Polystyrene resin supported palladium(0) (Pd@PR) nanocomposite catalyzed synthesis of *β*–aryl and *β,β*–diaryl unsaturated scaffolds following tandem approaches

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General information

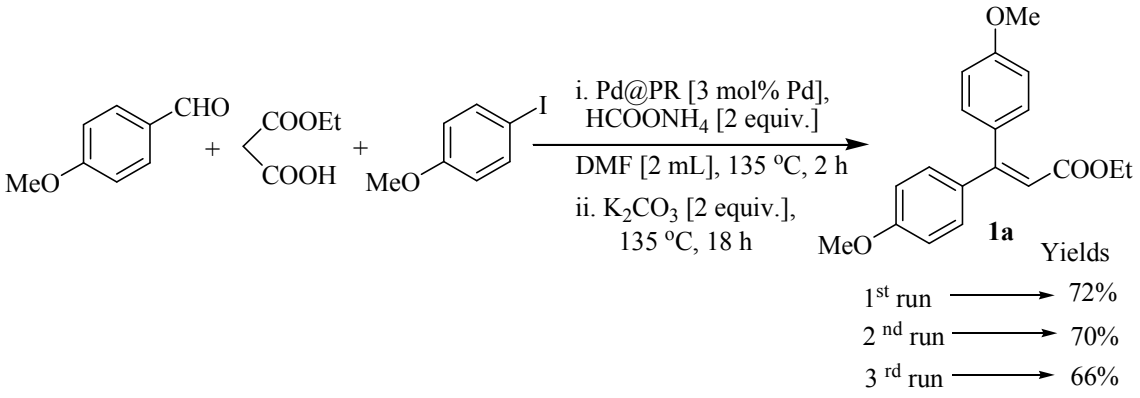
Reagents of high quality were purchased from Sigma Aldrich. Silica gel (60-200 mesh size) for column chromatography was procured from Sd Fine-chem Ltd. Reagents and solvents were of analytical grade and were purified by standard procedures prior to use. Thin layer chromatography was performed using precoated silica gel plates (Aliminium plates) 60 F^{254} (Merck) in UV light detector. ICP–AES analysis carried out on ARCOS from M/S. Spectro, Germany. A TEM image was taken using a carbon coated copper grid (Microscopy sciences) in a transmission electron microscope JEOL 2100F and FEI Tecnoi G20, 200 kV, Netherland. ESIMS spectra were determined using a Waters Micromass Q-TOF Ultima Spectrometer. All the melting points are uncorrected and were determined on a Barnsd Electrothermal 9100 capillary melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance 300 spectrometer/ Bruker Avance 600 spectrometer operating at 300 MHz (^{1}H) and 75 MHz (^{13}C)/ 600 MHz (^{1}H) and 150 MHz (^{13}C) respectively. Spectra were recorded at 25 °C in $CDCl_3$ and MeOD [residual $CHCl_3$ (δH 7.26 ppm) or $CDCl_3$ (δ_C 77.0 ppm), MeOD (δ_H 3.30, 4.78 ppm) or (δ_C 49.0 ppm) and DMSO-d_6 (δ_H 2.50) or (δ_C 39.5) as international standard] with TMS as internal standard. Chemical shifts were recorded in δ (ppm) relative to the TMS, coupling constants (*J*) are given in Hertz (Hz) and multiplicities of signals are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet.

Preparation of Pd@PR nanocomposite catalyst:

The solution of 25 mg of NaBH4 in 10 ml of water was added to 1 g of Amberlite IRA 900 Cl^- form resin (Across, BE) in a 25 ml round bottom flask. The mixture was stirred for 4 h at room temperature. Then the resin was washed with water till the pH became neutral and then with acetone to remove water from the solid surface. The partially borohydride exchanged resin beads were dried under reduced pressure. The dried borohydride exchanged resin beads were added into the warm (100 °C) solution of palladium acetate (10 mg) in DMF (3 ml) then the mixture was stirred for 1 h or till the brown colored solution changed to colorless and simultaneously white solid beads turned black. After cooling, the beads were filtered through a cotton bed, washed with water and acetone, and dried under reduced pressure.

Recyclability Experiment of Pd@PR catalyst

The recyclability experiment of Pd@PR was carried out using 4-anisalaldehyde, monoethylmalonate and 4-iodoanisole as model substrates under the standardized condition. The catalyst was recoverd after each cycle washed with water, then with acetone and dried under reduced pressure. The catalyst was further applied in the next reaction. The isolated yields of product **1a** were found to have slight variation up to third run.



Mercury poisoning experiment:

The heterogeneity of Pd@PR nanocomposite was tested by Mercury poisoning experiment in standard CDH reaction for **1a** synthesis. Mercury test was conducted by using 300 equiv. of Hg (metal) with respect to Pd (Pd@PR). Initially the catalyst was stirred with mercury metal for 30 minutes at room temperature and then the reaction was carried under standard condition. The product 1a was isolated in low yield 11% indicating the participation of Pd NPs tightly bound with the heterogeneous support.

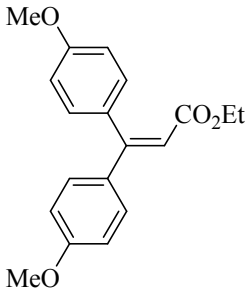
Pd Leaching experiment (ICP-AES analysis):

In the recyclability experiments (mentioned above) we have used 738 mg of Pd@PR (3 mol% Pd). 738 mg of Pd@PR contains 3.49 mg palladium metal as 10 mg $Pd(OAc)_2$ was used with 1 gm of borohydride exchanged polystyrene resin ((Amberlite IRA 900 resin (chloride form) (Across, BE)). The reaction mixture was analyzed for ICP-MS after proper acidic digestion (total sample volume 60 ml each). The results are summarized below.

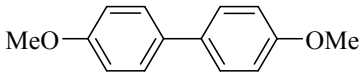
Cycles	**Pd leached (ppm)**	**Pd leached (%) with respect to initial metal content**
1 st	**0.057**	**0.097**
2 nd	**0.048**	**0.082**
3 rd	**0.039**	**0.067**

Typical experimental procedures and spectral data:

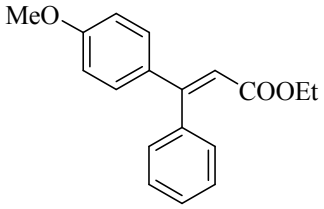
Typical experimental procedure for the synthesis of Ethyl 3,3-bis(4-methoxyphenyl)acrylate **1a**



To a mixture of 4-methoxybenzaldehyde (150 mg, 1.10 mmol), 4-iodoanisole (309.70 mg, 1.32 mmol), mono-ethylmalonate (174.24 mg, 1.32 mmol), ammonium formate (138.91 mg, 1.65 mmol) and Pd@PR (738 mg, 3 mol% Pd) in 40 ml reaction vial was added 2 ml of dry DMF. The reaction mixture was stirred in preheated silicone oil bath at 135 ^{o}C for 2 hours and then to add K_2CO_3 (303.60 mg, 2.20 mmol). After addition of K_2CO_3 the reaction was again continued at the same temperature. The progress of the reaction was monitored by TLC. On completion, the cooled reaction mixture was extracted with ethyl acetate (3×3 ml) by addition of 2 ml of water and dried over anhydrous Na_2SO_4. Evaporation of the combined organic layer followed by column chromatography (Hexane:EtOAc= 95:5) over silica gel (mesh 60-200) afforded Ethyl 3,3-bis(4-methoxyphenyl)acrylate **1a** as light yellow semi solid (248.05 mg, 72%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.16 (t, *J*= 6.9 Hz, 3H), 3.81 (s, 3H), 3.84 (s, 3H), 4.07 (q, *J*= 6.0 Hz, 2H), 6.23 (s, 1H), 6.84 (d, *J*= 7.8 Hz, 2H), 6.91(d, *J*=8.4 Hz, 2H), 7.15 (d, *J*= 7.8 Hz, 2H), 7.25 (d, *J*= 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.16, 55.22, 55.31, 59.85, 113.22 (2C), 113.70 (2C), 114.94, 129.99 (2C), 130.86 (2C), 132.24, 133.85, 156.37, 159.68, 160.76, 166.45; ESIMS data: m/z calcd. for $[M+H]^+$ $C_{19}H_{21}O_4$ 313.3676 obsd. 313.3643.



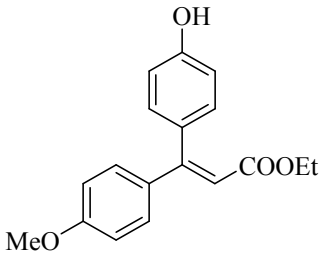
4, 4′-dimethoxybiphenyl was obtained as by-product under the reaction conditions of Table 1, entries 3, 5, 6 and 7. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.96-7.00 (m, 4H), 7.48-7.52 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.74 (2C), 114.58 (4C), 128.13 (4C), 133.89 (2C), 159.11(2C).



Ethyl 3-(4-methoxyphenyl)-3-phenylacrylate (1b) (*E/Z*= 59.5:40.5): Prepared as described the method for **1a**, starting form 4-methyoxybenzaldehyde (150 mg, 1.10 mmol), iodobenzene (269.30 mg, 1.32 mmol), momo-ethylmalonate (174.24 mg, 1.32 mmol), ammonium formate (103.95 mg, 1.65 mmol), K_2CO_3 (303.60 mg, 2.20 mmol) and Pd@PR (738 mg, 3 mol% Pd) gave, after purification with silica gel (60-200 mesh) column chromatography (Hexane:EtOAc = 95:5) **1b** as light yellow liquid (227.10 mg, 68%).

(E)- Ethyl 3-(4-methoxyphenyl)-3-phenylacrylate : ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.21 (t, *J*= 7.2 Hz, 3H), 3.85 (s, 3H), 4.13 (q, *J*= 7.2 Hz, 2H), 6.33 (s, 1H), 6.94 (d, *J*= 8.4 Hz, 2H), 7.20 (d, *J*= 8.4 Hz, 2H), 7.24-7.25 (m, 2H), 7.33-7.34 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.82, 55.01, 59.58, 112.98 (2C), 116.64, 127.58, 128.06 (2C), 128.85, 130.71 (3C), 130.77, 141.30, 156.29, 159.53, 165.96.

(Z)- Ethyl 3-(4-methoxyphenyl)-3-phenylacrylate :1.14 (t, *J*= 7.2 Hz, 3H), 3.82 (s, 3H), 4.07 (q, *J*= 7.2 Hz, 2H), 6.37 (s, 1H), 6.86 (d, *J*= 8.4 Hz, 2H), 7.27 (d, *J*= 8.4 Hz, 2H), 7.36-7.38 (m, 2H), 7.41-7.42 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.79, 54.91, 59.70, 113.53 (2C), 115.13, 127.73, 128.30 (2C), 129.08, 129.49, 132.84, 139.05, 155.99, 160.55, 165.94.

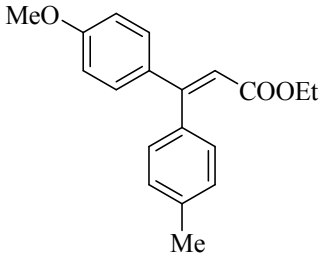


Ethyl 3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)acrylate (1c) (*E/Z*= 54:46): Prepared as described the method for **1a**, starting form 4-hydroxybenzaldehyde (150 mg, 1.22 mmol), 4-iodoanisole (344 mg, 1.47 mmol), momo-ethylmalonate (194 mg, 1.47 mmol), ammonium formate (115.30 mg, 1.51 mmol), K_2CO_3 (336.70 mg, 2.44 mmol) and Pd@PR (818.60 mg, 3 mol% Pd) gave, after purification with silica gel (60-200 mesh) column

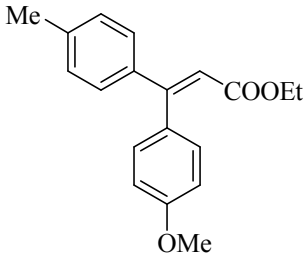
chromatography (Hexane:EtOAc = 90:10) **1c** as white crystalline solid (293.15 mg, 80%); ESIMS data: m/z calcd. for $[M+H]^+$ $C_{18}H_{18}O_4$ 299.3331 obsd. 299.3323.

(E)-Ethyl 3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)acrylate : ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.2 Hz, 3H), 3.80 (s, 3H), 4.08 (q, *J* = 7.2 Hz, 2H), 6.22 (s, 1H), 6.57 (brs, OH), 6.70 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 6.6 Hz, 2H), 7.24 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.03, 55.16, 60.09, 113.19 (2C), 114.30, 115.24 (2C), 130.81 (2C), 131.25 (2C), 133.71, 156.42, 157.52 (2C), 167.11, 167.38.

(Z)-Ethyl 3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)acrylate : 1.20 (t, *J* = 7.2 Hz, 3H), 3.82 (s, 3H), 4.11 (q, *J* = 7.2 Hz, 2H), 6.23 (s, 1H), 6.61 (brs, OH), 6.72 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H),7.15 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.01, 55.30, 60.25, 113.64 (2C), 114.17, 114.98 (2C), 130.08 (2C), 130.13 (2C), 130.59, 130.84 (2C), 133.29, 156.99, 159.61, 160.78.



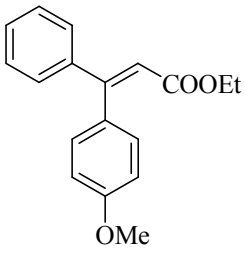
Ethyl 3-(4-methoxyphenyl)-3-*p*-tolylacrylate (1d): Prepared as described the method for **1a**, starting form 4-methoxybenzaldehyde (150 mg, 1.10 mmol), 4-iodotoluene (287.76 mg, 1.32 mmol), momo-ethylmalonate (172.24 mg, 1.32 mmol), ammonium formate (104 mg, 1.65 mmol), K_2CO_3 (303.60 mg, 2.20 mmol) and Pd@PR (738 mg, 3 mol% Pd) gave, after purification with silica gel (60-200 mesh) column chromatography (Hexane:EtOAc = 90:10) **1d** as colourless liquid (261.50 mg, 80%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, *J* = 6.9 Hz, 3H), 2.44 (s, 3H), 3.83 (s, 3H), 4.11(q, *J* = 6.0 Hz, 2H), 6.33 (s, 1H), 6.86-6.97 (m, 2H), 7.14-7.31 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.90, 21.16, 55.05, 59.58, 113.52 (2C), 114.12, 128.34 (2C), 128.84 (2C), 129.47 (2C), 133.25, 136.03, 137.60, 156.01, 160.56, 166.04; ESIMS data: m/z calcd. for $[M+H]^+$ $C_{19}H_{20}O_3$ 297.3603 obsd. 297.3649.



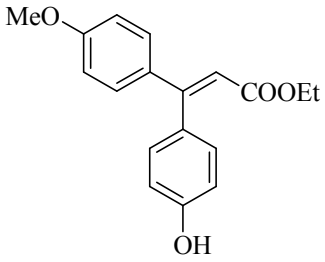
Ethyl 3-(4-methoxyphenyl)-3-*p*-tolylacrylate (1e) (*E/Z* = 66:34): Prepared as described the method for **1a**, starting form 4-methylbenzaldehyde (150 mg, 1.24 mmol), 4-iodanisole (350.60 mg, 1.49 mmol), momo-ethylmalonate (196.41 mg, 1.49 mmol), ammonium formate (117.18 mg, 1.86 mmol), K_2CO_3 (342.24 mg, 2.48 mmol) and Pd@PR (832 mg, 3 mol% Pd) gave, after purification with silica gel (60-200 mesh) column chromatography (Hexane:EtOAc = 90:10) **1e** as colourless liquid (281.21 mg, 76%).

(E)-Ethyl 3-(4-methoxyphenyl)-3-p-tolylacrylate : ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.16 (t, *J*= 7.2 Hz, 3H), 2.41 (s, 3H), 3.81 (s, 3H), 4.70 (q, *J* = 7.2 Hz, 2H), 6.29 (s, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.20-7.21 (m, 2H), 7.27 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.00, 15.10, 59.73, 113.58 (2C), 115.82, 128.39, 129.02 (2C), 129.72, 131.06, 133.84, 133.87, 136.07, 138.54, 156.54, 159.55, 160.61, 166.19.

(Z)-Ethyl 3-(4-methoxyphenyl)-3-p-tolylacrylate : ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.2 Hz, 3H), 2.37 (s, 3H), 3.85 (s, 3H), 4.09 (q, *J* = 7.2 Hz, 2H), 6.28 (s, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 9.0 Hz, 2H), 7.21-7.22 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.04, 15.04, 59.80, 113.06, 113.58, 114.63, 114.93, 128.39, 129.02,129.72 (2C), 130.78, 133.33, 137.85, 139.46, 156.54, 159.55, 160.61, 166.26.



