

Supporting Information for

N-heterocyclic carbene-catalyzed Stereoselective Construction of Olefinic Carbon-Sulfur Bonds via Cross-Coupling Reaction of *gem*-difluoroalkenes and Thiols

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Experimental Section

All reactions were conducted under nitrogen atmosphere in oven-dried glassware with magnetic stirring bar. ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3) and ^{19}F NMR (376 MHz, CDCl_3) spectra were recorded using deuterated chloroform as solvent, with tetramethylsilane as an internal standard and reported in ppm (δ). *Gem*-difluoroalkenes were synthesized according to literature procedure.¹⁹ Thiols and other chemicals were obtained from Adamas-beta and used without purification. Anhydrous THF and toluene were distilled from sodium and benzophenone. DMF, CH_2Cl_2 and CH_3CN were distilled from calcium hydride.

General procedure for NHCs-catalyzed nucleophilic substitution reaction of *gem*-difluoroalkenes and thiols: IPr **A** (7.8 mg, 10 mol%) was dissolved in 2.0 mL dry CH_3CN with molecular sieve (0.2 g). *Gem*-difluoroalkenes **1a** (0.2 mmol, 44 mg) and ethanethiol **2a** (0.3 mmol, 21 μL) were added via a syringe under N_2 . The reaction mixture was stirred at room temperature until full consume of the starting *gem*-difluoroalkene indicated by TLC. Then, the mixture was washed with EtOAc (5.0 mL $\times$ 3) and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (PE) to give the desired product **3a** as an inseparable 11:1 *Z/E* mixture.

Procedure for deuterium labeling experiment: IPr **A** (7.8 mg, 10 mol%) was dissolved in 2.0 mL dry CH_3CN with 4Å MS (0.2 g). *Gem*-difluoroalkenes **1a** (0.3 mmol, 66 mg) and deuterium labeled thiophenol **2I'** (0.2 mmol, 22 mg) were added via a syringe under N_2 . The reaction mixture was stirred at room temperature for 15 h

until full consume of the starting deuterium labeled thiophenol indicated by TLC. Then the mixture was washed with EtOAc (5.0 mL×3) and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (PE) to give the product.

(Z/E)-(2-(4-Bromophenyl)-1-fluorovinyl)(ethyl) sulfane (3a): colorless oil; yield 45.4 mg (87%) as an inseparable 11:1 Z/E mixture; R_f (petroleum ether) 0.65; Data for Z-**3a**: ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.5$ Hz, 2H), 7.38 (d, $J = 8.6$ Hz, 2H), 6.51 (d, $J = 18.0$ Hz, 1H), 2.91 (q, $J = 7.4$ Hz, 2H), 1.36 (t, $J = 7.4$ Hz, 3H). Selected data for E-**3a**: ^1H NMR (400 MHz, CDCl_3) δ 6.02 (d, $J = 33.4$, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.2 (d, $J = 295.4$ Hz), 131.9 (d, $J = 10.4$ Hz), 131.4, 130.2 (d, $J = 3.2$ Hz), 121.0 (d, $J = 1.9$ Hz), 114.2, 113.9, 26.1 (d, $J = 2.9$ Hz), 15.14; Data for Z-**3a**: ^{19}F NMR (376 MHz, CDCl_3) δ -82.46 (s, 1F). Data for E-**3a**: ^{19}F NMR (376 MHz, CDCl_3) δ -85.17 (s, 1F); FTIR (film) 2966, 2928, 1627, 1487, 1398, 1262, 1071, 1050, 1008, 866, 810, 691 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{11}\text{BrFS}^+$ ($\text{M}+\text{H}$) $^+$ 260.9743, found 260.9741.

(Z/E)-(2-(4-Bromophenyl)-1-fluorovinyl)(propyl) sulfane (3b): colorless oil; yield 50.1mg (91%) as an inseparable 8:1 Z/E mixture; R_f (petroleum ether) 0.71; Data for Z-**3b**: ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 6.48 (d, $J = 18.0$ Hz, 1H), 2.86 (t, $J = 7.3$ Hz, 2H), 1.72 (q, $J = 145.71$ Hz, 2H), 1.01 (t, $J = 7.4$ Hz, 3H). Selected data for E-**3b**: ^1H NMR (400 MHz, CDCl_3) δ 6.00 (d, $J = 33.5$ Hz, 1H); Data for Z-**3b**: ^{13}C NMR (100 MHz, CDCl_3) δ 155.4 (d, $J = 295.5$ Hz), 131.8 (q, $J = 20.0$ Hz), 131.4, 130.2 (d, $J = 3.3$ Hz), 121.0 (d, $J = 1.9$ Hz), 113.7 (d, $J = 32.8$ Hz), 33.7 (d, $J = 2.6$ Hz), 23.3 (d, $J = 1.1$ Hz), 13.2. Selected data for E-**3b**: ^{13}C NMR (100 MHz, CDCl_3) δ 49.8, 41.2, 31.2; Data for Z-**3b**: ^{19}F NMR (376

MHz, CDCl₃) δ -82.27 (s, 1F). Data for *E*-**3b**: ¹⁹F NMR (376 MHz, CDCl₃) δ -85.20 (s, 1F); FTIR (film) 2966, 1686, 1629, 1488, 1073, 1010, 905, 868, 728, 649 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₁H₁₃BrFS⁺(M+H)⁺ 274.9900, found 274.9907.

(Z/E)-(2-(4-Bromophenyl)-1-fluorovinyl)(butyl) sulfane (3c): colorless oil; yield 56.7 mg (96%) as an inseparable 8:1 *Z/E* mixture; *R_f* (petroleum ether) 0.71; Data for *Z*-**3c**: ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.45 (m, 2H), 7.41-7.36 (m, 2H), 6.48 (d, *J* = 18.0 Hz, 1H), 2.88 (t, *J* = 7.4 Hz, 2H), 1.72 - 1.63 (m, 2H), 1.48 - 1.42 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). Selected data for *E*-**3c**: ¹H NMR (400 MHz, CDCl₃) δ 6.00 (d, *J* = 3.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 155.4 (d, *J* = 295.3 Hz), 131.9 (d, *J* = 10.5 Hz), 131.4, 130.2 (d, *J* = 3.3 Hz), 121.0 (d, *J* = 1.9 Hz), 113.7 (d, *J* = 32.8 Hz), 38.9, 31.6 (d, *J* = 52.1 Hz), 21.7, 13.5; Data for *Z*-**3c**: ¹⁹F NMR (376 MHz, CDCl₃) δ -82.25 (s, 1F). Data for *E*-**3c**: ¹⁹F NMR (376 MHz, CDCl₃) δ -85.20 (s, 1F); FTIR (film) 2957, 2929, 2871, 1687, 1628, 1487, 1071, 1009, 867, 799, 734, 688, 622 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₂H₁₅BrFS⁺(M+H)⁺ 289.0056, found 289.0063.

(Z/E)-(2-(4-Bromophenyl)-1-fluorovinyl)(octadecyl) sulfane (3d): white solid; mp 42.4-47.0 °C; yield 82.6 mg (85%) as an inseparable 11:1 *Z/E* mixture; *R_f* (petroleum ether) 0.75; Data for *Z*-**3d**: ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.45 (m, 2H), 7.40 – 7.36 (m, 2H), 6.48 (d, *J* = 18.0 Hz, 1H), 2.87 (t, *J* = 7.3 Hz, 2H), 1.74-1.62 (m, 2H), 1.28 - 1.26 (m, 30H), 0.90 (t, *J* =

6.6 Hz, 3H). Selected data for *E*-**3d**: ^1H NMR (400 MHz, CDCl_3) δ 5.99 (d, J = 33.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4 (d, J = 295.5 Hz), 131.9 (d, J = 10.4 Hz), 131.4, 130.2 (d, J = 3.3 Hz), 121.0 (d, J = 1.8 Hz), 113.7 (d, J = 32.7 Hz), 32.0, 31.8 (d, J = 2.5 Hz), 31.7, 29.8 (d, J = 1.1 Hz), 29.8–29.7 (m), 29.6 (d, J = 8.7 Hz), 29.5, 29.4, 29.1, 28.5, 22.7, 14.1; Data for *Z*-**3d**: ^{19}F NMR (376 MHz, CDCl_3) δ -82.17 (d, J = 7.6 Hz, 1F). Data for *E*-**3d**: ^{19}F NMR (376 MHz, CDCl_3) δ -85.17 (d, J = 7.1 Hz, 1F); FTIR (film) 2914, 2847, 1628, 1472, 1462, 1063, 1008, 867, 857, 818, 729, 719 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{42}\text{BrFS}^+$ ($\text{M}+\text{H}$) $^+$ 484.2169, found 484.2164.

(*Z/E*)-Benzyl(2-(4-bromophenyl)-1-fluorovinyl) sulfane (3e): colorless oil; yield 59.6 mg (92 %) as an inseparable 11:1 *Z/E* mixture; R_f (petroleum ether) 0.45; Data for *Z*-**3e**: ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, J = 8.5 Hz, 2H), 7.36 – 7.29 (m, 5H), 7.17 (d, J = 8.4 Hz, 2H), 6.50 (d, J = 17.3 Hz, 1H), 4.10 (s, 2H). Selected data for *E*-**3e**: ^1H NMR (400 MHz, CDCl_3) δ 5.89 (d, J = 33.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.6 (d, J = 295.3 Hz), 136.6, 131.6 (d, J = 10.1 Hz), 131.3, 130.2 (d, J = 3.3 Hz), 128.9, 128.7, 127.6, 121.2, 115.2 (d, J = 32.3 Hz), 36.2 (d, J = 1.8 Hz); Data for *Z*-**3e**: ^{19}F NMR (376 MHz, CDCl_3) δ -81.56 (s, 1F). Data for *E*-**3e**: ^{19}F NMR (376 MHz, CDCl_3) δ -85.15 (s, 1F); FTIR (film) 3028, 1627, 1487, 1454, 1398, 1053, 1008, 908, 810, 765, 696 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{13}\text{BrFS}^+$ ($\text{M}+\text{H}$) $^+$ 322.9900, found 322.9903.

(Z/E)-(2-(4-Bromophenyl)-1-fluorovinyl)(isopropyl) sulfane (3f):

colorless oil; yield 50.2 mg (91%) as an inseparable 14:1 Z/E mixture; R_f (petroleum ether) 0.65; Data for Z-**3f**: ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.45 (m, 2H), 7.43 – 7.38 (m, 2H), 6.54 (d, J = 17.8 Hz, 1H), 3.58–3.47 (m, 1H), 1.38 (s, 4H), 1.36 (s, 3H). Selected data for E-**3f**: ^1H NMR (400 MHz, CDCl_3) δ 6.06 (d, J = 32.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4 (d, J = 294.6 Hz), 131.9 (d, J = 10.2 Hz), 131.4, 130.3 (d, J = 3.4 Hz), 121.2 (d, J = 1.9 Hz), 115.2 (d, J = 33.7 Hz), 37.5, 23.3 (d, J = 1.1 Hz); Data for Z-**3f**: ^{19}F NMR (376 MHz, CDCl_3) δ -77.50 (s, 1F). Data for E-**3f**: ^{19}F NMR (376 MHz, CDCl_3) δ -80.54 (s, 1F); FTIR (film) 2965, 2926, 2865, 1626, 1487, 1461, 1398, 1243, 1051, 1009, 867, 811, 734, 692 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{13}\text{BrFS}^+$ ($\text{M}+\text{H}$) $^+$ 274.9900, found 274.9907.

(Z/E)-(2-(4-Bromophenyl)-1-fluorovinyl)(cyclohexyl) sulfane (3g):

colorless oil; yield 62.5 mg (99%) as an inseparable 6:1 Z/E mixture; R_f (petroleum ether) 0.55; Data for Z-**3g**: ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.45 (m, 2H), 7.44 – 7.40 (m, 2H), 6.52 (d, J = 17.7 Hz, 1H), 3.34 – 3.25 (m, 1H), 2.06 – 2.01 (m, 2H), 1.81 – 1.75 (m, 2H), 1.69 – 1.59 (m, 2H), 1.48 – 1.44 (m, 2H), 1.39 – 1.33 (m, 2H). Selected data for E-**3g**: ^1H NMR (400 MHz, CDCl_3) δ 6.04 (d, J = 32.7 Hz, 1H); Data for Z-**3g**: ^{13}C NMR (100 MHz, CDCl_3) δ 155.1 (d, J = 295.0 Hz), 132.0 (d, J = 10.2 Hz), 131.7 (d, J = 4.2 Hz), 131.4, 130.3 (d, J = 3.3 Hz), 115.3 (d, J = 33.9 Hz), 45.4, 33.4 (d, J = 1.0 Hz), 26.0, 25.5. Selected data for E-**3g**: ^{13}C NMR (100 MHz, CDCl_3) δ 131.2,

130.1 (d, $J = 8.4$ Hz), 50.0 (d, $J = 5.0$ Hz), 42.9, 32.9 (d, $J = 2.6$ Hz); Data for **Z-3g**: ^{19}F NMR (376 MHz, CDCl_3) δ -76.86 (s, 1F). Data for **E-3g**: ^{19}F NMR (376 MHz, CDCl_3) δ -80.14 (s, 1F); FTIR (film) 2929, 2853, 1682, 1627, 1487, 1448, 1263, 1072, 1009, 906, 867, 729, 649 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{BrFS}^+ (\text{M}+\text{H})^+$ 315.0213, found 315.0211.

