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SUPPLEMENTARY INFORMATION

Regio- and stereoselective manganese-catalyzed hydrosulfonylation of alkynes: facile access to *Z*-vinyl sulfones

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Contents

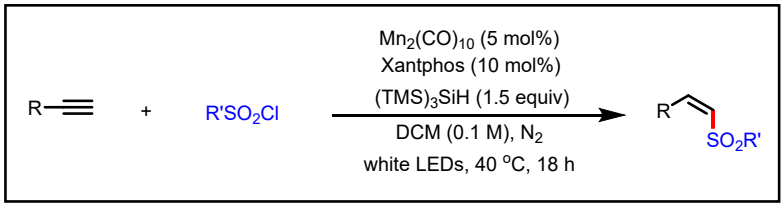
1. General information

All reactions were conducted in oven- or flame-dried glassware under an atmosphere of nitrogen unless otherwise noted. Unless otherwise noted, all reagents were used as received and handled under air atmosphere. The decacarbonyldimanganese was purchased from HWRK Chem, Energy Chemical and Laajoo reagent suppliers and used after column purification and recrystallization. The commercial ligands were purchased from Energy Chemical, Laajoo, J & K scientific Ltd., TCI (Shanghai) Ltd. and Aladdin for direct use. $CDCl3_1$ was purchased from J & K Scientific Ltd.

NMR spectra were recorded on a Bruker Ultra-shield 500 MHz spectrometer. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR are recorded on an NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H, ^{13}C, and ^{19}F NMR spectra are reported in parts per million (ppm). The ^{19}F NMR spectra is {1H} decoupled and the ^{13}C NMR spectra is {1H} decoupled. The residual solvent signals were used as standard, and the chemical shifts were converted to the corresponding scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm). All coupling constants (*J* values) were reported in hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). The high-resolution mass spectra (HRMS) were detected with the ESI mode of the Micromass Q-TOF instrument. The IR spectrum was recorded on a Brucker Alpha FT/IR instrument. The 45 W white LEDs light (λ = 400-700 nm, λ_{max} = 464 nm) was purchased from Kessil (A360NE/WE). Schlenk tubes (10 mL and 100 mL) were purchased from synthware. Toppette was purchased from DLAB Scientific Co., Ltd. The compound names were generated by the computer program ChemDraw according to the guidelines specified by the International Union of Pure and Applied Chemistry (IUPAC).

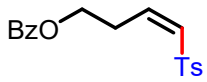
All substrates were used as received from commercial suppliers unless otherwise stated. Bromides and olefins were purchased from commercial suppliers, Aladdin, TCI (Shanghai) Development Co., Ltd, Energy Chemical reagent suppliers, J & K scientific Ltd., Bide Pharmatech Ltd, Alfa-Aesar and Sigma-Aldrich unless otherwise noted.

2. General procedure for the hydrosulfonylation of alkynes



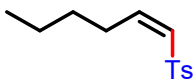
To an oven-dried 10 mL sealed tube, $Mn_2(CO)_{10}$ (5 mol%, 0.01 mmol), Xantphos (10 mol%, 0.02 mmol), $(TMS)_3SiH$ (1.5 equiv, 0.3 mmol), terminal alkyne (0.2 mmol), sulfonyl chloride (0.6 mmol) and DCM (2 mL) were added and the tube was backfilled with nitrogen. The resulting reaction mixture was vigorously stirred under the irradiation of two 45 W white LEDs (distance app. 4.0 cm from the bulb) at 40 °C for 18 h. After the reaction finished, the solvent was removed under vacuum, and the resulting residue was purified by column chromatography (eluent: PE/EA = 1:20 to 1:1) to afford the corresponding product.

3. Characterization data for the products



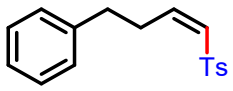
*(Z)-4-tosylbut-3-en-1-yl benzoate (**3a**)*

White solid (54.8 mg, 83%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.41 – 6.29 (m, 2H), 4.42 (t, *J* = 6.2 Hz, 2H), 3.24 – 3.17 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 144.6, 141.8, 138.4, 133.2, 132.8, 130.0, 129.9, 129.7, 128.5, 127.4, 63.2, 27.4, 21.7. HRMS (ESI) calcd for $C_{18}H_{19}O_4S$ $[M+H]^+$: 331.0999; found: 331.0989.



*(Z)-1-(hex-1-en-1-ylsulfonyl)-4-methylbenzene (**3b**)*

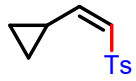
Colorless oil (41.5 mg, 87%, *Z*/*E* = 19:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.32 – 6.17 (m, 2H), 2.65 (q, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 1.41 – 1.29 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 144.3, 139.1, 130.7, 129.9, 127.4, 30.9, 27.6, 22.4, 21.7, 13.9. HRMS (ESI) calcd for $C_{13}H_{19}O_2S$ $[M+H]^+$: 239.1100; found: 239.1094.



*(Z)-1-methyl-4-((4-phenylbut-1-en-1-yl)sulfonyl)benzene (**3c**)*

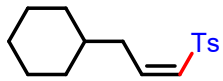
Colorless oil (51.5 mg, 90%, *Z*/*E* = 11:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.31 – 7.23 (m, 4H), 7.22 – 7.18 (m, 1H), 7.17 – 7.12 (m, 2H), 6.29 – 6.16 (m, 2H), 3.03 – 2.95 (m, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 144.4, 140.4, 138.8, 131.2, 129.9, 128.61, 128.57, 127.4, 126.4, 34.9, 29.2,

21.7. HRMS (ESI) calcd for $C_{17}H_{19}O_2S$ $[M+H]^+$: 287.1100; found: 287.1089.



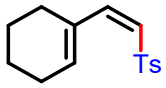
*(Z)-1-((2-cyclopropylvinyl)sulfonyl)-4-methylbenzene (**3d**)*

Colorless oil (35.6 mg, 80%, *Z*/*E* = 17:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.14 (d, *J* = 11.0 Hz, 1H), 5.45 (t, *J* = 11.1 Hz, 1H), 2.83 – 2.75 (m, 1H), 2.43 (s, 3H), 1.06 – 1.01 (m, 2H), 0.59 – 0.54 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 144.1, 139.4, 129.9, 127.6, 127.2, 21.7, 10.9, 9.5. HRMS (ESI) calcd for $C_{12}H_{15}O_2S$ $[M+H]^+$: 223.0787; found: 223.0784.



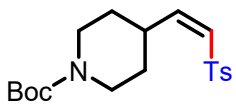
*(Z)-1-((3-cyclohexylprop-1-en-1-yl)sulfonyl)-4-methylbenzene (**3e**)*

Colorless oil (52.3 mg, 94%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.31 – 6.19 (m, 2H), 2.55 (t, *J* = 6.7 Hz, 2H), 2.43 (s, 3H), 1.71 – 1.64 (m, 4H), 1.62 – 1.59 (m, 1H), 1.40 – 1.31 (m, 1H), 1.21 – 1.10 (m, 3H), 0.98 – 0.88 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 144.3, 139.1, 131.2, 129.9, 127.5, 38.0, 35.2, 33.0, 26.3, 26.3, 21.7. HRMS (ESI) calcd for $C_{16}H_{23}O_2S$ $[M+H]^+$: 279.1413; found: 279.1401.



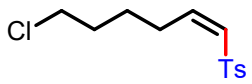
*(Z)-1-((2-(cyclohex-1-en-1-yl)vinyl)sulfonyl)-4-methylbenzene (**3f**)*

Yellow oil (28.9 mg, 55%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 15.1 Hz, 1H), 6.27 (t, *J* = 4.2 Hz, 1H), 6.18 (d, *J* = 15.1 Hz, 1H), 2.42 (s, 3H), 2.25 – 2.19 (m, 2H), 2.06 – 2.01 (m, 2H), 1.68 – 1.64 (m, 2H), 1.62 – 1.56 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 144.1, 141.5, 138.6, 133.5, 130.0, 127.6, 124.1, 26.7, 24.3, 22.0, 21.9, 21.7. HRMS (ESI) calcd for $C_{15}H_{19}O_2S$ $[M+H]^+$: 263.1100; found: 263.1093.



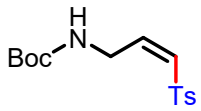
*tert-butyl (Z)-4-(2-tosylvinyl)piperidine-1-carboxylate (**3g**)*

Pale yellow solid (51.9 mg, 71%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 6.22 (d, *J* = 11.1 Hz, 1H), 5.96 (t, *J* = 10.7 Hz, 1H), 4.19 – 3.97 (m, 2H), 3.59 – 3.46 (m, 1H), 2.85 – 2.68 (m, 2H), 2.43 (s, 3H), 1.64 – 1.57 (m, 2H), 1.44 (s, 9H), 1.26 – 1.20 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 148.8, 144.6, 138.8, 130.2, 130.1, 127.8, 127.4, 79.7, 34.8, 31.0, 28.6, 21.8. HRMS (ESI) calcd for $C_{19}H_{28}NO_4S$ $[M+H]^+$: 366.1734; found: 366.1720.



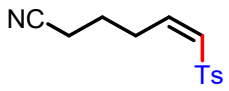
*(Z)-1-((6-chlorohex-1-en-1-yl)sulfonyl)-4-methylbenzene (**3h**)*

Pale yellow oil (44.7 mg, 82%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.32 – 6.28 (m, 1H), 6.23 – 6.16 (m, 1H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.74 – 2.66 (m, 2H), 2.44 (s, 3H), 1.82 – 1.75 (m, 2H), 1.62 – 1.55 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.8, 144.5, 138.9, 131.4, 130.0, 127.4, 44.7, 32.0, 26.9, 26.0, 21.8. HRMS (ESI) calcd for $C_{13}H_{18}ClO_2S$ $[M+H]^+$: 273.0711; found: 273.0705.



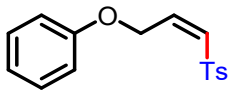
*tert-butyl (Z)-(3-tosylallyl)carbamate (**3i**)*

Yellow solid (39.8 mg, 64%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.29 (d, *J* = 12.5 Hz, 2H), 4.96 (s, 1H), 4.33 (t, *J* = 5.6 Hz, 2H), 2.44 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 143.3, 138.1, 131.3, 130.2, 127.6, 37.5, 28.5, 21.8. HRMS (ESI) calcd for $C_{15}H_{22}NO_4S$ $[M+H]^+$: 312.1264; found: 312.1253.



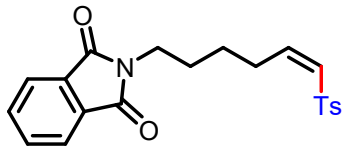
*(Z)-6-tosylhex-5-enenitrile (**3j**)*

Brown oil (26.9 mg, 54%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.39 – 6.34 (m, 1H), 6.22 – 6.15 (m, 1H), 2.86 – 2.78 (m, 2H), 2.45 (s, 3H), 2.40 (t, *J* = 7.3 Hz, 2H), 1.88 – 1.81 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 143.1, 138.4, 132.9, 130.2, 127.5, 119.2, 26.8, 24.9, 21.8, 16.9. HRMS (ESI) calcd for $C_{13}H_{16}NO_2S$ $[M+H]^+$: 250.0896; found: 250.0888.



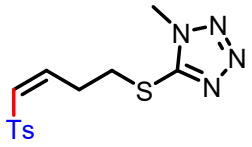
*(Z)-1-methyl-4-((3-phenoxyprop-1-en-1-yl)sulfonyl)benzene (**3k**)*

Pale yellow solid (28.8 mg, 50%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.9 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.51 – 6.45 (m, 1H), 6.37 – 6.31 (m, 1H), 5.24 (dd, *J* = 4.9, 2.3 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 145.1, 142.5, 137.7, 130.5, 130.2, 129.8, 127.6, 121.5, 114.8, 64.1, 21.8. HRMS (ESI) calcd for $C_{16}H_{17}O_3S$ $[M+H]^+$: 289.0893; found: 289.0885.



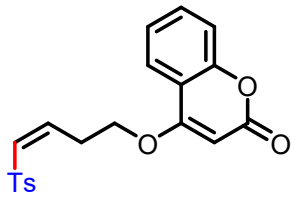
(Z)-2-(6-tosylhex-5-en-1-yl)isoindoline-1,3-dione ***(3l)***

Colorless oil (64.4 mg, 84%, *Z*/*E* = 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.72 – 7.69 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.30 – 6.25 (m, 1H), 6.20 – 6.14 (m, 1H), 3.66 (t, *J* = 7.1 Hz, 2H), 2.71 – 2.65 (m, 2H), 2.40 (s, 3H), 1.69 – 1.63 (m, 2H), 1.48 – 1.41 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 146.0, 144.4, 138.9, 134.0, 132.2, 131.3, 129.9, 127.4, 123.3, 37.7, 28.2, 27.2, 26.0, 21.7. HRMS (ESI) calcd for $C_{21}H_{22}NO_4S$ $[M+H]^+$: 384.1264; found: 384.1252.



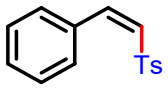
(Z)-1-methyl-5-((4-tosylbut-3-en-1-yl)thio)-1H-tetrazole ***(3m)***

Colorless oil (48.7 mg, 75%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.39 – 6.23 (m, 2H), 3.91 (s, 3H), 3.46 (t, *J* = 7.0 Hz, 2H), 3.19 (q, *J* = 7.3 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 144.8, 141.9, 138.3, 133.2, 130.1, 127.5, 33.6, 31.9, 27.5, 21.8. HRMS (ESI) calcd for $C_{13}H_{17}N_4O_2S_2$ $[M+H]^+$: 325.0787; found: 325.0777.



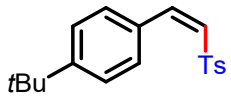
(Z)-4-((4-tosylbut-3-en-1-yl)oxy)-2H-chromen-2-one ***(3n)***

White solid (38.5 mg, 52%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.70 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.50 – 6.42 (m, 1H), 6.41 – 6.32 (m, 1H), 5.66 (s, 1H), 4.24 (t, *J* = 6.1 Hz, 2H), 3.39 – 3.31 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 162.8, 153.4, 145.0, 140.4, 138.3, 133.6, 132.7, 130.2, 127.5, 124.1, 123.1, 116.9, 115.5, 90.9, 67.6, 27.1, 21.8. HRMS (ESI) calcd for $C_{20}H_{19}O_5S$ $[M+H]^+$: 371.0948; found: 371.0935.



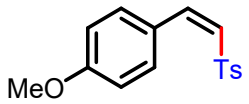
(Z)-1-methyl-4-(styrylsulfonyl)benzene ***(3p)***

Pale yellow solid (43.4 mg, 84%, *Z*/*E* = 4:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 2H), 7.58 – 7.54 (m, 2H), 7.36 – 7.33 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 12.1 Hz, 1H), 6.50 (d, *J* = 12.1 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 141.2, 131.4, 130.3, 129.7, 129.2, 128.6, 128.2, 127.8, 127.7, 21.7. HRMS (ESI) calcd for $C_{15}H_{15}O_2S$ $[M+H]^+$: 259.0787; found: 259.0782.



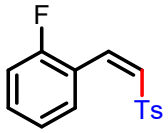
*(Z)-1-(tert-butyl)-4-(2-tosylvinyl)benzene (**3q**)*

White solid (42.1 mg, 67%, *Z*-isomer, which was isolated by column chromatography). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.44 – 7.38 (m, 4H), 7.33 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 15.4 Hz, 1H), 2.43 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 144.4, 142.0, 138.1, 130.0, 129.8, 128.5, 127.8, 126.7, 126.2, 35.1, 31.2, 21.7. HRMS (ESI) calcd for $C_{19}H_{23}O_2S$ $[M+H]^+$: 315.1413; found: 315.1405.



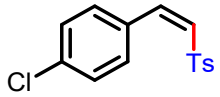
*(Z)-1-methoxy-4-(2-tosylvinyl)benzene (**3r**)*

White solid (38.6 mg, 67%, *Z*/*E* = 15:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 15.3 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 15.3 Hz, 1H), 3.82 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1, 144.2, 141.8, 138.3, 130.4, 130.0, 127.7, 125.2, 124.9, 114.6, 55.5, 21.7. HRMS (ESI) calcd for $C_{16}H_{17}O_3S$ $[M+H]^+$: 289.0893; found: 289.0887.



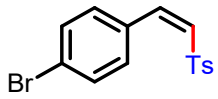
*(Z)-1-fluoro-2-(2-tosylvinyl)benzene (**3s**)*

White solid (35.4 mg, 64%, *Z*-isomer, which was isolated by column chromatography). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (td, *J* = 7.7, 1.7 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.32 (m, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.19 – 7.11 (m, 2H), 7.01 – 6.96 (m, 1H), 6.59 (d, *J* = 12.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1 (d, *J* = 249.5 Hz), 144.6, 137.8, 133.8 (d, *J* = 3.8 Hz), 133.4, 132.4 (d, *J* = 2.5 Hz), 131.7 (d, *J* = 8.8 Hz), 129.8, 127.8, 123.8 (d, *J* = 3.8 Hz), 120.6 (d, *J* = 13.9 Hz), 115.1 (d, *J* = 20.2 Hz), 21.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.0 (s). HRMS (ESI) calcd for $C_{15}H_{14}FO_2S$ $[M+H]^+$: 277.0693; found: 277.0685.



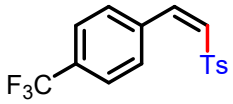
*(Z)-1-chloro-4-(2-tosylvinyl)benzene (**3t**)*

Pale yellow solid (38.6 mg, 66%, *Z*-isomer, which was isolated by column chromatography). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 12.1 Hz, 1H), 6.50 (d, *J* = 12.1 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7, 139.5, 138.0, 136.0, 131.9, 131.6, 130.9, 129.8, 128.4, 127.7, 21.7. HRMS (ESI) calcd for $C_{15}H_{14}ClO_2S$ $[M+H]^+$: 293.0398; found: 293.0388.



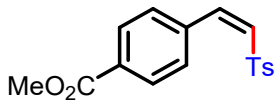
*(Z)-1-bromo-4-(2-tosylvinyl)benzene (**3u**)*

White solid (23.6 mg, 35%, *Z*-isomer, which was isolated by column chromatography). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 12.1 Hz, 1H), 6.51 (d, *J* = 12.1 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7, 139.6, 138.0, 132.1, 131.8, 131.42, 131.35, 129.9, 127.7, 124.4, 21.8. HRMS (ESI) calcd for $C_{15}H_{14}BrO_2S$ $[M+H]^+$: 336.9892; found: 336.9882.



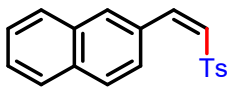
*(Z)-1-methyl-4-((4-(trifluoromethyl)styryl)sulfonyl)benzene (**3v**)*

White solid (37.9 mg, 58%, *Z*-isomer, which was isolated by column chromatography). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.70 – 7.62 (m, 3H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 140.0, 137.3, 136.0, 132.6 (q, *J* = 32.8 Hz), 130.5, 130.2, 128.8, 128.0, 126.2 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 269.6 Hz), 21.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.0 (s). HRMS (ESI) calcd for $C_{16}H_{14}F_3O_2S$ $[M+H]^+$: 327.0661; found: 327.0655.



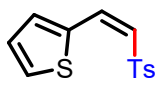
*methyl (Z)-4-(2-tosylvinyl)benzoate (**3w**)*

Yellow solid (37.9 mg, 60%, *Z*-isomer, which was isolated by column chromatography). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 12.1 Hz, 1H), 6.59 (d, *J* = 12.1 Hz, 1H), 3.93 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 144.8, 139.8, 137. 9, 137.0, 133.3, 130.9, 129.94, 129.85, 129.3, 127.8, 52.4, 21.7. HRMS (ESI) calcd for $C_{17}H_{17}O_4S$ $[M+H]^+$: 317.0842; found: 317.0836.



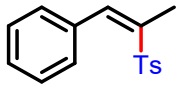
*(Z)-2-(2-tosylvinyl)naphthalene (**3x**)*

White solid (16.0 mg, 26%, *Z*-isomer, which was isolated by column chromatography). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.88 – 7.79 (m, 6H), 7.56 – 7.50 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 15.3 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 142.1, 138.0, 134.6, 133.3, 131.0, 130.12, 130.05, 129.1, 128.8, 128.0, 127.9, 127.8, 127.1, 123.6, 21.8. HRMS (ESI) calcd for $C_{19}H_{17}O_2S$ $[M+H]^+$: 309.0944; found: 309.0936.



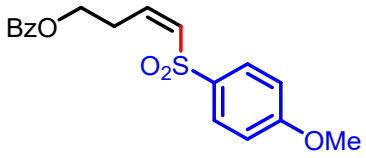
*(Z)-2-(2-tosylvinyl)thiophene (**3y**)*

Pale yellow solid (31.7 mg, 60%, *Z*-isomer, which was isolated by column chromatography). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 15.1 Hz, 1H), 7.42 (d, *J* = 5.1 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 3.5 Hz, 1H), 7.06 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.63 (d, *J* = 15.1 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 138.0, 137.2, 134.7, 132.4, 130.1, 130.0, 128.4, 127.8, 125.9, 21.8. HRMS (ESI) calcd for $C_{13}H_{13}O_2S_2$ $[M+H]^+$: 265.0351; found: 265.0346.



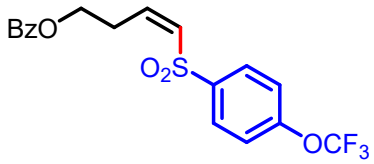
*(Z)-1-methyl-4-((1-phenylprop-1-en-2-yl)sulfonyl)benzene (**3z**)*

Colorless oil (40.8 mg, 75%, *Z*/*E* = 7:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.24 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.05 (s, 1H), 2.39 (s, 3H), 2.21 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 138.5, 137.5, 137.1, 134.3, 129.4, 129.0, 128.2, 128.0, 127.7, 21.7, 20.9. HRMS (ESI) calcd for $C_{16}H_{17}O_2S$ $[M+H]^+$: 273.0944; found: 273.0936.



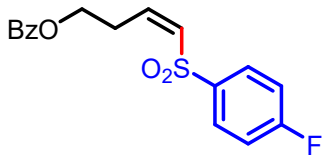
*(Z)-4-((4-methoxyphenyl)sulfonyl)but-3-en-1-yl benzoate (**4a**)*

Colorless oil (50.6 mg, 73%, *Z*/*E* = 14:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.86 – 7.79 (m, 2H), 7.59 – 7.53 (m, 1H), 7.42 (dd, *J* = 8.4, 7.1 Hz, 2H), 6.99 – 6.91 (m, 2H), 6.44 – 6.26 (m, 2H), 4.43 (t, *J* = 6.2 Hz, 2H), 3.84 (s, 3H), 3.24 – 3.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 163.8, 141.2, 137.3, 133.2, 133.1, 133.0, 129.73, 129.65, 128.5, 114.7, 63.2, 55.8, 27.4. HRMS (ESI) calcd for $C_{18}H_{19}O_5S$ $[M+H]^+$: 347.0948; found: 347.0935.



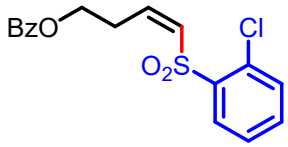
*(Z)-4-((4-(trifluoromethoxy)phenyl)sulfonyl)but-3-en-1-yl benzoate (**4b**)*

Colorless oil (40.8 mg, 51%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.98 (m, 2H), 7.97 – 7.92 (m, 2H), 7.60 – 7.55 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.47 – 6.34 (m, 2H), 4.47 (t, *J* = 6.1 Hz, 2H), 3.27 – 3.22 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 153.0, 143.2, 140.0, 133.4, 132.0, 129.9, 129.77, 129.75, 122.3 (q, *J* = 260.8 Hz), 121.2, 119.3, 63.1, 27.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -57.7 (s). HRMS (ESI) calcd for $C_{18}H_{16}F_3O_5S$ $[M+H]^+$: 401.0665; found: 401.0659.



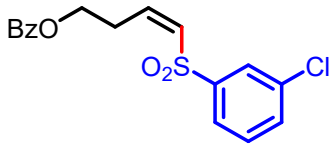
*(Z)-4-((4-fluorophenyl)sulfonyl)but-3-en-1-yl benzoate (**4c**)*

Colorless oil (42.8 mg, 64%, *Z*/*E* = 10:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 7.94 – 7.89 (m, 2H), 7.60 – 7.55 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 8.5 Hz, 2H), 6.43 – 6.36 (m, 2H), 4.45 (t, *J* = 6.2 Hz, 2H), 3.25 – 3.20 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 165.8 (d, *J* = 257.0 Hz), 142.6, 137.4 (d, *J* = 2.5 Hz), 133.3, 132.4, 130.3 (d, *J* = 10.1 Hz), 129.9, 129.7, 128.6, 116.8 (d, *J* = 11.1 Hz), 63.1, 27.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -103.6 (s). HRMS (ESI) calcd for $C_{17}H_{16}FO_4S$ $[M+H]^+$: 335.0748; found: 335.0729.



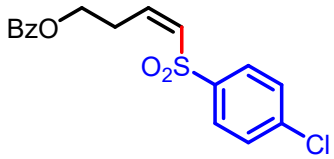
*(Z)-4-((2-chlorophenyl)sulfonyl)but-3-en-1-yl benzoate (**4d**)*

Colorless oil (43.5 mg, 62%, *Z*/*E* = 10:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.58 – 7.49 (m, 2H), 7.48 – 7.41 (m, 4H), 6.65 – 6.59 (m, 1H), 6.54 – 6.45 (m, 1H), 4.39 (t, *J* = 6.2 Hz, 2H), 3.16 – 3.08 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 143.9, 139.0, 134.7, 133.2, 133.0, 132.0, 131.4, 130.5, 129.9, 129.7, 128.5, 127.5, 63.0, 27.8. HRMS (ESI) calcd for $C_{17}H_{16}ClO_4S$ $[M+H]^+$: 351.0452; found: 351.0439.



*(Z)-4-((3-chlorophenyl)sulfonyl)but-3-en-1-yl benzoate (**4e**)*

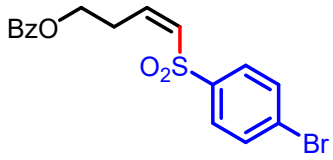
Colorless oil (54.7 mg, 78%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.90 (t, *J* = 1.9 Hz, 1H), 7.80 – 7.77 (m, 1H), 7.58 – 7.53 (m, 2H), 7.45 – 7.40 (m, 3H), 6.48 – 6.37 (m, 2H), 4.45 (t, *J* = 6.2 Hz, 2H), 3.25 – 3.20 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 143.5, 143.0, 135.7, 133.8, 133.3, 131.9, 130.8, 129.9, 129.7, 128.5, 127.5, 125.5, 63.0, 27.6. HRMS (ESI) calcd for $C_{17}H_{16}ClO_4S$ $[M+H]^+$: 351.0452; found: 351.0440.



*(Z)-4-((4-chlorophenyl)sulfonyl)but-3-en-1-yl benzoate (**4f**)*

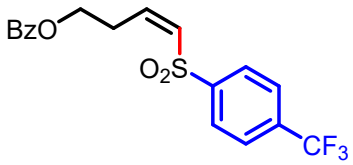
White solid (49.1 mg, 70%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.86 – 7.80 (m, 2H), 7.60 – 7.55 (m, 1H), 7.47 – 7.41 (m, 4H), 6.44 – 6.36 (m, 2H), 4.45 (t, *J* = 6.1 Hz, 2H), 3.22 (q, *J* = 6.0 Hz, 2H). ^{13}C NMR (126 MHz,

$CDCl_3$) δ 166.4, 143.1, 140.4, 139.8, 133.3, 132.1, 129.9, 129.8, 129.7, 128.9, 128.6, 63.1, 27.6. HRMS (ESI) calcd for $C_{17}H_{16}ClO_4S$ $[M+H]^+$: 351.0452; found: 351.0441.



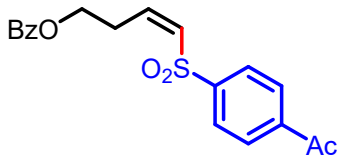
*(Z)-4-((4-bromophenyl)sulfonyl)but-3-en-1-yl benzoate (**4g**)*

Colorless oil (64.0 mg, 81%, *Z*/*E* = 14:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.78 – 7.72 (m, 2H), 7.62 – 7.55 (m, 3H), 7.46 – 7.40 (m, 2H), 6.47 – 6.34 (m, 2H), 4.45 (t, *J* = 6.1 Hz, 2H), 3.21 (q, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 142.1, 139.3, 132.3, 131.8, 131.7, 131.1, 128.9, 128.7, 128.6, 128.3, 128.0, 127.5, 62.0, 26.6. HRMS (ESI) calcd for $C_{17}H_{16}BrO_4S$ $[M+H]^+$: 394.9947; found: 394.9937.



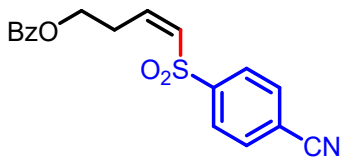
*(Z)-4-((4-(trifluoromethyl)phenyl)sulfonyl)but-3-en-1-yl benzoate (**4h**)*

Colorless oil (50.7 mg, 66%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 6.53 – 6.45 (m, 1H), 6.43 – 6.33 (m, 1H), 4.47 (t, *J* = 6.1 Hz, 2H), 3.29 – 3.21 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 144.8, 144.1, 135.3 (q, *J* = 32.8 Hz), 133.4, 131.6, 129.9, 129.7, 128.6, 128.1, 126.6 (q, *J* = 3.8 Hz), 123.2 (q, *J* = 273.4 Hz), 63.0, 27.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.2 (s). HRMS (ESI) calcd for $C_{18}H_{16}F_3O_4S$ $[M+H]^+$: 385.0716; found: 385.0711.



*(Z)-4-((4-acetylphenyl)sulfonyl)but-3-en-1-yl benzoate (**4i**)*

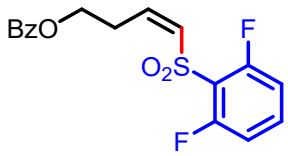
White solid (49.5 mg, 69%, *Z*/*E* = 9:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.93 (m, 6H), 7.58 – 7.54 (m, 1H), 7.44 – 7.38 (m, 2H), 6.50 – 6.38 (m, 2H), 4.47 – 4.44 (m, 2H), 3.28 – 3.19 (m, 2H), 2.62 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 166.4, 145.1, 143.9, 140.8, 133.3, 132.4, 131.9, 129.7, 129.2, 128.6, 127.8, 63.0, 27.7, 27.0. HRMS (ESI) calcd for $C_{19}H_{19}O_5S$ $[M+H]^+$: 359.0948; found: 359.0936.



*(Z)-4-((4-cyanophenyl)sulfonyl)but-3-en-1-yl benzoate (**4j**)*

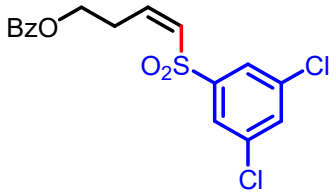
White solid (56.0 mg, 82%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR

(500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.98 – 7.93 (m, 2H), 7.76 – 7.70 (m, 2H), 7.62 – 7.57 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 6.55 – 6.47 (m, 1H), 6.43 – 6.35 (m, 1H), 4.47 (t, *J* = 6.1 Hz, 2H), 3.27 – 3.19 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 145.4, 144.9, 133.5, 133.2, 131.3, 129.8, 129.7, 128.6, 128.1, 117.4, 117.2, 62.9, 27.9. HRMS (ESI) calcd for $C_{18}H_{16}NO_4S$ $[M+H]^+$: 342.0795; found: 342.0789.



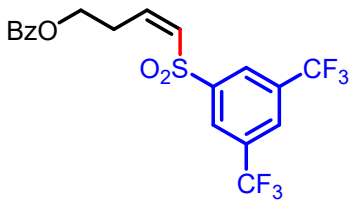
*(Z)-4-((2,6-difluorophenyl)sulfonyl)but-3-en-1-yl benzoate (**4k**)*

Colorless oil (59.9 mg, 85%, *Z*/*E* > 20:1, which was detected by ^1H NMR spectroscopy). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.59 – 7.48 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 8.4 Hz, 2H), 6.66 – 6.60 (m, 1H), 6.58 – 6.50 (m, 1H), 4.44 (t, *J* = 6.1 Hz, 2H), 3.28 – 3.21 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 161.3 (d, *J* = 3.8 Hz), 158.8 (d, *J* = 5.0 Hz), 144.6, 135.7 (d, *J* = 13.8 Hz), 133.3, 132.6, 129.9, 129.7, 128.5, 113.4 (dd, *J* = 27.7, 3.8 Hz), 63.0, 27.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -106.5 (s). HRMS (ESI) calcd for $C_{17}H_{15}F_2O_4S$ $[M+H]^+$: 353.0654; found: 353.0640.



*(Z)-4-((3,5-dichlorophenyl)sulfonyl)but-3-en-1-yl benzoate (**4l**)*

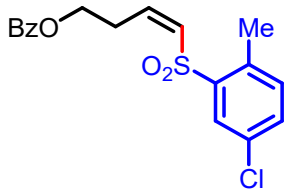
White solid (63.9 mg, 83%, *Z*/*E* > 20:1, which was detected by ^1H NMR spectroscopy). ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.78 (d, *J* = 1.8 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 6.53 – 6.46 (m, 1H), 6.42 – 6.35 (m, 1H), 4.46 (t, *J* = 6.1 Hz, 2H), 3.25 – 3.18 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 144.6, 144.2, 136.5, 133.7, 133.3, 131.3, 130.0, 129.7, 128.5, 125.8, 62.9, 27.8. HRMS (ESI) calcd for $C_{17}H_{15}Cl_2O_4S$ $[M+H]^+$: 385.0063; found: 385.0049.



*(Z)-4-((3,5-bis(trifluoromethyl)phenyl)sulfonyl)but-3-en-1-yl benzoate (**4m**)*

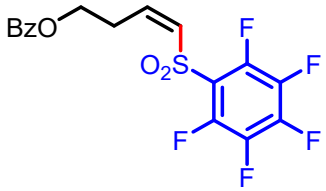
White solid (71.5 mg, 79%, *Z*/*E* > 20:1, which was detected by ^1H NMR spectroscopy). ^1H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 1.6 Hz, 2H), 8.10 (s, 1H), 8.00 – 7.95 (m, 2H), 7.58 – 7.54 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 6.61 – 6.53 (m, 1H), 6.46 – 6.40 (m, 1H), 4.48 (t, *J* = 6.2 Hz, 2H), 3.28 – 3.23 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 145.4, 144.0, 133.3 (q, *J* = 35.3 Hz), 133.2, 130.7, 129.60, 129.55, 129.4, 128.4, 127.7 (q, *J* = 3.8 Hz), 127.2 – 127.1 (dt, m), 122.3 (q, *J* = 273.4 Hz), 62.7, 27.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9 (s). HRMS (ESI) calcd for

$C_{19}H_{15}F_6O_4S$ $[M+H]^+$: 453.0590; found: 453.0587.



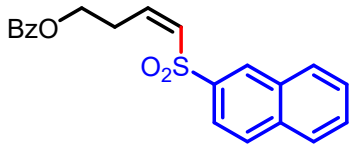
*(Z)-4-((5-chloro-2-methylphenyl)sulfonyl)but-3-en-1-yl benzoate (**4n**)*

White solid (39.5 mg, 54%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.68 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 6.43 – 6.37 (m, 2H), 4.45 (t, *J* = 6.2 Hz, 2H), 3.25 – 3.19 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 142.9, 142.7, 140.3, 135.6, 133.3, 132.3, 131.9, 129.9, 129.7, 128.5, 128.0, 125.5, 63.1, 27.6, 20.5. HRMS (ESI) calcd for $C_{18}H_{18}ClO_4S$ $[M+H]^+$: 365.0609; found: 365.0594.



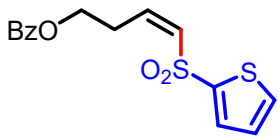
*(Z)-4-((perfluorophenyl)sulfonyl)but-3-en-1-yl benzoate (**4o**)*

White solid (56.8 mg, 70%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 6.75 – 6.56 (m, 2H), 4.48 (t, *J* = 6.1 Hz, 2H), 3.25 (q, *J* = 6.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 147.1, 144.9 (dm, *J* = 278.4 Hz), 138.0 (dm, *J* = 262.1 Hz), 133.4, 132.3, 131.7, 129.7, 129.6, 129.5, 128.6, 62.8, 27.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.99 – -1436.09 (m), -143.35 – -143.47 (m), -157.82 – -157.95 (m). HRMS (ESI) calcd for $C_{17}H_{12}F_5O_4S$ $[M+H]^+$: 407.0371; found: 407.0370.



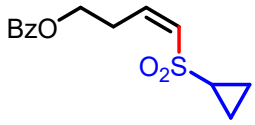
*(Z)-4-(naphthalen-2-ylsulfonyl)but-3-en-1-yl benzoate (**4p**)*

White solid (38.1 mg, 52%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.99 – 7.91 (m, 4H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.85 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.64 – 7.59 (m, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 6.51 – 6.45 (m, 1H), 6.43 – 6.36 (m, 1H), 4.46 (t, *J* = 6.2 Hz, 2H), 3.32 –3.25 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 142.5, 138.2, 135.3, 133.2, 132.5, 132.3, 129.9, 129.8, 129.7, 129.6, 129.4, 129.0, 128.5, 128.1, 127.8, 122.3, 63.2, 27.6. HRMS (ESI) calcd for $C_{21}H_{19}O_4S$ $[M+H]^+$: 367.0999; found: 367.0980.



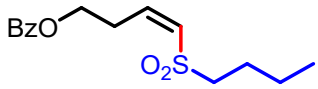
*(Z)-4-(thiophen-2-ylsulfonyl)but-3-en-1-yl benzoate (**4q**)*

Brown oil (39.3 mg, 61%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.58 – 7.54 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.10 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.53 – 6.47 (m, 1H), 6.42 – 6.35 (m, 1H), 4.45 (t, *J* = 6.2 Hz, 2H), 3.26 – 3.21 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 142.8, 142.2, 134.0, 133.4, 133.3, 133.0, 129.9, 129.8, 128.5, 128.1, 63.1, 27.5. HRMS (ESI) calcd for $C_{15}H_{15}O_4S_2$ $[M+H]^+$: 323.0406; found: 323.0396.



*(Z)-4-(cyclopropylsulfonyl)but-3-en-1-yl benzoate (**4r**)*

Pale yellow oil (47.1 mg, 84%, *Z*/*E* = 2.5:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.51 – 7.47 (m, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 6.40 – 6.29 (m, 2H), 4.39 (t, *J* = 6.3 Hz, 2H), 3.14 – 3.07 (m, 2H), 2.41 – 2.32 (m, 1H), 1.20 – 1.17 (m, 2H), 0.95 – 0.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 142.4, 133.3, 131.0, 130.0, 129.7, 128.5, 63.2, 32.0, 27.6, 5.1. HRMS (ESI) calcd for $C_{14}H_{17}O_4S$ $[M+H]^+$: 281.0842; found: 281.0830.

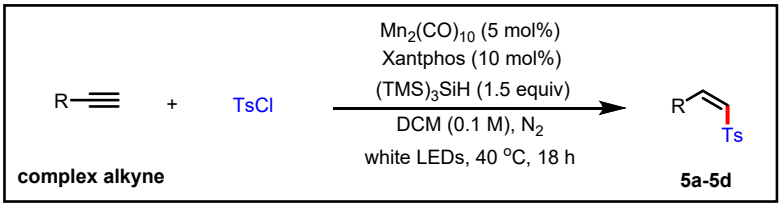


*(Z)-4-(butylsulfonyl)but-3-en-1-yl benzoate (**4s**)*

Colorless oil (30.8 mg, 52%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.60 – 7.53 (m, 1H), 7.48 – 7.41 (m, 2H), 6.56 – 6.46 (m, 1H), 6.33 – 6.26 (m, 1H), 4.46 (t, *J* = 6.2 Hz, 2H), 3.22 – 3.14 (m, 2H), 3.01 – 2.94 (m, 2H), 1.81 – 1.72 (m, 2H), 1.45 – 1.35 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 144.2, 133.3, 130.1, 130.3, 129.7, 128.6, 63.2, 55.5, 27.6, 24.3, 21.7, 13.7. HRMS (ESI) calcd for $C_{15}H_{21}O_4S$ $[M+H]^+$: 297.1155; found: 297.1143.

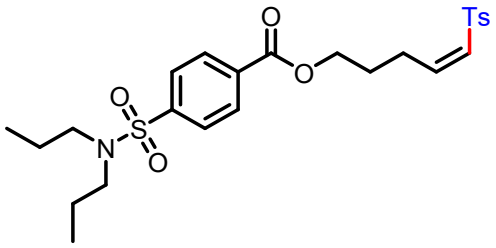
4. Synthetic Application

4.1 Hydrosulfonylation of structurally complex natural products and drugs



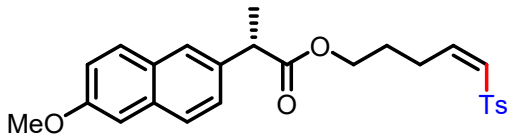
To an oven-dried 10 mL sealed tube, $Mn_2(CO)_{10}$ (5 mol%, 0.01 mmol), Xantphos (10 mol%, 0.02 mmol), $(TMS)_3SiH$ (1.5 equiv, 0.3 mmol), complex alkyne (0.2 mmol), TsCl (0.6 mmol) and DCM

(2 mL) were added and the tube was backfilled with nitrogen. The resulting reaction mixture was vigorously stirred under the irradiation of two 45 W white LEDs (distance app. 4.0 cm from the bulb) at 40 °C for 18 h. After the reaction finished, the solvent was removed under vacuum, and the resulting residue was purified by column chromatography (eluent: PE/EA = 1:5 to 1:1) to afford the corresponding product.



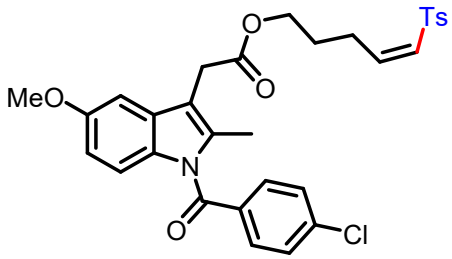
*(Z)-5-tosylpent-4-en-1-yl 4-(N,N-dipropylsulfamoyl)benzoate (**5a**)*

White solid (51.8 mg, 51%, *Z*/*E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.34 – 6.22 (m, 2H), 4.37 (t, *J* = 6.3 Hz, 2H), 3.11 – 3.06 (m, 4H), 2.88 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.98 – 1.92 (m, 2H), 1.57 – 1.50 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 144.8, 144.6, 144.4, 138.6, 133.5, 131.8, 130.4, 130.0, 127.4, 127.1, 64.8, 50.1, 28.0, 24.6, 22.1, 21.7, 11.3. HRMS (ESI) calcd for $C_{25}H_{34}NO_6S_2$ $[M+H]^+$: 508.1822; found: 508.1811.



*(Z)-5-tosylpent-4-en-1-yl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (**5b**)*

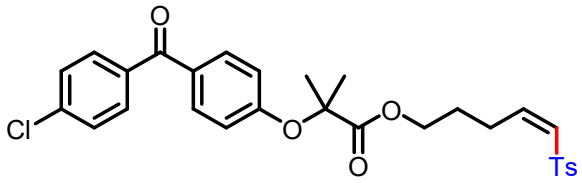
Pale yellow oil (69.8 mg, 77%, *Z*/*E* = 3:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.70 – 7.67 (m, 3H), 7.40 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.28 – 7.26 (m, 2H), 7.15 – 7.10 (m, 2H), 6.15 – 6.11 (m, 1H), 6.07 – 6.03 (m, 1H), 4.08 (t, *J* = 6.3 Hz, 2H), 3.90 (s, 3H), 3.85 (t, *J* = 7.1 Hz, 1H), 2.69 – 2.64 (m, 2H), 2.40 (s, 3H), 1.72 – 1.67 (m, 2H), 1.57 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 144.8, 144.6, 144.4, 138.6, 133.5, 131.82, 131.76, 130.4, 130.3, 130.0, 127.8, 127.4, 127.2, 127.1, 64.8, 50.1, 28.0, 24.6, 22.1, 21.7, 11.3. HRMS (ESI) calcd for $C_{26}H_{29}O_5S$ $[M+H]^+$: 453.1730; found: 453.1716.



*(Z)-5-tosylpent-4-en-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (**5c**)*

Pale yellow oil (62.6 mg, 54%, *Z*/*E* = 17:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H),

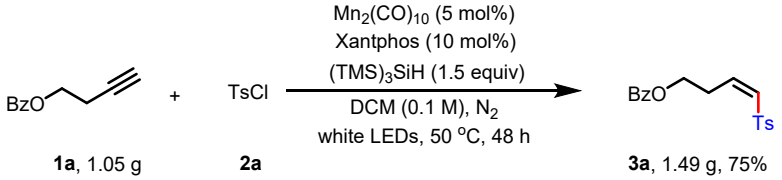
7.31 (d, J = 7.9 Hz, 2H), 6.97 (d, J = 2.5 Hz, 1H), 6.88 (d, J = 9.0 Hz, 1H), 6.66 (dd, J = 9.0, 2.6 Hz, 1H), 6.26 – 6.20 (m, 1H), 6.15 – 6.08 (m, 1H), 4.12 (t, J = 6.4 Hz, 2H), 3.82 (s, 3H), 3.68 (s, 2H), 2.73 (q, J = 7.0 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H), 1.81 – 1.74 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 168.4, 156.2, 144.8, 144.6, 139.4, 138.7, 136.1, 134.0, 131.6, 131.3, 131.0, 130.8, 130.0, 129.2, 127.4, 115.1, 112.7, 111.8, 101.5, 64.2, 55.9, 30.5, 27.9, 24.4, 21.8, 135. HRMS (ESI) calcd for $C_{31}H_{31}ClNO_6S$ $[M+H]^+$: 580.1555; found: 580.1539.



*(Z)-5-tosylpent-4-en-1-yl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (**5d**)*

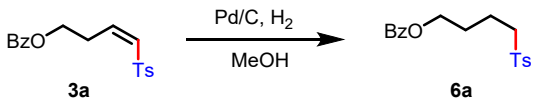
Colorless oil (57.3 mg, 53%, Z/E = 7:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 4H), 7.70 – 7.67 (m, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.88 – 6.85 (m, 2H), 6.27 – 6.22 (m, 1H), 6.11 (d, J = 11.1 Hz, 1H), 4.19 (t, J = 6.4 Hz, 2H), 2.67 (q, J = 7.9 Hz, 2H), 2.42 (s, 3H), 1.79 – 1.72 (m, 2H), 1.68 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 157.7, 145.1, 144.4, 138.7, 135.7, 133.8, 131.3, 130.0, 129.4, 129.0, 127.7, 127.4, 126.3, 126.1, 119.1, 105.7, 64.0, 55.4, 45.6, 27.8, 24.5, 18.5. HRMS (ESI) calcd for $C_{29}H_{30}ClO_6S$ $[M+H]^+$: 541.1446; found: 541.1430.

