Chapter 5

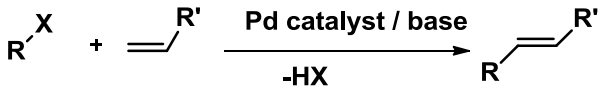
APPLICATION OF HETEROGENEOUS Pd CATALYST IN C-C COUPLING REACTIONS

Contents

5.1. *Introduction*

Palladium-catalysed cross-coupling reactions such as Mizoroki-Heck, Suzuki–Miyaura, Stille, Sonogashira, etc. have gained enormous importance during the last few decades since many valuable products can be efficiently synthesized using these reactions with high efficiency.[1]

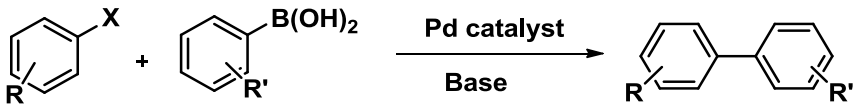
The reaction of alkyl- or aryl-substituted alkenes containing at least one hydrogen atom at the C=C double bond with aryl, benzyl, and vinyl halides or triflates, proceeds in presence of suitable catalyst resulting in the formation of new C–C bond and affords a substituted alkene, generally referred as Mizoroki-Heck coupling (or Mizoroki–Heck reaction) [**Scheme 1**].



R = Ar, Bn, vinyl
R' = H, Alk, Ar, COOAlk
X = Cl, Br, I, OTf

Scheme 1: Mizoroki-Heck reaction

It is generally catalysed by palladium species generated *in situ* from various Pd(II) salts or complexes and requires bases (organic or inorganic) to neutralize the acid HX formed during the reaction.[2] A wide range of functional groups, both in the alkene and in the halide portion, are compatible with the Mizoroki-Heck coupling,[2] which renders the reaction synthetically robust and thus practically widely applicable. Another important reaction is the palladium catalyzed Suzuki–Miyaura reaction in which cross-coupling reaction of aryl halides with arylboronic acids, representing the most successful method for the preparation of biaryls [**Scheme 2**].



Scheme 2: Suzuki–Miyaura reaction

For all these palladium catalysed reaction development of catalyst is of prime concern.

In regards to the current challenges arising from the demands of industrial and fine chemistry, catalysts should have high activity and selectivity to the target products and also have to be easily accessible, environmentally favourable, stable (robust) and recyclable.[3] Generally the catalysts are divided as homogeneous and heterogeneous types, each having their advantages. Although the former category is believed to be more

efficient due to effective interactions between reactant species being in the same phase, there are some distinct advantages of the latter type. The advantages of heterogeneous metal catalysts include easy separation from the reaction mixture, reusability of the catalysts, less contamination of the toxic metal ions in the products, cost benefits and some environmental considerations. Processes using the heterogeneous catalysts can be modified in to continuous flow procedures for the practical applications. The key aspect of the development of heterogeneous catalyst involves loading of transition metal ion to the solid surface. This concept of loading catalyst on solid support involves attaching a suitable ligand on the appropriate surface and then exposing this to metal ions to form anchored complex for the applications as heterogeneous catalysis.[4,5] Adequate care needs to be taken during the process of making the heterogeneous catalysts. The activity of the metal complex needs to be retained to perform the role of the catalysis, offer access to the reacting species and prevent leaching the metal ions during the reaction as well as the work-up steps and hence maintaining the reusability for subsequent catalytic cycles. Organic polymers are often chosen as supports to anchor metal ions to prepare heterogeneous catalysts. The development in the field of polymer chemistry has lead to the availability of polymeric materials which are insoluble in many organic solvents, the materials can be easily functionalized and its porosity can be tuned to modify permeability. The area of polymer-anchored metal complexes and their applications as heterogeneous catalysts for many useful organic transformations is widely investigated.[6,7] Various supports include the use of soluble polymer support[8], dendrimers[9], polysiloxanes[10], self-supported polymeric catalysis[11], nano-particles[12], metal ions anchored on clays and zeolites[13], metal oxides and mesoporous materials[14] etc. Till date, many heterogeneous palladium catalytic systems were developed for the C–C cross-coupling reactions, such as Pd(II)– Schiff base complex supported on multi-walled carbon nanotubes,[15] Pd catalyst supported on amine-functionalized glycidylmethacrylate gel type terpolymers,[16] mesoporous silica-supported Pd catalyst,[17] Pd–pyridine complex immobilized on hydrotalcite,[18] Pd-grafted porous metal–organic framework material,[19] and polymer-supported Pd–NHC complex,[20] just to mention the few.

In the area of heterogeneous catalysis modified silica is the most commonly utilized support for immobilizing Pd-complexes. Shimizu *et al.*,[21] Bedford *et al.*[22] and Crudden *et al*[23,24,25] have shown that mesoporous silica can be modified with commercially available thiol ligands, resulting in recoverable catalysts for cross-coupling reactions, such as the Suzuki–Miyaura and Heck reactions. A novel catalytic system is reported by H. Gruber-

Woelfler *et al* where $Pd(OAc)_2$ is attached to a bis(oxazoline) ligand that is covalently bonded to 3-mercaptopropyl-functionalized silica gel and to show its catalytic utility for Suzuki-Miyaura reaction [**Figure 1**].[26]

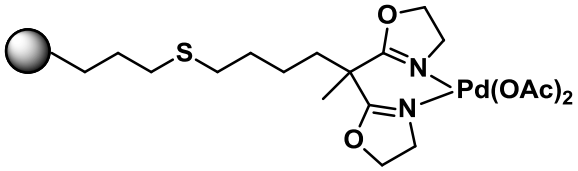


Figure 1

M. Ghiaci *et al* reported development of efficient heterogeneous Pd catalytic system based on immobilization of Pd nanoparticles (PNPs) on a silica-bonded propylamine-cyanuric-cysteine (SiO_2-PA-Cyan-Cys) substrate [**Figure 2**].

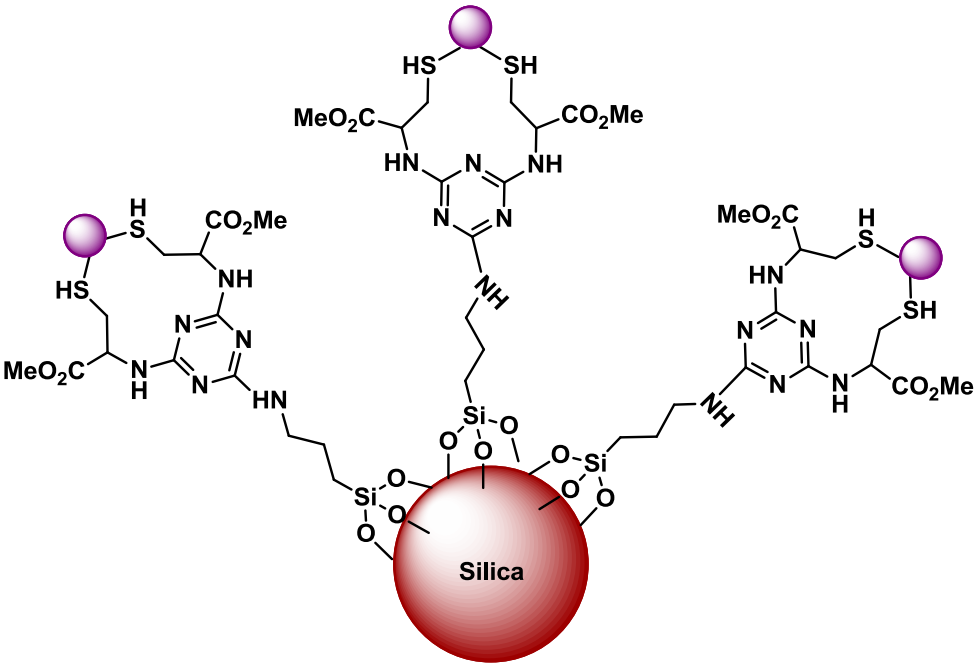


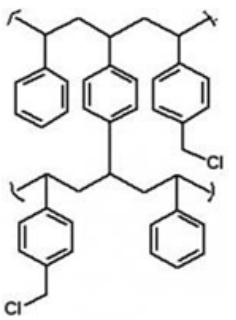
Figure 2

The catalytic activity of this system was investigated in the Suzuki and Sonogashira cross-coupling reactions. The catalyst showed excellent performance in these two reactions, including various aryl halide derivatives with phenylboronic acid and phenyl acetylene under green conditions. Also the catalyst was recycled for several runs without any significant loss of catalytic activity.[27]

Apart from the inorganic supports some natural biopolymers, such as chitosan,[28] cellulose,[29] wool,[30] etc. have also been used as efficient polymer supports in several important palladium-catalyzed transformations. In this context, Lei *et al* have reported the use of animal fibres (wool) due to the facts that the animal fibres themselves could be used as a solid phase ligand with no further functionalization. Furthermore, the loaded

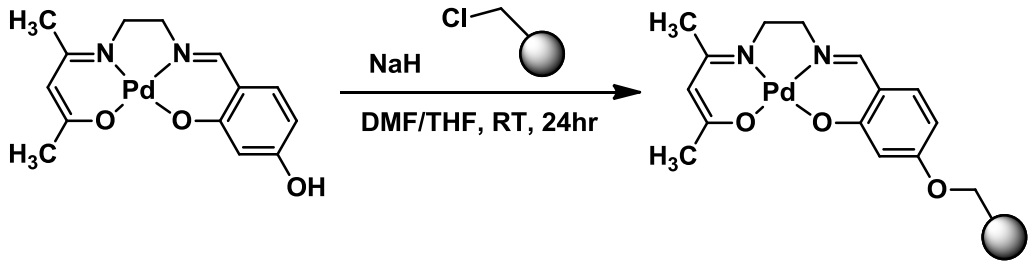
palladium particles could be distributed evenly on the surface of the fibers because of the structurally ordered amino acid chains. A heterogeneous biopolymer complex wool–Pd catalyst was applied under aqueous coupling reaction condition for aryl iodides and bromides with arylboronic acid. The results showed that the reactions could be conducted in neat water under atmospheric conditions with water-insoluble or even solid aryl halides and the catalyst system has the advantages of excellent yields, environmental friendliness, and catalyst recyclability.[31]

Amongst the polymer supported organic transformations, Merrifield first reported the concept of solid-phase synthesis for peptide synthesis with the concept that if peptide is attached to some insoluble support then the unreacted reagents can be simply removed by washings which can greatly reduce the purification time. This concept was realized by Merrifield in his pioneering use of heterogeneous chloromethylated polystyrene with cross-linking by divinylbenzene. This materials widely known as Merrifield resin and has been used in various ways to facilitate synthesis and product purification in large number of processes.[32]



Merrifield resin

It is important not only as a support for solid-phase synthesis but also for reagent and catalyst immobilization. Since then many polymer supported catalysts have been developed. Phan *et al* have reported immobilisation of salen-type palladium (II) complex onto Merrifield resin[33] [**Scheme 3**].



Scheme 3

The supported complex was shown to be effective recyclable heterogeneous catalyst for the Suzuki cross-coupling reaction without the use of phosphine ligands. Leaching of the metal into solution from the supported catalyst was also negligible. A novel polymer-supported N-heterocyclic carbene (NHC) system has been prepared by Lee *et al* [**Figure 3**] from chloromethyl polystyrene resin using a simple procedure and used as the ligand for palladium catalyst. The polymer-

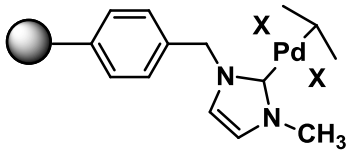
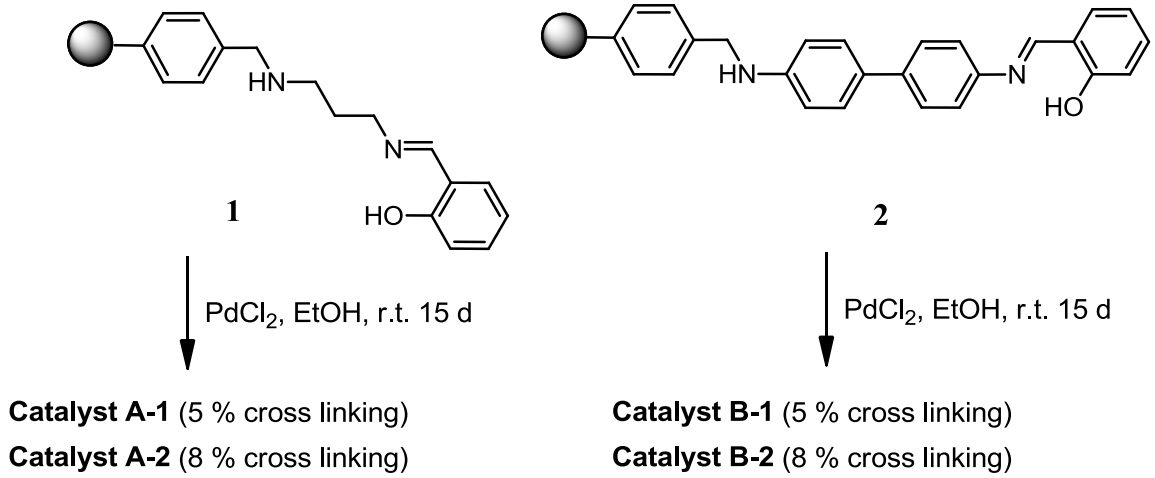


Figure 3

supported Pd-NHC complexes were shown to be efficient for the catalytic Suzuki cross-coupling reaction.[34]

5.2. *Result and Discussion*

In the present chapter we present the screening of polymer anchored palladium catalyst for Heck reaction, Suzuki reaction and one-pot *O*-Alkylation-Suzuki reaction. The two set of polymer anchored Schiff base-Palladium complexes were screened for its catalytic activity. Polymers **1** with different cross linking (5 or 8 %) afforded two polymer-supported palladium catalysts **A-1** and **A-2 [Scheme 4**]. Similarly **2** afforded another set of palladium catalysts **B-1** and **B-2**.



Scheme 4: Synthesis of polymer anchored Schiff bases

Depending on different cross linking in the polymer support and the different linking groups four different catalysts **A-1**, **A-2**, **B-1** and **B-2** which are designated as shown below were screened for its catalytic activity.

A-1: 5% poly(S-DVB)Pd(II) (1,3-DAP-SB)

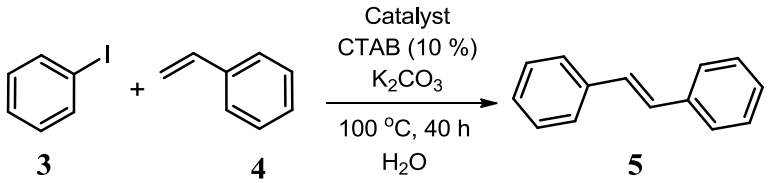
A-2: 8% poly(S-DVB)Pd(II) (1,3-DAP-SB)

B-1: 5% poly(S-DVB)Pd(II) (4,4-DABP-SB)

B-2: 8% poly(S-DVB)Pd(II) (4,4-DABP-SB)

5.2.1 *Screening of supported catalysts for standard Mizoroki-Heck reaction*

The polymer anchored Pd-catalysts were screened for the standard reaction of synthesis of stilbene by reaction of iodobenzene and styrene in presence of base [**Scheme 5**].



Scheme 5: Standard Mizoroki–Heck reaction

The results are presented in **Table 1**. All the four catalysts prepared were quite effective and the products were obtained in good yield with respectable TON for the reactions. Catalyst **A-2** was slightly more active since its crosslink and loading is also higher. The reaction was carried out in water at 100 ^{o}C with a small quantity of CTAB to increase solubility of reagents. While toluene gave poor yield probably due to the poor swelling of beads and hence ineffective penetration of reagents to reach the active sites, the other solvents, DMA and DMF are found to be active for this reaction.

Table 1: Screening of supported catalysts for standard Mizoroki–Heck reaction.[a]

No	Catalyst	Pd content[b] (g/g resin)	Crosslink (%)	Yield[c] (%)	TON
1	No Catalyst	-	-	No Reaction	-
2	A-1	1.0×10^{-4}	5	73	7301
3	A-2	2.5×10^{-4}	8	96	9580
4	B-1	2.0×10^{-4}	5	93	9294
5	B-2	1.7×10^{-4}	8	89	8897

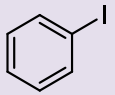
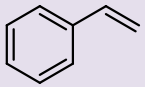
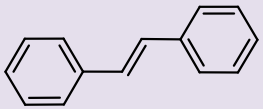
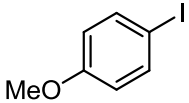
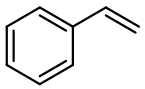
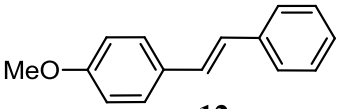
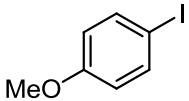
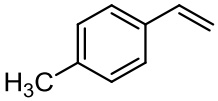
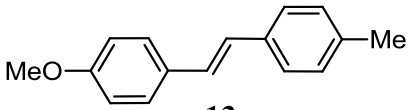
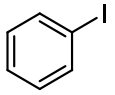
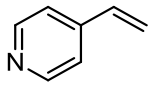
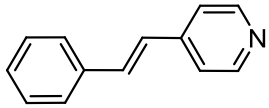
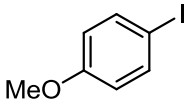
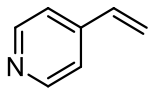
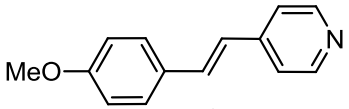
[a] All reactions were run for 40 h at 100 ^{o}C with CTAB (10 mol%).

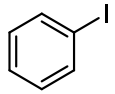
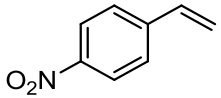
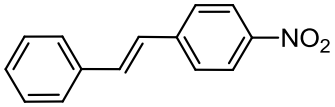
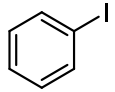
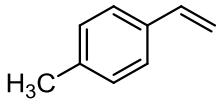
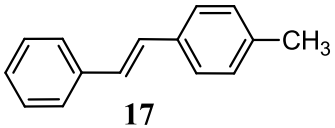
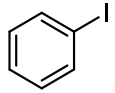
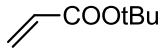
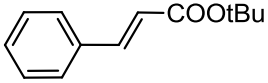
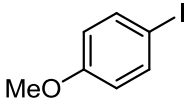
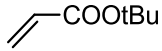
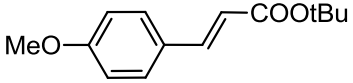
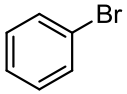
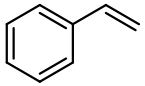
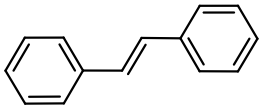
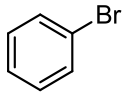
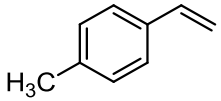
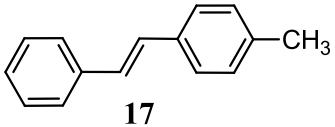
[b] Pd content (0.01 mol%) for all reactions.

[c] Isolated product, pure trans isomer.

Having established that the catalyst **A-2** and **B-1** are more effective among catalysts studied, number of different aryl iodides and aryl bromides were screened with styrene and its derivatives to see the generality of the system. The results are summarized in **Table 2**. For this study a slightly higher quantity of the catalyst is taken (0.05 mol% of Pd) and a combination of water and DMA is used. The choice of solvent is based on the solubility of aryl halides and styrenes. From the point of view of environmental safety it is beneficial to explore the possibility to use water as solvent, preferably fully or as combination with some polar organic solvent. In all the reactions it is very important to stir the contents continuously but carefully using a small spherical shaped magnetic stirrer bar in order to keep the beads in good shape. The Mizoroki–Heck reaction involves three main steps in the catalytic cycle, *viz* oxidative addition of aryl halide to Pd, insertion of styrene and finally reductive elimination of stilbene. As expected the addition of aryl bromide was less effective due to stronger Ar–Br bond than the corresponding iodides, hence slightly lower yields were observed for them. Under the present catalytic condition aryl chlorides were almost completely ineffective for the olefination reaction.

Table 2: Application of the catalyst for palladium catalyzed Mizoroki–Heck reaction[a]

No.	Arylhalide ArX	Olefin	Solvent Ratio [Temp^{o}C]	Catalyst A-2 (mol% of Pd)	Stilbenes Ar-CH=CH-Ar'	%Y[b]	TON
1	 **3**	 **4**	DMA [140]	**0.001**	 **5**	89	**88,408**
2	 **6**	 **4**	H_2O[c] [100]	0.01	 **12**	91	9089
3	 **6**	 **7**	DMA [140]	0.05	 **13**	95	1886
4	 **3**	 **8**	DMA:H_2O {2:1} [120]	0.05	 **14**	83	1675
5	 **6**	 **8**	DMA:H_2O {2:1} [120]	0.05	 **15**	65	1290

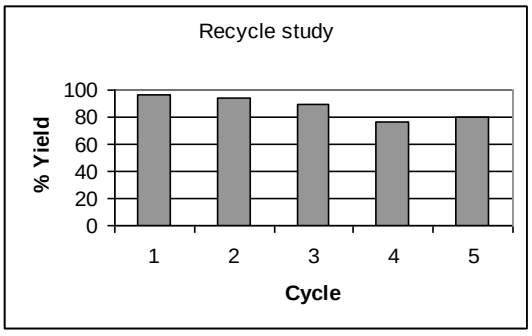
6	 **3**	 **9**	DMA [140 °C]	0.05	 **16**	89	1784
7	 **3**	 **7**	DMA [140 °C]	0.05	 **17**	94	1878
8	 **3**	 **10**	DMA [140 °C]	0.05	 **18**	85	1700
9	 **6**	 **10**	DMA [140 °C]	0.05	 **19**	83	1660
10	 **11**	 **4**	DMA [140 °C]	0.05	 **5**	41	812
11	 **11**	 **7**	DMA [140 °C]	0.05	 **17**	50	1004

[a] All reactions run for 40 h with K_2CO_3 (2 eq.). [b] Isolated yield, mostly trans isomer. [c] With CTAB (10%).

Catalyst recycle study for Heck Reaction

The ease of separation and reuse of the polymer anchored Pd catalyst is important consideration. The catalyst beads were separated carefully from first cycle where water was used as solvent with CTAB (10%) and washed several times with water, then with methanol and dried under vacuum. The recovered catalyst when reused for identical reaction showed only marginal drop in the conversion [**Figure 4**] in next two cycles. However, there was noticeable drop in the yield in the fourth cycle and the beads started to get coated with white material –most likely polystyrene, formed by the polymerization of styrene. However, the catalyst beads from the fourth cycle when subjected to additional cleaning with toluene before reuse in the fifth cycle showed some recovery in activity, confirming the possibility of polystyrene being deposited and blocking the access of reagents to catalytic sites in the earlier cycle.

Hence, these supported complexes were found to be very effective catalysts for Mizorok-Heck reaction for aryl iodides and aryl bromides with number of styrenes.



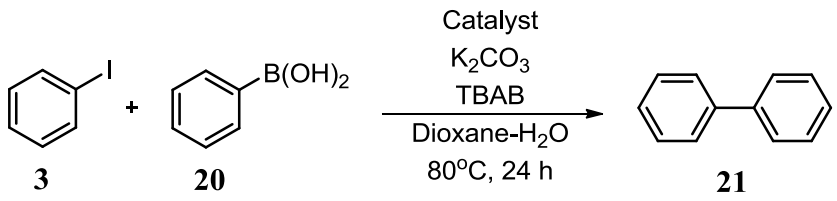
No. of Cycles	Yield (%)	TON
1	96	9580
2	93.8	9354
3	90	8957
4	75.6	7540
5	80	7982

Figure 4: Recycle study of the catalyst **A-2** for standard reaction of iodobenzene and styrene

5.2.2 *Application of polymer supported catalyts for Suzuki reaction*

Synthesis of biaryls can be efficiently achieved by palladium mediated Suzuki-Miyaura reaction[35] of aryl halide and arylboronic acid, as against Ullmann coupling reaction[36] which requires drastic conditions. In this part of the chapter we present our findings to utilize the present series of polymer supported palladium catalysts for the Suzuki-Miyaura reaction and a combination of one-pot *O*-alkylation-Suzuki reaction.

The catalysts of both the sets with known amount of cross linking and palladium loading were screened for the standard Suzuki-Miyaura reaction with phenyl iodide **3** and phenyl boronic acid **20** [**Scheme 6**, **Table 3**]. All the catalysts were found to be very effective as evident from the high isolated yields and Turn Over Numbers (TON).



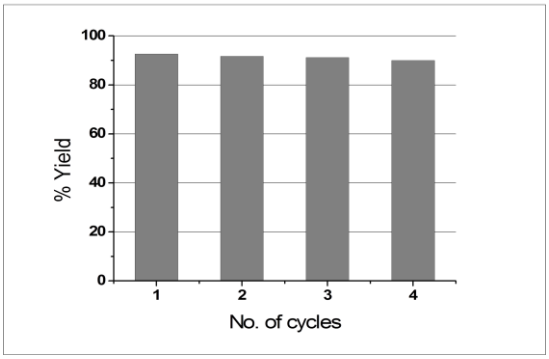
Scheme 6: Standard Suzuki-Miyaura reaction

Table 3: Screening of supported catalysts for standard Suzuki-Miyaura reaction

No	Catalyst	Pd content (g/g resin)	Crosslink (%)	Yield (%)	TON
1	No Catalyst	-	-	No Reaction	-
2	**A-1**	1.0×10^{-4}	5	93	7398
3	**B-1**	2.0×10^{-4}	5	98	9737
4	**A-2**	2.5×10^{-4}	8	96.67	9607
5	**B-2**	1.7×10^{-4}	8	98.66	9803

The catalyst **B-2** was then scanned for a series of aryl bromides as they are more readily accessible and are stable substrates compared to their iodo derivatives. The catalyst works consistently well for many examples [**Table 4**] and can tolerate several functional groups for the Suzuki-Miyaura coupling reaction with very low palladium loading (0.01 mol%). Two derivatives of aryl boronic acids were scanned for the reaction where the products were isolated in good yields.

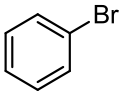
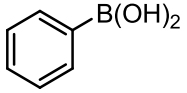
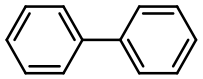
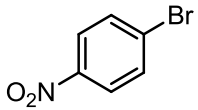
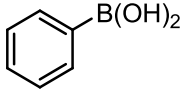
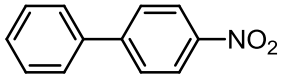
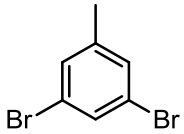
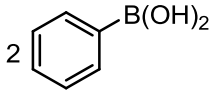
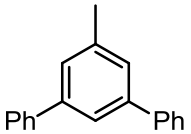
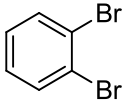
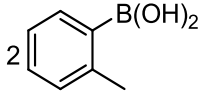
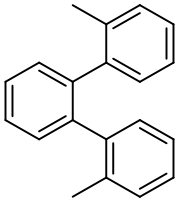
The efficiency of the heterogeneous catalyst for Suzuki reaction tested by conducting four reactions with identical conditions with recycled catalyst **A-1** [**Figure 5**]. As can be seen the catalyst showed negligible loss in activity, which was observed during recycle study of Mizoroki-Heck reaction due to polymerization of styrene used in Heck reaction. Hence it confirms the reusability of the polymer anchored Pd catalyst.

