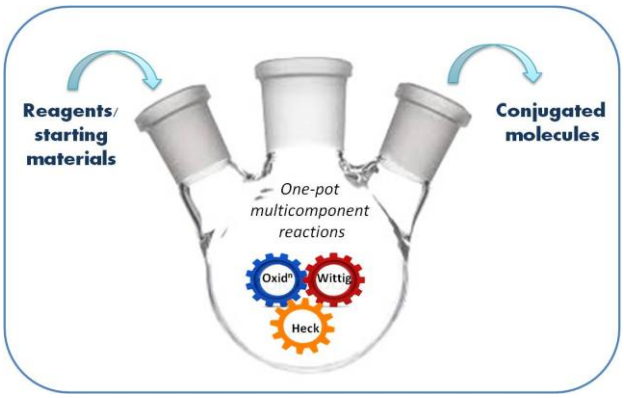
Chapter 2

ONE POT METHODOLOGIES FOR THE SYNTHESIS OF CONJUGATED MOLECULES

Contents



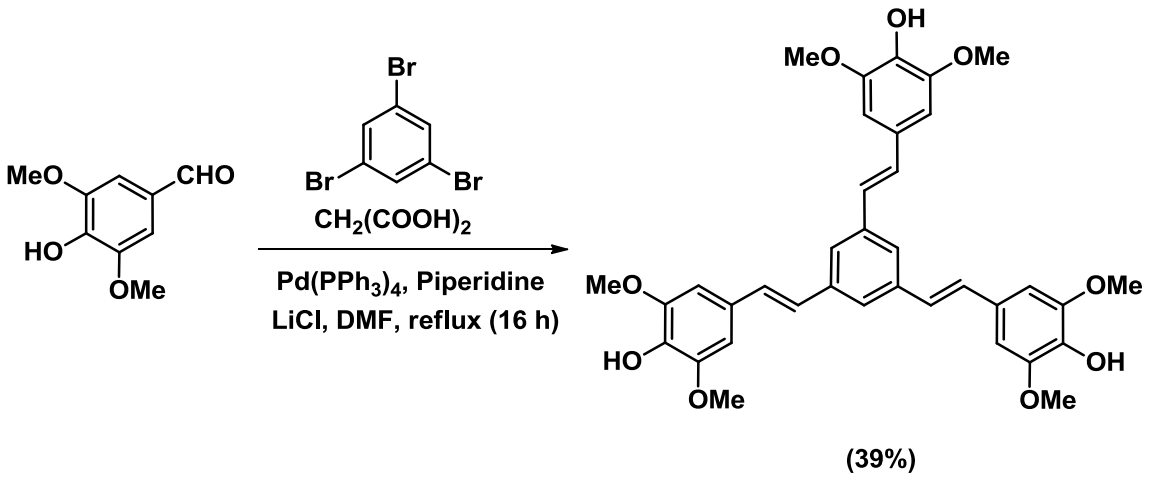
2.1 Introduction

In modern organic synthesis, purification processes are probably the most time consuming, cost-demanding and waste producing operations. However to avoid various compatibility issues and thus ensuring that the consecutive reactions proceed smoothly, intermediate purification steps often seems to be obligatory in synthetic routes. As a rival to this traditional "stop-and-go" approach to synthesis with its obvious drawbacks stands the "one-pot" strategy, in which multiple chemical transformations are performed sequentially in a single reaction vessel without intermediary purification steps.[1] Synthetic protocols in which more than one step is carried out simultaneously or as one-pot process, offer a number of advantages to the chemists. Mainly the combination of operations results in the lower overall consumption of reagents required for reaction/work-up, reduction in the total reaction time, avoids purification of unstable, toxic, or volatile intermediates, and often fulfil some of the requirements of the alternative greener synthesis. In recent decades several procedures have been developed for making useful molecules and intermediates by adopting one-pot or domino or tandem synthetic schemes. Recently many attempts have been made to develop efficient protocols to achieve one-pot synthesis of certain useful molecules.

As discussed in the introduction conjugated molecules are important class of compounds due to their applications in the area of material chemistry. Molecules with π-conjugation are capable of allowing the mobility of electrons through continuous delocalization due to structural and orbital arrangements. The nature of substitution and the length of conjugation of these molecules mainly influence their properties. Typically the mobility of electrons is controlled by choosing electron releasing or electron withdrawing groups placed at the appropriate positions of the organic molecule. As a part of our interest in the synthesis of conjugated molecules we have developed three one pot methodologies for the synthesis of stilbene and its analogous derivatives. These synthetic developments will be presented in this chapter. Discussion will be divided mainly in two parts, firstly the development of one-pot Oxidation-Wittig-Heck methodology for the synthesis of stilbene derivatives and secondly development of *O*-Alkylation-Wittig and *O*-Alkylation-Wittig-Heck methodology towards the synthesis of alkyloxy stilbenes and its analogous conjugated derivatives.

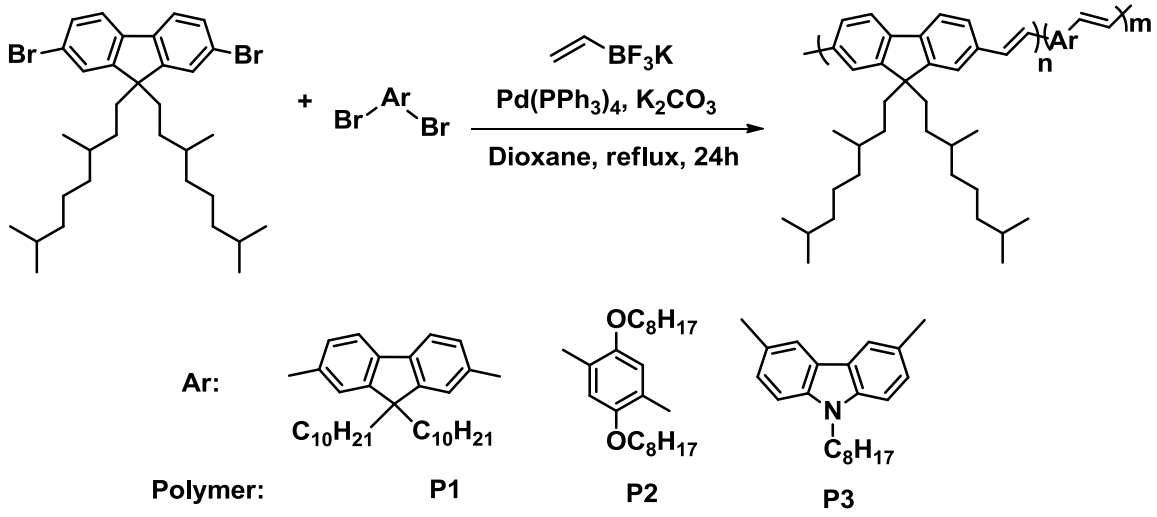
The development of new strategies for sequential formation of multiple C–C bonds in the same pot, or flask, is one of the ultimate goals of organic synthesis.

Interesting one-pot method has been developed by Sinha and co-workers for the synthesis of certain conjugated molecules.[2] The method involves direct olefination of benzaldehydes into hydroxyl functionalized oligo(*p*-phenylenevinylene)s *via* Pd-catalysed heterodomino Knoevenagel-decarboxylation-Heck sequence. Moreover among conjugated molecules distyrylbenzenes (DSBs) are also an important class of oligo(*p*-phenylenevinylene)s (OPVs) having multifarious applications.[3] In particular, the DSBs[4] with hydroxy substitution have recently generated much interest as novel H-bonding supramolecular organogels[4b] as potent candidates for detection[4d] and treatment[4c] of neurodegenerative Alzheimer's disease. The methodology also led to new oxygen based OPV scaffolds capable of selective and visible fluoride recognition in organic or aqueous medium. The application of this methodology was proved by the preparation of more complex molecule like octupolar OPV *via* reaction of hydroxyl benzaldehyde derivative, malonic acid and 1,3,5-tribromobenzene in 39% overall yield [**Scheme 1**].



Scheme 1: One-pot Knoevenagel-decarboxylation-Heck sequence

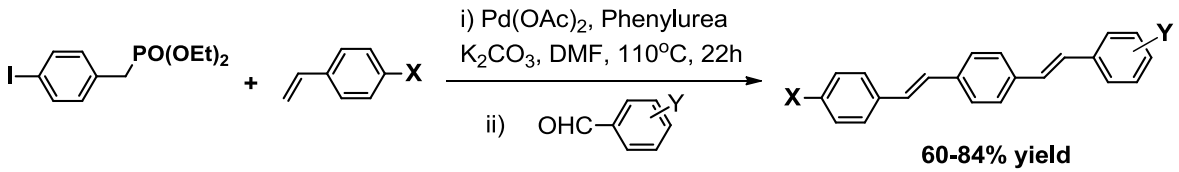
Since the discovery of electroluminescence from poly(phenylenevinylene) (PPV), continuous research efforts have been devoted to the synthesis of differently structured PPV derivatives, which can be considered the most promising organic materials to be used in light-emitting diodes (LEDs). As a contributing part of this study, Grisorio *et al* reported the synthesis of poly(fluorenylenevinylene)s **P_1-P_3** by one-pot cascade Suzuki–Heck reaction from dibromofluorene derivative and variety of aryldibromides [**Scheme 2**]. This approach differs from the known syntheses of PFVs, which require a multistep approach for the synthesis of the monomers, inevitably leading to unsatisfactory overall yields and the most important advantage of this method is the use of easily accessible substrates and potassium vinyltrifluoroborate as ethylene equivalent in this high-yielding reaction.[5]



Scheme 2: One-pot cascade Suzuki–Heck reaction for the synthesis of poly(fluorenylenevinylene)s

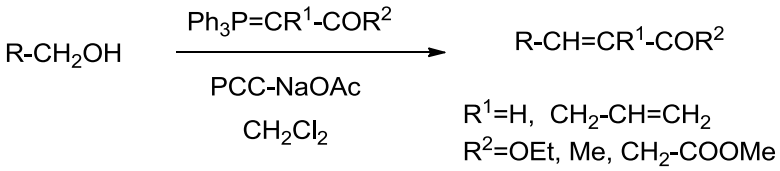
Another class of conjugated compounds is bis-styrylbenzenes. One-step syntheses of symmetrical bis-styrylbenzenes using classical Wittig (Horner-Wadsworth-Emmons or HWE) couplings between benzaldehydes and ylides derived from tetraethyl *p*-xylylenediphosphonate have been described in the literature.[6,7] Other report describes double HWE reaction sequence that could be applied to the synthesis of unsymmetrical bis-styrylbenzenes, but these require intervening adjustment of oxidation state,[8,9] adding extra steps to the synthesis. Other syntheses[10-12] employ alternating HWE and Heck reactions in a step-wise manner to form polymeric bis-styrylbenzenes known as oligo(phenylenevinylene)s; in these syntheses, unsymmetrical bis-styrylbenzene are often synthetic intermediates. Another report[13] describes a one-pot sequential Heck cross-coupling using aryl dihalides to form unsymmetrical bis-styrylbenzenes.

Vennerstrom and co-workers were the first to report one-pot synthesis of unsymmetrical bis-styrylbenzenes using a Heck/HWE sequence.[14] The yields were shown to be comparable or higher than those reported from HWE/Heck stepwise reactions. This method should be applicable to the synthesis of structurally diverse unsymmetrical bis-styrylbenzenes [**Scheme 3**].



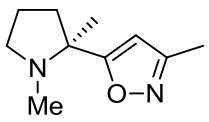
Scheme 3

One-pot methods have also found application in the total synthesis of some natural products. Tilve and co-workers have reported domino oxidation of primary alcohols to α,β-unsaturated compounds using the combination of PCC-NaOAc and stabilized Wittig reagent and its application towards total synthesis of ABT-418 and 4-oxonon-2-enoic acid.[15] The method involves benzyl alcohol as the substrate, oxidized with PCC to form aldehydes, which react with stable Wittig reagent [(carboethoxymethylene)triphenylphosphorane] in appropriate molar ratios in CH_2Cl_2 to afford ethyl cinnamate in excellent yield of 96% [**Scheme 4**]. Pyridinium chlorochromate, being an acidic reagent has been buffered with NaOAc effectively.

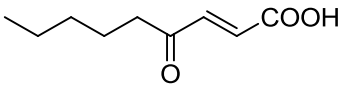


Scheme 4

Further studies using long chain as well as branched aliphatic alcohols with different Wittig reagents revealed the usefulness of this method. This method was applied for the total synthesis of ABT-418 and 4-oxonon-2-enoic acid.

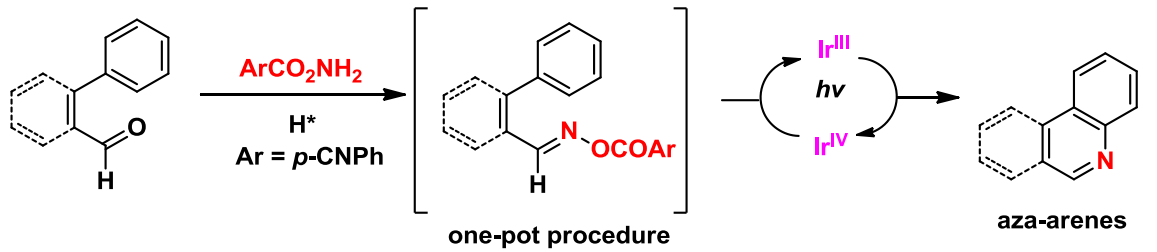


ABT-418



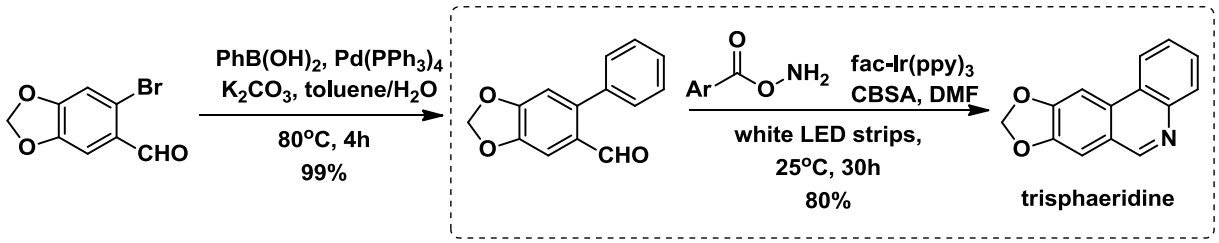
4-oxonon-2-enoic acid

Also Shouyun Yu *et al* have reported a one pot synthesis of phenanthridines and quinoline from commercially available or easily prepared aldehydes.[16] Here *O*-(4-cyanobenzoyl)hydroxylamine was utilized as the nitrogen source to *in situ* generate *O*-acyl oximes, which was then subjected to photoredox catalyzed cyclization [**Scheme 5**]. Various phenanthridines and quinolines have been synthesized by Bronsted acid (*p*-Cl-benzenesulfonic acid (CBSA)) assisted photocatalyst under visible light at room temperature with satisfactory yields. These advantages may bring this method an application in the synthesis of biologically important N-containing heterocycles, as well as natural products.



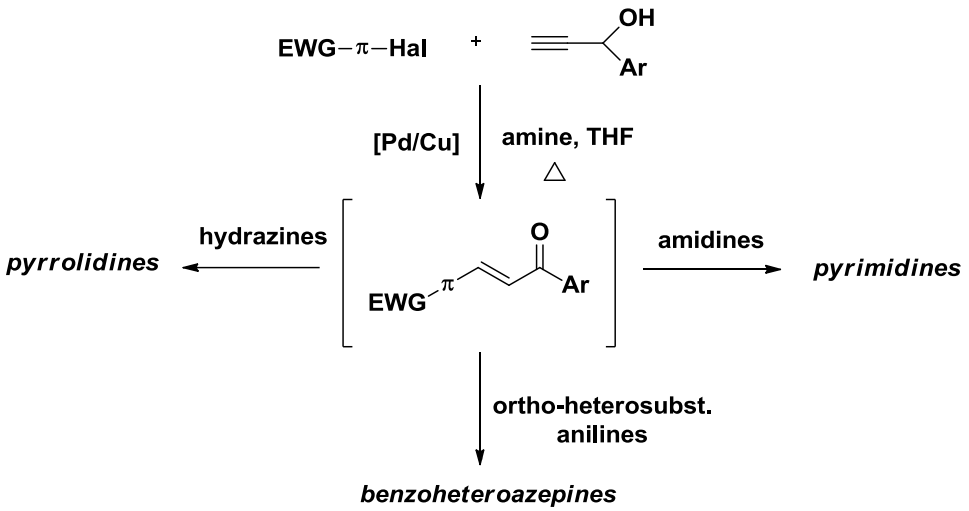
Scheme 5

This method was extended for the synthesis of alkaloid trisphaeridine, possessing excellent antitumor effects and antiretroviral activity [**Scheme 6**].



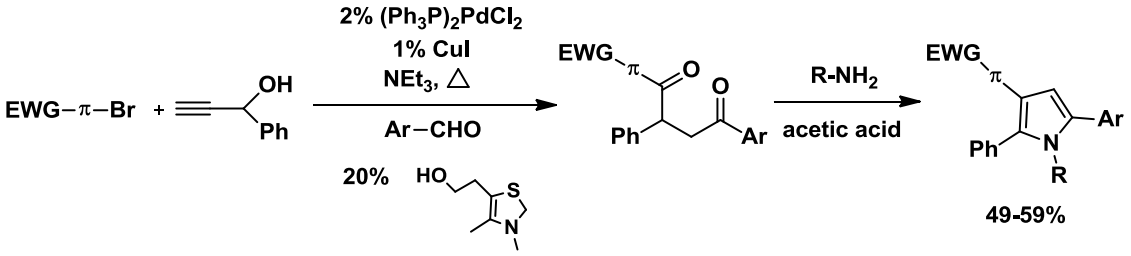
Scheme 6

The prospect of extending one-pot reactions into combinatorial and solid-phase syntheses[17,18] promises manifold opportunities for developing novel lead structures of pharmaceuticals, catalysts, and even novel materials. Mullar and co-workers have reported a novel one-pot palladium-copper-catalyzed domino synthesis of pyrrole *via* a coupling-isomerization-Stetter-Paal-Knorr sequence. With this crosscoupling-isomerisation sequence of electron-poor halogen substituted π-systems and 1-aryl prop-2-yn-1-ols furnishing 1,3-di(hetero)aryl enones (i.e., chalcones), synthesis of pyrrolidines, pyrimidines and 1,5-benzoheteroazepines can be achieved [**Scheme 7**].[19]



Scheme 7: One-Pot Syntheses of Pyrazolines, Pyrimidines,and Benzoheteroazepines Based upon a Coupling-Isomerization

The authors have applied this coupling-isomerization concept for the synthesis of pyrroles by further combining a Stetter reaction, furnishing the 1,4-diketones and a subsequent Paal-Knorr cyclocondensation. **[Scheme 8**]



Scheme 8: Four-Component Pyrrole Synthesis Based upon a Coupling-Isomerization-Stetter-Paal-Knorr Sequence

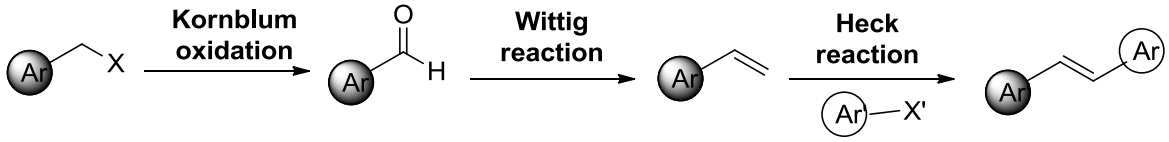
2.2 *Result and Discussion*

Owing to the importance and the applicability of one-pot methods as shown above we will be discussing about development of three one-pot synthetic methodologies for the synthesis of conjugated molecules in this chapter.

2.2.1 Oxidation-Wittig-Heck Reaction

Functional groups such as aldehydes and ketones are crucial starting materials for building many products by a number of important reactions. Several of these starting materials are commercially available or can be easily synthesized. Oxidation of 1^{o} alcohols gives inherently unstable aldehydes and the strategy of their *in situ* one-pot reaction is an attractive option. In this connection several reagents have been applied for *in situ* oxidation of alcohols for subsequent variety of organic transformations. Similarly, substituted styrenes are often not readily available due to their tendency of polymerization, and hence are also good substrates for investigations for one-pot *in situ* reactions.

In this section we present synthesis of symmetrical and unsymmetrical stilbene derivatives by a combination of one-pot Oxidation-Wittig-Heck sequence. The approach starts with oxidation of benzyl halide to the aldehyde, and then the Wittig reaction with readily available one carbon phosphonium salt (CH_3PPh_3I) to furnish styrene as the intermediate for further coupling with differently substituted aryl halide by a Pd mediated Mizoroki–Heck reaction [**Scheme 9**].



Scheme 9: One-pot Oxidation-Wittig-Heck sequence

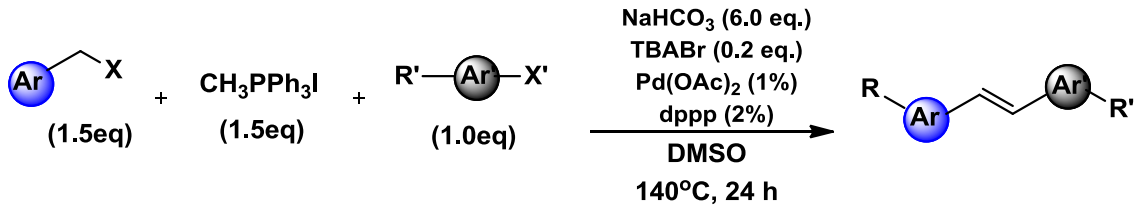
Easy availability of aryl halides compared to benzyl halides may increase the usefulness of this approach. This novel combination of oxidation-Wittig–Heck reactions is compatible with a base mediated reaction and quite suitable for one-pot exploration. This approach widens the scope of the present one-pot synthesis of stilbene derivatives. Reaction conditions were optimized by performing preliminary experiments and the selected conditions are summarized in **Table 1**. Longer reaction time furnished lower yield in the case of some examples of this sequence.

Table 1: Optimization of reaction conditions for One-pot Oxidation-Wittig-Heck Methodology

Sr. No.	Benzyl halide	Aryl halide (**2**)	Base	Catalyst ratio $Pd(OAc)_2$:dppp	%Y
1	Benzyl chloride (**1**)	Iodobenzene (1 eq)	K_2CO_3	0.5:1	52
2	Benzyl chloride (**1**)	Iodobenzene (1 eq)	Cs_2CO_3	0.5:1	32
3	Benzyl chloride (**1**)	Iodobenzene (1 eq)	Na_2CO_3	0.5:1	39
4	Benzyl chloride (**1**)	Iodobenzene (1 eq)	$NaHCO_3$	0.5:1	65
5	Benzyl chloride (**1**)	Iodobenzene (1 eq)	$NaHCO_3$	1:2	75
6	Benzyl chloride (**1**)	Iodobenzene (1 eq)	K_2CO_3	1:2	57
7	Benzyl chloride (**1**)	Iodobenzene (1.2 eq)	$NaHCO_3$	1:2	77
8	Benzyl bromide (**3**)	Iodobenzene (1.2 eq)	$NaHCO_3$	1:2	75

Conditions: CH_3PPh_3I (1 eq), TBAB (20%), DMSO (solvent), 24h, 130-140^oC

General scheme for the method is described in **Scheme 10**. A number of combinations are screened to test the validity of this approach and variety of stilbenes was isolated.



Scheme 10: One-pot Oxidation-Wittig-Heck sequence

The proposed mechanism for Oxidation-Wittig-Heck sequence is as shown in **Figure 1**.

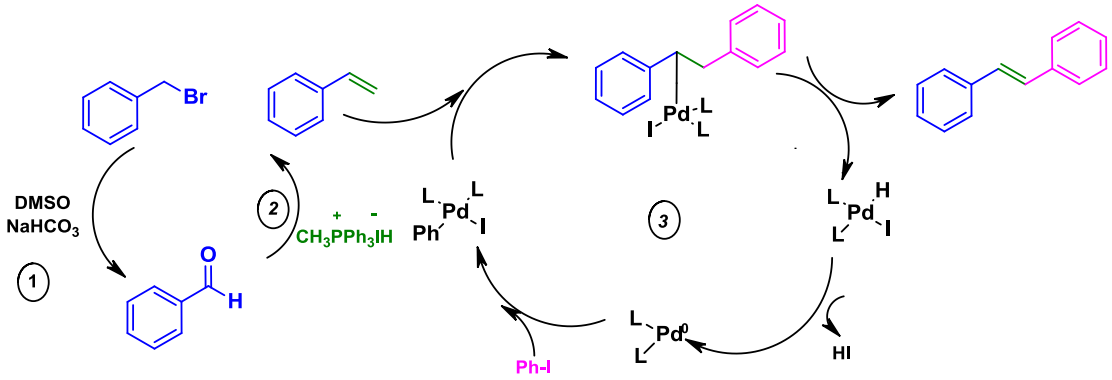
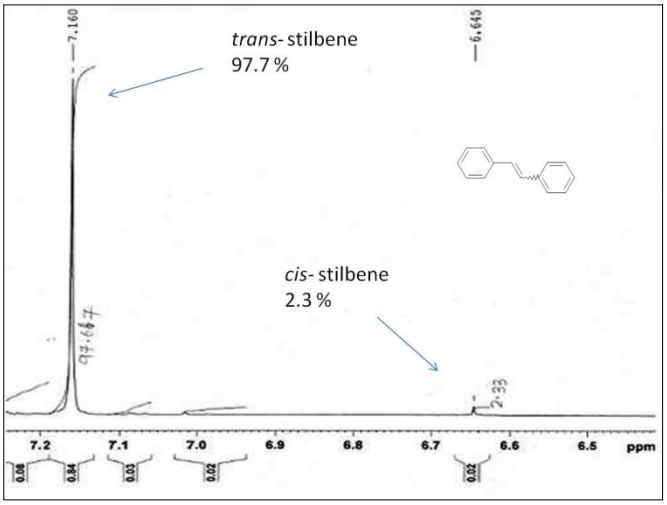


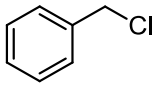
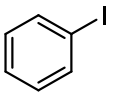
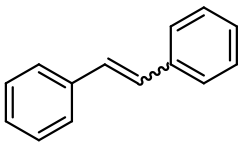
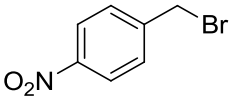
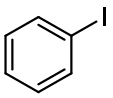
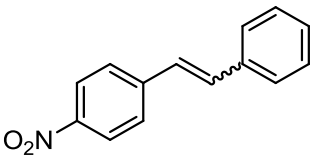
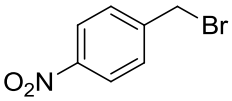
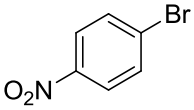
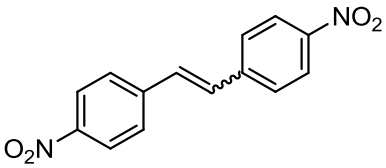
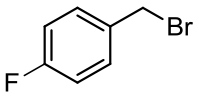
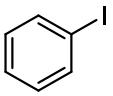
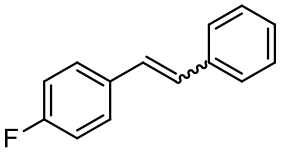
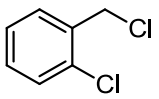
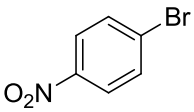
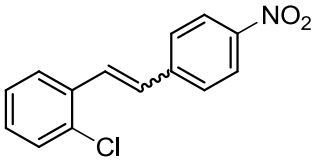
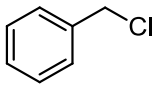
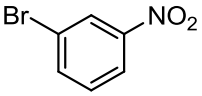
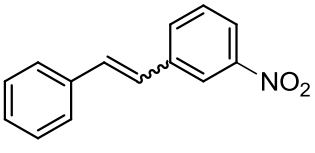
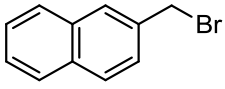
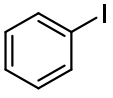
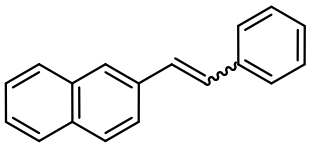
Figure 1: Proposed mechanism for one-pot Oxidation-Wittig-Heck

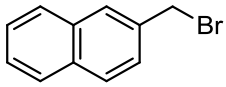
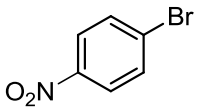
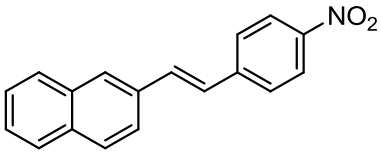
The reaction sequence can be categorised as Cascade reaction as the product of first step is used for the second reaction and the product of second undergoes third reaction to give the final product. As the stereochemistry of the final stilbene is determined primarily during the Mizoroki–Heck reaction step, as in most of the cases with triphenylphosphine ligands, such as dppp, the *E* isomer is predominantly formed in the cases investigated, which was determined by ^{1}H-NMR as shown below.



Examples for this methodology have been presented in **Table 2**.

