Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supplementary Information

A photocatalyst-free visible-light mediated solvent-switchable route to stilbenes/vinyl sulfones from β-nitrostyrenes and arylazo sulfones

Ruchi Chawla,[a]* Shefali Jaiswal,[a] P. K. Dutta[a] and Lal Dhar S. Yadav [b]

[a] *Polymer Research Laboratory, Department of Chemistry, Motilal Nehru National Institute of Technology Allahabad, Prayagraj 211004, India*

[b] *Green Synthesis Lab, Department of Chemistry, University of Allahabad, Prayagraj 211 002, India*

E-mail: *ruchi@mnnit.ac.in (R. Chawla).*

Table of Contents

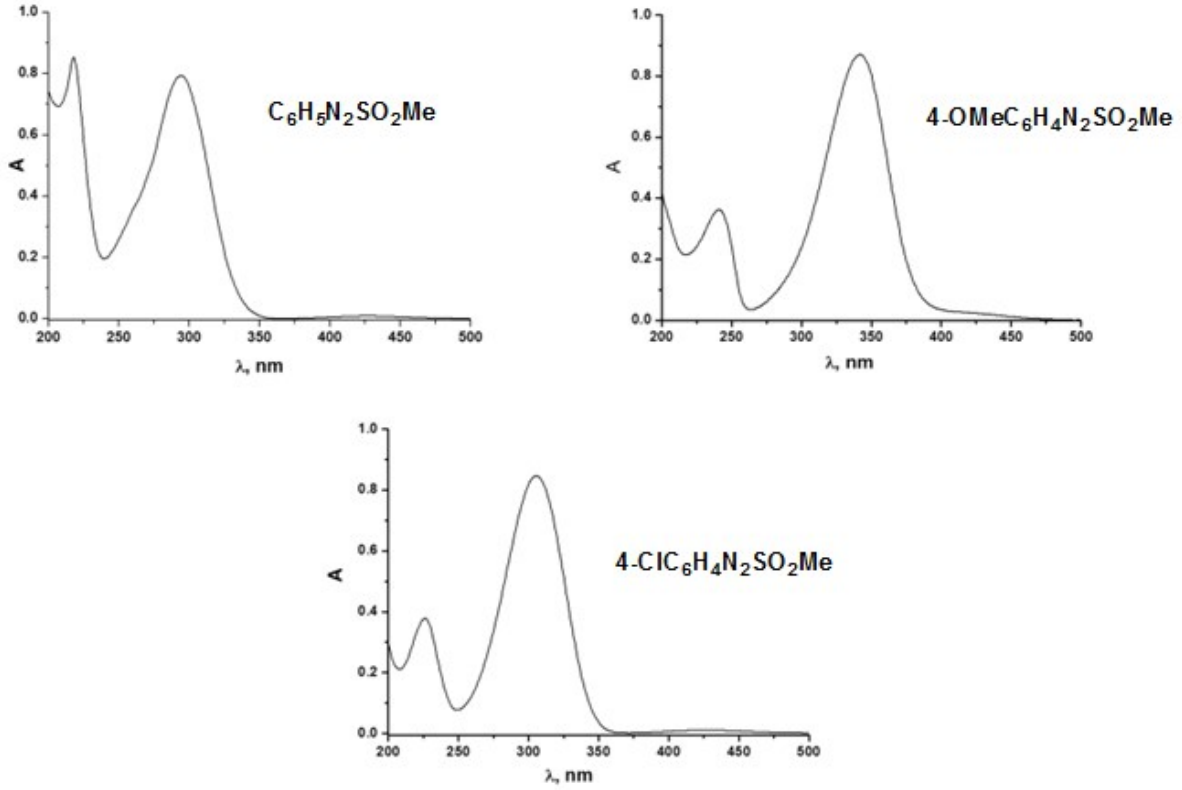
General Information:

Reagents were obtained from commercial suppliers, and used without further purification unless otherwise specified by a reference. All reactions were performed under ambient air. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF_{254} (Merck) plates. ^{1}H NMR spectra were recorded on a Bruker Advance II 400 MHz/ Bruker Advance Neo 500 MHz NMR spectrometer in $CDCl_3$ using TMS as internal reference with chemical shift value being reported in ppm. All coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded on the same instruments at 100/126 MHz in $CDCl_3$ and TMS was used as internal reference. The following abbreviations have been used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). HRMS were recorded on a Waters Q-ToF Micro mass spectrometer.

General procedure for the synthesis of arylazo sulfones 2:

Arylazo sulfones **2** were synthesized following the literature procedure[1a] and the identity and purity was checked by comparison of their melting points.[1]

Figure 1. UV absorption spectra of some arylazo sulfones **2** in acetonitrile (5×10^{-5} M)



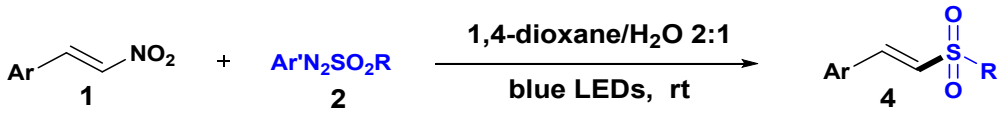
The detection of phenol in the model reaction system

A mixture of nitrostyrene **1a** (0.5 mmol) and arylazo sulfone **2a** (2.5 equiv.) in 1,4-dioxane:H_2O 2:1 (1 mL) was irradiated with visible-light (blue light emitting diodes (LEDs), λ_{max} = 455 nm, 3.0 W) with stirring at rt for 15 h (Table 1, entry 20) in an open-flask. After completion of the reaction, the solution was concentrated in vacuum. The side product phenol was detected by TLC and LC-MS analysis of the crude reaction mixture. In addition to the desired product **4a** (66%), the stilbene **3a** and phenol were isolated in 13% and 18% yield respectively.

General procedure for the synthesis of *trans*-stilbenes 3:

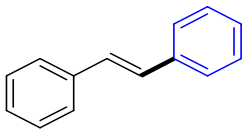
A mixture of nitrostyrene **1** (0.5 mmol) and arylazo sulfone **2** (2.5 equiv.) in CH_3CN was irradiated with visible-light (blue light emitting diodes (LEDs), λ_{max} = 455 nm, 3.0 W) with stirring at rt for 12-18 h (Table 2). Upon completion of the reaction (monitored by TLC), water (5 mL) was added and the mixture was extracted with EtOAc (3 x 15 mL). The combined organic phase was dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (EtOAc/*n*-hexane, 0:100 to 1:49) to afford an analytically pure sample of *trans*-stilbenes **3** (Table 2).

General procedure for the synthesis of (*E*)-vinyl sulfones 4:

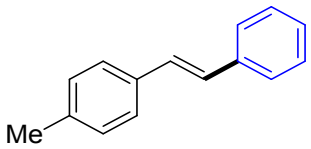


A mixture of nitrostyrene **1** (0.5 mmol) and arylazo sulfone **2** (2.5 equiv.) in 1,4-dioxane:H_2O 2:1 (1 mL) was irradiated with visible-light (blue light emitting diodes (LEDs), λ_{max} = 455 nm, 3.0 W) with stirring at rt for 12-18 h (Table 3) in an open-flask. Upon completion of the reaction (monitored by TLC), water (5 mL) was added and the mixture was extracted with EtOAc (3 x 15 mL). The combined organic phase was dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (EtOAc/*n*-hexane, 1:19) to afford an analytically pure sample of vinyl sulfones **4** (Table 3).

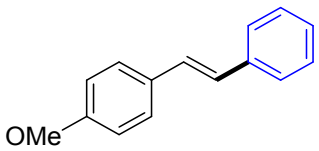
Characterization data of compounds 3



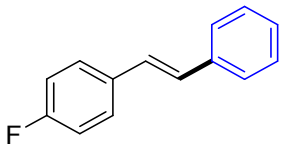
(*E*)-1,2-Diphenylethene (3a):[2-5] White solid (76% yield). M.p. 119-120 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.5 Hz, 2H, ArH), 7.37 (t, *J* = 7.5 Hz, 2H, ArH), 7.29-7.25 (m, 1H, ArH), 7.13 (s, 1H, CH). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.4, 128.8, 128.6, 127.7, 126.6. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{14}H_{13}$ 181.1012; Found 181.1015.



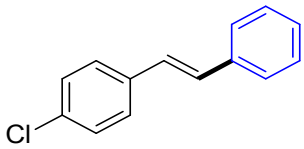
(*E*)-1-Methyl-4-styrylbenzene (3b):[2-5] White solid (78% yield). M.p. 116-117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.2 Hz, 2H, ArH), 7.41 (d, *J* = 8.4 Hz, 2H, ArH), 7.35 (t, *J* = 7.5 Hz, 2H, ArH), 7.24 (d, *J* = 7.2 Hz, 1H, ArH), 7.17 (d, *J* = 7.8 Hz, 2H, ArH), 7.08 (d, *J* = 4.8 Hz, 2H, CH), 2.36 (s, 3H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.6, 137.6, 134.6, 129.5, 128.7, 128.7, 127.8, 127.5, 126.5, 126.5, 21.3. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{15}H_{15}$ 195.1168; Found 195.1166.



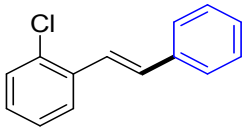
(*E*)-1-Methoxy-4-styrylbenzene (3c):[2-4] White solid (81% yield). M.p. 132-133 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.8 Hz, 1H, ArH), 7.45-7.36 (m, 4H, ArH), 7.26 (t, *J* = 7.2 Hz, 2H, ArH), 7.16 (d, *J* = 16.2 Hz, 1H, CH), 7.00 (d, *J* = 9.2 Hz, 1H, ArH), 6.94 (d, *J* = 16.2 Hz, 1H, CH), 6.86 (d, *J* = 9.0 Hz, 1H, ArH), 3.75 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.4, 137.7, 130.1, 128.6, 128.3, 127.8, 127.3, 126.7, 126.3, 114.2, 55.4. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{15}H_{15}O$ 211.1117; Found 211.1114.



(*E*)-1-Fluoro-4-styrylbenzene (3d):[2,4,5] White solid (65% yield). M.p. 124-125 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44-7.40 (m, 4H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.19-7.18 (m, 1H), 7.00-6.96 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.8 ($^{1}J_{C\text{-}F}$ = 247.8 Hz), 137.3, 133.6, 128.8, 128.6, 128.0, 127.7, 127.6, 126.5, 115.7 ($^{2}J_{C\text{-}F}$ = 21.7 Hz). HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{14}H_{12}F$ 199.0918; Found 199.0919.

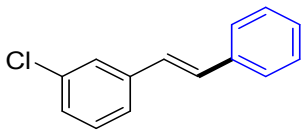


(*E*)-1-Chloro-4-styrylbenzene (3e):[2-5] Yellow solid (61% yield). M.p. 127-128 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.0 Hz, 2H, ArH), 7.42 (d, *J* = 8.0 Hz, 2H, ArH), 7.37-7.30 (m, 4H, ArH), 7.27-7.24 (m, 1H, ArH), 7.07 (d, *J* = 16.2 Hz, 1H, CH), 7.02 (d, *J* = 16.2 Hz, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.9, 135.9, 133.2, 129.4, 128.9, 128.8, 127.8, 127.7, 127.4, 126.5. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{14}H_{12}Cl$ 215.0622; Found 215.0622.

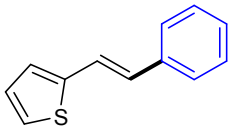


(*E*)-1-Chloro-2-styrylbenzene (3f):[3,4] White solid (59% yield). M.p. 67-68 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 7.8 Hz, 1H, ArH), 7.49-7.43 (m, 3H, ArH), 7.32-7.27 (m, 3H, ArH), 7.23-7.19 (m, 2H, 1ArH and 1CH), 7.12 (t, *J* = 8.0 Hz, 1H, ArH), 7.11 (d, *J* = 16.5 Hz, 1H, CH). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.2, 135.5, 133.5, 131.3, 129.9,

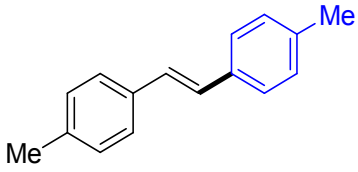
128.8, 128.6, 128.1, 127.0, 126.9, 126.6, 124.9. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{14}H_{12}Cl$ 215.0622; Found 215.0620.



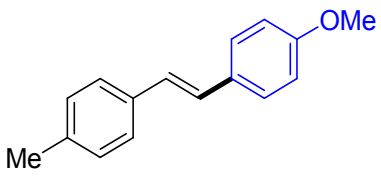
(*E*)-1-Chloro-3-styrylbenzene (3g):[3,4] White solid (63% yield): M.p. 70-71 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51-7.50 (m, 3H, ArH), 7.38-7.35 (m, 3H, ArH), 7.28 (t, *J* = 7.8 Hz, 2H, ArH), 7.22 (d, *J* = 7.5 Hz, 1H, ArH), 7.11 (d, *J* = 16.0 Hz, 1H, CH), 7.03 (d, *J* = 16.5 Hz, 1H, CH). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 139.2, 136.8, 134.6, 130.1, 129.9, 128.8, 128.0, 127.5, 127.2, 126.6, 126.3, 124.7. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{14}H_{12}Cl$ 215.0622; Found 215.0621.



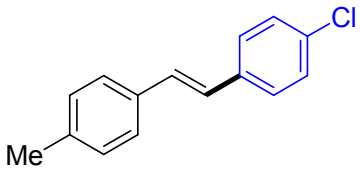
(*E*)-2-Styrylthiophene (3h):[2,4,5] Yellow solid (62% yield). M.p. 127-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.24-7.17 (m, 3H), 7.05 (d, *J* = 4.0 Hz, 1H), 7.00-6.98 (m, 1H), 6.91 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 136.9, 136.7, 128.7, 128.3, 127.6, 126.3 126.1, 124.3, 121.7. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{12}H_{11}S$ 187.0576; Found 187.0580.



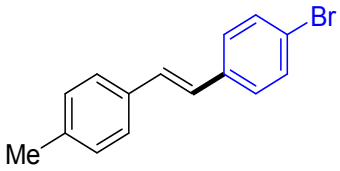
(*E*)-1,2-Di-*p*-tolylethene (3i):[4] White solid (82% yield). M.p. 177-178 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 7.6 Hz, 4H), 7.09 (d, *J* = 7.6 Hz, 4H), 6.97 (s, 2H), 2.29 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 136.8, 134.6, 129.7, 129.1, 128.8, 21.4. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{16}H_{17}$ 209.1325; Found 209.1322.



(*E*)-1-Methoxy-4-(4-methylstyryl)benzene (3j):[2,4] White solid (85% yield). M.p. 155-157 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.5 Hz, 2H), 7.17-7.14 (m, 3H), 6.92-6.90 (m, 3H), 6.70-6.68 (m, 2H), 3.69 (s, 3H), 2.33 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 160.0, 144.6, 135.2, 132.1, 130.1, 129.6, 128.7, 124.8, 120.3, 114.1, 55.3, 21.7. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{16}H_{17}O$ 225.1274; Found 225.1273.

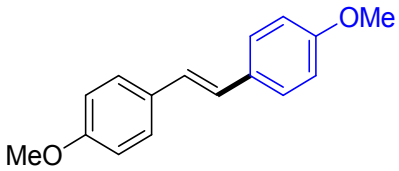


(*E*)-1-Chloro-4-(4-methylstyryl)benzene (3k):[3,4] White solid (70% yield). M.p.: 200-202 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36-7.32 (m, 4H, ArH), 7.24 (d, *J* = 9.0, 2H, ArH), 7.10 (d, *J* = 7.5 Hz, 2H, ArH), 6.98 (d, *J* = 16.5 Hz, 1H, CH), 6.92 (d, *J* = 16.5 Hz, 1H, CH), 2.29 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.9, 136.1, 134.3, 133.0, 129.5, 129.3, 128.9, 127.6, 126.5, 126.4, 21.3. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{15}H_{14}Cl$ 229.0779; Found 229.0780.

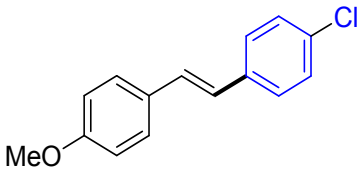


(*E*)-1-bromo-4-(4-methylstyryl)benzene (3l):[3] White solid (72% yield). M.p. 189 - 190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.8 Hz, 2H, ArH), 7.33 - 7.29 (m, 3H, ArH), 7.18 - 7.08 (m, 3H, ArH), 6.99 (d, J = 16.4 Hz, 1H, CH), 6.90 (d, J = 16.0 Hz, 1H, CH),

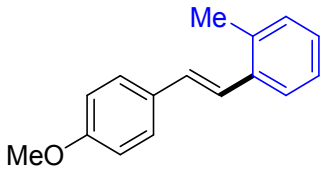
2.28 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.4, 134.1, 131.7, 129.4, 129.3, 127.8, 126.4, 126.4, 121.0, 21.3. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{15}H_{14}Br$ 273.0273; Found 273.0275.



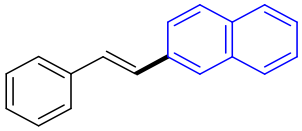
(*E*)-1,2-Bis(4-methoxyphenyl)ethene (3m):[2,4,5] Yellowish solid (87% yield). M.p. 215-216 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 4H), 6.92 (s, 2H), 6.87 (d, *J* = 8.0 Hz, 4H), 3.81 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 130.4, 127.4, 126.1, 114.1, 55.5. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{16}H_{17}O_2$ 241.1223; Found 241.1222.



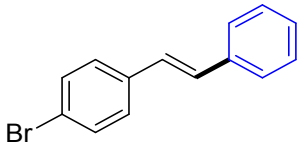
(*E*)-1-chloro-4-(4-methoxystyryl)benzene (3n):[3,5] Yellow solid (72% yield). M.p. 163 - 166 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H, ArH), 7.42 (d, *J* = 8.4 Hz, 2H, ArH), 7.30 (d, *J* = 8.4 Hz, 2H, ArH), 7.04 (d, *J* = 16.2 Hz, 1H, CH), 6.93-6.89 (m, 2H, ArH and 1H, CH), 3.83 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 136.1, 132.6, 129.8, 128.8, 128.7, 127.7, 127.3, 125.2, 114.1, 55.3. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{15}H_{14}ClO$ 245.0728; Found 245.0731.



(*E*)-1-(4-Methoxystyryl)-2-methylbenzene (3o):[5] Off-white solid (80% yield). M.p. 77–78 °C (recrystallized with *n*-pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.24–7.17 (m, 4H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 136.6, 135.5, 130.5, 130.4, 129.5, 127.8, 127.2, 126.2, 125.1, 124.4, 114.1, 55.3, 20.0. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{16}H_{17}O$ 225.1274; Found 225.1271.

