Supporting Information for

Copper catalyzed direct tert-butyl sulfonylation of alkynes with t-butylsulfinamide leading to (*E*)-vinyl tert-butyl sulfones

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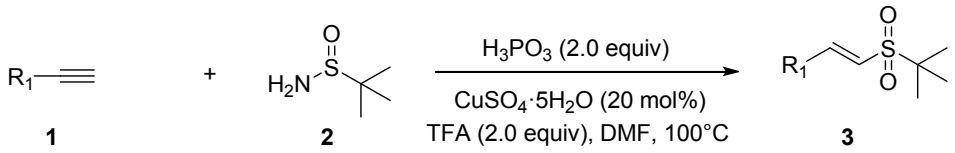
1. General:

NMR spectra were recorded with a 400 NMR spectrometer for ^{1}H-NMR, 100 MHz for ^{13}C-NMR. Proton chemical shifts δ were given in ppm relative to tetramethylsilane (0.00 ppm) in $CDCl_3$. High resolution mass spectra were taken with a 3000 mass spectrometer, using Waters Q-Tof MS/MS system. For column chromatography 200-300 mesh silica gel (GF254) was used as the stationary phase. All reactions were monitored by thin layer chromatography (TLC). All reactions were set up in air (with no use of a glove box). All substrates were purchased commercially and used without further purification.

2. Typical experiment procedure:

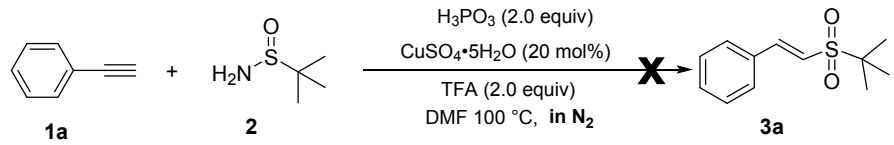


1 **2** **3**

A 50-mL round-bottom flask containing a stirbar was charged with 1.0 mmol of alkynes, 1.2 mmol t-butylsulfinamide, 2.0 mmol of H_3PO_3, 20 mol% of $CuSO_4$•$5H_2O$, 2.0 mmol TFA. The reaction was stirred at 100 °C for 12 h (monitored by TLC). Upon completion of the reaction, the mixture was diluted with brine (20 mL) and extracted with dichloromethane (20.0 mL × 3). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, and filtered. The solvents were removed via rotary evaporator under reduced pressure and the residue was purified with flash chromatography (silica gel, gradient eluent of petroleum ether/ ethyl acetate = 3:1) to yield the desired product. All products shows *E* configuration, indicating a high stereo-selectivity of the this reaction (the related ^{1}HNMR data for supporting the *E* configuration).

3. Experiments on the investigation of mechanism

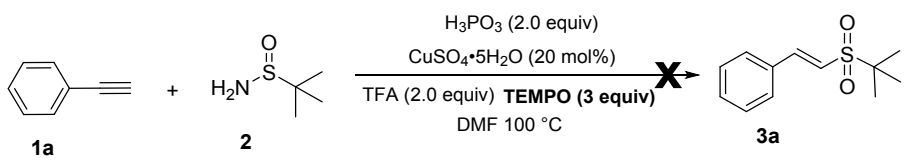
(a) Role of air as the oxidant:



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

1a (1.0 mmol), **2** (1.2 mmol), H_3PO_3 (2.0 mmol), $CuSO_4$•$5H_2O$ (20 mol%), TFA (2.0 mmol) at 100 °C under nitrogen atmosphere for 12 h.

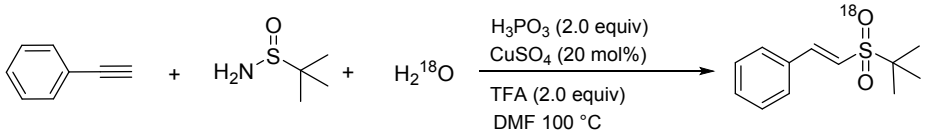
(b) Evidence in support of a radical pathway:



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

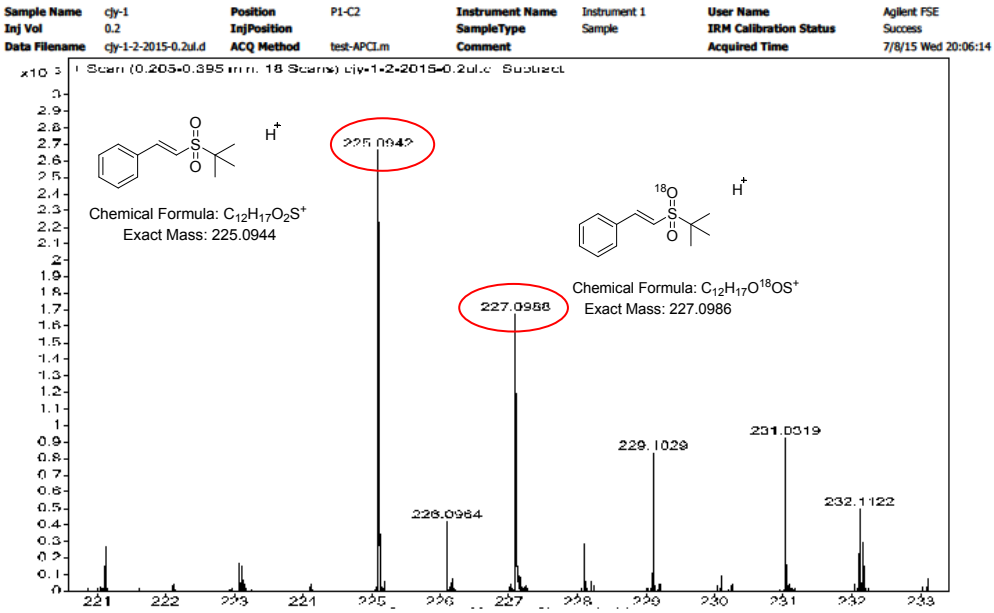
1a (1.0 mmol), **2** (1.2 mmol), H_3PO_3 (2.0 mmol), $CuSO_4$•$5H_2O$ (20 mol%), TFA (2.0 mmol), TEMPO (3 equiv) at 100 °C for 12 h.

(c) Role of $H_2{}^{18}O$:



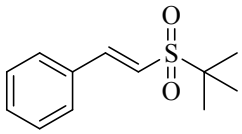
1a (1.0 mmol), **2** (1.2 mmol), $H_2{}^{18}O$ (10 equiv), H_3PO_3 (2.0 mmol), $CuSO_4$ (20 mol%), TFA (2.0 mmol), at 100°C for 12 h.

The HRMS spectra of products was listed as bellow:



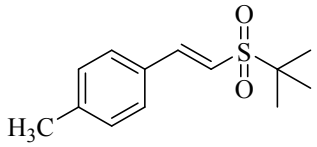
4. Characterization of compounds

(*E*)-(2-(tert-butylsulfonyl)vinyl)benzene (3a)



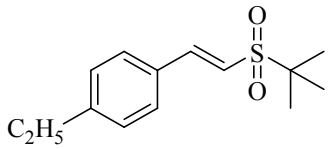
Yellow solid Mp:98~100 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.59 (d, *J*=15.6 Hz, 1H), 7.55-7.53 (m, 2H), 7.46-7.43 (m, 3H), 6.83 (d, *J*=15.6 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 146.5, 132.5, 131.3, 129.2, 128.6, 120.6, 59.0, 23.4; HRMS: $C_{12}H_{16}O_2S$ $[M+Na]^+$ 247.0763, found 247.0768.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)-4-methylbenzene (3b)



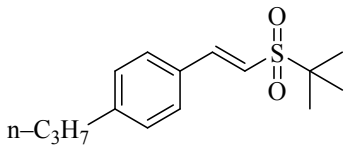
Yellow solid Mp:127~133 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.55 (d, *J*=15.2Hz, 1H), 7.43(d, *J*=8.4 Hz, 2H), 7.23 (d, *J*=8.0 Hz, 2H), 6.77 (d, *J*=15.2 Hz, 1H), 2.40 (s, 3H), 1.42(s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 146.5, 141.9, 129.9, 129.8, 128.6, 119.3, 58.9, 23.5, 21.6; HRMS: $C_{13}H_{18}O_2S$ $[M+Na]^+$ 261.0920, found 261.0923.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)-4-ethylbenzene (3c)



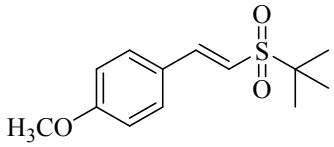
Yellow solid Mp:51~57 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.56 (d, *J*=15.6 Hz, 1H), 7.46 (d, *J*=8.0 Hz, 2H), 7.26 (d, *J*=6.4 Hz, 2H), 6.77 (d, *J*=15.6 Hz, 1H), 2.69 (q, *J*=7.2 Hz, 2H), 1.42 (s, 9H), 1.25 (t, *J*=7.6 Hz, 3H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 146.5, 141.9, 129.9, 129.8, 128.6, 119.3, 58.9, 23.5, 21.6; HRMS: $C_{14}H_{20}O_2S$ $[M+Na]^+$ 275.1076, found 275.1081.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)-4-propylbenzene (3d)



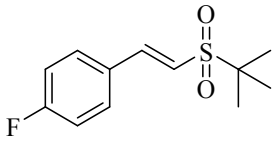
Yellow solid Mp:33~35 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.56 (d, *J*=15.2 Hz, 1H), 7.45 (d, *J*=8.0 Hz, 2H), 7.24 (d, *J*=8.0 Hz, 2H), 6.77 (d, *J*=15.6 Hz, 1H), 2.62 (t, *J*=7.6 Hz, 2H), 1.65(m, 2H), 1.42(s, 9H), 0.95 (t, *J*=7.4 Hz, 3H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 146.7, 146.5, 130.1, 129.3, 128.6, 119.4, 58.9, 37.9, 24.3, 23.5, 13.8; HRMS: $C_{15}H_{22}O_2S$ $[M+Na]^+$ 289.1233, found 289.1237.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)-4-methoxybenzene (3e)



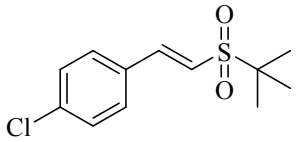
Yellow oil, ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.46-7.39 (t, Ar-H 2H and Ar-CH=CH$SO_2C_4H_9$ 1H), 6.85 (d, *J*=8.8 Hz, 2H), 6.59 (d, *J*=15.2 Hz, 1H), 3.77 (s, 3H), 1.33 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 162.1, 146.1, 130.4, 125.2, 117.6, 114.5, 58.9, 55.5, 23.5; HRMS: $C_{13}H_{18}O_3S$ $[M+H]^+$ 255.1049, found 255.1045.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)-4-fluorobenzene (3f)



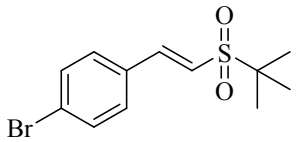
Yellow solid Mp:80~84 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.57-7.52 (m, Ar-H 2H and Ar-CH=CH$SO_2C_4H_9$ 1H), 7.13 (t, *J*=8.4 Hz, 2H), 6.76 (d, *J*=15.2 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 164.4 (*J*=251.6 Hz),, 145.1, 130.6 (*J*=8.6 Hz), 128.8 (*J*=3.5 Hz), 120.5 (*J*=2.2 Hz), 116.4 (*J*=21.9 Hz), 58.4, 23.4; HRMS: $C_{12}H_{15}FO_2S$ $[M+H]^+$ 243.0850, found 243.0846.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)-4-chlorobenzene (3g)



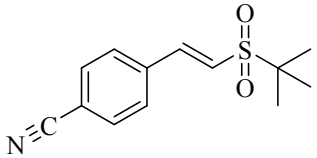
Yellow solid Mp:119~121 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.54 (d, *J*=15.6Hz 1H), 7.47 (d, *J*=8.8 Hz, 2H), 7.40 (d, *J*=8.8 Hz, 2H), 6.83 (d, *J*=15.6 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 144.9, 137.3, 131.0, 129.7, 129.5, 121.4, 59.0, 23.4; HRMS: $C_{12}H_{15}ClO_2S$ $[M+H]^+$ 259.0554, found 259.0552.

(*E*)-1-bromo-4-(2-(tert-butylsulfonyl)vinyl)benzene (3h)



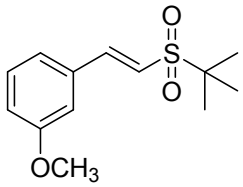
Yellow solid Mp:86~89 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.57 (t, *J*=8.4 Hz 2H), 7.53 (d, *J*=15.6 Hz, 1H), 7.40 (d, *J*=8.4 Hz, 2H), 6.83 (d, *J*=15.6 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 145.0, 132.4, 131.4, 129.9, 125.7, 121.5, 59.0, 23.4; HRMS: $C_{12}H_{15}BrO_2S$ $[M+H]^+$ 303.0049, found 303.0046.

(*E*)-4-(2-(tert-butylsulfonyl)vinyl)benzonitrile (3i)



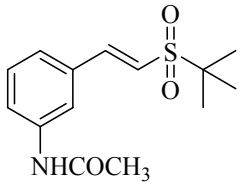
Yellow solid Mp:152~155 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.74 (d, *J*=8.4 Hz, 2H), 7.65 (d, *J*=8.4 Hz, 2H), 7.61 (d, *J*=15.6 Hz, 1H), 6.98 (d, *J*=15.6 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm)143.9, 136.7, 132.9, 128.9, 124.7, 118.0, 114.4, 59.2, 23.4; HRMS: $C_{13}H_{15}NO_2S$ $[M+H]^+$ 250.0896, found 250.0893.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)-3-methoxybenzene (3j)



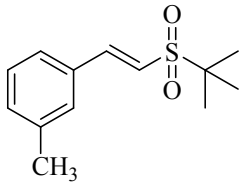
Yellow oil ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.55 (d, *J*=15.6 Hz, 1H), 7.34 (t, *J*=8.0 Hz, 1H), 7.13 (d, *J*=8.0 Hz, 1H), 7.04 (s, 1H), 6.99 (dd, *J*=2.8 Hz, *J*=8.4 Hz, 1H), 6.82(d, *J*=15.6 Hz, 1H), 3.84 (s, 3H), 1.42 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 160.0, 146.4, 133.8, 130.2, 121.1, 120.9, 117.0, 113.5, 60.4, 55.4, 23.4; HRMS: $C_{13}H_{18}O_3S$ $[M+H]^+$ 255.1049, found 255.1047.

(*E*)-N-(3-(2-(tert-butylsulfonyl)vinyl)phenyl)acetamide (3k)



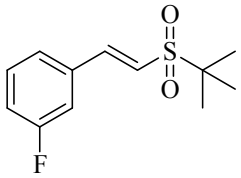
Yellow solid Mp:47~49 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.79 (s, -NH- 1H and Ar-H), 7.58 (d, *J*=8.4 Hz, 1H), 7.53 (d, *J*=15.6 Hz, 1H), 7.35 (t, *J*=7.8 Hz, 1H), 7.23 (d, *J*=7.6 Hz, 1H), 6.84 (d, *J*=15.6 Hz, 1H), 2.20 (s, 3H), 1.42 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 168.8, 146.2, 138.9, 133.2, 129.7, 124.4, 122.5, 121.1, 119.4, 59.0, 24.6, 23.4; HRMS: $C_{14}H_{19}NO_3S$ $[M+H]^+$ 282.1158，found 282.1156.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)-3-methylbenzene (3l)



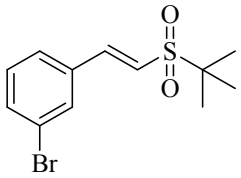
Yellow solid Mp:68~72 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.56 (d, *J*=15.6 Hz, 1H), 7.34-7.42 (t, 3H), 7.27-7.25 (d, 1H), 6.81 (d, *J*=15.6 Hz, 1H), 2.39 (s, 3H), 1.42 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 146.7, 138.9, 132.5, 132.1, 129.2, 129.0, 125.8, 120.4, 58.9, 23.5, 21.3; HRMS: $C_{13}H_{18}O_2S$ $[M+H]^+$ 239.1100, found 239.1097F.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)-3-fluorobenzene (3m)



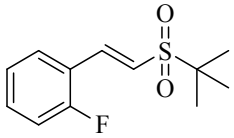
Yellow solid Mp:85~89 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.56 (d, *J*=15.6 Hz, 1H), 7.44-7.39 (m, 1H), 7.31 (d, 1H), 7.25-7.22 (m, 1H), 7.18-7.13 (m, 1H), 6.84 (d, *J*=15.6 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 163.0 (*J*=246 Hz), 145.0, 134.7(*J*=8.0 Hz), 130.8 (*J*=8.0 Hz) , 124.6 (*J*=3.0 Hz), 122.3, 118.2 (*J*=21.0 Hz), 114.8 (*J*=22.0 Hz), 59.0, 23.4; HRMS: $C_{12}H_{15}FO_2S$ $[M+H]^+$ 243.0850, found 243.0848.

