Supporting Information

Formal allylic C(sp^3)−H alkylation of *a*-alkylstyrenes by rearrangement of intermediate alkenyl sulfonium salts

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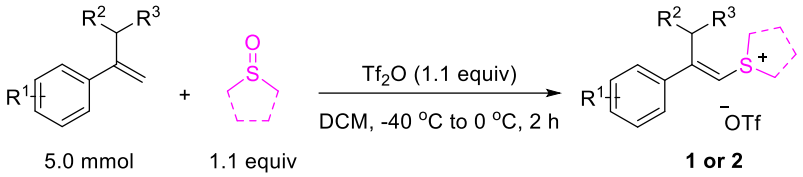
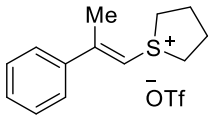
1. General Information

All solvents were dried over molecular sieves. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The products were isolated by column chromatography on silica gel (300-400 mesh) by using petroleum ether (PE, 30-60 ℃) and ethyl acetate (EA) as eluents. Silica gel for column chromatography was purchased from AnhuiLiangchen Chemical Co, Lt. All yields described herein are the isolated yields after column chromatography. Reaction progress and product mixtures were routinely monitored by TLC using TLC SiO_2 sheets, and compounds were visualized under ultraviolet light. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AVANCE III 400 MHz or 500 MHz spectrometer. Chemical shifts are reported in ppm with the residual solvent signal as the internal standard. For ^{1}H NMR: $CDCl_3$, δ 7.26; CD_3OD, δ 3.31. For ^{13}C NMR: $CDCl_3$, δ 77.00; CD_3OD, δ 49.00; Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), brs (broad singlet). High–Resolution Mass Spectra (HRMS) were recorded on Agilent 1290UPLC-QTOF-MS (6546). Melting points were measured with a melting point instrument (Shanghai Yidian Physical Optical Instrument Co., Ltd., SGW, and X-4A) and were uncorrected.

2. Synthesis of Styryl Sulfonium Salts



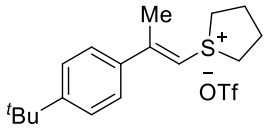
General experimental procedure for the synthesis of styryl sulfonium salts: Under an argon atmosphere, related sulfoxide (1.1 equiv, 5.5 mmol) and anhydrous DCM (20 mL) were added to a 100 mL round bottom flask at -40 °C. The Tf_2O (1.1 equiv, 5.5 mmol) was added dropwise under argon, then styrene derivative (1.0 equiv, 5.0 mmol) was added gradually. The reaction mixture was stirred at -40 °C for 30 min before warming to 0 °C. Upon completion monitored by the TLC, the solvent was removed under reduced pressure. The resulted crude product was dissolved in a small amount of anhydrous DCM, which was slowly dropped into anhydrous ether (20 mL) to precipitate out the styryl sulfonium salts solid. The solid was collected by filtration and washed three times with ether to afford the sulfonium salts (**1** and **2**), or the crude product was purified by column chromatography on silica gel (DCM/MeOH, from 50:1 to 20:1) to afford the sulfonium salts (**1** and **2**).



1a

(*E*)-1-(2-Phenylprop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1a)

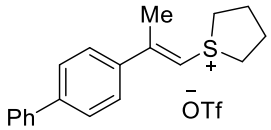
1a was synthesized following the general procedure on 10.0 mmol scale. Styryl sulfonium salt **1a** was obtained by recrystallization as a white solid in 91% yield (3.22 g). **^{1}H NMR** (500 MHz, CD_3OD) δ 7.64 – 7.61 (m, 2H), 7.47 – 7.43 (m, 3H), 6.59 (q, *J* = 1.1 Hz, 1H), 3.84 – 3.77 (m, 2H), 3.55 – 3.50 (m, 2H), 2.54 (d, *J* = 1.1 Hz, 3H), 2.53 – 2.45 (m, 2H), 2.34 – 2.29 (m, 2H). The data is in accordance with the literature [1]



1b

(*E*)-1-(2-(4-(tert-butyl)phenyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1b)

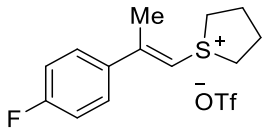
1b was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1b** was obtained by recrystallization as a white solid in 89% yield (1.81 g). M.p. = 125-127 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.60 – 7.56 (m, 2H), 7.51 – 7.48 (m, 2H), 6.58 (q, *J* = 1.2 Hz, 1H), 3.84 – 3.77 (m, 2H), 3.55 – 3.48 (m, 2H), 2.54 (d, *J* = 1.2 Hz, 3H), 2.53 – 2.45 (m, 2H), 2.36 – 2.26 (m, 2H), 1.33 (s, 9H). **^{13}C NMR** (101 MHz, CD_3OD) δ 159.1, 155.3, 136.7, 127.6, 126.9, 111.9, 48.9, 35.7, 31.5, 29.9, 19.2. **^{19}F NMR** (376 MHz, CD_3OD) δ -76.07. **HRMS** m/z (ESI) calcd for $C_{17}H_{25}S$ (M-OTf)$^+$ 261.1671, found 261.1671.



1c

(*E*)-1-(2-([1,1'-Biphenyl]-4-yl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1c)

1c was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1c** was obtained by recrystallization as a white solid in 88% yield (1.89 g). M.p. = 108-110 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.82 (s, 4H), 7.80 – 7.73(m, 2H), 7.53 – 7.49 (m, 2H), 7.44 – 7.40 (m, 1H), 6.86 (d, *J* = 1.3 Hz, 1H), 3.80 – 3.73 (m, 2H), 3.59 – 3.52 (m, 2H), 3.38 (s, 3H), 2.44 – 2.35(m, 2H), 2.26 – 2.17 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 154.1, 141.8, 139.0, 136.9, 129.1, 128.1, 127.4, 126.9, 126.8, 113.2, 47.6, 28.6, 18.6. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -73.00. **HRMS** m/z (ESI) calcd for $C_{19}H_{21}S$ (M-OTf)$^+$ 281.1358, found 281.1358.

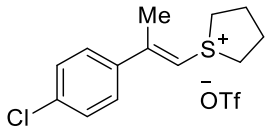


1d

(*E*)-1-(2-(4-Fluorophenyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1d)

1d was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1d** was obtained by recrystallization as a white solid in 85% yield (1.58 g). M.p. = 115-117 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.71 – 7.66 (m, 2H), 7.20 – 7.15 (m, 2H), 6.60 (s, 1H), 3.84 – 3.77 (m, 2H), 3.56 – 3.50 (m, 2H), 2.56 (s, 3H), 2.55 – 2.46 (m, 2H), 2.37 – 2.27 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ 165.4 (d, *J* = 249.8 Hz), 157.9, 135.9, 130.2 (d, *J* = 8.7 Hz), 121.8 (d, *J* = 318.5 Hz), 116.7 (d, *J* = 22.1 Hz), 113.0, 48.9, 29.9, 19.4. **^{19}F NMR** (376 MHz, CD_3OD) δ -76.03,

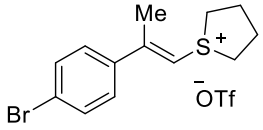
-108.34. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}FS$ $(M\text{-}OTf)^+$ 223.0951, found 223.0950.



1e

(*E*)-1-(2-(4-Chlorophenyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1e)

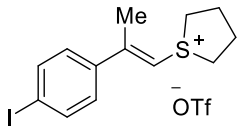
1e was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1e** was obtained by recrystallization as a white solid in 87% yield (1.70 g). M.p. = 107-109 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.65 – 7.62 (m, 2H), 7.46 – 7.43 (m, 2H), 6.64 (q, *J* = 1.2 Hz, 1H), 3.83 – 3.78 (m, 2H), 3.56 – 3.51 (m, 2H), 2.54 (d, *J* = 1.2 Hz, 3H), 2.53 – 2.46 (m, 2H), 2.35 – 2.28 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ 157.7, 138.2, 137.5, 130.0, 129.5, 113.7, 48.8, 29.9, 19.3. **^{19}F NMR** (376 MHz, CD_3OD) δ -79.86. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}ClS$ $(M\text{-}OTf)^+$ 239.0656, found 239.0656.



1f

(*E*)-1-(2-(4-Bromophenyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1f)

1f was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1f** was obtained by recrystallization as a white solid in 86% yield (1.86 g). M.p. = 129-131 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.62 – 7.54 (m, 4H), 6.64 (s, 1H), 3.84 – 3.77 (m, 2H), 3.57 – 3.50 (m, 2H), 2.55 (s, 3H), 2.52 – 2.45 (m, 2H), 2.36 – 2.28 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ 157.8, 138.7, 133.1, 129.6, 125.7, 113.8, 48.8, 29.9, 19.3. **^{19}F NMR** (376 MHz, CD_3OD) δ -76.01. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}BrS$ $(M\text{-}OTf)^+$ 283.0151, found 283.0150.

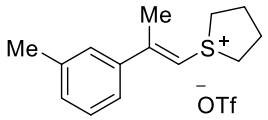


1g

(*E*)-1-(2-(4-Iodophenyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1g)

1g was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1g**

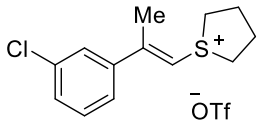
was obtained by recrystallization as a white solid in 82% yield (1.96 g). M.p. = 128-130 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.83 – 7.80 (m, 2H), 7.41– 7.38 (m, 2H), 6.64 (q, *J* = 1.1 Hz, 1H), 3.83 – 3.77 (m, 2H), 2.56 – 2.51 (m, 2H), 2.53 – 2.46 (m, 5H), 2.36 – 2.30 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ 157.9, 139.2, 139.1, 129.6, 113.7, 97.6, 48.8, 29.9, 19.2. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.25. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}IS$ $(M\text{-}OTf)^+$ 331.0012, found 331.0013.



1h

(*E*)-1-(2-(*m*-Tolyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1h)

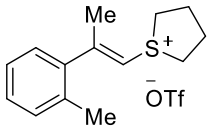
1h was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1h** was obtained by recrystallization as a white solid in 72% yield (1.32 g). M.p. = 109-111 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 4H), 6.49 (d, *J* = 1.3 Hz, 1H), 3.91 – 3.84 (m, 2H), 3.49 – 3.42 (m, 2H), 2.54 – 2.48 (m, 5H), 2.37 – 2.30 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 138.8, 137.5, 131.5, 128.7, 127.2, 123.7, 120.6 (d, *J* = 320.6 Hz, *CF_3*-), 110.4, 48.0, 28.9, 21.2, 19.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.29. **HRMS** m/z (ESI) calcd for $C_{14}H_{16}S$ $(M\text{-}OTf)^+$ 219.1202, found 219.1202.



1i

(*E*)-1-(2-(3-Chlorophenyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1i)

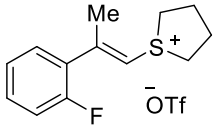
1i was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1i** was obtained by recrystallization as a light-yellow solid in 80% yield (1.55 g). M.p. = 95-97 ℃. **^{1}H NMR** (500 MHz, CD_3OD) δ 7.80 (t, *J* = 1.9 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 6.65 (q, *J* = 1.2 Hz, 1H), 3.84 – 3.78 (m, 2H), 3.58 – 3.53 (m, 2H), 2.52 (d, *J* = 1.2 Hz, 3H), 2.54 – 2.46 (m, 2H), 2.36 – 2.28 (m, 2H). **^{13}C NMR** (126 MHz, CD_3OD) δ 157.6, 141.9, 134.4, 131.7, 130.7, 126.7, 123.8, 114.6, 48.8, 30.0, 19.5. **^{19}F NMR** (471 MHz, CD_3OD) δ -79.94. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}ClS$ $(M\text{-}OTf)^+$ 239.0656, found 239.0656.



1j

(*E*)-1-(2-(o-Tolyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1j)

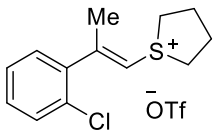
1j was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1j** was obtained by recrystallization as a white solid in 75% yield (1.38 g). M.p. = 99-101 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.29 – 7.17 (m, 4H), 6.25 (q, *J* = 1.3 Hz, 1H), 3.85 – 3.79 (m, 2H), 3.54 – 3.48 (m, 2H), 2.47 – 2.40 (m, 5H), 2.34 – 2.27 (m, 5H). **^{13}C NMR** (101 MHz, CD_3OD) δ 162.1, 141.3, 135.4, 131.7, 130.0, 128.3, 127.1, 115.7, 48.6, 29.9, 22.0, 19.7. **^{19}F NMR** (376 MHz, CD_3OD) δ -79.89. **HRMS** m/z (ESI) calcd for $C_{14}H_{19}S$ $(M\text{-}OTf)^+$ 219.1202, found 219.1204.



1k

(*E*)-1-(2-(2-Fluorophenyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1k)

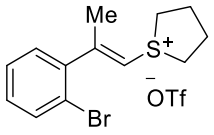
1k was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1k** was obtained by recrystallization as a white solid in 81% yield (1.50 g). M.p. = 115-117 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.52 – 7.44 (m, 2H), 7.28 – 7.17 (m, 2H), 6.54 (q, *J* = 1.3 Hz, 1H), 3.86 – 3.80 (m, 2H), 3.58 – 3.52 (m, 2H), 2.53 (d, *J* = 1.3 Hz, 3H), 2.52 – 2.45 (m, 2H), 2.36 – 2.29 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ 160.7 (d, *J* = 249.4 Hz), 155.3, 133.0 (d, *J* = 8.7 Hz), 130.8 (d, *J* = 2.8 Hz), 128.3 (d, *J* = 12.8 Hz), 125.9 (d, *J* = 3.6 Hz), 117.2 (d, *J* = 30.1 Hz), 117.1 (d, *J* = 3.0 Hz), 48.8, 29.9, 20.6 (d, *J* = 4.0 Hz). **^{19}F NMR** (376 MHz, CD_3OD) δ -76.02, -111.63. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}FS$ $(M\text{-}OTf)^+$ 223.0951, found 223.0951.



1l

(*E*)-1-(2-(2-Chlorophenyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1l)

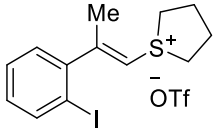
1l was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1l** was obtained by recrystallization as a light-yellow solid in 78% yield (1.51 g). M.p. = 115-117 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.49 – 7.47 (m, 1H), 7.42 – 7.36 (m, 3H), 6.42 (q, *J* = 1.3 Hz, 1H), 3.87 – 3.81 (m, 2H), 3.57 – 3.52 (m, 2H), 2.48 (d, *J* = 1.3 Hz, 3H), 2.47 – 2.41 (m, 2H), 2.36 – 2.29 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ 158.9, 140.1, 132.2, 131.8, 131.1, 130.5, 128.6, 117.9, 48.7, 30.0, 21.3. **^{19}F NMR** (376 MHz, CD_3OD) δ -76.11. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}ClS$ $(M\text{-}OTf)^+$ 239.0656, found 239.0656.



1m

(*E*)-1-(2-(2-Bromophenyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1m)

1m was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1m** was obtained by recrystallization as a white solid in 79% yield (1.71 g). M.p. = 175-176 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.36 – 7.30 (m, 2H), 6.40 (d, *J* = 1.4 Hz, 1H), 3.87 – 3.80 (m, 2H), 3.58 – 3.52 (m, 2H), 2.50 – 2.40 (m, 5H), 2.38 – 2.28 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ 160.2, 142.1, 134.3, 131.8, 130.3, 129.1, 121.3, 117.8, 48.6, 30.0, 21.6. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.30. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}BrS$ $(M\text{-}OTf)^+$ 283.0151, found 283.0151.

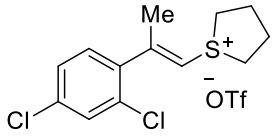


1n

(*E*)-1-(2-(2-Iodophenyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1n)

1n was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1n** was obtained through column chromatography on silica gel (DCM/MeOH, from 50:1 to 20/1) as a colorless oil in 75% yield (1.80 g). **^{1}H NMR** (400 MHz, CD_3OD) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.46 (td, *J* = 7.5, 1.1 Hz, 1H), 7.32 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H), 6.35 (d, *J* = 1.5 Hz, 1H), 3.86 – 3.80 (m, 2H), 3.62 – 3.56 (m, 2H), 2.49 – 2.42 (m, 5H), 2.42 – 2.31 (m, 2H). **^{13}C**

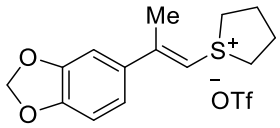
NMR (101 MHz, CD_3OD) δ 162.9, 145.9, 140.8, 131.6, 129.8, 129.0, 117.8, 95.8, 48.3, 30.0, 22.1. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.40. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}IS$ $(M\text{-}OTf)^+$ 331.0012, found 331.0012.



1o

(*E*)-1-(2-(2,4-Dichlorophenyl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1o)

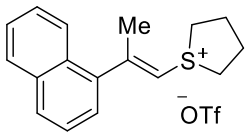
1o was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1o** was obtained by recrystallization as a white solid in 78% yield (1.68 g). M.p. = 179–181 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.59 – 7.56 (m, 1H), 7.43 – 7.37 (m, 2H), 6.46 (s, 1H), 3.87 – 3.81 (m, 2H), 3.58 – 3.52 (m, 2H), 2.46 (s, 3H), 2.48 – 2.41 (m, 2H), 2.37 – 2.28 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ 157.6, 138.8, 136.8, 133.2, 131.8, 130.8, 128.8, 118.5, 48.7, 30.0, 21.2. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.31. HRMS m/z (ESI) calcd for $C_{13}H_{15}Cl_2S$ $(M\text{-}OTf)^+$ 273.0266, found 273.0267.



1p

(*E*)-1-(2-(Benzo[d][1,3]dioxol-5-yl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1p)

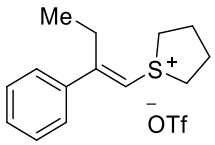
1p was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1p** was obtained by recrystallization as a white solid in 81% yield (1.61 g). M.p. = 125–127 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.40 (s, 1H), 6.00 (s, 2H), 3.94 – 3.89 (m, 2H), 3.49 – 3.44 (m, 2H), 2.57 – 2.51 (m, 2H), 2.47 (s, 3H), 2.42 – 2.34 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.1, 150.1, 148.4, 131.5, 121.7, 108.9, 108.5, 106.7, 101.8, 48.3, 29.0, 19.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.27. **HRMS** m/z (ESI) calcd for $C_{14}H_{17}O_2S$ $(M\text{-}OTf)^+$ 249.0944, found 249.0943.



1q

(*E*)-1-(2-(Naphthalen-1-yl)prop-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1q)

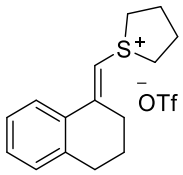
1q was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1q** was obtained by recrystallization as a light-yellow solid in 77% yield (1.56 g). M.p. = 85–87 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.92 – 7.89 (m, 3H), 7.59 – 7.48 (m, 3H), 7.44 – 7.40 (m, 1H), 6.44 (d, *J* = 1.3 Hz, 1H), 3.89 – 3.82 (m, 2H), 3.61 – 3.52 (m, 2H), 2.58 (d, *J* = 1.3 Hz, 3H), 2.46 – 2.36 (m, 2H), 2.34 – 2.28 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ 161.2, 139.4, 135.1, 131.0, 130.5, 129.7, 128.1, 127.5, 126.3, 126.1, 125.7, 121.8 (d, *J* = 318.7 Hz, *CF_3*-), 116.7, 48.7, 29.9, 22.7. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.22. **HRMS** m/z (ESI) calcd for $C_{17}H_{19}S$ $(M\text{-}OTf)^+$ 255.1202, found 255.1202.



1r

(*E*)-1-(2-Phenylbut-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1r)

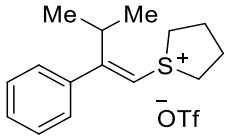
1r was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1r** was obtained by recrystallization as a light-yellow solid in 78% yield (1.43 g). M.p. = 91–93 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.59 – 7.55 (m, 2H), 7.52 – 7.44 (m, 3H), 6.47 (s, 1H), 3.86 – 3.80 (m, 2H), 3.56 – 3.50 (m, 2H), 3.03 (q, *J* = 7.5 Hz, 2H), 2.55 – 2.44 (m, 2H), 2.36 – 2.26 (m, 2H), 1.10 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, CD_3OD) δ 165.6, 138.5, 131.4, 130.0, 128.2, 112.4, 49.1, 30.0, 27.0, 13.6. **^{19}F NMR** (376 MHz, CD_3OD) δ -79.93. **HRMS** m/z (ESI) calcd for $C_{14}H_{19}S$ $(M\text{-}OTf)^+$ 219.1202, found 219.1204.



1s

(*E*)-1-((3,4-Dihydronaphthalen-1(2H)-ylidene)methyl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (1s)

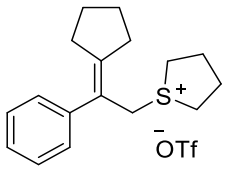
1s was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1s** was obtained by recrystallization as a white solid in 62% yield (1.17 g). M.p. = 119–121 ℃. **^{1}H NMR** (500 MHz, CD_3OD) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.22 (m, 2H), 6.77 (s, 1H), 3.83 – 3.77 (m, 2H), 3.54 – 3.48 (m, 2H), 2.99 – 2.96 (m, 2H), 2.90 (t, *J* = 6.2 Hz, 2H), 2.56 – 2.49 (m, 2H), 2.35 – 2.28 (m, 2H), 1.99 – 1.94 (m, 2H). **^{13}C NMR** (126 MHz, CD_3OD) δ 157.9, 141.3, 132.5, 132.2, 130.6, 127.8, 126.8, 108.7, 48.8, 30.7, 30.5, 29.9, 23.8. **^{19}F NMR** (471 MHz, CD_3OD) δ -79.90. **HRMS** m/z (ESI) calcd for $C_{15}H_{19}S$ $(M\text{-}OTf)^+$ 231.1202, found 231.1202.



1t

(*E*)-1-(3-Methyl-2-phenylbut-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1t)

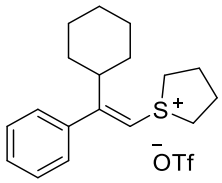
1t was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1t** was obtained by recrystallization as a white solid in 85% yield (1.62 g). M.p. = 109–111 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.54 – 7.48 (m, 3H), 7.30 – 7.28 (m, 2H), 6.41 (d, *J* = 1.3 Hz, 1H), 3.63 – 3.47 (m, 4H), 2.95 – 2.88 (m, 1H), 2.50 – 2.42 (m, 2H), 2.27 – 2.18 (m, 2H), 1.15 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, CD_3OD) δ 172.1, 137.9, 130.5, 130.0, 129.2, 113.9, 48.9, 38.8, 30.0, 21.0. **^{19}F NMR** (376 MHz, CD_3OD) δ -76.00. **HRMS** m/z (ESI) calcd for $C_{15}H_{21}S$ $(M\text{-}OTf)^+$ 233.1358, found 233.1358.



1u'

1-(2-Cyclopentylidene-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1u')

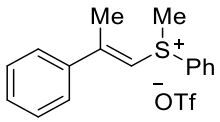
1u' was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1u'** was obtained by recrystallization as a white solid in 75% yield (1.52 g). M.p. = 93–95 ℃. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.44 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.33 (m, 3H), 4.40 (s, 2H), 3.47 – 3.40 (m, 2H), 3.34 – 3.28 (m, 2H), 2.61 – 2.57 (m, 2H), 2.40 – 2.31 (m, 4H), 2.31 – 2.20 (m, 2H), 1.89 – 1.82 (m, 2H), 1.72 – 1.65 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ 155.5, 140.5, 130.0, 129.7, 129.0, 121.7, 48.5, 43.3, 34.3, 32.7, 29.6, 27.5, 27.2. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.31. **HRMS** m/z (ESI) calcd for $C_{17}H_{23}S$ $(M\text{-}OTf)^+$ 259.1515, found 259.1515.



1v

(*E*)-1-(3-Methyl-2-phenylbut-1-en-1-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1v)

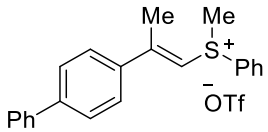
1v was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **1v** was obtained by recrystallization as a white solid in 82% yield (1.73 g). M.p. = 178–180 ℃. **^{1}H NMR** (500 MHz, CD_3OD) δ 7.52 – 7.44 (m, 3H), 7.28 – 7.26 (m, 2H), 6.38 (d, *J* = 1.2 Hz, 1H), 3.60 – 3.53 (m, 2H), 3.52 – 3.46 (m, 2H), 2.58 – 2.53 (m, 1H), 2.49 – 2.42 (m, 2H), 2.26 – 2.19 (m, 2H), 1.88 – 1.79 (m, 4H), 1.72 – 1.67 (m, 1H), 1.38 – 1.17 (m, 5H). **^{13}C NMR** (126 MHz, CD_3OD) δ 171.3, 138.1, 130.4, 130.0, 129.1, 114.1, 49.0, 48.5, 32.2, 30.0, 27.2, 26.9. **^{19}F NMR** (471 MHz, CD_3OD) δ -81.24. **HRMS** m/z (ESI) calcd for $C_{18}H_{25}S$ $(M\text{-}OTf)^+$ 273.1671, found 273.1671.



2a

(*E*)-Methyl(phenyl)(2-phenylprop-1-en-1-yl)sulfonium trifluoromethanesulfonate (2a)

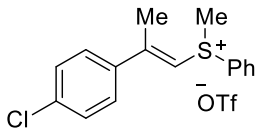
2a was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2a** was obtained through column chromatography on silica gel (DCM/MeOH, from 50:1 to 20/1) as a yellow oil in 76% yield (1.48 g). **^{1}H NMR** (500 MHz, CD_3OD) δ 8.06 – 8.03 (m, 2H), 7.77 – 7.68 (m, 3H), 7.67 – 7.62 (m, 2H), 7.48 – 7.40 (m, 3H), 6.99 (q, *J* = 1.1 Hz, 1H), 3.47 (s, 3H), 2.56 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (126 MHz, CD_3OD) δ 160.9, 139.1, 135.1, 132.3, 131.9, 130.3, 130.0, 129.1, 127.8, 112.4, 30.1, 19.6. **^{19}F NMR** (376 MHz, CD_3OD) δ -79.74. **HRMS** m/z (ESI) calcd for $C_{16}H_{17}S$ $(M\text{-}OTf)^+$ 241.1045, found 241.1046.



2b

(*E*)-(2-([1,1'-Biphenyl]-4-yl)prop-1-en-1-yl)(methyl)(phenyl)sulfonium trifluoromethanesulfonate (2b)

2b was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2b** was obtained through column chromatography on silica gel (DCM/MeOH, from 50:1 to 20/1) as a yellow oil in 79% yield (1.84 g). **^{1}H NMR** (500 MHz, CD_3OD) δ 8.03 – 8.01 (m, 2H), 7.74 – 7.66 (m, 5H), 7.65 – 7.61 (m, 2H), 7.57 – 7.55 (m, 2H), 7.41 – 7.37 (m, 2H), 7.32 – 7.29 (m, 1H), 7.01 (q, *J* = 1.1 Hz, 1H), 3.43 (s, 3H), 2.51 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (126 MHz, CD_3OD) δ 160.1, 144.6, 140.7, 137.6, 135.1, 132.3, 130.3, 130.0, 129.1, 129.0, 128.4, 128.2, 127.9, 111.9, 30.2, 19.4. **^{19}F NMR** (471 MHz, CD_3OD) δ -79.49. **HRMS** m/z (ESI) calcd for $C_{22}H_{21}S$ $(M\text{-}OTf)^+$ 317.1358, found 317.1358.

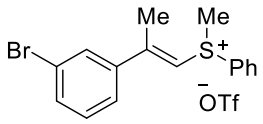


2c

(*E*)-(2-(4-Chlorophenyl)prop-1-en-1-yl)(methyl)(phenyl)sulfonium trifluoromethanesulfonate (2c)

2c was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2c** was obtained through column chromatography on silica gel (DCM/MeOH, from 50:1 to 20/1) as a yellow oil in 78% yield (1.65 g). **^{1}H NMR** (400 MHz, CD_3OD) δ 8.08 – 8.06 (m, 2H), 7.78 – 7.70 (m, 3H), 7.67 – 7.62 (m, 2H), 7.39 – 7.36 (m, 2H), 7.06 (q, *J* = 1.2 Hz, 1H), 3.50 (s, 3H), 2.55 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (101 MHz, CD_3OD) δ 159.2, 137.7, 137.5, 135.1, 132.3, 130.4, 130.0,

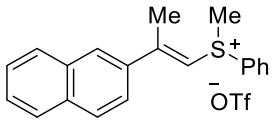
129.5, 128.8, 113.1, 30.1, 19.5. **^{19}F NMR** (376 MHz, CD_3OD) δ -79.38. **HRMS** m/z (ESI) calcd for $C_{16}H_{16}ClS$ $(M\text{-}OTf)^+$ 275.0656, found 275.0656.



2d

(*E*)-(2-(3-Bromophenyl)prop-1-en-1-yl)(methyl)(phenyl)sulfonium trifluoromethanesulfonate (2d)

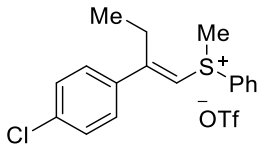
2d was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2d** was obtained through column chromatography on silica gel (DCM/MeOH, from 50:1 to 20/1) as a yellow oil in 74% yield (1.73 g). **^{1}H NMR** (400 MHz, CD_3OD) δ 8.06 – 8.03 (m, 2H), 7.82 – 7.71 (m, 4H), 7.63 – 7.61 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 3.50 (s, 3H), 2.56 (s, 3H). **^{13}C NMR** (101 MHz, CD_3OD) δ 159.3, 141.4, 135.5, 134.7, 132.4, 131.8, 130.7, 130.5, 128.9, 126.7, 123.9, 114.3, 30.0, 19.7. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.43. **HRMS** m/z (ESI) calcd for $C_{16}H_{16}BrS$ $(M\text{-}OTf)^+$ 319.0151, found 319.0151.



2e

(*E*)-Methyl(2-(naphthalen-2-yl)prop-1-en-1-yl)(phenyl)sulfonium trifluoromethanesulfonate (2e)

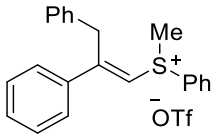
2e was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2e** was obtained through column chromatography on silica gel (DCM/MeOH, from 50:1 to 20/1) as a light-yellow oil in 79% yield (1.73 g). **^{1}H NMR** (400 MHz, CD_3OD) δ 8.16 (d, *J* = 2.0 Hz, 1H), 8.07 – 8.05 (m, 2H), 7.96 – 7.94 (m, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.86 – 7.84 (m, 1H), 7.80 – 7.70 (m, 4H), 7.57 – 7.49 (m, 2H), 7.13 (q, *J* = 1.1 Hz, 1H), 3.50 (s, 3H), 2.66 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, CD_3OD) δ 160.7, 136.2, 135.7, 135.2, 134.4, 132.4, 130.4, 130.0, 129.8, 129.3, 128.9, 128.7, 128.4, 128.0, 124.4, 112.7, 30.2, 19.6. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.21. **HRMS** m/z (ESI) calcd for $C_{20}H_{19}S$ $(M\text{-}OTf)^+$ 291.1202, found 291.1202.



2f

(*E*)-(2-(4-Chlorophenyl)but-1-en-1-yl)(methyl)(phenyl)sulfonium trifluoromethanesulfonate (2f)

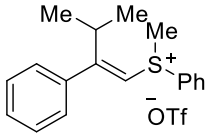
2f was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2f** was obtained through column chromatography on silica gel (DCM/MeOH, from 50:1 to 20:1) as a white solid in 77% yield (1.70 g). M.p. = 85-87 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 8.09 – 8.06 (m, 2H), 7.80 – 7.72 (m, 3H), 7.62 – 7.59 (m, 2H), 7.49 – 7.45 (m, 2H), 6.93 (s, 1H), 3.49 (s, 3H), 3.09 – 3.02 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, CD_3OD) δ 165.5, 137.8, 136.6, 135.3, 132.5, 130.5, 130.3, 129.9, 129.5, 112.9, 30.4, 27.2, 13.4. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.30. **HRMS** m/z (ESI) calcd for $C_{17}H_{18}ClS$ $(M\text{-}OTf)^+$ 289.0812, found 289.0811.



2g

(*E*)-(2,3-Diphenylprop-1-en-1-yl)(methyl)(phenyl)sulfonium trifluoromethanesulfonate (2g)

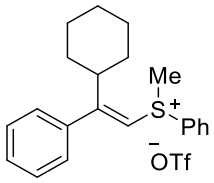
2g was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2g** was obtained through column chromatography on silica gel (DCM/MeOH, from 50:1 to 20:1) as a light-yellow solid in 79% yield (1.84 g). M.p. = 80-82 °C. **^{1}H NMR** (500 MHz, CD_3OD) δ 7.88 – 7.85 (m, 2H), 7.70 – 7.67 (m, 1H), 7.63 – 7.58 (m, 4H), 7.38 – 7.35 (m, 3H), 7.15 (s, 1H), 7.13 – 7.08 (m, 3H), 7.01 –7.00 (m, 2H), 4.48 (d, *J* = 16.0 Hz, 1H), 4.38 (d, *J* = 15.9 Hz, 1H), 3.42 (s, 3H). **^{13}C NMR** (126 MHz, CD_3OD) δ 163.1, 138.4, 137.7, 135.1, 132.1, 131.9, 130.5, 130.0, 129.9, 129.4, 128.8, 128.5, 128.0, 114.2, 39.1, 30.5. **^{19}F NMR** (471 MHz, CD_3OD) δ -79.42. **HRMS** m/z (ESI) calcd for $C_{22}H_{21}S$ $(M\text{-}OTf)^+$ 317.1358, found 317.1358.



2h

(*E*)-methyl(3-methyl-2-phenylbut-1-en-1-yl)(phenyl)sulfonium (2h)

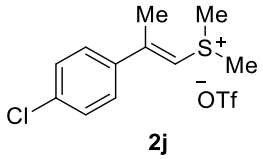
2h was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2h** was obtained through column chromatography on silica gel (DCM/MeOH, from 50:1 to 20:1) as a light-yellow solid in 82% yield (1.71 g). M.p. = 63-65 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.79 – 7.73 (m, 3H), 7.69 – 7.65 (m, 2H), 7.49 – 7.44 (m, 3H), 7.16 – 7.13 (m, 2H), 6.82 (d, *J* = 1.3 Hz, 1H), 3.36 (s, 3H), 2.99 – 2.90 (m, 1H), 1.17 (dd, *J* = 6.9, 3.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 137.8, 135.1, 132.3, 130.8, 130.4, 129.7, 128.7, 113.9, 39.0, 30.2, 21.0, 20.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.23. **HRMS** m/z (ESI) calcd for $C_{18}H_{21}S$ $(M\text{-}OTf)^+$ 269.1358, found 269.1359.



2i

(*E*)-(2-Cyclohexyl-2-phenylvinyl)(methyl)(phenyl)sulfonium trifluoromethanesulfonate (2i)

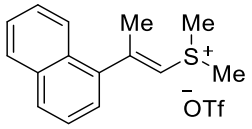
2i was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2i** was obtained through column chromatography on silica gel (DCM/MeOH, from 50:1 to 20:1) as a white solid in 81% yield (1.85 g). M.p. = 112-114 °C. **^{1}H NMR** (500 MHz, CD_3OD) δ 7.77 – 7.75 (m, 2H), 7.66 – 7.63 (m, 1H), 7.59 – 7.56 (m, 2H), 7.41 – 7.34 (m, 3H), 6.96 – 6.94 (m, 2H), 6.90 (d, *J* = 1.1 Hz, 1H), 3.32 (s, 3H), 2.51 – 2.46 (m, 1H), 1.84 – 1.73 (m, 4H), 1.63 – 1.59 (m, 1H), 1.28 – 1.19 (m, 4H), 1.15 – 1.10 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.3, 136.3, 134.1, 131.2, 129.6, 129.5, 128.89, 127.9, 127.2, 112.5, 47.6, 30.9, 30.8, 30.2, 25.9, 25.9, 25.4. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.19. **HRMS** m/z (ESI) calcd for $C_{21}H_{25}S$ $(M\text{-}OTf)^+$ 309.1671, found 309.1672.



2j

(*E*)-(2-(4-Chlorophenyl)prop-1-en-1-yl)dimethylsulfonium trifluoromethanesulfonate (2j)

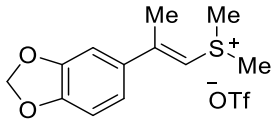
2j was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2j** was obtained by recrystallization as a white solid in 85% yield (1.54 g). M.p. = 164-166 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.65 – 7.62 (m, 2H), 7.48 – 7.45 (m, 2H), 6.64 – 6.63 (m, 1H), 3.08 (s, 6H), 2.51 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101MHz, CD_3OD) δ 158.8, 138.0, 137.7, 130.1, 129.4, 113.6, 28.8, 19.4. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.34. **HRMS** m/z (ESI) calcd for $C_{11}H_{14}ClS$ $(M\text{-}OTf)^+$ 213.0499, found 213.0450.



2k

(*E*)-(2-(4-Chlorophenyl)prop-1-en-1-yl)dimethylsulfonium trifluoromethanesulfonate (2k)

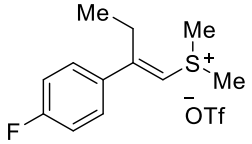
2k was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2k** was obtained by recrystallization as a white solid in 84% yield (1.59 g). M.p. = 158-160 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.93– 7.91 (m, 3H), 7.48 – 7.59 (m, 3H), 7.41 (d, *J* = 7.0 Hz, 1H), 6.39 (s, 1H), 3.13 (s, 6H), 2.58 (s, 3H). **^{13}C NMR** (101MHz, CD_3OD) δ 162.4, 139.2, 135.1, 130.9, 130.6, 129.7, 128.1, 127.5, 126.3, 125.9, 125.6, 116.7, 28.5, 22.9. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.30. **HRMS** m/z (ESI) calcd for $C_{15}H_{17}S$ $(M\text{-}OTf)^+$ 229.1045, found 229.1044.



2l

(*E*)-(2-(Benzo[d][1,3]dioxol-5-yl)prop-1-en-1-yl)dimethylsulfonium trifluoromethanesulfonate (2l)

2l was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2l** was obtained by recrystallization as a light-yellow solid in 88% yield (1.63 g). M.p. = 135-137°C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.20 – 7.17 (m, 2H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.51 (s, 1H), 6.02 (s, 2H), 3.05 (s, 6H), 2.48 (s, 3H). **^{13}C NMR** (101 MHz, CD_3OD) δ 159.4, 151.3, 149.8, 133.2, 122.8, 111.0, 109.3, 107.7, 103.3, 29.0, 19.4. **^{9}F NMR** (376 MHz, CD_3OD) δ -81.35. **HRMS** m/z (ESI) calcd for $C_{12}H_{15}O_2S$ $(M\text{-}OTf)^+$ 223.0787, found 223.0787.

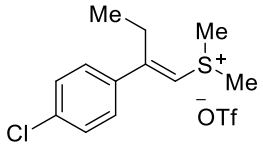


2m

(*E*)-(2-(4-Fluorophenyl)but-1-en-1-yl)dimethylsulfonium trifluoromethanesulfonate (2m)

2m was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2m** was obtained by recrystallization as a white solid in 85% yield (1.53 g). M.p. = 140-142 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.66 – 7.62 (m, 2H), 7.24 – 7.19 (m, 2H), 6.47 (s, 1H), 3.08 (s, 6H), 2.99 (q, *J* = 7.5 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, CD_3OD) δ 165.4 (d, *J* = 251.0 Hz), 165.3, 134.5 (d, *J* = 3.3 Hz), 130.6 (d, *J* = 8.6 Hz), 121.8 (d, *J* = 320.0 Hz, CF_3), 117.0 (d, *J* = 22.2

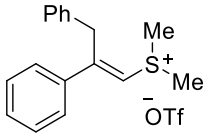
Hz), 112.5, 29.2, 27.2, 13.7. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.32, -113.53. **HRMS** m/z (ESI) calcd for $C_{12}H_{16}FS$ $(M\text{-}OTf)^+$ 211.0951, found 211.0953.



2n

(*E*)-(2-(4-Chlorophenyl)but-1-en-1-yl)dimethylsulfonium trifluoromethanesulfonate (2n)

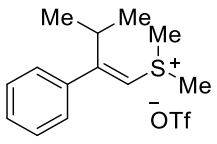
2n was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2n** was obtained by recrystallization as a white solid in 86% yield (1.62 g). M.p. = 145-147 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.59 – 7.57 (m, 2H), 7.49 – 7.46 (m, 2H), 6.51 (s, 1H), 3.09 (s, 6H), 2.98 (q, *J* = 7.5 Hz, 2H), 1.08 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, CD_3OD) δ 165.0, 137.5, 136.9, 130.2, 129.9, 113.2, 29.1, 27.1, 13.7. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.30. **HRMS** m/z (ESI) calcd for $C_{12}H_{16}ClS$ $(M\text{-}OTf)^+$ 227.0656, found 227.0657.



2o

(*E*)-(2,3-Diphenylprop-1-en-1-yl)dimethylsulfonium trifluoromethanesulfonate (2o)

2o was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2o** was obtained by recrystallization as a white solid in 86% yield (1.74 g). M.p. = 120-122 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.38 – 7.34 (m, 3H), 7.26 – 7.22 (m, 2H), 7.20 – 7.17 (m, 1H), 7.06 (d, *J* = 7.4 Hz, 2H), 6.77 (d, *J* = 1.3 Hz, 1H), 4.25 (s, 2H), 2.93 (s, 6H). **^{13}C NMR** (101MHz, $CDCl_3$) δ 161.7, 136.8, 136.7, 130.9, 129.1, 129.0, 128.1, 127.3, 127.2, 112.6, 38.3, 28.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.33. **HRMS** m/z (ESI) calcd for $C_{22}H_{21}S$ $(M\text{-}OTf)^+$ 317.1358, found 317.1358.

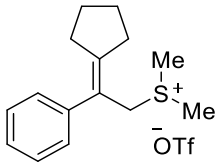


2p

(*E*)-Dimethyl(3-methyl-2-phenylbut-1-en-1-yl)sulfonium trifluoromethanesulfonate (2p)

2p was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2p** was obtained by recrystallization as a white solid in 82% yield (1.46 g). M.p. = 154-156 °C. **^{1}H**

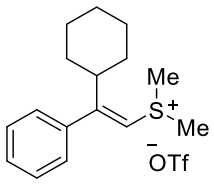
NMR (400 MHz, CD_3OD) δ 7.52 – 7.49 (m, 3H), 7.31 – 7.29 (m, 2H), 6.43 (s, 1H), 3.04 – 2.88 (m, 7H), 1.17 – 1.15 (m, 6H). **^{13}C NMR** (101 MHz, CD_3OD) δ 173.3, 137.9, 130.6, 130.0, 128.8, 113.7, 38.8, 28.8, 20.9. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.34. **HRMS** m/z (ESI) calcd for $C_{13}H_{19}S$ (M-OTf)$^+$ 207.1202, found 207.1203.



2q'

(2-Cyclopentylidene-2-phenylethyl)dimethylsulfonium trifluoromethanesulfonate (2q')

2q' was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2q'** was obtained by recrystallization by recrystallization as a white solid in 78% yield (1.49 g). M.p. = 110-112 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.44 – 7.39 (m, 2H), 7.36 – 7.30 (m, 3H), 4.48 (s, 2H), 2.81 (s, 6H), 2.62 – 2.58 (m, 2H), 2.36 – 2.30 (m, 2H), 1.87 – 1.80 (m, 2H), 1.71 – 1.64 (m, 2H). **^{13}C NMR** (101MHz, CD_3OD) δ 155.9, 140.7, 130.0, 129.7, 128.9, 120.6, 49.8, 34.4, 32.8, 27.4, 27.2, 24.6. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.32. **HRMS** m/z (ESI) calcd for $C_{15}H_{21}S$ (M-OTf)$^+$ 233.1358, found 233.1359.

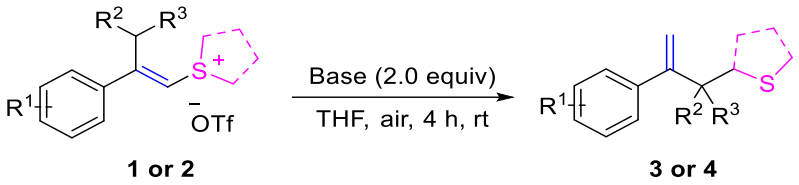


2r

***(E)*-(2-Cyclohexyl-2-phenylvinyl)dimethylsulfonium trifluoromethanesulfonate (2r)**

2r was synthesized following the general procedure on 5.0 mmol scale. Styryl sulfonium salt **2r** was obtained by recrystallization by recrystallization as a white solid in 86% yield (1.70 g). M.p. = 174-176 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.52 – 7.48 (m, 3H), 7.29 – 7.27 (m, 2H), 6.39 (s, 1H), 2.94 (s, 6H), 2.59 – 2.53 (m, 1H), 1.88 – 1.79 (m, 4H), 1.39 – 1.17 (m, 6H). **^{13}C NMR** (101 MHz, CD_3OD) δ 172.5, 138.1, 130.6, 130.0, 128.8, 113.8, 48.5, 32.2, 28.8, 27.2, 26.9. **^{19}F NMR** (376 MHz, CD_3OD) δ -81.33. **HRMS** m/z (ESI) calcd for $C_{16}H_{23}S$ (M-OTf)$^+$ 247.1515, found 247.1515.

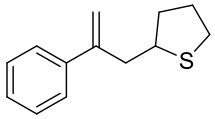
3. General Procedures for the Desired Products



1 or 2 **3 or 4**

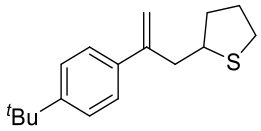
General procedure for the synthesis of compound 3 or 4: A 25.0 mL Schlenk tube with a stirring bar was added styryl sulfonium salt **1** or **2** (0.3 mmol, 1.0 equiv), ^{t}BuOK or ^{t}BuONa (0.6 mmol, 2.0 equiv) and THF (2.0 mL). Then, the reaction mixture was stirred at room temperature for 4 h in air. After complete consumption of the styryl sulfonium salt (monitored by the TLC), the resulting solution was concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA, from 100:1 to 50:1) to afford corresponding products **3** or **4**.

4. Characterization Data of Products



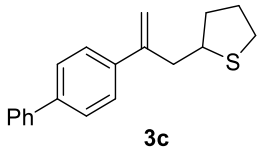
3a

2-(2-Phenylallyl)tetrahydrothiophene (3a): 3a was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA =100:1) as a colorless oil in 93% yield (56.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.25 (m, 1H), 5.30 (d, *J* = 1.5 Hz, 1H), 5.12 (d, *J* = 1.3 Hz, 1H), 3.48 – 3.39 (m, 1H), 2.93 – 2.87 (m, 1H), 2.85 – 2.76 (m, 3H), 2.11 – 1.96 (m, 2H), 1.89 – 1.80 (m, 1H), 1.65 – 1.57 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0, 140.7, 128.3, 127.5, 126.2, 113.9, 47.0, 43.5, 36.8, 32.3, 30.1. **HRMS** m/z (ESI) calcd for $C_{13}H_{17}S$ $(M+H)^+$ 205.1045, found 205.1045. The data is in accordance with the literature [2]



3b

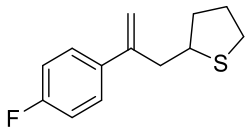
2-(2-(4-(Tert-butyl)phenyl)allyl)tetrahydrothiophene (3b): 3b was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 80% yield (62.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 5.31 (s, 1H), 5.10 (s, 1H), 3.51 – 3.44 (m, 1H), 2.93 – 2.89 (m, 1H), 2.86 – 2.79 (m, 3H), 2.11-2.00 (m, 2H), 1.89 – 1.81 (m, 1H), 1.67 – 1.59 (m, 1H), 1.33 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 146.6, 137.6, 125.8, 125.2, 113.2, 47.0, 43.4, 36.8, 34.5, 32.3, 31.3, 30.1. **HRMS** m/z (ESI) calcd for $C_{17}H_{25}S$ $(M+H)^+$ 261.1671, found 261.1671.



3c

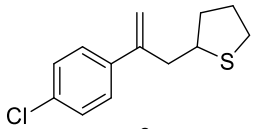
2-(2-([1,1'-Biphenyl]-4-yl)allyl)tetrahydrothiophene (3c): 3c was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a white solid in 85% yield (71.4 mg). M.p. = 64-65 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 4H), 7.50 – 7.43 (m, 4H), 7.37 – 7.33 (m, 1H), 5.39 (s, 1H), 5.17 (s, 1H), 3.52 – 3.48(m, 1H), 2.95 – 2.92 (m, 1H), 2.86 – 2.82 (m, 3H), 2.13 – 2.02 (m, 2H),

1.91 – 1.84 (m, 1H), 1.68 – 1.61 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.5, 140.7, 140.3, 139.6, 128.7, 127.3, 127.0, 126.9, 126.6, 113.9, 47.0, 43.4, 36.8, 32.4, 30.2. **HRMS** m/z (ESI) calcd for $C_{19}H_{21}S$ $(M+H)^+$ 281.1358, found 281.1357.



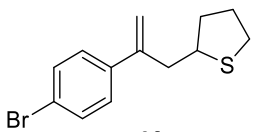
3d

2-(2-(4-Fluorophenyl)allyl)tetrahydrothiophene (3d): 3d was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 84% yield (56.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 5.24 (s, 1H), 5.11 (s, 1H), 3.42 – 3.37(m, 1H), 2.91 – 2.87 (m, 1H), 2.85 – 2.70 (m, 3H), 2.11 – 1.97 (m, 2H), 1.88 – 1.80 (m, 1H), 1.63 – 1.55 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.4 Hz), 146.0, 136.7 (d, *J* = 3.3 Hz), 127.8 (d, *J* = 7.9 Hz), 115.1 (d, *J* = 21.3 Hz), 113.9, 46.9, 43.5, 36.8, 32.3, 30.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -115.05. **HRMS** m/z (ESI) calcd for $C_{13}H_{15}FNaS$ $(M+Na)^+$ 245.0071, found 245.0072.



3e

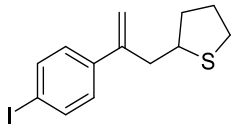
2-(2-(4-Chlorophenyl)allyl)tetrahydrothiophene (3e): 3e was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 76% yield (54.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 4H), 5.28 (s, 1H), 5.14 (s, 1H), 3.42 – 3.37(m, 1H), 2.91 – 2.87 (m, 1H), 2.85 – 2.70 (m, 3H), 2.11 – 1.97 (m, 2H), 1.88 – 1.83 (m, 1H), 1.63 – 1.55 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.9, 139.1, 133.3, 128.5, 127.5, 114.5, 46.9, 43.3, 36.8, 32.3, 30.1. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}ClS$ $(M+H)^+$ 239.0656, found 239.0657.



3f

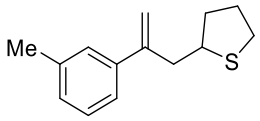
2-(2-(4-Bromophenyl)allyl)tetrahydrothiophene (3f): 3f was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash

column (PE/EA = 100:1) as a colorless oil in 80% yield (67.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.27 – 7.24 (m, 2H), 5.29 (s, 1H), 5.15 (s, 1H), 3.43 – 3.37(m, 1H), 2.93 – 2.88 (m, 1H), 2.84 – 2.70 (m, 3H), 2.11 – 1.97 (m, 2H), 1.88 – 1.81 (m, 1H), 1.64 – 1.56 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.0, 139.7, 131.4, 127.9, 121.4, 114.5, 46.9, 43.3, 36.8, 32.3, 30.1. **HRMS** m/z (ESI) calcd for $C_{13}H_{15}BrNaS$ $(M+Na)^+$ 304.9970, found 304.9968.



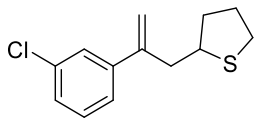
3g

2-(2-(4-Iodophenyl)allyl)tetrahydrothiophene (3g): 3g was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1 to 50:1) as a light-yellow solid in 78% yield (77.2 mg). M.p. = 45-47 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.29 (s, 1H), 5.13 (s, 1H), 3.43 – 3.36 (m, 1H), 2.93 – 2.69 (m, 4H), 2.10 – 1.97 (m, 2H), 1.89 – 1.79 (m, 1H), 1.63 – 1.54 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.0, 140.2, 137.4, 128.1, 114.6, 93.0, 46.9, 43.2, 36.8, 32.4, 30.1. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}IS$ $(M+H)^+$ 331.0012, found 331.0014.



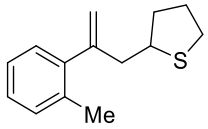
3h

2-(2-(m-tolyl)allyl)tetrahydrothiophene (3h): 3h was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 73% yield (47.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 3H), 7.09 (d, *J* = 7.0 Hz, 1H), 5.28 (s, 1H), 5.10 (s, 1H), 3.47 – 3.40 (m, 1H), 2.94 – 2.88 (m, 1H), 2.85 – 2.78 (m, 3H), 2.36 (s, 3H), 2.10 – 1.97 (m, 2H), 1.88 – 1.83 (m, 1H), 1.64 – 1.57 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.2, 140.8, 137.8, 128.3, 128.2, 127.0, 123.3, 113.7, 47.0, 43.6, 36.8, 32.3, 30.2, 21.5. **HRMS** m/z (ESI) calcd for $C_{14}H_{19}S$ $(M+H)^+$ 219.1202, found 219.1201.



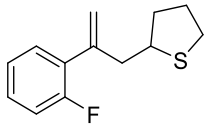
3i

2-(2-(3-Chlorophenyl)allyl)tetrahydrothiophene (3i): 3i was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 61% yield (43.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.24 – 7.22 (m, 3H), 5.29 (s, 1H), 5.14 (s, 1H), 3.42 – 3.35 (m, 1H), 2.91 – 2.68 (m, 4H), 2.07 – 1.98 (m, 2H), 1.87 – 1.79 (m, 1H), 1.62 – 1.52 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.9, 142.7, 134.2, 129.6, 127.5, 126.4, 124.4, 115.1, 46.8, 43.3, 36.8, 32.4, 30.2. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}ClS$ $(M+H)^+$ 239.0656, found 239.0655.



3j

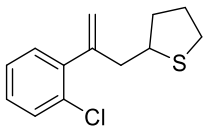
2-(2-(o-tolyl)allyl)tetrahydrothiophene (3j): 3j was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 84% yield (55.0 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 – 7.18 (m, 2H), 7.17 – 7.14 (m, 1H), 7.14 – 7.10 (m, 1H), 5.28 (d, *J* = 1.6 Hz, 1H), 4.95 (d, *J* = 1.9 Hz, 1H), 3.39 – 3.33 (m, 1H), 2.93 – 2.88 (m, 1H), 2.86 – 2.81 (m, 1H), 2.76 – 2.71 (m, 1H), 2.62 – 2.57 (m, 1H), 2.34 (s, 3H), 2.12 – 2.03 (m, 2H), 1.92 – 1.83 (m, 1H), 1.66 – 1.59 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.2, 142.0, 134.8, 130.1, 128.5, 126.9, 125.4, 115.5, 46.7, 45.8, 37.0, 32.3, 30.2, 19.9. **HRMS** m/z (ESI) calcd for $C_{14}H_{19}S$ $(M+H)^+$ 219.1202, found 219.1201.



3k

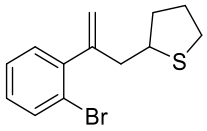
2-(2-(2-Fluorophenyl)allyl)tetrahydrothiophene (3k): 3k was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 77% yield (51.3 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.11 – 7.08 (m, 1H), 7.06 – 6.99 (m, 1H), 5.28 (d, *J* = 1.4 Hz, 1H), 5.18 (d, *J* = 1.5, 1H), 3.36 –3.31 (m, 1H), 2.91 – 78 (m, 3H), 2.74 – 2.70 (m, 1H), 2.10 – 1.99 (m, 2H), 1.88 – 1.81 (m, 1H), 1.63 – 1.56 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8 (d, *J* = 247.3

Hz), 143.6, 130.3 (d, *J* = 4.3 Hz), 129.2 (d, *J* = 14.4 Hz), 128.9 (d, *J* = 8.2 Hz), 124.0 (d, *J* = 3.5 Hz), 117.3 (d, *J* = 2.1 Hz), 115.7 (d, *J* = 22.6 Hz), 47.1, 44.5 (d, *J* = 2.9 Hz), 36.8, 32.3, 30.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -115.03. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}FS$ $(M+H)^+$ 223.0951, found 223.0951.



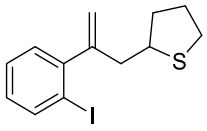
3l

2-(2-(2-Chlorophenyl)allyl)tetrahydrothiophene (3l): 3l was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 84% yield (60.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 1H), 7.22 – 7.19 (m, 3H), 5.31 (s, 1H), 5.04 (s, 1H), 3.33 – 3.26 (m, 1H), 2.92 – 2.78 (m, 3H), 2.69 – 2.63 (m, 1H), 2.09 – 2.01 (m, 2H), 1.90 – 1.80 (m, 1H), 1.65 – 1.56 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.9, 141.0, 132.0, 130.6, 129.5, 128.4, 126.6, 117.1, 46.9, 44.7, 36.9, 32.3, 30.2. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}ClS$ $(M+H)^+$ 239.0656, found 239.0656.



3m

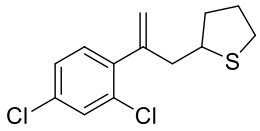
2-(2-(2-Bromophenyl)allyl)tetrahydrothiophene (3m): 3m was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 81% yield (68.5 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.27 (td, *J* = 7.4, 1.2 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.14 – 7.11 (m, 1H), 5.30 (d, *J* = 1.4 Hz, 1H), 5.02 (d, *J* = 1.4 Hz, 1H), 3.34 – 3.29 (m, 1H), 2.92 – 2.80 (m, 3H), 2.66 – 2.62 (m, 1H), 2.12 – 2.03 (m, 2H), 1.90 – 1.82 (m, 1H), 1.66 – 1.58 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.3, 143.1, 132.8, 130.6, 128.6, 127.2, 121.9, 117.0, 46.8, 44.8, 37.0, 32.4, 30.3. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}BrS$ $(M+H)^+$ 283.0151, found 283.0152.



3n

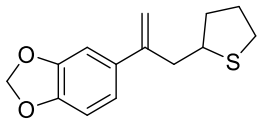
2-(2-(2-Iodophenyl)allyl)tetrahydrothiophene (3n): 3n was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash

column (PE/EA = 100:1) as a colorless oil in 85% yield (84.2mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 5.30 (s, 1H), 4.99 (s, 1H), 3.38 – 3.31 (m, 1H), 2.93 – 2.80 (m, 3H), 2.59 (dd, *J* = 14.6, 8.1 Hz, 1H), 2.12 – 2.03 (m, 2H), 1.92 – 1.82 (m, 1H), 1.68 – 1.59 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7, 147.0, 139.3, 129.5, 128.6, 127.9, 117.1, 97.5, 46.6, 45.1, 37.1, 32.4, 30.3. **HRMS** m/z (ESI) calcd for $C_{13}H_{16}IS$ $(M+H)^+$ 331.0012, found 331.0012.



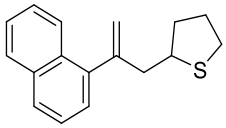
3o

2-(2-(2,4-Dichlorophenyl)allyl)tetrahydrothiophene (3o): 3o was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 78% yield (63.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 2.1 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.15 – 7.13 (m, 1H), 5.32 (s, 1H), 5.03 (s, 1H), 3.28 – 3.24 (m, 1H), 2.90 – 2.81 (m, 3H), 2.64 – 2.58 (m, 1H), 2.08 – 2.02 (m, 2H), 1.87 – 1.83 (m, 1H), 1.62 – 1.56 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.9, 139.5, 133.5, 132.8, 131.4, 129.3, 126.9, 117.8, 46.9, 44.5, 37.0, 32.4, 30.2. **HRMS** m/z (ESI) calcd for $C_{13}H_{14}Cl_2NaS$ $(M+Na)^+$ 295.0085, found 295.0087.



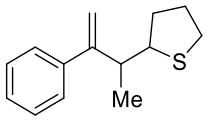
3p

5-(3-(Tetrahydrothiophen-2-yl)prop-1-en-2-yl)benzo[d][1,3]dioxole (3p): 3p was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 50:1) as a colorless oil in 89% yield (66.2 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.90 – 6.85 (m, 2H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.95 (s, 2H), 5.20 (d, *J* = 1.4 Hz, 1H), 5.04 (d, *J* = 1.4 Hz, 1H), 3.46 – 3.40 (m, 1H), 2.92 – 2.87 (m, 1H), 2.84 – 2.80 (m, 1H), 2.79 – 2.70 (m, 2H), 2.10 – 1.98 (m, 2H), 1.89 – 1.80 (m, 1H), 1.63 – 1.57 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.7, 147.0, 146.5, 135.0, 119.7, 113.0, 108.0, 106.8, 101.0, 47.0, 43.7, 36.7, 32.3, 30.1. **HRMS** m/z (ESI) calcd for $C_{14}H_{17}O_2S$ $(M+H)^+$ 249.0944, found 249.0944.



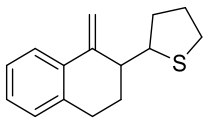
3q

2-(2-(Naphthalen-1-yl)allyl)tetrahydrothiophene (3q): 3q was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 87% yield (67.8 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 1H), 7.88 – 7.85 (m, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.32 (m, 3H), 7.33 (dd, *J* = 7.0, 1.3 Hz, 1H), 5.50 (d, *J* = 1.6 Hz, 1H), 5.17 (d, *J* = 1.9 Hz, 1H), 3.39 – 7.34 (m, 1H), 2.95 – 2.88 (m, 2H), 2.85 – 2.75 (m, 2H), 2.11 – 2.01 (m, 2H), 1.89 – 1.80 (m, 1H), 1.66 – 1.59 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.1, 140.4, 133.7, 131.2, 128.3, 127.4, 125.8, 125.7, 125.7, 125.3, 125.2, 117.0, 47.0, 46.7, 37.0, 32.3, 30.3. **HRMS** m/z (ESI) calcd for $C_{17}H_{19}S$ $(M+H)^+$ 255.1202, found 255.1203.



3r

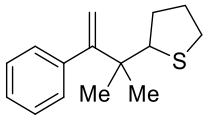
2-(3-Phenylbut-3-en-2-yl)tetrahydrothiophene (3r): 3r was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 83% yield (54.3 mg, dr = 1.8:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.34 – 7.24 (m, 3H), 5.21 (s, 1H), 5.13 (s, 1H), 3.54 – 3.48 (m, 1H), 2.88 – 2.80 (m, 2H), 2.80 – 2.72 (m, 1H), 2.21 – 2.13 (m, 2H), 1.91 – 1.80 (m, 1H), 1.53 – 1.49 (m, 1H), 1.18 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.3, 142.6, 128.1, 127.2, 127.0, 112.6, 53.7, 45.9, 34.8, 32.3, 31.3, 19.2. **HRMS** m/z (ESI) calcd for $C_{14}H_{19}S$ $(M+H)^+$ 219.1202, found 219.1202.



3s

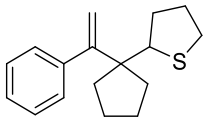
2-(1-Methylene-1,2,3,4-tetrahydronaphthalen-2-yl)tetrahydrothiophene (3s): 3s was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 50:1) as a light-yellow oil in 80% yield (55.2 mg, dr = 1.5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 1H), 7.22 – 7.10 (m, 3H), 5.45

(s, 1H), 5.00 (s, 1H), 3.47 – 3.41 (m, 1H), 3.03 – 2.84 (m, 3H), 2.81 – 2.77 (m, 1H), 2.60 – 2.55 (m, 1H), 2.22 – 2.15 (m, 1H), 2.12 – 1.99 (m, 2H), 1.98 – 1.93 (m, 1H), 1.86 – 1.77 (m, 1H), 1.76 – 1.67 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.2, 136.5, 134.0, 129.0, 127.7, 126.0, 125.1, 109.6, 49.2, 49.0, 36.1, 32.3, 30.3, 28.0, 25.5. **HRMS** m/z (ESI) calcd for $C_{15}H_{19}S$ $(M+H)^+$ 231.1202, found 231.1202.



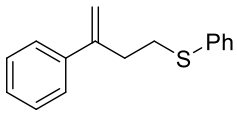
3t

2-(2-Methyl-3-phenylbut-3-en-2-yl)tetrahydrothiophene (3t): 3t was synthesized using ^{t}BuONa as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 80% yield (55.7 mg, dr = 1.5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 3H), 7.21 – 7.219 (m, 2H), 5.25 (d, *J* = 1.5 Hz, 1H), 4.87 (d, *J* = 1.5 Hz, 1H), 3.59 (dd, *J* = 8.9, 6.7 Hz, 1H), 2.81 – 2.78 (m, 2H), 2.17 – 2.11 (m, 1H), 1.97 – 1.91 (m, 1H), 1.89 – 1.82 (m, 1H), 1.66 – 1.59 (m, 1H), 1.21 (s, 3H), 1.17 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.7, 142.7, 129.2, 127.4, 126.5, 114.1, 57.1, 42.3, 32.5, 31.8, 24.3, 24.0. **HRMS** m/z (ESI) calcd for $C_{15}H_{21}S$ $(M+H)^+$ 233.1358, found 233.1360.



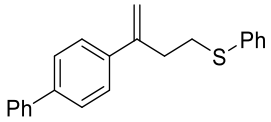
3u

2-(1-(1-Phenylvinyl)cyclopentyl)tetrahydrothiophene (3u): 3u was synthesized using ^{t}BuONa as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 72% yield (55.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ7.31 – 7.27 (m, 3H), 7.25 – 7.22 (m, 2H), 5.31 (d, *J* = 1.4 Hz, 1H), 5.03 (d, *J* = 1.4 Hz, 1H), 3.89 (dd, *J* = 9.4, 6.4 Hz, 1H), 2.83 – 2.79 (m, 2H), 2.16 – 2.11 (m, 1H), 2.05 – 1.95 (m, 2H), 1.94 – 1.85 (m, 2H), 1.83 – 1.78(m, 1H), 1.74 – 1.65 (m, 4H), 1.63 – 1.55 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.9, 143.1, 128.7, 127.6, 126.6, 115.6, 56.1, 55.5, 35.9, 33.2, 32.4, 31.5, 31.4, 24.1, 24.0. **HRMS** m/z (ESI) calcd for $C_{17}H_{23}S$ $(M+H)^+$ 259.1515, found 259.1515.



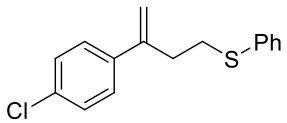
4a

Phenyl(3-phenylbut-3-en-1-yl)sulfane (4a): 4a was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 90% yield (64.8 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.40 – 7.36 (m, 4H), 7.36 – 7.32 (m, 3H), 7.25 – 7.22 (m, 1H), 5.41 (d, *J* = 1.2 Hz, 1H), 5.19 (d, *J* = 1.4 Hz, 1H), 3.09 – 3.06 (m, 2H), 2.92 – 2.89 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.4, 140.2, 136.2, 129.3, 128.8, 128.4, 127.6, 126.0, 125.9, 113.6, 35.2, 32.3. The data is in accordance with the literature [3]



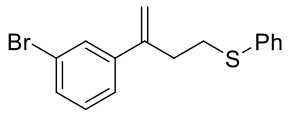
4b

(3-([1,1'-Biphenyl]-4-yl)but-3-en-1-yl)(phenyl)sulfane (4b): 4b was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a white solid in 81% yield (87.7 mg). M.p. = 92-94 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 – 7.61 (m, 2H), 7.59 – 7.57 (m, 2H), 7.48 – 7.44 (m, 4H), 7.38 – 7.35 (m, 3H), 7.32 – 7.29 (m, 2H), 7.22 – 7.19 (m, 1H), 5.43 (d, *J* = 1.2 Hz, 1H), 5.17 (d, *J* = 1.4 Hz, 1H), 3.08 – 3.05 (m, 2H), 2.90 – 2.87 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.0, 140.6, 140.5, 139.1, 136.3, 129.4, 128.9, 128.8, 127.3, 127.1, 127.0, 126.5, 126.0, 113.7, 35.2, 32.5. **HRMS** m/z (ESI) calcd for $C_{22}H_{21}S$ $(M+H)^+$ 317.1358, found 317.1358.



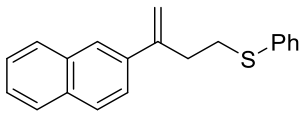
4c

(3-(4-Chlorophenyl)but-3-en-1-yl)(phenyl)sulfane (4c): 4c was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a white solid in 83% yield (68.3 mg). M.p. = 38-40 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 6H), 7.24 – 7.21 (m, 1H), 5.37 (d, *J* = 1.1 Hz, 1H), 5.17 (d, *J* = 1.3 Hz, 1H), 3.04 – 3.01 (m, 2H), 2.85 – 2.82 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.3, 138.6, 136.1, 133.3, 129.4, 128.8, 128.5, 127.3, 126.0, 114.2, 35.0, 32.3. HRMS m/z (ESI) calcd for $C_{16}H_{16}ClS$ $(M+H)^+$ 275.0656, found 275.0655.



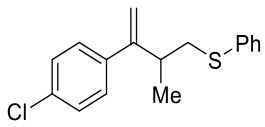
4d

(3-(3-Bromophenyl)but-3-en-1-yl)(phenyl)sulfane (4d): 4d was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 58% yield (55.3 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (t, *J* = 1.9 Hz, 1H), 7.43 – 7.41 (m, 1H), 7.35 – 7.27 (m, 5H), 7.23 – 7.18 (m, 2H), 5.35 (d, *J* = 1.0 Hz, 1H), 5.17 (d, *J* = 1.2 Hz, 1H), 3.02 – 2.99 (m, 2H), 2.82 – 2.79 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.3, 142.5, 136.0, 130.5, 129.9, 129.4, 129.2, 128.9, 126.1, 124.7, 122.6, 115.0, 35.1, 32.3. **HRMS** m/z (ESI) calcd for $C_{16}H_{16}BrS$ $(M+H)^+$ 319.0151, found 319.0150.



4e

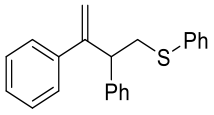
(3-(Naphthalen-2-yl)but-3-en-1-yl)(phenyl)sulfane (4e): 4e was synthesized a using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a white solid in 72% yield (62.7 mg). M.p. = 50-52 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 4H), 7.59 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.40 – 7.38 (m, 2H), 7.34 – 7.31 (m, 2H), 7.25 – 7.22 (m, 1H), 5.54 (d, *J* = 1.1 Hz, 1H), 5.27 (d, *J* = 1.2 Hz, 1H), 3.12 – 3.09 (m, 2H), 3.01 – 2.98(m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.3, 137.4, 136.2, 133.3, 132.8, 129.4, 128.9, 128.1, 128.0, 127.5, 126.2, 126.0, 125.9, 124.7, 124.5, 114.3, 35.3, 32.6. **HRMS** m/z (ESI) calcd for $C_{20}H_{19}S$ $(M+H)^+$ 291.1202, found 291.1202.



4f

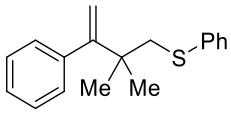
(3-(4-Chlorophenyl)-2-methylbut-3-en-1-yl)(phenyl)sulfane (4f): 4f was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 84% yield (72.6 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 6H), 7.17 – 7.14 (m, 3H), 5.22 (s, 1H), 5.12 (s, 1H), 3.09 (dd, *J* = 12.7, 4.9 Hz, 1H), 2.88 – 2.83 (m, 1H), 2.74 (dd, *J* = 12.7, 8.4 Hz, 1H), 1.26 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 140.3, 136.6, 133.2, 129.5, 128.8, 128.4, 128.0, 126.0, 112.9, 40.1, 37.7, 19.0. **HRMS** m/z (ESI) calcd for $C_{17}H_{18}ClS$ $(M+H)^+$ 289.0812, found 289.0810.



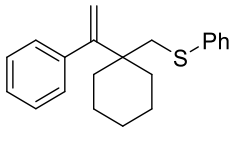
4g

(2,3-Diphenylbut-3-en-1-yl)(phenyl)sulfane (4g): 4g was synthesized using ^{t}BuONa as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 50:1) as a white solid in 82% yield (77.8 mg). M.p. = 102-104 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 8H), 7.31 – 7.24 (m, 6H), 7.23 – 7.19 (m, 1H), 5.54 (s, 1H), 5.29 (s, 1H), 4.32 – 4.04 (m, 1H), 3.55 (dd, *J* = 12.8, 7.1 Hz, 1H), 3.39 (dd, *J* = 12.8, 8.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.9, 141.6, 141.3, 136.7, 129.4, 128.8, 128.4, 128.2, 128.1, 127.4, 126.8, 126.7, 126.0, 114.3, 49.9, 39.0. **HRMS** m/z (ESI) calcd for $C_{22}H_{21}S$ $(M+H)^+$ 317.1358, found 317.1358.



4h

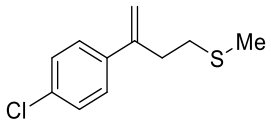
(2,2-Dimethyl-3-phenylbut-3-en-1-yl)(phenyl)sulfane (4h): 4h was synthesized using ^{t}BuONa as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 50:1) as a colorless oil in 76% yield (61.1 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.31 – 7.28 (m, 3H), 7.27 – 7.245 (m, 4H), 7.18 – 7.15 (m, 1H), 5.31 (d, *J* = 1.3 Hz, 1H), 4.99 (d, *J* = 1.4 Hz, 1H), 3.04 (s, 2H), 1.30 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.8, 142.3, 138.1, 129.0, 128.8, 128.7, 127.5, 126.6, 125.5, 114.6, 45.5, 40.3, 27.4. **HRMS** m/z (ESI) calcd for $C_{18}H_{21}S$ $(M+H)^+$ 269.1358, found 269.1359.



4i

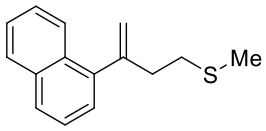
Phenyl((1-(1-phenylvinyl)cyclohexyl)methyl)sulfane (4i): 4i was synthesized using ^{t}BuONa as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 50:1) as a colorless oil in 60% yield (55.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.28 – 7.24 (m, 7H), 7.17 – 7.12 (m, 1H), 5.31 (d, *J* = 1.4 Hz, 1H),

5.11 (d, *J* = 1.4 Hz, 1H), 3.06 (s, 2H), 1.83 – 1.87 (m, 2H), 1.62 – 1.54 (m, 4H), 1.510 – 1.42 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.5, 142.4, 138.2, 129.0, 128.9, 128.8, 127.6, 126.6, 125.5, 126.9, 42.9, 42.6, 34.8, 26.2, 22.7. **HRMS** m/z (ESI) calcd for $C_{21}H_{25}S$ $(M+H)^+$ 309.1671, found 309.1672.



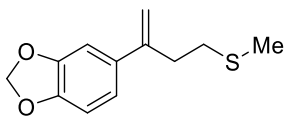
4j

(3-(4-Chlorophenyl)but-3-en-1-yl)(methyl)sulfane (4j): 4j was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA =100:1) as a light-yellow oil in 89% yield (56.6mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 5.32 (d, *J* = 1.1 Hz, 1H), 5.14 (d, *J* = 1.2 Hz, 1H), 2.78 – 2.75 (m, 2H), 2.60 – 2.56 (m, 2H), 2.11 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.6, 138.8, 133.3, 128.5, 127.3, 113.9, 35.1, 32.8, 15.5. **HRMS** m/z (ESI) calcd for $C_{11}H_{14}ClS$ $(M+H)^+$ 213.0499, found 213.0500.



4k

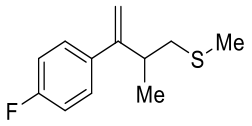
Methyl(3-(naphthalen-1-yl)but-3-en-1-yl)sulfane (4k): 4k was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 91% yield (62.3 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 – 8.06 (m, 1H), 7.89 – 7.87 (m, 1H), 7.80 (d, *J* = 8.1, 1H), 7.53 – 7.45 (m, 2H), 7.46 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.34 (dd, *J* = 7.0, 1.3 Hz, 1H), 5.49 (d, *J* = 1.6 Hz, 1H), 5.19 (d, *J* = 1.9 Hz, 1H), 2.87 – 2.83 (m, 2H), 2.60 – 2.57 (m, 2H), 2.09 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.9, 140.3, 133.7, 131.2, 128.3, 127.4, 125.8, 125.7, 125.6, 125.2, 125.1, 116.6, 38.2, 32.7, 15.5. **HRMS** m/z (ESI) calcd for $C_{15}H_{17}S$ $(M+H)^+$ 229.1045, found 229.1045.



4l

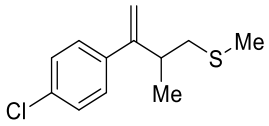
5-(4-(Methylthio)but-1-en-2-yl)benzo[d][1,3]dioxole (4l): 4l was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel

flash column (PE/EA = 50:1) as a colorless oil in 89% yield (59.3 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.91 – 6.87 (m, 2H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.95 (s, 2H), 5.23 (d, *J* = 1.2 Hz, 1H), 5.04 (d, *J* = 1.3 Hz, 1H), 2.76 – 2.72 (m, 2H), 2.61 – 2.58 (m, 2H), 2.11 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.7, 147.1, 146.3, 134.7, 119.5, 112.4, 108.0, 106.6, 101.0, 35.5, 33.0, 15.6. **HRMS** m/z (ESI) calcd for $C_{12}H_{15}O_2S$ $(M+H)^+$ 223.0787, found 223.0787.



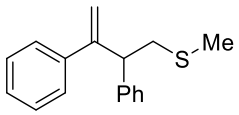
4m

(3-(4-Fluorophenyl)-2-methylbut-3-en-1-yl)(methyl)sulfane (4m): 4m was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 90% yield (56.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.03 – 6.99 (m, 2H), 5.20 (s, 1H), 5.09 (s, 1H), 2.90 – 2.85 (m, 1H), 2.68 (dd, *J* = 12.8, 5.2 Hz, 1H), 2.42 (dd, *J* = 12.8, 8.4 Hz, 1H), 2.07 (s, 3H), 1.24 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.2 Hz), 152.1, 138.1 (d, *J* = 3.1 Hz), 128.3 (d, *J* = 7.8 Hz), 115.0 (d, *J* = 21.1 Hz), 112.2, 40.9, 38.2, 19.2, 16.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.38. **HRMS** m/z (ESI) calcd for $C_{12}H_{16}FS$ $(M+H)^+$ 211.0951, found 211.0950.



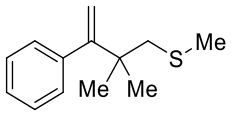
4n

(3-(4-Chlorophenyl)-2-methylbut-3-en-1-yl)(methyl)sulfane (4n): 4n was synthesized using ^{t}BuOK as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 92% yield (62.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 4H), 5.20 (s, 1H), 5.09 (s, 1H), 2.87 – 2.81 (m, 1H), 2.64 (dd, *J* = 12.7, 5.1 Hz, 1H), 2.39 (dd, *J* = 12.7, 8.3 Hz, 1H), 2.04 (s, 3H), 1.21 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.0, 140.6, 133.2, 128.4, 128.0, 112.6, 40.9, 38.0, 19.2, 16.3. **HRMS** m/z (ESI) calcd for $C_{12}H_{16}S$ $(M+H)^+$ 227.0656, found 227.0655.



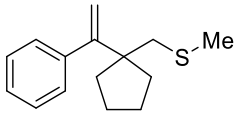
4o

(2,3-Diphenylbut-3-en-1-yl)(methyl)sulfane (4o): 4o was synthesized using ^{t}BuONa as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 85% yield (64.8 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 6H), 7.25 – 7.21 (m, 4H), 5.48 (d, *J* = 0.8 Hz, 1H), 5.24 (t, *J* = 1.0 Hz, 1H), 4.10 (t, *J* = 7.0 Hz, 1H), 3.11 (dd, *J* = 12.8, 6.7 Hz, 1H), 2.94 (dd, *J* = 12.8, 8.4 Hz, 1H), 2.05 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.3, 141.9, 141.7, 128.4, 128.2, 128.1, 127.3, 126.8, 126.7, 114.0, 50.4, 39.8, 16.4. **HRMS** m/z (ESI) calcd for $C_{17}H_{19}S$ $(M+H)^+$ 255.1202, found 255.1201.



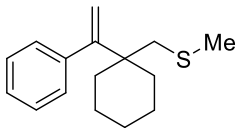
4p

(2,2-Dimethyl-3-phenylbut-3-en-1-yl)(methyl)sulfane (4p): 4p was synthesized using ^{t}BuONa as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a colorless oil in 88% yield (54.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 3H), 7.22 – 7.20 (m, 2H), 5.23 (d, *J* = 1.5 Hz, 1H), 4.92 (d, *J* = 1.5 Hz, 1H), 2.58 (s, 2H), 2.10 (s, 3H), 1.22 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.4, 142.6, 128.9, 127.4, 126.5, 114.1, 47.1, 40.7, 27.2, 17.6. **HRMS** m/z (ESI) calcd for $C_{13}H_{19}S$ $(M+H)^+$ 207.1202, found 207.1202.



4q

Methyl((1-(1-phenylvinyl)cyclopentyl)methyl)sulfane (4q): 4q was synthesized using ^{t}BuONa as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 63% yield (43.9 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 5H), 5.26 (d, *J* = 1.5 Hz, 1H), 5.04 (d, *J* = 1.5 Hz, 1H), 2.65 (s, 2H), 2.10 (s, 3H), 1.92 – 1.88 (m, 2H), 1.77 – 1.68 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.2, 143.0, 128.5, 127.5, 126.6, 114.9, 53.0, 43.6, 36.6, 23.2, 17.2. **HRMS** m/z (ESI) calcd for $C_{15}H_{21}S$ $(M+H)^+$ 233.1358, found 233.1360.

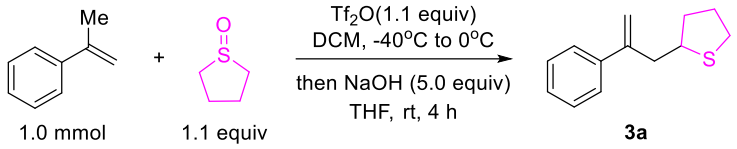


4r

Methyl((1-(1-phenylvinyl)cyclohexyl)methyl)sulfane (4r): 4r was synthesized using ^{t}BuONa as a base at room temperature following the general procedure, and it was purified through a silica gel flash column (PE/EA = 100:1) as a light-yellow oil in 62% yield (45.8 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 5H), 5.23 (d, *J* = 1.5 Hz, 1H), 5.05 (d, *J* = 1.5 Hz, 1H), 2.63 (s, 2H), 2.11 (s, 3H), 1.76 – 1.72 (m, 2H), 1.55 – 1.41 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.9, 142.7, 128.9, 127.5, 126.5, 116.5, 44.4, 43.4, 34.6, 26.2, 22.3, 17.2. **HRMS** m/z (ESI) calcd for $C_{16}H_{23}S$ $(M+H)^+$ 247.1515, found 247.1516.

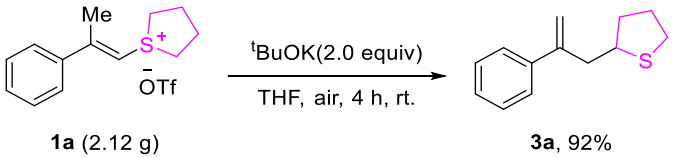
5. Synthetic Applications

5.1 One-pot synthesis



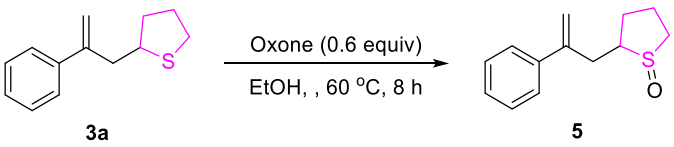
General procedure: Under argon atmosphere, sulfoxide (98.8 μL, 1.1 mmol, 1.1 equiv) and anhydrous DCM (5.0 mL) were added to a 25.0 mL flask at -40 °C. The Tf_2O (184.8 μL, 1.1 mmol, 1.1 equiv) was added dropwise under argon, then ***α***-methyl styrene (130.0 μL, 1.0 mmol, 1.0 equiv) was added gradually. The reaction mixture was stirred at -40 °C for 30 min before warming to 0 °C. After stirring for 2 h, the reaction mixture was filtered and the solvent was removed under reduced pressure. Then NaOH (200.0 mg, 5.0 mmol, 5.0 equiv) and THF (6.0 mL) were added. The reaction mixture was stirred at room temperature for 4 h. The crude product was purified by column chromatography on silica gel (PE/EA=100:1) to afford product **3a** (147.0 mg, 72% for two steps).

5.2 Scale-up Reaction



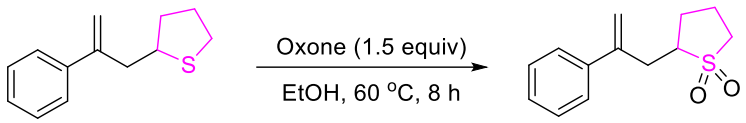
General procedure: To a round-bottom flask (100 mL) equipped with a stirring bar were added styryl sulfonium salt **1a** (2.12 g, 6.0 mmol, 1.0 equiv), ^tBuOK (1.35 g, 12.0 mmol, 2.0 equiv) and THF (40.0 mL). Then, the reaction mixture was stirred at room temperature for 4 h in air. The crude product was concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA=100:1) to afford product **3a** (1.13 g, 92%).

5.3 Product Derivatization



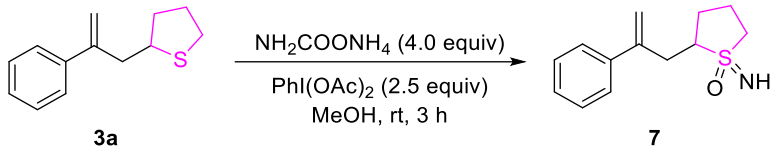
Following the relative literature [3]: General procedure for compound 5: To a 10 mL flask, compound **3a** (61.2 mg, 0.3 mmol), Oxone (100.7 mg, 0.18 mmol), and ethanol (4.0 mL) were

added, and the mixture was stirred at 60 ℃ for 8 hours. The mixture was cooled to room temperature, added with brine (10.0 mL), and then extracted by ethyl acetate (15.0 mL × 3). After drying with anhydrous sodium sulfate, it was concentrated and purified with flash column chromatography, eluted by ethyl acetate, to give corresponding sulfoxide **5** as a pair of diastereomers in 85% combined yield, in 1.5:1 ratio as determined by crude ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 7.35 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 5.38 (s, 1H), 5.15 (s, 1H), 3.15 – 3.10 (m, 1H), 2.98 (dd, *J* = 14.7, 6.9 Hz, 1H), 2.90 – 2.77 (m, 2H), 2.47 (dd, *J* = 14.9, 9.2 Hz, 1H), 2.44 – 2.34 (m, 2H), 2.16 – 2.09 (m, 1H), 1.67 – 1..59 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.8, 139.7, 128.5, 127.9, 126.2, 115.2, 68.7, 52.7, 36.0, 31.1, 25.0. **HRMS** m/z (ESI) calcd for $C_{13}H_{17}OS$ $(M+H)^+$ 221.0995, found 221.0994.



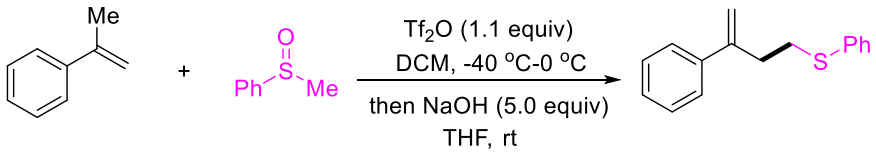
3a **6**

Following the relative literature[3]: **General procedure for compound 6:** To a 10 mL flask, compound **3a** (61.2 mg, 0.3 mmol), Oxone (276.6 mg, 0.45 mmol), and ethanol (4.0 mL) were added, and the mixture was stirred at 60 ℃ for 8 hours. The mixture was cooled to room temperature, added with brine (10.0 mL), and then extracted by ethyl acetate (15.0 mL × 3). After drying with anhydrous sodium sulfate, it was concentrated and purified with flash column chromatography, eluted by petroleum ether/ethyl acetate (4:1), to give corresponding sulfone **6** as a light-yellow oil in 75% yield (51.3 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.38 (m, 2H), 7.36 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 5.38 (s, 1H), 5.21 (s, 1H), 3.25 (dd, *J* = 14.6, 5.0 Hz, 1H), 3.12 – 3.07 (m, 1H), 3.03 – 2.94 (m, 2H), 2.59 (dd, *J* = 14.6, 10.0 Hz, 1H), 2.19 – 2.94 (m, 2H), 2.01 – 1.90 (m, 1H), 1.81 – 1.72 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.8, 139.4, 128.5, 127.9, 126.1, 115.6, 58.9, 51.1, 33.4, 28.6, 19.7. **HRMS** m/z (ESI) calcd for $C_{13}H_{17}O_2S$ $(M+H)^+$ 237.0944, found 237.0945.



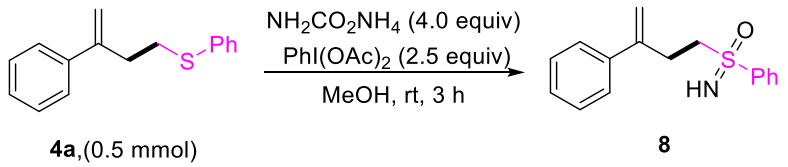
3a **7**

Following the relative literature[4]: **General procedure for compound 7:** The compound **3a** (102.1 mg, 0.5 mmol), (diacetoxyiodo)benzene (402.6 mg, 1.25 mmol, 2.5 equiv) and ammonium carbamate (156.0 mg, 2.0 mmol, 4.0 equiv) were added to a flask containing a stirrer bar. MeOH (1 mL, 0.5 M) was added and the reaction was stirred at 25 ℃ for 3 h. The solvent was removed under reduced pressure. Purification by flash chromatography (petroleum ether/ethyl acetate, 4:1) afforded the sulfoximine product **7** (light-yellow oil) as a pair of diastereomers in 81% combined yield, in 1.2:1 ratio as determined by crude ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, mixture of diastereomers) δ 7.40 – 7.37 (m, 4H), 7.34 – 7.31 (m, 4H), 7.29 – 7.26 (m, 2H), 5.37 (s, 1H), 5.37 (s, 1H), 5.22 – 5.21 (m, 2H), 3.25 – 3.03 (m, 8H), 2.64 – 2.59 (m, 2H), 2.48 (brs, 2H), 2.20 – 2.06 (m, 4H), 2.01 – 1.91 (m, 2H), 1.87 – 1.70 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.27, 144.20, 139.62, 139.50, 128.54, 128.50, 127.90, 127.88, 126.05, 126.02, 115.48, 115.26, 62.30, 62.0, 55.34, 54.30, 34.33, 33.79, 30.25, 29.79, 20.71, 20.38. **HRMS** m/z (ESI) calcd for $C_{13}H_{18}NOS$ $(M+H)^+$ 236.1104, found 236.1105.



