Chapter - 2

Synthesis and Applications of Aminobenzyl Naphthols

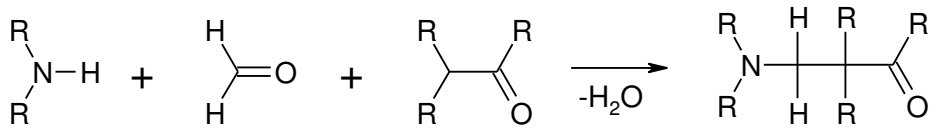
PART - I: Synthesis of Aminobenzyl Naphthols by Mannich reaction

PART - II: Applications in C - C bond Formation reaction

INTRODUCTION

PART - I: Synthesis of Aminobenzyl Naphthols by Mannich Reaction

Mannich reaction is an organic reaction used to convert a primary or secondary amine and two carbonyl compounds (one non-enolizable and one enolizable) to a β-amino carbonyl compound; the product is also known as a Mannich base, using an acid or base catalyst. The reaction is named after German chemist Carl Mannich.



Scheme 1: Mannich reaction

In the acid catalyzed mechanism both carbonyl compounds get protonated at the oxygen. The enolizable carbonyl compound, with a α-Hydrogen then gets deprotonated to form an enol intermediate. The other, non-enolizable carbonyl compound reacts with the amine to form an imminium ion. The enol intermediate then attacks the imminium ion which after deprotonation provides the final Mannich base product.[1]

In the Mannich reaction, primary or secondary amines or ammonia, are employed for the activation of formaldehyde. Tertiary amines without N-H proton do not form the intermediate enamine. Compounds (nucleophiles) with α-CH – acidic hydrogen include carbonyl compounds, nitriles, acetylenes, aliphatic nitro compounds, α-alkyl-pyridines or imines. It is also possible to use activated phenyl groups and electron-rich hetero cycles such as furan, pyrrole and thiophene Indole is a particularly active substrate; the Mannich reaction of Indol provides gramine derivatives.

Thus the Mannich reaction is an example of nucleophilic addition of an amine to a carbonyl group followed by dehydration to the Schiff base. The schiff base is an electrophile which reacts in the second step in an electrophilic addition with a compound containing an acidic proton (which is, or had become an enol). This reaction is also considered a condensation reaction.

Mechanism for Mannich Reaction

The mechanism of the Mannich Reaction starts with the formation of an iminium ion from the amine and the non-enolizable carbonyl compound. The

enolizable carbonyl compound tautomerizes to the enol form, after which it can attack the iminium ion to give β-amino carbonyl product.

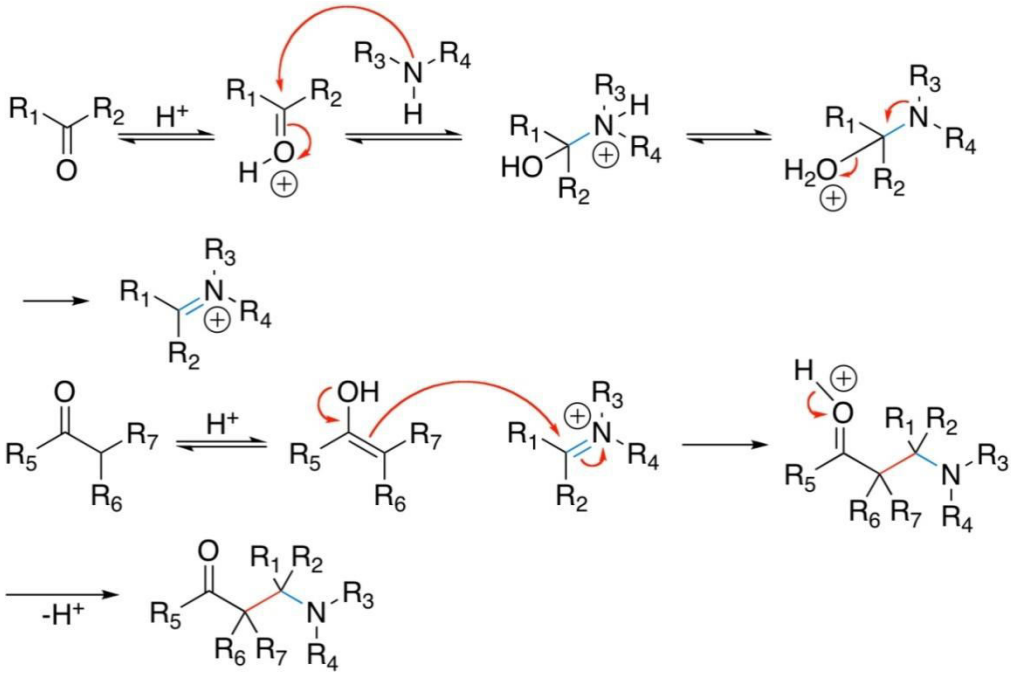


Figure 1: Mechanism for Mannich reaction

PART - II: Application in C-C Bond formation Reaction

The significance of palladium catalysis and cross-coupling reactions[2] has been recognized by the award of a Nobel Prize for chemistry in 2010 to scientists who carried out pioneering work in this area. As discussed in chapter 1, the palladium catalyzed cross-coupling reactions, like Mizoroki-Heck, Suzuki-Miyaura and Sonogashira reactions have been used extensively for the synthesis of natural products, pharmaceutical intermediates, conducting polymers, pesticides and liquid crystals.

(A) MIZOROKI – HECK REACTION

Palladium catalyzed attachment of vinyl moiety to aryl halides, often referred as "Mizoroki-Heck reaction", is an extremely useful and routinely employed method of the formation of carbon-carbon bond. In this reaction *trans* olefins are predominantly formed as major product. In the late 1960s, Heck and Mizoroki independently discovered arylation and alkenylation of olefins, known after Heck[3] or Mizoroki-Heck[3] reaction. This reaction was further developed by Heck described in number of fundamental papers in to a general method of organic chemistry. The reaction is catalyzed by Pd in the presence of base and solvent.

Scheme 2: Mizoroki-Heck reaction

The catalyst in the standard Heck reaction is a Pd(0) species stabilized by suitable ligands. The reaction mechanism includes four steps (**Figure 2**):

1) A σ-aryl-Pd (II) complex is formed via oxidative addition.
2) Either one of the ligands or halide anion dissociates from the complex, leaving behind a vacant coordination site that is occupied by the olefin substrate. Insertion of the olefin at the aryl-Pd bond takes place subsequently.
3) An intramolecular β-hydride elimination occurs, which gives the coupling product.
4) PdL_2 catalyst is regenerated after the removal of HX from the complex mediated by the base.

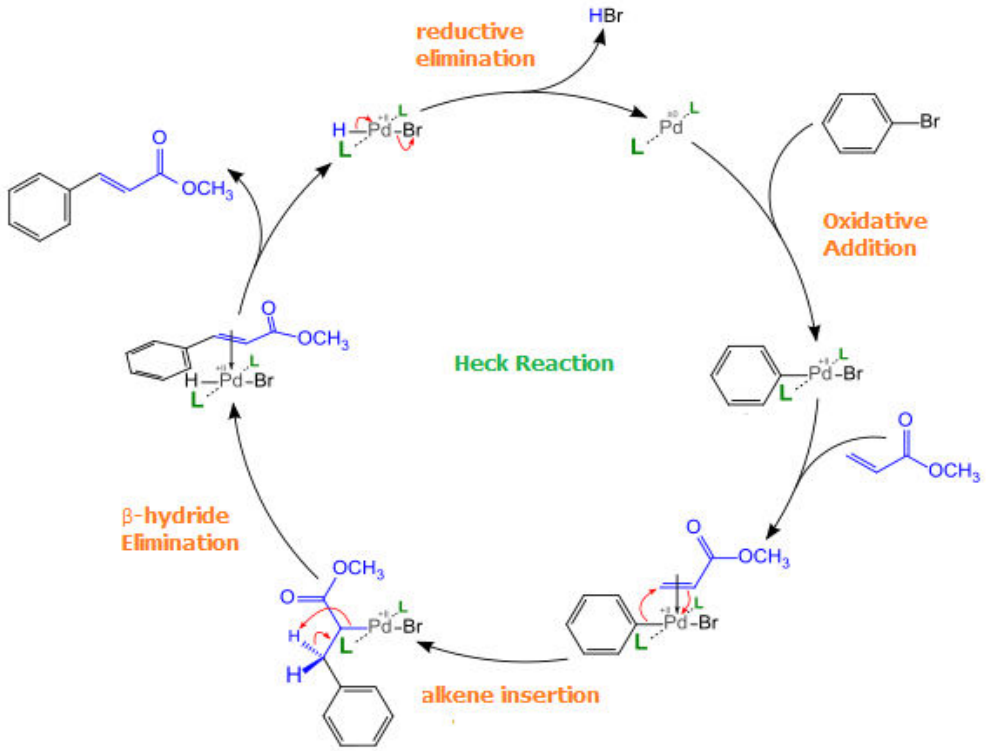
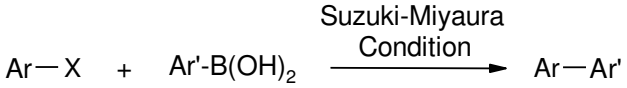


Figure 2: Mechanism of Mizoroki-Heck reaction

(B) SUZUKI - MIYAURA REACTION

The coupling of aryl halide with aryl boronic acid in presence of base and the Pd-Ligand catalyst system known as Suzuki-Miyaura reaction is also an important method of carbon-carbon bond formation.



Scheme 3: Suzuki-Miyaura reaction

It was first published in 1979 by Prof. Akira Suzuki who shared the 2010 Nobel Prize in chemistry with Prof. Richard F. Heck and Prof. Ei-ichi Negishi for their effort for discovery and development of Palladium catalyzed cross coupling in organic synthesis. In many publications this reaction is referred by "Suzuki-Miyaura reaction."

The Suzuki reaction is providing to be an increasingly popular tool for the construction of unsymmetrical biaryl. The reagents organoboranes are air and moisture stable and with relatively low toxicity.[4a] Suzuki coupling for the production of biaryls has been applied under microwave[4b] or ultrasonic irradiation.[4c] Both conditions, in general, lead to reduction of reaction time and can offer some advantages.

Mechanism for Suzuki - Miyaura Reaction

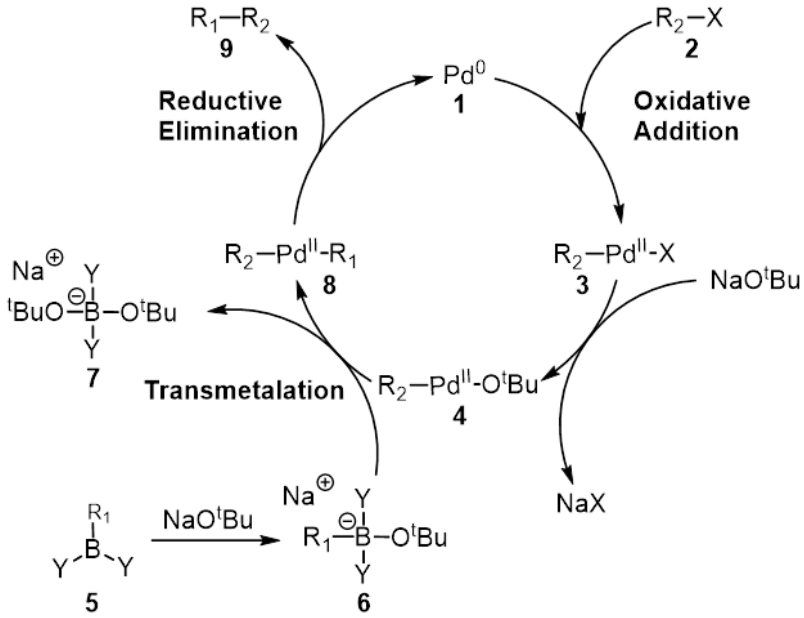
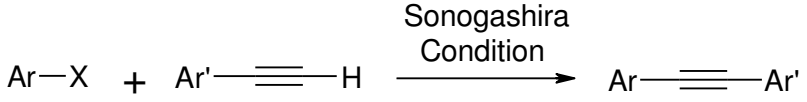


Figure 3: Mechanism of Suzuki reaction

The mechanism of the Suzuki reaction is best viewed from the perspective of the palladium catalyst. The first step is the oxidative addition of Pd to the halide **2** to form the organopalladium species, **3**. Reaction with base gives intermediate **4**, which via transmetalation with the boron-ate complex **6** forms the organopalladium species **8**. Reductive elimination of the desired product **9** restores the original palladium catalyst **1** which completes the catalytic cycle (**Figure 3**).

(C) SONOGASHIRA REACTION

The Sonogashira cross-coupling reaction is the organic reaction of an organohalide with a terminal alkyne to give the coupled product using a palladium catalyst, a copper catalyst and a base. It was first reported by Kenkichi Sonogashira, Yasuo Tohda and Nobue Hagihara in their 1975 publication.[5]



Scheme 4: Sonogashira reaction

Mechanism for Sonogashira Reaction

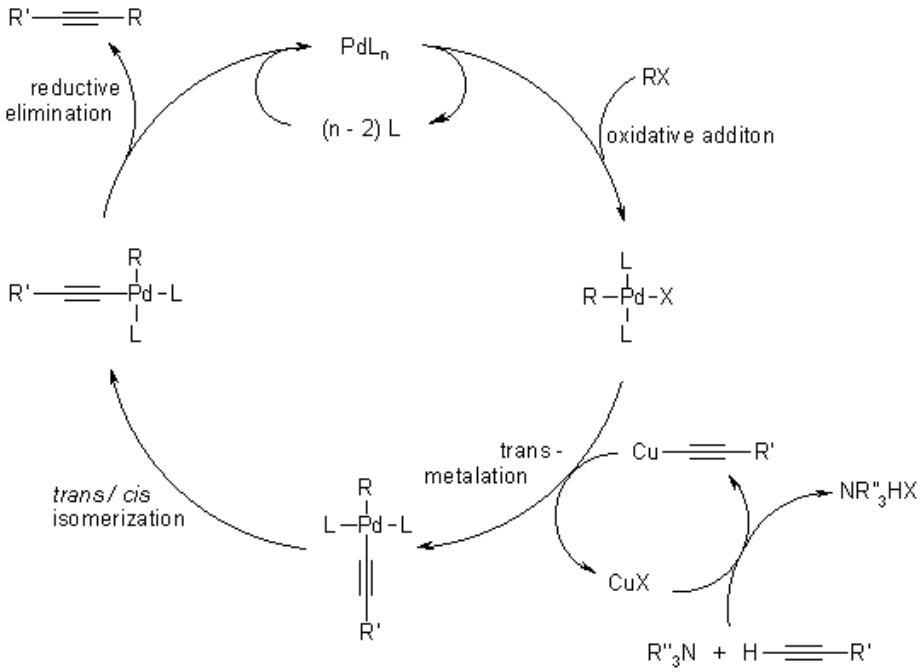


Figure 4: Mechanism of Sonogashira reaction

The palladium catalyzed mechanism begins with oxidative addition of the organohalide to the Pd(0) to form a Pd(II) complex. Transmetalation with the

organocopper reagent formed from the terminal alkyne and the copper catalyst, then follows. The alkynyl anion replaces the halide on the palladium complex and regenerates the copper halide catalyst. Reductive elimination then gives the final coupled product, regenerates the palladium catalyst and the catalytic cycle can begin again.

Modification – "copper-free Sonogashira Reaction"

While a copper co-catalyst is added to the Sonogashira reaction to increase reactivity, the presence of copper can result in the formation of alkyne dimers. This leads to Glacer coupling reaction, which is an undesired formation of homocoupling products of acetylene derivatives upon oxidation. As a result, when carrying out a Sonogashira reaction with a copper co-catalyst, it is necessary to run the reaction in an inert atmosphere to avoid the unwanted dimerization. Copper-free variations to the Sonogashira reaction have been developed to avoid the formation of homocoupling products.[6]

Mechanism of Copper-free Sonogashira reaction

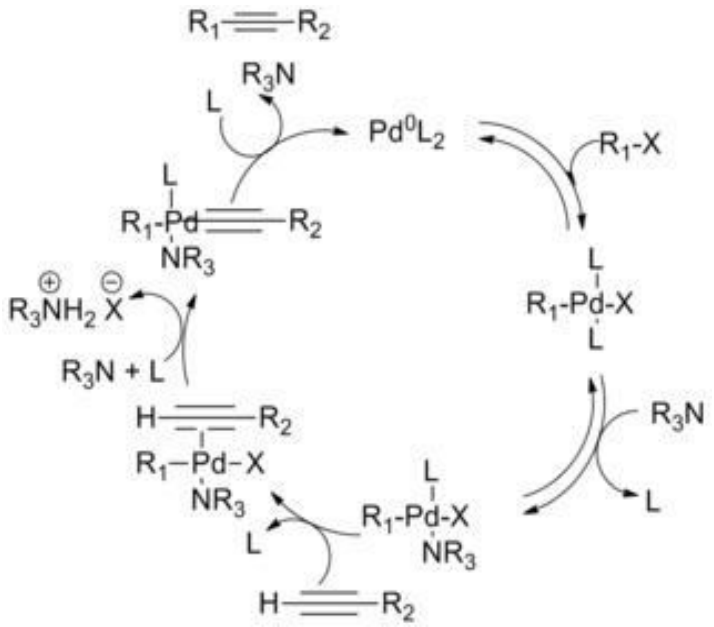


Figure 5: Mechanism of Copper-free Sonogashira reaction

As in the original mechanism, oxidative addition of the aryl halide or triflate to the Pd(0) catalysts. Since the amines associated with this reaction are not basic enough to deprotonate the reacting alkyne, it is believed that complexation to the

Pd(0) catalyst requires displacement of one ligand to create an intermediate complex. As a result, this new intermediate can then facilitate deprotonation of the terminal alkyne proton and subsequent ligand exchange with the leaving group X. reductive elimination gives rise to the desired coupling product.

These cross-coupling reactions; normally performed with 1-5 mol% of Pd catalyst along with equal or higher molar amounts of phosphine ligands, still suffer from two significant problems.[7] Firstly, palladium is expensive and its contamination has to be particularly regulated in the case of consumption for biological systems. Second, many phosphine ligands are not readily available, and are not simple to work with owing to their toxic character, air sensitivity and tendency of degradation. However, most of these catalysts containing phosphines are generally sensitive to moisture and air, and require air-free conditions to minimize oxidation. Moreover, their large-scale application is limited in industry owing to their high cost and toxic nature.[7] These reasons offer an opportunity to develop Pd catalysts that can utilize inexpensive phosphine-free ligands. In this endeavor, a number of nitrogen and/or oxygen donor ligands have been examined for palladium-catalyzed reactions as discussed in chapter 1.

Aminonaphthols are established as efficient and widely accepted ligands for various organic transformations due to their easy accessibility and better binding ability with metals which have been summarized in chapter 1. As discussed in the chapter 1, we have synthesized some aminonaphthols as phosphine free catalysts and screened them for palladium catalyzed reactions, which will be discussed in this chapter.

Results and Discussion

PART - I: Synthesis of Aminobenzyl Naphthols by Mannich Reaction

Aminonaphthols have been synthesized by a simple alteration of the three-component modified Mannich reaction (mMR) in which formaldehyde is replaced by an aromatic aldehyde, the secondary amine by ammonia, and the C-H acid by an electron rich aromatic compound such as 1- or 2- naphthol, quinolinol or isoquinolinol.[8] They are established as efficient and widely accepted ligands due to their easy accessibility, air stability and better binding ability, which have been discussed in chapter 1. In accordance with the previous chapter, we have synthesized number of aminobenzylnaphthol derivatives. This chapter deals with the different variants of mMR. The subsections are divided according to the amine source applied.

I. Synthesis of Achiral ligands

(a) Synthesis with monoamine as N source

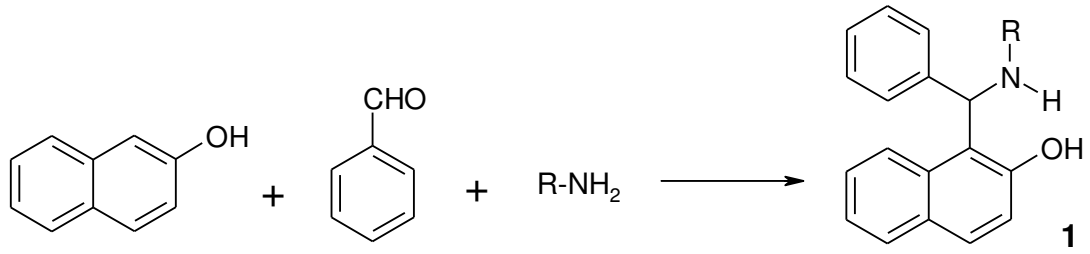
(b) Synthesis with di-amine as N source

II. Applications of Chiral ligands

For the practical application, these aminobenzyl naphthols were screened as phosphine-free ligands in Pd catalyzed cross-coupling reactions. Details of these experiments would be discussed in part II of this chapter.

I. Synthesis of achiral ligands

Consideration of 1^o or 2^o amines with aldehydes and 2-naphthols similar to the classical Mannich reaction gives 1-(α-aminobenzyl)-2-naphthols **1** in good yields (**Eq.1**).



Equation 1: Modified Mannich reaction

(a) Synthesis with monoamine as N source:

We have chosen monoamines for example, piperidine, morpholine, dimethyl amine and benzyl amine as N source for the synthesis of the racemic aminobenzylnaphthols. We have carried out this mMR in two different conditions.

Method A: r.t., N_2 atmosphere, 24 - 48 h, EtOH

Method B: 60^oC, N_2 atmosphere, 24 h, no solvent

We observed that the reaction carried out at higher temperature gave better yield compared to reaction at room temperature (**Table 1**).

Table 1: Synthesis of achiral ligands with monoamines

Ligand	R	% Yield in Method A	% Yield in Method B
1a	- CH_2-$(CH_2)_3$-CH_2-	46	62
1b	-$(CH_2)_2$-O-$(CH_2)_2$-	46	65
1c	-$(CH_3)_2$-	71	80
1d	Ph-CH_2-	-	30

The proton NMR analysis of ligand showed some interesting pattern. The two alkyl groups attached to nitrogen appeared as broad signal at around 2.5 δ when NMR was run at 21^oC in $CDCl_3$. The variable temperature ^{1}H-NMR analysis indicated that at lower temperature (0^oC) the two methyl groups of **1c** clearly separate as two sharp singlets while they merge as one slightly broad single singlet at higher temperature (40^oC). This separation of two signals could be due to two possible reasons, (i) the hydrogen bonding between the phenolic hydroxyl and nitrogen or (ii) due to restriction of rotation across Ar – $^{\alpha}$C or $^{\alpha}$C – N bonds. As expected the rotation will be slower at lower temperature and

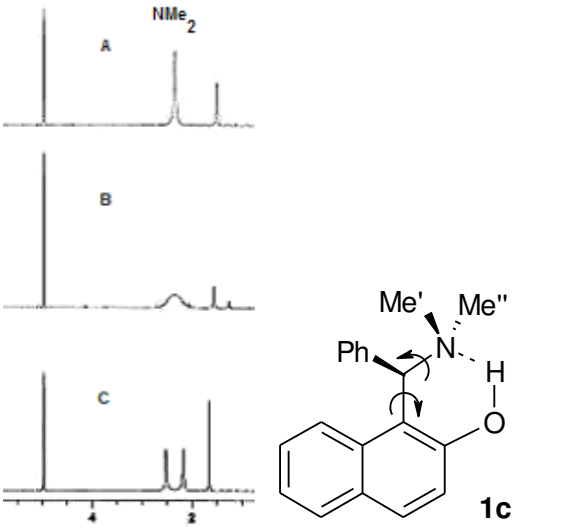
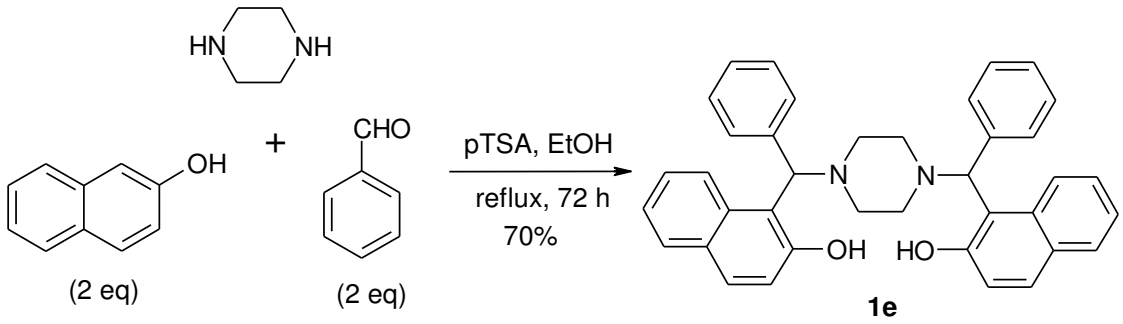


Figure 6: H-NMR of **L-1c** at 40^oC(A), 21^oC(B), 0^oC(C)

hence two signals were seen for NMe_2 at 0^oC, (**Figure 6**). A similar broadening of signals of NCH_2- of **1a** and **1b** confirms this observation.

(b) <u>Synthesis with Di-amines as N source:</u>

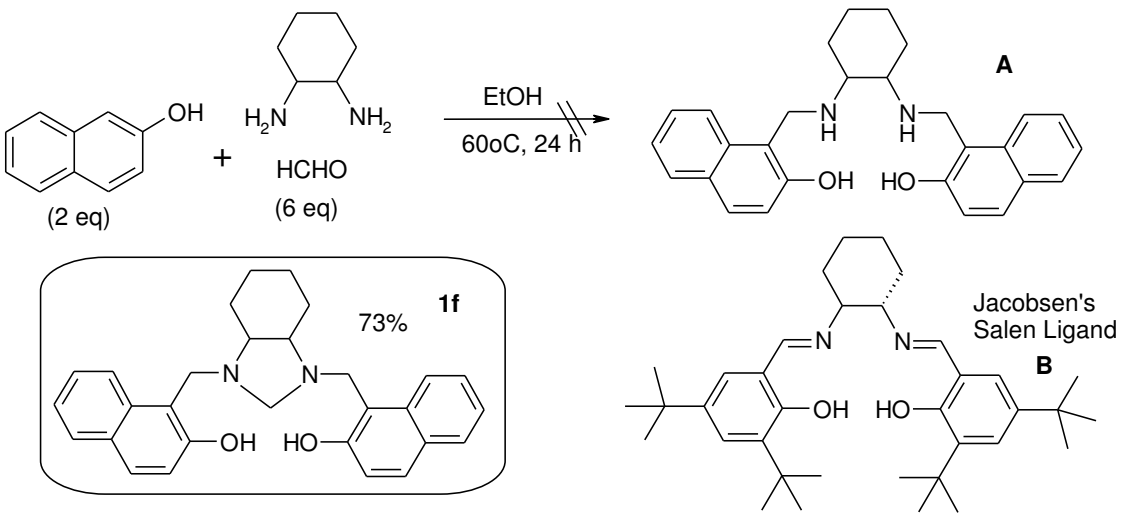
We have used Piperazine and 1, 2-Diaminocyclohexane as Nitrogen source. Reaction of Piperazine with 2-naphthol (2 eq.) and benzaldehyde (2 eq.) in the presence of stoicheometric amount of pTSA in ethanol solvent under reflux condition for 72 h yielded Bis-aminobenzylnaphthol **1e** in good yield (70%) (**Scheme 5**).



Scheme 5: Synthesis of Ligand **1e**

Using 1,2-Diaminocyclohexane, our aim was to prepare the bis-aminonaphthol derivative **A** which is quite similar in structure to that of Jacobson's Salen catalyst **B**. The Salen ligand **B** was prepared and extensively utilized by Jacobsen for a number of early transition metal mediated asymmetric reactions. Several oxidations and Lewis acid promoted epoxide ring opening reactions with Mn, Cr, Co etc have been successfully carried out with good selectivity.

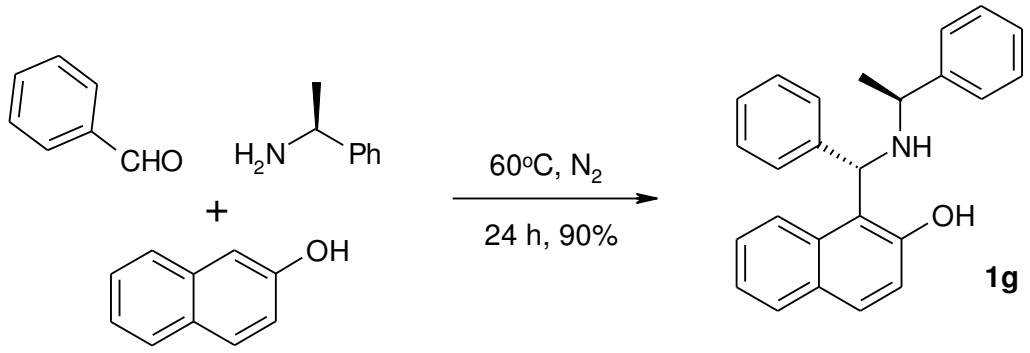
Here we proposed to prepare ligands like **A** and study their reactions. However, the Mannich reaction of 1, 2-diaminocyclohexane with 2-naphthol (2 eq.) and excess of formaldehyde, the expected bis-Mannich base product was not formed but unexpected cyclized bis-aminonaphthol **1f** type product was obtained in good yield (73 %).

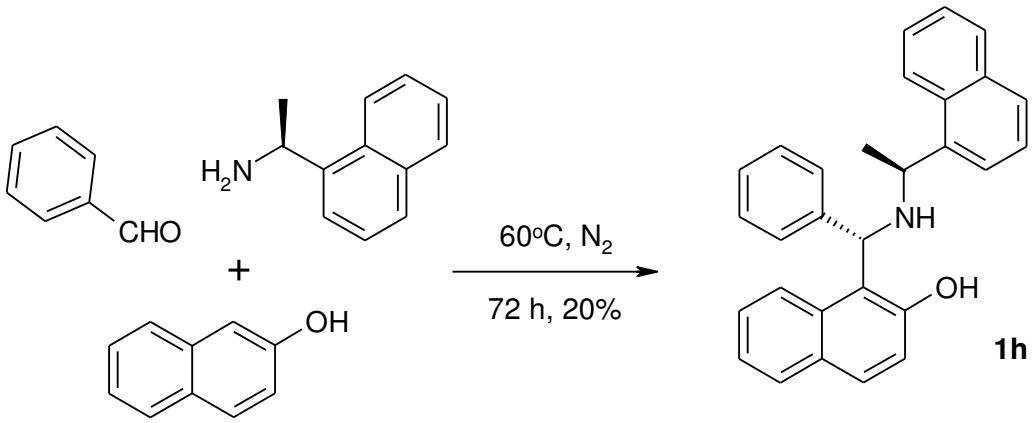


Scheme 6: Synthesis of Ligand **1f**

II. **Synthesis of Chiral ligands**

In this part we have used two chiral amines as Nitrogen source to synthesize corresponding chiral aminobenzylnaphthols. The Mannich reaction of 2-naphthol, benzaldehyde and *S*-(-)-phenylethylamine at 60 ^{o}C, under N_2 atmosphere and solvent-free conditions yielded chiral aminobenzylnaphthol (*S*,*S*)-**1g** in excellent yield (90%). However when chiral *S*-(-)-phenylethylamine was replaced with *S*-(-)-1-naphthylethylamine then the yield of the corresponding chiral aminobenzylnaphthol **1h** was decreased even though with longer reaction time. The lower yield may be due to steric hindrance.





Scheme 7: Synthesis of Chiral ligands

The achiral aminobenzylnaphthols (**1a**-**1d**) prepared so far, have an attractive arrangement of two heteroatoms (N and O) at a suitable distance to form a six-member stable chelate with metal ions, a prerequisite for the applications as a ligand in metal-catalyzed reactions and few examples of them are available in the literature as discussed in chapter 1.

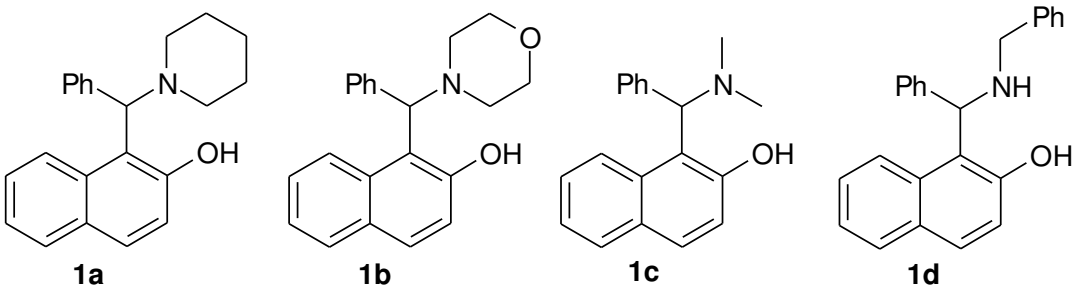
All the ligands were characterized by ^{1}H-NMR, IR and Mass analysis. In ^{1}H-NMR spectra, -OH proton in 2-naphthyl ring of ligand shows the most downfield singlet around 13 δ. The methine -CH- proton appears as singlet as 5 δ. The two sets of -CH_3 protons of ligand **1c** give broad singlet at 2.3 δ as discussed earlier in variable temperature NMR study. The benzylic protons in ligand **1d** shows two doublets at δ = 4.05 and 3.83 ppm (J = 12.9 Hz).

PART-II Applications in C-C Bond formation Reaction

To demonstrate the practical application of aminobenzylnaphthol ligands **1a**-**1d**, we have screened these ligands in palladium catalyzed Mizoroki-Heck, Suzuki-Miyaura and Sonogashira coupling reactions.

