CHAPTER 3

HETEROGENIZATION OF POLYANILINE ON SOLID SUPPORT: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF CELITE-PANI-Pd FOR ORGANIC TRANSFORMATIONS

Contents

Section-I

Synthesis, characterization and applications of Celite-PANI-Pd for Suzuki, sunlight Suzuki and one-pot combinations with Suzuki reaction

3.1.1 Introduction

The preparation of heterogeneous catalysts have been explored by anchoring active metal ions on various types of materials. There are different modes of binding metal ions, involving chemical, physical and supramolecular forces. Metal ions are known to be loaded on inorganic supports[1] like silica[2], zeolites[3], clay[4] or materials like dendrimers[5] and polymers.[6] Amongst all these approaches, polymer supported metal catalysts are very significant. Polymers having amino functional groups are suitable as they can form complexes or chelates with metal ions for diverse catalytic applications.[7]

Various methods have been described for generating organic polymer on inorganic materials, which include surface polymerization from particle-bound initiators, cross linking of polymeric micelles surrounding the inorganic cores, layer-by-layer deposition and vapor deposition polymerization.[8] These materials can be good candidates for appropriate modifications to solid reagents for useful chemical transformations. Such inorganic-organic hybrid materials have been prepared recently and used for some transformations.[9]

Importance of polyaniline and its applications as polyaniline loaded with metal ions have been already discussed in earlier chapters. However, in some cases such catalysts system of polyaniline loaded with metal ions or metal complexes face difficulty due to partial solubility of PANI in some solvents, particularly at higher temperature. Due to which the system can't be completely heterogeneous and hence faces difficulty in recovering and recycling the catalyst in efficient manner. Also the use of amount of PANI for the synthesis of the desired product is fairly high, which may become a matter of concern due to some aspects of its toxicity.[10]Few composite materials with PANI have been prepared by researchers and have investigated for their properties. Results showed that in some cases after incorporating polyaniline with inorganic materials can enhance the conducting properties.[11] Recently micrometer-size hollow particles[12] and nanoparticles of composites of PANI[13,14] have also been synthesized and studied.

We have designed a strategy to heterogenize PANI over some solid materials. Although few of reports were available on supporting PANI on silica gel, we have chosen celite as a less acidic, solid inorganic support for its heterogenization. So during polymerization of PANI it will be coated around celite as shown in Figure 1. This supported PANI was further treated with metal ions to prepare more robust heterogeneous catalyst. The prepared catalysts were then characterized and scanned to evaluate their efficacy to influence useful catalytic transformation. As a part of our continuous interest in PANI palladium mediated chemical transformations, as also discussed in Section 1 of Chapter 2, we have presently chosen palladium chloride to finally yield Pd-PANI on celite.

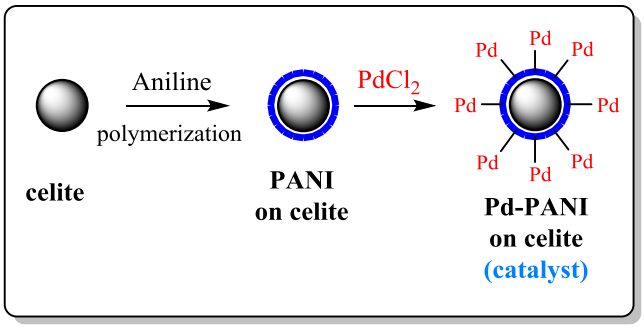


Figure 1: Anchoring palladium on heterogenized PANI on celite

3.1.2 Results and discussion

In this part we present our findings for the immobilization of palladium salts on polyaniline support, its preliminary characterization and applications in Suzuki, sunlight Suzuki and one pot Suzuki-aldol, Suzuki-aldol-*O*-alkylation reactions.

3.1.2.1 Synthesis and characterization of Celite-PANI-Pd

The typical procedure for synthesis of PANI involves oxidative polymerization of aniline hydrochloride with ammonium persulfate in aqueous medium.[15] The polymerization of aniline was performed in its aqueous solution of hydrochloric acid in the presence of suspension of celite to load PANI on the solid surface. The particles of celite were found to be coated with a layer of PANI, which was separated by filtration. The excess of PANI, its oligomers and excess of aniline were removed by proper washing with different solvents. The material was vacuum dried till constant weight was observed. The free flowing dry powder of Celite-PANI was characterized by usual techniques to establish its composition. For the present study a sample was prepared with celite (5.0 g) and aniline (5.0 g), being referred as

Celite-PANI. The dry sample of Celite-PANI (1.0 g) was stirred with $PdCl_2$ (three different quantities, 0.05 g, 0.10 g and 0.20 g) in acetonitrile (24 h) and the material was filtered, washed and dried. Thus, the three samples of catalysts were prepared with different loading of palladium. The amount of palladium present in each of the three catalysts was estimated by ICP-AES analysis (Table 1).

Table 1 Three catalysts prepared with palladium loading

No	Catalyst Code	Amount of $PdCl_2$ for Celite-PANI (1.0 g)	Amount of $PdCl_2$ (%) per gram of catalyst[a]
1	Celite-PANI-Pd-A	0.05 g	0.34
2	Celite-PANI-Pd-B	0.10 g	0.42
3	Celite-PANI-Pd-C	0.20 g	0. 50

[a]Determined by ICP-AES analysis

The catalysts were characterized by IR spectroscopy and compared with spectral features of PANI to confirm the loading (Figure 2). The spectrum of pure PANI displays a broad band at 3272 cm,$^{-1}$ attributed to N–H stretching mode of aromatic amine, absorption bands at 1587, 1684 and 1495 cm^{-1}, can be assigned to the C=C stretching vibration of quinoid and benzenoid units of PANI chain, band at 1307 cm^{-1} may be attributed to C-N stretching in aromatic amine and a strong absorption at 1144 cm,$^{-1}$ which is attributed to the plane bending vibration of C–H, related to the quinoid (N=Q=N) and the protonic forms which is formed during the protonation. The spectrum of celite presents a strong and broad absorption band at 1052 cm,$^{-1}$ assigned to Si–O–Si symmetric stretching vibration.The spectrum of the Celite-PANI composite contains contributions from both components. Celite-PANI-Pd does not show any significant change in stretching frequencies.[16] So presence of Pd is confirmed by other techniques.

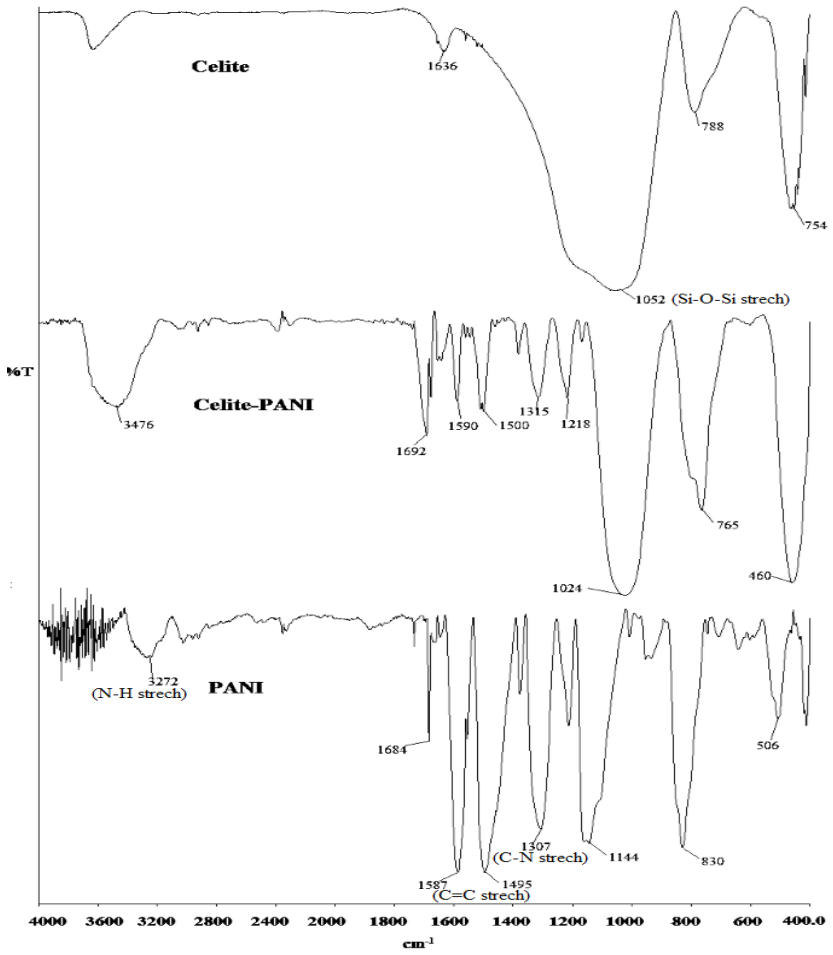


Figure 2: Comparison of IR spectrum of Celite, PANI and Celite-PANI

The morphology and composition of Celite and Celite-PANI by SEM and EDX demonstrates the successful polymerization of PANI onto the surface of Celite (Figure 3a & 3b). Further loading of Palladium on Celite-PANI is also confirmed by SEM images where palladium is seen as nano-sized particles between the range of 50-170 nm (Figure 3c & 3d). Furthermore, EDX spectrum also confirms the presence of other ions attributing to celite as well as PANI, confirming the composition of the catalyst as shown in Figure 4.

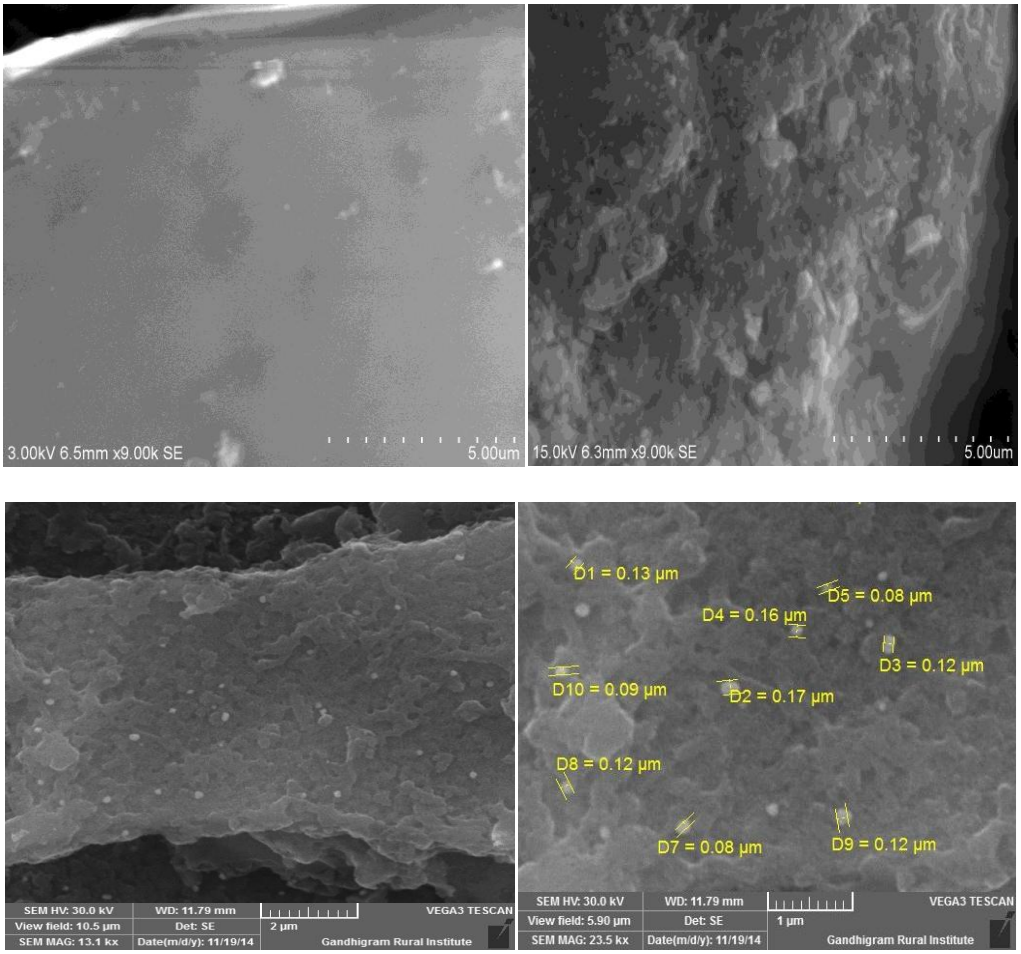
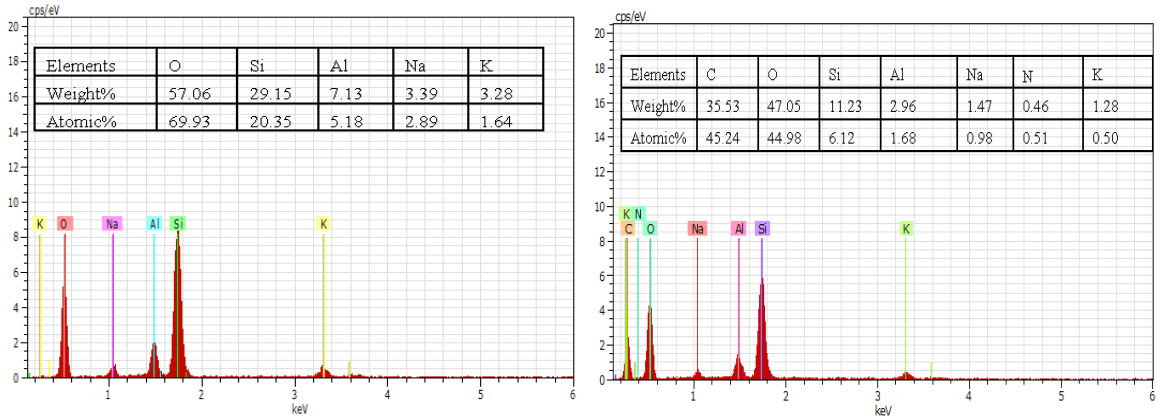


Figure 3: SEM images: (a) bare celite (top left); (b) Celite-PANI (top right); (c) Celite-PANI-Pd-B (bottom left); (d) enlarged image of Celite-PANI-Pd-B (bottom right)



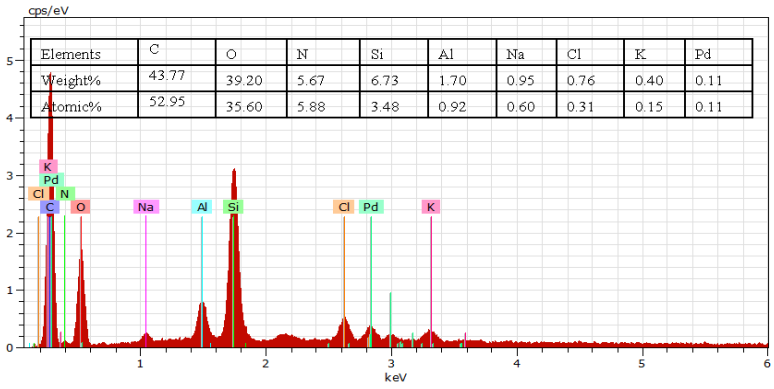


Figure 4: EDX: (a) celite (top left); (b) Celite-PANI (top right); (c) Celite-PANI-Pd-B (bottom)

The X-ray diffraction (XRD) analysis of the samples Celite-PANI and Celite-PANI-Pd were performed (Figure 5a). The broad peak corresponding to 2 *theta* value 25 indicate the amorphous nature of Celite-PANI. The XRD analysis of Celite-PANI-Pd clearly showed the two characteristic signals corresponding to 2*theta* values at 40 and 46 which are characteristic peaks for Pd.[17]

Thermogravimetric analysis (TGA) of Celite-PANI-Pd-B confirmed its stability up to ~350^{o}C, which shows its appropriateness for the use as heterogeneous catalyst in standard reaction parameters (Figure 5b).

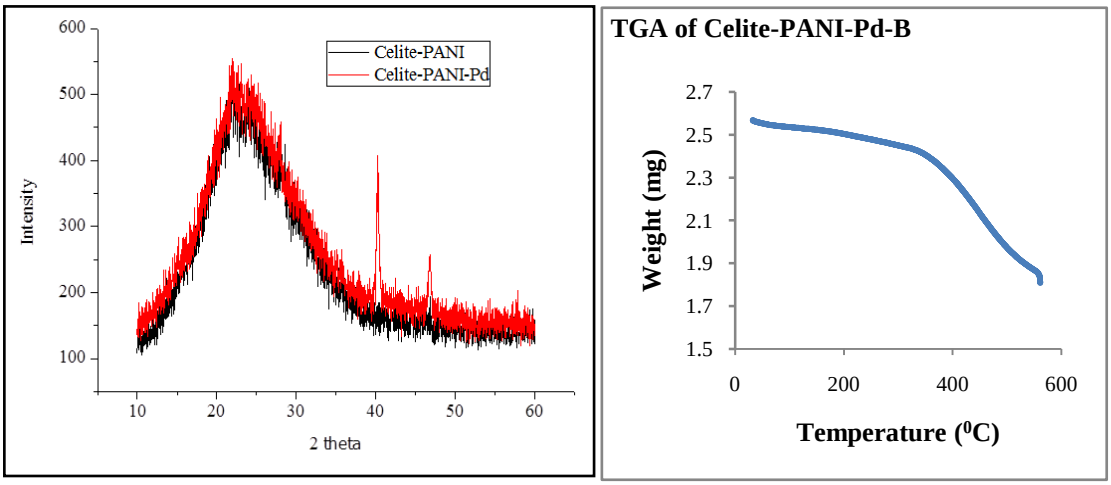


Figure 5: (a) XRD of Celite-PANI and Celite-PANI-Pd-B (left) and (b) TGA of Celite-PANI-Pd (right)

Brunauer-Emmet-Teller (BET) surface analysis of Celite-PANI and Celite-PANI-Pd-B shows specific area of Celite-PANI is 5.11 m^2/g, which increased to 6.02 m^2/g in Celite-PANI-Pd-B. The average pore diameter is 204 A^o and 178 A^o for Celite-PANI and Celite-

PANI-Pd-B, respectively (Table 2). It can be assumed that pores are filled with active phase which decreased the average pore diameter.

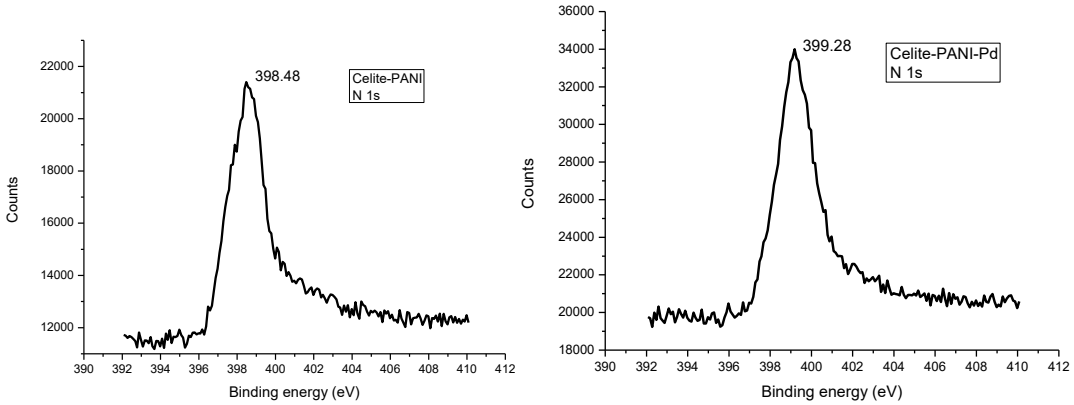
Table 2 BET analysis data for Celite-PANI and Celite-PANI-Pd-B

Sample	S_{BET} m^2/g	Pore volume cm^3/g	Pore Diameter A^0
Celite-PANI	5.11	0.21	203
Celite-PANI-Pd	6.05	0.02	178

The XPS (X-ray photo-electron spectroscopy) analysis of Celite-PANI and palladium supported catalyst are summarized in Table-3. The observed binding energy peaks of N 1s for PANI is observed at 398, for Celite-PANI and Celite-PANI-Pd are observed at 398.48 and 399.38 respectively as shown in Figure-6. This electron modification suggests coordination of palladium chloride with nitrogen of PANI. The Pd 3d region of XPS spectra shows presence of Pd $3d_{3/2}$ and $3d_{5/2}$with binding energy 337.78 and 342.88 eV respectively as shown in Figure-6. The observed binding energy is in accordance with Pd +2 state.[16]

Table 2 XPS data for Celite-PANI and Celite-PANI-Pd-B

Entry	Catalyst	Binding energy (eV)		
		N 1s	Pd $3d_{3/2}$	Pd $3d_{5/2}$
1	PANI	398[16]	--	--
2	Celite-PANI	398.48	--	--
3	Celite-PANI-Pd-B	399.28	337.78	342.88



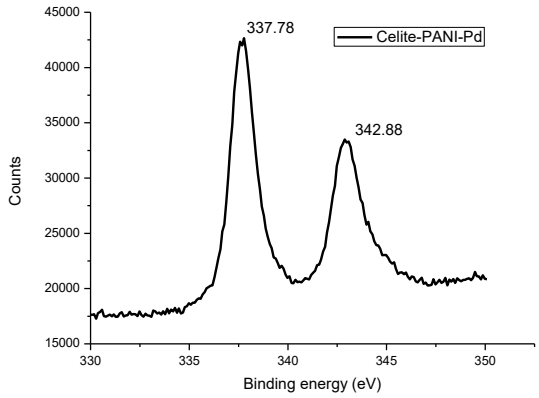
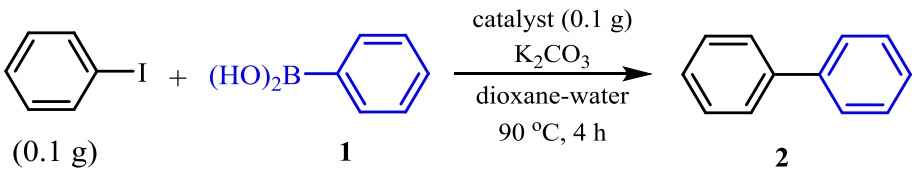


Figure 6: (a) XPS of Celite-PANI (top-left) and Celite-PANI-Pd-B (top-right) for N 1s and (b) XPS of Celite-PANI-Pd (bottom) for Pd 3d.

3.1.2.2 Applications of catalyst for Suzuki reaction

Coupling of aryl boronic acid with aryl halide, also known as Suzuki reaction is a well-known and well-studied under homogeneous palladium catalyzed reaction conditions. The reaction is also studied with several useful heterogeneous palladium catalysts.[18] In our earlier chapter we have used palladium catalyst anchored on PANI for Mizoroki-Heck, Suzuki-Miyaura and their one-pot combination with Wittig reaction. We have observed few difficulties in some cases, due to partial solubility of PANI in some solvents at higher temperature. In order to address some of these issues we have scanned the series of heterogenized Celite-PANI-Pd as catalysts for Suzuki-Miyaura reaction, and also extend the application by performing its one-pot combination with aldol reaction. The above catalysts were screened for testing their efficacy for the standard Suzuki-Miyaura reaction with iodobenzene and phenylboronic acid **1** (Scheme 1), where the product biphenyl **2** was isolated by column chromatography in very good yield.



Scheme 1: Suzuki-Miyaura reaction

The results of the experiment with the three catalysts are summarized in Table 3, where the data suggested effectiveness of all the three systems. Moreover, the efficiency of any heterogeneous catalyst system is also judged by the recyclability and reusability in

subsequent cycles of the reaction. The catalyst Celite-PANI-Pd-B recovered from the above reaction was washed with suitable solvents, dried and used for five more cycles to check this property (Table 4). Reactions carried out under identical conditions resulted in consistent conversions, establishing the recyclability of the catalyst system.

Table 4 Catalyst screening for synthesis of biphenyl **2**

No	Catalyst	Yield (%)
1	Celite-PANI-Pd-A	94
2	Celite-PANI-Pd-B	96
3	Celite-PANI-Pd-C	96
Recycle study with Celite-PANI-Pd-B		
4	2^{nd} Cycle	93
5	3^{rd} Cycle	90
6	4^{th} Cycle	91
7	5^{th} Cycle	90
8	6^{th} Cycle	89

Conditions: Aryl halide (1.0 equiv), K_2CO_3 (2.0 equiv), boronic acid (1.2 equiv),90^{o}C, dioxane-water (1:1), 4 h

Moreover heteroginity test was also performed to study the leaching of Pd during the reaction. For this purpose a standard Suzuki-Miyaura reaction with iodobenzene and phenyl boronic acid was selected. Two sets of above reaction were carried out under optimized condition (Figure 7) out of which one set of reaction was quenched after one hour and product was isolated (35 % Yield). In other set, the catalyst was separated after one hour by filtration and the reaction was allowed to continue for three more hours, which resulted in almost no further conversion (37 % Yield) The experimental result shows no significance change in the yield after catalyst separation which clearly indicates very low leaching of palladium.

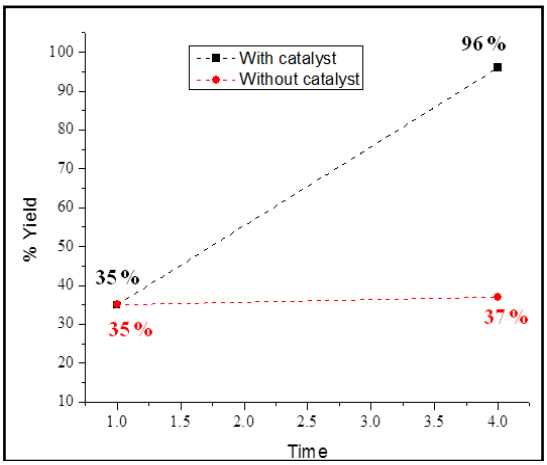


Figure 7: Result of hot filtration test

The particle size distribution was studied using dynamic light scattering (DLS) with a BIC 90 Plus (Brookhaven) equipped with 35.0mW solid state lasers operating at 660 nm and an avalanche photodiode detector. The particle size of PANI-Pd was observed in the ranges from 150 to 300 nm and that of Celite-PANI-Pd-B was increased to 428 nm in ethylene glycol at 25 °C. The particle size of the catalyst was also found to be much larger as compared to PANI-Pd, which opens up possibilities to explore the use in continuous flow reactors and also free flowing nature of the catalyst particles helps in its easy filtration and handling making it more useful for the synthetic applications.

One of the objectives of the present study was to reduce the consumption of PANI for the production of the coupling product. Even though the reaction was efficiently catalyzed by PANI-Pd system as seen earlier, the consumption of PANI for the preparation of biphenyl was found to be quite high (0.44 g PANI/ g of biphenyl). In this part of work coating of celite with PANI is done to facilitate the adhering the metal ions to prepare the active heterogeneous catalyst. The catalyst was taken in pre-weighed porcelain crucible and decomposed at high temperature (Bunsen burner). The process was repeated till constant weight of the residue, subtracting from the original value we could estimate the amount of PANI present in Celite-PANI. This was observed to be about 0.167 g PANI in 1.0 g of Celite-PANI, which was in agreement with expected data based on increased weight of celite when coated with PANI. Based on this information and the experimental yields of Suzuki-Miyaura reaction we estimated the consumption of PANI for the production of biphenyl (Table 5). The optimization done with the catalysts clearly indicate that by choosing Celite-PANI-Pd-C which has higher amount of palladium loading, we could increase the conversion. These

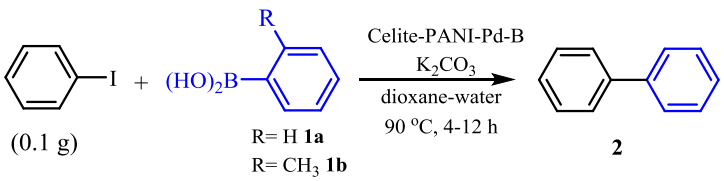
results indicate the possibility to reduce the requirement of PANI by nearly ten folds as compared to the previous work (chapter-2) in which usage of PANI was 0.44 g PANI/ 1 g of **2** (entry 7, Table 5). Besides the low use of PANI, this also offers advantages like more stability due to less aggregation, effectively more surface area for efficient loading of palladium metal for wider applications. The heterogeneous catalytic system becomes more robust by reducing the quantity of the material (PANI) which has chance of being less stable under reaction conditions.

Table 5 Estimation of consumption of PANI for the preparation of biphenyl

No	PhI [g]	Catalyst [g]	Yield of **2** % [g]	PANI consumed per g of **2**
1	0.1	Celite-PANI-Pd-A [0.1]	94 [0.071]	0.237
2	0.1	Celite-PANI-Pd-B [0.1]	96 [0.072]	0.233
3	0.1	Celite-PANI-Pd-C [0.1]	96 [0.072]	0.233
4	0.2	Celite-PANI-Pd-C [0.1]	93 [0.140]	0.119
5	0.4	Celite-PANI-Pd-C [0.1]	93 [0.281]	0.059
6	0.4	Celite-PANI-Pd-C [0.05]	68 [0.206]	0.040
7	0.2	PANI-Pd [0.06]	91[0.136]	0.441

Conditions: Aryl halide (1.0 equiv), K_2CO_3 (2 equiv), boronic acid (1.2 equiv),TBAB (10 %), 90 ^oC, dioxane-water (1:1), 4 h

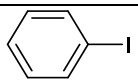
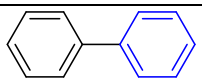
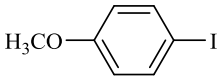
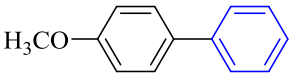
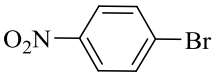
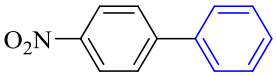
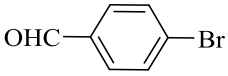
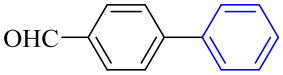
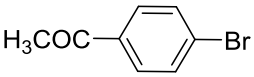
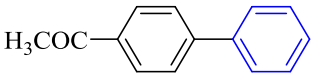
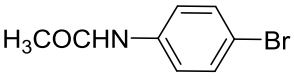
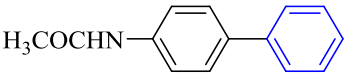
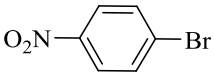
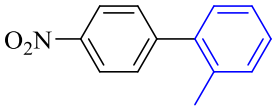
Having recognized significant advantages of palladium catalysts supported on the heterogeneous support of Celite-PANI we have screened them for Suzuki-Miyaura coupling reaction (Scheme 3). The reactions were conducted with the catalyst Celite-PANI-Pd-B as it has optimum quantity of palladium required for efficient catalysis.

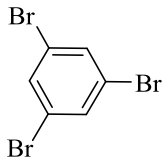
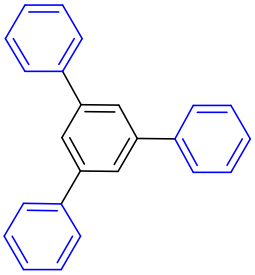
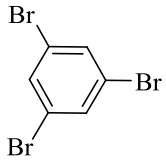
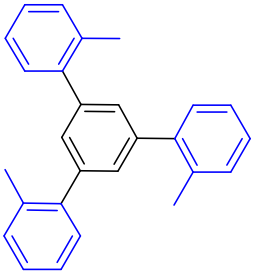
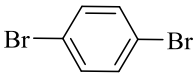
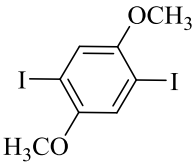
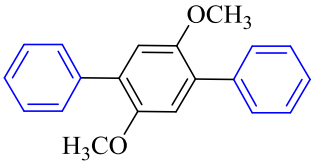
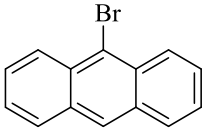
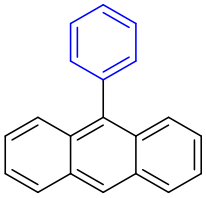
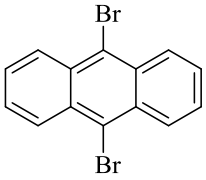
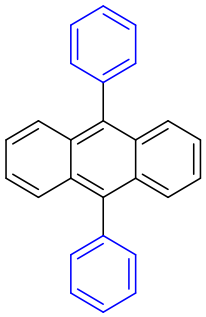


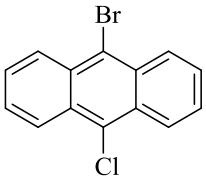
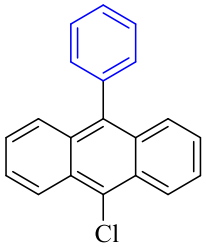
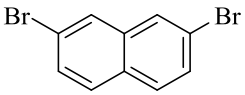
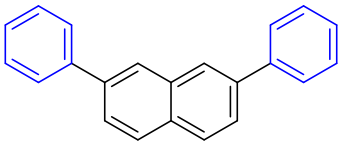
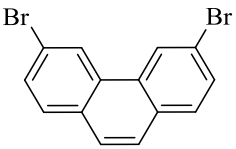
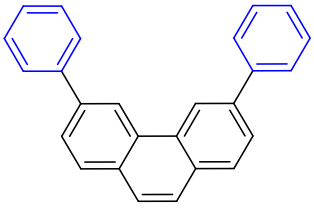
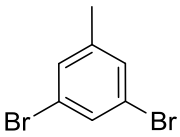
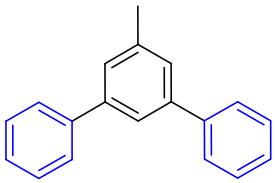
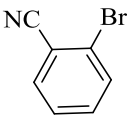
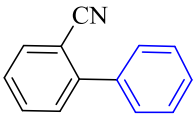
Scheme 3 Standardization of Suzuki-Miyaura reaction

The reactions were done with Ar-X (1.0 eq.), Ar'B(OH)$_2$ (1.2 eq. per halogen), K_2CO_3 (2.0 eq. per halogen), TBAB (10 mol %), in dioxane or aqueous dioxane depending upon the solubility or reagents for 4-12 h. The present catalyst system showed excellent activity for Suzuki reaction for Aryl iodides and aryl bromides, while aryl chlorides remained quite inert under these conditions. We observed that when both bromine and chlorine are present, the reaction proceeds selectively replacing the former (entry 14, Table 6). After the completion of reaction, the catalyst was simply separated by filtration and the products were purified by column chromatography over silica gel. The yields mentioned in Table 6 refer to the isolated yield and the products have been characterized by usual spectroscopic techniques.

Table 6 Suzuki-Miyaura reaction with Celite-PANI-Pd-B

Entry	Aryl halide	Product	Time (h)	Isolated Yield (%)
1		 **2**	4	96
2		 **3**	4	94
3		 **4**	8	91
4		 **5**	8	85
5		 **6**	8	93
6		 **7**	8	90
7		 **8**	8	90

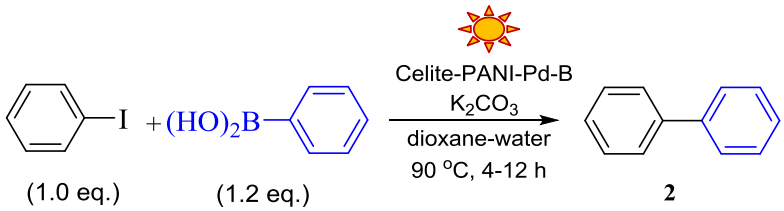
8		 **9**	12	71
9		 **10**	12	73
10		 **11**	10	78
11		 **12**	6	80
12		 **13**	10	84
13		 **14**	10	73

14		 **15**	10	83
15		 **16**	12	87
16		 **17**	12	60
17		 **18**	10	80
18		 **19**	8	89

Conditions:ArX (1.0 equiv), K_2CO_3 (2 equiv), boronic acid (1.2 equiv), TBAB (10%), 90 ^oC, 4-12 h, Dioxane:H_2O (1:1) for **2**-**4**, **6**-**8**, **12**, **19**, Dioxane for, 9-11, 13-18, Toluene for compound **5**, ArI for **2**, **3**, **12** and ArBr for **4**-**11**, **13**-**19**. boronic acid 1b was used for product **7**&**9**.

One of the twelve principles of "Green Chemistry" proposed by Anastas and Warner refer to the use of energy efficient synthetic processes.[19] The sixth principle says "the energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. The sunlight mediated chemical transformations have been known for some time,[20,21] but mostly it is used as a photon source for photochemical or photothermal reactions, dimerisation[22a] or isomerisation of the conjugated compounds[22b]and the related reactions. Beside these, a few other sunlight mediated reactions have been developed over the years and are summarized in recent articles.[23,24] In our ongoing

interest to develop useful chemical transformations performed under the direct sunlight irradiation we have previously developed homogeneous palladium catalyzed coupling reactions.[25] We have scanned our present heterogeneous catalyst system for the Suzuki-Miyaura reaction under the direct sunlight, as outlined in Scheme 4.



Scheme 4 Sunlight promoted Suzuki-Miyaura reaction

The reaction proceeds well with very good conversions as shown in Table 7, though the reaction time is much longer. The yield of the examples studied, with the comparison of their conversions under thermal reactions, is presented here, establishing the efficiency of this method. The results of effective use of heterogeneous catalysis in sunlight promoted reactions are encouraging as most of such reactions are performed in homogeneous conditions.[25] The chemical yields of this reaction were marginally better in some cases compared to our earlier study.