(*E*)-1-bromo-3-(2-(tert-butylsulfonyl)vinyl)benzene (3n)



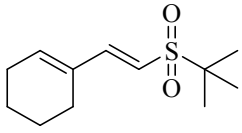
Yellow solid Mp:43~47 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.68 (s, 1H), 7.58 (d, *J*=8.0 Hz, 1H), 7.52 (d, *J*=15.6 Hz, 1H), 7.45 (d, *J*=8.0 Hz, 1H), 7.31 (t, *J*=8.0 Hz, 1H), 6.84 (d, *J*=15.6 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 144.7, 134.6, 134.0, 131.1, 130.7, 127.2, 123.3, 122.4, 59.0, 23.4; HRMS: $C_{12}H_{15}BrO_2S$ $[M+H]^+$ 303.0049, found 303.0047.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)-2-fluorobenzene (3o)



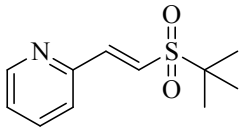
Yellow solid Mp:80~84 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.97 (d, *J*=15.2 Hz, 1H), 7.58 (d, *J*=7.6 Hz, 1H), 7.46 (d, *J*=8.0 Hz, 1H), 7.38 (t, *J*=7.2 Hz, 1H), 7.33 (t, *J*=7.2 Hz, 1H), 6.86 (d, *J*=15.6 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 142.8, 135.1, 131.9, 131.1, 130.4, 128.5, 127.3, 123.9, 59.0, 23.4; HRMS: $C_{12}H_{15}FO_2S$ $[M+H]^+$ 243.0850, found 243.0849.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)cyclohex-1-ene (3p)



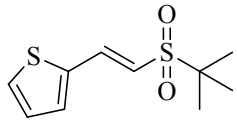
Yellow solid Mp:32~36 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.16 (d, *J*=15.2 Hz, 1H), 6.28 (t, *J*=4.0 Hz, 1H), 6.12 (d, *J*=15.2 Hz, 1H), 2.26-2.25 (d, 2H), 2.24-2.14 (d, 2H), 1.75-1.69 (m, 2H), 1.67-1.61 (m, 2H), 1.37 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 149.7, 141.6, 133.4, 116.7, 58.7, 26.5, 24.3, 23.4, 21.83, 21.76; HRMS: $C_{12}H_{20}O_2S$ $[M+H]^+$ 229.1257, found 229.1254.

(*E*)-2-(2-(tert-butylsulfonyl)vinyl)pyridine (3q)



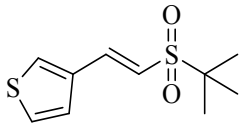
Yellow oil, ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 8.67 (d, *J*=4.8Hz, 1H), 7.78-7.74 (m, 1H), 7.59 (d, *J*=15.2 Hz, 1H), 7.46 (d, *J*=15.2 Hz, 1H), 7.42 (d, *J*=8.0 Hz, 1H), 7.35-7.31 (m, 1H), 1.44 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 151.0, 150.4, 144.5, 137.1, 125.5, 125.5, 125.1, 58.8, 23.4; HRMS: $C_{11}H_{15}NO_2S$ $[M+H]^+$ 226.0896, found 226.0893.

(*E*)-2-(2-(tert-butylsulfonyl)vinyl)thiophene (3r)



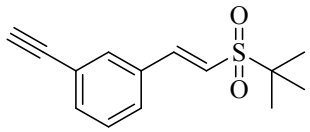
Yellow solid Mp:40~47 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.68 (d, *J*=15.2 Hz, 1H), 7.47 (d, *J*=4.8 Hz, 1H), 7.33 (d, *J*=3.6 Hz, 1H), 7.11-7.09 (m, 1H), 6.60 (d, *J*=15.2 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 138.8, 137.1, 132.4, 129.9, 128.4, 118.8, 59.0 23.4; HRMS: $C_{10}H_{14}O_2S_2$ $[M+H]^+$ 231.0508, found 231.0506.

(*E*)-3-(2-(tert-butylsulfonyl)vinyl)thiophene (3s)



Yellow oil, ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.61-7.55 (m, 2H, Ar-H and $CH_3SO_2CH=C\underline{H}$), 7.40-7.38 (m, 1H), 7.29 (d, *J*=2.8 Hz, 1H), 6.66 (d, *J*=15.6 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 139.8, 135.4, 130.0, 127.6, 125.2, 120.0, 58.9, 23.4; HRMS: $C_{10}H_{14}O_2S_2$ $[M+H]^+$ 231.0508, found 231.0505.

(*E*)-1-(2-(tert-butylsulfonyl)vinyl)-3-ethynylbenzene (3t)



Yellow solid Mp:91~94 °C ^{1}H NMR($CDCl_3$, 400 MHz): δ(ppm) 7.66 (s, 1H), 7.57-7.50 (m, 3H, Ar-H and $CH_3SO_2CH=C\underline{H}$), 7.40 (t, *J*=15.4 Hz 1H), 6.85 (d, *J*=15.5 Hz, 1H), 3.15 (s, 1H), 1.42 (s, 9H); ^{13}C NMR($CDCl_3$, 100 MHz): δ(ppm) 145.23, 134.51, 132.80, 131.82, 129.21, 128.82, 123.30, 121.91, 82.40, 78.54, 58.99, 23.42. HRMS: $C_{14}H_{16}OS_2$ $[M+H]^+$ 249.0944, found 249.0941.