(Z/E)-2-(((2-(4-Bromophenyl)-1-fluorovinyl)thio) methyl)furan (3h):

colorless oil; yield 46.5 mg (74%) as an inseparable 10:1 *Z/E* mixture; R_f (petroleum ether) 0.35; Data for **Z-3h**: ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.40 (m, 2H), 7.35 (dd, $J = 1.9, 0.9$ Hz, 1H), 7.24 – 7.19 (m, 2H), 6.53 (d, $J = 17.1$ Hz, 1H), 6.30 (dd, $J = 3.2, 1.8$ Hz, 1H), 6.24 (dd, $J = 3.2, 0.8$ Hz, 1H), 4.09 (s, 2H). Selected data for **E-3h**: ^1H NMR (400 MHz, CDCl_3) δ 5.94 (d, $J = 33.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.1 (d, $J = 295.3$ Hz), 149.7, 142.6, 131.5 (d, $J = 9.9$ Hz), 131.4, 130.2 (d, $J = 3.3$ Hz), 121.3 (d, $J = 1.9$ Hz), 115.9 (d, $J = 32.6$ Hz), 110.7, 108.6, 28.4 (d, $J = 1.7$ Hz); Data for **Z-3h**: ^{19}F NMR (376 MHz, CDCl_3) δ -82.19 (s, 1F). Data for **E-3h**: ^{19}F NMR (376 MHz, CDCl_3) δ -85.83 (s, 1F); FTIR (film) 1631, 1488, 1151, 1072, 1011, 903, 869, 723, 649 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{BrOFS}^+ (\text{M}+\text{H})^+$ 312.9693, found 312.9688.

(Z/E)-((2-(4-Bromophenyl)-1-fluorovinyl)thio)methyl acetate (3i):

colorless oil; yield 57.5 mg (94%) as an inseparable 8:1 *Z/E* mixture; R_f (1:20 EtOAc/petroleum ether) 0.22; Data for **Z-3i**: ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.46 (m, 2H), 7.40 – 7.35 (m, 2H), 6.54 (d, $J = 17.4$ Hz, 1H),

3.73 (s, 3H), 3.62 (s, 2H). Selected data for *E*-**3i**: ^1H NMR (400 MHz, CDCl_3) δ 6.11 (d, $J = 33.1$ Hz, 1H), ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 153.1 (d, $J = 296.3$ Hz), 131.5, 131.2 (d, $J = 9.9$ Hz), 130.3 (d, $J = 3.2$ Hz), 121.6 (d, $J = 1.8$ Hz), 115.0 (d, $J = 31.1$ Hz), 52.8, 32.8 (d, $J = 2.5$ Hz); Data for *Z*-**3i**: ^{19}F NMR (376 MHz, CDCl_3) δ -84.58 (s, 1F). Data for *E*-**3i**: ^{19}F NMR (376 MHz, CDCl_3) δ -87.44 (s, 1F); FTIR (film) 1739, 1488, 1300, 1073, 1010, 903, 722, 649 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{BrO}_2\text{FS}^+$ ($\text{M}+\text{H}$) $^+$ 304.9642, found 304.9643.

(*Z/E*)-2-((2-((4-Bromophenyl)-1-fluorovinyl)thio) ethoxy)ethan-1-ol

(3j): colorless oil; yield 61.1 mg (95%) as an inseparable 10:1 *Z/E* mixture; R_f (1:5 EtOAc/petroleum ether) 0.18; Data for *Z*-**3j**: ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.45 (m, 2H), 7.41 – 7.35 (m, 2H), 6.50 (d, $J = 17.8$ Hz, 1H), 3.75 – 3.69 (m, 4H), 3.58 – 3.53 (m, 2H), 3.07 (t, $J = 6.3$ Hz, 2H). Selected data for *E*-**3j**: ^1H NMR (400 MHz, CDCl_3) δ 6.05 (d, $J = 33.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.5 (d, $J = 295.7$ Hz), 131.6 (d, $J = 10.2$ Hz), 131.5, 130.2 (d, $J = 3.3$ Hz), 121.3 (d, $J = 1.9$ Hz), 121.3 (d, $J = 1.9$ Hz), 114.3 (d, $J = 32.4$ Hz), 114.1, 72.1, 69.8 (d, $J = 1.0$ Hz), 61.7, 31.2 (d, $J = 2.0$ Hz); Data for *Z*-**3j**: ^{19}F NMR (376 MHz, CDCl_3) δ -82.52 (s, 1F). Data for *E*-**3j**: ^{19}F NMR (376 MHz, CDCl_3) δ -85.58 (s, 1F); FTIR (film) 2865, 1629, 1488, 1399, 1355, 1286, 1207, 1117, 1071, 1009, 906, 866, 727, 648 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{BrFO}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 320.9955, found 320.9955.

(Z/E)-(2-(4-Bromophenyl)-1-fluorovinyl)(tert-butyl) sulfane(3k):

colorless oil; yield 49.3 mg (85%) as an inseparable 2:1 Z/E mixture; R_f (petroleum ether) 0.75; Data for Z-**3k**: ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.47 (m, 4H), 6.66 (d, $J = 16.7$ Hz, 1H), 1.44 (s, 9H). Data for E-**3k**: ^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.39 (m, 4H), 6.13 (d, $J = 31.3$ Hz, 1H), 1.47 (s, 9H); Data for Z-**3k**: ^{13}C NMR (100 MHz, CDCl_3) δ 155.8 (d, $J = 295.7$ Hz), 131.9 (d, $J = 9.5$ Hz), 131.3, 130.5 (d, $J = 3.7$ Hz), 121.4 (d, $J = 2.2$ Hz), 118.8 (d, $J = 36.2$ Hz), 49.8 (d, $J = 3.7$ Hz), 31.7 (d, $J = 2.1$ Hz). Data for E-**3k**: ^{13}C NMR (100 MHz, CDCl_3) δ 155.5 (d, $J = 309.3$ Hz), 132.2 (d, $J = 6.4$ Hz), 131.7, 130.3 (d, $J = 8.6$ Hz), 121.8 (d, $J = 3.8$ Hz), 118.9 (d, $J = 16.0$ Hz), 48.1 (d, $J = 4.3$ Hz), 31.4 (d, $J = 1.7$ Hz); Data for Z-**3k**: ^{19}F NMR (376 MHz, CDCl_3) δ -68.30 (s, 1F). Data for E-**3k**: ^{19}F NMR (376 MHz, CDCl_3) δ -74.42 (s, 1F); FTIR (film) 1624, 1487, 1368, 1157, 1038, 1010, 903, 814, 723, 649 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{BrFS}^+$ ($\text{M}+\text{H}$) $^+$ 289.0056, found 289.0054.

(Z/E)-(2-(4-Bromophenyl)-1-fluorovinyl)(phenyl) sulfane (3l): white

solid; mp 48.5-56.0 $^{\circ}\text{C}$; yield 51.4 mg (83%) as an inseparable 11:1 Z/E mixture; R_f (petroleum ether) 0.45; Data for Z-**3l**: ^1H NMR (400 MHz, CDCl_3) δ 7.52 - 7.49 (m, 2H), 7.48 – 7.44 (m, 4H), 7.39 – 7.32 (m, 3H), 6.71 (d, $J = 15.9$ Hz, 1H). Selected data for E-**3l**: ^1H NMR (400 MHz, CDCl_3) δ 6.24 (d, $J = 32.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.1 (d, $J = 297.7$ Hz), 131.6, 131.5 (d, $J = 9.1$ Hz), 130.6 (d, $J = 2.5$ Hz), 130.3 (d, $J = 3.3$ Hz),

130.1 (d, $J = 0.9$ Hz), 129.4, 127.9, 121.9 (d, $J = 1.8$ Hz), 117.4 (d, $J = 32.4$ Hz); Data for **Z-3l**: ^{19}F NMR (376 MHz, CDCl_3) δ -78.71 (s, 1F). Data for **E-3l**: ^{19}F NMR (376 MHz, CDCl_3) δ -84.39 (s, 1F); FTIR (film) 1629, 1582, 1478, 1439, 1398, 1074, 1048, 1008, 882, 863, 820, 732, 684 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{10}\text{BrFS}^+ (\text{M}+\text{H})^+$ 307.9665, found 307.9661.

(Z/E)-(2-(4-Chlorophenyl)-1-fluorovinyl)(ethyl) sulfane (3m): colorless oil; yield 37.0 mg (85%) as an inseparable 10:1 *Z/E* mixture; R_f (petroleum ether) 0.61; Data for **Z-3m**: ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.42 (m, 2H), 7.34 – 7.31 (m, 2H), 6.53 (d, $J = 18.0$ Hz, 1H), 2.91 (qd, $J = 7.4, 0.8$ Hz, 2H), 1.36 (t, $J = 7.4$ Hz, 3H). Selected data for **E-3m**: ^1H NMR (400 MHz, CDCl_3) δ 6.04 (d, $J = 33.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.1 (d, $J = 295.1$ Hz), 132.9 (d, $J = 1.9$ Hz), 131.4 (d, $J = 10.4$ Hz), 129.9 (d, $J = 3.3$ Hz), 128.4, 114.0 (d, $J = 32.7$ Hz), 26.1 (d, $J = 2.9$ Hz), 15.1 (d, $J = 1.2$ Hz); Data for **Z-3m**: ^{19}F NMR (376 MHz, CDCl_3) δ -82.73 (s, 1F). Data for **E-3m**: ^{19}F NMR (376 MHz, CDCl_3) δ -85.52 (s, 1F); FTIR (film) 1629, 1490, 1093, 1014, 870, 723, 649 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{11}\text{FCIS}^+ (\text{M}+\text{H})^+$ 217.0249, found 217.0249.

(Z/E)-Ethyl(1-fluoro-2-(4-methoxyphenyl)vinyl) sulfane (3n): colorless oil; yield 37 mg (87%) as an inseparable 20:1 *Z/E* mixture; R_f (petroleum ether) 0.18; Data for **Z-3n**: ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.45 (m, 2H), 6.93 – 6.88 (m, 2H), 6.57 (d, $J = 18.2$ Hz, 1H), 3.84 (s, 3H), 2.89 (qd, $J = 7.3, 0.9$ Hz, 2H), 1.36 (t, $J = 7.4$ Hz, 3H). Selected data for **E-3n**: ^1H NMR

(400 MHz, CDCl₃) δ 6.06 (d, J = 33.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 158.8 (d, J = 1.6 Hz), 153.1 (d, J = 291.6 Hz), 130.0 (d, J = 3.2 Hz), 125.3 (d, J = 9.6 Hz), 115.2 (d, J = 32.3 Hz), 113.7, 55.3, 26.2 (d, J = 1.9 Hz), 15.1 (d, J = 1.2 Hz); Data for **Z-3n**: ¹⁹F NMR (376 MHz, CDCl₃) δ -85.45 (s, 1F), Data for **E-3n**: ¹⁹F NMR (376 MHz, CDCl₃) δ -88.62 (s, 1F); FTIR (film) 1607, 1509, 1250, 1179, 1034, 904, 874, 724, 649 cm⁻¹; HRMS (ESI) m/z calcd for C₁₁H₁₄FOS⁺ (M+H)⁺ 213.0744, found 213.0744.

(Z/E)-Ethyl(1-fluoro-2-(p-tolyl)vinyl)sulfane (3o): colorless oil; yield 31.9 mg (81%) as an inseparable 17:1 Z/E mixture; R_f (petroleum ether) 0.55; Data for **Z-3o**: ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 6.59 (d, J = 18.3 Hz, 1H), 2.90 (qd, J = 7.4, 0.9 Hz, 2H), 2.38 (s, 3H), 1.36 (t, J = 7.4 Hz, 3H). Selected data for **E-3o**: ¹H NMR (400 MHz, CDCl₃) δ 6.08 (d, J = 33.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 153.9 (d, J = 292.8 Hz), 137.2 (d, J = 1.8 Hz), 130.0 (d, J = 9.9 Hz), 129.0, 128.6 (d, J = 3.2 Hz), 115.3 (d, J = 31.7 Hz), 26.2 (d, J = 2.5 Hz), 21.2, 15.1 (d, J = 1.2 Hz); Data for **Z-3o**: ¹⁹F NMR (376 MHz, CDCl₃) δ -84.61 (s, 1F). Data for **E-3o**: ¹⁹F NMR (376 MHz, CDCl₃) δ -86.93 (s, 1F); FTIR (film) 2966, 2927, 1628, 1510, 1449, 1261, 1036, 818, 806, 712, 679, 628, 576 cm⁻¹; HRMS (ESI) m/z calcd for C₁₁H₁₄FS⁺ (M+H)⁺ 197.0795, found 197.0791.

(Z/E)-Ethyl(1-fluoro-2-(2-methoxyphenyl)vinyl) sulfane (3p): colorless oil; yield 34.5 mg (81%) as an inseparable 17:1 Z/E mixture; R_f (petroleum ether) 0.28; Data for **Z-3p**: ¹H NMR (400 MHz, CDCl₃) δ 7.62 -

7.60 (m, 1H), 7.28 (td, $J = 7.8, 1.7$ Hz, 1H), 6.99 (td, $J = 7.6, 1.1$ Hz, 1H), 6.89 (d, $J = 8.2$ Hz, 1H), 6.83 (d, $J = 18.4$ Hz, 1H), 3.87 (s, 3H), 2.88 (qd, $J = 7.4, 0.8$ Hz, 2H), 1.35 (t, $J = 7.4$ Hz, 3H). Selected data for *E*-**3p**: ^1H NMR (400 MHz, CDCl_3) δ 6.54 (d, $J = 35.0$ Hz, 1H); Data for *Z*-**3p**: ^{13}C NMR (100 MHz, CDCl_3) δ 156.8 (d, $J = 3.4$ Hz), 154.6 (d, $J = 293.0$ Hz), 129.6 (d, $J = 2.2$ Hz), 128.7 (d, $J = 1.3$ Hz), 121.96 (d, $J = 9.7$ Hz), 120.1, 110.3, 110.0 (d, $J = 33.3$ Hz), 55.5, 26.01 (d, $J = 2.9$ Hz), 15.05 (d, $J = 1.2$ Hz). Selected data for *E*-**3p**: ^{13}C NMR (100 MHz, CDCl_3) δ 29.7; Data for *Z*-**3p**: ^{19}F NMR (376 MHz, CDCl_3) δ -84.11 (s, 1F), Data for *E*-**3p**: ^{19}F NMR (376 MHz, CDCl_3) δ -87.40 (s, 1F); FTIR (film) 2927, 1626, 1598, 1486, 1462, 1244, 1116, 1050, 1028, 908, 874, 748, 730, 628 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{14}\text{FOS}^+$ ($\text{M}+\text{H}$) $^+$ 213.0744, found 213.0746.