1.0 mmol 1.1 equiv **4a**, 65%

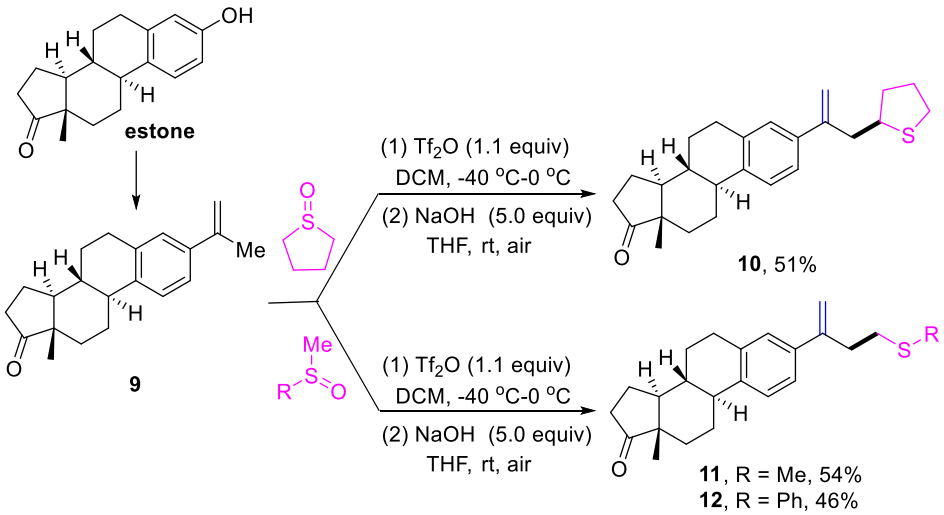
One-pot reaction for the synthesis of compound 4a: Under an argon atmosphere, sulfoxide (137.9 μL, 1.1 mmol, 1.1 equiv) and anhydrous DCM (5.0 mL) were added to a 25.0 mL flask at -40 °C. The Tf_2O (184.8 μL, 1.1 mmol, 1.1 equiv) was added dropwise under argon, then ***α***-methylstyrene (130.0 μL, 1.0 mmol, 1.0 equiv) was added gradually. The reaction mixture was stirred at -40 °C for 30 min before warming to 0 °C.. After stirring for 2 h, the reaction mixture was filtered and the solvent was removed under reduced pressure. Then NaOH (200.0 mg, 5.0 mmol, 5.0 equiv) and THF (6.0 mL) were added. The reaction mixture was stirred at room temperature for 4 h. The crude product was purified by column chromatography on silica gel (PE/EA=100:1) to afford product **4a** (156.1 mg, 65% for two steps).

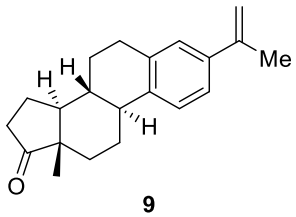


4a,(0.5 mmol) **8**

Following the relative literature[4]: **General procedure for compound 8:** The compound **4a** (120.1 mg, 0.5 mmol), (diacetoxyiodo)benzene (402.6 mg, 1.25 mmol, 2.5 equiv) and ammonium carbamate (156.0 mg, 2.0 mmol, 4.0 equiv) were added to a flask containing a stirrer bar. MeOH (1 mL, 0.5 M) was added and the reaction was stirred at 25 ℃ for 3 h. The solvent was removed under reduced pressure. Purification by flash chromatography (petroleum ether/ethyl acetate, 2:1) afforded the sulfoximine product **8** (light-yellow oil) in 83% yield (112.5 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 – 7.99 (m, 2H), 7.68 – 7.64 (m, 1H), 7.60 – 7.56 (m, 2H), 7.34 – 7.25 (m, 5H), 5.33 (s, 1H), 5.10 (d, *J* = 1.2 Hz, 1H), 3.34 – 3.21 (m, 2H), 3.05 – 2.97 (m, 1H), 2.94 – 2.86 (m, 1H), 2.63 (brs, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.3, 141.7, 139.2, 133.0, 129.1, 128.5, 128.3, 127.8, 125.8, 114.1, 56.1, 28.8. **HRMS** m/z (ESI) calcd for $C_{16}H_{18}NOS$ $(M+H)^+$ 272.1104, found 272.1103.

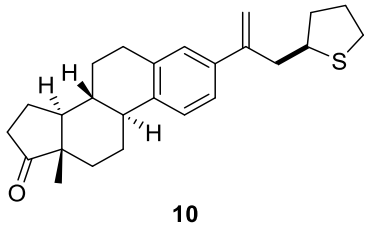
5.4 Late-stage Functionalization





9

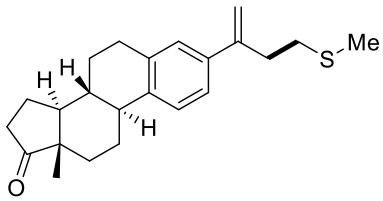
(8R,9S,13S,14S)-13-Methyl-3-(prop-1-en-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (9): Compound **9** was synthesized from estone according to the literature.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.77 (m, 2H), 7.21 (s, 1H), 5.34 (s, 1H), 5.05 (s, 1H), 2.94 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.51 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.47 – 2.42 (m, 1H), 2.35 – 2.28 (m, 1H), 2.20 – 1.95 (m, 7H), 1.67 – 1.43 (m, 6H), 0.92 (s, 3H). The data is in accordance with the literature [6]



10

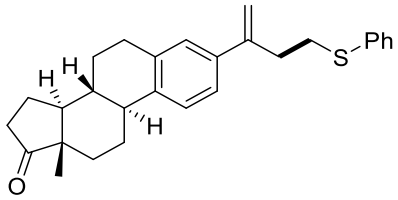
(8R,9S,13S,14S)-13-Methyl-3-(3-((R)-tetrahydrothiophen-2-yl)prop-1-en-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (10): Under argon atmosphere, tetramethylene sulfoxide (45.0 μL, 0.55 mmol, 1.1 equiv) and anhydrous DCM (3.0 mL) were added to a 25.0 mL flask at -40 °C. The Tf_2O (92.4 μL, 0.55 mmol, 1.1 equiv) was added dropwise under argon, then compound **9** (147.1 mg, 0.5 mmol, 1.0 equiv) was added gradually. The reaction mixture was stirred at -40 °C for 30 min before warming to 0 °C. After stirring for 2 h, the reaction mixture was filtered and the solvent was removed under reduced pressure. Then NaOH (100.0 mg, 2.5 mmol, 5.0 equiv) and THF (6.0 mL) were added. The reaction mixture was stirred at room temperature for 4 h. The crude product was purified by column chromatography on silica gel (PE/EA=50:1) to afford compound **10** as a colorless oil (97.0 mg, 51% for two steps). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.2 Hz, 1H), 7.17 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 5.27 (d, *J* = 1.5 Hz, 1H), 5.07 (d, *J* = 1.6 Hz, 1H), 3.48 – 342 (m, 1H), 2.95 – 2.87 (m, 3H), 2.83 – 2.79 (m, 1H), 2.77 (d, *J* = 7.3 Hz, 2H), 2.50 (dd, *J* = 18.9, 8.7 Hz, 1H), 2.45 – 2.40 (m, 1H), 2.29 (td, *J* = 10.9, 4.0 Hz, 1H), 2.17 – 2.12 (m, 1H), 2.10 – 1.99 (m, 4H), 1.98 – 1.94 (m, 1H), 1.88 – 1.81 (m, 1H), 1.67 – 1.57 (m, 3H), 1.56 – 1.40 (m,

4H), 0.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 220.7, 146.6, 139.1, 138.1, 136.3, 126.6, 125.2, 123.5, 113.2, 50.4, 47.9, 46.9 (d, *J* = 2.1 Hz), 44.3, 43.3, 38.0, 36.7 (d, *J* = 2.5 Hz), 35.8, 32.3, 31.5, 30.1, 29.4, 26.4, 25.6, 21.5, 13.8. **HRMS** m/z (ESI) calcd for $C_{25}H_{33}OS$ $(M+H)^+$ 381.2247, found 381.2246.



11

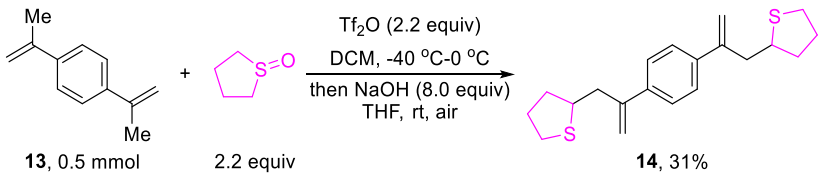
(8R,9S,13S,14S)-13-Methyl-3-(4-(methylthio)but-1-en-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (11): Under argon atmosphere, dimethyl sulfoxide (35.5 μL, 0.55 mmol, 1.1 equiv) and anhydrous DCM (3.0 mL) were added to a 25.0 mL flask at -40 °C. The Tf_2O (92.4 μL, 0.55 mmol, 1.1 equiv) was added dropwise under argon, then compound **9** (147.1 mg, 0.5 mmol, 1.0 equiv) was added gradually. The reaction mixture was stirred at -40 °C for 30 min before warming to 0 °C. After stirring for 2 h, the reaction mixture was filtered and the solvent was removed under reduced pressure. Then NaOH (100.0 mg, 2.5 mmol, 5.0 equiv) and THF (6.0 mL) were added. The reaction mixture was stirred at room temperature for 4 h. The crude product was purified by column chromatography on silica gel (PE/EA=50:1) to afford compound **11** as a colorless oil (95.6 mg, 54% for two steps). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.25 (m, 1H), 7.21 – 7.19 (m, 1H), 7.15 (s, 1H), 5.32 (d, *J* = 1.4 Hz, 1H), 5.08 (d, *J* = 1.2 Hz, 1H), 2.93 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.80 – 2.77 (m, 2H), 2.63 – 2.60 (m, 2H), 2.51 (dd, *J* = 18.9, 8.3 Hz, 1H), 2.45 – 2.41 (m, 1H), 2.33 – 2.28 (m, 1H), 2.18 – 2.10 (m, 4H), 2.09 – 2.01 (m, 2H), 1.99 – 1.95 (m, 1H), 1.67 – 1.59 (m, 2H), 1.58 – 1.43 (m, 4H), 0.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 220.7, 146.4, 139.2, 137.8, 136.3, 126.5, 125.3, 123.4, 112.7, 50.4, 47.9, 44.3, 38.1, 35.8, 35.2, 33.0, 31.5, 29.4, 26.4, 25.6, 21.5, 15.5, 13.8. **HRMS** m/z (ESI) calcd for $C_{23}H_{31}OS$ $(M+H)^+$ 355.2090, found 355.2090.



12

(8R,9S,13S,14S)-13-Methyl-3-(4-(phenylthio)but-1-en-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (12): Under argon atmosphere, methyl phenyl sulfoxide (69.0 μL, 0.55 mmol, 1.1 equiv) and anhydrous DCM (3.0 mL) were added to a 25.0 mL flask at -40 °C. The Tf_2O (92.4 μL, 0.55 mmol, 1.1 equiv) was added dropwise under argon, then compound **9** (147.1 mg, 0.5 mmol, 1.0 equiv) was added gradually. The reaction mixture was stirred at -40 °C for 30 min before warming to 0 °C. After stirring for 2 h, the reaction mixture was filtered and the solvent was removed under reduced pressure. Then NaOH (100.0 mg, 2.5 mmol, 5.0 equiv) and THF (6.0 mL) were added. The reaction mixture was stirred at room temperature for 4 h. The crude product was purified by column chromatography on silica gel (PE/EA=50:1) to afford compound **12** as a white soild (95.7 mg, 46% for two steps). M.p. = 119-121 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.31 – 7.26 (m, 3H), 7.21 – 7.17 (m, 2H), 7.12 (d, *J* = 1.9 Hz, 1H), 5.34 (d, *J* = 1.4 Hz, 1H), 5.10 (d, *J* = 1.4 Hz, 1H), 3.05 – 3.02 (m, 2H), 2.92 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.84 – 2.81 (m, 2H), 2.52 (dd, *J* = 18.9, 8.7 Hz, 1H), 2.46 – 2.42 (m, 1H), 2.32 (td, *J* = 10.9, 4.1 Hz, 1H), 2.16 (dt, *J* = 18.8, 8.9 Hz, 1H), 2.10 – 2.01 (m, 2H), 2.01 – 1.97 (m, 1H), 1.69 – 1.59 (m, 2H), 1.58 – 1.43 (m, 4H), 0.93 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 220.7, 146.1, 139.3, 137.6, 136.3, 129.2, 128.8, 126.5, 125.9, 125.4, 123.5, 113.0, 50.4, 47.9, 44.3, 38.1, 35.8, 35.1, 32.4, 31.5, 29.4, 26.4, 25.6, 21.5, 13.8. **HRMS** m/z (ESI) calcd for $C_{28}H_{33}OS$ $(M+H)^+$ 417.2247, found 417.2248.

5.5 Double Allylic C(sp^3)-H Alkylation

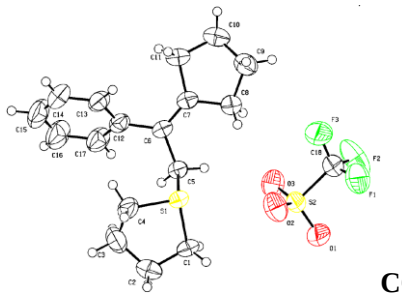


13, 0.5 mmol 2.2 equiv **14**, 31%

1,4-Bis(3-(tetrahydrothiophen-2-yl)prop-1-en-2-yl)benzene (14): Under argon atmosphere, tetramethylene sulfoxide (90.0 μL, 1.1 mmol, 2.2 equiv) and anhydrous DCM (5.0 mL) were added to a 25.0 mL flask at -40 °C. The Tf_2O (184.8 μL, 1.1 mmol, 2.2 equiv) was added

dropwise under argon, then commercially available 1,4-diisopropenylbenzene **13** (84.0 μL, 0.5 mmol, 1.0 equiv) was added gradually. The reaction mixture was stirred at -40 °C for 30 min before warming to room temperature. After stirring for 2 h, the reaction mixture was filtered and the solvent was removed under reduced pressure. Then NaOH (160.0 mg, 4.0 mmol, 8.0 equiv) and THF (6.0 mL) were added. The reaction mixture was stirred at room temperature for 4 h. The crude product was purified by column chromatography on silica gel (PE/EA=50:1) to afford compound **14** as a white solid (51.2 mg, 31% for two steps). M.p. = 57-59 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.34 (m, 4H), 5.32 (d, *J* = 1.5 Hz, 1H), 5.12 (d, *J* = 1.4 Hz, 1H), 3.47 – 3.42 (m, 2H), 2.94 – 2.88 (m, 2H), 2.85 – 2.77 (m, 6H), 2.11 – 1.98 (m, 4H), 1.89 – 1.81 (m, 2H), 1.63 – 1.59 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.49, 146.47, 139.83, 139.82, 126.16, 126.15, 113.83, 46.99, 46.98, 43.35, 43.33, 36.79, 32.35, 30.16. **HRMS** m/z (ESI) calcd for $C_{20}H_{27}S$ $(M+H)^+$ 331.1549, found 331.1550.

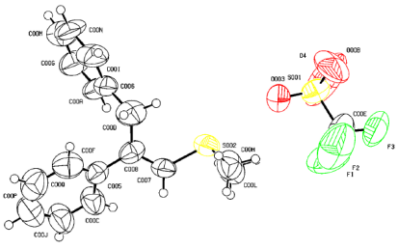
6. Single Crystal X-ray Structure of 1u', 2o and 3g



CCDC: 2253421

Table 1 Crystal data and structure refinement for 1u'.

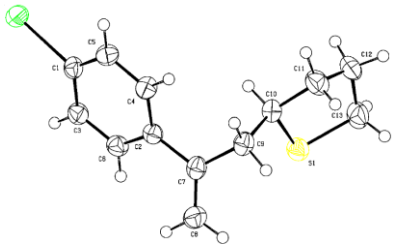
Identification code	1u'_auto
Empirical formula	$C_{18}H_{23}F_3O_3S_2$
Formula weight	408.48
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.89231(14)
b/Å	8.53641(10)
c/Å	23.7023(3)
α/°	90
β/°	101.8925(13)
γ/°	90
Volume/Å^3	1958.57(5)
Z	4
ρ_{calc}g/cm^3	1.385
μ/mm^{-1}	2.855
F(000)	856.0
Crystal size/mm^3	0.06 × 0.05 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.624 to 136.206
Index ranges	-11≤ h ≤ 11, -10 ≤ k ≤10, -28 ≤ l ≤ 20
Reflections collected	15882
Independent reflections	3477 [R_{int} = 0.0394, R_{sigma} = 0.0281]
Data/restraints/parameters	3477/0/235
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.1229
Final R indexes [all data]	R_1 = 0.0462, wR_2 = 0.1250
Largest diff. peak/hole / e Å^{-3}	0.37/-0.39



CCDC: 2259304

Table 1 Crystal data and structure refinement for 2o.

Identification code	**2o**
Empirical formula	$C_{18}H_{19}F_3O_3S_2$
Formula weight	404.45
Temperature/K	293
Crystal system	monoclinic
Space group	P21/c
a/Å	14.2669(8)
b/Å	11.9380(6)
c/Å	12.6553(6)
α/°	90
β/°	112.820(7)
γ/°	90
Volume/Å^3	1986.7(2)
Z	4
ρcalcg/cm^3	1.352
μ/mm^{-1}	2.814
F(000)	840.0
Crystal size/mm^3	0.07 × 0.06 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.722 to 136.54
Index ranges	-17 ≤ h ≤ 17, -12 ≤ k ≤ 14, -11 ≤ l ≤ 15
Reflections collected	15019
Independent reflections	3554 [Rint = 0.1124, Rsigma = 0.0654]
Data/restraints/parameters	3554/0/237
Goodness-of-fit on F^2	1.252
Final R indexes [I>=2σ (I)]	R1 = 0.1047, wR2 = 0.3049
Final R indexes [all data]	R1 = 0.1196, wR2 = 0.3351
Largest diff. peak/hole / e Å^{-3}	0.69/-0.51



CCDC: 2192921

Table 2. Crystal data and structure refinement for 3g.

Identification code	3g	
Empirical formula	C_{13} $H_{15}IS$	
Formula weight	330.21	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.0770(15) Å	a= 90 °.
	b = 6.3879(10) Å	b= 99.329(6) °.
	c = 22.529(4) Å	g = 90 °.
Volume	1289.0(4) $Å^3$	
Z	4	
Density (calculated)	1.702 Mg/m^3	
Absorption coefficient	2.613 mm^{-1}	
F(000)	648	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	2.310 to 27.533 °.	
Index ranges	-11<=h<=11, -8<=k<=8, -29<=l<=20	
Reflections collected	11036	
Independent reflections	2945 [R(int) = 0.0770]	
Completeness to theta = 25.242 °	99.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2945/0/136	
Goodness-of-fit on F^2	0.813	
Final R indices [I > 2 sigma (I)]	R1 = 0.0432, wR2 = 0.1177	
R indices (all data)	R1 = 0.0487, wR2 = 0.1244	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.669 and -0.831 $e.Å^{-3}$	

7. References

[1] L.-H. Zou, B. Liu, C. Wang, Z. Shao, J. Zhou, A. Shao, J. Wen, **S**elective synthesis of alkyl amines and *N*-vinylazoles from vinyl sulfonium salts with *N*-nucleophiles**.** *Org. Chem. Front.* **2022**, *9*, 3231−3236.

[2] S.-V. Patil, J.-M. Tanko, Radical additions of acyclic and cyclic ethers to alkenes via an allyl transfer reaction involving phthalimido-*N*-oxyl radical**.** *Tetrahedron* **2016**, *72*, 7849−7858.

[3] G. Hu, J. Xu, P. Li, Sulfur Mediated Allylic C–H Alkylation of Tri- and Disubstituted Olefins. *Org. Lett.* **2014,** *16*, 6036–6039.

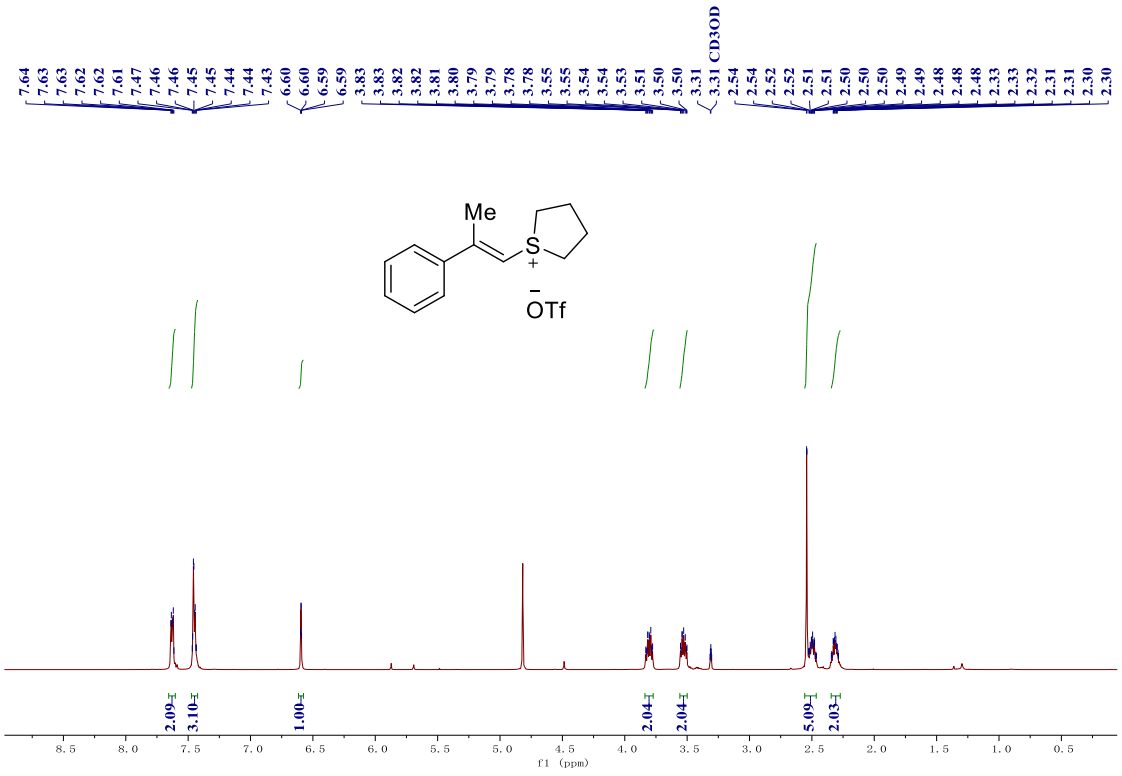
[4] A. Tota, M. Zenzola, S.-J. Chawner, S.-S. John-Campbell, C. Carlucci, G. Romanazzi, L. Degennaro, J. A. Bull, R. Luisi, Synthesis of NH-sulfoximines from sulfides by chemoselective one-pot N- and O-transfers**.** *Chem. Commun.* **2017**, *53*, 348–351.

[5] A. Jana, K. Misztal, A. Żak, K. Grela, Synthesis of Selectively Substituted or Deuterated Indenes via Sequential Pd and Ru Catalysis. *J. Org. Chem.* **2017**, *82*, 4226–4234.

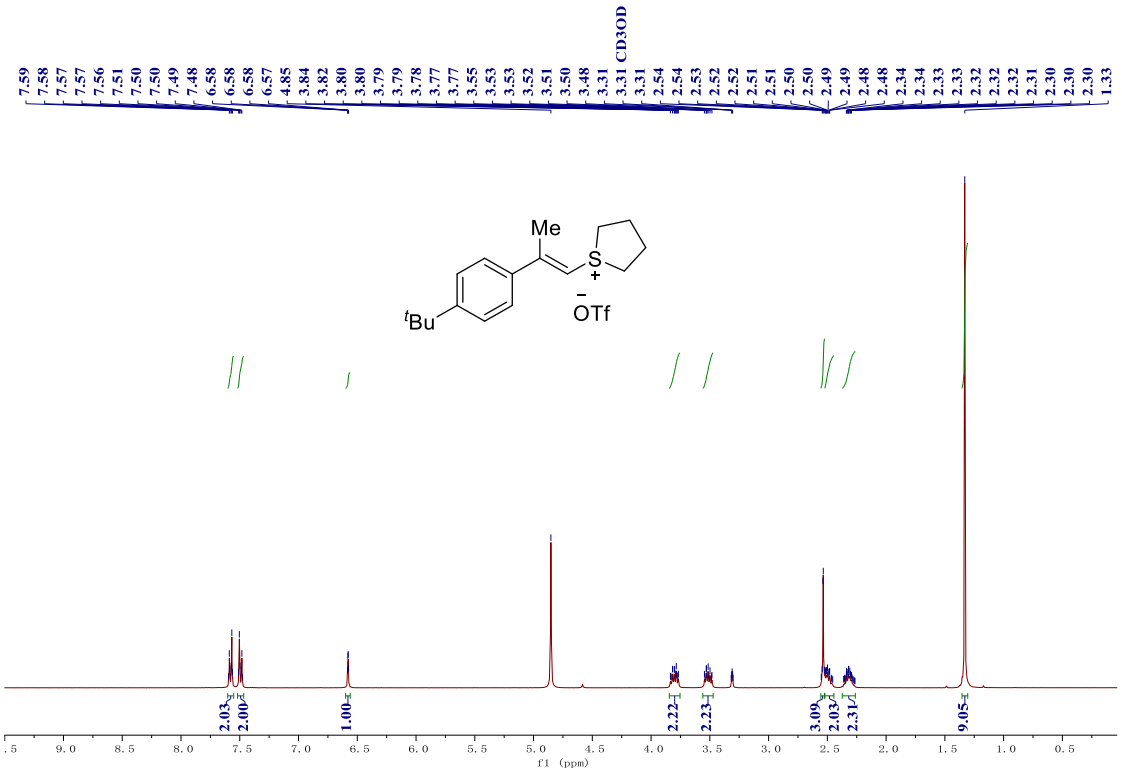
[6] B. Xiong, X. Zeng, S. Geng, S. Chen, Y. He, Z. Feng, Thiyl radical promoted chemo- and regioselective oxidation of C＝C bonds using molecular oxygen *via* iron catalysis. *Green Chem.* **2018**, *20*, 4521−4527.

8. ^{1}H, ^{13}C, and ^{19}F NMR Spectra

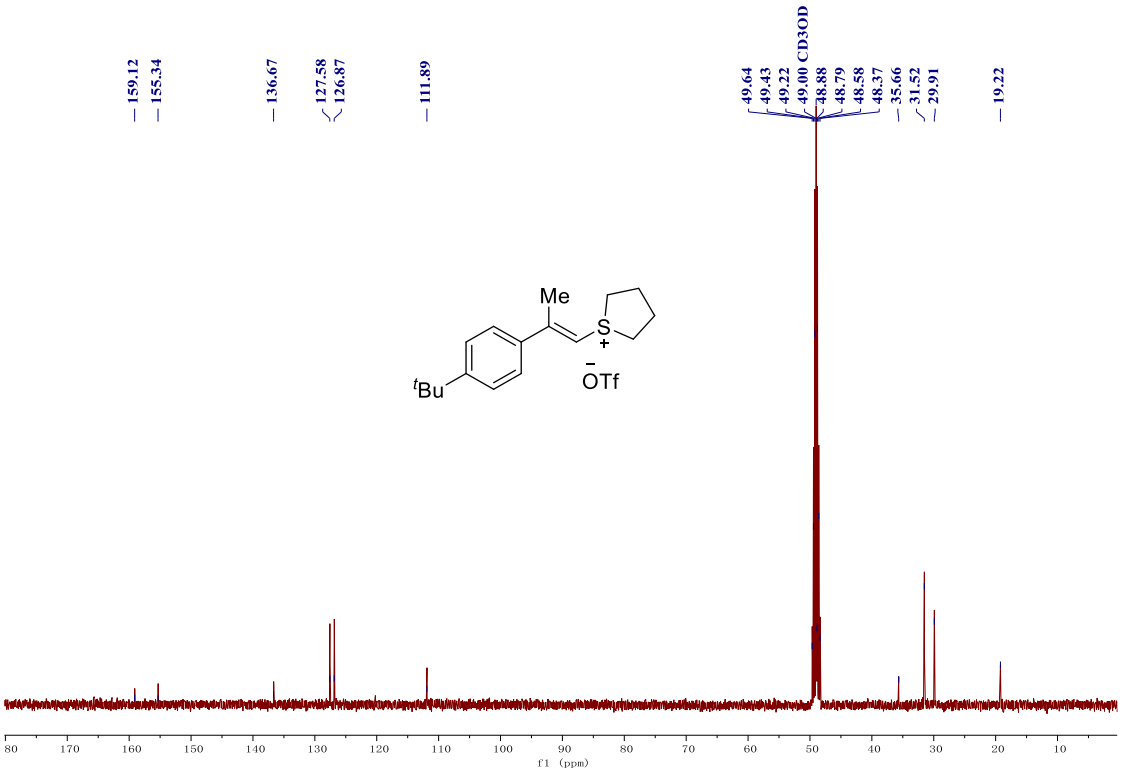
^{1}H NMR Spectra of compound 1a (500 MHz, CD_3OD)



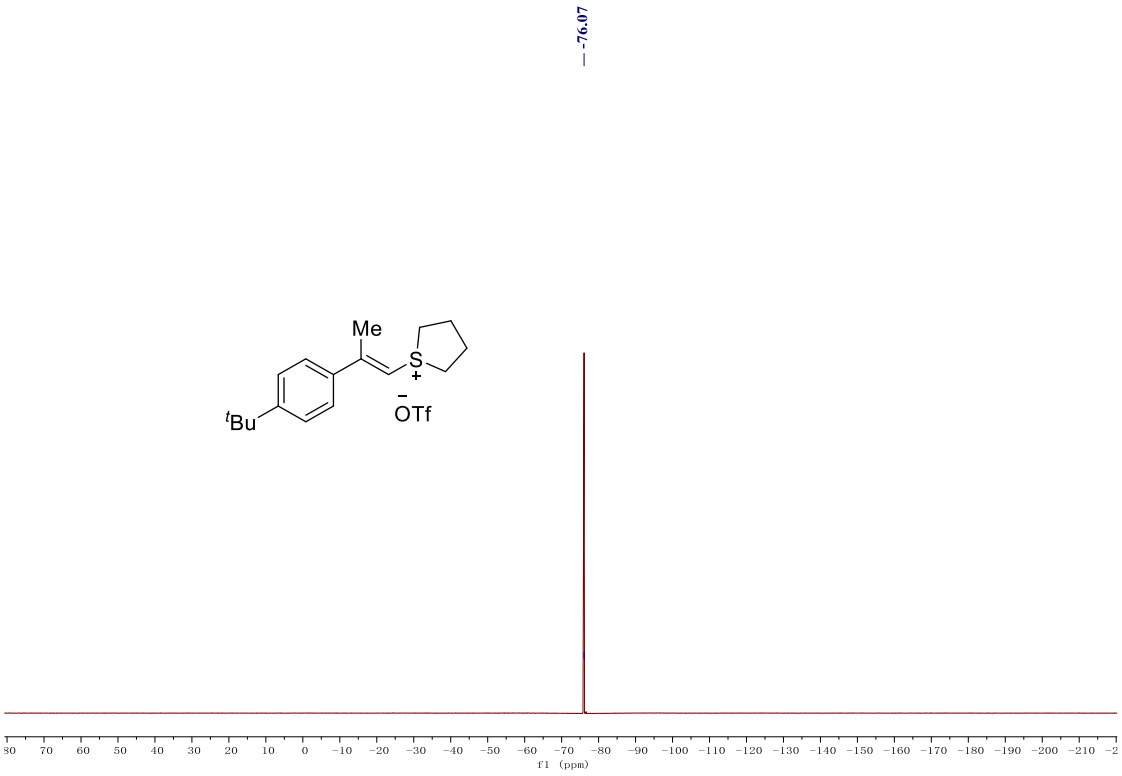
^{1}H NMR Spectra of compound 1b (400 MHz, CD_3OD)



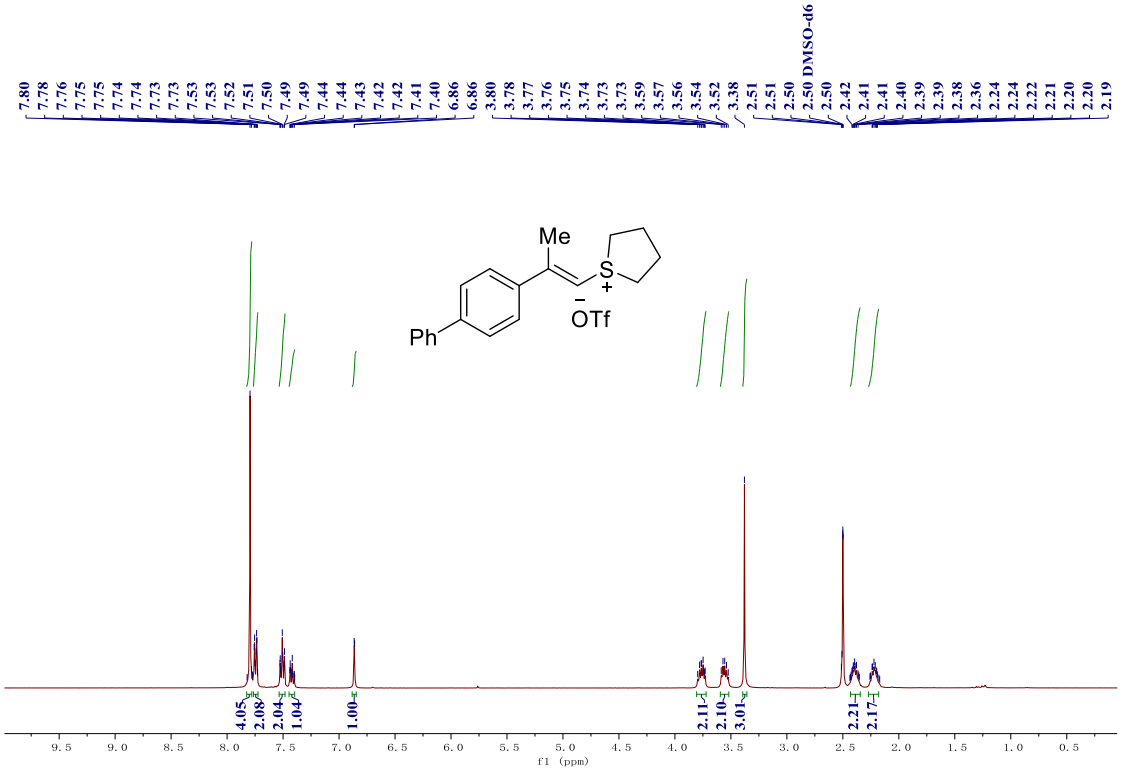
^{13}C NMR Spectra of compound 1b (101 MHz, CD_3OD)



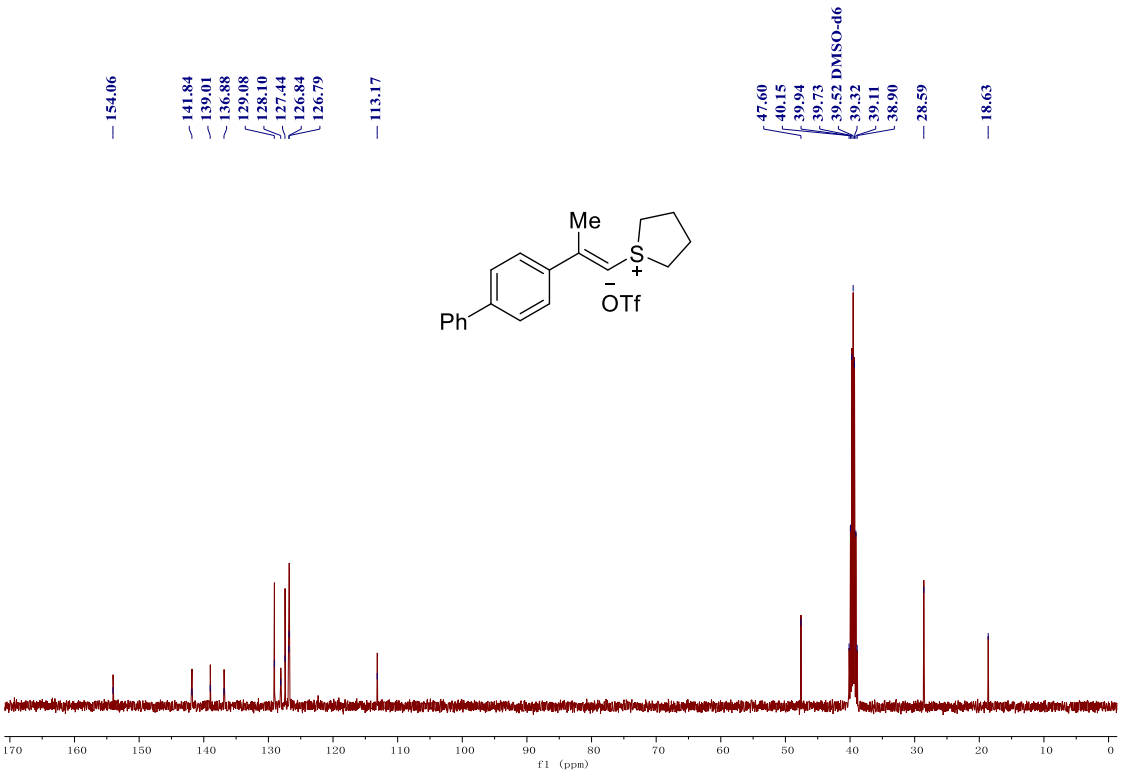
^{19}F NMR Spectra of compound 1b (376 MHz, CD_3OD)



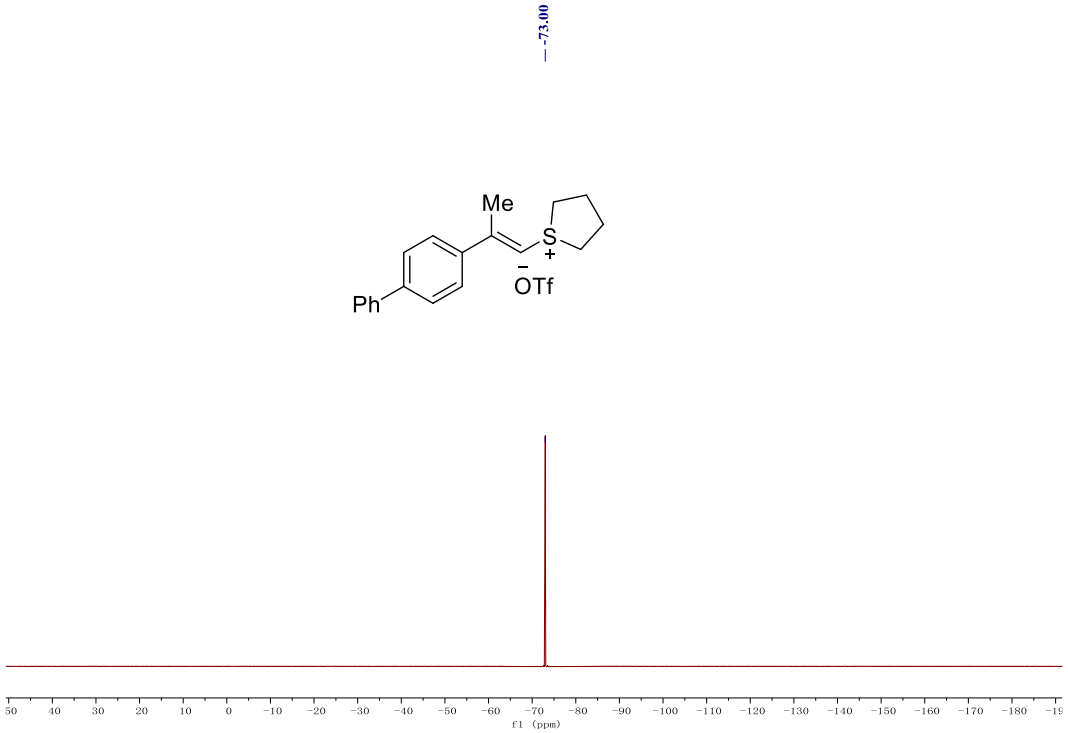
^{1}H NMR Spectra of compound 1c (400 MHz, DMSO-d_6)



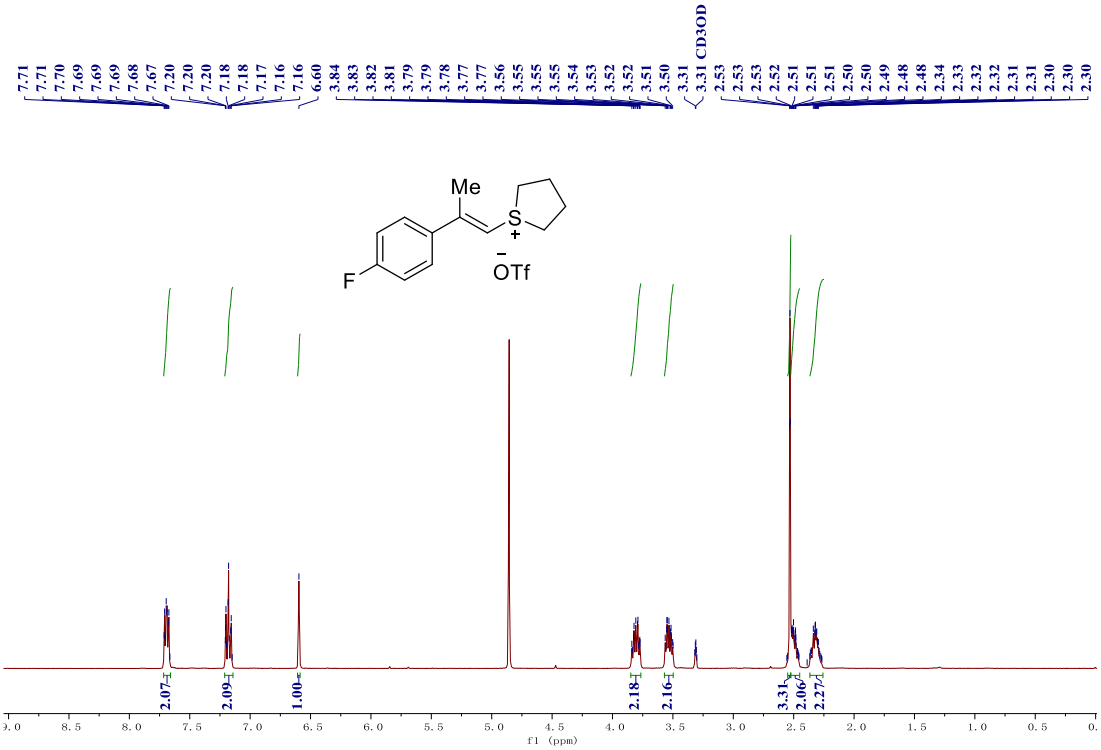
^{13}C NMR Spectra of compound 1c (101 MHz, DMSO-d_6)



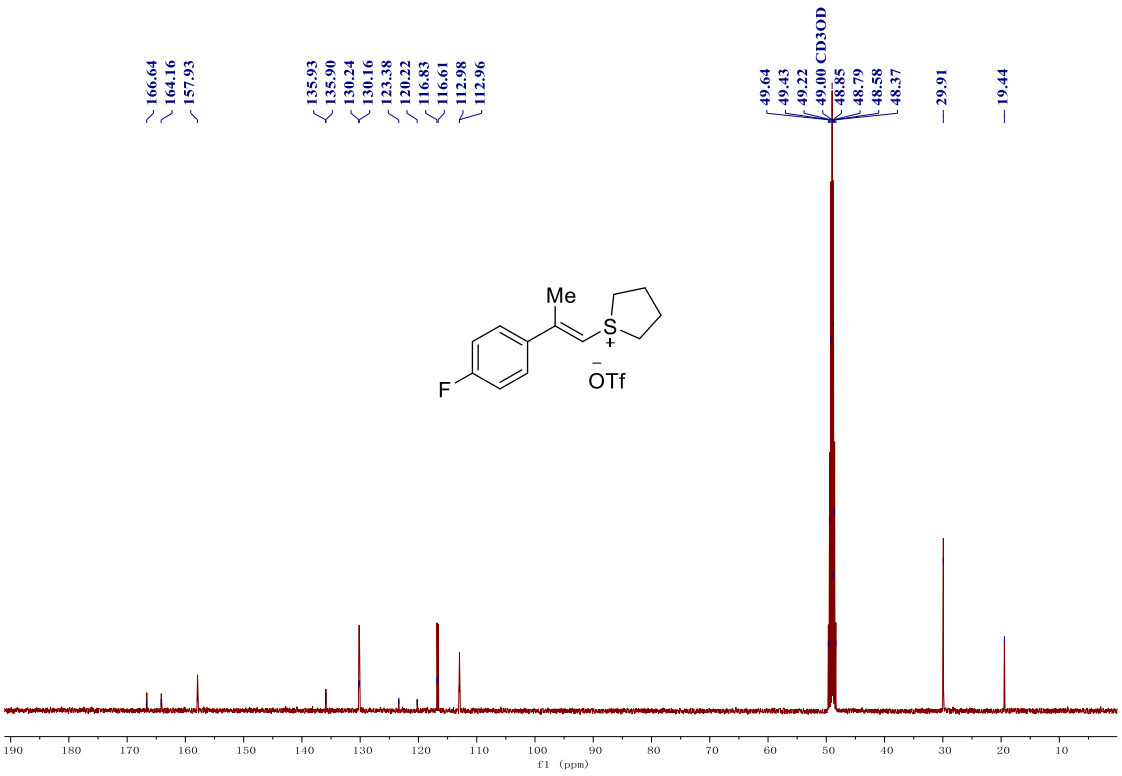
^{19}F NMR Spectra of compound 1c (376 MHz, DMSO-d_6)



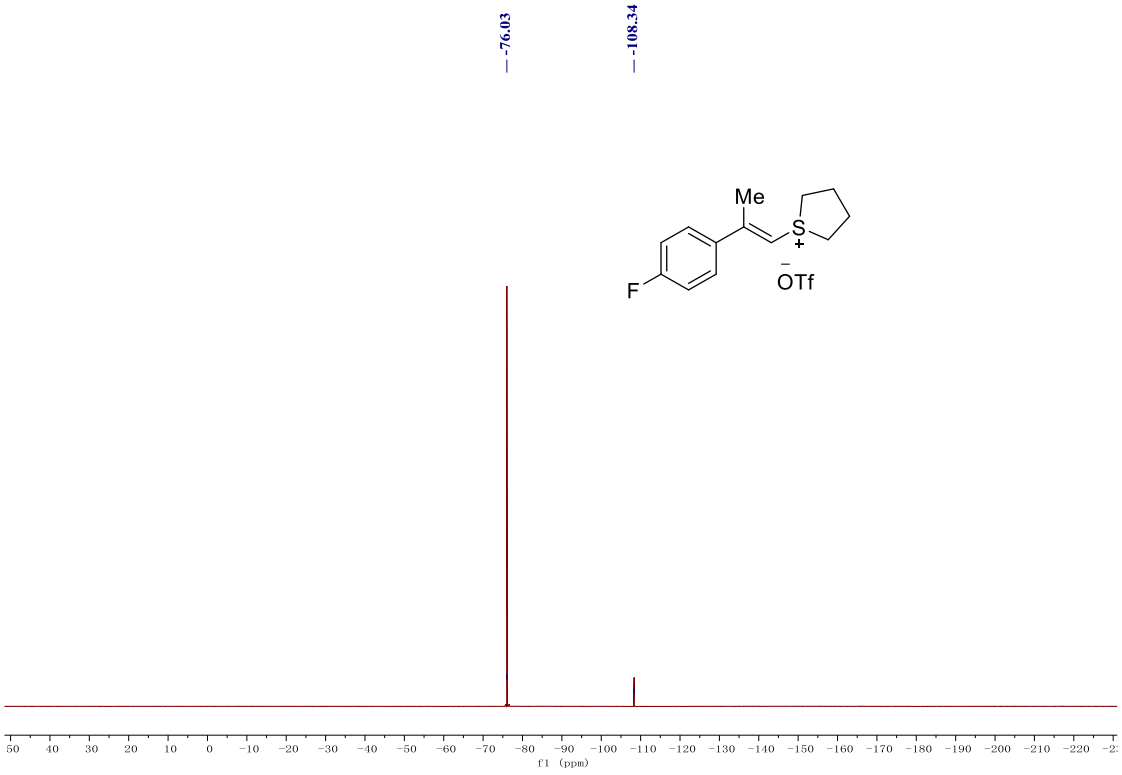
^{1}H NMR Spectra of compound 1d (400 MHz, CD_3OD)



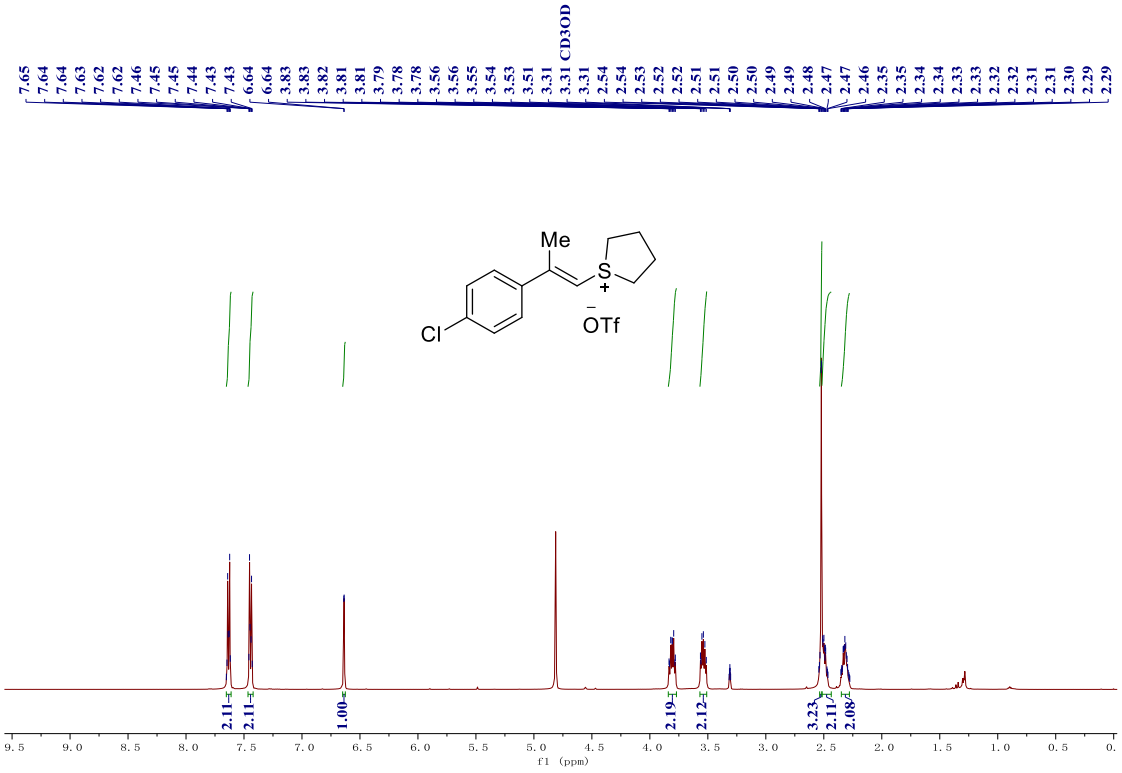
^{13}C NMR Spectra of compound 1d (101 MHz, CD_3OD)



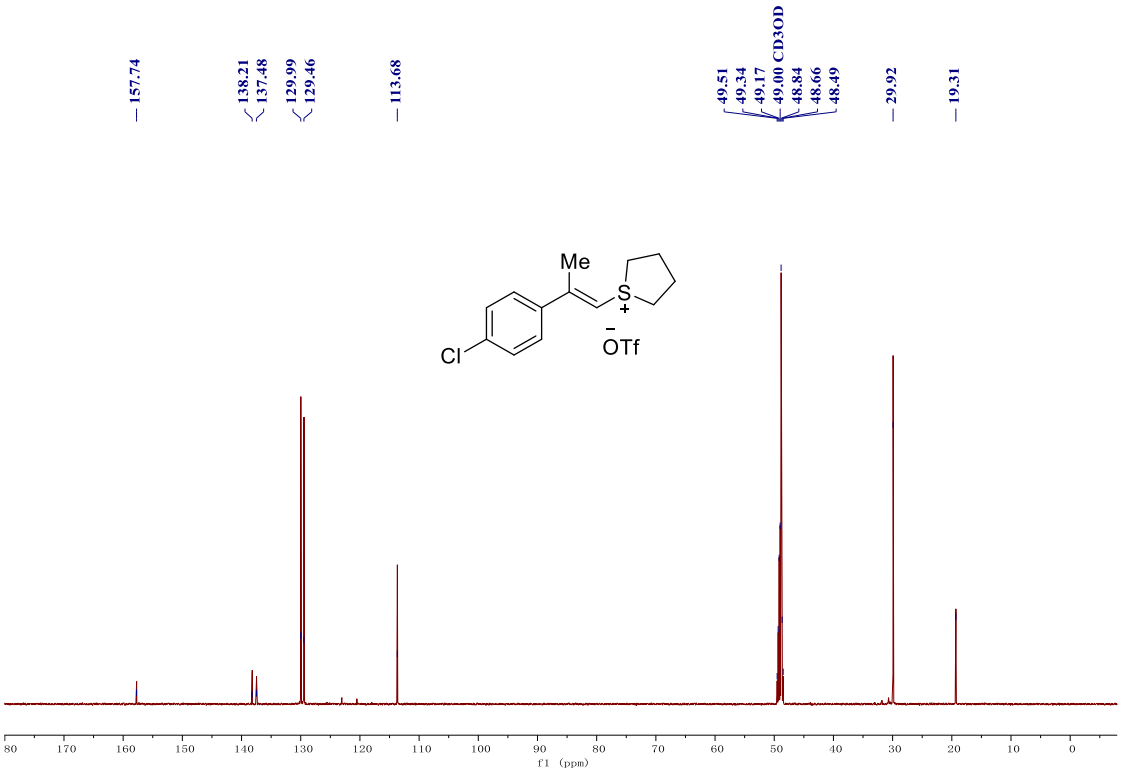
^{19}F NMR Spectra of compound 1d (376 MHz, CD_3OD)



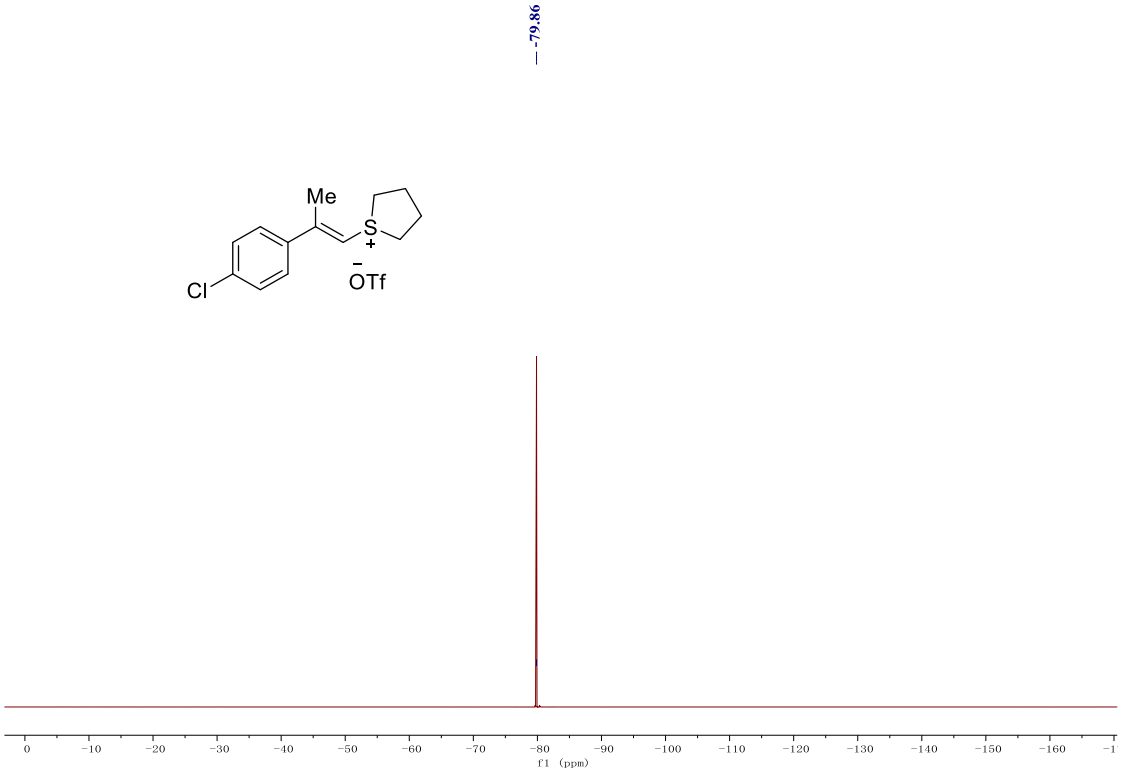
^{1}H NMR Spectra of compound 1e (400 MHz, CD_3OD)



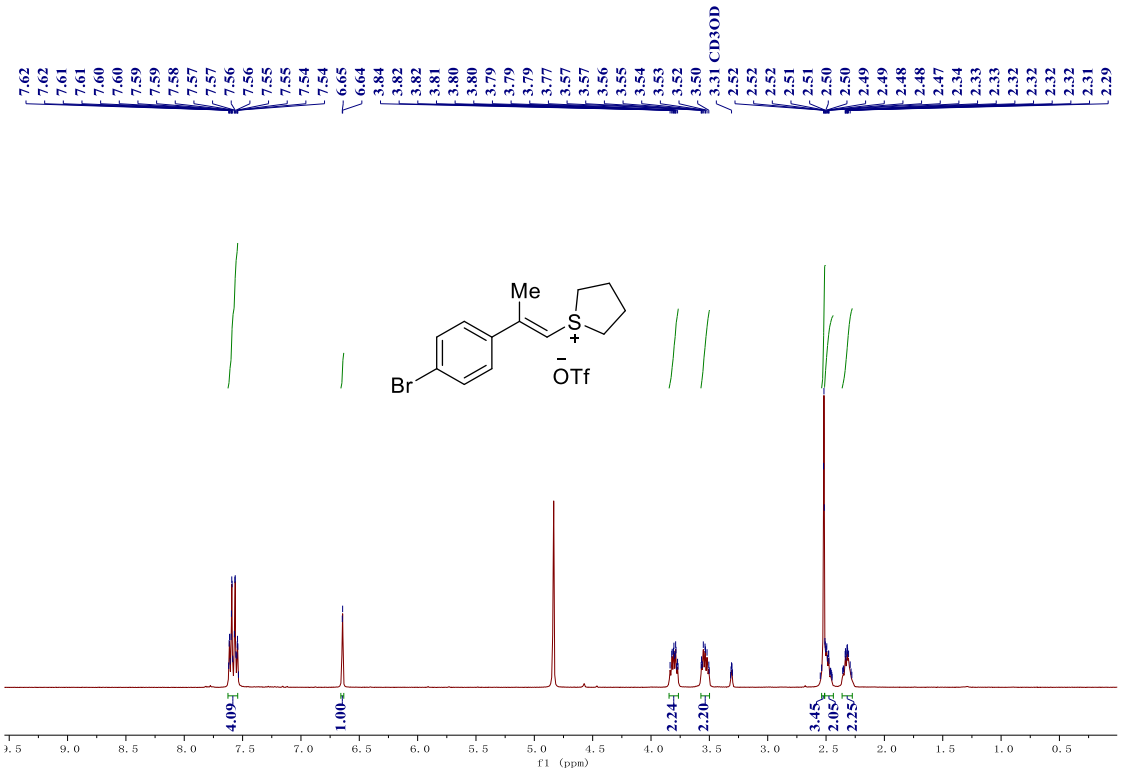
^{13}C NMR Spectra of compound 1e (101 MHz, CD_3OD)



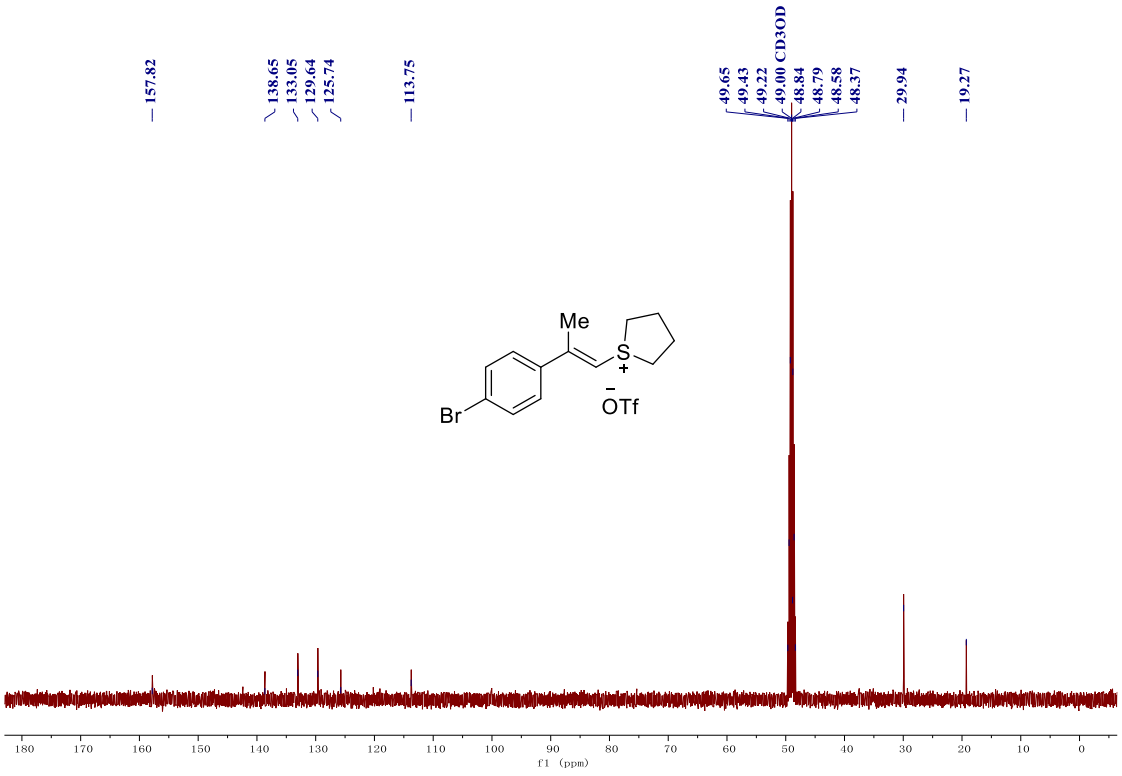
^{19}F NMR Spectra of compound 1e (376 MHz, CD_3OD)



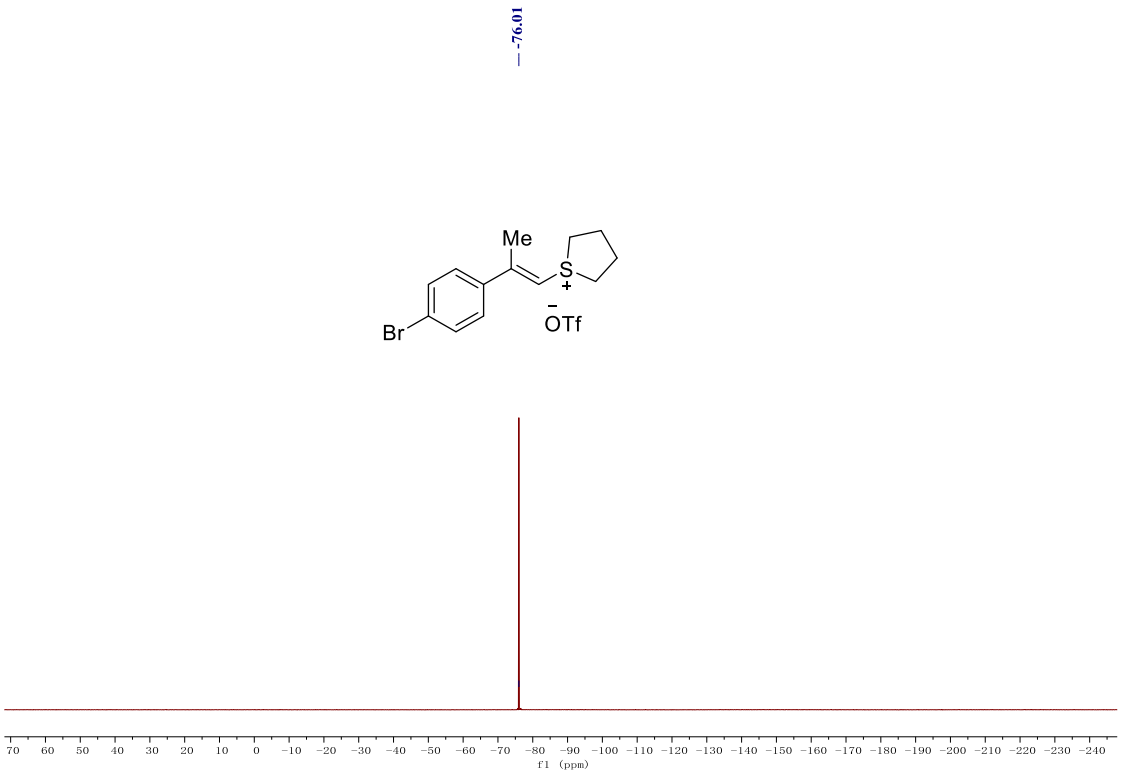
^{1}H NMR Spectra of compound 1f (400 MHz, CD_3OD)



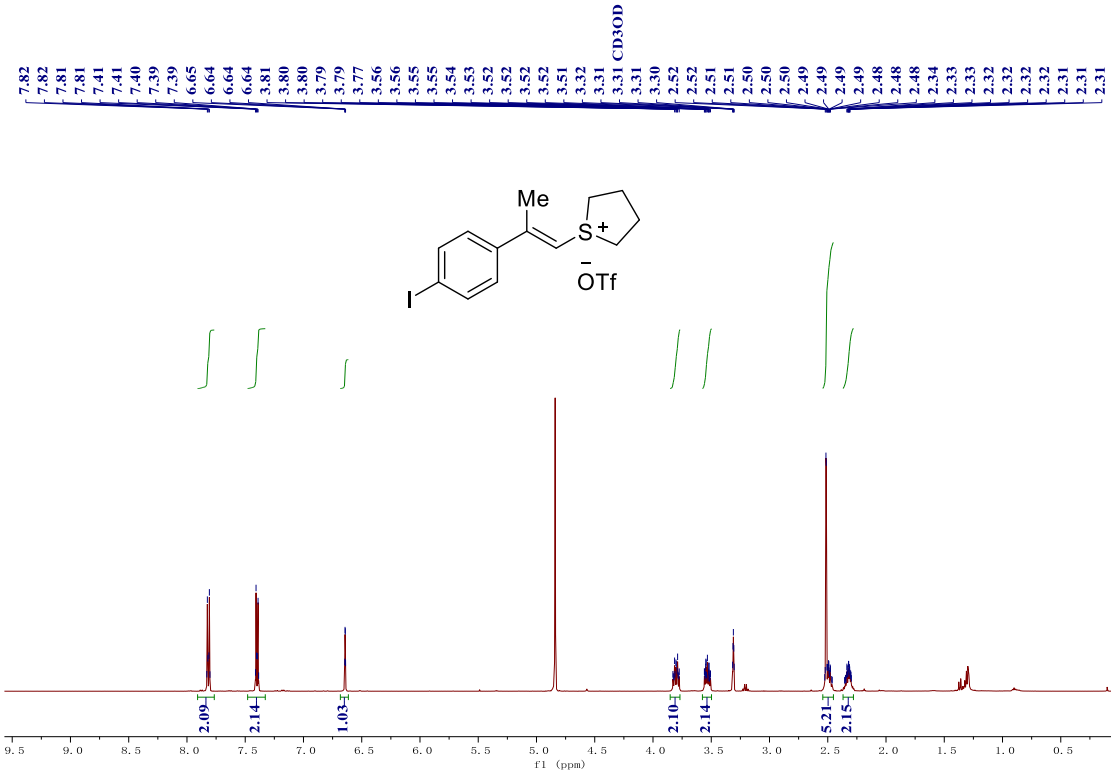
^{13}C NMR Spectra of compound 1f (101 MHz, CD_3OD)



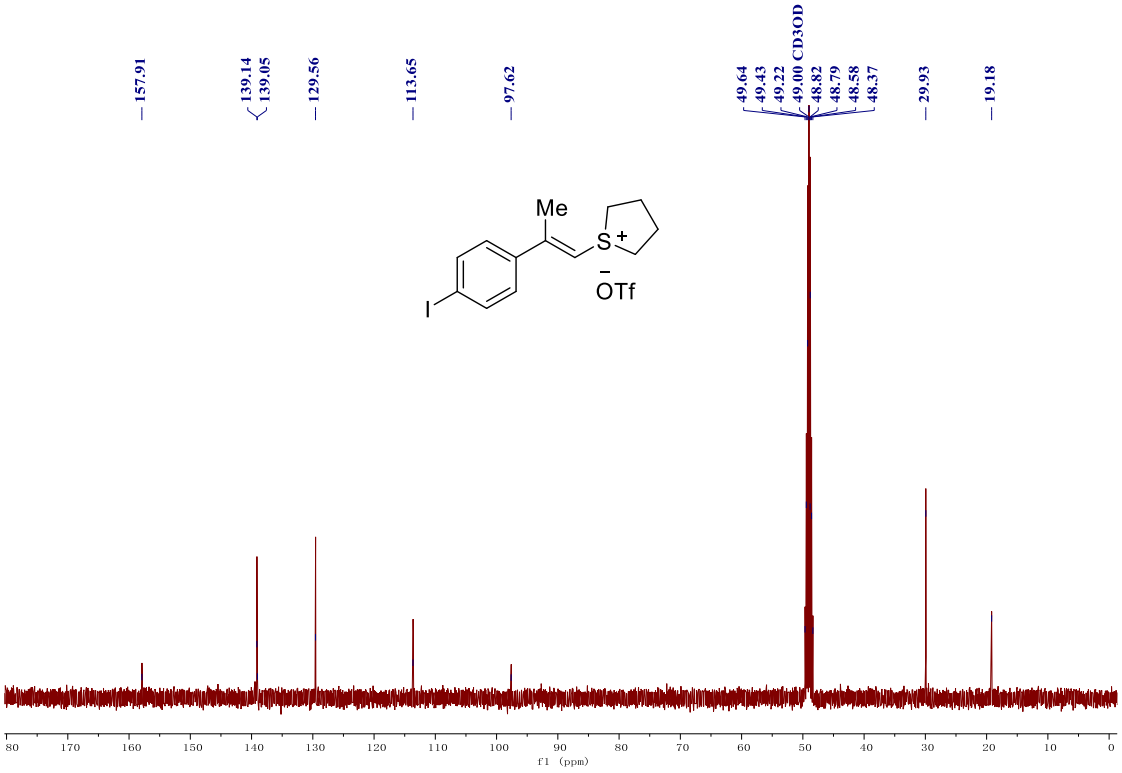
^{19}F NMR Spectra of compound 1f (376 MHz, CD_3OD)



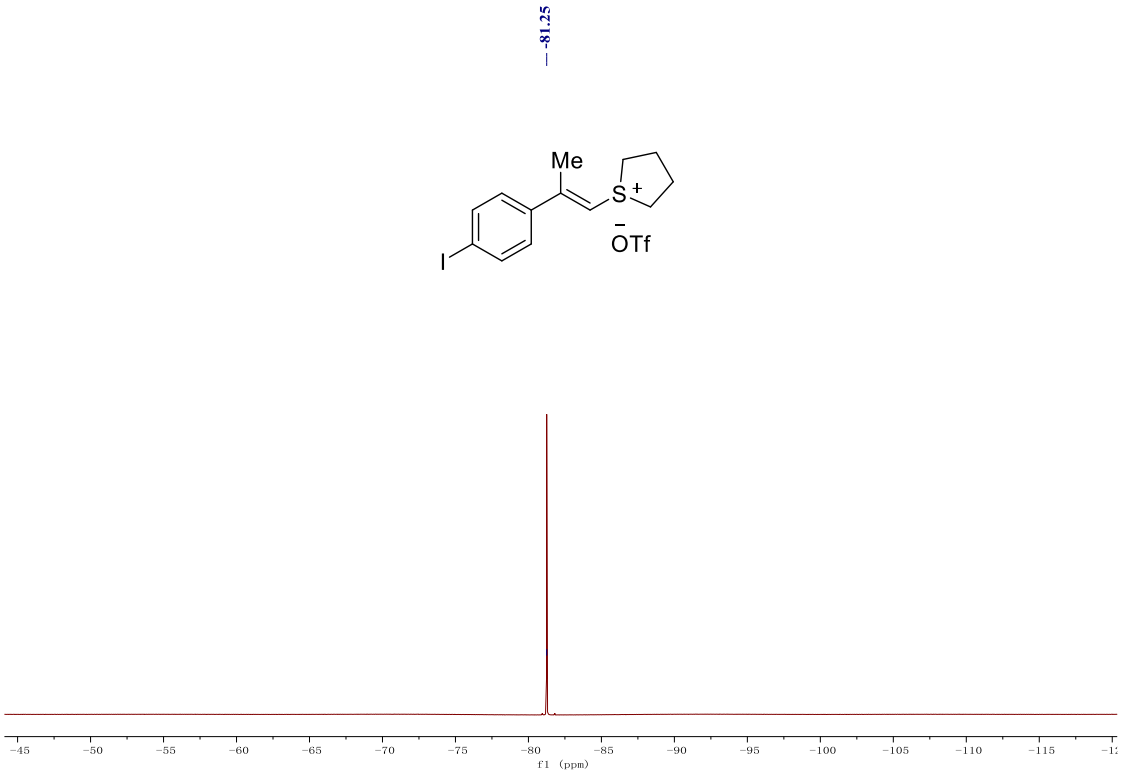
^{1}H NMR Spectra of compound 1g (400 MHz, CD_3OD)



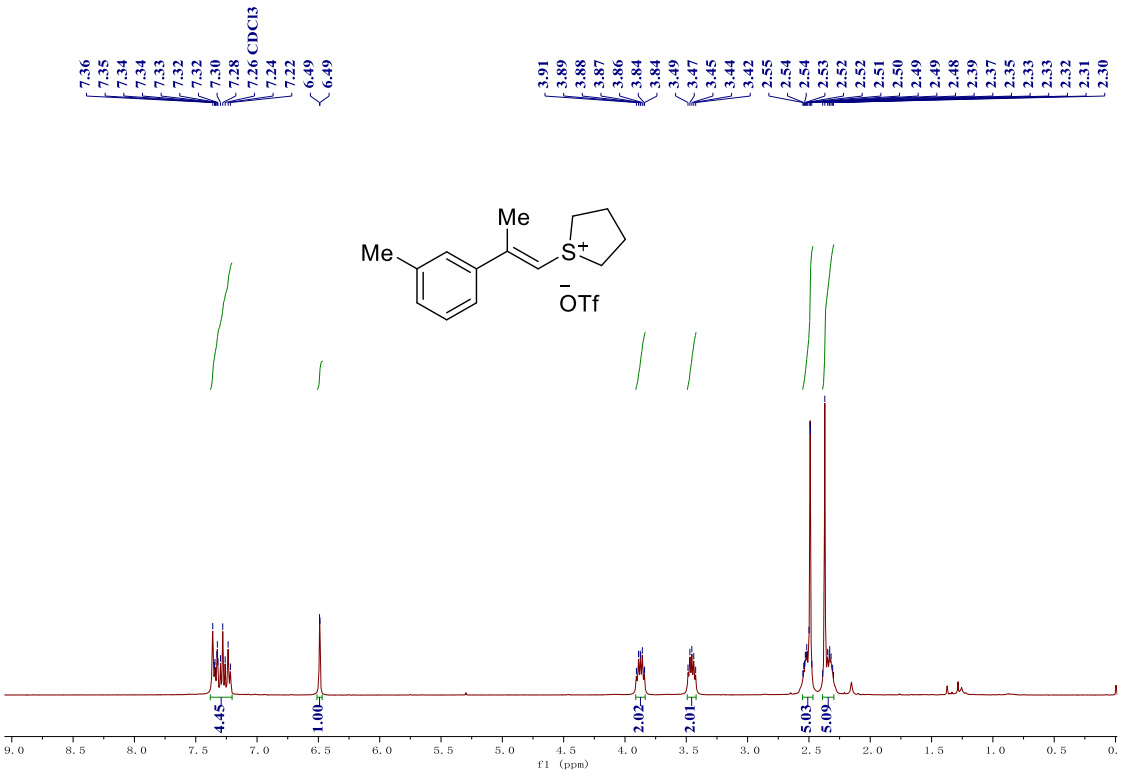
^{13}C NMR Spectra of compound 1g (101 MHz, CD_3OD)



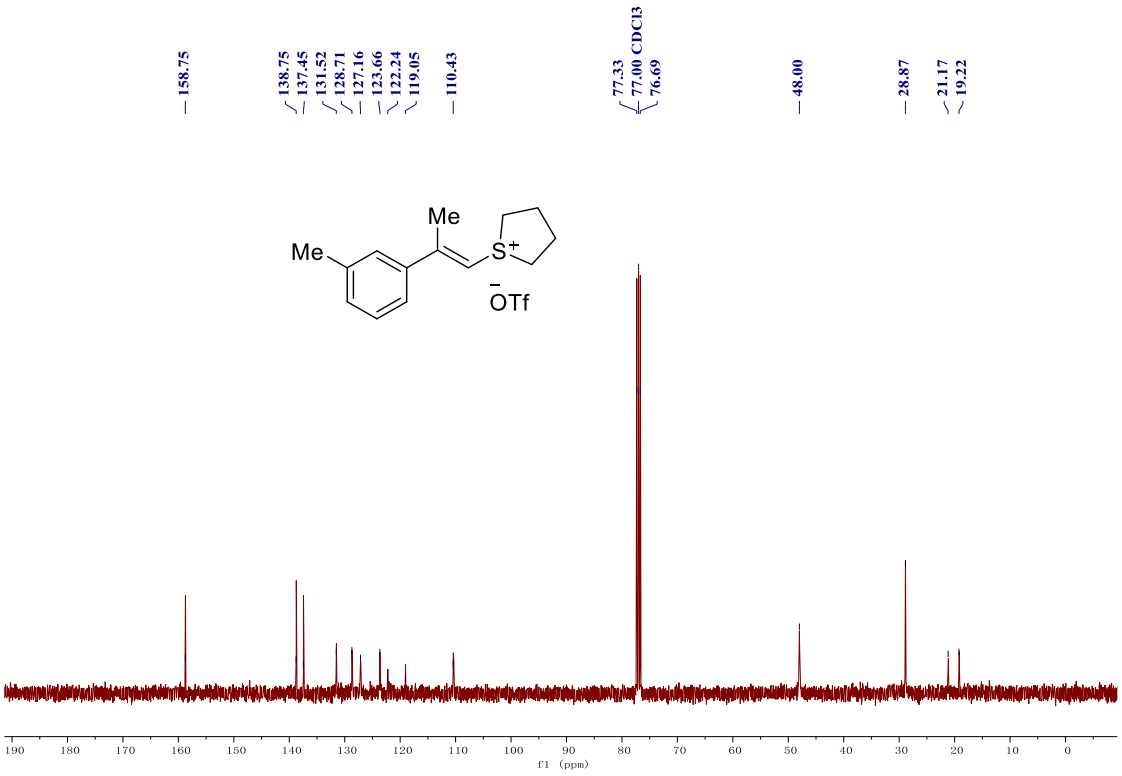
^{19}F NMR Spectra of compound 1g (376 MHz, CD_3OD)



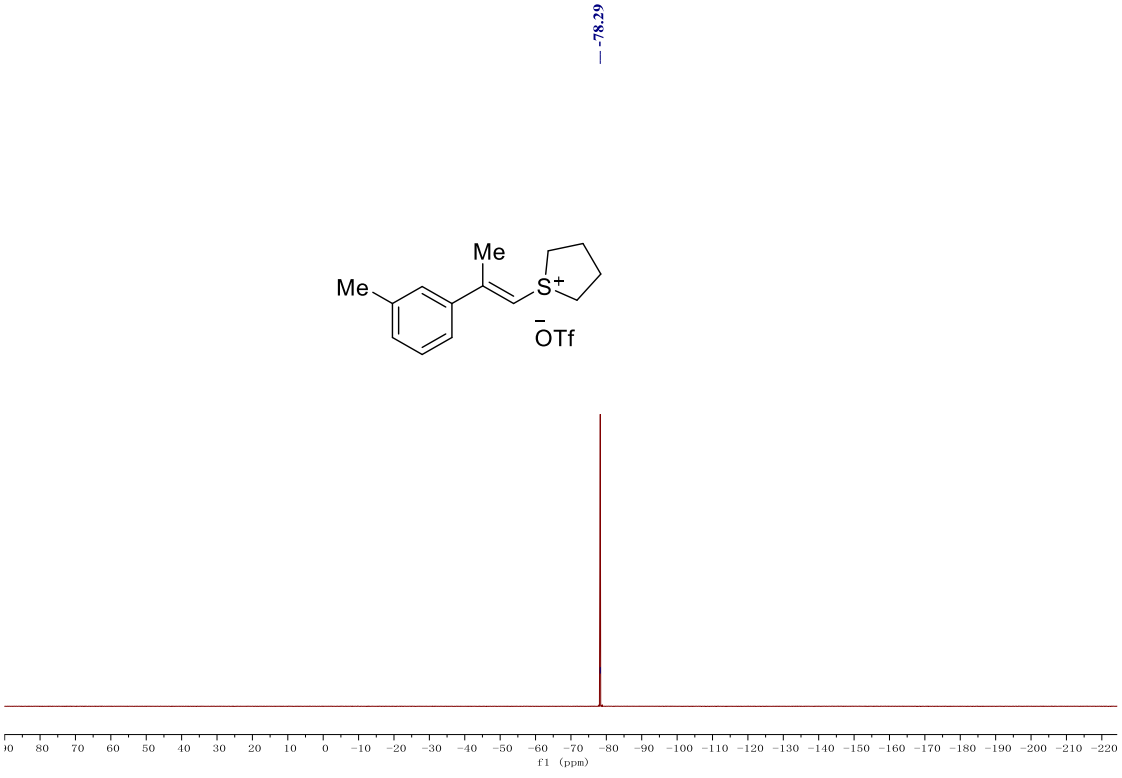
^{1}H NMR Spectra of compound 1h (400 MHz, $CDCl_3$)



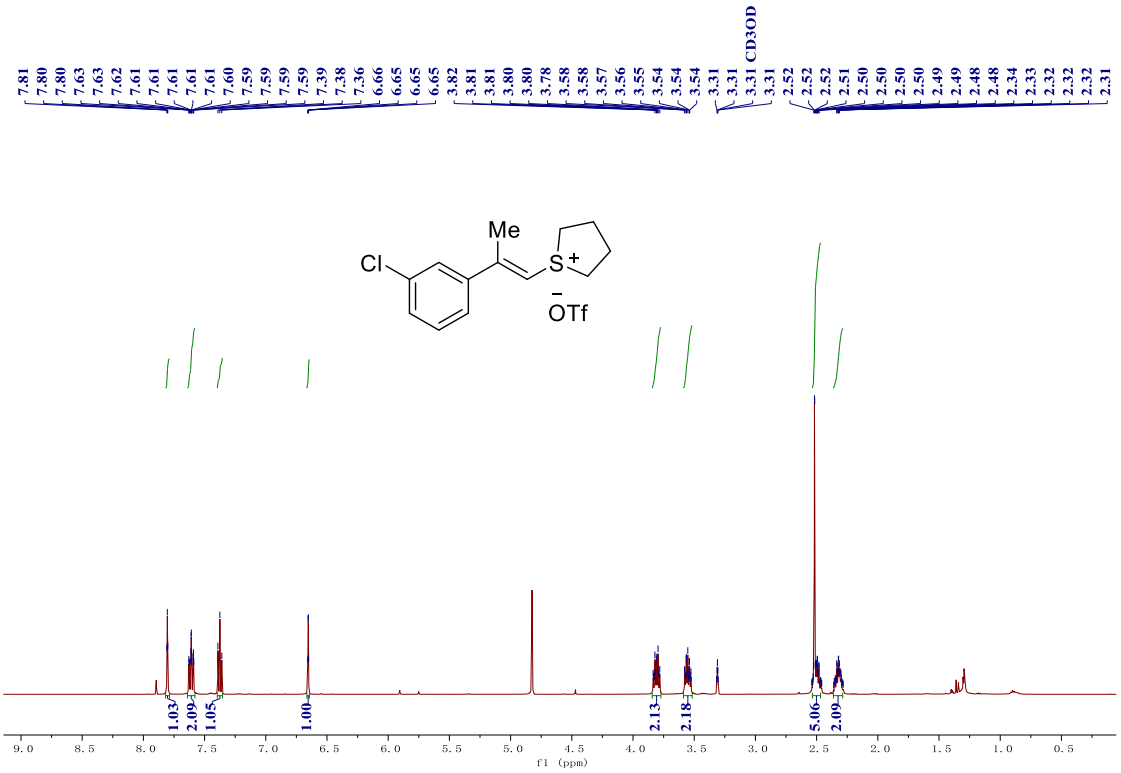
^{13}C NMR Spectra of compound 1h (101 MHz, $CDCl_3$)



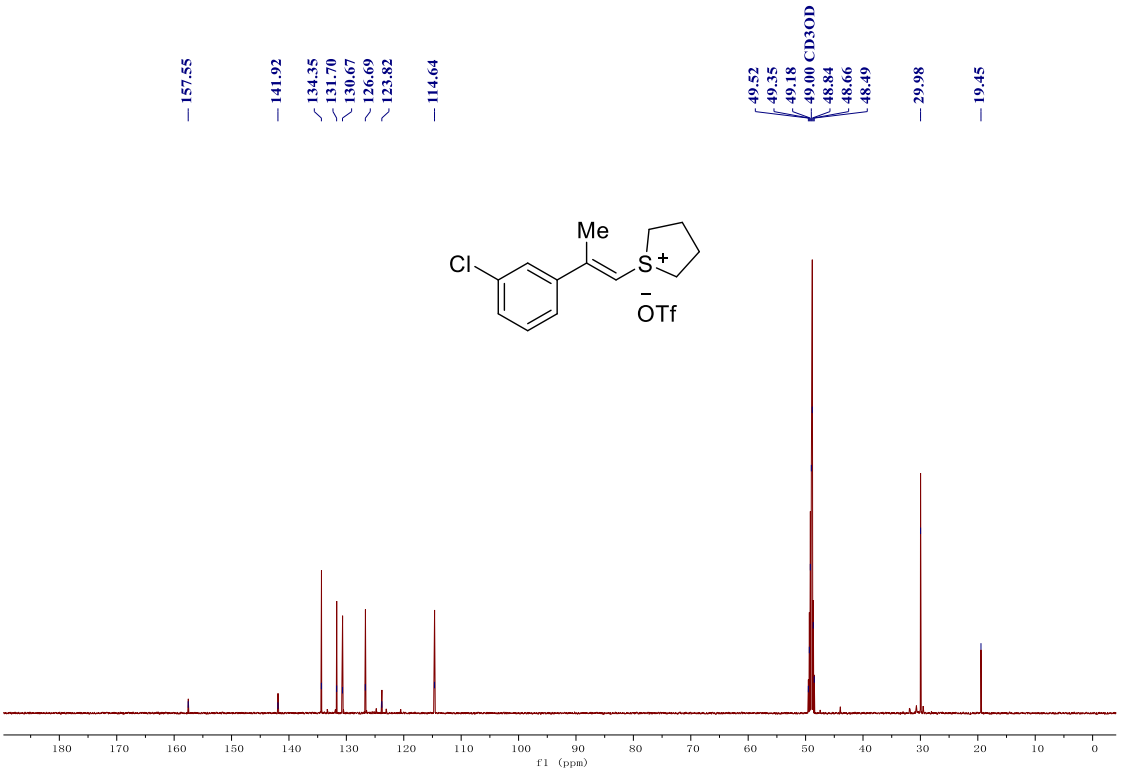
^{19}F NMR Spectra of compound 1h (376 MHz, $CDCl_3$)



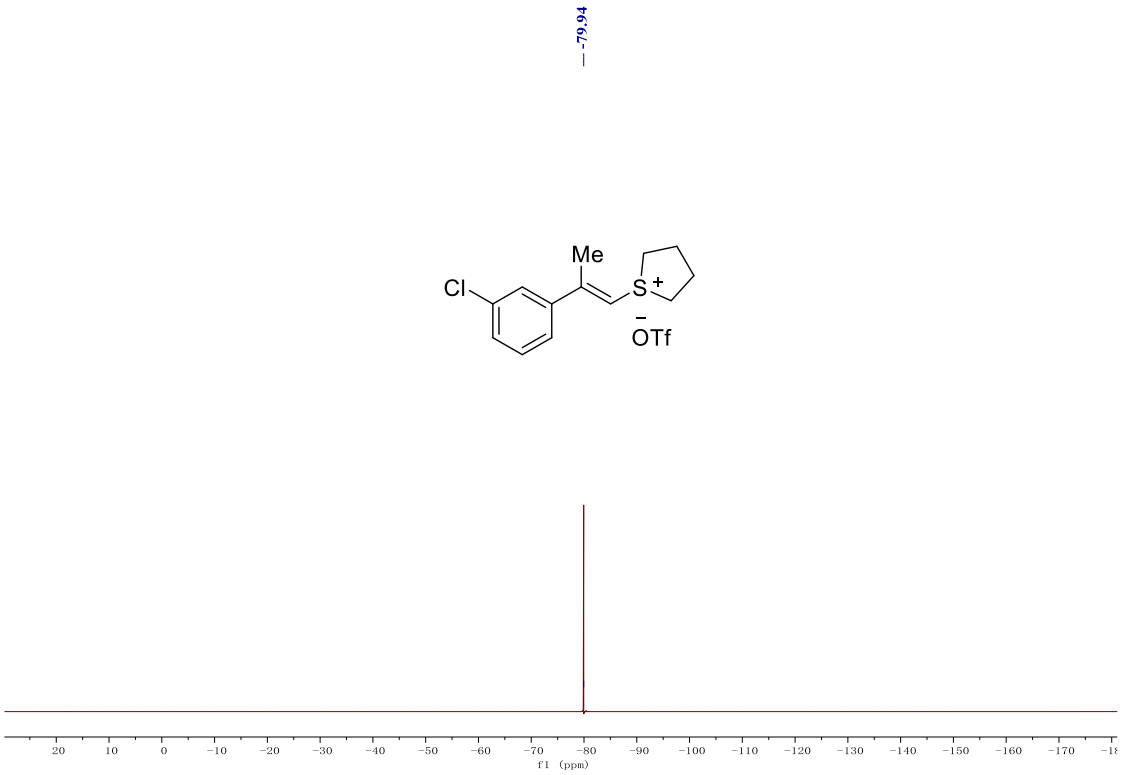
^{1}H NMR Spectra of compound 1i (500 MHz, CD_3OD)