5. **^{1}H NMR, and ^{13}C NMR copies of products**

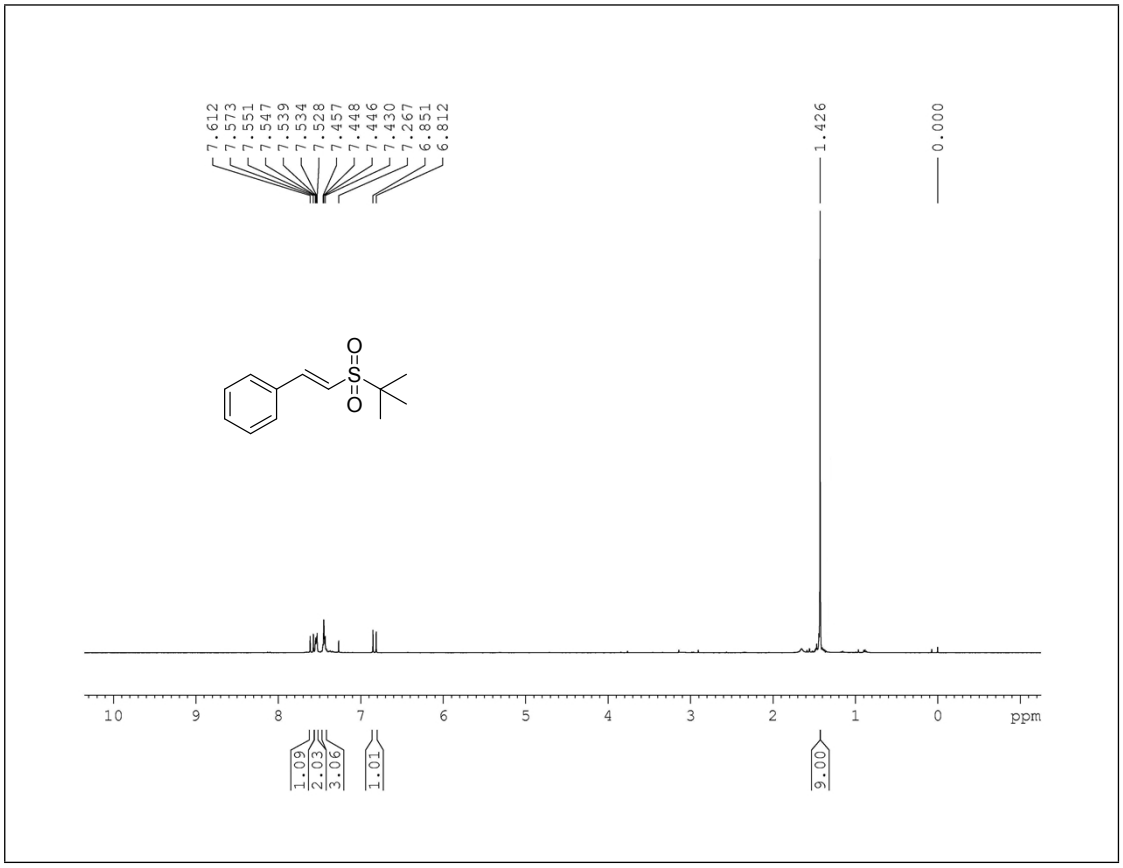


Fig 1. ^{1}H-NMR spectrum of **3a**

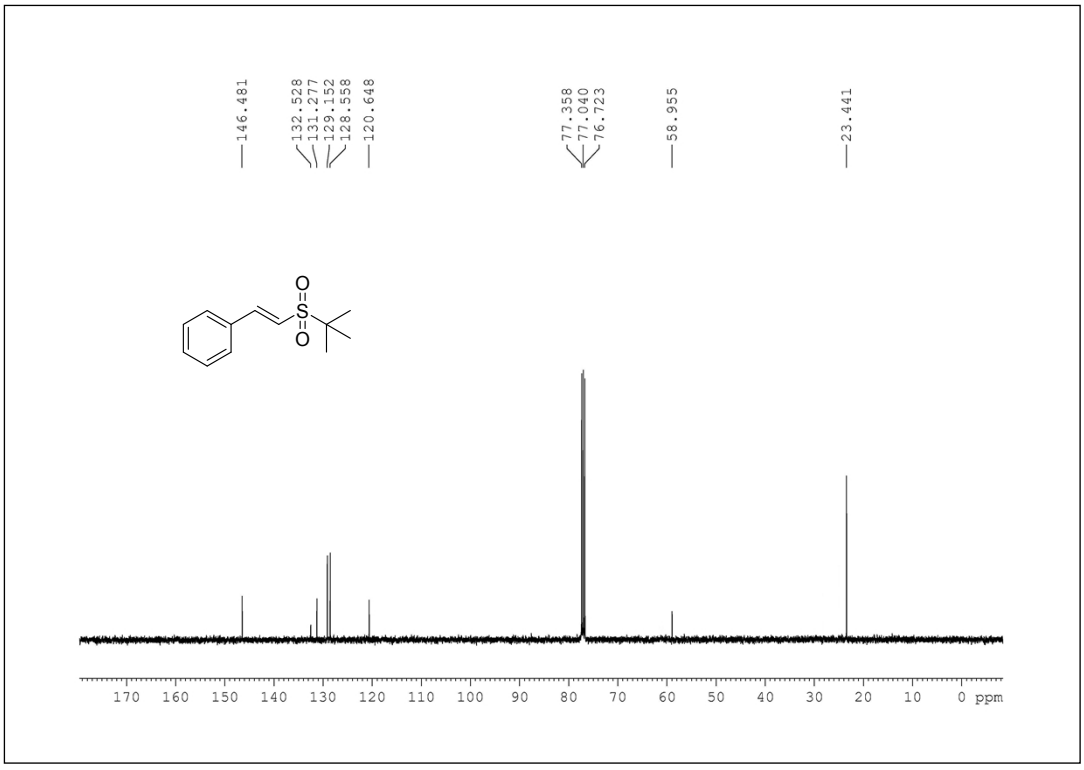


Fig 2. ^{13}C-NMR spectrum of **3a**

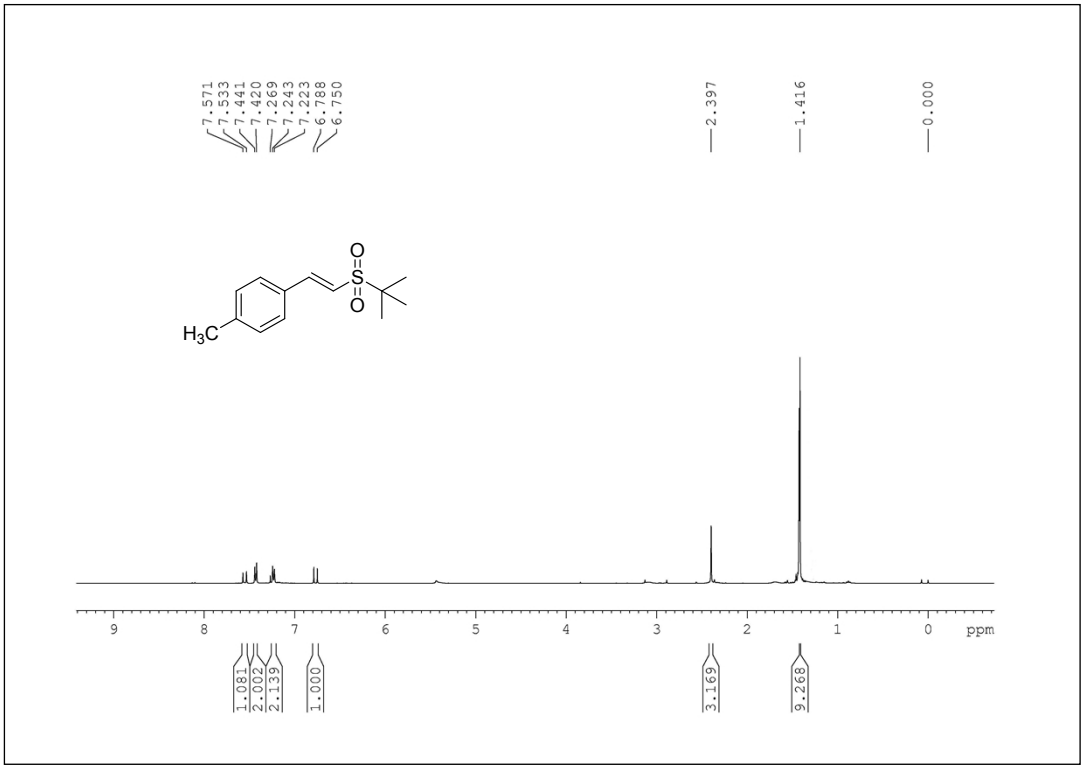


Fig 3. ^{1}H-NMR spectrum of **3b**

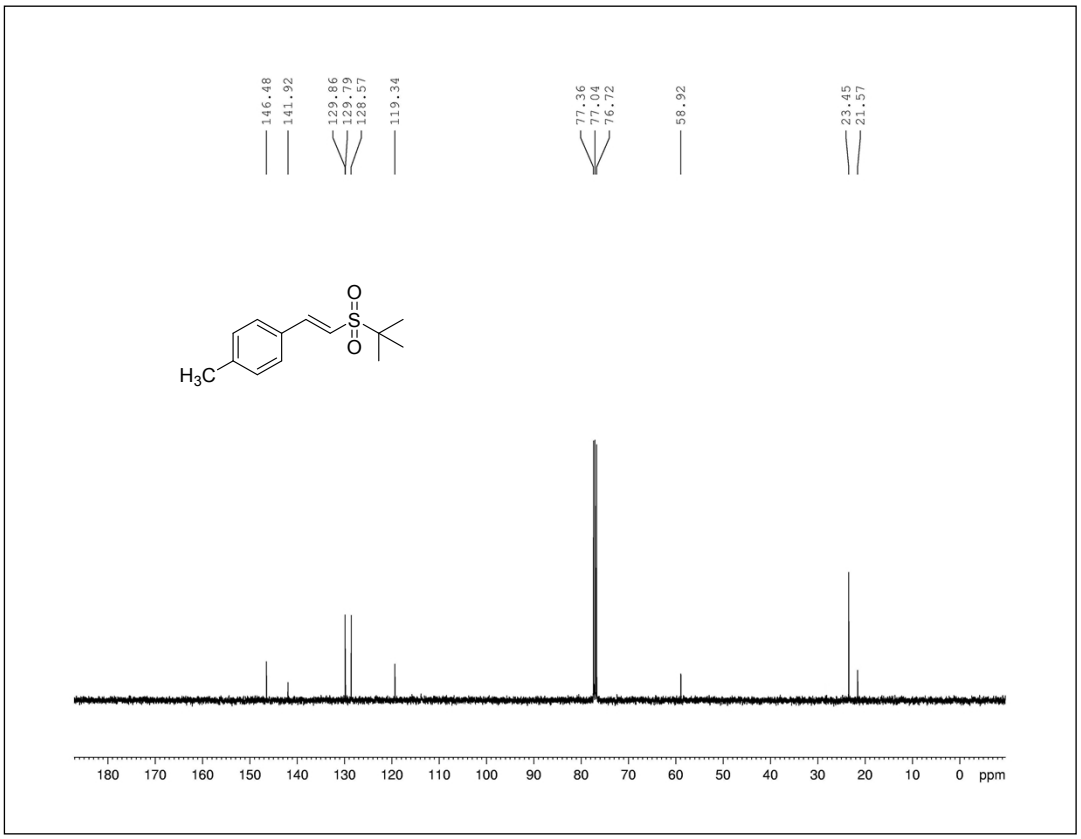


Fig 4. ^{13}C-NMR spectrum of **3b**

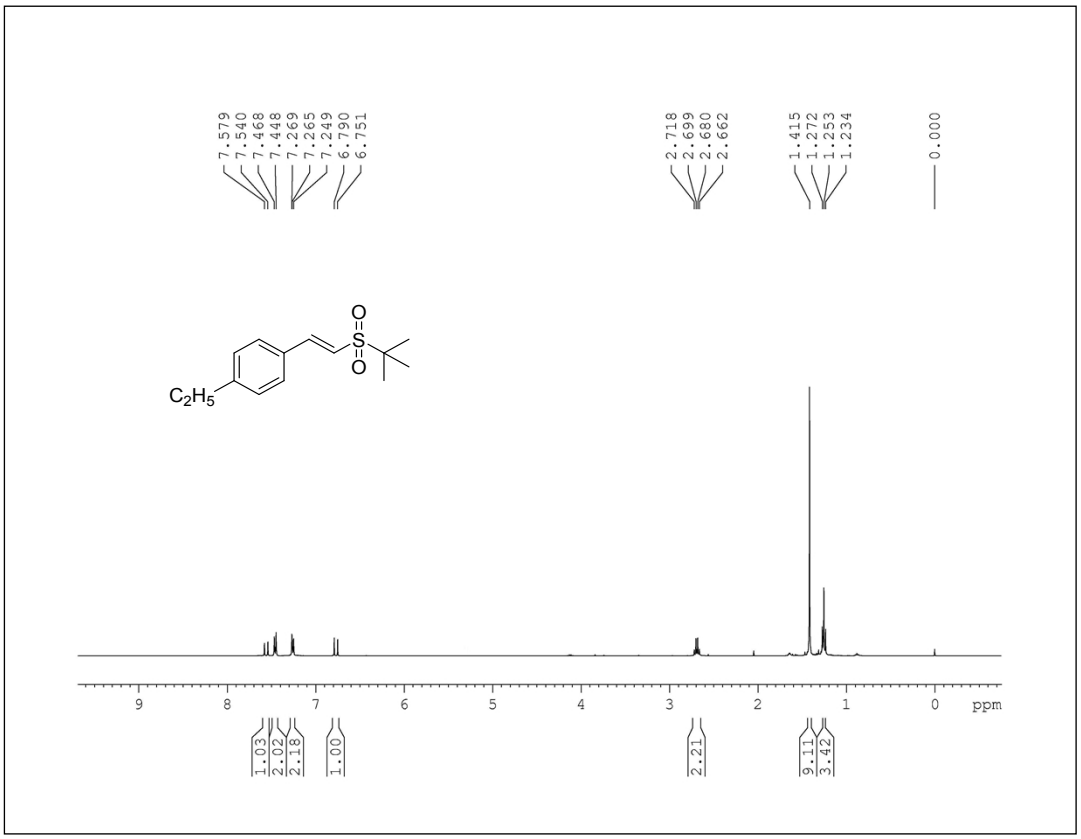


Fig 5. ^{1}H-NMR spectrum of **3c**

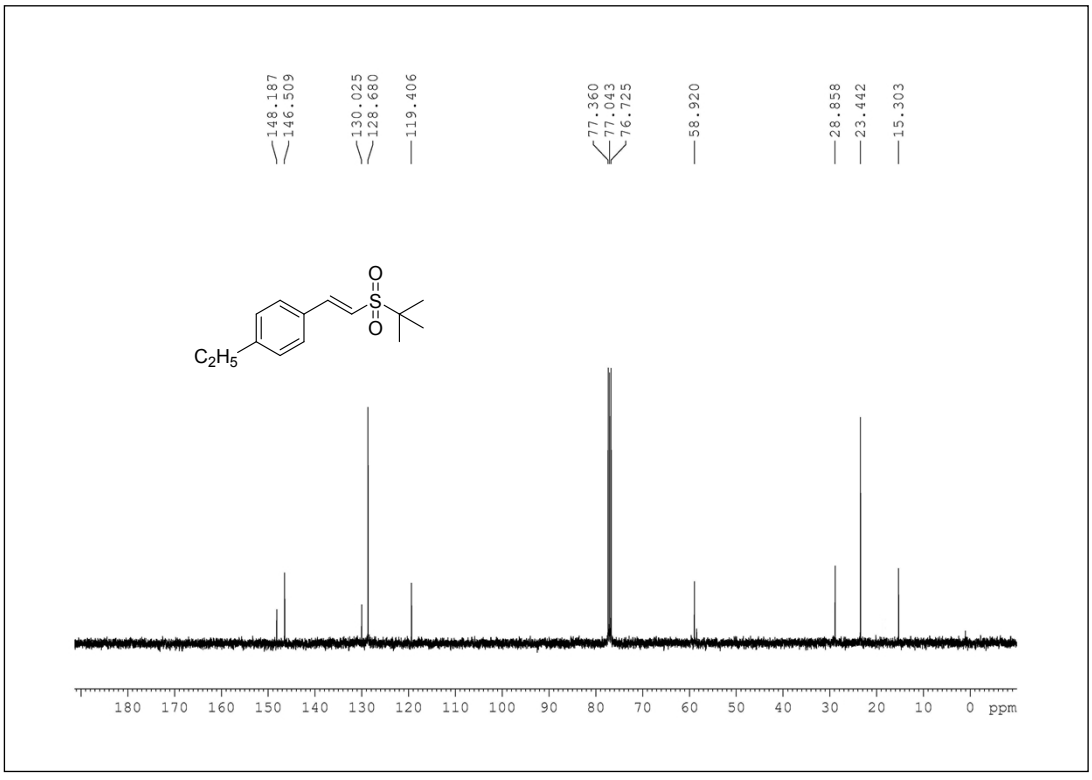


Fig 6. ^{13}C-NMR spectrum of **3c**