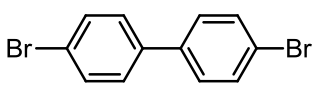
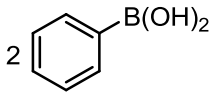
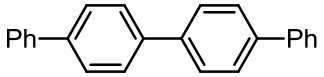
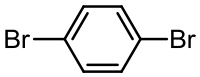
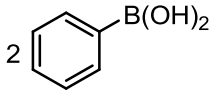
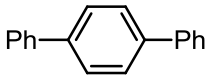
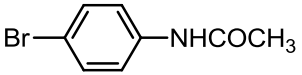
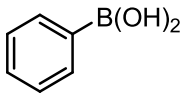
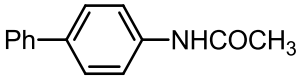
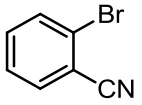
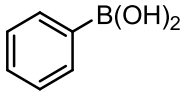
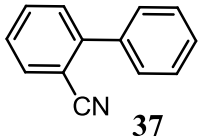
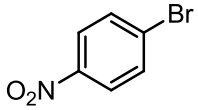
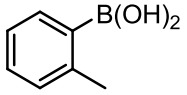
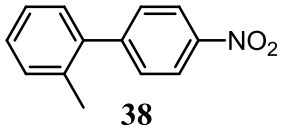
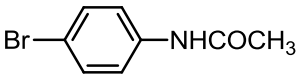
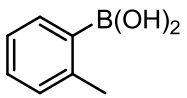
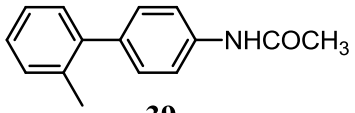


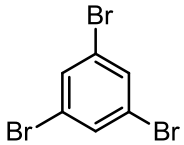
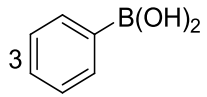
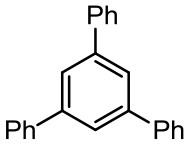
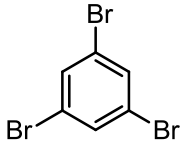
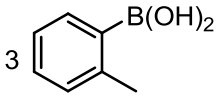
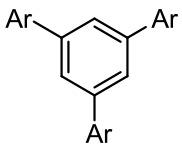
No. of Cycles	Yield(%)	TON
1	92.7	9207
2	91.7	9074
3	91.2	9008
4	90.0	8942

Figure 5: Recycle study of catalyst **A-1** for the standard reaction of iodobenzene and $PhB(OH)_2$.

Table 4: Application of the catalyst for palladium catalyzed Suzuki-Miyaura reaction

No.	Arylhalide ArX	Boronic acid	Catalyst B-2 (mol% of Pd)	Biphenyl Ar-Ar'	%Y	TON
1	 **11**	 **20**	0.01	 **21**	93.87	9379
2	 **22**	 **20**	0.01	 **31**	91.15	9074[a]
3	 **23**	 **20**	0.01	 **32**	90.41	4500
4	 **24**	 **30**	0.01	 **33**	86.0	4300

5	 **25**	 **20**	0.01	 **34**	76.87	3840[a]
6	 **26**	 **20**	0.01	 **35**	94.52	4724[a]
7	 **27**	 **20**	0.01	 **36**	95.23	9466[a]
8	 **28**	 **20**	0.01	 **37**	94.55	9424[a]
9	 **22**	 **30**	0.01	 **38**	94.30	9421[a]
10	 **27**	 **30**	0.01	 **39**	94.90	9448

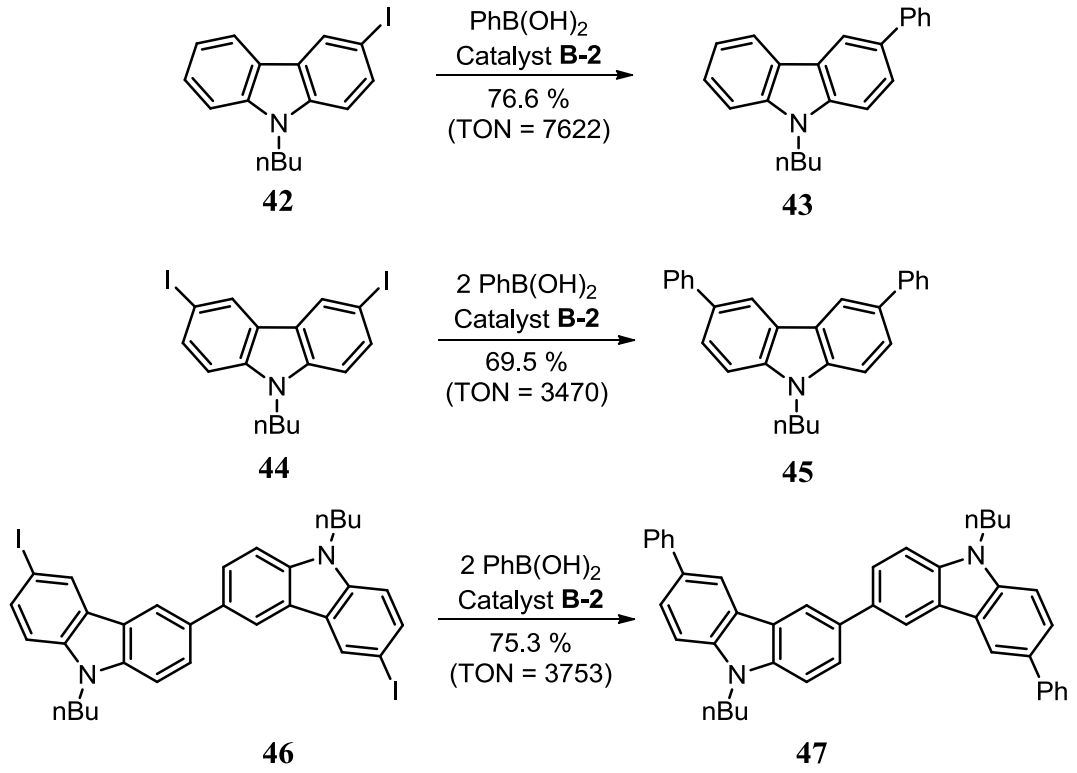
11	 **29**	 **20**	0.01	 **40**	96.55	3202
12	 **29**	 **30**	0.01	 Ar = 2-$CH_3C_6H_4$ **41**	84.24	2810

With Pd (0.01 mol %) and K_2CO_3 (2.0 eq) for one Br, TBAB (20mol%), Dioxane-water as solvent, 24h, 80^{o}C

TON : Turn Over Number

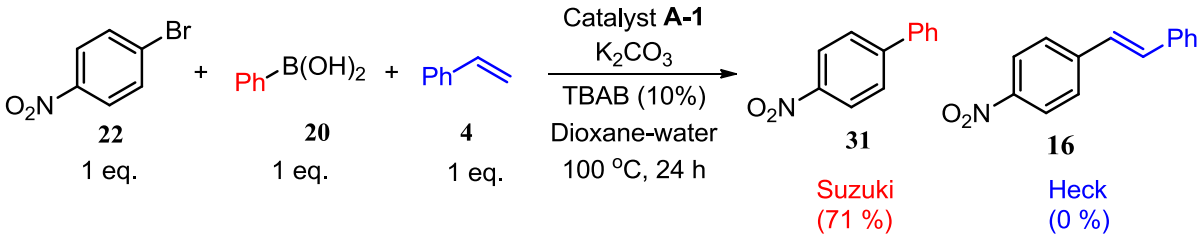
[a] With recovered catalyst **B-2**

In this brief study we also prepared aryl derivatives of carbazoles by Suzuki-Miyaura coupling with the corresponding iodo analogues [**Scheme 7**]. Structurally similar arylated carbazoles have been studied as hole-transport materials,[37] as fluorophores,[38] light emitting diode,[39] photovoltaic devices[40] and for other electron transfer applications [41] etc. The required iodo derivatives of the carbazole **42** and **44** or bis-carbazole **46** were prepared according to the literature procedures[39a,42] and then subjected to the Suzuki-Miyaura reaction with the present catalyst. The products **43**, **45** and **47** were isolated in good yields and characterized by usual spectral techniques.



Scheme 7: Synthesis of aryl carbazoles by Suzuki-Miyaura reaction

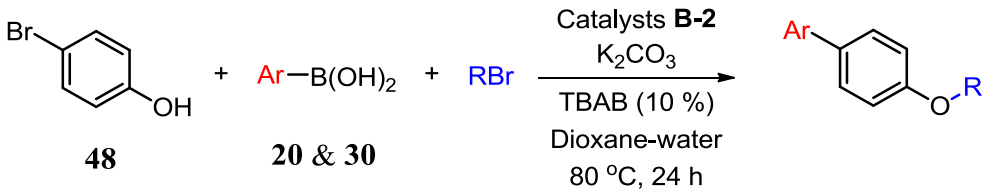
In the present study we found the Suzuki-Miyaura reaction to be more facile compared to the Mizoroki-Heck reaction with aryl bromide by our using catalysts. This was established by performing a controlled experiment of 4-nitro bromobenzene **22** with equivalent amount of phenyl boronic acid and styrene in presence of catalyst **A-1** (0.01 % Pd), potassium carbonate (2.0 eq.), TBAB (10%) in aqueous dioxane. The careful analysis of the product confirmed the formation of 4-nitro biphenyl **11** in good yield along with small quantity of biphenyl **21**, while 4-nitro stilbene **16** was not detected [**Scheme 8**]. The absence of 4-nitro stilbene **16** confirmed the selectivity in favour of Suzuki-Miyaura reaction with active aryl bromide.



Scheme 8: Selectivity of Suzuki-Miyaura reaction over Mizoroki-Heck reaction with catalyst **B-2**

5.2.3 *Application of polymer supported catalyts for O-Alkylation-Suzuki reaction*

Many alkoxy substituted derivatives of biphenyl or biaryl compounds have been studied for their specific properties. Compounds containing alkoxy functional groups have been studied as materials with thermal properties.[43] Several such compounds show liquid crystalline properties.[44] Alkoxy substituent is required for appropriate crystal packing and hence are responsible for the specific thermal behaviour. Usually the introduction of alkoxy substituent is carried out as a separate chemical operation. We have also developed a couple of one-pot *O*-alkylation-Wittig and *O*-alkylation-Wittig-Heck reactions to synthesize alkoxy stilbenes. In this work we have extended the strategy to synthesize *O*-alkoxy biphenyls and *O*-alkoxy biaryls by simultaneously conducting Suzuki-Miyaura and *O*-alkylation reaction on bromo phenols [**Scheme 9**]. As outlined the three components of this version include bromo phenol **48**, arylboronic acid **20** & **30** and the alkyl halide treated with catalyst **B-2** in presence of suitable base, PTC in aqueous dioxane.



Scheme 9: One-pot *O*-alkylation and Suzuki-Miyaura reaction

A series of examples were tested to establish this one-pot reaction and the results are presented in **Chart 1**. Consistently good conversions and isolated yields were observed for the examples studied in this work.

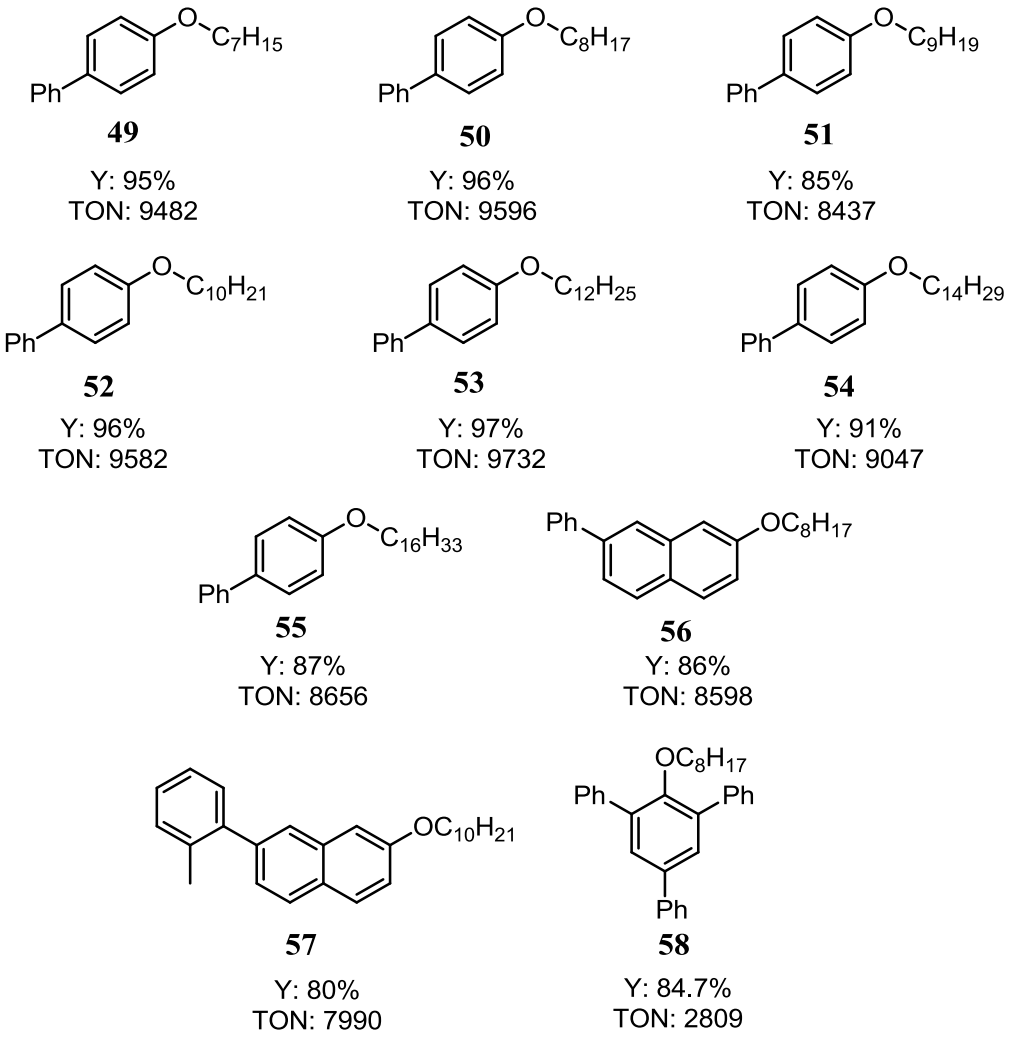


Chart 1: Examples of one-pot *O*-alkylation-Suzuki reaction

5.3 *Conclusion*

In conclusion to chapter 5, we have presented applications of polymer anchored amines as heterogeneous ligands for palladium catalyzed Mizoroki-Heck and Suzuki-Miyaura coupling reactions of aryl halides. The catalysts system was also scanned for the one-pot *O*-alkylation-Suzuki combination to synthesize a series of alkoxy biaryl systems and the catalyst was found to be efficient. The catalyst was easily separable and reused for subsequent catalytic cycles confirming the reusability of the bead shaped solid catalysts.

5.4 *Experimental Section*

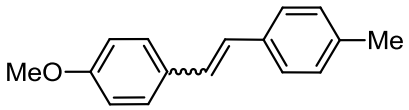
All reactions were carried out in oven-dried glassware with magnetic stirring. Purification of reaction products was carried out by column chromatography using silica gel (60-120 mesh). Thin layer chromatography was performed on TLC Silica Gel 60 F_{254} (Merck). The spots were visualized under UV light or with iodine vapour. ^{1}H-NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer (400 MHz) and were run in $CDCl_3$ unless otherwise stated. Signal multiplicity is denoted as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument; IR spectra were recorded on Perkin-Elmer FTIR RXI spectrometer as KBr pallets unless stated. Melting points were recorded in Thiele's tube using paraffin oil and are uncorrected.

Solvents were dried and purified by distillation under reduced pressure and stored on molecular sieves. All chemicals were purchased from Sigma-Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens, Avara Chemicals Limited etc., and used without further purification.

5.4.1. *Screening of supported catalysts for standard Mizoroki-Heck reaction*

Typical procedure for the Mizoroki-Heck reaction:

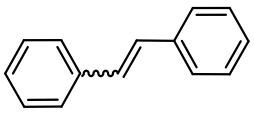
Synthesis of *trans*-4-methoxy-4'-methylstilbene (13)



A two neck round bottom flask was charged with 4-iodoanisole (0.1 g, 0.427 mmol), catalyst **A-2** (0.091 g, 0.000213 mmol Pd, 0.05 mol %), dry potassium carbonate (0.118 g, 0.855 mmol) and dimethylacetamide (6 mL) under the nitrogen atmosphere. This mixture was slowly heated. As soon as the temperature reaches 65^{o}C, a solution of 4-methylstyrene (0.076 g, 0.64 mmol) in DMA (2 mL) was introduced. The reaction mixture was then heated to 140 ^{o}C and continued for 40 h. 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 *trans*-4-methoxy-4'-methylstilbene (0.09 g, 94.7 %) as white solid. m.p. = 164^{o}C (reported 163-164^{o}C).

Stilbene (5)

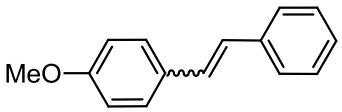
White solid (0.169g, 96%)



^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.56(d, *J*=7.2Hz, 4H), 7.42 – 7.38 (m,

4H), 7.32 – 7.28 (m, 2H), 7.16 (s, 2H).

1-methoxy-4-styrylbenzene (12)



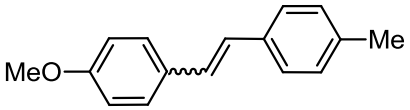
White solid (0.163g, 91.1%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.50 - 7.44 (m, 4 H), 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): 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).

1-methoxy-4-(4-methylstyryl)benzene (13)

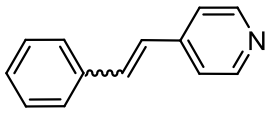


White solid (0.090g, 94.7%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.45 – 7.42 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 16.2 Hz), 6. 94 (d, *J* = 16.2 Hz, 1H), 6.90 - 6.88 (m, 2H), 3.82 (s, 3H), 2.35 (s, 3H).

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

4-styrylpyridine (14)



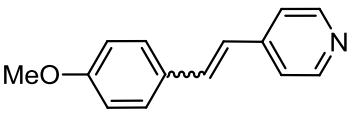
White solid (0.074g, 83.4%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.60 – 8.58 (dd, *J* = 1.6 & 4.8 Hz, 2H), 7.43 – 7.35 (m, 4H), 7.57 – 7.55 (m, 2H), 7.32 (d, *J* = 16.2 Hz, 1H), 7.04 (d, *J* = 16.2 Hz, 1H).

IR (KBr): 3022, 1590, 1564, 1485, 1309, 1187, 1022, 962, 800, 752 cm.$^{-1}$

MS (EI) (m/z): 180 (M^{-1}, 100), 181 (M^+, 80.57), 97 (29), 71 (21).

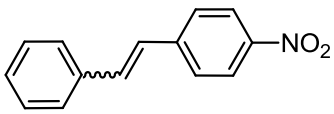
4-(4-methoxystyryl)pyridine (15)



Pale yellow (0.058g, 65%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.57 (d, *J* = 5.2 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 4.8 Hz, 2H), 7.28 (d, *J* = 16.4 Hz, 1H), 6.96-6.88 (m, 3H, a doublet with *J* = 16.4 Hz merged in it), 3.68 (s, 3H).

1-nitro-4-styrylbenzene (16)



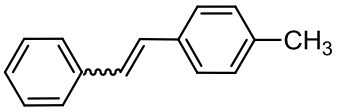
Yellow solid (0.098, 89%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.74 (d, *J* = 9.2 Hz, 1H), 7.90 - 7.60 (m, 2H), 7.60 - 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) 2922, 1590, 1340, 1107, 970, 694 cm.$^{-1}$

MS (EI) (m/z): 225 (M^+, 100), 179 (43), 167 (8.9), 89 (12.5), 77(5.86).

1-methyl-4-styrylbenzene (17)



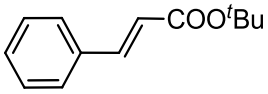
White solid (0.089g, 93.7%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.54 – 7.52 (m, 2H), 7.44 (d, *J* = 8 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.29 – 7.25 (m, 1H), 7.20 (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): 2925, 1588, 1355, 1117, 980, 714 cm.$^{-1}$

MS (EI) (m/z): 195 (M^+, 93.5), 179 (100), 89 (11), 76 (5.3).

tert-butyl cinnamate (18)

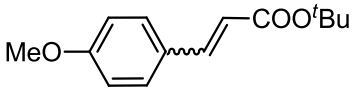


Colourless oil (0.170g, 85%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, *J* = 16Hz, 1H), 7.52 – 7.49 (m, 2H), 7.37 – 7.35 (m, 3H), 6.37 (d, *J*=16Hz, 1H), 1.53 (s, 9H).

IR (neat): 2978, 1711, 1635, 1578, 1496, 1475, 1450, 1392, 1367, 1328, 1257, 1207, 1150 cm.$^{-1}$

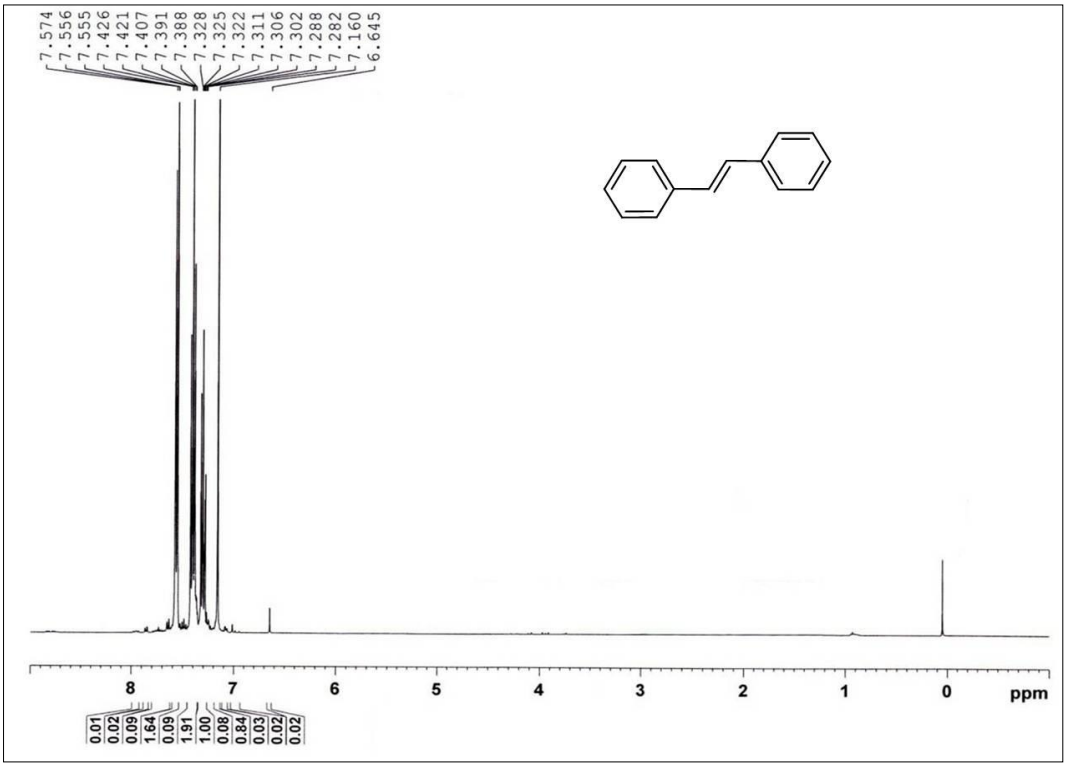
tert-butyl 3-(4-methoxyphenyl)acrylate (19)



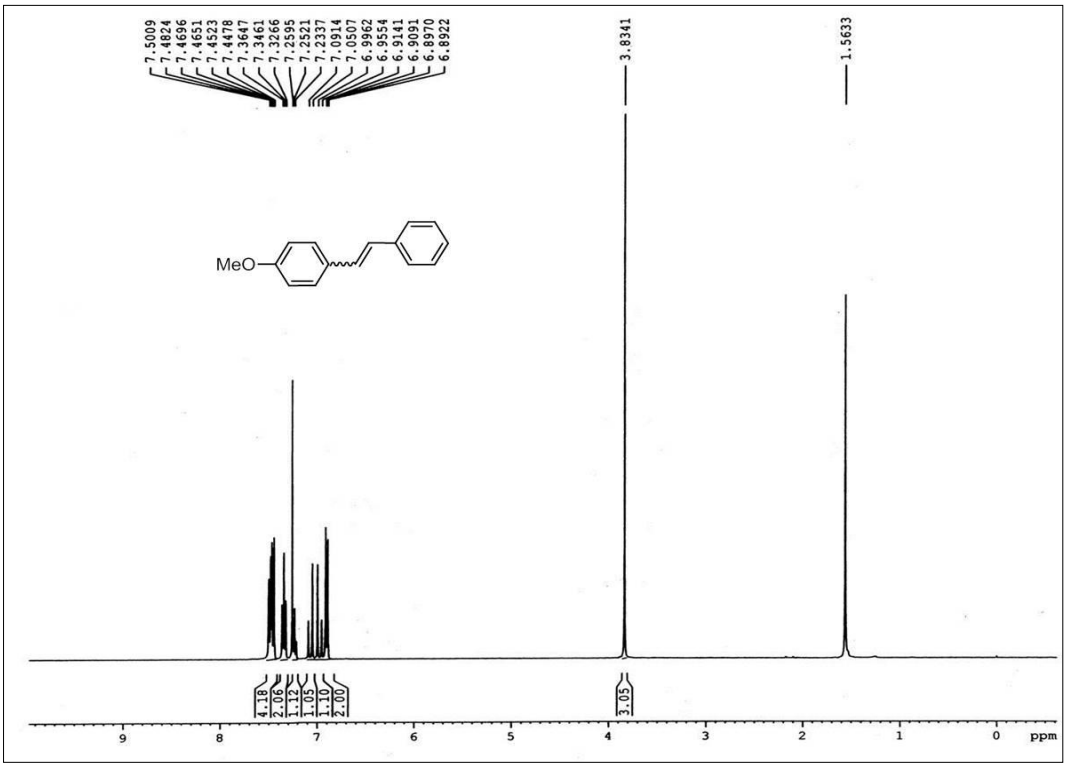
Colourless oil (0.166g, 83%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, *J* = 16Hz, 1H), 7.47 (d, *J*=8.8Hz, 2H), 6.90 (d, *J* = 8.8Hz, 2H), 6.25 (d, *J* = 16Hz, 1H), 3.84 (s, 3H), 1.54 (s, 9H).