4.2 Gram scale synthesis of **3a**

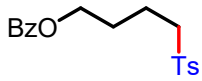


To an oven-dried 100 mL sealed flask, $Mn_2(CO)_{10}$ (5 mol%, 0.3 mmol, 117 mg), Xantphos (10 mol%, 0.6 mmol, 347 mg), $(TMS)_3SiH$ (1.5 equiv, 9 mmol, 2.24 g), but-3-yn-1-yl benzoate (6 mmol, 1.05 g) **1a**, TsCl **2a** (18 mmol, 3.43 g) and DCM (60 mL) were added and the flask was backfilled with nitrogen. The resulting reaction mixture was vigorously stirred under the irradiation of two 45 W white LEDs (distance app. 6.0 cm from the bulb) at 50 °C for 48 h. After the reaction finished, the solvent was removed under vacuum, and the resulting residue was purified by column chromatography on silica gel to afford the corresponding product **3a** in 1.49 g, 75% yield, >20:1 Z/E ratio.

4.3 The procedure for the synthesis of **6a**



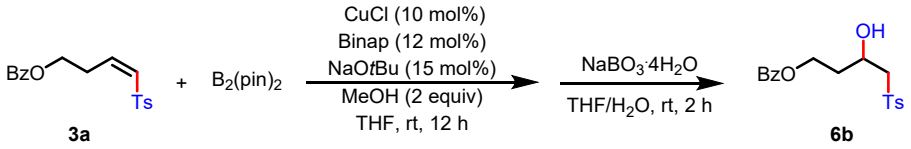
A solution of **3a** (66 mg, 0.2 mmol) in MeOH (4 mL) was added 10% Pd/C, then the mixture was stirred under H_2 (1 atm, balloon) overnight. The catalyst was removed by filtration over celite and the filtrate was concentrated *in vacuo* to provide the residue, which was purified by the column chromatography to give the target product **6a**.



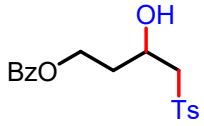
*4-tosylbutyl benzoate (**6a**)*

Colorless oil (63.1 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.28 (t, *J* = 5.7 Hz, 2H), 3.18 – 3.10 (m, 2H), 2.43 (s, 3H), 1.91 – 1.82 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 144.9, 136.1, 133.2, 130.13, 130.05, 129.7, 128.5, 128.2, 63.9, 55.9, 27.5, 21.8, 19.9. HRMS (ESI) calcd for $C_{18}H_{21}O_4S$ $[M+H]^+$: 333.1155; found: 333.1142.

4.4 The procedure for the synthesis of **6b**[1]



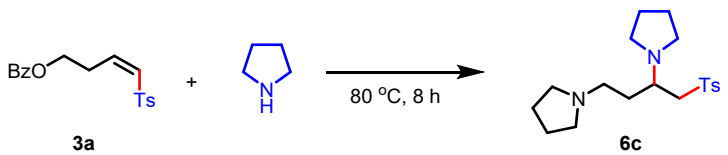
To a mixture of the **3a** (66 mg, 0.20 mmol), CuCl (2.0 mg, 0.020 mmol, 10 mol%), NaOtBu (2.9 mg, 0.030 mmol, 15 mol%), Binap (14.9 mg, 0.024 mmol, 12 mol%) and bis(pinacolato)diboron (55.9 mg, 0.22 mmol, 1.1 equiv) in anhydrous THF (0.4 mL), at room temperature under argon atmosphere, was added MeOH (16 µL, 0.40 mmol, 2.0 equiv). The mixture was stirred for 12 h and then it was quenched with MeOH (1 mL). After 5 min of further stirring at room temperature, the mixture was filtered through a pad of Celite and the filtrate was concentrated to dryness. The residue was dissolved in a 1:1 mixture of THF/H_2O (2 mL) and sodium perborate tetrahydrate (92.3 mg, 0.60 mmol, 3.0 equiv) was added. The mixture was stirred at room temperature for 2 h before it was extracted with EtOAc (2 x 10 mL). The combined organic phase was dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired β-hydroxysulfone **6b**.



*3-hydroxy-4-tosylbutyl benzoate (**6b**)*

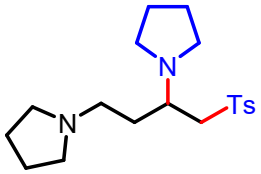
Colorless oil (51.6 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.50 – 4.38 (m, 2H), 4.36 – 4.28 (m, 1H), 3.64 (s, 1H), 3.35 – 3.19 (m, 2H), 2.41 (s, 3H), 1.97 – 1.89 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 145.3, 136.2, 133.2, 130.2, 130.0, 129.7, 128.5, 128.1, 63.4, 62.3, 61.0, 35.6, 21.8. HRMS (ESI) calcd for $C_{18}H_{21}O_5S$ $[M+H]^+$: 349.1104; found: 239.1092.

4.5 The procedure for the synthesis of **6c**[2]



A mixture of **3a** (66 mg, 0.20 mmol) tetrahydropyrrole (0.33 mL, 20 equiv) was stirred at 80 °C for 6 h. After the completion of reaction, saturated ammonium chloride solution (10 mL) was added to

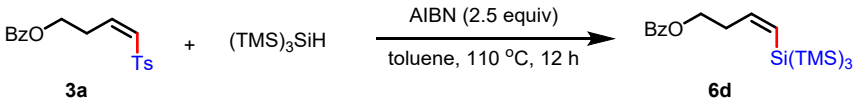
the reaction system to quench the reaction. Then EtOAc (20 mL) was poured into the reaction mixture. The organic layers were extracted with water (3 × 10 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and filtered and solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel t to afford the desired product **6c** with 92% yield.



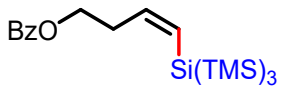
*1,1'-(4-tosylbutane-1,3-diyl)dipyrrolidine (**6c**)*

Yellow oil (64.5 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.30 – 3.22 (m, 2H), 3.08 (dd, *J* = 15.2, 7.8 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.58 – 2.50 (m, 4H), 2.49 – 2.43 (m, 3H), 2.42 (s, 3H), 2.36 – 2.28 (m, 2H), 1.86 – 1.74 (m, 6H), 1.62 – 1.52 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 137.5, 129.8, 128.0, 56.7, 54.2, 54.0, 53.3, 47.9, 31.5, 23.6, 23.5, 21.7. HRMS (ESI) calcd for $C_{19}H_{31}N_2O_2S$ $[M+H]^+$: 351.2101; found: 351.2088.

4.6 The procedure for the synthesis of **6d**



A solution of **3a** (66 mg, 0.2 mmol), $Si(TMS)_3H$ (149 mg, 3 equiv) and AIBN (2,2'-Azobis(2-methylpropionitrile), 82 mg, 2.5 equiv) in toluene (2 mL) was stirred at 110 °C for 12 h. After the completion of reaction, EtOAc (20 mL) was poured into the reaction mixture. The organic layers were extracted with water (3 × 10 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and filtered and solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel using afford **6d** with 87% yield, >20:1 *Z/E* ratio.

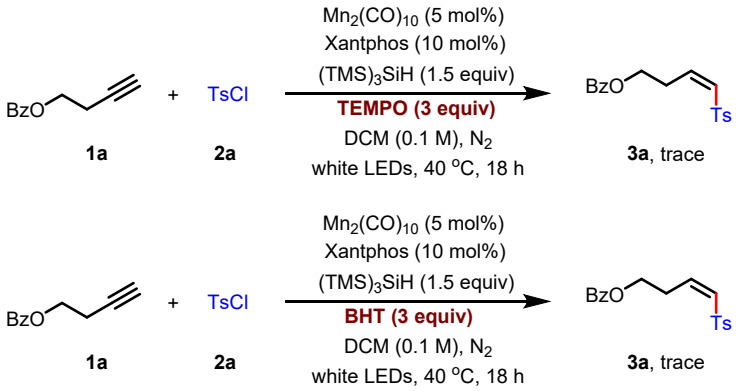


*(Z)-4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)but-3-en-1-yl benzoate (**6d**)*

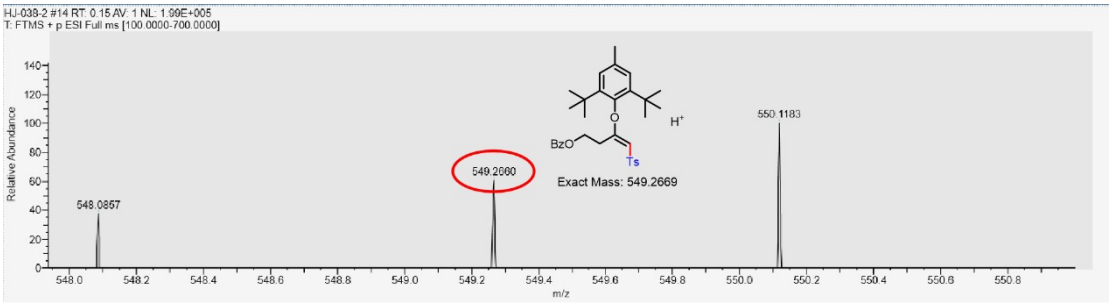
Colorless oil (73.6 mg, 87%, *Z/E* > 20:1, which was detected by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 6.08 – 5.98 (m, 1H), 5.77 – 5.67 (m, 1H), 4.36 (t, *J* = 6.6 Hz, 2H), 2.61 – 2.54 (m, 2H), 0.14 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 142.7, 132.0, 129.5, 128.7, 127.4, 124.3, 63.3, 35.9, -0.10. HRMS (ESI) calcd for $C_{20}H_{39}O_2Si_4$ $[M+H]^+$: 423.2022; found: 423.2007.

5. Mechanistic Studies

5.1 Radical trapping experiments



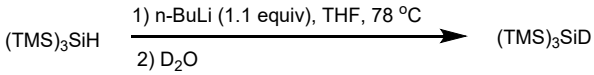
To an oven-dried 10 mL sealed tube, $Mn_2(CO)_{10}$ (5 mol%, 0.01 mmol), Xantphos (10 mol%, 0.02 mmol), $(TMS)_3SiH$ (1.5 equiv, 0.3 mmol), but-3-yn-1-yl benzoate (0.2 mmol), TsCl (0.6 mmol), TEMPO (0.8 mmol) or BHT (0.8 mmol), and DCM (2 mL) were added and the tube was backfilled with nitrogen. The resulting reaction mixture was vigorously stirred under the irradiation of two 45 W white LEDs (distance app. 4.0 cm from the bulb) at 40 °C for 18 h. After the reaction finished, the reaction mixture was analyzed by GC and HR-MS. Trace yield of desired product **3** was detected. These results indicated that a radical mechanism might be operative.



Supplementary Figure 1. The HR-MS result for radical trapping with BHT.

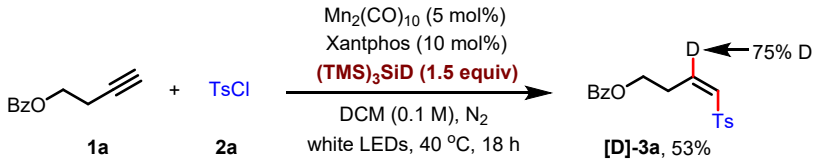
5.2 Deuterium-labeling experiment

5.2.1 The preparation of $(TMS)_3SiD$

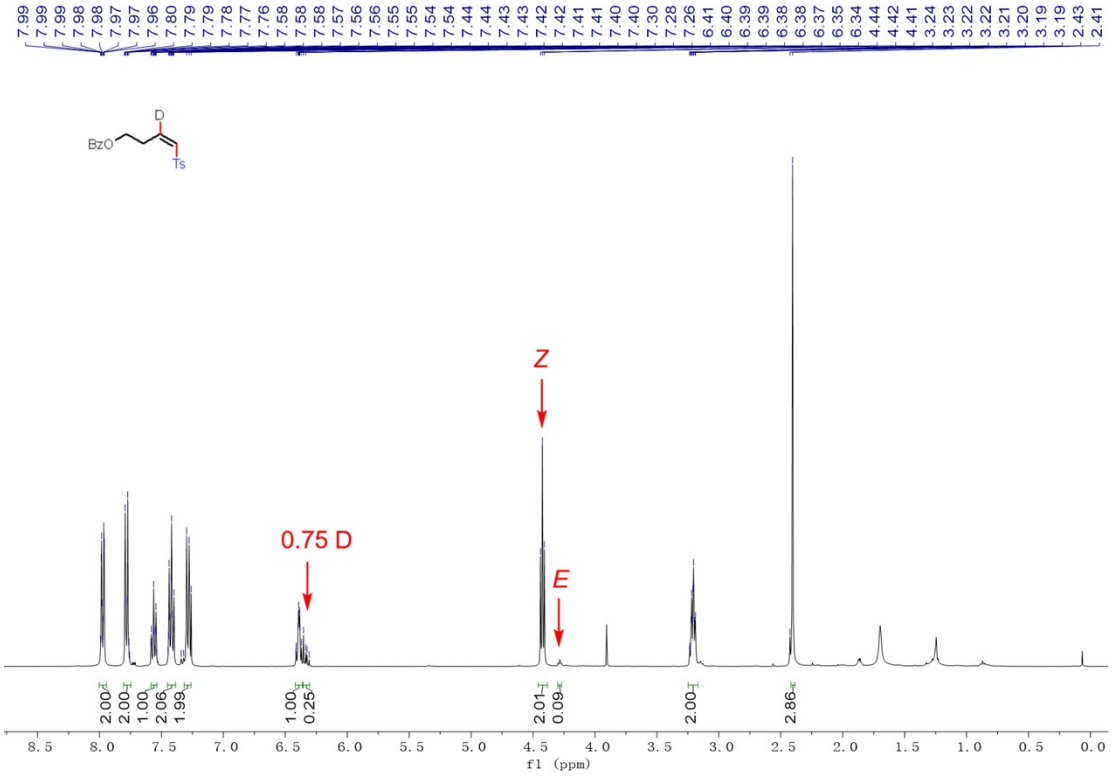


To a solution of $(TMS)_3SiH$ (248 mg, 1 mmol) in THF (3 mL) was dropwise added n-BuLi (1.1 equiv) at -78 °C. And the reaction mixture was stirred at the same temperature for 2 hours. Then 20 equiv D_2O was added to the mixture and the mixture was stirred at room temperature for 30 min. After the completion of reaction, EtOAc (10 mL) was poured into the reaction mixture. The organic layers were extracted with water (3 × 10 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and filtered and solvent was removed under reduced pressure. The product could be used directly without purification.

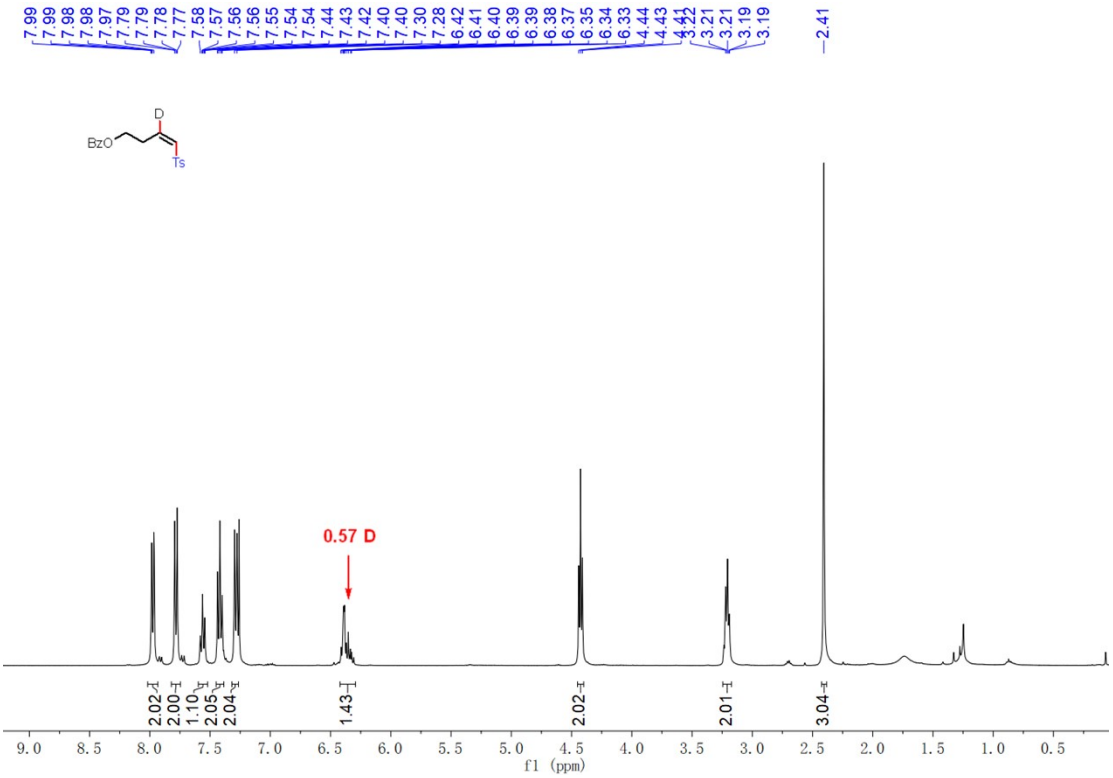
5.2.2 The model reaction with $(TMS)_3SiD$



To an oven-dried 10 mL sealed tube, $Mn_2(CO)_{10}$ (5 mol%, 0.01 mmol), Xantphos (10 mol%, 0.02 mmol), $(TMS)_3SiD$ (1.5 equiv, 0.3 mmol), but-3-yn-1-yl benzoate (0.2 mmol), TsCl (0.6 mmol), and DCM (2 mL) or DCM (4 mL) were added and the tube was backfilled with nitrogen. The resulting reaction mixture was vigorously stirred under the irradiation of two 45 W white LEDs (distance app. 4.0 cm from the bulb) at 40 °C for 18 h. After the reaction finished, the solvent was removed under vacuum, and the resulting residue was purified by column chromatography on silica gel to afford the corresponding product **[D]-3a** in 53% yield, *Z*/*E* > 20:1. The deuterated ratios of the product were determined by 1H NMR. This result confirms that H atom source mainly comes from the $(TMS)_3SiH$.

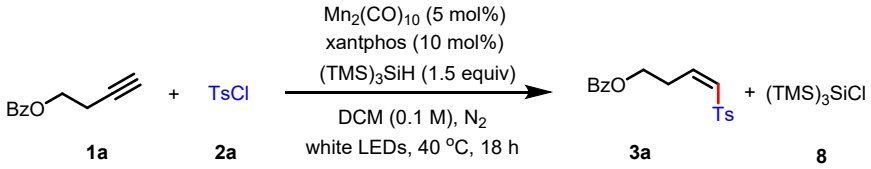


Supplementary Figure 2. The ^1H NMR of **[D]-3a** (in 0.1 M CH_2Cl_2).

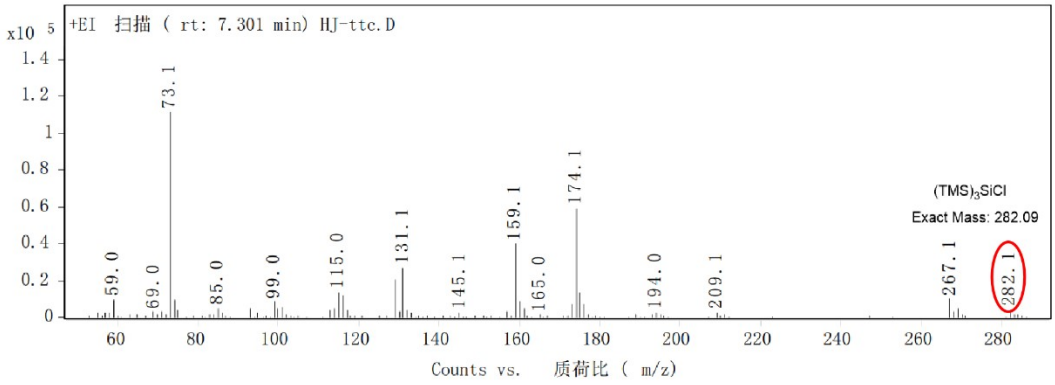


Supplementary Figure 3. The ^{1}H NMR of **[D]-3a** (in 0.05 M CH_2Cl_2).

5.3 Formation and detection of $(TMS)_3SiCl$

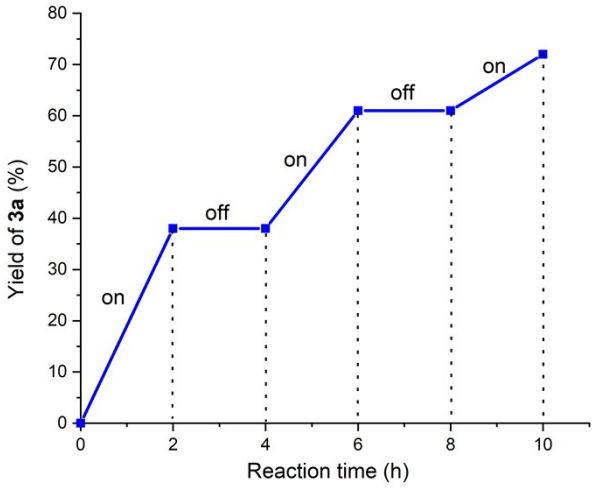


The model reaction was conducted under standard conditions, and the reaction mixture was detected by GC-MS.



Supplementary Figure 4. The GC-MS result of $(TMS)_3SiCl$

5.4 Turn on/off profile experiment[3]

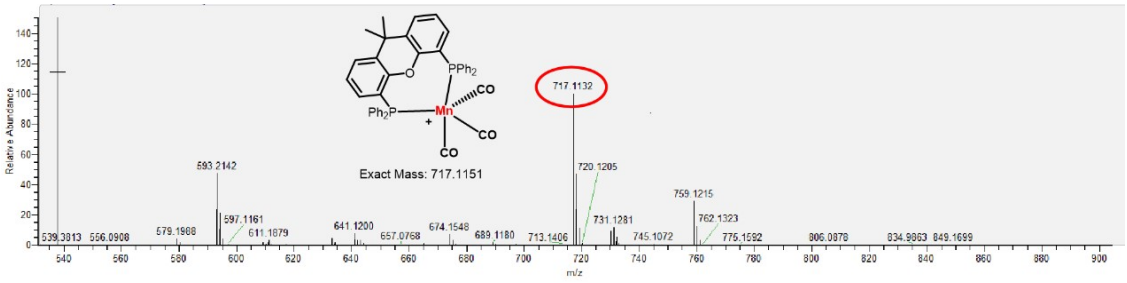


Supplementary Figure 5. Time profile of photocatalytic reaction with and without white light.

To an oven-dried 10 mL sealed tube, $Mn_2(CO)_{10}$ (5 mol%, 0.01 mmol), Xantphos (10 mol%, 0.02 mmol), $(TMS)_3SiH$ (1.5 equiv, 0.3 mmol), but-3-yn-1-yl benzoate (0.2 mmol), TsCl (0.6 mmol), and DCM (2 mL) were added and the tube was backfilled with nitrogen. The resulting reaction mixture was vigorously stirred under the irradiation of two 45 W white LEDs (distance app. 4.0 cm from the bulb) at 40 °C. The process of photocatalytic reaction with and without light was monitored by GC, the yields were detected using dodecane as internal standard. It was found that the formation of **3a** needed continuous irradiation of white light.

5.5 HRMS analysis of reaction mixture of $Mn_2(CO)_{10}$ and **L1**

The reaction mixture of $Mn_2(CO)_{10}$ (19 mg) and Xantphos (**L1**) (58 mg) in DCM under the irradiation of two 45 W white LEDs (distance app. 4.0 cm from the bulb) at 40 °C. 1 hour later, the mixture was subjected to HRMS analysis, the mass of $[\mathbf{L1}Mn(CO)_3]^+$ could be detected, since the $\mathbf{L1}Mn(CO)_3\cdot$ readily loses one electron during the HRMS analysis. This result supports the existence of $\mathbf{L1}Mn(CO)_3\cdot$ and the manganese center was coordinated with ligand **L1**.



Supplementary Figure 6. The HR-MS result for $[\mathbf{L1}Mn(CO)_3]^+$.

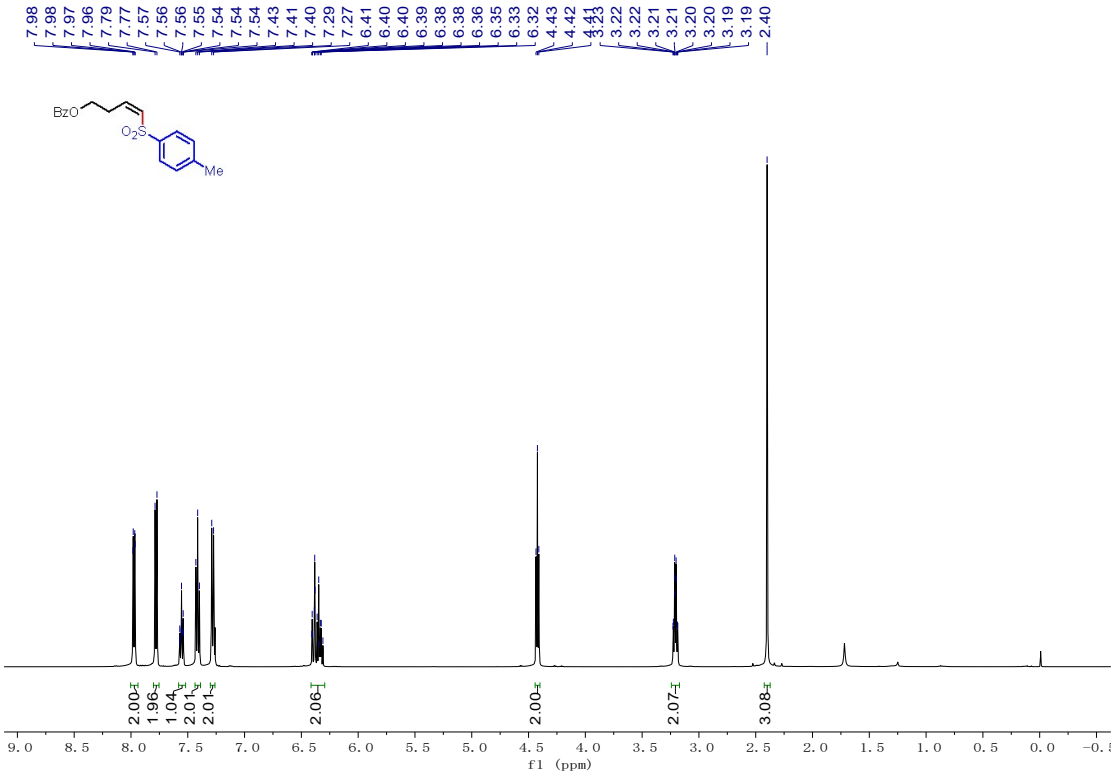
6. Supplementary references

[1] A. L. Moure, R. G. Arrayás, J. C. Carretero. *Chem. Commun.* **2011**, *47*, 6701–6703.

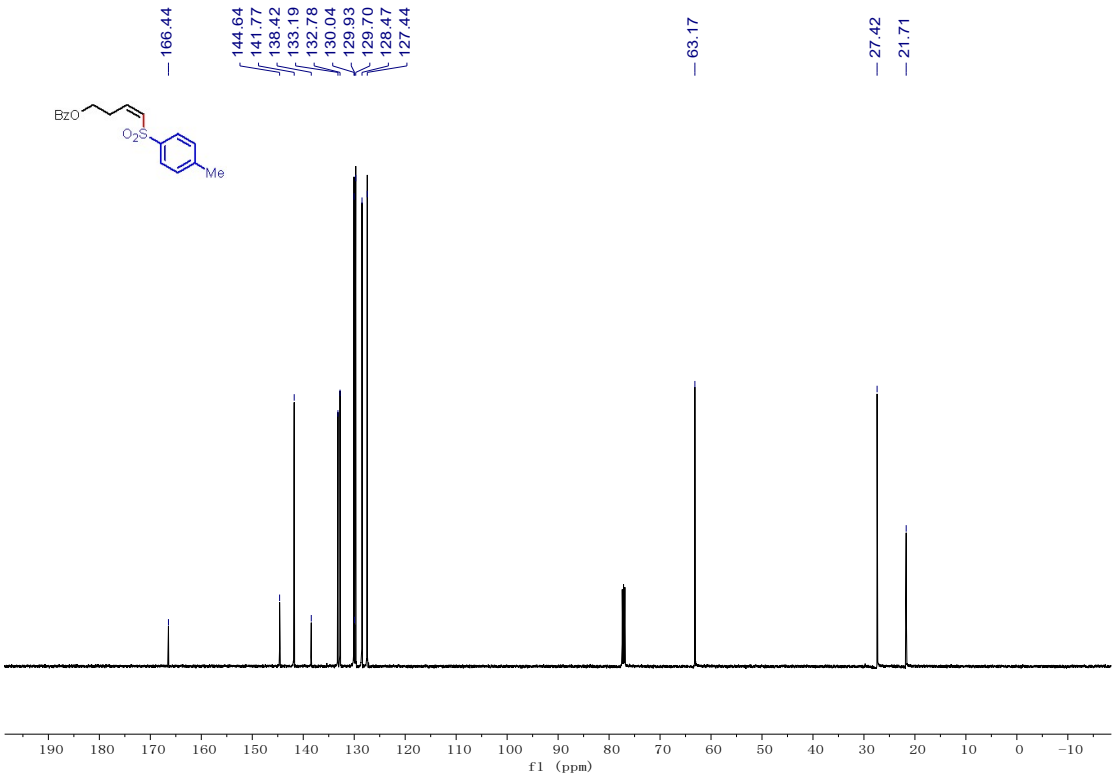
[2] Z. Zhang, Q. Song, C. Feng, Z. Wang, W. Zhao, Y. Ning, Y. Wu. *Chem Asian J.* **2022**, *17*, e202200299.

[3] J. Han, J. Han, S. Chen, T. Zhong, Y. He, X. Yang, G. Wang, C. Zhu, J. Xie, *Nat. Syn.* **2022**, *1*, 475-486