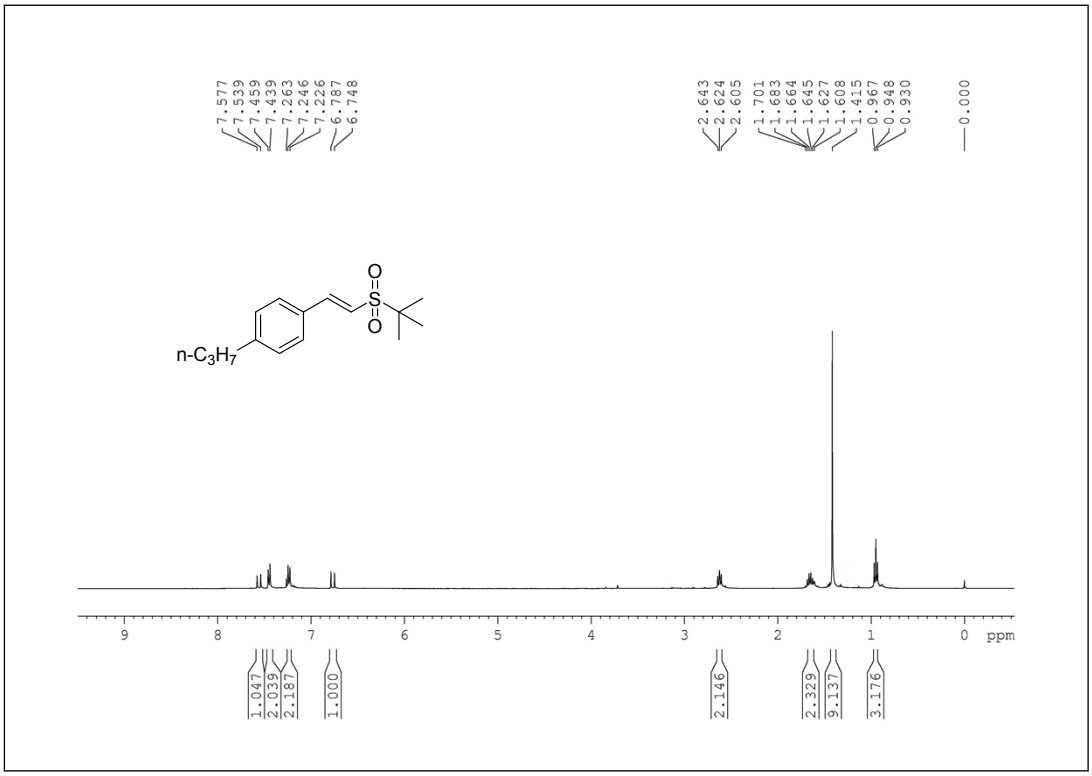


Fig 7. ^{1}H-NMR spectrum of **3d**

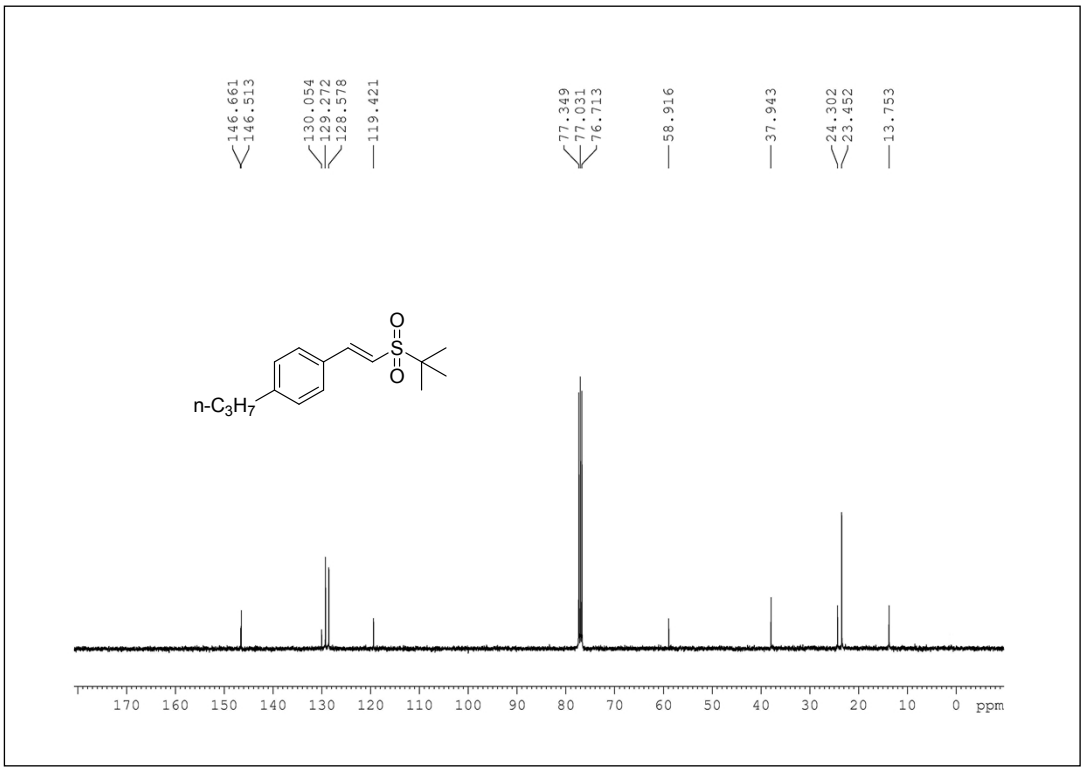


Fig 8. ^{13}C-NMR spectrum of **3d**

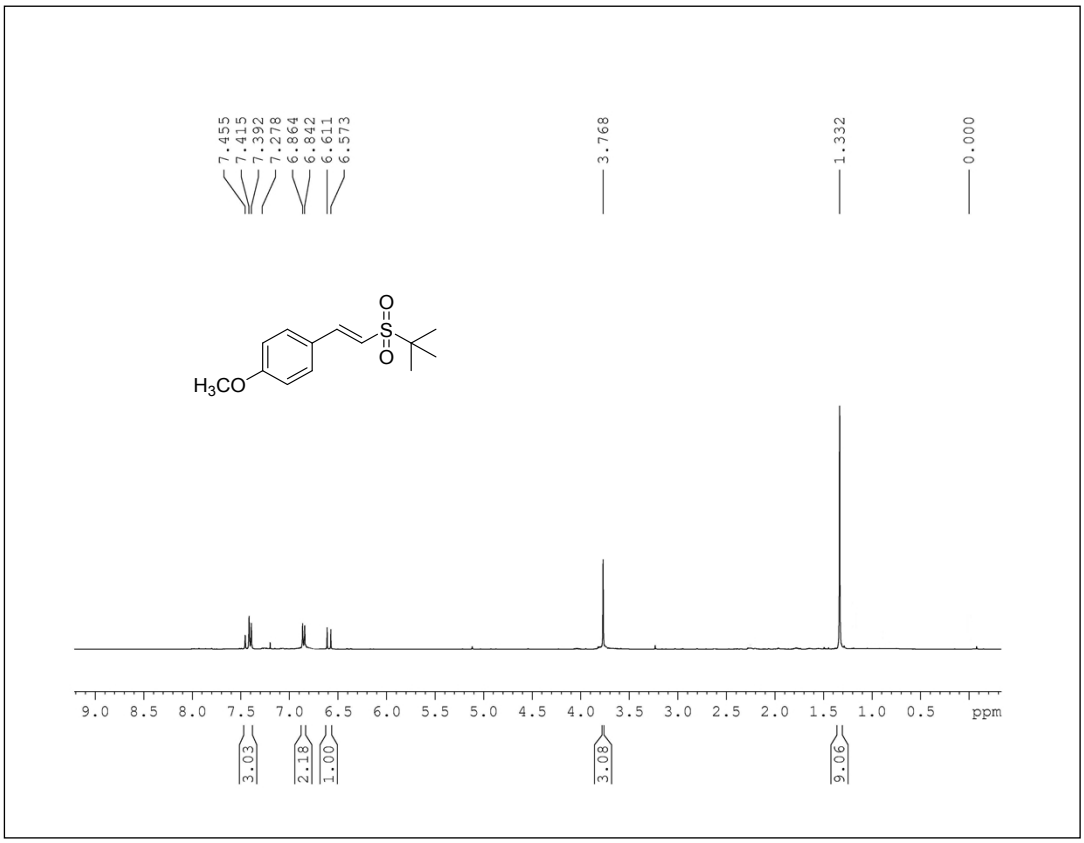


Fig 9. ^{1}H-NMR spectrum of **3e**

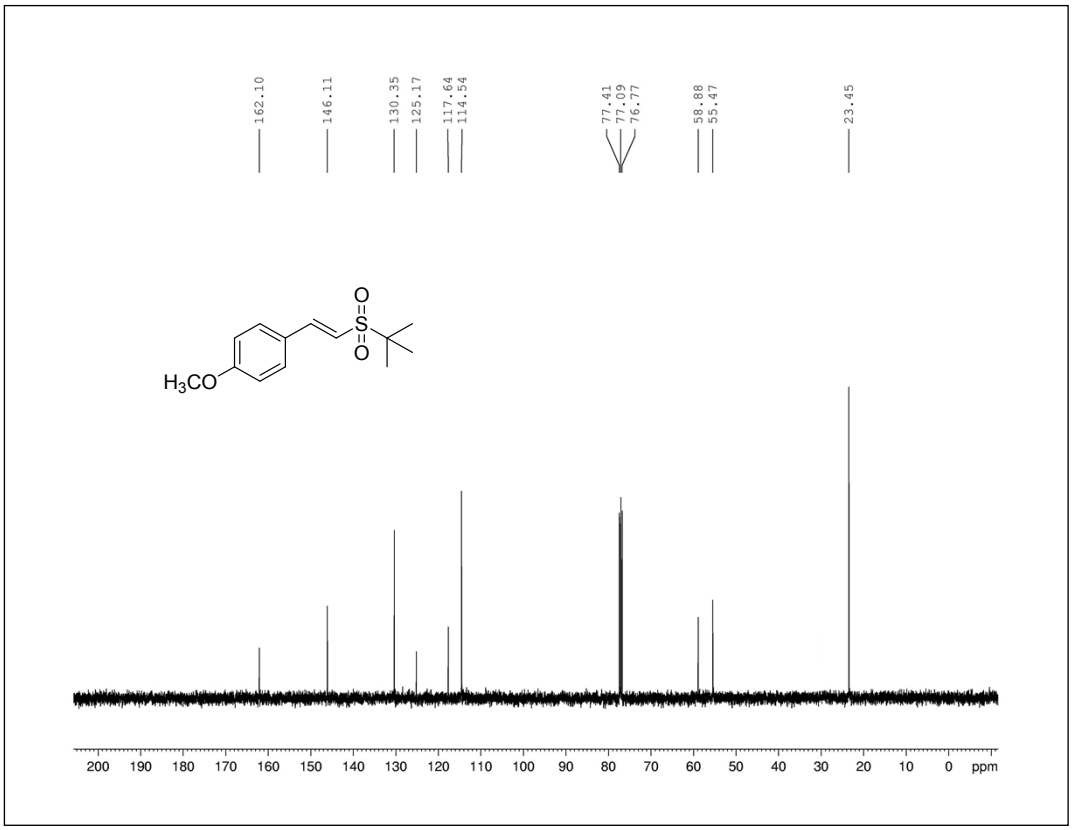


Fig 10. ^{13}C-NMR spectrum of **3e**

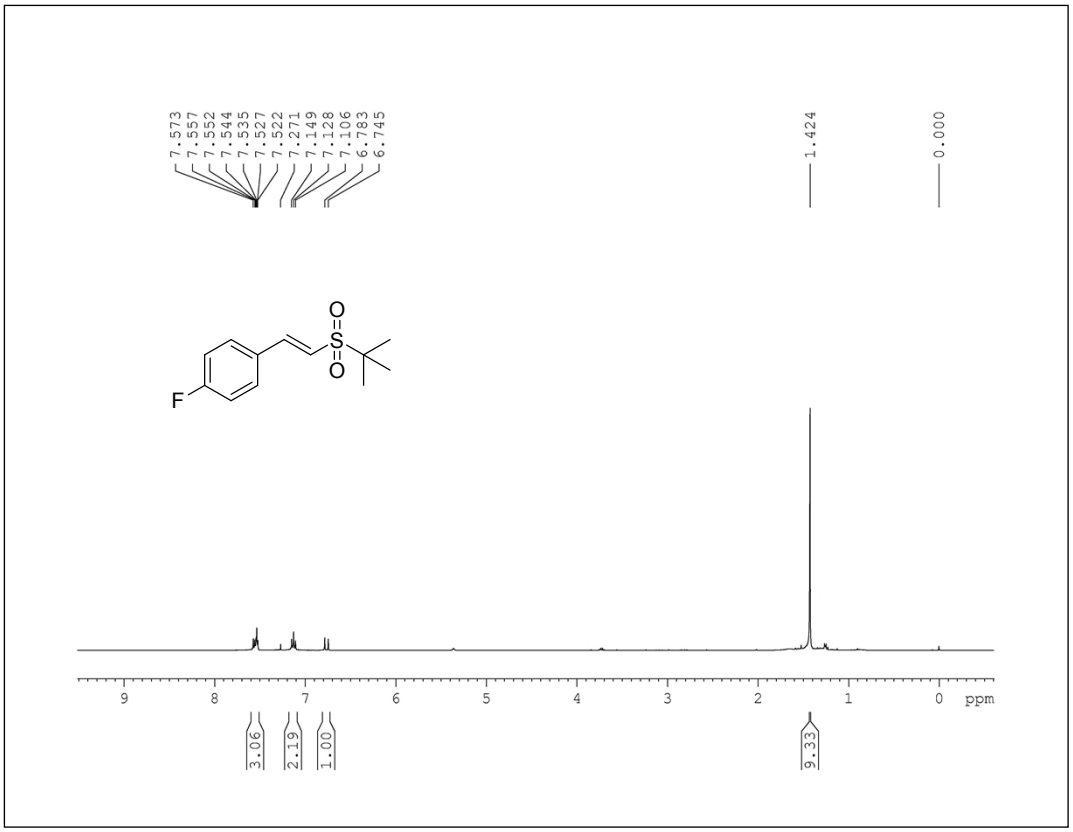


Fig 11. ^{1}H-NMR spectrum of **3f**

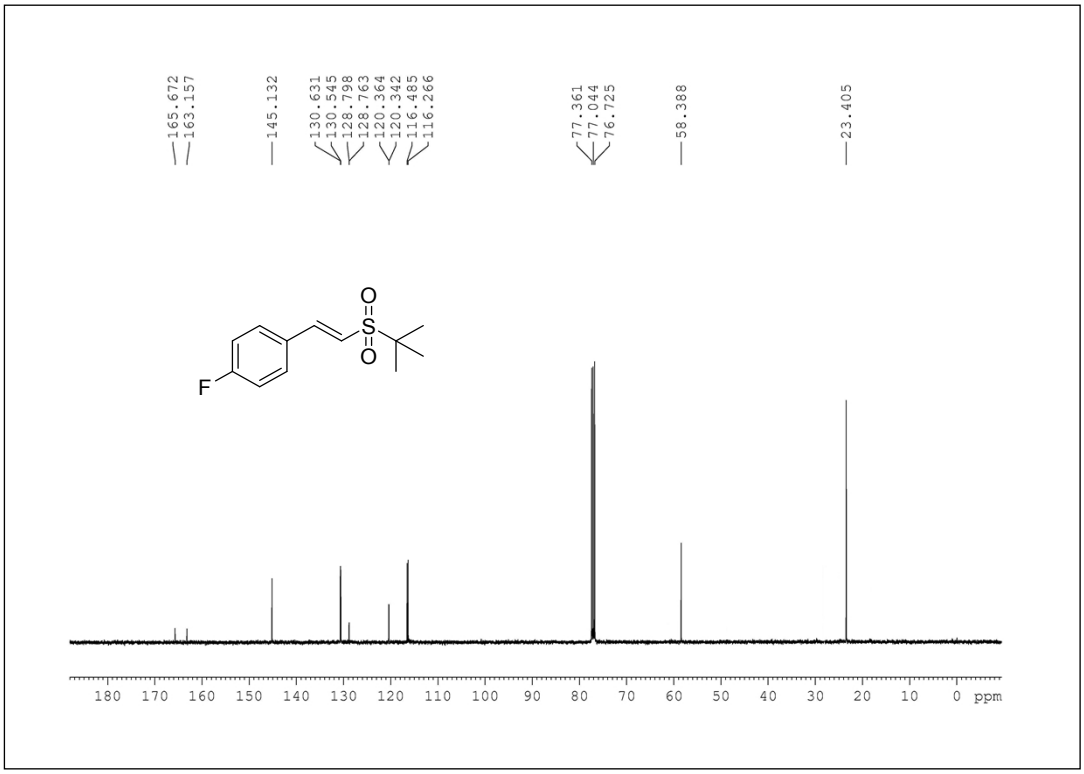


Fig 12. ^{13}C-NMR spectrum of **3f**

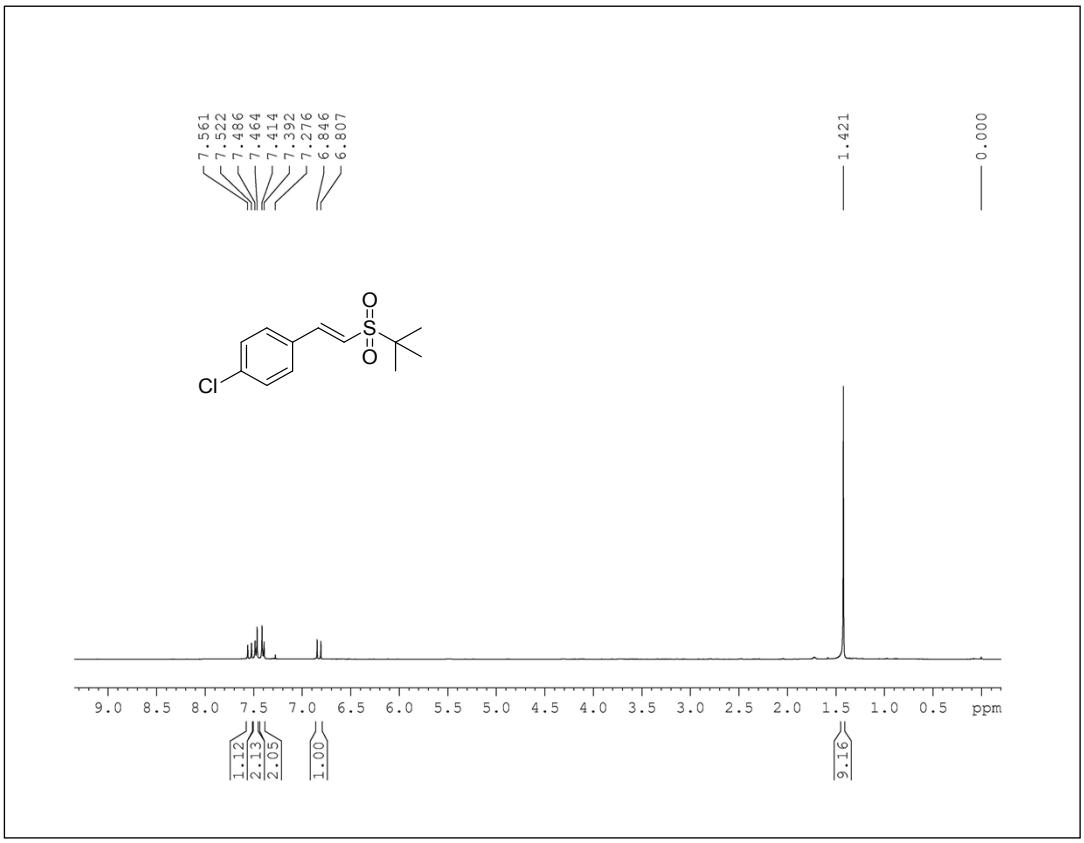


