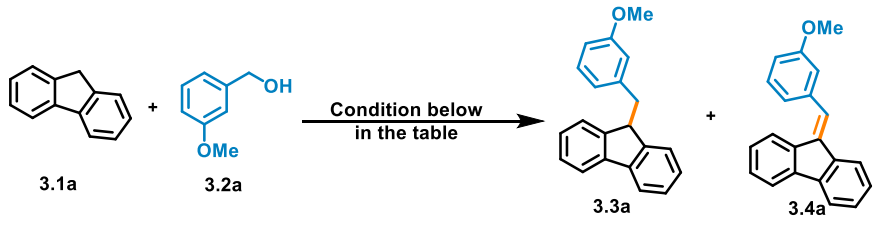
Figure 3.2: Previous reports on C-alkylation/alkenylation of 9H-Fluorene

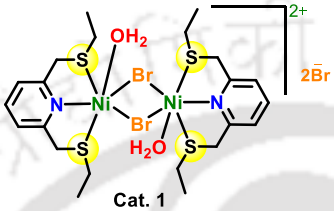
The use of nickel in this transformation would be beneficial because of its unique importance.[18] Parallelly, Adhikari and coworkers[14c] reported that a non-innocent Ni complex catalysed the C-alkylation of fluorene (figure **3.2**). Although they have demonstrated a wide range of alcohols, the substrate scope is limited to 9H-fluorenes. Moreover, alkenylation of fluorenes was not achieved. These open up avenues to explore such an important area. Intrigued by our continuous interest in 3d-metal catalyzed (de)hydrogenative reactions,[19] herein, this works involves the further catalytic application of SNS–nickel [20] catalysed switchable alkylation and alkenylation of fluorenes. Moreover, the primary focus of the chapter is on applying the developed protocol for the synthesis of functionally important fluorene derivatives in such a way that it can be further post functionalized into some important organic moieties.

3.3. Present work

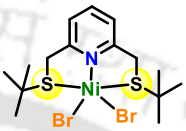
The initial investigation began with 9H-fluorene and 3-methoxybenzyl alcohol as a model substrate to explore the optimized reaction conditions, which are summarized in table **3.1**. Initially, fluorene (1 equiv.) and 3-methoxybenzyl alcohol (1 equiv.) were treated in the presence of Cat. **1** (3 mol%) and toluene (1.5 mL) at 140 °C for 24 h without any base (table **3.1**, entry **1**). The reaction results in no product formation. However, by addition of 1 equiv. of KO^{t}Bu, keeping all the conditions unchanged, 62% **3.3a** and 35% **3.4a** were formed (table **3.1**, entry **2**). This result clearly suggests the critical role of the base in both dehydrogenation of alcohol and generating a nucleophilic center at the 9-position of fluorene. After achieving the initial result, other reaction parameters such as the amount of the alcohol, nature of the base, solvent and catalyst were also screened. Increasing the amount of alcohol further improved the yield of **3.3a** (table **3.1**, entries **3** and **4**). Also, the amount of the base has a profound effect on improving the yield of the product. When the base amount was decreased to 0.8 equiv., the yield of the product was not affected, but further decreasing the amount of base has an adverse effect on the reaction system (table **3.1**, entries **4**–**6**). Interestingly, by changing KO^{t}Bu to KOH without altering other reaction parameters, 85% of the isolated product was achieved (table **3.1**, entry **7**). Considering the mild and cost-effective nature of KOH, it is chosen as a suitable candidate for the present reaction system. Afterward, decreasing the catalyst loading from 3 mol% to 2 mol% was found suitable, but further decreasing Cat. **1** to 1.5 mol% shows a detrimental effect (table **3.1**, entries **7** and **8**). The reaction was also investigated using Cat. **2**.

Table 3.1: Optimization of C-alkylation/alkenylation of 9H-fluorene[a]





Cat. 1



Cat. 2

Entry	3.1a (in mmol)	3.2a (in mmol)	Catalyst (in mol%)	Base (in equiv.)	Solvent (in mL)	% Yield[b] 3.3a	% Yield[b] 3.4a
1	0.5	0.5	Cat. 1 (3)	-	tol(2)	-	-
2	0.5	0.5	Cat. 1 (3)	KO^{t}Bu(1)	tol(2)	62	35
3	0.5	0.6	Cat. 1 (3)	KO^{t}Bu(1)	tol(2)	70	30
4	0.5	0.75	Cat. 1 (3)	KO^{t}Bu(0.8)	tol(2)	99	-
5	0.5	0.75	Cat. 1 (3)	KO^{t}Bu(0.7)	tol(2)	80	20
6	0.5	0.75	Cat. 1 (3)	KOH(0.8)	tol(2)	99	-
7	0.5	0.75	Cat. 1 (2)	KOH(0.8)	tol(2)	99(85)	-
8	0.5	0.75	Cat. 1 (1.5)	KOH(0.8)	tol(2)	70	25
9	0.5	0.55	Cat. 1 (2)	KOH(0.8)	tol(2)	55	40
10	0.5	0.55	Cat. 1 (2)	KOH(0.4)	tol(2)	46	48
11	0.5	0.55	Cat. 1 (2)	KO^{t}Bu(0.4)	tol(2)	52	38
12	0.5	0.55	Cat. 1 (2)	NaO^{t}Bu(0.4)	tol(2)	-	30
13	0.5	0.55	Cat. 1 (2)	K_2CO_3(0.40	tol(2)	-	-
14	0.5	0.55	Cat. 1 (2)	NaOH(0.4)	tol(2)	trace	-
15	0.5	0.75	Cat. 2 (4)	KOH(0.8)	tol(2)	80	15
16	0.5	0.55	Cat. 1 (2)	KOH(0.4)	Xyl(2)	30	63
17	0.5	0.55	Cat. 1 (1.5)	KOH(0.4)	Xyl(2)	20	75(65)
18	0.5	0.55	Cat. 1 (1.5)	KOH(0.4)	dioxane(2)	-	20
19	0.5	0.65	Cat. 1 (1.5)	KOH(0.4)	Xyl(2)	45	52
20	0.5	0.55	Cat. 1 (1)	KOH(0.4)	Xyl(2)	10	62
21	0.5	0.55	-	KOH(0.4)	Xyl(2)	-	12

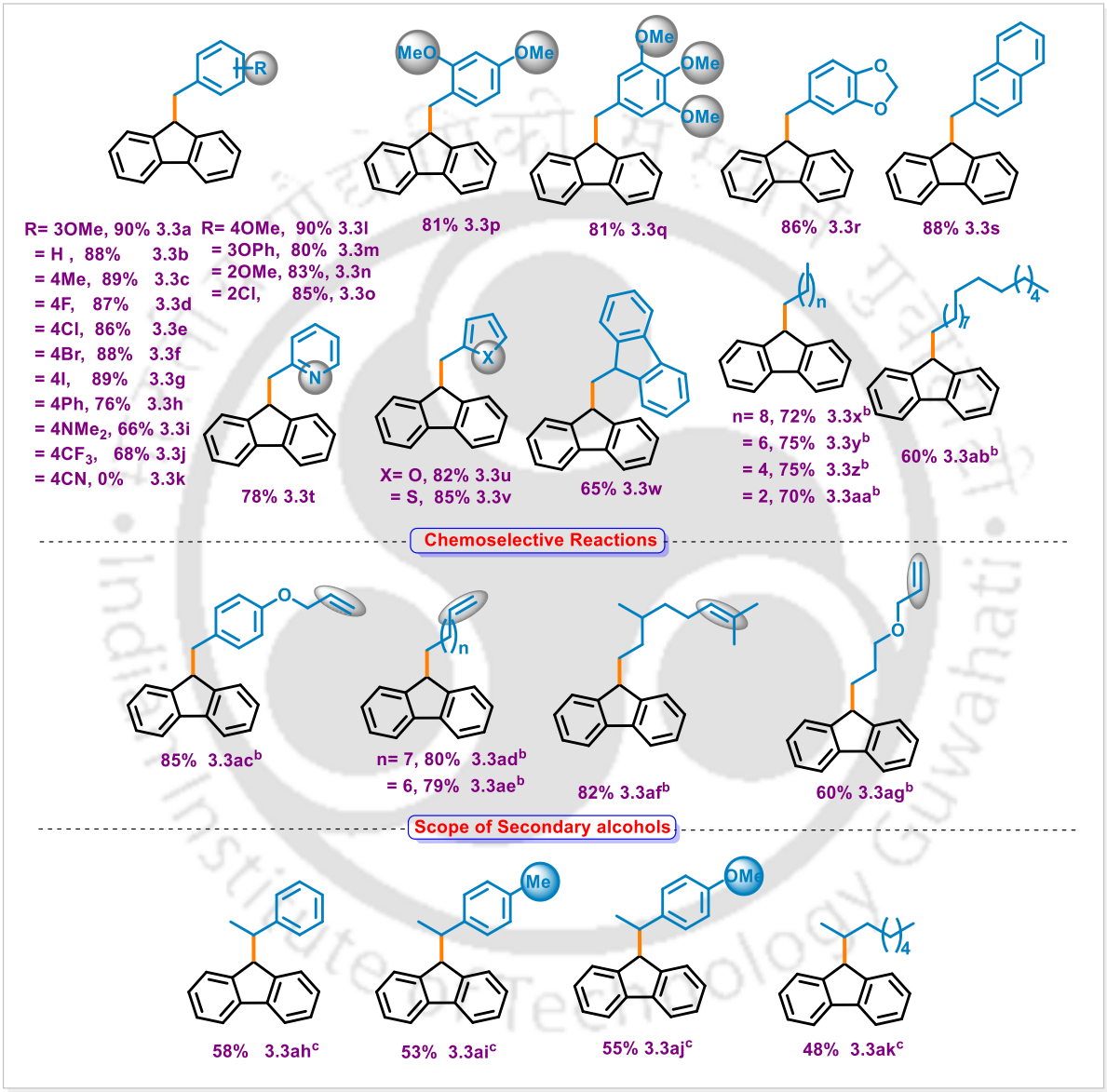
[a]Reaction Condition: **3.1a** (0.5 mmol), **3.2a** (0.55 - 0.75 mmol), Cat. (1 – 4 mol%), Base (0.2 – 0.5 mmol), Solvent (2 mL) temperature = 130 °C, [b]NMR yield using acetonitrile as internal standard and isolated yield in parenthesis.

The reaction was found less efficient, and we chose Cat. **1** for further study (table **3.1**, entry **15**). While screening the reaction conditions, we also observed the formation of an alkenylated product. Hence, it was hypothesized that tuning both amounts of alcohol and base could improve the formation of **3.4a** in good yield. Gratifyingly, 1.5 mol% Cat. **1** in the presence of 0.4 equiv. of KOH results in 65% of the isolated **3.4a** along with hydrogenated **3.3a** (table **3.1**, entry **17**). Interestingly, out of all the solvents, xylene appears to be suitable for the reaction (table **3.1**, entry **17**). Further, decreasing the catalyst loading hampers the reaction system (table **3.1**, entry **20**). Finally, a control experiment was conducted in the absence of catalyst where 12% **3.4a** was formed (table **3.1**, entry **21**) which indicates that both catalysts, as well as the base, have an active role in driving the reaction.

Fascinated by the initial result, the present protocol was promoted to explore the scope of various alcohol derivatives. Delightfully, the protocol is compatible with a wide range of alcohol derivatives with benzyl alcohols bearing electron donating groups (OMe, Me, NMe_2), as well as halo substituents in the 3 and 4-positions, delivering the alkylated product in 76–90% isolated yield (table **3.2**, **3.3a** – **3.3g**). Also, electron withdrawing substituent (such as Ph, CF_3) containing benzyl alcohols were also compatible with the optimized reaction conditions (table **3.2**, **3.3h** and **3.3j**). In addition, a similar trend was observed when substituents were placed in the 3 and 2 positions of the phenyl ring (table **3.2**, **3.3l** – **3.3o**). Alcohols containing a heterocyclic moiety such as pyridine, furan and thiophene work smoothly to deliver excellent yields of the desired products (table **3.2**, **3.3t** – **3.3v**). Intrigued by the result so far, the strategy also intends to probe the efficacy of the catalyst to activate aliphatic alcohols in the present reaction system. Delightfully, good yields of the desired alkylated products were obtained using aliphatic alcohols having various chain lengths (table **3.2**, **3.3x** – **3.3ab**). Direct lignocellulose-derived alcohols (cetyl alcohol) also couple with fluorene quite efficiently delivering **3.3ab** in 60% yield. Chemoselective alkylation of fluorene with aliphatic alcohols containing a distal double bond is envisioned as an interesting approach due to the potential for further synthetic diversification of the resulting products.[21] Delightfully, the alcohols couple chemoselectively with 9H-fluorene giving alkylated products without hydrogenating the distal double bond in good to excellent yields (table **3.2**, **3.3ac** – **3.3ag**). In order for catalytic hydrogenation of alkene, there must be strong coordination of metal center and alkene moiety. Moreover, in C-alkylation of fluorene, the reaction goes via the formation of alkenylated

fluorene. Now, alkenylated fluorene being polar reduced faster than that possessing distal or terminal alkene (apolar). The coupling of challenging secondary alcohols with fluorene delivered moderate yields, which might be due to steric hindrance (table **3.2**, **3.3ah** – **3.3ak**).

Table 3.2: Scope of Various Alcohols[a]

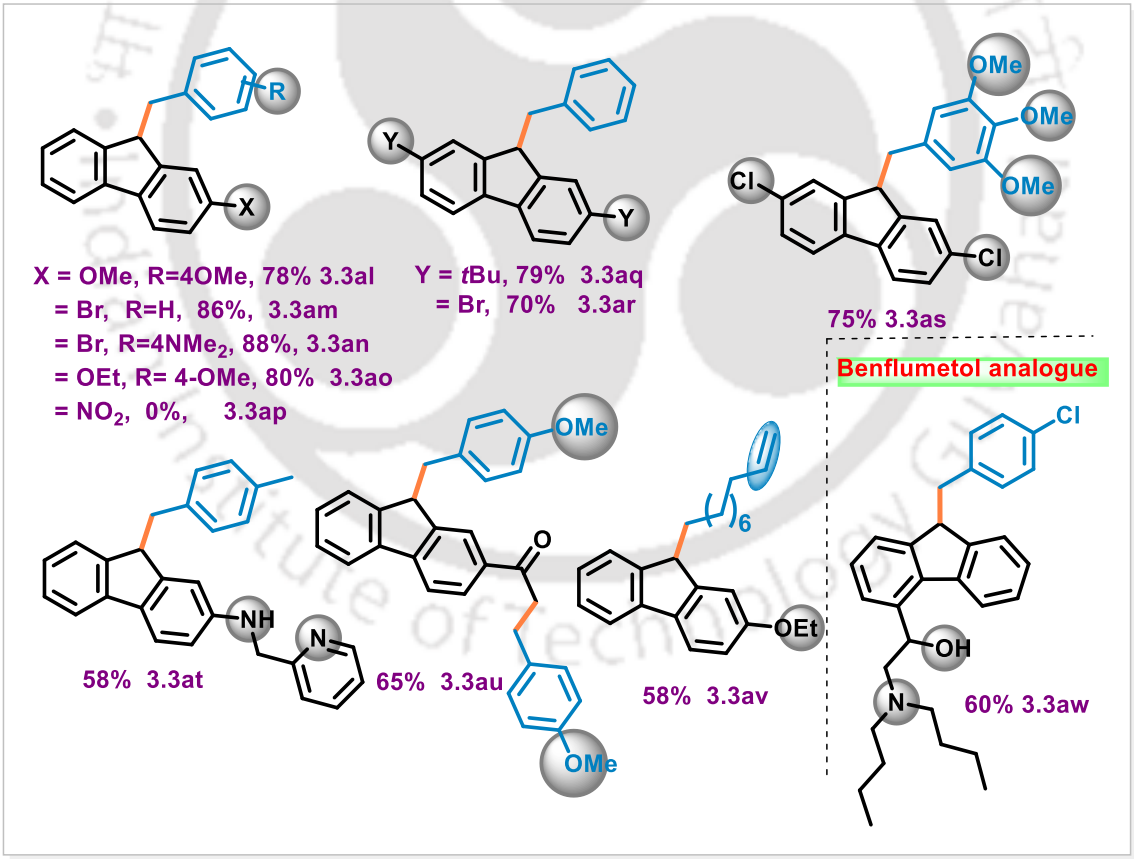


[a]Reaction Condition: **3.1a** (0.5 mmol), **3.2** (0.75 mmol), Cat. **1** (2 mol%), KOH (80 mol%), Toluene (2 mL), 130 °C, 24 h, under argon. [b] Cat. **1** (3 mol%), KOH (100 mol%). [c] Cat. 1 (3 mol%), KOH (150 mol%).

Subsequently, the scope of various substituted fluorenes for the present protocol was investigated. Pleasantly, substituted fluorene derivatives (Br, OMe, NMe_2) couple efficiently

with various benzyl alcohols, providing the alkylated product in excellent yields (table **3.3**, **3.3al** – **3.3ap**). Further, disubstituted fluorenes in the 2 and 7-positions furnish a good yield of the respective desired products (table **3.3**, **3.3aq** and **3.3ar**). When fluorene with a N-(2-pyridyl) group was treated with 4-methylbenzyl alcohol, 58% of the desired alkylated product was obtained (table **3.3**, **3.3at**). Interestingly, 2-acetylfluorene ended up being alkylated at both the 9-position and CH_3 of the acetyl group, delivering a good yield of the desired product (table **3.3**, **3.3au**). Fluorene with a nitro substituent in the 2-position failed to provide any desired product. Moreover, 2-ethoxyfluorene couples with an aliphatic alcohol (containing a distal double bond) efficiently resulting in 58% of the desired product **3.3av**. To highlight the synthetic utility of the developed protocol, an analogue of antimalarial drug benflumetol, 3aw, was synthesized with a good yield.

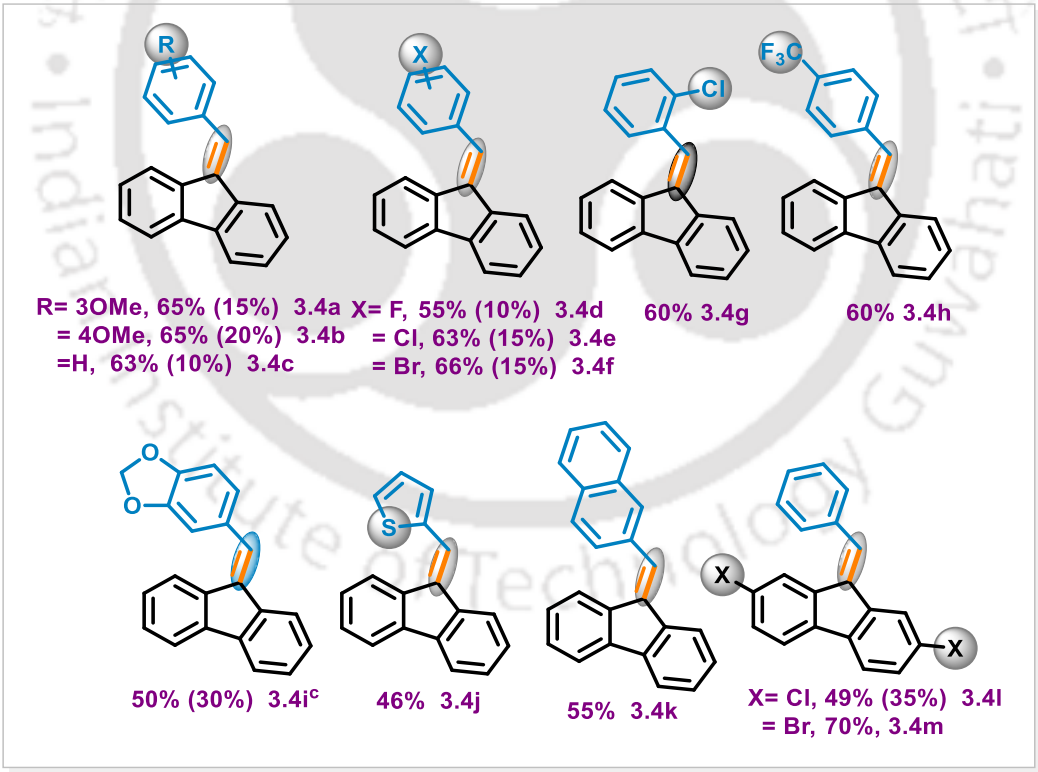
Table 3: Scope of Various Fluorene Derivatives[a]



[a]Reaction Condition: **3.1** (0.5 mmol), **3.2** (0.75 mmol), Cat. **1** (2 mol%), KOH (80 mol%), Toluene (2 mL), 130 °C, 24 h, under argon.

Subsequently, the selective construction of the alkenylated product 9-alkylidenefluorene was investigated. An interesting outcome was observed during experimental optimization: **3.4a** was obtained as the major product after properly tuning the reaction conditions. Intrigued by the result, the efficacy of the reaction conditions for various benzyl alcohols and fluorene derivatives was also explored. With the established reaction conditions in hand, electron neutral, electron donating and halo substituent bearing benzyl alcohols deliver the respective alkenylated product in moderate yield (table **3.4**, **3.4a**–**g**). Piperonyl alcohol and thiophene alcohol work well under the present conditions and deliver good yields of the respective alkenylated products (table **3.4**, **3.4i** and **3.4j**). In addition, a polyaromatic alcohol also shows a similar trend furnishing **3.4k** in 60% yield. Moreover, substituted fluorenes deliver the desired product in moderate yield (table **3.4**, **3.4l** and **3.4m**). The reason behind the low yield of alkenylated products is the subsequent formation of hydrogenated products.

Table 4: Scope for Alkenylation of Fluorene[a]



[a]Reaction Condition: **3.1** (0.5 mmol), **3.2** (0.55 mmol), Cat. **1** (1.5 mol%), KOH (40 mol%), Toluene (2 mL), 130 °C, 24 h, under argon. Yield of alkylated product in parenthesis.

In order to understand the reaction path, sets of control experiments and time dependent kinetic studies were conducted. The reaction profile revealed that the reaction goes via alkenylated fluorene species (Fig. **3.3**, **3.4l**). Initially, up to 3 h of the reaction, alkylated product **3.3l** was not formed. However, after 3 h, alkylated product **3.3l** starts forming and at 12 h, the concentration of alkenylated fluorene species **3.4l** reaches the maximum, and gradually decreases to zero via simultaneous conversion to **3.3l**. This underpins the formation of an alkenylated fluorene intermediate. This is further supported by the reaction of fluorene and benzaldehyde to give **3.4l** exclusively, which under standard conditions resulted in alkylated product **3.3l**. When **3.1a** was reacted with **3.8´** in the absence of a catalyst, **3.4l** was obtained, but in the absence of a base, the reaction was silent (table **3.5**, **4A**). To prove the role of the catalyst in the borrowing hydrogen step, a reaction between **3.4l** and **3.2a** in the absence of the catalyst was conducted, which results in a trace amount of product (table **3.5**, **4B**); however, the alkylated product formed exclusively under standard conditions (table **3.5**, **4C**).

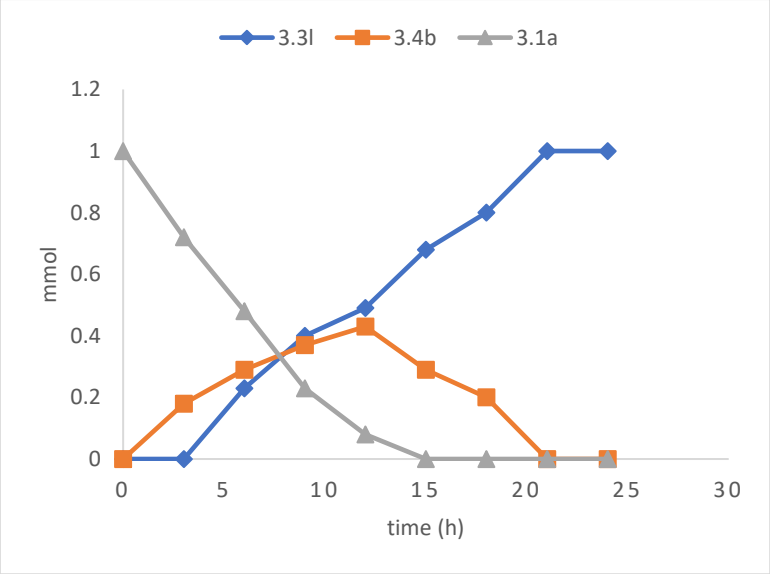
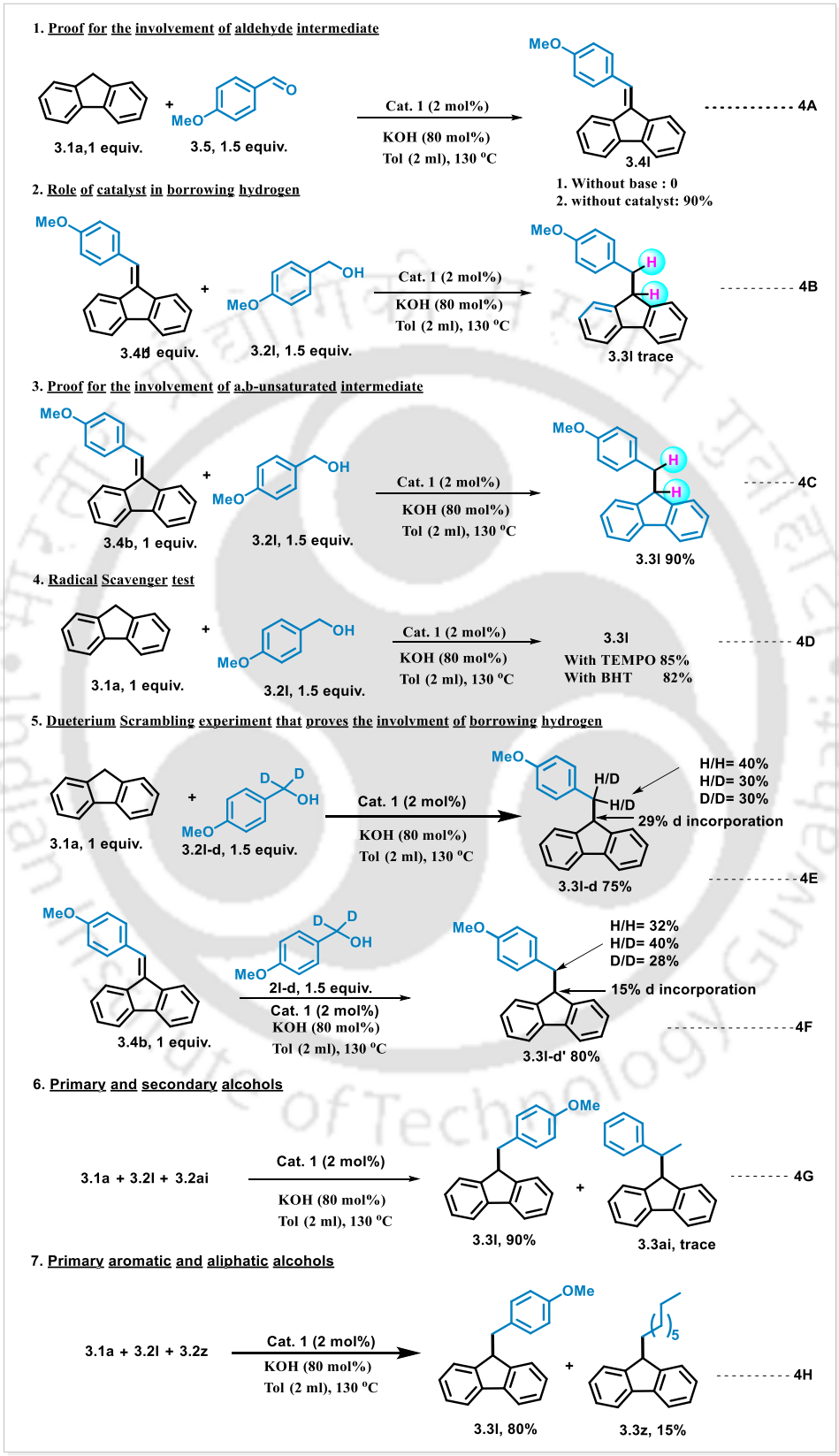


Figure 3.3: Kinetic profile diagram for reaction between 9H-fluorene and benzyl alcohol

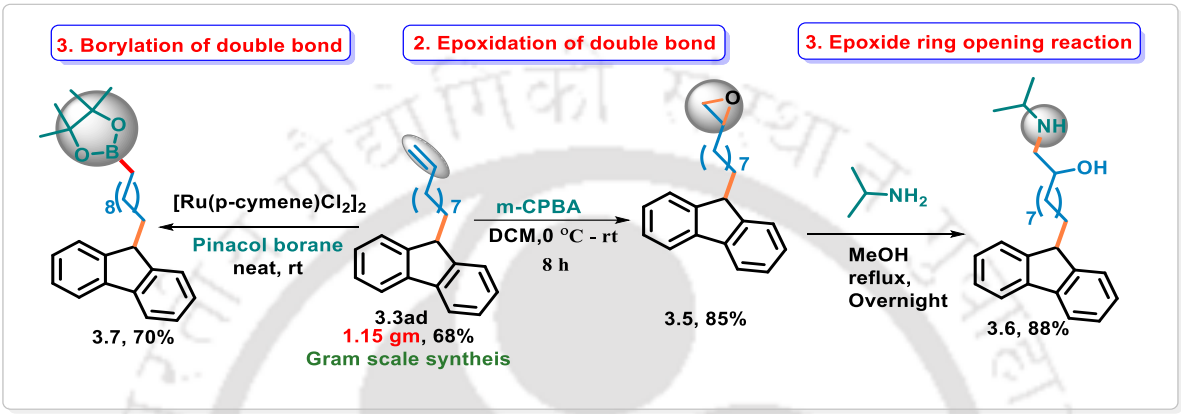
In addition, the radical scavenger test ruled out the involvement of radical species in the reaction mechanism (table **3.5**, **4D**). Finally, deuterium-scrambling experiments were conducted, where deuterium incorporation was observed; however, in experiment **4E**, the deuterium incorporation is comparatively lower because of rapid H/D exchange [10a,

Table 3.5: Table of Control and Competitive Experiments



14a–c,18g] (table **3.5**, **4E** and **4F**). Hence, the above experiments show the involvement of the borrowing hydrogen approach in the reaction mechanism. Competitive experiments were also conducted which shows that primary benzyl alcohols react faster than primary aliphatic alcohols and secondary alcohols (table **3.5**, **4G** and **4H**).

Table 3.6: Post Modification of Fluorene Derivative



Further, this thesis work also shows keen interested in post-functionalizing an interesting fluorene derivative containing a distal unsaturated center (table **3.6**). This distal unsaturated position can be functionalized further to interesting compounds. **3.3ad** was first synthesized on a gram scale applying the present protocol in 68% yield (i.e., 1.15 g). Next, **3.3ad** was treated with m-CPBA to give **3.5** in 85% yield which was further mixed with isopropylamine to result in ring opening amino alcohol product **3.6**. This amino alcohol can be further utilized for the synthesis of structurally important heterocycles such as pyrrole.[22] Secondly, **3.3ad** was also applied for borylation reaction using pinacolborane to furnish borylated product **3.7** in 70% yield (Table **6**) which can further be utilized for various transformations.[23]

Based on controlled experiments, attempts to isolate possible catalytic intermediate and the literature,[24] a catalytic pathway was proposed as shown in Fig. **3.3**. It was unfortunate that isolation of the crystals and hence the crystal structure of the reactive catalytic intermediate was unsuccessful. However, an indirect way of detecting catalytic intermediate was carried out via recording the mass spectrometry of the reaction mixture containing catalyst, base and alcohol. Based on the data obtained, following catalytic intermediates and hence following catalytic pathway was proposed as shown in figure **3**.

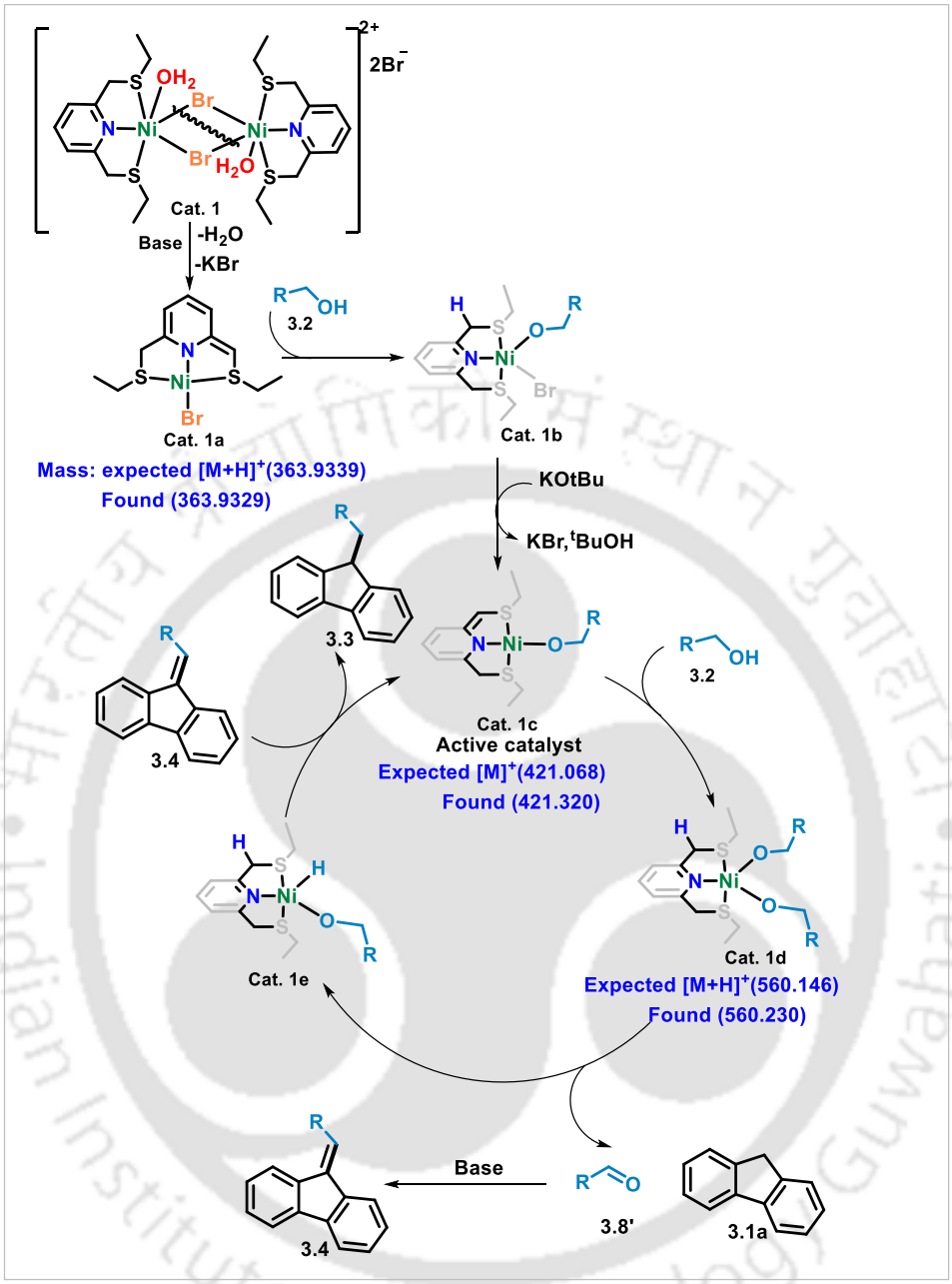


Figure 3.3: Proposed catalytic pathway

First, dearomatized Cat. **1a** (detected from mass spectrometry [M+H$^+$] = 363.9329) is generated in the presence of a base and under heating conditions. Subsequently, through metal-ligand cooperation, aromatized Ni-alkoxo complex Cat. **1b** is formed which further upon reaction of base, converted to dearomatized Cat. **1c** (detected from mass spectrometry [M$^+$] = 421.320). Further, Cat. **1c** react with another molecule of and convert to Ni-dialkoxo complex Cat. **1d** (detected from mass spectrometry [M+H$^+$] = 560.230). Now, the one alcohol molecule gets

activated and convert to corresponding aldehyde and Ni-Hydride complex Cat. **1e**. In the meantime, condensation product **3.4** is produced when the aldehyde gradually couples with amine derivatives in the presence of a base. This intermediate **3.4** is then subjected to transfer hydrogenation (via hydride transfer through Cat. **1e**), resulting in the corresponding alkylated product **3.3** and the regeneration of the active catalyst, Cat. **1c**, thereby allowing the catalytic cycle to proceed further.

3.4. Conclusion:

In summary, the chapter demonstrates the application of the Ni-SNS complex for C-alkylation of 9H-fluorenes with various alcohols. Along with benzylic alcohols, various aliphatic alcohols including alcohols containing distal double bond also efficiently couple with 9H-fluorene. Using present protocol, an important analogue of antimalarial drug i.e., benflumetol was successfully synthesized. Further, various post-modification of alkylated product of fluorene was also conducted successfully. Various control experiments suggest the reaction involves borrowing hydrogen approach.

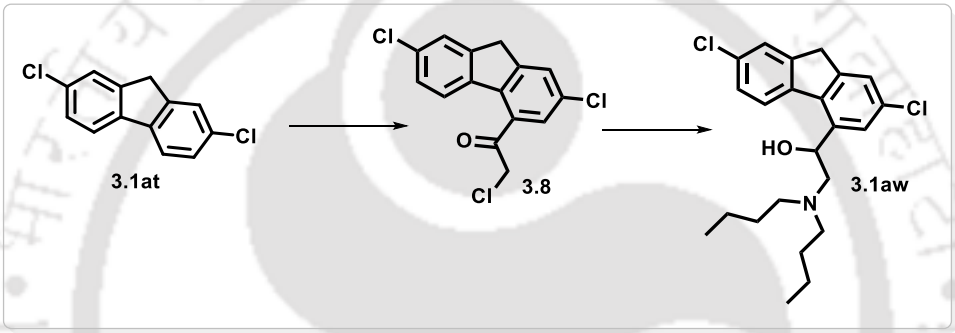
3.5. Experimental Section

3.5.1. General Considerations.

Unless otherwise mentioned, all chemicals were purchased from common commercial sources and used as received. All solvents were dried by using standard procedure. All catalytic reactions were carried out under argon atmosphere using dried glassware and standard syringe/septa techniques. DRX-400 Varian spectrometer and Bruker Avance III 600, 500 and 400 spectrometers were used to record ^{1}H and ^{13}C NMR spectra using $CDCl_3$ as solvent and TMS as an internal standard. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (J) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dt = doublet of triplet, td = triplet of doublet and brs = broad singlet. Q-TOF ESI-MS instrument (model HAB 273) was used for recording mass spectra. SRL silica gel (100-200 mesh) was used for column chromatography.

3.5.2. Experimental Procedure for the Synthesis of 2-(dibutylamino)-1-(2,7-dichloro-9H-fluoren-4-yl)ethan-1-ol:

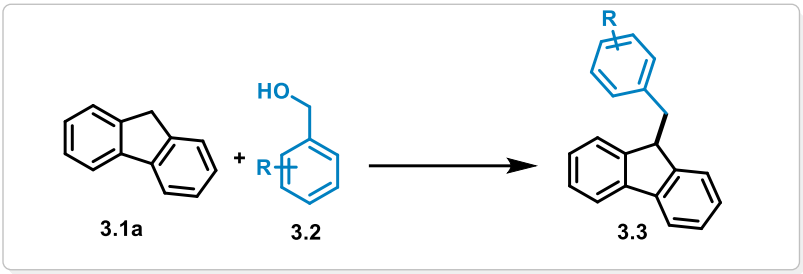
A mixture of chloroacetyl chloride (1.47 g, 13 mmol), $AlCl_3$ (1.99 g, 15 mmol), and dichloromethane (15 mL) was cooled to 0 °C. A solution of 1at (2.34 g, 10 mmol) dissolved in dichloromethane (10 mL) was added. After 3-10 h, the deep-red reaction mixture was transferred to 15% aqueous hydrochloric acid (75 mL). After phase separation, the organic phase was washed twice with water. Dichloromethane was distilled off, while ethanol was added at the same rate. The crude mixture was purified through column chromatography (5% ethyl acetate in hexane) and isolated 3.8 in 65% (2.0 g) yield.



To a slurry of 3.8 (1.54 g, 5 mmol) in ethanol (25 mL) was added sodium borohydride (0.55 g, 15 mmol) portionwise at -5 to 5 °C within 1 h. As the viscosity increased, good mixing was necessary to reach complete conversion. After agitating for 1 h, dibutylamine (2.6 g, 20 mmol) was added, and the mixture was heated up to distill off the ethanol. The mixture was heated to 140 °C for 3 h, cooled down to below 90 °C, and quenched with 10% aqueous sodium hydroxide (50 mL). After phase separation, the organic phase was washed with brine (2 × 50 mL). The organic layer was concentrated under reduced pressure and purified under column chromatography (30% ethyl acetate in hexane) and isolated **3.1aw** 75% (1.95 g) yield.

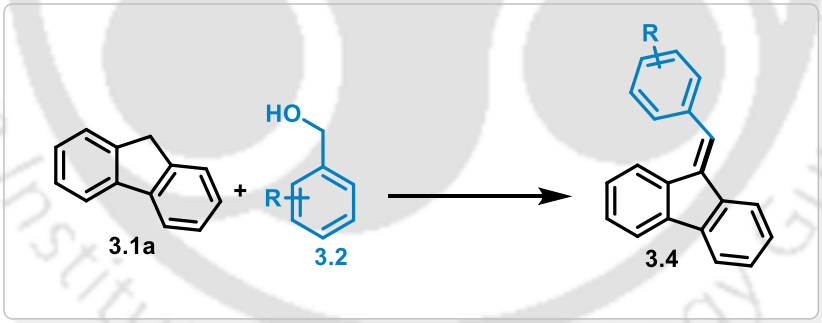
Yellow gummy liquid, Yield: 75%, 1.95 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.43 (s, 1H), 7.32 (s, 1H), 7.25 (dd, *J* = 8.3, 1.6 Hz, 1H), 5.31 (dd, *J* = 10.1, 3.3 Hz, 1H), 3.78 (s, 2H), 2.80 (dd, *J* = 13.0, 3.5 Hz, 1H), 2.69 – 2.55 (m, 2H), 2.47 – 2.36 (m, 3H), 1.46 – 1.36 (m, 4H), 1.34 – 1.23 (m, 4H), 0.89 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.5, 145.3, 139.8, 139.2, 135.6, 133.3, 132.4, 127.1, 125.4, 124.5, 123.9, 65.6, 60.0, 53.4, 36.9, 29.1, 20.6, 14.1.

3.5.3. General Experimental Procedure for The Alkylation of Fluorene Derivatives.



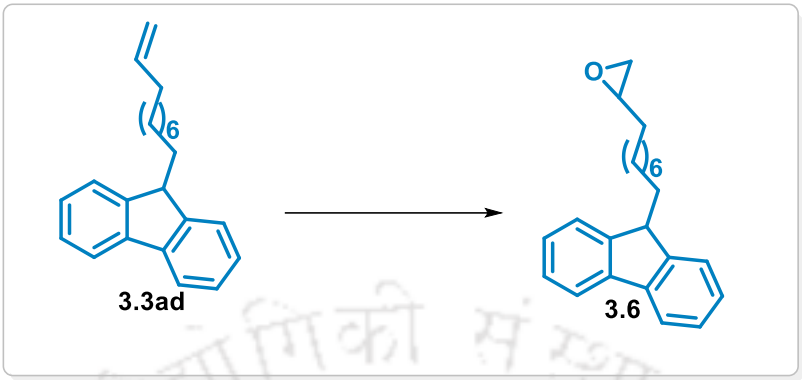
To an oven dried 10 mL round bottom flask, Fluorene **1a** (0.083 g, 0.5 mmol), alcohols **2** (0.75 mmol), KOH (0.023, 80 mol%) and **Cat. 1** (0.009 g, 2 mol%) were taken under argon atmosphere, after that 2 ml of toluene was added to the reaction mixture. The resulting mixture was heated in an oil bath at 130 °C for 24 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using hexane or 1%-10% ethyl acetate in hexane to get pure C-alkylated compound **3**.

3.5.4. General Experimental Procedure for The Alkenylation of Fluorene Derivatives.



To an oven dried 10 mL round bottom flask, 9H-fluorene **1a** (0.083 g, 0.5 mmol), alcohols **2** (0.55 mmol), KOH (0.011 g, 40 mol%) and **Cat. 1** (0.007 g, 1.5 mol%) were taken under argon atmosphere, after that 2 mL of toluene was added to the reaction mixture. The resulting mixture was heated in an oil bath at 130 °C for 24 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using hexane or 0%-5% ethyl acetate in hexane to get pure C-alkenylated compound **4**.

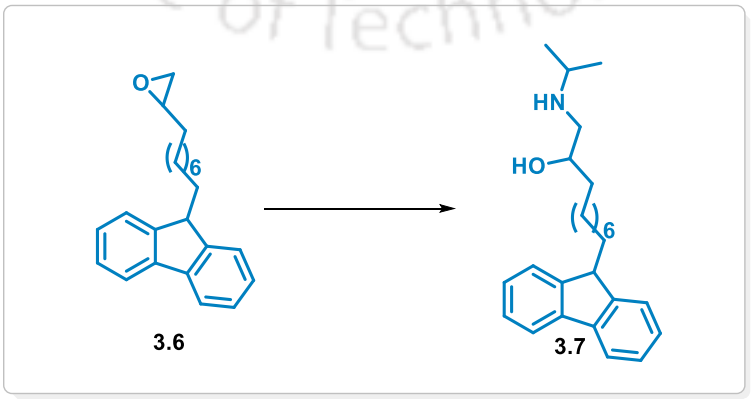
3.5.5. Experimental Procedure for the Epoxidation of 3.3ad:



To a 10 mL RB equipped with a stir bar was added 3.**3ad** (0.152 g, 0.5 mmol, 1.0 equiv.), $NaHCO_3$ (0.063 g, 0.75 mmol, 1.5 equiv.) and DCM (2 mL). The mixture was cooled to 0 °C before m-CPBA (0.129 g, 0.75 mmol, 1.5 equiv.) was added. After being stirred at 0 °C for 2 h, the reaction was further stirred overnight. The mixture was then diluted with DCM (10 mL) and quenched with saturated Na_2SO_3 (5 mL). The mixture was further stirred for 10 min and the organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude mixture was purified by silica flash chromatography to afford the desired product **3.6** as a yellow oil (0.136 g, 85% yield).

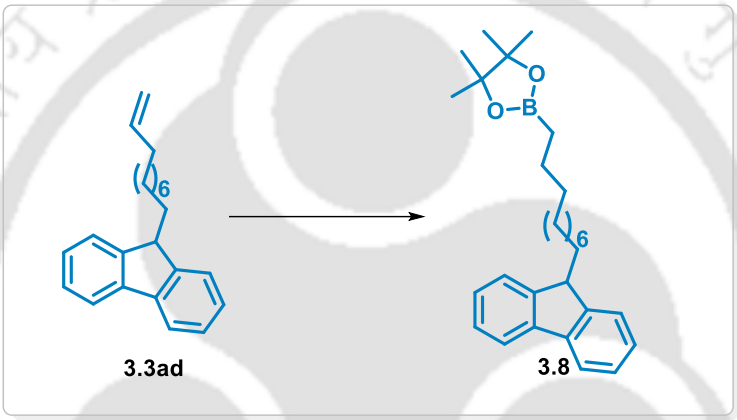
3.5.6. Experimental Procedure for the Ring Opening of 3.6 using Isopropylamine:

To a 10 ml RB, was equipped with a stir bar was added **3.7** (0.08 g, 0.25 mmol), and isopropyl amine (10 equiv.) in methanol was heated to reflux overnight. After completion of the reaction, the methanol and excess of isopropyl amine was evaporated and the organic compound was extracted with DCM in the presence of brine. The compound **3.7** thus isolated in 88% (0.083 g) was directly analysed through NMR.



3.5.7. Experimental Procedure for the Borylation of 3.3ad:

The synthesis of **3.8** was carried out according to the literature procedure. To a screw cap scintillation vial **3.3ad** (0.152 g, 0.5 mmol), $RuCl_2$(p-cymene) (1 mol%), and pinacolborane (0.064 g, 0.5 mmol) were charged in the argon filled glove box. The reaction mixture was allowed to stir at room temperature for 12 h. Reaction progress was monitor by GC. Upon completion, the resulted boronate ester product was separated by silica-gel column chromatography using Ethyl acetate in hexane (5:90) as an eluent to give colorless oil as a title compound. The compound was further analysed via ^{1}H, ^{13}C NMR and HRMS spectrometry.