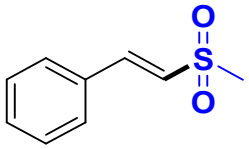


(*E*)-2-Styrylnaphthalene (3p):[5] White solid (63% yield). M.p. 143–146 °C (recrystallized with *n*-pentane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84-7.79 (m, 4H), 7.73-7.72 (m, 1H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.47-7.41 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.28-7.20 (m, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 136.2, 133.6, 132.5, 131.8, 127.8, 127.6, 127.5, 127.1, 126.8, 126.5, 126.5, 125.4, 125.4, 125.1, 124.7, 122.3. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{18}H_{15}$ 231.1168; Found 231.1167.

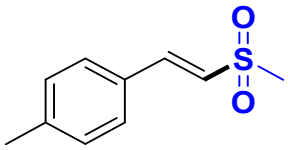


(*E*)-1-bromo-4-styrylbenzene (3q):[3,5] White solid (55% yield). M.p. 125 – 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.46 (m, 4H, ArH), 7.38-7.34 (m, 4H, ArH), 7.27 (d, *J* = 8.0 Hz, 1H, ArH), 7.09 (d, *J* = 16.0 Hz, 1H, CH), 7.02 (d, *J* = 16.0 Hz, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 136.2, 131.8, 129.4, 128.7, 127.9, 127.9, 127.4, 126.5, 121.3. HRMS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{14}H_{12}Br$ 259.0117; Found 259.0119.

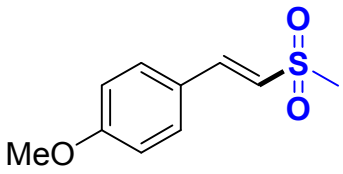
Characterization data of compounds 4



(*E*)-(2-(Methylsulfonyl)vinyl)benzene (4a):[6,7] Yellow solid (66% yield). M.p. 72-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 15.2 Hz, 1H), 7.53-7.51 (m, 2H), 7.45-7.39 (m, 3H), 6.93 (d, J = 15.4 Hz, 1H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 143.8, 132.1, 131.3, 129.1, 128.6, 126.2, 43.3. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_9H_{11}O_2S$ 183.0474; Found 183.0477.

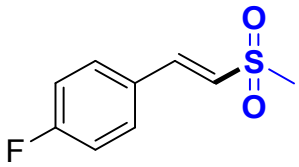


(*E*)-1-Methyl-4-(2-(methylsulfonyl)vinyl)benzene (4b):[7] Yellow solid (69% yield). M.p. 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, J = 15.6 Hz, 1H), 7.42 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 6.88 (d, J = 15.6 Hz, 1H), 3.03 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 142.2, 130.0, 129.3, 128.6, 124.9, 43.2, 21.5. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{10}H_{13}O_2S$ 197.0631; Found 197.0630.

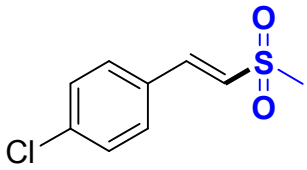


(*E*)-1-Methoxy-4-(2-(methylsulfonyl)vinyl)benzene (4c):[6,7] Yellow solid (71% yield). M.p. 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 15.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 15.6 Hz, 1H), 3.85 (s, 3H), 3.02 (s,

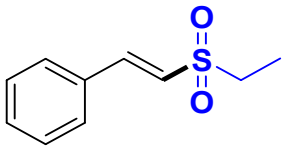
3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 143.7, 130.4, 124.8, 123.4, 114.5, 55.5, 43.5. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{10}H_{13}O_3S$ 213.0580; Found 213.0577.



(*E*)-1-Fluoro-4-(2-(methylsulfonyl)vinyl)benzene (4d):[6,7] Yellow solid (55% yield). M.p. 121-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 15.6 Hz, 1H), 7.55-7.52 (m, 2H), 7.11(t, J = 8.8 Hz, 2H), 6.88 (d, J = 15.6 Hz, 1H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4 (J = 252.0 Hz), 142.7, 130.6 (J = 9.2 Hz), 128.3 (J = 3.0 Hz), 125.8, 116.5 (J = 22.2 Hz), 43.4. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_9H_{10}FO_2S$ 201.0380; Found 201.0382.

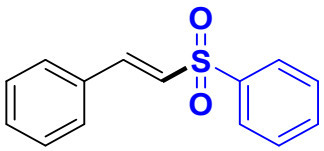


(*E*)-1-Chloro-4-(2-(methylsulfonyl)vinyl)benzene (4e):[7] Yellow solid (58% yield). M.p. 128-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 15.6 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 15.6 Hz, 1H), 3.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 137.4, 130.7, 129.8, 129.4, 126.7, 43.3. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_9H_{10}ClO_2S$ 217.0085; Found 217.0084.

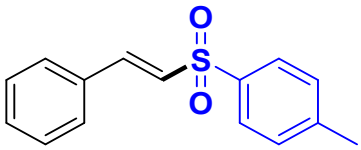


(*E*)-(2-(Ethylsulfonyl)vinyl)benzene (4f):[8] White solid (71% yield). M.p. 65−67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 15.2 Hz, 1H), 7.56−7.51 (m, 2H), 7.47−7.42

(m, 3H), 6.83 (d, *J* = 15.2 Hz, 1H), 3.08 (q, *J* = 7.8 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 144.7, 131.7, 130.9, 128.8, 128.2, 123.5, 48.9, 6.7. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{10}H_{13}O_2S$ 197.0631; Found 197.0633.



(*E*)-(2-(Phenylsulfonyl)vinyl)benzene (4g):[9] Pale yellow solid (74% yield). M.p. 61−62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.98 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 15.6 Hz, 1H), 7.64−7.58 (m, 1H), 7.55−7.51 (m, 2H), 7.49−7.46 (m, 2H), 7.39−7.36 (m, 3H), 6.86 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 142.4, 140.6, 133.4, 132.2, 131.2, 129.2, 128.9, 128.3, 127.5, 127.1. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{14}H_{13}O_2S$ 245.0631; Found 245.0635.

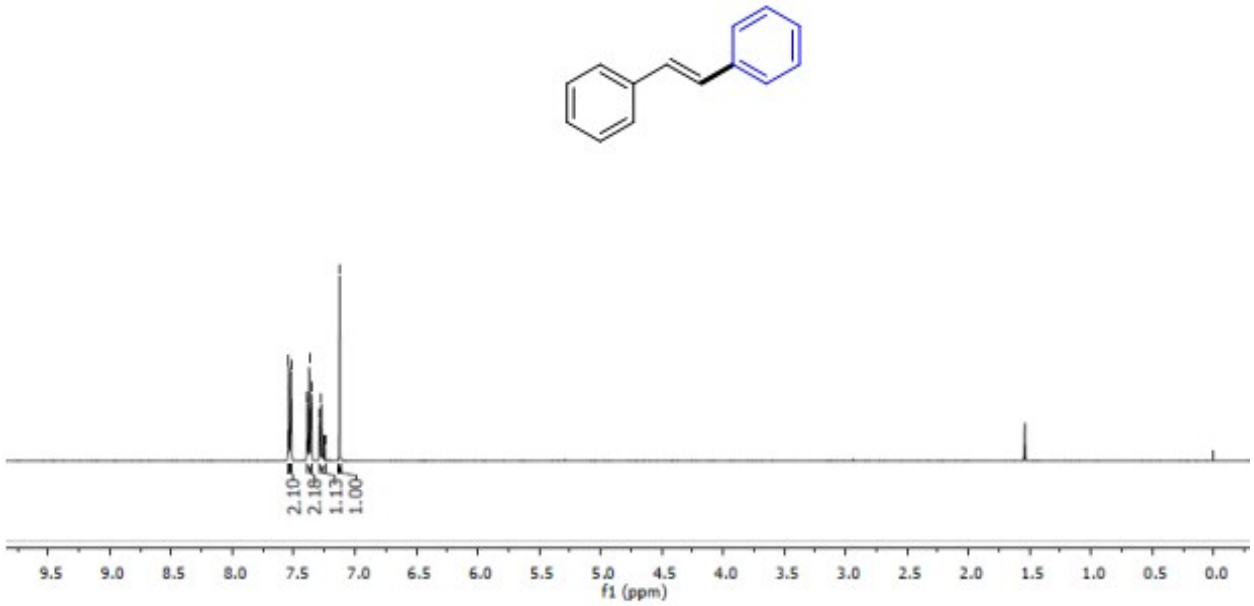


(*E*)-1-Methyl-4-(styrylsulfonyl)benzene (4h):[9] White solid (84% yield). M.p. 112−115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.84 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 15.6 Hz, 1H), 7.47−7.43 (d, *J* = 7.2 Hz, 2H), 7.39−7.33 (m, 5H), 6.88 (d, *J* = 15.6 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 144.3, 141.8, 137.87, 132.3, 131.0, 129.7, 128.9, 128.3, 127.6, 127.5, 21.3. HRMS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{15}H_{15}O_2S$ 259.0787; Found 259.0784.

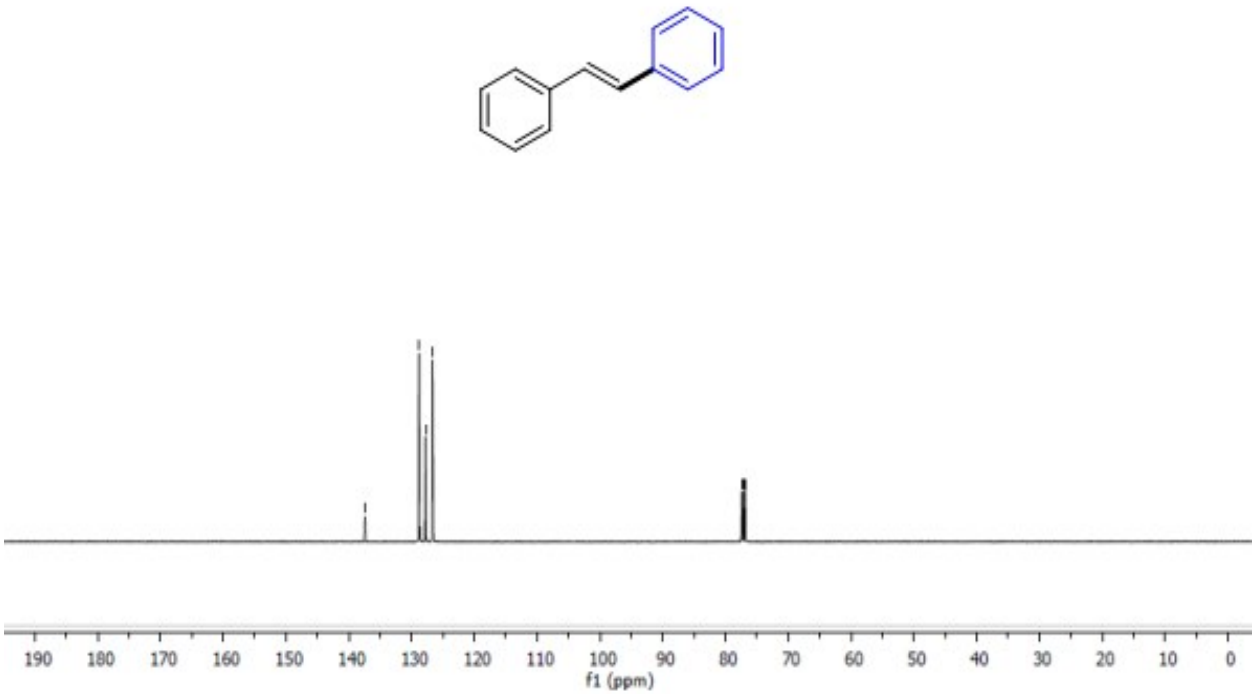
References

1. a) S. Crespi, S. Protti and M. Fagnoni, *J. Org. Chem.,* 2016, **81**, 9612; b) Y. Xu, X. Yang and H. Fang, *J. Org. Chem.,* 2018, **83**, 12831; c) N. Kamigata and M. Kobayashi, *Sulfur Reports*, 1982, **2**, 87; d) Q. Liu, F. Liu, H. Yue, X. Zhao, J. Li and W. Wei, *Adv. Synth. Catal.,* 2019, **361**, 5277.
2. P. Puthiyaraj and K. Pitchumani, *Green Chem*., 2014, **16**, 4223.
3. N. Zhang, Z.-J. Quan, Z. Zhang, Y.-X. Da and X.-C. Wang, *Chem. Commun*., 2016, **52**, 14234.
4. A. K. Yadav and K. N. Singh, *New J. Chem.,* 2017, **41**, 14914.
5. G. Wagh, S. Autade, P. C. Patil and K. G. Akamanchi, *New J. Chem.,* 2018, **42**, 3301.
6. Y. Jiang and T.-P. Loh, *Chem. Sci.,* 2014, **5**, 4939.
7. J.-Y. Chen, X.-L. Chen, X. Li, L.-B. Qu, Q. Zhang, L.-K. Duan, Y.-Y. Xia, X. Chen, K. Sun, Z.-D. Liu and Y.-F. Zhao, *Eur. J. Org. Chem.,* 2015, 314.
8. G. Rong, J. Mao, H. Yan, Y. Zheng and G. Zhang, *J. Org. Chem.,* 2015, **80**, 7652.
9. P. Qian, M. Bi, J. Su, Z. Zha and Z. Wang, *J. Org. Chem.,* 2016, **81**, 4876.

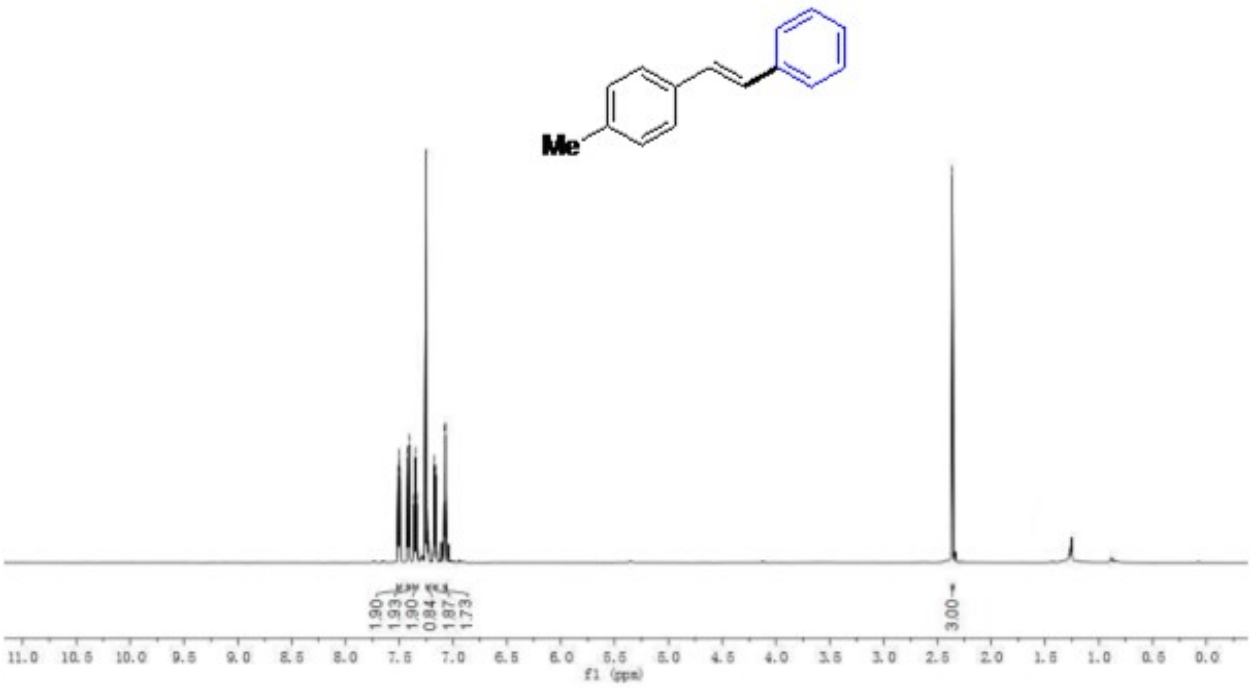
Copies of ^{1}H and ^{13}C NMR spectra of compounds **3a**-**3q** and **4a**-**4h**



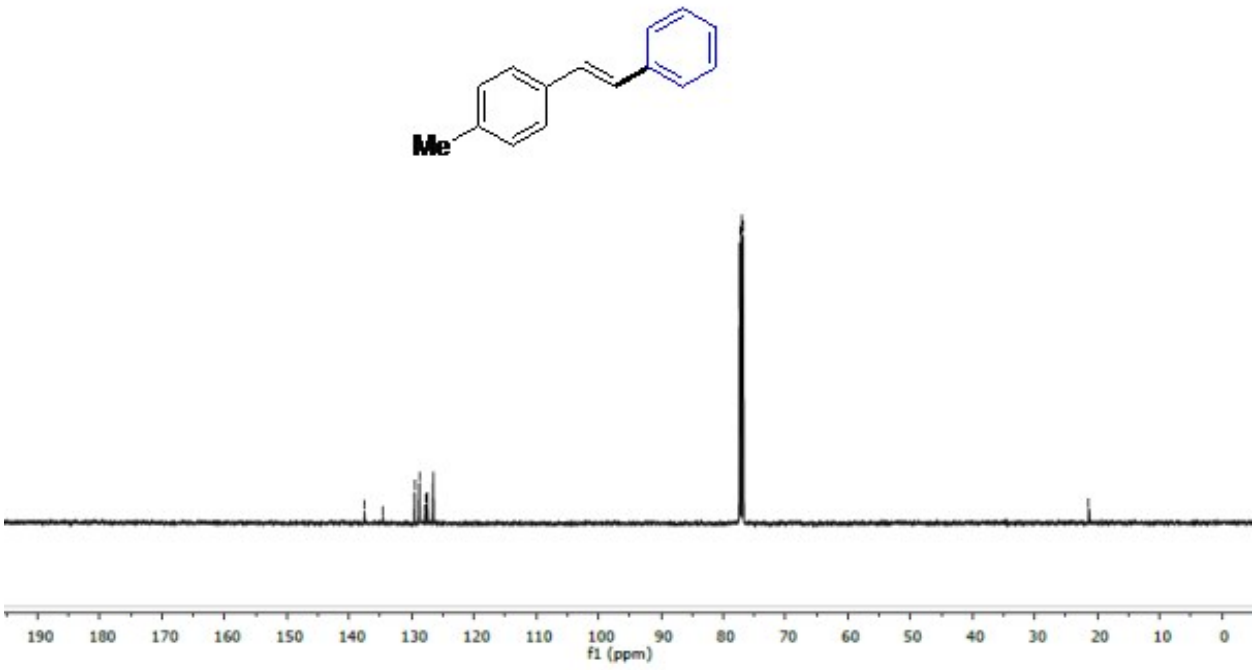
^{1}H NMR spectrum of compound **3a** in $CDCl_3$