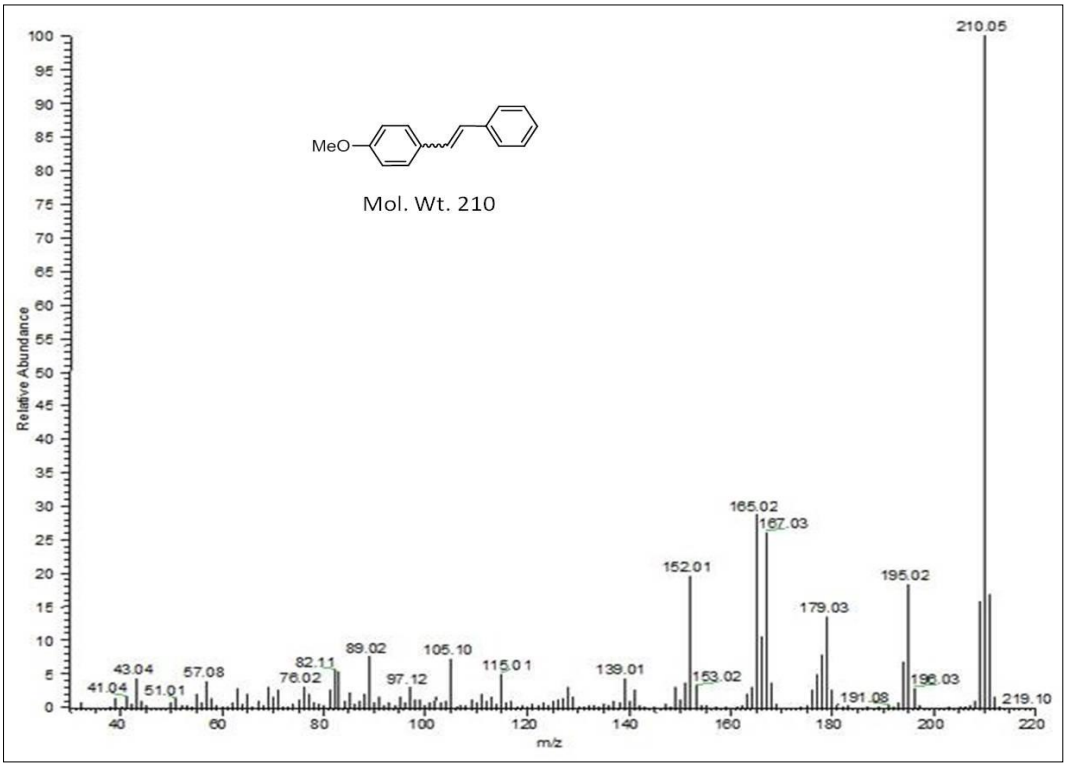
Spectral data for stilbene derivatives (Section 5.2.1)



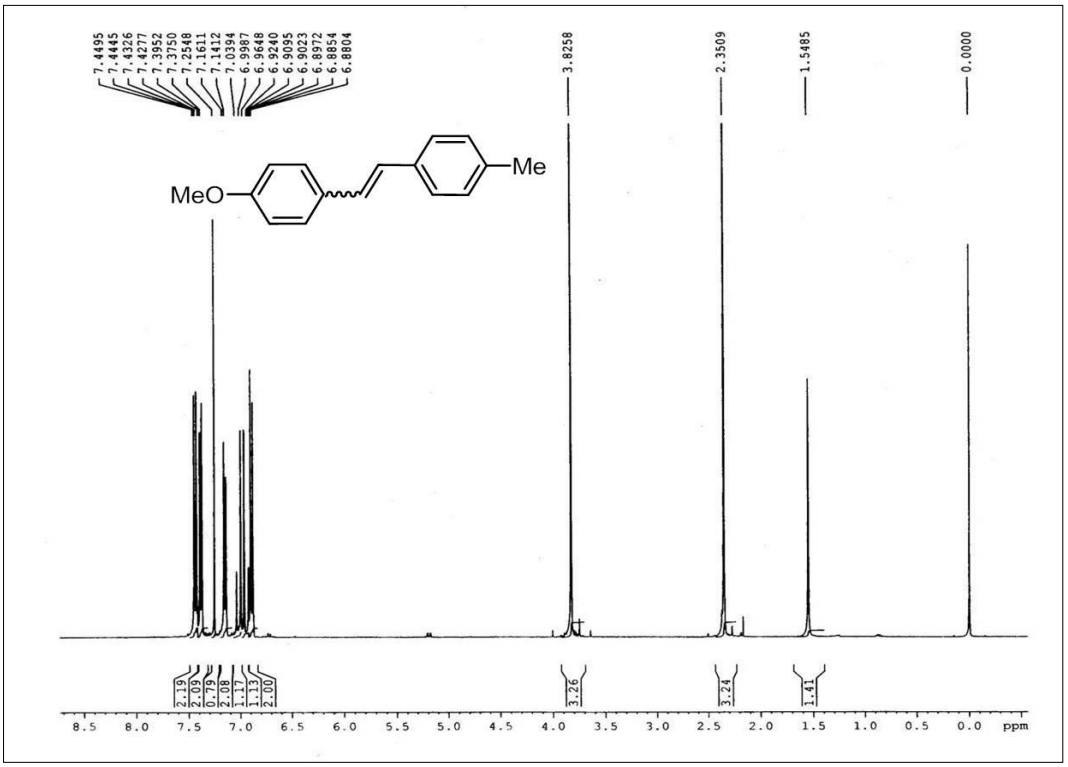
^{1}H-NMR of compound 5



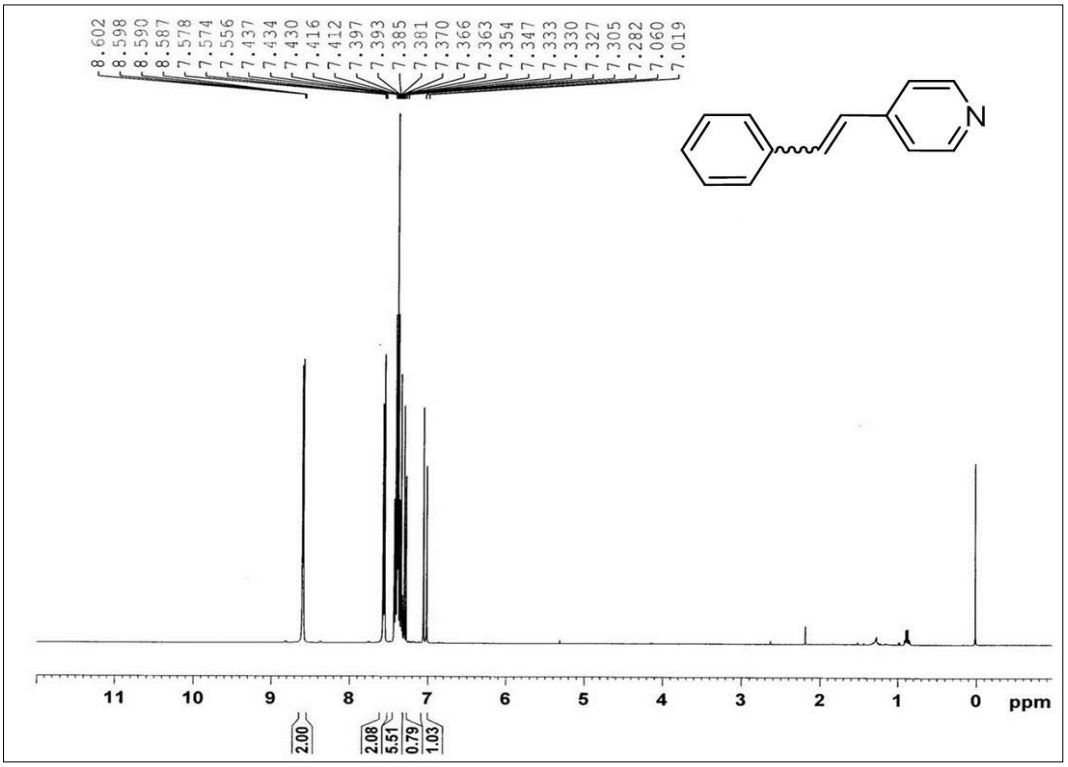
^{1}H-NMR of compound 12



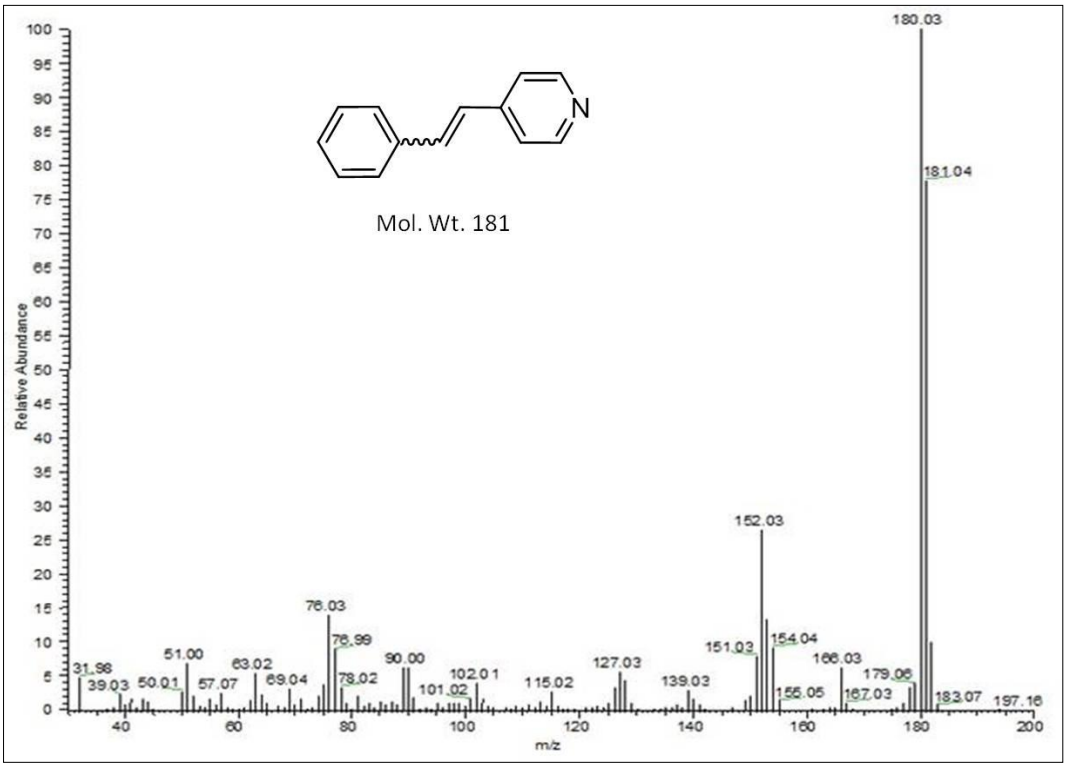
Mass spectra of compound 12



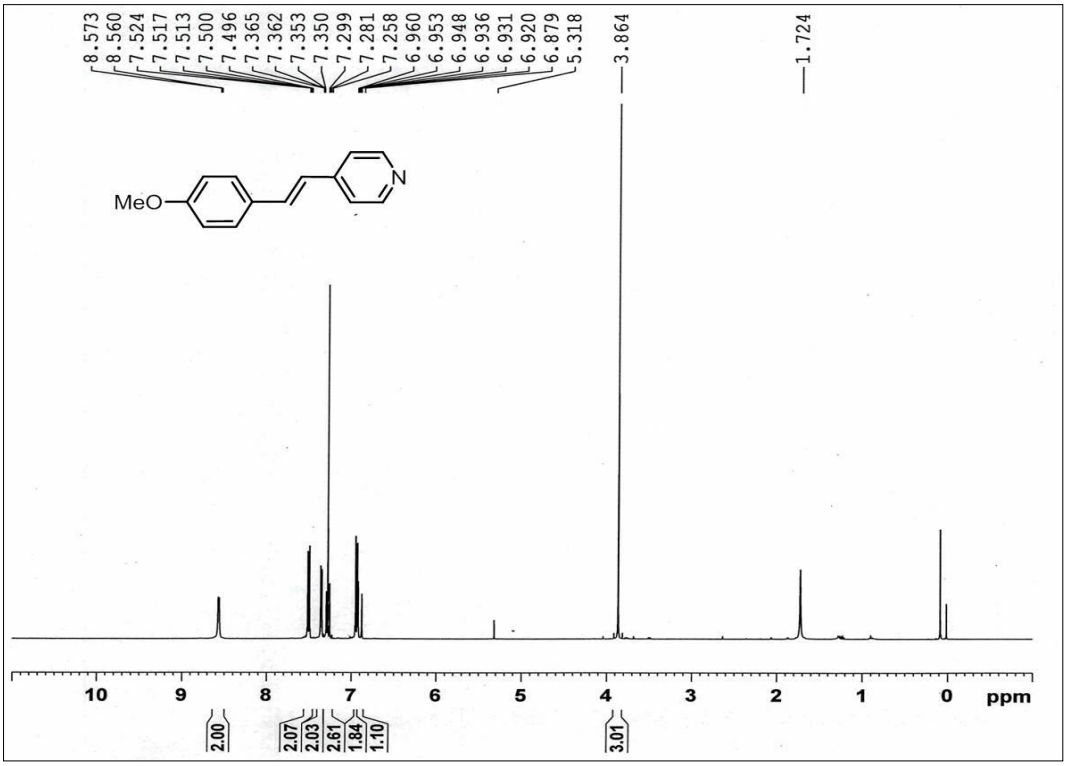
^{1}H-NMR of compound 13



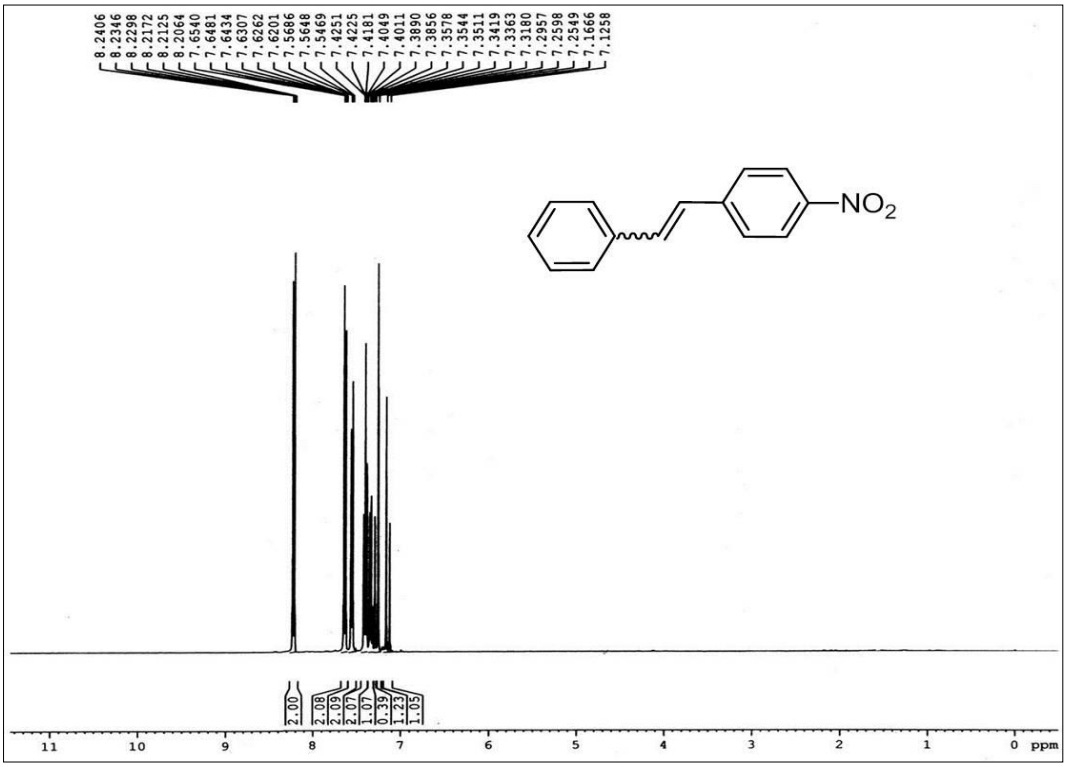
^{1}H-NMR of compound 14



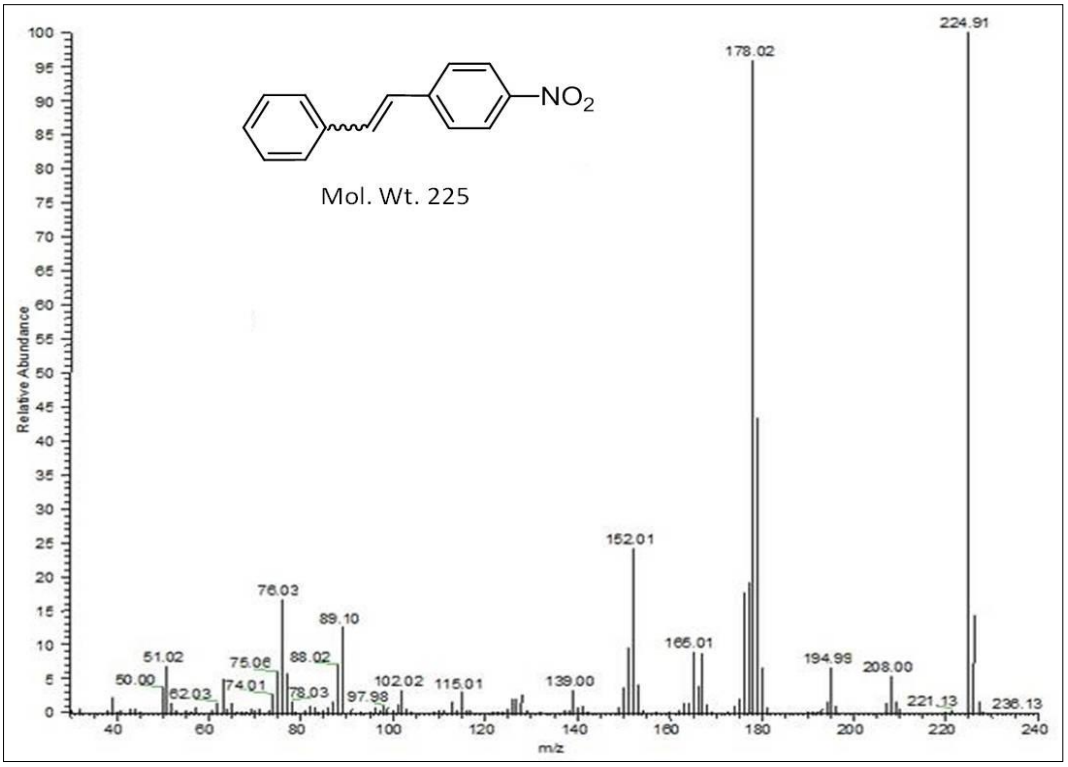
Mass spectra of compound 14



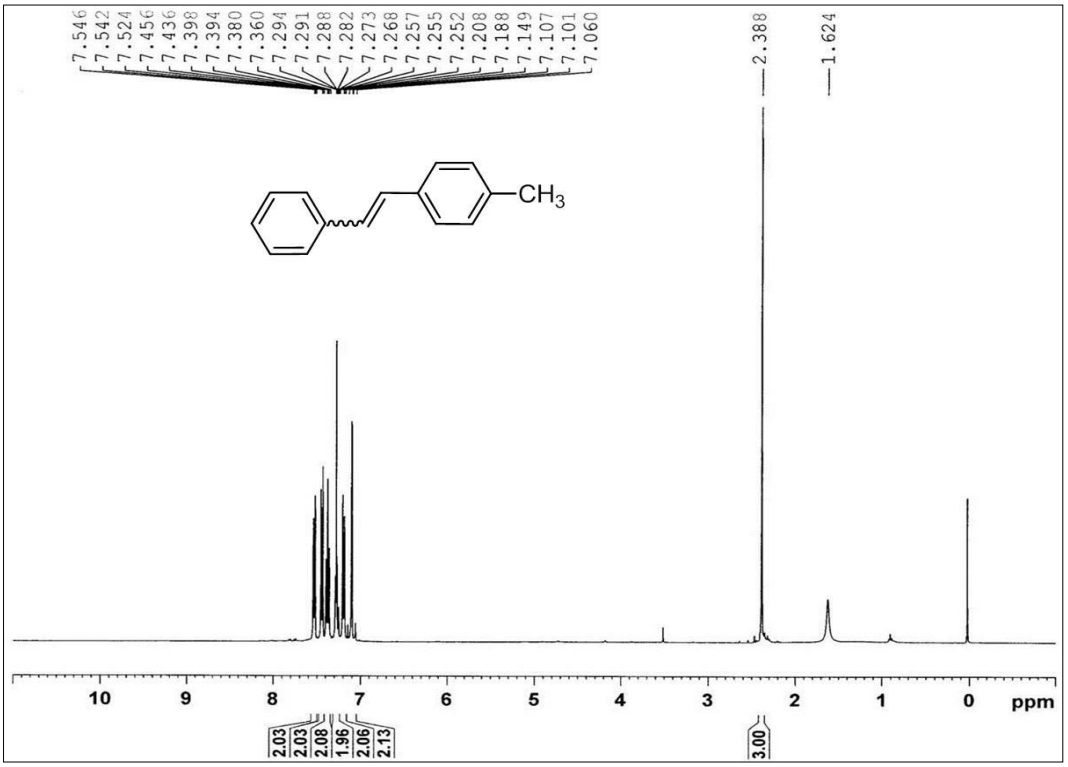
^{1}H-NMR of compound 15



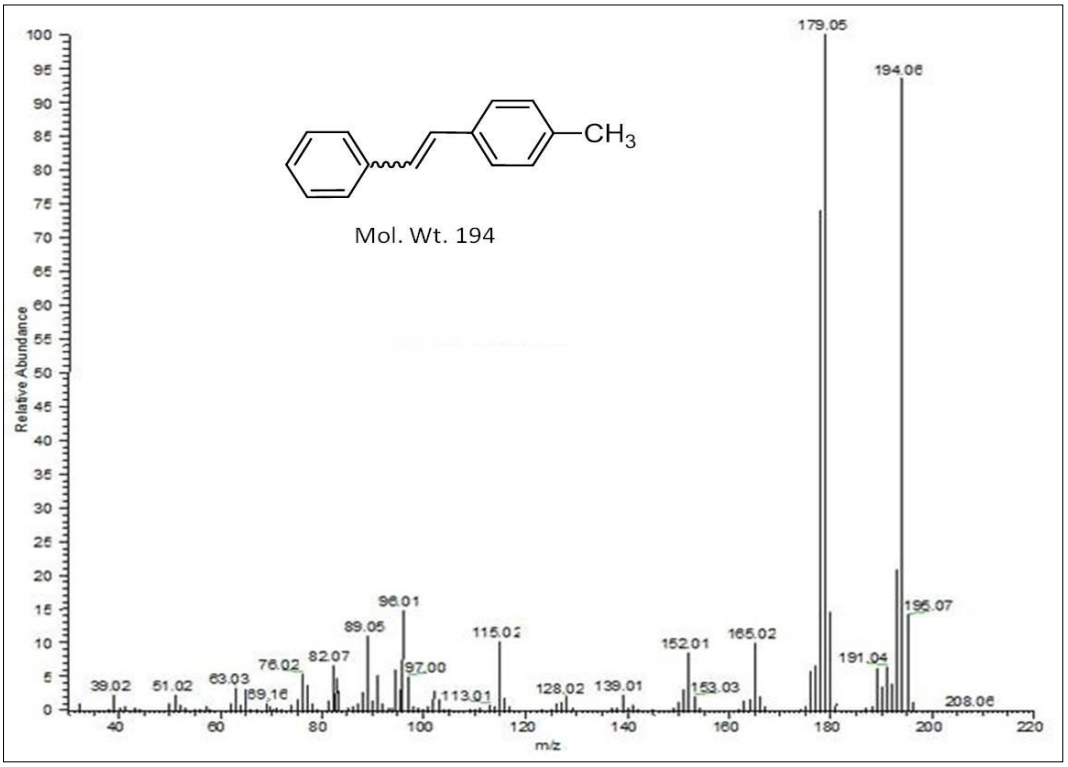
^{1}H-NMR of compound 16



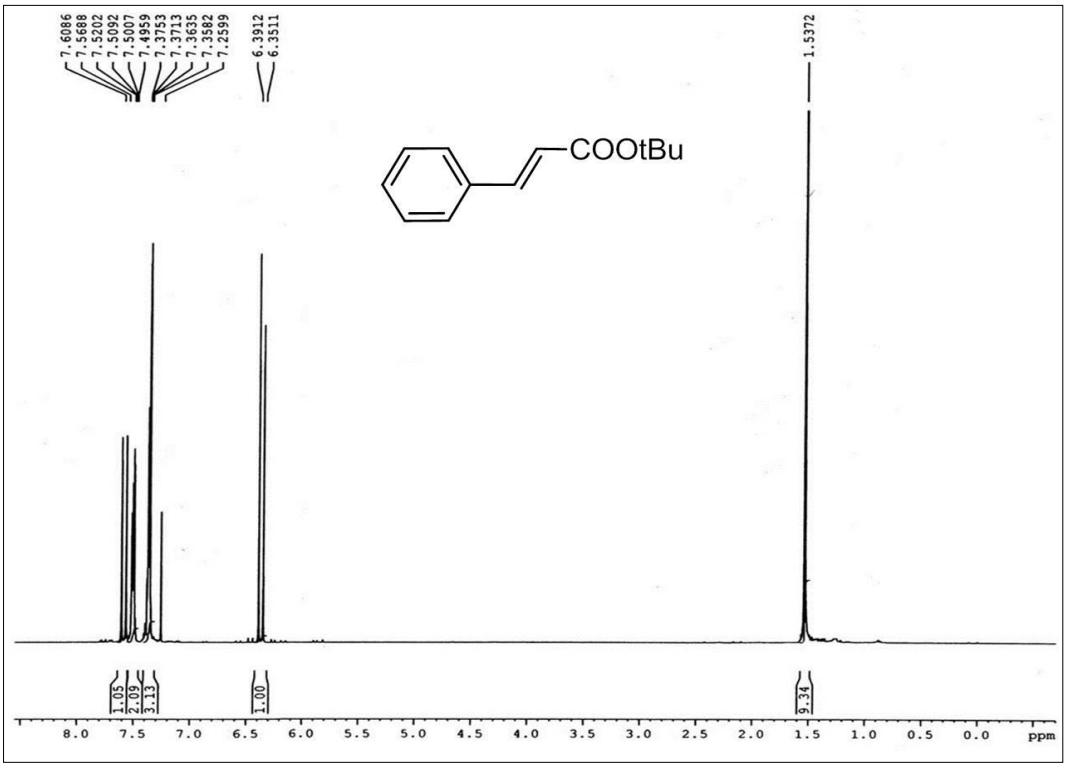
Mass spectra of compound 16



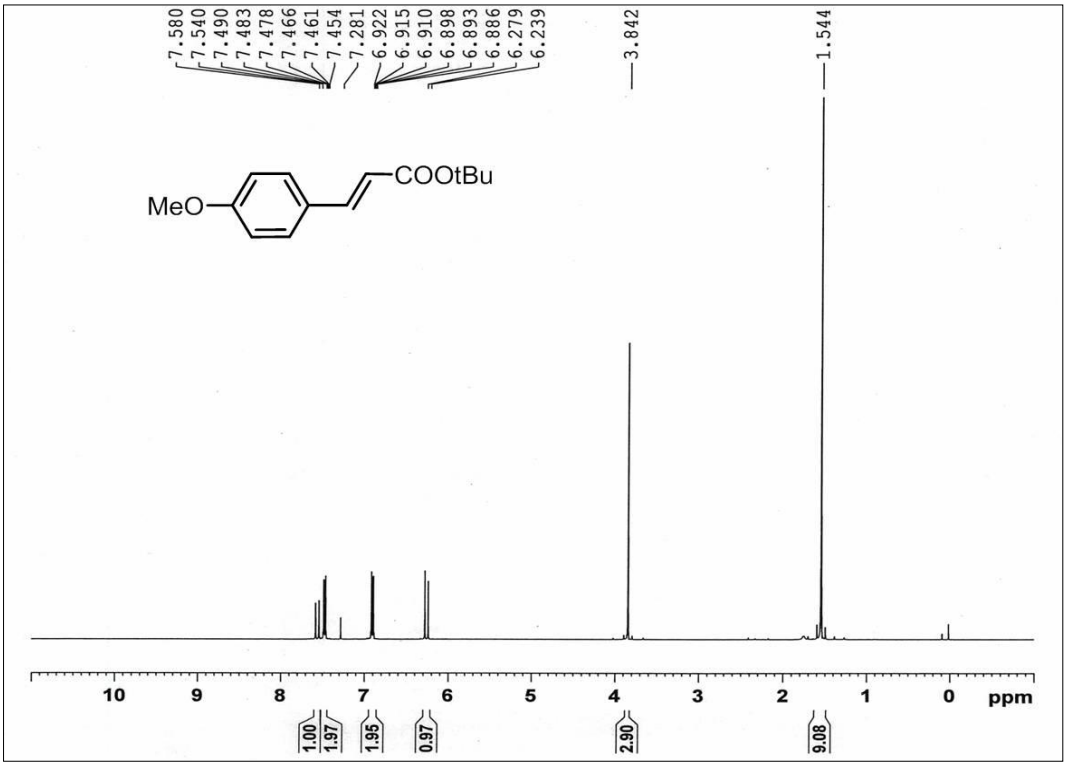
^{1}H-NMR of compound 17



Mass spectra of compound 17



^{1}H-NMR of compound 18



^{1}H-NMR of compound 19

5.4.2 *Application of polymer supported catalyts for Suzuki reaction*

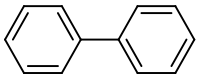
Typical procedure for Suzuki-Miyaura reaction:

Synthesis of biphenyl (**21**):

A round bottom flask was charged with iodobenzene (0.2 g, 0.980 mmol), catalyst **B-2** (0.061 g, 0.000098 mmol Pd, 0.01 mol%), phenyl boronic acid (0.143 g, 1.176 mmol), dry potassium carbonate (0.270 g, 1.960 mmol), TBAB (0.063 g, 0.196 mmol) and dioxane-water (1:1; 10 mL) as solvent. This mixture was heated to 80^{o}C and continued for 24 h. The reaction mixture was filtered to remove the catalyst and was quenched with water and extracted with ethyl acetate (3x25 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 biphenyl (0.148 g, 98.7 %) as white solid [m.p. 66-67 ^{o}C, reported 68-70 ^{o}C].