(*Z/E*)-Ethyl(1-fluoro-2-(3-methoxyphenyl)vinyl) sulfane (3q): colorless oil; yield 37.5 mg (88%) as an inseparable 10:1 *Z/E* mixture; R_f (petroleum ether) 0.18; Data for *Z*-**3q**: ^1H NMR (400 MHz, CDCl_3) δ 7.30 – 7.27 (m, 1H), 7.14 (t, $J = 2.1$ Hz, 1H), 7.07 (dt, $J = 7.6, 0.9$ Hz, 1H), 6.83 (dd, $J = 8.2, 2.6$ Hz, 1H), 6.57 (d, $J = 18.6$ Hz, 1H), 3.85 (s, 3H), 2.91 (qd, $J = 7.3, 0.9$ Hz, 2H), 1.37 (t, $J = 7.4$ Hz, 3H). Selected data for *E*-**3q**: ^1H NMR (400 MHz, CDCl_3) δ 6.07 (d, $J = 33.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.4, 154.8 (d, $J = 294.0$ Hz), 134.2 (d, $J = 10.2$ Hz), 129.2, 121.5 (d, $J = 3.3$ Hz), 115.0 (d, $J = 32.2$ Hz), 114.0 (d, $J = 3.3$ Hz), 113.0 (d, $J = 1.8$ Hz), 55.2, 26.1 (d, $J = 3.0$ Hz), 15.2 (d, $J = 1.3$ Hz); Data for *Z*-**3q**: ^{19}F NMR (376

MHz, CDCl₃) δ -83.41 (s, 1F). Data for *E*-**3q**: ¹⁹F NMR (376 MHz, CDCl₃) δ -85.48 (s, 1F); FTIR (film) 2928, 1628, 1597, 1576, 1488, 1453, 1431, 1264, 1159, 1039, 865, 773, 690 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₁H₁₄FOS⁺ (M+H)⁺ 213.0744, found 213.0738.

(Z/E)-(2-(3-Bromophenyl)-1-fluorovinyl)(ethyl) sulfane (3r): colorless oil; yield 46.6 mg (89%) as an inseparable 6:1 *Z/E* mixture; *R_f* (petroleum ether) 0.65; Data for *Z*-**3r**: ¹H NMR (400 MHz, CDCl₃) δ 7.68 (t, *J* = 1.9 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.50 (d, *J* = 18.0 Hz, 1H), 2.92 (qd, *J* = 7.4, 0.8 Hz, 2H), 1.37 (t, *J* = 7.4 Hz, 3H). Selected data for *E*-**3r**: ¹H NMR (400 MHz, CDCl₃) δ 6.00 (d, *J* = 33.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 155.8 (d, *J* = 296.1 Hz), 135.1 (d, *J* = 10.6 Hz), 131.4 (d, *J* = 3.2 Hz), 130.1 (d, *J* = 1.5 Hz), 129.7, 127.3 (d, *J* = 3.0 Hz), 122.3, 113.6 (d, *J* = 32.7 Hz), 26.1 (d, *J* = 3.3 Hz), 15.2 (d, *J* = 1.2 Hz); Data for *Z*-**3r**: ¹⁹F NMR (376 MHz, CDCl₃) δ -81.83 (s, 1F). Data for *E*-**3r**: ¹⁹F NMR (376 MHz, CDCl₃) δ -84.32 (s, 1F); FTIR (film) 3054, 2965, 2927, 1625, 1507, 1449, 1376, 1261, 1176, 1049, 967, 894, 861, 813, 764, 743 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₀H₁₁BrFS⁺ (M+H)⁺ 260.9743, found 260.9743.

(Z/E)-Ethyl(1-fluoro-2-(naphthalen-1-yl)vinyl)sulfane (3s): colorless oil; yield 41.0 mg (88%) as an inseparable 11:1 *Z/E* mixture; *R_f* (petroleum ether) 0.45; Data for *Z*-**3s**: ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.99 (m, 1H), 7.93 – 7.89 (m, 1H), 7.86 (d, *J* = 7.1 Hz, 1H), 7.58 – 7.50 (m, 4H), 7.12 (d, *J* = 16.2 Hz, 1H), 2.86 (q, *J* = 7.4 Hz, 2H), 1.33 (t, *J* = 7.4 Hz, 3H). Selected

data for *E*-**3s**: ^1H NMR (400 MHz, CDCl_3) δ 6.79 (d, J = 31.7 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.3 (d, J = 296.0 Hz), 133.5, 131.8 (d, J = 3.0 Hz), 130.2 (d, J = 9.5 Hz), 128.6, 128.2 (d, J = 0.5 Hz), 127.5 (d, J = 2.5 Hz), 126.2, 126.0, 125.3, 124.3, 112.0 (d, J = 30.3 Hz), 25.8 (d, J = 3.2 Hz), 15.0 (d, J = 1.2 Hz); Data for *Z*-**3s**: ^{19}F NMR (376 MHz, CDCl_3) δ -84.92 (s, 1F). Data for *E*-**3s**: ^{19}F NMR (376 MHz, CDCl_3) δ -87.44 (s, 1F); FTIR (film) 1630, 1087, 903, 799, 781, 722, 648 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{FS}^+$ ($\text{M}+\text{H}$) $^+$ 233.0795, found 233.0795.

(Z/E)-Ethyl(1-fluoro-2-(naphthalen-2-yl)vinyl)sulfane (3t): colorless oil; yield 37.3 mg (80%) as an inseparable 6:1 *Z/E* mixture; R_f (petroleum ether) 0.45; Data for *Z*-**3t**: ^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.86-7.82 (m, 3H), 7.73 (dd, J = 8.6, 1.8 Hz, 1H), 7.52 – 7.49 (m, 2H), 6.77 (d, J = 18.3 Hz, 1H), 2.95 (qd, J = 7.4, 0.9 Hz, 2H), 1.40 (t, J = 7.4 Hz, 3H). Selected data for *E*-**3t**: ^1H NMR (400 MHz, CDCl_3) δ 6.27 (d, J = 33.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9 (d, J = 294.3 Hz), 133.3, 132.5 (d, J = 1.0 Hz), 130.4 (d, J = 10.2 Hz), 128.0 (m), 127.8, 127.6, 126.5 (d, J = 2.3 Hz), 126.3, 126.1 (d, J = 0.9 Hz), 115.3 (d, J = 32.1 Hz), 26.2 (d, J = 2.8 Hz), 15.2 (d, J = 1.2 Hz); Data for *Z*-**3t**: ^{19}F NMR (376 MHz, CDCl_3) δ -82.89 (s, 1F). Data for *E*-**3t**: ^{19}F NMR (376 MHz, CDCl_3) δ -85.80 (s, 1F); FTIR (film) 1628, 1591, 1557, 1476, 1260, 1075, 904, 779, 726, 685 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{FS}^+$ ($\text{M}+\text{H}$) $^+$ 233.0795, found 233.0792.

(Z)-Ethyl(1-fluoro-4-phenylbut-1-en-1-yl)sulfane (3u): colorless oil; yield 5.1 mg (12%); R_f (petroleum ether) 0.65; ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.30 (m, 2H), 7.26 – 7.18 (m, 3H), 5.60 (dt, $J = 15.5, 7.8$ Hz, 1H), 2.75 – 2.66 (m, 4H), 2.55 – 2.46 (m, 2H), 1.27 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.9 (d, $J = 290.9$ Hz), 141.1, 128.6, 128.4, 126.0, 115.2 (d, $J = 24.6$ Hz), 35.8 (d, $J = 2.9$ Hz), 29.3 (d, $J = 3.4$ Hz), 15.0 (d, $J = 1.2$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -87.63. FTIR (film) 3027, 2929, 1683, 1647, 1603, 1496, 1454, 1287, 1261, 1074, 968, 908, 730, 698 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{16}\text{FS}^+$ ($\text{M}+\text{H}$) $^+$ 211.0951, found 211.0952.

(2-(4-Bromophenyl)ethene-1,1-diyl)bis(ethylsulfane) (3v): colorless oil; yield 15.1 mg (25%); R_f (petroleum ether) 0.45; ^1H NMR (400 MHz, CDCl_3) δ 7.54 – 7.45 (m, 4H), 6.93 (s, 1H), 2.87 (q, $J = 7.3$ Hz, 4H), 1.33 (t, $J = 7.3$ Hz, 3H), 1.25 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 135.4, 133.5, 133.0, 131.2, 130.9, 121.0, 28.1, 27.7, 14.9, 14.2. FTIR (film) 2963, 2924, 2868, 1550, 1484, 1447, 1395, 1373, 1257, 1074, 1009, 915, 808 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{16}\text{BrS}_2^+$ ($\text{M}+\text{H}$) $^+$ 302.9871, found 302.9872.

Ethyl(1-fluoro-2,2-diphenylvinyl)sulfane (3w): colorless oil; yield 45.0 mg (87%); R_f (petroleum ether) 0.31; ^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.35 (m, 6H), 7.35 – 7.25 (m, 4H), 2.88 (qd, $J = 7.4, 0.8$ Hz, 2H), 1.39 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.0 (d, $J = 302.7$ Hz), 138.6 (d, $J = 4.8$ Hz), 137.3 (d, $J = 2.3$ Hz), 130.5 (d, $J = 3.2$ Hz), 129.6 (d, $J = 5.3$ Hz),

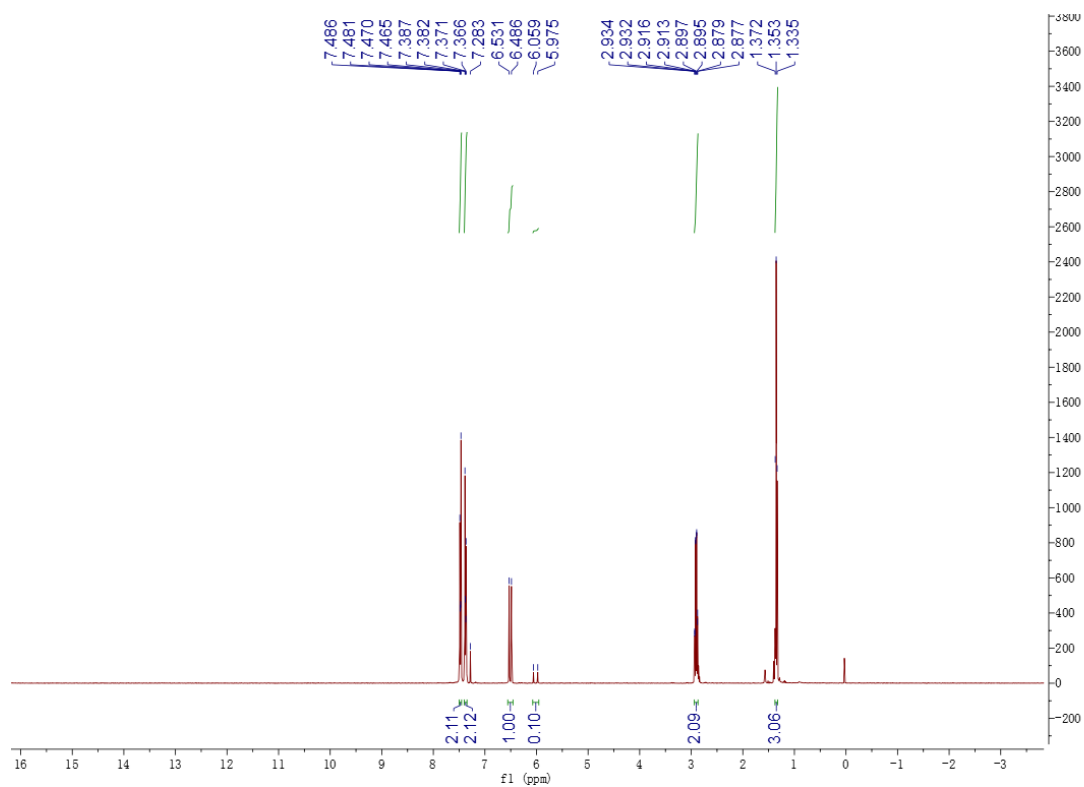
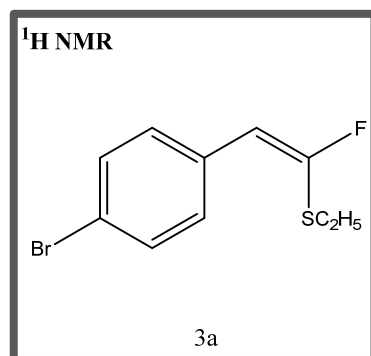
128.2, 128.1, 127.6, 127.4 (d, $J = 1.3$ Hz), 126.9 (d, $J = 17.1$ Hz), 26.3 (d, $J = 2.8$ Hz), 15.1 (d, $J = 1.2$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -91.51 (s, 1F); FTIR (film) 2253, 1495, 1443, 1275, 1090, 903, 723, 698, 649 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{FS}^+$ ($\text{M}+\text{H}$) $^+$ 258.0873, found 258.0870.

