Chapter - 4

Sunlight promoted Pd catalyzed Coupling reaction using 1-(α-Aminobenzyl)-2-naphthol as Phosphine - free ligand

INTRODUCTION

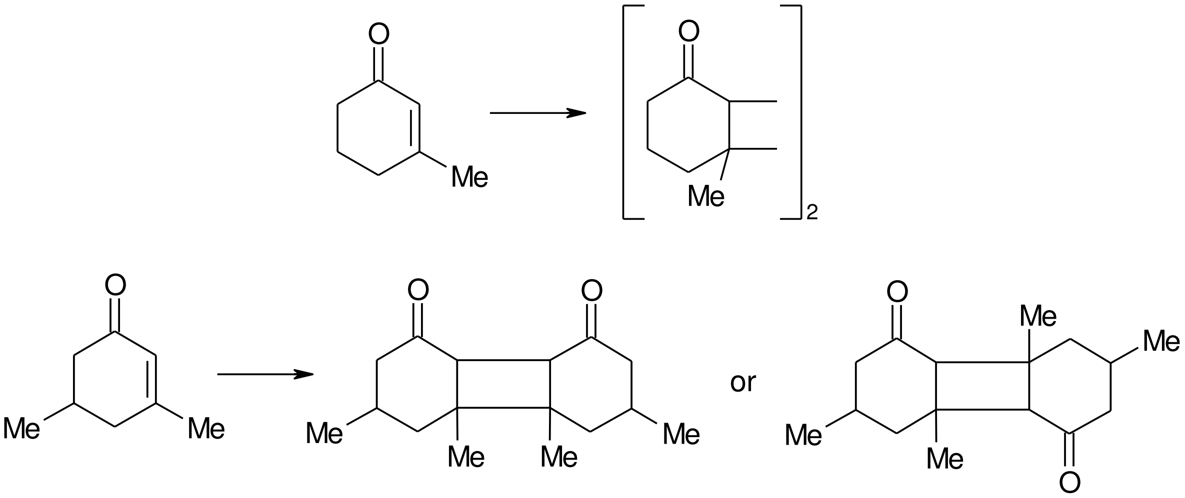
The sun has been a source of energy and inspiration from the earliest civilizations. From religion to art and dance to science and astronomy, the sun has played a prominent part in human history. In fact most of the ancient civilizations had a Sun God of some sort in their mythology and religious faith. From science point of view also, we know that the most basic life support process, the photosynthesis is totally dependent on sunlight and it is the greatest sunlight mediated chemical operation.

Moving towards the synthetic use of sunlight that mankind has adopted to utilize this unlimited source of free energy to make life easier and better e.g. earliest application of solar energy was in space, then the discovery of solar car, solar street light, solar heater etc. Several state governments including Gujarat, Rajashtan and Tamilnadu have actively implemented energy generation units based on solar energy. One such plant of **600 MW solar power generation capacity in Charanka village of Patan district was commissioned in April 19 of 2012, while many more are either operational or are in the pipeline.**

One of the twelve principles of ‘Green Chemistry’ proposed by Anastas and Warner refers to the use of energy efficient synthetic processes.[1] The sixth principle says ‘the energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure’. The solar energy is the greenest source of energy, it is abundant, cheaper and a cleaner alternative to any process of generation of energy. It is the most powerful form of renewable energy.

The use of solar energy to drive chemical transformations was recognized very early[2, 3] and many efforts are made to explore different reactions under the natural sunlight. The direct sunlight or concentrated sunlight is utilized either as a photon source for photochemical or photothermal reactions. Some of the sunlight induced reactions are summarized in this chapter.

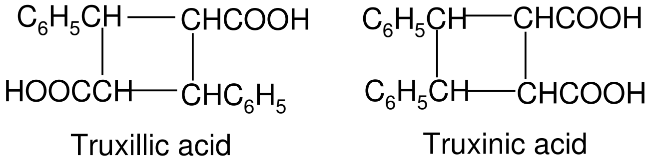
Some of the sunlight induced reactions involve dimerization[4] of alkenes and conjugated compounds. For example, 3-methylcyclohexenone and 3,5-dimethylcyclohexenone undergoes photodimerization when their solutions in dilute alcohol are exposed to sunlight.



Scheme 1: Photodimerization of Cyclohexenone derivative

When a benzene solution of stilbene is exposed to sunlight, it acquires a pale yellow color and partially undergoes polymerization, forming a compound having the formula $(C_{14}H_{12})_2$.

When solid cinnamic acid or its aqueous suspensions are exposed to sunlight, dimerization is accompanied by stereoisomerization. While α-*trans*-cinnamic acid yields mainly the dimer α-truxillic acid with a small amount of the β-truxinic acid, whereas the metastable β -form of cinnamic acid (*trans*), which is much more readily isomerized than the stable a *trans* - cinnamic acid, yields much β - truxinic acid and a small amount of α-truxillic acid.

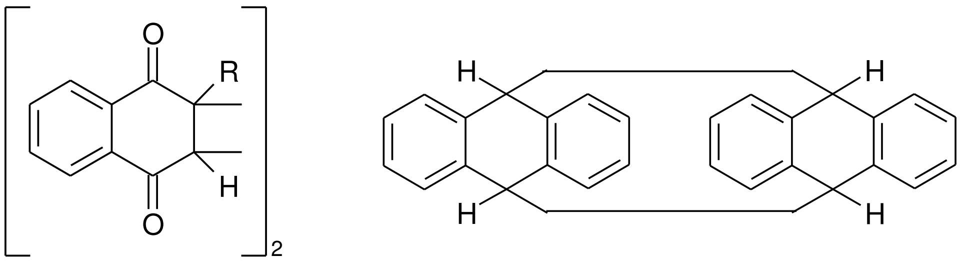


Truxillic acid

Truxinic acid

Figure 1: Photodimerization followed by stereoisomerization of Cinnamic acid

When the benzene solution of the yellow α-naphthoquinone is exposed to sunlight, the colorless photodimer is formed, it decomposes when heated at 270°C, with regeneration of α-naphthoquinone.



(a) R = H, (b) R = C_6H_5

Figure 2: Dimers of α-naphthoquinone and anthracene

In 1867 Fritzsche found that anthracene was capable of forming a photodimer when its solutions were irradiated with sunlight, which was recognized as dianthracene. The formation of dianthracene is a true photochemical process; anthracene was found to be stable in the dark.

Cis-trans isomerisation[5] of alkenes and the conjugated compounds in the presence of sunlight have also been reported. The *cis-trans* isomerization of α-carotene was reinvestigated by Nash and Zscheile; their results confirmed the findings of Zechmeister and Polgar concerning the structure of this pigment. Axerophthene, a recently discovered carotenoid, was found to undergo photochemical and catalytic isomerization in a manner typical of all-*trans* carotenoids.

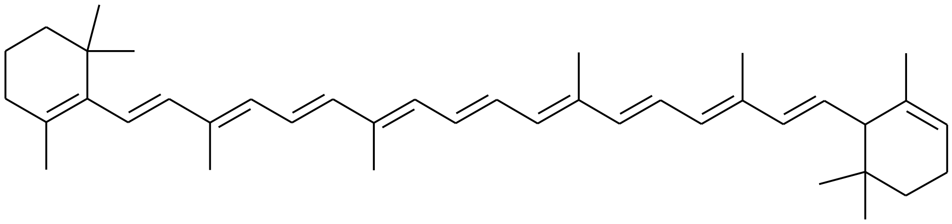


Figure 3: α-carotene

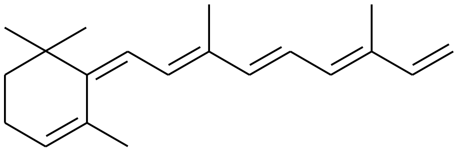
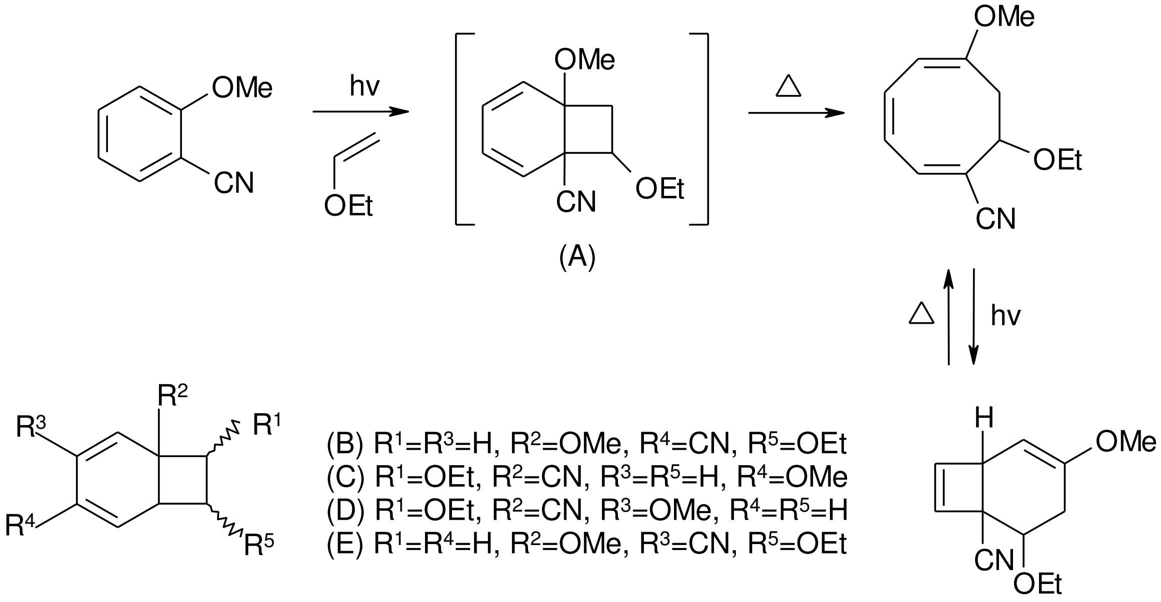


Figure 4: Axerophthene

The photochemical isomerization of stilbene was first studied by Smakula. He reported that upon irradiation with monochromatic light of 313 mμ wave length, *trans*-stilbene was completely converted to the *cis* isomer and that the reaction occurred even at liquid-air temperatures.

Among the aromatic monoolefins of higher molecular weight, *trans*-sym-di-ρ-toluylethylene was similarly reported to undergo isomerization to the *cis* form, when irradiated in dilute acetone solution with light of 4047 Å wave length.

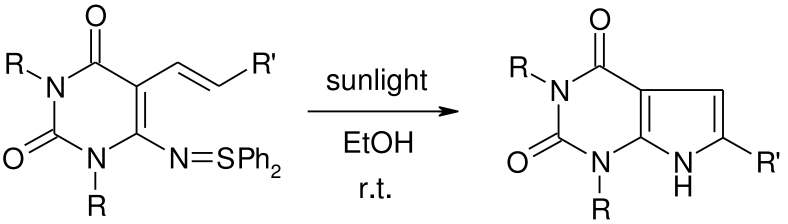
Gilbert et al. reported specific ortho photocycloaddition of enol ethers to 2-substituted anisoles resulted into facile synthesis of bicyclo[4.2.0]octa-2,7-dienes in sunlight.[6] They have investigated the photoreactions of anisoles having an electron withdrawing substituent in the 2-position with polarized ethenes. These systems were chosen since the interaction of the addends resulting from the polarization effects within the arene and ethene should be well oriented. They reported that irradiation of such arenes in the presence of enol ethers leads to a high-yielding specific photoaddition and the formation of bicyclo[4.2.0]octa-2,7-dienes as the photostable products (**Scheme 2**).



Scheme 2: Specific ortho photocycloaddition of enol ether to 2-substituted anisole

This present "one-pot" sequence of reactions to give derivatives of bicyclo[4.2.0]octa-2,7-dienes was very convenient and occurred in good yields from readily available starting materials and hence provided an attractive direct access to such systems.

Sulfilimines are known to be useful building blocks for heterocycles. Since some pyrrolo[2,3-*d*]pyrimidine-2,4-diones show antibacterial, anticancer or antiviral activity, the development of a method for efficient synthesis of this ring system has been reported by Matsumoto et al.[7] They carried out a novel synthesis of pyrrolo[2,3-*d*]pyrimidine-2,4-diones by sunlight photolysis of an N-(5-vinyluracil-6-y1)sulfilimines (**Scheme 3**).



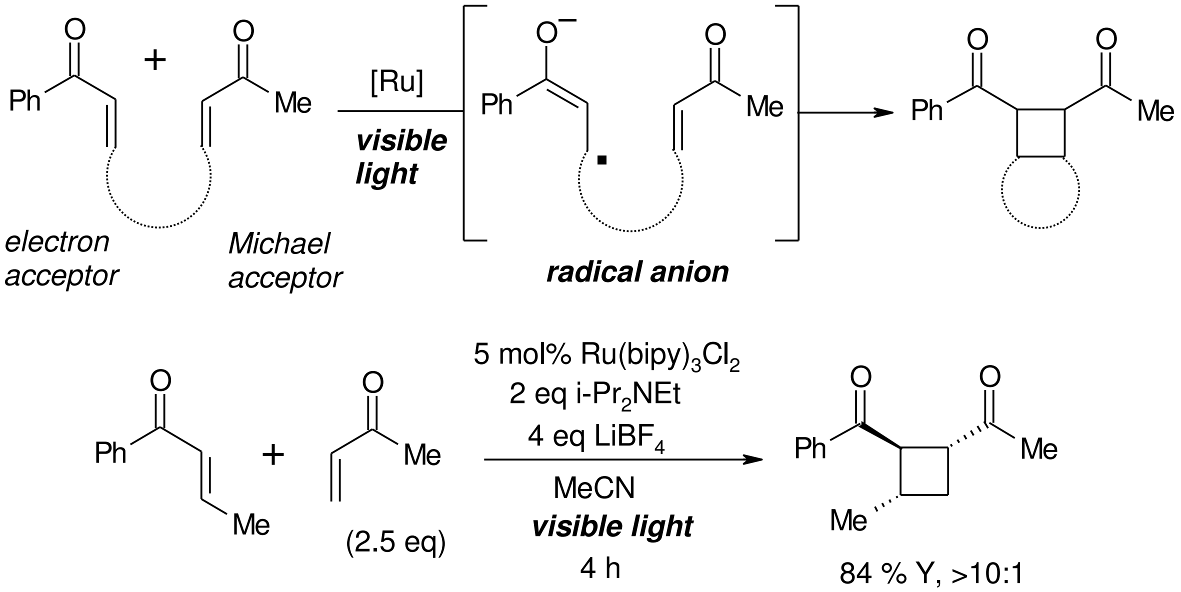
a: R=Me, R'=$COCF_3$, **b**: R=iso-Pr, R'=$COCF_3$
c: R=Me, R'= Ph, **d**: R=Me, R'=p-Tolyl
e: R=Me, R'=p-Chlorophenyl

Scheme 3: Sunlight photolysis of sulfilimine derivatives

They prepared uracil derivatives having a vinyl group at the C-5 position and a sulfilimine moiety at the C-6 position and cyclized to 1,3,6-trisubstituted pyrrolo[2,3-*d*]pyrimidine-2,4-diones by sunlight photolysis in good yields.

The first example of a photoinitiated [2+2] enone cycloaddition was reported by Ciamician in 1908 and involved the intramolecular cyclobutanation of carvone upon prolonged exposure to intense sunlight.[8] In the century since this initial discovery, [2+2] enone cycloaddition reactions promoted by UV irradiation have become recognized as an efficient method for the construction of cyclobutane-containing structures.[9] Hence Du et al. have developed an efficient method for crossed [2+2] cycloadditions of acyclic enones promoted by visible light[10] (**Scheme 4**).

The excellent chemo- and stereoselectivity observed in this reaction represents a considerable advance in the construction of strained four-membered rings and should have a significant impact on the approach towards synthesis of cyclobutane-containing structures.

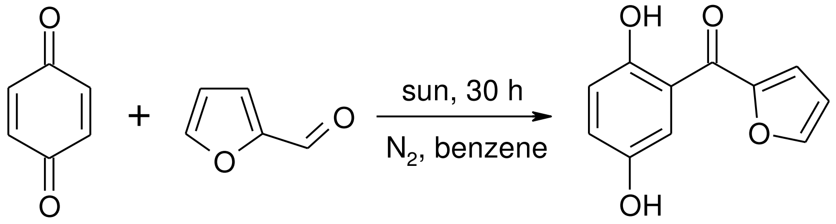


Scheme 4: Crossed intermolecular [2+2] cycloaddition of acyclic enone *via* visible light photocatalysis

They first set out to probe the feasibility of the intermolecular heterocoupling process by studying the reaction shown in **Scheme-4**. They selected methyl vinyl ketone, which should be less easily reduced than enone, but, due to the lack of a β-substituent, should serve as a better electrophilic reaction partner for the radical anion intermediate. In this reaction, they observed highly chemoselective formation of the crossed [2+2] cycloadduct in high yield. Only trace amounts of products arising from the homocoupling of enone and none of the product from dimerization of methyl vinyl ketone could be observed upon NMR analysis of the reaction mixture. In addition, the cycloaddition proceeded with excellent diastereoselectivity (>10:1 *dr*).

An important feature of this process is that the reaction is initiated by photoexcitation of the ruthenium catalyst and does not access electronically excited states of the enone. Thus this method avoids some of the synthetic limitations of cycloadditions conducted under standard UV photolysis conditions.

Benites et al. studied the application of the solar chemistry to the synthesis of heteroacylhydroquinones from 1,4-benzo- and 1,4-naphthoquinones and various heteroaromatic aldehydes.[11] They firstly explored the photolysis of 1,4-benzoquinone in the presence of 7.5 eq of furan-2-carbaldehyde in order to inhibit competing photodimerizations of the quinone in benzene solution and also containing a catalytic amount of benzophenone to facilitate the eventual photoacylation (**Scheme 5**).



Scheme 5: Photoacylation of 1,4-quinone with furan-2-carbaldehyde

Solar irradiation was employed to induce the acylation and the reaction course was daily monitored by thin layer chromatography. After 30h of light irradiation (six days), the reaction went to completion to give heteroacylhydroquinone as the sole product in 88% isolated yield (**Scheme 5**). Thus they described a facile, efficient, cheap and high yielding procedure to prepare heteroacylhydroquinones. This method involves commercially available precursors and an efficient solar photoacylation of 1,4-benzo- and 1,4-naphthoquinone. This work demonstrates that the use of green photochemistry with sunlight is achievable for the acylation of 1,4-quinones with heteroaromatic aldehydes.

In all these above reports, the focus of research has mostly been directed to the chemistry of molecules which are capable of absorbing light for the desired bond modifications leading to chemical changes.

The palladium catalyzed coupling reactions are now well established tools of modern synthetic chemists as discussed in chapter 1 and 2. Mizoroki-Heck reaction to synthesize stilbenes or cinnamates,[12] Suzuki-Miyaura reaction[13] for biaryls or substituted alkenes and Sonogashira reaction[14] for the preparation of substituted alkynes are the three main reactions of this class. These reactions are traditionally carried out in the thermal conditions in the presence of catalysts and suitable additives. Use of microwave or ultrasound irradiation to drive these reactions has also been explored with varied success.[15]

In this chapter we present our efforts to perform these important reactions under the direct solar irradiation without the need of any special apparatus or conditions.

Result and Discussion

In this chapter, we present results of the palladium catalyzed coupling reactions (Mizoroki-Heck, Suzuki-Miyaura and Sonogashira) performed under the direct solar irradiation without the need of any special apparatus or conditions.

The intended driving force is the photothermal energy received from sunrays. As discussed in chapter-2, we have screened a series of 1-(α-aminobenzyl)-2-naphthols as phosphine-free ligands for these three reactions with reasonably good conversations at conventional heating conditions.[16] Here also we have carried out these coupling reactions using same phosphine-free catalyst system (**Figure 5**). Initially we optimize reaction conditions for Heck reaction under solar irradiation.

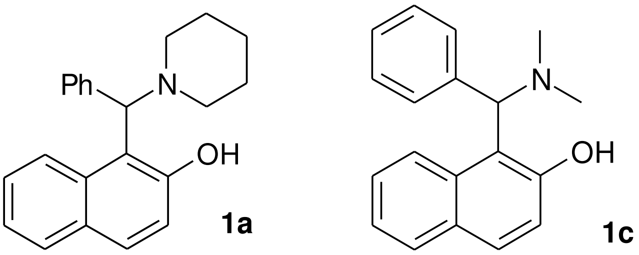
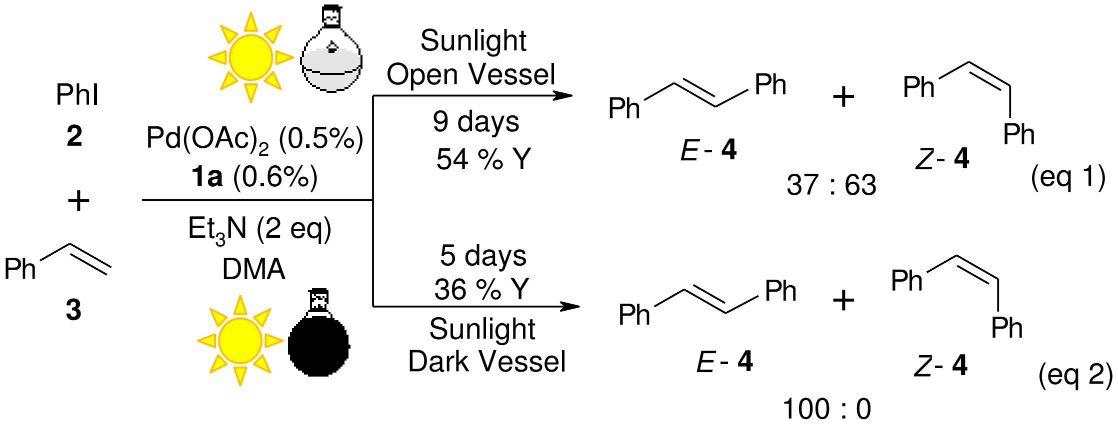


Figure 5: Ligands for the present study

Initially, Mizoroki-Heck reaction of iodobenzene with styrene was investigated under the conditions presented in **Scheme 6**. The reaction was performed in a simple assembly of an Erlenmeyer flask fitted with a guard tube and a magnetic stirrer. The reaction was simply exposed to bright sunlight continuously for several days and then the product was isolated. For better results the flask is placed on the top of a simple mirror to utilize the reflected sunrays.