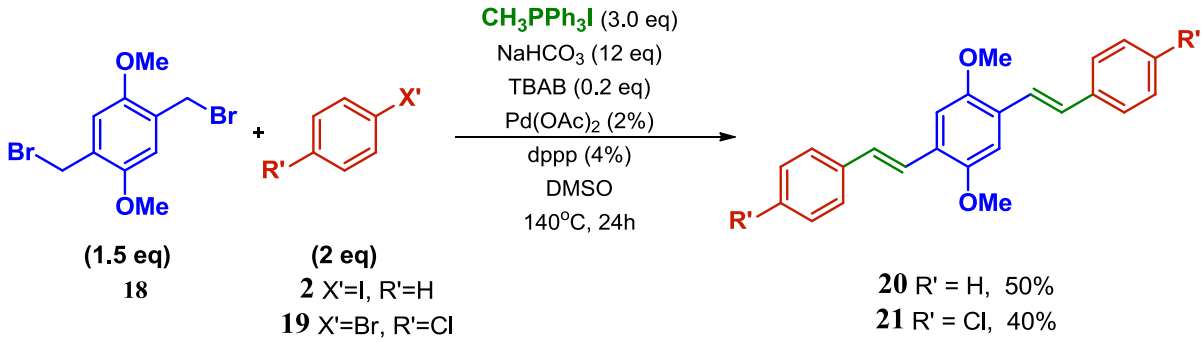
Table 2: Examples of Oxidation-Wittig-Heck reaction

No.	Benzyl halide $ArCH_2X$	Aryl halide Ar'X'	Stilbene Ar-CH=CH-Ar'	% Y	*Z:E*
1.	 **1**	 **2**	 **10**	75	2:98[a]
2.	 **4**	 **2**	 **11**	76	9:91[a]
3.	 **4**	 **5**	 **12**	73	nd
4.	 **6**	 **2**	 **13**	46	10:90[b]
5.	 **7**	 **5**	 **14**	50	8:92[a]
6.	 **1**	 **8**	 **15**	65	12:88[a]
7.	 **9**	 **2**	 **16**	73	7:93[c]

8.	 **9**	 **5**	 **17**	44	nd

[a] Isolated Yield. (*Z*:*E*) Ratio determined by H NMR. [b](*Z*:*E*) Ratio determined by GC analysis.
[c] (*Z*:*E*) Ratio determined by HPLC analysis. nd = not determined

Certain conjugated molecules have important applications in material chemistry due to their ability to transport electrons from one part to the other within its framework.[20] Some of the distyrylbenzenes (C6-C2-C6-C2-C6) have useful optical properties.[21] The present procedure is applied for the synthesis of 2,4-dimethoxy-1,4-bis(phenylethynyl)benzene **20** or its dichloro analogue **21** [**Scheme 11**]. Accordingly the bis-bromomethyl derivative **18** was separately synthesized from 1,4-dimethoxybenzene by the reaction of formaldehyde and hydrobromic acid.[22] Double oxidation-Wittig–Heck sequence on this compound furnished the desired molecules **20** and **21** almost exclusively in the *E* form. Although the yield was moderate the simplicity of the reagents, convenient reaction conditions, and high stereoselectivity for the coupling reaction may make this a useful synthetic procedure for such conjugated molecules.



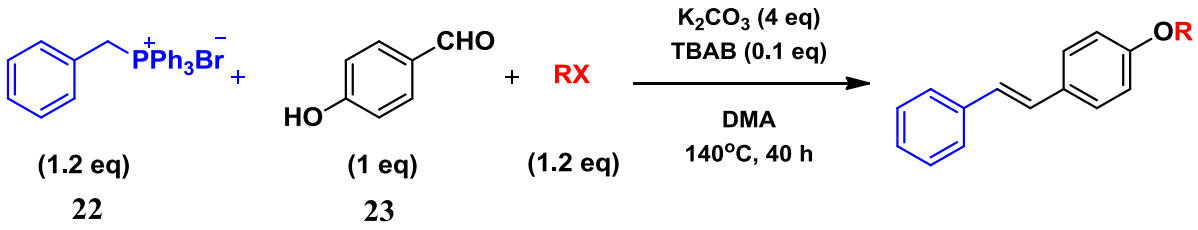
Scheme 11: Synthetic scheme for distyrylbenzenes derivatives

As described in the introduction the classical yield expression is not very informative or accurate for one pot processes we have also calculated the yield per bond formation (Y_{PBF}) and yield per manual operations (Y_{PMO}) for **20** and **21** and it was found that Y_{PBF} was 84% and 80% where as Y_{PMO} was 79% and 74% respectively showing the efficiency of the three- step one-pot reaction procedure.

2.2.2 O-Alkylation-Wittig Reaction and O-Alkylation-Wittig-Heck Reaction

In this part of the chapter we present one pot synthetic approach towards the preparation of alkyloxy stilbenes and related derivatives. As conjugated molecules are important class of compounds for application in material science, the nature of substitution and the length of conjugation of these molecules mainly influence their properties. Typically the mobility of electrons is controlled by choosing electron releasing or electron withdrawing groups placed at the appropriate positions of the organic molecule. 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 organic solvents.[23] This class of compounds also shows mesomorphism with appropriated core molecules. In this section we will present two approaches for the synthesis of alkyloxy stilbenes.

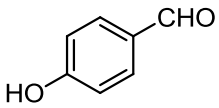
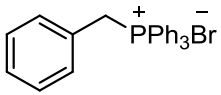
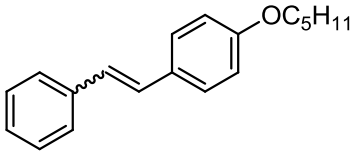
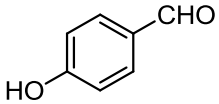
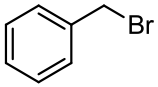
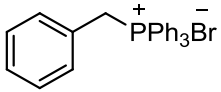
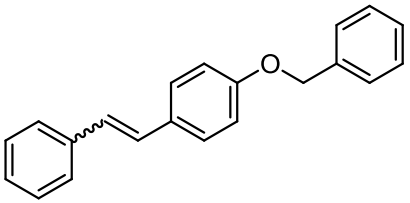
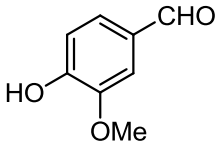
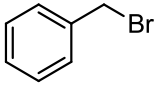
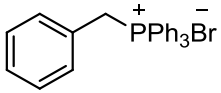
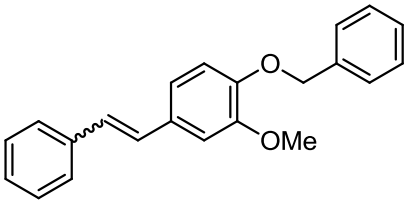
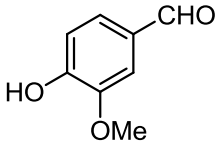
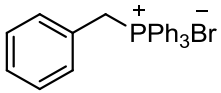
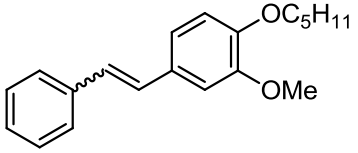
In Path A, 4-hydroxybenzaldehyde **23** was subjected to two chemical transformations; firstly the aldehyde will undergo the Wittig reaction with an ylide generated from the phosphonium salt **22** of benzylhalide and secondly the *O*-alkylation of hydroxyl group with an appropriate alkylhalide. Since both the steps are taking place in the basic medium one can conduct them simultaneously [**Scheme 12**].

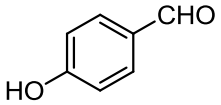
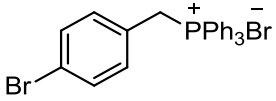
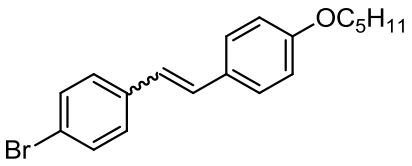
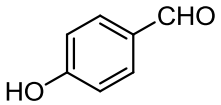
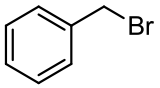
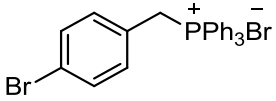
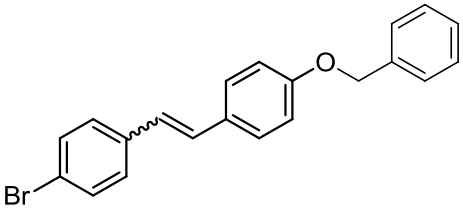
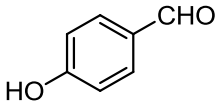
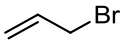
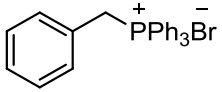
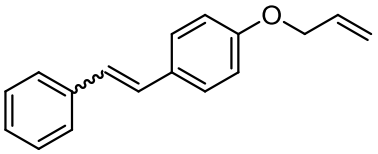
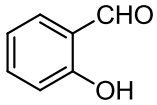
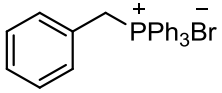
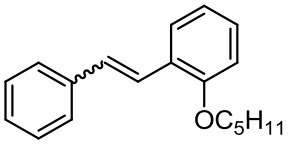


Scheme 12: One-pot *O*-Alkylation-Wittig reaction (Path A)

Synthesis of alkyloxystilbenes by Path A was investigated and the products were formed in good yields. As expected for a typical Wittig reaction,[24] the stilbenes were formed in a mixture of isomers with *E* olefin being formed in excess. Number of examples was carried out to show the validity of the developed method and the results are summarized in **Table 3**.

Table 3: Examples of synthesis of O-Alkyloxy stilbenes by one-pot O-Alkylation-Wittig methodology[a]

No.	Aldehyde	Alkyl halide	Phosphonium salt	Alkyloxy stilbene	Yield %[b]	E:Z[c]
1.	 **23**	$C_5H_{11}Br$ **24**	 **22**	 **29**	83	69:31
2.	 **23**	 **3**	 **22**	 **30**	72	76:24
3.	 **25**	 **3**	 **22**	 **31**	80	57:43
4.	 **25**	$C_5H_{11}Br$ **24**	 **22**	 **32**	84	72:28

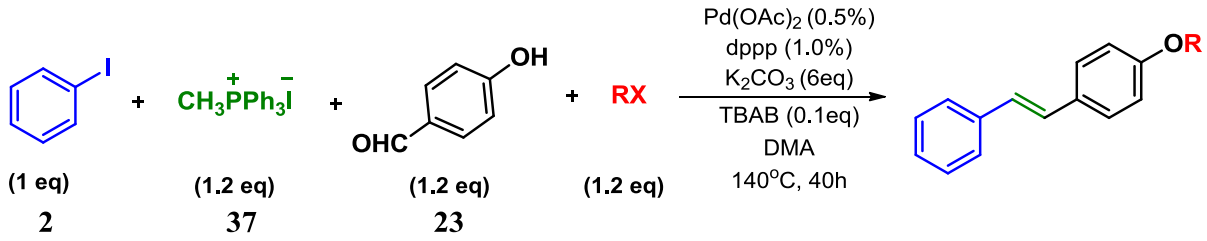
5.	 **23**	$C_5H_{11}Br$ **24**	 **26**	 **33**	56	65:35
6.	 **23**	 **3**	 **26**	 **34**	55	57:43
7.	 **23**	 **27**	 **22**	 **35**	74	71:29
8.	 **28**	$C_5H_{11}Br$ **24**	 **22**	 **36**	84	84:16

[a]Conditions: phosphonium salt (1.2 equiv), aldehyde (1.0 equiv), alkyl halide (1.2 equiv), K_2CO_3 (4 equiv), tetrabutylammonium bromide (TBAB) (10%), DMA, 140°C, 40 h.

[b] Isolated yield.

[c] E/Z Ratio was determined by ^1H NMR.

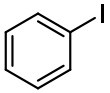
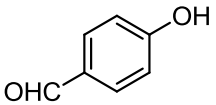
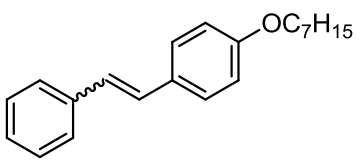
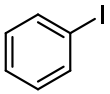
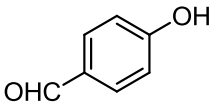
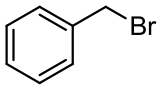
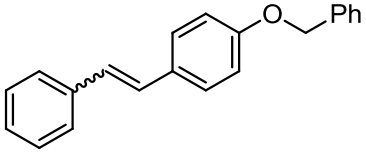
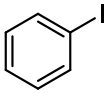
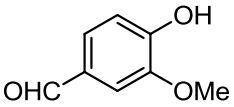
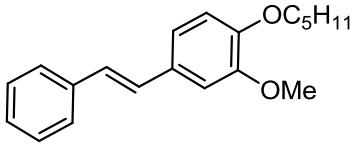
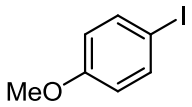
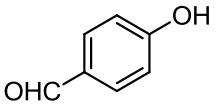
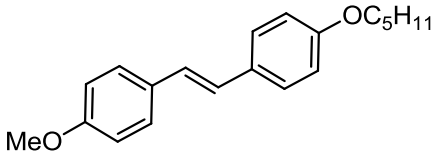
The availability of benzylhalide for the Wittig reaction can be an issue of concern for this approach. This was addressed by adopting another approach, Path B, where the 4-hydroxybenzaldehyde **23** may be converted into 4-alkyloxystyrene by the Wittig reaction with one carbon phosphonium salt **37** (CH_3PPh_3I) and alkylation of hydroxyl group. The *in situ* generated 4-alkyloxystyrene can undergo the Pd catalyzed Mizoroki–Heck reaction with an appropriate aryl halide [**Scheme 13**].

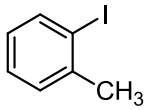
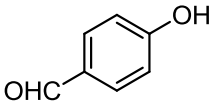
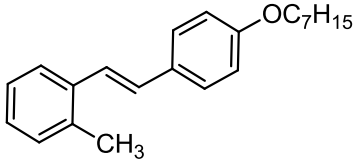
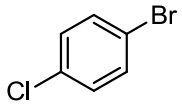
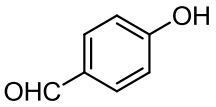
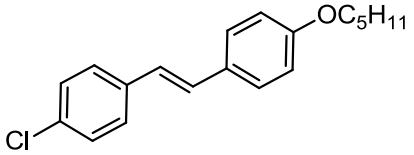
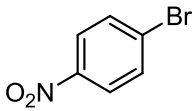
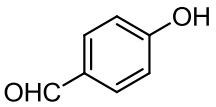
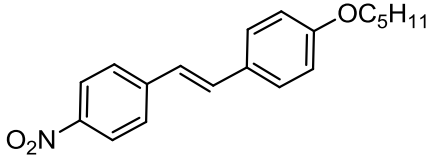
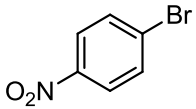
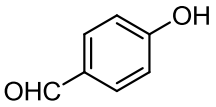
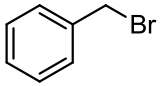
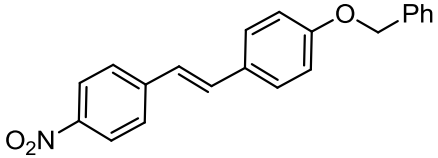
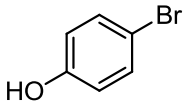
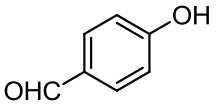
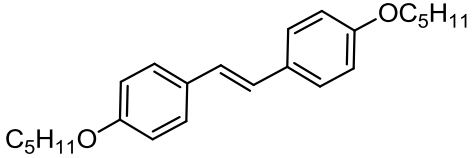


Scheme 13: One-pot O-Alkylation-Wittig-Heck reaction (Path B)

This approach may have wider applications due to the easy availability of functionalized aryl halides. This Path B was screened for a number of aldehydes and aryl halides under the homogeneous $Pd(OAc)_2$-dppp catalyst system with good overall yields, see **Table 4**. In this protocol the Mizoroki–Heck step determines the stereochemistry of alkene and as expected the product was predominantly formed as *E* isomer.[25] In Path B the *in situ* generated styrene by the reaction of ylide from one carbon phosphonium salt **37** and a variety of aldehydes, was trapped to build stilbenes by the catalytic coupling reaction. The approach involved an additional step in the one-pot sequence but still the conversions were comparable with the first process.

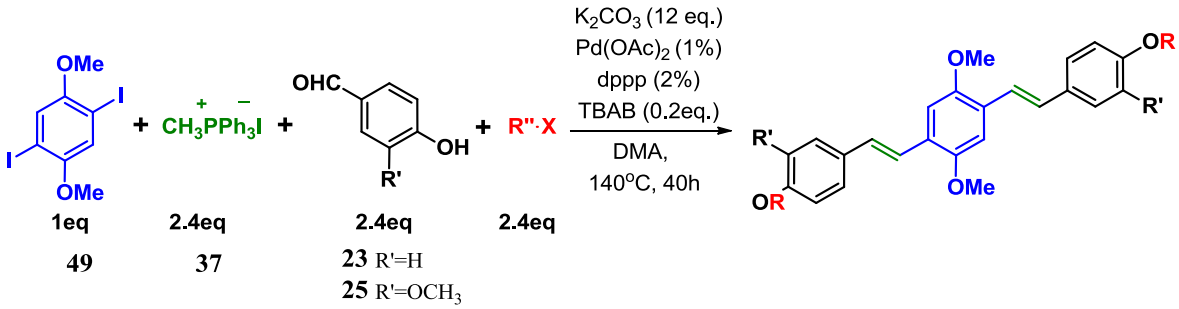
Table 4: Examples of synthesis of O-Alkyloxy stilbenes by one-pot O-Alkylation-Wittig-Heck methodology[a]

No.	Aryl halide	Aldehyde	Alkyl halide	Alkyloxystilbene	Yield (%)[b]	Y_{PBF}
1.	 **2**	 **23**	$C_7H_{15}Br$ **38**	 **42**	76	91.25
2.	 **2**	 **23**	 **3**	 **30**	78	92.05
3.	 **2**	 **25**	$C_5H_{11}Br$ **24**	 **32**	75	90.85
4.	 **39**	 **23**	$C_5H_{11}Br$ **24**	 **43**	79	92.44

5.	 **40**	 **23**	$C_7H_{15}Br$ **38**	 **44**	71	89.21
6.	 **19**	 **23**	$C_5H_{11}Br$ **24**	 **45**	59	83.87
7.	 **5**	 **23**	$C_5H_{11}Br$ **24**	 **46**	61	84.80
8.	 **5**	 **23**	 **3**	 **47**	77	91.65
9.	 **41**	 **23**	$C_5H_{11}Br$ **24**	 **48**	75	90.85

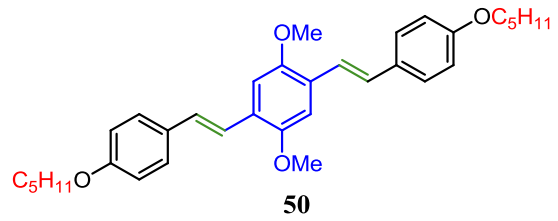
[a]Conditions: phosphonium salt **37** (1.2 equiv), aldehyde (1.2 equiv), alkyl halide (1.2 equiv), Aryl halide (1.0 equiv), K_2CO_3 (6 equiv), $Pd(OAc)_2$ (0.5%), dppp (1.0%), TBAB (10%), DMA, 140^{o}C, 40 h, alkyl halide (2.4 equiv). [b] Isolated yield; Mostly *E* isomer was formed.

Certain small conjugated molecules also have significant applications in material chemistry due to their ability to transport electrons from one part to the other within their framework.[23,26] Some of the distyrylbenzenes with suitably placed alkyloxy substitutions have useful optical properties.[21] The present method was then extended for the preparation of distyrylbenzenes having a C6–C2–C6–C2–C6 framework [**Scheme 14**].

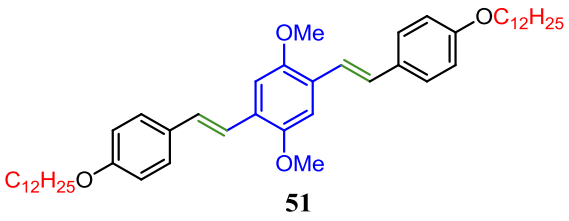


Scheme 14: Synthetic scheme for alkyloxy distyrylbenzene derivatives

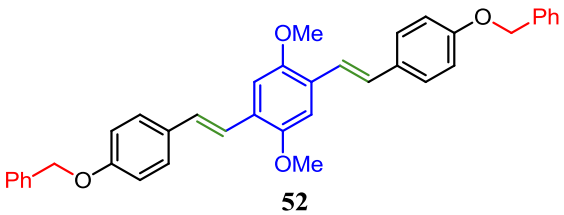
The reaction of 2,5-dimethoxy-1,4-diiodobenzene **49** with aldehyde **23** or **25**, phosphonium salt **37**, and appropriate alkyl halide primarily gave the E,E isomers of distyrylbenzenes **50**–**53** by Path B, *O*-alkylation-Wittig–Heck one-pot sequence, in good isolated yield. This process involved simultaneous two sets of such operations in one reaction setup. Here the number of new bond formed is six and number of manual operation is three. The Y_{PBF} and Y_{PMO} were calculated and it was found to be in the range of 80-90% showing that the reaction sequence is fairly efficient.



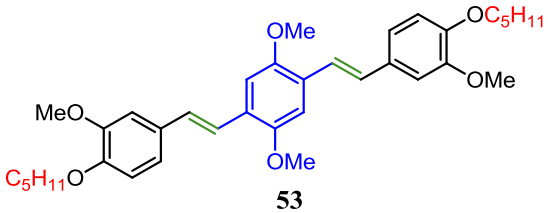
50



51



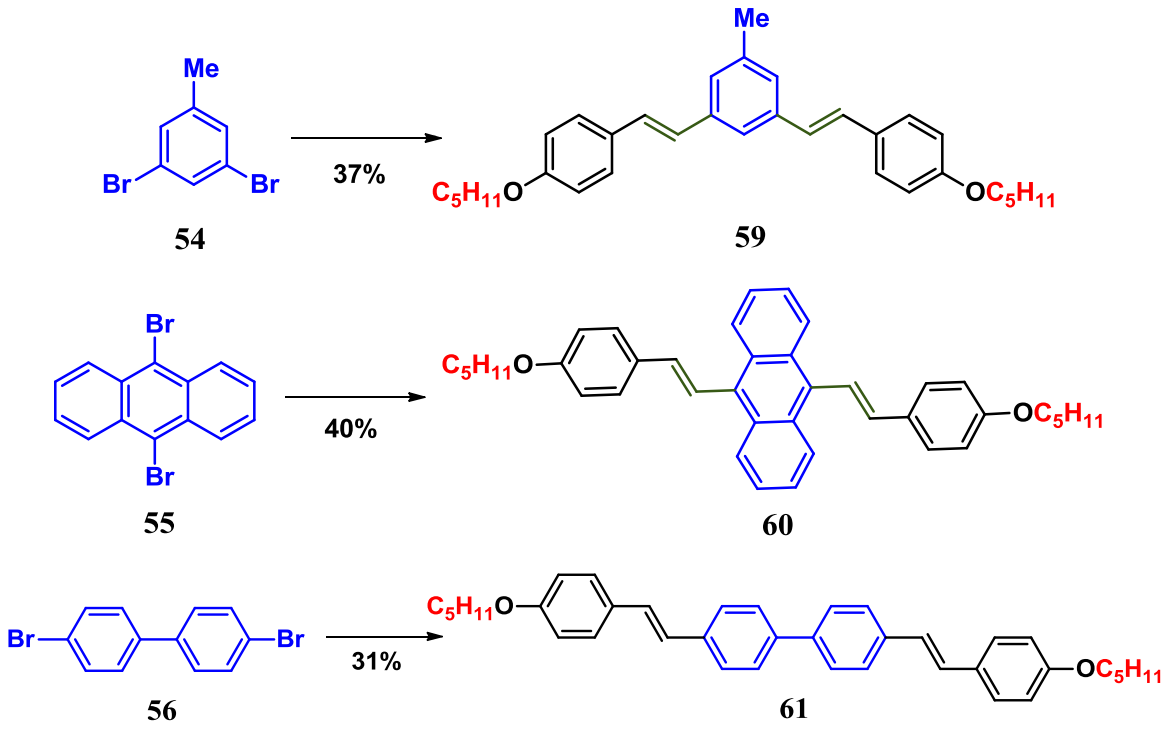
52



53

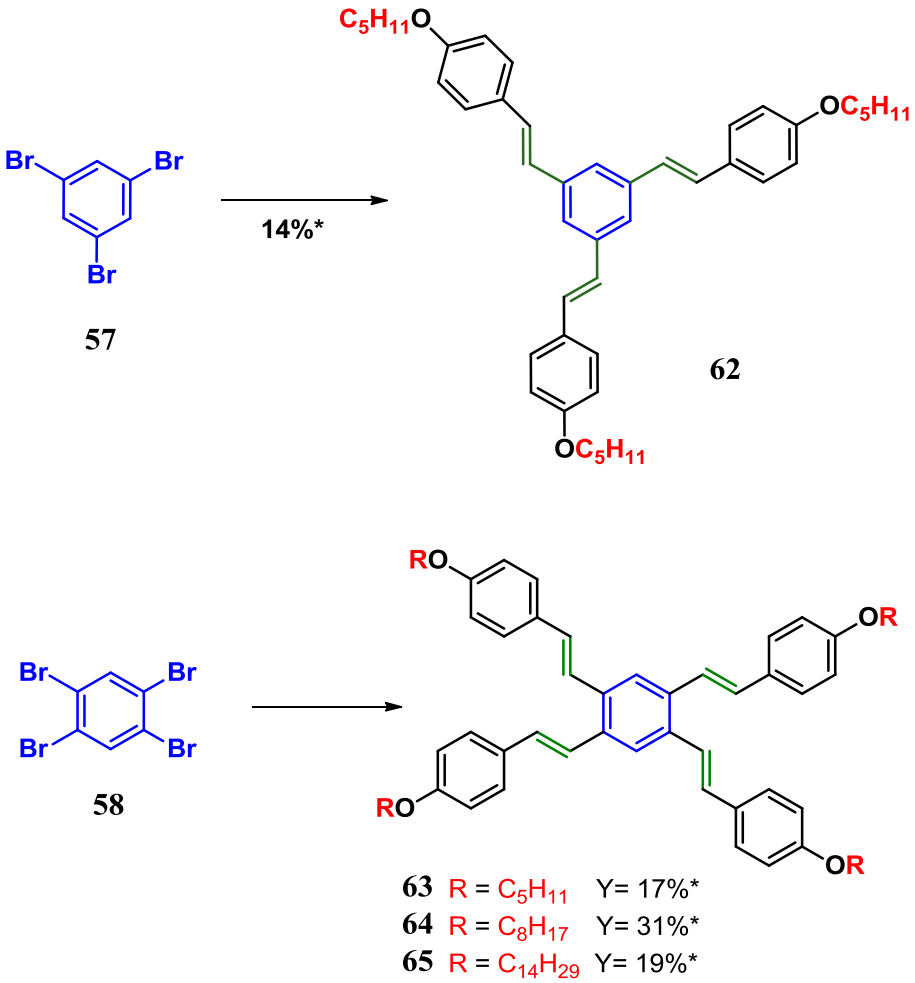
Compound	Classical Yield [%]	Y_{PBF} [%]	Y_{PMO} [%]
50	62	92.34	85.27
51	53	89.95	80.92
52	71	94.45	89.21
53	62	92.34	85.27

Encouraged by the above result a set of polybrominated aromatic compounds were subjected to the similar *O*-alkylation- Wittig–Heck reaction sequence and the results are outlined in [**Schemes 15**] and [**Scheme 16**]. As representative examples, the dibromo arenes **54**, **55**, and **56** were converted into the corresponding bis-alkyloxy alkene derivatives **59**, **60**,[27] and **61**, respectively. Several UV active spots were detected in the reaction mixture but only the desired *E*,*E*-isomer was isolated by column chromatography. Similarly 1,3,5-tribromobenzene **57** and 1,2,4,5-tetrabromobenzene **58** were converted into the corresponding tri- and tetra-stilbene derivatives **62** and **63**-**65**, respectively.[23c,28] The Pd-catalyzed Mizoroki–Heck reaction predominantly produces the *E* isomers of **62** and **63**-**65** which were isolated in low yield from the complex reaction mixture by careful column chromatography. The synthesis was achieved by simultaneously performing several one-pot chemical operations for tri- and tetra derivatives, where the low yield could be compensated by the simplicity and the practicability of the entire one-pot process, although the Y_{PBF} and Y_{PMO} were found to be good for the reaction sequences.



Compound	Classical yield	nmo	nbf	Y_{PBF} [%]	Y_{PMO}[%]
59	37	3	6	84.72	71.79
60	40	3	6	85.83	73.68
61	31	3	6	82.26	67.67

Scheme 15: Synthesis of conjugated compounds from dibromo arenes by Path B



*Isolated yield of E isomer

Compound	nmo	nbf	Y_{PBF} [%]	Y_{PMO}[%]
62	3	9	80.37	51.92
63	3	12	86.27	55.39
64	3	12	90.70	67.67
65	3	12	87.07	57.48

Scheme 16: Synthesis of conjugated compounds from tribromobenzene and tetrabromobenzene

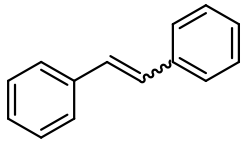
2.3 Conclusion

In conclusion in this chapter we have developed three one pot synthetic methodologies. These methods offer simple and efficient procedures for the preparation of highly conjugated molecules that can be a good candidate for the applications in the material science. Y_{PBF} and Y_{PMO} showed that the methods were efficient for the synthesis. Several polybrominated aryl halides were also subjected to the reaction sequence and the *trans* product were isolated. The yields were low in such cases but that could be compensated by the simplicity and practicability of the entire one-pot process.

2.4 Experimental Section

2.4.1 Procedure for synthesis of stilbenes by Oxidation-Wittig-Heck reaction [Scheme-10]:

Stilbene (10)

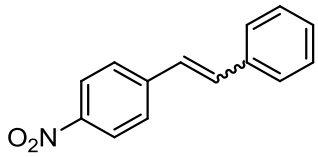


A two neck round bottom flask was charged with iodobenzene (0.200 g, 0.980 mmol), benzyl chloride (0.186 g, 1.470 mmol), methyl triphenyl phosphonium iodide (0.597 g, 1.470 mmol), sodium bicarbonate (0.494 g, 5.882 mmol), palladium acetate (0.0022 g, 0.0098 mmol), dppp (0.0080 g, 0.0196 mmol), tetrabutylammonium bromide (0.0316 g, 0.098 mmol) and dimethyl sulphoxide (10 mL) under the nitrogen atmosphere. This mixture was slowly heated to 130 ^{o}C and continued for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulphate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford stilbene (0.131 g, 74.6%).

White solid; Yield 75% (*Z:E=2:98*)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.28–7.57 (complex m, aromatic protons of both isomers), 7.16 (s, *E* olefinic protons), 6.64 (s, *Z* olefinic protons).