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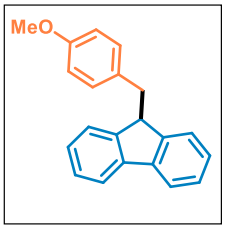
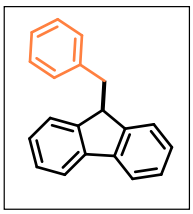
3.7. Characterisation Data for the Compounds:

9-(4-methoxybenzyl)-9H-fluorene (**3.3a**)



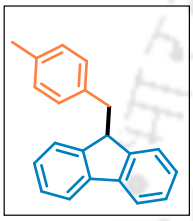
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 90% Yield, 0.128 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.24 – 7.17 (m, 4H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.17 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 3.05 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 146.9, 140.9, 131.9, 130.4, 127.1, 126.6, 124.9, 119.8, 113.7, 55.3, 48.9, 39.2.

9-benzyl-9H-fluorene (**3.3b**)



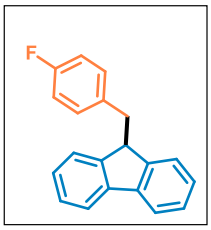
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 88% Yield, 0.112 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 6.2 Hz, 2H), 7.35 – 7.33 (m, 2H), 7.30 – 7.24 (m, 5H), 7.20 (d, *J* = 7.4 Hz, 2H), 4.27 (t, *J* = 7.6 Hz, 1H), 3.15 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.8, 140.8, 139.8, 129. 6, 128.3, 127.1, 126. 7, 126.4, 124.9, 119.8, 48.7, 40.1.

9-(4-methylbenzyl)-9H-fluorene (**3.3c**)



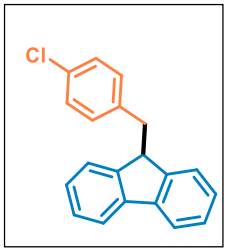
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 89% Yield, 0.120 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.14 (m, 4H), 7.13 – 7.09 (m, 4H), 4.20 (t, *J* = 7.6 Hz, 1H), 3.07 (d, *J* = 7.6 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.0, 140.8, 136.7, 135.8, 129.4, 129.0, 127.1, 126.6, 124. 9, 119.8, 48.8, 39.7, 21.1.

9-(4-fluorobenzyl)-9H-fluorene (**3.3d**)



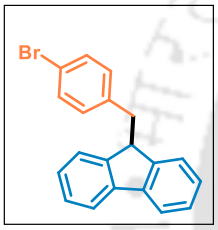
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 87% Yield, 0.119 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.17 – 7.15 (m, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 4.23 (t, *J* = 7.4 Hz, 1H), 3.15 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6 (d, *J* = 243 Hz), 146.5, 140.9, 135.2, 130.9 (d, *J* = 7.5 Hz), 127.2, 126.7, 124.8, 119.9, 115.0 (d, *J* = 21 Hz), 48.7, 39.1.

9-(4-chlorobenzyl)-9H-fluorene (**3.3e**)



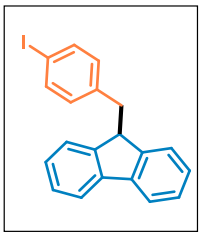
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 86% Yield, 0.125 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.21 (m, 6H), 7.12 (d, *J* = 8.2 Hz, 2H), 4.23 (t, *J* = 7.3 Hz, 1H), 3.14 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 140.9, 138.0, 132.1, 130.9, 128.3, 127.3, 126.7, 124.7, 119.9, 48.5, 39.3.

9-(4-bromobenzyl)-9H-fluorene (**3.3f**)



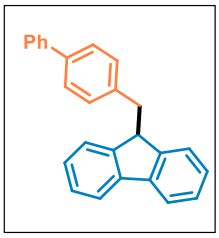
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 88% Yield, 0.147 g. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.18 – 7.11 (m, 4H), 6.95 (d, *J* = 8.3 Hz, 2H), 4.11 (t, *J* = 7.3 Hz, 1H), 3.01 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 140. 9, 138.5, 131.3, 131.3, 127.3, 126.7, 124.7, 120.2, 119.9, 48.4, 39.3.

9-(4-iodobenzyl)-9H-fluorene (**3.3g**)



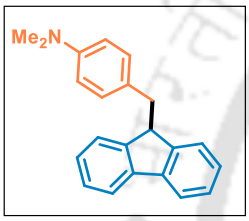
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 89% Yield, 0.170 g. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.21 – 7.08 (m, 4H), 6.85 (d, *J* = 8.2 Hz, 2H), 4.11 (t, *J* = 7.3 Hz, 1H), 3.00 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 140. 9, 139.2, 137.7, 131.3, 127.3, 126.7, 124.7, 119.9, 91.6, 48.4, 39.3.

9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene (**3.3h**)



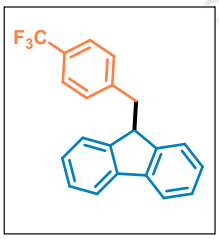
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 76% Yield, 0.127 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.32 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.22 (m, 4H), 4.26 (t, *J* = 7.5 Hz, 1H), 3.15 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 140.9, 140.9, 139.2, 138.9, 129.9, 128.8, 127.2, 127.0, 126.9, 126.7, 124.9, 119.9, 48.7, 39.8.

4-((9H-fluoren-9-yl)methyl)-N,N-dimethylaniline (**3.3i**)



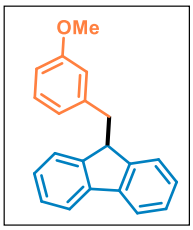
yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:4). 67% Yield, 0.099 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 6.3 Hz, 2H), 7.25 – 7.22 (m, 4H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.67 (d, *J* = 6.2 Hz, 2H), 4.11 (t, *J* = 7.7 Hz, 1H), 2.94 (d, *J* = 7.7 Hz, 2H), 2.89 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.2, 140.8, 135.0, 130.1, 129.1, 127.0, 126.6, 125.0, 120.3, 119.7, 49.1, 41.0, 39.2. HRMS (ESI) m/z: $[M + H]^+$ $C_{22}H_{21}N$: 300.1752; found 300.1752.

9-(4-(trifluoromethyl)benzyl)-9H-fluorene (**3.3j**)



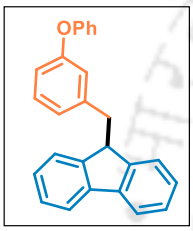
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 68% Yield, 0.110 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.20 – 7.16 (m, 4H), 7.13 (t, *J* = 7.4 Hz, 2H) 4.17 (t, *J* = 7.2 Hz, 1H), 3.13 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.2, 143.7, 140.9, 129.8, 128.7 (q, *J* = 33 Hz), 127.4, 126.8, 125.1 (q, *J* = 4.5 Hz), 124.7, 124.3 (q, *J* = 270 Hz) 120.0, 48.3, 39.7.

9-(3-methoxybenzyl)-9H-fluorene (**3.3l**)



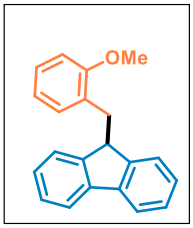
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 90% Yield, 0.128 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.16 (m, 4H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 4.18 (t, *J* = 7.5 Hz, 1H), 3.80 (s, 3H), 3.05 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 146.8, 141.4, 140.9, 129.2, 127.1, 126.7, 124.7, 121.9, 119.8, 114.9, 112.0, 55.2, 48.6, 40.1.

9-(3-phenoxybenzyl)-9H-fluorene (**3.3m**)



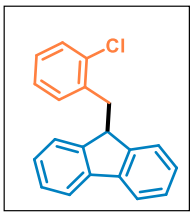
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 80% Yield, 0.128 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.34 (m, 4H), 7.29 – 7.26 (m, 5H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.96 – 6.87 (m, 4H), 6.84 (s, 1H), 4.19 (t, *J* = 7.3 Hz, 1H), 3.10 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.4, 156.9, 146.6, 141.7, 140.9, 129.7, 129.5, 127.2, 126.7, 124.8, 124.7, 123.0, 120.2, 119.9, 118.6, 117.3, 48.5, 39.8.

9-(2-methoxybenzyl)-9H-fluorene (**3.3n**)



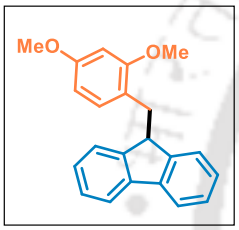
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 83% Yield, 0.118 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.26 – 7.24 (m, 2H), 7.21 (d, *J* = 7.4 Hz, 2H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 4.41 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 3H), 3.10 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 147.7, 140.8, 131.6, 128.6, 127.9, 126.9, 126.6, 125.1, 120.2, 119.7, 110.3, 55.3, 46.7, 35.6.

9-(2-chlorobenzyl)-9H-fluorene (**3.3o**)



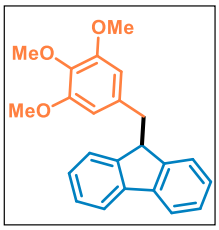
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 85% Yield, 0.123 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.18 – 7.11 (m, 4H), 7.07 – 7.04 (m, 3H), 4.29 (t, *J* = 7.7 Hz, 1H), 3.07 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 140.8, 137.8, 134.7, 132.3, 129.8, 128.1, 127.2, 126.8, 126.6, 125.0, 119.9, 46.5, 38.6.

9-(2,4-dimethoxybenzyl)-9H-fluorene (**3.3p**)



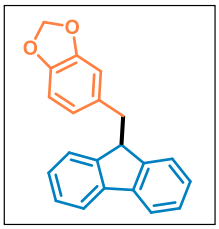
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 81% Yield, 0.128 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.20 (m, 4H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.58 (d, *J* = 2.2 Hz, 1H), 6.47 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.35 (t, *J* = 7.7 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.03 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 158.9, 147.8, 140.8, 131.8, 126.8, 126.5, 125.1, 121.1, 119.7, 103.6, 98.5, 55.4, 55.3, 46.9, 34.9.

9-(3,4,5-trimethoxybenzyl)-9H-fluorene (**3.3q**)



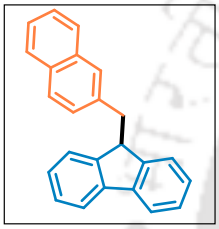
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:5). 81% Yield, 0.140 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.29 – 7.20 (m, 4H), 6.34 (s, 2H), 4.21 (t, *J* = 7.2 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 6H), 3.08 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 146.6, 141.0, 136.6, 135.0, 127.2, 126.6, 124.9, 119.9, 106.6, 60.94, 56.1, 48.7, 40.2.

5-((9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole (**3.3r**)



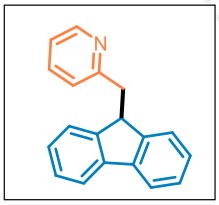
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 86% Yield, 0.129 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.24 (m, 4H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.98 (s, 2H), 4.19 (t, *J* = 7.6 Hz, 1H), 3.06 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.5, 146.7, 146.0, 140.8, 133.6, 127.1, 126.7, 124.9, 122.6, 119.8, 109.7, 108.0, 100.9, 48.9, 39.8.

9-(naphthalen-2-ylmethyl)-9H-fluorene (**3.3s**)



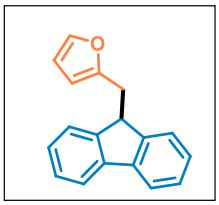
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 88% Yield, 0.135 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.78 (m, 2H), 7.77 – 7.73 (m, 3H), 7.63 (s, 1H), 7.49 – 7.40 (m, 3H), 7.35 – 7.32 (m, 2H), 7.20 – 7.16 (m, 4H), 4.34 (t, *J* = 7.6 Hz, 1H), 3.27 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 140.8, 137.4, 133.5, 132.3, 128.0, 127.9, 127.9, 127.7, 127. 7, 127.2, 126.7, 126.0, 125.4, 124.9, 119.9, 48. 6, 40.4.

2-((9H-fluoren-9-yl)methyl)pyridine (**3.3t**)



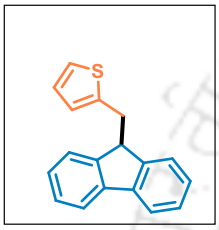
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 78% Yield, 0.100 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.68 (d, *J* = 4.2 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.60 (td, *J* = 7.6, 1.8 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 1H), 4.63 (t, *J* = 7.7 Hz, 1H), 3.23 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 149.6, 147.1, 140.8, 136.3, 127.1, 126.8, 124.7, 124.4, 121.7, 119.9, 47.2, 42.5.

2-((9H-fluoren-9-yl)methyl)furan (**3.3u**)



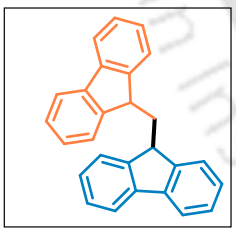
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 82% Yield, 0.101 g. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.12 (d, *J* = 5.0 Hz, 1H), 6.89 – 6.86 (m, 1H), 6.70 (d, *J* = 3.4 Hz, 1H), 4.23 (t, *J* = 7.0 Hz, 1H), 3.39 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 142.1, 141.0, 127.3, 126.8, 126.6, 126.0, 124.7, 123.8, 119.9, 49.0, 34.0.

2-((9H-fluoren-9-yl)methyl)thiophene (**3.3v**)



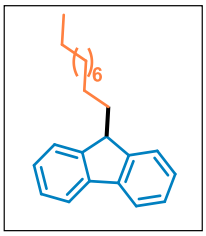
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 85% Yield, 0.111 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.37 – 7.26 (m, 4H), 7.17 (d, *J* = 5.1 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.76 (s, 1H), 4.29 (t, *J* = 7.0 Hz, 1H), 3.45 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.2, 142.1, 141.1, 127.4, 126.9, 126.6, 126.0, 124.7, 123.8, 119.9, 49.0, 34.0.

di(9H-fluoren-9-yl)methane (**3.3w**)



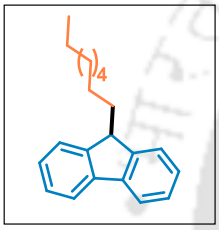
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 65% Yield, 0.112 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.6 Hz, 4H), 7.60 (d, *J* = 7.5 Hz, 4H), 7.44 (t, *J* = 7.5 Hz, 4H), 7.33 (t, *J* = 7.4 Hz, 4H), 4.46 (t, *J* = 7.7 Hz, 2H), 2.26 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.4, 141.0, 127.3, 127.0, 125.1, 120.1, 45.8, 38.9.

9-decyl-9H-fluorene (**3.3x**)



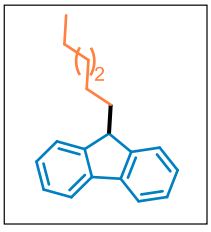
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 72% Yield, 0.110 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 3.95 (t, *J* = 5.8 Hz, 1H), 2.00 – 1.95 (m, 2H), 1.27 – 1.16 (m, 16H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 144.8, 140.9, 140.5, 125.8, 125.7, 125.7, 125.5, 124.1, 123.3, 118.6, 118.5, 51.4, 36.1, 33.5, 30.9, 28.7, 28.6, 28.3, 26.9, 21.7, 14.7, 13.1.

9-octyl-9H-fluorene (**3.3y**)



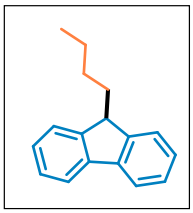
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 75% Yield, 0.104 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 4.03 (t, *J* = 5.9 Hz, 1H), 2.07 – 2.03 (m, 2H), 1.35 – 1.23 (m, 12H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.7, 141.1, 126.9, 126.8, 124.4, 119.8, 47.5, 33.2, 31.9, 30.0, 29.4, 29.3, 25.8, 22.7, 14.2.

9-hexyl-9H-fluorene (**3.3z**)



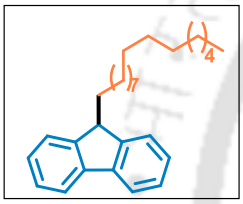
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 75% Yield, 0.094 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 4.02 (t, *J* = 5.9 Hz, 1H), 2.08 – 2.01 (m, 2H), 1.36 – 1.20 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.7, 141.1, 126.8, 126.8, 124.4, 119.8, 47.5, 33.2, 31.7, 29.7, 25.7, 22.7, 14.1.

9-butyl-9H-fluorene (**3.3aa**)



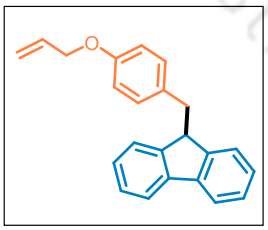
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 70% Yield, 0.078 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 6.9 Hz, 2H), 4.00 (t, *J* = 5.8 Hz, 1H), 2.05 – 2.01 (m, 2H), 1.33 – 1.27 (m, 2H), 1.23 – 1.12 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 141.1, 126.8, 126.8, 124.4, 119.8, 47.5, 32.8, 27.8, 23.1, 14.0.

9-hexadecyl-9H-fluorene (**3.3ab**)



Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 60% Yield, 0.117 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 4.00 (t, *J* = 5.3 Hz, 1H), 2.04 – 2.00 (m, 2H), 1.28 – 1.23 (m, 28H), 0.91 (t, *J* = 5.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.7, 141.1, 126.8, 126.8, 124.4, 119.8, 47.5, 33.1, 31.9, 30.0, 29.7, 29.6, 29.4, 29.4, 25.7, 22.7, 14.1.

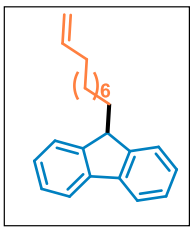
9-(4-(allyloxy)benzyl)-9H-fluorene (**3.3ac**)



Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 85% Yield, 0.133 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.14 – 6.08 (m, 1H), 5.46 (dd, *J* = 17.3, 1.56 Hz, 1H), 5.33 (dd, *J* = 11.8, 1.32 Hz, 1H), 4.58 – 4.56 (m, 2H), 4.21 (t, *J* = 7.6 Hz, 1H), 3.08 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.2, 146.9, 140.8, 133.4, 132.1, 130.4, 127.1, 126.6, 124.9, 119.8,

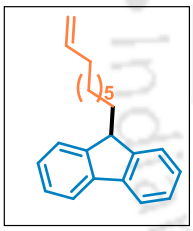
117.6, 114.5, 68.9, 48.9, 39.2. HRMS (ESI) m/z: $[M + Na]^+$ $C_{23}H_{20}O$: 335.1412; found 335.1412.

9-(dec-9-en-1-yl)-9H-fluorene (**3.3ad**)



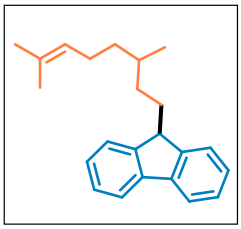
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 80% Yield, 0.122 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 5.85 – 5.78 (m, 1H), 5.03 – 4.97 (m, 1H), 4.94 (d, J = 10.6 Hz, 1H), 4.00 (t, *J* = 5.9 Hz, 1H), 2.05 – 1.98 (m, 4H), 1.39 – 1.31 (m, 2H), 1.27 – 1.17 (m, 10H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 141.1, 139.3, 126.8, 126.8, 124.4, 119.8, 114.1, 47.5, 33.8, 33.1, 30.0, 29.5, 29.4, 29.1, 28.9, 25.6. HRMS (ESI) m/z: $[M - H]^+$ $C_{23}H_{28}$: 303.2111; found 303.2098.

9-(non-8-en-1-yl)-9H-fluorene (**3.3ae**)



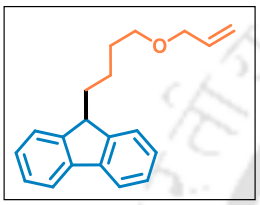
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 79% Yield, 0.114 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 5.85 – 5.78 (m, 1H), 5.00 (d, J = 17.1 Hz, 1H), 4.94 (d, J = 10.1 Hz, 1H)., 4.00 (t, *J* = 5.9 Hz, 1H), 2.04 – 2.00 (m, 4H), 1.37 – 1.32 (m, 2H), 1.29 – 1.18 (m, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 141.1, 139.2, 126.8, 126.8, 124.3, 119.8, 114.1, 47.5, 33.8, 33.1, 29.9, 29.2, 29.1, 28.9, 25.7. HRMS (ESI) m/z: $[M - H]^+$ $C_{22}H_{26}$: 289.1955; found 289.1944.

9-(3,7-dimethyloct-6-en-1-yl)-9H-fluorene (**3.3af**)



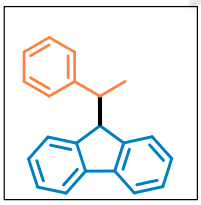
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 82% Yield, 0.125 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 4.97 (t, *J* = 7.0 Hz, 1H), 3.89 (t, *J* = 5.8 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.88 – 1.73 (m, 2H), 1.47 (d, *J* = 8.4 Hz, 5H), 1.32 – 0.89 (m, 6H), 0.75 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 147.6, 141.1, 131.0, 126.8, 126.7, 124.9, 124.3, 124.3, 119.8, 47.6, 36.7, 32.6, 32.4, 30.3, 25.7, 25.5, 19.5, 17.6.

9-(4-(allyloxy)butyl)-9H-fluorene (**3.3ag**)



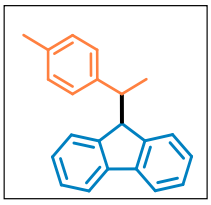
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 60% Yield, 0.083 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 5.94 – 5.87 (m, 1H), 5.26 (d, *J* = 17.2 Hz, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 4.01 (t, *J* = 5.7 Hz, 1H), 3.93 (d, *J* = 5.6 Hz, 2H), 3.37 (t, *J* = 6.7 Hz, 2H), 2.08 – 2.04 (m, 2H), 1.62 – 1.57 (m, 2H), 1.32 – 1.27 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.4, 141.1, 135.0, 126.9, 126.8, 124.4, 119.8, 116.7, 71.8, 70.2, 47.4, 33.0, 30.1, 22.4. HRMS (ESI) m/z: $[M + Na]^+$ $C_{20}H_{22}O$: 279.1749; found 279.1749.

(S)-9-(1-phenylethyl)-9H-fluorene (**3.3ah**)



White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 58% Yield, 0.078 g. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.65 (m, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.22 (m, 8H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 4.28 (d, *J* = 4.5 Hz, 1H), 3.73 – 3.61 (m, 1H), 0.91 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 144.6, 144.6, 141.8, 141.4, 128.2, 128.1, 127.1, 127.1, 126.8, 126.3, 126.3, 125.7, 124.3, 119.7, 119.6, 54.2, 41.9, 13.9.

(S)-9-(1-(p-tolyl)ethyl)-9H-fluorene (**3.3ai**)

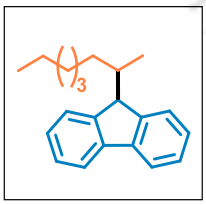


White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 53% Yield, 0.075 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 – 7.68 (m, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.0 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 4.27 (d, *J* = 4.3 Hz, 1H), 3.66 – 3.60 (m, 1H), 2.36 (s, 3H), 0.89 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 144.7, 141.8, 141.6, 141.4, 135.7, 128.8, 127.9, 127.0, 126.9, 126.8, 126.2, 125.7, 124.3, 119.7, 119.6, 54.3, 41.5, 21.1, 13.9.

(S)-9-(1-(4-methoxyphenyl)ethyl)-9H-fluorene (**3.3aj**)

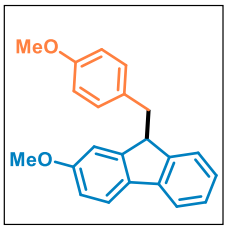
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 55% Yield, 0.083 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.72 (m, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.92 – 6.88 (m, 3H), 4.29 (d, *J* = 4.5 Hz, 1H), 3.86 (s, 3H), 3.70 – 3.62 (m, 1H), 0.94 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 146.6, 144.7, 141.8, 141.4, 136.7, 128.9, 127.0, 127.0, 126.8, 126.2, 125.7, 124.3, 119.7, 119.6, 113.5, 55.3, 54.4, 41.1, 14.2.

9-(octan-2-yl)-9H-fluorene (**3.3ak**)



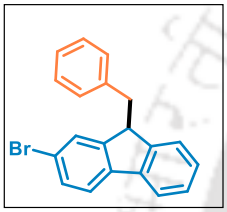
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 48% Yield, 0.067 g.^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 – 7.71 (m, 2H), 7.53 – 7.47 (m, 2H), 7.35 (td, *J* = 7.3, 3.3 Hz, 2H), 7.30 – 7.27 (m, 2H), 3.99 (d, *J* = 3.1 Hz, 1H), 2.43 – 2.33 (m, 1H), 1.49 – 1.27 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.60 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 145.8, 141.9, 141.5, 126.8, 126.7, 126.7, 126.5, 125.1, 124.4, 119.6, 119.5, 52.5, 37.2, 34.5, 31.9, 29.4, 27.9, 22.7, 15.7, 14.1.

(S)-2-methoxy-9-(4-methoxybenzyl)-9H-fluorene (**3.3al**)



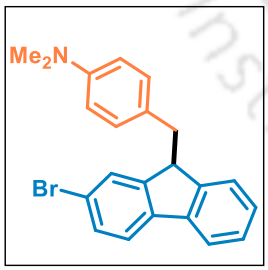
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:4). 78% Yield, 0.123 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.15 – 7.12 (m, 4H), 6.88 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 2.1 Hz, 1H), 4.12 (t, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.10 – 2.96 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 158.2, 148.7, 146.5, 140.8, 133.8, 131.8, 130.5, 127.1, 125.5, 124. 7, 120.5, 119.0, 113.7, 113.3, 110.5, 55.4, 55.3, 49.0, 39.3.

(S)-9-benzyl-2-bromo-9H-fluorene (**3.3am**)



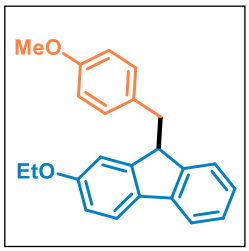
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 86% Yield, 0.145 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 9.1 Hz, 1H), 7.39 – 7.25 (m, 6H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 1H), 4.23 (t, *J* = 7.6 Hz, 1H), 3.16 – 3.09 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.8, 146.5, 139.8, 139.8, 139.2, 130.2, 129.5, 128.4, 128.2, 127.3, 127.1, 126.6, 124.9, 121.1, 120.4, 119.9, 48.7, 39.9.

(S)-4-((2-bromo-9H-fluoren-9-yl)methyl)-N,N-dimethylaniline (**3.3an**)



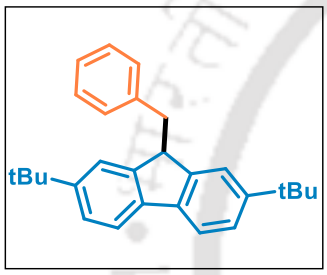
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:4). 88% Yield, 0.188 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 7.7 Hz, 2H), 4.18 (t, *J* = 7.6 Hz, 1H), 3.10 – 3.00 (m, 2H), 2.98 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.2, 146.9, 139.8, 139.8, 137.1, 130.1, 130.0, 128.2, 127.2, 127.0, 125.1, 121.0, 120.5 120.4, 119.8, 112.9, 49.2, 40.9, 39.0. HRMS (ESI) m/z: $[M + H]^+$ $C_{22}H_{20}BrN$: 378.0857; found 378.0851.

(S)-2-ethoxy-9-(4-methoxybenzyl)-9H-fluorene (**3.3ao**)



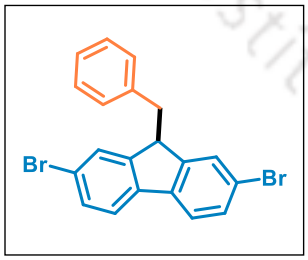
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:4). 80% Yield, 0.132 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 (t, *J* = 8.3 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.14 – 7.12 (m, 4H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.70 (s, 1H), 4.11 (t, *J* = 7.5 Hz, 1H), 4.00 – 3.95 (m, 2H), 3.81 (s, 3H), 3.08 – 2.99 (m, 2H), 1.39 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 158.2, 148.7, 146.4, 140. 9, 133.7, 131.9, 130.5, 127.0, 125.4, 124.7, 120.4, 118.9, 113.9, 113.7, 111.0, 63.6, 55.3, 48.9, 39.3, 14.9.

9-benzyl-2,7-di-tert-butyl-9H-fluorene (**3.3aq**)



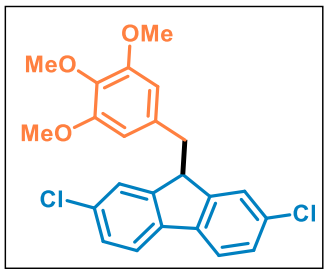
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 79% Yield, 0.145 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.27 – 7.24 (m, 4H), 7.11 (s, 2H), 4.14 (t, *J* = 7.8 Hz, 1H), 3.06 (d, *J* = 7.8 Hz, 2H), 1.28 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 146.9, 140.4, 138.2, 129.7, 128.3, 126.3, 124.0, 121. 9, 118.9, 49.0, 40.7, 34.8, 31.5.

9-benzyl-2,7-dibromo-9H-fluorene (**3.3ar**)



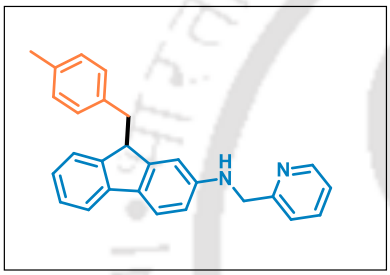
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 70% Yield, 0.144 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 4.20 (t, *J* = 7.6 Hz, 1H), 3.11 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.4, 138.8, 138.6, 130.5, 129.4, 128.5, 128.3, 126.8, 121.2, 120.9, 48.7, 39.7.

2,7-dichloro-9-(3,4,5-trimethoxybenzyl)-9H-fluorene (**3.3as**)



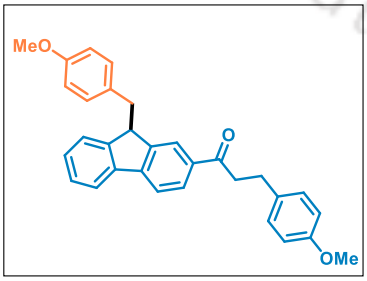
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:5). 75% Yield, 0.155 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.27 (s, 2H), 6.32 (s, 2H), 4.18 (t, *J* = 7.1 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 6H), 3.08 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.0, 148.0, 138.5, 136.8, 133.8, 132.7, 127.6, 125.4, 120.9, 106.6, 61.0, 56.1, 48.8, 40.0.

(R)-9-benzyl-N-(pyridin-2-ylmethyl)-9H-fluoren-2-amine (**3.3at**)



White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). 58% Yield, 0.105 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 4.5 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.18 – 7.15 (m, 1H), 7.10 – 7.03 (m, 6H), 6.64 (d, *J* = 8.1 Hz, 1H), 6.47 (s, 1H), 4.40 (s, 2H), 4.08 (t, *J* = 7.6 Hz, 1H), 3.01 (d, *J* = 7.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 149.2, 148.9, 147.3, 146.0, 141.5, 136.9, 136.7, 135.7, 131.2, 129.5, 128.9, 126.9, 124.7, 124.6, 122.1, 121.7, 120.6, 118.4, 112.5, 109.5, 49.4, 48.7, 39.9, 21.1.

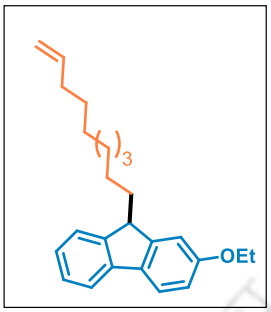
(R)-1-(9-(4-methoxybenzyl)-9H-fluoren-2-yl)-3-(4-methoxyphenyl)propan-1-one (**3.3au**)



White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:5). 65% Yield, 0.145 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 2H), 7.76 (s, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 6.12 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J*

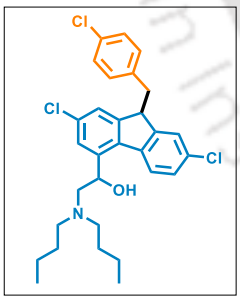
= 8.5 Hz, 2H), 4.23 (t, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.21 (t, *J* = 7.6 Hz, 2H), 3.14 – 3.06 (m, 2H), 3.03 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.3, 158.3, 158.0, 148.2, 146.9, 145.6, 139.6, 135.2, 133.4, 131.3, 130.5, 129.4, 127.9, 127.7, 127.4, 125.1, 124.8, 120.8, 119.7, 113.9, 113.7, 55.3, 55.2, 49.0, 40.7, 39.0, 29.5.

(R)-2-ethoxy-9-(non-8-en-1-yl)-9H-fluorene (**3.3av**)



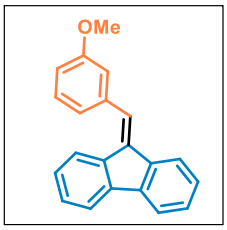
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 58% Yield, 0.097 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.97 (s, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 5.75 – 5.67 (m, 1H), 4.89 (d, *J* = 17.1 Hz, 1H), 4.83 (d, *J* = 10.0 Hz, 1H), 4.02 (q, *J* = 6.9 Hz, 2H), 3.83 (t, *J* = 5.7 Hz, 1H), 1.95 – 1.86 (m, 4H), 1.37 (t, *J* = 6.9 Hz, 3H), 1.29 – 1.23 (m, 2H), 1.16 – 1.13 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 149.5, 147.1, 141.2, 139.2, 134.1, 126.8, 125.6, 124.1, 120.4, 118.9, 114.1, 113.1, 110.9, 63.7, 47.5, 33.8, 33.2, 29.9, 29.4, 29.3, 29.1, 28.9, 25.5, 14.9. HRMS (ESI) m/z: $[M + H]^+$ $C_{25}H_{32}O$: 349.2531; found 349.2531.

2-(dibutylamino)-1-((S)-2,7-dichloro-9-(4-chlorobenzyl)-9H-fluoren-4-yl)ethan-1-ol (**3.3aw**)



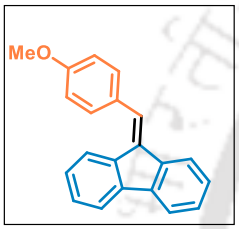
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.62 – 7.57 (m, 1H), 7.30 (d, *J* = 7.1 Hz, 1H), 7.22 – 7.14 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.35 – 5.31 (m, 1H), 4.22 – 4.05 (m, 1H), 3.12 – 3.08 (m, 2H), 2.84 – 2.73 (m, 1H), 2.70 – 2.63 (m, 2H), 2.54 – 2.43 (m, 3H), 1.49 – 1.47 (m, 4H), 1.41 – 1.30 (m, 4H), 1.26 – 1.21 (m, 1H), 0.98 – 0.94 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 136.6, 136.4, 134.7, 133.4, 132.6, 132.4, 130.70, 128.45, 128.3, 127.6, 125.2, 124.9, 124.1, 123.9, 123.6, 121.0, 65.6, 60.0, 53.5, 48.2, 39.4, 39.2, 29.1, 20.6, 14.0. HRMS (ESI) m/z: $[M + H]^+$ $C_{30}H_{34}ONCl_2$: 530.1784; found 530.1772.

9-(3-methoxybenzylidene)-9H-fluorene (**3.4a**)



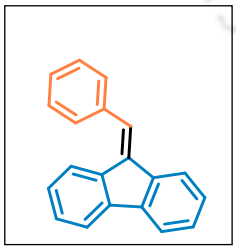
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 65% Yield, 0.092 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.71 (dd, *J* = 7.5, 3.2 Hz, 2H), 7.66 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.28 (m, 4H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.12 (s, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.94 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 141.1, 139.7, 138.9, 136.6, 135.5, 130.9, 129.1, 128.3, 127.9, 127.4, 126.9, 126.6, 124.2, 120.1, 119.7, 119.6, 113.9, 55.4.

9-(4-methoxybenzylidene)-9H-fluorene (**3.4b**)



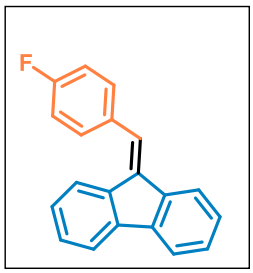
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 65% Yield, 0.092 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.76 – 7.73 (m, 3H), 7.68 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 141.1, 139.7, 139.0, 136.6, 135.5, 130.9, 129.1, 128.3, 127.9, 127.4, 126.9, 126.6, 124.2, 120.1, 119.7, 119.6, 114.0, 55.4.

9-benzylidene-9H-fluorene (**3.4c**)



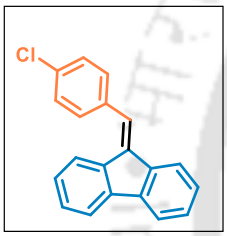
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 63% Yield, 0.080 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.72 – 7.69 (m, 4H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.30 (m, 4H), 7.04 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 139.5, 139.2, 136.9, 136.6, 136.5, 129.3, 128.5, 128.2, 128.0, 127.3, 127.0, 126.7, 124.4, 120.2, 119.7, 119.6.

9-(4-fluorobenzylidene)-9H-fluorene (**3.4d**)



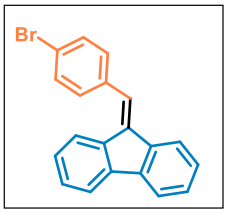
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 55% Yield, 0.075 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.65 (s, 1H), 7.61 – 7.56 (m, 3H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.18 (t, *J* = 8.5 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5 (d, *J* = 247.5 Hz), 141.3, 139.3 (d, *J* = 21.5 Hz), 136.7, 136.4, 132.8 (d, *J* = 3.6 Hz), 131.1, 131.1, 128.7, 128.3, 127.0, 126.7, 126.0, 124.2, 120.2, 119.8, 119.6, 115.7, 115.6.

9-(4-chlorobenzylidene)-9H-fluorene (**3.4e**)



Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 63% Yield, 0.091 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.62 (s, 1H), 7.56 – 7.54 (m, 3H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.4, 139.3, 139.2, 137.1, 136.3, 135.3, 133.9, 130.7, 128.8, 128.8, 128.4, 127.1, 126.8, 125.7, 124.3, 120.3, 119.8, 119.7.

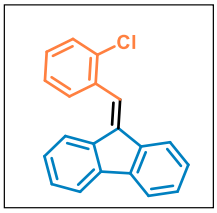
9-(4-bromobenzylidene)-9H-fluorene (**3.4f**)



Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 66% Yield, 0.109 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.64 – 7.57 (m, 3H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.10 (t, *J* = 8.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ

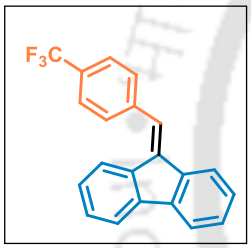
141.4, 139.3, 137.1, 136.3, 135.8, 131.8 131.0, 128.8, 128.5, 127.1, 126.8, 125.7, 124.3, 122.1, 120.3, 119.9, 119.7.

9-(2-chlorobenzylidene)-9H-fluorene (**3.4g**)



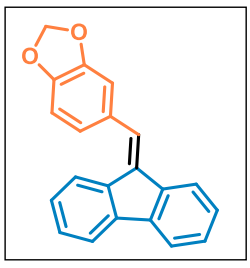
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 60% Yield, 0.086 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.65 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.34 (m, 6H), 7.08 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.4, 139.4, 139.1, 137.5, 136.4, 135.4, 134.1, 131.5, 129.8, 129.5, 128.8, 128.6, 127.1, 126.8, 126.6, 124.4, 124.0, 120.6, 119.8, 119.7.

9-(4-(trifluoromethyl)benzylidene)-9H-fluorene (**3.4h**)



Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 60% Yield, 0.097 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.75 – 7.72 (m, 6H), 7.66 (s, 1H), 7.49 – 7.41 (m, 2H), 7.38 – 7.35 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.5, 140.7, 139.4, 139.1, 137.9, 136.1, 129.9 (q, *J* = 32.5 Hz), 129.6, 129.1, 128.7, 127.4, 127.2, 126.9, 125.5 (q, *J* = 3.7 Hz), 125.0, 124.2 (q, *J* = 270 Hz), 120.4, 119.9, 119.7.

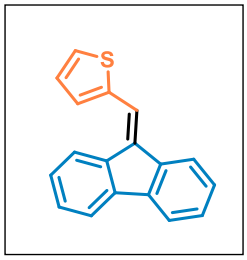
5-((9H-fluoren-9-ylidene)methyl)benzo[d][1,3]dioxole (**3.4i**)



Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 50% Yield, 0.074 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 3H), 7.62 (s, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.17 – 7.09 (m,

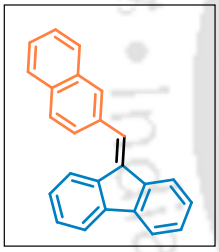
3H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.07 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.8, 147.5, 141.2, 139.6, 139.0, 136.4, 135.9, 130.6, 128.4, 128.1, 127.1, 126.9, 126.7, 124.4, 123.5, 120.1, 119.7, 119.6, 109.6, 108.5, 101.3.

2-((9H-fluoren-9-ylidene)methyl)thiophene (**3.4j**)



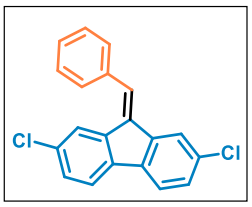
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 46% Yield, 0.060 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.72 (m, 2H), 7.64 – 7.55 (m, 4H), 7.54 – 7.51 (m, 3H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.0, 138.7, 137.9, 136.6, 135.7, 134.7, 133.1, 132.6, 129.9, 129.1, 128.8, 128.8, 128.7, 128.4, 124.5, 120.7, 120.6.

9-(naphthalen-2-ylmethylene)-9H-fluorene (**3.4k**)



Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 55% Yield, 0.084 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.96 – 7.93 (m, 2H), 7.92 – 7.85 (m, 3H), 7.80 – 7.74 (m, 3H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.3, 139.6, 139.2, 136.7, 136.6, 134.4, 133.4, 133.0, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 127.3, 127.2, 127.0, 126.7, 126.7, 126.5, 126.4, 124.4, 120.3, 119.8, 119.6.

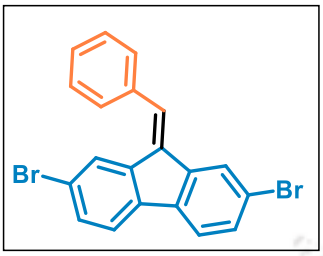
9-benzylidene-2,7-dichloro-9H-fluorene (**3.4l**)



Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 49% Yield, 0.079 g. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 1.8 Hz, 1H), 7.70 (s,

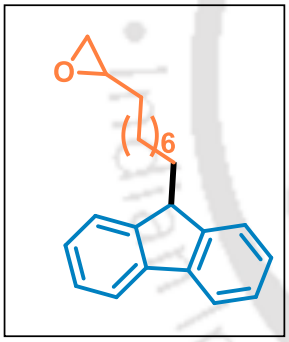
1H), 7.60 – 7.53 (m, 4H), 7.53 – 7.43 (m, 4H), 7.34 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.28 (dd, *J* = 8.1, 1.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.7, 137.9, 136.6, 135.7, 134.7, 133.2, 132.6, 129.9, 129.4, 129.1, 128.8, 128.8, 128.7, 128.4, 124.6, 120.7, 120.6.

9-benzylidene-2,7-dibromo-9H-fluorene (**3.4m**)



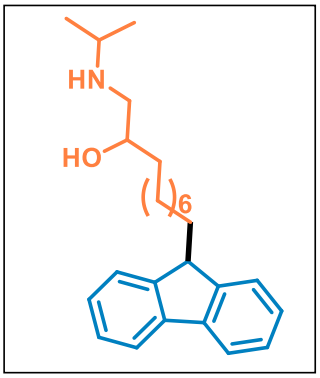
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 70% Yield, 0.143 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.73 – 7.71 (m, 2H), 7.62 – 7.55 (m, 4H), 7.55 – 7.50 (m, 3H), 7.47 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.1, 139.1, 138.0, 137.0, 135.7, 134.5, 131.5, 131.2, 130.0, 129.2, 128.9, 128.8, 127.4, 123.7, 121.2, 121.0, 120.9, 120.8.

2-(8-(9H-fluoren-9-yl)octyl)oxirane (**3.6**)



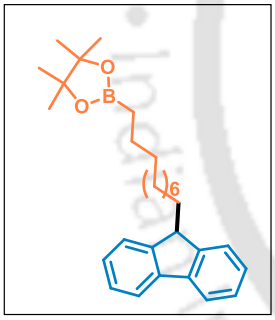
Gummy yellow liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 85% Yield, 0.136 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 4.00 (t, *J* = 5.8 Hz, 1H), 2.93 – 2.90 (m, 1H), 2.77 (t, *J* = 4.4 Hz, 1H), 2.48 (dd, *J* = 4.9, 2.7 Hz, 1H), 2.04 – 2.01 (m, 2H), 1.55 – 1.51 (m, 2H), 1.48 – 1.37 (m, 3H), 1.32 – 1.16 (m, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 141.1, 126.8, 126.8, 124.3, 119.8, 52.4, 47.5, 47.2, 33.1, 32.5, 29.9, 29.5, 29.4, 29.3, 25.9, 25.6. HRMS (ESI) m/z: $[M + H]^+$ $C_{25}H_{32}O$: 321.2218; found 321.2247.

10-(9H-fluoren-9-yl)-1-(isopropylamino)decan-2-ol (**3.7**)



Gummy brown liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). 88% Yield, 0.083 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 3.96 (t, *J* = 5.7 Hz, 1H), 3.57 – 3.44 (m, 1H), 2.83 – 2.68 (m, 2H), 2.45 – 2.26 (m, 1H), 2.07 – 1.90 (m, 2H), 1.72 (bs, 2H) 1.48 – 1.30 (m, 4H), 1.25 – 1.13 (m, 10H), 1.16 – 1.05 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 141.1, 126.8, 126.8, 124.4, 119.8, 70.0, 52.8, 48.7, 47.5, 35.2, 33.1, 29.9, 29.7, 29.5, 29.3, 25.7, 25.7, 23.4, 23.0. HRMS (ESI) m/z: $[M + H]^+$ $C_{26}H_{37}NO$: 380.2953; found 380.2953.

2-(10-(9H-fluoren-9-yl)decyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3.8**)



Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:5). 70% Yield, 0.151 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 3.96 (t, *J* = 5.8 Hz, 1H), 2.07 – 1.89 (m, 2H), 1.39 – 1.34 (m, 2H), 1.28 – 1.16 (m, 25H), 0.89 – 0.84 (m, 1H), 0.75 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 141.1, 126.8, 126.7, 124.3, 119.7, 82.8, 47.5, 33.1, 32.4, 30.0, 29.6, 29.5, 29.4, 29.4, 25.7, 24.8, 24.0. HRMS (ESI) m/z: $[M + H]^+$ $C_{26}H_{41}BO_2$: 433.3278; found 433.3238.

3.8. NMR spectra of some representative compounds:

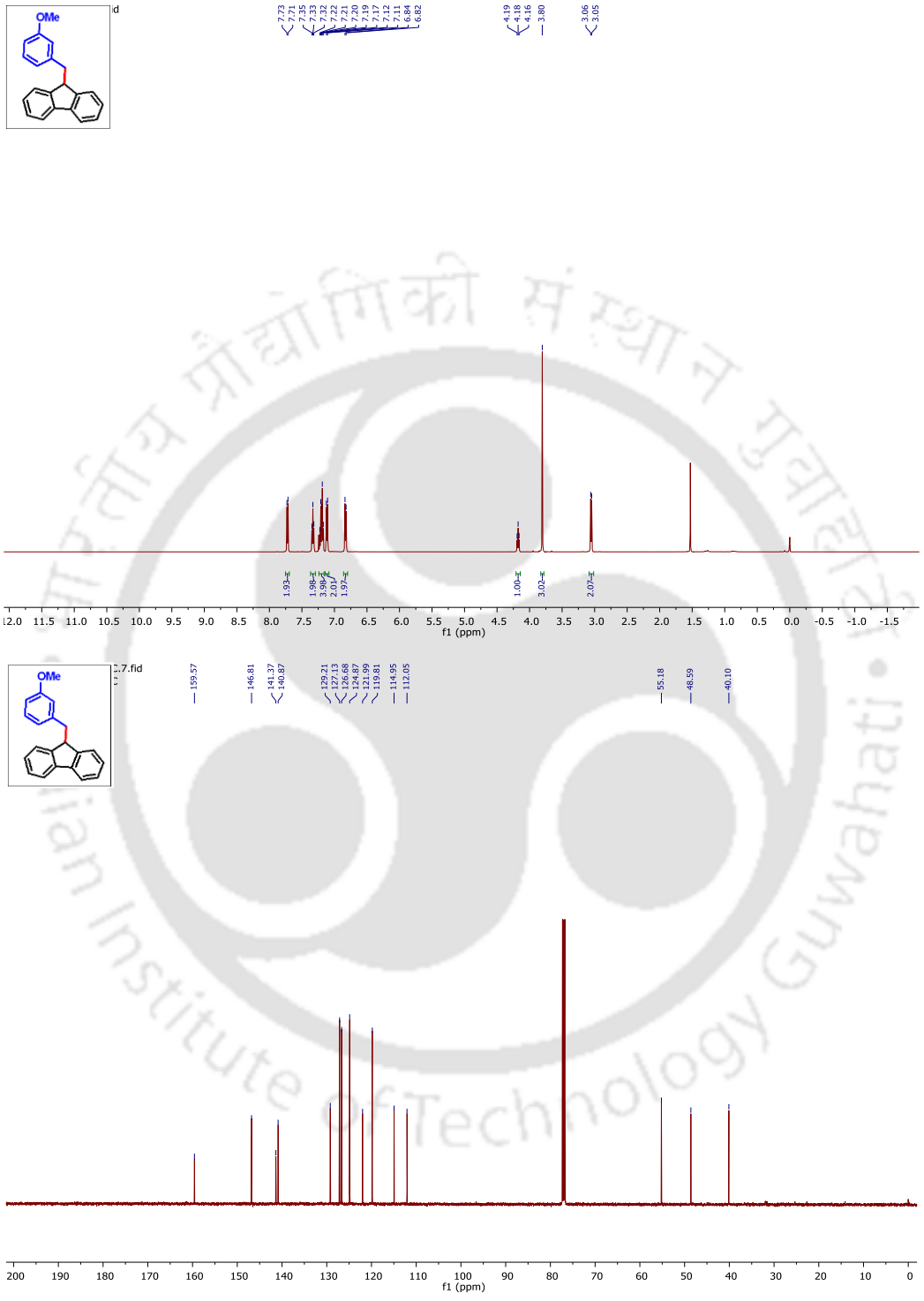


Fig 3.4: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 9-(3-methoxybenzyl)-9H-fluorene (**3.3a**) in $CDCl_3$.