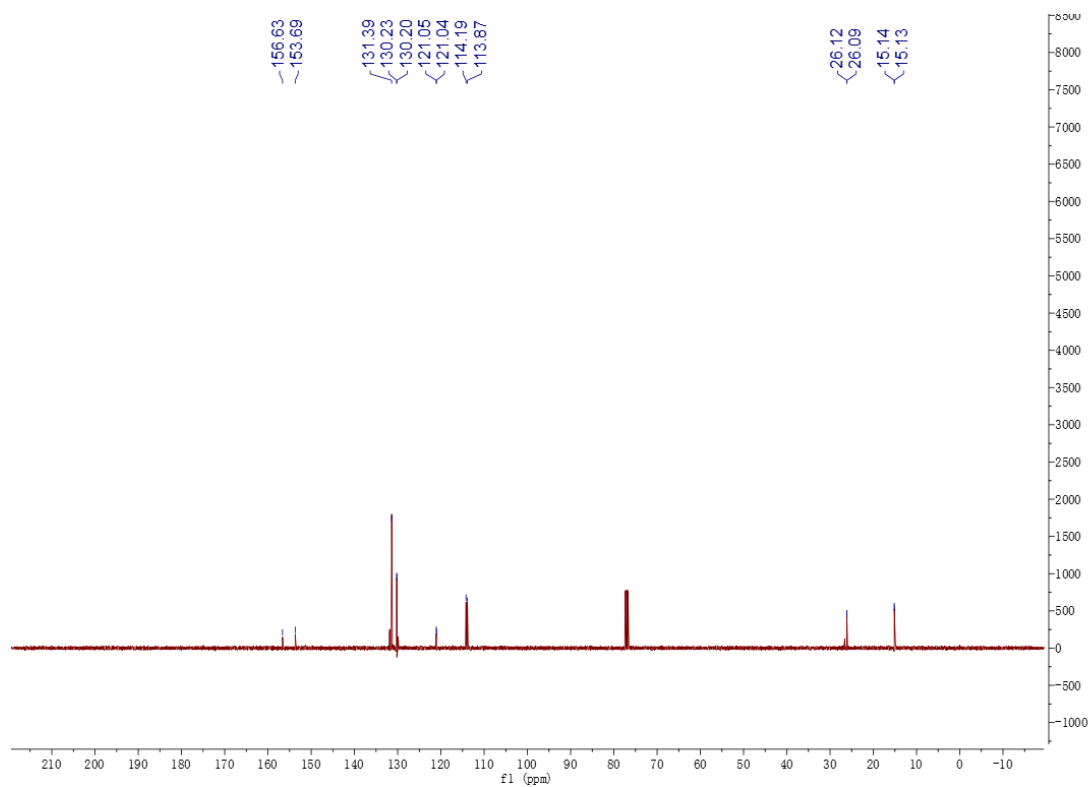
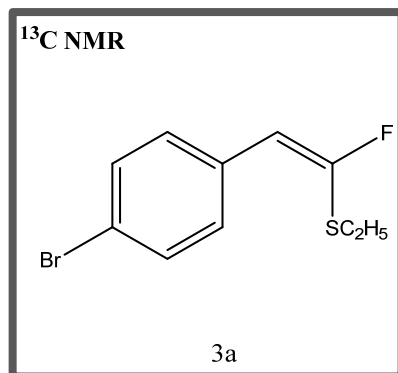
(2,2-Bis(4-chlorophenyl)-1-fluorovinyl)(ethyl)sulfane (3x): colorless oil; yield 57.7 mg (88%); R_f (petroleum ether) 0.45; ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.26 (m, 2H), 7.25 – 7.14 (m, 2H), 2.86 (qd, $J = 7.4, 0.8$ Hz, 2H), 1.36 (d, $J = 14.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.8 (d, $J = 304.5$ Hz), 136.6 (d, $J = 4.9$ Hz), 135.3 (d, $J = 2.6$ Hz), 133.8, 133.3 (d, $J = 1.5$ Hz), 131.9 (d, $J = 3.3$ Hz), 130.8 (d, $J = 5.6$ Hz), 128.6, 128.4, 124.4 (d, $J = 17.6$ Hz), 26.3 (d, $J = 3.2$ Hz), 15.1 (d, $J = 1.2$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -89.99 (s, 1F); FTIR (film) 3675, 2988, 2960, 2923, 1617, 1491, 1399, 1265, 1088, 1015, 927, 809, 767, 689 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{13}\text{Cl}_2\text{FS}^+$ ($\text{M}+\text{H}$) $^+$ 326.0094, found 326.0091.

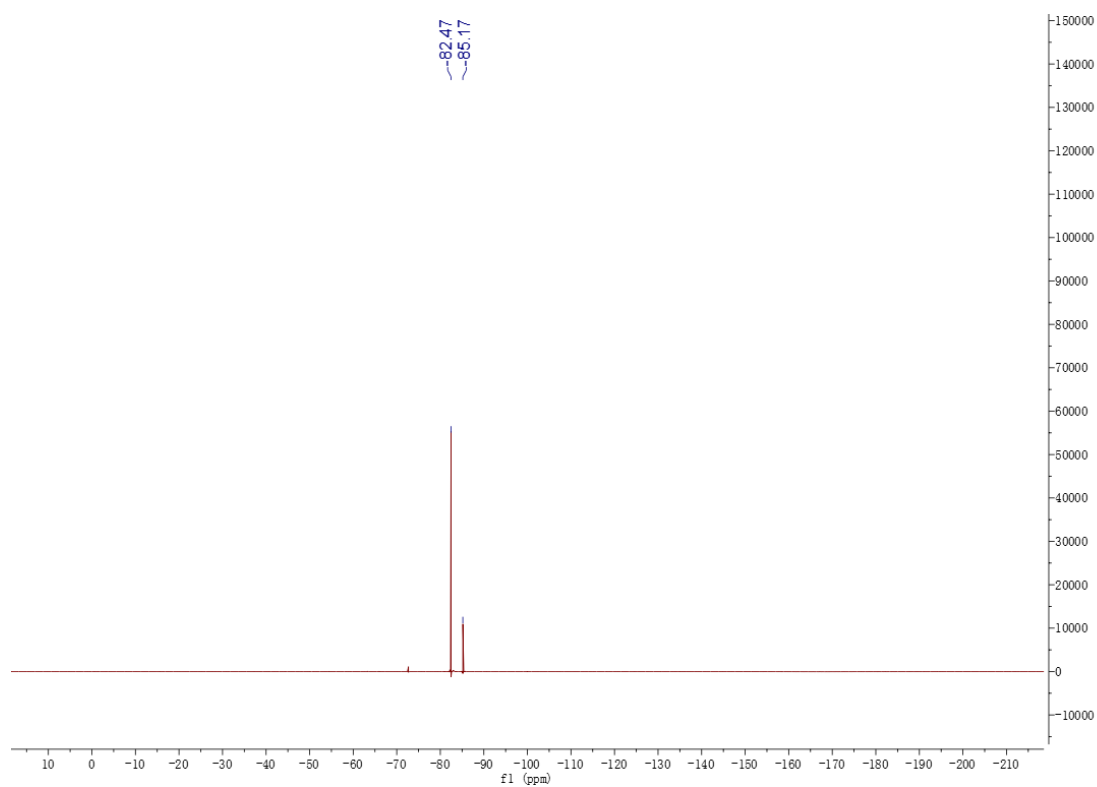
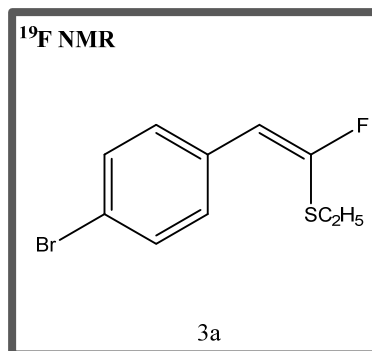
(*E/Z*)-(1-Chloro-2-phenylvinyl)(ethyl)sulfane (3y): colorless oil; yield 9.9 mg (25%) as an inseparable 9:1 *E/Z* mixture; R_f (petroleum ether) 0.60; Data for *E*-**3y**: ^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.52 (m, 2H), 7.40 – 7.33 (m, 2H), 7.32 – 7.29 (m, 1H), 7.04 (s, 1H), 2.98 (q, $J = 7.3$ Hz, 2H), 1.32 (t, $J = 7.3$ Hz, 3H). Data for *Z*-**3y**: ^1H NMR (400 MHz, CDCl_3) δ 7.00 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 134.9, 134.4, 129.2, 128.2, 127.8, 28.2, 14.7. FTIR (film) 3058, 2926, 2870, 1568, 1491, 1444, 1376, 1259, 1056,

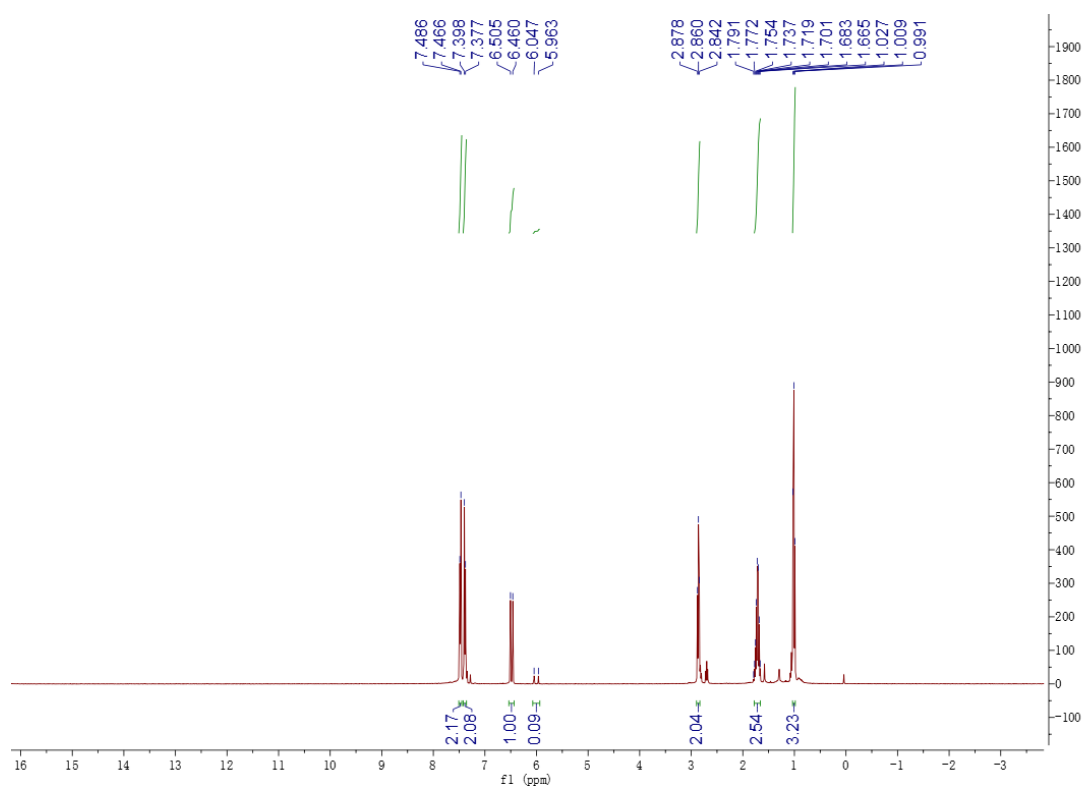
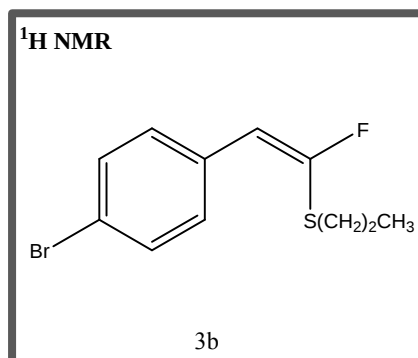
910, 797, 750, 692 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{12}\text{ClS}^+$ ($\text{M}+\text{H}$) $^+$

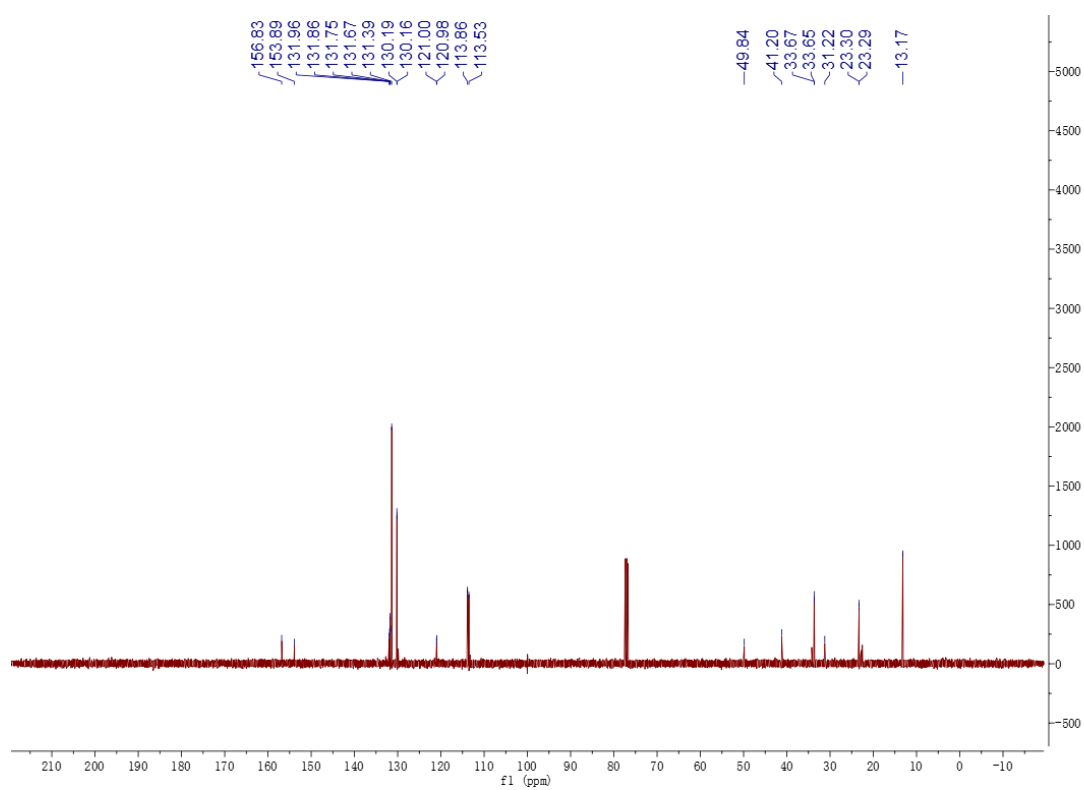
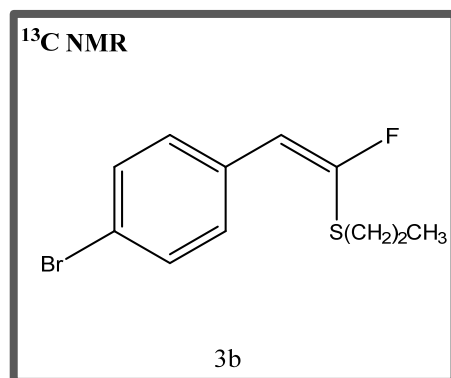
199.0343, found 199.0342.