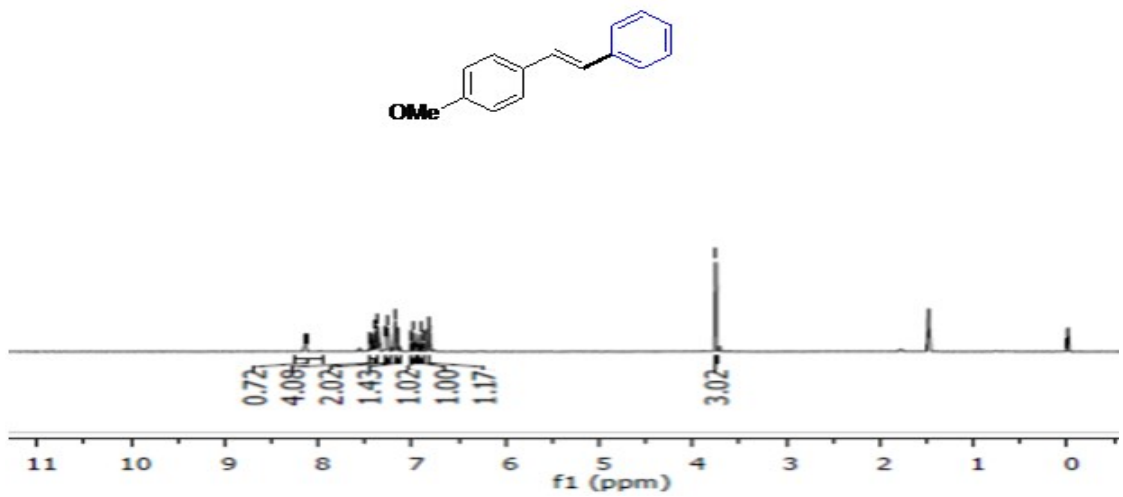
^{13}C NMR spectrum of compound **3a** in $CDCl_3$



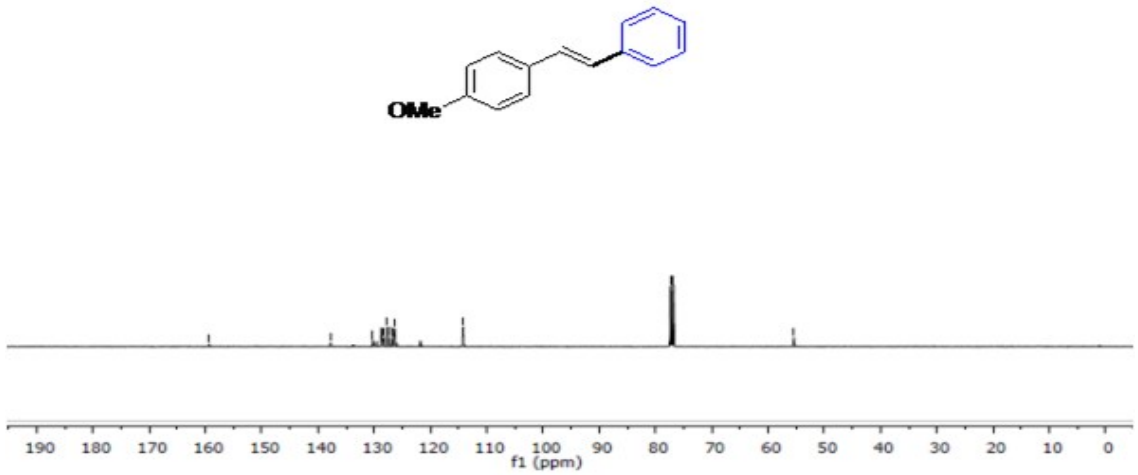
^{1}H NMR spectrum of compound **3b** in $CDCl_3$



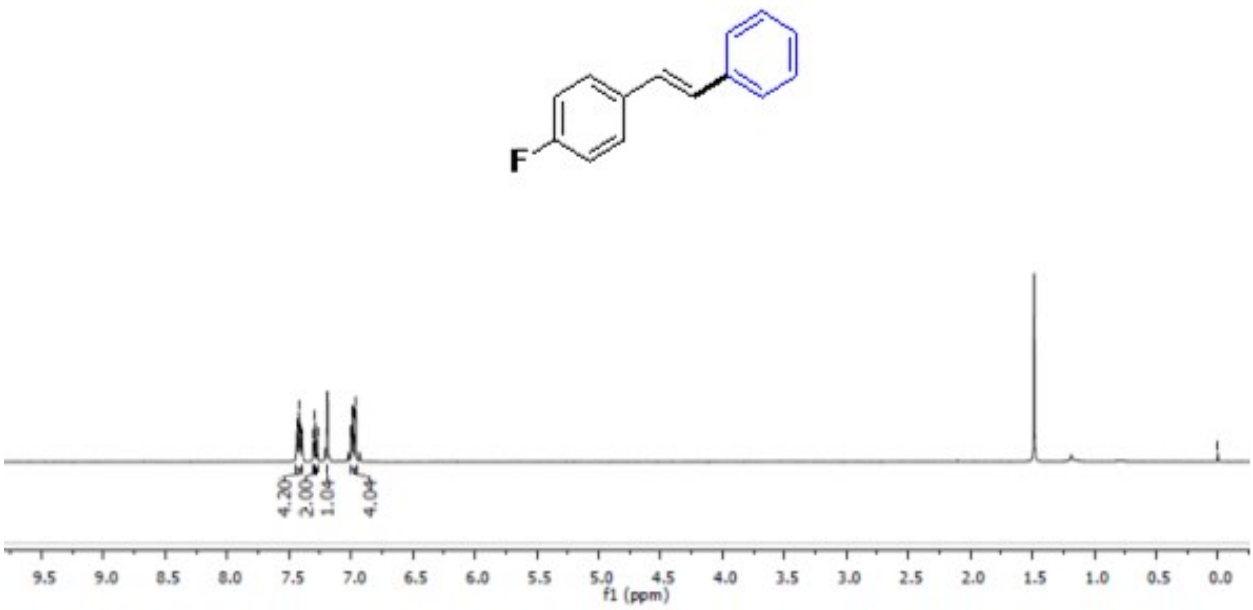
^{13}C NMR spectrum of compound **3b** in $CDCl_3$



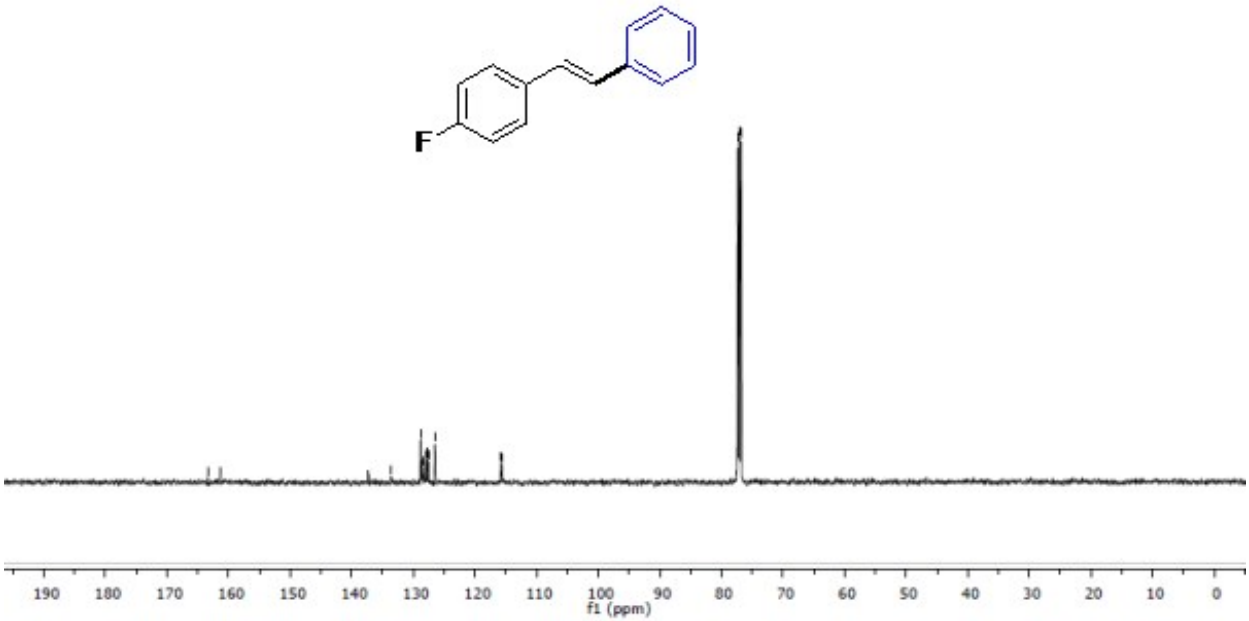
^{1}H NMR spectrum of compound **3c** in $CDCl_3$



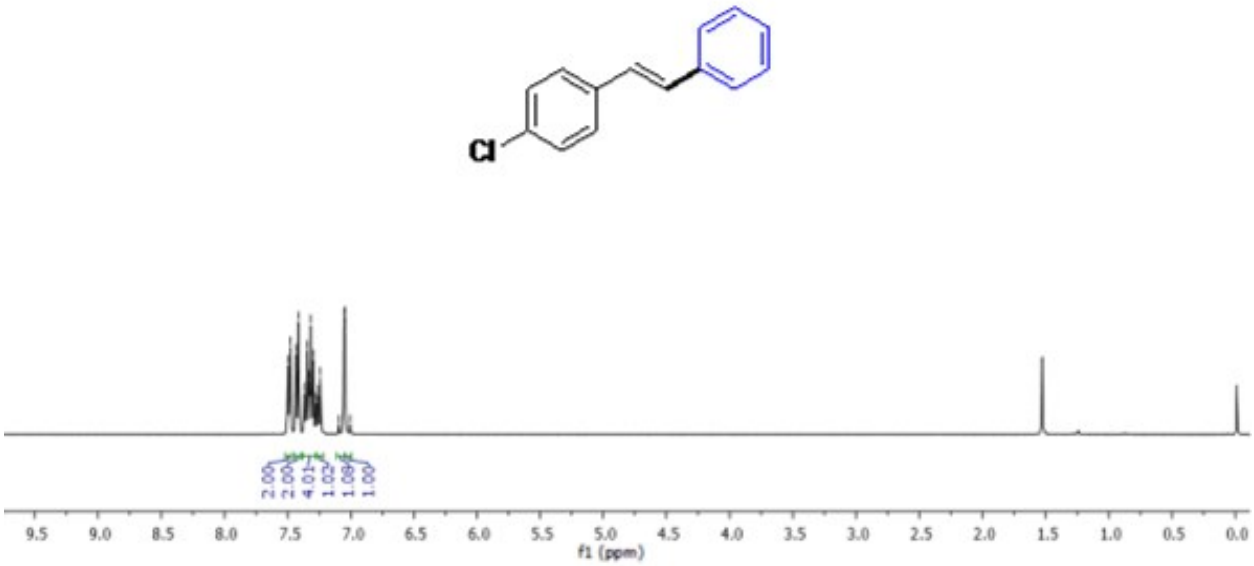
^{13}C NMR spectrum of compound **3c** in $CDCl_3$



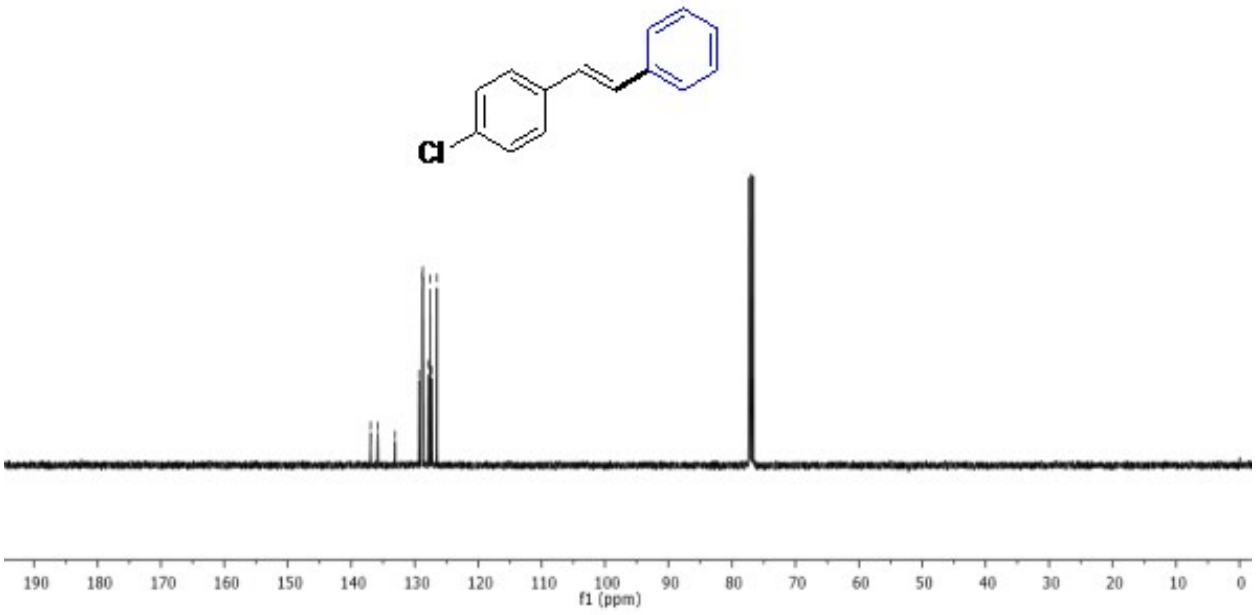
^{1}H NMR spectrum of compound **3d** in $CDCl_3$



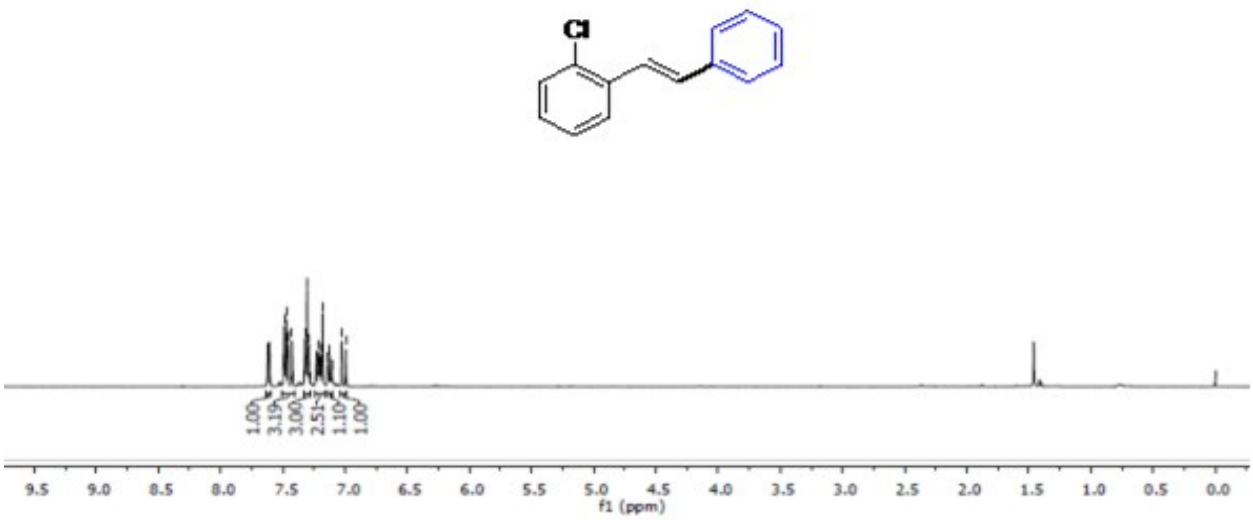
^{13}C NMR spectrum of compound **3d** in $CDCl_3$



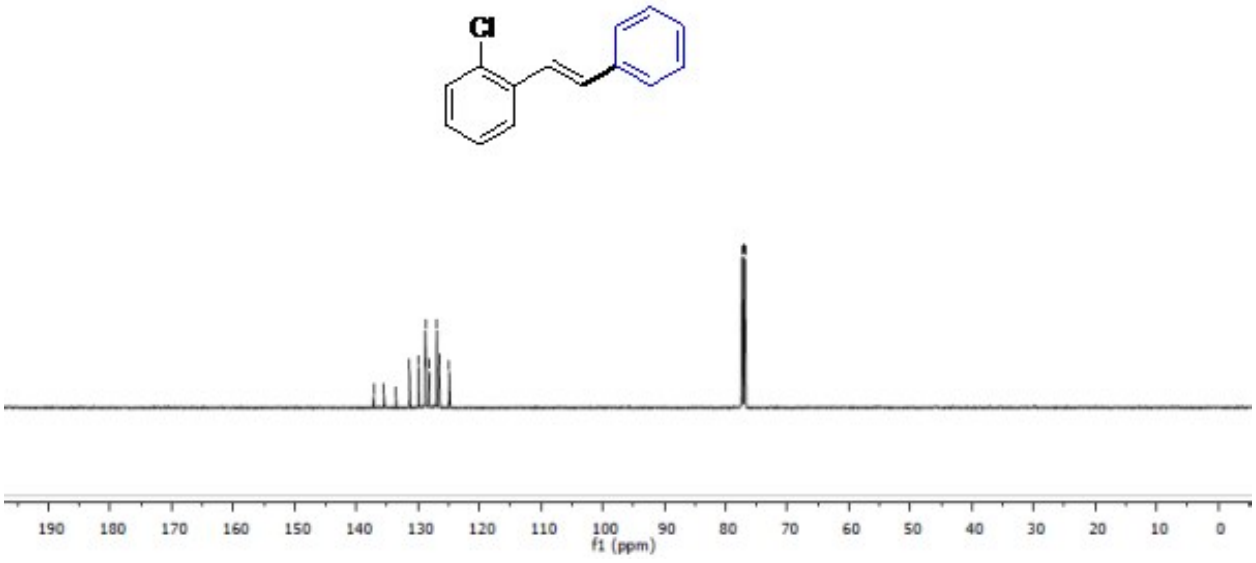
^{1}H NMR spectrum of compound **3e** in $CDCl_3$



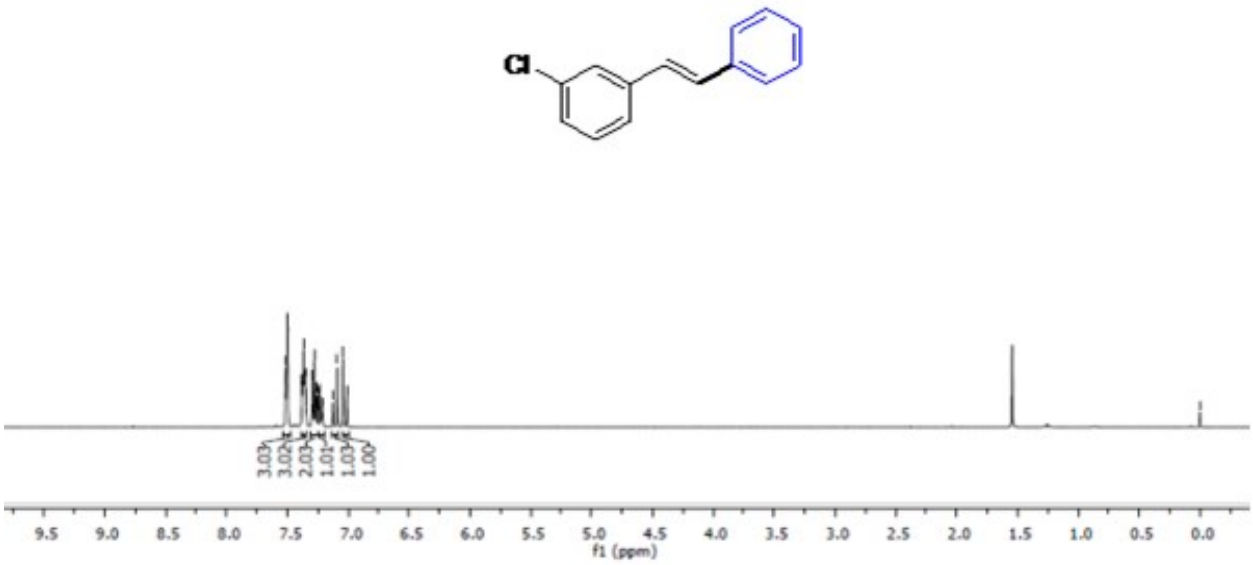
^{13}C NMR spectrum of compound **3e** in $CDCl_3$