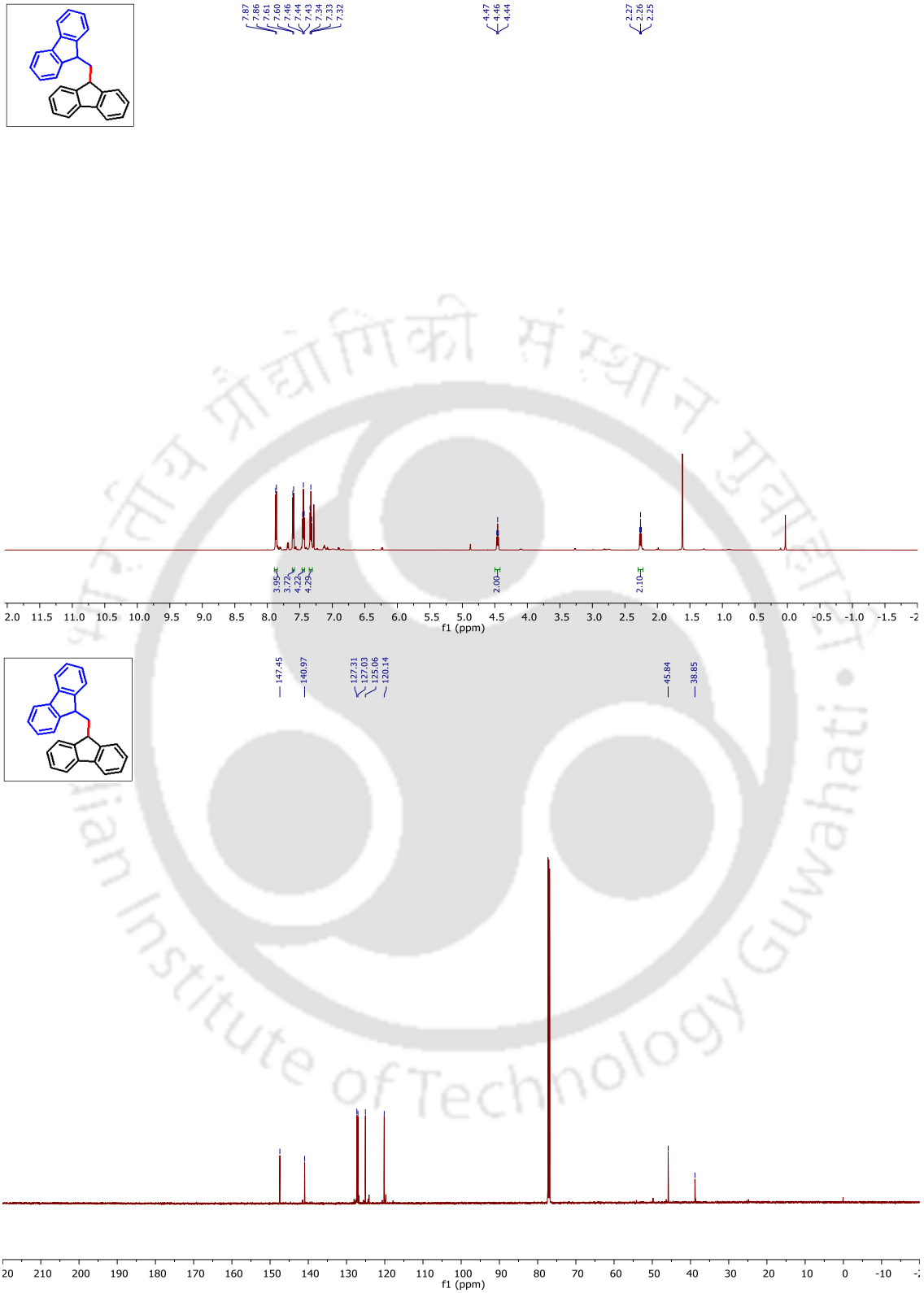


Fig 3.5: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of di(9H-fluoren-9-yl)methane (**3.3w**) in $CDCl_3$.

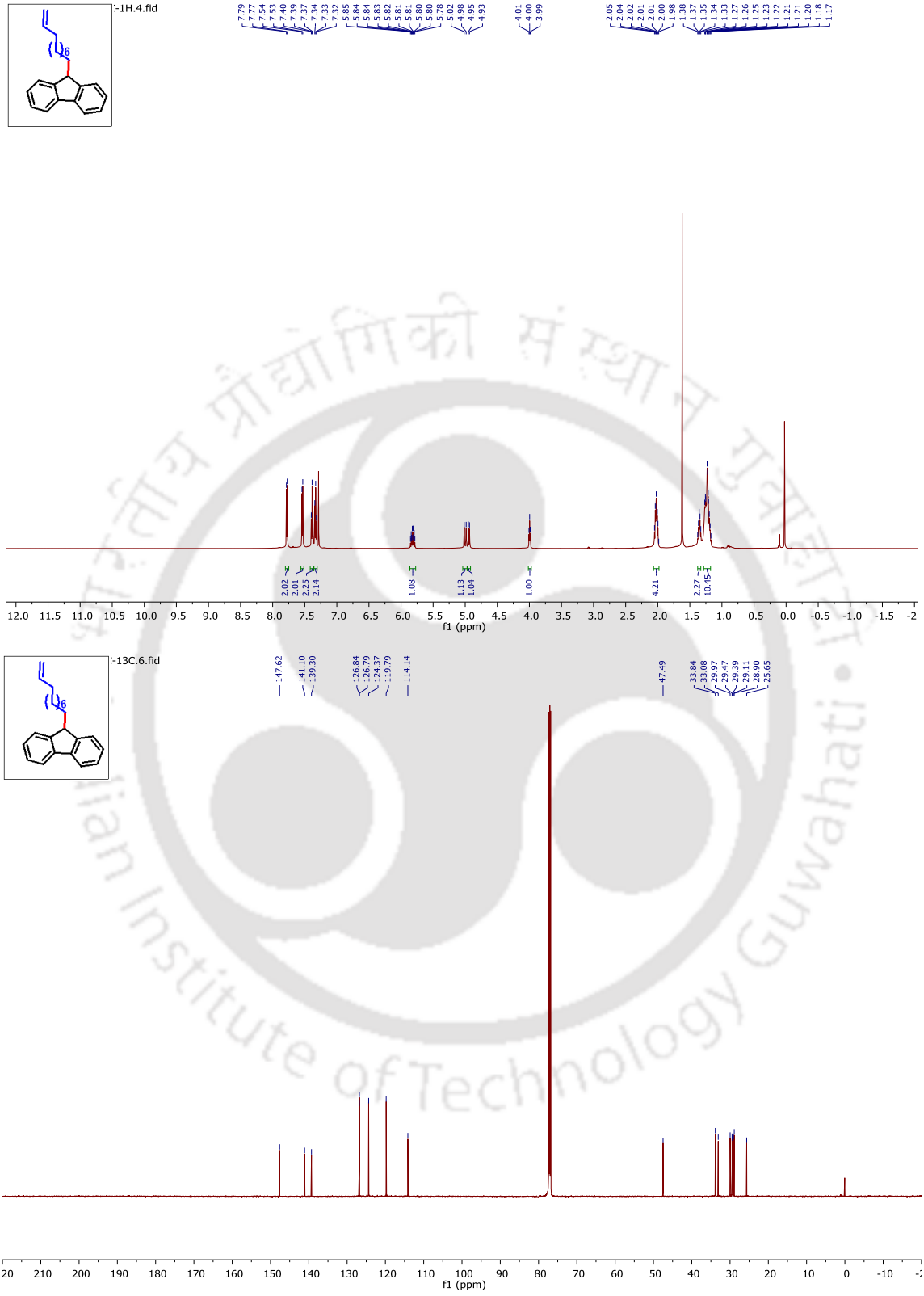


Fig 3.6: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(dec-9-en-1-yl)-9H-fluorene (**3.3ad**) in $CDCl_3$.

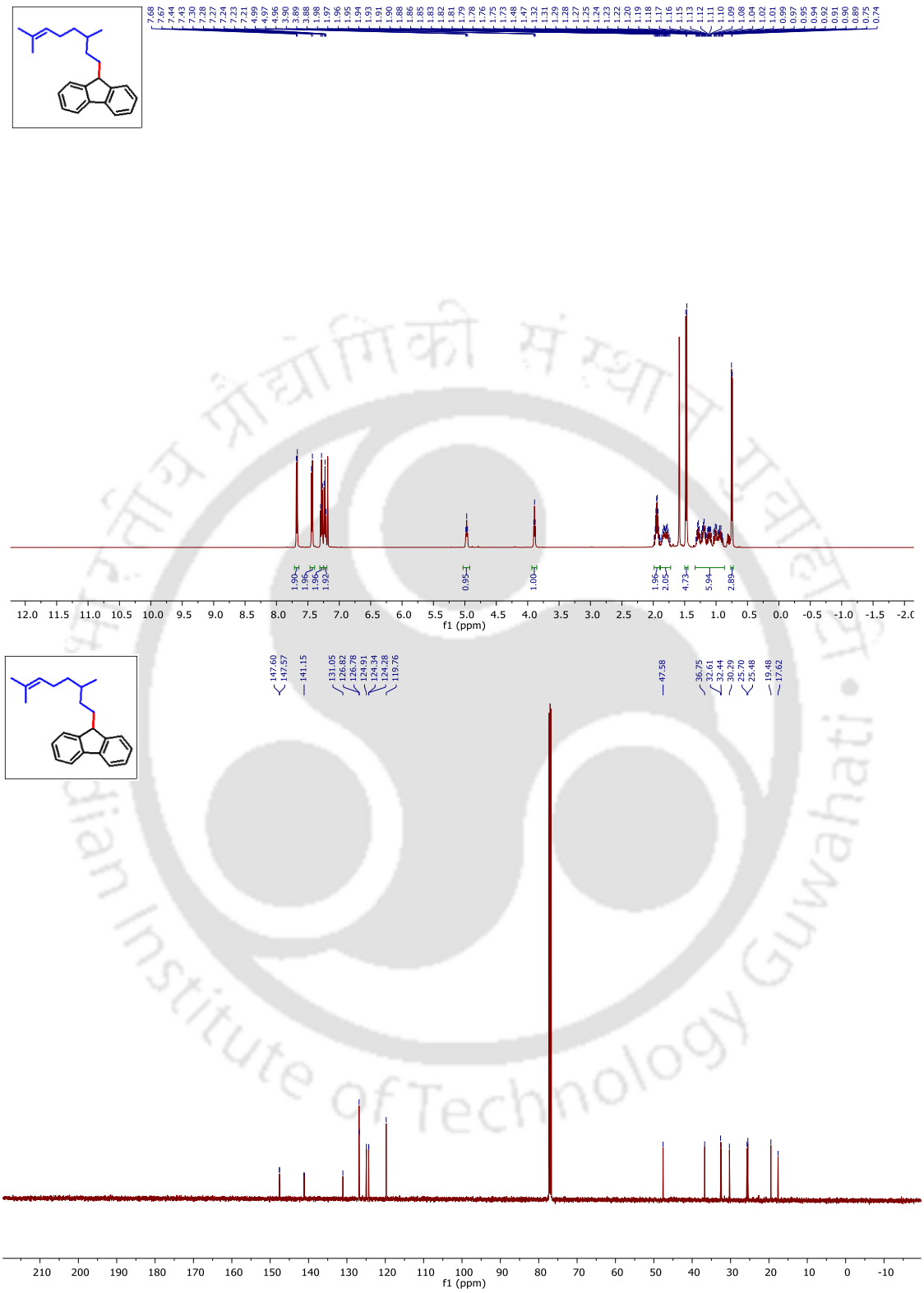


Fig 3.7: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 9-(3,7-dimethyloct-6-en-1-yl)-9H-fluorene (**3.3af**) in $CDCl_3$

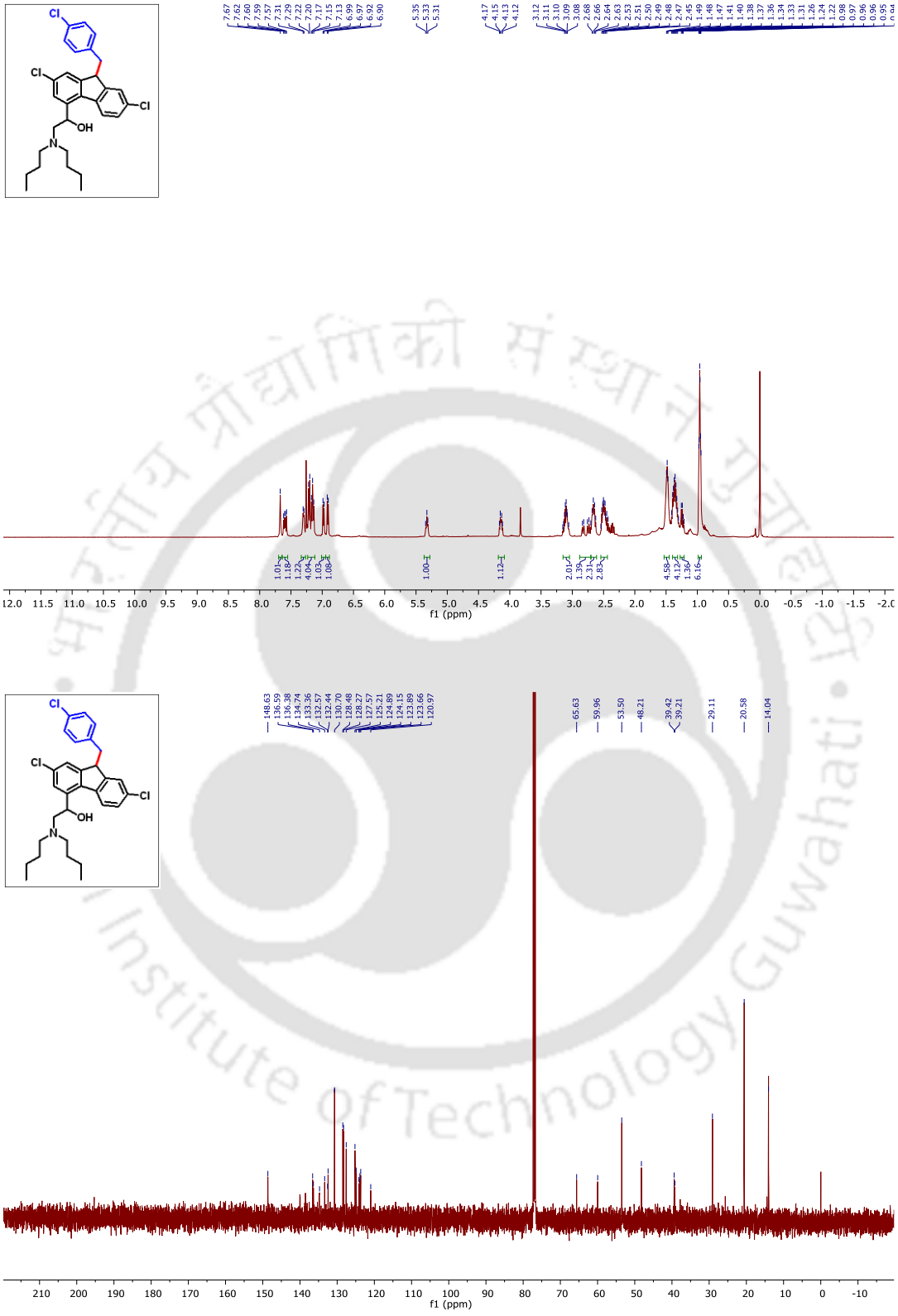


Fig 3.8: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 2-(dibutylamino)-1-((S)-2,7-dichloro-9-(4-chlorobenzyl)-9H-fluoren-4-yl)ethan-1-ol (**3.3aw**) in $CDCl_3$.

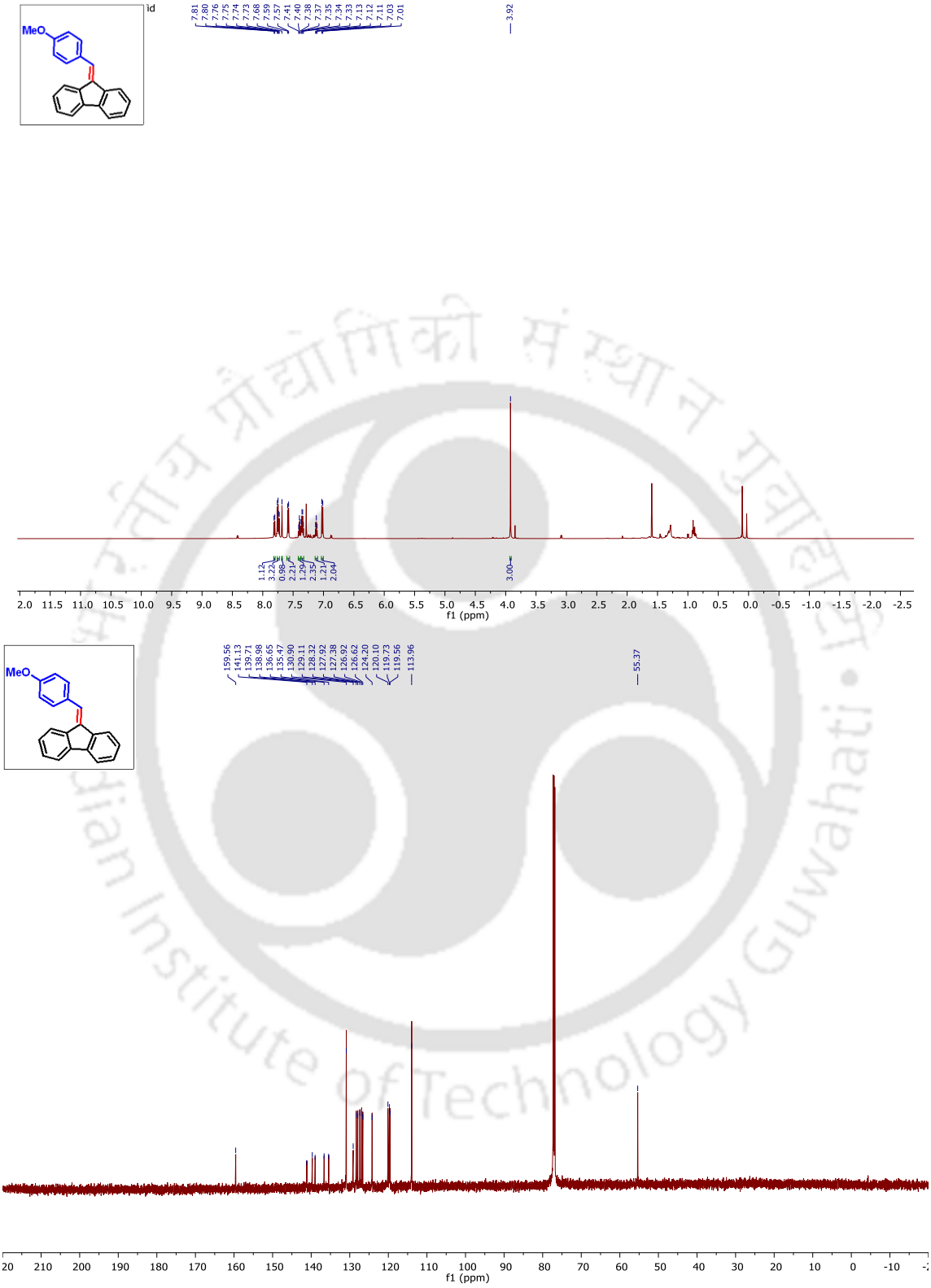


Fig 3.9: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(4-methoxybenzylidene)-9H-fluorene (**3.4b**) in $CDCl_3$.

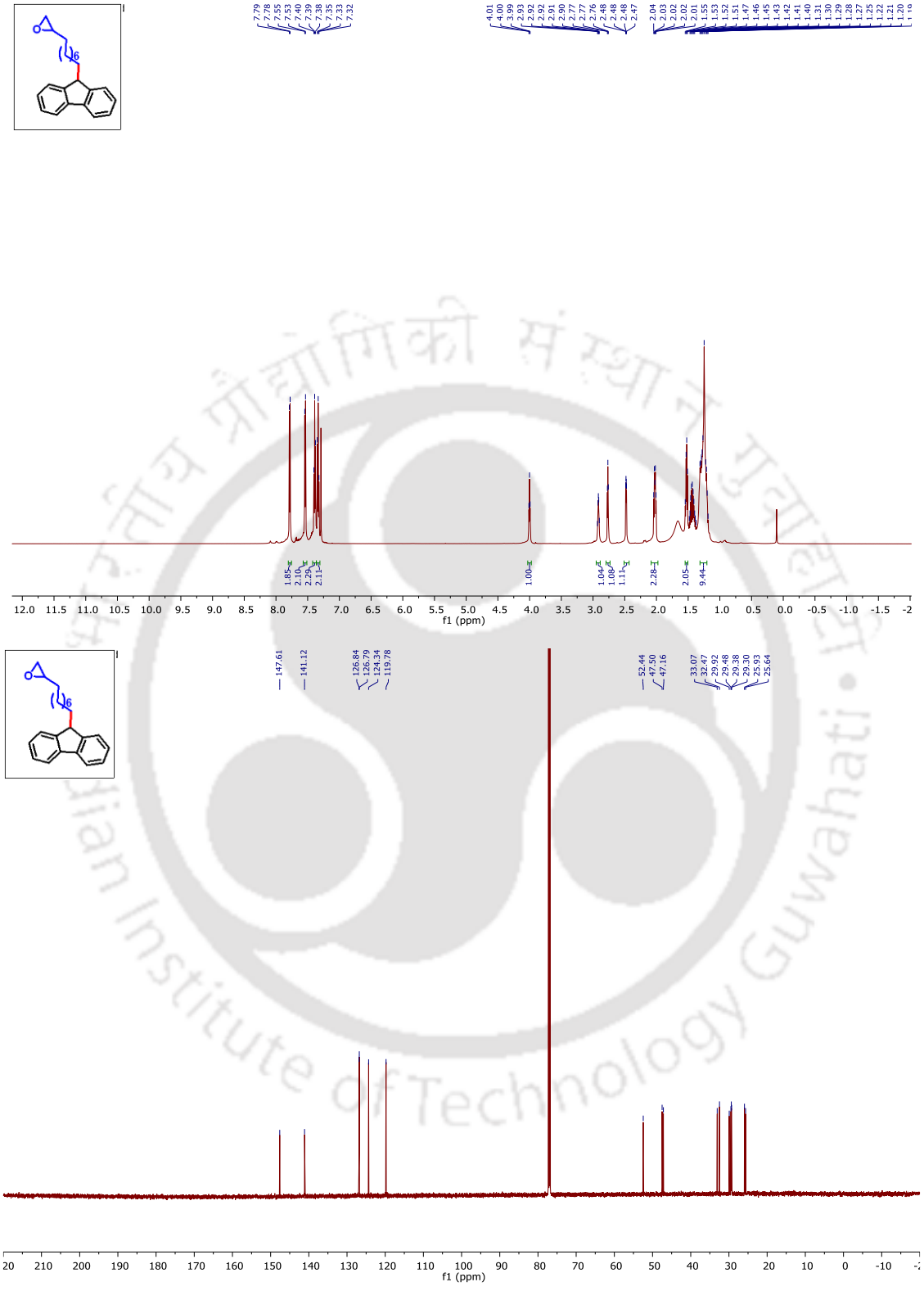


Fig 3.10: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 2-(8-(9H-fluoren-9-yl)octyl)oxirane (**3.6**) in $CDCl_3$.

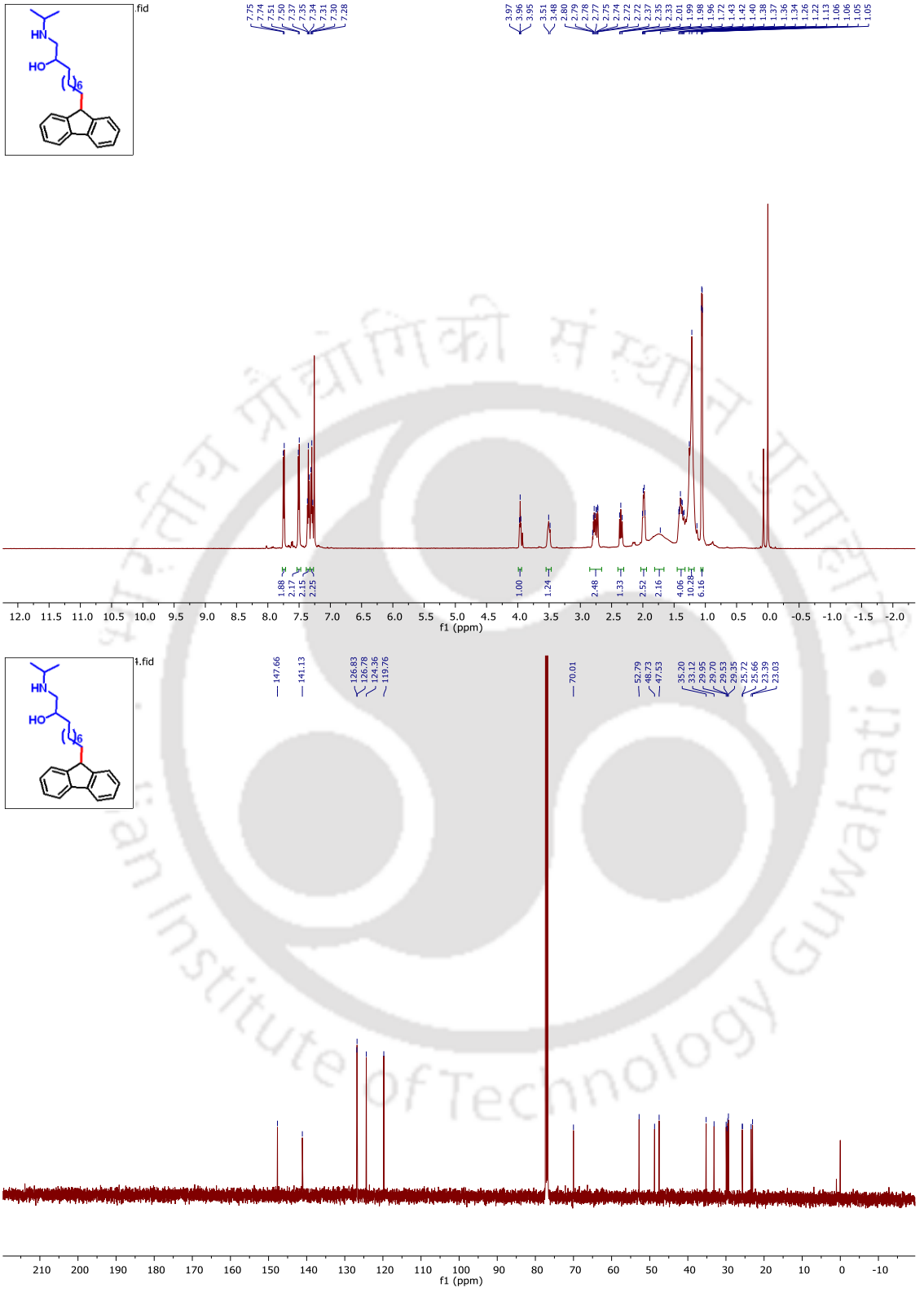


Fig 3.11: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 10-(9H-fluoren-9-yl)-1-(isopropylamino)decan-2-ol (**3.7**) in $CDCl_3$.

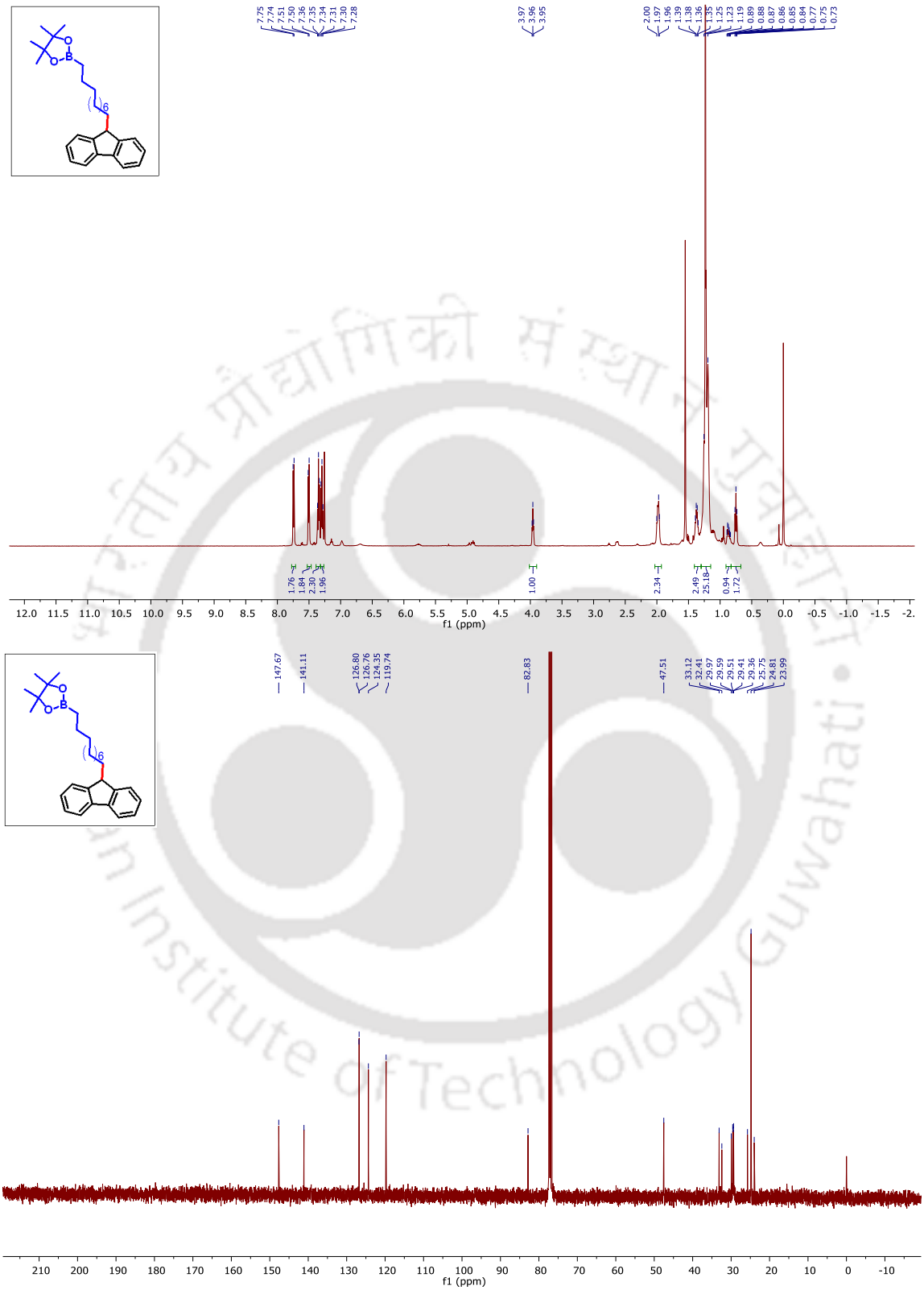
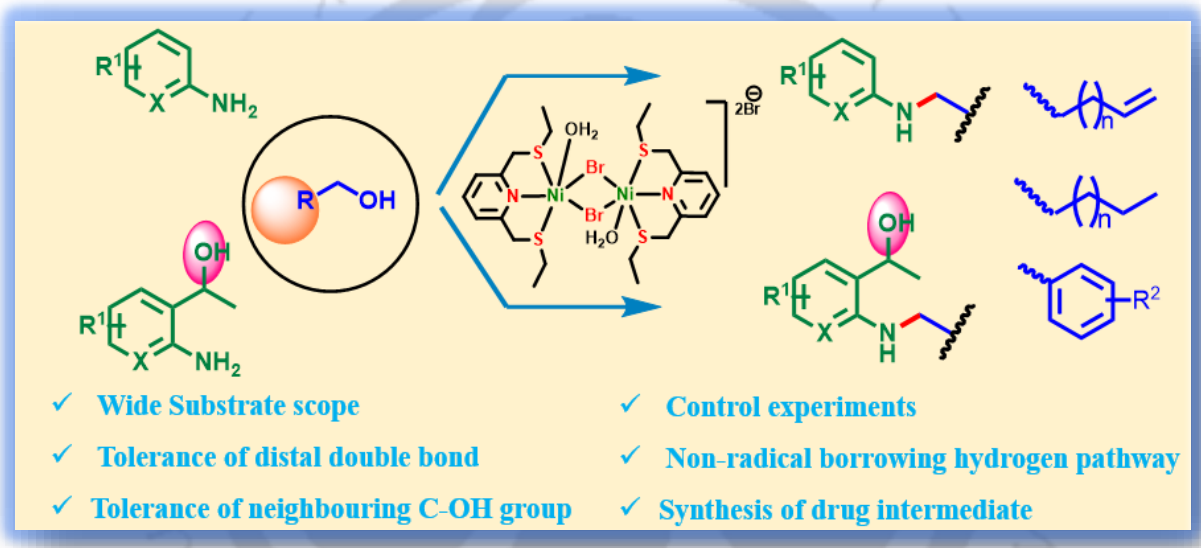


Fig 3.12: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 2-(10-(9H-fluoren-9-yl)decyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3.8**) in $CDCl_3$.

Chapter 4

Unveiling the Potential of SNS-Ni Complex for Establishing C-N Bonds: An Approach Toward Chemoselectivity



4.1. Introduction

This chapter discusses the further application of SNS-Ni complex for the coupling of amines with alcohol derivatives. In this work, the protocol shows efficiency toward the reactivity of amines over other potential reacting center. The details of the work will be discussed in the upcoming sections

Research on the sustainable construction of C-N bonds is crucial since these bonds are found in a variety of fungicides, medicines, agrochemicals, and compounds used in material science and the dye industry (Figure **4.1**). [1,2] However, the conventional process of creating a C-N bond from amines uses organic halides, produces hazardous waste, and compromises selectivity by over-alkylating primary amines into tertiary or quarternary amines.[3]

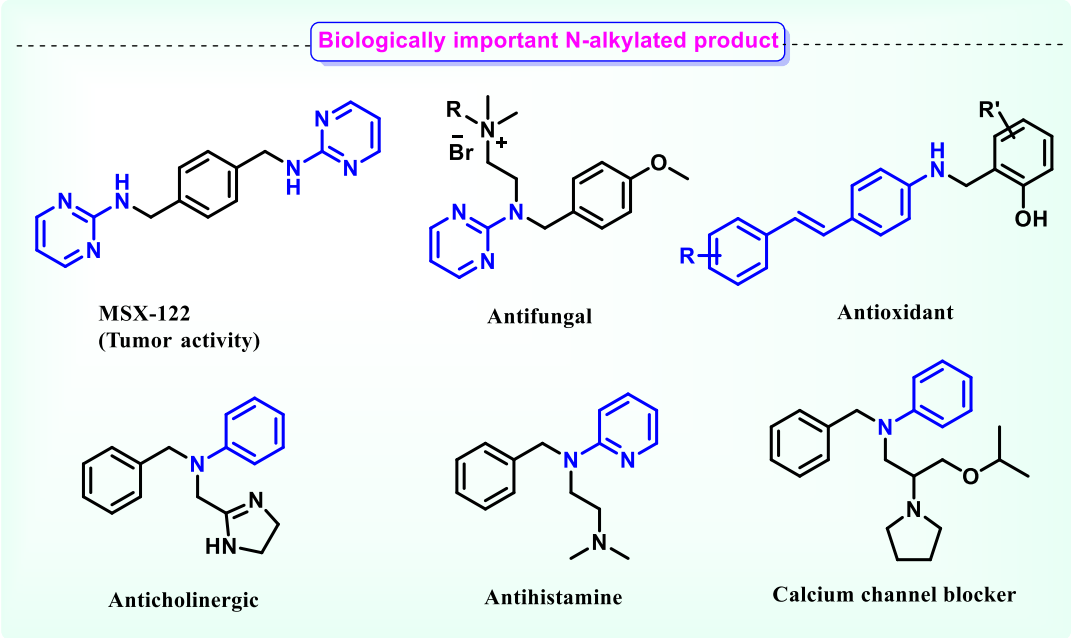


Figure 4.1: Important biological compounds containing C-N bonds

In contrast, various efficient catalytic routes were developed such as Buchwald-Hartwig[4] and Ullmann coupling,[5] nevertheless, the process required non-renewable starting materials along with the generation of a substantial amount of side products or wastes. On the other hand, alcohols are used as a renewable starting material in Borrowing Hydrogen mediated C-N bond formation, which involves the loss of water as a clean byproduct that makes the process green.[6] Several groups understood and applied the approach by employing various noble metal-based complexes.[7] However, the use of cheap, earth-abundant, and less toxic 3d-metals

based catalytic systems is always highly demanding and has proven to be a sustainable application.[8] Hence, efforts were devoted to the development of 3d-metal-based catalytic systems having equal potential to carry out such chemical transformations.

4.2. Literature Survey

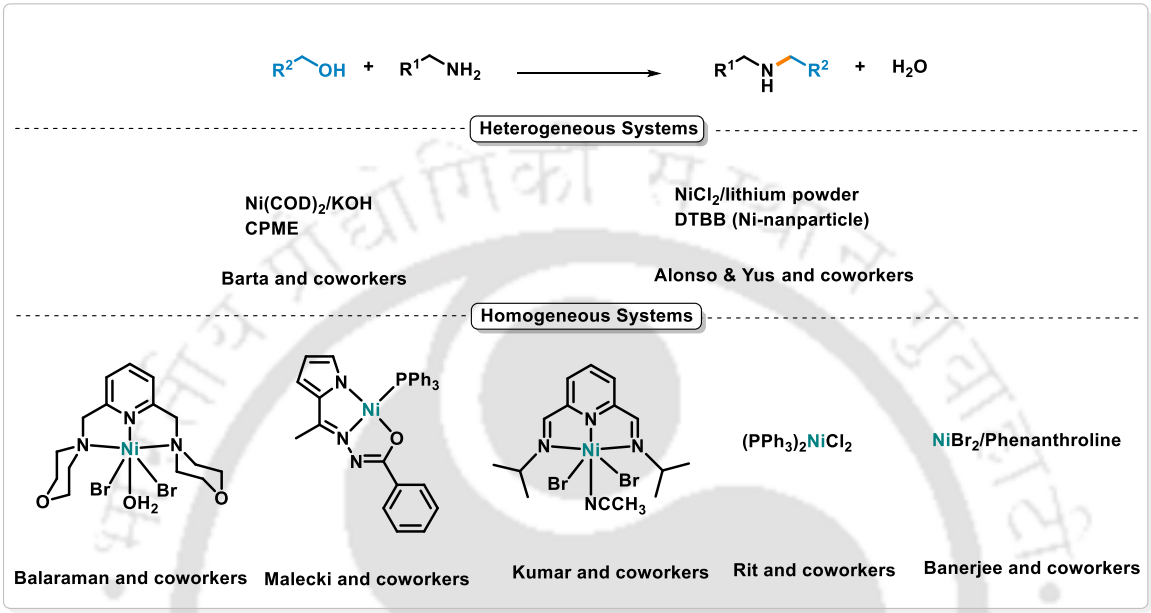


Figure 4.2: Previous reports on Ni-catalysed N-alkylation

The literature survey on N-alkylation of amine with alcohol derivatives was discussed in details in Chapter **1** section **1.5.1**. However, in this section, the work on nickel is again brought into light. Nickel, which is also one such abundant and cheap element in the periodic table has recently been explored by various groups (figure **4.2**).[12] Banerjee and coworkers[13a] reported the first Ni-catalysed N-alkylation reactions using 10 mol% of $NiBr_2$ and 20 mol% of the ligand. Adhikari and coworkers[13b] developed a non-innocent ligand-decorated Ni-complex (7 mol%) for N-alkylating anilines with various alcohols. Later on, Maleki and coworkers[13c] demonstrated NNO-Ni complexes (4 mol%) and allowed the coupling of diverse amines, including heteroaromatic amines. Very recently, Rit and coworkers reported N-alkylation of amines using commercially available $(PPh_3)_2NiCl_2$. Previously, a few heterogenous Ni-catalyst systems were also investigated. The coupling of alcohols with amines was established by Yus et al. [13d] using nickel nanoparticles as a heterogeneous catalyst. Furthermore, the nickel nanoparticle for monoalkylation of amines using alcohols as a substrate was described by Barta and chis group.[13e]

4.3. Result and Discussions

The present chapter aims to demonstrates the application of SNS-Ni complexes [14] for the N-alkylation of amines with various alcohols including benzylic, heterocyclic as well as C4-C16 aliphatic alcohols. Amines are alkylated with various fatty alcohols keeping the distal unsaturation intact. Further, the chapter also describes investigating the potential of the developed catalyst for selective N-alkylation over possible C-alkylation.

In the present study, three SNS-Ni complexes are employed for the investigation of N-alkylation of amine with alcohol (figure **4.3**). The cat. **2** was newly synthesized which is fully characterized using various techniques such as mass spectrometry, and single crystal XRD and the synthetic procedure and spectroscopic analysis is described in the experimental section.

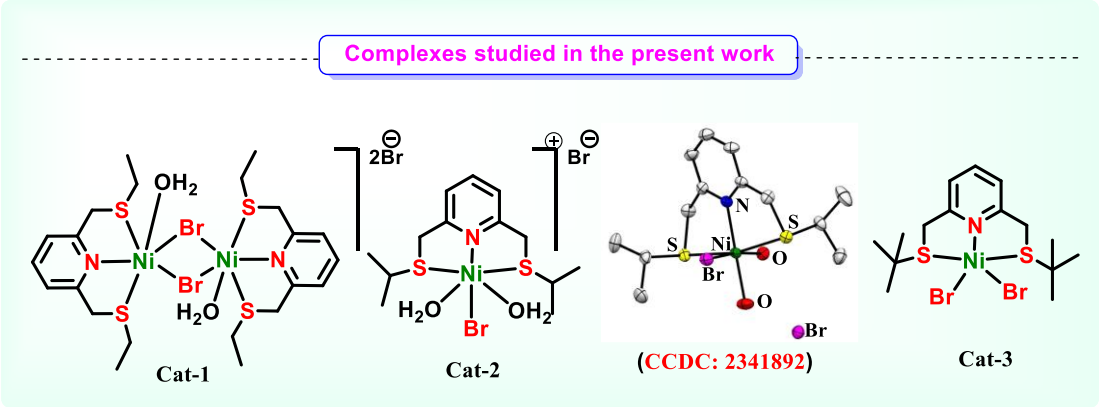
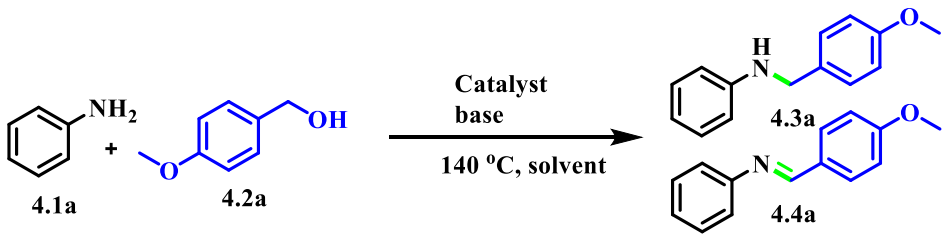


Figure 4.3: Catalyst used in the present work

After the synthesis of SNS-Ni complexes, the investigation was carried forward to obtain the optimized reaction conditions by applying 4-methoxybenzyl alcohol and aniline as model substrates. Initially, **4.1a** and **4.2a** were used in a 1:2 ratio in the presence of 3 mol% of the Ni-SNS catalyst and 1 equivalent of KO^{t}Bu in a toluene medium at 140 °C for 24 h (table **4.1** entry **1**). The reaction results in 73% (NMR yield) N-alkylated product (**4.3a**) and 25% of imine product (**4.4a**). Next, changing the nature of the base (KOH), results in **4.3a** in 65% and **4.4a** of 30% NMR yield (table **4.1** entry **2**). On further changing the base to NaO^{t}Bu, NaOH, K_2CO_3, and Cs_2CO_3, the yield of the product was not improved (table **4.1** entries **3**-**6**). Pleasingly upon increasing the amount of alcohol from 1.2 to 1.5 equivalent results in 100% of the **4.3a** (90%isolated) (table **4.1** entry **7**). Solvent optimization shows that toluene is the best candidate over the xylene in our catalytic system (table 4.1 entry 9). Lowering the catalyst

Table 4.1: Investigation of Optimization Condition



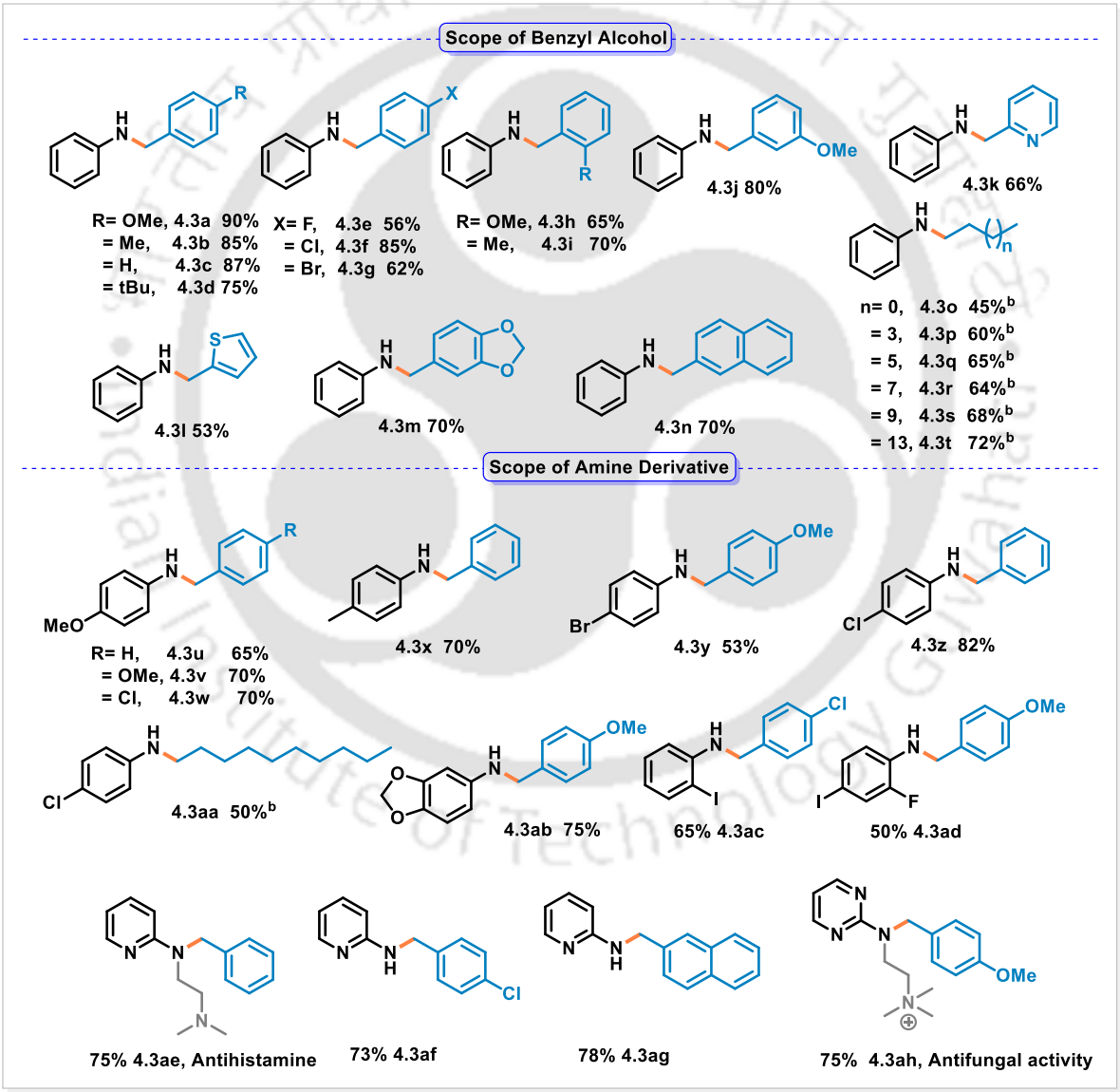
Entry	4.1a (in mmol)	4.2a (in mmol)	Cat (mol%)	Base (mmol)	Solvent	4.3a in %	4.4a in %
1	1	1.0	Cat. 1 (3)	KO^{t}Bu (1)	Tol	55	18
2	1	1.2	Cat. 1 (3)	KO^{t}Bu (1)	Tol	73	25
3	1	1.2	Cat. 1 (3)	KOH (1)	Tol	65	30
4	1	1.2	Cat. 1 (3)	NaO^{t}Bu (1)	Tol	trace	25
5	1	1.2	Cat. 1 (3)	NaOH(1)	Tol	trace	20
6	1	1.2	Cat. 1 (3)	K_2CO_3(1)	Tol	-	-
7	1	1.2	Cat. 1 (3)	Cs_2CO_3(1)	Tol	trace	-
8	1	1.5	Cat. 1 (3)	KO^{t}Bu (1)	Tol	100 (90)	-
9	1	1.5	Cat. 1 (1.5)	KO^{t}Bu (1)	Tol	75	5
10	1	1.5	Cat. 1 (3)	KO^{t}Bu (1)	Xylene	56	41
11	1	1.5	Cat. 1 (3)	KO^{t}Bu (1)	DMSO,DMF, MeOH,EtOH	trace	
12	1	1.5	Cat. 2 (6)	KO^{t}Bu (1)	Tol	95	trace
13	1	1.5	Cat. 3 (6)	KO^{t}Bu (1)	Tol	70	25
14	1	1.5	$NiBr_2$	KO^{t}Bu (1)	Tol	15	trace
15	1	1.5	-	KO^{t}Bu (1)	Tol	<20	trace
16	1	1.5	Cat. 1 (3)	-	Tol	trace	-
17	1	1.5	"	KO^{t}Bu (0.75)	Tol	68	32
18[b]	1	1.5	"	KO^{t}Bu (1)	Tol	<30	trace

[a]Reaction Condition: **1a** (0.5 mmol), **2a** (0.6 – 0.75 mmol), Cat. **1** – **3** (1 – 6 mol%), base (0.75 – 1 equiv.), 140 °C, Solvent (2 mL), 24 h; [b]100 °C; [c]NMR yield using acetonitrile as internal standard (isolated yield in parenthesis)

loading to 1.5 mol% shows a detrimental effect (table **4.1** entry **8**) resulting in approx. 60% of **4.3a**. Moreover, changing the catalyst to & $NiBr_2$ keeping all other parameters unchanged, shows lower conversion to the N-alkylated product (table **4.1** entries **10**-**12**), however, Cat. **2**

is also found to be equally efficient. The control experiment involving the absence of only catalyst (table **4.1** entry **13**) and only KO^{t}Bu (table **4.1** entry **14**), results in less than 20% of **4.3a** formation indicating clearly that both nickel catalyst and base have a tremendous role in driving the reaction further. In addition, when the reaction was investigated in lower loading of the KO^{t}Bu to 0.75 equiv., a mixture of **4.3a** and **4.4a** product was obtained (table **4.1** entry **15**). Finally, lowering the temperature to 110 °C also shows a negative effect on product formation (table **4.1** entry **16**).