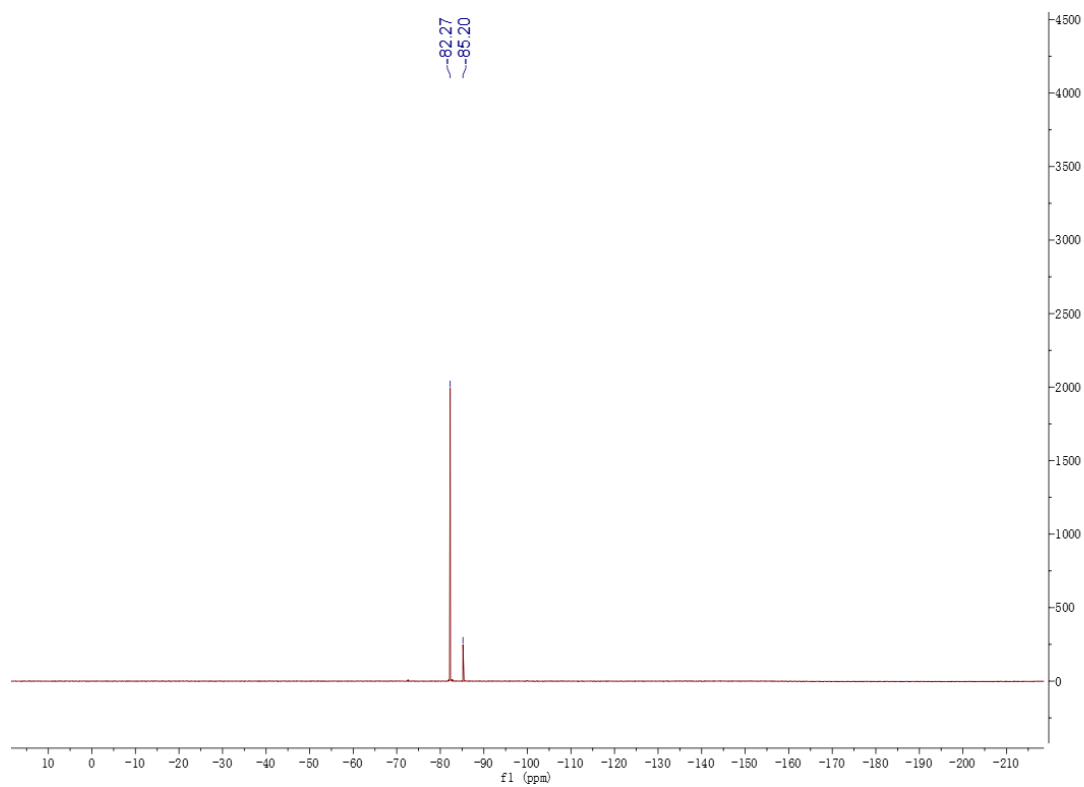
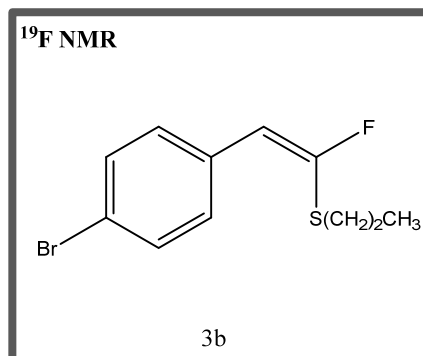


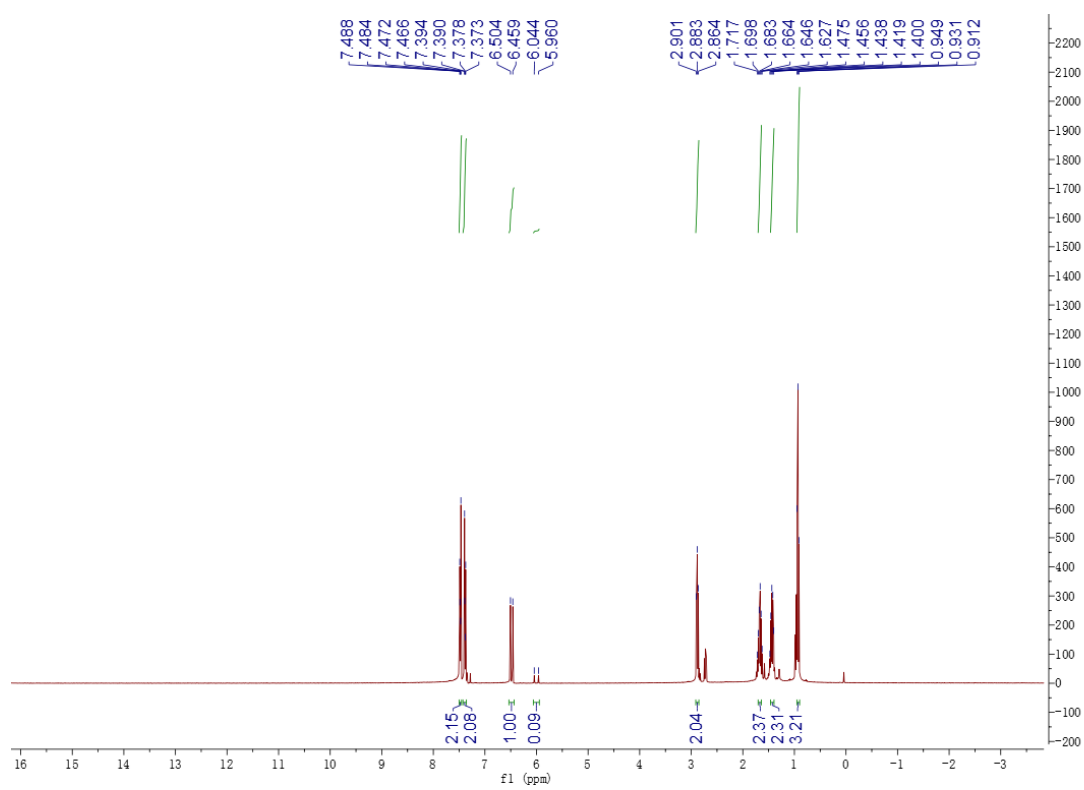
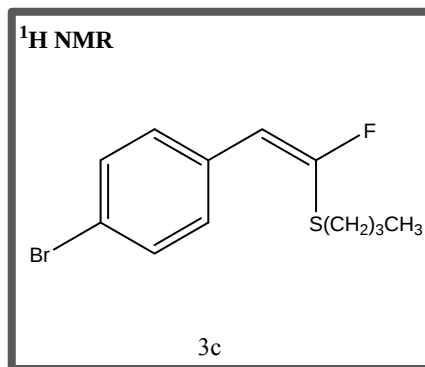


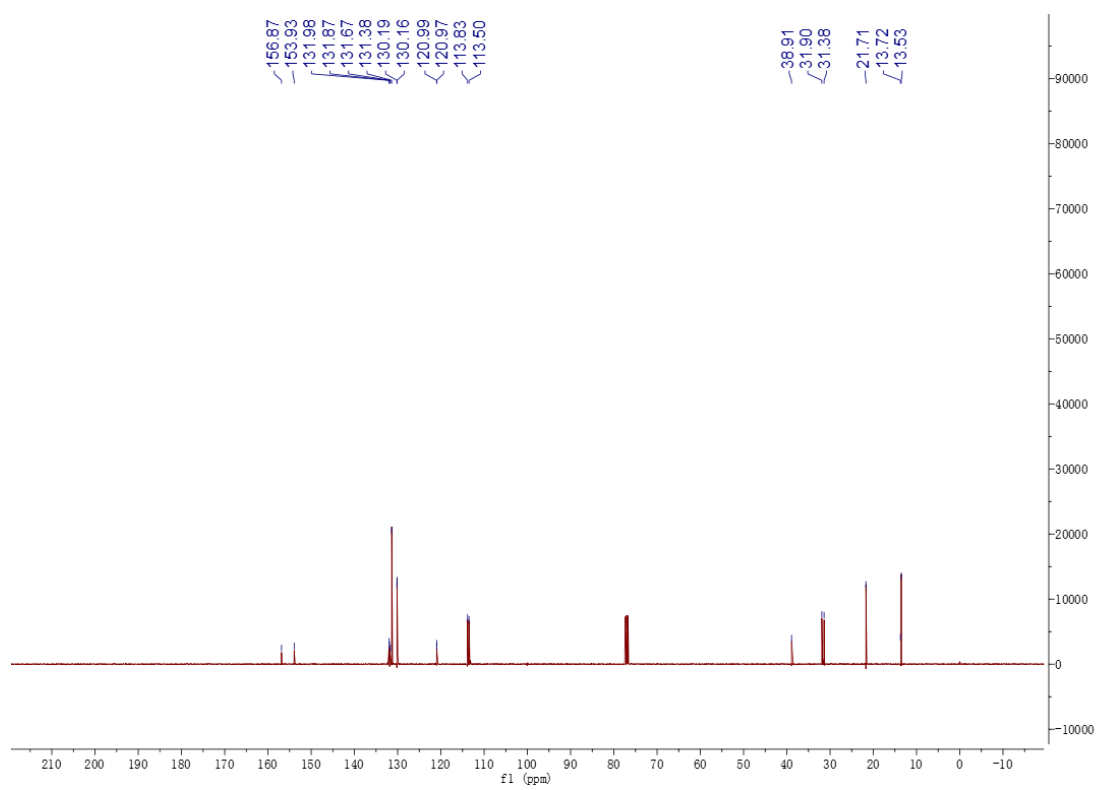
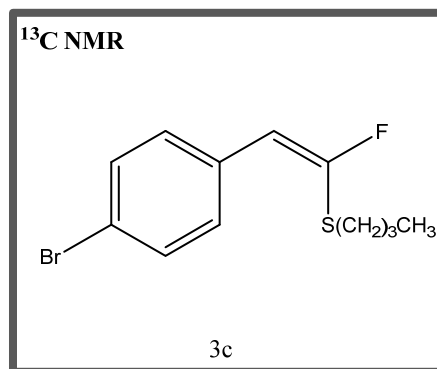


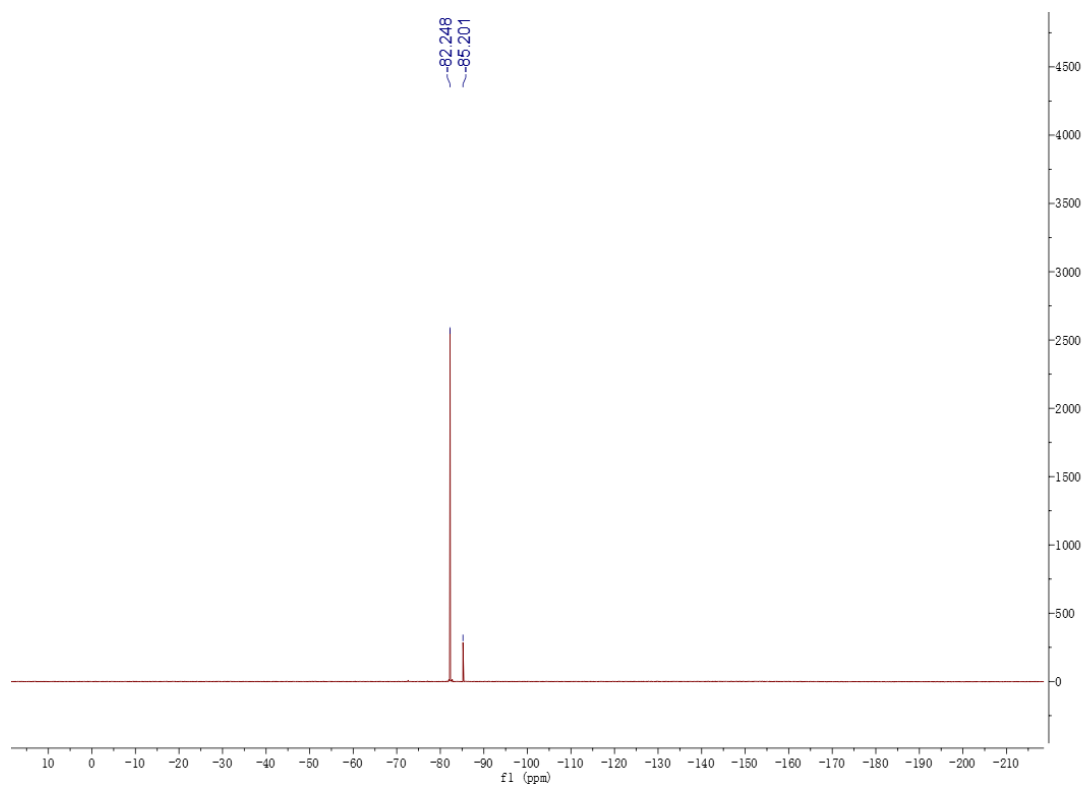
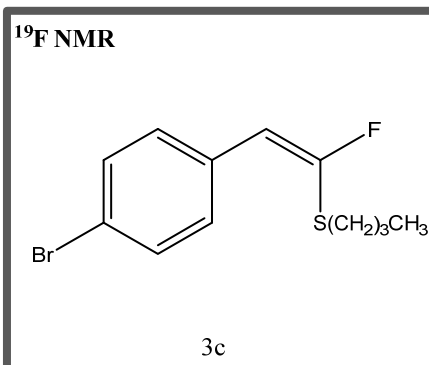