Biphenyl (21)

White solid (0.184 g, 93.9 %)

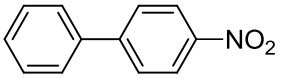


^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.64 - 7.62 (m, 4H), 7.5 - 7.46 (m, 4H), 7.4 - 7.36 (m, 2H).

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

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

4-Nitro biphenyl (31)



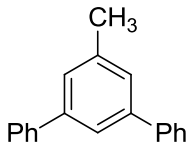
Yellow solid (0.134 g, 91.2 %)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.32 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.66-7.64 (m, 2H), 7.55-7.45 (m, 3H).

IR (KBr): υ 2927, 1598, 1514, 1447, 1346, 1103, 853, 774, 740 $cm.^{-1}$

MS (EI) (m/z) : 199 (63), 169 (35), 152 (56), 97 (59), 69 (100).

5'-Methyl-[1,1',3',1'']terphenyl (32)



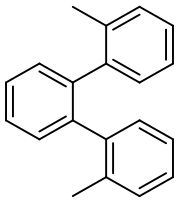
White solid (0.132 g, 90.5 %)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.68-7.64 (m, 5H), 7.49-7.46 (m, 4H), 7.42-7.42 (m, 2H), 7.39-7.36 (m, 2H), 2.51 (s, 3H).

IR (KBr): υ 3025, 2911, 1595, 1493, 1408, 1316, 1177, 1072, 1025, 868, 762, 700 $cm.^{-1}$

MS (EI) (*m/z*): 244 (51) [M^+], 243 (100), 228 (15).

2,2''-Dimethyl-[1,1',2',1'']terphenyl (33)



Colourless liquid (0.141 g, 86.0 %)

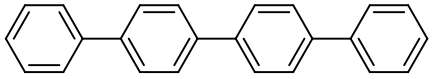
^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.45 - 7.37 (m, 2H), 7.32 (br s, 2H), 7.07 - 6.95 (m, 7H), 6.87 - 6.8 (m, 1H), 2.14 - 2.05 (two s, 6H).

IR (KBr):

υ 3057, 3017, 2923, 2864,1468, 1379, 1277, 1120, 1029, 1006, 751, 727 $cm.^{-1}$

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

1,1':4',1'':4''.1'''-Quaterphenyl (34)



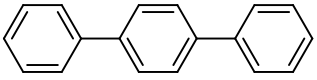
White solid (0.113 g, 76.9 %)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.75-7.65 (m, 2H), 7.59-7.54 (m, 1H), 7.49-7.43 (m, 2H).

IR (KBr): υ 2918, 2849, 1469, 1381, 1219, 1067, 999, 815, 764 $cm.^{-1}$

MS (EI) (*m/z*): [M^+] 307 (100), 228 (31), 149 (35).

1,1':4',1''-Terphenyl (35)



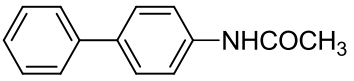
White solid (0.138 g, 94.5 %).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.71 (s, 2H), 7.69-7.67 (m, 2H), 7.51-7.48 (m, 2H), 7.42-7.37 (m, 1H).

IR (KBr): υ 3057, 3031, 1478, 1402, 837, 745, 686 cm.$^{-1}$

MS (EI) (*m/z*): [M^+] 230 (12), 147 (19), 128 (100), 71 (81), 70 (61).

***N*-Biphenyl-4-yl-acetamide (36)**



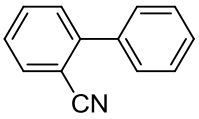
White solid (0.140 g, 95.2%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.61-7.56 (m, 6H), 7.47-7.43 (m, 2H), 7.37-7.33 (m, 1H), 2.23 (s, 3H).

IR (KBr): υ 3302, 1663, 1603, 1543, 1402, 836, 761 cm.$^{-1}$

MS (EI) (*m/z*): 211 (30) [M^+], 169 (32), 149 (80), 148 (60), 111 (100).

[1,1'-biphenyl]-2-carbonitrile (37)



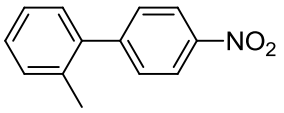
Colourless liquid (0.139 g, 94.6%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.79 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.67 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.60-7.58 (m, 2H), 7.55-7.45 (m, 5H).

IR (neat): υ 3063, 3032, 2224, 1595, 1476, 1434, 1268, 1164, 1075, 1008, 759, 700 cm^{-1}.

MS (EI) (*m/z*): 179 (47) [M^+], 178 (32), 69 (100).

2-Methyl-4'-nitro-1,1'-biphenyl (38)



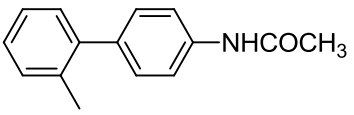
Yellow solid (0.149 g, 94.3%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.31 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8Hz, 2H), 7.36-7.29 (m, 3H), 7.24 (d, *J* = 7.6 Hz, 1H).

IR (KBr): υ 3098, 2927, 1597, 1513, 1475, 1346, 1103, 852, 773, 749 cm^{-1}

MS (EI) (*m/z*): 213 (72) [M^+], 165 (67), 149 (54), 111 (100).

N-(2'-Methyl-[1,1'-biphenyl]-4-yl)acetamide (39)



White solid (0.149 g, 94.9%)

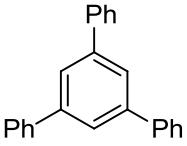
^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, *J* = 8.4Hz, 2H), 7.31-7.22 (m, 7H), 2.29 (s, 3H), 2.23 (s, 3H).

IR (KBr): υ 3304, 1664, 1601, 1533, 1318, 839, 758 cm.$^{-1}$

MS (EI) (*m/z*): 225 (100) [M^+], 183 (66), 182 (58).

5'-Phenyl-1,1':3',1''-terphenyl (40)

White solid (0.140 g, 96.6 %)

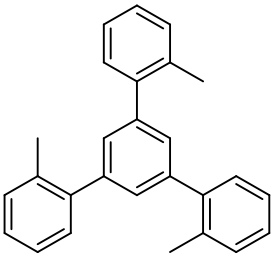


^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.82 (s, 1H), 7.73 (d, *J* = 7.2Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.44-7.40 (m, 1H).

IR (KBr): υ 3056, 3031, 1593, 1496, 1410, 1075, 1027, 872, 765, 750, 690, 609 $cm.^{-1}$

MS (EI) (*m/z*): 306 (100) [M^+], 305 (79), 228 (13).

2,2''-Dimethyl-5'-(o-tolyl)-1,1':3',1''-terphenyl (41)



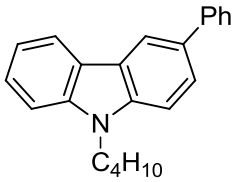
White solid (0.139 g, 84.2 %)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.38-7.35 (m, 1H), 7.33-7.28 (m, 4H), 2.41 (s, 3H)

IR (KBr): υ 3060, 3015, 2922, 1589, 1486, 890, 755, 723 $cm.^{-1}$

MS (EI) (*m/z*): 348 (53) [M^+], 347 (100), 241 (16), 215 (13).

9-butyl-3-phenyl-9H-carbazole (**43**):



Pale white solid (0.098g, 76.6%).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, *J* = 1.6 Hz, 1H, Ar-*H*), 8.18 (dd, *J* = 7.2, 0.8 Hz, 1H, Ar-*H*), 7.77-7.74 (m, 3H, Ar-*H*), 7.54- 7.45 (m, 5H, Ar-*H*), 7.40- 7.36 (m, 1H, Ar-*H*), 7.31- 7.27 (m, 1H, Ar-*H*), 4.36 (t, *J* = 7.2 Hz, 2H, -N-CH_2-), 1.96- 1.88 (m, 2H, -N-CH_2-CH_2-), 1.49- 1.43 (m, 2H, -N-CH_2-CH_2-CH_2-), 0.99 (t, *J* = 7.2 Hz, 3H, -CH_3).

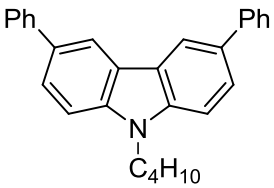
^{13}C-NMR ($CDCl_3$, 100 MHz) δ 142.22, 140.93, 139.98, 132.28, 128.80, 127.34, 126.42, 125.81, 125.19, 123.34, 122.99, 120.45, 118.92, 108.94, 108.87, 42.98, 31.21, 20.64, 13.96.

IR (KBr): υ 3055, 2958, 2930, 2872, 1627, 1599, 1472, 1349, 1257, 1212, 802 $cm.^{-1}$

MS (EI) (*m/z*): 299 (98) [M^+], 255 (100).

HRMS (ESI^+): Calculated for $C_{22}H_{21}N$ $[M+H]^+$ 300.1752, found 300.1744

9-Butyl-3,6-diphenyl-9H-carbazole (45)



Pale yellow solid (0.082g, 69.5%).

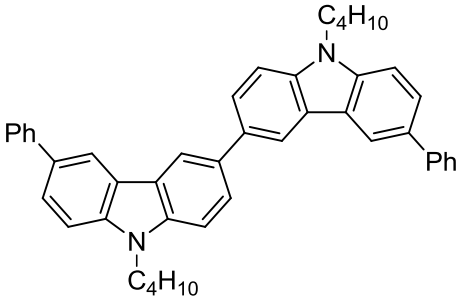
^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.39 (d, *J* = 1.2 Hz, 2H), 7.77-7.75 (m, 7H), 7.53-7.48 (m, 7H), 7.39-7.35 (m, 2H), 4.38 (t, *J* = 7.2 Hz, 2H), 1.97-1.89 (m, 2H), 1.52-1.41 (m, 2H), 1.00 (t, *J* = 7.6 Hz,3H).

IR (KBr):

υ 3036, 2954, 2869, 1599, 1475, 1210, 875, 807, 758 $cm.^{-1}$

MS (EI) (*m/z*): 375 (45), 374 (72), 331 (100).

6,6'-Diphenyl-3,3'-di(N-butyl carbazole) (47)



Pale yellow solid (0.128 g, 75.3 %)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.52-8.39 (m, 2H, Ar-*H*), 7.90-7.84 (m, 1H, Ar-*H*), 7.79-7.76 (m, 3H, Ar-*H*), 7.56-7.49 (m, 4H, Ar-*H*), 7.39-7.37 (m, 1H, Ar-*H*), 4.41 (t, *J* = 7.2Hz, 2H, -N-C*H*$_2$-), 1.99-1.90 (m, 2H, -N-CH_2-C*H*$_2$-), 1.52-1.45 (m, 2H, -N-CH_2-CH_2-C*H*$_2$-), 1.02 (t, *J* = 7.2 Hz, 3H, -C*H*$_3$).

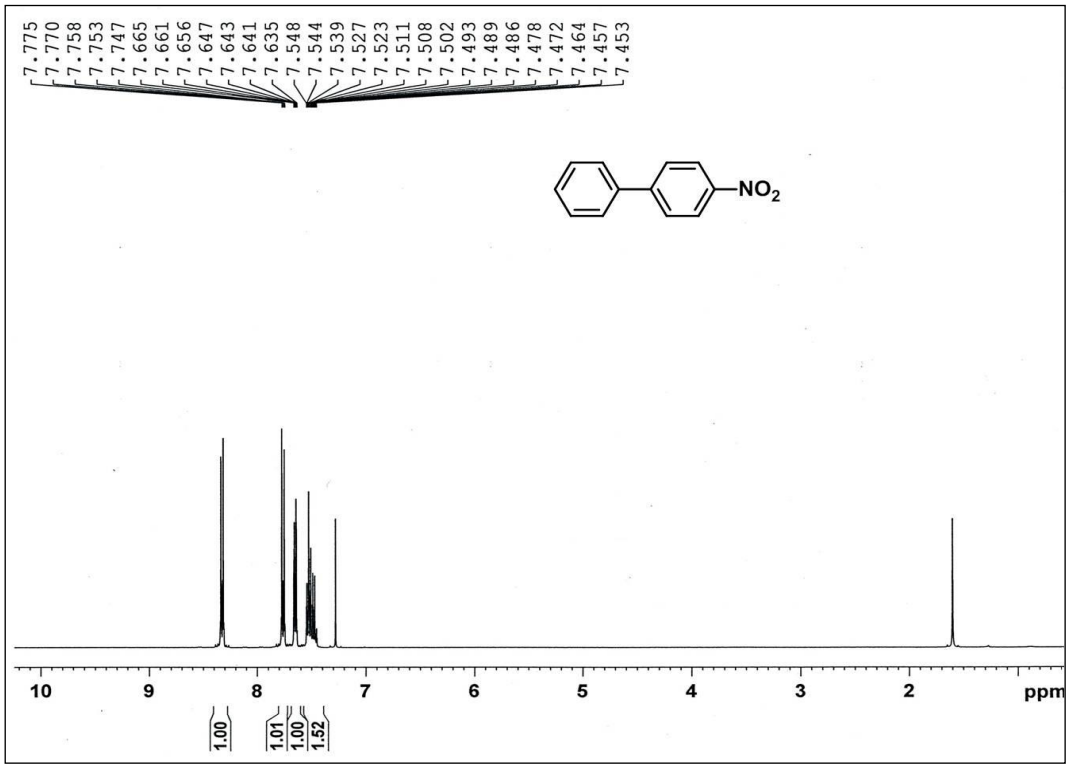
^{13}C-NMR ($CDCl_3$, 100 MHz) δ 142.19, 140.45, 140.05, 133.41, 132.29, 128.81, 127.33, 126.43, 125.69, 125.24, 123.61, 119.02, 118.99, 109.12, 109.07, 43.12, 31.30, 20.67, 14.00

IR (KBr): υ 3035, 2954, 2871, 1600, 1475, 1379, 1349, 1268, 1210, 1130, 874, 798, 757 cm^{-1}

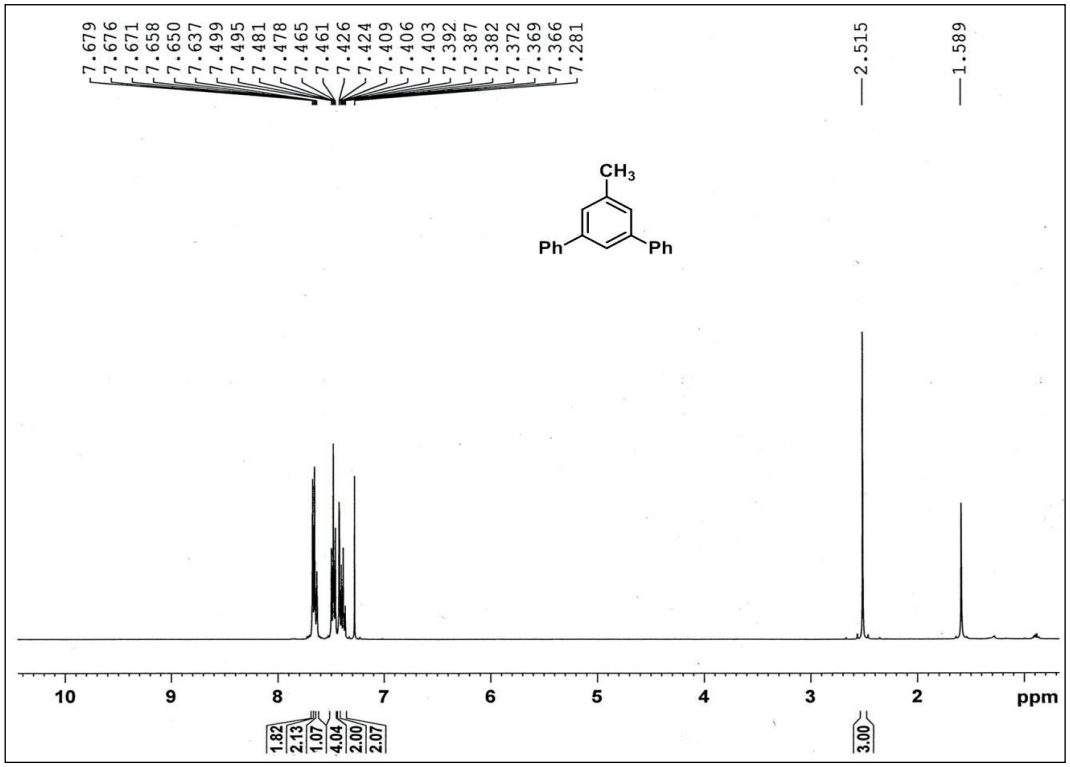
MS (EI) (*m/z*): 596 (3) [M^+], 576 (10), 520 (22), 451 (38), 407 (35), 312 (30).

HRMS (ESI^+): Calculated for $C_{44}H_{40}N_2$ $[M+K]^+$ 635.2829, found 635.2828

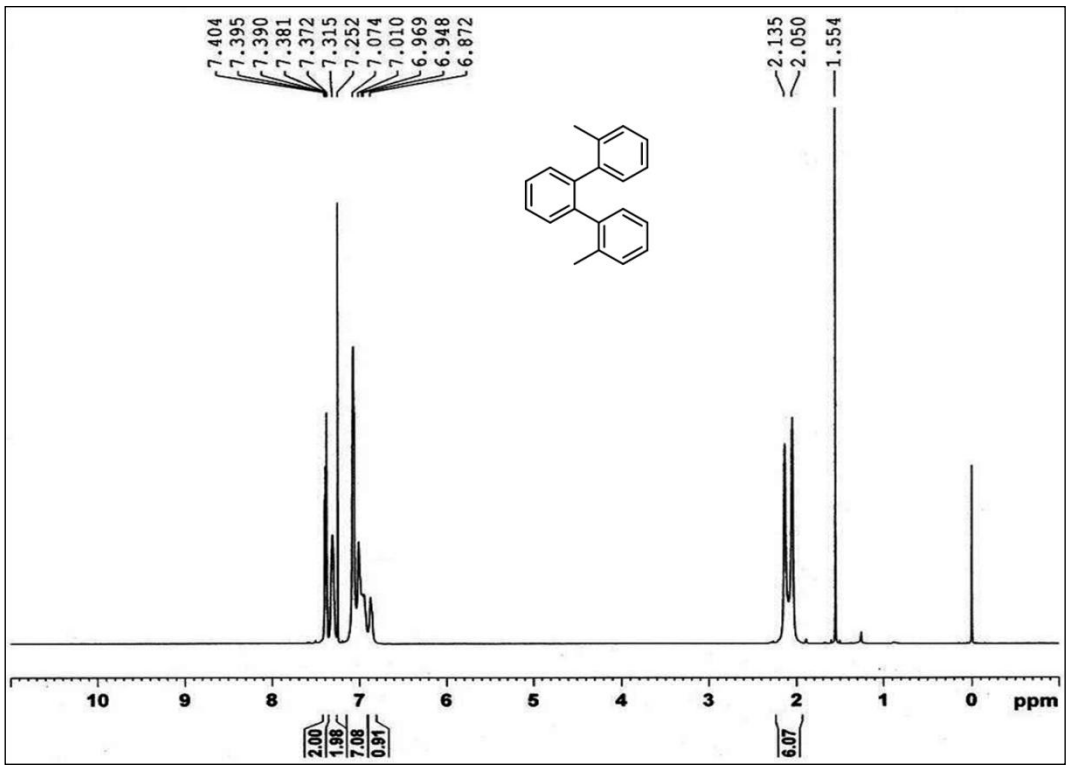
Spectral data for examples of Suzuki reaction (Section 5.2.2)