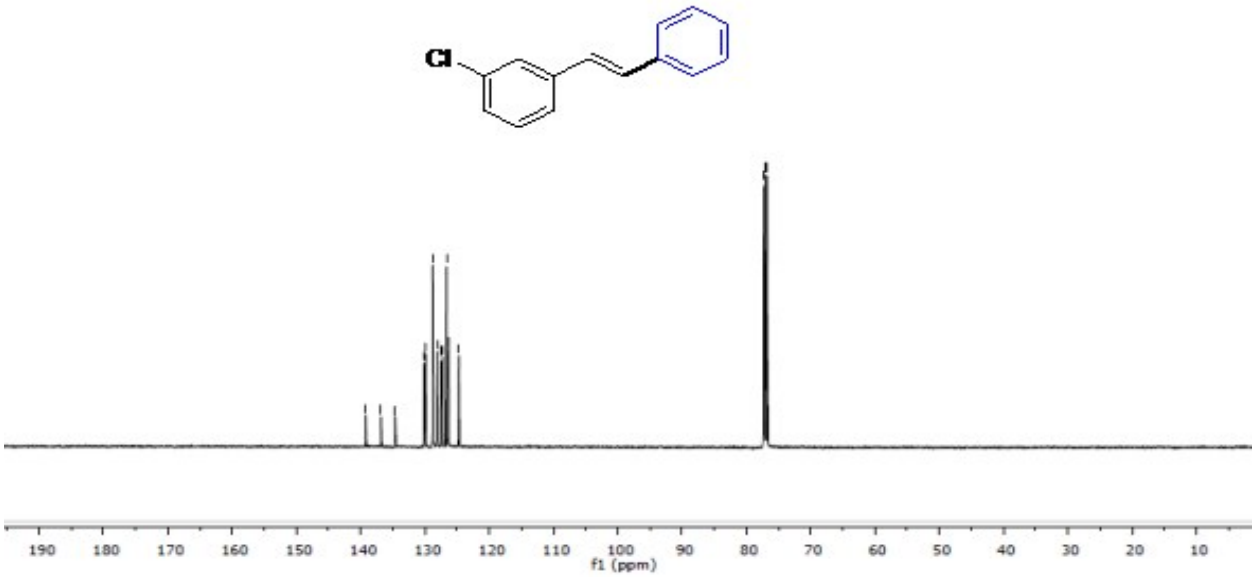
^{1}H NMR spectrum of compound **3f** in $CDCl_3$



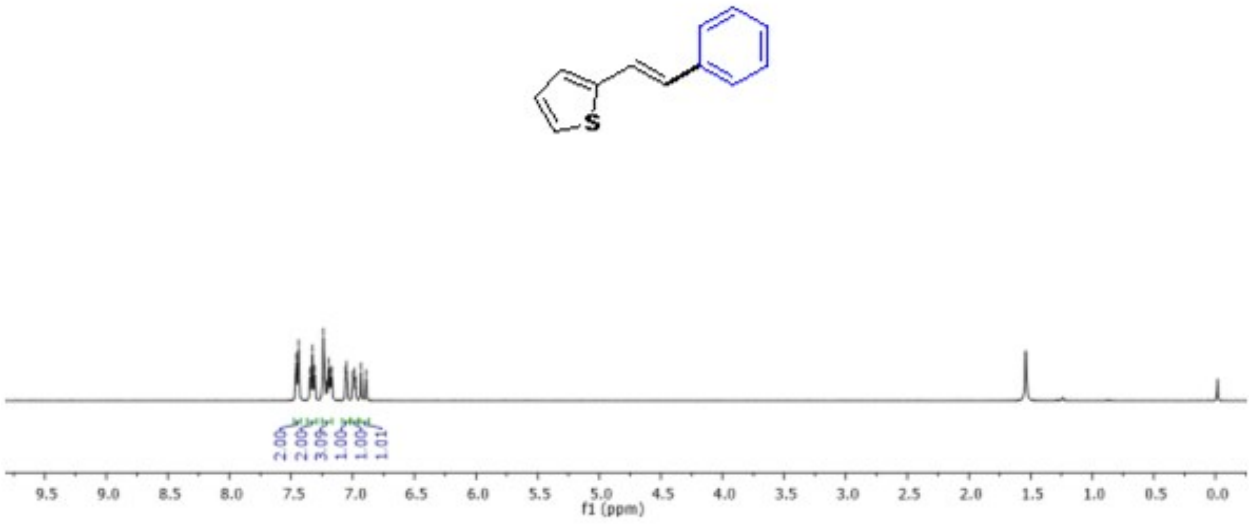
^{13}C NMR spectrum of compound **3f** in $CDCl_3$



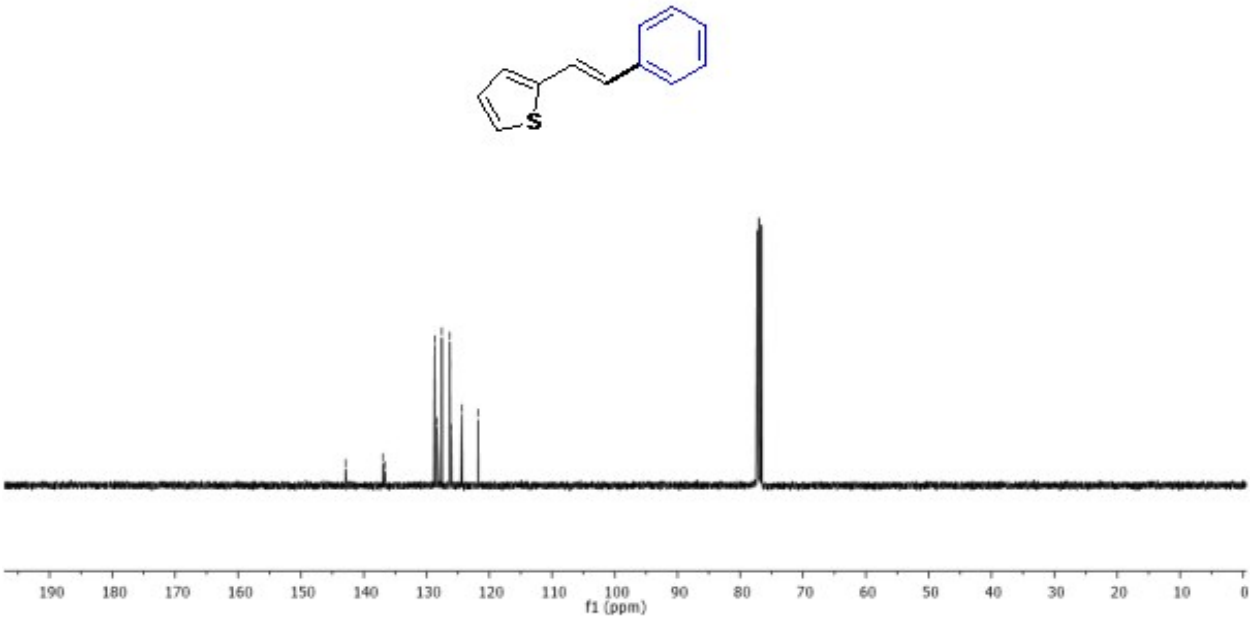
^{1}H NMR spectrum of compound **3g** in $CDCl_3$



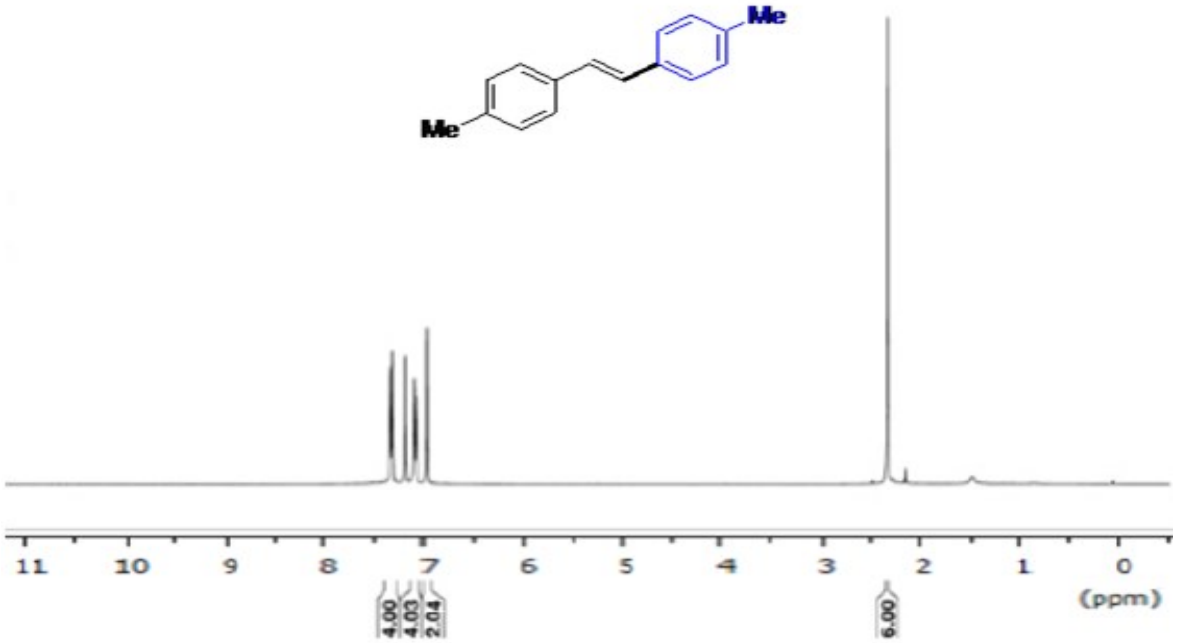
^{13}C NMR spectrum of compound **3g** in $CDCl_3$



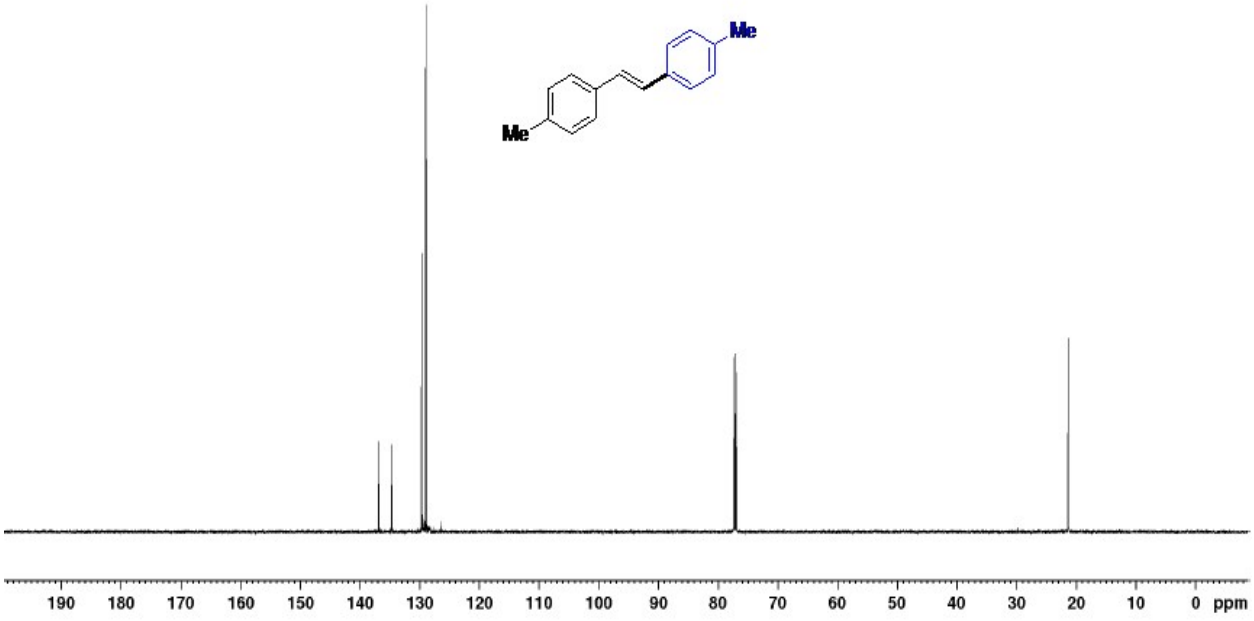
^{1}H NMR spectrum of compound **3h** in $CDCl_3$



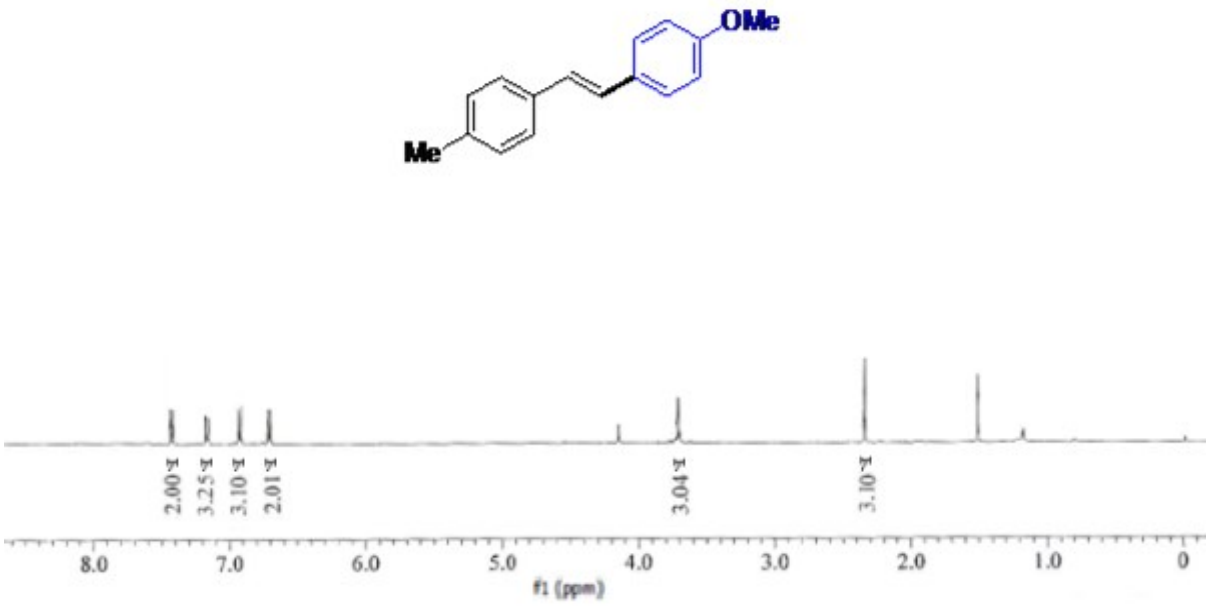
^{13}C NMR spectrum of compound **3h** in $CDCl_3$



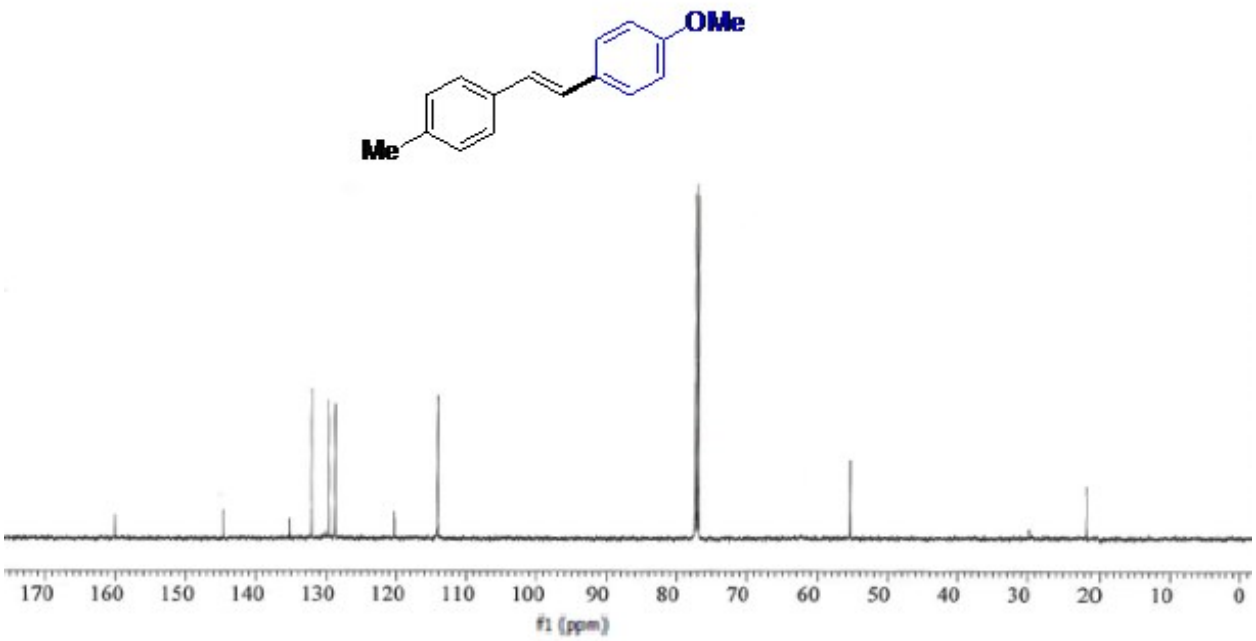
^{1}H NMR spectrum of compound **3i** in $CDCl_3$