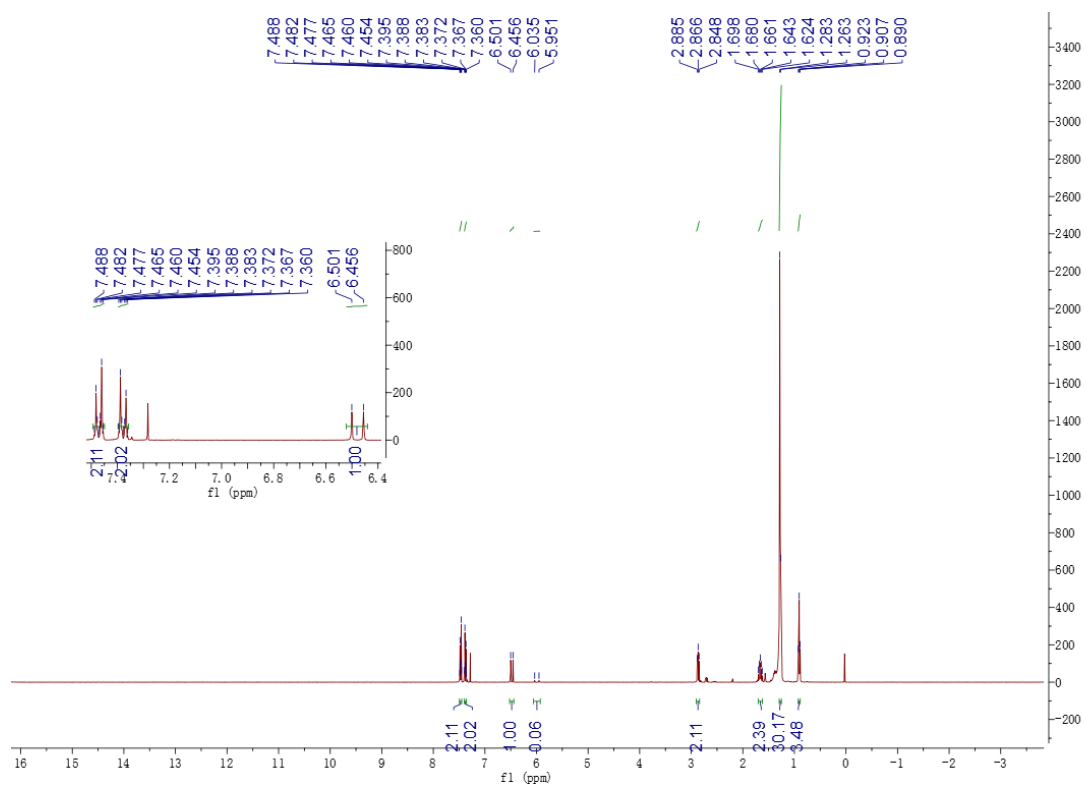
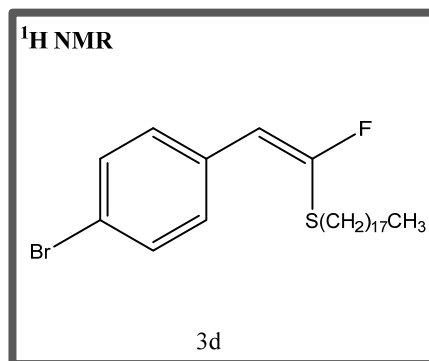


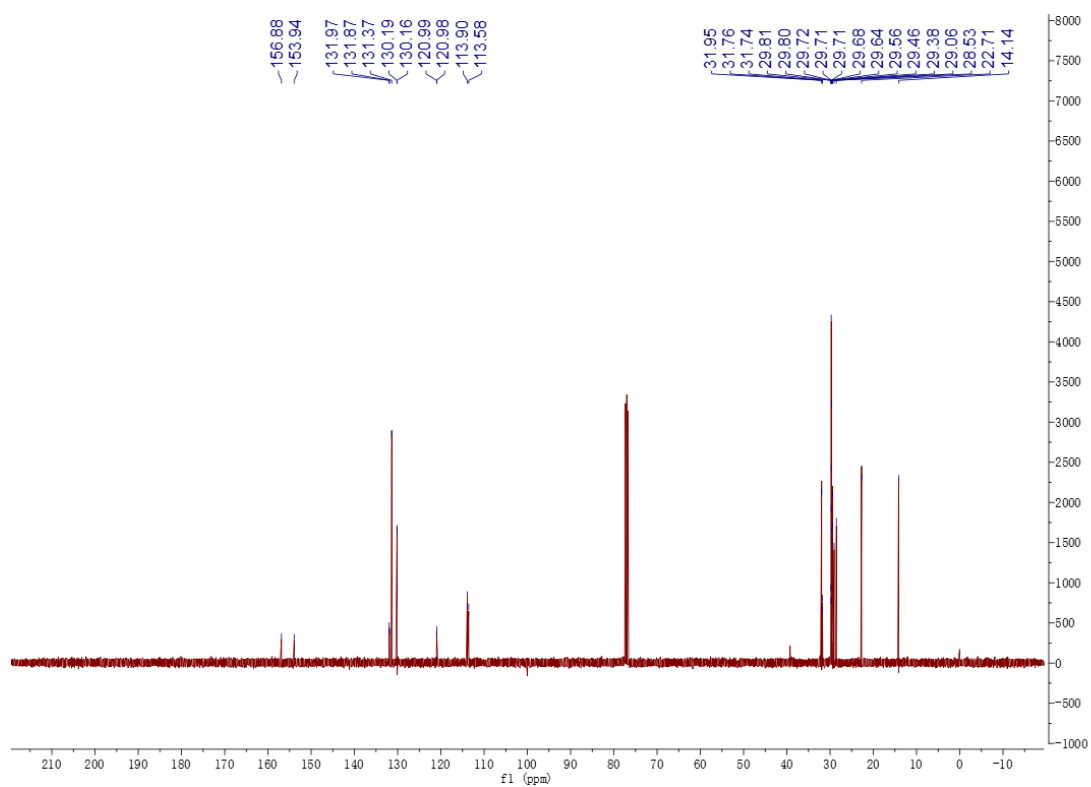
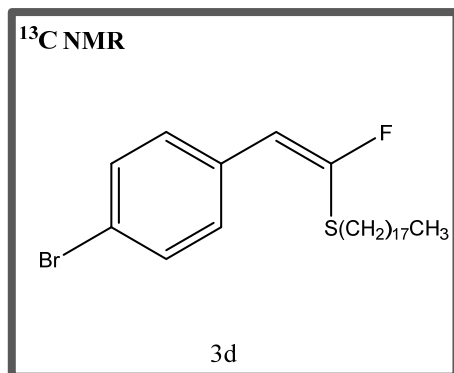


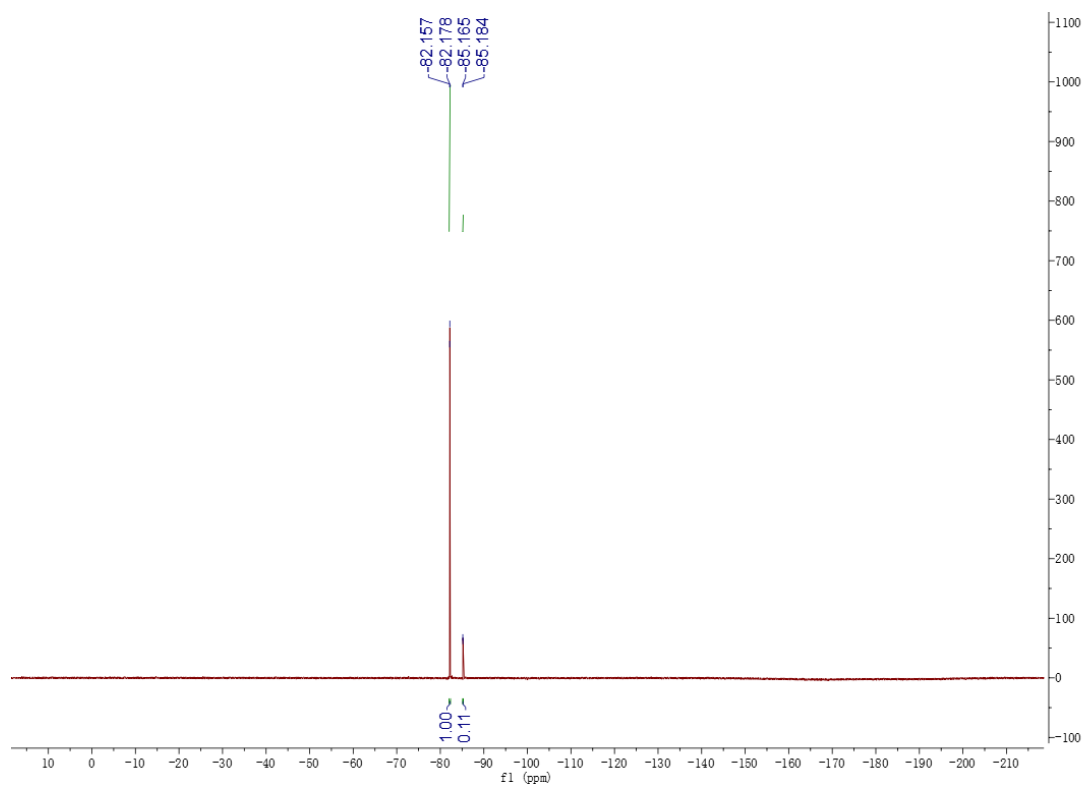
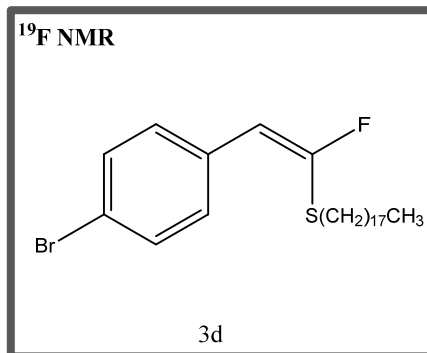


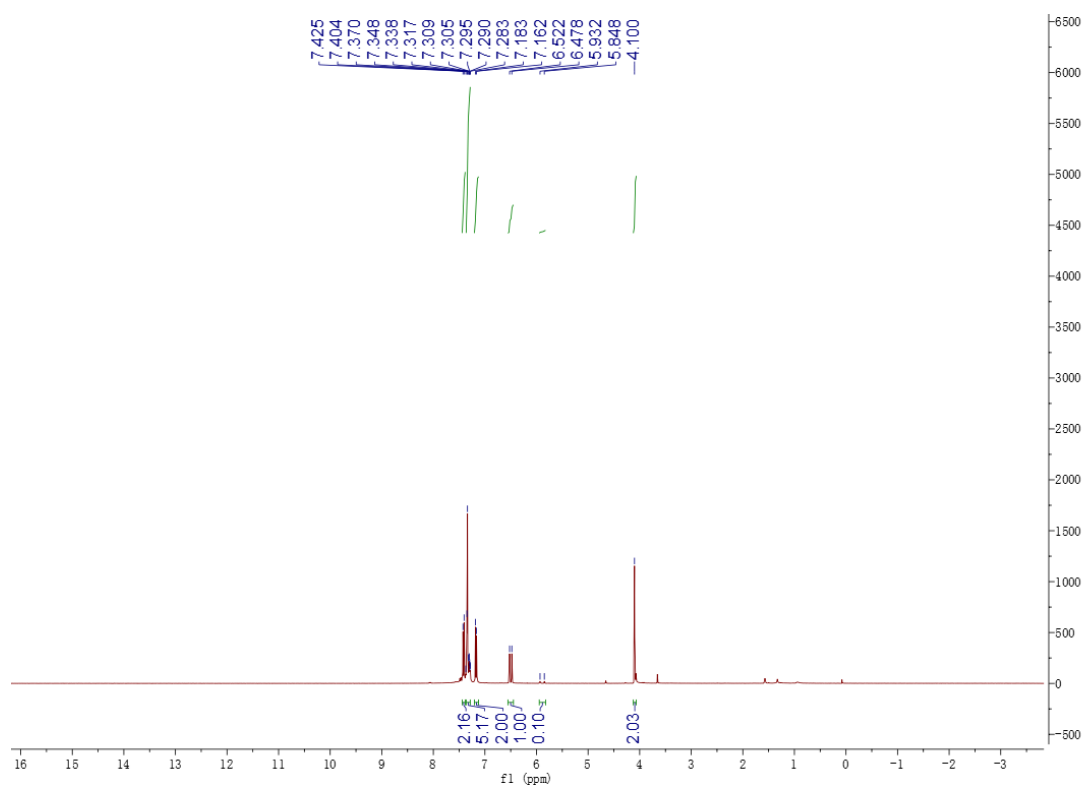
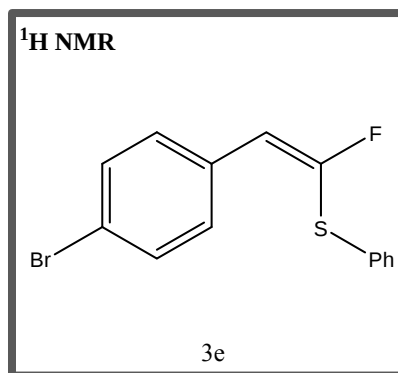