Table 7 Sunlight promoted Suzuki-Miyaura reaction with Celite-PANI-Pd-B[a]

No	Aryl Halide	Product (See Table 5)	Time[b] (h)	Yield %	Yield %
1	Iodobenzene	**2**	10	94	96
2	1-iodo-4-methoxybenzene	**3**	10	94	94
3	4-nitrobromobenzene	**4**	13	96	91
4	4-bromoacetophenone	**6**	13	90	93
5	4-bromoacetanilide	**7**	13	90	90
6	4-nitrobromobenzene	**8**	13	88	90
7	1,4-dibromobenzene	**11**	15	78	78
8	1,4-diiodo-2,5-dimethoxybenzene	**12**	13	87	80
9	1,3-dibromo-5-methylbenzene	**18**	15	70	80
10	2-bromobenzonitrile	**19**	13	91	89

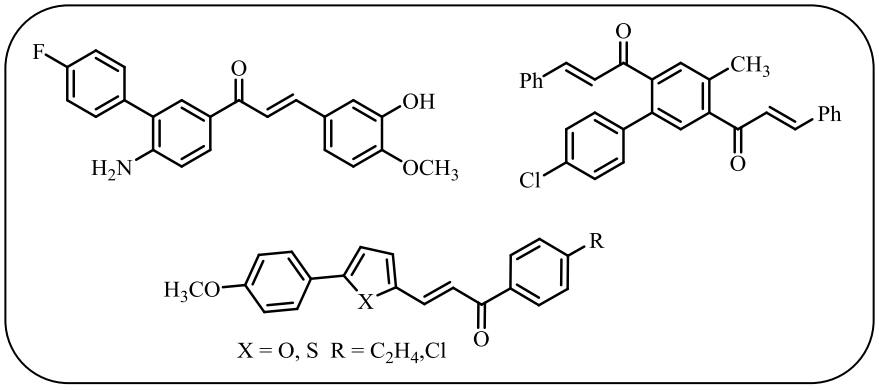
[a]Reactions were run with ArX (0.1 g, 1.0 eq.), $ArB(OH)_2$ (1.2 eq. per number of halogens), catalyst (0.1 g), K_2CO_3 (2.0 eq. for each halogen), TBAB (10 mol %), in dioxane-water (1:1), under magnetic stirring in conical flask. [b]Actual sunlight exposure time.

The sunlight mediated coupling reaction probably involves a combination of photochemical and photothermal effects.[19]Initial step involves insertion of palladium followed by photochemical cleavage of aryl-halogen bond. The positive role of sunlight was established by performing the reaction by covering flask to cut off the rays of light. This experiment resulted in almost no conversion (tlc), clearly establishing the role of photo irradiation. There is a possibility that the sunlight helps to cleave Ar-X bond, and subsequent insertion of metal ion.

3.1.2.3 Applications in one-pot reactions

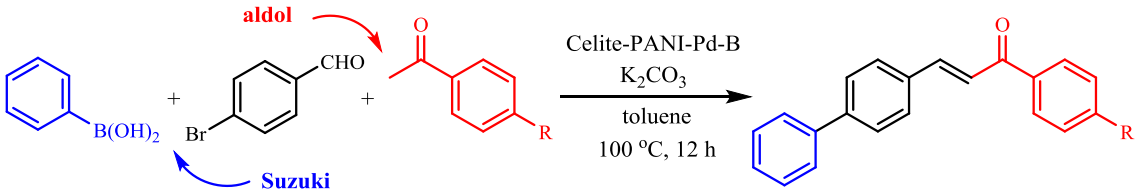
As discussed in earlier chapter the importance of one-pot synthesis like reduces purification steps, reduce the consumption of reagents and cuts on reaction time etc. is now well recognized. It is the approach in which different reaction are performed in single flask also called as cascade, tandem or domino reaction. As a part of our interest we further extend our work in the present section about combination of new one pot Suzuki-aldol and Suzuki-aldol-*O*-alkylation reaction catalyzed by Celite-PANI-Pd catalyst.

Among various organic transformations Suzuki–Miyaura cross-coupling and aldol condensation reaction aldol condensation reaction between an aldehyde and a ketone with acidic α-hydrogen occupy esteemed position as both reactions tend to enrich molecular diversity by formation of C-C and C=C bonds. Biarylchalcones have gained significance in the field of medicinal chemistry because of their anticancer activities.[26] Some biarylchalcones showing anticancer activities are shown in Scheme 5.



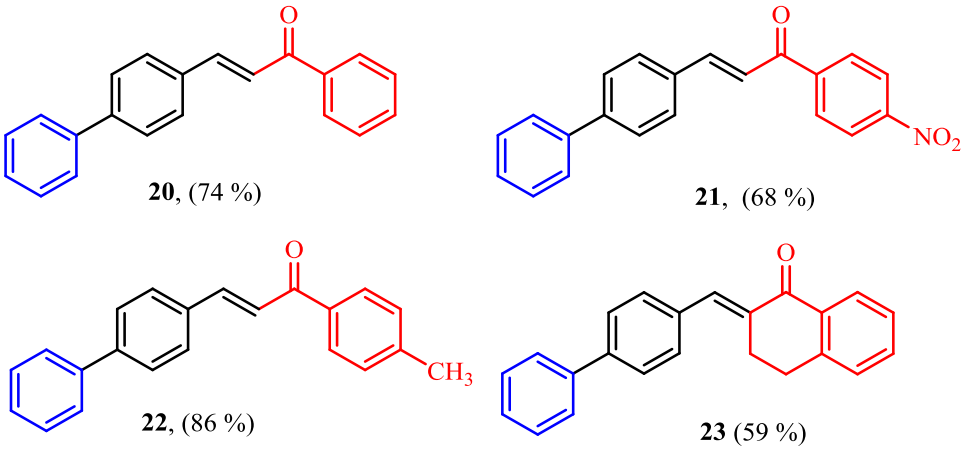
Scheme 5: Some biarylchalcones showing anti-cancer activity

As both the reactions are well-matched under similar condition and so we decide to extend our methodology to investigate this combination. Initially we started with substituted acetophenones and bromobenzaldehye as the aldol partners, while performing the reaction under the Suzuki-Miyaura condition along with a boronic acid. The chalcone unit formed by dehydration of base mediated aldol reaction of acetophenone with 4-bromoaldehyde, while the aryl bromine can couple with boronic acid to furnish an interesting building block (Scheme 6). Celite-PANI-Pd-B as catalyst in toluene and potassium carbonate as base were used as the standard reaction condition.



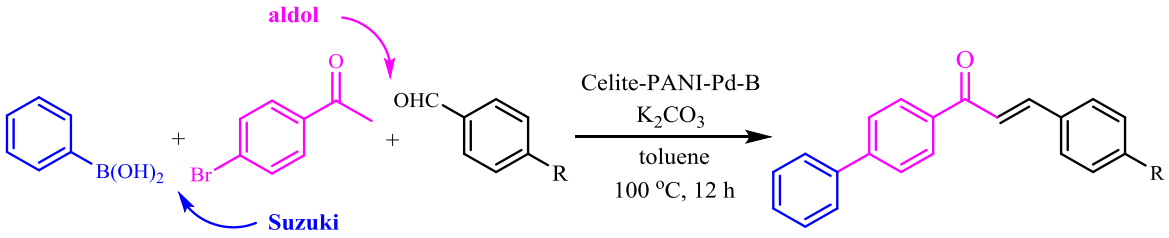
Scheme 6: One-pot Suzuki-aldol reaction (Type A)

A number examples were studied by using different derivatives of acetophenoneas shown in Scheme 7(**20-22**). At the same time α-tetralone can be substituted as the source of anion to produce compound **23**, in good yields. All the compounds were separated by column chromatography over silica gel, and the stereochemistry of the isolated major product was established to be *E* as expected in such cases.



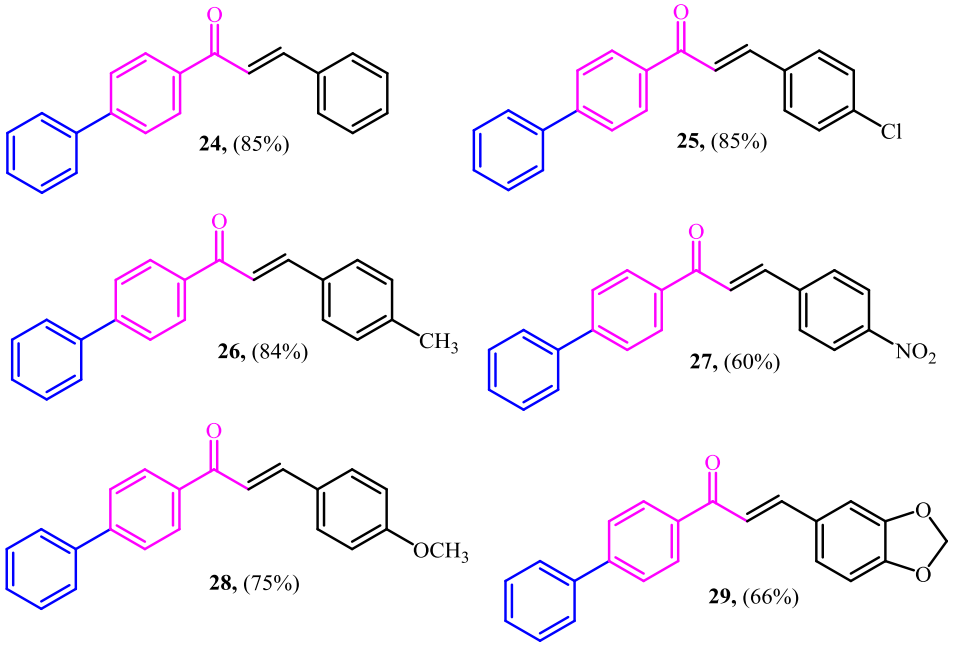
Scheme 7: Examples of one-pot Suzuki-aldol reaction (Type A)

Multi substituted chalcone can be easily synthesized by doing variation in two components of chalcones i.e. substituted aldehyde or acetophenone. To developed this other combination where 4-bromoacetophenone was chosen as aldol and Suzuki reaction partner, while substituted benzaldehydes can complete the aldol reaction as shown in Scheme 8.



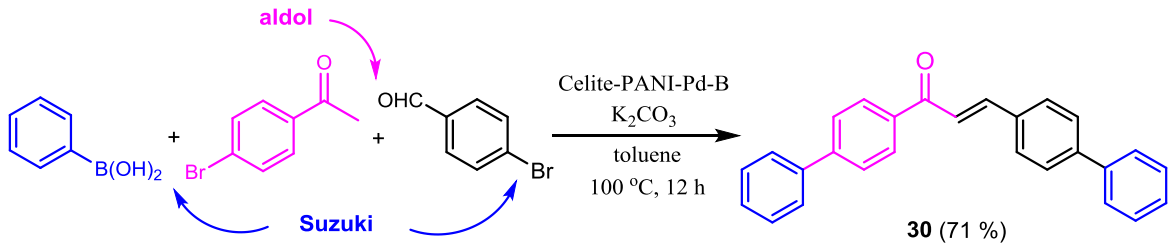
Scheme 8: One-pot Suzuki-aldol reaction (Type B)

This reaction was catalyzed by Celite-PANI-Pd-B in toluene under the standard condition and a similar series of compounds were isolated by column chromatography in good yields (Scheme 9). By introducing such variations in one-pot aldol-Suzuki reaction one may offer easyaccess to synthesize such compounds and may also explore different permutations and combinations.



Scheme 9: Examples of one-pot Suzuki-aldol reaction (Type B)

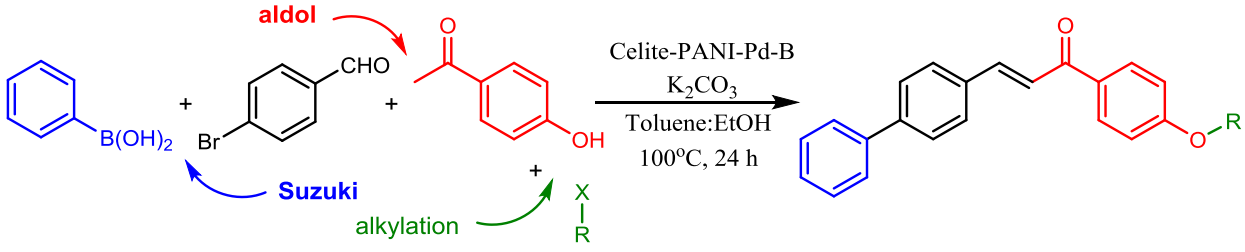
Similarly the methodology can be extended further, by choosing 4-bromoacetophenone and 4-bromobenzaldehyde for the aldol reaction along with excess of phenylboronic acid **1a**, under the same reaction parameters. The reaction involves a combination of double Suzuki reaction and an aldol condensation to produce 4,4'-diphenyl chalcone **30**, in good yield as shown in Scheme 10.



Scheme 10: One-pot Suzuki-aldol-Suzuki reaction (Type B)

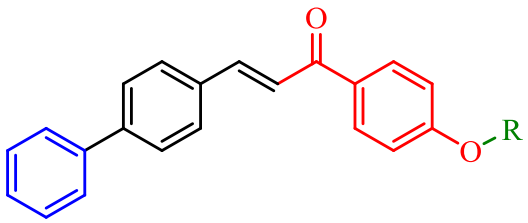
Synthesis of conjugated molecules with adequate substituents which may find wider applications in material chemistry[27] was further investigated. The design of such molecules is often based on electronic considerations where either electron donating or withdrawing substitutions are selected to play with the push-pull concept. In many studies the alkyloxy groups are selected as electron releasing groups due to the simplicity of their synthesis from corresponding phenols and the reasonable solubility of the resultant materials in routine solvents.

Hence we further extended our catalyst system to design a one-pot methodology consisting of aldol-Suzuki-*O*-alkylation reactions as all three reactions are compatible under similar reaction (Scheme 11).The reaction was performed with catalyst Celite-PANI-Pd-B in toluene:ethanol(1:1) as the standard condition. We chose 4-hydroxyacetophenone, which possesses hydroxyl which under the basic reaction conditions can be easily alkylated with appropriate alkyl halide, while acetophenone will react with 4-bromoaldehyde followed by dehydration to yield chalcone unit. The bromine can further couple with boronic acid by Suzuki reaction to give compounds with much functional group modifications.



Scheme 11: One-pot Suzuki-aldol-*O*-alkylation reaction (Type A)

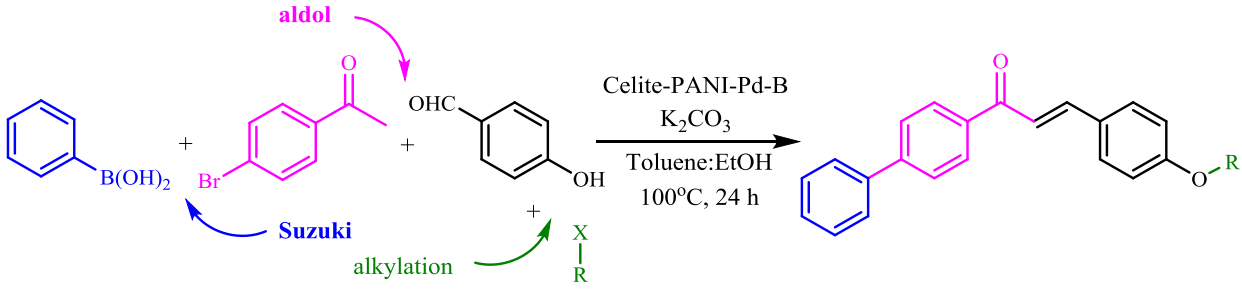
We selected five alkyl halides for *insitu* introduction of alkoxy substituent on the aromatic ring of the chalcone generated by aldol reaction (Scheme 12). The products were adequately characterized and the compound isolated showed *E* stereochemistry.



31, R = *n*-C_6H_{13} (75%)
32, R = *n*-C_8H_{17} (72%)
33, R = *n*-$C_{10}H_{21}$ (74%)
34, R = *n*-$C_{12}H_{25}$ (79%)
35, R = *n*-$C_{14}H_{29}$ (74%)

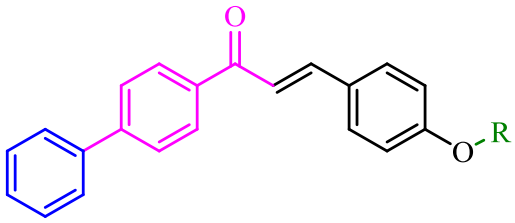
Scheme 12: Examples of one-pot Suzuki-aldol-*O*-alkylation reaction (Type A)

As in the previous case another variant was also investigated where 4-hydroxybenzaldehyde was chosen along with 4-bromoacetophenone for aldol reaction, thus the former is expected to give *O*-alkylation and the later to undergo Suzuki reaction (Scheme 13).



Scheme 13: One-pot Suzuki-aldol-*O*-alkylation reaction (Type B)

By changing the alkyl halides structurally analogous alkoxy chalcones were synthesized in good overall yield (Scheme 14).



36, R = *n*-C_7H_{15} (69%)
37, R = *n*-$C_{10}H_{21}$ (70%)
38, R = *n*-$C_{12}H_{25}$ (71%)
39, R = *n*-$C_{14}H_{29}$ (69%)
40, R = *n*-$C_{16}H_{33}$ (72%)

Scheme 14: Examples of one-pot Suzuki-aldol-*O*-alkylation reaction (Type B)

All the compounds were properly purified and adequately characterized by usual spectral techniques. The stereochemistry of the double bond is also established by NMR analysis.

3.1.3 Conclusion

We present here the preparation of celite supported PANI particles and its loading with palladium ions.The catalyst was fully characterized by various analytical techniques and Celite-PANI-Pd heterogeneous catalysts were scanned for Suzuki-Miyaura reaction under thermal as well as sunlight irradiation. Furthermore, their applications in one-pot Suzuki-aldol and Suzuki-aldol-*O*-alkylation reactions were investigated. The resultant catalyst works well as a robust, recyclable system.

3.1.4 Experimental section

3.1.4.1 Preparation of catalyst

Procedure for the synthesis of Celite-PANI:

Freshly distilled aniline (5 mL, 54.9 mmol) was dissolved in minimum amount of aqueous HCl (1.5 M). To this solution, 5 g of celite was added and a solution of ammonium persulfate (6.27 g, 27.5 mmol) in HCl (1.5 M, 25 mL) was added to it at 0 °C. Since, aniline polymerization is strongly exothermic, the oxidant must be added slowly over a period of 1 h. After the addition of the oxidant, the reaction was stirred overnight. The coated celite-polyaniline hydrochloride was separated by filtration and washed consecutively with water (3x30 mL), methanol (2x25 mL), and diethyl ether (2x15 mL) to remove the oligomers and the reaction side products. The polymer was then vacuum-dried until constant mass. Deprotonation of polyaniline hydrochloride was achieved with aqueous ammonia (3 wt %). Deprotonated polymer was again washed with water, methanol, and diethyl ether and dried until constant mass (5.962 g).

Procedure for the synthesis of Celite-PANI-Pd:

Celite-PANI (5 g) was charged into a round-bottomed flask containing an acetonitrile solution (150 mL) of palladium chloride and stirred under nitrogen atmosphere for 48 h. The resultant catalyst was filtered off and washed with acetonitrile followed by acetone. The residue was dried in air for 24 h to afford the grey colored powder of Celite-PANI-Pd.

3.1.4.2 Screening of supported catalysts for standard Suzuki reaction

General procedure for Suzuki-Miyaura reaction (Scheme 3):

To an oven-dried two necked round bottom flask equipped with a stirrer bar was charged iodobenzene (0.2 g, 0.98 mmol), potassium carbonate (0.27 g, 1.96 mmol), Celite-PANI-Pd-B (0.2 g, 0.0079 mmol of Pd) in dioxane:water (1:1).To the reaction mixture phenylboronic acid (0.14 g, 1.17 mmol) was added and heated at 95 ^{o}C for 4 h. The reaction mixture 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 crude product was purified by column chromatography on silica gel to afford biphenyl **2** as white solid**.** (0.145 g, 96 %). M.p. 71 ^{o}C [Lit.[28] 71 ^{o}C]

General procedure for sunlight promoted Suzuki-Miyaura reaction (Scheme 4):

To an oven-dried flat bottom flask equipped with a stirrer bar was charged iodobenzene (0.2 g, 0.98 mmol), potassium carbonate (0.27 g, 1.96 mmol), Celite-PANI-Pd-B (0.2 g, 0.0079 mmol of Pd) in dioxane:water. To the reaction mixture phenylboronic acid (0.14 g, 1.17 mmol) was added and kept in sunlight for 10 h. The reaction mixture 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 crude product was purified by column chromatography on silica gel to afford biphenyl **2** as white solid**.** (0.142 g, 94 %).

Spectral data for compounds reported in Table **5**:

4-Methoxy-1,1'-biphenyl (**3**)

Yield: 94% (Off white solid)

M.p. 93 ^{o}C [Lit.[29] 88-89 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.67 (s, 3H), 7.43-7.45 (m, 1H), 7.48-7.52 (m, 2H), 7.64-7.67 (m, 2H), 7.70-7.72 (m, 2H), 8.04-8.07 (m, 2H).

IR[KBr]: υ 3001, 2961, 2835, 1606, 1522, 1487, 1439, 1250, 1184, 833, 760, 688 cm^{-1}.

4-Nitro-1,1'-biphenyl (**4**)

Yield: 91% (Pale Yellow solid)

M.p. 114-116 ^{o}C [Lit.[30]113-115 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.45-7.55 (m, 3H), 7.63-7.66 (m, 2H), 7.75-7.78 (m, 2H), 8.33 (d, *J* =8.8 Hz, 2H).

IR[KBr]: υ 1598, 1574, 1518, 1478, 1448, 1346, 853, 740, 698 cm^{-1}.

[1,1'-Biphenyl]-4-carbaldehyde **(5)**

Yield: 85% (reaction performed in toluene) ;

41% (in Dioxane:water) (Pale yellow solid)

M.p. 60 ^{o}C [Lit. [31] 60-61^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.45-7.53(m, 3H), 7.65-7.68 (m, 2H), 7.77-7.79 (m, 2H), 7.97-7.99 (m, 2H), 10.01 (s, 1H).

IR[KBr]: υ 1700, 1602, 1449, 1213, 1168, 837, 762, 696 cm^{-1}.

Mass (EI): (*m/z*) 182(M^{+}, 73), 181(M^{-1},100), 153(42), 129(53), 69(74).

1-([1,1'-Biphenyl]-4-yl)ethan-1-one (**6**)

Yield: 93% (off-White solid)

M.p. 116-118 ^{o}C [Lit.[32] 117-119 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.67 (s, 1H), 7.43-7.45 (m, 1H), 7.48-7.52 (m, 2H), 7.65-7.67 (m, 2H), 7.70-7.72 (m, 2H), 8.05-8.07 (m, 2H).

IR[KBr]: υ 1650, 1598, 1486, 1409, 1331, 1224, 1180, 985, 815, 762, 690 cm^{-1}.

Mass (EI): (*m/z*) 196(M^{+},20), 196(56), 181(100), 152(79), 129(28).

N-([1,1'-Biphenyl]-4-yl)acetamide (**7**)

Yield: 90% (Pale yellow solid)

M.p. 172 ^{o}C [Lit.[32] 168-170^{o}C]

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

IR[KBr]: υ 3302, 3111, 1663, 1603, 1543, 1487, 1321, 836, 762, 673 cm^{-1}.

Mass (EI): (*m/z*) 211(M^{+}, 30), 168(50), 149(80), 111(100).

2-Methyl-4'-nitro-1,1'-biphenyl (**8**)

Yield: 90% (Off white solid)

M.p. 102 ^{o}C [Lit.[33]100-102 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.23-7.25 (m, 1H), 7.28-7.39 (m, 3H), 7.50-7.56 (m, 2H), 8.29-8.32 (m, 2H).

IR[KBr]: υ 3072, 2955, 1596, 1514, 1479, 1383, 1346, 857, 752, 775, 699 cm^{-1}.

Mass (EI): (*m/z*) 213(M^+, 72), 165(68), 149(54), 111(100).

5'-Phenyl-1,1':3',1''-terphenyl (**9**)

Yield: 71% (Off white solid)

M.p. 175 ^oC [Lit.[34]173 ^oC]

^1H-NMR ($CDCl_3$, 400 MHz): δ 7.40-7.44 (m, 1H), 7.47-7.53 (m, 2H), 7.72-7.75 (m, 2H), 7.82 (s, 1H).

IR[KBr]: υ 3057, 3032, 1644, 1595, 1560, 1496, 872, 764 cm^{-1}.

Mass (EI): (*m/z*) 306(M^+, 100), 305(79), 289(13), 228(13).

2,2''-Dimethyl-5'-(o-tolyl)-1,1':3',1''-terphenyl (**10**)

Yield: 73% (Off white solid)

M.p. 137-140 ^oC [Lit.[35] 138-140 ^oC]

^1H-NMR ($CDCl_3$, 400 MHz): δ 2.41 (s, 3H), 7.29-7.33 (m, 4H), 7.36-7.39 (m, 1H).

IR[KBr]: υ 3061, 3018, 2922, 2858, 1591, 1488, 1455, 1377, 892, 754 cm^{-1}.

Mass (EI): (*m/z*) 348(M^+, 53), 347(M-1, 100), 241(16).

1,1',4',1''-Terphenyl (**11**)

Yield: 78% (White solid)

M.p. 214 ^oC [Lit.[36]211-212 ^oC]

^1H-NMR ($CDCl_3$, 400 MHz): δ 7.49 (m, 2H), 7.66-7.68 (m, 4H), 7.71 (s, 2H).

IR[KBr]: υ 3059, 1668, 1550, 1532, 1480, 1455, 839, 746, 688 cm^{-1}.

Mass (EI): (*m/z*) 230 (M^+, 100), 228 (11), 152 (6), 115 (10).

2',5'-Dimethoxy-1,1':4',1''-terphenyl (**12**)

Yield: 80% (White solid)

M.p.145-148 ^oC [Lit.[37] 147-149 ^oC]

^1H-NMR ($CDCl_3$, 400 MHz): δ 3.83(s, 3H), 7.02(s, 1H), 7.37-7.41 (m, 1H), 7.46-7.50 (m, 2H), 7.62-7.65 (m, 2H).

IR[KBr]: υ 2954, 1515, 1484, 1448, 1389, 1207, 1058, 1036, 1018,752, 699, 677 cm^{-1}.

Mass (EI): (*m/z*) 290(M^+, 100), 275(30), 260(32), 202(12).

9-Phenylanthracene (**13**)

Yield: 84% (Pale yellow solid)

M.p. 152-154 ^{o}C [Lit.[38] 153-154 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.35-7.40 (m, 2H), 7.46-7.63 (m, 9H), 7.70 (d, *J* =8.8 Hz, 2H), 8.53 (s, 1H).

IR[KBr]: υ 2957, 1731, 1683, 1550, 1441, 1378, 877, 736, 700, 609 cm^{-1}.

Mass (EI): (*m/z*) 254(M^+, 86), 253(100), 85(67), 69(73).

9,10-Diphenylanthracene (**14**)

Yield: 73% (Pale yellow solid)

M.p. 245 ^{o}C [Lit.[39] 247-248^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.37-7.40 (m, 1H), 7.54-7.56 (m, 1H), 7.59-7.72 (m, 2H), 7.75-7.80 (m, 1H).

IR[KBr]: υ 3064, 1596, 1491, 1387, 1159, 1072, 1030, 769, 702, 660 cm^{-1}.

Mass (EI): (*m/z*) 330(M^+, 100), 329(58), 253(16), 252(44).

9-Chloro-10-phenylanthracene (**15**)

Yield: 84% (Yellow solid)

M.p. 175 ^{o}C [40]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.36-7.50 (m, 5H), 7.58-7.64 (m, 4H), 7.70 (d, *J* = 8.8 Hz, 1H), 8.62 (d, *J* = 9.2 Hz, 1H).

IR[KBr]: υ 3055, 1551, 1435, 1346, 943, 757, 698, 611 cm^{-1}.

Mass (EI): (*m/z*) 289(M+1, 18), 288(M^+, 100), 252(42), 126(16).

2,7-Diphenylnaphthalene (**16**)

Yield: 87% (White solid)

M.p. 141-143 ^{o}C [Lit.[41] 142 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.43-7.47 (m, 1H), 7.532-7.57 (m, 2H), 7.79-7.82 (m, 3H), 7.98 (d, *J* = 8.4 Hz, 1H), 8.15 (s, 1H).

IR[KBr]: υ 3054, 1597, 1484, 1456, 1440, 1075, 905, 846, 755, 699, 524 cm^{-1}.

Mass (EI): (*m/z*) 280(M^+, 32), 148(20), 128(28), 83(61), 81(78), 69(100).

3,6-Diphenylphenanthrene (**17**)

Yield: 60% (Light brown solid)

M.p.: 180-184 ^{o}C

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.44-7.45 (m, 1H), 7.57 (t, *J* = 7.2 Hz, 2H), 7.81-7.84 (m, 3H), 7.88-7.90 (m, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 8.98 (s, 1H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 121.2, 126.2, 126.7, 127.5, 127.7, 128.9, 129.1, 130.6,131.5, 139.6, 141.6

IR[KBr]: υ 3050, 3026, 1679, 1598, 1488, 1227, 1075, 876, 840, 753, 699 cm^{-1}.

Mass (EI): (*m/z*) 330(M^+, 100), 329(79), 252(11).

5'-Methyl-1,1':3',1''-terphenyl (**18**)

Yield: 80% (Off-white solid)

M.p. 130 - 132^{o}C [Lit.[42] 135 - 138^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.39-7.44 (m, 4H), 7.48-7.52 (m, 4H), 7.66-7.70 (m, 5H).

IR[KBr]: υ 3026, 1595, 1494, 1075, 1025, 868, 762, 701 cm^{-1}.

Mass (EI): (*m/z*) 244(M^+, 51), 243(100), 228(15), 165(13)

[1,1'-Biphenyl]-2-carbonitrile (**19**)

Yield: 89% (Brown solid)

M.p. 46 ^{o}C [Lit.[43] 37 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.45-7.56 (m, 5H), 7.58-7.60 (m, 2H), 7.65-7.70 (m, 1H), 7.78-7.80 (m, 1H).

IR[KBr]: υ 3033, 3064, 2225, 1596, 1564, 1477, 1451, 1434, 760, 735, 699 cm^{-1}.

3.1.4.3 Screening of supported catalysts for one-pot reactions:

General procedure for One-pot Suzuki-aldol reaction reaction (Scheme 6 and 8):

To an oven-dried two necked round bottom flask equipped with a stirrer bar was charged 4-bromobenzaldehyde (0.2 g, 1.08 mmol),acetophenone (0.13 g, 1.08 mmol), potassium carbonate (0.60 g, 4.32 mmol), Celite-PANI-Pd-B (0.2 g, 0.0079 mmol of Pd), phenylboronic acid (0.14 g, 1.17 mmol) in toluene were added and heated at 100^{o}C for 12 h. Excess of toluene was distlilled under vacuum and then reaction mixture 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 crude product

was purified by column chromatography on silica gel to afford (*E*)-3-([1,1'-biphenyl]-4-yl)-1-phenylprop-2-en-1-one (**20)**as white solid**.** (0.23g, 74 %).

Spectral data for compounds:

(*E*)-3-([1,1'-Biphenyl]-4-yl)-1-phenylprop-2-en-1-one (**20)**

M.p. 118-120^{o}C [Lit.[26b]119-121^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.42-7.43 (m, 1H), 7.48-7.59 (m, 5H), 7.61-7.70 (m, 6H), 7.75-7.77 (m, 2H), 7.891 (d, *J* = 15.6 Hz, 1H), 8.06-8.08 (m, 2H).

IR[KBr]: υ 3055, 3031, 1690, 1600, 1458, 1446, 1216, 834, 690, 758 cm^{-1}.

Mass (EI):*(m/z)* 284(M^+, 41), 283(100), 207(41.35), 178(53), 77(30).

(*E*)-3-([1,1'-Biphenyl]-4-yl)-1-(4-nitrophenyl)prop-2-en-1-one (**21**)

Yield: 68% (yellow solid)

M.p. 207 ^{o}C [Lit.[26b] 205-208 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.42-7.44 (m, 1H), 7.48-7.57 (m, 3H), 7.65-7.78 (m, 6H), 7.92 (d, *J* =15.6 Hz, 1H), 8.19 (dd, *J1* = 6.8 Hz, *J2* = 2 Hz, 2H), 8.39 (dd, *J1* = 6.8 Hz, *J2* = 2 Hz, 2H).

IR[KBr]: υ 1658, 1602, 1521, 1337, 1223, 1030, 827, 752, 696 cm^{-1}.

Mass (EI):(*m/z*) 329(M^+, 46), 328(100), 252(31), 178(55), 76(20).

(*E*)-3-([1,1'-Biphenyl]-4-yl)-1-(p-tolyl)prop-2-en-1-one (**22**)

Yield: 86% (off-white solid)

M.p. 178-181 ^{o}C [Lit.[44] 179-180^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.47 (s, 3H) 7.34 (d, *J* = 8 Hz, 2H), 7.39-7.43 (m, 1H), 7.48-7.51 (m, 2H), 7.61 (d, *J* = 15.6 Hz, 1H), 7.64-7.69 (m, 4H), 7.74-7.76 (m, 2H), 7.86-7.90 (d, *J* = 15.6 Hz, 1H), 7.88 (dd, *J1*=6.4 Hz, *J2*=1.6 Hz, 2H).

IR[KBr]: υ 3073, 2998, 1678, 1601, 1560, 1485, 1404, 1359, 1264, 960, 765, 691, 593 cm^{-1}.

Mass (EI):(*m/z*) 298(M^+,46), 297(100), 221(32), 177(26), 91(28).

(*E*)-2-([1,1'-Biphenyl]-4-ylmethylene)-3,4-dihydronaphthalen-1(2H)-one (**23**)

Yield: 59% (Brown solid)

M.p.: 125-128 ^{o}C [45]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.98-3.01 (m, 2H), 3.20-3.22 (m, 2H),7.28-7.30 (m, 1H), 7.38-7.42 (m, 2H), 7.48 (d, *J* = 8 Hz, 2H), 7.50-7.57 (m, 3H), 7.65-7.69 (m, 4H), 7.94 (s, 1H), 8.17 (d, *J* = 7.6 Hz, 1H).

^{13}C-NMR ($CDCl_3$, 400 MHz): δ 27.3, 28.8, 127.1, 127.1, 127.7, 128.2, 128.2, 128.9, 130.5, 133.3, 133.5, 134.8, 135.4, 136.3, 140.4, 141.4, 143.2.

IR[KBr]: υ 3029, 1665, 1603, 1485, 1317, 1249, 1135, 950, 844, 765, 692 cm^{-1}.

Mass (EI):(*m/z*) 310(M^+, 37), 309(100), 232(20).

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-phenylprop-2-en-1-one (**24**)

Yield: 85% (Pale yellow solid)

M.p. 154-156^{o}C [Lit.[46] 155-156^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.44-7.53 (m, 6H), 7.62 (d, 1H, 15.6 Hz), 7.67-7.71 (m, 4H), 7.76 (dd, *J1* = 6.8 Hz, *J2* = 2H), 7.88 (d, 1H, 15.6Hz), 8.14 (dd, *J1* = 6.8 Hz, *J2* = 2H).

IR[KBr]: υ 3051, 1657, 1599, 1446, 1338, 1290, 1034, 837, 751, 686 cm^{-1}.

Mass (EI):(*m/z*) 284(M^+, 5), 207(30), 129(39), 83(61), 69(69), 55(100).

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (**25**)

Yield: 75% (Yellow solid)

M.p. 95^{o}C [Lit.[46]94-95^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.88(s, 3H), 6.97 (dd, *J1* = 6.8, *J2* = 2.0 Hz, 2H), 7.43-7.45 (m, 1H), 7.48-7.53 (m, 3H), 7.64-7.69 (m, 4H), 7.75 (dd, *J1* = 6.8 Hz, *J2* = 2H), 7.86 (d, *J* = 15.2 Hz, 1H), 8.13 (dd, *J1* = 6.8 Hz, *J2* = 2H).

IR[KBr]: υ 3057, 2836, 1658, 1596, 1507, 1334, 1255, 1171, 1037, 978, 823, 739, 694 cm^{-1}.

Mass (EI):(*m/z*) 314(M^+, 81), 313(100), 299(29), 151(42).

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(4-chlorophenyl)prop-2-en-1-one (**26**)

Yield: 85% (Yellow solid)

M.p. 183-184 ^{o}C [Lit.[46] 184-185 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.42-7.46 (m, 3H), 7.49-7.56 (m, 2H),7.58 (d, *J* = 15.6 Hz, 1H) 7.60-7.63 (m, 2H), 7.67-7.69 (m, 2H), 7.76 (dd, *J1* = 6.8, *J2* = 2 Hz, 2H), 7.82 (d, *J* = 16 Hz, 1H), 8.13 (dd, *J1* = 6.8, *J2* = 2 Hz, 2H).

IR[KBr]: υ 1658, 1589, 1487, 1406, 1320, 1086, 1009, 969, 819, 733, 687, 499 cm^{-1}.

Mass (EI):(*m/z*) 320(26), 319(M^+, 43), 318(87), 317(100), 283(40), 152 (68).

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(p-tolyl)prop-2-en-1-one (**27**)

Yield: 84% (Off-white solid)

M.p. 105^{o}C [Lit.[46] 103-104 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.43 (s, 3H), 7.26-7.28 (m, 2H), 7.43-7.45 (m, 1H), 7.49-7.60 (m, 5H), 7.67-7.69 (m, 2H), 7.76(m, 2H), 7.86 (dd, *J* = 15.6 Hz, 1H), 8.12-8.15 (m, 2H) .

IR[KBr]: υ 3029, 2914, 1660, 1597, 1486, 1331, 1223, 1037, 984, 814, 691 cm^{-1}.