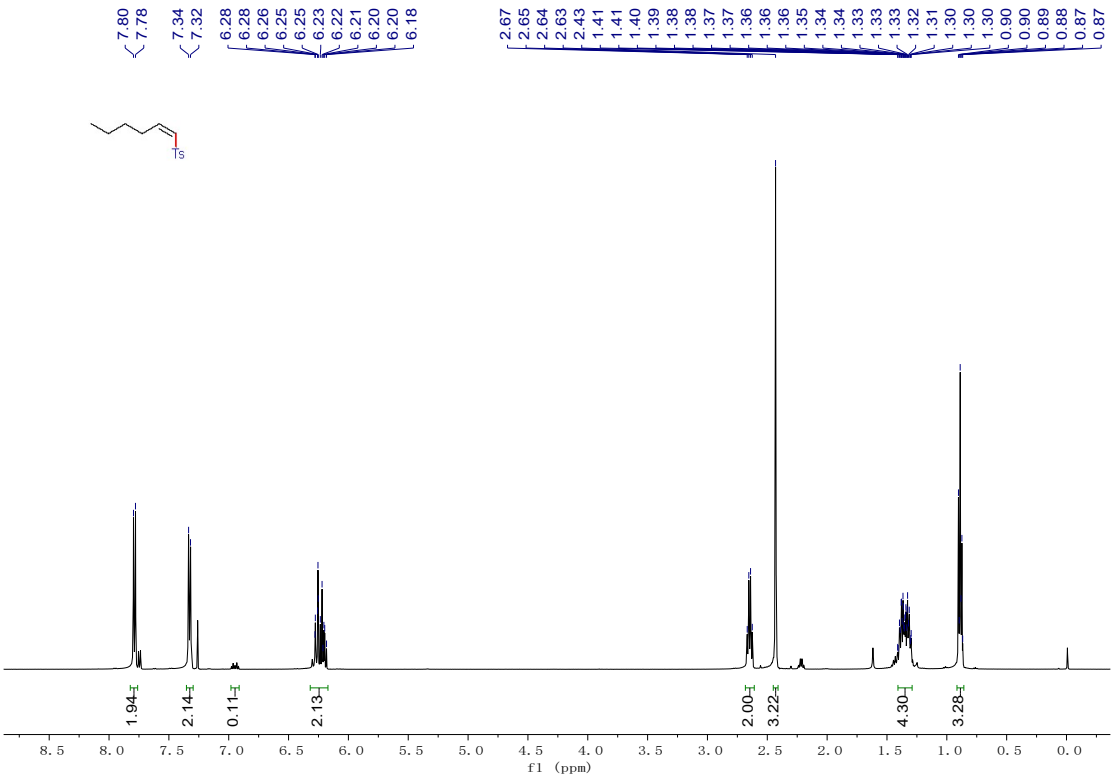
7. NMR Spectra



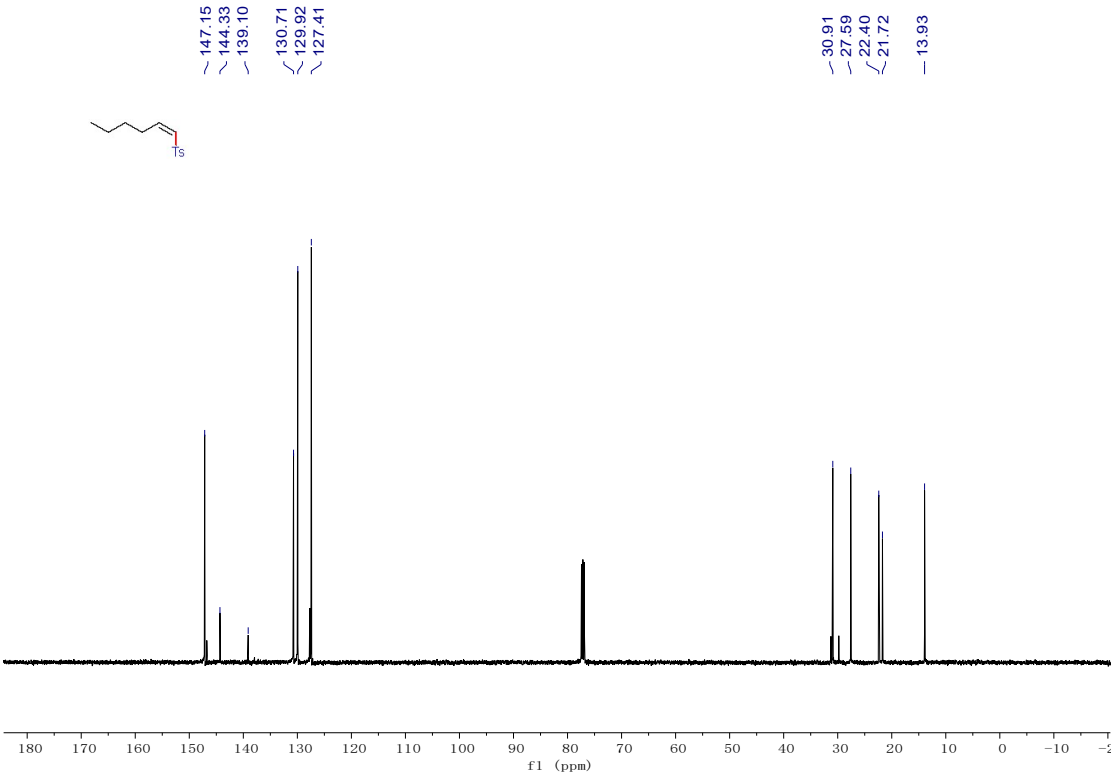
^{1}H NMR spectrum of **3a**



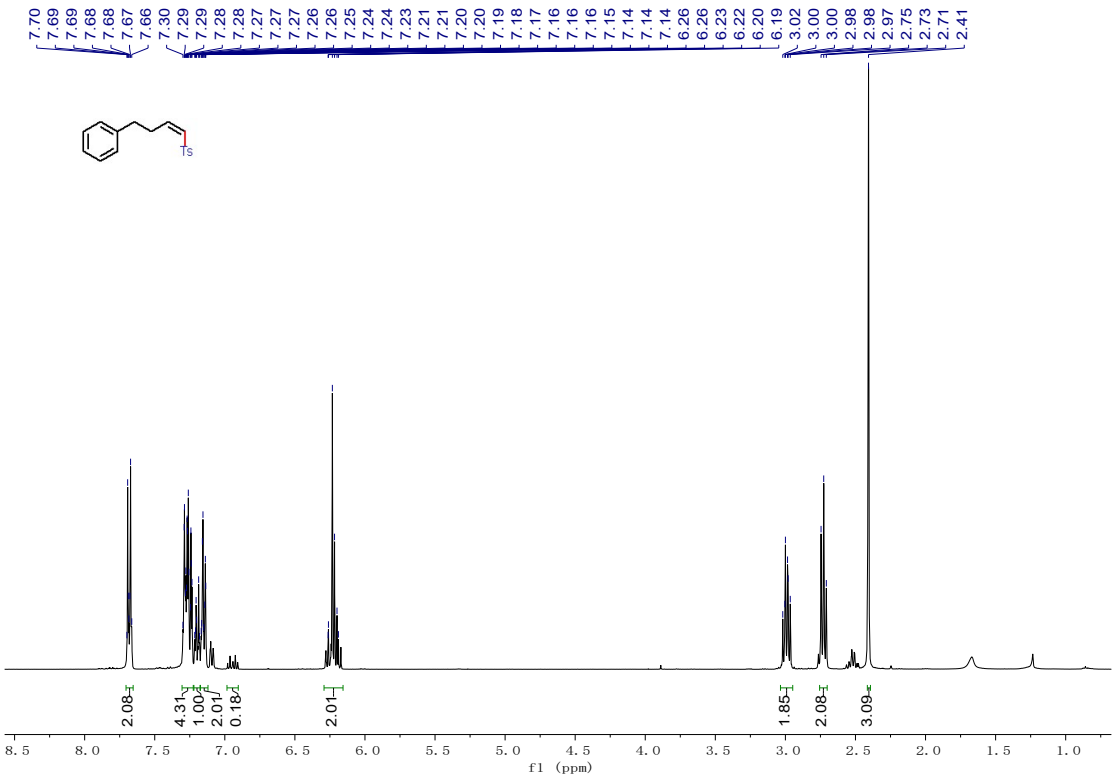
^{13}C NMR spectrum of **3a**



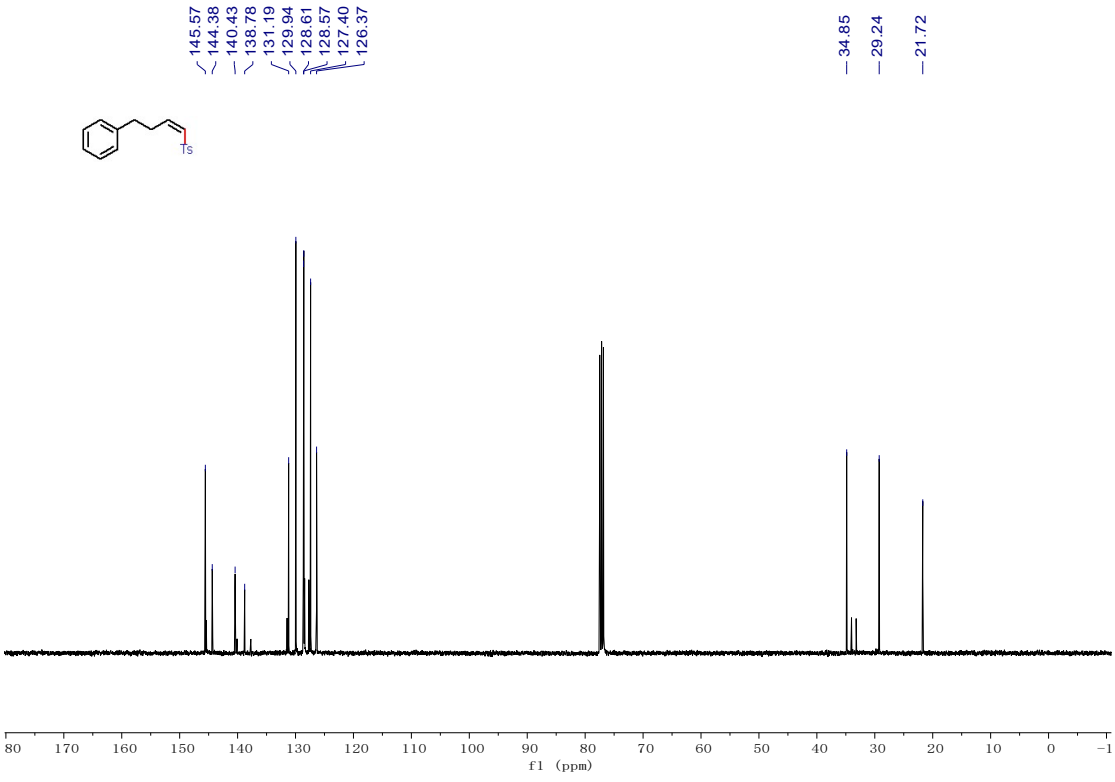
^{1}H NMR spectrum of **3b**



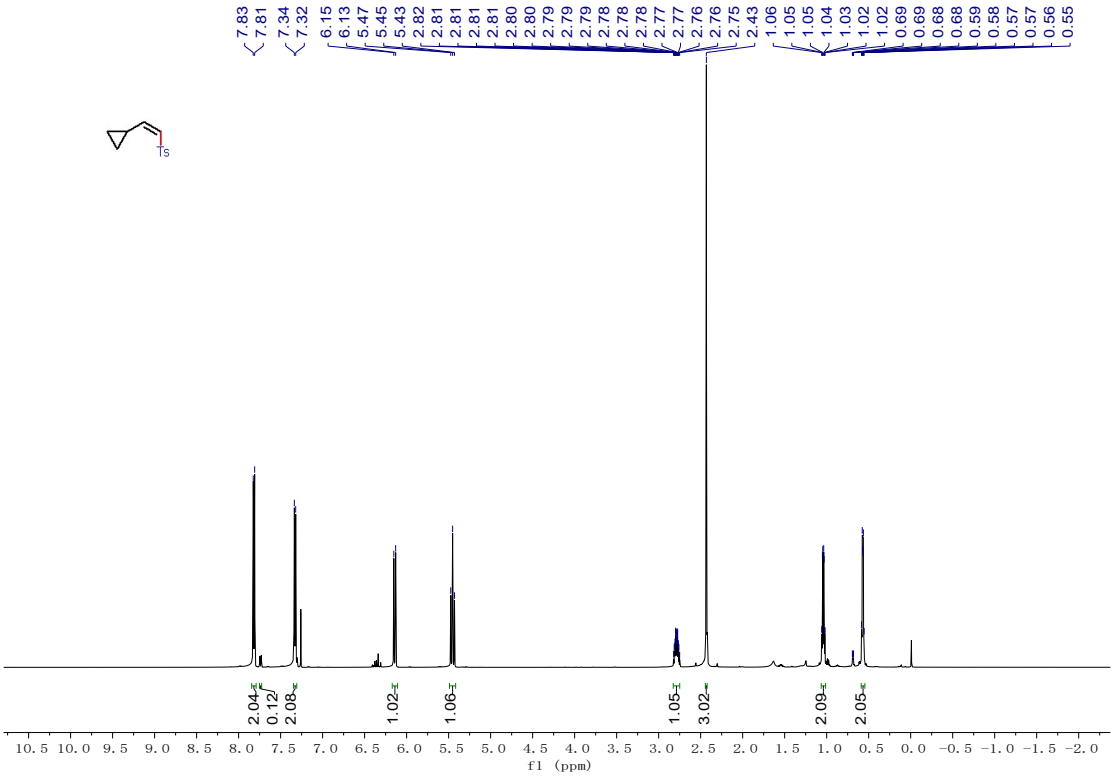
^{13}C NMR spectrum of **3b**



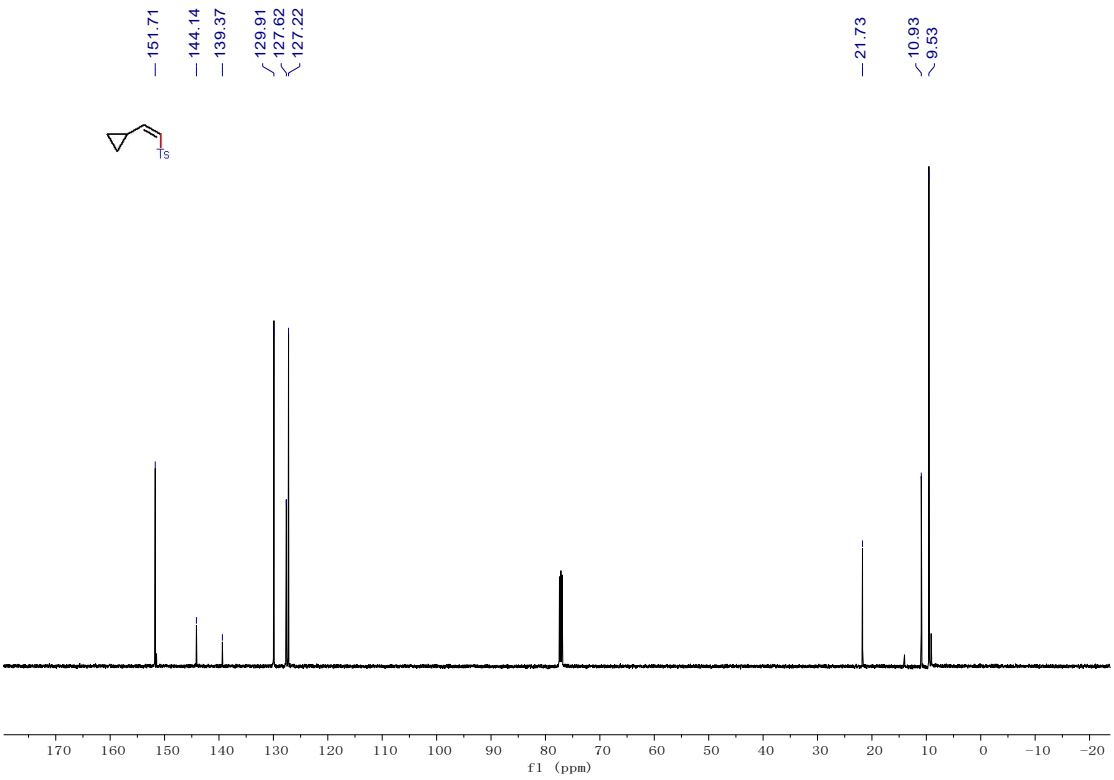
^{1}H NMR spectrum of **3c**



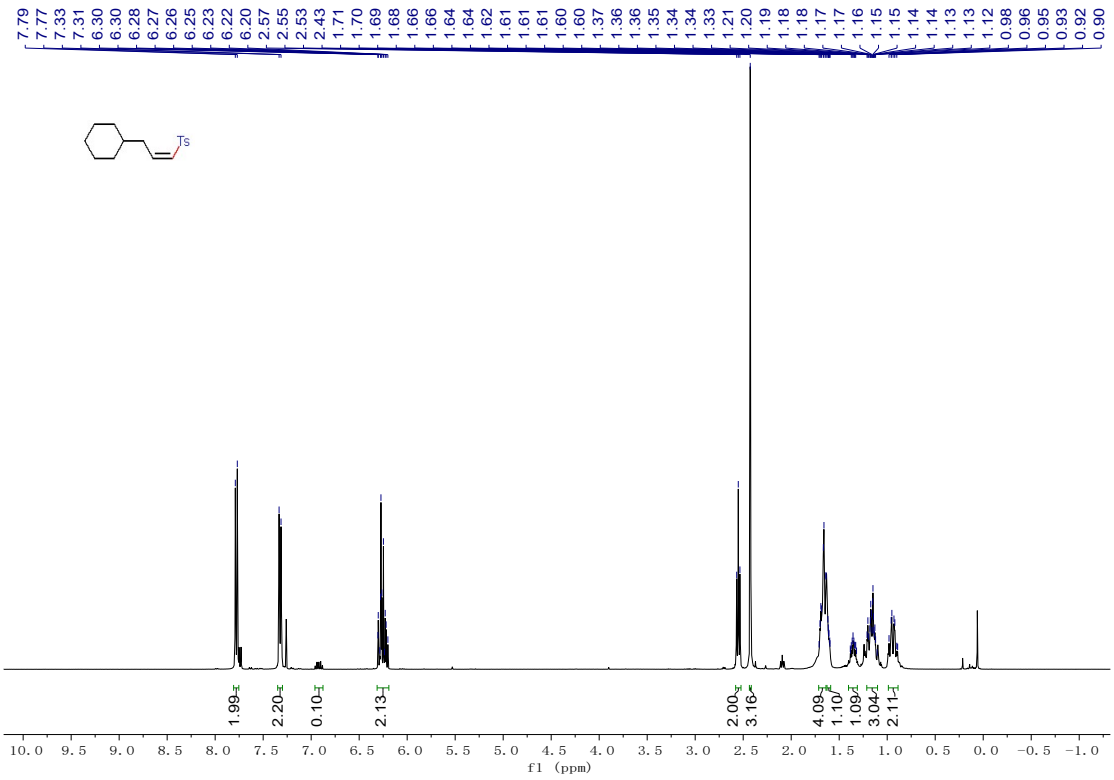
^{13}C NMR spectrum of **3c**



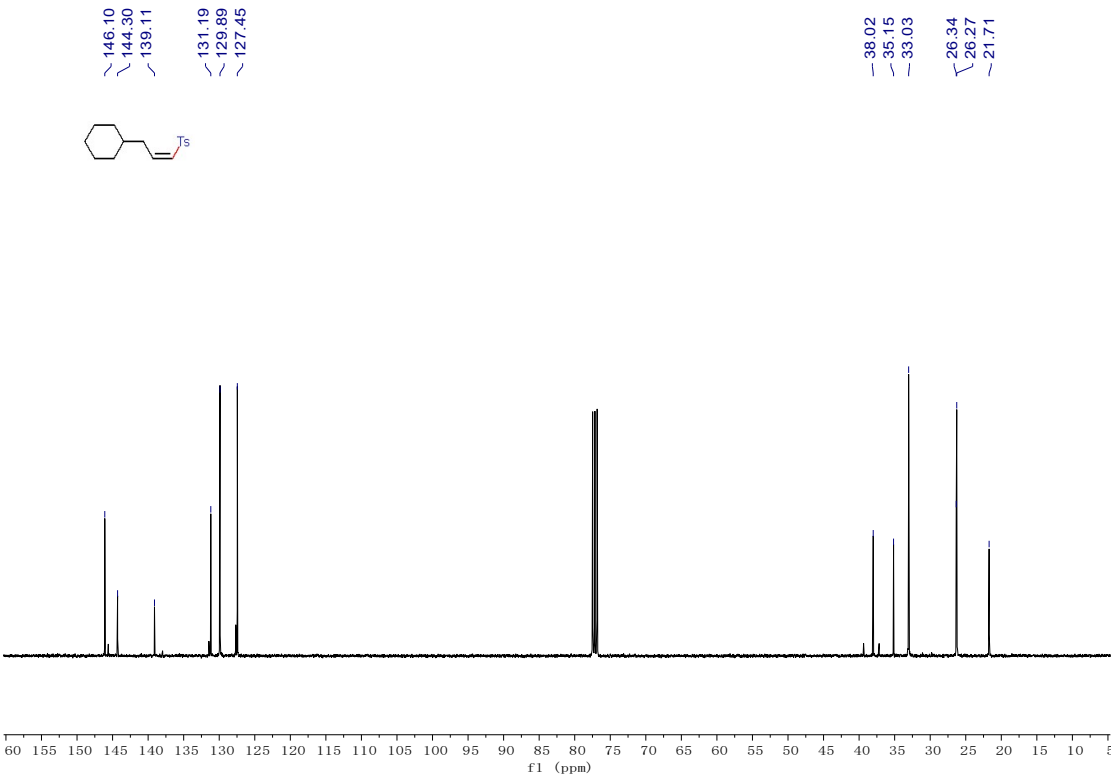
^{1}H NMR spectrum of **3d**



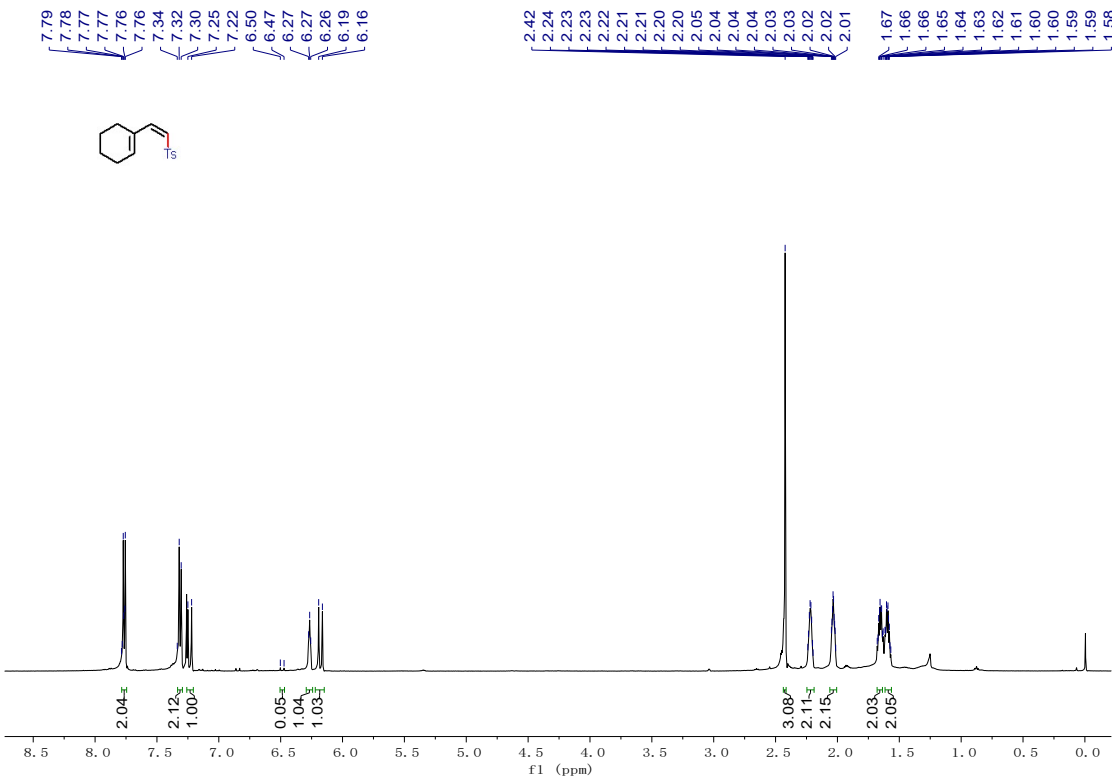
^{13}C NMR spectrum of **3d**



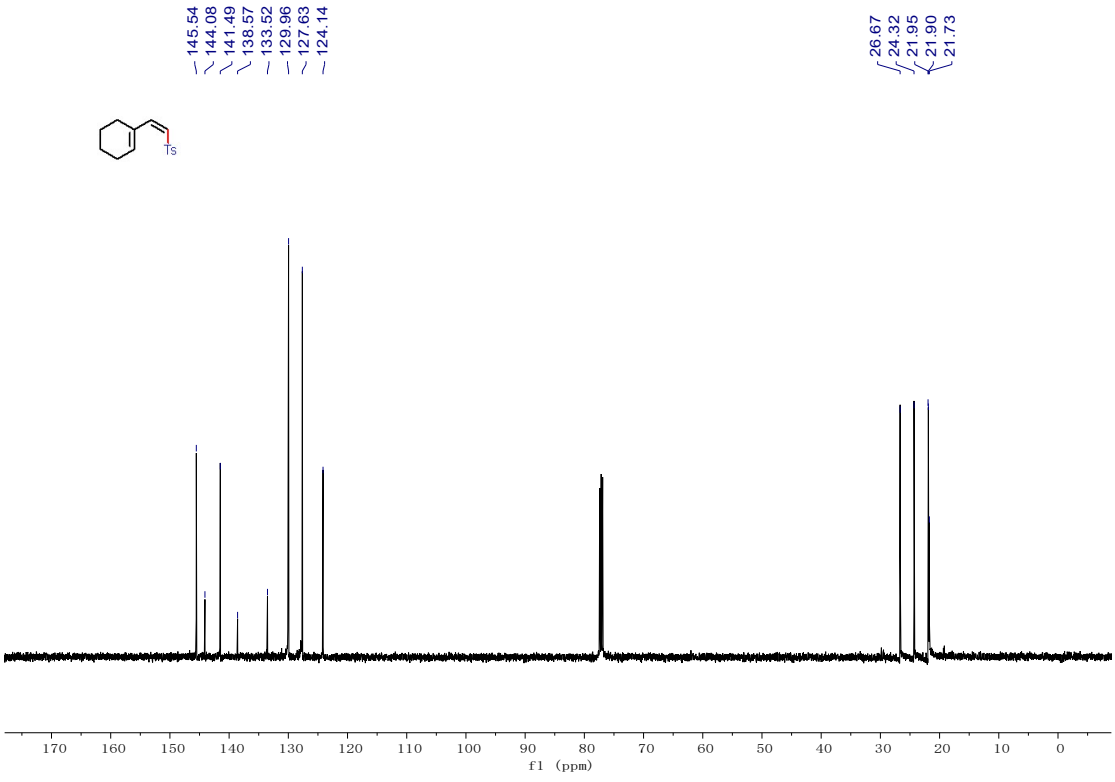
^{1}H NMR spectrum of **3e**



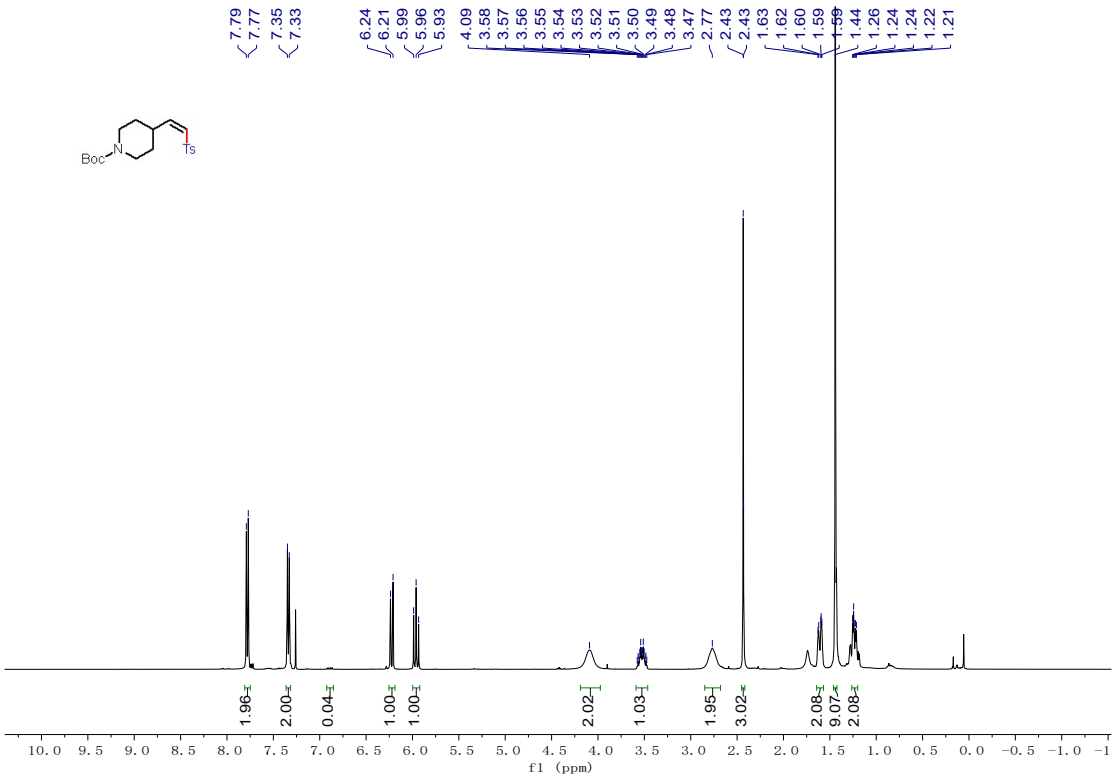
^{13}C NMR spectrum of **3e**



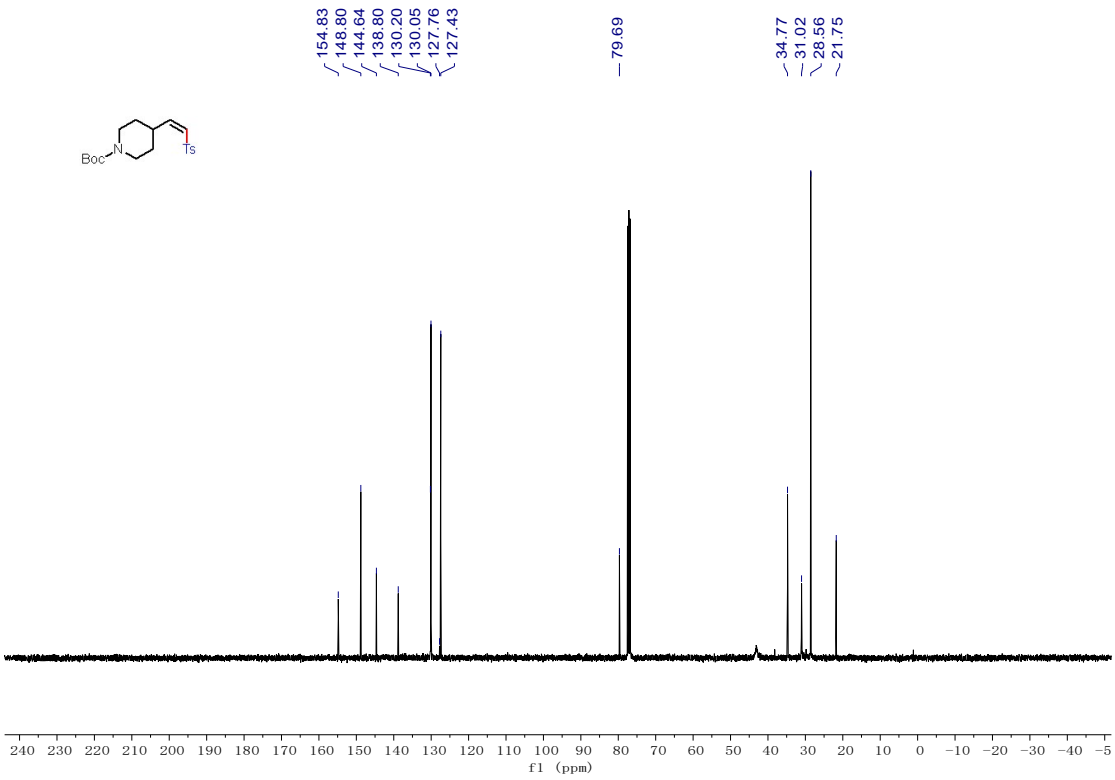
^{1}H NMR spectrum of **3f**



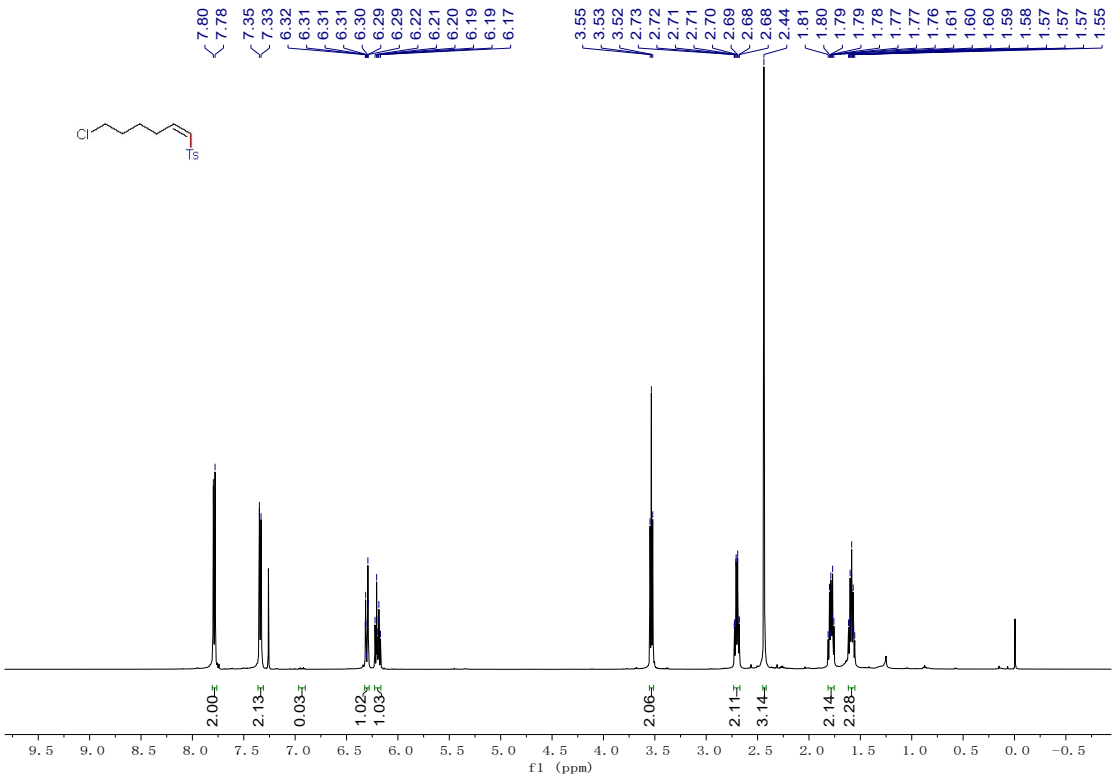
^{13}C NMR spectrum of **3f**



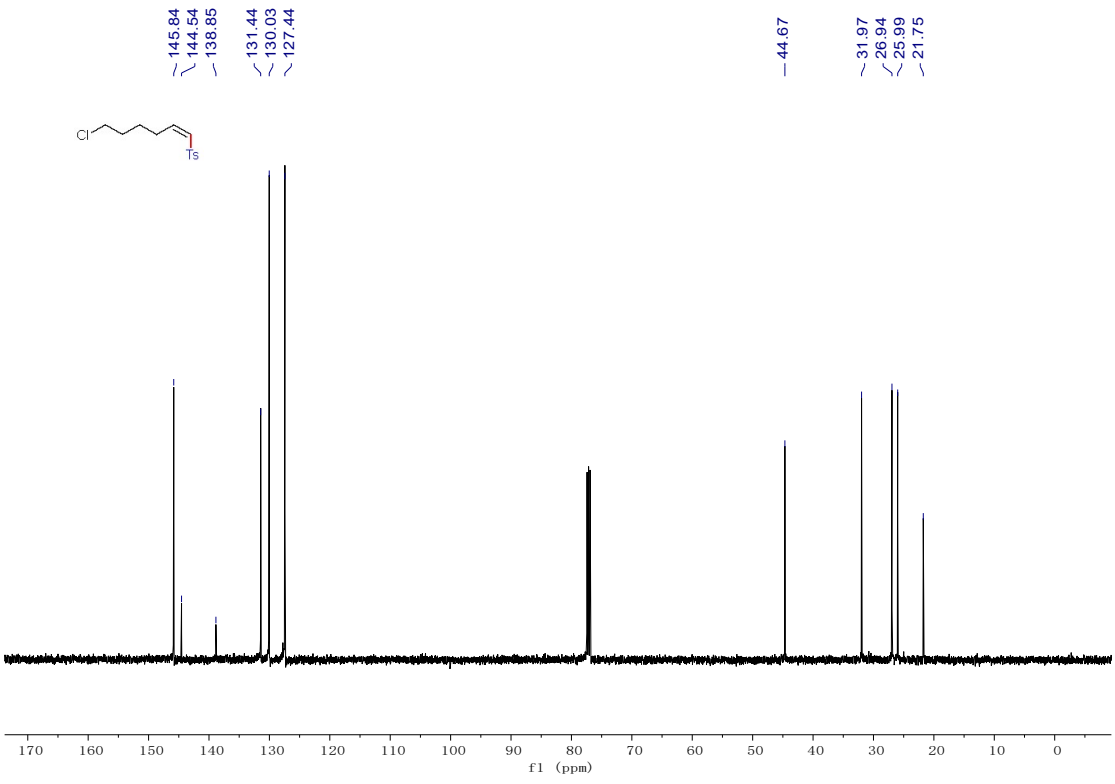
^{1}H NMR spectrum of **3g**



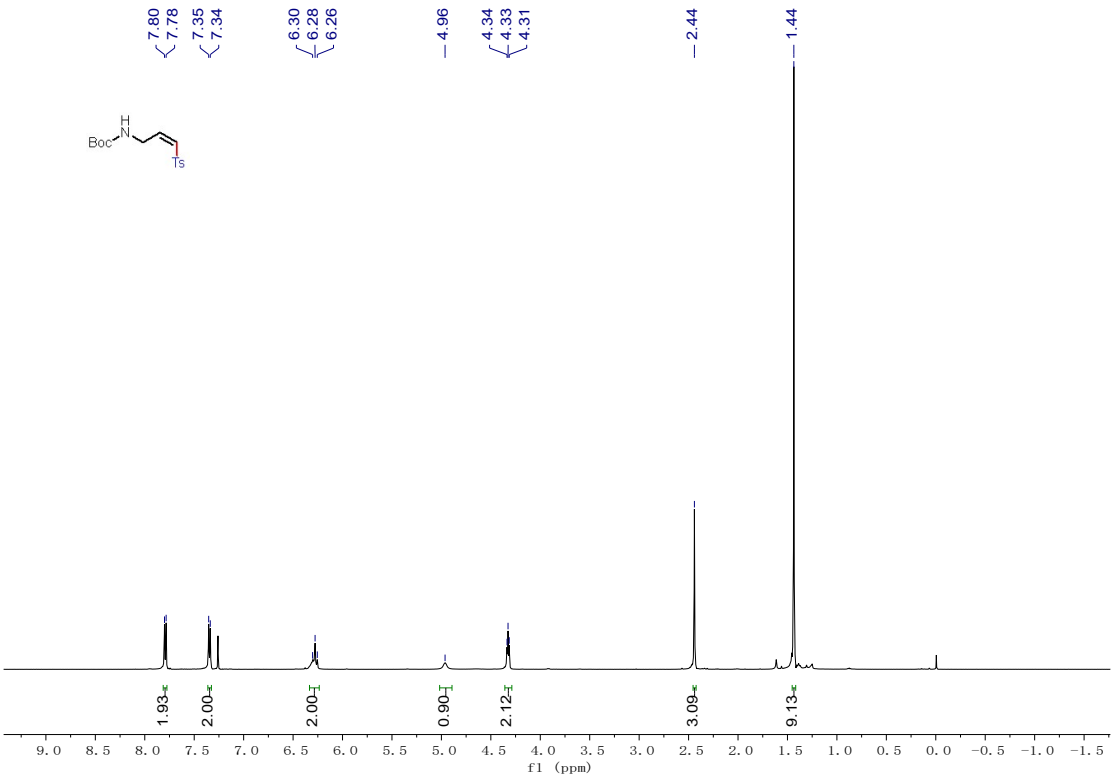
^{13}C NMR spectrum of **3g**



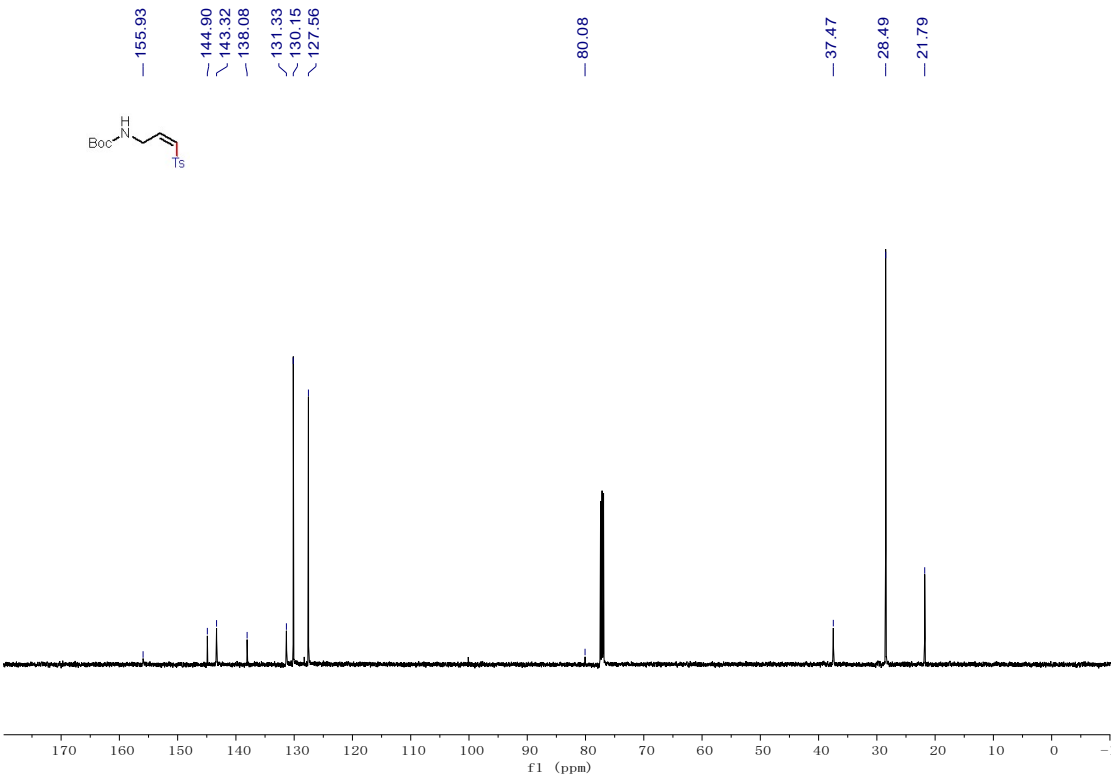
^{1}H NMR spectrum of **3h**



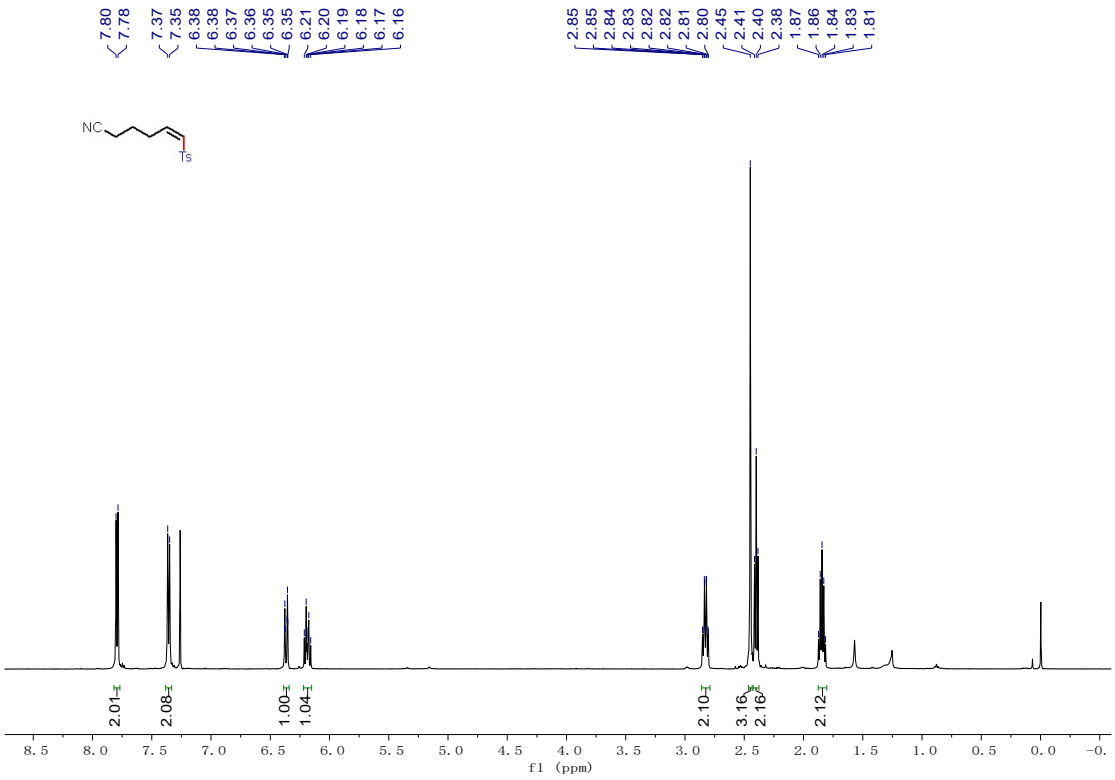
^{13}C NMR spectrum of **3h**



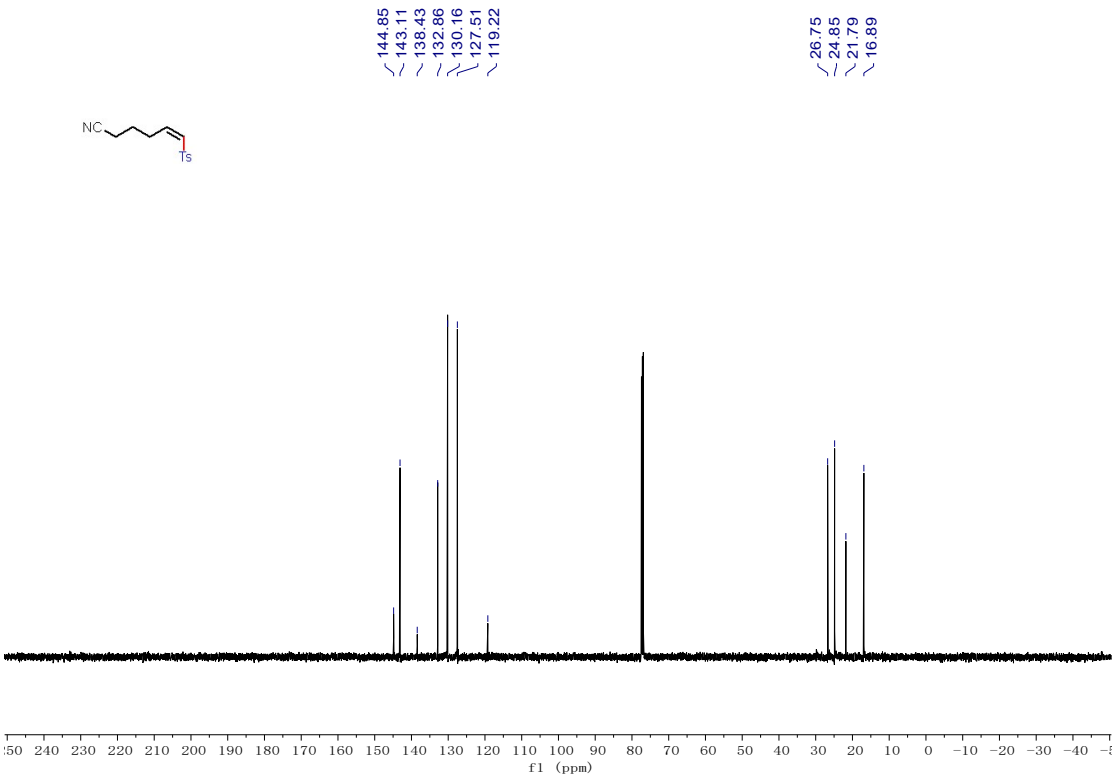
^{1}H NMR spectrum of **3i**



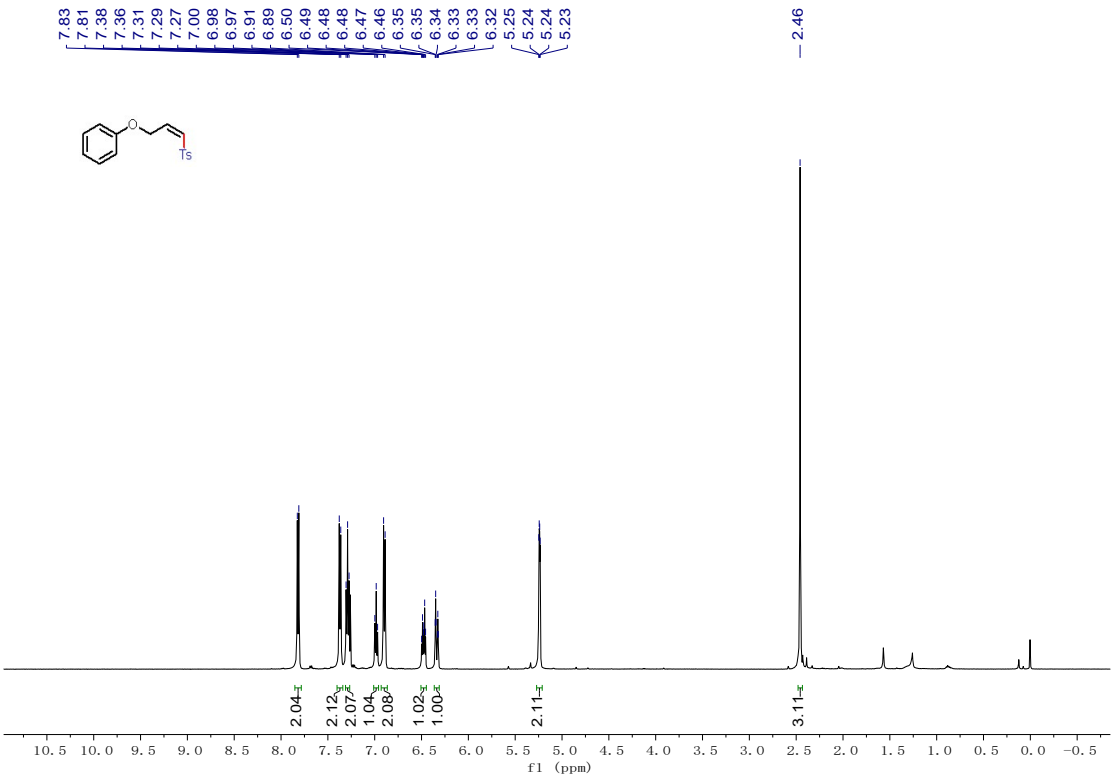