Fig 13. ^{1}H-NMR spectrum of **3g**

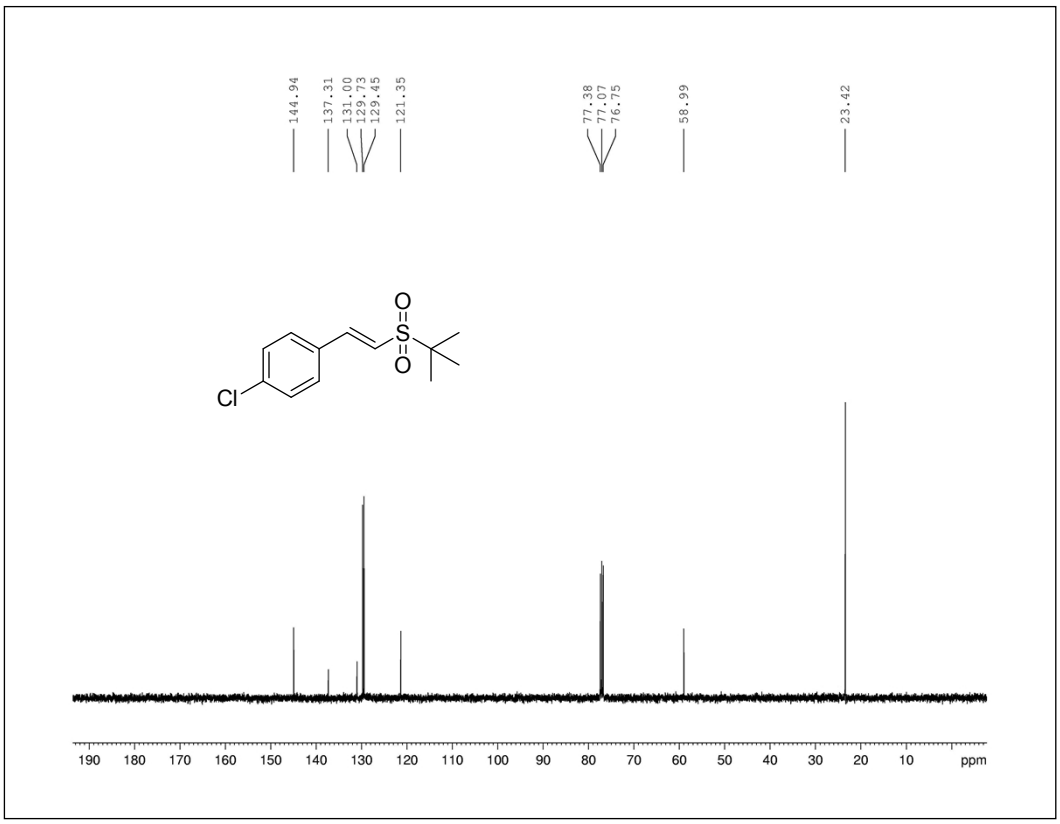


Fig 14. ^{13}C-NMR spectrum of **3g**

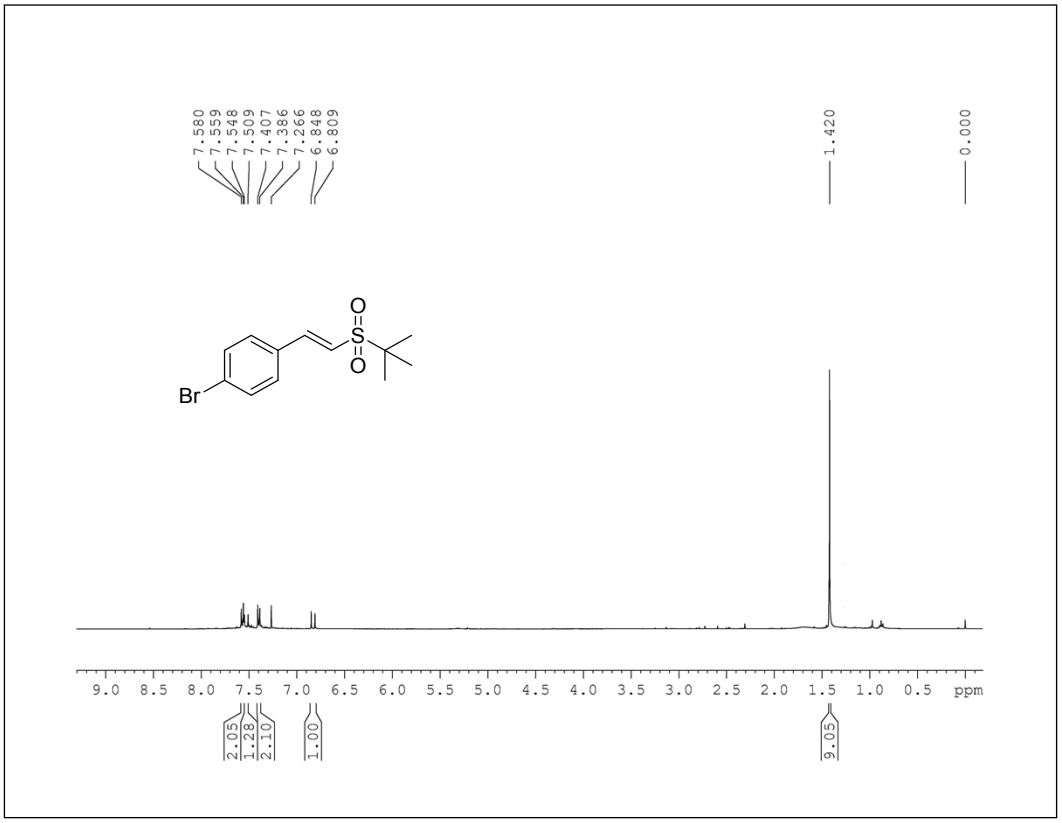


Fig 15. ^{1}H-NMR spectrum of **3h**

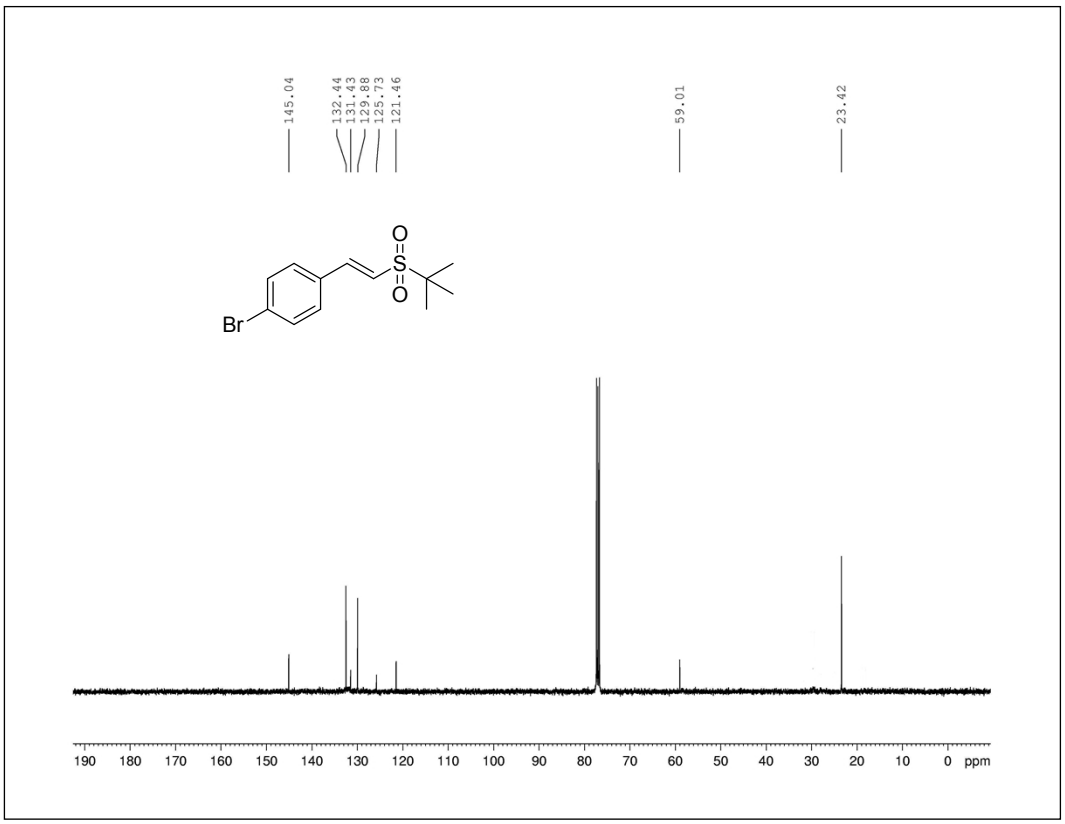


Fig 16. ^{13}C-NMR spectrum of **3h**

Fig 17. ^{1}H-NMR spectrum of **3i**

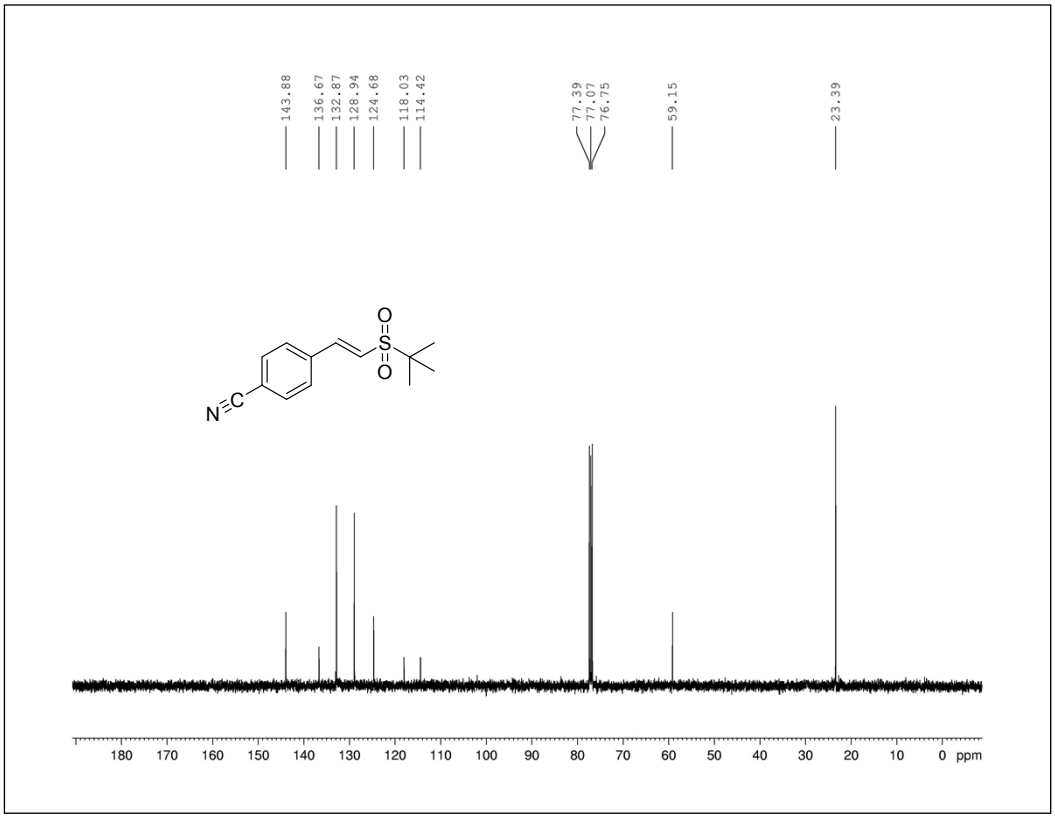


Fig 18. ^{13}C-NMR spectrum of **3i**

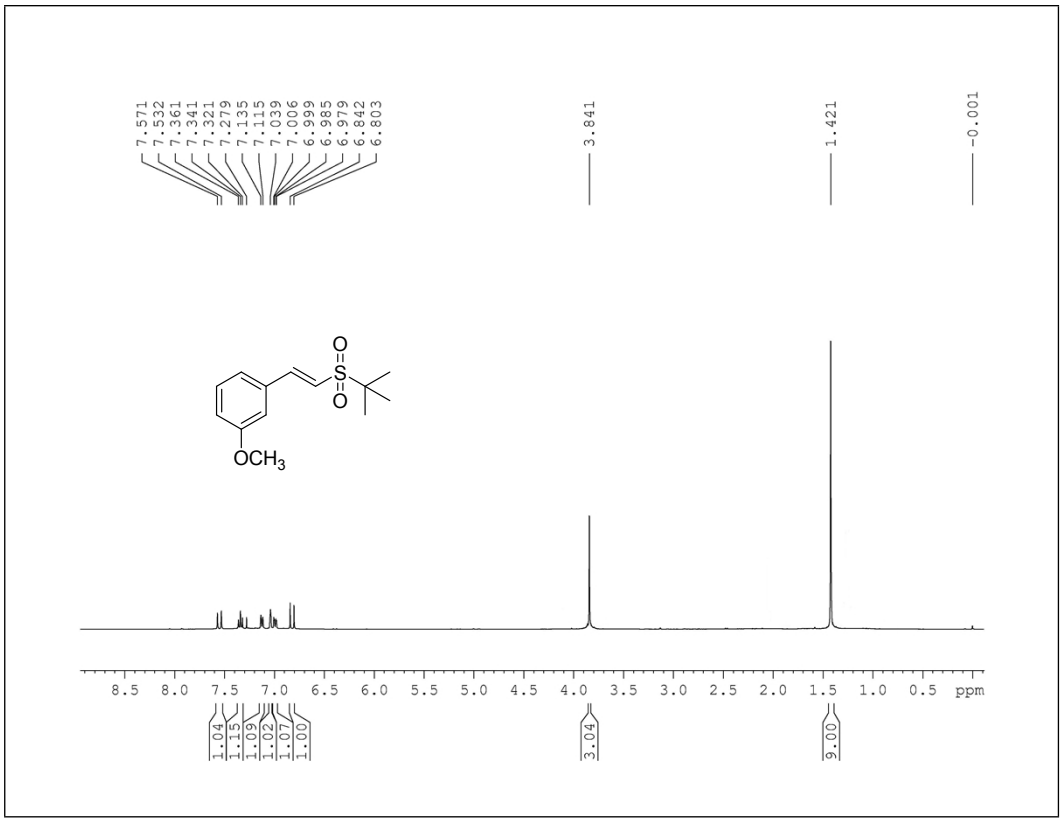


Fig 19. ^{1}H-NMR spectrum of **3j**

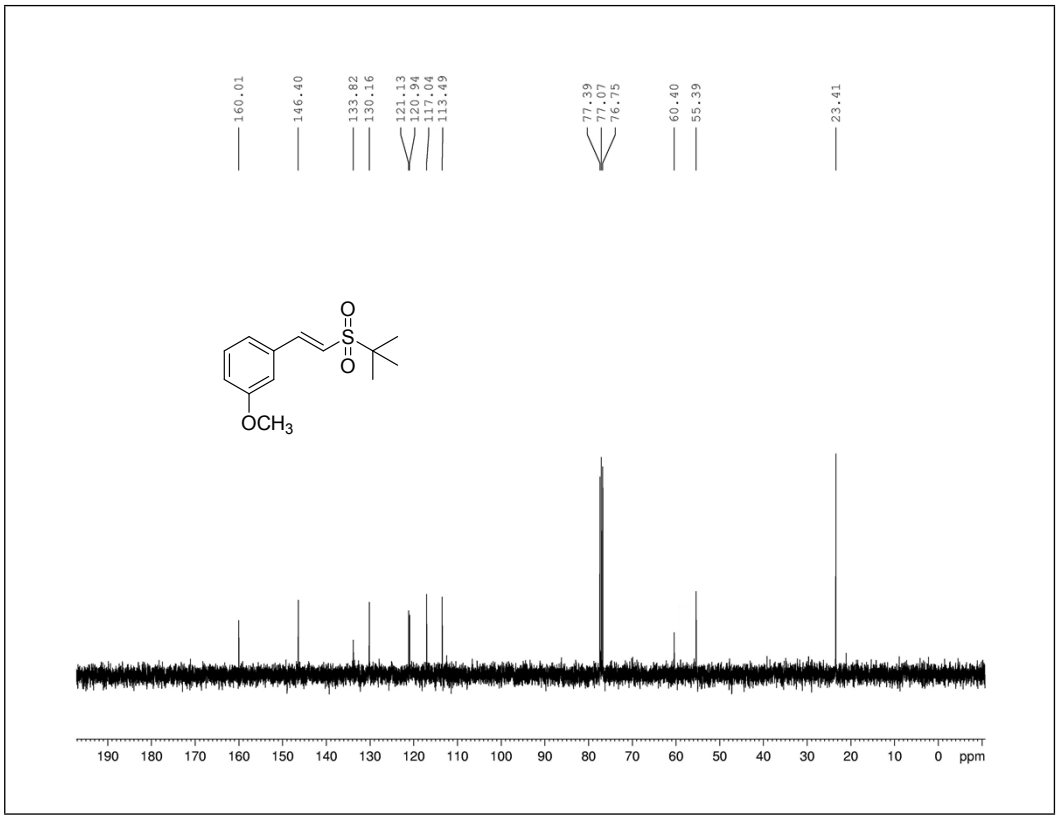