(A) MIZOROKI-HECK REACTION

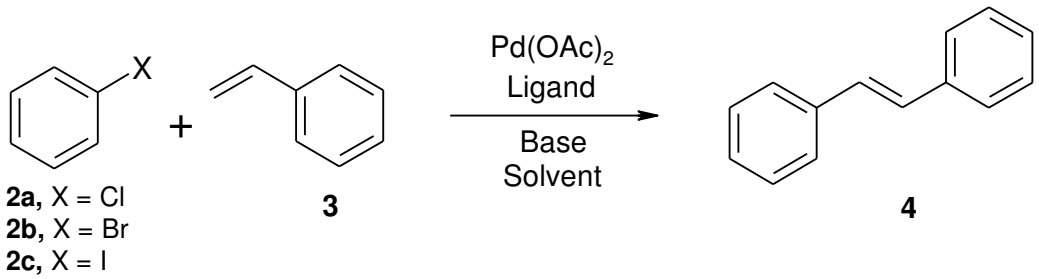
In this chapter we present our findings where air-stable easily accessible Mannich bases 1-(α-aminobenzyl)-2-naphthols **1a**-**1d** are used as efficient ligands for phosphine-free Pd catalyzed Mizoroki-Heck reaction. We have chosen the following representative ligands for this study.



1a **1b** **1c** **1d**

Figure 7: List of Ligands Screened for the Mizoroki-Heck reaction

The ligands **1a**-**1d** were systematically screened in the standard Heck reaction of aryl halides **2a**-**2c** and styrene for the search of best condition (**Scheme 8**) and the results are summarized in **Table 2**. Here we have studied the effect of variation in aryl halides, ligands, solvent and the amount of catalyst.



2a, X = Cl
2b, X = Br
2c, X = I

3 **4**

Scheme 8: Mizoroki-Heck reaction

Table 2: Search for suitable conditions for Heck reaction with ligand **1**

No	Aryl halide (1 mol eq.)	Ligand (mol %)	$Pd(OAc)_2$ (mol %)	Solvent	Isolated yield (%) of **4**	TON
1	PhCl	**1a** (1.2)[a]	1.0	DMA	--	--
2	PhBr	**1a** (0.12)	0.1	DMA	60	597
3	PhI	**1a** (0.12)	0.1	DMA	97	975
4	PhI	**1a** (0.55)	0.5	DMA	96	194
5	PhI	**1b** (0.55)	0.5	DMA	93	187
6	PhI	**1c** (0.55)	0.5	DMA	87	175
7	PhI	**1d** (0.55)	0.5	DMA	84	170
8	PhI	**1a** (0.55)	0.5	DMF	89	180
9	PhI	**1a** (0.55)	0.5	NMP	69	139
10	PhI	**1a** (0.012)	0.01	DMA	79	7890
11	PhI	**1a** (0.006)	0.005	DMA	68	13594
12	PhI	**1a** (0.12)[b]	0.1	DMA	89	889
13	PhI	**1a** (0.55)	0.25	DMA	97	390

Solvent: **A**: DMA; **B**: DMF; **C**: NMP. All reactions run with styrene (1.5 eq.), K_2CO_3 (2.5 eq.) at 140 °C, except entry 12. [a]With TBAB (0.25 eq.); [b]With NEt_3 (2.5 eq.). TON = **T**urn **O**ver **N**umber.

The present ligands prepared either from 1° or 2° amines are very effective for the Heck reactions with either K_2CO_3 or with organic amine Et_3N and the stilbene is obtained almost as a single *trans* isomer. Initially a combination of slightly higher amount of Pd (0.5 mol %) and ligand **1a** (0.55 mol %) was used to assess the efficiency and as expected iodobenzene **2c** and styrene **3** gave the desired *trans*-stilbene **4** in very good yield [Entry 4, Table 2] but with rather low turnover number (TON). As expected, chlorobenzene **2a** was inert even in the presence of tetrabutylammonium bromide (TBAB) as additive for this reaction. On the other side bromobenzene **2b** and iodobenzene **2c** gave *trans*-stilbene **4** as exclusive product in 60% and 97% respectively under identical condition [Entry 1-3, Table 2].

Further reaction with lower amount of catalyst/ligand were encouraging and reasonably low concentrations (0.005/0.006 mol %) gave good isolated yield of stilbene **4** with excellent turn over number [Entry-11, Table 2]. Solvent study indicated dimethylacetamide (DMA) or dimethylfoamamide (DMF) to be good solvents [Entry-4, 8, 9] and all the ligands were almost equally efficient in reactions [Entry 4-7, Table 2].

The well-established catalytic cycle of the Heck reaction starts with reduction of Pd(II) to Pd(0), often referred to as preactivation, followed by oxidative addition of arylhalide, insertion of olefin and finally reductive elimination. In the case of phosphine-free reaction conditions, it is possible that the initial reduction of palladium during preactivation is assisted by nucleophilic amine of the ligands rather from alkene.

The role of ligand in this reaction was established by performing two sets of experiment with relatively less reactive bromobenzene **2b** with styrene under our standard condition for 8, 24 and 40h, one in the presence of ligand and other in the absence of ligand. The increase in the conversion and yield of *trans*-stilbene in the experiment with ligand compared to the experiment without ligand clearly establishes the role of ligand. The results are presented in graphical manner as below.

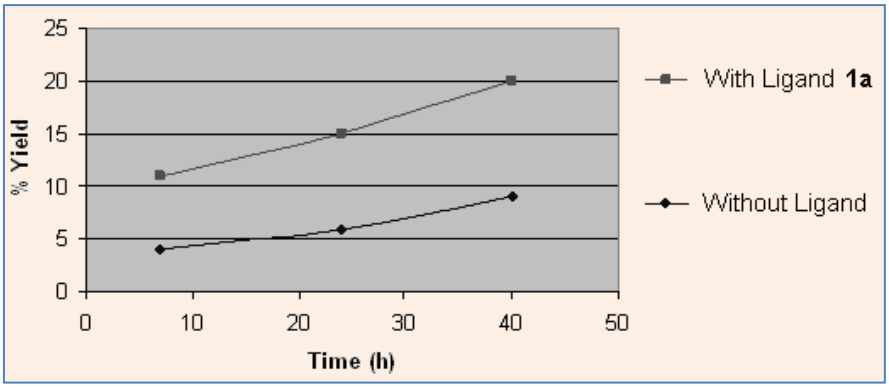
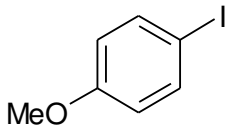
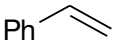
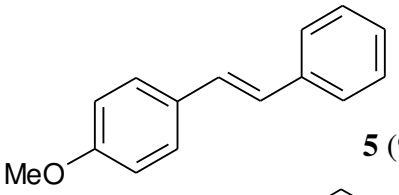
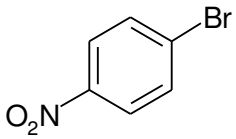
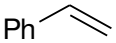
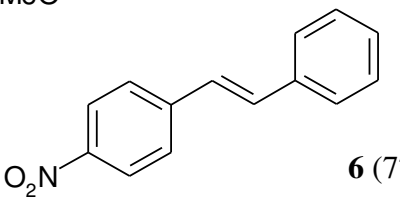
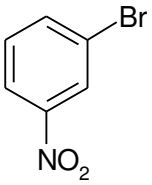
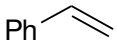
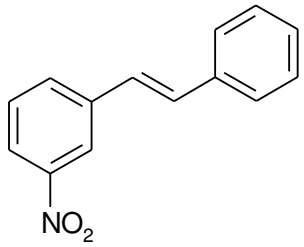
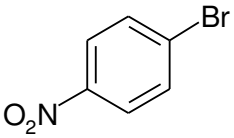
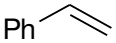
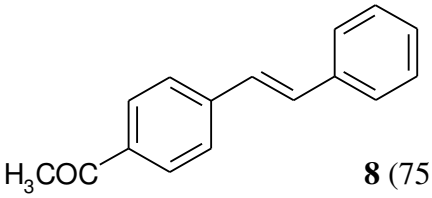
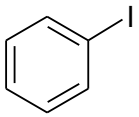
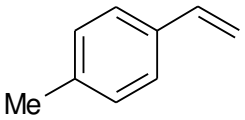
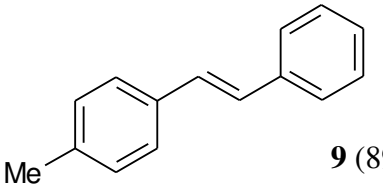
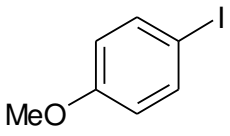
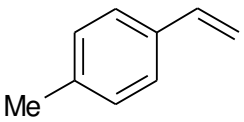
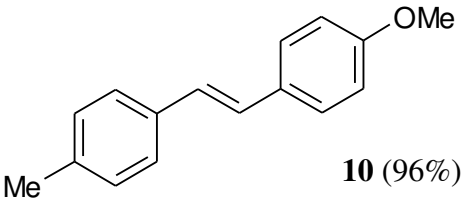
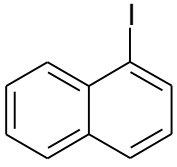
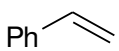
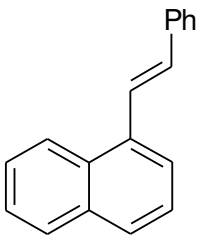


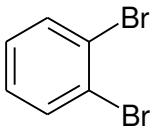
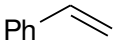
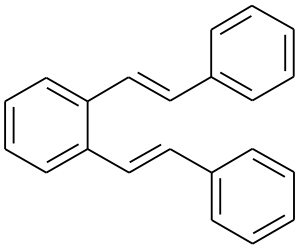
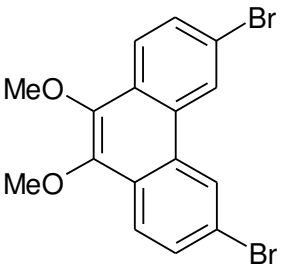
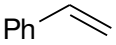
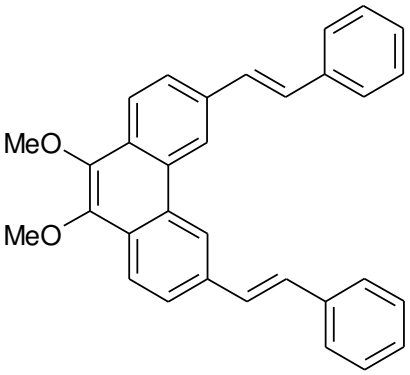
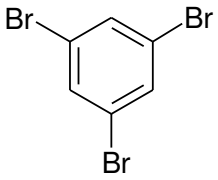
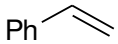
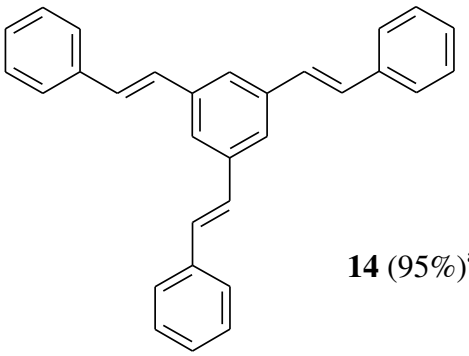
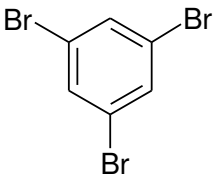
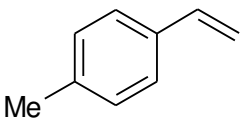
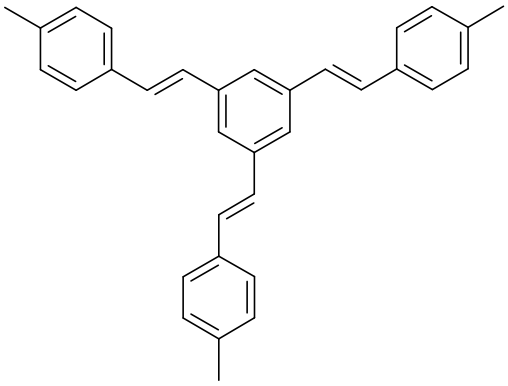
Figure 8: Graphical presentation for the role of ligand in Mizoroki-Heck reaction

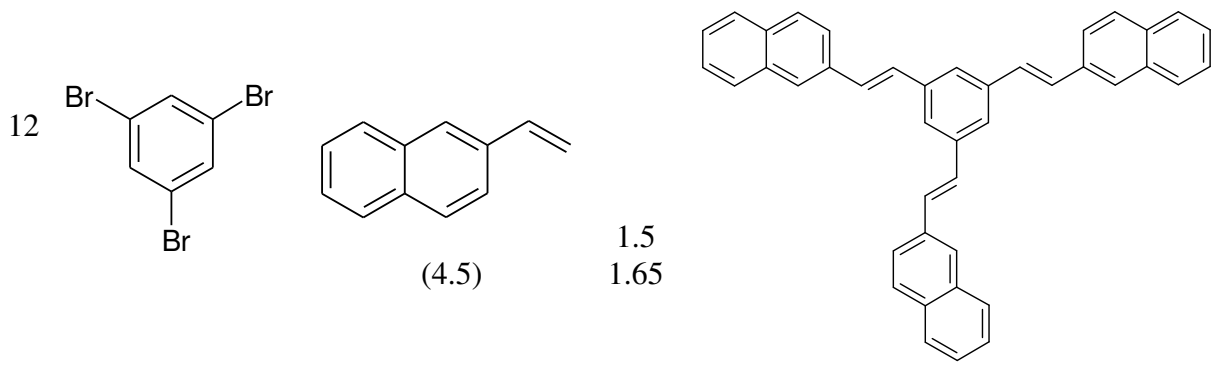
Having established the standard reaction parameters we have applied this system for several examples of this reaction to produce variety of olefins and the results are presented in **Table 3**. The products were separated by careful chromatography and characterized by ^{1}H-NMR analysis, in most of the cases almost no *cis*-product.

A number of different derivatives **5** to **11** of stilbenes were prepared by using ligand-Pd ratio (**1a**/$Pd(OAc)_2$ = 0.12/0.1mol%) in good yield [Entry 1-7, table 3], while for **12**-**16** a greater ratio of styrene and catalyst was needed [Entry 8-12, Table 3].

Table 3: Examples of Mizoroki-Heck reaction

No	Aryl Halides	Olefin (eq)	$Pd(OAc)_2$ Ligand **1a** (mol%)	Product (Yield, %)
1		 (1.5)	0.1 0.12	 **5** (93%)
2		 (1.5)	0.1 0.12	 **6** (77%)[a]
3		 (1.5)	0.1 0.12	 **7** (97%)[a]
4		 (1.5)	0.1 0.12	 **8** (75%)[a]
5		 (1.2)	0.1 0.12	 **9** (89%)
6		 (1.2)	0.1 0.12	 **10** (96%)
7		 (1.5)	0.1 0.12	 **11** (91%)

8		 (3.0)	0.2 0.24	 **12** (94%)[a]
9		 (4.0)	1.0 1.2	 **13** (93%)[a]
10		 (6.0)	1.5 1.65	 **14** (95%)[a]
11		 (4.5)	1.5 1.65	 **15** (87%)[a]



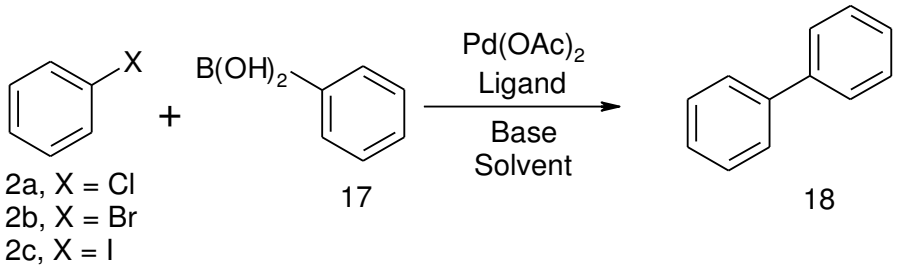
All reactions in DMA with K_2CO_3 (2.0 eq), 140°C, N_2 atmosphere; [a]With TBAB (20% per halogen atom).

The photocyclization of substituted styrene is a standard method of preparation of the derivatives of phenanthrenes.[9a] This is also a widely employed method for the synthesis of polycyclic aromatic compounds.[9b] Considering this, we have prepared a series of such derivatives of stilbenes (**13**, **14**, **15** & **16**) from the corresponding bromo compounds in very good yields [Entry 9-12, Table 3]. It is noteworthy that we were able to prepare **13** and 1,3,5-*trans*-(styryl)-benzenes **14** in good yields compared to other olefination methods.[10]

The *trans* olefinic proton shows signal at δ = 7 ppm (*J* = 16.4 Hz) in compound **12**, δ = 7.15 ppm (*J* = 16.4 Hz) in compound **14** and δ = 7.3 ppm (*J* = 16.0 Hz) in compound **16**. In the ^{1}H-NMR spectra of compound **13**, the *trans* olefinic protons get merged with the multiplet given by aromatic protons, while the two -OMe protons appear as singlet at δ = 4.11 ppm.

(B) SUZUKI-MIYAURA REACTION

The results obtained in an application of our phosphine-free ligands for the palladium-catalyzed Heck reaction prompted us to extend our studies towards the palladium-catalyzed Suzuki coupling reactions.



Scheme 9: Suzuki-Miyaura reaction

As we know, one of the basic types of reactivity in palladium driven catalytic cycles is due to the ability of Pd(0) species to undergo oxidative addition to various C-X bonds and here our ligand **1** stabilizes the Pd catalysts via formation of Pd(0) species and thus accelerates coupling in the reaction. We have chosen the following representative ligands for this study.

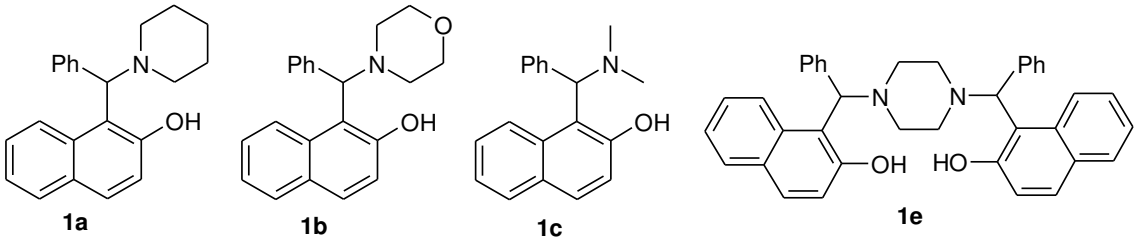


Figure 9: List of Ligands screened for the Suzuki-Miyaura reaction

The ligands were screened to determine optimum reaction conditions for the Suzuki-Miyaura reaction with aryl halides and aryl boronic acid in the presence of a suitable base (**Scheme 9**) under different reaction conditions. The results are presented in (**Table 4**).

We have varied aryl halides, ligands, reaction temperature and mole ratio of catalyst to optimize reaction conditions. The results of the study of Suzuki-Miyaura coupling indicate very efficient conversion with aryl iodides and aryl bromides with a small quantity of tetra-n-butylammoniumbromide (TBAB) when aqueous dioxane was used as solvent [Entry 3, 6 Table-4].

Table 4: Search for suitable condition for Suzuki reaction with Ligand **1**.

No	Aryl halide (1 eq.)	Ligand (mol %)	$Pd(OAc)_2$ (mol %)	Temp ^{o}C [Time/h]	Isolated yield (%) of **18**	TON
1	PhI	1a (0.12)	0.1	95 [4]	92	920
2	PhI	1b (0.12)	0.1	95 [4]	89	890
3	PhI	1c (0.12)	0.1	95 [4]	96	964
4	PhI	-	0.1	95 [4]	20	200
5	PhI	1e(0.12)	0.1	95 [4]	85	854
6	PhBr	1c (0.12)	0.1	95 [20]	82[a]	629
7	PhCl	1c (0.12)	0.1	95 [30]	26[a]	146
8	PhI	1c (0.012)	0.01	95 [24]	93	9390
9	PhI	1c (0.60)	0.5	Sonication Temp≤40 ^{o}C [2]	70	140
10	PhI	--	0.1	Sonication Temp≤40 ^{o}C [2]	40	400
11	PhI	1c (0.12)	0.1	Sonication Temp≤40 ^{o}C [2]	60	603
12	PhI	1c (0.12)	0.1	Room Temp [2]	10	100

All reactions in dioxane-water (1:1) with Phenyl boronic acid (1.2 eq), K_2CO_3 (2.0 eq); [a]With TBAB (20% per halogen atom);

Chlorobenzene was considerably less reactive after a long reaction time [Entry 7, Table-4] but iodobenzene gave biphenyl with good conversion even with very low catalyst quantity. Variation of the amount of catalyst to as low as 0.01 mol% of Pd resulted in the formation of biphenyl in high yield and turnover number (TON) [Entry 8, Table-4].

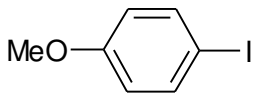
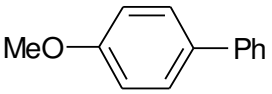
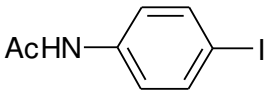
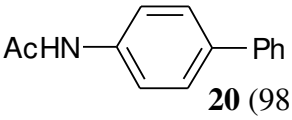
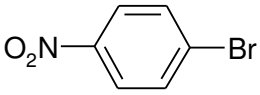
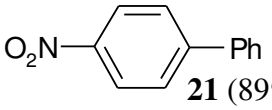
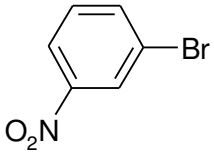
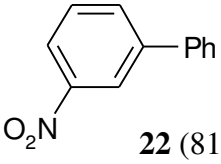
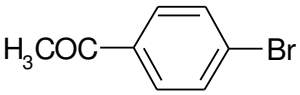
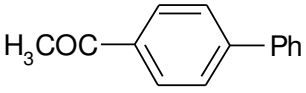
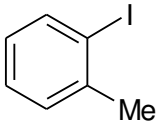
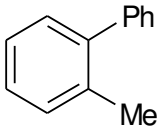
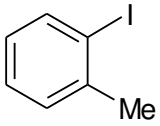
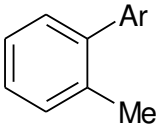
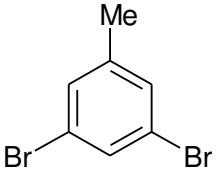
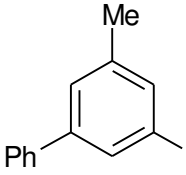
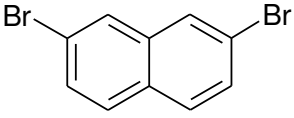
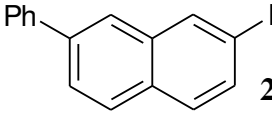
The efficacy of different ligands was ascertained by separate experiments [Entries 1-3 and 5, Table-4]. It was found that in the absence of any ligand, only $Pd(OAc)_2$ [Entry 4, table-4] could catalyze the Suzuki reaction, but the yield of biphenyl was low (20%). The reaction with ligand **1c** under controlled conditions increased the yield to 96% [Entry 3, Table-4], clearly establishing the role of the ligand. Similarly, reaction carried out at room temperature (with neither heating nor sonication) gave the biphenyl in very poor yield [Entry 12, Table-4], indicating the effect of ultrasonic irradiation.

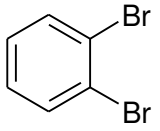
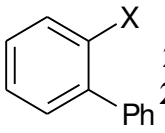
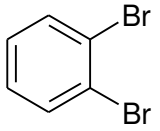
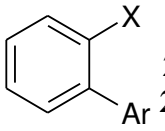
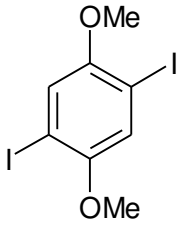
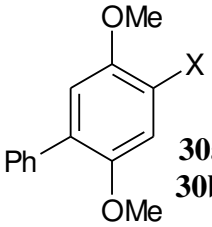
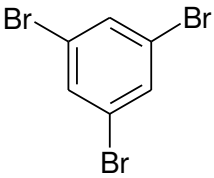
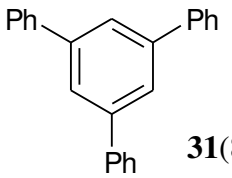
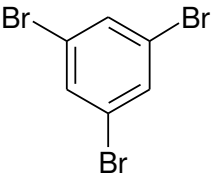
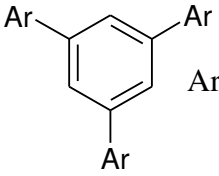
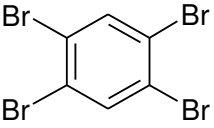
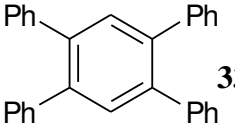
I. Suzuki reaction under Thermal condition

The method of using readily accessible ligands was further extended for a number of examples (**Table 5**). A series of different biaryls **19**-**23** were prepared by using a ligand-Pd ratio (**1**/$Pd(OAc)_2$) of 0.12/0.1 mol% while for dibromo, tribromo and tetrabromo substrates a higher ratio of phenylboronic acid and catalyst was needed. This method worked well for a series of compounds, establishing the generality of the present ligand system for the Suzuki-Miyaura coupling reaction.

The derivatives of biphenyls obtained after column chromatography and characterized by ^{1}H-NMR, IR and Mass analysis. In the ^{1}H-NMR spectra of terphenyl derivative **29b**, the two sets of methyl protons show two singlet at δ = 2.14 and δ = 2.05 ppm due to asymmetry of the compound whereas the two sets of methoxy protons of compound **30b** give only one singlet at 3.84 δ and three sets of methyl protons of compound **32** shows only one singlet at δ = 2.4 ppm. The reason of the less number of peaks is the presence of symmetry element in both compounds. The -CH_2OH protons of compound **38** appear as singlet at δ = 4.78 ppm while -OH proton gives a broad singlet at 2.17 δ.

Table 5: Examples of Suzuki-Miyaura reaction under Thermal condition

No.	Aryl halide	$Pd(OAC)_2$-**1** (mol%)	Temp ^oC (Time h)	Product (% Yield)
1		**1c** [0.1:0.12]	95 [4]	 **19** (98%)
2		**1c** [0.1:0.12]	95 [8][a]	 **20** (98%)
3		**1c** [0.1:0.12]	95 [15]	 **21** (89%)
4		**1a** [0.1:0.12]	95 [15]	 **22** (81%)
5		**1a** [0.1:0.12]	95 [15]	 **23** (90%)
6		**1c** [0.5:0.6]	95 [15]	 **24** (94%)
7		**1c** [0.5:0.6]	95 [15]	 Ar=2-MePh **25** (96%)
8		**1c** [2:2.2]	95 [24]	 **26** (51%)
9		**1c** [0.2:0.24]	95 [15][a,b]	 **27** (77%)

10		**1c** [0.2:0.24]	95 [15][b]	 **28a** (X=Br, 24%) **28b** (X=Ph, 68%)
11		**1c** [2:2.2]	95 [24][b,c]	 Ar=2-MePh **29a** (X=Br, 24%) **29b** (X=Ar, 74%)
12		**1c** [1:1.2]	95 [24][a]	 **30a** (X=Br, 10%) **30b** (X=Ph, 71%)
13		**1c** [3:3.3]	95 [15][b,c]	 **31**(89%)
14		**1c** [3:3.3]	95 [15][b,c]	 Ar=2-MePh **32** (86%)
15		**1c** [4:4.4]	95 [40][a,b]	 **33** (90%)

All reactions in dioxane-water (1:1) with arylborobicacid (1.2 eq); K_2CO_3 (2.0 eq); [a]Dioxane-H_2O (2:1); [b]With TBAB (20% per halogen atom); [c]Dioxane-H_2O (3:1).

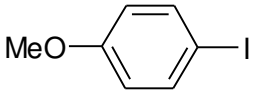
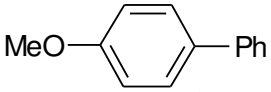
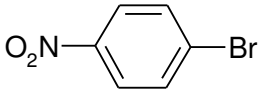
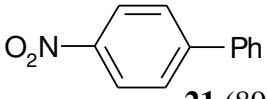
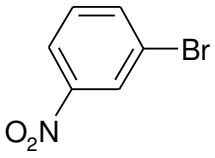
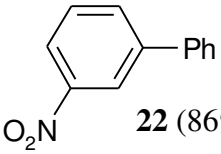
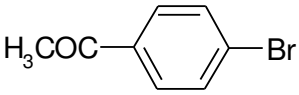
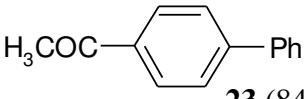
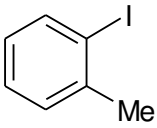
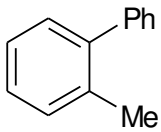
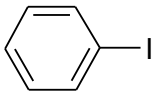
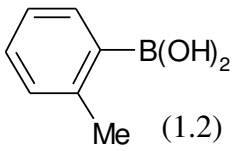
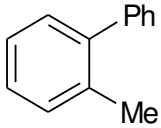
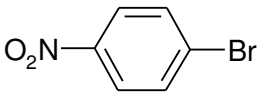
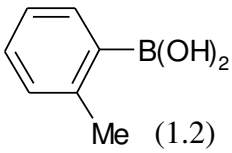
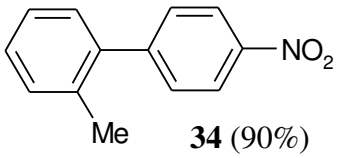
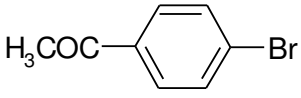
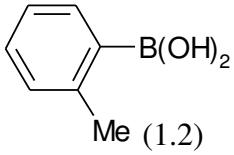
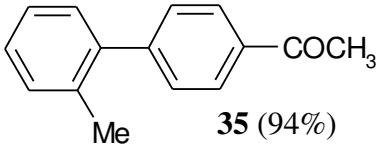
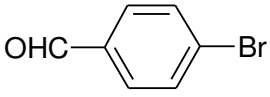
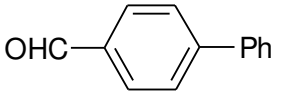
II. Suzuki Reaction Under Ultrasonication condition:

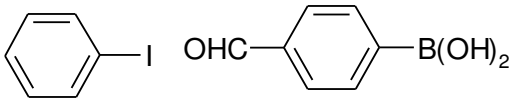
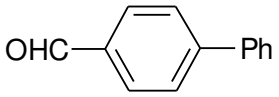
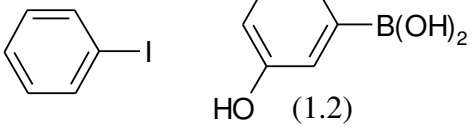
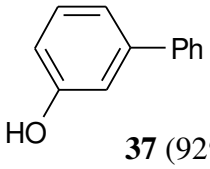
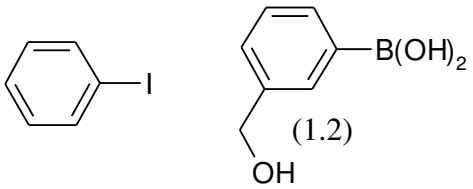
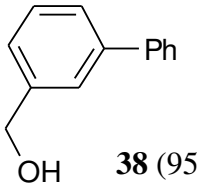
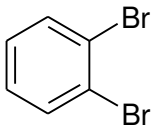
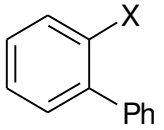
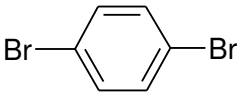
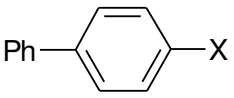
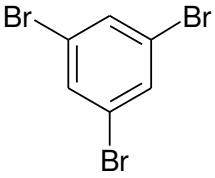
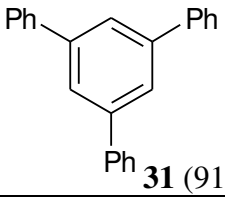
Ultrasound accelerated chemical reactions are well known and proceed *via* the formation and adiabatic collapse of transient cavitation bubbles. Ultrasonic irradiation can be utilized as an alternative energy source for organic reactions ordinarily accomplished by heating. It increases the reaction rate many fold when compared with conventional reaction conditions. It is also known to accelerate diverse types of organic reactions and it is established as an important technique in organic synthesis.

Many reactions have been conducted with homogenous and heterogeneous catalysts, in which the rate of the reaction was accelerated by sonication. Several reports on diverse reactions carried out using ultrasonication[11] include a low temperature Heck reaction with Pd/C by Samant et al., Reformatsky reactions by Bartsch and co-workers, sonochemical preparation of ionic liquids by Varma et al. and Sonogashira coupling by Gholap et al.

We have investigated the present reaction system under ultrasonic/sonication conditions. The reaction was conducted in a normal cleaning immersion sonication bath and the reaction medium was agitated by a mechanical stirrer. We took care to maintain the bath temperature below 40^{o}C by careful water circulation. A wide variety of substrates and boronic acids were used for Suzuki-Miyaura coupling under sonication and the results are summarized in **Table 6**.

Table 6: Examples of Suzuki-Miyaura reaction under Ultrasoniction condition

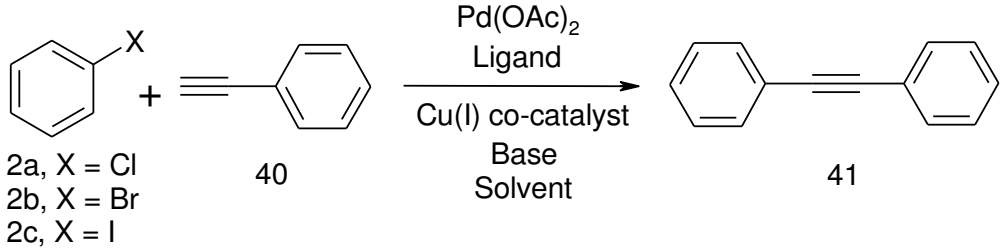
No	Aryl halide (1 eq.)	Boronic acid (eq)	$Pd(OAc)_2$-**1c** (mol%) [Time(h)]	Product (% Yield)
1		Ph-$B(OH)_2$ (1.2)	0.5:0.6 [4 h]	 **19** (34%)
2		Ph-$B(OH)_2$ (1.2)	0.5:0.6 [5 h]	 **21** (89%)
3		Ph-$B(OH)_2$ (1.2)	0.5:0.6 [5 h]	 **22** (86%)
4		Ph-$B(OH)_2$ (1.2)	0.5:0.6 [5 h]	 **23** (84%)
5		Ph-$B(OH)_2$ (1.2)	0.5:0.6 [5 h]	 **24** (47%)
6		 (1.2)	0.5:0.6 [5 h]	 **24** (66%)
7		 (1.2)	0.5:0.6 [5 h]	 **34** (90%)
8		 (1.2)	0.5:0.6 [5 h]	 **35** (94%)
9		Ph-$B(OH)_2$ (1.2)	0.5:0.6 [7 h]	 **36** (89%)

10	 (1.2)		0.5:0.6 [4 h]	 **36** (57%)
11	 (1.2)		0.5:0.6 [4 h]	 **37** (92%)
12	 (1.2)		0.5:0.6 [4 h]	 **38** (95%)
13		Ph-B(OH)$_2$ (4.0)	1.0:1.2 [5 h][a]	 **28a** (X=Br, 10%) **28b** (X=Ph, 87%)
14		Ph-B(OH)$_2$ (4.0)	1.0:1.2 [5 h][a]	 **39a** (X=Br, 27%) **39b** (X=Ph, 52%)
15		Ph-B(OH)$_2$ (6.0)	3.0:3.3 [5 h][a]	 **31** (91%)

All reactions in dioxane-water (1:1) with K_2CO_3 (2.0 eq); [a]With TBAB (20% per halogen atom).