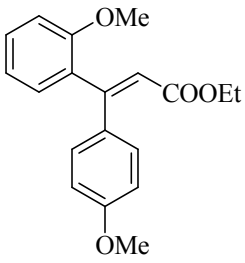
Ethyl 3-(4-methoxyphenyl)-3-phenylacrylate (1f): Prepared as described the method for **1a**, starting form benzaldehyde (150 mg, 1.14 mmol), 4-iodoanisole (397 mg, 1.69 mmol), momo-ethylmalonate (223 mg, 1.69 mmol), ammonium formate (107.73 mg, 1.71 mmol), K_2CO_3 (314.64 mg, 2.28 mmol) and Pd@PR (765 mg, 3 mol% Pd) gave, after purification with silica gel (60-200 mesh) column chromatography (Hexane:EtOAc = 95:5) **1f** as light yellow liquid (275.35 mg, 69%); ^{1}H NMR (300 MHz, CD_3COCD_3) δ 1.05 (t, *J* = 7.2 Hz, 3H), 3.67 (s, 3H), 3.80 (s, 3H), 3.94 (q, *J* = 7.2 Hz, 2H), 6.39 (s, 1H), 6.87-7.03(m, 5H), 7.28-7.39 (m, 4H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 13.95, 55.19, 55.37, 59.46, 111.36, 114.13 (2C), 116.53, 120.45, 129.17 (2C), 129.45, 130.32, 132.85, 152.55, 157.23, 161.14, 165.62; ESIMS data: m/z calcd. for $[M+H]^+$ $C_{18}H_{18}O_3$ 283.3337 obsd. 283.3314.



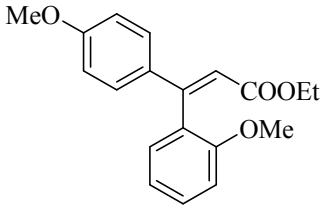
Ethyl 3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)acrylate (*E/Z* = 83.5: 16.5) **(1g):** Prepared as described the method for **1a**, starting form 4-methoxybenzaldehyde (150 mg, 1.10 mmol), 4-iodophenol (290.40 mg, 1.32 mmol), momo-ethylmalonate (174.24 mg, 1.32 mmol), ammonium formate (104 mg, 1.65 mmol), K_2CO_3 (303.60 mg, 2.20 mmol) and Pd@PR (738 mg, 3 mol% Pd) gave, after purification with silica gel (60-200 mesh) column chromatography (Hexane:EtOAc = 90:10) **1g** as white crystalline solid (213.65 mg, 65%).

(E)-Ethyl 3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)acrylate : ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.2 Hz, 3H), 3.81 (s, 3H), 5.82 (brs, OH), 6.22 (s, 1H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H) , 7.24 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.12, 55.33, 60.09, 113.66 (2C), 114.45, 114.94 (2C), 130.05 (2C), 130.19, 130.89 (2C), 133.74, 156.19, 157.10, 160.79, 166.97.

(Z)-Ethyl 3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)acrylate : ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.15 (t, *J* = 7.2 Hz, 3H), 3.83 (s, 3H), 5.82 (brs, OH), 6.21 (s, 1H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H).



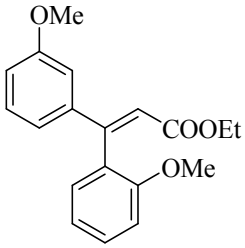
Ethyl 3-(2-methoxyphenyl)-3-(4-methoxyphenyl)acrylate (1h): Prepared as described the method for **1a**, starting form 2-methyoxybenzaldehyde (150 mg, 1.10 mmol), iodobenzene (269.30 mg, 1.32 mmol), momo-ethylmalonate (174.24 mg, 1.32 mmol), ammonium formate (103.95 mg, 1.65 mmol), K_2CO_3 (303.60 mg, 2.20 mmol) and Pd@PR (738 mg, 3 mol% Pd) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 95:5) **1e** as light yellow liquid (234 mg, 68%); ^{1}H NMR (300 MHz, C_6D_6) δ 0.97 (t, *J* = 6.9 Hz, 3H), 3.29 (s, 3H), 3.37 (s, 3H), 4.03 (q, *J* = 7.2 Hz, 2H), 6.67-6.74 (m, 3H), 6.99-7.03 (m, 1H), 7.03-7.38 (m, 5H); ^{13}C NMR (75 MHz, C_6D_6) δ 14.15, 54,70, 55.12, 59.47, 111.00, 124.03 (2C), 116.92, 120.48, 129.20 (4C), 133.04, 152.77, 157.26, 160.95, 165.61; ESIMS data: m/z calcd. for $[M+H]^+$ $C_{19}H_{21}O_4$ 313.3676 obsd. 313.3659.



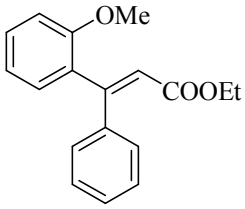
Ethyl 3-(2-methoxyphenyl)-3-(4-methoxyphenyl)acrylate (1i) (*E/Z* = 72:28) : Prepared as described the method for **1a**, starting form 4-methyoxybenzaldehyde (150 mg, 1.10 mmol), 2-iodoanisole (308.90 mg, 1.32 mmol), momo-ethylmalonate (174.24 mg, 1.32 mmol), ammonium formate (103.95 mg, 1.65 mmol), K_2CO_3 (303.60 mg, 2.20 mmol) and Pd@PR (738 mg, 3 mol% Pd) gave, after purification with silica gel (60-200 mesh) column chromatography (Hexane:EtOAc = 95:5) **1i** as light yellow liquid (186 mg, 54%).

(E)-Ethyl 3-(2-methoxyphenyl)-3-(4-methoxyphenyl)acrylate : ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.10 ((t, *J* = 6.9 Hz, 3H), 3.57 (s, 3H), 3.73 (s, 3H), 4.03 (q, *J* = 6.0 Hz, 2H), 6.10 (s, 1H), 6.74-6.77 (m, 3H), 7.10 (d, *J* = 6 Hz, 2H), 7.17 (d, *J* = 6.9 Hz, 2H), 7.21-7.22 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.08, 55.10, 55.60, 59.89, 112.75 (2C), 113.12, 113.61, 113.68, 119.32, 129.86, 130.19 (3C), 131.94, 153.65, 157.20, 159.31, 166.56.

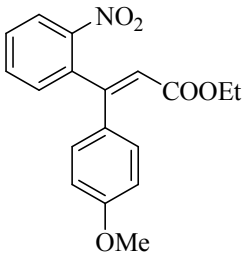
(Z)-Ethyl 3-(2-methoxyphenyl)-3-(4-methoxyphenyl)acrylate : ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.09 (t, *J* = 6.9 Hz, 3H), 3.73 (s, 3H), 3.76 (s, 3H), 4.00 (q, *J* = 6.0 Hz, 2H), 6.15 (s, 1H), 6.81 (d, *J* = 6 Hz, 1H), 6.83-6.85 (m, 2H), 7.04-7.08 (m, 4H), 7.21-7.22 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.13, 55.14, 55.27, 59.79, 111.59, 112.75 (2C), 114.81, 119.37, 128.82, 129.92, 130.19 (3C), 131.39, 153.65, 157.20, 159.31, 166.56.



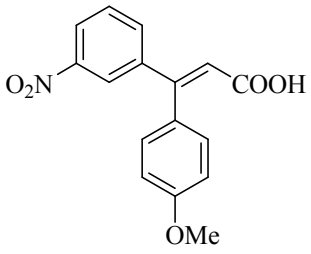
Ethyl 3-(2-methoxyphenyl)-3-(3-methoxyphenyl)acrylate (1j): Prepared as described the method for **1a**, starting form 2-methyoxybenzaldehyde (150 mg, 1.10 mmol), 3-methoxyiodobenzene (308.88 mg, 1.32 mmol), ammonium formate (103.95 mg, 1.65 mmol), K_2CO_3 (303.60 mg, 2.20 mmol) and Pd@PR (738 mg, 3 mol% Pd) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 95:5) **1j** as light yellow liquid (223.92 mg, 65%); ^{1}H NMR (300 MHz, C_6D_6) δ 0.95 (t, *J* = 7.2 Hz, 3H), 3.28 (s, 3H), 3.35 (s, 3H), 4.01 (q, *J* = 6.9 Hz, 2H), 6.58-6.81 (m, 3H), 6.97-7.26 (m, 6H); ^{13}C NMR (75 MHz, C_6D_6) δ 14.07, 54.58, 55.09, 59.62, 111.00, 113.12, 115.09, 119.33, 120.43 (2C), 130.69, 131.49, 132.83, 142.44, 153.03, 157.20, 160.16, 165.42



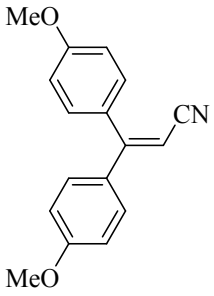
Ethyl 3-(2-methoxyphenyl)-3-phenylacrylate (1k): Prepared as described the method for **1a**, starting form 2-methyoxybenzaldehyde (150 mg, 1.10 mmol), iodobenzene (269.30 mg, 1.32 mmol), momo-ethylmalonate (174.24 mg, 1.32 mmol), ammonium formate (103.95 mg, 1.65 mmol), K_2CO_3 (303.60 mg, 2.20 mmol) and Pd@PR (738 mg, 3 mol% Pd) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 95:5) **1k** as light yellow liquid (220.86 mg, 71%); ^{1}H NMR (300 MHz, CD_3COCD_3) δ 1.06 (t, *J* = 7.2 Hz, 3H), 3.67 (s, 3H), 3.97 (q, *J* = 7.2 Hz, 2H), 6.45 (s, 1H), 6.95-7.06 (m, 3H), 7.28-7.38 (m, 6H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 13.13, 54.60, 58.86, 110.66, 118.08, 119.70, 126.91 (2C), 128.00 (2C), 128.68, 128.84, 129.63, 140.07, 151.97, 156.46, 164.71.



Ethyl 3-(4-methoxyphenyl)-3-(2-nitrophenyl)acrylate (1l): Prepared as described the method for **1a**, starting form 2-nitrobenzaldehyde (150 mg, 0.99 mmol), 4-iodanisole (278.73 mg, 1.19 mmol), momo-ethylmalonate (156.81 mg, 1.19 mmol), ammonium formate (93.55 mg, 1.48 mmol), K_2CO_3 (273.24 mg, 1.98 mmol) and Pd@PR (664.30 mg, 3 mol% Pd) gave, after purification with silica gel (60-200 mesh) column chromatography (Hexane:EtOAc = 90:10) **1l** as light yellow solid (227.44 mg, 70%); mp 100-102 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (t, *J* = 6.9 Hz, 3H), 3.82 (s, 3H), 4.00 (q, *J* = 6.9 Hz, 2H), 6.43 (s, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 7.26-7.29 (m, 3H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 8.20 (d, *J* = 9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.93, 55.31, 60.07, 114.03 (2C), 114.96, 124.46, 128.67, 128.91 (2C), 130.86, 130.98, 133.08, 135.31, 147.91, 152.89, 161.00, 165.57; ESIMS data: m/z calcd. for $[M+H]^+$ $C_{18}H_{17}NO_5$ 328.3312 obsd. 328.3373.

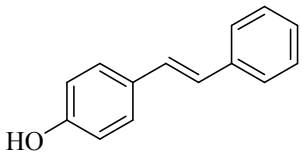


3-(4-methoxyphenyl)-3-(3-nitrophenyl)acrylic acid (1m): Prepared as described the method for **2a**, starting form 3-nitrobenzaldehyde (150 mg, 0.99 mmol), 4-methoxyiodobenzene (369.60 mg, 1.19 mmol), ammonium formate (132.30 mg, 1.48 mmol), Et_3N (199.98 mg, 1.98 mmol) and Pd@PR (664.27 mg, 3 mol% Pd) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 50:50) **1m** as light yellow crystalline solid (181.21 mg, 61%); ^{1}H NMR (600 MHz, CD_3OD) δ 3.69 (s, 3H), 6.34 (s, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.43-7.52 (m, 2H), 7.92 (s, 1H), 8.13 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 55.87, 115.19 (2C), 117.72, 123.73, 125.10, 130.21, 130.73 (2C), 133.13, 136.53, 142.42, 149.32, 155.49, 162.74, 168.96

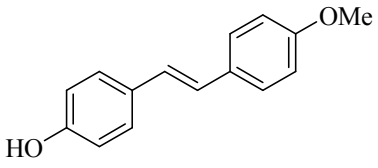


3,3-bis(4-methoxyphenyl)acrylonitrile (1n): Prepared as described the method for **1a**, starting form 4-methoxybenzaldehyde (150 mg, 1.10 mmol), 4-iodoanisole (309 mg, 1.32 mmol), ammonium formate (95.50 mg, 1.51 mmol), K_2CO_3 (278.80 mg, 2.02 mmol) and Pd@PR (677.70 mg, 3 mol% Pd) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 90:10) **1n** as light yellow solid (163.70 mg, 56%); mp 105-108 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.88 (s, 3H), 5.56 (s, 1H), 6.90 (d, *J* = 6.9 Hz, 2H), 6.97 (d, *J* = 6.0 Hz, 2H), 7.26 (d, *J* = 6.9 Hz, 2H), 7.41 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.33, 55.39, 91.50, 113.82 (2C), 113.94 (2C), 118.74, 129.51, 130.14 (2C), 131.27 (2C), 131.67, 160.95, 161.43, 162.31; ESIMS data: m/z calcd. for $[M+H]^+$ $C_{17}H_{16}NO_2$ 266.3144 obsd. 266.3148.

Typical experimental procedure for the synthesis of 4-styrylphenol (1o):

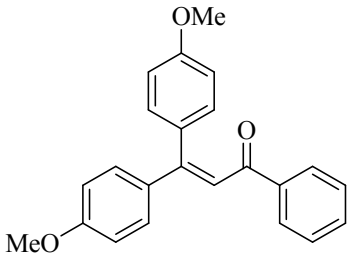


To a mixture of 4-hydroxybenzaldehyde (150 mg, 1.22 mmol), iodobenzene (300.68 mg, 1.47 mmol), malonic acid (152.25 mg, 1.46 mmol), ammonium formate (115.30 mg, 1.83 mmol) and Pd@PR (818.60 mg, 3 mol% Pd) in 40 ml reaction vial was added 2 ml of dry DMF. The reaction mixture was stirred in preheated silicone oil bath at 135 ^{o}C for 2 hours and then K_2CO_3 (336.72 mg, 2.44 mmol) was added to the reaction mixture. The progress of the reaction was monitored by TLC. On completion, the cooled reaction mixture was extracted with ethyl acetate (3×3 ml) by addition of 2 ml of water and dried over anhydrous Na_2SO_4. Evaporation of the combined organic layer followed by column chromatography (Hexane:EtOAc= 90:10) over silica gel (mesh 60-200) afforded 4-styrylphenol **1o** as white crystalline solid (147.20 mg, 61%); mp 187-189 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 16.2 Hz, 1H), 7.05 (d, *J* = 16.2 Hz, 1H), 7.22-7.26 (m, 1H), 7.33-7.36 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 115.62 (2C), 126.27 (2C), 126.76, 127.25, 127.92 (2C), 128.16, 128.64 (2C), 130.44, 137.63, 155.26.

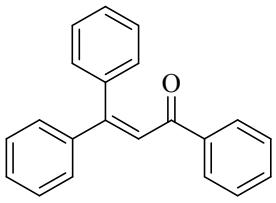


4-methoxyphenyl-4-hydroxyphenylethene (1p): Prepared as described the method for **1a**, starting form 4-hydroxybenzaldehyde (150 mg, 1.22 mmol), 4-iodoanisole (342.57 mg, 1.46 mmol), malonic acid (152.25 mg, 1.46 mmol), ammonium formate (115.30 mg, 1.83 mmol), K_2CO_3 (336.72 mg, 2.44 mmol) and Pd@PR (818.60 mg, 3 mol% Pd)gave, after purification with silica gel (60-200 mesh) column chromatography (Hexane:EtOAc = 90:10) **1p** as light brown solid (180.65 mg, 65%), mp 205-207 ^{o} C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.75 (s, 3H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.90-6.96 (m, 4H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 9.51 (brs, OH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 55.05, 114.08 (2C), 115.49 (2C), 124.76, 126.19, 127.22 (2C), 127.45 (2C), 128.40, 130.17, 156.91, 158.47; ESIMS data: m/z calcd. for $[M+H]^+$ $C_{15}H_{14}O_2$ 227.2704 obsd. 227.2718.