^{13}C NMR spectrum of **3i**



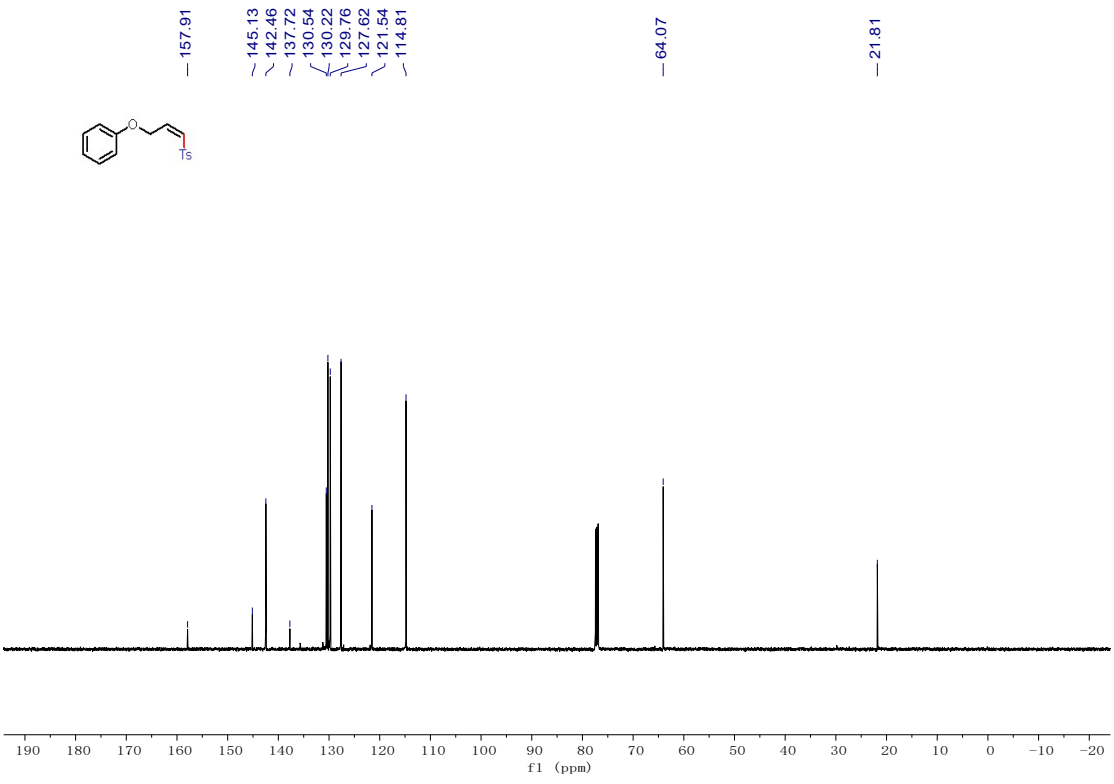
^{1}H NMR spectrum of **3j**



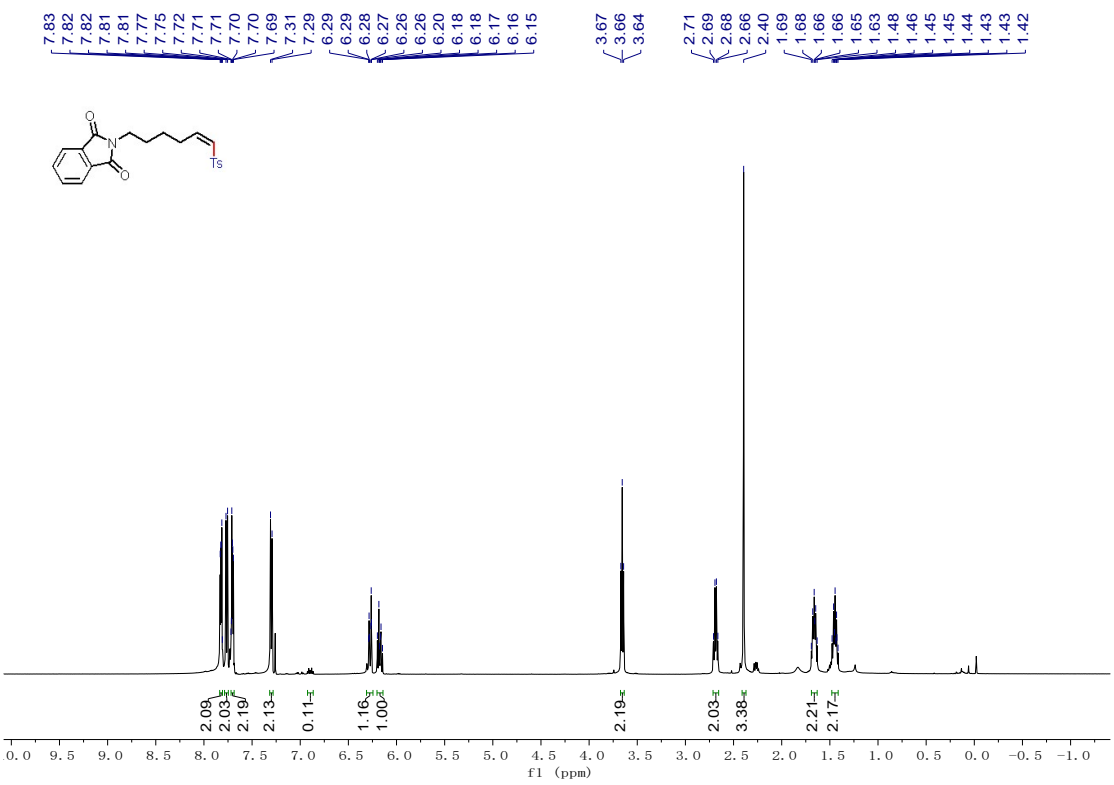
^{13}C NMR spectrum of **3j**



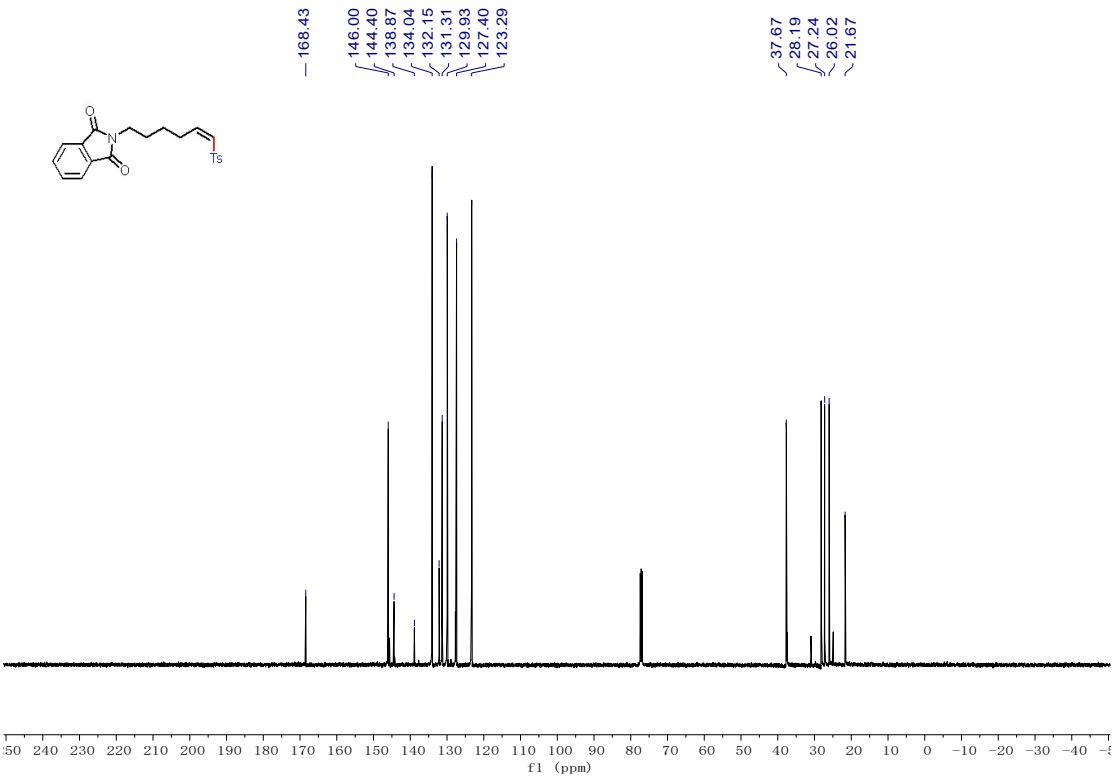
^{1}H NMR spectrum of **3k**



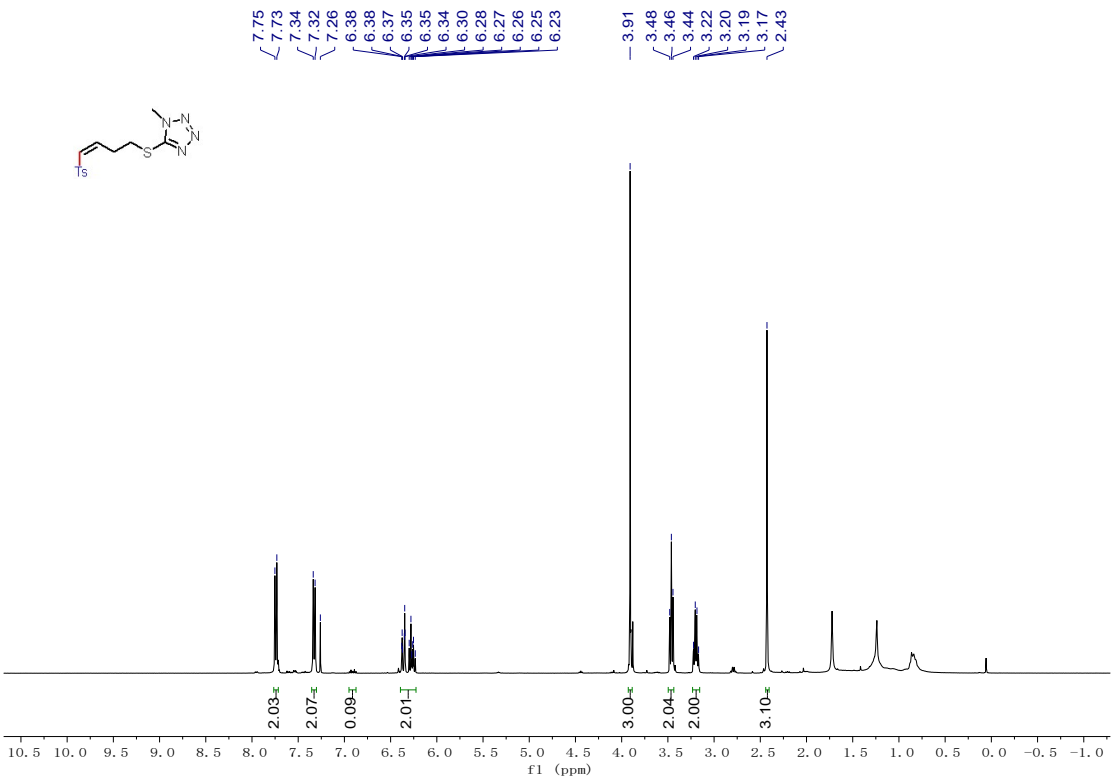
^{13}C NMR spectrum of **3k**



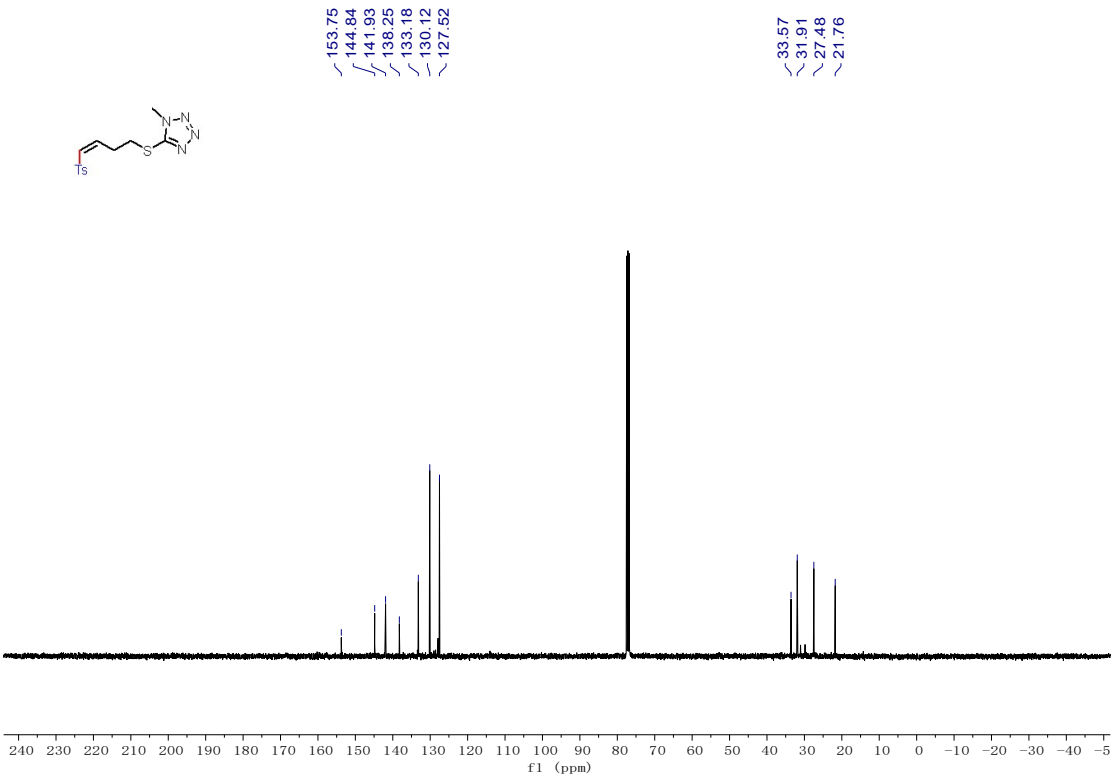
^{1}H NMR spectrum of **3l**



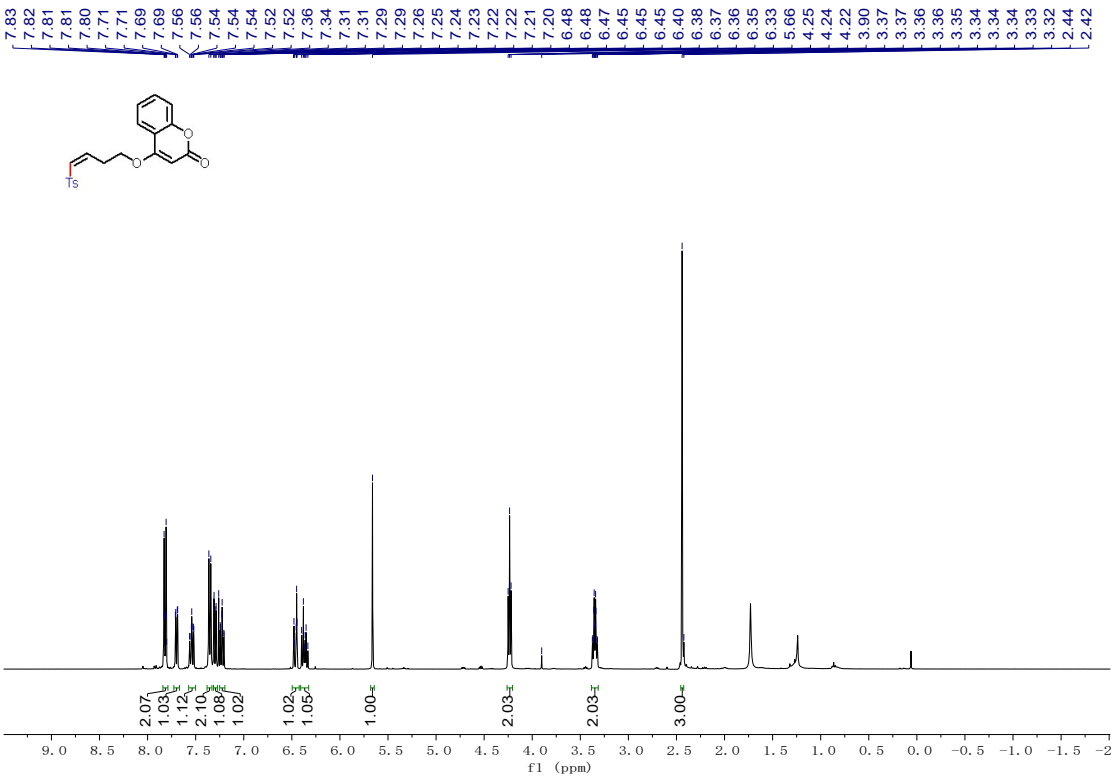
^{13}C NMR spectrum of **3l**



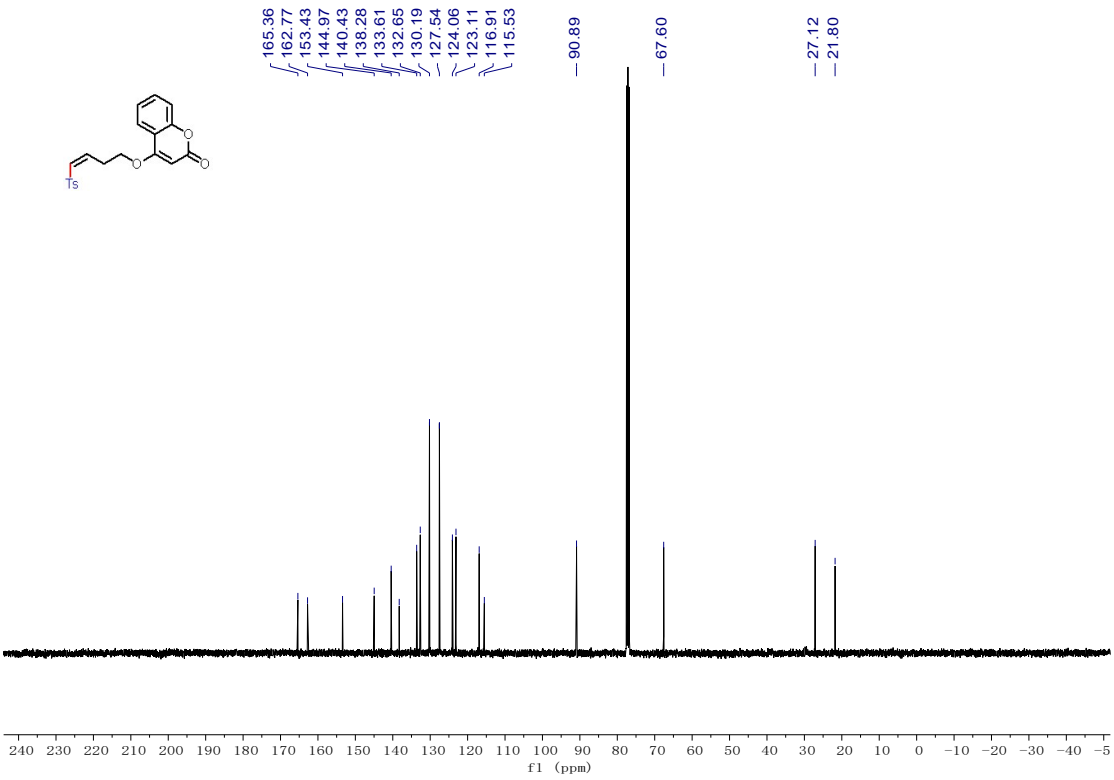
^{1}H NMR spectrum of **3m**



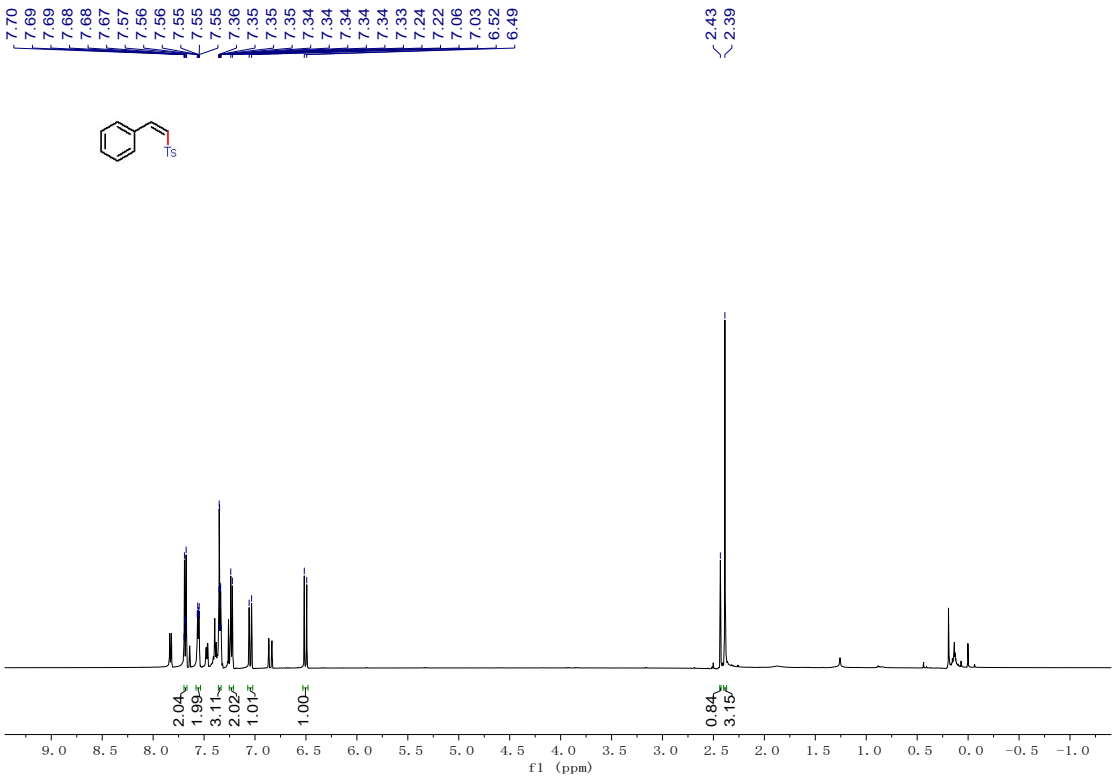
^{13}C NMR spectrum of **3m**



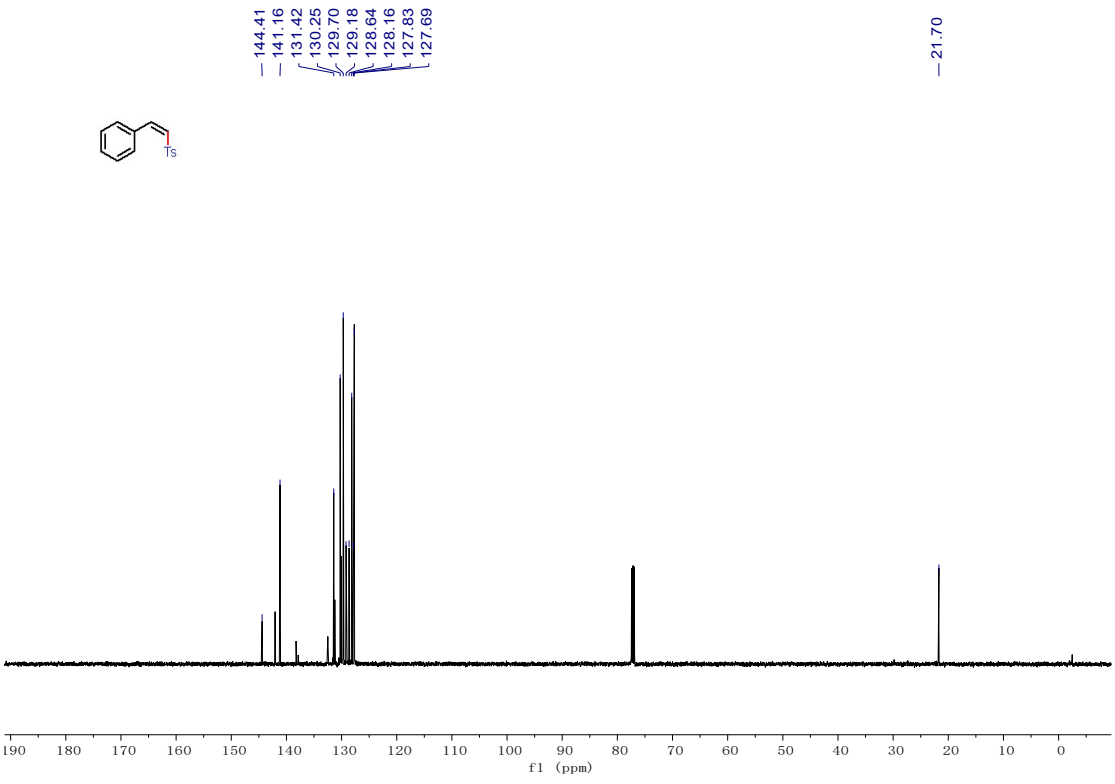
^{1}H NMR spectrum of **3n**



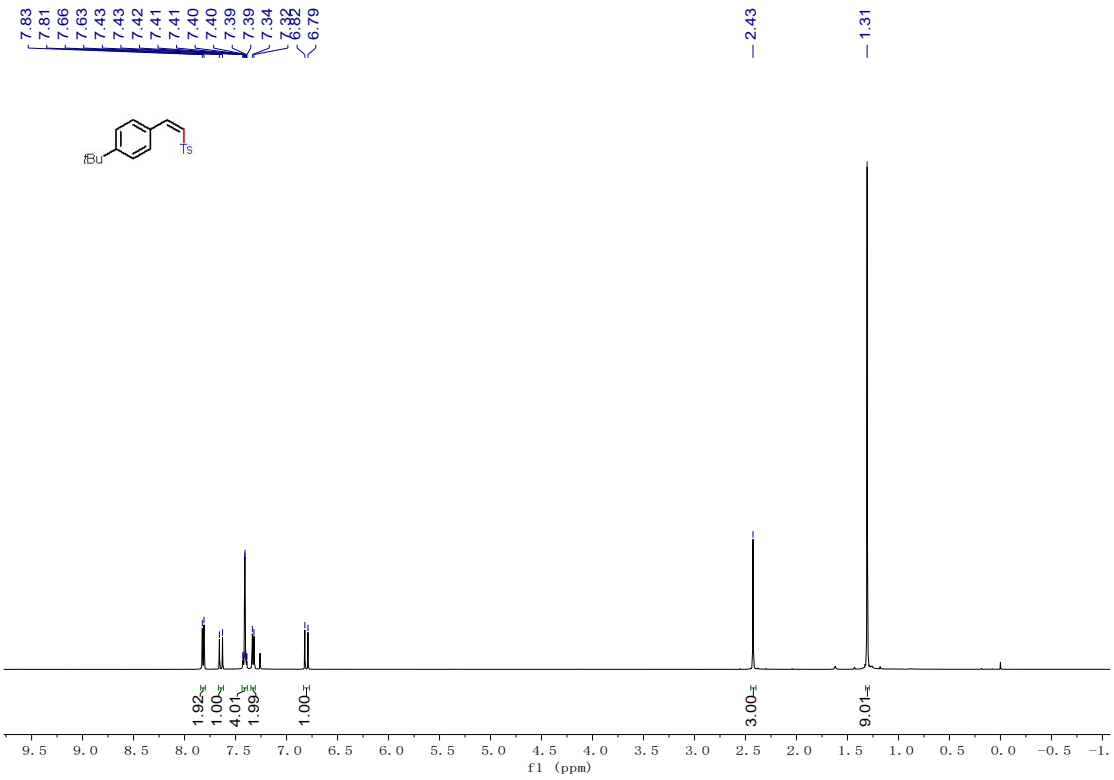
^{13}C NMR spectrum of **3n**



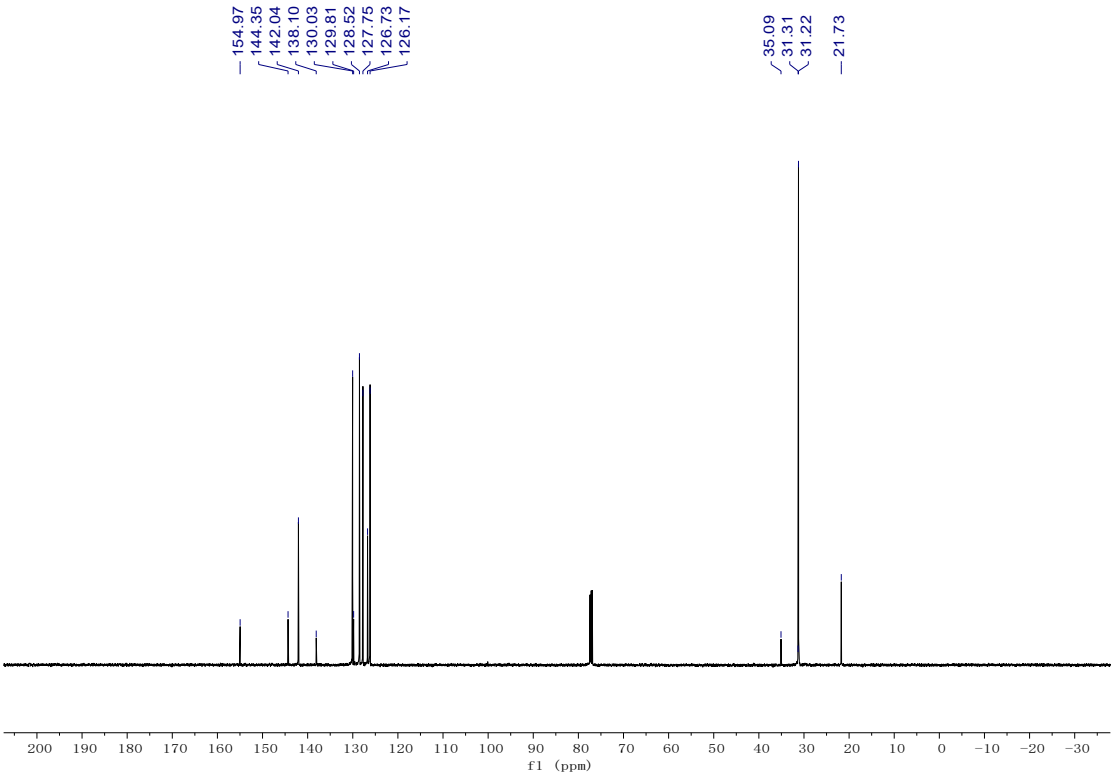
^{1}H NMR spectrum of **3p**



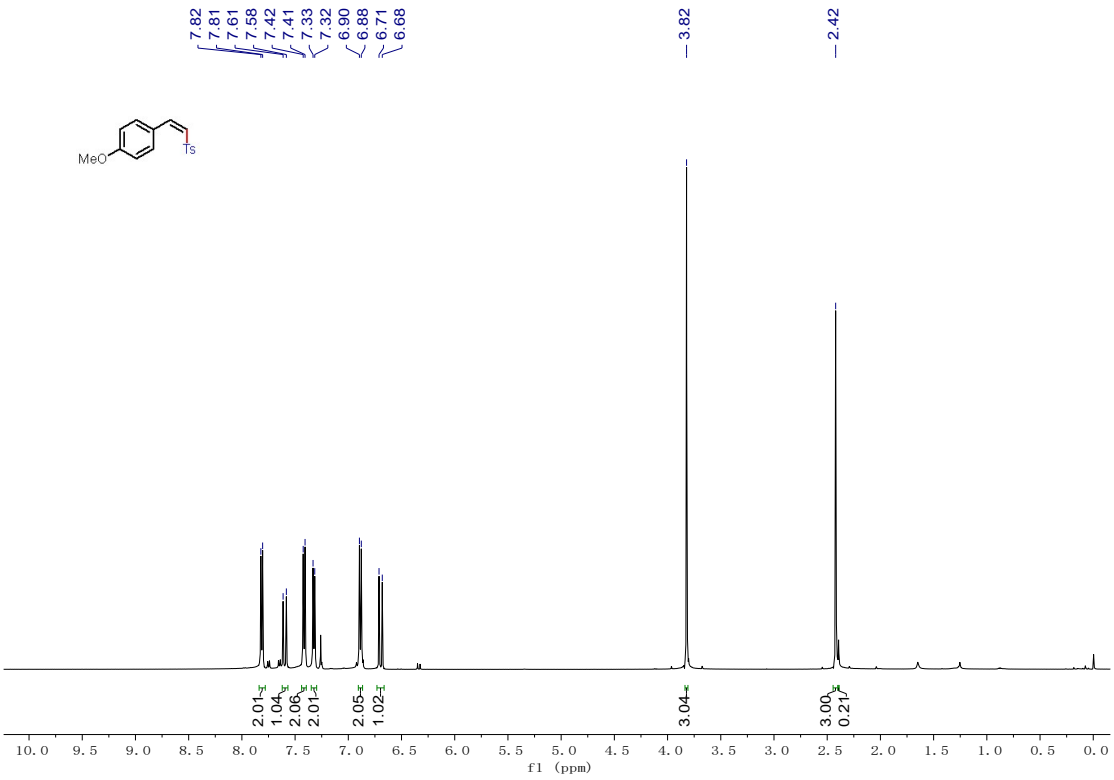
^{13}C NMR spectrum of **3p**



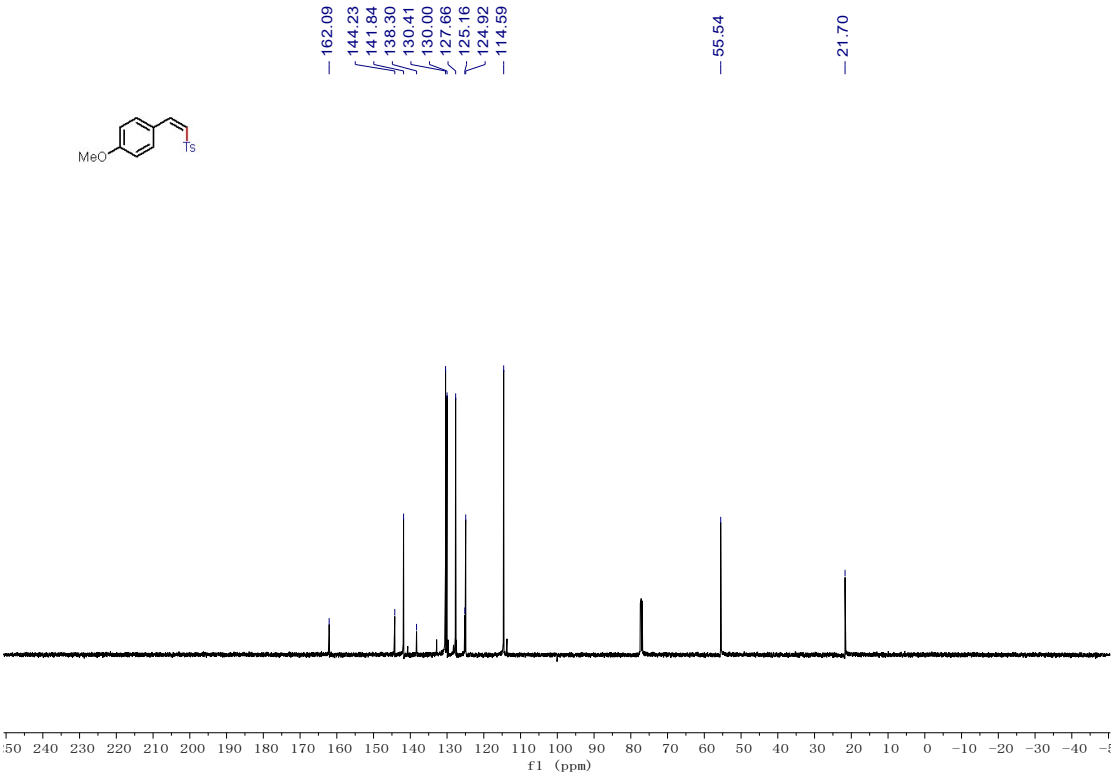
^{1}H NMR spectrum of **3q**



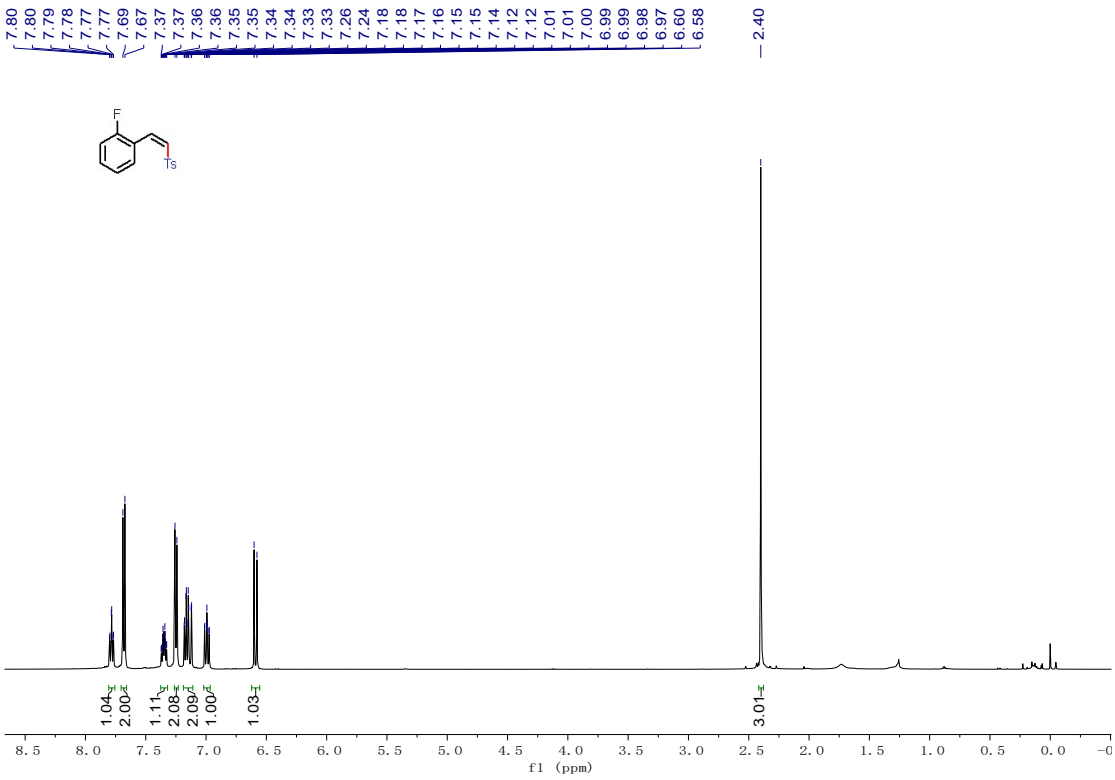
^{13}C NMR spectrum of **3q**



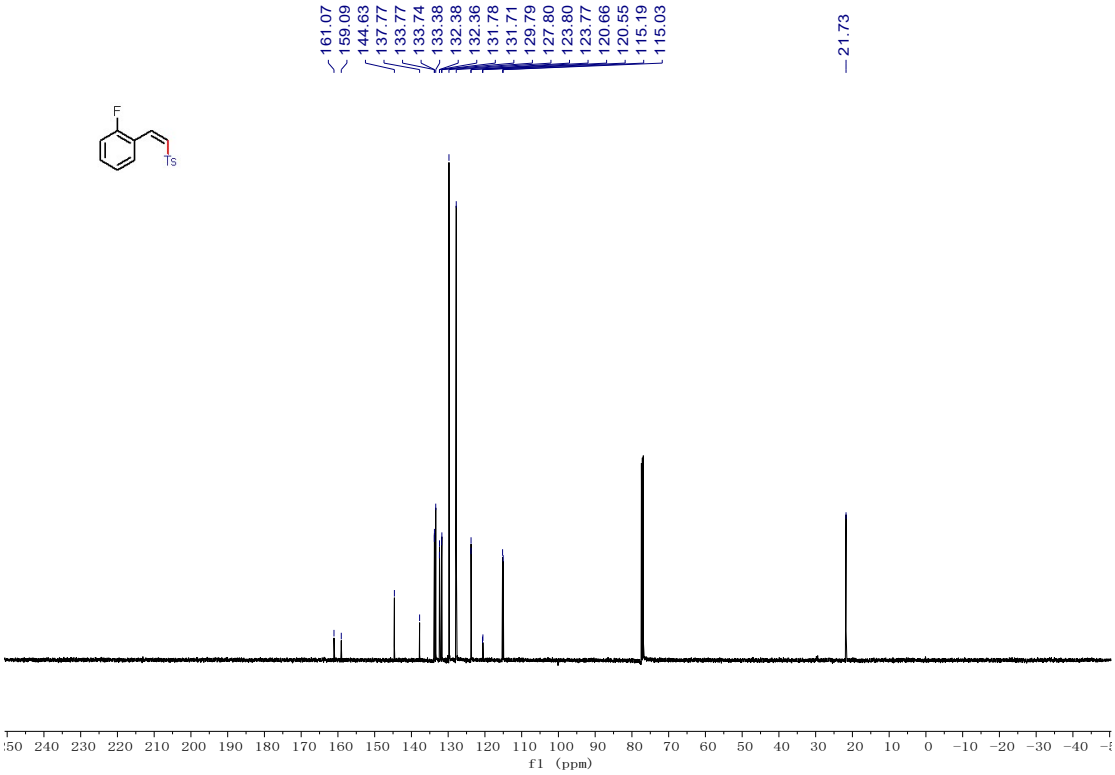
^{1}H NMR spectrum of **3r**



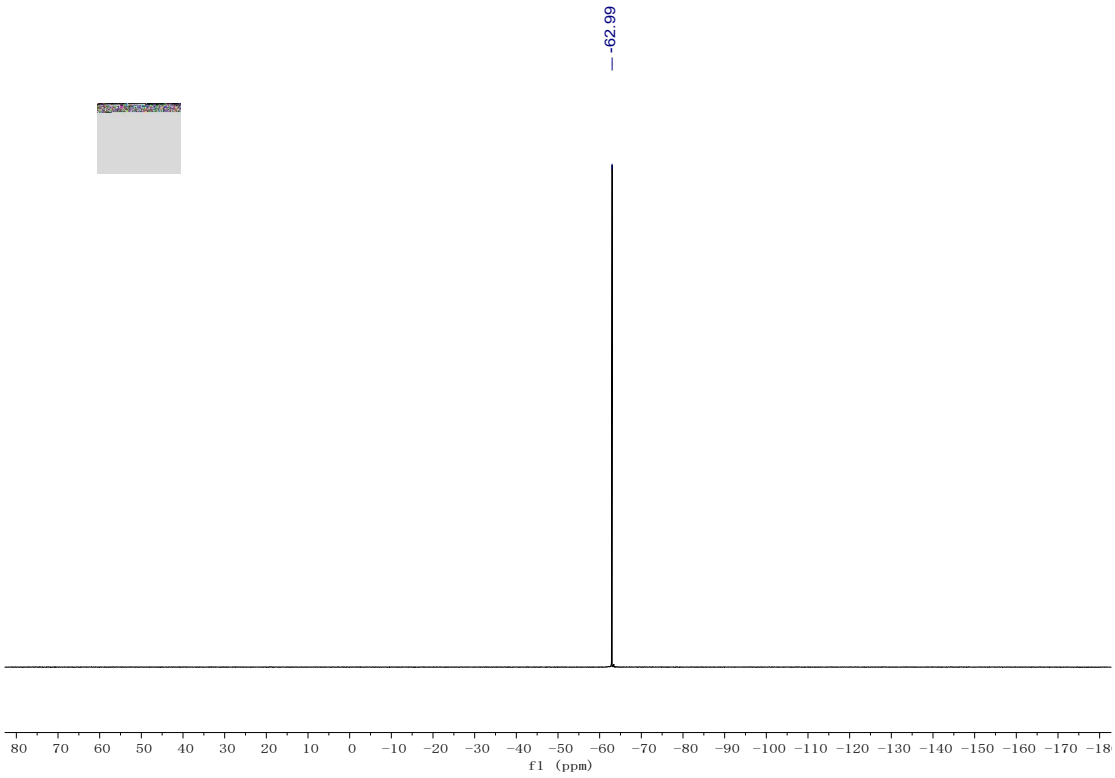
^{13}C NMR spectrum of **3r**



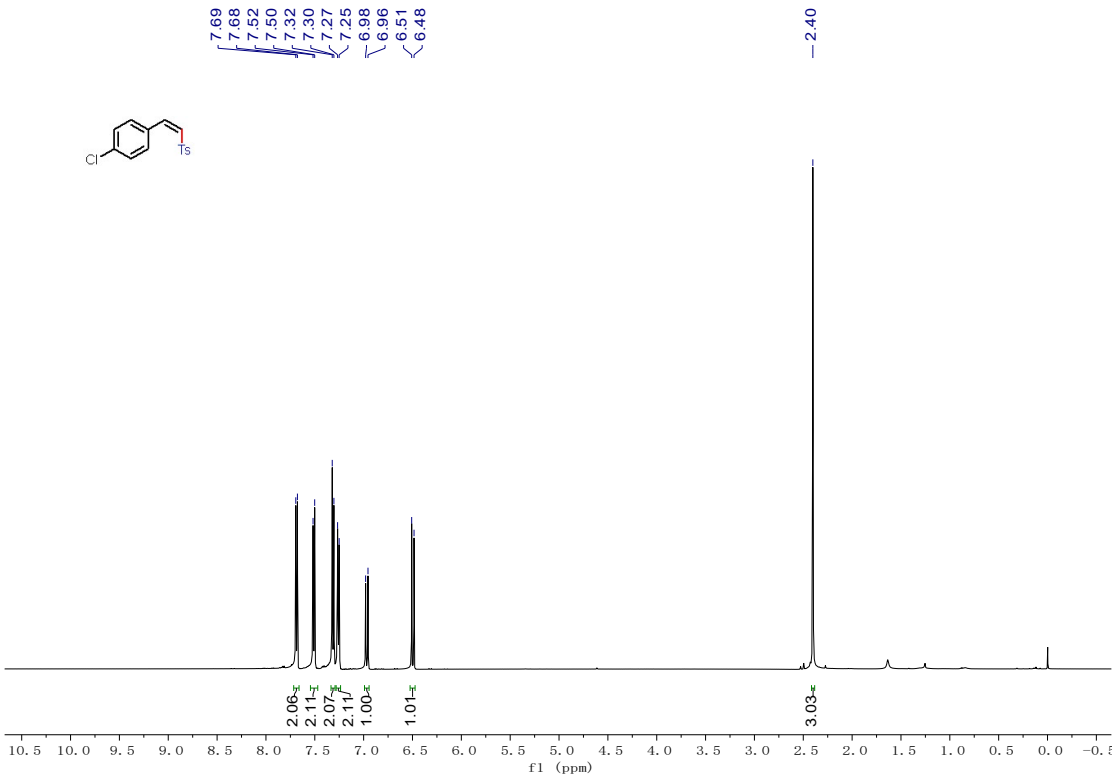
^{1}H NMR spectrum of **3s**



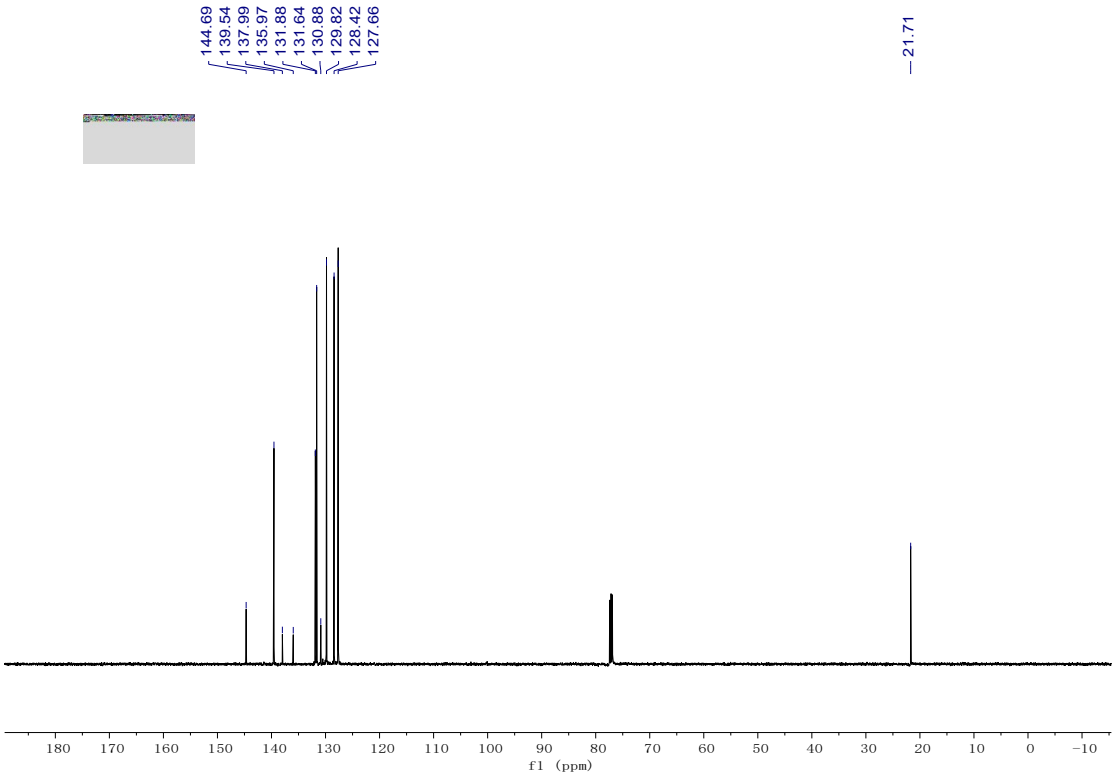
^{13}C NMR spectrum of **3s**