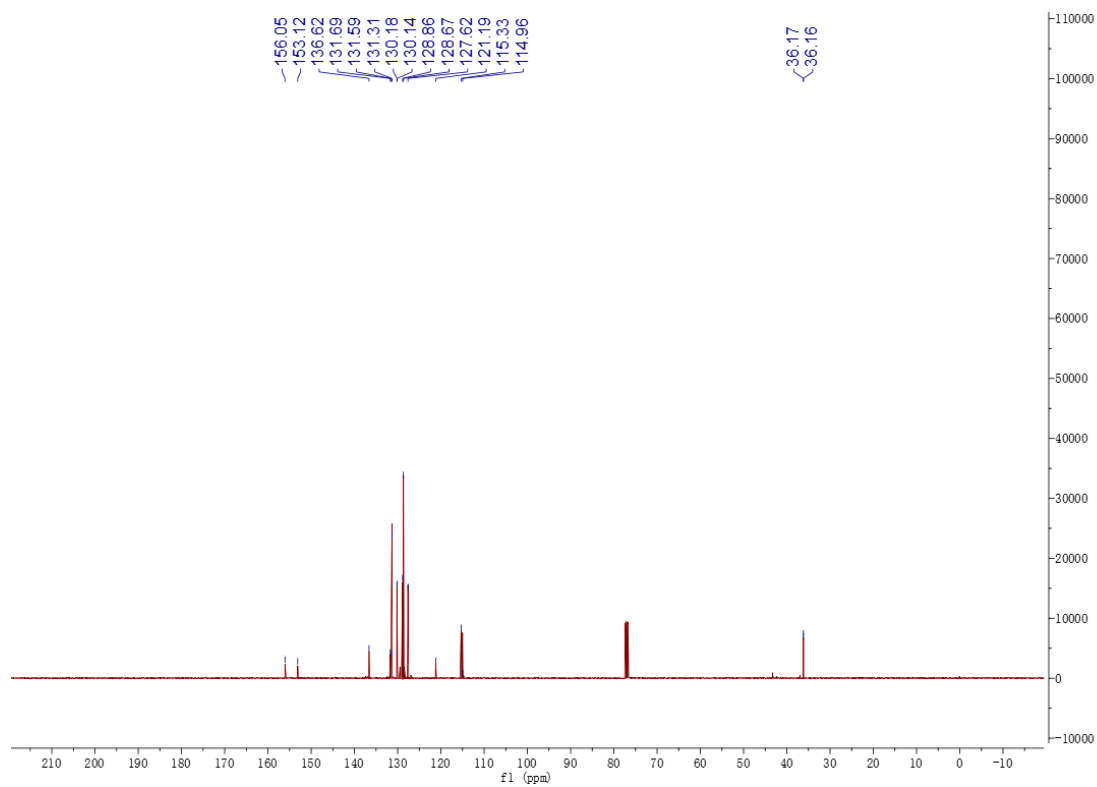
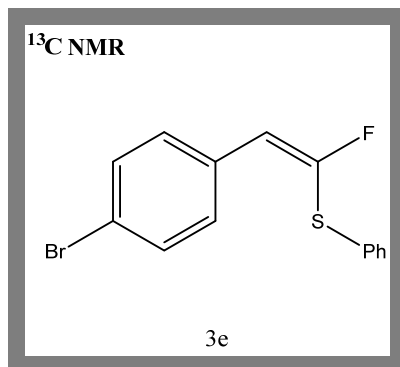


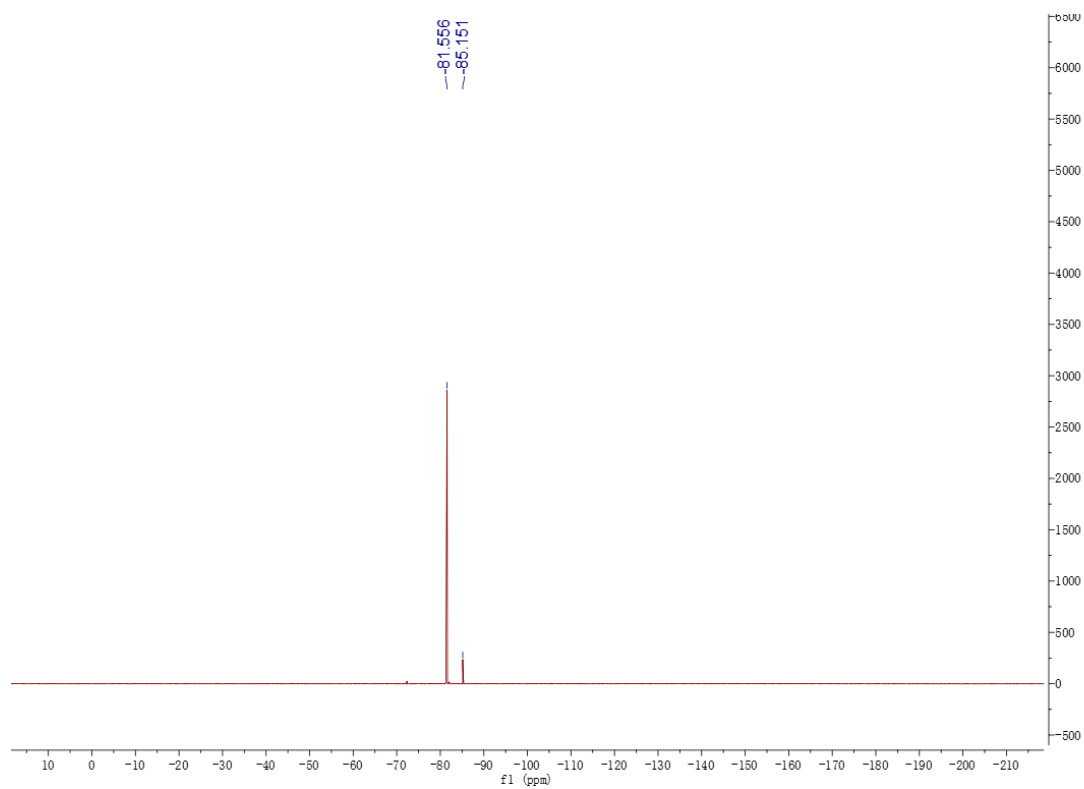
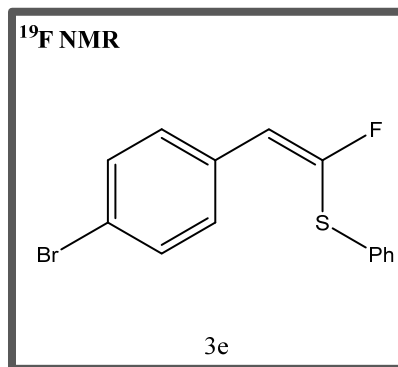


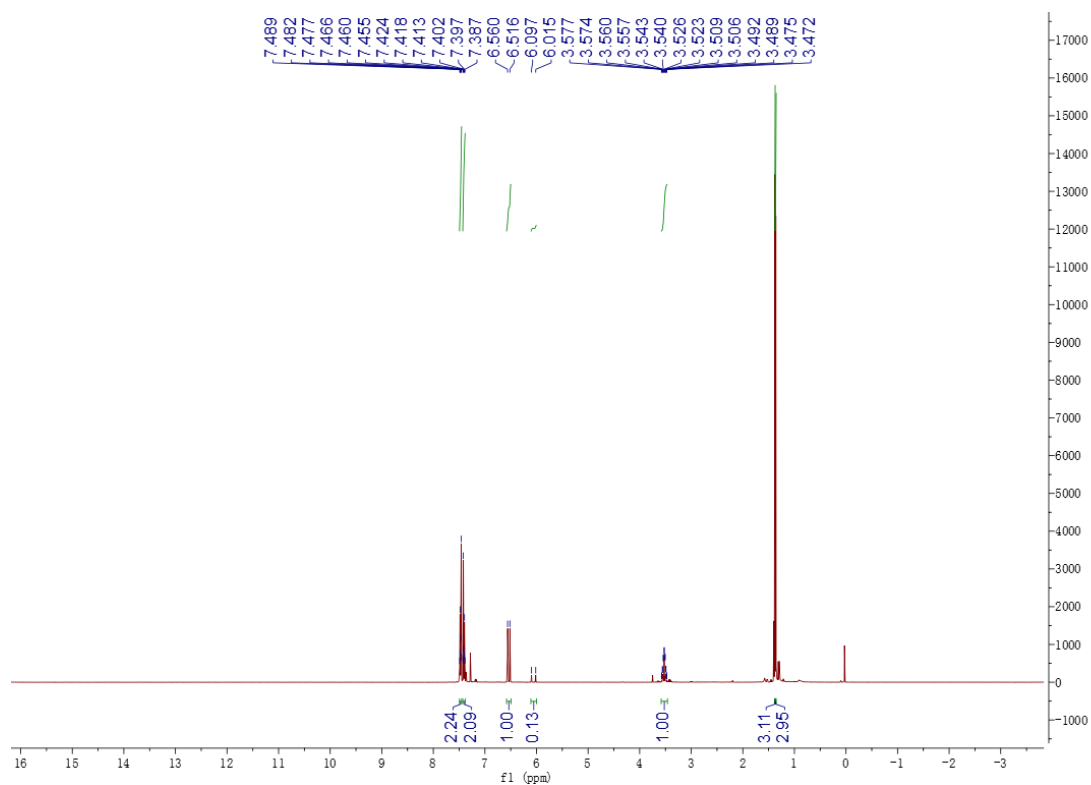
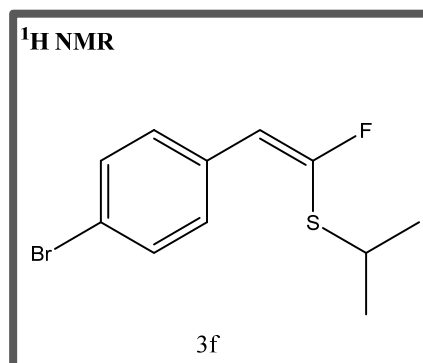


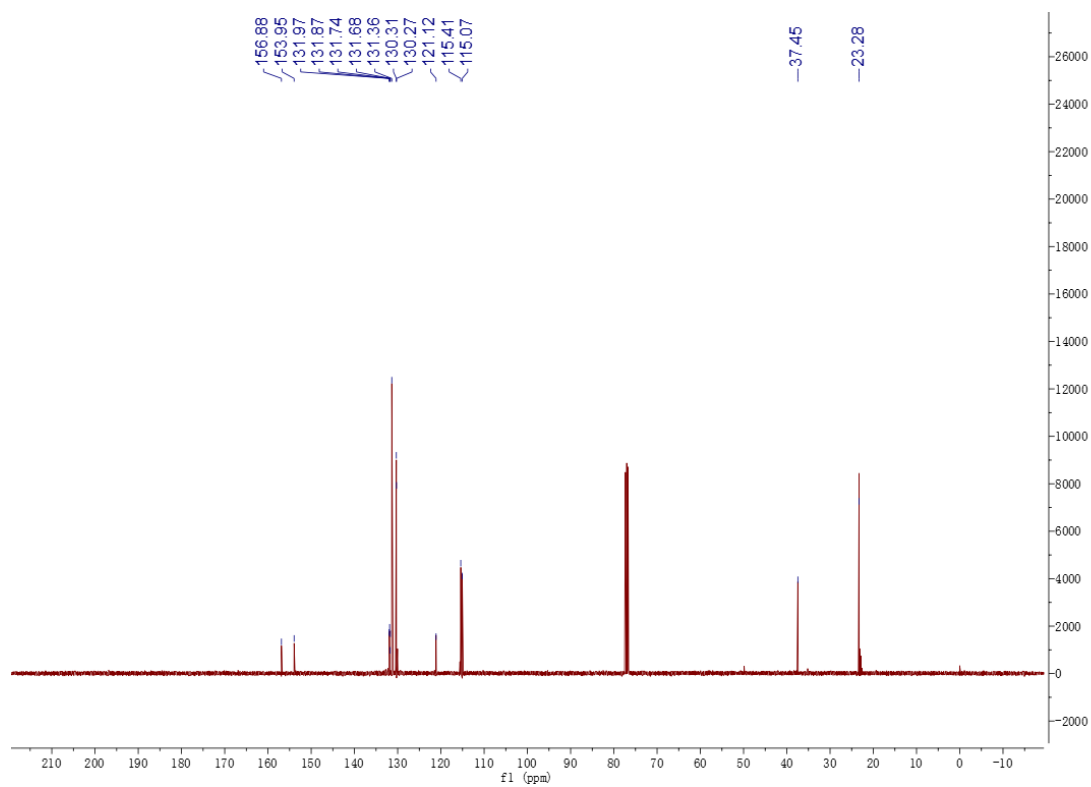
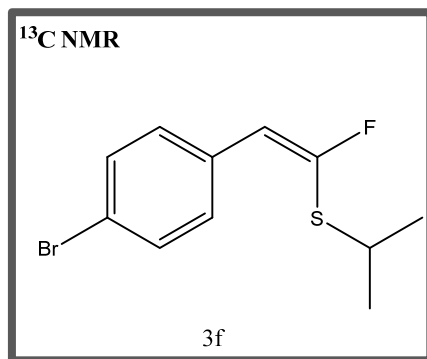