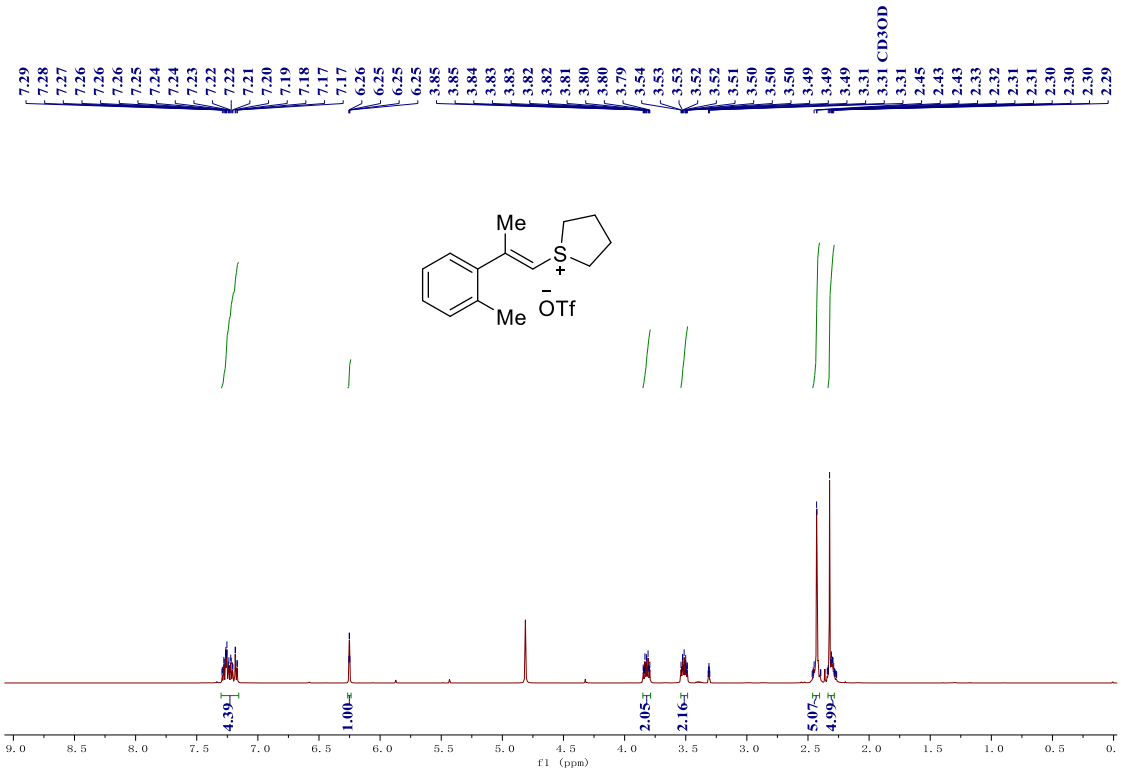
^{13}C NMR Spectra of compound 1i (126 MHz, CD_3OD)



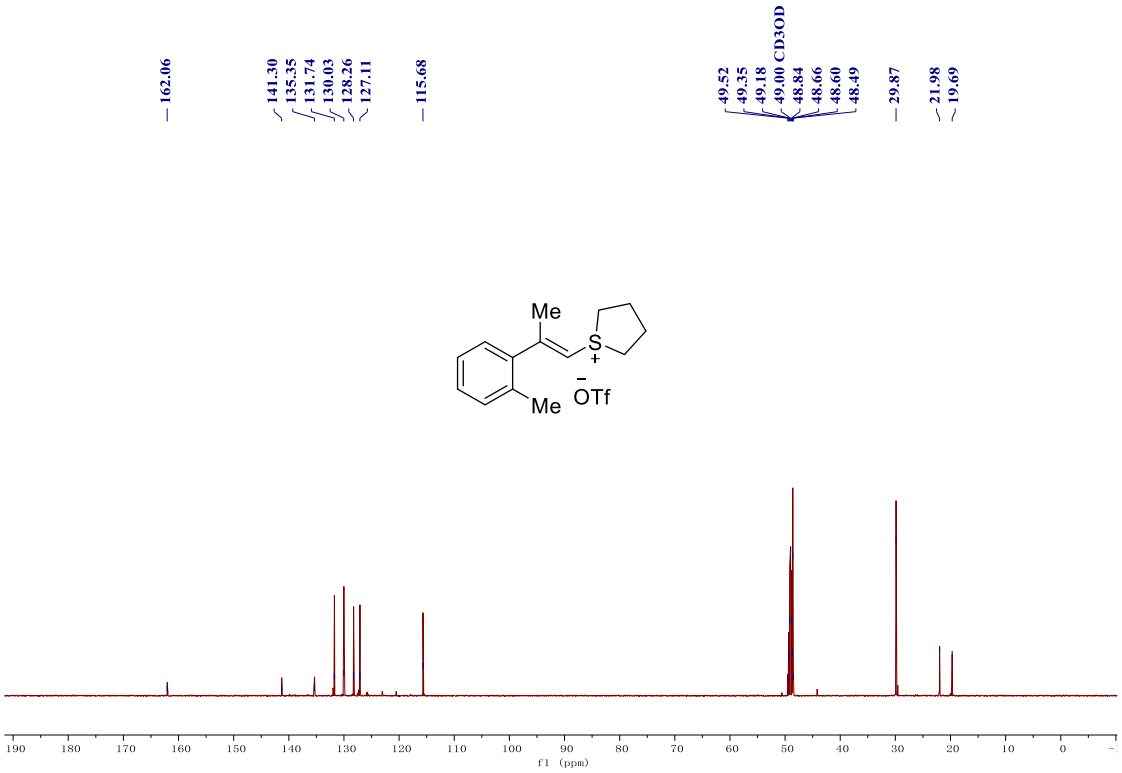
^{19}F NMR Spectra of compound 1i (471 MHz, CD_3OD)



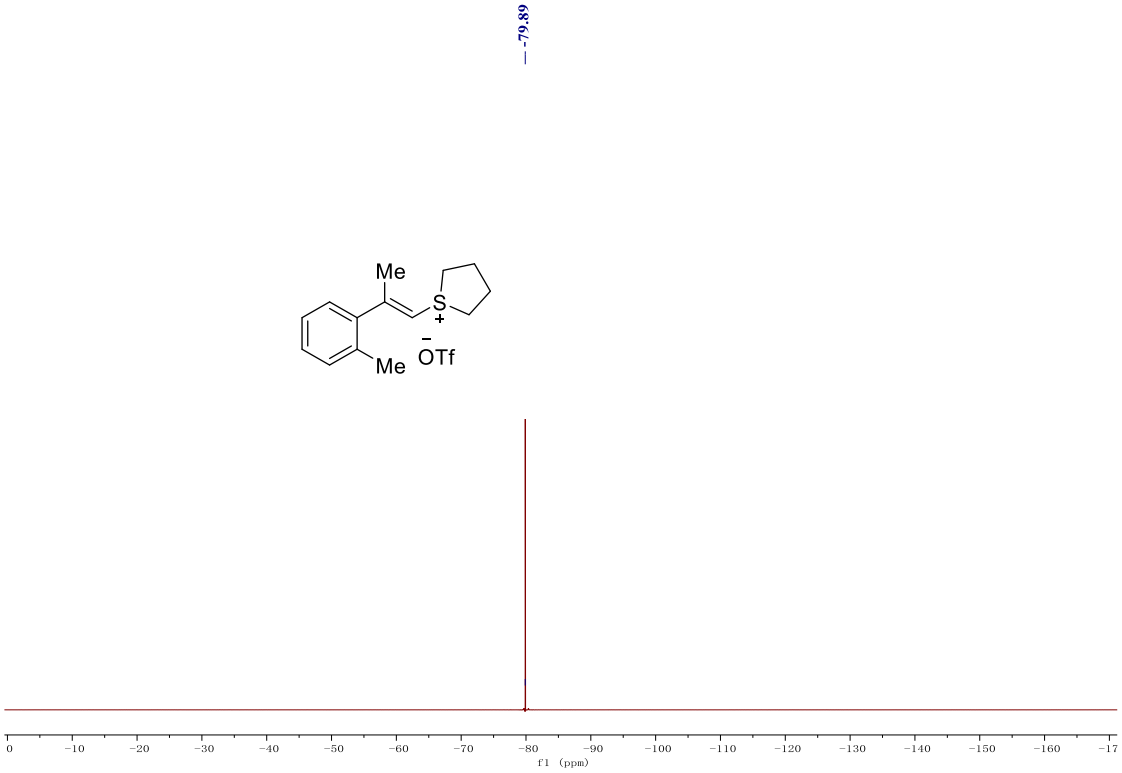
^{1}H NMR Spectra of compound 1j (400 MHz, CD_3OD)



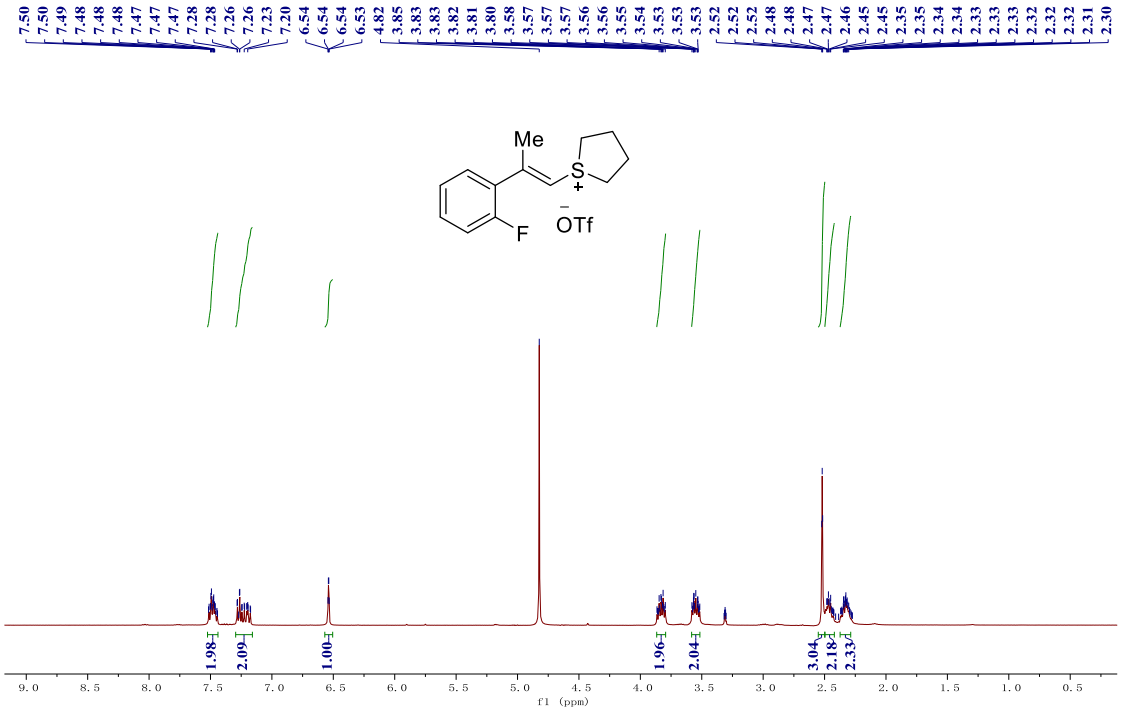
^{13}C NMR Spectra of compound 1j (101 MHz, CD_3OD)



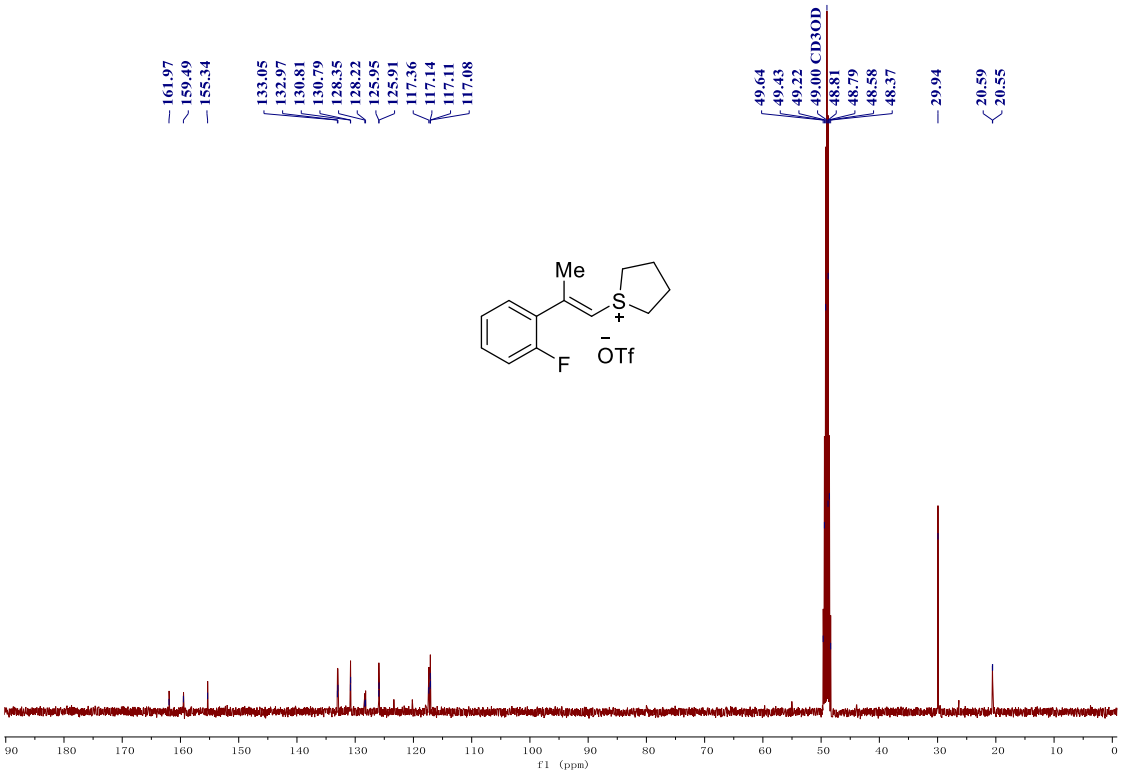
^{19}F NMR Spectra of compound 1j (376 MHz, CD_3OD)



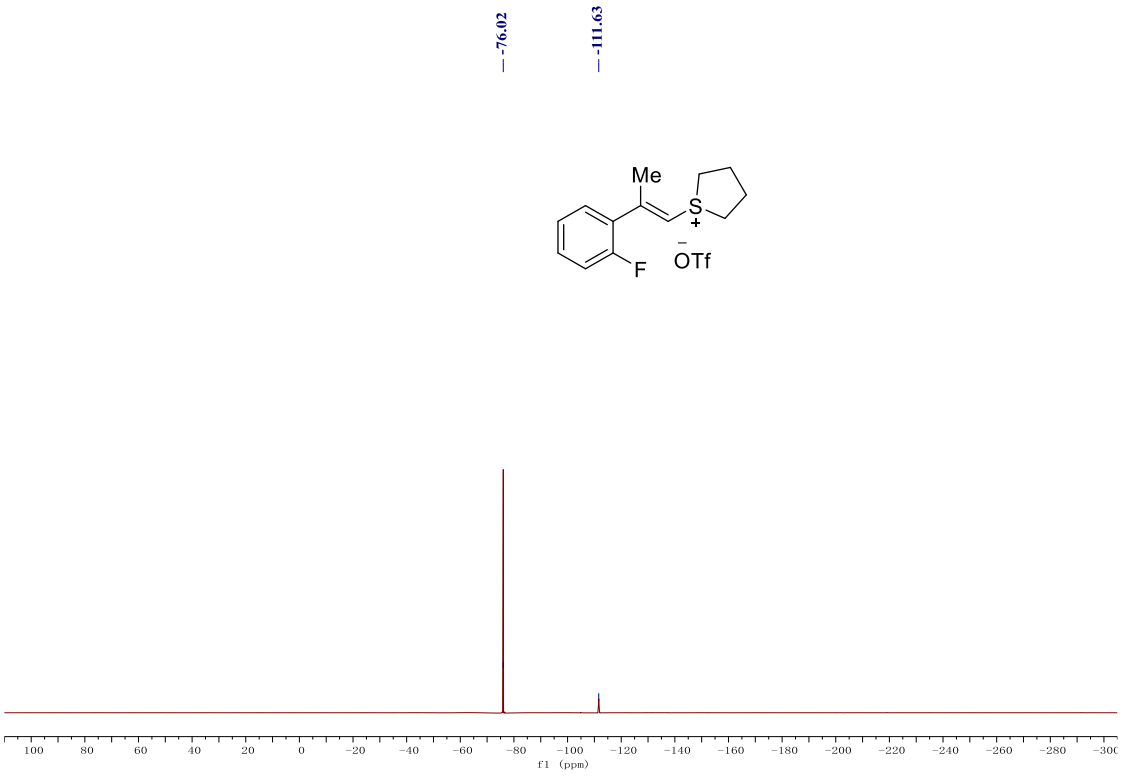
^{1}H NMR Spectra of compound 1k (400 MHz, CD_3OD)



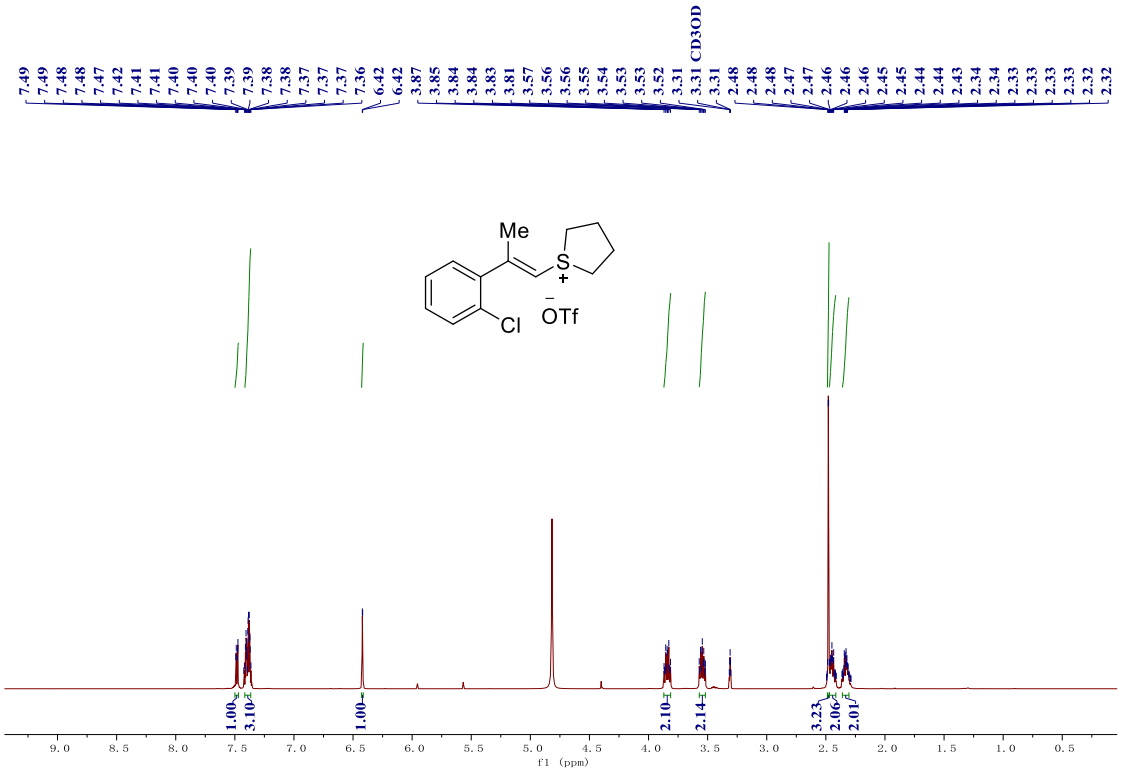
^{13}C NMR Spectra of compound 1k (101 MHz, CD_3OD)



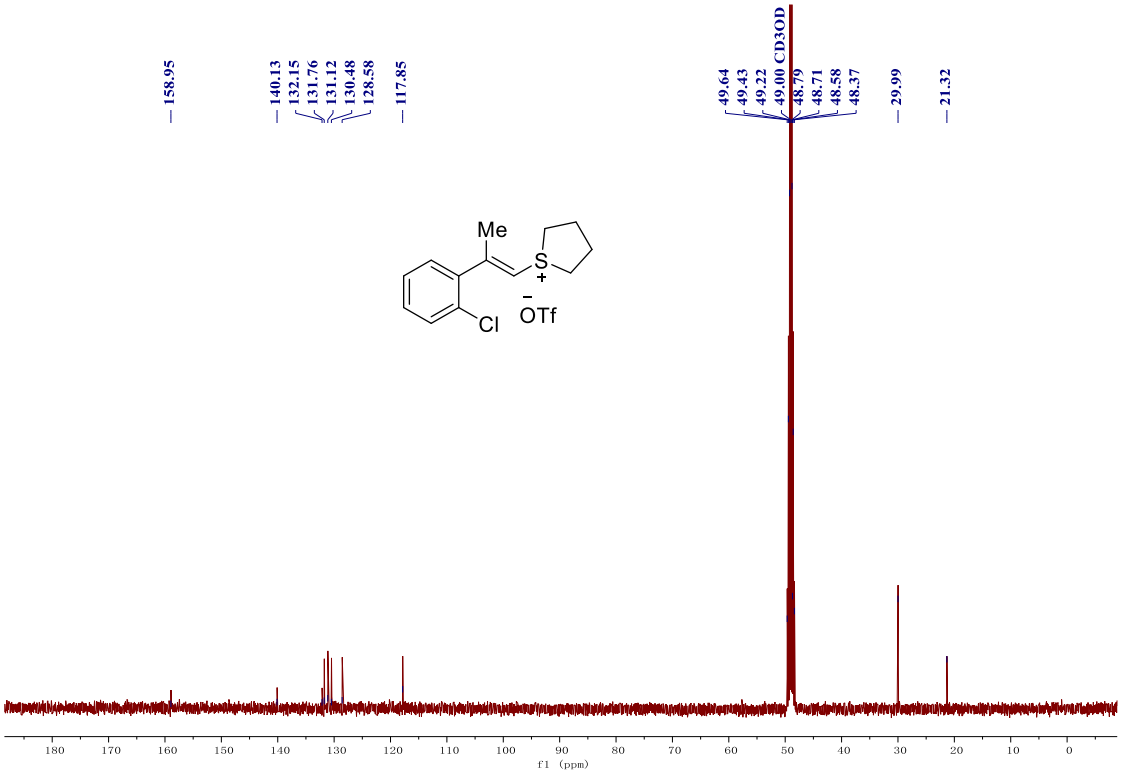
^{19}F NMR Spectra of compound 1k (376 MHz, CD_3OD)



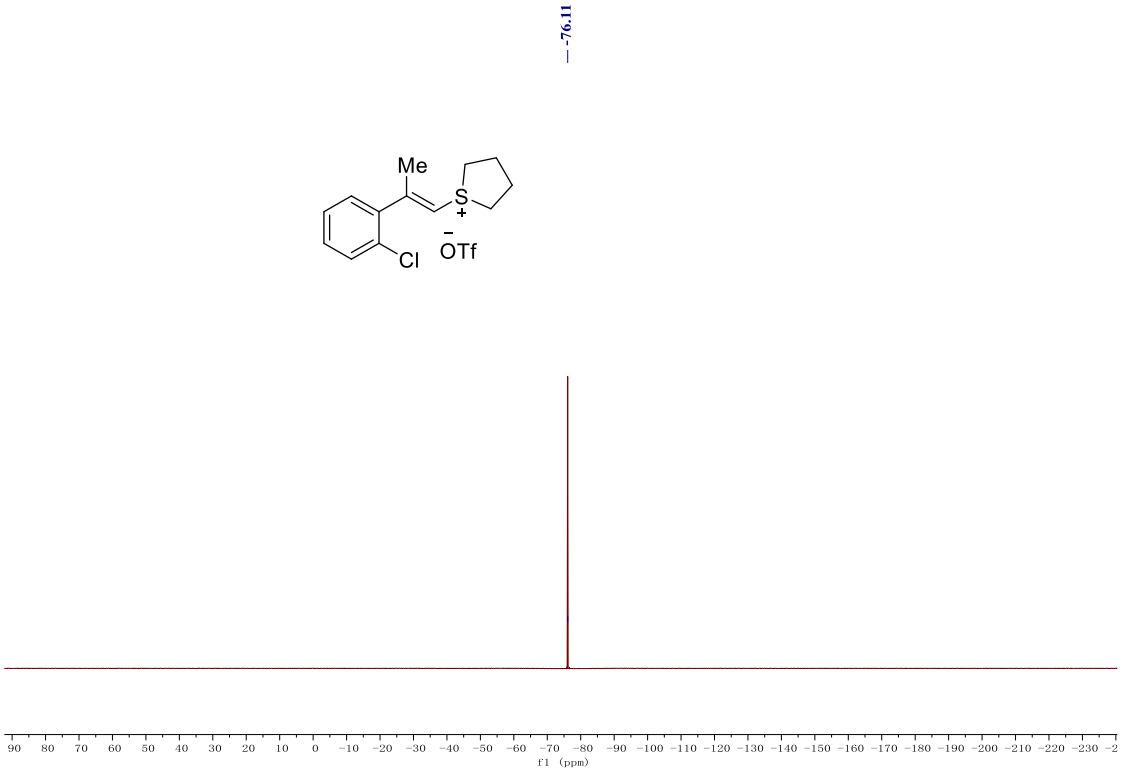
^{1}H NMR Spectra of compound 1l (400 MHz, CD_3OD)



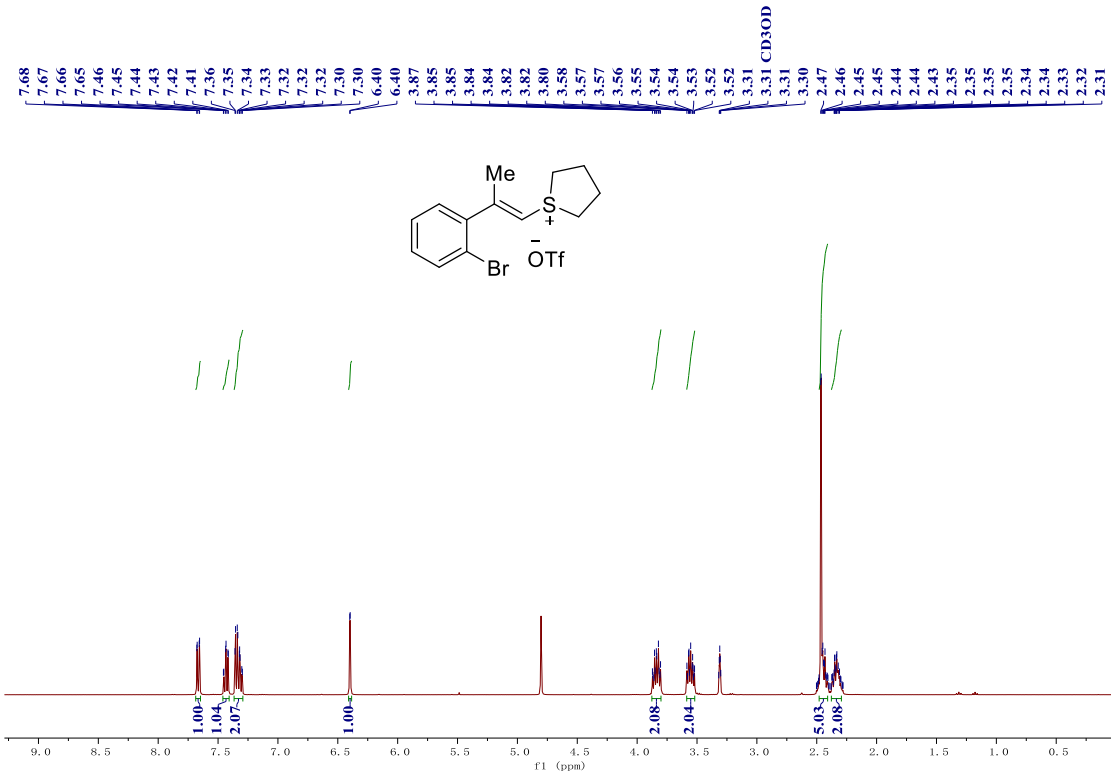
^{13}C NMR Spectra of compound 1l (101 MHz, CD_3OD)



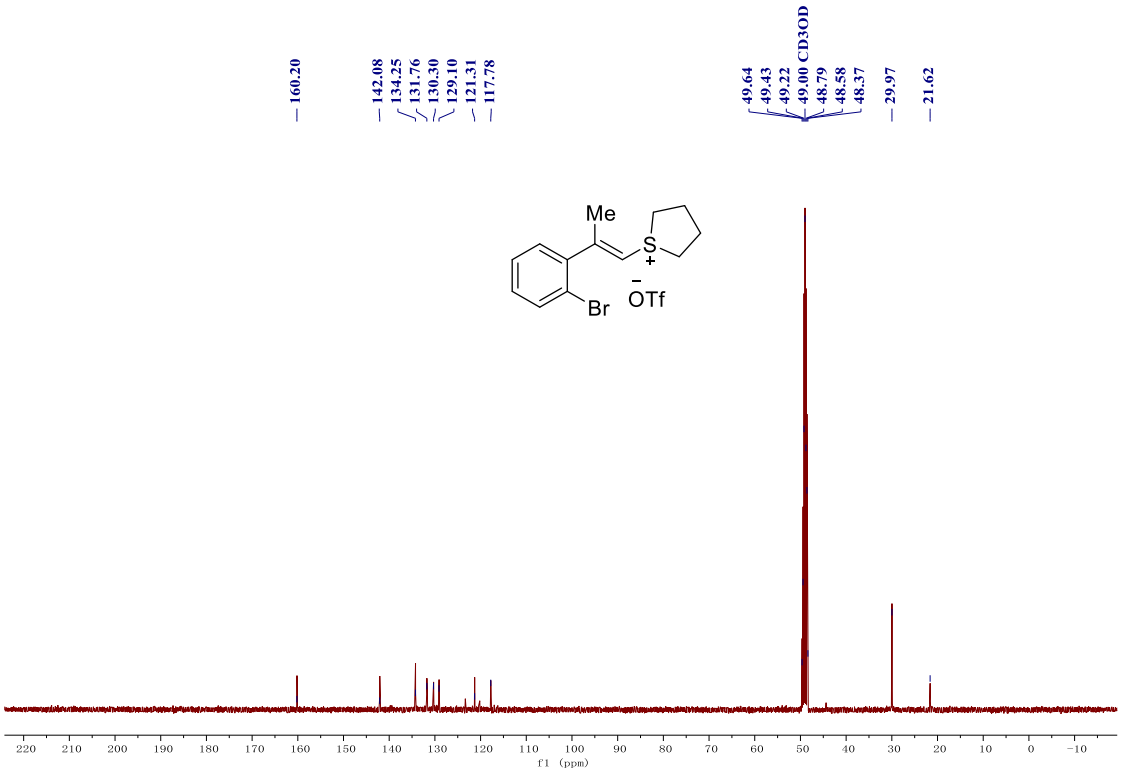
^{19}F NMR Spectra of compound 1l (376 MHz, CD_3OD)



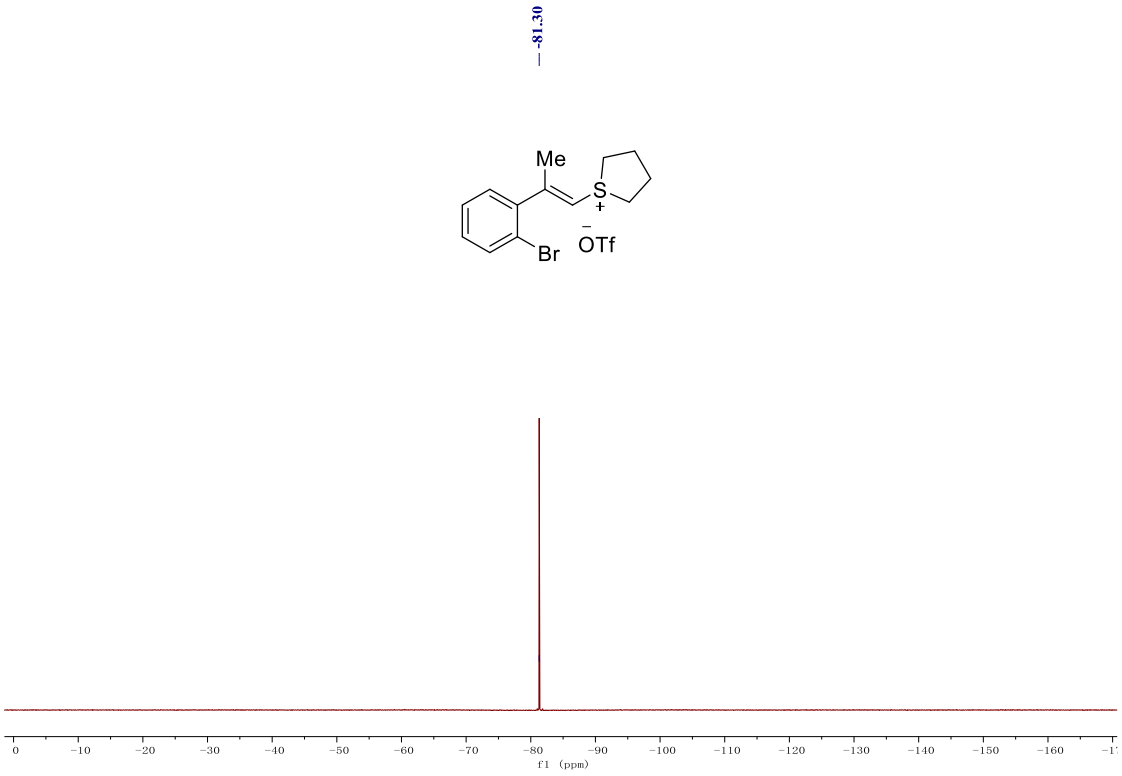
^{1}H NMR Spectra of compound 1m (400 MHz, CD_3OD)



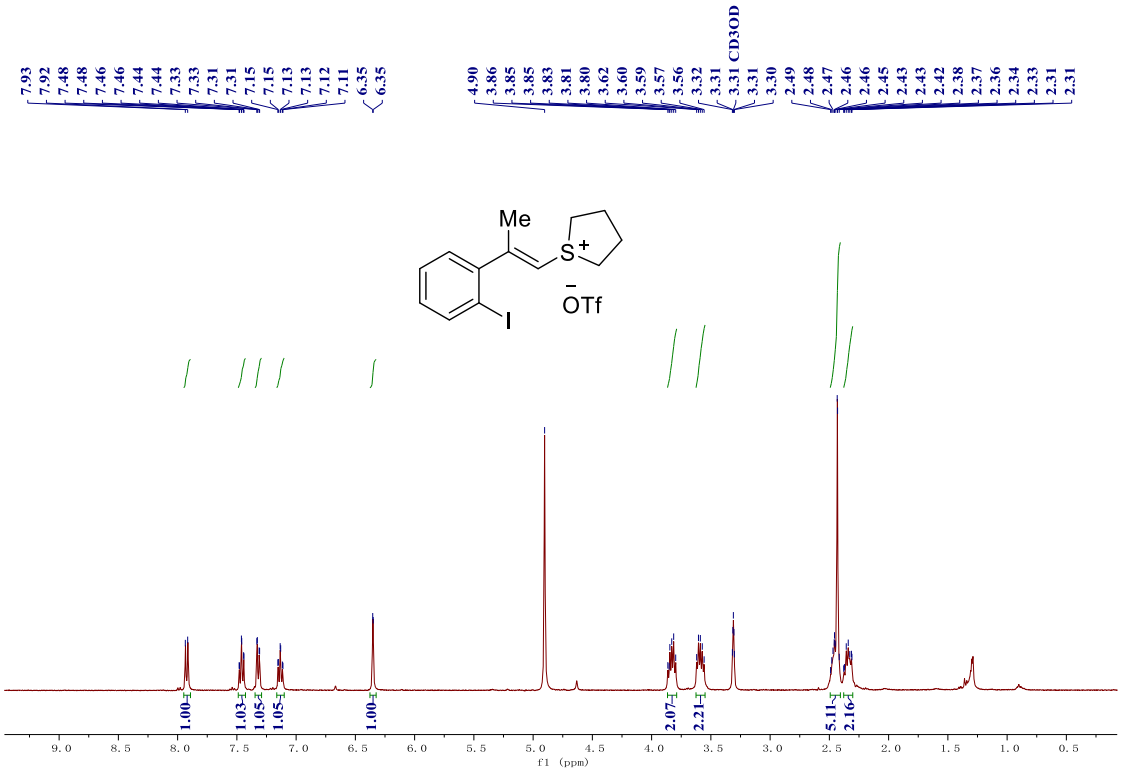
^{13}C NMR Spectra of compound 1m (101 MHz, CD_3OD)



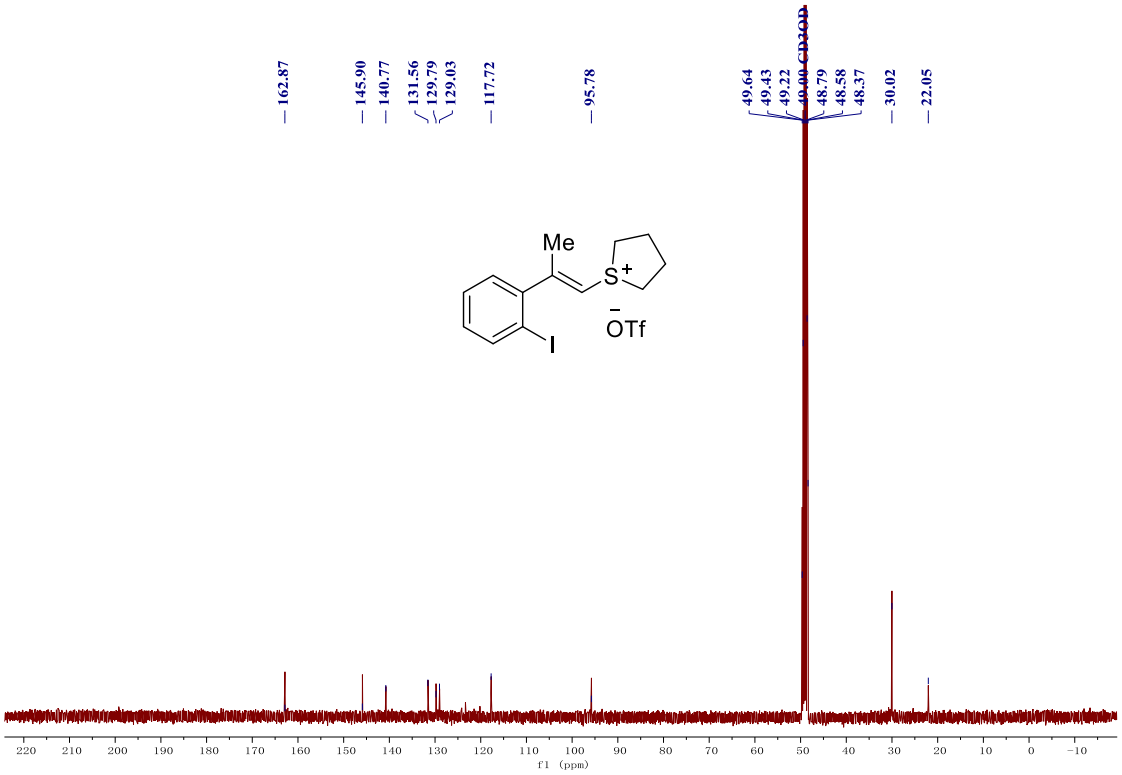
^{19}F NMR Spectra of compound 1m (376 MHz, CD_3OD)



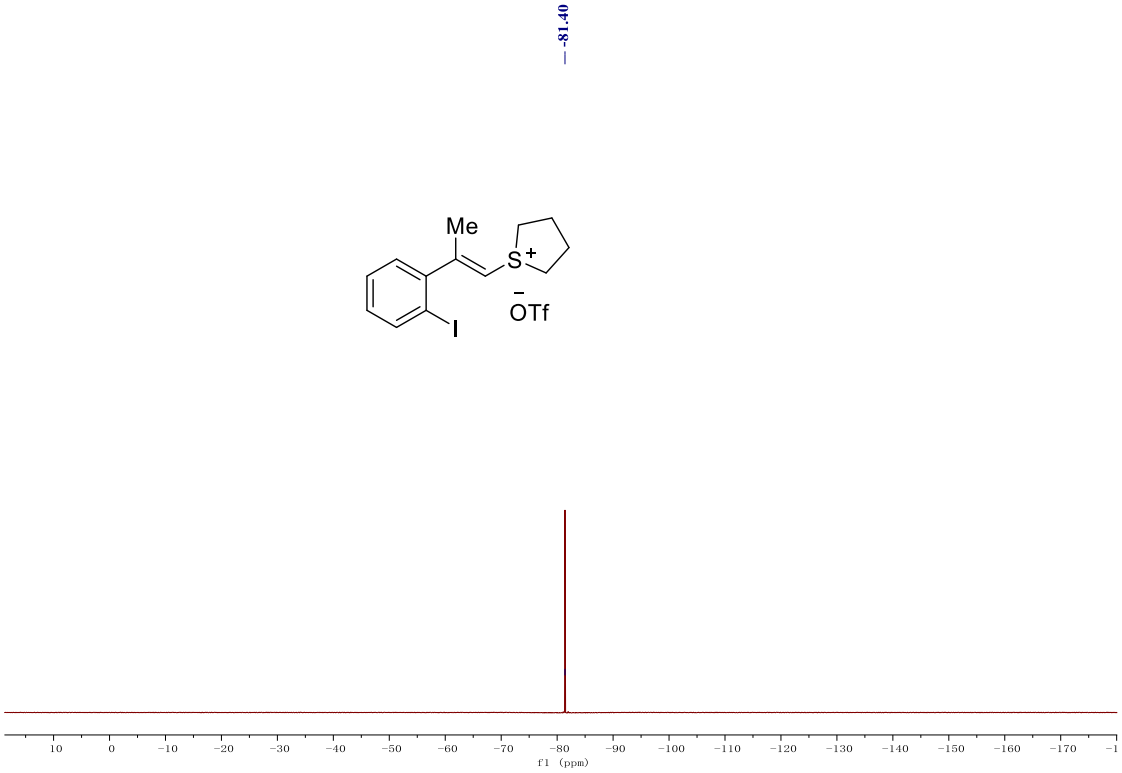
^{1}H NMR Spectra of compound 1n (400 MHz, CD_3OD)



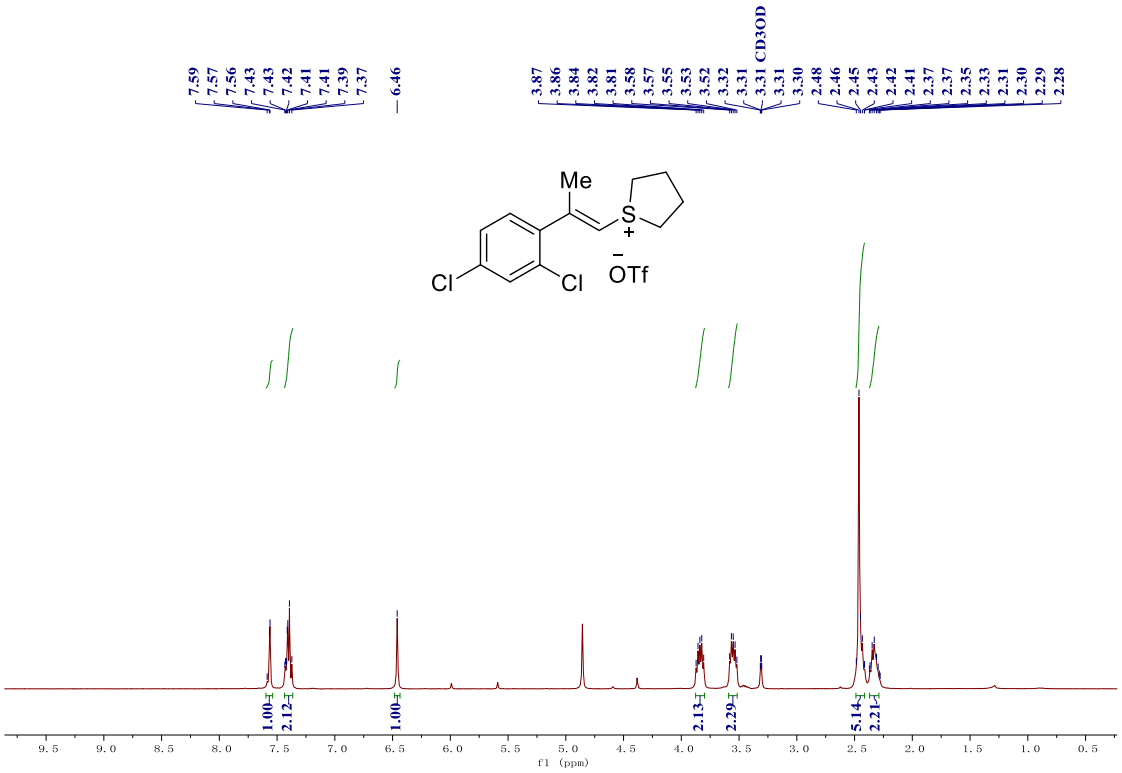
^{13}C NMR Spectra of compound 1n (101 MHz, CD_3OD)



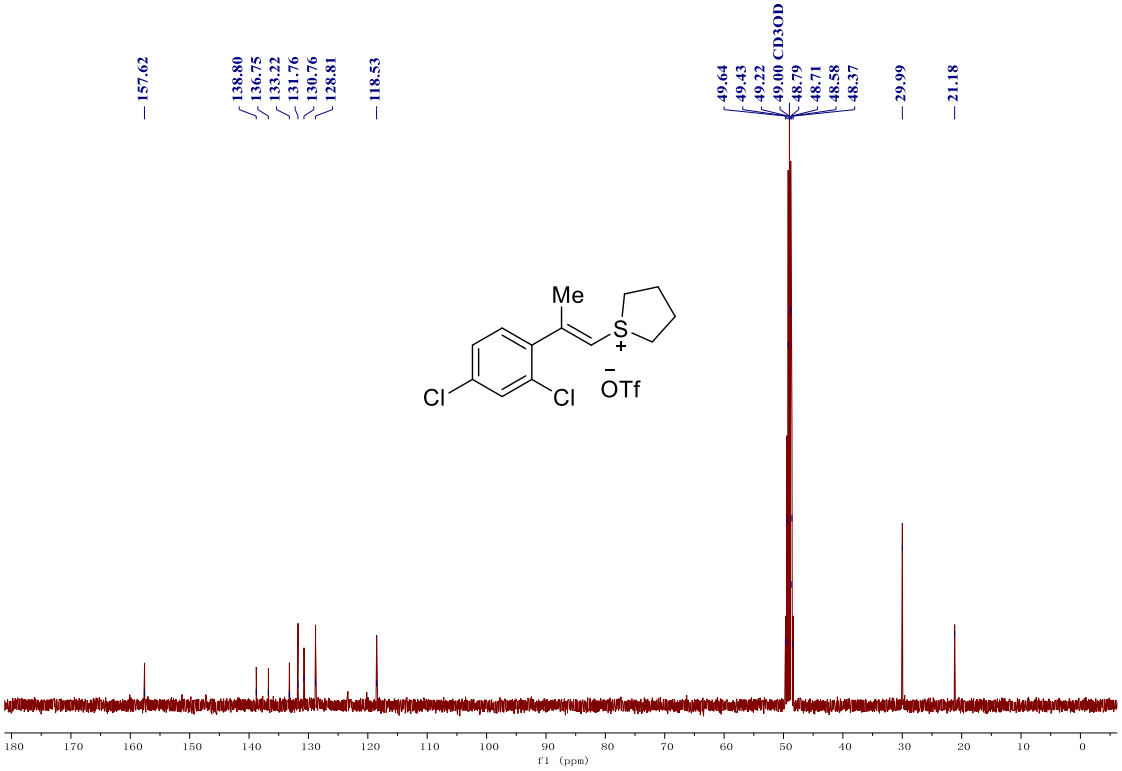
^{19}F NMR Spectra of compound 1n (376 MHz, CD_3OD)



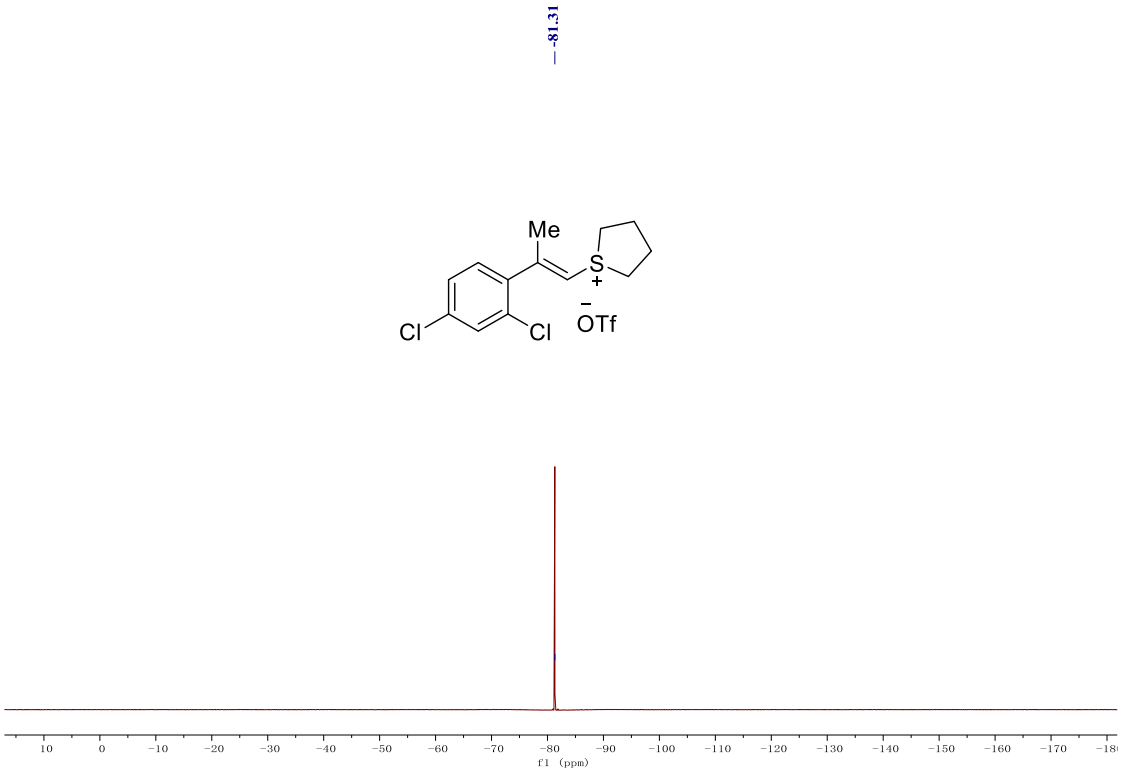
^{1}H NMR Spectra of compound 1o (400 MHz, CD_3OD)



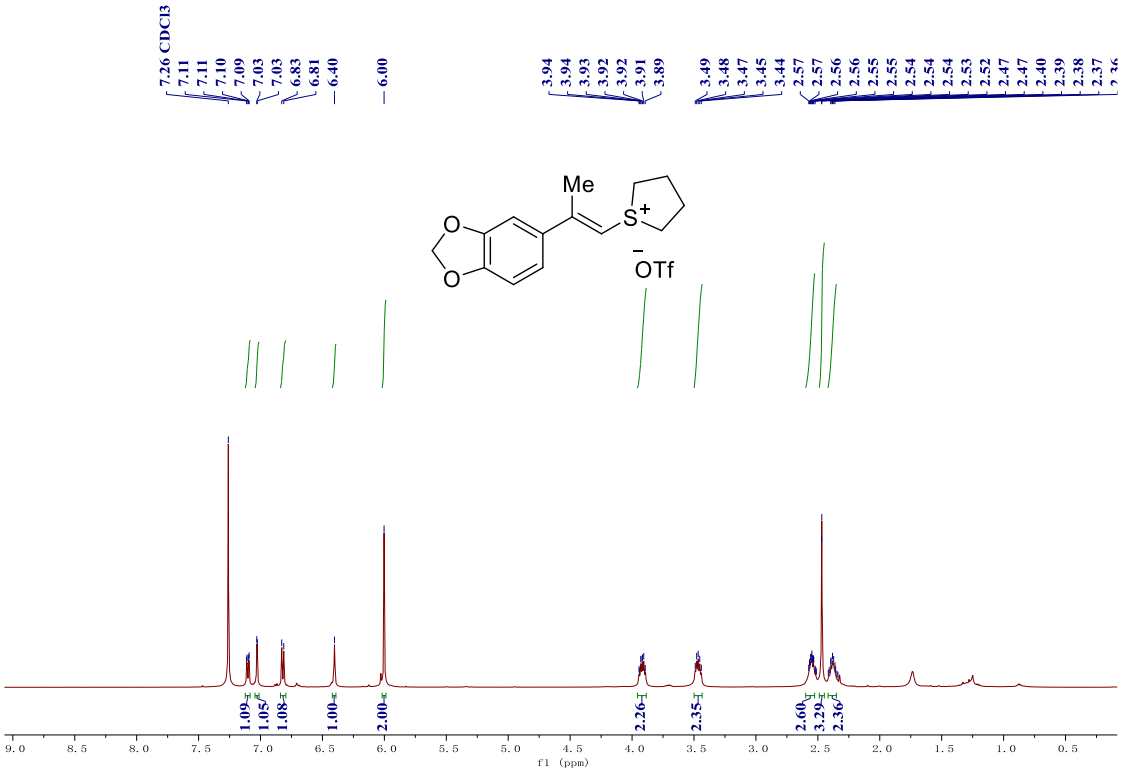
^{13}C NMR Spectra of compound 1o (101 MHz, CD_3OD)



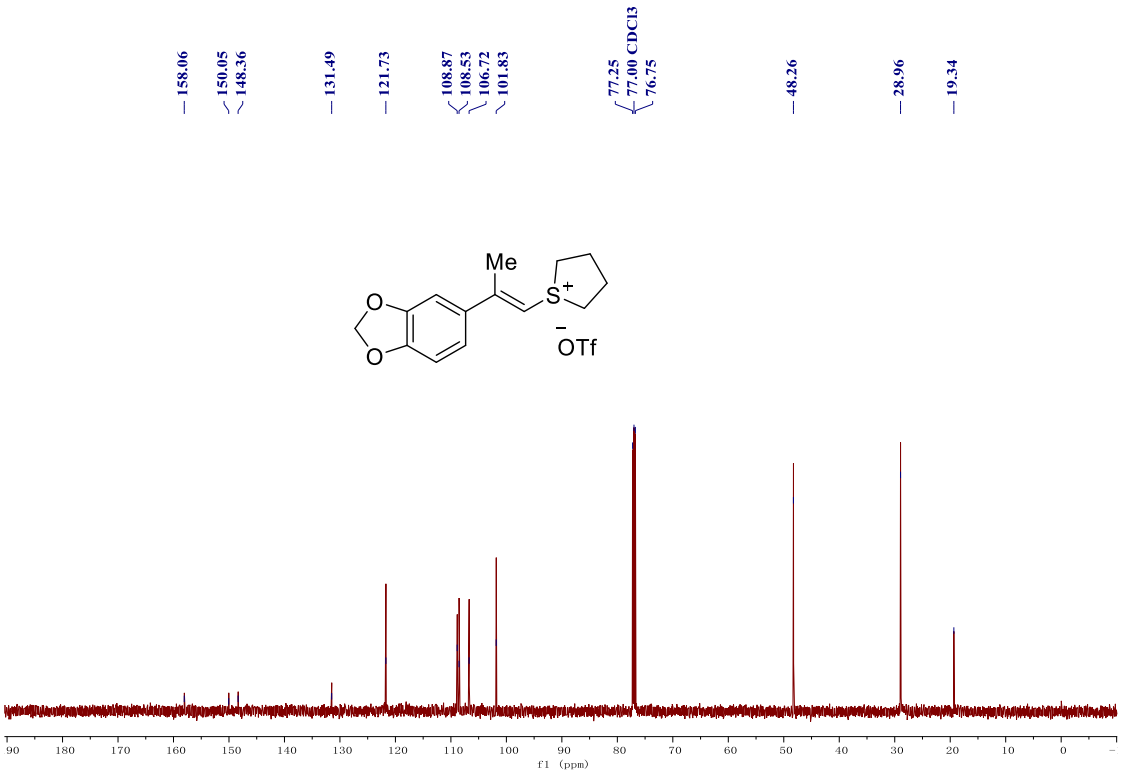
^{19}F NMR Spectra of compound 1o (376 MHz, CD_3OD)



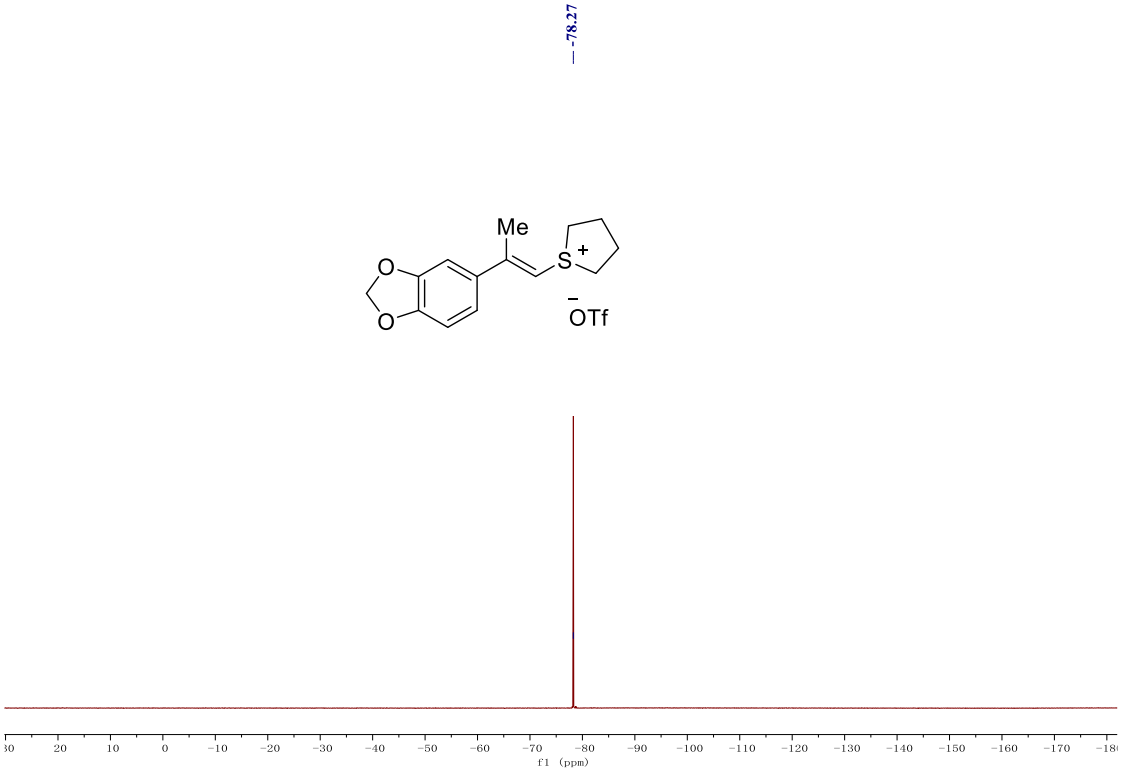
^{1}H NMR Spectra of compound 1p (500 MHz, $CDCl_3$)



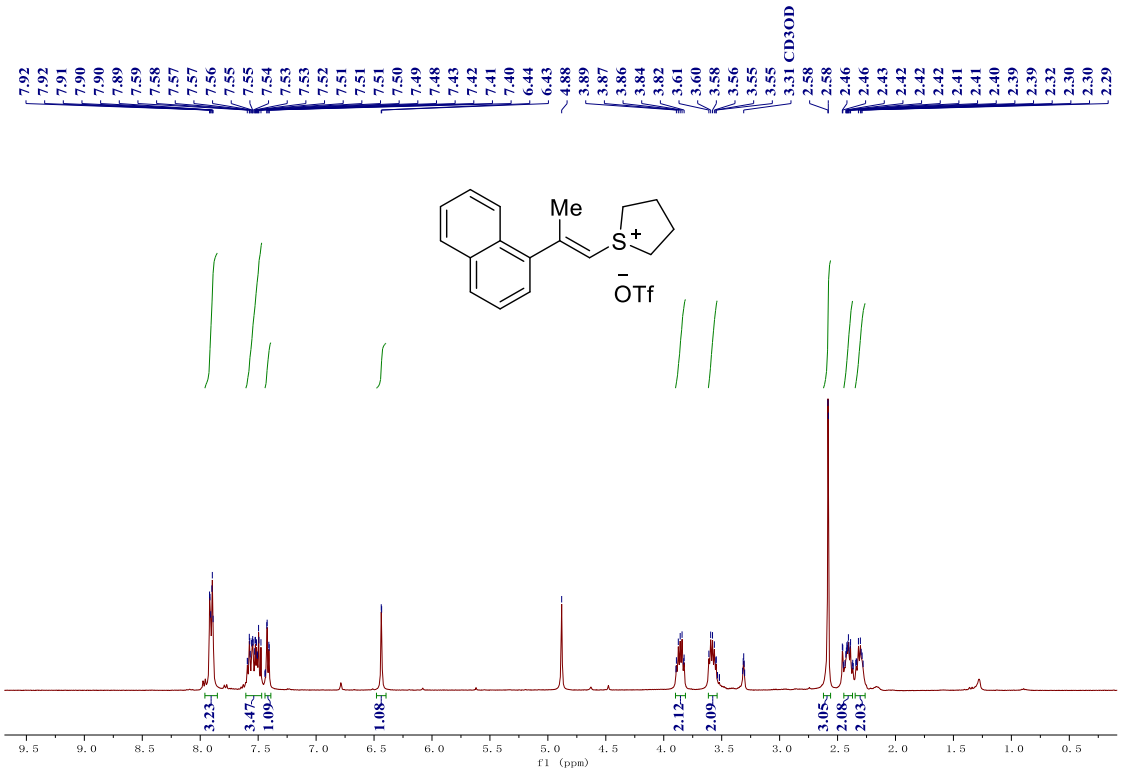
^{13}C NMR Spectra of compound 1p (126 MHz, $CDCl_3$)



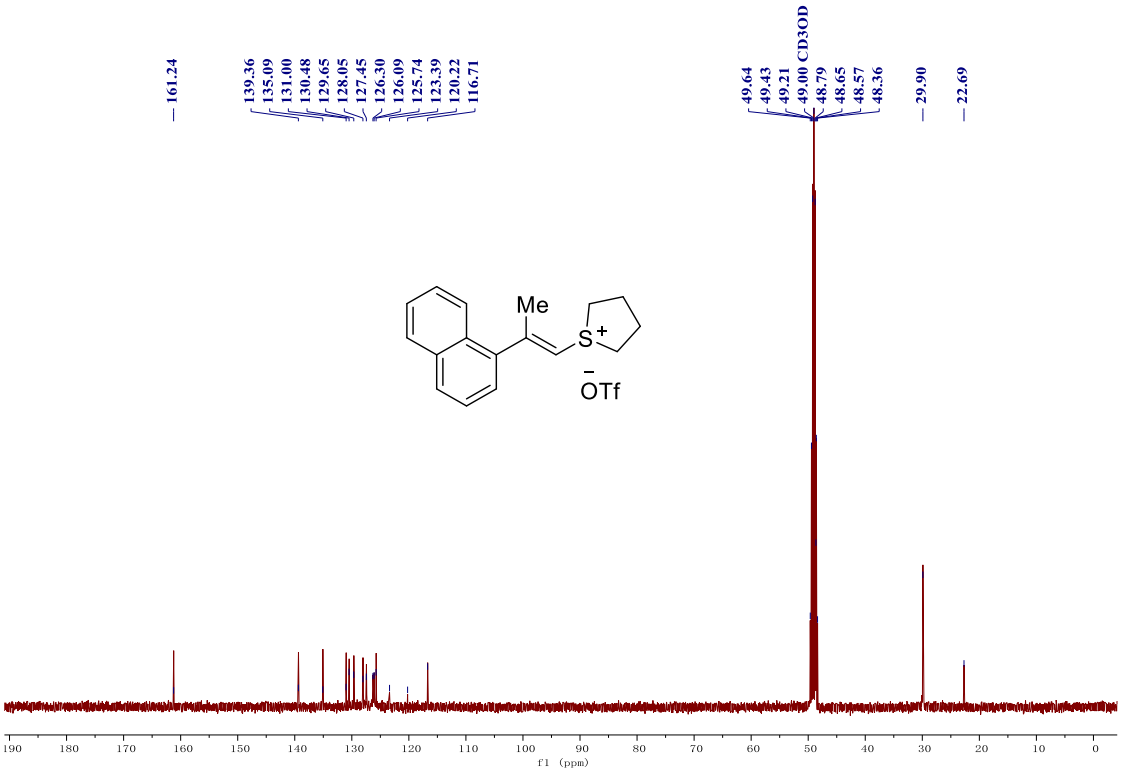
^{19}F NMR Spectra of compound 1p (471 MHz, $CDCl_3$)



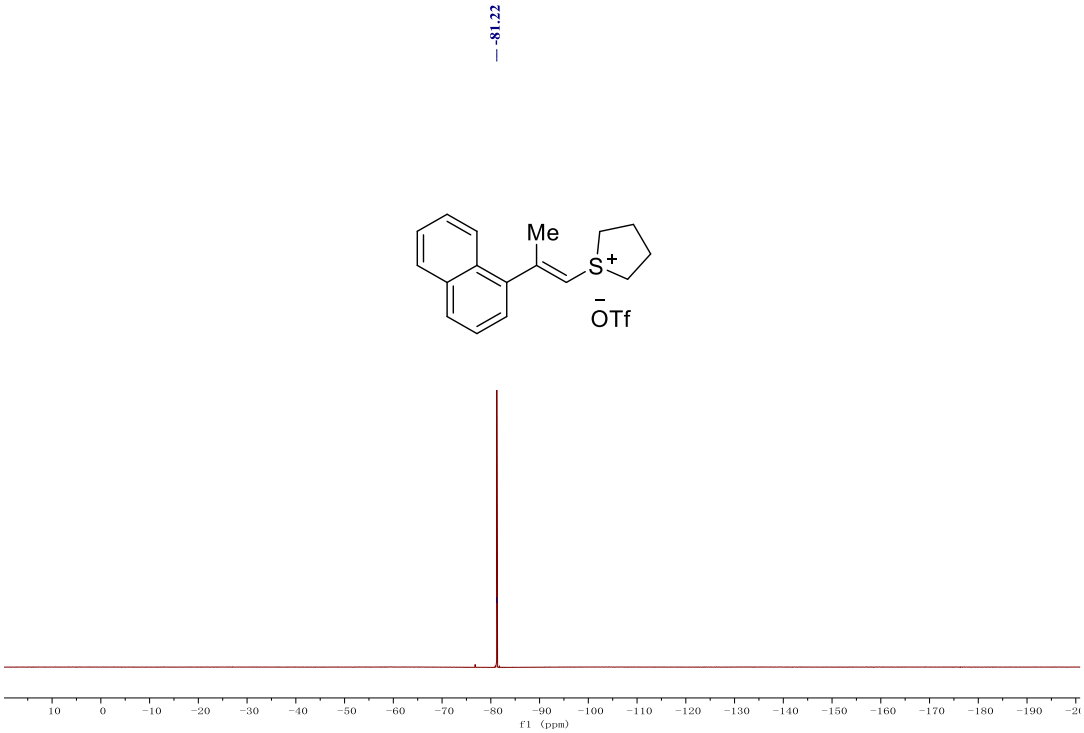
^{1}H NMR Spectra of compound 1q (400 MHz, CD_3OD)



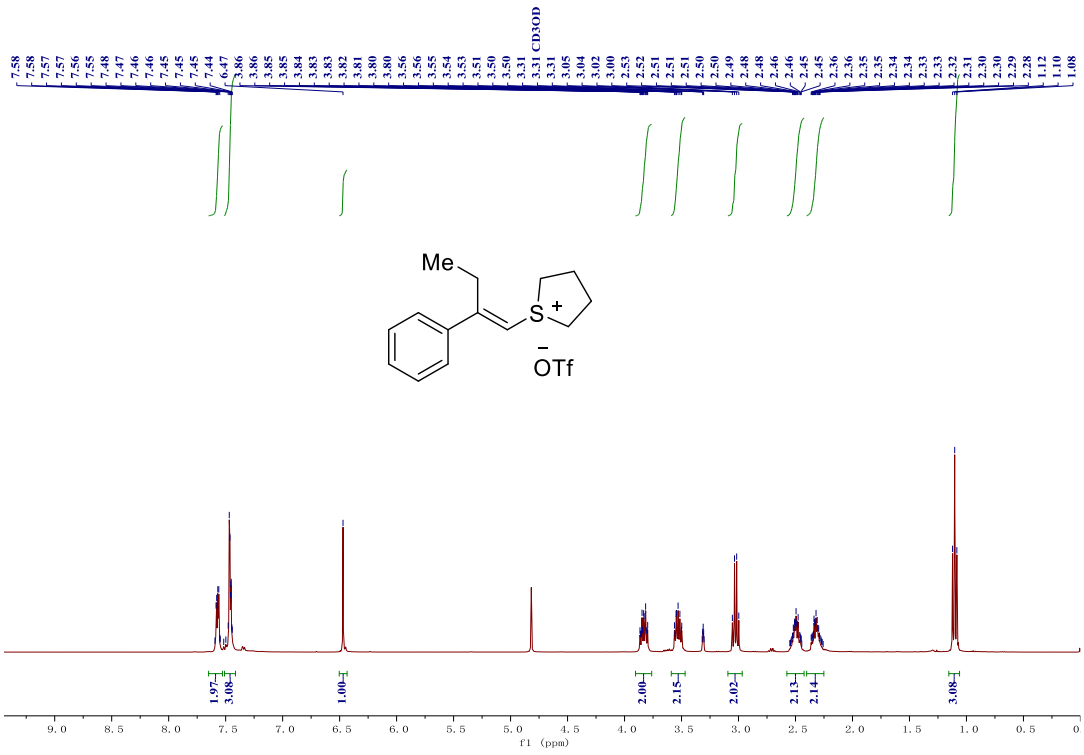
^{13}C NMR Spectra of compound 1q (101 MHz, CD_3OD)



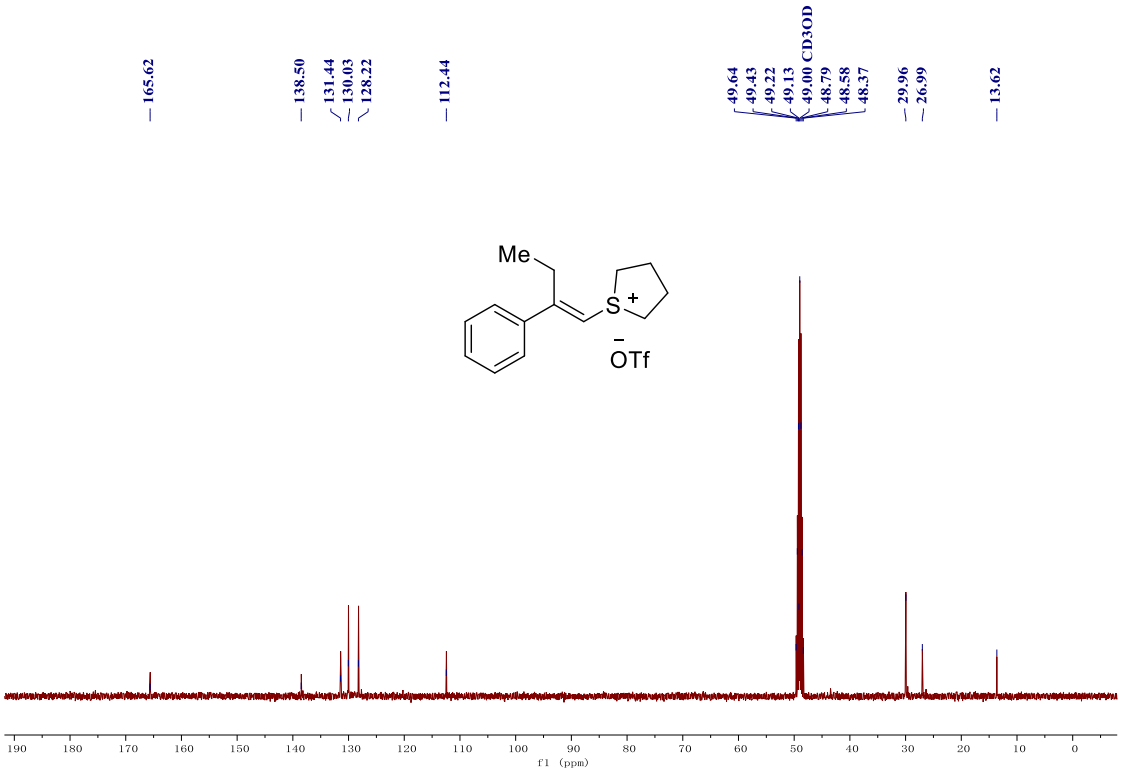
^{19}F NMR Spectra of compound 1q (376 MHz, CD_3OD)



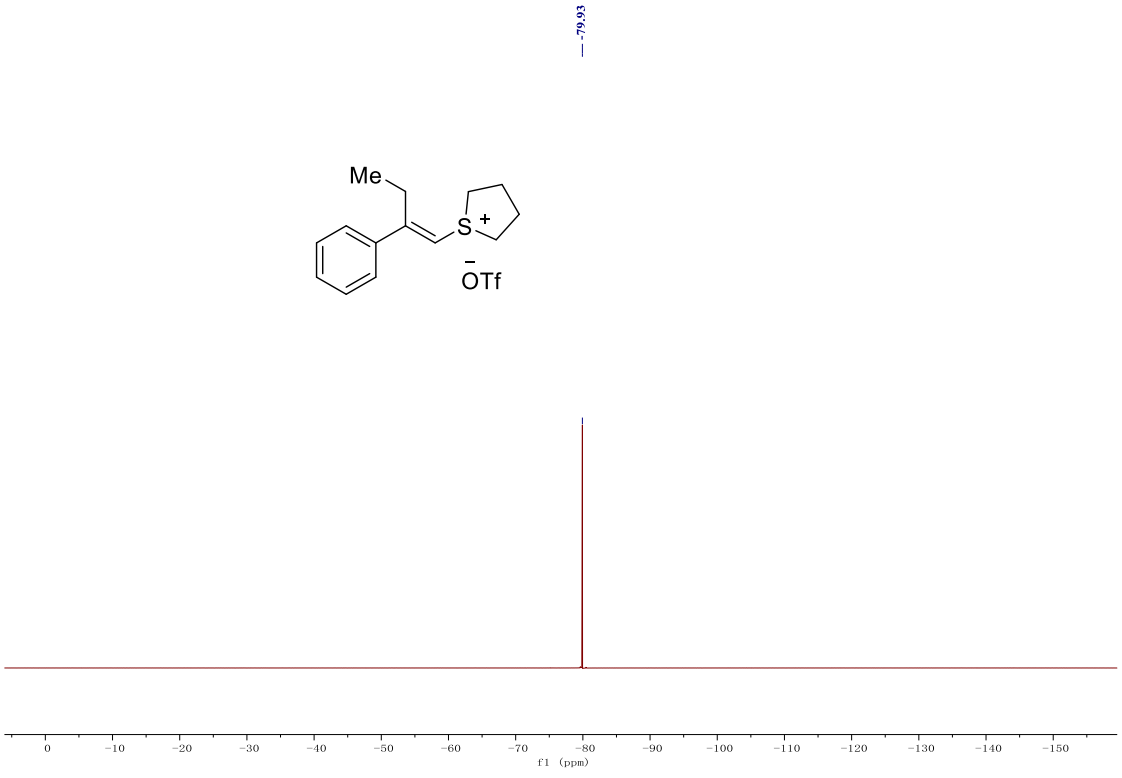
^{1}H NMR Spectra of compound 1r (400 MHz, CD_3OD)



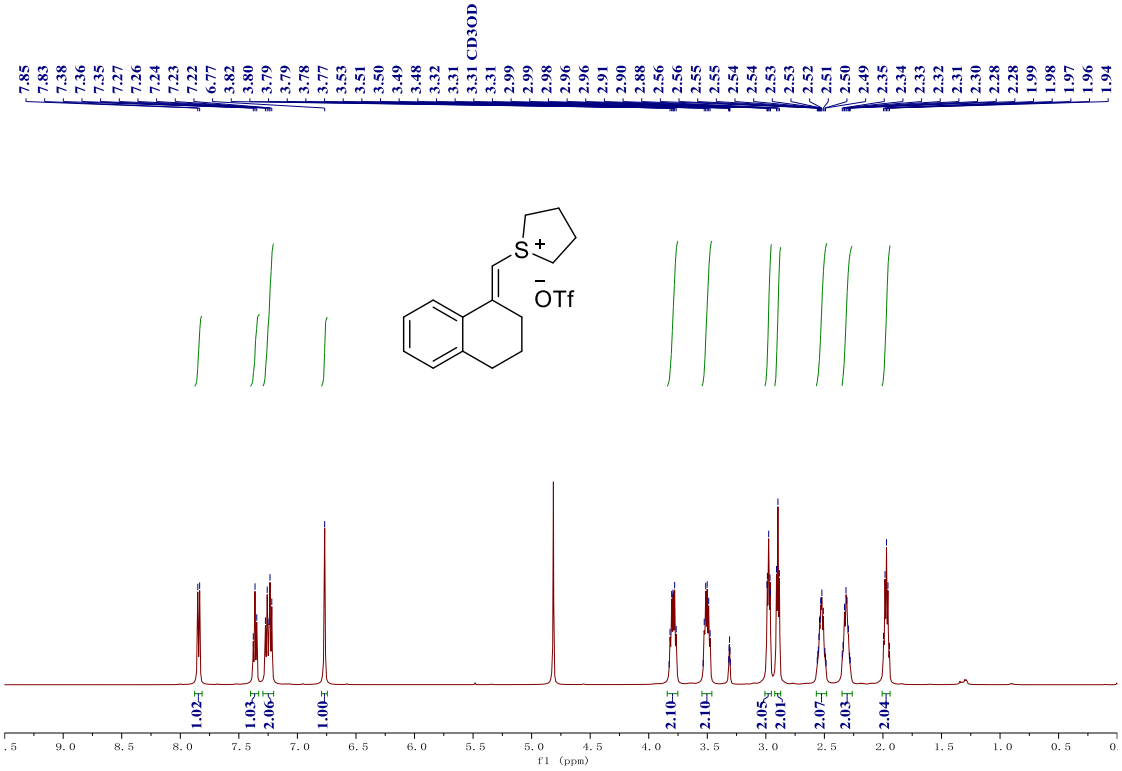
^{13}C NMR Spectra of compound 1r (101 MHz, CD_3OD)



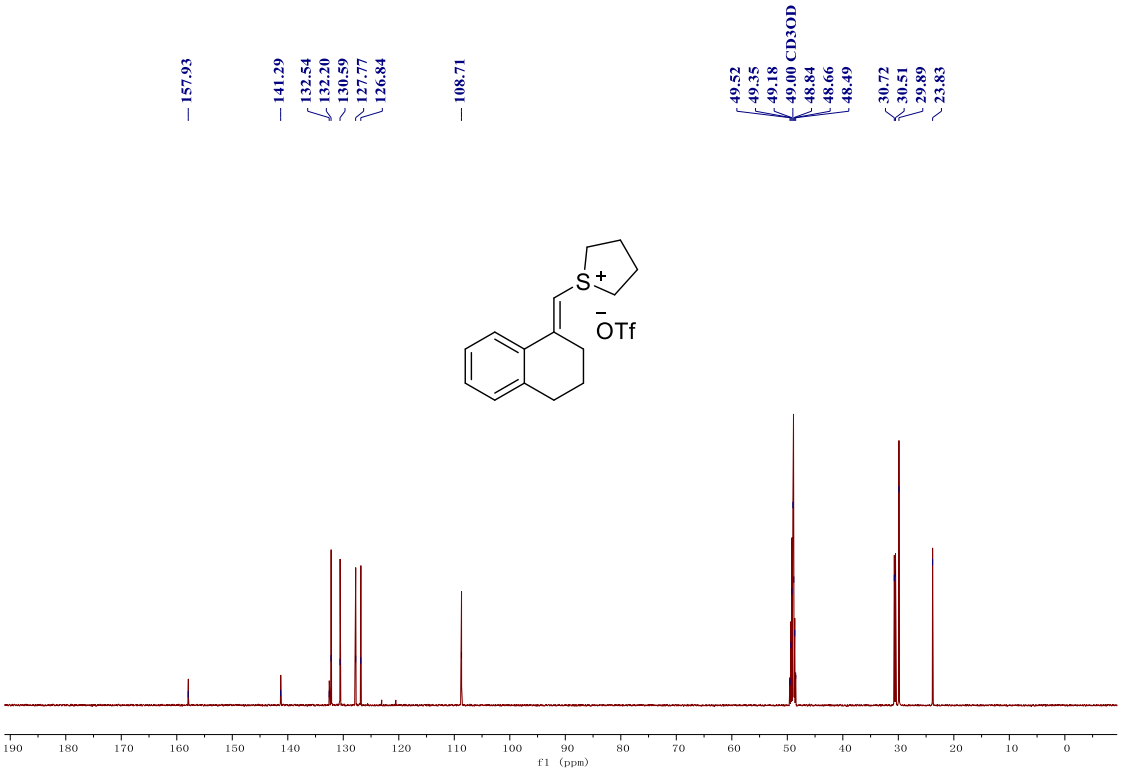
^{19}F NMR Spectra of compound 1r (376 MHz, CD_3OD)



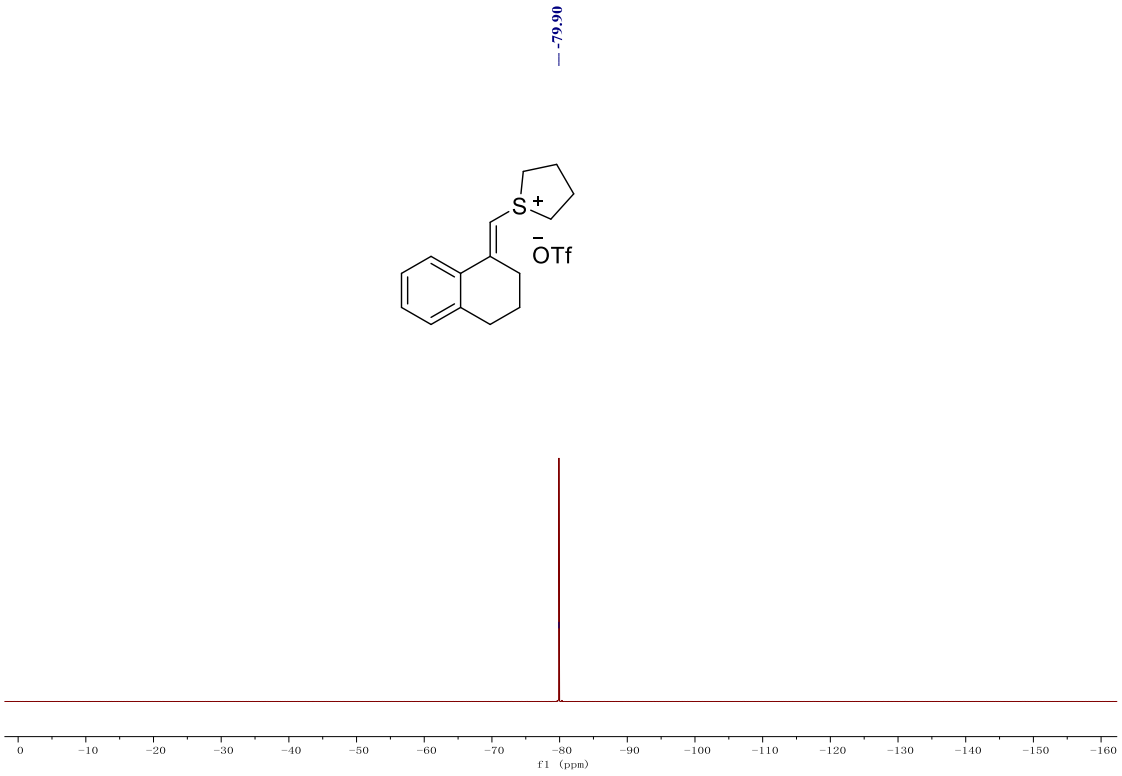
^{1}H NMR Spectra of compound 1s (500 MHz, CD_3OD)



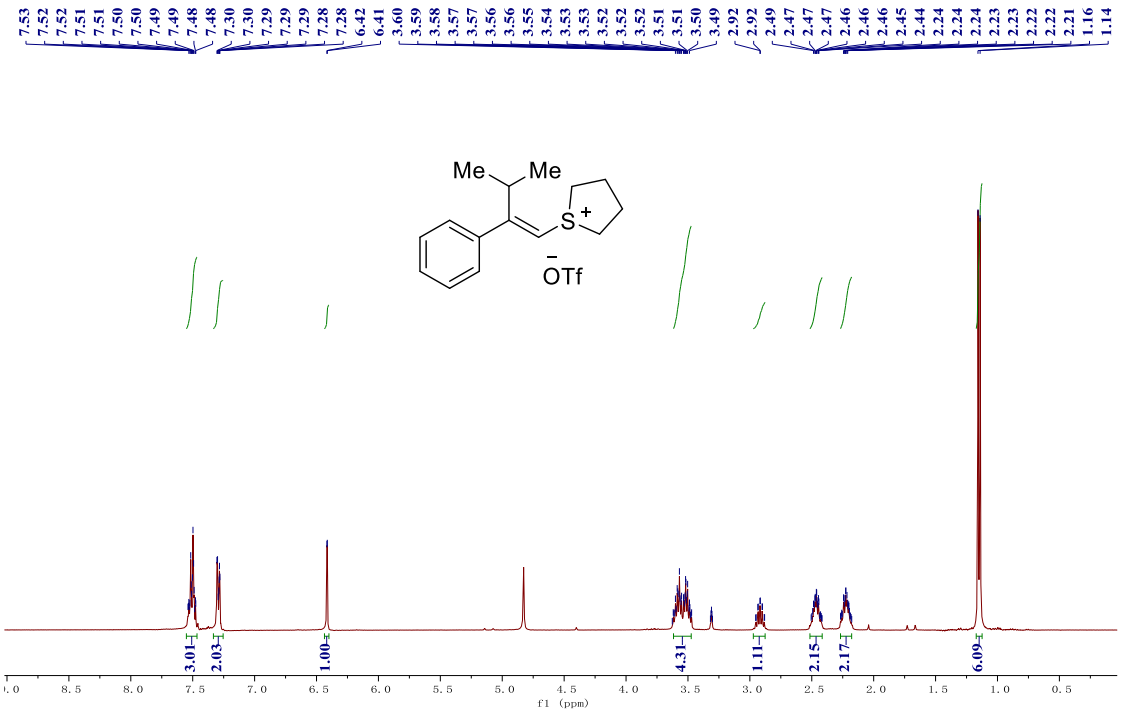
^{13}C NMR Spectra of compound 1s (126 MHz, CD_3OD)



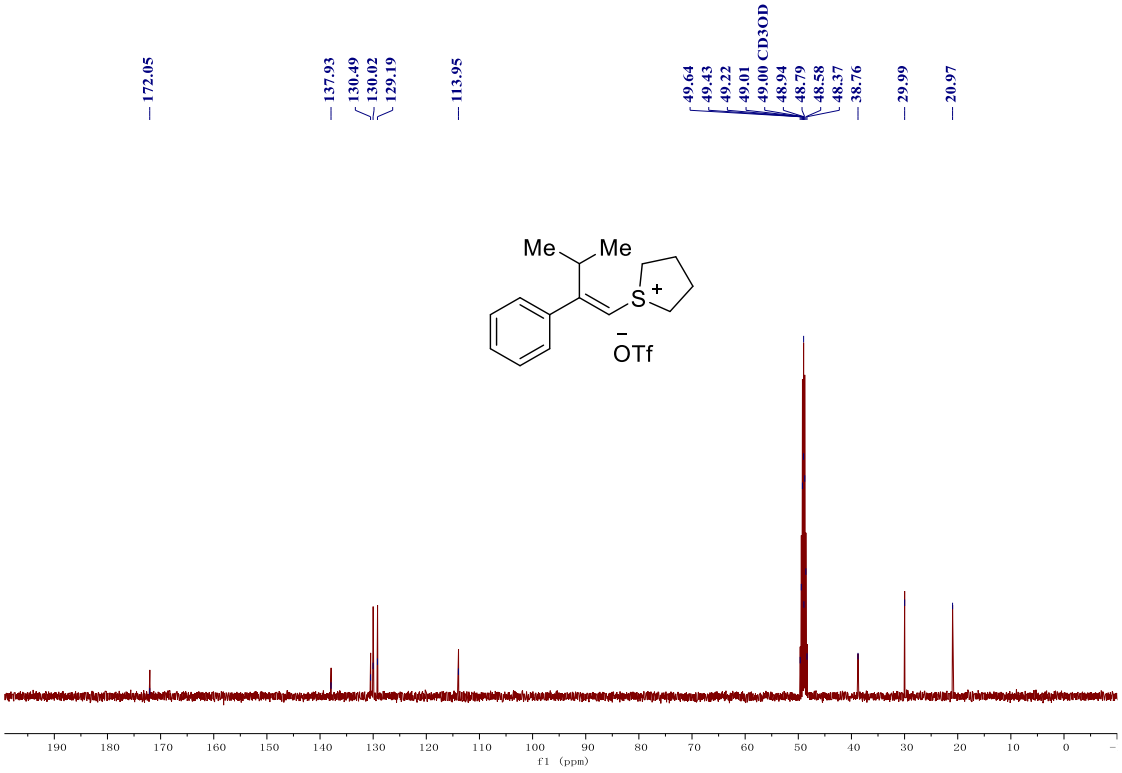
^{19}F NMR Spectra of compound 1s (471 MHz, CD_3OD)



