Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Magnetically separable nano-copper catalyzed unprecedented stereoselective synthesis of *E*-vinyl sulfones from tosylmethyl isocyanide and alkynes: TosMIC as a source of sulfonyl group

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1. General Techniques:

All reagents were purchased from Sigma Aldrich and Alfa Aesar and were used without further purification. All experiments were carried out under oxygen atmosphere. All the solvents used for the reaction were distilled before use. The product purification by column chromatography was accomplished using silica gel 100-200 mesh. Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. Infrared spectra were recorded using a FT-IR spectrophotometer and values reported in cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded with 300, 400 and 500 MHz NMR instruments with tertramethylsilane (TMS) as an internal standard. High-resolution mass spectra (ESI-HRMS) were recorded on ESI-QTOP mass spectrometer. Chemical shifts (δ =) are reported in ppm using TMS as an internal standard, and spin -spin coupling constants (J) are given in Hz. Multiplicities in the ^{1}H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, bs = broad singlet; coupling constants are reported in Hz. Low (MS) and high (HRMS) resolution mass spectra were recorded on a Waters 2695 and Thermo Scientific Exactive spectrometer respectively and mass/charge (m/z) ratios are reported as values in atomic mass units. All the melting points are uncorrected. X-ray powder diffraction (XRD) data were collected on a Simens/D-5000

diffractometer using Cu Kα radiation. XPS spectra were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. The pressure in the spectrometer was about 10^{-9} Torr. The particle size and external morphology of the samples were observed on a JEOL JEM-2100 high resolution transmission electron microscope (HRTEM). Auger electron spectroscopic (AES) analysis is conducted, at a base pressure of 10^{-10} Torr, within the K.E. range of 110-700 eV (beam voltage of 3 kV, eV/step 1 eV, time/step 50 ms). X-ray absorption spectra were recorded using a Rigaku spectrometer with a rotating anode X-ray generator (Ru-200B, Rigaku, Japan).

2. Synthesis of copper nanoparticles on Fe_3O_4:

The stable copper nanoparticles on Fe_3O_4, $Cu(0)/Fe_3O_4$ were synthesized from copper-Iron hydrotalcite successively by coprecipitaion and Hydrothermal methods followed reduction by with Hydrogen gas. The detailed procedure is provided in our experimental procedure.

Copper- Iron Hydrotalcite Cu- Fe HT (Cu-Fe HT):

In a 250 mL four necked round bottomed flask with an overhead stirrer a mixture of copper nitrate trihydrate (0.0375 mole, 9.03 gm) and $FeNO_3.9H_2O$ (0.15 moles, 6.06 gm) metal nitrates. NaOH (1.5 moles, 6.0 gm) and Na_2CO_3 (0.5 moles, 5.5 gm) were added from their respective additional burettes into the flask under stirring condition and precipated at pH 8 with continious stirring condition. After complete addition of metal nitrates, the greenish brown coloured precipitate was obtained which was aged at 333 K for 2h followed by filtration, washing with copious amount of distilled water to make the solid catalyst free from base and then dried in an oven at 383 K for 12h. The dried catalyst is then crushed into fine powder to obtain copper iron hydrotalcite Cu Fe HT.

Synthesis of calcined copper iron hydrotalcite (CuO/ Fe_3O_4)

5.0 gm of Cu Fe HT catalyst was taken in a tubular furnace and calcined in a static of air at 200 ^oC for a period of 5h. Calcined copper iron hydrotalcite CuO/Fe_3O_4 is obtained as a grey powder.

Synthesis of copper nanoparticles $Cu(0)/ Fe_3O_4$:

2.0 gm of calcined CuO/Fe_3O_4 was placed in the sample holder of the closed furnace. The furnace was facilitated with gas inlet and outlet. The inlet was connected to hydrogen gas with the flow rate 1 mL/ min. The furnace was slowly heated to 250 °C and CuO/Fe_3O_4 was kept at this temperature for 2 h. CuO/Fe_3O_4 which was in grey colour was reduced to $Cu(0)/Fe_3O_4$ (black powder). The furnace was cooled to room temperature under the N_2 flow (for 6-7h).

Iron ratio (Cu:Fe) in the synthesized catalysts was determined by Inductively Coupled Plasma-Atomic Optical Emission Spectroscopy (ICP-OES) and it is found to be 3:1 and showed 8 wt % of copper in $Cu(0)/Fe_3O_4$.

$Cu/\alpha\text{-}Al_2O_3$, Cu/La_2O_3, Cu/Y_2O_3, Cu/CeO_2, Cu/ZrO_2, Cu/TiO_2, Cu/Nb_2O_5, Cu/SnO_2 with same 8wt% of copper (ICP-OES) was reduced in same procedure as $Cu(0)/Fe_3O_4$. Copper nanoparticles on Fe_3O_4 $Cu(0)/Fe_3O_4$ was characterized and confirmed by various XRD, XPS, OES, and BET analytical methods.

3. **Characterizations of $Cu(0)/Fe_3O_4$:**

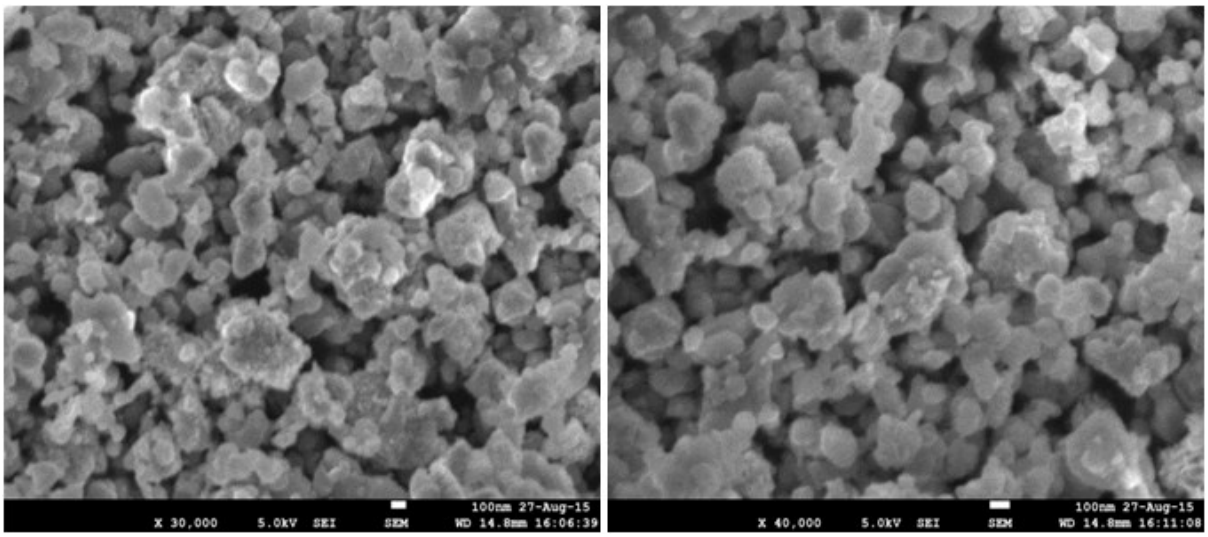


Figure S1: FE-SEM images of $Cu(0)/Fe_3O_4$

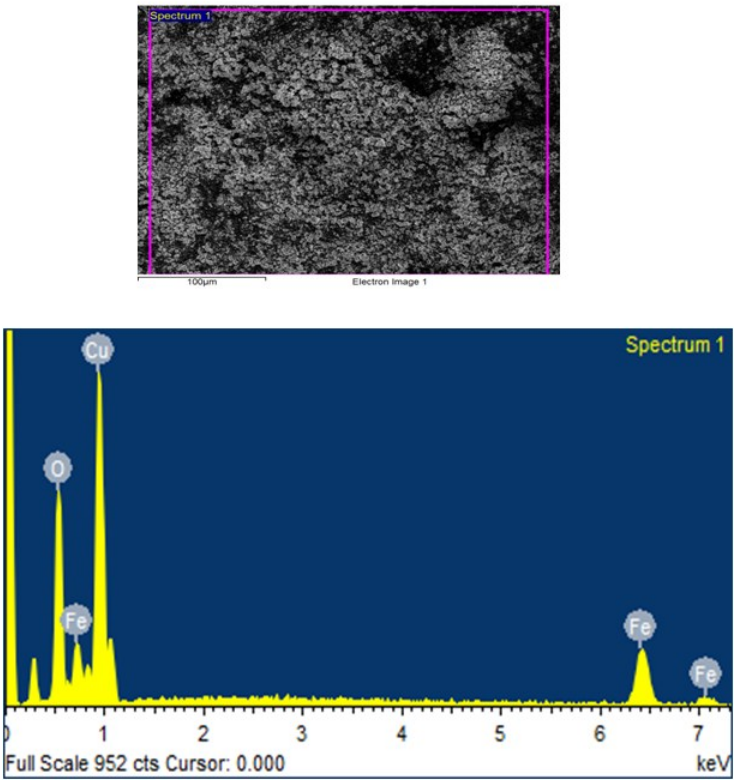


Figure S2: Energy dispersive X-ray spectrum of Cu(0)/Fe_3O_4

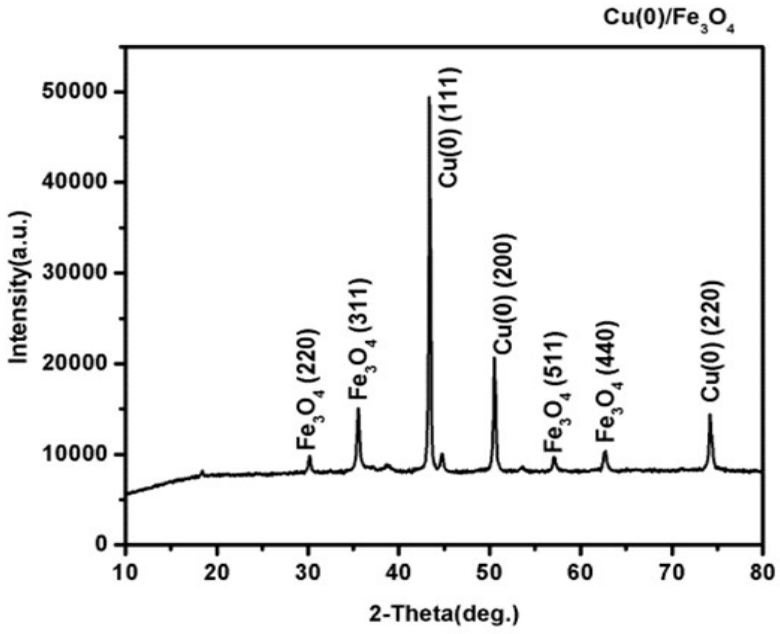


Figure S3: Wide angle powder X-ray diffraction pattern of Cu(0)/Fe_3O_4

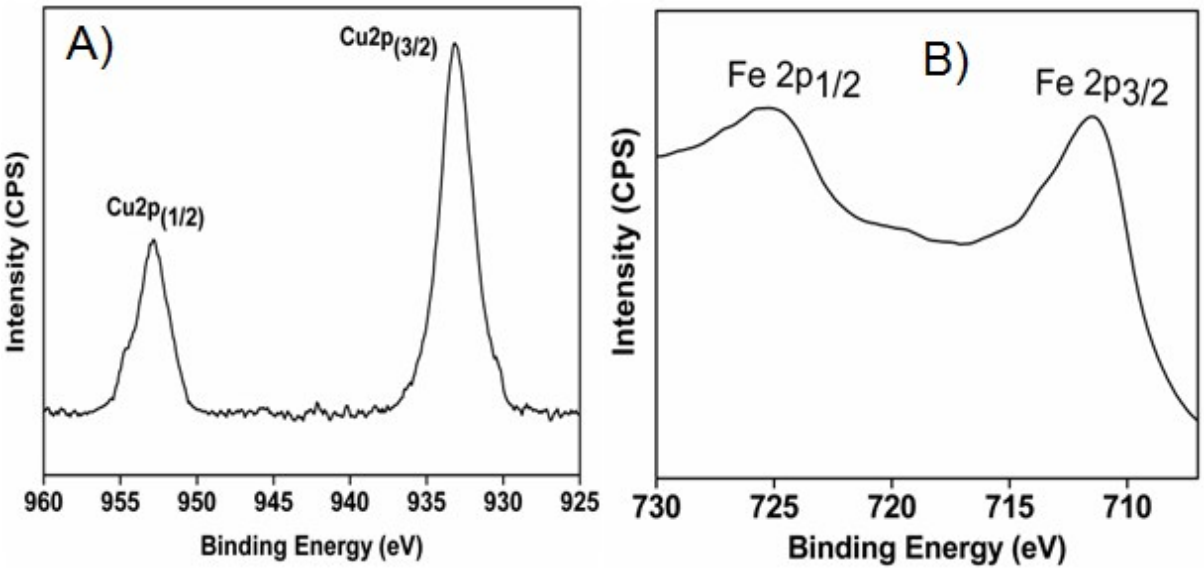


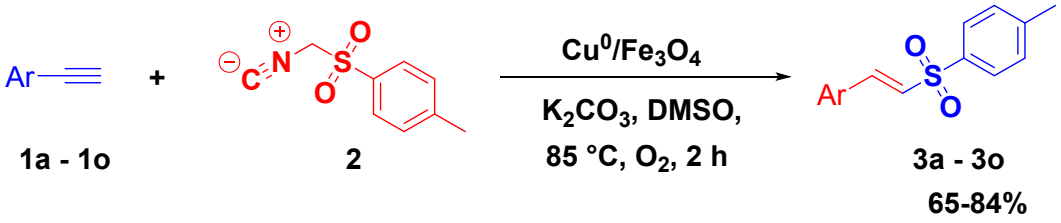
Figure S4: XPS spectra of Cu 2p region (A) and Fe 2p region (B) of $Cu(0)/Fe_3O_4$

4. Reusability of $Cu(0)/Fe_3O_4$:

Magnetic separation is a more attractive and simple technique than the filtration or centrifugation techniques as it prevents the loss of the catalyst and increases the reusability of the catalyst. Due to the superparamagnetic nature of Fe_3O_4 nanoparticles at room temperature separation of the $Cu(0)/Fe_3O_4$ nanocatalyst from the reaction mixture becomes very easy. In the magnetic separation technique the catalyst became adsorbed onto the magnetic stirring bar when the stirring was stopped. Then the catalyst was washed with diethyl ether, oven dried at 100 ^oC and then directly used for the next cycle reaction without further purification.

A recyclability test was performed under optimised conditions using fresh phenyl acetylene, isocyanides and anhydrous K_2CO_3. Recyclable potential plot of $Cu(0)/Fe_3O_4$ nanocatalyst suggested that the nanocatalyst can be effectively reused for five consecutive catalytic cycles (ESI, Fig. XX) without significant loss in catalytic activity. A slight drop in the conversion (%) from the 5^{th} to 6^{th} cycles is observed which is due to the clogging of some catalytic active sites with organic reagents during the course of reaction. In every case our recovery of catalyst from the reaction mixture is almost 100%. We have also provided the distribution of product yield which remains consistent in each catalytic cycle.

General experimental procedures for the synthesis of *E*-Vinyl Sulfones (3a – 3o):

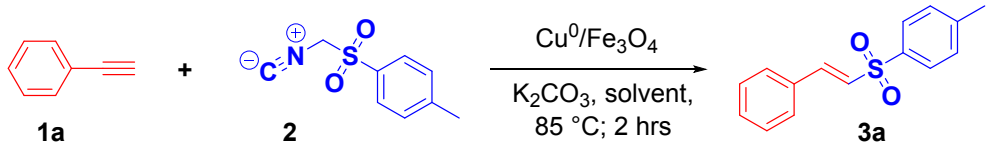


1a - 1o **2** **3a - 3o**

65-84%

A mixture of aryl alkynes (1.0 mmol), Tosylmetylisocyanide (1.0 mmol), K_2CO_3 (1.0 mmol) and Cu^0/Fe_3O_4 (40 mg) in distilled DMSO (4.0 mL) was heated at 85 °C for 2 hrs under oxygen atmosphere. The stirring was stopped and mixture allowed to attain room temperature. Catalyst was separated with the help of external magnate and water (10.0 mL) was added to the reaction mixture. The aqueous layer was further washed with ethyl acetate (3 x 10 mL). The organic layer was washed with brine (10.0 mL) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure to give crude *E*-vinyl sulfones (**3a – 3o**) which was purified by column chromatography using 100-200 mesh silica gel.