(C) SONOGASHIRA REACTION

Another palladium catalyzed C-C bond formation process which is able to couple a terminal sp hybridized carbon from an alkyne with a sp^2 carbon of an aryl or vinyl halide (or triflate) is commonly termed as a Sonogashira coupling.



Scheme 10: Sonogashira reaction

Here we have used **1c** as efficient phosphine-free ligands for Sonogashira reaction. We screened a variety of coupling conditions which is shown in **Table 7**.

Table 7: Search for suitable conditions for Sonogashira reaction with ligand **1c**

No	$Pd(OAc)_2$ (mol %)	Ligand (mol%) **1c**	CuI (mol%)	PTC	base	solvent	Temp (^oC)	Time (h)	Yield (%)
1	0.5	0.6	1.0	-	NEt_3	H_2O	80	4	17
2	0.5	0.6	1.0	-	NEt_3	NMP	80	20	23
3	0.5	0.6	1.0	-	NEt_3	DMA	80	20	18
4	0.5	0.6	1.0	-	K_2CO_3	NMP	80	24	49
5	0.5	0.6	-	-	NEt_3	NMP	80	24	18
6	0.5	0.6	-	-	K_2CO_3	NMP	80	24	34
7	0.5	0.6	1.0	-	K_2CO_3	NMP	100	40	18
8	0.5	0.6	1.0	-	K_2CO_3	-	100	40	20
9	0.5	0.6	1.0	-	K_2CO_3	NMP	80	48	37
10	0.5	0.6	0.5	-	K_2CO_3	NMP	80	15	72
11	0.5	0.6	1.0	18-C-6	K_2CO_3	NMP	80	15	51
12	0.5	0.6	1.0	18-C-6	K_2CO_3	NMP	60	24	67
13	0.5	0.6	0.5	18-C-6	K_2CO_3	NMP	60	24	76
14	0.5	0.6	0.5	18-C-6	K_2CO_3	ACN	60	24	73
15	1.0	1.2	-	-	K_2CO_3	ACN	60	24	80

Initially, we employed the CuI co-catalyzed coupling reaction of iodobenzene and phenylacetylene. Various solvents (Such as H_2O, NMP, DMA) were tested at

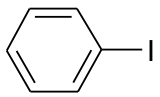
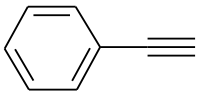
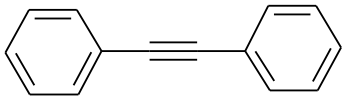
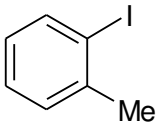
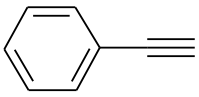
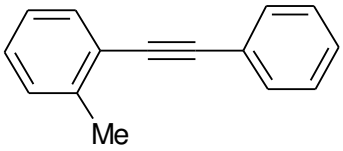
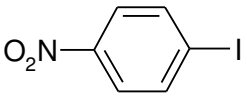
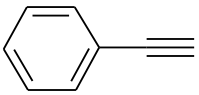
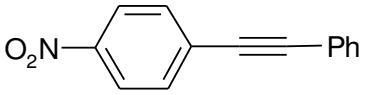
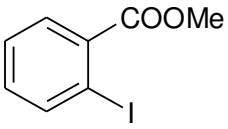
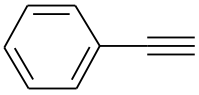
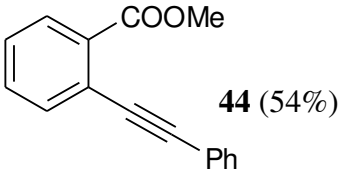
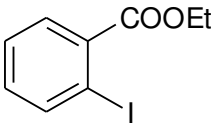
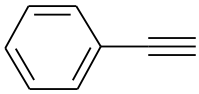
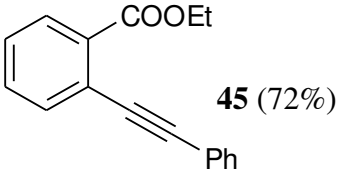
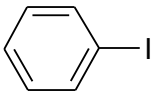
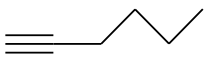
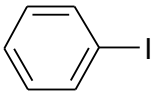
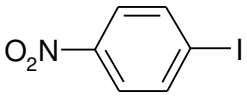
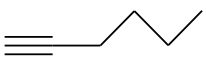
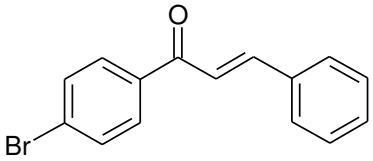
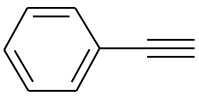
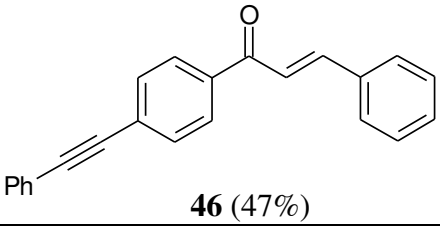
similar conditions but NMP gave better results comparatively. Among the bases used [NEt_3, K_2CO_3], K_2CO_3 was found to be of the best choice. To further increase the yield, we tested the same reaction condition using additive 18-crown-6 which can act as phase transfer catalyst, but we did not see much improvement [Entry 11, Table-7].

Further screening experiments were conducted. To avoid undesirable formation of alkyne homocoupling through copper (Glaser reaction), we eliminated copper salt in the so called "copper-free Sonogashira reaction." The best results were obtained when we increased the amount of catalyst in Cu-free reaction at 60^oC, 24 h in acetonitrile solvent and K_2CO_3 base without any additive, under inert atmosphere of nitrogen gas (Entry 15, Table-7). This is a promising result, since no Cu salt was required.

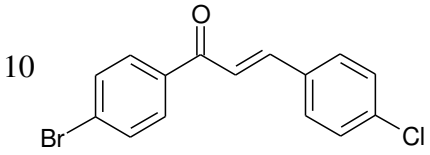
Using our phosphine-free catalyst system, we have synthesized different derivatives of Diphenyl acetylenes, (summarized in **Table 8**) in moderate to good yields. As we expected aryl iodides are more reactive compared to aryl bromide while aryl chlorides are inert. (Entry 1-5, 9, 10, Table-8).

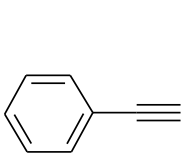
Moreover we found that the Sonogashira coupling reaction between the aryl halides and aliphatic alkynes gave poor results. Therefore, we can conclude that Sonogashira coupling reaction of aromatic alkynes are more favorable than those of aliphatic alkynes.

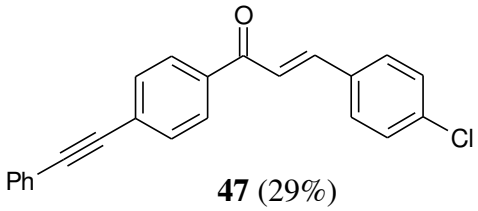
Table 8: Examples of Sonogashira reaction

No	Aryl halide (1 eq)	Alkyne (1.2 eq)	Product (% Yield)
1			 **41** (80%)
2			 **42** (40%)
3			 **43** (72%)
4			 **44** (54%)
5			 **45** (72%)
6			---
7		TMSA	---
8			---
9			 **46** (47%)

10







47 (29%)

All reactions in ACN with Ligand **1c** (1.2 %), $Pd(OAc)_2$ (1.0 %), K_2CO_3(2.0 eq.), 24 h, 60°C.

The derivatives of diphenylacetylenes were purified using column chromatography on silica gel and characterized by ^{1}H-NMR, IR and Mass analysis. In the IR spectra the characteristic band of alkyne derivatives appear at 2215 cm^{-1} due to C≡C stretching. Due to presence of -COOMe and -COOEt group in compound **44** and **45**, this band shifts to higher frequency value i.e., 2275 and 2260$cm.^{-1}$ In the ^{1}H-NMR spectra of compound **46** the two aromatic protons near the -CO- group give the most downfield doublet at δ = 8 ppm (J = 8 Hz). The one of the *trans* olefinic protons appear at 7.8 δ (J = 15.6 Hz), while the second olefinic proton appears to have got merged into the multiplet of the aromatic protons.

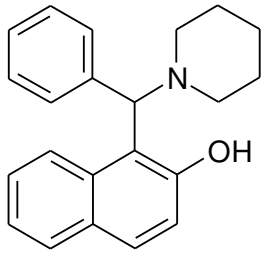
Experimental Section

Reagents were purchased from Sigma-Aldrich Chemicals Limited, S. D. Fine, Sisco, Qualigens Limited etc. DMA was distilled and stored 24 h over molecular sieves (4 Å). Thin layer chromatography was performed on Merck 60 F254 Aluminium coated plates. The spots were visualized under UV light or with iodine vapour. All the compounds were purified by column chromatography using SRL made silica gel (60-120 mesh) unless mentioned otherwise. ^{1}H-NMR Spectra were recorded on Bruker Avance 200 or 400 and Inova-500 Spectrometers and were run in $CDCl_3$ unless otherwise stated. Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument. IR spectra were recorded on a Perkin-Elmer FTIR RXI spectrometer as KBr pallets. Melting points were recorded in Thiele's tube using paraffin oil and are uncorrected.

PART 1: Synthesis of Aminonaphthol Ligands (1a-1f)

General Procedure for Synthesis of Ligand:

Method - A for the preparation of 1-(Phenyl-piperidin-1-yl-methyl)-naphthalen-2-ol (1a):



A solution of β-naphthol (1.0 g, 6.93 mmol) and benzaldehyde (0.74 g, 6.93 mmol) was prepared in absolute alcohol (2 mL). To this solution piperidine (0.59 g, 6.93 mmol) was slowly added and mixture stirred for 48 h at room temperature. The solid was filtered off and washed twice with cold ethyl alcohol (2 x 3 mL). It was recrystallized from a mixture of pet ether and ethyl acetate to get colorless crystals of **1a** (1.02 g, 46 %).

M.P. 195 - 198^{o}C (lit.[12a] 198 - 199^{o}C).

Method - B for the preparation of (1a): Alternatively the above mixture of β-naphthol, benzaldehyde and piperidine (same quantities as A) was stirred at 60 ^{o}C for 24 h under nitrogen atmosphere. The reaction mixture was dispersed at room temperature with ethanol (5 mL). The white solid separated were collected and

washed with cold ethanol (2 x 3 mL). The crystalline white residue was purified by recrystalization from a mixture of pet ether and ethyl acetate to get **1a** (1.37 g, 62 %).

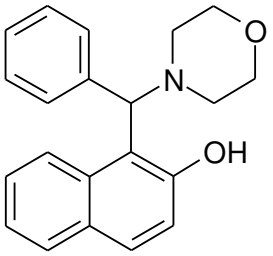
M.P. 196 - 198°C (lit.[12a] 198 - 199°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 13.84 (br s, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.77 - 7.68 (dd, J_1 = 8.08 & J_2 = 0.8 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 6.1 Hz, 2H), 7.38 - 7.17 (m, 6H), 5.10 (s, 1H), 3.34 (br s, 1H), 2.68 (br s, 1H), 2.17 - 1.70 (m, 8H).

IR (KBr): υ 3459, 3065, 2971, 2939, 1599, 1519, 1491, 1238, 1155, 1035, 717 cm^{-1}.

Analytical data for other ligands:.

1- (Morpholin-4-yl-phenyl-methyl)-naphthalen-2-ol (1b):



Ligand **1b** was prepared by procedure (**A**).

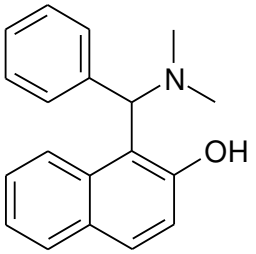
Yield: 46% (1.027 g), White solid.

M.P. 176 - 179°C (lit.[12a] 181 - 183°C).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 13.07 (s, 1H), 7.84 (d, *J* = 8.56 Hz, 1H), 7.71 - 7.66 (m, 2H), 7.58 (d, *J* = 7.64 Hz, 2H), 7.44 - 7.19 (m, 5H), 7.16 (d, *J* = 8.84 Hz, 1H), 5.14 (s, 1H), 3.82 - 3.66 (m, 4H), 3.13 (br s, 1H), 2.45 - 2.30 (m, 3H).

IR (KBr): υ 3465, 3057, 2971, 2841, 1618, 1593, 1515, 1411, 1315, 1238, 1157, 1028, 869, 824, 746 cm^{-1}.

1-(Dimethylamino-phenyl-methyl)-naphthalen-2-ol (1c):



Ligand **1c** was prepared by procedure (**A**).

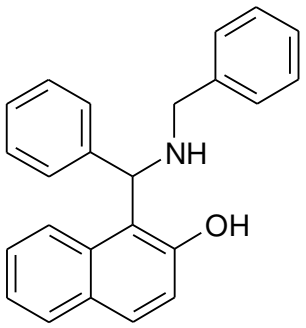
Yield: 71% (1.373 g), Colorless crystals.

M.P. 162 - 164°C (lit.[12b] 164 - 164.5°C).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 13.76 (s, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.70 - 7.68 (d, *J* = 7.95 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.39 - 7.34 (m, 1H), 7.28 - 7.18 (m, 4H), 7.16 - 7.15 (d, *J* = 8.7 Hz, 1H), 4.84 (s, 1H), 2.34 (br s, 6H).

IR (KBr): υ 3270, 3057, 2991, 2953, 2858, 1599, 1517, 1409, 1374, 1351, 1238, 1161, 1033, 870, 704 cm^{-1}.

1-(Benzylamino-phenyl-methyl)-naphthalen-2-ol (1d):



Ligand **1d** was prepared by procedure (**B**).

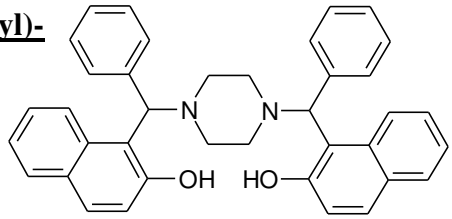
Yield: 30%, (0.7 g), White solid.

M.P. 134 - 136°C (lit.[12c] 136 - 137°C).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 13.26 (br s, 1H), 7.76 - 7.73 (m, 2H), 7.69 - 7.66 (d, *J* = 8.52 Hz, 1H), 7.39 - 7.19 (m, 13H), 5.76 (s, 1H), 4.05 (d, *J* = 12.9 Hz, 1H), 3.83 (d, *J* = 12.9 Hz, 1H).

IR (KBr): υ 3325, 3025, 1619, 1598, 1515, 1413, 1384, 1344, 1270, 1239, 1156, 1073, 1027, 861, 827 cm^{-1}.

<u>Synthesis of N, N'-Bis-[(2-hydroxynaphthalen-1-yl)-phenyl-methyl]piperazine (1e):</u>



Yield: 67% (2.15 g), White solid.

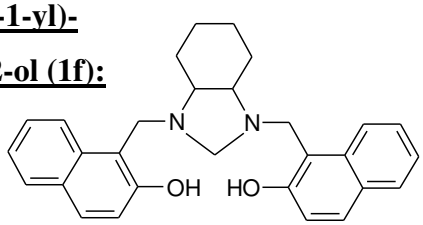
M.P. 242 - 244°C (Lit.[12d] 241 - 242°C).

The mixture of 2-Naphthol (1.76 g, 12.21 mmol), benzaldehyde (1.36 g, 12.25 mmol) and piperazine (0.5 g, 5.8 mmol) was stirred at 95°C for 24 h under nitrogen atmosphere. The reaction mixture was dispersed at room temperature with cold ethanol (10 mL). The white solid was separated, collected and washed with ethanol (2 x 5 mL). The white solid was purified by recrystalization from a mixture of petroleum ether-ethyl acetate to get **1e**.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 13.12 (s, 2H), 7.84 - 7.82 (d, *J* = 8.8 Hz, 2H), 7.72 - 7.67 (two d, J_1 = 8, J_2 = 8.8 Hz, 4H), 7.56 - 7.54 (d, *J* = 7.6 Hz, 4H), 7.42 - 7.37 (m, 2H), 7.27 - 7.2 (m, 8H), 7.15 - 7.13 (d, *J* = 8.8 Hz, 2H), 5.15 (s, 2H), 3.27 (br s, 2H), 2.6 - 2.43 (m, 6H).

IR (KBr): υ 3426, 3057, 2991, 2841, 2122, 1618, 1519, 1411, 1238, 1161, 1035, 870, 746 cm^{-1}.

<u>Synthesis of 1-((Octahydro-1-((2-hydroxynaphthalen-1-yl)-methyl)benzo[d]imidazole-3-yl)methyl)naphthalene-2-ol (1f):</u>



Yield: 73% (1.4 g), Pale yellow solid.

M.P. 178 - 180°C.

In a 50 ml r. b. flask attached with water condenser and guard tube, 1,2-Cyclohexane diamine (0.5 g, 4.4 mmol) and formaldehyde (1.95 ml, 26.3 mmol) were taken in ethanol (10 mL) and stirred for 10-15 mins. To this reaction mixture 2-naphthol (1.26 g, 8.8 mmol) was added and reaction mixture was heated at 60^{o}C for 24 h. The solid product get separated, was filtered, washed with ethanol and then with pet ether. The product was dried under vacuum. The solid was recrystalised in petroleum ether-ethyl acetate.

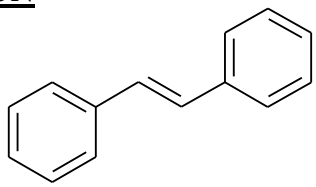
^{1}H-NMR (400 MHz, $CDCl_3$): δ 11.9 (br s, 2H), 7.79 - 7.74 (*d*, J = 8.5 Hz, 2H), 7.71 - 7.64 (d, *J* = 8.16 Hz, 2H), 7.63 - 7.6 (d, *J* = 8.82 Hz, 2H), 7.48 - 7.37 (m, 2H), 7.28 - 7.21 (m, 2H), 7.08 - 7.0 (d, *J* = 8.84 Hz, 2H), 4.44 - 4.17 (two d, *J* = 14 Hz, 4H), 3.66 (s, 2H), 2.55 (m, 2H), 2.25 - 1.2 (m, 8H).

IR (KBr): υ 3432, 2952, 2853, 1620, 1596, 1517, 1466, 1234, 1065, 858 cm^{-1}.

PART-II Application in C-C Bond formation Reaction

(A) MIZOROKI-HECK REACTION

General Procedure for the Heck reaction:



(*E*)- 1, 2-Diphenylethene or trans-Stilbene (4):

Catalyst solution: A solution of palladium acetate (0.055 mg, 0.00024 mmol) and ligand **1a** (0.093 mg, 0.00029 mmol) was made in dry dimethylacetamide (2 mL) under the nitrogen atmosphere. This was sonicated for 2-3 min to degas and to make the solution homogeneous.

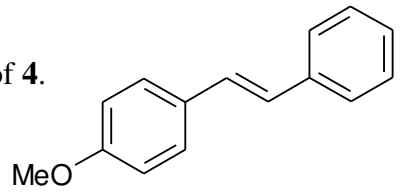
In another two-necked flask, a mixture of iodobenzene (0.5 g, 2.4 mmol), dry potassium carbonate (0.85 g, 6.13 mmol) and dry dimethylacetamide (5 mL) was made and heated under a nitrogen atmosphere. When the temperature attained 60^{o}C, styrene (0.38 g, 3.7 mmol) was slowly introduced by syringe. The mixture was then heated to 100^{o}C and the previously prepared catalyst solution was added. The temperature was further raised to 140^{o}C and continued for another 40h. The reaction mixture was quenched with water, neutralized using aqueous HCl (6 N, 5 mL), and extracted with dichloromethane (3 x 25 mL). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed in vacuum, and the crude product was purified by column chromatography on silica gel to afford trans-stilbene as white solid (0.35 g, 79%).

M.P. 120 - 122°C.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.57 - 7.55 (m, 4H), 7.42 - 7.38 (m, 4H), 7.32 - 7.28 (m, 2H), 7.16 (s, 2H).

MS (EI): (*m/z)* 180 (M^+, 100), 179 (94), 178 (66), 165 (50), 152 (12), 89 (24), 76 (16).

(*E*)-1-Methoxy-4-styrylbenzene (5):



Compound **5** was prepared by same procedure as that of **4**.

Yield: 93% (0.832 g), White solid.

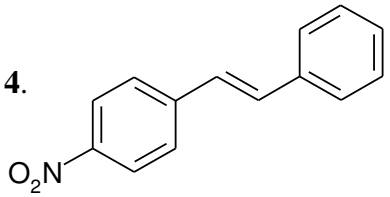
M.P. 130 - 132°C (Lit.[13a] 134 - 135°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.5 - 7.44 (m, 4H), 7.36 - 7.32 (m, 2H), 7.25 - 7.23 (m, 1H), 7.07 (d, *J* = 16.31 Hz, 1H), 6.97 (d, *J* = 16.31 Hz, 1H), 6.91 - 6.89 (m, 2H), 3.83 (s, 3H).

IR (KBr): υ 3002, 2853, 1641, 1511, 1446, 1384, 1296, 1179 cm^{-1}.

MS (EI): (*m/z*) 210 (M^+, 100), 179 (14), 167 (27), 105 (7), 76 (3).

(*E*)-1-Nitro-4-styrylbenzene (6):



Compound **6** was prepared by same procedure as that of **4**.

Yield: 77% (0.858 g), Yellow solid.

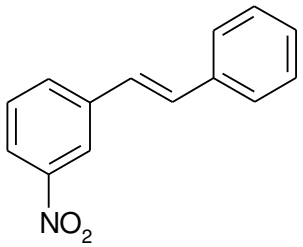
M.P. 146 - 150°C (Lit. [10b] 146 - 149°C).

^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.74 (d, *J* = 9.2 Hz, 1H), 7.9 - 7.6 (m, 2H), 7.6 - 7.58 (m, 2H), 7.42 - 7.36 (m, 2H), 7.33 - 7.31 (m, 2H), 7.28 (d, *J* = 16.3 Hz, 1H), 7.14 (d, *J* = 16.3 Hz, 1H).

IR (KBr): υ 2922, 1590, 1340, 1107, 970, 694 cm^{-1}.

MS (EI): (*m/z*) 225 (M^+, 100), 179(43), 167(9), 89(12), 77(6).

(*E*)-1-Nitro-3-styrylbenzene (7):



Compound **7** was prepared by same procedure as that of **4**.

Yield: 97% (1.08 g), Yellow Solid.

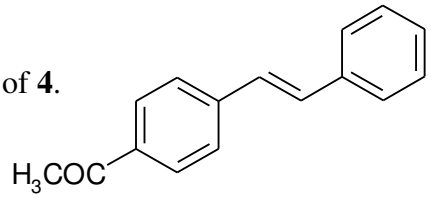
M.P. 108 - 112°C (Lit.[13b] 111 - 112°C).

^{1}H-NMR (DMSO, 400Hz): δ 8.44 (s, 1H), 8.12 - 8.07 (m, 2H), 7.7 - 7.66 (m, 3H), 7.53 - 7.40 (m, 4H), 7.34 - 7.31 (m, 1H).

IR (KBr): υ 2925, 1588, 1355, 1117, 980, 714 cm^{-1}.

MS (EI): (*m/z*) 225 (M^+, 60), 178(100), 152(23), 76(12).

(*E*)-1-Acetoxy-4-styrylbenzene (8):



Compound **8** was prepared by same procedure as that of **4**.

Yield: 75% 0.21 g), White solid.

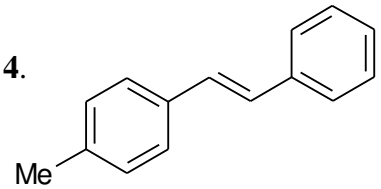
M.P. 138 - 140°C (Lit.[10c] 139 - 140°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.97 - 7.94 (m, 2H), 7.6 - 7.58 (m, 2H), 7.55 - 7.53 (m, 2H), 7.4 - 7.3 (m, 3H), 7.21 - 7.11 (m, 2H), 2.61 (s, 3H).

IR (KBr): υ 2850, 1675, 1595, 1410, 1355, 1268, 1170, 1075, 966, 868, 825, 756, 720, 692, 594 cm^{-1}.

MS (EI): (*m/z*) 222 (M^+, 90), 207 (100), 178 (55), 152 (20), 102 (8), 96 (5), 89 (20), 76 (10), 63 (7).

(*E*)-1-Methyl-4-styrylbenzene (9):



Compound **9** was prepared by same procedure as that of **4**.

Yield: 89% (0.426 g), White solid.

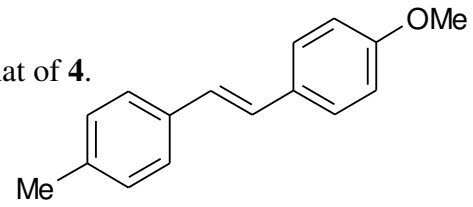
M.P. 114 - 116°C (Lit.[13a] 114 - 116°C).

^{1}H-NMR ($CDCl_3$, 400MHz): δ 7.54 - 7.52 (m, 2H), 7.44 (d, *J* = 8 Hz, 2H), 7.4 - 7.36 (m, 2H), 7.29 - 7.25 (m, 1H), 7.2 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 16.2 Hz, 1H), 7.08 (d, *J* = 16.2 Hz, 1H), 2.38 (s, 3H).

IR (KBr): υ 2925, 1588, 1355, 1117, 980, 714 cm^{-1}.

MS (EI): (*m/z*) 195 (M^+, 93.5), 179 (100), 89 (11), 76 (5).

(*E*)-1-Methoxy-4-(4-methylstyryl)benzene (10):



Compound **10** was prepared by same procedure as that of **4**.

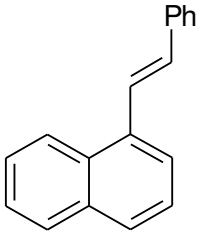
Yield: 96% (0.23 g), White solid.

M.P. 166 - 168°C (Lit.[13a] 162°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.45 - 7.42 (m, 2H), 7.38 (d, *J* = 8 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 16.2 Hz, 2H), 6.94 (d, *J* = 16.2 Hz, 1H), 6.9 - 6.88 (m, 2H), 3.82 (s, 3H), 2.35 (s, 3H).

IR (KBr): υ 3014, 2913, 2840, 1605, 1510, 1250, 1172, 1037, 967, 825 cm^{-1}.

1-((*E*)-Styryl)-naphthalene (11):



Compound **11** was prepared by same procedure as that of **4**.

Yield: 91% (0.178 g), White solid.

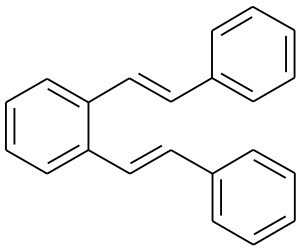
M.P. 62 - 64°C (Lit.[13c] 68 - 72°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.23 - 8.21 (m, 1H), 7.9 - 7.86 (m, 2H), 7.81 - 7.79 (d, *J* = 8.4 Hz, 1H), 7.75 - 7.74 (d, *J* = 7.2 Hz, 1H), 7.62 - 7.59 (m, 2H), 7.56 - 7.47 (m, 3H), 7.42 - 7.38 (m, 2H), 7.32 - 7.28 (m, 1H), 7.17 - 7.13 (d, *J* = 16 Hz, 1H).

IR (KBr): υ 3024, 1595, 1480, 1378, 1350, 1141, 1075, 1012, 969, 956, 794, 773, 756, 690 cm^{-1}.

MS (EI): (*m/z*) 230 (M^+, 100), 229 (40), 189 (35), 176 (50), 152 (30), 128 (15), 115 (25), 101 (30), 91 (5), 77 (10).

1,2-Di ((*E*)-styryl)benzene (12):



Compound **12** was prepared by same procedure as that of **4**.

Yield: 94% (0.564 g), White Solid.

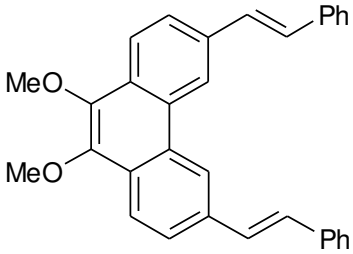
M.P. 108 - 110°C (Lit.[10d] 111 - 112°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.6 - 7.58 (m, 2H), 7.54 - 7.51 (m, 4H), 7.46 (d, *J* = 16.4 Hz, 2H), 7.38 - 7.34 (m, 4H), 7.3 - 7.24 (m, 4H), 7.0 (d, *J* = 16.4 Hz, 2H).

IR (KBr): υ 3086, 3053, 3019, 1600, 1491, 1213, 1158, 1071, 956, 758, 691 cm^{-1}.

MS (EI): (*m/z*) 223 (M+1, 8.9), 282 (M^+, 38), 191 (100), 178 (6), 91 (12).

9, 10-Dimethoxy-3,6-di((*E*)styryl)-phenanthrene (13):



Compound **13** was prepared by same procedure as that of **4**.

Yield: 93% (1.038 g), White solid.

M.P. 116 - 120°C.

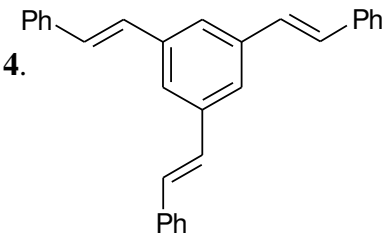
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.714 - 8.711 (d, *J* = 1.2 Hz, 2H), 8.23 - 8.21 (d, *J* = 8.4 Hz, 2H), 7.89 - 7.87 (dd, J_1 = 8.8, J_2 = 1.6 Hz, 2H), 7.64 - 7.62 (m, 4H), 7.44 - 7.28 (m, 10H, overlapping the *trans* coupling proton signals, d, *J* = 16.4 Hz), 4.11 (s, 6H).

^{13}C-NMR ($CDCl_3$, 50 MHz): δ 144.79, 138.04, 135.49, 129.43, 128.37, 127.25, 125.17, 123.29, 122.25, 61.69.

IR (KBr): υ 3438, 3024, 2931, 2835, 1602, 1503, 1446, 1419, 1364, 1327, 1243, 1202, 1121, 1062, 986, 954, 816, 751 cm^{-1}.

MS (EI): (*m/z*) 443 (M+1, 33), 442 (M^+,100), 428 (13), 427 (41), 399 (23), 221 (53), 213 (10), 192 (10), 191 (14), 184 (15), 183 (13), 182 (18), 177 (23), 176 (34), 175 (12), 169 (32), 163 (11).

1,3,5-tri ((*E*)-styryl)benzene (14):



Compound **14** was prepared by same procedure as that of **4**.

Yield: 95% (0.582 g), White solid.

M.P. 196 - 200°C (Lit.[10a] 200 - 202°C).

^{1}H-NMR ($CDCl_3$, MHz): δ 7.57 - 7.55 (m, 9H), 7.4 - 7.36 (m, 6H), 7.3 - 7.26 (m, 3H), 7.21 (d, *J* = 16.4 Hz, 3H), 7.15 (d, *J* = 16.4 Hz, 3H).

IR (KBr): υ 3025, 1595, 1494, 1263, 1073, 956, 883, 750 cm^{-1}.

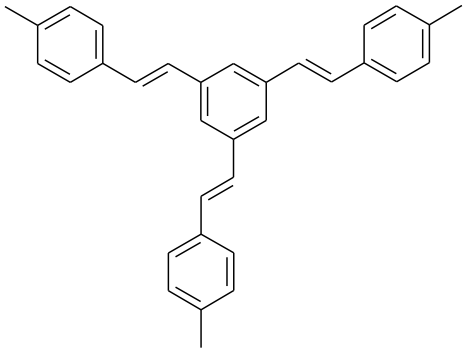
MS (EI): (*m/z*) 384 (M^+, 100), 278 (12), 227 (10), 202 (14), 153 (14), 103 (12), 91 (20), 77 (10).

1,3,5-tri ((*E*)-4-methylstyryl)benzene (15):

Compound **15** was prepared by same procedure as that of **4**.

Yield: 87% (0.586 g), White solid.

M.P. 216 - 220°C (Lit.[13d] 213 - 217°C).



^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.53 - 7.52 (m, 3H), 7.46 - 7.44 (d, *J* = 8 Hz, 6H), 7.2 - 7.07 (m, 12H), 2.38 (s, 9H).

IR (KBr): υ 3081, 3022, 1897, 1631, 1584, 1448, 1328, 1298, 1039, 958, 885, 708 cm^{-1}.

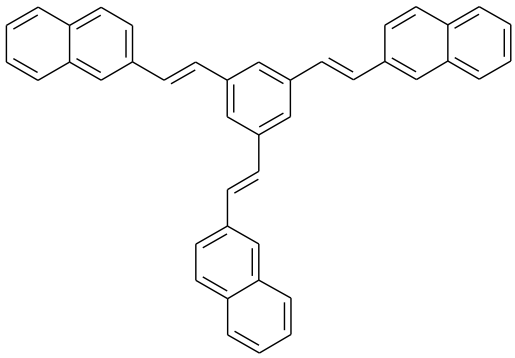
MS (EI): (*m/z*) 427 (M+1, 30), 426 (M^+, 100), 306 (10), 227 (12), 152 (16), 105 (32), 91 (12).

1,3,5-tri ((*E*)-2'-naphthylstyryl)benzene (16):

Compound **16** was prepared by same procedure as that of **4**.

Yield: 69% (0.26 g), Yellow solid.

M.P. 260 - 264°C (Lit.[13e] 266 - 267°C).