Scheme 6: Comparison of Mizoroki-Heck reaction under the solar irradiation performed in open or dark vessel

However, it was interesting to observe the formation of *Z* - stilbene (*Z* - **4**) as a major product compared to *E* - stilbene (*E* - **4**) contrary to the usual selectivity of the reaction (**Equation 1**). This could be due to the photochemical isomerization of stilbene like compounds when exposed to sunlight.[17] Another experiment was conducted under identical condition but the flask was completely covered with a black paper to prevent exposure to UV rays of the sunlight (**Equation 2**). This Dark vessel experiment gave exclusively *trans* - stilbene (*E* - **4**) as earlier observed for the same catalyst system for the classical thermal conditions.[16a]

Identical results were obtained when iodobenzene was treated with acrylates to form *Z*/*E* cinnamates. To provide further evidence to the possibility that the initially formed *E* olefin was getting isomerized to *Z* olefin over a period of sunlight exposure, we carried out a separate experiment (**Table 1**). In this study the pure *E* - ethyl cinnamate **6** was gradually converted into *Z* isomer till it reached the equilibrium or photostationary phase in about 56 h of actual sunlight (**Figure 6**).

Table 1: Kinetic study of *trans* to *cis* isomerization on exposure to sunlight

Time (h)	*cis* isomer	*trans* isomer
0	0	100
8	16	84
16	21	79
24	22	78
40	23	77
56	28	72

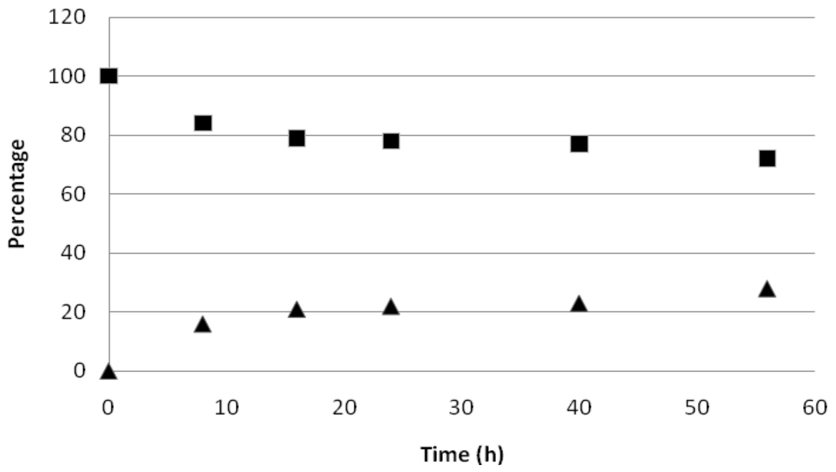


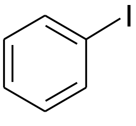
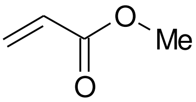
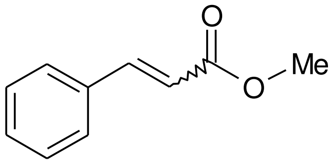
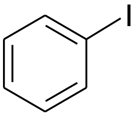
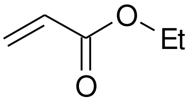
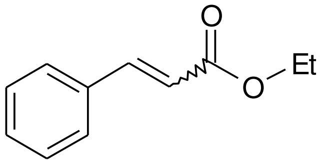
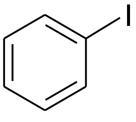
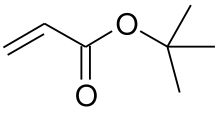
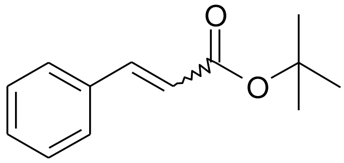
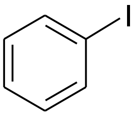
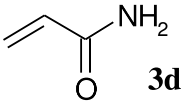
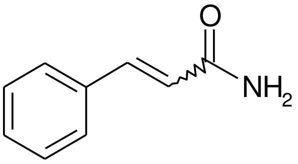
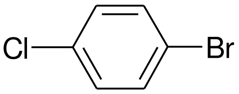
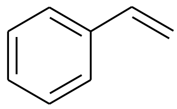
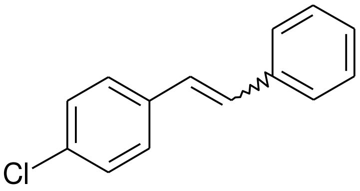
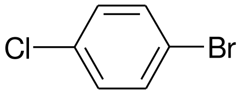
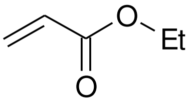
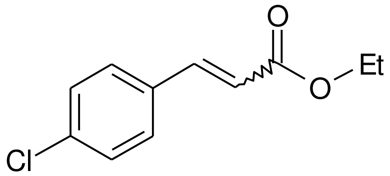
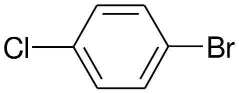
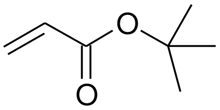
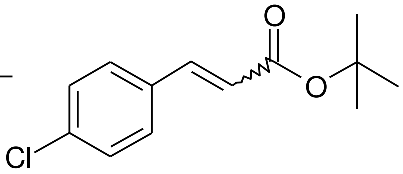
Figure 6: Isomerization of ethyl cinnamate under sunlight irradiation

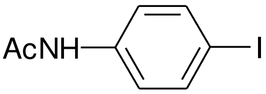
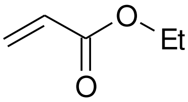
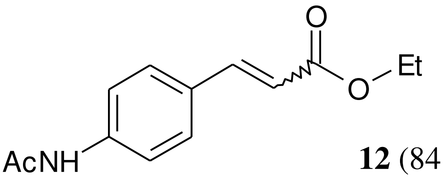
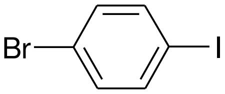
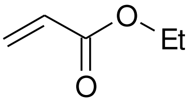
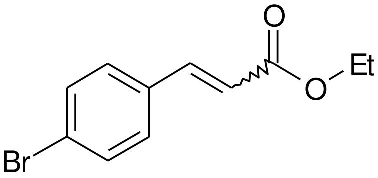
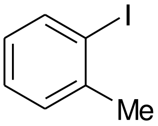
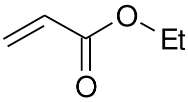
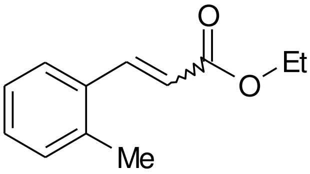
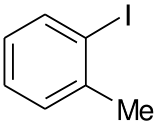
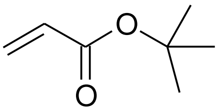
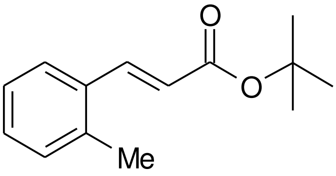
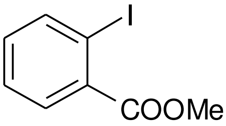
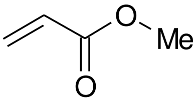
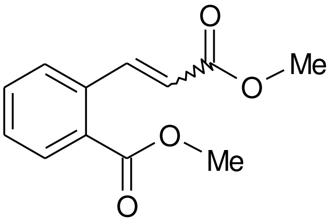
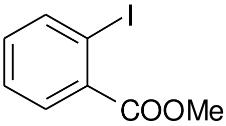
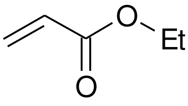
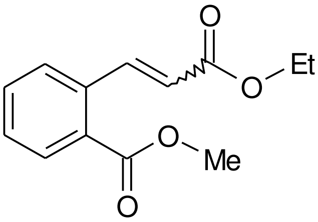
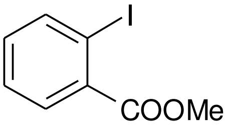
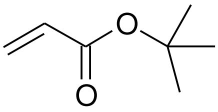
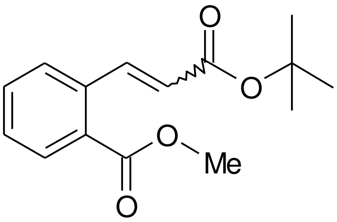
We also observed a very poor conversion when the same reaction was performed at room temperature without exposure to the sunlight (only 9% Y) or with only $Pd(OAc)_2$ in sunlight in the absence of ligand (18% Y). Both these experiments clearly indicate that the sunlight and ligand are essential for the efficient reaction. The reaction proceeds mainly due to the photothermal reaction as we have measured the reaction temperature to reach about 56-58^{o}C in the day time when the brightest sunlight falls on the reaction medium.

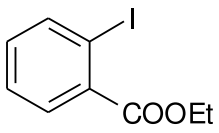
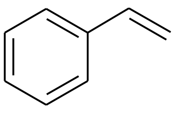
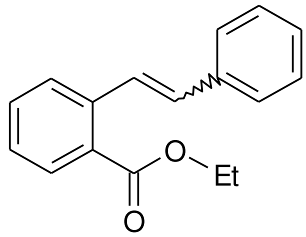
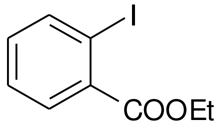
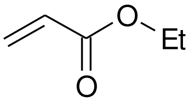
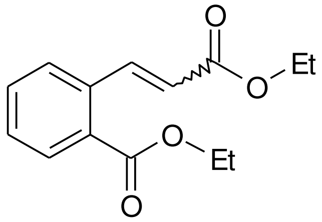
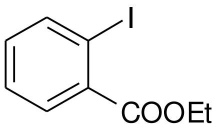
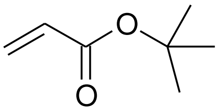
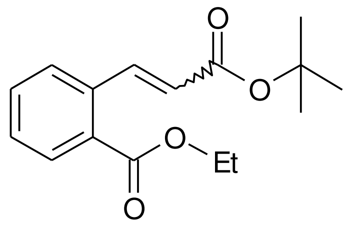
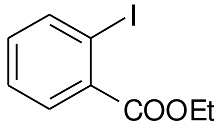
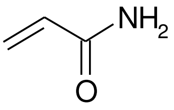
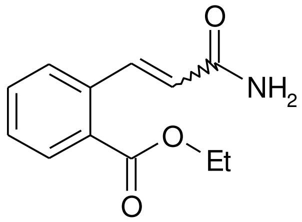
However, the role of photochemical cleavage of Ar-I bond for the $S_{RN}1$ type substitution reaction assisted by sunlight cannot be ruled out.[18] This also accounts for the observation of low reactivity of Ar-Br in this reaction under the solar conditions. The reduction of Pd(II) to Pd(0) can also be assisted under the photochemical conditions as postulated by Kohler.[19] This is the only known report on the beneficial effect of artificial light on the Mizoroki-Heck reaction to best of our knowledge.

Having reasonably establishing the conditions of optimized conversion, a series of substrates were screened with moderate to good results (**Table 2**). The stilbenes or cinnamic acid derivatives formed were found to have a considerable amount of the *Z* isomer in most of the cases.

Table 2: Examples of Photothermal Mizoroki-Heck reaction

No	Aryl halide (1 eq)	Olefin (1.5 eq)	Product	Yield (%) [*Z* : *E*]
1	 **2a**	 **3a**		**5** (73 %) [37 : 63]
2	 **2a**	 **3b**		**6** (90 %) [25 : 75]
3	 **2a**	 **3c**		**7** (85 %) [20 : 80]
4	 **2a**	 **3d**		**8** (76 %) [48 : 52]
5	 **2b**	 **3e**		**9** (32 %) [N.D.]
6	 **2b**	 **3b**		**10** (43%) [28 : 72]
7	 **2b**	 **3c**		**11** (41%) [21 : 79]

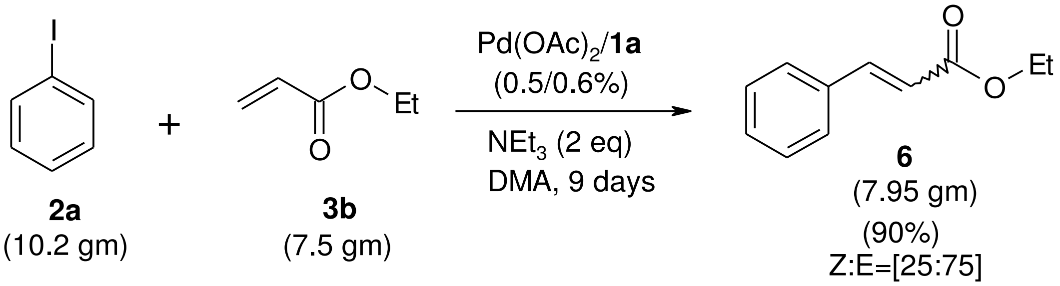
8	 **2c**	 **3b**	 **12** (84%) [55 : 45]
9	 **2d**	 **3b**	 **13** (83%) [43 : 57]
10	 **2e**	 **3b**	 **14** (90%) [80 : 20]
11	 **2e**	 **3c**	 **15** (87%) [41 : 59]
12	 **2f**	 **3a**	 **16** (71%) [56 : 44]
13	 **2f**	 **3b**	 **17** (69%) [70 : 30]
14	 **2f**	 **3c**	 **18** (78%) [78 : 22]

15	 **2g**	 **3e**		**19** (78%) [69 : 31]
16	 **2g**	 **3b**		**20** (28%) [68 : 32]
17	 **2g**	 **3c**		**21** (74%) [75 : 25]
18	 **2g**	 **3d**		**22** (67%) [67 : 33]

All reactions run with Ar-I (1 eq.), Styrene (1.5 eq.), $Pd(OAc)_2$ (0.5 %), **1a** (0.6 %), NEt_3 (2 eq.) in DMA.

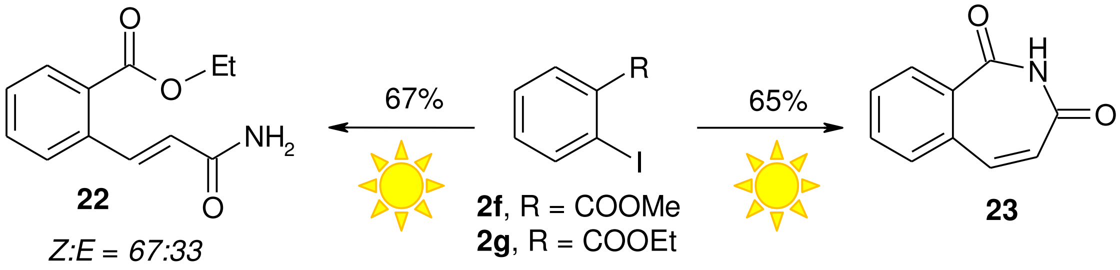
The methods available for the synthesis of *Z* alkenes include selective hydrogenation of corresponding alkynes,[20] from aldehydes by modified Wittig reactions,[21] Favoraskii reaction,[22] Negishi coupling,[23] aldol reaction,[24] Peterson reaction,[25] photoisomerization of *E* alkenes[26] etc. Special conditions for Mizoroki-Heck reaction for selective formation of *Z* alkene has also been developed by some groups[27] which involves the design of ligand or other parameters. The similar olefinic moiety with *Z* stereochemistry is present in some bioactive molecules discovered recently.[28]

For practical application, we have carried out this reaction on a multigram scale of iodobenzene (10.2 g, 0.05 mol) and ethyl acrylate (7.5 g, 0.075 mol) to afford the ethyl cinnamate **6** in high yield (90% Yield, *Z* : *E* = 25 : 75).



Scheme 7: Multigram synthesis

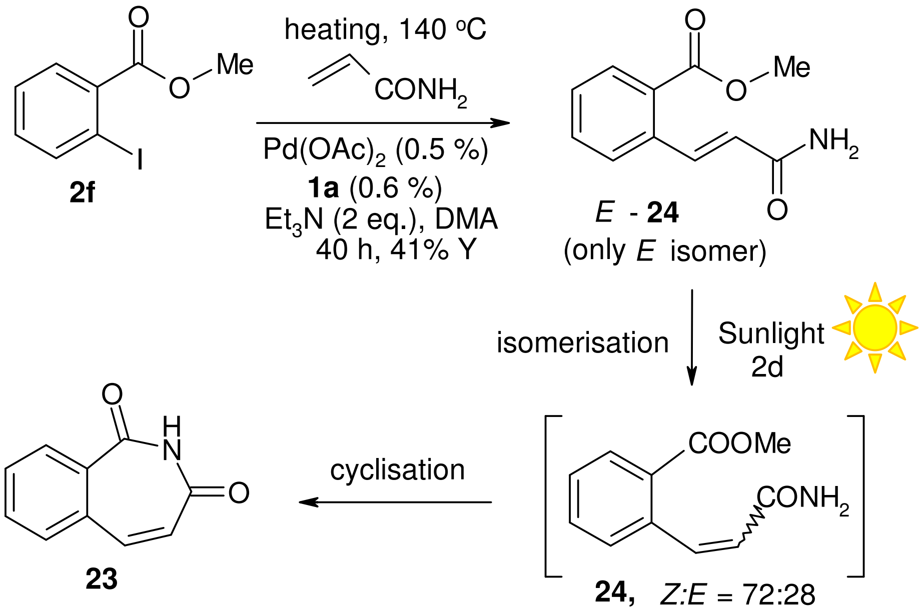
Reaction of ethyl-2-iodobenzoate **2g** with acrylamide under the same conditions afforded desired compound, **22** in similar manner, but notably the reaction of methyl 2-iodobenzonate **2f** under the identical reaction conditions furnished a cyclized product, 2*H*-2-benzazepine-1,3-dione **23** (**Scheme 8**).[29]



CH_2=CH-$CONH_2$, sunlight, Pd(OAc)$_2$ (0.5%), **1a** (0.6%), Et_3N (2 eq), DMA, 9 d

Scheme 8: Unexpected cyclization in Mizoroki-Heck reaction in solar condition

However, when we performed the latter reaction under thermal conditions, it furnished the expected product **24** exclusively as the *E* isomer (**Scheme 9**). This unexpected observation for the sunlight induced Mizoroki-Heck reaction could be explained by the initial isomerization of compound from *E* - **24** to *Z* - **24** followed by intramolecular cyclization.



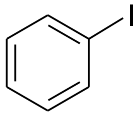
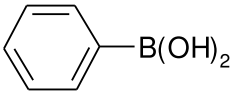
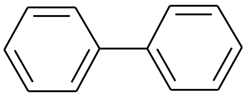
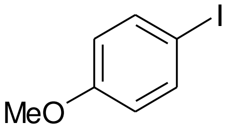
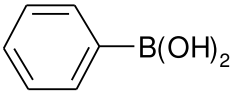
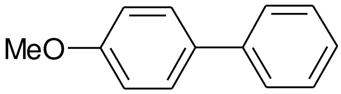
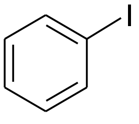
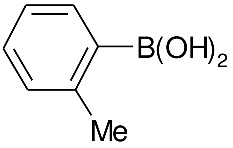
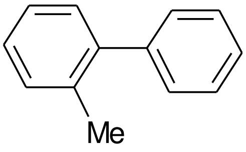
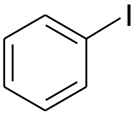
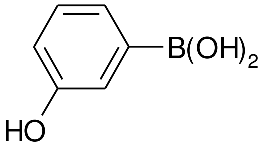
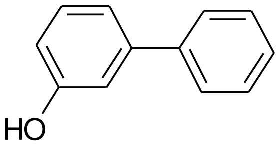
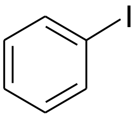
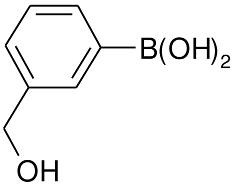
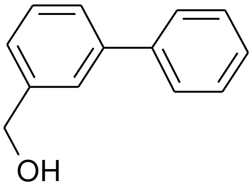
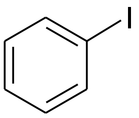
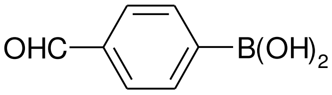
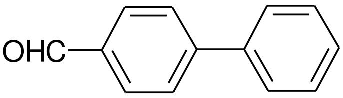
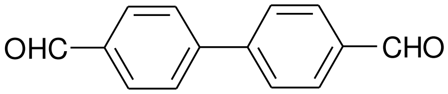
Scheme 9: Probable route for the formation of **24**

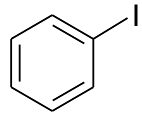
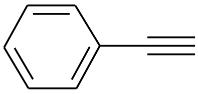
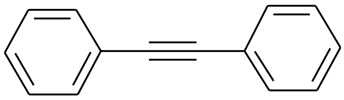
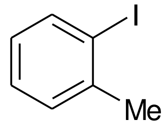
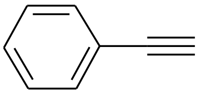
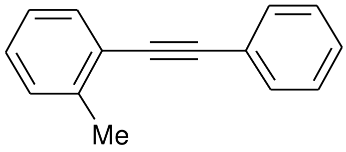
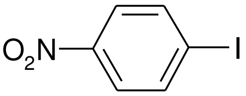
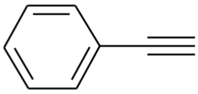
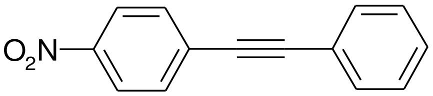
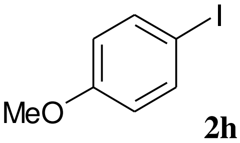
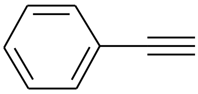
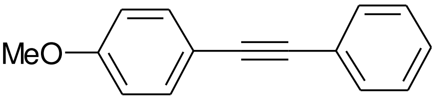
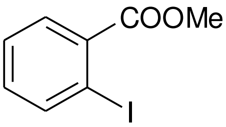
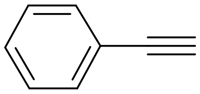
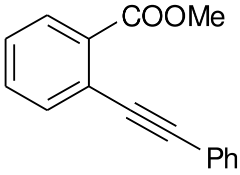
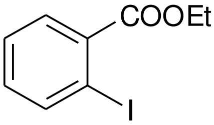
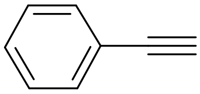
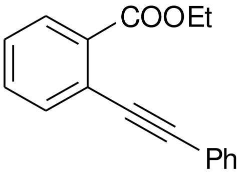
The less favorable cyclization on ethyl ester as compared to methyl ester may be the reason for this observation in the case of **2g** and **2f**. This hypothesis was confirmed when a pure sample of *E* - **24** was initially converted into *Z* - **24** when exposed to sunlight and later cyclized to 2H-2-benzazepine-1,3-dione **23**.