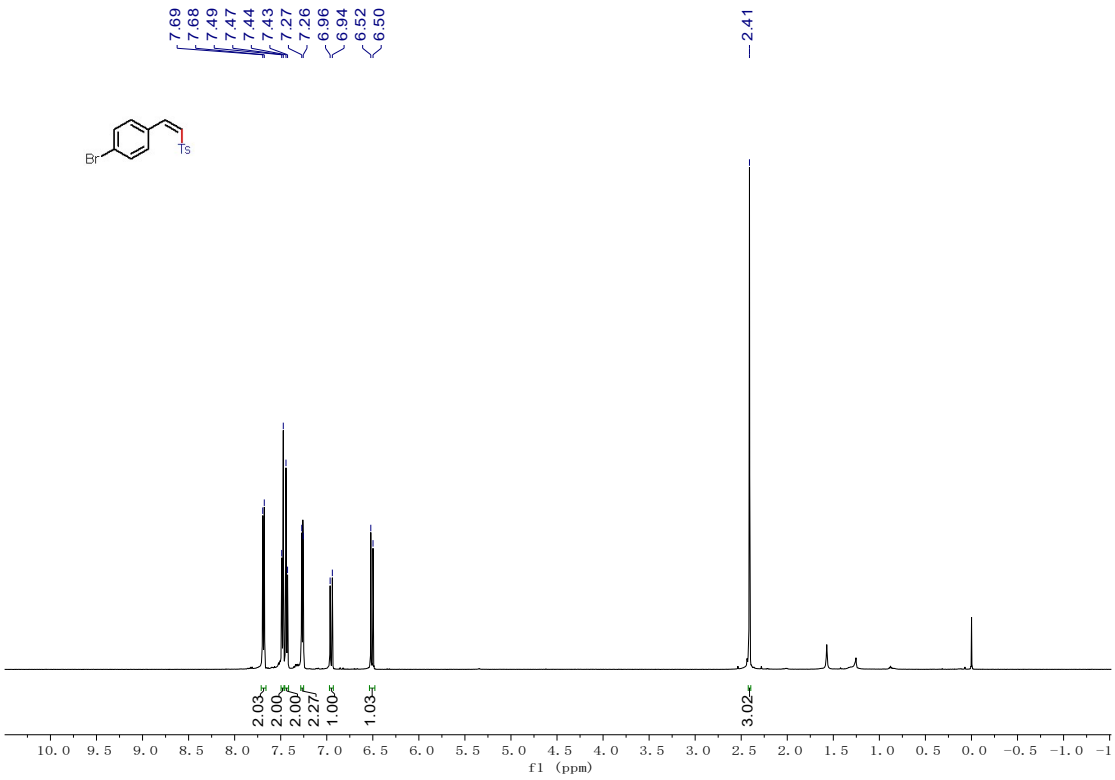
^{19}F NMR spectrum of **3s**



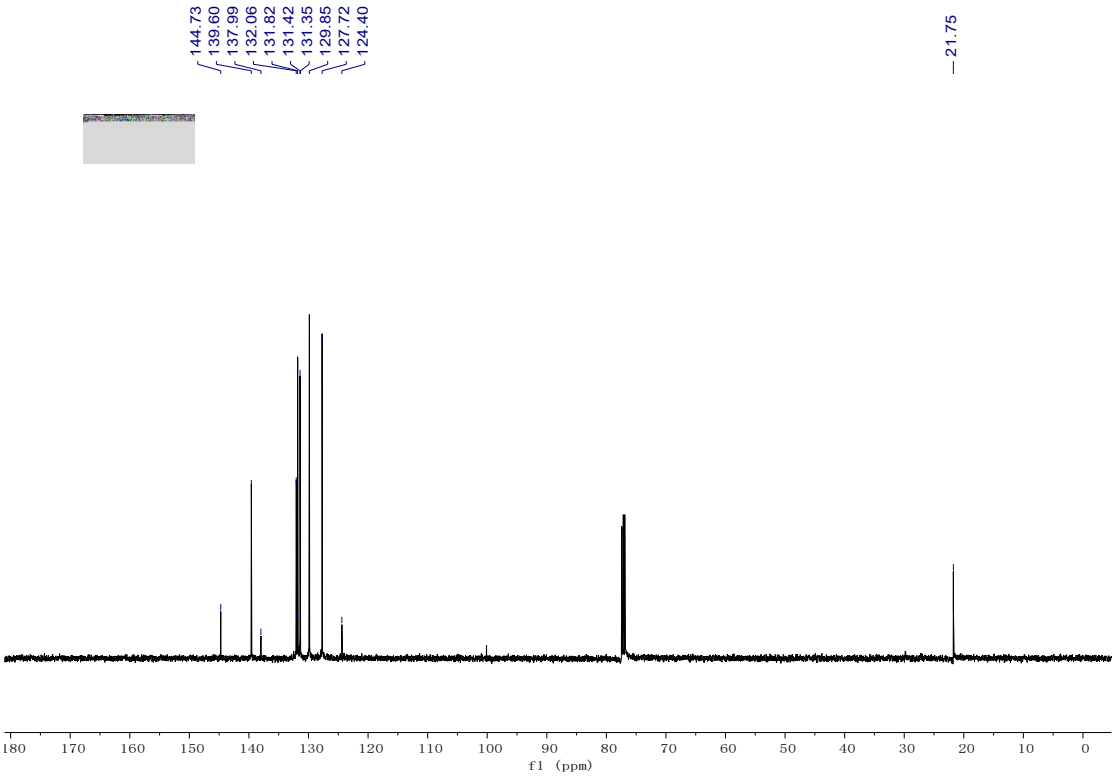
^{1}H NMR spectrum of **3t**



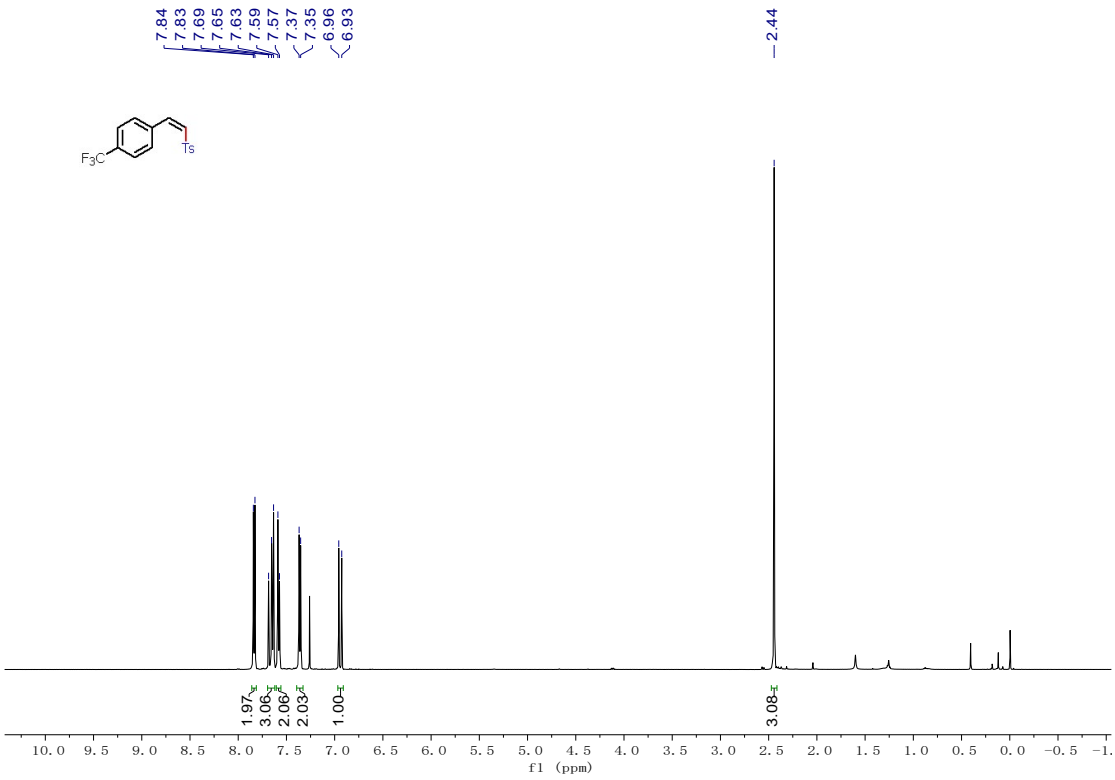
^{13}C NMR spectrum of **3t**



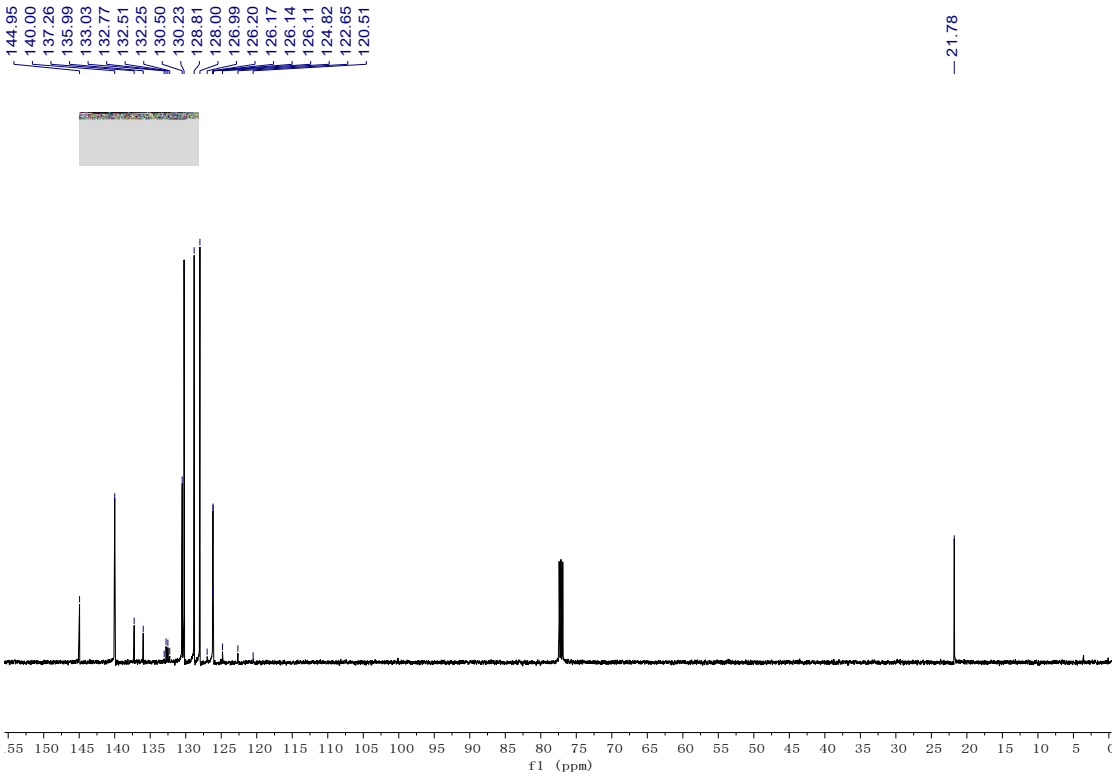
^{1}H NMR spectrum of **3u**



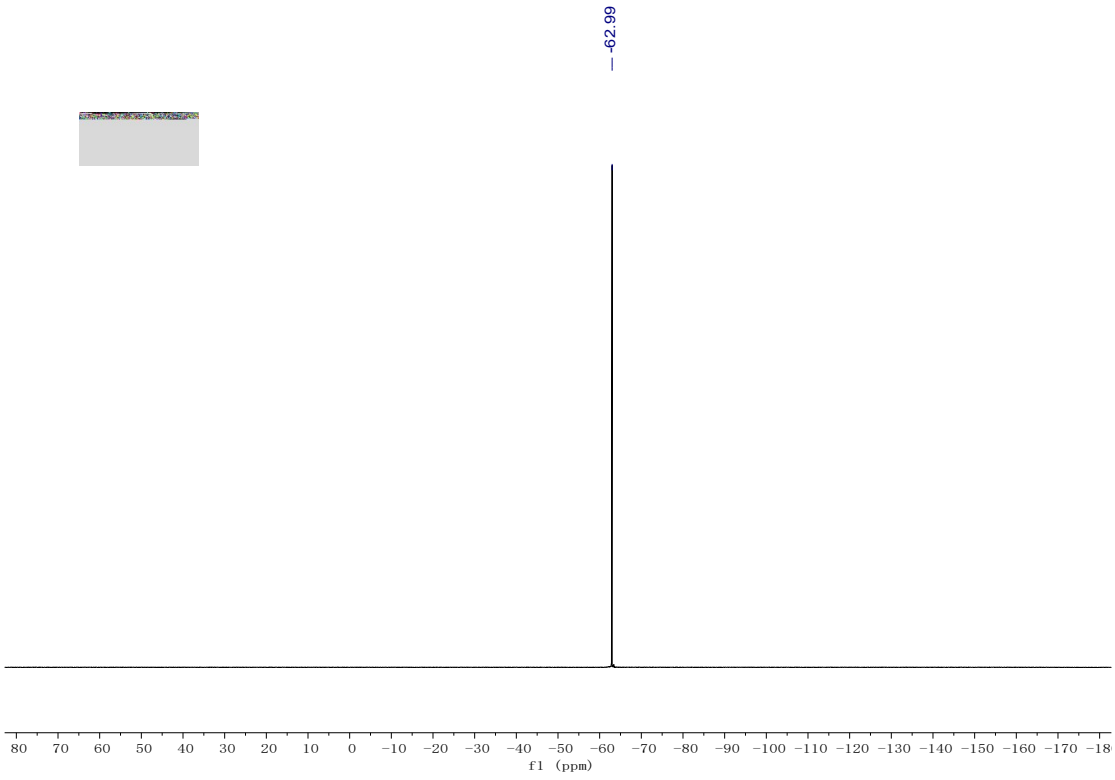
^{13}C NMR spectrum of **3u**



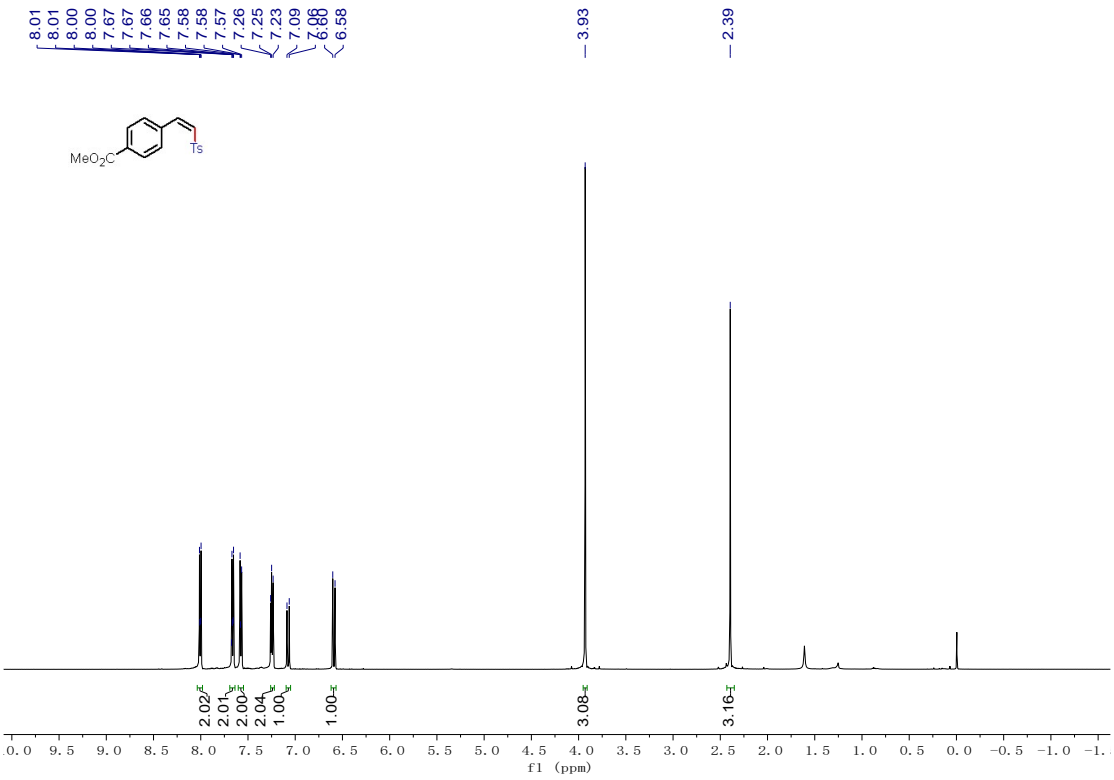
^{1}H NMR spectrum of **3v**



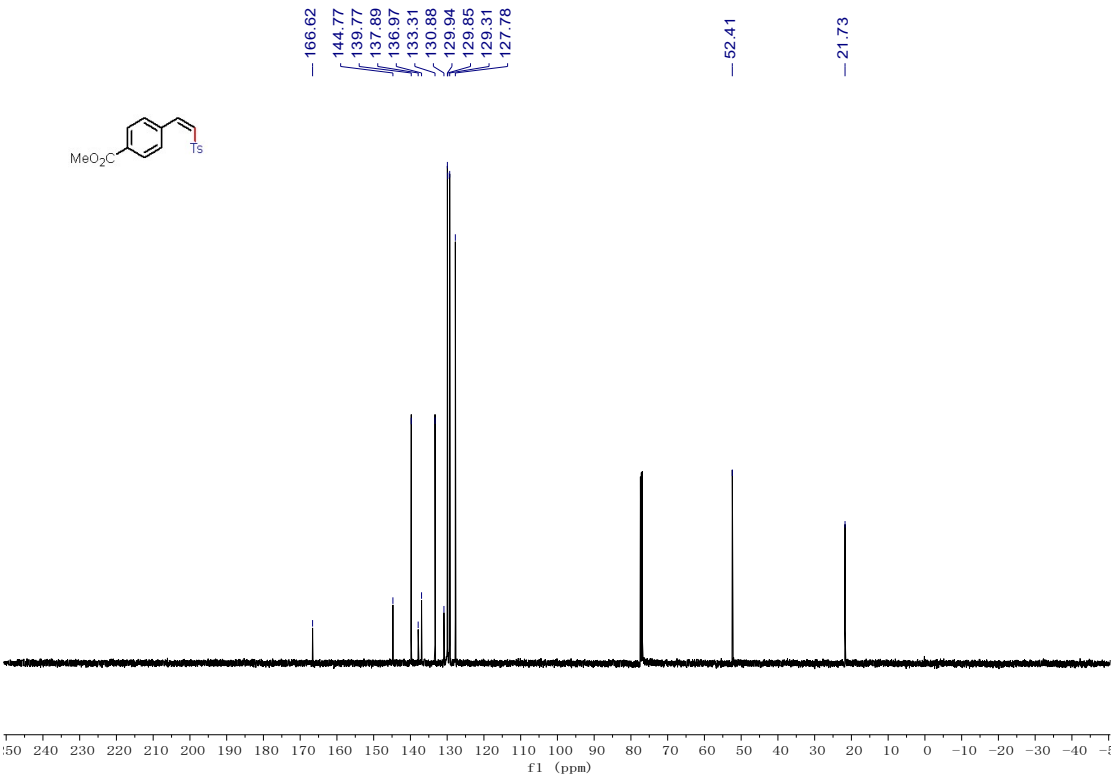
^{13}C NMR spectrum of **3v**



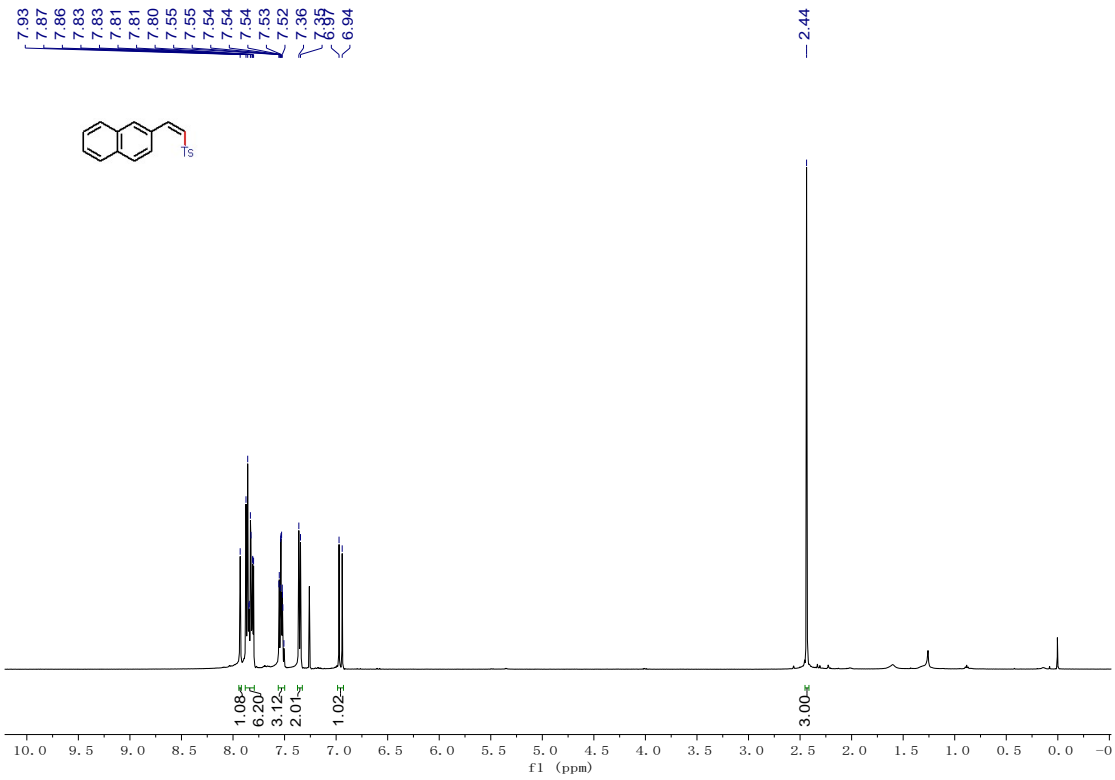
^{19}F NMR spectrum of **3v**



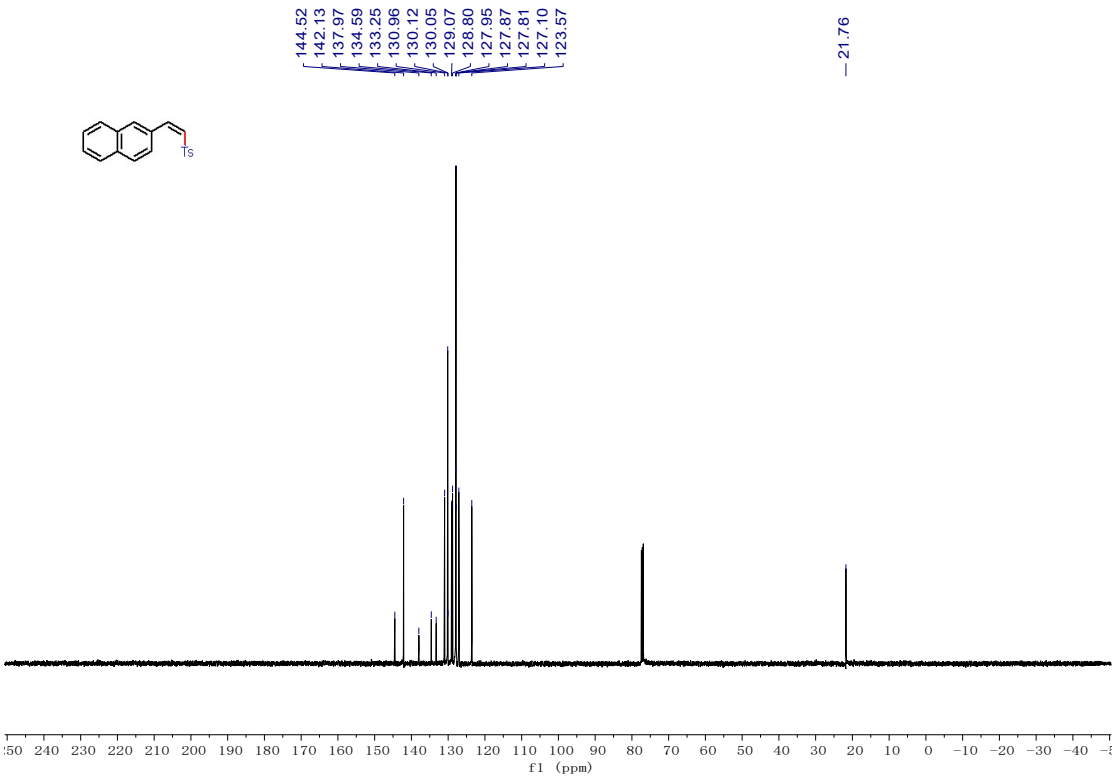
^{1}H NMR spectrum of **3w**



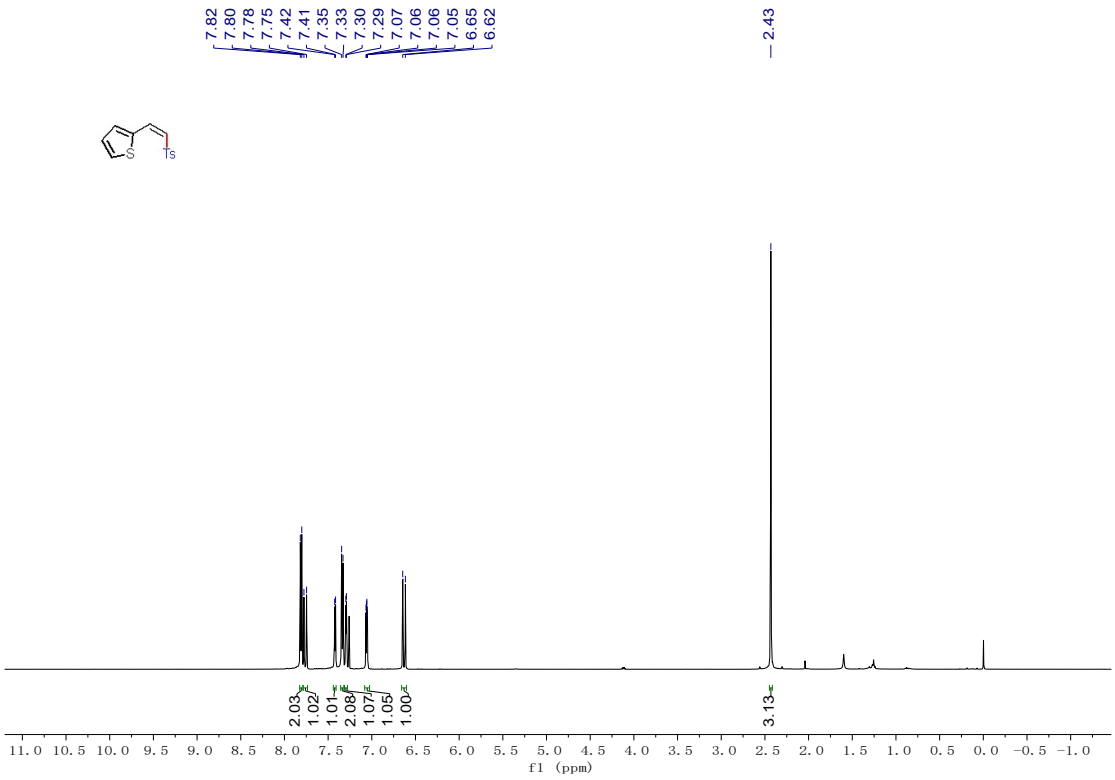
^{13}C NMR spectrum of **3w**



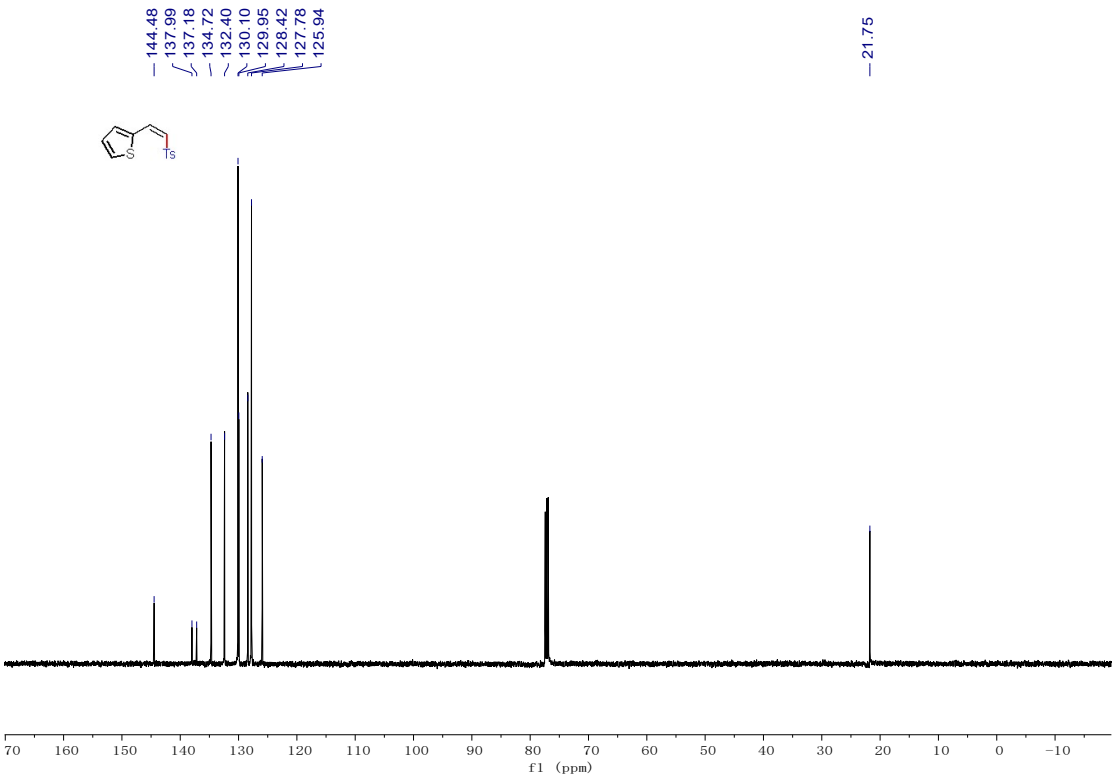
^{1}H NMR spectrum of **3x**



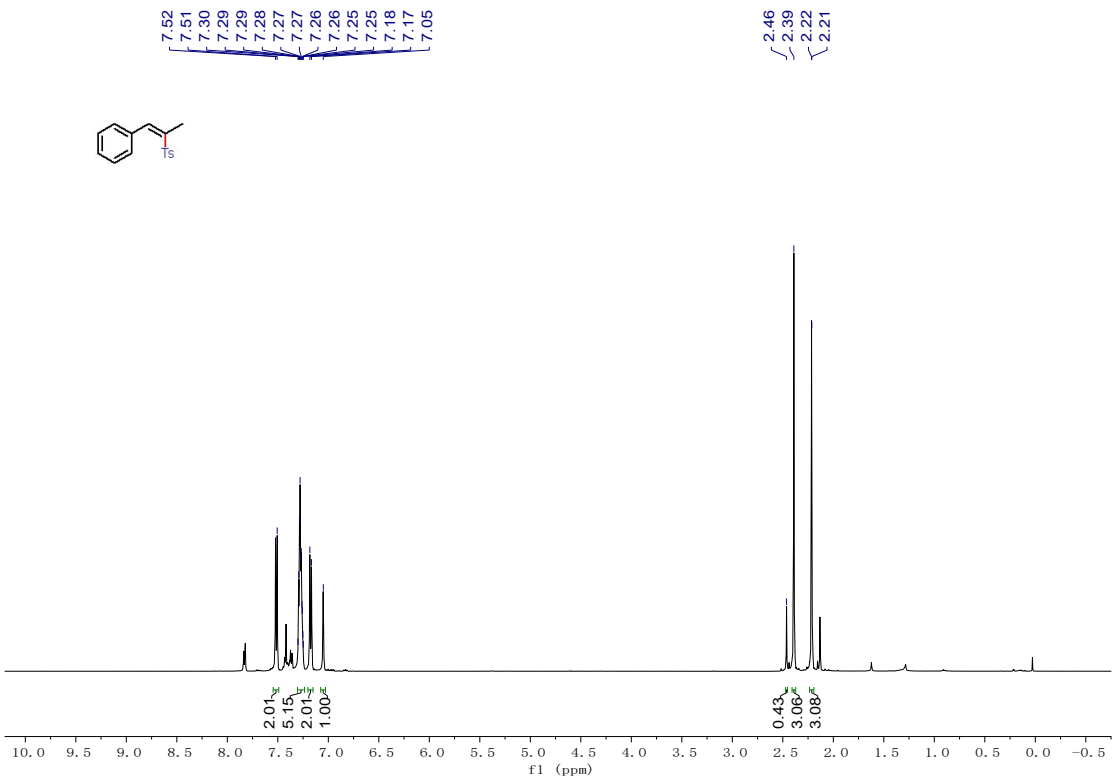
^{13}C NMR spectrum of **3x**



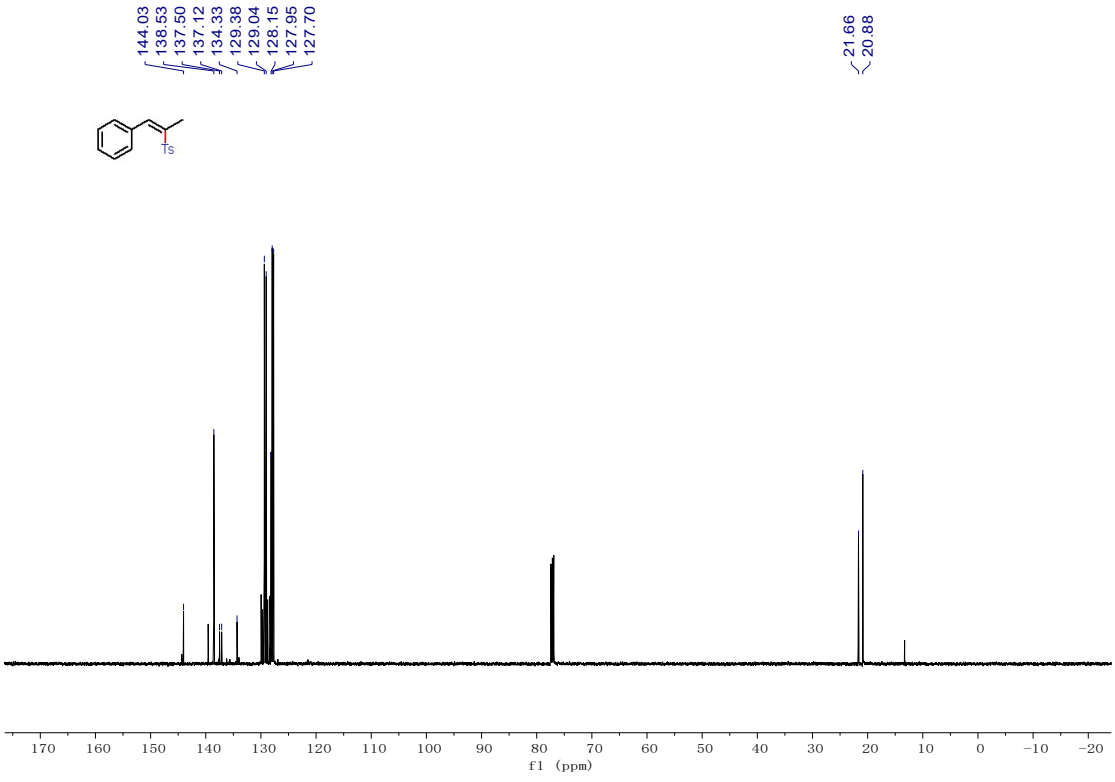
^{1}H NMR spectrum of **3y**



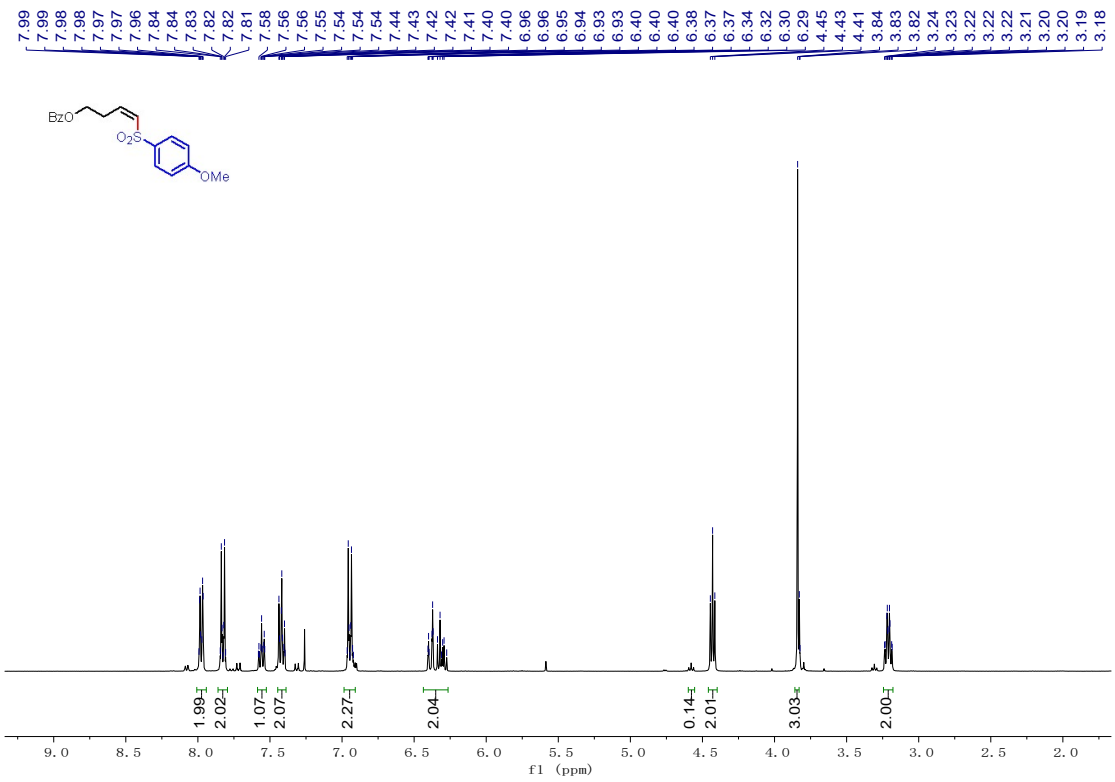
^{13}C NMR spectrum of **3y**



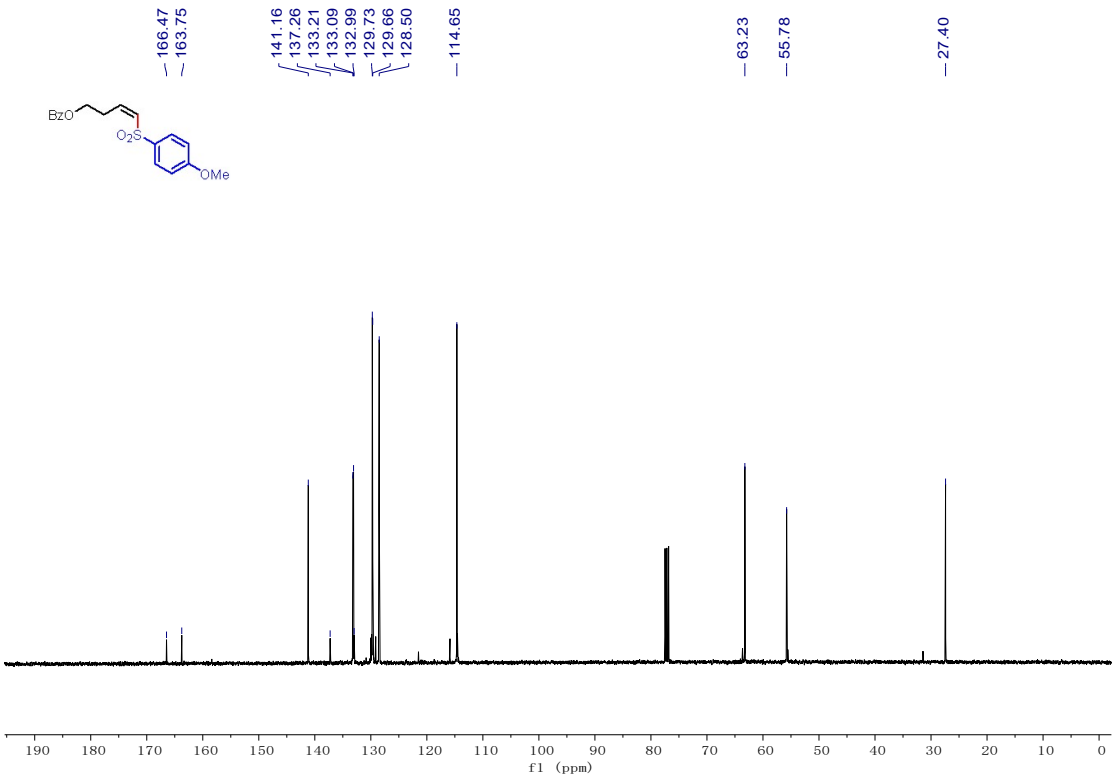
^{1}H NMR spectrum of **3z**



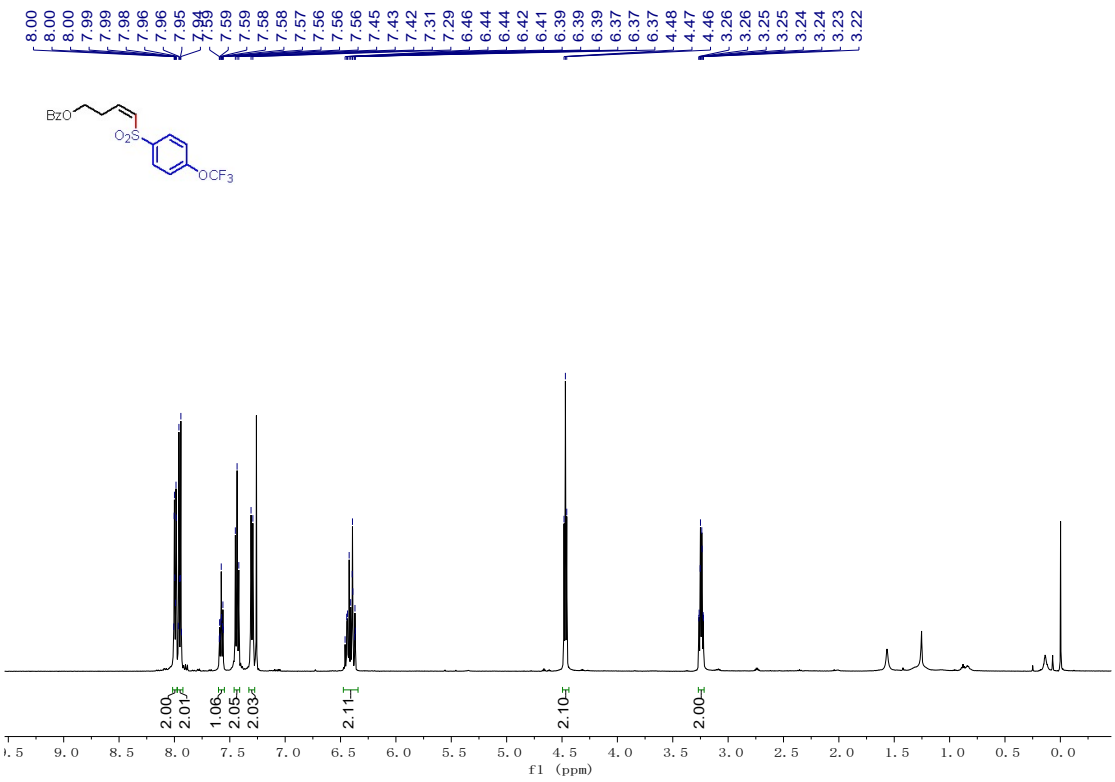
^{13}C NMR spectrum of **3z**



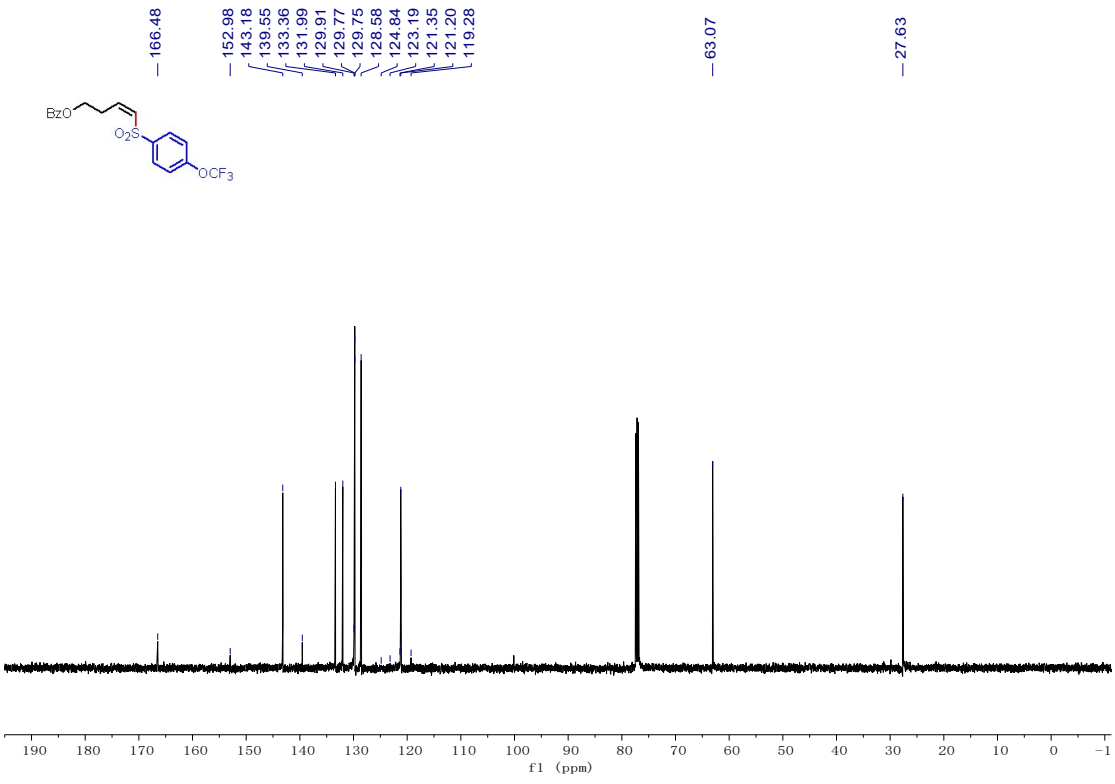
^{1}H NMR spectrum of **4a**



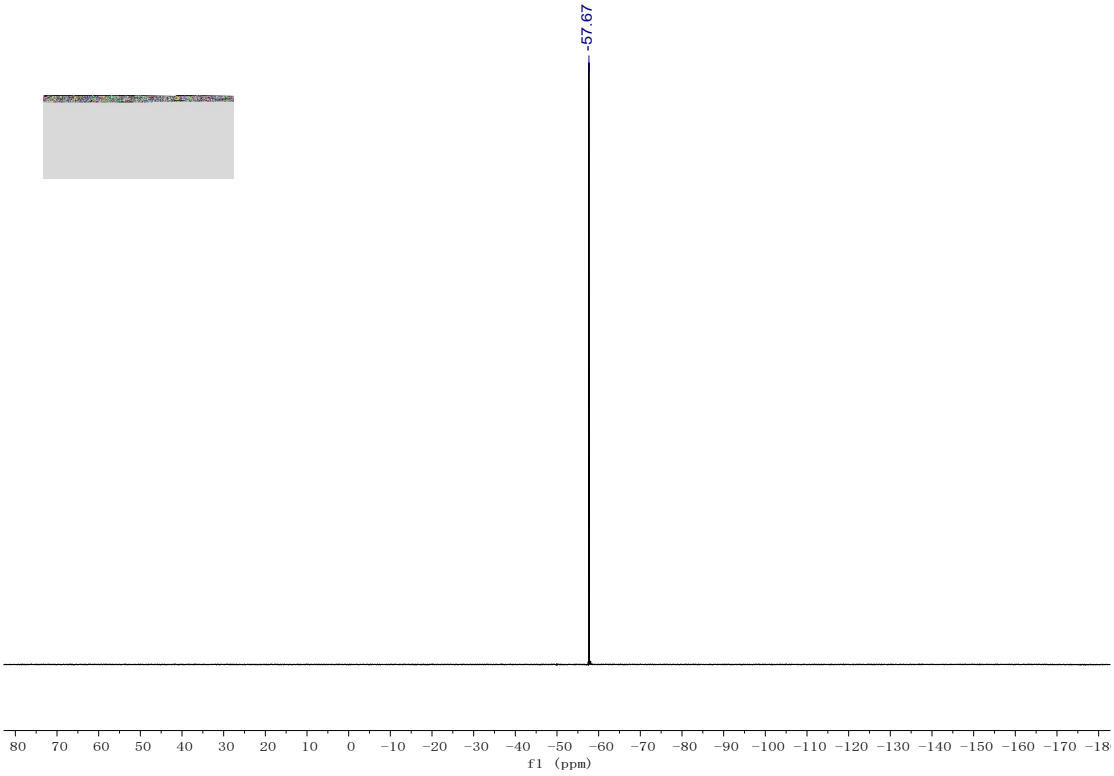
^{13}C NMR spectrum of **4a**



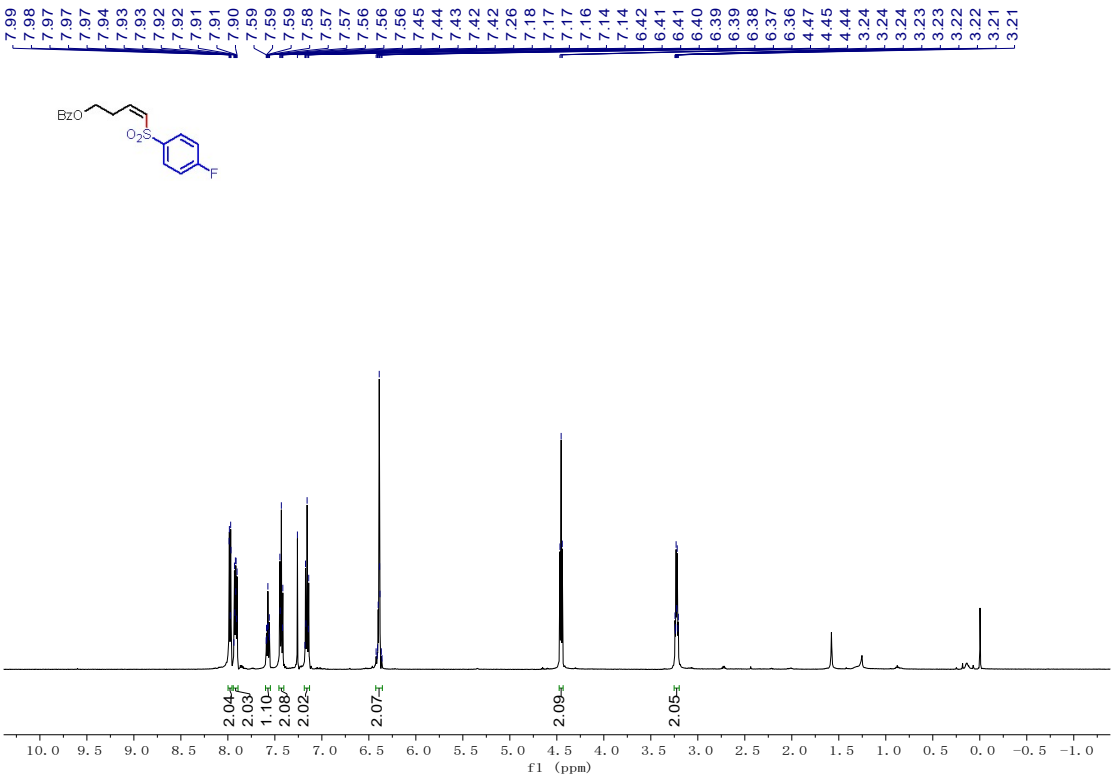