4-Nitrostilbene (11)



A two neck round bottom flask was charged with iodobenzene (0.150 g, 0.735 mmol), p-nitrobenzyl bromide (0.238 g, 1.102 mmol), methyl triphenyl phosphonium iodide (0.448 g, 1.102 mmol), sodium bicarbonate (0.370 g, 4.41 mmol), palladium acetate (0.00165 g, 0.0073 mmol), dppp (0.0060 g, 0.014 mmol), tetrabutylammonium bromide (0.0237 g, 0.073 mmol) and dimethyl sulphoxide (10 mL) under the nitrogen atmosphere. This mixture was slowly heated to 130 ^{o}C and continued for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulphate. Solvent was

removed in vacuum and the crude product was purified by column chromatography on silica gel to afford 4-nitro stilbene (0.126 g, 76.4 %).

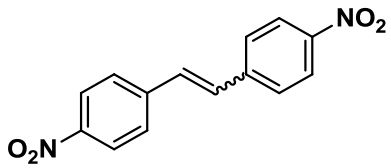
Yellow solid; Yield 76% (*Z:E=9:91*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.24 (d, *J* = 8.0 Hz, aromatic protons of both isomers), 7.65 (d, *J* = 8.8 Hz, aromatic protons both isomers), 7.58 (d, *J* = 8.8 Hz, aromatic protons of both isomers), 7.27 – 7.44 (m, aromatic protons of both isomers and signal of *E* olefinic protons merged in it), 7.16 (d, *J* = 16.4 Hz, E olefinic protons), 6.83 (d, *J* = 12.0 Hz, Z olefinic protons), 6.63 (d, *J* = 12.0 Hz, *Z* olefinic protons).

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

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

4,4'-dinitrostilbene (12)

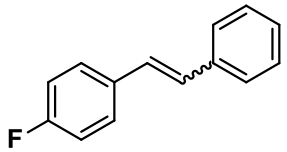


A two neck round bottom flask was charged with 4-bromo nitrobenzene (0.070 g, 0.346 mmol), 4-nitrobenzyl bromide (0.112 g, 0.519 mmol), methyl triphenyl phosphonium iodide (0.211 g, 0.519 mmol), sodium bicarbonate (0.174 g, 2.0 mmol), palladium acetate (0.00077 g, 0.0034 mmol), dppp (0.0028 g, 0.0069 mmol), tetrabutylammonium bromide (0.011 g, 0.034 mmol) and dimethyl sulphoxide (10 mL) under the nitrogen atmosphere. This mixture was slowly heated to 130 ^oC and continued for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulphate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford 4, 4'-dinitrostilbene (0.068 g, 73.1 %).

Pale yellow solid, Yield 73% (*Z:E* not determined)

MS (EI) (m/z): 271 (M^{+1}, 16), 270 (M^+, 100), 178 (10), 176 (12).

***trans* 4-Fluorostilbene (13)**



A two neck round bottom flask was charged with iodobenzene (0.100 g, 0.49 mmol), 4-floro benzylbromide (0.138 g, 0.735 mmol), methyl triphenyl phosphonium iodide (0.298 g, 0.735 mmol), sodium bicarbonate (0.247 g, 2.941 mmol), palladium acetate (0.0011 g,

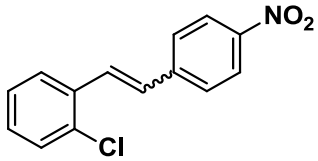
0.0049 mmol), dppp (0.0040 g, 0.0098 mmol), tetrabutylammonium bromide (0.0158 g, 0.049 mmol) and dimethyl sulphoxide (10 mL) under the nitrogen atmosphere. This mixture was slowly heated to 130 ^{o}C and continued for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulphate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford stilbene (0.041 g, 46%).

White solid, Yield 46 % *(Z:E=10:90*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.02–7.14 (complex m, aromatic protons and *E* olefinic protons with *J* = 16.4 Hz), 7.27–7.53 (complex m, aromatic protons).

MS (EI) (m/z): 199 (M^{+1}, 16), 198 (M^{+}, 100), 183 (28), 177 (16), 98 (15), 89 (5.2), 77(3).

1-(4-Nitrostyryl)-2-(2-chlorobenzene) (**14**):



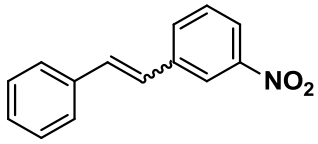
A two neck round bottom flask was charged with 4-bromo nitrobenzene (0.200 g, 0.99 mmol), 2-chloro benzylchloride (0.239 g, 1.485 mmol), methyl triphenyl phosphonium iodide (0.603 g, 1.485 mmol), sodium bicarbonate (0.498 g, 5.99 mmol), palladium acetate (0.0022 g, 0.0099 mmol), dppp (0.0081 g, 0.019 mmol), tetrabutylammonium bromide (0.031 g, 0.099 mmol) and dimethyl sulphoxide (10 mL) under the nitrogen atmosphere. This mixture was slowly heated to 130^{o}C and continued for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulphate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford 1-(4-Nitrostyryl)-2-(2-chlorobenzene) (0.127 g, 50 %).

Pale yellow solid, Yield: 50% (*Z:E* = 8:92)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.24–8.26 (d, *J* = 8.8 Hz, aromatic protons of both isomers), 7.68–7.74 (m, aromatic protons of both isomers), 7.43–7.46 (m, aromatic protons of both isomers), 7.26–7.34 (m, aromatic protons of both isomers and signal for *E* olefinic protons merged in it), 7.14 (d, *J* = 16.0 Hz, *E* olefinic protons), 6.91 (d, *J* = 12.0 Hz, *Z* olefinic protons), 6.77 (d, *J* = 12.0 Hz, *Z* olefinic protons).

MS (EI) (m/z): 261 (M^{+2}, 71), 259 (M^{+}, 92), 212 (28), 178 (80), 1176 (100), 88 (43), 75(33).

3-Nitrostilbene (**15**):



A two neck round bottom flask was charged with 3-bromo nitrobenzene (0.200 g, 0.99 mmol), benzyl chloride (0.187 g, 1.485 mmol), methyl triphenyl phosphonium iodide (0.603 g, 1.485 mmol), sodium bicarbonate (0.498 g, 5.99 mmol), palladium acetate (0.0022 g, 0.0099 mmol), dppp (0.0081 g, 0.019 mmol), tetrabutylammonium bromide (0.031 g, 0.099 mmol) and dimethyl sulphoxide (10 mL) under the nitrogen atmosphere. This mixture was slowly heated to 130 ^{o}C and continued for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulphate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford 3-nitrostilbene (0.143g, 65%).

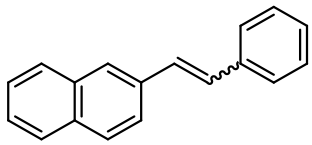
Pale yellow solid, yield: 64% (*Z:E=12:88*)

^{1}H-NMR (DMSO, 400 MHz): δ 8.35–8.38 (m, aromatic protons of both isomers), 8.17–8.2 (m, aromatic protons of both isomers), 8.08–8.1 (m, aromatic protons of both isomers), 7.81–7.85 (m, aromatic protons of both isomers), 7.33–7.56 (m, aromatic protons of both isomers), 7.24 (, *J* = 16.4 Hz, *E* olefinic protons), 7.13 (d, *J* = 16.4 Hz, *E* olefinic protons), 6.79 (d, *J* = 12.0 Hz, *Z* olefinic protons), 6.61 (d, *J* = 12.0 Hz, *Z* olefinic protons).

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

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

2-Styrylnaphthalene (16)



A two neck round bottom flask was charged with iodobenzene (0.200 g, 0.980 mmol), napthyl bromide (0.324 g, 1.470 mmol), methyl triphenyl phosphonium iodide (0.597 g, 1.470 mmol), sodium bicarbonate (0.494 g, 5.882 mmol), palladium acetate (0.0022 g, 0.0098 mmol), dppp (0.0080 g, 0.0196 mmol), tetrabutylammonium bromide (0.0316 g, 0.098 mmol) and dimethyl sulphoxide (10 mL) under the nitrogen atmosphere. This

mixture was slowly heated to 130 ^{o}C and continued for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulphate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford stilbene (0.164 g, 73%).`

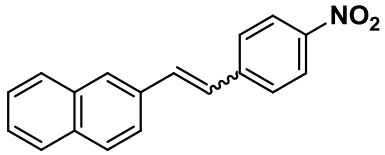
White solid, yield 73%, (*Z:E=7:93*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.72 – 7.84 (m, aromatic protons of both isomers), 7.55 – 7.57 (m, aromatic protons of both isomers), 7.36 – 7.49 (m, aromatic prtotons of both isomers), 7.25 – 7.34 (m, aromatic protons and signal of *E* olefinic protons merged in with *J* = 16.4 Hz), 6.75 (d, *J* = 12.0 Hz, *Z* olefinic protons), 6.67 (d, *J* = 12.0 Hz, *Z* olefinic protons).

IR (KBr): υ 3077, 3045, 1595, 1510, 1496, 1448, 1350, 1074, 957, 794, 775 cm.$^{-1}$

MS (EI) (m/z): 230 (M^{+}, 100), 215 (21), 115 (15), 107 (9).

2-(4-Nitrostyryl)-naphthalene (**17**):



A two neck round bottom flask was charged with 4-bromo nitrobenzene (0.200 g, 0.99 mmol), napthyl bromide (0.328 g, 1.485 mmol), methyl triphenyl phosphonium iodide (0.603 g, 1.485 mmol), sodium bicarbonate (0.498 g, 5.99 mmol), palladium acetate (0.0022 g, 0.0099 mmol), dppp (0.0081 g, 0.019 mmol), tetrabutylammonium bromide (0.0319 g, 0.099 mmol) and dimethyl sulphoxide (10 mL) under the nitrogen atmosphere. This mixture was slowly heated to 130 ^{o}C and continued for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulphate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford 3-nitro stilbene (0.120 g, 44 %).

Pale yellow solid, Yield 44%, (*Z:E* ratio not determined)

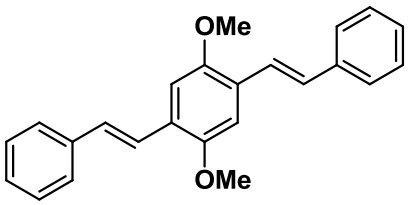
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.26 – 8.28 (m, aromatic protons of both isomers), 8.08 – 8.13 (m, aromatic protons of both isomers), 7.70 – 7.90 (m, aromatic protons of both isomers), 7.50 – 7.63 (m, aromatic protons of both isomers and singal of *E* olefinic protons with *J* = 16.4 Hz), 6.99 (d, *J* = 12.0 Hz, *Z* olefinic protons), 6.72 (d, *J* = 12.0 Hz, *Z* olefinic protons),

IR (KBr): υ 3431, 2922, 1625, 1589, 1509, 1335, 1179, 1105, 965, 861, 831, 745, 688 cm.$^{-1}$

MS (EI) (m/z): 276 (M^{+1}, 20), 275 (M^{+}, 100), 229 (33), 228 (85), 227 (33), 226 (36), 202 (24), 83 (12).

Procedure for synthesis of distytylbenzene derivatives by Oxidation-Wittig-Heck reaction (Scheme-11)*:*

trans **2,5-Dimethoxy-1,4-distyrylbenzene** (**20**):



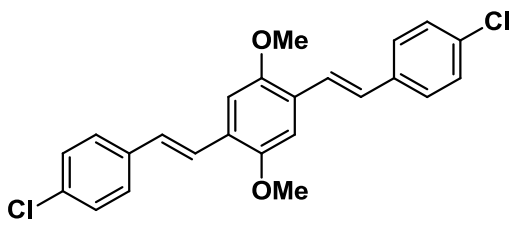
A two neck round bottom flask was charged with iodobenzene (0.150 g, 0.735 mmol), 1,4-bis(bromomethyl)-2,5-dimethoxybenzene (0.178 g, 0.551 mmol), methyl triphenyl phosphonium iodide (0.224 g, 0.551 mmol), sodium bicarbonate (0.741 g, 8.82 mmol), palladium acetate (0.0033 g, 0.0147 mmol), dppp (0.0121 g, 0.0294 mmol), tetrabutylammonium bromide (0.047 g, 0.147 mmol) and dimethyl sulphoxide (10 mL) under the nitrogen atmosphere. This mixture was slowly heated to 130 ^{o}C and continued for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulphate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford stilbene (0.063 g, 51%).

Pale yellow solid, Yield: 50%, m.p. 184 - 186 ^{o}C (Lit.[29]177 - 178 ^{o}C)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, *J* = 7.2 Hz, aromatic protons of terminal benzene ring), 7.52 (d, *J* =16.4 Hz, *E* olefinic protons), 7.37–7.41 (m, aromatic protons of terminal benzene rings), 7.26–7.30 (m, aromatic protons of terminal benzene rings), 7.17 (s, aromatic protons of tetra substituted benzene ring), 7.15 (d, *J* = 16.4 Hz, *E* olefinic protons), 3.96 (s, 6H).

MS (EI) (m/z): 343 (M^{+1}, 25), 342 (M^{+}, 100), 171 (11), 105 (35).

trans **1,4-Bis(4-chlorostyryl)-2,5-dimethoxybenzene** (**21**):



A two neck round bottom flask was charged with 1-bromo chlorobenzene (0.200 g, 1.044 mmol), 1,4-bis(bromomethyl)-2,5-dimethoxybenzene (0.253 g, 0.780 mmol), methyl triphenyl phosphonium iodide (0.318 g, 0.783 mmol), sodium bicarbonate (1.053 g, 12.53 mmol), palladium acetate (0.00469 g, 0.0208 mmol), dppp (0.0172 g, 0.0417 mmol), tetrabutylammonium bromide (0.067 g, 0.208 mmol) and dimethyl sulphoxide (10 mL) under the nitrogen atmosphere. This mixture was slowly heated to 130 ^{o}C and continued for 24 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulphate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford stilbene (0.170 g, 40%).

Pale yellow solid, Yield: 40%, m.p. 212 ^{o}C (Lit.[29] 214-216 ^{o}C)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, *J* = 8.4Hz, 4H), 7.47 (d, *J* = 16.4Hz, 2H), 7.34(d, *J* = 8.4Hz, 4H), 7.13 (s, 2H), 7.09 (d, *J* = 16.4 Hz, 2H), 3.95 (s, 6H).

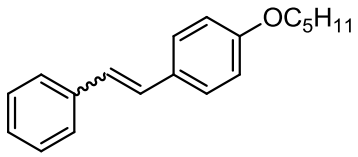
MS (EI) (m/z): 412 (M^{+2}, 60), 410 (M^{+}, 84), 139 (100), 126 (46).

2.4.2 General procedure for synthesis of alkyloxy stilbene derivatives by O-Alkylation-Wittig reaction [Scheme-12]:

Synthesis of 4-benzyloxy stilbene 30 (Table 3, entry 2):

A two-neck round bottom flask was charged with p-hydroxy benzaldehyde (0.20 g, 1.63 mmol), benzyl triphenyl phosphine chloride (0.76 g, 1.96 mmol), benzyl bromide (0.34 g, 1.96 mmol), dry potassium carbonate (0.91 g, 6.55 mmol), tetrabutylammonium bromide (0.05 g, 0.16 mmol), and dimethylacetamide (8 mL) under the nitrogen atmosphere. This reaction mixture was stirred at 140 ^{o}C for 40 h and quenched with water and extracted with ethyl acetate (3 x 25 mL). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel and ethyl acetate petroleum ether (2:98) was used as eluent to give 4-benzyloxy stilbene (0.34 g, 72%) (*Z:E=77:23*).

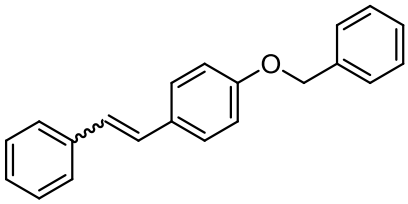
1-(pentyloxy)-4-styrylbenzene (29)



White solid (0.359 g, 83%, *Z:E = 31:69*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.48-7.41 (m, 5H), 7.35-7.15 (m, 8H), 7.05 (d, *J*=16.4Hz, olefinic proton of *E* isomer, 1H), 6.95 (d, *J*=16.4Hz, olefinic proton of *E* isomer, 1H), 6.73 (d, *J*= 8.8Hz, 1H), 6.52 (d, *J*=12Hz, olefinic protons of *Z* isomer), 6.48 (d, *J*=12Hz, olefinic protons of *Z* isomer), 3.95 (t, *J*=6.4,-O*CH*$_2$- protons of *E* isomer, 2H), 3.90 (t, *J*=6.4,-O*CH*$_2$- protons of *Z* isomer), 1.78-1.76 (m, 4H), 1.43-1.37 (m, 8H), 0.95-0.90 (m, -*CH*$_3$ protons of *Z* and *E* isomer merged together).

1-(benzyloxy)-4-styrylbenzene (30)



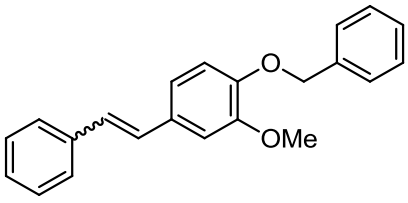
White solid (0.336 g, 72%, *Z:E = 24:76*)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37–7.54 (m, aromatic protons of *Z* and *E* isomers), 7.22–7.32 (m, aromatic protons of *Z* and *E* isomers), 7.11(d, olefinic proton of *E* isomer), 7.00–7.05 (m, aromatic protons of *Z* and *E* isomers and signal of *E* olefinic proton with *J*=16.4 Hz merged in it), 6.86– 6.89 (m, aromatic protons of both the isomers), 6.53–6.60 (m, olefinic protons of *Z* isomer), 5.12 (s, –CH_2 protons of *E* isomer), 5.07(s, –CH_2 protons of *Z* isomer).

MS (EI) (m/z): 287(M+1, 40), 286 (M+, 36), 285 (61), 196 (16), 195 (40), 194 (100), 164 (72), 151 (58), 91 (75), 90 (52).

IR (KBr): υ 3028, 2860, 1949, 1879, 1598, 1449, 1381, 1295, 1248, 1012, 964, 812, 689, 538 $cm.^{-1}$

1-(benzyloxy)-2-methoxy-4-styrylbenzene (31)

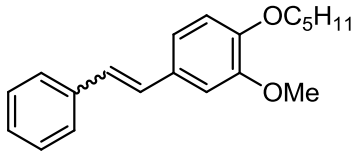


White solid (0.330 g, 80%, *Z:E = 43:57*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.58 - 7.17 (m, 18H), 7.17-7.03 (m, 4H), 6.94-6.84 (m, 4H), 6.64-6.57 (two doublets with *J*= 12Hz, olefinic protons of *Z* isomer) 5.23 (s, -O*CH*$_2$-Ph, for *E* isomer, 2H), 5.19 (s, -O*CH*$_2$-Ph, for *Z* isomer) 4.01 (s, ,-O*CH*$_3$ protons of *E* isomer, 3H), 3.66 (s, ,-O*CH*$_3$ protons of *Z* isomer).

MS (EI) (m/z): 316 (M^+, 59), 225 (100), 91(47).

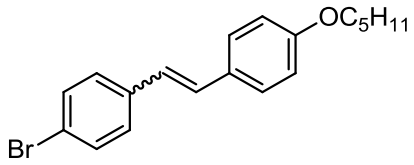
2-methoxy-1-(pentyloxy)-4-styrylbenzene (32)



White solid (0.243 g, 84%, *Z:E = 28:72*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.58 - 7.56 (d, *J*=7.2Hz, 2H), 7.39 - 7.36 (t, *J*=7.6Hz, 2H), 7.34-7.19 (m, 4H), 7.11-7.05 (m,3H), 7.0 (d, *J* = 16 Hz, olefinic proton of *E* isomer, 1H), 6.89(d, *J*= 8.4Hz, 1H), 6.84- 6.76 (m, 1H), 6.90-6.30 (two doublets with *J*= 12Hz, olefinic protons of *Z* isomer) 4.063 (t, *J*=6.8,-OCH_2- protons of *E* isomer, 2H), 4.01 (t, *J*=6.8,-OCH_2- protons of *Z* isomer), 3.96 (s, 3H, -OCH_2- proton of *E* isomer), 3.60 (s, -OCH_2- proton of *Z* isomer) 1.93-1.83 (m, 3H), 1.52-1.29 (m, 7H), 1.01-0.89 (m, -CH_3 protons of *Z* and *E* isomer merged together).

1-bromo-4-(4-(pentyloxy)styryl)benzene (33)

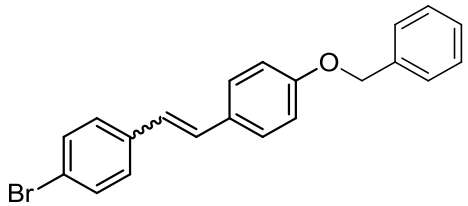


White solid (0.315 g, 56%, *Z:E = 35:65*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.49–7.34 (m, 12H), 7.19 - 7.16 (m, 4H), 7.07 (d, *J* = 16 Hz, olefinic proton of *E* isomer, 2H), 6.96-6.86 (m, a doublet with *J* = 16 Hz, olefinic proton of *E* isomer merged together, 5H), 6.58 (d, *J*=12Hz, olefinic proton of *Z* isomer, 1H), 6.43 (d, *J*=12.4 Hz, olefinic proton of *Z* isomer, 1H), 1.92-1.77 (m, 6H), 1.52-1.36 (m, 12H), 0.99-0.92 (two triplets for -CH_3 protons of *Z* and *E* isomer merged together).

MS (EI) (m/z): 344 (M^+, 100), 274 (93), 164 (68).

1-(benzyloxy)-4-(4-bromostyryl)benzene (34)

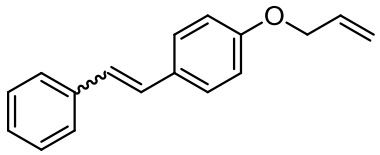


White solid (0.330 g, 55%, *Z:E = 43:57*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.58 - 7.56 (d, *J*=7.2Hz, 2H), 7.39 - 7.36 (t, *J*=7.6Hz, 2H), 7.47-7.36 (m, 15H), 7.19-7.15 (m, 4H), 7.09-6.86 (m, a doublet with *J* = 16.4Hz for olefinic proton of *E* isomer mergrd within, 5H), 6.59-6.42 (two doublets with *J*= 12.4 Hz

for olefinic protons of *Z* isomer), 5.11(s, -O*CH*$_2$-Ph of *Z* isomer), 5.06(s, -O*CH*$_2$-Ph of *E* isomer, 2H).

1-(allyloxy)-4-styrylbenzene (35)

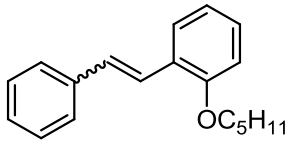


White solid (0.287 g, 74%, *Z:E = 71:29*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.56 - 7.49 (m, 7H), 7.41 (t, *J*=7.6Hz, 3H), 7.35-7.23 (m, 2H), 7.12 (d, *J* = 16.4 Hz, of *E* olefinic protons 1H), 7.03 (d, *J* = 16.4 Hz, of *E* olefinic protons , 1H), 6.97 (d, *J*=8.8Hz, 3H), 6.83 (d, *J*=8.8Hz, 3H), 6.83 (d, *J*=8.8Hz, 1H) 6.61-6.55 (two doublets with *J*=12Hz of *Z* olefinic protons merged together, 1H), 6.17-6.05 (m, 2H), 5.48-5.44 (m, 2H), 5.37-5.32 (m, 2H), 4.60 (d, *J*=5.2Hz, 3H of *E* isomer), 4.55 (d, *J*=5.2Hz, 3H of *Z* isomer).

MS (EI) (m/z): 266 (M^+, 100), 194 (92), 164 (61).

1-(pentyloxy)-2-styrylbenzene (36)



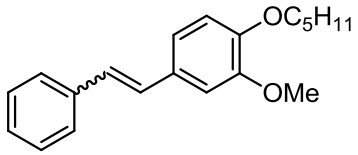
Colorless oil (0.364 g, 84%, *Z:E = 16:84*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.58 - 7.56 (dd, *J*= 8Hz, J=1.6Hz, 1H), 7.52 - 7.47 (m, 3H), 7.35 - 7.32 (t, *J*=7.6 Hz 2H), 7.25-7.12 (m, a doublet with *J* = 16.4 Hz merged within, 5H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.87-6.83 (m, 1H), 3.99 (t, *J*=6.4,-OCH_2- protons of *E* isomer, 2H), 3.93 (t, *J*=6.4,-OCH_2- protons of *Z* isomer), 1.88-1.81 (m, -OCH_2-*CH_2*-, aliphatic protons of *E* isomer, 2H), 1.75-1.68 (m, -OCH_2-*CH_2*-, aliphatic protons of *Z* isomer), 1.53-1.29 (m, 5H), 0.96-0.89(m, -*CH_3* protons of *Z* and *E* isomer merged together).

MS (EI) (m/z): 266 (M^+, 100), 194 (92), 164 (61).

2.4.3 General procedure for synthesis of alkyloxy stilbene derivatives by O-Alkylation-Wittig-Heck reaction (Scheme-13)*:*

Synthesis of 3-methoxy-4-pentyloxy stilbene 32 (Table 4, entry 3):



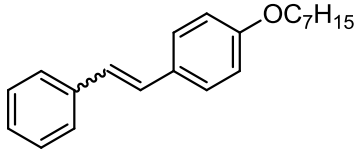
A two-neck round bottom flask was charged with iodobenzene (0.200 g, 0.98 mmol), 4-hydroxy 3-methoxy benzaldehyde (0.18 g, 1.176 mmol), methyl triphenyl phosphine iodide (0.48 g, 1.176 mmol), pentyl bromide (0.18 g, 1.176 mmol), dry potassium carbonate (0.81 g, 5.88 mmol), palladium acetate (0.001 g, 0.0049 mmol), dppp (0.004 g, 0.0098 mmol), tetrabutylammonium bromide (0.032 g, 0.098 mmol), and dimethylacetamide (8 mL) under the nitrogen atmosphere. This reaction mixture was stirred at 140^{o}C for 40 h and quenched with water and extracted with ethyl acetate (3 x 25 mL). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel and ethyl acetate:petroleum ether (*2*:*98*) was used as eluent to give 3-methoxy 4-pentyloxy stilbene (0.22 g, 75 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49–7.51 (m, 2H), 7.33–7.37 (m, 2H), 7.22–7.26 (m, 1H), 7.02–7.08 (m, 3H, aromatic protons and doublet of olefinic proton with J = 16 Hz merged in it), 6.86 (d, J = 8.4 Hz, 1H), 6.97 (d, J = 16 Hz, 1H, olefinic proton), 4.03 (t, J = 7.2 Hz, 2H, – OCH_2– protons of alkyl chain), 3.93 (s, 3H,–OCH_3 protons), 1.83–1.90 (m, 2H, –CH_2 protons of alkyl chain), 1.33–1.49 (m, 4H, –CH_2–CH_2 protons of alkyl chain), 0.93 (t, J = 7.2 Hz, 3H, –CH_3 protons of alkyl chain).

MS (EI) (m/z): 296(M+, 100), 226(88), 225(55), 164(38), 152(17), 151(11).

IR (KBr): υ 2983, 2909, 2831, 1712, 1591, 1468, 1382, 1287, 1227, 1176, 1026, 968, 912, 802, 756, 696, 612, 542cm.$^{-1}$

1-(heptyloxy)-4-styrylbenzene (42)



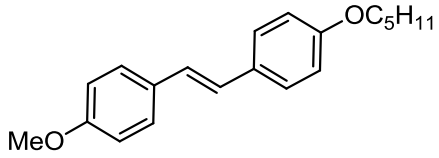
White solid (0.220 g, 76%, *Z:E = 8:92*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, *J*=7.2Hz, Ar-H of *E* isomer), 7.49 (d, *J*=8.8Hz, Ar-H of *E* isomer) 7.39 (t, *J*=7.2Hz, Ar-H of *E* isomer), 7.32-7.21 (m, Ar-H of *Z* and *E*

isomer), 7.11 (d, *J*=16.4Hz, olefinic proton of *E* isomer), 7.02 (d, *J*=16.4Hz, olefinic proton of *E* isomer), 6.95-6.89 (m, Ar-H for *Z* and *E* isomer), 6.79 (d, *J*=8.8Hz, Ar-H for *Z* isomer), 6.58 (d, *J*=12.4Hz, olefinic proton of *Z* isomer), 6.54 (d, *J*=12.4Hz, olefinic proton of *Z* isomer), 4.02-3.94 (two triplets with *J*=6.4Hz for –O*CH*$_2$- protons of *Z* and *E* isomers merged together), 1.86-1.82 (m, aliphatic protons of *Z* and *E* isomer), 1.51-1.43 (m, aliphatic protons of *Z* and *E* isomer), 0.99-0.97 (two triplets with *J*=7.2Hz, of -*CH*$_3$ protons of *Z* and *E* isomer merged together).

MS (EI) (m/z): 294 (M^+, 10), 265 (59), 195 (100), 119 (97), 86 (80).

1-methoxy-4-(4-(pentyloxy)styryl)benzene (43)

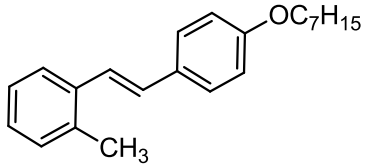


White solid (0.186 g, 79%)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.43-7.40 (m, 4H), 6.92-6.86 (m, 6H), 3.96 (t, *J*=6.8, 2H), 3.83 (s, 3H), 1.83-1.76 (m, 2H), 1.48-1.36 (m, 4H), 0.95 (t, *J*=7.2Hz, 3H).

MS (EI) (m/z): 296 (M^+, 100), 226 (40), 165 (29).

1-(4-(heptyloxy)styryl)-2-methylbenzene (44)

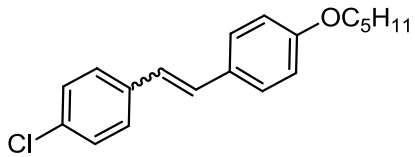


White solid (0.199 g, 71%)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, *J*=7.6Hz, 1H), 7.498 (d, *J*=8.8Hz, 2H), 7.25-7.20 (m, 4H), 6.99 (d, *J*=16Hz, 2H), 6.94 (d, *J*=8.8Hz, 2H), 4.02 (t, *J*=6.8Hz, 2H), 2.46 (s, 3H), 2.11-1.82 (m, 2H), 1.49-1.33 (m, 8H), 1.0-0.97 (t, *J*=7.2Hz, 3H).