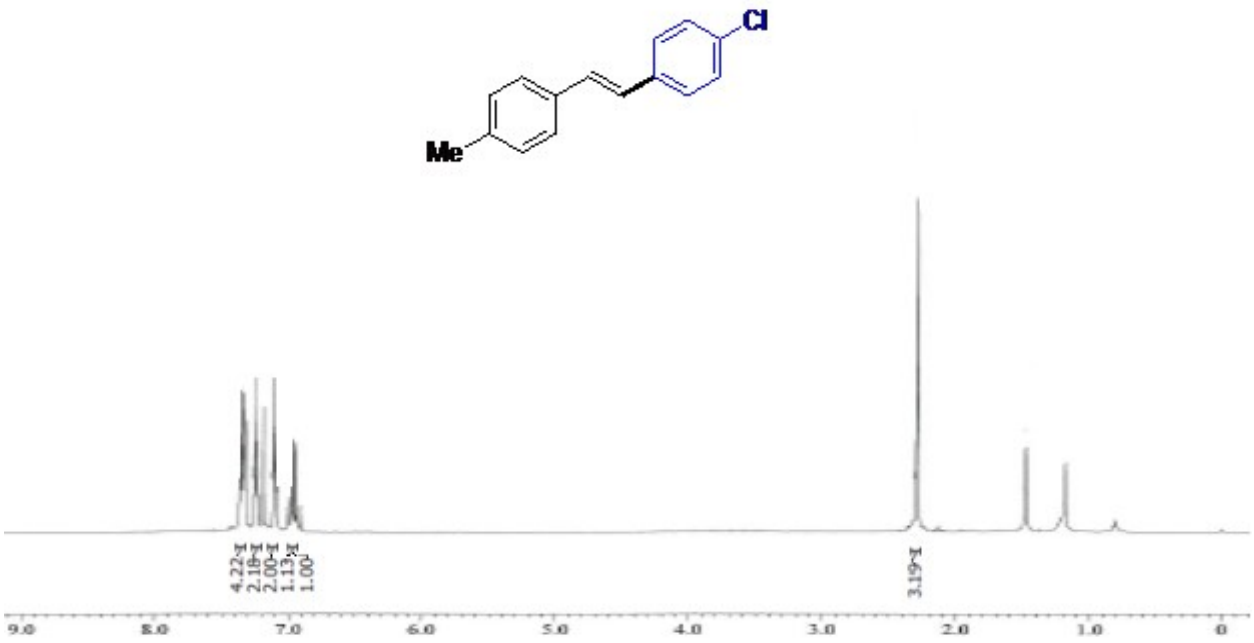
^{13}C NMR spectrum of compound **3i** in $CDCl_3$



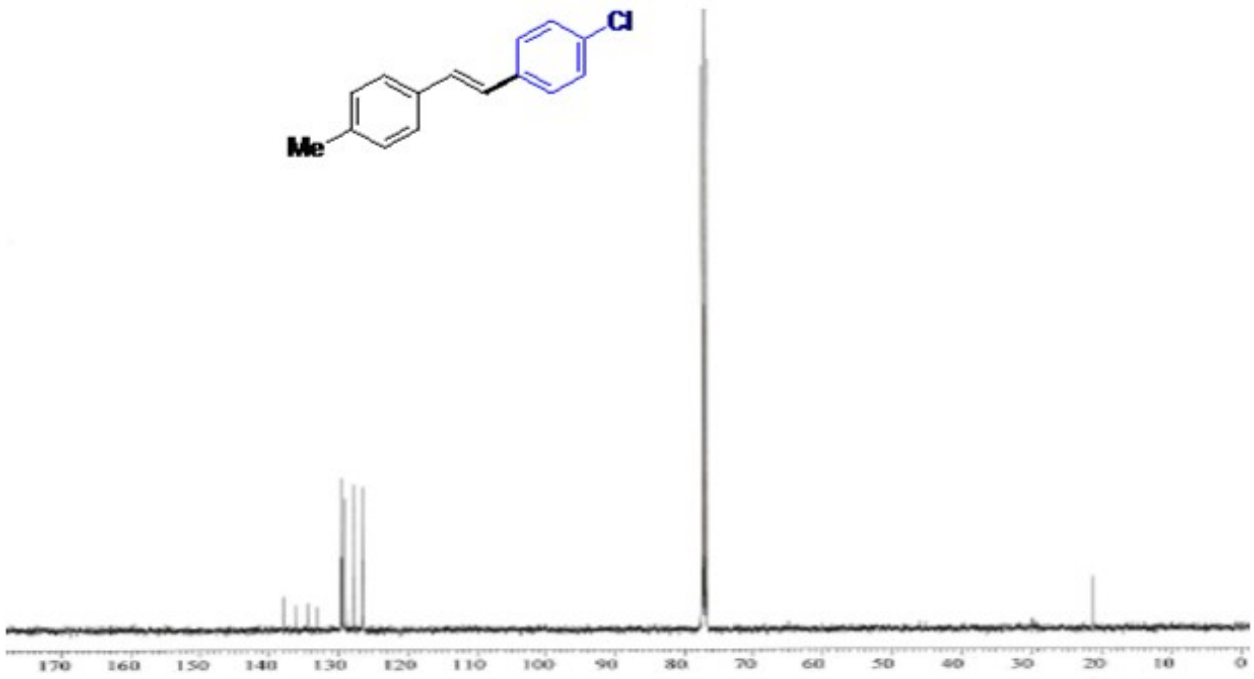
^{1}H NMR spectrum of compound **3j** in $CDCl_3$



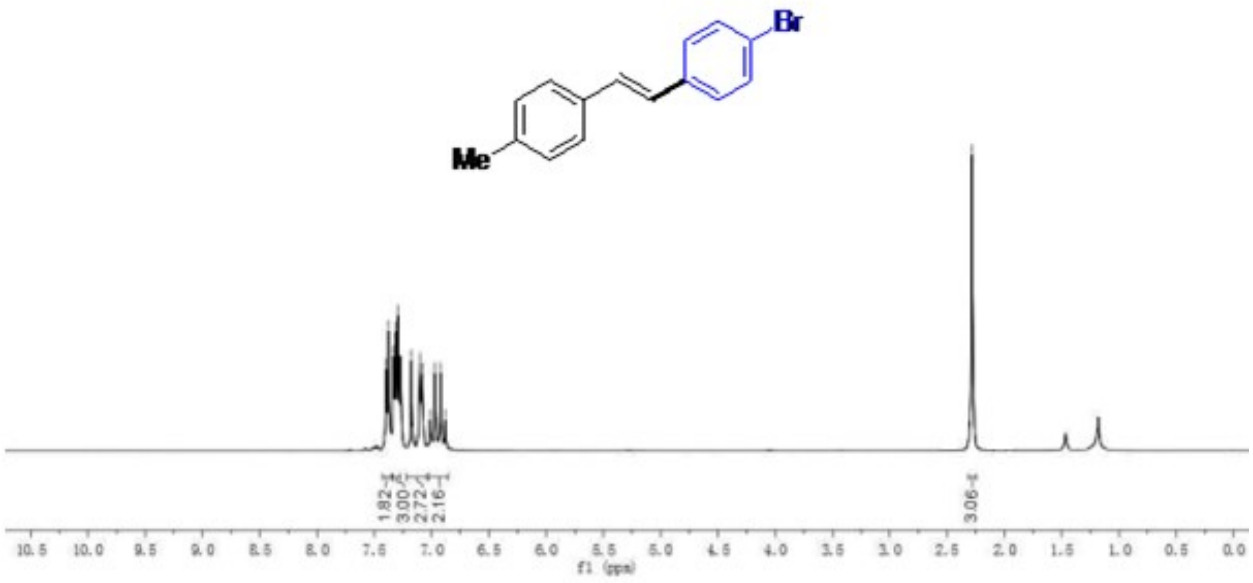
^{13}C NMR spectrum of compound **3j** in $CDCl_3$



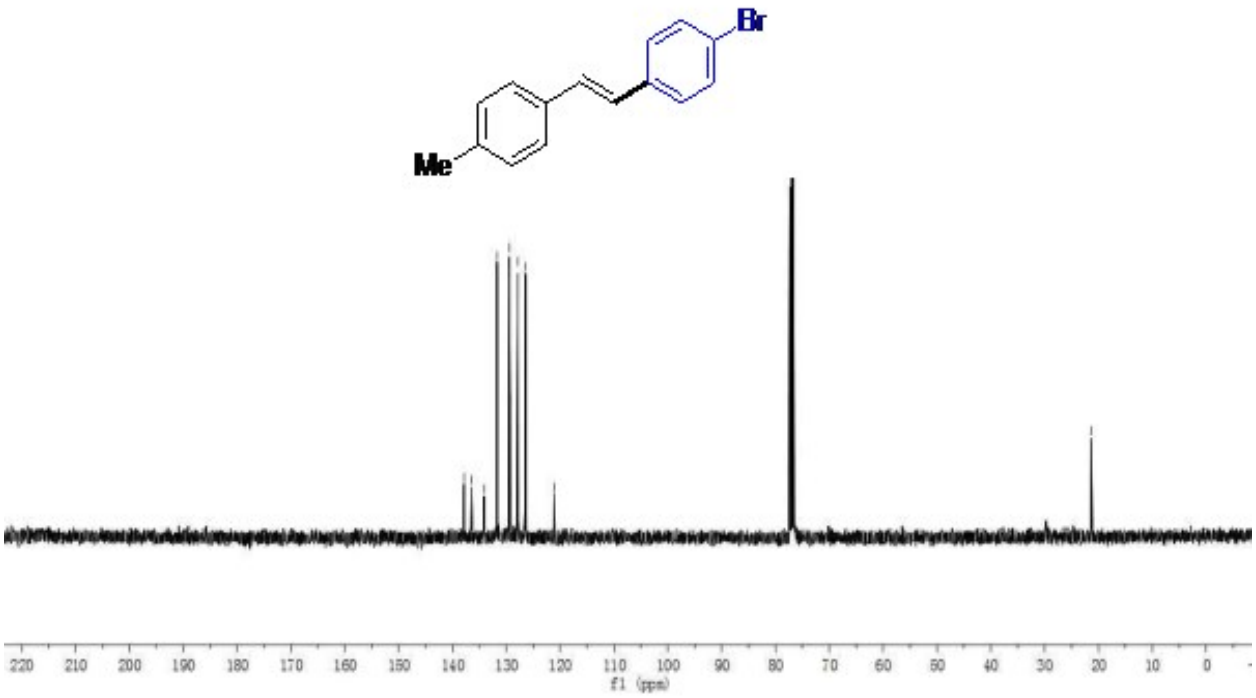
^{1}H NMR spectrum of compound **3k** in $CDCl_3$



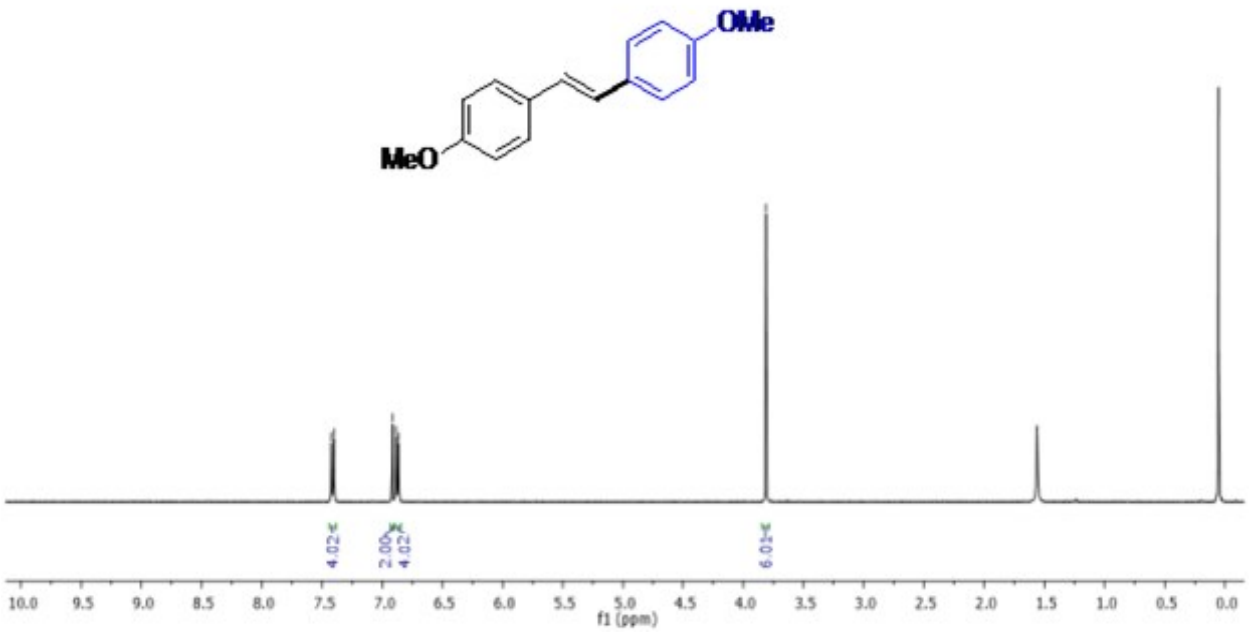
^{13}C NMR spectrum of compound **3k** in $CDCl_3$



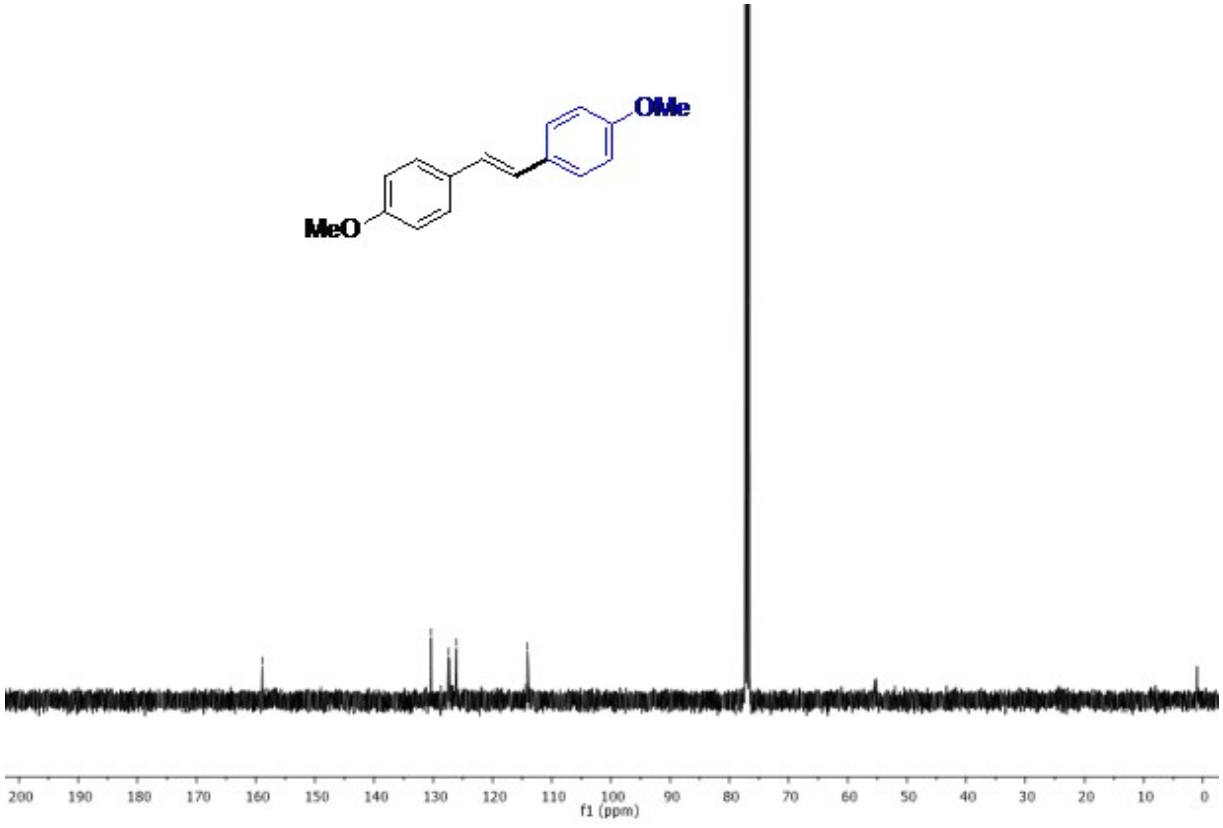
^{1}H NMR spectrum of compound **3l** in $CDCl_3$



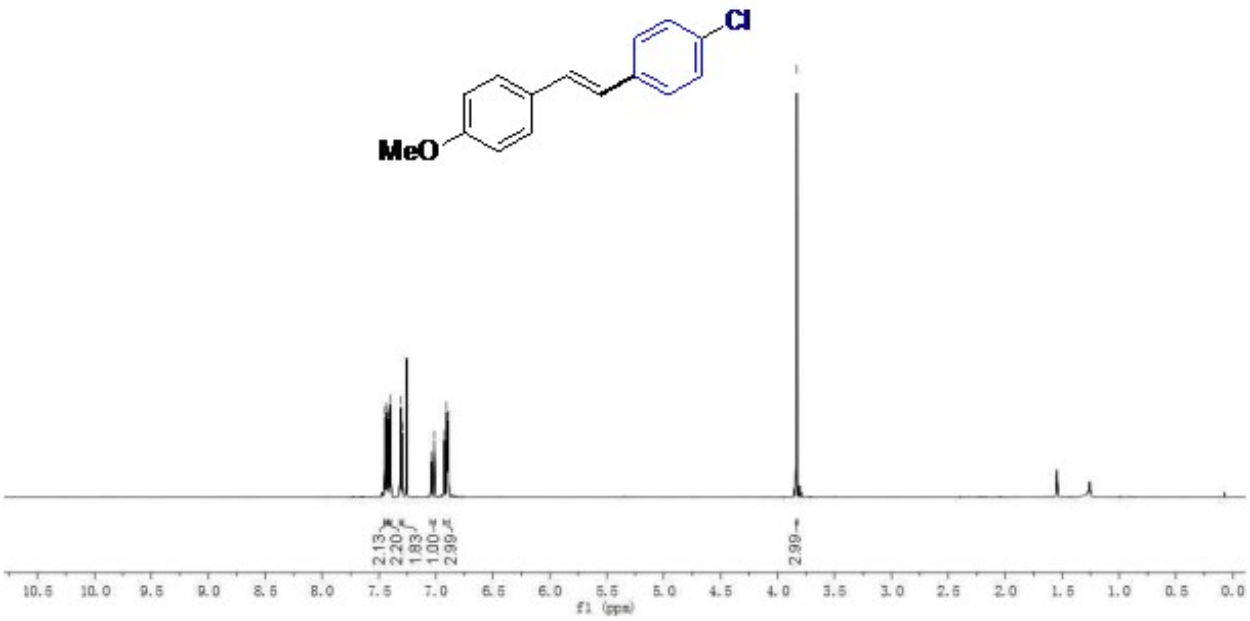
^{13}C NMR spectrum of compound **3l** in $CDCl_3$