General experimental procedure for gram scale synthesis of *E*-Vinyl Sulfone (3a):

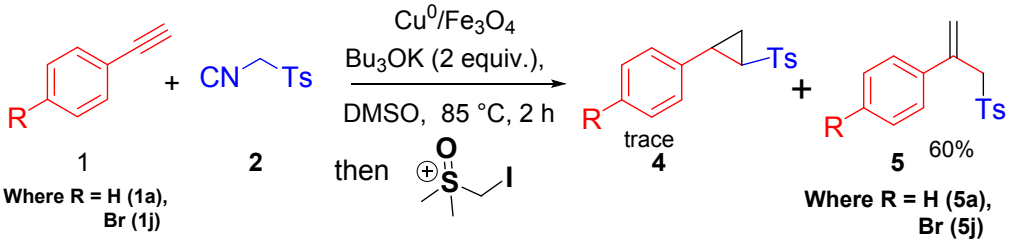


1a **2** **3a**

10.0 mmol **10.0 mmol** **75% isolated yield**

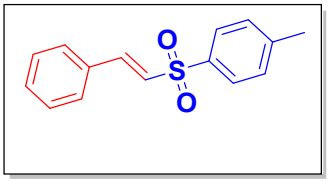
A mixture of phenyl acetylene (**1a**) (1.02 gm, 10.0 mmol), tosylmetylisocyanide (**2**) (1.95 gm, 10.0 mmol), K_2CO_3 (1.38 gm, 10.0 mmol) and Cu^0/Fe_3O_4 (400 mg) in distilled DMSO (400 mL) was heated at 85 °C for 2 hrs under oxygen atmosphere. The stirring was stopped and mixture allowed to attain room temperature. Catalyst was separated with the help of external magnate and water (50.0 mL) was added to the reaction mixture. The aqueous layer was further washed with ethyl acetate (3 x 50 mL). The organic layer was washed with brine (50.0 mL) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure to give crude *E*-vinyl sulfones (**3a**) which was purified by column chromatography to give **3a** as white solid (1.93 gm) in 75% yield.

General procedure for one pot synthesis of allylic sulfones (5a & 5j):



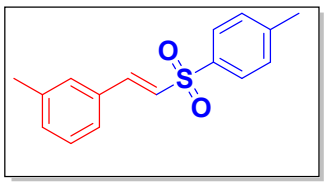
A mixture of Aryl alkynes (1.0 mmol), Tosylmetylisocyanide (1.0 mmol), *t*-BuOK (3.0 mmol) and Cu^0/Fe_3O_4 (40 mg) in DMSO (4.0 mL) was heated at 80 °C for 2 hrs under oxygen atmosphere. Trimethyl sulfoxonium iodide (0.22 gm, 1.0 mmol) was added in three batches at 80 °C. The reaction mixture was further stirred at same temperature for another 12 hrs; and quenched with water (10.0 mL). The aqueous layer was washed with ethyl acetate (3 x 10 mL) and the organic layer was further washed with brine (10.0 mL) and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure to give crude allylic sulfone which was purified by column chromatography using 100 – 200 mesh silica gel.

(*E*)-1-methyl-4-(styrylsulfonyl)benzene (3a):



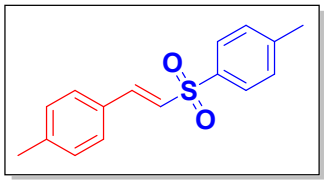
Yield 84%; white solid, m. p. 121-123 °C.; (Lit. 120-122 °C)[1]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 15.4 Hz, 1H), 7.47 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 15.4 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 144.45, 141.97, 137.76, 132.46, 131.15, 130.02, 129.10, 128.56, 127.74, 127.65, 21.66. **FT-IR** (KBr): 3042, 2924, 2853, 1595, 1304, 1143, 1085, 747, 535 cm^{-1}; HRMS (ESI, Orbitrap) calcd for $C_{15}H_{15}O_2S$ $[M+H]^+$ is 259.07873 and found 259.07889.

(*E*)-1-methyl-3-(2-tosylvinyl)benzene (3b):



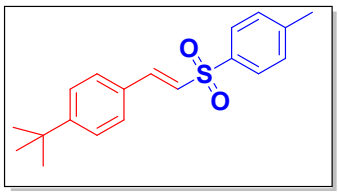
Yield 76%; yellow solid; m. p. 98-99 °C.; (Lit. 97-99 °C)[1]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.83 – 7.81 (dd, *J* = 1.74, 8.33 Hz, 2H), 7.62 (d, *J* = 15.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.22 (m, 3H), 7.22 – 7.20 (m, 1H), 6.83 (d, *J* = 15.4 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 144.36, 142.15, 138.82, 137.86, 132.41, 131.97, 129.98, 129.44, 129.12, 128.97, 127.71, 127.39, 125.80, 21.65, 21.29; **FT-IR** (KBr) 2923, 1604, 138, 1138, 1091, 656 cm^{-1}; HRMS (ESI, Orbitrap) calcd for $C_{16}H_{17}O_2S$ $[M+H]^+$ is 273.09438 and found 273.09458.

(*E*)-1-methyl-4-((4-methylstyryl)sulfonyl)benzene (3c):



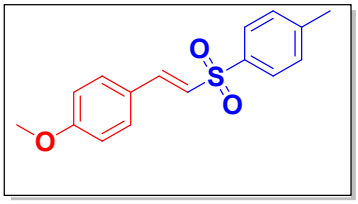
Yield 75%, yellow solid; m. p. 152 - 144 °C.; (Lit. 152-155)[1]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 15.4 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 15.4 Hz, 1H), 2.43 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 144.29, 142.04, 141.73, 137.93, 129.96, 129.81, 129.70, 128.57, 127.68, 126.36, 21.66, 21.56. **FT-IR** (KBr) 2921, 1607, 1303, 1142, 1084, 795, 658 cm^{-1}. HRMS (ESI, Orbitrap) calcd for $C_{16}H_{17}O_2S$ $[M+H]^+$ is 273.09438 and found 273.09463.

***(E)*-1-(tert-butyl)-4-(2-tosylvinyl)benzene (3d):**



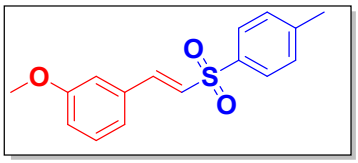
Yield 74%; yellow solid, m. p. 115 - 117 °C.; (Lit. 116-118)[1]; **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.47 – 7.36 (bs, 4H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 15.4 Hz, 1H), 2.43 (s, 3H), 1.31 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.88, 144.27, 141.97, 137.98, 129.94, 129.71, 128.43, 127.66, 126.59, 126.08, 35.01, 31.13, 21.65. **FT-IR** (KBr) 3421, 2964, 1594, 1316, 1143, 1084, 801, 651 cm^{-1}; HRMS (ESI, Orbitrap) calcd for $C_{19}H_{23}O_2S$ $[M+H]^+$ is 315.14133 and found 315.14149.

(*E*)-1-methoxy-4-(2-tosylvinyl)benzene (3e):



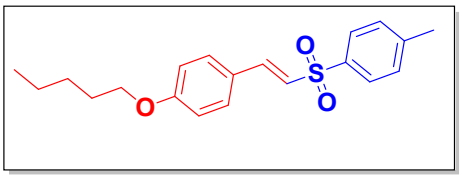
Yield 72%, Yellow solid, m. p. 94 - 96 °C.; (Lit 92-94)[1]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 15.3 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 15.3 Hz, 1H), 3.83 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 162.01, 144.15, 141.76, 138.23, 130.33, 129.92, 127.58, 125.09, 124.86, 114.52, 55.46, 21.62; **FT-IR** (KBr) 3045, 2970, 2941, 1604, 1510, 1461, 1315, 1141 cm^{-1}; HRMS (ESI, Orbitrap) calcd for $C_{16}H_{17}O_3S$ $[M+H]^+$ is 289.08929 and found 289.08955

(*E*)-1-methoxy-3-(2-tosylvinyl)benzene (3f):



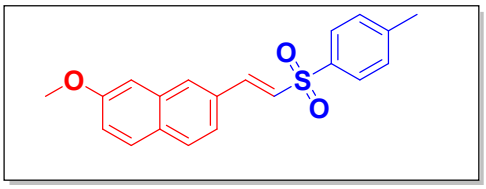
Yield 70%, sticky solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 15.5 Hz, 1H), 7.84 – 7.82 (dd, J = 1.8, 8.7 Hz, 2H), 7.41 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 15.5 Hz, 1H), 6.95 (td, *J* = 7.6, 0.9 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 3.87 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.83, 144.05, 138.27, 138.04, 132.39, 130.75, 129.88, 128.24, 127.68, 121.32, 120.79, 111.25, 55.52, 21.63; **FT-IR** (KBr) 2931, 1604, 1489, 1308, 1251, 1143, 1085 cm^{-1}.; HRMS (ESI, Orbitrap) calcd for $C_{16}H_{17}O_3S$ $[M+H]^+$ is 289.08929 and found 289.08959

(*E*)-1-methyl-4-((4-(pentyloxy)styryl)sulfonyl)benzene (3g):



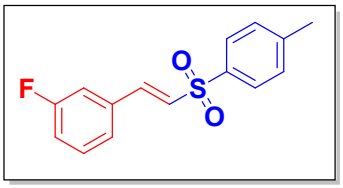
Yield 71%, white solid, m. p. 110-113 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 15.3 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 15.3 Hz, 1H), 3.97 (t, *J* = 6.5 Hz, 2H), 2.43 (s, 3H), 1.79 (dt, *J* = 13.2, 6.4 Hz, 2H), 1.48 – 1.29 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 161.61, 144.11, 141.86, 138.21, 133.83, 132.66, 130.32, 129.90, 129.52, 127.56, 124.79, 124.53, 114.95, 68.21, 28.78, 28.11, 22.42, 21.60, 14.01. **FT-IR** (KBr) 3289, 2955, 1602, 1572, 1468, 1256, 1085, 835 cm^{-1}. HRMS (ESI, Orbitrap) calcd for $C_{20}H_{25}O_3S$ $[M+H]^+$ is 345.15189 and found 345.15201.

(*E*)-2-methoxy-7-(2-tosylvinyl)naphthalene (3h):



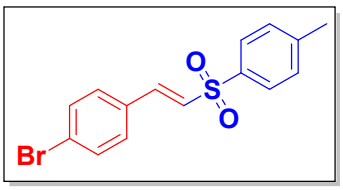
Yield 69%; light yellow solid; m. p. 148-150 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.91 – 7.83 (m, 3H), 7.78 (d, *J* = 15.4 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.51 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.17 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.11 (d, *J* = 2.2 Hz, 2H), 6.89 (d, *J* = 15.3 Hz, 1H), 3.93 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.21, 144.27, 142.29, 138.09, 136.05, 132.80, 130.66, 130.26, 129.97, 128.52, 127.69, 127.00, 126.39, 124.18, 119.77, 106.01, 55.43, 21.64. **FT-IR** (KBr) 3432, 2925, 1595, 1461, 1319, 1084, 1025, 799 cm^{-1}; **HRMS** (ESI, Orbitrap) calcd for $C_{20}H_{19}O_3S$ $[M+Na]^+$ is 361.08743 and found 361.08738.

(*E*)-1-fluoro-3-(2-tosylvinyl)benzene (3i):



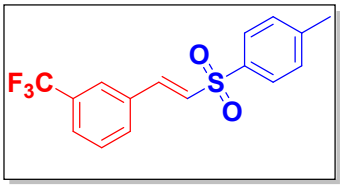
Yield 81%, white solid, m. p. 77-79 °C (Lit. 75 -78 °C)[2]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 15.4 Hz, 1H), 7.42 – 7.30 (m, 3H), 7.25 – 7.05 (m, 3H), 6.85 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 162.58 (d, *J* = 248 Hz); 144.69, 140.45, 137.36, 130.77 (d, *J* = 8.2 Hz), 130.01, 129.18, 127.833, 124.57, 117.10 (d, *J* = 21.5 Hz), 114.11 (d, *J* = 22.1 Hz); **FT-IR** (KBr) 3054, 1606, 1514, 1309, 1230, 1145 cm^{-1}; **HRMS** (ESI, Orbitrap) calcd for $C_{15}H_{14}FO_2S$ [M+H] is 277.06931 and found 277.06939

(*E*)-1-bromo-4-(2-tosylvinyl)benzene (3j):



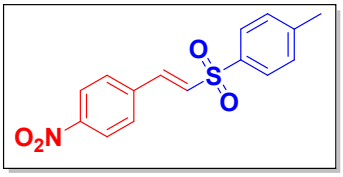
Yield 82%; light yellow solid; m. p. 161-163 °C.; (Lit. 162-164 °C)[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 15.4 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 4H), 6.84 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 144.60, 140.51, 137.49, 132.36, 131.41, 130.05, 129.87, 128.39, 127.79, 125.53, 21.65.

(*E*)-1-(2-tosylvinyl)-3-(trifluoromethyl)benzene (3k):



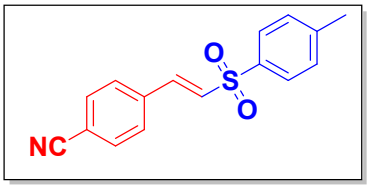
Yield 82%; white solid; m.p. 104-107 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.02 (dd, *J* = 15.3, 1.8 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.49 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 15.2 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 144.80, 137.90, 137.03, 132.27, 131.48, 130.34, 130.10, 128.33, 127.96, 126.39, 126.35, 124.82, 122.64, 21.68; **FT-IR** (KBr) 3291, 2922, 1687, 1577, 1404, 1213, 1015, 825 cm^{-1}.; **HRMS** (ESI, Orbitrap) calcd for $C_{16}H_{14}F3O_2S$ [M+H] is 327.06611 and found 327.06610

(*E*)-1-methyl-4-((4-nitrostyryl)sulfonyl)benzene (3l):



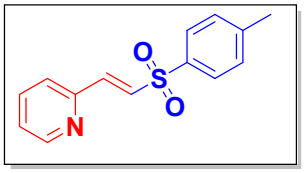
Yield 85%; White solid; m. p. 173-175 °C (Lit. 172-175 °C)[4]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 15.5 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 15.5 Hz, 1H), 2.46 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.51, 145.61, 143.38, 140.56, 140.02, 133.45, 130.00, 129.64, 123.81, 21.80.

(*E*)-4-(2-tosylvinyl)benzonitrile (3m):



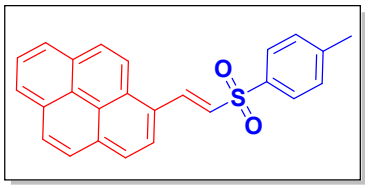
Yield 84%; white solid; m. p. 126-128 °C (Lit. 125-127 °C)[3]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.3 Hz, 2H), 7.69 – 7.65 (m, 3H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 15.4 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.03, 139.24, 136.90, 136.76, 132.79, 131.41, 130.19, 128.89, 127.96, 118.05, 114.26, 21.70.