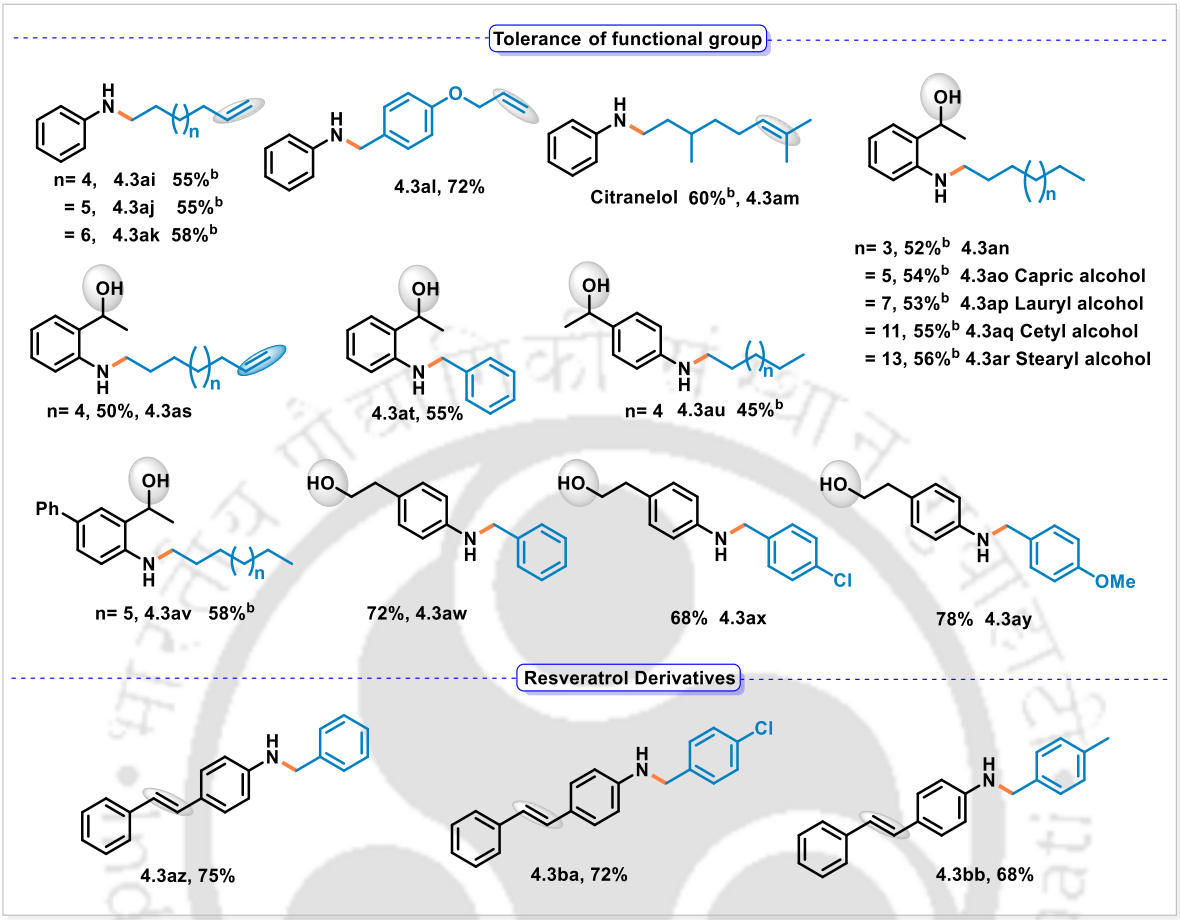
Table 4.2: Scope of Aniline and Alcohol Derivatives



[a]Reaction Condition: **1** (0.5 mmol), **2** (0.75 mmol), Cat. **1** (3 mol%), KO^{t}Bu (1 equiv.), 140 °C, Toluene (2 mL), 24 h; [b] 2 (1 mmol), Cat. **1** (5 mol%).

After achieving the optimized reaction conditions, the practical applicability of the catalytic system was explored toward a diverse range of substrates as depicted in Table **2**. Initially, the efficacy of the present protocol for electronically neutral to bias alcohols was investigated. Electron neutral to electron-rich species in the para position works excellently, furnishing N-alkylated product in 75 – 90% isolated yield (table **4.2**, **4.3a** – **4.3d**). Next, various halide-substituted benzyl alcohols in the para position was tested and found them to tolerate well in the catalytic system (table **4.2**, **4.3e** – **4.3g**). Further, the substitution in ortho and meta position (2-OMe, 2-Me, and 3-OMe) of benzyl alcohols also underwent the reaction smoothly, delivering moderate to good yield of the desired product (table **4.2**, **4.3h** – **4.3j**). Notably, a heterocyclic unit containing alcohols works moderately in the present catalytic protocol delivering 53 – 66% of the desired N-alkylated product (table **4.2**, **4.3k** & **4.3l**). Importantly, piperonyl alcohol and β-naphthyl alcohol also underwent the reaction, delivering a good yield of the desired product (table **4.2**, **4.3m** & **4.3n**). It is also worth noting that, challenging alcohols such as aliphatic alcohols from C4 to C16 chains show good activity, more importantly, the longer chain length (from C8 onward) is more active than the shorter chain length (table **4.2**, **4.3o** – **4.3t**). It could be because the shorter chain alcohols need greater enthalpy of activation to convert it to corresponding aldehydes. Intrigued by the initial result, next the scopes of various substituted amines were investigated. Electron-donating substituents in para position (4-OMe & 4-Me) of aniline work efficiently with various benzyl alcohols furnishing N-alkylated products in good yield (table **4.2**, **4.3u** – **4.3x**). 4-bromoaniline also underwent an N-alkylation reaction albeit with debromination as a side product (table **4.2**, **4.3y**). In addition, 4-chloroaniline couples with both benzylic alcohol and octanol in moderate to good yield (table **4.2**, **4.3z** & **4.3aa**). 3,4-(Methylenedioxy)aniline, a pharmaceutically important derivative of aniline also couples with 4-methoxybenzyl alcohol very effectively furnishing 75% yield of desired product (table **4.2**, **4.3ab**). The substituent in *ortho* position and multi-substituted aniline tolerates the present protocol delivering the respective N-alkylated product in moderate yield (table **4.2**, **4.3ac** & **4.3ad**). Pyridine-based molecular system contributes towards the most important structural motif in various medicinal compounds. Delightfully, the 2-aminopyridine derivatives coupled with electronically biased benzyl alcohols delivering 70 – 80% of the desired N-alkylated products (table **4.2**, **4.3ae** – **4.3ah**). It is also worth mentioning that, the present catalytic protocol leads to the synthesis of intermediate antihistamine **4.3ae** & antifungal **4.3ah** drugs.

Table 4.3: **Chemoselective Approach in N-alkylation Reactions**



[a]**Reaction Condition**: **1** (0.5 mmol), **2** (0.75 mmol), Cat. **1** (3 mol%), KO^{t}Bu (1 equiv.), 140 °C, Toluene (2 mL), 24 h; [b] 2 (1 mmol), **Cat. 1** (5 mol%).

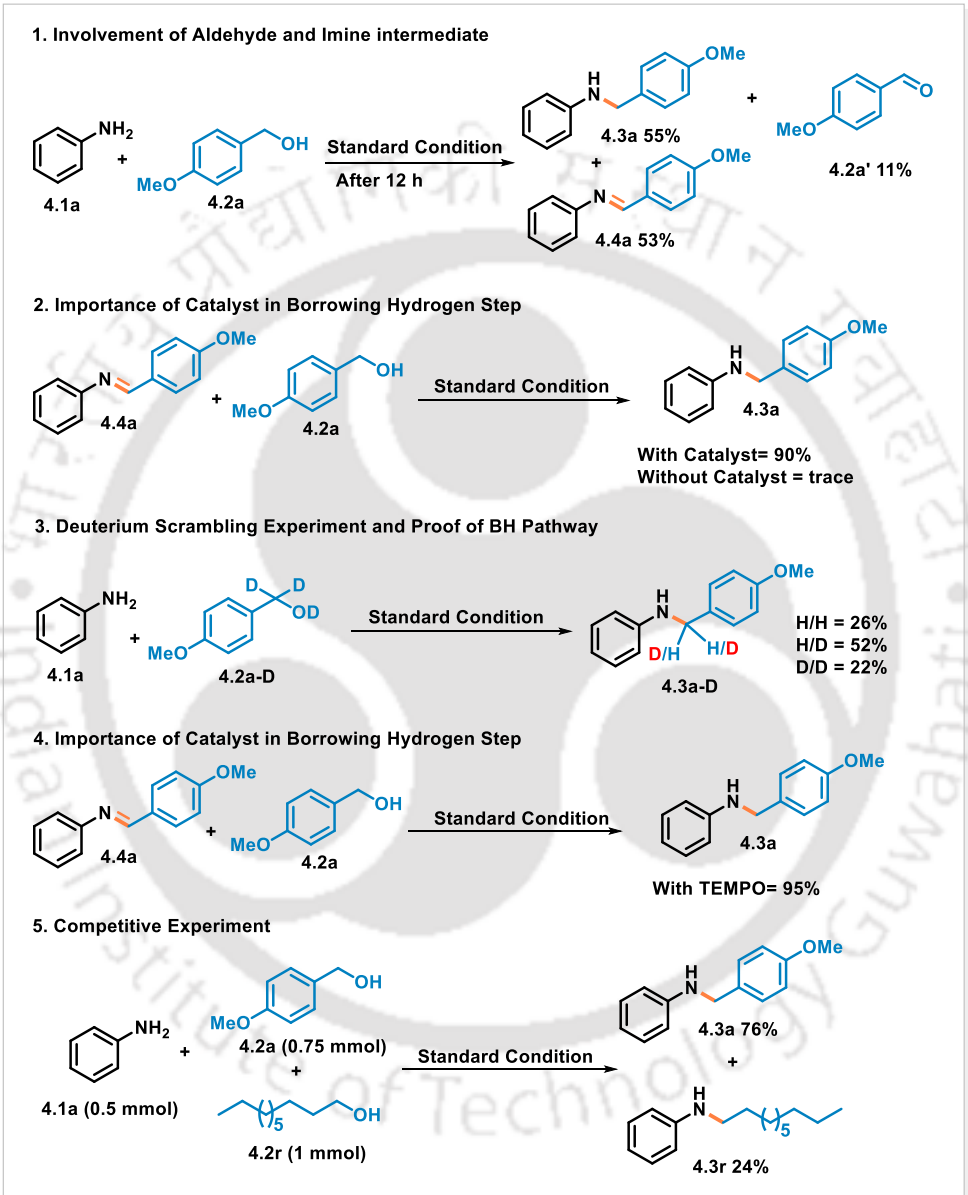
Delighted by the initial results, the chemoselective N-alkylation of aniline with various potential functional groups bearing alcohols and aromatic amines was also investigated. In this respect, aliphatic alcohols with distal double bonds were chosen, keeping in mind that a chemically reactive unsaturation can be employed for a variety of post-synthesis transformations.[15] Interestingly, the chemoselective concept is much less explored in the context of Borrowing Hydrogen mediated N-alkylation chemistry. It is worth noting that, unsaturated alcohol bearing distal double bond with varied chain lengths works well toward coupling with aniline, although the product yield is moderate 55 – 60% (table **4.2**, **4.3ai** – **4.3ak**). Similarly, distal double bonds containing benzyl alcohol couples with aniline efficiently delivering N-alkylated products in good yield (table **4.2**, **4.3al**). Structurally important terpenoids, such as citronellol, are tolerated in the present protocol retaining the

double bond (table **4.2**, **4.3am**). It was further envisaged that this chemoselectivity might be investigated in aminoalcohols, where the possibility of both N and C-alkylation exists. Making a C-N bond selectively rather than a potential C-C bond would be intriguing. Moreover, the presence of potential C-Centre at *ortho* position of amine could lead to further cyclisation product.[16] However, it is interesting to note that in the present protocol C-center remains silent over the potential N-centre. Various aliphatic alcohols with chain lengths C-8 to C-18 have been explored and found to be efficient, delivering the product to good yields (table **4.2**, **4.3an** – **4.3as**). Moreover, *para*-substituted amino-alcohol also works well with decanol delivering 55% of the desired product (table **4.2**, **4.3av**). Interestingly, 2-(4-aminophenyl)ethanol having both amine and alcohol groups selectively couple with different benzyl alcohols without producing self-coupling product (table **4.2**, **4.3aw** – **4.3ay**). In addition, the synthetic applicability of the present protocol was also proved by the synthesis of resveratrol derivatives from 4-amino stilbene and benzyl alcohol derivatives. The desired products are obtained in good yield (table **4.2**, **4.3az** – **4.3bb**).

A few control tests were also conducted to provide further insight into the reaction process. When the reaction between **4.1a** and **4.2a** ceased at around 12 h, the product **4.3a** was found in 55% and **4.4a** in 53% along with the formation of benzaldehyde from the crude ^{1}HNMR (table **4.4**, **1**). This result shows that the reaction runs via the involvement of both aldehyde and imine. Only a trace amount of N-alkylated product was produced by the reaction between the intermediate imine and alcohol in the absence of a catalyst (table **4.4**, **2**). However, in the presence of a catalyst, the imine is hydrogenated with alcohol to form 90% yield of the desired N-alkylated product (table **4.4**, **2**). Moreover, the deuterium scrambling experiment shows 74% of D incorporation in the benzylic carbon (table **4.4**, **3**). This result suggests the transfer of hydrogens from the alcohols to the intermediate imine to give an N-alkylated product i.e., involvement of "Hydrogen Autotransfer". In addition, a radical scavenging experiment shows that TEMPO has no detrimental effect on the efficacy of the reaction (table **4.4**, **4**; crude NMR). Further, a competitive experiment of N-alkylation between benzylic alcohol and aliphatic alcohol shows that benzylic alcohol reacts faster (table **4.4**, **5**) and hence infers that it requires less activation energy to reach the desired product.

As seen in figure **4.2**, a catalytic route was proposed that was derived from controlled experiments, detection of possible catalytic intermediate and substantiated by existing literature.[17] First, dearomatized Cat. **1a** (detected from mass spectrometry [M+H$^+$] =

Table 4.4: Control Experiments



363.9329) is generated in the presence of a base and under heating conditions. Subsequently, through metal-ligand cooperation, aromatized Ni-alkoxo complex Cat. **1b** is formed which further upon reaction of base, converted to dearomatized Cat. **1c**. Further, Cat. **1c** react with another molecule of and convert to Ni-dialkoxo complex Cat. **1d**. Now, the one alcohol molecule gets activated and convert to corresponding aldehyde and Ni-hydride complex Cat.

1e. In the meantime, condensation product **4.4** is produced when the aldehyde gradually couples with amine derivatives in the presence of a base. This intermediate **4.4** is then subjected to transfer hydrogenation (via hydride transfer through Cat. **1e**), resulting in the corresponding alkylated product **4.3** and the regeneration of the active catalyst, Cat. **1c**, thereby allowing the catalytic cycle to proceed further.

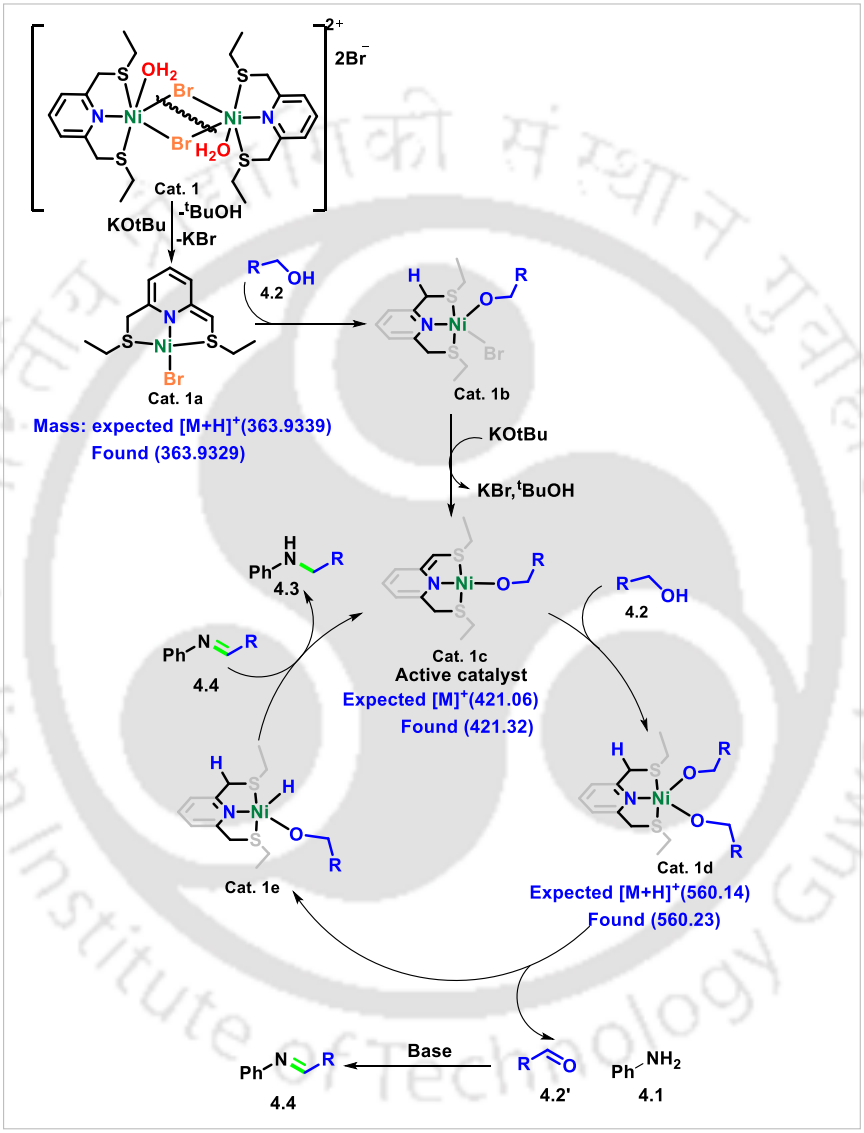


Figure 4.2: Proposed catalytic cycle for Ni-catalysed N-alkylation of amines

4.4. Conclusion

In conclusion, the chapter primarily demonstrates the use of the SNS-Ni complex for the N-alkylation of amines via activating various alcohols. Diverse amines and varieties of alcohols including challenging aliphatic alcohols were also explored. Fatty alcohols were well tolerated

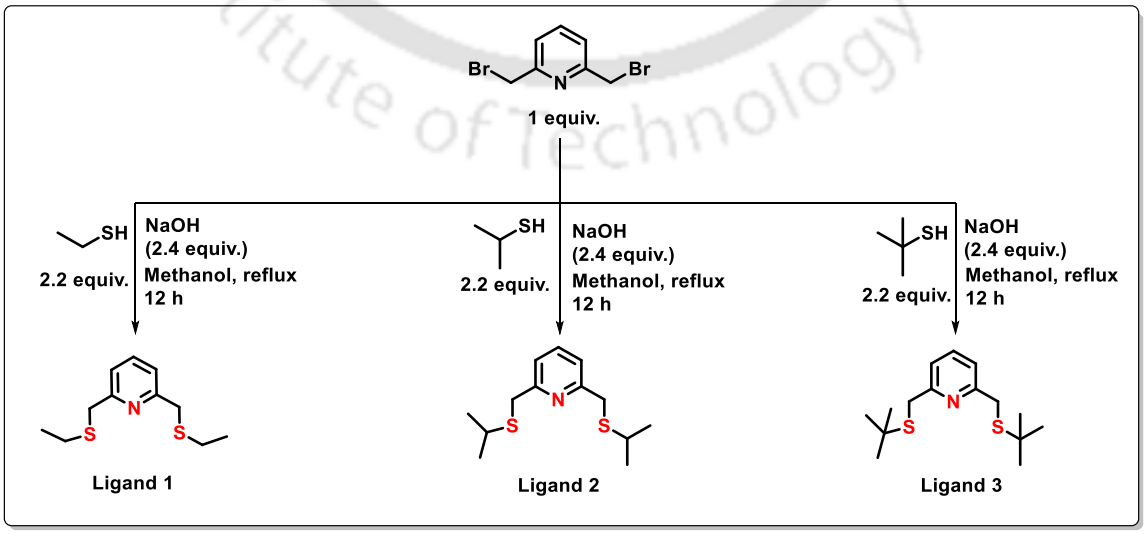
and N-alkylated product was chemoselectively produced having the distal double bond intact. Moreover, the developed catalyst selectively produces the N-alkylated product without any C-alkylation. In addition, the successful synthesis of intermediate of antihistamine, antifungal, and resveratrol derivatives carried out.

4.5. General Consideration

4.5.1. Experimental Section

Unless otherwise mentioned, all chemicals were purchased from common commercial sources and used as received. All solvents were dried by using standard procedure. All catalytic reactions were carried out under argon atmosphere using dried glassware and standard syringe/septa techniques. DRX-400 Varian spectrometer and Bruker Avance III 600, 500 and 400 spectrometers were used to record ^{1}H and ^{13}C NMR spectra using $CDCl_3$ as solvent and TMS as an internal standard. Chemical shifts (δ) are reported in ppm and spin-spin cou-pling constant (J) are expressed in Hz, and other data are reported as follows: s=singlet, d=doublet, t=triplet, m=multiplet, q=quartet, dt=doublet of triplet, td=triplet of doublet and brs=broad singlet. X-ray crystallographic data were collected using BRUKER D8 VENTURE SC-XRD. QTOF ESI-MS instrument (model HAB 273) was used for recording mass spectra. SRL silica gel (100–200 mesh) was used for column chromatography. Ligands [$(PyCH_2)HN(CH_2CH_2SR)$, R=Et, tBu] were synthesized according to the literature report. And synthesis of its corresponding Ni-complexes is already present in our previous report.[14a]

4.5.2. SNS Ligands Synthesis

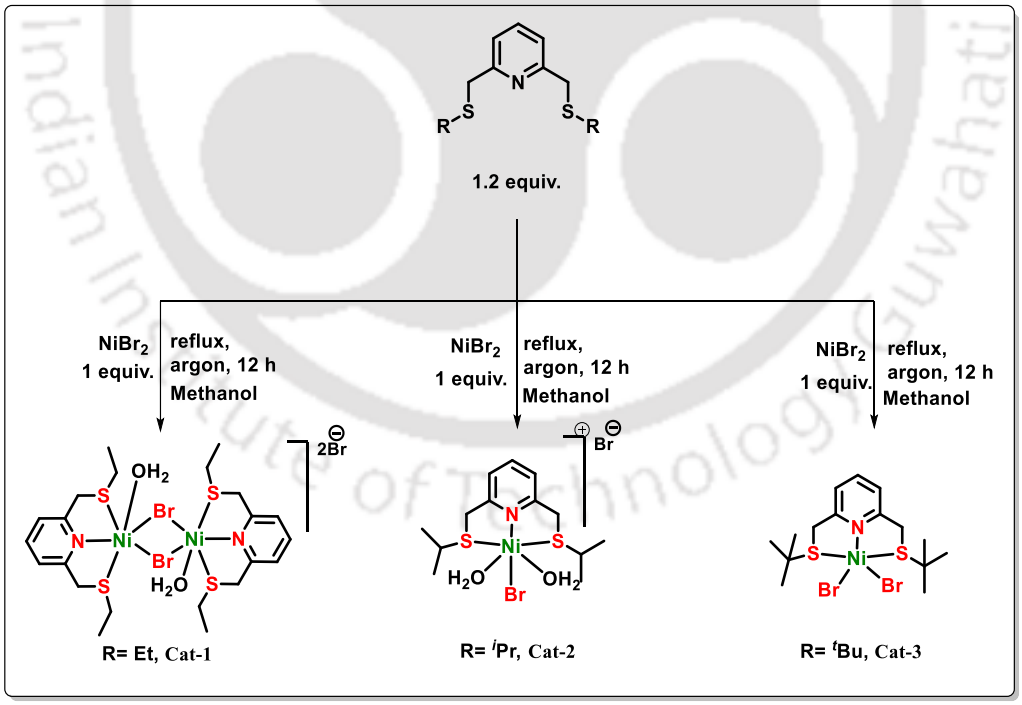


Ligand 1 and Ligand 3 are prepared according to the literature procedure.[14a]

Synthetic procedure of Ligand 2: The ligands [($PyCH_2$)HN(CH_2CH_2SR), R=^{i}Pr] were prepared following a previously documented procedure. Isopropyl thiol (2.2 equiv.) was combined with MeOH containing 2.4 equiv. of NaOH. Subsequently, 2,6-bis(bromomethyl)pyridine (2 mmol) was added in one portion while stirring at room temperature. The mixture was then heated to reflux and stirred overnight. Upon evaporation of the solvent, the resulting slurry was dissolved in diethyl ether and subjected to two washes with a saturated aqueous solution of $NaHCO_3$. The organic layer was dehydrated using anhydrous Na_2SO_4, then filtered. Solvent evaporation yielded the ligands as colorless or slightly yellow oils in typical yields of approximately 90%, which were utilized without further purification.

HRMS (ESI) of [($PyCH_2$)HN(CH_2CH_2SR), R=^{i}Pr] m/z: $[M + H]^+$ $C_{13}H_{21}NS_2$: 256.1194; found 256.1190. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.60 (t, J = 7.7 Hz, 1H), 7.26 (d, J = 7.7 Hz, 2H), 3.86 (s, 4H), 2.94 – 2.86 (m, 2H), 1.26 (d, J = 6.7 Hz, 12H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 137.2, 120.9, 37.1, 34.8, 23.2.

4.5.3. Synthetic Method for Complexes (Cat-1, Cat-2 and Cat-3)

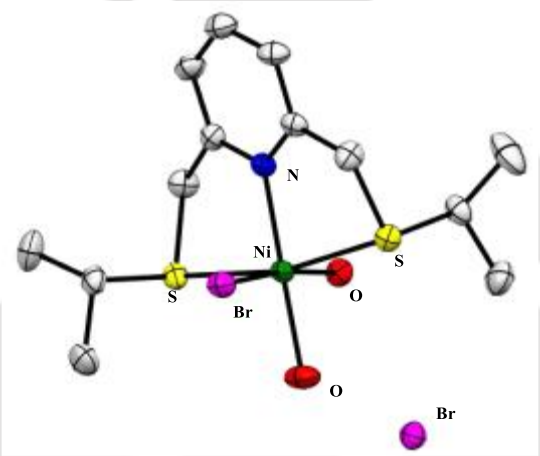


The synthetic procedure for the catalysts (Cat. 1 and Cat.3) are reported in the literature by our group.[14a]

Cat.2 is newly synthesized following the literature procedure. The ligand [($Py(CH_2CH_2SR)_2$, R=*i*Pr)] (1.2 mmol) was dissolved in 5 mL of MeOH and added dropwise to an orange suspension of [$NiBr_2$] (1.0 mmol) in 10 mL of MeOH. The resulting suspension was refluxed overnight under an argon atmosphere. Upon completion of the reaction, the mixture was cooled to room temperature, and the solvent was evaporated to yield a residue. This residue was washed with diethyl ether and then dried under vacuum to obtain a striking green solid of the Ni-complex. Recrystallization was performed by layering diethyl ether solvent over the methanolic solution of the prepared Ni-complex.

HRMS (ESI) m/z: $[M - H_2O - Br]^+$ $C_{13}H_{21}BrNiNS_2$: 391.9652; found 391.9648.

Single crystal XRD analysis and complete crystal data of Cat-2:



Empirical formula	C_{13} H_{25} Br_2 N Ni O_2 S_2
Formula weight	509.99
Temperature, T	273 K
Crystal system	monoclinic
Space group	P 21/c
Unit cell dimensions	a=16.1217(8)Å, α=90 ° b=24.1556(11) Å, β=95.045(1)° c=10.1659(5)Å, γ=90°
Volume, V (Å3)	3943.6(3)
Z	8
Density (calculated),	1.718

Absorption coefficient, μ (mm−1)	5.251
F(000)	2048.0
Crystal size, mm3	0.28 0.26 0.22
Theta range for data collection	2.61to 26.69
Index ranges	-20 ≤ h ≤ 20, -30 ≤ k ≤ 30, -13 ≤ l ≤ 13
Reflections collected	9709
Independent reflections	8689
Completeness to theta	0.999
Absorption correction	multi-scan
Refinement method	'SHELXL-2018/3'
Data / restraints / parameters	8689/0/407
Goodness-of-fit on F2	1.004
Final R indices [I>2sigma(I)]	R1 = 0.0377(6637), wR2= 0.1080(8689)
R indices (all data)	R1= 0.0609, WR2=0.0924
Extinction coefficient	5.251
Selected bond lengths	**Selected bond angles**
Bond lengths [Å]	**Bond angles [°]**
Br01 Ni04 2.5482(6) Br02 Ni05 2.5333(6) Ni04 N00F 2.038(3) Ni04 O2 2.047(3) Ni04 O1 2.105(3) Ni04 S007 2.4105(11) Ni04 S009 2.4509(11) Ni05 O3 2.028(3) Ni05 N00E 2.048(3) Ni05 O4 2.133(3) Ni05 S008 2.4375(11) Ni05 S00A 2.4702(11) S007 C00L 1.810(4) S007 C00Z 1.836(4) S008 C00M 1.808(4) S008 C00X 1.835(4) S009 C00S 1.810(4) S009 C00V 1.833(4) S00A C00R 1.809(4) S00A C00P 1.838(4) N00E C00H 1.342(5) N00E C00K 1.345(5)	N00F Ni04 O2 178.04(13) N00F Ni04 O1 97.66(12) O2 Ni04 O1 82.56(12) N00F Ni04 S007 83.74(9) O2 Ni04 S007 98.19(10) O1 Ni04 S007 94.27(10) N00F Ni04 S009 84.76(9) O2 Ni04 S009 93.35(10) O1 Ni04 S009 82.49(9) S007 Ni04 S009 167.52(4) N00F Ni04 Br01 89.21(8) O2 Ni04 Br01 90.58(9) O1 Ni04 Br01 173.11(9) S007 Ni04 Br01 86.00(3) S009 Ni04 Br01 98.67(3) O3 Ni05 N00E 179.28(16) O3 Ni05 O4 84.43(12) N00E Ni05 O4 95.65(12) O3 Ni05 S008 95.84(13) N00E Ni05 S008 83.45(9) O4 Ni05 S008 92.51(9) O3 Ni05 S00A 96.67(13) N00E Ni05 S00A 84.04(9)

N00F C00I 1.342(5) N00F C00J 1.348(5) C00J C00N 1.379(5) C00J C00S 1.502(6) C00K C00O 1.382(5) C00K C00R 1.501(5)	O4 Ni05 S00A 84.71(9) S008 Ni05 S00A 166.85(4) O3 Ni05 Br02 89.02(10) N00E Ni05 Br02 90.88(8) O4 Ni05 Br02 173.13(8) S008 Ni05 Br02 86.11(3) S00A Ni05 Br02 98.11(3)

4.5.4. General Experimental Procedure for the N-Alkylation of Aniline Derivatives.

In a 100 mL pressure tube, previously dried in an oven, aniline derivatives **4.1** (0.5 mmol), alcohols **4.2** (0.75 - 1 mmol), KO^{t}Bu (1 – 1.5 equiv.), and Cat-1 (3 mol%, 11.5 mg) were combined under an argon atmosphere. Following this, 2 mL of toluene was introduced to the reaction mixture. The resulting blend was then heated in an oil bath at 140 °C for 24 hours. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate. After filtration through celite, the filtrate was concentrated under reduced pressure. The resulting residue was further purified using silica gel column chromatography with either hexane or a mixture of 2%–10% ethyl acetate in hexane to obtain the pure N-alkylated compound.

4.5.6. Nickel Catalysed Alkylation of Aniline by Deuterated Labelled Alcohol (5a–d2).

In an oven-dried 100 mL pressure tube, Aniline **4.1a** (0.5 mmol), deuterated 4-methoxybenzyl alcohol **4.2a–d2** (0.75 mmol), KO^{t}Bu (1 equiv.), and Cat-**1** (3 mol%, 11.5 mg) were combined, followed by the addition of 2 mL of toluene under an argon atmosphere. The resulting mixture was then subjected to heating in a preheated oil bath at 140 °C for 24 hours under argon atmosphere. Upon completion, the reaction was cooled to room temperature, and ethyl acetate was added before filtration through celite. The filtrate was concentrated under vacuum, and the residue was purified using column chromatography over silica gel (100–200 mesh) with a hexane/ethyl acetate mixture (0–2%) as the eluent. The percentage of 3a–d obtained represented a mixture of deuterated N-alkylated product. The degree of deuterium incorporation was assessed using 1H NMR spectroscopy, as depicted below.

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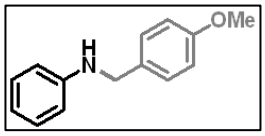
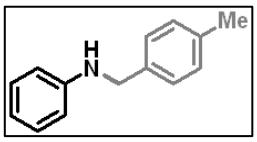
4.7. Characterization Data of Compounds

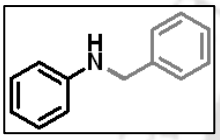
4.3a: **(N-(4-methoxybenzyl)aniline) Yield 90%; Yellow solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v):** ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.6 Hz, 2H), 7.23 – 7.17 (m, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 2H), 4.28 (s, 2H), 4.03 (s, 1H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 158.9, 148.2, 131.4, 129.3, 128.8, 117.6, 114.0, 112.9, 55.3, 47.8.



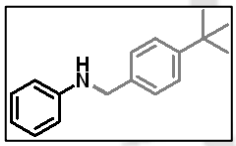
4.3b: (**N-(4-methylbenzyl)aniline**) **Yield 85%; White solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 30:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.17 (m, 4H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 4.31 (s, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.2, 136.9, 136.3, 129.3, 129.3, 127.5, 117.6, 112.9, 48.1, 21.1.



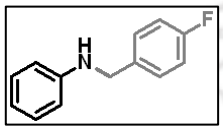
4.3c: (**N-benzylaniline**) **Yield 87%; Pale yellow liquid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 30:1 (v/v)**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 4H), 7.20 (d, *J* = 7 Hz, 1H) , 7.10 (t, *J* = 7.9 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 2H), 4.26 (s, 2H), 3.94 (bs, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.2, 139.5, 129.3, 128.6, 127.5, 127.2, 117.6, 112.9, 48.4.



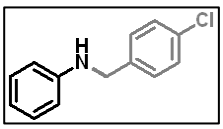
4.3d: (**N-(4-(tert-butyl)benzyl)aniline**) **Yield 75%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 30:1 (v/v)**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.7 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 2H), 4.21 (s, 2H), 3.88 (s, 1H), 1.24 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 150.3, 148.3, 136.4, 129.2, 127.4, 125.5, 117.5, 112.8, 48.1, 34.5, 31.4.



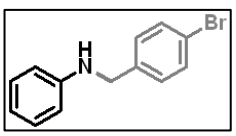
4.3e: (**N-(4-fluorobenzyl)aniline**) **Yield 56%; Pale yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 30:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 – 7.32 (m, 2H), 7.21 (t, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 2H), 4.33 (s, 2H), 4.05 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, CDCl3) δ 162.1 (d, *J* = 243.6 Hz), 147.9, 135.1 (d, *J* = 3.0 Hz), 129.3, 129.0 (d, *J* = 7.8 Hz), 117.8, 115.4 (d, *J* = 21.3 Hz), 112.9, 47.6.



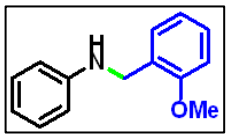
4.3f: (**N-(4-chlorobenzyl)aniline**) **Yield 85%; White solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 30:1 (v/v)**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 – 7.22 (m, 4H), 7.09 (t, *J* = 7.9 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 2H), 4.24 (s, 2H), 3.98 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.8, 138.0, 132.9, 129.3, 128.7, 128.7, 117.9, 112.9, 47.7.



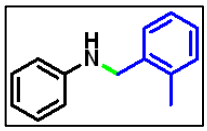
4.3g: (**N-(4-bromobenzyl)aniline**) **Yield 62%; White solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 30:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 2H), 4.32 (s, 2H), 4.09 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.8, 138.5, 131.7, 129.3, 129.1, 120.9, 117.8, 112.9, 47.7.



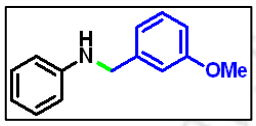
4.3h: (**N-(2-methoxybenzyl)aniline**) **Yield 65%; White solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v)**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.15 (t, *J* = 7.8 Hz, 2H), 6.94 – 6.86 (m, 2H), 6.67 (dd, *J* = 17.8, 7.7 Hz, 3H), 4.33 (s, 2H), 4.10 (s, 1H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.4, 148.5, 129.2, 128.9, 128.3, 127.4, 120.5, 117.4, 113.1, 110.3, 55.3, 43.5.



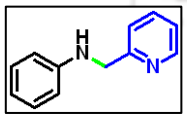
4.3i: (**N-(2-methylbenzyl)aniline**) **Yield 70%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 30:1 (v/v):** ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.13 (m, 5H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 2H), 4.26 (s, 2H), 3.81 (s, 1H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.3, 137.0, 136.3, 130.4, 129.3, 128.3, 127.4, 126.2, 117.5, 112.7, 46.4, 18.9.



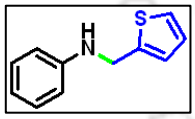
4.3j: (**N-(3-methoxybenzyl)aniline**) **Yield 80%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v)**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.09 (t, *J* = 7.9 Hz, 2H), 6.91 – 6.84 (m, 3H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.63 (d, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 3H), 4.23 (s, 2H), 3.94 (s, 1H), 3.72 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 160.0, 148.2, 141.2, 129.6, 129.2, 119.7, 117.6, 113.1, 112.9, 112.7, 55.2, 48.4.



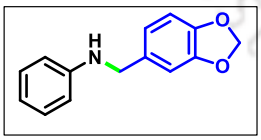
4.3k: (**N-(pyridin-2-ylmethyl)aniline**) **Yield 66%; White Solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 6.9 Hz, 3H), 6.73 – 6.66 (m, 3H), 4.46 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 149.2, 147.9, 136.6, 129.2, 122.1, 121.6, 117.6, 113.1, 49.3.



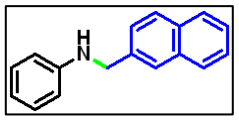
4.3l: (**N-(thiophen-2-ylmethyl)aniline**) **Yield 53%; Brown oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v)**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.16 – 7.07 (m, 3H), 6.96 – 6.91 (m, 1H), 6.91 – 6.86 (m, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 2H), 4.44 (s, 2H), 3.95 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.6, 143.0, 129.3, 126.8, 125.0, 124.5, 118.1, 113.2, 43.5.



4.3m: (**N-(benzo[d][1,3]dioxol-5-ylmethyl)aniline**) **Yield 70%; White solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-d) δ 7.20 (t, *J* = 7.4 Hz, 2H), 6.90 (d, *J* = 6.9 Hz, 1H), 6.86 (s, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 2H), 5.97 (s, 2H), 4.27 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.9, 147.7, 146.8, 133.1, 129.3, 120.7, 117.9, 113.1, 108.3, 108.1, 101.0, 48.3.



4.3n: (**N-(naphthalen-2-ylmethyl)aniline**) **Yield 70%; Pale yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 30:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.84 (m, 4H), 7.54 – 7.49 (m, 3H), 7.22 (t, *J* = 7.6 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 2H), 4.53 (s, 2H), 4.17 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.2, 137.0, 133.5, 132.8, 129.3, 128.4, 127.8, 127.7, 126.2, 125.9, 125.8, 117.7, 113.0, 48.5.



4.3o: (**N-butylaniline**) **Yield 45%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 40:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.22 – 7.16 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6. 63 (d, *J* = 8.4 Hz, 1H), 3.13 (t, *J* = 7.1 Hz, 2H), 1.65 – 1.60 (m, 2H), 1.49 – 1.42 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.5, 129.2, 117.1, 112.7, 43.7, 31.7, 20.3, 13.9.

4.3p: (**N-hexylaniline**) **Yield 60%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 40:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 – 7.18 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 3.68 (s, 1H), 3.13 (t, *J* = 7.2 Hz, 2H), 1.66 – 1.61 (m, 2H), 1.45 – 1.40 (m, 2H), 1.37 – 1.33 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.5, 129.2, 117.1, 112.7, 44.1, 31.7, 29.5, 26.9, 22.6, 14.0.

4.3q: (**N-octylaniline**) **Yield 65%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 40:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.22 – 7.17 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 1.64 (q, *J* = 7.2 Hz, 2H), 1.33 – 1.29 (m, 10H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.6, 129.2, 117.1, 112.7, 44.0, 31.8, 29.6, 29.4, 29.3, 27.2, 22.7, 14.1.

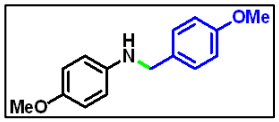
4.3r: (**N-decylaniline**) **Yield 64%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 40:1 (v/v)**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.17 (t, *J* = 7.9 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 3.10 (t, *J* = 7.1 Hz, 2H), 1.64 – 1.56 (m, 2H), 1.42 – 1.27 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.5, 129.2, 117.1, 112.7, 44.0, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 27.2, 22.7, 14.1.

4.3s: (**N-dodecylaniline**) **Yield 68%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 40:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.23 – 7.16 (m, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 1.66 – 1.61 (m, 2H), 1.46 – 1.38 (m, 2H), 1.36 – 1.26 (m, 16H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.5, 129.2, 117.1, 112.7, 44.1, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 27.2, 22.7, 14.1.

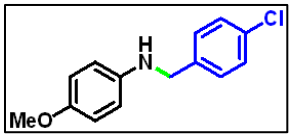
4.3t: (**N-hexadecylaniline**) **Yield 72%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 40:1 (v/v)**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (t, *J* = 7.9 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 3.59 (s, 1H), 3.10 (t, *J* = 7.1 Hz, 2H), 1.66 – 1.55 (m, 3H), 1.40 – 1.24 (m, 26H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.6, 129.2, 117.1, 112.7, 44.0, 31.9, 29.7, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 27.2, 22.7, 14.1.

4.3u: (**N-benzyl-4-methoxyaniline**) **Yield 65%; Pale yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v)**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 3H), 7.27 – 7.25 (m, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.28 (s, 2H), 3.74 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.3, 142.5, 139.7, 128.6, 127.5, 127.2, 115.0, 114.2, 55.8, 49.3.

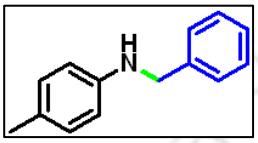
4.3v: (**4-methoxy-N-(4-methoxybenzyl)aniline**) **Yield 70%; White solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v)**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 4.21 (s, 2H), 3.80 (s, 3H), 3.74 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.9, 152.3, 142.5, 131.8, 128.8, 115.0, 114.2, 114.0, 55.8, 55.3, 48.8.



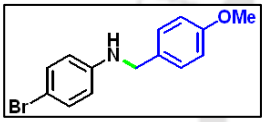
4.3w: (**N-(4-chlorobenzyl)-4-methoxyaniline**) **Yield 70%; Pale yellow solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v)**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 4H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 4.26 (s, 2H), 3.73 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.4, 142.1, 138.3, 132.8, 128.7, 128.7, 115.0, 114.2, 55.8, 48.6.



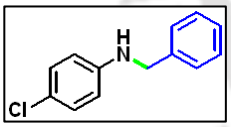
4.3x: (**N-benzyl-4-methylaniline**) **Yield 68%; Pale yellow solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 30:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 – 7.32 (m, 4H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.61 (d, *J* = 8.1 Hz, 2H), 4.35 (s, 2H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 145.9, 139.7, 129.8, 128.6, 127.5, 127.2, 126.8, 113.1, 48.7, 20.4.



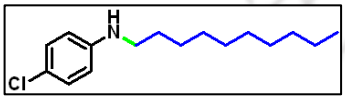
4.3y: (**4-bromo-N-(4-methoxybenzyl)aniline**) **Yield 53%; Pale yellow solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v)**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.26 – 7.22 (m, 4H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 7.9 Hz, 2H), 4.21 (s, 2H), 3.97 (s, 1H), 3.80 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.0, 147.2, 131.9, 130.9, 128.7, 114.4, 114.2, 109.1, 55.3, 47.8.



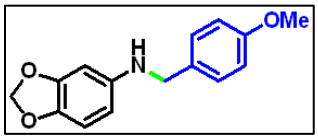
4.3z: (**N-benzyl-4-chloroaniline**) **Yield 82%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 30:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.37 (m, 4H), 7.33 – 7.30 (m, 1H), 7.14 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 4.33 (s, 1H), 4.15 (d, *J* = 7.1 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 146.6, 138.9, 129.3, 128.7, 127.4, 127.4, 122.2, 114.0, 48.4.



4.3aa: (**4-chloro-N-decylaniline**) **Yield 50%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 40:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 1H), 3.09 (t, *J* = 7.2 Hz, 2H), 1.69 – 1.56 (m, 2H), 1.41 – 1.21 (m, 14H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.0, 129.0, 121.7, 113.8, 64.7, 44.2, 31.9, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1.