^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.93 - 7.79 (m, 15H), 7.68 (s, 3H), 7.51 - 7.47 (m, 6H), 7.44 - 7.4 (d, *J* = 16 Hz, 3H), 7.34 - 7.3 (d, *J* = 16 Hz, 3H).

IR (KBr): υ 3023, 1623, 1588, 1426, 1270, 1016, 957, 889, 744 cm^{-1}.

MS (EI): (*m/z*) 534 (M^+, 20), 281 (12), 252 (10), 207 (100), 191 (26), 111 (32), 97 (70), 83 (98).

(B) SUZUKI-MIYAURA REACTION

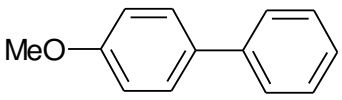
Typical experimental procedure for the Suzuki reaction under conventional conditions (in thermal condition):

4-methoxybiphenyl (19):

To an oven dried two-necked round-bottom flask equipped with a stir bar was charged 4-iodoanisole (0.25 g, 1.07 mmol), potassium carbonate (0.29 g, 2.14 mmol), palladium acetate (0.24 mg, 0.001 mmol) and **1c** (0.36 mg, 0.0013 mmol) in dioxane - water (1:1, 6 mL). To this reaction mixture phenylboronic acid (0.16 g, 1.28 mmol) was added. The reaction was heated at 95°C for 4 h. Following confirmation of consumption of starting material by TLC, the reaction mixture was quenched with water, and extracted with ethyl acetate (3 x 25 mL). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford 4-methoxybiphenyl **19** (0.194 g, 98 %) (Table 5, entry 1).

Yield: 98%, White solid.

M.P. 86 - 88°C (Lit.[14a] 83 - 84°C).



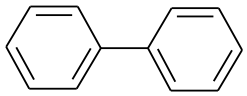
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.59 - 7.54 (m, 4H), 7.46 - 7.42 (m, 2H), 7.35 - 7.32 (m, 1H), 7.03 - 6.99 (m, 2H), 3.88 (s, 3H).

IR (KBr): υ 3059, 2999, 2960, 2834, 1887, 1647, 1604, 1521, 1484, 1285, 1248, 1198, 1118, 1036, 832, 759, 687, 570 cm^{-1}.

MS (EI): (*m/z*) 184 (M^+, 46), 169 (30), 129 (41), 97 (57), 81 (61), 69 (100), 57 (81).

Biphenyl (18):

Compound **18** was prepared by same procedure as that of **19**.



Yield: 96% (0.182 g), White solid.

M.P. 66 - 68°C (Lit.[14b] 68 - 70°C).

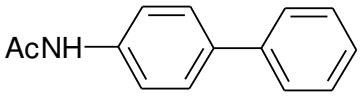
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.64 - 7.62 (m, 4H), 7.5 - 7.46 (m, 4H), 7.4 - 7.36 (m, 2H).

IR (KBr): υ 3032, 1946, 1568, 1475, 1427, 902, 729, 694 cm^{-1}.

MS (EI): (*m/z*) 154 (M^+, 100), 153 (42), 149 (74), 85 (40), 71 (50).

N-Biphenyl-4-yl-acetamide (20):

Compound **20** was prepared by same procedure as that of **19**.



Yield: 98% (0.2 g), White solid.

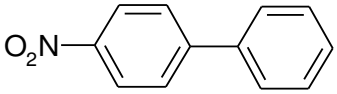
M.P. 172 - 174°C (Lit.[14a] 168 - 170°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.61 - 7.56 (m, 6H), 7.47 - 7.43 (m, 2H), 7.37 - 7.35 (m, 1H), 2.23 (s, 3H).

MS (EI): (*m/z*) 211 (M^+, 25), 170 (10), 169 (65), 141 (5), 115 (5), 43 (10), 32 (25), 28 (100), 18 (70).

4-Nitrobiphenyl (21):

Compound **21** was prepared by same procedure as that of **19**.



Yield: 89% (0.22 g), Yellow solid.

M.P. 110 - 114°C (Lit.[14b] 113 - 115°C).

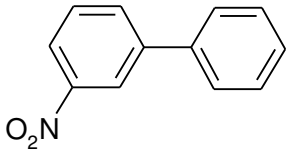
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.34 - 8.31 (m, 2H), 7.78 - 7.75 (m, 2H), 7.66 - 7.64 (m, 2H), 7.55 - 7.49 (m, 3H).

IR (KBr): υ 3074, 2926, 1926, 1596, 1513, 1478, 1448, 1398, 1345, 926, 853, 774, 740, 696 cm^{-1}.

MS (EI): (*m/z*) 199 (M^+, 100), 167 (20), 153 (63), 152 (96), 145 (57), 97 (31), 71 (35).

3-Nitrobiphenyl (22):

Compound **22** was prepared by same procedure as that of **19**.



Yield: 81% (0.2 g), Yellow solid.

M.P. 60 - 62°C (Lit.[14b] 59 - 60°C).

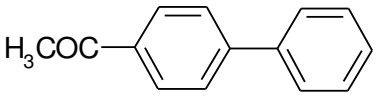
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.49 - 8.48 (t, 1H), 8.24 - 8.21 (m, 1H), 7.96 - 7.93 (m, 1H), 7.67 - 7.62 (m, 3H), 7.55 - 7.44 (m, 3H).

IR (KBr): υ 3081, 2860, 1974, 1620, 1578, 1526, 1344, 872, 812, 766, 689 cm^{-1}.

MS (EI): (*m/z*) 199 (M^+, 100), 169 (39), 153 (29), 152 (96), 141 (28), 77 (7).

4-Acetoxybiphenyl (23):

Compound **23** was prepared by same procedure as that of **19**.



Yield: 90% (0.222 g), Pale yellow solid.

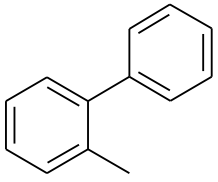
M.P. 114 - 116°C (Lit.[14a] 117 - 119°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.08 - 8.04 (dt, J_1 = 8.4, J_2 = 2 Hz, 2H), 7.73 - 7.7 (dt, J_1 = 8.4, J_2 = 1.6 Hz, 2H), 7.67 - 7.64 (m, 2H), 7.52 - 7.48 (m, 2H), 7.45 - 7.41 (tt, J_1 = 7.6, J_2 = 1.2 Hz, 1H), 2.67 (s, 3H).

IR (KBr): υ 2924, 2855, 1679, 1601, 1484, 1361, 1264, 1181, 1083, 960, 838, 765, 721, 688 cm^{-1}.

MS (EI): (*m/z*) 196 (M^+, 8), 184 (10), 167 (36), 149 (100), 83 (82), 77 (20).

2-Methylbiphenyl (24):[15a]



Compound **24** was prepared by same procedure as that of **19**.

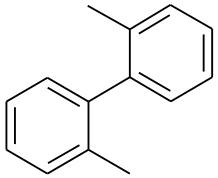
Yield: 94% (0.364 g), Colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.43 - 7.39 (m, 2H), 7.36 - 7.31 (m, 3H), 7.27 - 7.22 (m, 4H), 2.27 (s, 3H).

IR (KBr): υ 3059, 3021, 2953, 2924, 2865, 1599, 1479, 1440, 1381, 1267, 1157, 1119, 1073, 1051, 1034, 1009, 942, 915, 866, 772, 748, 726, 702, 619, 562 cm^{-1}.

MS (EI): (*m/z*) 168 (M^+, 53), 167 (100), 165 (40), 153 (18), 152 (16).

2, 2'-Dimethyl-biphenyl (25):[15b]



Compound **25** was prepared by same procedure as that of **19**.

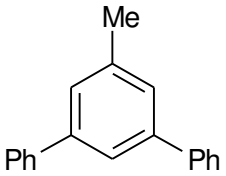
Yield: 96% (0.16 g), Colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.33 - 7.26 (m, 6H), 7.17 - 7.15 (m, 2H), 2.11 (s, 3H).

IR (KBr): υ 3441, 2919, 2853, 1629, 1572, 1465, 1384, 1112, 753, 732, 664 cm^{-1}.

MS (EI): (*m/z*) 183 (M+1, 15), 182 (M^+, 65), 181 (13), 168 (13), 167 (91), 166 (17), 165 (33), 152 (13), 115 (5), 91 (5).

5'-Methyl-[1,1',3',1'']terphenyl (26):



Compound **26** was prepared by same procedure as that of **19**.

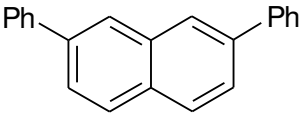
Yield: 51% (0.1 g), White solid.

M.P. 130 - 132°C (Lit.[16a] 135 - 138°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.65 - 7.61 (m, 5H), 7.47 - 7.43 (m, 4H), 7.4 - 7.34 (m, 4H), 2.48 (s, 3H).

MS (EI): (*m/z*) 251 (M+1, 82), 250 (M^+, 53), 249 (51), 171 (100), 169 (40), 168 (65), 90 (45), 89 (48).

2,7-Diphenyl-naphthalene (27):



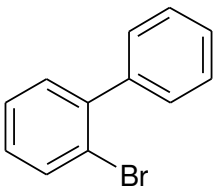
Compound **27** was prepared by same procedure as that of **19**.

Yield: 77% (0.15 g), White solid.

M.P. 142 - 146°C (Lit.[16b] 142°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.13 (s, 2H), 7.98 - 7.96 (m, 2H), 7.8 - 7.77 (m, 6H), 7.55 - 7.51 (t, *J* = 15.2 Hz, 4H), 7.44 - 7.4 (t, *J* = 14.4 Hz, 2H).

2-Bromo-biphenyl (28a):[15a]



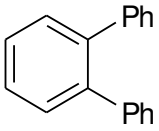
Compound **28a** was prepared by same procedure as that of **19**.

Yield: 24% (0.06 g), Colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.72 - 7.69 (d, *J* = 7.2 Hz, 1H), 7.4 - 7.36 (m, 4H), 7.33 (t, *J* = 7 Hz, 1H), 7.26 - 7.22 (m, 2H), 7.16 - 7.12 (m, 1H).

MS (EI): (*m/z*) 234 (M+1, 90), 233 (M^+, 15), 232 (95), 153 (45), 152 (100), 77 (10), 76 (35).

[1,1',2',1'']Terphenyl (28b):



Compound **28b** was prepared by same procedure as that of **19**.

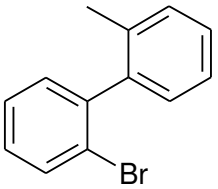
Yield: 68% (0.167 g), White solid.

M.P. 60 - 62°C (Lit.[17a] 58 - 60°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.48 - 7.43 (m, 4H), 7.26 - 7.22 (m, 6H), 7.2 - 7.16 (m, 4H).

MS (EI): (*m/z*) 230 (M^+, 100), 229 (60), 215 (40), 114 (35), 101 (30), 77 (5).

2-Bromo-2'-methyl-biphenyl (29a):[17b]

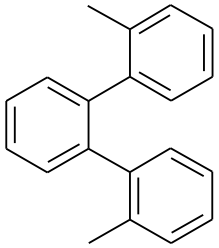


Compound **29a** was prepared by same procedure as that of **19**.

Yield: 24% (0.052 g), Colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.64 - 7.59 (m, 1H), 7.32 - 7.12 (m, 6H), 7.08 (d, *J* = 7.6 Hz, 1H), 2.09 (s, 3H).

2,2''-Dimethyl-[1,1',2',1'']terphenyl (29b):



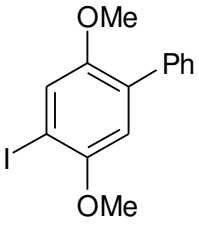
Compound **29b** was prepared by same procedure as that of **19**.

Yield: 74% (0.0162 g), Colorless oil (Lit.[18] 39 - 41°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.4 - 7.37 (m, 2H), 7.32 (br s, 2H), 7.07 - 6.95 (m, 7H), 6.87 - 6.8 (m, 1H), 2.14 - 2.05 (two s, 6H).

MS (EI): (*m/z*) 259 (M+1, 54), 258 (M^+, 100), 244 (10), 243 (98), 229 (25), 228 (72), 215 (30), 178 (20), 165 (24).

4-Iodo,2,5-dimthoxy-biphenyl (30a):



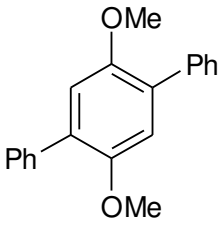
Compound **30a** was prepared by same procedure as that of **19**.

Yield: 10% (0.02g), Colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.54 - 7.52 (m, 2H), 7.46 - 7.44 (m, 2H), 7.39 (s, 1H), 7.38 - 7.36 (m, 1H), 6.79 (s, 1H), 3.89 (s, 3H), 3.78 (s, 3H).

MS (EI): (*m/z*) 342 (M+1, 18), 340 (M^+, 60), 326 (22), 254 (8), 242 (20), 214 (50).

2',5'-Dimthoxy-[1,1',4',1'']terphenyl (30b):



Compound **30b** was prepared by same procedure as that of **19**.

Yield: 71% (0.132 g), White solid.

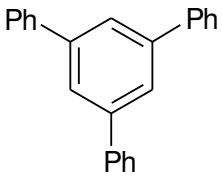
M.P. 144 - 146°C (Lit.[19] 147 - 149°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.67 - 7.65 (d, *J* = 7.2 Hz, 4H), 7.52 - 7.48 (t, *J* = 15.2 Hz, 4H), 7.43 - 7.39 (t, *J* = 14.8 Hz, 2H), 7.04 (s, 2H), 3.84 (s, 6H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 150.65, 138.36, 130.42, 129.52, 128.17, 127.19, 114.78, 56.46.

MS (EI): (*m/z*) 291 (M+1, 100), 290 (M^+, 54), 276 (10).

1,3,5-Triphenylbenzene (31):



Compound **31** was prepared by same procedure as that of **19**.

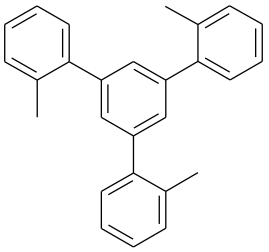
Yield: 89% (0.086 g), White solid.

M.P. 166 - 168°C (Lit.[20a] 172°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.82 - 7.81 (d, *J* = 0.8 Hz, 3H), 7.74 - 7.72 (m, 6H), 7.54 - 7.5 (t, *J* = 15.2 Hz, 6H), 7.44 - 7.4 (m, 3H).

MS (EI): (*m/z*) 307 (M+1, 24), 306 (M^+, 100), 289 (11), 228 (8), 153 (7).

1,3,5-Tris(2-methylphenyl)benzene (32):



Compound **32** was prepared by same procedure as that of **19**.

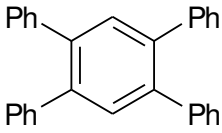
Yield: 86% (0.095 g), White solid.

M.P. 134 - 136°C (Lit.[20b] 138 - 140°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.37 - 7.34 (m, 3H), 7.32 - 7.26 (m, 12H), 2.4 (s, 3H).

IR (KBr): υ 3024, 2919, 2855, 1629, 1573, 1491, 1423, 1218, 932, 753, 732, 664 cm^{-1}.

1,2,4,5-Tetraphenylbenzene (33):



Compound **33** was prepared by same procedure as that of **19**.

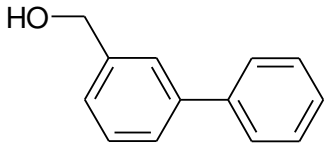
Yield: 90% (0.087 g), White solid.

M.P. 260 - 262°C (Lit.[21] 267 - 268°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.56 (s, 2H), 7.28 - 7.24 (m, 20H).

MS (EI): (*m/z*) 383 (M+1, 30), 382 (M^+, 100), 302 (13), 289 (14), 183 (16).

General Procedure for the Suzuki reaction under sonochemical conditions (in ultrasonication):



3-(hydroxymethyl)biphenyl (38):

To the mixture of iodobenzene (0.05 mL, 0.45 mmol), palladium acetate (0.5 mg, 0.002 mmol), **1c** (0.74 mg, 0.002 mmol), potassium carbonate (0.18 mg, 1.34 mmol) in dioxane - water (1:1, 4 mL) was added 3-(hydroxymethyl)phenyl boronic acid (0.082 g, 0.54 mmol). The reaction mixture was then sonicated for the time as mentioned in Table 3. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched with water, and extracted with ethyl acetate (3 x 25 mL). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford 3-(hydroxymethyl)biphenyl **38** (0.078 g, 95%) (Table 6, entry 12).

Yield: 95%, Pale yellow solid.

M.P. 50 - 52^{o}C (Lit.[22a] 51^{o}C).

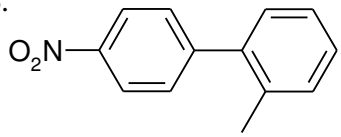
^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.64 - 7.62 (m, 3H), 7.57 - 7.55 (m, 1H), 7.5 - 7.45 (m, 3H), 7.41 - 7.36 (m, 2H), 4.78 (s, 2H), 2.17 (br s, 1H).

IR (KBr): υ 3300 - 3100 (b), 2860, 1954, 1894, 1597, 1573, 1478, 1452, 1417, 1323, 1184, 1122, 1067, 1029, 893, 800, 756, 698, 613 cm^{-1}.

MS (EI): (*m/z*) 185 (M+1, 14), 184 (M^{+}, 100), 183 (23), 167 (9), 166 (16), 165 (30), 155 (49), 152 (25), 77 (7).

2-Methyl-4'-nitro-biphenyl (34):[22b]

Compound **34** was prepared by same procedure as that of **38**.



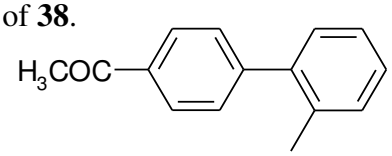
Yield: 90% (0.095 g), Yellow solid.

M.P. 66 - 68^{o}C.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ 8.32 - 8.29 (m, 2H), 7.54 - 7.5 (td, J_1 = 9.2, J_2 = 2 Hz, 2H), 7.38 - 7.29 (m, 2H), 7.25 - 7.23 (d, J = 8 Hz, 1H), 2.3 (s, 3H).

1-(2'-Methyl-biphenyl-4-yl)-ethanone (35):[22b]

Compound **35** was prepared by same procedure as that of **38**.



Yield: 94% (0.199 g), Pale yellow solid.

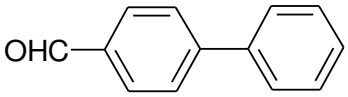
M.P. 90 - 92°C.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.06 - 8.02 (m, 2H), 7.47 - 7.44 (m, 2H), 7.33 - 7.24 (m, 4H), 2.68 (s, 3H), 2.3 (s, 3H).

IR (KBr): υ 3345, 3064, 2929, 2855, 1684, 1610, 1573, 1491, 1423, 1265, 932, 753, 732, 664 cm^{-1}.

2'Methyl-biphenyl-4-carbaldehyde (36):

Compound **36** was prepared by same procedure as that of **38**.



Yield: 89% (0.176 g), Pale yellow soild.

M.P. 58 - 60°C (Lit.[17a] 55 - 57°C).

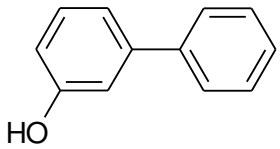
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 10.08 (s, 1H), 7.99 - 7.97 (m, 2H), 7.79 - 7.77 (m, 2H), 7.68 - 7.65 (m, 2H), 7.53 - 7.49 (m, 2H), 7.47 - 7.43 (tt, J_1 = 7.2, J_2 = 1.2 Hz, 1H).

IR (KBr): υ 3059, 3032, 2924, 2828, 2735, 1700, 1604, 1565, 1515, 1485, 1450, 1412, 1384, 1308, 1281, 1214, 1170, 1076, 1007, 917, 838, 762, 729, 697, 646, 629, 547 cm^{-1}.

MS (EI): (*m/z*) 183 (M+1, 18), 182 (M^+, 59), 181 (65), 180 (53), 153 (51), 152 (100), 150 (26), 77 (13), 76 (36).

Biphenyl-3-ol (37):

Compound **37** was prepared by same procedure as that of **38**.



Yield: 92% (0.07 g), Pale yellow solid.

M.P. 54 - 56°C (Lit.[23a] 56 - 57°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.61 - 7.59 (m, 2H), 7.48 - 7.44 (m, 2H), 7.4 - 7.32 (m, 2H), 7.21 - 7.18 (m, 1H), 7.1 - 7.09 (m, 1H), 6.86 - 6.83 (two dd, J_1 = 2.4, J_2 = 1.2 Hz, 1H), 4.9 (s, 1H).

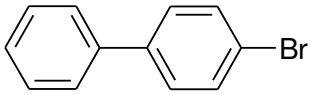
IR (KBr): υ 3502, 3414, 3035, 1596, 1483, 1426, 1300, 1166, 1084, 1026, 993, 913, 882, 856, 791, 756, 718, 696, 613 cm^{-1}.

MS (EI): (*m/z*) 170 (M^+, 53), 169 (100), 141 (23), 115 (27).

4-Bromo-biphenyl (39a):

Compound **39a** was prepared by same procedure as that of **38**.

Yield: 27% (0.026 g), White solid.



M.P. 84 - 86°C (Lit.[23b] 88 - 90°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.62 - 7.56 (m, 4H), 7.5 - 7.45 (m, 4H), 7.41 - 7.36 (m, 1H).

MS (EI): (*m/z*) 234 (M+1, 98), 233 (M^+, 15), 232 (100), 152 (70), 126 (10), 76 (25).

[1,1',4',1'']Terphenyl (39b):

Compound **39b** was prepared by same procedure as that of **38**.

Yield: 52% (0.051 g), White solid.

M.P. 208 - 210°C (Lit.[14b] 212°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.71 (s, 4H), 7.69 - 7.66 (m, 4H), 7.51 - 7.47 (m, 4H), 7.41 - 7.37 (tt, J_1 = 7.2, J_2 = 1.2 Hz, 2H).

MS (EI): (*m/z*) 230 (M^+, 100), 229 (11), 228 (12), 202 (5), 152 (6), 115 (9), 101 (4), 76 (2).

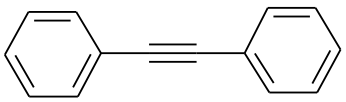
(C) SONOGASHIRA REACTION

General procedure for Sonogashira coupling Reaction :

Diphenylactylene (41):

In a two-neck 50ml r. b. flask with a magnetic stir bar and reflux condenser attached to a nitrogen balloon, iodobenzene (0.25 g, 1.22 mmol), K_2CO_3 (0.34 g, 2.45 mmol), $Pd(OAc)_2$ (1.38 mg, 0.74 mmol) and ligand **1c** (2.47 mg, 0.89 mmol) in acetonitrile (10 mL) were taken. The reaction mixture was purged with nitrogen gas. To this reaction mixture phenyl acetylene (0.11 g, 1.05 mmol) was added under nitrogen atmosphere and reaction was heated at 60°C for 24h. After 24h the reaction mixture was quenched with water and extracted with ethyl acetate (2 x 50mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether as an eluent to yield the pure product.

Yield: 80% (0.174 g), White solid.



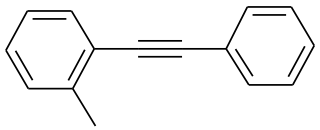
M.P. 72°C (Lit.[24a] 60 - 61°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.63 - 7.54 (m, 4H), 7.44 - 7.36 (m, 6H).

IR (KBr): υ 3056, 2213, 1596, 1490, 1438, 912, 752, 684 cm^{-1}.

MS (EI): (*m/z*) 178 (M^+, 84), 149 (26), 85 (57), 71 (54), 69 (75), 57 (99), 55 (57), 43 (100), 41 (52).

1-Methyl-2-phenylethynyl-benzene (42):[24b]



Compound **42** was prepared by same procedure as that of **41**.

Yield: 40% (0.109 g), Colourless oil.

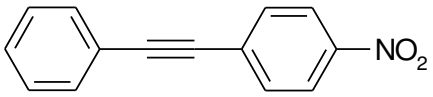
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.59 - 7.51 (m, 3H), 7.41 - 7.36 (m, 3H), 7.27 - 7.19 (m, 3H), 2.55 (s, 3H).

IR (KBr): υ 3045, 2215, 1594, 1495, 1375, 915, 860, 768 cm^{-1}.

MS (EI): (*m/z*) 193 (14), 192 (100), 189 (40), 165 (30), 95 (18).

1-Nitro-4-phenylethynyl-benzene (43):

Compound **43** was prepared by same procedure as that of **41**.



Yield: 72% (0.12 g), Yellow solid.

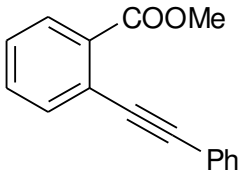
M.P. 125°C (Lit.[24a] 120 - 122°C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.26 - 8.23 (m, 2H), 7.7 - 7.67 (m, 2H), 7.6 - 7.57 (m, 2H), 7.44 - 7.39 (m, 3H).

IR (KBr): υ 3103, 2213, 1967, 1591, 1510, 1345, 1104, 921, 857, 764 cm^{-1}.

MS (EI): (*m/z*) 224 (M+1, 14), 223 (M^+, 100), 193 (28), 176 (54), 165 (20), 151 (16).

2-Phenylethynyl-benzoic acid methyl ester (44):[25]



Compound **44** was prepared by same procedure as that of **41**.

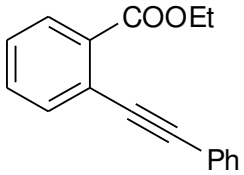
Yield: 54% (0.092 g), Colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.01 - 7.99 (m, 1H), 7.69 - 7.66 (m, 1H), 7.62 - 7.59 (m, 2H), 7.54 - 7.5 (m, 1H), 7.43 - 7.37 (m, 4H), 3.99 (s, 3H).

IR (KBr): υ 3061, 2950, 2275, 1725, 1597, 1567, 1494, 1440, 1292, 1255, 1129, 1078, 963, 757, 694 cm^{-1}.

MS (EI): (*m/z*) 236 (M^+, 99), 235 (52), 221 (100), 193 (32), 176 (41), 175 (43), 165 (77), 150 (39).

2-Phenylethynyl-benzoic acid ethyl ester (45):



Compound **45** was prepared by same procedure as that of **41**.

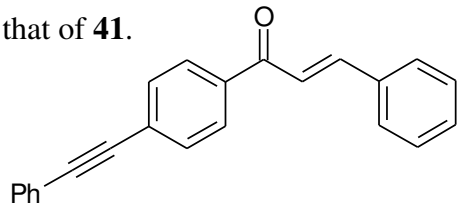
Yield: 72% (0.13 g), Colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.01 - 7.99 (m, 1H), 7.68 - 7.59 (m, 4H), 7.53 - 7.22 (m, 4H), 4.47 - 4.42 (q, *J* = 7.2 Hz, 2H), 1.44 - 1.4 (t, 3H).

IR (KBr): υ 3061, 2982, 2260, 2149, 1723, 1597, 1568, 1494, 1444, 1389, 1366, 1290, 1250, 1130, 1076, 1040, 1019, 858, 757, 693 cm^{-1}.

MS (EI): (*m/z*) 250 (80), 222 (76), 221 (82), 193 (25), 176 (63), 175 (27), 165 (100), 149 (19).

(*E*)-3-Phenyl-1-(4-phenylethynyl-phenyl)-propenone (46):



Compound **46** was prepared by same procedure as that of **41**.

Yield: 47% (0.05 g), Pale yellow solid.

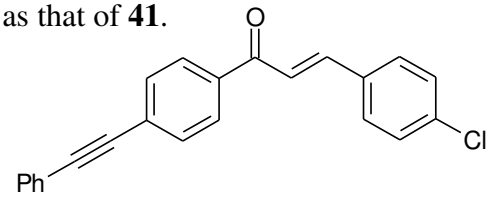
M.P. 128°C.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.06 - 8.04 (d, *J* = 8 Hz, 2H), 7.88 - 7.84 (d, *J* = 15.6 Hz, 1H), 7.69 - 7.67 (m, 4H), 7.6 - 7.55 (m, 3H), 7.46 - 7.44 (m, 3H), 7.41 - 7.39 (m, 3H).

IR (KBr): υ 3053, 2216, 1657, 1598, 1485, 1445, 1336, 1215, 1010, 988, 835, 767, 754, 688 cm^{-1}.

MS (EI): (*m/z*) 309 (M+1, 50), 308 (M^+, 63), 307 (57), 306 (80), 279 (39), 278 (31), 205 (55), 176 (100), 153 (58), 150 (27), 131 (26), 103 (42), 77 (23).

(E)-3-(4-Chloro-phenyl)-1-(4-phenylethynyl-phenyl)-propenone (47):



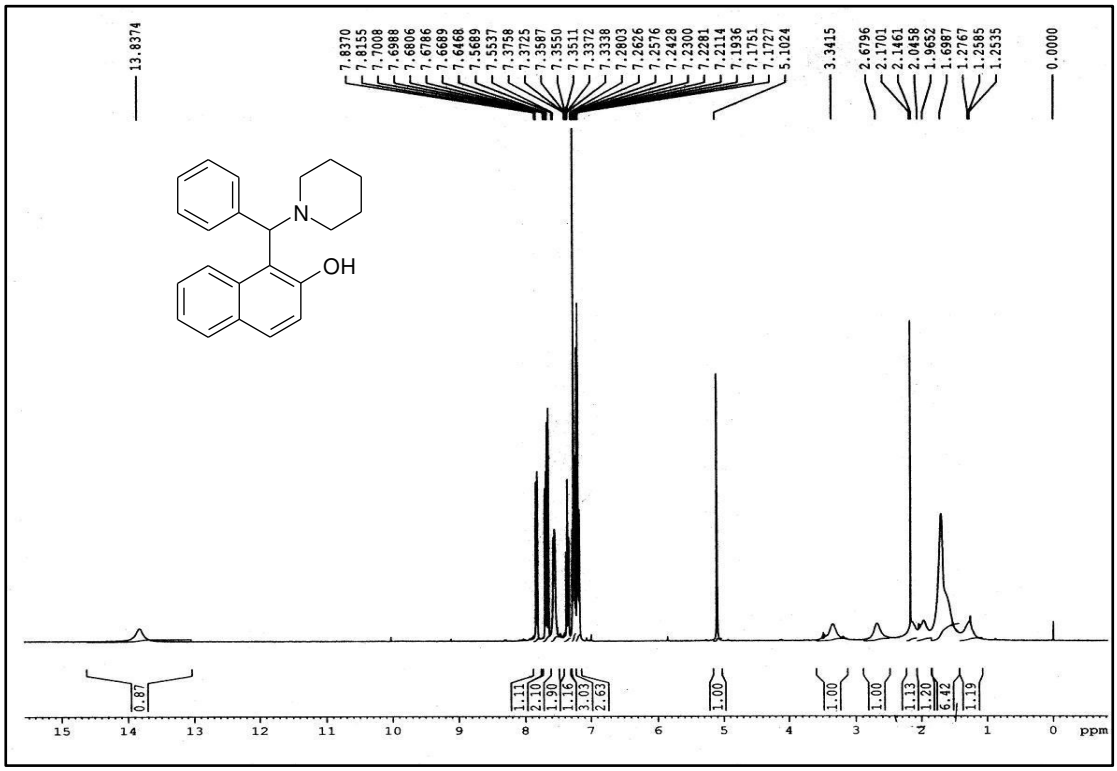
Compound **47** was prepared by same procedure as that of **41**.

Yield: 29% (0.046 g), Pale yellow oil.

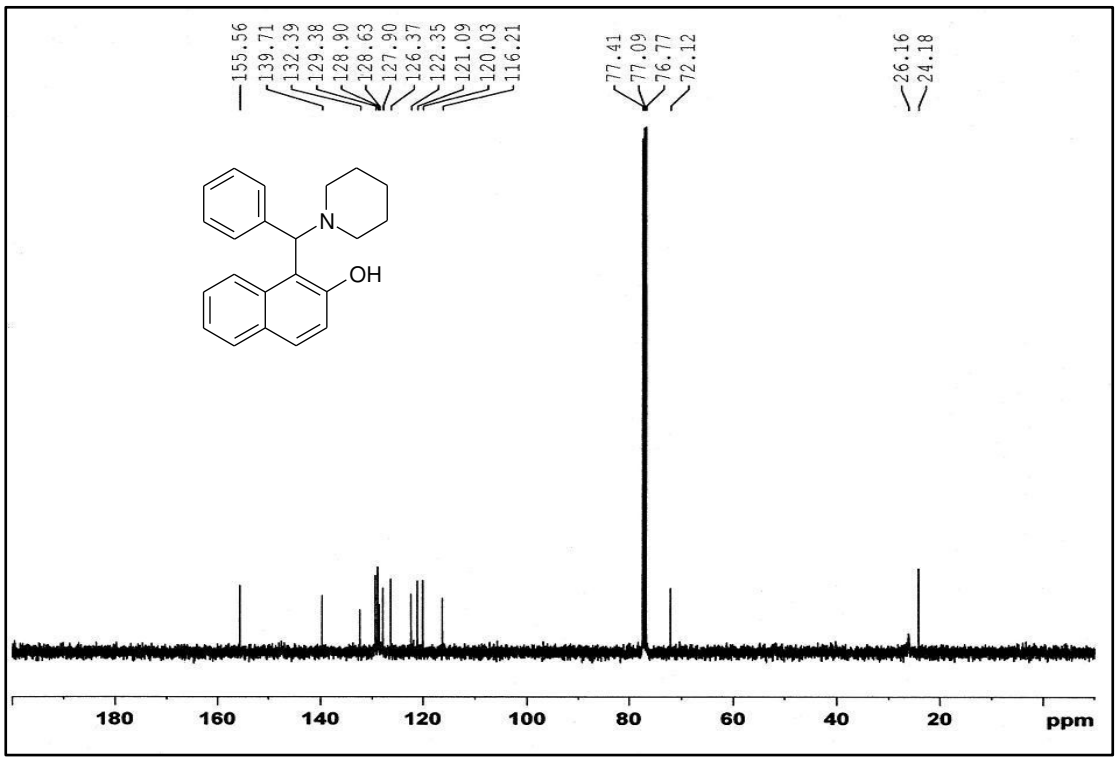
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.05 - 8.03 (dd, J_1 = 6.8, J_2 = 1.6 Hz, 2H), 7.82 - 7.78 (d, *J* = 16 Hz, 1H), 7.69 - 7.67 (m, 2H), 7.62 - 7.52 (m, 5H), 7.44 - 7.38 (m, 5H).