(*E*)-2-(2-tosylvinyl)pyridine (3n):



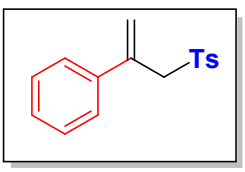
Yield 65%; White solid; m. p. 99-101 °C; (Lit. 98-99 °C)[1]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.61 (d, *J* = 4.3 Hz, 1H), 7.97 – 7.87 (m, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.73 (td, *J* = 7.7, 1.8 Hz, 1H), 7.62 (d, *J* = 14.9 Hz, 1H), 7.44 (d, *J* = 15.0 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.28 (m, 1H), 2.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.14, 150.29, 144.62, 140.02, 137.06, 132.20, 130.01, 127.96, 125.39, 124.95, 21.66; **FT-IR** (KBr) 1580, 1436, 1320, 1144 cm^{-1}.

(*E*)-1-(2-tosylvinyl)pyrene (3o):



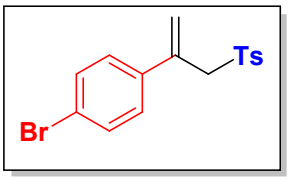
Yield 75%; White solid; m.p. 188-191 °C (Lit. 189-190 °C)[5]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.78 (d, *J* = 15.2 Hz, 1H), 8.44 (d, *J* = 9.3 Hz, 1H), 8.26 – 8.22 (m, 2H), 8.20 (d, *J* = 9.3 Hz, 1H), 8.14 – 8.10 (m, 3H), 8.08 – 8.01 (m, 3H), 7.95 – 7.93 (dd, *J* = 1.7, 8.3 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 15.1 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 144.44, 138.68, 137.92, 131.25, 130.60, 130.08, 129.11, 127.85, 127.25, 126.49, 126.36, 126.18, 125.86, 125.00, 124.45, 122.08, 21.68.

1-methyl-4-((2-phenylallyl)sulfonyl)benzene (5a):



Yield 60%; White solid; m.p. 96- 98 °C.; (Lit m.p. 97-98 °C)[6]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.65 (d, J = 8.5 Hz, 2H), 7.28 – 7.20 (m, 7H), 5.59 (s, 1H), 5.21 (s, 1H), 4.25 (s, 2H), 2.39 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 144.61, 138.90, 136.62, 135.48, 130.94, 129.52, 128.86, 128.70, 128.37, 127.94, 126.25, 121.75, 62.19, 21.61.

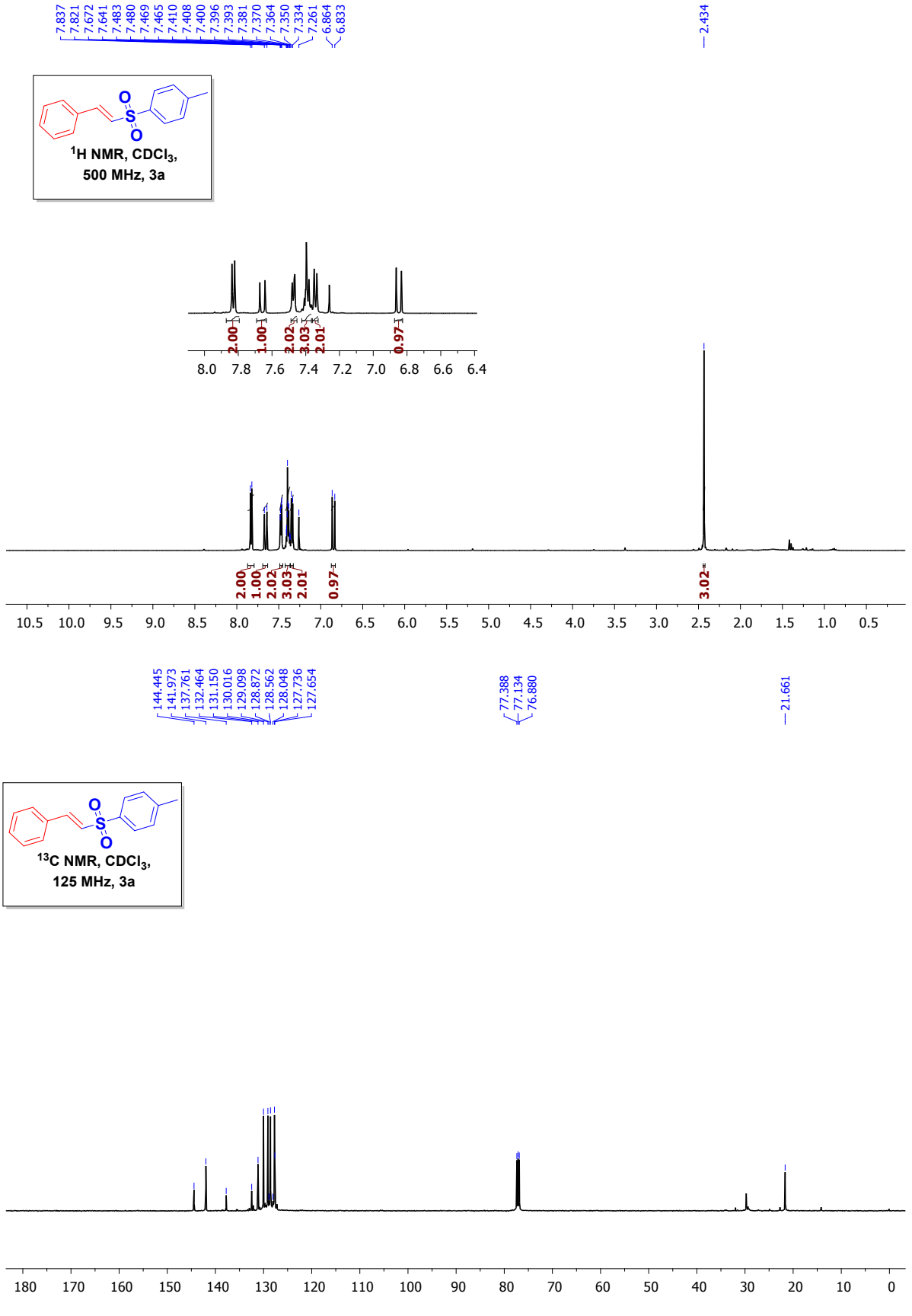
1-bromo-4-(3-tosylprop-1-en-2-yl)benzene (5j):



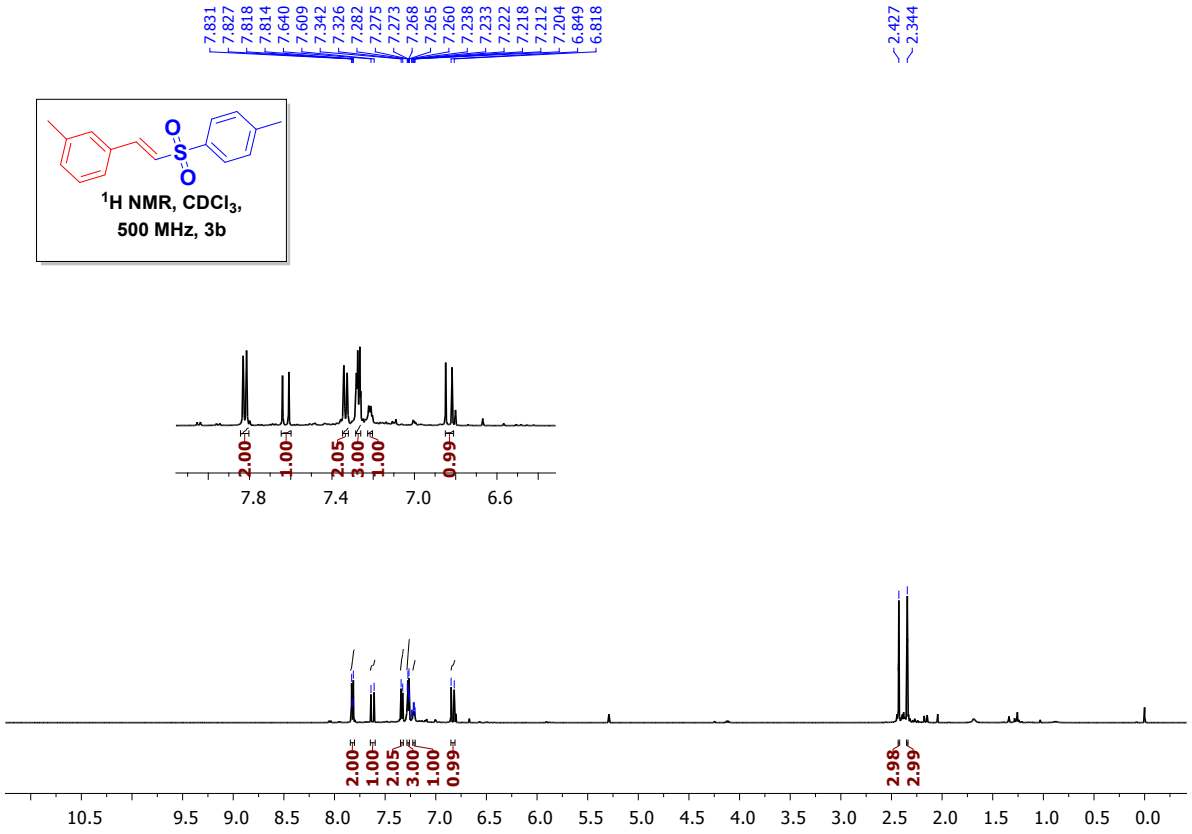
Yield 60%; White solid; m.p. 131-133 °C; (Lit. 130-132 °C)[6]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 5.58 (s, 1H), 5.22 (s, 1H), 4.20 (s, 2H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.90, 137.77, 135.75, 135.34, 131.49, 129.61, 128.65, 127.95, 122.35, 122.15, 77.37, 77.05, 76.74, 62.11, 21.65.

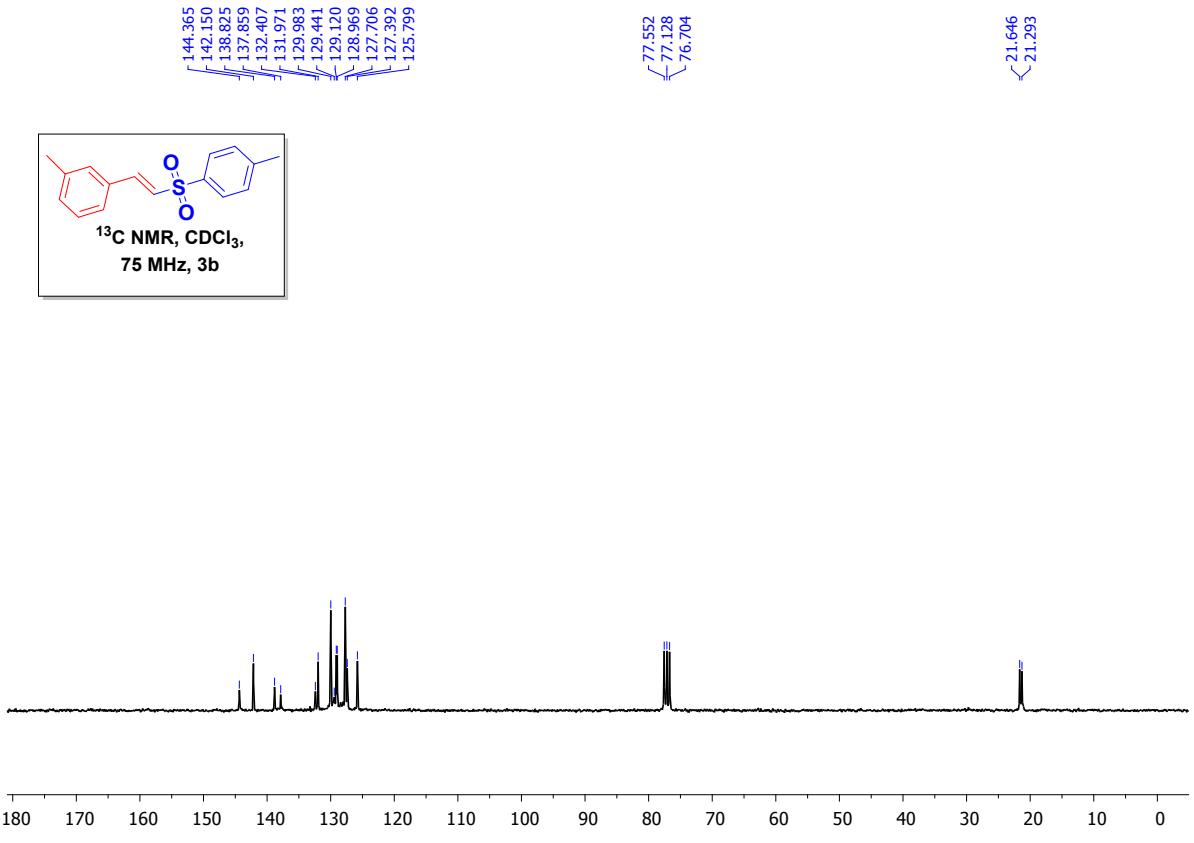
References:

1. G. M. Selke, V. K. Rao, K. Pericherla, and A. Kumar, *Synlett*, 2014, **25**, 2345.
2. T. Sawangphon, P. Katrun, K. Chaisiwamongkhol, M. Pohmakotr, V. Reutrakul, T. Jaipetch, D. Soorukram, and C. Kuhakarn *Synth. Commun.*, 2013, **43**, 1692
3. G. W. Rong, J. C. Mao, H. Yan, Y. Zheng and G. Q. Zhang, *J. Org. Chem.,* 2015, **80**, 4697.
4. X. Li, Y. Xu, W. Wu, C. Jiang, C. Qi, H. Jiang, *Chem. Eur. J.,* 2014, **20**, 7911.
5. N. Reddy; *Indian Journal of Chemistry*, 1975, **13**, 543.
6. X. Li, X. Xu and C. Zhou, *Chem. Commun*., 2012, **48**, 12240.