4.3ab: (**N-(4-methoxybenzyl)benzo[d][1,3]dioxol-5-amine**) **Yield 75%; Brown oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.3 Hz, 1H), 6.31 (s, 1H), 6.11 (d, *J* = 8.3 Hz, 1H), 5.88 (s, 2H), 4.21 (s, 2H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 158.9, 148.3, 143.7, 139.8, 131.2, 128.9, 114.0, 108.6, 104.7, 100.6, 96.2, 55.3, 48.9.



4.3ac: (**2-iodo-N-(4-methoxybenzyl)aniline**) **Yield 65%; Yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 30:1 (v/v)**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.48 (d, *J* = 8.1 Hz, 1H), 6.37 (t, *J* = 7.5 Hz, 1H), 4.47 (s, 1H), 4.25 (s, 2H), 3.73 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.0, 147.1, 139.0, 130.6, 129.4, 128.5, 118.8, 114.2, 111.0, 85.3, 55.3, 47.9.

4.3ad: (**2-fluoro-4-iodo-N-(4-methoxybenzyl)aniline**) **Yield 50%; Yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.20 (m, 4H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.46 (t, *J* = 8.7 Hz, 1H), 4.29 (s, 2H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 159.1, 151.3 (d, *J* = 243 Hz), 136.5 (d, *J* = 11.3 Hz), 133.5 (d, *J* = 10 Hz), 130.3, 128.7, 128.6, 123.1 (d, *J* = 21 Hz), 114.2, 113.9 (d, *J* = 3.7 Hz), 55.3, 47.1.

4.3ae: (**N-(4-methoxybenzyl)pyridin-2-amine**) **Yield 75%; White solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 4.3 Hz, 1H), 7.46– 7.34 (m, 5H), 7.30 (d, *J* = 7.1 Hz, 1H), 6.65 – 6.58 (m, 1H), 6.40 (d, *J* = 8.4 Hz, 1H), 4.90 (s, 1H), 4.53 (d, *J* = 5.7 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 158.6, 148.2, 139.2, 137.5, 128.6, 127.4, 127.3, 113.2, 106.8, 46.3.

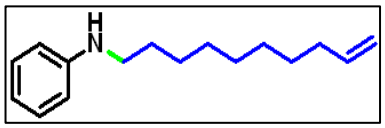
4.3af: (**N-(4-chlorobenzyl)pyridin-2-amine**) **Yield 73%; White solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 – 8.06 (m, 1H), 7.46 – 7.26 (m, 5H), 6.69 – 6.56 (m, 1H), 6.38 (d, *J* = 8.4 Hz, 1H), 4.87 (s, 1H), 4.52 (d, *J* = 5.9 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 158.4, 148.2, 137.8, 137.5, 132.9, 128.8, 128.7, 113.4, 106.9, 45.6.

4.3ag: (**N-(naphthalen-2-ylmethyl)pyridin-2-amine**) **Yield 78%; White solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 4.6 Hz, 1H), 7.89 – 7.75 (m, 4H), 7.55 – 7.45 (m, 3H), 7.43 (t, *J* = 7.7 Hz, 1H), 6.65 – 6.58 (m, 1H), 6.43 (d, *J* = 8.4 Hz, 1H), 5.01 (s, 1H), 4.70 (d, *J* = 5.8 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 158.7, 148.3, 137.6, 136.7, 133.5, 132.8, 128.4, 127.7, 127.7, 126.2, 125.8, 125.7, 125.7, 113.3, 106.9, 46.5.

4.3ah: (**N-(4-methoxybenzyl)pyrimidin-2-amine**) **Yield 75%; White solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (s, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.54 (t, *J* = 4.5 Hz, 1H), 5.76 (s, 1H), 4.58 (d, *J* = 5.6 Hz, 2H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 162.3, 158.9, 158.1, 131.1, 128.9, 114.0, 110.7, 55.3, 44.9.

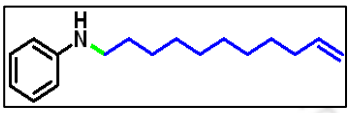
4.3ai: (**N-(non-8-en-1-yl)aniline**) **Yield 55%; Colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 40:1 (v/v)**: HRMS $C_{15}H_{23}N$: $[M+H]^+$ expected 218.1909; found 218.1904. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.4 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 2H), 5.89 – 5.75 (m, 1H), 5.02 (dd, *J* = 17.1, 1.9 Hz, 1H), 4.96 (dd, *J* = 10.2, 1.9 Hz, 1H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.08 – 2.05 (m, 2H), 1.69 – 1.60 (m, 2H), 1.43 – 1.38 (m, 4H), 1.36 – 1.34 (m, 4H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 139.1, 129.2, 117.2, 114.3, 114.2, 112.8, 44.1, 33.8, 29.5, 29.3, 29.0, 28.9, 27.1.

4.3aj: (**N-(dec-9-en-1-yl)aniline**) **Yield 55%; Colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 40:1 (v/v)**:



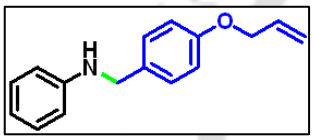
HRMS $C_{16}H_{25}N$: $[M+H]^+$ expected 232.2065; found 232.2068. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 7.8 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 5.90 – 5.78 (m, 1H), 5.02 (dd, *J* = 17.1, 1.9 Hz, 1H), 4.96 (d, *J* = 10.1, 1.9 Hz, 1H), 3.13 (t, *J* = 7.1 Hz, 2H), 2.09 – 2.05 (m, 2H), 1.66 – 1.62 (m, 2H), 1.33 – 1.28 (m, 4H), 1.27 – 1.21 (m, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 148.5, 139.2, 129.2, 117.1, 114.2, 112.7, 44.0, 33.8, 29.6, 29.4, 29.4, 29.1, 28.9, 27.2.

4.3ak: (**N-(undec-10-en-1-yl)aniline**) **Yield 58%; Colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 40:1 (v/v)**:



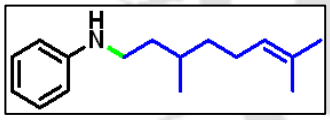
HRMS $C_{17}H_{27}N$: $[M+H]^+$ expected 246.2222; found 246.2215. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.7 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 5.87 – 5.80 (m, 1H), 5.01 (d, *J* = 17.1 Hz, 1H), 4.95 (d, *J* = 10.1 Hz, 1H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.08 – 2.04 (m, 2H), 1.66 – 1.60 (m, 2H), 1.42 – 1.38 (m, 4H), 1.36 – 1.28 (m, 8H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 148.4, 139.2, 129.2, 117.12, 114.1, 112.8, 44.1, 33.8, 29.5, 29.4, 29.4, 29.1, 28.9, 27.2.

4.3al: (**N-(4-(allyloxy)benzyl)aniline**) **Yield 72%; Yellow solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 20:1 (v/v)**:



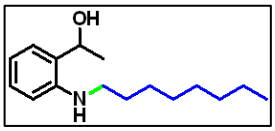
HRMS C16H17NO: $[M+H]^+$ expected 240.1388; found 240.1381. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.6 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 6.14 – 6.01 (m, 1H), 5.44 (d, *J* = 18.8, 1.5 Hz, 1H), 5.32 (d, *J* = 11.8, 1.5 Hz, 1H), 4.56 (d, *J* = 5.3 Hz, 2H), 4.28 (s, 2H), 4.00 (s, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 157.9, 148.2, 133.3, 131.6, 129.3, 128.8, 117.7, 117.5, 114.9, 112.9, 68.9, 47.8.

4.3am: (**N-(3,7-dimethyloct-6-en-1-yl)aniline**) **Yield 60%; Colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 40:1 (v/v)**:



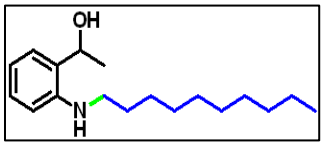
^1H NMR (500 MHz, Chloroform-*d*) δ 7.17 (t, *J* = 7.9 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 2H), 5.10 (t, *J* = 6.4 Hz, 1H), 3.54 (s, 1H), 3.21 – 2.96 (m, 2H), 2.07 – 1.93 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.51 – 1.12 (m, 5H), 0.94 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 148.6, 131.4, 129.2, 124.7, 117.1, 112.7, 42.0, 37.1, 36.7, 30.4, 25.7, 25.5, 19.6, 17.7.

4.3an: (**1-(2-(octylamino)phenyl)ethan-1-ol**) **Yield 52%; Yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**:



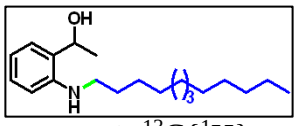
HRMS $C_{16}H_{27}NO$: $[M+H]^+$ expected 250.2171; found 250.2151. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.71 – 6.65 (m, 2H), 4.94 (q, *J* = 6.6 Hz, 1H), 3.18 – 3.11 (m, 2H), 1.69 (p, *J* = 7.1 Hz, 2H), 1.63 (d, *J* = 6.6 Hz, 3H), 1.47 – 1.42 (m, 2H), 1.37 – 1.27 (m, 8H), 0.91 (t, *J* = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 146.9, 128.9, 127.5, 126.3, 116.2, 111.1, 70.0, 43.7, 31.8, 31.6, 29.4, 29.3, 27.3, 22.7, 21.4, 14.1.

4.3ao: (**1-(2-(decylamino)phenyl)ethan-1-ol**) **Yield 54%; Yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**:

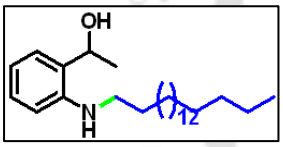


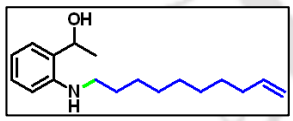
HRMS $C_{18}H_{31}NO$: $[M+H]^+$ expected 278.2484; found 278.2476. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.71 – 6.66 (m, 2H), 4.94 (q, *J* = 6.6 Hz, 1H), 3.18 – 3.10 (m, 2H), 1.72 – 1.65 (m, 2H), 1.63 (d, *J* = 6.6 Hz, 3H), 1.46 – 1.41 (m, 2H), 1.37 –

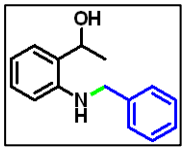
1.26 (m, 12H), 0.91 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 147.0, 128.9, 127.4, 126.3, 116.1, 111.0, 70.0, 43.7, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 27.3, 22.7, 21.4, 14.1.

4.3ap: (**1-(2-(dodecylamino)phenyl)ethan-1-ol**) **Yield 53%; Yellow solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**: HRMS $C_{20}H_{35}NO$: $[M+H]^+$ expected 306.2797; found 306.2790. 
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.71 – 6.65 (m, 2H), 4.94 (q, *J* = 6.6 Hz, 1H), 3.18 – 3.11 (m, 2H), 1.68 (p, *J* = 7.1 Hz, 2H), 1.63 (d, *J* = 6.6 Hz, 3H), 1.46 – 1.41 (m, 2H), 1.37 – 1.27 (m, 16H), 0.91 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 147.0, 128.9, 127.4, 126.3, 116.1, 110.9, 70.0, 43.7, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 27.3, 22.7, 21.4, 14.1.

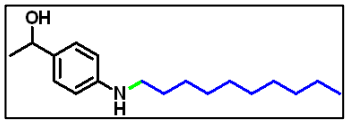
4.3aq: (**1-(2-(hexadecylamino)phenyl)ethan-1-ol**) **Yield 55%; Yellow solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**: HRMS $C_{24}H_{43}NO$: $[M+H]^+$ expected 362.3423; found 362.3421. 
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.71 – 6.65 (m, 2H), 4.94 (q, *J* = 6.6 Hz, 1H), 3.18 – 3.10 (m, 2H), 1.68 (p, *J* = 7.1 Hz, 2H), 1.63 (d, *J* = 6.6 Hz, 3H), 1.46 – 1.41 (m, 2H), 1.38 – 1.26 (m, 24H), 0.91 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 147.0, 128.9, 127.4, 126.3, 116.0, 110.9, 70.0, 43.6, 31.9, 29.7, 29.7, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 27.3, 22.7, 21.4, 14.1.

4.3ar: (**1-(2-(octadecylamino)phenyl)ethan-1-ol**) **Yield 56%; Yellow Solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**: 
HRMS $C_{26}H_{47}NO$: $[M+H]^+$ expected 390.3736; found 390.3729. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.73 – 6.66 (m, 2H), 4.95 (q, *J* = 6.6 Hz, 1H), 3.18 – 3.11 (m, 2H), 1.71 – 1.62 (m, 2H), 1.63 (d, *J* = 6.6 Hz, 3H), 1.46 – 1.41 (m, 2H), 1.38 – 1.26 (m, 28H), 0.90 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 135.7, 128.9, 127.1, 126.3, 116.4, 111.3, 70.0, 43.9, 31.9, 29.7, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.4, 27.3, 22.7, 21.5, 14.1.

4.3as: (**1-(2-(dec-9-en-1-ylamino)phenyl)ethan-1-ol**) **Yield 50%; Pale yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**: 
HRMS $C_{18}H_{29}NO$: $[M+K]^+$ expected 328.2043; found 328.2154. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.70 – 6.67 (m, 2H), 5.87 – 5.80 (m, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.96 (d, *J* = 13.2 Hz, 1H), 3.18 – 3.11 (m, 2H), 2.07 (q, *J* = 7.1 Hz, 3H), 1.71 – 1.66 (m, 2H), 1.62 (d, *J* = 6.6 Hz, 3H), 1.45 – 1.37 (m, 4H), 1.34 – 1.31 (m, 6H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 147.0, 139.2, 128.9, 127.5, 126.3, 116.1, 116.1, 114.2, 111.0, 111.0, 70.0, 43.7, 43.7, 33.8, 29.4, 29.4, 29.0, 28.9, 27.3, 21.4.

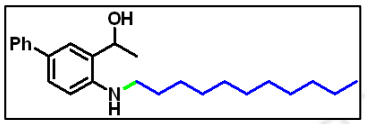
4.3at: (**1-(2-(benzylamino)phenyl)ethan-1-ol**) **Yield 55%; Yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**: 
HRMS $C_{15}H_{17}NO$: $[M+H]^+$ expected 228.1388; found 228.1380.^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 5.00 (q, *J* = 6.6 Hz, 1H), 4.41 (s, 2H), 1.67 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 146.6, 139.6, 128.9, 128.6, 127.7, 127.3, 127.1, 126.4, 116.6, 111.4, 70.1, 47.8, 21.5.

4.3au: (**1-(4-(decylamino)phenyl)ethan-1-ol**) **Yield 45%; Yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**:



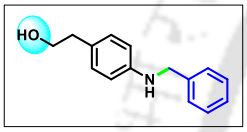
HRMS $C_{18}H_{31}NO$: $[M+H]^+$ expected 278.2484; found 278.2477. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.5 Hz, 2H), 6.61 (d, *J* = 8.5 Hz, 2H), 4.82 (q, *J* = 6.4 Hz, 1H), 3.12 (t, *J* = 7.1 Hz, 2H), 1.66 – 1.61 (m, 2H), 1.49 (d, *J* = 6.4 Hz, 3H), 1.43 – 1.40 (m, 2H), 1.35 – 1.26 (m, 10H), 0.91 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 148.1, 134.3, 126.7, 112.6, 70.3, 44.1, 31.8, 29.6, 29.4, 29.3, 27.2, 24.7, 22.7, 14.1.

4.3av: (**1-(4-(decylamino)-[1,1'-biphenyl]-3-yl)ethan-1-ol**) **Yield 58%; Pale yellow solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**:



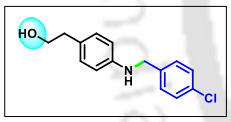
HRMS $C_{24}H_{35}NO$: $[M+H]^+$ expected 354.2797; found 354.2801. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 2.1 Hz, 1H), 7.28 (d, *J* = 5.3 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.01 (q, *J* = 6.6 Hz, 1H), 3.23 – 3.16 (m, 2H), 1.73 – 1.70 (m, 2H), 1.67 (d, *J* = 6.6 Hz, 3H), 1.48 – 1.43 (m, 2H), 1.37 – 1.27 (m, 14H), 0.91 (t, *J* = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl3) δ 146.4, 141.3, 129.0, 128.7, 127.7, 127.4, 126.3, 126.0, 125.3, 111.3, 70.4, 43.7, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 27.3, 22.7, 21.5, 14.1.

4.3aw: (**2-(4-(benzylamino)phenyl)ethan-1-ol**) **Yield 72%; Yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 4:1 (v/v)**:



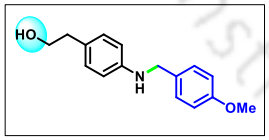
^1H NMR (600 MHz, Chloroform-d) δ 7.41 – 7.35 (m, 2H), 7.30 (t, *J* = 7.1 Hz, 0H), 7.09 – 7.04 (m, 1H), 6.66 – 6.60 (m, 1H), 4.34 (s, 1H), 3.82 (t, *J* = 6.6 Hz, 1H), 2.78 (t, *J* = 6.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 146.8, 139.5, 129.9, 128.7, 127.5, 127.3, 127.0, 113.1, 64.0, 48.5, 38.3.

4.3ax: (**2-(4-((4-chlorobenzyl)amino)phenyl)ethan-1-ol**) **Yield 68%; Yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 4:1 (v/v)**:



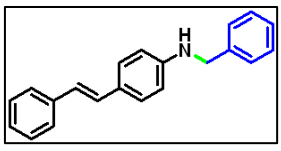
^1H NMR (600 MHz, Chloroform-d) δ 7.33 (s, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 4.32 (s, 1H), 3.81 (t, *J* = 6.5 Hz, 1H), 2.78 (t, *J* = 6.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 146.5, 138.0, 132.9, 129.9, 128.8, 128.7, 113.2, 63.9, 47.8, 38.3.

4.3ay: (**2-(4-((4-methoxybenzyl)amino)phenyl)ethan-1-ol**) **Yield 78%; Yellow oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 4:1 (v/v)**:



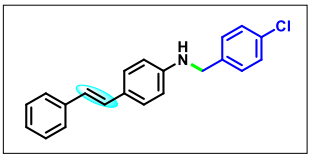
^1H NMR (600 MHz, Chloroform-d) δ 7.31 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 4.26 (s, 1H), 3.83 (s, 1H), 3.81 (t, *J* = 6.6 Hz, 1H), 2.78 (t, *J* = 6.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 158.8, 146.9, 131.4, 129.9, 128.8, 127.0, 114.0, 113.1, 64.0, 55.3, 48.0, 38.3.

4.3ba: (**(E)-N-benzyl-4-styrylaniline**) **Yield 75%; Yellow solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**:



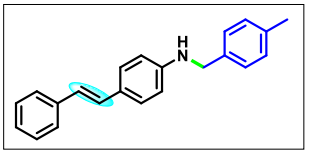
^1H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.43 – 7.29 (m, 11H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 16.3 Hz, 1H), 6.93 (d, *J* = 16.3 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 2H), 4.40 (s, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 147.7, 139.1, 139.1, 138.1, 129.1, 128.8, 128.7, 128.6, 128.2, 127.8, 127.5, 127.4, 127.1, 126.8, 126.1, 125.3, 124.7, 113.0, 113.0, 48.3.

4.3bb: (**(E)-N-(4-chlorobenzyl)-4-styrylaniline**) **Yield 72%; Yellow solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**:



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.31 (m, 8H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 16.3 Hz, 1H), 6.93 (d, *J* = 16.3 Hz, 1H), 6.63 (d, *J* = 8.6 Hz, 2H), 4.37 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.4, 138.0, 137.7, 133.0, 128.8, 128.7, 128.7, 128.6, 127.8, 127.8, 127.4, 126.8, 126.1, 124.9, 113.1, 47.6.

4.3bc: (**(E)-N-(4-methylbenzyl)-4-styrylaniline**) **Yield 68%; Yellow solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v)**:



^{1}H NMR (600 MHz, Chloroform-d) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 16.3 Hz, 1H), 6.94 (d, *J* = 16.3 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 2H), 4.35 (s, 2H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.9, 138.1, 137.0, 136.1, 129.4, 128.8, 128.6, 127.8, 127.5, 127.0, 126.8, 126.1, 124.6, 113.0, 48.0, 21.7.

4.8. NMR Spectra of Some Representative Compounds

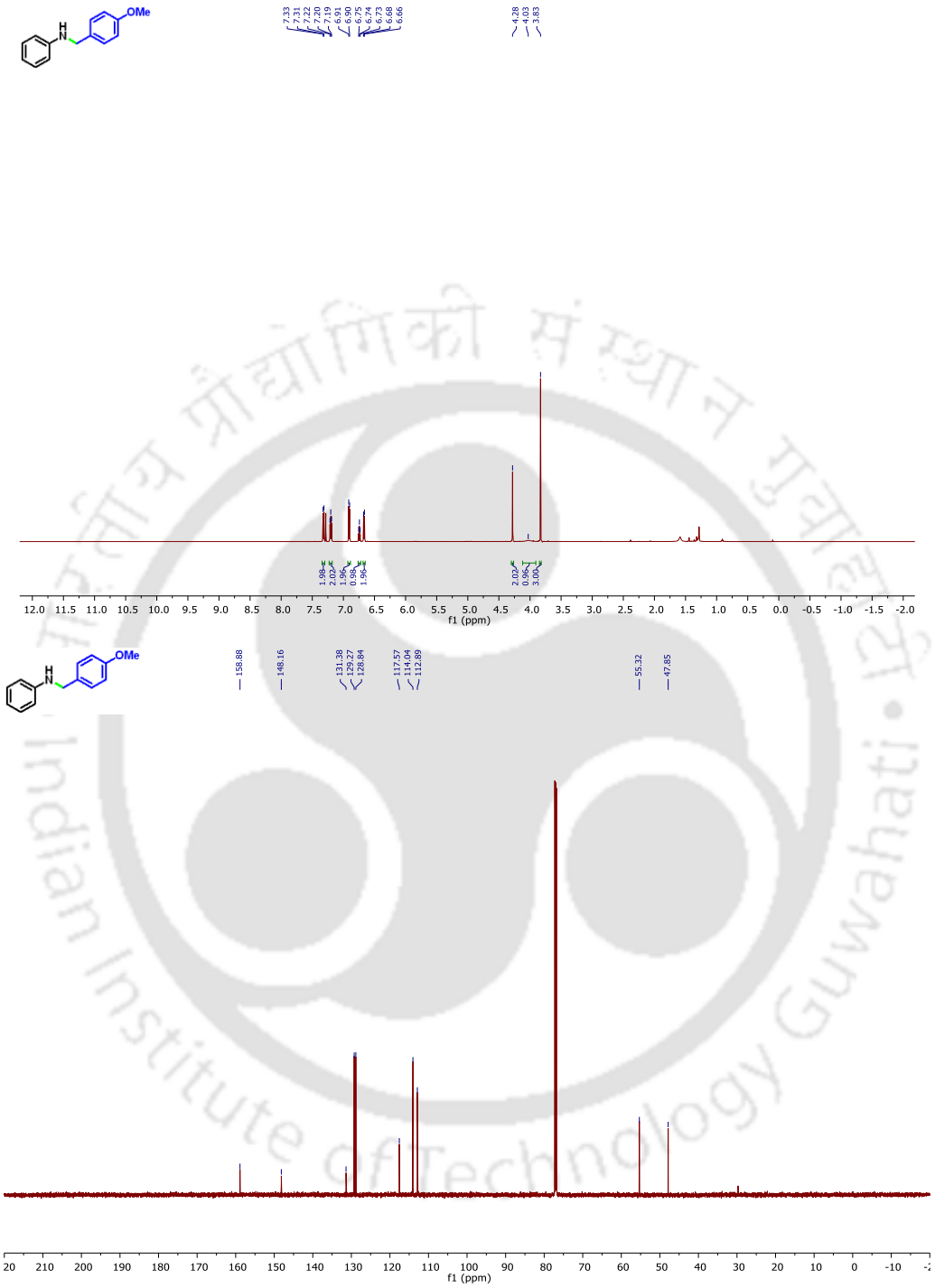


Fig S3: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of **N-(4-methoxybenzyl)aniline** (**4.3a)** in $CDCl_3$.

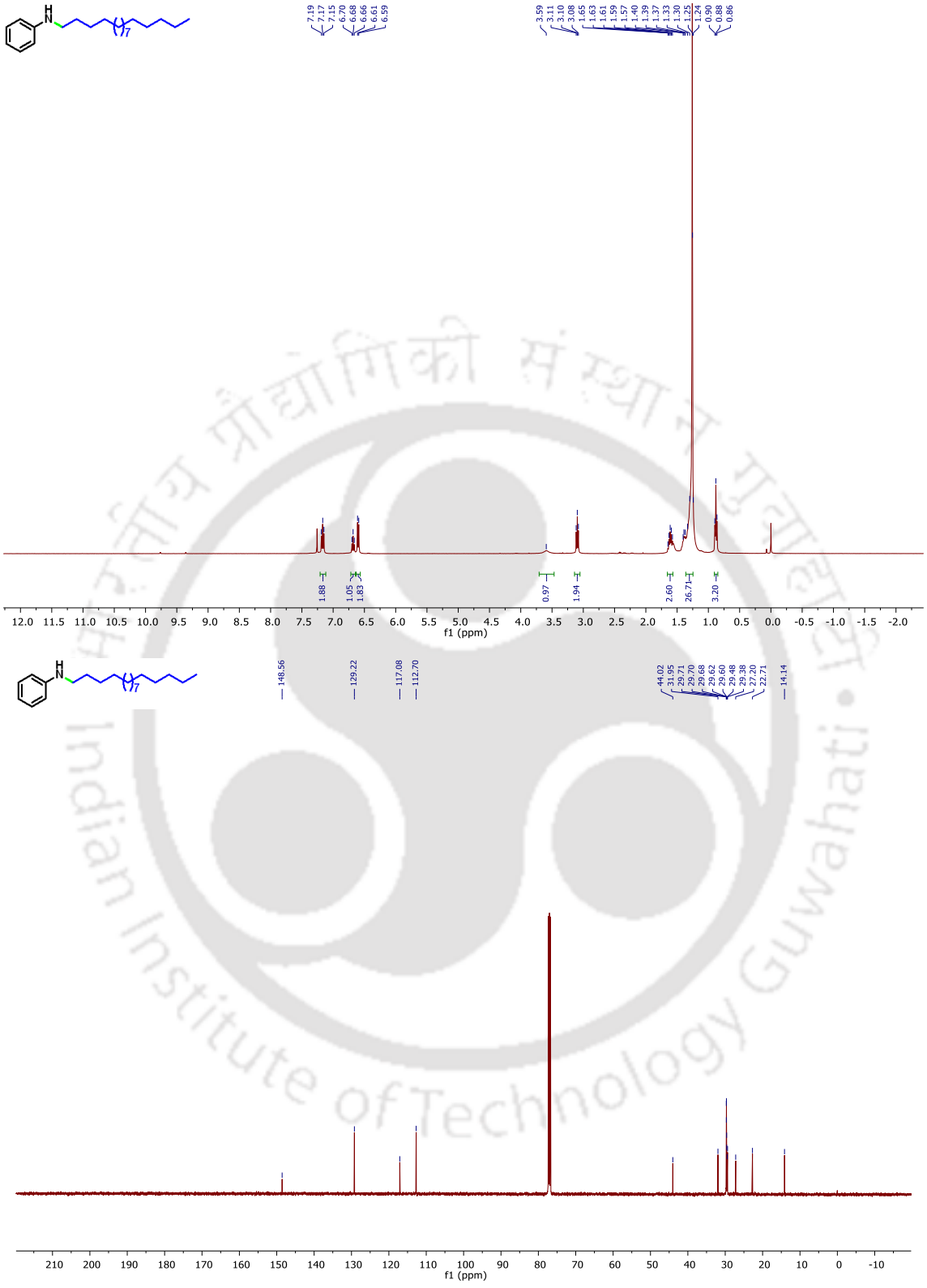


Fig S22: ^{1}H (400 MHz) & $^{13}C\{^{1}H\}$ (125 MHz) NMR Spectra of **N-hexadecylaniline** (**4.3t**) in $CDCl_3$.

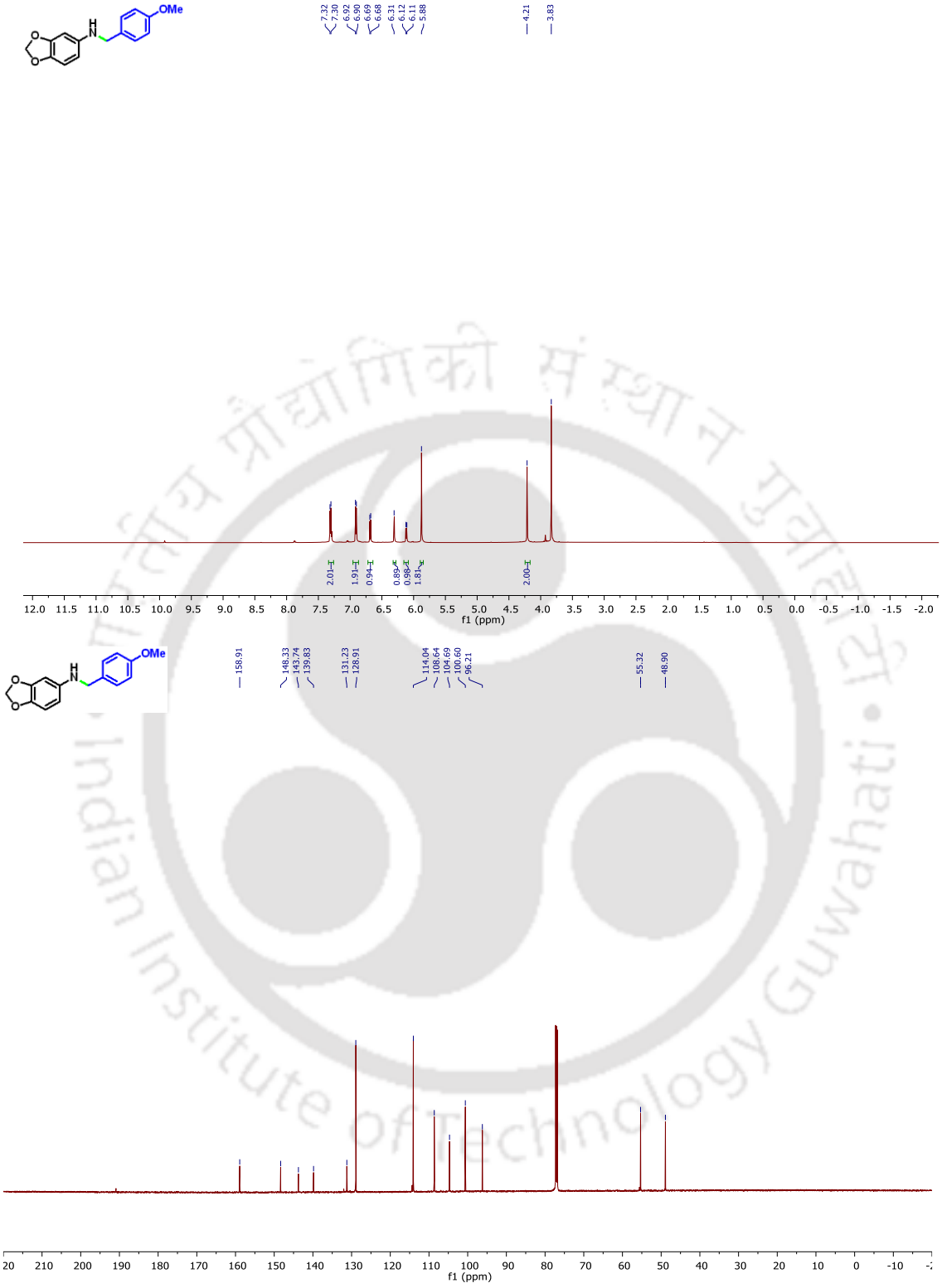


Fig S30: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of **N-(4-methoxybenzyl)benzo[d][1,3]dioxol-5-amine** (**4.3ab**) in $CDCl_3$.

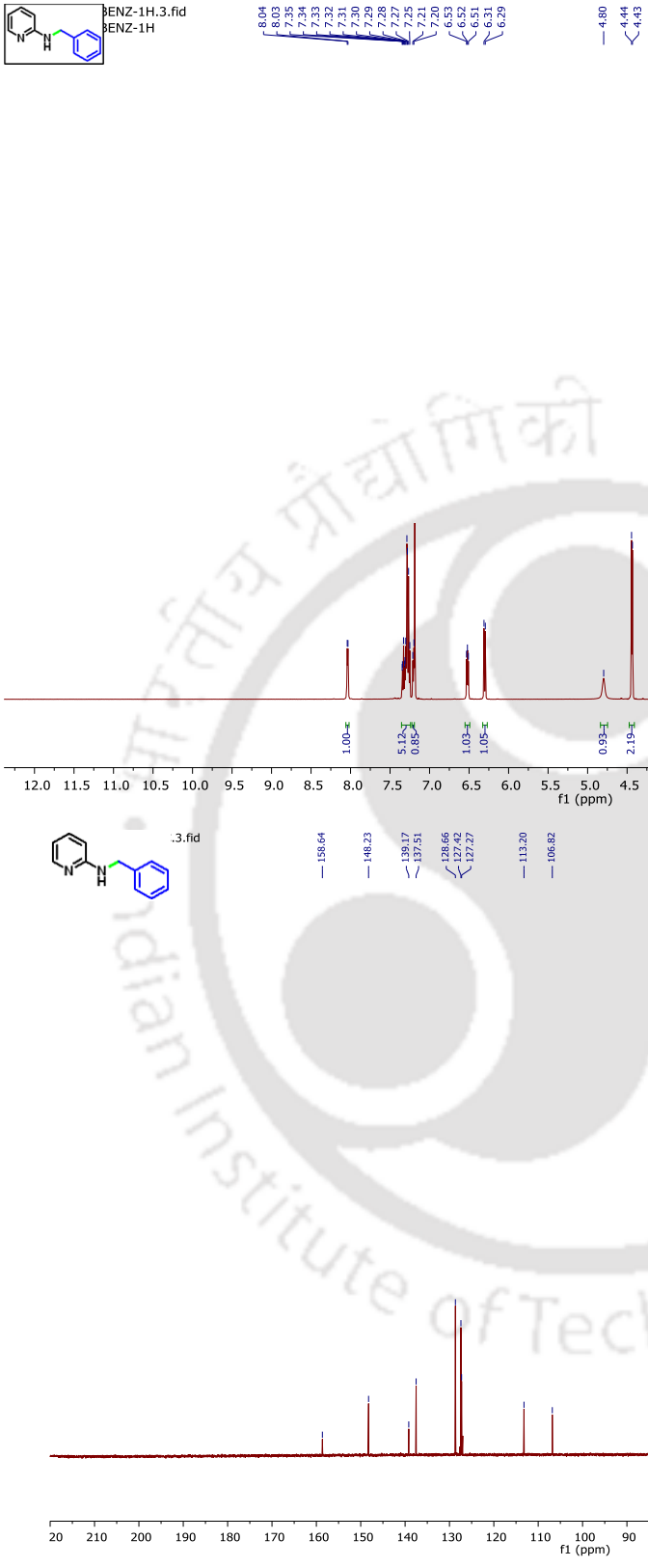


Fig S33: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of **N-(4-methoxybenzyl)pyridin-2-amine** (**4.3ae**) in $CDCl_3$.

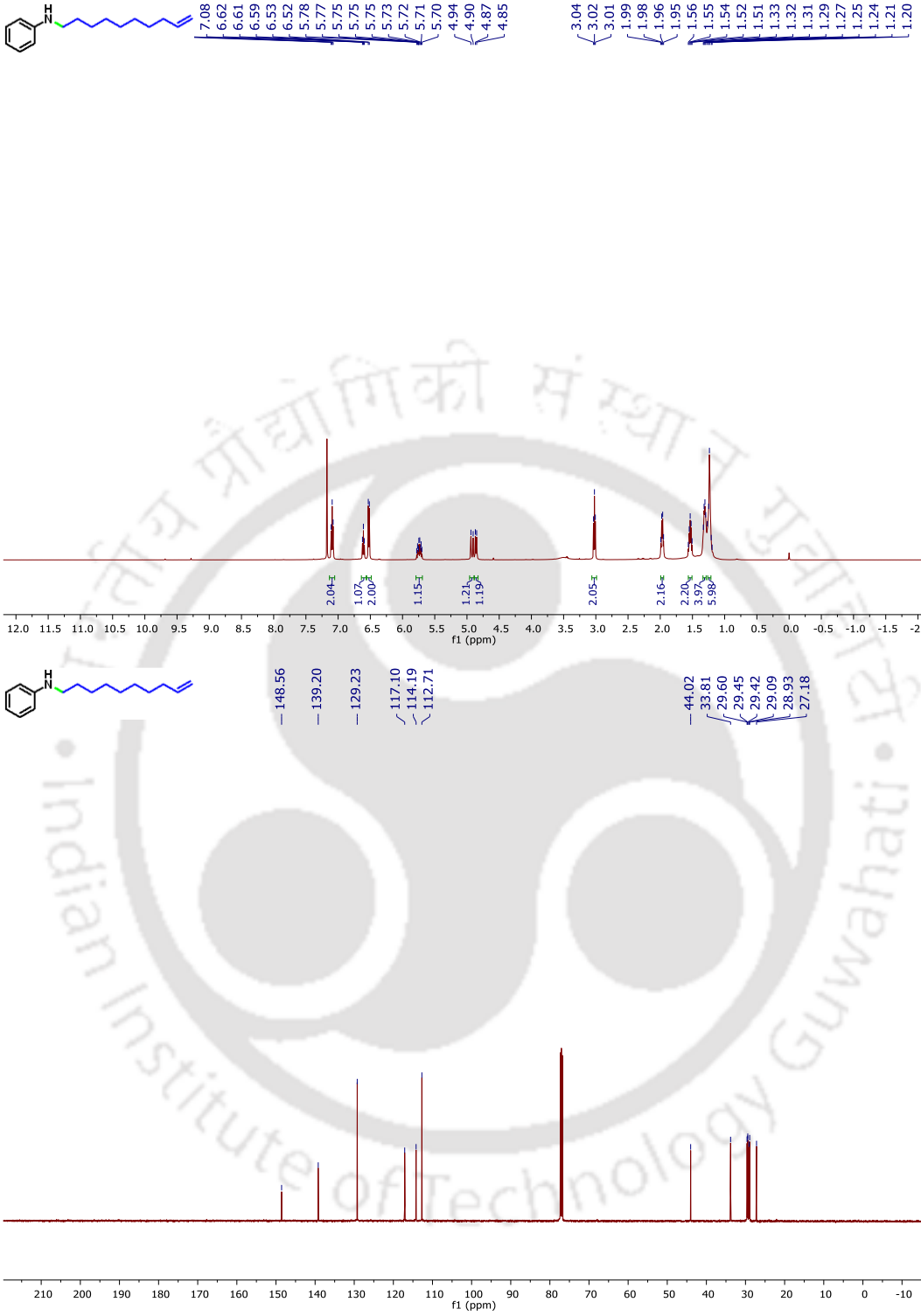


Fig S38: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of **N-(dec-9-en-1-yl)aniline** (**4.3aj**) in $CDCl_3$.

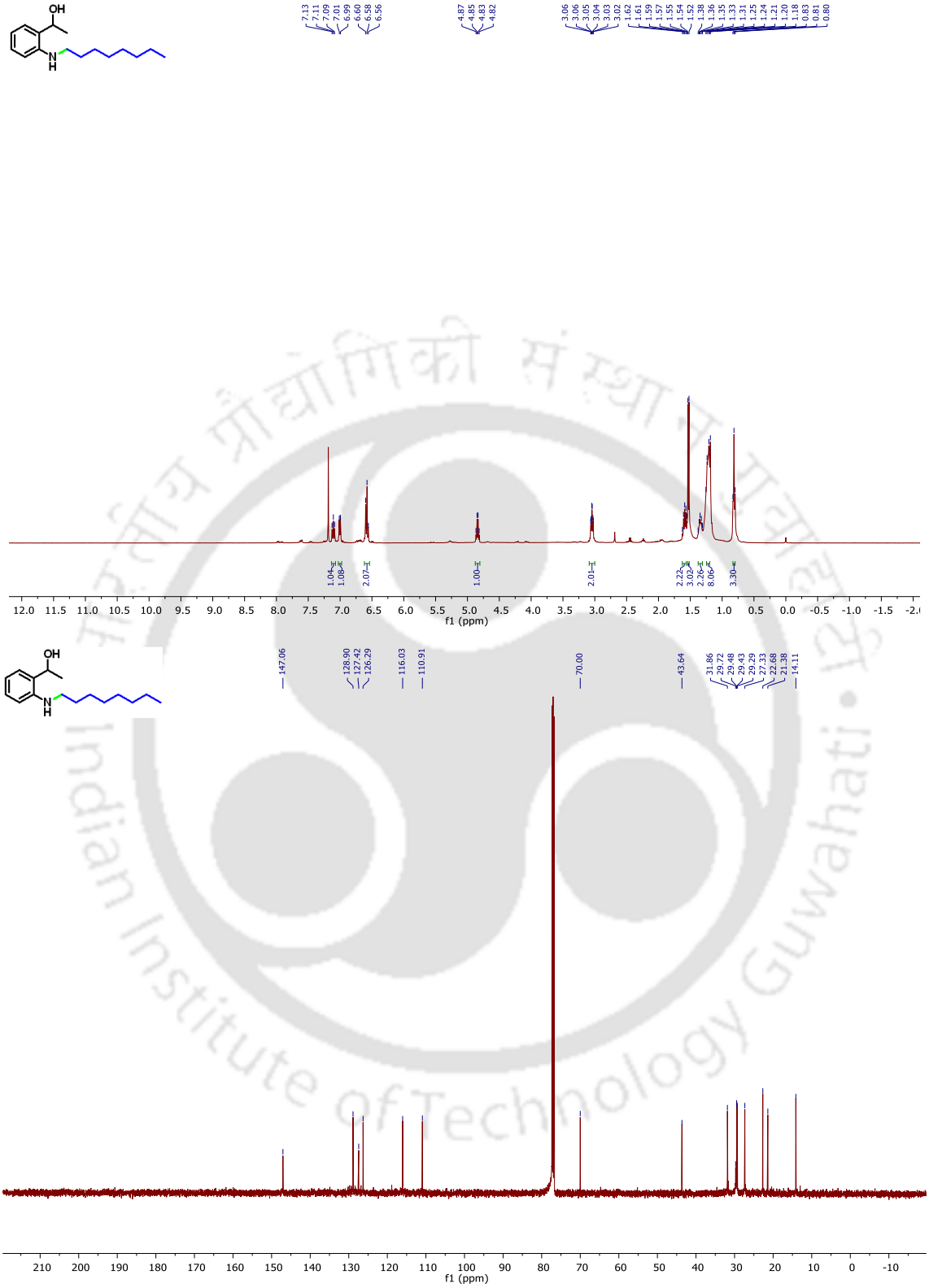


Fig S42: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of **1-(2-(octylamino)phenyl)ethan-1-ol** (**4.3an**) in $CDCl_3$.

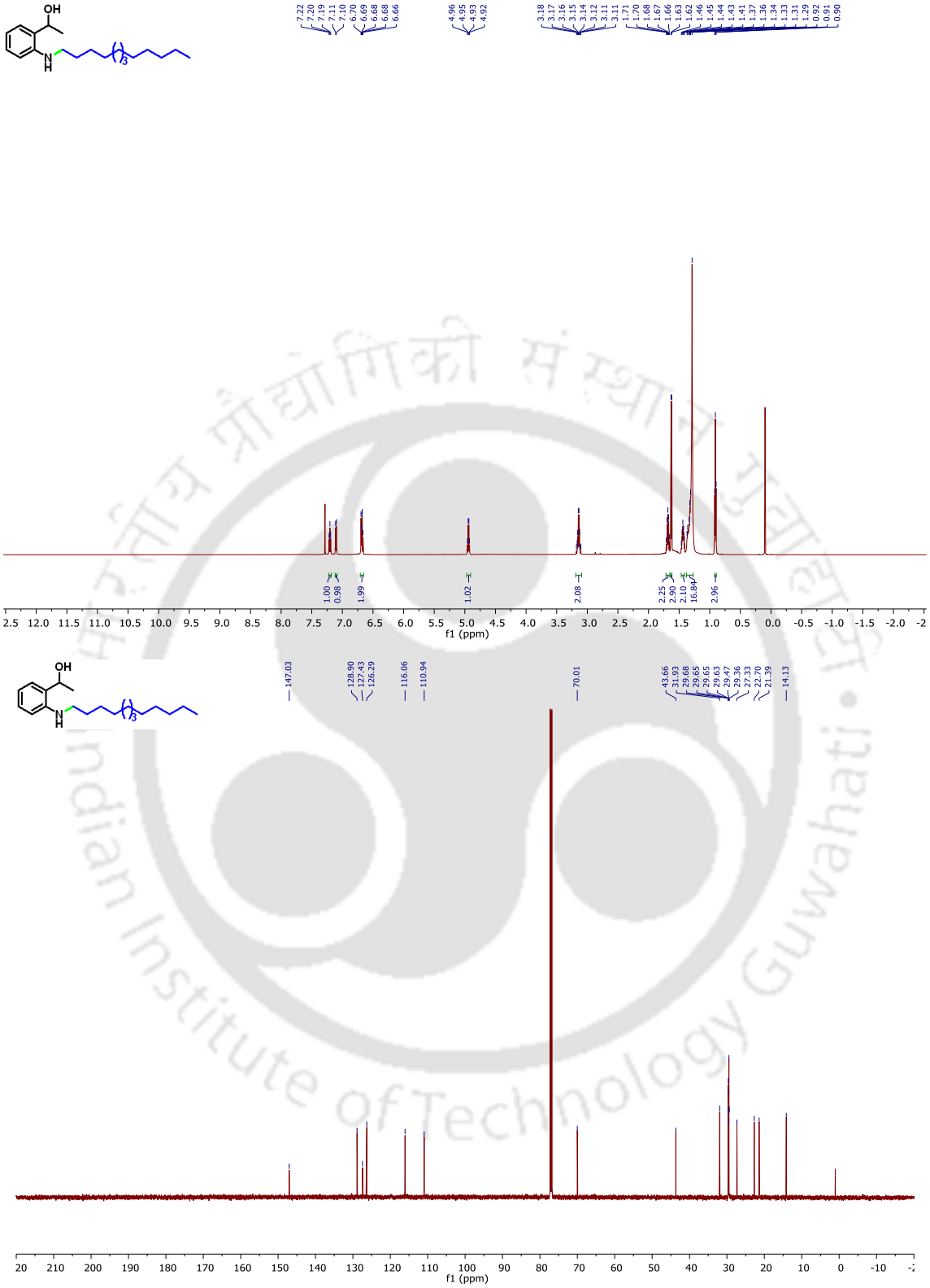


Fig S44: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of **1-(2-(dodecylamino)phenyl)ethan-1-ol** (**4.3ap**) in $CDCl_3$.