Fig 20. ^{13}C-NMR spectrum of **3j**

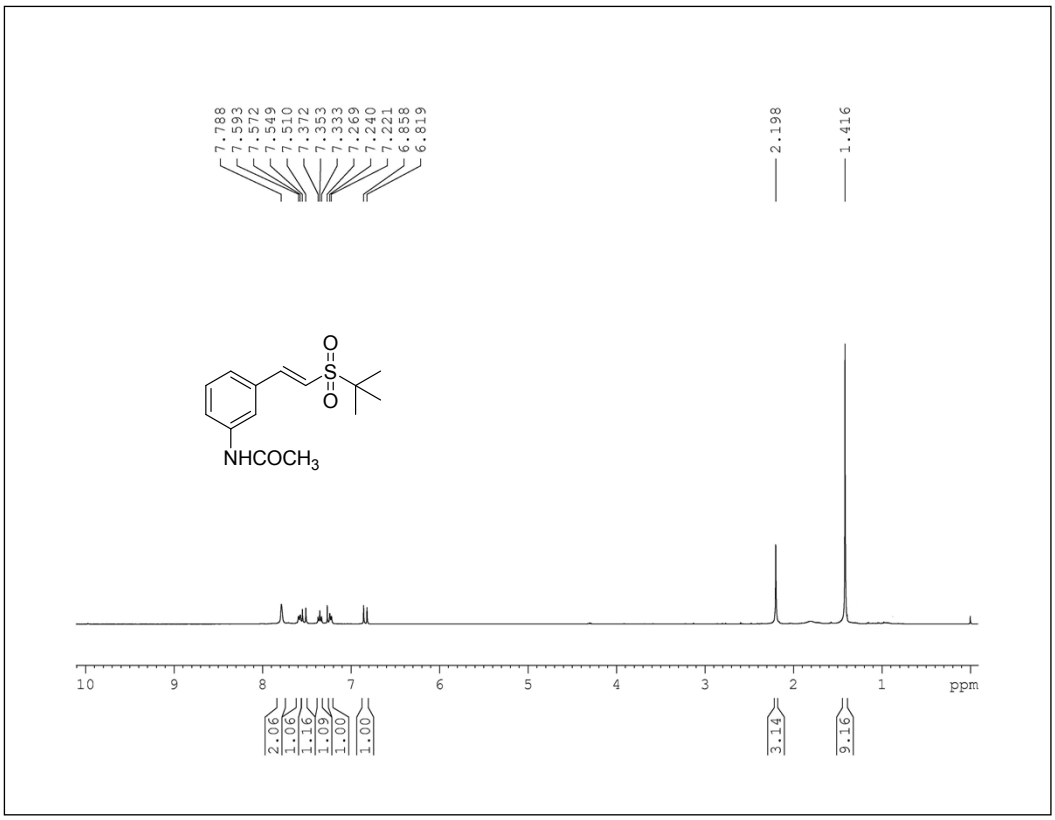


Fig 21. ^{1}H-NMR spectrum of **3k**

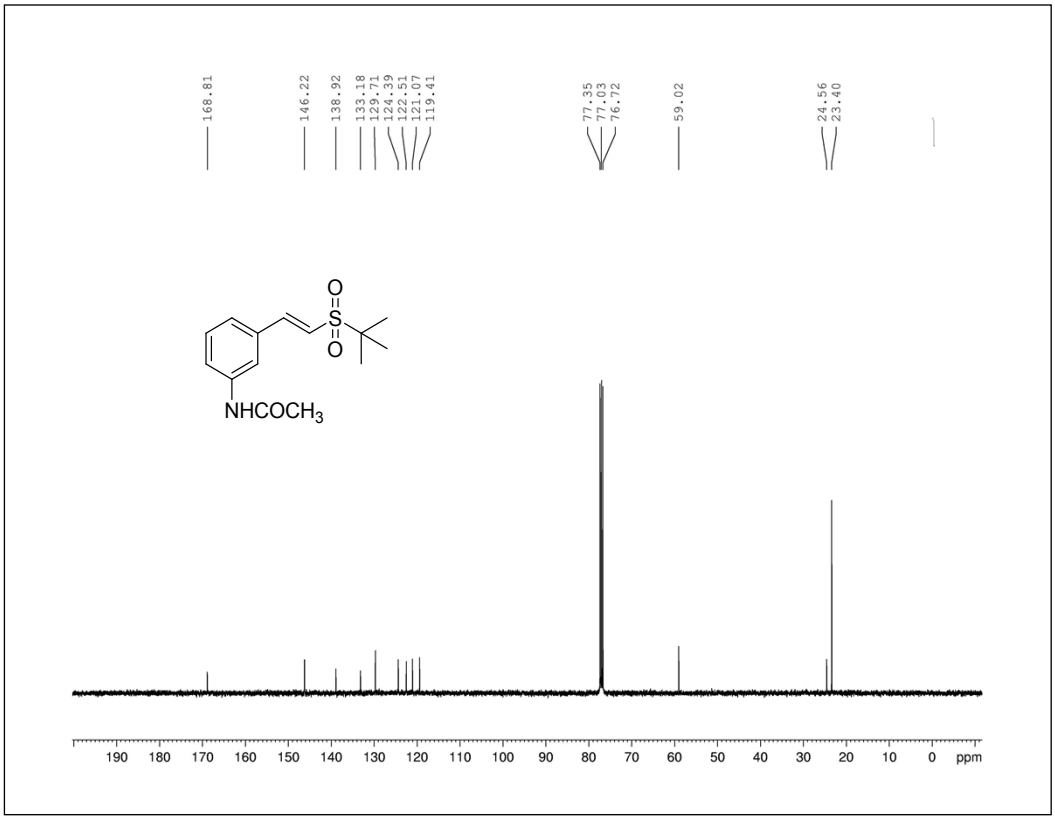


Fig 22. ^{13}C-NMR spectrum of **3k**

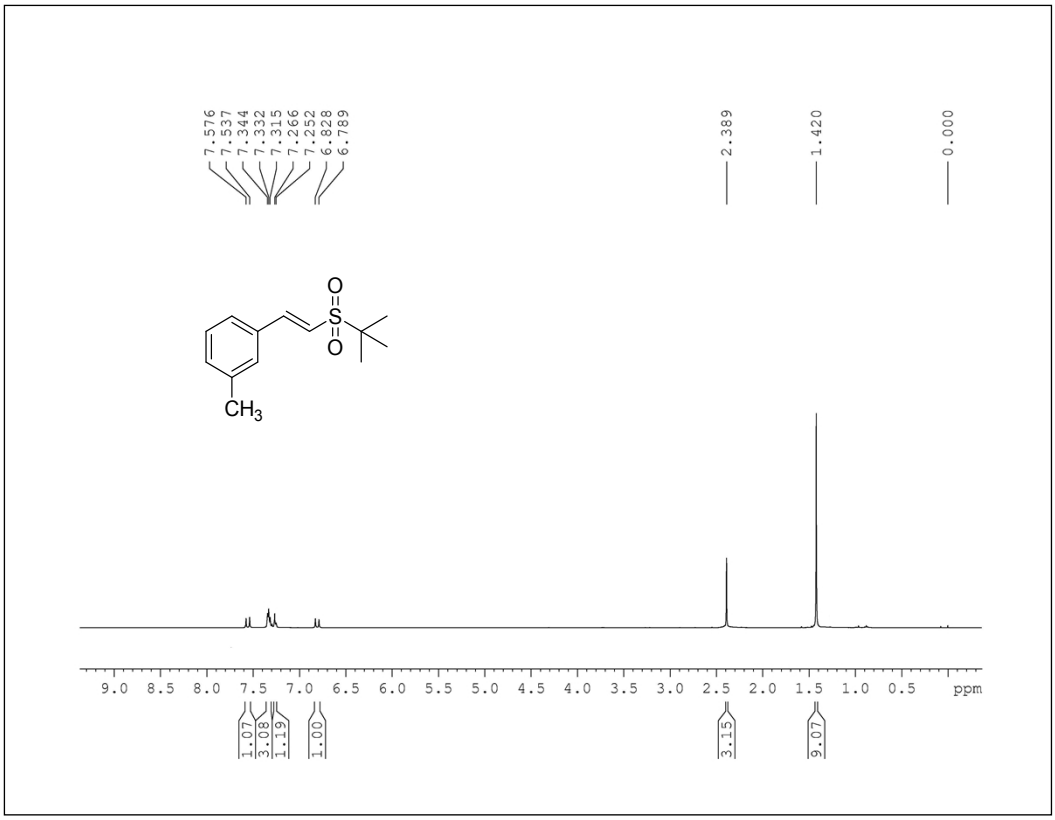


Fig 23. ^{1}H-NMR spectrum of **3l**

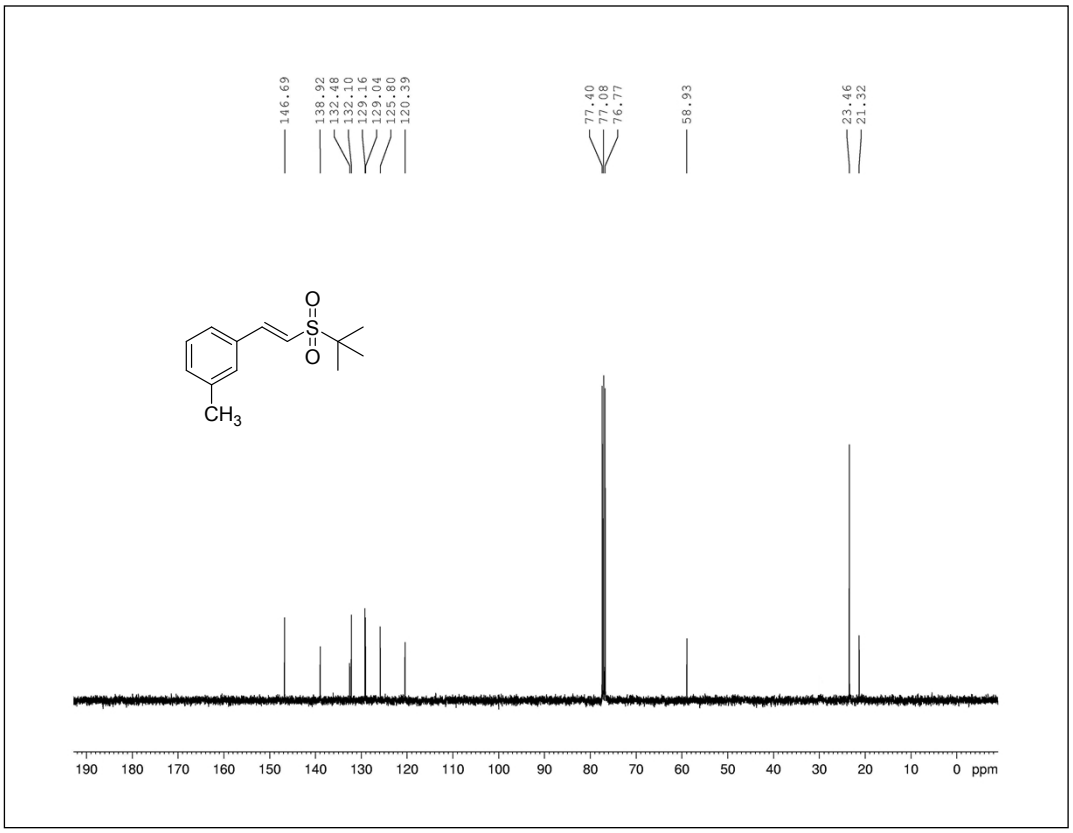


Fig 24. ^{13}C-NMR spectrum of **3l**

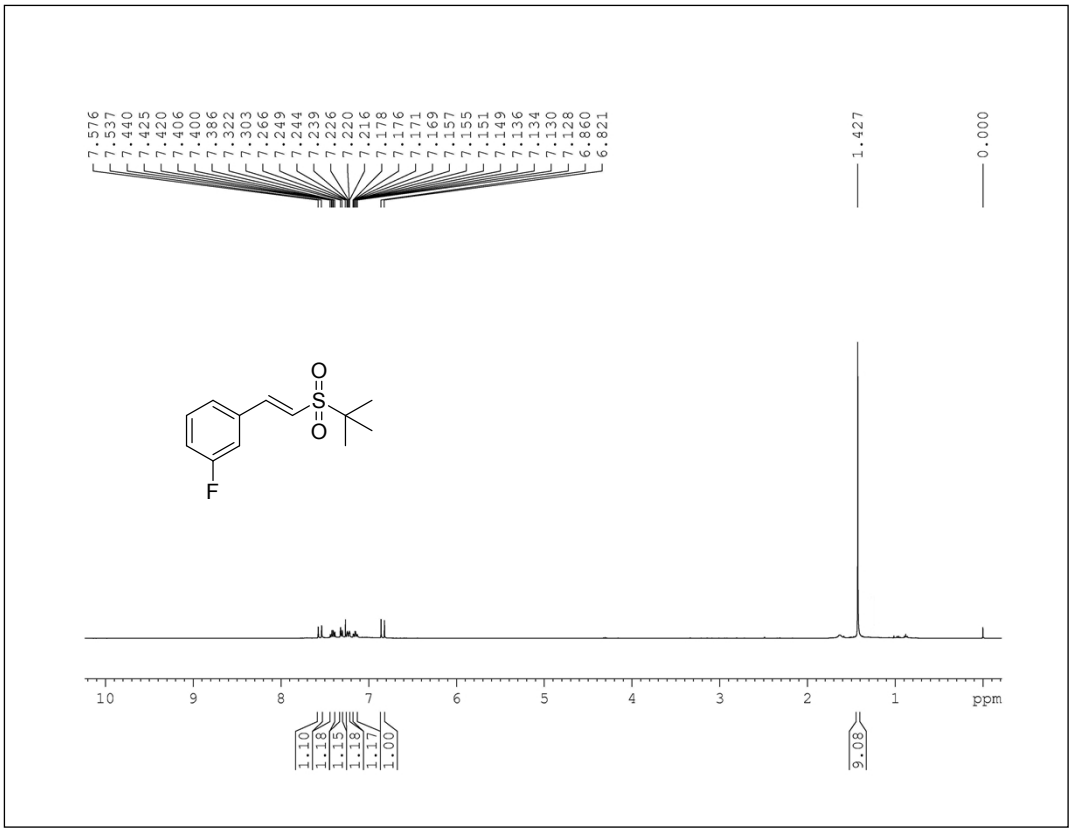


Fig 25. ^{1}H-NMR spectrum of **3m**

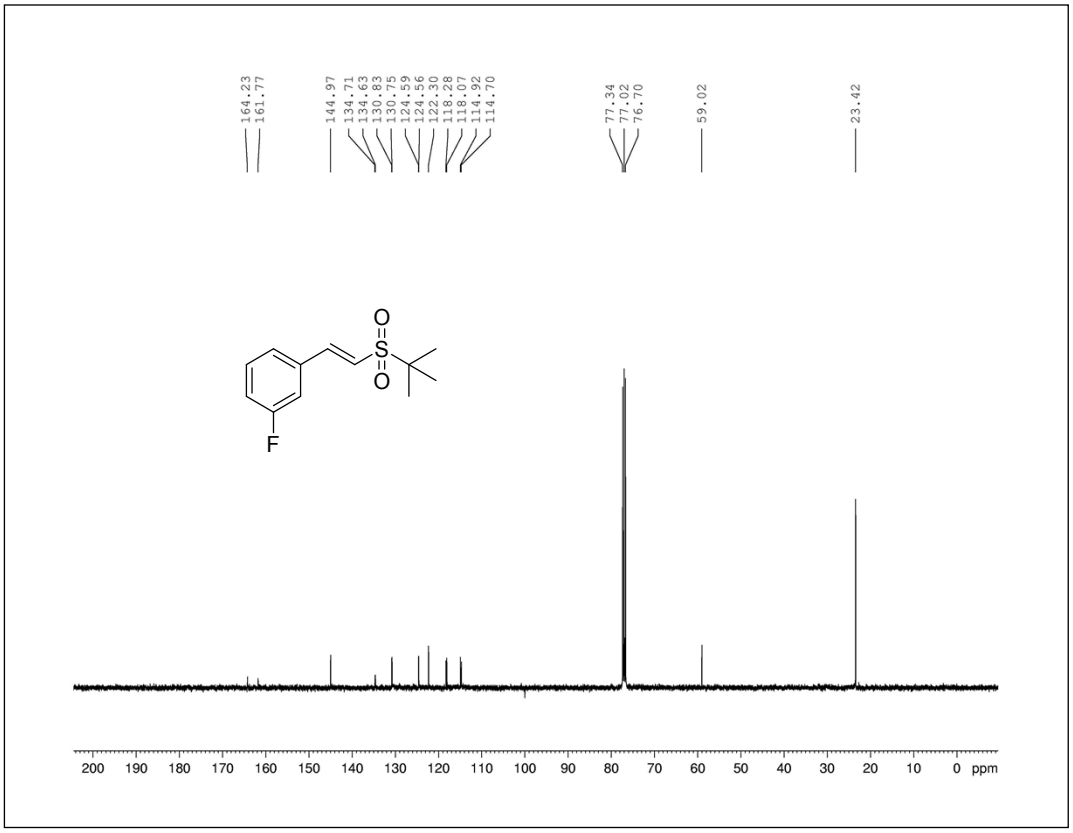


Fig 26. ^{13}C-NMR spectrum of **3m**