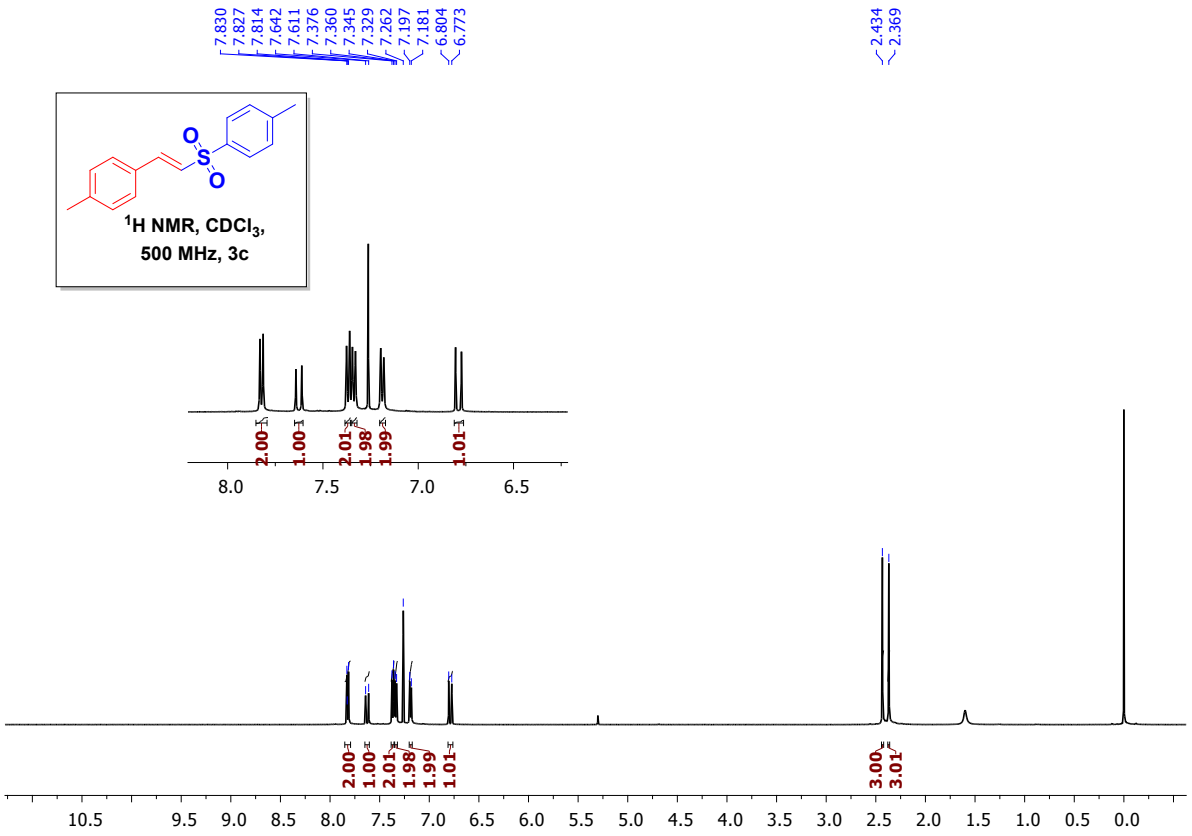


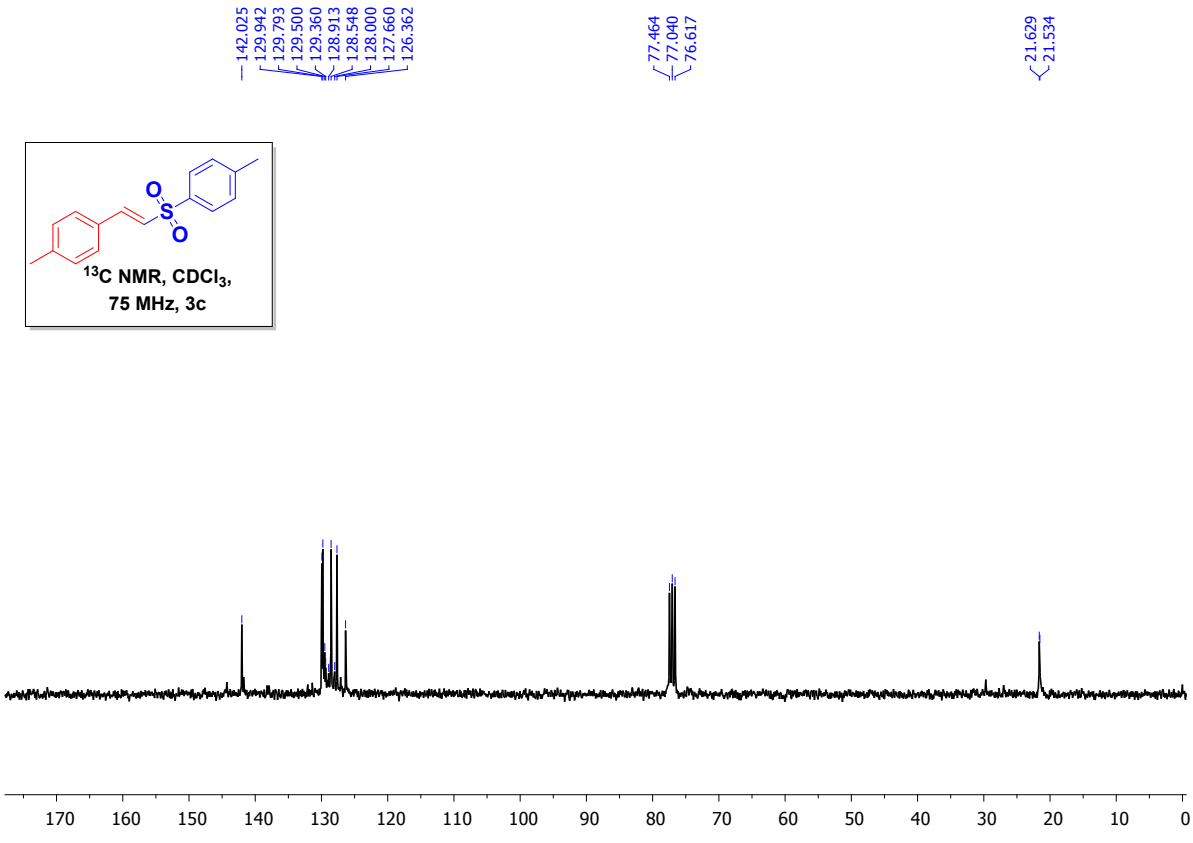
^{1}H and ^{13}C NMR of **3a**



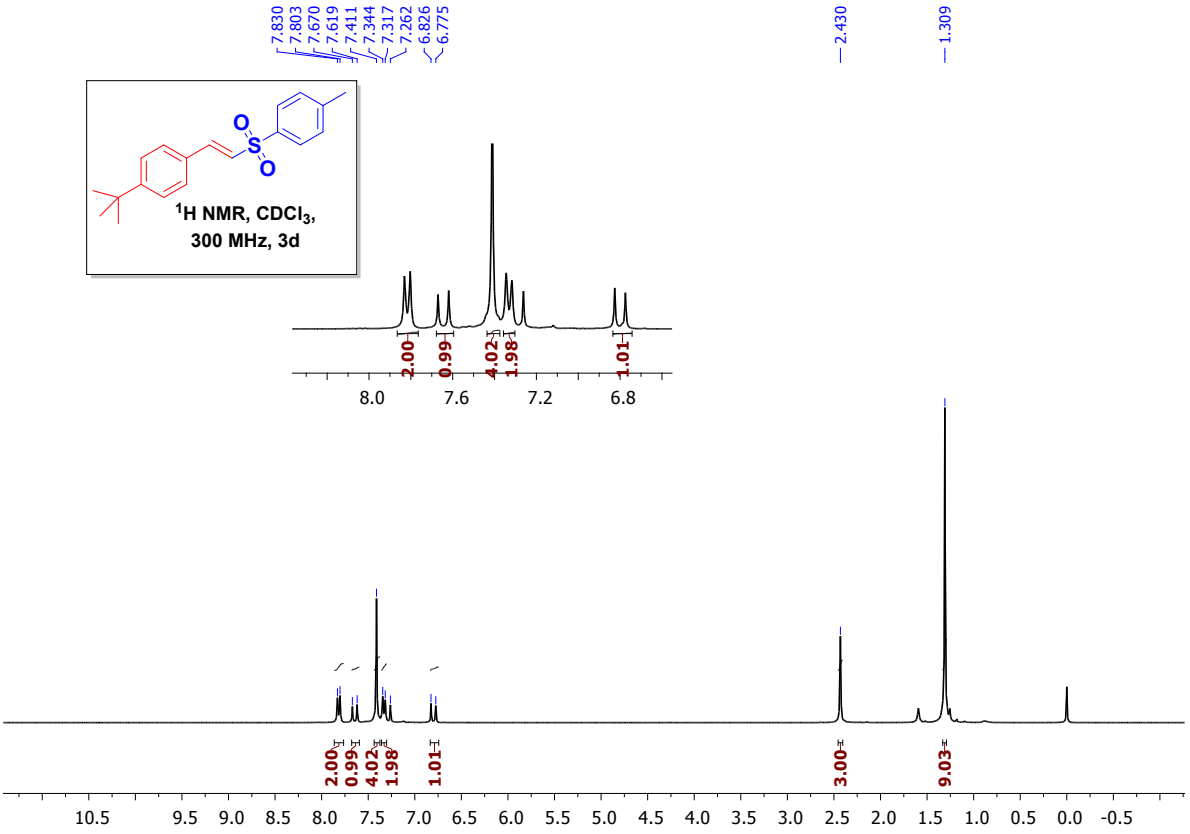


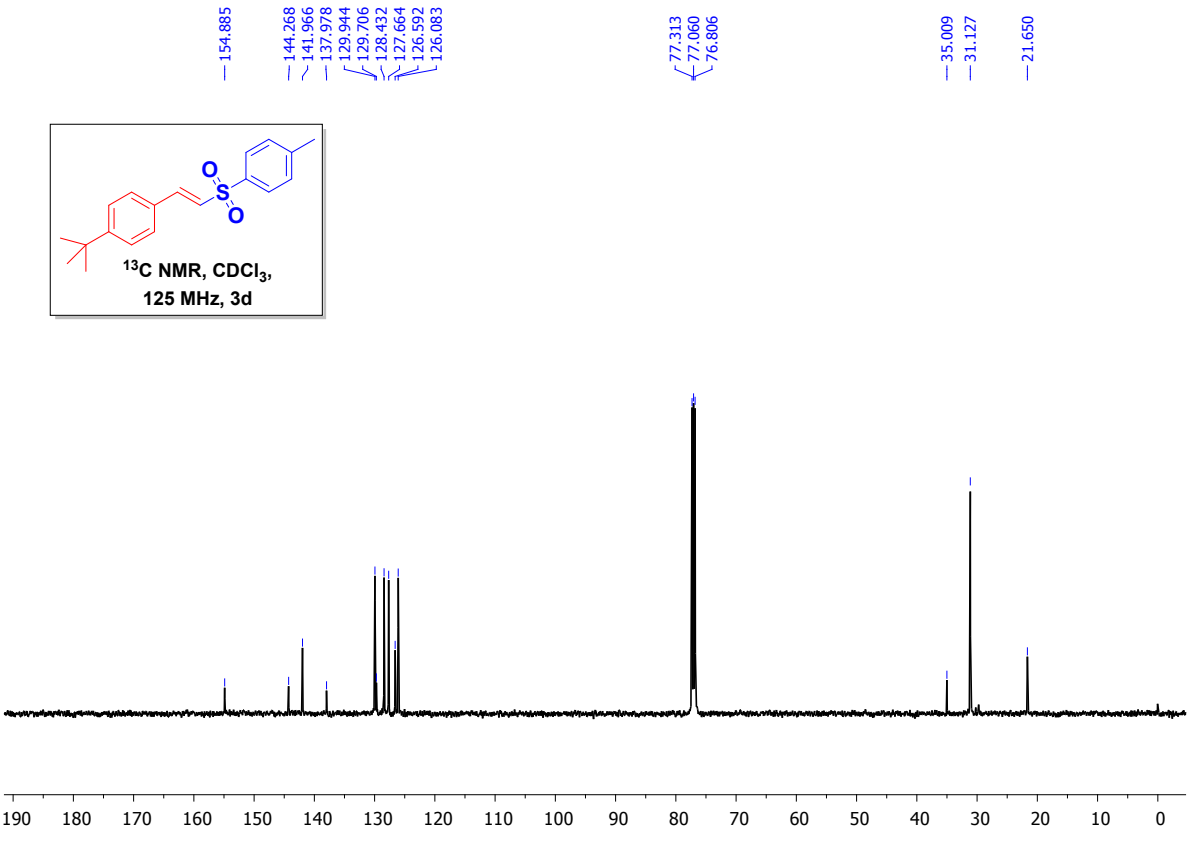
^{1}H and ^{13}C NMR of **3b**



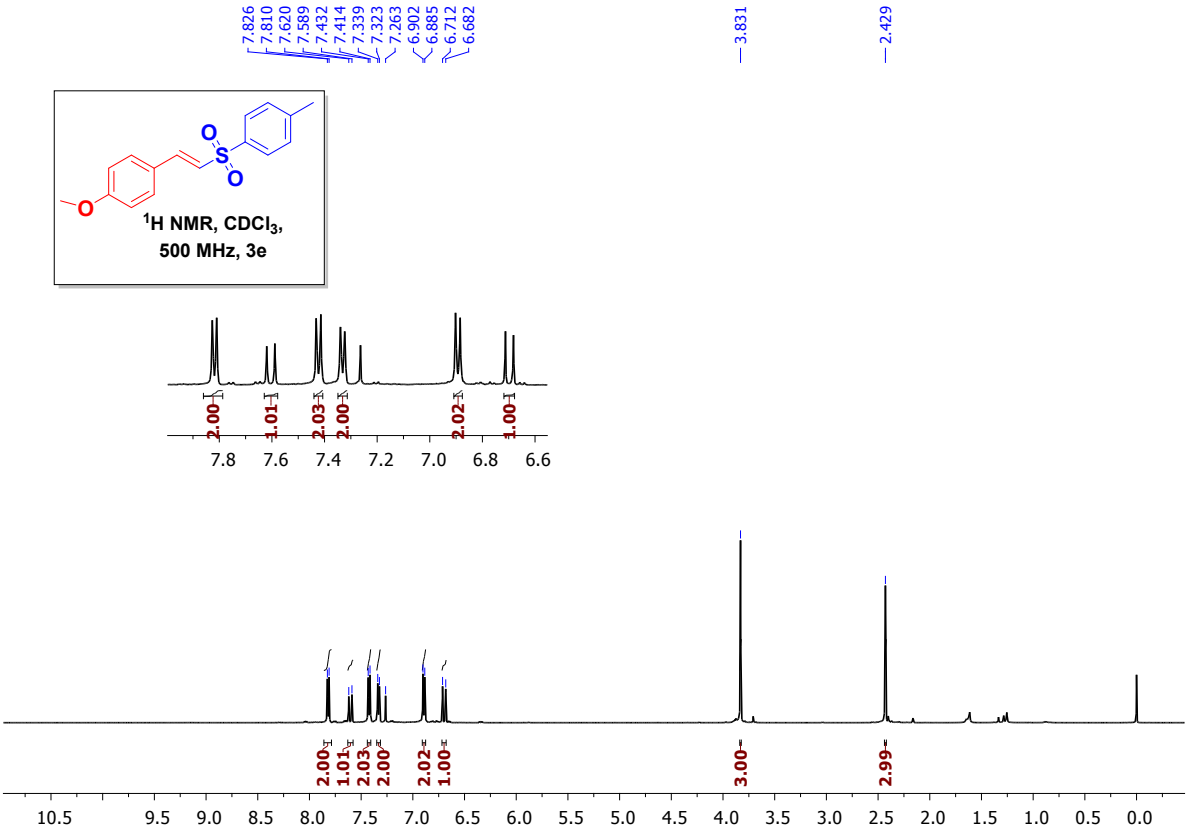


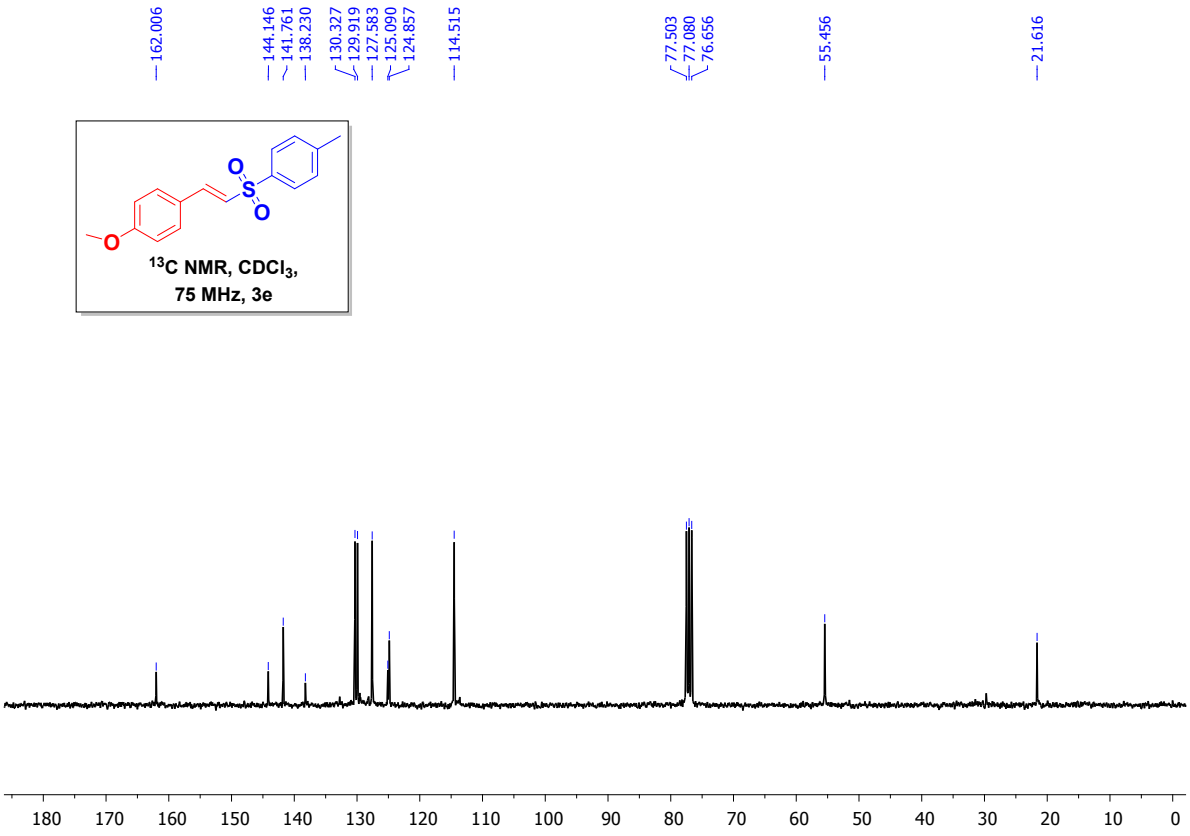
^{1}H and ^{13}C NMR of **3c**



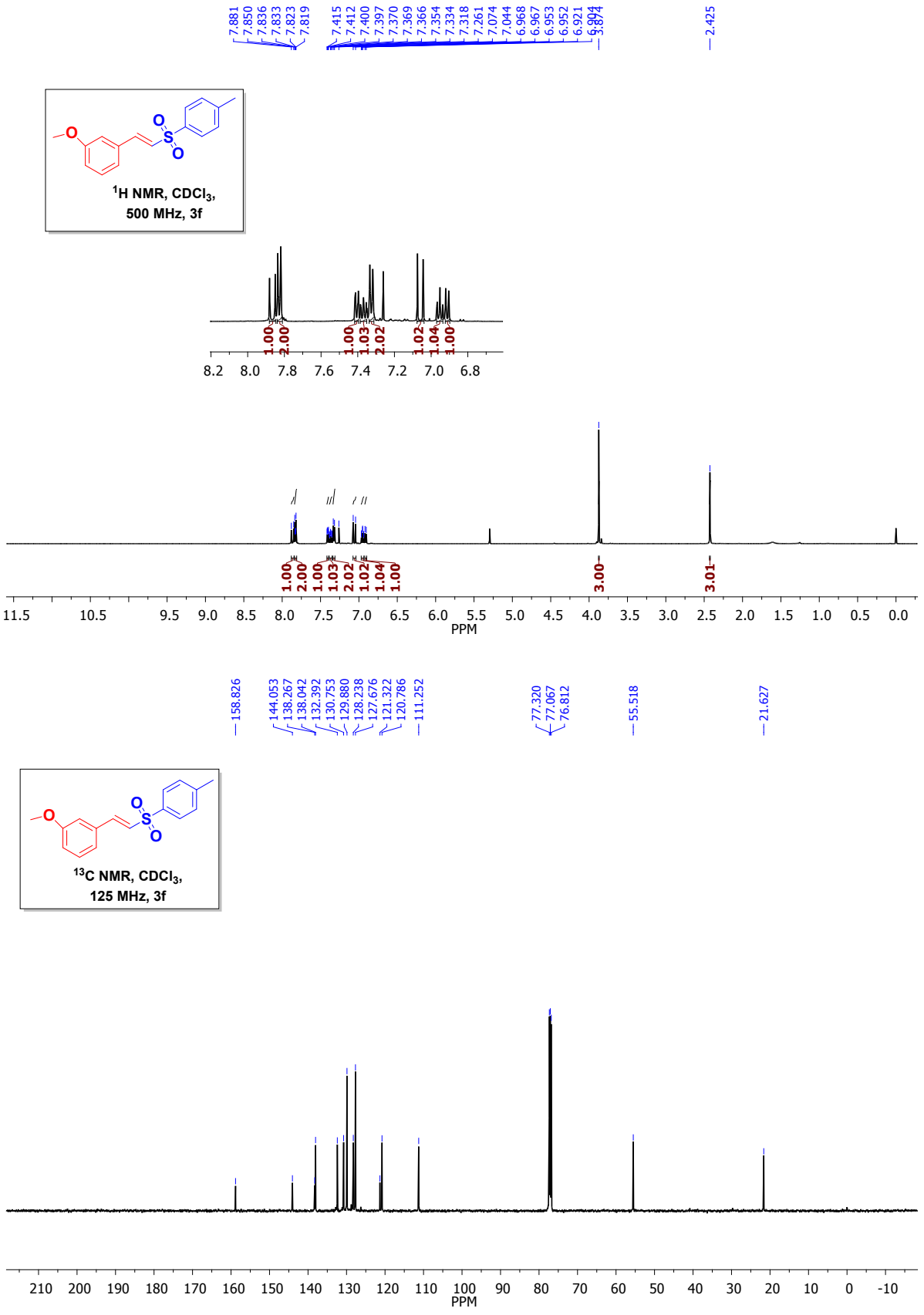


^{1}H and ^{13}C NMR of **3d**

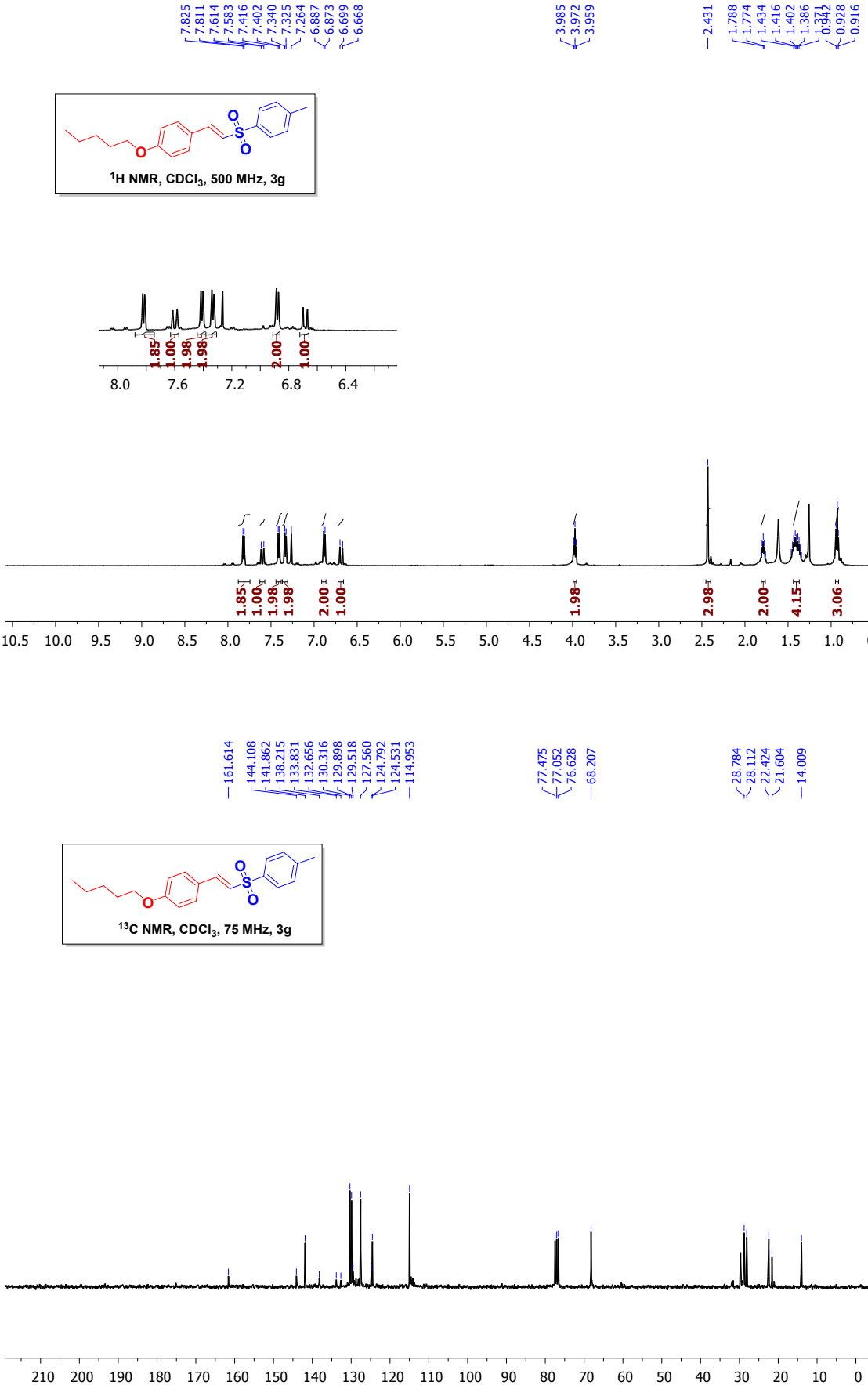




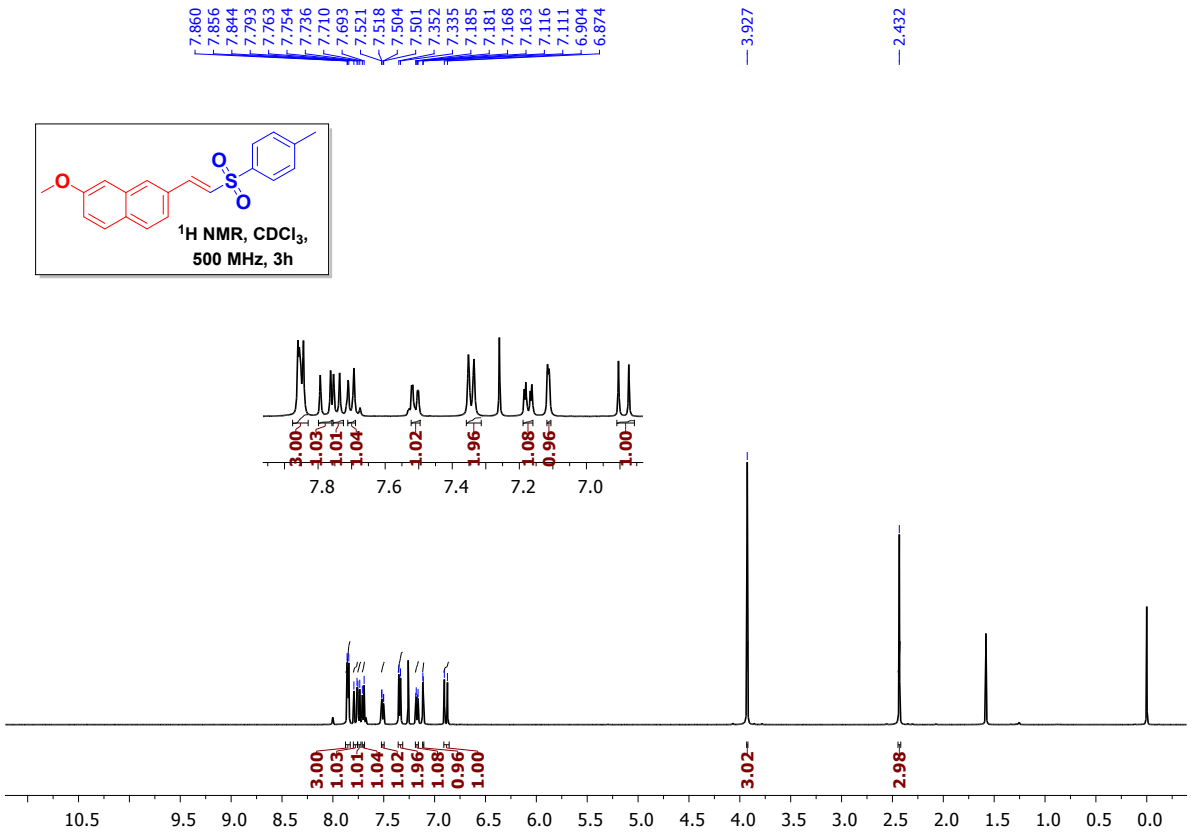
^{1}H and ^{13}C NMR of **3e**

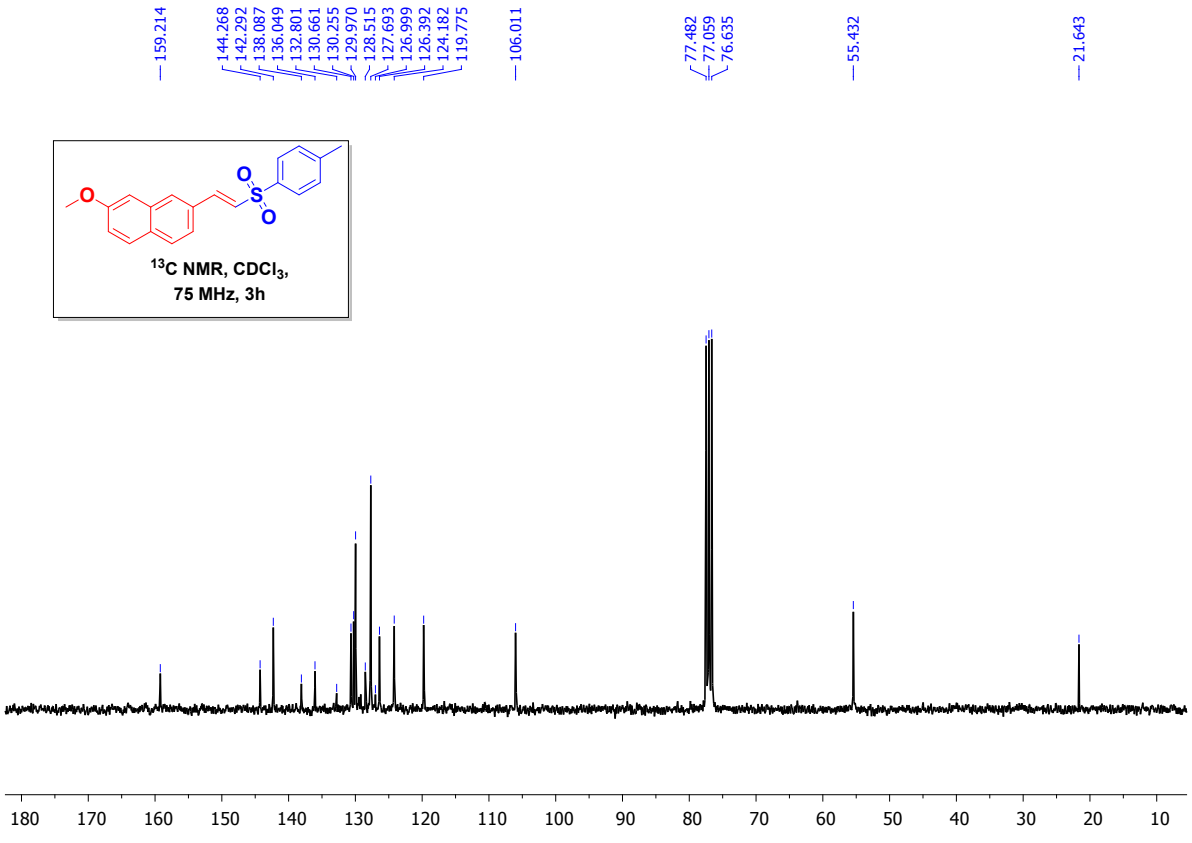


^{1}H and ^{13}C NMR of **3f**

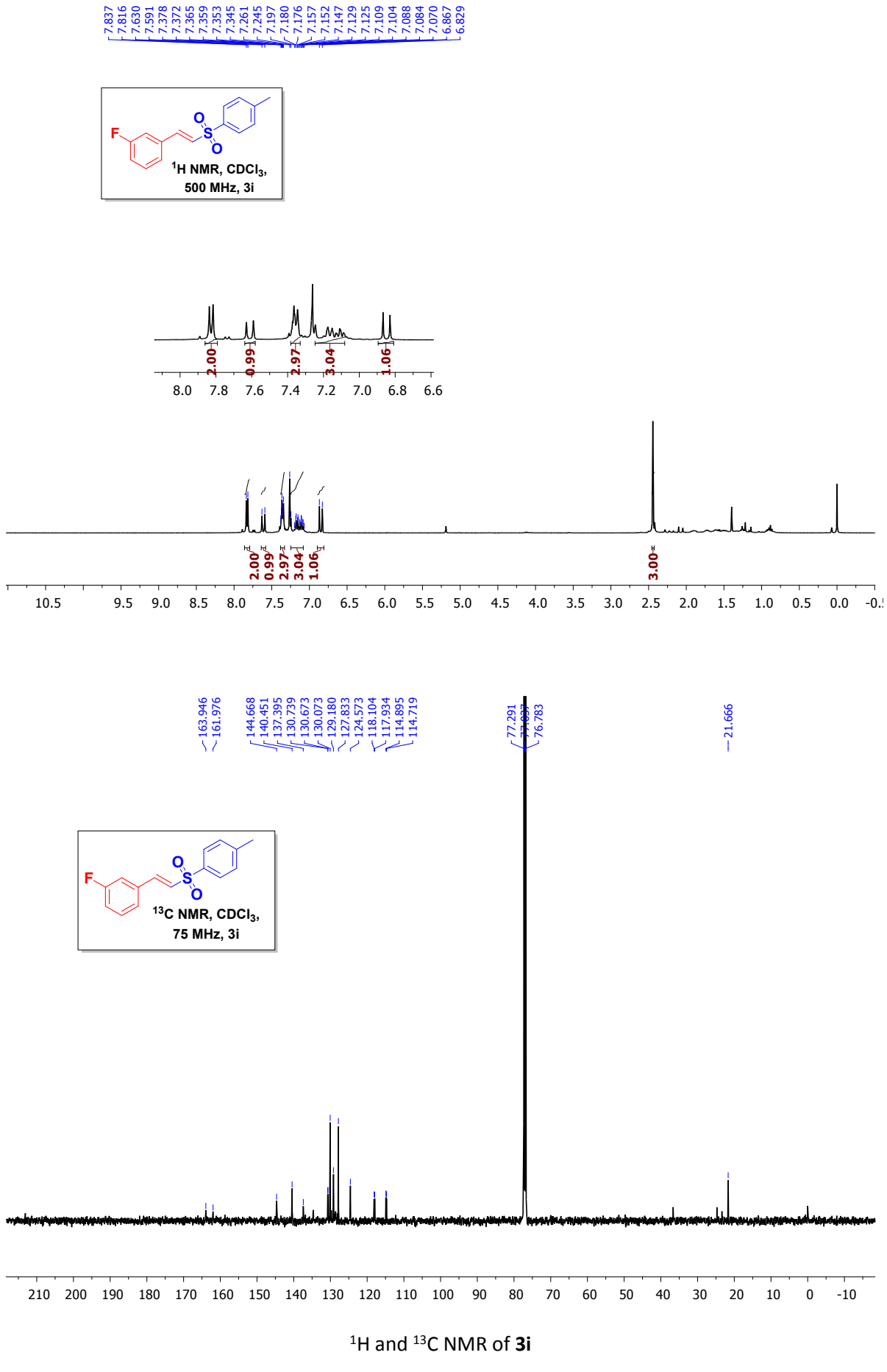


^{1}H and ^{13}C NMR of **3g**