Mass (EI):(*m/z*) 298(M^+, 51), 297(100), 283(91), 151(50).

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(4-nitrophenyl)prop-2-en-1-one (**28**)

Yield: 60% (yellow solid)

M.p.187-189 ^{o}C [Lit.[46] 189-190 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.45-7.47 (m, 1H), 7.50-7.54 (m, 2H), 7.67-7.74 (m, 3H), 7.79-7.85 (m, 4H), 7.89 (d, *J* = 15.6 Hz, 1H), 8.15 (dd, *J1* = 6.8 Hz, *J2* = 2 Hz, 2H), 8.31 (dd, *J1* = 6.8 Hz, *J2* = 2H).

IR[KBr]: υ 1658, 1601, 1521, 1337, 1223, 1107, 837, 752, 696, 482 cm^{-1}.

Mass (EI):(*m/z*) 329(M^+, 36), 151(33), 97(100), 82(75).

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one (**29**)

Yield: 66% (Yellow solid)

M.p. 190-193 ^{o}C [47]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 6.06 (s, 2H), 6.88 (d, *J* = 8Hz, 1H), 7.17 (dd, *J1* = 8 Hz, *J2* = 1.6 Hz, 1H),7.22 (d, *J* = 1.6 Hz, 1H), 7.43-7.53 (m, 4H), 7.67-7.76 (m, 4H), 7.80 (d, *J* = 15.6 Hz, 1H), 8.10-8.13 (m, 2H).

IR[KBr]: υ 3455, 2918, 1657, 1603, 1585, 1503, 1366, 1252, 1037, 995, 839, 773, 740, 697 cm^{-1}.

Mass (EI):(*m/z*) 328(M^+,79), 327(100), 241(13), 151(21), 121(21).

(*E*)-1,3-di([1,1'-Biphenyl]-4-yl)prop-2-en-1-one (**30**)

Yield: 71% (yellow solid)

M.p. 176-179 ^{o}C [Lit.[26b]179-181 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.42-7.45 (m, 2H), 7.46-7.54 (m, 4H), 7.64-7.71 (m, 7H), 7.77 (d, *J* = 8 Hz, 4H), 7.93 (d, *J* = 15.6 Hz, 1H), 8.16 (dd, *J1* = 6.8 Hz, *J2* = 2Hz, 2H) .

IR[KBr]: υ 3053, 3032, 1660, 1601, 1484, 1405, 1331, 1225, 1037, 981, 827, 759, 689 cm.$^{-1}$

Mass (EI):(*m/z*) 360(M^+, 61), 359(100), 283(27), 152(34).

General procedure for One-pot Suzuki-aldol-O-alkylation reaction (Scheme 11 and 13):

To an oven-dried two necked round bottom flask equipped with a stirrer bar was charged with 4-bromobenzaldehyde (0.1 g, 0.54 mmol),4-hydroxy acetophenone (0.073 g, 0.54 mmol), n-octyl bromide (0.1 g, 0.54 mmol),potassium carbonate (0.45 g, 3.24 mmol), Celite-PANI-Pd-B(0.1 g, 0.004 mmol of Pd), phenylboronic acid (0.14 g, 1.17 mmol) in toluene:ethanol (1:1) were added and heated at 100^{o}C for 15 h. Excess ofsolventwas distilled under vacuum and then reaction mixture 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 crude product was purified by column chromatography on silica gel to afford (*E*)-3-([1,1'-Biphenyl]-4-yl)-1-(4-(octyloxy)phenyl)prop-2-en-1-one (**32**) as white solid**.** (0.16 g, 72. %).

Spectral data for compounds:

(*E*)-3- ([1,1'-Biphenyl]-4-yl)-1-(4-(octyloxy)phenyl)prop-2-en-1-one (**32**)

M.p. 124 ^{o}C

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.90-0.94 (m, 3H), 1.32-1.48 (m, 8H), 1.50-1.52 (m, 2H), 1.80-1.89 (m, 2H), 4.06 (t, 2H, *J* = 6.8 Hz), 7.00 (dd, 2H, *J1* = 6.8 Hz, *J2* = 2 Hz), 7.40-7.42 (m, 1H), 7.47-7.51 (m, 2H), 7.61 (d, 1H, *J* = 16.0 Hz), 7.63-7.76 (m, 6H), 7.86 (d, 1H, *J* = 15.6 Hz), 8.07 (dd, 2H, *J1* = 6.8 Hz, *J2* = 2 Hz).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 14.15, 22.69, 26.02, 29.14, 29.26, 29.36, 31.83, 68.32, 114.33, 121.71, 127.07, 127.58, 127.87, 128.91, 128.93, 129.04, 130.85, 134.08, 140.19, 143.07, 143.44, 163.12, 188.65.

IR[KBr]: υ 3036, 2922, 2854, 1662, 1628, 1602, 1574, 1469, 1253, 1253, 1306, 1174, 987, 822, 765, 688 cm^{-1}.

Mass (EI): *(m/z)* 412 (M^+,47), 411(100), 335(9), 299(39), 271(13).

(*E*)-3-([1,1'-Biphenyl]-4-yl)-1-(4-(hexyloxy)phenyl)prop-2-en-1-one **(31)**

Yield: 75.0% (White solid)

M.p.: 98-100^{o}C

^{1}H-NMR ($CDCl_3$, 400 MHz): δ.0.93-0.96 (m, 3H), 1.36-1.42 (m, 4H), 1.47-1.54 (m, 2H), 1.81-1.88 (m, 2H), 4.07 (t, 2H, *J* = 6.8 Hz), 6.98-7.02 (m, 2H), 7.38-7.42 (m, 1H), 7.46-7.51

(m, 2H), 7.61 (d, 1H, *J* = 15.6 Hz), 7.64-7.75 (m, 6H), 7.86 (d, 1H, *J* = 15.6 Hz), 8.05-8.08(m, 2H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 14.08, 22.62, 25.69, 29.10, 31.57, 68.31, 114.32, 121.70, 127.08, 127.59, 127.87, 128.90, 128.93, 130.84, 130.87, 134.08, 140.20, 143.07, 143.44, 163.11, 188.66.

IR[KBr]: υ 3036, 2867, 1660, 1602, 1506, 1413, 1329, 1304, 1253, 987, 826, 765 cm^{-1}.

Mass (EI): 384(M^+,100), 300(52), 178(47), 121(54)

(*E*)-3-([1,1'-Biphenyl]-4-yl)-1-(4-(decyloxy)phenyl)prop-2-en-1-one **(33)**

Yield: 74.0% (White solid)

M.p.: 118-120^{o}C

^{1}H-NMR ($CDCl_3$, 400 MHz): δ.0.88-0.92 (m, 3H), 1.30-1.40 (m, 12H), 1.46-1.51 (m, 2H), 1.80-1.86 (m, 2H), 4.07 (t, 2H, *J* =6.8 Hz), 6.98-7.02 (m, 2H), 7.40-7.42 (m, 1H), 7.47-7.51 (m, 2H), 7.62 (d, 1H, *J* =15.6 Hz), 7.64-7.68 (m, 4H), 7.75 (d, 2H, *J* = 8 Hz), 7.87 (d, 1H, *J* = 15.6 Hz), 8.07 (dd, 2H, *J1* = 7.2 Hz, *J2* = 2 Hz)

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 14.16, 22.71, 26.01, 29.13, 29.34, 29.39, 29.58(2C), 31.92, 68.31, 114.32, 121.70, 127.08, 127.59, 127.87, 128.90, 128.93, 130.84, 134.08, 140.20, 143.07, 143.44, 163.11, 188.66.

IR[KBr]:υ 3037, 2852, 1662, 1601, 1504, 1469, 1319, 1266, 1024, 820, 736, 691 cm^{-1}.

Mass (EI): 441(M^{+1}), 243, 157, 117.

(*E*)-3-([1,1'-Biphenyl]-4-yl)-1-(4-(dodecyloxy)phenyl)prop-2-en-1-one (**34**)

Yield: 79.0% (White solid)

M.p.: 120-122 ^{o}C

^{1}H-NMR ($CDCl_3$, 400 MHz): δ.0.89-0.92 (m, 3H), 1.29-1.38 (m, 16H), 1.46-1.51 (m, 2H), 1.81-1.86 (m, 2H), 4.07 (t, 2H, *J* = 6.8 Hz), 7.00 (dd, 2H, *J1* = 7.2 Hz, *J2* = 2 Hz),7.40-7.43 (m, 1H), 7.47-7.51 (m, 2H), 7.62 (d, 1H, *J* = 15.6 Hz), 7.64-7.76 (m, 6H), 7.87(d, 1H, *J* = 15.6 Hz), 8.07 (dd, 2H, *J1* = 7.2 Hz, *J2* = 2 Hz).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 14.15, 22.71, 26.01, 29.14, 29.37, 29.38, 29.58, 29.61, 29.65, 29.68, 31.93, 68.32, 114.33, 121.75, 127.07, 127.57, 127.86, 128.89, 128.92, 130.83, 130.89, 134.10, 140.21, 143.07, 143.43, 163.12, 188.65.

IR[KBr]: υ 3038, 2918, 2849, 1628, 1601, 1510, 1468, 1266, 1176, 988, 836, 767, 688 cm^{-1}.

Mass (EI): 468(M^+, 100), 300.11(68.26), 120.96(44.13).

(*E*)-3-([1,1'-Biphenyl]-4-yl)-1-(4-(tetradecyloxy)phenyl)prop-2-en-1-one (**35**)

Yield: 74.0 % (White solid)

M.p.: 125-127 ^{o}C

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.89-0.92 (m, 3H), 1.29-1.38 (m, 20H), 1.48-1.52 (m, 2H), 1.82-1.86 (m, 2H), 4.07 (t, 2H, *J* = 6.4 Hz), 7.00 (dd, 2H, *J1* = 7.2 Hz, *J2* = 2 Hz),7.40-7.42 (m, 1H), 7.47-7.51 (m, 2H), 7.67 (d, 1H, *J* = 15.6 Hz), 7.64-7.76 (m, 6H), 7.87 (d, 1H, *J* = 16 Hz), 8.07 (dd, 2H, *J1* = 7.2 Hz, *J2* = 2 Hz).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 14.15, 22.72, 26.01, 29.14, 29.39(2C), 29.58, 29.61, 29.68(2C), 29.70, 29.71, 31.94, 68.32, 114.33, 121.74, 127.07, 127.57, 127.86, 128.89, 128.92, 130.83, 130.89, 134.10, 140.20, 143.07, 143.42, 163.12, 188.64.

IR[KBr]: υ 3037, 2918, 2849, 1612, 1628, 1603, 1403, 1468, 1254, 1175, 986, 822, 765, 688 cm^{-1}.

Mass (EI): 496(M^{+}, 100), 367(49), 312(38), 299(34), 207(54).

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(4-(heptyloxy)phenyl)prop-2-en-1-one (**36**)

Yield: 69.0 % (White solid)

M.p.: 112-115 ^{o}C

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.90-0.94 (m, 3H), 1.30-1.39 (m, 6H), 1.40-1.51 (m, 2H), 1,79-1.85 (m, 2H), 4.03 (t, 2H, *J* = 6.8 Hz), 6.94-6.97 (m, 2H), 7.41-7.52 (m, 4H), 7.62-7.76 (m, 6H), 7.84 (d, 1H, *J* = 15.6 Hz), 8.11-8.14 (dd, 2H, *J1* = 6.8 Hz, *J2* = 2 Hz).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 14.13, 22.63, 25.99, 29.07, 29.17, 31.79, 68.21, 114.92, 119.47, 127.26, 127.31, 127.39, 128.17, 128.97, 129.05, 130.30, 137.23, 140.03, 144.79, 145.29, 161.35, 190.04.

IR[KBr]: υ 2929, 2857, 1660, 1627, 1510, 1471, 1398, 1308, 1266, 1177, 1013, 987, 820, 767, 736, 690 cm^{-1}.

Mass (EI): 400 (M^{+1}), 399 (M^{+})

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(4-(decyloxy)phenyl)prop-2-en-1-one (**37**)

Yield: 70.0 % (White solid)

M.p.: 127-128 ^{o}C

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.92 (m, 3H), 1.30-1.36 (m, 12H), 1.45-1.51 (m, 2H), 1,79-1.86 (m, 2H), 4.03 (t, 2H, *J*=6.8 Hz), 6.96 (d, 2H, *J* = 8.8 Hz), 7.41-7.52 (m, 4H), 7.63-7.69

(m, 4H), 7.75 (d, 2H, *J* = 8.4 Hz), 7.85 (d, 1H, *J* = 15.6 Hz), 8.13 (dd, 2H, *J1* = 6.8 Hz, *J2* = 2 Hz) .

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 14.15, 22.70, 26.02, 29.18, 29.34, 29.39, 29.58(2C), 31.92, 68.22, 114.94, 119.49, 127.25, 127.30, 127.41, 128.16, 128.96, 129.05, 130.29, 137.25, 140.03, 144.77, 145.28, 161.36, 190.01.

IR[KBr]: υ 3038, 2920, 2851, 1628, 1601, 1501, 1469, 1309, 1266, 1246, 1177, 1021, 820, 736, 690 cm^{-1}.

Mass (EI): 440(M^+, 100), 300(47), 206(20), 152(12).

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(4-(dodecyloxy)phenyl)prop-2-en-1-one (**38**)

Yield: 71.0% (White solid)

M.p.: 118-119 ^oC

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.89-0.92 (m, 3H), 1.34-1.37 (m, 16H), 1.47-1.51 (m, 2H), 1.80-1.84 (m, 2H), 4.03 (t. 2H, *J* = 6.4 Hz), 6.96 (d, 2H, *J* = 8.8 Hz), 7.41-7.51 (m, 4H), 7.67-7.69 (m, 4H), 7.75 (dd, 2H, *J1* = 6.8 Hz, *J2* = 1.6 Hz), 7.85 (d, 1H, *J* = 15.6 Hz), 8.13 (dd, 2H, *J1* = 6.8 Hz, *J2* = 1.6 Hz).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 14.14, 22.71, 26.02, 29.17, 29.36, 29.39, 29.58, 29.60, 29.65, 29.67, 31.93, 68.22, 114.94, 119.51, 127.25, 127.30, 127.41, 128.15, 128.96, 129.04, 130.28, 137.26, 140.04, 144.77, 145.29, 161.36, 190.03.

IR[KBr]: υ 2919, 2850, 1628, 1602, 1511, 1307, 1252, 1177, 1021, 821, 766, 689 cm^{-1}.

Mass (EI): 469(M+1), 249, 243.

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(4-(tetradecyloxy)phenyl)prop-2-en-1-one (**39**)

Yield 69 % (White solid)

M.p.: 120^oC

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.88-0.92 (m, 3H), 1.29 (m, 20H), 1.47-1.51 (m, 2H), 1.80-1.84 (m, 2H), 4.03 (t. 2H, *J* = 6.8 Hz), 6.96 (d, 2H, *J* = 8.4 Hz), 7.42-7.52 (m, 4H), 7.63-7.69 (m, 4H), 7.75 (d, 2H, *J* = 8.4 Hz), 7.85 (d, 1H, *J* = 15.6 Hz), 8.12 (d, 2H, *J* = 8.4 Hz)

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 14.16, 22.72, 26.03, 29.18, 29.39(2C), 29.59, 29.62, 29.68(2C), 29.71, 29.72, 31.95, 68.22, 114.93, 119.48, 127.25, 127.30, 127.40, 128.16, 128.96, 129.05, 130.29, 137.25, 140.03, 144.78, 145.28, 161.36, 190.01.

IR[KBr]: υ 2918, 2849, 1629, 1602, 1512, 1309, 1268, 1178, 1020, 820, 737, 690 $cm.^{-1}$

Mass (EI):496(M^+, 100), 299(30).

(*E*)-1-([1,1'-Biphenyl]-4-yl)-3-(4-(hexadecyloxy)phenyl)prop-2-en-1-one (**40**)

Yield: 72.0% (White solid)

M.p.: 100-102 ^{o}C

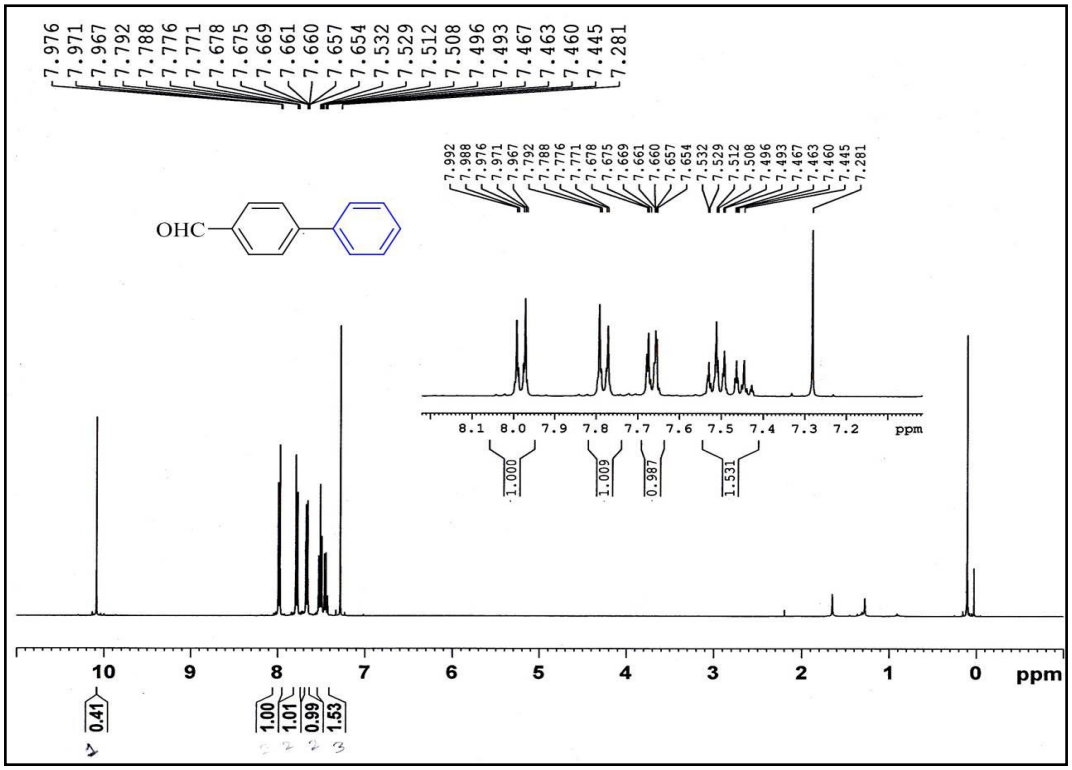
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.88-0.91 (m, 3H), 1.27-1.50 (m, 26H), 4.03 (t. 2H, *J*=6.4 Hz), 6.96 (d, 2H, *J* = 8.8 Hz), 7.43-7.52 (m, 4H), 7.62-7.91 (m, 4H), 7.75 (dd, 2H, *J1*=6.8 Hz, *J2*=1.6 Hz), 7.85 (d, 1H, *J*=15.6 Hz), 8.13 (dd, 2H, *J1*=6.8 Hz, *J2*=1.6 Hz).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ 14.17, 22.73, 26.02, 29.17, 29.40(2C), 29.59(3C), 29.62, 29.69, 31.95, 68.22, 114.92, 119.45, 127.26, 127.31, 127.38, 128.17, 128.97, 129.05, 130.30, 137.23, 140.03, 144.80, 145.29, 161.35, 190.03.

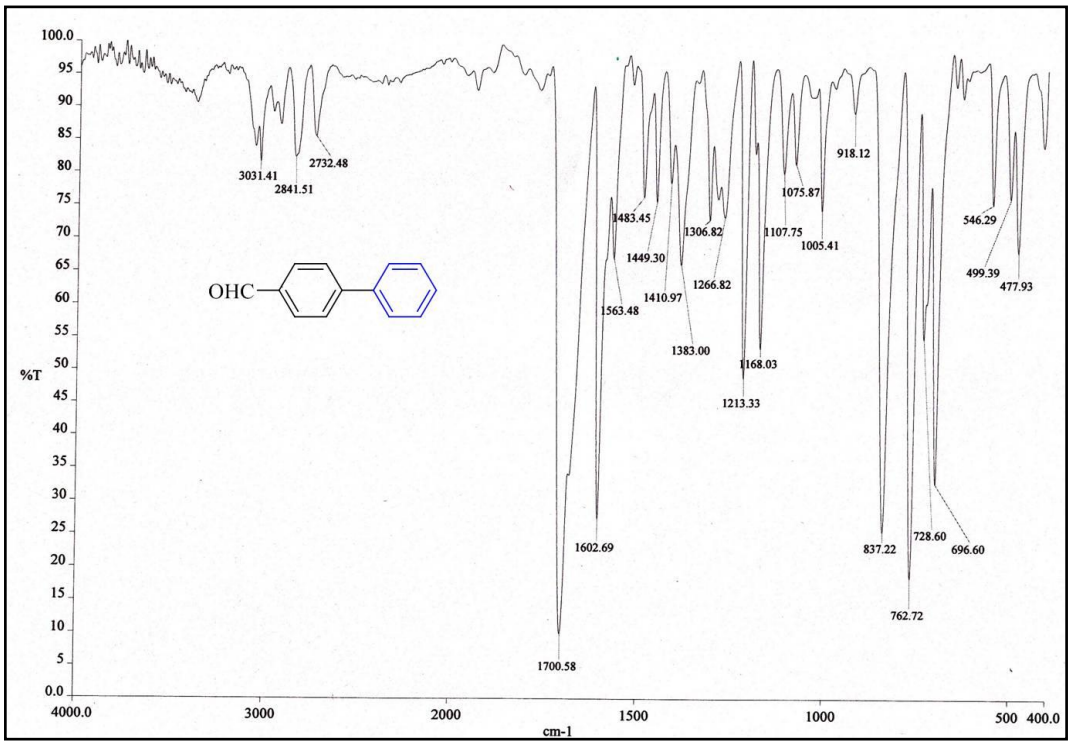
IR[KBr]: υ 2918, 2849, 1628, 1601, 1511, 1309, 1276, 1177, 1082, 989, 767, 689 cm^{-1}.

Mass (EI): 525 (M^{+1}), 157.

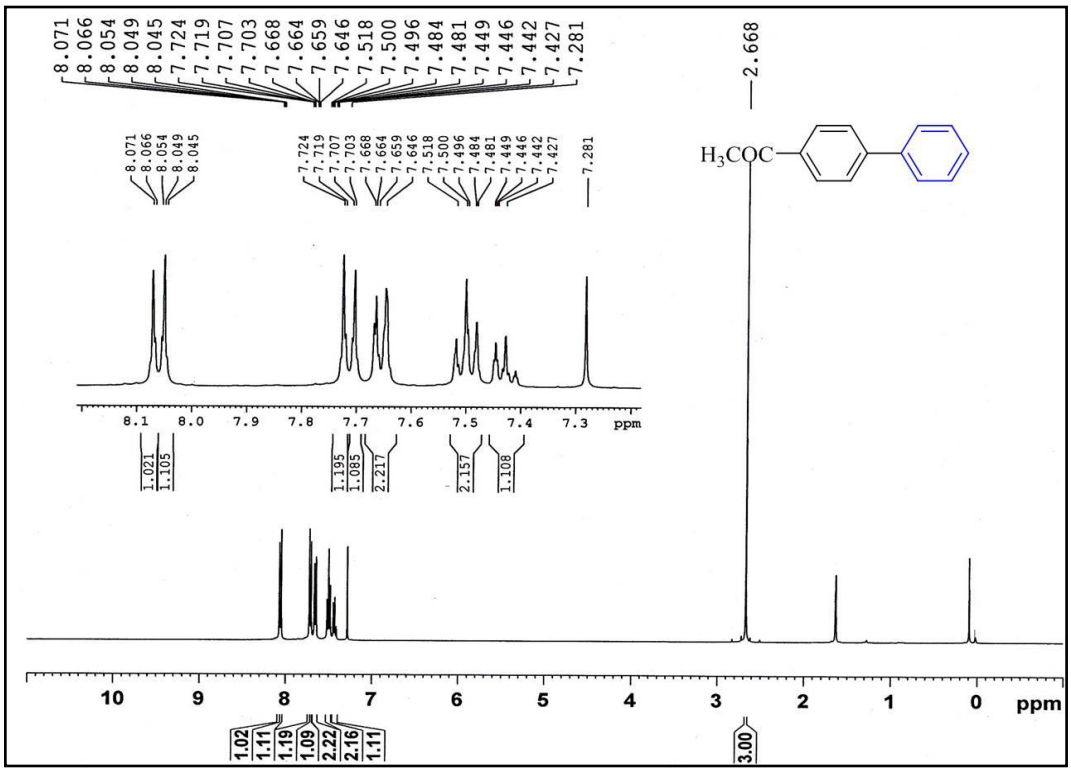
Spectral Data:



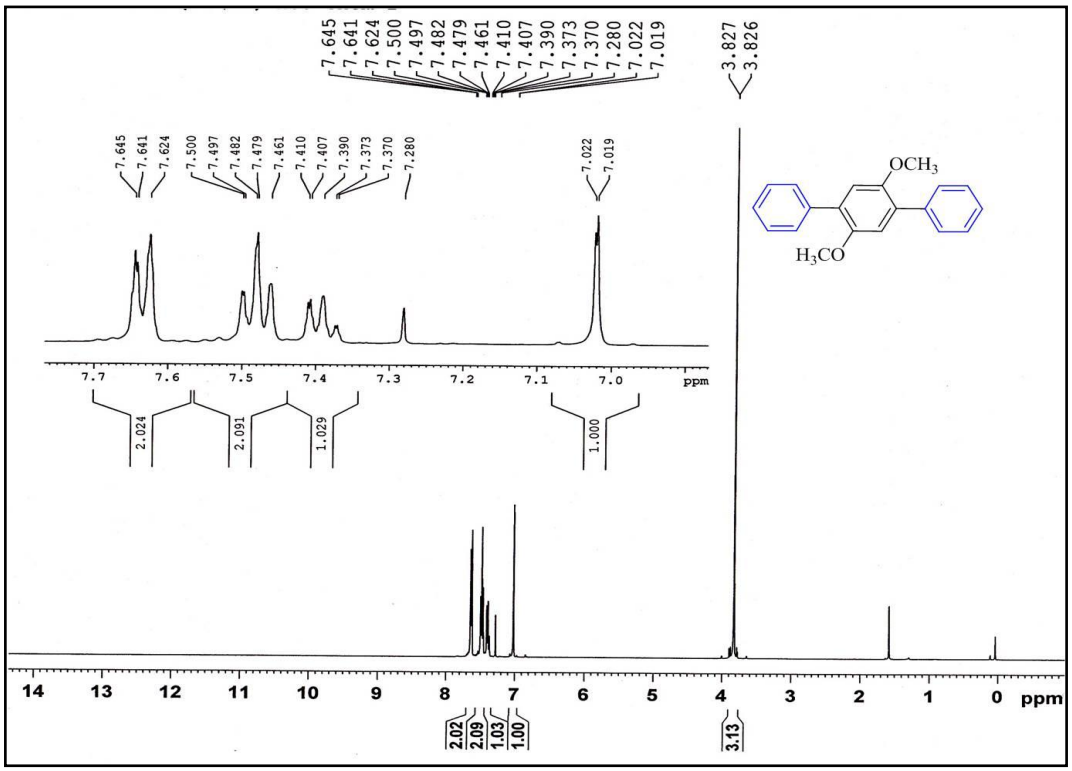
^{1}H NMR of compound **5**



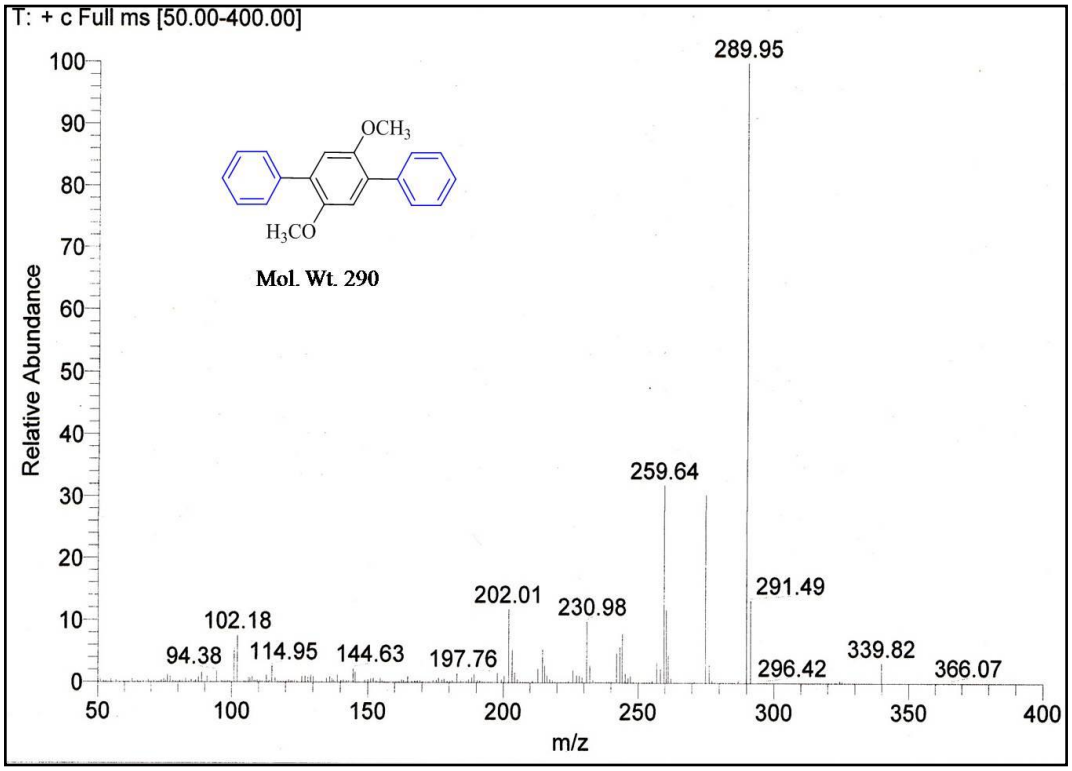
IR of compound **5**



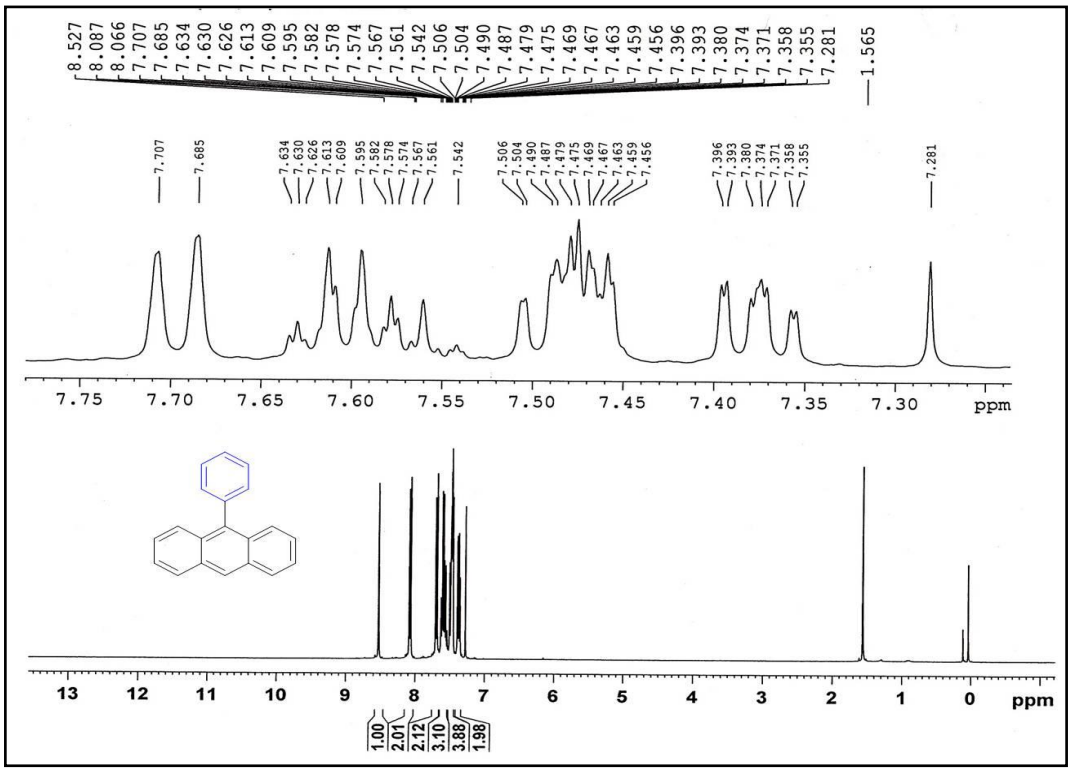
^{1}H NMR of compound **6**



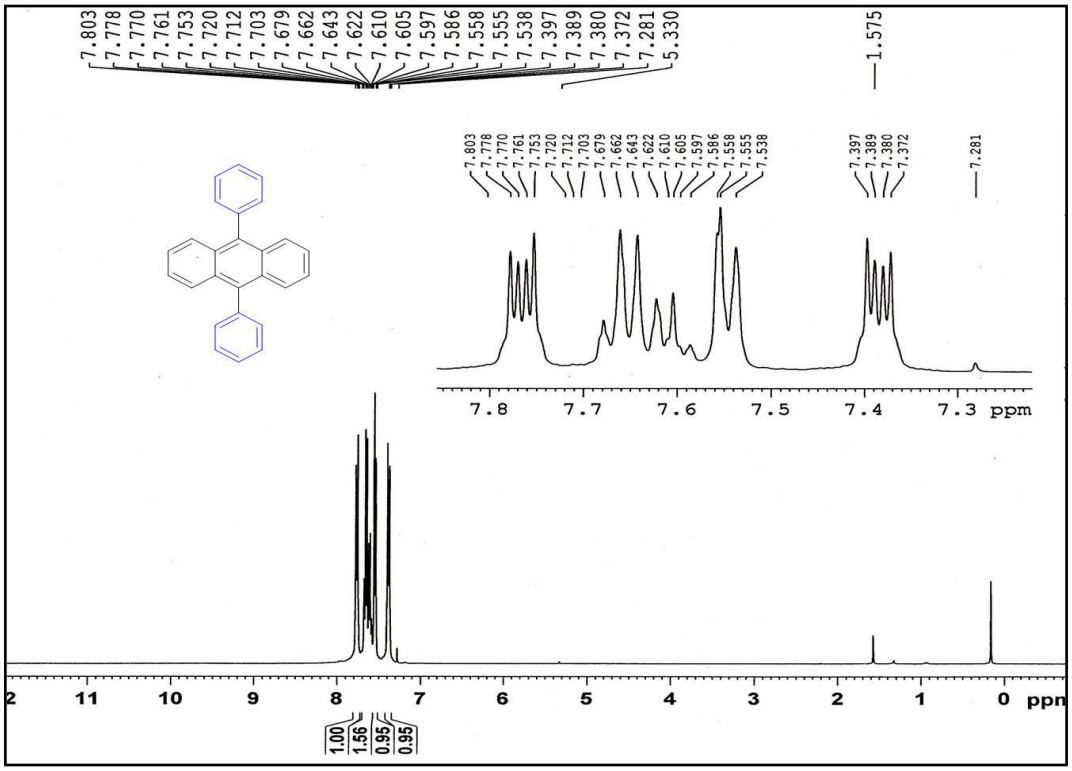
^{1}H NMR of compound **12**



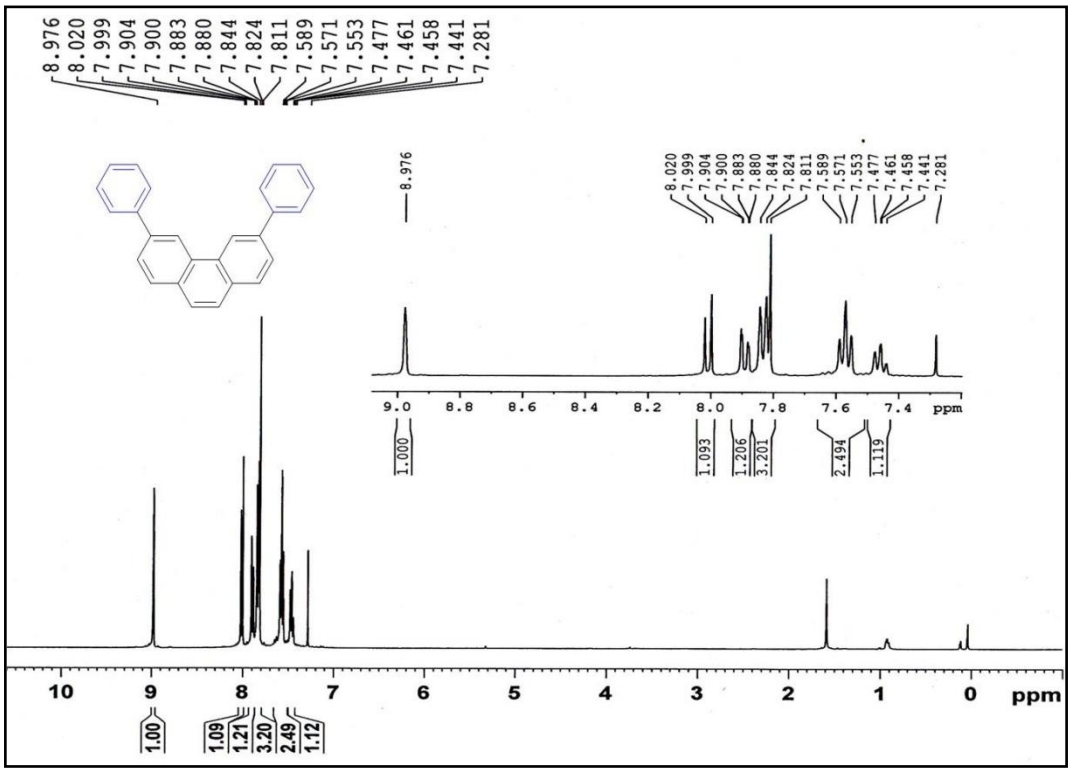
Mass Spectra of compound **12**



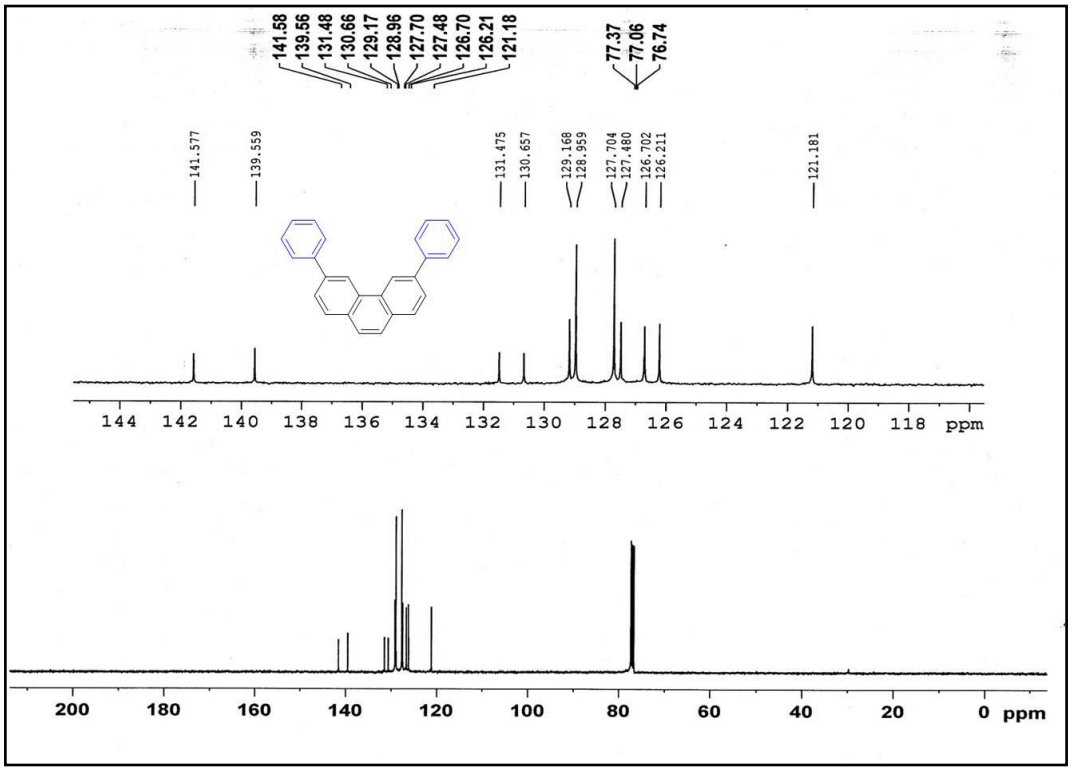
^{1}H NMR of compound **12**



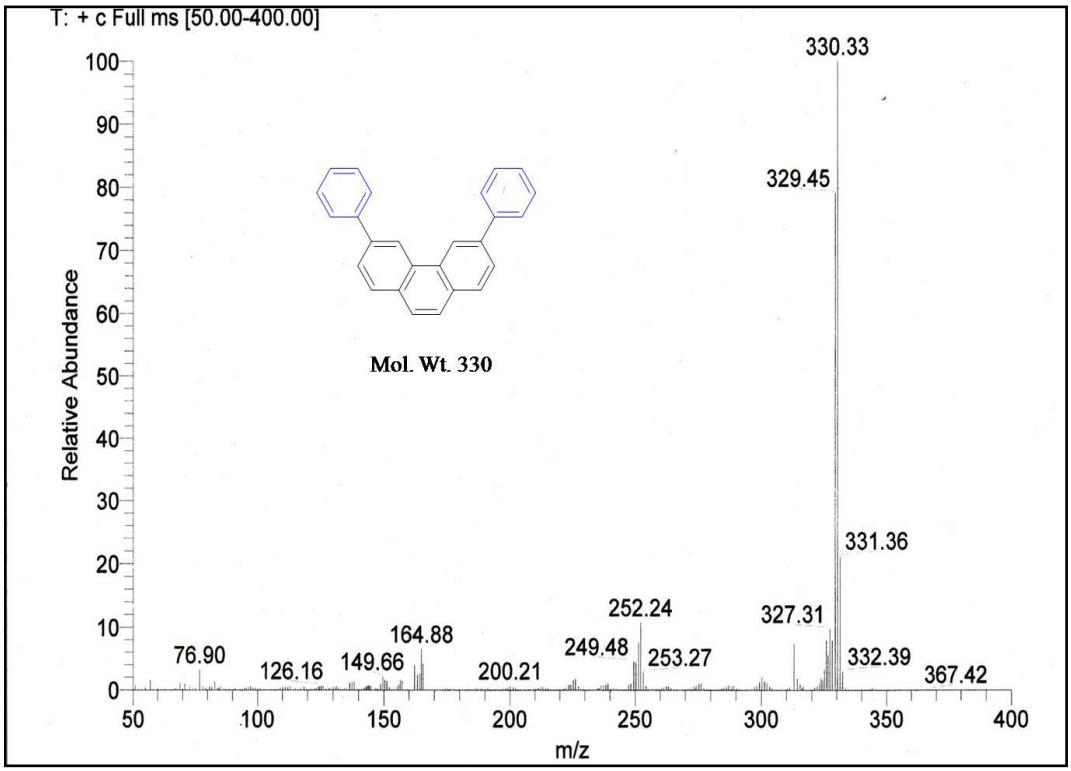
^{1}H NMR of compound **14**



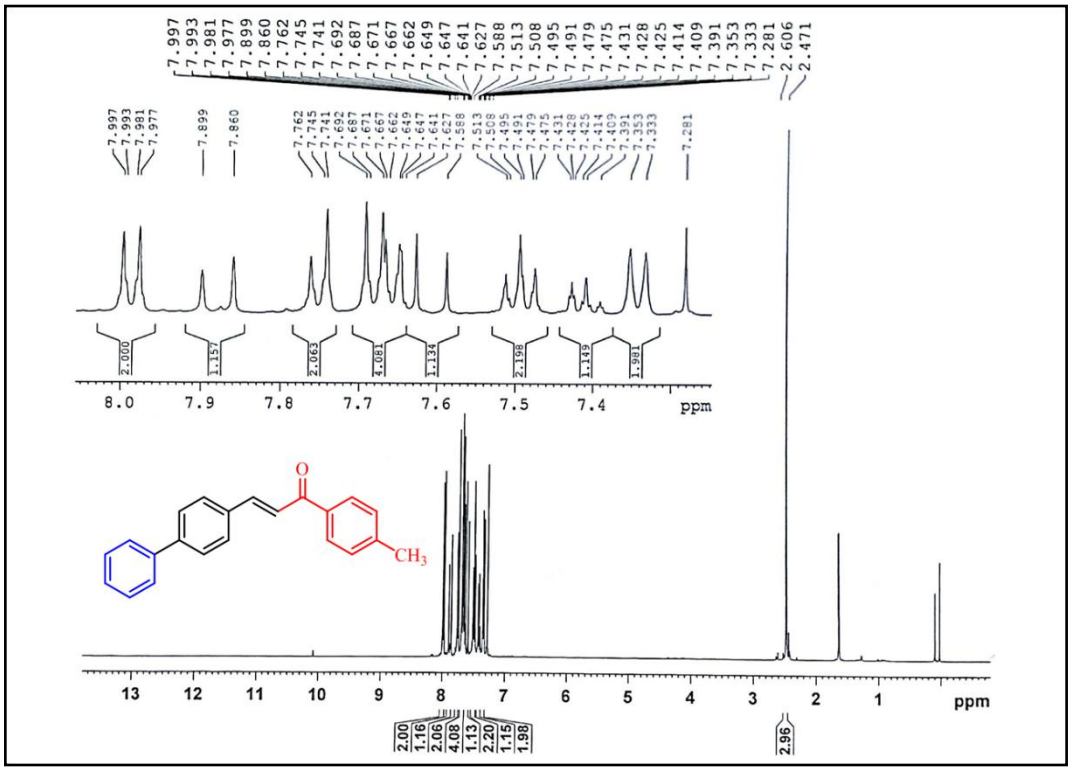
^{1}H NMR of compound **17**



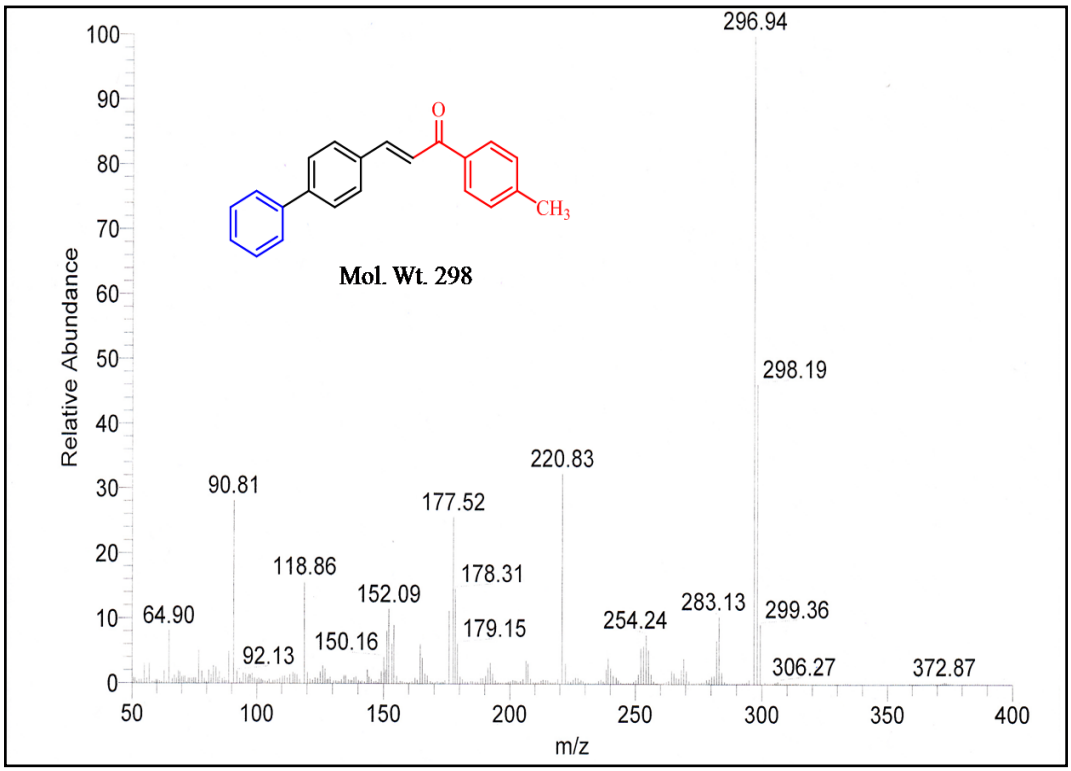
^{13}C NMR of compound **14**



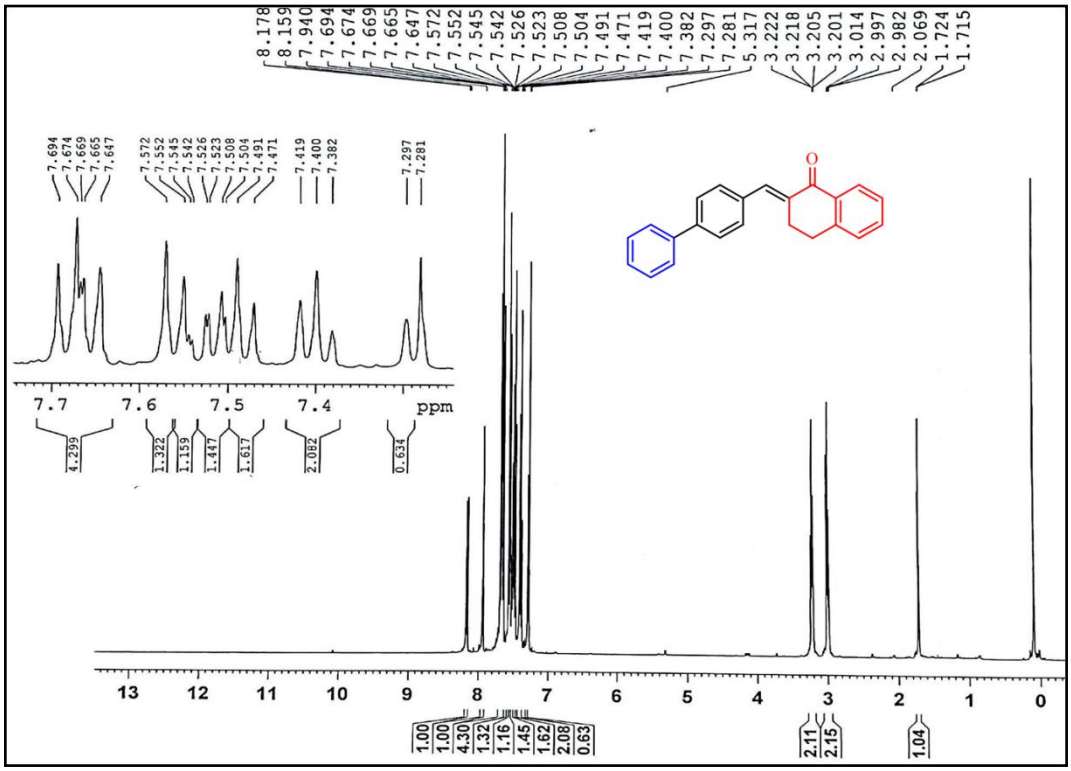
Mass Spectra of compound **14**



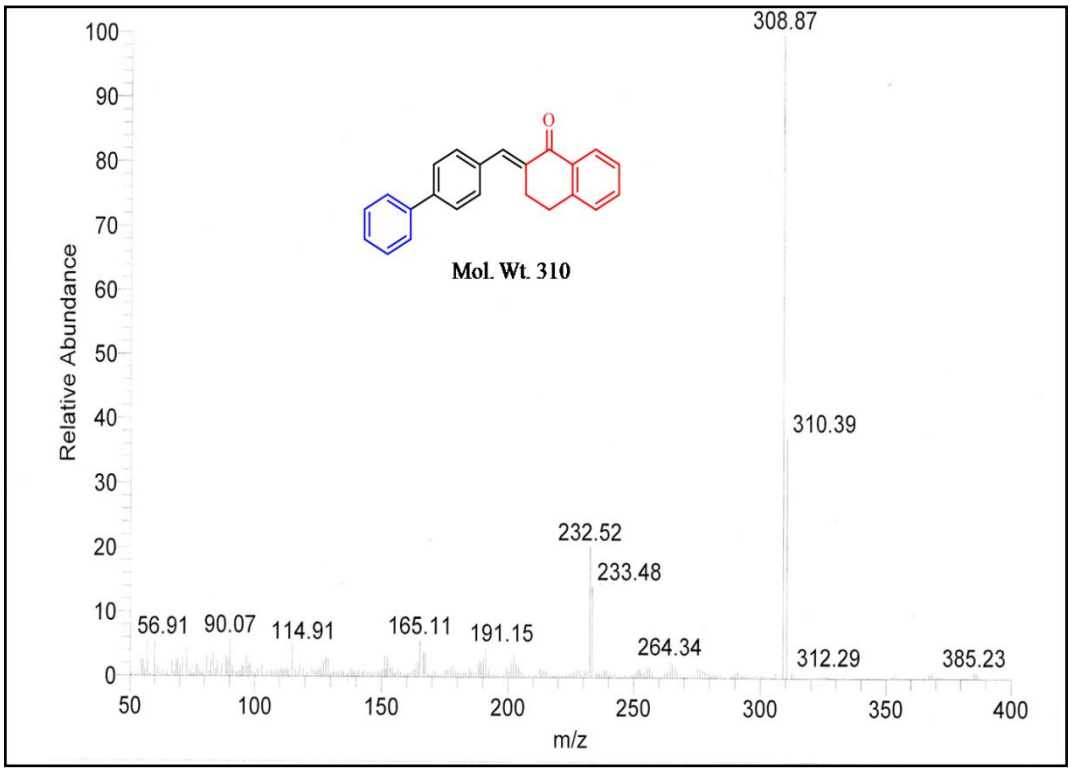
^{1}H NMR of compound **22**



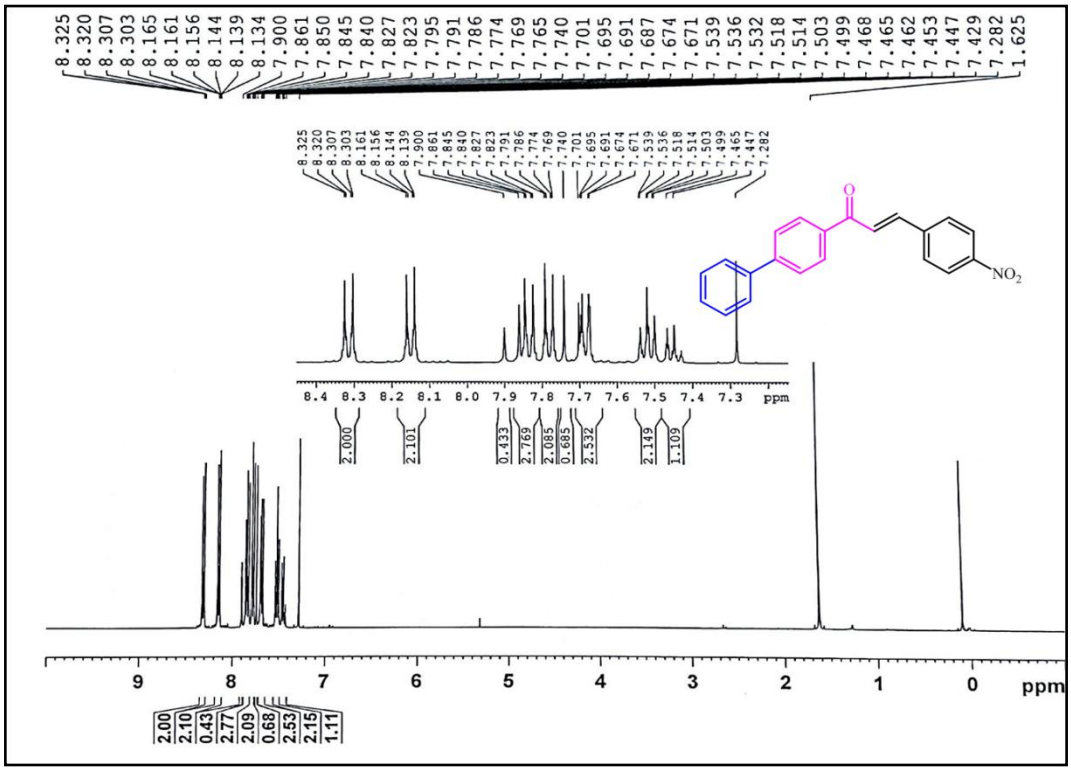
Mass Spectra of compound **22**



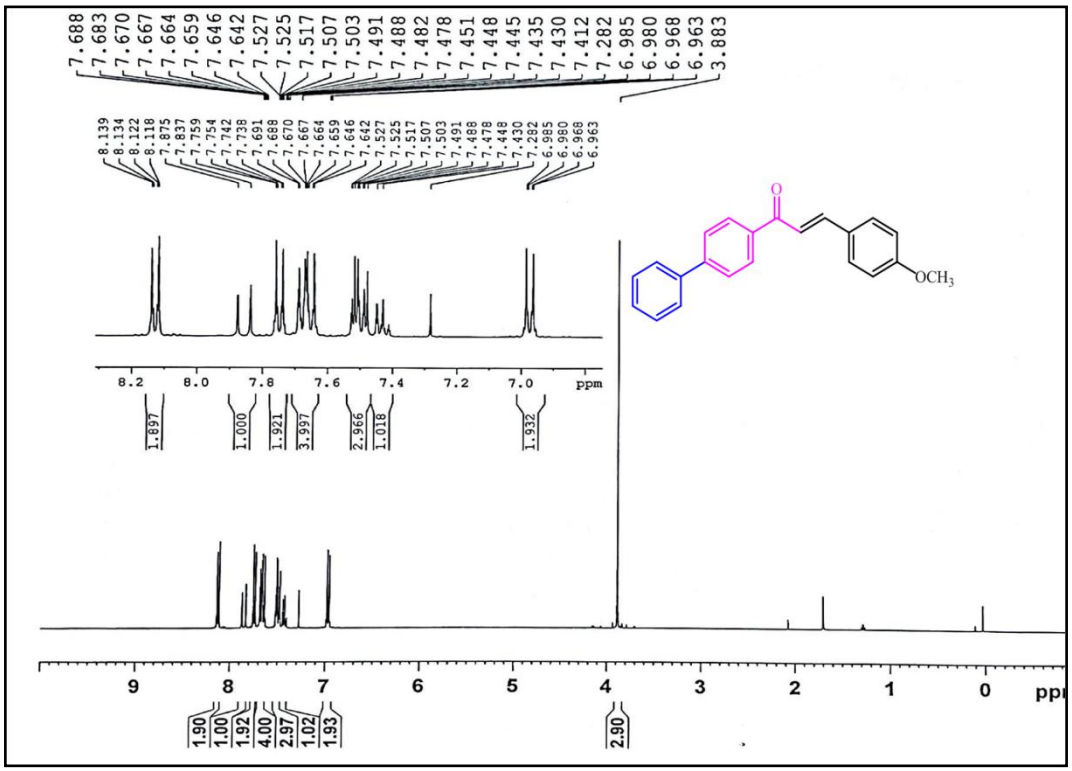
^{1}H NMR of compound **23**



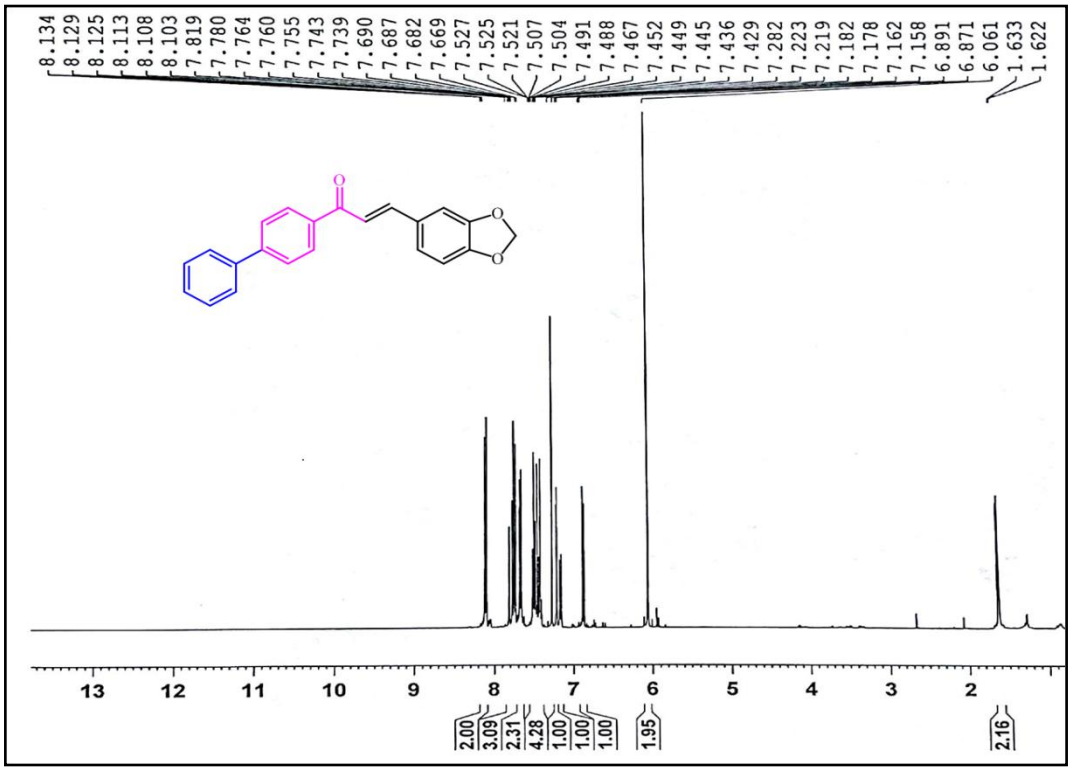
Mass Spectra of compound **23**



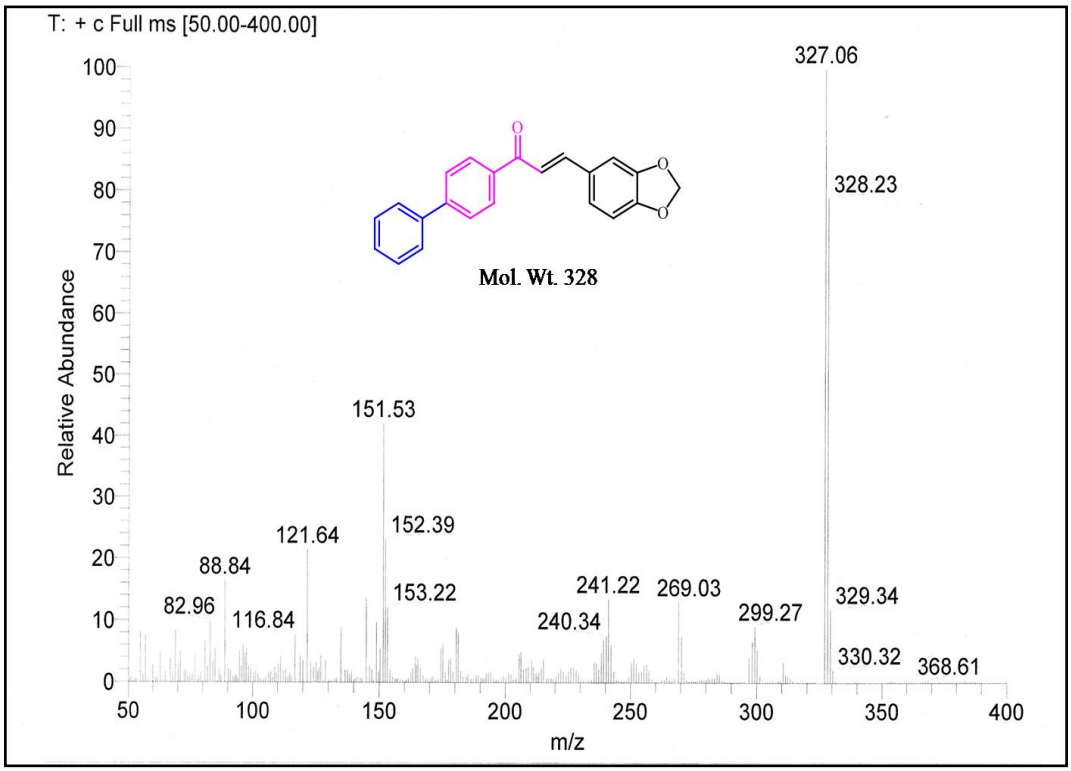
^{1}H NMR of compound **27**



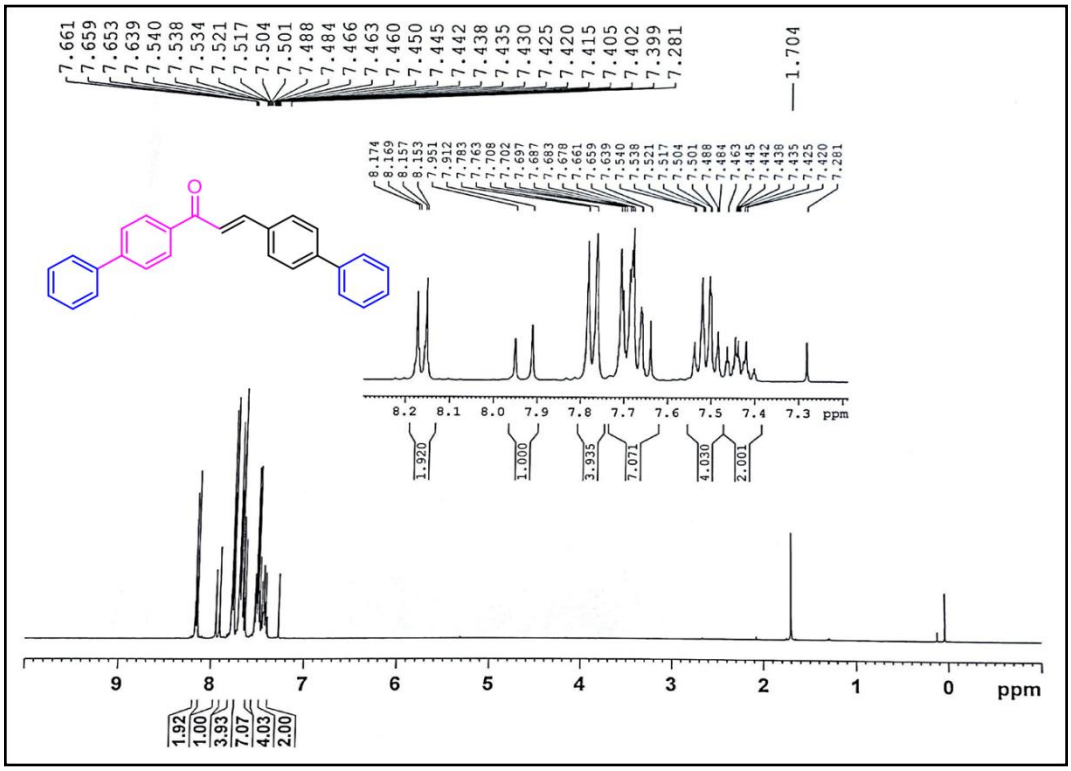
^{1}H NMR of compound **28**



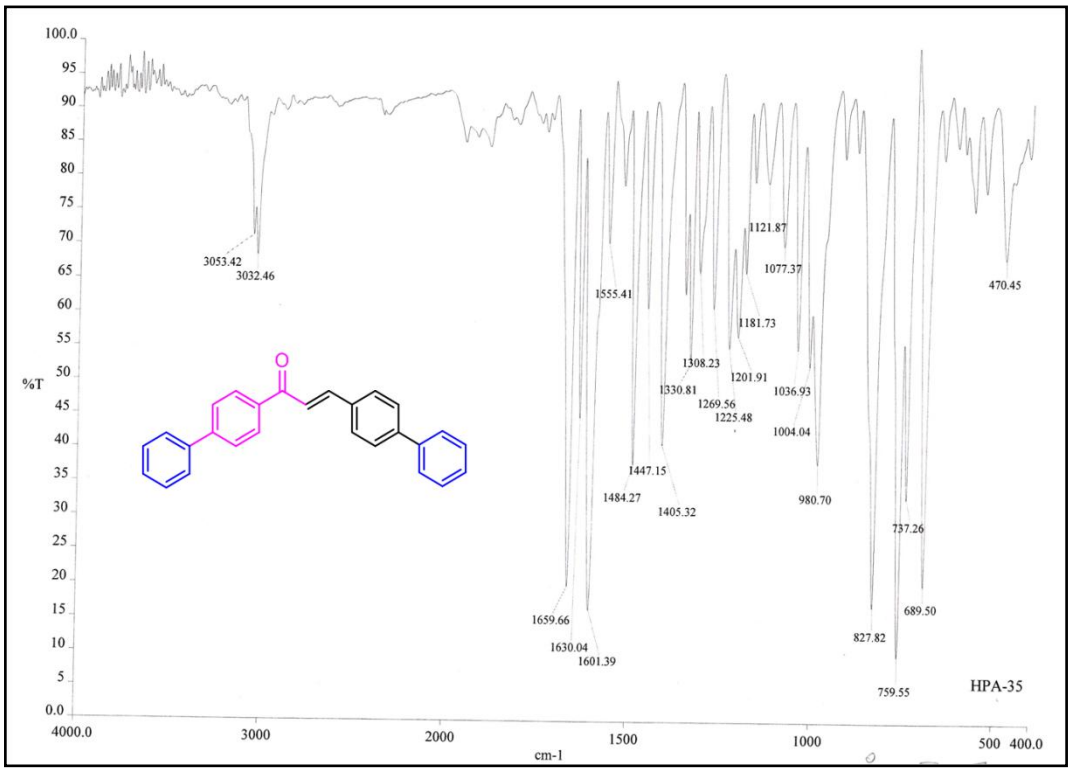
^{1}H NMR of compound **29**



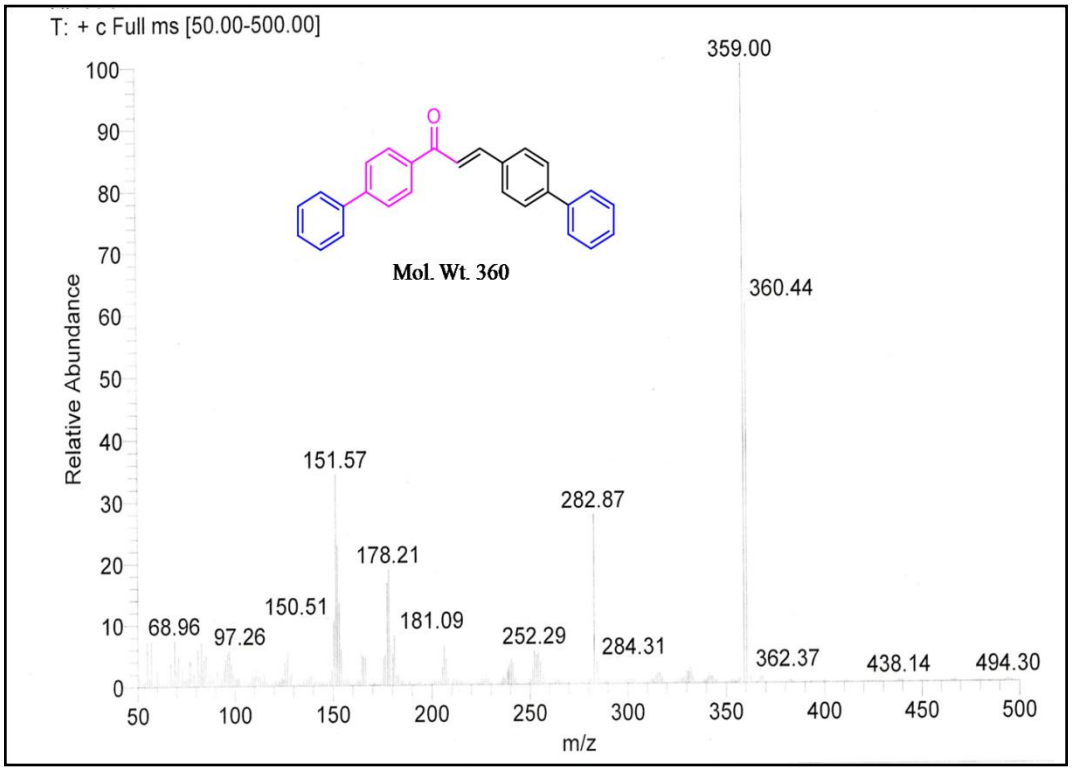
Mass Spectra of compound **29**



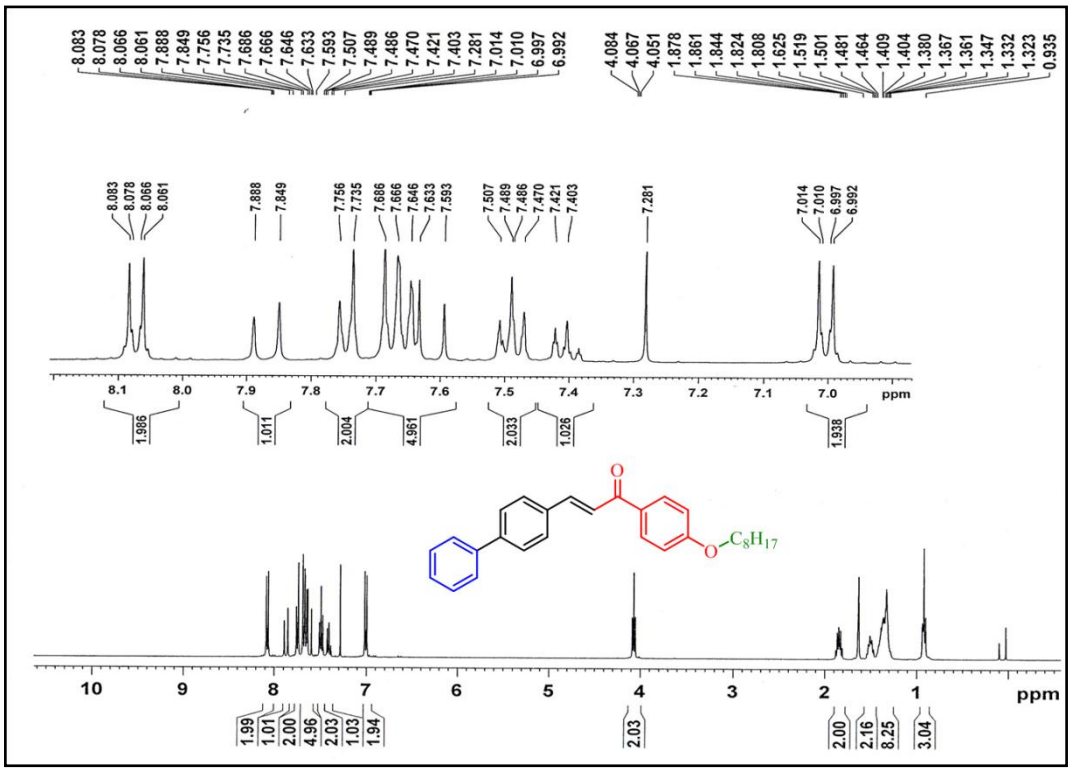
^{1}H NMR of compound **30**



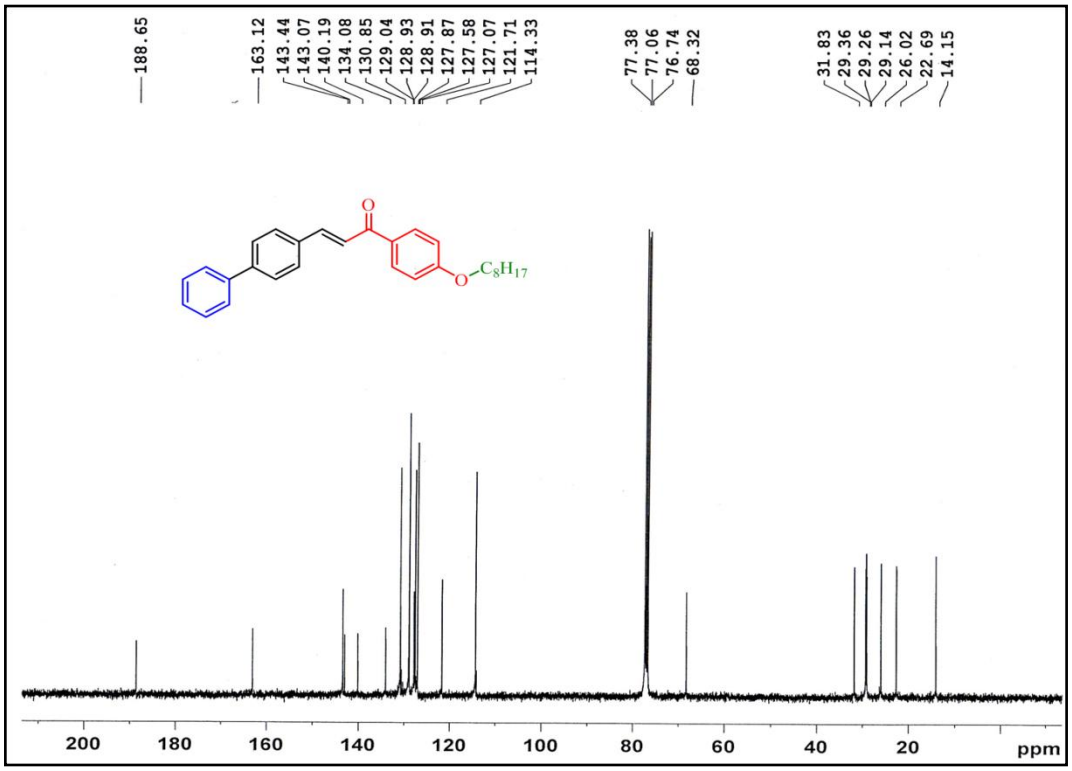
IR Spectra of compound **30**



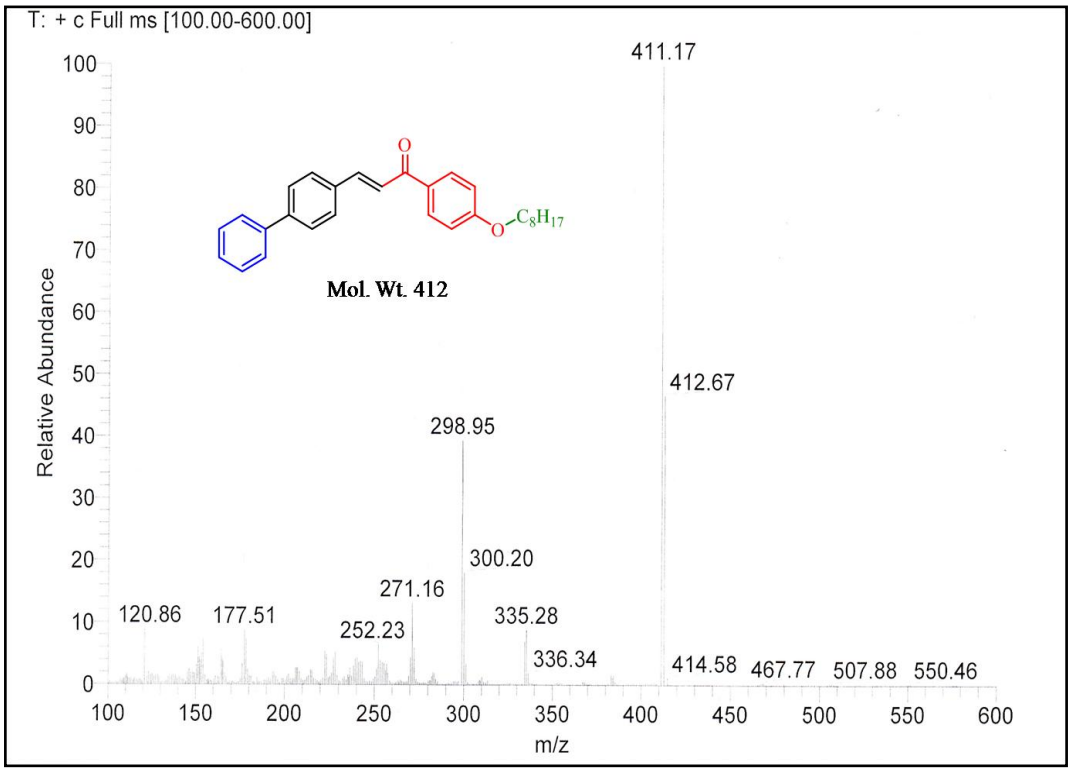
Mass Spectra of compound **30**



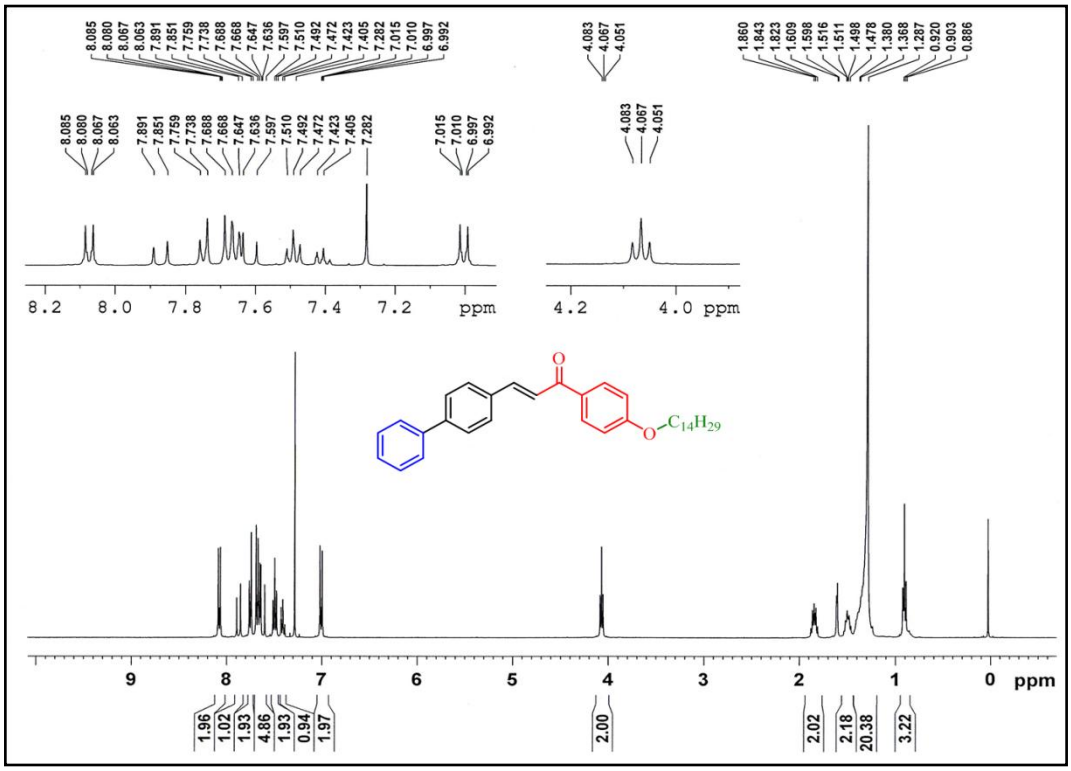
^{1}H NMR of compound **32**



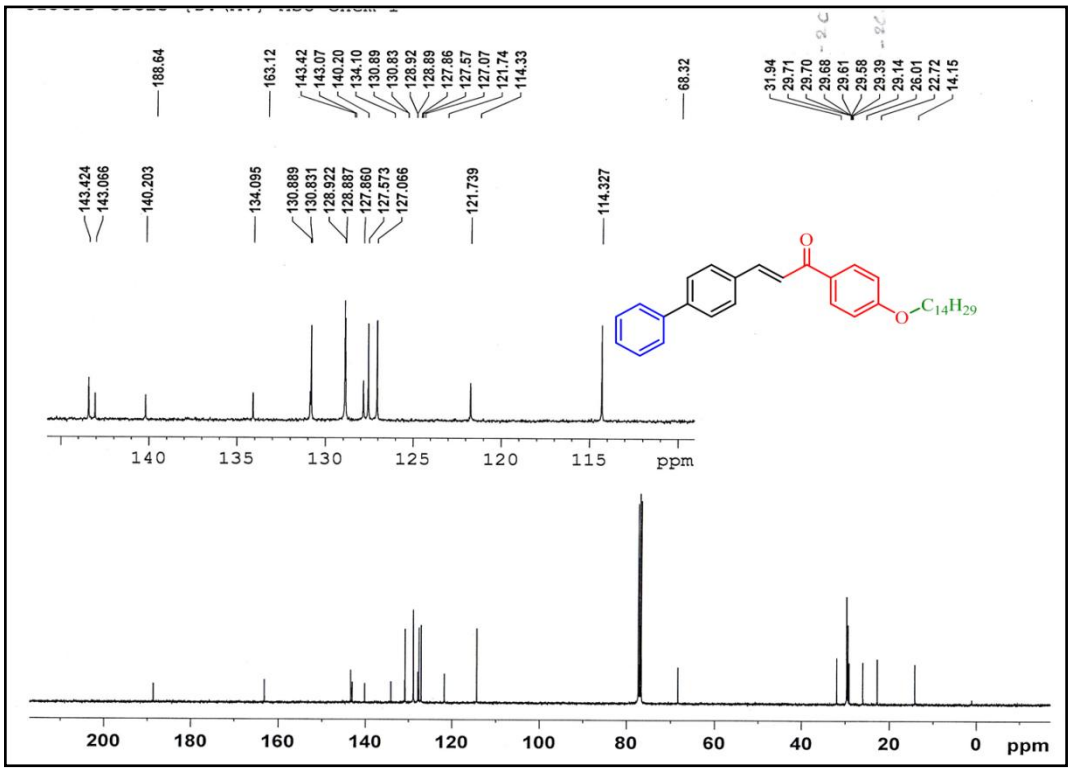
^{13}C NMR of compound **32**



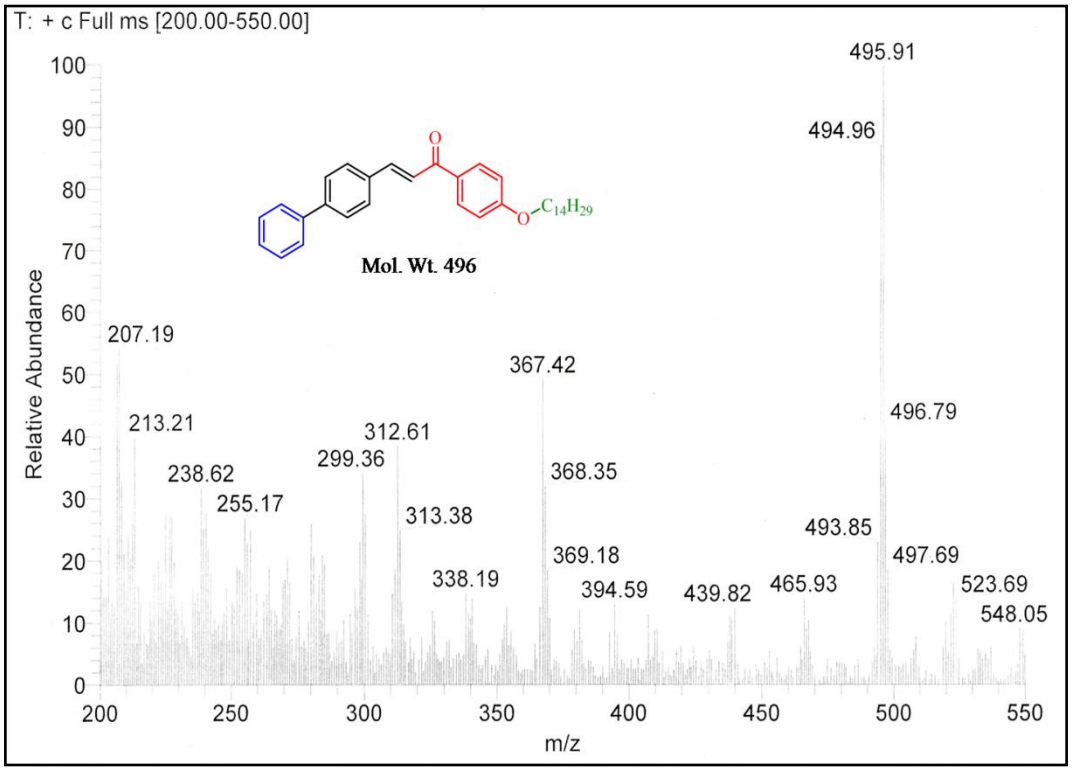
Mass Spectra of compound **32**



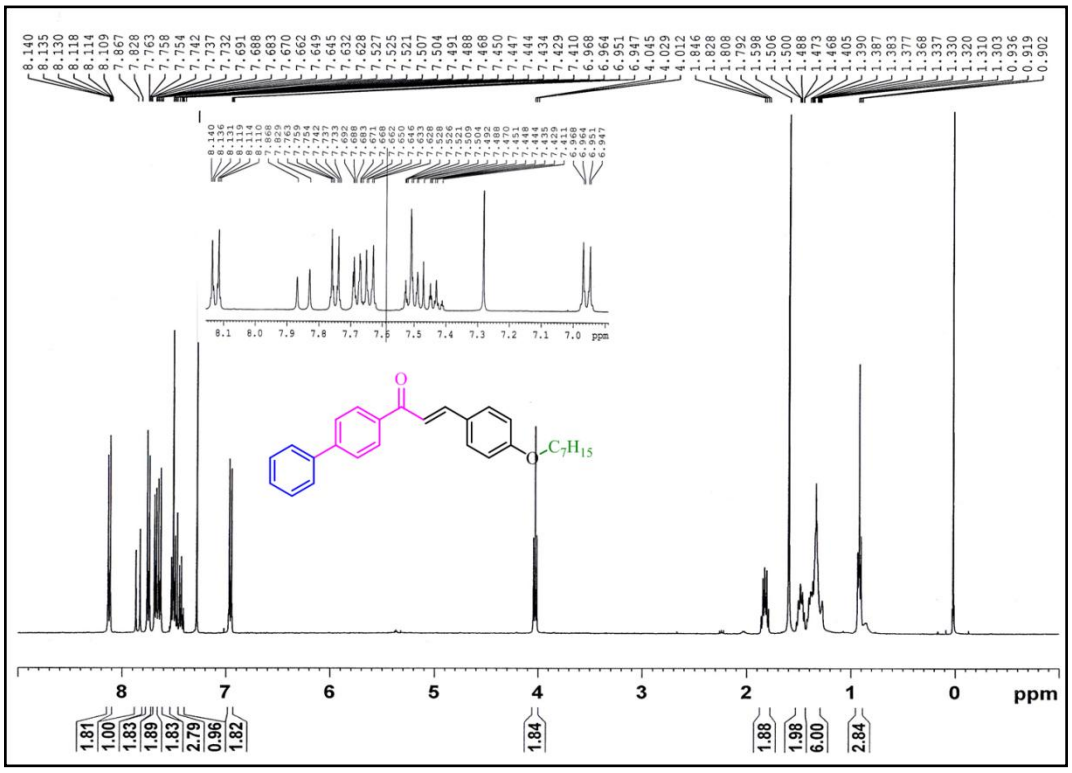
^{1}H NMR of compound **35**



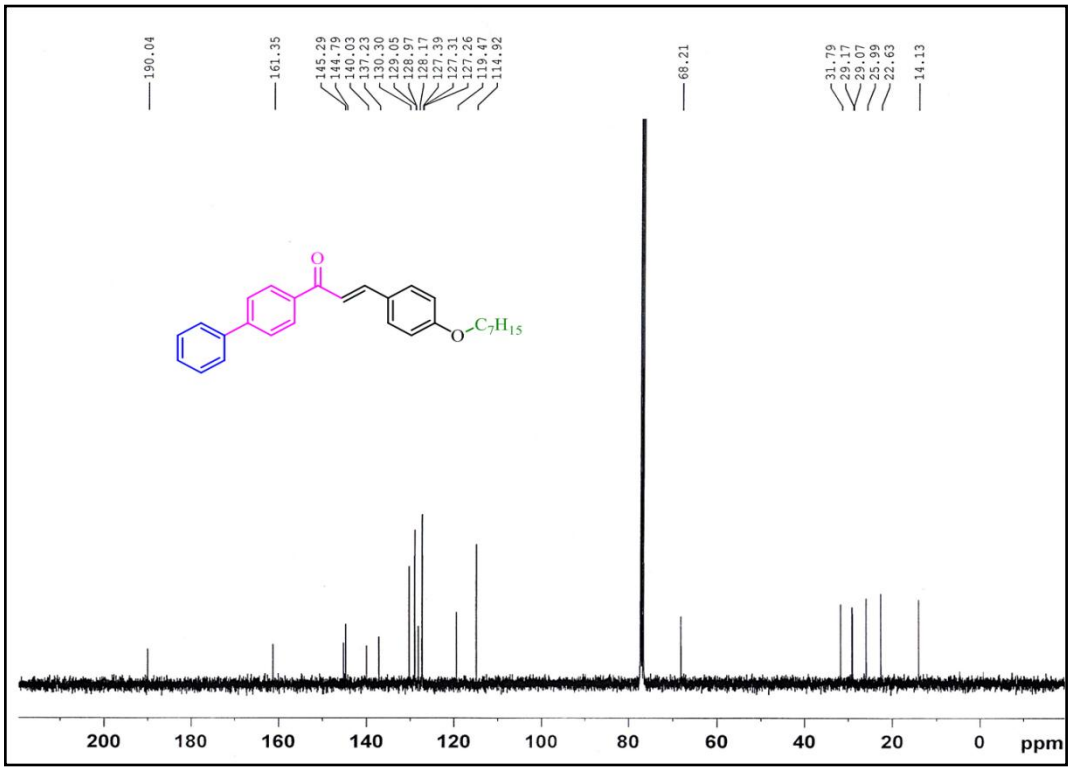
^{13}C NMR of compound **35**



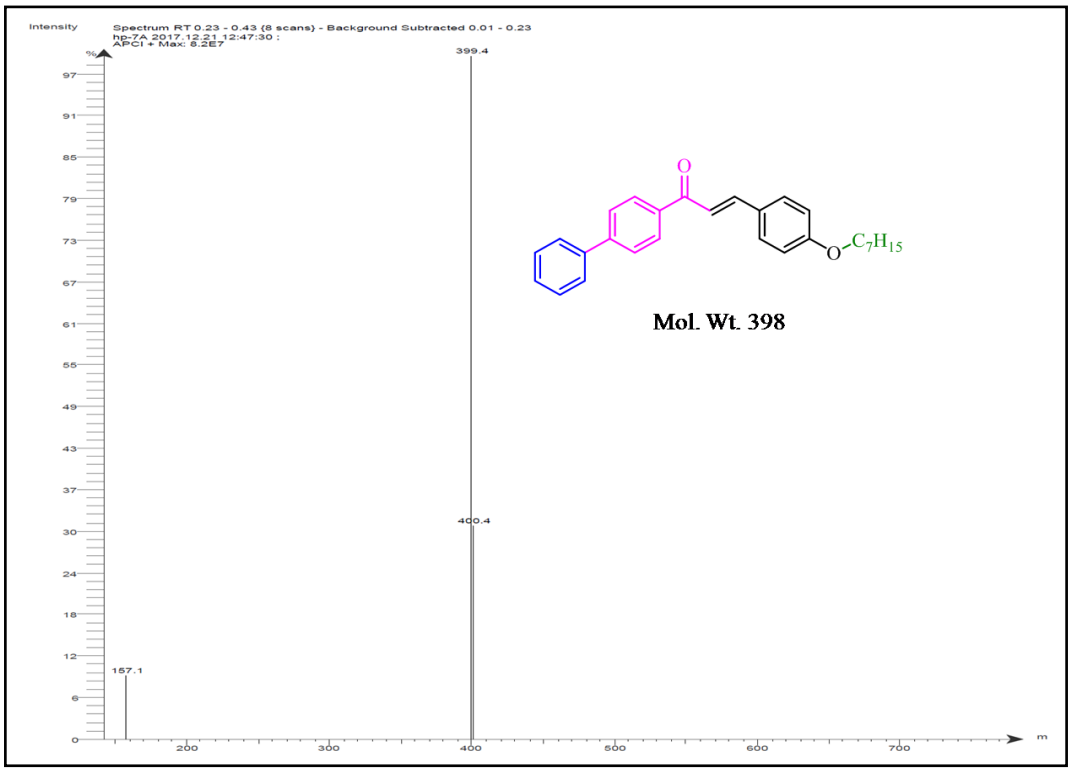
Mass Spectra of compound **35**



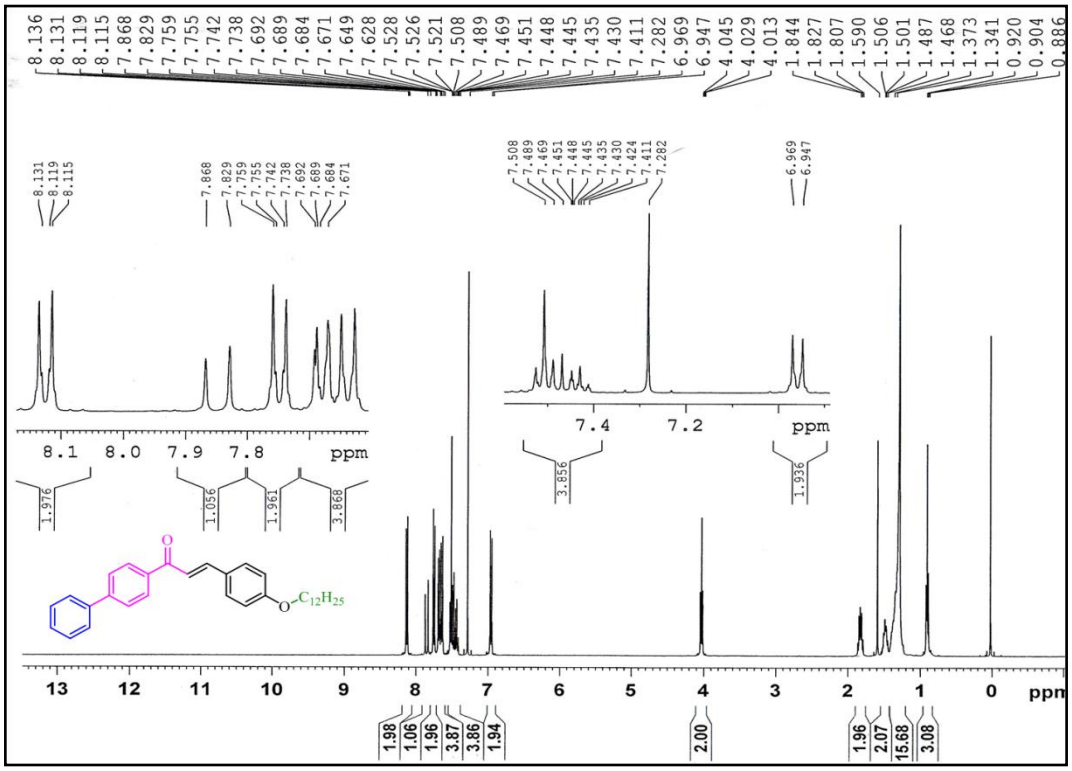
^{1}H NMR of compound **36**



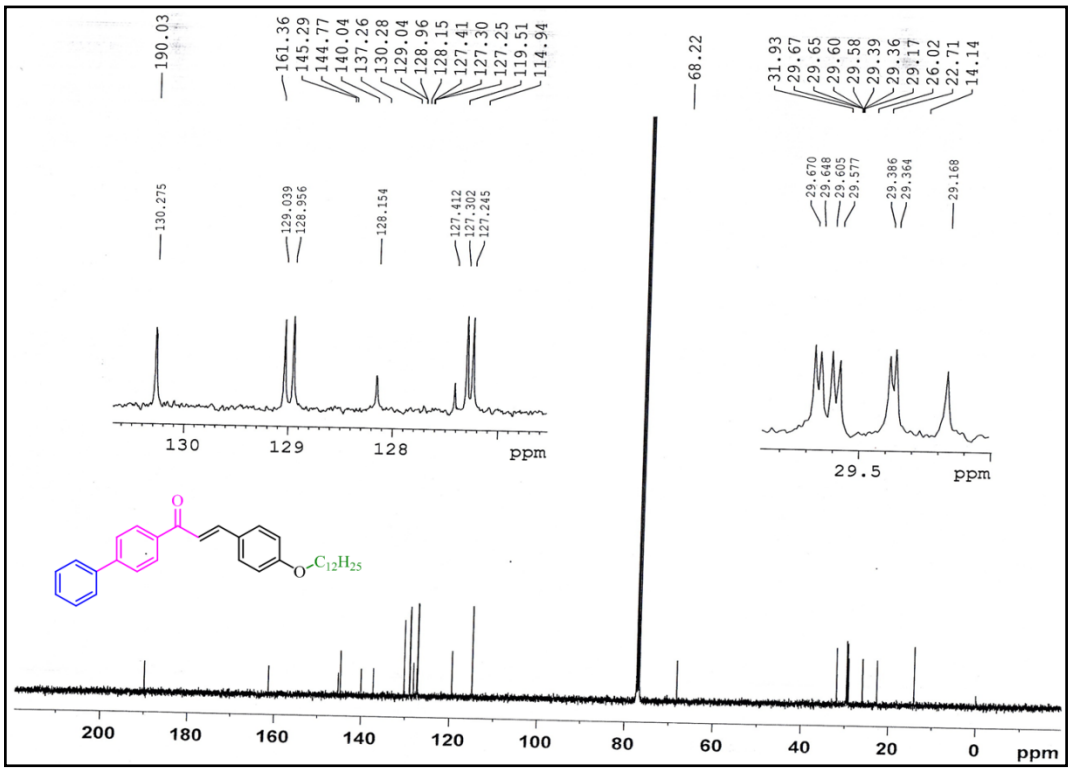
^{13}C NMR of compound **36**



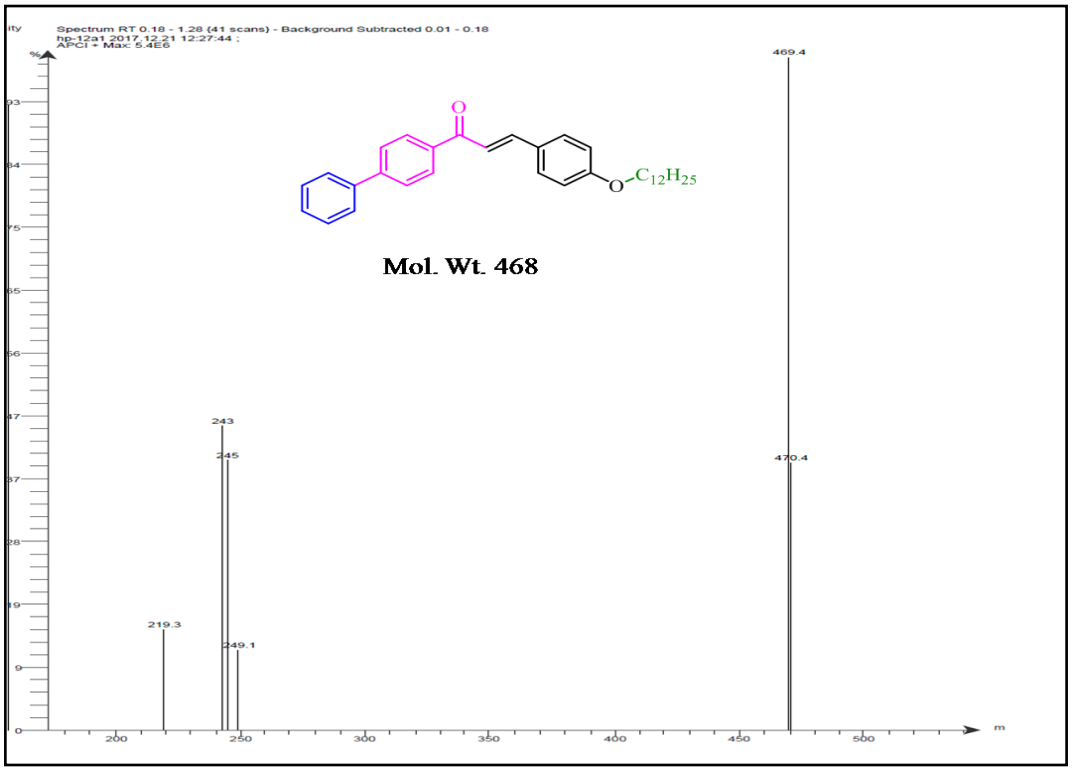
Mass Spectra of compound **36**



^{1}H NMR of compound **38**



^{13}C NMR of compound **38**



Mass Spectra of compound **38**

3.1.5 References

1. J.M. Fraile, in *Heterogenization on inorganic supports: methods and applications*, p. 65-121, *Heterogenized homogeneous catalysis for fine chemicals production*, (Eds: P. Barbaro, F. Liguori), Springer, 2010.
2. (a) H.-Y. Lee, S. Ryu, H. Kang, Y. Jun, J. Cheon, *Chem. Commun.* **2006**, 1325. (b) S. Jana, B. Dutta, R. Bera, S. Koner, *Inorg. Chem.* **2008**, *47*, 5512.
3. (a) S. S. Prockl, W. Kleist, M. A. Gruber, K. Kohler, *Angew. Chem. Int. Ed.* **2004**, *43*, 1881. (b) S. Noel, C. Luo, C. Pinel, L. Djakovitch, *Adv. Synth. Catal.* **2007**, *349*, 1128.
4. E. Mas-Marza, A. M. Segarra, C. Claver, E. Peris, E. Fernandez, *Tetrahedron Lett.* **2003**, *44*, 6595.
5. (a) V.A. Yazerski, in *Heterogenization of homogeneous catalysts on dendrimers*, p. 171-201, *Heterogenized homogeneous catalysis for fine chemicals production*, (Eds P. Barbaro, F. Liguori), Springer, 2010. (b) B. Helms, J.M.J. Fréchet, *Adv. Synth. Catal.* **2006**, *348*, 1125.
6. (a) D.C. Bailey, S.H. Langer, *Chem. Rev.* **1981**, *81*, 109. (b) A.D. Pomogailo, in *Catalysis by polymer-immobilized metal complexes*, (Eds Gordon and Breach), Australia, 1998.
7. (a) P. Hodge, *Chem. Soc. Rev*. **1997**, *26*, 417. (b) J. Chen, G. Yang, H. Zhang, Z. Chen. *React. Funct. Polym.* **2006**, *66*, 1434. (c) K. Ding, Z. Wang, L. Shi, *Pure Appl. Chem.* **2007**, *79*, 1531. (d) S.A. Patel, K.N. Patel, S. Sinha, B.V. Kamath, A.V. Bedekar, *J. Mol. Catal. A: Chem*. **2010**, *332*, 70.
8. J. Jang, J. Ha, B. Lim, *Chem. Commun.* **2006**, 1622 and references cited therein.