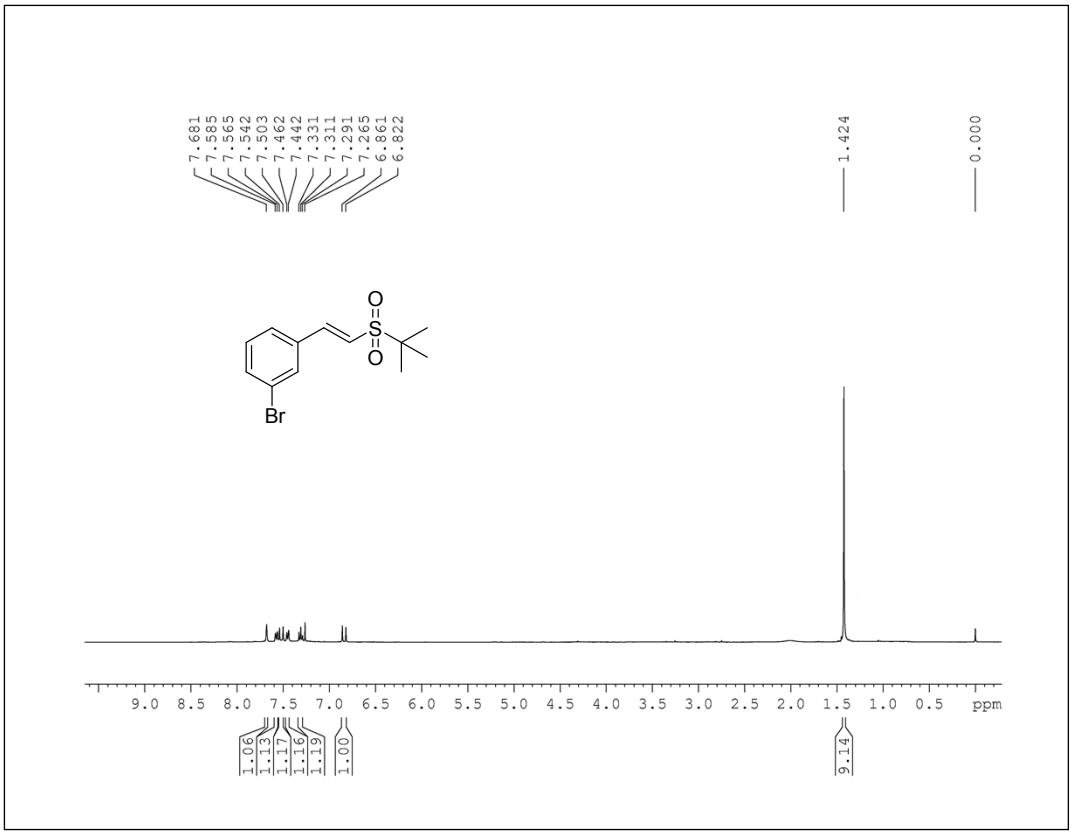


Fig 27. ^{1}H-NMR spectrum of **3n**

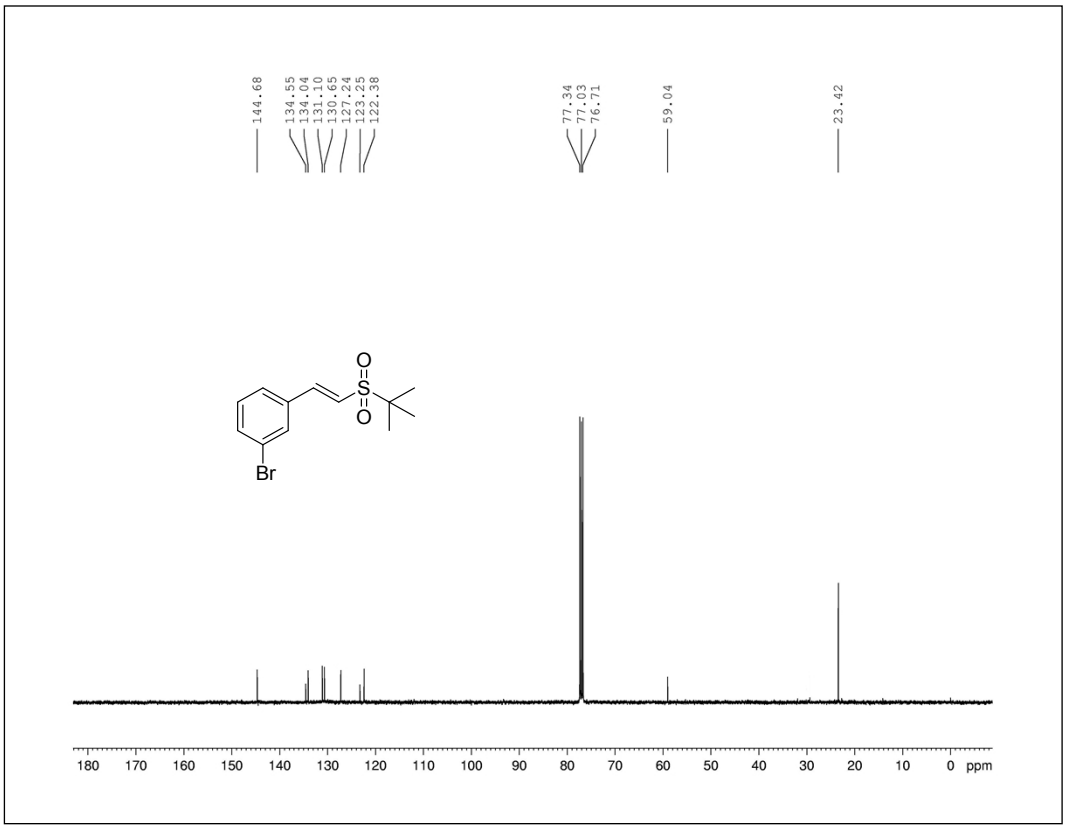


Fig 28. ^{13}C-NMR spectrum of **3n**

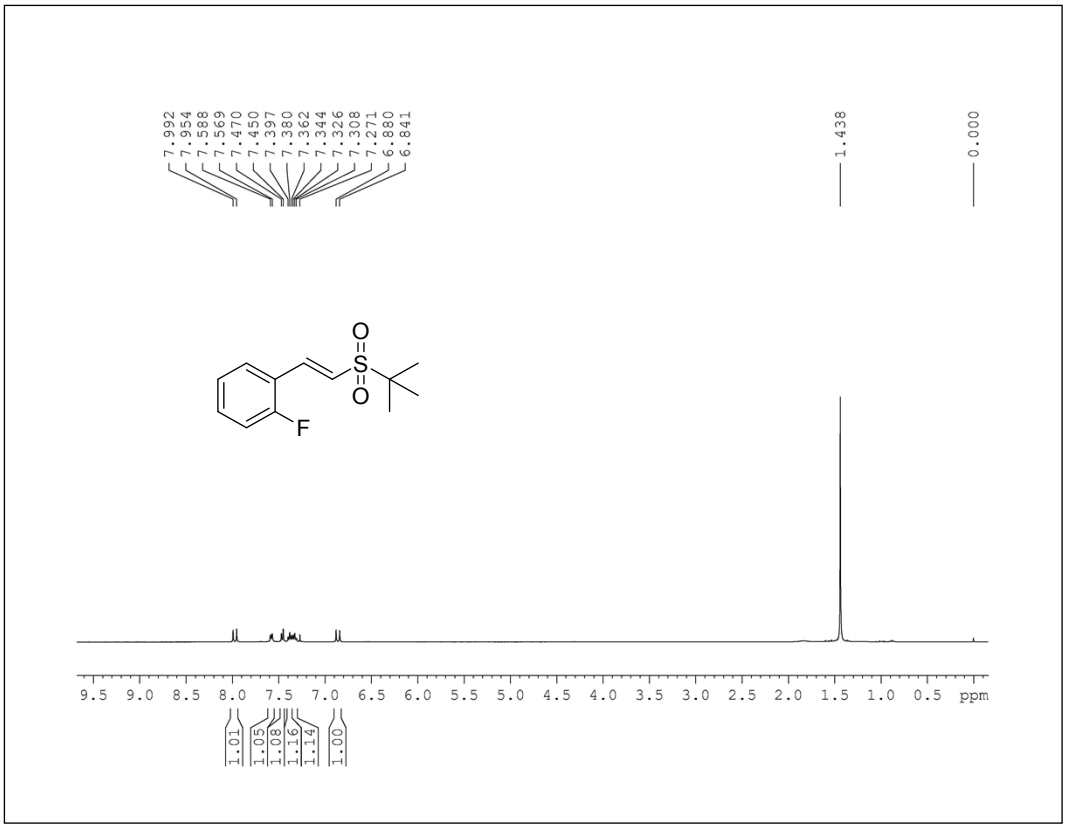


Fig 29. ^{1}H-NMR spectrum of **3o**

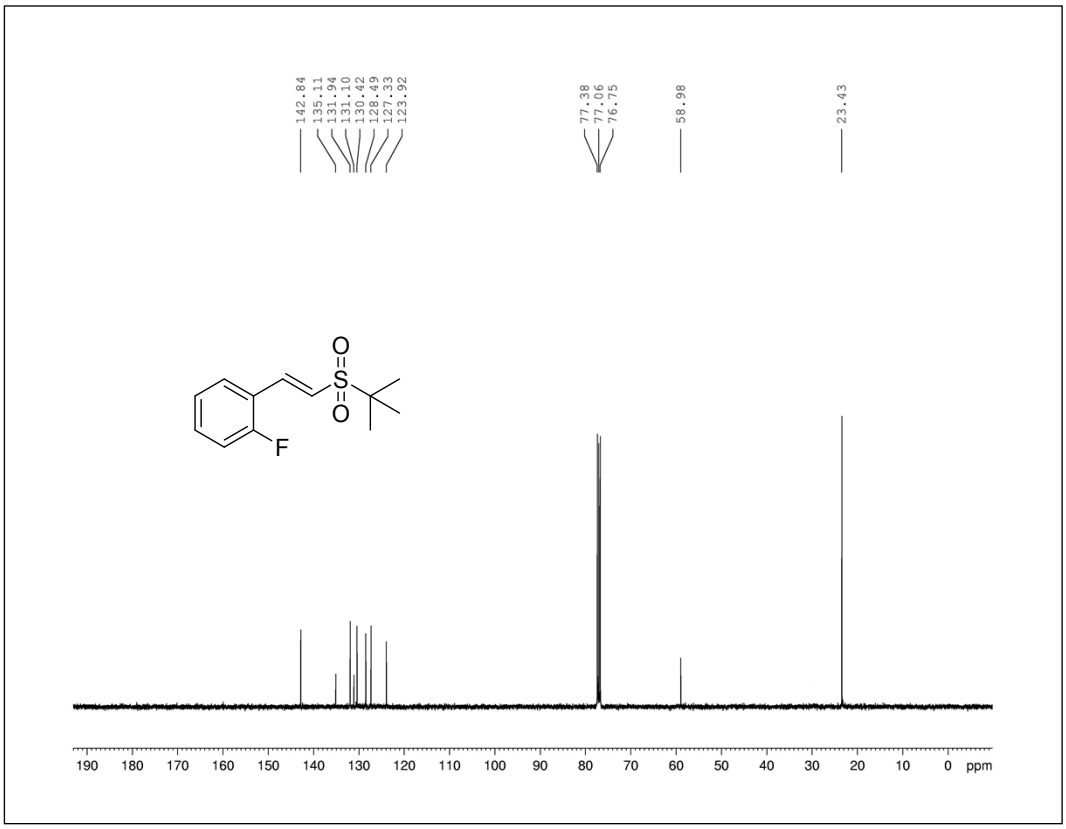


Fig 30. ^{13}C-NMR spectrum of **3o**

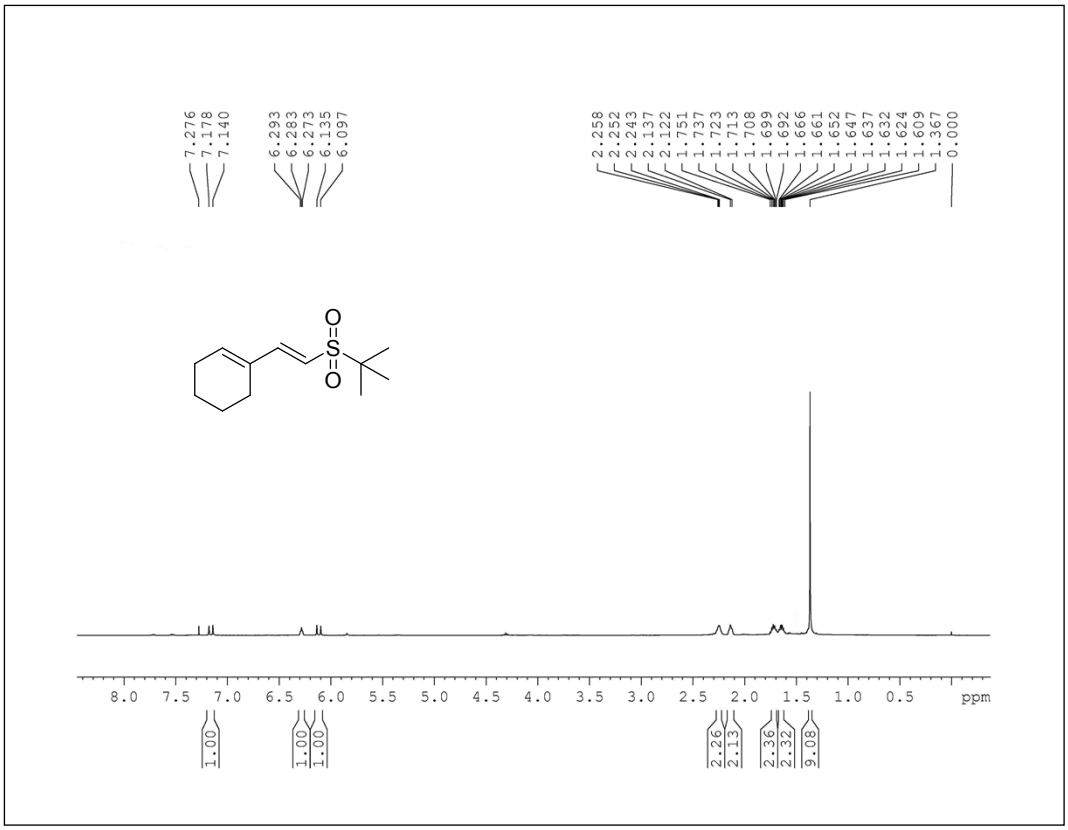


Fig 31. ^{1}H-NMR spectrum of **3p**

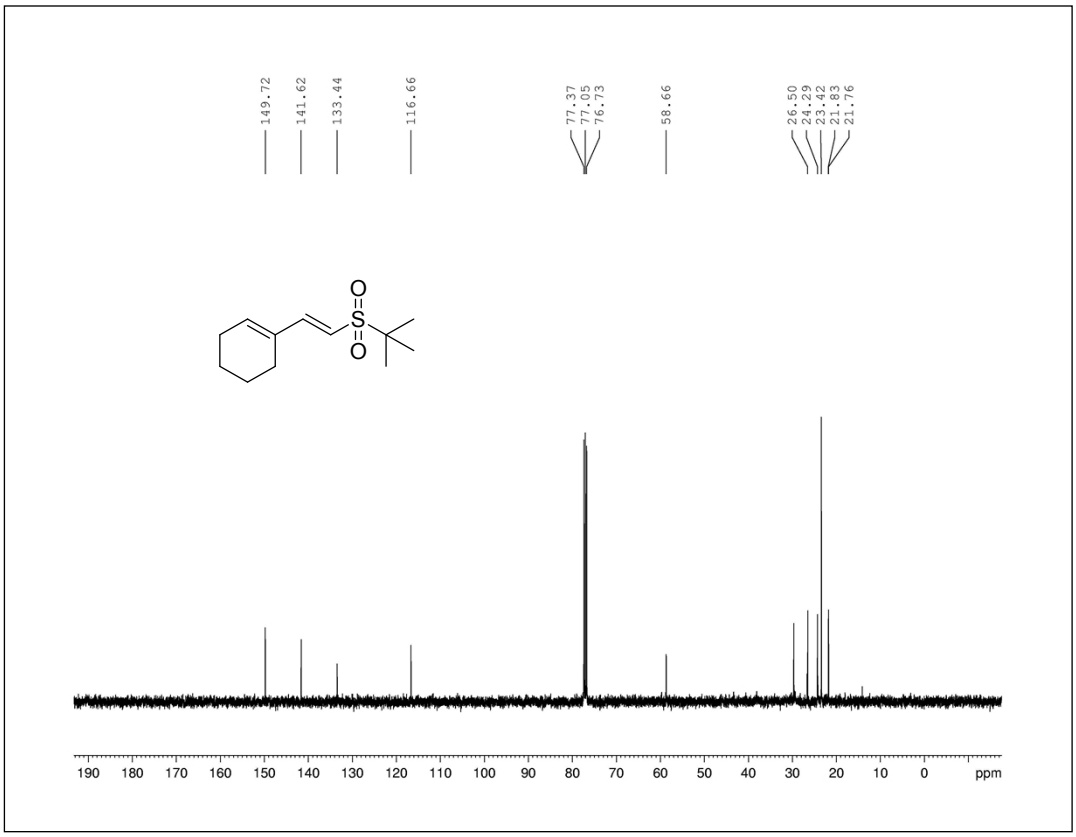


Fig 32. ^{13}C-NMR spectrum of **3p**

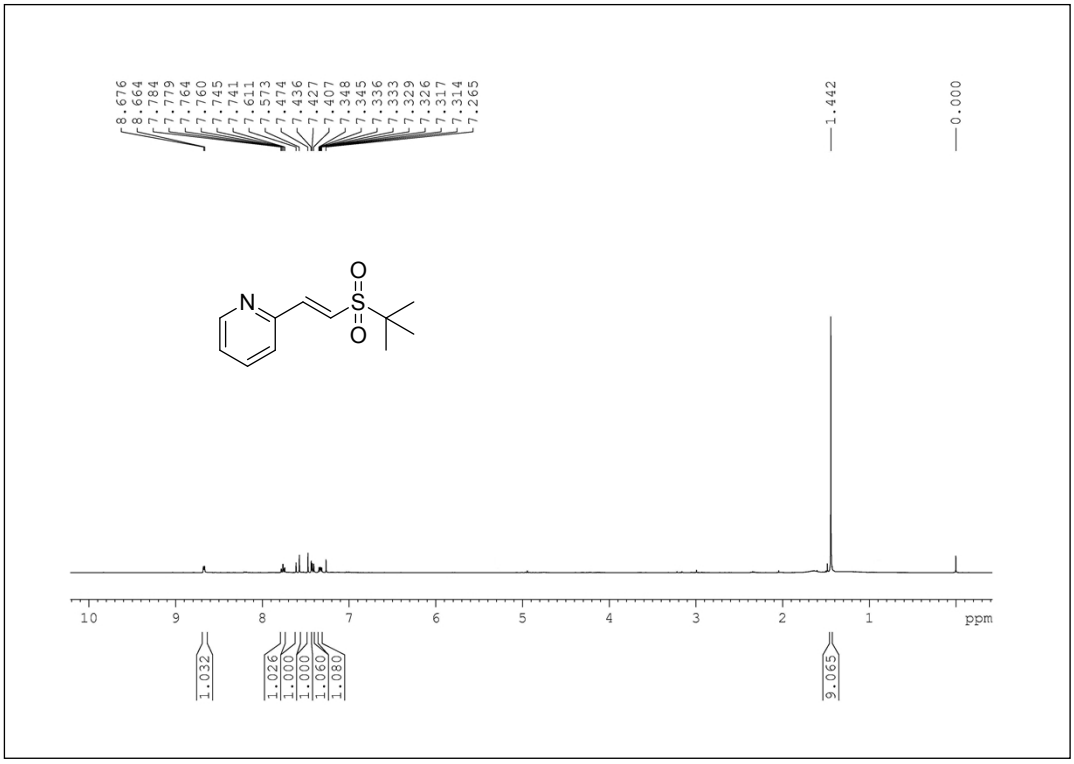