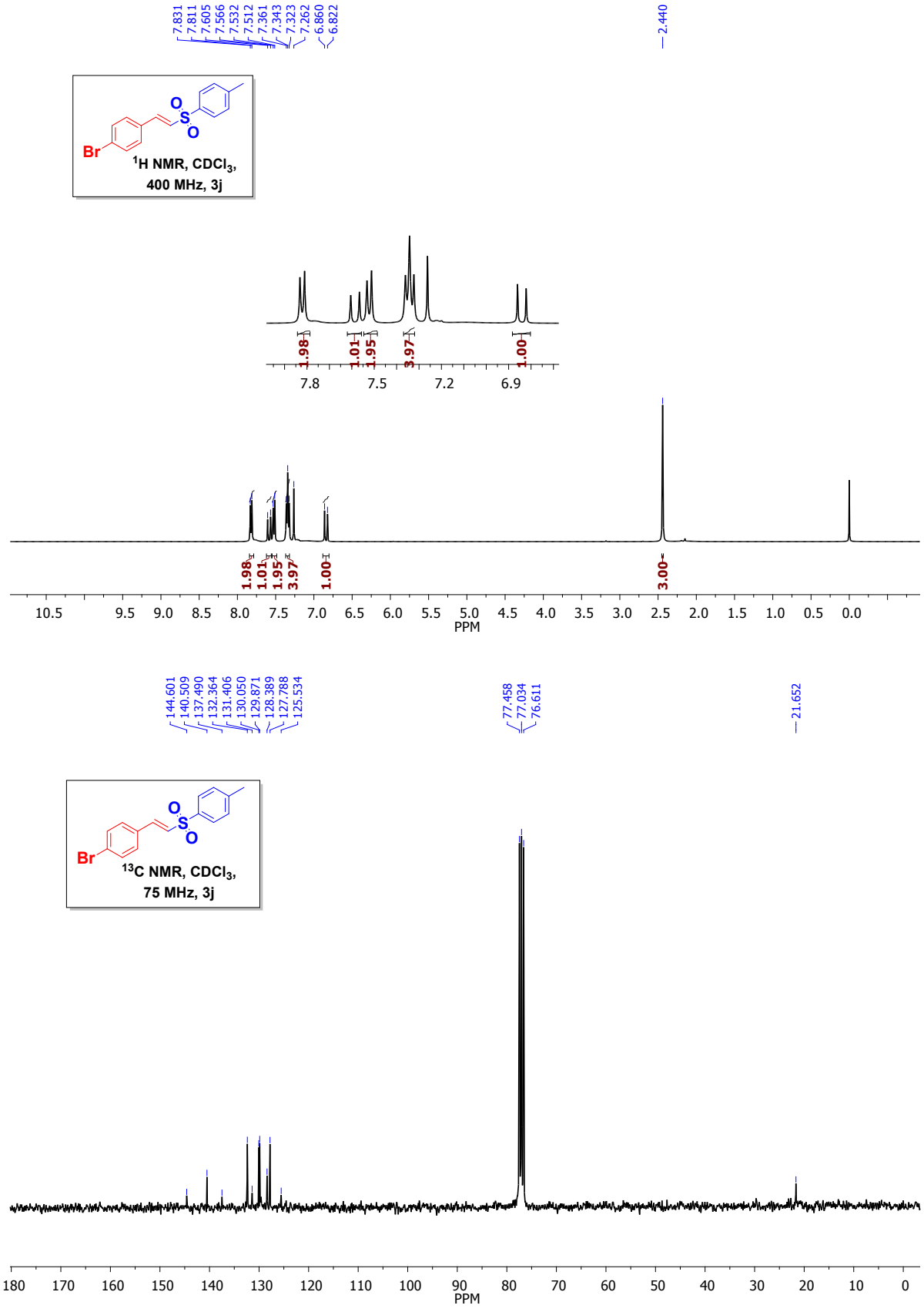




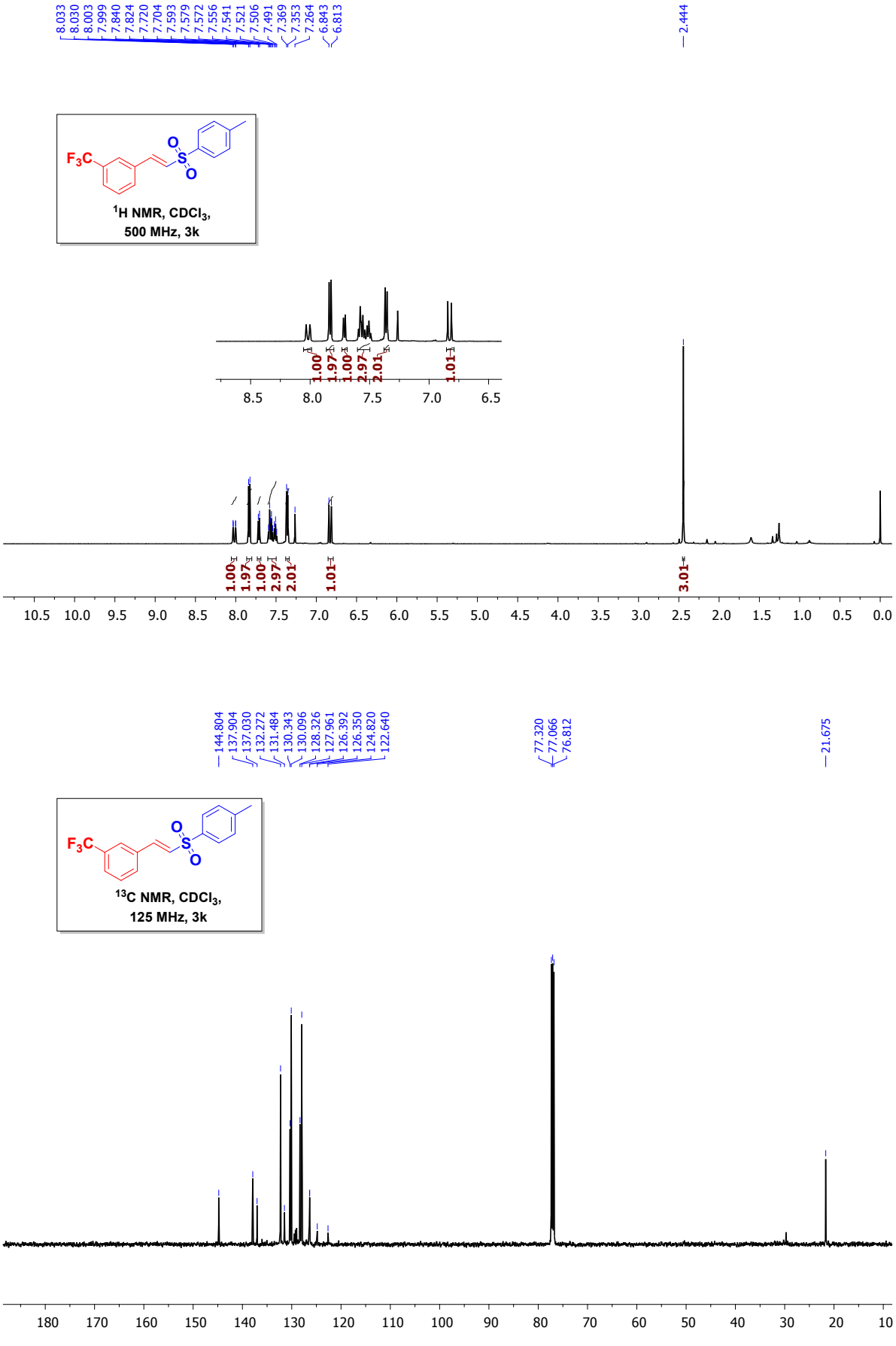
^{1}H and ^{13}C NMR of **3h**



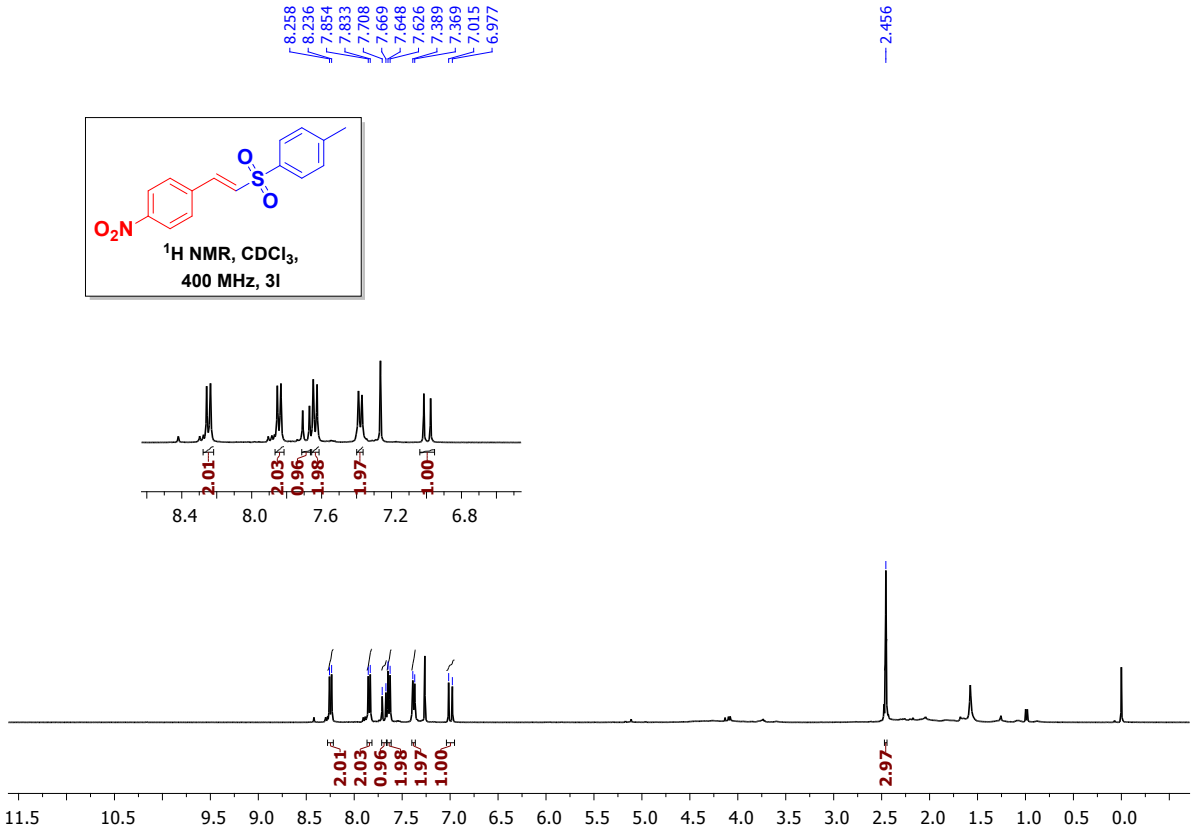
^{1}H and ^{13}C NMR of **3i**

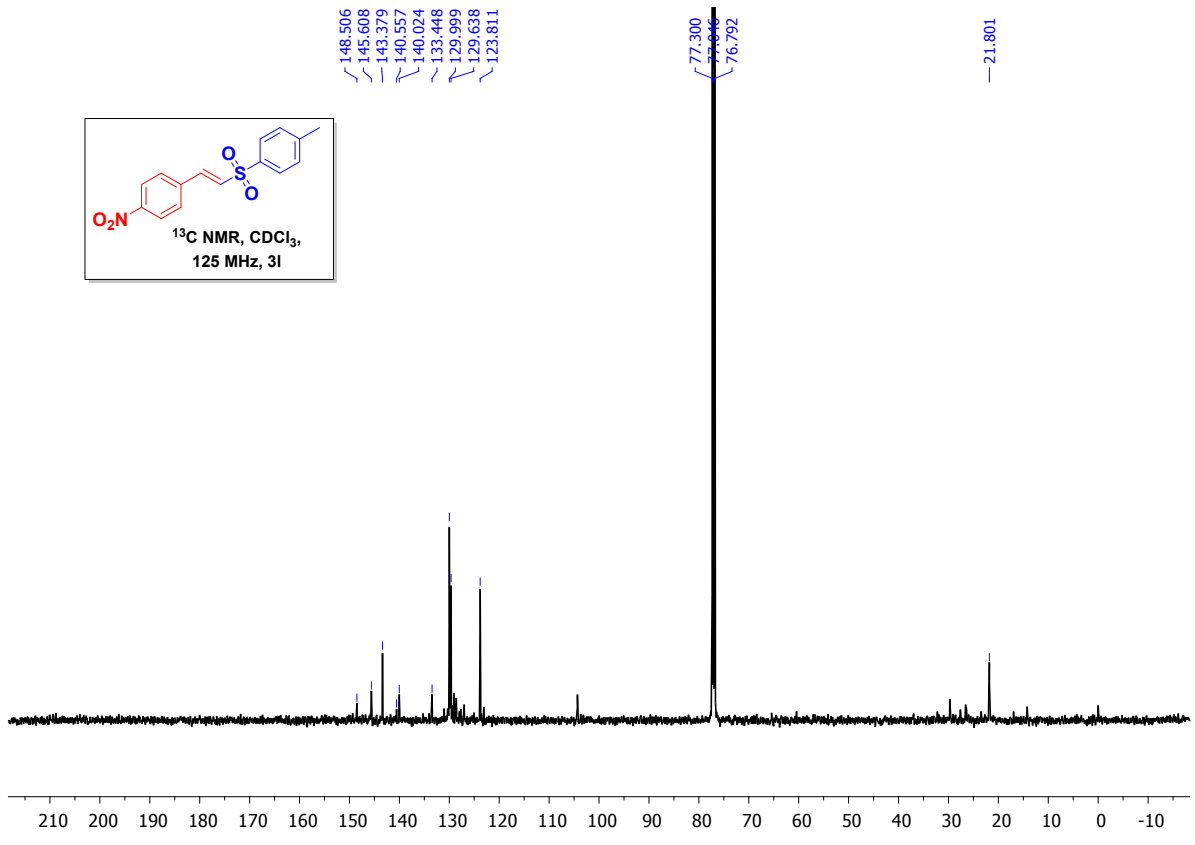


^{1}H and ^{13}C NMR of **3j**

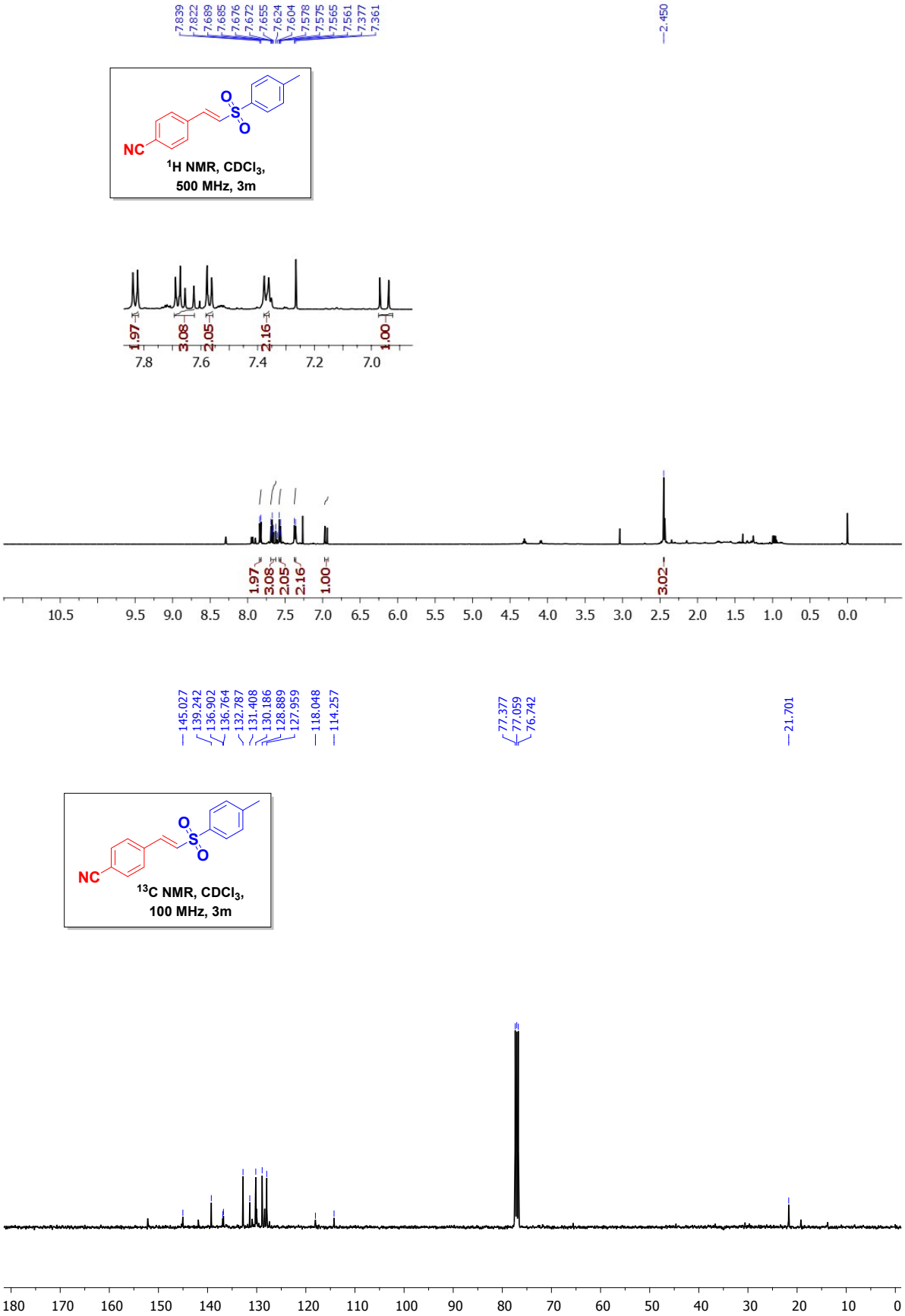


^{1}H and ^{13}C NMR of **3k**

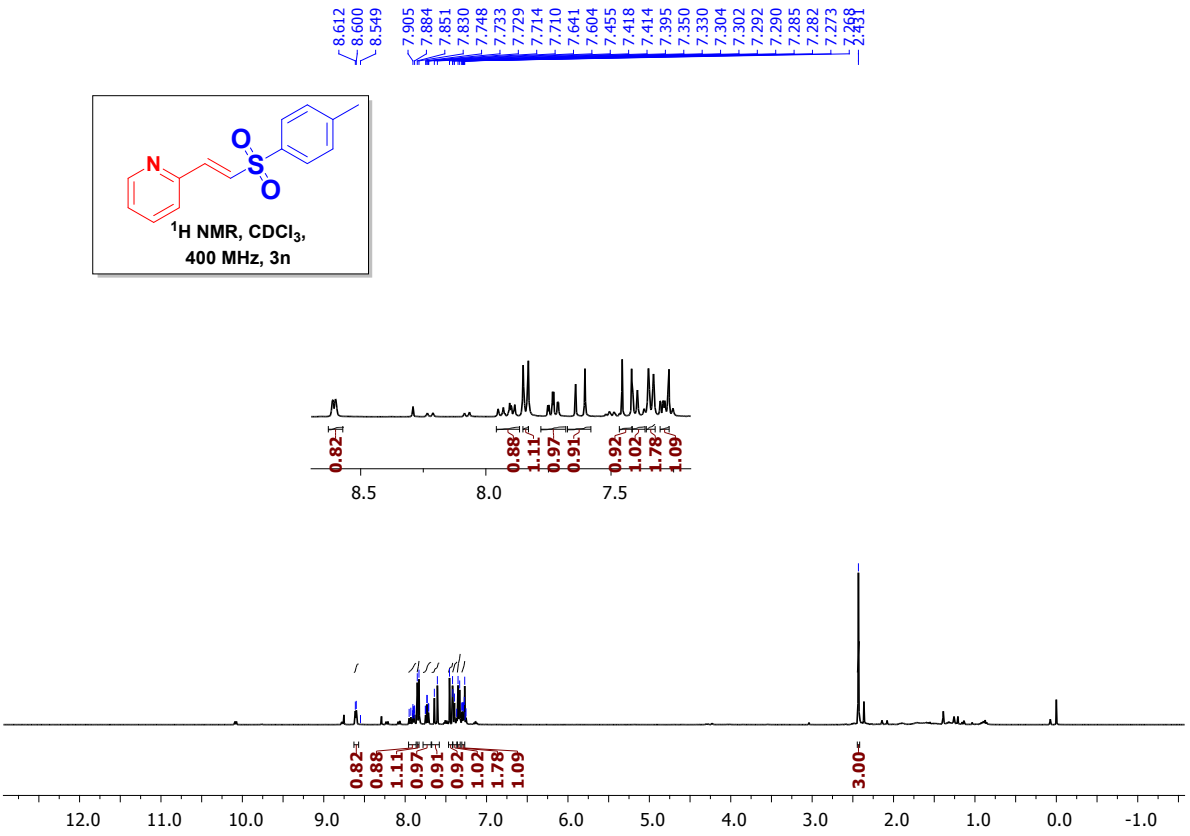


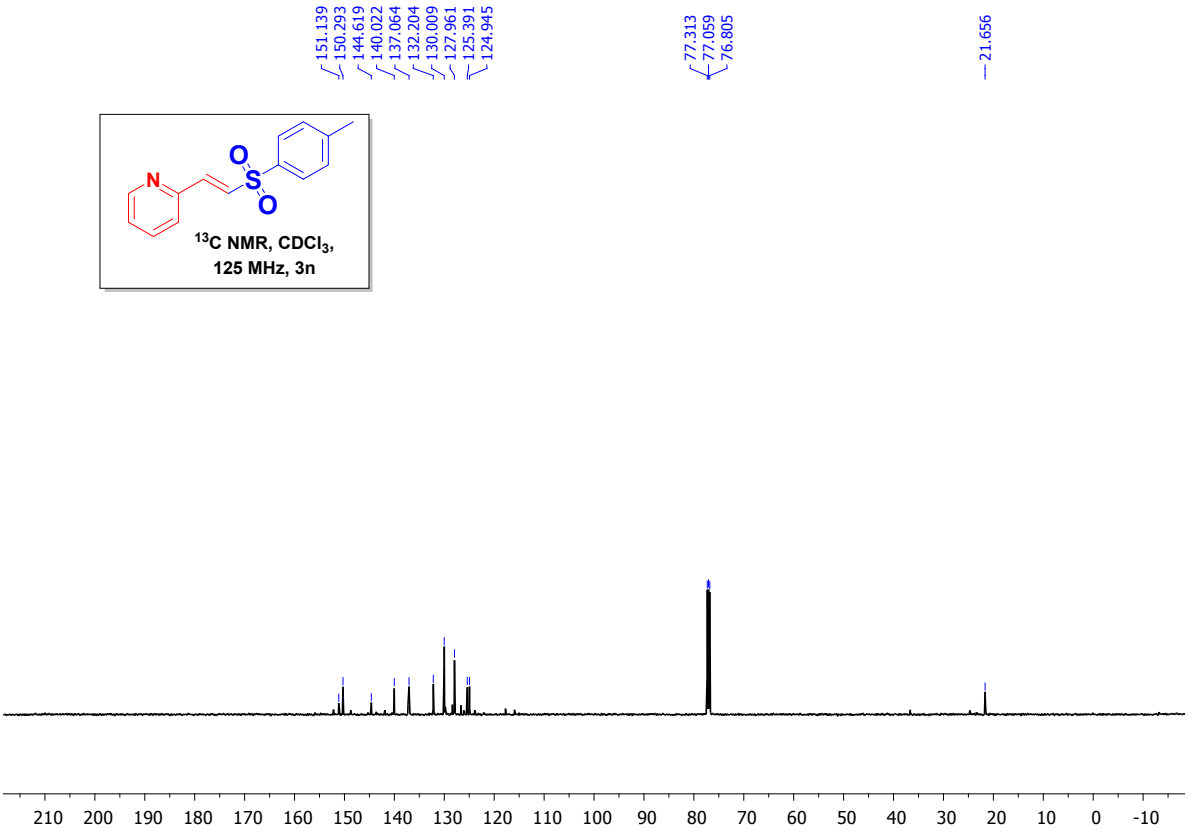


^{1}H and ^{13}C NMR of **3l**

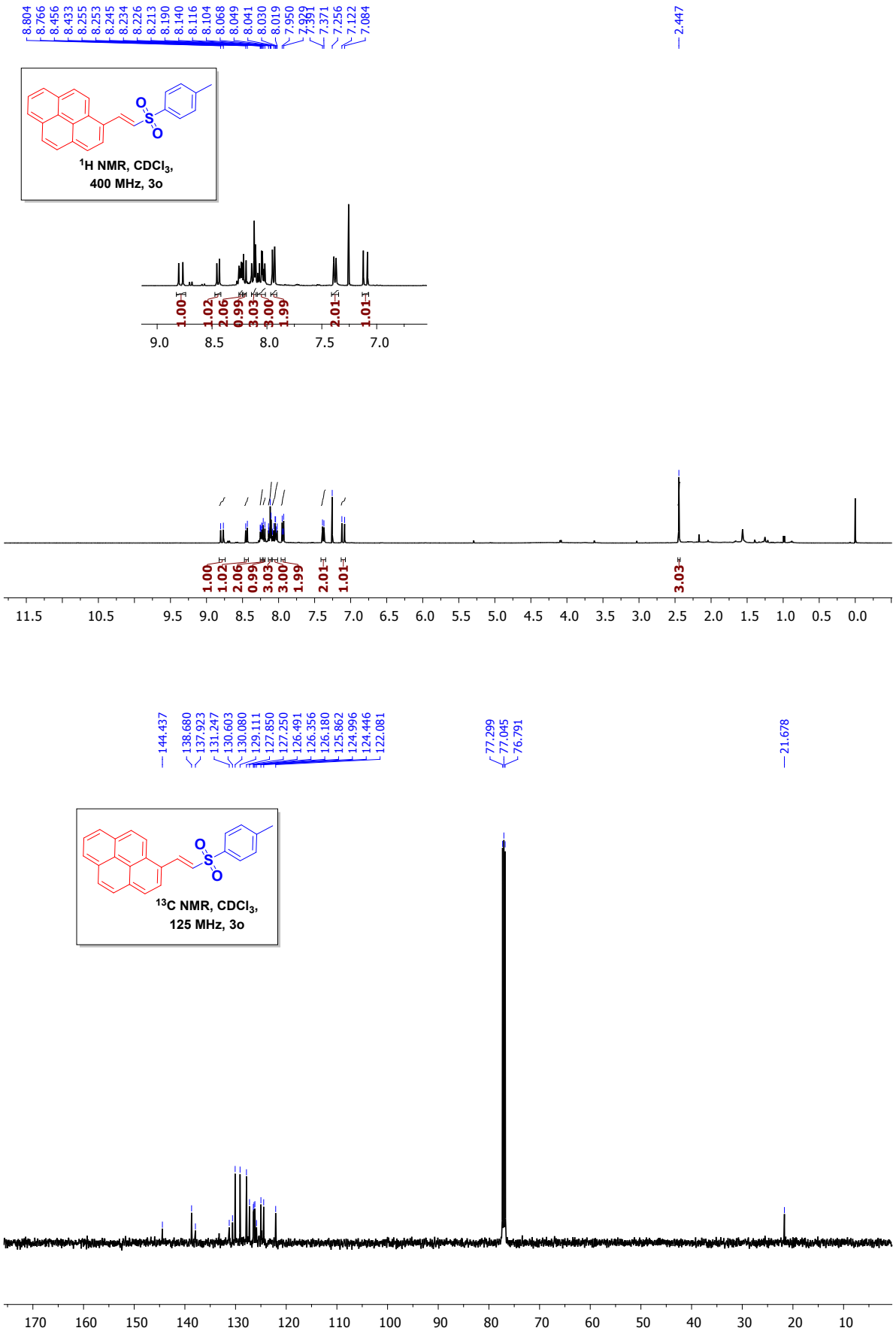


^{1}H and ^{13}C NMR of **3m**

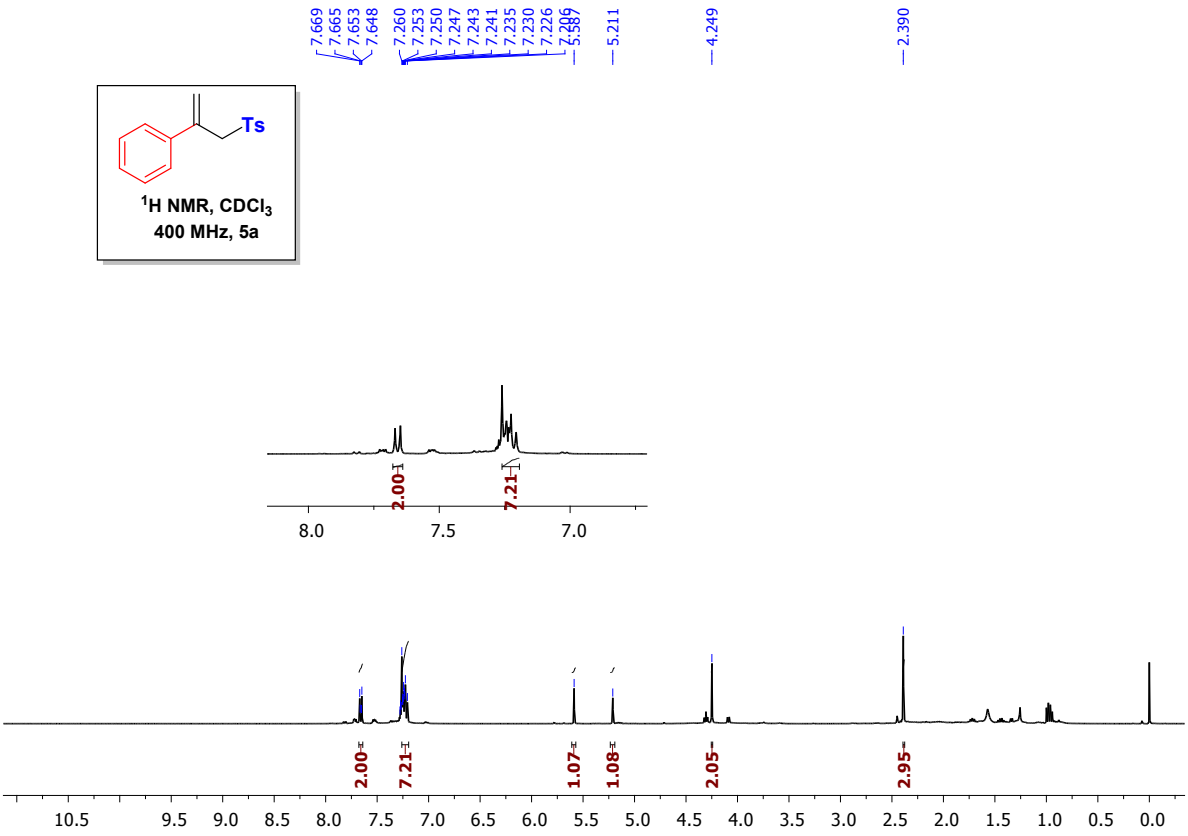


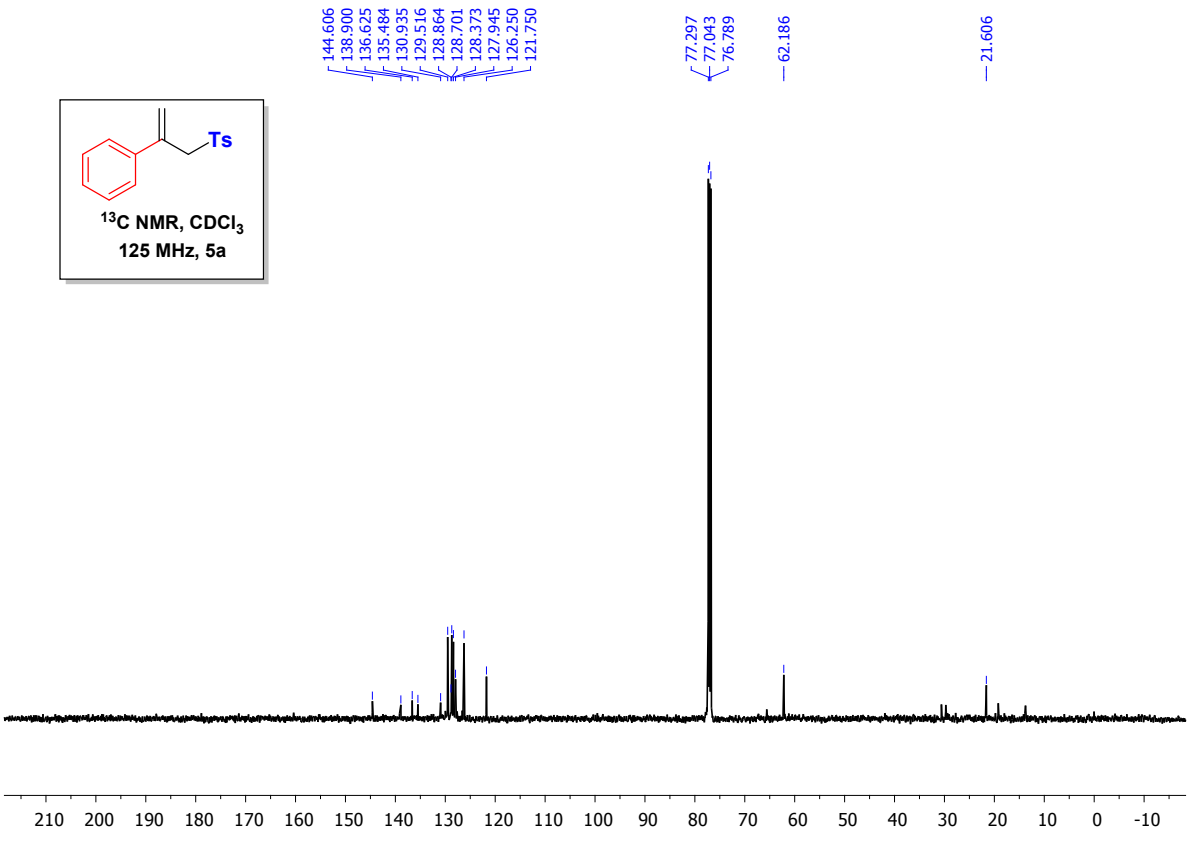


^{1}H and ^{13}C NMR of **3n**

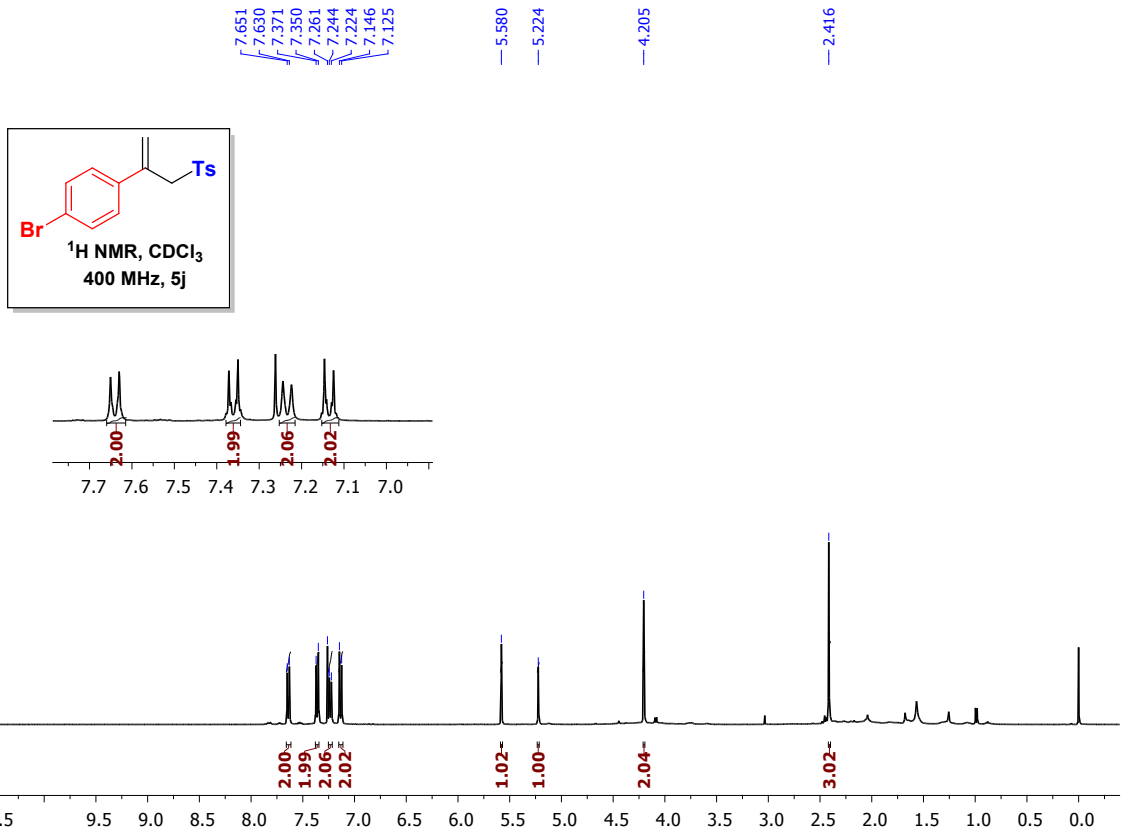


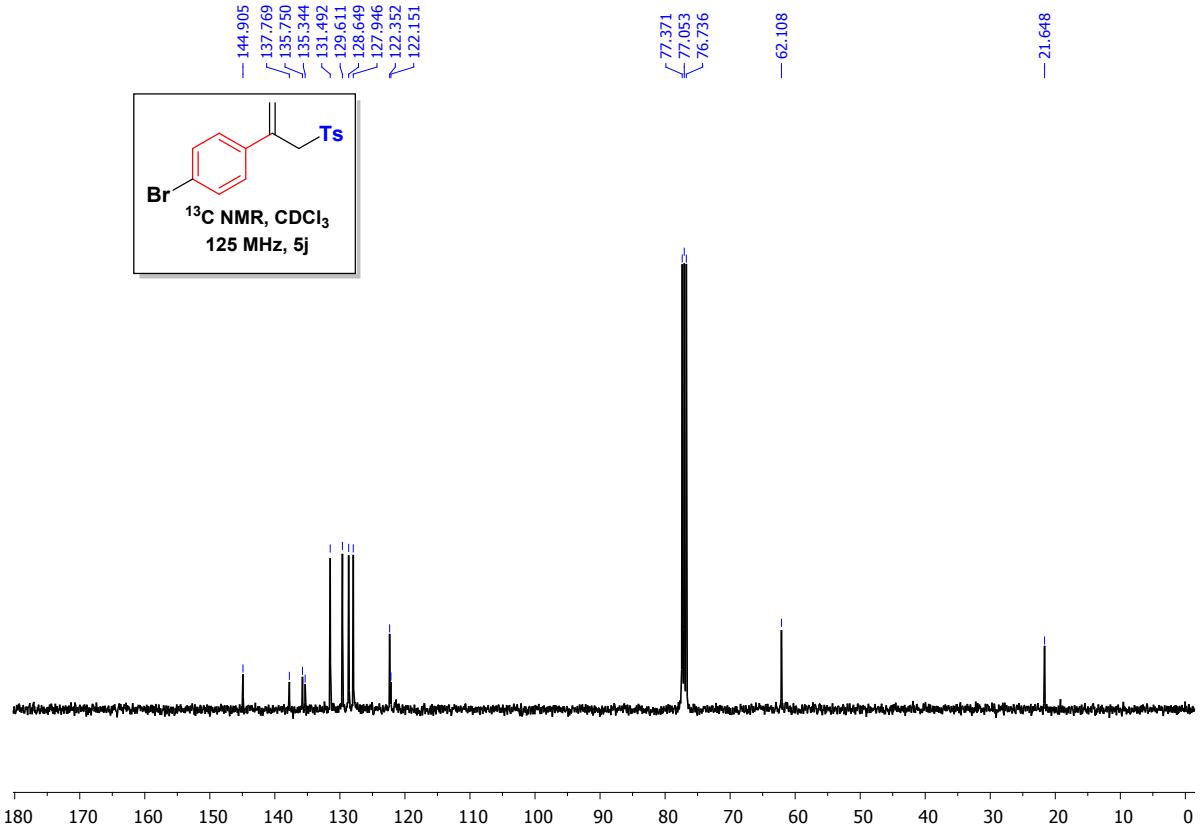