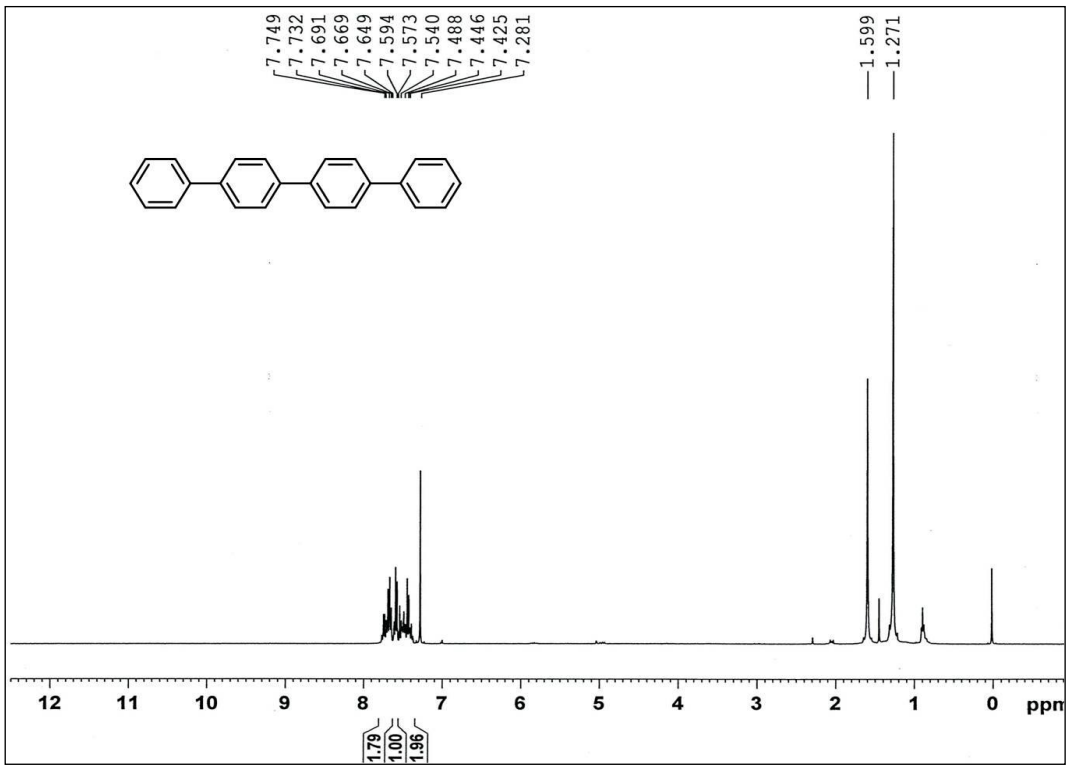
^{1}H-NMR of compound 31



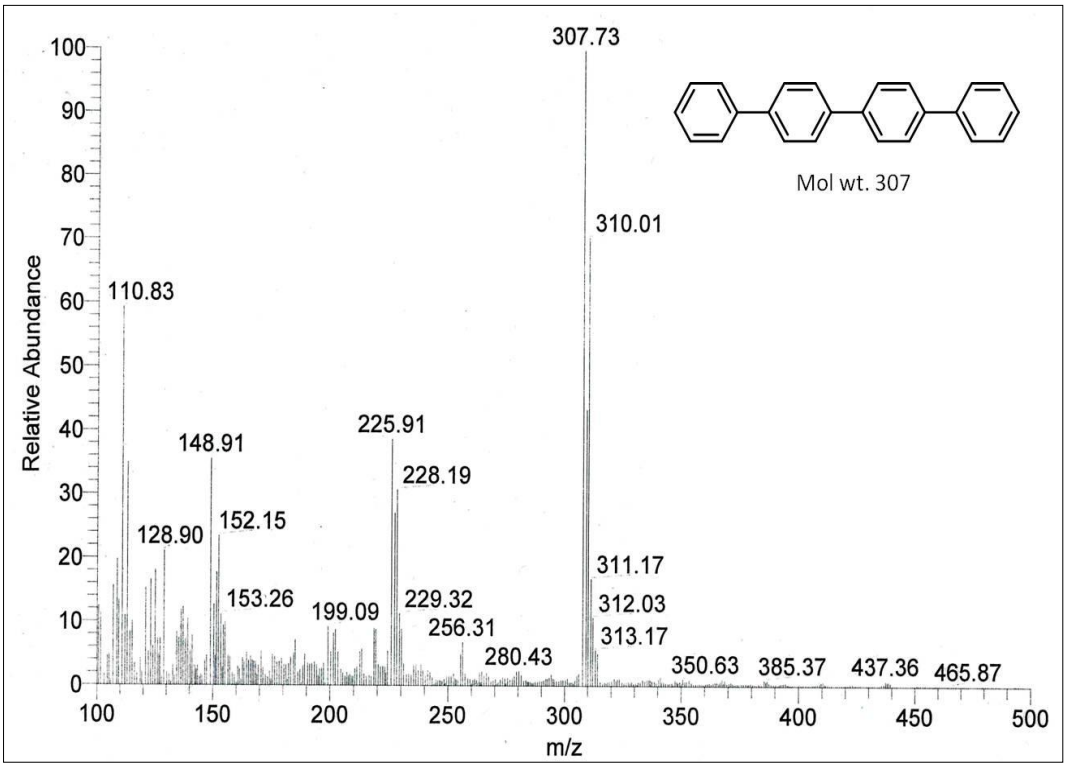
[1]H-NMR of compound 32



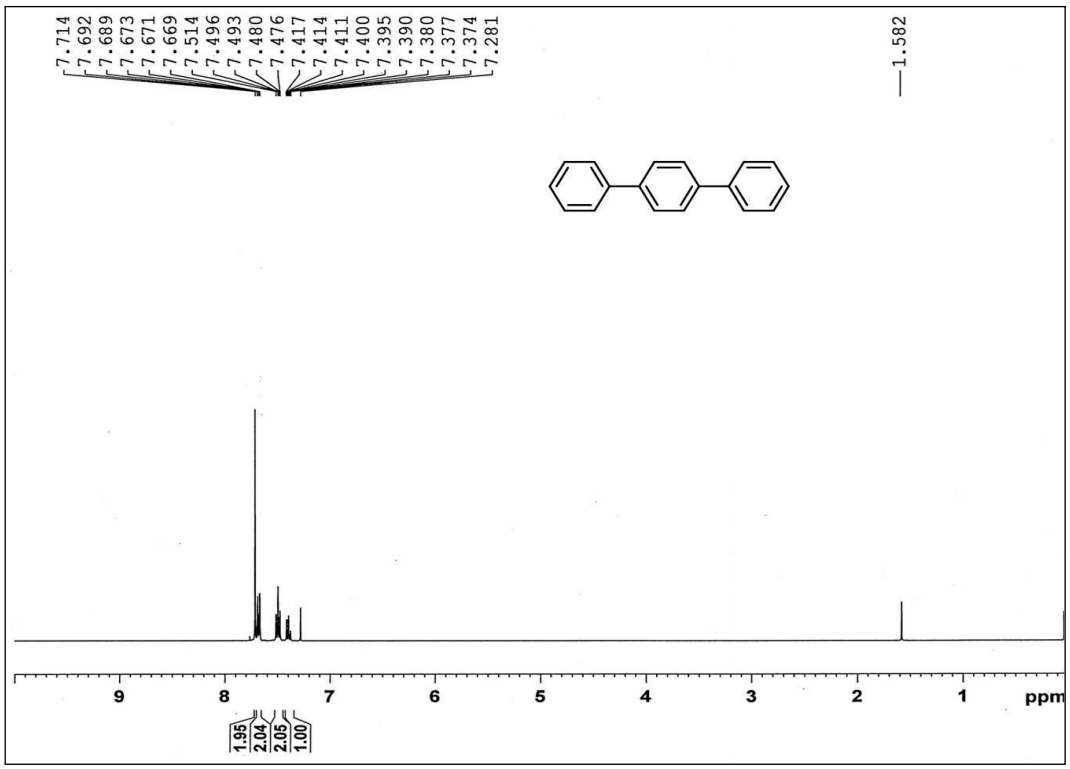
[1]H-NMR of compound 33



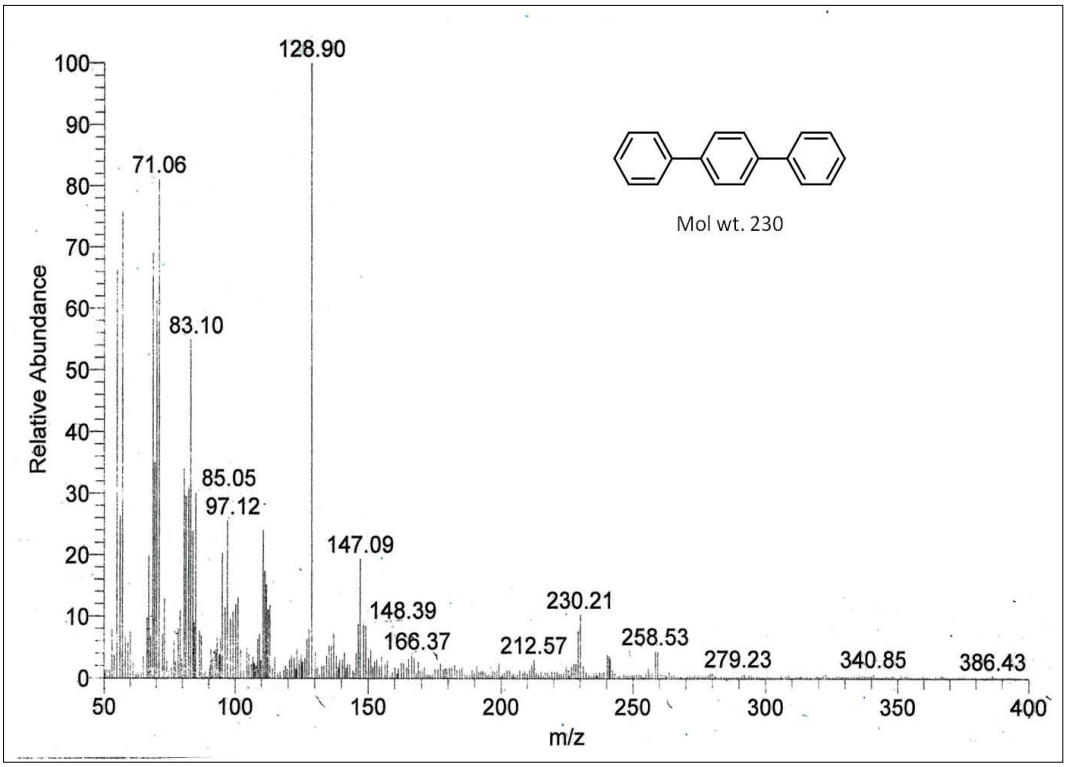
^{1}H-NMR of compound 34



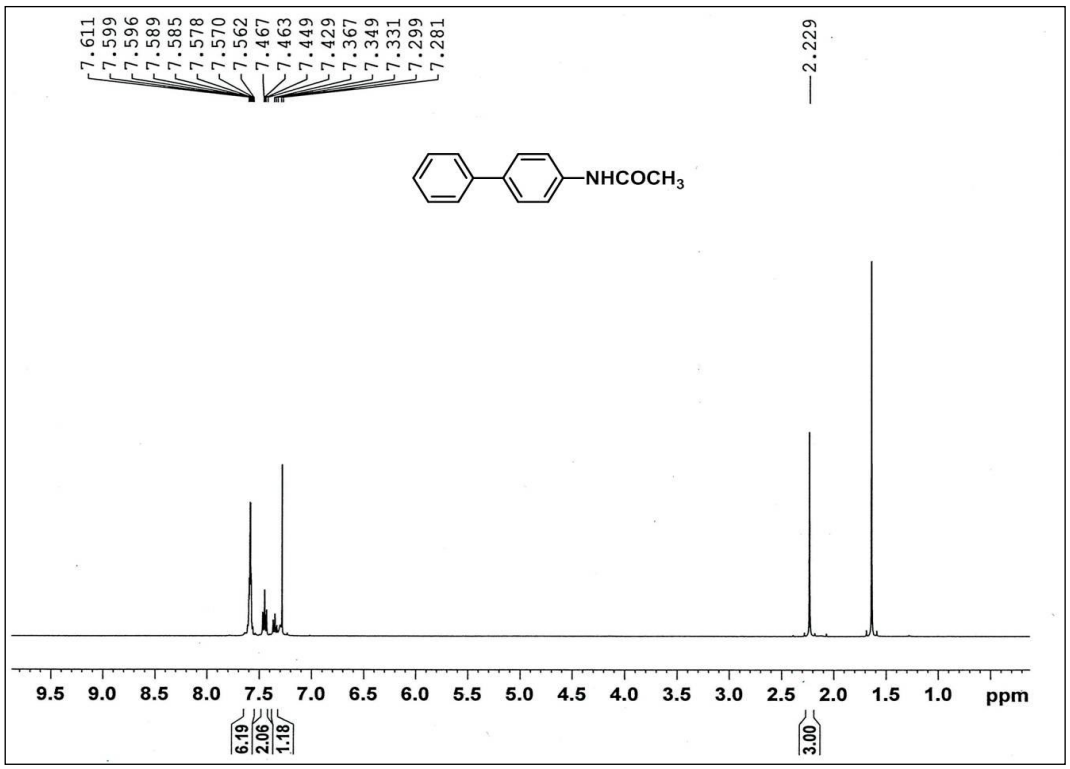
Mass spectra of compound 34



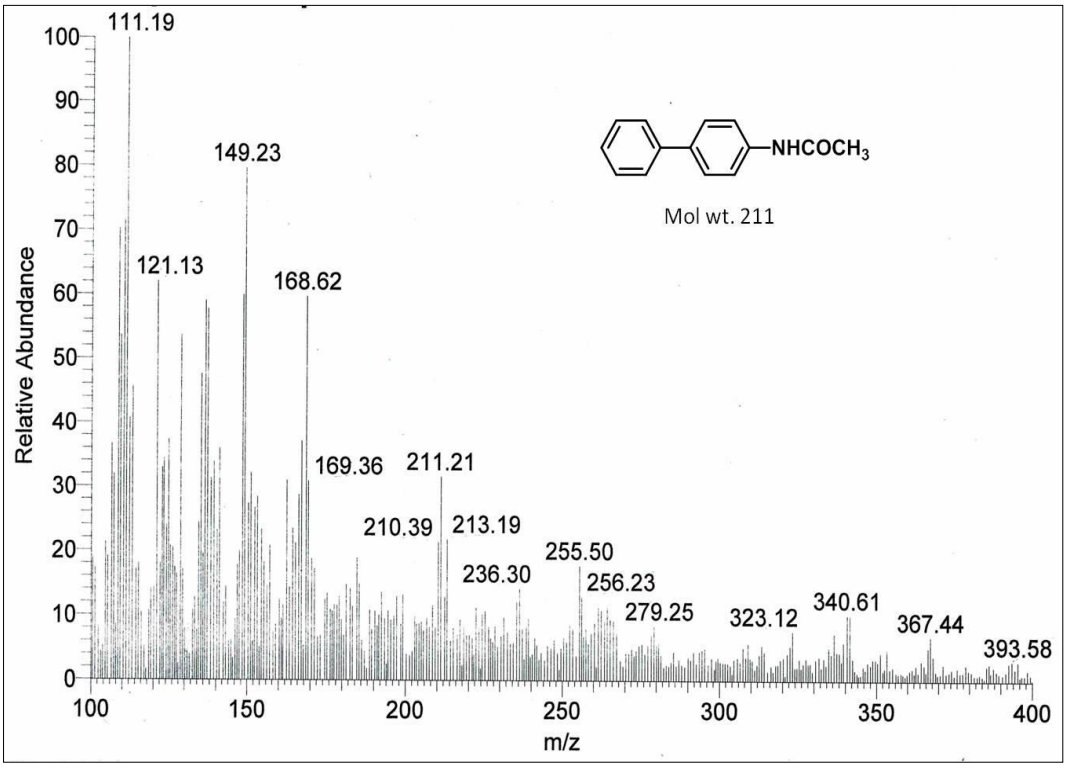
^{1}H-NMR of compound 35



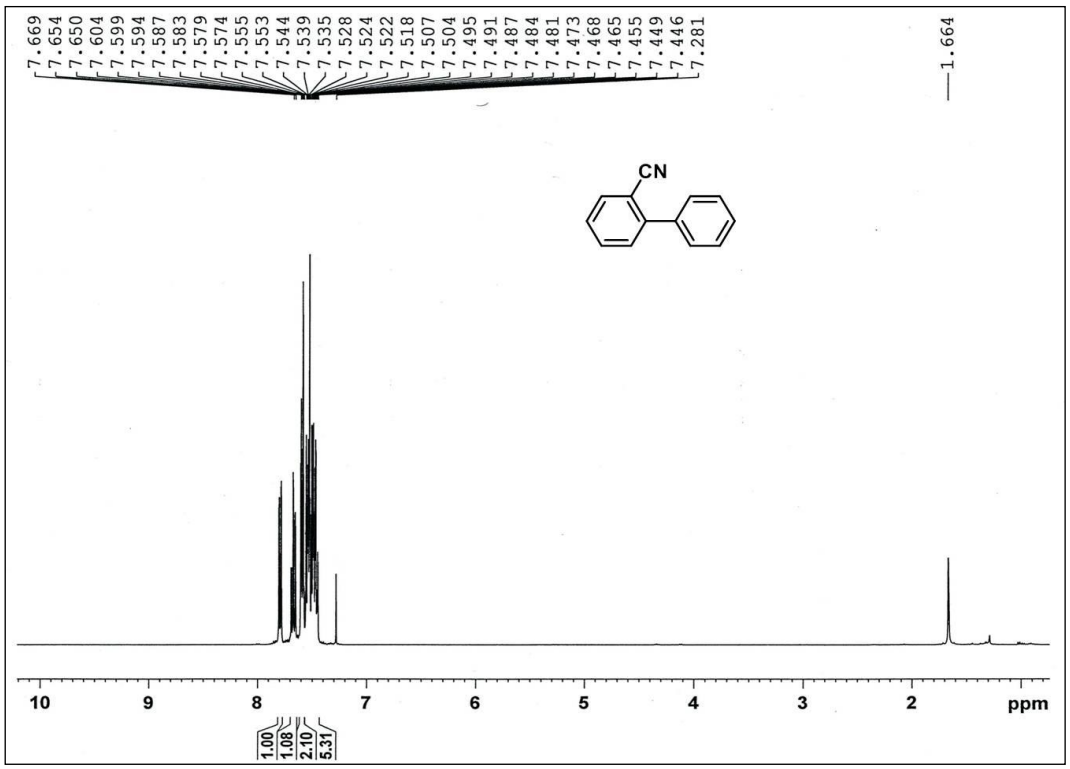
Mass spectra of compound 35



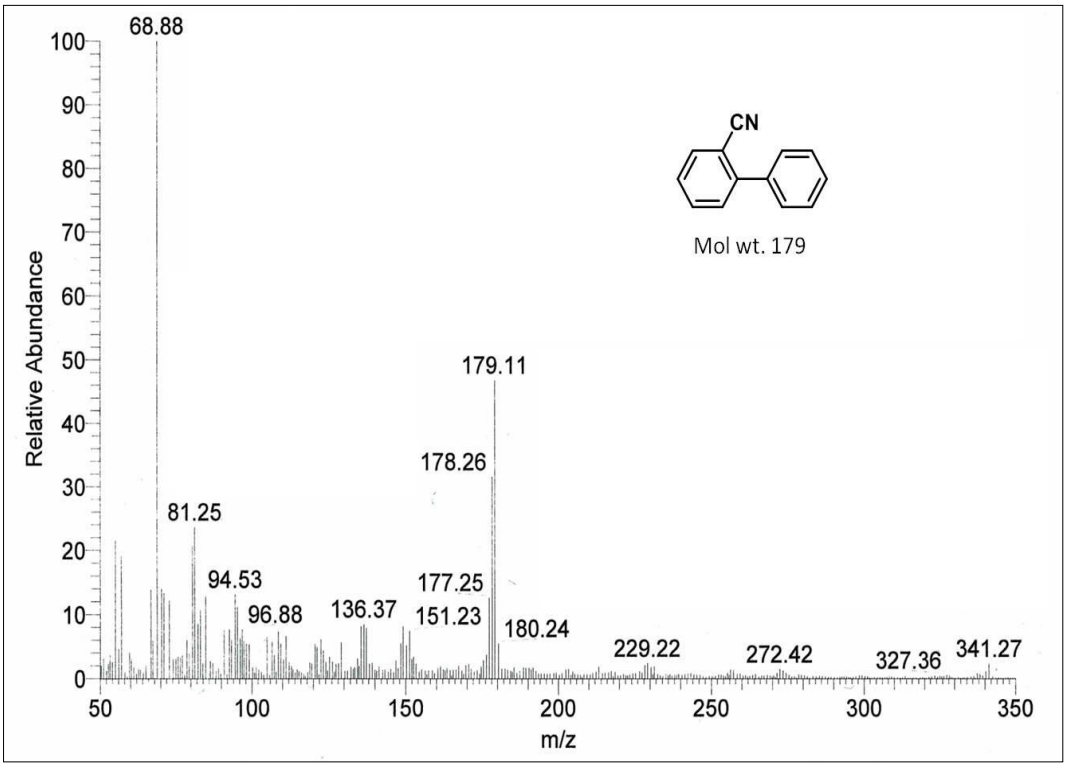
^{1}H-NMR of compound 36



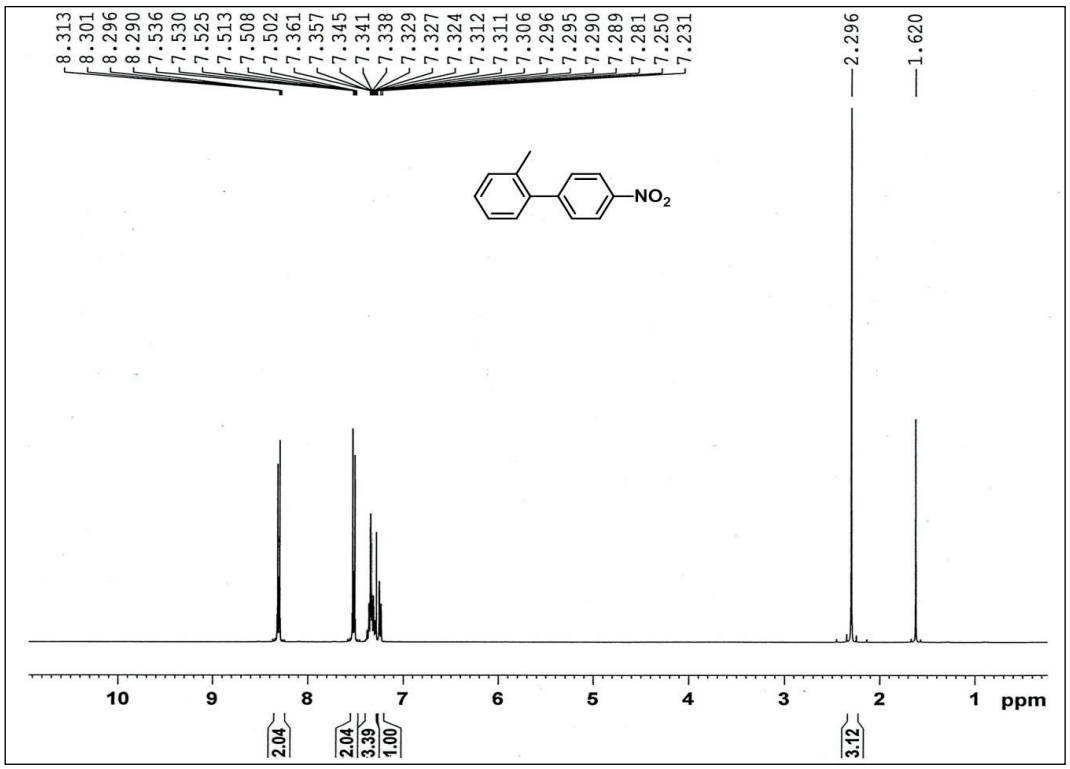
Mass spectra of compound 36



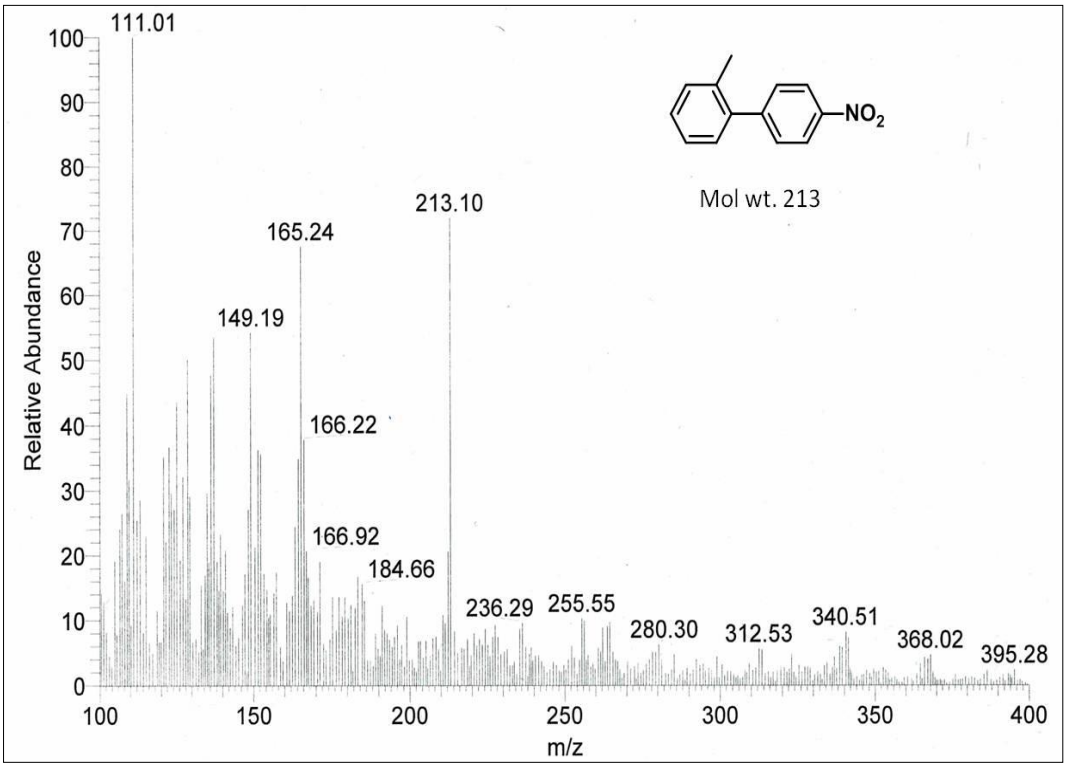
^{1}H-NMR of compound 37



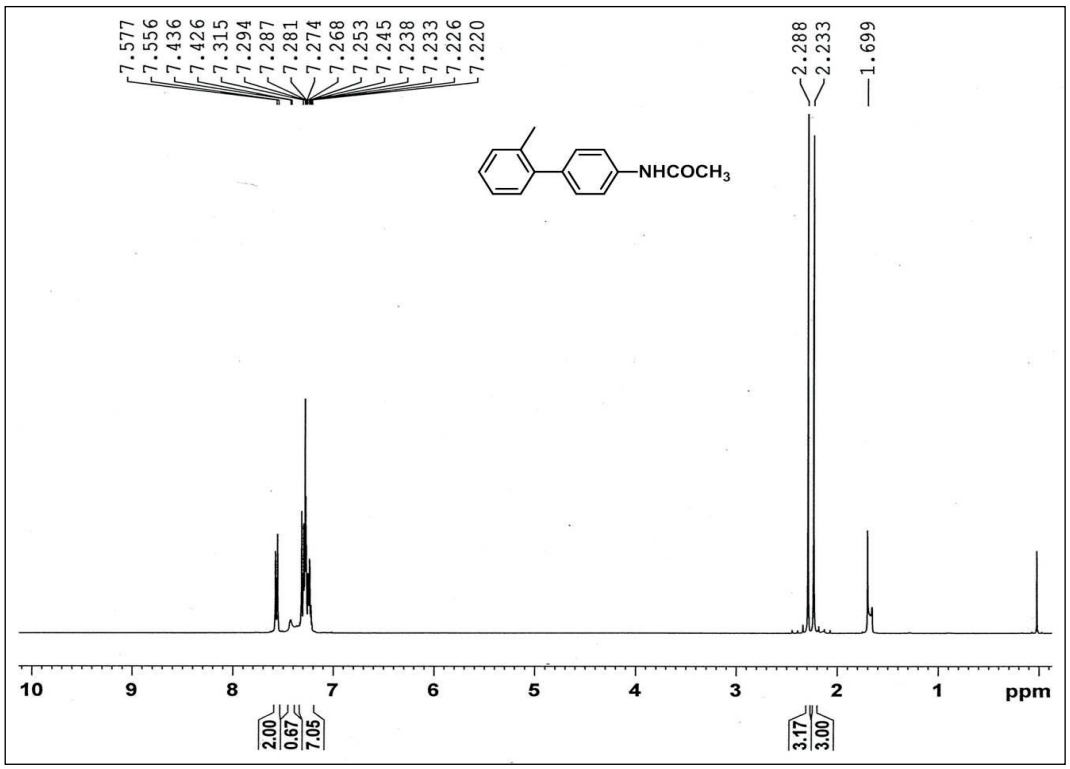
Mass spectra of compound 37



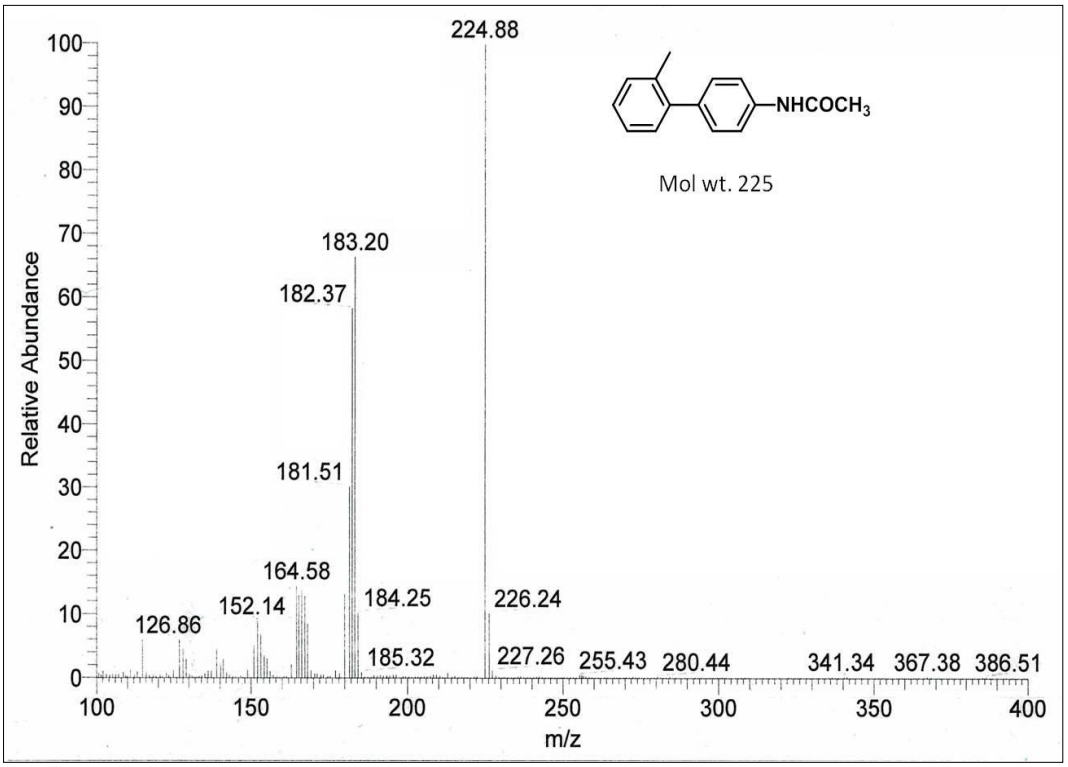
^{1}H-NMR of compound 38



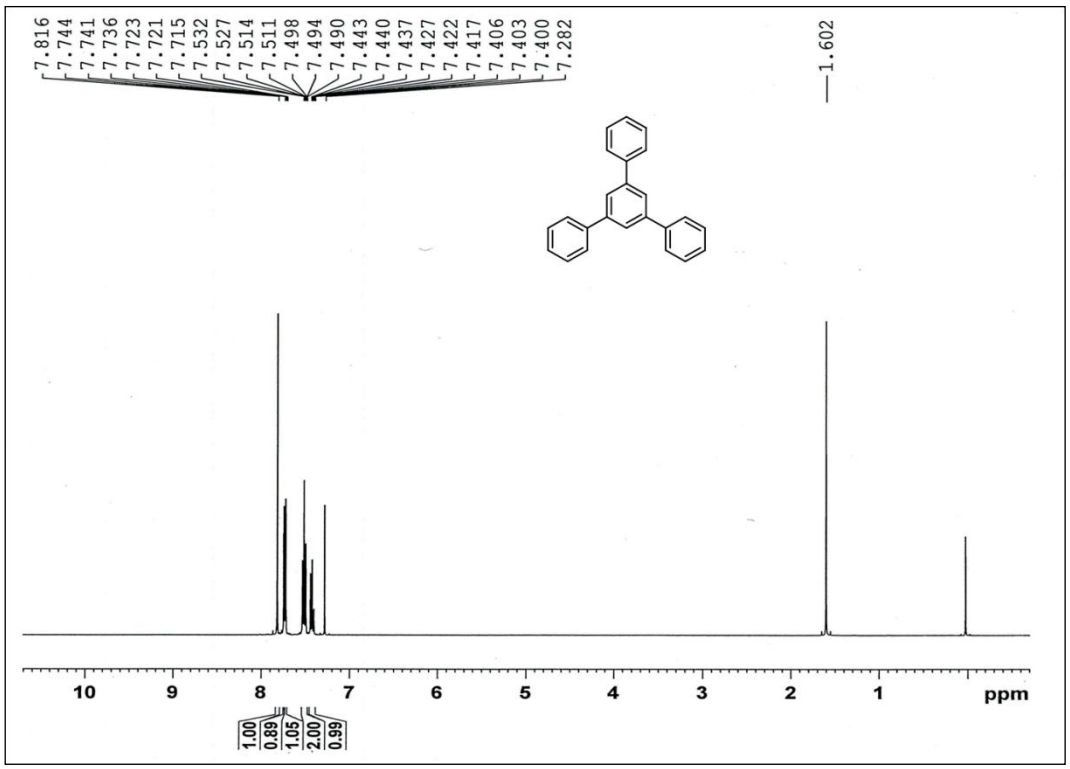
Mass spectra of compound 38



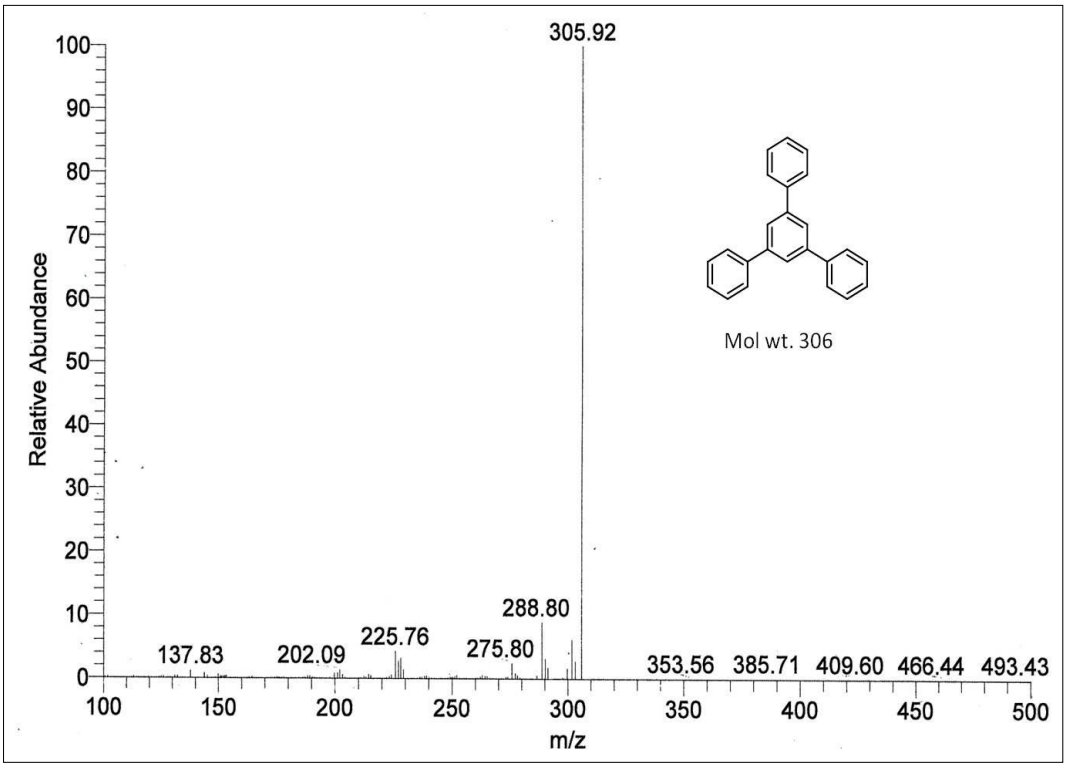
^{1}H-NMR of compound 39



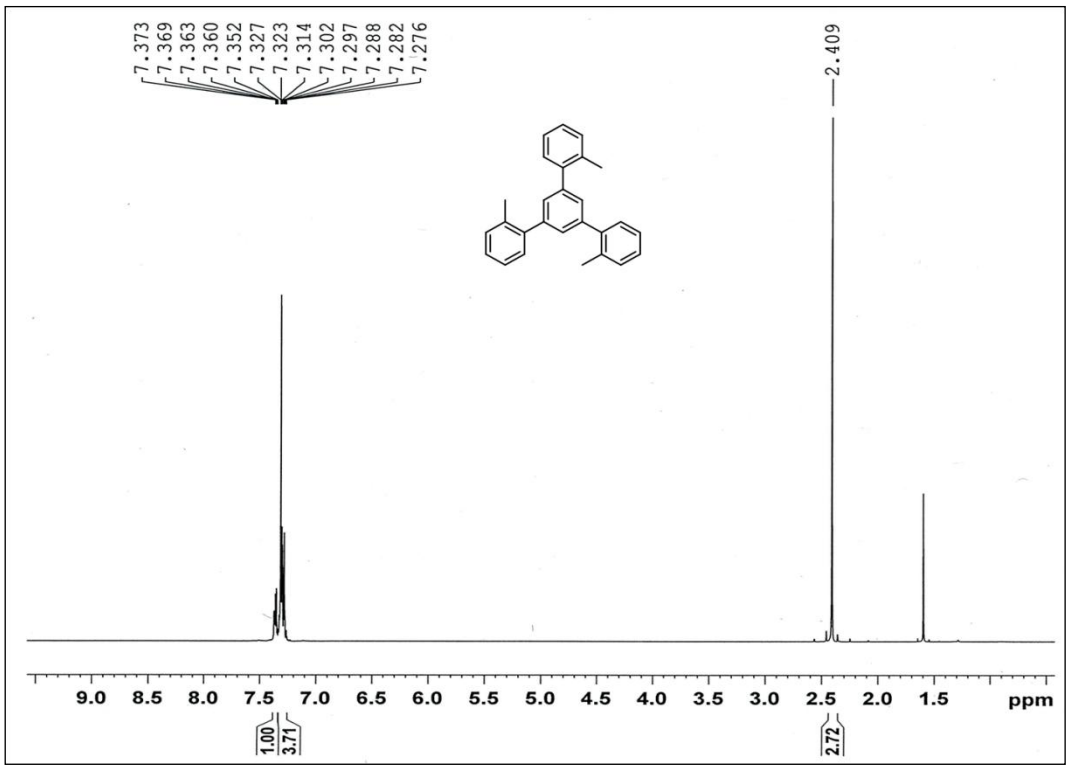
Mass spectra of compound 39



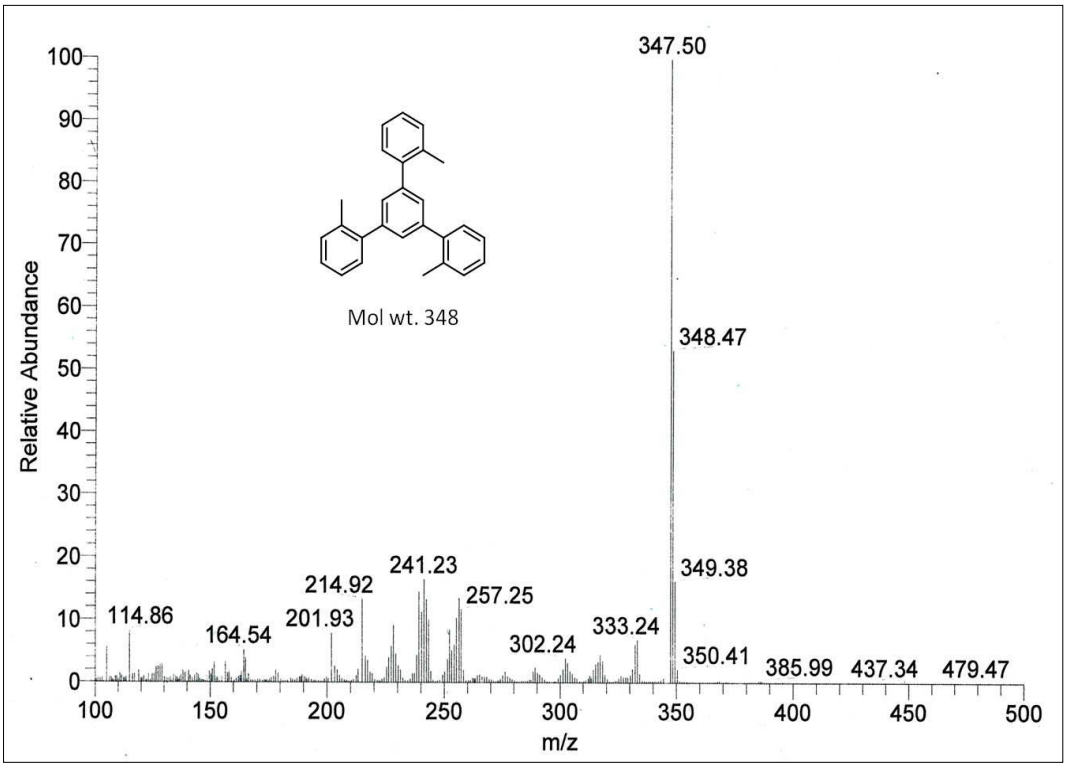
^{1}H-NMR of compound 40



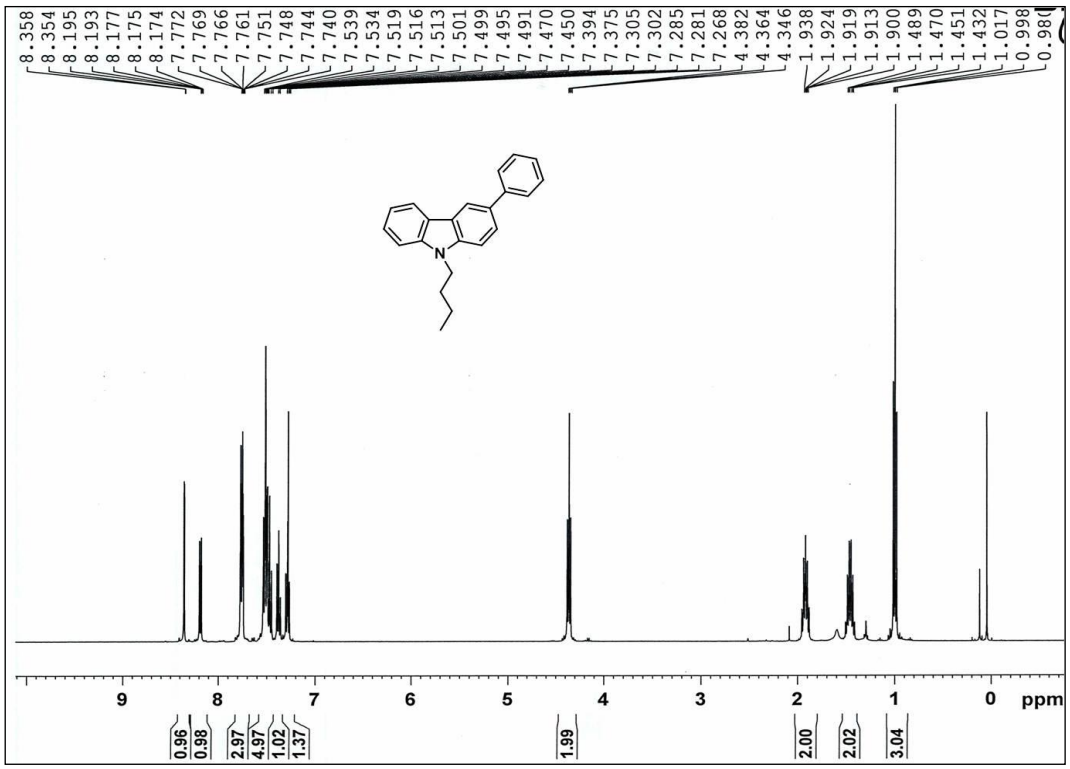
Mass spectra of compound 40



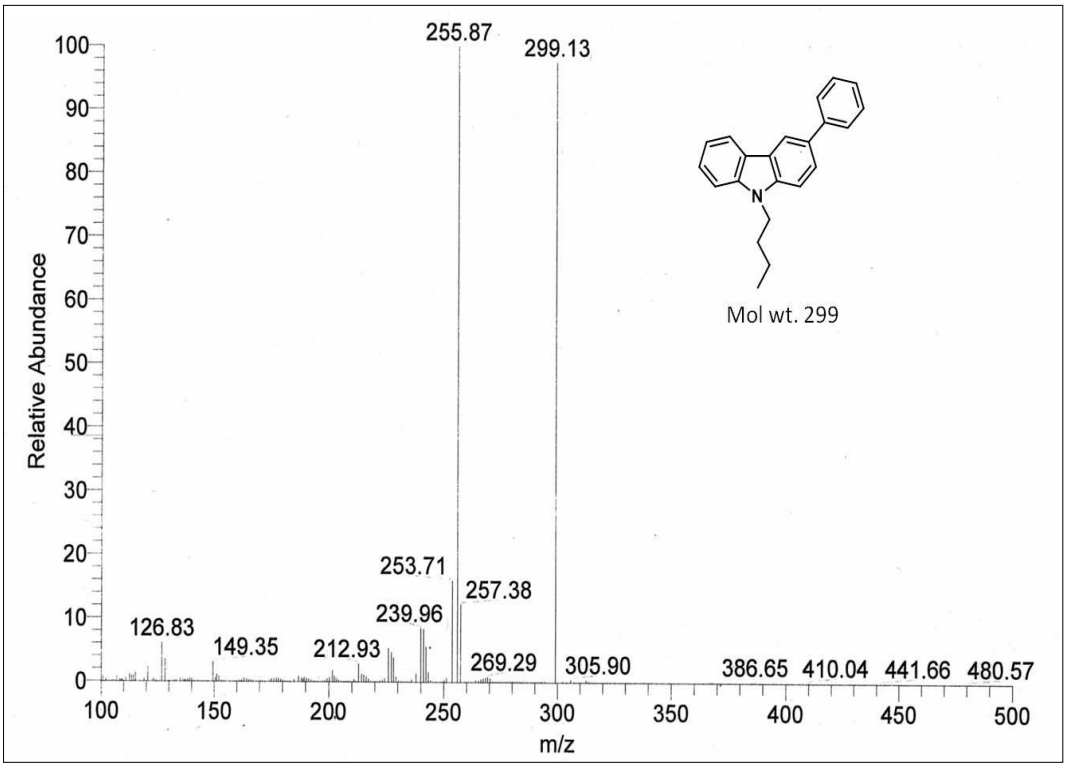
^{1}H-NMR of compound 40



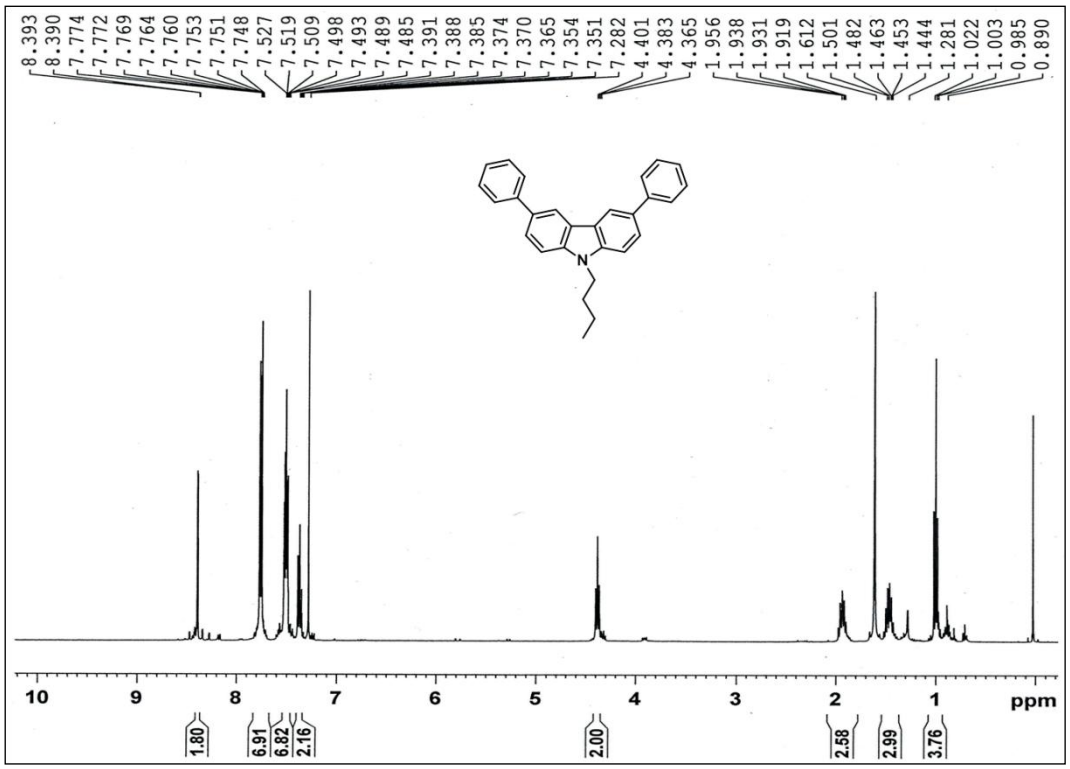
Mass spectra of compound 40



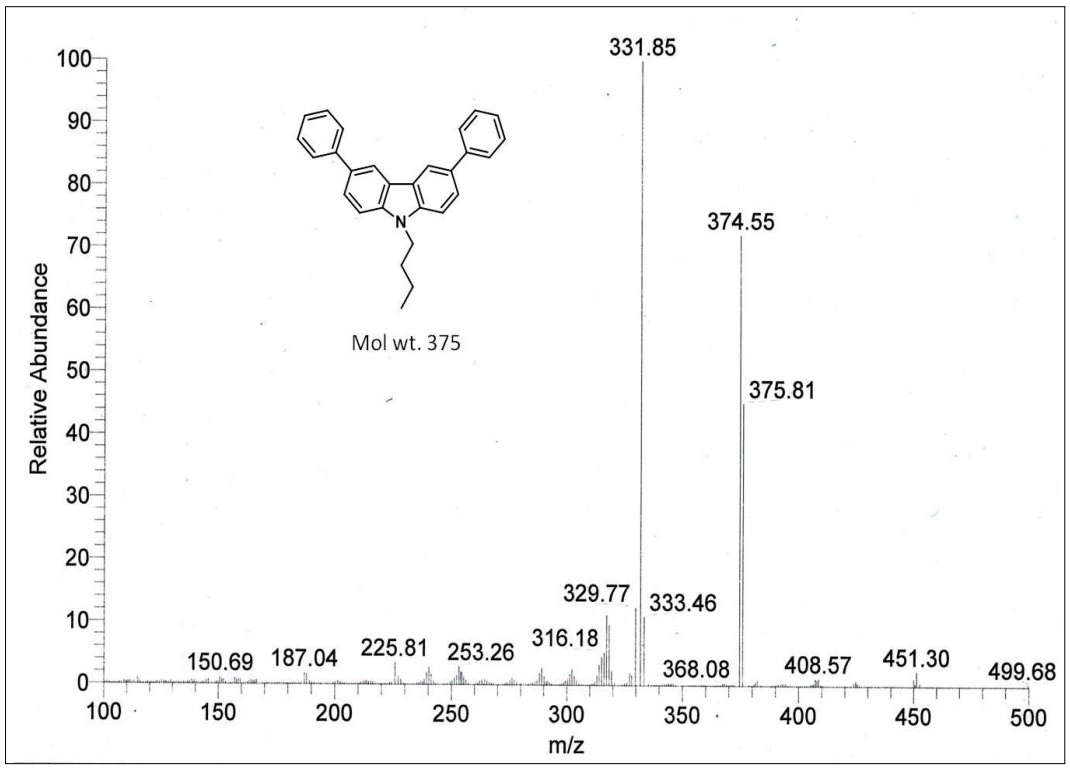
^{1}H-NMR of compound 43



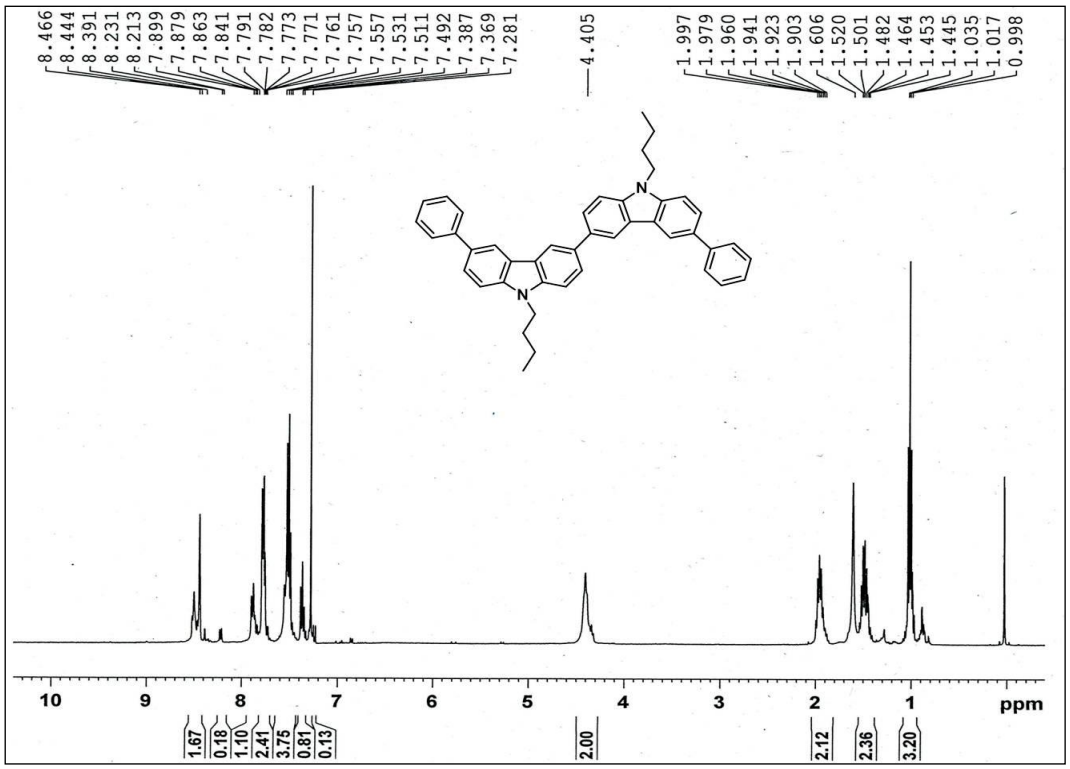
Mass spectra of compound 43



^{1}H-NMR of compound 45



Mass spectra of compound 45



^{1}H-NMR of compound 47

5.4.3 *Application of polymer supported catalyts for One pot O-Alkylation-Suzuki reaction*

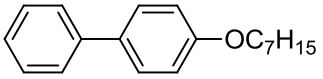
Typical procedure for O-Alkylation-Suzuki reaction:

Synthesis of 4-(octyloxy)-1,1'-biphenyl (**50**)