9. (a) G. Schooter, *Chem. Mater*. **2001**, *13*, 4322. (b) B. Bruno, R. Corriu, *Chem. Commun*. **2002**, 795. (c) Y. Leng, F. Chen, L. Zuo, W. Duan, *Tetrahedron Lett*. **2010**, *51*, 2370. (d) A. Khalafi-Nezhad, E.S. Shahidzadeh, S. Sarikhani, F. Panahi, *J. Mol. Catal. A: Chem.* **2013**, *379*, 1.
10. (a) P. Villalba, M.K. Ram, H. Gomez, V. Bhethanabotla, M.N. Helms, A. Kumar, A. Kumar, *Mater. Sci. and Engin*. **2012**, *32C*, 594. (b) E.I. Yslas, L.E. Ibarra, D.O. Peralta, C.A. Barbero, V.A. Rivarola, M.L. Bertuzzi, *Chemosphere* **2012**, *87*, 1374.and references cited therein.
11. (a) Y. Wang, X. Wang, J. Li, Z. Mo, X. Zhao, X. Jing, F. Wang, *Adv. Mater*. **2001**, *13*, 1582. (b) J. Stejskal, O. Quadrat, I. Sapurina, J. Zemek, A. Drelinkiewicz, M. Hasik, I. Krivka, J. Prokeš, *Eur. Polym. J.* **2002**, *38*, 631.

12. (a) D.B. Cairns, S.P. Armes, *Langmuir* **1999**, *15*, 8052. (b) Z. Niu, Z. Yang, Z. Hu, Y. Lu, C.C. Han, *Adv. Funct. Mater*. **2003**, *13*, 949.
13. (a) M. Kim, S. Cho, J. Song, S. Son, J. Jang, *ACS Appl. Mater. Interfaces* **2012**, *4*, 4603.
14. A.R. Modarresi-Alam, S. Zafari, A.R. Miandashti, *Polym. Adv. Technol.* **2015**, *26*, 645.
15. E.N. Prabhakaran, J. Iqbal, *J. Org. Chem.* **1999**, *64*, 3339.
16. M. Lakshmi Kantam, M. Roy, S. Roy, B. Sreedhar, S. S. Madhavendra, B. M. Chaudhary, R. L. De, *Tetrahedron* **2007**, *63*, 8002.
17. (a) N.N. Mallikarjuna, S.K. Manohar, P.V. Kulkarni, A. Venkataraman, T.M. Aminabhavi, *J. Appl. Polym. Sci.* **2005**, *97*, 1868. (b) K. Lee, S. Cho, S. H. Park, A. J. Heeger, C.-W. Lee, S.-H. Lee, *Nature* **2006**, *441*, 65. (c) M.M. Bidgoli, M. Mohsennia, F.A. Boroumand, *Mater. Res. Bull* .**2015**, *72*, 29. (d) L. Li, G. Yan, J. Wu, X. Yu, Q. Guo, Z. Ma, Z. Huang, *J Polym Res*. **2009**, *16*, 421.
18. (a) M. Mora, C. Jiménez-Sanchidrián, J. R. Ruiz, *Curr. Org. Chem*. **2012**, *16*, 1128. (b) A. Taher, D. Nandi, M. Choudhary, K. Mallick, *New J. Chem*. **2015**, *39*, 5589. (c) P. Das, W. Linert, *Coord. Chem. Rev*. **2016**, *311*, 1. (d) S. Sobhani, Z. M. Falatooni, S. Asadi, M. Honarmand, *Catal. Lett*. **2016**, *146*, 255.
19. (a) P.T. Anastas, J. C. Warner, in *Green Chemistry: Theory and practice*, Oxford University Press: New York, 1998, p. 30. (b) I. T. Horváth, P. T. Anastas, *Chem. Rev.* **2007**, *107*, 2169.
20. E. Paterno, *Gazz. Chim. It.* **1909**, *39(I)*, 237. Its English translation: M. D'Auria, (Ed.) Emanuele Paternò, *Synthesis in Organic Chemistry by Means of Light*, Societa Chimica Italiana, Rome, 2009.
21. (a) G. Ciamician, *Science* **1912**, *36*, 385. (b) G. Ciamician, P. Silber, *Chem. Ber*. **1908**, *41*, 1928. (c) A. Albini, M. Fagnoni, *ChemSusChem* **2008**, ***1***, 63.
22. (a) A. Mustafa, *Chem. Rev*. **1952**, *51*, 1. (b) G.M. Wyman, *Chem. Rev*. **1955**, *55*, 625.
23. (a) B. Pohlmann, H.-D. Scharf, U. Jarolimek, P. Mauermann, *Sol. Energy* **1997**, *61*, 159. (b) M. Oelgemöller, C. Jung, J. Mattay, *Pure Appl. Chem.* **2007**, *79*, 1939. (c) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev*. **2011**, *40*, 102. (d) S. Protti, M. Fagnoni, *Photochem. Photobiol. Sci*. **2009**, *8*, 1499.
24. (a) A. Gilbert, P. Heath, *Tetrahedron Lett.* **1987**, *28*, 5909. (b) C. Schiel, M. Oelgemöller, J. Ortner, J. Mattay, *Green Chemistry* **2001**, *3*, 224. (c) M. Oelgemöller,

N. Healy, L. de Oliveira, C. Jung, J. Mattay, *Green Chem*. **2006**, *8*, 831. (d) J. Du, T.P. Yoon, *J. Am. Chem. Soc.* **2009**, *131*, 14604. (e) M. A. Ischay, Z. Lu, T. P. Yoon, *J. Am. Chem. Soc* .**2010**, *132*, 8572. (f) J. Benites, D. Rios, P. Díaz, J.A. Valderrama, *Tetrahedron Lett*. **2011**, *52*, 609. (g) T. Wu, L.-H. Weng, G.-X. Jin, *Chem. Commun*. **2012**, *48*, 4435. (h) J.W. Tucker, C.R.J. Stephenson, *Org. Lett.* **2011**, *13*, 5468.and references cited therein for light induced recent reactions.