MS (EI) (m/z): 308 (M^+, 64), 280 (81), 209 (90), 194 (100), 164 (42).

1-chloro-4-(4-(pentyloxy)styryl)benzene (45)

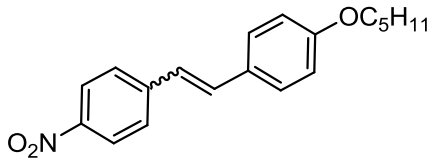


White solid (0.185 g, 59%, *Z:E = 9:91*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.46–7.39 (t, *J*=8.4Hz, 4H), 7.312-7.29 (d, *J*=6.8Hz, 2H), 7.02 (d, *J* = 16 Hz, olefinic proton of *E* isomer, 1H), 6.92-6.87 (m, a doublet with *J*=16 Hz, olefinic proton of *E* isomer merged together, 3H), 6.75 (d, *J*=8.8Hz, aromatic proton of *Z* isomer), 6.54 (d, *J*=12.4 Hz, olefinic proton of *Z* isomer), 6.42 (d, *J*=12.4 Hz, olefinic proton of *Z* isomer), 3.98-3.91 (two triplets with *J*=6.4Hz for –O*CH*$_2$- protons of *Z* and *E* isomers merged together), 1.83-1.76 (m, 2H), 1.48-1.34 (m, 4H), 0.95-0.92 (two triplets with *J*=7.2Hz, for -*CH*$_3$ protons of *Z* and *E* isomer merged together).

MS (EI) (m/z): 300 (M^+, 100), 230 (44), 229 (49), 165 (38).

1-nitro-4-(4-(pentyloxy)styryl)benzene (46)

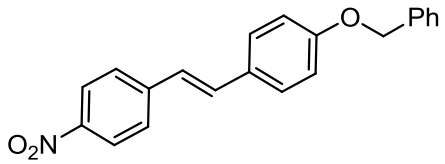


Yellow solid (0. 188 g, 61%, *Z:E = 6:94*)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.22 (d, *J*=8.8Hz, aromatic protons for *E* product), 8.10 (d, *J*=8.8Hz, aromatic protons for *Z* isomer), 7.99 (d, *J*=8.8Hz, olefinic proton of *Z* isomer), 7.61 (, *J*=8.8Hz, aromatic protons for *E* product), 7.50 (d, *J*=8.4Hz, aromatic protons for *E* product), 7.32-7.14 (m, aromatic protons of *Z* and *E* isomers and a doublet with *J*=16 Hz, olefinic proton of *E* isomer merged together), 7.02(d, *J*=16.4 Hz, olefinic proton of *E* isomer) 6.93 (d, *J*=8.8Hz, aromatic proton of *E* isomer), 4.01 (t, *J*=6.4Hz, –O*CH*$_2$- protons of *E* isomer) 3.95 (t, *J*=6.4Hz, –O*CH*$_2$- protons of *E* isomer) 1.83 (m, aliphatic protons of both isomers), 1.47-1.22 (m, aliphatic protons of both isomers), 0.96 (t, *J*=7.2Hz, for -*CH*$_3$ protons of *E* isomer), 0.88- 0.84 (m, aliphatic protons of both isomers), 0.73 (t, *J*=7.2Hz, for -*CH*$_3$ protons of *Z* isomer).

MS (EI) (m/z): 311 (M^+, 67), 240 (100), 164 (80).

1-(benzyloxy)-4-(4-nitrostyryl)benzene (47)

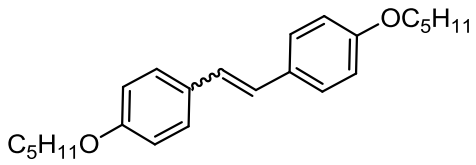


Yellow solid (0. 252 g, 77%)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.22 (d, *J*=8.8Hz, 2H), 7.62 (d, *J*=8.8Hz, 2H), 7.51 (d, *J*=8.8Hz, 2H), 7.48-7.33 (m, 6H), 7.24 (d, *J*=16.4Hz, 1H), 7.05-7.01 (m, 3H), 5.13 (s, 2H).

MS (EI) (m/z): 331 (M^+, 25), 164 (26), 91 (100).

1,2-bis(4-(pentyloxy)phenyl)ethane (48)

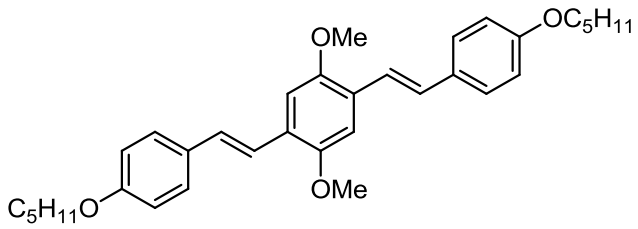


White solid (0. 303 g, 75%)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.43 (d, *J*=8.8Hz, 2H), 6.94 (s, 1H), 6.89 (d, *J*=8.8Hz, 2H), 3.98 (t, *J*=6.8, 2H), 1.84-1.77 (m, 2H), 1.48-1.38 (m, 4H), 0.95 (t, *J*=7.2Hz, 3H).

MS (EI) (m/z): 352 (M^+, 100), 211 (30).

1,4-dimethoxy-2,5-bis(E)-[2-(4-pentyloxyphenyl)vinyl]benzene (50)



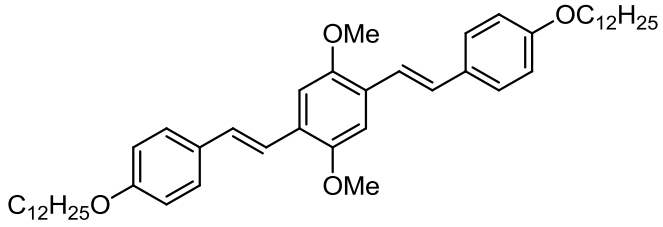
Pale yellow solid (0.162 g, 62%)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.51 (m, 2H), 7.36 (d, *J* = 16.4 Hz, 1H), 7.13 (s, 1H), 7.08 (d, *J* = 16 Hz, 1H), 6.90-6.92 (m, 2H), 4.00 (t, *J* = 6.8 Hz, 2H), 3.94 (s, 3H), 1.78-1.85 (q, *J* = 6.8 Hz, 2H), 1.40-1.495 (m, 4H), 0.96 (t, *J* = 7.2, 3H).

MS (EI) (m/z): 514 (M+, 84), 513 (61), 129 (45), 97 (29), 95 (28), 83 (40), 81 (41), 73 (38), 71 (55), 68 (81), 57 (79), 56 (46), 55 (100).

IR (KBr): υ 3036, 3005, 2939, 2866, 1605, 1572, 1513, 1459, 1408, 1393, 1295, 1250, 1207, 1175, 1044, 1021, 964, 849, 804, 592, 523 $cm.^{-1}$

1,4-Dimethoxy-2,5-bis(E)-[2-(4-dodecyloxyphenyl)vinyl]benzene (51)



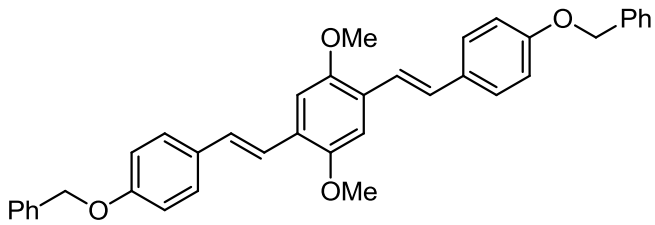
White solid (0.192 g, 53%)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, *J*=8.8Hz, 2H), 7.36 (d, *J*=16.4Hz, 1H), 7.05-7.12 (m, 2H, one doublet of olefinic proton with *J*=16.4Hz and a one singlet of aromatic proton), 6.90 (d, *J*=8.8Hz, 2H), 3.97-4.01 (t, *J*=6.8Hz, 2H), 3.93 (s, 3H), 1.77-1.82 (m, 2H), 1.44-1.49 (m, 2H), 1.28-1.34 (m, 17H), 0.88-0.91 (t, *J*=6.8Hz, 3H).

MS (EI) (m/z): 711(M^{+1}, 67), 710(M^{+}, 100), 709(76), 708(41), 526(59), 525(64), 57(50).

IR (KBr): υ 3045, 3005, 2921, 2849, 1602, 1509, 1251, 1041, 963, 848, 585 $cm.^{-1}$

1,4-Dimethoxy-2,5-bis(E)-[2-(4-benzyloxyphenyl)vinyl]benzene (52)



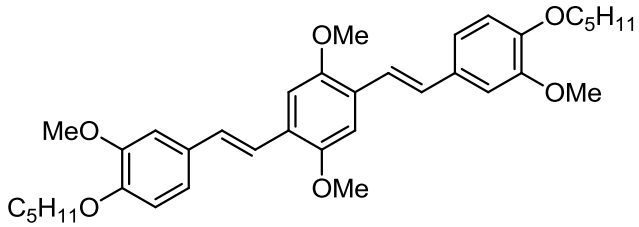
Yellow solid (0.201 g, 71%)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.44-7.52 (m, 4H), 7.31-7.42 (m, 4H), 7.11(s, 1H), 7.06 (d, *J*=16.4Hz, 1H), 6.96-7.00 (m, 2H), 5.09 (s,2H), 3.91 (s,3H).

MS (EI) (m/z): 515(M^{+1}, 30), 514(M^{+}, 100), 513(62), 512(56), 91(51), 83(37), 80(29), 72(41), 70(35), 69(44), 68(50), 57(68), 55(79).

IR (KBr): υ 2939, 2869, 2833, 1600, 1572, 1510, 1242, 1042, 1012, 850, 743, 696, 526 $cm.^{-1}$

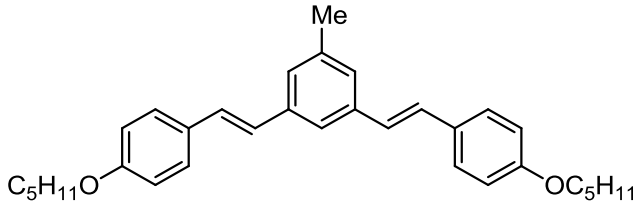
1,4-Dimethoxy-2,5-bis(E)-[2-(3-methoxy-4-pentyloxyphenyl)vinyl]benzene (53)



Yellow solid (0.168 g, 62%)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.33 (d, *J*=16.4Hz, 1H), 7.04-7.11(m, 4H), 6.86(d, *J*=8.4Hz, 1H), 4.01-4.05 (t, *J*=7.2Hz, 2H), 3.942 (s, 3H), 3.93 (s, 3H), 1.83-1.90(m, 2H), 1.36-1.47 (m, 4H), 0.91-0.95 (t, *J*=7.2, 3H).

4,4'-((1E,1'E)-(5-methyl-1,3-phenylene)bis(ethene-2,1-diyl))bis((pentyloxy)benzene) (59)

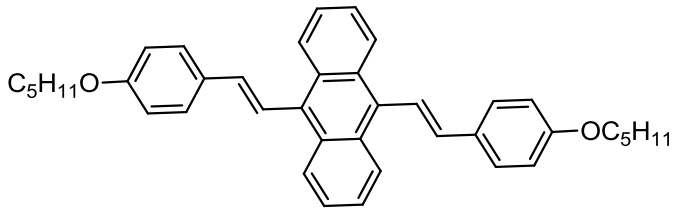


White solid (0. 140 g, 37%)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, *J*=8.8Hz, 2H), 7.19 (s, 1H), 7.09 (d, *J*=16.4Hz, 1H), 6.96 (d, *J*=16.4Hz, 1H), 6.89 (d, *J*=8.8Hz, 2H), 3.98 (t, *J*=6.8, 2H), 1.83-1.76 (m, 2H), 1.49-1.34 (m, 4H), 0.94 (t, *J*=7.2Hz, 3H).

MS (EI) (m/z): 468 (M^+, 100), 327 (24).

9,10-bis((E)-4-(pentyloxy)styryl)anthracene (60)



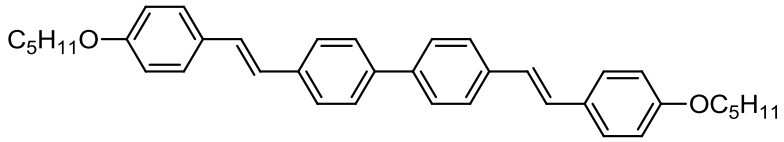
Pale yellow solid (0.131 g, 40%)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38–8.42 (m, 2H), 7.78 (d, *J* = 16.4 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.44–7.48 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 16.4 Hz, 1H), 6.84–6.89 (m, 2H), 4.03 (t, *J* = 6.8 Hz, 2H), 1.80– 1.87 (m, 2H), 1.37–1.52 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H).

MS (EI) (m/z): 555 (M+1,21), 554 (M+,100), 553 (56), 552 (35), 368 (9), 319 (6.6), 264 (6).

IR (KBr): υ 3010, 2932, 2866, 1603, 1573, 1510, 1469, 1246, 1173, 1021, 967, 760 $cm.^{-1}$

4,4'-bis((E)-4-(pentyloxy)styryl)-1,1'-biphenyl (61)



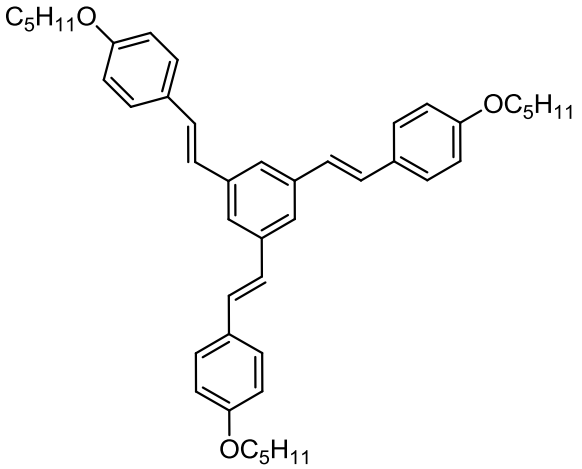
Pale yellow solid (0.101 g, 31%)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57–7.65 (m, 5H), 7.43–7.51 (m, 3H), 7.31–7.38 (m, 1H), 7.13 (d, *J* = 16.4 Hz, 1H), 6.99–7.04 (m, 1H), 6.88–6.93 (m, 2H), 3.99 (t, *J* = 6.8 Hz, 2H), 1.78– 1.85 (m, 2H), 1.36–1.51 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H).

MS (EI) (m/z): 531 (M+1,22), 530 (M+), 529 (32), 454 (11), 266 (19), 205 (17), 190 (37), 104 (100), 91 (13).

IR (KBr): υ 3067, 3037, 2968, 2930, 2823, 1617, 1582, 1534, 1470, 1272, 993, 880, 738, 577, 490 $cm.^{-1}$

1,3,5-tris((E)-4-(pentyloxy)styryl)benzene (62)



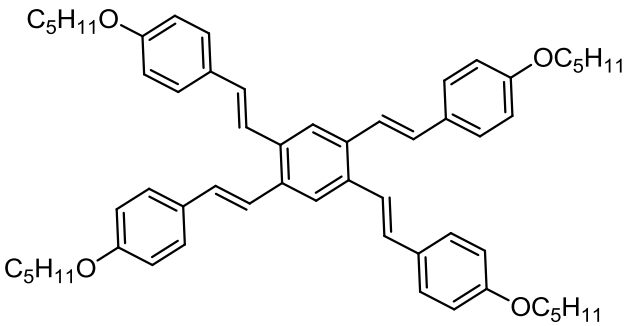
Pale yellow solid (0.055 g, 14%)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47–7.49 (3H, doublet with *J* = 7.6 Hz (2H) and a singlet of aromatic proton (1H) merged together), 7.14 (d, *J* = 16.4 Hz, 1H), 7.01 (d, *J* = 16 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.98 (t, *J* = 6.8 Hz, 2H), 1.77–1.84 (m, 2H), 1.35-1.50 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H).

MS (EI) (m/z): 642 (M+,62), 641 (100), 482 (72), 481 (70), 106 (18), 55 (13).

IR (KBr) υ 3024, 2936, 2866, 1694, 1606, 1583, 1510, 1472, 1250, 1173, 1025, 961, 840, 680, 550, 523 cm.$^{-1}$

1,2,4,5-tetrakis(*E*)-[2-(4-pentyloxyphenyl)vinyl]benzene (63)



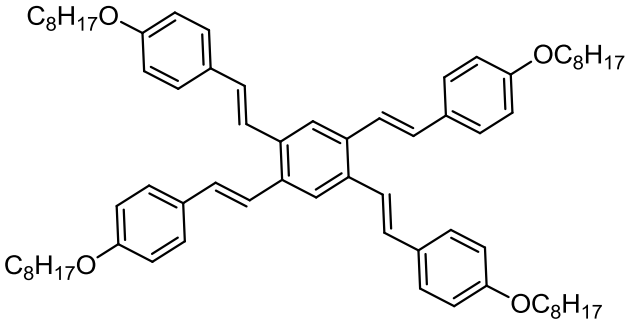
Pale yellow solid (0.070 g, 17%)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (s, 1H), 7.48–7.54 (m, 2H), 7.23 (d, *J* = 16.4 Hz, 1H), 7.02 (d, *J* = 16 Hz, 1H), 6.91–6.93 (m, 2H), 3.99–4.02 (t, *J* = 6.8 Hz, 2H), 1.79– 1.86 (m, 2H), 1.37–1.51 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H).

MS (EI) (m/z): 846 (M+1), 610 (100), 470 (15), 107 (13).

IR (KBr): υ 3036, 2945, 2863, 1672, 1603, 1511, 1466, 1253, 1172, 1050, 959, 821, 589, 519 cm.$^{-1}$

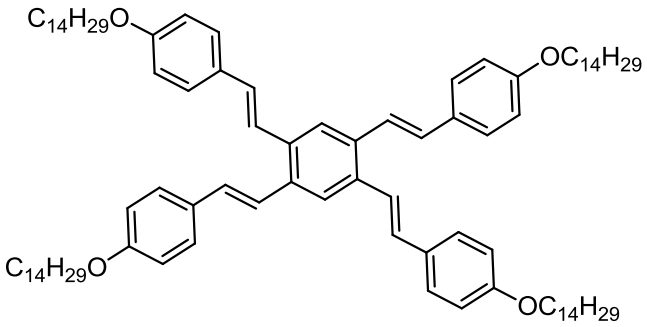
1,2,4,5-tetrakis(*E*)-[2-(4-octyloxyphenyl)vinyl]benzene (64)



Pale yellow solid (0.160 g, 31%)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (s, 1H), 7.48 (d, *J* = 8.4Hz, 2H), 7.35 (d, *J* = 16.4 Hz, 2H), 7.05 (d, *J* = 16Hz, 2H), 6.93 (d, *J*=8.8Hz, 2H), 4.0 (t, *J* = 6.8Hz, 2H), 1.84–1.78(m, 2H), 1.50–1.45(m, 2H), 1.37-1.31 (m, 8H), 0.91 (t, *J* = 6.4 Hz, 3H).

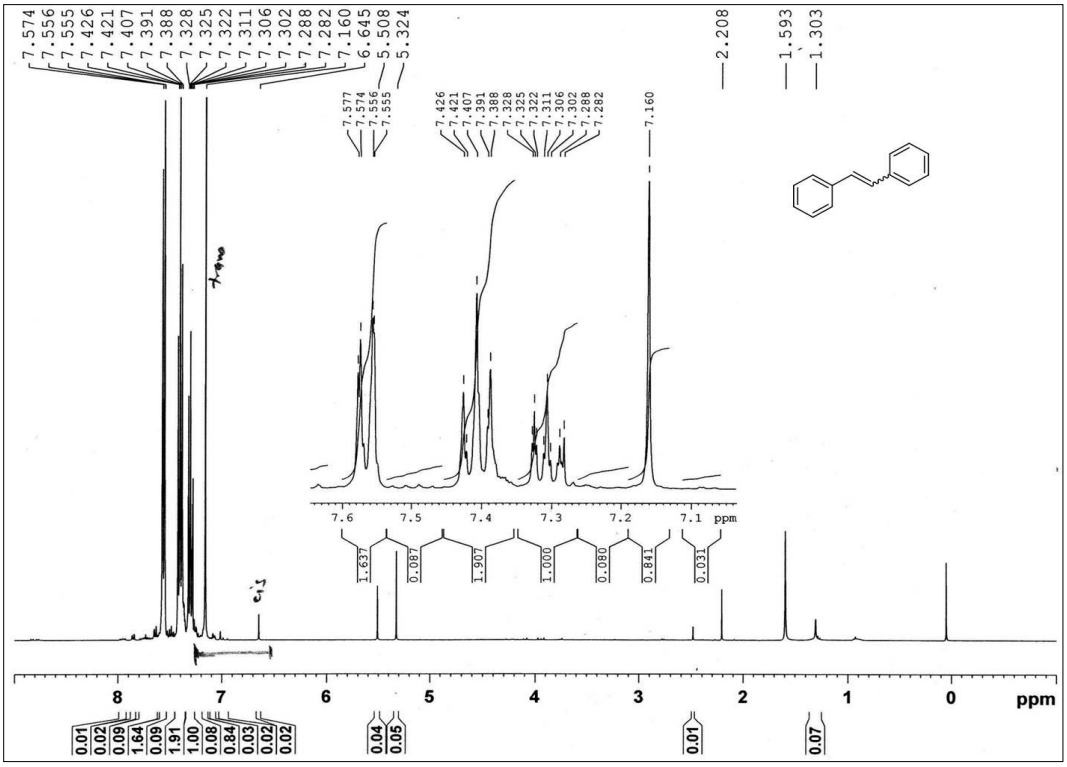
1,2,4,5-tetrakis(*E*)-[2-(4-tetradecyloxyphenyl)vinyl]benzene (65)



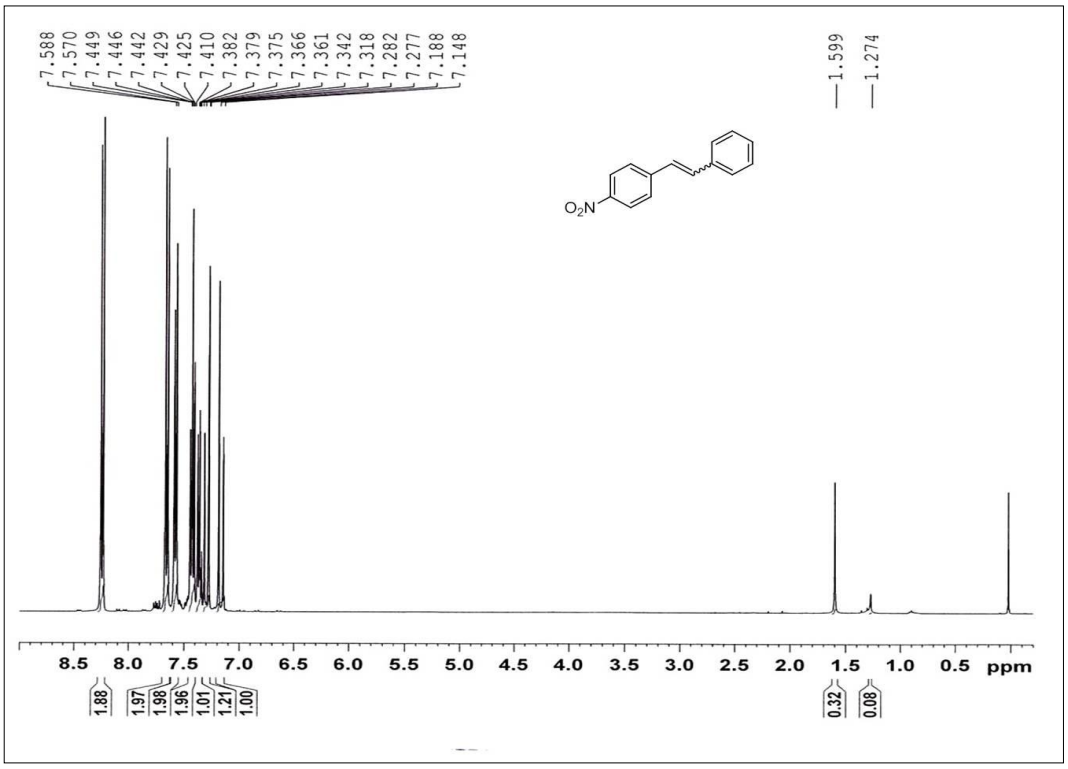
Pale yellow solid (0.128, 19%)

^{1}H NMR (CDCl3, 400 MHz) δ 7.86 (s, 1H), 7.50 (d, *J* = 8.8Hz, 2H), 7.23 (d, *J* = 16.4 Hz, 1H), 7.02 (d, *J* = 16.4 Hz, 1H), 6.92 (d, *J* = 8.4Hz, 2H), 4.0 (t, *J* = 6.4Hz, 2H), 1.85–1.77 (m, 2H), 1.50–1.44 (m, 2H), 1.30-1.28 (m, 20H), 0.90 (t, *J* = 6.8 Hz, 3H).

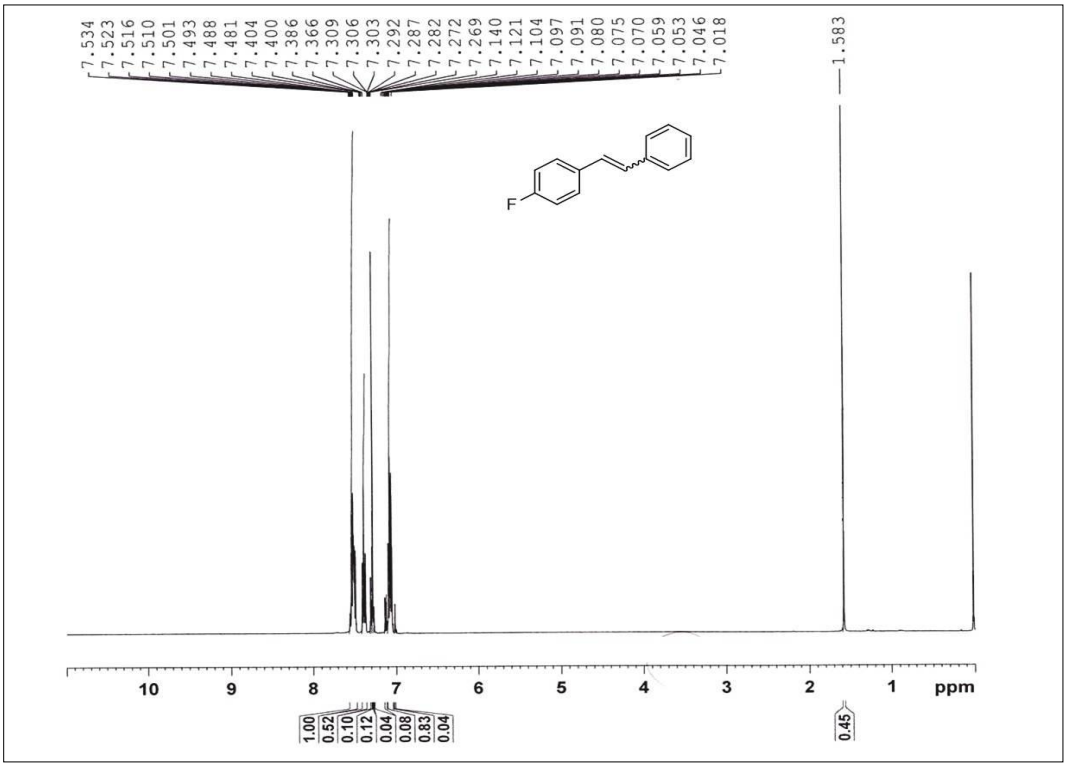
2.4.4 Spectral Data for the examples of Oxidation-Wittig-Heck