Typical experimental procedure for the synthesis of 3,3-bis(4-methoxyphenyl)-1-phenylprop-2-en-1-one (2a):



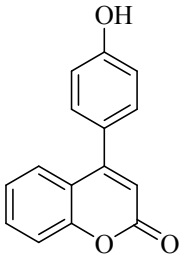
To a mixture of 4-methoxybenzaldehyde (150 mg, 1.10 mmol), 4-iodoanisole (309.70 mg, 1.32 mmol), acetophenone (158.58 mg, 1.32 mmol), ammonium formate (103.95 mg, 1.65 mmol) and Pd@PR (738 mg, 3 mol% Pd) in 40 ml reaction vial was added 2 ml of dry DMF. The reaction mixture was stirred in preheated silicone oil bath at 135 ^{o}C for 2 hours and then K_2CO_3 (402.96 mg, 2.92 mmol) added to the reaction mixture. The progress of the reaction was monitored by TLC. On completion, the cooled reaction mixture was extracted with ethyl acetate (3×3 ml) by addition of 2 ml of water and dried over anhydrous Na_2SO_4. Evaporation of the combined organic layer followed by column chromatography (Hexane:EtOAc= 95:5) over silica gel (mesh 60-200) afforded 3,3-bis(4-methoxyphenyl)-1-phenylprop-2-en-1-one **2a** as yellow semi solid (246.90 mg, 65%); ^{1}H NMR (300 MHz, CD_3COCD_3) δ 3.76 (s, 3H), 3.83 (s, 3H), 6.80-7.09 (m, 7H), 7.25-7.90 (m, 5H), 7.91 (d, J = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 54.61, 54.83, 113.19 (2C), 114.75 (2C), 121.74, 128.31 (2C), 128.45 (2C), 130.09 (2C), 131.38 (2C), 131.59, 132.24, 134.01, 138.72, 153.56, 159.81, 160.84, 192.82; ESIMS data: m/z calcd. for $[M+H]^+$ $C_{23}H_{20}O_3$ 345.4031 obsd. 345.4012.



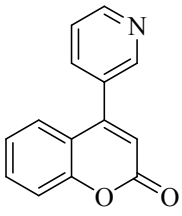
1,3,3-triphenylprop-2-en-1-one (2b): Prepared as described the method for **2a**, starting form benzaldehyde (150 mg, 1.41 mmol), iodobenzene (345.16 mg, 1.69 mmol),

acetophenone (203.27 mg, 1.69 mmol), ammonium formate (115.30 mg, 2.11 mmol), K_2CO_3 (389.16 mg, 2.82 mmol) and Pd@PR (946 mg, 3 mol% Pd) gave, after purification with silica gel (60-200 mesh) column chromatography (Hexane:EtOAc = 95:5) **2b** as yellow semisolid (257.23 mg, 64%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.97 (m, 15H), 7.99 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.92, 127.89 (2C), 128.21 (3C), 128.31 (2C), 128.43 (2C), 128.58 (2C), 129.20, 129.62 (2C), 132.50, 138.09, 138.88, 141.21, 154.46, 192.49

Typical experimental procedure for the synthesis of 4-(4-hydroxyphenyl)-2H-chromen-2-one (3a):



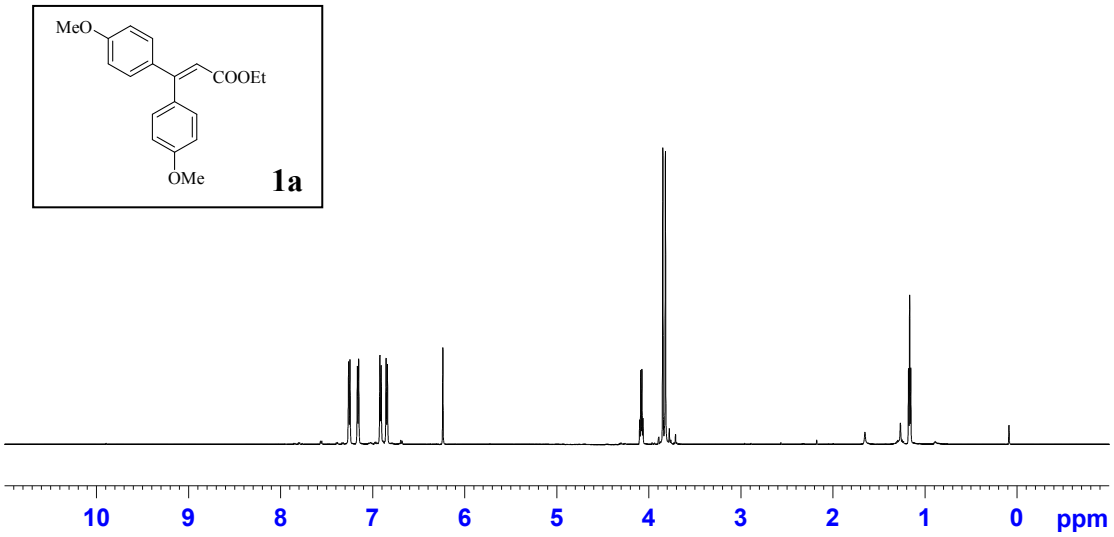
To a mixture of 4-hydroxybenzaldehyde (150 mg, 1.10 mmol), 2-hydroxyiodobenzene (431.20 mg, 1.32 mmol), mono-ethylmalonate (258.19 mg, 1.95 mmol), ammonium formate (291.17 mg, 2.44 mmol) and Pd@PR (738 mg, 3 mol% Pd) in 40 ml reaction vial was added 2 ml of dry DMF. The reaction mixture was stirred in preheated silicone oil bath at 135 ^{o}C for 2 hours and then K_2CO_3 (303.60 mg, 2.20 mmol) added to the reaction mixture. The progress of the reaction was monitored by TLC. On completion, the cooled reaction mixture was extracted with ethyl acetate (3×3 ml) by addition of 2 ml of water and dried over anhydrous Na_2SO_4. Evaporation of the combined organic layer followed by column chromatography (Hexane:EtOAc= 30:70) over silica gel (mesh 60-200) afforded 4-(4-hydroxyphenyl)-2H-chromen-2-one **3a** as white crystalline solid (193.12 mg, 66%) mp 211-213 ^{o}C; ^{1}H NMR (600 MHz, CD_3OD) δ 6.25 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 7.21-7.24 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz), 7.51-7.60 (m, 2H); ^{13}C NMR (150 MHz, CD_3OD) δ 114.28, 116.5 (2C), 117.88, 119.97, 125.20, 126.85, 128.07, 130.86 (2C), 132.84, 154.92, 157.59, 159.88, 162.88; ESIMS data: m/z calcd. for $[M+H]^+$ $C_{15}H_{11}O_3$ 239.2460 obsd. 239.2423.



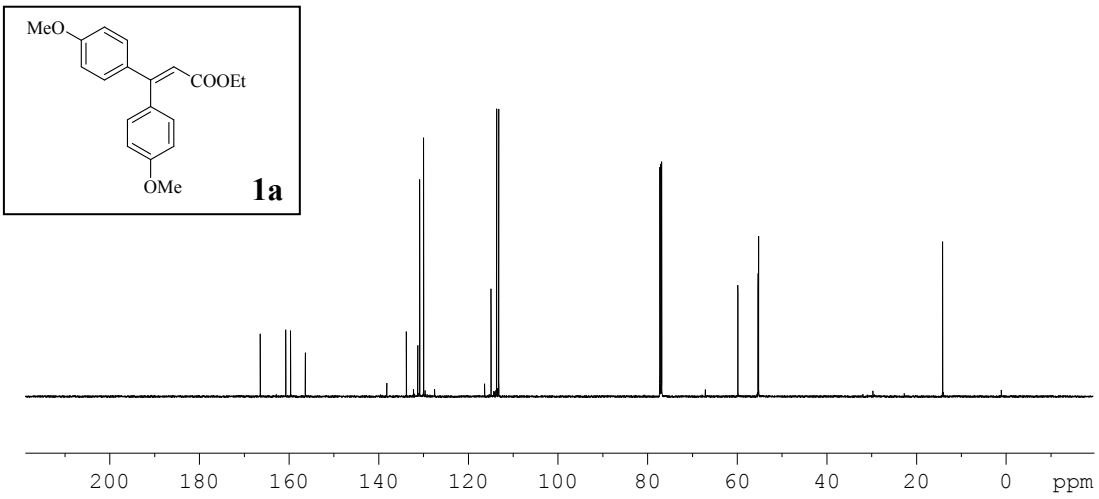
4-(pyridin-3-yl)-2H-chromen-2-one (3b): Prepared as described the method for **4a**, starting form 3-formylpyridine (150 mg, 1.40 mmol), 2-hydroxyiodobenzene (369.60 mg, 1.68 mmol), ammonium formate (132.30 mg, 2.1 mmol), K_2CO_3 (386.40 mg, 2.80 mmol) and Pd@PR (939.40 mg, 3 mol% Pd) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 60:40) 3**b** as light yellow semi solid (181.31 mg, 58%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.40 (s 1H), 7.25-7.28 (m, 1H), 7.39-7.44 (m, 2H), 7.49-7.51 (m, 1H), 7.57-7.59 (m, 1H), 7.80-7.82 (m, 1H), 8.73-8.78 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 116.10, 117.56, 118.44, 123.60, 124.49, 126.33, 131.14, 132.41, 135.98, 148.79, 150.84, 152.10, 154.12, 160.10.

^{1}H, ^{13}C NMR and selected ESIMS spectra of the synthesised compounds

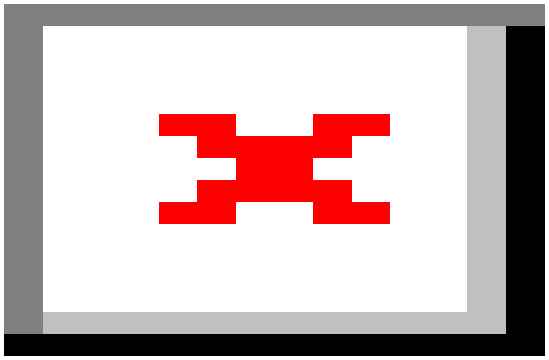
Ethyl 3,3-bis(4-methoxyphenyl)acrylate **(1a)** (^{1}H NMR in $CDCl_3$ (600 MHz))



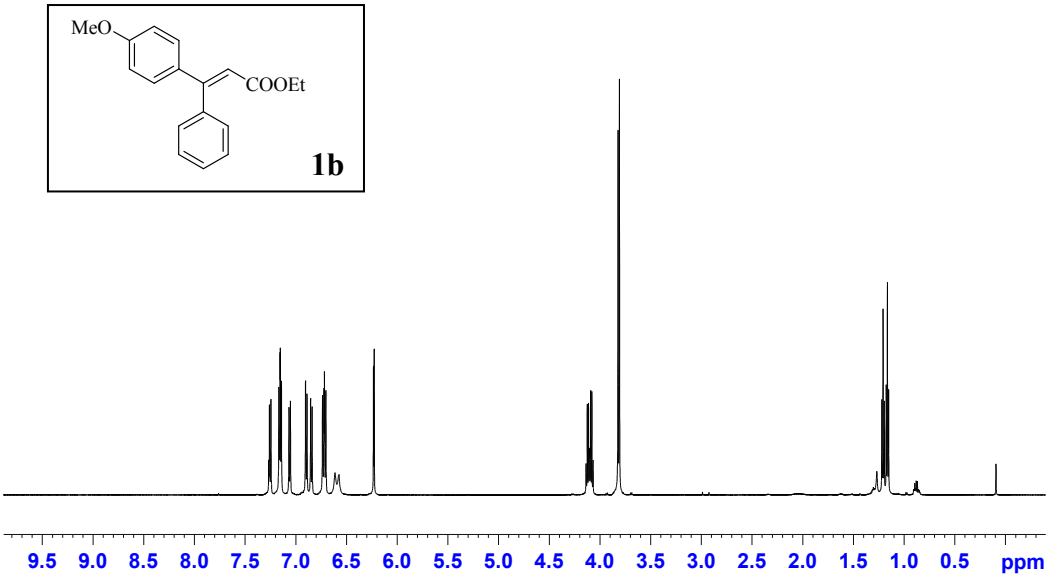
Ethyl 3,3-bis(4-methoxyphenyl)acrylate **(1a)** (^{13}C NMR in $CDCl_3$ (150 MHz))



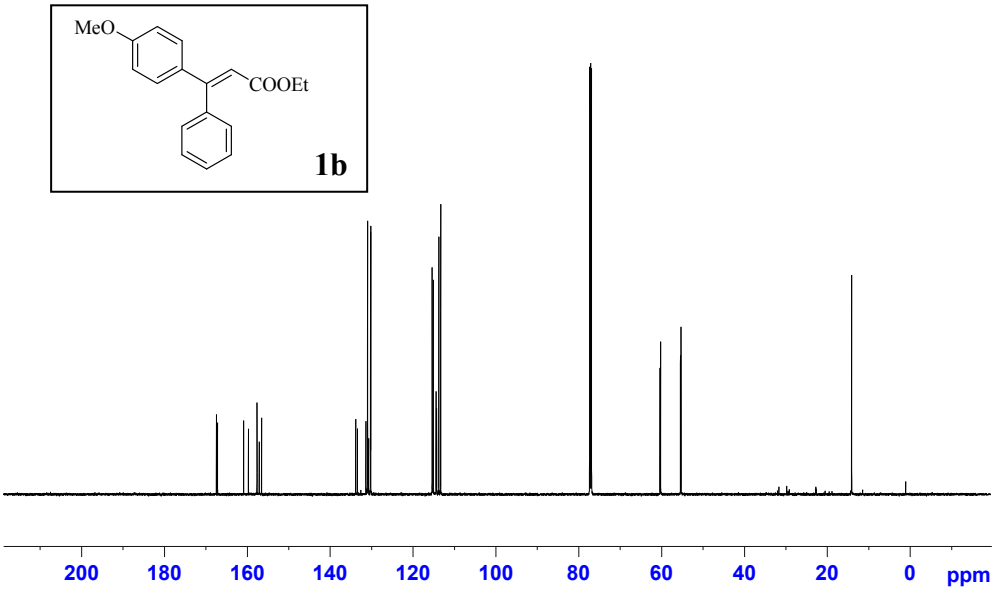
Ethyl 3,3-bis(4-methoxyphenyl)acrylate **(1a) (**ESI MS in MeCN/H_2O (1:1))



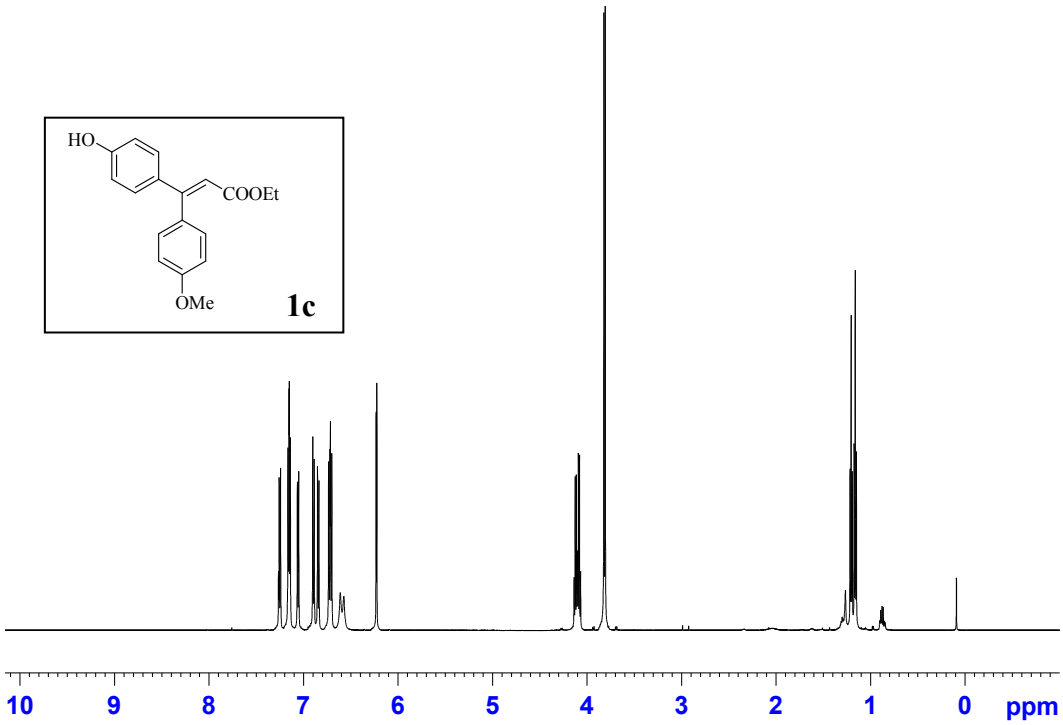
Ethyl 3-(4-methoxyphenyl)-3-phenylacrylate (**1b**) (*E/Z*= 59.5:40.5) (^{1}H NMR in CDCl3 (600 MHz))