25. (a) A.S. Saiyed, A.V. Bedekar, *Tetrahedron Lett.* **2010**, *51*, 6227. (b) K.N. Patel, A.V. Bedekar, *Tetrahedron Lett.* **2015**, *56*, 6617. (c)A.R. Chaudhary, A.V. Bedekar, *Appl. Organomet. Chem*. **2012**, *26*, 430.(d) A.S. Saiyed, K.N. Patel, B.V. Kamath, A.V. Bedekar, *Tetrahedron Lett.* **2012**, *53*, 4692. (e) K.N. Patel, B.V. Kamath, A.V. Bedekar, *Tetrahedron Lett.* **2013**, *54*, 80.
26. (a) J.K. Kim, Y.H. Kim, H.T. Nam, B.T. Kim, J.-N. Heo, *Org. Lett.* **2008**, *10*, 3543. (b) R. Kumar, Richa, N. H. Andhare, A. Shard, A. K. Sinha, *Chem. Eur. J.* **2013**, *19*, 14798.
27. (a) C. Wang, A.S. Batsanov, M.R. Bryce, *J. Org. Chem*. **2006**, *71*, 108. (c) C. Coya, A. de Andrés, C. Zaldo, A.L. Álvarez, B. Arredondo, R. Gómez, J.L. Segura, C. Seoane, *J. Appl. Phys.* **2009**, *105*, 044510. (d) A. Ajayaghosh, V.K. Praveen, *Acc. Chem. Res*. **2007**, *40*, 644.
28. L. Bai, J.-X. Wang, *Adv. Synth. Catal*. **2008**, *350*, 315.
29. H. Zhao, G. Zheng, W. hao, M. Cai, *Appl. Organometal. Chem*. **2010**, *24*, 92
30. P. Das, D. Sharma, A.K. Shil, A. Kumari, *Tetrahedron Lett*. **2011**, *52*, 1176.
31. Zhang, Guolin, *J. Chem. Res.* **2004**, *9*, 593-595.
32. V. Percec, G.M. Golding, J. Smidrkal, O. Weichold, *J. Org. Chem.* **2004**, *69*, 3447.
33. M.-H. Hsu, C.-M. Hsu, J.-C. Wang, C.-H. Sun, *Tetrahedron* **2008**, *64*, 4268.
34. .A. Cade, A. Pilbeam, *Tetrahedron Lett.* **1964**, *20*, 519.
35. M.-T. Kao, J.-H. Chen, Y.Y. Chu, K.-P. Tseng, C.-H. Hsu, K.-T. Wong, C.-W. Chang, C.-P. Hsu, Y.H. Liu, *Org. Lett.* **2011**, *13*, 1714.
36. X.-H. Fan, L.-M. Yang, *Eur. J. Org. Chem.* **2010**, *13*, 2457.
37. K.-S Lee,J.-P. Kim, J.-S. Lee, *Polymer* **2010**, *51*, 632.
38. S.-K.Cho, H.-K.Kim, H.-s. Yim, M.-R. Kim, J.-K. Lee, J.-J. Kim, Y.-J. Yoon, *Tetrahedron* **2007**, *63*, 1345.
39. E. Yagodkin, C. J. Douglas, *Tetrahedron Letters* **2010**, *51*, 3037.
40. S.C. To, F.Y. Kwong, *Chem. Commun*. **2011**, *47*, 5079.

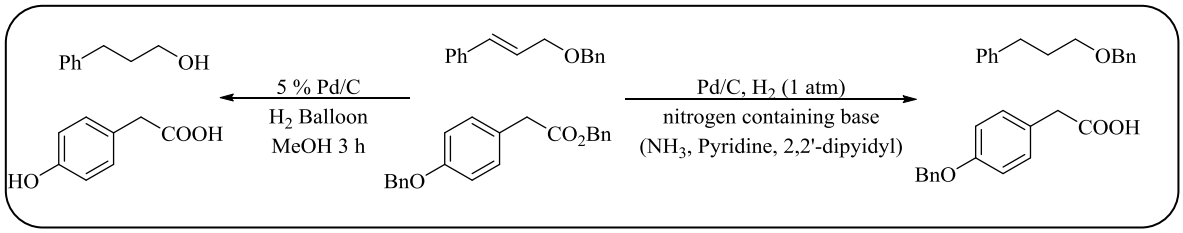
41. E.D. Bergmann, Sh. Blumberg, P. Bracha, Sh.Epstein, *Tetrahedron* **1964**, *20*, 195.
42. P. Rajakumar, K. Ganesan, *Synth. Commun.* **2004**, *34*, 2009.
43. O.Grossman, C. Azerraf, D.Gelman, *Organometallics* **2006**, *25*, 375.
44. N. S. Kozlov ; Z. A. Abramova, Z. A., *Obshchei Khimii*. 1961, **31**, 2236.
45. T. M. Al-Nakibl, N. J. Miller, S. Rashid, M. Meegan, *Drug and Chemical Toxicology* 1990, **13**, 195.
46. G.Thirunarayanan; G. Vanangamudi, *E-Journal of Chemistry* 2007, **4**, 90.
47. L. C.C. Vieira, M. W. Paixão, A. G. Corrêa, *Tetrahedron Lett.* 2012, **53**, 2715.

Section-II

Application of Celite-PANI-Pd for chemoselective hydrogenation reactions

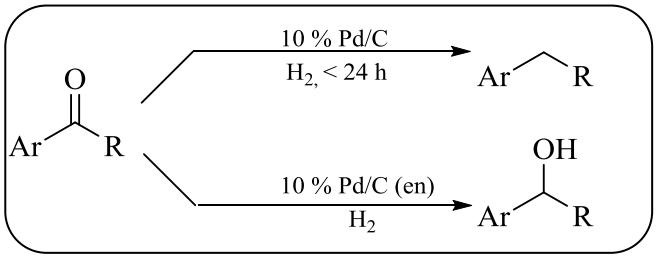
3.2.1 Introduction

Catalytic hydrogenation of specific functionalities within molecule using heterogeneous catalyst is one of the most important topics in organic chemistry even at industrial level.[1] The commonly used heterogeneous catalyst is Pd on charcoal (Pd/C) due to its high catalytic activity, cost efficiency, high stability and good recyclability as it is convenient to recover.[2] But due to its high catalytic activity, chemoselective hydrogenation was not achieved. To get chemoselectivity by toning down the reactivity of the catalysts, researches have added suitable catalyst poisons such as sulphur or nitrogen containing compounds which have the ability to coordinate with palladium species[3], few examples include Lindlar catalyst Pd/$CaCO_3$(or $BaSO_4$) poisoned by $Pb(OAc)_2$ and quinoline is widely used catalyst for partial hydrogenation of alkyne to alkene[4] ,catalyst poisons such as NH_3, pyridine, or 2,2'-dipyridyl[5] were reported to give chemoselective hydrogenation of olefin or benzyl ester without deprotection of the *O*-benzyl and other protecting groups.



Scheme 1: Chemoselective hydrogenation of olefin or benzyl ester by adding catalyst poison

Hittori *et al* developed carbon-supported Pd-ethylenediamine complex [Pd/C(en)] which possess less catalytic activity than commercially available Pd/C as it coordinates with polyethylene diamine and hence acts as catalyst poision.[6] Chemoselective hydrogenation of aromatic aldehydes/ketones to benzyl alcohol using 10 % Pd/C (en), while Pd/C-catalyzed hydrogenation removed the carbonyl oxygen from the aromatic ketone derivatives.



Scheme 2: Chemoselective hydrogenation by Pd/C(en)

Sulphur containing catalyst poison such as thiophene or butylmercaptan selectively reduce olefin in the presence of *O*-benzyl functionality[7] while Pd/C-Ph_2S (Diphenyl sulphide) catalyzed chemoselective hydrogenation of olefin and acetylene functionalities without hydrogenolysis of aromatic carbonyls, halogens, benzyl esters and N-Cbz protective groups.[8]

On the other hand, instead of activated carbon as support for palladium, many other heterogenous support were used depending on its special features such as structural functionality, pore volume and surface area. These include hydroxide supports palladium[9], polysiloxane encapsulated Pd nanoclusters[10], Palladium-supported ionic liquid catalyst (Pd-SH-SILC) immobilized on mercaptopropyl silica gel[11], polymer supported Pd-N-heterocyclic carbine[12] , polysilane-supported Pd nanoparticles[13], Pd nanoparticles stabilized by an alkylated polyethyleneimine (PEI)[14], Pd nanoparticles containing mixture of Bu_4NBr and Bu_3N[15] and catalyst supports such as silk fibroin Pd/Fib[16], polyethyleneimine Pd/PEI[17], boron nitride Pd/BN[18] and molecular sieves Pd/MS[19] were reported for chemoselective hydrogenation. All these catalysts facilitate immobilization of Pd metal and heteroatoms contained in that leads to suppression of original hydrogenation catalyst activity based on their coordination abilities to the Pd metal.

3.2.2 Results and discussion

In the present work, we have prepared different catalyst i.e. Celite-PANI-Pd by varying amount of aniline and palladium and scanned for hydrogenation reaction after doing optimization study. We have observed that polyaniline being basic material leads to suppression of the power of original hydrogenation and making the catalyst system milder and hence more selective in hydrogenation reaction.

3.2.2.1 Synthesis of Celite-PANI-Pd

In the present study the polymerization of aniline was done in aqueous solution of hydrochloric acid in the presence of suspension of celite. The particles of celite were found to be coated with a layer of PANI, which was separated by filtration. The solid material was treated in aqueous ammonia, excess of aniline and its oligomers were removed by proper washing with different solvents. The material was vacuum dried till constant weight was observed. For the present work celite (5.0 g) and aniline (5.0 g), being referred as Celite-PANI was prepared with celite (5.0 g) and aniline (three different quantities, 1.0 g, 2.5 g, 5.0 g), being referred as Celite-PANI **(1)**, Celite-PANI **(2)** and Celite-PANI **(3)** respectively.

Table 1: Three catalyst with different aniline quantities

Sr No.	Catalyst Code	Amount of aniline used during Polymerisation	Amount of catalyst obtained after polymerisation
1	Celite-PANI **(1)**	1.0 g	5.35 g
2	Celite-PANI **(2)**	2.5 g	5.62 g
3	Celite-PANI **(3)**	5.0 g	6.05 g

The dry sample of Celite-PANI (1.0 g) of above three catalyst was stirred with $PdCl_2$ (four different quantities, 0.05, 0.10, 0.15, 0.20 g) in acetonitrile for (24 h) and the material was filtered, washed and dried. Thus, the four samples of catalysts were prepared with different loading of palladium. The amount of palladium present in Celite-PANI-Pd-B **(3)** and Celite-PANI-Pd-C **(3)** was estimated by ICP analysis and it was found to be as 0.42 and 0.50 % per gm of catalyst respectively.

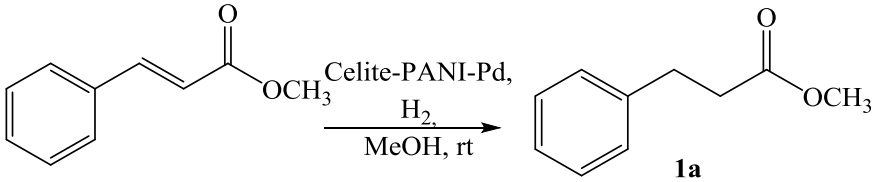
Table 2: Four catalysts prepared with palladium loading

Sr No.	Catalyst Code	Amount of $PdCl_2$ for Celite-PANI (1.0 g)
1	Celite-PANI-Pd **(1)**	0.05
2	Celite-PANI-Pd **(2)**	0.10
3	Celite-PANI-Pd-B **(3)**	0.15
4	Celite-PANI-Pd-C **(3)**	0.20

The other characterization techniques like IR, SEM, EDX, XRD and TGA were used to establish the loading of palladium onto Celite-PANI in our earlier portion.

3.2.2.2 Optimization study for hydrogenation reaction

All the catalysts were systematically screened for hydrogenation reaction of methyl cinnamate using balloon filled with hydrogen gas at atmospheric pressure as shown in scheme 2 by varying the amount of catalyst, and the results are summarized in Table 3.



Scheme 2: Hydrogenation of methyl cinnamate

Table 3: Optimization study varying amount of all 4 catalysts for hydrogenation reaction

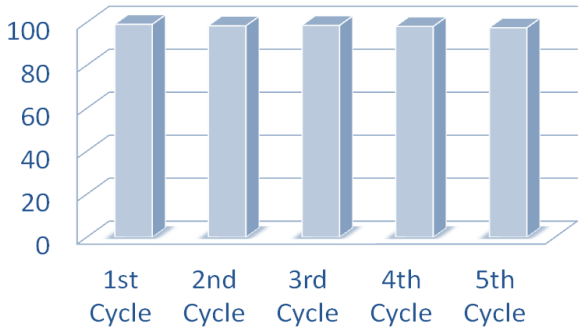
Entry	Catalyst code[a]	Amount of catalyst used	% Yield[b]
1	Celite-PANI-Pd **(1)**	0.05 g	NR
2	Celite-PANI-Pd **(1)**	0.1 g	NR
3	Celite-PANI-Pd **(2)**	0.05 g	55.1 %
4	Celite-PANI-Pd **(2)**	0.1 g	71.6 %
5	Celite-PANI-Pd-B **(3)**	0.05 g	89.1 %
6	**Celite-PANI-Pd-B (3)**	**0.1 g**	**99.4 %**
7	Celite-PANI-Pd-C **(3)**	0.05 g	94.1 %
8	Celite-PANI-Pd-C **(3)**	0.1 g	99.1 %

NR= No Reaction[a]All the reactions were run with methyl cinnamate (0.10 g), reaction time = 5.0 h, [b]Isolated yield.

Recycle Study:

The success of a heterogeneous catalyst is measures by its ability to be recycled and reused for subsequent reactions. This was established by performing a reaction with methyl cinnamate in the presence of Celite-PANI-Pd-B at the standard condition. As can be seen from Table 4, the catalyst could be easy separated by filtration and reused upto five cycles without losing much catalytic activity, fulfilling the primary requirement of a heterogeneous catalyst.

Table 4: Recycle study of Celite-PANI-Pd-B with methyl cinnamate



	% yield of product[b]
1st Cycle	99.1
2nd Cycle	98.4
3rd Cycle	98.6
4th Cycle	98.1
5th Cycle	97.5

reaction time = 5.0 h, [b]Isolated yield.

To monitor the reaction, it was quenched (after 2 h), filtered and the catalyst was dried and analyzed by XPS. It was observed that Pd(II) catalyst was reduced to Pd(0) as Pd $3d_{3/2}$ and $3d_{5/2}$with binding energy 337.78 and 342.88 eV shifted to 335.08 and 340.58 eV as shown in Figure 1. The binding energy values are in accordance with Pd(0) which indicates Pd(0) is the actual catalyst taking part in the reaction.

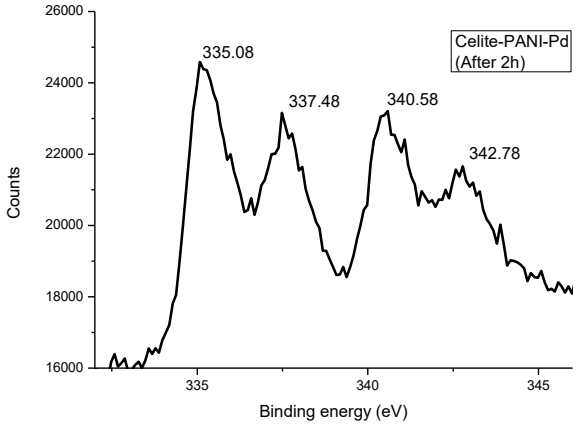


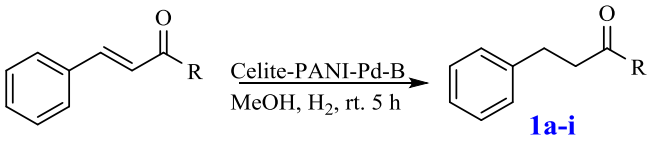
Figure 1: XPS of Celite-PANI-Pd for Pd 3d after 2h reaction.

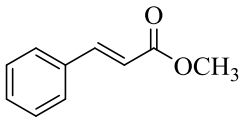
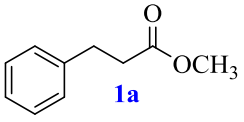
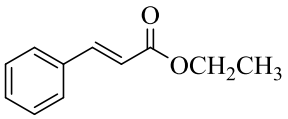
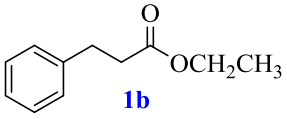
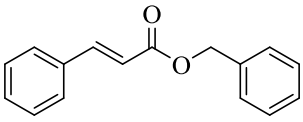
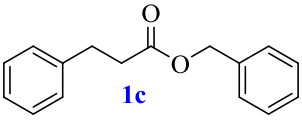
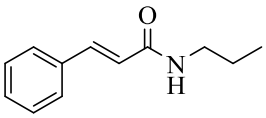
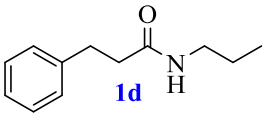
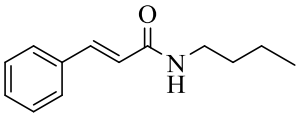
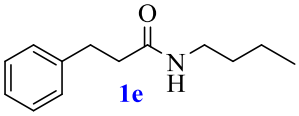
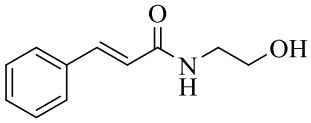
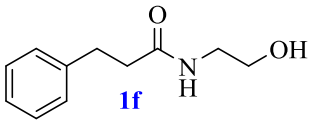
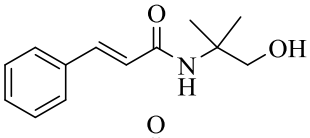
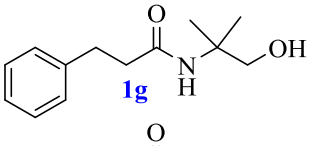
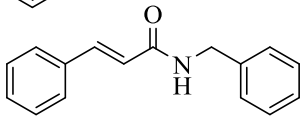
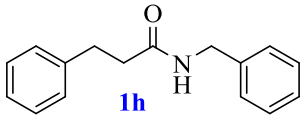
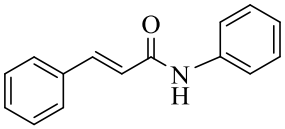
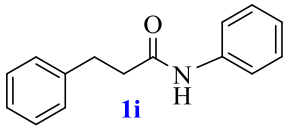
3.2.2.3 Applications of catalyst for chemoselective hydrogenation reaction

The Celite-PANI-Pd-B catalyst system was initially scanned to establish effective catalytic activity for the hydrogenation of olefin in presence ester and amides groups (Table 5). All the reactions were run for 5 h with hydrogen filled in a balloon (atmospheric pressure) using methanol as solvent. The carbon-carbon double undergoes reduction with preference and high selectivity when the reaction is run for a limited time, in all the examples scanned. The suppression of reduction of benzyl group (entry no. 3 and 8) was also successfully

achieved to afford only the olefin-hydrogenated product with excellent yield even when reaction was stirred for 24 h. The product was isolated by column chromatography over silica gel and characterized by ^{1}H NMR. In all the cases the absence of olefin group was easily established by ^{1}H NMR analysis.

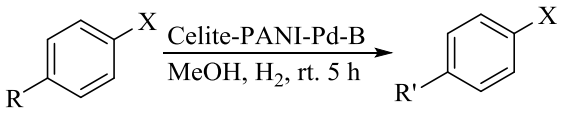
Table 5: Suppression of hydrogenation of benzyl group and selective hydrogenation of olefin in the presence of ester and amide group by using Celite-PANI-Pd-B as catalyst:



Entry	Substrate	Product	Yield(%)[a]
1.		 1a	99 %
2.		 1b	98 %
3.		 1c	99 %[b]
4.		 1d	98 %
5.		 1e	97 %
6.		 1f	96 %
7.		 1g	99 %
8.		 1h	98 %[b]
9.		 1i	99 %

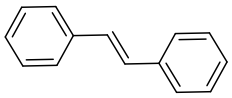
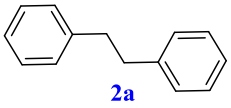
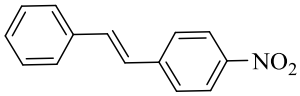
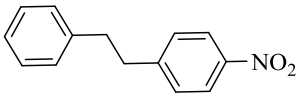
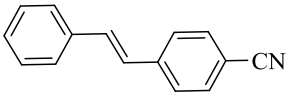
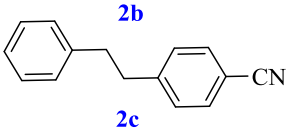
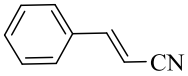
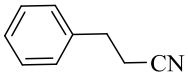
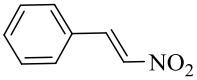
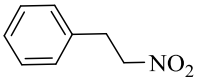
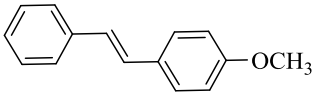
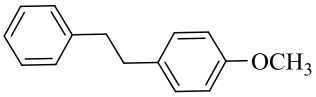
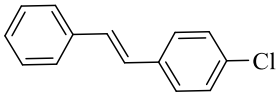
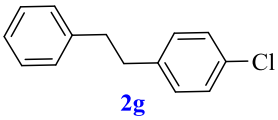
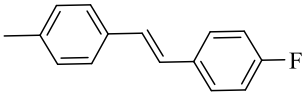
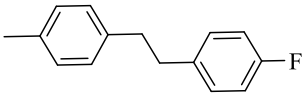
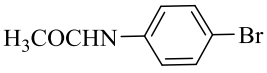
[a] Isolated Yield, [b] Rection was stirred for 24 h.

Table 6: Selective hydrogenation of alkene in presence of nitro, cyano and halides Using Celite-PANI-Pd-B as catalyst.



X= CN, NO_2, Cl, F, Br

2a-h

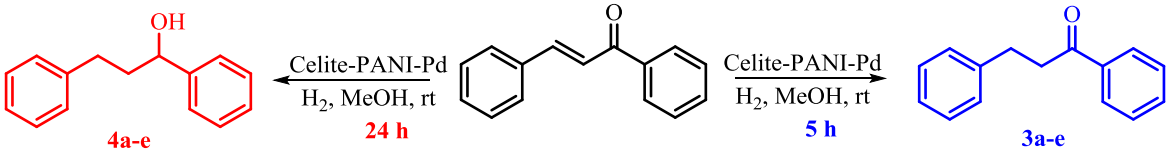
Entry	Substrate	Product	Yield(%)[a]
1.		 **2a**	**99 %**
2.		 **2b**	**98 %[b]**
3.		 **2c**	**99 %[b]**
4.		 **2d**	**97 %**
5.		 **2e**	**96 %**
6.		 **2f**	**98 %**
7.		 **2g**	**99 %**
8.		 **2h**	**97 %**
9.		Recovered	**99 %**

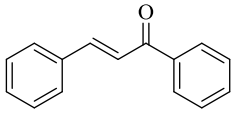
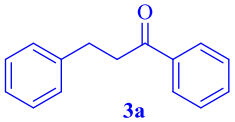
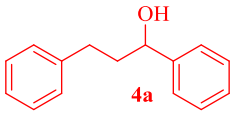
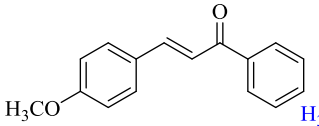
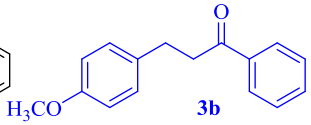
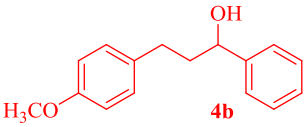
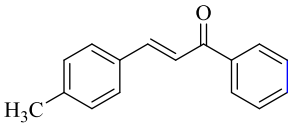
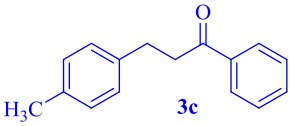
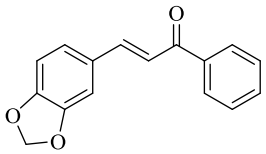
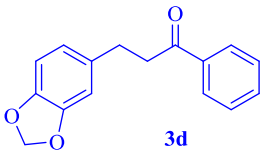
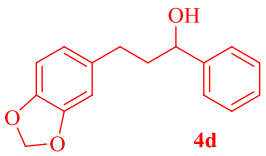
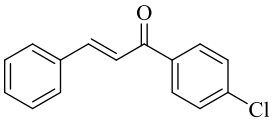
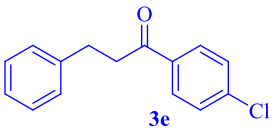
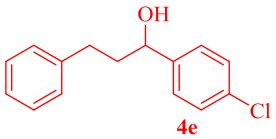
[a] Isolated Yield, [b] Reaction was stirred for 24 h

The selective hydrogenation of olefin in presence of other active π-systems, such as cyano or aromatic halides was examined and the out outcome is as presented in Table 6. Aromatic cyano group and nitro groups are known to be easily reduced under Pd/C catalyzed conditions.[2a] With the present catalyst Celite-PANI-Pd-B, a good selectivity in reduction of

olefin moiety in presence of nitro and cyano groups is seen (entry no. **2-5** in Table 6). Moreover, complete inhibition of hydrogenolysis of aromatic halides were obtained using our catalyst system as shown in entry no. **7-9** of Table 6.

Table 7: Chemoselective hydrogenation of chalcones using Celite-PANI-Pd-B as catalyst.



Entry	Substrate	Product[a]	Product[b]	% Yield[c]
1.		 **3a**	 **4a**	5h **98 %** 24h **92 %**
2.		 **3b**	 **4b**	5h **97 %** 24h **94 %**
3.		 **3c**	 **4c**	5h **97 %** 24h **91 %**
4.		 **3d**	 **4d**	5h **97 %** 24h **95 %**
5.		 **3e**	 **4e**	5h **96 %** 24h **94 %**

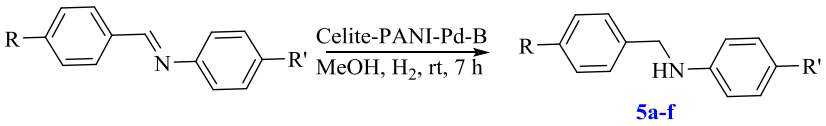
[a] Product isolated after 5h, [b] Product isolated after 24h, [c] Isolated yield

However, chalcone have two reducible functional groups, the carbon-carbon double bond and a carbonyl group. We were interested to explore if the catalysts system developed here can also reduce the latter group. In order to explore this possibility the reaction time was extended for the catalytic hydrogenation procedure and the progress of the reaction was carefully monitored. We observed that on longer hydrogenation reaction using same amount of the catalyst, two different products were obtained. It reduces the double bond in lesser time (5 h) of reaction time, while undergoes further reduction of the carbonyl to alcohol on much longer time (24 h). However, no further reduction i.e. no formation of $PhCH_2CH_2CH_2Ph$ was

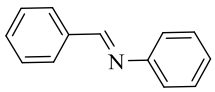
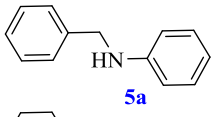
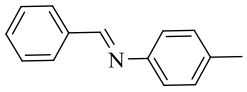
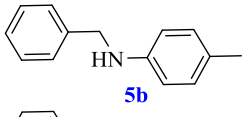
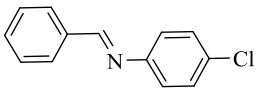
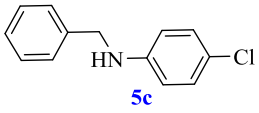
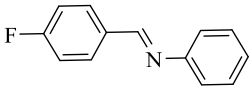
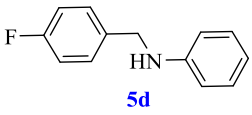
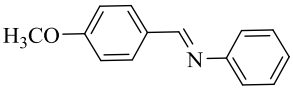
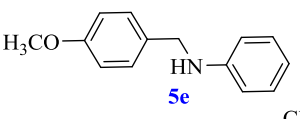
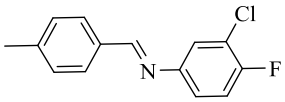
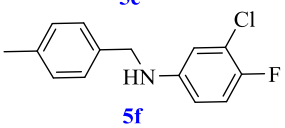
detected in our reaction. Such type of complete hydrogenation of chalcone was observed by Sajiki *et. al.* with much stronger catalyst in H_2/Pd-C system.[8b] This observation indicates that our present catalyst, Celite-PANI-Pd-B is much milder reducing agent as compared to H_2/Pd-C. This type of selective mild reaction was confirmed by several examples shown in Table 7.

The reduction of imines to the corresponding secondary amines is a very useful transformation in organic synthesis since amines constitute important precursors to compounds that are of much interest in pharmaceutical and agriculture industries. The reduction of imines either by borohydride type reagents or by catalytic hydrogenation is still best established method for to produce secondary amines in good yields.[20] So, using our catalyst reduction of imines was also successfully carried out system under H_2 balloon at room temperature.

Table 8: Catalytic hydrogenation of imines using Celite-PANI-Pd-B as catalyst.



5a-f

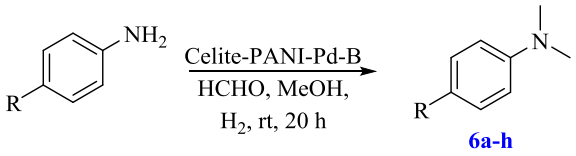
Entry	Substrate	Product	Yield(%)[a]
1.		 5a	86 %
2.		 5b	93 %
3.		 5c	84 %
4.		 5d	81 %
5.		 5e	91 %
6.		 5f	70 %

[a] Isolated yield

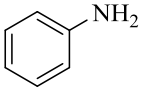
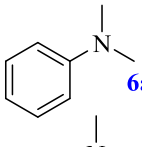
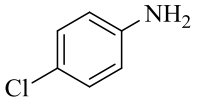
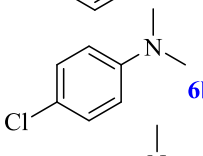
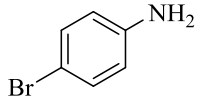
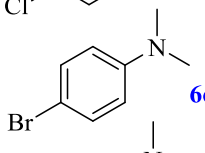
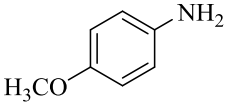
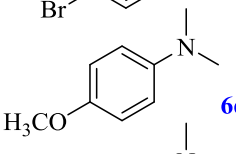
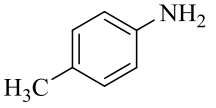
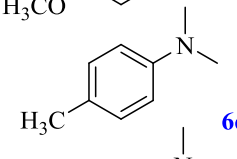
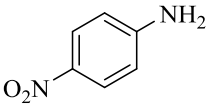
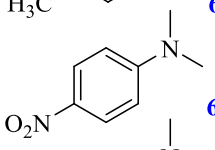
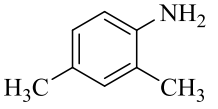
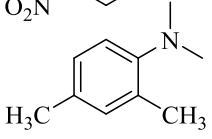
N-methyl amines are considered as important class of compounds, as they are used as intermediate steps in the synthesis of various dyes, surfactants, preservatives, pesticides etc.[21]

Leuckart–Wallach (LW) reaction is condensation of carbonyl with amines to give imines and formic acid is used as a reducing agent.[22] Another attractive protocol is the reductive N-alkylation of amines with aldehydes and ketones catalyzed by the transition metal, such as Pd, Ni, Pt and so on.[23] Moreover, these catalysts can be recovered and reused.[24] The mechanism involves reductive N-alkylation of amines that proceed by addition of aldehydes or ketones with amines, hemiaminal dehydration and imine hydrogenation.[25] Dimethylation of primary amines with aqueous formaldehyde is an efficient and cheap option to access such derivatives. Reductive N-methylation of primary amines using Celite-PANI-Pd-B as the catalyst, formaldehyde as carbon source, was carried out (20 h)in presence of hydrogen filled balloon at ambient conditions. Anilines bearing electron withdrawing groups showed low yield compared to electron releasing groups as shown in Table 9.

Table 9: Reductive N-methylation of primary amines using Celite-PANI-Pd-B as catalyst.



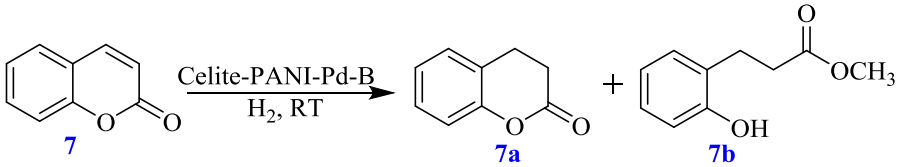
6a-h

Entry	Substrate	Product	% Yield[a]
1.		 6a	74 %
2.		 6b	71 %
3.		 6c	73 %
4.		 6d	86 %
5.		 6e	85 %
6.		 6f	43 %
7.		 6g	56 %

[a] Isolated yield

In the next application we have investigated the reduction of the carbon-carbon π-bond of coumarin. Coumarins are an important class of compounds, in which reduced coumarins i.e. 3,4-dihydrocoumarins are widely distributed in nature and exhibit some interesting biological activities, such as anti-herpetic, anti-inflammatory, anti-oxidative, anti-aging, and anti-cancer activities.[26] Therefore, development of efficient methods for the synthesis of dihydrocoumarins have attracted great interest in recent years.[27] The most conventional method for hydrogenation of coumarin is by using transition metals.[28]

Table 10: Hydrogention study of Coumarin



7 7a 7b

No	Solvent	Time(h)	Catalyst (amount in % w/w)	Yield[a] (%) 7:7a:7b
1	MeOH	7	100	65:4:31
2	MeOH	24	100	35:7:58
3	MeOH	42	100	0:0:100
4	MeOH	7	200	71:6:23
5	EtOAc	12	100	90:10:0
6	THF	20	100	84:16:0
7	THF	40	100	62:38:0
8	THF	80	100	7:93:0
9	THF	80	150	0:100:0

[a]The % yield ratio was determined by ^{1}H NMR

We have reported that the choice of solvent and time, plays an important factor for hydrogenation of coumarin. In former case with MeOH initially we got mixture of products (entry 1 and 2 in Table 10) while after 42 h of reaction we got 100 % product 7b (entry 3), while in latter case with EtOAc and THF no ring opened product was observed (entry 5-8) but after 80 h 100 % product 7a was obtained (entry 9).

3.2.3 Conclusion

The heterogeneous catalyst was prepared by loading palladium metal on Celite-PANI. The Celite-PANI-Pd works effectively for hydrogenation reaction having different functionality and can be reused as it shows good yield till 5th cycle. It showed suppression of reduction of benzyl and different functionalities like nitro, cyano and halides which can get easily reduced with H_2/Pd-C. It is chemoselective towards hydrogenation of chalcones and coumarin. With this result we may conclude that the PANI, being a basic material may act like a kind of catalyst poison and making the catalyst system milder and hence more selective in hydrogenation reaction.

3.2.4 Experimental Section

General procedure for hydrogenation using Celite-PANI-Pd-B as catalyst:(Table 5-8):

The reactions were run with starting material (0.1 g) and Celite-PANI-Pd-B (0.1 g) in methanol under H_2balloon at room temperature at different time intervals as given in tables. Generally, the reactions were monitored by performing thin layer chromatography, catalyst was simply separated by filtration and the products were purified by filter column chromatography over silica gel. The yields mentioned refer to the isolated yield and the products have been characterized by ^{1}H-NMR. The wide range of different substituents indicates the generality of the catalyst system.

General procedure for Reductive N-methylation of primary amines using Celite-PANI-Pd-B as catalyst (Table 9):

The reactions were run with aniline (0.1 g, 1.07 mmol), formaldehyde(0.34 ml, 3.22 mmol) and Celite-PANI-Pd-B(0.1 g) in methanol under H_2balloon at room temperature for 20 h.The catalyst was simply separated by filtration and the products were purified by column chromatography over silica gel. The yields mentioned refer to the isolated yield and the products have been characterized by ^{1}H-NMR.

3-Phenylpropanoate (**1a**)

M.p. 144 ^{o}C [Lit.[29] 142-145^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 3.69 (s, 3H), 2.64-2.68 (t, *J* = 8 Hz, 2H), 2.96-3.0 (t, *J* = 8 Hz), 7.21-7.25 (m, 3H), 7.30-7.33 (m, 2H).

Ethyl 3-phenylpropanoate (**1b**)

M.p. 122 ^{o}C [Lit.[30] 122-124^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$: δ 1.23-1.27 (t, *J* =7.2 Hz, 3H), 2.62-2.66 (t, *J* = 7.6 Hz, 2H), 2.95-2.97(t, *J* = 7.6 Hz, 2H), 4.12-4.17 (q, *J* = 7.2 Hz, 2H), 7.20-7.23 (m, 3H), 7.21-7.33 (m ,2H).

Benzyl 3-phenylpropanoate **(1c)**

Thick liquid at room temperature[31]

^{1}H NMR (400 MHz, $CDCI_3$): 2.70-2.74 (t, *J*=7.6 Hz, 3H), 2.98-3.02 (t, *J*=7.6 Hz, 3H), 5.14(s, 2H), 7.21-7.25 (m, 3H), 7.29-7.39(m, 7H).