The present protocol of sunlight assisted coupling was further extended to other two important coupling reactions – Suzuki-Miyaura for the synthesis of biphenyl derivatives and Sonogashira reactions for the synthesis of substituted diphenyl actylenes. The outcome of all three reactions with either ligand is almost similar.

Initially we have optimized reaction conditions for these two coupling reactions using our phosphine free catalyst system. The outcome of the Suzuki-Miyaura reaction in the absence of light was same as in open vessel indicating the sunlight is merely acting as a heating source (Table-3, entry 1). For both coupling reactions K_2CO_3 was found to be better base than NEt_3.

Table 3: Sunlight induced Suzuki-Miyaura and Sonogashira reactions

No	Aryl halide (1 eq)	Reagent (1.5 eq)	Product	Yield (%)
1	 **2a**	 **25a**		**26** (91%) (88 %)[a]
2	 **2h**	 **25a**		**27** (53%)
3	 **2a**	 **25b**		**28** (83%)
4	 **2a**	 **25c**		**29** (82%)
5	 **2a**	 **25d**		**30** (77%)
6	 **2a**	 **25e**	 	**31** (55%) **32** (47%)

7	 **2a**	 **33**		**34** (84%) (39)[b]
8	 **2e**	 **33**		**35** (44%)
9	 **2i**	 **33**		**36** (80%)
10	 **2h**	 **33**		**37** (38%)
11	 **2f**	 **33**		**38** (75%)
12	 **2g**	 **33**		**39** (74%)

General conditions for Suzuki reaction: **1-c** (0.6%), $Pd(OAc)_2$ (0.5%), K_2CO_3 (2 eq.) Dioxane-H_2O (1:1, 10 mL), sunlight, 1 d. [a]The reaction is conducted in dark vessel.

General conditions For Sonogashira reaction: **1-c** (1.2%), $Pd(OAc)_2$ (1.0%), K_2CO_3(2.0 eq.), NMP (10 mL), sunlight, 3 d. [b] With Et_3N.

Mechanistic considerations:

To understand mechanism of these sunlight mediated cross-coupling reactions, few experiments were carried. When the solution of iodobenzene was exposed to sunlight for number of hours, the solution was found acquire light pink to dark pink colour, which indicates evolution of iodine in the solution (**Figure 7**). The iodine was established by its UV-visible absorption spectra of this colored solution, as it showed same absorption maxima as that of standard iodine solution (**Figure 8**). This indicates that sunlight is probably assisting the cleavage of Ph - I bond.

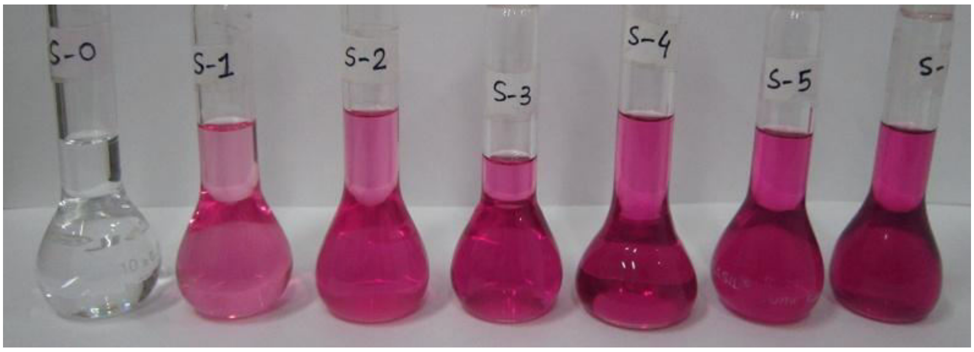


Figure 7: Evolution of I_2 from iodobenzene in sunlight

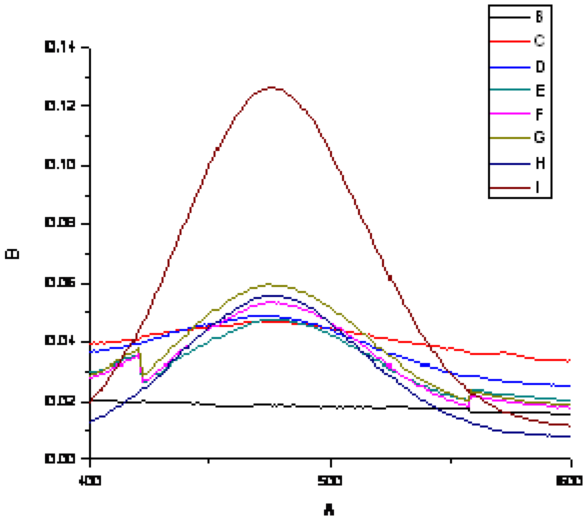
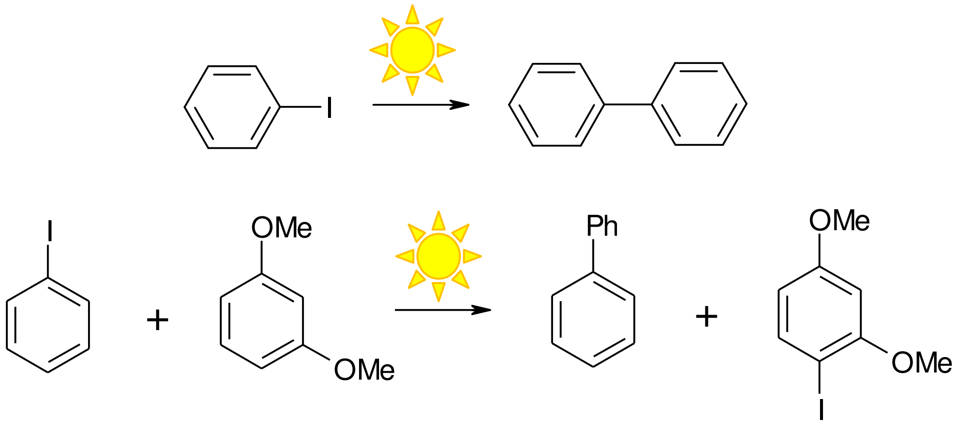


Figure 8: UV-Visible absorption spectra of colored solution (B-H).
I-standard iodine solution

Furthermore evidence is provided by another two reactions (**Scheme 10**). When iodobenzene was exposed to sunlight, it resulted into iodine evolution along with formation of some amount of biphenyl (detected by GC-MS). Another reaction of iodobenzene gave biphenyl along with 4-iodo-1,3-dimethoxybenzene (detected by GC-MS). Both the experiments support the initial cleavage of Ar-I bond.



Scheme 10: Reactions of iodobenzene in sunlight

These reactions and experiments support our hypothesis that sunlight is assisting the cleavage of Ar-I bond in these coupling reactions.

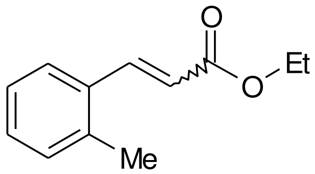
All the compounds were purified by column chromatography and characterized by ^{1}H-NMR, IR and Mass analysis. The *cis* - *trans* ratio of the Heck reaction products was determined by ^{1}H-NMR. In the NMR spectra of compound **4**, the *cis* and *trans* olefinic protons show two singlets at δ = 6.59 and 7.11 ppm. The olefinic protons Ar-CH= and =CH-C=O in compound **23** give doublet at δ = 7.18 - 7.15 (J = 12.8 Hz) and *dd* at δ = 6.41 - 6.38 (J = 12.4, 2.4 Hz) respectively. The –NH proton appears as broad singlet at 8.66 δ. The mass spectra of compound **13** shows ratio of relative abundance [M]:[M+1] = 1:1 due to presence of -Br and the base peak at 101 m/z is produced after loss of -Br and -COOEt groups. In case of compound **38**, the base peak at 221 m/z is generated after loss of -CH_3 group.

Experimental Section

Reagents were purchased from Sigma-Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens, Avara Chemicals Limited etc. All solvents that were used were stored on oven dried molecular sieves (4Å). All commercial products were used without further purification. Thin Layer Chromatography was performed on Merck 60 F254 Aluminium coated plates. The spots were visualized under UV light or with iodine vapour. All the compounds were purified by column chromatography using silica gel (60-120 mesh) purchased from Sisco Research Laboratory, Pvt. Limited. ^{1}H and ^{13}C NMR spectra are recorded on a 400 MHz Bruker Avance 400 Spectrometer spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument. IR spectra were recorded on a Perkin-Elmer FTIR RXI spectrometer as KBr pallets.

General Procedure for the Heck Reaction under Photochemical irradiation

To an oven-dried Erlenmeyer flask equipped with a stirrer bar and guard tube was charged 2-iodotoluene **2e** (0.25 g, 1.147 mmol), triethyl amine (0.232g, 2.293 mmol), palladium acetate (1.29 mg, 0.006 mmol) and **1a** (2.18 mg, 0.007 mmol) in DMA (10 mL). To this reaction mixture ethyl acrylate **3b** (0.172 g, 1.72 mmol) was added. The reaction mixture was exposed to sunlight for 9 days. After completion of the reaction, the mixture was quenched with water and extracted with ethyl acetate (3 x 25 mL). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel to afford ethyl (2-methyl)cinnamate **14** (0.195 g, 90%) (Table 2, entry 10).



Ethyl (2-methyl) cinnamate (14):[30a]

Yield: 90%, (0.195 g).

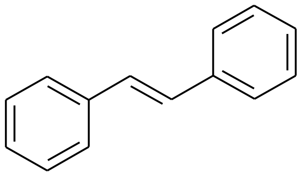
Colorless oil, ***Z* : *E*** = 80 : 20.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.0 **-** 7.1 (m, 5H, which also contains one set of *trans* & *cis* olefinic protons), 6.38 - 6.34 and 6.04 - 6.01 (two d, *J* = 16 Hz & *J* = 12 Hz, 1H, second set of *trans* & *cis* olefinic protons), 4.3 - 4.06 (two q, 2H, $-CH_2$ of –COOEt group of *trans* & *cis* isomer), 2.44 & 2.3 (two s, 3H, Ar-CH_3 of *trans* & *cis* isomer), 1.36 - 1.13 (two t, 3H, $-CH_3$ of -COOEt group of *trans* & *cis* isomer).

IR (Neat): υ 3062, 2981, 1722, 1633, 1602, 1530, 1485, 1459, 1407, 1384, 1312, 1275, 1185, 1162, 1098, 1032, 982, 950, 839, 760, 730, 598 cm^{-1}.

MS (EI): (*m/z*) 190 (M^+, 11), 175 (5), 145 (56), 144 (63), 117 (29), 116 (59), 115 (100), 91 (25).

Stilbene (4):[30b]



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

Yield: 36%, (0.08 g), ***Z* : *E*** = 0 : 100.

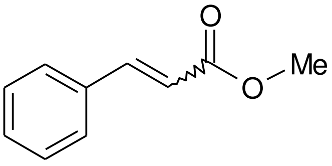
White solid, **M.P.** 64 - 66°C (Lit 65 - 67°C, Sigma Aldrich Catalogue).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 - 7.5 (m, 2H), 7.38 - 7.33 (m, 2H), 7.28 - 7.24 (m, 1H), 7.11 (s, 1H).

IR (KBr): υ 3056, 3019, 1596, 1575, 1493, 1449, 1399, 1123, 983, 962, 907, 763, 691, 603 cm^{-1}.

MS (EI): (*m/z*) 180(M^+, 70), 179 (100), 178 (79), 165 (33), 89 (12), 77 (6).

Methyl cinnamate or methyl 3-phenylprop-2-enoate (5):[30b]



Compound **5** was prepared by same procedure as that of **14**.

Yield: 73%, (0.144 g).

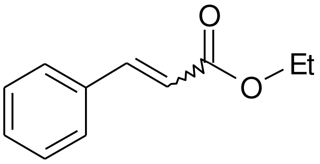
Colorless oil, ***Z* : *E*** = 37 : 63.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.74 - 7.7 (d, *J* = 16 Hz, 1H, olefinic proton of *trans* isomer), 7.62 - 7.35 (m, 5H), 6.99 - 5.96 (three d, *J* = 16 Hz, *J* = 12.4 Hz, olefinic proton of *trans* and *cis* isomer), 3.83 - 3.73 (two s, 3H, -CH_3 of *trans* and *cis* isomer).

IR (Neat): υ 2348, 1715, 1631, 1498, 1453, 1312, 1273, 1168, 976, 865, 766, 715, 683 cm^{-1}.

MS (EI): (*m/z*) 162 (M^+, 85), 131 (100), 117 (6), 105 (95), 91 (12), 77 (56), 51 (35), 39 (6).

Ethyl cinnamate or ethyl 3-phenylprop-2-enoate (6):[30b]



Compound **6** was prepared by same procedure as that of **14**.

Yield: 86% (0.186 g).

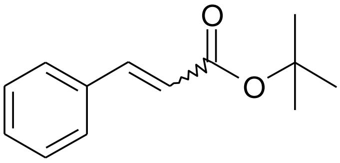
Colorless oil, ***Z* : *E* =** 25 : 75.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 - 7.69 (d, *J* = 16 Hz, *trans* olefinic proton), 7.56 - 7.54 (m, 2H), 7.42 - 7.34 (m, 3H), 6.99 - 6.96 (d, *J* = 12 Hz, *cis* olefinic proton), 6.48 - 6.44 and 5.99 - 5.96 (two d, *J* = 16 Hz & *J* = 12 Hz, 1H *trans* & *cis* olefinic proton respectively), 4.32 - 4.17 (two q, 2H, -CH$_2$ protons of *trans* & *cis* isomer), 1.38 - 1.25 (two t, 3H, -CH$_3$ protons of *trans* & *cis* isomer).

IR (Neat): υ 3061, 3029, 2982, 2936, 1713, 1637, 1578, 1495, 1449, 1390, 1367, 1311, 1270, 1177, 1095, 1034, 982, 865, 835, 767, 687 cm^{-1}.

MS (EI): (*m/z*) 178 (M+2, 28), 177 (M+1, 27), 176 (M$^+$, 26), 149 (77), 148 (100), 147 (29), 131 (34), 103 (22), 77 (33).

***tert*-butyl cinnamate (7):**[31a]



Compound **7** was prepared by same procedure as that of **14**.

Yield: 85 %, (0.212 g).

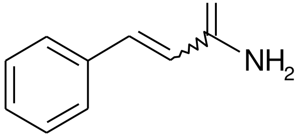
Colorless oil, ***Z : E*** **=** 19 : 81.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.63 - 7.59 (d, *J* = 16 Hz, *trans* olefinic proton), 7.54 - 7.51 (m, 2H), 7.4 - 7.32 (m, 3H), 6.9 - 6.87 (d, *J* = 12 Hz, *cis* olefinic proton), 6.42 - 6.38 and 5.92 - 5.89 (two d, *J* = 16 Hz and *J* = 12 Hz, *trans* & *cis* olefinic protons), 1.67 - 1.45 (two s, 9H of ^{t}Bu group of *trans* & *cis* isomer).

IR (Neat): υ 3061, 3028, 2978, 2932, 1709, 1637, 1578, 1527, 1495, 1475, 1451, 1392, 1367, 1326, 1285, 1254, 1208, 1150, 1072, 1030, 980, 920, 870, 836, 767, 709, 687 cm^{-1}.

MS (EI): (*m/z*) 204 (M$^+$, 4), 189 (2), 149 (19), 148 (48), 147 (100), 131 (46), 103 (17), 102 (13), 77 (24), 57 (25).

Cinnamamide (8):[31b]



Compound **8** was prepared by same procedure as that of **14**.

Yield: 76 %, (0.136 g), ***Z : E*** **=** 48 : 52.

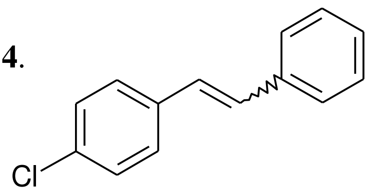
Off white solid, **M.P.** 106 - 108°C (of *Z : E* mixture).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.68 - 6.86 (m, 6H, which also contains one set of *trans* & *cis* olefinic protons), 6.51 - 6.47 and 6.02 - 5.99 (two d, *J* = 16 Hz and *J* = 12 Hz, 1H, second set of *trans* & *cis* olefinic protons), 5.87 - 5.54 (br s, 2H, -NH$_2$ of *trans* & *cis* isomers).

IR (KBr): υ 3371, 3300, 3169, 1661, 1607, 1577, 1492, 1449, 1399, 1345, 1287, 1193, 1122, 1001, 968, 932, 925, 862, 845, 757, 692, 656, 644 cm^{-1}.

MS (EI): (*m/z*) 147 (M$^+$, 27), 146 (100), 131 (25), 103 (44), 102 (15), 77 (19).

4-Chloro stilbene (9):[32a]



Compound **9** was prepared by same procedure as that of **14**.

Yield: 43%, (0.12 g), ***Z* : *E*** not determined.

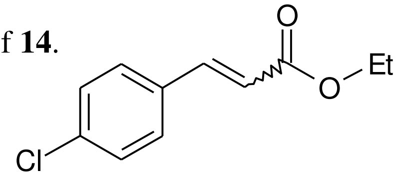
White solid, **M.P.** 128°C (Lit[32a] 128 - 129°C).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 - 7.32(m, 4H), 7.3 - 7.24 (m, 3H), 7.23 - 7.09 (m, 2H, which also contains *trans* olefinic protons), 6.68 - 6.55 (two d, *J* = 12.4 Hz, *cis* olefinic protons, 2H).

IR (KBr): υ 2922, 2850, 1595, 1494, 1448, 1400, 1192, 1136, 1123, 1011, 965, 863, 835, 817, 750, 706, 691, 656, 644, 603 cm^{-1}.

MS (EI): (*m/z*) 215.7 (18), 215 (M+1, 14), 214.5 (M^+, 34), 213.5 (57), 179 (72), 178 (100), 176 (26), 149 (22).

4-Chloro-ethyl cinnamate (10):[32b]



Compound **10** was prepared by same procedure as that of **14**.

Yield: 43%, (0.118 g).

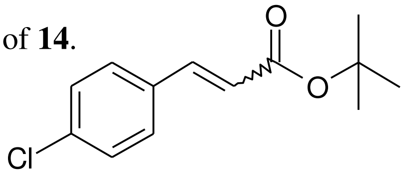
Colorless oil, ***Z* : *E* =** 28 : 72.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.67 - 7.63 (d, *J* = 16 Hz, 1H, *trans* olefinic proton), 7.57 - 7.32 (m, 4H), 6.92 - 5.96 (three doublets, *J* = 12.4 and *J* = 16 Hz, *cis* and *trans* olefinic protons), 4.27 - 4.11 (two q, *J* = 7.2 Hz, -CH_2- of *trans* and *cis* isomer), 1.37 - 1.28 (two t, *J* = 7.2 Hz, -CH_3 of *trans* and *cis* isomer).

IR (Neat): υ 2986, 1723, 1682, 1595, 1570, 1494, 1441, 1377, 1323, 1267, 1192, 1134, 1085, 1035, 968, 881, 829, 765, 705, 695, 646 cm^{-1}.

MS (EI): (*m/z*) 212 (16), 210 (M^+, 50), 191 (27), 182 (26), 181 (12), 167 (35), 166 (13), 165 (100), 137 (28), 102 (30), 101 (28).

4-Chloro-*tert*-butyl cinnamate (11):[32c]



Compound **11** was prepared by same procedure as that of **14**.

Yield: 41%, (0.127 g).

Colorless oil, ***Z* : *E* =** 21 : 79.

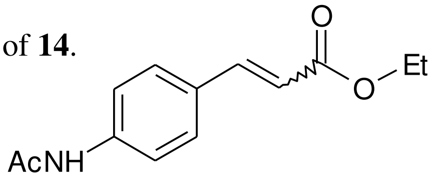
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 - 7.53 (d, *J* = 16 Hz, *trans* olefinic proton), 7.51 - 7.44 (m, 2H), 7.37 - 7.32 (m, 2H), 6.83 - 6.8 (d, *J* = 12 Hz, *cis* olefinic proton), 6.38

- 6.34 and 5.93 - 5.9 (two d, *J* = 16 Hz & *J* = 12 Hz, *trans* & *cis* olefinic protons), 1.55 and 1.46 (two s, 9H, ^{t}Bu group of *trans* & *cis* isomers).

IR (Neat): υ 2925, 2855, 1710, 1637, 1593, 1491, 1458, 1368, 1319, 1256, 1207, 1153, 1092, 1013, 981, 872, 822, 768, 739 cm^{-1}.

MS (EI): (*m/z*) 238.5 (M^+, 11), 238 (48), 184 (52), 183 (59), 183 (28), 182 (70), 181 (79), 167 (23), 166 (18), 165 (100), 137 (17), 136 (20), 102 (27), 101 (43).