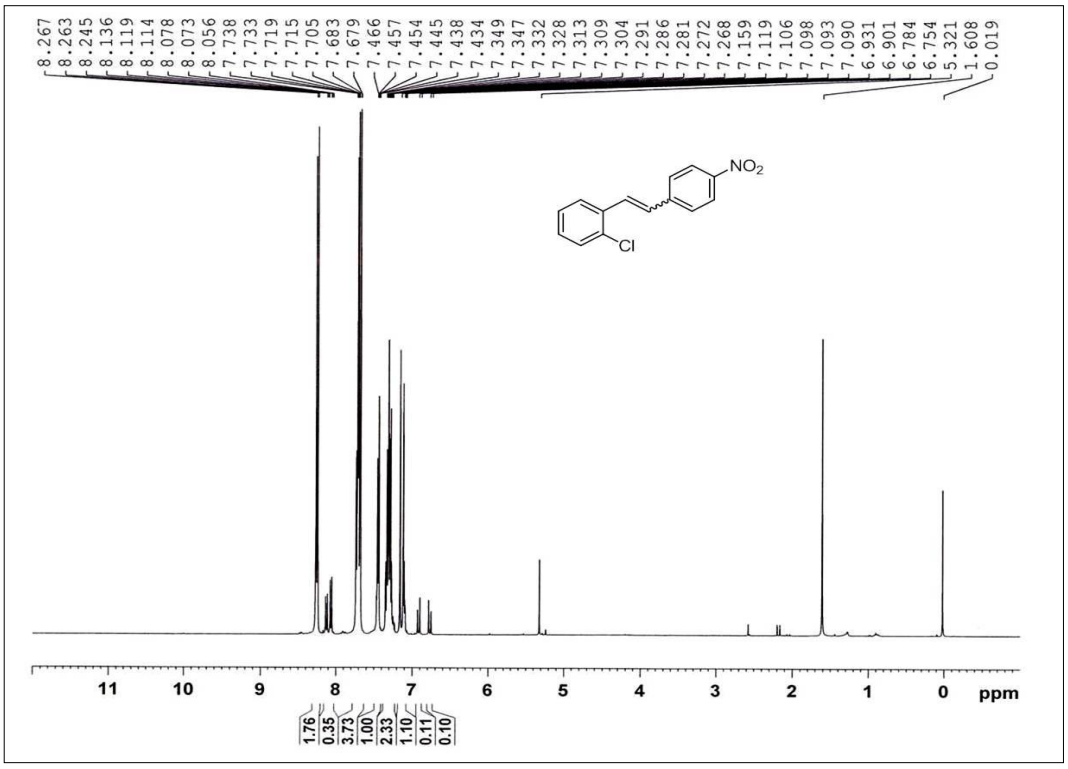
^{1}H-NMR of compound 10



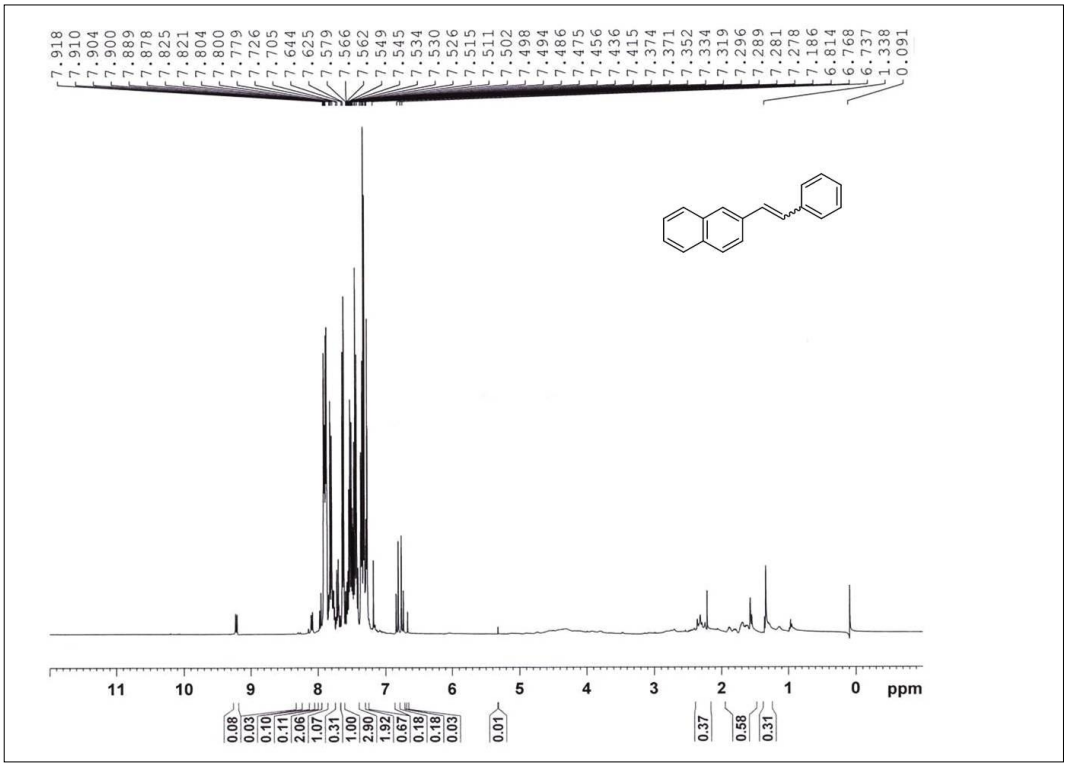
^{1}H-NMR of compound 11



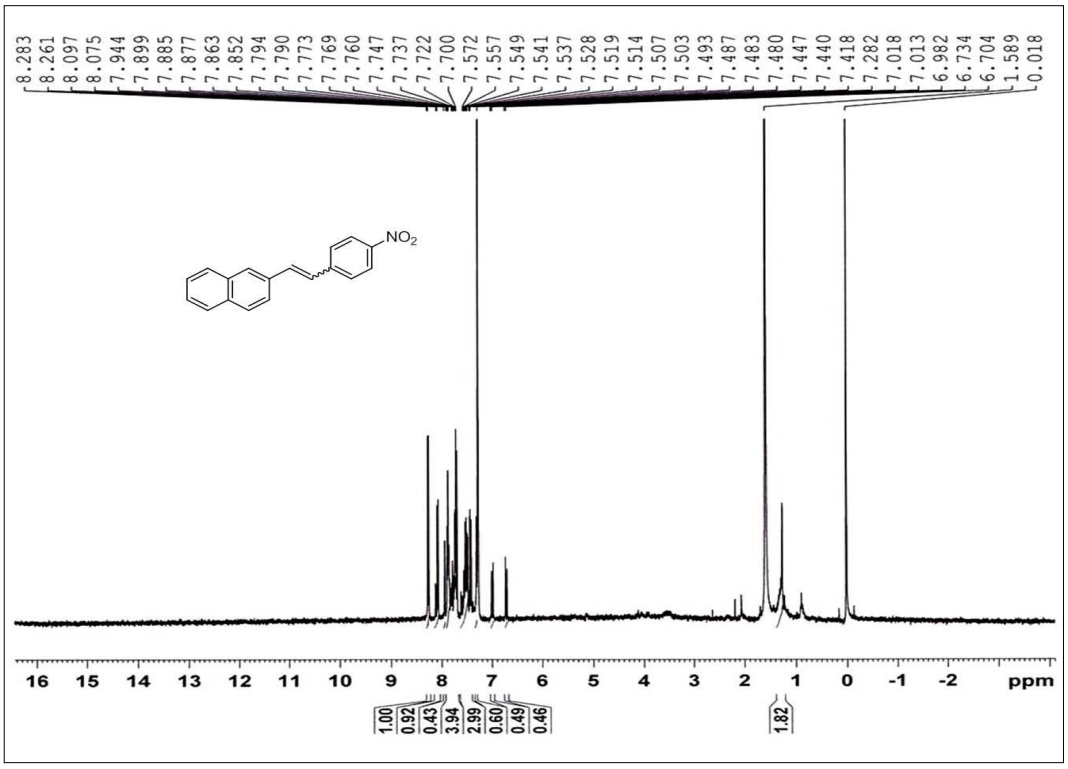
[1]H-NMR of compound 13



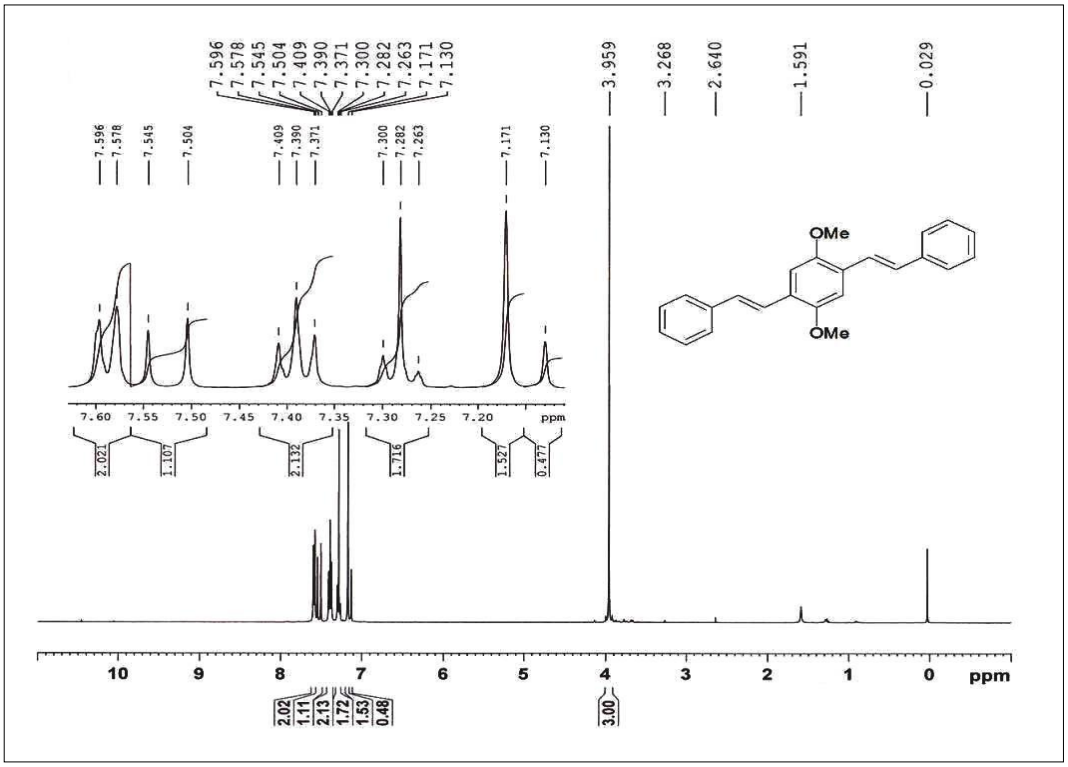
[1]H-NMR of compound 14



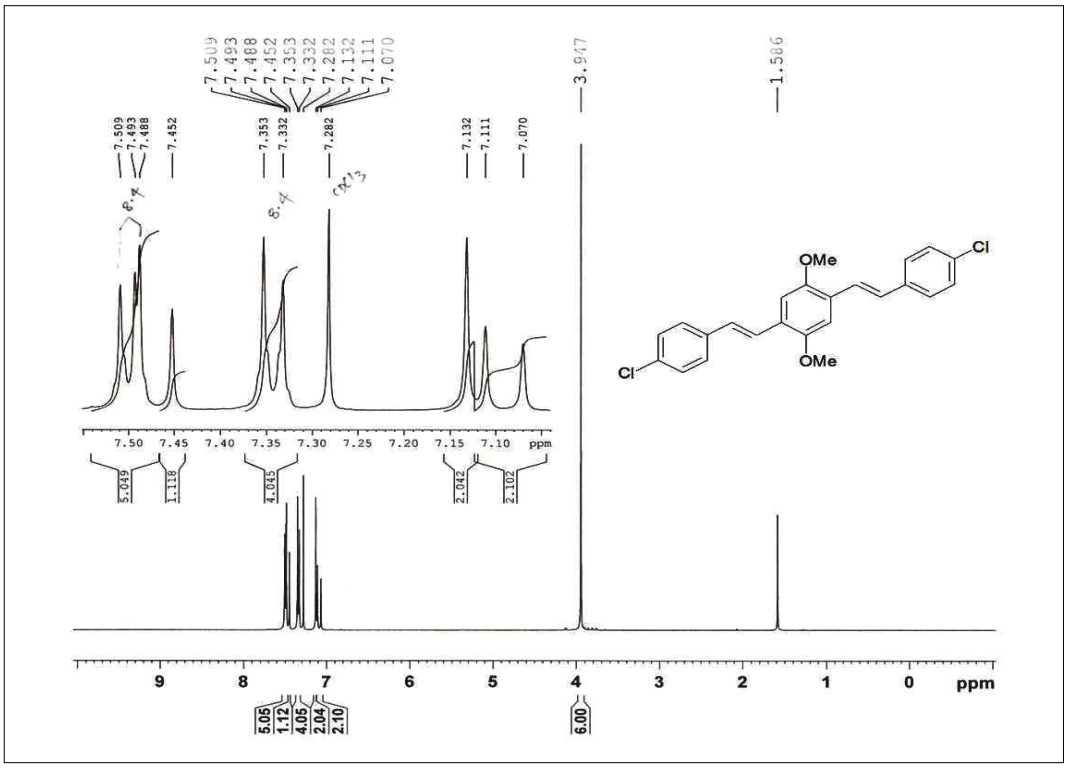
^{1}H-NMR of compound 16



^{1}H-NMR of compound 17

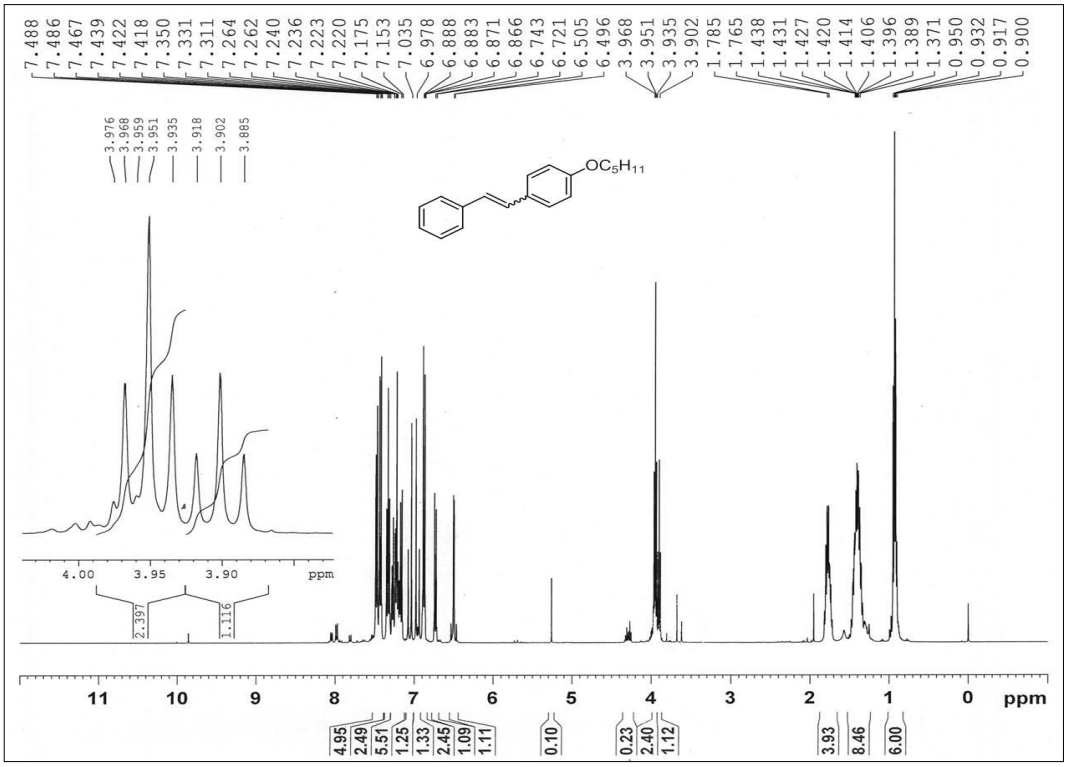


^{1}H-NMR of compound 20

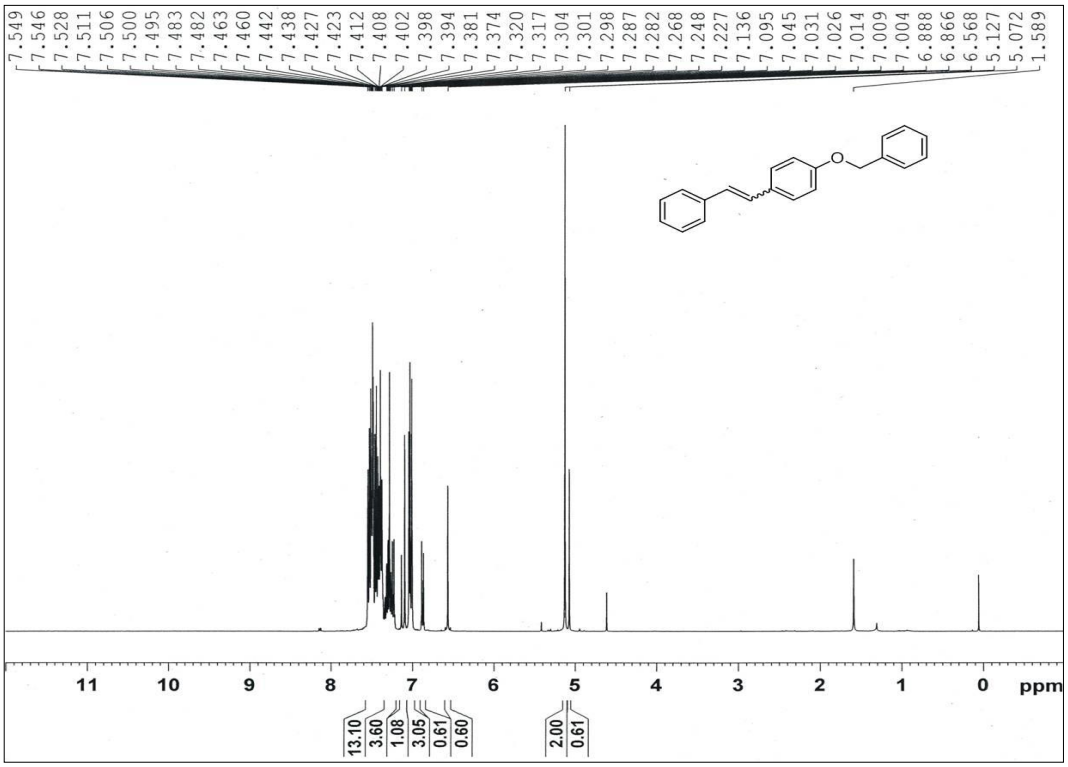


^{1}H-NMR of compound 21

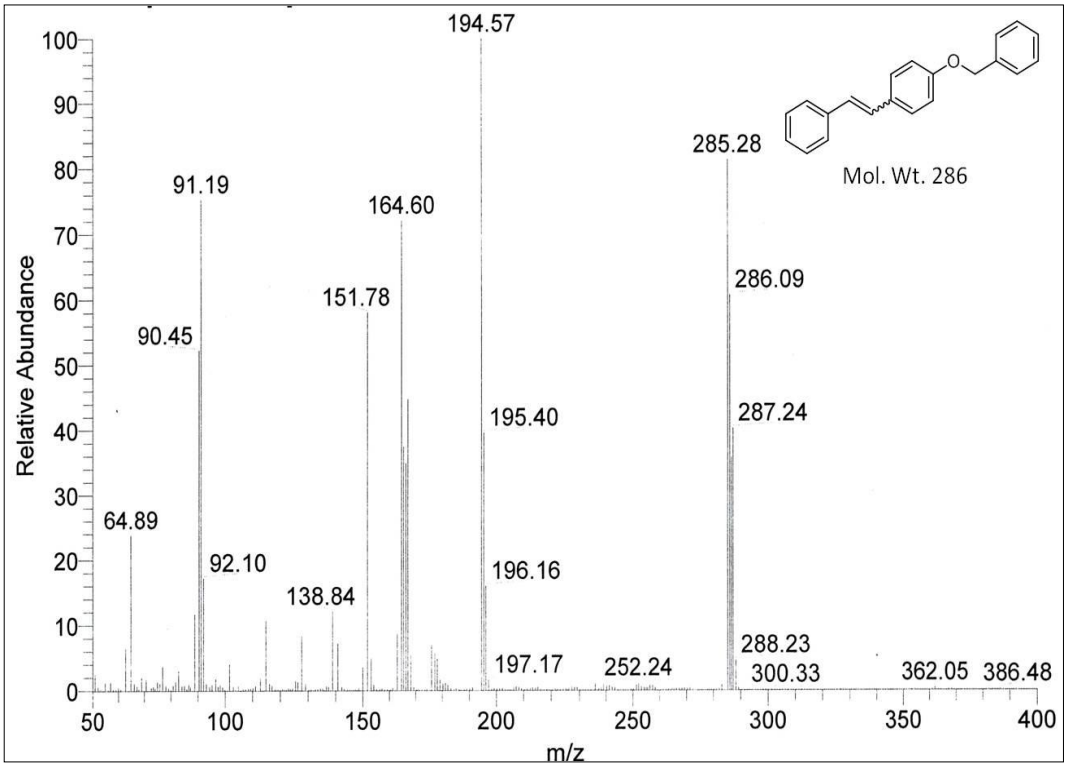
2.4.5 Spectral Data for the examples of O-Alkylation-Wittig