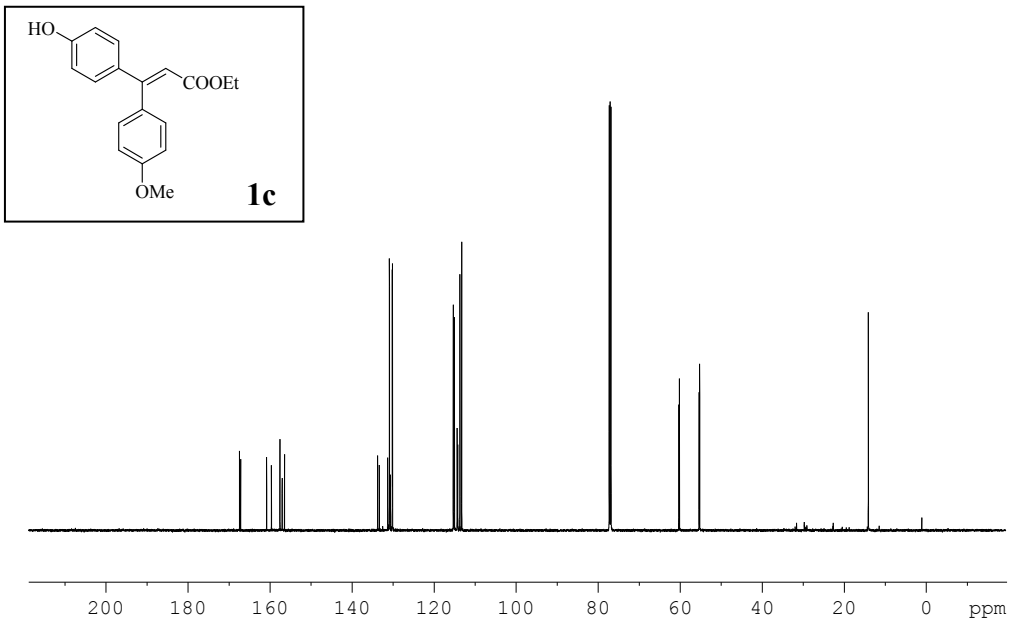
Ethyl 3-(4-methoxyphenyl)-3-phenylacrylate (**1b**) (*E/Z*= 59.5:40.5) (^{13}C NMR in CDCl3 (150 MHz))



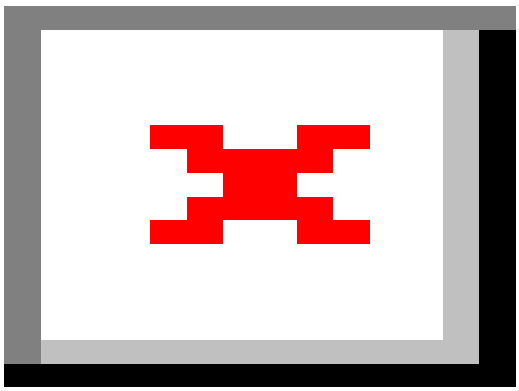
Ethyl 3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)acrylate (**1c** and **1g**) (*E/Z*= 54:46) (^{1}H NMR in $CDCl_3$ (600 MHz))



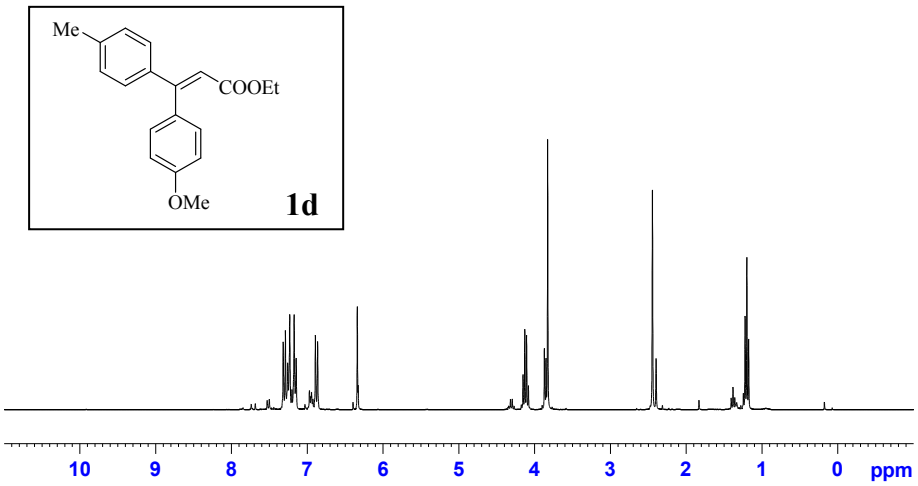
Ethyl 3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)acrylate (**1c**) (*E/Z*= 54:46) (^{13}C NMR in $CDCl_3$ (150 MHz))



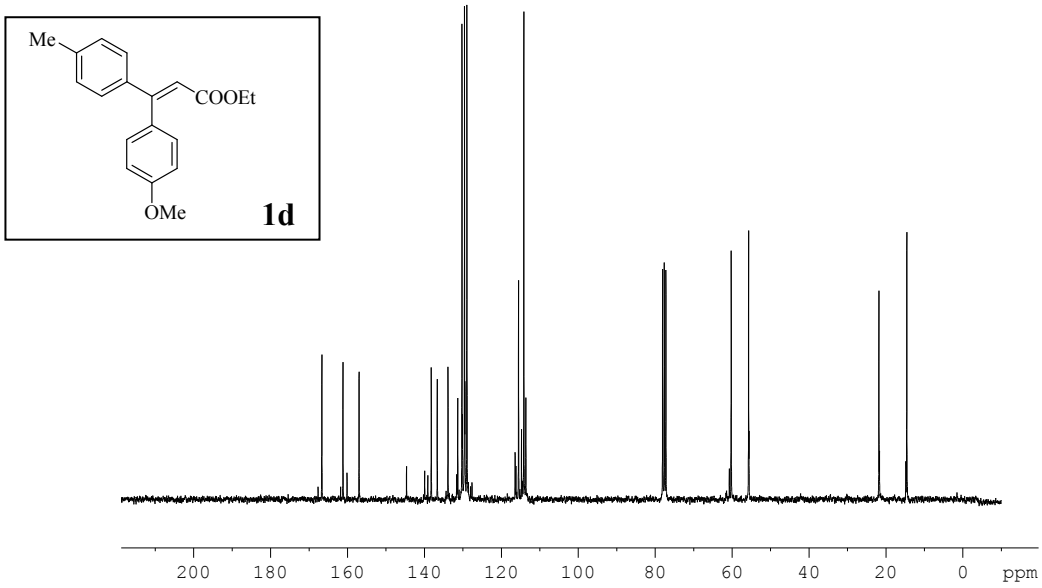
Ethyl 3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)acrylate (**1c** and **1g**) (*E/Z*= 54:46) (ESI MS in $MeCN/H_2O$ (1:1)



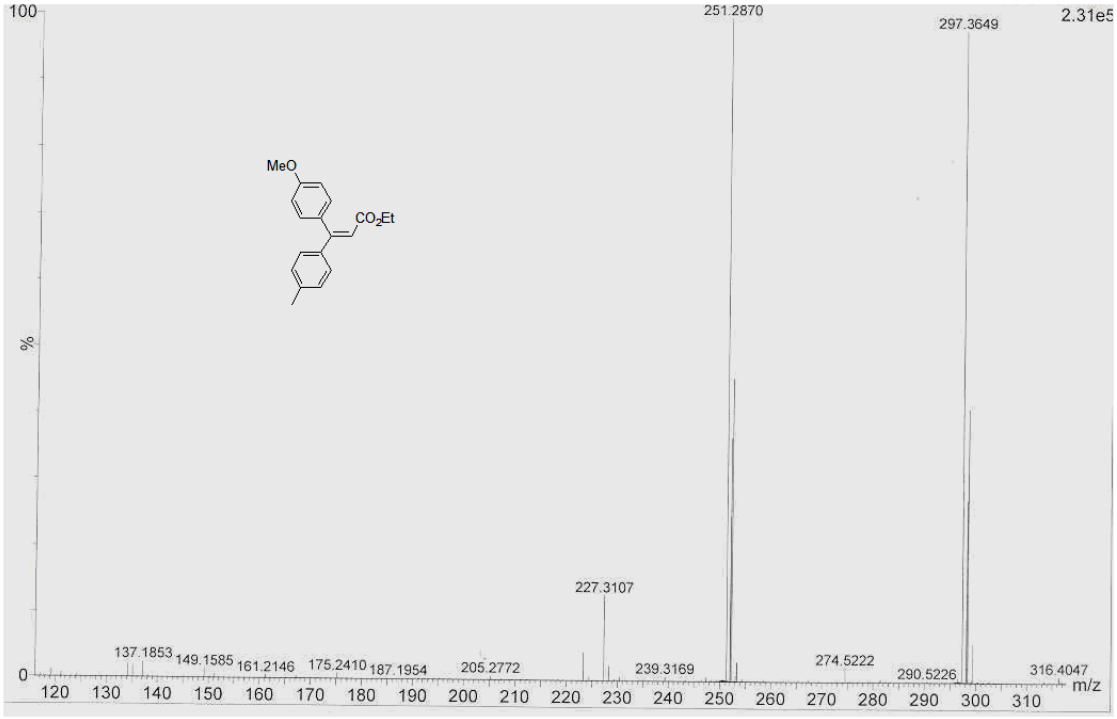
Ethyl 3-(4-methoxyphenyl)-3-p-tolylacrylate (**1d)** (^{1}H NMR in $CDCl_3$ (300 MHz))



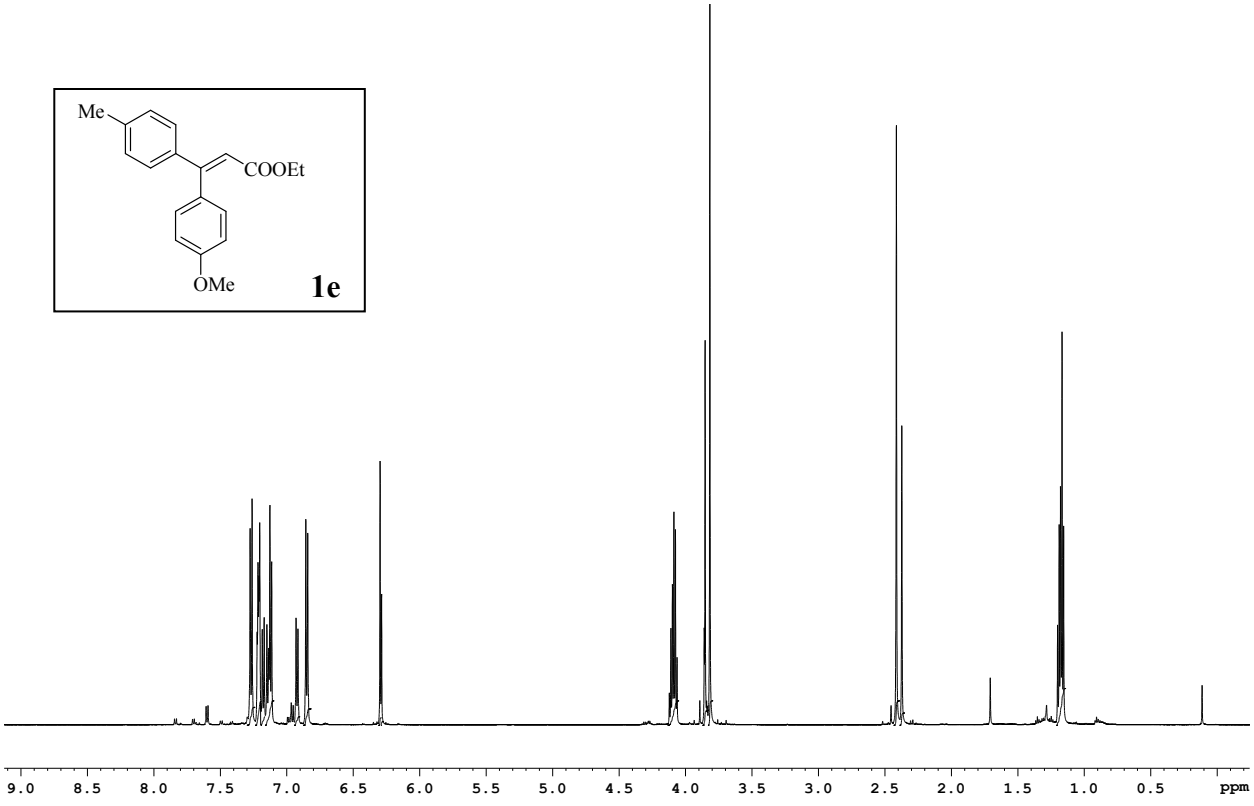
Ethyl 3-(4-methoxyphenyl)-3-p-tolylacrylate (**1d)** (^{13}C NMR in $CDCl_3$ (75 MHz))



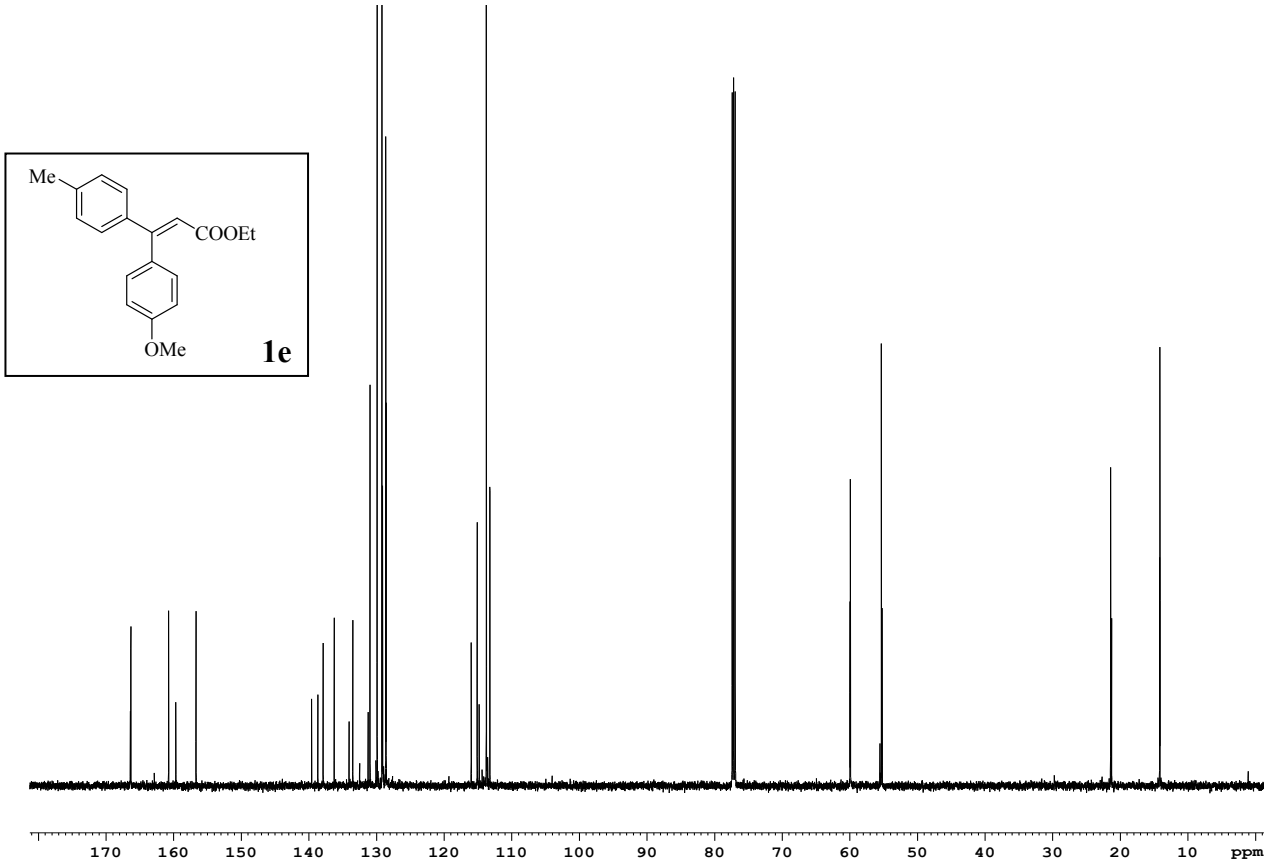
Ethyl 3-(4-methoxyphenyl)-3-p-tolylacrylate (**1d)** (ESI MS in MeCN/H_2O (1:1))



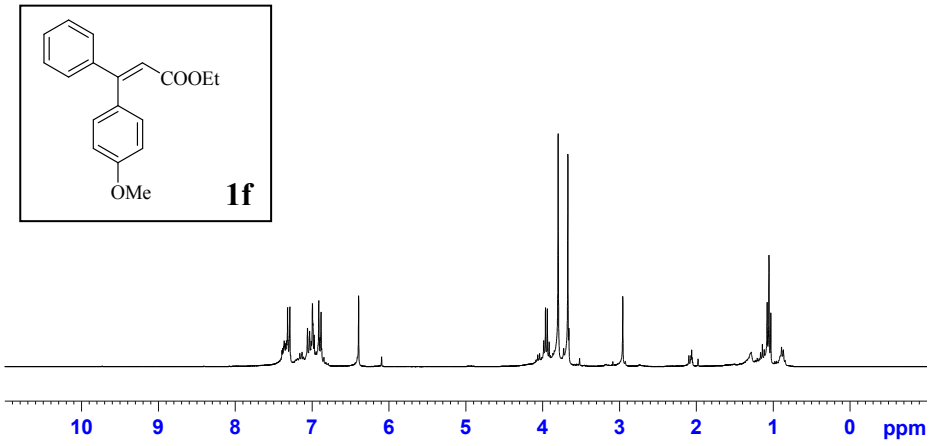
Ethyl 3-(4-methoxyphenyl)-3-p-tolylacrylate (**1e**) (^{1}H NMR in $CDCl_3$ (600 MHz))