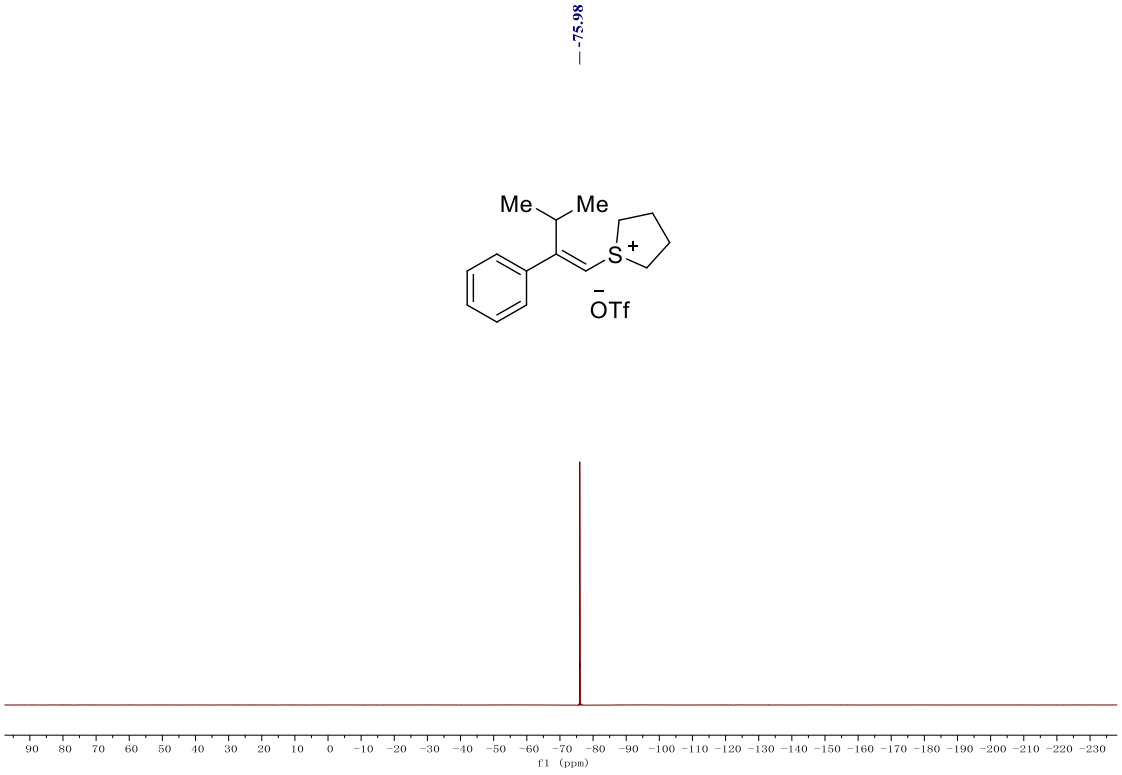
^{1}H NMR Spectra of compound 1t (400 MHz, CD_3OD)



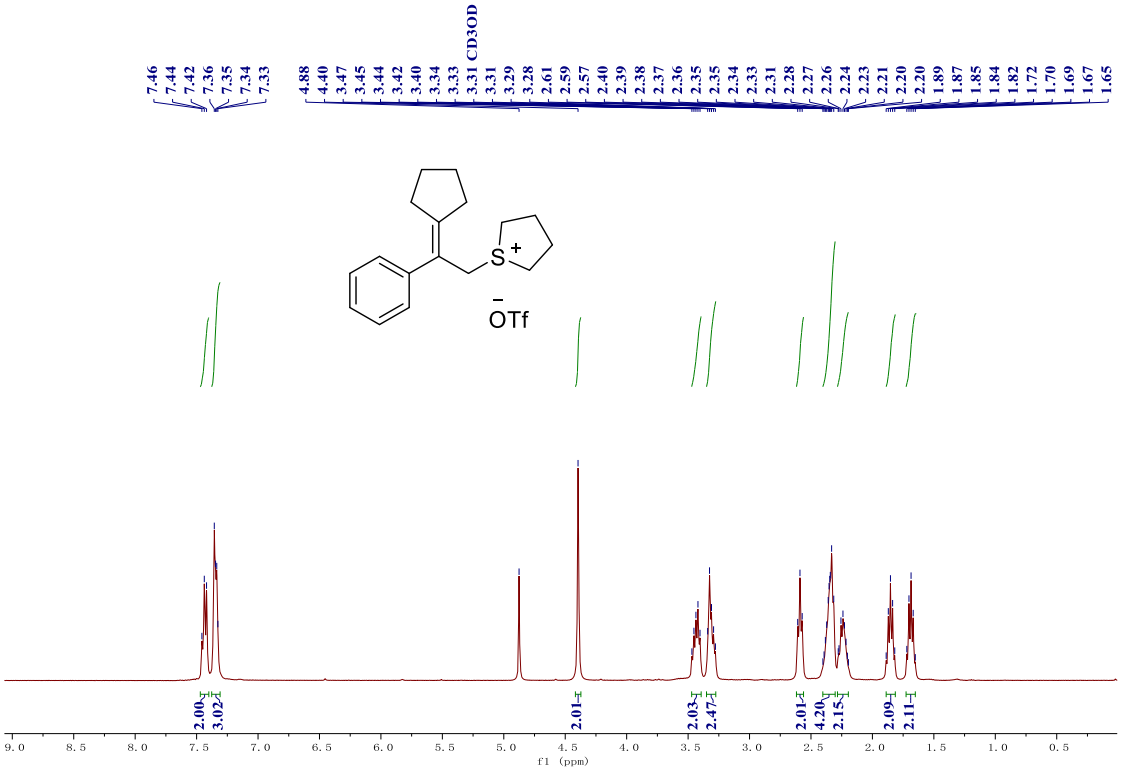
^{13}C NMR Spectra of compound 1t (101 MHz, CD_3OD)



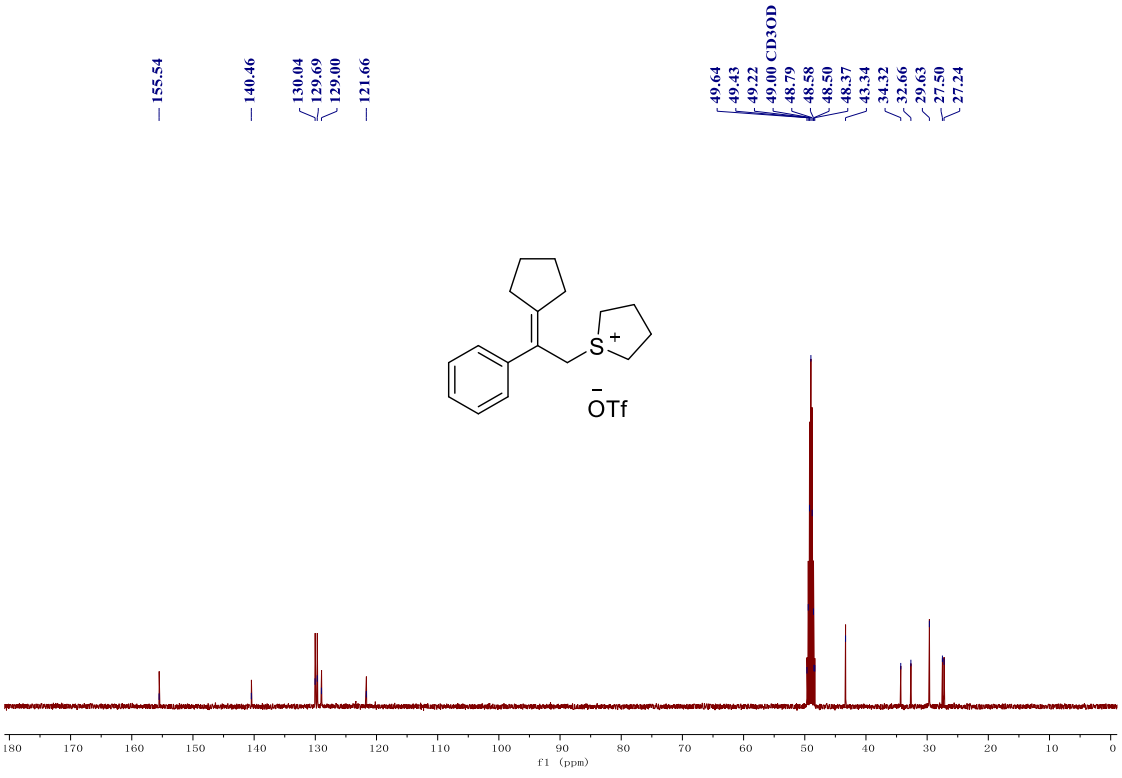
^{19}F NMR Spectra of compound 1t (376 MHz, CD_3OD)



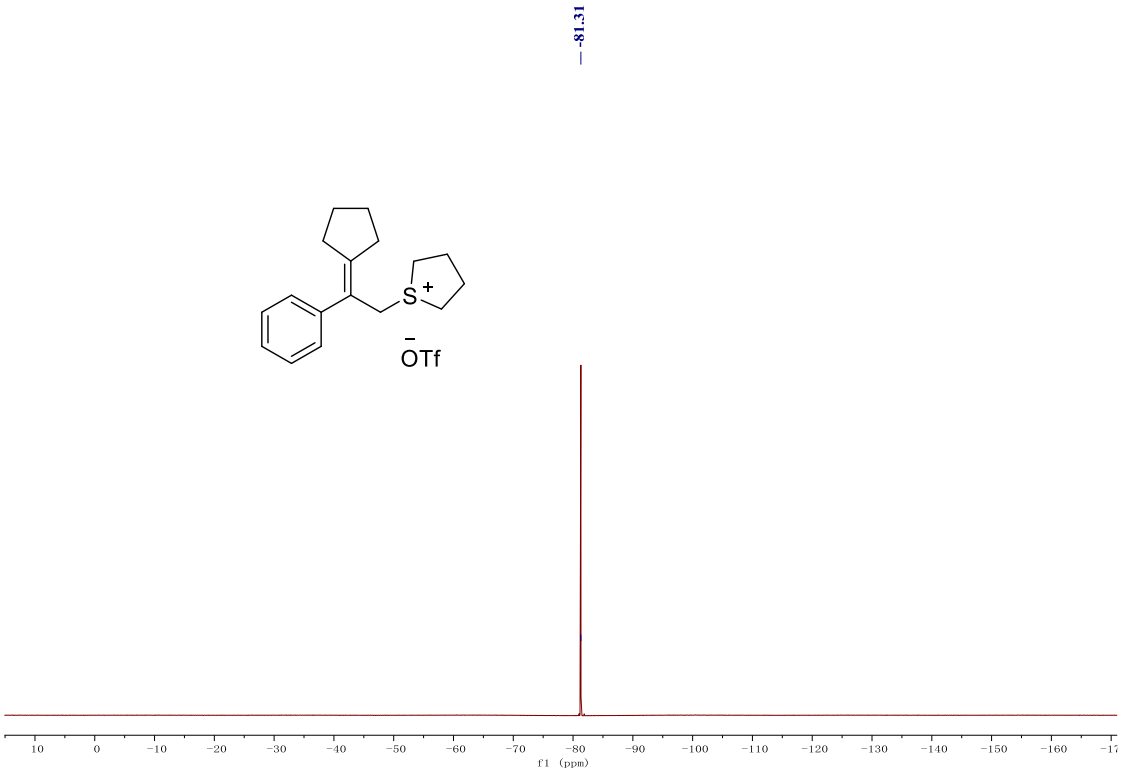
^{1}H NMR Spectra of compound 1u' (400 MHz, CD_3OD)



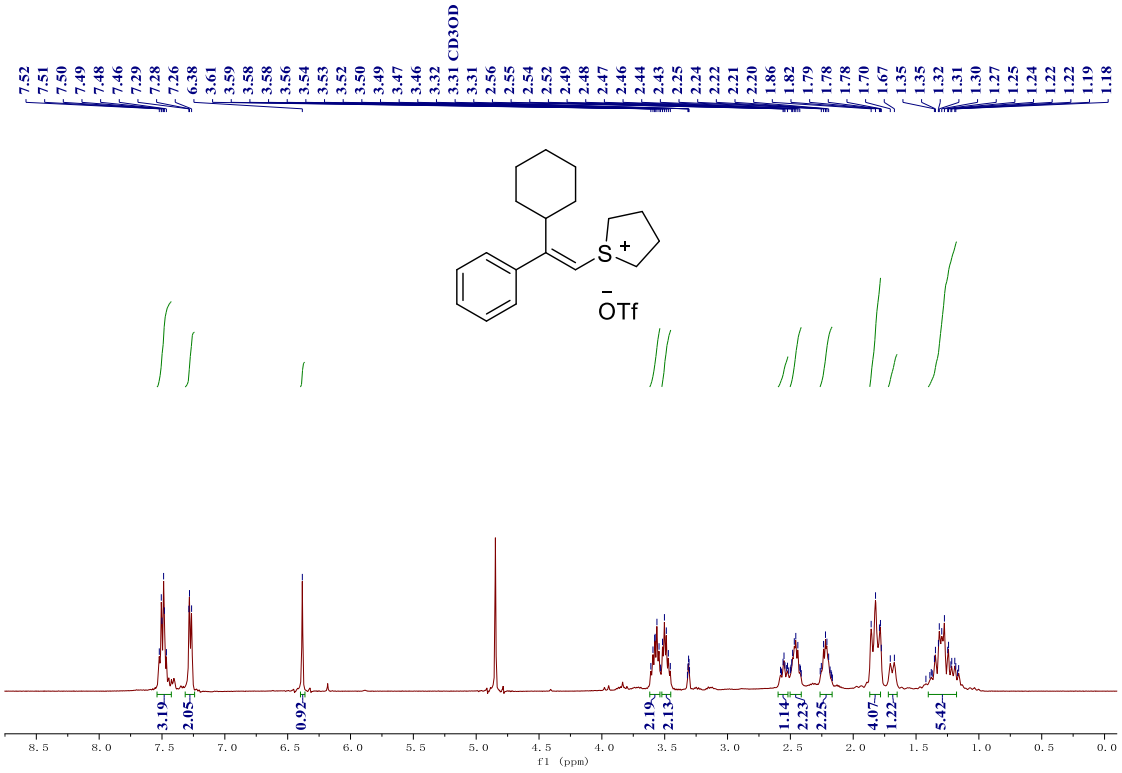
^{13}C NMR Spectra of compound 1u' (101 MHz, CD_3OD)



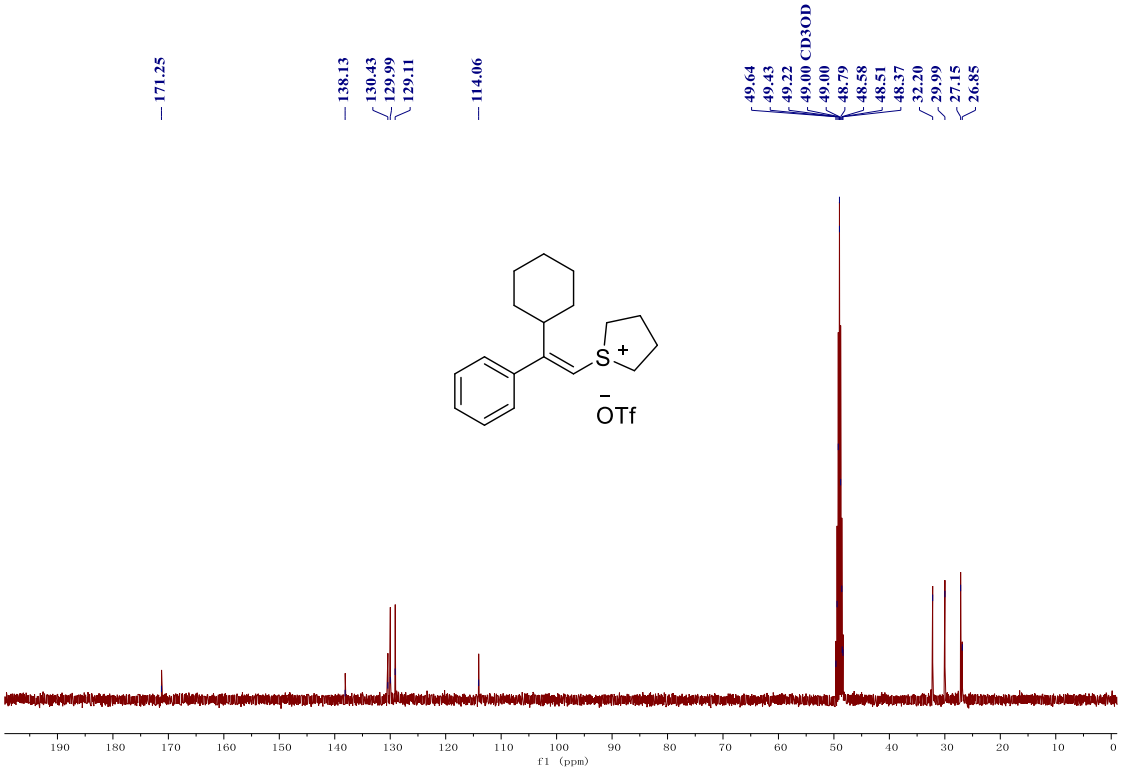
^{19}F NMR Spectra of compound 1u (376 MHz, CD_3OD)



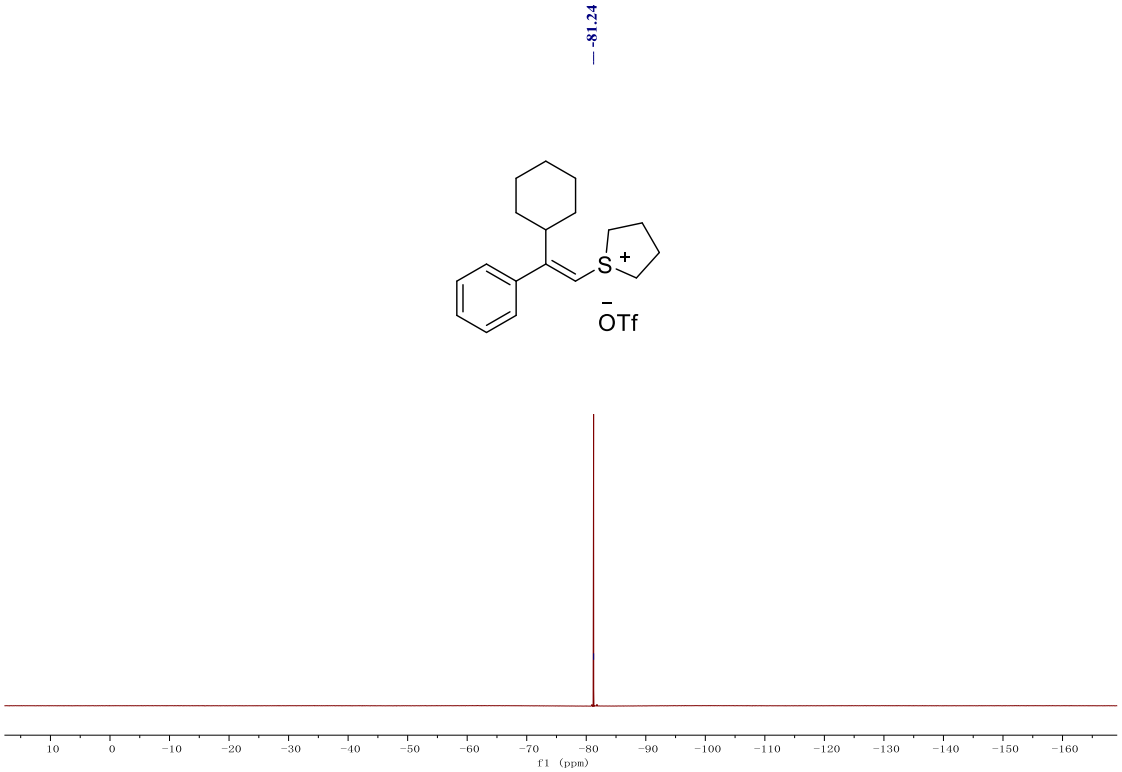
^{1}H NMR Spectra of compound 1v (500 MHz, CD_3OD)



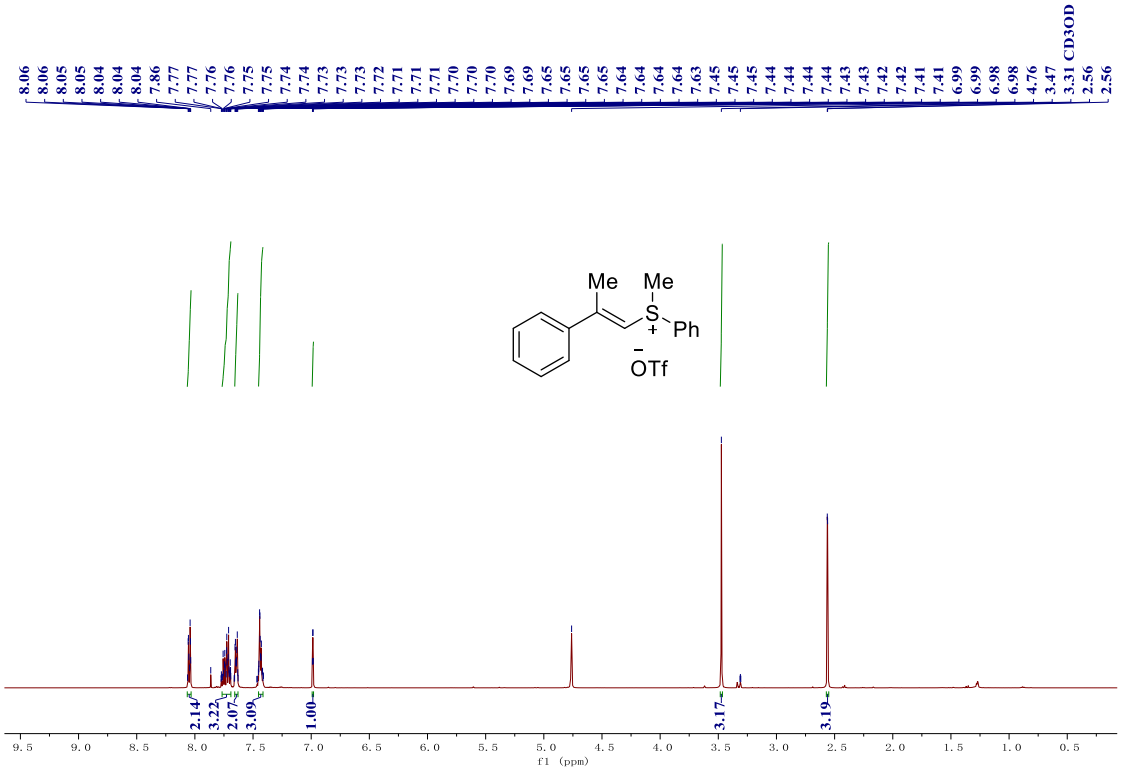
^{13}C NMR Spectra of compound 1v (126 MHz, CD_3OD)



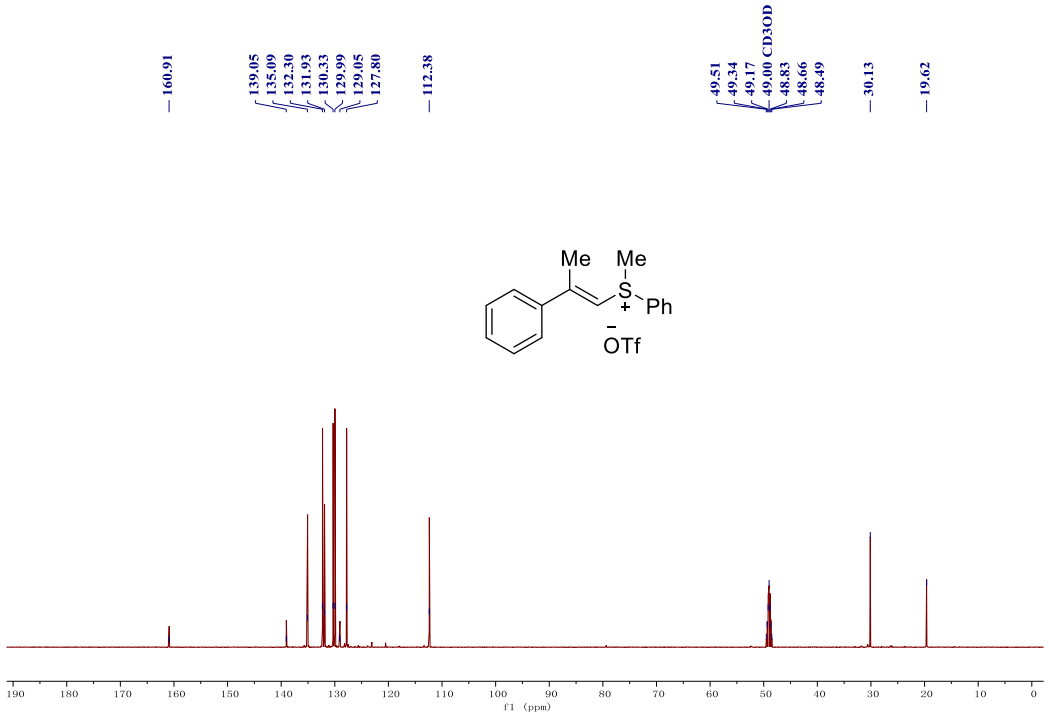
^{19}F NMR Spectra of compound 1v (471 MHz, CD_3OD)



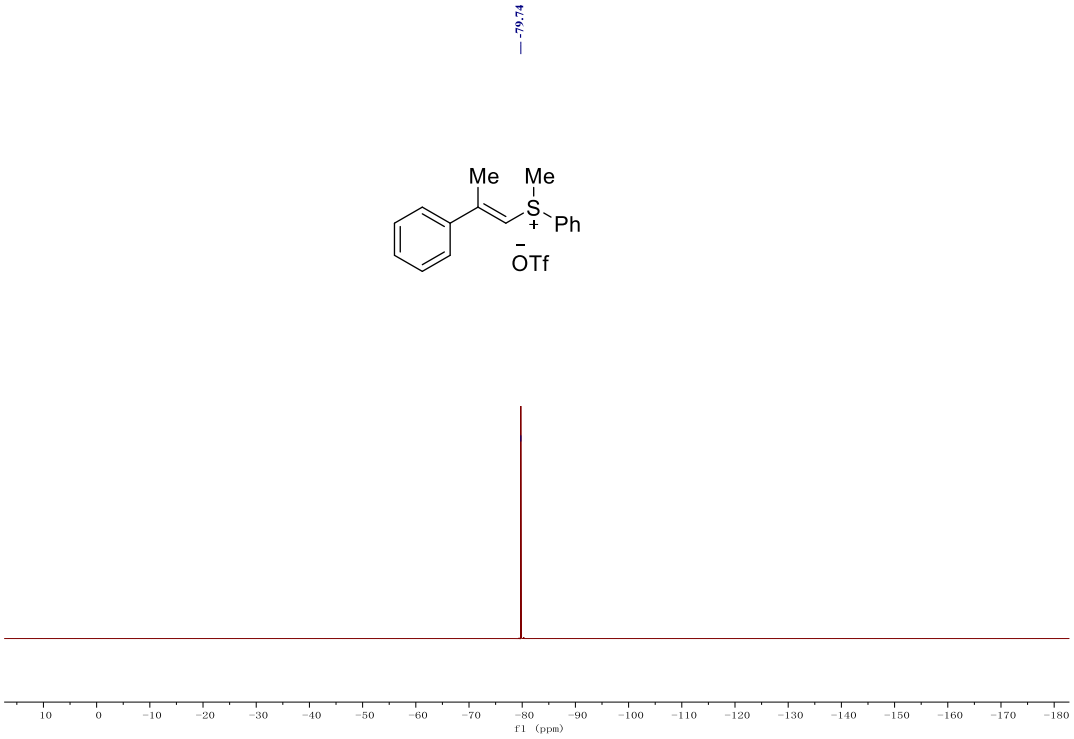
^{1}H NMR Spectra of compound 2a (500 MHz, CD_3OD)



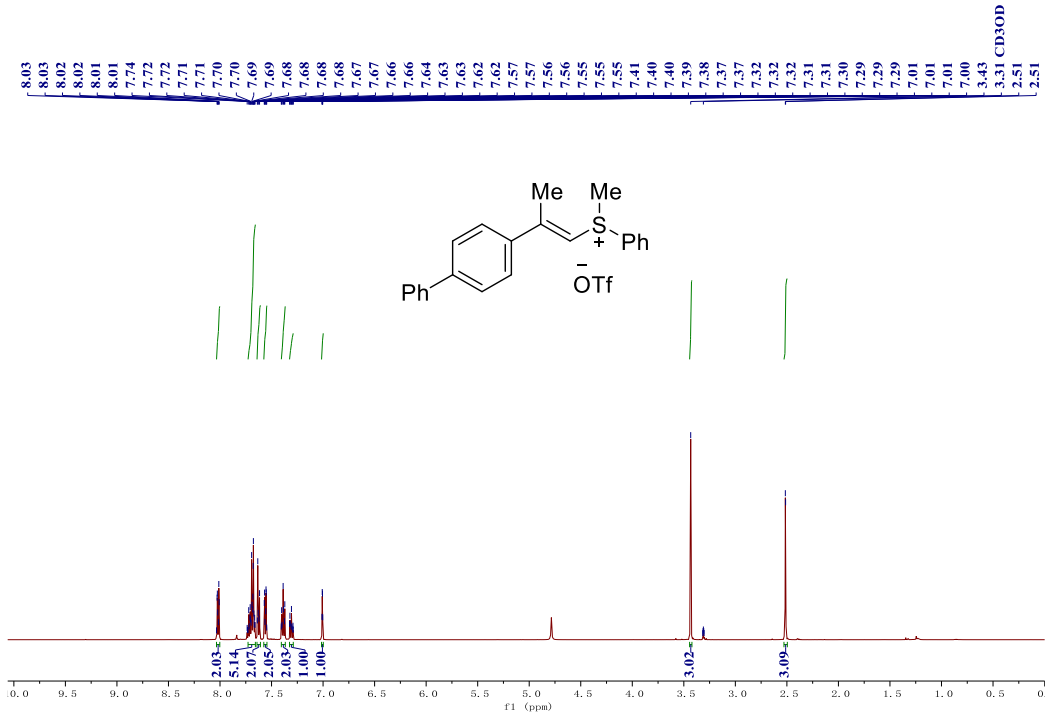
^{13}C NMR Spectra of compound 2a (126 MHz, CD_3OD)



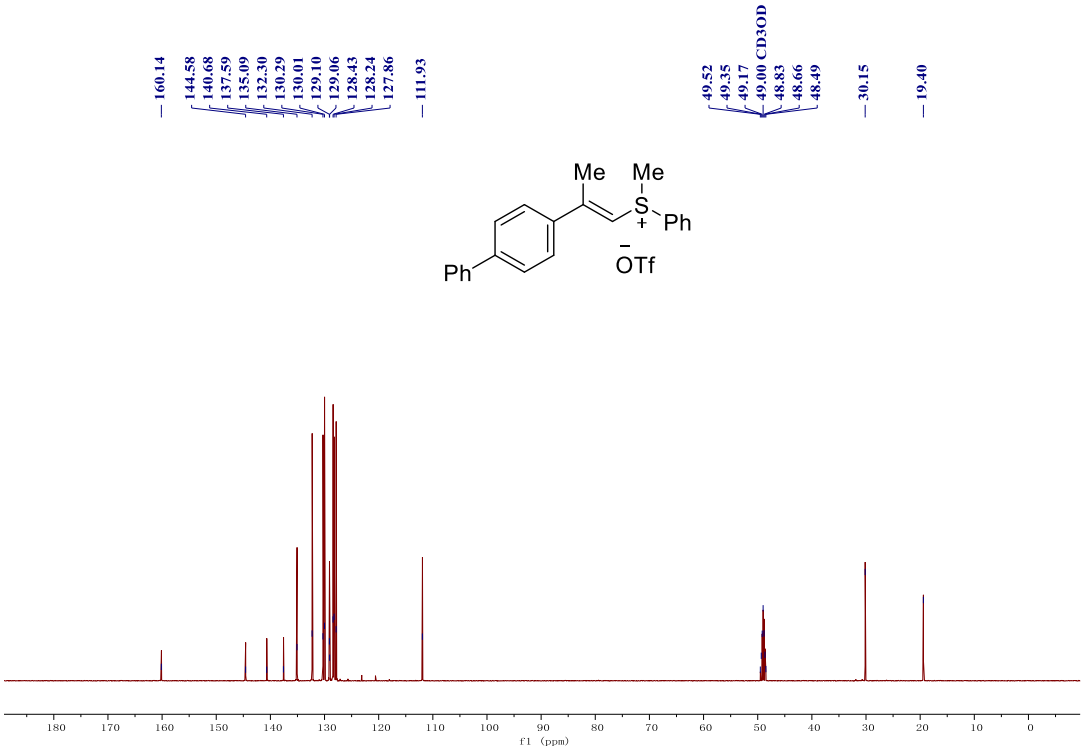
^{19}F NMR Spectra of compound 2a (471 MHz, CD_3OD)



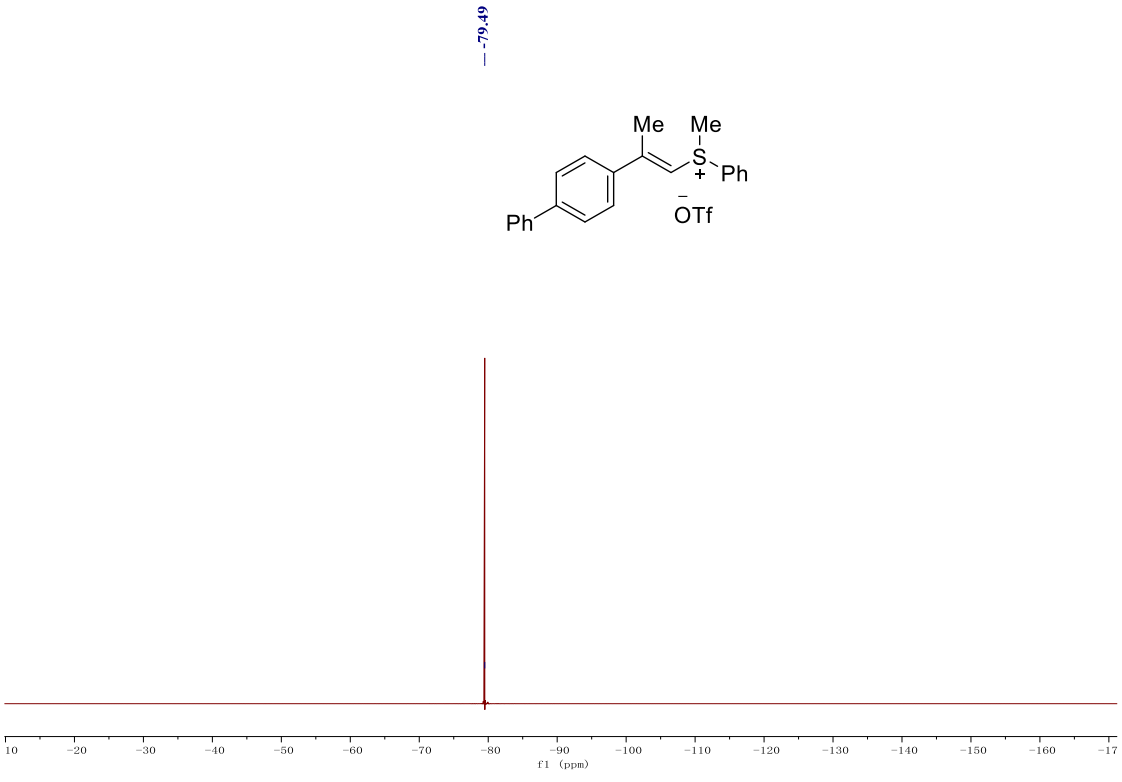
^{1}H NMR Spectra of compound 2b (500 MHz, CD_3OD)



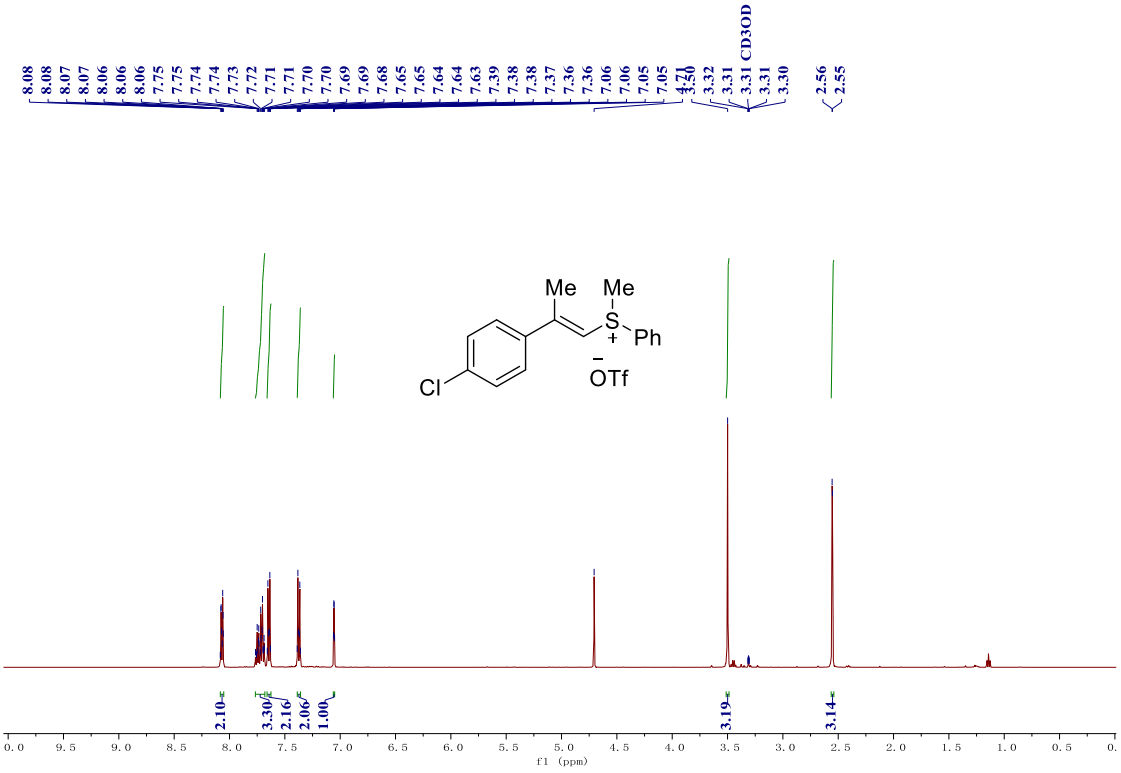
^{13}C NMR Spectra of compound 2b (126 MHz, CD_3OD)



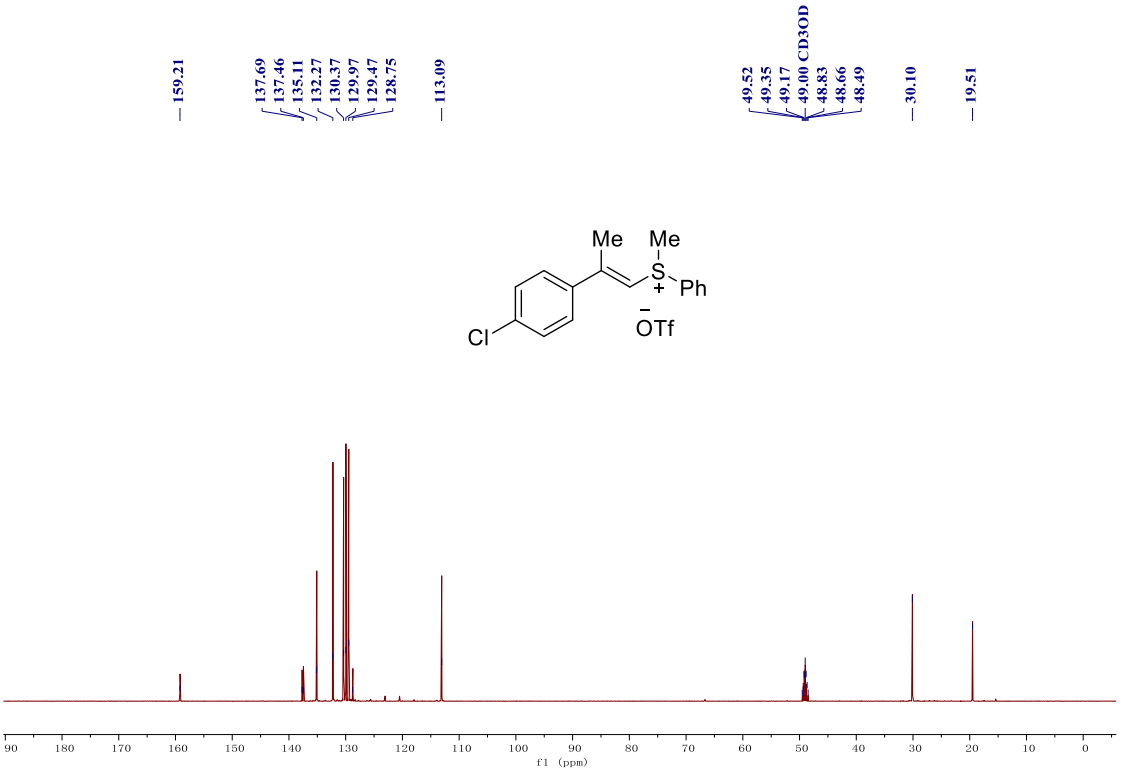
^{19}F NMR Spectra of compound 2b (471 MHz, CD_3OD)



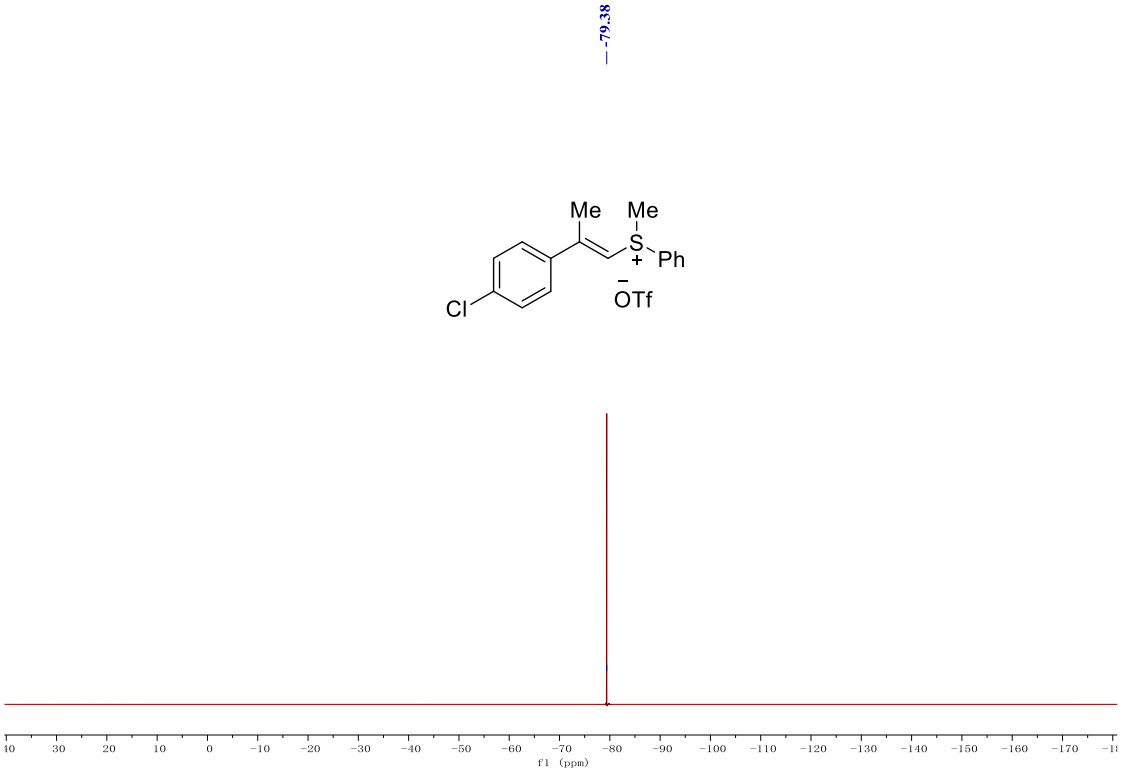
^{1}H NMR Spectra of compound 2c (400 MHz, CD_3OD)



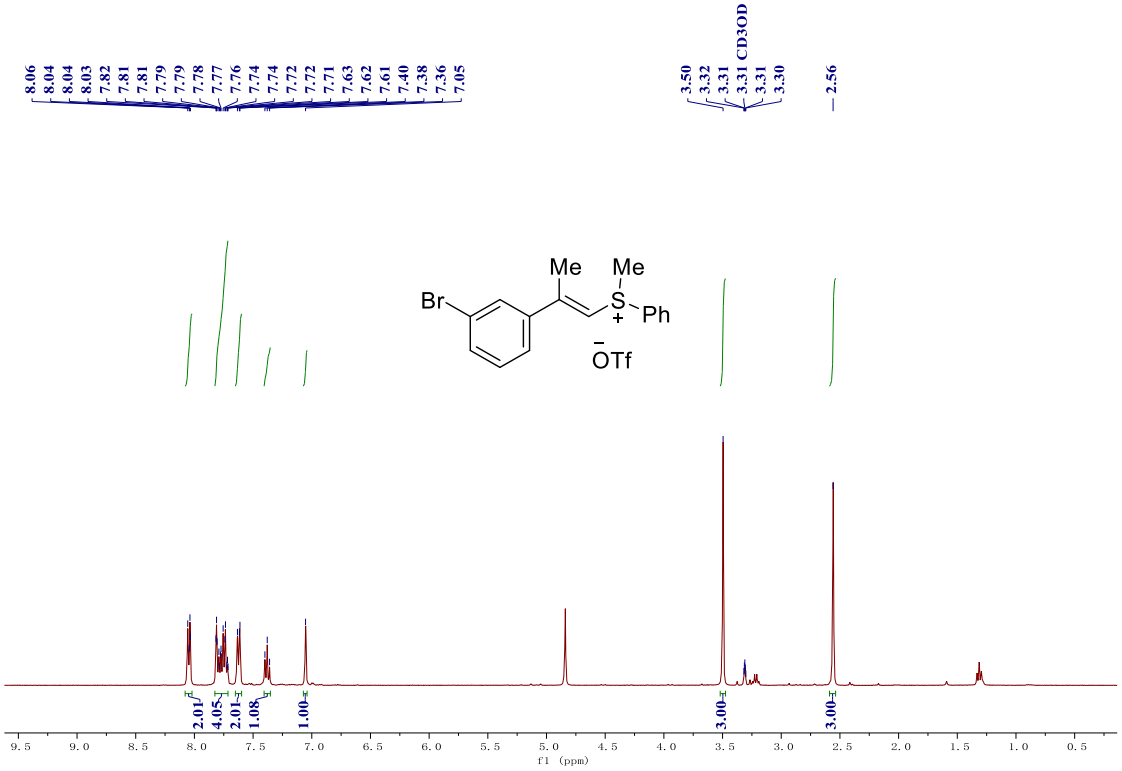
^{13}C NMR Spectra of compound 2c (101 MHz, CD_3OD)



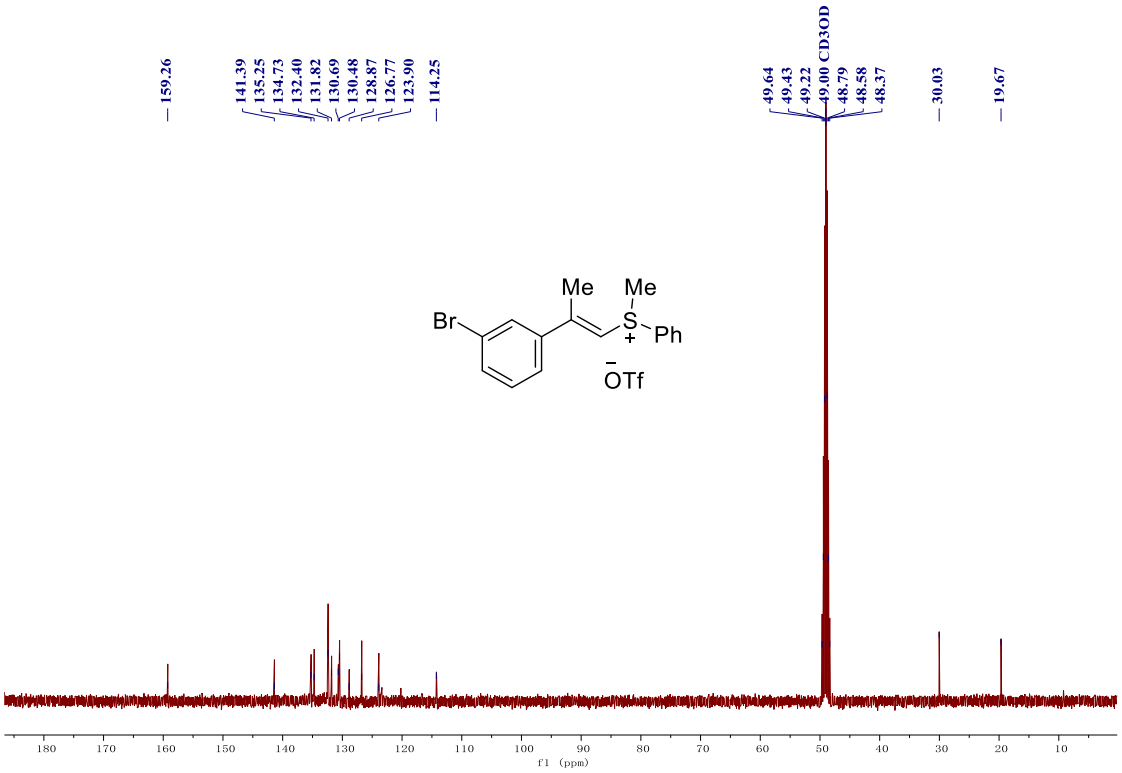
^{19}F NMR Spectra of compound 2c (376 MHz, CD_3OD)



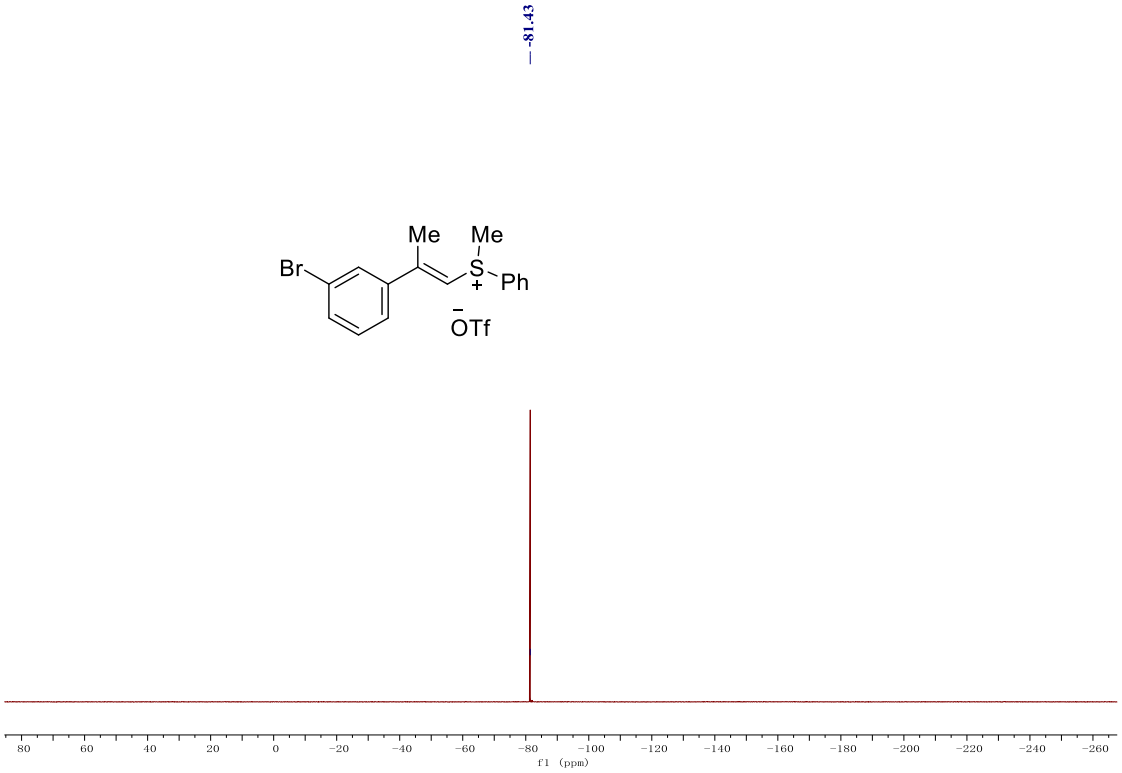
^{1}H NMR Spectra of compound 2d (400 MHz, CD_3OD)



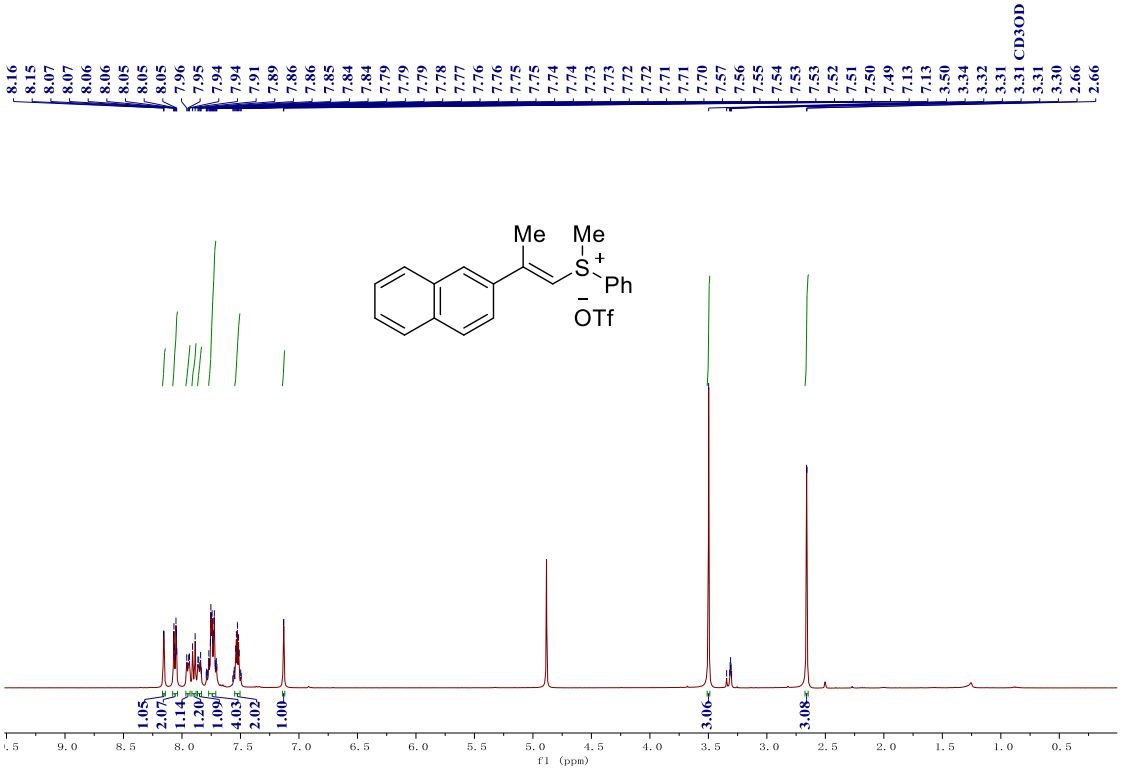
^{13}C NMR Spectra of compound 2d (101 MHz, CD_3OD)



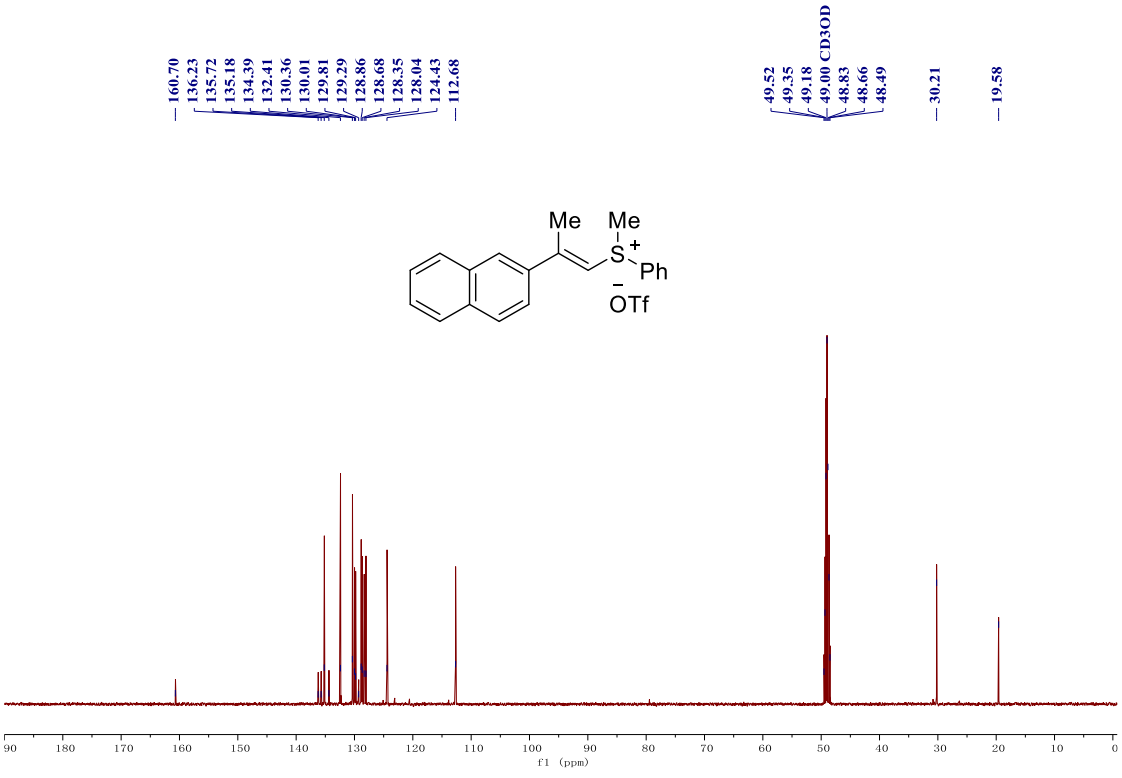
^{19}F NMR Spectra of compound 2d (376 MHz, CD_3OD)



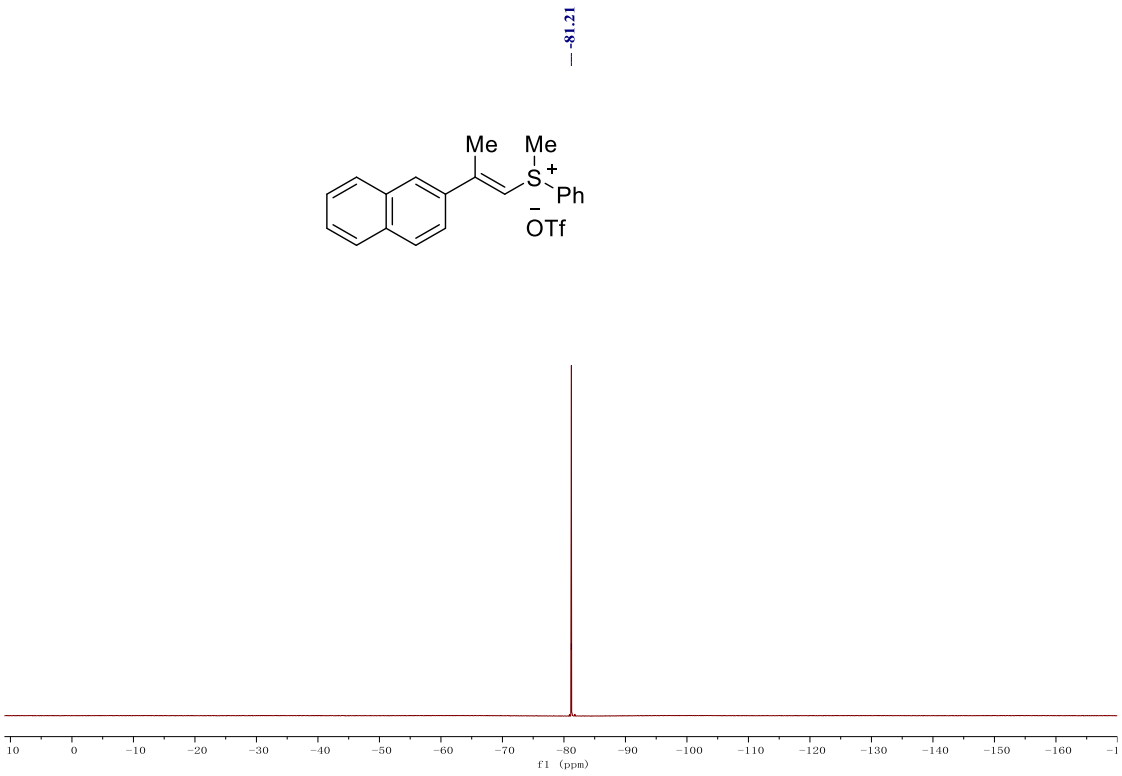
^{1}H NMR Spectra of compound 2e (400 MHz, CD_3OD)



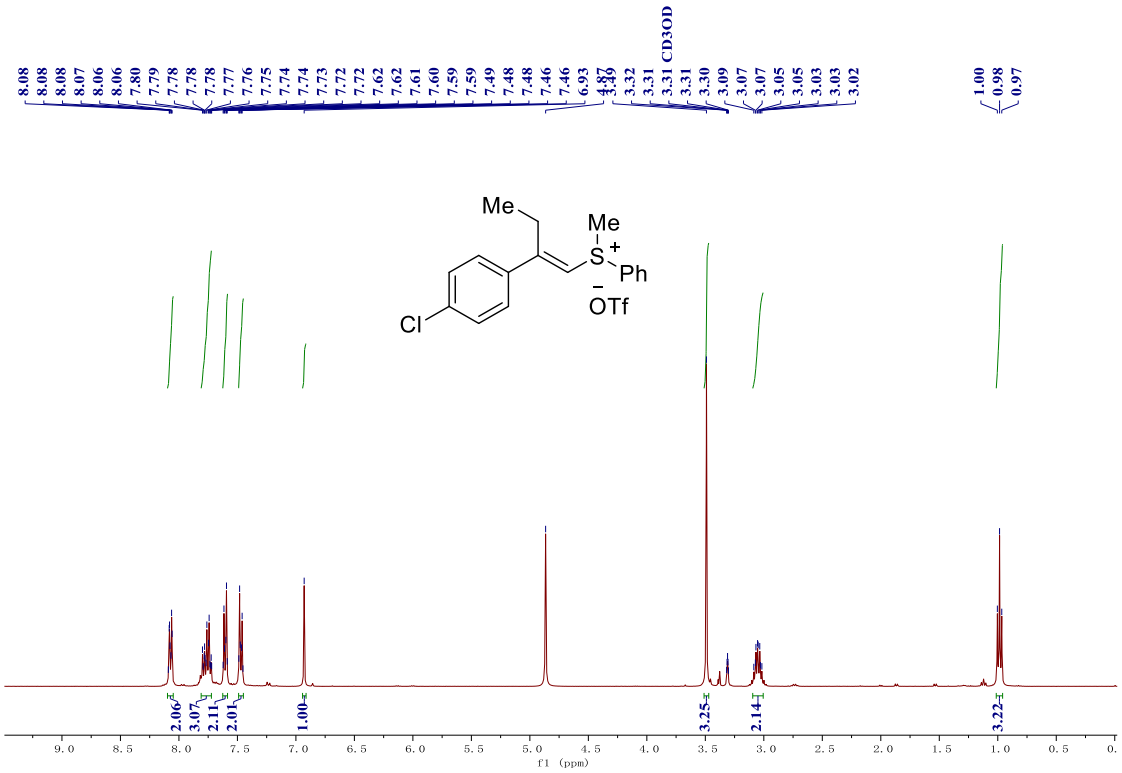
^{13}C NMR Spectra of compound 2e (101 MHz, CD_3OD)



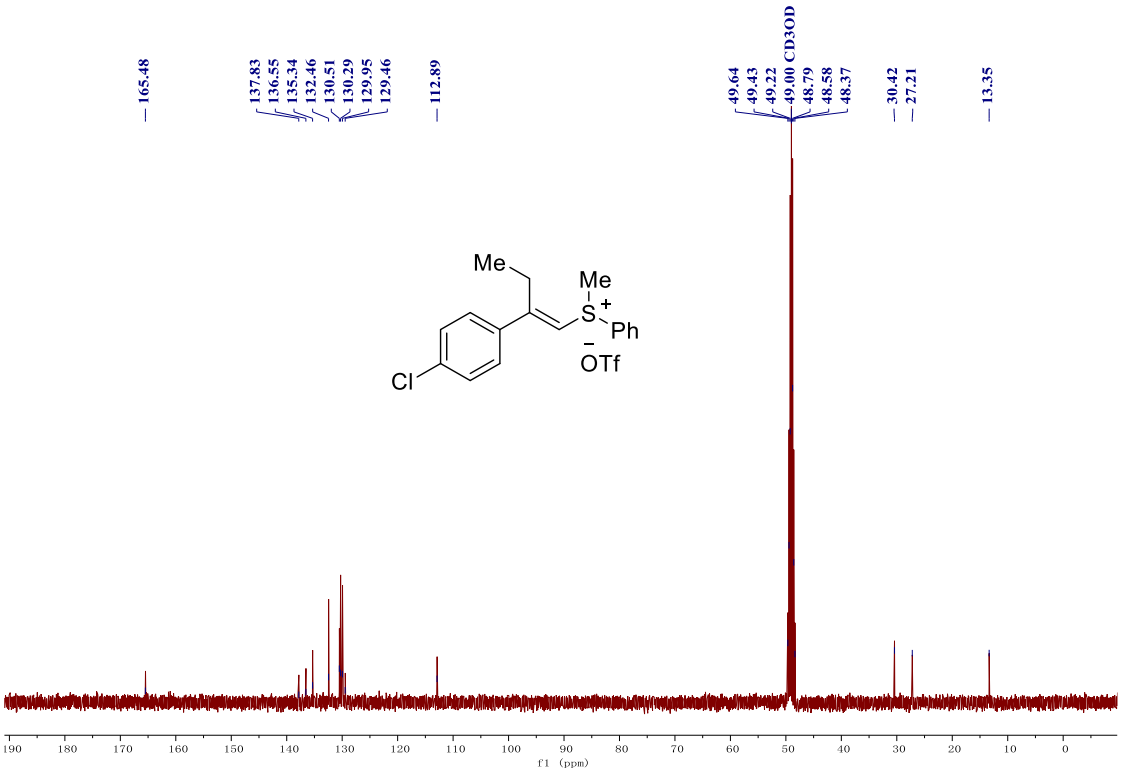
^{19}F NMR Spectra of compound 2e (376 MHz, CD_3OD)



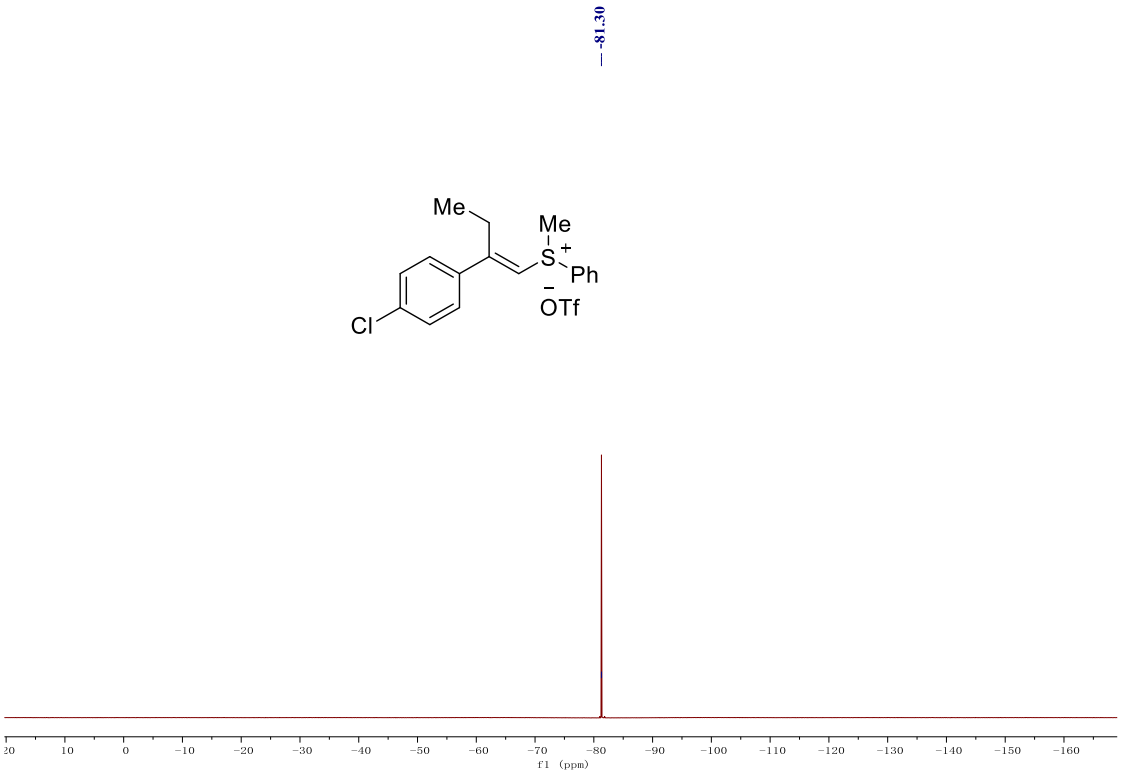
^{1}H NMR Spectra of compound 2f (400 MHz, CD_3OD)



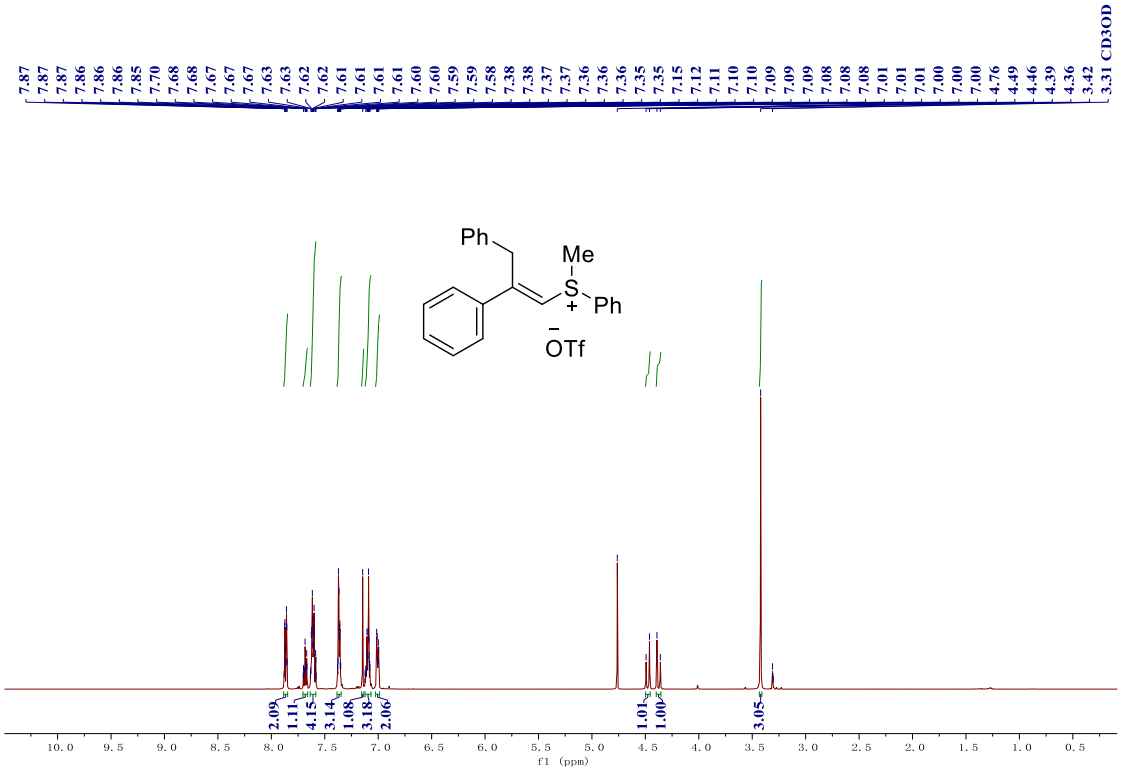
^{13}C NMR Spectra of compound 2f (101 MHz, CD_3OD)



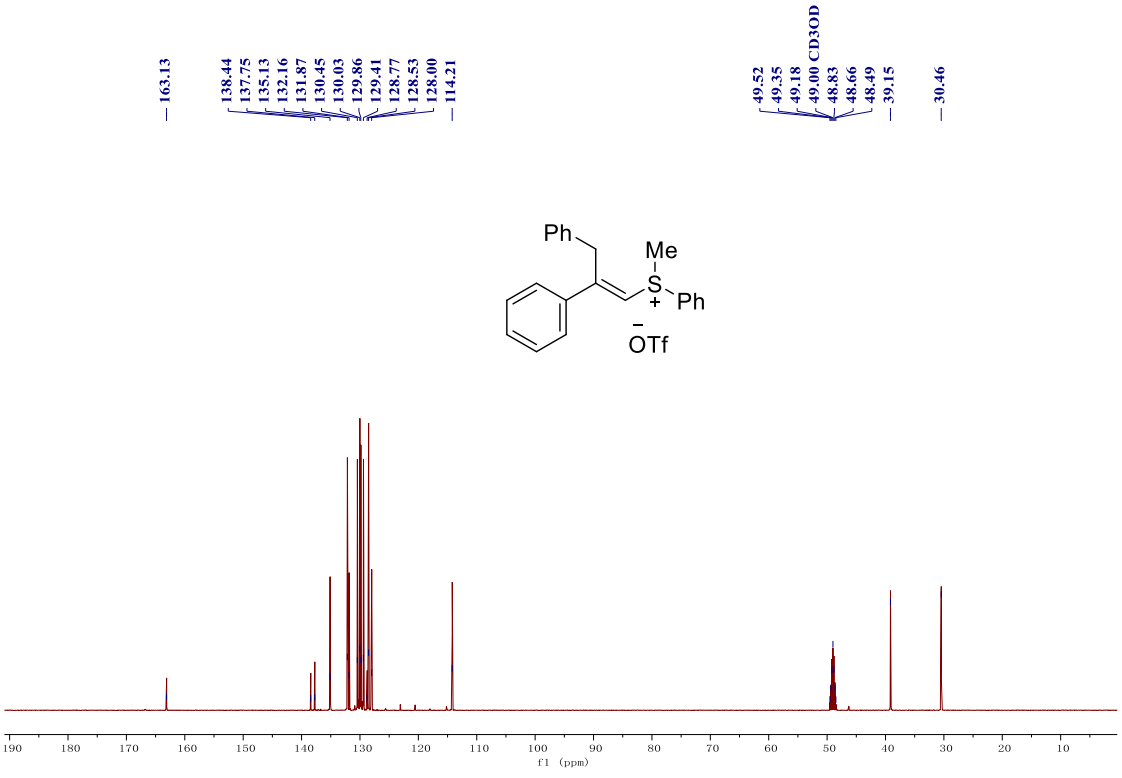
^{19}F NMR Spectra of compound 2f (376 MHz, CD_3OD)



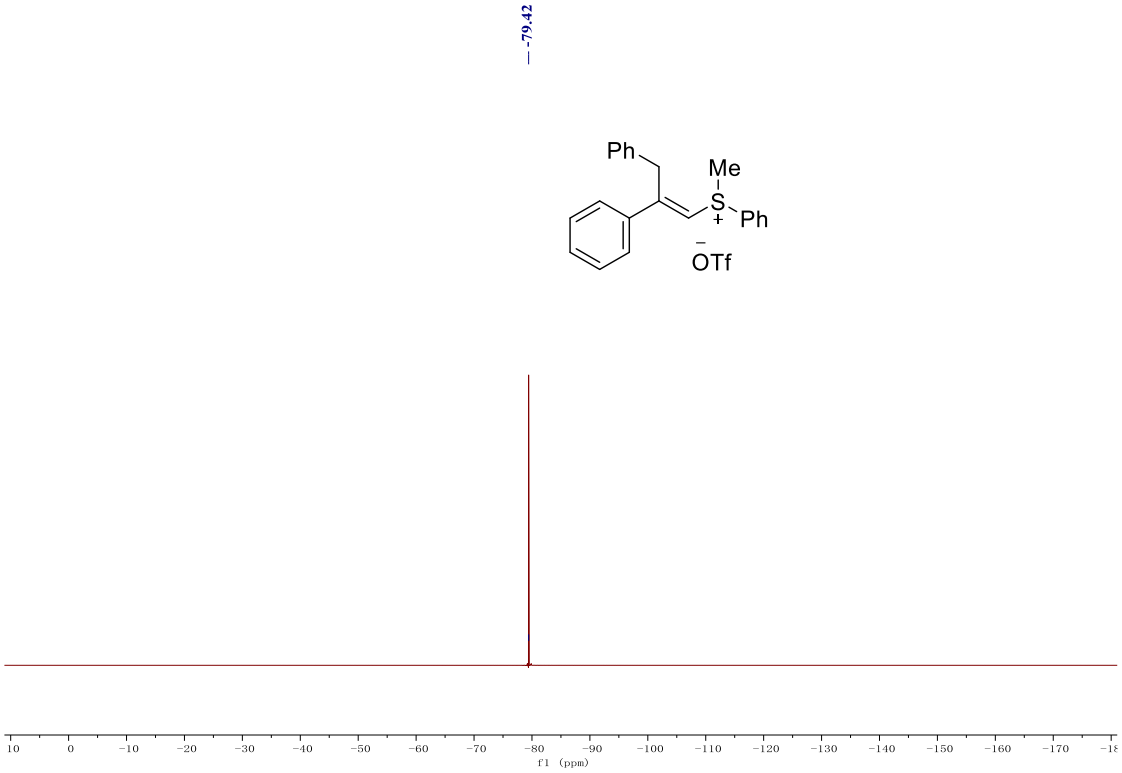
^{1}H NMR Spectra of compound 2g (500 MHz, CD_3OD)



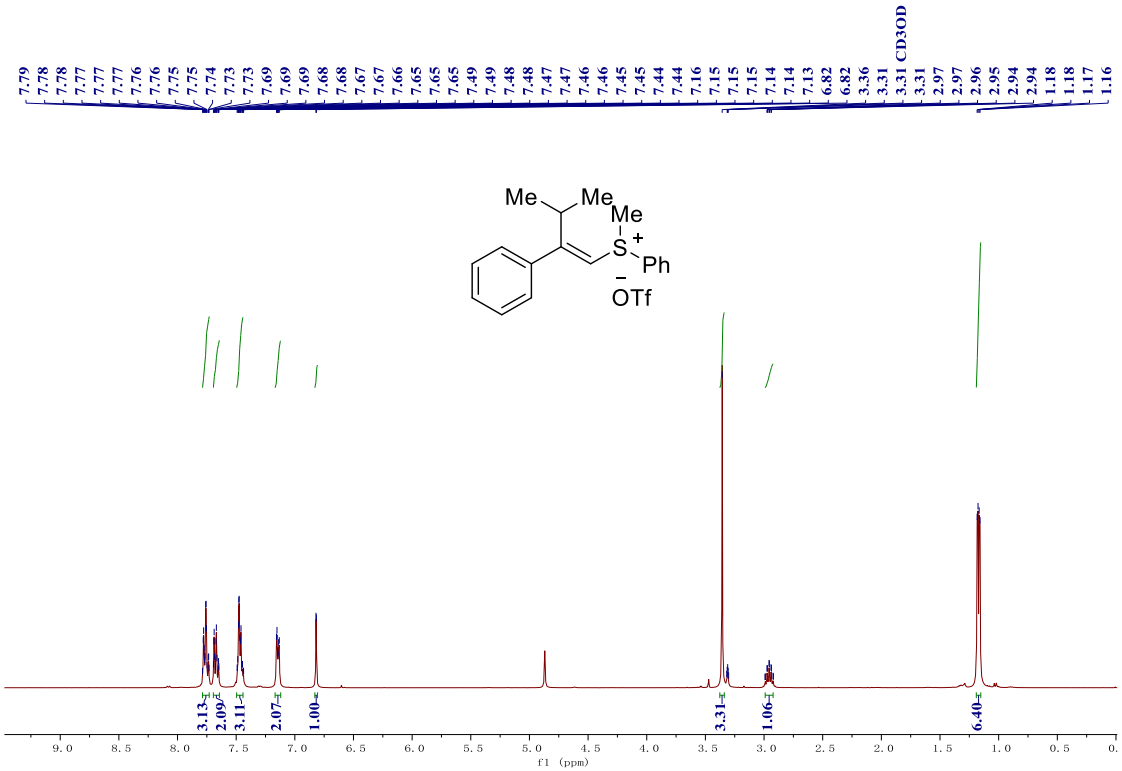
^{13}C NMR Spectra of compound 2g (126 MHz, CD_3OD)



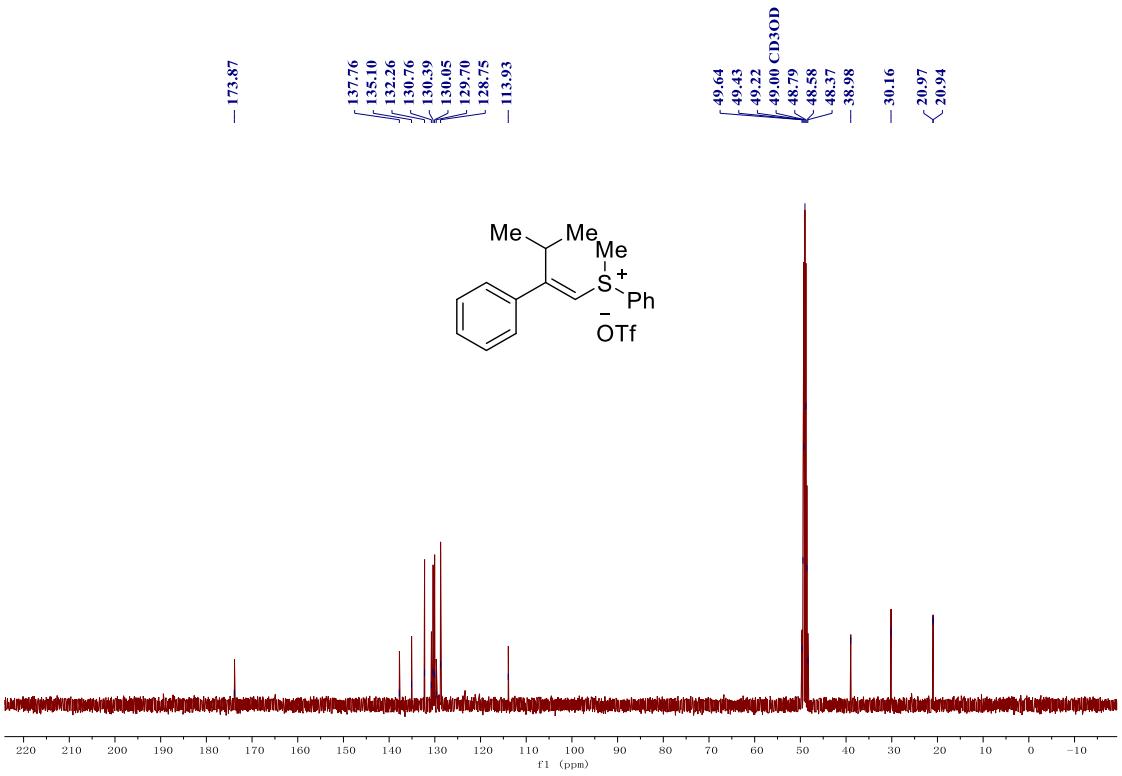
^{19}F NMR Spectra of compound 2g (471 MHz, CD_3OD)



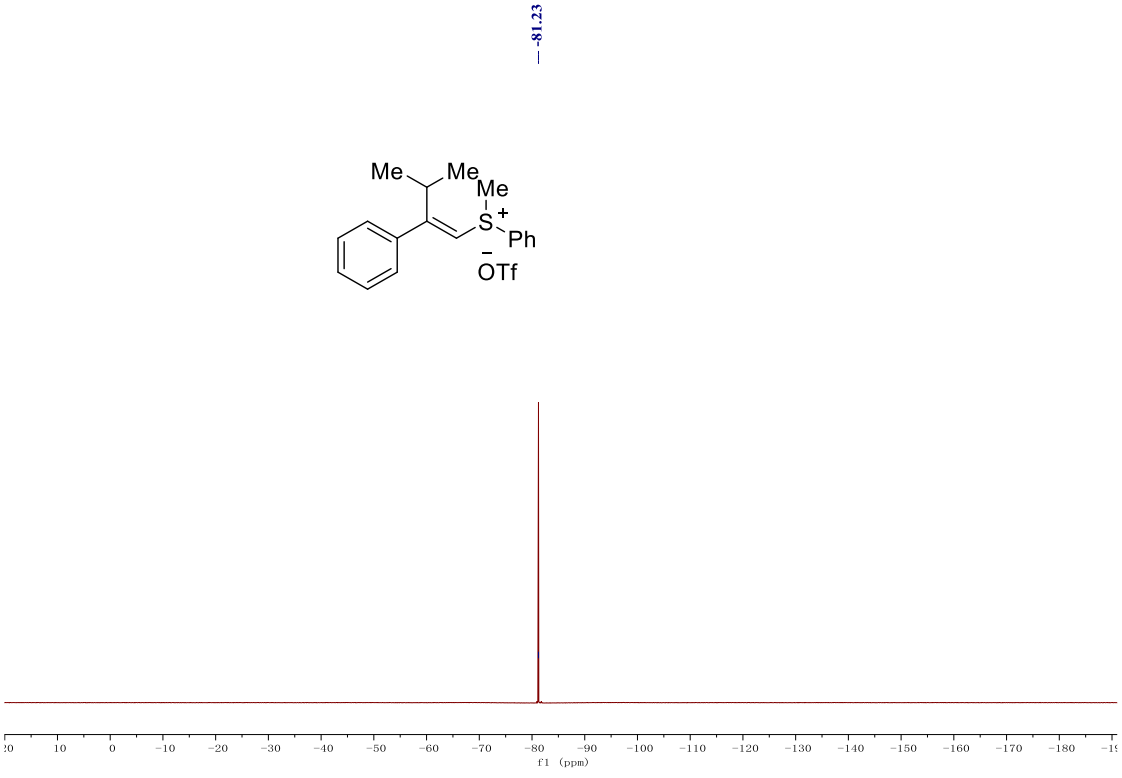
^{1}H NMR Spectra of compound 2h (400 MHz, CD_3OD)



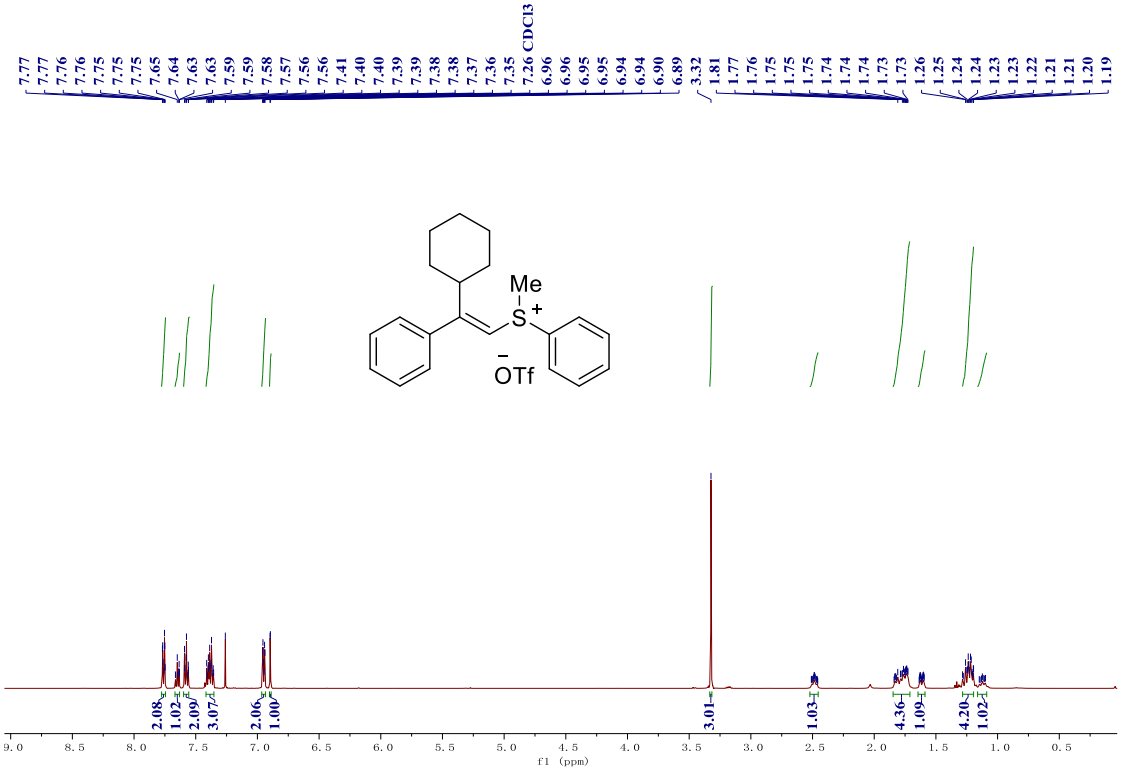
^{13}C NMR Spectra of compound 2h (101 MHz, CD_3OD)



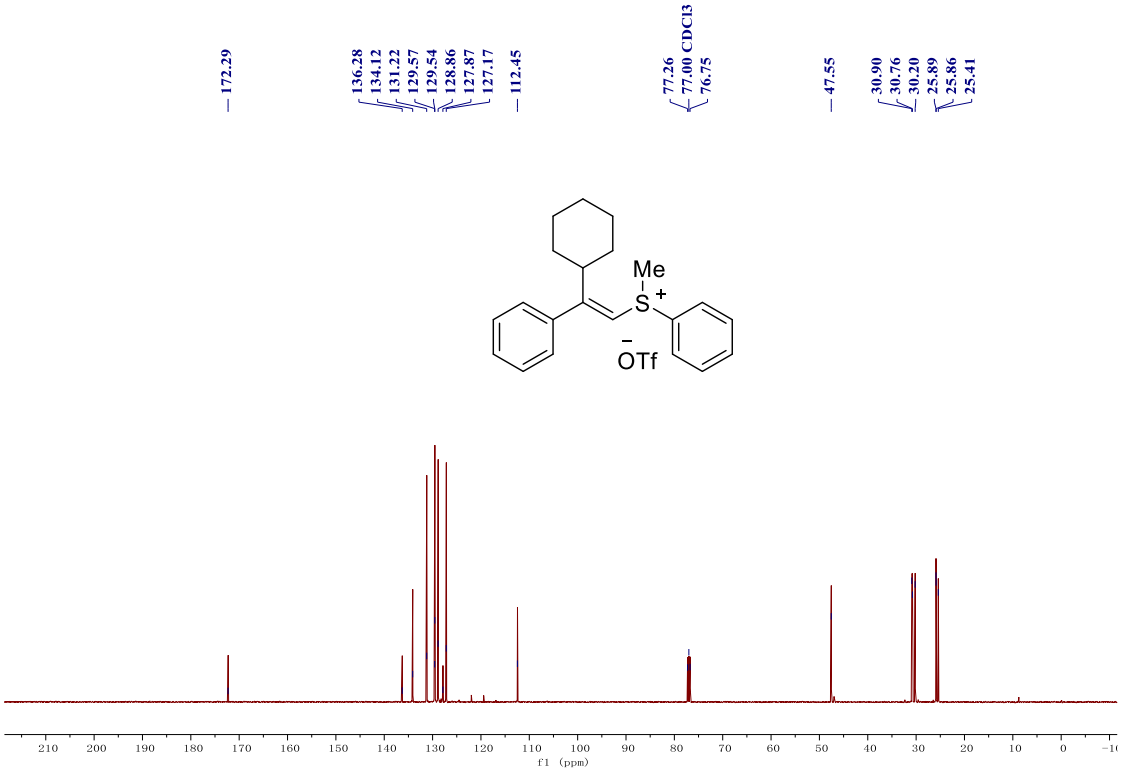
^{19}F NMR Spectra of compound 2h (376 MHz, CD_3OD)