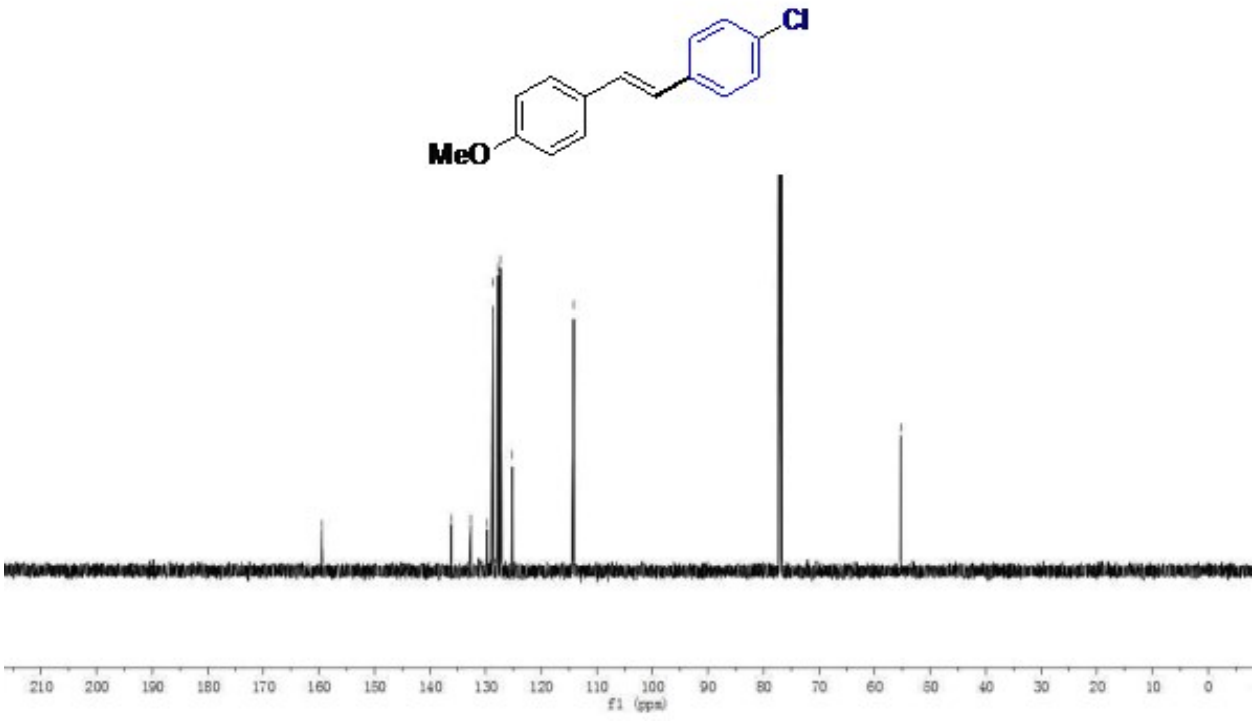
^{1}H NMR spectrum of compound **3m** in $CDCl_3$



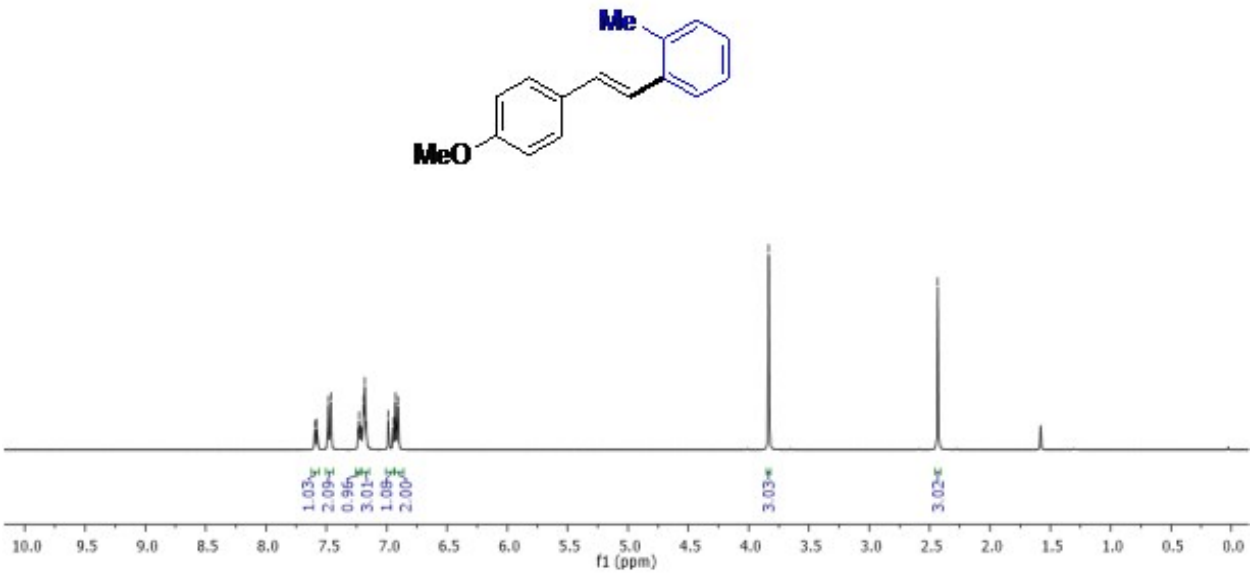
^{13}C NMR spectrum of compound **3m** in $CDCl_3$



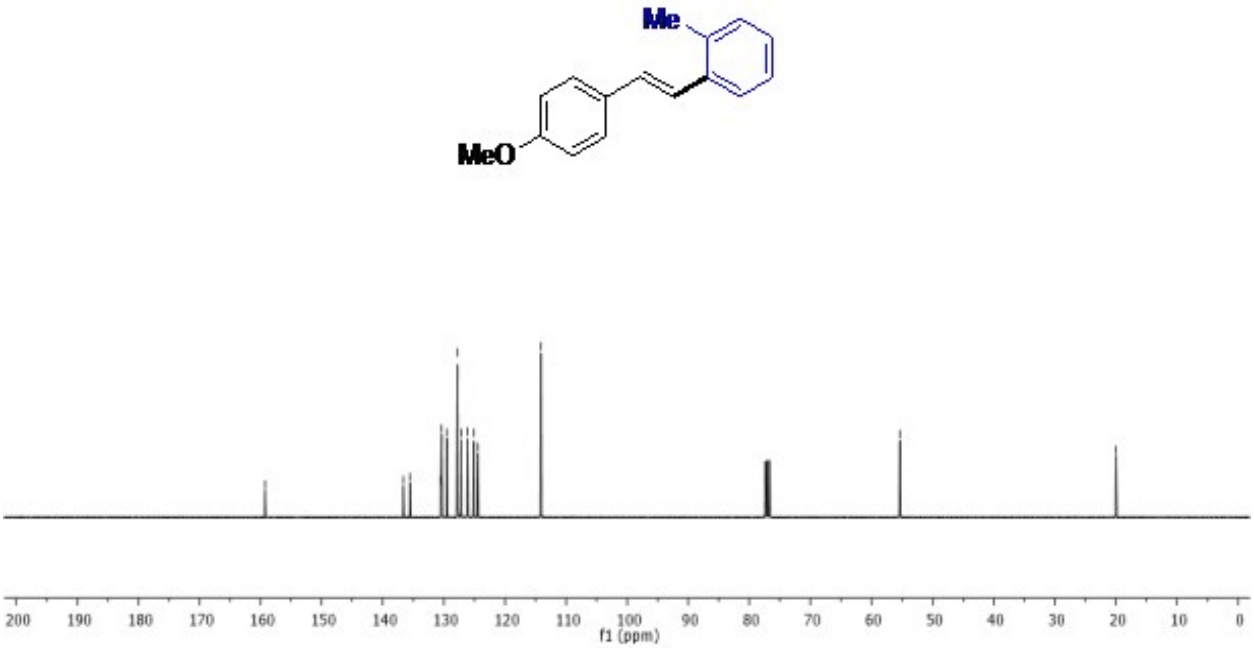
^{1}H NMR spectrum of compound **3n** in $CDCl_3$



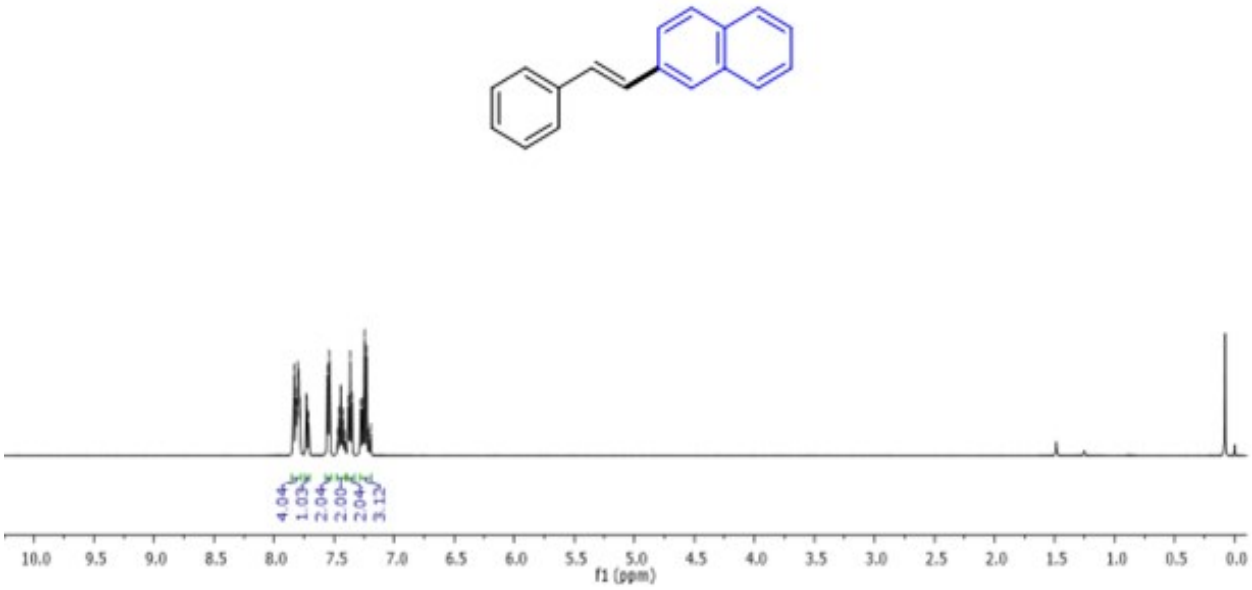
^{13}C NMR spectrum of compound **3n** in $CDCl_3$



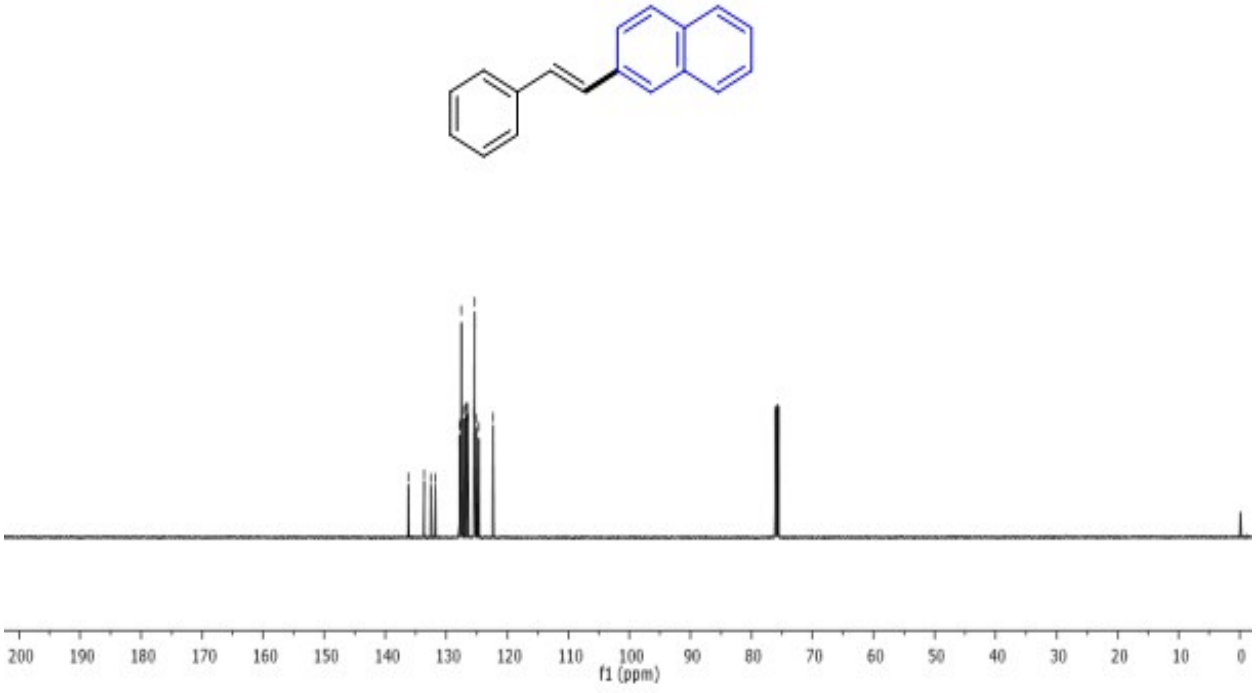
^{1}H NMR spectrum of compound **3o** in $CDCl_3$



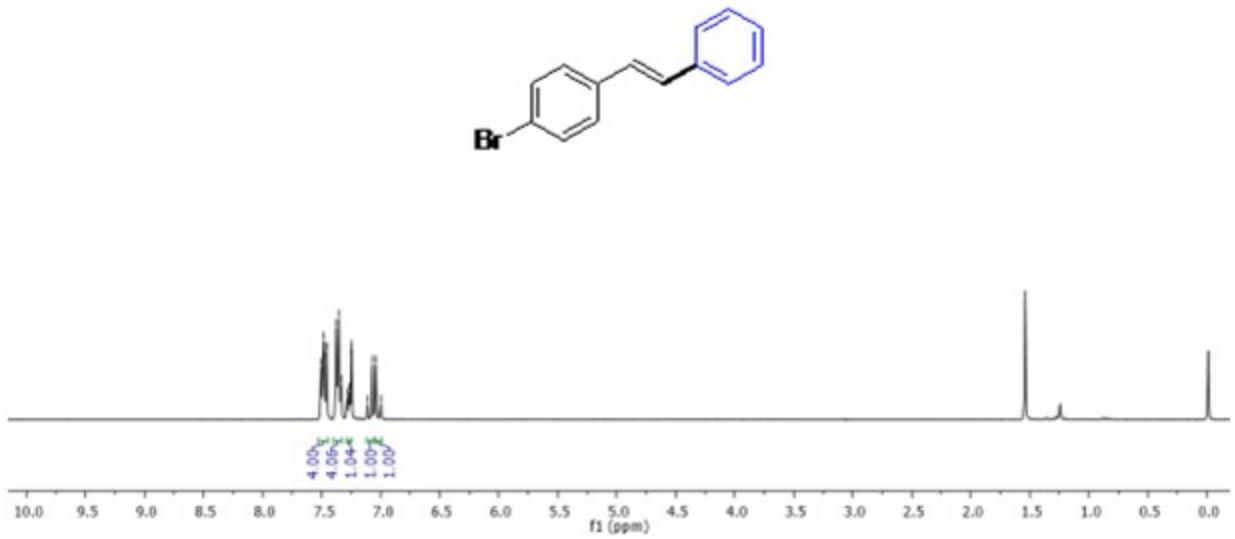
^{13}C NMR spectrum of compound **3o** in $CDCl_3$



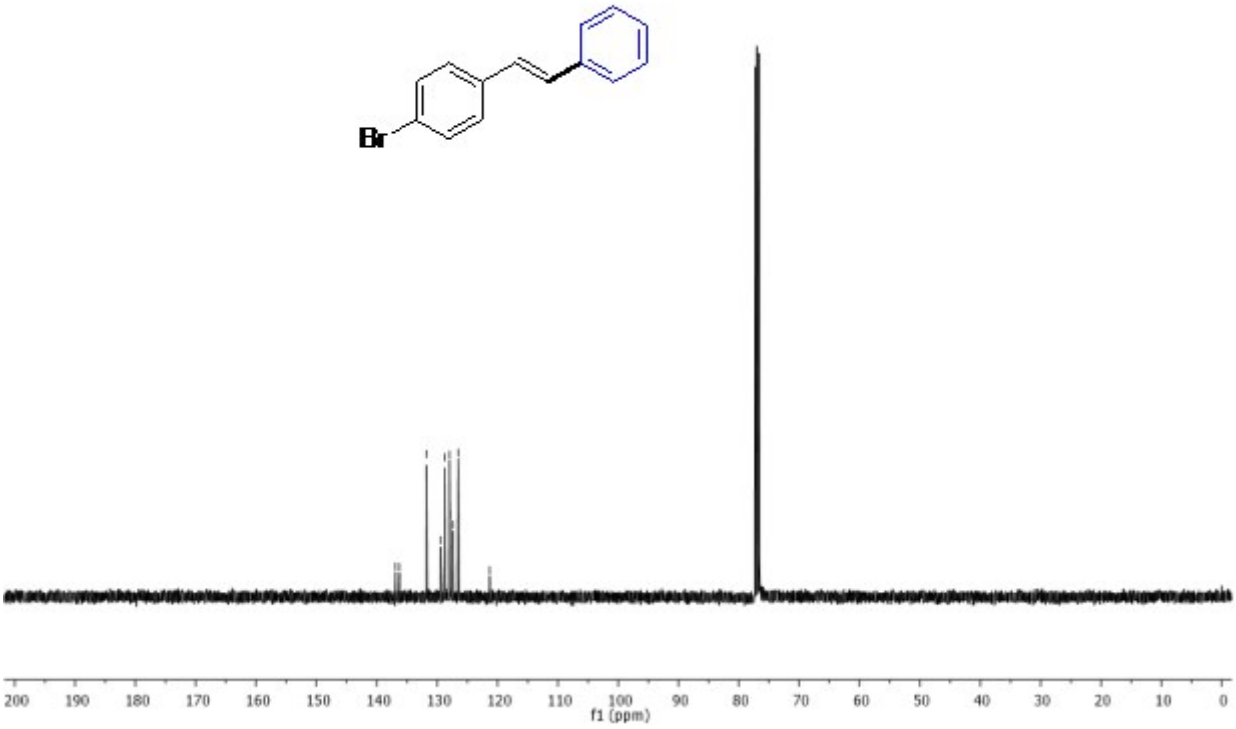
^{1}H NMR spectrum of compound **3p** in $CDCl_3$