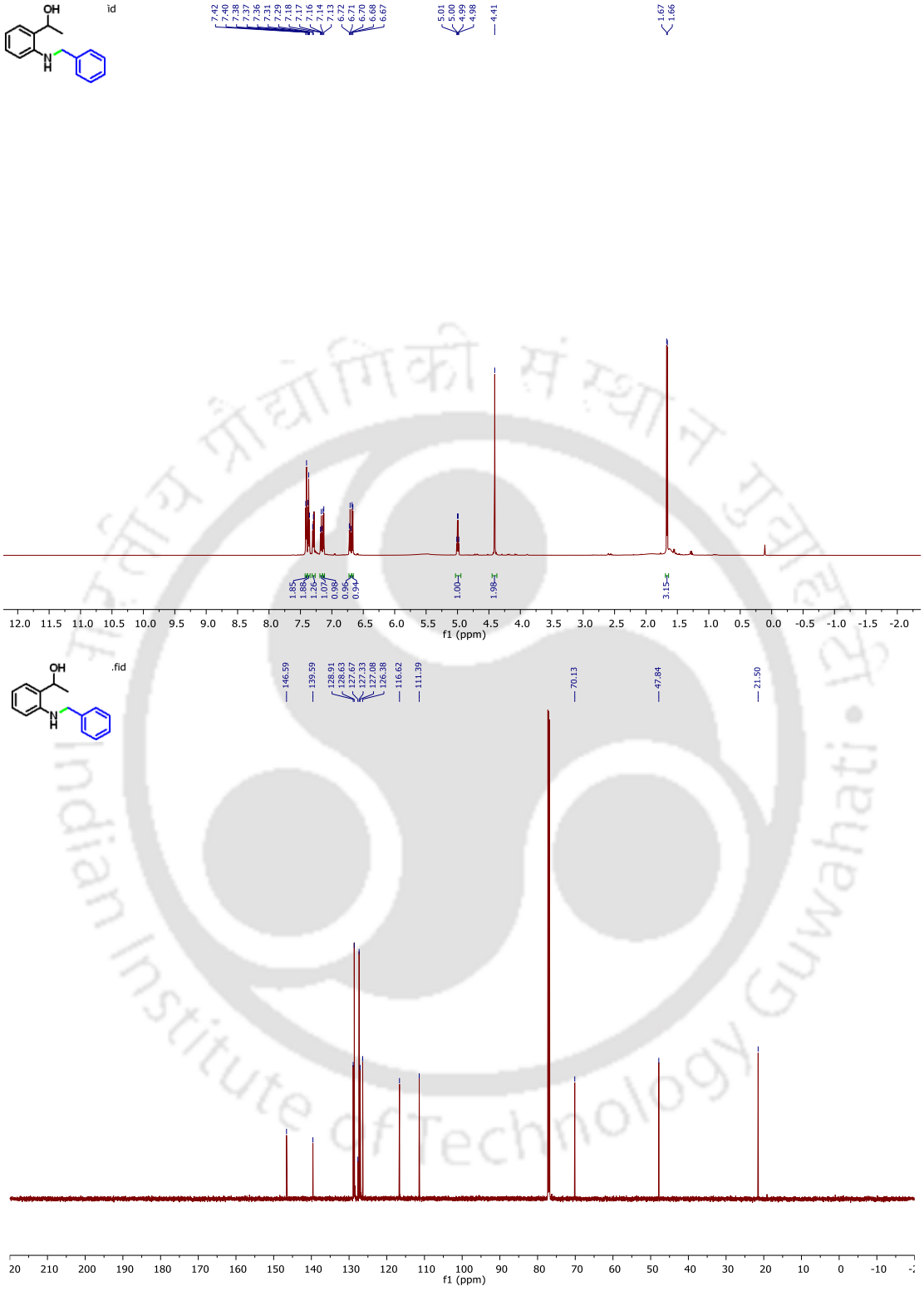


Fig S48: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of **1-(2-(benzylamino)phenyl)ethan-1-ol** (**4.3at**) in $CDCl_3$.

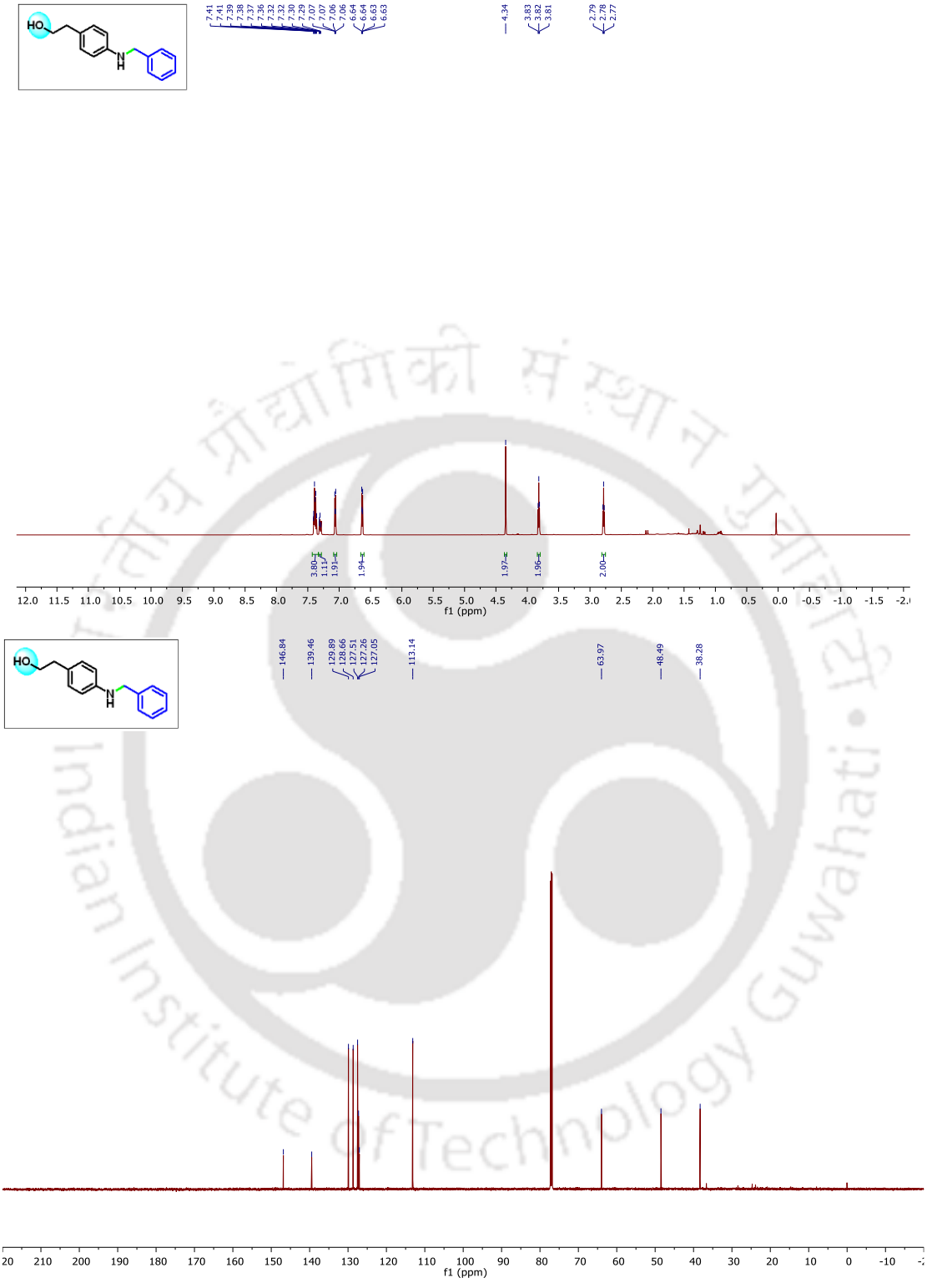


Fig S51: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of **2-(4-(benzylamino)phenyl)ethan-1-ol** (**4.3aw**) in $CDCl_3$.

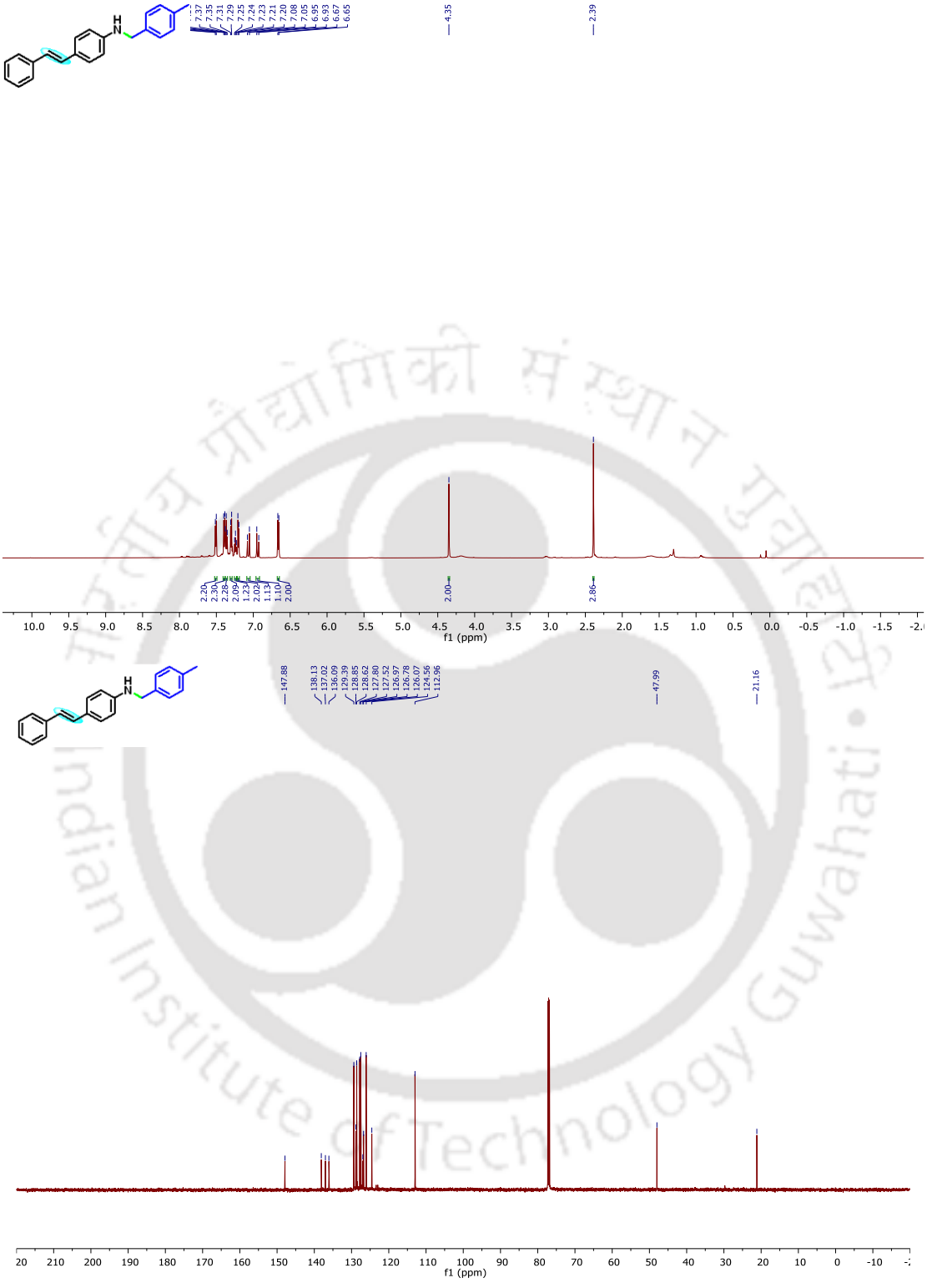
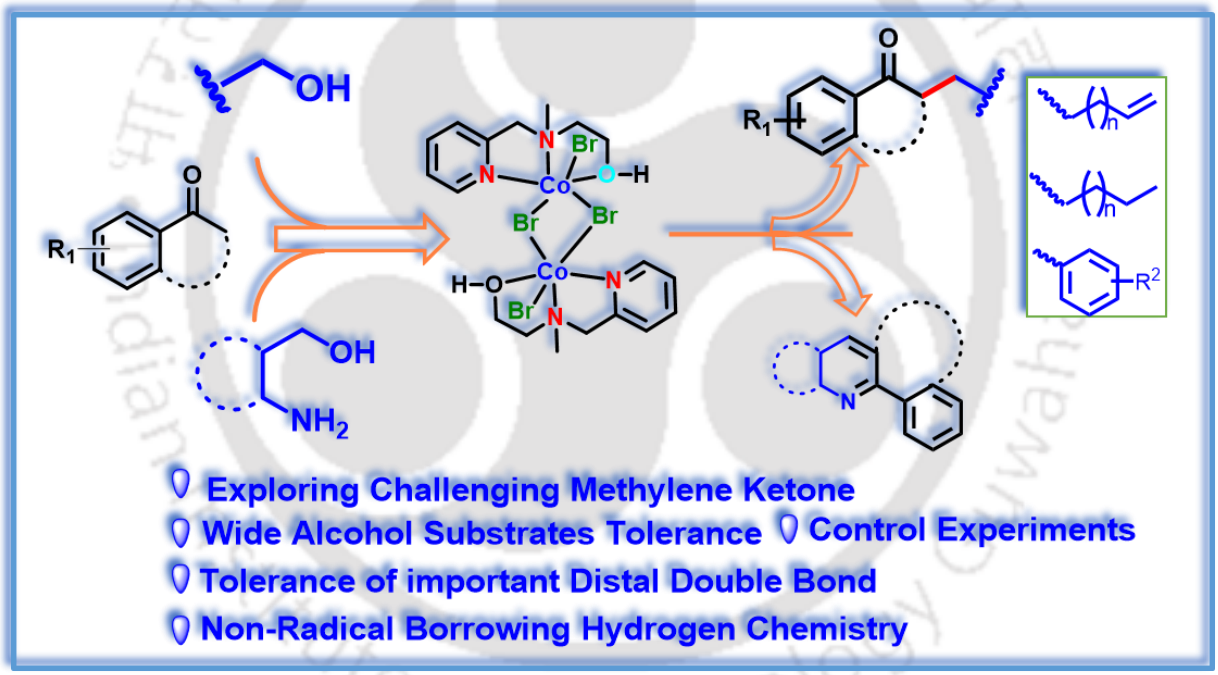


Fig S56: ^{1}H (600 MHz) & $^{13}C\{^{1}H\}$ (150 MHz) NMR Spectra of **(E)-N-(4-methylbenzyl)-4-styrylaniline** (**4.3bb**) in $CDCl_3$.

Chapter 5

Exploring the Potential of Non-Phosphine Cobalt System for the Alcohol Activation: Expedition of C-C and C-N Bond Formation



5.1. Introduction

This Chapter introduces non-phosphine based NNO-Co and NNN-Co pincer complexes. To further probe the practical applicability of the complexes, the catalytic activity of the said complexes toward the C-alkylation of challenging methylene ketones was investigated. This work encompasses a diverse range of alcohols, including those bearing significant functional groups in distal positions. Moreover, the protocol also efficient toward the multisubstituted quinoline synthesis. The details of the work is presented below.

Constructing C-C bonds from ketones is one of the major events in organic synthesis due to its extensive applications as an important reaction intermediate and basic building block in the chemical industry.[1] Conventional methods for C-alkylation of ketones include the use of organic halide or aldehydes in the presence of reducing agents which results in the elimination of quantitative toxic wastes.[2] Despite significant progress in the alkylation of methyl ketones to respective linear ketones,[3] it was observed that the alkylation of methylene ketones to α,α′-dialkylated (branched) ketones using the borrowing hydrogen technique was very limited. The major challenges include the steric factors obtained due to increased chain length on the α-carbon and also involve various competitive side reactions. However, with the progress of time, utmost dedication was observed to design a catalytic protocol that can efficiently transform methylene ketone to α, α′-dialkylated ketones which are illustrated in the next section.

5.2. Literature Survey

To achieve the C-alkylation of methylene ketones, several noble metals-based catalytic systems were employed. Donohoe and coworkers reported Ir and Rh-complexes with appropriate phosphine ligand systems for C-alkylation of methylene ketones using methanol as methylating agents.[4,5] The same group also extended the work with Ir-catalyst and various aliphatic and benzylic alcohols were employed as an alcohol counterpart.[6] However, the protocol utilizes a superstoichiometric amount of base and approximately 10 equiv. of alcohols for alkylation. Afterward, Glorious and Zhang groups also contributed toward the α-alkylation of methylene ketones and provided milder reaction conditions than previously reported (**figure 5.1**).[7,8] However, the implementation of renewable resources in combination with earth-abundant metal catalysts is always an attractive solution.[9] In this respect very limited contribution has been reported to date which includes the application of Mn, Fe, and Ni catalytic system,[10] providing room for further development (**figure 5.1**). Despite being the reported protocols very

effective, the need for more general and sustainable protocols is highly demanding. In this respect, it was observed that cobalt catalysis attracted the utmost attention in the scientific community because of its effective contribution in nature in the form of Vitamin B12 to the

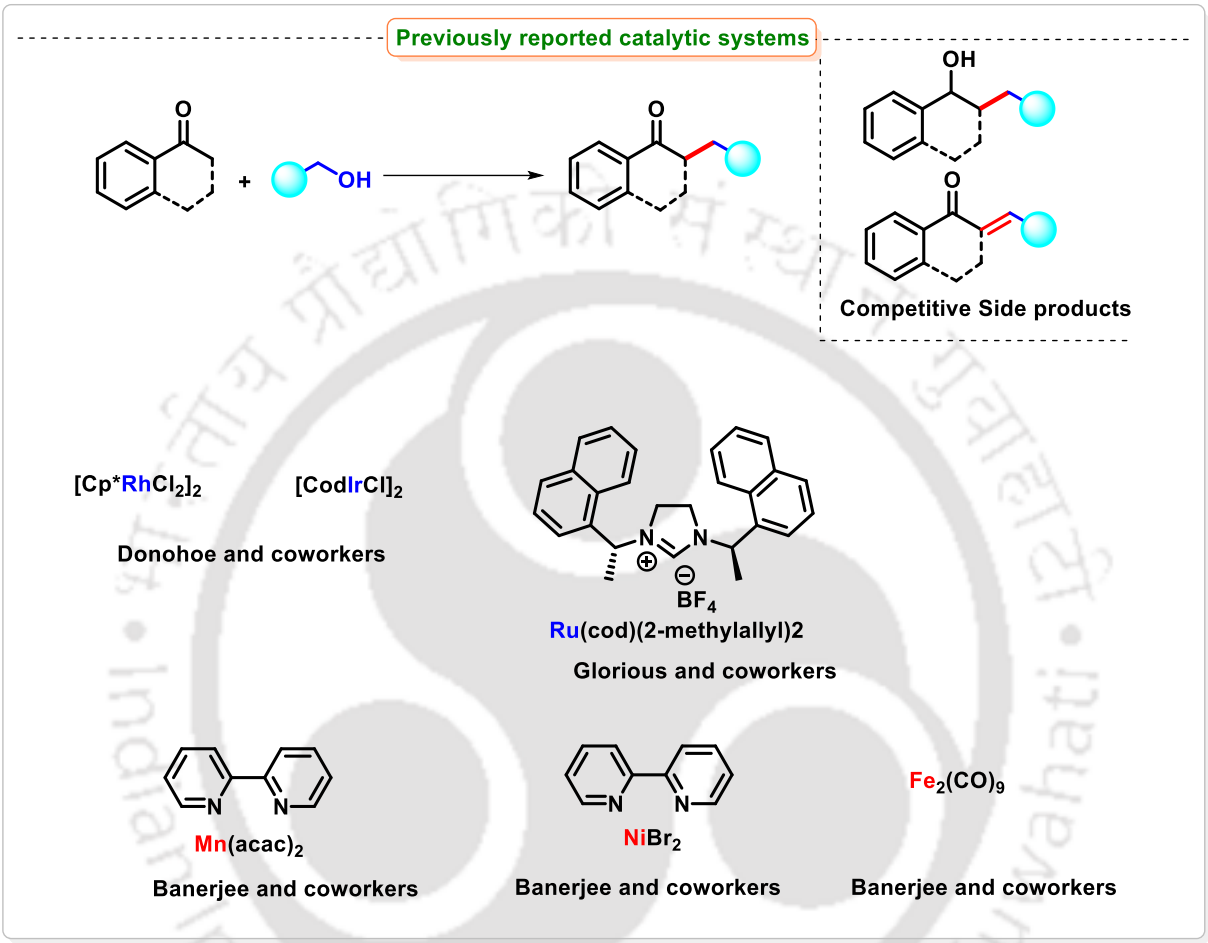


Figure 5.1: Previous reports on the C-alkylation of methylene ketone

synthetic world (e.g., Pauson-Khand reactions, various coupling reactions, cyclization reactions, and C-H activation reactions).[11] Recently, various Co-based catalyst system was explored for the "Acceptorless Dehydrogenation" and "Borrowing Hydrogen" mediated reactions.[12] As a part of our continuous endeavour for the development of catalytic pathways via the green route,[13] an affordable NNO ligand-based Co complex was developed. [14] To find the practical applicability of the synthesized complexes, the Co-catalysis in the C-alkylation of methylene ketones exclusively were not reported and hence, in this chapter, the developed NNO-Co complexes were investigated for C-alkylation of methylene ketones.

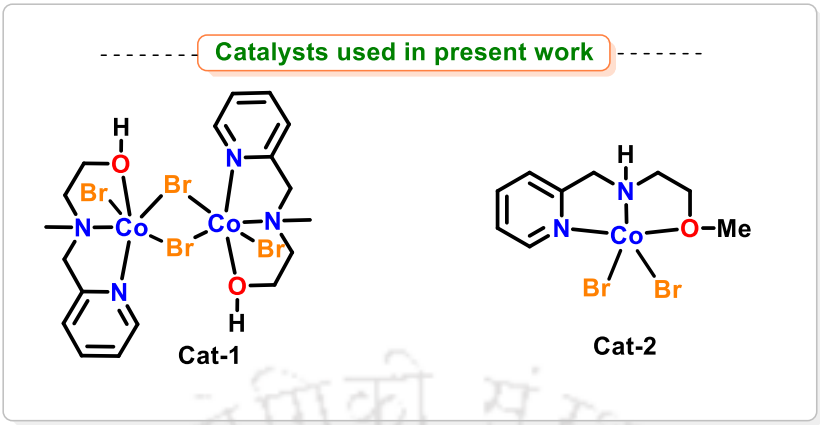
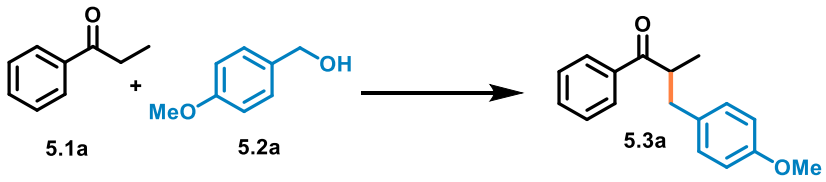


Figure 5.2: Catalysts used in the present work

5.3. Present Work

The investigation started with the optimization of reaction conditions for the reaction between methylene ketone and benzyl alcohol to give α-alkylated branched ketone product. Initially, when propiophenone **5.1a** (1 equiv.) and benzyl alcohol **5.2a** (1.5 equiv.) reacted in the presence of Cat. **1** (3 mol%) and 1 equiv. of KO^{t}Bu at 140 °C for 24 h to afford 75% of the alkylated product **5.3a** (table **5.1** entry **1**). Concerning Cat. **2**, keeping all the conditions identical, the yield of the **3a** was found to decrease (table **5.1** entry **2**). This result shows that the presence of a strong acidic proton in the ligand helps the catalyst to perform well to drive the reaction forward. So, Cat. **1** is considered as a suitable catalyst for the reaction and further proceed to change other reaction parameters. Upon decreasing the KO^{t}Bu loading to 50 mol%, the yield of the **5.3a** increased, while decreasing further, lowers the yield of **5.3a** (table **5.1** entry **3**). However, when the reaction was carried out in the presence of 50 mol% of KO^{t}Bu with increasing the reaction duration to 36 h, the yield of the **5.3a** was improved to 82% (table **5.1** entry **6**). Upon conducting the control experiment either in the absence of a catalyst or KO^{t}Bu, the reaction shows a trace amount of the formation of **5.3a** (table **5.1** entries **7** & **8**). These results indicate the participation of both the catalyst and base in driving the reaction forward. Further, under uniform conditions, various bases (such as KOH, NaO^{t}Bu, NaOH, K_2CO_3) and solvents (such as xylene and dioxane) do not enhance the efficiency of the reaction (table **5.1** entries **9** - **14**). Further on decreasing the catalyst loading displays lower yield of the desired product (table **5.1** entry **15**). Moreover, the application of ligand free cobalt bromide also shows detrimental effect proving the importance of ligand in driving the reaction(table **5.1** entry **16**).

Table 5.1: Optimization of C-alkylation of methylene ketone with benzyl alcohol[a]



Sl. no.	5.1a (in mmol)	5.2a (in mmol)	Cat (mol%)	Base (mol%)	solvent (in ml)	time (in h)	5.3a (% yield)[b]
1	0.5	0.75	Cat-1 (3)	KO^{t}Bu (100)	tol (2)	24	75
2	0.5	0.75	Cat-2 (6)	KO^{t}Bu (100)	tol (2)	24	60
3	0.5	0.75	Cat-1 (3)	KO^{t}Bu (50)	tol (2)	24	71
4	0.5	0.75	Cat-1 (3)	KO^{t}Bu (30)	tol (2)	24	62
5	0.5	0.55	Cat-1 (3)	KO^{t}Bu (50)	tol (2)	24	51
6	0.5	0.75	Cat-1 (3)	KO^{t}Bu (50)	tol (2)	36	85
7	0.5	0.75	-	KO^{t}Bu (50)	tol (2)	36	20
8	0.5	0.75	Cat-1 (3)	-	tol (2)	36	-
9	0.5	0.75	Cat-1 (3)	KOH (50)	tol (2)	36	62
10	0.5	0.75	Cat-1 (3)	NaO^{t}Bu (50)	tol (2)	36	30
11	0.5	0.75	Cat-1 (3)	NaOH (50)	tol (2)	36	20
12	0.5	0.75	Cat-1 (3)	K_2CO_3 (50)	tol (2)	36	trace
13	0.5	0.75	Cat-1 (3)	KO^{t}Bu (50)	Xylene (2)	36	40
14	0.5	0.75	Cat-1 (3)	KO^{t}Bu (50)	dioxane (2)	36	trace
15	0.5	0.75	Cat-1 (1.5)	KO^{t}Bu (50)	tol (2)	36	58%
16	0.5	0.75	$CoBr_2$ (3)	KO^{t}Bu (50)	tol (2)	36	trace

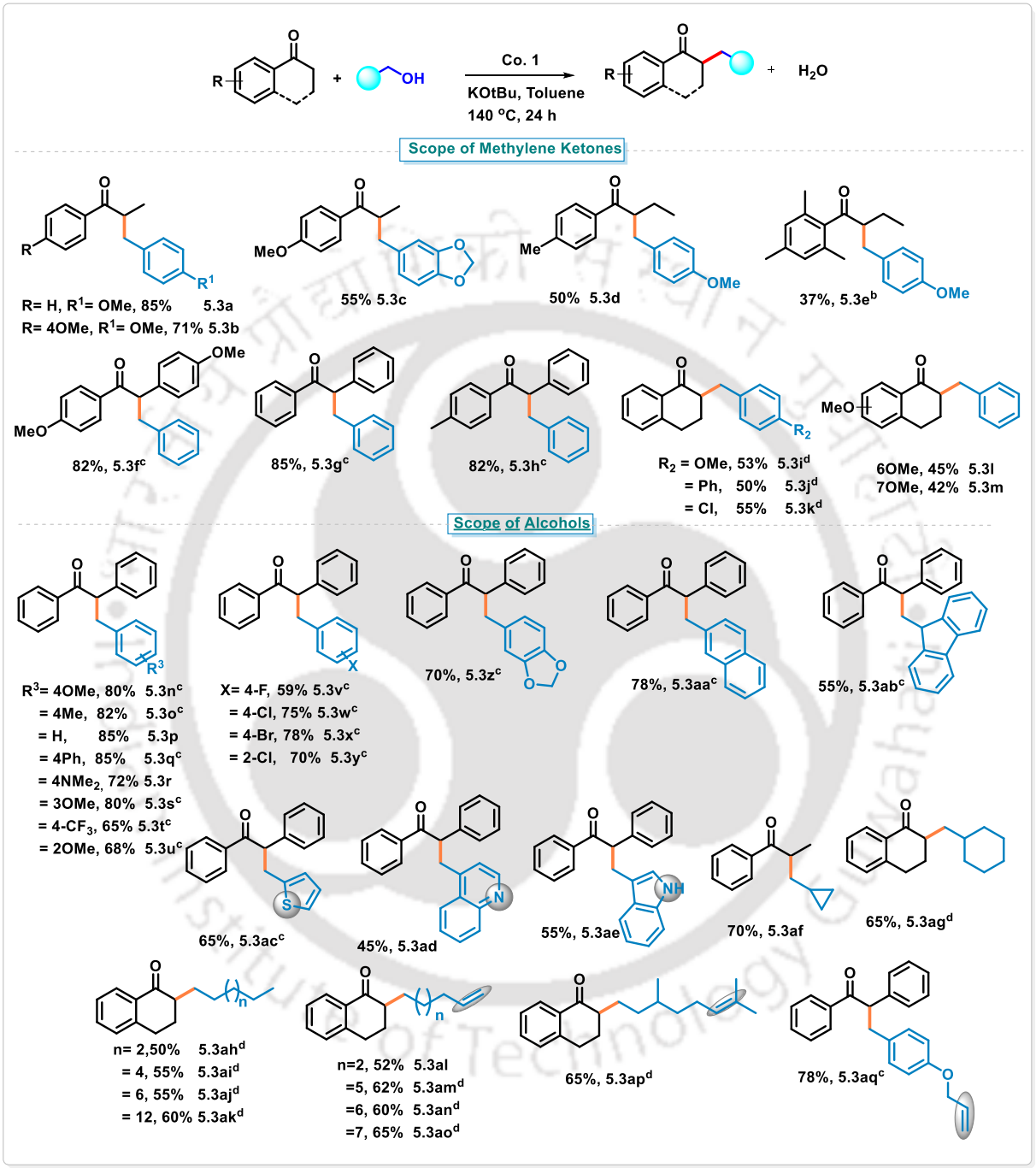
[a]**Reaction Condition**: **1a** (0.5 mmol), **2a** (0.55 - 0.75 mmol), Cat. (3 – 6 mol%), Base (0.1 – 0.5 mmol), Solvent (2 mL), Temperature = 140 °C, [b]Isolated yield.

After achieving the optimized reaction conditions, a wide range of substrates were explored which is summarized in table **5.2**. Initially, various methylene ketone derivatives and benzyl alcohols were explored. The 4-methoxypropiophenone works well with 4-methoxybenzyl alcohol and piperonyl alcohol, delivering the C-alkylated product in good yield (table **5.2**, **5.3b**

& **5.3c**). Further, increasing the chain length in the methylene part increases steric congestion and as a result, was less efficiently coupled with alcohol and requires higher loading of the base to achieve the alkylated product (table **5.2**, **5.3d** & **5.3e**). Notably, derivatives of 2-phenylpropiophenone derivatives reacted efficiently with alcohol counterparts delivering an excellent yield (82 – 85%) of the desired C-alkylated product (table **5.2**, **5.3f** – **5.3h**). Interestingly, α-tetralone and its derivatives (OMe in 6 and 7 positions) also work well delivering the desired product in uniformly moderate yields (table **5.2**, **5.3i** – **5.3m**).

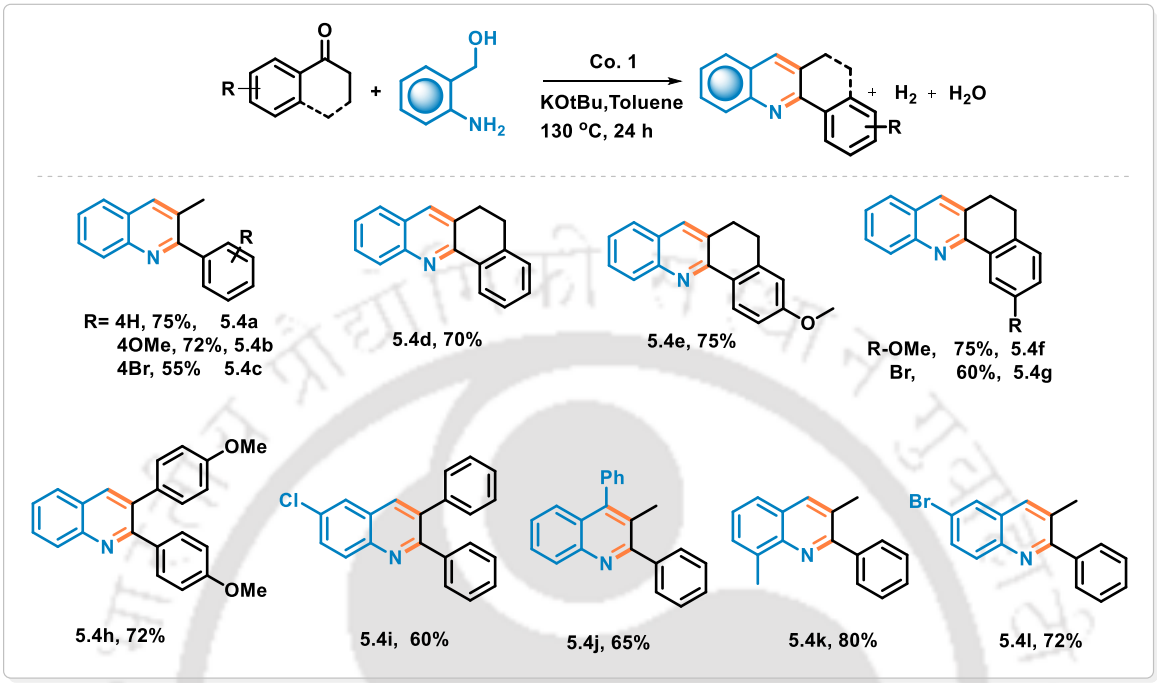
Moving forward, the substrate scope of structurally diverse alcohols was investigated for the catalytic cross-coupling of methylene ketones and alcohols. Alcohols bearing electron donating group (4-OMe, Me, Ph, NMe_2), when reacted with 2-phenylpropiophenone, excellent yield of the desired C-alkylated product were obtained (table **5.2**, **5.3n** – **5.3r**). Further, the electron-withdrawing group (3-OMe, 4-CF_3) is also efficient toward the reaction, although CF_3-bearing benzyl alcohol was found to be less active delivering 65% of the desired product (table **5.2**, **5.3s** & **5.3t**). Further, substituent in ortho position (2-OMe) also works well in the present condition delivering good yield of the desired product (table **5.2**, **5.3u**). Halogen (4-F, Cl, Br, 2-Cl) containing benzyl alcohol underwent facile coupling with methylene ketone delivering 59 – 79% of the desired C-alkylated products (table **5.2**, **5.3v** – **5.3y**). In addition, piperonyl alcohol and 2-naphthyl methanol efficiently reacted with methylene ketones (table **5.2**, **5.3z** & **5.3aa**). Moreover, the sterically congested fluorenyl alcohol furnishes 55% of the desired C-alkylated product (table **5.2**, **5.3ab**). Remarkably, heterocyclic units bearing benzyl alcohols (such as thiophene, quinoline, and indole) were also effectively coupled with methylene ketones that further probe the scope of the reaction (table **5.2**, **5.3ac** – **5.3ae**). While more challenging un-activated aliphatic alcohols (such as cyclopropyl methanol, and cyclohexyl methanol) moderately reacted with propiophenone and α-tetralone respectively (table **5.2**, **5.3af** & **5.3ag**). Notably, aliphatic alcohols with varied chain lengths including lignocellulosic biomass-derived cetyl alcohol when allowed to react with tetralone, interestingly moderate to a good yield of the desired C-alkylated product were obtained (table **5.2**, **5.3ah** – **5.3ak**). Pleasingly, aliphatic alcohol containing distal double bonds (has potential for various post-modification) and structurally important citronellol also displays uniform activity (52 – 65%) toward C-alkylated product formation (table **5.2**, **5.3al** – **5.3aq**).

Table 5.2: Scope of Various Methylene Ketones & Alcohols[a]



[a]**Reaction Condition**: **1** (0.5 mmol), **2** (0.75 mmol), Cat. **1** (3 mol%), KO^{t}Bu (50 mol%), Toluene (2 mL), 140 °C, 24 h, under argon. [b]Cat. **1** (3 mol%), KO^{t}Bu (100 mol%). [c]Cat. **1** (3 mol%), KO^{t}Bu (30 mol%). [d]Cat. **1** (3 mol%), KO^{t}Bu (80 mol%)

Table 5.3: Reaction with branch ketones and amino alcohols for highly branch quinoline synthesis[a]

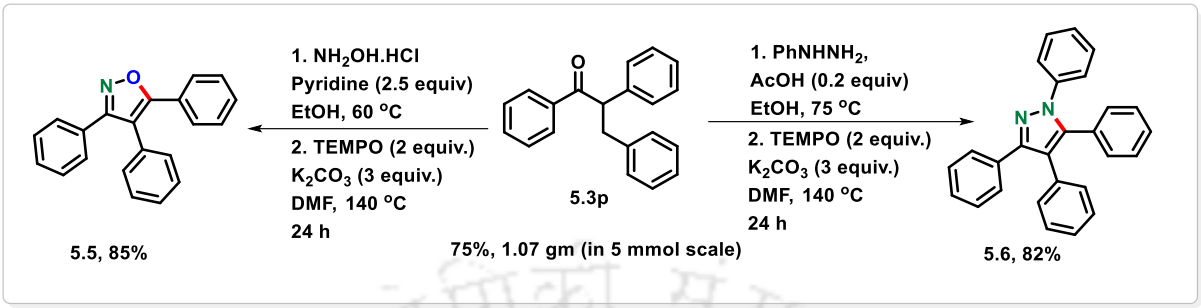


[a]**Reaction Condition**: **1** (0.5 mmol), **2** (0.75 mmol), Cat. **1** (3 mol%), KO^{t}Bu (50 mol%), Toluene (2 mL), 140 °C, 24 h, under argon.

Further, when derivatives of 2-aminobenzyl alcohols were treated with methylene ketone derivative, it resulted in the formation of multi-substituted quinoline derivatives. Various substituted and unsubstituted propiophenones (4OMe and 4Br) couple well with 2-aminobenzyl alcohol giving the desired quinoline product in moderate to good yield (table **5.3**, **5.4a** – **5.4c**). In addition, tetralone derivatives also show equal potential toward the formation of multi-ring containing quinoline derivatives (table **5.3**, **5.4d** – **5.4g**). Moreover, bulky methylene ketones couple with amino alcohol derivatives moderately (table **5.3**, **5.4h** & **5.4i**). In addition, the present catalytic system enables the reaction between 2-aminobenzhydrol with propiophenone effectively to deliver highly substituted quinoline (table **5.3**, **5.4j**). Pleasingly, the methyl and bromo substituted 2-aminobenzyl alcohol couples with propiophenone efficiently delivering 72 – 80% yield of the desired quinoline derivatives (table **5.3**, **5.4k** & **5.4l**).

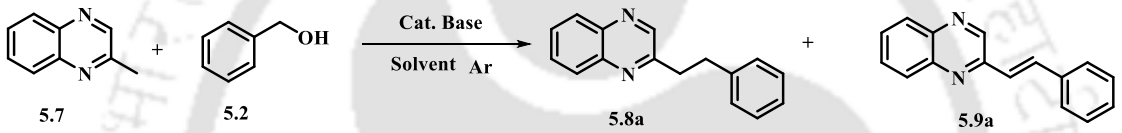
The attempt toward gram-scale synthesis of **5.3p** demonstrates good efficiency, isolating 75% of the product. This interesting moiety was found to have the potential for the synthesis of

important heterocycles (scheme **5.1**). Thus, oxazole (**5.5**), and pyrazole (**5.6**) were synthesized with good yield using starting material **3d**. [15 17]



Scheme 5.1: Post-synthetic modification of multi-substituted ketone to isooxazole and pyrazole derivative

Table 5.4: Table of Optimisation of C-alkylation 2-Methylquinoxaline



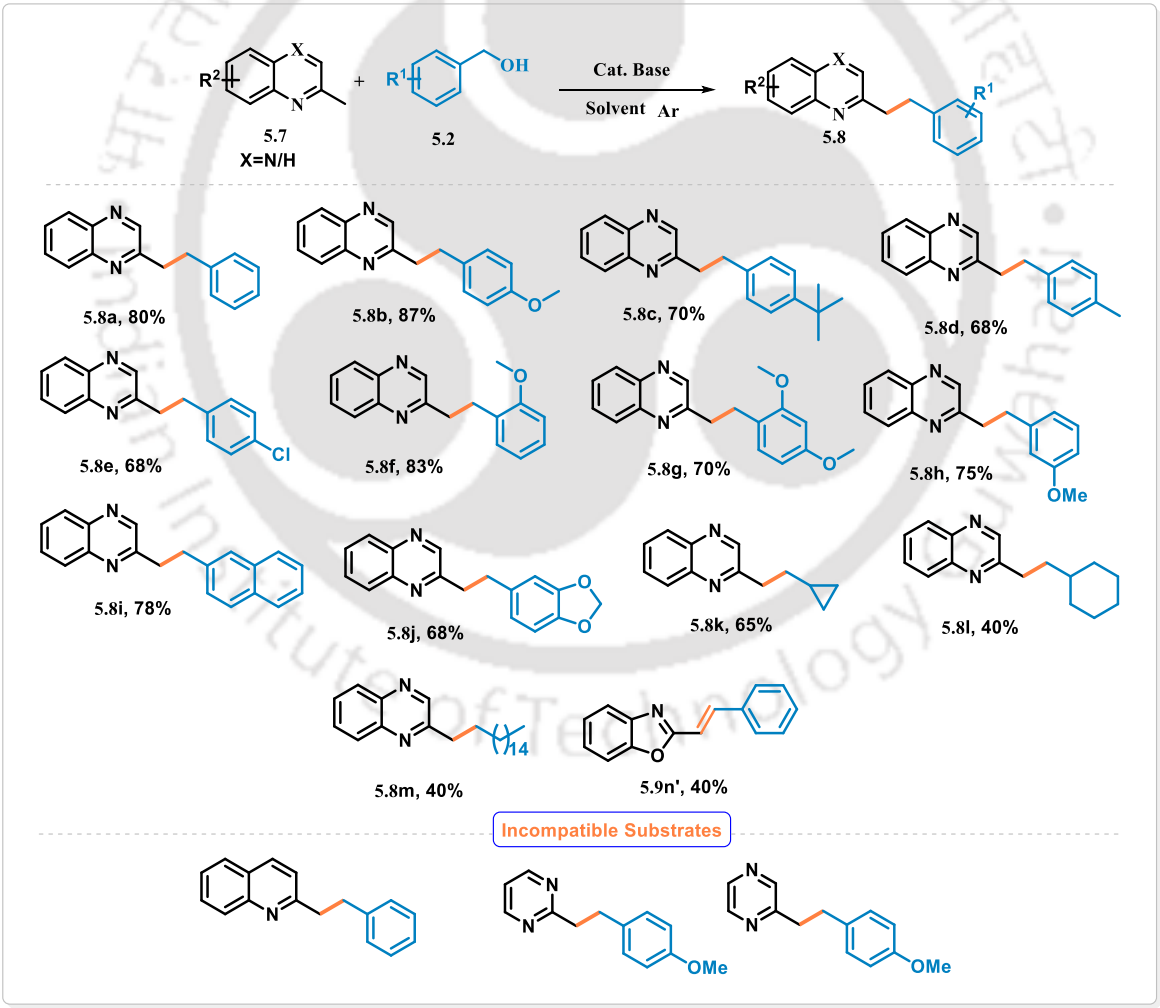
S.No.	5.7 (mmol)	5.2 (eq)	Catalyst(mol%)	Base (mol%)	Solvent	Temp (°C)	Time (h)	5.8a (%)	5.9a (%)
1	0.5	0.5	cat.-1 (3)	KO^{t}Bu (100)	Toluene	140	24	20	40
2	0.5	0.6	cat.-1 (3)	KO^{t}Bu (100)	Toluene	140	24	50	35
3	0.5	0.6	cat.-2 (6)	KO^{t}Bu (100)	Toluene	140	24	-	40
4	0.5	0.6	cat.-3 (6)	KO^{t}Bu (100)	Toluene	140	24	30	
5	0.5	0.75	cat. - 1 (3)	KO^{t}Bu (100)	Toluene	140	24	80	
6	0.5	0.75	cat. - 1 (3)	KO^{t}Bu (100)	Toluene	120	24	40	
7	0.5	0.75	cat. - 1 (3)	NaO^{t}Bu (100)	Toluene	140	24	15	70
8	0.5	0.75	cat. - 1 (3)	KOH (100)	Toluene	140	24	94	-
9	0.5	0.75	cat. - 1 (3)	KOH (100)	Xylene	140	24	45	
10	0.5	0.75	cat. -1 (3)	KOH (100)	Dioxane	140	24	N.R.	
11	0.5	0.75	cat. - 1 (3)	-	Toluene	140	24	N.R.	-
12	0.5	0.75	-	KOH (100)	Toluene	140	24	N.R.	15
13	0.5	0.75	cat. - 1 (3)	KOH (100)	Toluene	140	12	50	40
14	0.5	0.75	cat. - 1 (3)	KOH (100)	Toluene	140	36	90	-

[a]**Reaction Condition**: **5** (0.5 mmol), **2** (0.75 mmol), Cat. **1-3** (3 – 6 mol%), Base (100 – 150 mol%), Solvent (2 mL), 140 °C, under argon. [b]yield of alkylated product in parenthesis.

Functionalized N-heterocycles attracted tremendous attention because of their wide significance in various areas of science. Thus, the synthesis of N-heterocycles and its post-functionalization are quite an important area to visit. To further probe the scope of the present

protocol, 2-methyl N-heteroarenes are chosen to be investigated for C-alkylation with benzyl alcohols as alkylating agents. In this regard 2-methylquinoxalines are taken as a primary component and various unsubstituted and substituted benzyl alcohols were investigated for the coupling reaction. During the examination of the optimisation condition, it was observed that 1 equiv. of 2-methyl quinoxaline and 1.5 equiv. of benzyl alcohols is necessary for product formation. In addition, out of three cobalt catalyst, NNO-Co system i.e., Co-**1** in 3 mol% is efficient for the C-alkylation of methylene ketone. Moreover, KOH (1 equiv.) is found to be a suitable candidate for the efficacy of the reaction. Also, toluene as a solvent medium and maintaining 140 °C is essential for the reaction to proceed smoothly (table **5.4**).

Table 5.5: Substrate scope of C-alkylation of 2-methyl N-heteroarenes

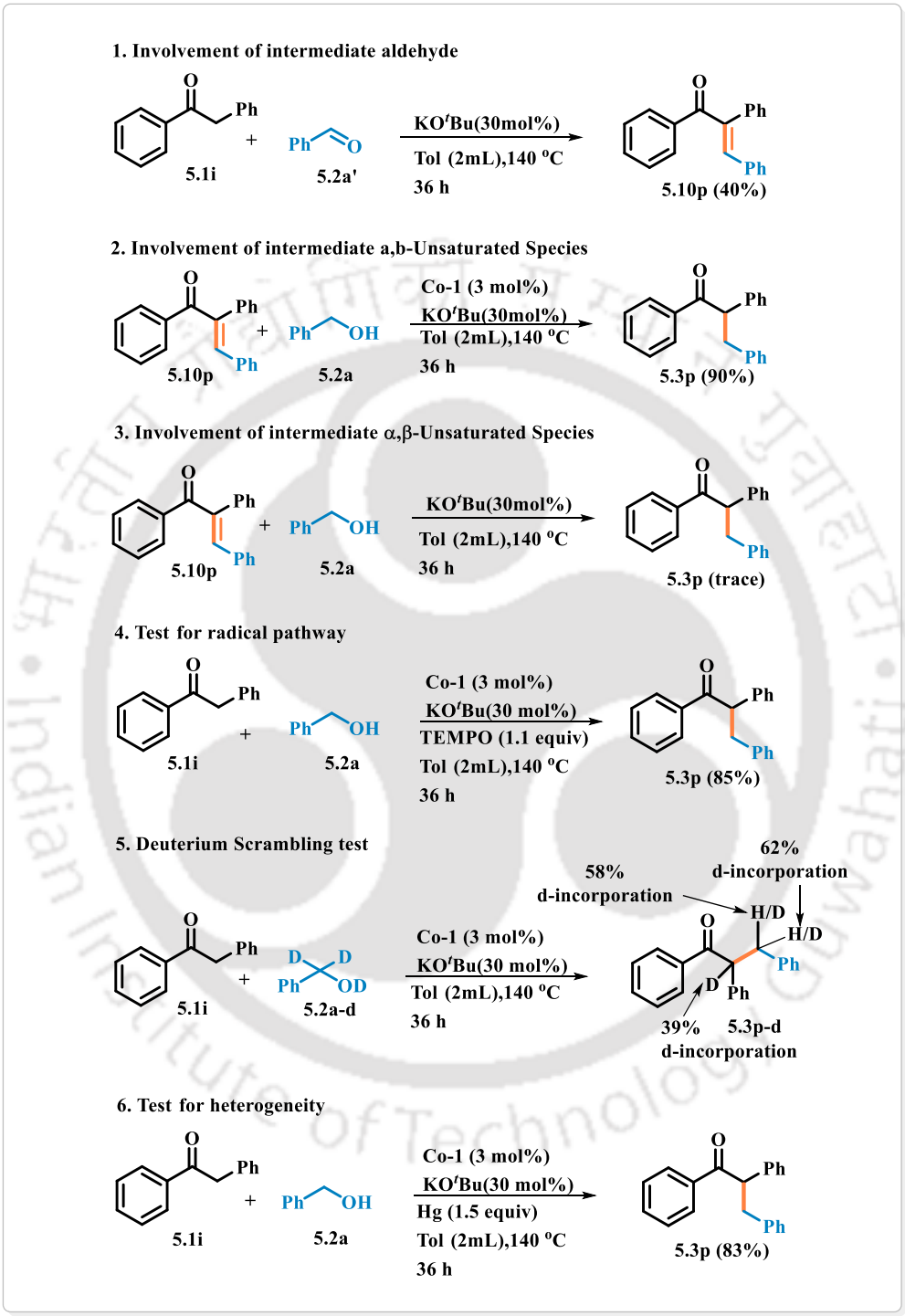


[a]**Reaction Condition**: **1** (0.5 mmol), **2** (0.75 mmol), Cat. **1** (5 mol%), KOH (100 mol%), Toluene (2 mL), 140 °C, 24 h, under argon

In this chapter, further the scope of the substrate was explored, where electron donating and halogen group containing benzyl alcohols (such as 4-OMe, 4-tBu, 4Me, 4Cl) deliver the alkylated product in good to excellent yield (table **5.6**, **5.8a** – **5.8e**). Gratifyingly, the substituents in the 2-position of benzyl alcohol also efficiently couple with the N-heteroarene to afford the desired product in good yield (table **5.6**, **5.8f** & **5.8g**). Moreover, OMe in 3 position of benzyl alcohol furnishes 75% of the desired product (table **5.6**, **5.8h**). In addition, 2-napthylmethanol and piperonyl alcohol was also employed effectively as an alkylating agent (table **5.6**, **5.8i** & **5.8j**). In case of cyclic alcohol bearing methanol, cyclopropylmethanol and cyclohexyl methanol couples with 2-methyl quinoxaline to furnish C-alkylated product in 65% and 40% respectively yield, respectively. Interestingly, direct biomass derived cetyl alcohol results in desired alkylated product in 40% yield (table **5.6**, **5.8m**). In addition, the reaction of 2-methylbenzoxazole with benzyl alcohol delivered alkenylated **5.9o´** exclusively in 40% yield (table **5.6**). 2-methylpyrazine, 2-methylpyrimidine and 2-methylquinoline are incompatible in the present catalytic protocol (table **5.6**) which indicate there could be some sort of poisoning by quinoline derivatives effectively by complexing with catalyst.