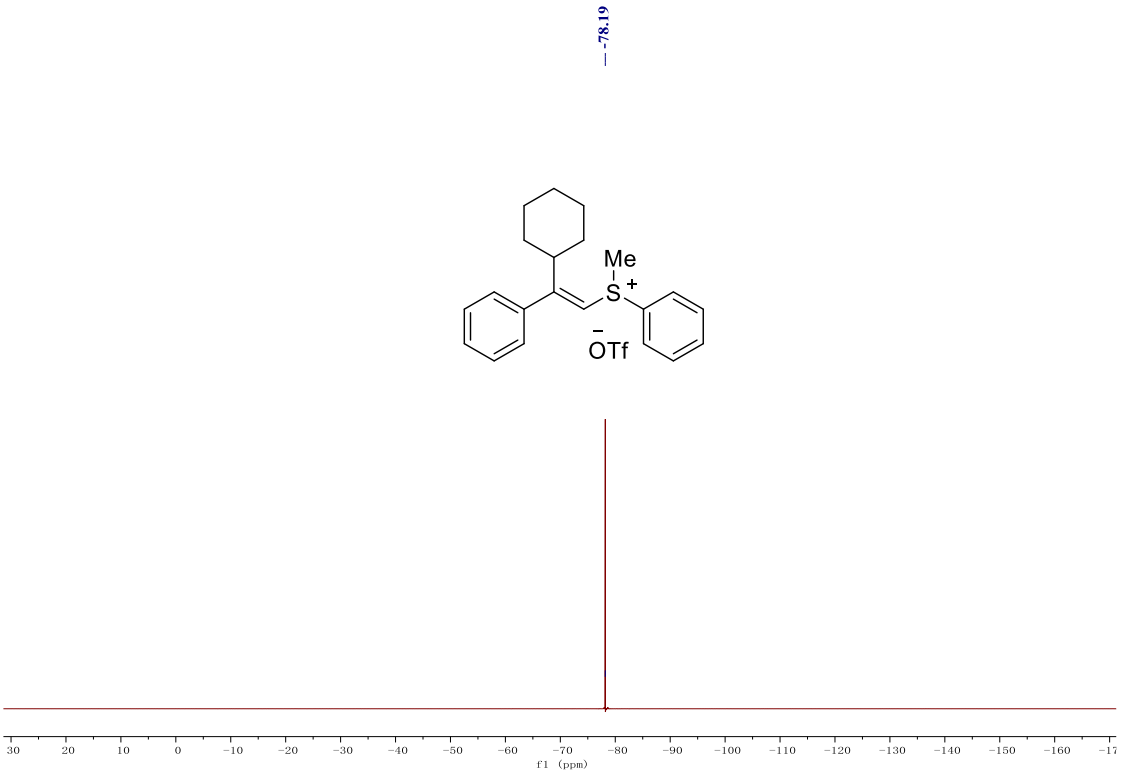
^{1}H NMR Spectra of compound 2i (500 MHz, CD_3OD)



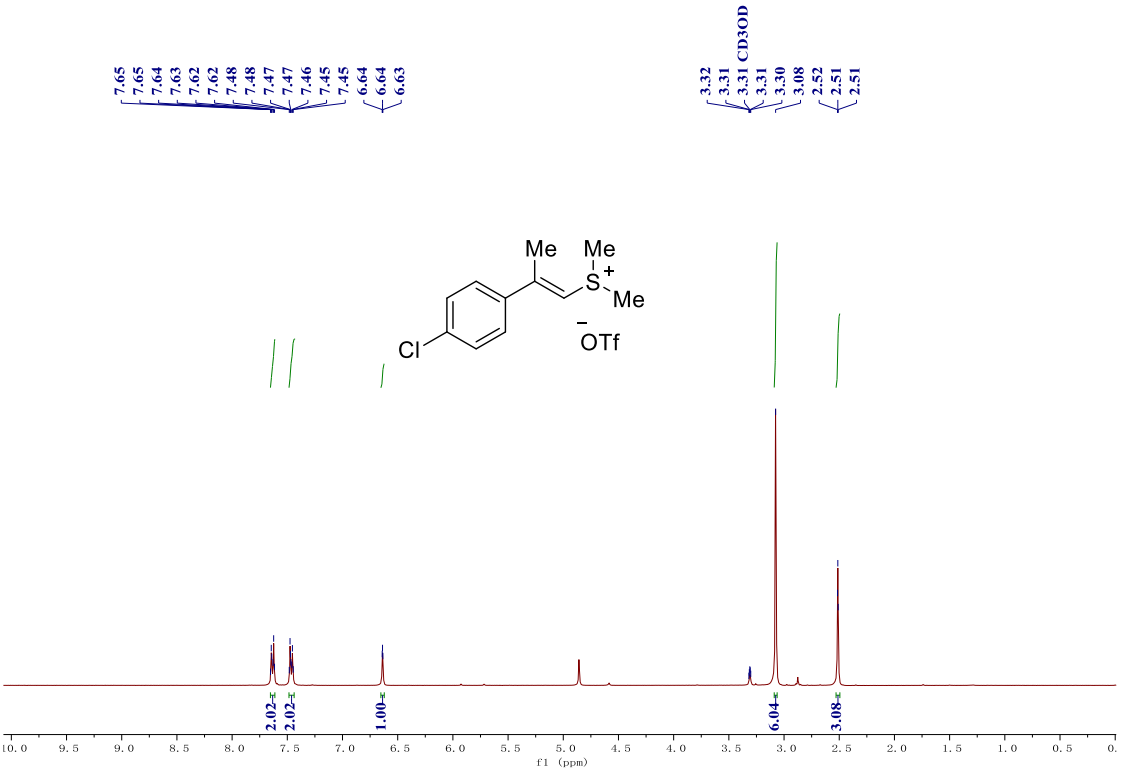
^{13}C NMR Spectra of compound 2i (126 MHz, CD_3OD)



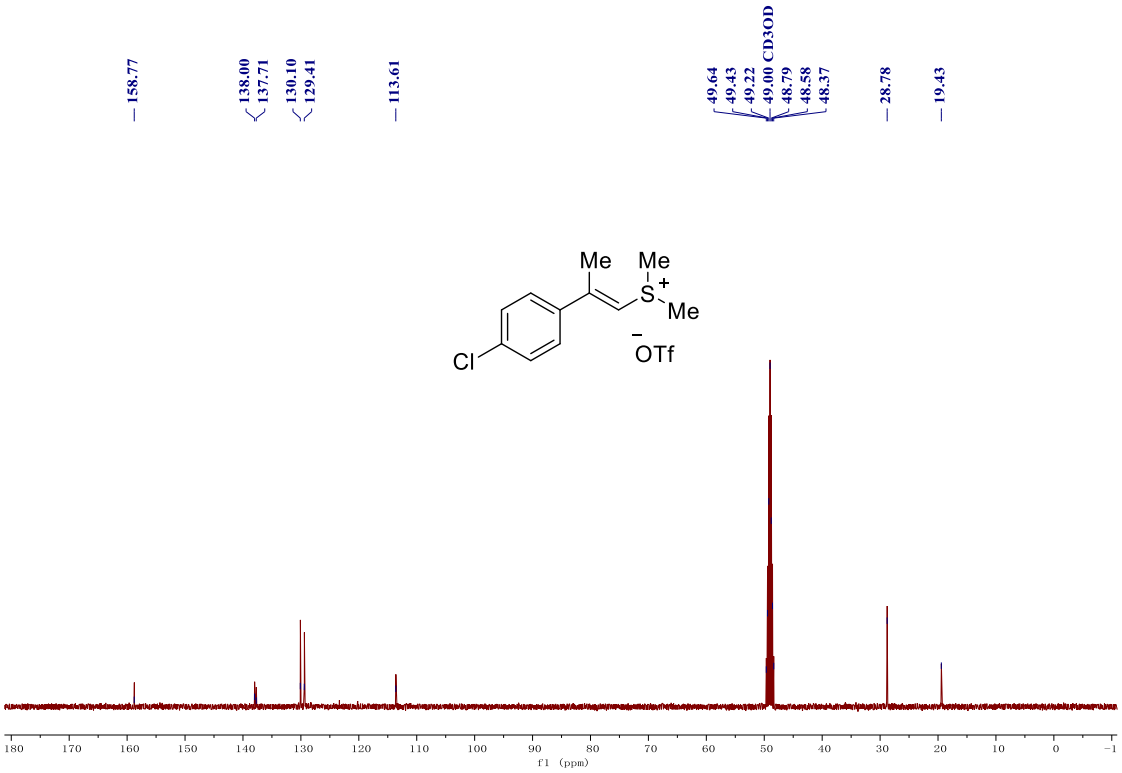
^{19}F NMR Spectra of compound 2i (471MHz, CD_3OD)



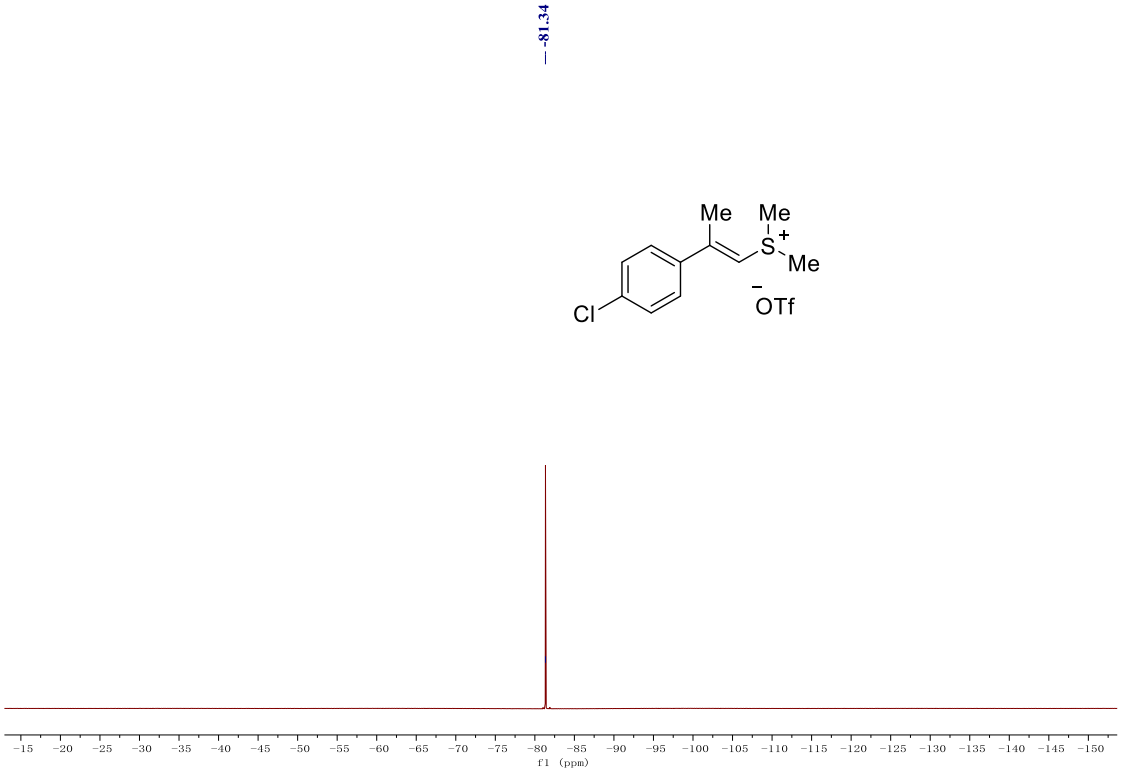
^{1}H NMR Spectra of compound 2j (400 MHz, CD_3OD)



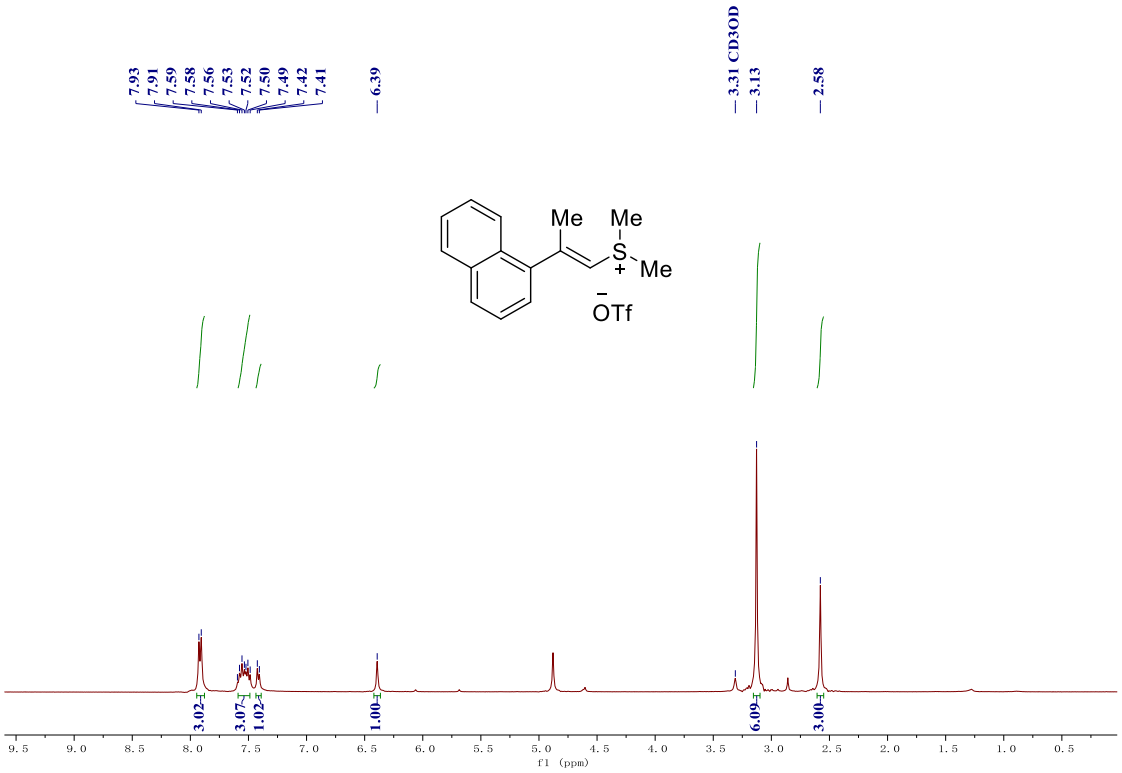
^{13}C NMR Spectra of compound 2j (126 MHz, CD_3OD)



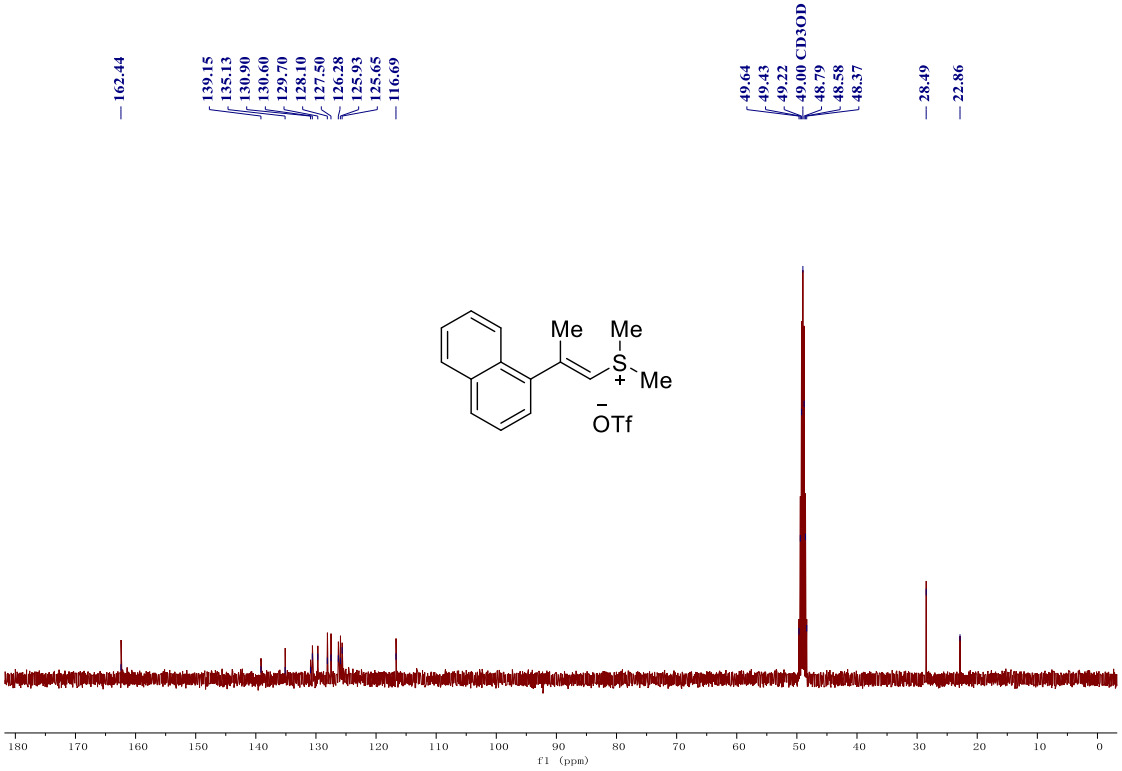
^{19}F NMR Spectra of compound 2j (376 MHz, CD_3OD)



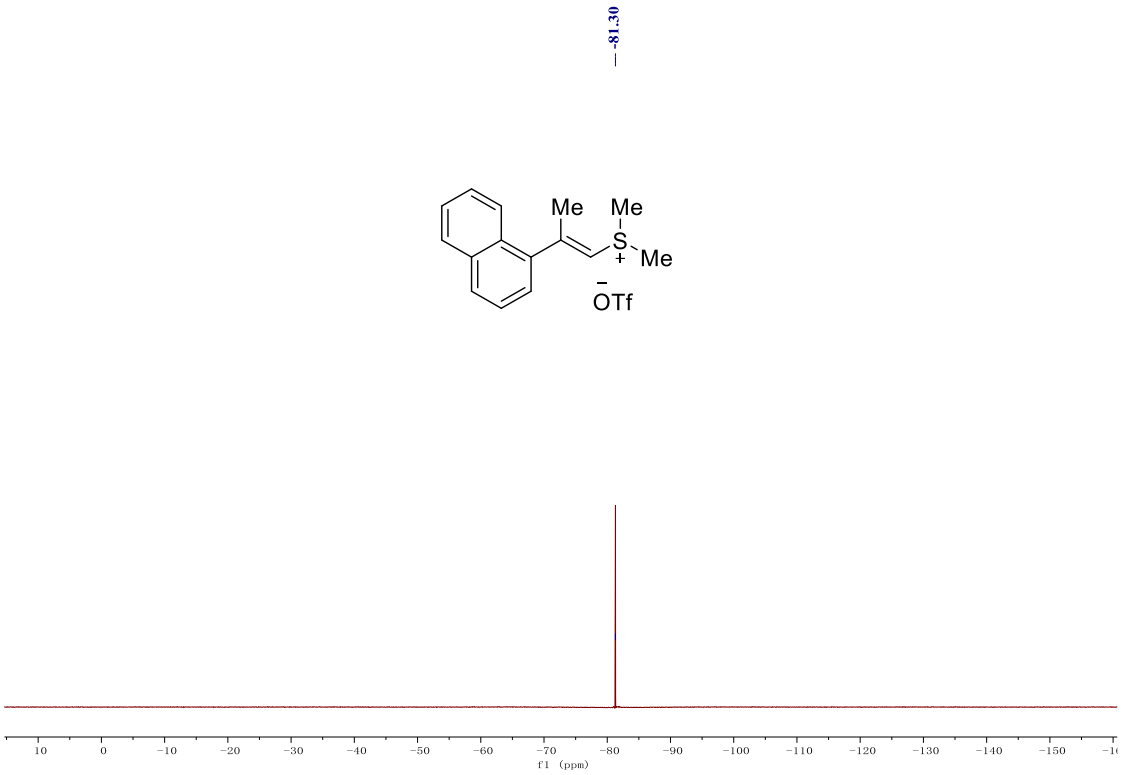
^{1}H NMR Spectra of compound 2k (400 MHz, CD_3OD)



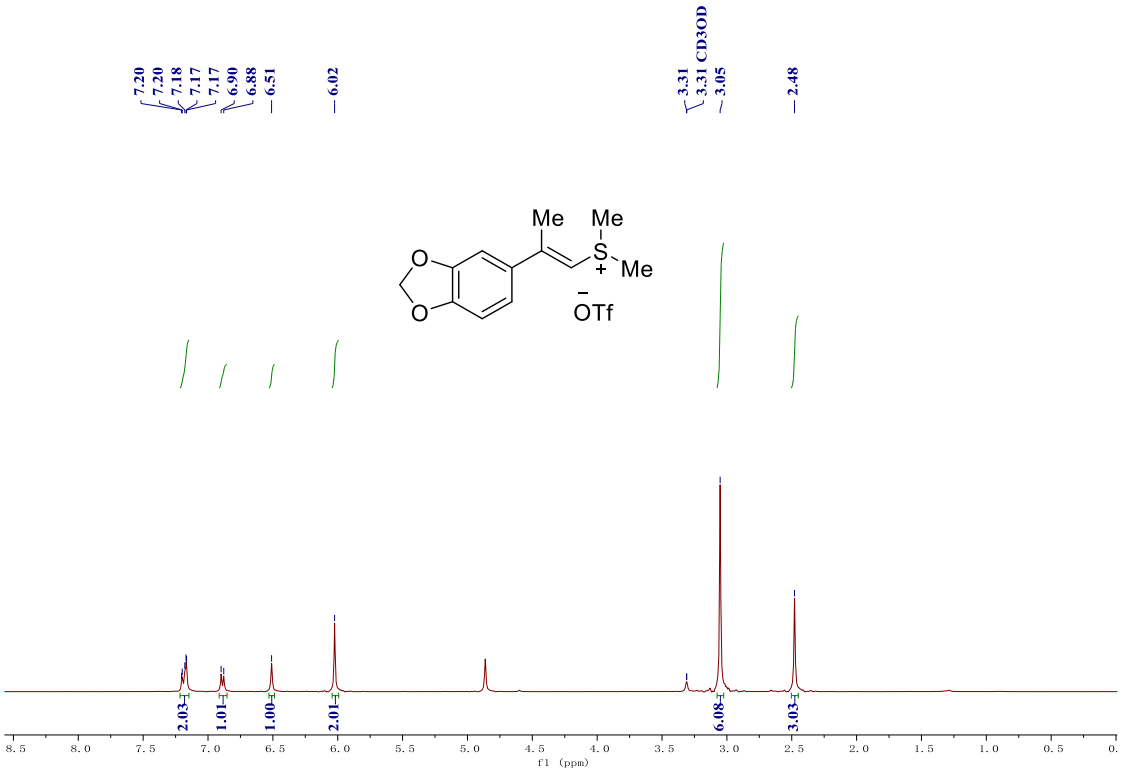
^{13}C NMR Spectra of compound 2k (101 MHz, CD_3OD)



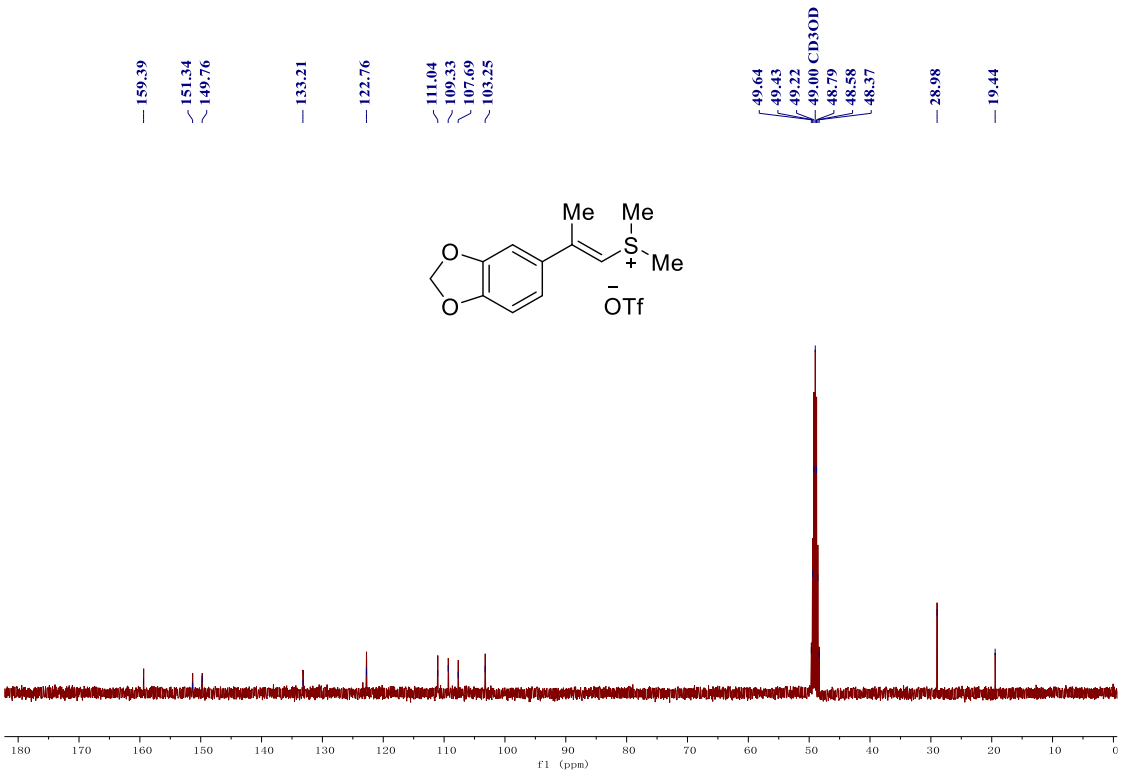
^{19}F NMR Spectra of compound 2k (376 MHz, CD_3OD)



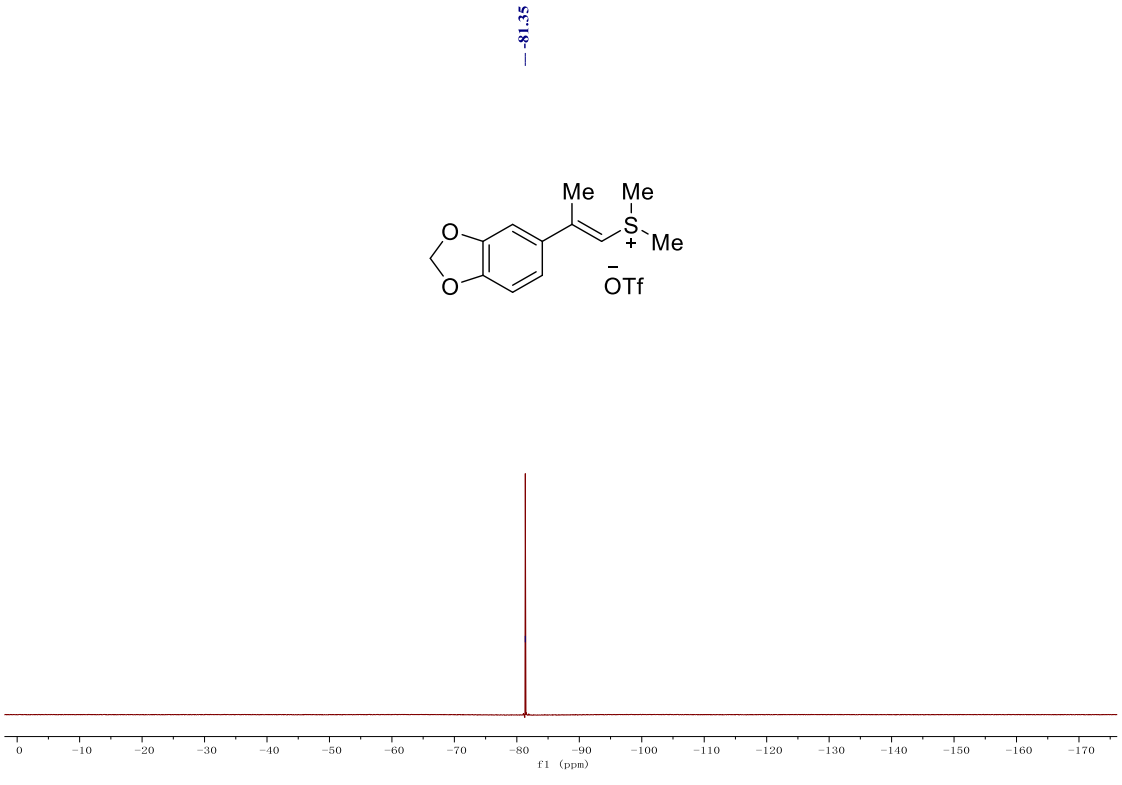
^{1}H NMR Spectra of compound 2l (400 MHz, CD_3OD)



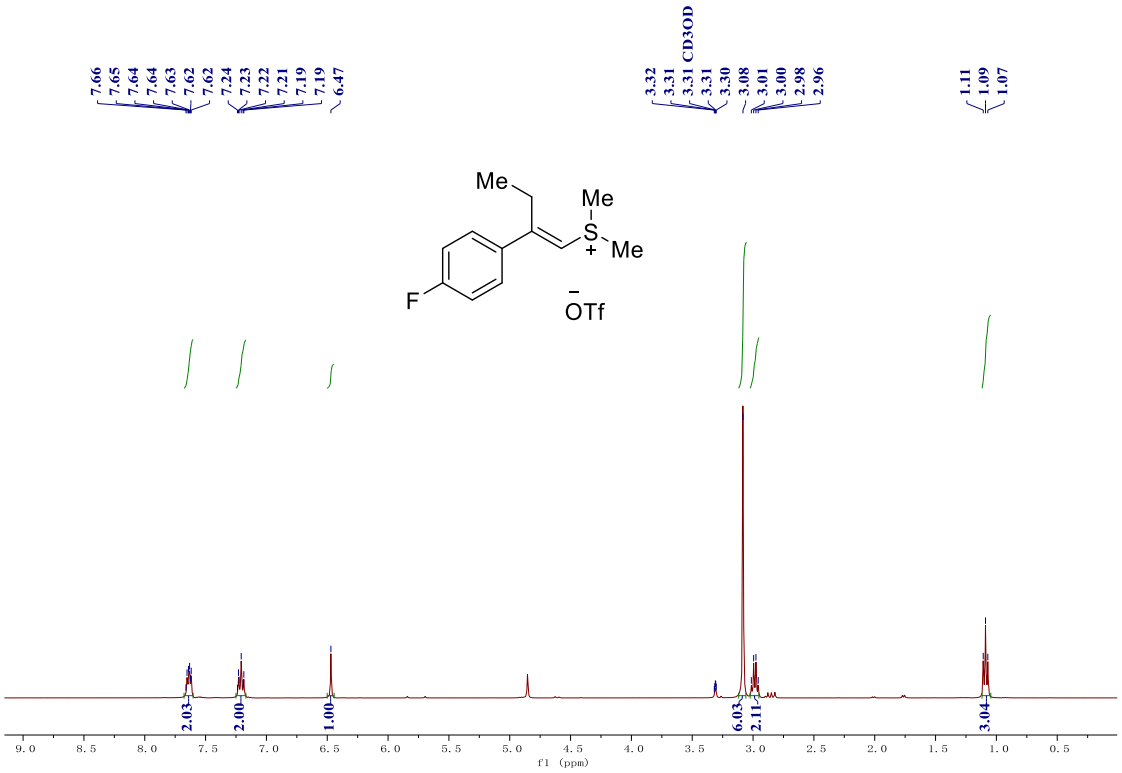
^{13}C NMR Spectra of compound 2l (101 MHz, CD_3OD)



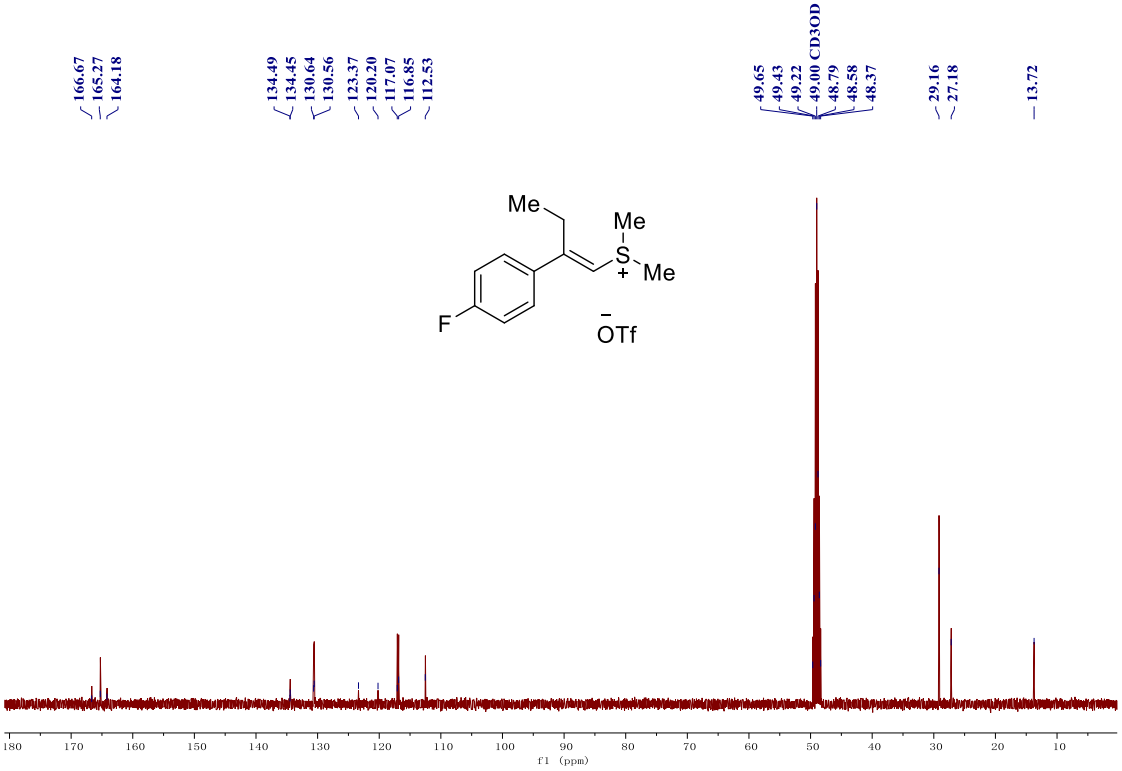
^{19}F NMR Spectra of compound 2l (376 MHz, CD_3OD)



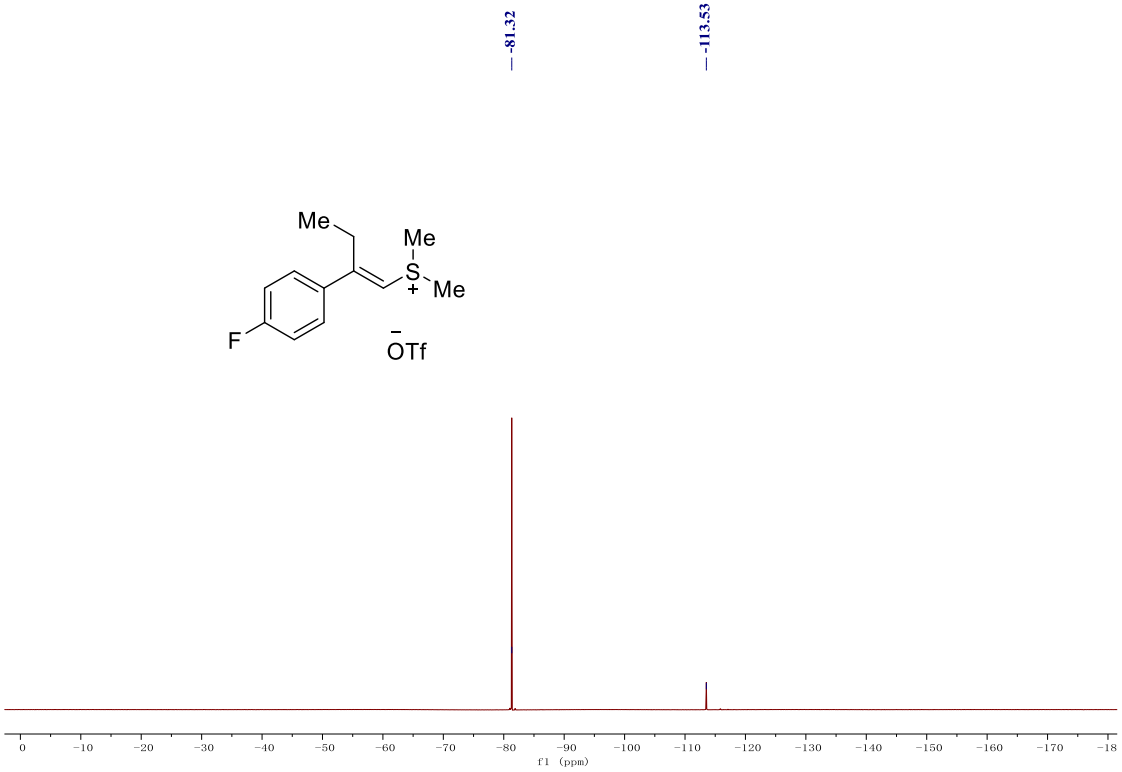
^{1}H NMR Spectra of compound 2m (400 MHz, CD_3OD)



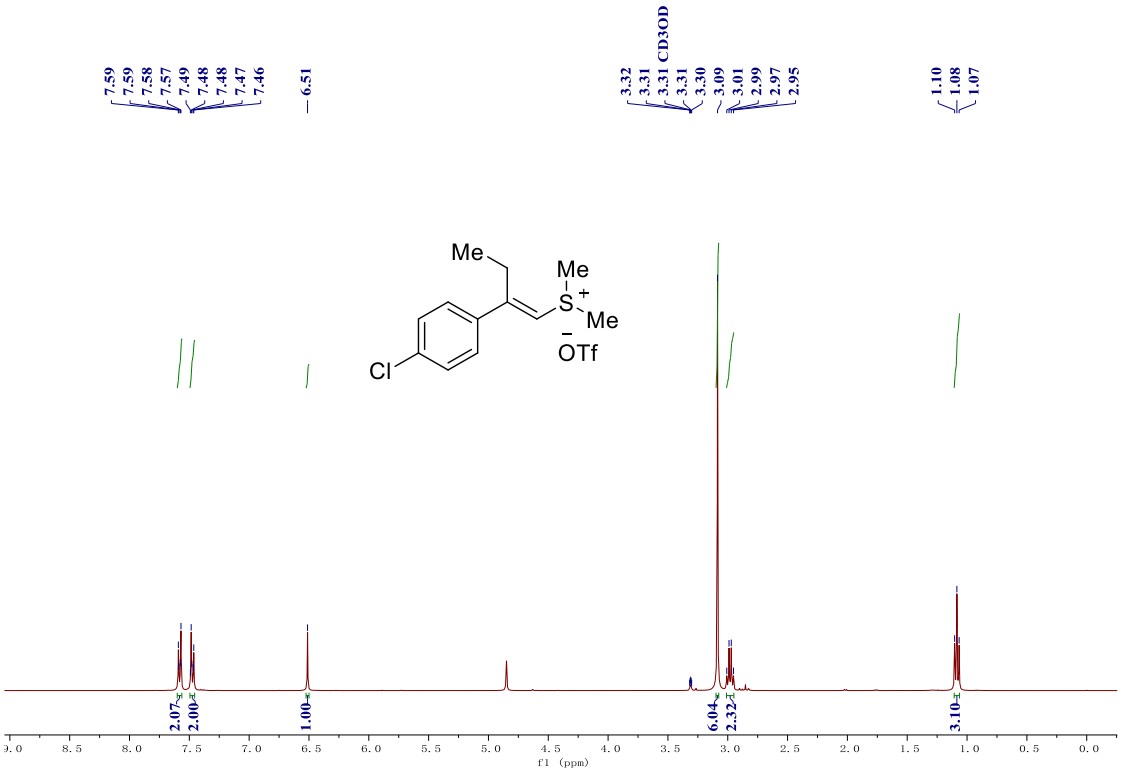
^{13}C NMR Spectra of compound 2m (101 MHz, CD_3OD)



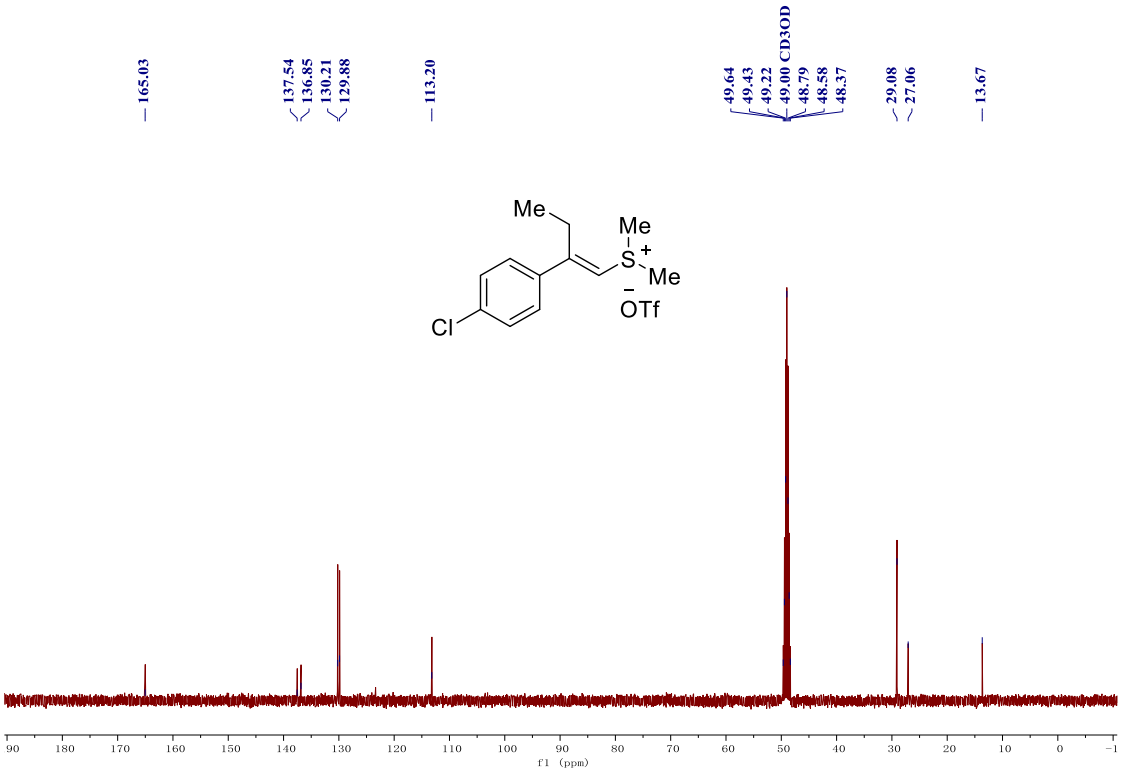
^{19}F NMR Spectra of compound 2m (376 MHz, CD_3OD)



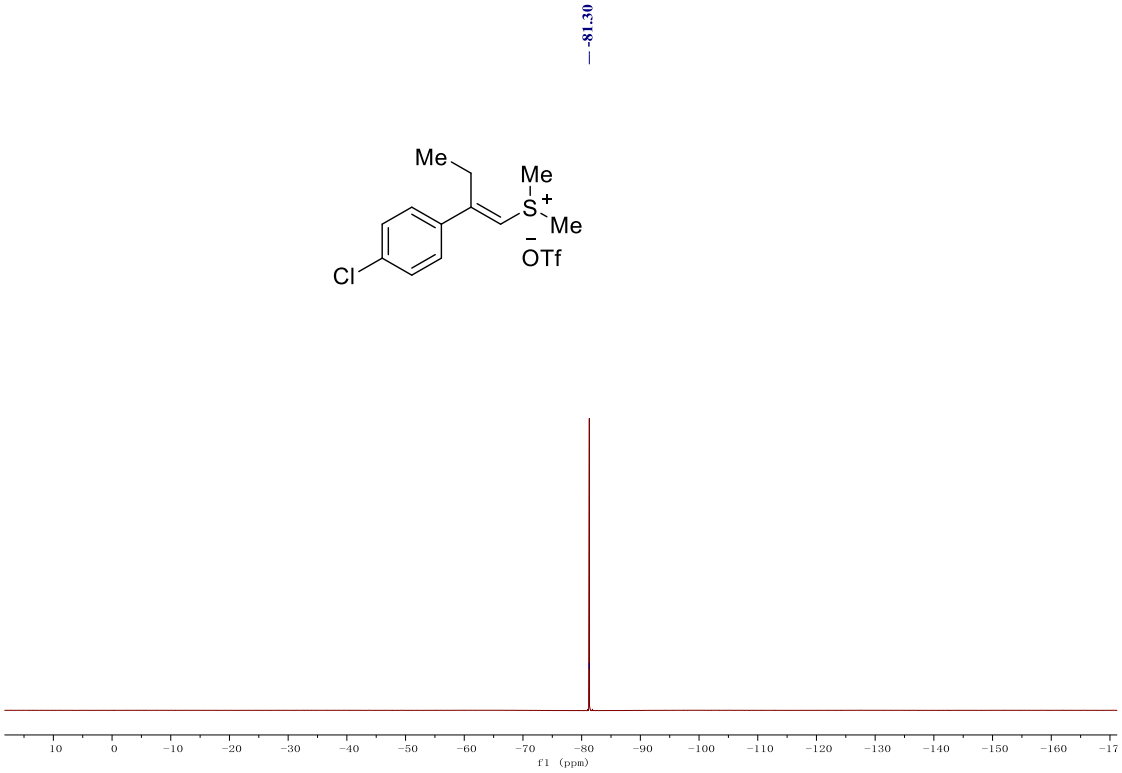
^{1}H NMR Spectra of compound 2n (400 MHz, CD_3OD)



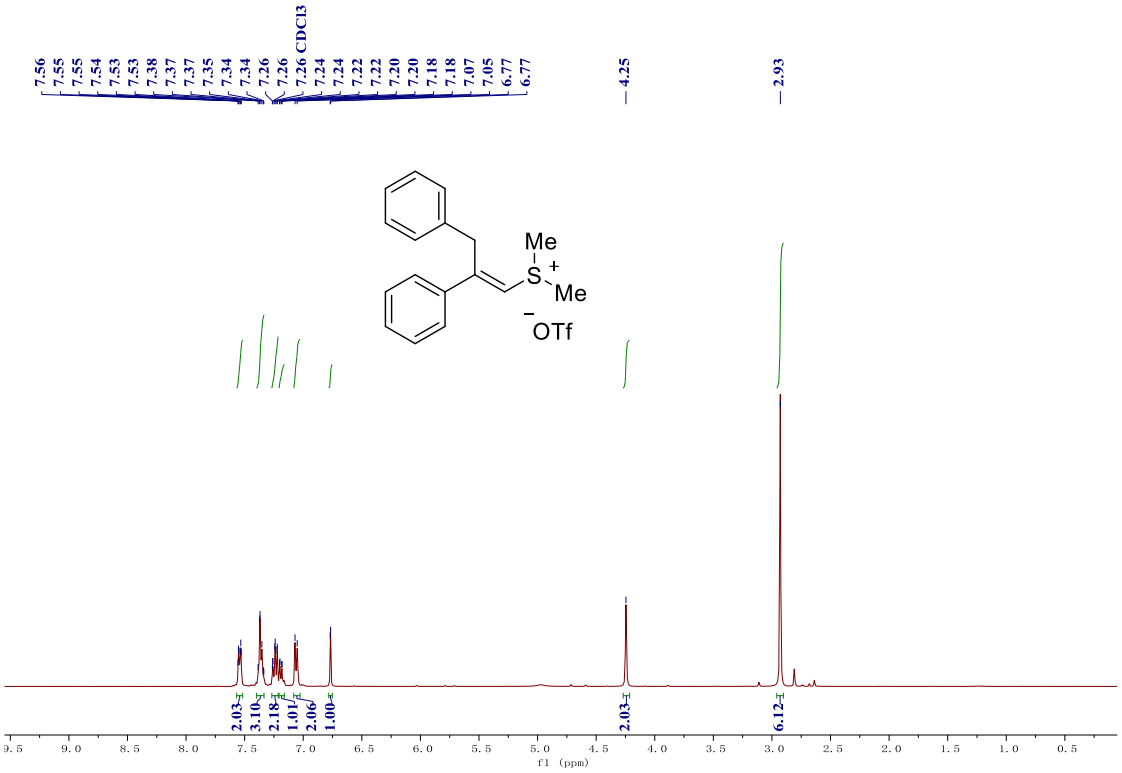
^{13}C NMR Spectra of compound 2n (101 MHz, CD_3OD)



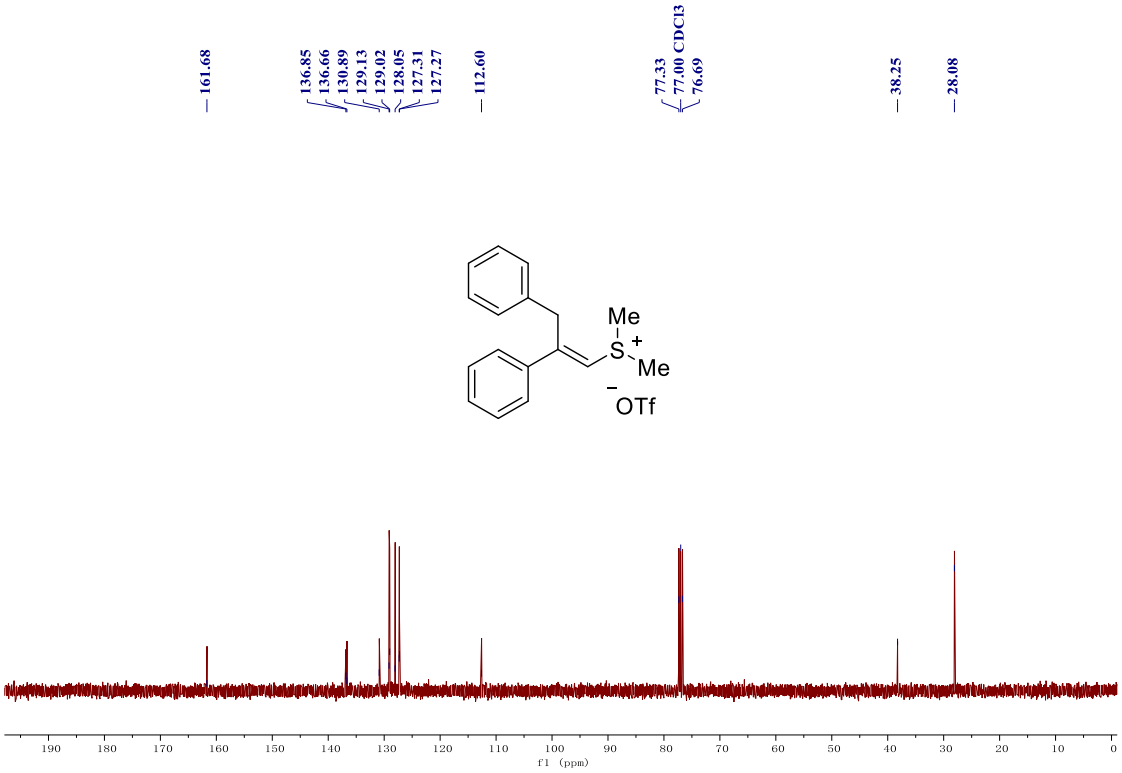
^{19}F NMR Spectra of compound 2n (376 MHz, CD_3OD)



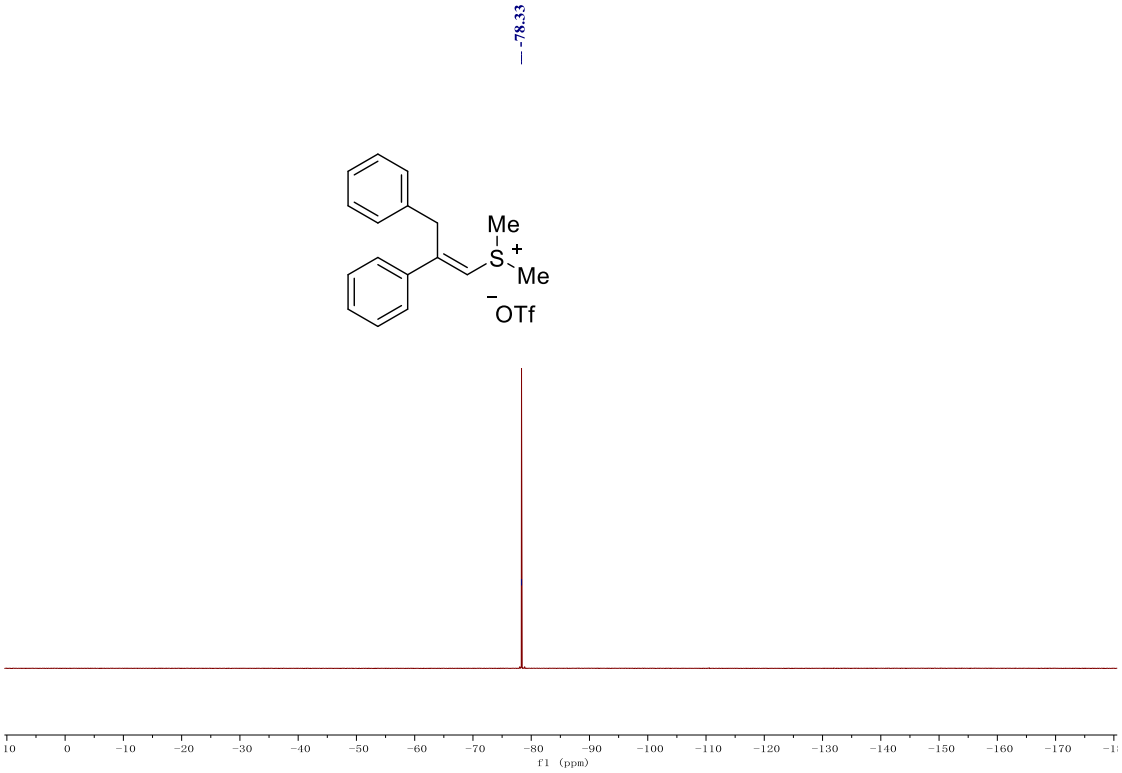
^{1}H NMR Spectra of compound 2o (400 MHz, $CDCl_3$)



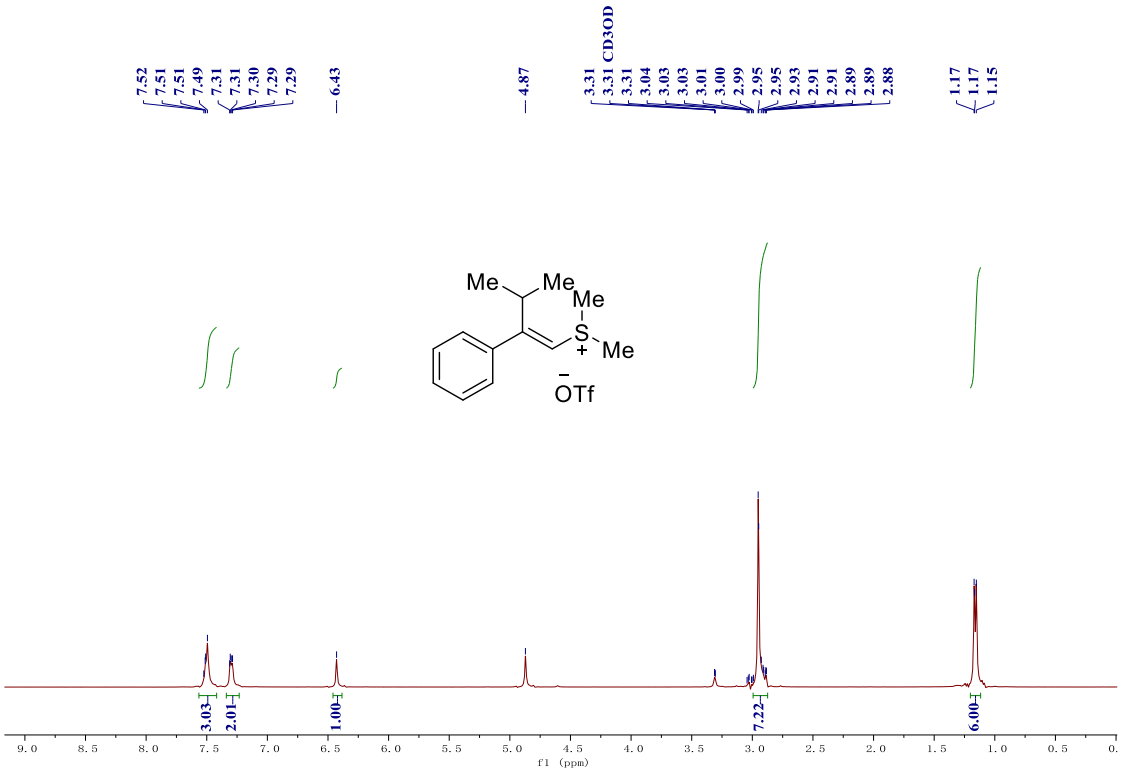
^{13}C NMR Spectra of compound 2o (101 MHz, $CDCl_3$)



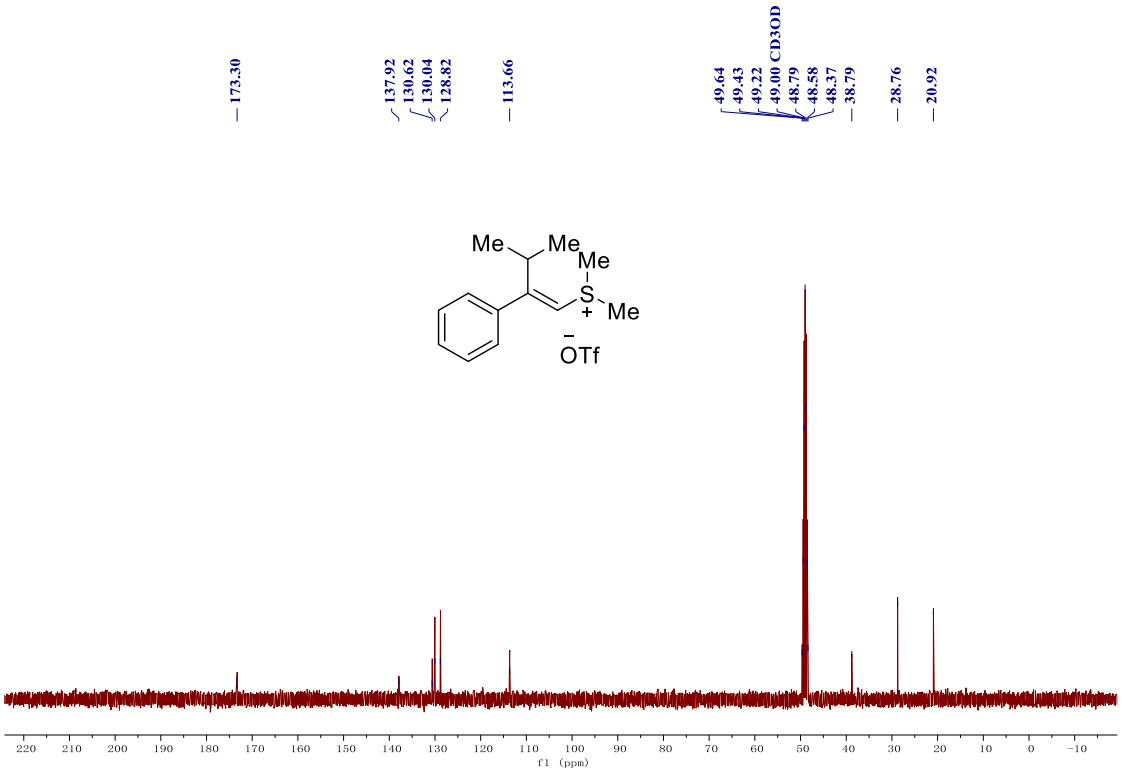
^{19}F NMR Spectra of compound 2o (376 MHz, $CDCl_3$)



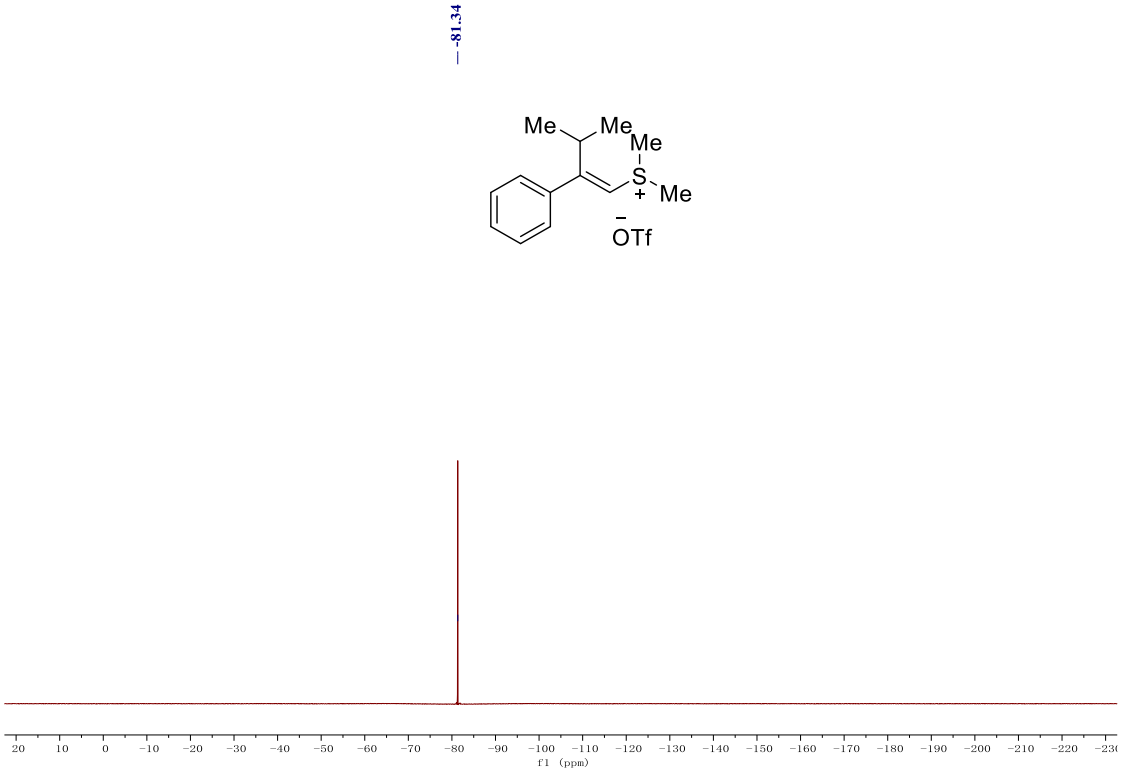
^{1}H NMR Spectra of compound 2p (400 MHz, CD_3OD)



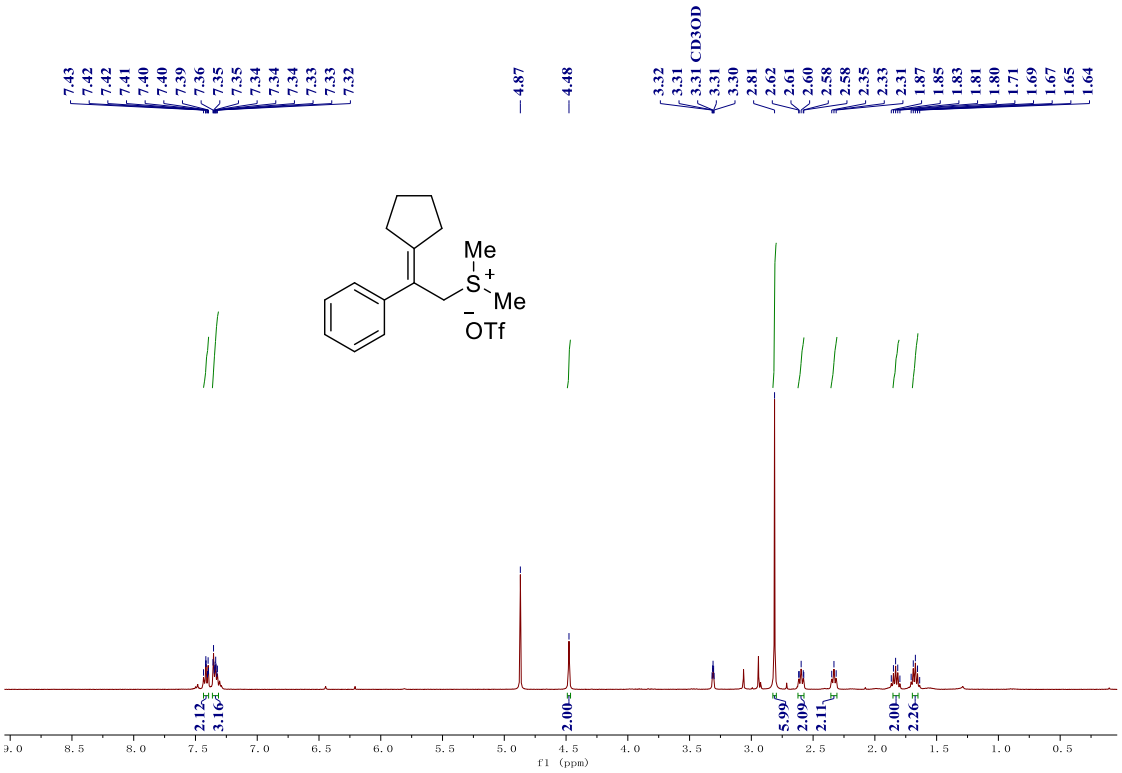
^{13}C NMR Spectra of compound 2p (101 MHz, CD_3OD)



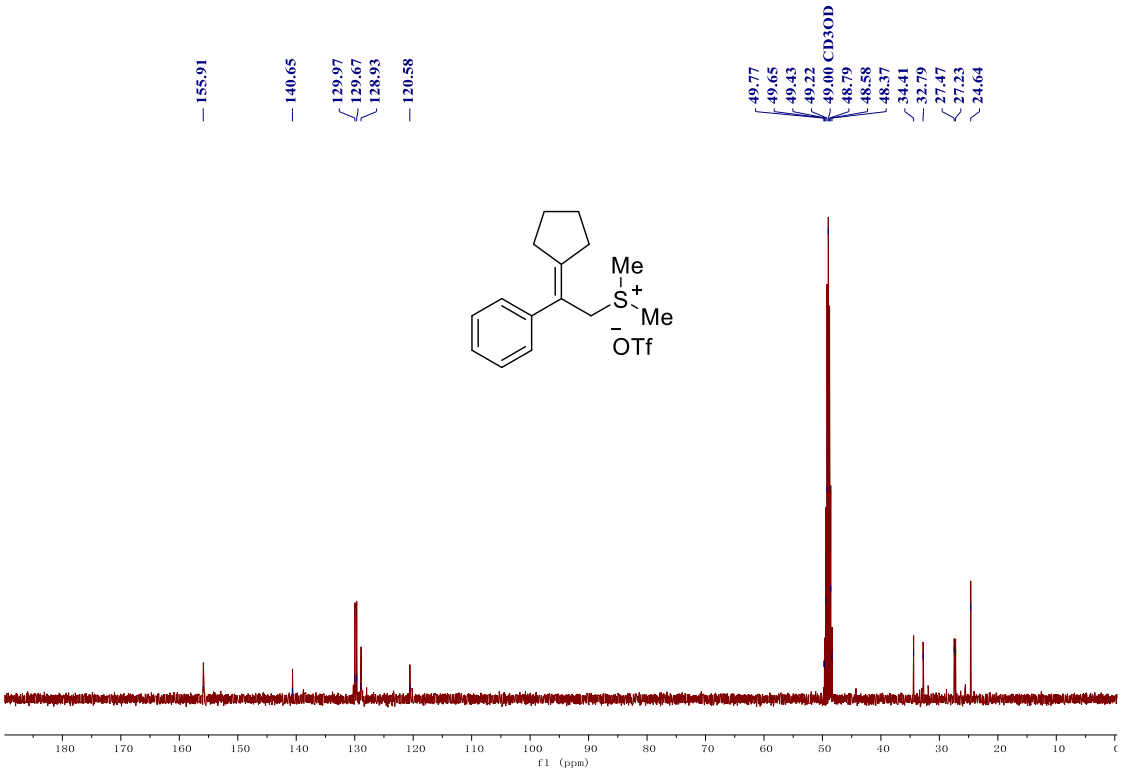
^{19}F NMR Spectra of compound 2p (376 MHz, CD_3OD)



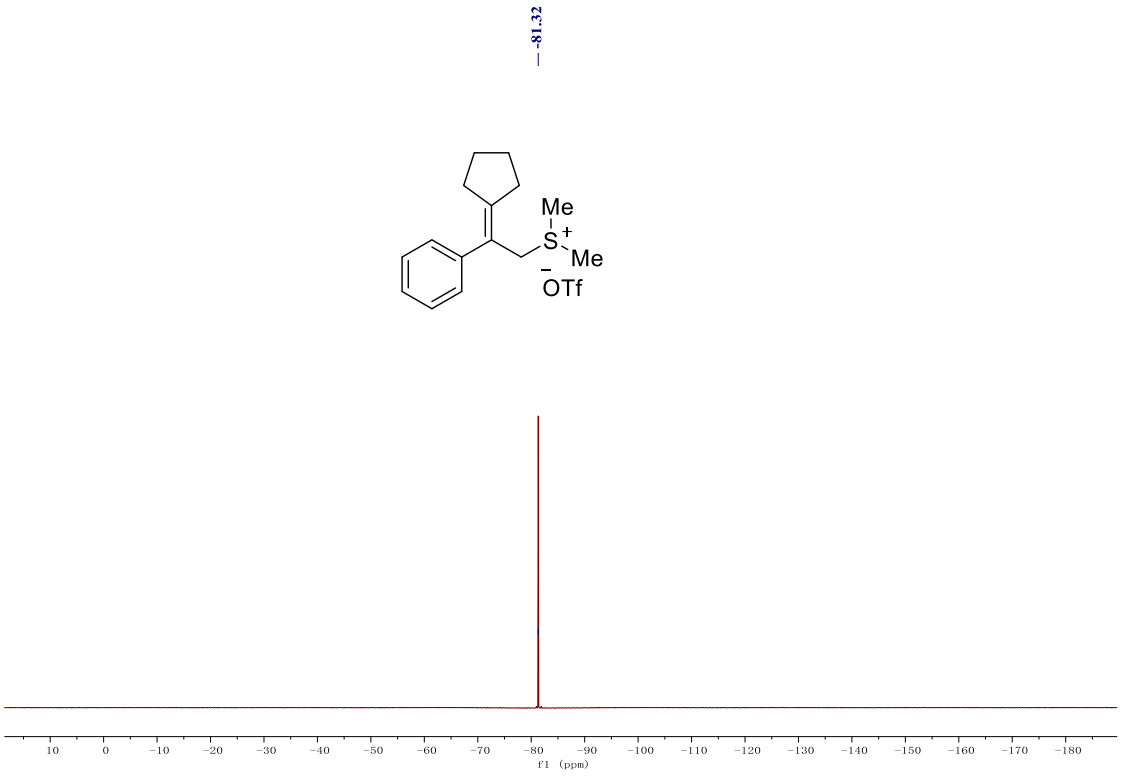
^{1}H NMR Spectra of compound 2q' (400 MHz, CD_3OD)



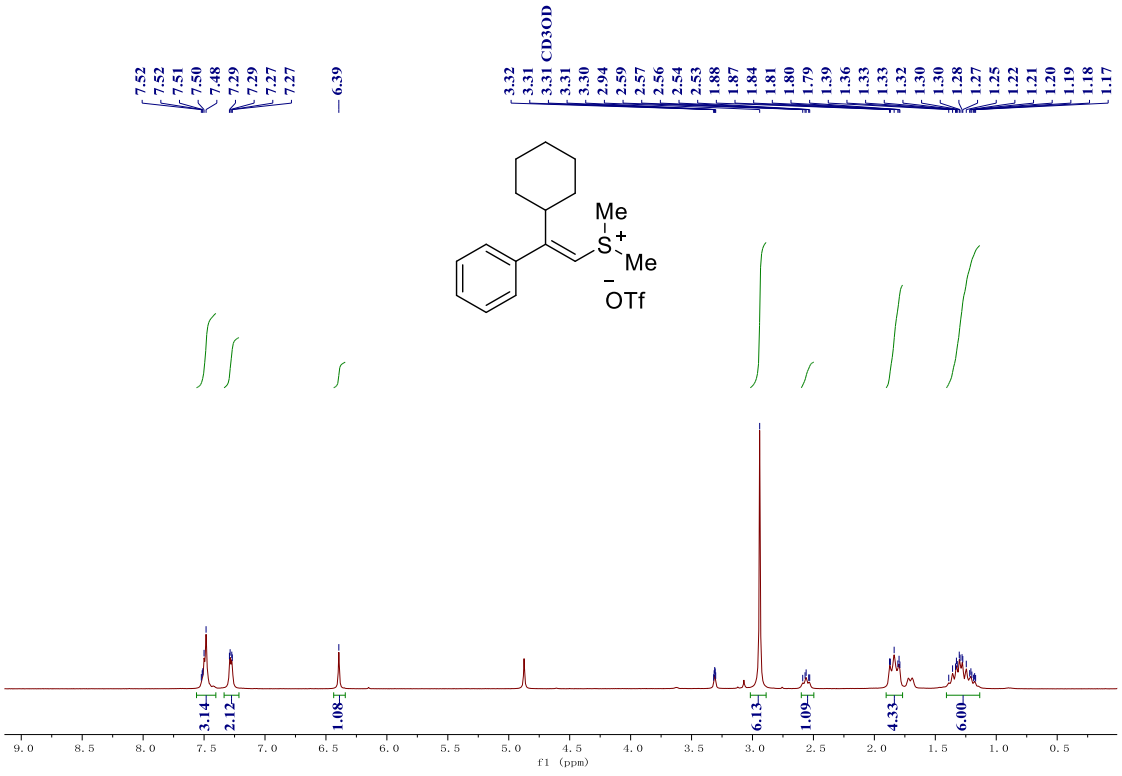
^{13}C NMR Spectra of compound 2q' (101 MHz, CD_3OD)



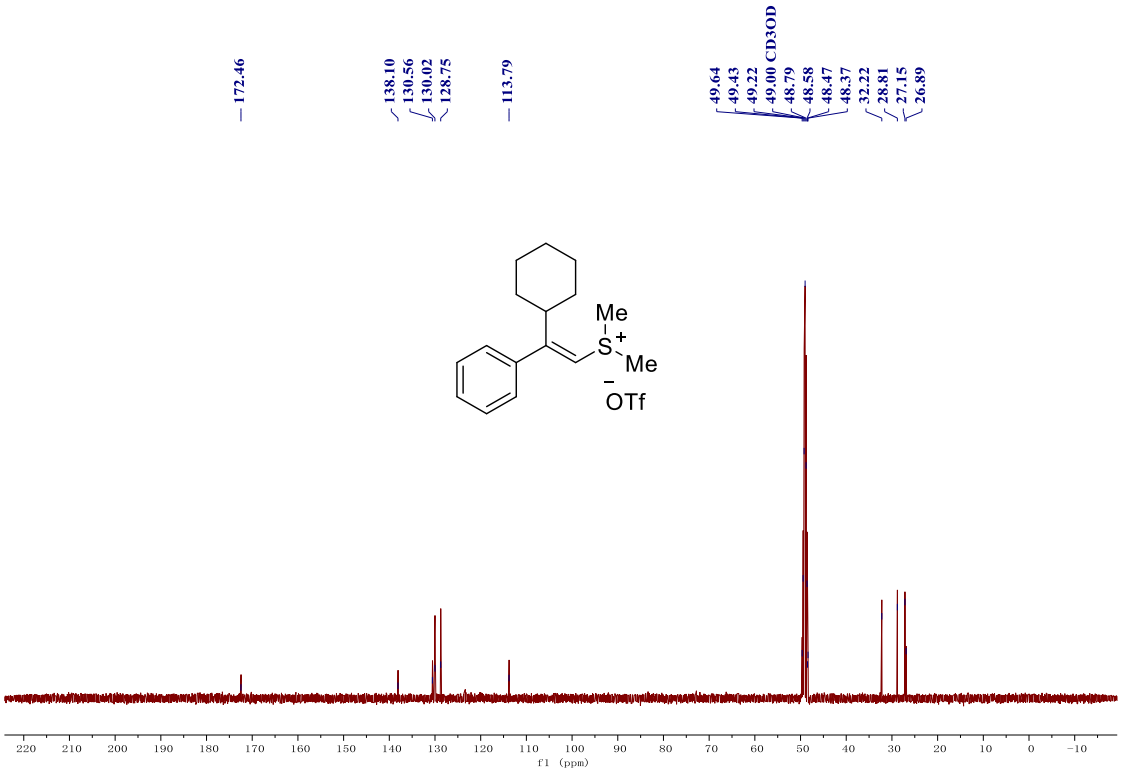
^{19}F NMR Spectra of compound 2q (376 MHz, CD_3OD)



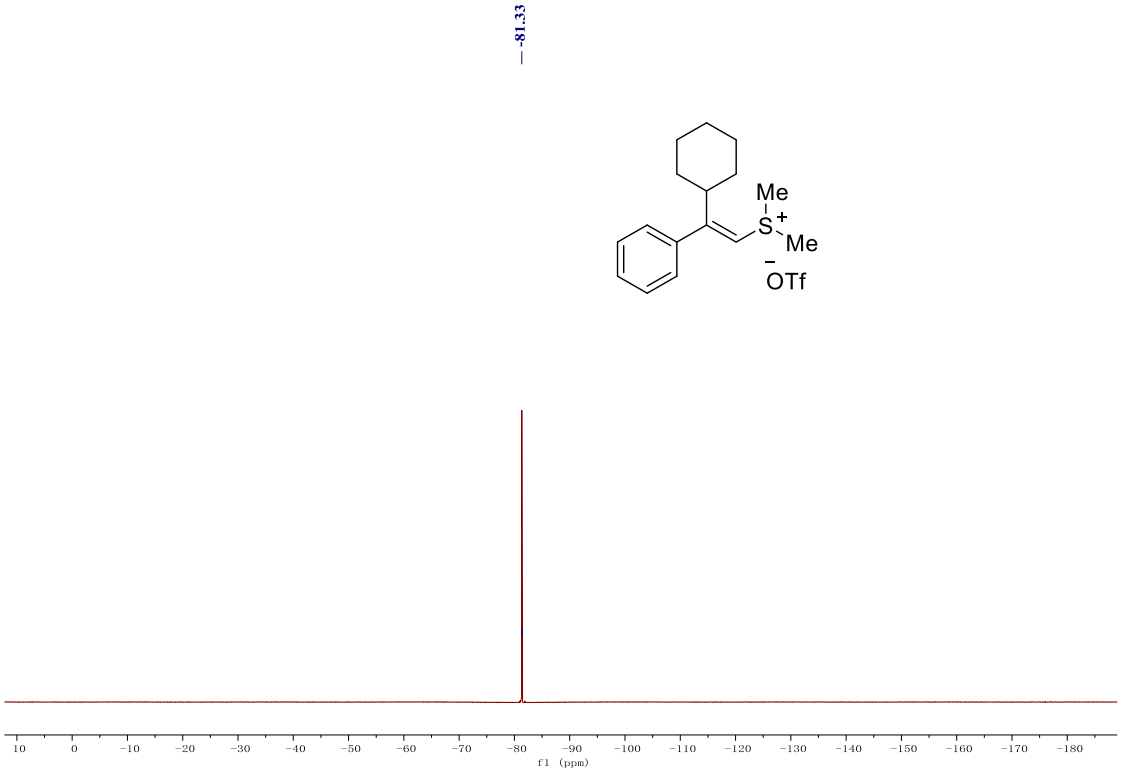
^{1}H NMR Spectra of compound 2r (400 MHz, CD_3OD)



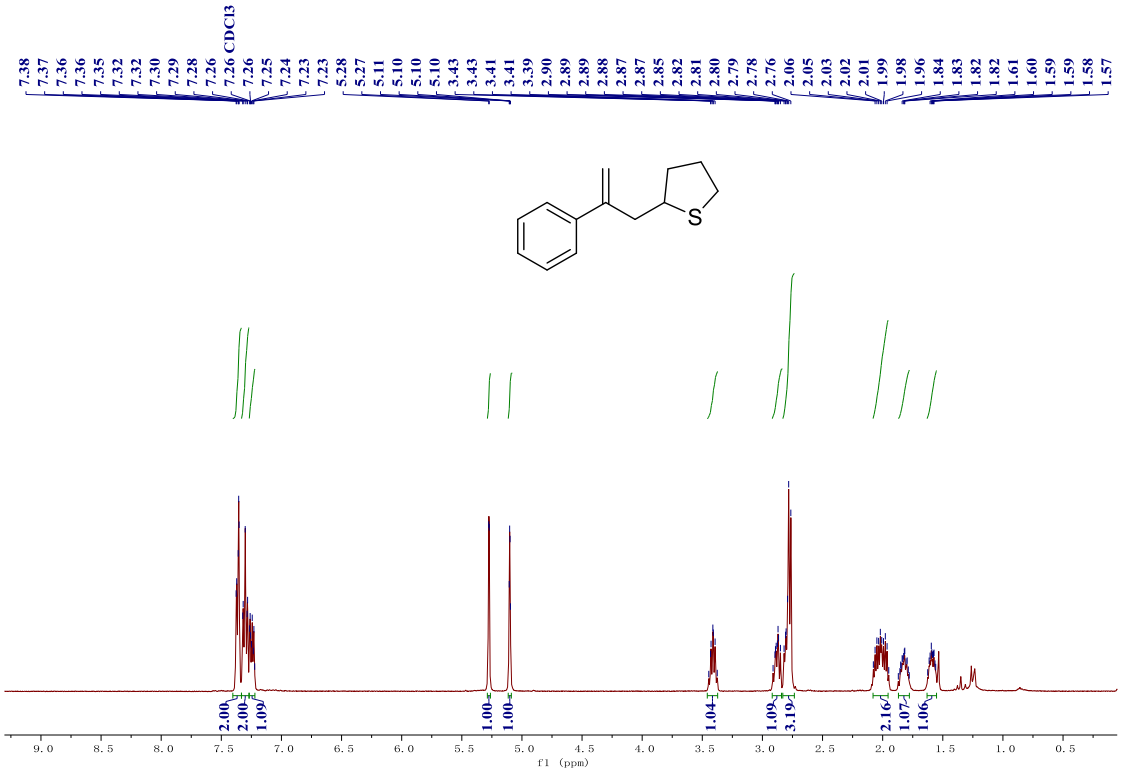
^{13}C NMR Spectra of compound 2r (101 MHz, CD_3OD)



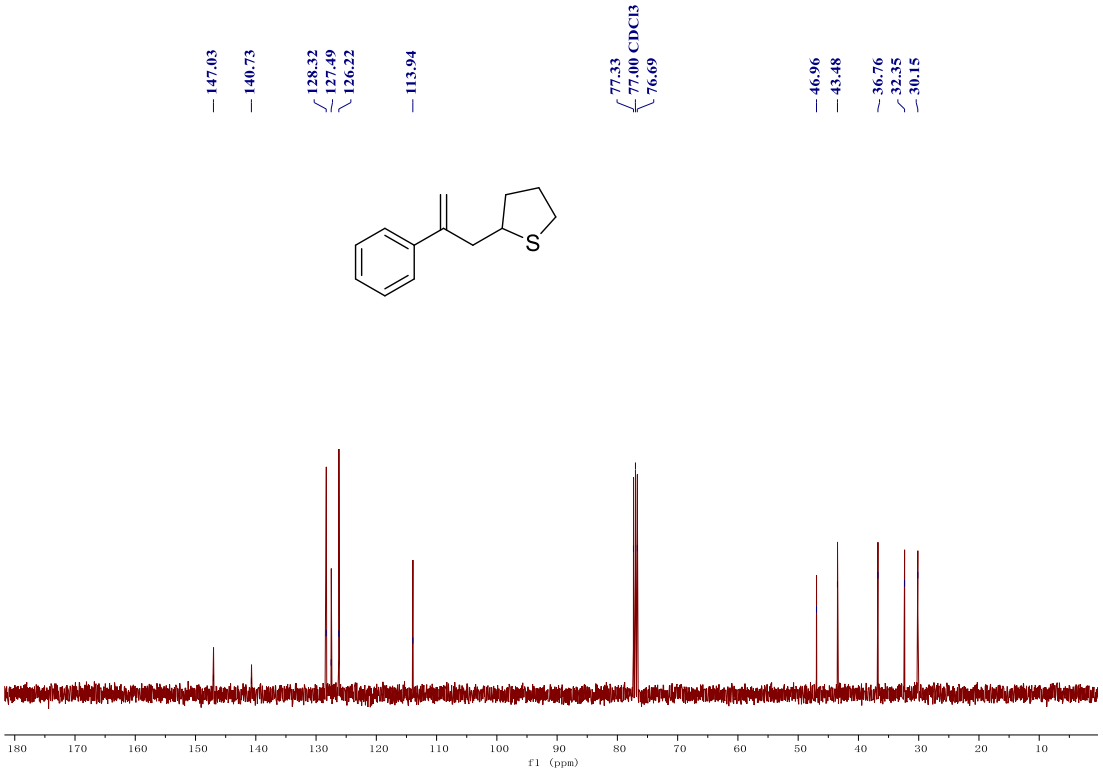
^{19}F NMR Spectra of compound 2r (376 MHz, CD_3OD)



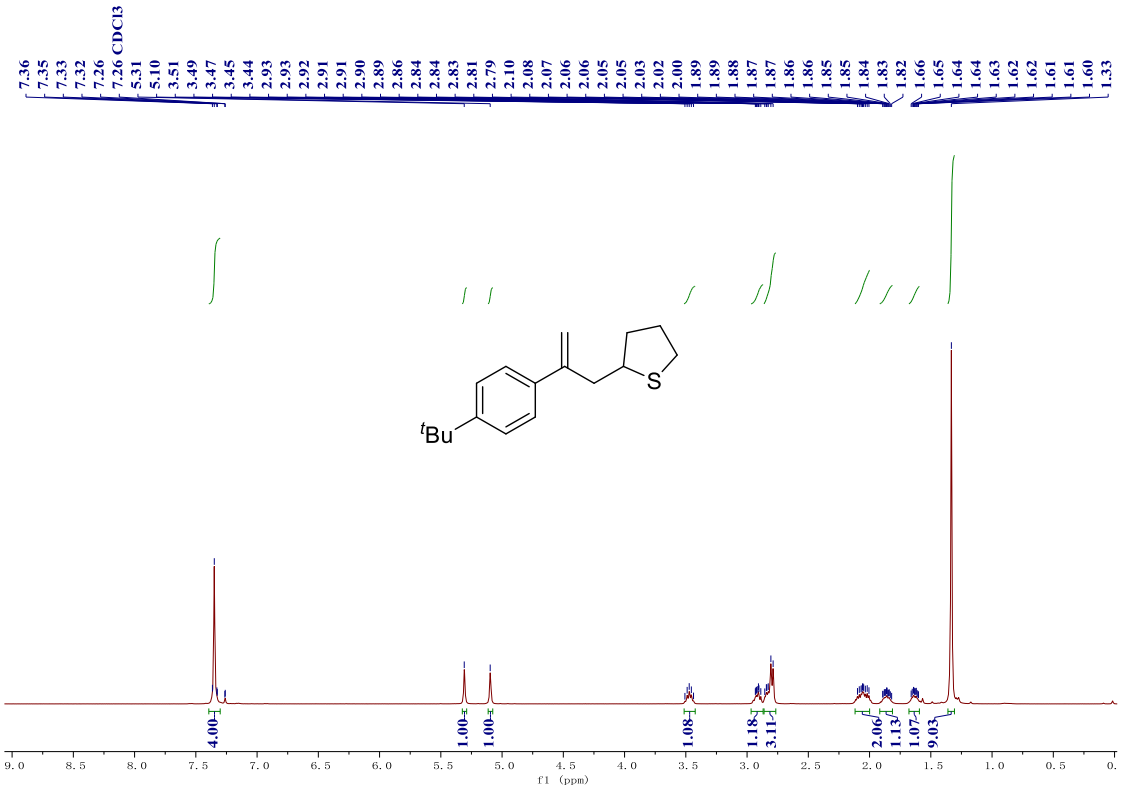
^{1}H NMR Spectra of compound 3a (400 MHz, $CDCl_3$)



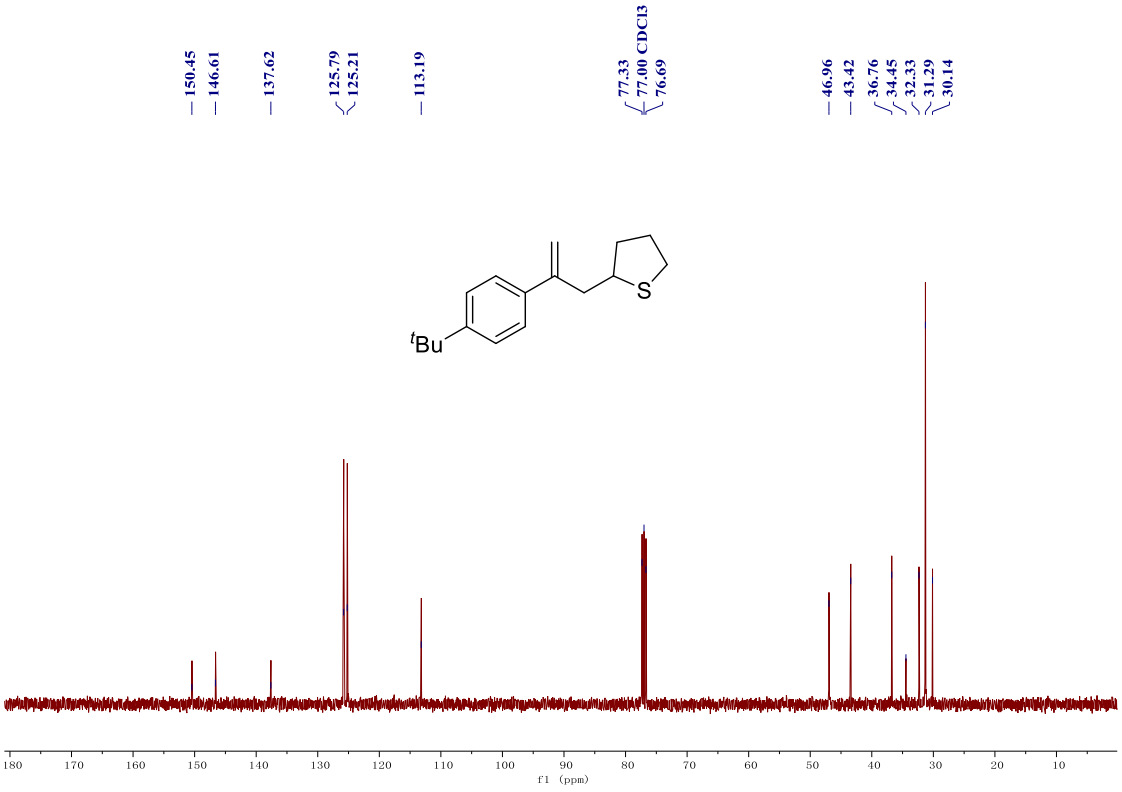
^{13}C NMR Spectra of compound 3a (101 MHz, $CDCl_3$)