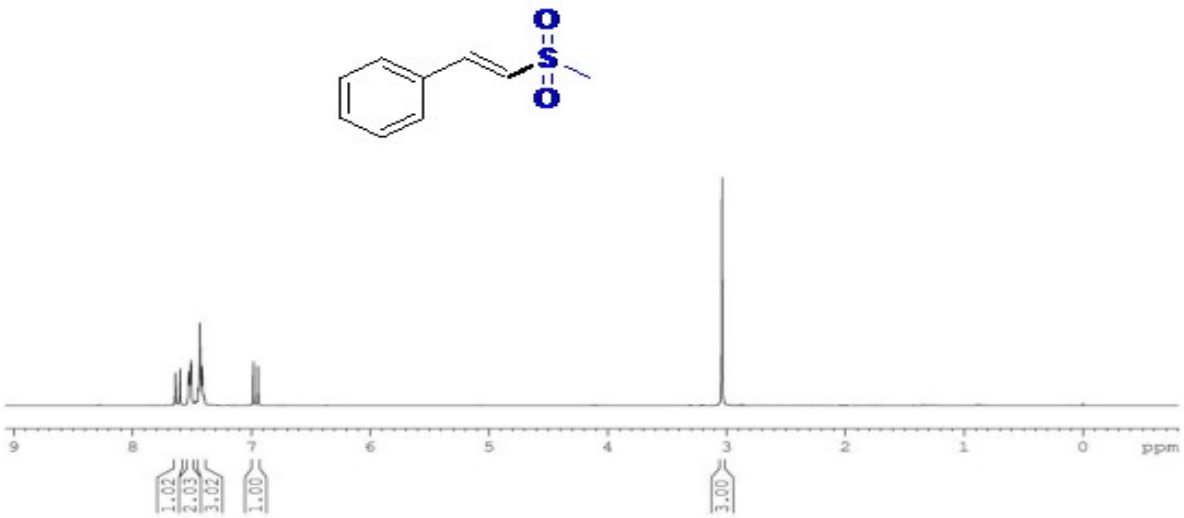
^{13}C NMR spectrum of compound **3p** in $CDCl_3$



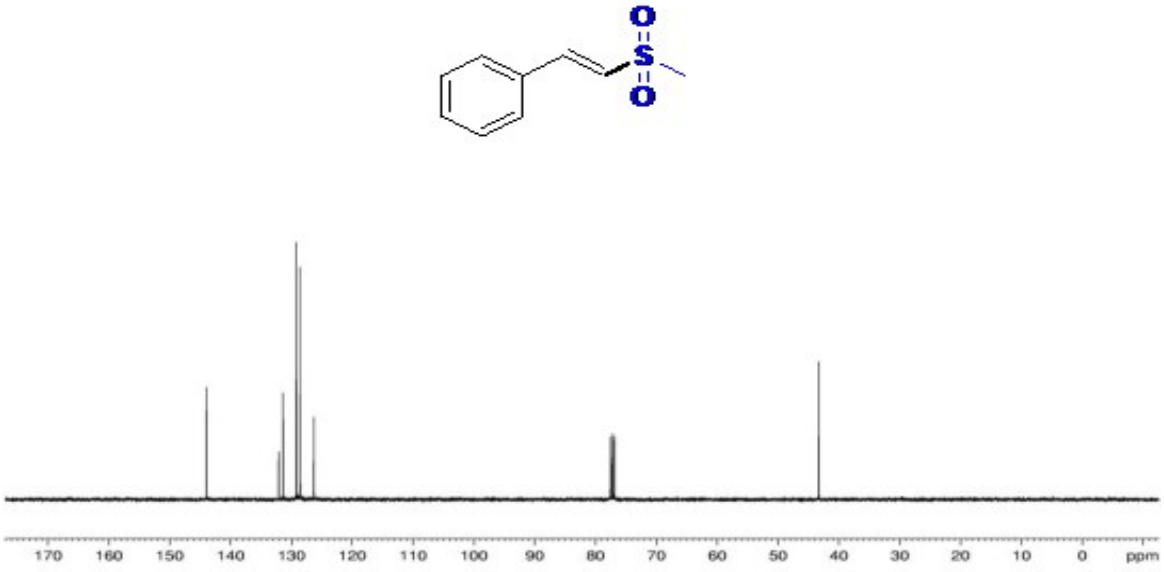
^{1}H NMR spectrum of compound **3q** in $CDCl_3$



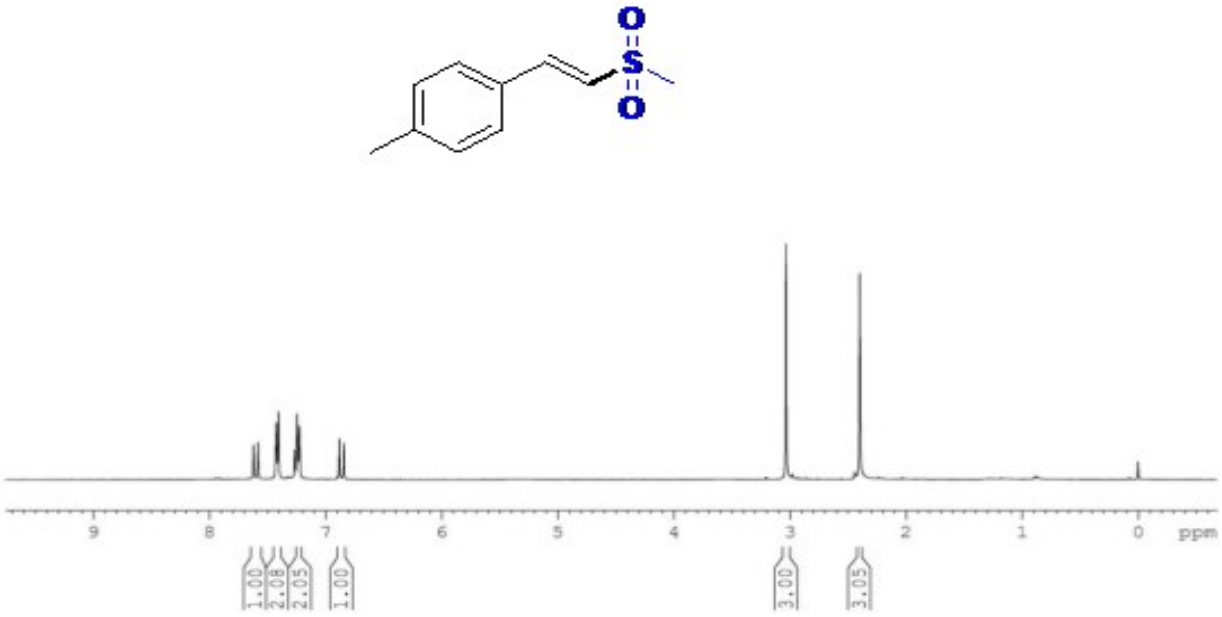
^{13}C NMR spectrum of compound **3q** in $CDCl_3$



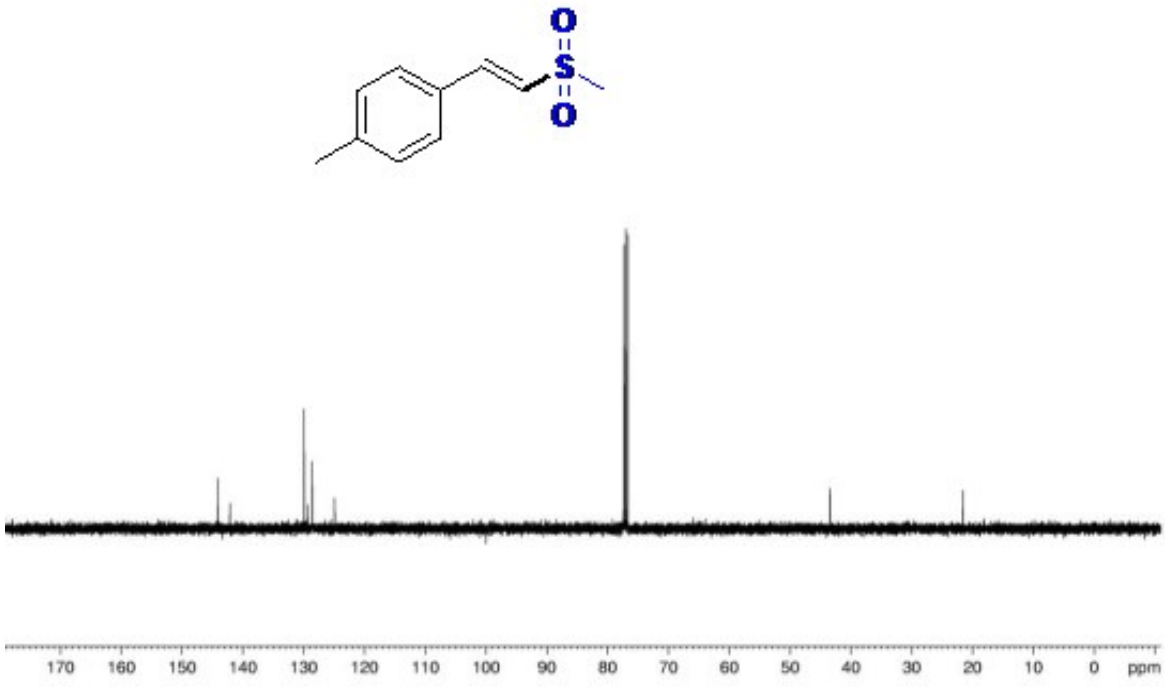
^{1}H NMR spectrum of compound **4a** in $CDCl_3$



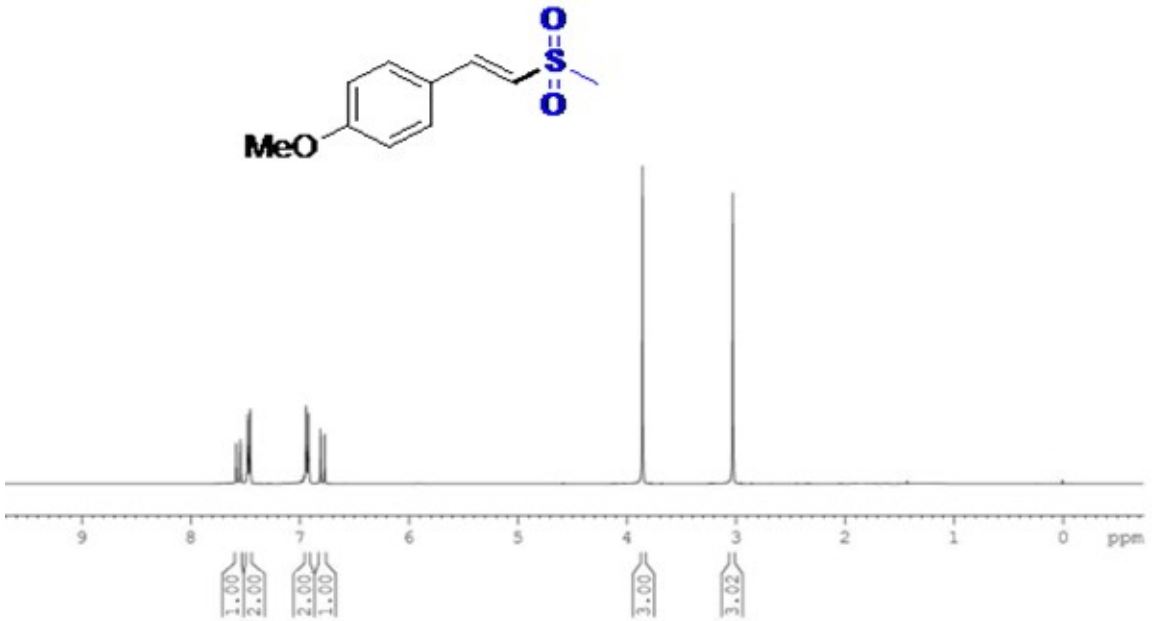
^{13}C NMR spectrum of compound **4a** in $CDCl_3$



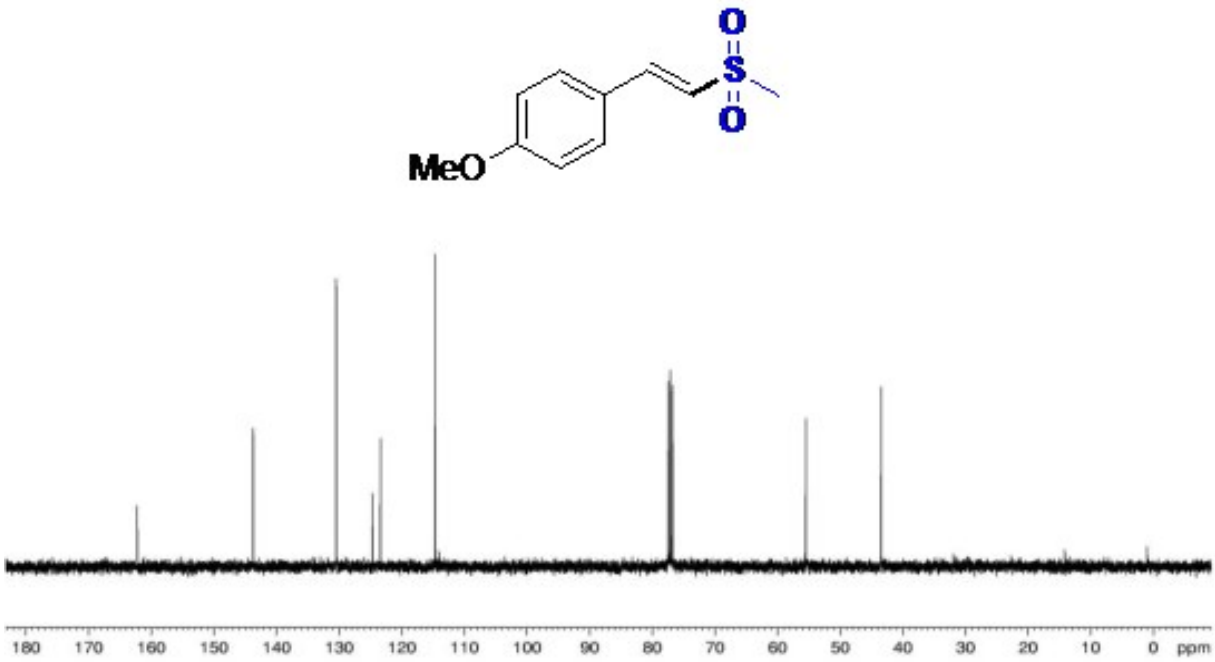
^{1}H NMR spectrum of compound **4b** in $CDCl_3$



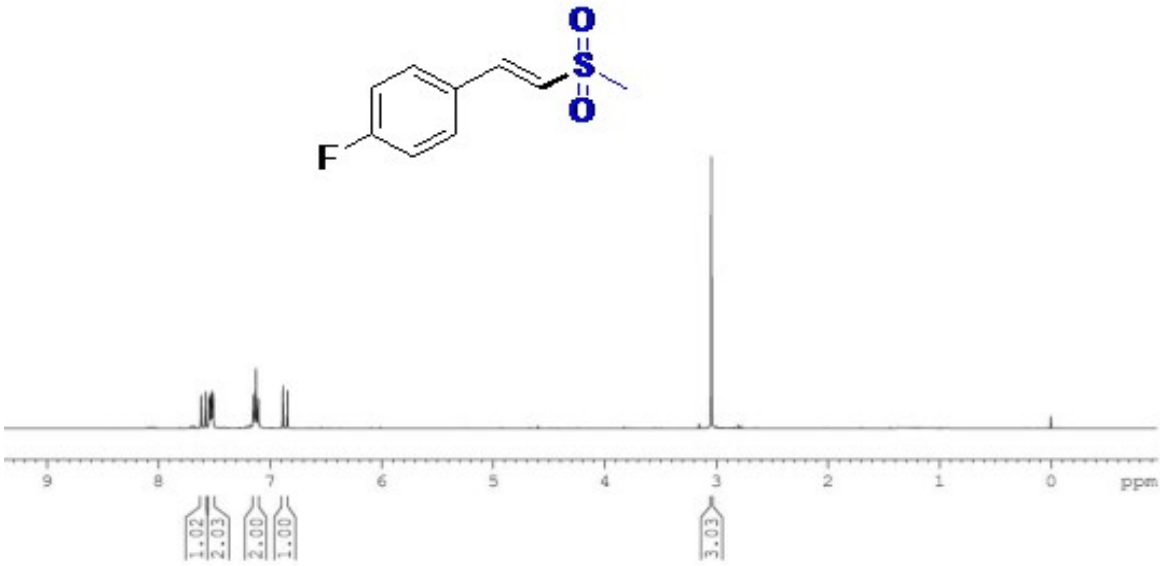
^{13}C NMR spectrum of compound **4b** in $CDCl_3$



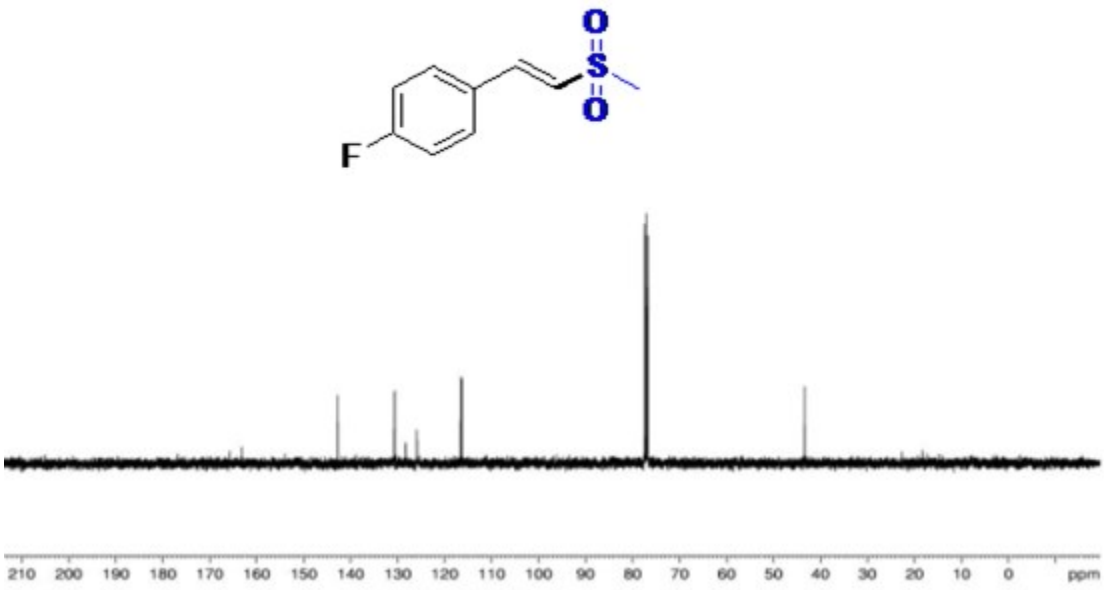
^{1}H NMR spectrum of compound **4c** in $CDCl_3$