^{1}H NMR spectrum of **4b**



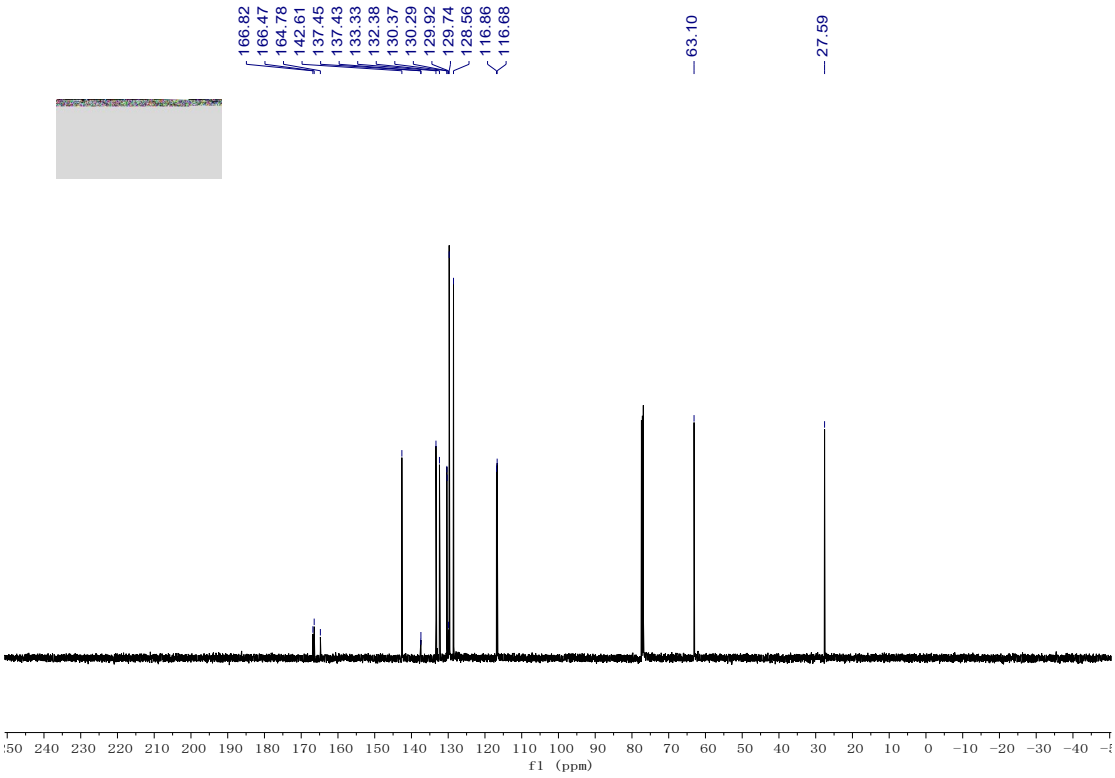
^{13}C NMR spectrum of **4b**



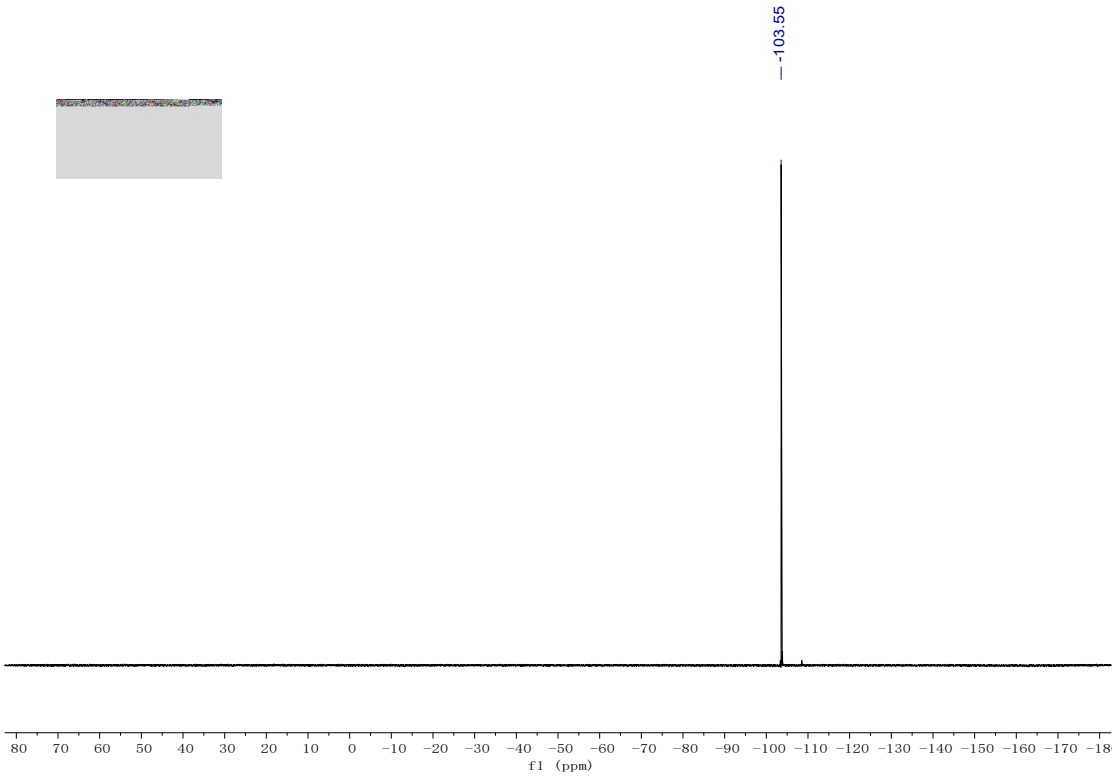
^{19}F NMR spectrum of **4b**



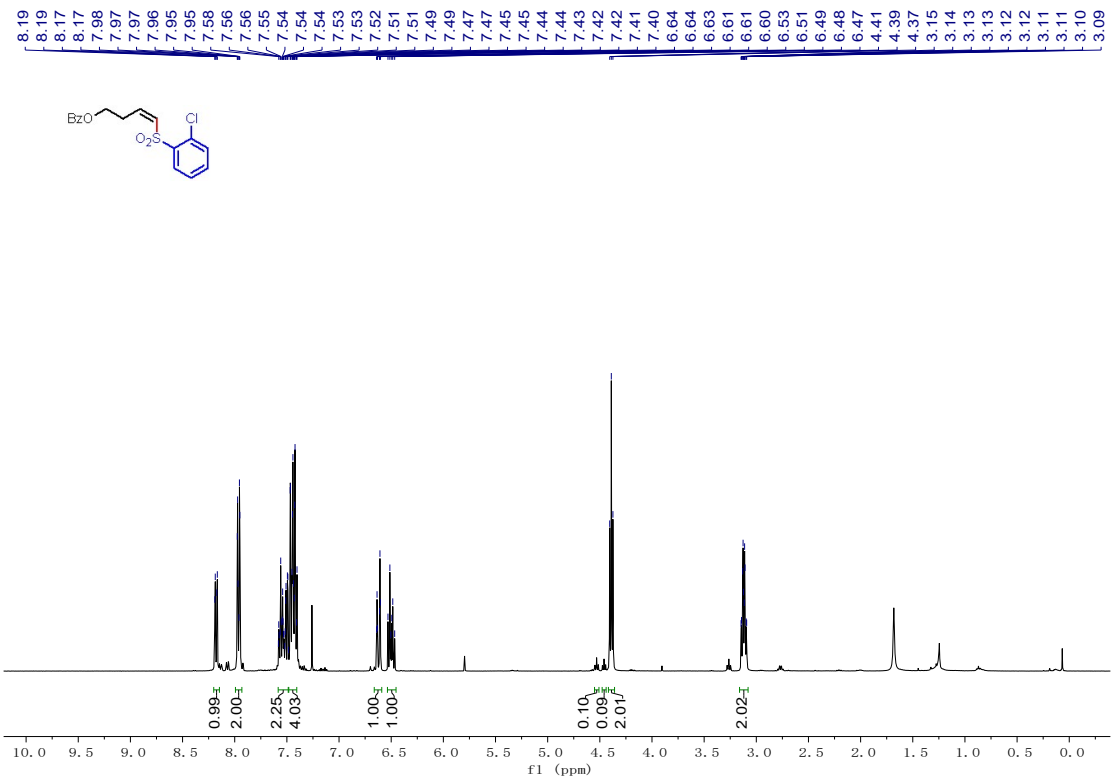
^{1}H NMR spectrum of **4c**



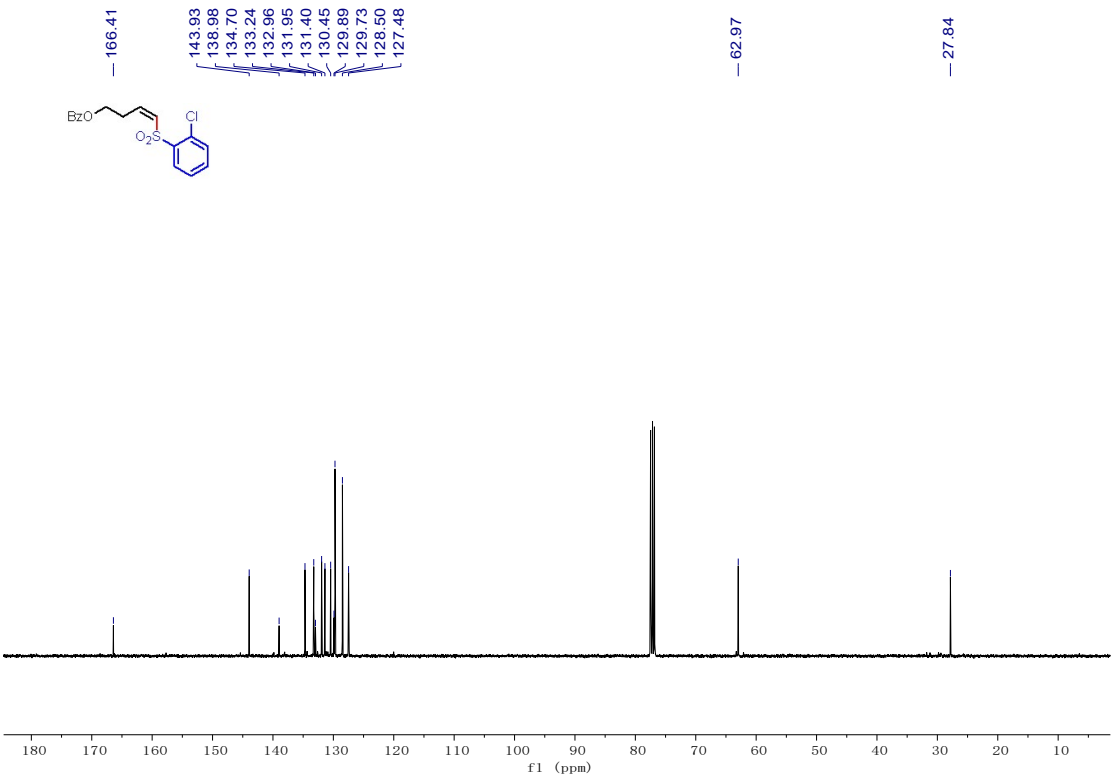
^{13}C NMR spectrum of **4c**



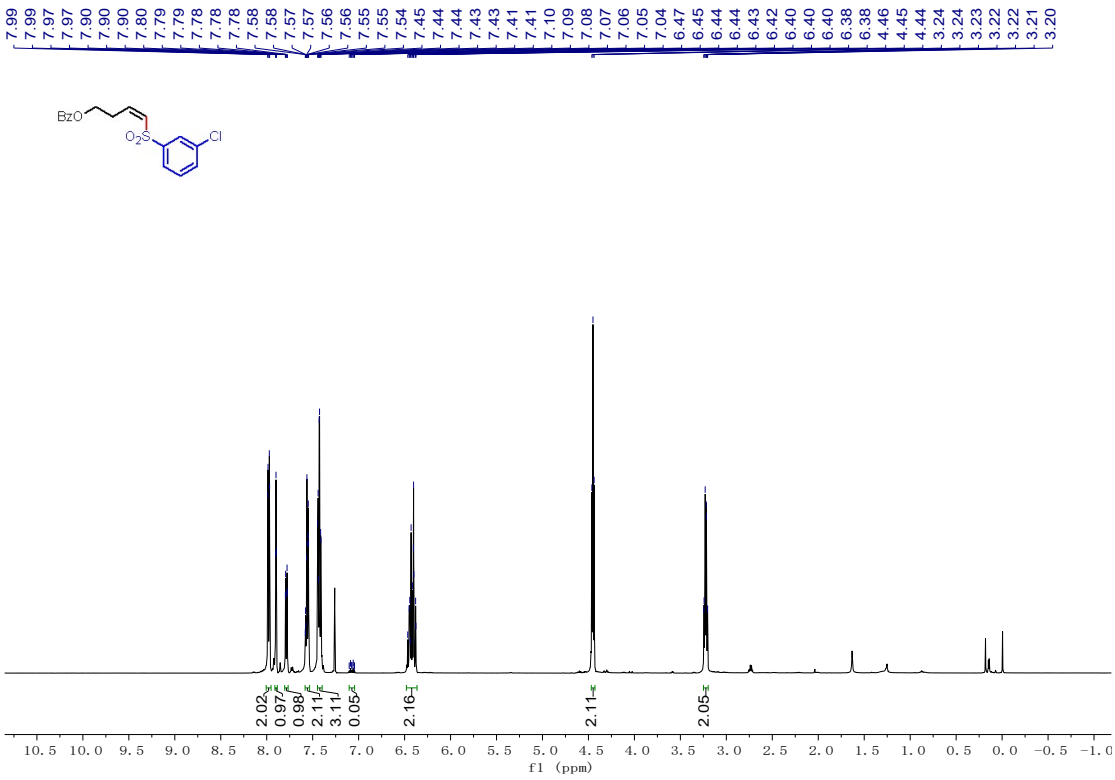
^{19}F NMR spectrum of **4c**



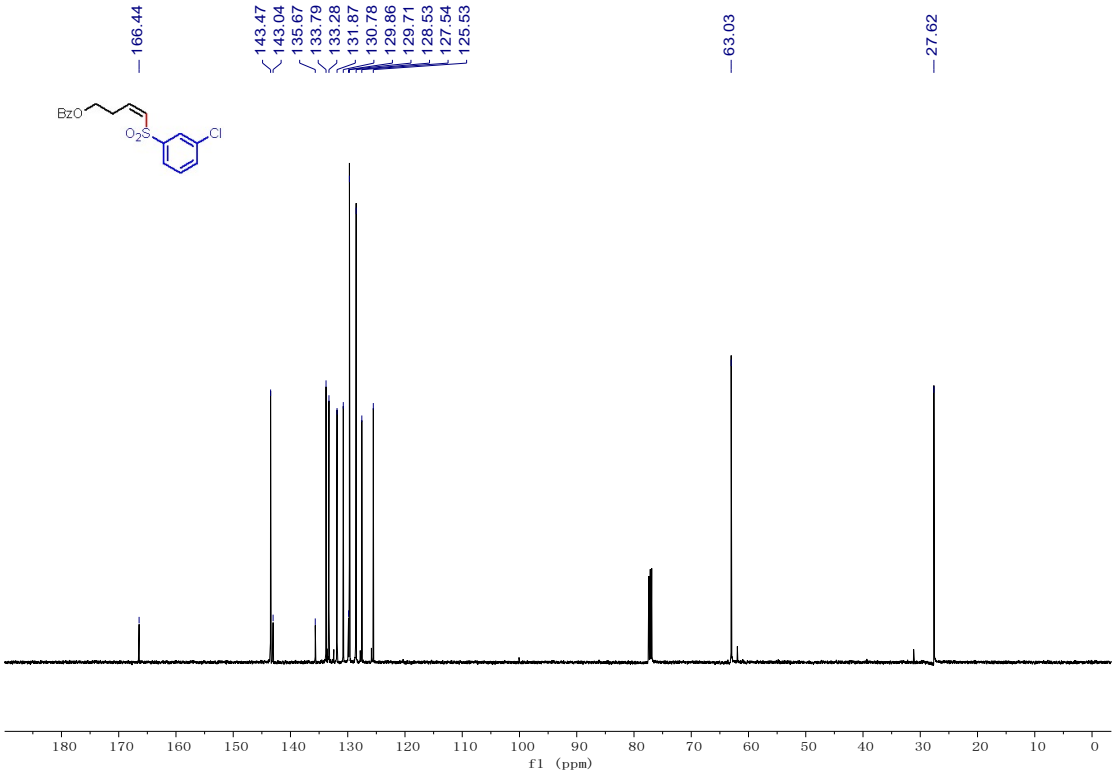
^{1}H NMR spectrum of **4d**



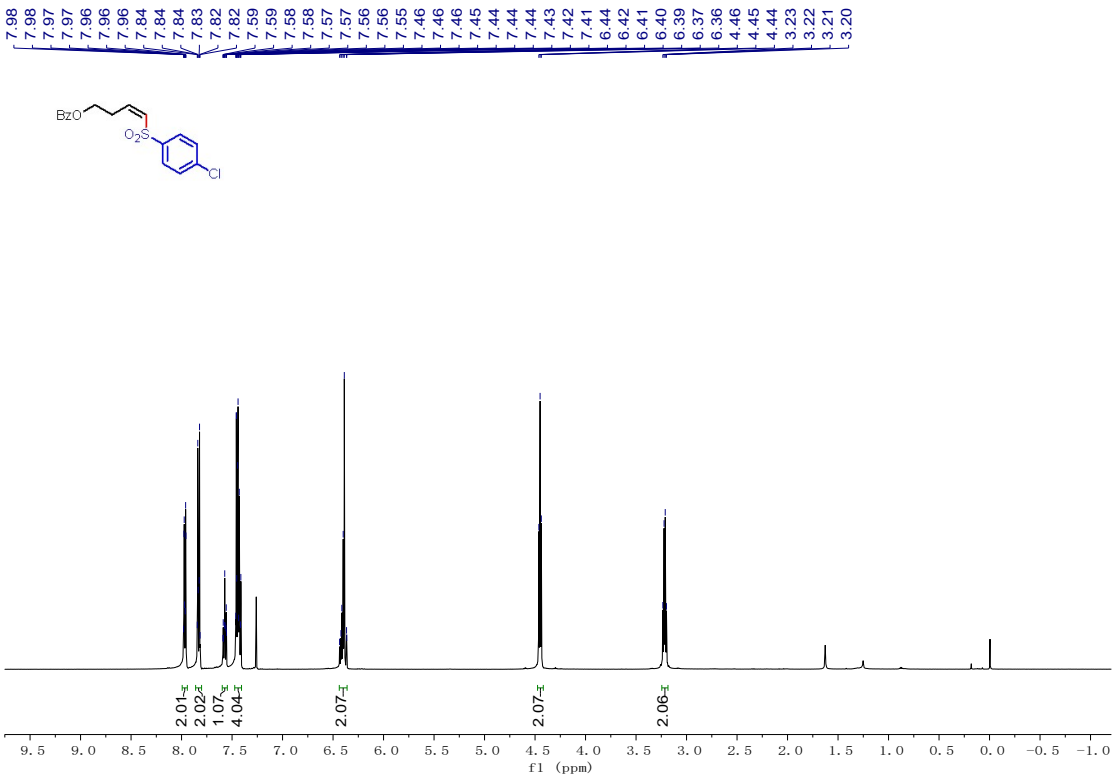
^{13}C NMR spectrum of **4d**



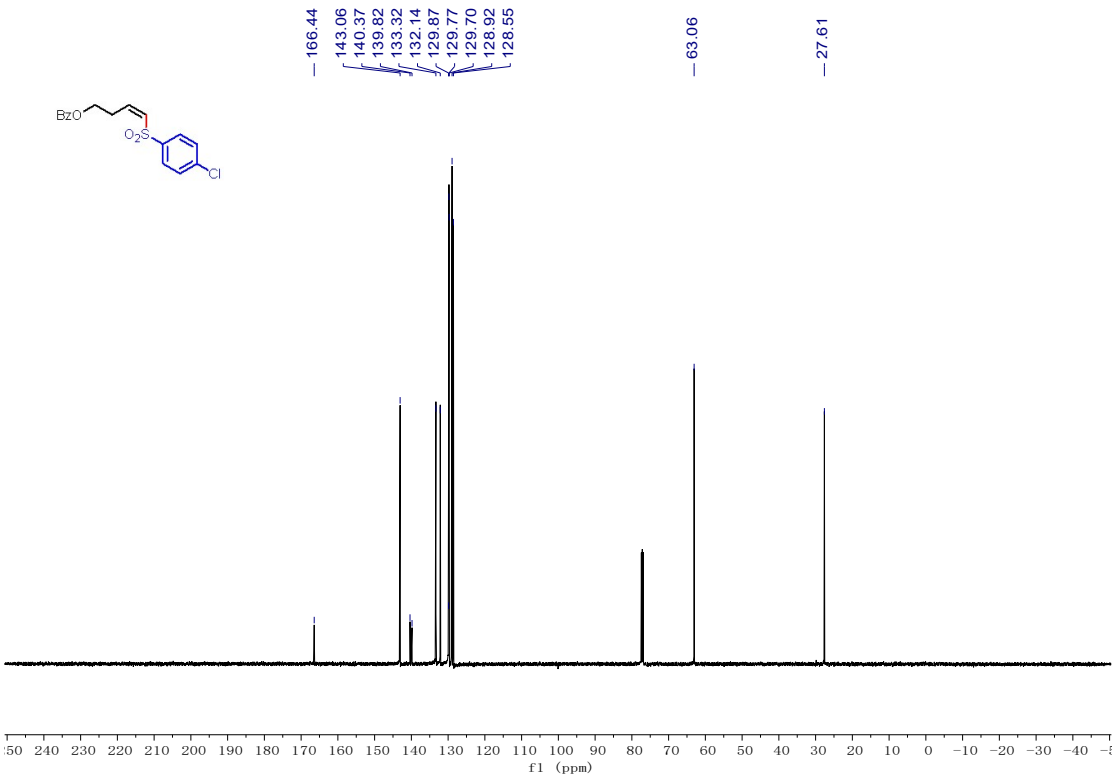
^{1}H NMR spectrum of **4e**



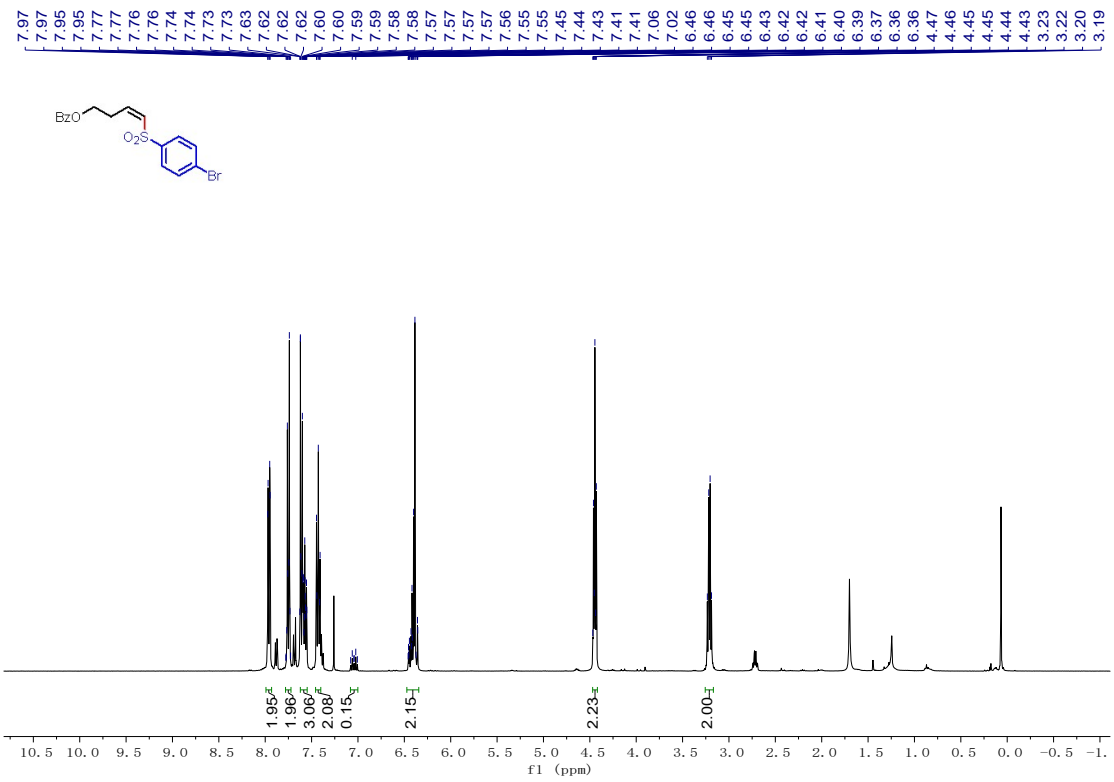
^{13}C NMR spectrum of **4e**



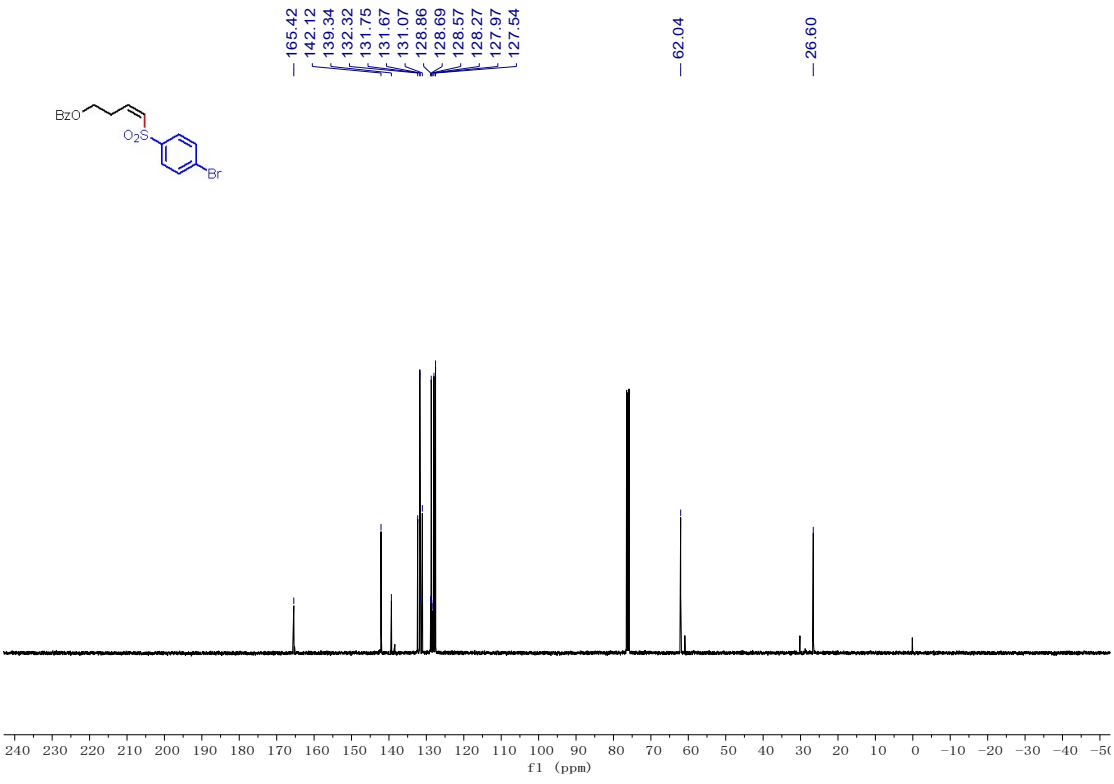
^{1}H NMR spectrum of **4f**



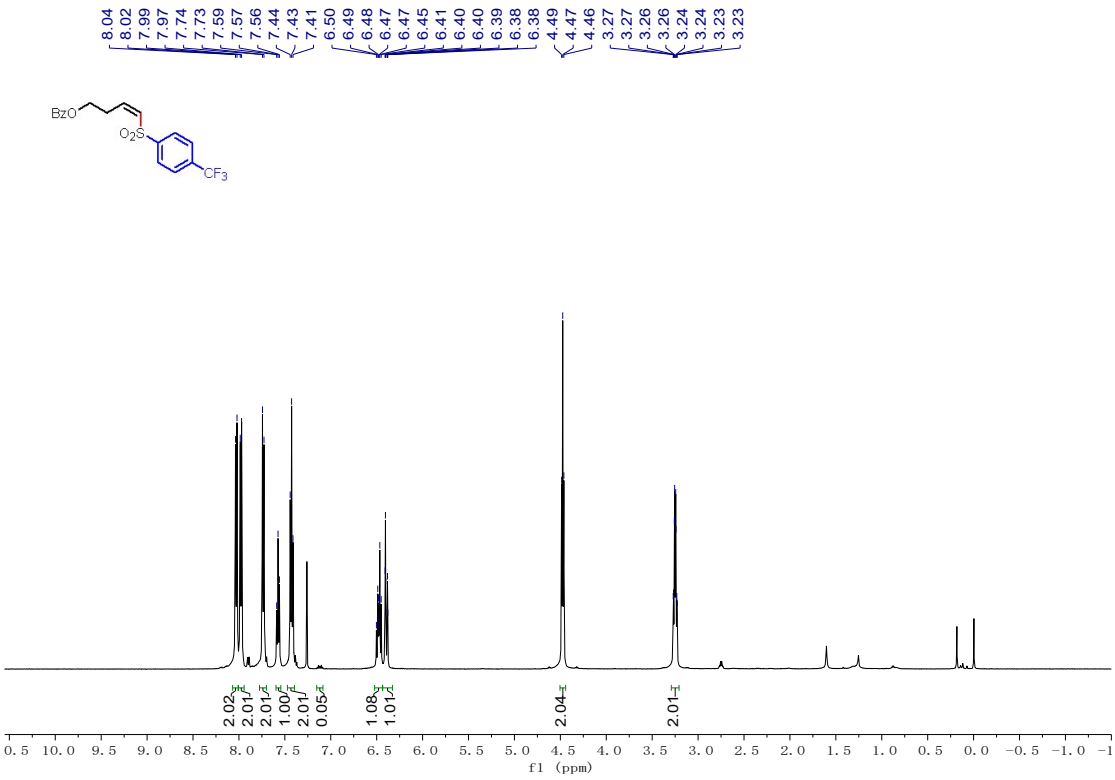
^{13}C NMR spectrum of **4f**



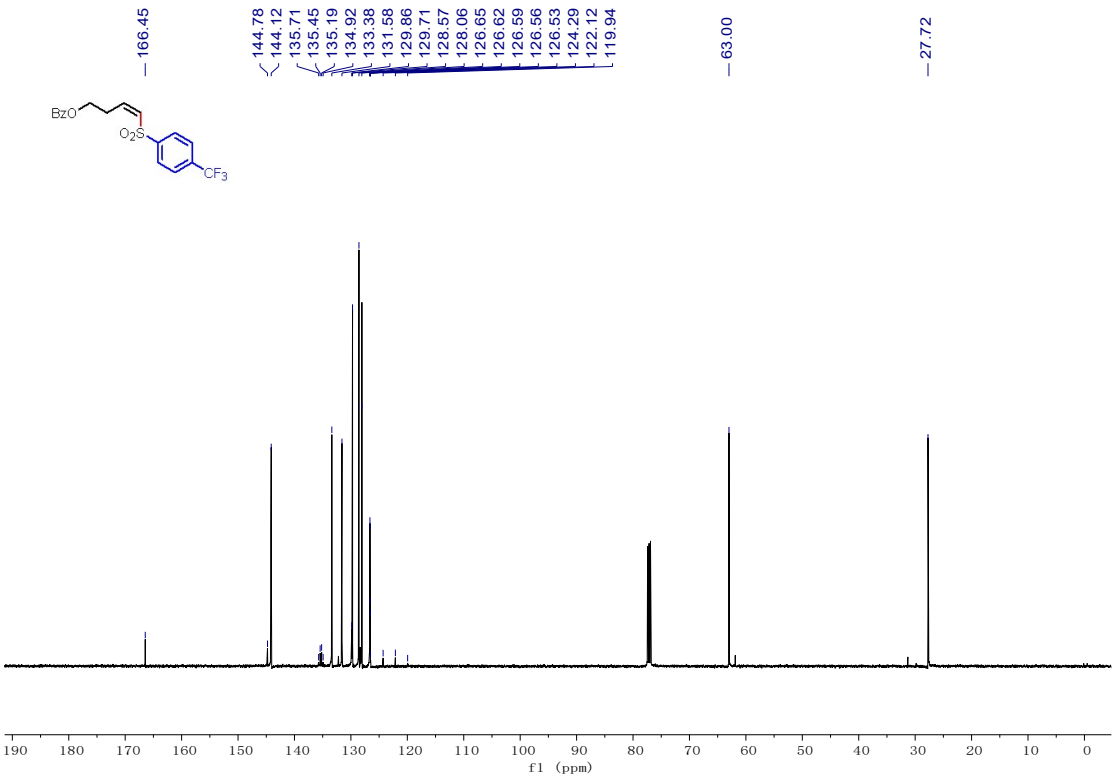
^{1}H NMR spectrum of **4g**



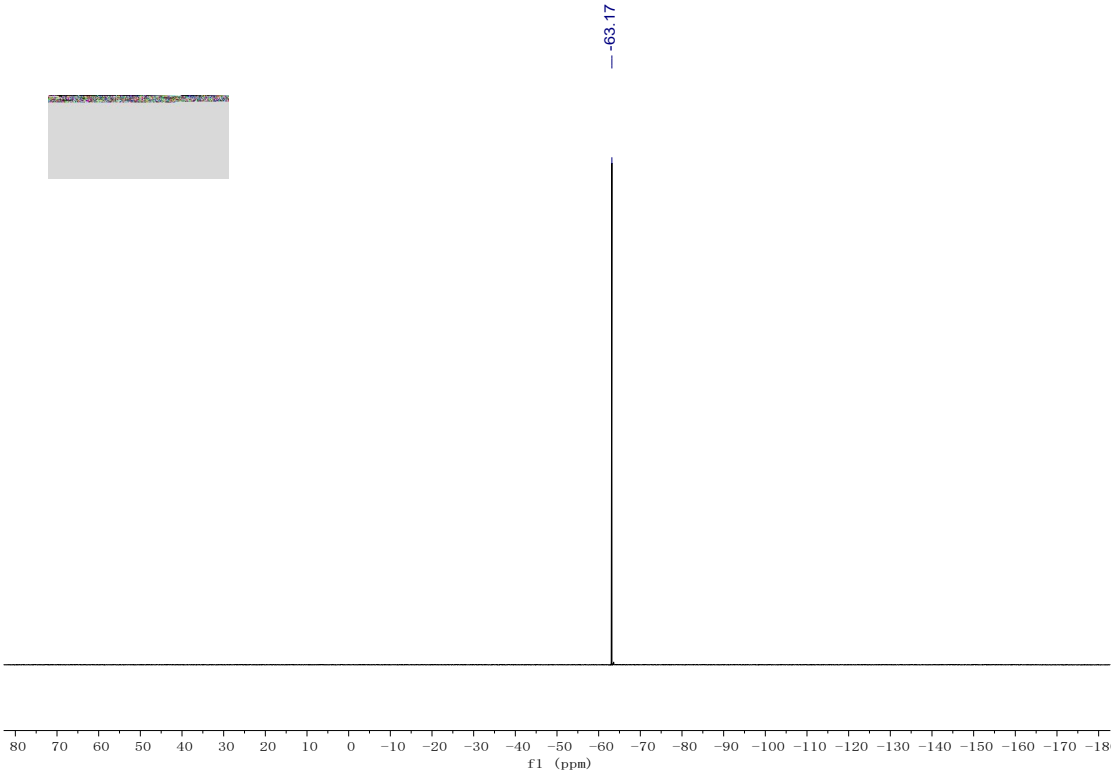
^{13}C NMR spectrum of **4g**



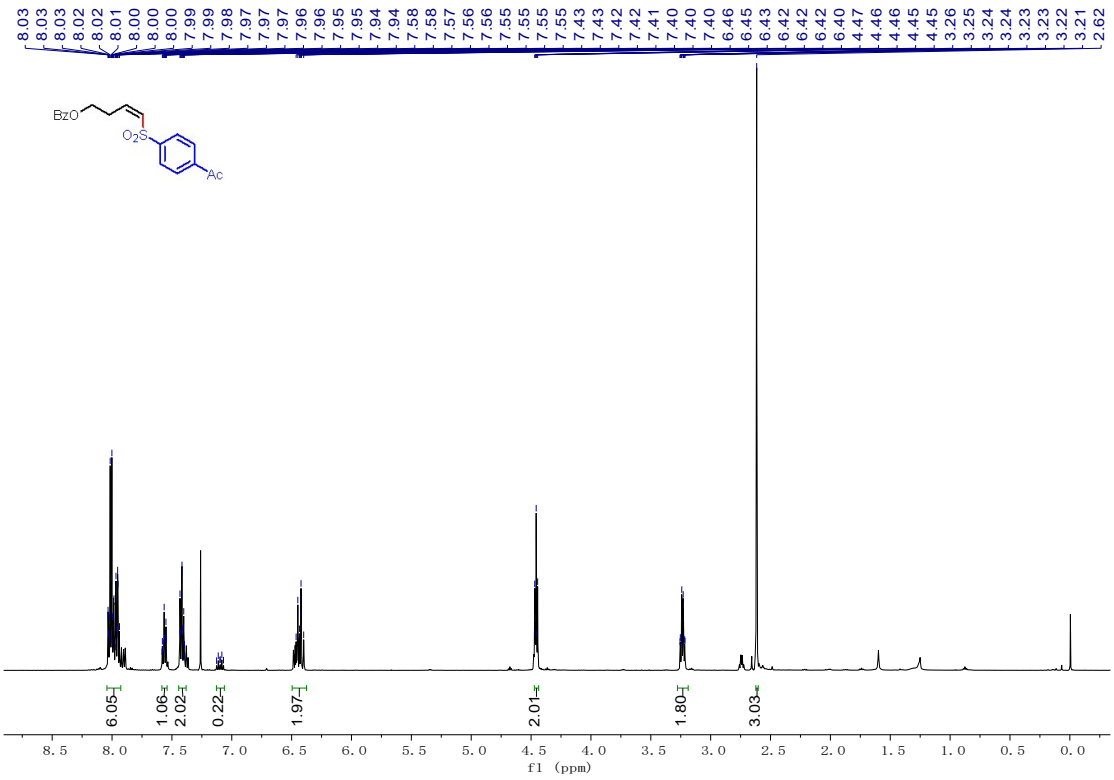
^{1}H NMR spectrum of **4h**



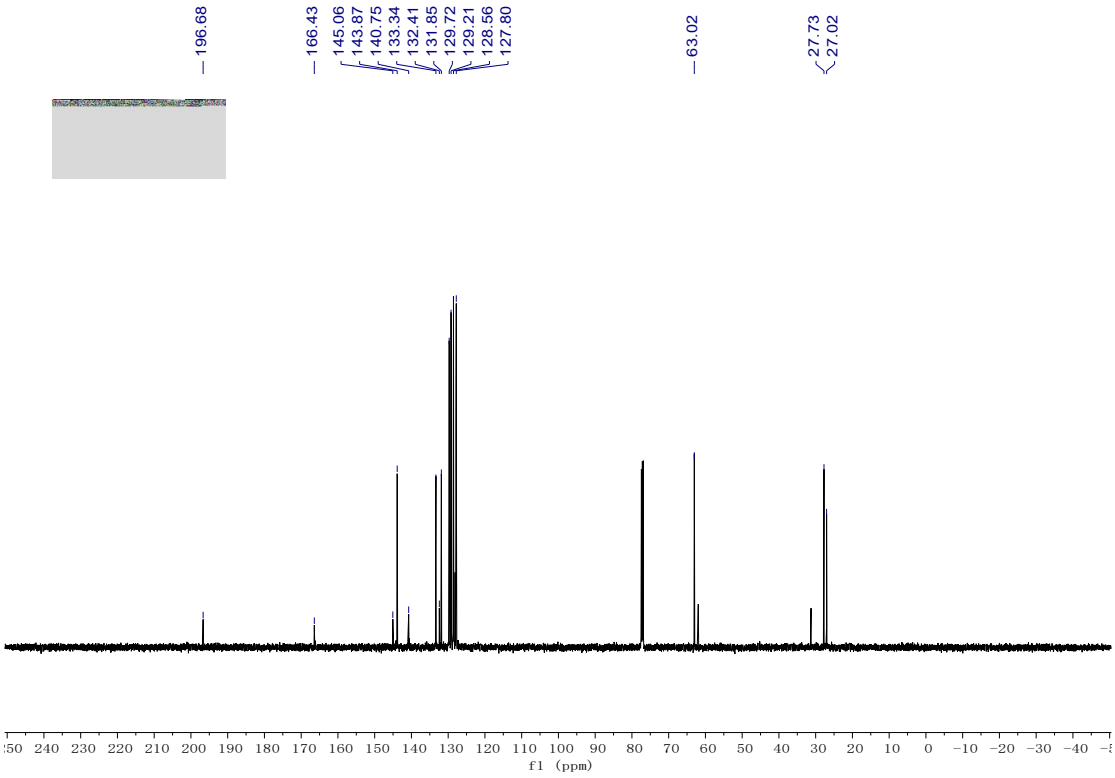
^{13}C NMR spectrum of **4h**



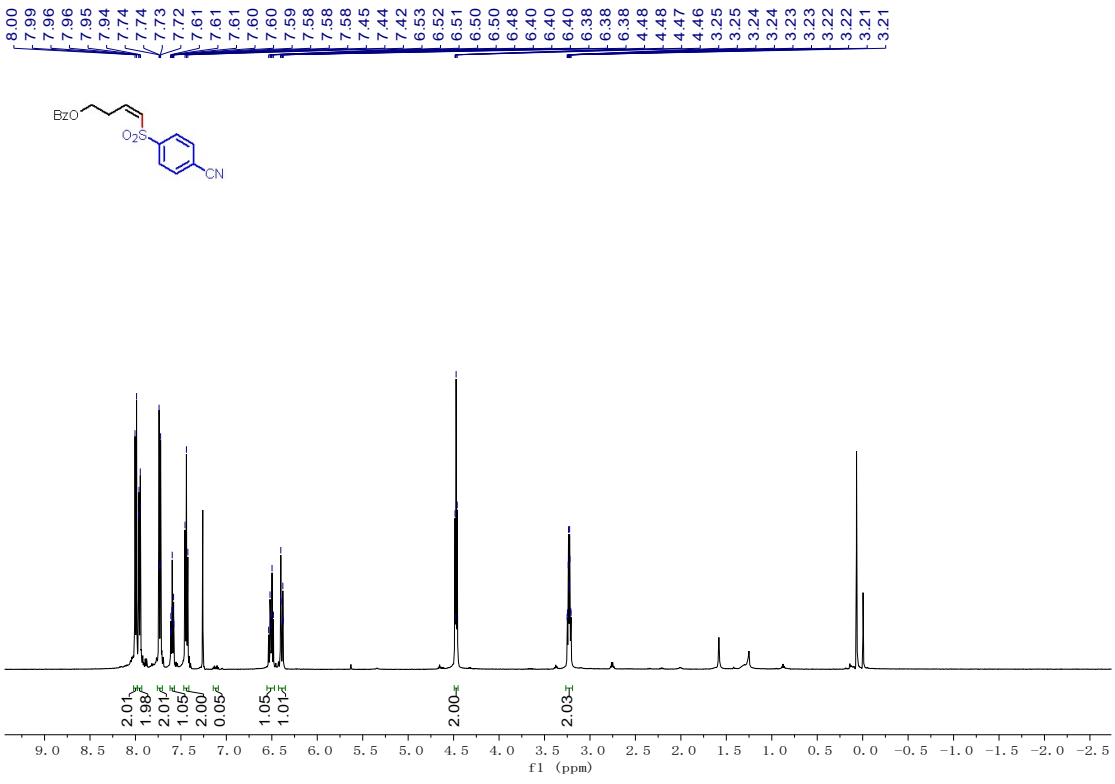
^{19}F NMR spectrum of **4h**



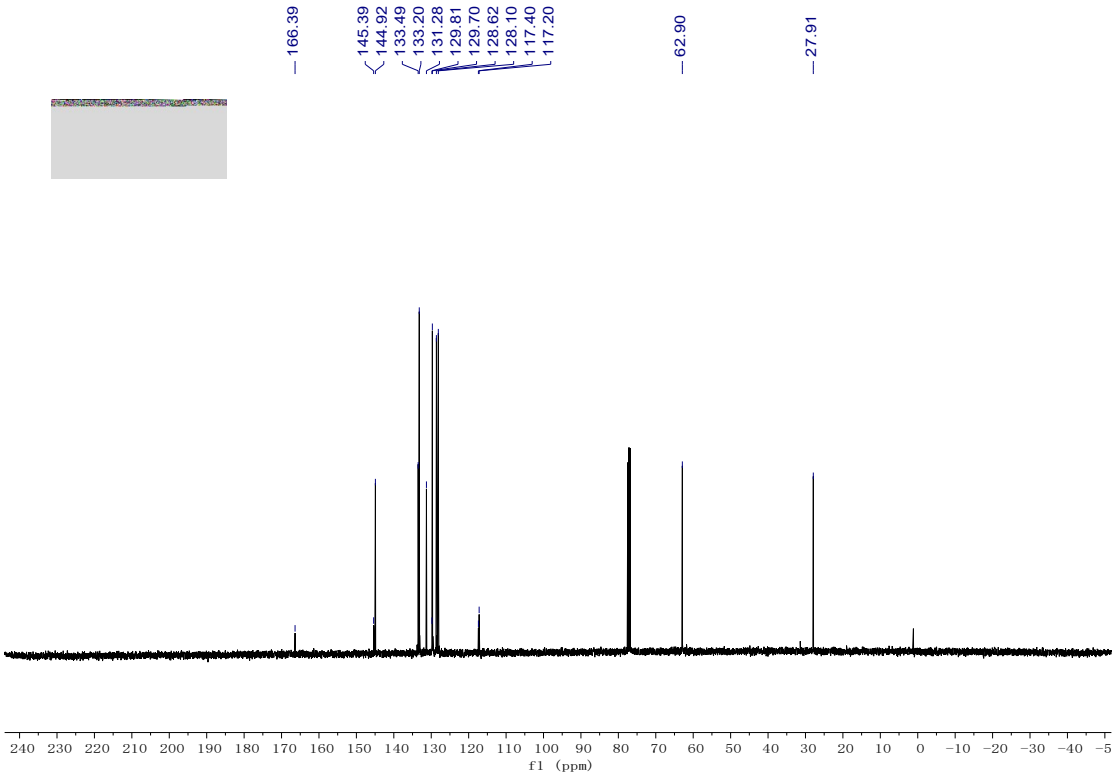
^{1}H NMR spectrum of **4i**



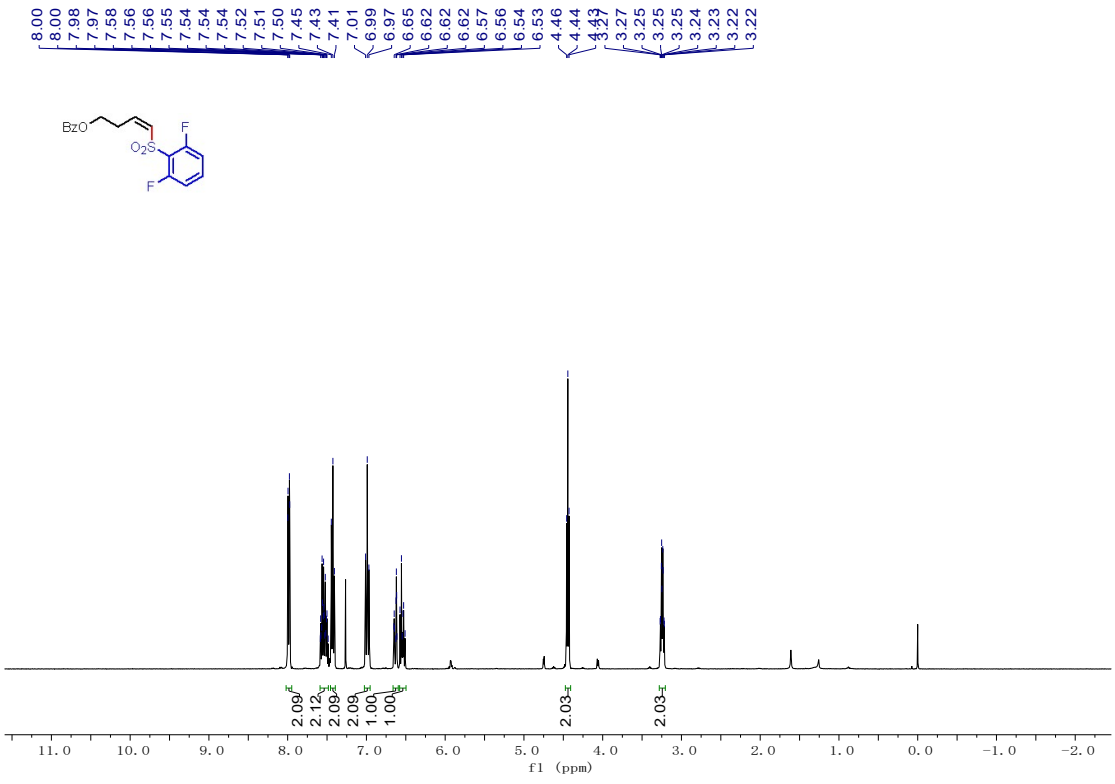
^{13}C NMR spectrum of **4i**