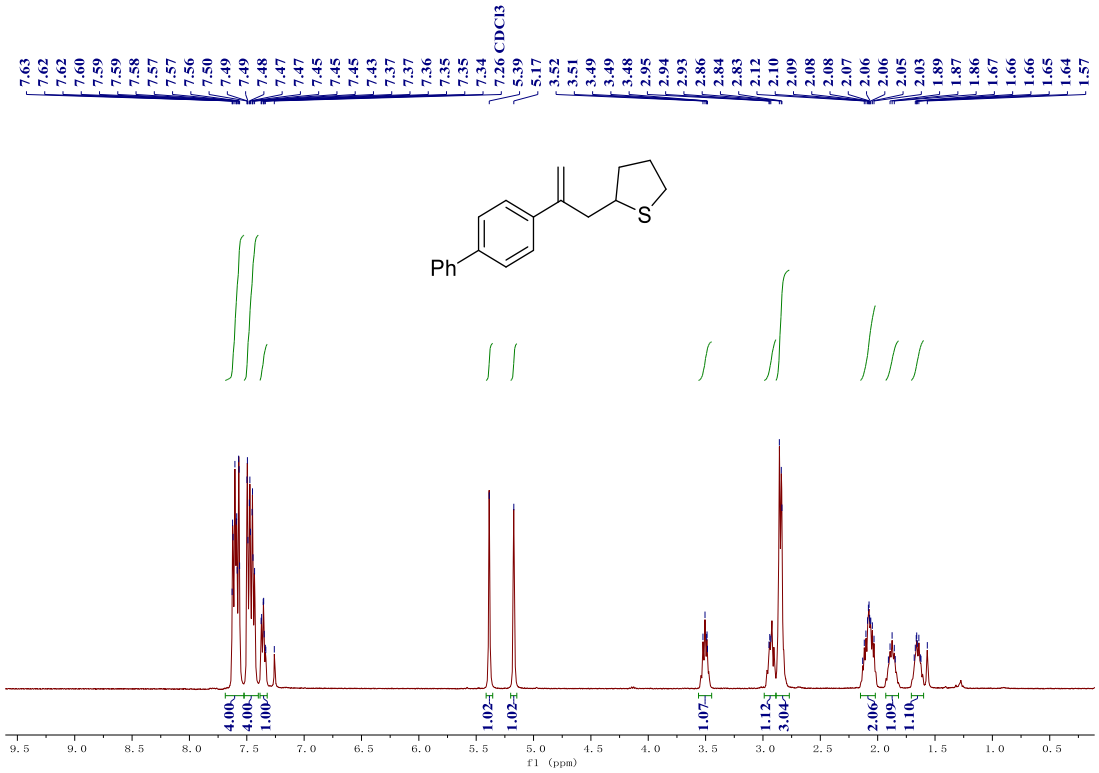
^{1}H NMR Spectra of compound 3b (400 MHz, $CDCl_3$)



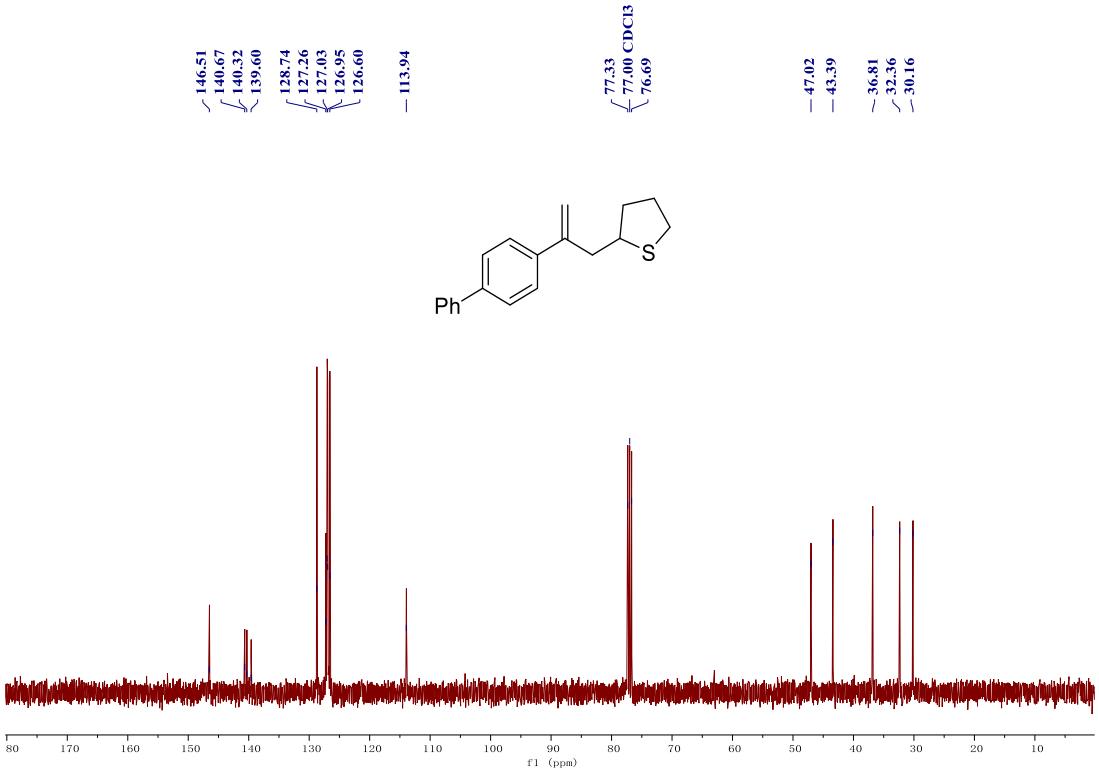
^{13}C NMR Spectra of compound 3b (101 MHz, $CDCl_3$)



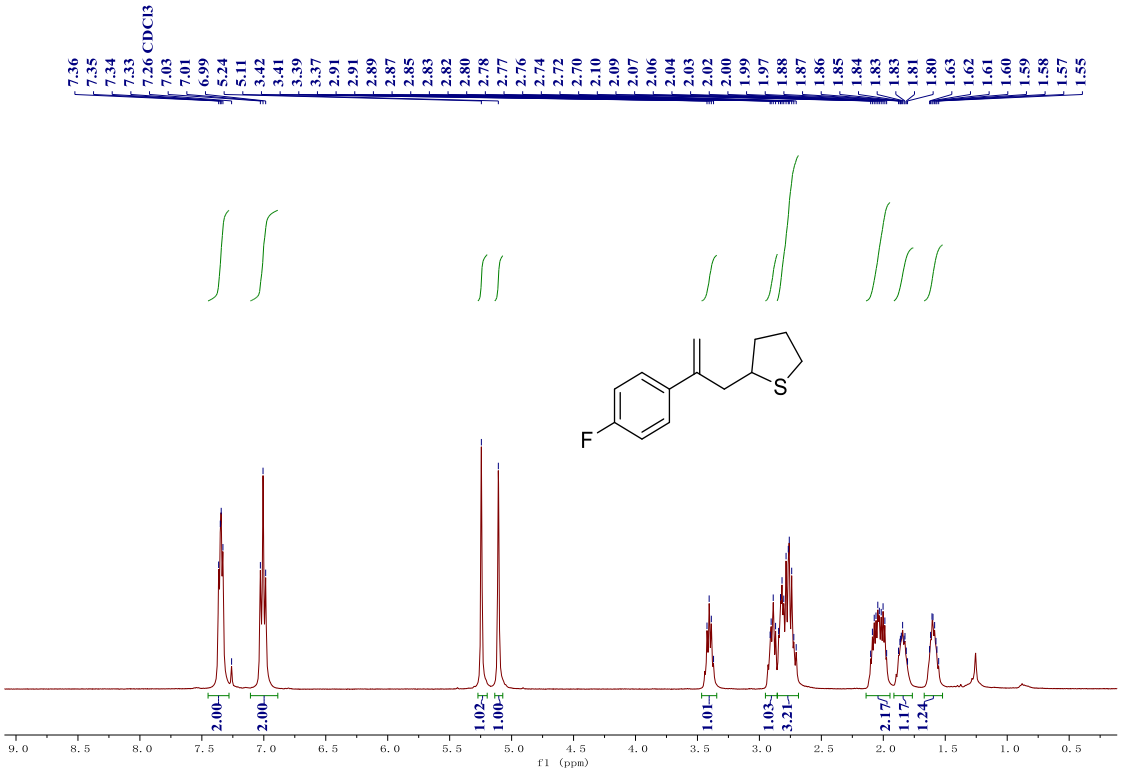
^{1}H NMR Spectra of compound 3c (400 MHz, $CDCl_3$)



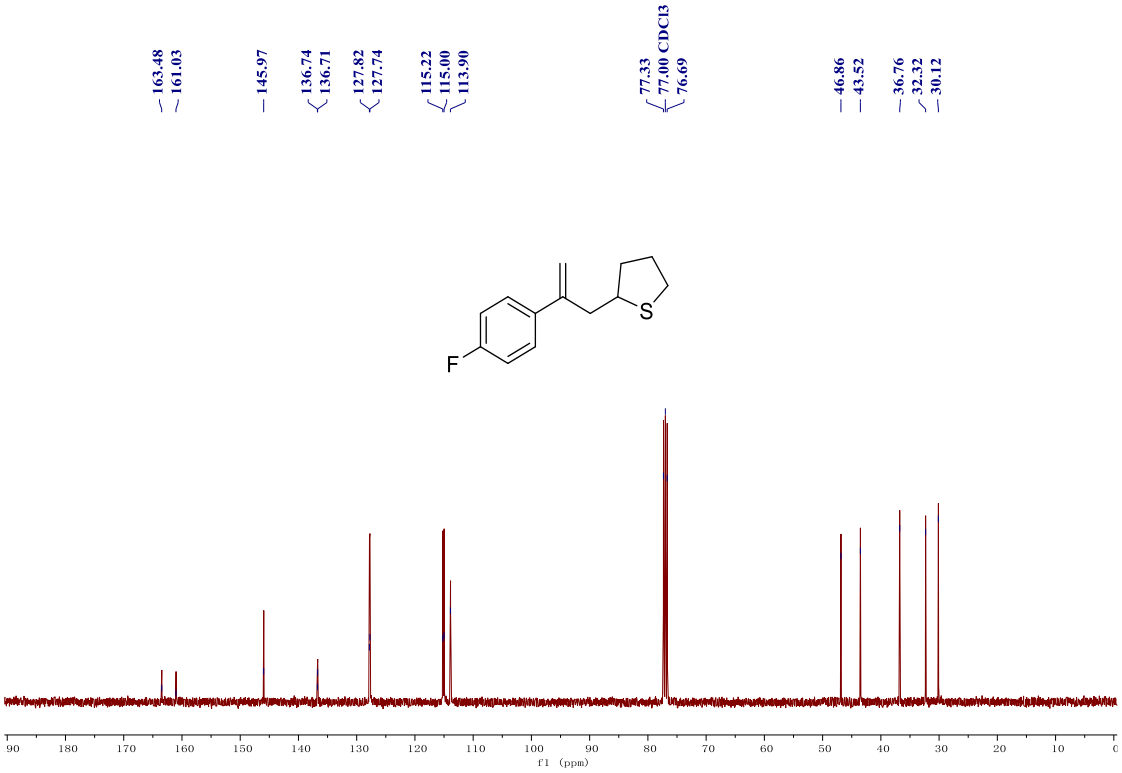
^{13}C NMR Spectra of compound 3c (101 MHz, $CDCl_3$)



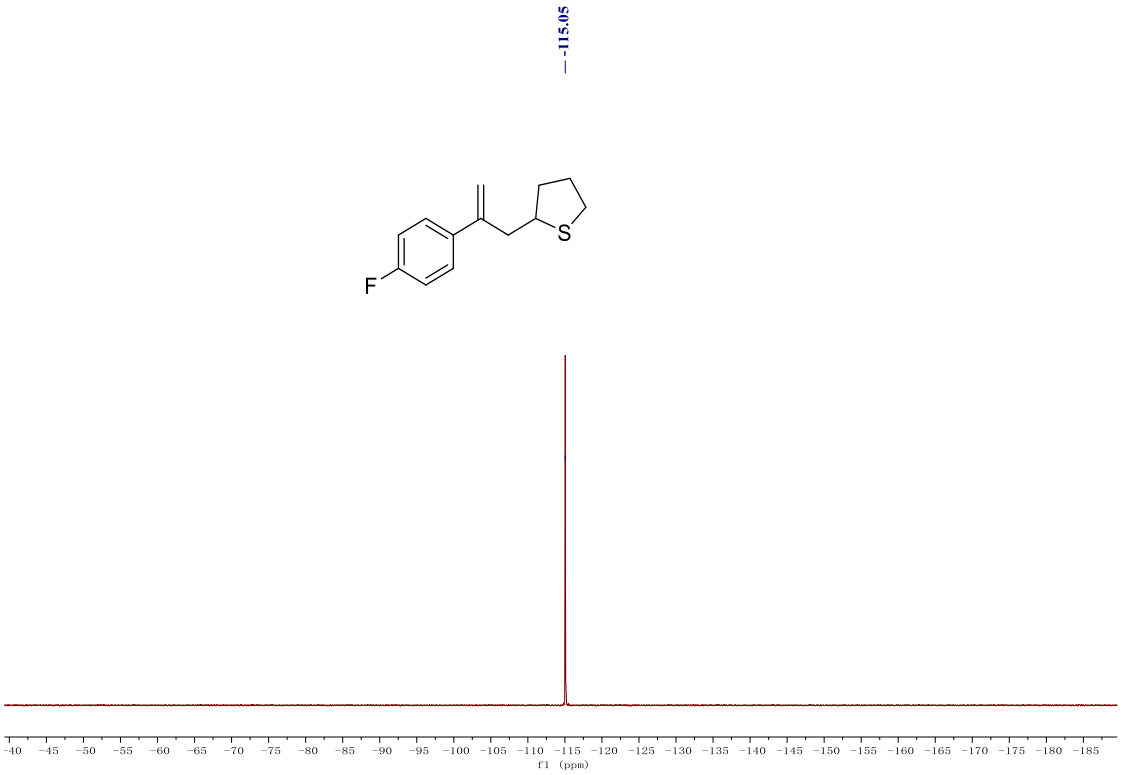
^{1}H NMR Spectra of compound 3d (101 MHz, $CDCl_3$)



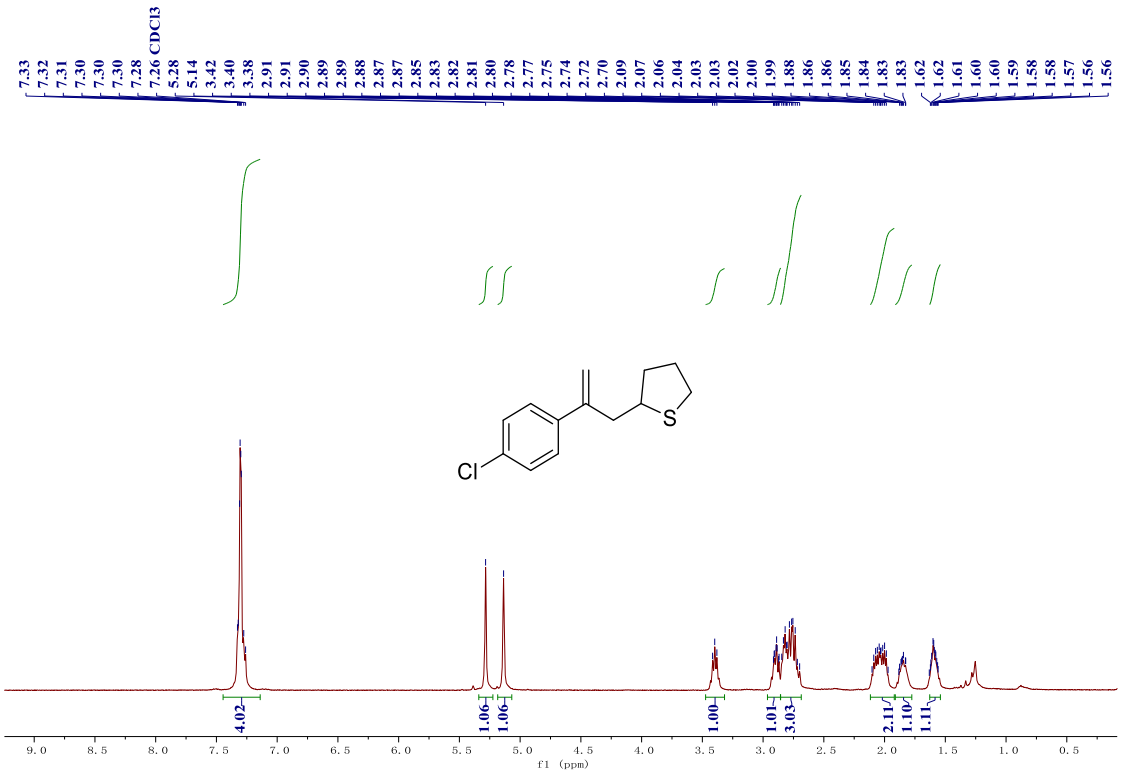
^{13}C NMR Spectra of compound 3d (101 MHz, $CDCl_3$)



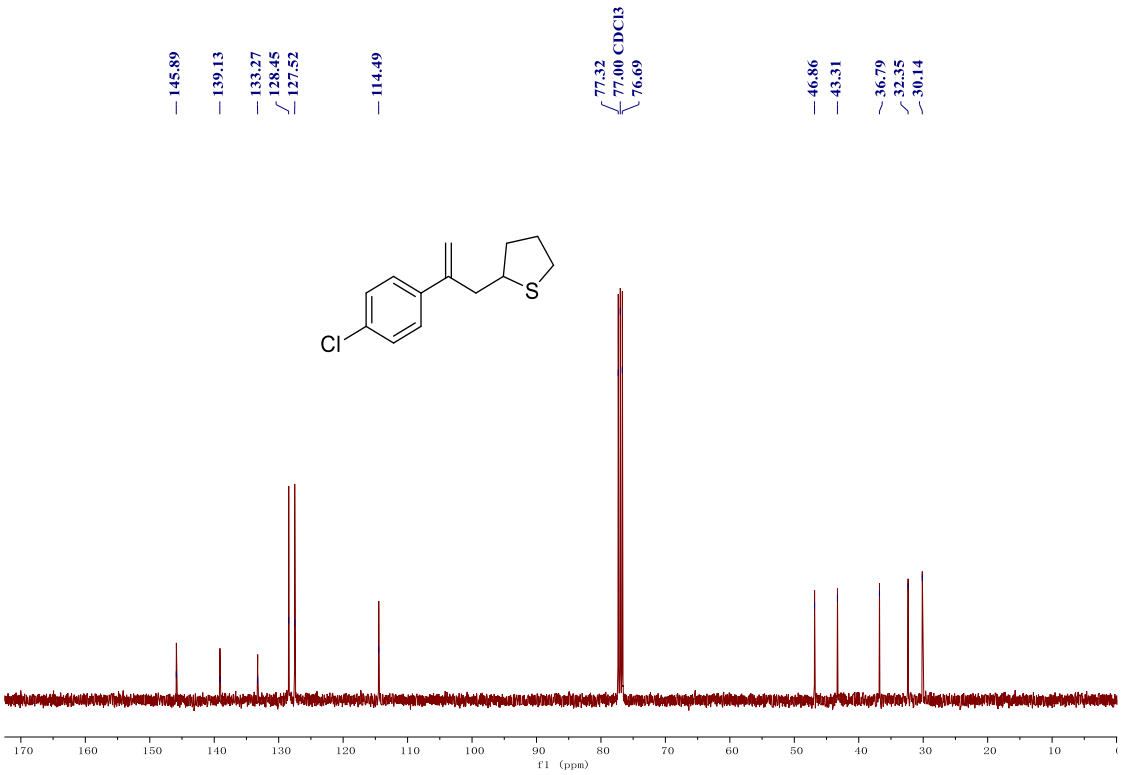
^{19}F NMR Spectra of compound 3d (376 MHz, $CDCl_3$)



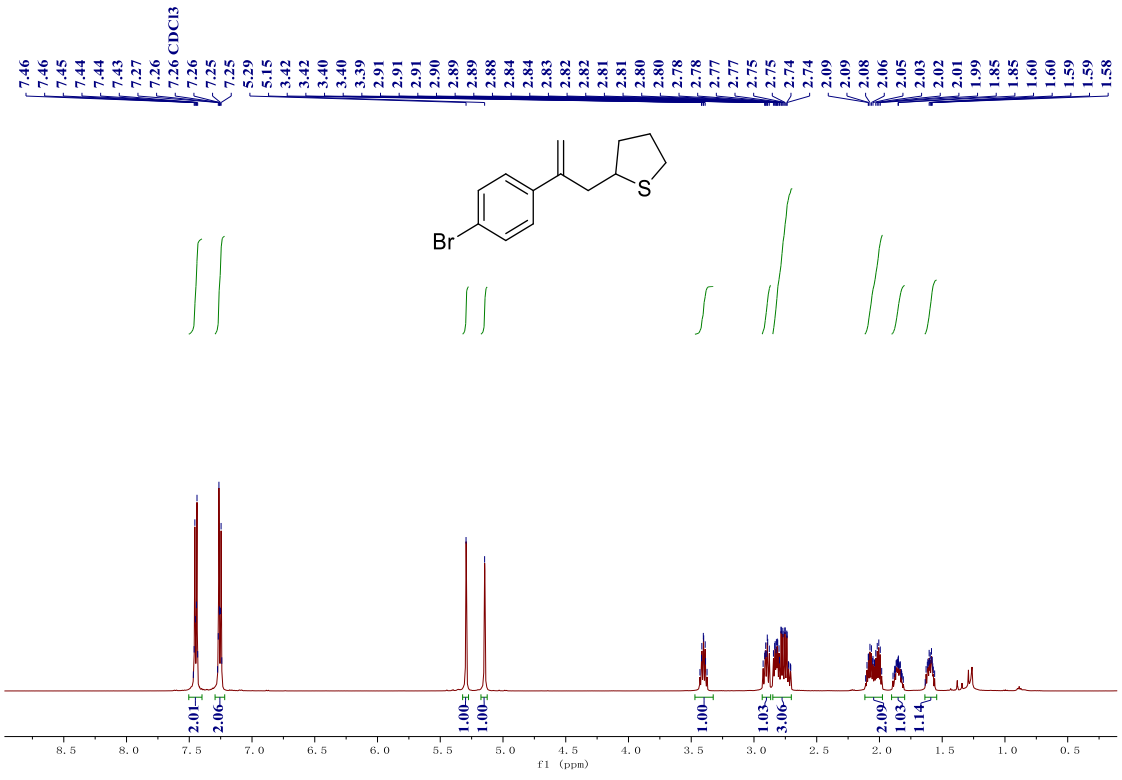
^{1}H NMR Spectra of compound 3e (400 MHz, $CDCl_3$)



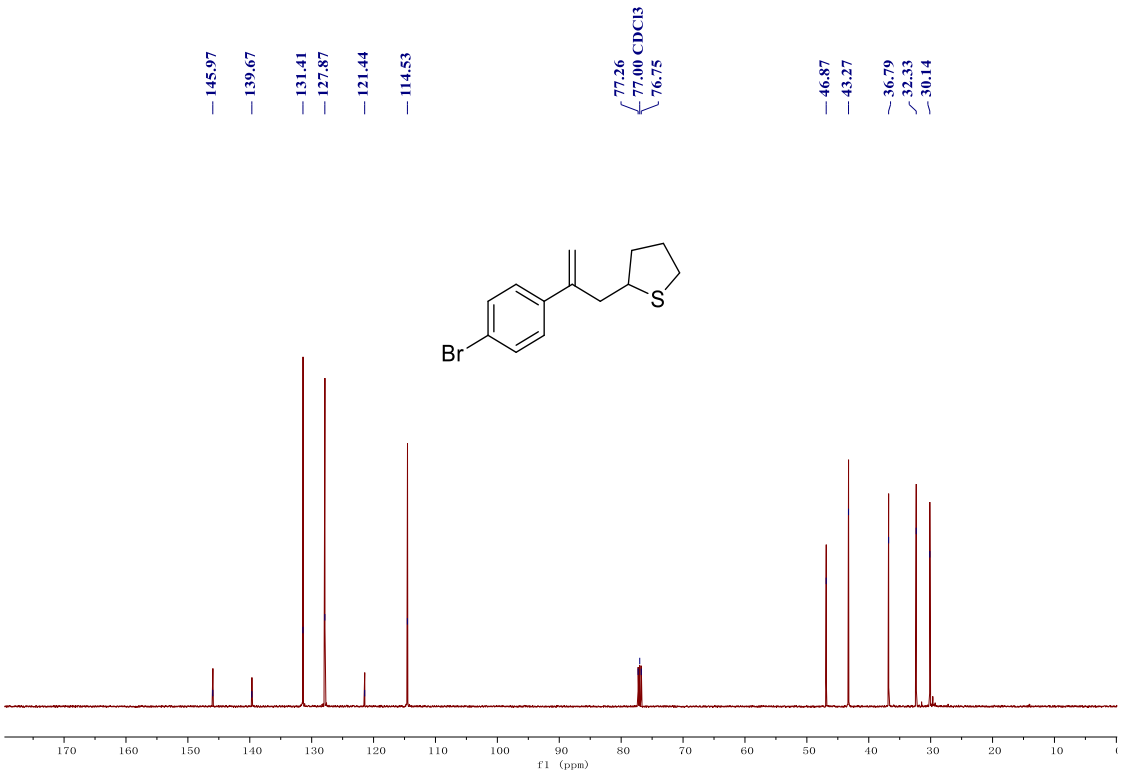
^{13}C NMR Spectra of compound 3e (101 MHz, $CDCl_3$)



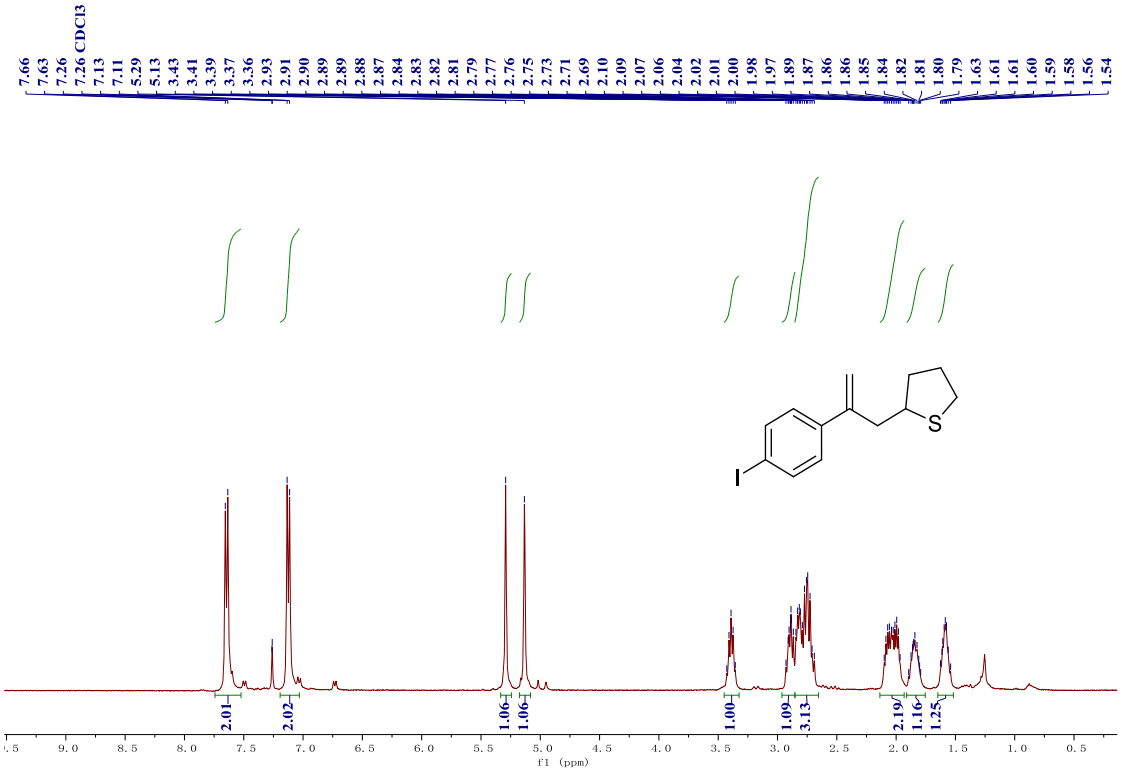
^{1}H NMR Spectra of compound 3f (400 MHz, $CDCl_3$)



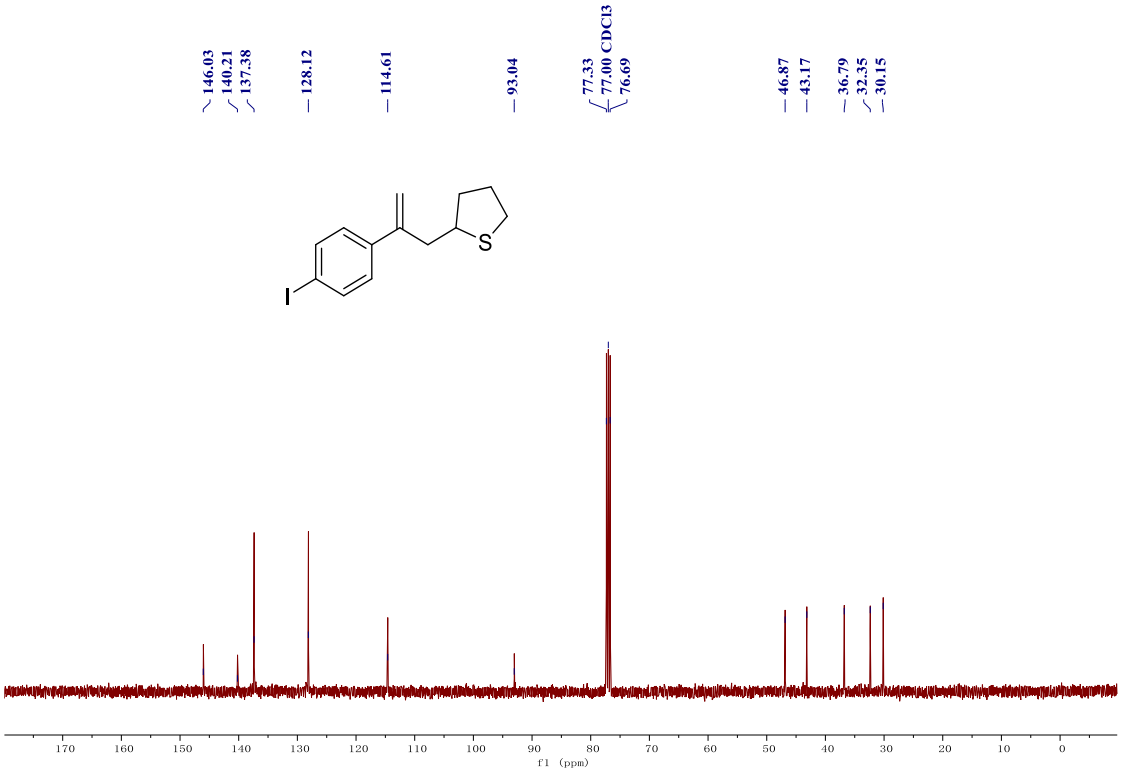
^{13}C NMR Spectra of compound 3f (101 MHz, $CDCl_3$)



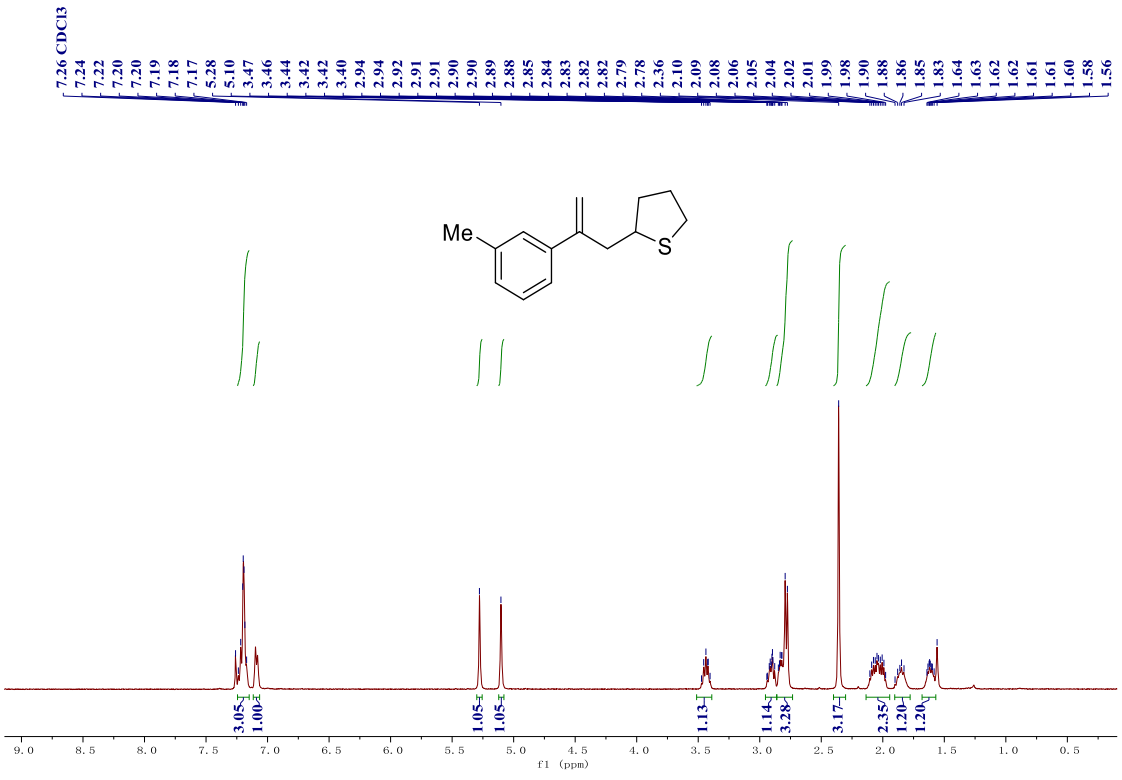
^{1}H NMR Spectra of compound 3g (400 MHz, $CDCl_3$)



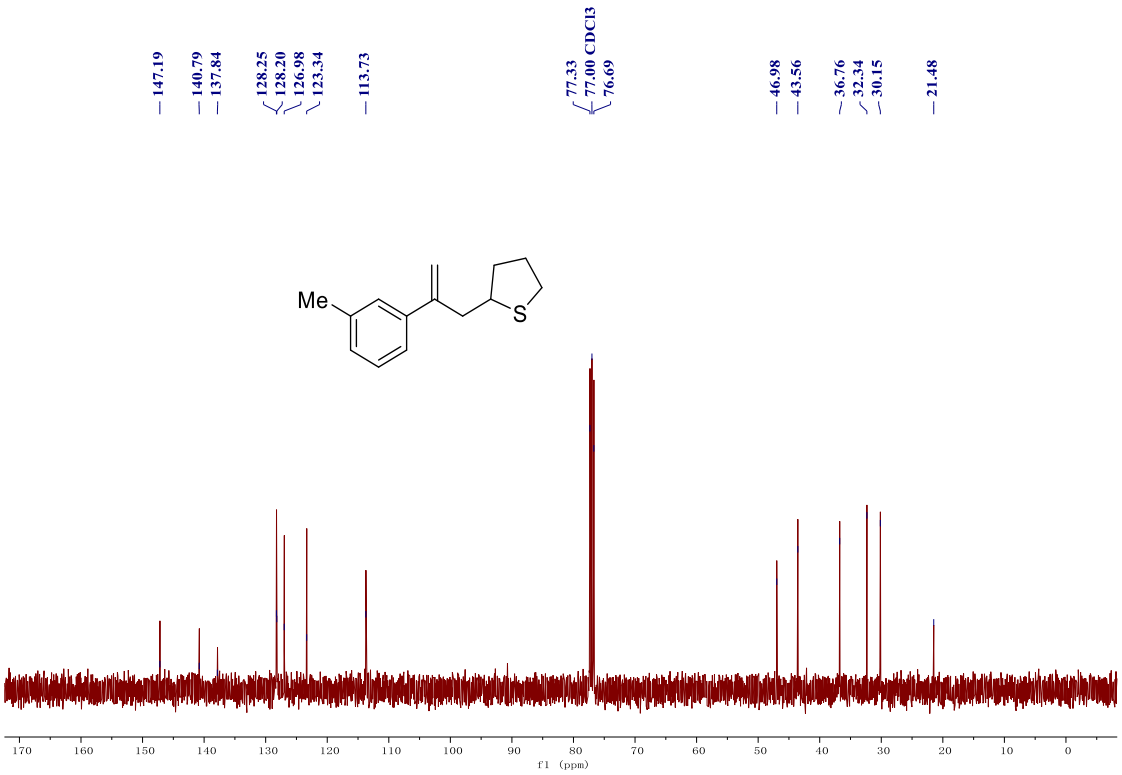
^{13}C NMR Spectra of compound 3g (101 MHz, $CDCl_3$)



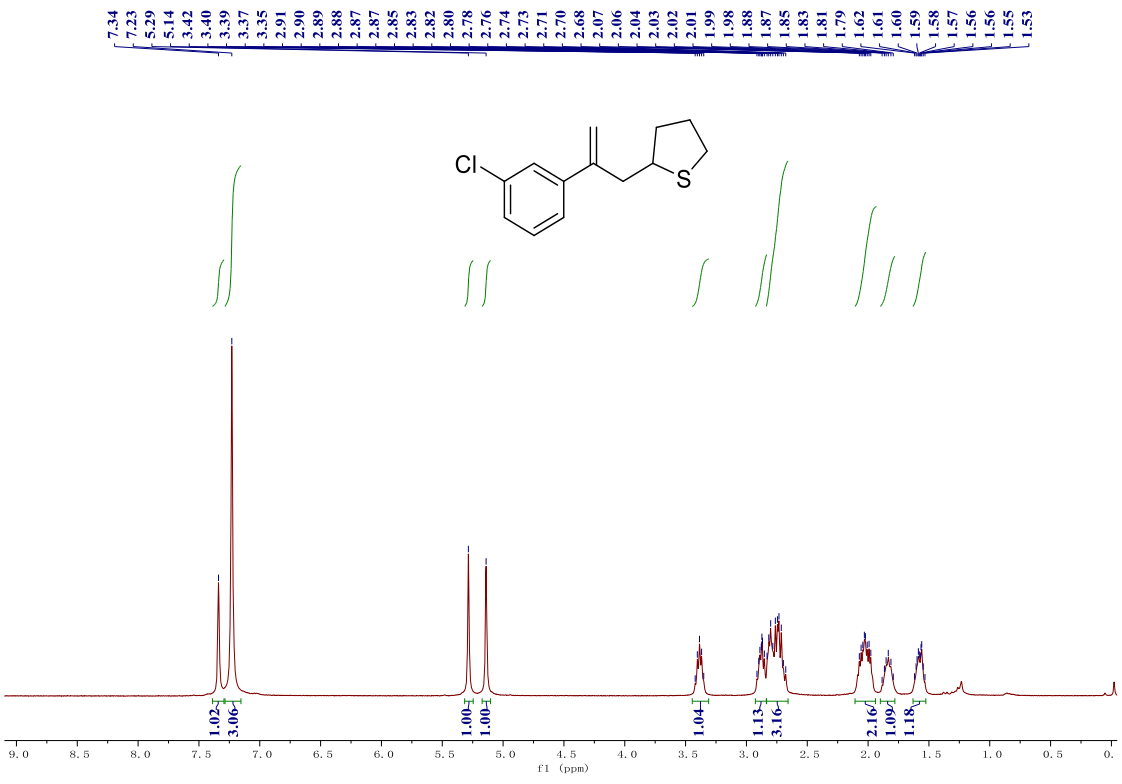
^{1}H NMR Spectra of compound 3h (400 MHz, $CDCl_3$)



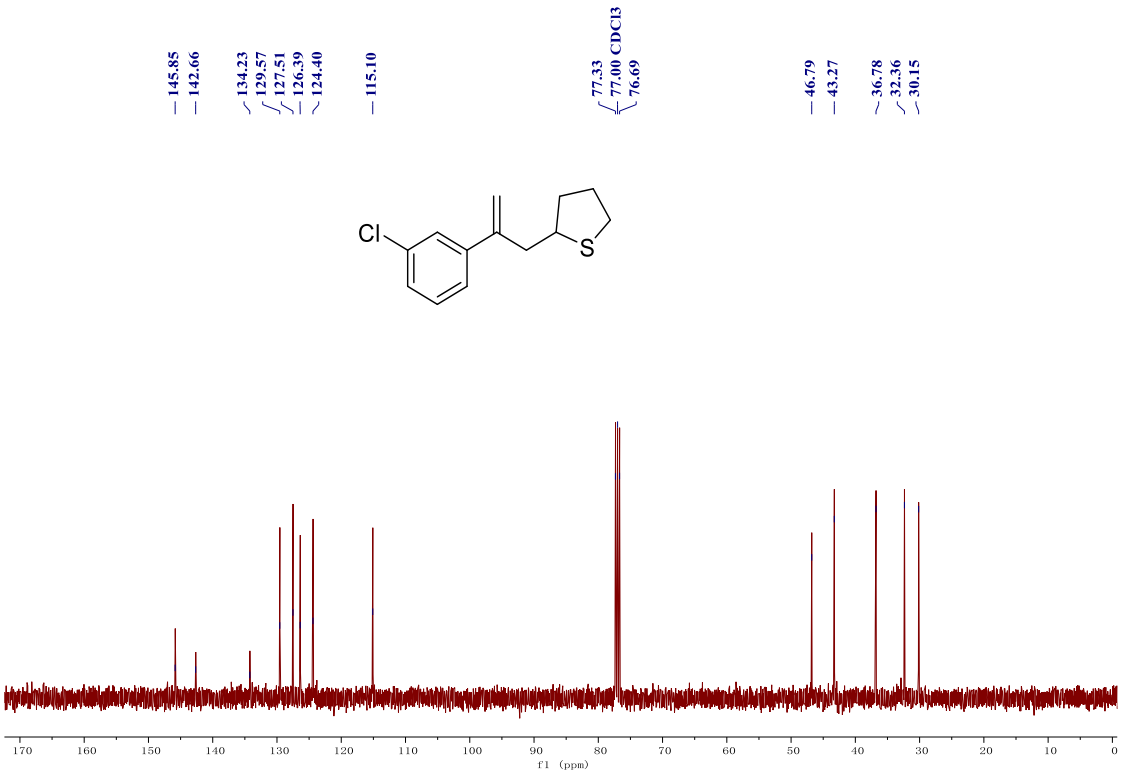
^{13}C NMR Spectra of compound 3h (101 MHz, $CDCl_3$)



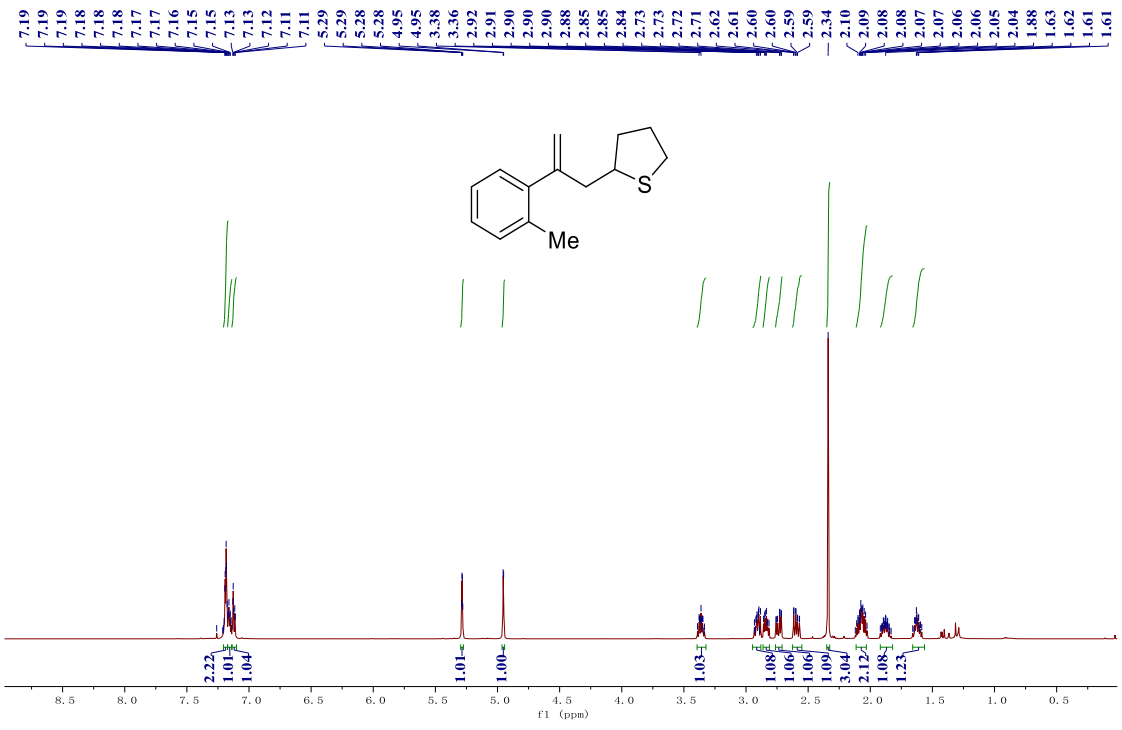
^{1}H NMR Spectra of compound 3i (400 MHz, $CDCl_3$)



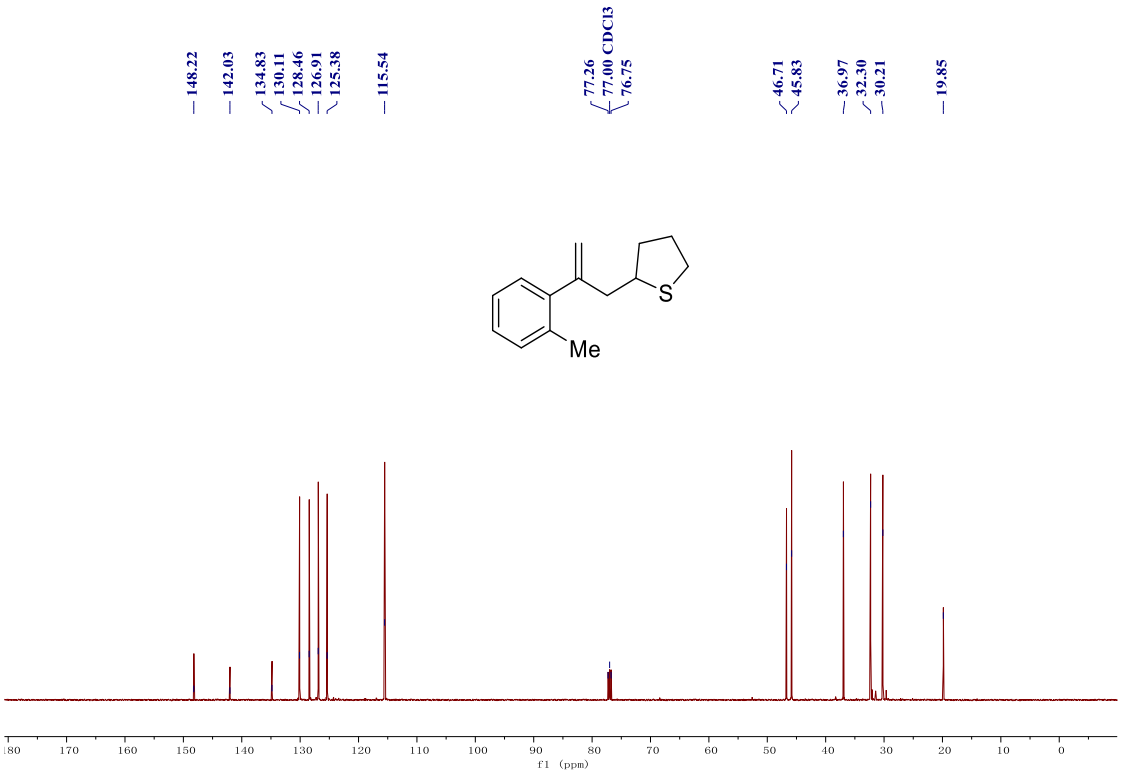
^{13}C NMR Spectra of compound 3i (101 MHz, $CDCl_3$)



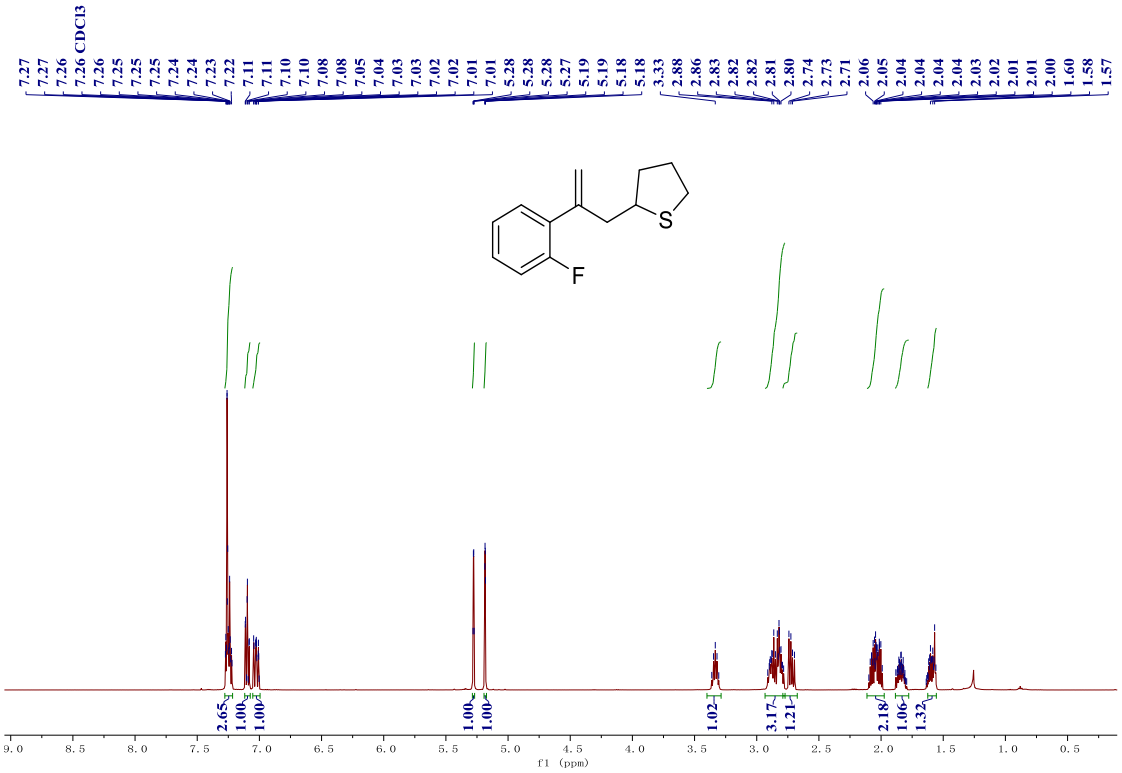
^{1}H NMR Spectra of compound 3j (500 MHz, $CDCl_3$)



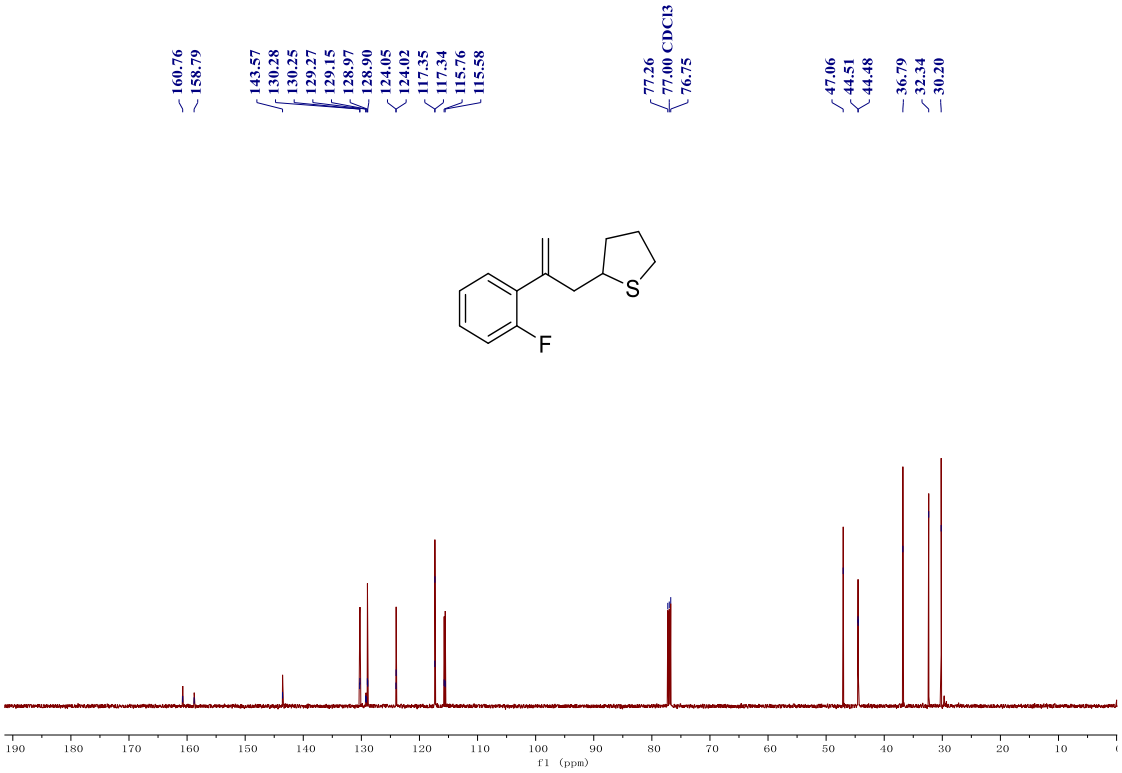
^{13}C NMR Spectra of compound 3j (126 MHz, $CDCl_3$)



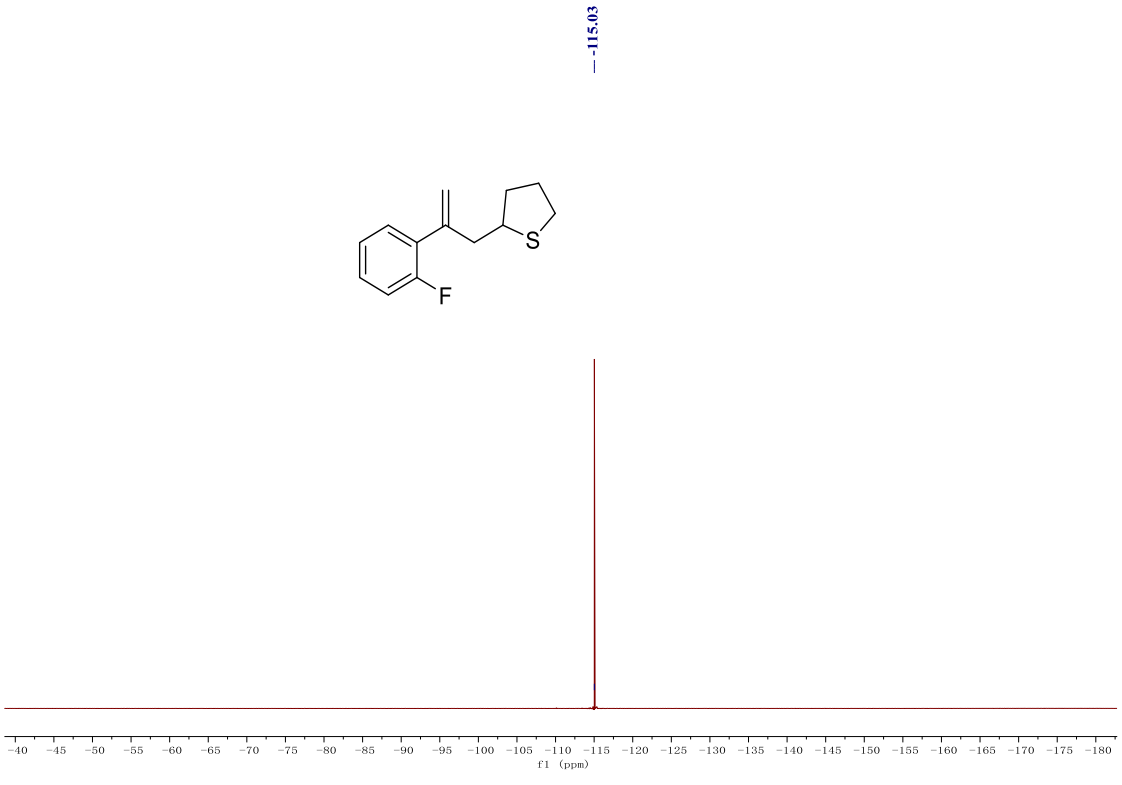
^{1}H NMR Spectra of compound 3k (500 MHz, $CDCl_3$)



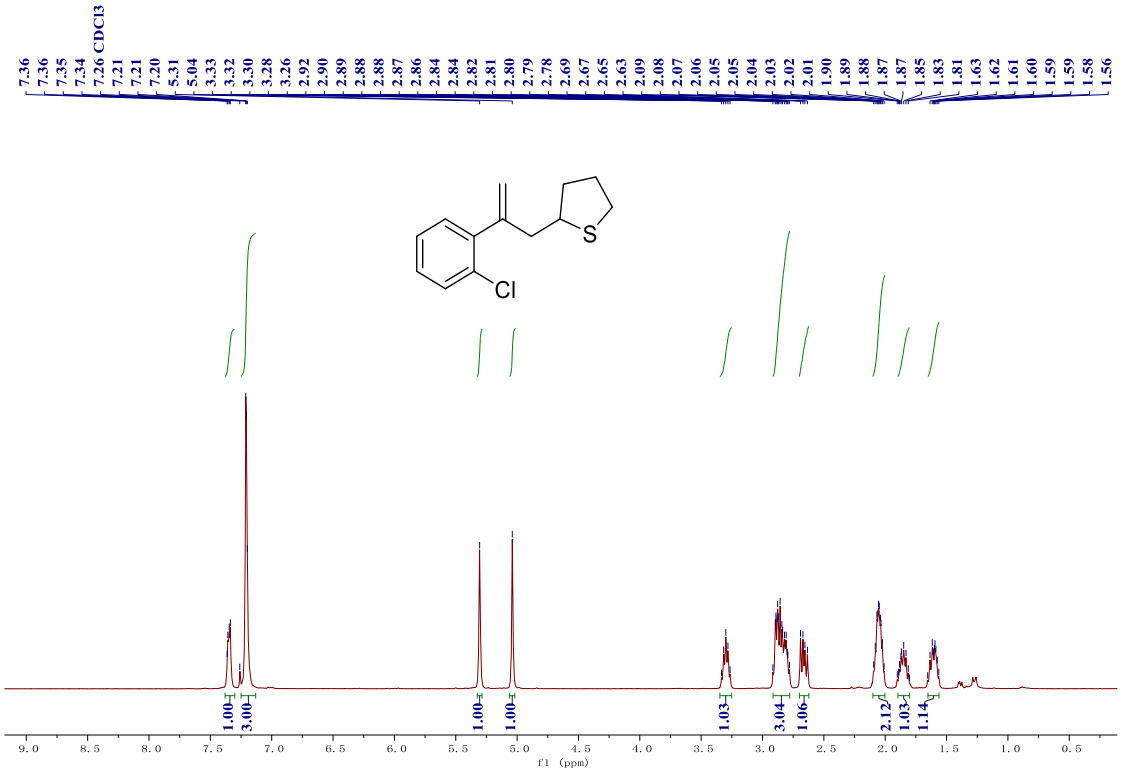
^{13}C NMR Spectra of compound 3k (126 MHz, $CDCl_3$)



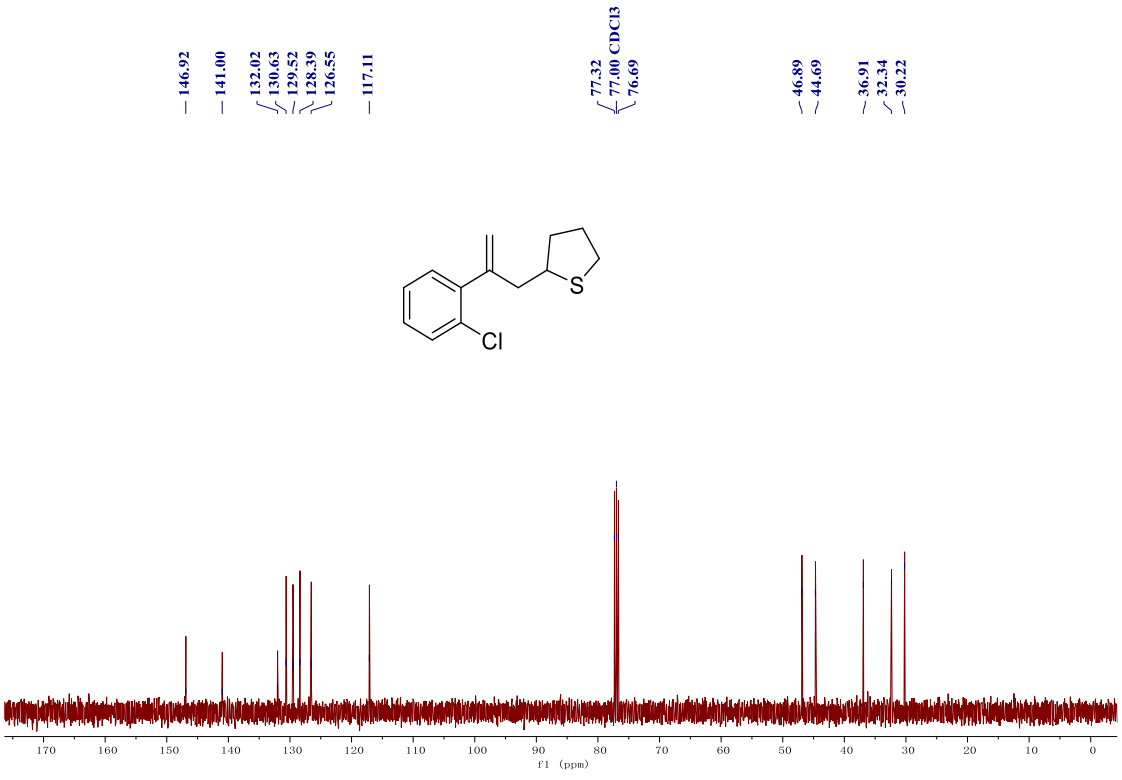
^{19}F NMR Spectra of compound 3k (471 MHz, $CDCl_3$)



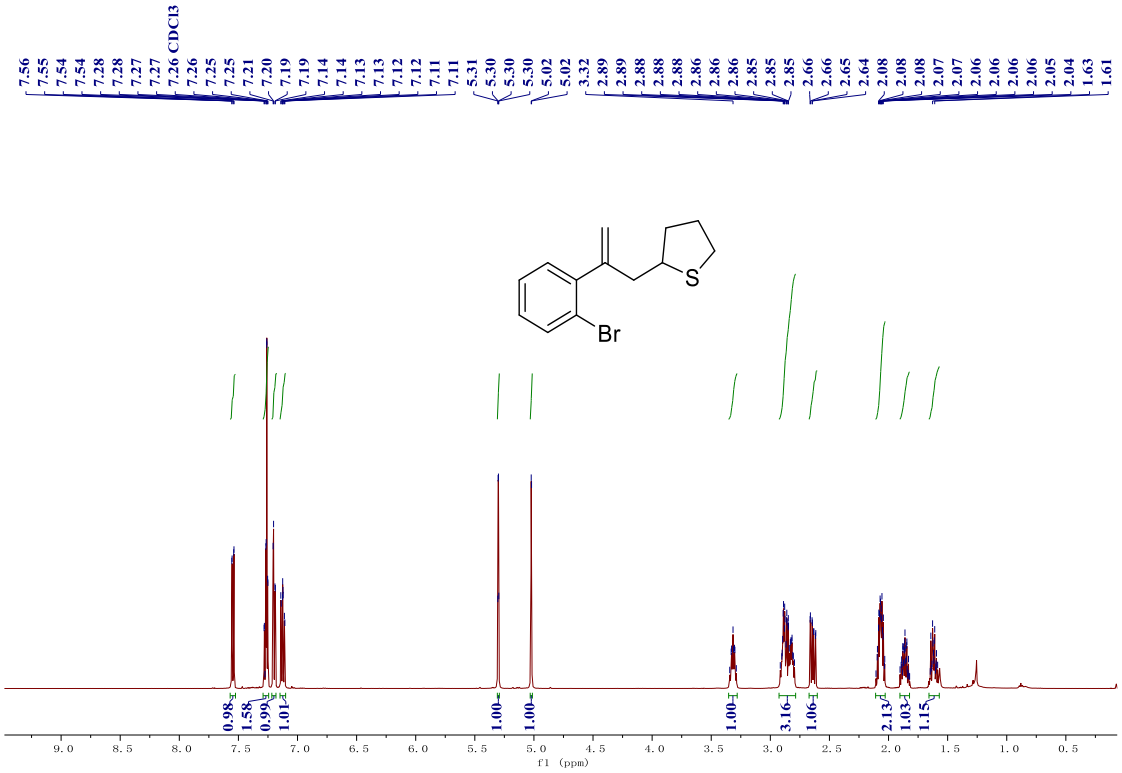
^{1}H NMR Spectra of compound 3l (400 MHz, $CDCl_3$)



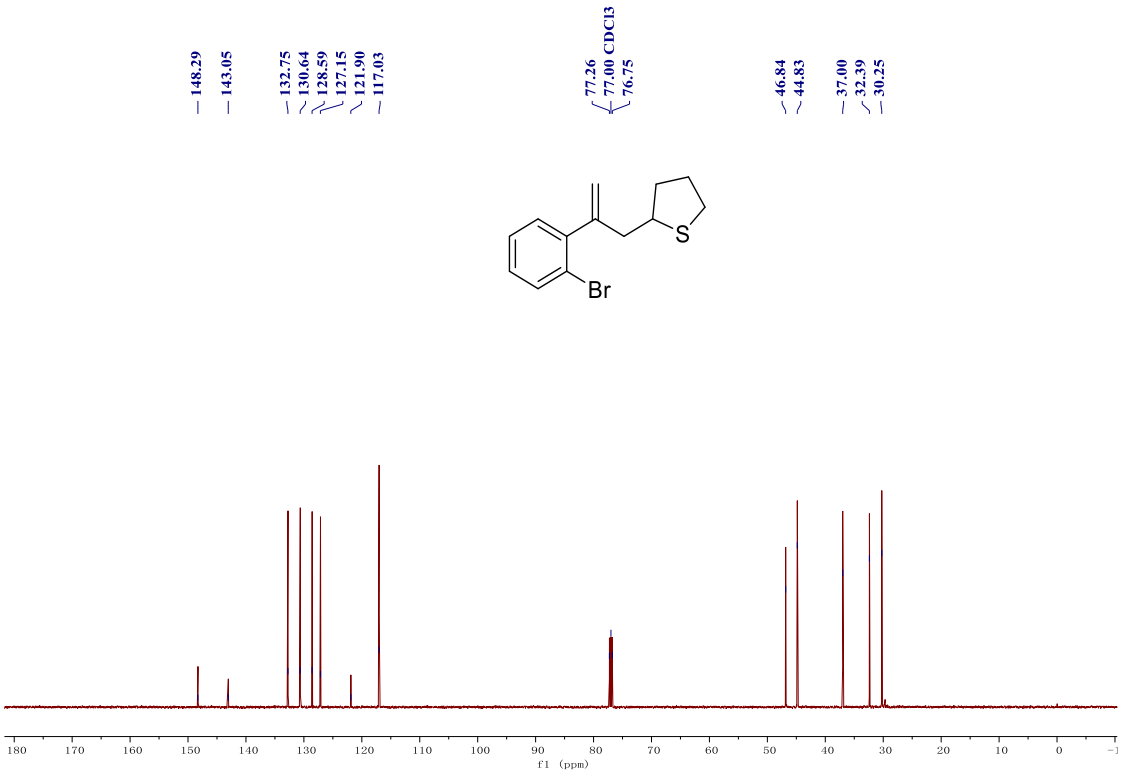
^{13}C NMR Spectra of compound 3l (101 MHz, $CDCl_3$)



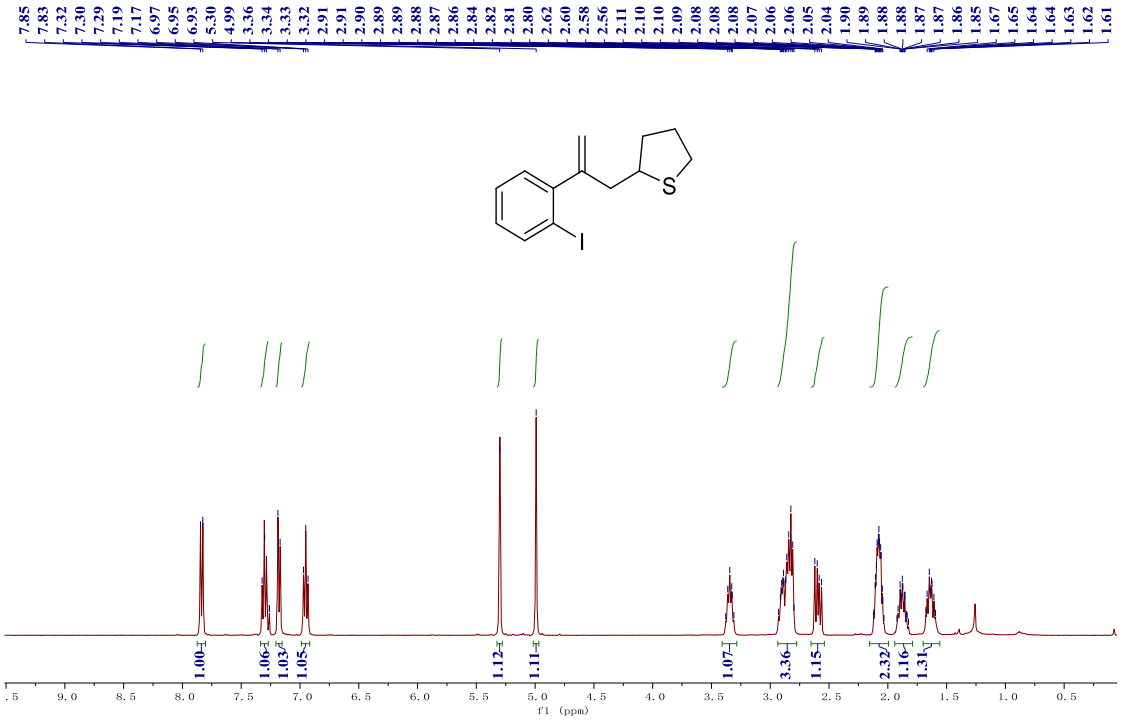
^{1}H NMR Spectra of compound 3m (500 MHz, $CDCl_3$)



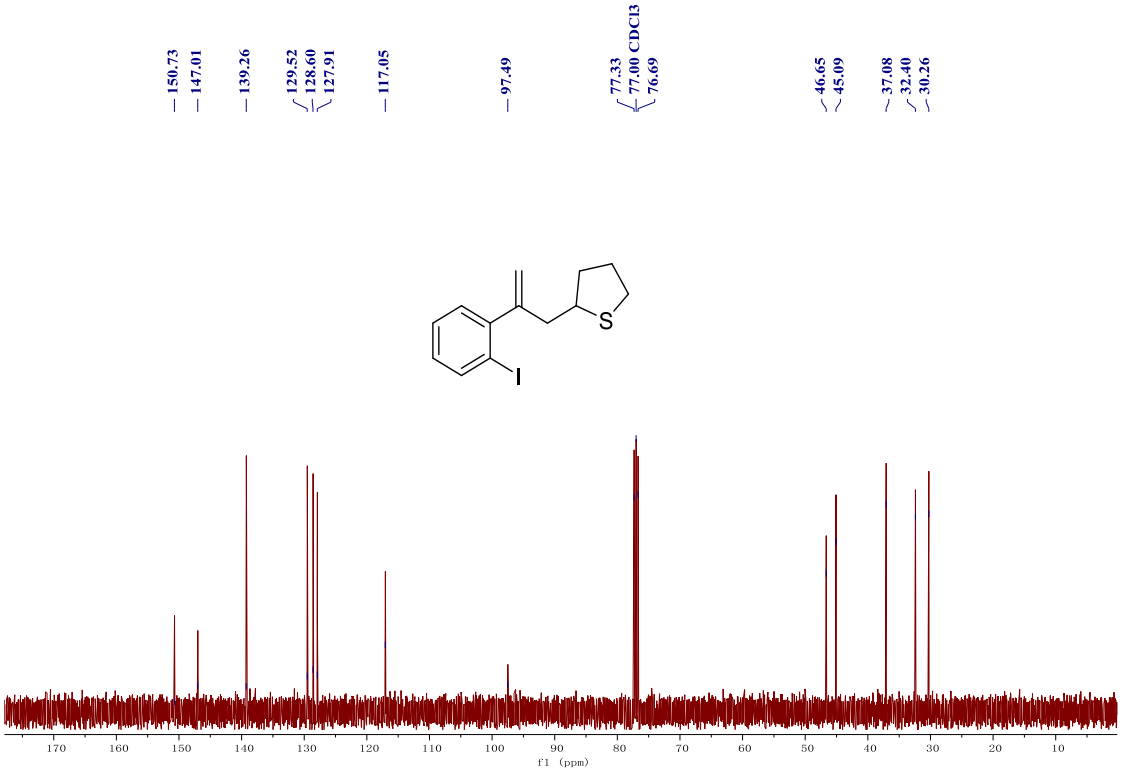
^{1}H NMR Spectra of compound 3m (126 MHz, $CDCl_3$)



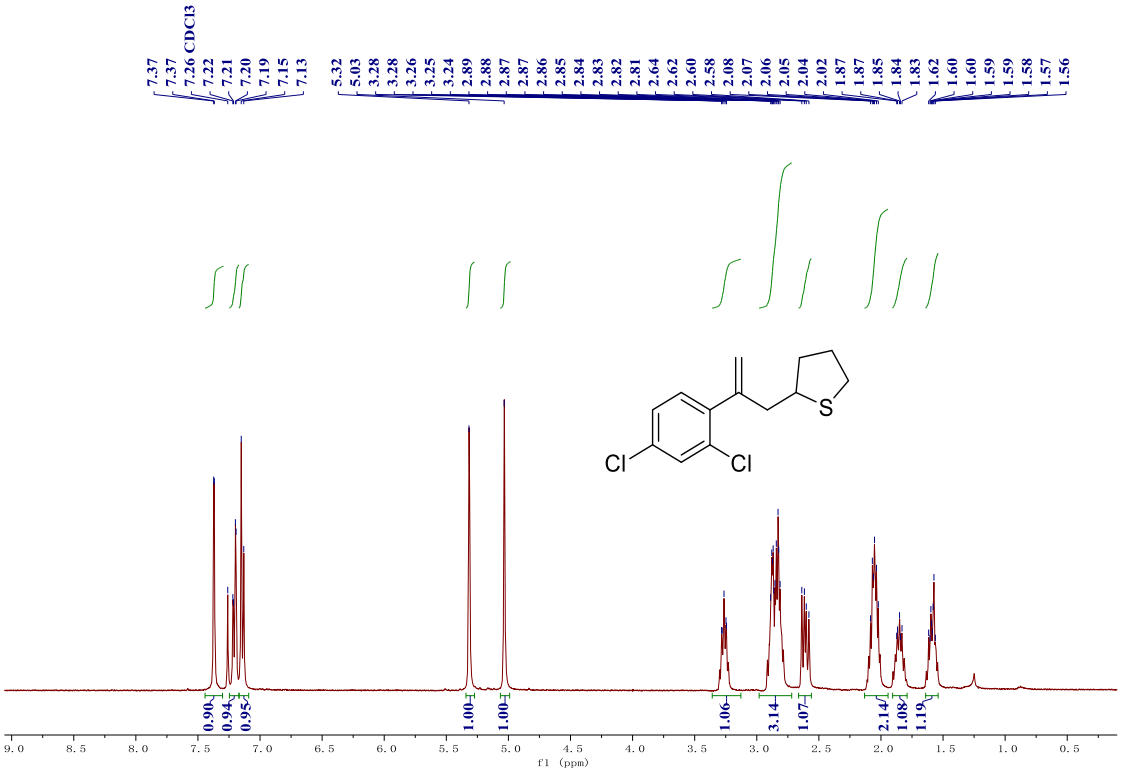
^{1}H NMR Spectra of compound 3n (400 MHz, $CDCl_3$)



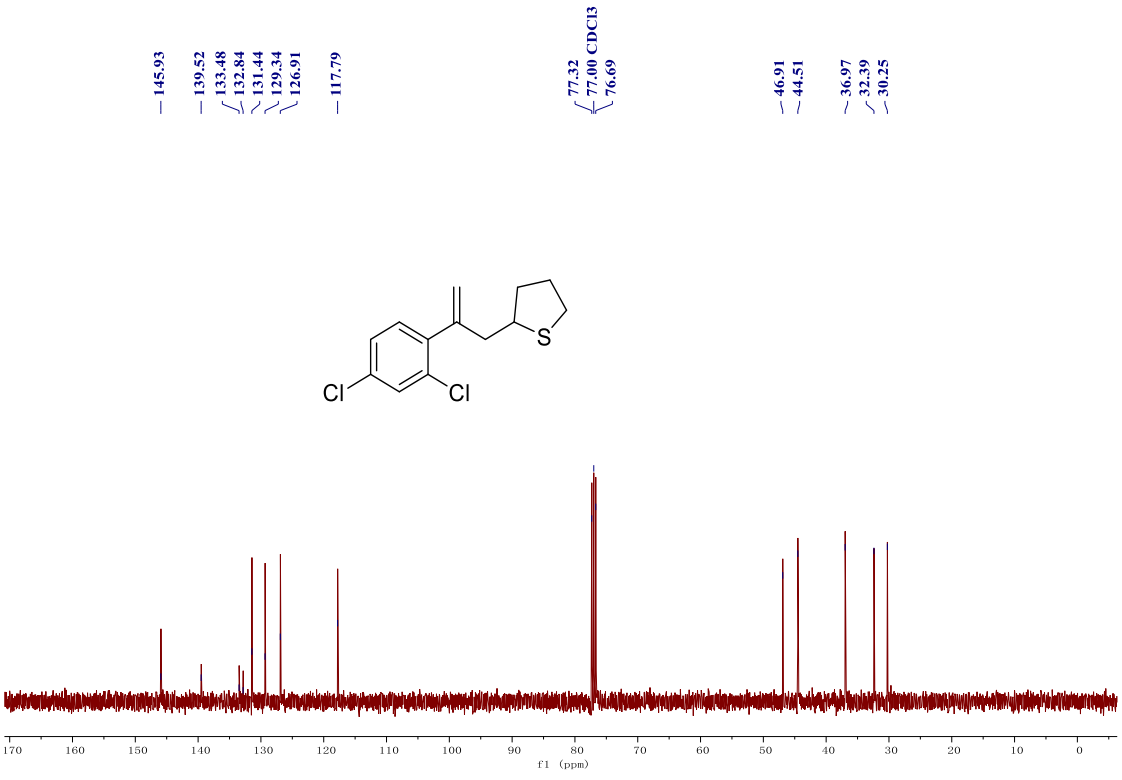
^{1}H NMR Spectra of compound 3n (101 MHz, $CDCl_3$)



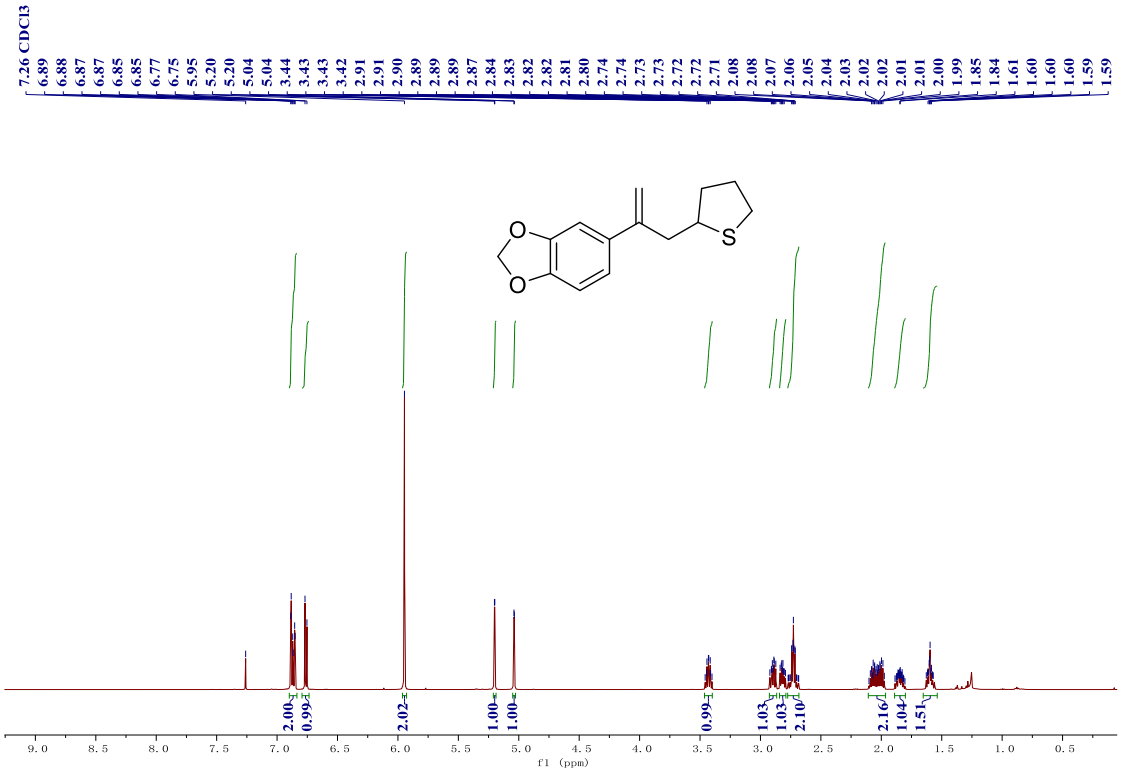
^{1}H NMR Spectra of compound 3o (400 MHz, $CDCl_3$)



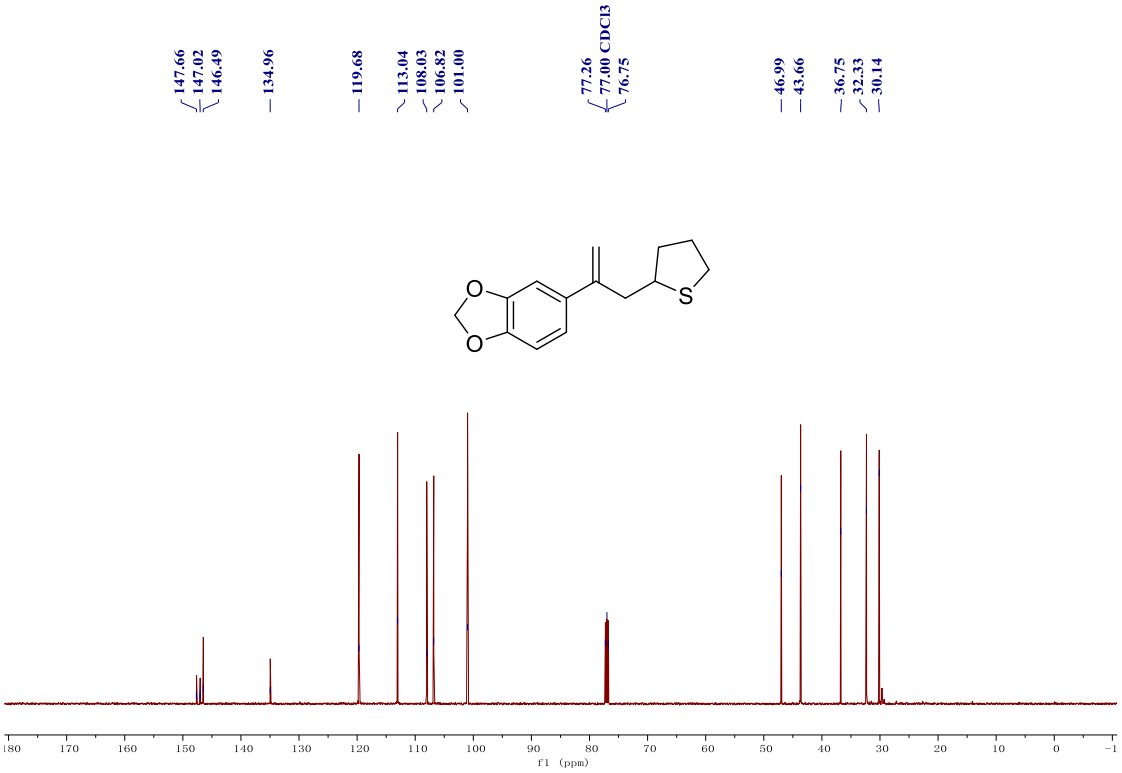
^{13}C NMR Spectra of compound 3o (101 MHz, $CDCl_3$)



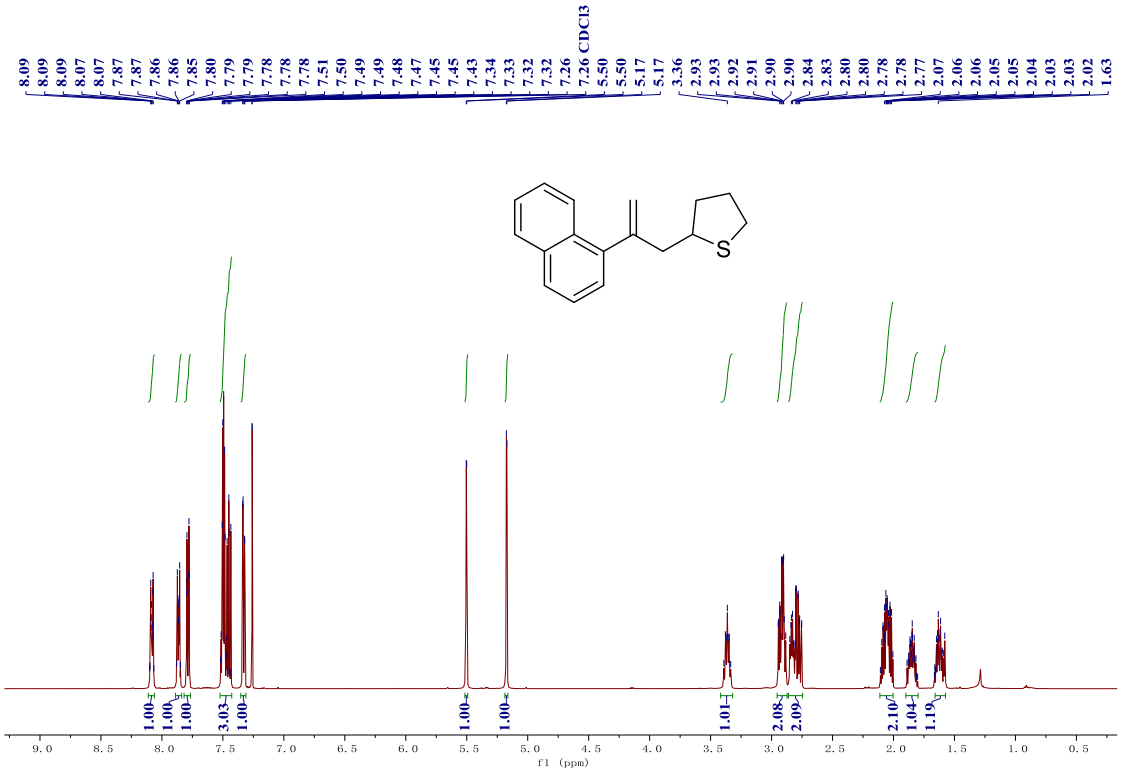
^{1}H NMR Spectra of compound 3p (500 MHz, $CDCl_3$)



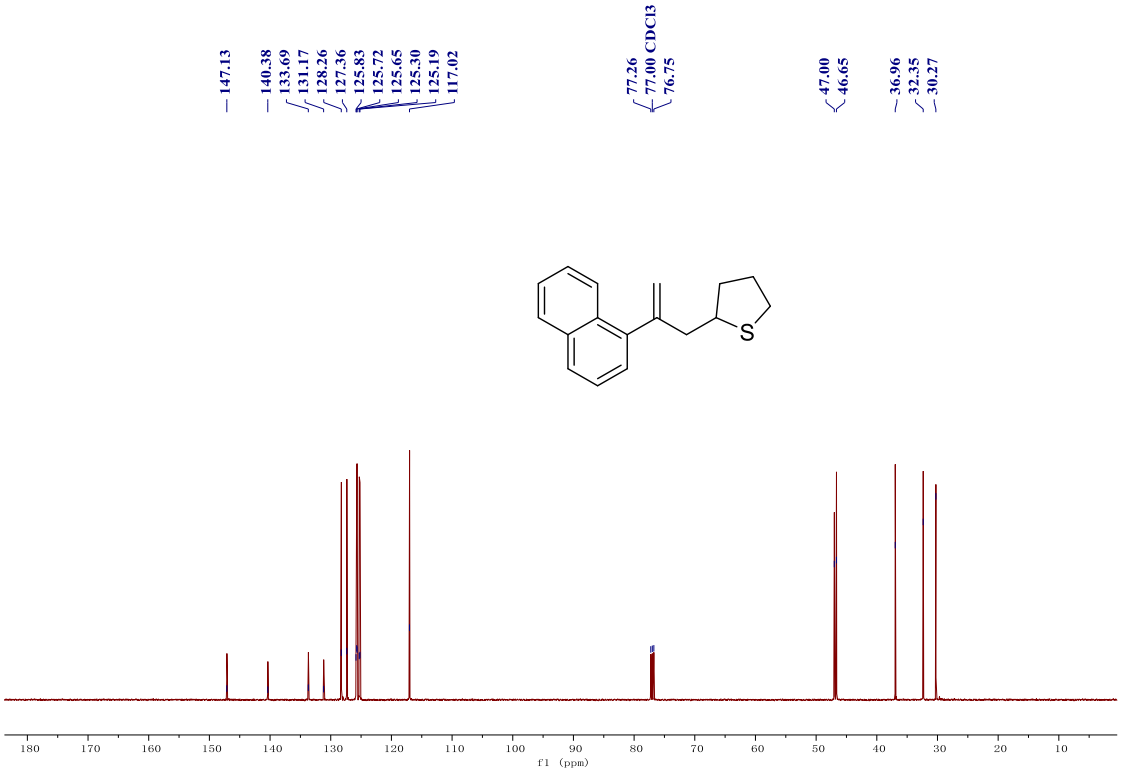
^{13}C NMR Spectra of compound 3p (126 MHz, $CDCl_3$)