Subsequently, various experimental studies were carried out to get a clear vision of the mechanistic pathway (table **5.6**). From the control experiments as described in the optimized table (table **5.1**, entry **8** & **9**) it was clear that in the absence of either the catalyst or the base, the reaction showed no result. Further, when 1a is reacted with benzaldehyde in the absence of a catalyst keeping all other conditions unchanged, the unsaturated intermediate is obtained in 40% yield (table **5.6** entry **1**). Further, the unsaturated intermediate upon reaction with corresponding alcohols in the absence of a catalyst shows the formation of only a trace amount of saturated C-alkylated product. However, the presence of a catalyst furnishes 90% of the product formation thus, demonstrating the role of catalyst in the borrowing hydrogen step (table **5.6** entries **2** & **3**). In addition, radical scavenger (TEMPO) is used to probe the involvement of radical pathways or ionic pathways and demonstrates the involvement of non-radical pathways (table **5.6** entry **4**). Further, deuterium scrambling experiments show the incorporation of deuterium in α (37%) and β (62 & 58%) position of C-alkylated product thus providing a hint of involvement of borrowing hydrogen pathway (table **5.6** entry **5**). When the C-alkylated reaction is carried out in the presence of 1.1 equiv. Hg and it does not harm the reaction efficiency, thus the result shows the Co-complex acts as a homogeneous catalyst (table **5.6** entry **6**).

Table 5.6: Table of Control and Competitive Experiments



Hereby, a catalytic pathway is proposed based on controlled experiments and literature support, also recorded mass spectrum of insitu reaction to understand the possible catalytic intermediate as shown in Figure **5.3**. Initially, in the presence of base and high temperature, mono-nuclear deprotonated Cat. **1a** is formed. It is then reacted with alcohol to result in Cat. **1b** (Mass Data

found=441.26), which further upon presence of base converts to deprotonated catalytic intermediate Cat. **1c** (Mass Data found=361.05). Upon reaction with another alcohol molecule to form Cat. **1d** (Mass Data found=499.07) and further metal-ligand cooperation activates the alcohol to aldehyde and gives Co-H (Cat. **1e**) species. In the presence of base, methylene ketone couples with aldehyde giving α,β-unsaturated product **5.10a**. **5.10a** upon hydrogenation (via hydride transfer) furnish corresponding alkylated product 3a and regenerates active catalyst i.e., Cat. **1a** which further continues the catalytic cycle (figure **5.3**).

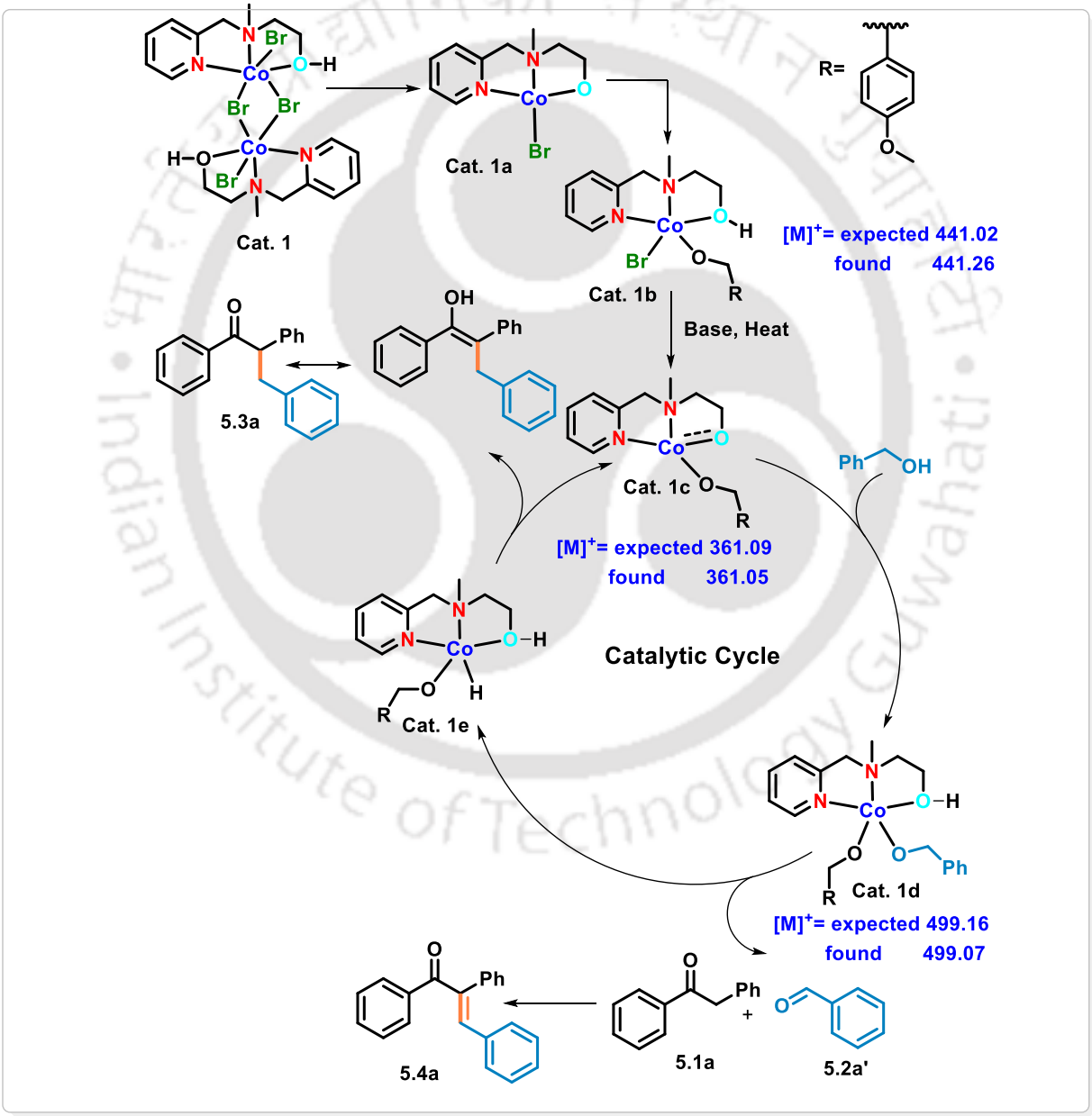


Figure 5.3: Proposed catalytic pathway

5.4. Conclusion

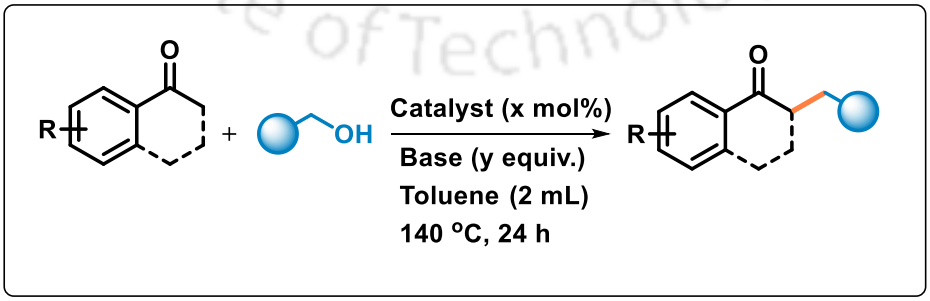
In summary, the chapter discussed on application of the Co-NNO complex for C-alkylation of challenging methylene ketones. The work was extended toward diverse substrate variations including activation of various benzylic and aliphatic alcohols. Applying the optimised protocol, multisubstituted quinoline was also successfully explored. Further, the catalyst can also be applied for the C-alkylation of 2-methylheteroarene. Various control experiments suggest the involvement of homogeneous non-radical behaviour of the Co-ONN complex.

5.5. General Considerations.

Unless otherwise mentioned, all chemicals were purchased from common commercial sources and used as received. All solvents were dried by using standard procedure. All catalytic reactions were carried out under argon atmosphere using dried glassware and standard syringe/septa techniques. DRX-400 Varian spectrometer and Bruker Avance III 600, 500 and 400 spectrometers were used to record ^{1}H and ^{13}C NMR spectra using $CDCl_3$ as solvent and TMS as an internal standard. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (*J*) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dt = doublet of triplet, td = triplet of doublet and brs = broad singlet. Q-TOF ESI-MS instrument (model HAB 273) was used for recording mass spectra. SRL silica gel (100-200 mesh) was used for column chromatography. Catalyst **1** and **2** were prepared according to the previously reported by our group.[14]

5.6. Experimental Section

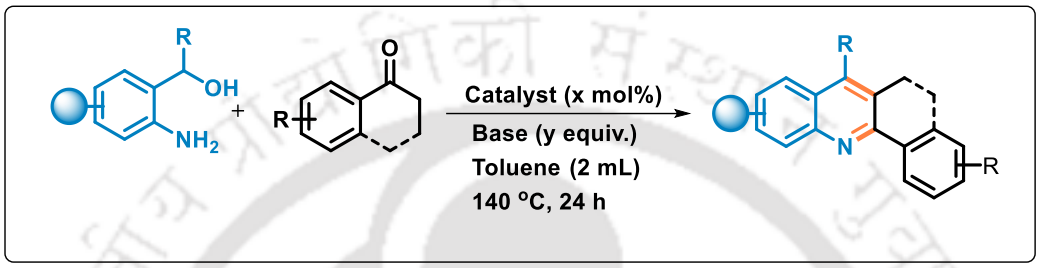
5.6.1. General Experimental Procedure for The Alkylation of methylene ketones with alcohols



To an oven dried 10 mL round bottom flask, Methylene ketones **1a** (0.5 mmol), alcohols **2** (0.75 mmol), KO^{t}Bu (50 – 80 mol%) and **Cat. 1** (3 mol%) were taken under argon atmosphere, after that 2 ml of toluene was added to the reaction mixture. The resulting mixture was heated

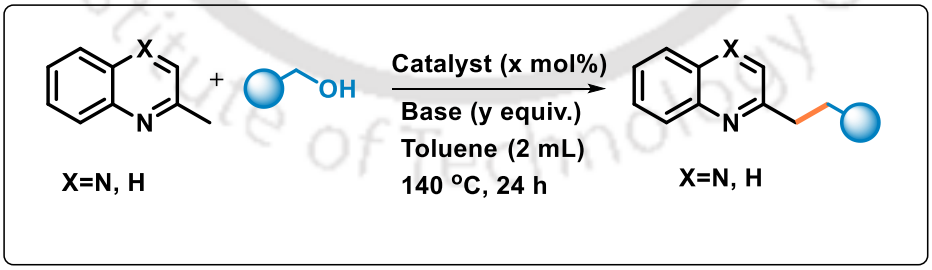
in an oil bath at 140 °C for 36 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using hexane or 1%-10% ethyl acetate in hexane to get pure C-alkylated compound **5.3**.

5.6.2. General Experimental Procedure for the synthesis of Quinolines



To an oven dried 10 mL round bottom flask, methylene ketones (0.083 g, 0.5 mmol), 2-aminobenzyl alcohol derivatives (0.75 mmol), KO^{t}Bu (50 mol%) and **Cat. 1** (3 mol%) were taken under argon atmosphere, after that 2 ml of toluene was added to the reaction mixture. The resulting mixture was heated in an oil bath at 140 °C for 24 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using hexane or 1%-10% ethyl acetate in hexane to get pure C-alkylated compound **5.**.

5.6.3. General Experimental Procedure for the C-alkylation of N-heteroarenes



To an oven dried 100 mL screw-capped pressure tube, 2-methyl-N-heteroarene (0.5 mmol), alcohol derivatives (0.75 mmol), KOH (100 mol%) and **Cat. 1** (3 mol%) were taken under argon atmosphere, after that 2 ml of toluene was added to the reaction mixture. The resulting mixture was heated in an oil bath at 140 °C for 24 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and

the residue was purified by silica gel column chromatography using hexane or 1%-10% ethyl acetate in hexane to get pure C-alkylated compound **5.7**.

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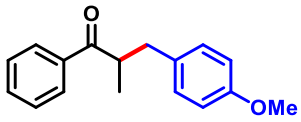
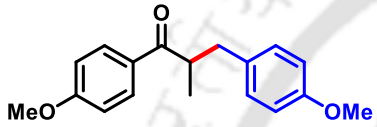
5.8. Characterisation Data of Compounds

3-(4-methoxyphenyl)-2-methyl-1-phenylpropan-1-one (**5.3a**):



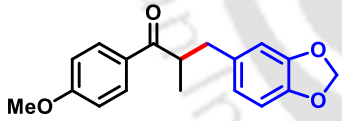
Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 85%, Yield: 0.108 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 3.70 (s, 3H), 3.63 (m, 1H), 3.03 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.56 (dd, *J* = 13.8, 7.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.9, 158.0, 136.6, 132.9, 132.0, 130.0, 128.6, 128.3, 113.8, 55.2, 43.0, 38.5, 17.3.

1,3-bis(4-methoxyphenyl)-2-methylpropan-1-one (**5.3b**):



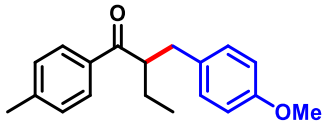
Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 71%, Yield: 0.101 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 3.77 (s, 3H), 3.71 – 3.59 (m, 1H), 3.08 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.62 (dd, *J* = 13.8, 7.7 Hz, 1H), 1.17 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.4, 163.4, 158.0, 132.2, 130.6, 130.0, 129.5, 113.8, 55.5, 55.2, 42.6, 38.7, 17.5.

3-(benzo[d][1,3]dioxol-5-yl)-1-(4-methoxyphenyl)-2-methylpropan-1-one (**5.3c**)[3]**:**



Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 55%, Yield: 0.082 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.62 – 6.60 (m, 2H), 6.55 (d, *J* = 7.9 Hz, 1H), 5.81 (s, 2H), 3.77 (s, 3H), 3.56 (m, 1H), 2.98 (dd, *J* = 13.8, 6.5 Hz, 1H), 2.52 (dd, *J* = 13.8, 7.6 Hz, 1H), 1.10 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.2, 162.4, 146.5, 144.8, 132.9, 129.5, 128.4, 121.0, 112.8, 108.4, 107.1, 99.7, 54.4, 41.5, 38.2, 16.5.

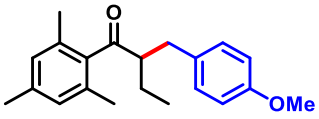
2-(4-methoxybenzyl)-1-(p-tolyl)butan-1-one (**5.3d**):



Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 50%, Yield: 0.070 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 3.78 (s, 3H), 3.62 (m, 1H), 3.06 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.73 (dd, *J* = 13.8, 6.6 Hz, 1H), 2.42 (s, 3H), 0.89 (t, *J* = 7.4

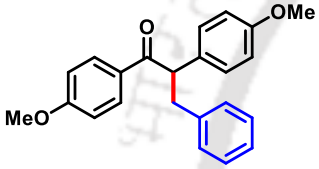
Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.6, 157.9, 143.6, 135.1, 132.2, 130.0, 129.3, 128.3, 113.7, 55.2, 49.8, 36.9, 25.3, 21.6, 11.7. HRMS $C_{19}H_{22}O_2$: $[M+Na]^+$ expected 305.1517; found 305.1483.

1-mesityl-2-(4-methoxybenzyl)butan-1-one (**5.3e**):



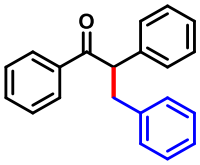
Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 37 %, Yield: 0.057 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.3 Hz, 2H), 6.83 – 6.82 (m, 6H), 3.81 (s, 3H), 3.13 – 3.07 (m, 2H), 2.67 – 2.63 (m, 1H), 2.29 (s, 3H), 2.12 (s, 6H), 1.77 – 1.70 (m, 1H), 1.52 – 1.46 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.8, 158.0, 138.5, 133.9, 132.3, 130.3, 128.9, 113.7, 56.7, 55.3, 34.2, 22.7, 21.0, 19.7, 11.2. HRMS $C_{21}H_{26}O_2$: $[M+H]^+$ expected 311.2011; found 311.2022

1,2-bis(4-methoxyphenyl)-3-phenylpropan-1-one (**5.3f):**



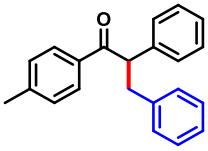
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 82 %, Yield: 0.142 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 2H), 7.07 – 7.04 (m, 3H), 6.99 (d, *J* = 7.3 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 4.63 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.67 (s, 3H), 3.44 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.95 (dd, *J* = 13.7, 7.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.0, 163.2, 158.6, 140.1, 131.6, 131.0, 129.8, 129.3, 129.1, 128.2, 126.0, 114.3, 113.6, 55.4, 55.2, 54.6, 40.2.

1,2,3-triphenylpropan-1-one (**5.3g)**:



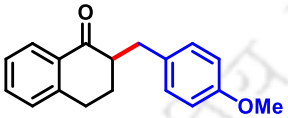
white solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 85 %, Yield: 0.117 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.21 (m, 4H), 7.22 (t, *J* = 7.5 Hz, 3H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.1 Hz, 2H), 4.84 (t, *J* = 7.3 Hz, 1H), 3.59 (dd, *J* = 13.7, 7.5 Hz, 1H), 3.09 (dd, *J* = 13.7, 7.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.3, 139.8, 139.1, 136.6, 132.9, 129.2, 128.9, 128.7, 128.5, 128.3, 128.3, 127.2, 126.2, 55.9, 40.1.

2,3-diphenyl-1-(p-tolyl)propan-1-one (**5.3h**):



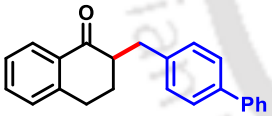
white solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 82 %, Yield: 0.123 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 2H), 7.08 – 7.03 (m, 3H), 7.02 – 6.94 (m, 4H), 4.70 (t, *J* = 7.6 Hz, 1H), 3.47 (dd, *J* = 13.7, 7.6 Hz, 1H), 2.96 (dd, *J* = 13.7, 7.6 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4, 139.9, 136.8, 136.1, 132.8, 129.6, 129.1, 128.7, 128.4, 128.3, 128.2, 128.1, 126.1, 55.5, 40.1, 21.0.

2-(4-methoxybenzyl)-3,4-dihydronaphthalen-1(2H)-one (**5.3i**):



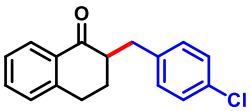
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 53 %, Yield: 0.070 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 3.43 (dd, *J* = 13.9, 4.1 Hz, 1H), 3.04 – 2.88 (m, 2H), 2.79 – 2.68 (m, 1H), 2.65 (m, 1H), 2.14 (m, 1H), 1.87 – 1.72 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.6, 158.0, 144.1, 133.3, 132.5, 132.0, 130.2, 128.7, 127.5, 126.6, 113.8, 55.3, 49.6, 34.8, 28.6, 27.6.

2-([1,1'-biphenyl]-4-ylmethyl)-3,4-dihydronaphthalen-1(2H)-one (**5.3j**):



Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 50 %, Yield: 0.078 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 7.1 Hz, 2H), 7.51 – 7.45 (m, 3H), 7.37 – 7.33 (m, 4H), 7.26 (d, *J* = 7.5 Hz, 1H), 3.55 (d, *J* = 13.6 Hz, 1H), 3.02 – 2.95 (m, 2H), 2.83 – 2.80 (m, 1H), 2.77 – 2.70 (m, 1H), 2.19 (d, *J* = 10.3 Hz, 1H), 1.90 – 1.83 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.4, 144.1, 141.0, 139.2, 139.1, 133.3, 132.5, 129.7, 128.7, 127.6, 127.4, 127.1, 127.1, 127.0, 126.7, 49.5, 35.4, 28.7, 27.8.

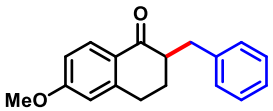
2-(4-chlorobenzyl)-3,4-dihydronaphthalen-1(2H)-one (**5.3k**):



Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 55%, Yield: 0.074 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 3.45 (dd, *J* = 13.4, 3.9 Hz, 1H), 3.00 – 2.94 (m, 3H), 2.11 (dq, *J*

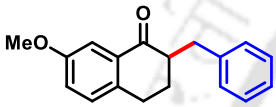
= 13.2, 4.3 Hz, 1H), 1.84 – 1.76 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.1, 143.9, 138.5, 133.4, 132.4, 131.9, 130.6, 128.7, 128.5, 127.6, 126.7, 49.4, 35.1, 28.7, 27.8.

2-benzyl-6-methoxy-3,4-dihydronaphthalen-1(2H)-one (**5.3l)**:



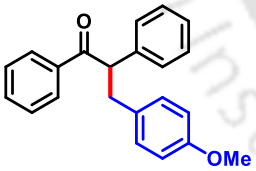
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 45 %, Yield: 0.060 g. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.24 – 7.19 (m, 3H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.66 (d, *J* = 2.2 Hz, 1H), 3.85 (s, 3H), 3.49 (dd, *J* = 13.3, 3.5 Hz, 1H), 2.95 – 2.82 (m, 2H), 2.76 – 2.56 (m, 2H), 2.11 – 2.04 (m, 1H), 1.81 – 1.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 163.5, 146.5, 140.3, 130.0, 129.3, 128.4, 126.2, 126.1, 113.2, 112.5, 55.4, 49.1, 35.8, 29.0, 27.7.

2-benzyl-7-methoxy-3,4-dihydronaphthalen-1(2H)-one (**5.3m)**:



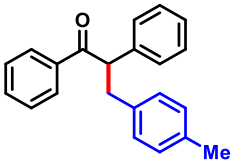
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 42 %, Yield: 0.056 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 2.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.20 (m, 3H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.05 (dd, *J* = 8.4, 2.7 Hz, 1H), 3.84 (s, 3H), 3.47 (dd, *J* = 13.6, 3.9 Hz, 1H), 2.96 – 2.78 (m, 2H), 2.77 – 2.69 (m, 1H), 2.67 – 2.63 (m, 1H), 2.12 – 2.07 (m, 1H), 1.81 – 1.73 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4, 158.4, 140.1, 136.6, 133.3, 129.9, 129.3, 128.4, 126.1, 121.7, 109.5, 55.5, 49.3, 35.7, 27.9, 27.8.

3-(4-methoxyphenyl)-1,2-diphenylpropan-1-one (**5.3n)**:



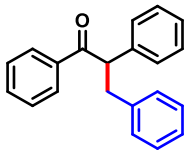
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 80 %, Yield: 0.126 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.26 (m, 4H), 7.22 (t, *J* = 6.9 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 4.80 (t, *J* = 7.3 Hz, 1H), 3.77 (s, 2H), 3.53 (dd, *J* = 13.9, 7.5 Hz, 1H), 3.03 (dd, *J* = 13.9, 7.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.4, 157.9, 139.2, 136.8, 132.8, 131.9, 130.1, 128.9, 128.7, 128.5, 128.3, 127.1, 113.6, 56.2, 55.2, 39.3.

1,2-diphenyl-3-(p-tolyl)propan-1-one (**5.3o)**:



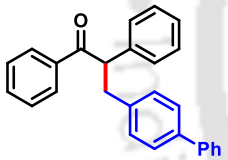
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 82 %, Yield: 0.123 g. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.21 – 7.04 (m, 5H), 6.92 – 6.87 (m, 4H), 4.71 (t, *J* = 7.2 Hz, 1H), 3.44 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.93 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.17 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 199.4, 139.2, 136.8, 136.7, 135.6, 132.8, 129.0, 128.9, 128.9, 128.7, 128.5, 128.3, 127.1, 56.0, 39.7, 21.0.

1,2,3-triphenylpropan-1-one (**5.3p)**:



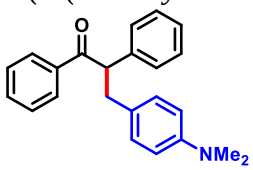
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 85 %, Yield: 0.121 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.24 (m, 4H), 7.22 (t, *J* = 7.4 Hz, 3H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 2H), 4.84 (t, *J* = 7.3 Hz, 1H), 3.59 (dd, *J* = 13.8, 7.5 Hz, 1H), 3.09 (dd, *J* = 13.8, 7.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.3, 139.8, 139.1, 136.8, 132.8, 129.1, 128.9, 128.7, 128.5, 128.3, 128.2, 127.2, 126.1, 55.9, 40.1.

3-([1,1'-biphenyl]-4-yl)-1,2-diphenylpropan-1-one (**5.3q)**:



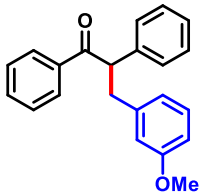
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 85 %, Yield: 0.154 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.47 – 7.24 (m, 12H), 7.23 – 7.17 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.85 (t, *J* = 7.2 Hz, 1H), 3.61 (dd, *J* = 13.8, 7.6 Hz, 1H), 3.10 (dd, *J* = 13.8, 6.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 140.9, 139.1, 139.0, 138.9, 136.8, 132.9, 129.5, 128.9, 128.7, 128.7, 128.5, 128.3, 127.2, 127.0, 126.9, 55.9, 39.8.

3-(4-(dimethylamino)phenyl)-1,2-diphenylpropan-1-one (**5.3r)**:



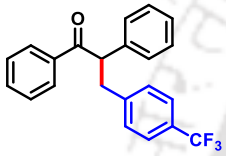
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 72 %, Yield: 0.118 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.15 (m, 4H), 7.15 – 7.07 (m, 1H), 6.88 (d, *J* = 6.9 Hz, 2H), 6.52 (d, *J* = 7.0 Hz, 2H), 4.70 (t, *J* = 7.2 Hz, 1H), 3.41 (dd, *J* = 13.1, 6.9 Hz, 1H), 2.89 (dd, *J* = 13.8, 6.7 Hz, 1H), 2.79 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 149.1, 139.4, 136.9, 132.7, 129.7, 128.8, 128.7, 128.4, 128.4, 128.0, 127.0, 112.8, 56.3, 40.8, 39.2. HRMS $C_{23}H_{23}NO$: $[M+H]^+$ expected 330.1858; found 330.1860.

3-(3-methoxyphenyl)-1,2-diphenylpropan-1-one (**5.3s)**:



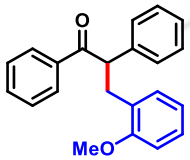
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 80 %, Yield: 0.126 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.23 (m, 5H), 7.18 (t, *J* = 6.6 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 2H), 6.58 (s, 1H), 4.80 (t, *J* = 7.2 Hz, 1H), 3.68 (s, 3H), 3.54 (dd, *J* = 13.7, 7.4 Hz, 1H), 3.04 (dd, *J* = 13.7, 7.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 159.4, 141.4, 139.1, 136.8, 132.8, 129.2, 128.9, 128.7, 128.5, 128.3, 127.2, 121.5, 114.7, 111.8, 55.8, 55.1, 40.2.

1,2-diphenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**5.3t)**:



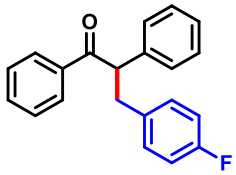
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 65 %, Yield: 0.115 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.44 (m, 3H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.25 (m, 2H), 7.24 – 7.16 (m, 5H), 4.79 (t, *J* = 7.3 Hz, 1H), 3.60 (dd, *J* = 13.7, 7.5 Hz, 1H), 3.12 (dd, *J* = 13.7, 7.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 143.9, 138.6, 136.4, 133.0, 129.5, 129.1, 128.7, 128.6, 128.5 (q, *J*=31 Hz), 128.2, 127.4, 125.1 (q, *J*=3.75 Hz), 124.3 (q, *J*=270 Hz), 55.6, 39.9.

3-(2-methoxyphenyl)-1,2-diphenylpropan-1-one (**5.3u)**:



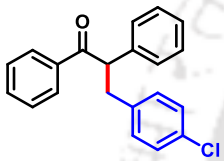
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 68 %, Yield: 0.107 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 4.4 Hz, 4H), 7.17 – 7.10 (m, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 4.95 (t, *J* = 7.1 Hz, 1H), 3.79 (s, 3H), 3.53 (dd, *J* = 13.4, 7.2 Hz, 1H), 3.08 (dd, *J* = 13.4, 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.8, 157.6, 139.8, 137.1, 132.6, 131.3, 128.7, 128.7, 128.4, 128.3, 128.0 127.5, 126.9, 120.3, 110.2, 55.3, 53.4, 35.3.

3-(4-fluorophenyl)-1,2-diphenylpropan-1-one (**5.3v)**:



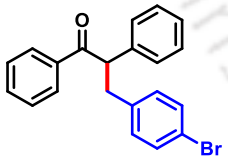
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 59 %, Yield: 0.090 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.08 (m, 5H), 6.96 – 6.93 (m, 2H), 6.79 (t, *J* = 8.5 Hz, 2H), 4.67 (t, *J* = 7.3 Hz, 1H), 3.44 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.96 (dd, *J* = 13.8, 7.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.1, 161.4 (d, *J*=243.7 Hz), 138.9, 136.7, 135.4 (d, J=2.5 Hz), 132.9, 130.6 (d, *J*=7.5 Hz), 128.9, 128.7, 128.5, 128.3, 127.2, 126.3, 115.0 (d, *J*=21.2 Hz), 56.1, 39.3.

3-(4-chlorophenyl)-1,2-diphenylpropan-1-one (**5.3w)**:



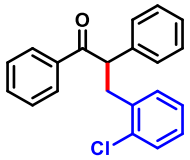
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 75 %, Yield: 0.120 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.18 (m, 5H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 4.74 (t, *J* = 7.3 Hz, 1H), 3.51 (dd, *J* = 13.8, 7.4 Hz, 1H), 3.03 (dd, *J* = 13.8, 7.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.9, 138.7, 138.2, 136.6, 133.0, 132.0, 130.5, 129.0, 128.7, 128.5, 128.3, 128.3, 127.3, 55.9, 39.4.

3-(4-bromophenyl)-1,2-diphenylpropan-1-one (**5.3x)**:



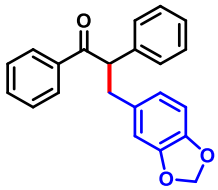
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 78 %, Yield: 0.126 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 6.3 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.25 – 7.24 (m, 3H), 6.98 (d, *J* = 8.3 Hz, 2H), 4.78 (t, *J* = 7.3 Hz, 1H), 3.53 (dd, *J* = 13.8, 7.4 Hz, 1H), 3.06 (dd, *J* = 13.8, 7.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.9, 138.8, 138.7, 136.6, 133.0, 131.3, 130.9, 129.0, 128.7, 128.5, 128.3, 127.3, 120.0, 55.8, 39.5.

3-(2-chlorophenyl)-1,2-diphenylpropan-1-one (**5.3y)**:



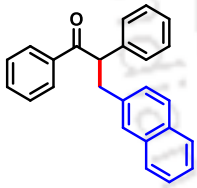
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 70 %, Yield: 0.112 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.31 – 7.29 (m, 4H), 7.25 – 7.21 (m, 1H), 7.14 – 7.11 (m, 1H), 7.06 (d, *J* = 4.2 Hz, 2H), 5.06 (t, *J* = 7.2 Hz, 1H), 3.70 (dd, *J* = 13.6, 7.7 Hz, 1H), 3.22 (dd, *J* = 13.6, 6.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.0, 139.0, 137.2, 136.7, 134.1, 132.9, 132.1, 129.4, 129.0, 128.7, 128.5, 128.2, 127.8, 127.2, 126.6, 53.1, 38.0.

3-(benzo[d][1,3]dioxol-5-yl)-1,2-diphenylpropan-1-one (**5.3z)**:



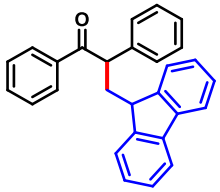
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 70 %, Yield: 0.115 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.23 (m, 4H), 7.19 (t, *J* = 6.9 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 6.58 (s, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 5.87 (s, 2H), 4.76 (t, *J* = 7.2 Hz, 1H), 3.48 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.97 (dd, *J* = 13.8, 6.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 147.4, 145.8, 139.0, 136.7, 133.6, 132.9, 128.9, 128.7, 128.5, 128.3, 127.2, 122.1, 109.6, 108.1, 100.7, 56.1, 39.9.

3-(naphthalen-2-yl)-1,2-diphenylpropan-1-one (**5.3aa)**:



White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 78 %, Yield: 0.131 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 7.0 Hz, 1H), 7.69 (t, *J* = 8.2 Hz, 2H), 7.53 (s, 1H), 7.45 – 7.38 (m, 3H), 7.33 (t, *J* = 7.9, 2H), 7.28 – 7.17 (m, 6H), 4.91 (t, *J* = 7.2 Hz, 1H), 3.73 (dd, *J* = 13.7, 7.5 Hz, 1H), 3.22 (dd, *J* = 13.7, 7.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.2, 139.1, 137.4, 136.4, 133.5, 132.9, 132.1, 129.0, 128.7, 128.5, 128.3, 127.8, 127.7, 127.6, 127.6, 127.5, 127.2, 125.8, 125.3, 56.0, 40.3.

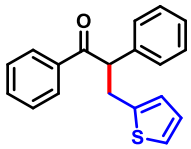
3-(9H-fluoren-9-yl)-1,2-diphenylpropan-1-one (**5.3ab)**:



White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 55 %, Yield: 0.103 g. HRMS $C_{28}H_{22}O$: $[M+H]^+$ expected 375.1749; found 375.1733.^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.0 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.36 – 7.25 (m, 3H), 7.21 – 7.17 (m, 4H), 7.15 – 7.07 (m, 6H),

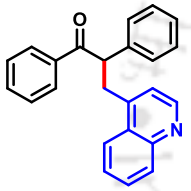
4.47 – 4.30 (m, 1H), 3.95 (t, *J* = 5.6 Hz, 1H), 3.09 – 3.03 (m, 1H), 2.44 – 2.25 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 147.0, 146.1, 141.3, 141.2, 139.8, 132.7, 129.9, 129.0, 128.8, 128.4, 128.2, 128.1, 127.2, 127.1, 127.0, 126.9, 126.8, 125.4, 124.6, 119.8, 119.7, 49.9, 46.0, 37.5.

1,2-diphenyl-3-(thiophen-2-yl)propan-1-one (**5.3ac)**



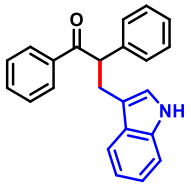
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 65 %, Yield: 0.095 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.28 (m, 4H), 7.28 – 7.21 (m, 1H), 7.09 (d, *J* = 5.1 Hz, 1H), 6.90 – 6.80 (m, 1H), 6.72 (s, 1H), 4.89 (t, *J* = 7.2 Hz, 1H), 3.83 (dd, *J* = 14.8, 7.9 Hz, 1H), 3.32 (dd, *J* = 14.8, 6.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.9, 142.1, 138.7, 136.6, 133.0, 129.0, 128.8, 128.5, 128.3, 127.4, 126.7, 125.7, 123.6, 56.1, 34.2.

(R)-1,2-diphenyl-3-(quinolin-4-yl)propan-1-one (**5.3ad)**:



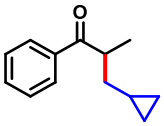
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 45 %, Yield: 0.076 g. HRMS $C_{24}H_{19}NO$: $[M+Na]^+$ expected 360.1364; found 360.1361.^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 4.3 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.11 (m, 5H), 6.93 (d, *J* = 4.3 Hz, 1H), 4.90 (t, *J* = 7.0 Hz, 1H), 4.00 (dd, *J* = 14.1, 7.2 Hz, 1H), 3.42 (dd, *J* = 14.1, 6.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 149.9, 148.3, 145.6, 138.7, 136.3, 133.1, 130.4, 129.2, 129.1, 128.7, 128.6, 128.1, 127.5, 127.5, 126.6, 123.2, 122.1, 54.2, 36.0.

(R)-3-(1H-indol-3-yl)-1,2-diphenylpropan-1-one (**5.3ae):**



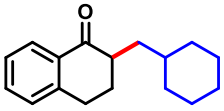
Greenish oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 55 %, Yield: 0.089 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.78 (m, 3H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.26 – 7.18 (m, 7H), 7.14 – 7.08 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.70 (s, 1H), 4.88 (t, *J* = 7.1 Hz, 1H), 3.67 (dd, *J* = 14.5, 8.0 Hz, 1H), 3.13 (dd, *J* = 14.5, 6.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.9, 139.8, 137.0, 136.1, 132.8, 128.9, 128.7, 128.4, 128.3, 127.5, 127.1, 122.7, 121.9, 119.3, 118.6, 113.9, 111.1, 54.6, 29.7.

3-cyclopropyl-2-methyl-1-phenylpropan-1-one (**5.3af)**:



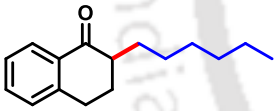
Colorless oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 70 %, Yield: 0.066 g ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 3.65 (q, *J* = 6.8 Hz, 1H), 1.76 – 1.72 (m, 1H), 1.43 – 1.38 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 3H), 0.75 – 0.70 (m, 1H), 0.45 – 0.41 (m, 2H), 0.07 – 0.06 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.7, 136.9, 132.8, 128.6, 128.3, 41.2, 38.9, 17.4, 9.3, 5.0, 4.6.

2-(cyclohexylmethyl)-3,4-dihydronaphthalen-1(2H)-one (**5.3ag)**:



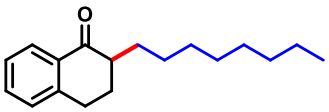
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 65 %, Yield: 0.078 g. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.45 (td, *J* = 7.4, 1.5 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 3.02 – 2.95 (m, 2H), 2.64 – 2.52 (m, 1H), 2.27 – 2.19 (m, 1H), 1.90 – 1.82 (m, 2H), 1.77 – 1.64 (m, 5H), 1.45 – 1.38 (m, 1H), 1.29 – 1.18 (m, 4H), 0.99 – 0.88 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.0, 143.9, 133.0, 132.6, 128.6, 127.5, 126.5, 44.6, 36.9, 34.9, 34.1, 32.6, 28.4, 28.2, 26.6, 26.4, 26.3.

2-hexyl-3,4-dihydronaphthalen-1(2H)-one (**5.3ah)**:



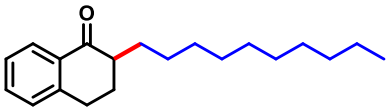
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 50 %, Yield: 0.057 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 3.06 – 2.96 (m, 2H), 2.51 – 2.47 (m, 1H), 2.28 – 2.24 (m, 1H), 2.00 – 1.87 (m, 2H), 1.55 – 1.48 (m, 2H), 1.40 – 1.28 (m, 12H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 144.0, 133.0, 132.6, 128.6, 127.5, 126.5, 47.5, 31.8, 29.4, 29.4, 28.3, 28.2, 27.0, 22.6, 14.1.

2-octyl-3,4-dihydronaphthalen-1(2H)-one (**5.3ai)**:



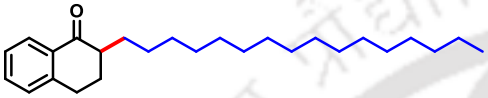
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 55 %, Yield: 0.071 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 3.06 – 2.96 (m, 2H), 2.51 – 2.47 (m, 1H), 2.28 – 2.24 (m, 1H), 1.99 – 1.88 (m, 2H), 1.39 – 1.29 (m, 13H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 144.0, 133.0, 132.6, 128.6, 127.5, 126.5, 47.5, 31.9, 29.8, 29.5, 29.4, 29.3, 28.3, 28.2, 27.1, 22.7, 14.1.

2-decyl-3,4-dihydronaphthalen-1(2H)-one (**5.3aj)**:



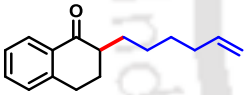
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 55 %, Yield: 0.078 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 3.06 – 2.94 (m, 2H), 2.51 – 2.47 (m, 1H), 2.28 – 2.24 (m, 1H), 1.98 – 1.88 (m, 2H), 1.54 – 1.47 (m, 1H), 1.42 – 1.23 (m, 16H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 144.0, 133.0, 132.6, 128.6, 127.5, 126.5, 47.5, 31.9, 29.8, 29.5, 29.4, 29.3, 28.3, 28.2, 27.1, 22.7, 14.1.

2-hexadecyl-3,4-dihydronaphthalen-1(2H)-one (**5.3ak)**:



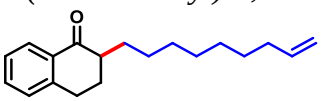
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 60 %, Yield: 0.111 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 3.06 – 2.96 (m, 2H), 2.52 – 2.46 (m, 1H), 2.28 – 2.23 (m, 1H), 1.98 – 1.87 (m, 2H), 1.53 – 1.47 (m, 1H), 1.32 – 1.24 (m, 28H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 144.0, 133.0, 132.6, 128.6, 127.5, 126.5, 47.5, 31.9, 29.8, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 28.3, 28.2, 27.1, 22.7, 14.1.

2-(hex-5-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (**5.3al)**:



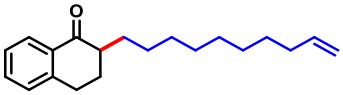
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 52 %, Yield: 0.059 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 5.77 – 5.69 (m, 2H), 4.92 (d, *J* = 15 Hz, 1H), 4.86 (d, *J* = 10.2 Hz, 1H), 2.92 – 2.89 (m, 2H), 2.42 – 2.36 (m, 1H), 2.18 – 2.12 (m, 1H), 2.02 – 1.98 (m, 2H), 1.91 – 1.75 (m, 2H), 1.41 – 1.30 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 142.9, 137.9, 132.0, 131.5, 127.6, 126.4, 125.5, 113.3, 46.4, 32.6, 28.2, 28.0, 27.3, 27.2, 25.5. HRMS: (ESI): Calc'd for.$C_{16}H_{20}O[M+Na]^+$: 251.1412; found = 251.1447

2-(non-8-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (**5.3am**):



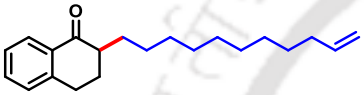
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 62 %, Yield: 0.084 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 5.86 – 5.74 (m, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.95 (d, *J* = 10.1 Hz, 1H), 3.04 – 2.96 (m, 2H), 2.51 – 2.46 (m, 1H), 2.28 – 2.23 (m, 1H), 2.08 – 2.04 (m, 2H), 1.99 – 1.88 (m, 2H), 1.54 – 1.48 (m, 1H), 1.42 – 1.31 (m, 10H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 143.9, 139.2, 133.0, 132.6, 128.6, 127.5, 126.5, 114.1, 47.5, 33.8, 29.7, 29.4, 29.4, 29.1, 28.9, 28.3, 28.2, 27.0. HRMS: (ESI): Calc'd for.$C_{19}H_{26}O[M+H]^+$: 271.2062; found = 271.2066

2-(dec-9-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (**5.3an**):



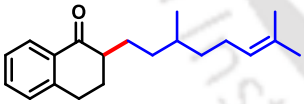
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). 60 %, Yield: 0.085 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 5.87 – 5.80 (m, 2H), 5.01 (d, *J* = 17.1 Hz, 1H), 4.95 (d, *J* = 10.2 Hz, 1H), 3.06 – 2.94 (m, 2H), 2.52 – 2.45 (m, 1H), 2.28 – 2.23 (m, 1H), 2.08 – 2.04 (m, 2H), 1.99 – 1.88 (m, 2H), 1.54 – 1.48 (m, 1H), 1.41 – 1.29 (m, 12H).^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 143.9, 139.2, 133.0, 132.6, 128.6, 127.5, 126.5, 114.1, 47.5, 33.8, 29.8, 29.5, 29.5, 29.4, 29.1, 28.9, 28.3, 28.2, 27.0. HRMS: (ESI): Calc'd for.C20H28O[M+H]$^{+}$: 285.2218; found = 285.2238

2-(undec-10-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (**5.3ao**):



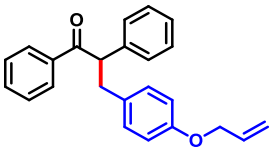
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). 65 %, Yield: 0.097 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 5.90 – 5.77 (m, 1H), 5.01 (d, *J* = 17.1 Hz, 1H), 4.95 (d, *J* = 10.2 Hz, 1H), 3.08 – 2.93 (m, 2H), 2.52 – 2.42 (m, 1H), 2.28 – 2.24 (m, 1H), 2.06 (q, *J* = 7.0 Hz, 3H), 2.01 – 1.83 (m, 2H), 1.42 – 1.23 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.6, 144.0, 139.3, 133.1, 132.6, 128.7, 127.5, 126.5, 114.1, 47.5, 33.8, 29.8, 29.6, 29.6, 29.5, 29.4, 29.1, 28.9, 28.3, 28.2, 27.0. HRMS: (ESI): Calc'd for.C21H30O[M+H]+: 299.2375; found = 299.2373.

2-(3,7-dimethyloct-6-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (**5.3ap**):



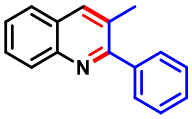
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). 65 %, Yield: 0.092 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 0H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 5.12 (t, *J* = 7.7 Hz, 1H), 3.06 – 2.95 (m, 2H), 2.49 – 2.43 (m, 1H), 2.28 – 2.23 (m, 1H), 2.08 – 1.86 (m, 4H), 1.70 (s, 3H), 1.62 (s, 3H), 1.53 – 1.34 (m, 4H), 1.29 – 1.13 (m, 2H), 0.94 – 0.91 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.4, 144.0, 133.0, 132.6, 132.6, 131.1, 131.1, 128.6, 127.5, 126.5, 125.0, 124.9, 47.9, 47.7, 37.1, 36.8, 34.3, 34.1, 32.7, 32.6, 28.3, 28.3, 28.3, 28.1, 26.9, 26.8, 25.7, 25.6, 25.5, 19.7, 19.5, 17.6. HRMS: (ESI):Calc'd for.C20H28O[M+H]+:285.2218; found = 285.2214

3-(4-(allyloxy)phenyl)-1,2-diphenylpropan-1-one (**5.3aq**):



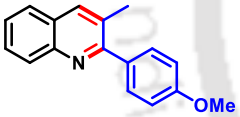
78 %, Yield: 0.133 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.25 (m, 4H), 7.22 (t, *J* = 6.9 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.08 – 6.02 (m, 1H), 5.41 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.28 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.80 (t, *J* = 7.3 Hz, 1H), 4.49 (d, *J* = 5.3 Hz, 2H), 3.53 (dd, *J* = 13.8, 7.5 Hz, 1H), 3.04 (dd, *J* = 13.8, 7.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.4, 157.0, 139.2, 136.8, 133.4, 132.8, 132.1, 130.1, 128.9, 128.7, 128.5, 128.3, 127.1, 117.5, 114.5, 68.8, 56.2, 39.3. HRMS $C_{24}H_{22}O_2$: $[M+H]^+$ expected 343.1698; found 343.1644.

3-methyl-2-phenylquinoline (**5.4a**):



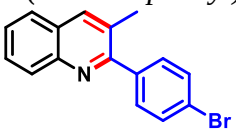
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). 75 %, Yield: 0.082 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.05 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.56 – 7.51 (m, 3H), 7.46 (d, *J* = 7.1 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.6, 146.7, 140.9, 136.7, 129.3, 129.2, 128.9, 128.8, 128.3, 128.2, 127.6, 126.7, 126.4, 20.6.