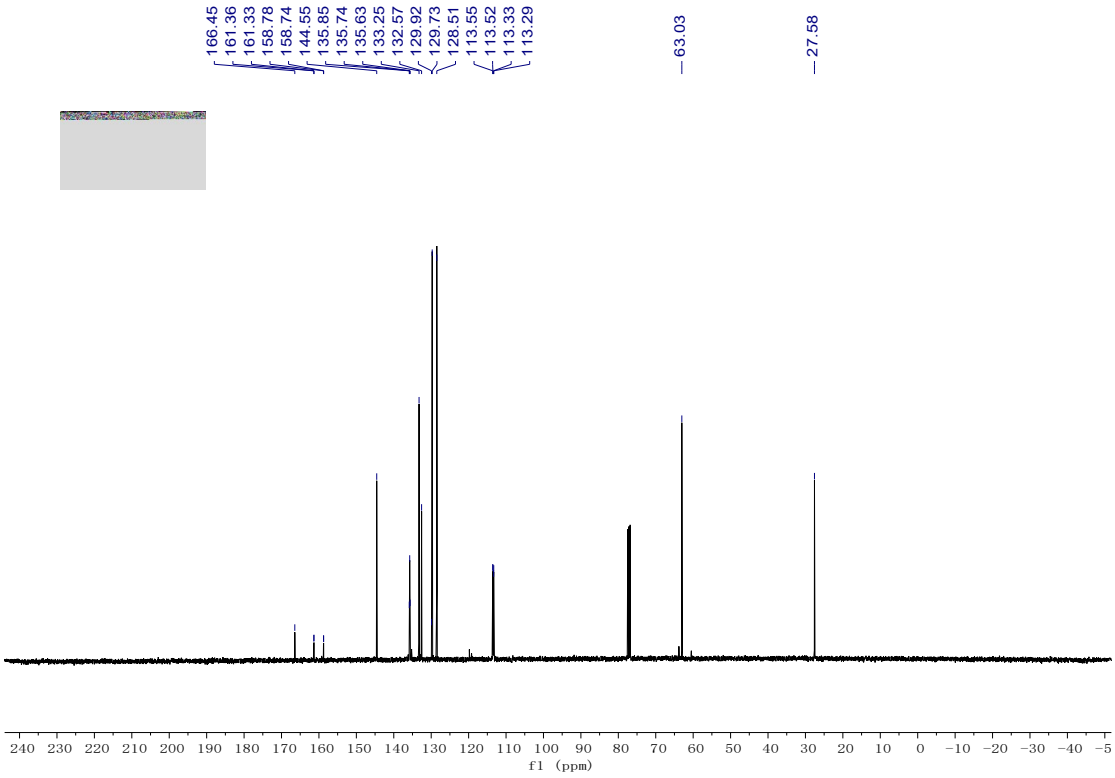
^{1}H NMR spectrum of **4j**



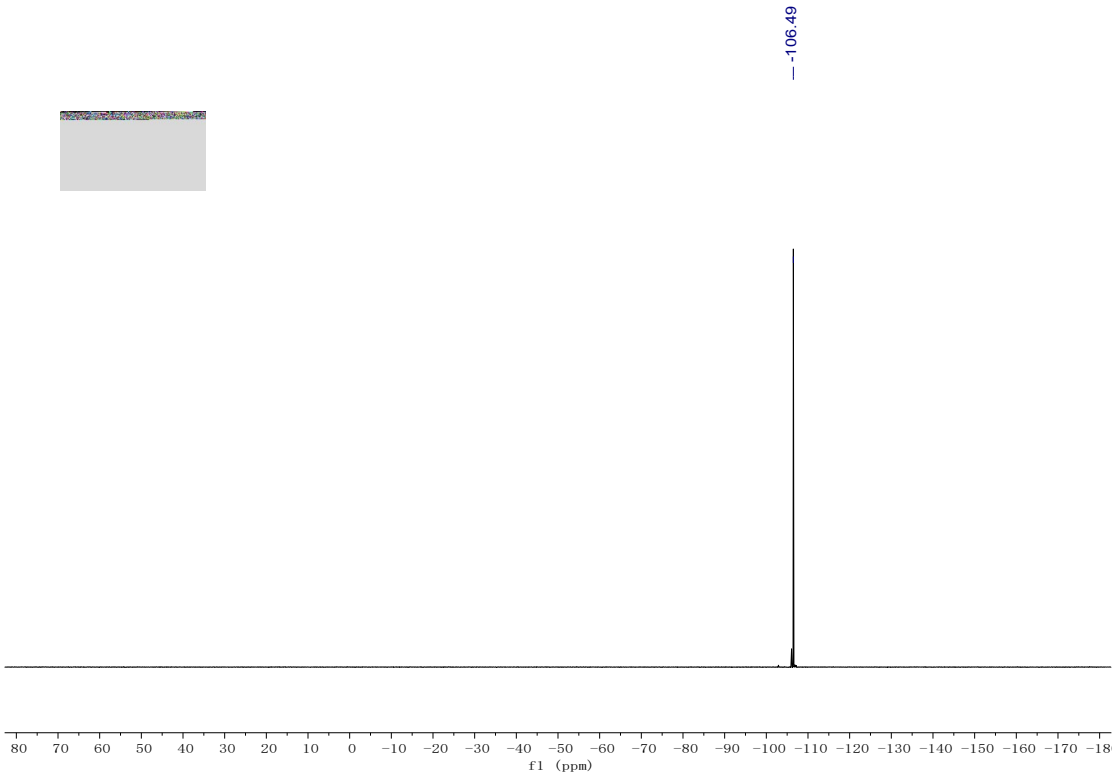
^{13}C NMR spectrum of **4j**



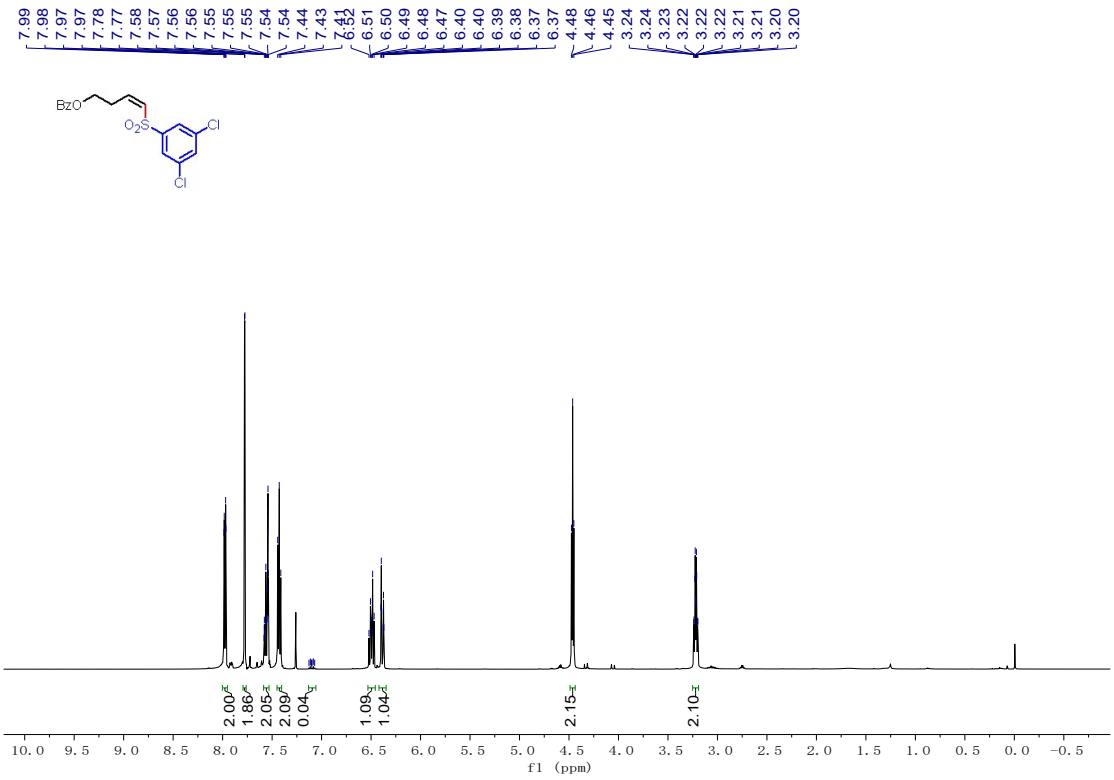
^{1}H NMR spectrum of **4k**



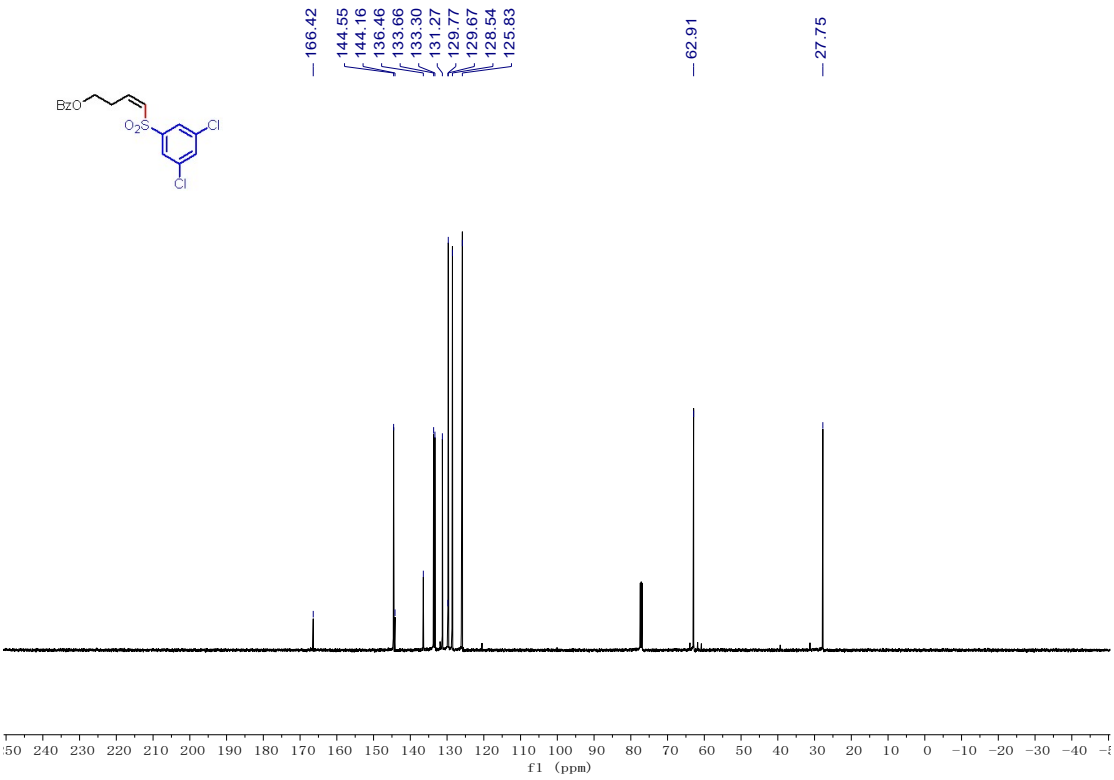
^{13}C NMR spectrum of **4k**



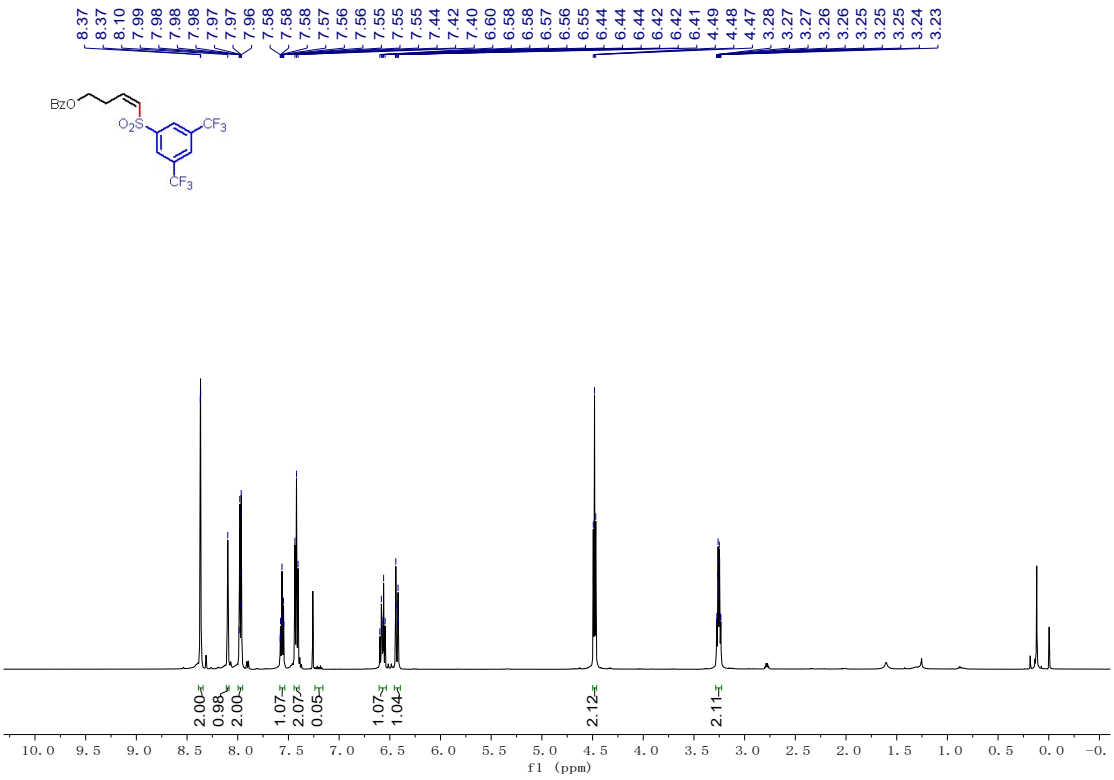
^{19}F NMR spectrum of **4k**



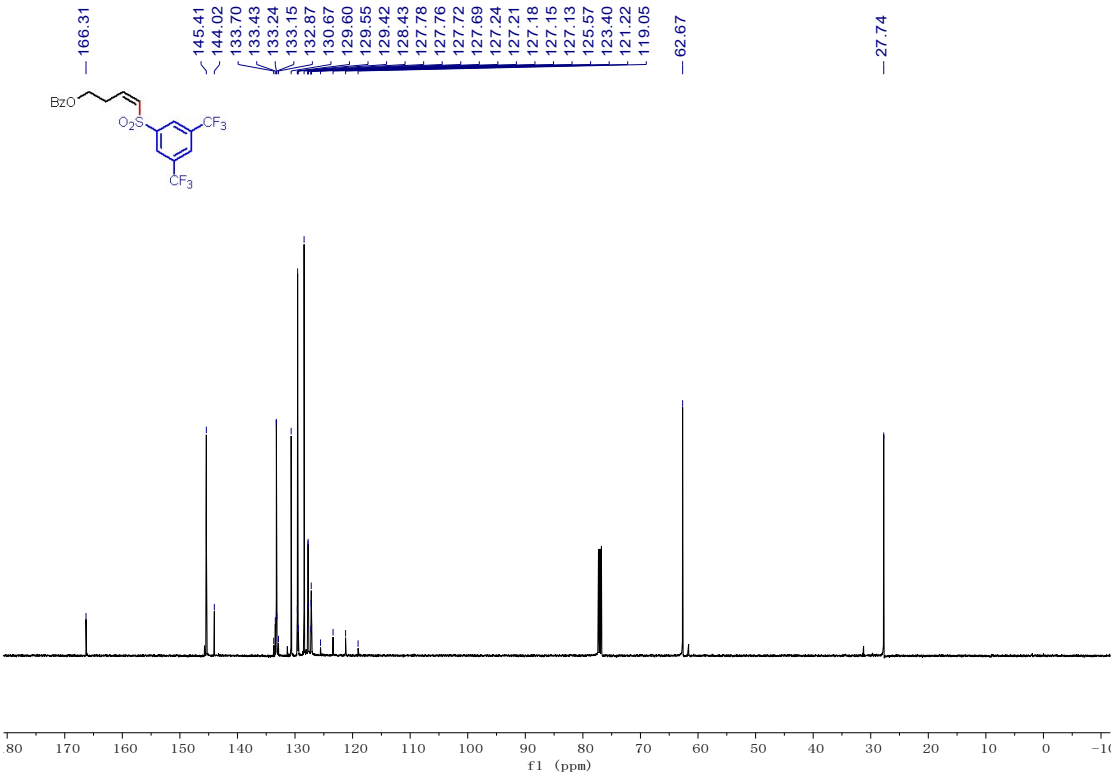
^{1}H NMR spectrum of **4l**



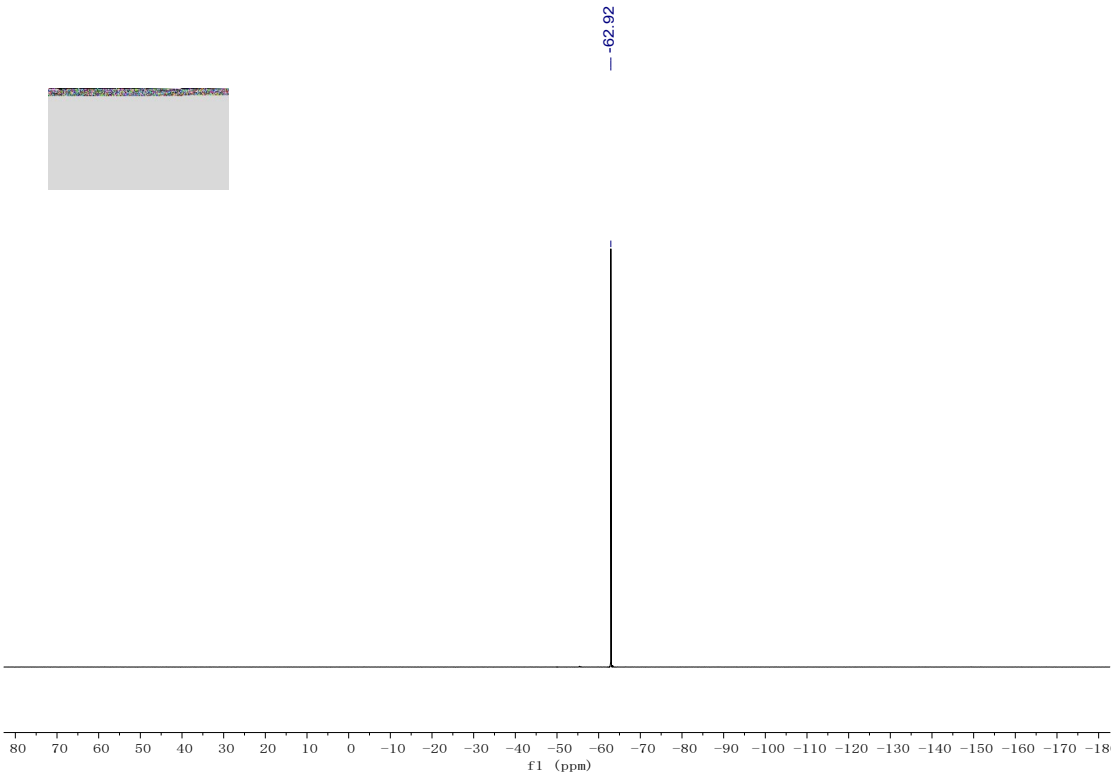
^{13}C NMR spectrum of **4l**



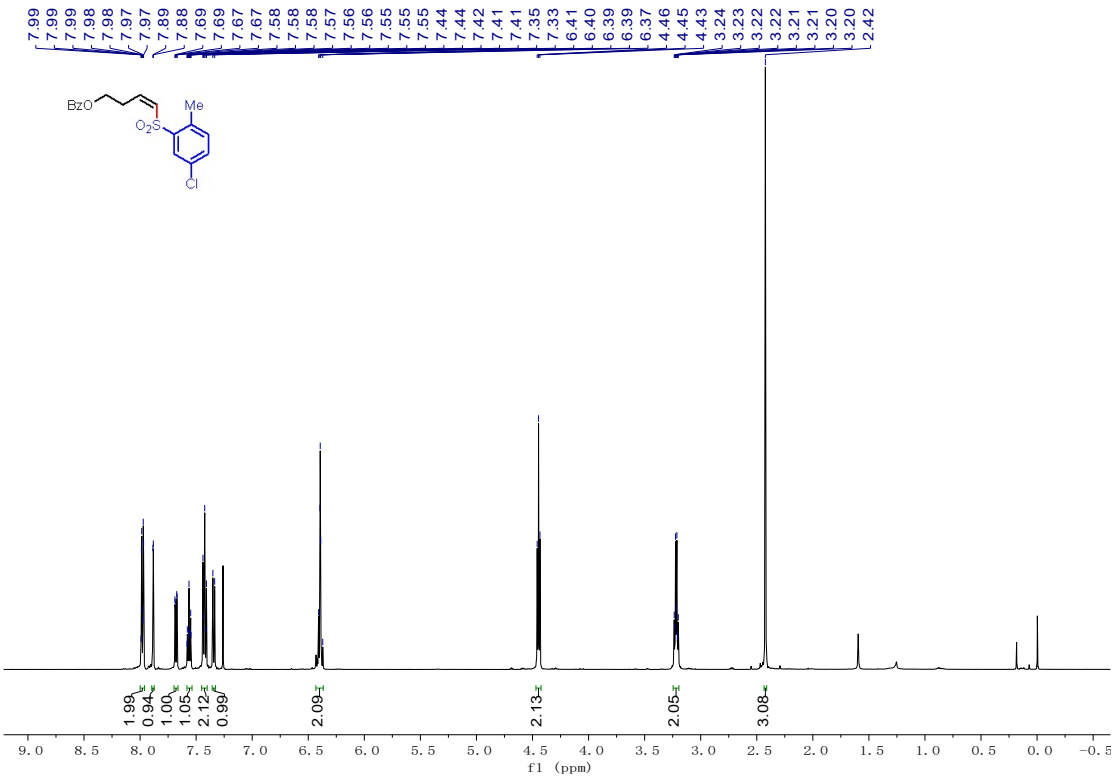
^{1}H NMR spectrum of **4m**



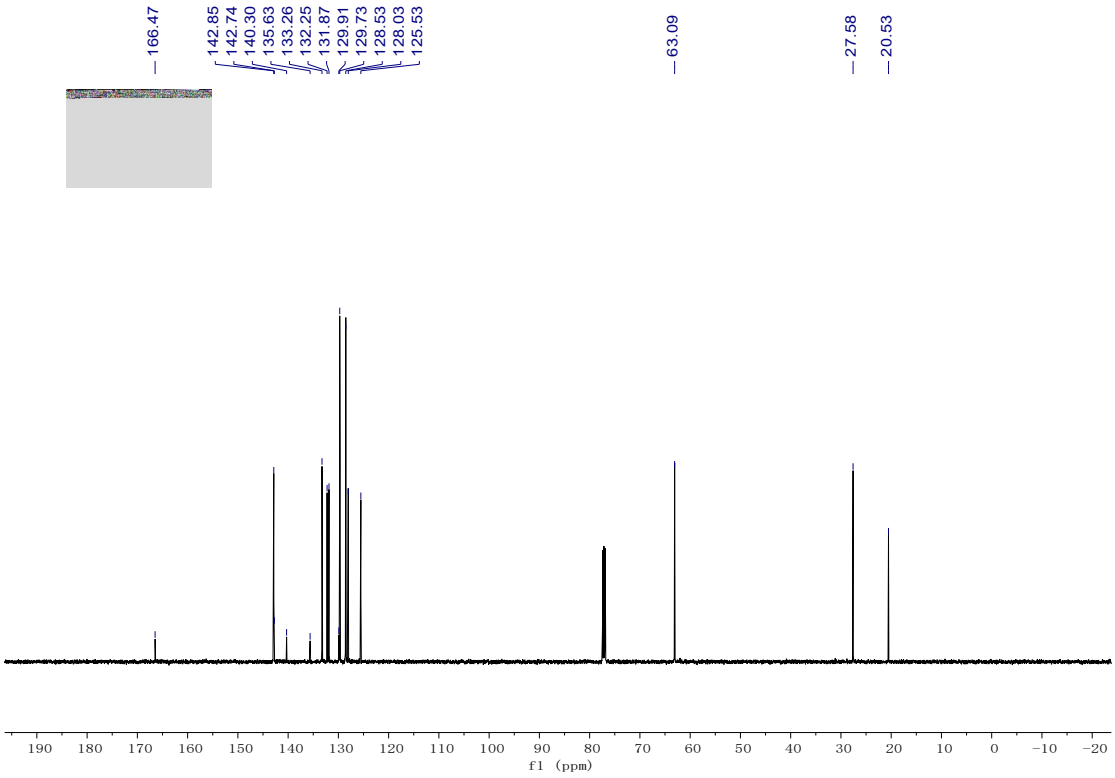
^{13}C NMR spectrum of **4m**



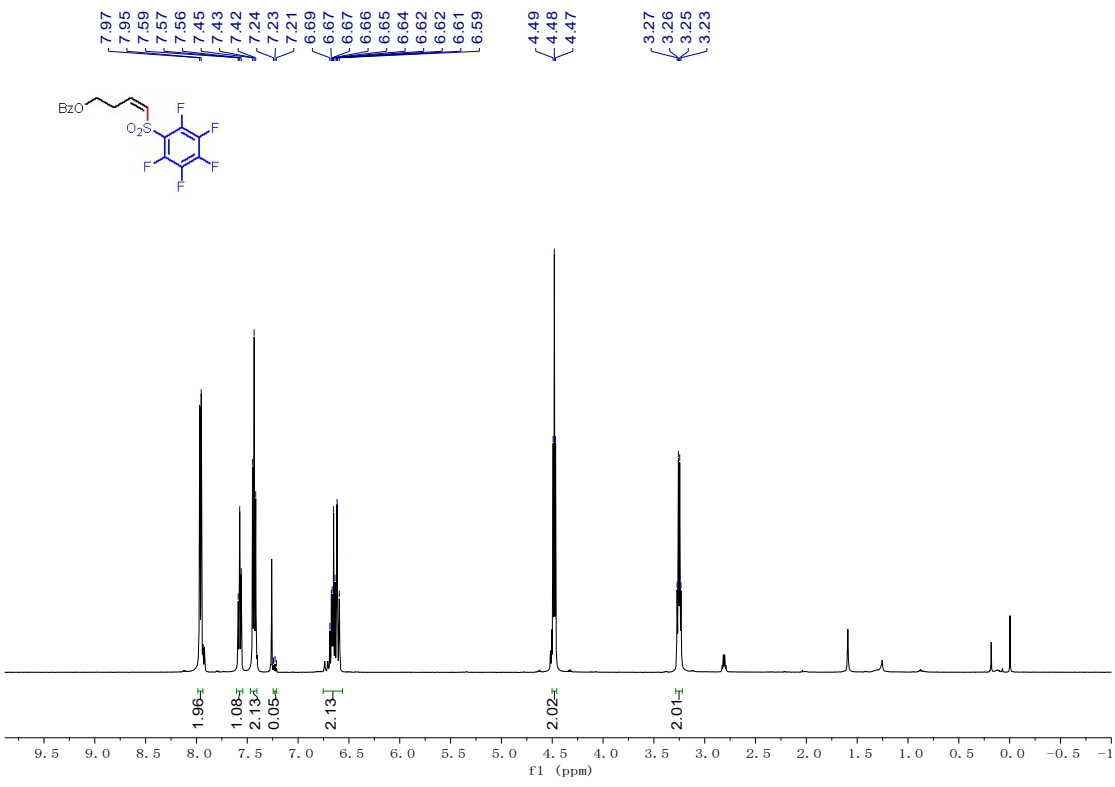
^{19}F NMR spectrum of **4m**



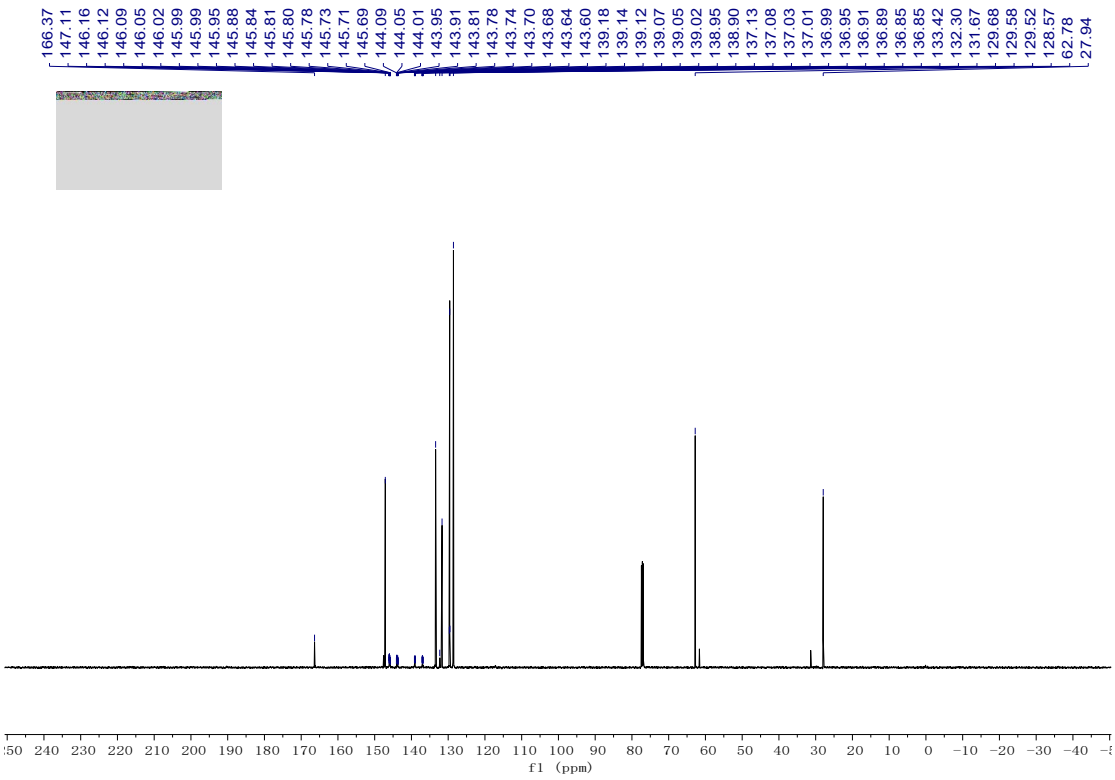
^{1}H NMR spectrum of **4n**



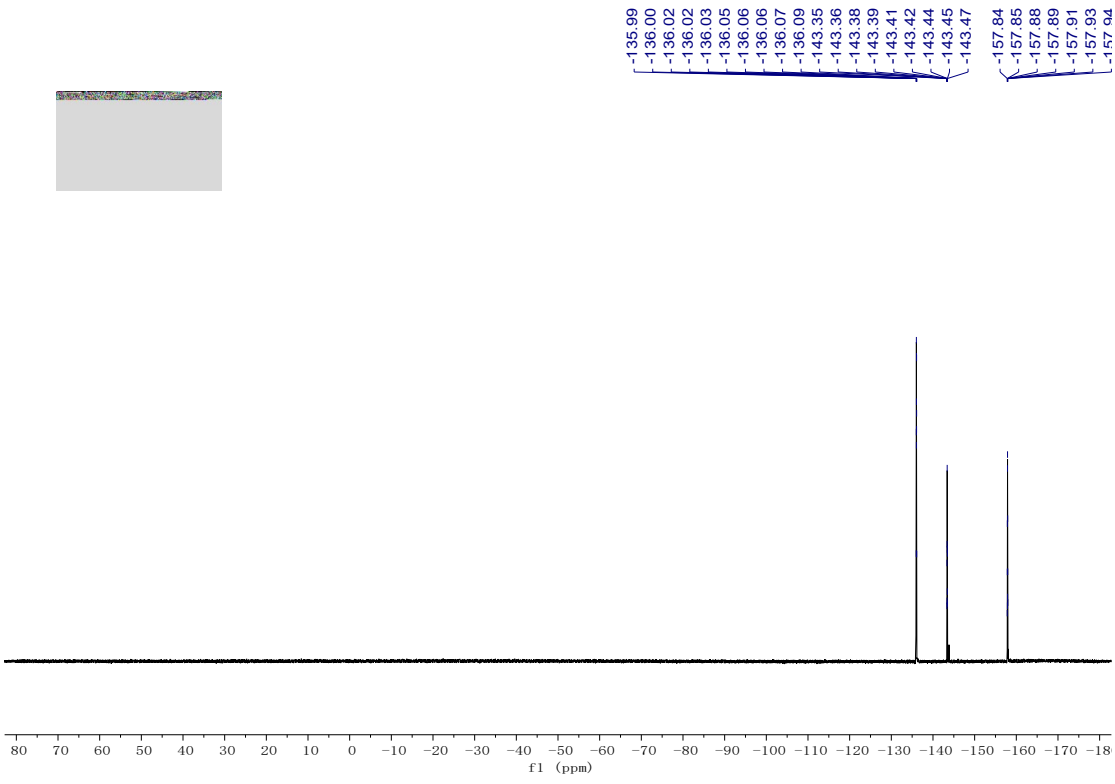
^{13}C NMR spectrum of **4n**



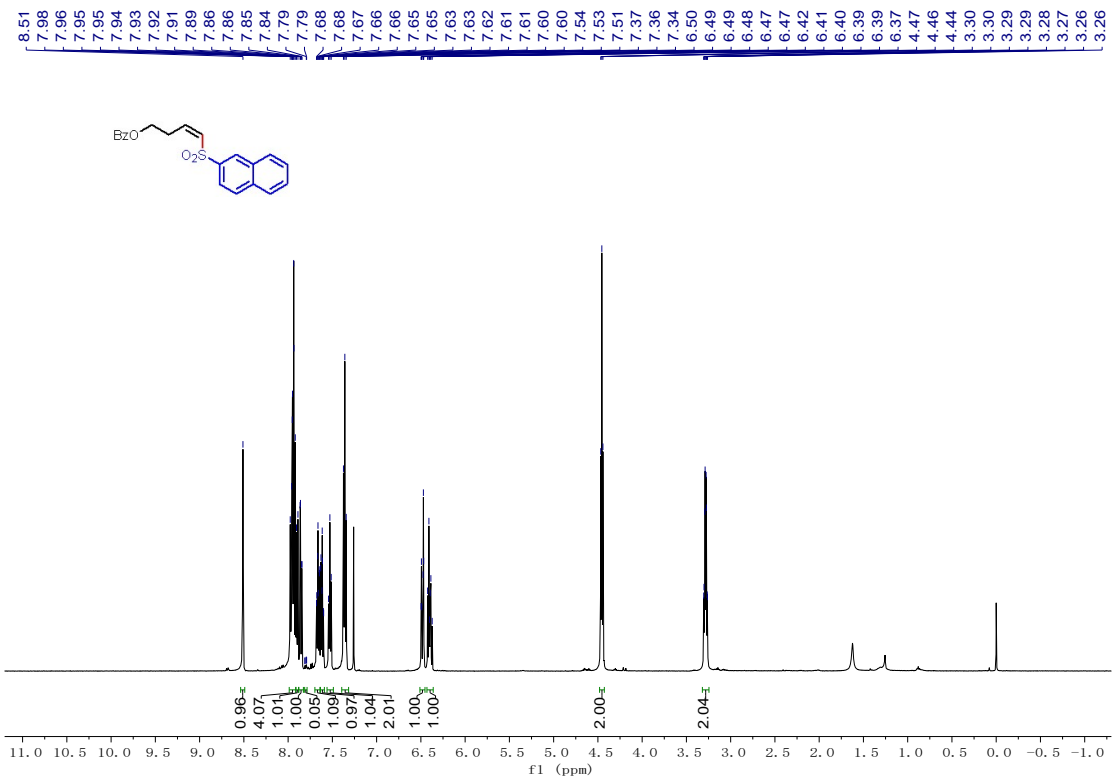
^{1}H NMR spectrum of **4o**



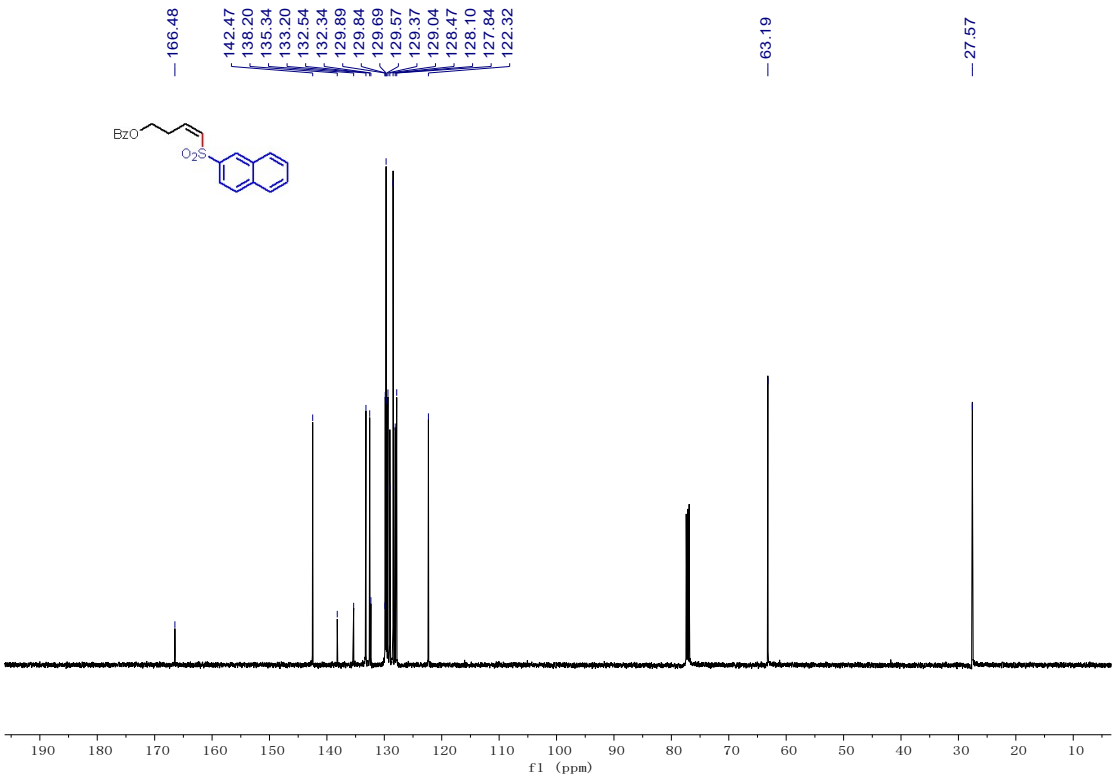
^{13}C NMR spectrum of **4o**



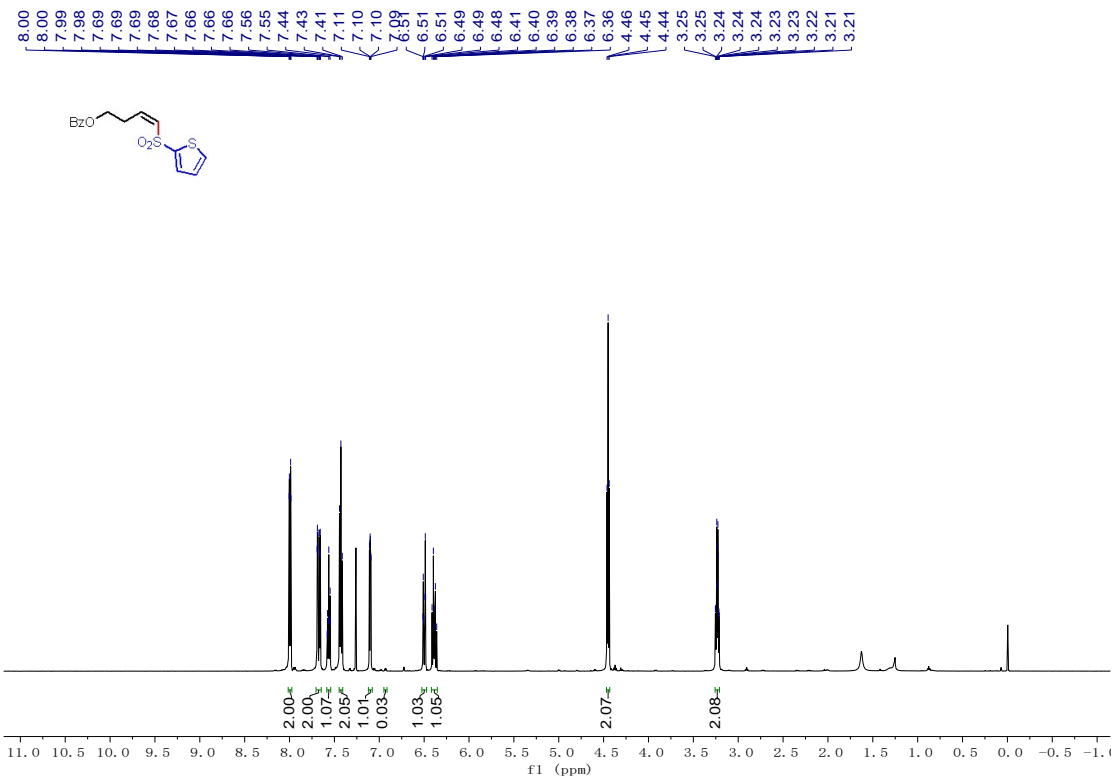
^{19}F NMR spectrum of **4o**



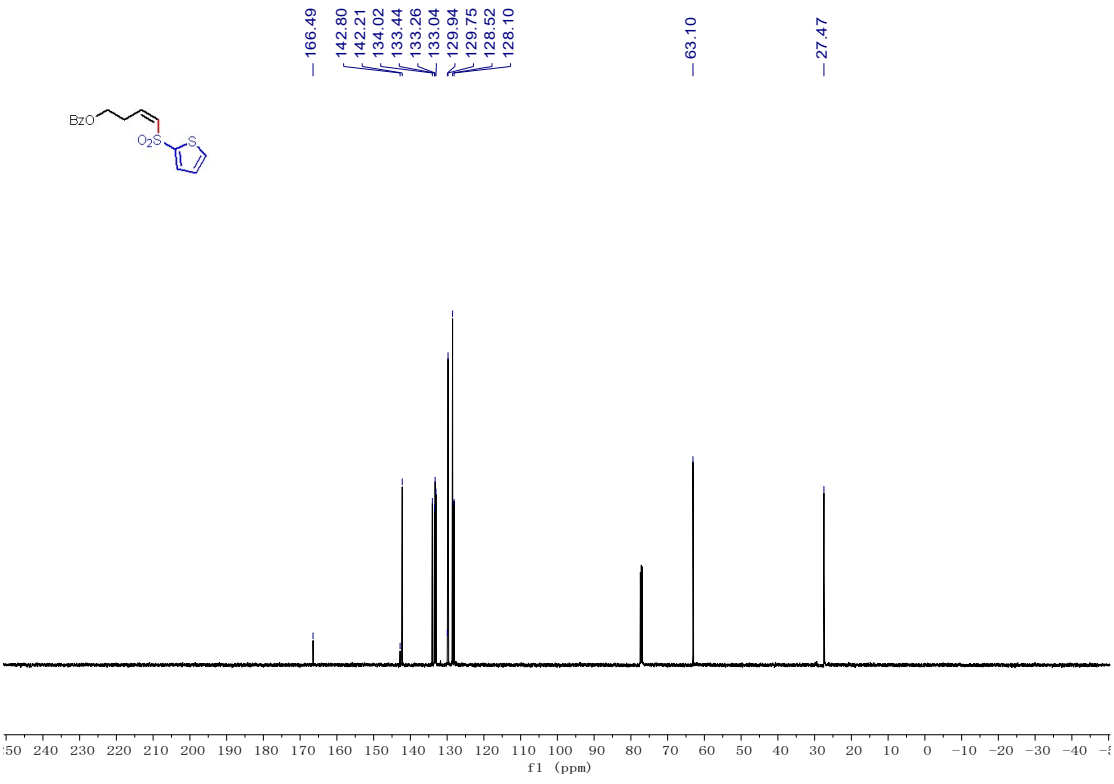
^{1}H NMR spectrum of **4p**



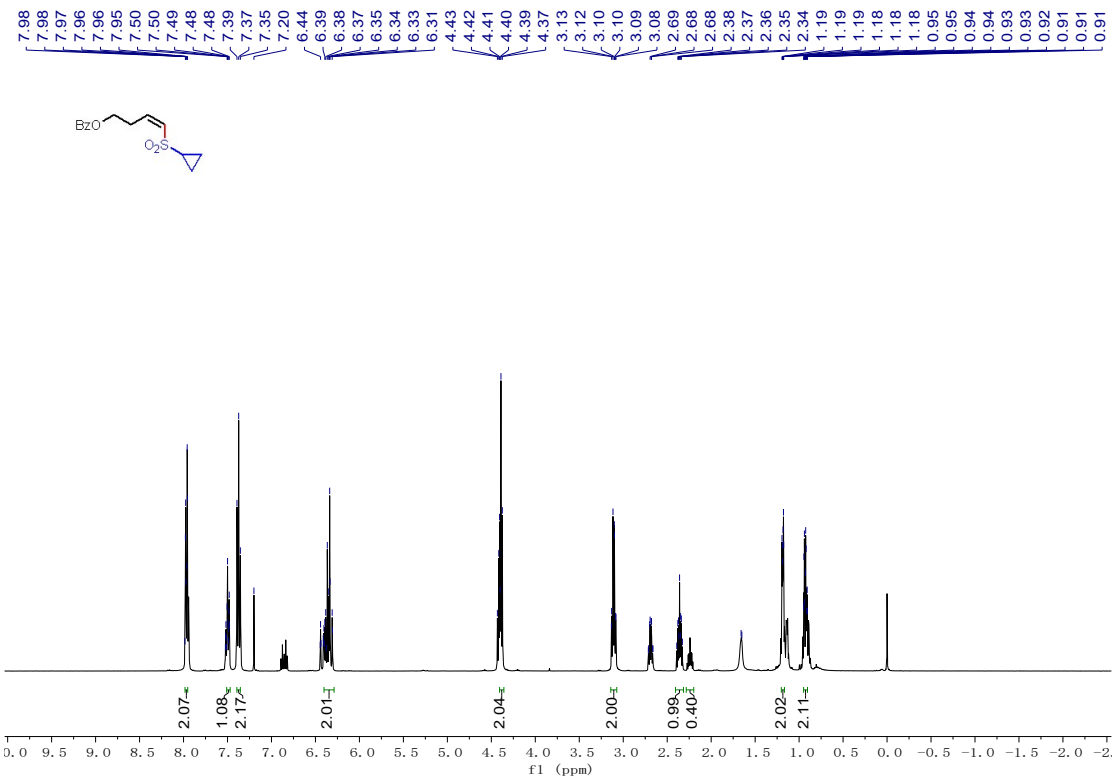
^{13}C NMR spectrum of **4p**



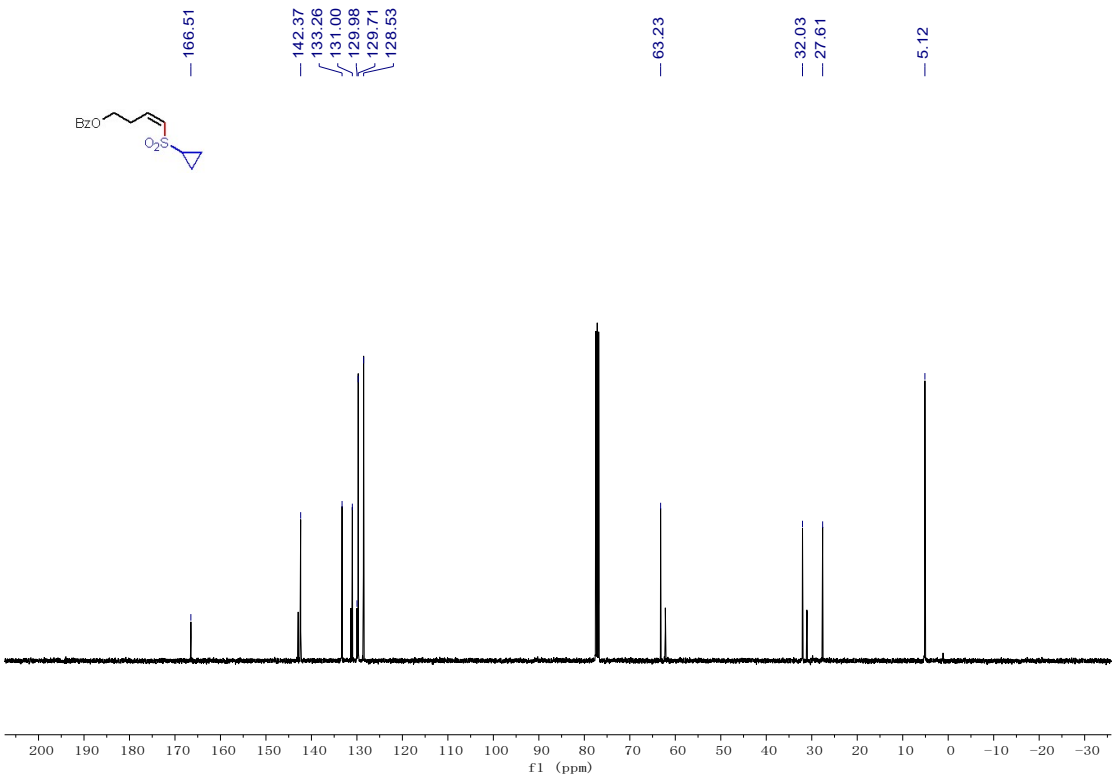
^{1}H NMR spectrum of **4q**



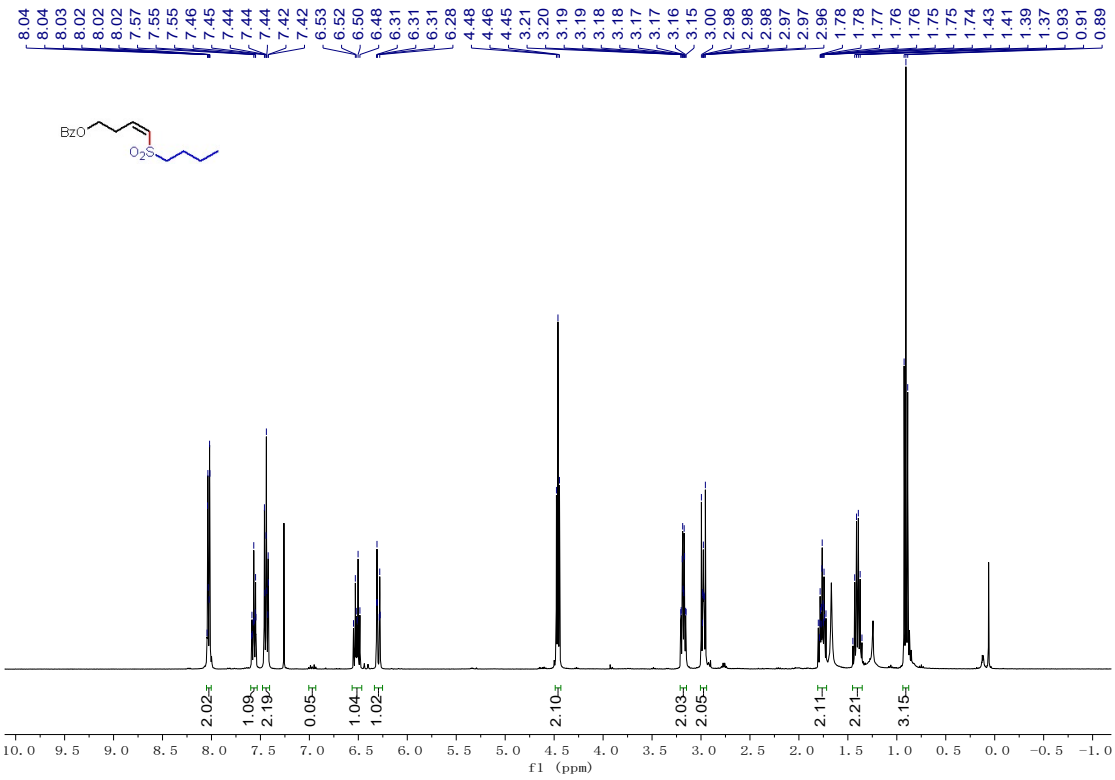