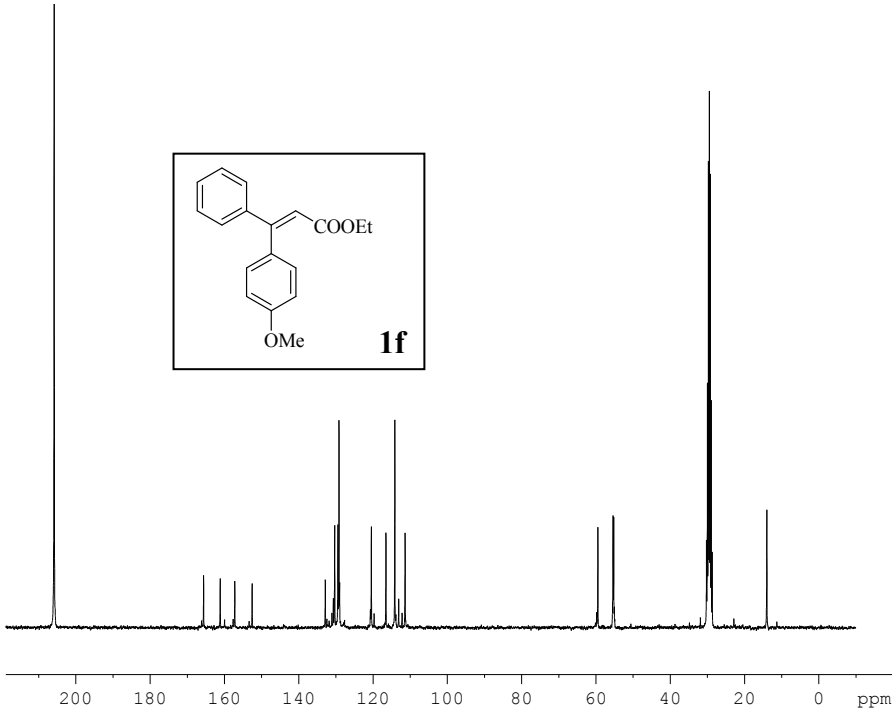
Ethyl 3-(4-methoxyphenyl)-3-p-tolylacrylate (**1e**) (^{13}C NMR in $CDCl_3$ (600 MHz))



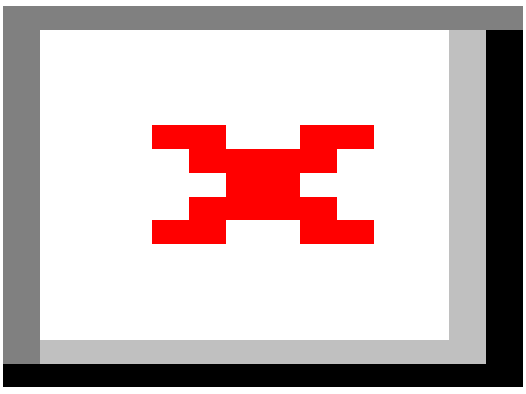
Ethyl 3-(4-methoxyphenyl)-3-phenylacrylate (**1f**) (^{1}H NMR in $CDCl_3$ (300 MHz))



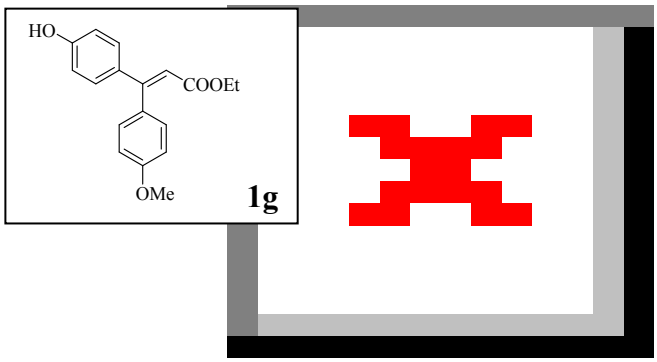
Ethyl 3-(4-methoxyphenyl)-3-phenylacrylate (**1f**) (^{13}C NMR in $CDCl_3$ (75 MHz))



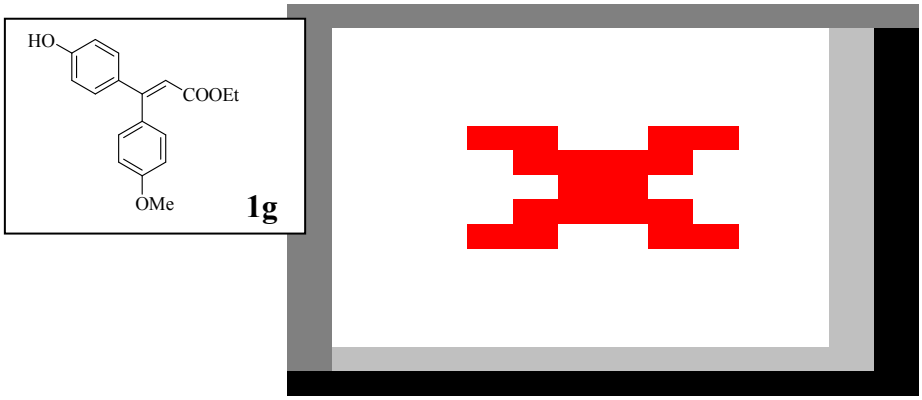
Ethyl 3-(4-methoxyphenyl)-3-phenylacrylate (**1f**) (ESI MS in $MeCN/H_2O$ (1:1))



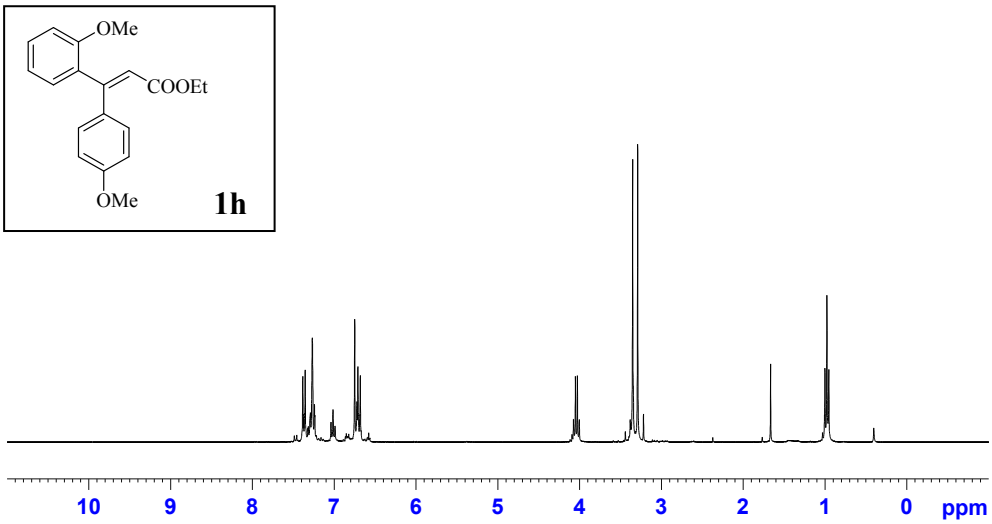
Ethyl 3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)acrylate (**1g**) (*E/Z*= 83.5:16.5) (^{1}H NMR in $CDCl_3$ (600 MHz))



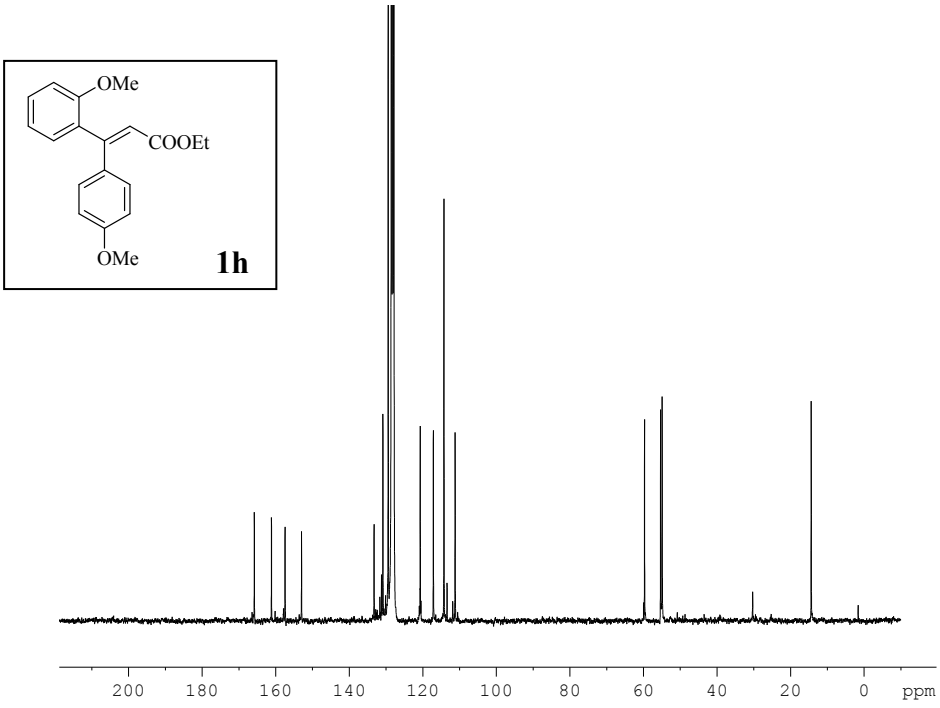
Ethyl 3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)acrylate (**1g**) (*E/Z*= 83.5:16.5) (^{1}H NMR in $CDCl_3$ (150 MHz))



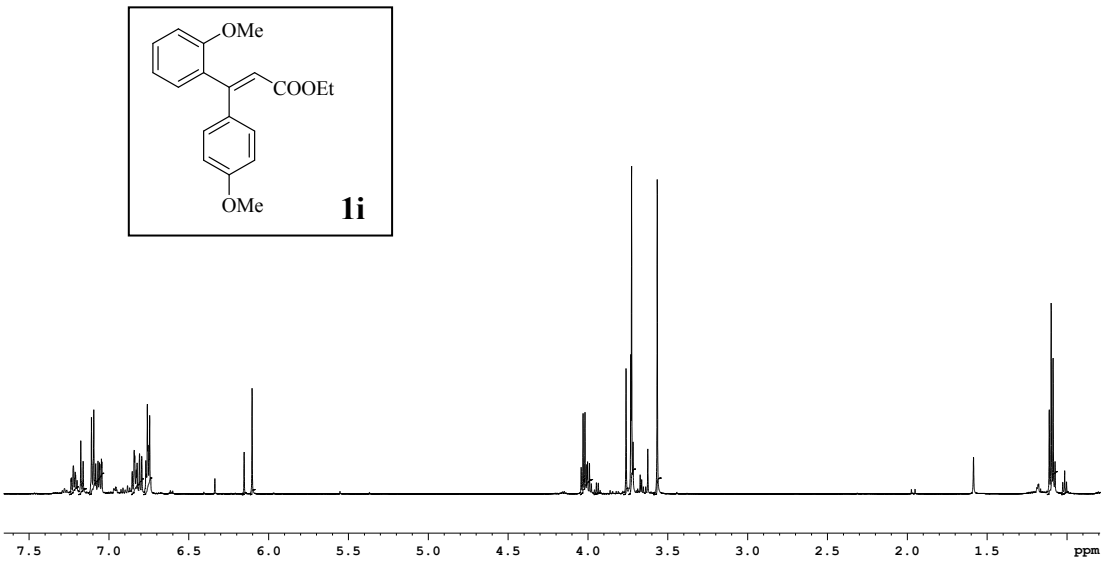
Ethyl 3-(2-methoxyphenyl)-3-(4-methoxyphenyl)acrylate (**1h**) (^{1}H NMR in C_6D_6 (300 MHz)



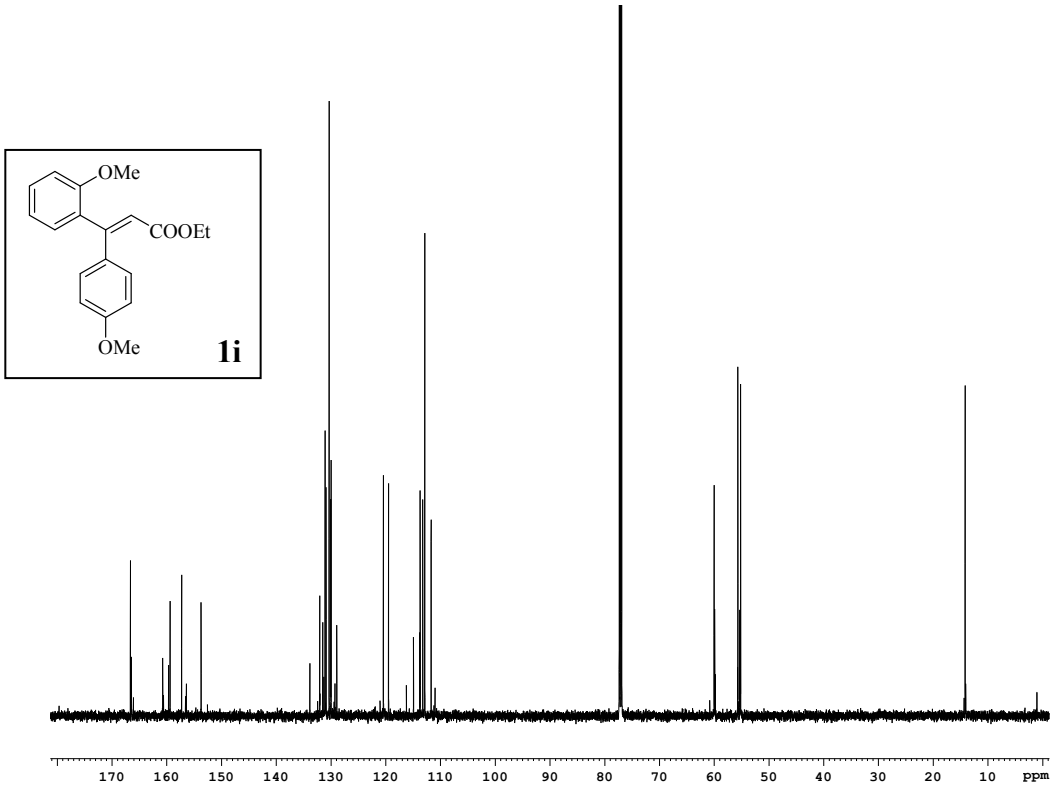
Ethyl 3-(2-methoxyphenyl)-3-(4-methoxyphenyl)acrylate (**1h**) (^{13}C NMR in C_6D_6 (75 MHz)



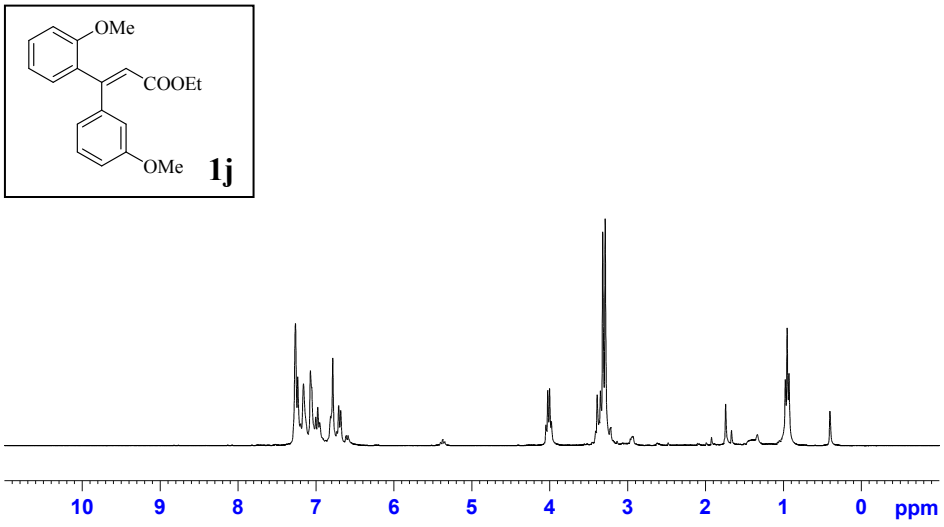
Ethyl 3-(2-methoxyphenyl)-3-(4-methoxyphenyl)acrylate (**1i**) (^{1}H NMR in $CDCl_3$ (600 MHz)