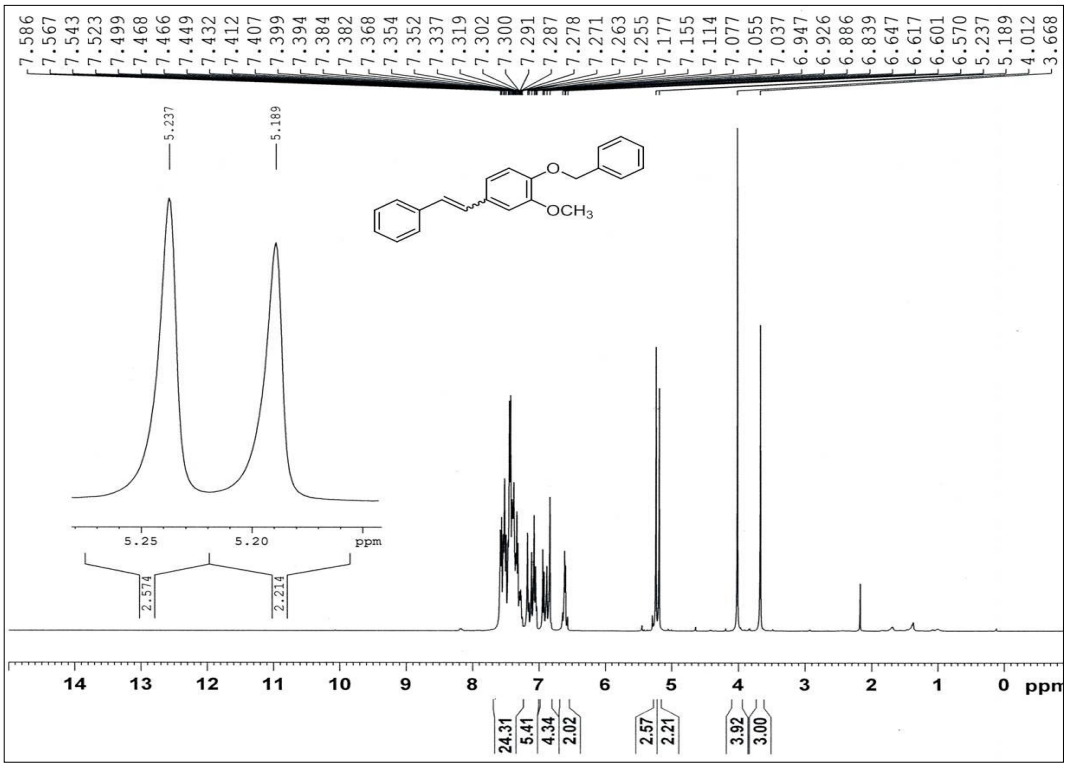
^{1}H-NMR of compound 29



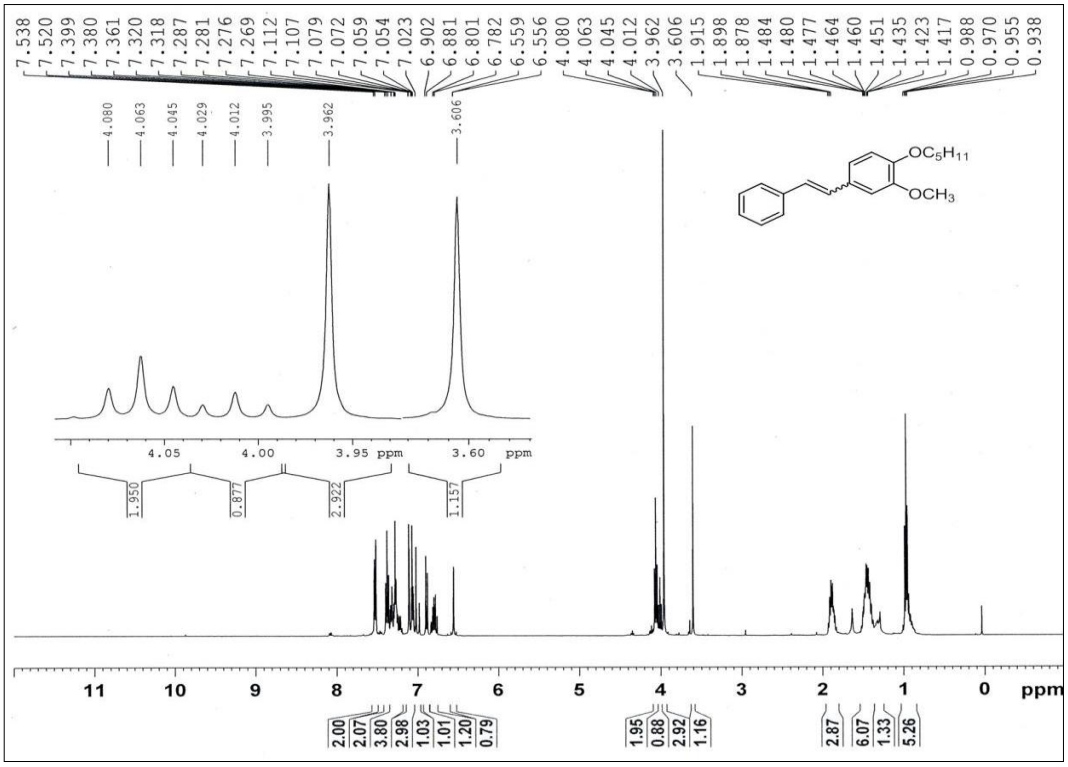
^{1}H-NMR of compound 30



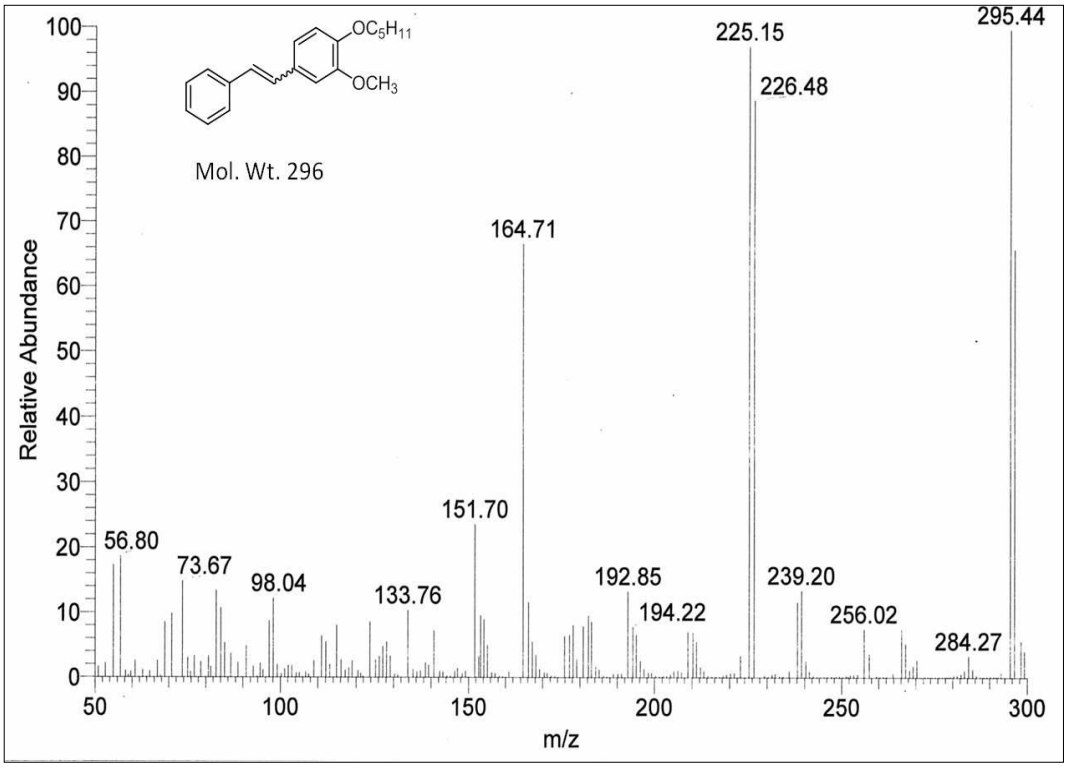
Mass spectra for compound 30



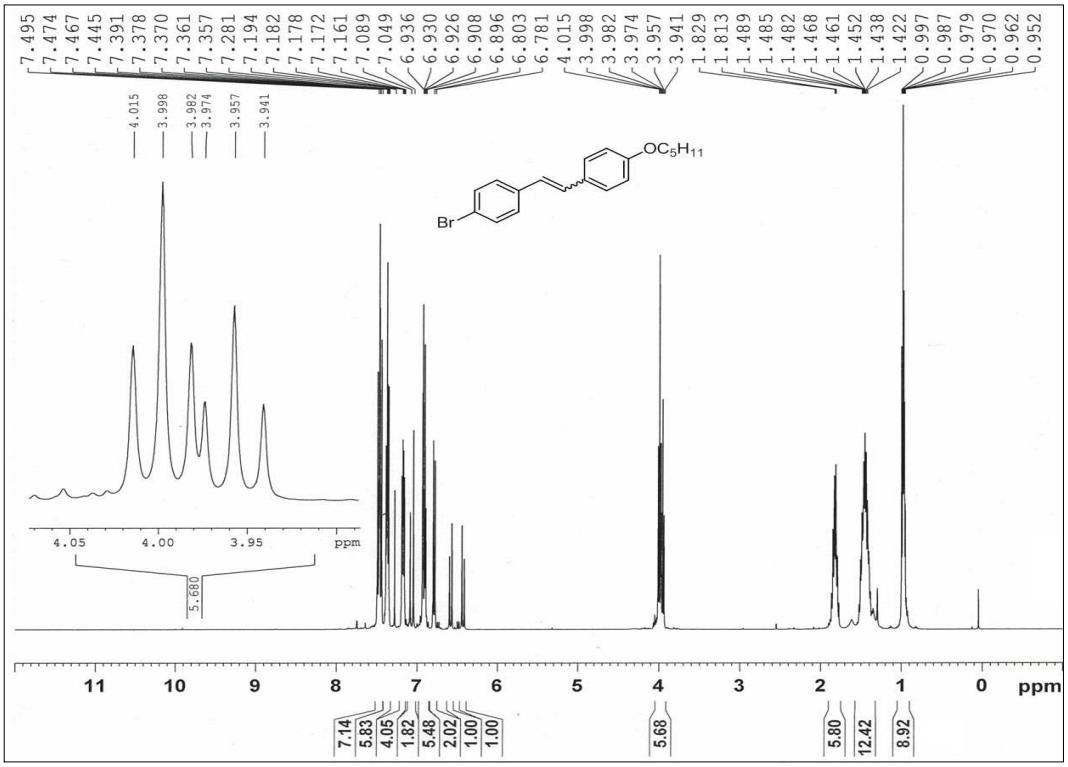
^{1}H-NMR of compound 31



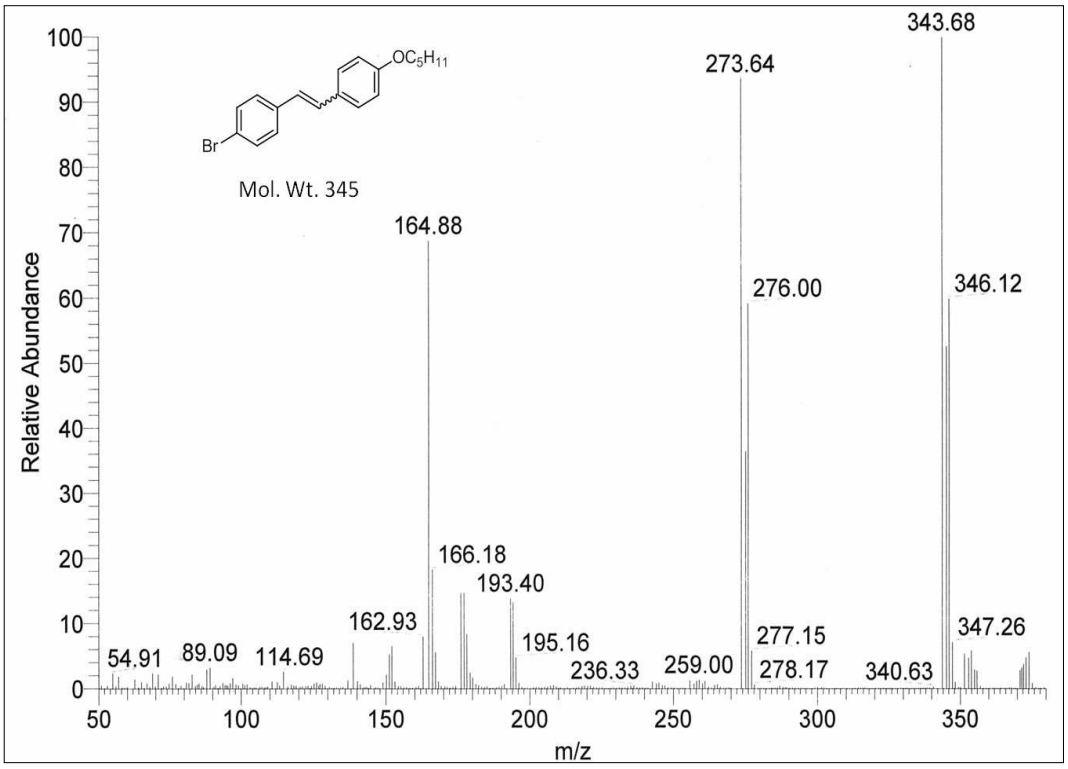
^{1}H-NMR of compound 32



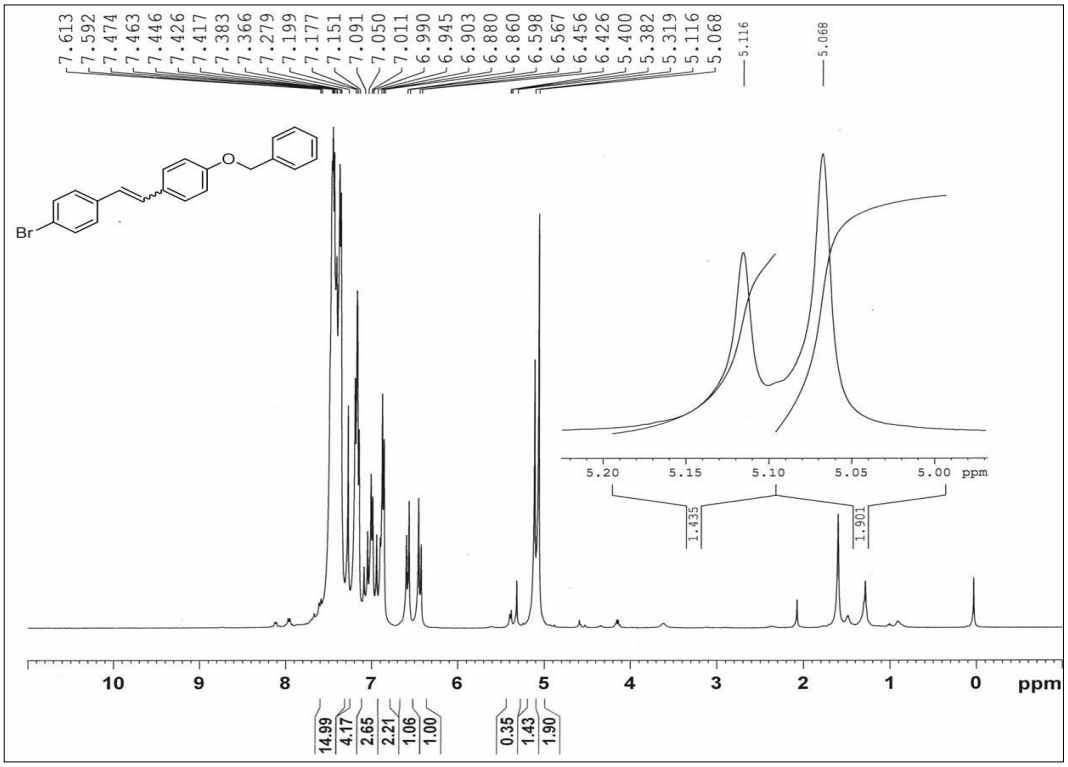
Mass spectra for compound 32



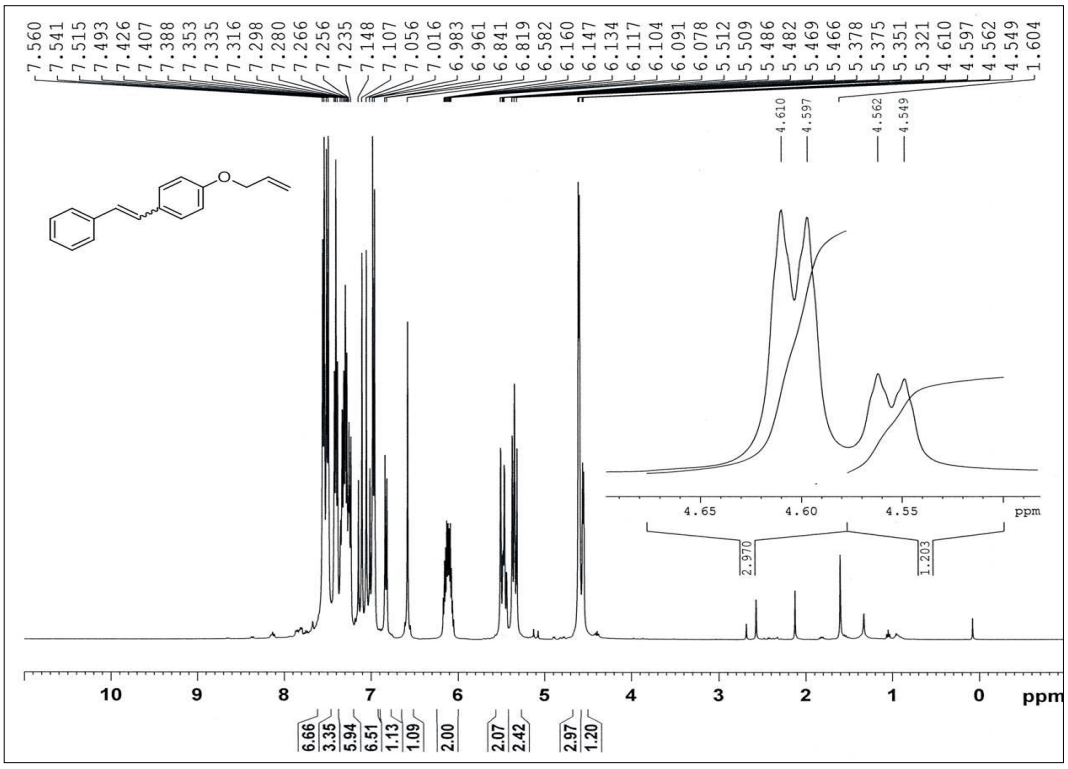
^{1}H-NMR of compound 33



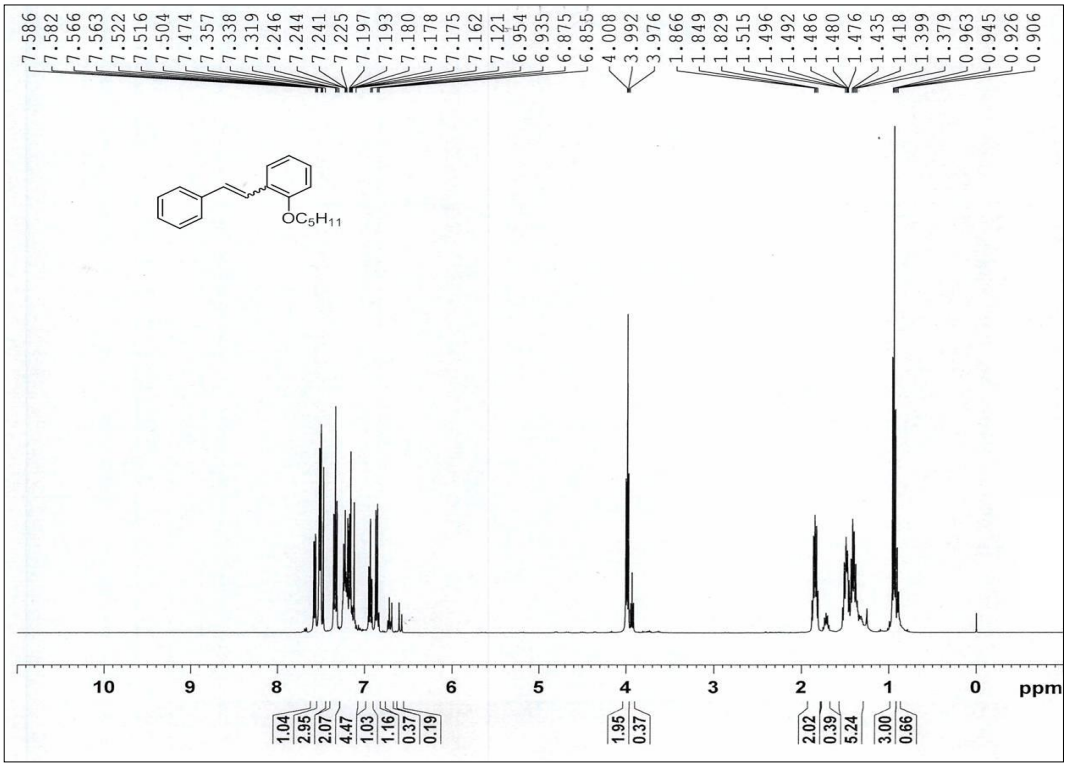
Mass spectra for compound 33



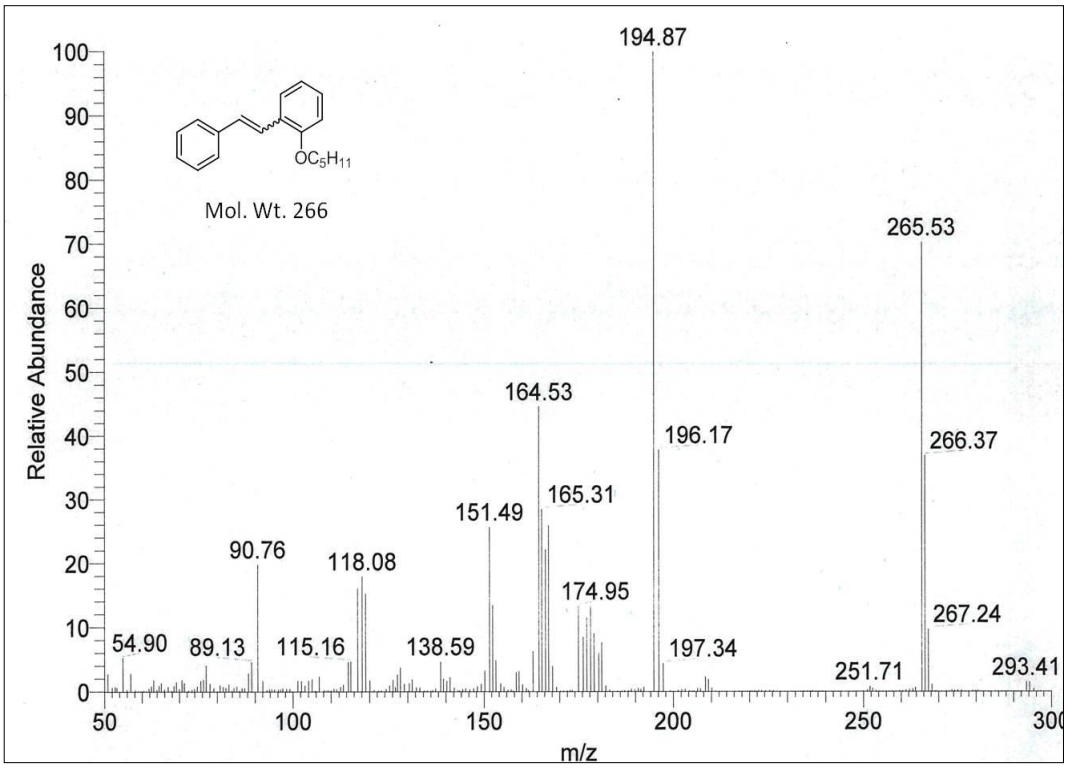
^{1}H-NMR of compound 34



^{1}H-NMR of compound 35

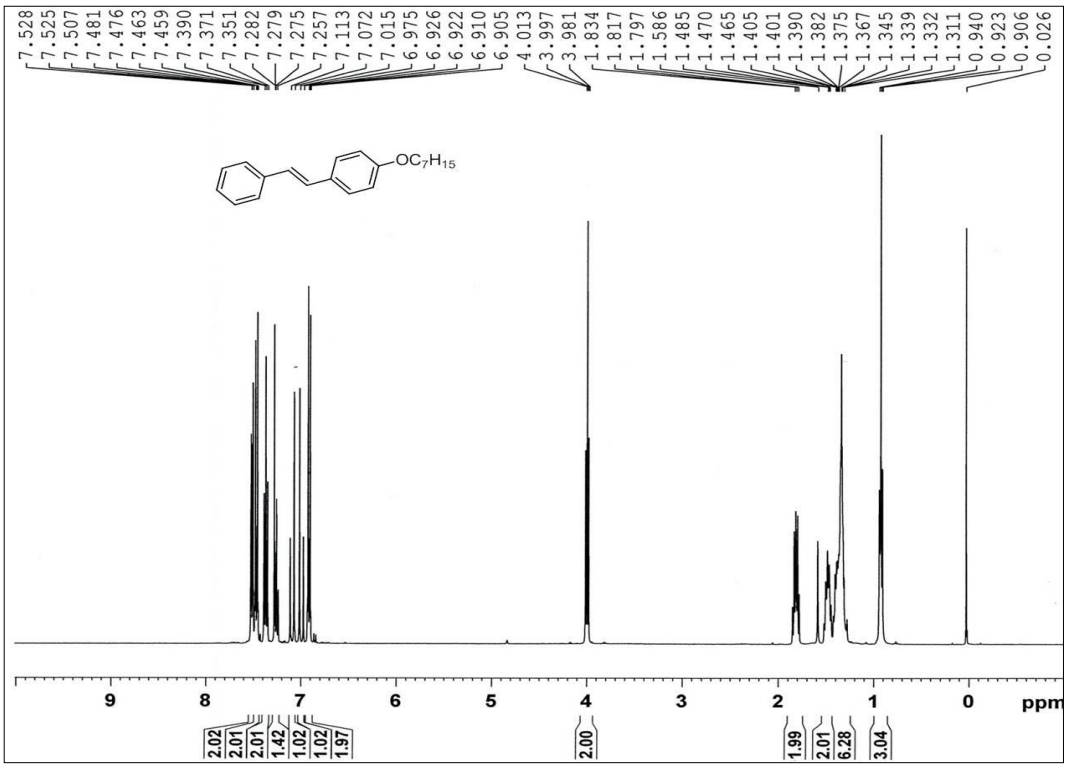


^{1}H-NMR of compound 36

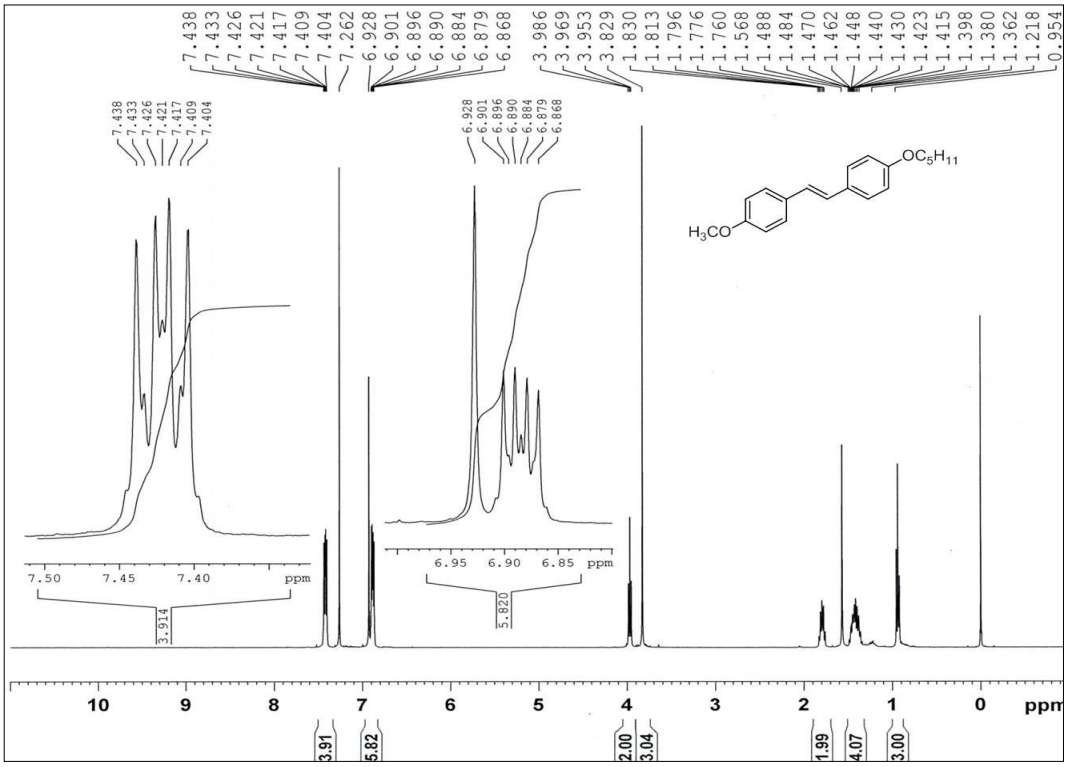


Mass spectra for compound 36

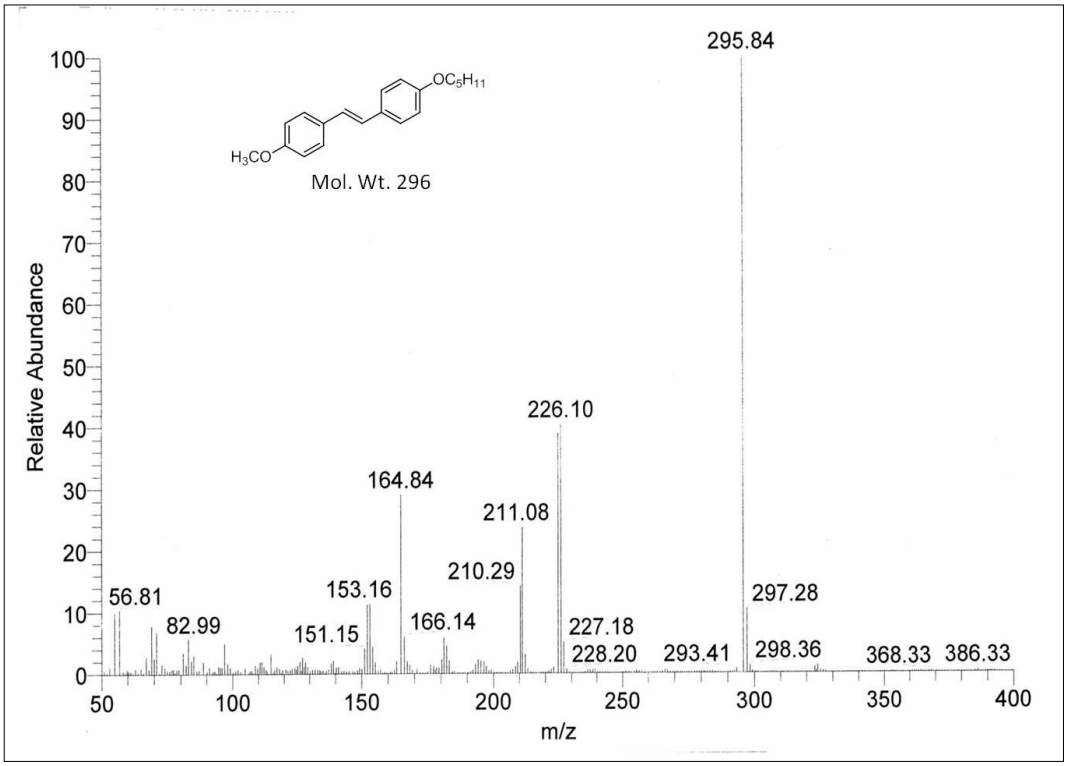
2.4.6 Spectral Data for the examples of O-Alkylation-Wittig