A round bottom flask was charged with 4-hydroxy phenol (0.20 g, 0.909 mmol), catalyst **B-2** (0.056 g, 0.0000909 mmol, 0.01 mol%), n-octyl bromide (0.21 g, 1.090 mmol), phenyl boronic acid (0.133 g, 1.090 mmol), dry potassium carbonate (0.502 g, 3.63 mmol), TBAB (0.058 g, 0.181 mmol) and dioxane-water (1:1, 10 mL) as solvent. This mixture was heated to 80^{o}C and continued for 24 h. The reaction mixture was filtered to remove catalyst and 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 sulphate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford 4-octyloxy biphenyl (**50**) (0.246 g, 96.2 %) as white solid.

4-(heptyloxy)-1,1'-biphenyl (49)

White solid (0.231 g, 95.0 %).



^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.58-7.53 (m, 4H, one doublet

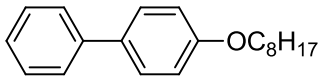
with *J* = 8.8 Hz merged together), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34-7.30 (m, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.02 (t, *J* = 6.8 Hz, 2H), 1.86-1.79 (m, 2H), 1.52-1.46 (m, 2H), 1.41-1.32 (m, 8H), 0.92 (t, *J* = 6.8 Hz, 3H).

IR (KBr): υ 3057, 3035, 2930, 2858, 1605, 1522, 1485, 1286, 1252, 1039, 835, 758 cm.$^{-1}$

MS (EI) (*m/z*): 268 (14) [M^+], 267 (31), 170 (40), 169 (100).

4-(octyloxy)-1,1'-biphenyl (50)

White solid (0.246 g, 96.0 %).



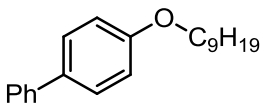
^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.58-7.52 (m, 4H, one doublet with *J* = 8.8 Hz merged together), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34-7.30 (m, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.02 (t, *J* = 6.8 Hz, 2H), 1.86-1.79 (m, 2H), 1.51-1.46 (m, 2H), 1.41-1.32 (m, 8H), 0.92 (t, *J* = 6.8 Hz, 3H).

IR (KBr): υ 3058, 3034, 2922, 2854, 1605, 1522, 1486, 1285, 1253, 1029, 835, 758 cm.$^{-1}$

MS (EI) (*m/z*): [M^+] 282 (15), 170 (41), 169 (45).