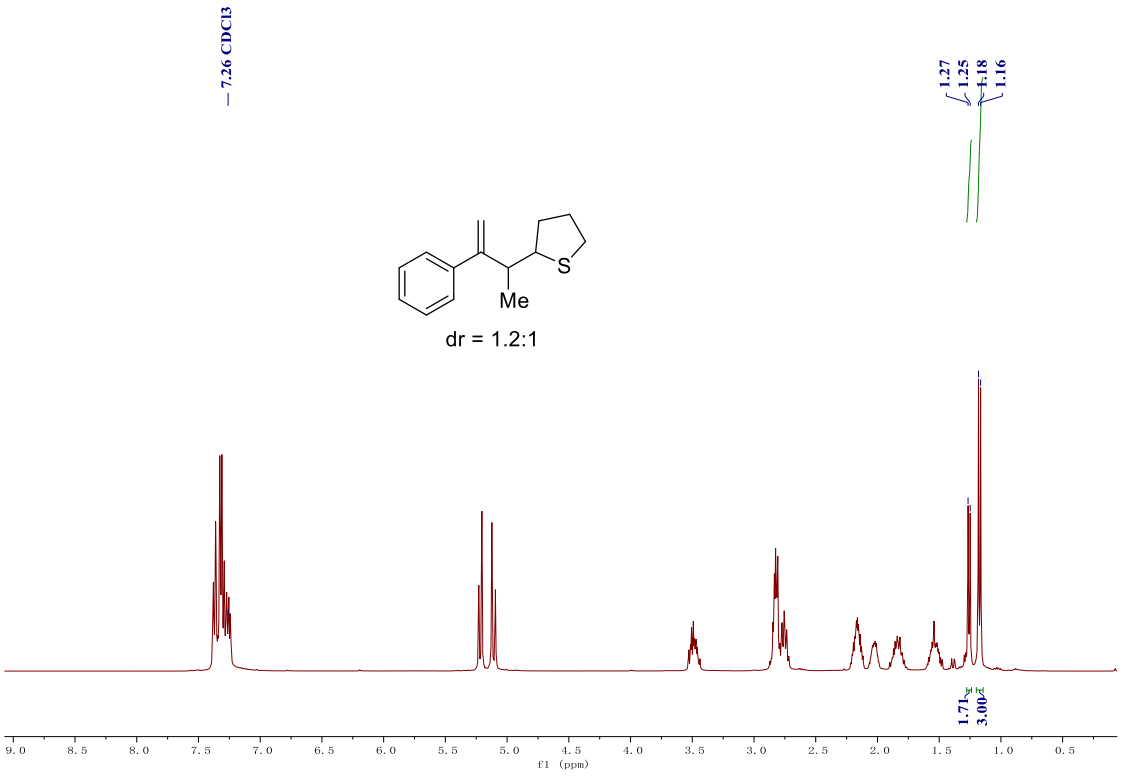
^{1}H NMR Spectra of compound 3q (500 MHz, $CDCl_3$)



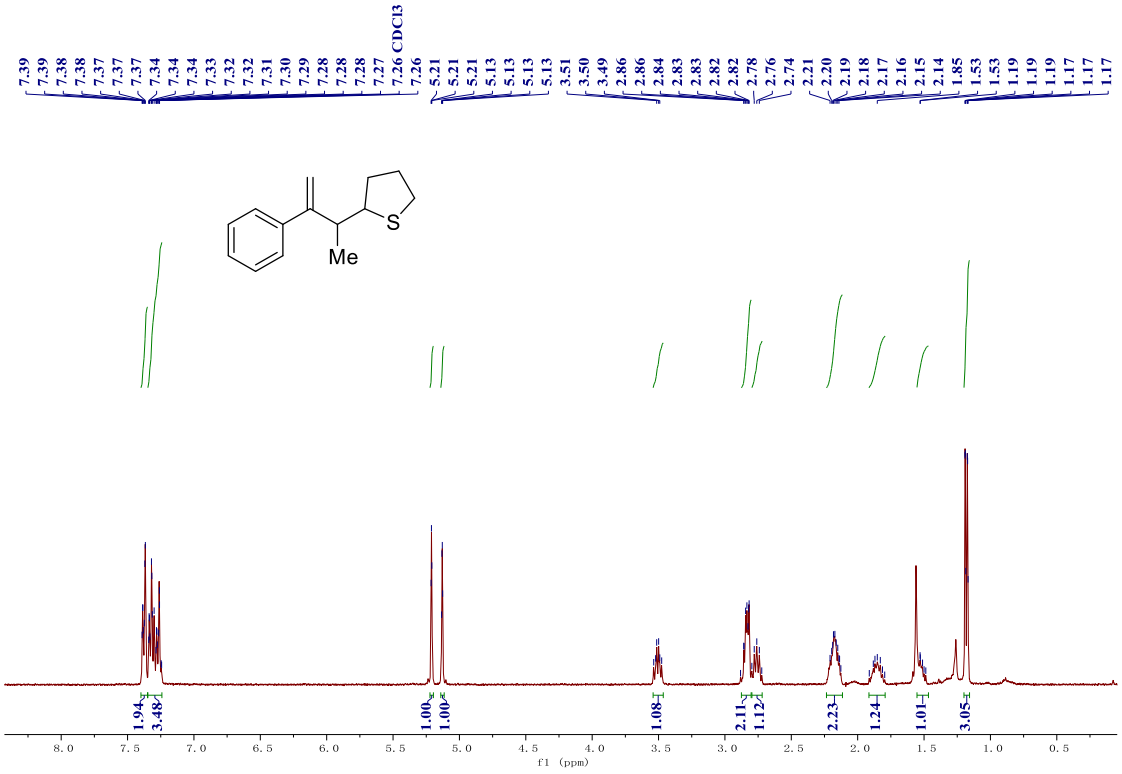
^{13}C NMR Spectra of compound 3q (126 MHz, $CDCl_3$)



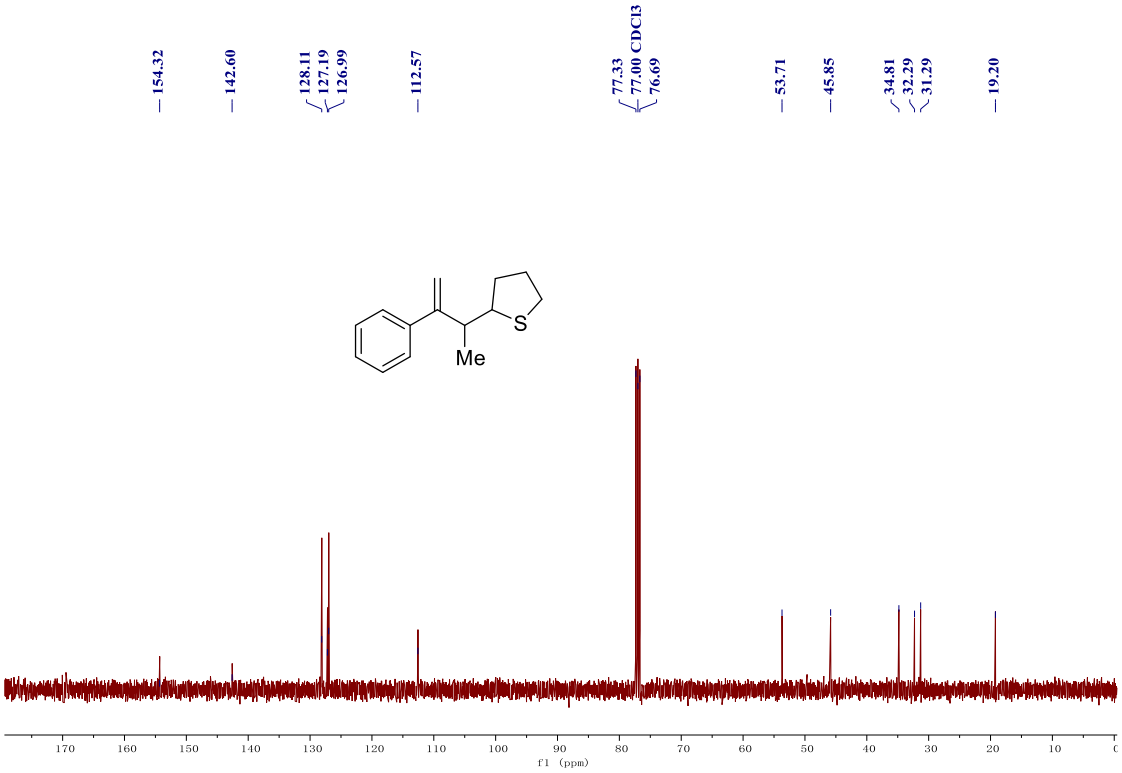
^{1}H NMR Spectra of compound 3r (400 MHz, $CDCl_3$)



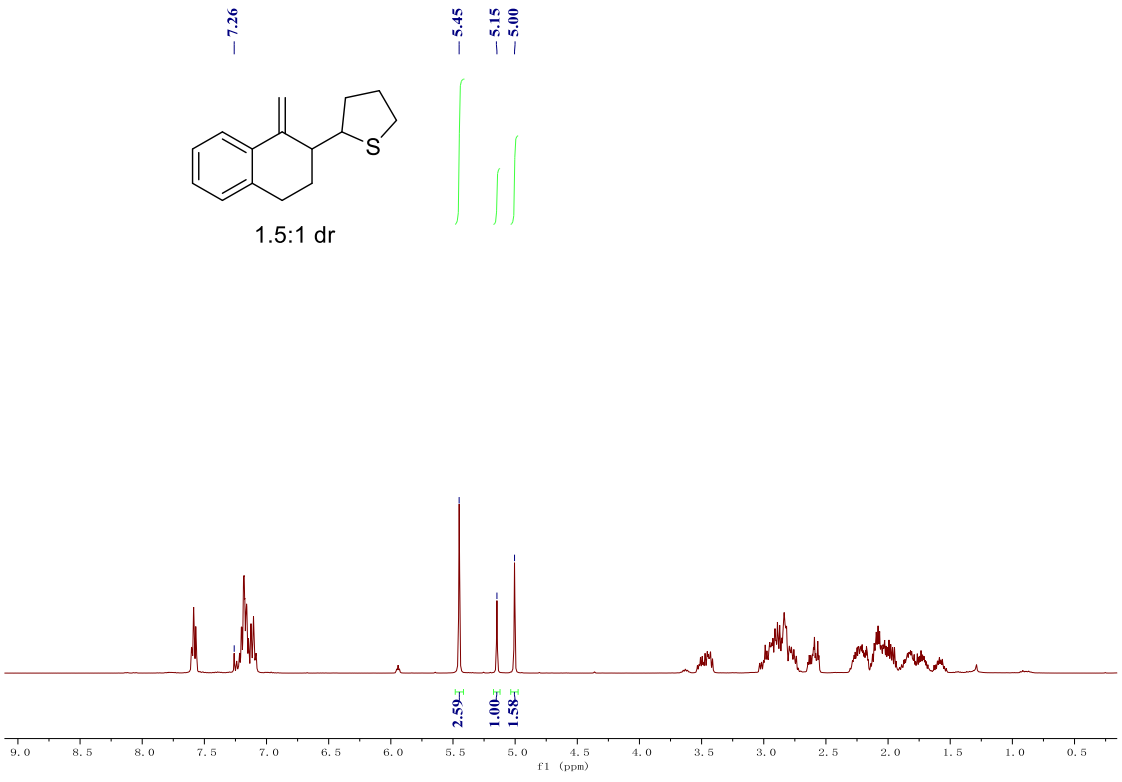
^{1}H NMR Spectra of compound 3r (400 MHz, $CDCl_3$)



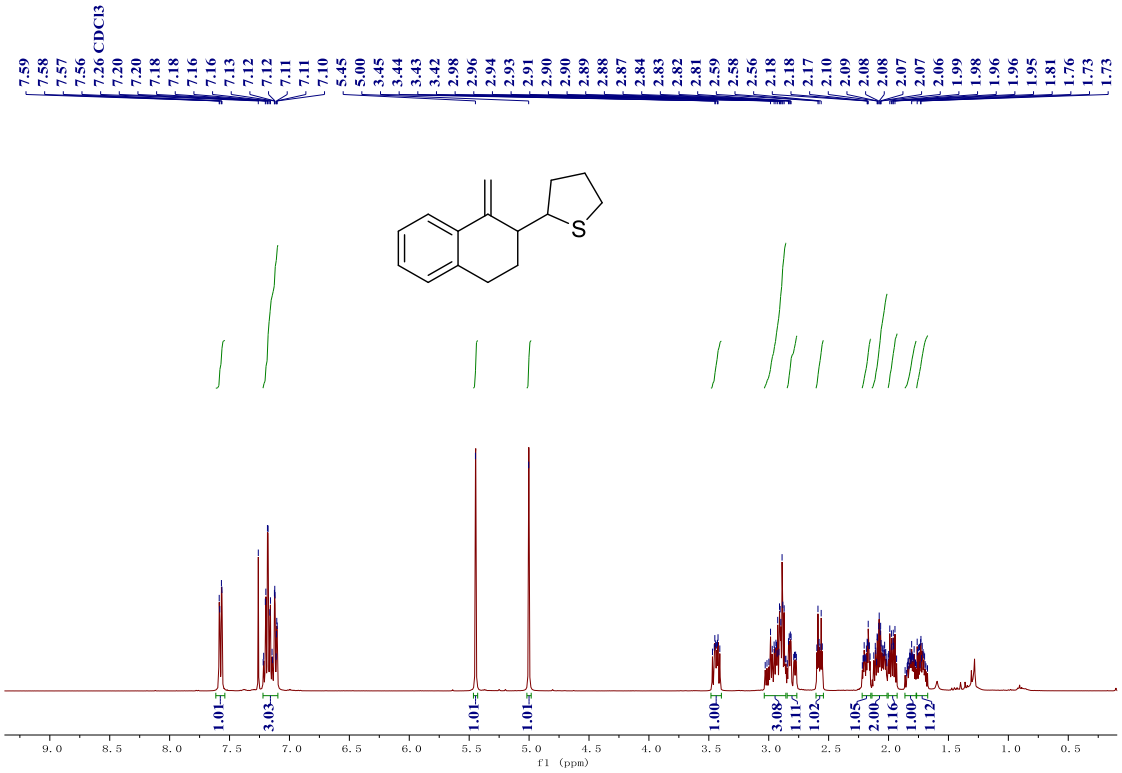
^{1}C NMR Spectra of compound 3r (101 MHz, $CDCl_3$)



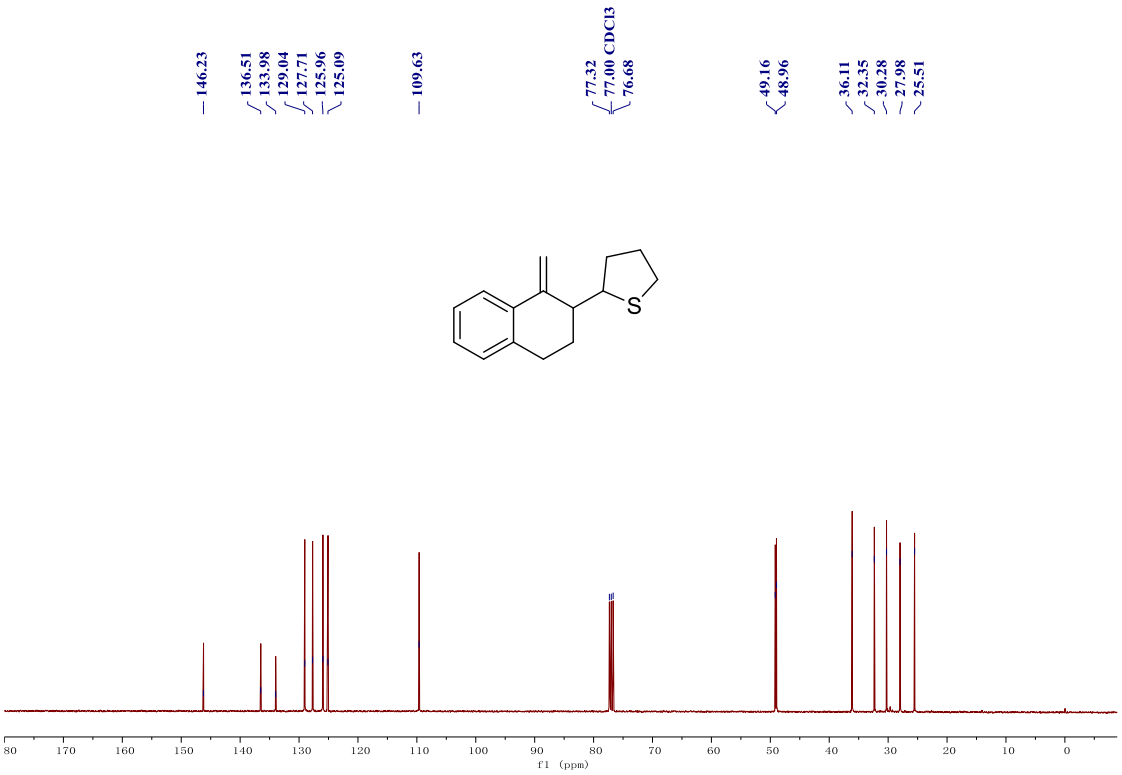
^{1}H NMR Spectra of compound 3s (500 MHz, $CDCl_3$)



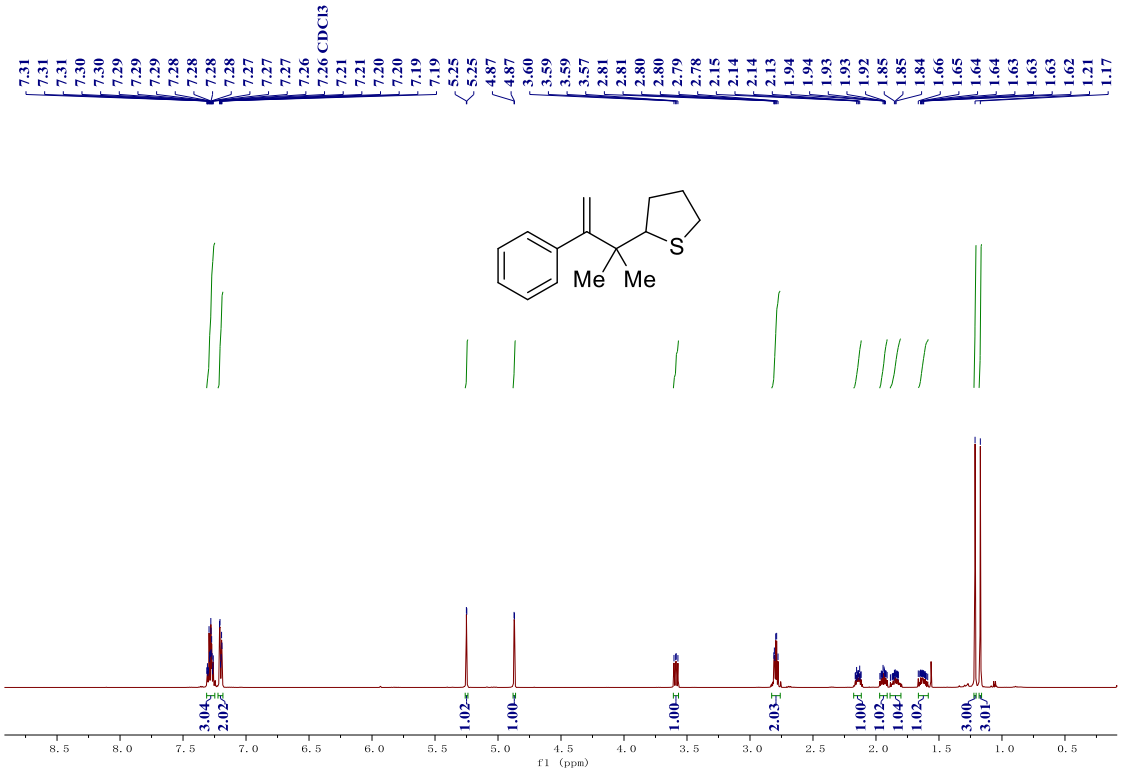
^{1}H NMR Spectra of compound 3s (500 MHz, $CDCl_3$)



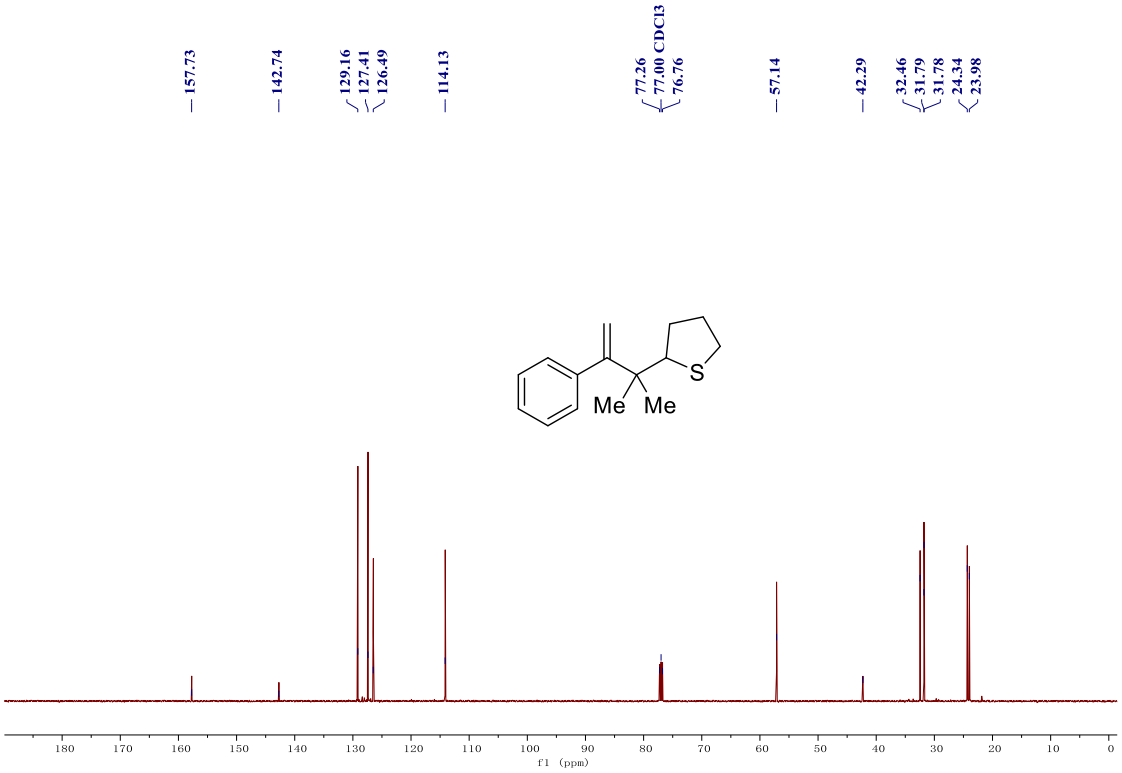
^{13}C NMR Spectra of compound 3s (126 MHz, $CDCl_3$)



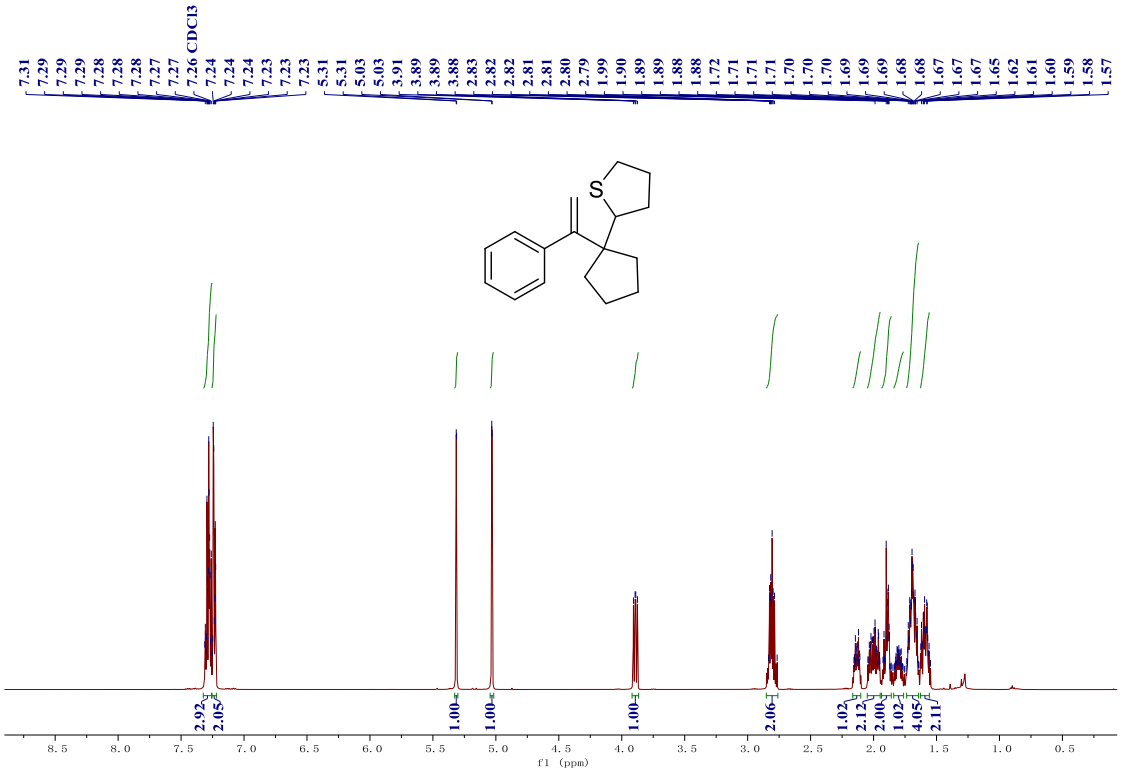
^{1}H NMR Spectra of compound 3t (500 MHz, $CDCl_3$)



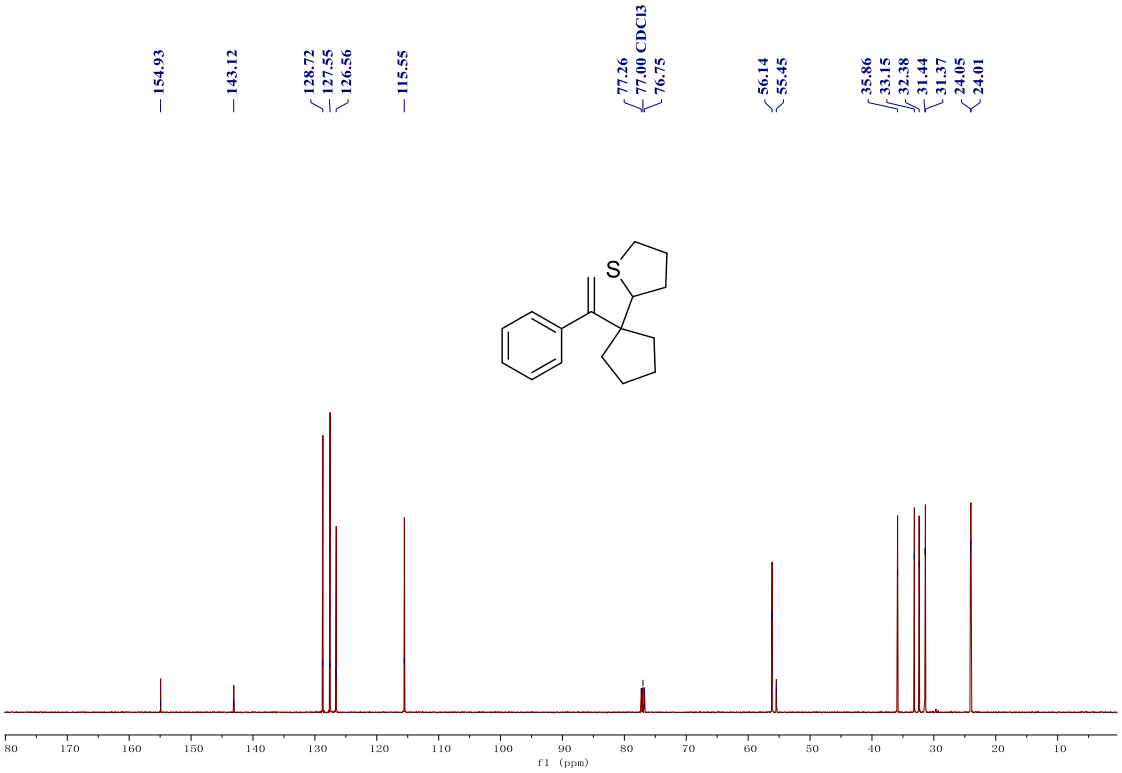
^{13}C NMR Spectra of compound 3t (126 MHz, $CDCl_3$)



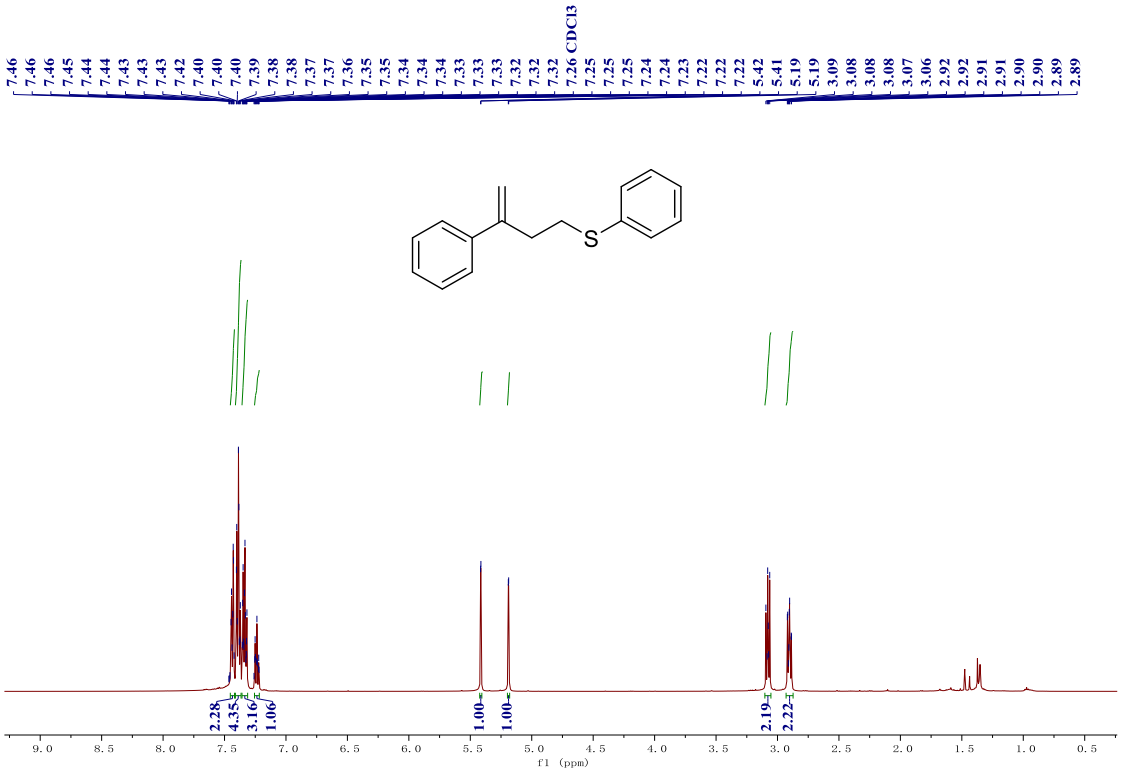
^{1}H NMR Spectra of compound 3u (500 MHz, $CDCl_3$)



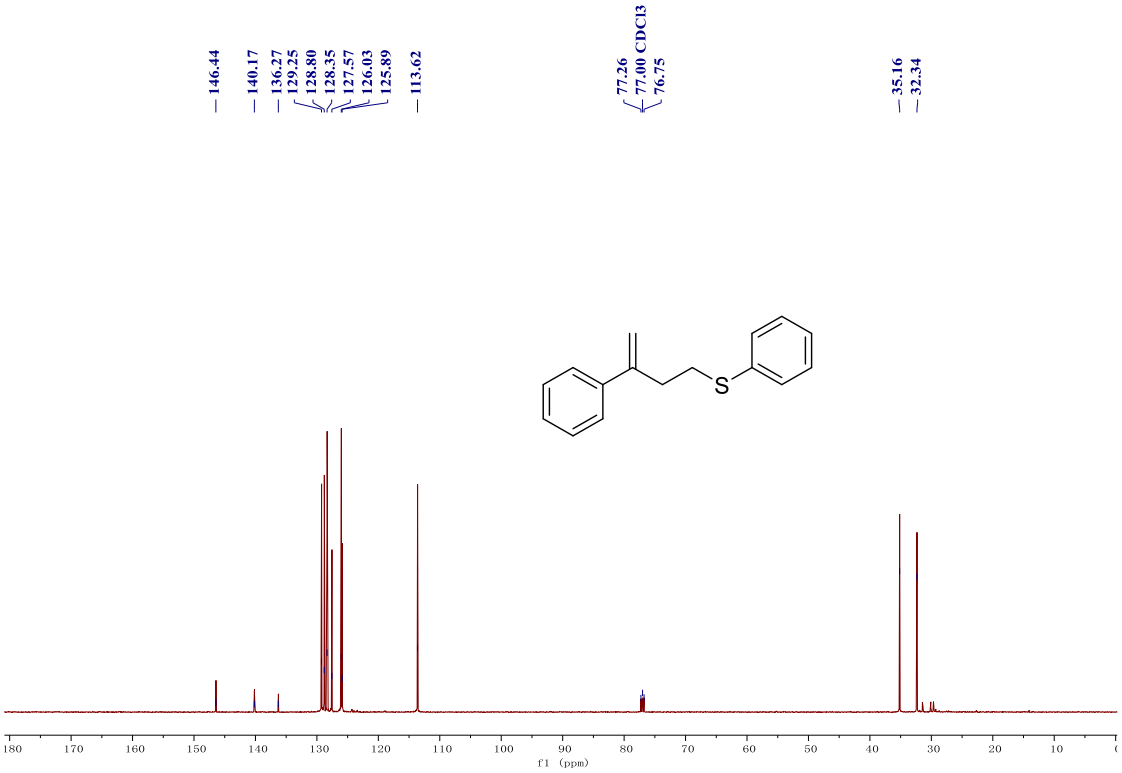
^{13}C NMR Spectra of compound 3u (126 MHz, $CDCl_3$)



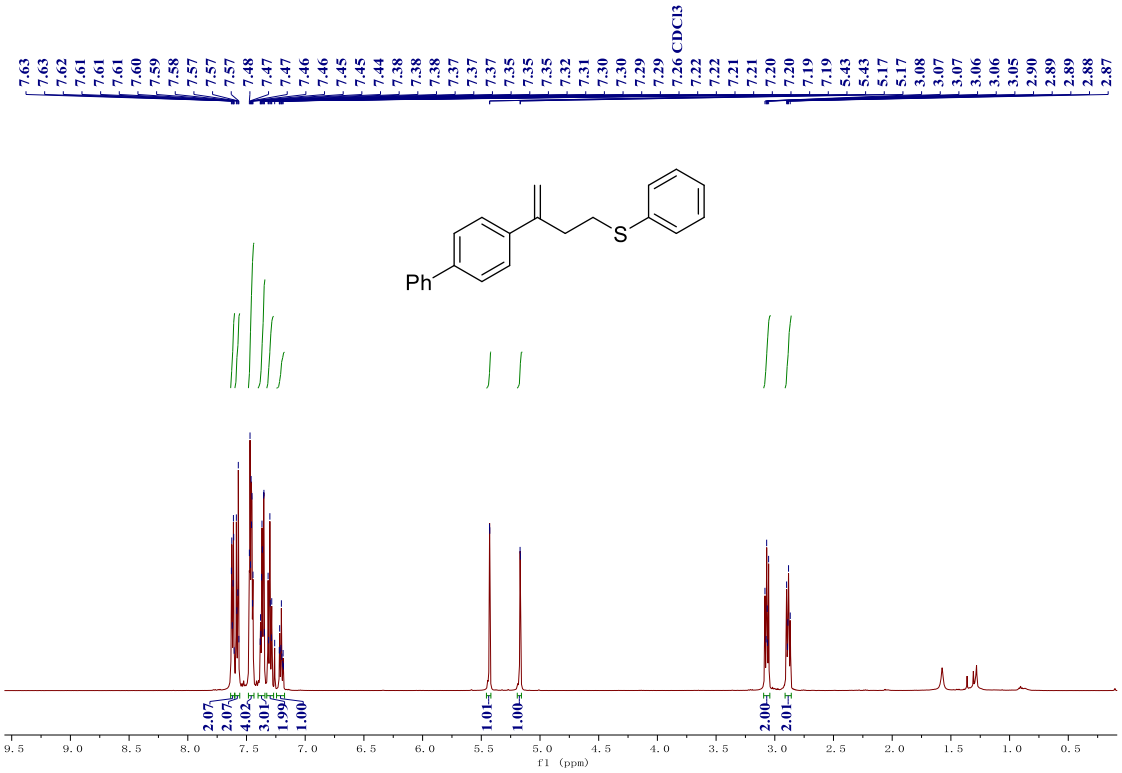
^{1}H NMR Spectra of compound 4a (500 MHz, $CDCl_3$)



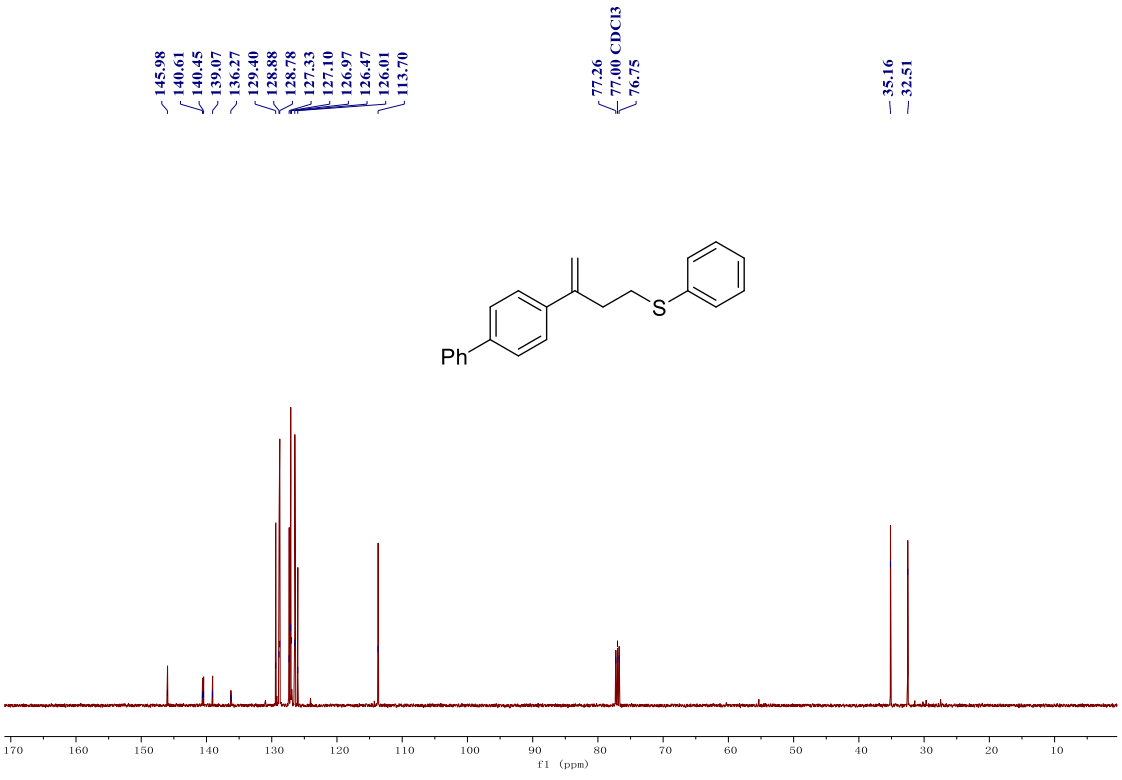
^{13}C NMR Spectra of compound 4a (126 MHz, $CDCl_3$)



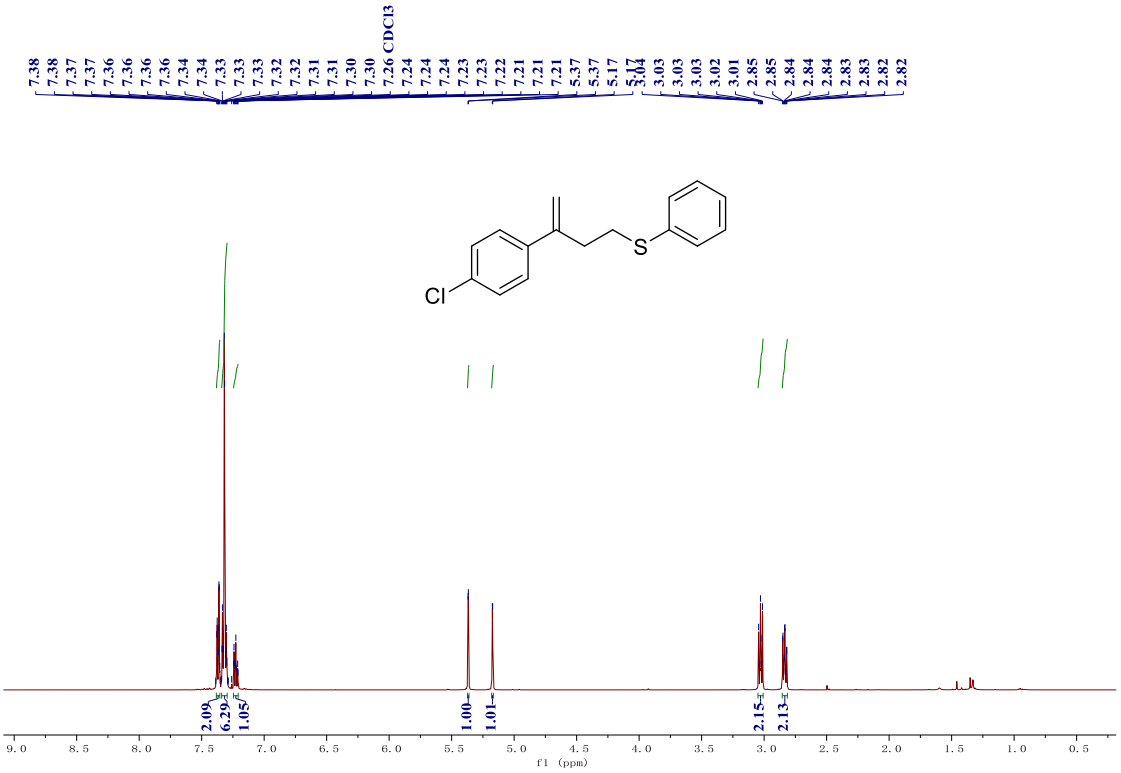
^{1}H NMR Spectra of compound 4b (500 MHz, $CDCl_3$)



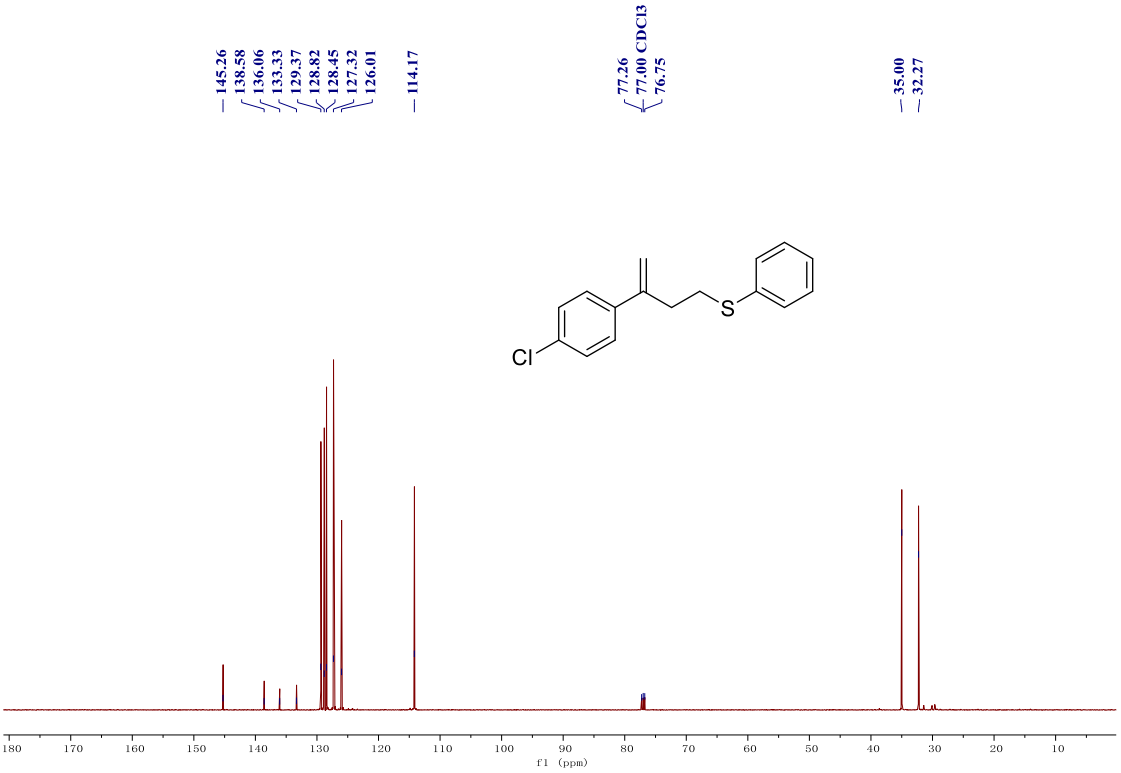
^{13}C NMR Spectra of compound 4b (126 MHz, $CDCl_3$)



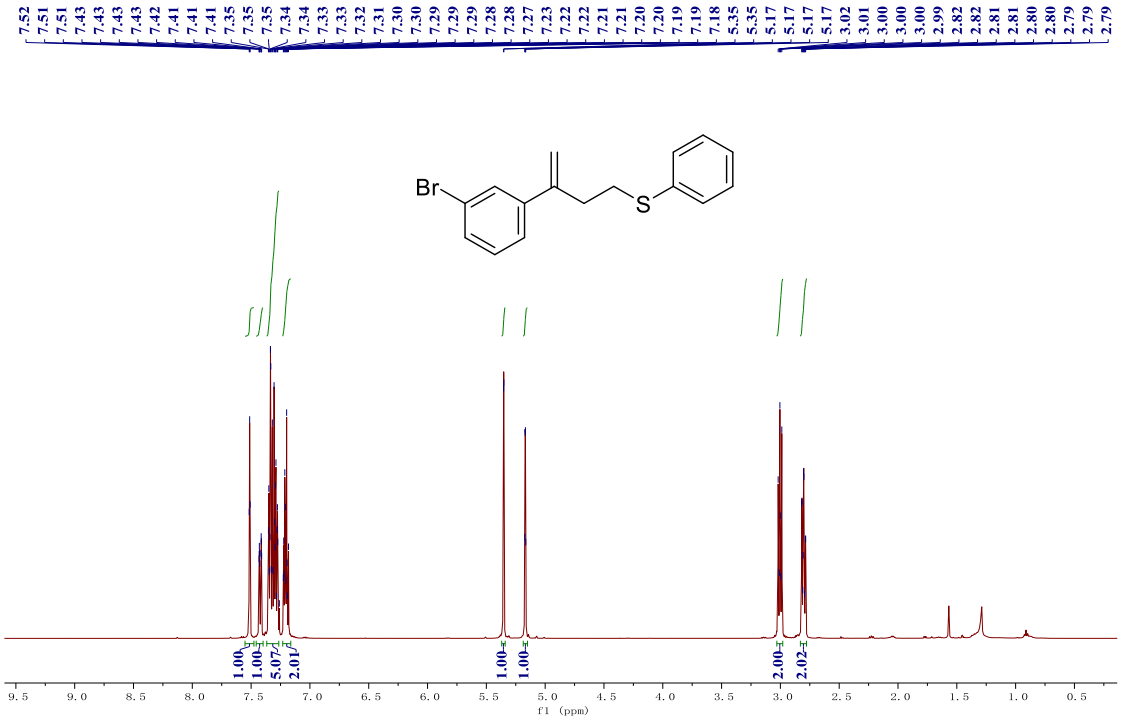
^{1}H NMR Spectra of compound 4c (500 MHz, $CDCl_3$)



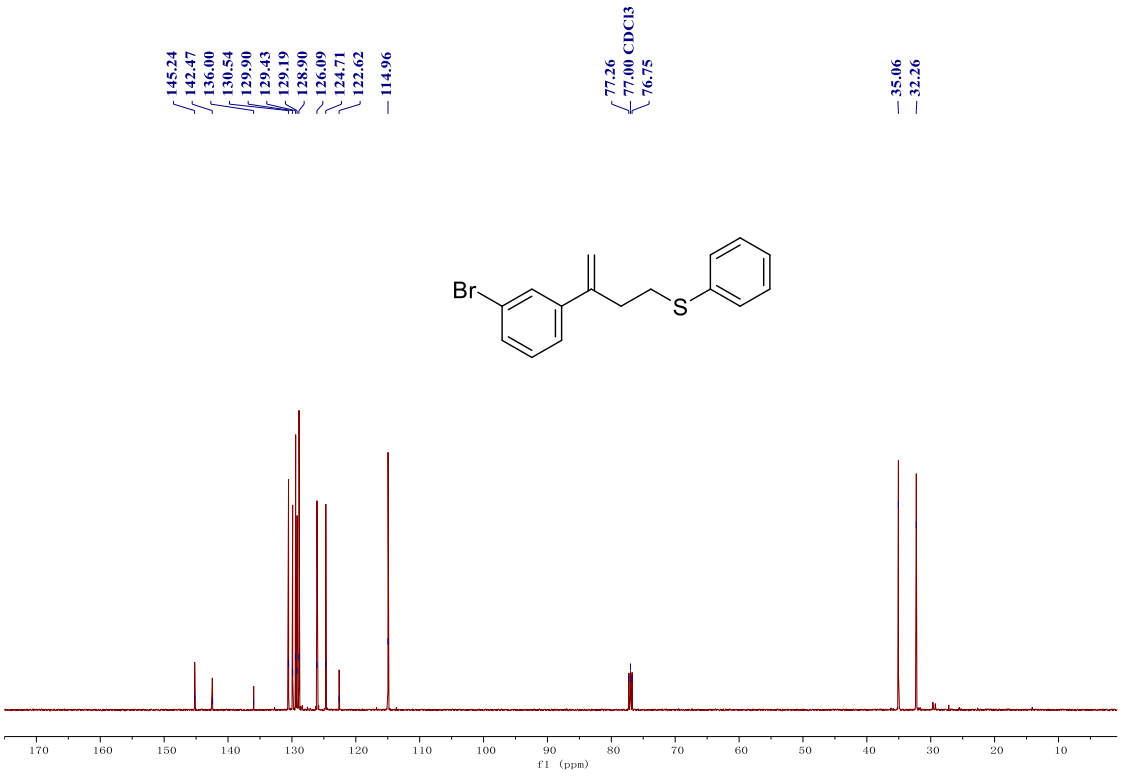
^{13}C NMR Spectra of compound 4c (126 MHz, $CDCl_3$)



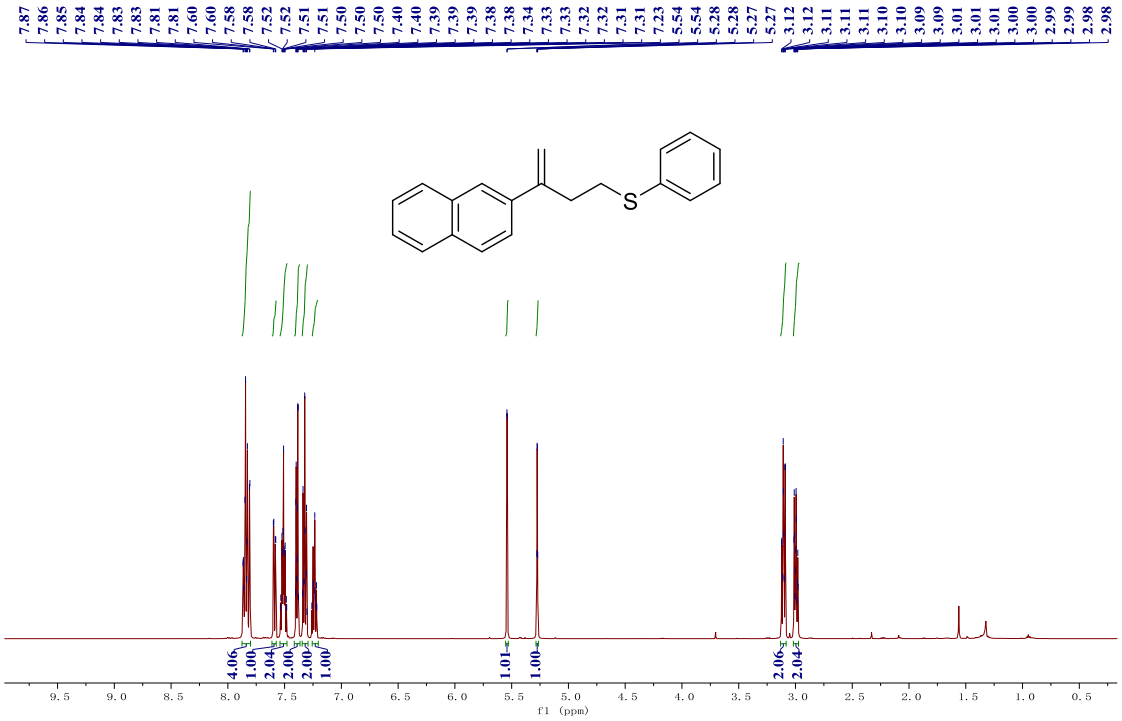
^{1}H NMR Spectra of compound 4d (500 MHz, $CDCl_3$)



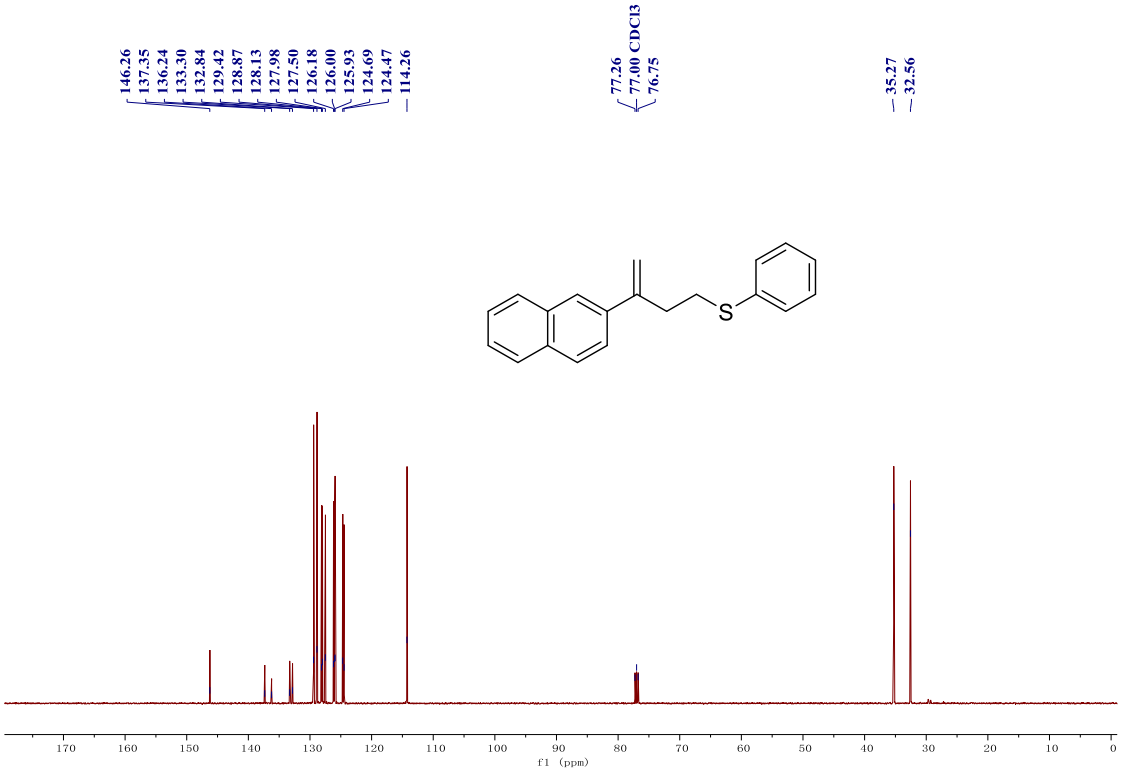
^{13}C NMR Spectra of compound 4d (126 MHz, $CDCl_3$)



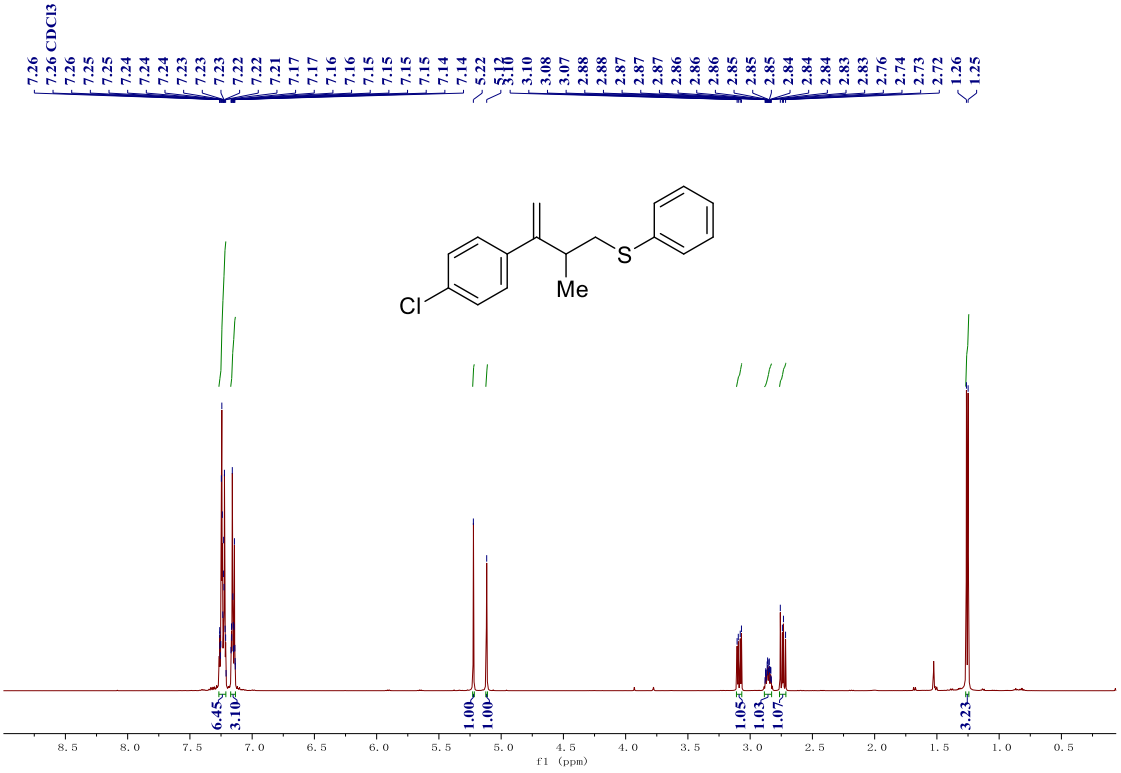
^{1}H NMR Spectra of compound 4e (500 MHz, $CDCl_3$)



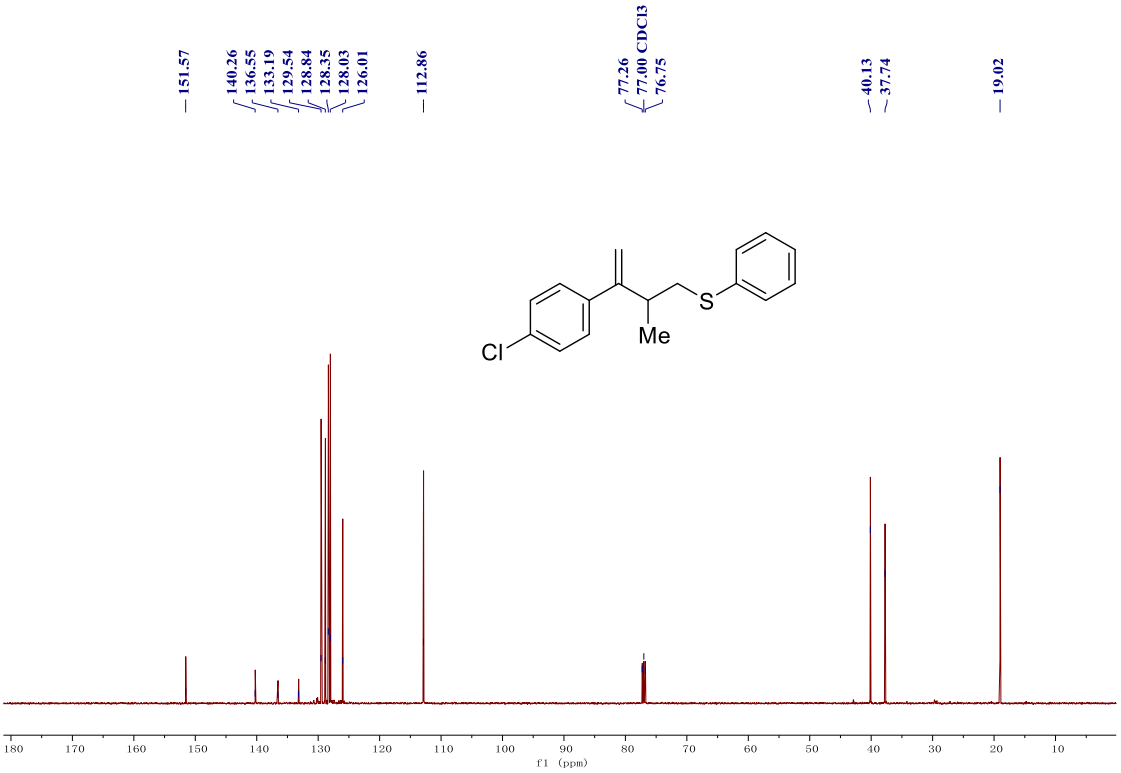
^{13}C NMR Spectra of compound 4e (126 MHz, $CDCl_3$)



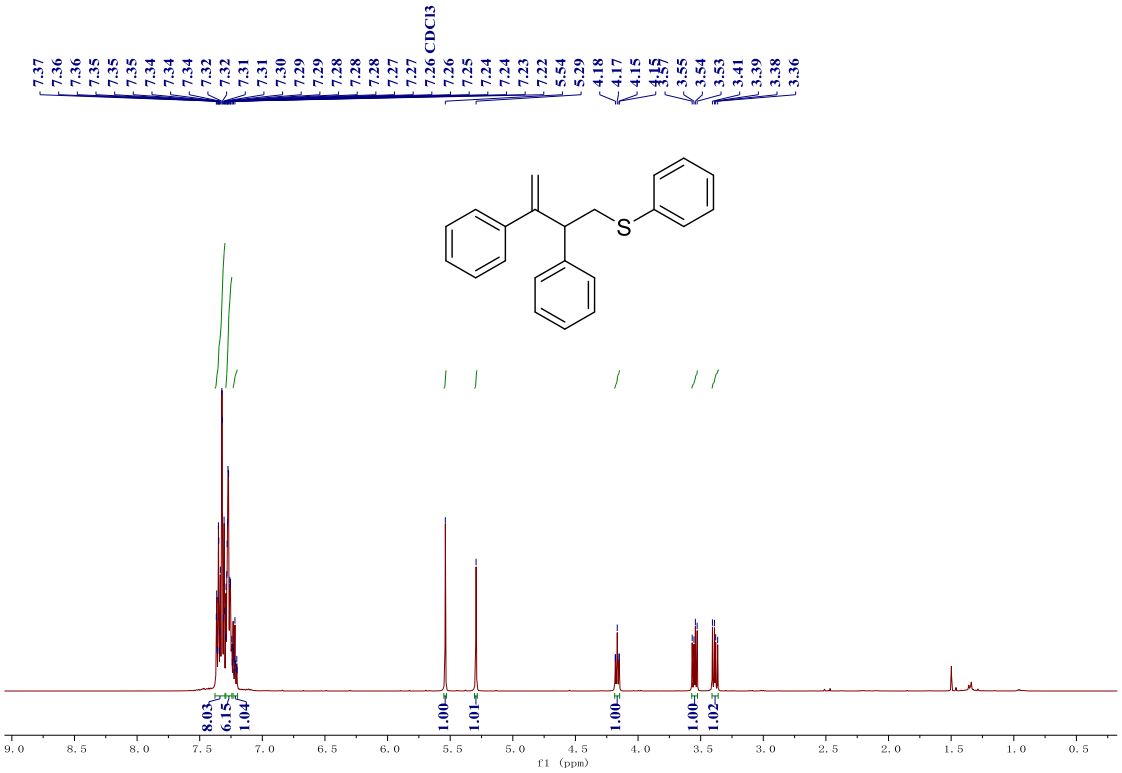
^{1}H NMR Spectra of compound 4f (500 MHz, $CDCl_3$)



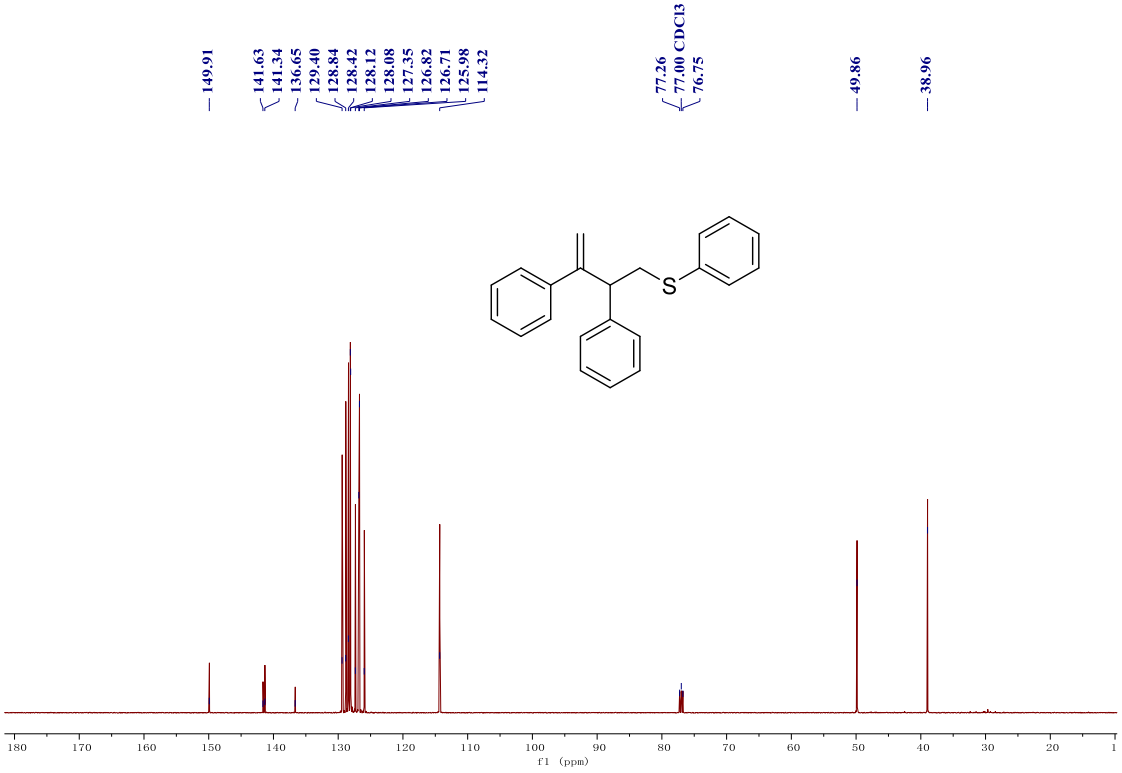
^{13}C NMR Spectra of compound 4f (126 MHz, $CDCl_3$)



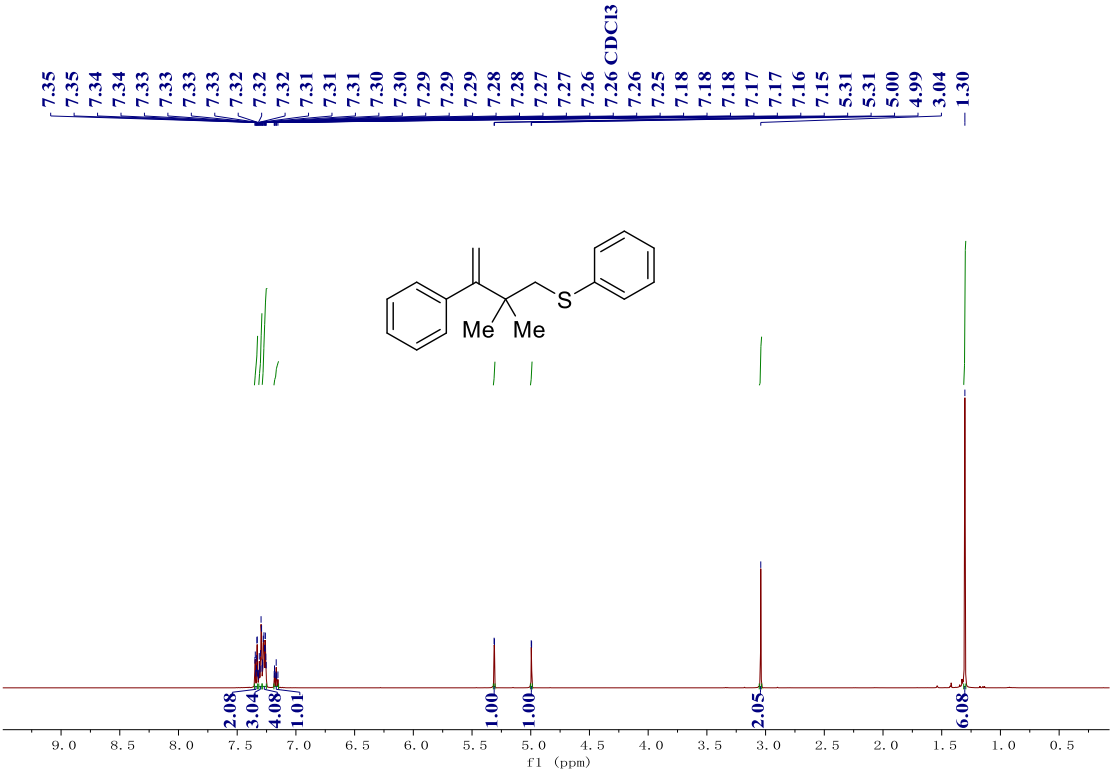
^{1}H NMR Spectra of compound 4g (500 MHz, $CDCl_3$)



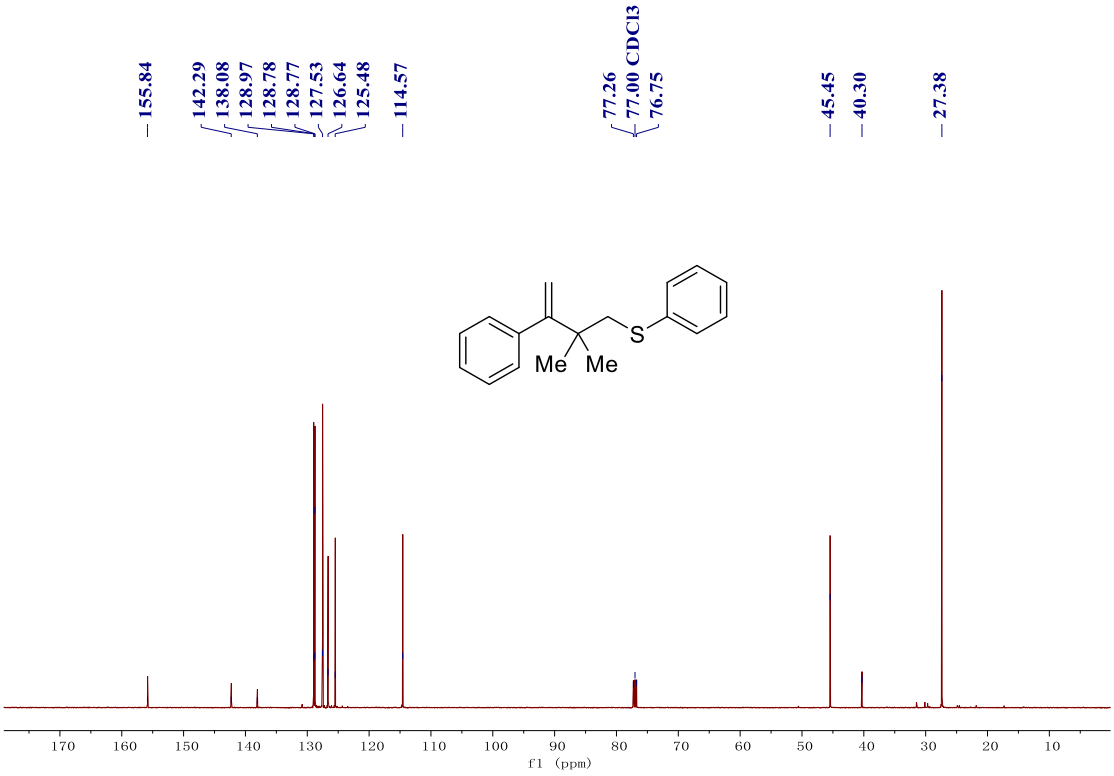
^{13}C NMR Spectra of compound 4g (126 MHz, $CDCl_3$)



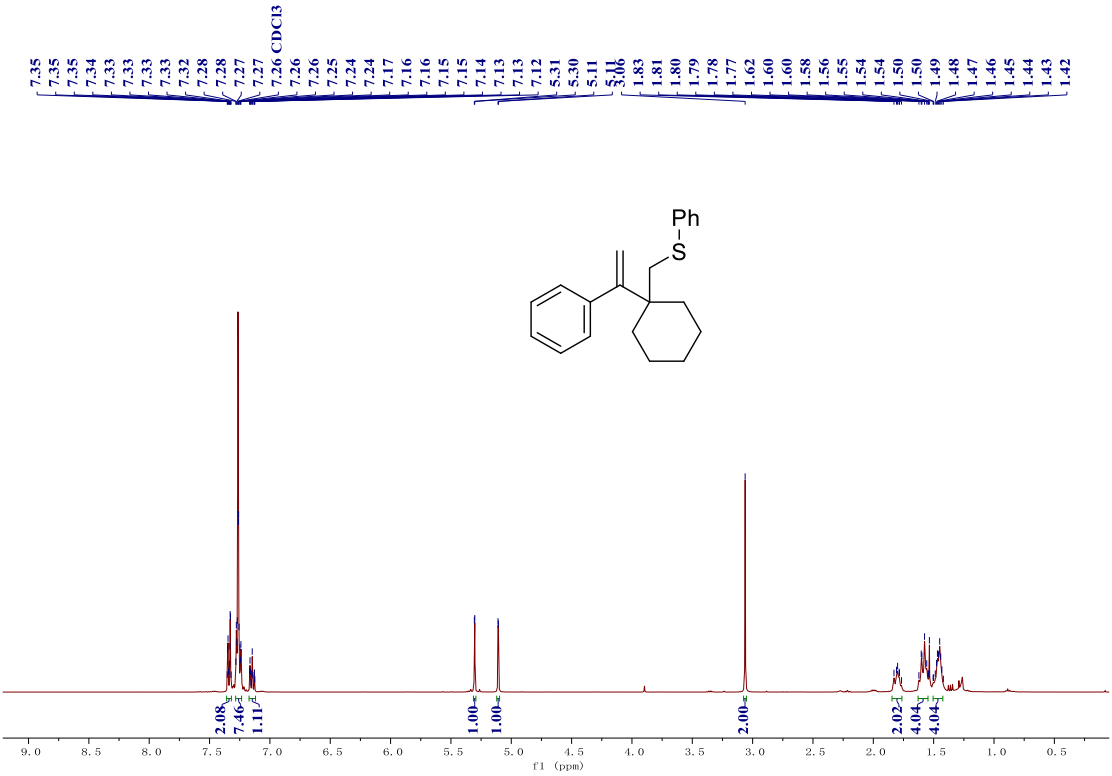
^{1}H NMR Spectra of compound 4h (500 MHz, $CDCl_3$)



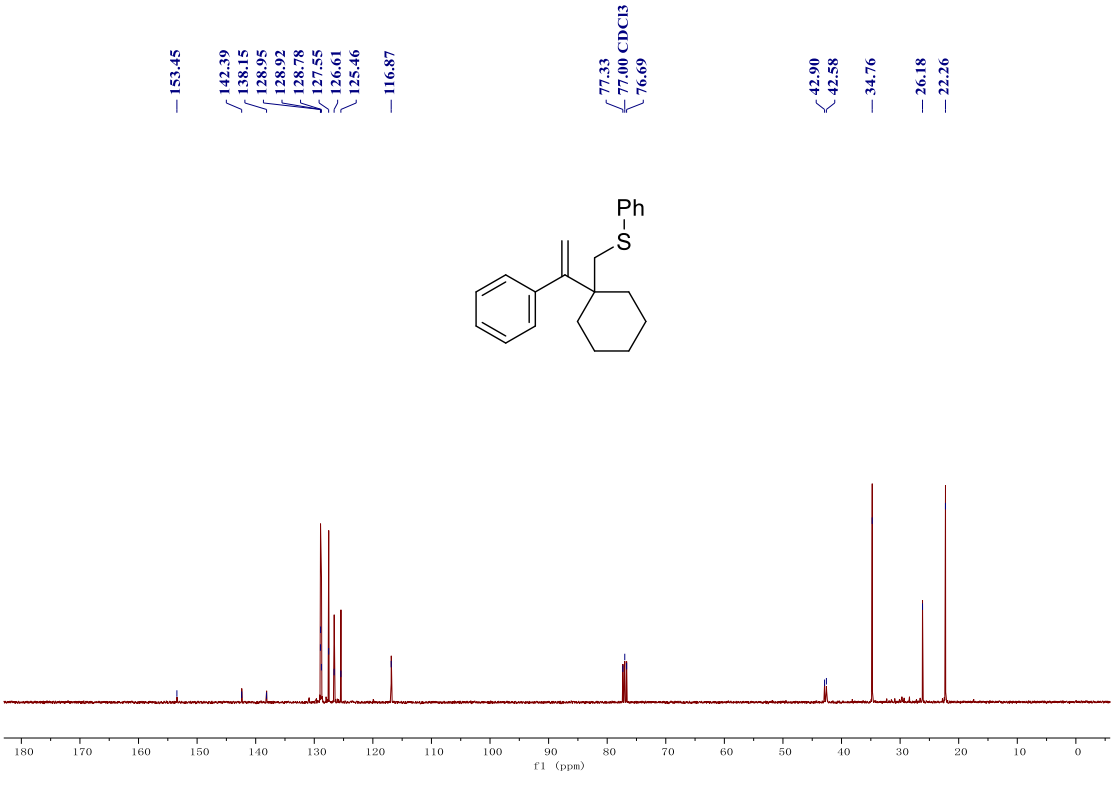
^{13}C NMR Spectra of compound 4h (126 MHz, $CDCl_3$)



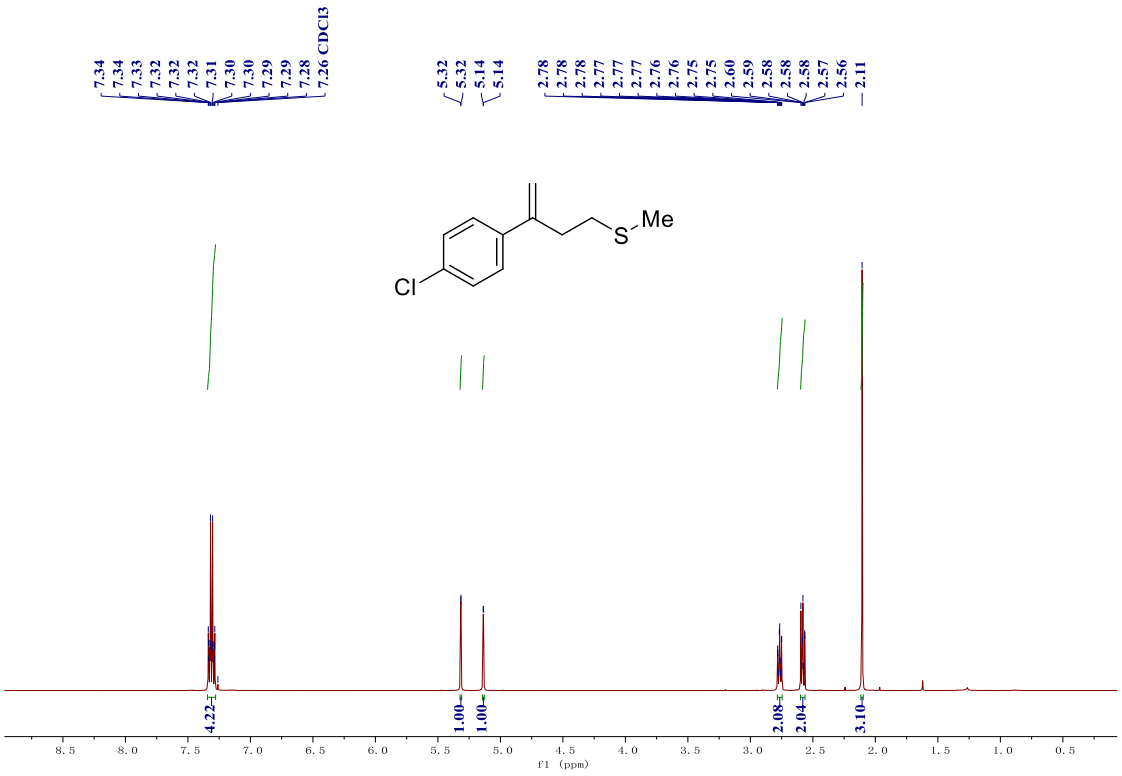
^{1}H NMR Spectra of compound 4i (400 MHz, $CDCl_3$)



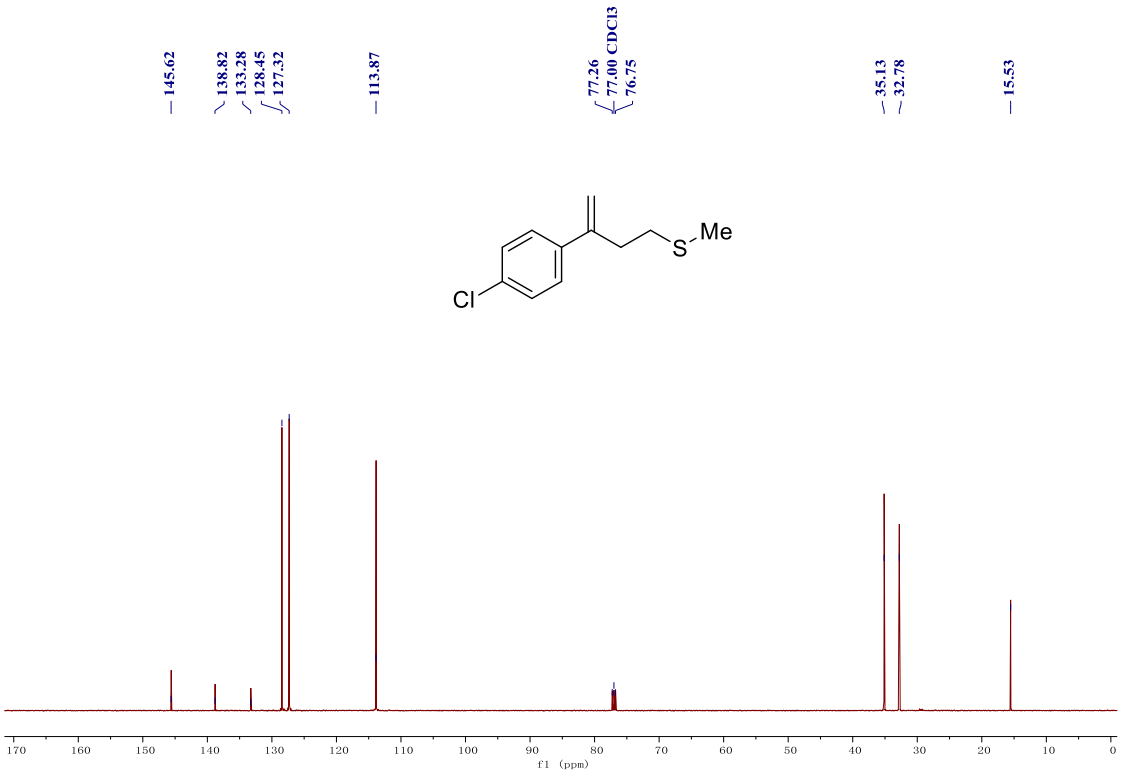
^{13}C NMR Spectra of compound 4i (101MHz, $CDCl_3$)



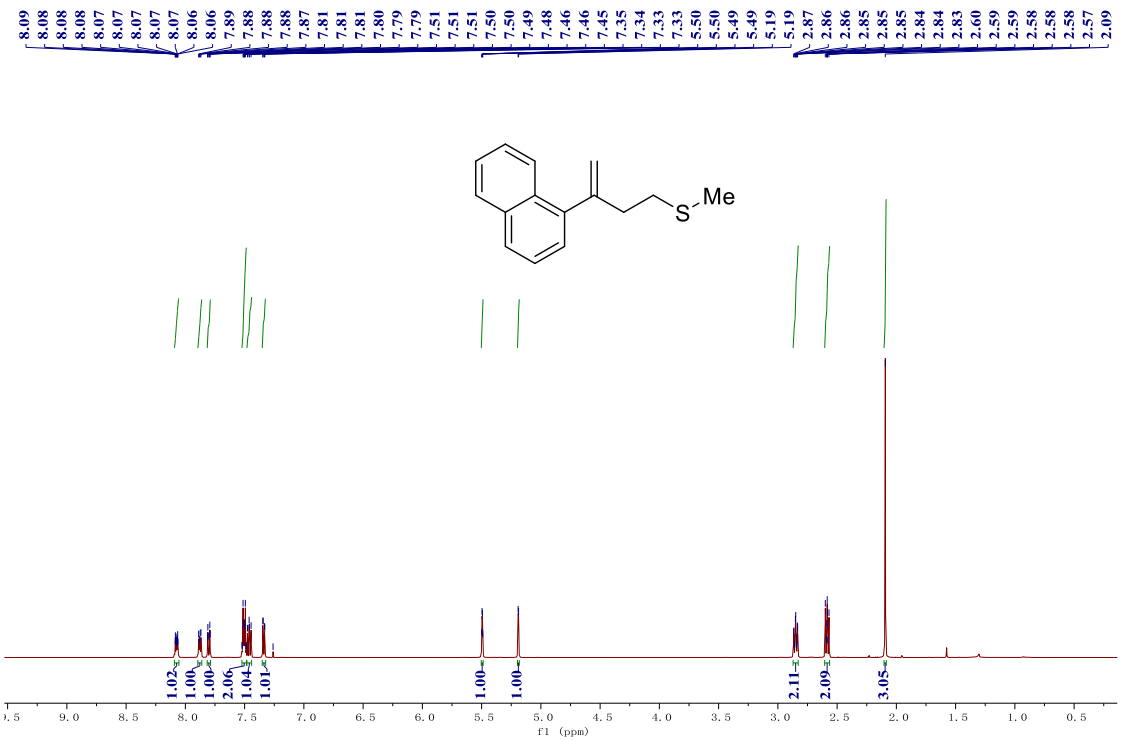
^{1}H NMR Spectra of compound 4j (500 MHz, $CDCl_3$)



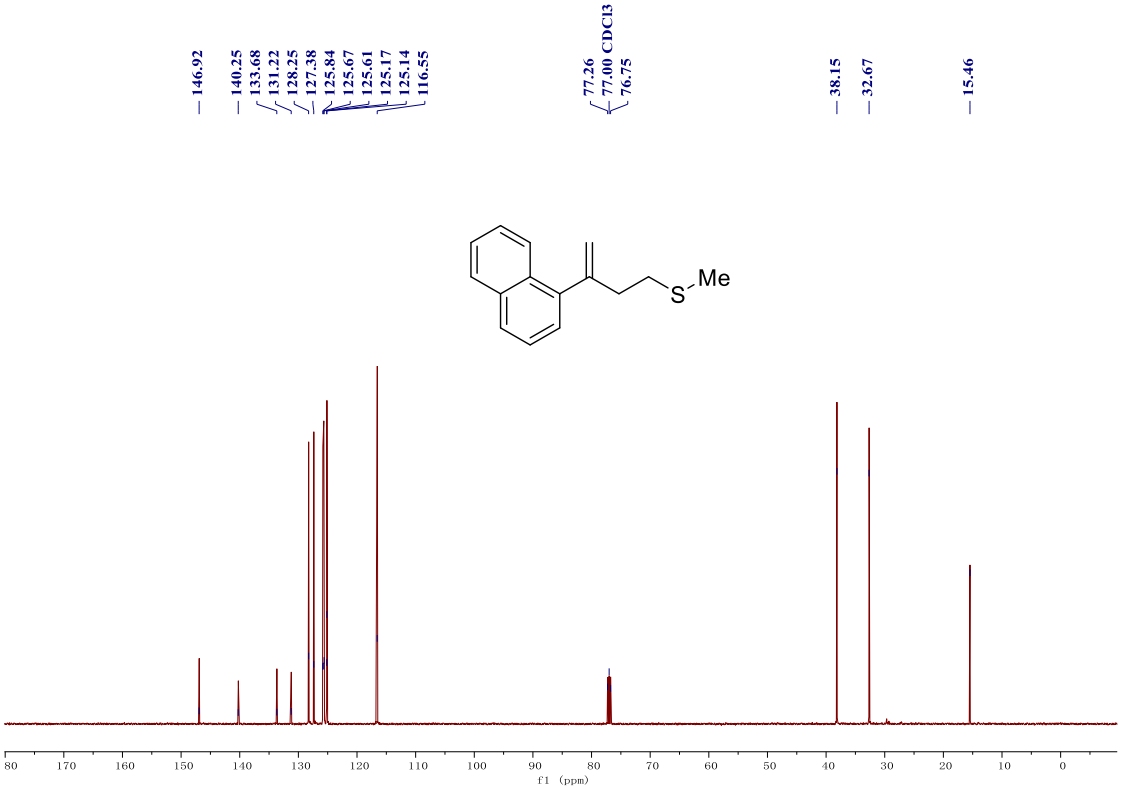
^{13}C NMR Spectra of compound 4j (126 MHz, $CDCl_3$)