Ethyl-4-Acetamidocinnamate (12):[33a]



Compound **12** was prepared by same procedure as that of **14**.

Yield: 84%, (0.15 g), ***Z* : *E*** = 55 : 45.

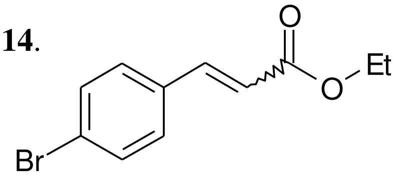
White solid, **M.P.** 90 - 92^{o}C (of *Z* : *E* mixture).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 - 8.17(m, 1H), 7.64 - 7.44 (m, 3H, which also contains *trans* olefinic proton), 6.88 - 6.85 (d, *J* = 12 Hz, *cis* olefinic proton), 6.38 - 6.34 and 5.91 - 5.88 (two d, *J* = 16 Hz and *J* = 12 Hz, olefinic protons of *trans* & *cis* isomer), 4.29 - 4.16 (two q, 2H, -CH_2 group of -COOEt of *trans* & *cis* isomer), 2.16 - 2.14 (two s, 3H, -CH_3 group of –$NHCOCH_3$ of *trans* & *cis* isomer), 1.36 - 1.26 (two t, 3H, Ar-CH_3 group of *trans* & *cis* isomer).

IR (KBr): υ 3292, 3100, 2981, 1720, 1682, 1589, 1537, 1441, 1411, 1367, 1322, 1289, 1251, 1208, 1032, 991, 883, 846, 823, 739, 687, 646 cm^{-1}.

MS (EI): (*m/z*) 233 (M^+, 8), 232 (12), 190 (6), 167 (37), 150 (7), 149 (100), 146 (16), 57 (34).

4-Bromo-ethyl cinnamate (13):[33b]



Compound **13** was prepared by same procedure as that of **14**.

Yield: 83%, (0.187 g).

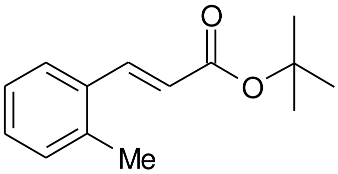
Colorless oil, ***Z* : *E*** = 43 : 57.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 - 6.85 (m, 5H, which also contains one set of *trans* & *cis* olefinic protons), 6.44 - 6.4 and 5.99 - 5.96 (two d, *J* = 16 Hz and *J* = 12 Hz, 1H, second set of *trans* & *cis* olefinic protons), 4.29 - 4.15 (two q, 2H, -CH_2 of –COOEt group of *trans* & *cis* isomers), 1.36 - 1.32 and 1.28 - 1.24 (two t, 3H, -CH_3 of –COOEt group of *trans* & *cis* isomers).

IR (Neat): υ 2981, 2934, 1715, 1636, 1587, 1487, 1445, 1400, 1367, 1311, 1271, 1249, 1178, 1108, 1072, 1033, 1011, 982, 848, 819, 744, 592 cm^{-1}.

MS (EI): (*m/z*) 256 (32), 255 (M^+, 28), 226 (27), 211 (70), 210 (47), 209 (40), 208 (77), 182 (38), 156 (8), 102 (75), 101 (100).

2-methyl-*tert*-butyl cinnamate (15):[33c]



Compound **15** was prepared by same procedure as that of **14**.

Yield: 87%, (0.103 g).

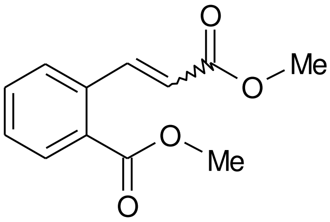
Colorless oil, ***Z* : *E*** = 41 : 59.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.91 - 7.87 (d, *J* = 16 Hz, 1H - *trans* olefinic proton), 7.56 - 7.0 (m, 4H, which also contains doublet of *cis* olefinic proton, *J* = 12.4 Hz, 4H), 6.32 - 5.93 (two d, *J* = 16 Hz, *J* = 12.4 Hz, 1H, olefinic proton of *trans* and *cis* isomer).

IR (Neat): υ 2975, 2954, 1723, 1635, 1596, 1574, 1485, 1452, 1391, 1364, 1296, 1214, 1151, 1082, 1045, 966, 892, 825, 756, 664 cm^{-1}.

MS (EI): (*m/z*) 218 (M^+, 15), 193 (29), 165 (18), 32 (100).

2-(2-Methoxy carbonyl-vinyl)-benzoic acid methyl ester or Methyl 2-(3-methoxy-3-oxoprop-1-en-1-yl)benzoate (16):[34a]



Compound **16** was prepared by same procedure as that of **14**.

Yield: 71%, (0.071 g).

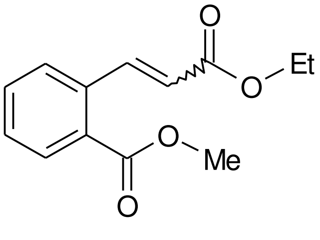
Colorless oil, ***Z* : *E*** = 56 : 44.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.47 - 8.43 (d, *J* = 16 Hz, 1H, *trans* olefinic proton), 8.05 - 7.96 (two dd, J_1 = 7.6, J_2 = 1.2 Hz, 1H), 7.61 - 7.34 (m, which also contains olefinic proton of *cis* isomer and doublet *J* = 7.6 Hz, 3H), 6.33 - 6.02 (two d, *J* = 15.6 Hz and *J* = 12.4 Hz, 1H, olefinic proton of *trans* and *cis* isomer).

IR (Neat): υ 3062, 2989, 2953, 1720, 1638, 1599, 1565, 1436, 1365, 1289, 1195, 1085, 969, 842, 765, 646 cm^{-1}.

MS (EI): (*m/z*) 220 (M^+, 56), 189 (100), 131 (35), 102 (17).

2-(2-Ethoxy carbonyl-vinyl)-benzoic acid methyl ester or Methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (17):[34b]



Compound **17** was prepared by same procedure as that of **14**.

Yield: 69%, (0.185 g).

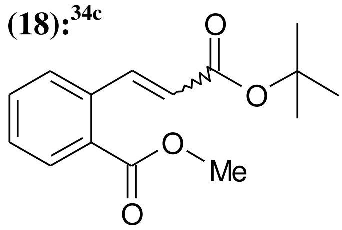
Colorless oil, ***Z* : *E*** = 70 : 30.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.46 - 7.33 (m, 5H, which also contains *trans* & *cis* olefinic protons), 6.33 - 6.29 and 6.04 - 6.01 (two d, *J* = 16 Hz and J = 12 Hz, 1H *trans* & *cis* olefinic protons respectively), 4.3 - 4.0 (two q, 2H, -CH$_2$ of –COOEt group of *trans* & *cis* isomer), 3.93 - 3.87 (two s, 3H, -CH$_3$ of Ar–COOCH$_3$ of *trans* & *cis* isomer), 1.37 - 1.08 (two t, 3H, -CH$_3$ of -COOEt group of *trans* & *cis* isomers).

IR (Neat): υ 3066, 2983, 2954, 2905, 1723, 1636, 1598, 1570, 1482, 1437, 1387, 1368, 1267, 1191, 1134, 1080, 1033, 967, 826, 762, 714, 664 cm^{-1}.

MS (EI): (*m/z*) 234 (M$^+$, 4), 203 (4), 189 (8), 175 (6), 161 (55), 160 (100), 146 (9).

2-(2-tert-Butoxy carbonyl-vinyl)-benzoic acid methyl ester (18):[34c]



Compound **18** was prepared by same procedure as that of **14**.

Yield: 78%, (0.133 g).

Colorless oil, ***Z* : *E*** = 78 : 22.

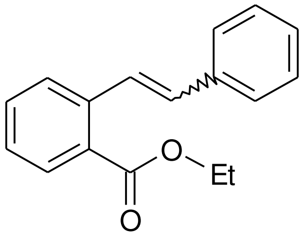
^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.37 - 7.31 (m, 5H which also contains *trans* & *cis* olefinic protons), 6.28 - 6.24 and 5.97 - 5.94 (two d, *J* = 16 Hz and *J* = 12 Hz, 1H *trans* & *cis* olefinic protons), 3.95 and 3.9 (two s, 3H, -CH$_3$ of –COOMe group of *trans* & *cis* isomer), 1.56 and 1.27 (two s, 9H, ^{t}Bu group of *trans* & *cis* isomer).

IR (Neat): υ 2978, 2954, 1722, 1633, 1598, 1570, 1482, 1450, 1435, 1391, 1367, 1295, 1264, 1214, 1151, 1080, 1045, 965, 890, 828, 756, 712, 664 cm^{-1}.

MS (EI): (*m/z*) 262 (M$^+$, 2), 206 (4), 189 (13), 161 (90), 160 (100).

2-Styryl-benzoic acid ethyl ester or

Benzoic acid, 2-(2-phenylethenyl)-ethyl ester (19):[35a]



Compound **19** was prepared by same procedure as that of **14**.

Yield: 78%, (0.106 g).

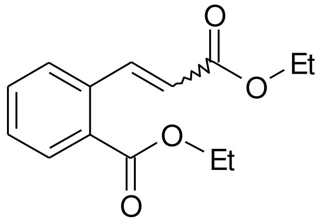
Colorless oil, ***Z* : *E*** = 69 : 31.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.01 - 7.04 (m, 10H, which also contains one set of *trans* & *cis* olefinic protons), 7.03 - 6.99 and 6.65 - 6.62 (two d, *J* = 16 Hz and *J* = 12 Hz, 1H, second set of *trans* & *cis* olefinic protons), 4.43 - 4.32 (two q, 2H, -CH$_2$ of –COOEt group of *trans* & *cis* isomers), 1.43 - 1.36 (two t, 3H, -CH$_3$ of –COOEt group of *trans* & *cis* isomers).

IR (Neat): υ 3061, 3024, 2981, 2933, 1717, 1599, 1583, 1527, 1494, 1465, 1447, 1390, 1366, 1274, 1172, 1131, 1107, 1075, 1044, 1017, 964, 919, 853, 778, 760, 713, 639 cm^{-1}.

MS (EI): (*m/z*) 252 (M$^+$, 100), 223 (10), 207 (21), 179 (53), 178 (91), 177 (42), 175 (34), 149 (14).

Ethyl-2-[(*E*)-2-(ethoxycarbonyl)ethenyl]benzoate (20):[30b]



Compound **20** was prepared by same procedure as that of **14**.

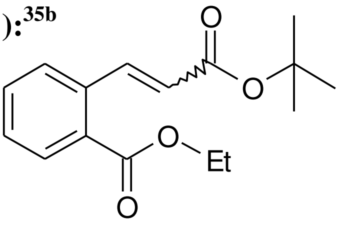
Yield: 28%, (0.043 g).

Colorless oil, ***Z* : *E* =** 68 : 32.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.91 - 7.87 (d, *J* = 15.6 Hz, 1H, olefinic proton of *trans* isomer), 7.56 - 7.01 (m, which also contains doublet of *cis* olefinic proton, *J* = 12.4 Hz, 4H), 6.32 - 5.93 (two d, *J* = 16 Hz and *J* = 12.4 Hz, 1H, olefinic proton of *trans* and *cis* isomer), 2.43 - 2.27 (two s, 3H, -CH$_3$ of *trans* and *cis* isomer), 1.54 and 1.3 (two s, 9H, ^{t}Bu group of *trans* and *cis* isomer).

IR (Neat): υ 2982, 1715, 1638, 1589, 1565, 1486, 1445, 1368, 1275, 1256, 1182, 1134, 1078, 1035, 975, 836, 766, 721 cm^{-1}.

2-(2-tert-Butoxy carbonyl-vinyl)-benzoic acid ethyl ester (21):[35b]



Compound **21** was prepared by same procedure as that of **14**.

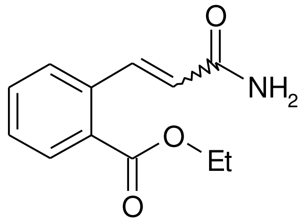
Yield: 74%, (0.226 g).

Colorless oil, ***Z* : *E* =** 75 : 25.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ 8.05 - 7.94 (two dd, *J$_1$* = 8, *J$_2$* = 1.2 Hz, 1H), 7.59 - 7.3 (m, 4H which also contains olefinic proton of *trans* and *cis* isomer), 6.26 - 5.92 (two d, *J* = 15.6 Hz and *J* = 12.4 Hz, 1H, olefinic proton of *trans* and *cis* isomer), 4.44 - 4.33 (two q, *J* = 7.2 Hz, 2H, -CH$_2$- of *trans* and *cis* isomer), 1.44 - 1.37 (two t, *J* = 7.2 Hz, 3H, -CH$_3$ of *trans* and *cis* isomer), 1.55 and 1.27 (two s, 9H, ^{t}Bu group of *trans* and *cis* isomer).

IR (Neat): υ 2988, 2945, 1722, 1635, 1598, 1572, 1485, 1452, 1434, 1393, 1367, 1296, 1264, 1153, 1080, 1033, 966, 892, 829, 757, 713, 665 cm^{-1}.

Ethyl 2-(3-amino-3-oxo-1-propen-1-yl)benzoate (22):



Compound **22** was prepared by same procedure as that of **14**.

Yield: 67%, (0.086 g), ***Z* : *E*** = 67 : 33.

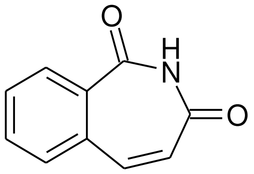
Pale yellow solid, **M.P.** 74 - 76°C (CAS No. 1000563-32-5).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.3 - 8.26 (d, *J* = 16 Hz, *trans* olefinic proton), 8.03 - 7.94 (two dd, 1H, $J_1 = J_2$ = 7.6 Hz), 7.58 - 7.39 (m, 3H), 7.37 - 7.34 (d, *J* = 12 Hz, *cis* olefinic proton), 6.33 - 6.29 and 6.07 - 6.04 (two d, *J* = 16 Hz, *J* = 12 Hz, 1H, second set of *trans* and *cis* olefinic protons), 5.94 - 5.43 (br s, 2H, $-NH_2$ of *trans* & *cis* isomer), 4.39 - 4.33 (two q, 2H, $-CH_2$ of –COOEt group of *trans* & *cis* isomer), 1.42 - 1.38 (two t, 3H, $-CH_3$ of –COOEt group of *trans* & *cis* isomers).

IR (KBr): υ 3402, 3350, 3209, 2988, 1684, 1614, 1566, 1479, 1451, 1432, 1391, 1366, 1299, 1270, 1194, 1137, 1009, 982, 945, 866, 821, 757, 710, 685, 642, 605 cm^{-1}.

MS (EI): (*m/z*) 219 (2), 176 (9), 175 (56), 174 (40), 147 (69), 146 (100), 145 (63), 103 (20).

2*H*-2-benzaepine-1,3-dione (23):[36a]



Compound **23** was prepared by same procedure as that of **14**.

Yield: 65%, (0.067 g).

Pale yellow solid, **M.P.** 134 - 136°C (Lit.[36a] 135 - 136°C).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (br s, 1H, -NH-), 8.55 - 8.53 (dd, J_1 = 8 Hz, J_2 = 7.6 Hz, 1H), 7.74 - 7.62 (m, 2H), 7.51 - 7.49 (m, 1H), 7.18 - 7.15 (d, *J* = 12.8 Hz, 1H, Ar-CH=), 6.41 - 6.38 (dd, J_1 = 12.4 Hz, J_2 = 2.4 Hz, 1H, =CH-C=O).

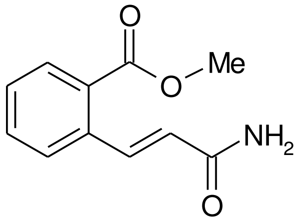
IR (KBr): υ 3316, 3183, 2926, 2855, 1683, 1653, 1624, 1591, 1453, 1420, 1401, 1361, 1311, 1193, 1123, 831, 761, 681, 656, 643, 599 cm^{-1}.

MS (EI): (*m/z*) 173 (M$^+$, 55), 172 (100), 145 (95), 144 (85), 117 (25), 102 (89), 76 (31), 69 (68).

***o*-Methoxycarbonyl-*trans*-cinnamamide (24):**[36b]

Catalyst solution: A solution of palladium acetate (0.44 mg, 0.002 mmol) and ligand **1a** (0.75 mg, 0.0024 mmol) was made in dry dimethylacetamide (2 mL) under the nitrogen atmosphere. This was sonicated for 2-3 min to degas and to make the solution homogeneous.

In another two-necked flask, a mixture of *o*-iodobenzoate **2f** (0.103 g, 0.393 mmol), dry potassium carbonate (0.109 g, 0.786 mmol) and dry dimethylacetamide (5 mL) was made and heated under a nitrogen atmosphere. When the temperature attained 60°C, acrylamide **3d** (0.042 g, 0.589 mmol) was slowly introduced by syringe. The mixture was then heated to 100°C and the previously prepared catalyst solution was added. The temperature was further raised to 120°C and continued for another 40h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 25 mL). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed in vacuum, and the crude product was purified by column chromatography on silica gel.



Yield: 41%, (0.033 g), ***Z* : *E*** = 0 : 100.

Pale yellow solid, **M.P.** 158 - 160°C (Lit[36b] 161°C).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 - 8.27 (d, *J* = 16 Hz, 1H, *trans* olefinic proton), 7.98 - 7.95 (m, 1H), 7.59 - 7.51 (m, 2H), 7.45 - 7.41 (m, 1H), 6.34 - 6.3 (d, *J* = 16 Hz, 1H *trans* olefinic proton), 5.75 - 5.62 (br s, 2H, -NH_2 of –$CONH_2$), 3.93 (s, 3H, -CH_3 of -COOMe).

IR (KBr): υ 3401, 3350, 3199, 2923, 2852, 1720, 1668, 1609, 1567, 1481, 1434, 1390, 1326, 1299, 1257, 1191, 1125, 1077, 982, 966, 949, 863, 758, 707, 656, 644, 604 cm^{-1}.

MS (EI): (*m/z*) 205 (M^+, 4), 173 (22), 161 (68), 160 (100), 146 (44), 145 (62).

Z* : *E = 72 : 28.

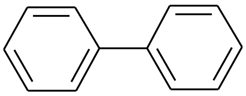
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 - 7.36 (m, 5H, which also contains one set of *trans* & *cis* olefinic protons), 6.34 - 6.3 and 6.08 - 6.05 (two d, *J* = 16 Hz and *J* = 12 Hz, 1H, second set of *trans* & *cis* olefinic protons), 5.83 - 5.37 (br s, 2H, -NH_2 of *trans* & *cis* isomer), 3.95 - 3.91 (two s, 3H, -CH_3 of -COOMe group of *trans* & *cis* isomer).

General Procedure for the Suzuki Reaction under Photochemical irradiation

To an oven-dried conical flask equipped with a stirrer bar and guard tube was charged iodobenzene **2a** (0.2 g, 0.98 mmol), K_2CO_3 (0.27 g, 1.96 mmol), palladium acetate (1.1 mg, 0.005 mmol) and **1c** (1.63 mg, 0.006 mmol) in dioxane-water (1:1, 10 mL). To this reaction mixture phenyl boronic acid **25a** (0.143 g, 1.176 mmol) was added.

The reaction mixture was exposed to sunlight for 1 day. After completion of reaction time, the reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 mL). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel to afford biphenyl **26**(0.137 g, 91%) (Table-3, entry 1).

Biphenyl (26):[37a]



Yield: 91%, (0.137 g).

White solid, **M.P.** 66 - 68°C (Lit.[37a] 68 - 70°C).

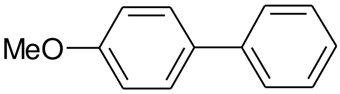
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 - 7.62 (m, 2H), 7.5 - 7.46 (m, 2H), 7.4 - 7.36 (m, 1H).

IR (KBr): υ 3059, 3032, 2950, 1568, 1475, 1170, 1086, 1040, 1004, 901, 729, 694, 608 cm^{-1}.

MS (EI): (*m/z*) 155 (M+1, 20), 154 (M$^+$, 100), 153 (44), 149 (76), 71 (50), 57 (65).

4-Methoxy biphenyl (27):[37b]

Compound **27** was prepared by same procedure as that of **26**.



Yield: 53%, (0.103 g).

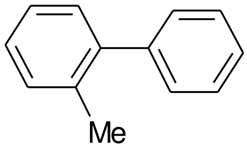
White solid, **M.P.** 82 - 86°C (Lit.[37b] 86 - 90°C).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 - 7.54 (m, 4H), 7.46 - 7.42 (m, 2H), 7.35 - 7.32 (m, 1H), 7.03 - 6.99 (m, 2H), 3.88 (s, 3H, -OCH_3).

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

MS (EI): (*m/z*) 185 (M+1, 24) , 184 (M$^+$, 50), 169 (28), 129 (36), 97 (54), 69 (100), 57 (94).

2-Methyl biphenyl (28):[37c]



Compound **28** was prepared by same procedure as that of **26**.

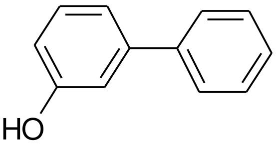
Yield: 83%, (0.136 g), colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 - 7.39 (m, 2H), 7.36 - 7.30 (m, 3H), 7.27 - 7.22 (m, 4 H), 2.27 (s, 3H).

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

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

3-Hydroxy biphenyl (29):[38a]



Compound **29** was prepared by same procedure as that of **26**.

Yield: 82%, (0.138 g).

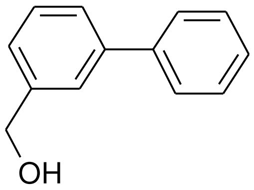
Pale yellow solid, **M.P.** 72°C (Lit.[38a] 73-74°C).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 - 7.59 (m, 2H), 7.48 - 7.44 (m, 2H), 7.4 - 7.32 (m, 2H), 7.21 - 7.19 (m, 1H), 7.1 - 7.09 (m, 1H), 6.86 - 6.84 (m, 1H), 4.9 (br s, 1H, -OH).