Fig 33. ^{1}H-NMR spectrum of **3q**

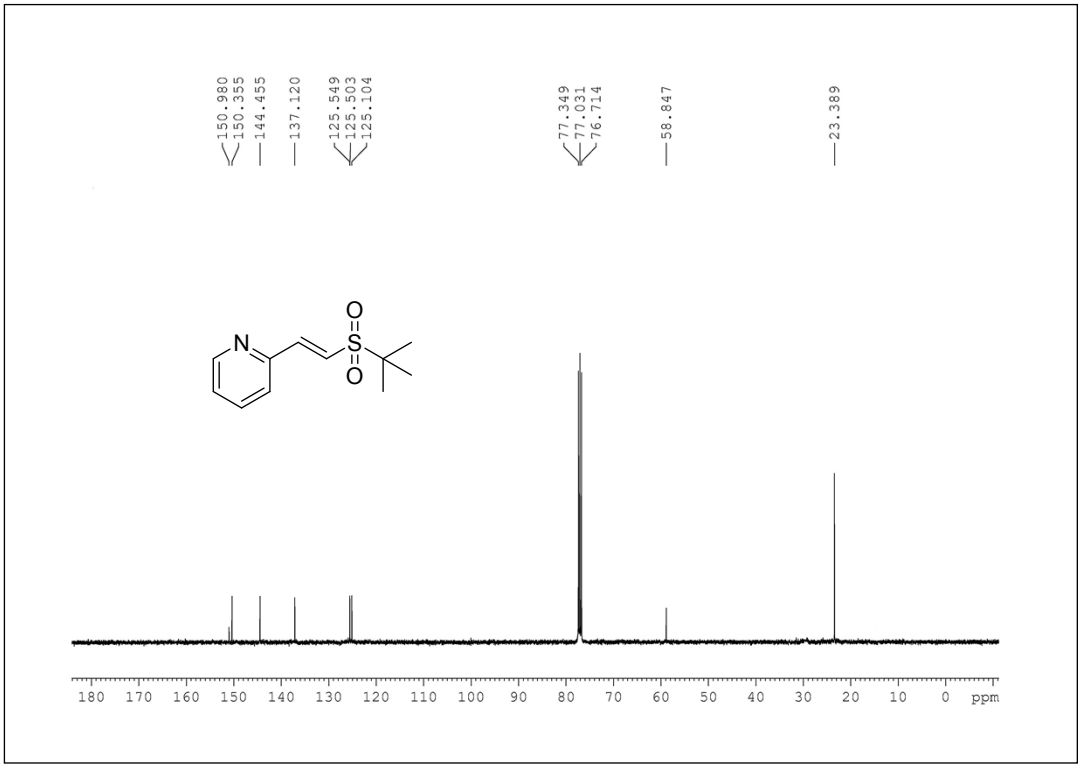


Fig 34. ^{13}C-NMR spectrum of **3q**

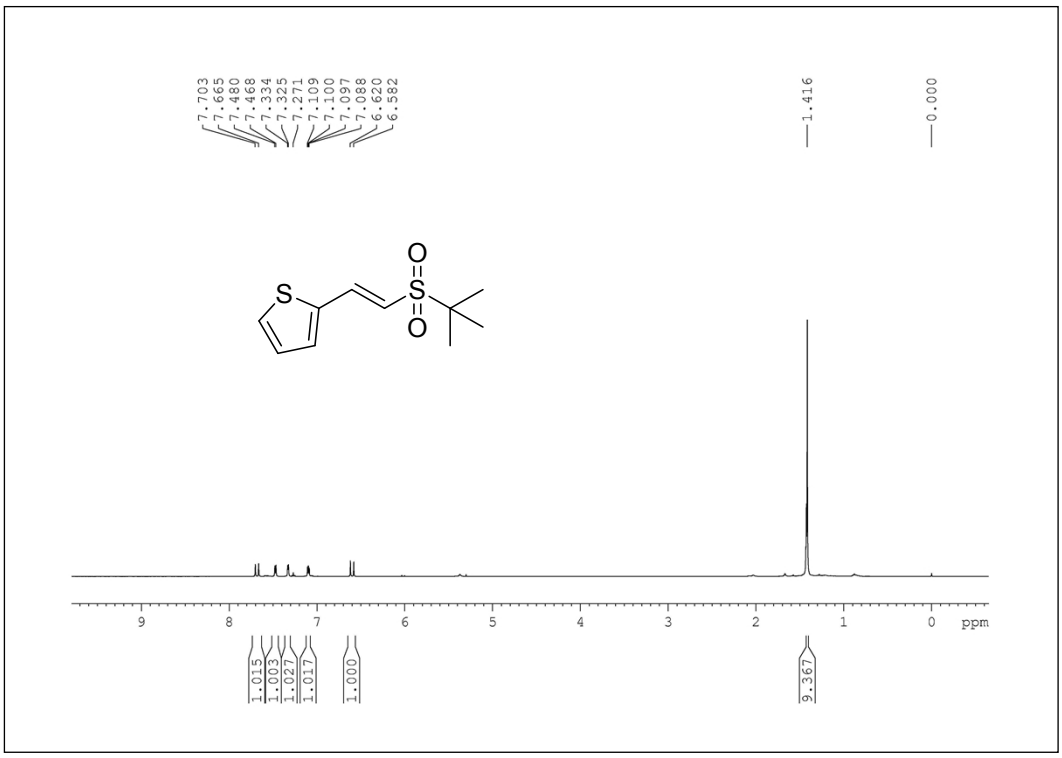


Fig 35. ^{1}H-NMR spectrum of **3r**

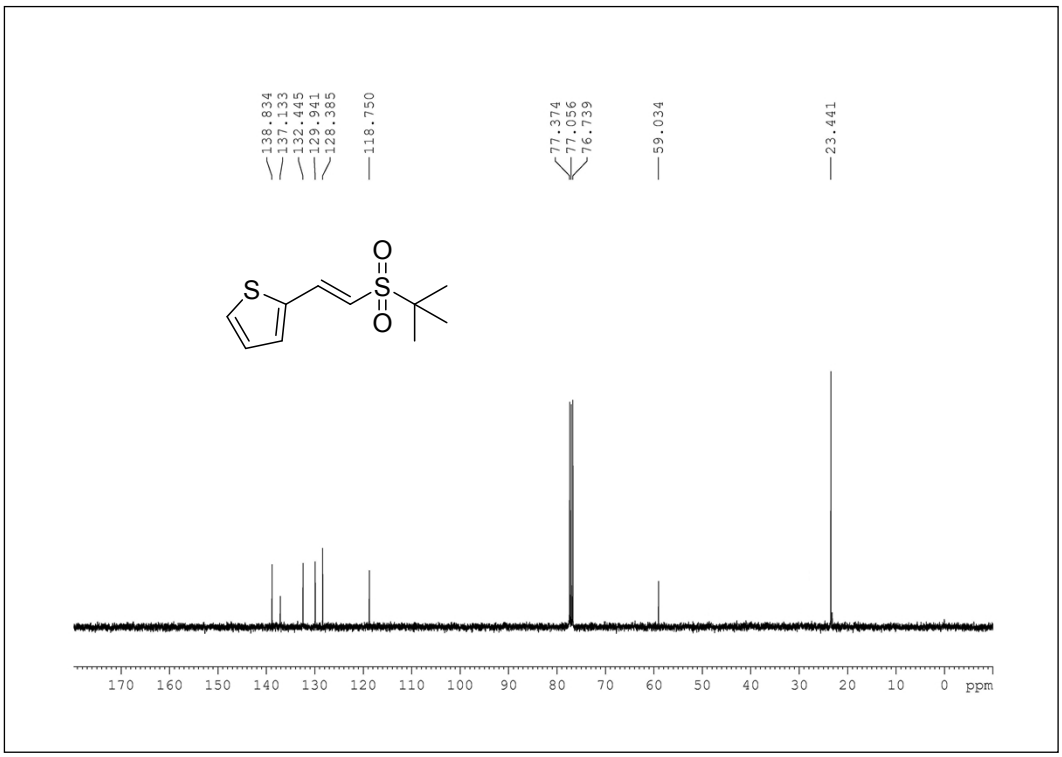


Fig 36. ^{13}C-NMR spectrum of **3r**

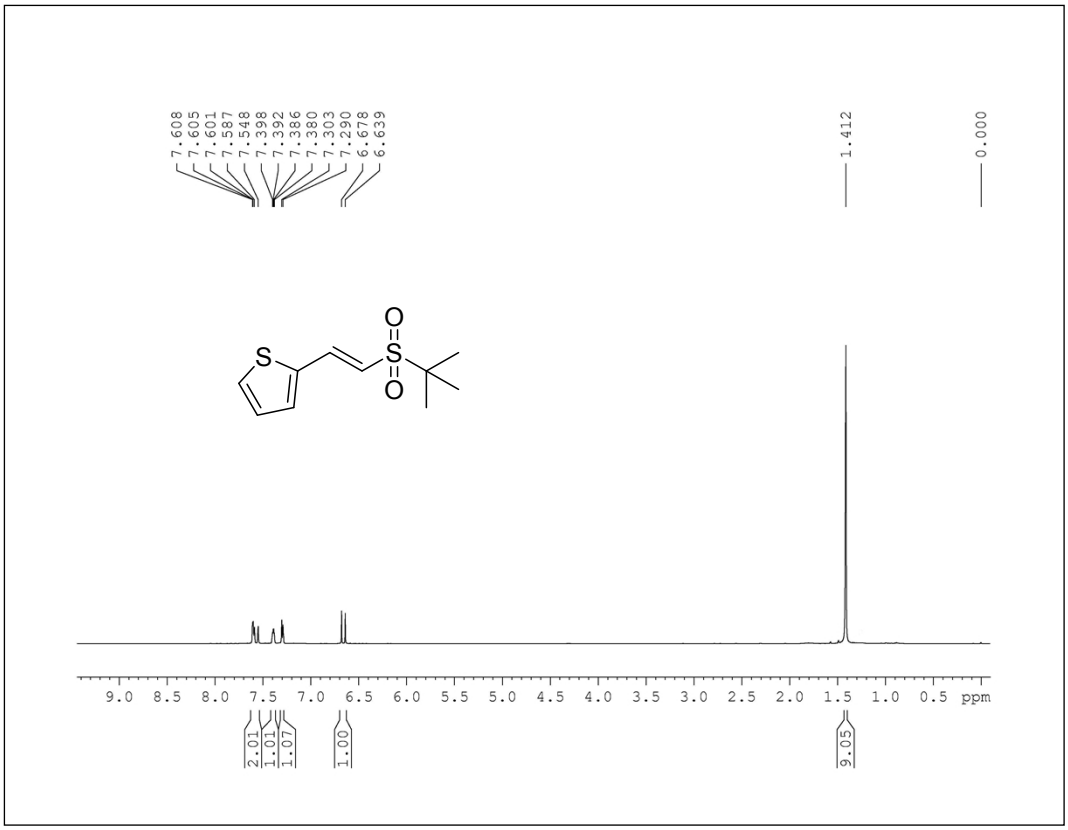


Fig 37. ^{1}H-NMR spectrum of **3s**

Fig 38. ^{13}C-NMR spectrum of **3s**

Fig 39. ^{1}H-NMR spectrum of **3t**

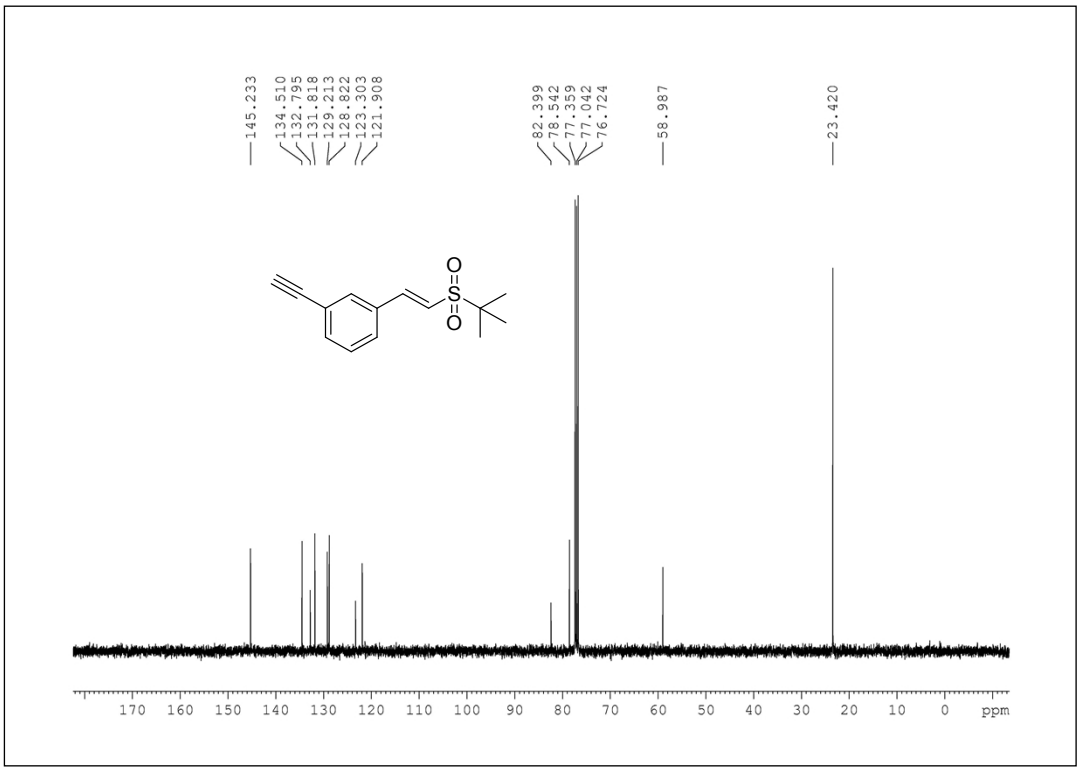


Fig 40. ^{13}C-NMR spectrum of **3t**