2-(4-methoxyphenyl)-3-methylquinoline (**5.4b**):



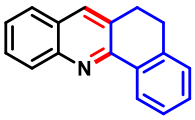
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). 72 %, Yield: 0.09 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.98 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 159.7, 146.7, 136.7, 133.5, 130.3, 129.3, 129.2, 128.6, 127.5, 126.7, 126.2, 113.7, 55.4, 20.8.

2-(4-bromophenyl)-3-methylquinoline (**5.4c**):



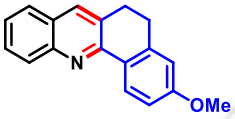
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). 55 %, Yield: 0.082 g. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.5 Hz, 1H), 8.02 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.62 (m, 3H), 7.55 – 7.47 (m, 3H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.2, 146.7, 139.7, 137.0, 131.5, 130.7, 129.3, 129.0, 128.9, 127.7, 126.8, 126.7, 122.6, 20.6.

5,6-dihydrobenzo[c]acridine (**5.4d**):



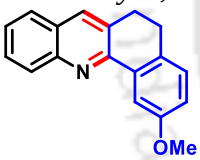
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). 70 %, Yield: 0.081 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.96 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 7.3 Hz, 1H), 3.17 (t, *J* = 6.8 Hz, 2H), 3.05 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.4, 147.7, 139.4, 134.7, 133.7, 130.6, 129.7, 129.4, 128.7, 128.0, 127.9, 127.4, 126.9, 126.1, 28.9, 28.4.

3-methoxy-5,6-dihydrobenzo[c]acridine (**5.4e)**:



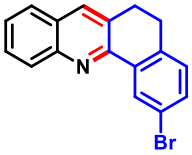
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). 75 %, Yield: 0.098 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 8.6 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.88 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.66 (dd, *J* = 8.4, 6.6 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.00 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.82 (d, *J* = 2.7 Hz, 1H), 3.90 (s, 2H), 3.12 (t, *J* = 7.0 Hz, 2H), 3.02 – 2.97 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.0, 153.4, 141.3, 133.6, 130.1, 129.0, 128.7, 127.9, 127.6, 126.9, 125.7, 113.1, 113.0, 55.4, 28.9, 28.8.

2-methoxy-5,6-dihydrobenzo[c]acridine (**5.4f)**:



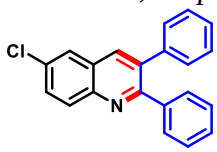
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 75 %, Yield: 0.112 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.08 – 8.07 (d, *J* = 8.2 Hz, 2H), 7.83 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 3.01 (t, *J* = 6.4 Hz, 2H), 2.85 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 152.2, 146.4, 134.5, 132.8, 130.9, 129.7, 128.3, 128.0, 127.7, 126.9, 125.9, 125.1, 116.0, 108.7, 54.6, 28.1, 26.5.

2-bromo-5,6-dihydrobenzo[c]acridine (**5.4g)**:



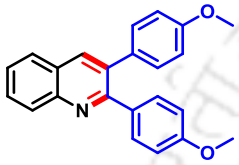
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 60 %, Yield: 0.093 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 1H), 3.12 (t, *J* = 6.6 Hz, 2H), 2.96 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 147.6, 138.1, 136.7, 133.9, 132.4, 130.2, 129.6, 129.5, 128.9, 128.9, 128.0, 126.9, 126.4, 121.3, 28.5, 27.9.

6-chloro-2,3-diphenylquinoline (**5.4h)**:



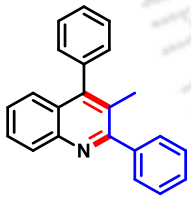
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 60 %, Yield: 0.094 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 8.05 (s, 1H), 7.79 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.28 – 7.09 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 137.1, 135.6, 130.9, 130.6, 130.1, 129.7, 128.5, 128.4, 128.0, 127.9, 127.6, 126.1.

2,3-bis(4-methoxyphenyl)quinoline (**5.4i)**:



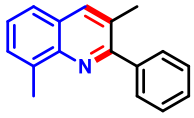
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 65 %, Yield: 0.111 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.4 Hz, 1H), 8.00 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.76 – 6.72 (m, 4H), 3.72 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 158.9, 158.1, 147.2, 137.3, 134.1, 133.2, 132.6, 131.4, 130.8, 129.3, 127.3, 127.2, 126.4, 113.8, 113.5, 55.3.

3-methyl-2,4-diphenylquinoline (**5.4j)**



Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 65 %, Yield: 0.096 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 6.9 Hz, 3H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.32 – 7.31 (m, 2H), 7.24 (d, *J* = 7.2 Hz, 3H), 2.08 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 147.9, 146.2, 141.4, 137.7, 129.4, 129.3, 129.0, 128.7, 128.6, 128.3, 128.1, 127.9, 127.1, 126.8, 126.3, 126.0, 18.6.

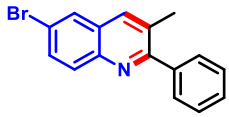
3,8-dimethyl-2-phenylquinoline (**5.4k)**:



Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 80 %, Yield: 0.093 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 3H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.45 –

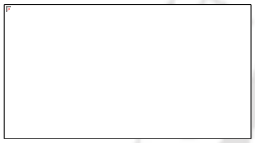
7.40 (m, 1H), 2.84 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.7, 145.8, 141.3, 137.4, 137.1, 129.4, 128.7, 128.7, 128.1, 127.4, 126.1, 124.6, 20.7, 17.9.

6-bromo-3-methyl-2-phenylquinoline (**5.4l**):



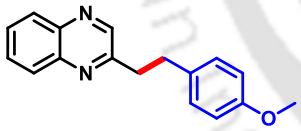
Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 72 %, Yield: 0.107 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.9 Hz, 1H), 7.97 – 7.93 (m, 2H), 7.74 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.60 (d, *J* = 9.4 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 2H), 7.48 – 7.46 (m, 1H), 2.49 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.9, 145.2, 140.4, 135.7, 132.2, 131.0, 130.4, 128.8, 128.7, 128.7, 128.4, 128.4, 120.2, 20.7.

2-phenethylquinoxaline (**5.8a**):



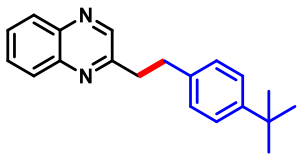
Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.36 – 7.18 (m, 5H), 3.37 (t, *J* = 7.5 Hz, 2H), 3.22 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.5, 145.8, 142.3, 141.3, 140.8, 130.0, 129.2, 129.1, 128.9, 128.6, 128.5, 126.3, 38.1, 35.3.

2-(4-methoxyphenethyl)quinoxaline (**5.8b**):



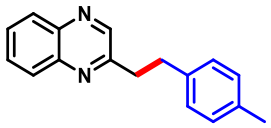
Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 8.07 (d, *J* = 8.1 Hz, 2H), 7.77 – 7.70 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 3H), 6.82 (d, *J* = 7.2 Hz, 3H), 3.78 (s, 3H), 3.30 (t, *J* = 7.7 Hz, 2H), 3.13 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 156.6, 145.9, 142.3, 141.3, 132.8, 130.0, 129.4, 129.2, 129.1, 128.9, 114.0, 55.3, 38.4, 34.5.

2-(4-(tert-butyl)phenethyl)quinoxaline (**5.8c**):



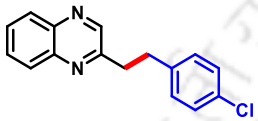
Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.80 – 7.68 (m, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 3.38 – 3.28 (m, 3H), 3.22 – 3.11 (m, 3H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 149.1, 145.9, 142.3, 141.3, 137.7, 130.0, 129.2, 129.1, 128.9, 128.1, 125.5, 38.2, 34.8, 34.4, 31.4.

2-(4-methylphenethyl)quinoxaline (**5.8d**):



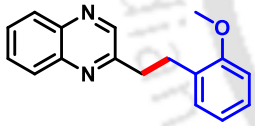
Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.76 (dt, *J* = 25.7, 6.9 Hz, 3H), 7.13 (q, *J* = 7.7 Hz, 5H), 3.34 (t, *J* = 7.9 Hz, 2H), 3.17 (t, *J* = 7.9 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.7, 146.0, 142.4, 141.4, 137.8, 135.9, 130.1, 129.4, 129.3, 129.2, 129.0, 128.5, 38.4, 35.1, 21.2.

2-(4-chlorophenethyl)quinoxaline (**5.8e**):



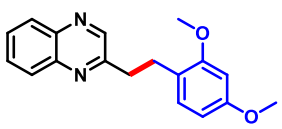
Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 8.09 (t, *J* = 8.7 Hz, 2H), 7.82 – 7.71 (m, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 3.33 (t, *J* = 7.9 Hz, 2H), 3.19 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.0, 145.7, 142.2, 141.3, 139.2, 132.1, 130.1, 129.8, 129.3, 129.2, 128.9, 128.7, 37.8, 34.4.

2-(2-methoxyphenethyl)quinoxaline (**5.8f**):



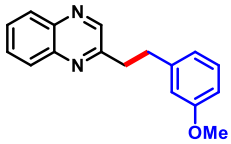
Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.63 (s, 1H), 8.07 (d, *J* = 9.6 Hz, 2H), 7.77 – 7.67 (m, 2H), 7.20 (t, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.86 (t, *J* = 7.3 Hz, 2H), 3.77 (s, 3H), 3.31 (t, *J* = 7.7 Hz, 2H), 3.17 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 157.2, 146.1, 142.2, 141.2, 130.1, 129.8, 129.2, 129.0, 128.9, 128.9, 127.6, 120.5, 110.3, 55.2, 36.6, 30.3.

2-(2,4-dimethoxyphenethyl)quinoxaline (**5.8g**):



Yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.65 (m, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.44 (d, *J* = 2.3 Hz, 1H), 6.38 (d, *J* = 8.2 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.27 (t, *J* = 7.7 Hz, 2H), 3.09 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 158.3, 157.3, 146.1, 142.2, 141.2, 130.3, 129.8, 129.2, 128.9, 128.8, 121.4, 103.9, 98.6, 55.3, 55.2, 36.9, 29.7. HRMS: (ESI):Calc'd for.$C_{18}H_{19}N_2O_2[M+H]^+$:296.1475; found = 296.1483.

2-(3-methoxyphenethyl)quinoxaline (**5.8h**):

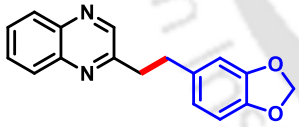


Brown oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.82 – 7.72 (m, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.81 (s, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 3.79 (s, 3H), 3.36 (t, *J* = 7.5 Hz, 2H), 3.19 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 156.4, 145.8, 142.4, 142.3, 141.3, 130.0, 129.5, 129.2, 129.1, 128.9, 120.8, 114.2, 111.7, 55.2, 38.0, 35.3.

2-(2-(naphthalen-2-yl)ethyl)quinoxaline (**5.8i**):

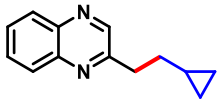
Brown solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.08 (t, *J* = 7.6 Hz, 2H), 7.76 (m, 5H), 7.68 (s, 1H), 7.48 – 7.35 (m, 3H), 3.43 (t, *J* = 7.5 Hz, 2H), 3.36 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 145.8, 142.3, 141.3, 138.3, 133.6, 132.2, 130.0, 129.3, 129.1, 128.9, 128.2, 127.6, 127.5, 127.1, 126.7, 126.0, 125.4, 38.0, 35.4.

2-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)quinoxaline (**5.8j**):



Brown oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 8.07 (dd, *J* = 8.4, 3.2 Hz, 2H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 6.76 – 6.69 (m, 2H), 6.64 (d, *J* = 7.9 Hz, 1H), 5.91 (s, 2H), 3.31 – 3.26 (m, 2H), 3.14 – 3.08 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.3, 147.7, 146.0, 145.8, 142.2, 141.3, 134.5, 130.0, 129.2, 129.1, 128.9, 121.3, 108.9, 108.3, 100.8, 38.3, 35.0.

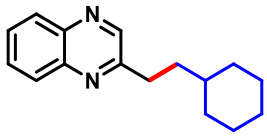
2-(2-cyclopropylethyl)quinoxaline (**5.8k**):



Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 (s, 1H), 8.10 – 8.02 (m, 2H), 7.78 – 7.67 (m, 2H), 3.19 – 3.07 (m, 2H), 1.77 (q, *J* = 7.2 Hz, 2H), 1.25 (s, 1H), 0.52 – 0.39 (m, 2H), 0.09 – 0.05 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 146.1, 142.4, 141.3, 130.0, 129.3, 129.0,

129.0, 36.73, 34.7, 10.9, 4.8. HRMS: (ESI):Calc'd for.$C_{13}H_{14}N_2[M+H]^+$:199.1230; found = 199.1235.

(E)-2-(2-cyclohexylvinyl)quinoxaline (**5.8l**):

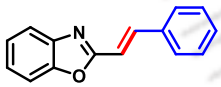


Pink oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.64 (s, 1H), 8.03 – 7.87 (m, 2H), 7.68 – 7.54 (m, 2H), 3.04 – 2.78 (m, 2H), 1.74 –1.71 (m, 2H), 1.69 – 1.61 (m, 4H), 1.62 – 1.50 (m, 1H), 1.26 (m, 1H), 1.19 – 1.02 (m, 3H), 0.96 – 0.78 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.1, 145.91, 142.3, 141.2, 129.9, 129.2, 128.9, 37.7, 37.2, 34.1, 33.3, 26.7, 26.4.

2-heptadecylquinoxaline (**5.8m**):

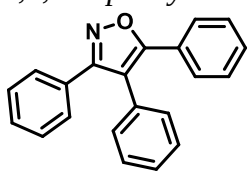
Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 8.09 – 8.04 (m, 2H), 7.76 – 7.70 (m, 2H), 3.05 – 2.97 (m, 2H), 1.85 (p, *J* = 7.7 Hz, 2H), 1.47 – 1.39 (m, 2H), 1.38 – 1.33 (m, 2H), 1.25 – 1.22 (m, 24H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.9, 146.0, 142.3, 141.34, 130.0, 129.3, 129.0, 36.7, 32.1, 29.8, 29.8, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 22.8, 14.3.

(E)-2-styrylbenzo[d]oxazole (**5.9o´**):



Pale yellow oil. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 16.3 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.38 – 7.36 (m, 3H), 7.11 (d, *J* = 16.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.9, 150.5, 142.3, 139.6, 135.3, 129.9, 129.1, 127.7, 125.4, 124.7, 120.0, 114.1, 110.5.

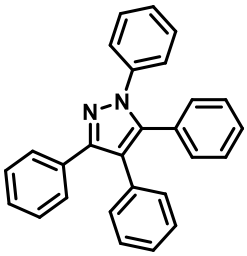
3,4,5-triphenylisoxazole **(5.5):**



White Solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.17 (m, 13H). ^{13}C NMR

(150 MHz, $CDCl_3$) δ 165.5, 162.2, 130.6, 130.5, 129.8, 129.4, 129.1, 129.0, 128.6, 128.5, 128.4, 128.2, 127.9, 127.0, 115.3.

1,3,4,5-tetraphenyl-1H-pyrazole **(5.6):**



White Solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 95:5). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.44 (m, 1H), 7.30 – 7.08 (m, 14H), 7.04 – 7.02 (m, 2H), 7.0 – 6.98 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 141.4, 140.0, 133.1, 133.1, 130.7, 130.4, 130.1, 128.8, 128.4, 128.3, 128.2, 128.1, 127.6, 127.2, 126.7, 125.3, 120.7.

5.9. NMR Spectra of some representative compounds

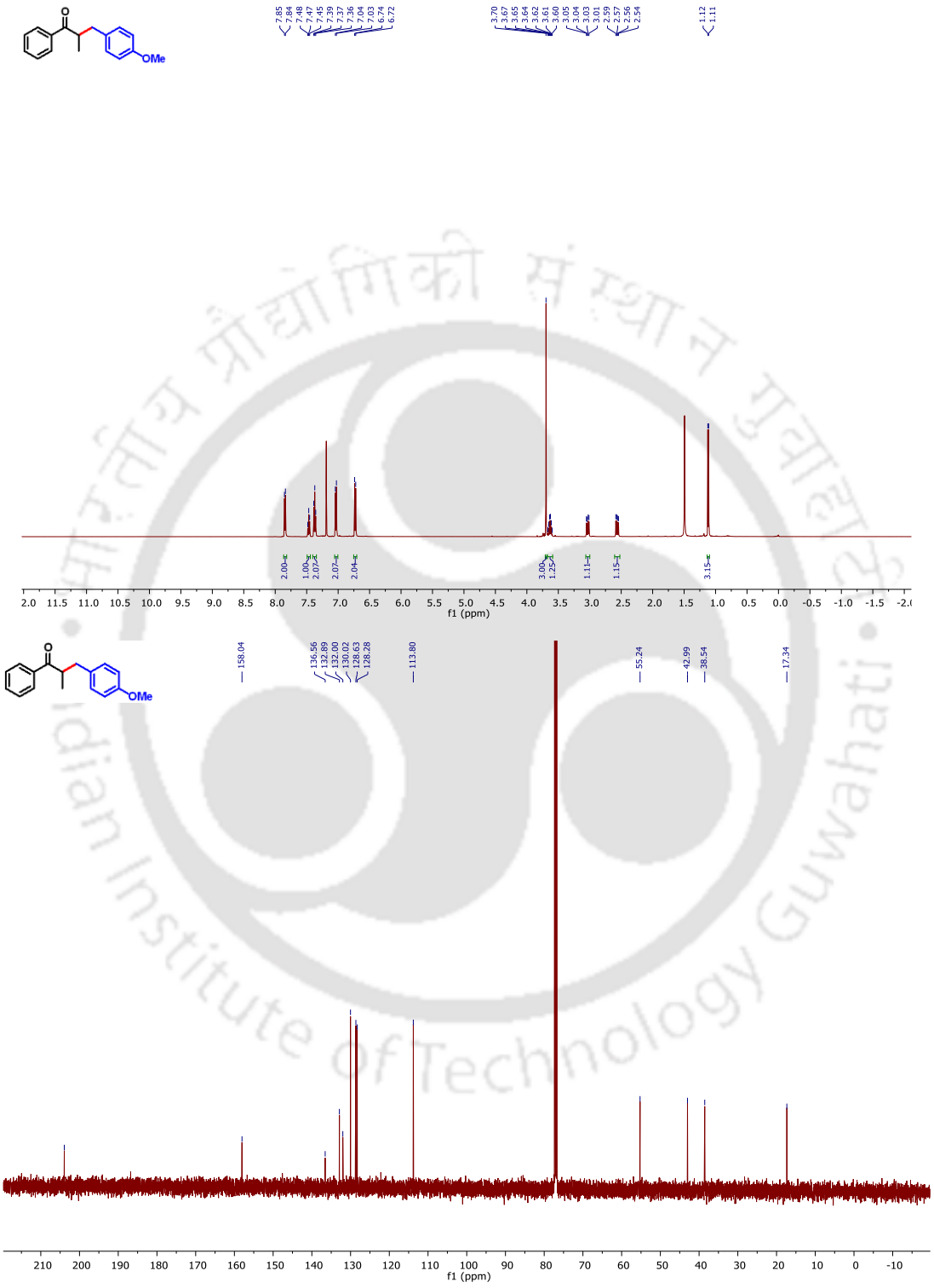


Figure **5.4**: ^{1}H and $^{13}C\{1H\}$ NMR of **5.3a** in $CDCl_3$

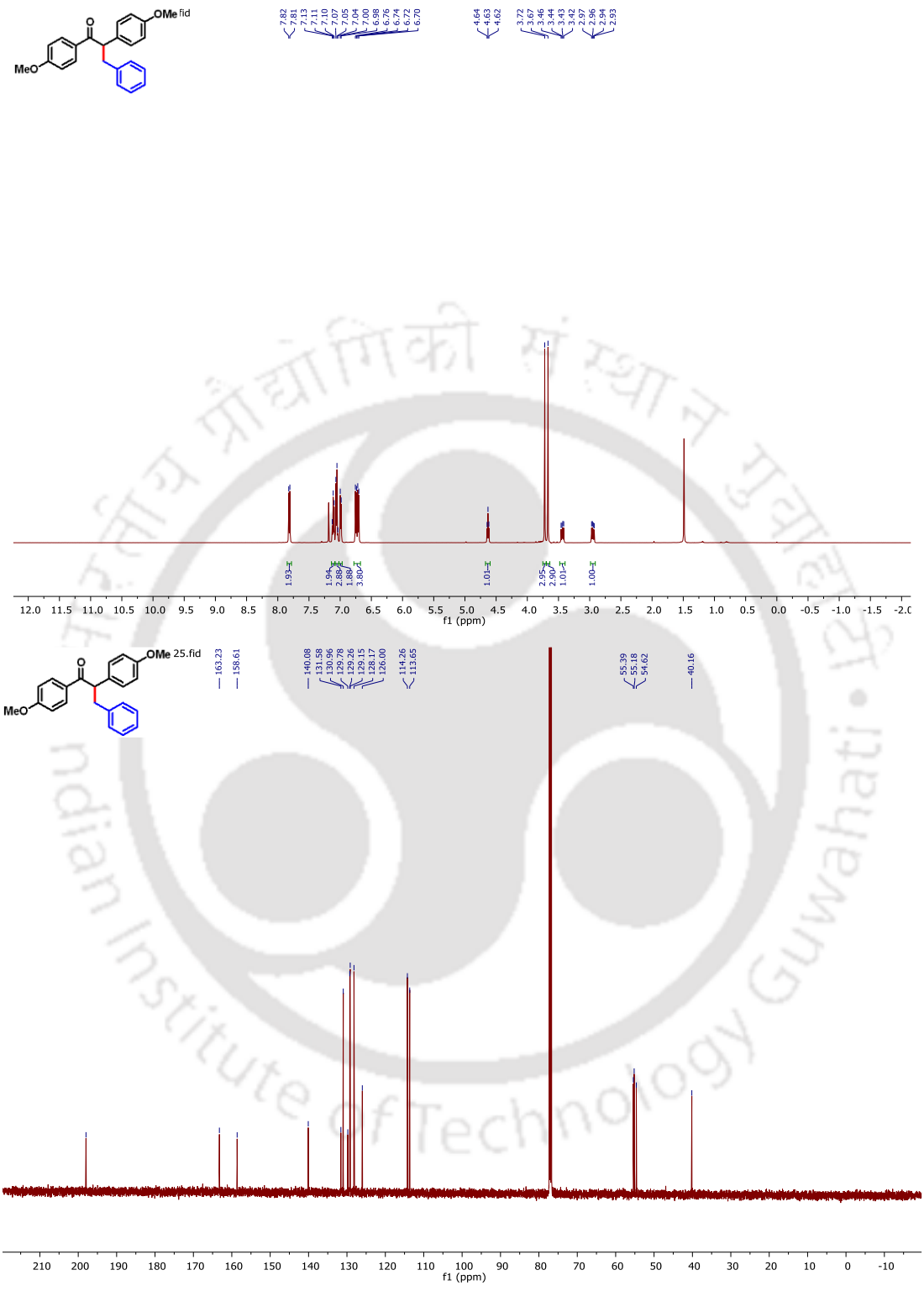


Figure **5.5**: ^{1}H and $^{13}C\{1H\}$ NMR of **5.3f** in $CDCl_3$

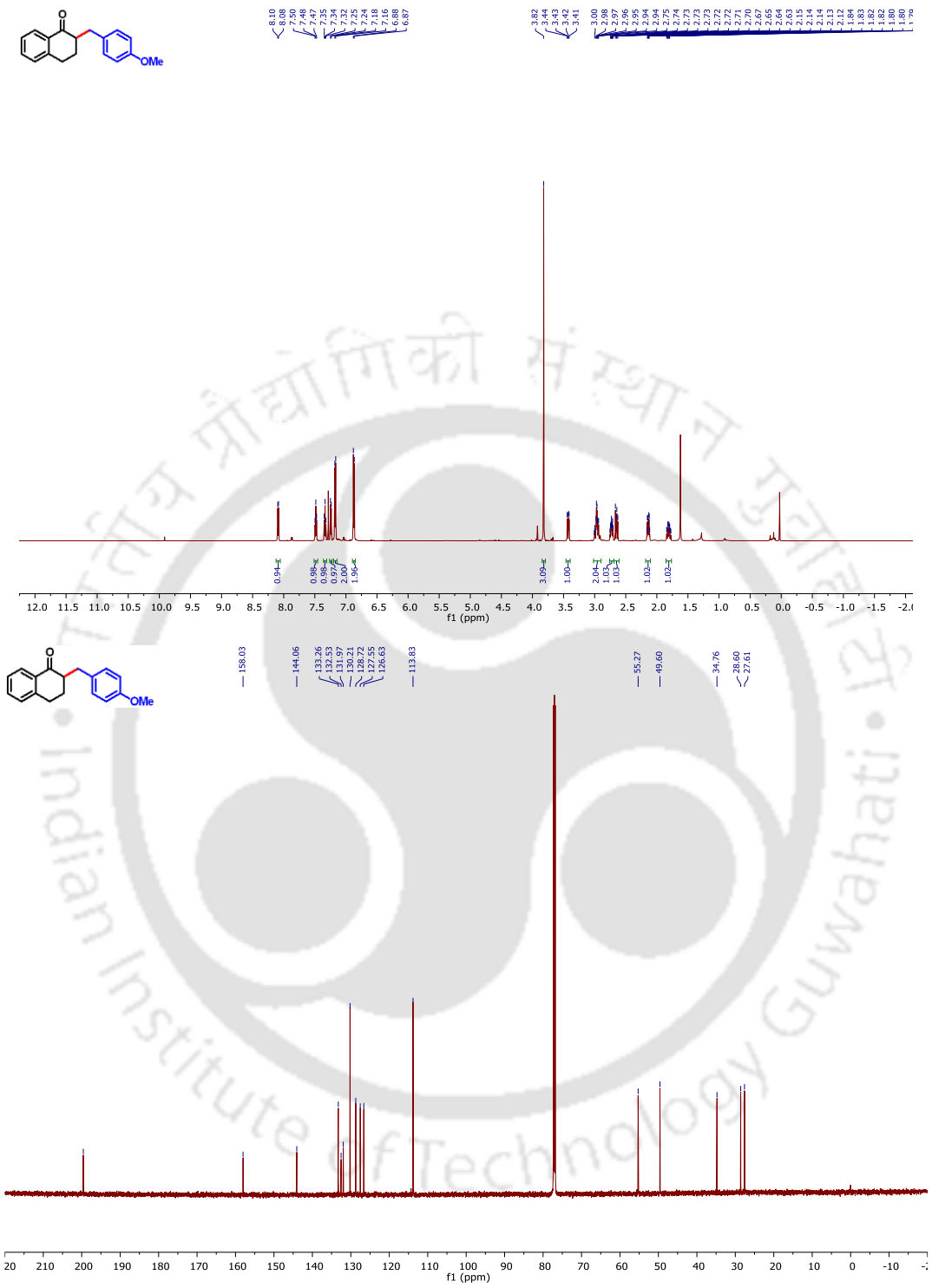


Figure **5.6**: ^{1}H and $^{13}C\{1H\}$ NMR of **5.3i** in $CDCl_3$

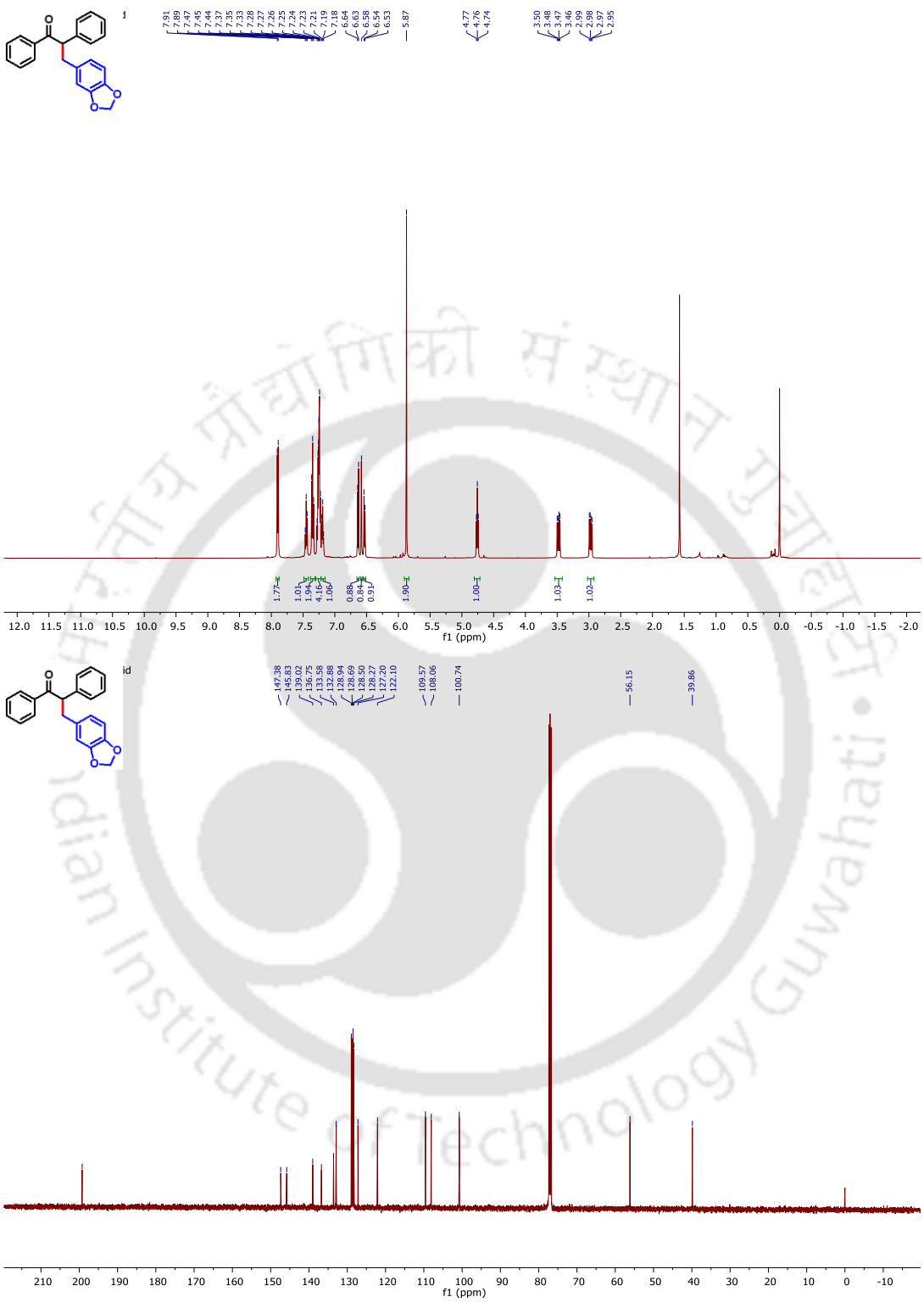


Figure **5.7**: ^{1}H and $^{13}C\{1H\}$ NMR of **5.3z** in $CDCl_3$

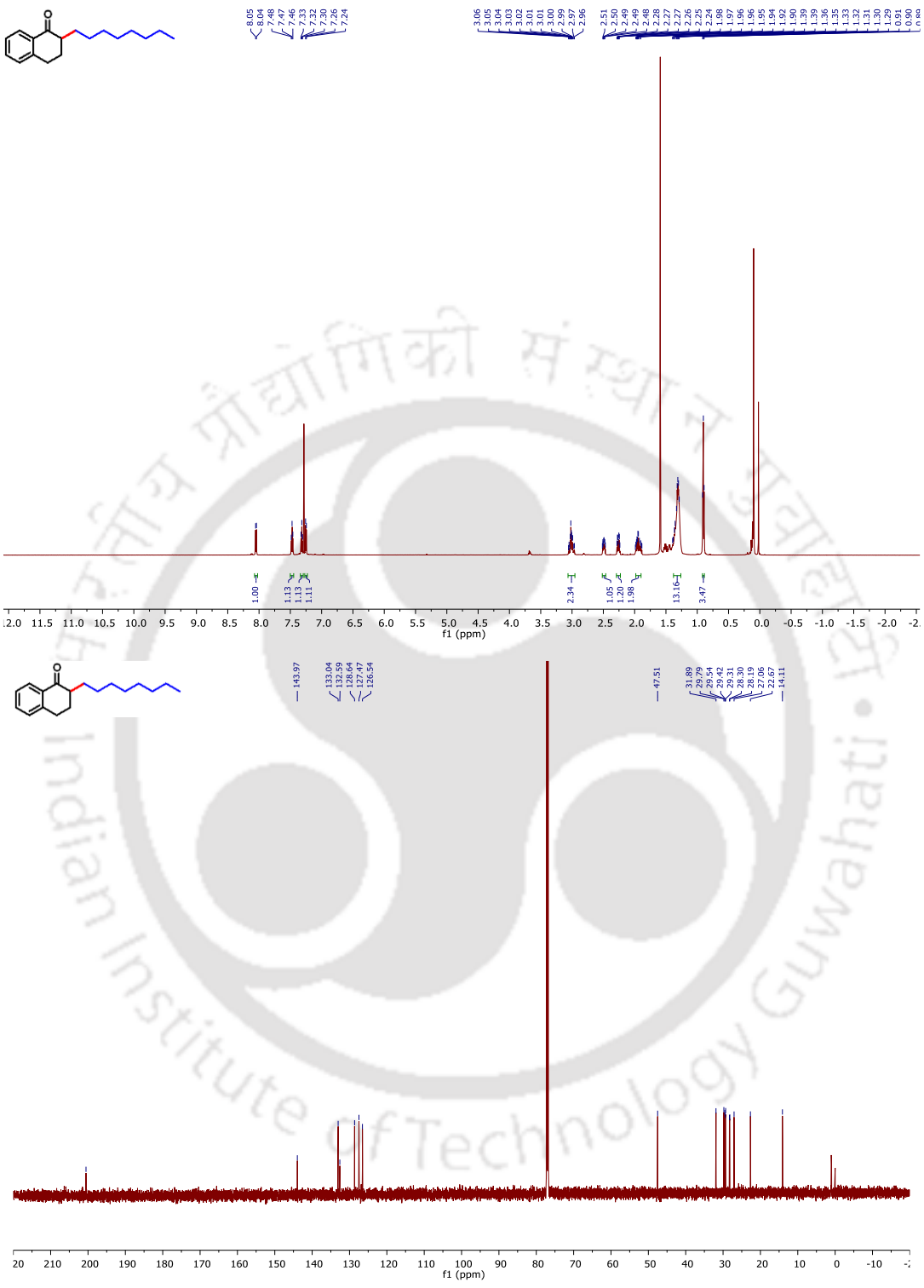


Figure **5.8**: ^{1}H and $^{13}C\{1H\}$ NMR of **5.3ai** in $CDCl_3$

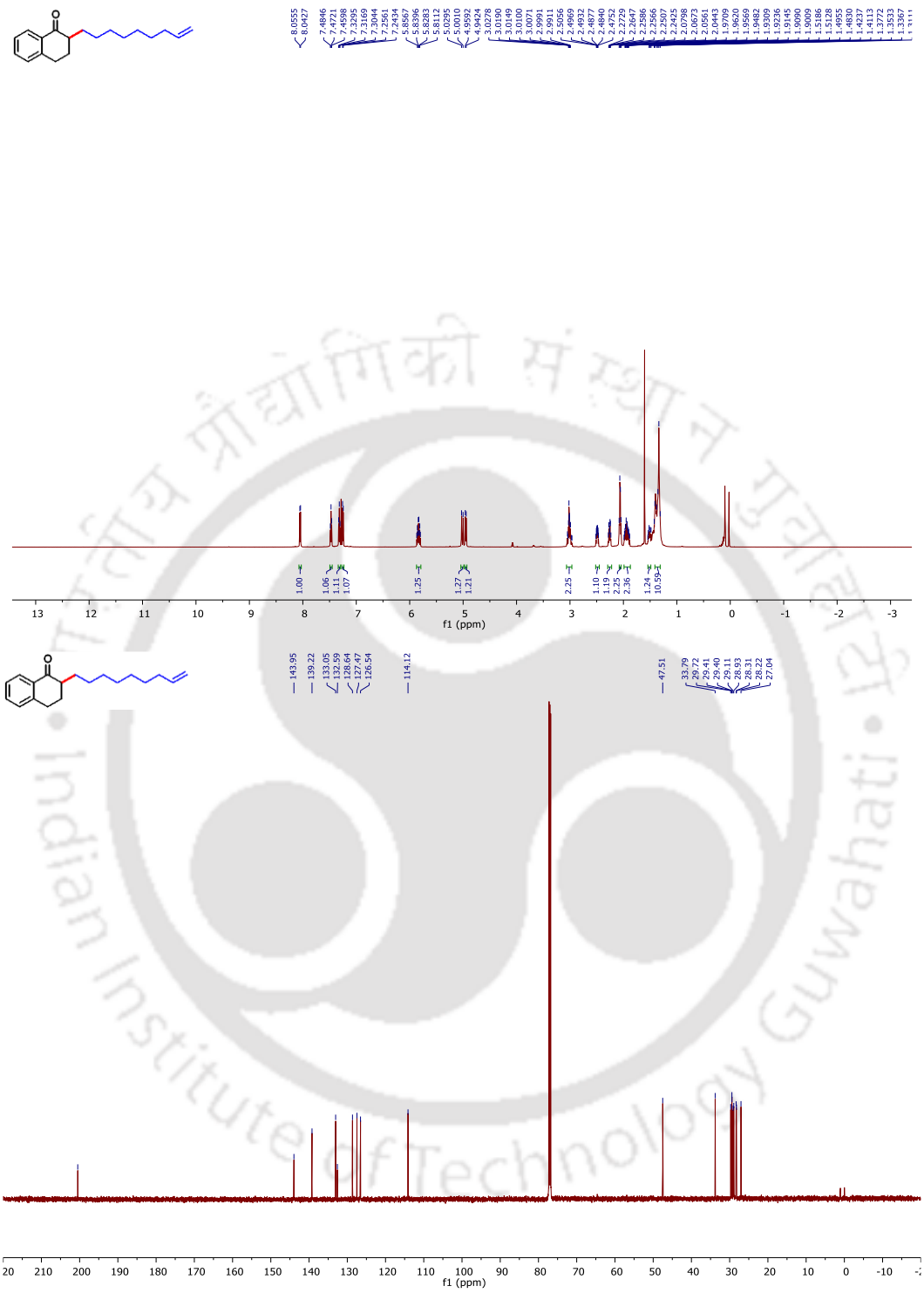


Figure **5.9**: ^{1}H and $^{13}C\{1H\}$ NMR of **5.3am** in $CDCl_3$

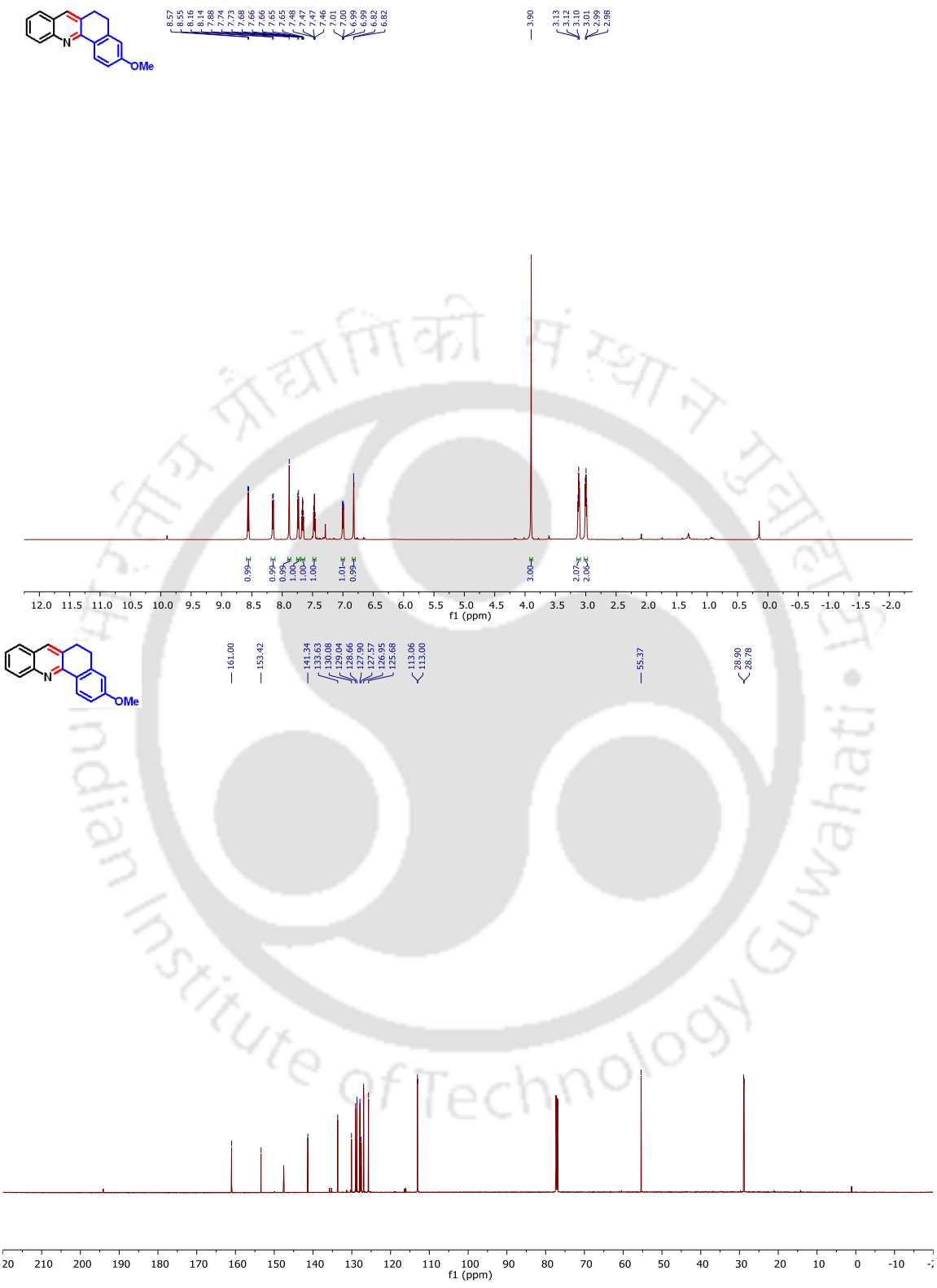


Figure **5.10**: ^{1}H and $^{13}C\{1H\}$ NMR of **5.4e** in $CDCl_3$

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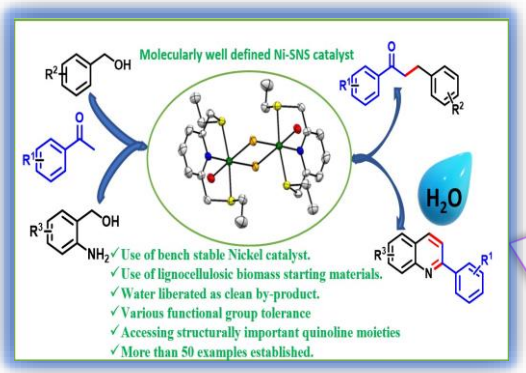

Chapter 2

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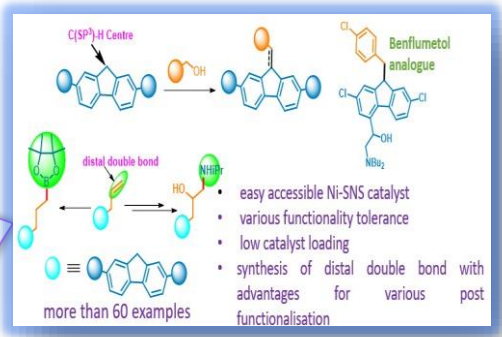
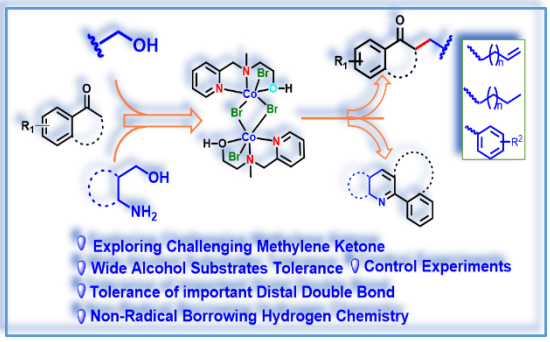


Chapter 3

Chapter 4



Chapter 5

List of publications:

Thesis works:

1. **R. Sharma**, A. Mondal, A. Samanta, N. Biswas, B. Das and D. Srimani*, Well-Defined Ni− SNS Complex Catalysed Borrowing Hydrogenative α-Alkylation of Ketones and Dehydrogenative Synthesis of Quinolines. *Adv. Synth. & Catal.* **2022**, *364*, 2429-2437.

2. **R. Sharma**, A. Mondal, A. Samanta and D. Srimani*, A strategic approach for Csp3–H functionalization of 9 H-fluorene: an acceptorless dehydrogenation and borrowing hydrogen approach. *Catal. Sci. & Technol.* **2023**, *13*, 611-617.

3. **R. Sharma**, A. Mondal, S. Maji, and D. Srimani*, Unveiling the Potential of SNS-Ni Complex for Establishing C–N Bonds: An Approach toward Chemoselectivity. *Organometallics* **2024**, 43, 2697 – 2702.

4. **R. Sharma**, K. Mohar, A. Mondal, E. Basumatary and D. Srimani*, Exploring the Potential of Non-Phosphine Cobalt System for the Alcohol Activation: Expedition of C-C and C-N Bond Formation. **Manuscript Under Preparation**.

Non-thesis works:

5. N Biswas, **R Sharma**, D Srimani*, Ruthenium Pincer Complex Catalyzed Selective Synthesis of C-3 Alkylated Indoles and Bisindolylmethanes Directly from Indoles and Alcohols. *Adv. Synth. & Catal.* **2020**, *362*, 2902-2910.

6. A Mondal, **R Sharma**, D Pal, D Srimani*, Recent Progress in the Synthesis of Heterocycles through Base Metal-Catalyzed Acceptorless Dehydrogenative and Borrowing Hydrogen Approach. *Euro. J. Org. Chem.* **2021**, *2021*, 3690-3720.

7. A. Mondal, **R. Sharma**, D. Pal and D. Srimani*, Manganese Catalyzed Switchable C-Alkylation/Alkenylation of Fluorenes and Indene with Alcohols. *Chem. Commun*. **2021**, *57*, 10363-10366.

8. A. Mondal, **R. Sharma**, B. Dutta D. Pal and D. Srimani*, Well-Defined NNS-Mn Complex Catalyzed Selective Synthesis of C-3 Alkylated Indoles and Bisindolylmethanes Using Alcohol. *J. Org. Chem*. **2022**, *87*, *6*, 3989–4000.

9. **R Sharma**, A Samanta, B Sardar, M Roy, D Srimani, Progressive study on ruthenium catalysis for de (hydrogenative) alkylation and alkenylation using alcohols as a sustainable source. *Org. & Biomol. Chem.* **2022**, *20*, 7998-8030.

10. N Biswas, **R Sharma**, B Sardar, D Srimani, Acridine-Based SNS–Ruthenium Pincer Complex-Catalyzed Borrowing Hydrogen-Mediated C–C Alkylation Reaction: Application to the Guerbet Reaction. *Synlett* **2023**, *34*, 622-628.

Conferences and workshop:

1. **Poster presentation with entitled:** "Ruthenium Pincer Complex Catalysed C-3 alkylated indole and Bisindolylmethane directly from indole and alcohol." **PFEOS-2021.**

2. **Poster presentation with entitled**: "Manganese Catalyzed Switchable C- Alkylation/Alkenylation of Fluorenes and Indene with Alcohols." **MTIC-IX.**

3. **Poster presentation with entitled:** "Ruthenium Catalyzed Alkylation of Alcohols Using SNS-Ru Catalyst via Borrowing Hydrogen Method." **RIC-2022**

4. **Poster presentation with entitled:** "A Sustainable Approach for the Synthesis of Heterocyclic Compounds via Hydrogen Autotransfer or Acceptorless Dehydrogenative Coupling by Phosphine-Free Manganese Complex." **NERC-2022.**

5. Oral presentation with entitled: "Lutidine Based SNS Ligand Decorated Ni-complex for Alcohol Activation and its Application for Various C-alkylation Reaction." **NCCTBSA24**

5. The 2 days' online workshop on **"Nuclear Magnetic Resonance: Technique and its Application"** held from 23rd to 24th August 2021, organized by **North East Centre for Biological Sciences and Healthcare Engineering**, Indian Institute of Technology Guwahati, Assam in collaboration with **Bruker**, **India**, with support of Department of Biotechnology, Govt. of India as part of **Azadi ka Amrit Mahotsav**.

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Unveiling the Potential of SNS-Ni Complex for Establishing C–N Bonds: An Approach toward Chemoselectivity

Author: Rahul Sharma, Avijit Mondal, Suman Maji, et al
Publication: Organometallics
Publisher: American Chemical Society
Date: Nov 1, 2024

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