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

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

(3-Hydroxymethyl)- biphenyl (30):[38b]



Compound **30** was prepared by same procedure as that of **26**.

Yield: 77%, (0.139 g).

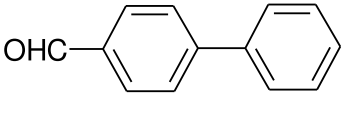
Pale yellow solid, **M.P.** 77°C (Lit.[38b] 51-52°C).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 - 7.62 (m, 3H), 7.57 - 7.55 (m, 1H), 7.5 - 7.45 (m, 3H), 7.41 - 7.36 (m, 2H), 4.78 (s, 2H, -CH_2), 2.16 (br s, 1H, -OH).

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

MS (EI): (*m/z*) 185 (M+1, 14), 184 (M^+, 100), 183 (23), 167 (9), 166 (16), 165 (30), 155 (49), 153 (19), 152 (25), 77 (7).

4-Formyl biphenyl (31):[39a]



Compound **31** was prepared by same procedure as that of **26**.

Yield: 55%, (0.097 g).

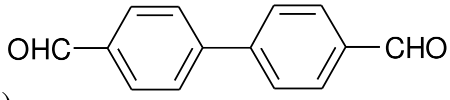
Yellow solid, **M.P.** 58 - 60°C (Lit.[39a] 61°C).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.08 (s, 1H, -CHO), 7.99 - 7.97 (m, 2H), 7.79 - 7.77 (m, 2H), 7.68 - 7.65 (m, 2H), 7.53 - 7.43 (m, 3H).

IR (KBr): υ 3059, 3032, 2924, 2828, 2735, 1700, 1604, 1565, 1515, 1485, 1450, 1412, 1384, 1308, 1281, 1214, 1170, 1109, 1076, 1007, 917, 838, 762, 729, 697, 646, 629, 547 cm^{-1}.

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

4, 4'-Diformyl biphenyl (32):[39b]



Yield: 47%, (0.058 g).

Yellow solid, **M.P.** 110 - 114°C (Lit.[39b] 113 - 114°C).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.86 (s, 1H, -CHO), 7.84 - 7.82 (d, *J* = 8 Hz, 2H), 7.0 - 6.98 (d, *J* = 8 Hz, 2H).

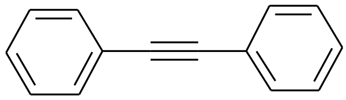
IR (KBr): υ 3165, 2877, 2619, 2016, 1905, 1668, 1600, 1517, 1453, 1386, 1315, 1287, 1217, 1160, 858, 833, 788, 707, 652, 642, 603 cm^{-1}.

MS (EI): (*m/z*) 210 (M^+, 6), 209 (10), 129 (7), 123 (13), 122 (78), 121 (78), 120 (57), 94 (8), 93 (100), 65 (73), 63 (18).

General Procedure for the Sonogashira Reaction under Photochemical irradiation

To an oven-dried conical flask equipped with a stirrer bar and guard tube was charged iodobenzene **2a** (0.2 g, 0.98 mmol), K_2CO_3 (0.27 g, 1.96 mmol), palladium acetate (2.2 mg, 0.01 mmol) and **1c** (3.3 mg, 0.012 mmol) in NMP (10 mL). To this reaction mixture Phenylacetylene **33** (0.15 g, 1.47 mmol) was added. The reaction mixture was exposed to sunlight for 3 days. After completion of reaction time, the reaction mixture was quenched with water and extracted with ethyl acetate (3 x 25 mL). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel to afford diphenyl actylene **34** (0.146 g, 84%) (Table-2, entry 7).

Diphenyl actylene (34):[40a]



Yield: 84%, (0.146 g).

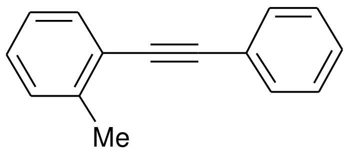
White solid, **M.P.** 72°C (Lit.[40a] 68 - 70°C).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 - 7.54 (m, 2H), 7.44 - 7.36 (m, 3H).

IR (KBr): υ 3056, 2921, 2213, 2147, 1951, 1881, 1596, 1570, 1490, 1438, 1067, 1023, 912, 752, 684 cm^{-1}.

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

1-Methyl-2-phenylethynyl-benzene (35):[40b]



Compound **35** was prepared by same procedure as that of **34**.

Yield: 44%, (0.083 g), Colourless oil.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.59 - 7.51 (m, 3H), 7.41 - 7.36 (m, 3H), 7.27 - 7.19 (m, 3H), 2.55 (s, 3H).

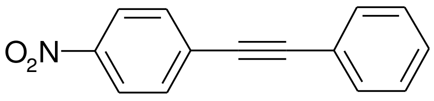
IR (KBr): υ 3045, 2215, 1594, 1495, 1375, 915, 860, 768 cm^{-1}.

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

4-Nitro-diphenyl actylene (36):[40a]

Compound **36** was prepared by same procedure as that of **34**.

Yield: 80%, (0.144 g).



Yellow solid, **M.P.** 125^{o}C (Lit.[40a] 121 - 123^{o}C).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.26 - 8.23 (m, 2H), 7.7 - 7.67 (m, 2H), 7.6 - 7.57 (m, 2H), 7.44 - 7.39 (m, 3H).

IR (KBr): υ 3103, 2924, 2213, 1967, 1591, 1510, 1441, 1378, 1345, 1286, 1175, 1104, 1071, 995, 921, 857, 831, 764, 747, 718, 688 cm^{-1}.

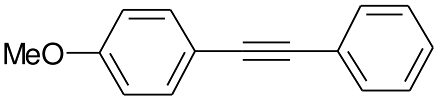
MS (EI): (*m/z*) 224 (M+1, 14), 223 (M^{+}, 100), 193 (28), 176 (54), 165 (20), 151 (16).

4-Methoxy-diphenyl actylene (37):

Compound **37** was prepared by same procedure as that of **34**.

Yield: 38%, (0.068 g).

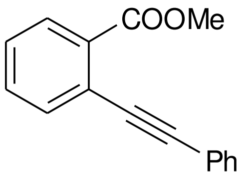
White solid, **M.P.** 62 - 64^{o}C (Lit.[40c] 56 - 58^{o}C).



^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.55 - 7.48 (m, 4H), 7.38 - 7.33 (m, 3H), 6.91 - 6.89 (m, 2H), 3.78 (s, 3H).

IR (KBr): υ 3038, 2966, 2933, 2859, 2226, 1605, 1508, 1463, 1244, 1010, 986, 835, 765, 753, 688 cm^{-1}.

MS (EI): (*m/z*) 209 (8), 208 (M^{+}, 100), 193 (40), 165 (43), 139 (9).



2-Phenylethynyl-benzoic acid methyl ester (38):[41a]

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

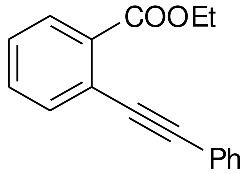
Yield: 75%, (0.092 g), colorless oil.

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

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

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

2-Phenylethynyl-benzoic acid ethyl ester (39):[41b]



Compound **39** was prepared by same procedure as that of **34**.

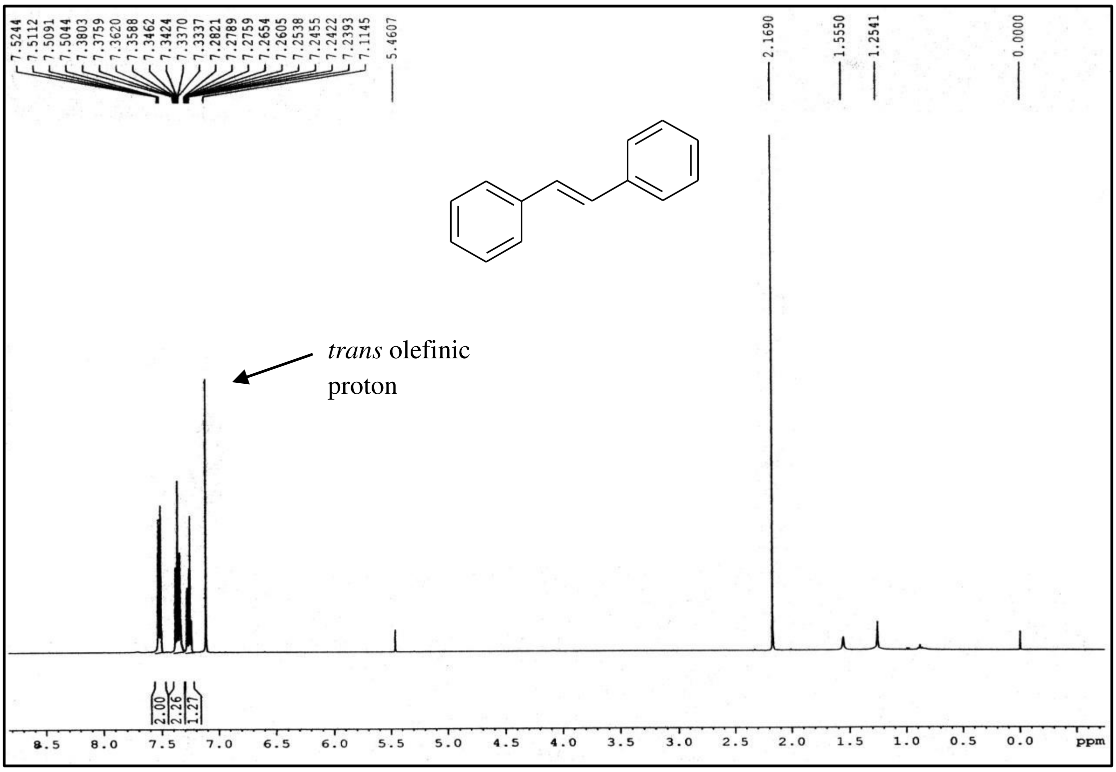
Yield: 74%, (0.137 g), colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 - 7.99 (m, 1H), 7.69 - 7.59 (m, 4H), 7.53 - 7.34 (m, 4H), 4.47 - 4.42 (q, 2H), 1.44 - 1.40 (t, 3H).

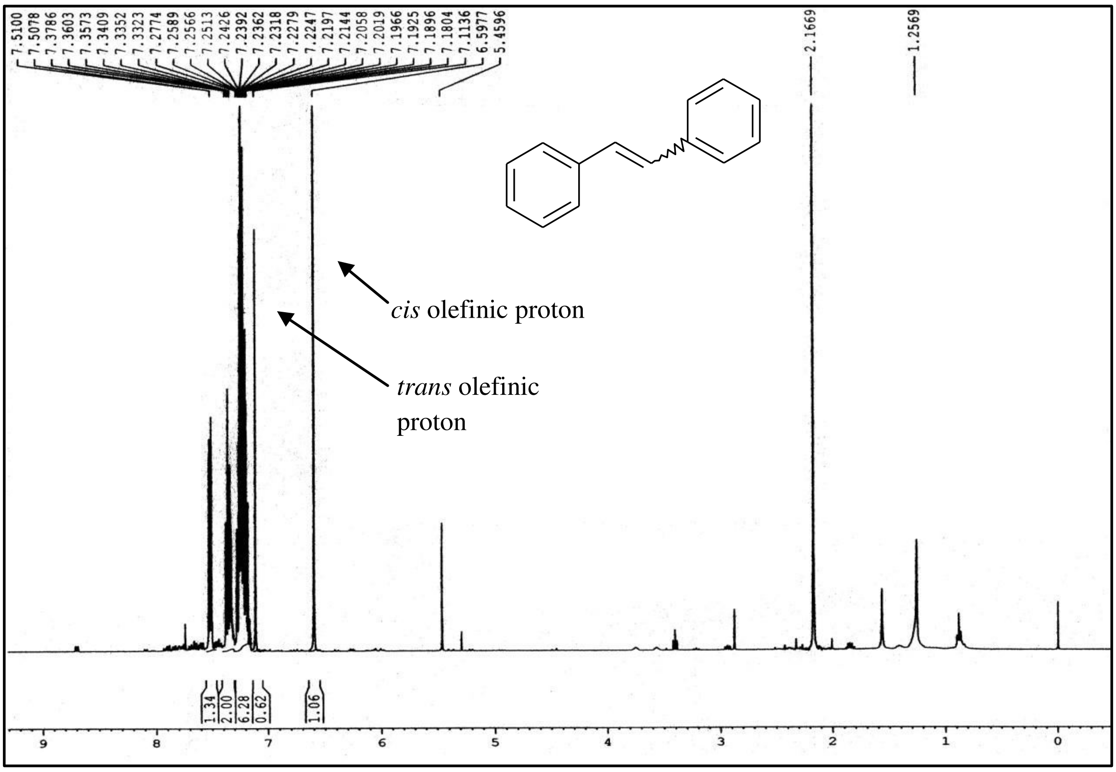
IR (Neat): υ 3061, 2982, 2931, 2332, 2260, 2215, 2149, 1951, 1723, 1597, 1568, 1494, 1444, 1389, 1366, 1290, 1250, 1168, 1130, 1076, 1040, 1019, 960, 915, 858, 757, 693, 658 cm^{-1}.

MS (EI): (*m/z*) 250 (M$^+$, 80) 222 (76), 221 (82), 205 (25), 193 (25), 176 (63), 175 (27), 165 (100), 149 (19).

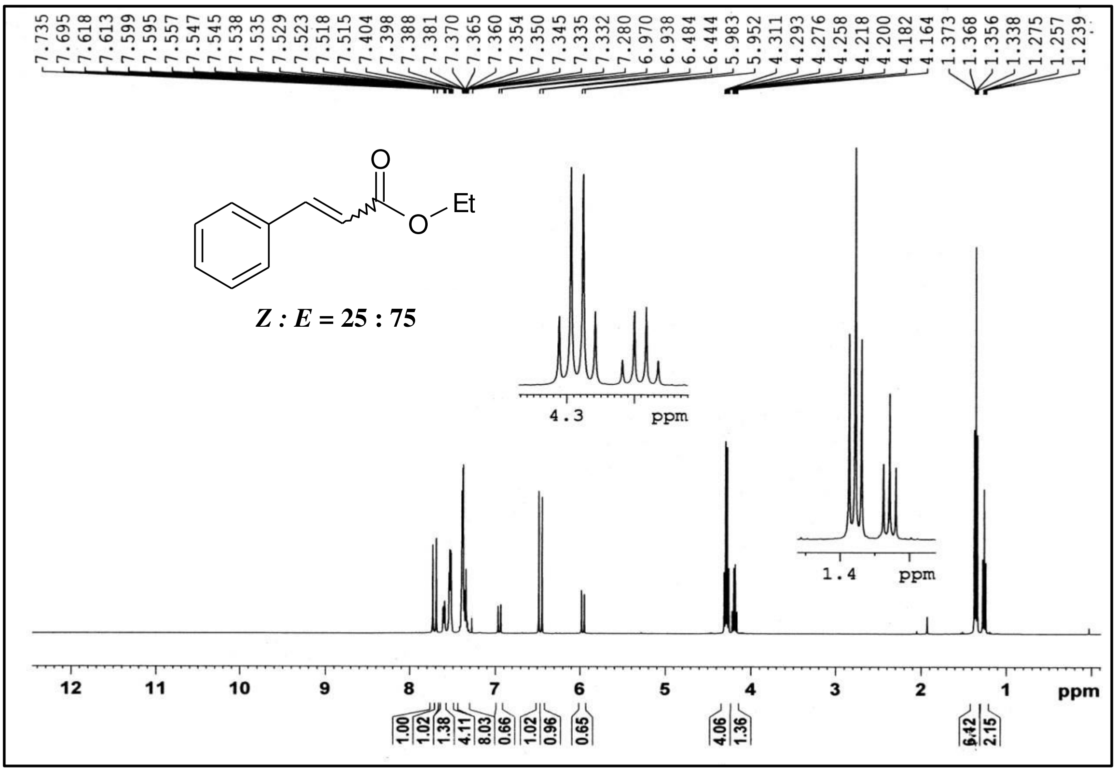
Spectral Data



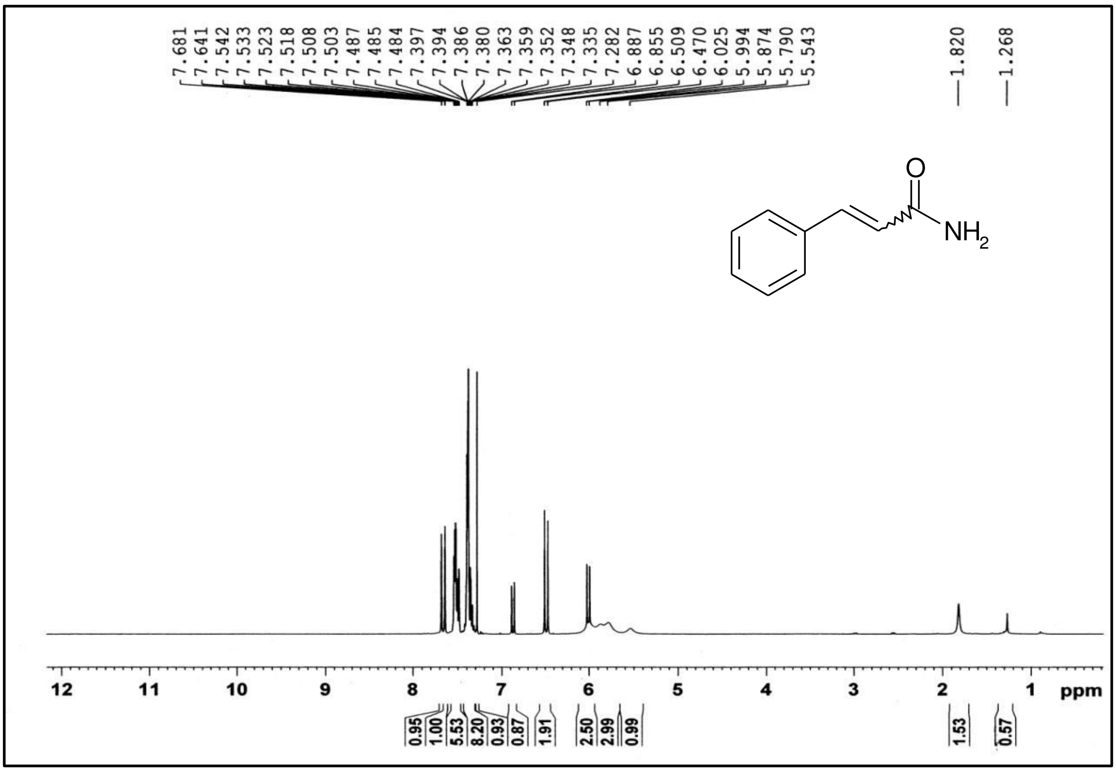
^{1}H-NMR Spectra of Compound 4 (*Z* : *E* = 0 : 100) (400 MHz, $CDCl_3$)



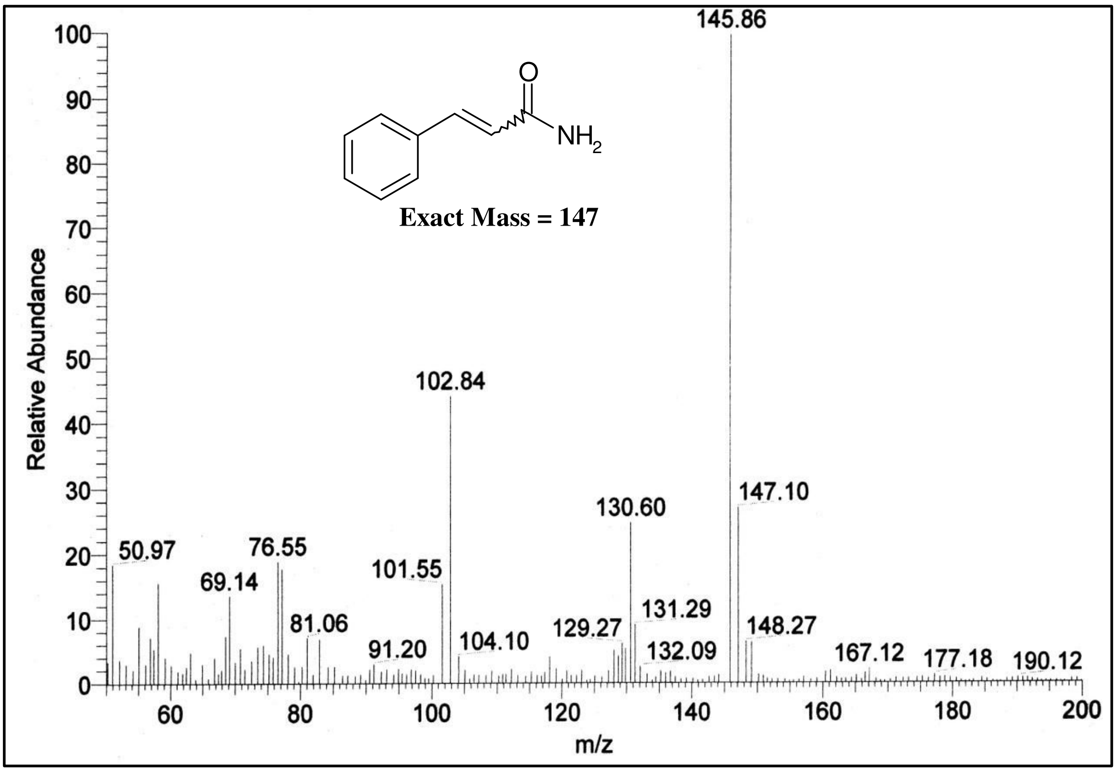
^{1}H-NMR Spectra of Compound 4 (*Z* : *E* = 63:37) (400 MHz, $CDCl_3$)