^{13}C NMR spectrum of **4q**



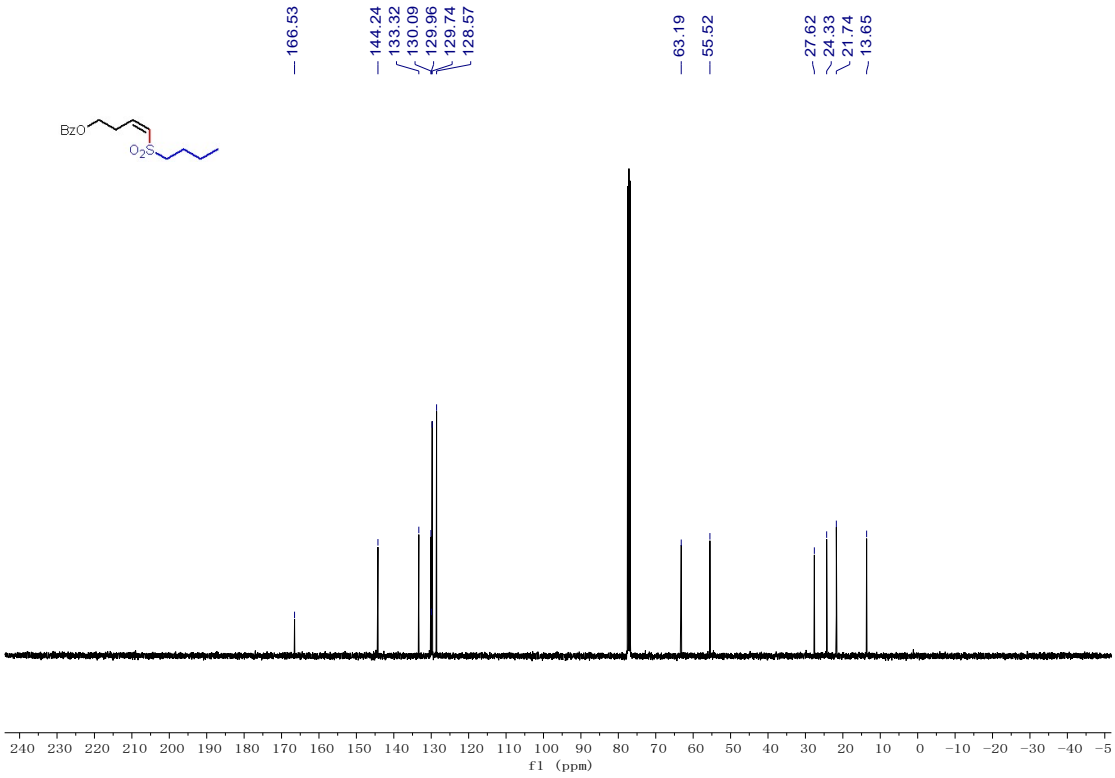
^{1}H NMR spectrum of **4r**



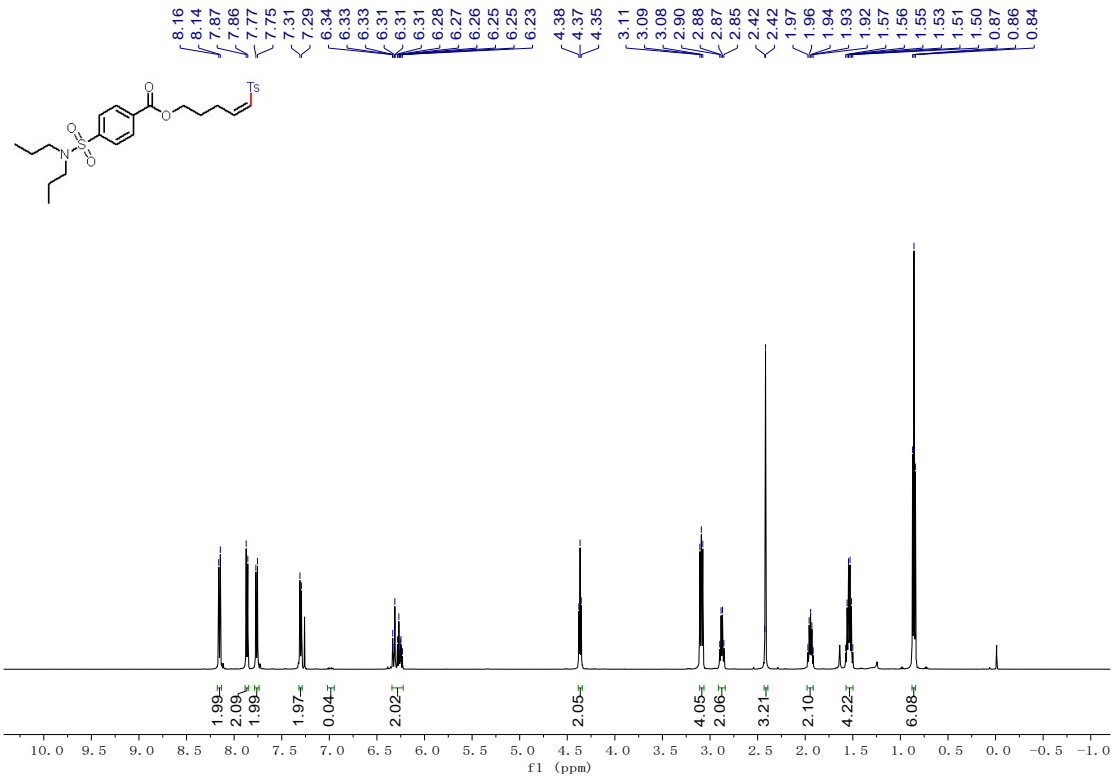
^{13}C NMR spectrum of **4r**



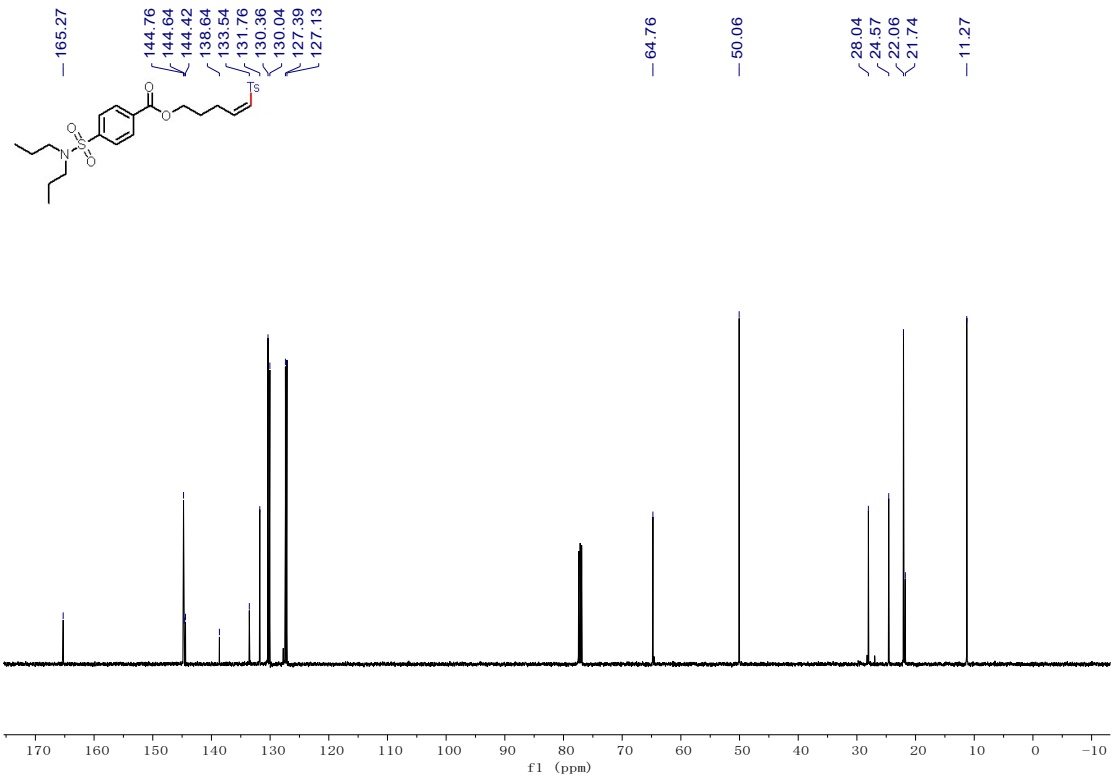
^{1}H NMR spectrum of **4s**



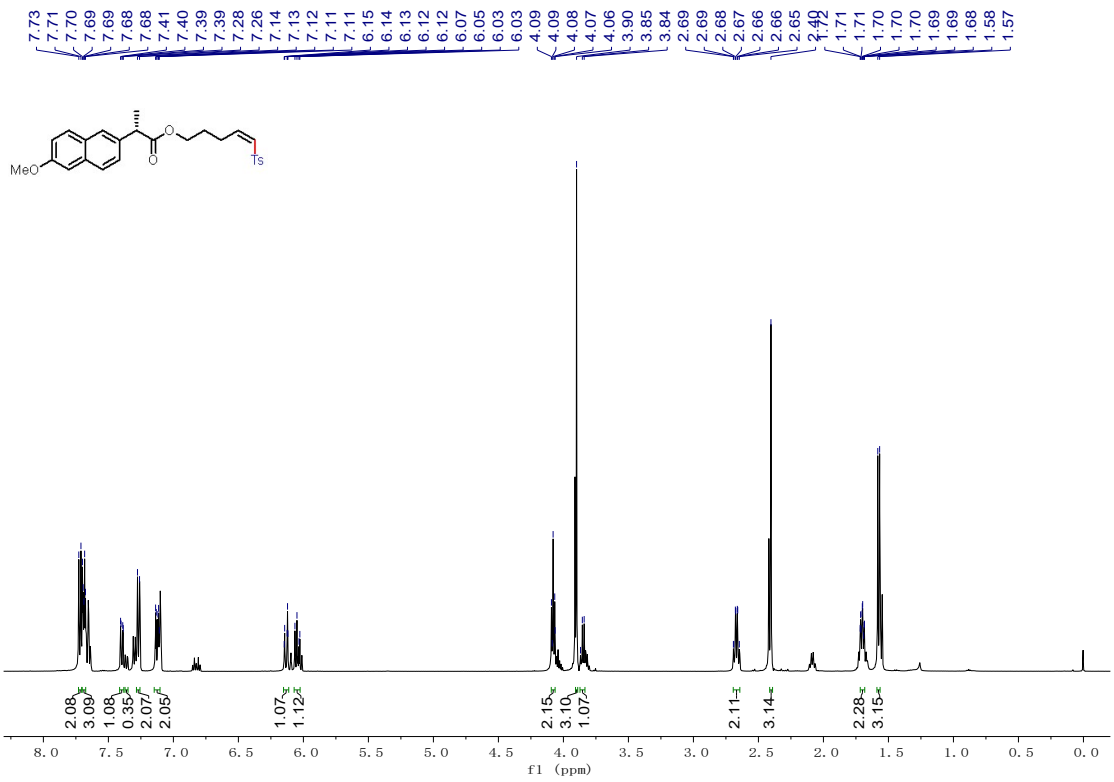
^{13}C NMR spectrum of **4s**



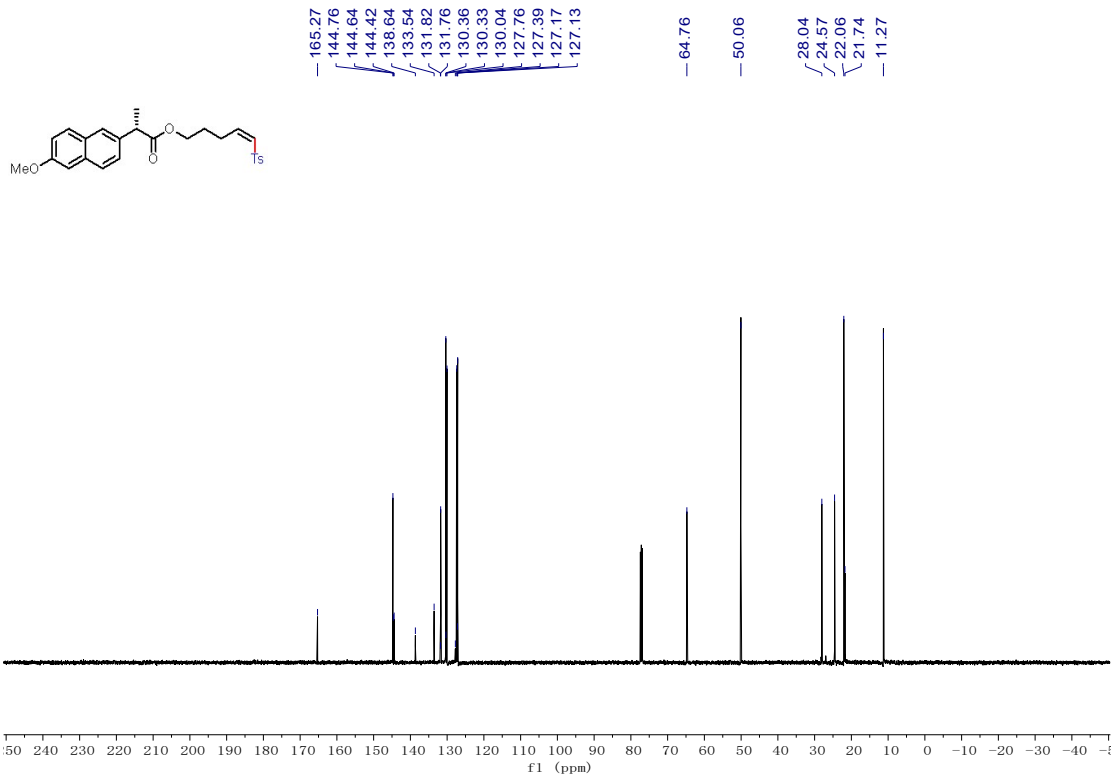
^{1}H NMR spectrum of **5a**



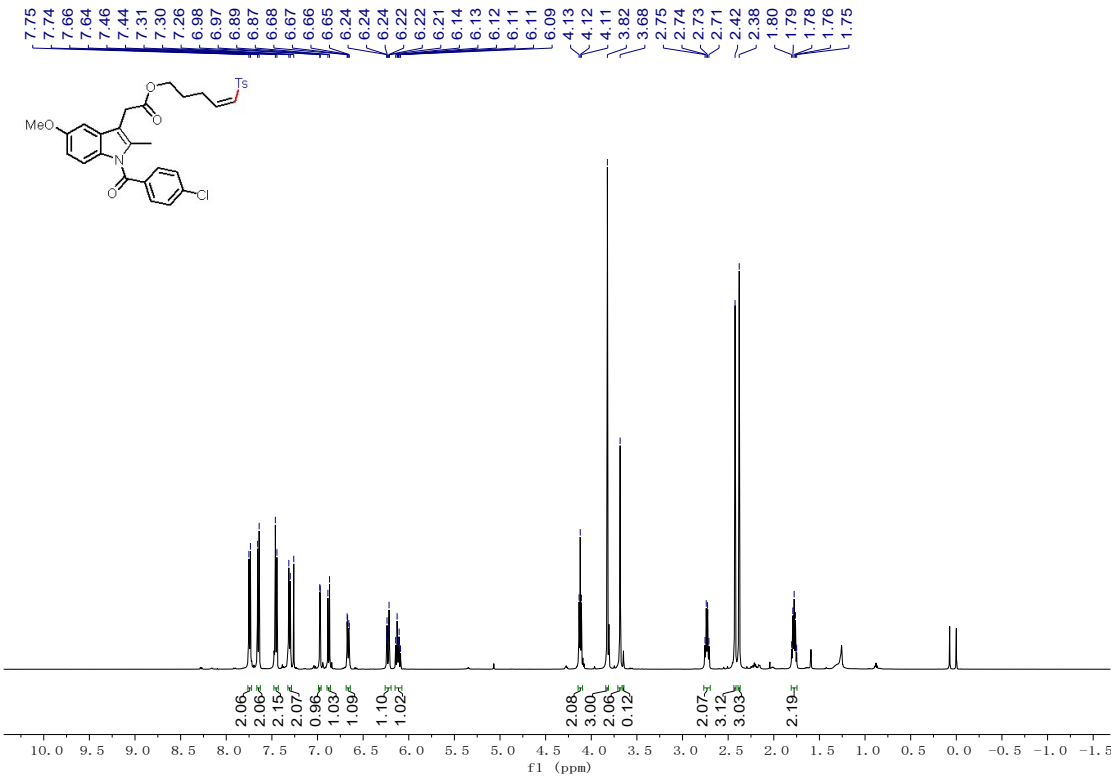
^{13}C NMR spectrum of **5a**



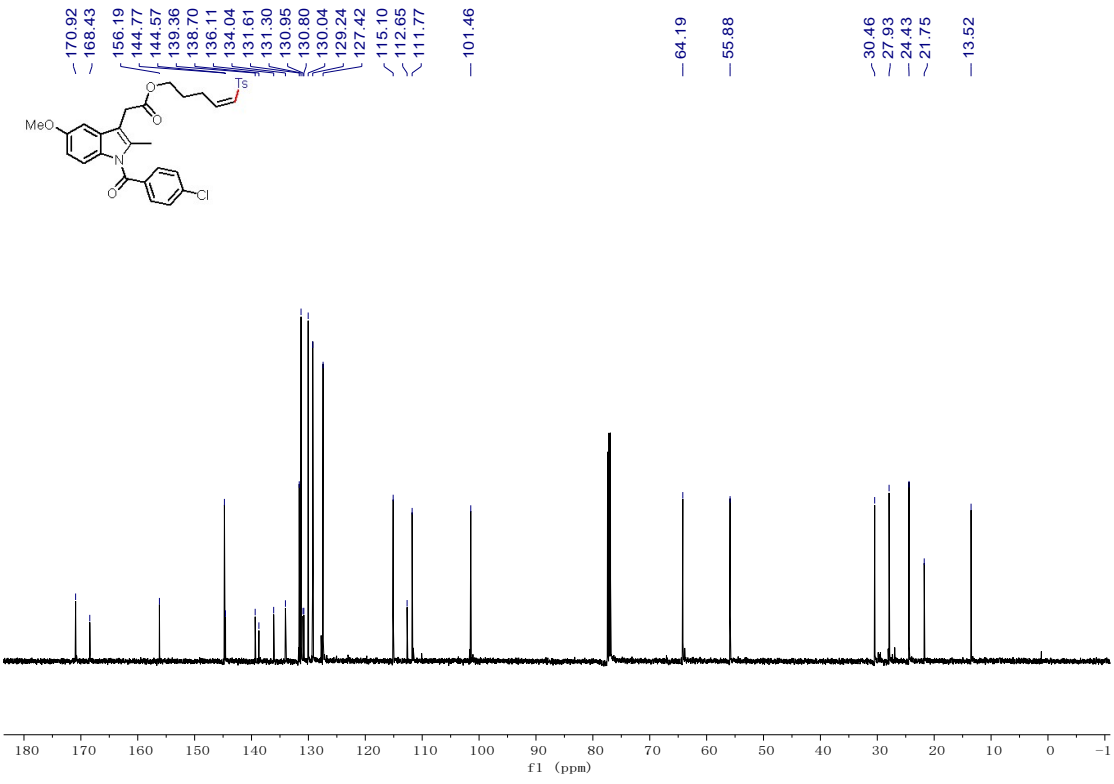
^{1}H NMR spectrum of **5b**



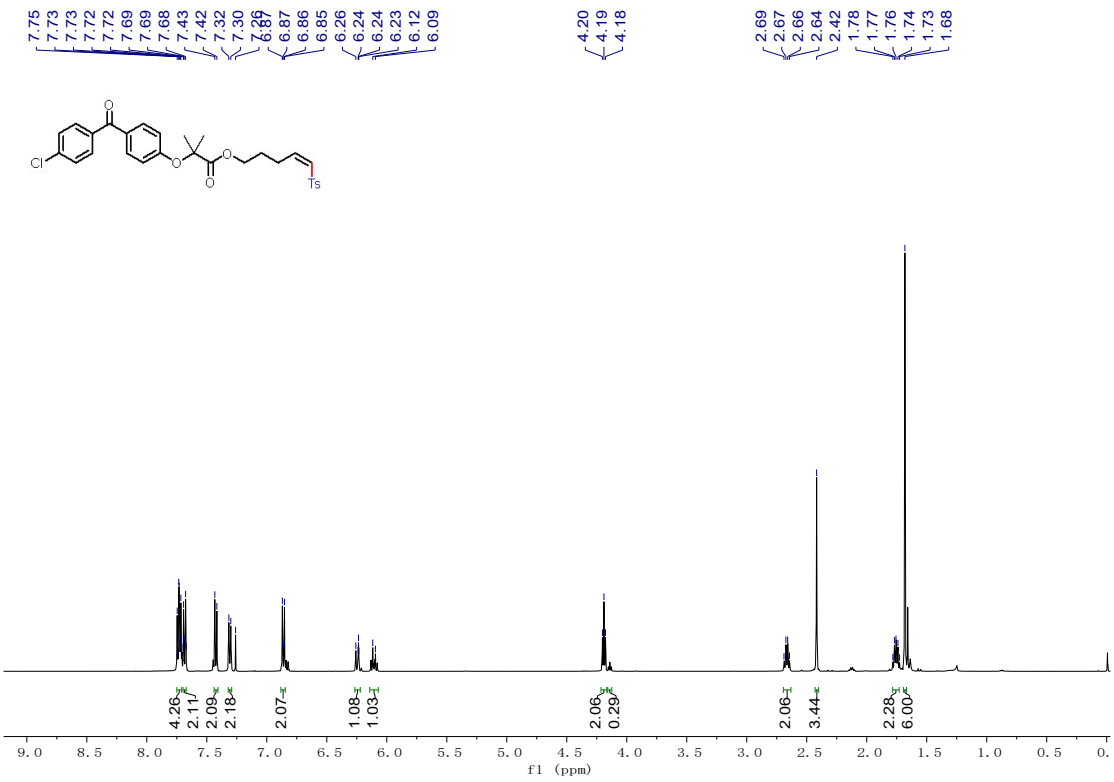
^{13}C NMR spectrum of **5b**



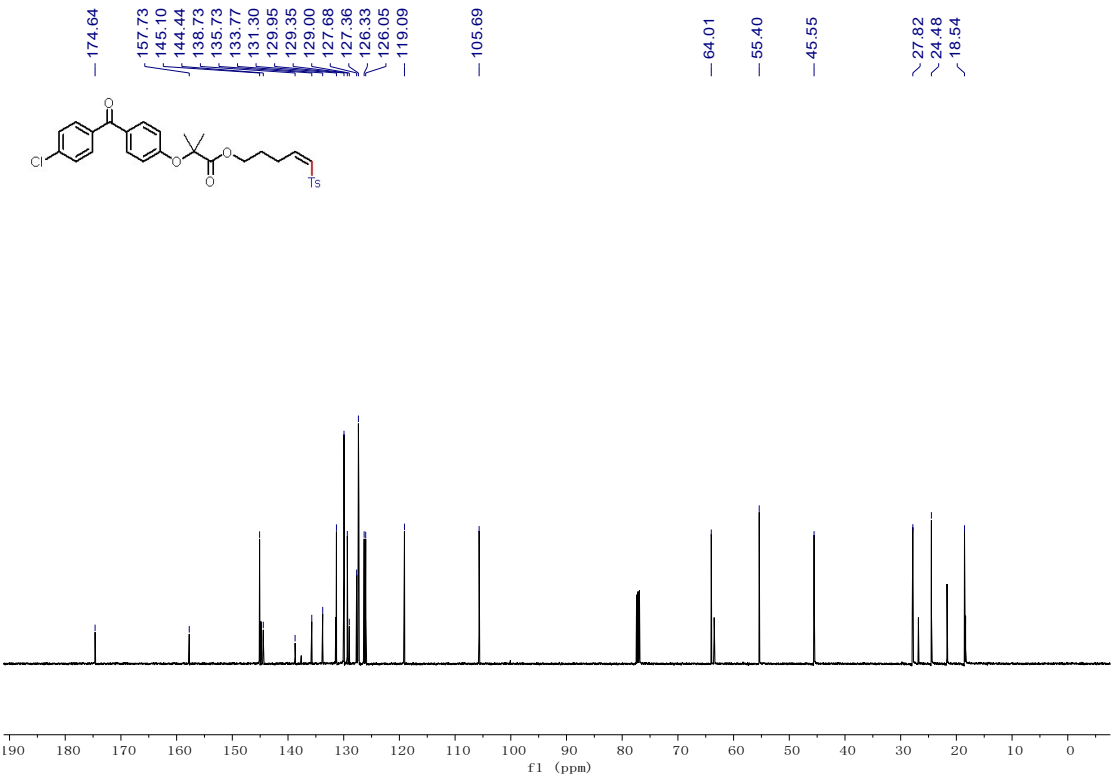
^{1}H NMR spectrum of **5c**



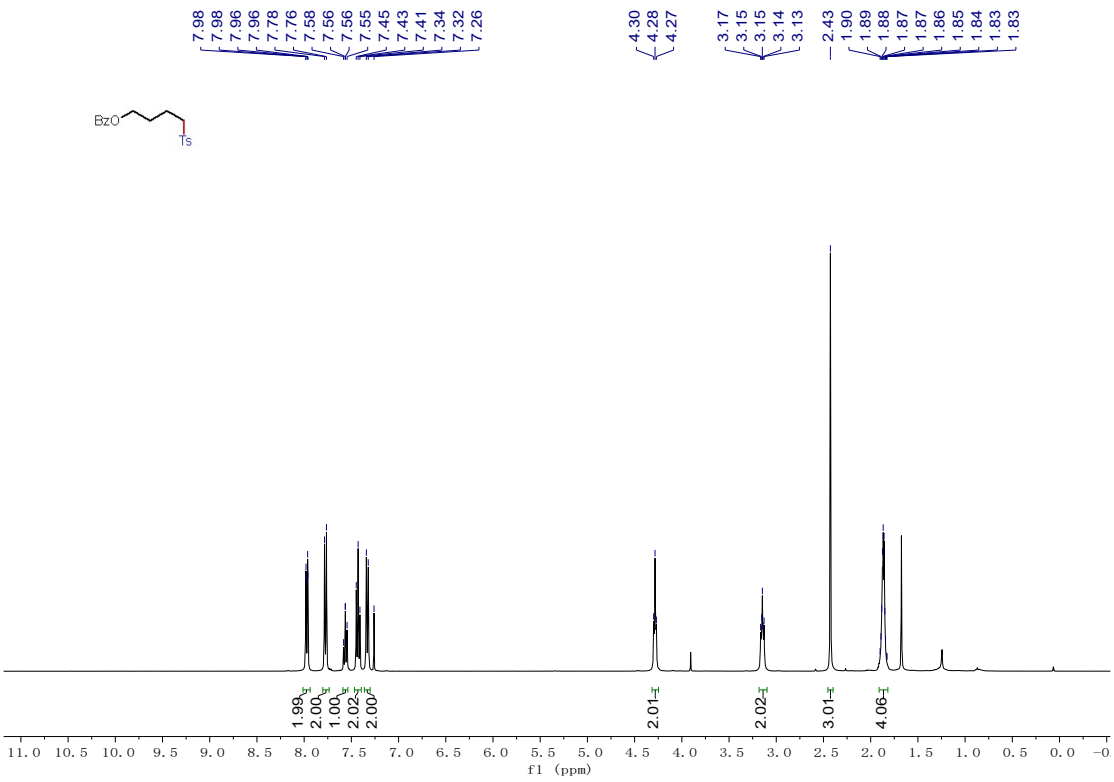
^{13}C NMR spectrum of **5c**



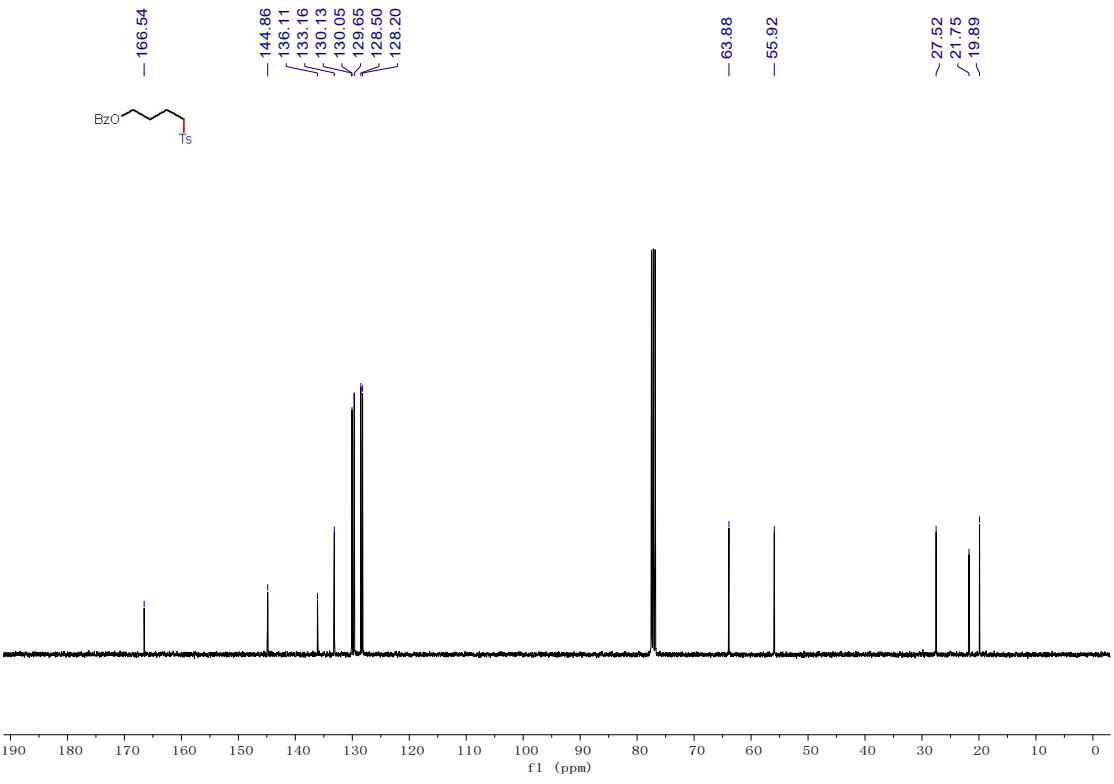
^{1}H NMR spectrum of **5d**



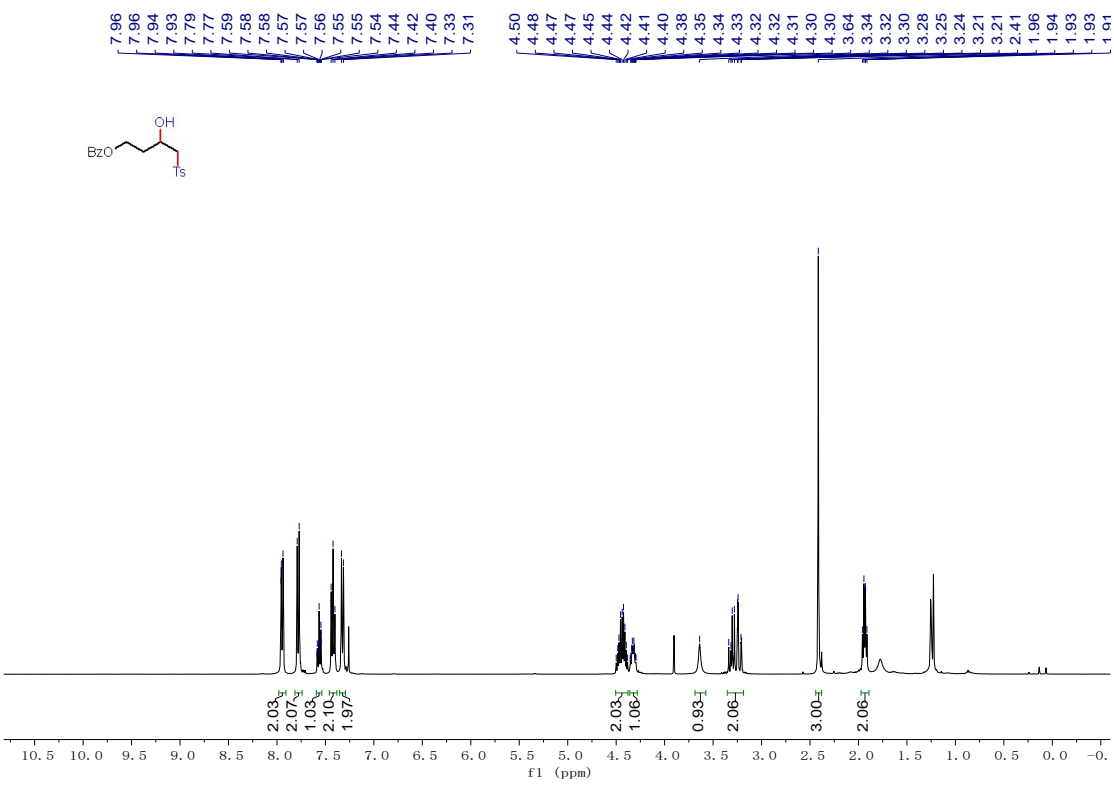
^{13}C NMR spectrum of **5d**



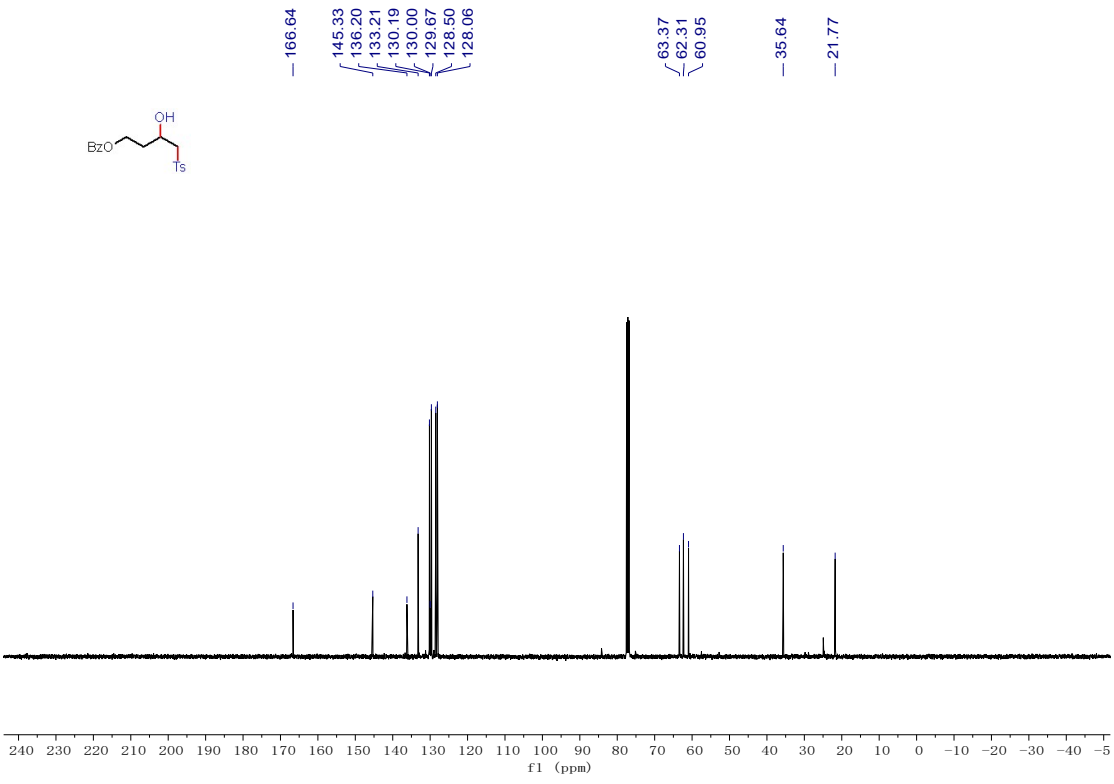
^{1}H NMR spectrum of **6a**



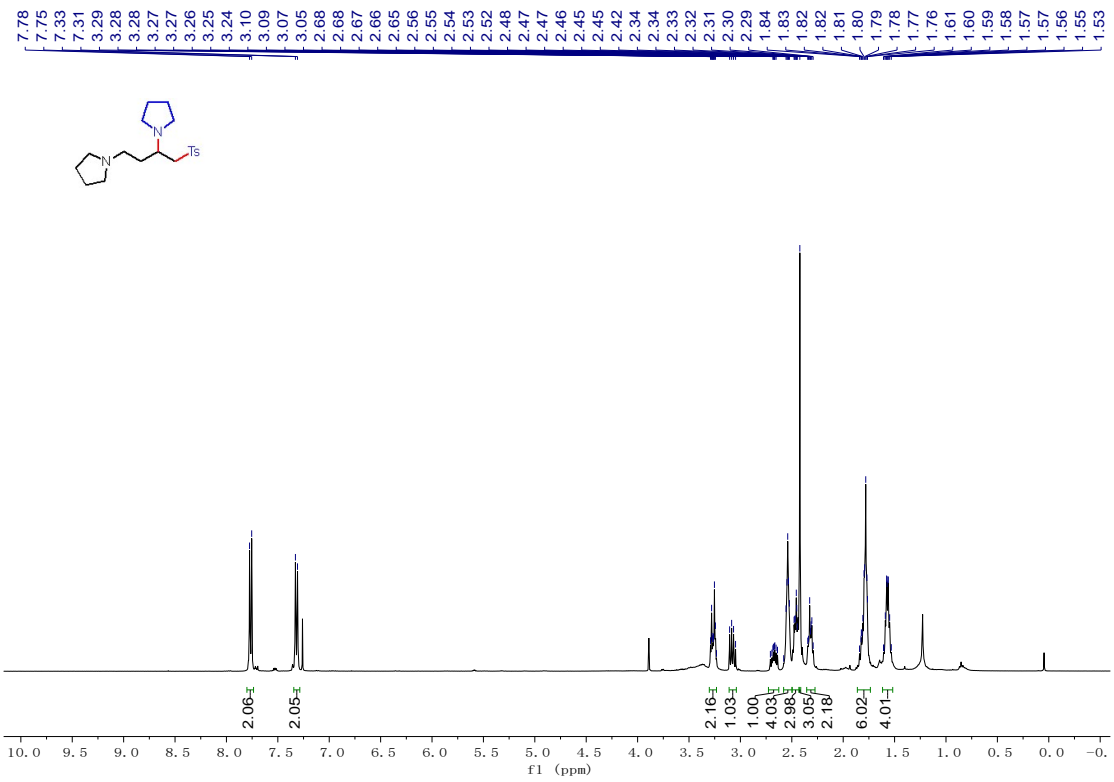
^{13}C NMR spectrum of **6a**



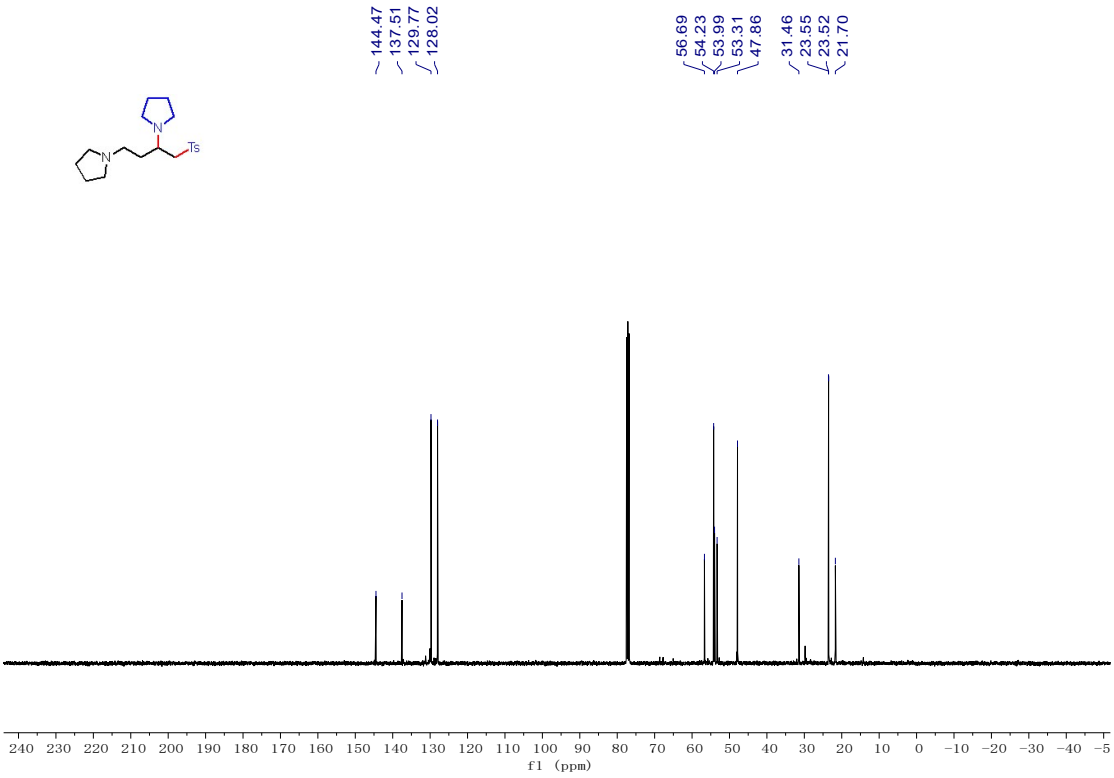
^{1}H NMR spectrum of **6b**



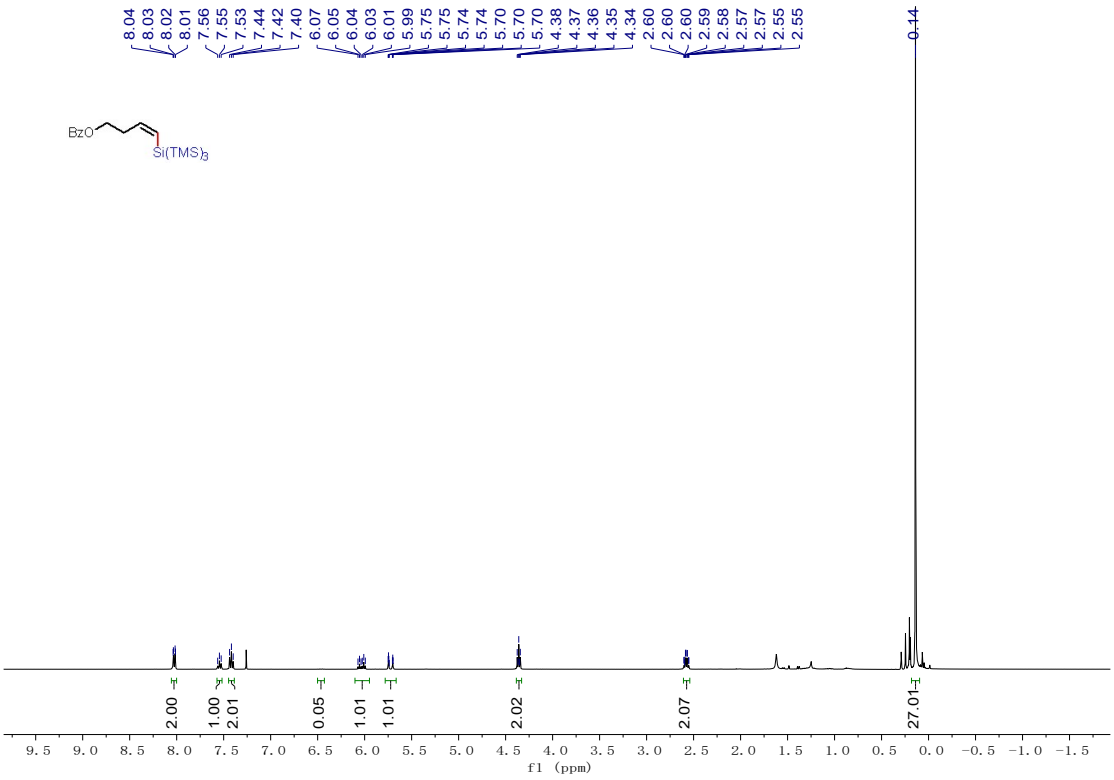
^{13}C NMR spectrum of **6b**



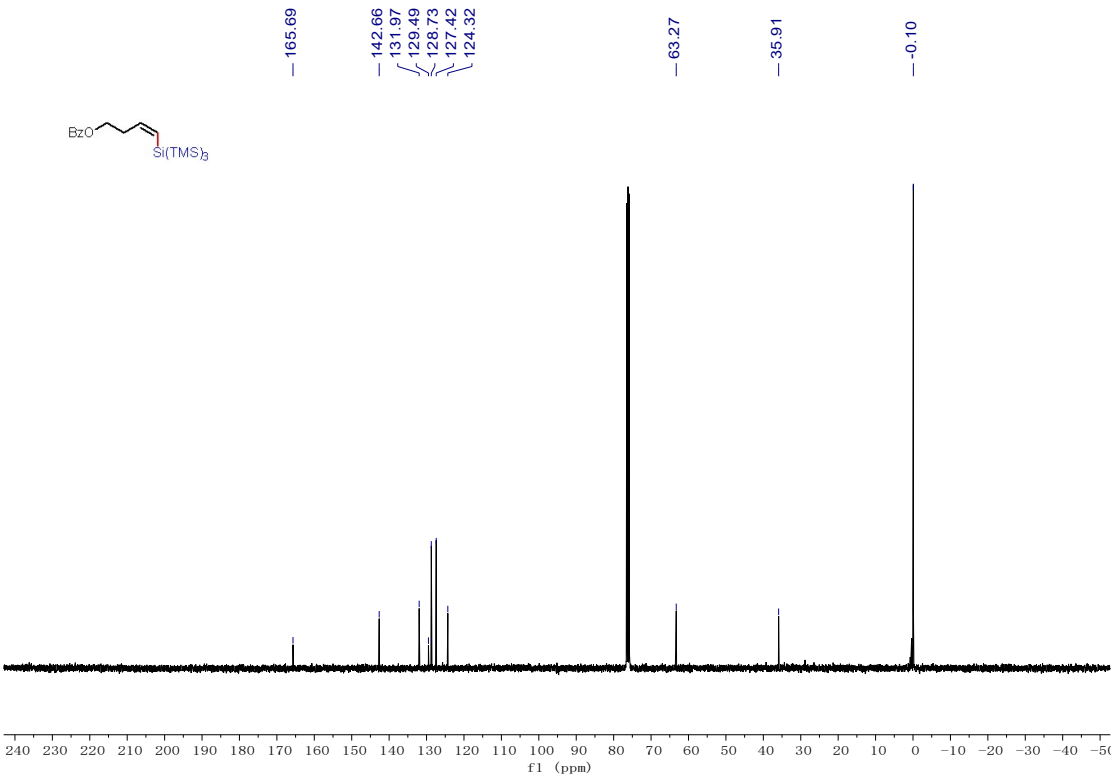
^{1}H NMR spectrum of **6c**



^{13}C NMR spectrum of **6c**



^{1}H NMR spectrum of **6d**



^{13}C NMR spectrum of **6d**