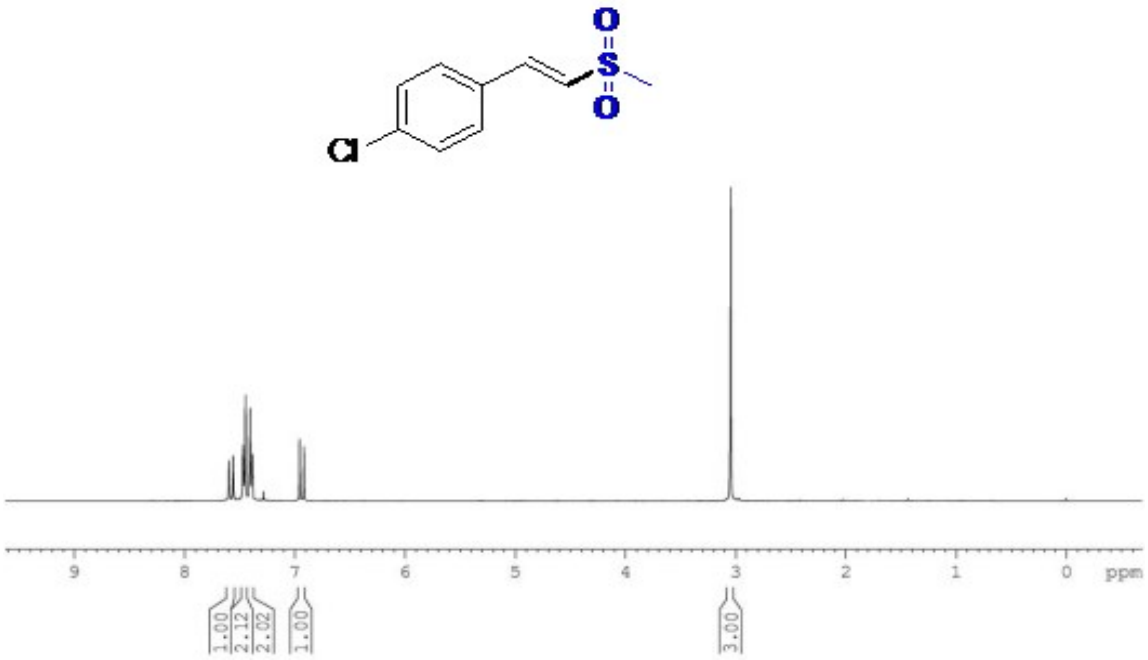
^{13}C NMR spectrum of compound **4c** in $CDCl_3$



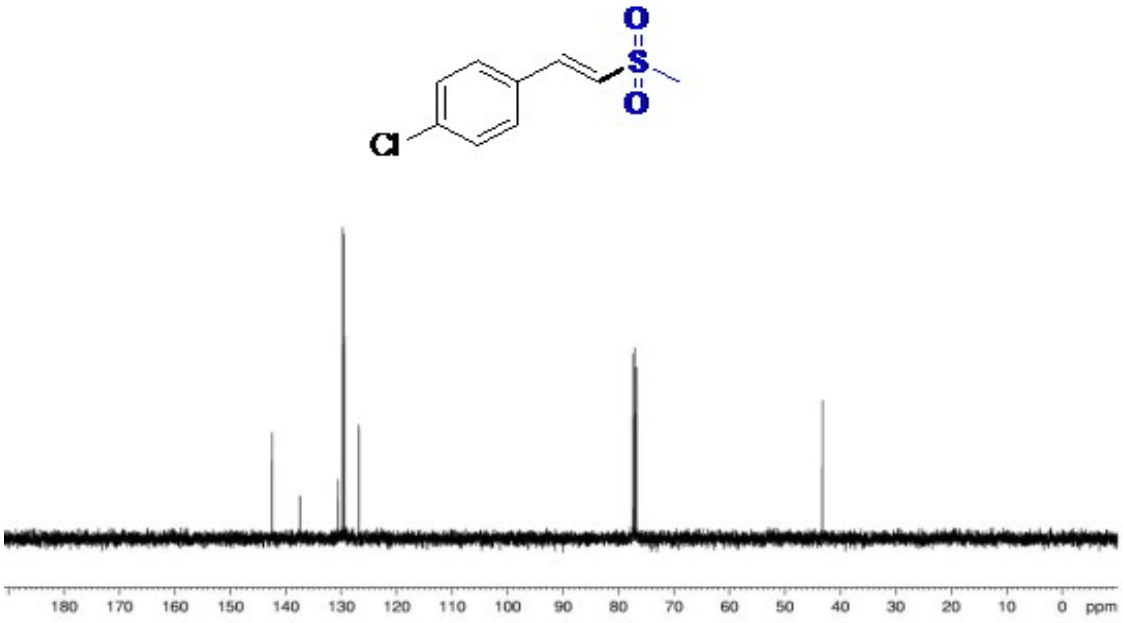
^{1}H NMR spectrum of compound **4d** in $CDCl_3$



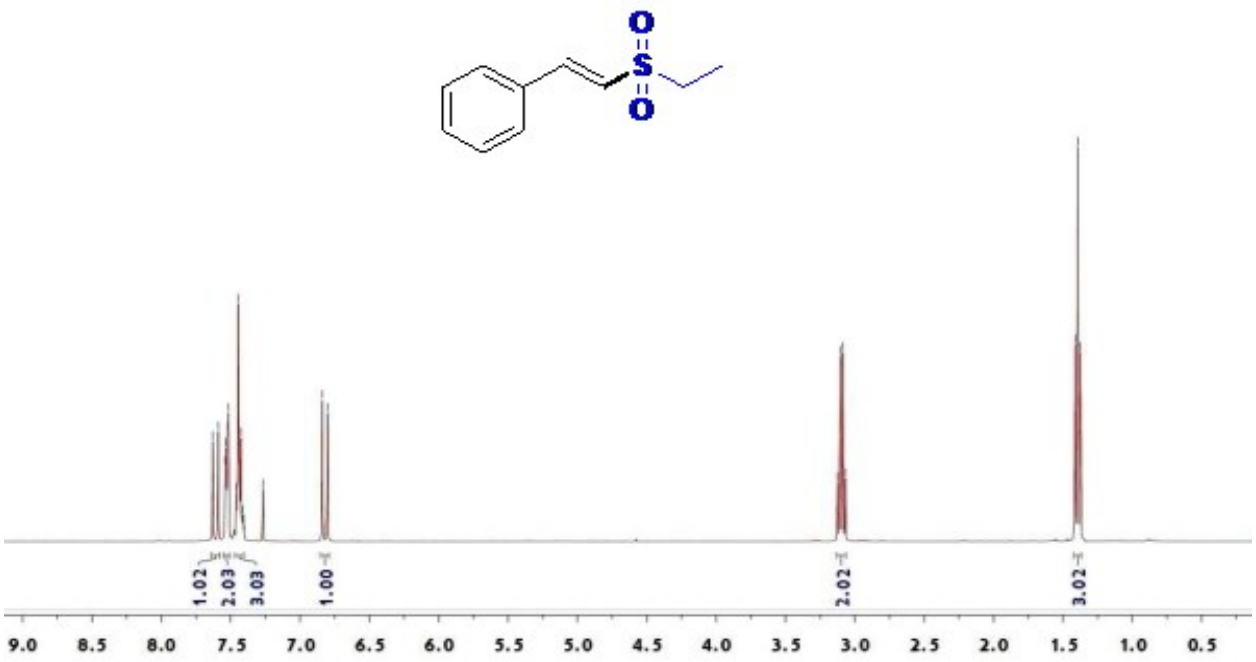
^{13}C NMR spectrum of compound **4d** in $CDCl_3$



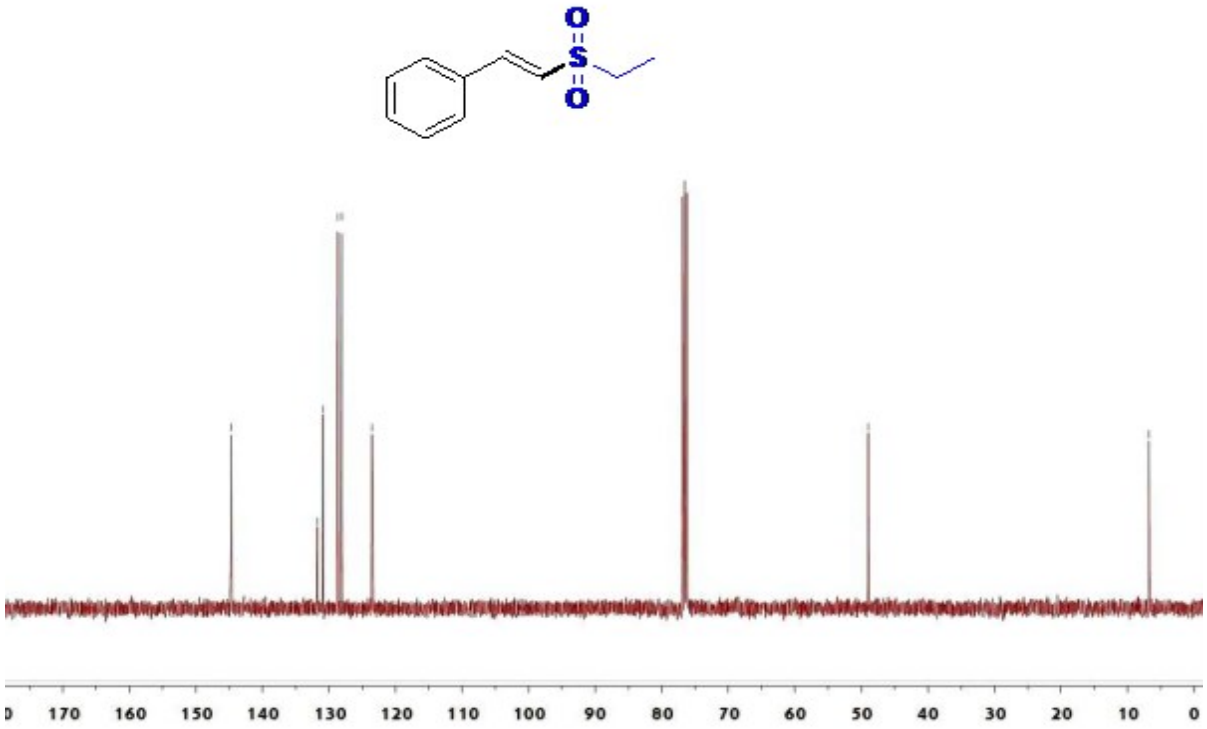
^{1}H NMR spectrum of compound **4e** in $CDCl_3$



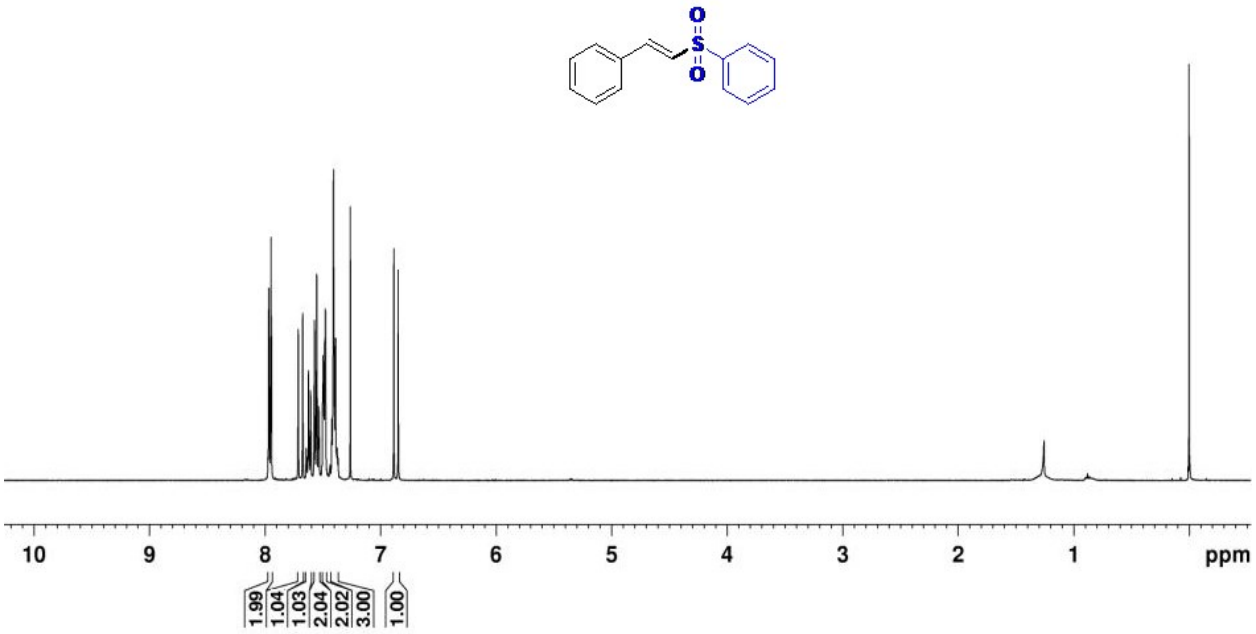
^{13}C NMR spectrum of compound **4e** in $CDCl_3$



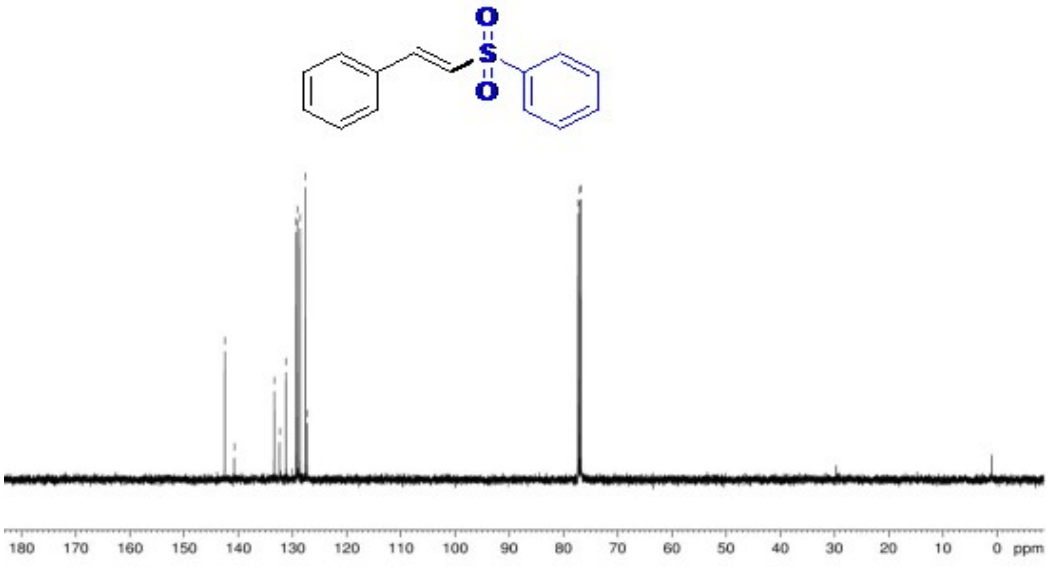
^{1}H NMR spectrum of compound **4f** in $CDCl_3$



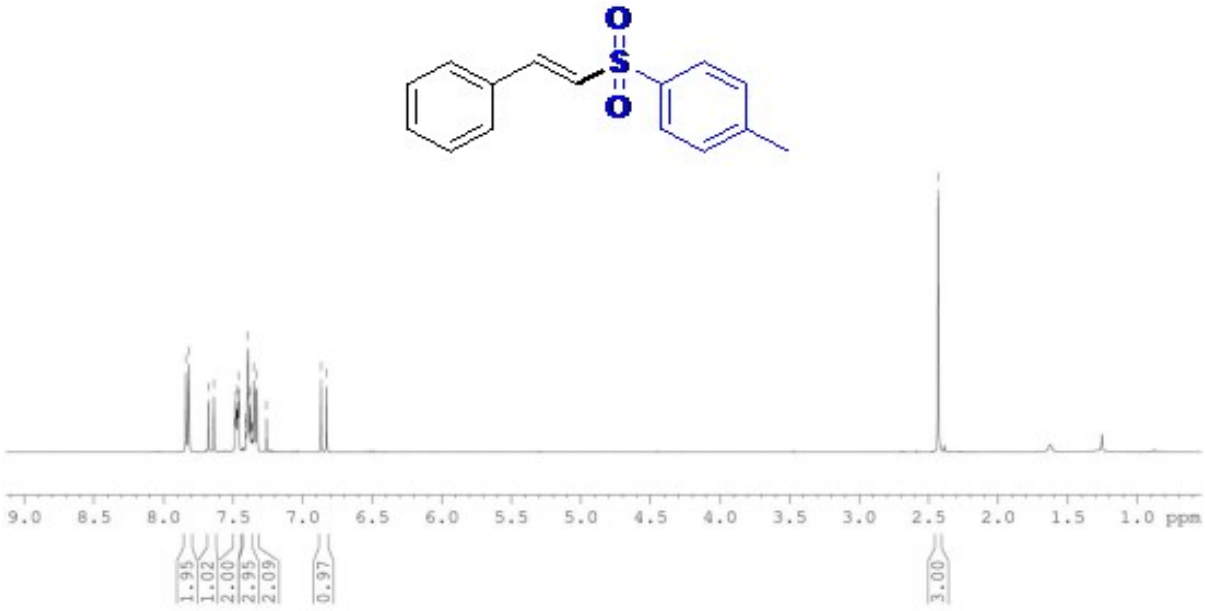
^{13}C NMR spectrum of compound **4f** in $CDCl_3$



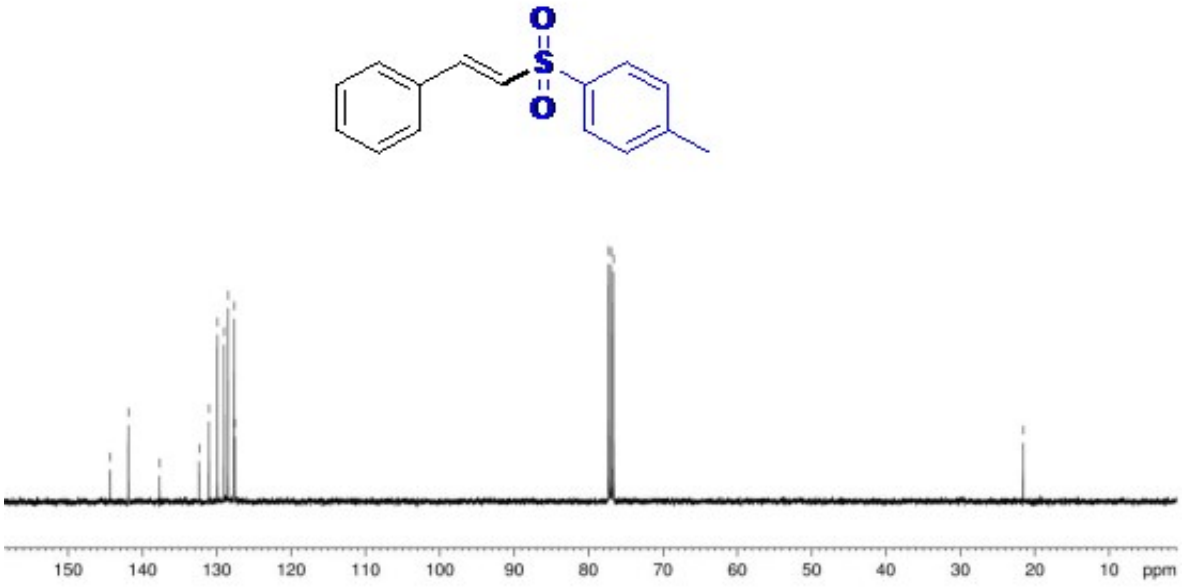
^{1}H NMR spectrum of compound **4g** in $CDCl_3$



^{13}C NMR spectrum of compound **4g** in $CDCl_3$



^{1}H NMR spectrum of compound **4h** in $CDCl_3$



^{13}C NMR spectrum of compound **4h** in $CDCl_3$