MS (EI): (*m/z*) 343 (M+1, 50), 342 (M^+, 74), 341 (100), 340 (23), 307 (18), 278 (11), 205 (11), 176 (16).

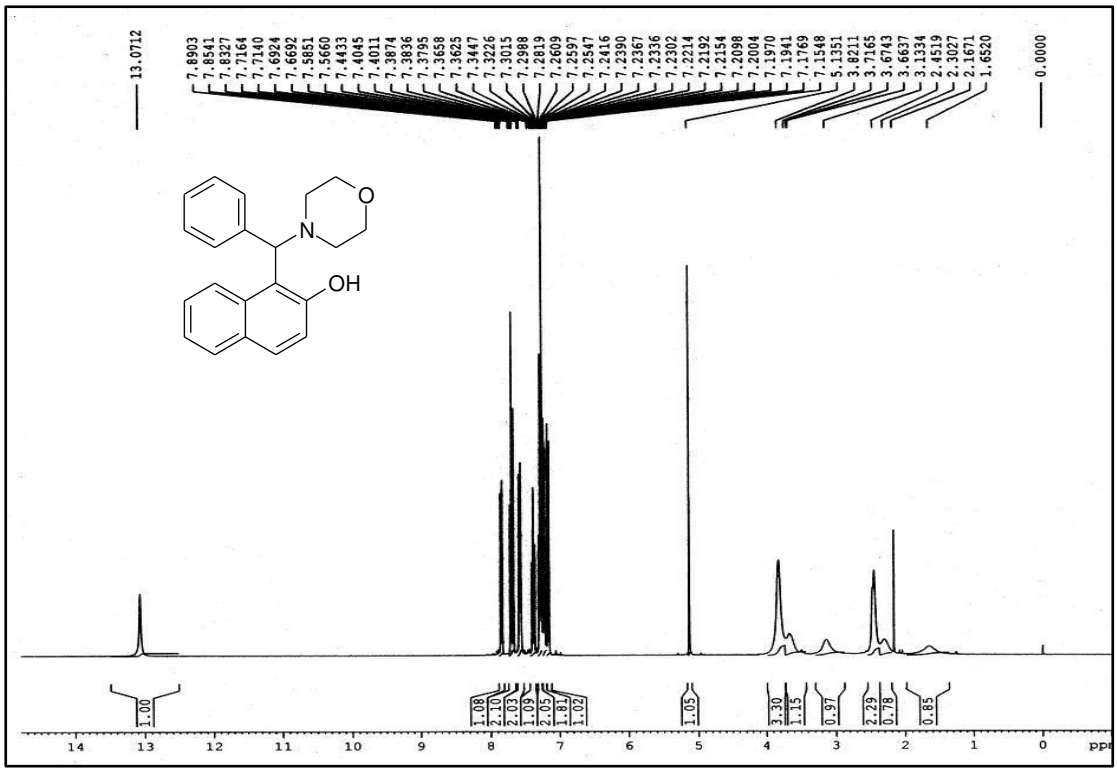
Spectral Data



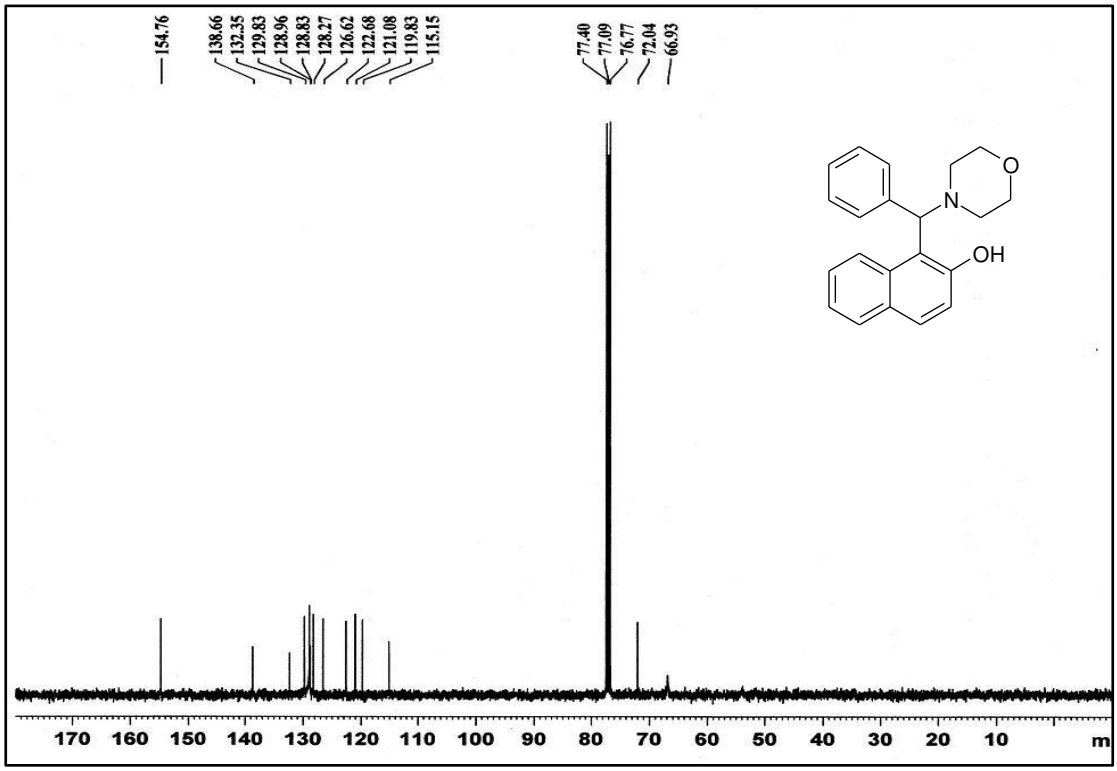
^{1}H-NMR Spectra of Compound 1a (400 MHz, $CDCl_3$)



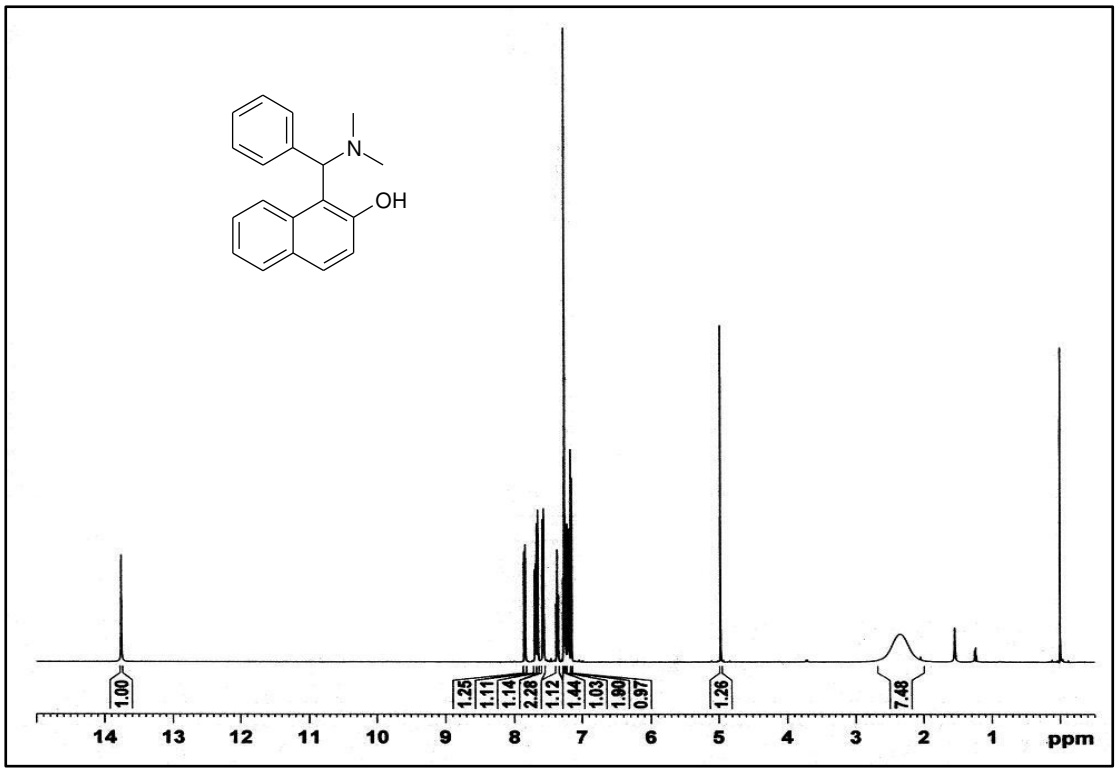
^{13}C-NMR Spectra of Compound 1a (100 MHz, $CDCl_3$)



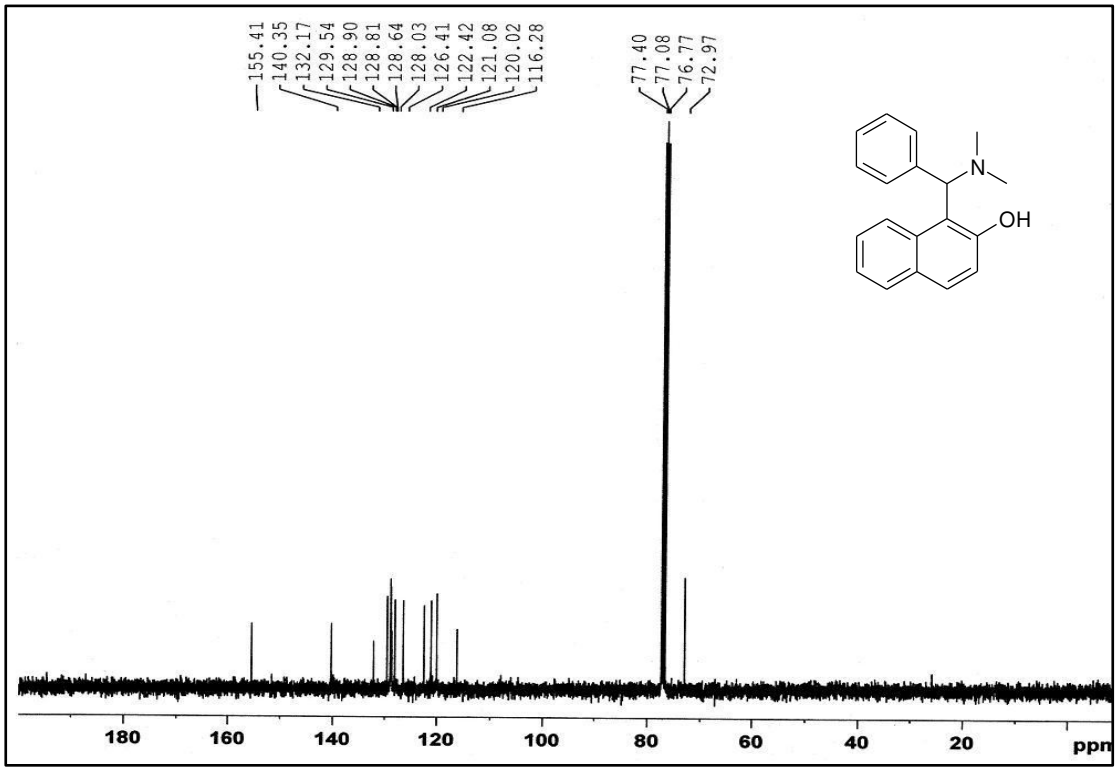
^{1}H-NMR Spectra of Compound 1b (400 MHz, $CDCl_3$)



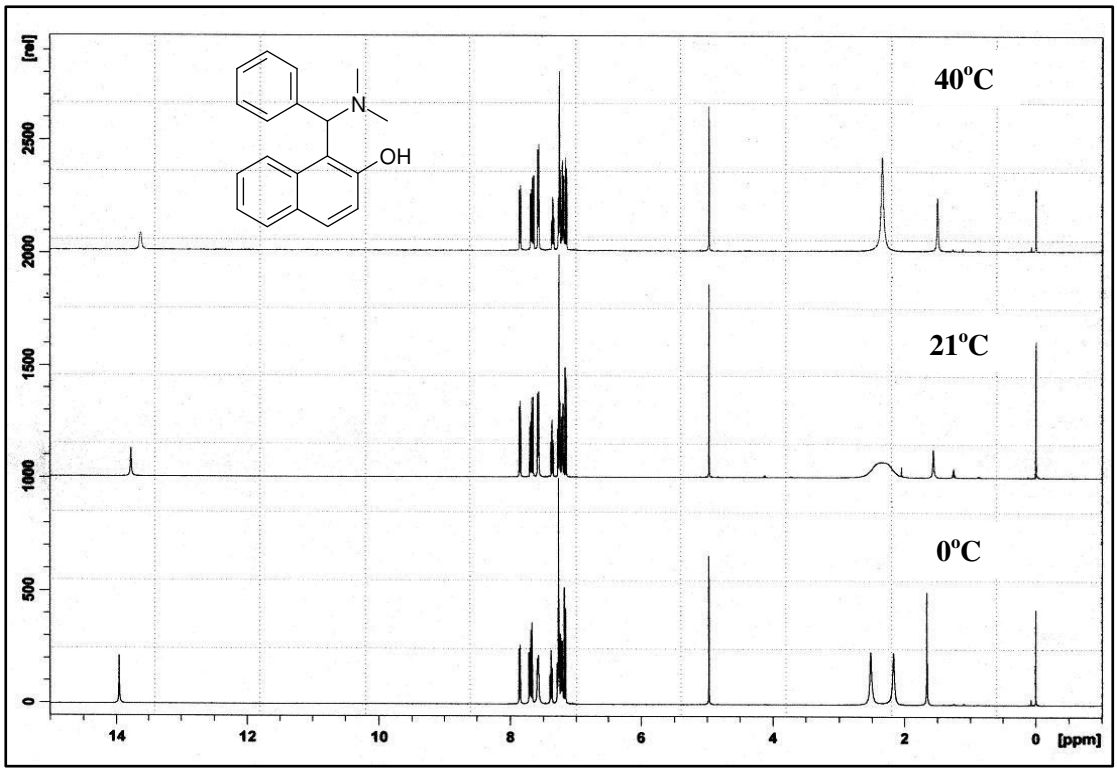
^{13}C-NMR Spectra of Compound 1b (100 MHz, $CDCl_3$)



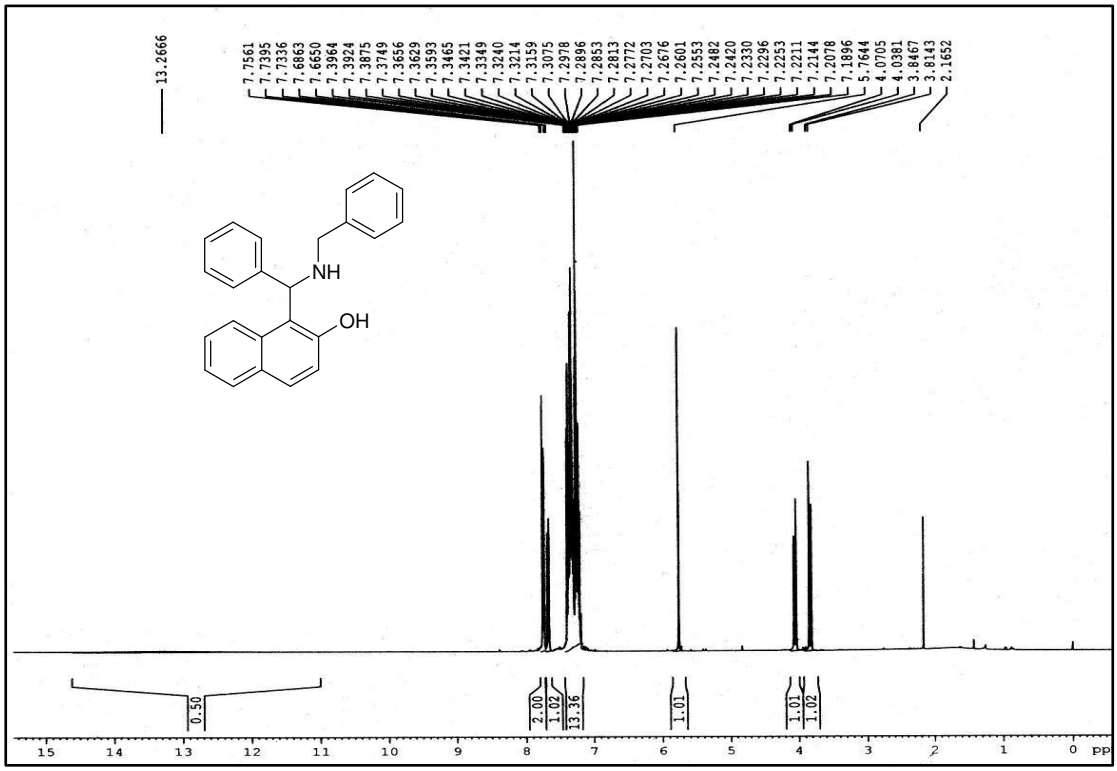
^{1}H-NMR Spectra of Compound 1c (400 MHz, $CDCl_3$)



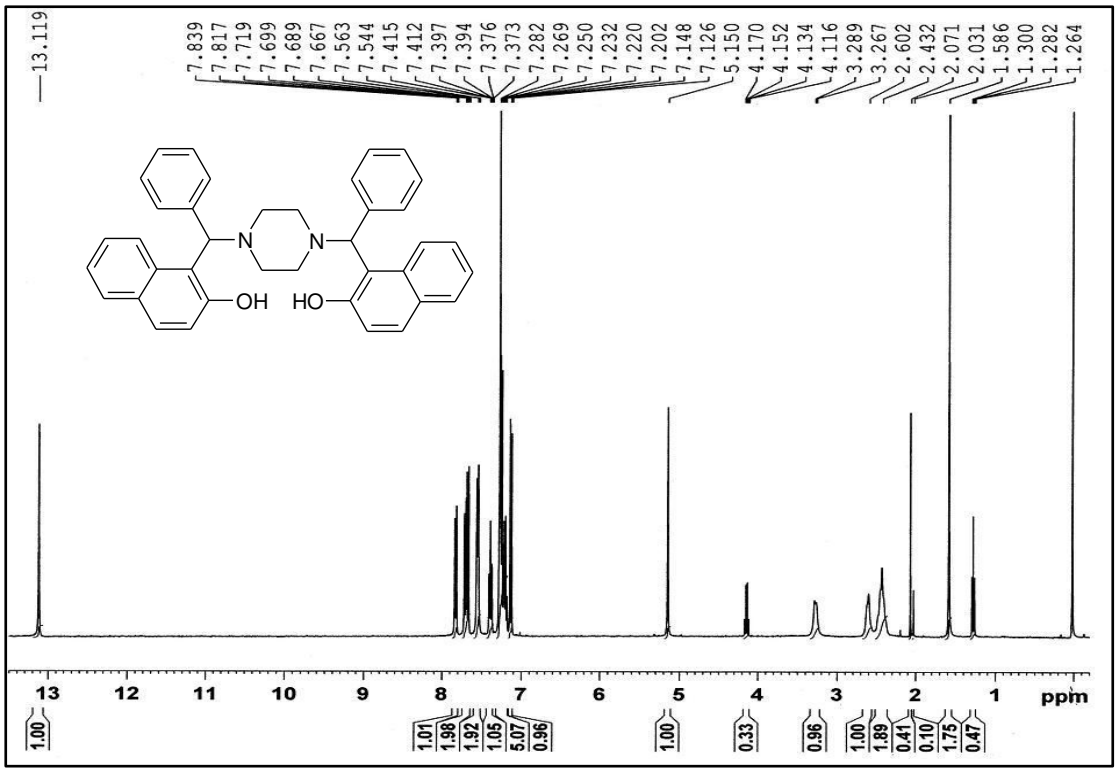
^{13}C-NMR Spectra of Compound 1c (100 MHz, $CDCl_3$)



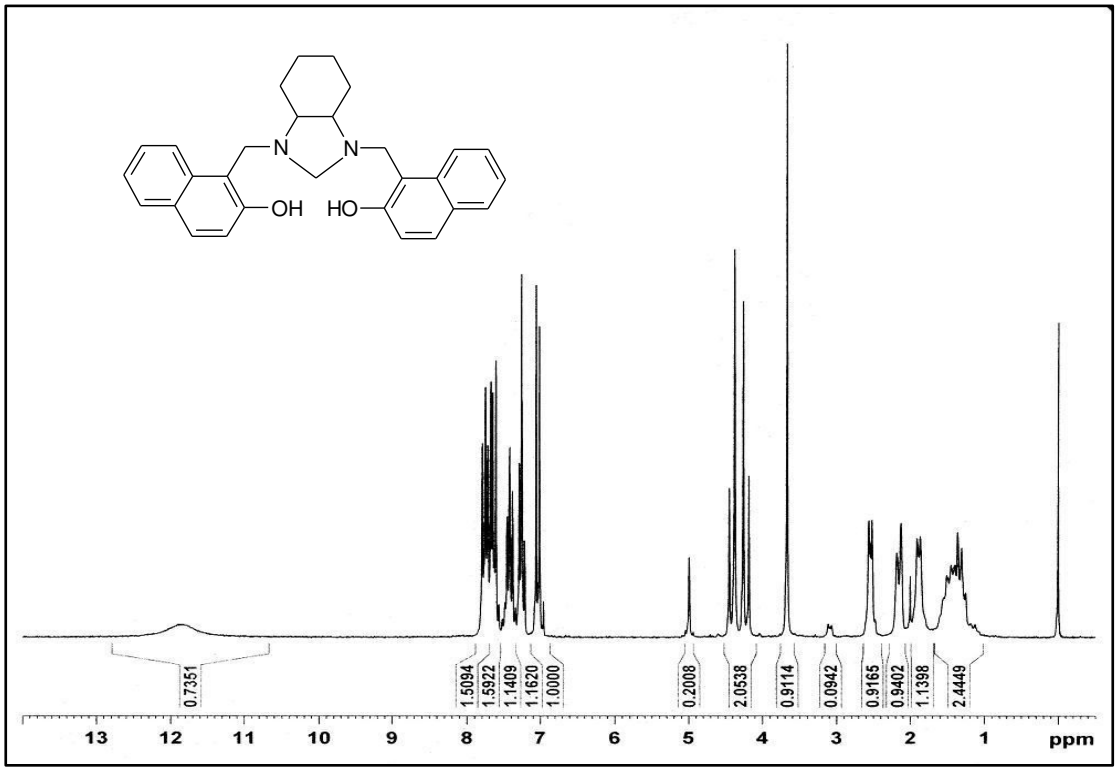
Variable temperature ^{1}H-NMR Spectra of Compound 1c (400 MHz, $CDCl_3$)



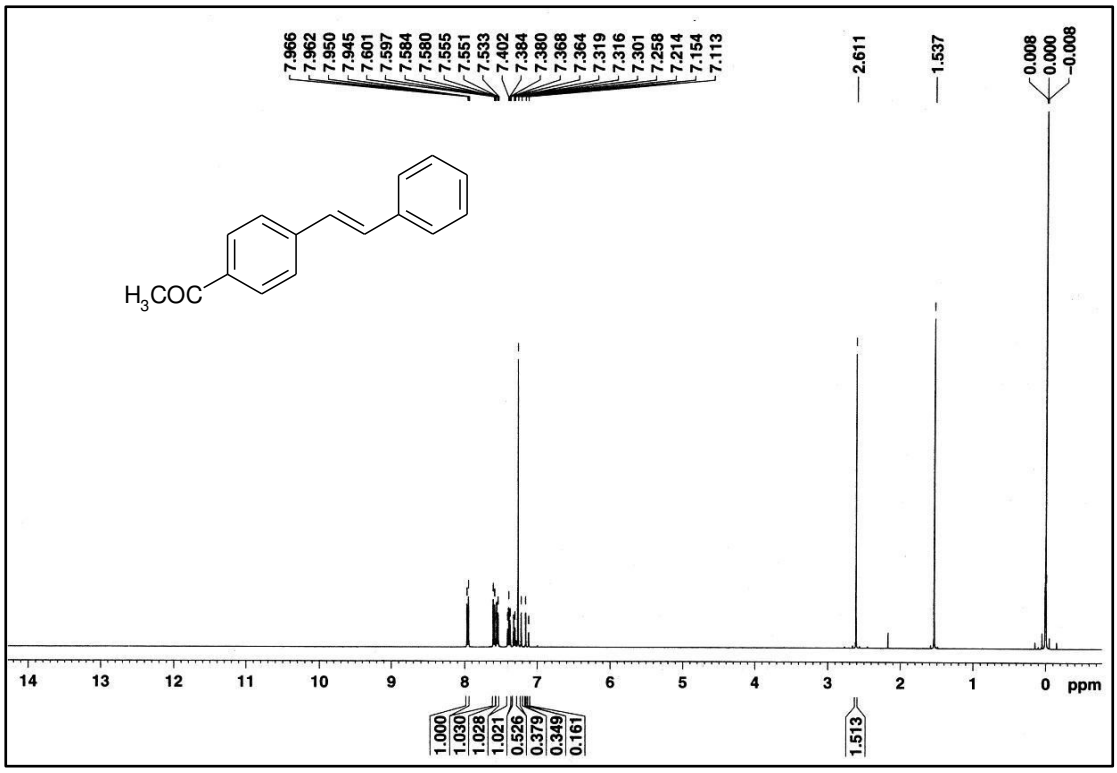
^{1}H-NMR Spectra of Compound 1d (400 MHz, $CDCl_3$)



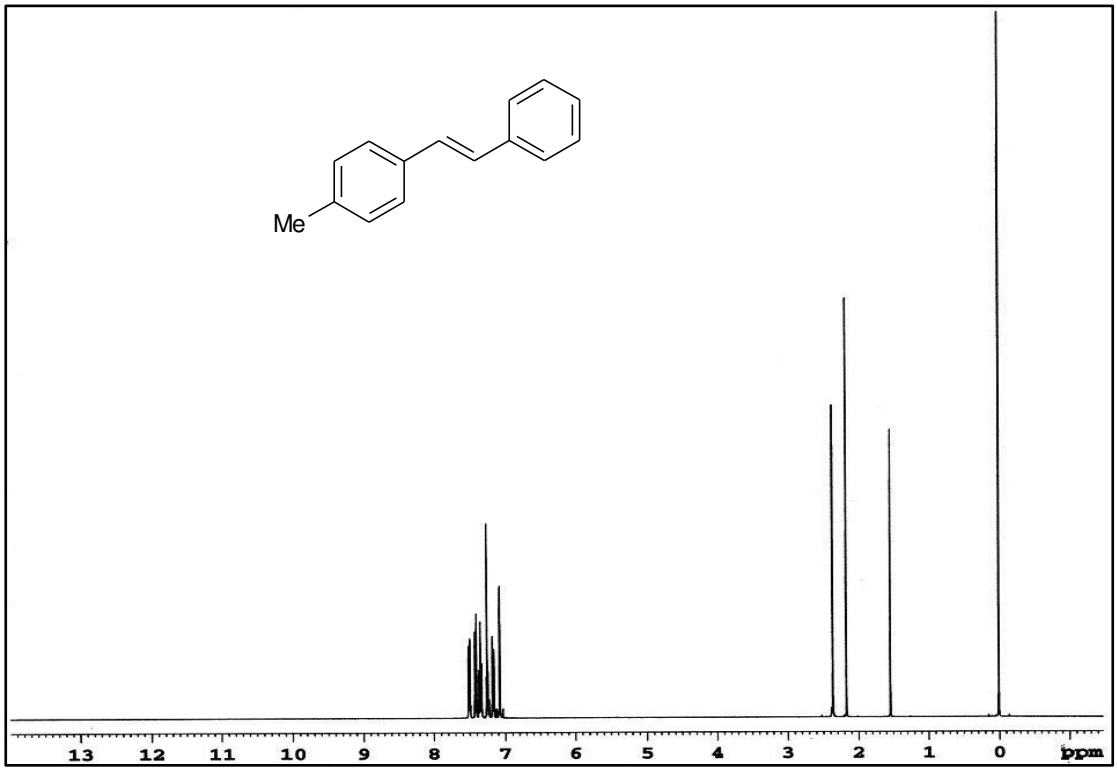
^{1}H-NMR Spectra of Compound 1e (400 MHz, $CDCl_3$)



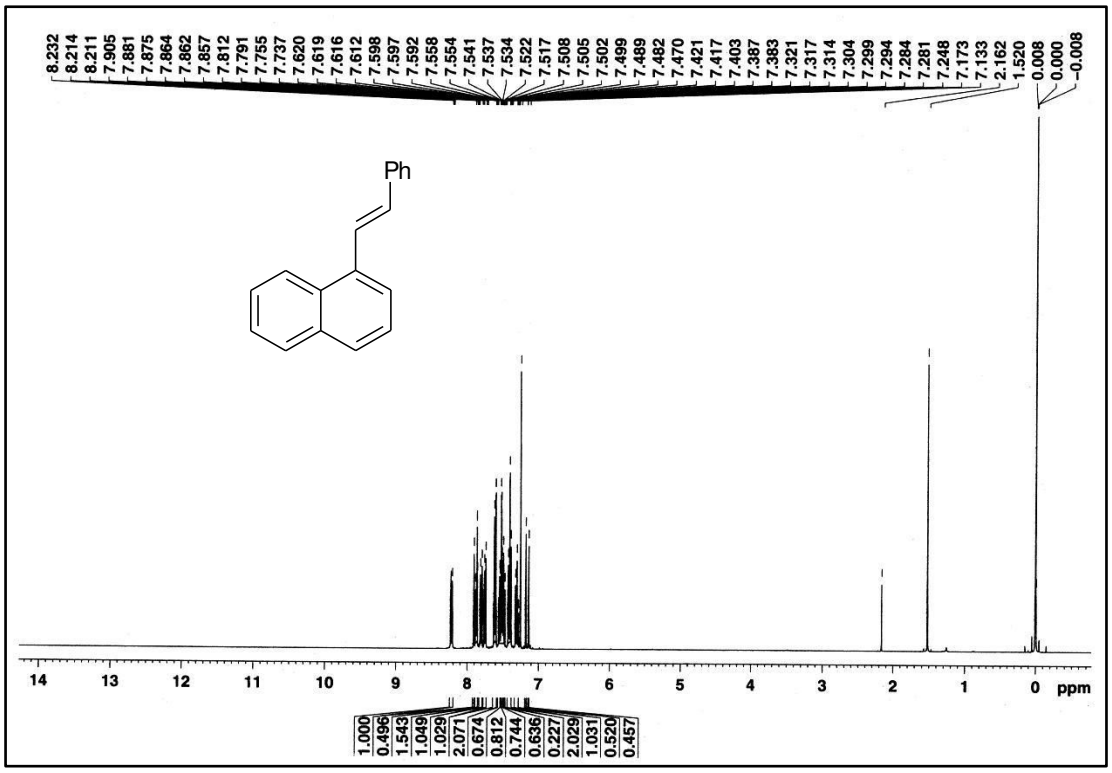
^{1}H-NMR Spectra of Compound 1f (400 MHz, $CDCl_3$)



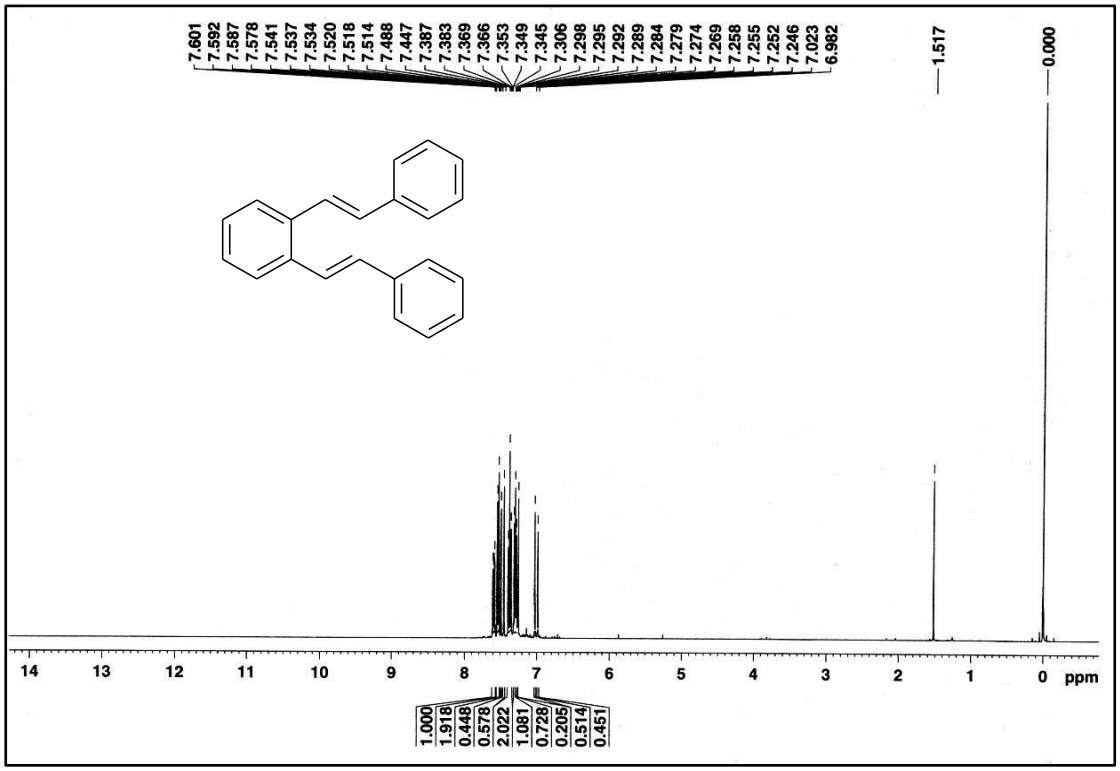
^{1}H-NMR Spectra of Compound 8 (400 MHz, $CDCl_3$)