^{1}H and ^{13}C NMR of **3o**





^{1}H and ^{13}C NMR of **5a**


7.651
7.630
7.371
7.350
7.261
7.244
7.224
7.146
7.125
5.580
5.224
4.205
2.416
Ts
Br
1H NMR, CDCl3
400 MHz, 5j
2.00
1.99
2.06
2.02
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
2.00
1.99
2.06
2.02
1.02
1.00
2.04
3.02
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

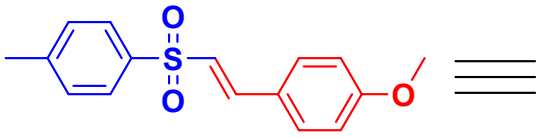

144.905
137.769
135.750
135.344
131.492
129.611
128.649
127.946
122.352
122.151
77.371
77.053
76.736
62.108
21.648
Ts
Br
13C NMR, CDCl3
125 MHz, 5j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

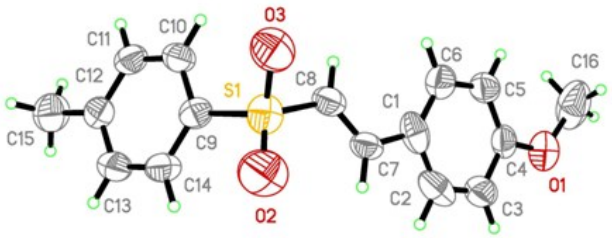
Single Crystal X-ray Data of compound (3e)