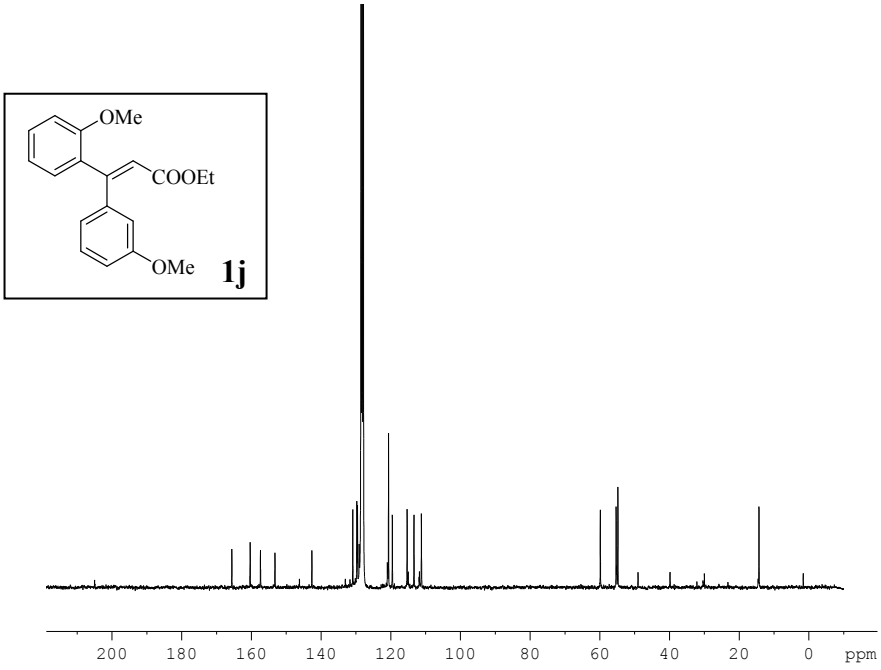
Ethyl 3-(2-methoxyphenyl)-3-(4-methoxyphenyl)acrylate (**1i**) (^{13}C NMR in $CDCl_3$ (600 MHz)



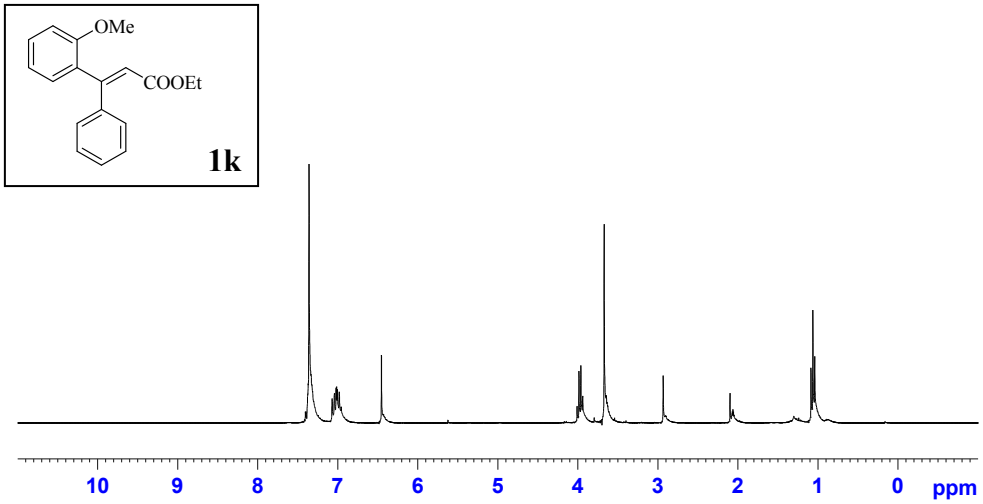
Ethyl 3-(2-methoxyphenyl)-3-(3-methoxyphenyl)acrylate (**1j**) (**(**^{1}H NMR in C_6D_6 (300 MHz)



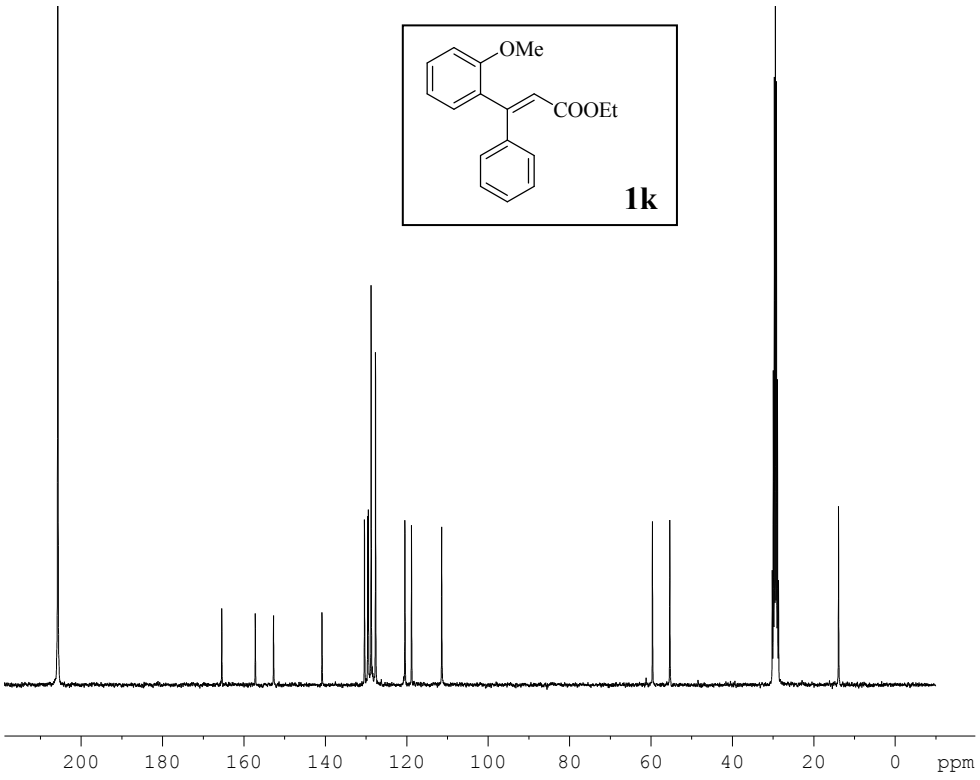
Ethyl 3-(2-methoxyphenyl)-3-(3-methoxyphenyl)acrylate (**1j**) (^{13}C NMR in C_6D_6 (75 MHz)



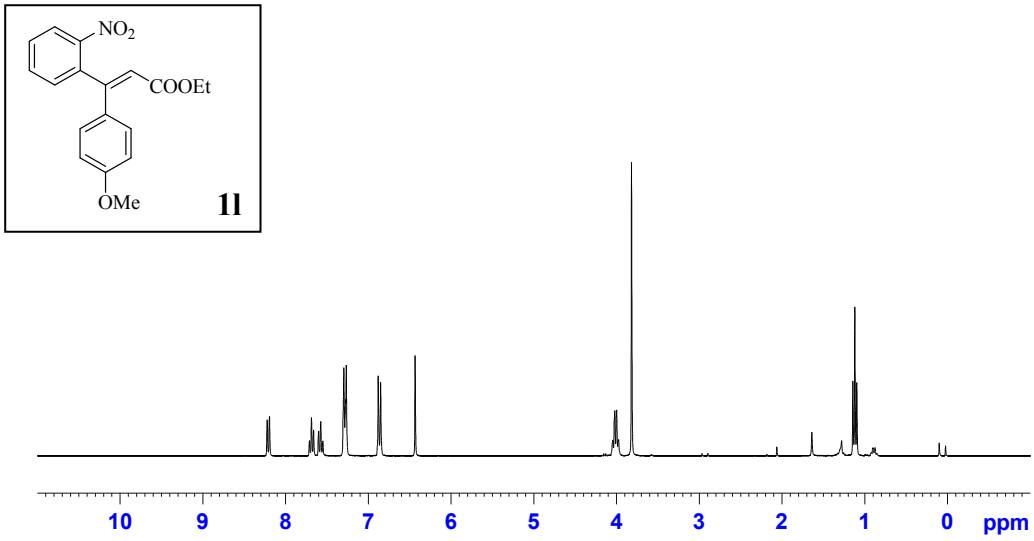
Ethyl 3-(2-methoxyphenyl)-3-phenylacrylate (**1k**) (^{1}H NMR in CD_3COCD_3 (300 MHz))



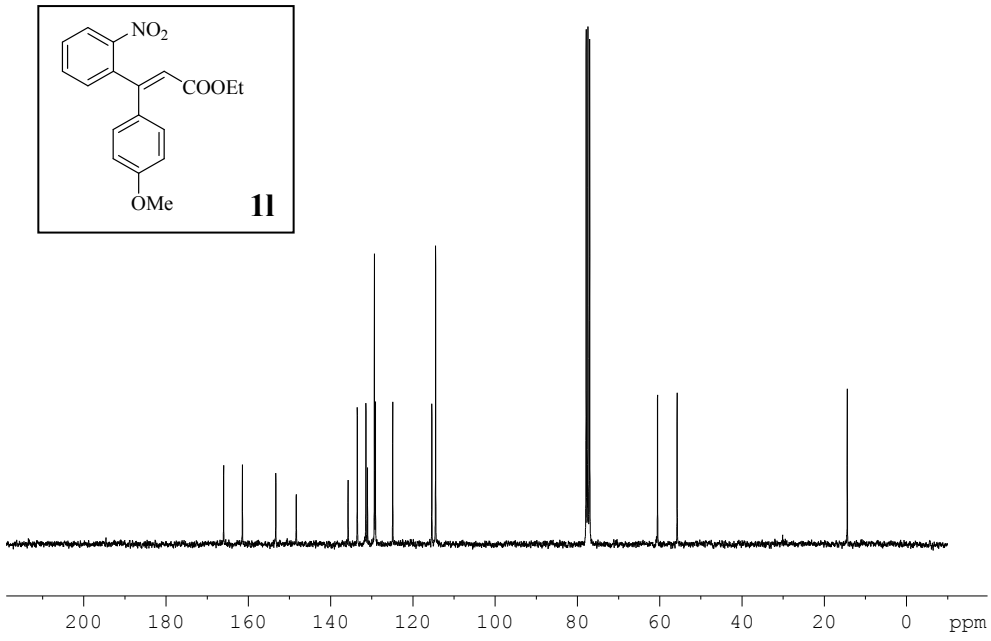
Ethyl 3-(2-methoxyphenyl)-3-phenylacrylate (**1k**) (^{13}C NMR in CD_3COCD_3 (75 MHz))



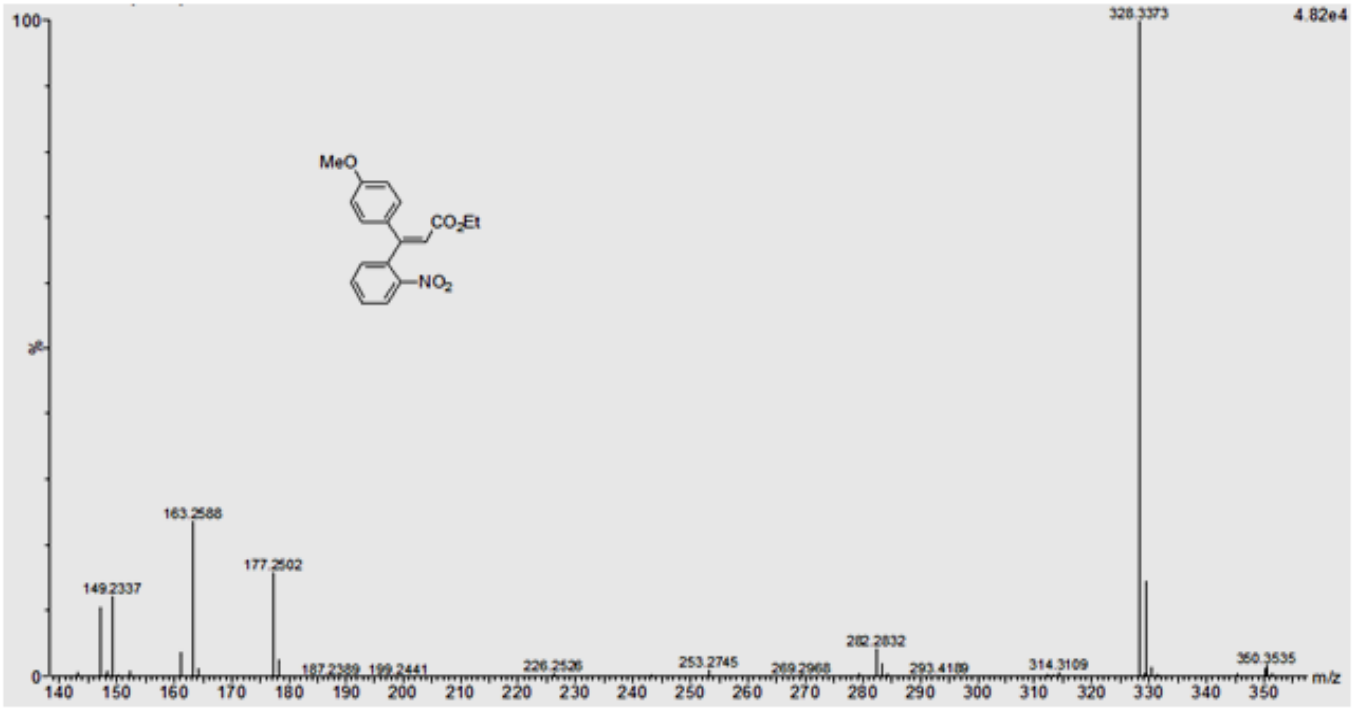
Ethyl 3-(4-methoxyphenyl)-3-(2-nitrophenyl)acrylate (**1l**) (^{1}H NMR in $CDCl_3$ (300 MHz))



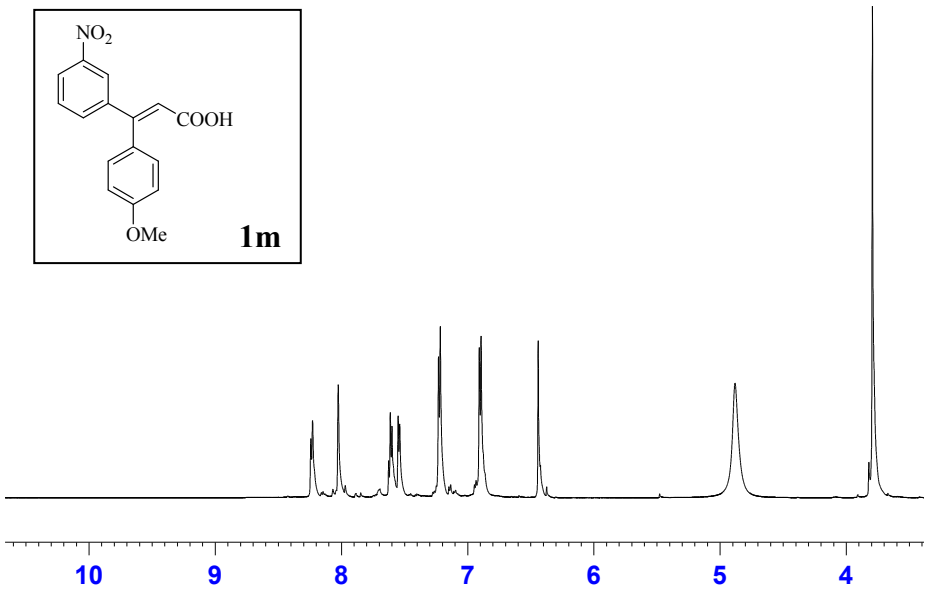
Ethyl 3-(4-methoxyphenyl)-3-(2-nitrophenyl)acrylate (**1l**) (^{13}C NMR in $CDCl_3$ (75 MHz))



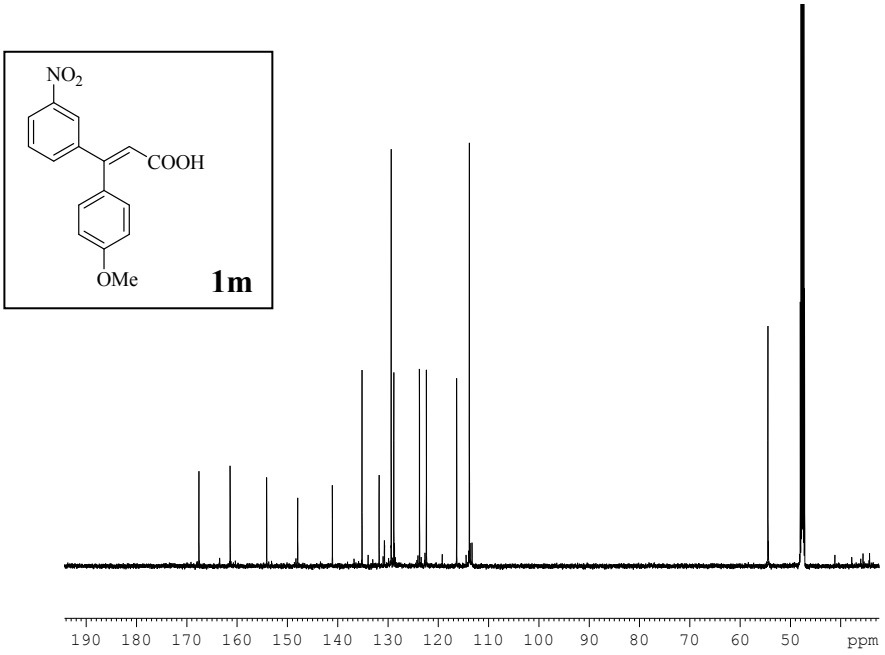
Ethyl 3-(4-methoxyphenyl)-3-(2-nitrophenyl)acrylate (**1l)** (ESI MS in MeCN/H_2O (1:1))