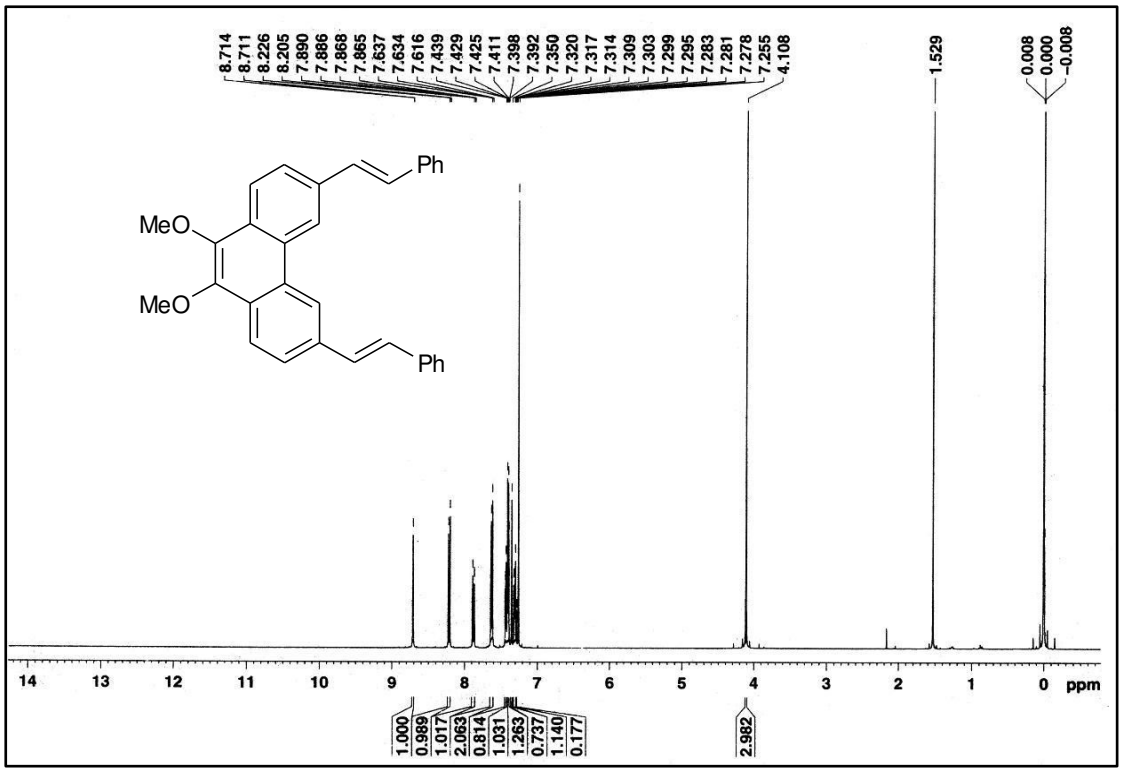
^{1}H-NMR Spectra of Compound 9 (400 MHz, $CDCl_3$)



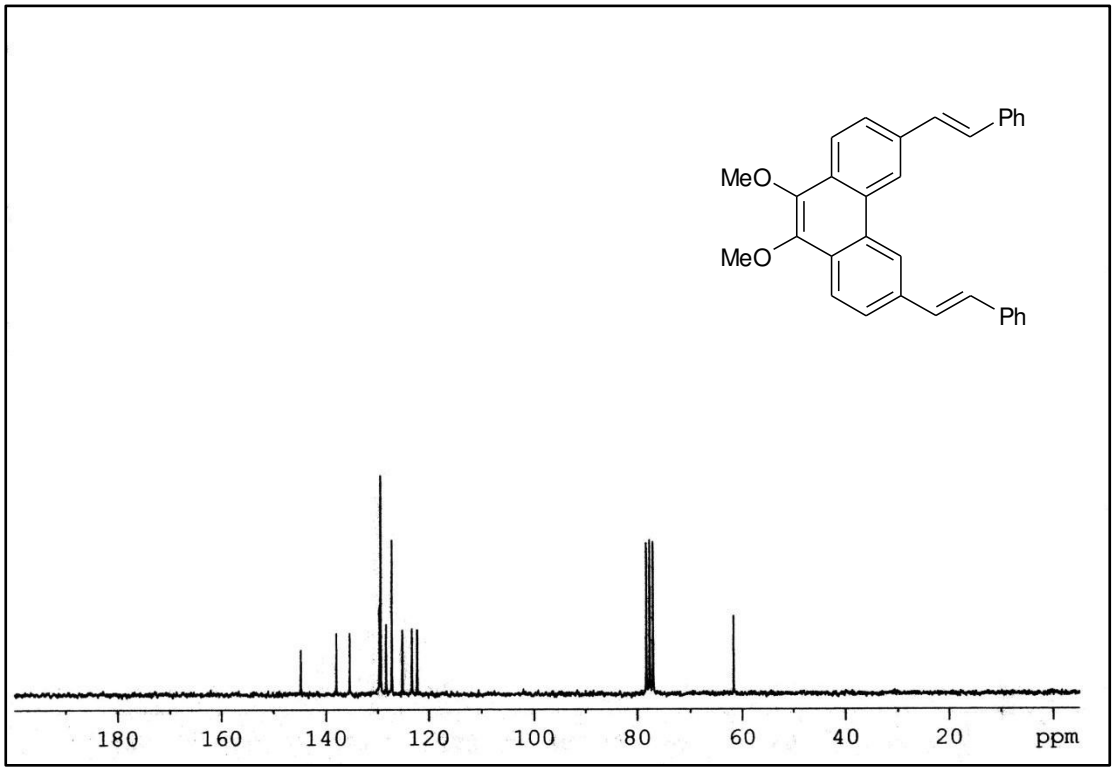
^{1}H-NMR Spectra of Compound 11 (400 MHz, $CDCl_3$)



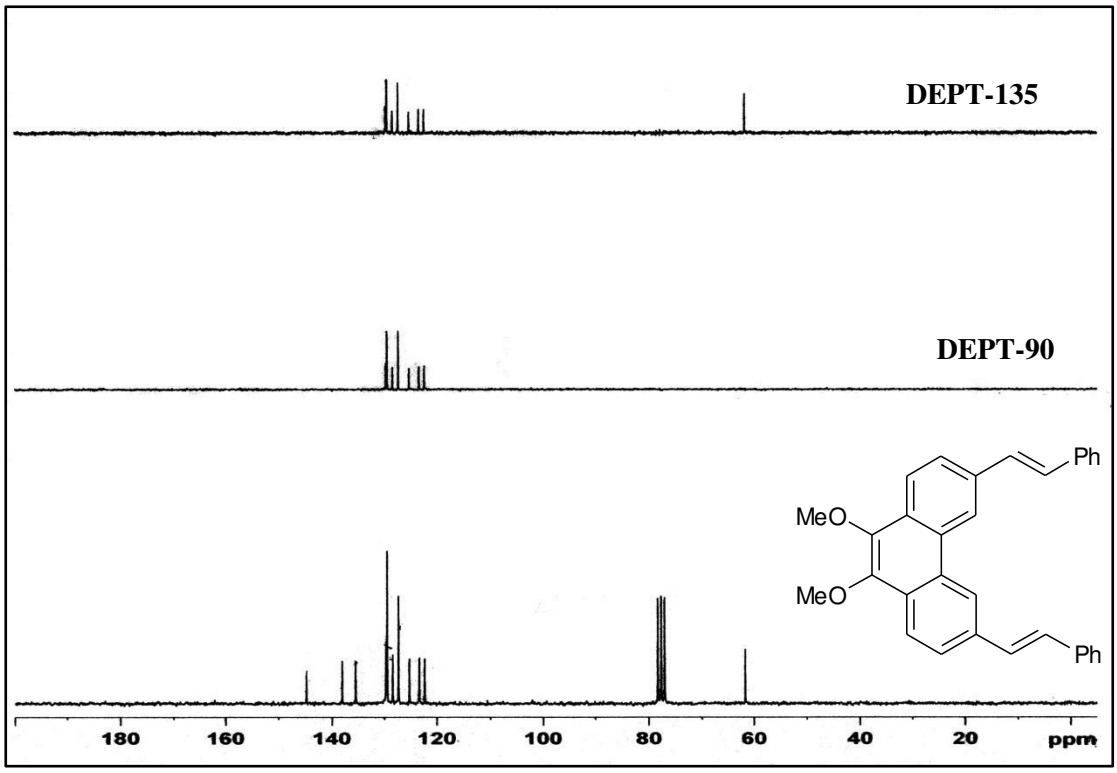
^{1}H-NMR Spectra of Compound 12 (400 MHz, $CDCl_3$)



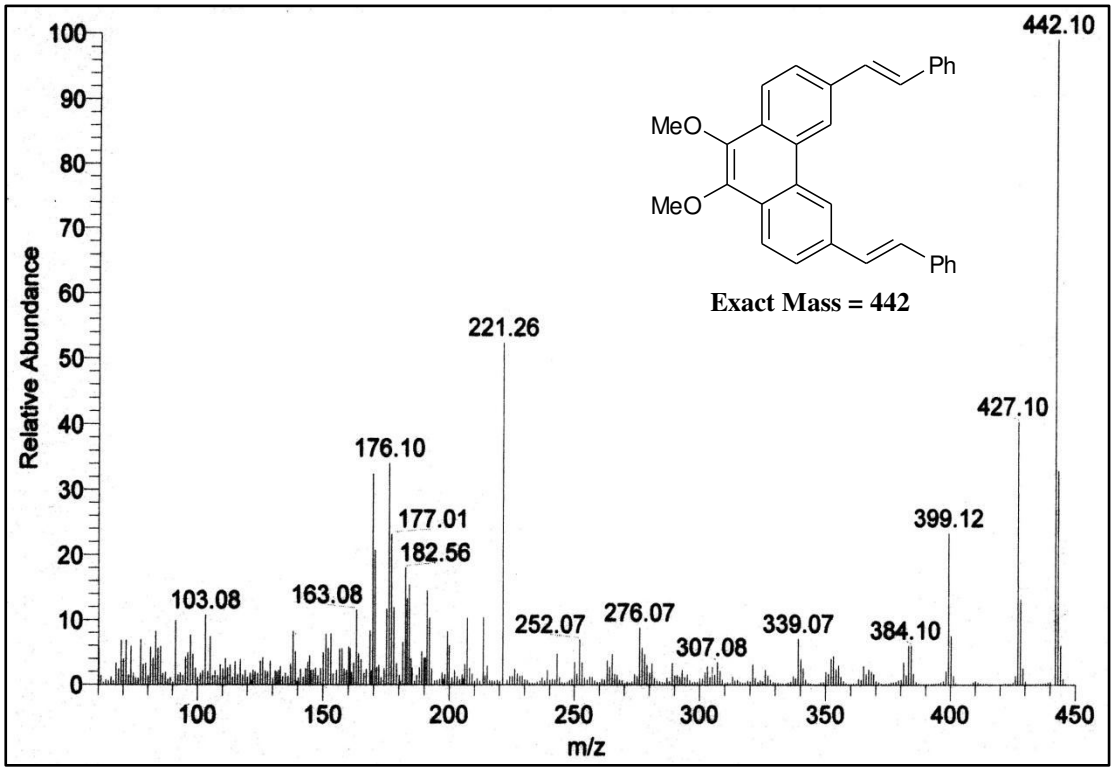
^{1}H-NMR Spectra of Compound 13 (400 MHz, $CDCl_3$)



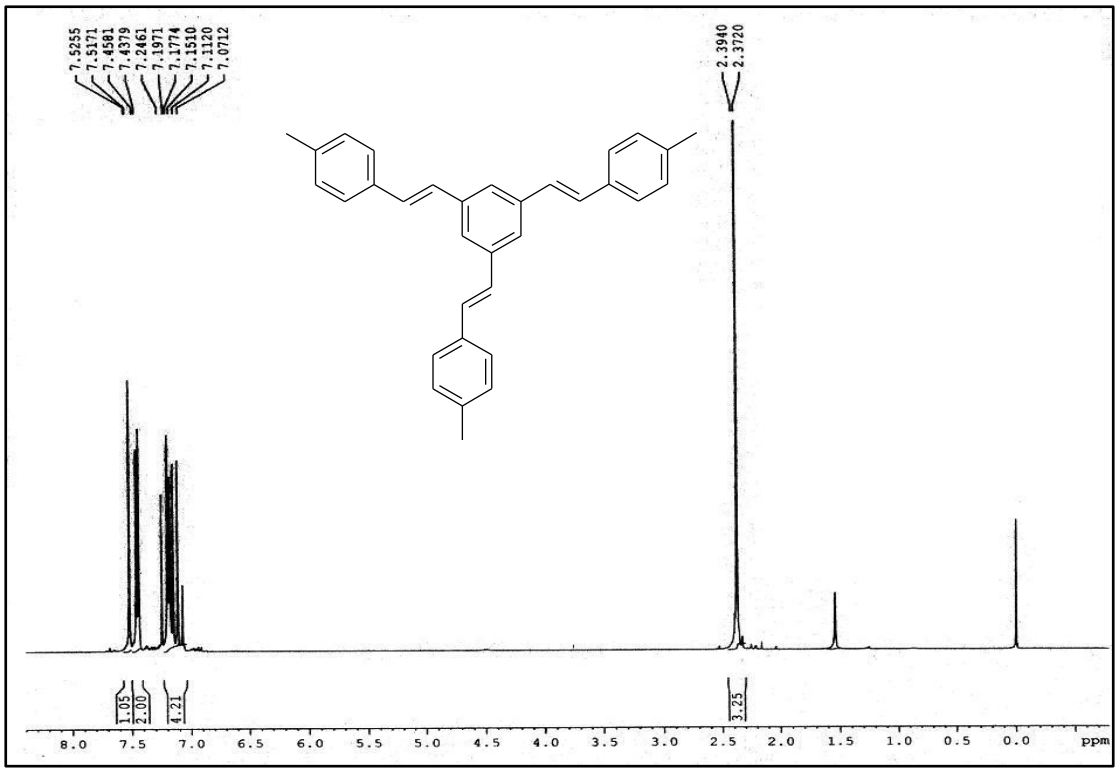
^{13}C-NMR Spectra of Compound 13 (400 MHz, $CDCl_3$)



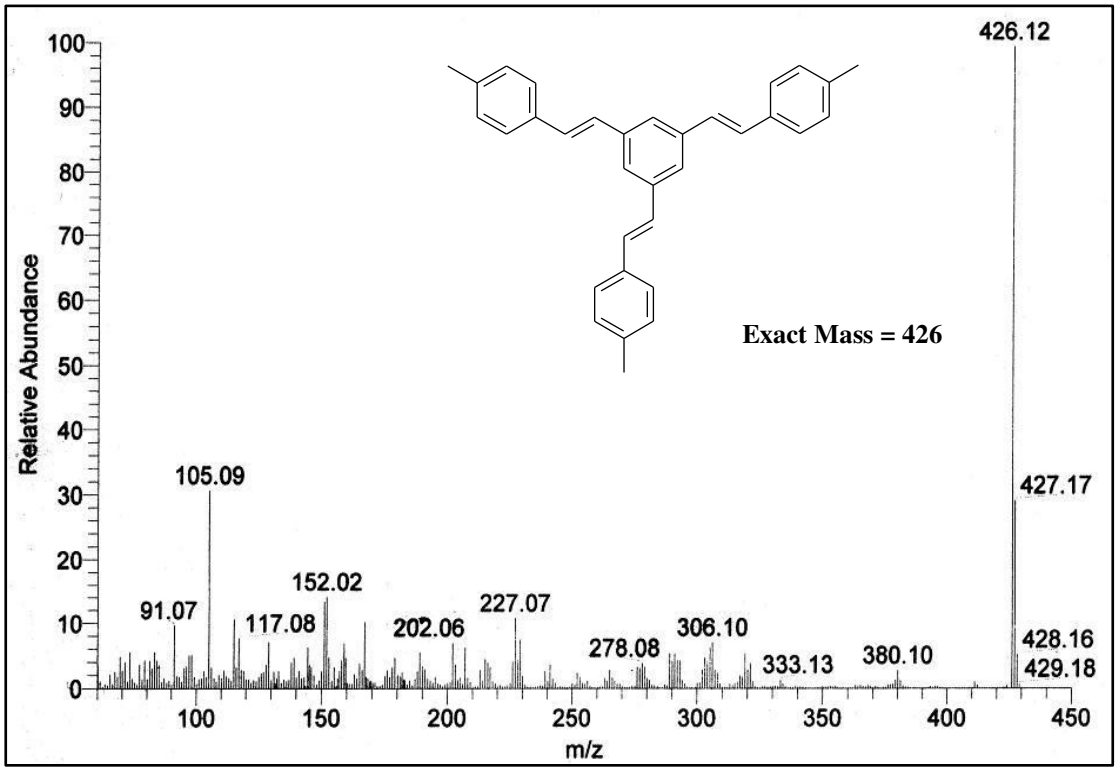
^{13}C-DEPT-NMR Spectra of Compound 13 (400 MHz, $CDCl_3$)



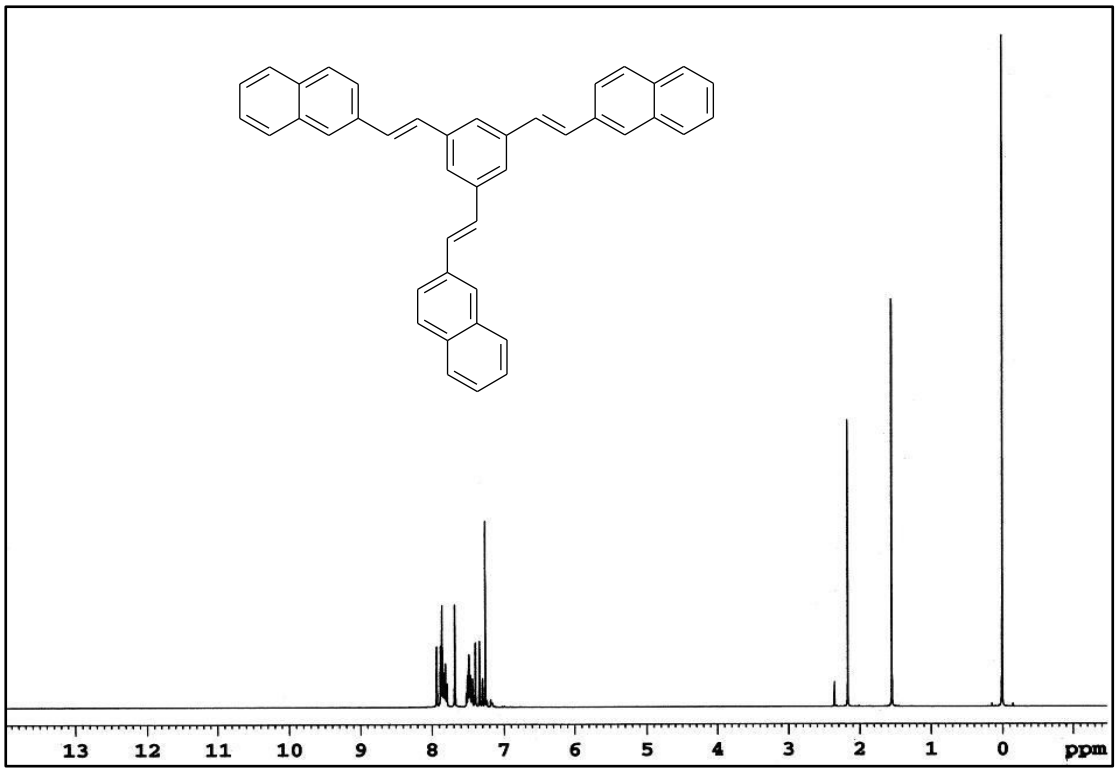
EI-Mass Spectra of Compound 13



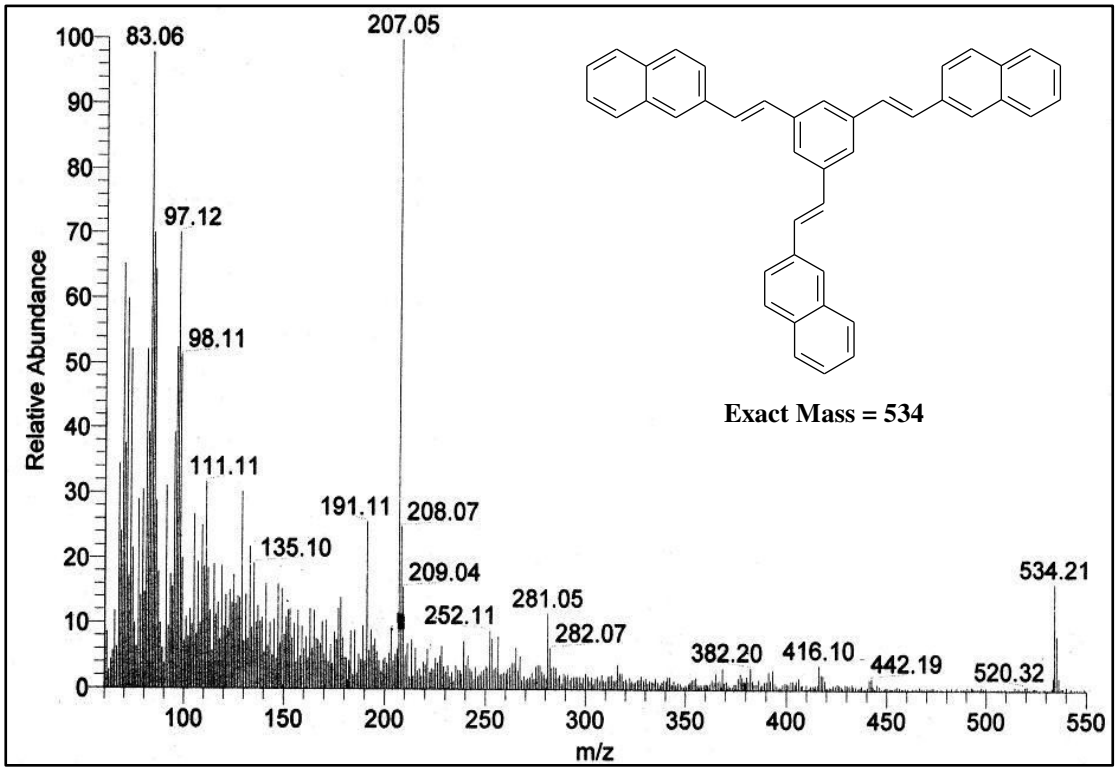
^{1}H-NMR Spectra of Compound 15 (400 MHz, $CDCl_3$)



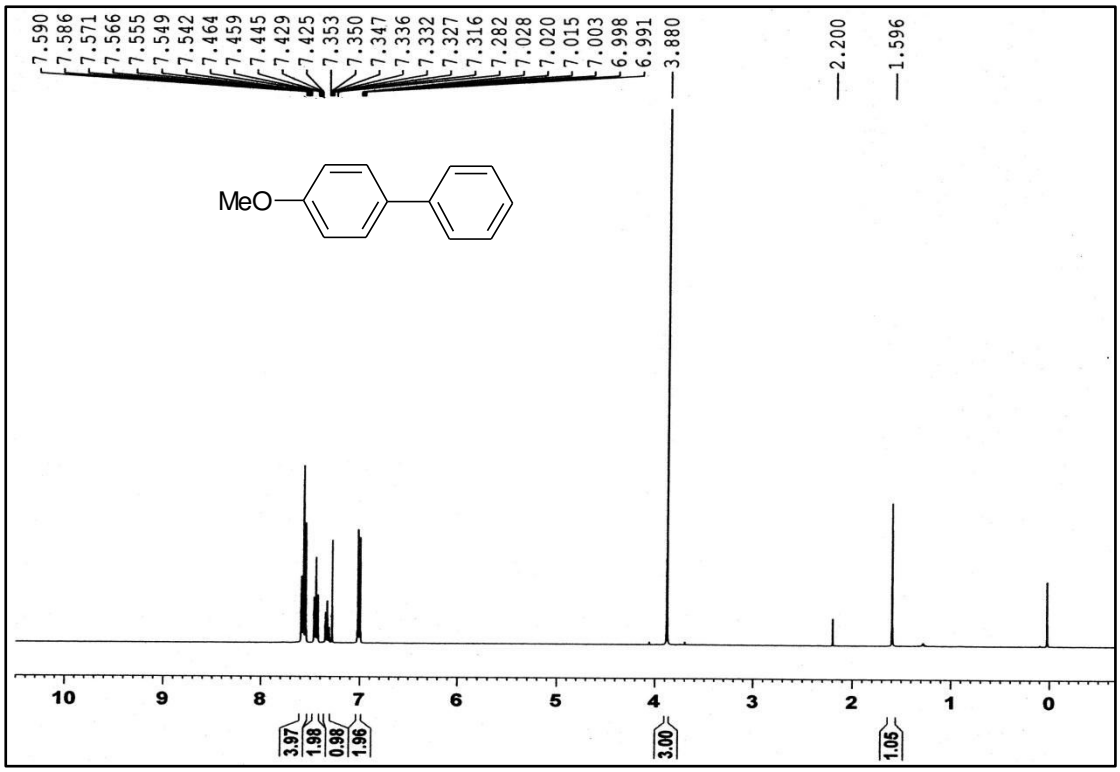
EI-Mass Spectra of Compound 15



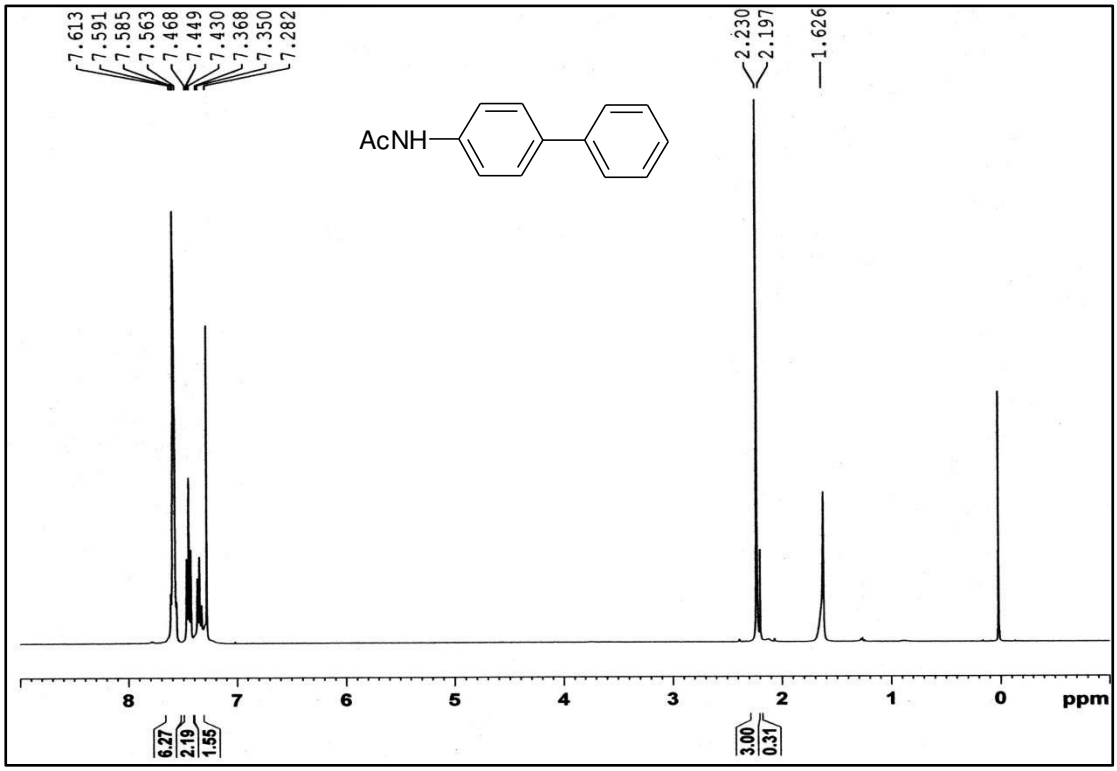
^{1}H-NMR Spectra of Compound 16 (400 MHz, $CDCl_3$)



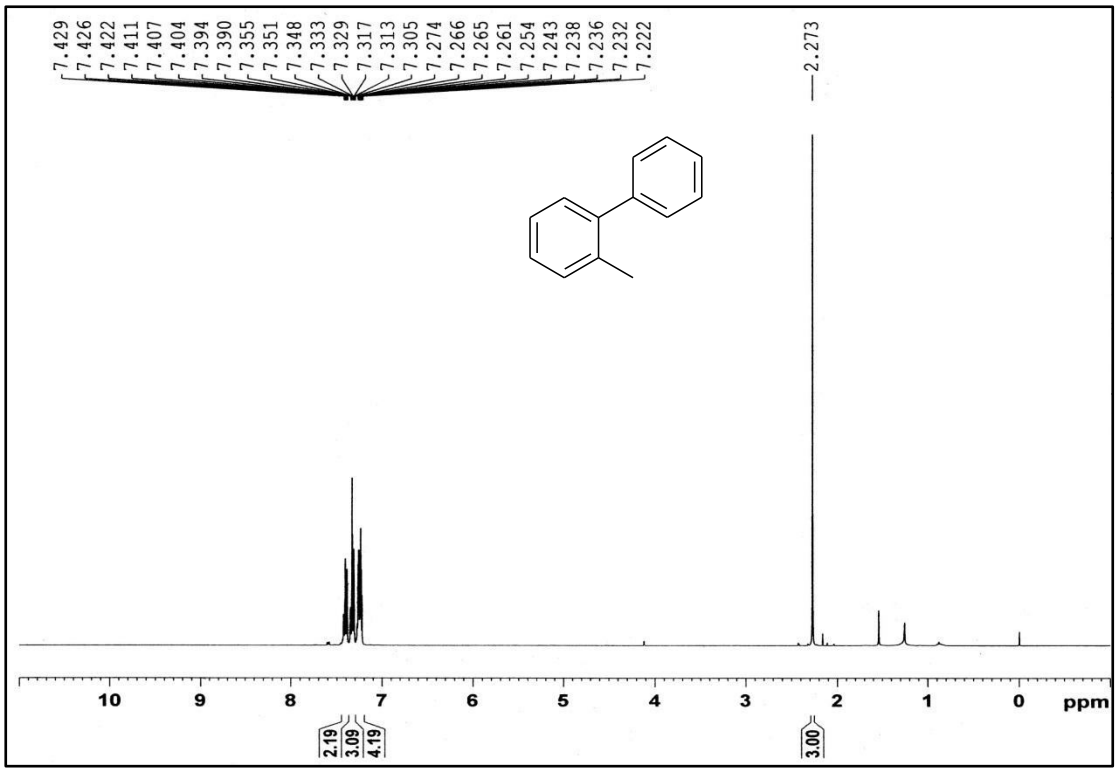
EI-Mass Spectra of Compound 16



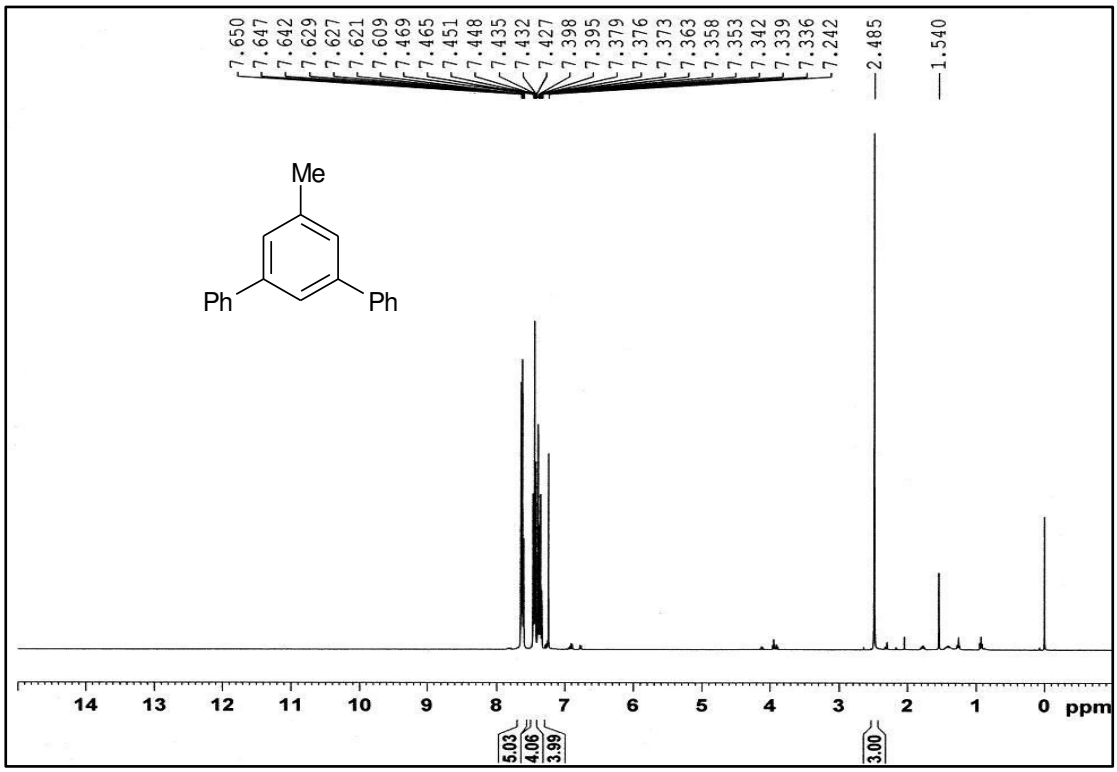
^{1}H-NMR Spectra of Compound 19 (400 MHz, $CDCl_3$)