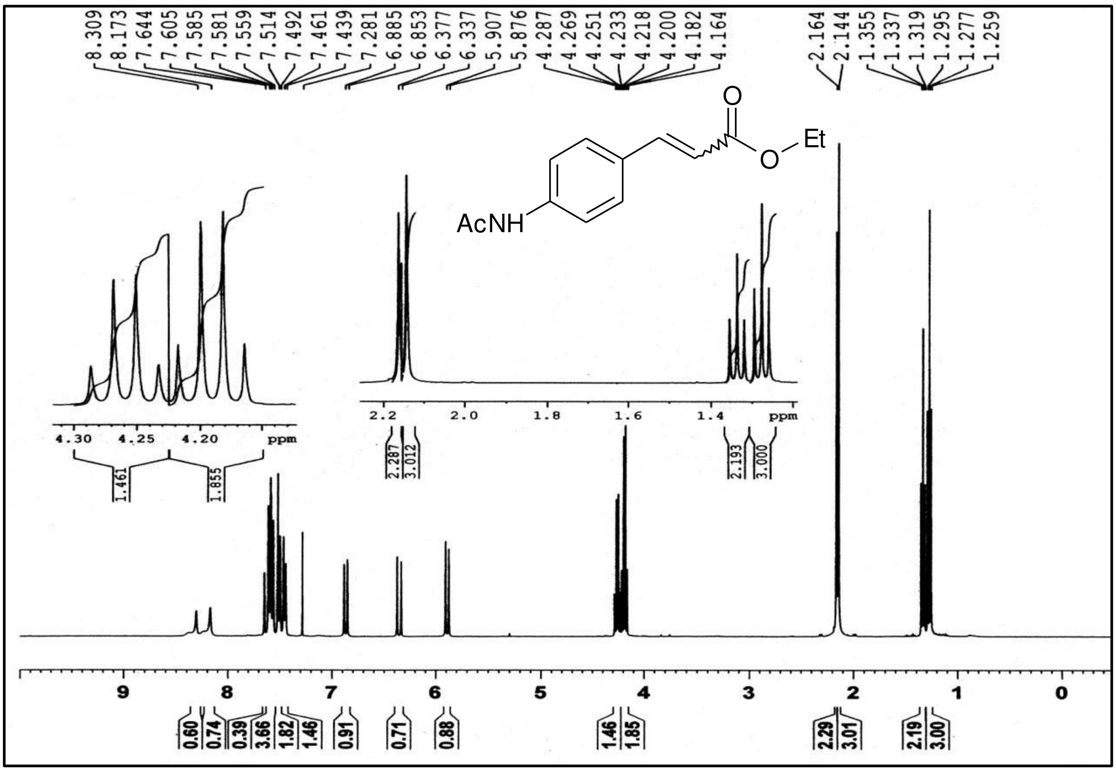
^{1}H-NMR Spectra of Compound 6 (Multi-gram Synthesis) (400 MHz, $CDCl_3$)



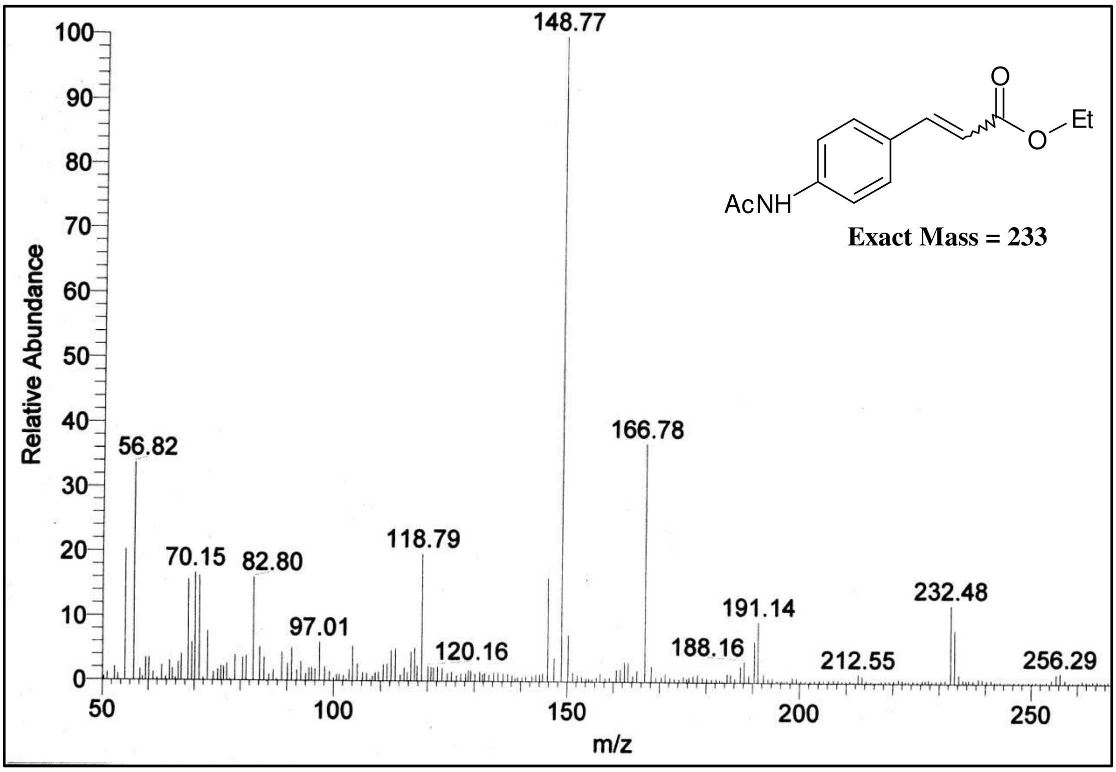
^{1}H-NMR Spectra of Compound 8 (*Z* : *E* = 48 : 52) (400 MHz, $CDCl_3$)



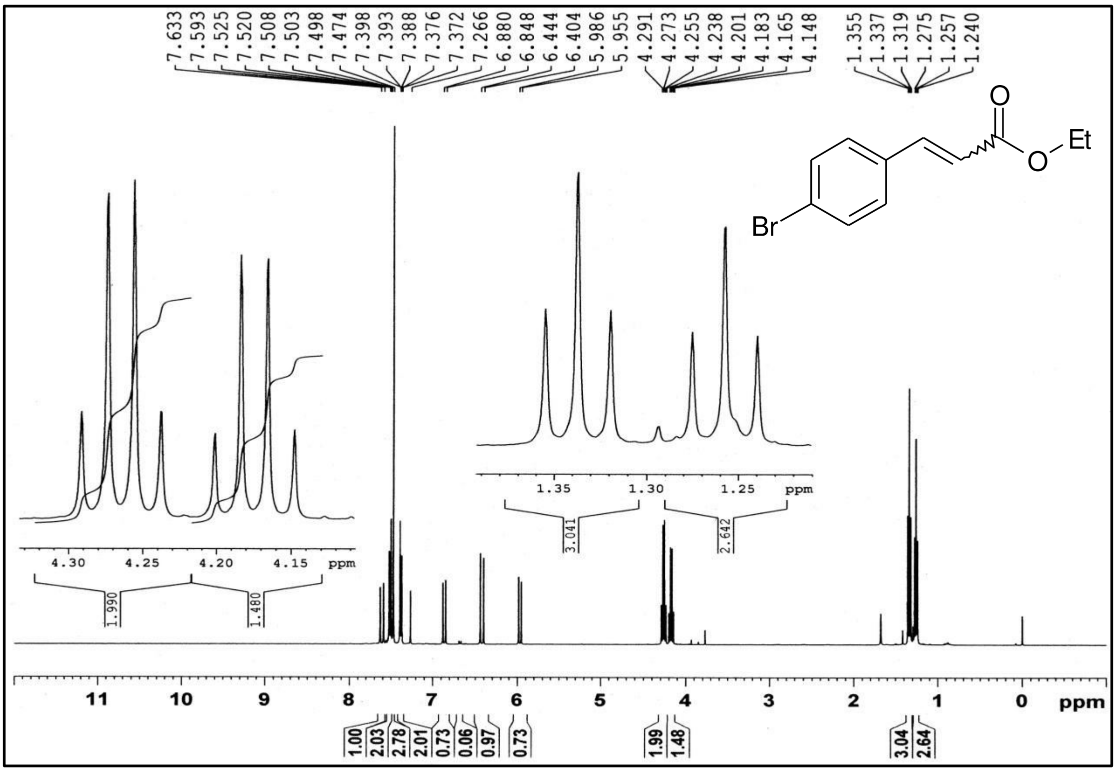
EI-Mass Spectra of Compound 8



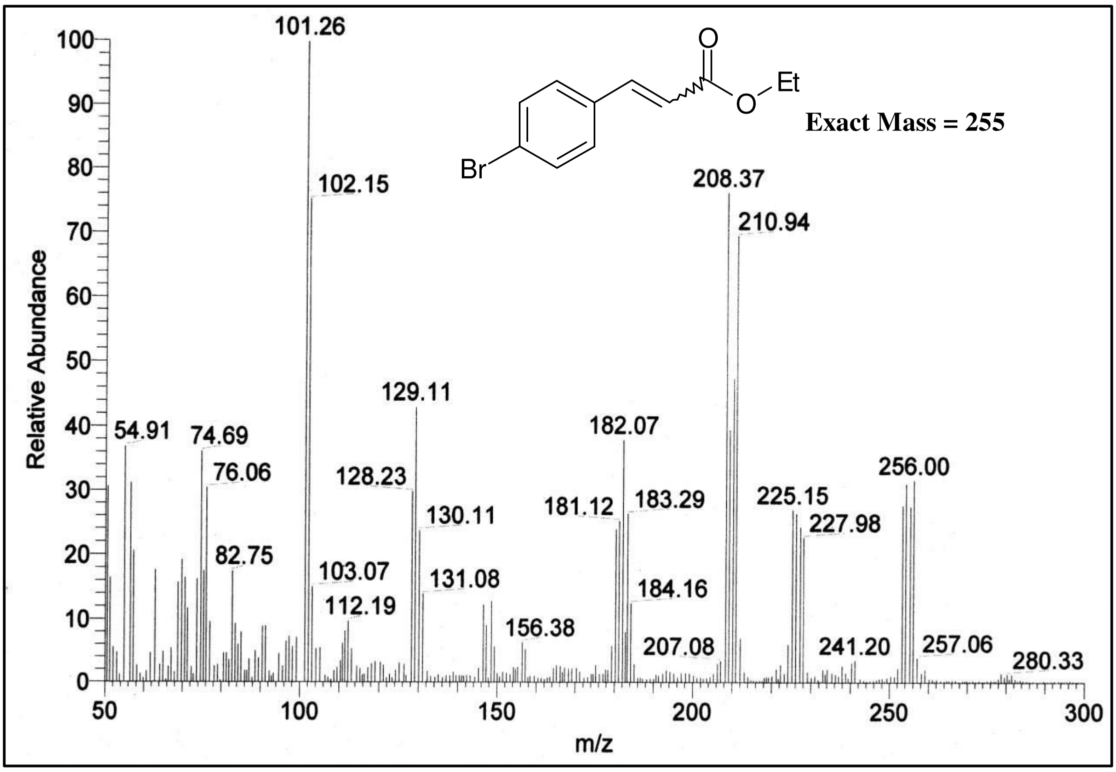
^{1}**H-NMR Spectra of Compound 12 (*Z* : *E* = 55 : 45) (400 MHz, $CDCl_3$)**



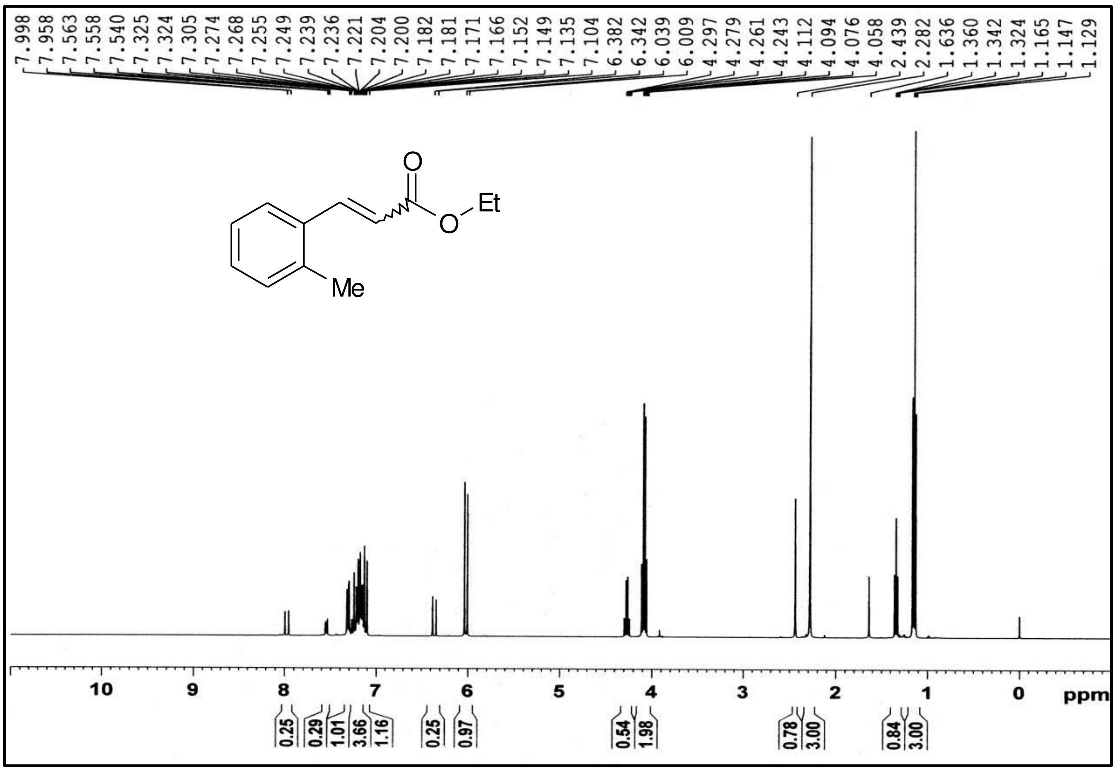
EI-Mass Spectra of Compound 12



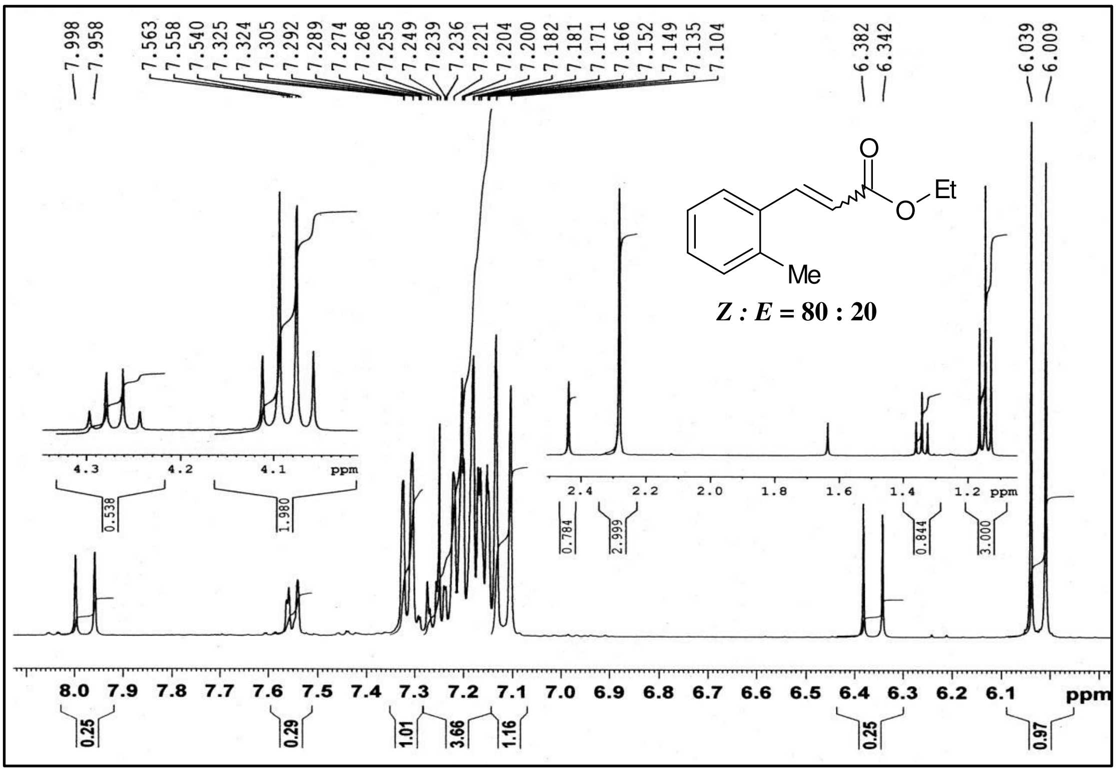
^{1}H-NMR Spectra of Compound 13 (*Z* : *E* = 43 : 57) (400 MHz, $CDCl_3$)



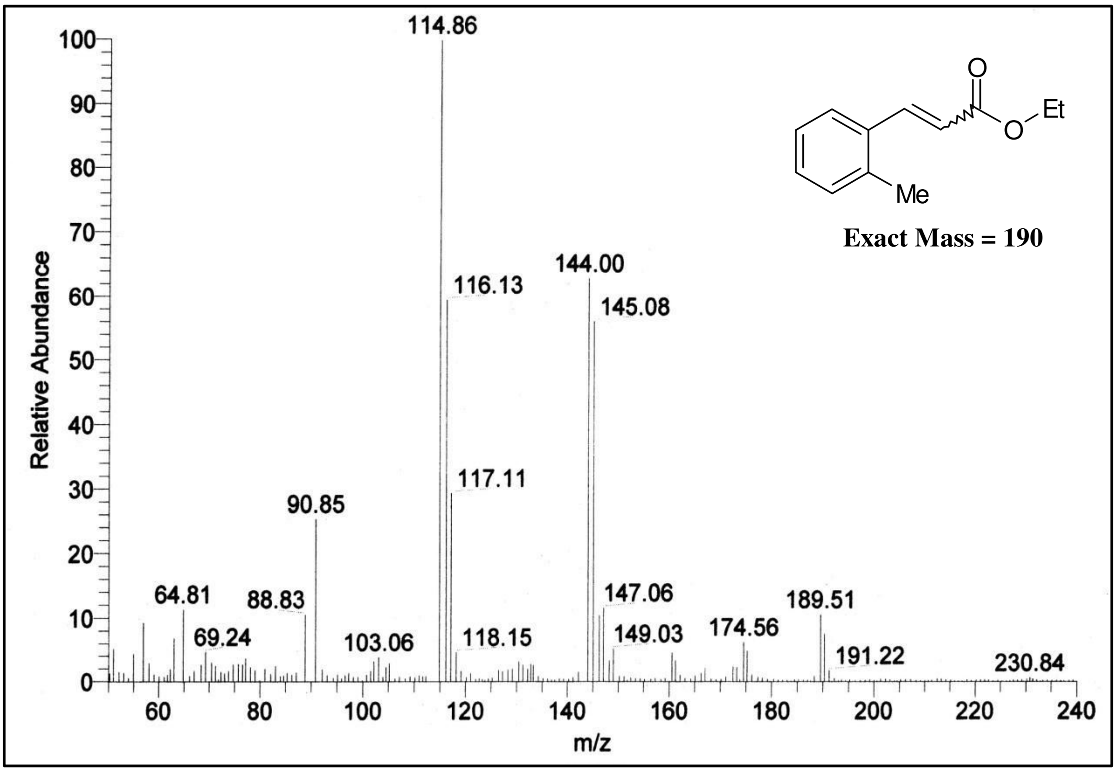
EI-Mass Spectra of Compound 13



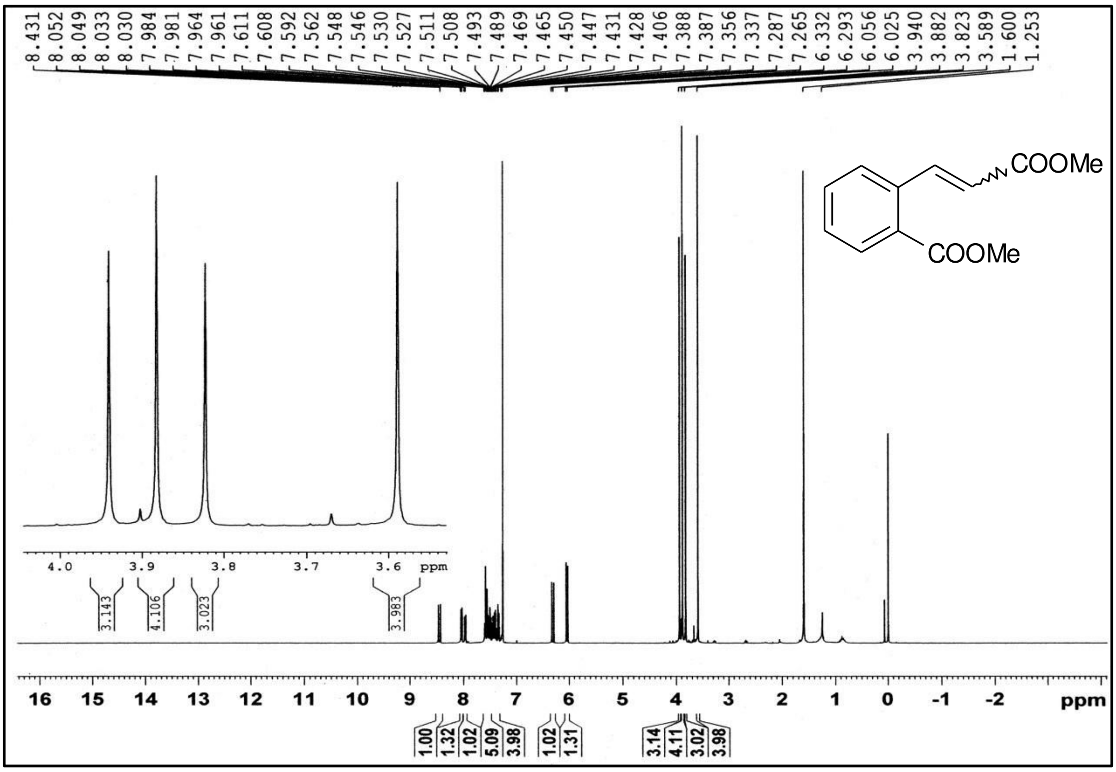
^{1}H-NMR Spectra of Compound 14 (*Z* : *E* = 80 : 20) (400 MHz, $CDCl_3$)