3-Phenyl-N-propylpropanamide **(1d)**

M.p. 50^{o}C [Lit.[32] 46-49^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): 0.84-0.88 (t, *J*=7.6 Hz, 3H), 1.43-1.48 (m, 2H), 2.46-2.50 (t, *J* = 7.6 Hz, 2H), 2.96-3.00 (t, *J* = 7.6 Hz, 2H), 3.16-3.21 (m, 2H), 5.44 (br s, 1H), 7.20-7.23 (m, 3H), 7.30-7.32 (m, 2H).

N-butyl-3-phenylpropanamide (**1e**)

Thick liquid at room temperature[33]

^{1}H NMR (400 MHz, $CDCI_3$) : δ 0.88-0.92 (t, *J* = 7.6 Hz, 3H), 1.24-1.29 (m, 2H), 1.37-1.39 (m, 2H), 2.45-2.49 (t, *J*=7.6 Hz, 2H), 2.95-2.99 (t, *J*=7.6 Hz, 2H), 3.18-3.23 (m, 2H), 5.46 (br s, 1H), 7.19-7.22 (m, 3H), 7.27-7.32 (m, 2H).

N-(2-hydroxyethyl)-3-phenylpropanamide (**1f**)

M.p.73 ^{o}C [Lit.[34] 72.5-73.5^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 2.50-2.53 (t, *J*=7.6 Hz, 2H), 2.95-3.03 (t, *J* = 7.6 Hz, 2H), 3.35-3.39 (q, *J* = 5.2 Hz, 2H,), 3.62-3.65 (t, *J* = 5.2 Hz, 2H), 7.21-7.24 (m, 3H), 7.28-7.33 (m, 2H).

N-(1-hydroxy-2-methylpropan-2-yl)-3-phenylpropanamide (**1g**)

M.p.93-95^{o}C [Lit.[35]95-97^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 1.12 (s, 6H), 2.44-2.45 (t, *J* = 7.6 Hz, 2H), 2.94-2.98(t, *J* = 7.6 Hz, 2H), 4.87(br s, 1H), 5.45(br s, 1H), 7.20-7.25(m, 3H), 7.28-7.33(m, 2H).

N-benzyl-3-phenylpropanamide (**1h**)

M.p. 85 ^{o}C [Lit.[36] 84.5-86.5^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$) : δ 2.51-2.55 (t, *J* = 7.6 Hz, 2H,), 3.02-3.04 (t, *J* = 7.6 Hz,), 4.41-4.42(d, *J* = 6 Hz, 2H), 5.65 (br s, 1H),7.15-7.17 (m, 2H), 7.21-7.25 (m, 3H), 7.28-7.33 (m, 5H).

N-phenyl-3-phenylpropionamide (**1i**)

M.p. 97-98 ^{o}C [Lit.[37] 96^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 2.65-2.68 (t, *J* = 7.6 Hz, 2H), 3.04-3.08 (t, *J* = 7.6 Hz, 2H), 7.09-7.13(m, 1H), 7.23-7.32 (m, 7H), 7.45-7.47 (m, 2H)

1,2-Diphenylethane (**2a**)

M.p. 54 ^{o}C [Lit.[38] 52^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 2.94 (s, 4H), 7.18-7.24 (m, 8H), 7.30-7.35 (m, 4H).

1-Nitro-4-phenethylbenzene (**2b**)

M.p. 55-57 ^{o}C [Lit.[39] 55-56^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 2.95-3.00 (m, 2H), 3.04-3.08 (m, 2H), 7.15-7.17 (m, 2H), 7.21-7.26 (m, 1H), 7.29-7.32 (m, 4H), 8.13-8.16 (m, 2H).

4-Phenethylbenzonitrile (**2c**)

Low melting solid [Lit.[40] 41-42^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 2.93-2.96 (m, 2H), 2.99-3.01 (m, 2H),7.14-7.16 (m, 2H), 7.23-7.32 (m, 6H), 7.56-5.59 (m, 2H).

3-Phenylpropanenitrile (**2d**)

Liquid at rt[41]

^{1}H NMR (400 MHz, $CDCI_3$): δ 2.63-2.76 (t, *J*=7.6 Hz, 2H), 2.97-3.00 (t, *J* = 7.6 Hz, 2H), 7.25-7.32 (m, 3H), 7.35-7.39 (m, 2H).

(2-Nitroethyl)benzene (**2e**)

Liquid at rt[42]

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.33-3.36 (t, *J* = 7.6 Hz, 2H), 4.62-4.66 (t, *J* = 7.6 Hz, 2H), 7.22-7.25 (m, 2H), 7.29-7.32 (m, 1H), 7.33-7.38 (m, 2H).

1-Methoxy-4-phenethylbenzene (**2f**)

M.p. 61-62^{o}C [Lit.[43] 58-60^{o}C]

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.91 (s, 4H), 3.82 (s, 3H), 6.85-6.87 (d, *J*=8.4 Hz, 2H), 7.12-7.14 (d, *J* = 8.4 Hz, 2H), 7.20-7.25 (m, 3H), 7.32-7.33 (m, 2H).

1-Chloro-4-phenethylbenzene (**2g**)

M.p. 51-52^{o}C [Lit.[44] 49^{o}C]

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.92 (s, 4H), 7.11-7.13 (d, *J* = 8.4 Hz, 2H), 7.18-7.20 (d, *J* = 8.4 Hz, 2H), 7.21-7.28 (m, 3H), 7.30-7.33 (m, 3H).

1-Fluoro-4-(4-methylphenethyl)benzene (**2h**)

M.p. 65 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.89 (t, *J* = 5.6 Hz, 4H), 6.96-7.00 (m, 2H), 7.07-7.09 (m, 2H), 7.11-7.16 (m, 4H).

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

M.p. 72-73^{o}C [Lit.[16b] 74-75^{o}C]

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.08-3.12 (t, *J* = 8 Hz, 2H), 3.20-3.35 (t, *J* = 8 Hz, 2H), 7.22-7.35 (m, 4H), 7.46-7.50 (m, 2H), 7.57-7.60 (m, 2H), 7.98-8.00 (m, 2H).

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

M.p. 66^{o}C [Lit.[16b] 64-65^{o}C]

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.02-3.05 (t, *J* = 8 Hz, 2H), 3.28-3.31 (t, *J* = 8 Hz, 2H), 6.85-6.88 (dd, *J1* = 6.8 Hz, *J2* = 2 Hz, 2H), 7.19-7.21 (d, *J* = 8.8Hz, 2H), 7.46-7.49 (m, 2H), 7.56-7.60 (m, 1H), 7.97-7.99 (m, 2H).

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

Low melting solid [Lit.[45] 37-38^{o}C]

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.04-3.07 (t, *J* = 8 Hz ,2H), 3.29-3.33 (t, *J* = 8 Hz ,2H), 7.13-7.19 (m, 4H), 7.46-7.49 (m, 2H), 7.56-7.58 (m, 1H), 7.97-7.99 (m, 2H).

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

M.p. 88-89^{o}C [Lit.[46] 87-88^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 2.99-3.03 (m, 2H), 3.26-3.30 (m, 2H), 5.94 (s, 2H), 6.71-6.77 (m, 3H), 7.46-7.50 (m, 2H), 7.56-7.60 (m, 1H), 7.96-7.99 (m, 2H)

1-(4-Chlorophenyl)-3-phenylpropan-1-one (**3e**)

M.p. 80^{o}C [Lit.[16b]78-80^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 3.06-3.10 (t, *J* = 8 Hz ,2H), 3.28-3.32 (m, 2H), 7.22-7.28 (m, 3H), 7.31-7.34 (m, 2H), 7.44-7.46 (m, 2H), 7.90-7.93 (dd, *J1* = 6.4 Hz, *J2* = 2 Hz, 2H).

1,3-Diphenylpropan-1-ol (**4a**)

Colourless oil[47]

^{1}H NMR (400 MHz, $CDCI_3$): δ 1.94 (br s,1H), 2.04-2.17 (m, 2H), 2.67-2.78 (m, 2H), 4.70-4.73 (m, 1H), 7.19-7.29 (m, 2H), 7.30-7.32 (m, 4H), 7.33-7.38 (m, 4H).

3-(4-Methoxyphenyl)-1-phenylpropan-1-ol (**4b**)

M.p. 62-63^{o}C [Lit.[47] 65^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 1.90 (br s, 1H), 1.91-2.14 (m, 2H), 2.60-2.72 (m, 2H), 4.68-4.72 (m, 1H), 6.83-6.87 (m, 2H), 7.12-7.38 (m, 7H).

1-Phenyl-3-(p-tolyl)propan-1-ol (**4c**)

M.p. 55-56^{o}C [Lit.[47] 54-56^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 2.02-2.16 (m, 2H), 2.38 (s, 3H), 2.65-2.74 (m, 2H), 4.69-4.73(q, 1H), 7.12-7.28 (m, 4H), 7.31-7.33 (m, 1H), 7.38-7.39 (m, 4H).

3-(Benzo[d][1,3]dioxol-5-yl)-1-phenylpropan-1-ol (**4d**)

M.p. 90-93^{o}C [Lit.[48] 93-94^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 1.61 (br s, 1H), 1.61-2.15 (m, 2H), 2.58-2.73 (m, 2H), 4.68-4.71 (dd, *J1* = 7.6 Hz, *J2* = 5.6 Hz, 1H), 5.94 (s, 2H), 6.65-6.76 (m, 3H), 7.29-7.40 (m, 5H).

1-(4-Chlorophenyl)-3-phenylpropan-1-ol (**4e**)

Low melting solid [Lit.[47] 42^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 1.95-2.15 (m, 3H), 2.74-2.74 (m, 2H), 4.67-4.70 (dd, *J1* = 8 Hz, *J2* = 5.2 Hz, 1H), 7.13-7.41 (m, 9H).

N-benzylaniline (**5a**)

Low melting solid [Lit.[49] 36-37^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 4.36 (s, 2H), 6.65-6.69 (m, 2H), 6.73-6.77 (m, 1H), 7.19-7.23 (m, 2H), 7.29-7.36 (m, 1H), 7.37-7.42 (m, 4H).

N-benzyl-4-methylaniline (**5b**)

M.p. 57-58^{o}C [Lit.[50] 59-60^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 2.38 (s, 3H), 4.02 (br s, 1H), 4.31 (s, 2H), 6.66-6.68 (d, *J* = 7.6 Hz, 2H), 6.73-6.76 (t, *J* = 7.6 Hz, 1H), 7.15-7.23 (m, 4H), 7.28-7.31 (m, 2H).

N-benzyl-4-chloroaniline (**5c**)

Thick oil [Lit.[50]]

^{1}H NMR (400 MHz, $CDCI_3$): δ 4.12 (br s, 1H), 4.33 (s, 2H), 6.55-6.59 (m, 2H), 7.11-7.15 (m, 2H), 7.28-7.38 (m, 5H).

N-(4-fluorobenzyl)aniline (**5d**)

M.p. 100-101^{o}C [Lit.[6a] 102^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 4.05 (br s, 1H), 4.32 (s, 2H), 6.63-6.66 (m, 2H), 6.73-6.77 (m, 1H), 7.03-7.08 (m, 2H), 7.17-7.23 (m,2H), 7.34-7.37 (m, 2H).

N-(4-methoxybenzyl)aniline (**5e**)

M.p. 47-48^{o}C [Lit.[49] 45-46^{o}C]

^{1}H NMR (400 MHz, $CDCI_3$): δ 3.92 (s, 3H), 4.01 (br s), 4.49 (s, 2H), 6.66-6.68 (m, 2H), 6.74-6.76 (m, 1H), 6.90-6.92 (m, 2H),7.19-7.23 (m, 2H), 7.31-7.33 (m, 2H).

3-chloro-4-fluoro-N-(4-methylbenzyl)aniline (**5f**)

^{1}H NMR (400 MHz, $CDCI_3$): δ 2.37 (s, 3H), 6.45-6.47 (m, 1H), 6.63-6.65 (m, 1H), 6.93-6.97 (t, *J* = 8.8 Hz, 1H), 7.17-7.19 (d, *J*=8 Hz, 2H), 7.24-7.26(d, *J* = 8 Hz, 2H).

N,N-dimethylaniline (**6a**)

B.p. 193^{o}C [Lit.[51] 193^{o}C]

^{1}H NMR(400 MHz, $CDCI_3$): δ 2.98 (s, 6H), 6.74-6.80 (m, 3H), 7.27-7.31 (m, 2H).

4-Chloro-N,N-dimethylaniline (**6b**)

Low melting solid [Lit.[52] 35-37^{o}C]

^{1}H NMR(400 MHz, $CDCI_3$): δ 2.92 (s, 6H), 6.74-6.80 (m, 2H), 7.17-7.20 (m, 2H).

4-Bromo-N,N-dimethylaniline (**6c**)

M.p. 56^{o}C [Lit.[53] 53-55^{o}C]

^{1}H NMR(400 MHz, $CDCI_3$): δ 2.93 (s, 6H), 6.74-6.80 (dd, *J1* = 6.8 Hz, *J2* = 2Hz, 2H), 7.07-7.08 (dd, *J1* = 6.8 Hz, *J2* = 2Hz, 2H).

4-Methoxy-N,N-dimethylaniline (**6d**)

M.p. 46^{o}C [Lit.[54] 46-48^{o}C]

^{1}H NMR(400 MHz, $CDCI_3$): δ 2.89 (s, 6H), 3.79 (s, 3H), 6.77-6.81 (m, 2H), 6.85-6.89 (m, 2H).

N,N, 4-trimethylaniline (**6e**)

B.p. 200^{o}C[Lit.[55] 204-206^{o}C]

^{1}H NMR(400 MHz, $CDCI_3$): δ 2.28 (s, 3H), 2.84 (s, 6H), 6.71-6.73 (d, *J* = 8.4 Hz, 2H), 7.07-7.10 (d, *J* = 8.4 Hz, 2H).

N,N-dimethyl-4-nitroaniline (**6f**)

M.p. 165-167^{o}C [Lit.[56] 164-166^{o}C]

^{1}H NMR(400 MHz, $CDCI_3$): δ 3.14 (s, 6H), 6.60-6.64 (dd, *J1* = 9.6 Hz, *J2* = 3.6 Hz, 2H), 8.13-8.16(dd, *J1* = 9.6 Hz, *J2* = 3.6 Hz, 2H).

N,N, 2,4-tetramethylaniline (**6g**)

Pale yellow liquid [Lit.[54]]

^{1}H NMR(400 MHz, $CDCI_3$): δ 2.29 (s, 3H), 2.32 (s, 3H), 2.69 (s, 6H), 6.98-7.01 (m, 3H).

chroman-2-one (**7a**)

Low melting solid [Lit.[27d] 23-26°C]

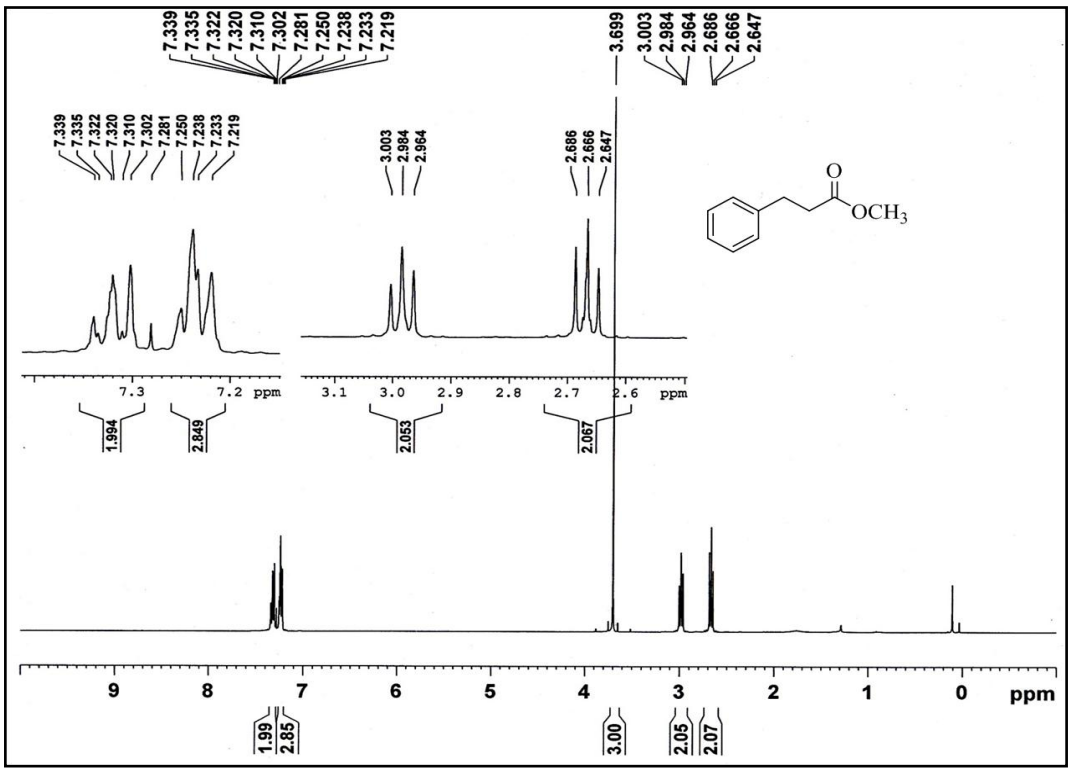
^{1}H NMR(400 MHz, $CDCI_3$): δ 2.79-2.83 (m, 2H), 3.01-3.04 (m, 2H), 7.06-7.14 (m, 2H), 7.21-7.29 (m, 2H)

Methyl 3-(2-hydroxyphenyl)propanoate (**7b**)

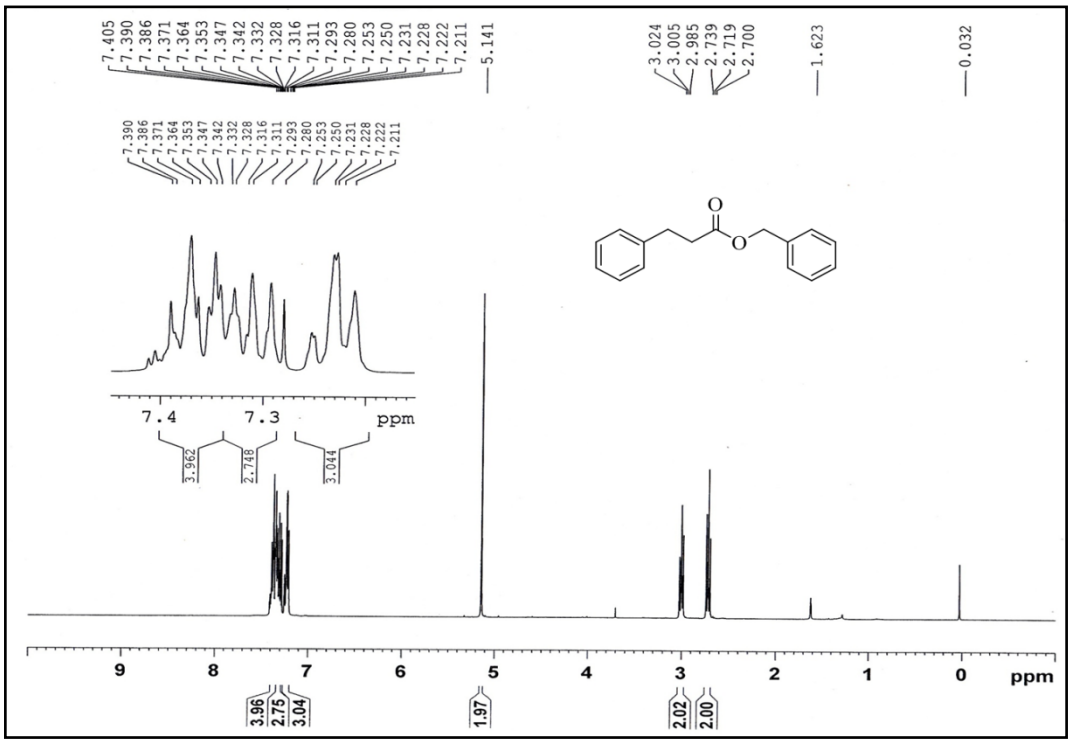
Low melting solid [Lit.[57] 41.5°C]

^{1}H NMR(400 MHz, $CDCI_3$): δ 2.73-2.76 (t, *J*=6.8 Hz, 2H), 2.91-2.95 (t, *J*=6.8 Hz, 2H), 6.87-6.91 (m, 2H), 7.10-7.16 (m, 2H), 7.19 (br s, 1H).

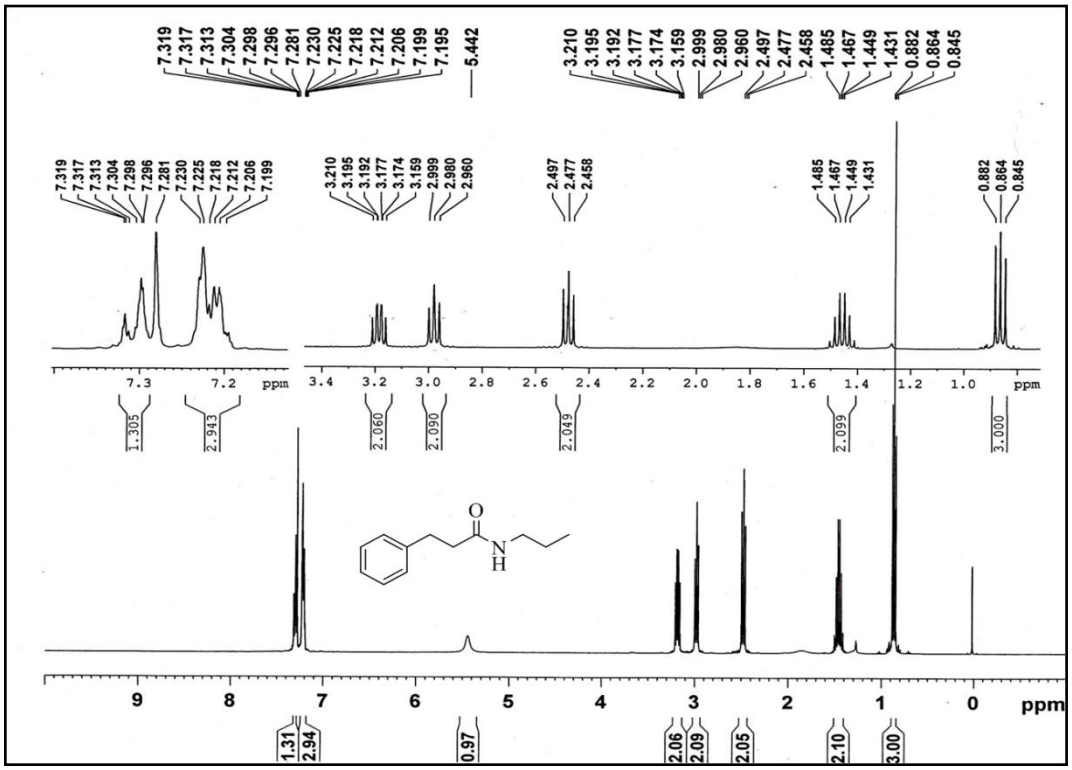
Spectral Data:



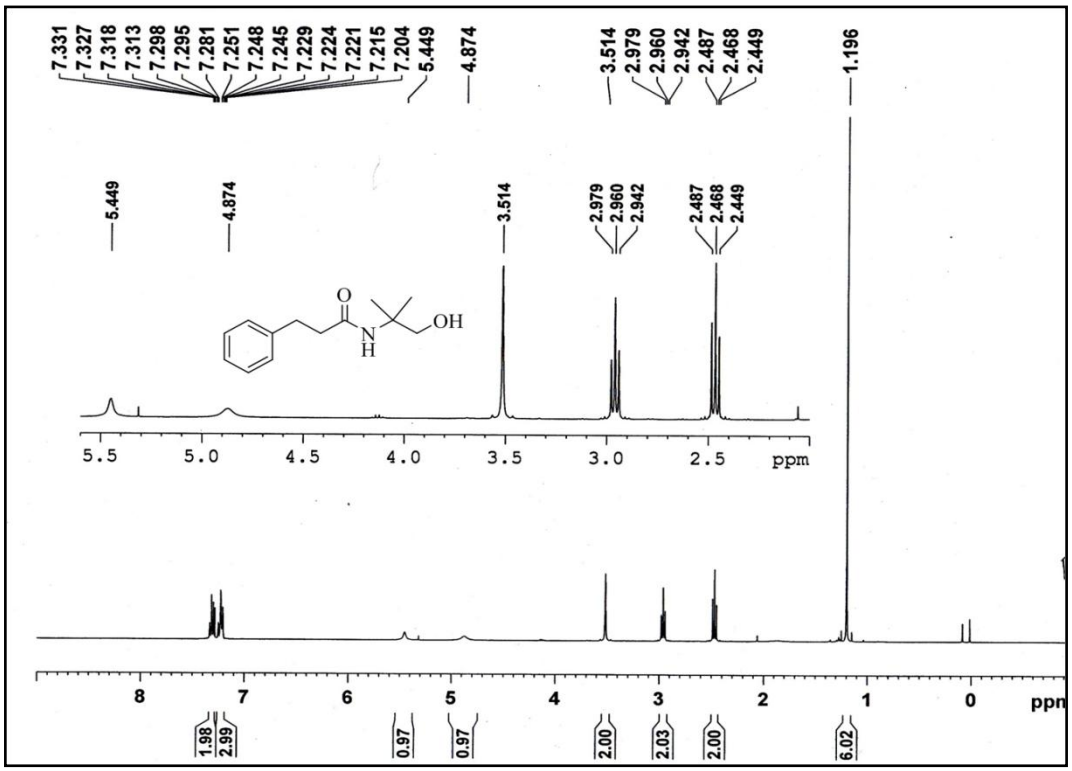
^{1}H-NMR of Compound **1a**



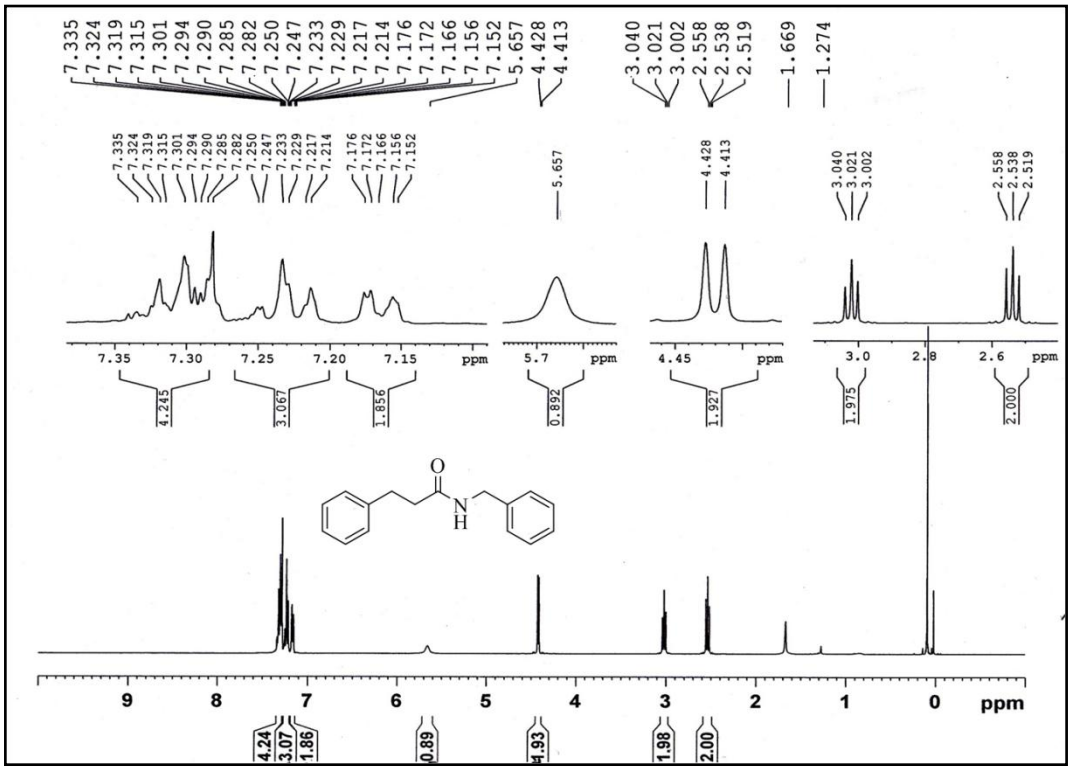
^{1}H-NMR of Compound **1c**



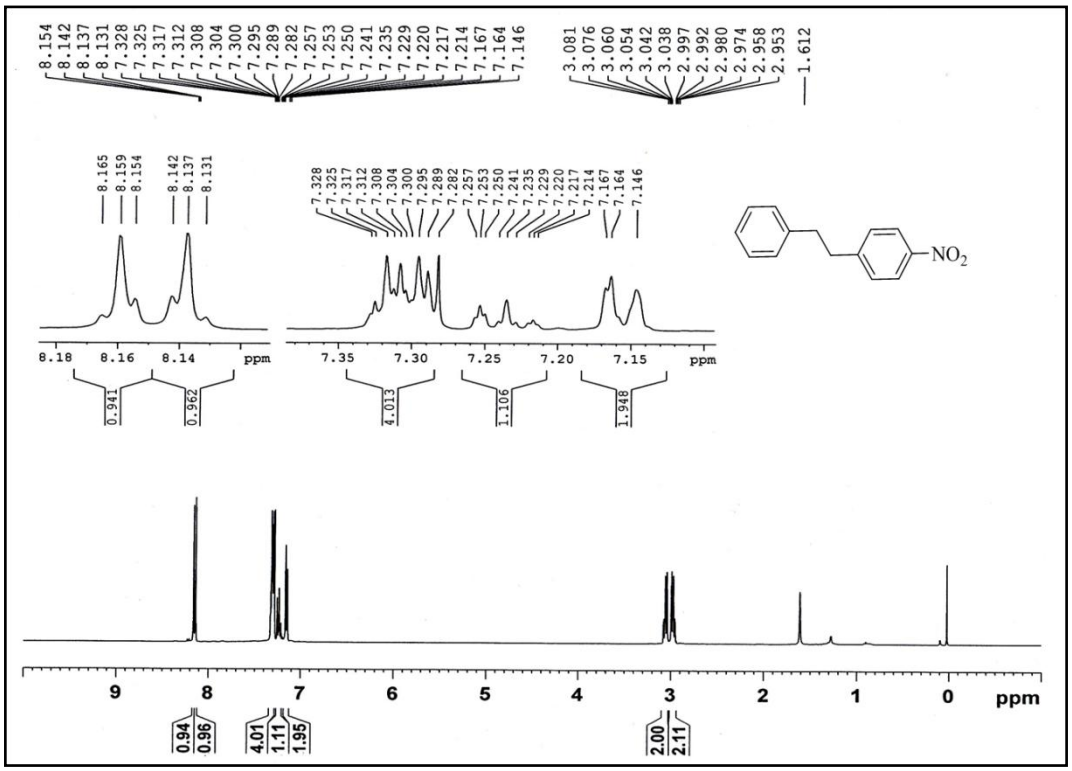
^{1}H-NMR of Compound **1d**



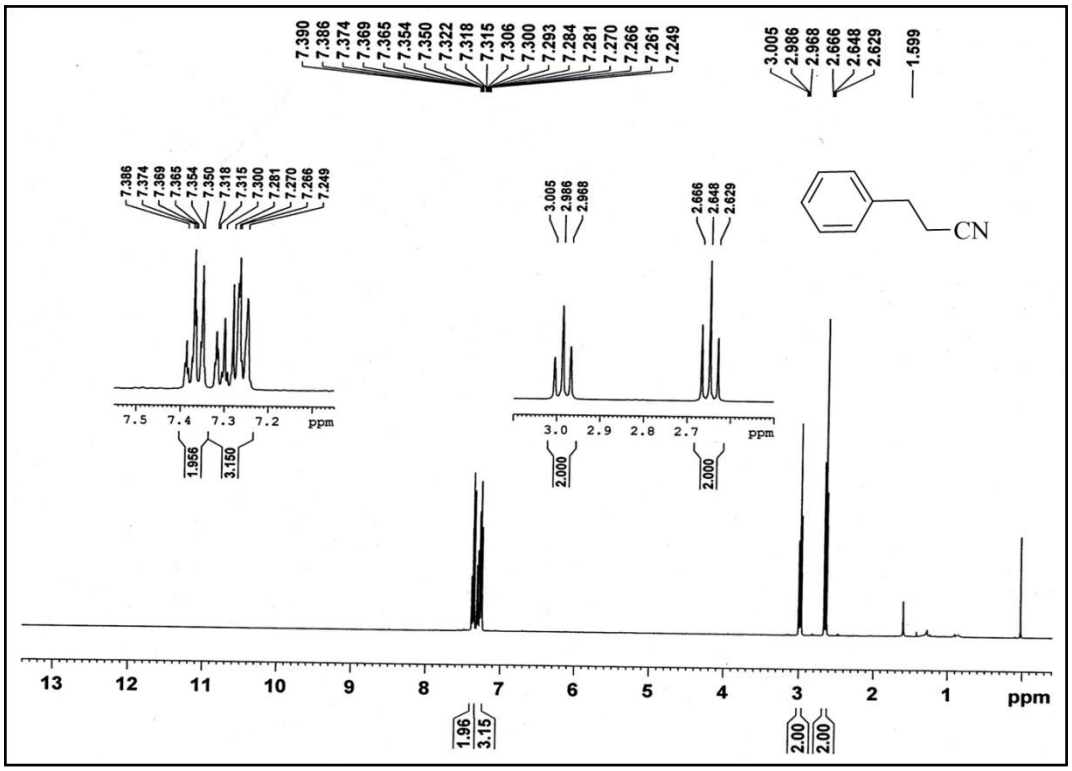
^{1}H-NMR of Compound **1g**



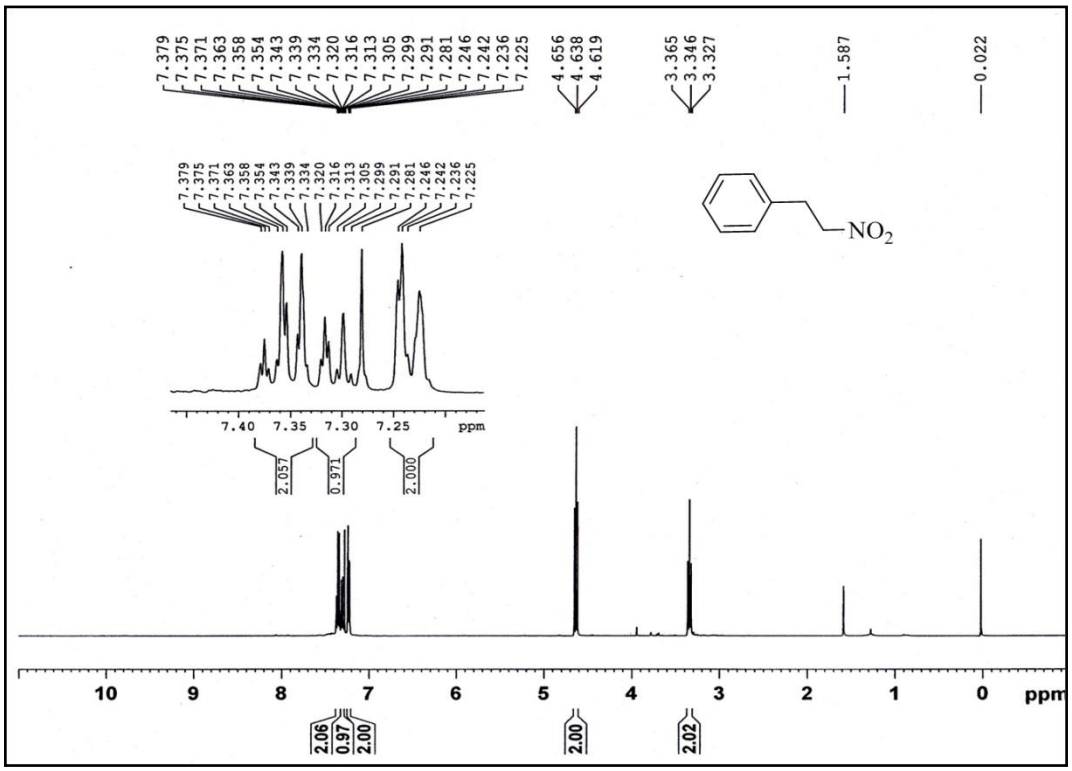
^{1}H-NMR of Compound **1h**



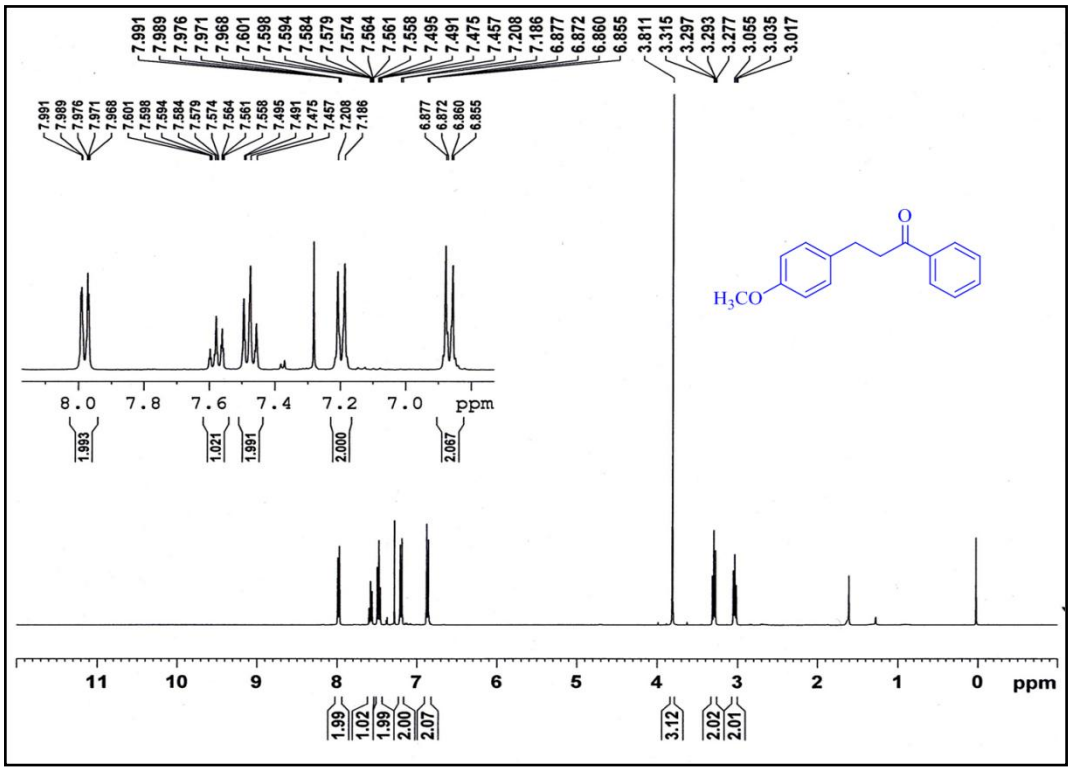
^{1}H-NMR of Compound **2b**



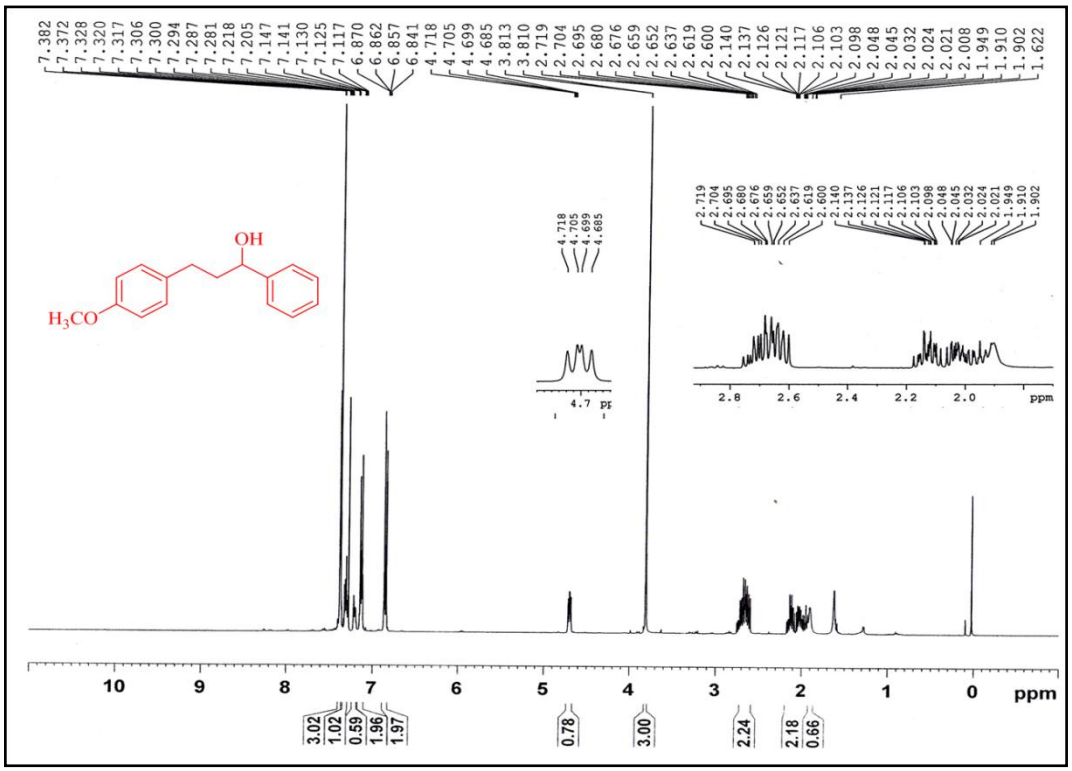
^{1}H-NMR of Compound **2d**



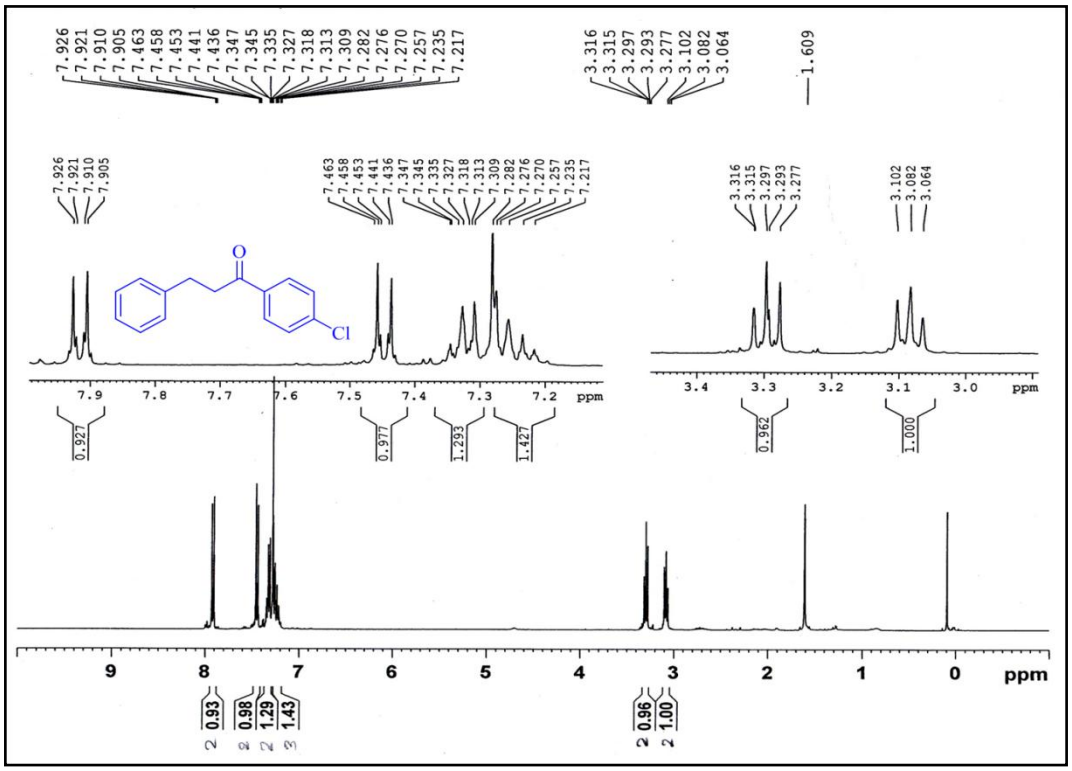
^{1}H-NMR of Compound **2e**



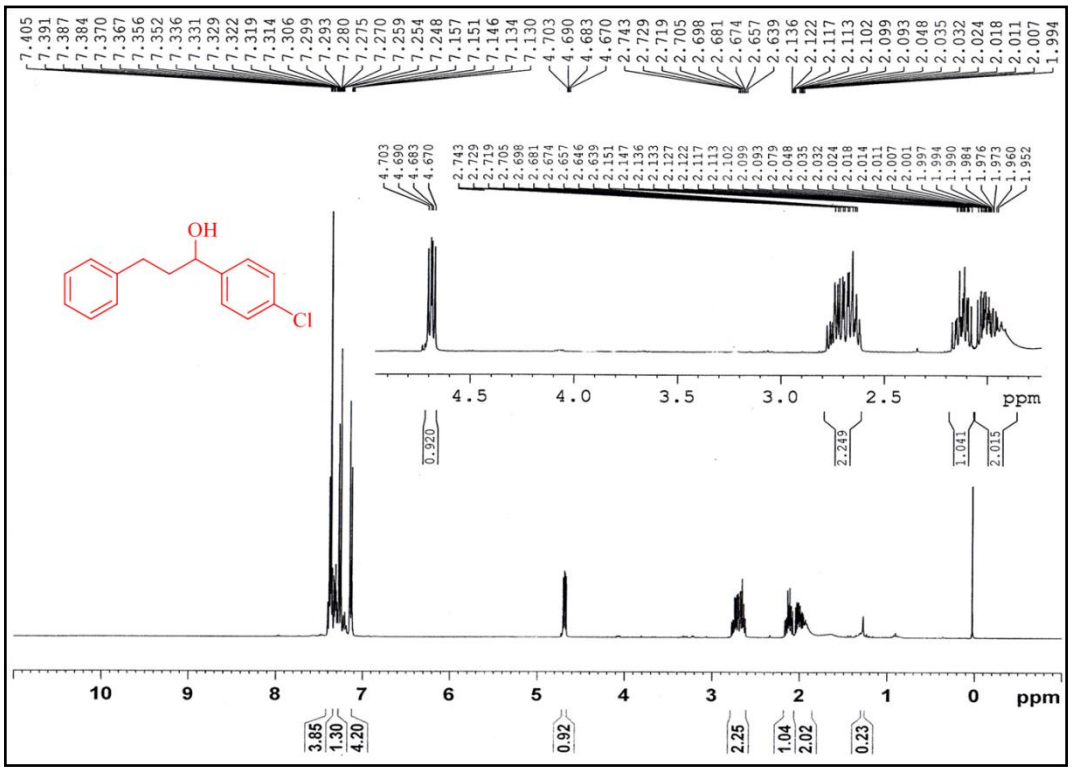
^{1}H-NMR of Compound **3b**



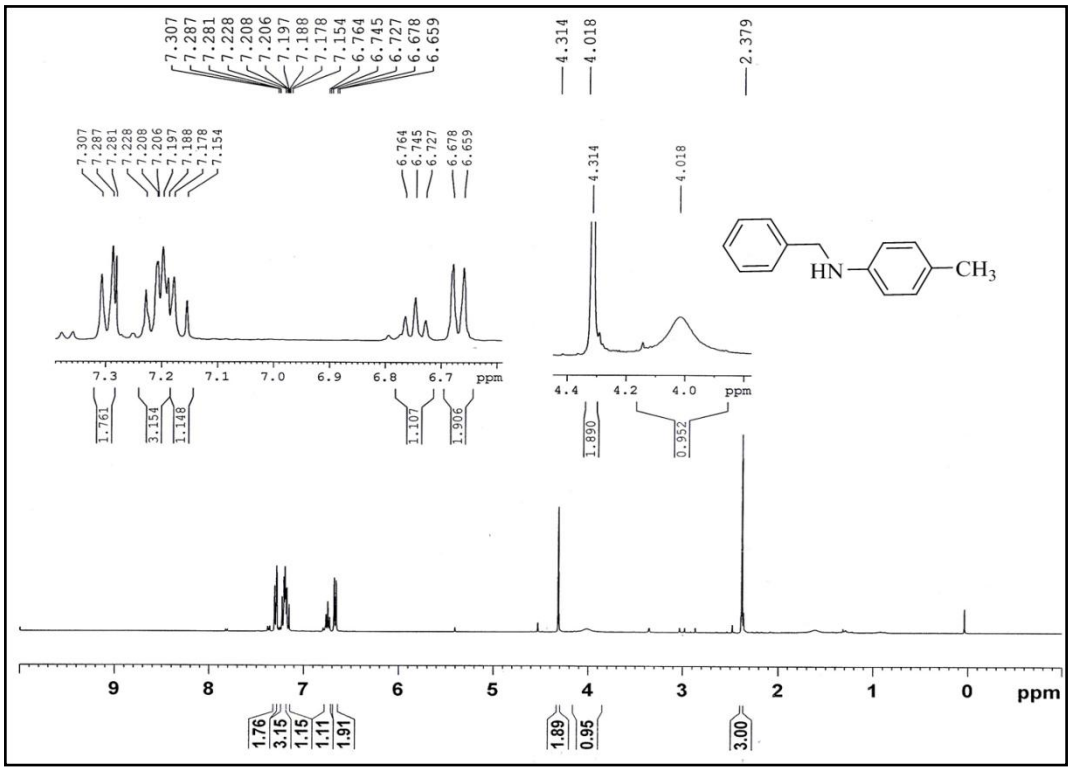
^{1}H-NMR of Compound **4b**



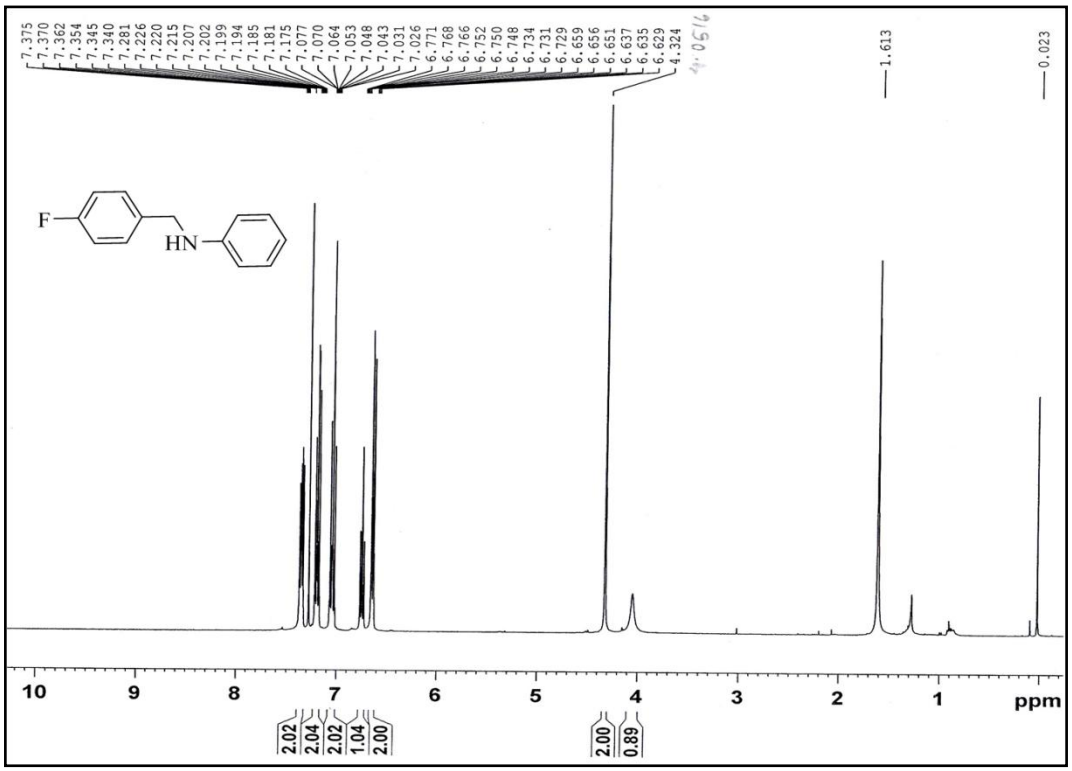
^{1}H-NMR of Compound **3e**



^{1}H-NMR of Compound **4e**

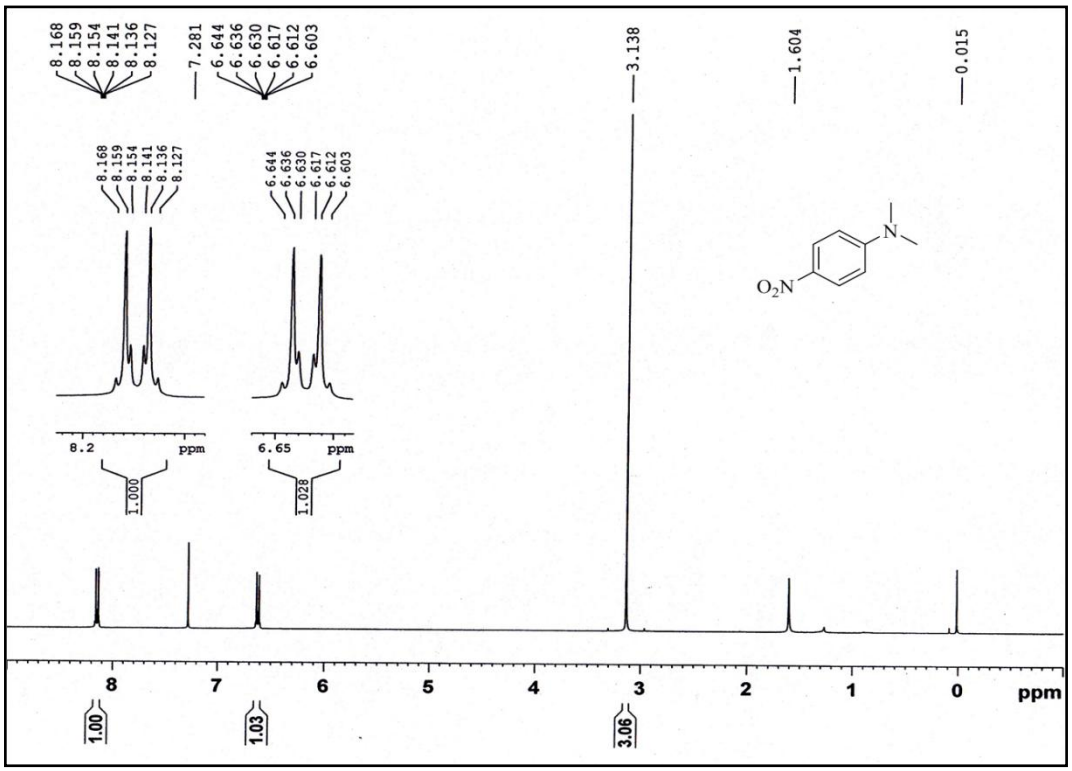


^{1}H-NMR of Compound **5b**

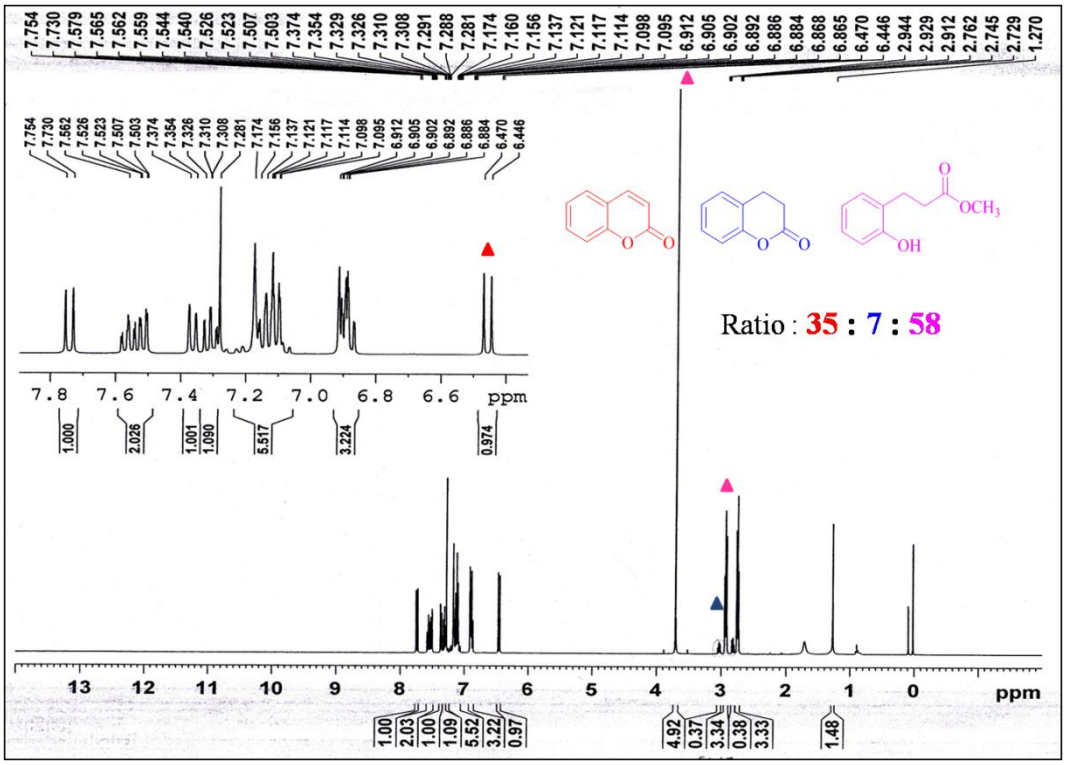


^{1}H-NMR of Compound **5d**

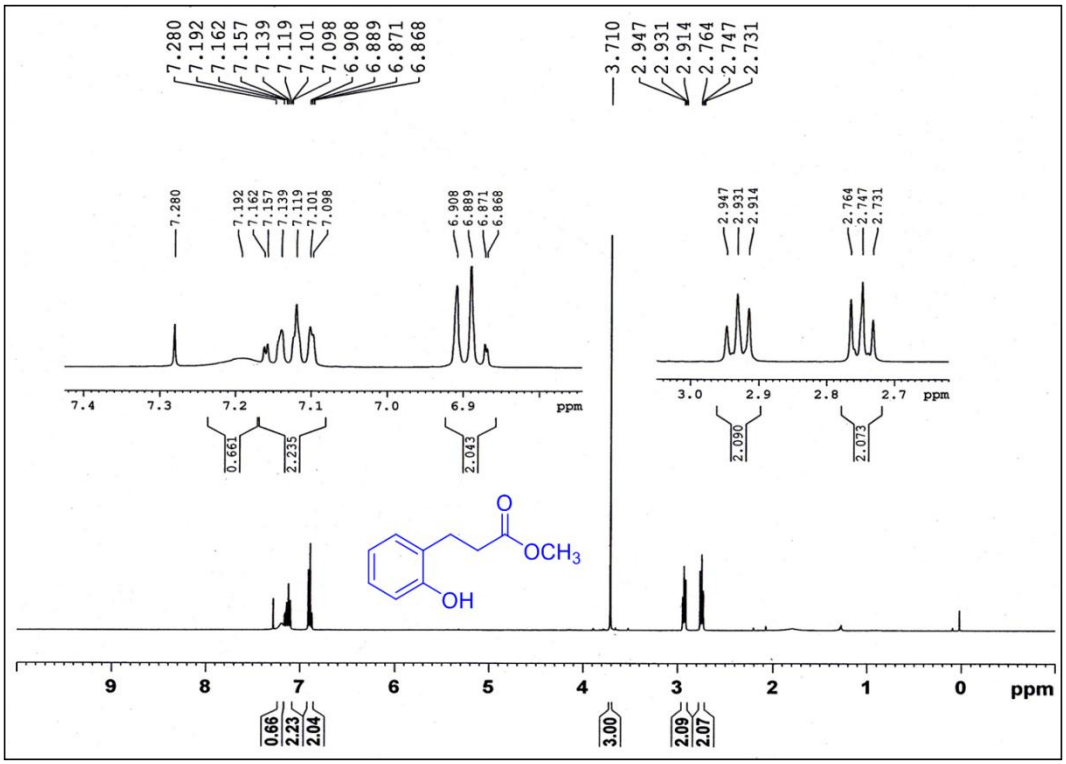
^{1}H-NMR of Compound **6c**



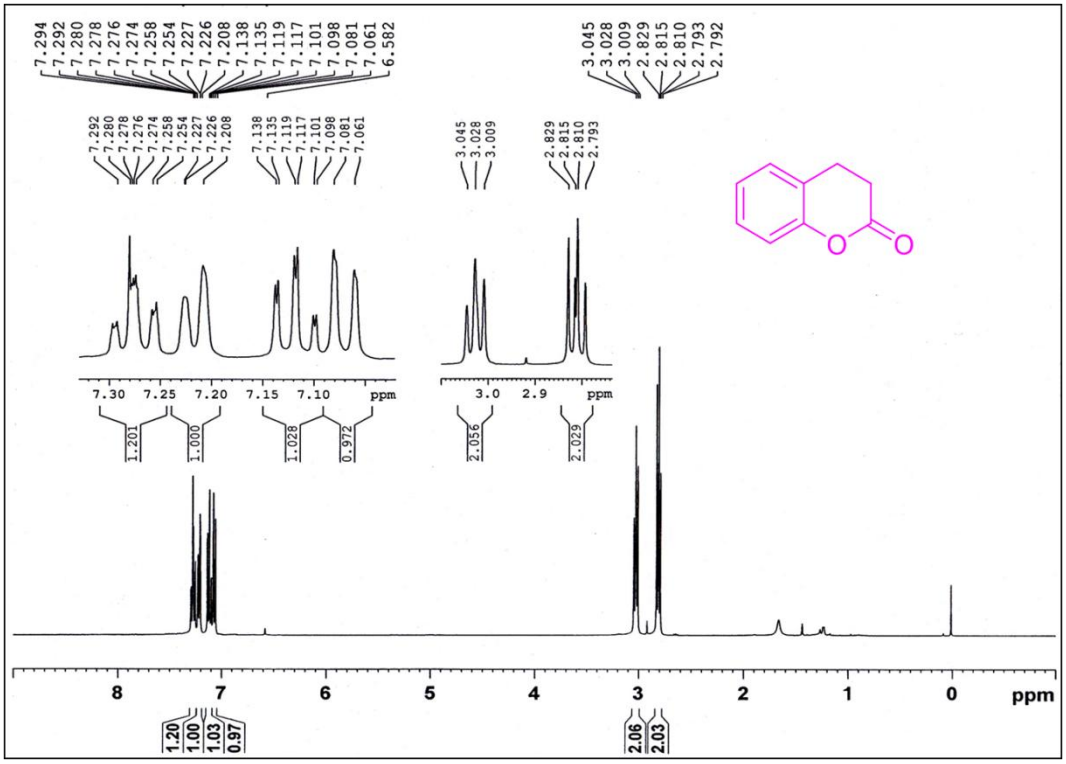
^{1}H-NMR of Compound **6f**



^{1}H-NMR of Coumarin in MeOH after 24 h



^{1}H-NMR of Compound **7b**



^{1}H-NMR of Compound **7a**

3.2.5 References

1. (a) Y. Monguchi, T. Ichikawa, H. Sajiki, *Chem. Pharma. Bull.***2017**, *65*, 2.(b) H. Sajiki, *J. Org. Synth. Chem. Jpn.* **2014**, *72*, 39. (c) H. Sajiki, Y. Monguchi, in *Pharmaceutical Process Chemistry* (Eds.: T. Shioiri, K. Izawa, T. Konoike), Wiley VCH : Weinheim, Germany, **2010**, pp. 77.
2. (a) S. Nishimura, *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, Wiley Interscience, **2001**.(b) R. Larock, *Comprehensive Organic Transformations*, Wiley-VCH : New York,NY, **1999**.(c) M. Hudlicky, *Reductions in Organic Chemistry*, American Chemical Society: Washington, DC, **1996**.
3. (a) H. Sajiki, *Tetrahedron Lett.* **1995**, *36*, 3465. (b) H. Sajiki, K. Hattori, K. Hirota, *J. Org. Chem.* **1998**, *63*, 7990. (c) H. Sajiki, H. Kuno, K. Hirota, *Tetrahedron Lett.* **1997**, *38*, 399. (d) H. Esaki, T. Hattori, A. Tsubone, S. Mibayashi, T. Sakata, *Chem. Pharma. Bull.* **2013**, *51*, 3629.
4. H. Lindlar, *Helv. Chim. Acta* **1952**, *35*, 446.
5. (a) H. Sajiki, *Yakugaku Zasshi* **2000**, *120*, 1091. (b) H.S. Ajiki, K.H. Irota, *Chem. Pharma. Bull.* **2003**, *51*, 320.
6. (a) H. Sajiki, K. Hattori, K. Hirota, *Chem. Commun.* **1999**, 1041. (b) K. Hattori, H. Sajiki, K. Hirota, *Tetrahedron Lett.* **2000**, *41*, 5711. (c) H. Sajiki, K. Hattori, K. Hirota, *Chem.-Eur. J.* **2000**, *6*, 2200. (d) K. Hattori, H. Sajiki, K. Hirota, *Tetrahedron* **2001**, *57*, 4817.
7. H. Oelschläger, *Archiv der Pharmazie* **1960**, *293*, 442.
8. (a) A. Mori, Y. Miyakawa, E. Ohashi, T. Haga, T. Maegawa, H. Sajiki, *Org. Lett.* **2006**, *8*, 3279. (b) A. Mori, T. Mizusaki, Y. Miyakawa, E. Ohashi, T. Haga, T. Maegawa, Y. Monguchi, H. Sajiki, *Tetrahedron* **2006**, *62*, 11925.
9. L. M. Kantam, P. T, M. S.V., *J. Mol. Catal. A: Chem.* **2012**, *365*, 115.
10. B. P. S. Chauhan, J. S. Rathore, T. Bandoo, *J. Am. Chem. Soc.* **2004**, *126*, 8493.
11. H. Hagiwara, T. Nakamura, T. Suzuki, *Green Chem.* **2011**, *13*, 1133.
12. D.B. Bagal, Z.S. Qureshi, K.P. Dhake, S.R. Khan, B.M. Bhanage, *Green Chem.* **2011**, *13*, 1490.
13. H. Oyamada, R. Akiyama, H. Hagio, T. Naito, *Chem. Commun.* **2006**, 4297.
14. M.V Vasylyev, G. Maayan, Y. Hovav, A. Haimov, R. Neumann, *Org. Lett.* **2006**, *8*, 5445.
15. N.M. Callis, E. Thiery, J. Le Bras, J. Muzart, *Tetrahedron Lett.* **2007**, *48*, 8128.

16. (a) H. Sajiki, T. Ikawa, K. Hirota, *Tetrahedron Lett.* **2003**, *44*, 8437. (b) T. Ikawa, H. Sajiki, K. Hirota, *Tetrahedron* **2005**, *61*, 2217. (c) Y. Kitamura, A. Tanaka, M. Sato, K. Oono, T. Maegawa, Y. Monguchi, H. Sajiki, *Synth. Commun.* **2007**, *37*, 4381. and references cited therein
17. (a) P. Catalyst, H. Sajiki, S. Mori, T. Ohkubo, T. Ikawa, *Chem.-Eur. J.* **2008**, *14*, 5109. (b) S. Mori, T. Ohkubo, T. Ikawa, A. Kume, T. Maegawa, Y. Monguchi, H. Sajiki, *J. Mol. Catal. A.* **2009**, *307*, 77.
18. (a) Y. Yabe, Y. Sawama, Y. Monguchi, H. Sajiki, *Chem.-Eur. J.* **2013**, *19*, 484. (b) A. Kawanishi, C. Miyamoto, Y. Yabe, M. Inai, T. Asakawa, Y. Hamashima, H. Sajiki, T. Kan, *Org. Lett.* **2013**, *15*, 1306. (c) Y. Yabe, Y. Sawama, T. Yamada, S. Nagata, Y. Monguchi, H. Sajiki, *ChemCatChem* **2013**, *5*, 2360.
19. (a) T. Maegawa, T. Takahashi, M. Yoshimura, H. Suzuka, Y. Monguchi, H. Sajiki, *Adv. Synth. Catal.* **2009**, *351*, 2091. (b) T. Takahashi, M. Yoshimura, H. Suzuka, T. Maegawa, *Tetrahedron* **2012**, *68*, 8293.
20. a) B.C. Ranu, A. Sarkar, A. Majee *J. Org. Chem.* **1997**, *62*, 1841. b) M.N. Cheemala, P Knochel, *Org. Lett.* **2007**, *9*, 3089.
21. a) A. Ricci, Modern Amination Methods, Wiley-VCH, New York, 2000. b) D. A. Horton, G. T. Bourne and M. L. Smythe, *Chem. Rev*. **2003**, *103*, 893.
22. a) P. L. Debenneville, J. H. Macartney, *J. Am. Chem. Soc.* **1950**, *72*, 3073. b) W.L. Borkowski, E.C. Wagner, *J. Org. Chem.*, **1952**, *17*, 1128. c) K. Ito, H. Oba, M. Sekiya, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2485.
23. a) S. Nishimura, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, Wiley, New York, 2001. b) A. W. Heinen, J. A. Peters, H. van Bekkum, *Eur. J. Org.Chem.* **2000**, 2501.
24. A. Corma and H. Garcia, *Chem. Rev*. *2003*, *103*, 4307.
25. X. Ge, C. Luo, C. Qian, Z. Yu, X. Che, *RSC Adv.* **2014**, *4*, 43195.
26. a) U. Matern, P.Luer, D. Kreusch, In Comprehensive Natural Products Chemistry; U Sankawa, Ed.; Pergamon: Oxford, 1999; Vol. 1, p 623. b) D. Yu, M Suzuki, L. Xie, S.L. Morris-Natschke, K.-H. Lee, *Med. Res. Rev.* **2003**, *23*, 322. c) X. Zhang, H. Wang, Y Song, L. Nie, L Wang, B. Liu, P Shen, Y. Liu, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 949.
27. a) K Zeitler, C.A. Rose, *J. Org. Chem.* **2009**, *74*, 1759. b) A. Shaabani, E. Soleimani, A.H. Rezayan, A. Sarvary, H.R. Khavasi, *Org. Lett.* **2008**, *10*, 2581. c) J. Barluenga,

F. Andina, F. Aznar, *Org. Lett.* **2006**, *8*, 2703. d) Y. Gu , K. Xue, *Tetrahedron Lett.* **2010**, *51*, 192.

28. a) M.A. McGuire, S.C. Shilcrat, E. Sorenson, *Tetrahedron Lett*. **1999**, *40*, 3293.
29. H.P. Hemantha, V.V. Sureshbabu, *Org. Biomol. Chem.* **2011**, ***9***, 2597.
30. K.U. Steiner, E. Sorkin, *Helvetica Chimica Acta* **1952**, *35*, 2486.
31. L. Zaramello, B.L. Albuquerque, J.B. Domingos, K. Philippot *Dalton Transactions* **2017**, *46*, 5082.
32. B. Stefane , S. Polanc *Tetrahedron* **2009**, *65*, 2339.
33. S.L. Shapiro, V.A. Parrino , L. Freedman , *J. Am. Chem. Soc.* **1959**, *81*, 3728
34. M. Kunishima, K. Yamamoto, Y. Watanabe, K. Hioki, S. Tani, *Chem. Commun*. **2005**, *21*, 2698.
35. Y. Kita, Y. Nishii, T. Higuchi, K. Mashima *Angew. Chem. Int. Ed*. **2012**, *51*, 5723.
36. S. Hanada, T. Ishida, Y. Motoyama, H. Nagashima, *J. Org. Chem.* **2007**, *72*, 7551.
37. Y. Saito, H. Ouchi, H. Takahata *Tetrahedron* **2008,** *64*, 11129.
38. G. Cahiez, A. Moyeux, J. Buendia, C. Duplais, *J. Am. Chem. Soc*. **2007**, 129, 13788.
39. S.W. Hadebe, S. Sithebe, R.S. Robinson, *Tetrahedron* **2011**, *67*, 4277.
40. E. M. Kaiser, J.D. Petty, *J. Organomet. Chem.* **1976**, *107*, 219.
41. M.M. Heravi, K. Bakhtiari, R.H. Shoar, H.A. Oskooie, *J. Chem. Res.* **2005**, *9*, 590.
42. J.M. Aizpurua, M. Oiarbide , C. Palomo, *Tetrahedron Lett.* **1987**, *28*, 5365.
43. S.D. Dreher, S.E. Lim, D.L. Sandrock, G.A. Molander, *J. Org. Chem.* **2009**, *74*, 3626.
44. F.Bergmann, J. Weizman, D. Schapiiro, *J. Org. Chem.* **1944**, *9*, 408.
45. Y. Zhou, Y. Wang, J. Wang, *J. Chem. Res.* **2004**, 118.
46. W.B. Mors, O.R. Gottlieb, C. Djerassi, *J. Am. Chem. Soc.* **1957**, 4507.
47. J.M. Khurana, Kiran, *J. Chem. Res.* **2006**, 374.
48. A.I. Khalaf, C.E. Badman, M.P. Ennis, W.M. Horspool, Q. Sultana, *Trends Photochem Photobiol* **2010,** *12*, 1.
49. K.A. Kumar, T. S. Sreelekha, K.N. Shivakumara, K. C. Prakasha, D. C. Gowda, *Synth. Commun.* **2009**, *39*, 1332.
50. F.M. Garibotto, M.A. Sortino, V.V. Kouznetsov, R.D. Enriz, S.A. Zacchinoa, ARKIVOC **2011**, 149.
51. N. Iranpoor , H. Firouzabadi, N. Nowrouzi, D. Khalili, *Tetrahedron* **2009**, *65*, 3893.
52. M. Oklobdzija, V. Sunjic, F. Kajfez, V. Caplar, D. Kolbah, *Synthesis* **1975,** *9*, 596.

53. S. Adimurthy, G. Ramachandraiah, A.V. Bedekar, S. Ghosh, B.C. Ranu, P.K. Ghosh, *Green Chem*. **2006**, *8*, 916.
54. B.K. Lee, M.R. Biscoe, S.L. Buchwald , *Tetrahedron Lett.* **2009**, *50*, 3672.
55. D. Thomas, J.H. Billmanan, C.E. Davis, *J. Am. Chem. Soc*. **1946**, *8*, 895.
56. M.A.K. Zarchi, F. Rahmani, *J. Appl. Polym. Sci.* **2011**, *121*, 582.
57. C.Meier, M.FM. Ruppel, D. Vukadinovic, J. Balzorini, *Nuceloside Nucleotide Nucleic acid* **2004**, *23*, 89.