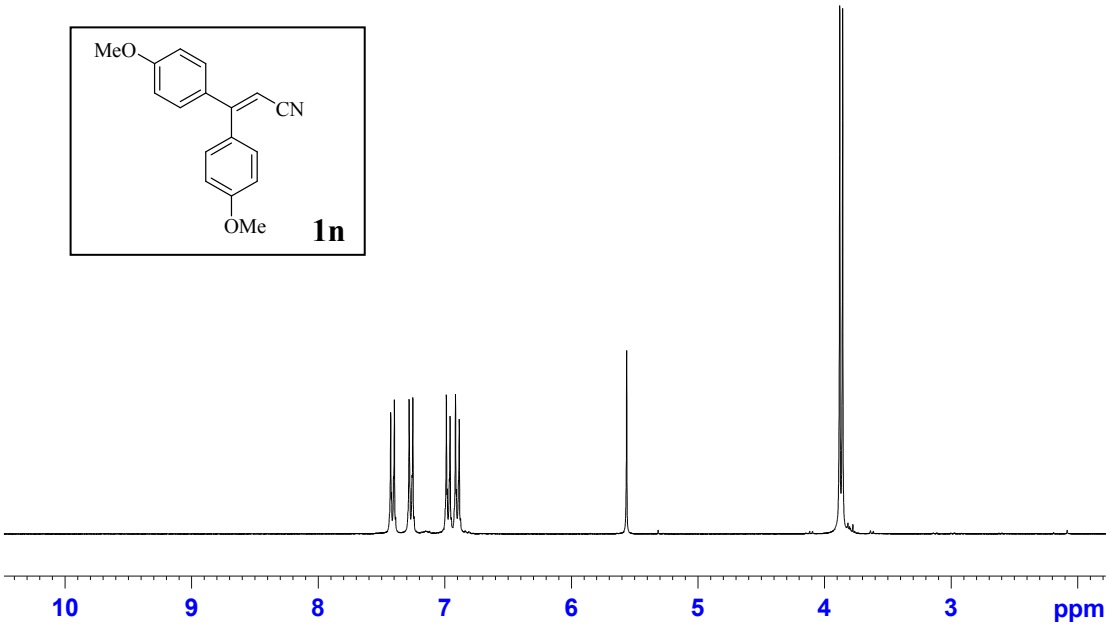
3-(4-methoxyphenyl)-3-(3-nitrophenyl)acrylic acid (**1m**) (^{1}H NMR in $CDCl_3$ (600 MHz))



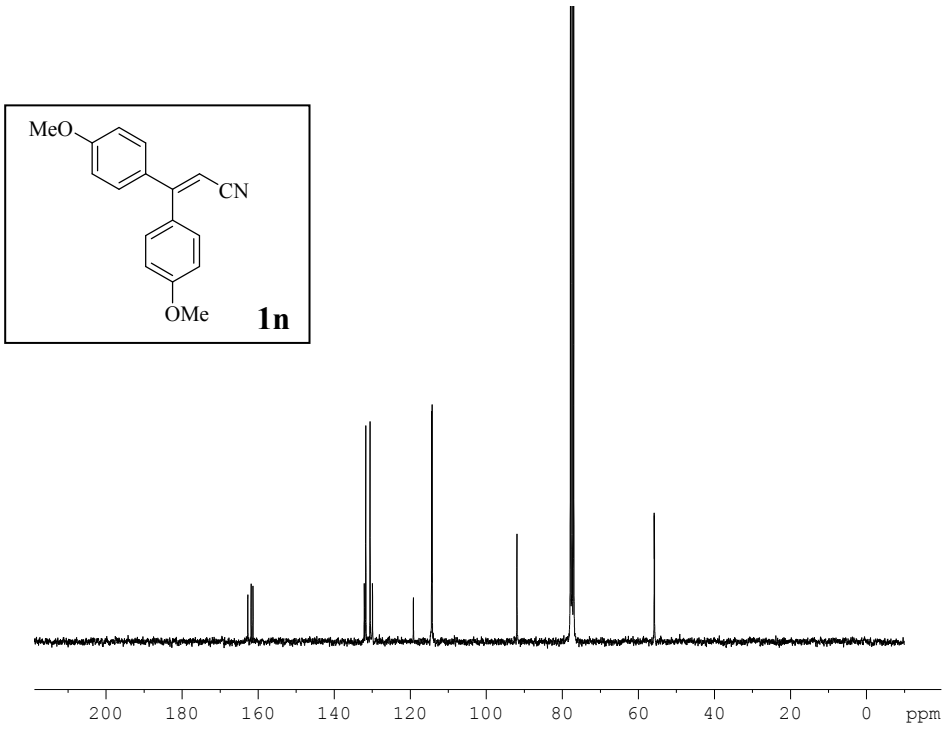
3-(4-methoxyphenyl)-3-(3-nitrophenyl)acrylic acid (**1m**) (^{13}C NMR in $CDCl_3$ (150 MHz))



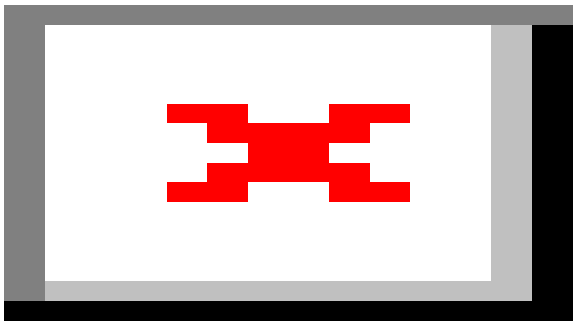
3,3-bis(4-methoxyphenyl)acrylonitrile (**1n**) (^{1}H NMR in C_6D_6 (300 MHz)



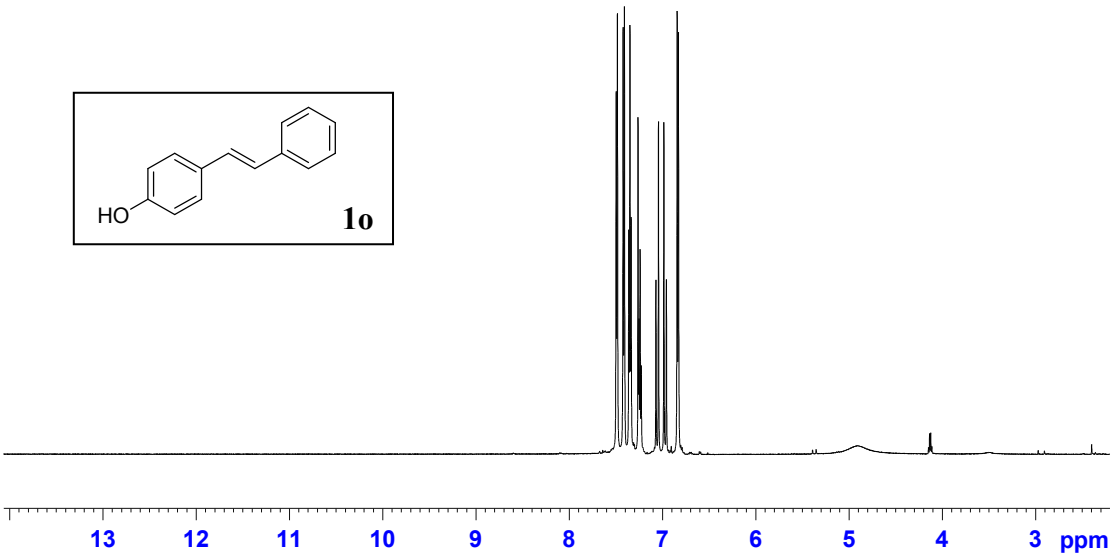
3,3-bis(4-methoxyphenyl)acrylonitrile (**1n**) (^{13}C NMR in C_6D_6 (75 MHz)



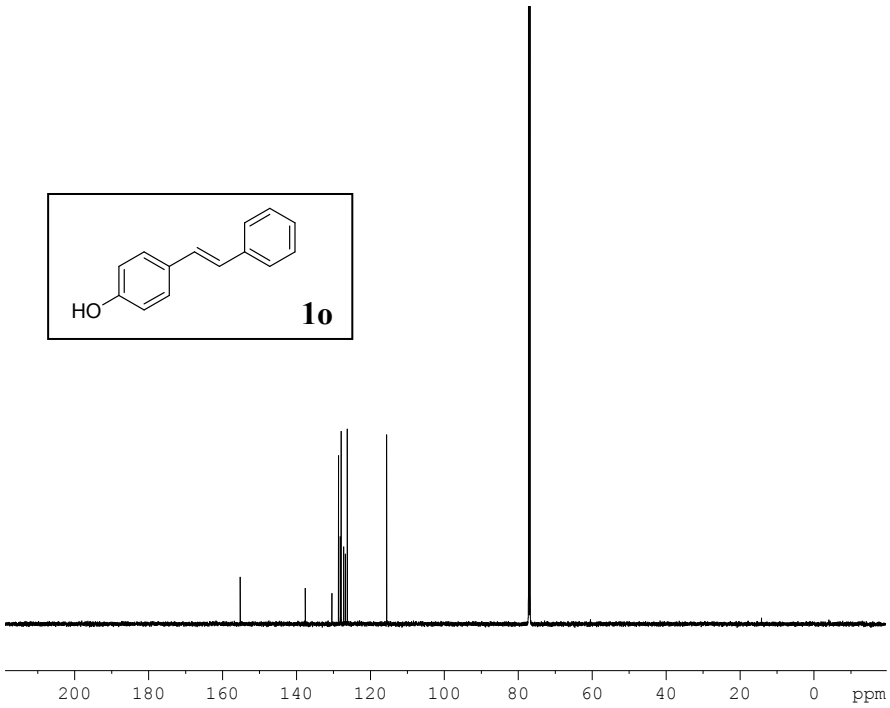
3,3-bis(4-methoxyphenyl)acrylonitrile (**1n**) (ESI MS in MeCN/H_2O (1:1))



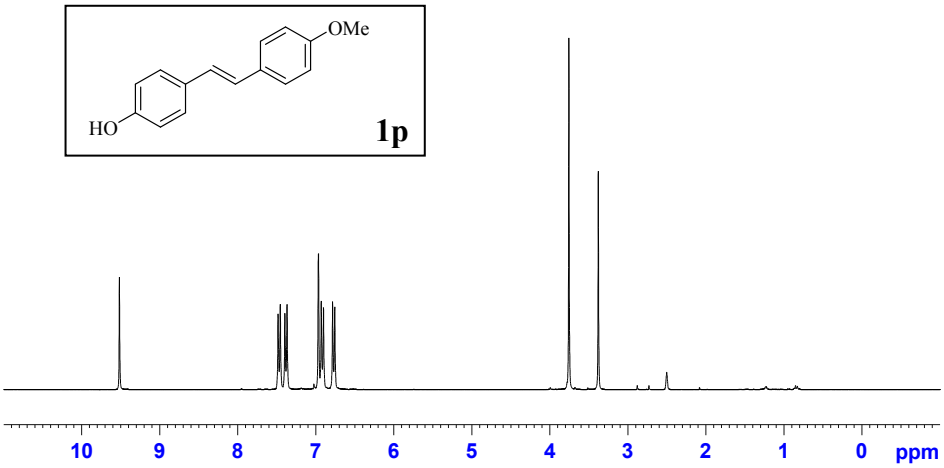
4-styrylphenol (**1o**) (^{1}H NMR in $CDCl_3$ (600 MHz))



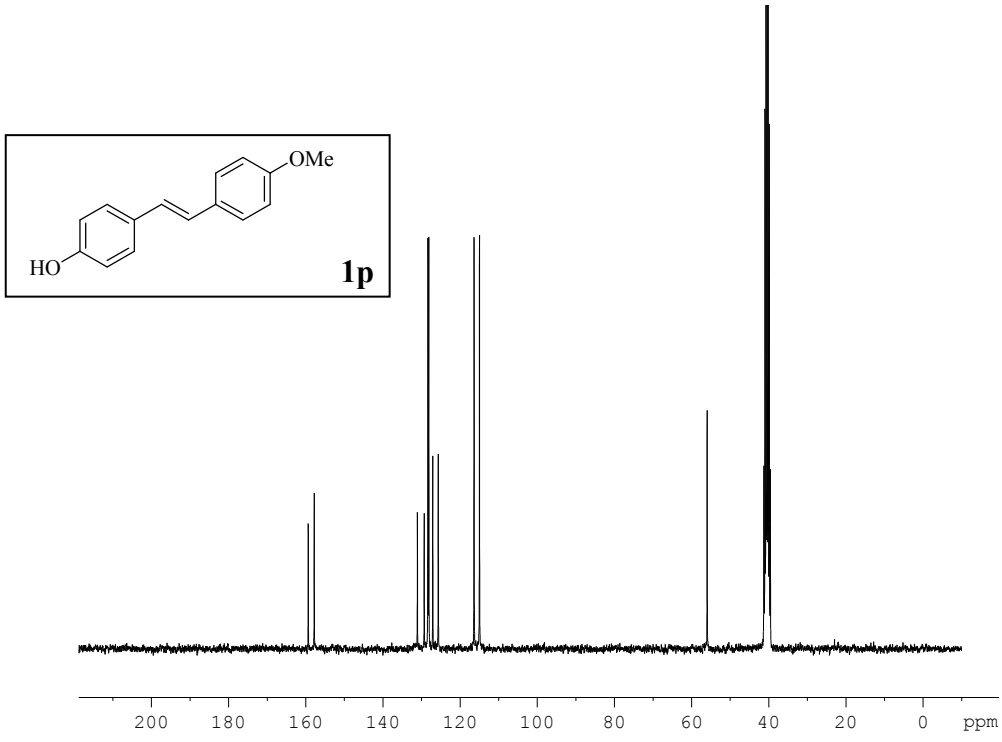
4-styrylphenol (**1o**) (^{13}C NMR in $CDCl_3$ (150 MHz))



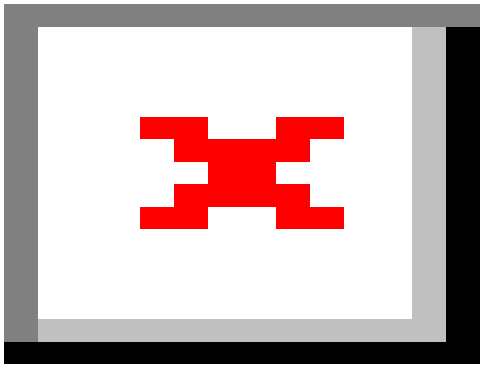
4-(4-methoxystyryl)phenol (**1p**) (^{1}H NMR in DMSO-d_6 (300 MHz))



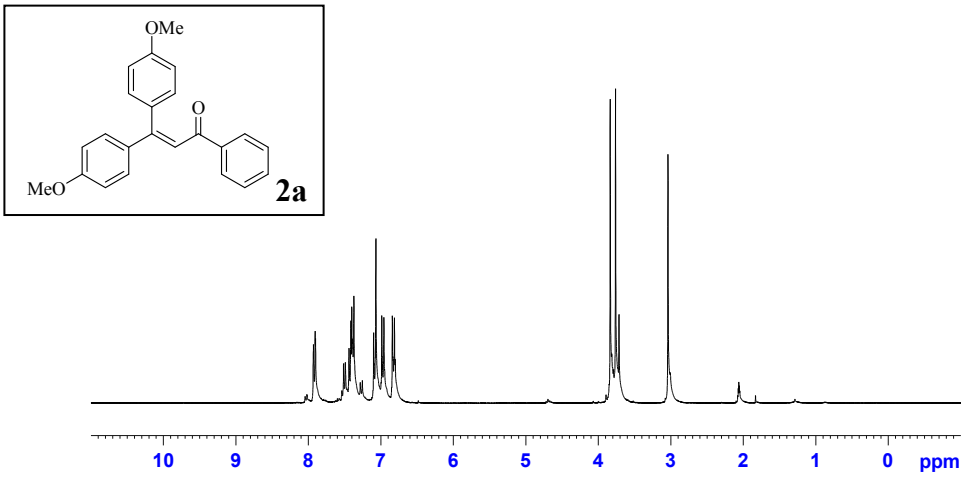
4-(4-methoxystyryl)phenol (**1p**) (^{13}C NMR in DMSO-d_6 (75 MHz))