X-ray data of compound was collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[1] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS[2] and refinement was carried out by full-matrix least-squares technique using SHELXL.[2] Anisotropic displacement parameters were included for all non-hydrogen atoms. The atoms C7-C8 were disordered over two sites (C7/C8 and C71/C81). The site-occupancy factors of disordered atoms were refined with same occupancies of 0.5. SIMU constraint was applied to the disordered atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(c) for other H atoms]. The methyl groups were allowed to rotate but not to tip.

Crystal Data for AY66: $C_{16}H_{16}O_3S$ (*M* =288.35): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 5.9262(4) Å, *b* = 8.0475(5) Å, *c* = 31.957(2) Å, *V* = 1524.08(17) Å^3, *Z* = 4, *T* = 294.15 K, μ(MoKα) = 0.216 mm^{-1}, *Dcalc* = 1.257 g/mm^3, 16245 reflections measured (5.098 ≤ 2Θ ≤ 52.482), 3077 unique (R_{int} = 0.0316) which were used in all calculations. The final R_1 was 0.0663 (I > 2σ(I)) and wR_2 was 0.1804 (all data).CCDC 1053806 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].





SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.

1. Sheldrick, G. M. (2015). Acta Cryst. C71, 3–8.

Figure caption: The molecular structure of AY83, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Minor component of the disordered atoms (C71/C81) have been omitted for clarity.