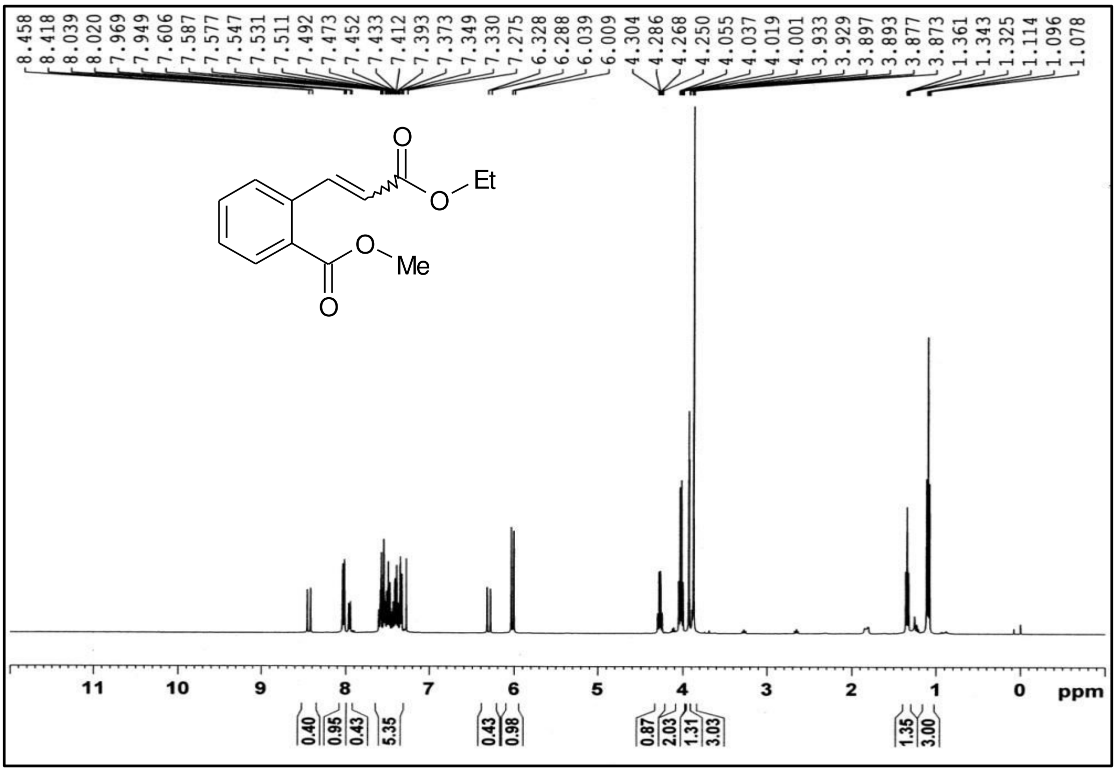
^{1}H-NMR Spectra of Compound 14 (expanded form) (400 MHz, $CDCl_3$)



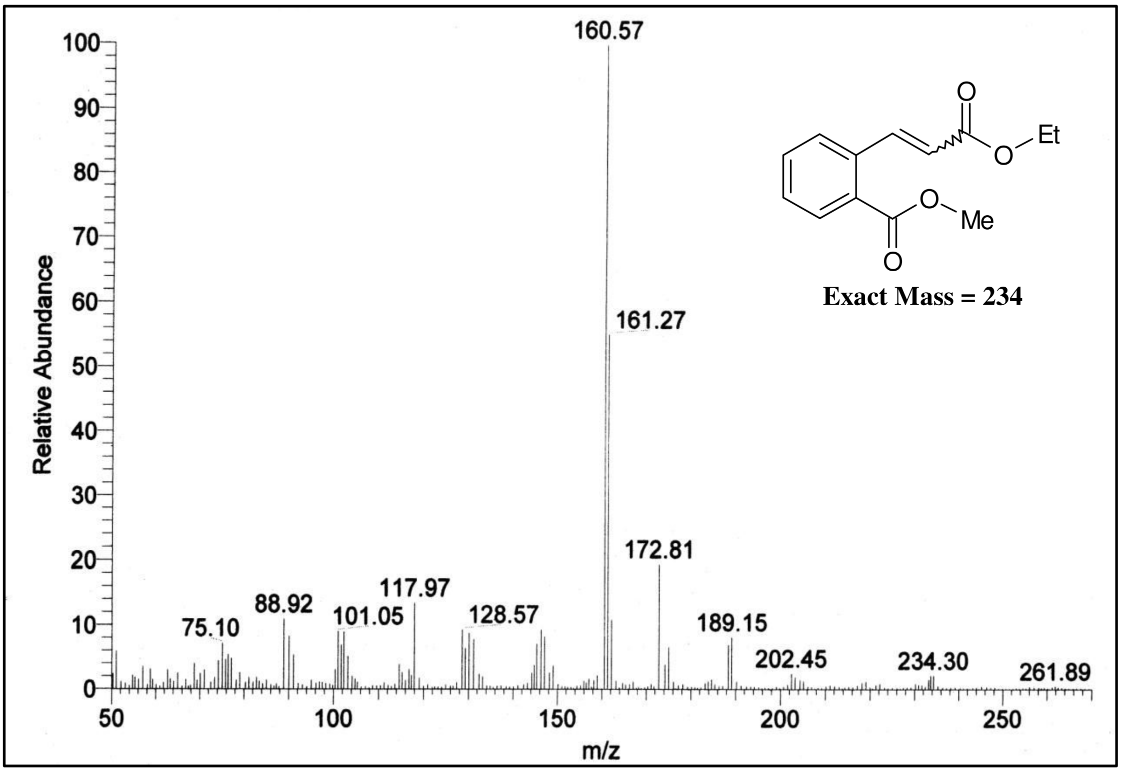
EI-Mass Spectra of Compound 14



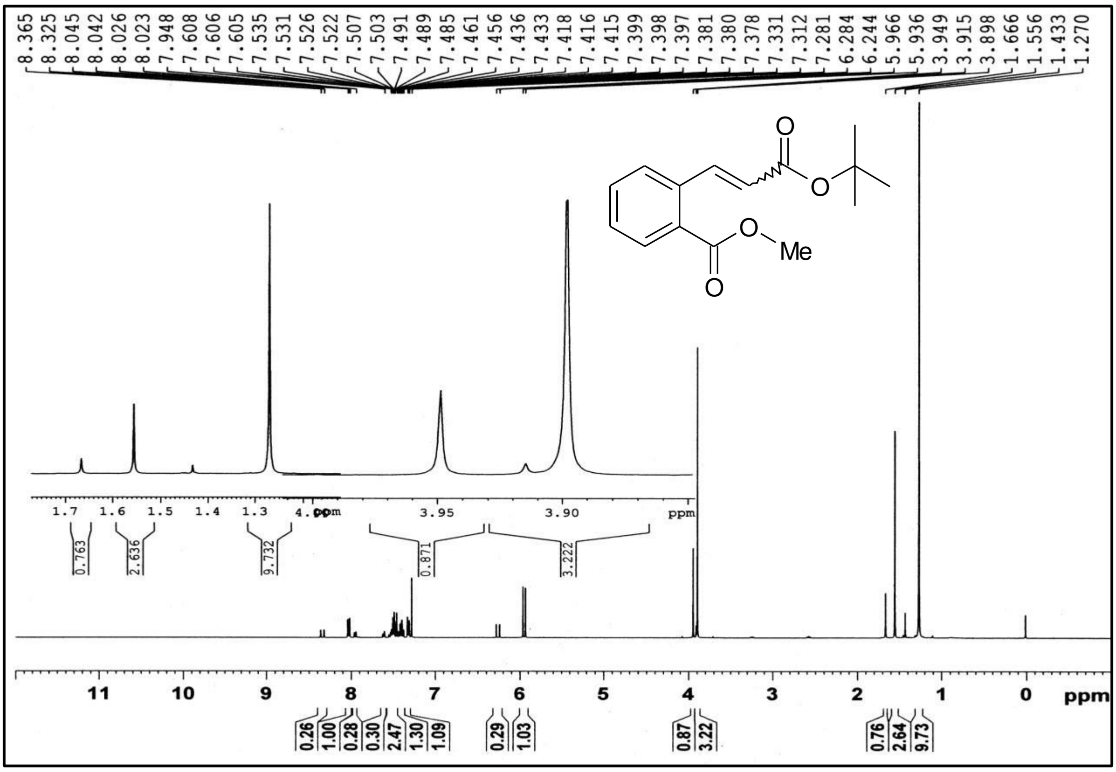
^{1}**H-NMR Spectra of Compound 16 (*Z* : *E* = 56 : 44) (400 MHz, CDCl$_3$)**



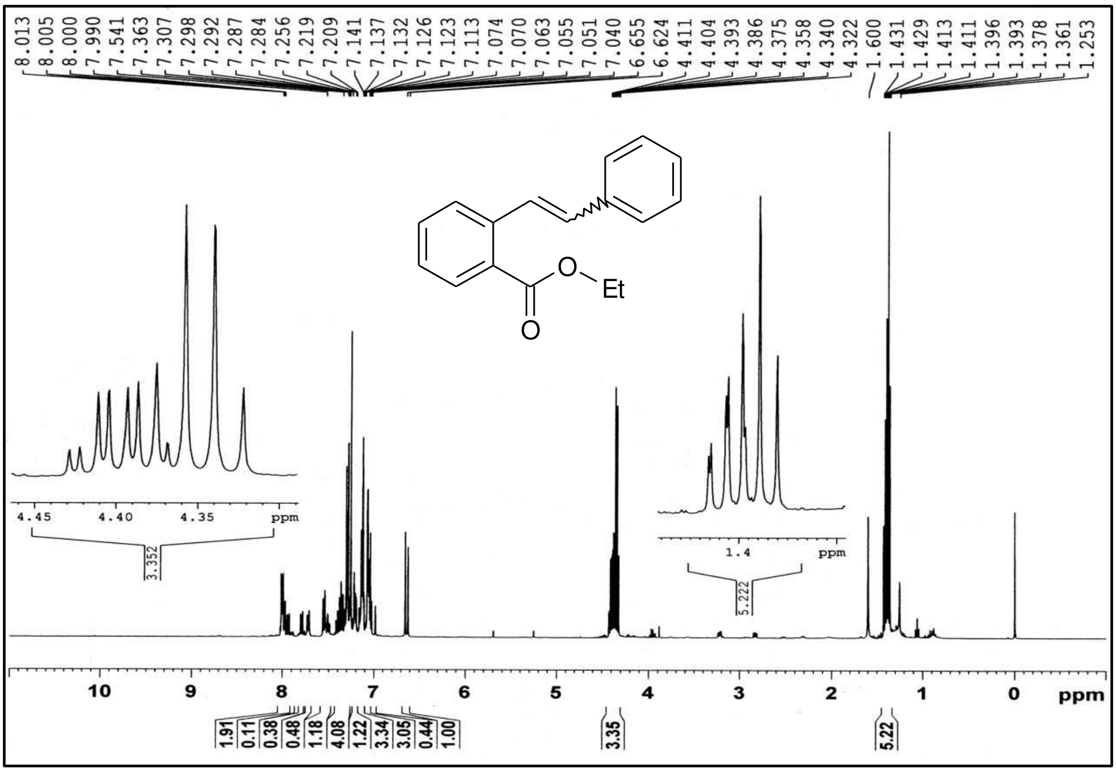
^{1}**H-NMR Spectra of Compound 17 (*Z* : *E* = 70 : 30) (400 MHz, CDCl$_3$)**



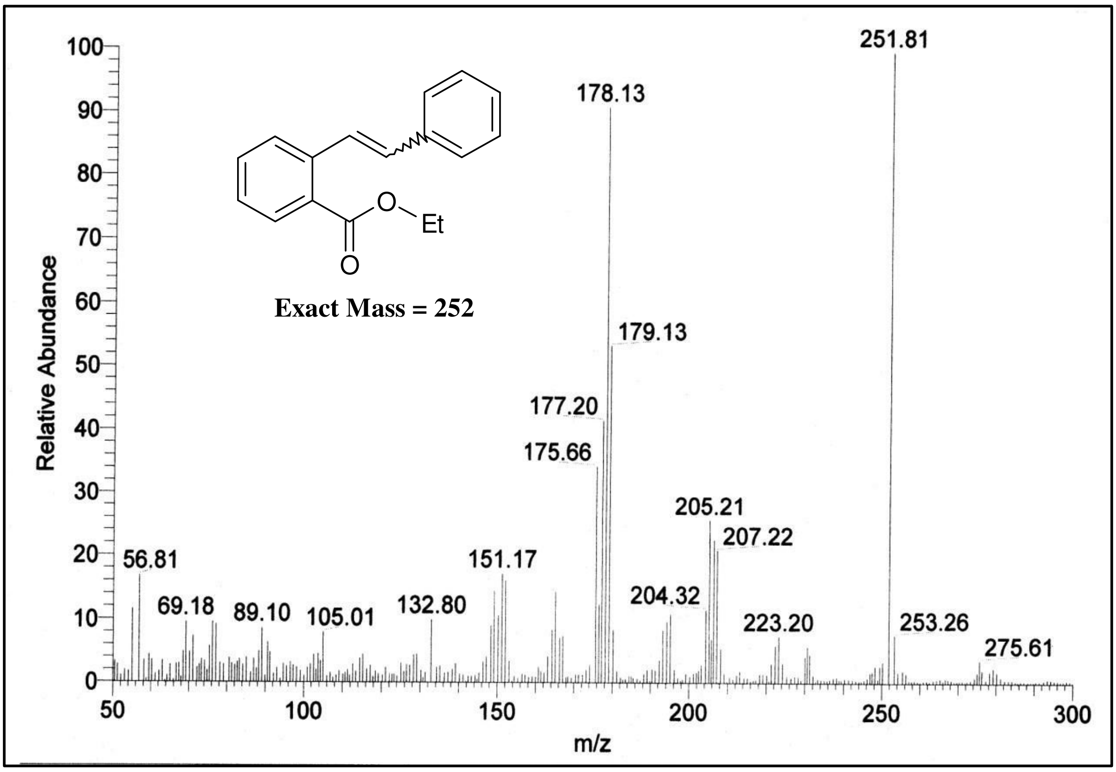
EI-Mass Spectra of Compound 17



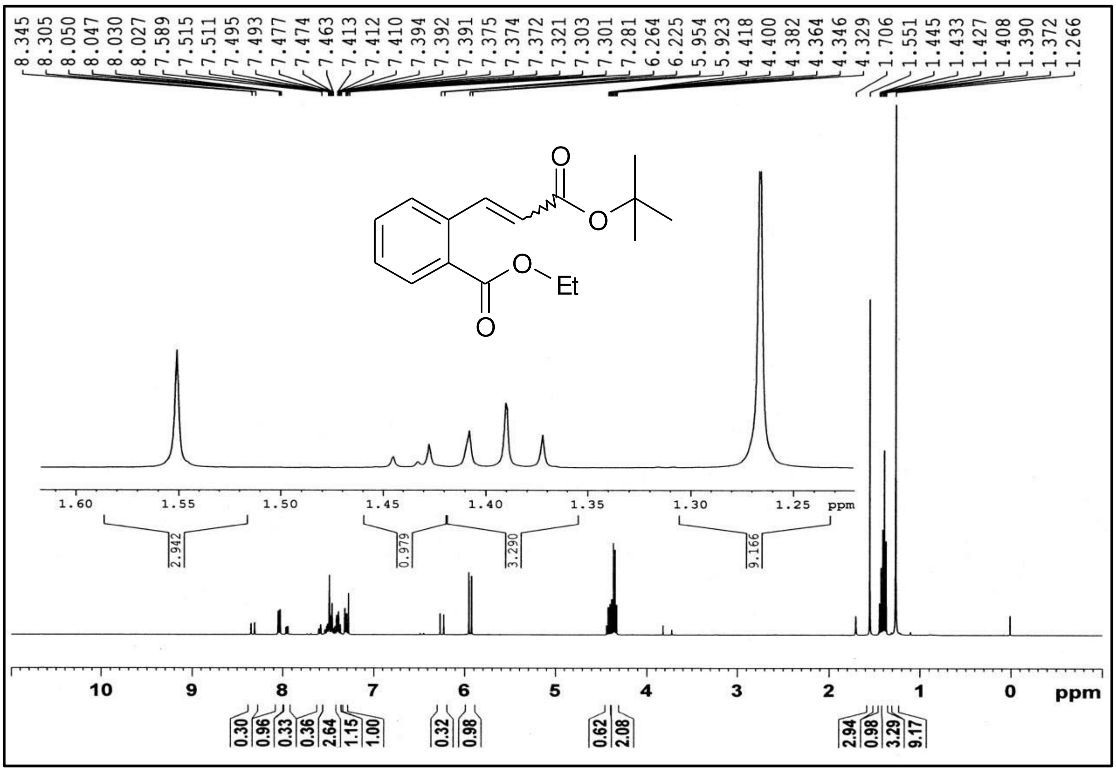
^{1}H-NMR Spectra of Compound 18 (*Z* : *E* = 78 : 22) (400 MHz, $CDCl_3$)



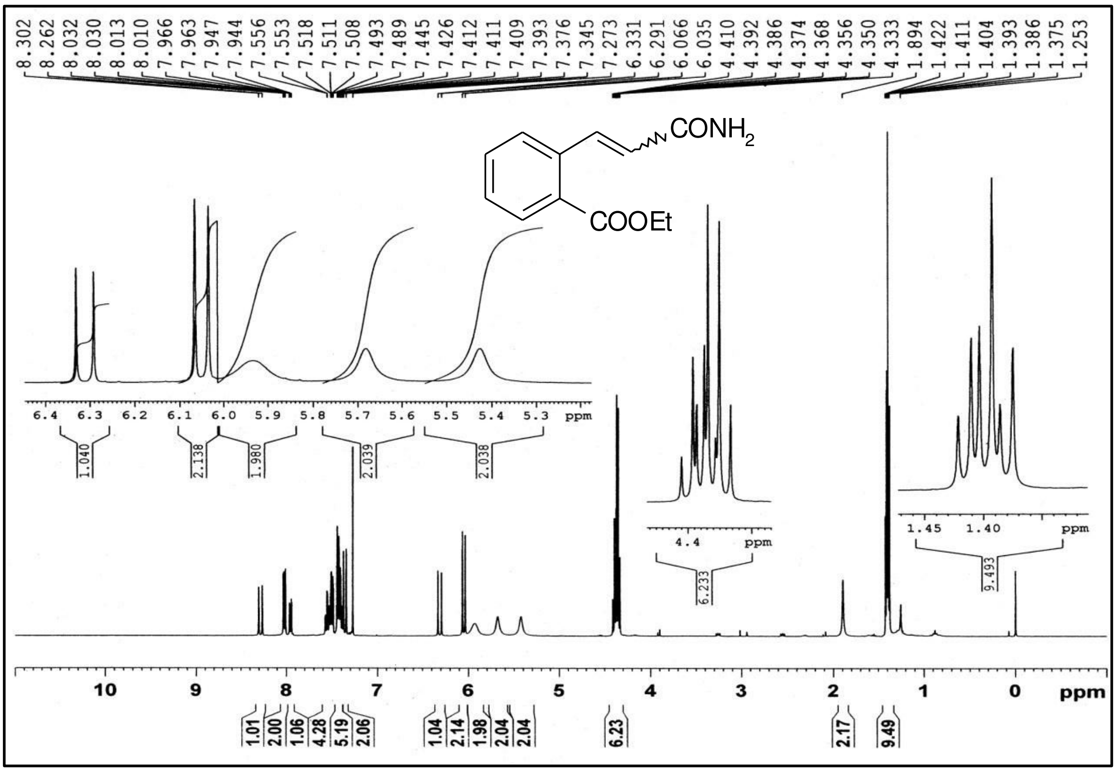
^{1}H-NMR Spectra of Compound 19 (*Z : E* = 69 : 31) (400 MHz, $CDCl_3$)