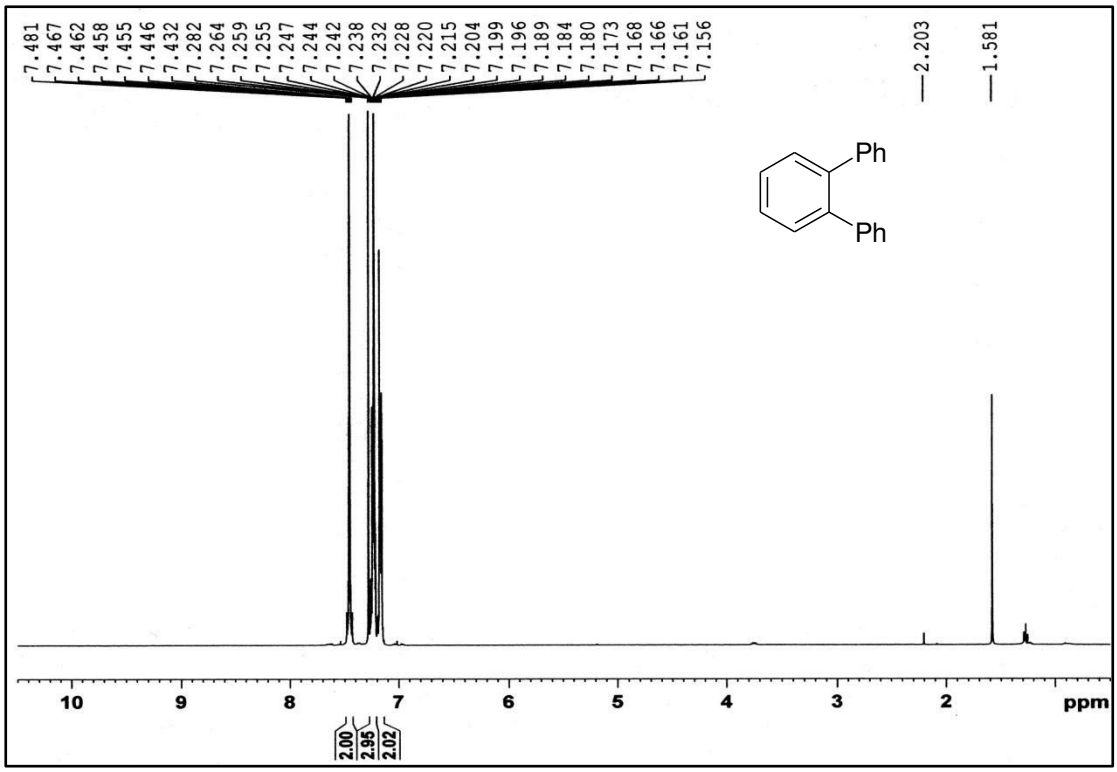
^{1}H-NMR Spectra of Compound 20 (400 MHz, $CDCl_3$)



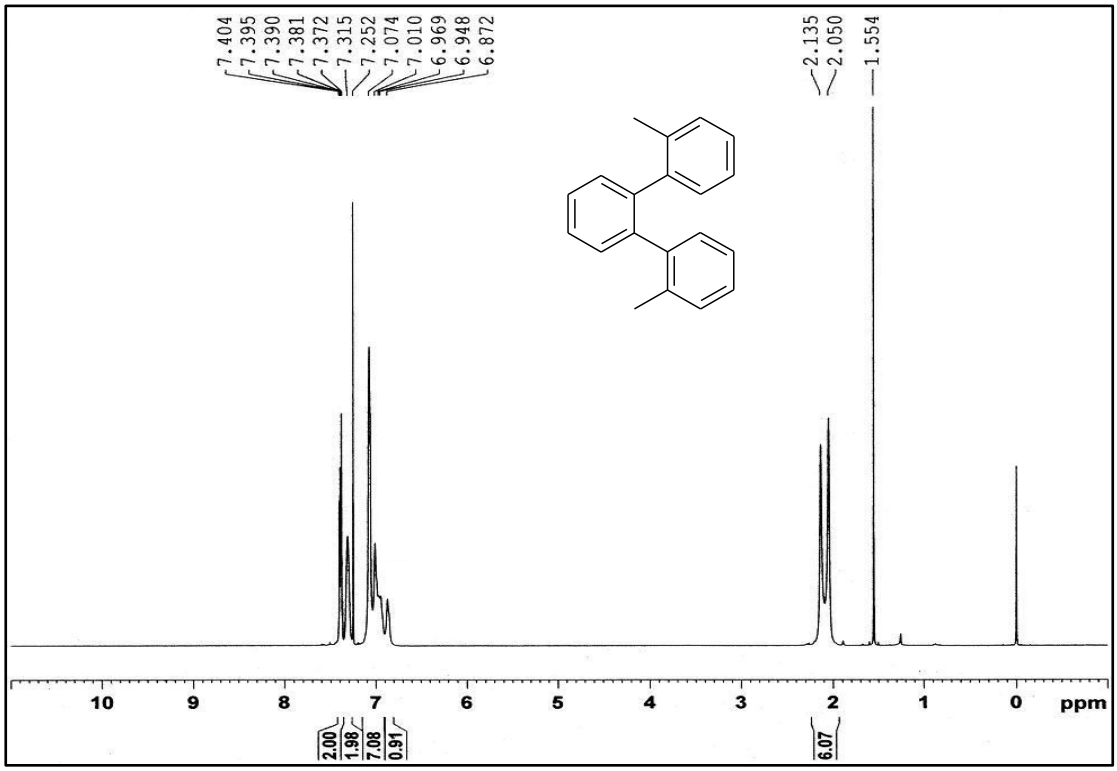
^{1}H-NMR Spectra of Compound 24 (400 MHz, $CDCl_3$)



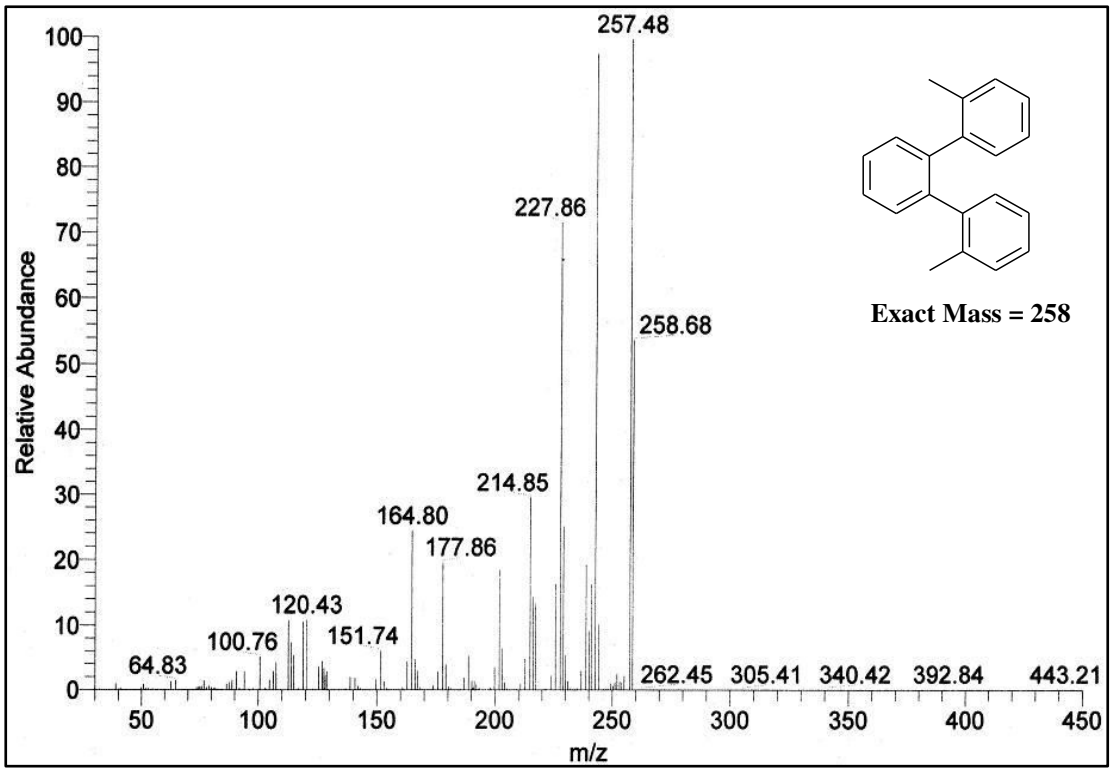
^{1}H-NMR Spectra of Compound 26 (400 MHz, $CDCl_3$)



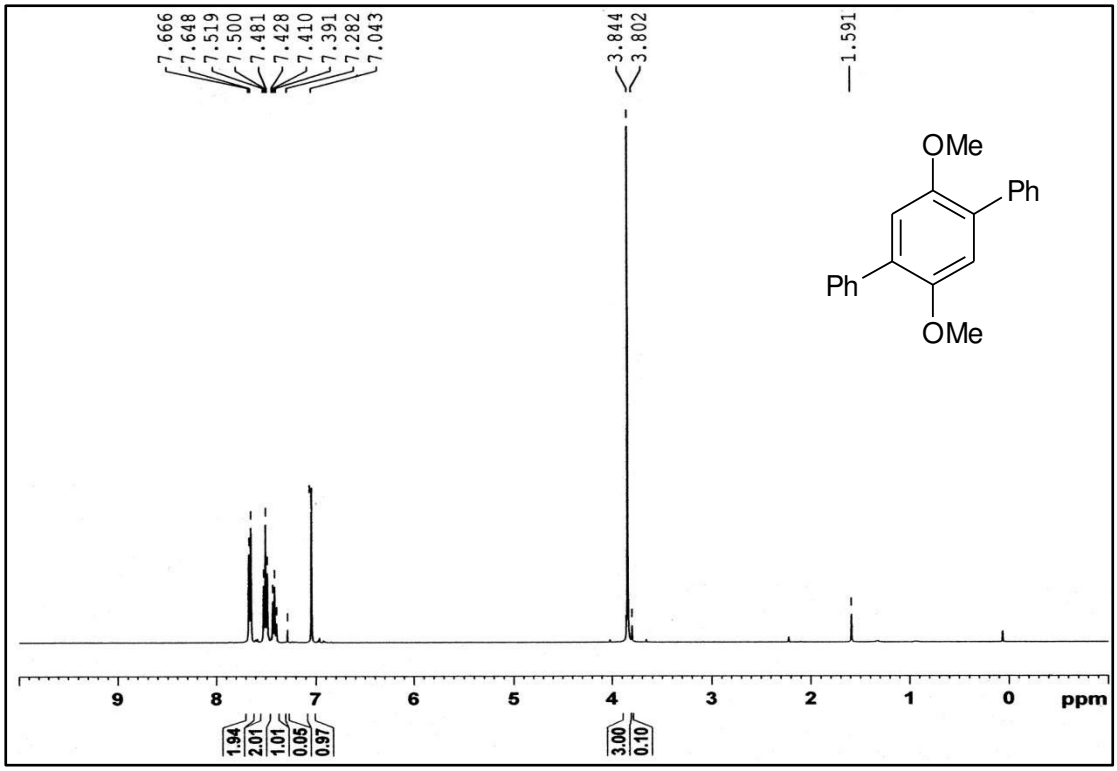
^{1}H-NMR Spectra of Compound 28b (400 MHz, $CDCl_3$)



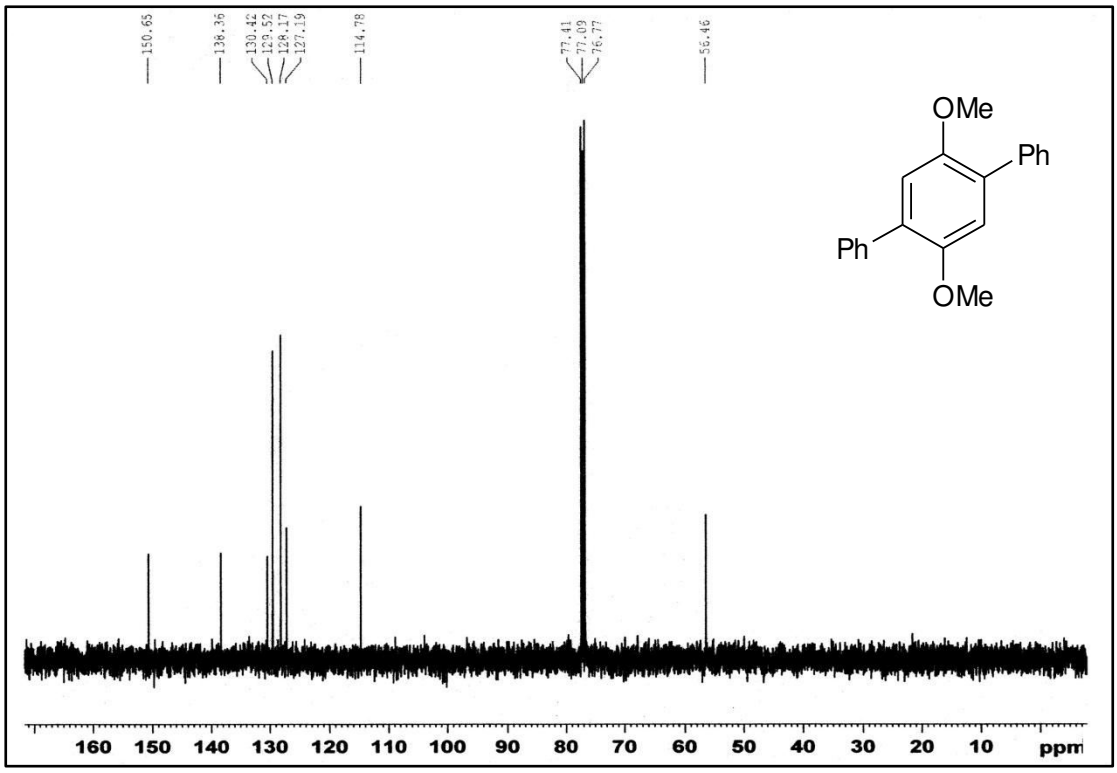
^{1}H-NMR Spectra of Compound 29b (400 MHz, $CDCl_3$)



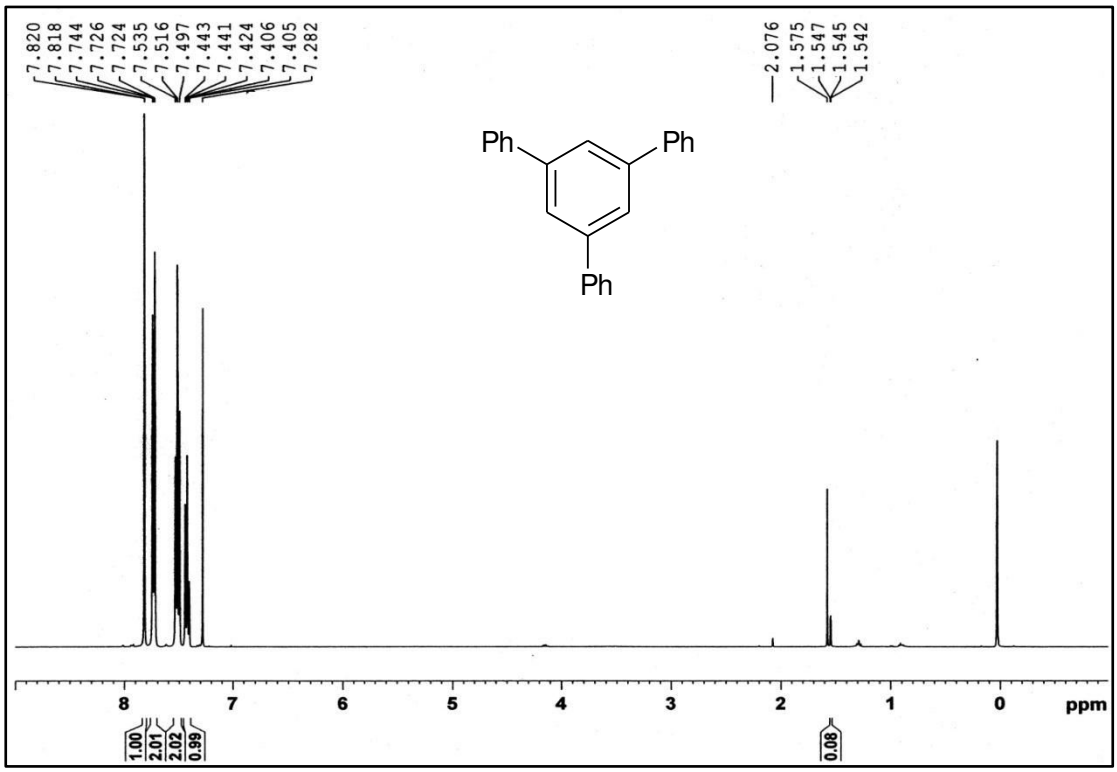
EI-Mass Spectra of Compound 29b



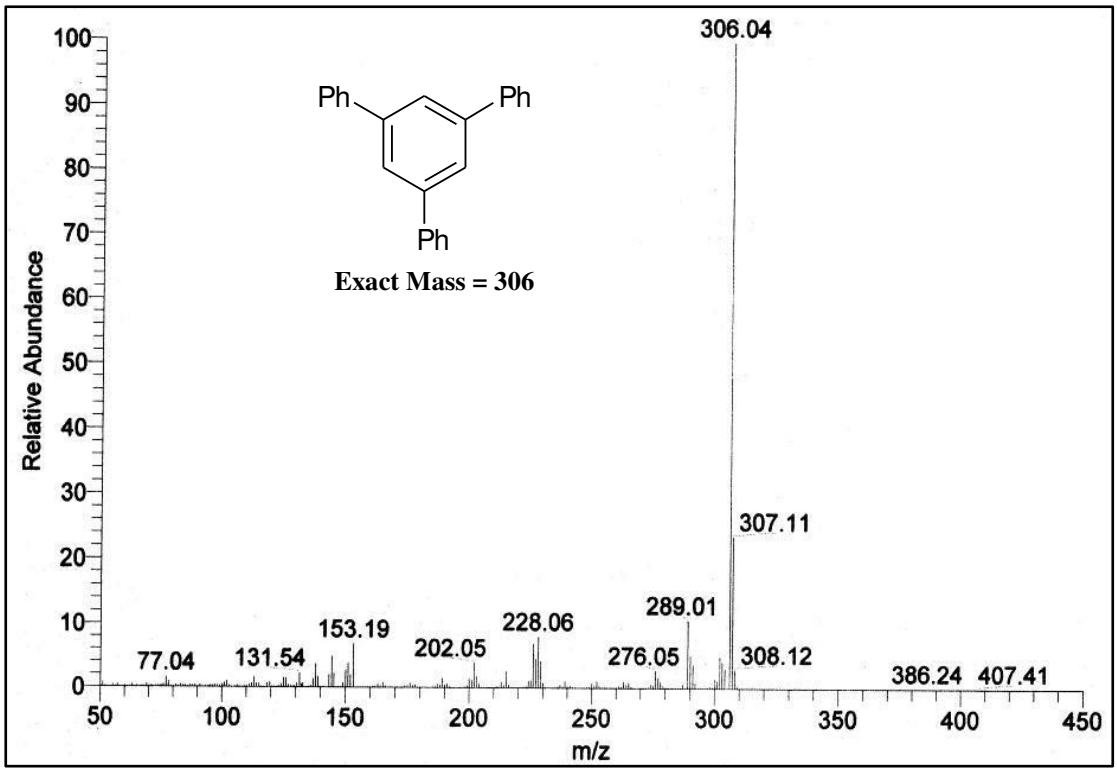
^{1}H-NMR Spectra of Compound 30b (400 MHz, $CDCl_3$)



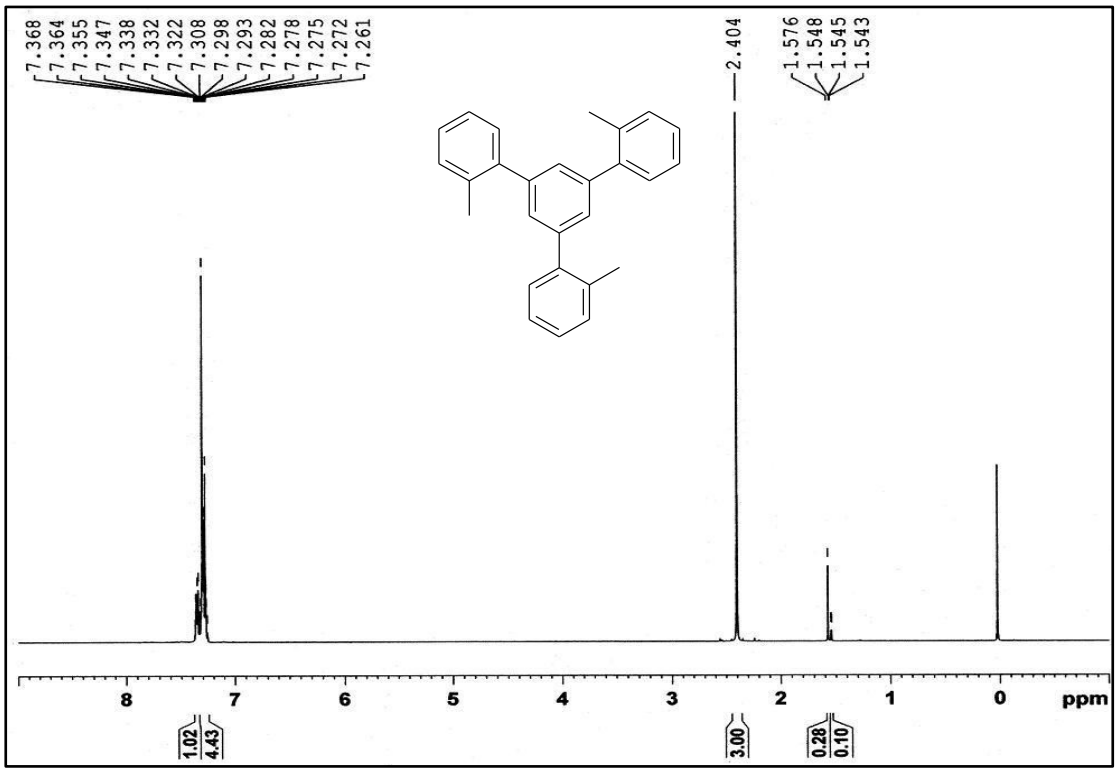
^{13}C-NMR Spectra of Compound 30b (400 MHz, $CDCl_3$)



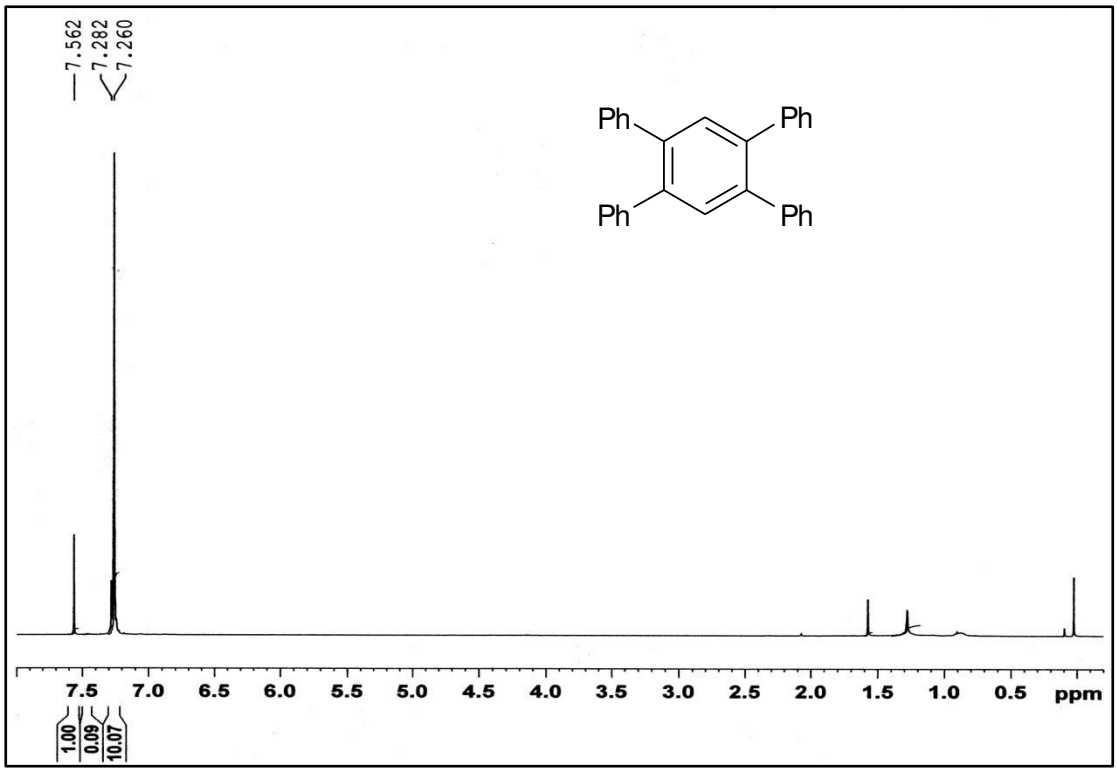
^{1}H-NMR Spectra of Compound 31 (400 MHz, $CDCl_3$)



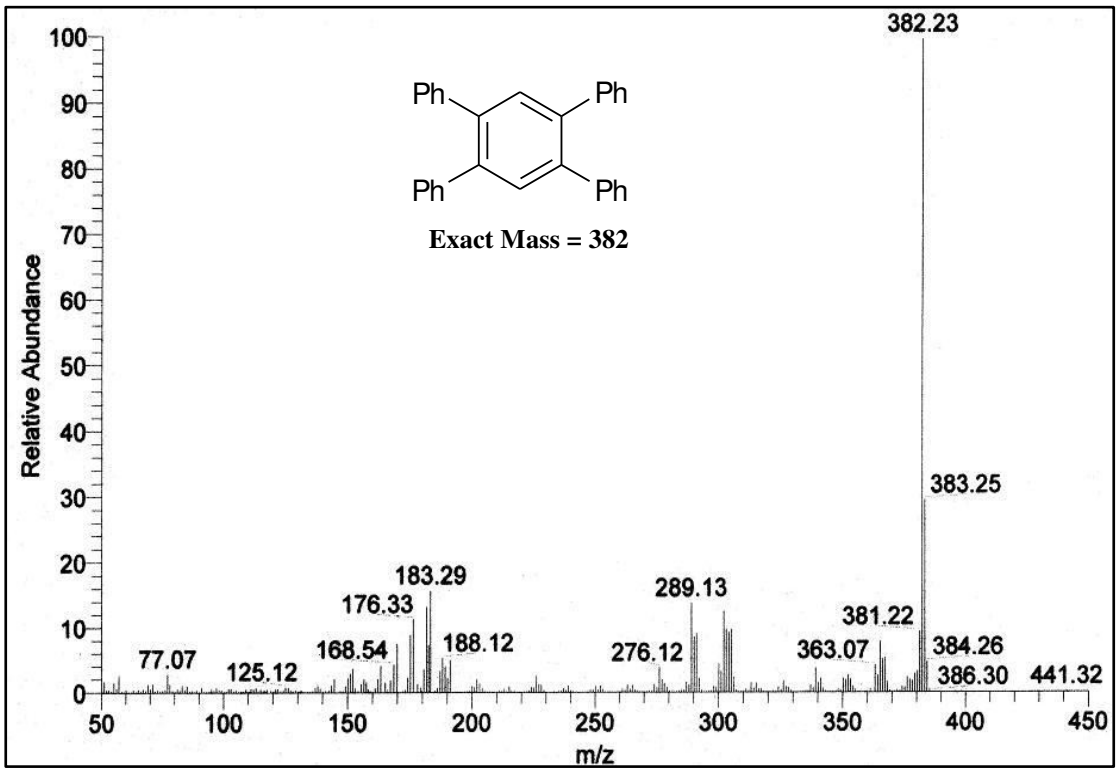
EI-Mass Spectra of Compound 31



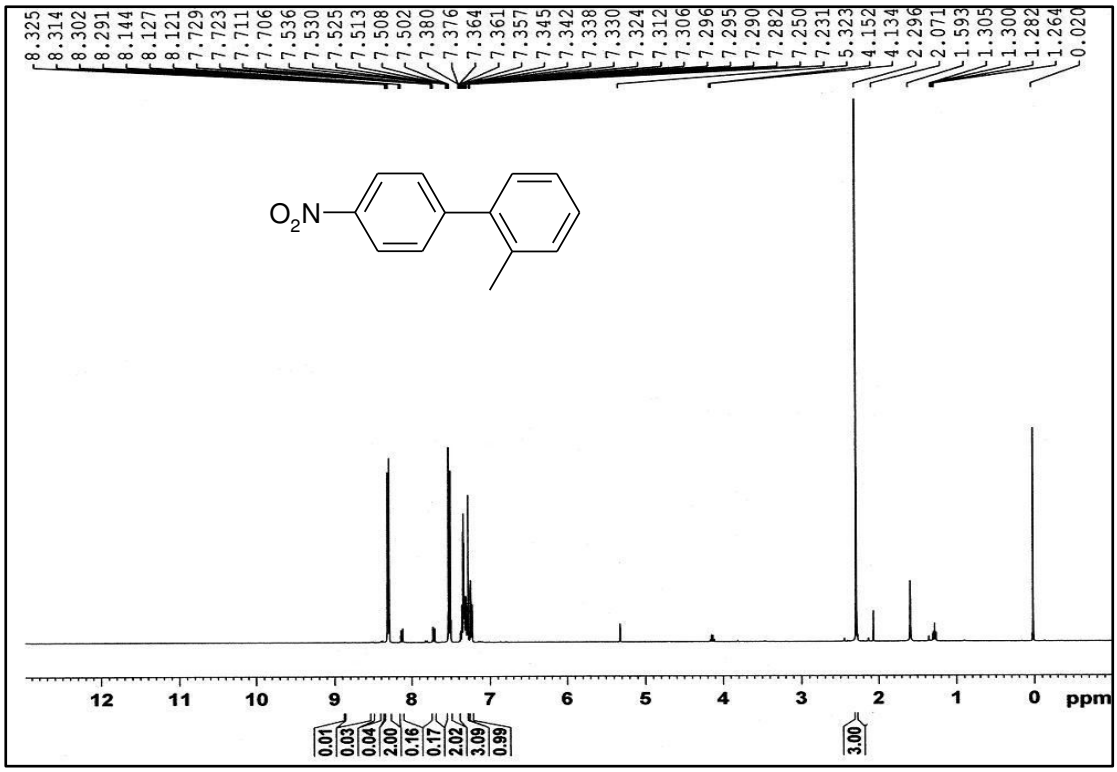
^{1}H-NMR Spectra of Compound 32 (400 MHz, $CDCl_3$)



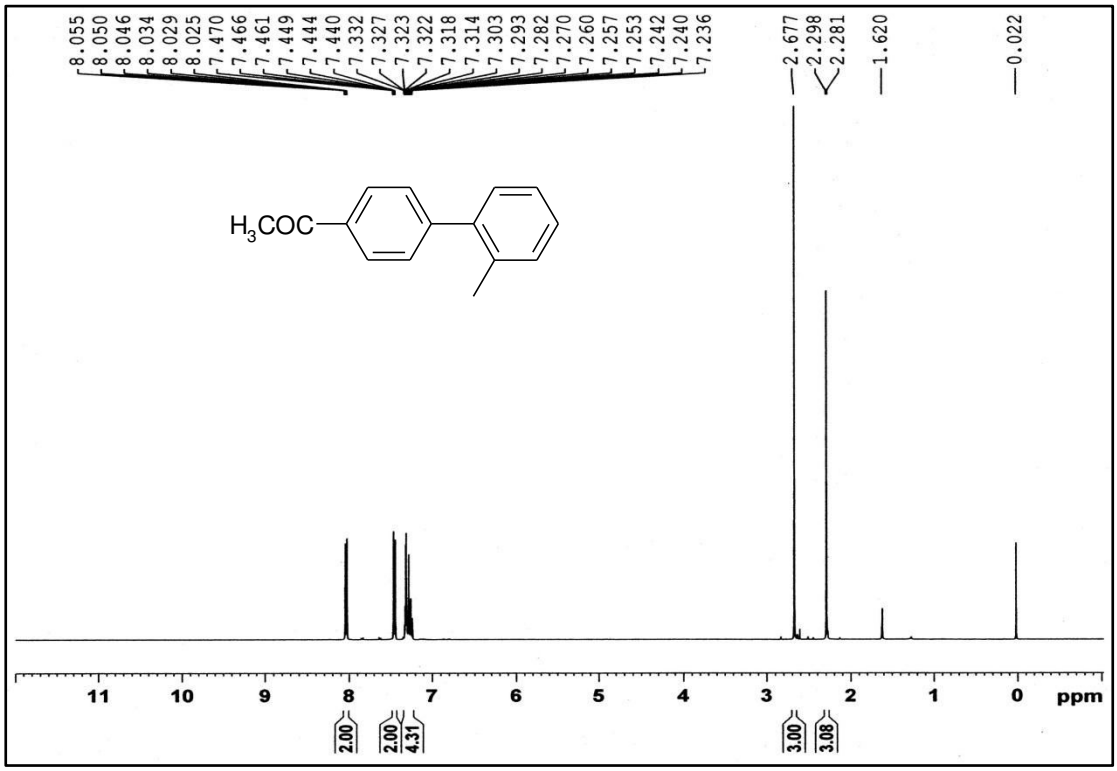
^{1}H-NMR Spectra of Compound 33 (400 MHz, $CDCl_3$)