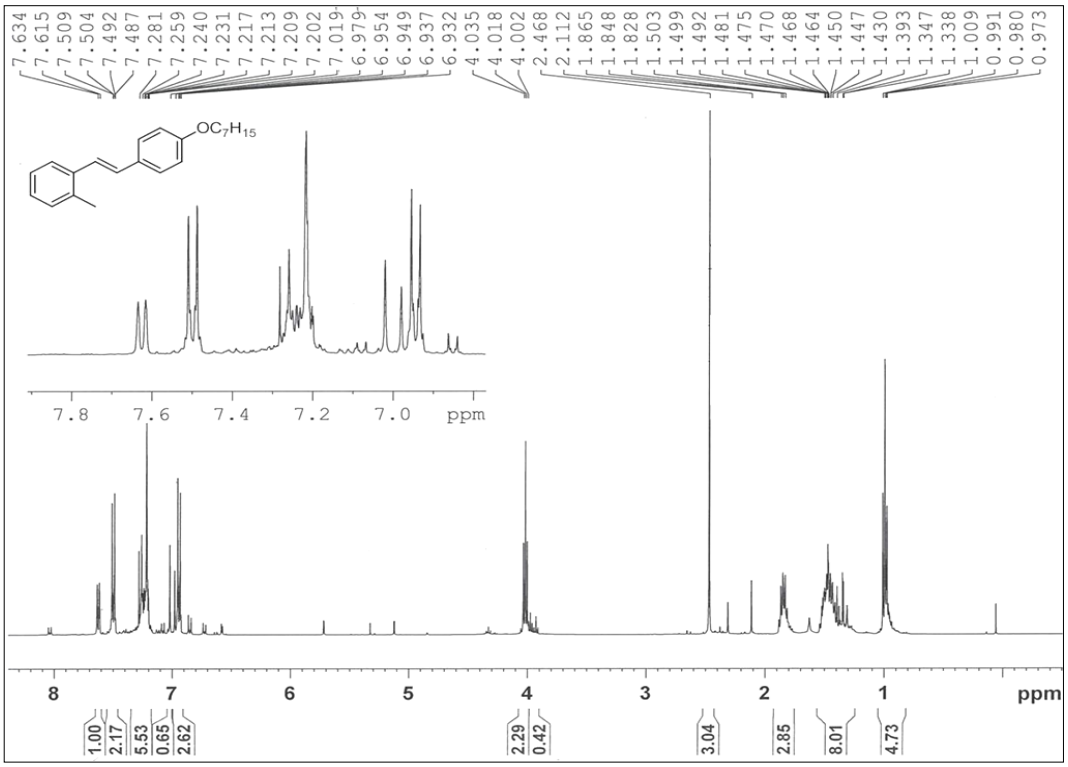
^{1}H-NMR of compound 42



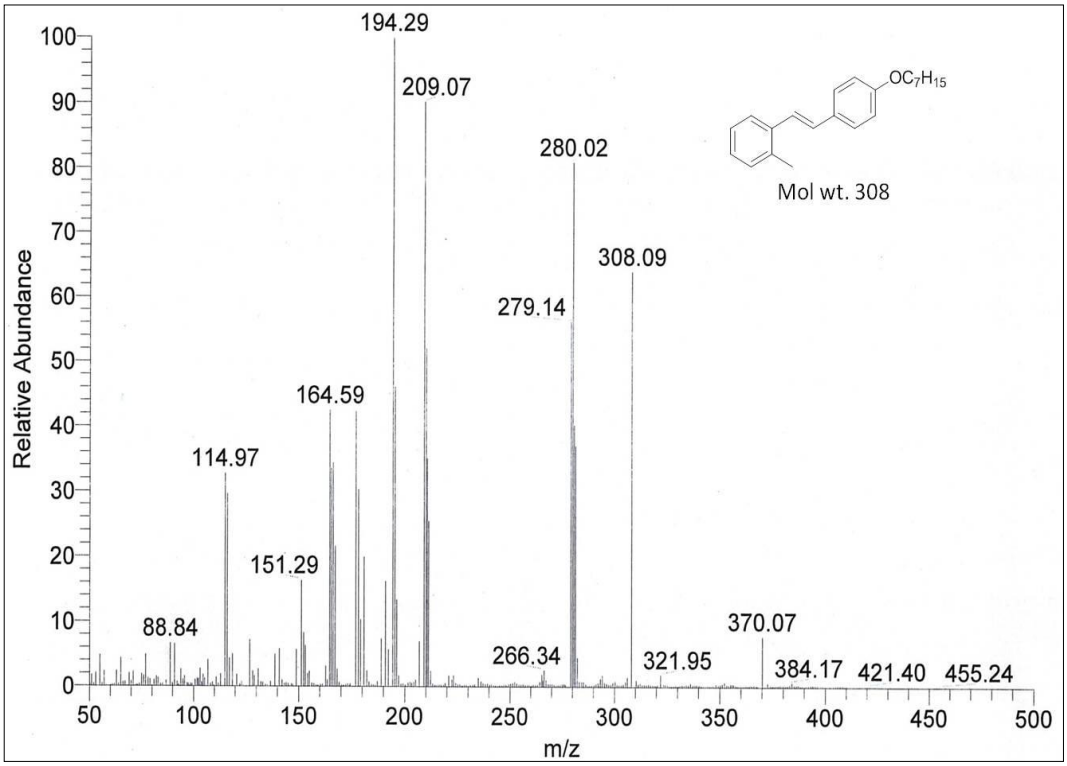
^{1}H-NMR of compound 43



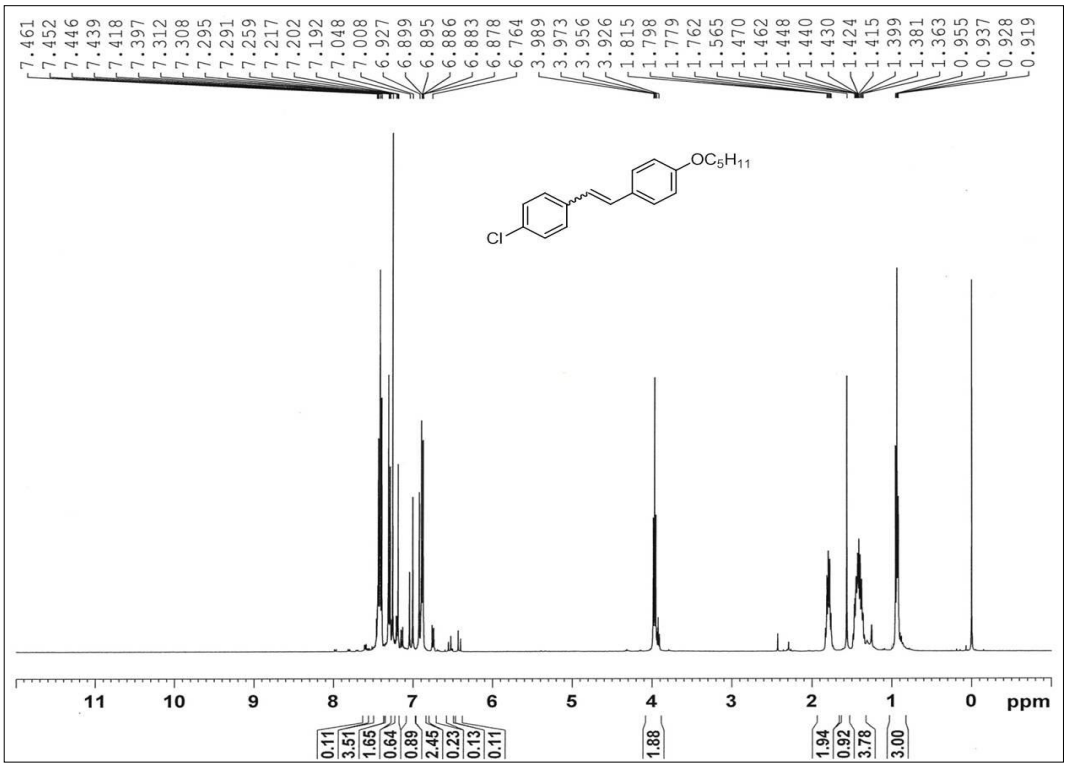
Mass spectra for compound 43



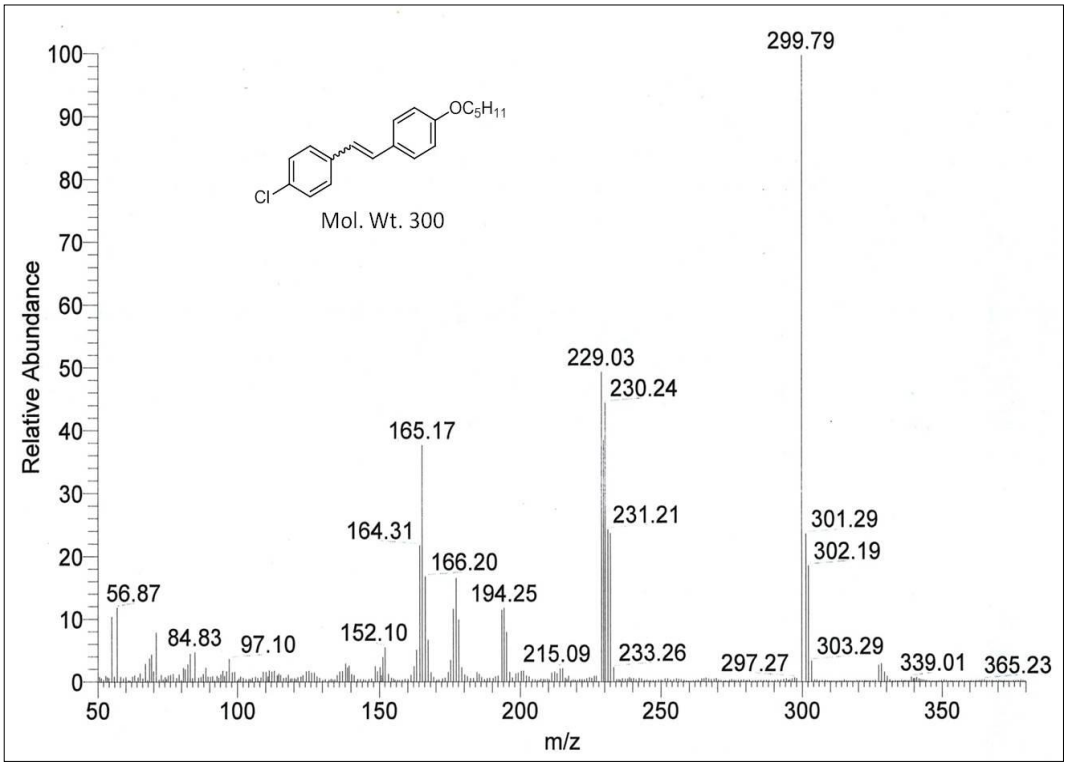
^{1}H-NMR of compound 44



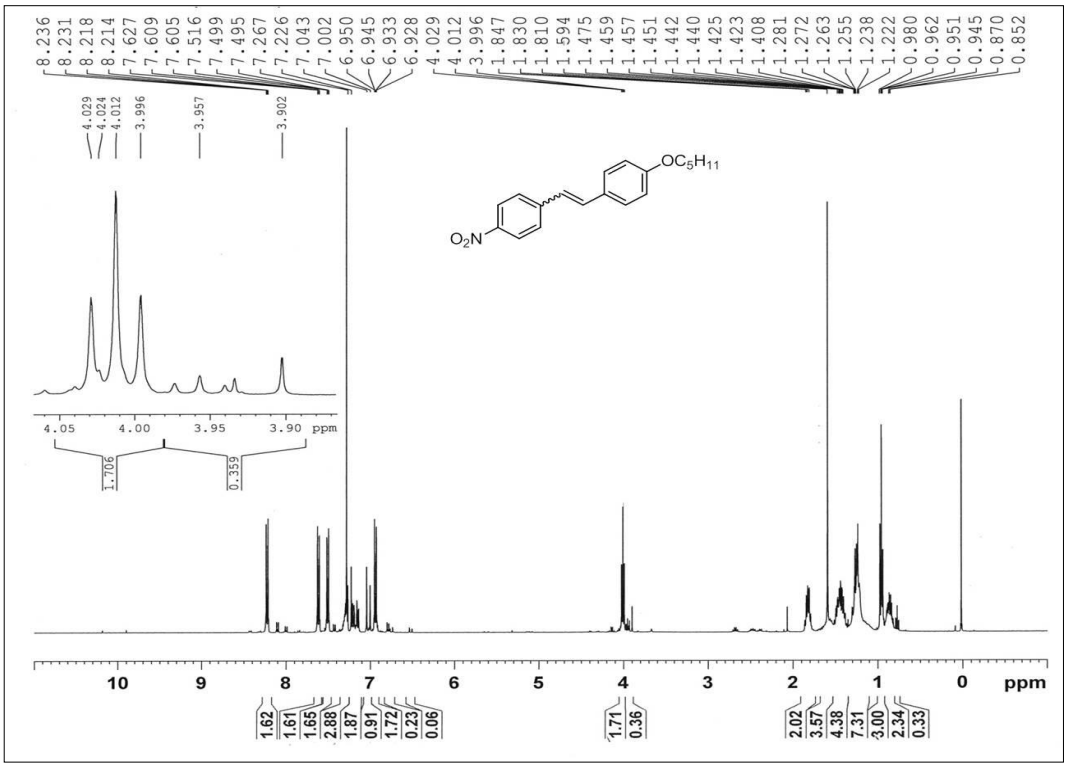
Mass spectra for compound 44



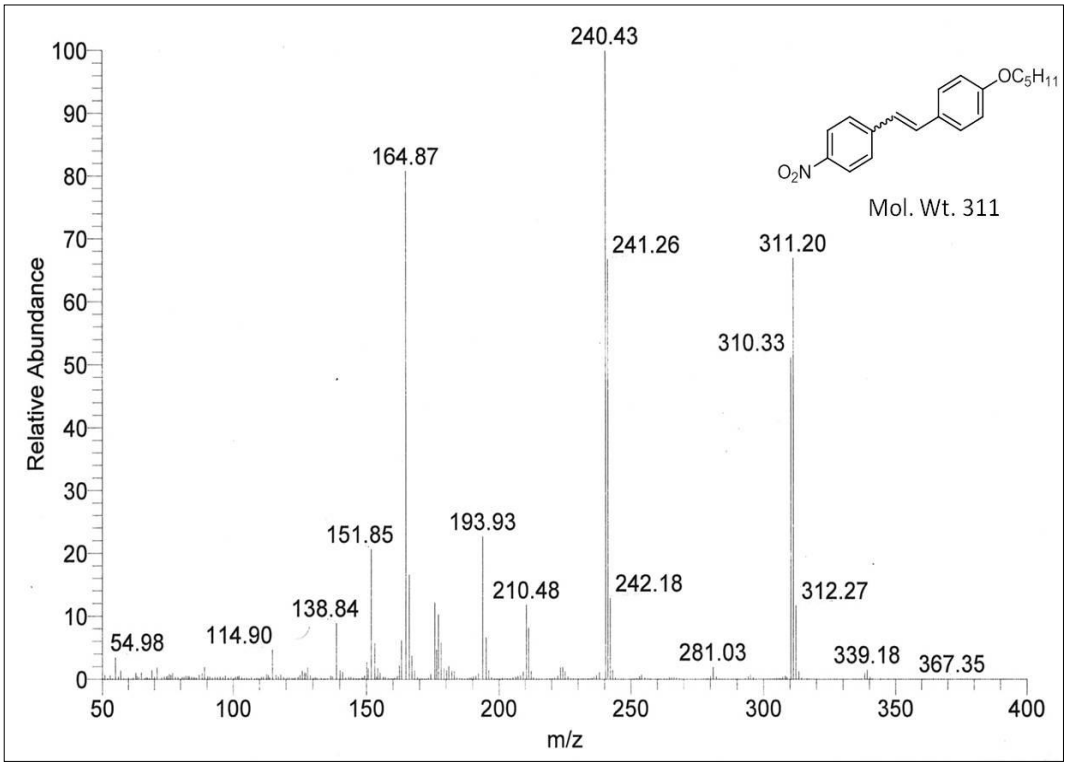
^{1}H-NMR of compound 45



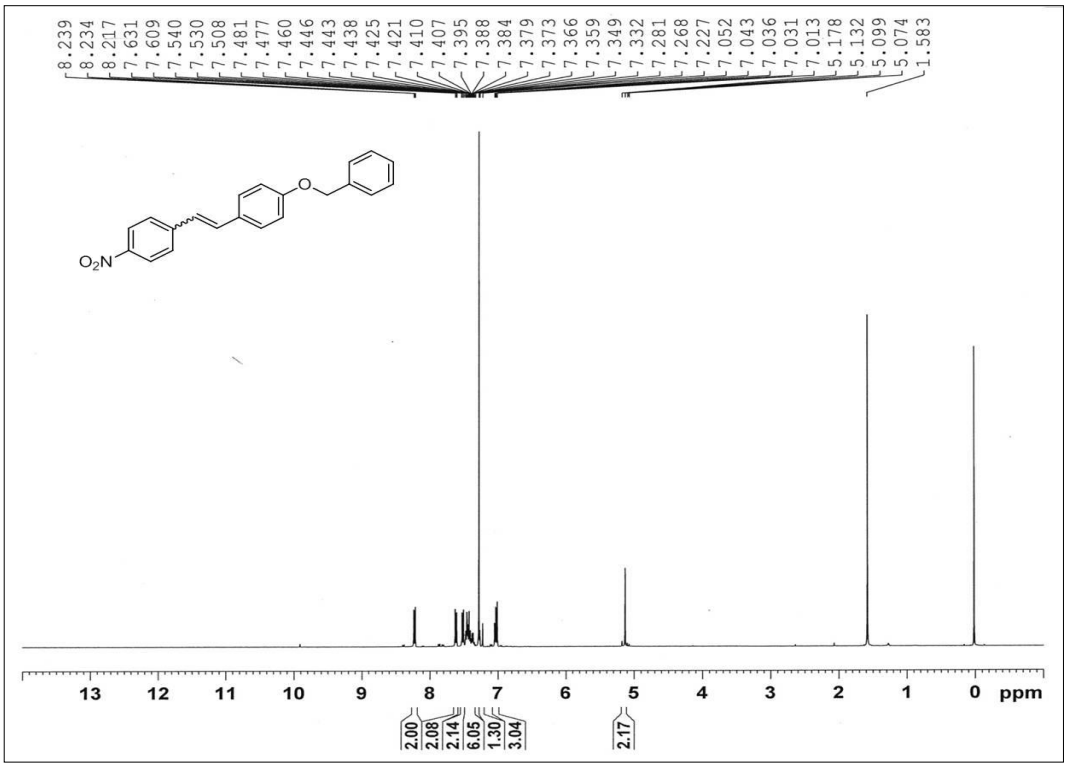
Mass spectra for compound 45



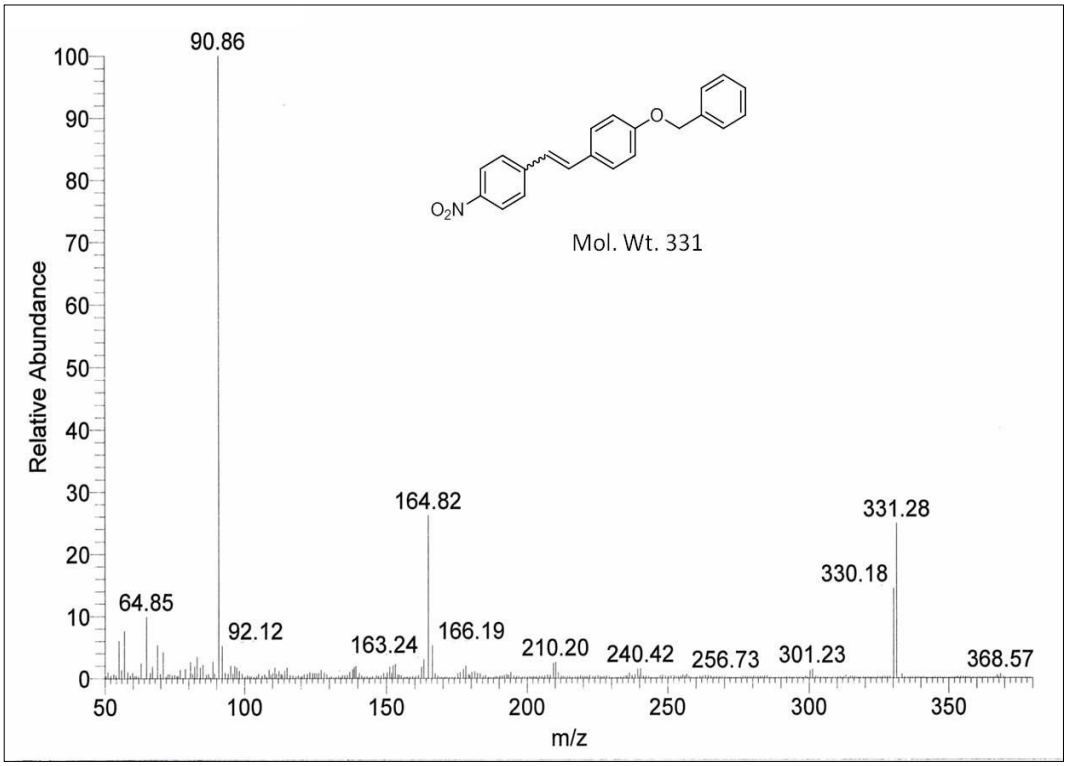
^{1}H-NMR of compound 46



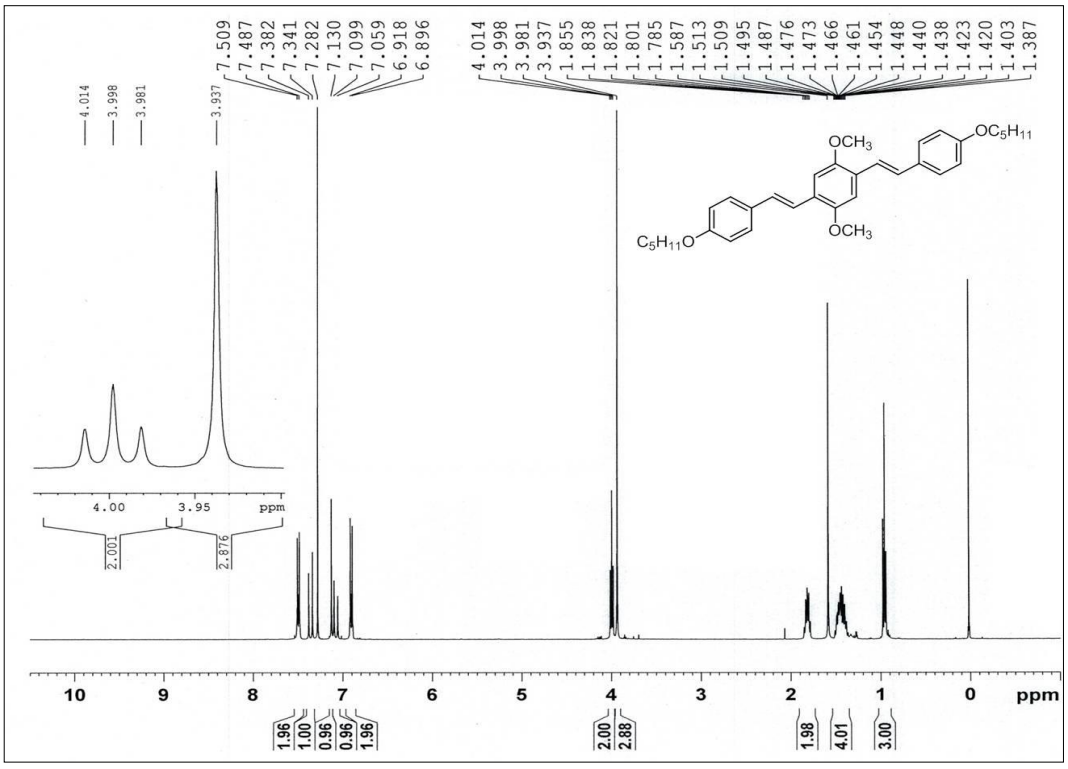
Mass spectra for compound 46



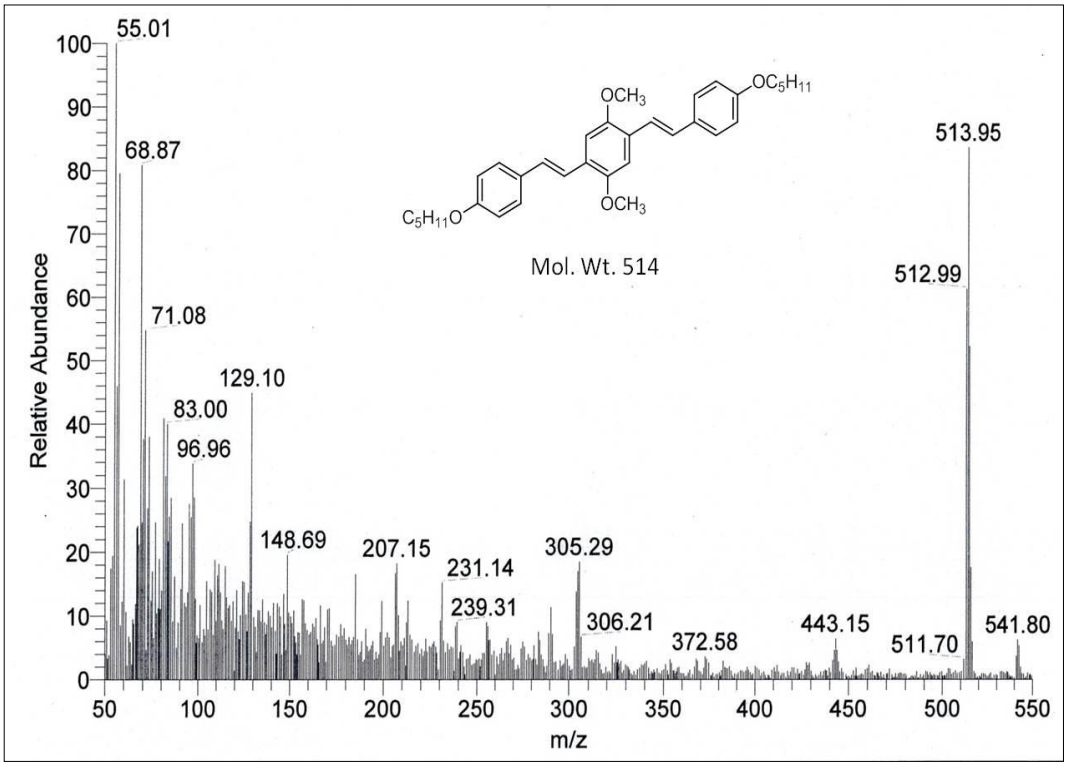
^{1}H-NMR of compound 47



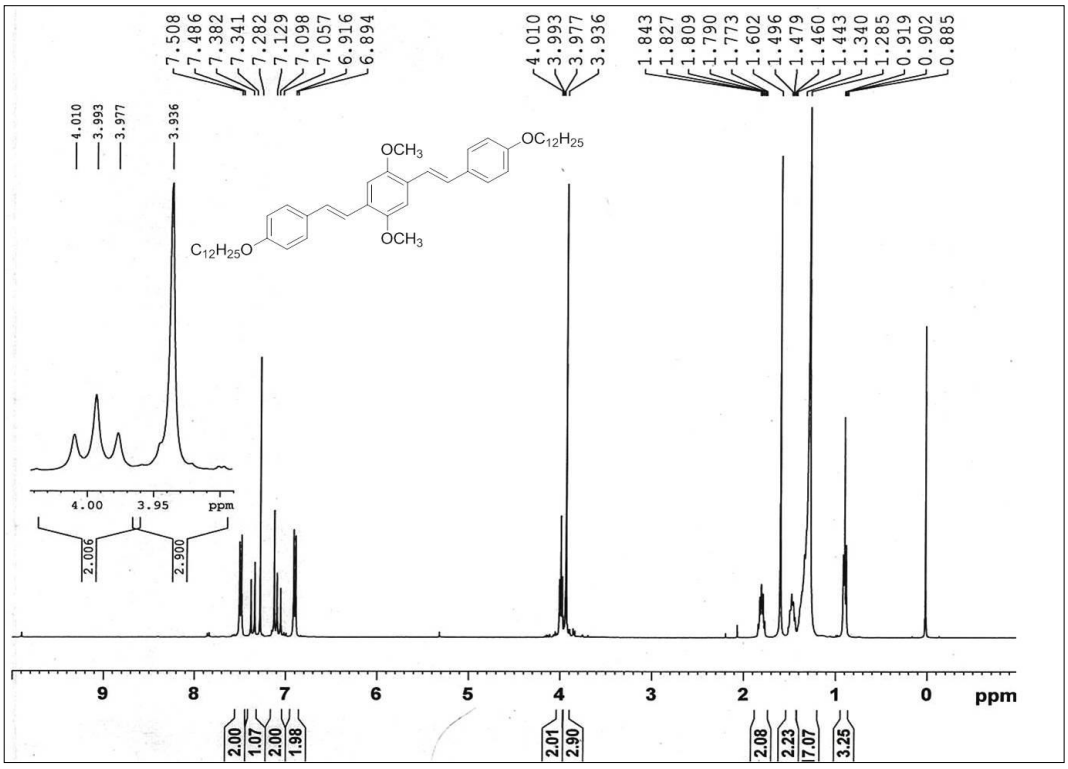
Mass spectra for compound 47



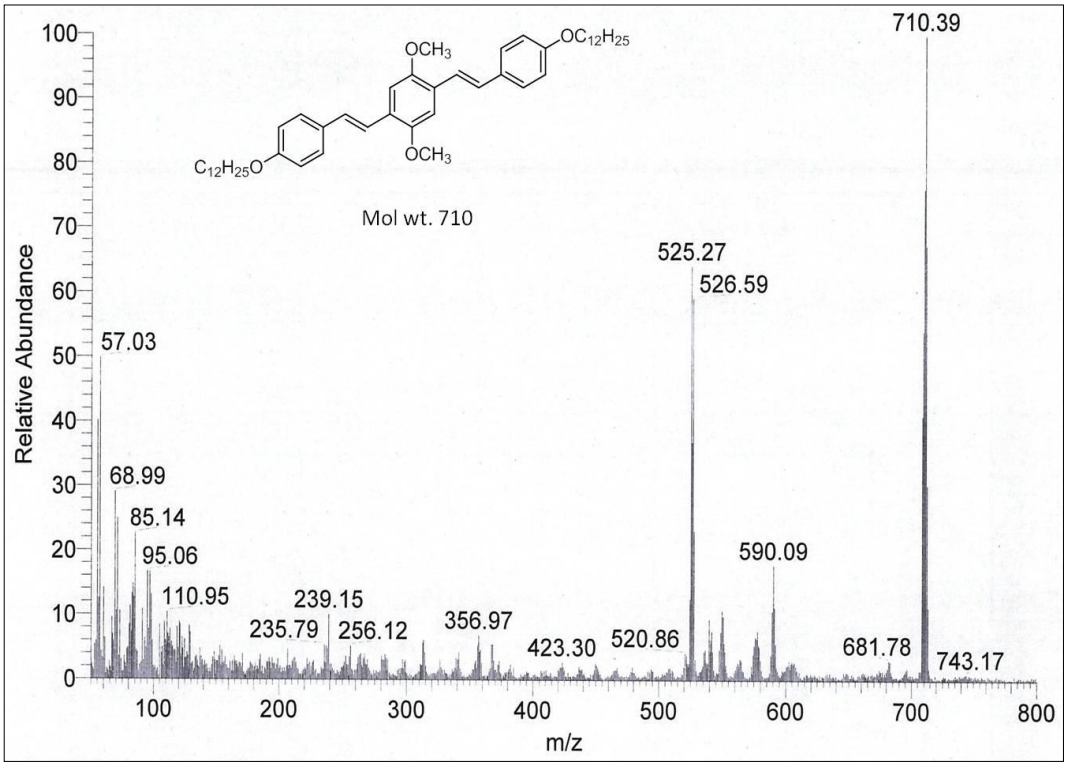
^{1}H-NMR of compound 50



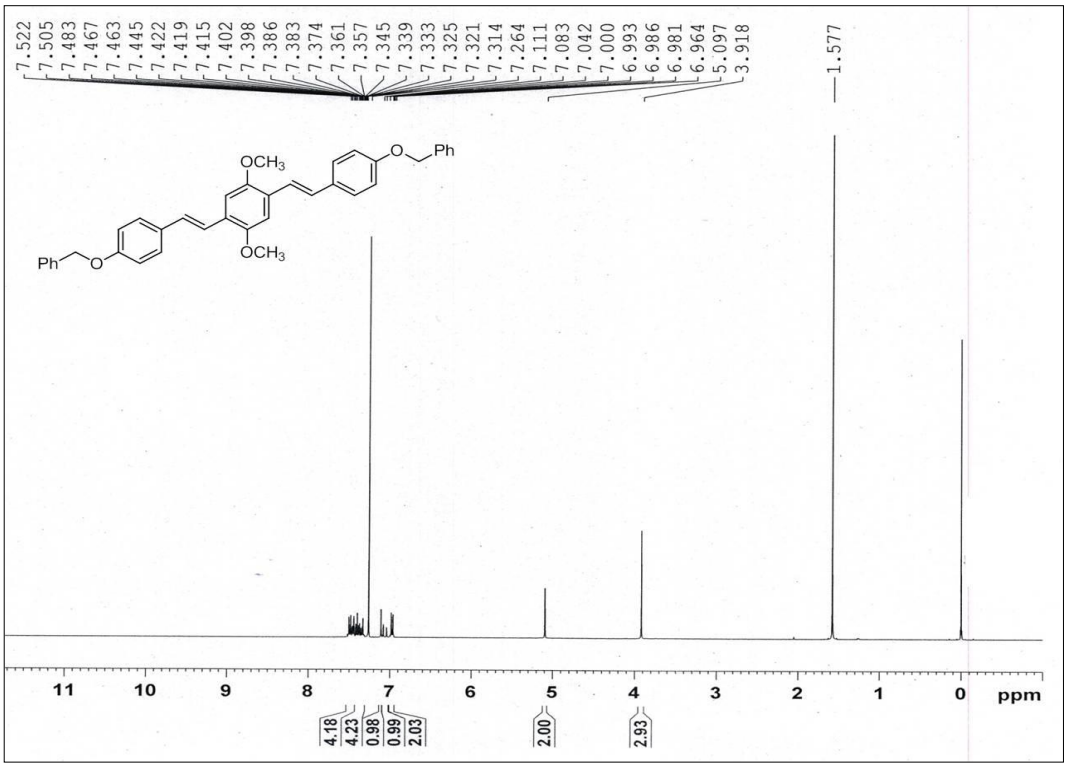
Mass spectra for compound 50



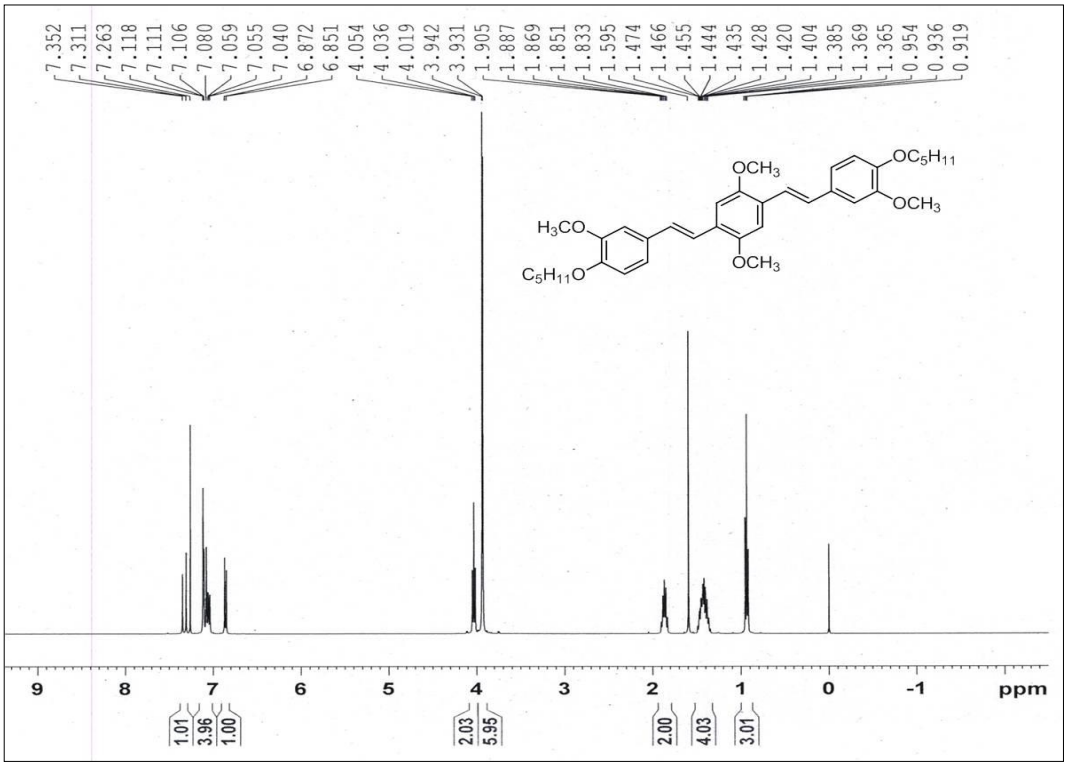
^{1}H-NMR of compound 51