4-(nonyloxy)-1,1'-biphenyl (51)

White solid (0.227g, 85.0%)



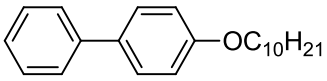
^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.59-7.53 (m, 4H, one doublet with *J* = 8.8 Hz merged together), 7.43 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.02 (t, *J* = 6.8 Hz, 2H), 1.84-1.81 (m, 2H), 1.51-1.47 (m, 2H), 1.40-1.31 (m, 10H), 0.91 (t, *J* = 6.8 Hz, 3H).

IR (KBr): υ 3035, 2919, 2849, 1605, 1522, 1488, 1473, 1286, 1255, 1201, 1037, 1024, 1009, 837, 758 cm.$^{-1}$

MS (EI) (*m/z*): [M^+] 296 (26), 295 (22), 170 (100), 169 (78).

4-(decyloxy)-1,1'-biphenyl (52)

White solid (0.270 g, 96.0 %).

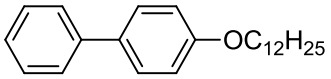


^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.63-7.52 (m, 4H, one doublet with *J* = 8.8 Hz merged together), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34-7.30 (m, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.02 (t, *J* = 6.8 Hz, 2H), 1.84-1.80 (m, 2H), 1.51-1.47 (m, 2H), 1.39-1.30 (m, 12H), 0.91 (t, *J* = 6.4 Hz, 3H).

IR (KBr): υ 3035, 2918, 2850, 1606, 1522, 1488, 1287, 1254, 1027, 836, 758 cm.$^{-1}$

MS (EI) (*m/z*): 310 (10) [M^+], 309 (20), 169 (100).

4-(dodecyloxy)-1,1'-biphenyl (53)



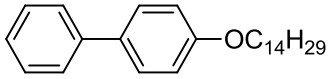
White solid (0.299 g, 97.0 %).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.58-7.53 (m, 4H, one doublet with *J* = 8.8 Hz merged together), 7.44 (t, *J* = 7.2 Hz, 2H), 7.34-7.30 (m, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.02 (t, *J* = 6.8 Hz, 2H), 1.84-1.79 (m, 2H), 1.51-1.47 (m, 2H), 1.36-1.30 (m, 16H), 0.91 (t, *J* = 6.8 Hz, 3H).

IR (KBr): υ 3035, 2919, 2850, 1606, 1522, 1488, 1287, 1255, 1028, 836, 758 cm.$^{-1}$

MS (EI) (*m/z*): 502 (5), 451 (24), 407 (32), 375 (64), 372 (45), 332 (100).

4-(tetradecyloxy)-1,1'-biphenyl (54)



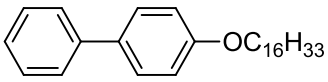
White solid (0.301 g, 91.0 %).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.59-7.53 (m, 4H, one doublet with *J* = 8.4 Hz merged together), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.02 (t, *J* = 6.8 Hz, 2H), 1.87-1.80 (m, 2H), 1.52-1.46 (m, 2H), xx-1.29 (m, 20H), 0.92 (t, *J* = 6.4 Hz, 3H).

IR (KBr): υ 3035, 2917, 2848, 1607, 1524, 1489, 1473, 1287, 1255, 1026, 837, 758 cm.$^{-1}$

MS (EI) (*m/z*): 366 (100) [M^+], 170 (36), 169 (58).

4-(hexadecyloxy)-1,1'-biphenyl (55)



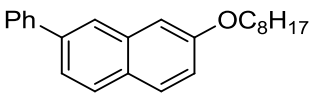
White solid (0.310 g, 87.0 %).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.58-7.52 (m, 4H, one doublet with *J* = 8.8 Hz merged together), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34-7.30 (m, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.02 (t, *J* = 6.8 Hz, 2H), 1.85-1.78 (m, 2H), 1.52-1.44 (m, 2H), 1.28-1.xx (m, 24H), 0.90 (t, *J* = 6.4 Hz, 3H).

IR (KBr): υ 3036, 2917, 2848, 1607, 1489, 1473, 1287, 1256, 1028, 837, 758 cm.$^{-1}$

MS (EI) (*m/z*): 394 (67) [M^+], 170 (100).

2-(octyloxy)-7-phenylnaphthalene (56)



White solid (0.192 g, 86%)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.95 (s, 1H, Ar-*H*), 7.85 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.90-7.73 (m, 3H, Ar-*H*), 7.61 (dd, *J* = 8.4 Hz, 1.6Hz, 1H, Ar-*H*), 7.50 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.40 (t, *J* = 7.2Hz, 1H, Ar-*H*), 7.21 (d, *J* = 2.4Hz, 1H, Ar-*H*), 7.17 (dd, *J* = 8.8Hz, 2.4 Hz, 1H, Ar-*H*), 4.12 (t, 6.4 Hz, 2H, -O-C*H*$_2$-), 1.90-1.87 (m, 2H, -O-CH$_2$-C*H*$_2$-), 1.59-1.52 (m, 2H, -O-CH$_2$-CH$_2$-C*H*$_2$-), 1.41-1.33 (m, 8H, *n*-(C*H*$_2$)$_4$-), 0.92 (t, *J* = 6.8 Hz, 3H, -C*H*$_3$).

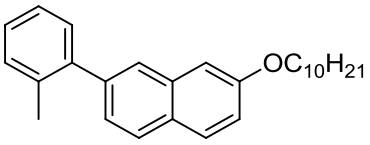
^{13}C-NMR ($CDCl_3$, 100 MHz) δ157.54, 141.37, 139.04, 134.95, 129.09, 128.85, 128.19, 128.09, 127.46, 127.32, 124.76, 123.27, 119.19, 106.84, 68.09, 31.91, 29.47, 29.34, 26.19, 22.75, 14.20

IR (KBr): υ 3059, 3032, 2924, 2851, 1625, 1604, 1460, 1391, 1211, 888, 840, 750, 690 cm.$^{-1}$

MS (EI) (*m/z*): 322 (31) [M^+], 331 (20), 219 (100).

HRMS (ESI^+): Calculated for $C_{24}H_{29}O$ $[M+H]^+$ 333.2218, found 333.2213

2-(decyloxy)-7-(o-tolyl)naphthalene (57)



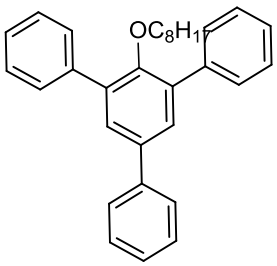
Colourless liquid (0.201 g, 80.0 %)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.83-7.79 (m, 2H), 7.68 (d, *J* = 1.2Hz, 1H), 7.36-7.29 (m, 5H), 7.21-7.17 (m, 2H), 4.11 (t, *J* = 6.8 Hz, 2H), 2.35 (s, 3H), 1.90-1.85 (m, 2H), 1.55-1.50 (m, 2H), 1.41-1.31 (m, 12H), 0.92 (t, *J* = 6.8 Hz, 3H).

IR (KBr): υ 3019, 2925, 2854, 1628, 1461, 1391, 1236, 1210, 1175, 839, 753 cm.$^{-1}$

MS (EI) (*m/z*): 374 (92) [M^+], 373 (100), 233 (74).

2'-(octyloxy)-5'-phenyl-1,1':3',1''-terphenyl (58)



Colourless liquid (0.166 g, 84.7 %)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.70-7.65 (m, 6H, Ar-*H*), 7.60 (s, 2H, Ar-*H*), 7.49-7.44 (m, 6H, Ar-*H*), 7.41-7.36 (m, 3H, Ar-*H*), 3.26 (t, *J* = 6.4 Hz, 2H, -O-CH_2-), 1.27-0.93 (m, 12H, *n*-(CH_2)$_6$-), 0.88 (t, *J* = 6.8 Hz, 3H, -CH_3).

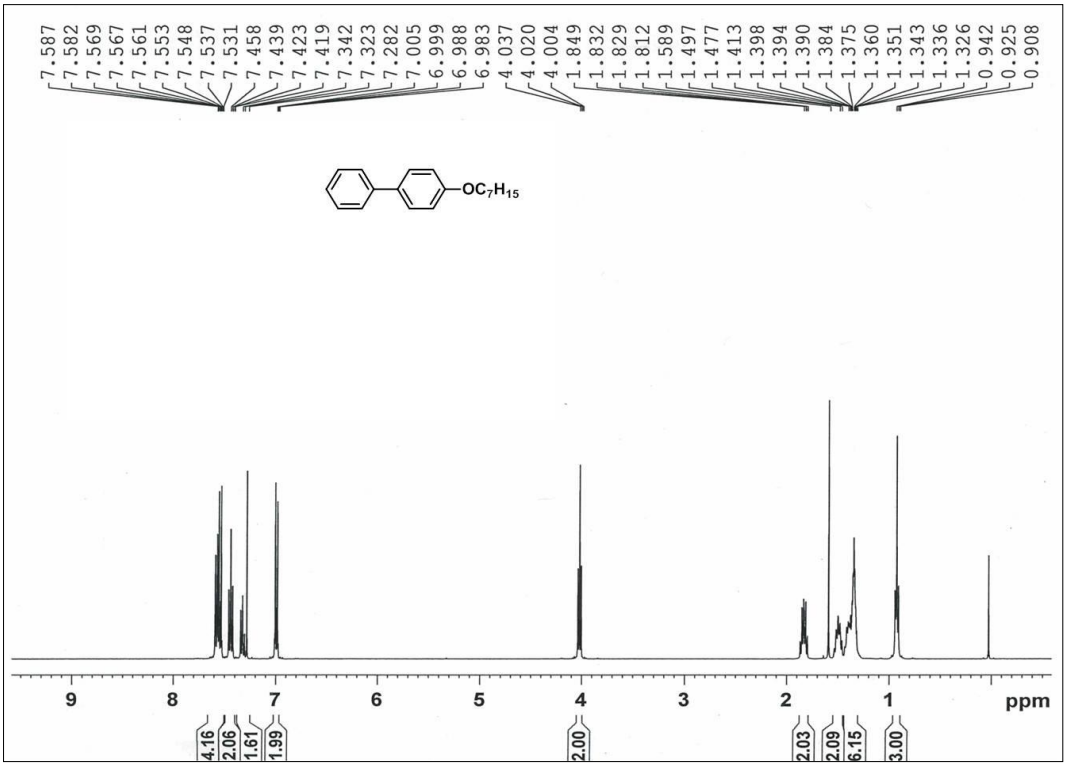
^{13}C-NMR ($CDCl_3$, 100 MHz) δ153.76, 140.56, 138.87, 136.95, 136.46, 129.58, 128.96, 128.90, 128.80, 128.09, 127.17, 127.05, 73.40, 31.78, 29.79, 29.13, 29.10, 25.73, 22.67, 14.17

IR (KBr): υ 3058, 3032, 2925, 2855, 1689, 1599, 1576, 1495, 1461, 1426, 1380, 1221, 1074, 963, 887, 753, 697 cm^{-1}

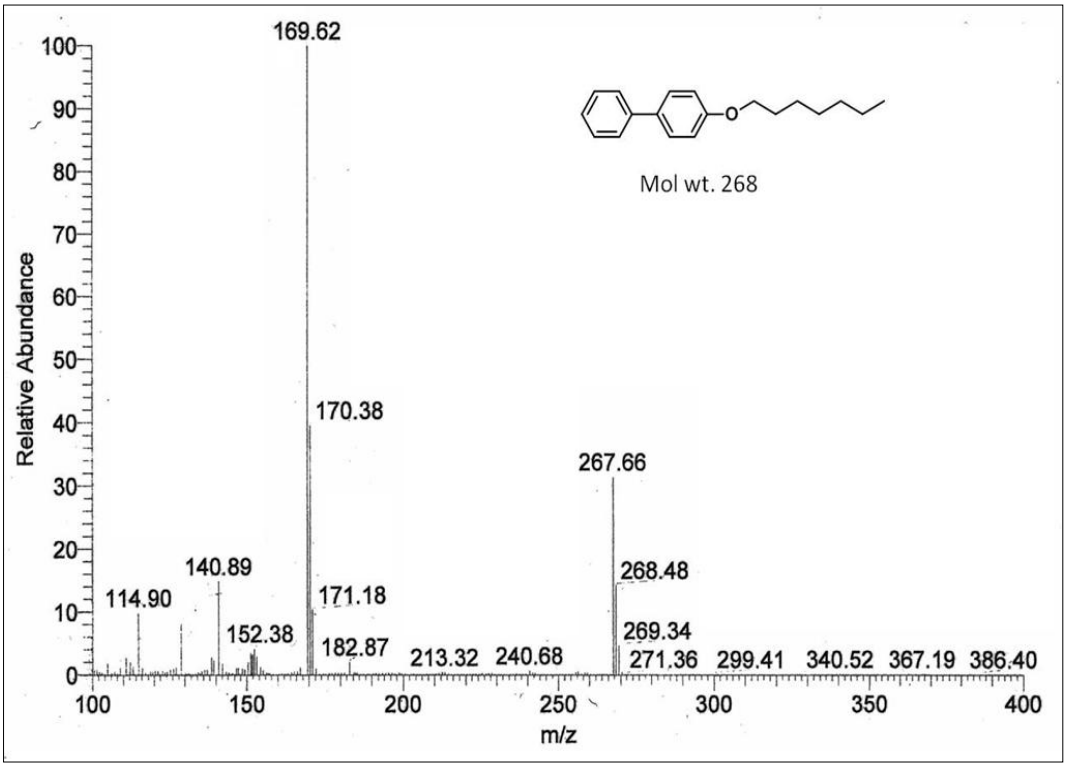
MS (EI) : (*m/z*) 434 (18) [M^+], 322 (100), 321 (98).

HRMS (ESI^+): Calculated for $C_{32}H_{34}O$ $[M+Na]^+$ 457.2507, found 457.2505

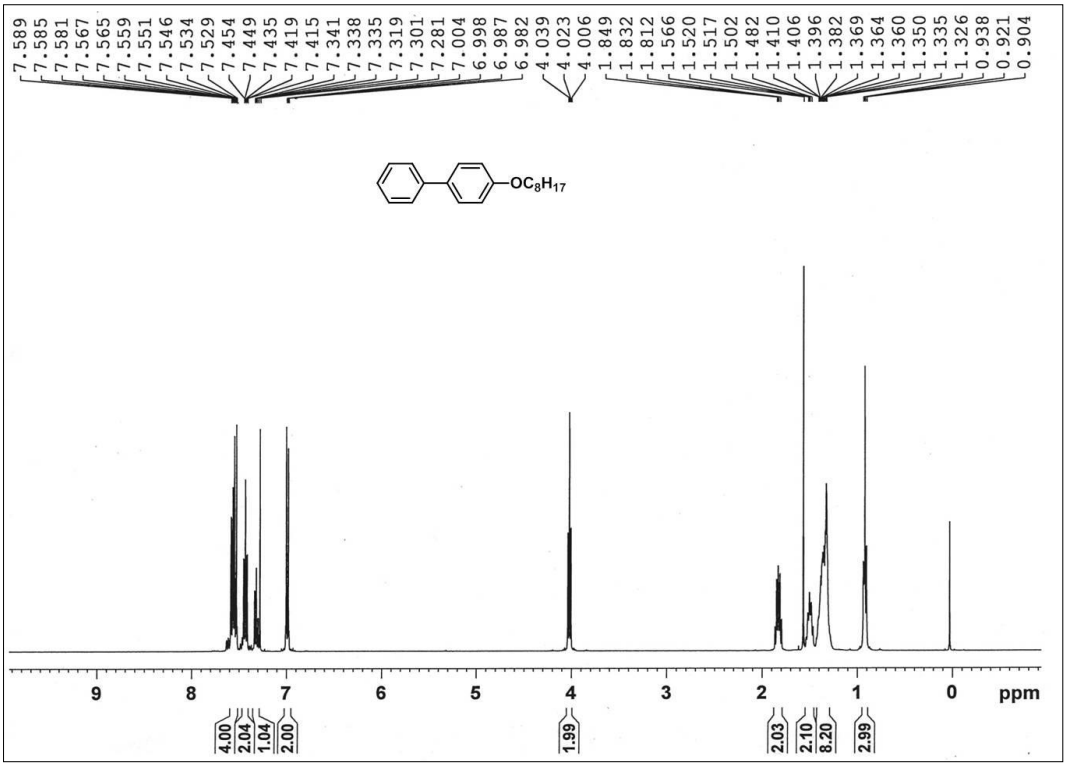
Spectral data for examples of O-Alkylation-Suzuki reaction (Section 5.2.3)