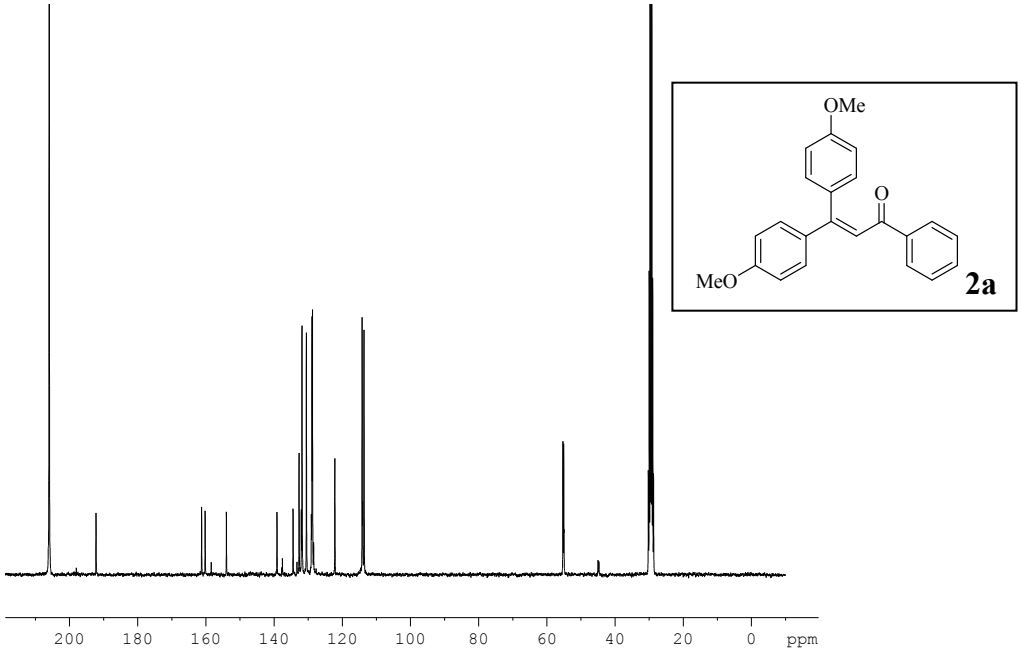
4-(4-methoxystyryl)phenol (**1p**) (ESI MS in MeCN/H_2O (1:1))



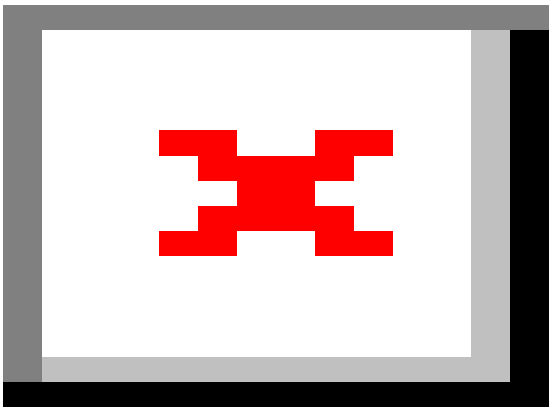
3,3-bis(4-methoxyphenyl)-1-phenylprop-2-en-1-one (**2a**) (^{1}H NMR in CD_3COCD_3 (300 MHz))



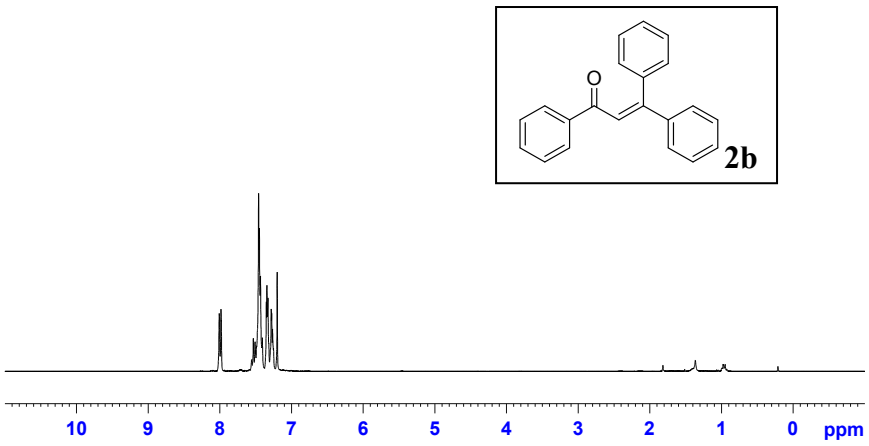
3,3-bis(4-methoxyphenyl)-1-phenylprop-2-en-1-one (**2a**) (^{13}C NMR in CD_3COCD_3 (75 MHz))



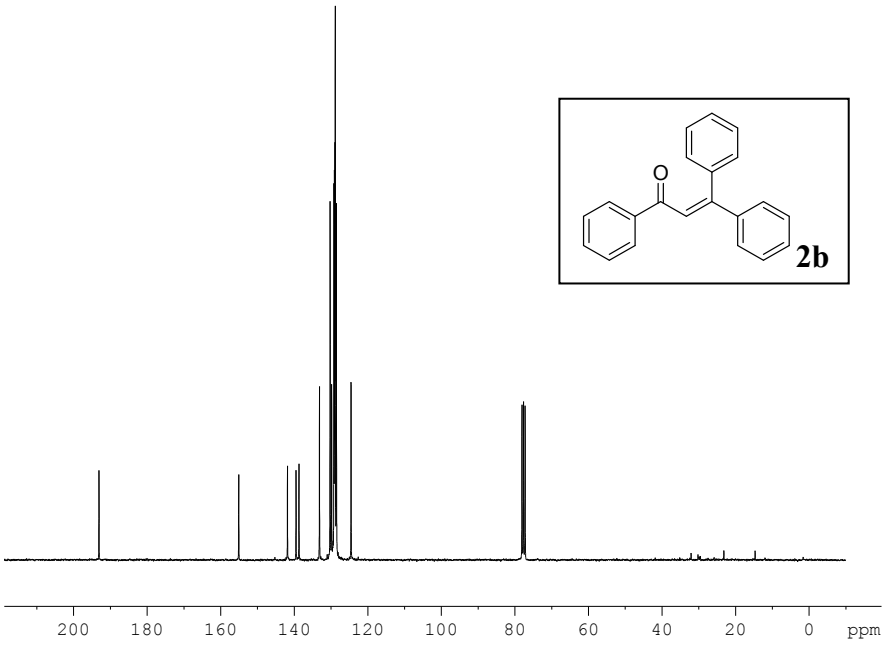
3,3-bis(4-methoxyphenyl)-1-phenylprop-2-en-1-one (**2a**) (ESI MS in MeCN/H_2O (1:1))



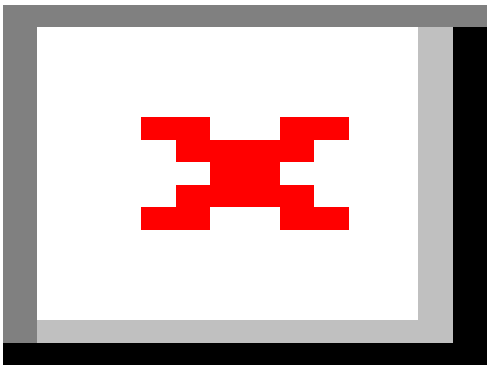
1,3,3-triphenylprop-2-en-1-one (**2b**) (^{1}H NMR in $CDCl_3$ (300 MHz))



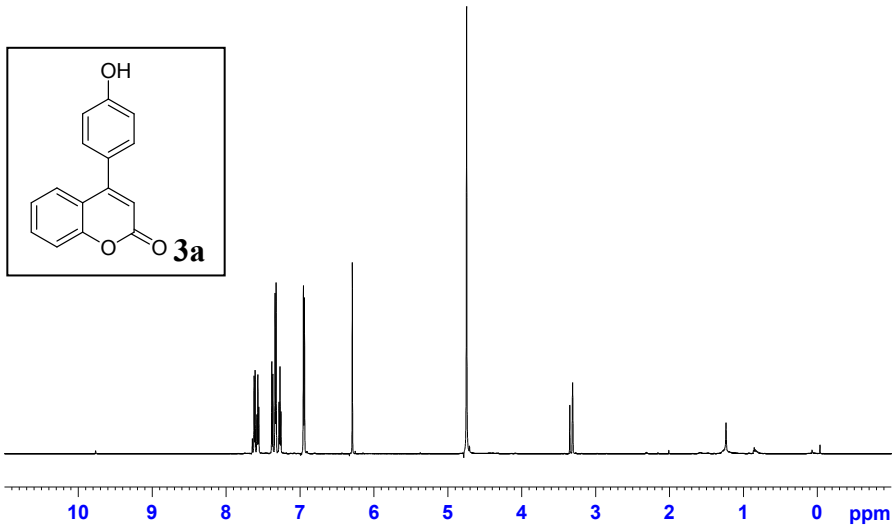
1,3,3-triphenylprop-2-en-1-one (**2b**) (^{13}C NMR in $CDCl_3$ (75 MHz))



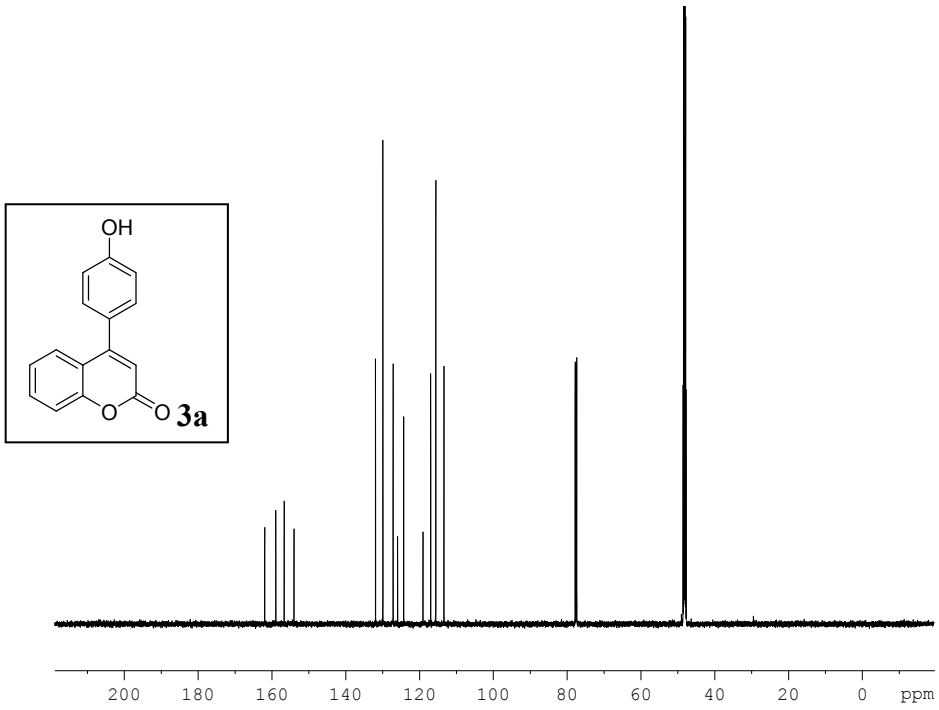
1,3,3-triphenylprop-2-en-1-one (**2b**) (ESI MS in MeCN/H_2O (1:1))



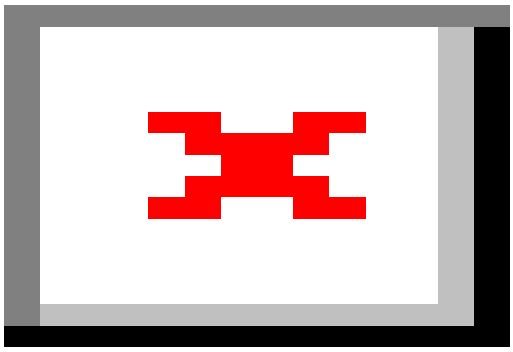
4-(4-hydroxyphenyl)-2*H*-chromen-2-one (**3a**) (^{1}H NMR in CD_3OD (600 MHz))



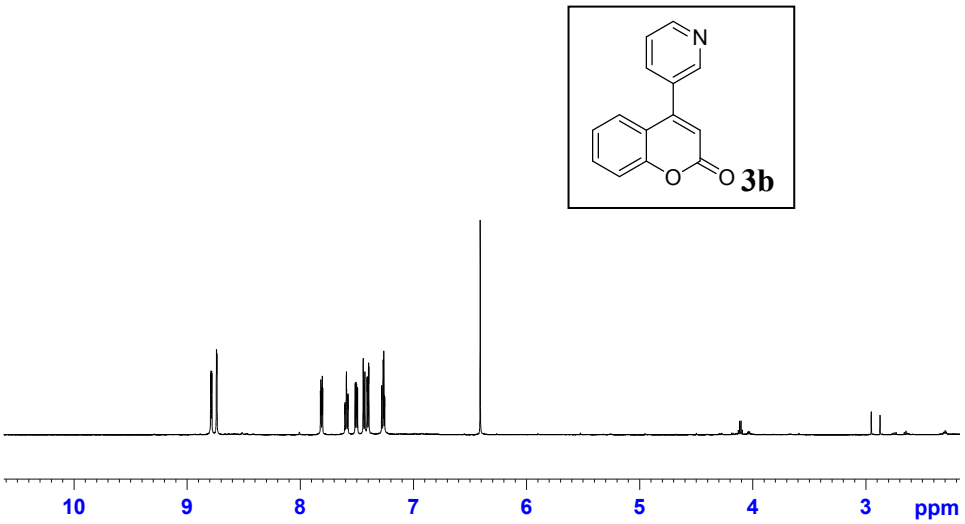
4-(4-hydroxyphenyl)-2*H*-chromen-2-one (**3a**) (^{13}C NMR in CD_3OD (150 MHz))



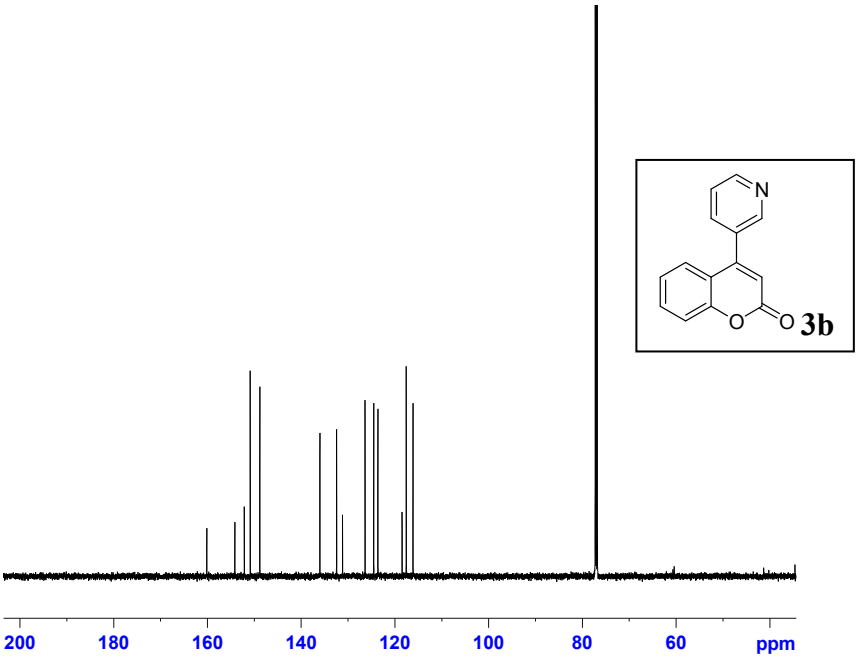
4-(4-hydroxyphenyl)-2*H*-chromen-2-one (**3a**) (ESI MS in MeCN/H_2O (1:1))



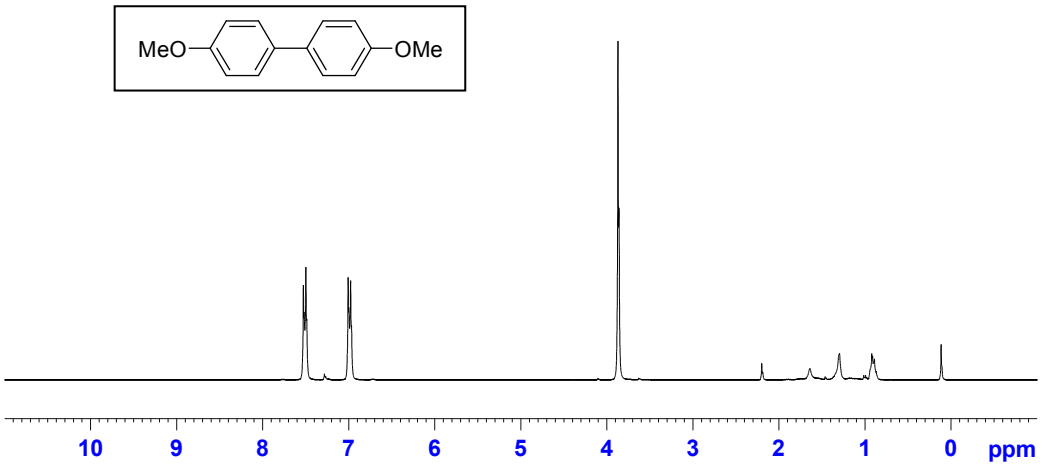
4-(pyridin-3-yl)-2H-chromen-2-one (**3b**) (^{1}H NMR in $CDCl_3$ (600 MHz))



4-(pyridin-3-yl)-2H-chromen-2-one (**3b**) (^{13}C NMR in $CDCl_3$ (150 MHz))



4, 4′-dimethoxybiphenyl (^{1}H NMR in $CDCl_3$ (300 MHz))



4, 4′-dimethoxybiphenyl (^{13}C NMR in $CDCl_3$ (75 MHz))