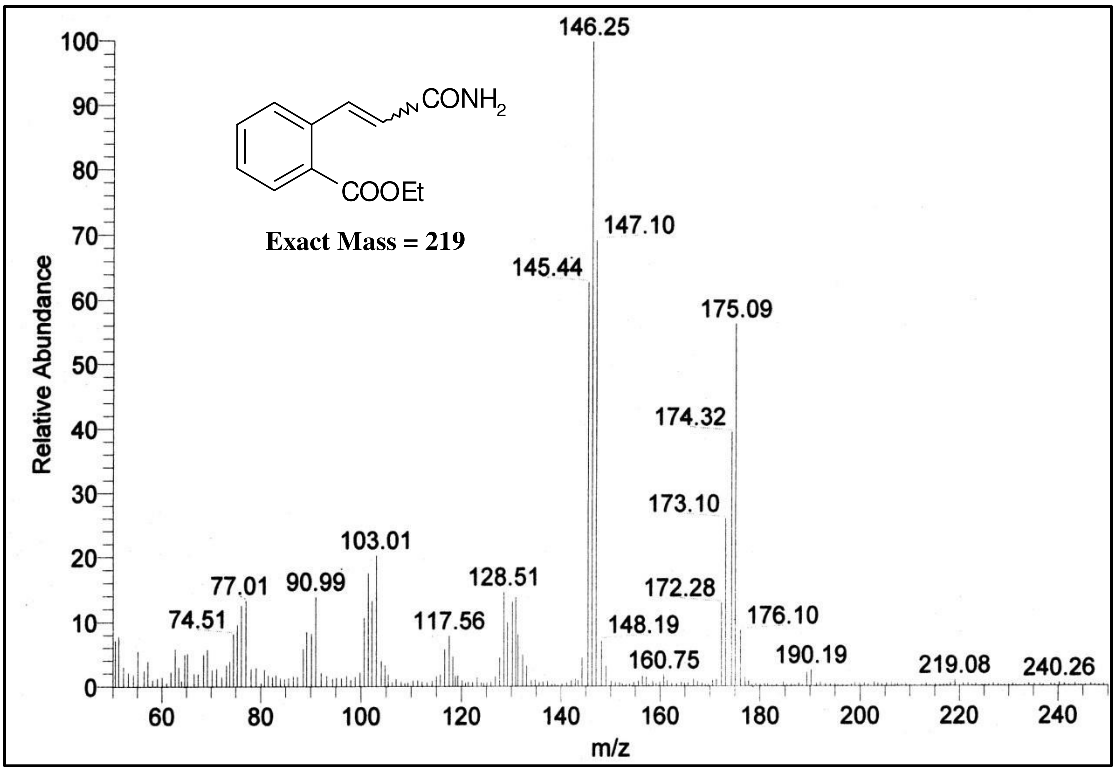
EI-Mass Spectra of Compound 19



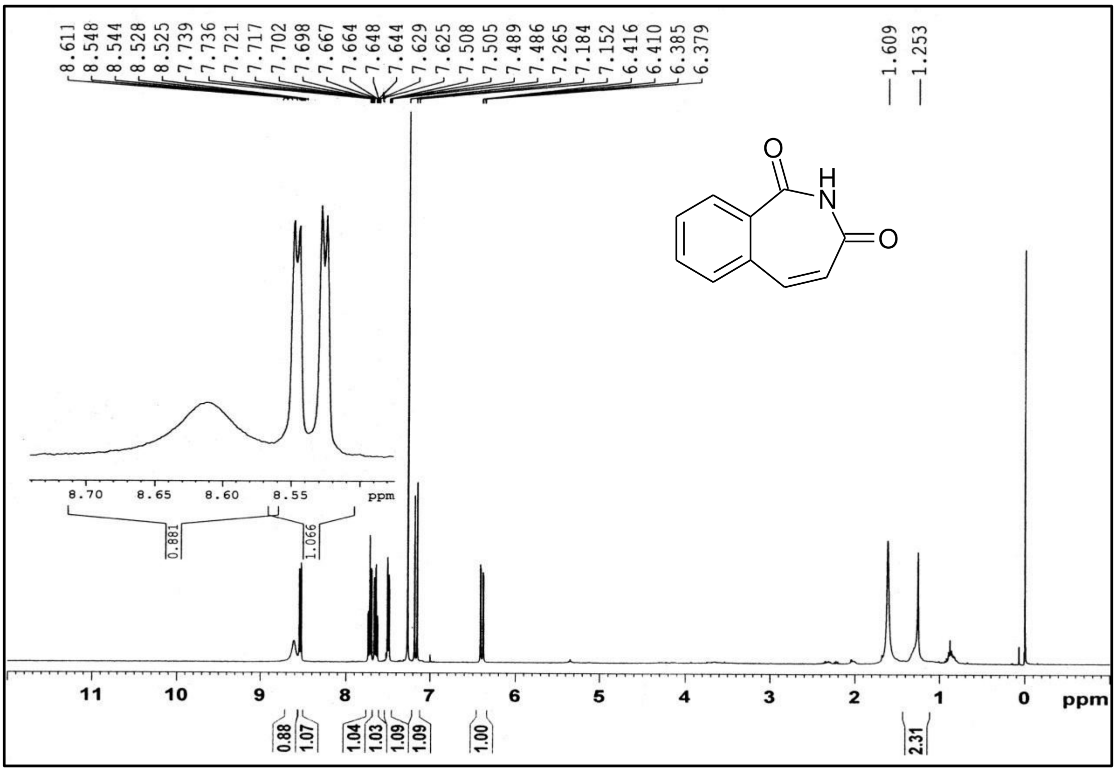
^{1}H-NMR Spectra of Compound 21 (*Z : E* = 75 : 25) (400 MHz, $CDCl_3$)



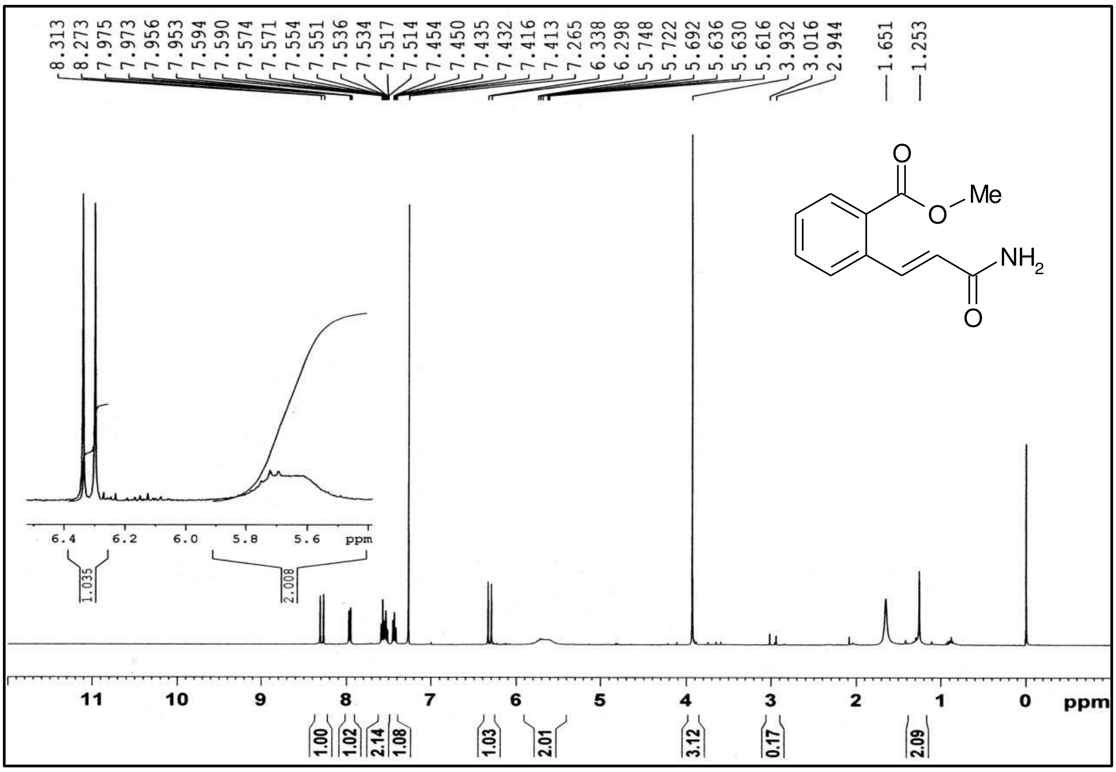
^{1}H-NMR Spectra of Compound 22 (*Z : E* = 67 : 33) (400 MHz, $CDCl_3$)



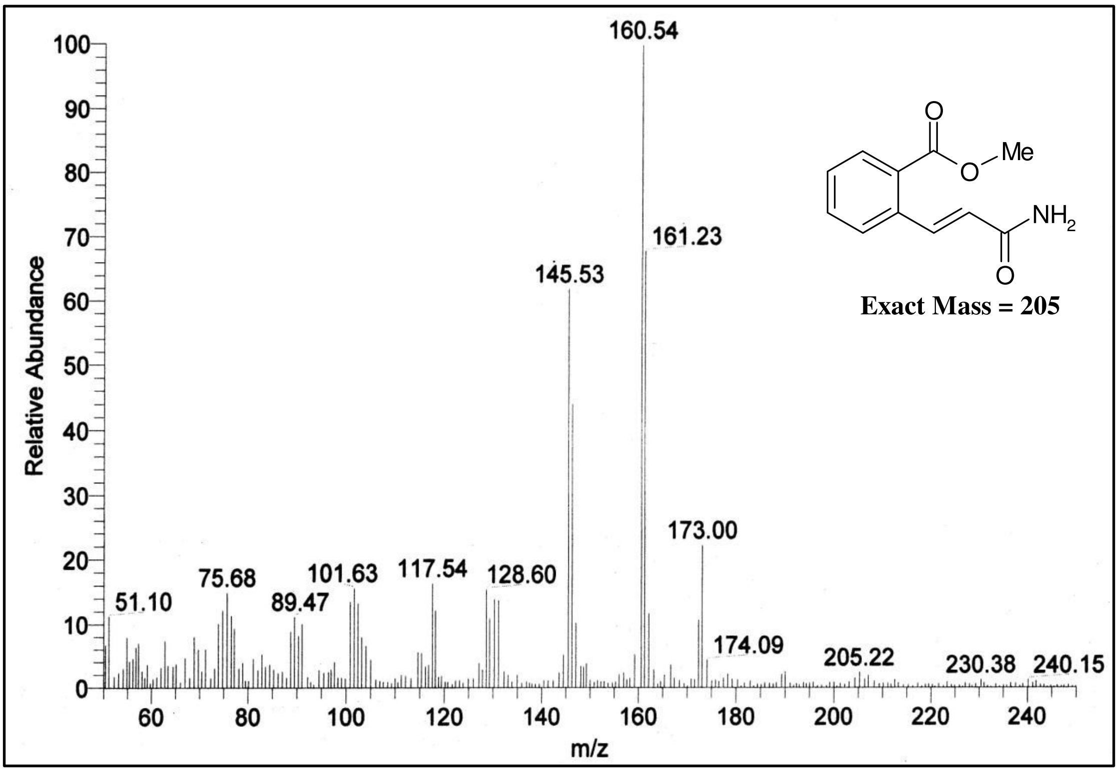
EI-Mass Spectra of Compound 22



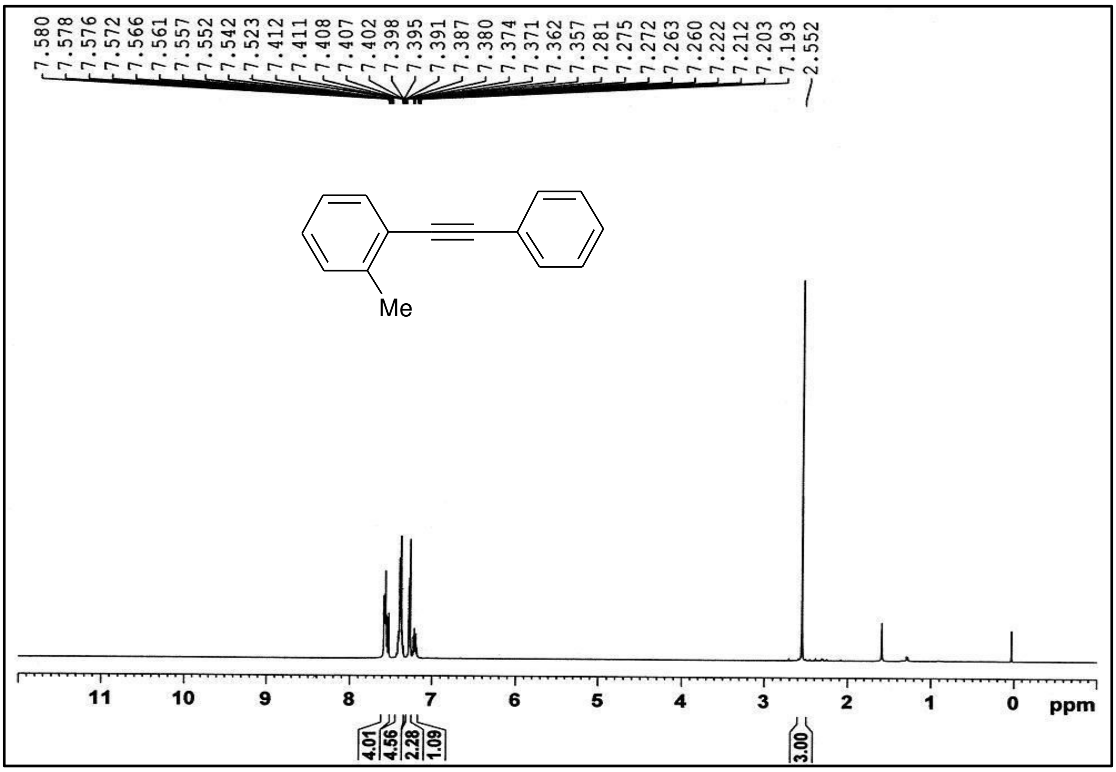
^{1}H-NMR Spectra of Compound 23 (400 MHz, CDCl$_3$)



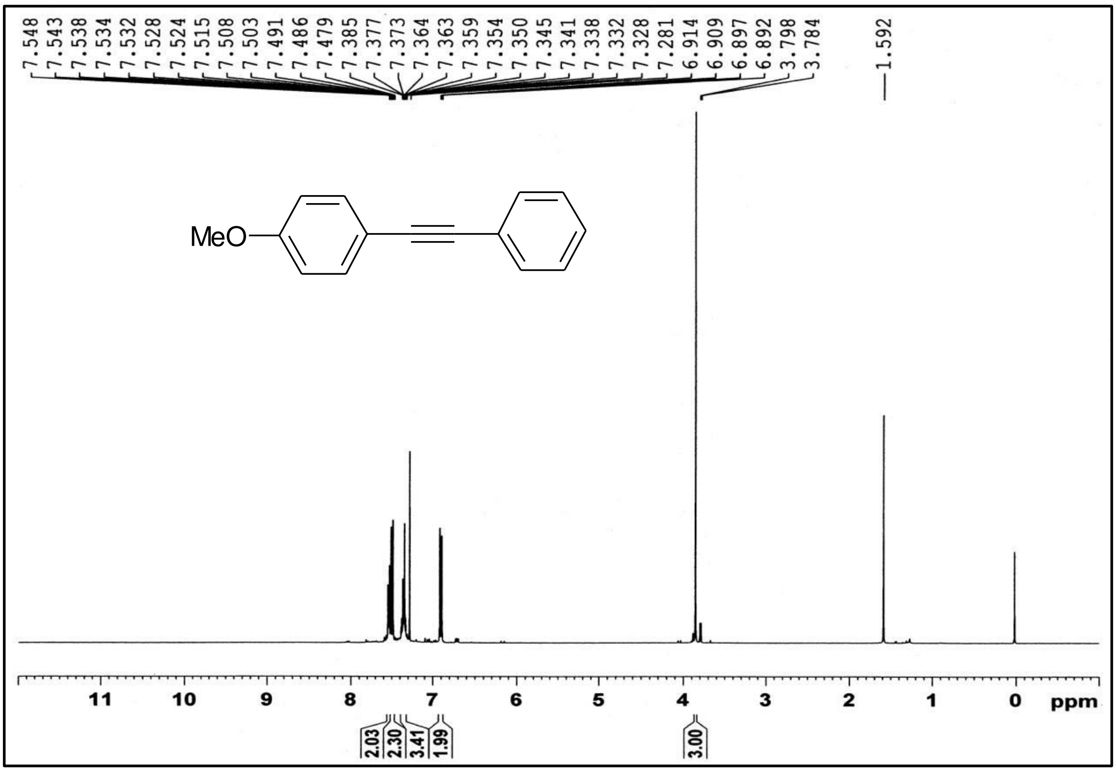
^{1}H-NMR Spectra of Compound 24 (*Z : E* = 0 : 100) (400 MHz, CDCl$_3$)



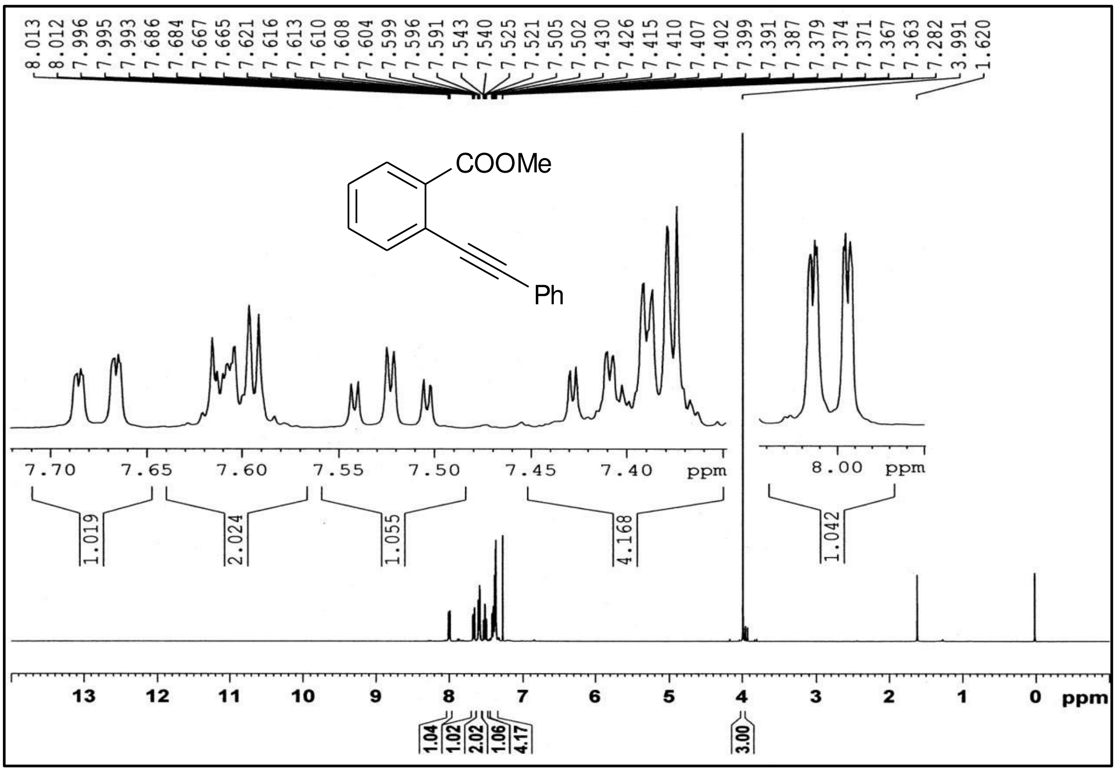
EI-Mass Spectra of Compound 24



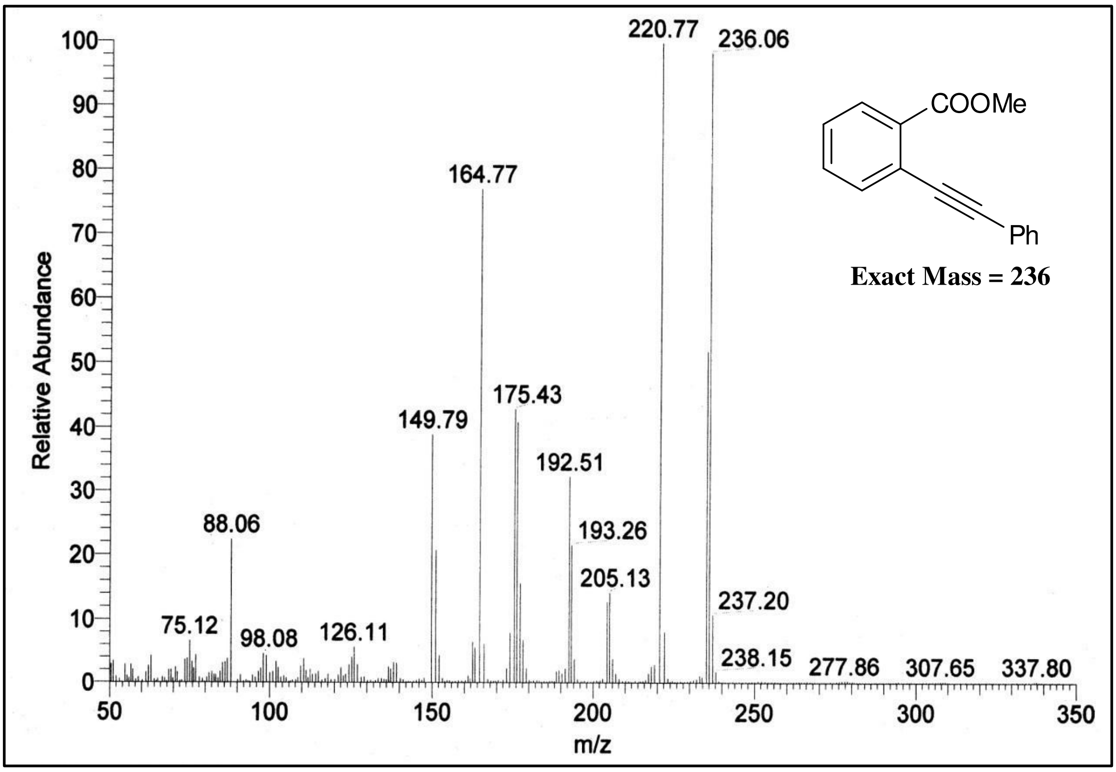
^{1}H-NMR Spectra of Compound 35 (400 MHz, $CDCl_3$)



^{1}H-NMR Spectra of Compound 37 (400 MHz, $CDCl_3$)



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



EI-Mass Spectra of Compound 38

CONCLUSION

The palladium catalyzed Mizoroki-Heck, Suzuki-Miyaura and Sonogashira reactions were successfully carried out under the sunlight irradiation.

The present “Green” reaction conditions require no special set-up while the Heck reaction gives considerable amount of *Z* product due to the photochemical isomerisation of initially formed *E* alkenes.

Reaction of methyl 2-iodobenzoate with acrylamide under solar condition furnished 2H-2-benzazepine-1,3-dione rather than the expected derivative of cinnamate while the same reaction with ethyl 2-iodobenzoate gave the desired cinnamide.

The present findings offer a simple way to utilize sunlight as renewable energy source for palladium catalyzed basic coupling reactions without the need for any special apparatus or reaction machinery. We hope this effort will be recognized as a small step towards the vision of Ciamician, Paterno (and others) of utilizing renewable solar energy for future chemical transformations and synthesis of fine chemicals.

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