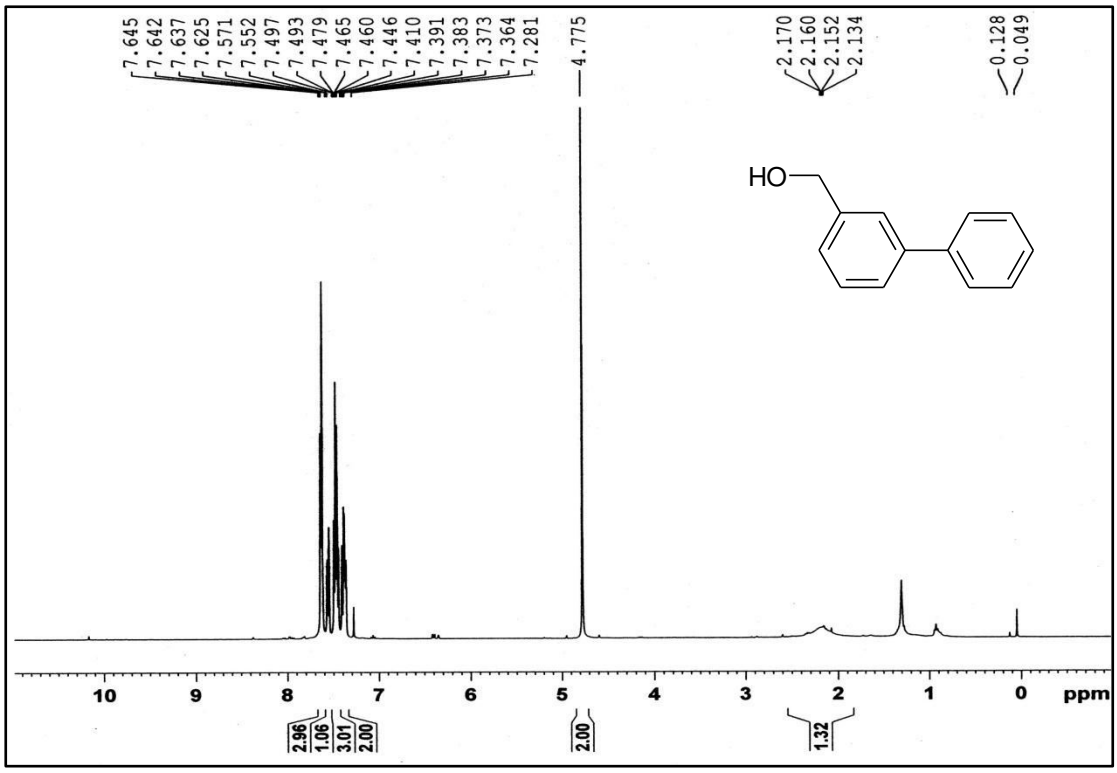
EI-Mass Spectra of Compound 33



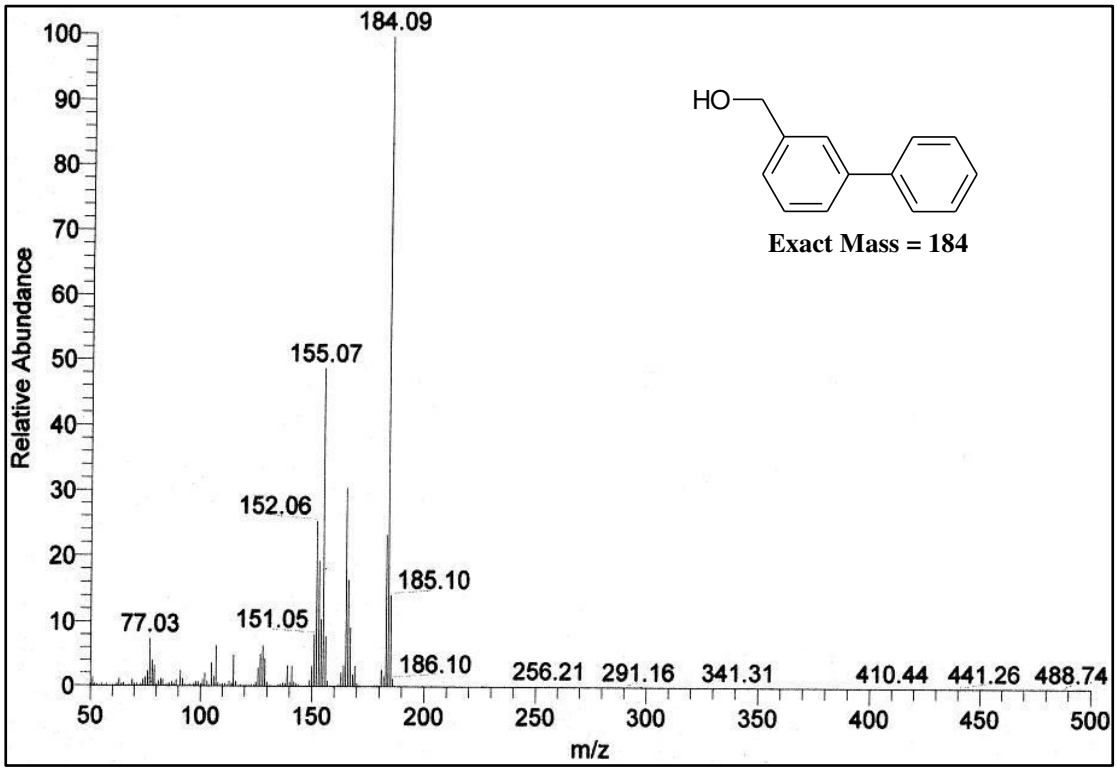
^{1}H-NMR Spectra of Compound 34 (400 MHz, $CDCl_3$)



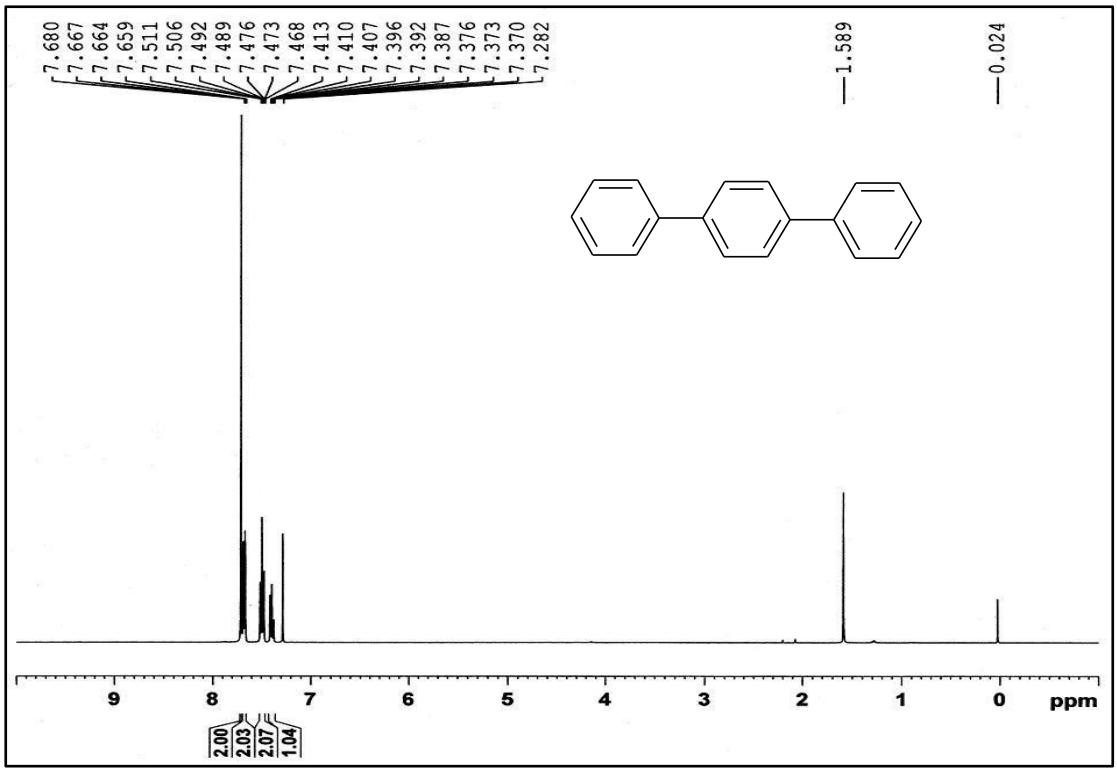
^{1}H-NMR Spectra of Compound 35 (400 MHz, $CDCl_3$)



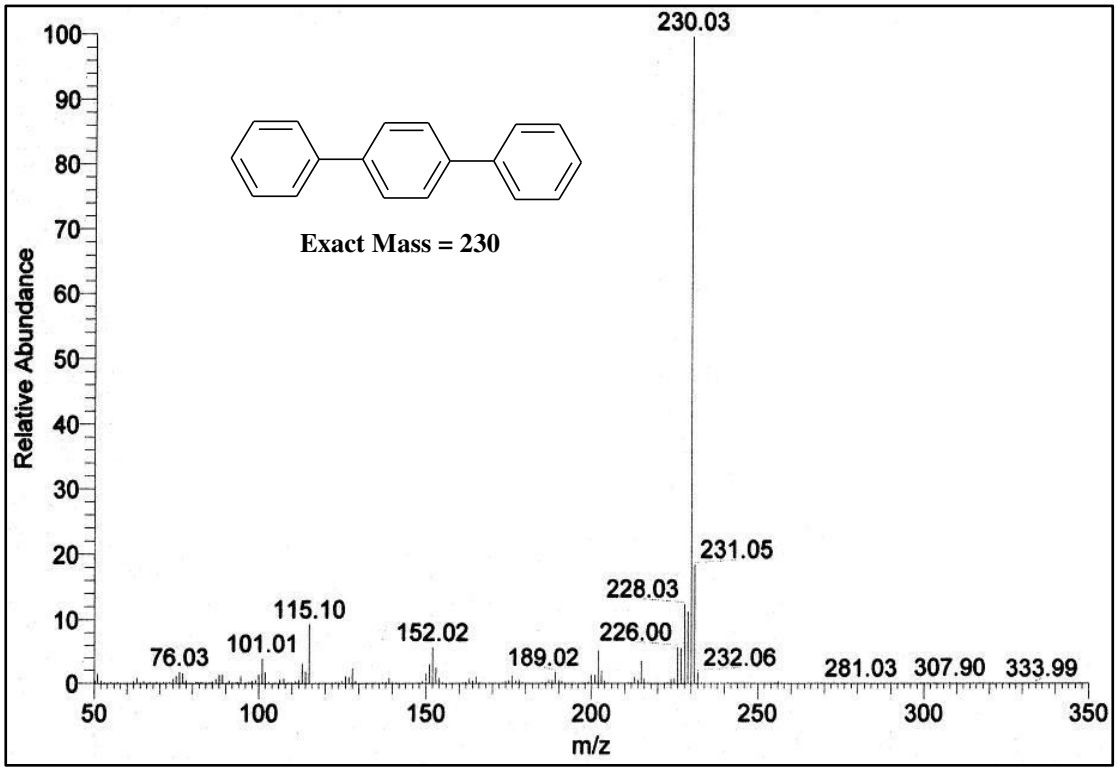
^{1}H-NMR Spectra of Compound 38 (400 MHz, $CDCl_3$)



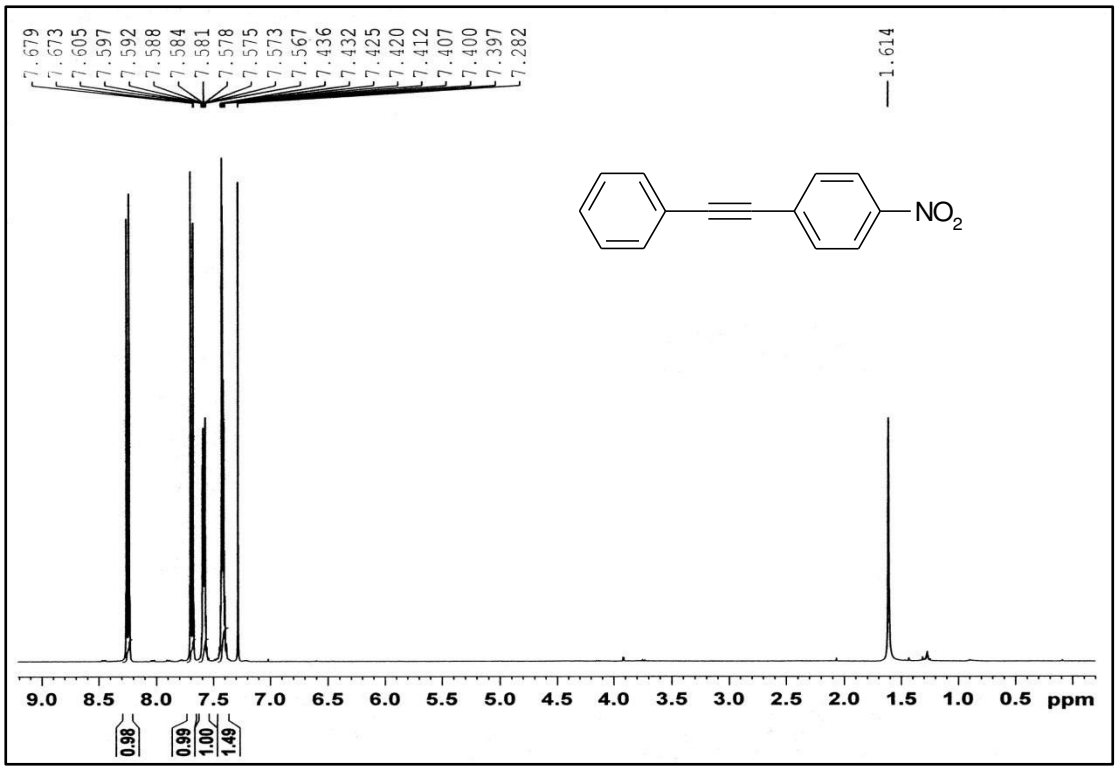
EI-Mass Spectra of Compound 38



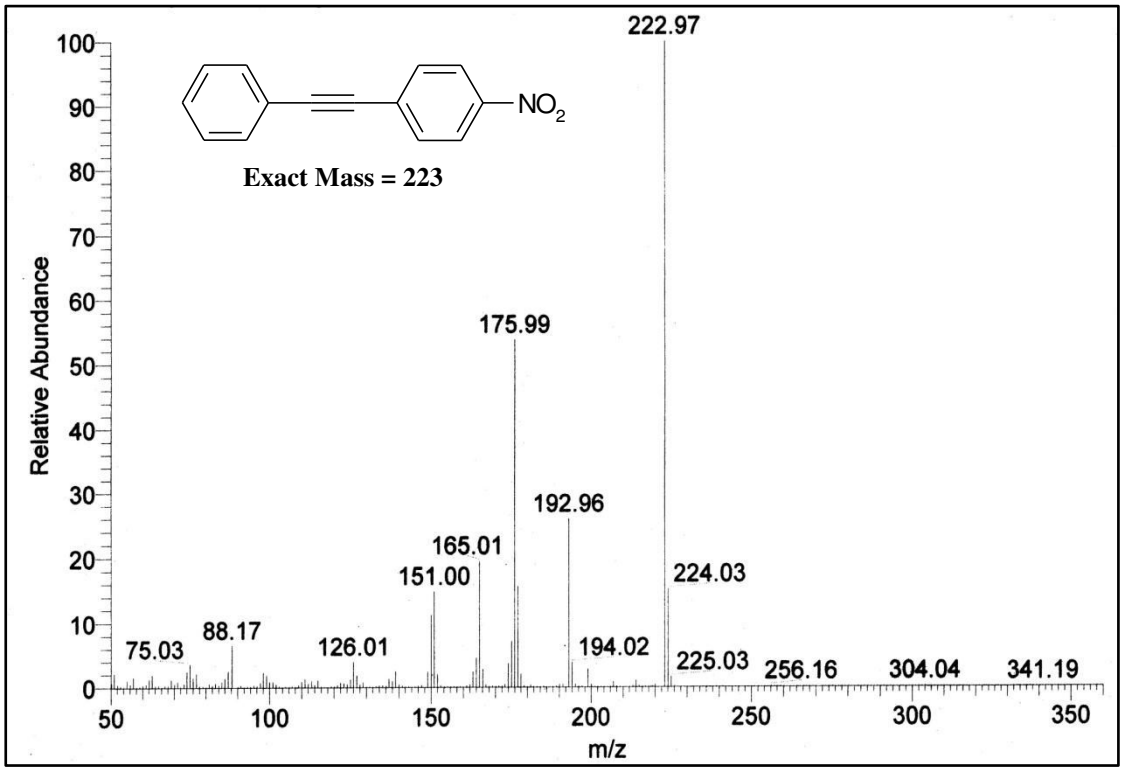
^{1}H-NMR Spectra of Compound 39b (400 MHz, $CDCl_3$)



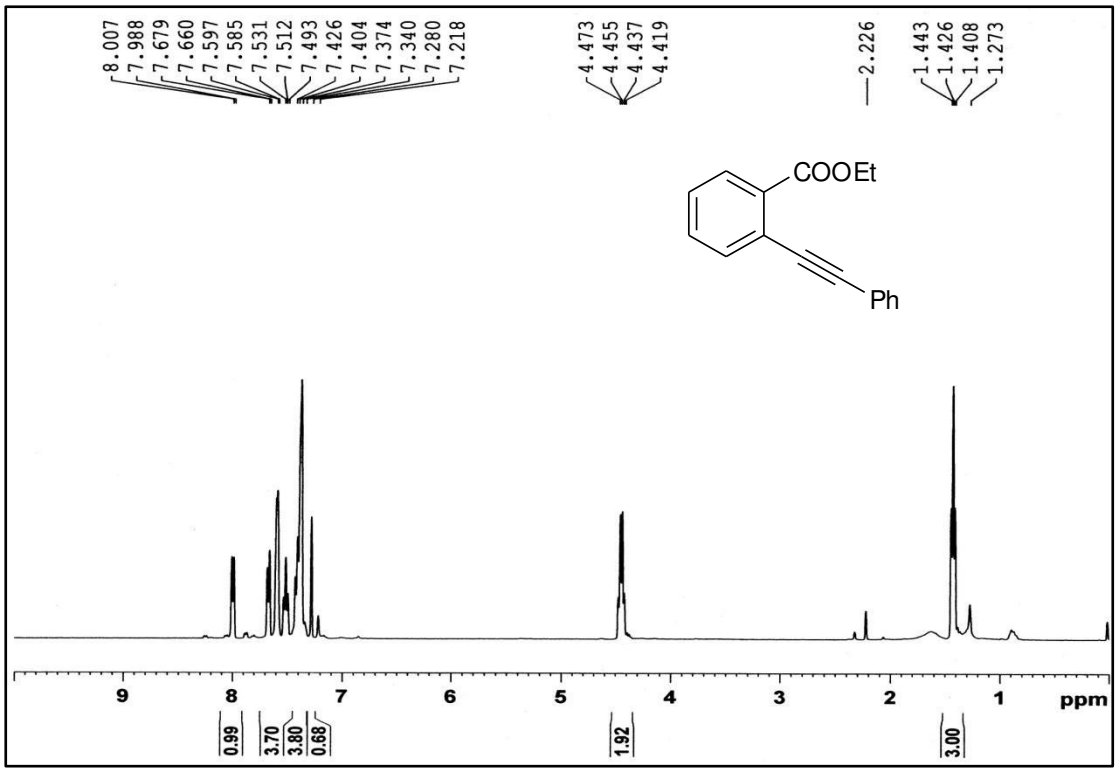
EI-Mass Spectra of Compound 39b



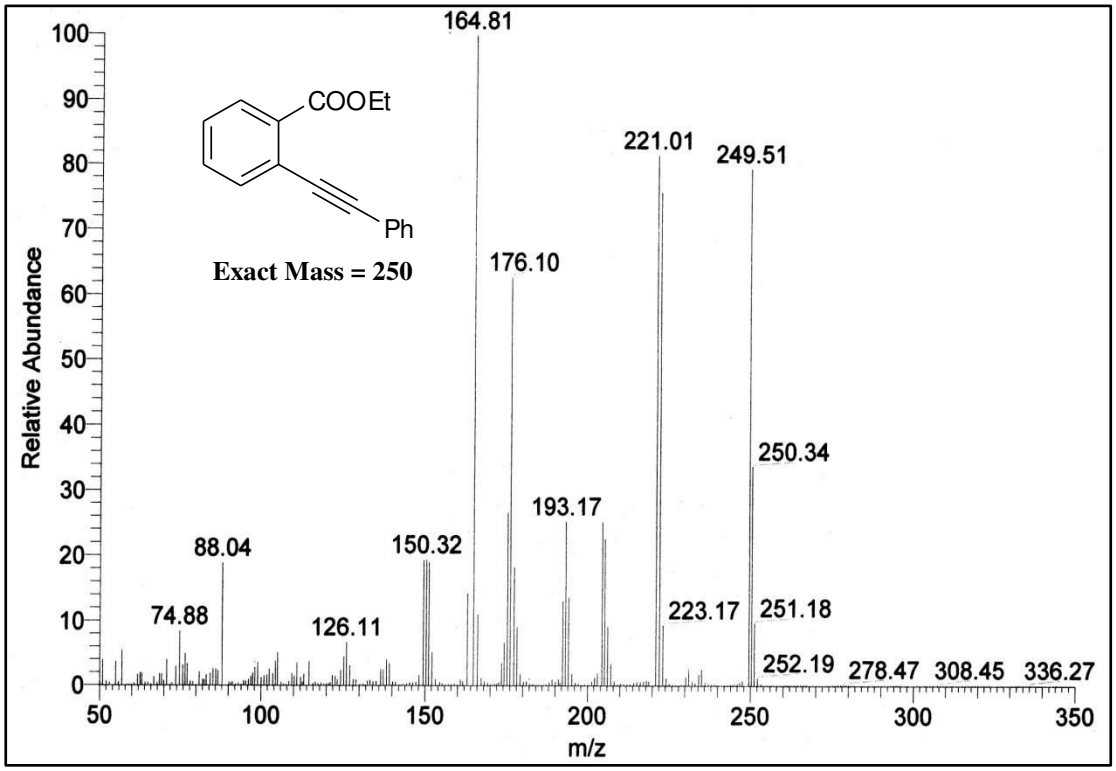
^{1}H-NMR Spectra of Compound 43 (400 MHz, $CDCl_3$)



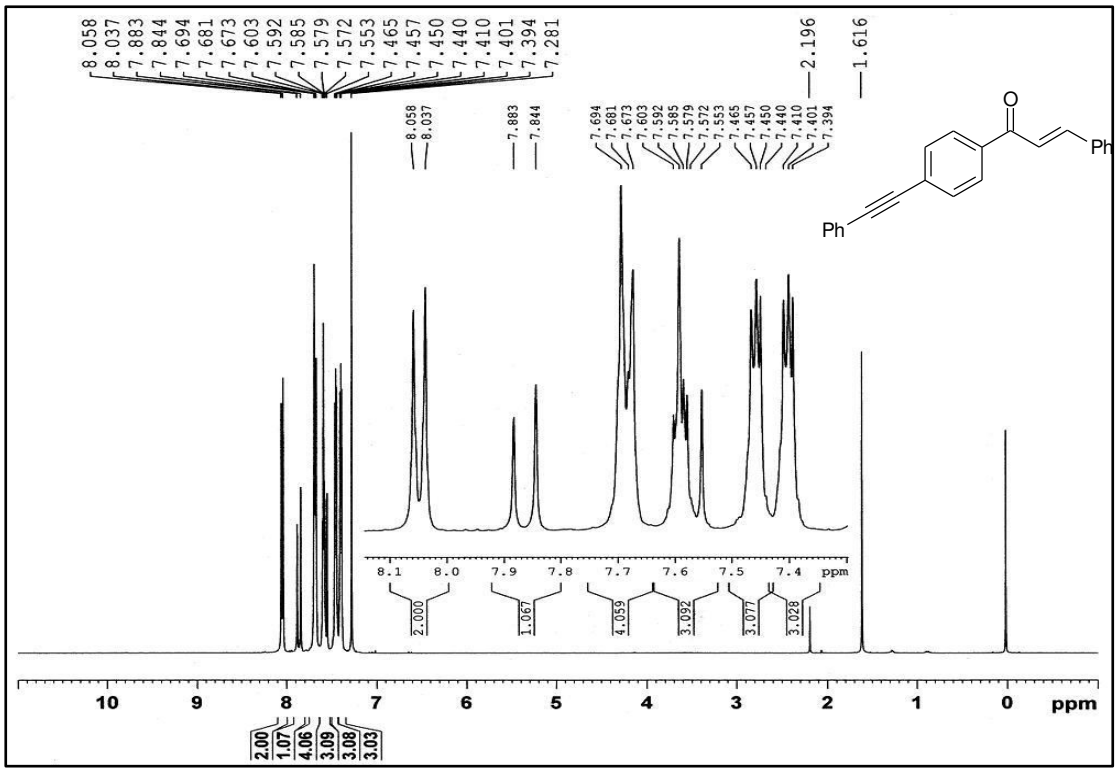
EI-Mass Spectra of Compound 43



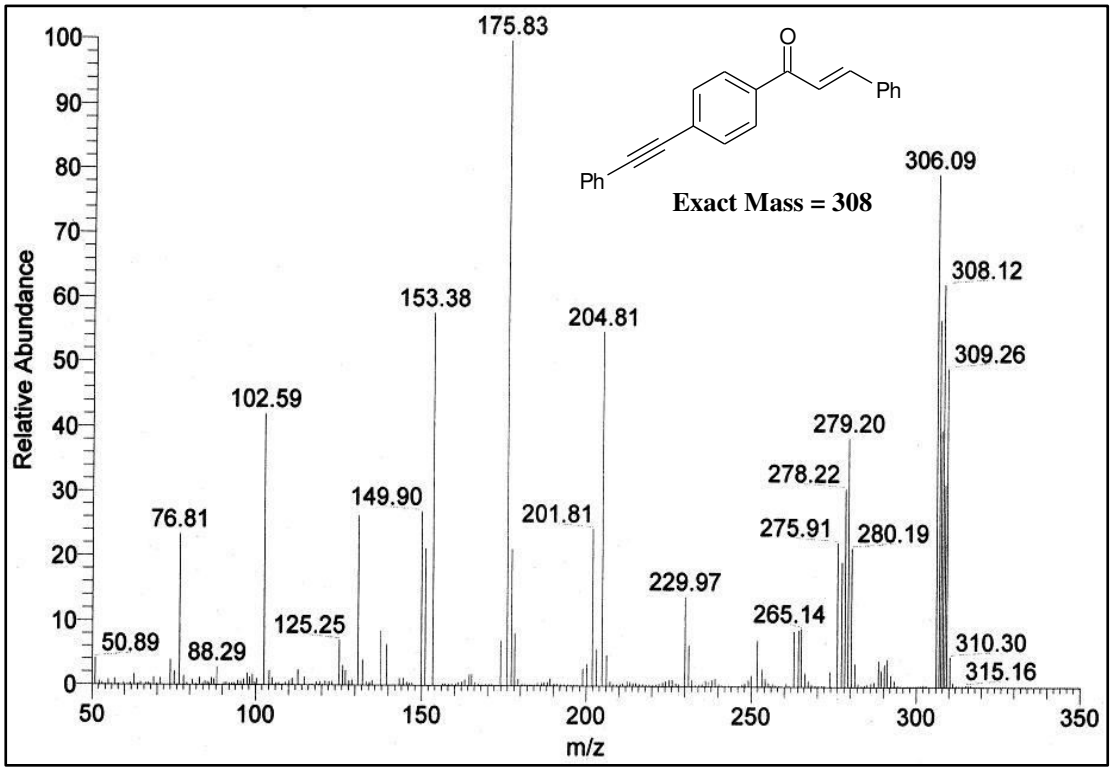
^{1}H-NMR Spectra of Compound 45 (400 MHz, $CDCl_3$)



EI-Mass Spectra of Compound 45



^{1}H-NMR Spectra of Compound 46 (400 MHz, $CDCl_3$)



EI-Mass Spectra of Compound 46

CONCLUSION

We have synthesized different derivatives of racemic aminobenzylnaphthols using modified Mannich Reaction (mMR) in good yields.

Air-stable, easily accessible Mannich bases, 1-(α-aminobenzyl)-2-naphthols, are used as efficient phosphine-free ligands in palladium catalyzed Mizoroki-Heck reaction and Suzuki-Miyaura reaction on variety of substrates under thermal as well as ultrasonic irradiation conditions.

Aryl bromides such as 1,2-dibromobenzene, 1,4-dibromobenzene, 2,7-dibromobenzene, 1,3,5-tribromobenzene and 1,2,4,5-tetrabromobenzene have been successfully used. Convenient synthesis of a variety of di-, tri- and even a 1,2,4,5-tetraarylated compound were prepared by use of this reaction.

Moreover 1-(α-Aminobenzyl)-2-naphthols are also screened as efficient phosphine-free ligands in palladium catalyzed "Copper-free Sonogashira reaction."

References

1. Mannich, C.; Krösche, W. *Arch. Pharm. Med. Chem.* **1912**, *250*, 647.
2. (a) De Meijere, F. Diederich (Eds), Metal-catalyzed cross-coupling reactions, Wiley-VCH, Weinheim, **2004.** (b) J. Tsuji, Palladium Reagents and Catalysts, Wiley, Chichester, **2004.**
3. (a) Heck, R. F.; Nolly, J. P. *J. Org. Chem.* **1972**, *37*, 2320. (b) Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581.
4. (a) Miyaura, A.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Glasnov, T.; Stadlbauer, W.; Kappe, C. *J. Org. Chem.* **2005,** *70*, 3864. (c) Polackova, V.; Hutka, M.; Toma, S. *Ultrason. Sonochem.* **2005**, *12*, 99
5. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467.
6. (a) Bohm, V. P. W.; Herrmann, W. A. *Eur. J. Org. Chem.* **2000**, *200*, 3679. (b) Mery, D.; Heuze, K.; Astruc, D. *Chem. Commun.* **2003**, *15*, 1934.
7. (a) Phan, N.; Sluys, M.; Jones, C. *Adv. Synth. Catal.* **2006**, *348*, 609. (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009
8. Szatmari, I.; Fulop, F. *Tetrahedron* **2013**, *69*, 1255.
9. (a) Mallory, F. B.; Wood, C.; Gordon, J. T. *J. Am. Chem. Soc.* **1964**, *86*, 3094. (b) Harvey, F. R. *Polycyclic Aromatic Hydrocarbons*, Willey-VCH, New York, **1997**.
10. (a) Winter, W.; Langjahr, U.; Meier, H.; Merkuschew, J.; Juriew, J. *Chem. Ber.* **1984**, *117*, 2452. (b) Dawood, K. M. *Tetrahedron* **2007**, *63,* 9642. (c) Alacid, E.; Najera, C. *J. Org. Chem.* **2009**, *74*, 2321. (d) Lansky, A.; Reiser, O.; De Meijere, A. *Synlett* **1990**, *7*, 405.
11. (a) Ambulgekar, G. V.; Bhanage, B. M.; Samant, S. D. *Tetrahedron Lett.* **2005**, *46*, 2483. (b) Ross, N. A.; MacGregor, R. R.; Bartsch, R. A. *Tetrahedron* **2004**, *60*, 2035. (c) Namboodiri, V. V.; Varma, R. S. *Org. Lett.* **2002**, *4*, 3161. (d) Gholap, A. R.; Venkatesan, K.; Pasricha, R.; Daniel, T.; Lahoti, R. J.; Srinivasan, K. V. *J. Org. Chem.* **2005**, *70*, 4869.
12. (a) Paul, N. K.; Dietrich, L.; Jha, A. *Synth. Commun*. **2007**, *37*, 877. (b) Littman, J. B.; Brode, W. R. *J. Am. Chem. Soc.* **1930**, *52*, 1655. (c) Cardellicchio, C.; Ciccarella, G.; Naso, F.; Schingaro, E.; Scordari, F. *Tetrahedron: Asymmetry* **1998**, *9*, 3667. (d) Huang, J.; Youssef, D.; Cameron, S.; Jha, A. *Arkivoc* **2008** (xvi), 165.
13. (a) Heynekamp, J. J.; Weber, W. M.; Hunsaker, L. A.; Gonzales, A. M.; Orlando, R. A.; Deck, L. M.; Vander Jagt D. L. *J. Med. Chem*. **2006**, *49*, 7182. (b) Wan, P.;

Davis, M. J.; Teo, M. A. *J. Org. Chem*. **1989**, *54,* 1354. (c) Cella, R.; Stefani, H. A. *Tetrahedron* **2006**, *62*, 5656. (d) Díez-Barra, E.; García-Martínez, J. C.; Merino, S.; del Rey, R.; Rodríguez-López, J.; Sánchez-Verdú, P.; Tejedac, J. *J. Org. Chem.* **2001**, *66*, 5664. (e) Malkes, L. Y.; *Zhurnal Obshchei Khimii.* **1966**, *2*, 297.

14. (a) Percec, V.; Golding, G. M.; Smidrkal, J.; Weichold O. *J. Org. Chem.* **2004**, *69*, 3447. (b) Desmarets, C.; Omar-Amrani, R.; Walcarius, A.; Lambert, J.; Champagne, B.; Fort, Y.; Schneider, R. *Tetrahedron* **2008**, *64*, 372.
15. (a) Demir, A. S.; Findik, H.; Saygili, N.; Subasi N. T. *Tetrahedron* **2010**, *66*, 1308. (b) Zeng, M.; Du, Y.; Qi, C.; Zuo, S.; Li, X.; Shao L.; Zhang, X. *Green Chem.*, **2011**, *13*, 350.
16. (a) Rajakumar, P.; Ganesan, K. *Synth. Commun.* **2004**, *34*, 2009. (b) Bergmann, E. D.; Blumberg, Sh.; Bracha, P.;Epstein, Sh. *Tetrahedron* **1964**, *20*, 195.
17. (a) Chandrasekhar, V.; Narayanan, R. S.; Thilagar P. *Organometallics* **2009,** *28*, 5883. (b) Nagaki, A.; Takabayashi, N.; Tomida, Y.; Yoshida, *J. Org. Lett.* **2008**, *10*, 3937.
18. Dong, C-G.; Hu, Q-S. *J. Am. Chem. Soc.* **2005**, *127*, 10006.
19. Lee, K.-S.; Kim, J.-P.; Lee, J.-S. *Polymer* **2010**, *51*, 632.
20. (a) Jing, X.; Xu, F.; Zhu, Q.; Ren, X.; Yan, C.; Wang, L.; Wang, J. *Synth. Commun.* **2005**, *35*, 3167. (b) Kao, M.-T.; Chen, J.-H.; Chu, Y.-Y.; Tseng, K.-P.; Hsu, C.-H.; Wong, K.-T.; Chang, C.-W.; Hsu, C.-P.; Liu, Y.-H. *Org. Lett.* **2011**, *13*, 1714.
21. Harada, K.; Hart, H.; Du, C.-J. F. *J. Org. Chem.* **1985**, *50*, 5524.
22. (a) Hammond, G. S.; Reeder, C. E. *J. Am. Chem. Soc.* **1958**, *80*, 573. (b) Song, C.; Ma, Y.; Chai, Q.; Ma, C.; Jiang, W.; Andrus, M. B. *Tetrahedron* **2005**, *61*, 7438.
23. (a) Freundlicha, J. S.; Landis, H. E. *Tetrahedron Lett.* **2006**, *47*, 4275. (b) Molander, G. A.; Cavalcanti, L. N. *J. Org. Chem.* **2011**, *76*, 7195.
24. (a) Li, P.; Wanga, L.; Li, H. *Tetrahedron* **2005**, *61*, 8633. (b) Kakusawa, N.; Yamaguchi, K.; Kurita, J. *J. Organometal. Chem.* **2005**, *690*, 2956.
25. Marchal, E.; Uriac, P.; Legouin, B.; Toupet, L.; Weghe, P. *Tetrahedron* **2007**, *63*, 9979.