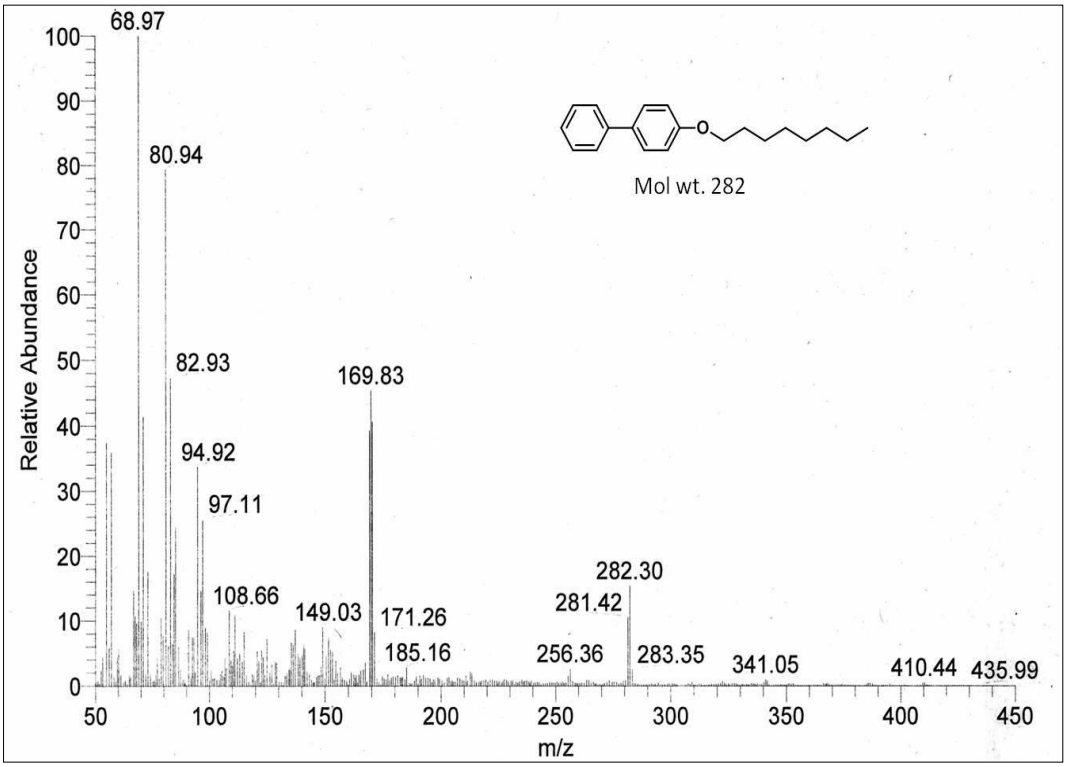
^{1}H-NMR of compound 49



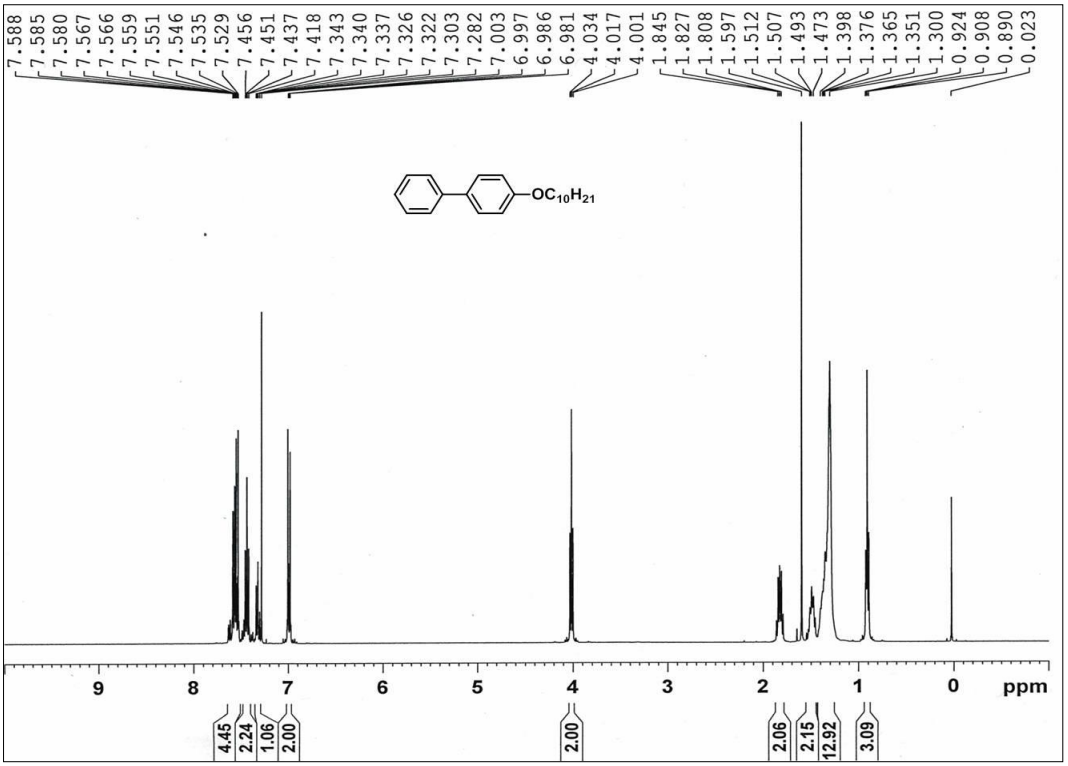
Mass spectra of compound 49



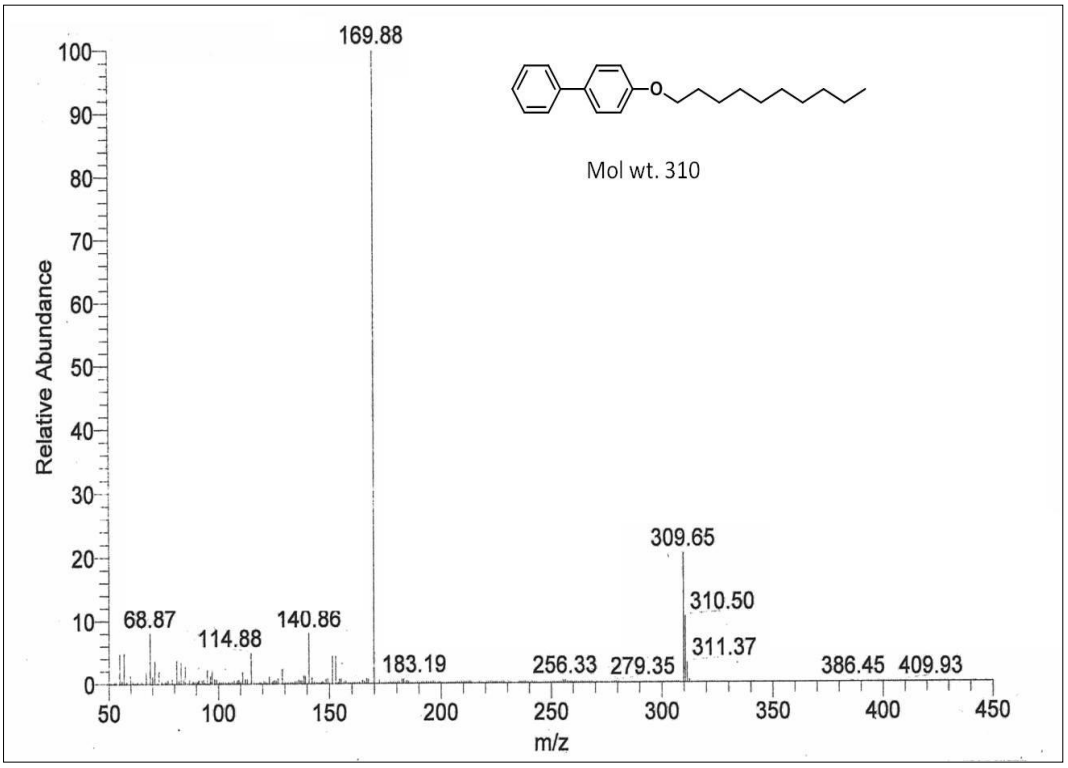
^{1}H-NMR of compound 50



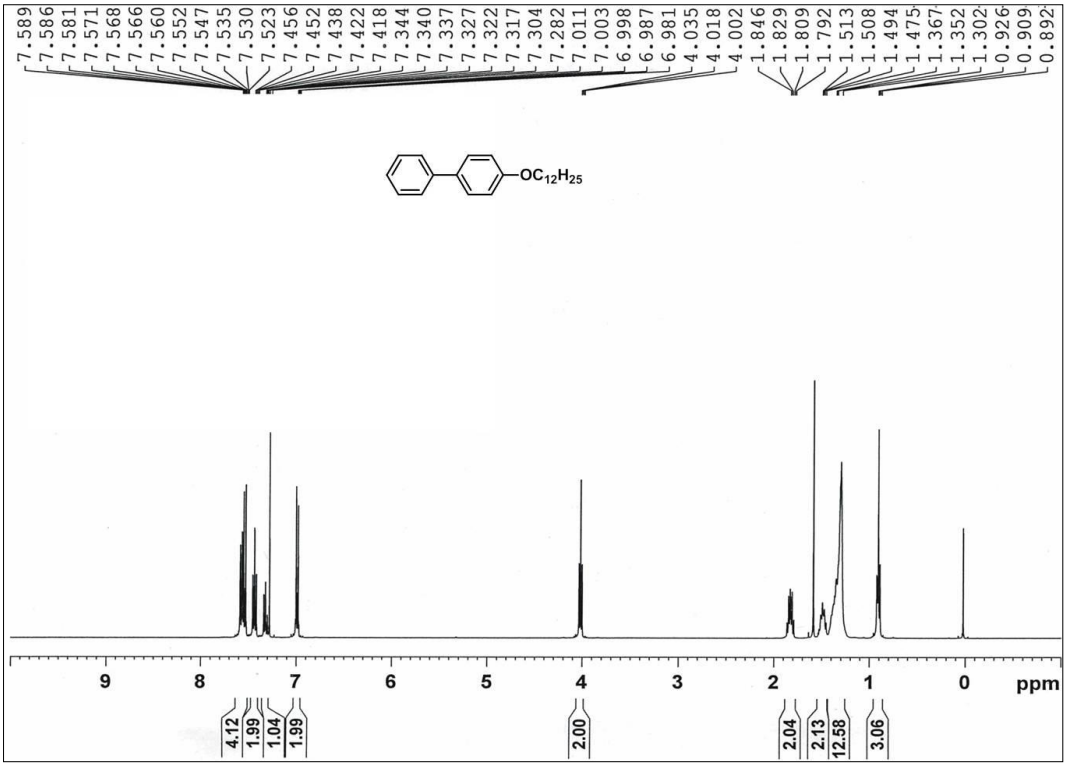
Mass spectra of compound 50



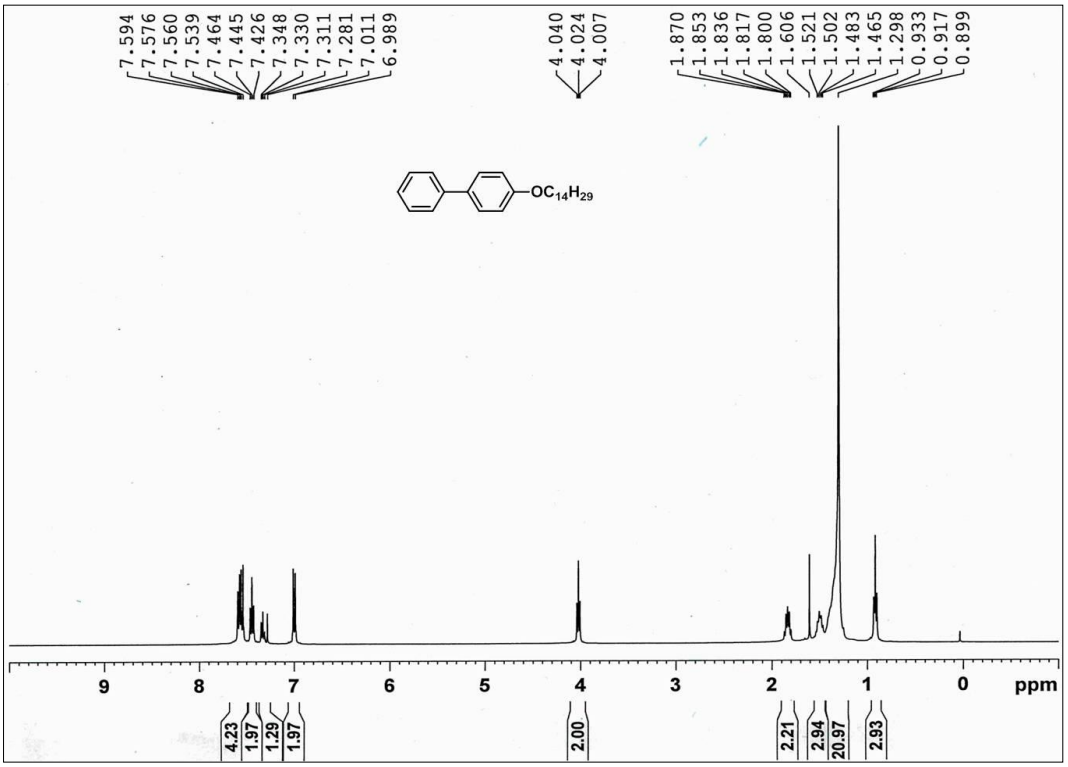
^{1}H-NMR of compound 52



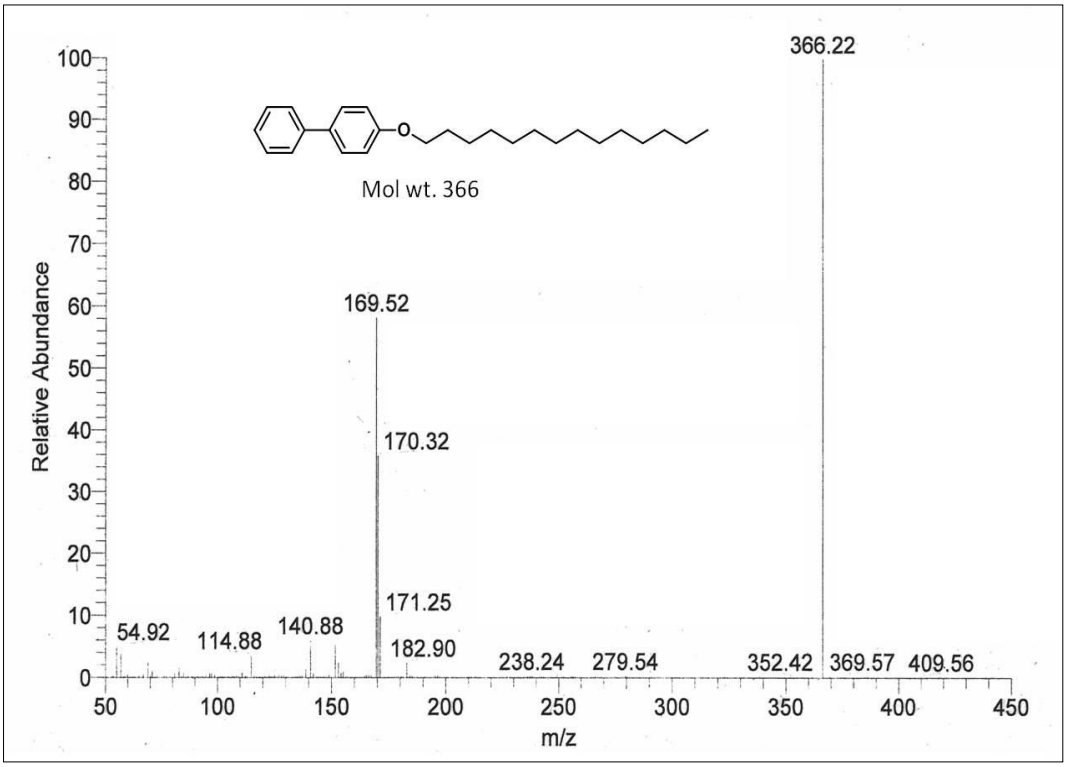
Mass spectra of compound 52



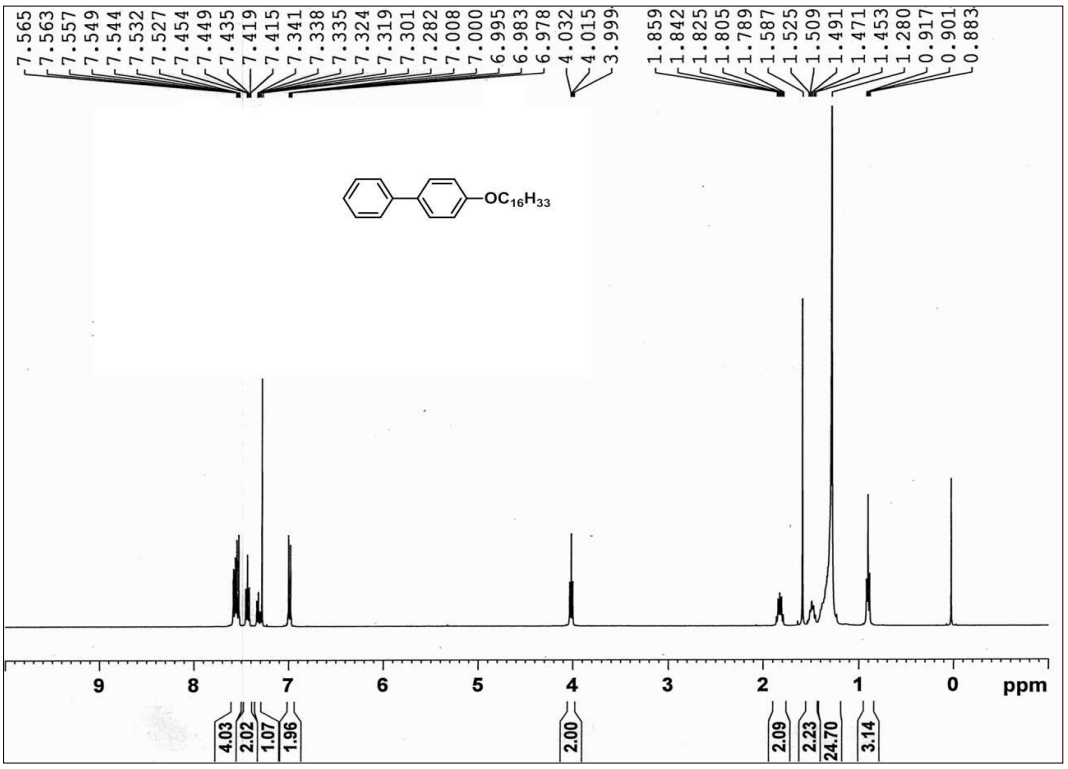
^{1}H-NMR of compound 53



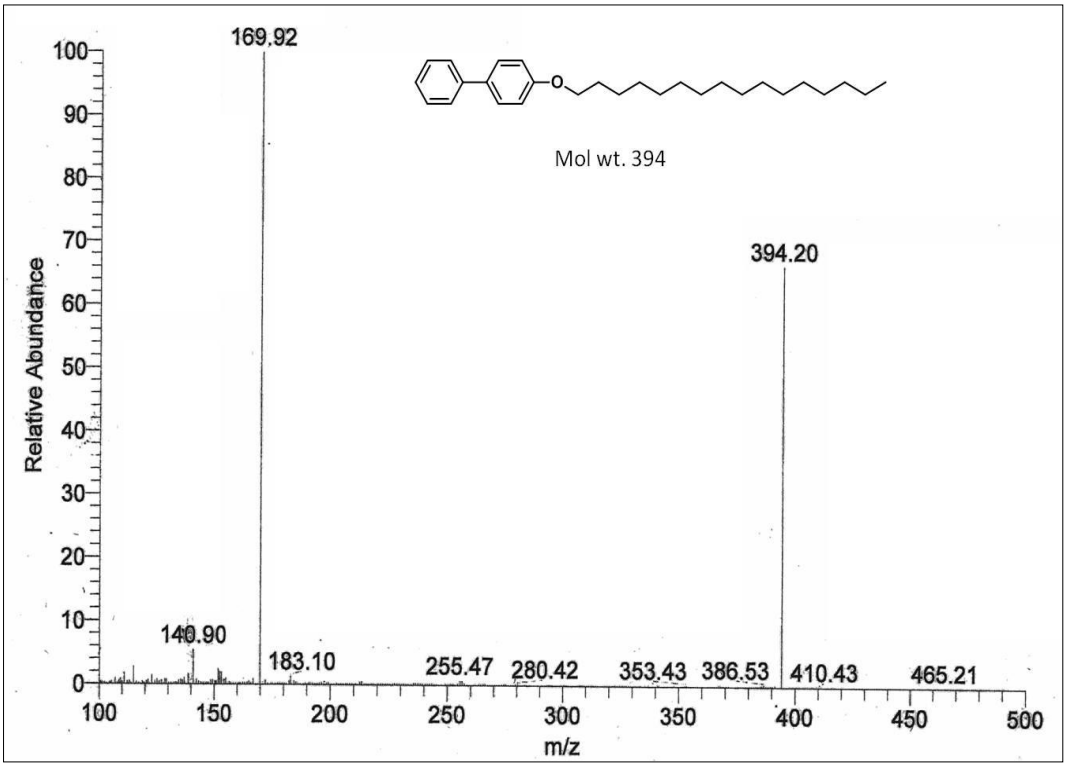
^{1}H-NMR of compound 54



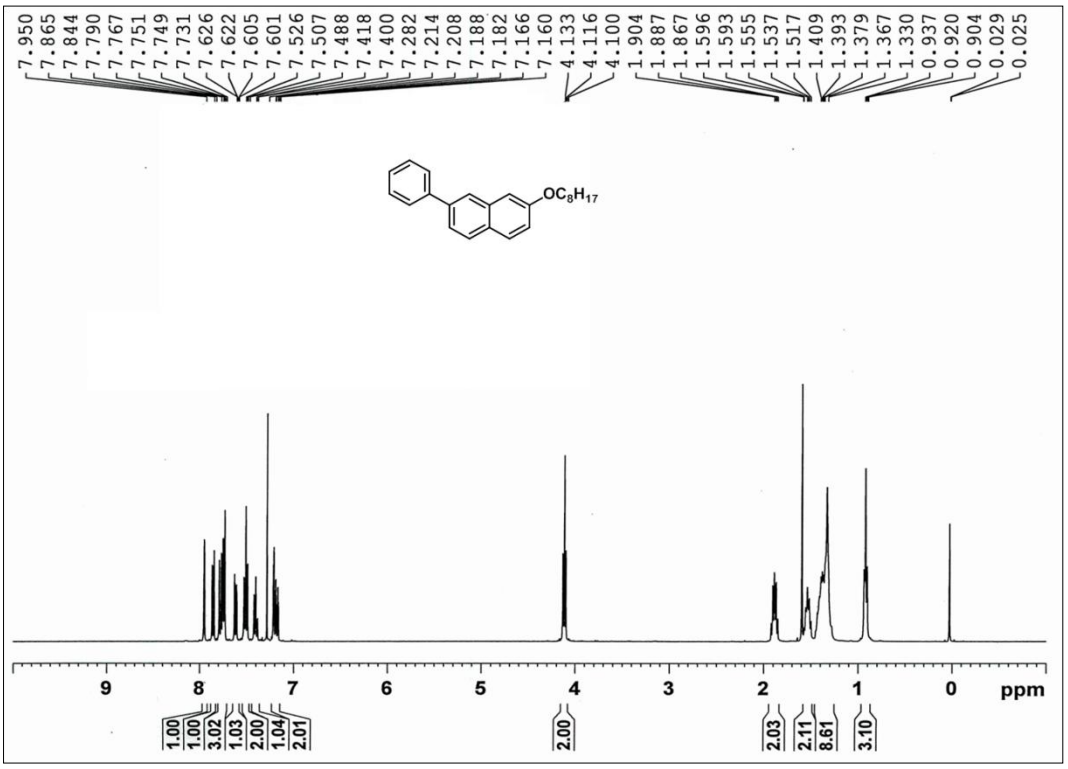
Mass spectra of compound 54



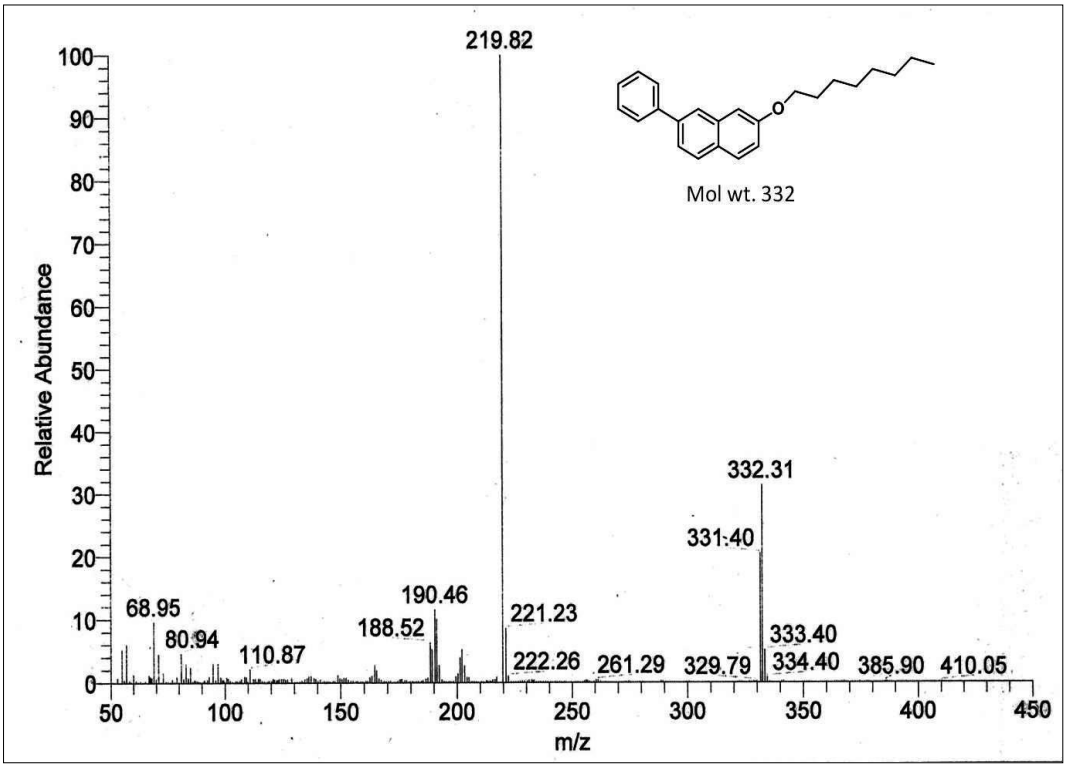
^{1}H-NMR of compound 55



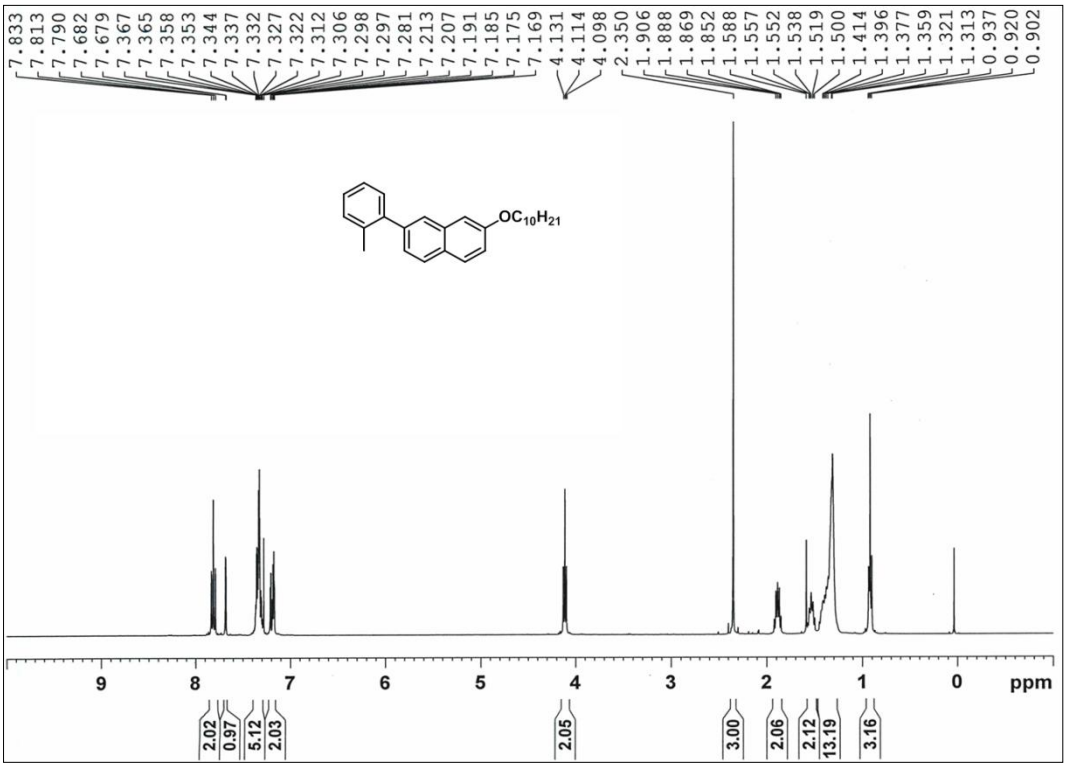
Mass spectra of compound 55



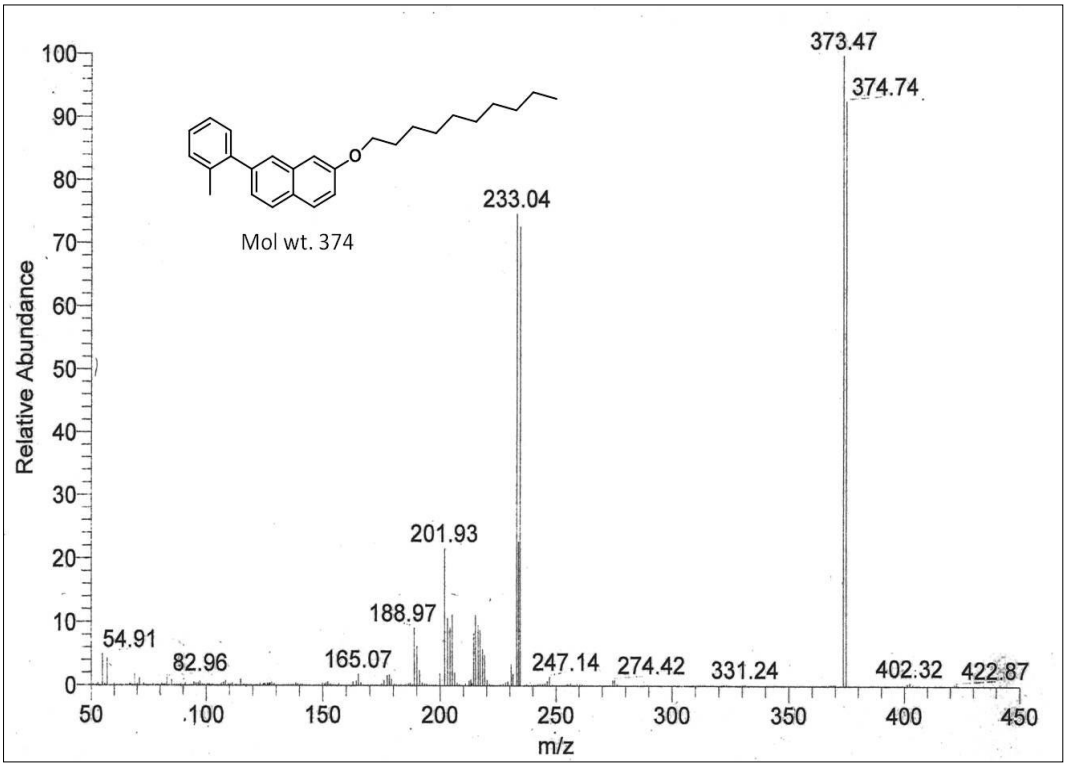
^{1}H-NMR of compound 56



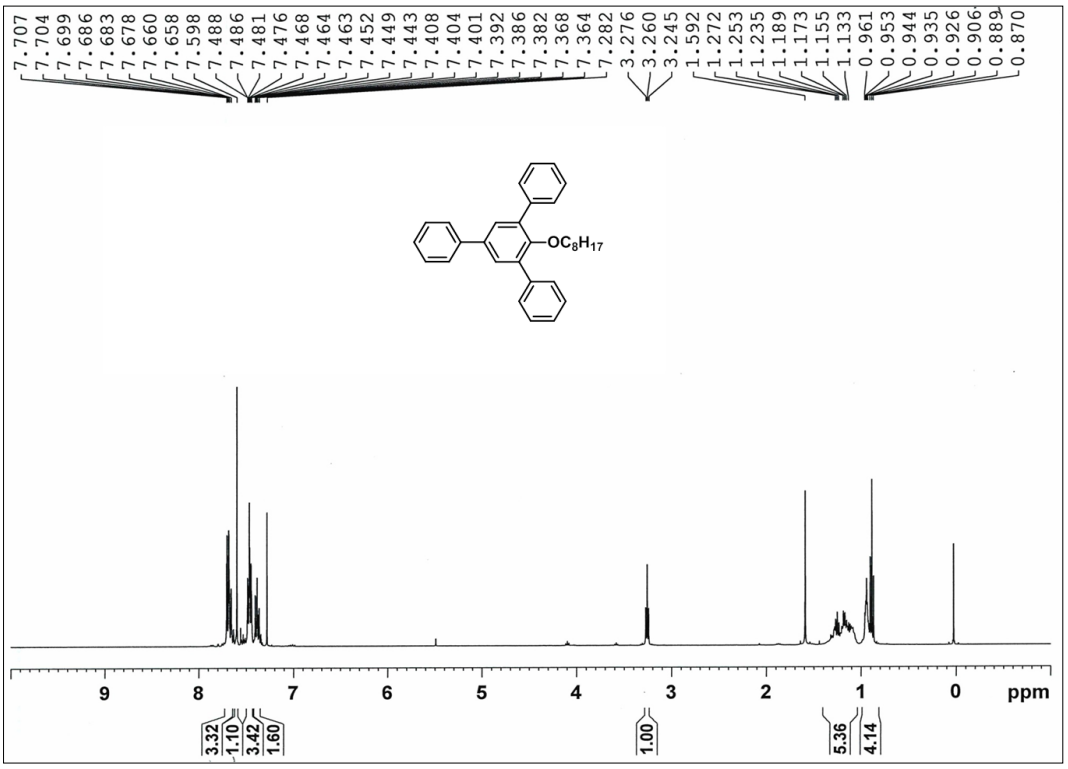
Mass spectra of compound 56



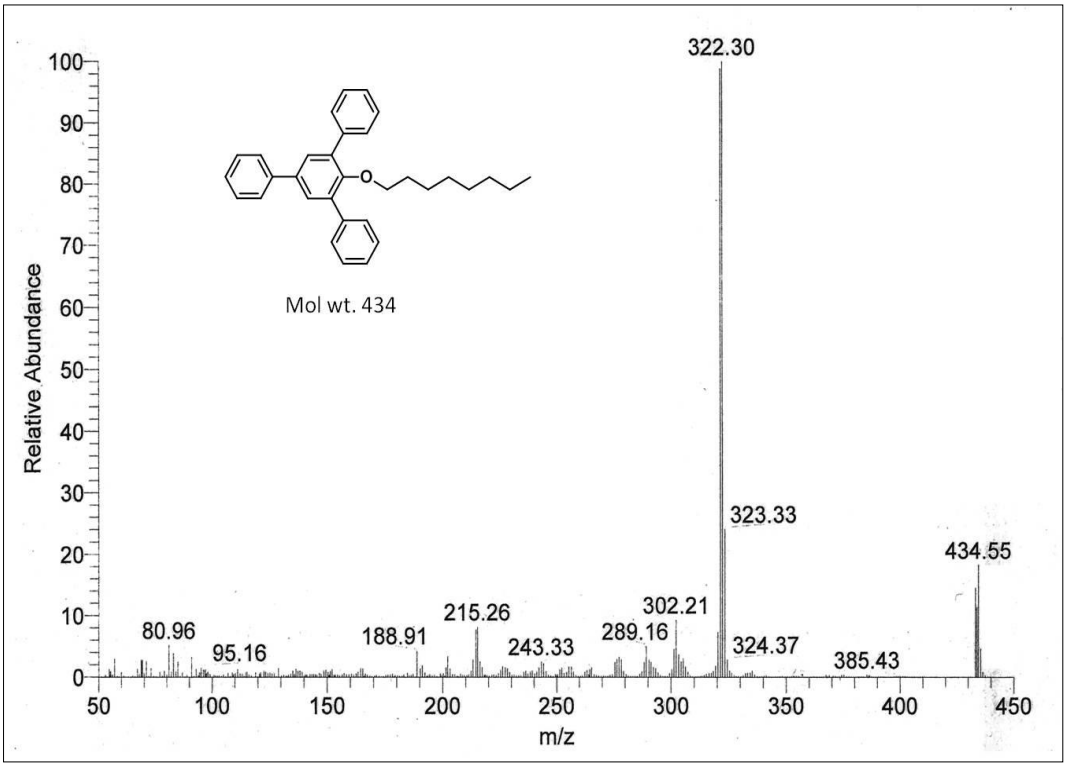
^{1}H-NMR of compound 57



Mass spectra of compound 57



^{1}H-NMR of compound 58



Mass spectra of compound 58

5.5. *References*

1. Yin, L.; Liebscher, J. *Chem. Rev*. **2007**, *107*, 133.
2. The Mizoroki–Heck Reaction, ed. Oestreich M., John Wiley & Sons Ltd, **2009**.
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