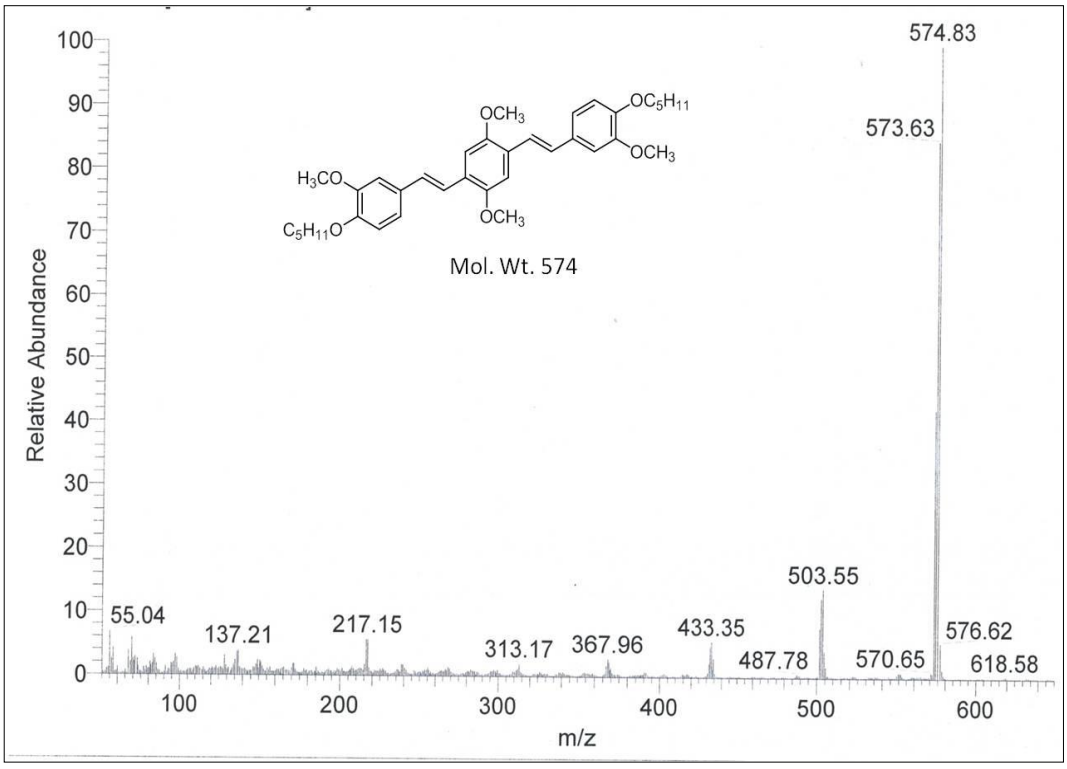
Mass spectra for compound 51



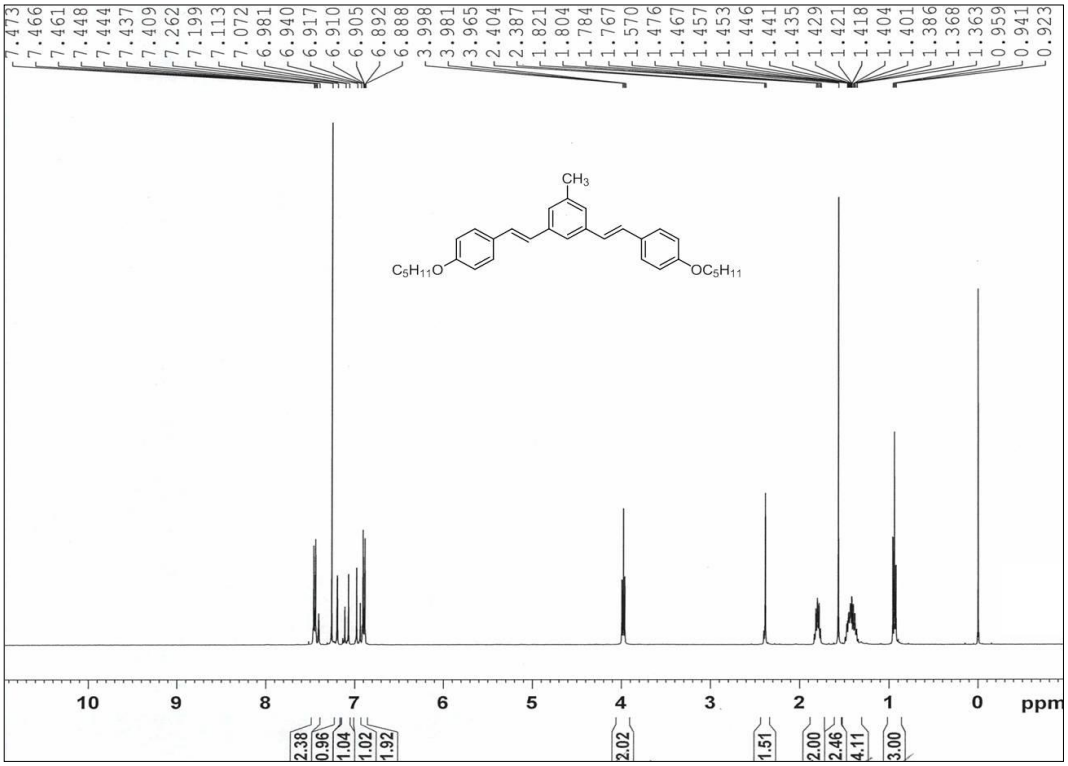
^{1}H-NMR of compound 52



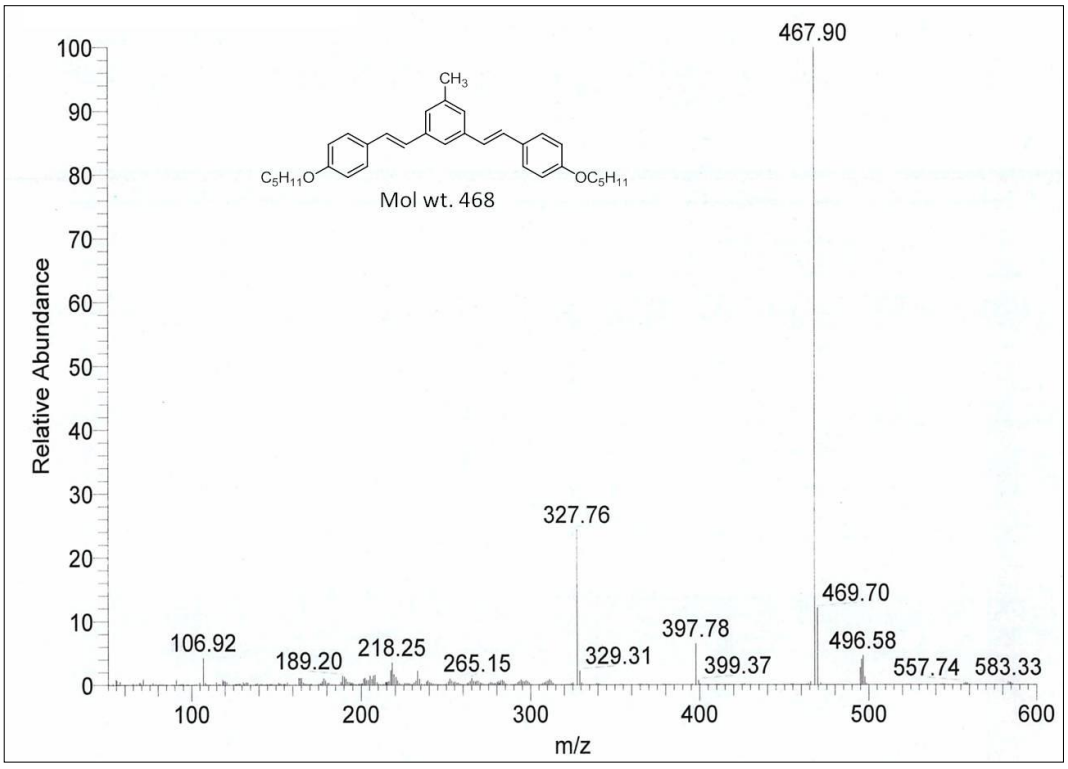
^{1}H-NMR of compound 53



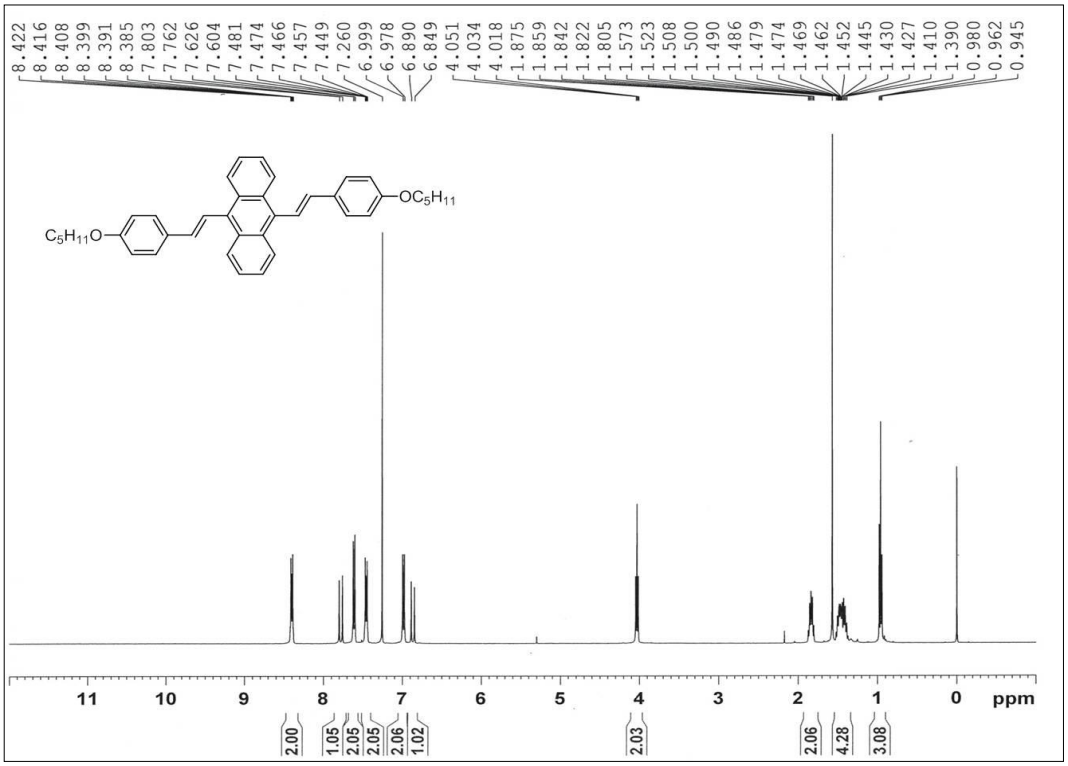
Mass spectra for compound 53



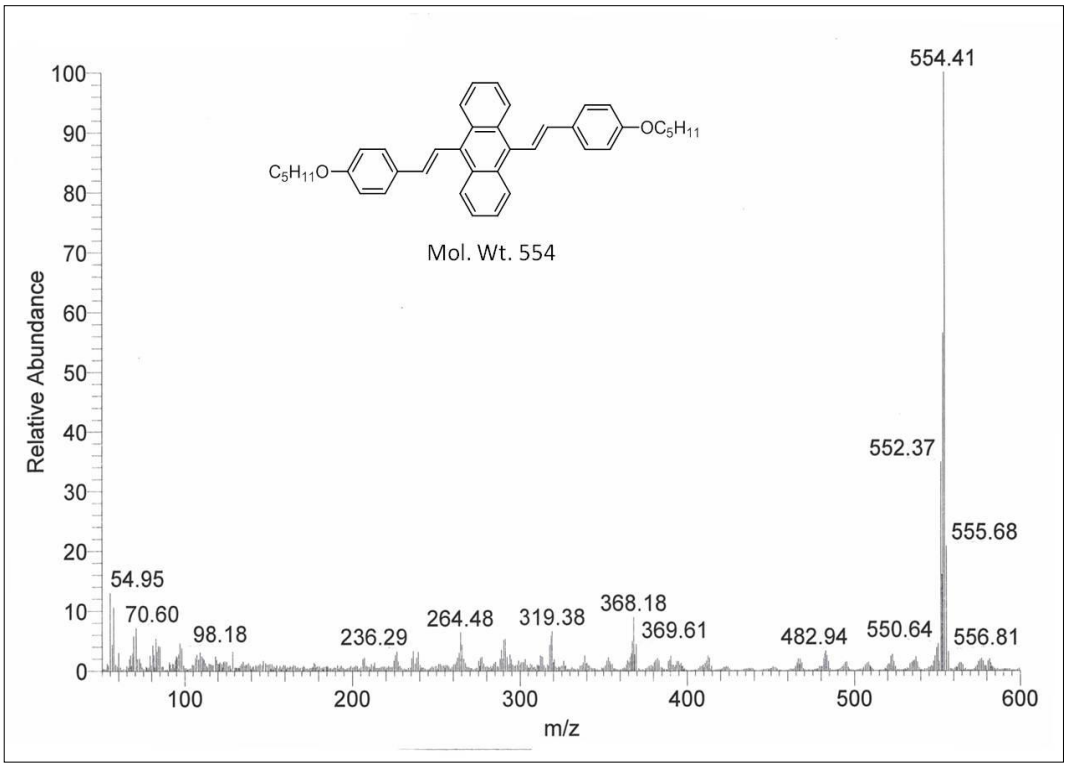
^{1}H-NMR of compound 59



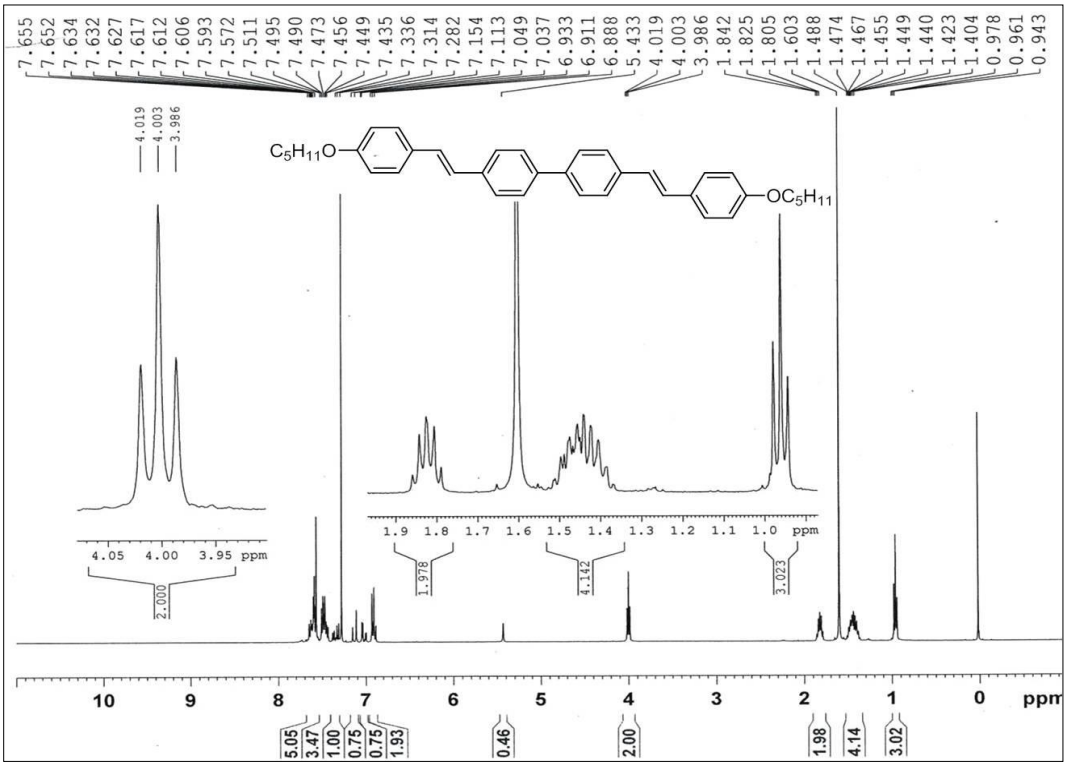
Mass spectra for compound 59



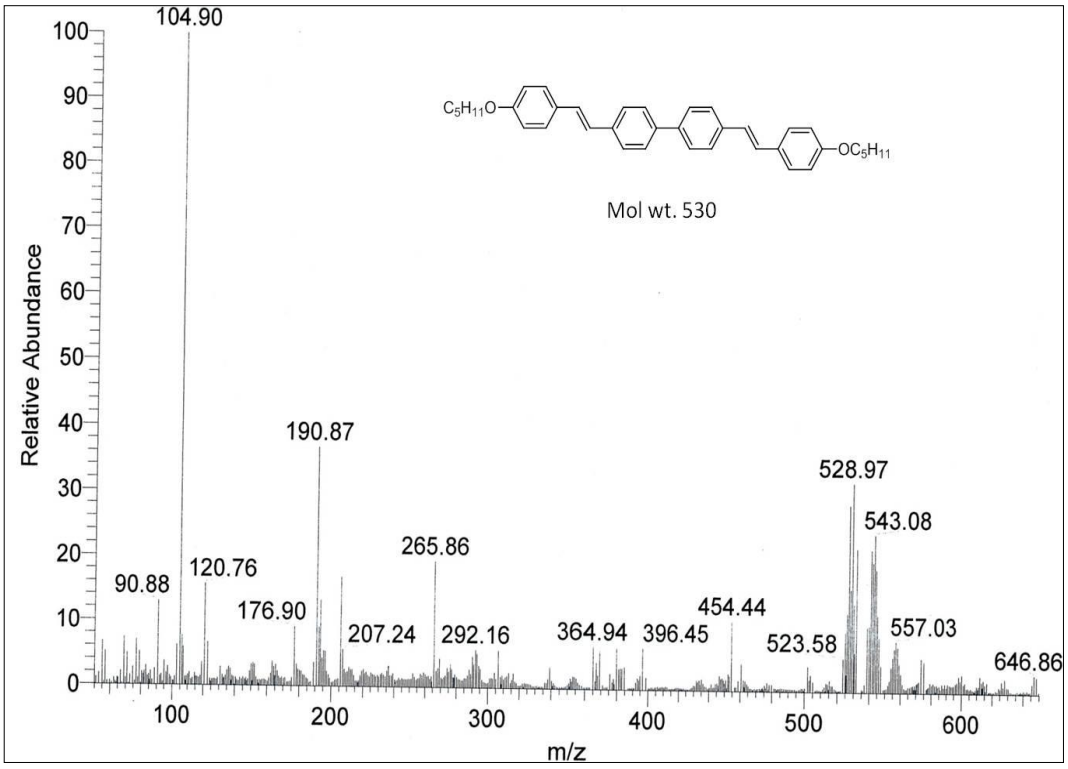
^{1}H-NMR of compound 60



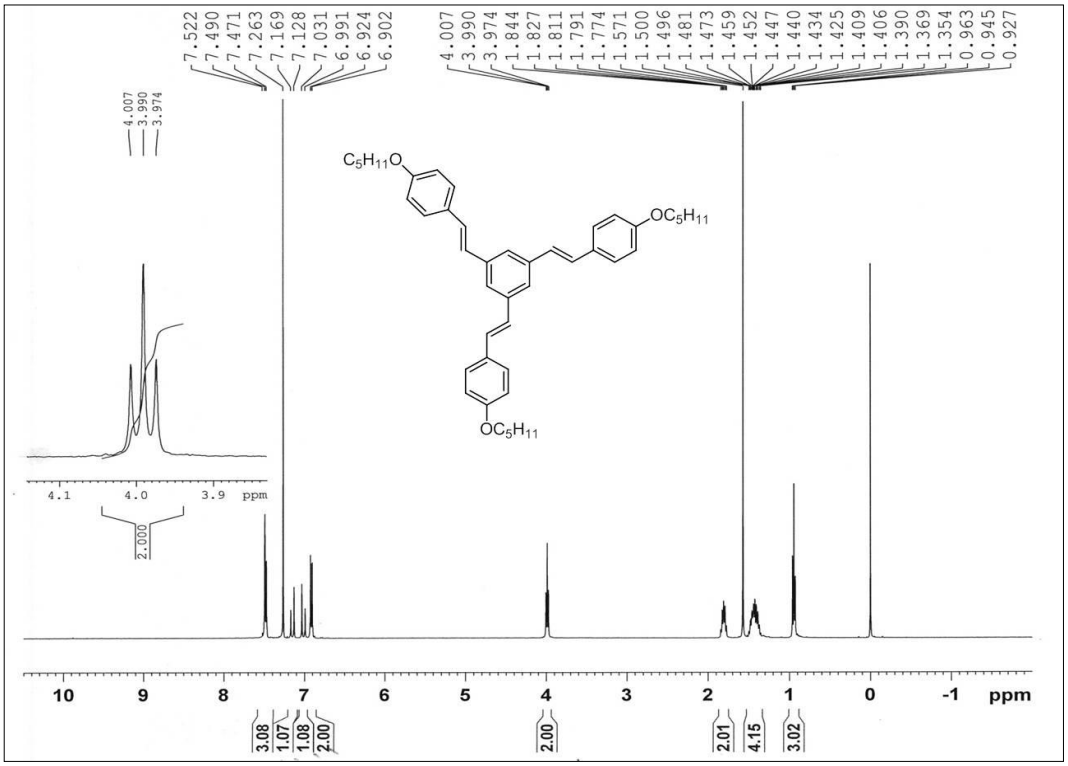
Mass spectra for compound 60



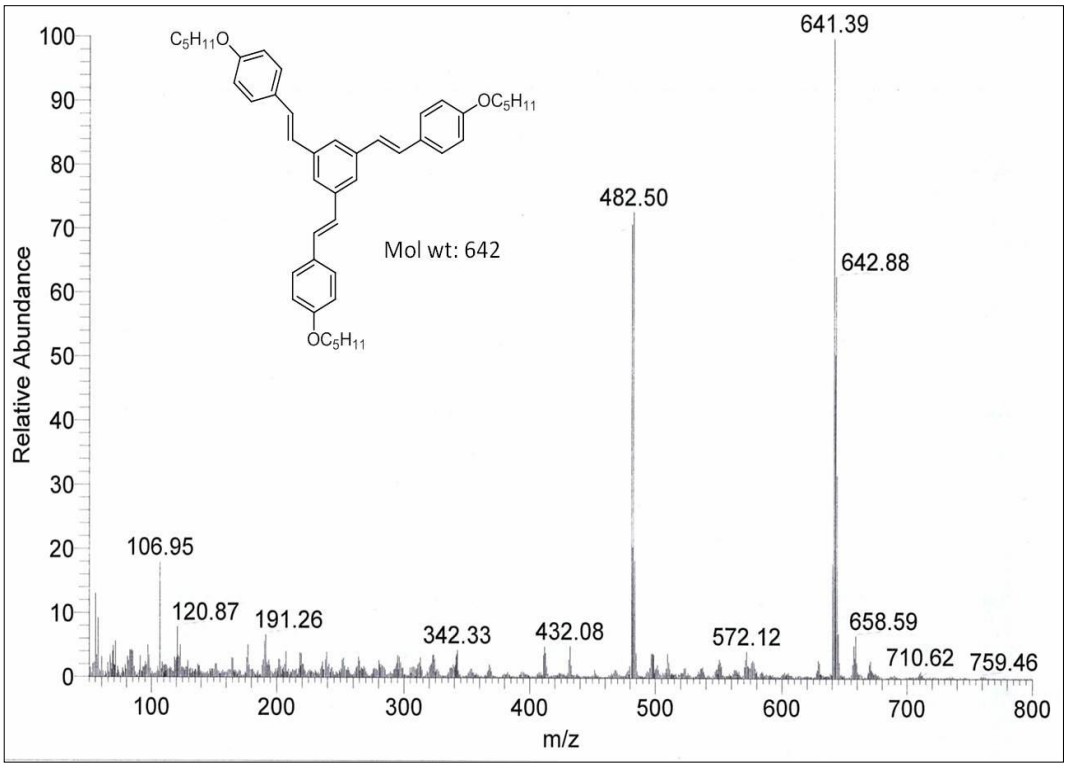
^{1}H-NMR of compound 61



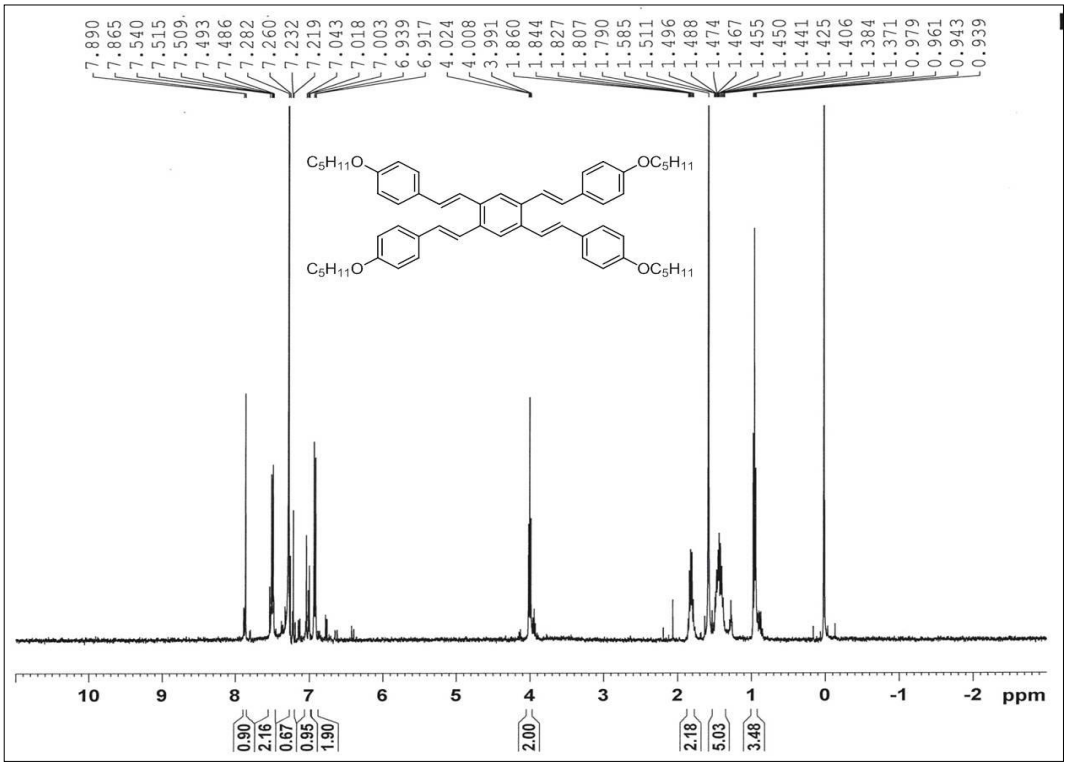
Mass spectra for compound 61



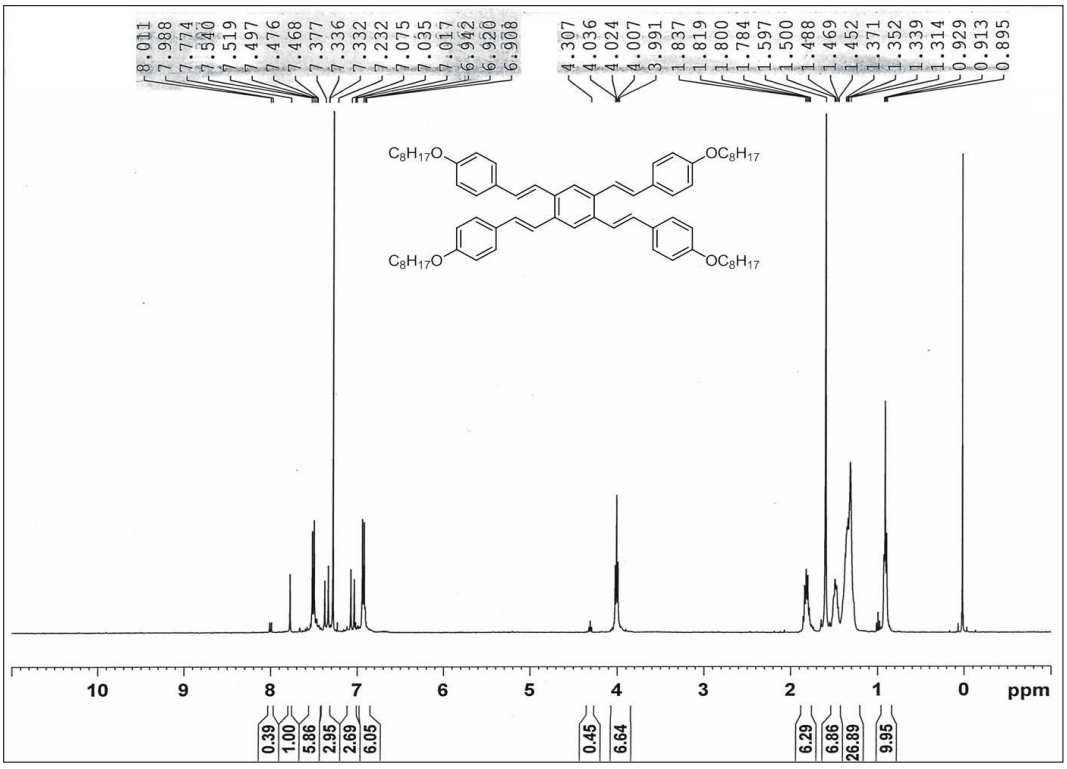
^{1}H-NMR of compound 62



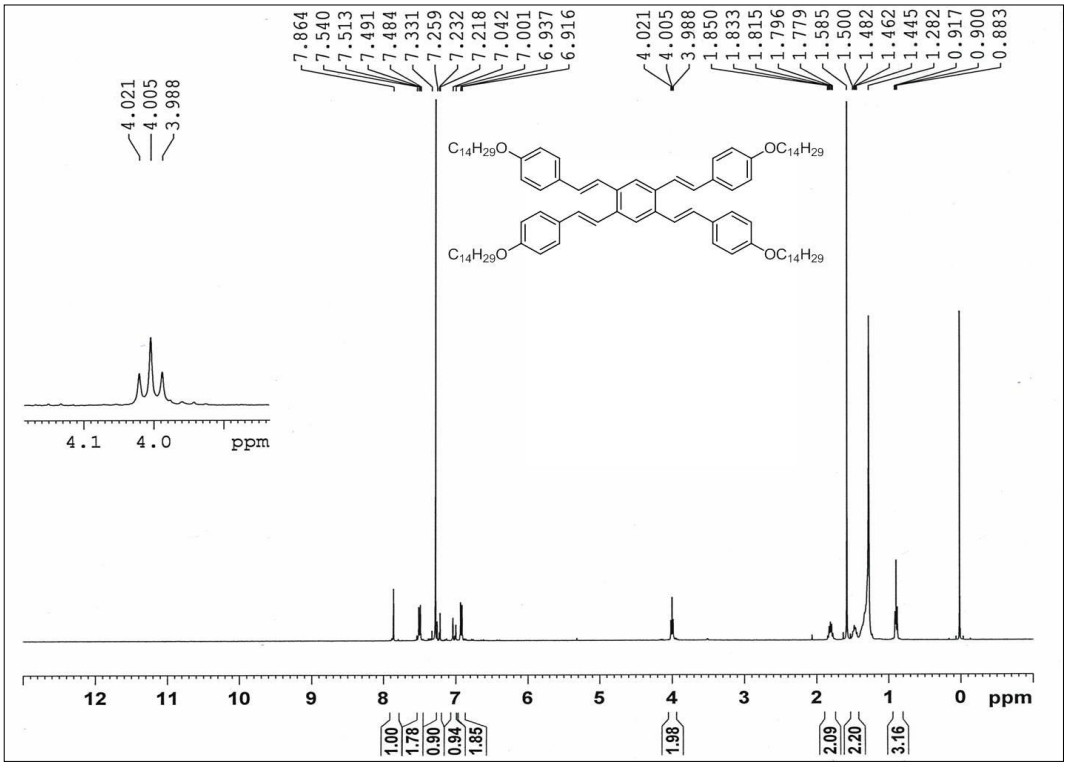
Mass spectra for compound 62



^{1}H-NMR of compound 63



^{1}H-NMR of compound 64



^{1}H-NMR of compound 65

2.5 References

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