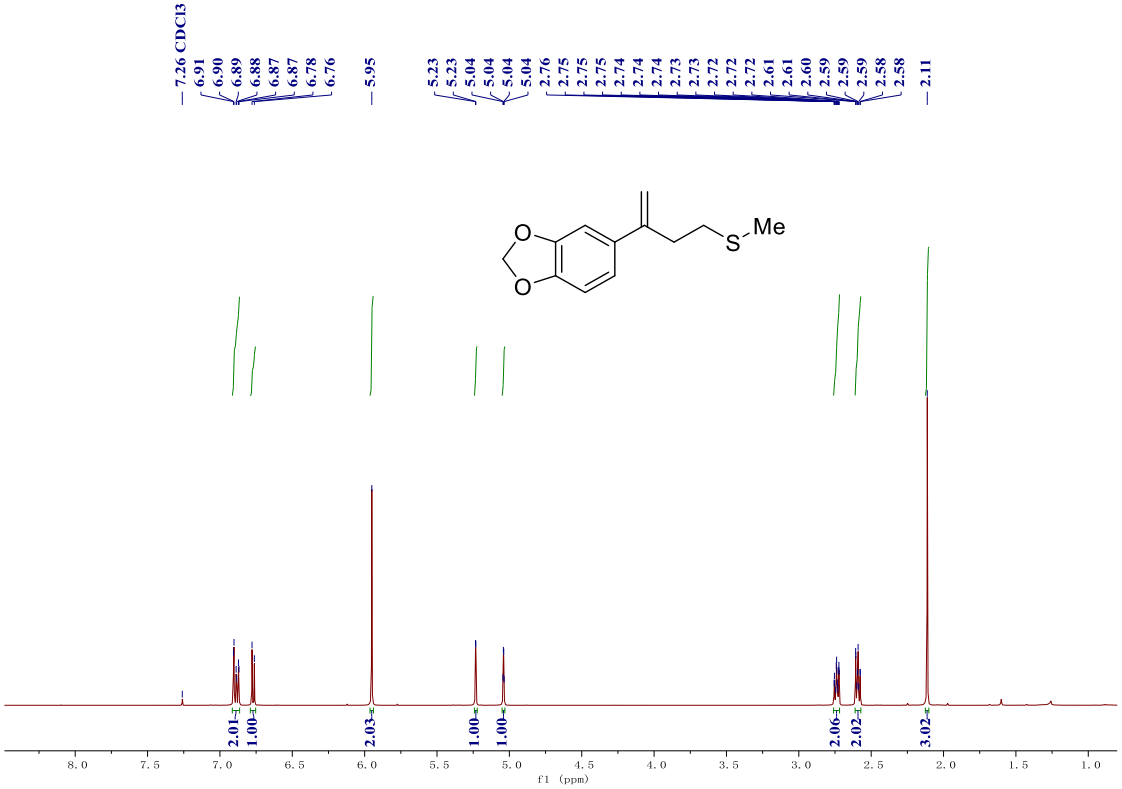
^{1}H NMR Spectra of compound 4k (500 MHz, $CDCl_3$)



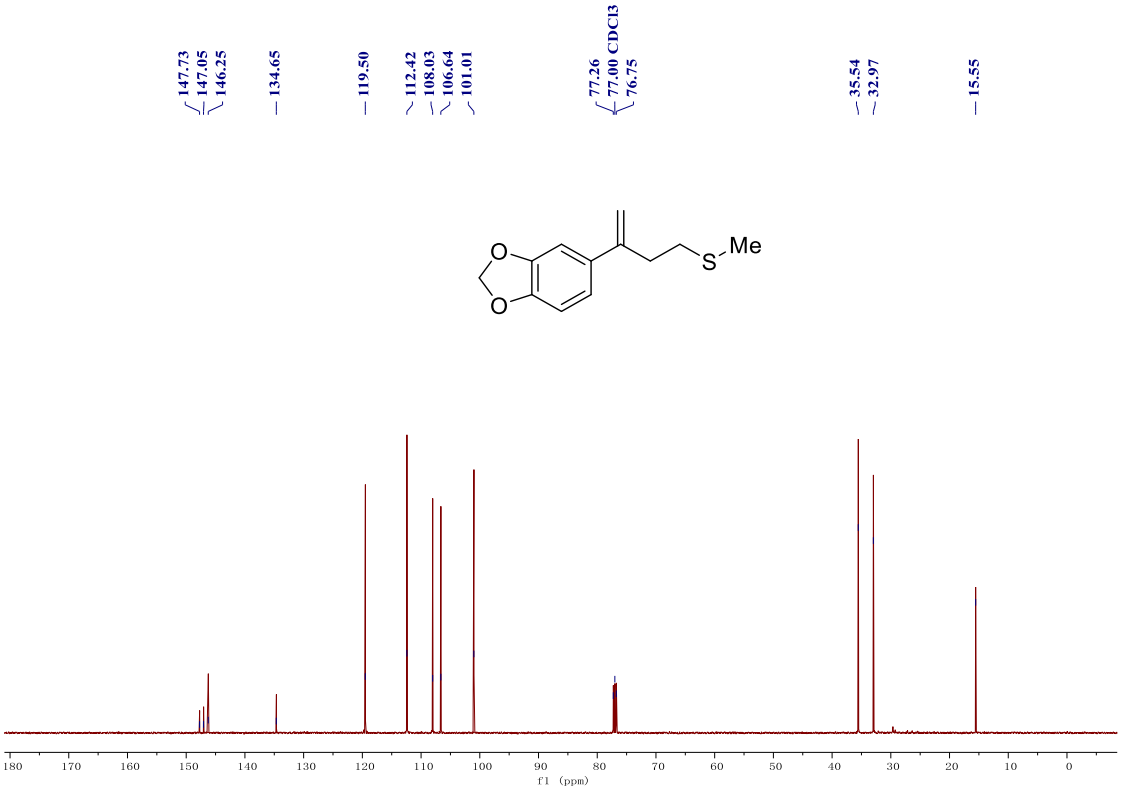
^{13}C NMR Spectra of compound 4k (126 MHz, $CDCl_3$)



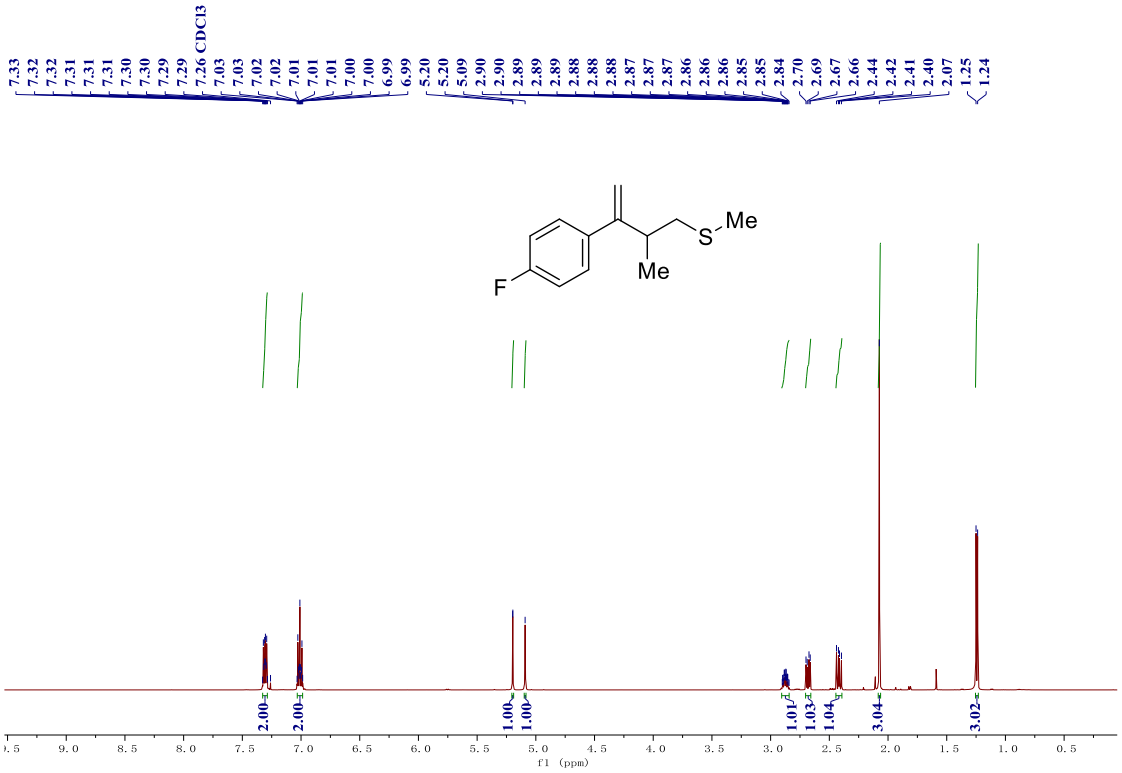
^{1}H NMR Spectra of compound 4l (500 MHz, $CDCl_3$)



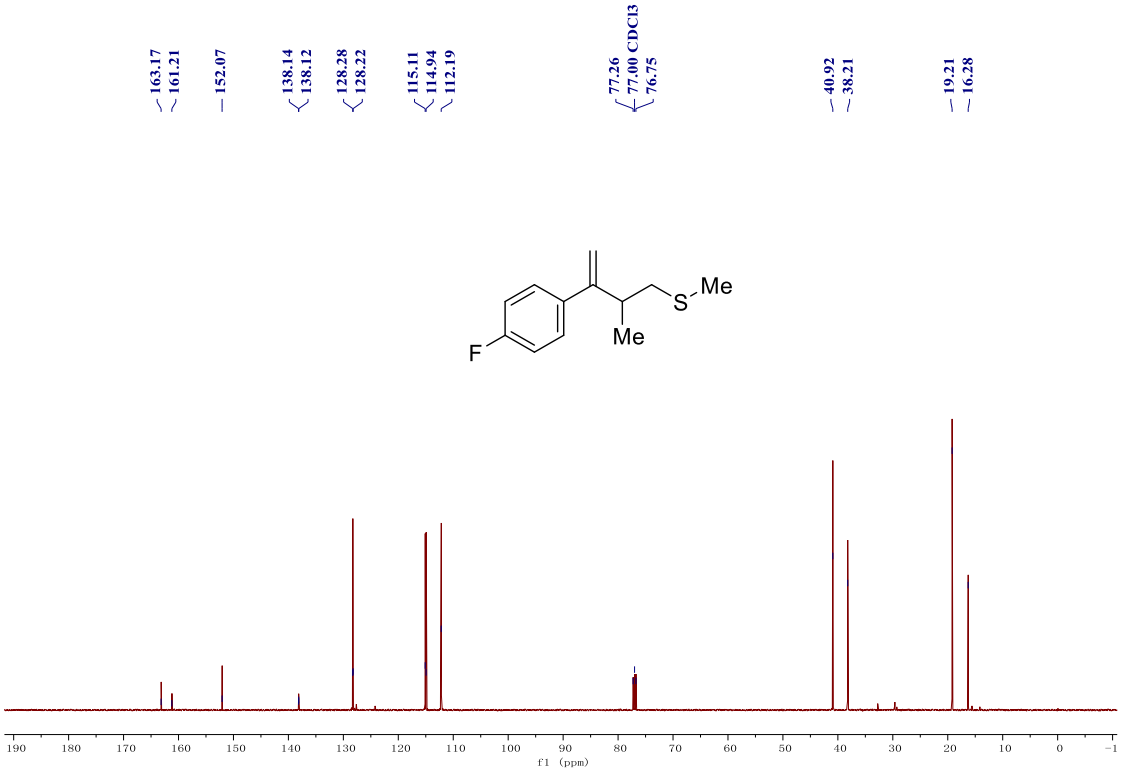
^{13}C NMR Spectra of compound 4l (126 MHz, $CDCl_3$)



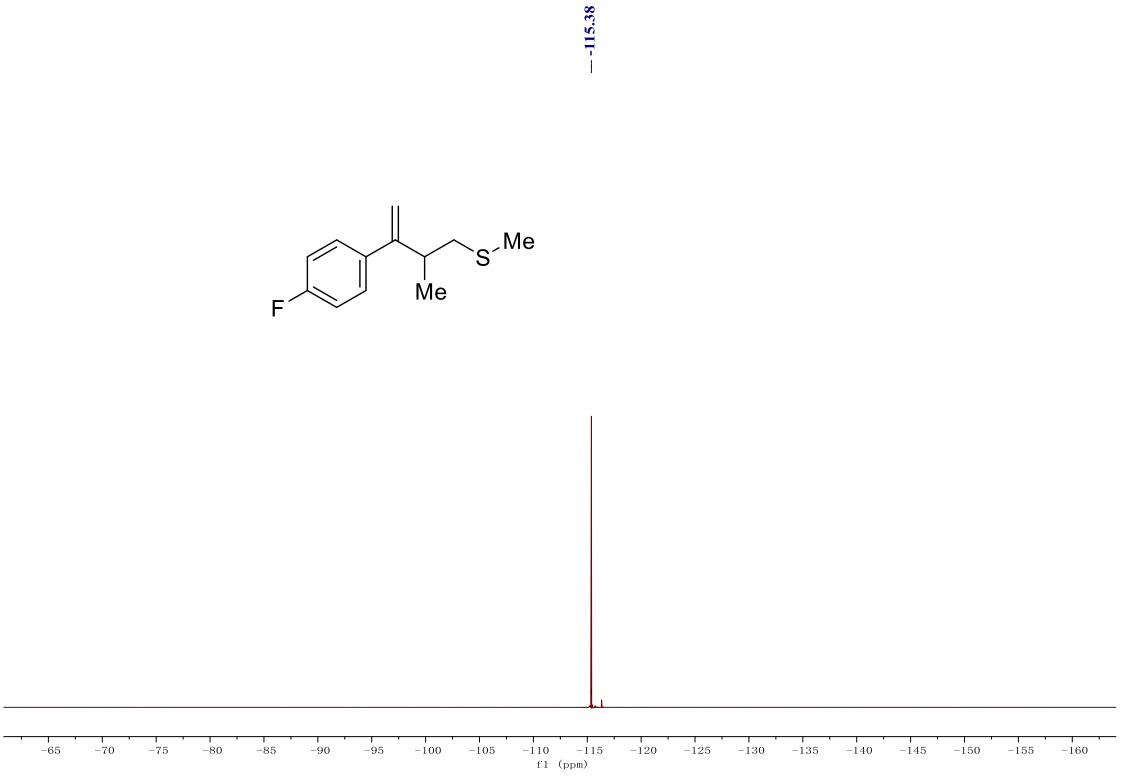
^{1}H NMR Spectra of compound 4m (500 MHz, $CDCl_3$)



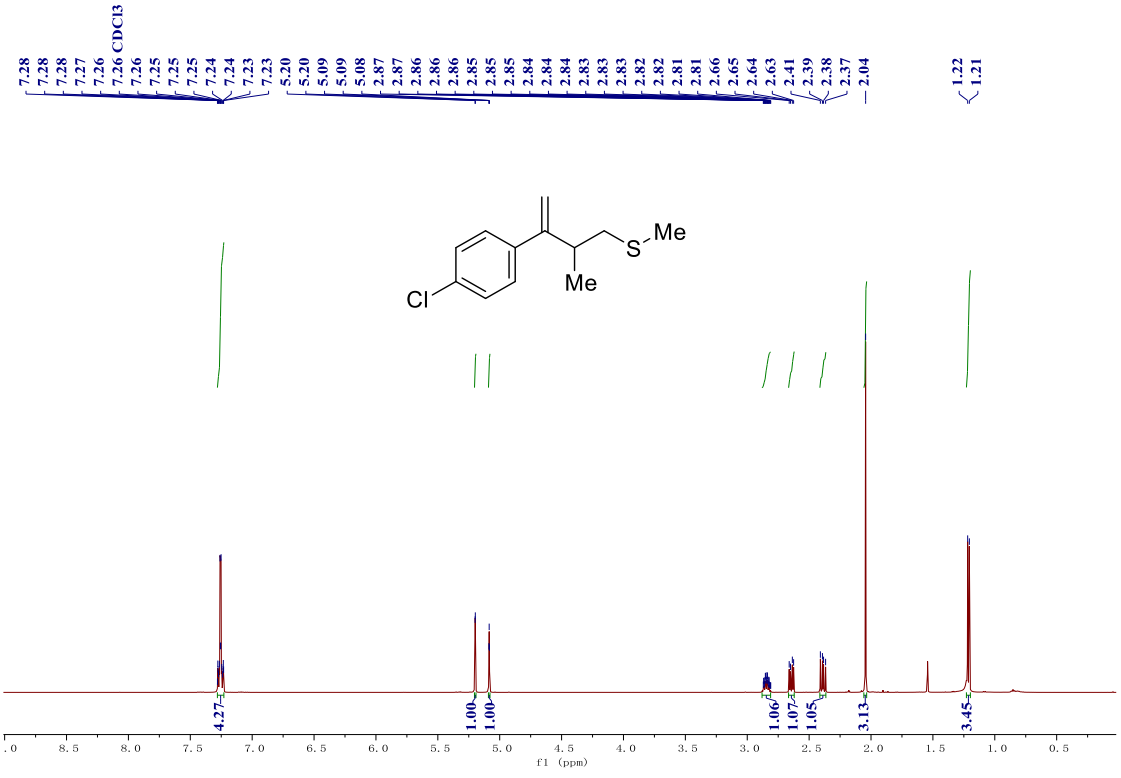
^{13}C NMR Spectra of compound 4m (126 MHz, $CDCl_3$)



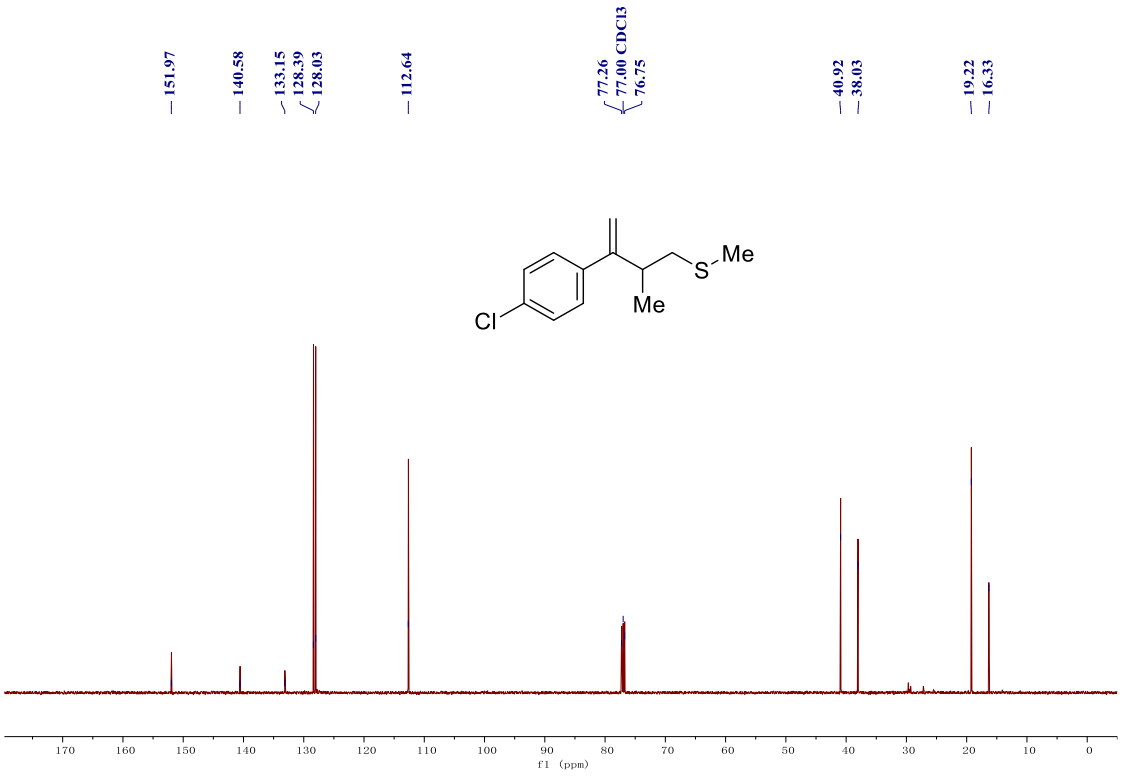
^{19}F NMR Spectra of compound 4m (471 MHz, $CDCl_3$)



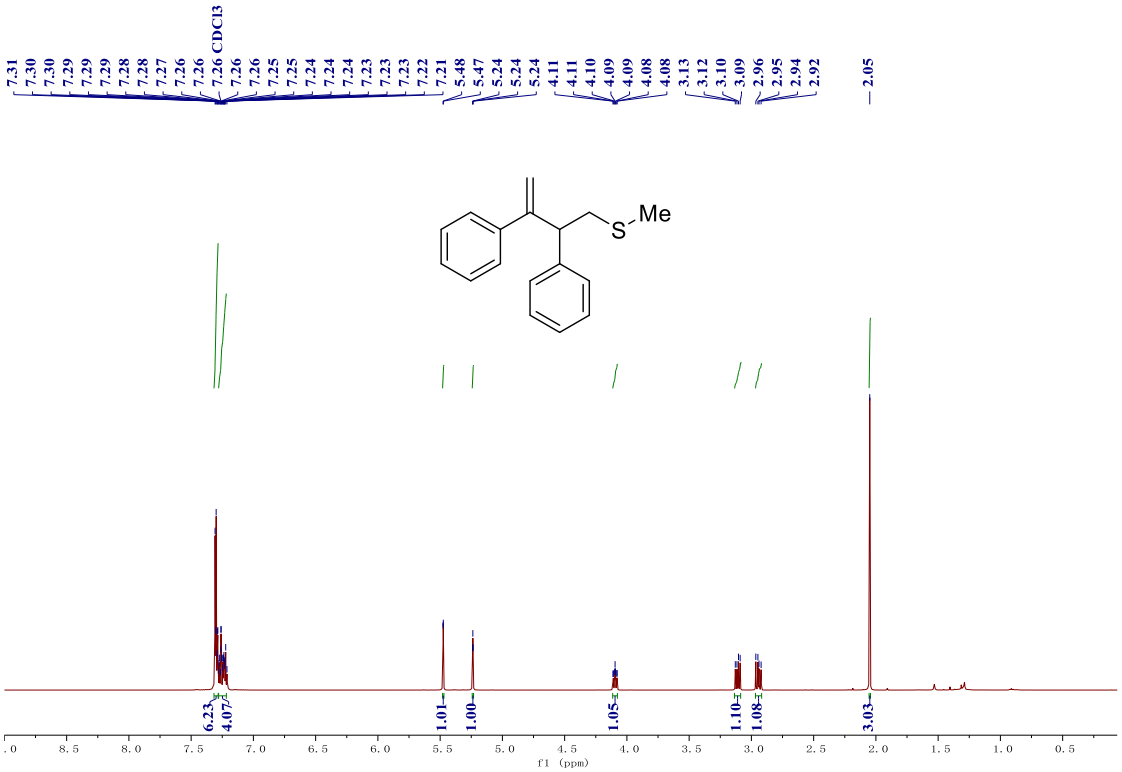
^{1}H NMR Spectra of compound 4n (500 MHz, $CDCl_3$)



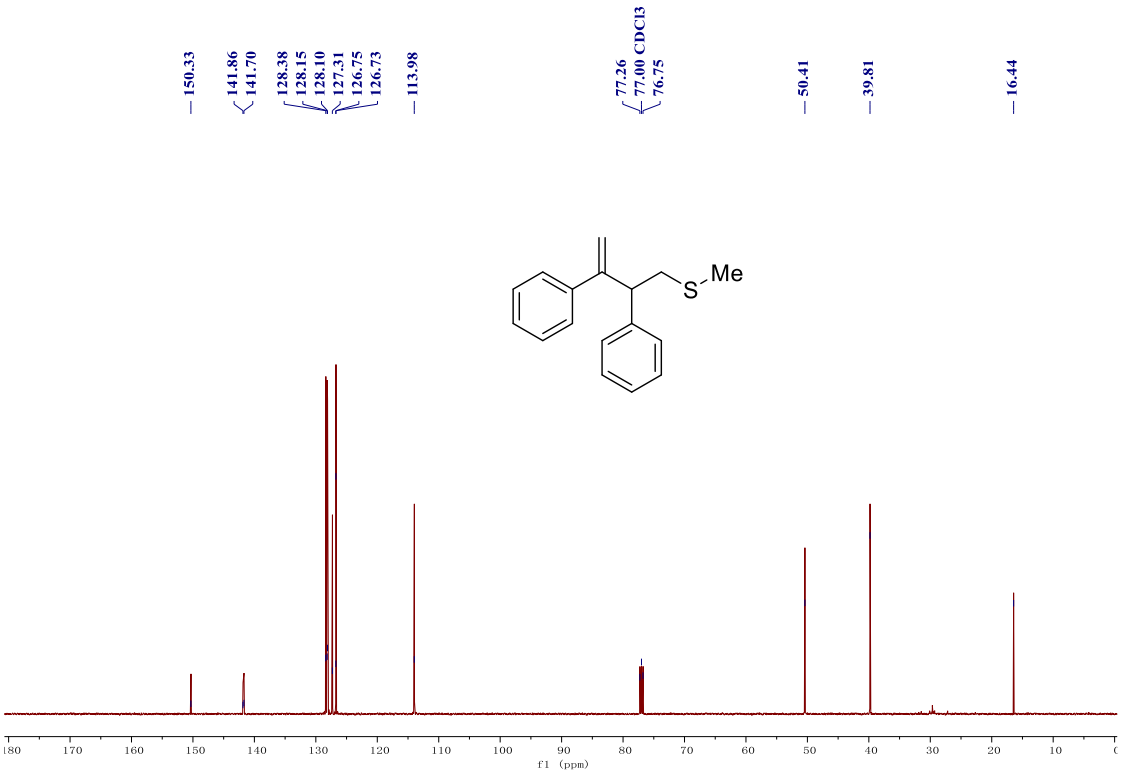
^{13}C NMR Spectra of compound 4n (126 MHz, $CDCl_3$)



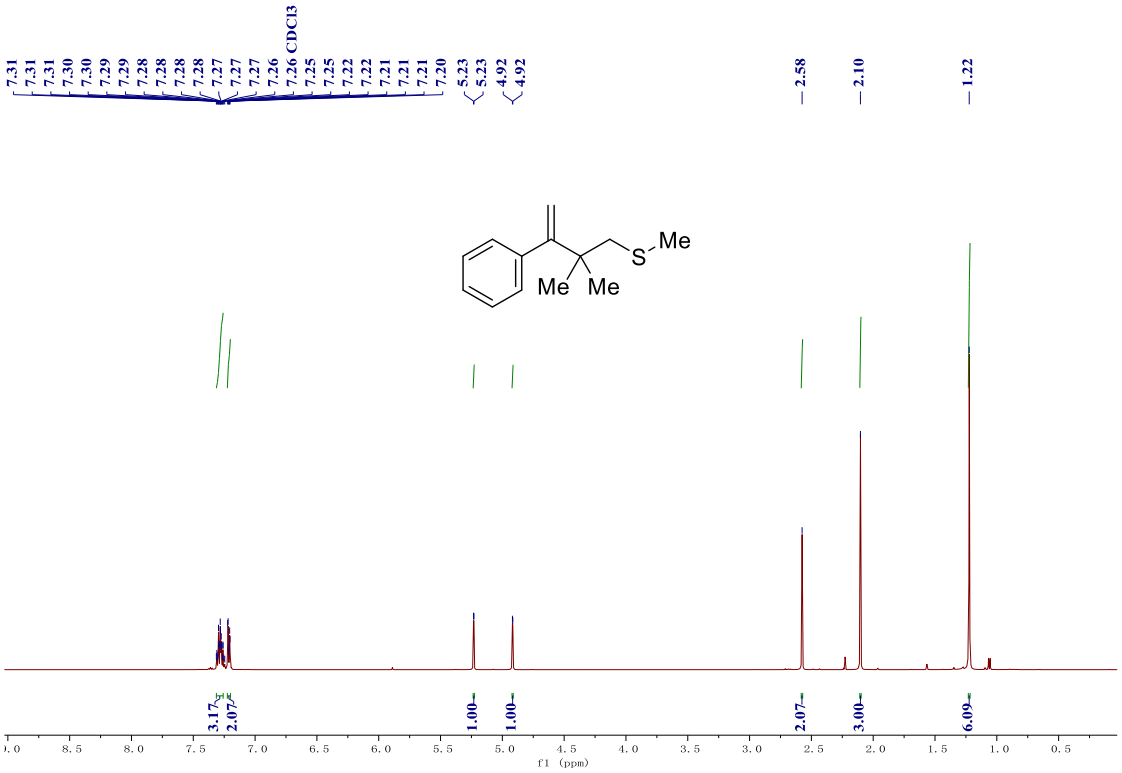
^{1}H NMR Spectra of compound 4o (500 MHz, $CDCl_3$)



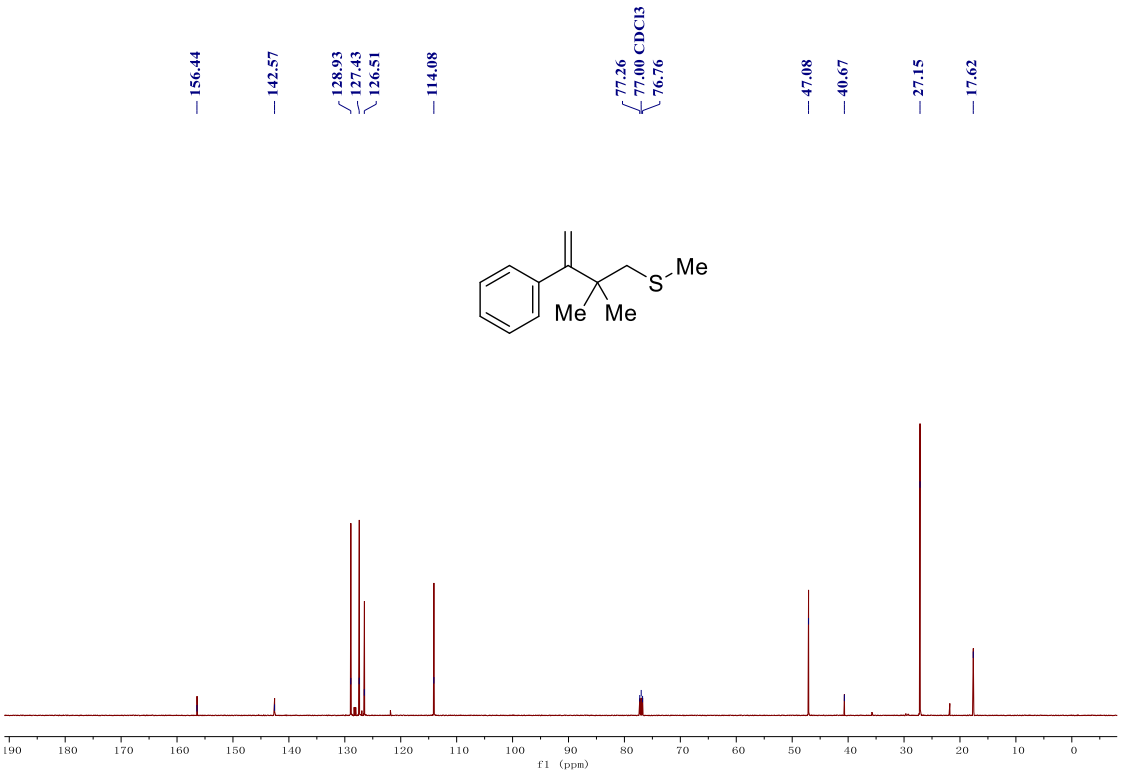
^{13}C NMR Spectra of compound 4o (126 MHz, $CDCl_3$)



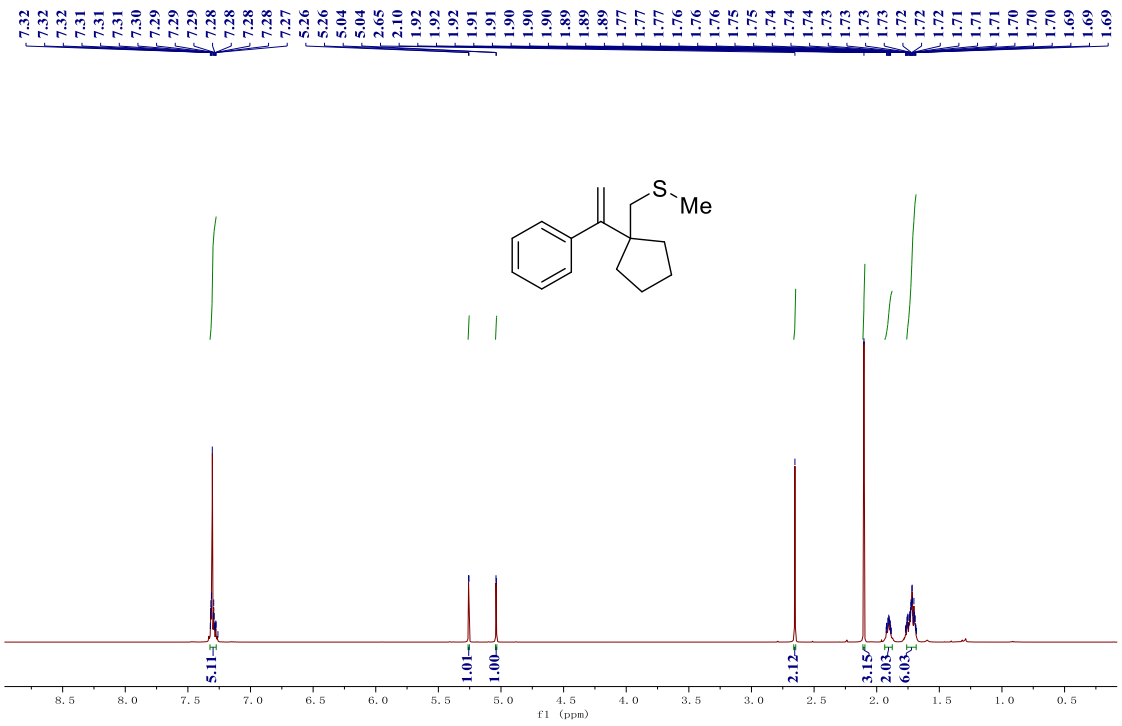
^{1}H NMR Spectra of compound 4p (500 MHz, $CDCl_3$)



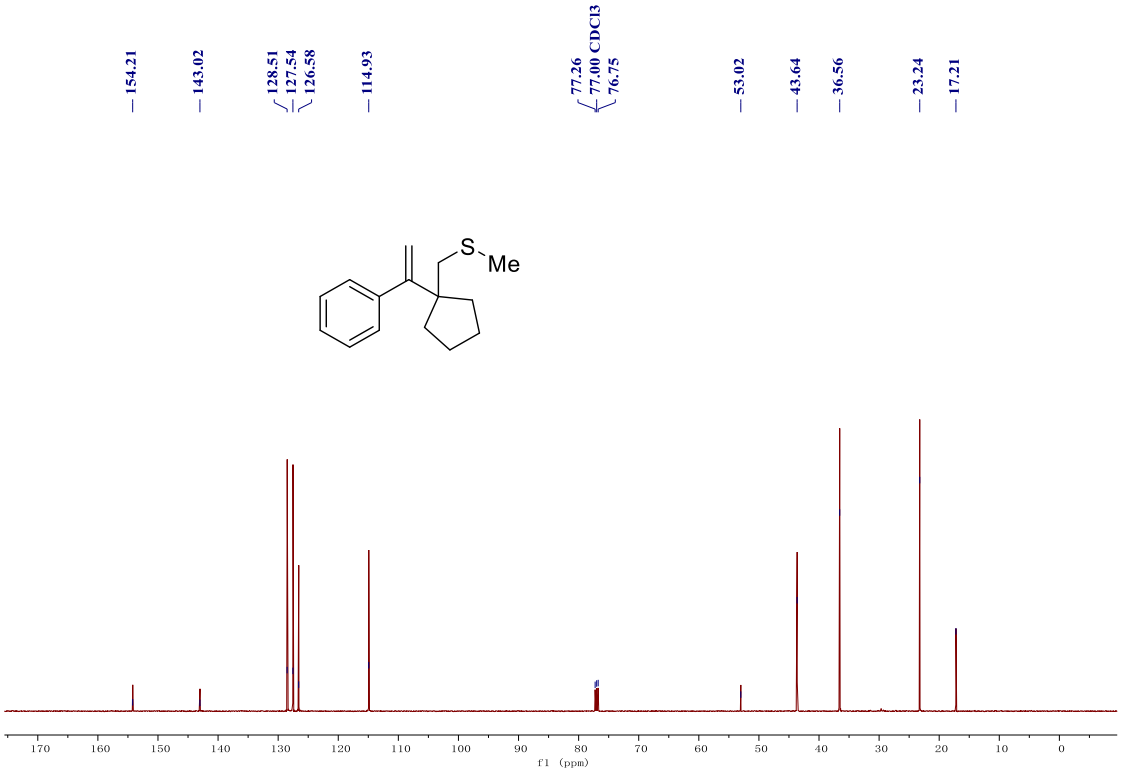
^{13}C NMR Spectra of compound 4p (126 MHz, $CDCl_3$)



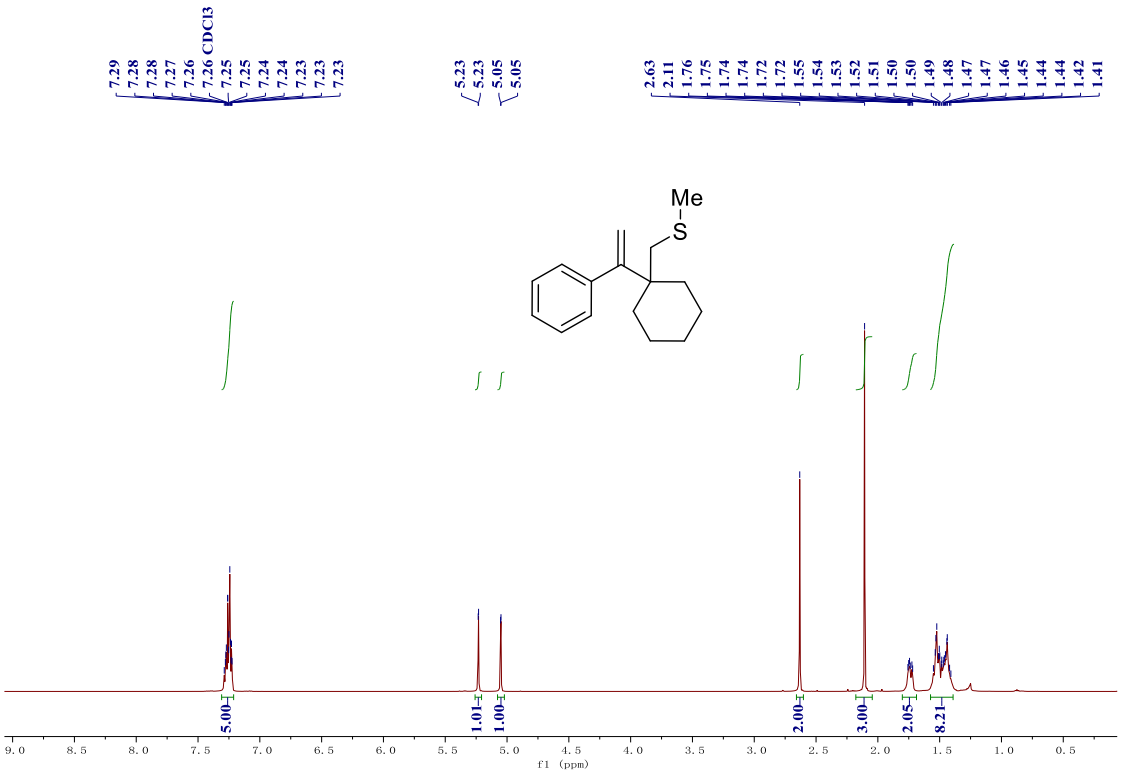
^{1}H NMR Spectra of compound 4q (500 MHz, $CDCl_3$)



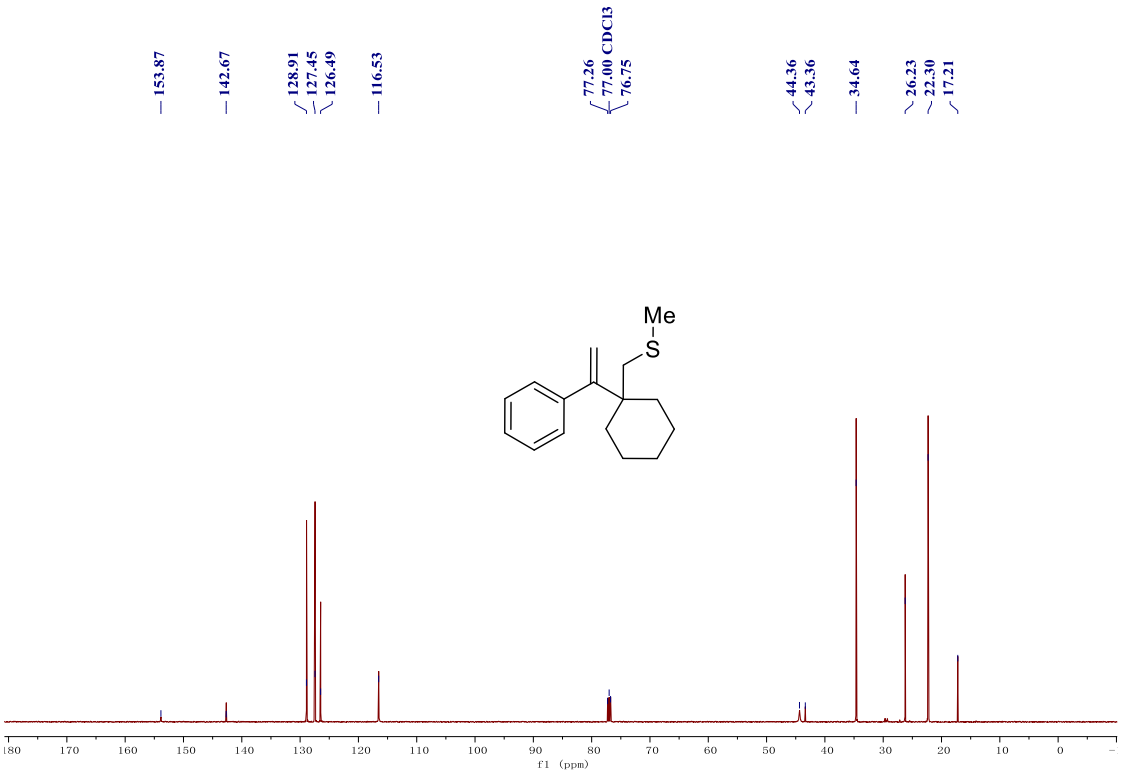
^{13}C NMR Spectra of compound 4q (126 MHz, $CDCl_3$)



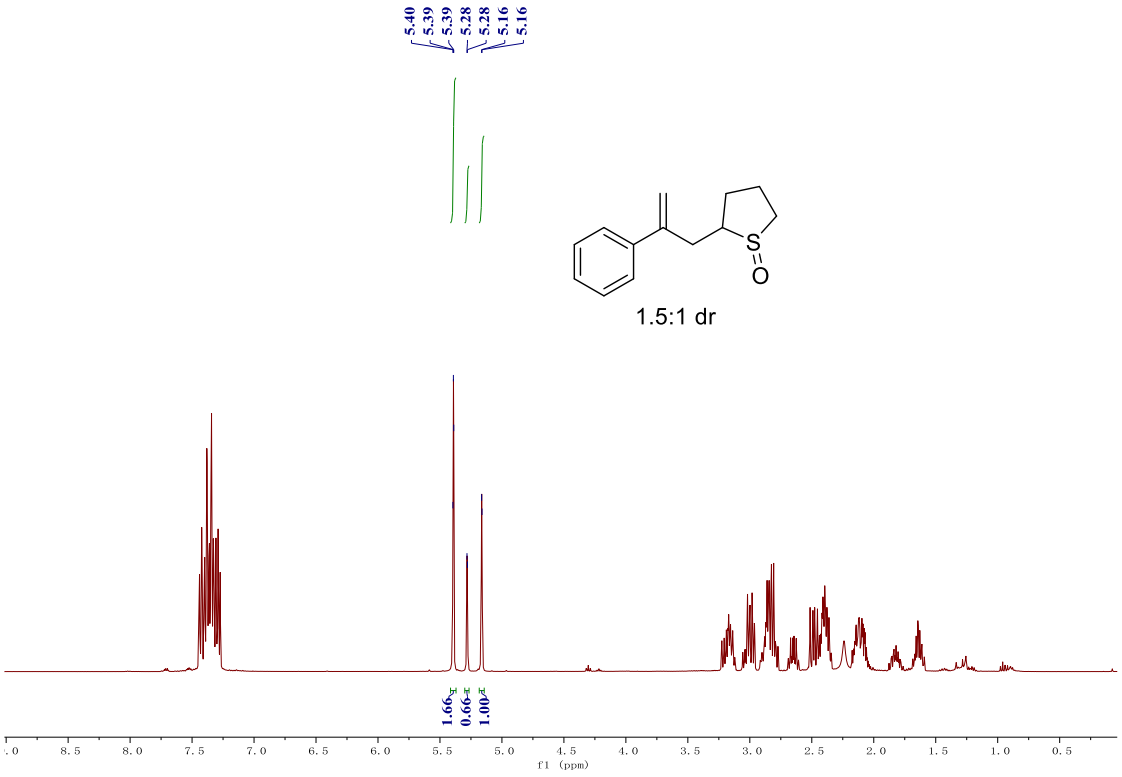
^{1}H NMR Spectra of compound 4r (500 MHz, $CDCl_3$)



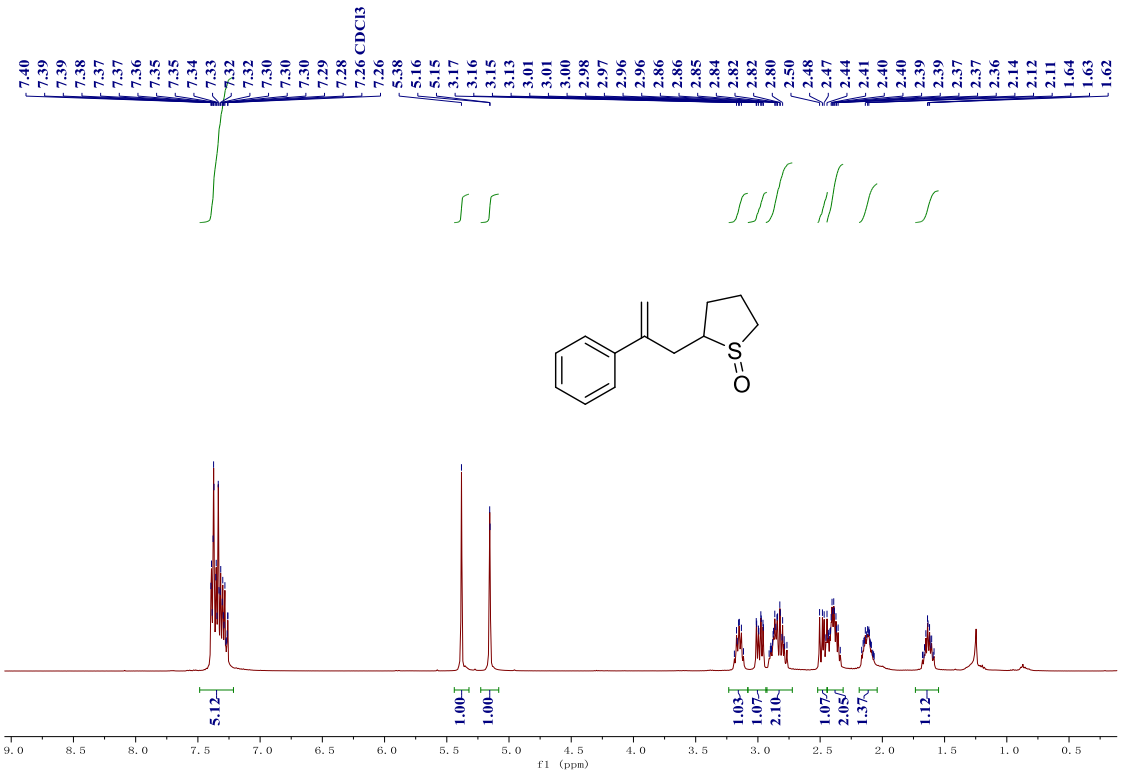
^{13}C NMR Spectra of compound 4r (126 MHz, $CDCl_3$)



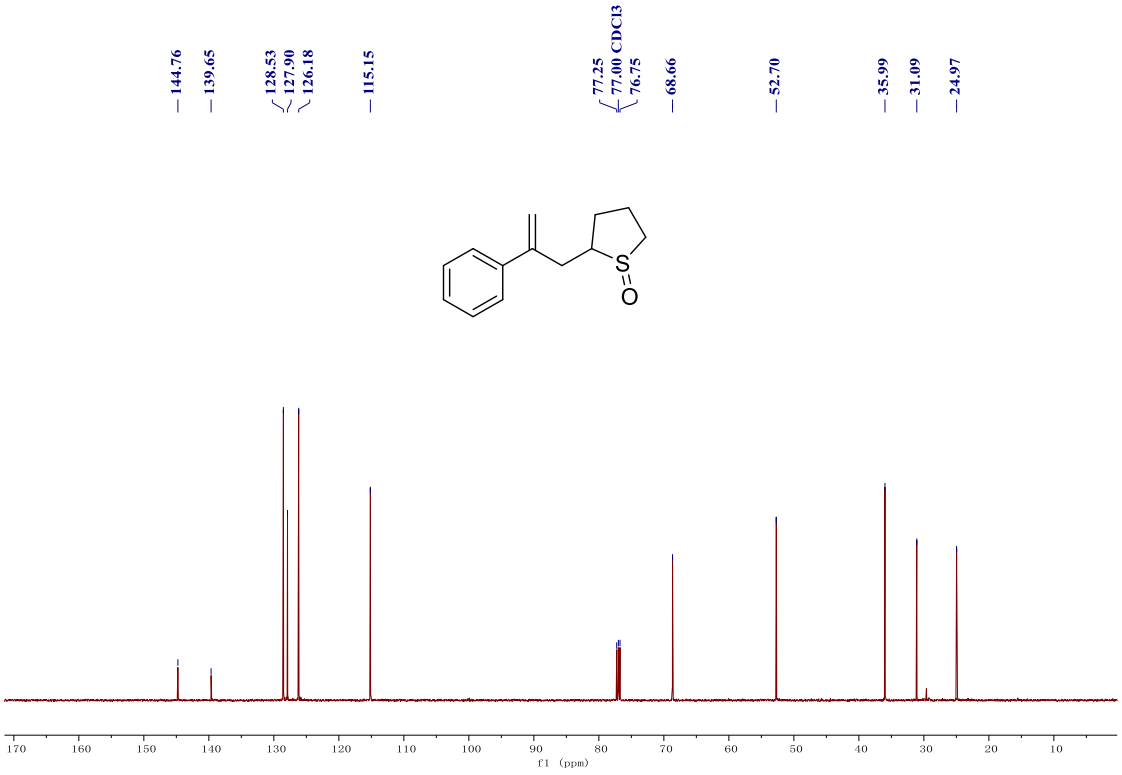
^{1}H NMR Spectra of compound 5 (400 MHz, $CDCl_3$)



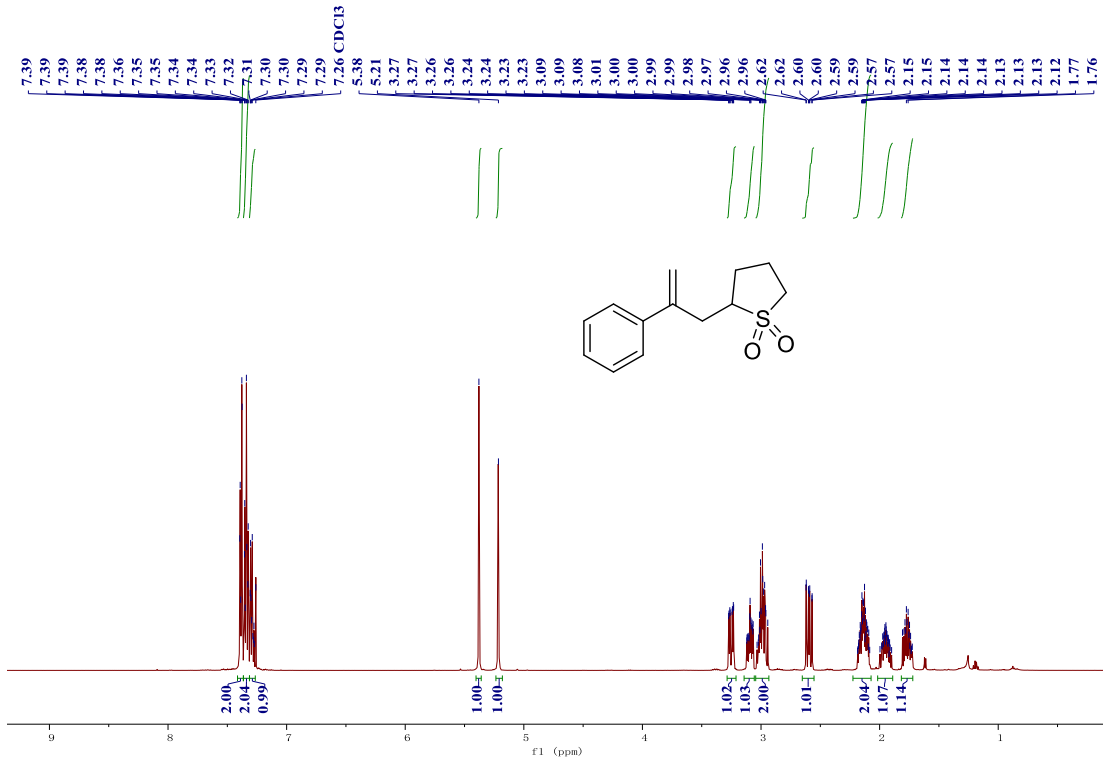
^{1}H NMR Spectra of compound 5 (500 MHz, $CDCl_3$)



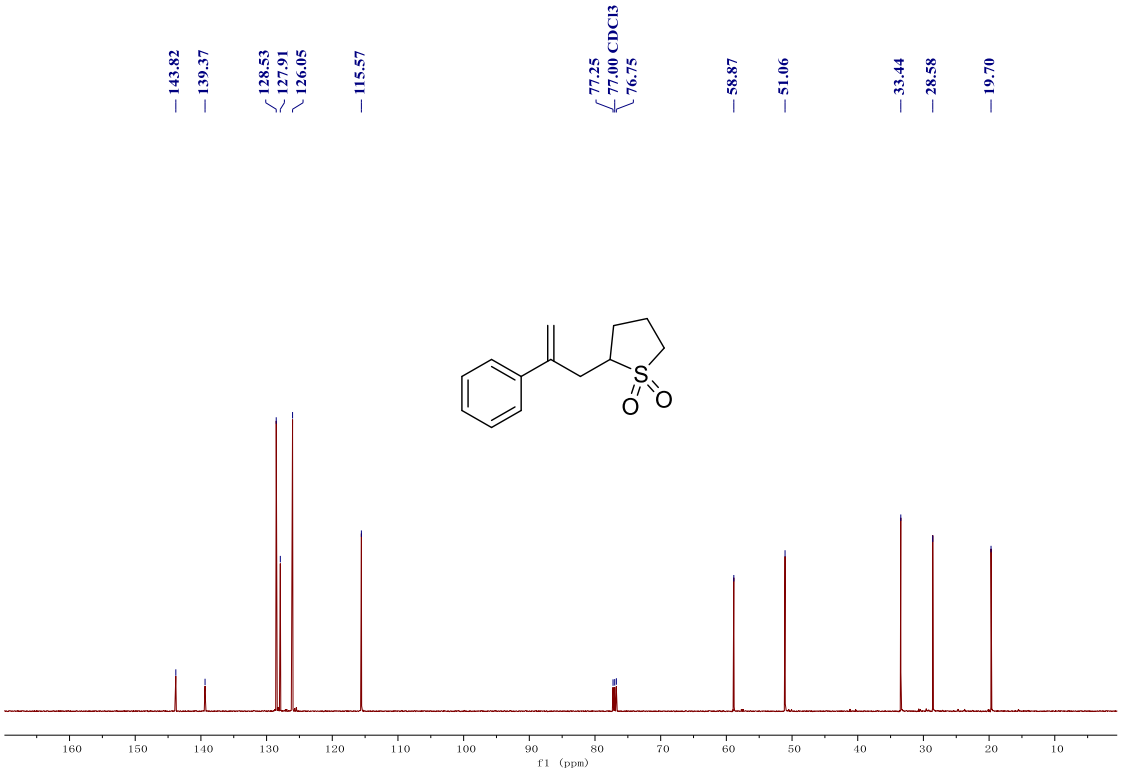
^{13}C NMR Spectra of compound 5 (126 MHz, $CDCl_3$)



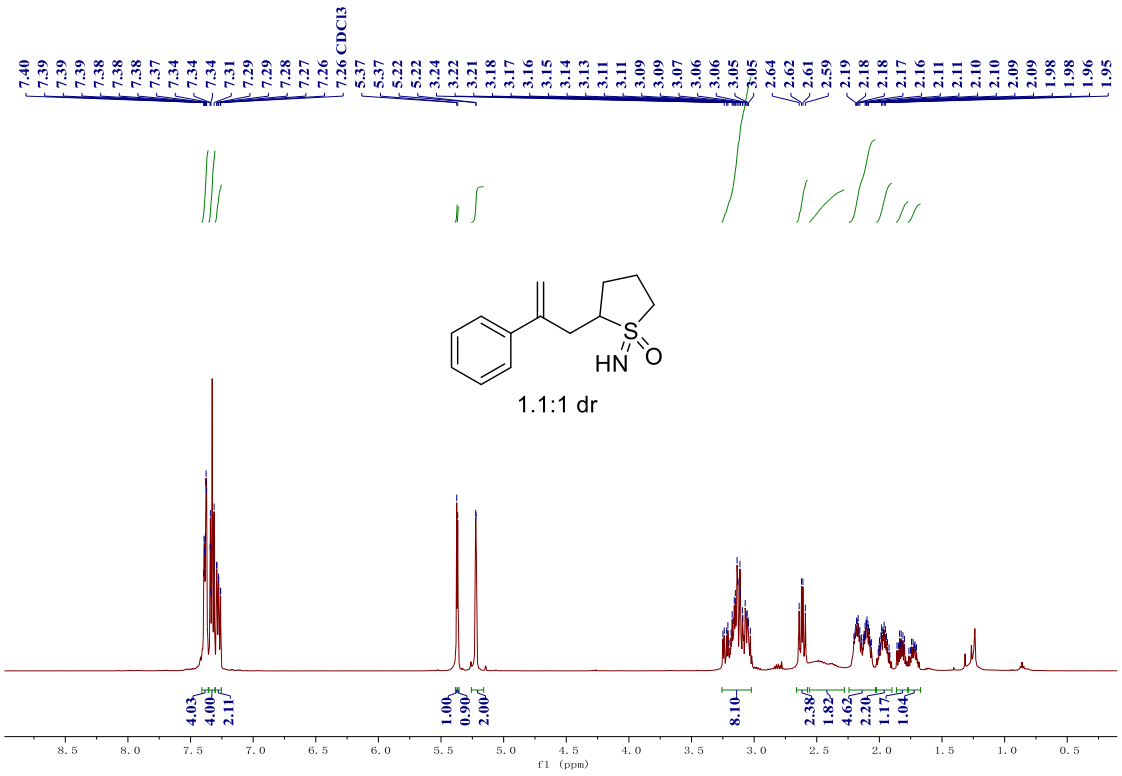
^{1}H NMR Spectra of compound 6 (500 MHz, $CDCl_3$)



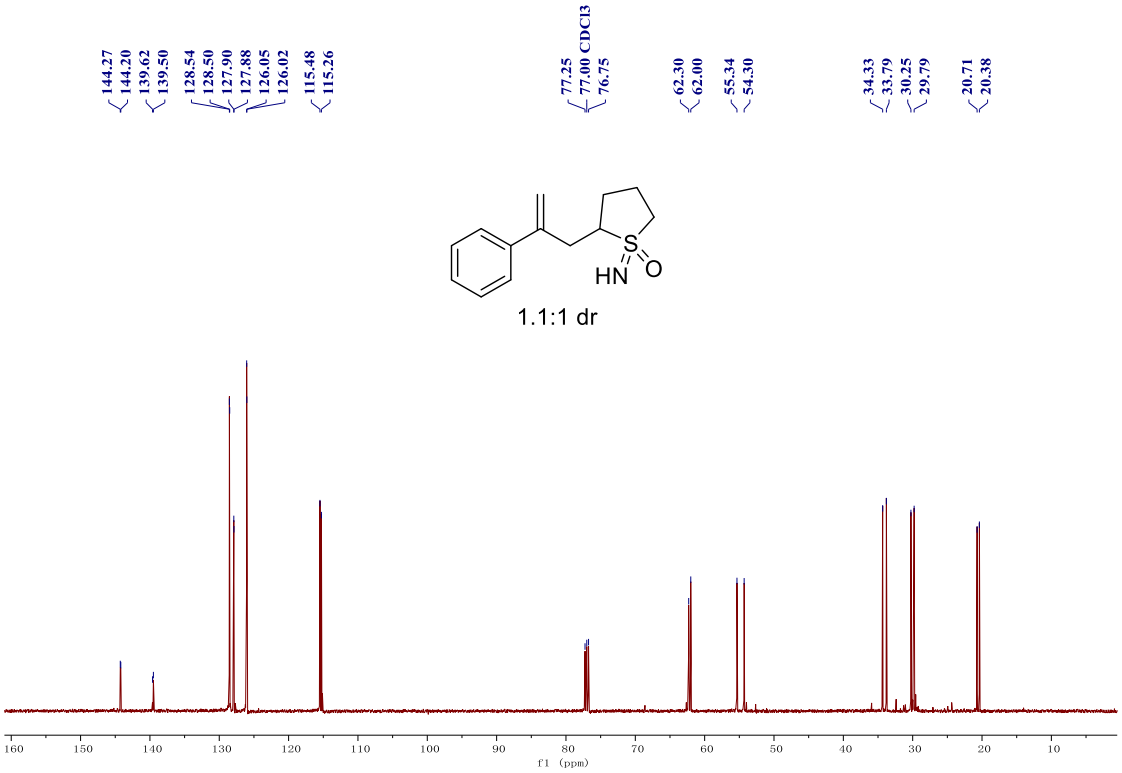
^{13}C NMR Spectra of compound 6 (126 MHz, $CDCl_3$)



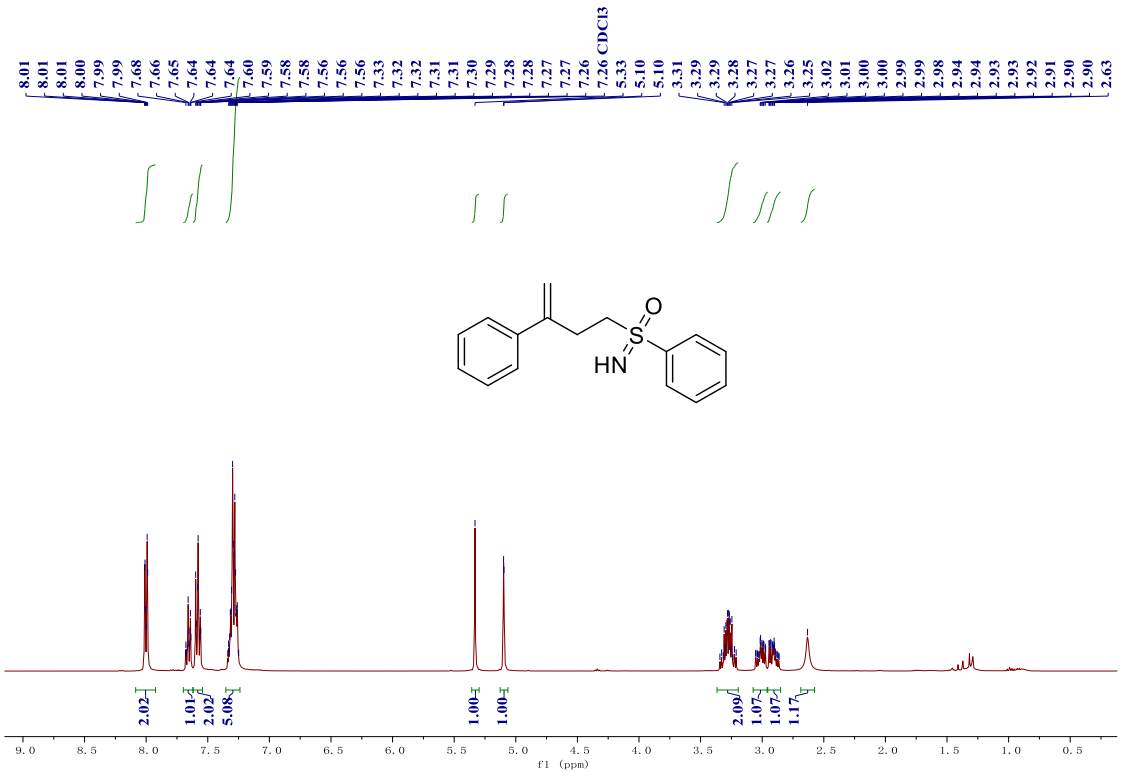
^{1}H NMR Spectra of compound 7 (500 MHz, $CDCl_3$)



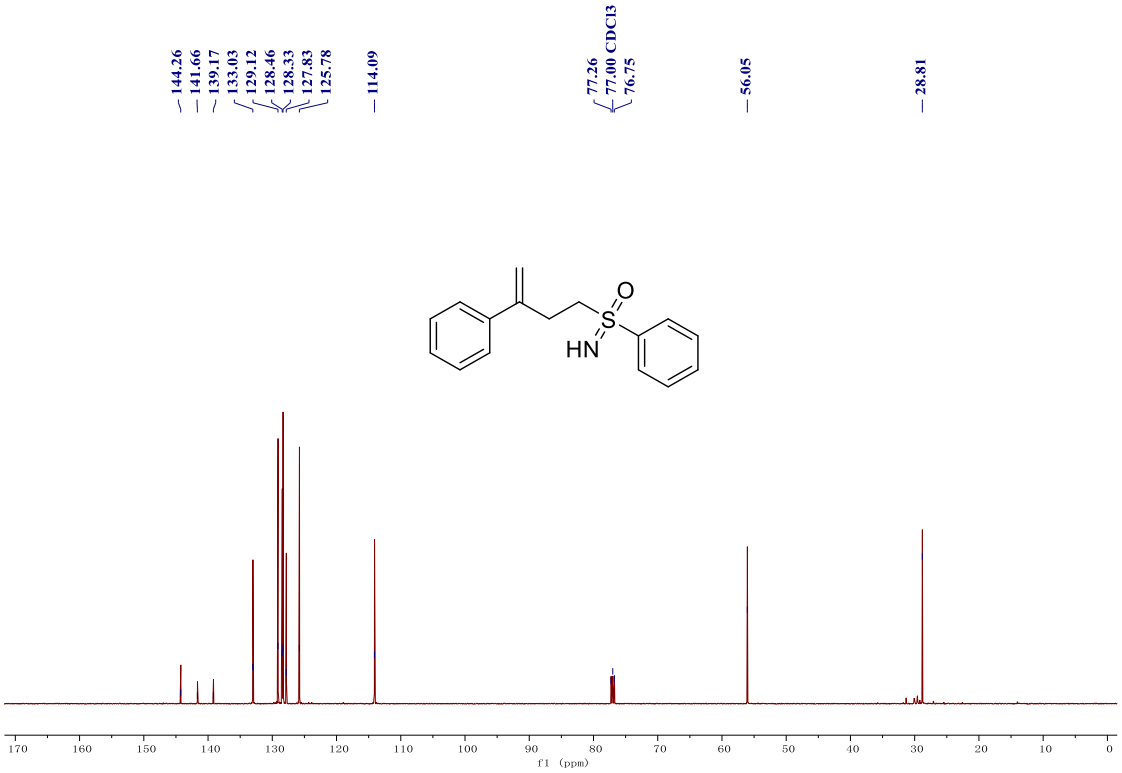
^{13}C NMR Spectra of compound 7 (126 MHz, $CDCl_3$)



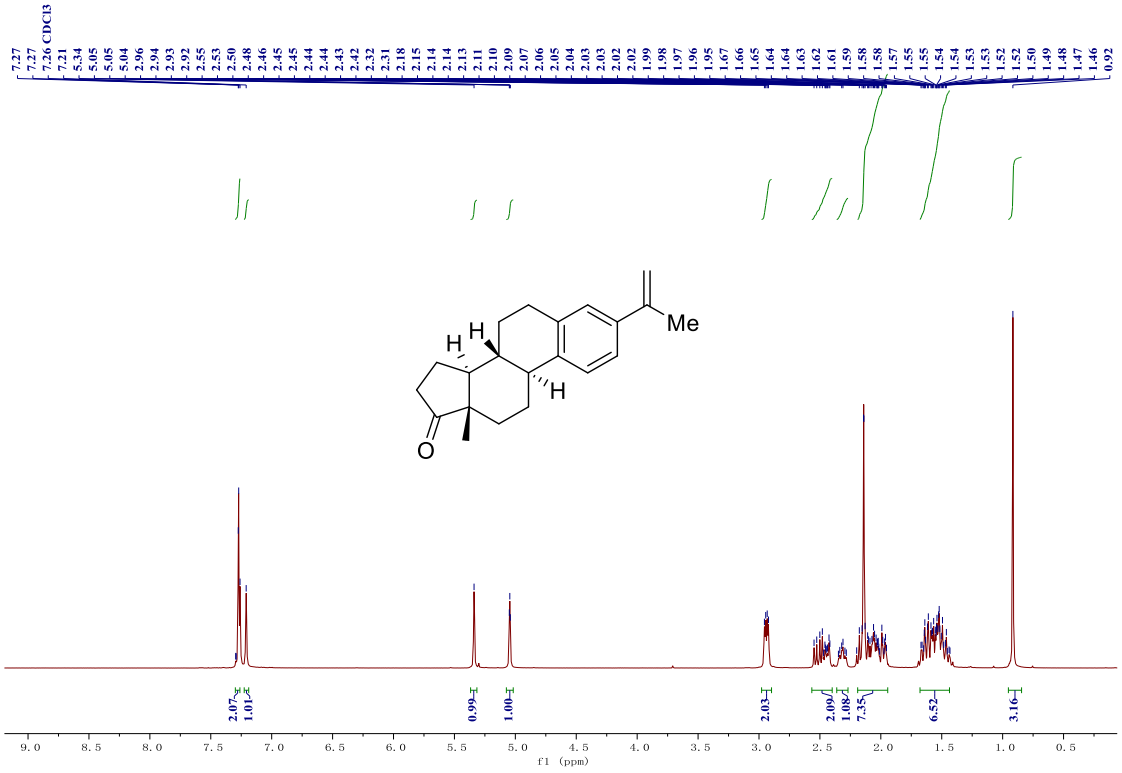
^{1}H NMR Spectra of compound 8 (500 MHz, $CDCl_3$)



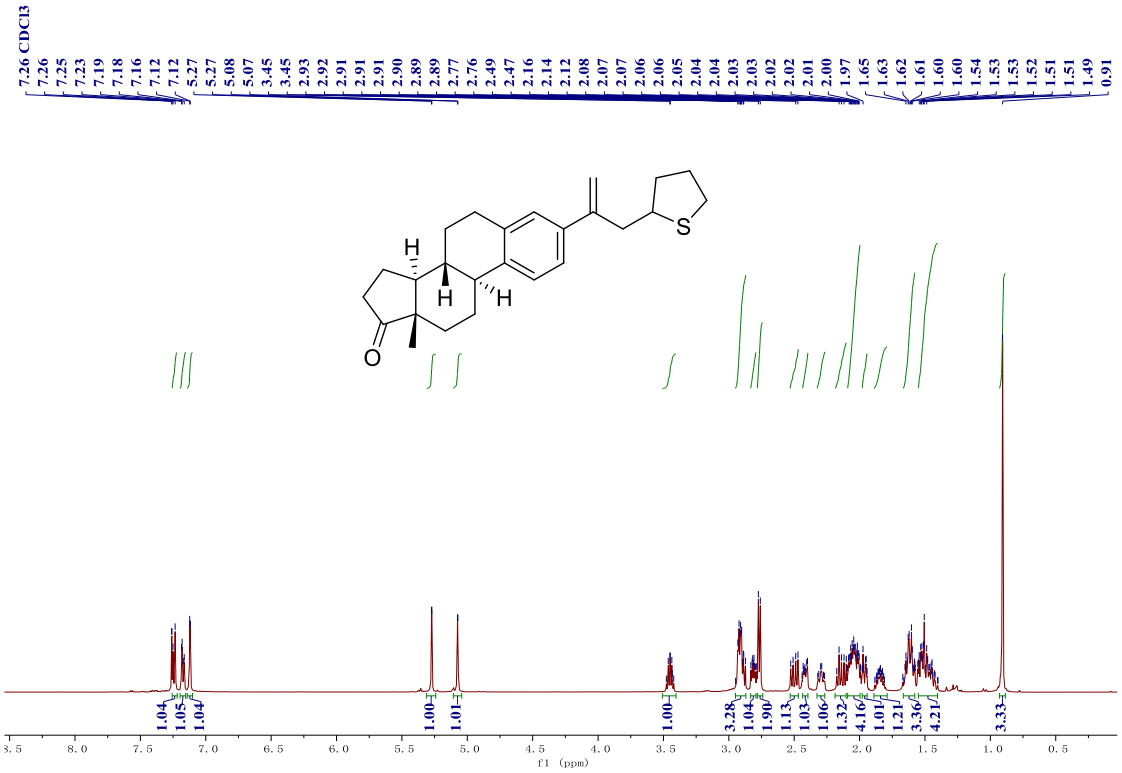
^{13}C NMR Spectra of compound 8 (126 MHz, $CDCl_3$)



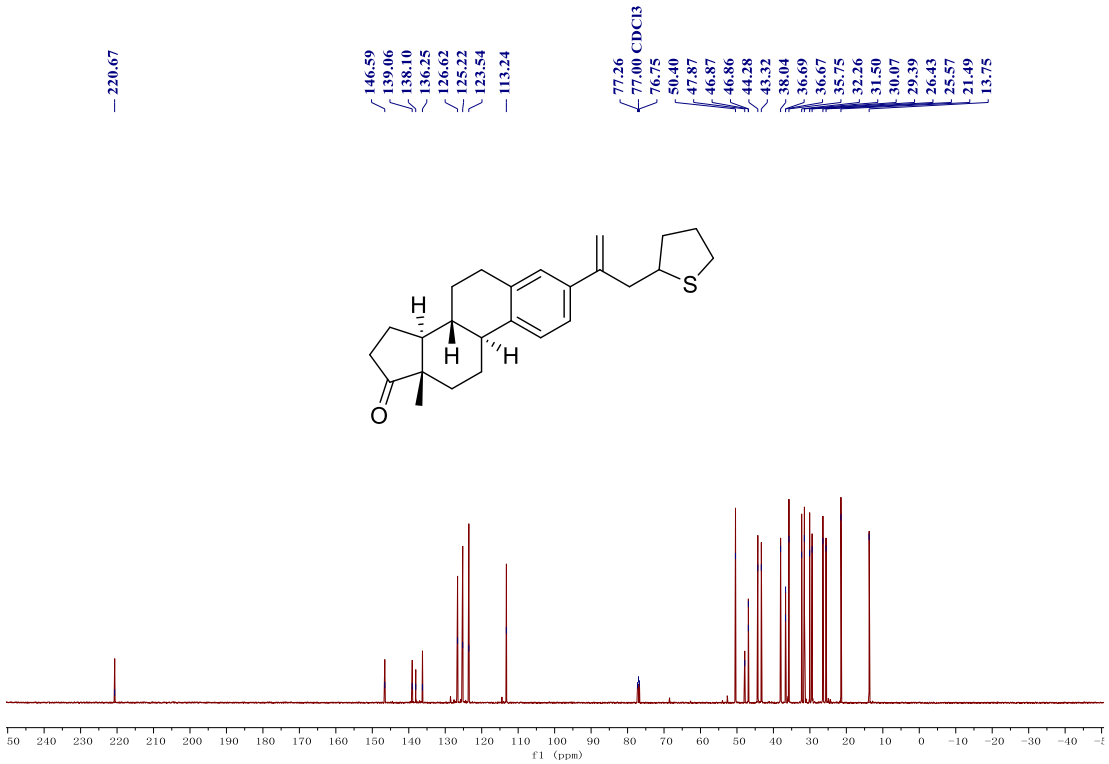
^{1}H NMR Spectra of compound 9 (400 MHz, $CDCl_3$)



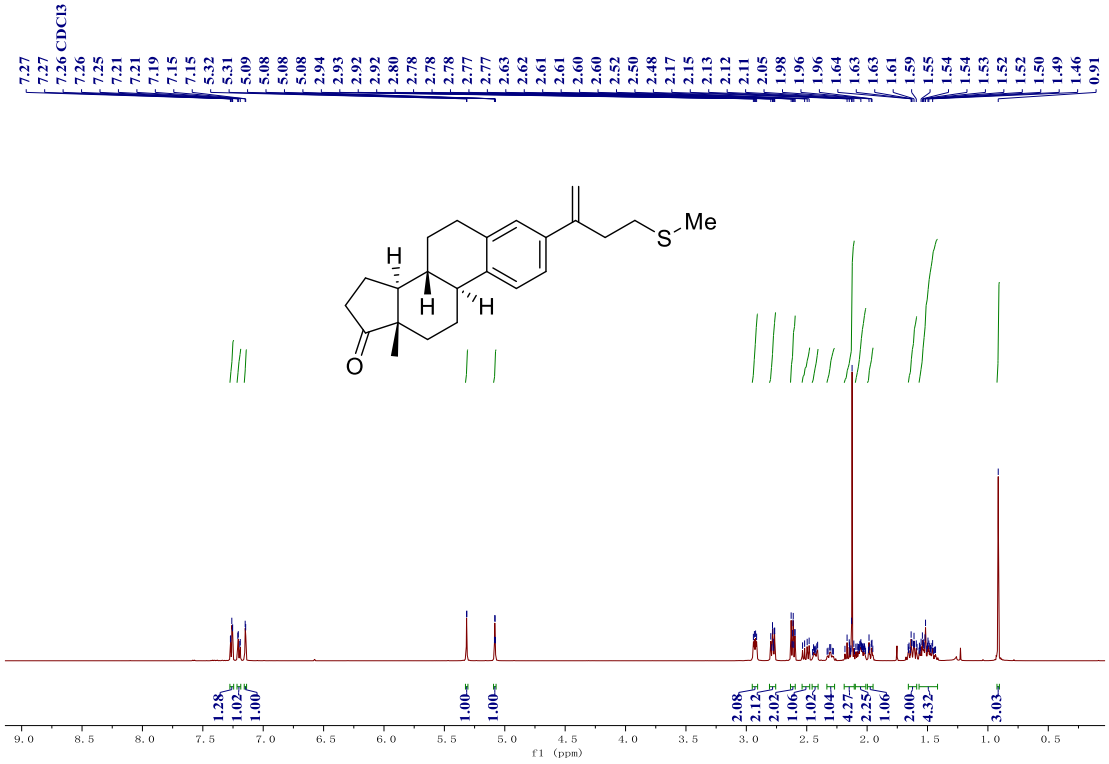
^{1}H NMR Spectra of compound 10 (500 MHz, $CDCl_3$)



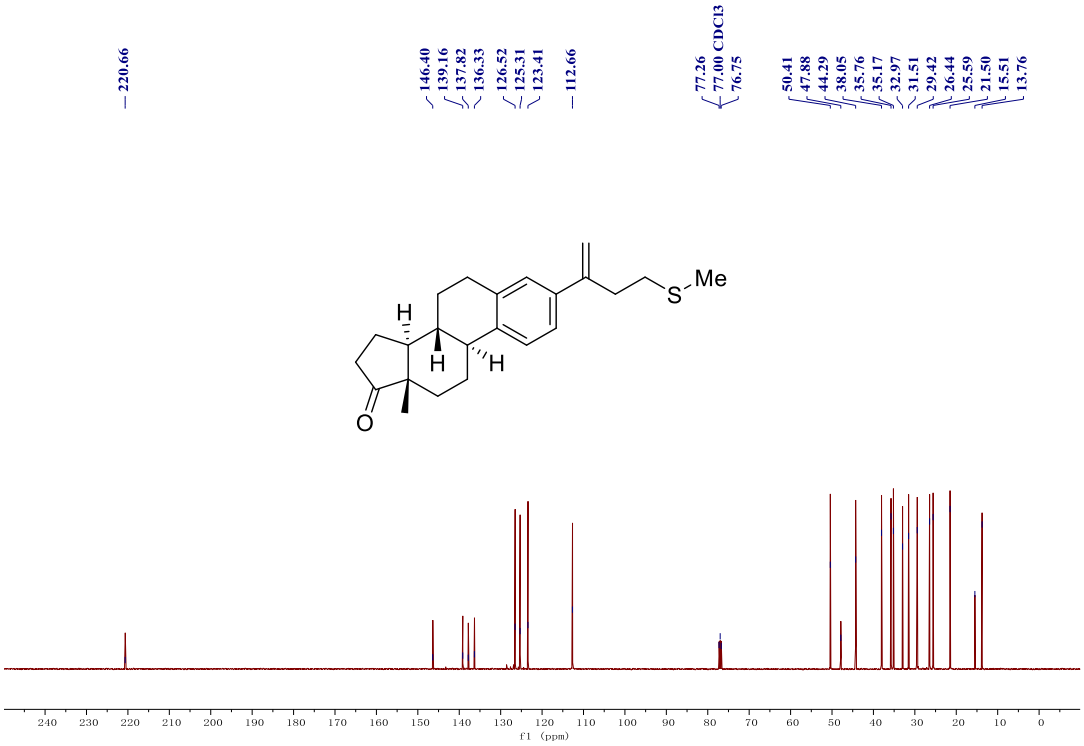
^{13}C NMR Spectra of compound 10 (126 MHz, $CDCl_3$)



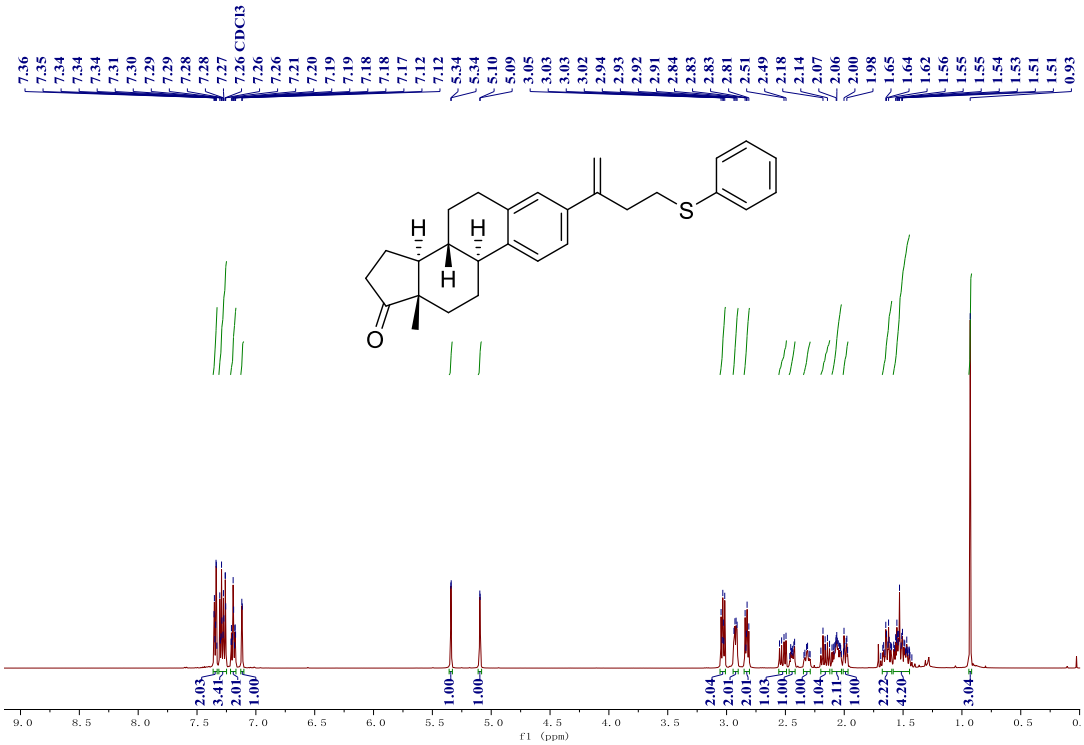
^{1}H NMR Spectra of compound 11 (500 MHz, $CDCl_3$)



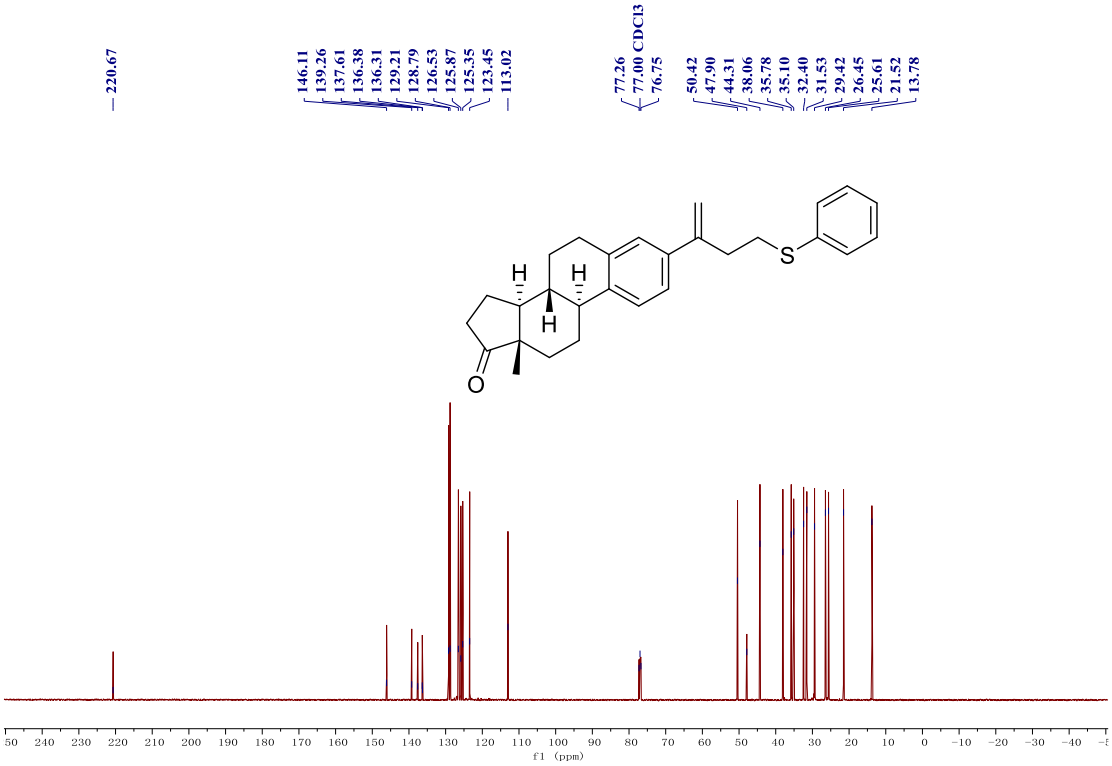
^{13}C NMR Spectra of compound 11 (126 MHz, $CDCl_3$)



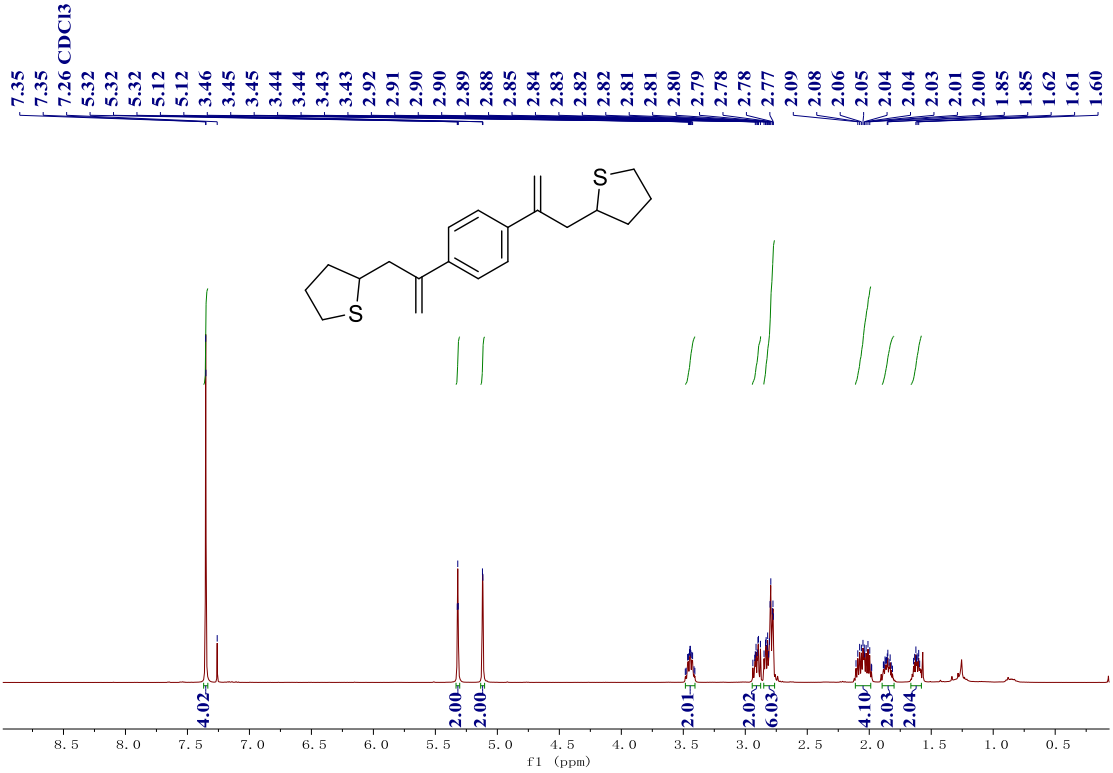
^{1}H NMR Spectra of compound 12 (500 MHz, $CDCl_3$)



^{13}C NMR Spectra of compound 12 (126 MHz, $CDCl_3$)



^{1}H NMR Spectra of compound 14 (400 MHz, $CDCl_3$)



^{13}C NMR Spectra of compound 14 (101 MHz, $CDCl_3$)