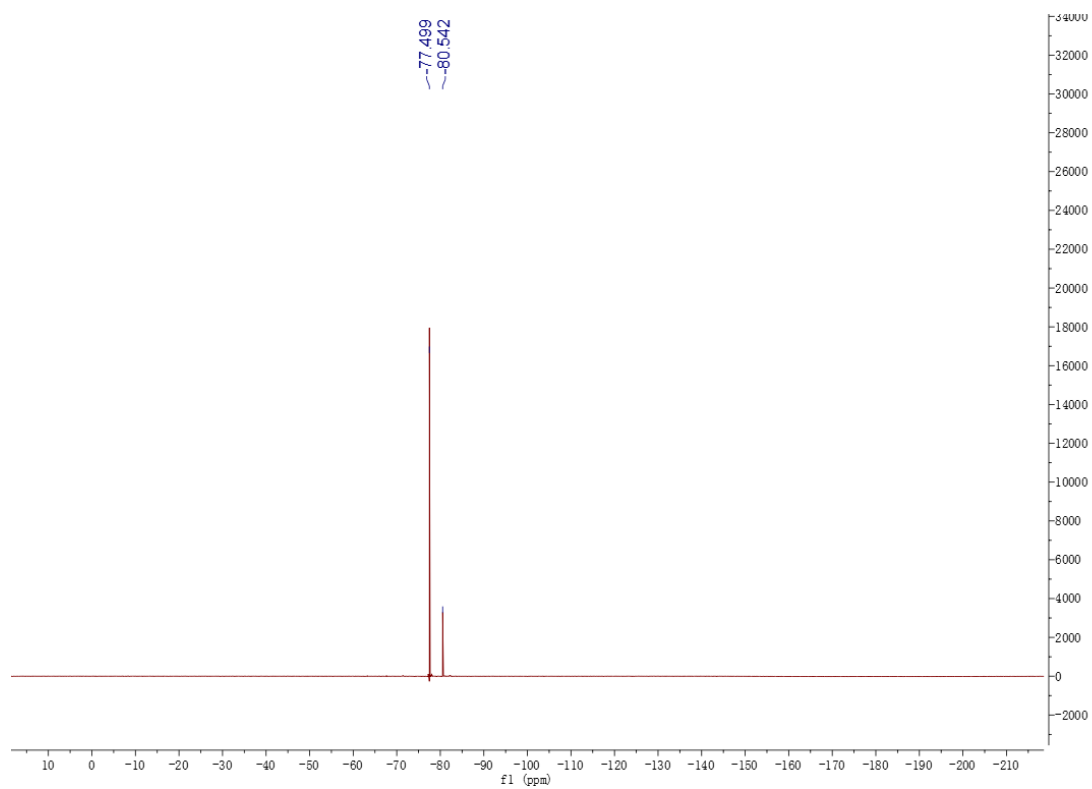
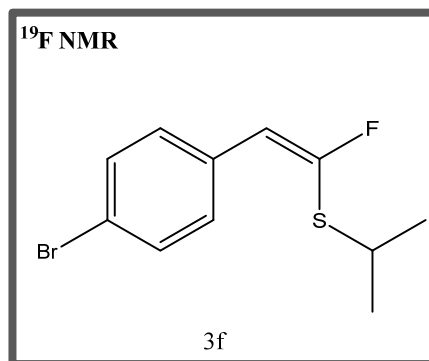


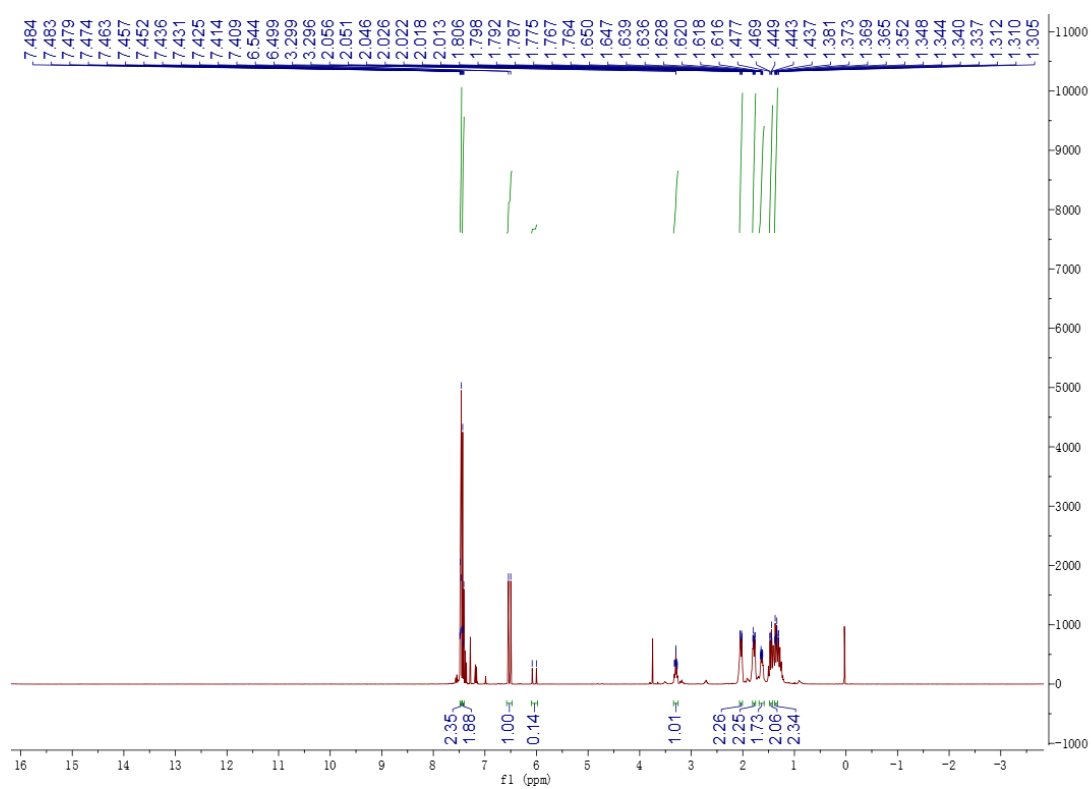
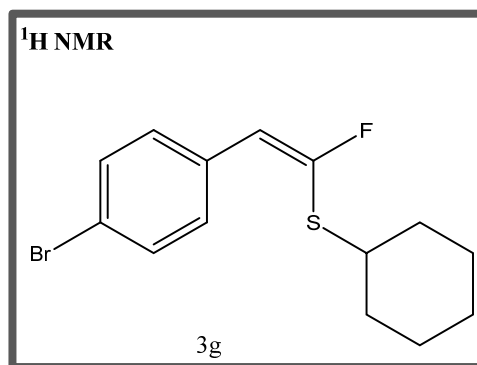


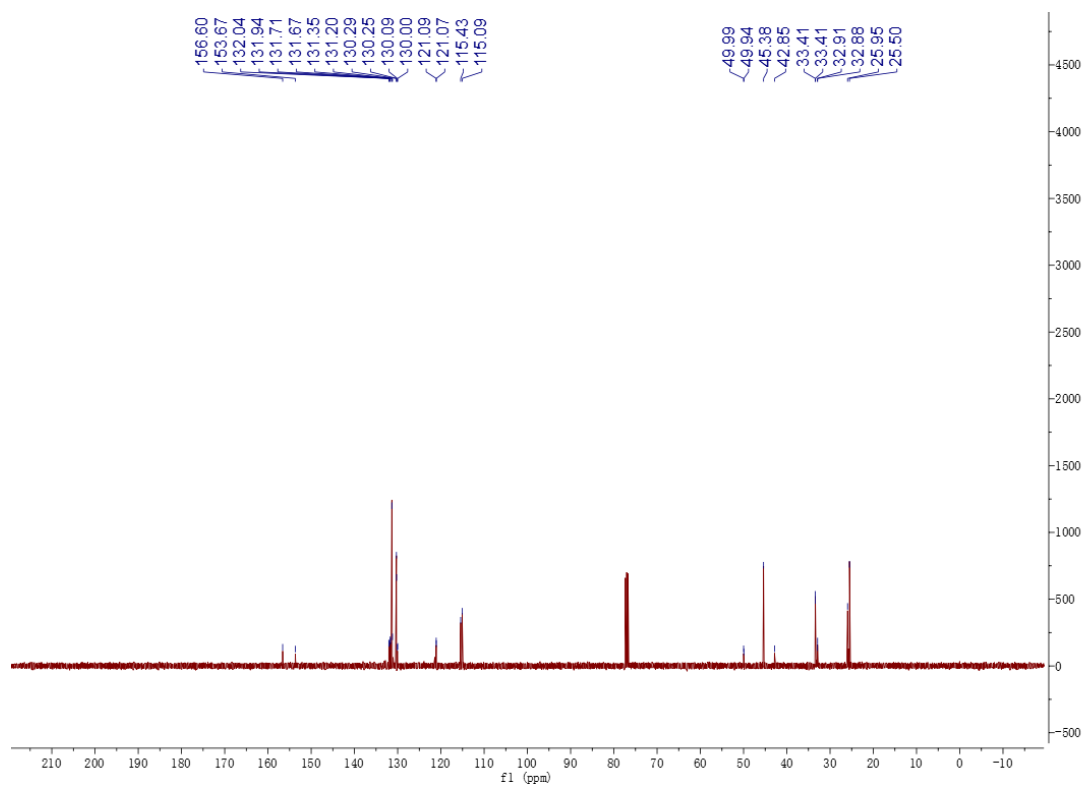
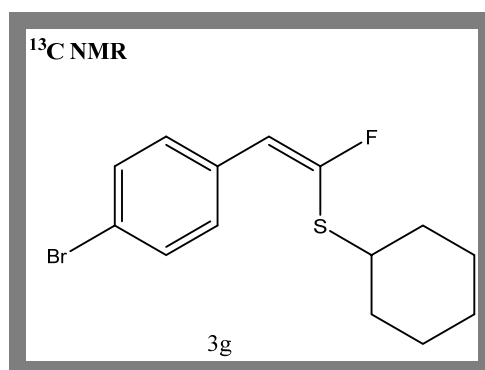


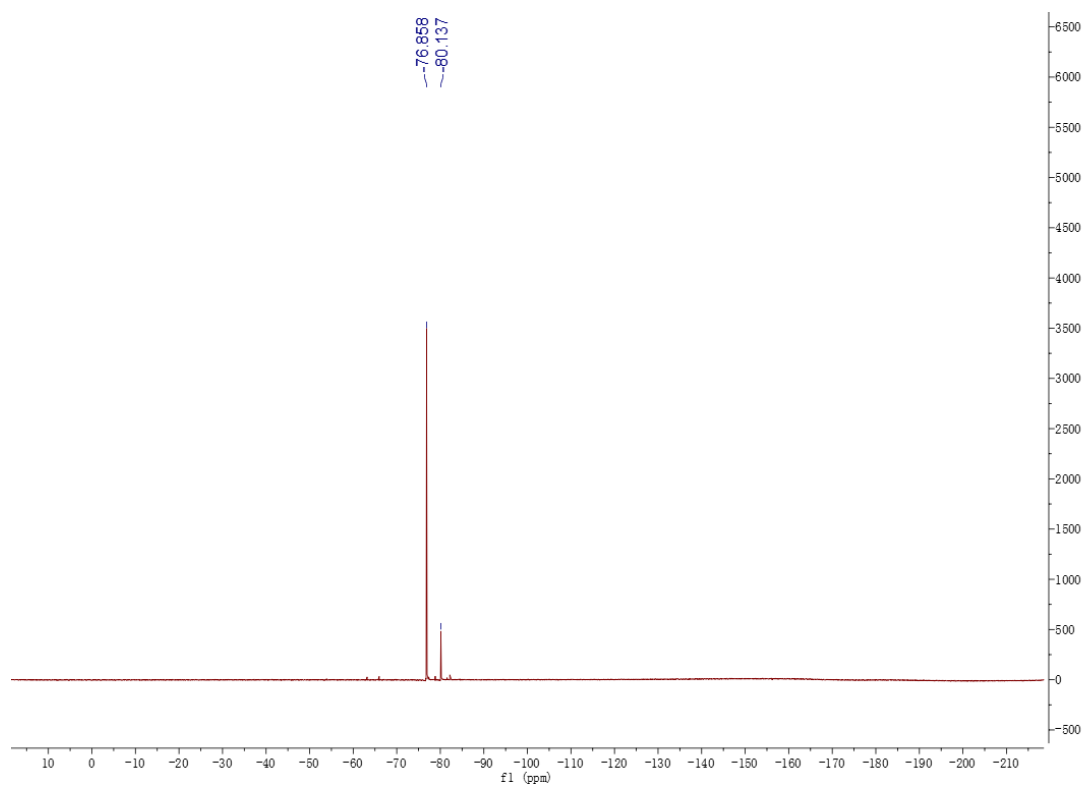
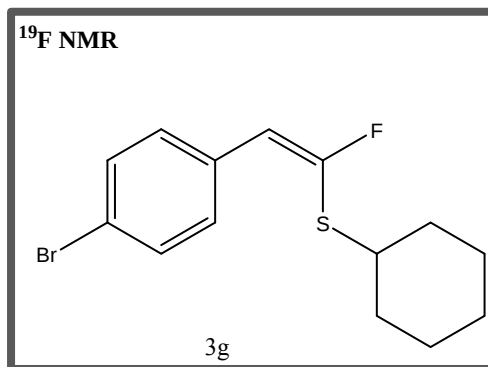


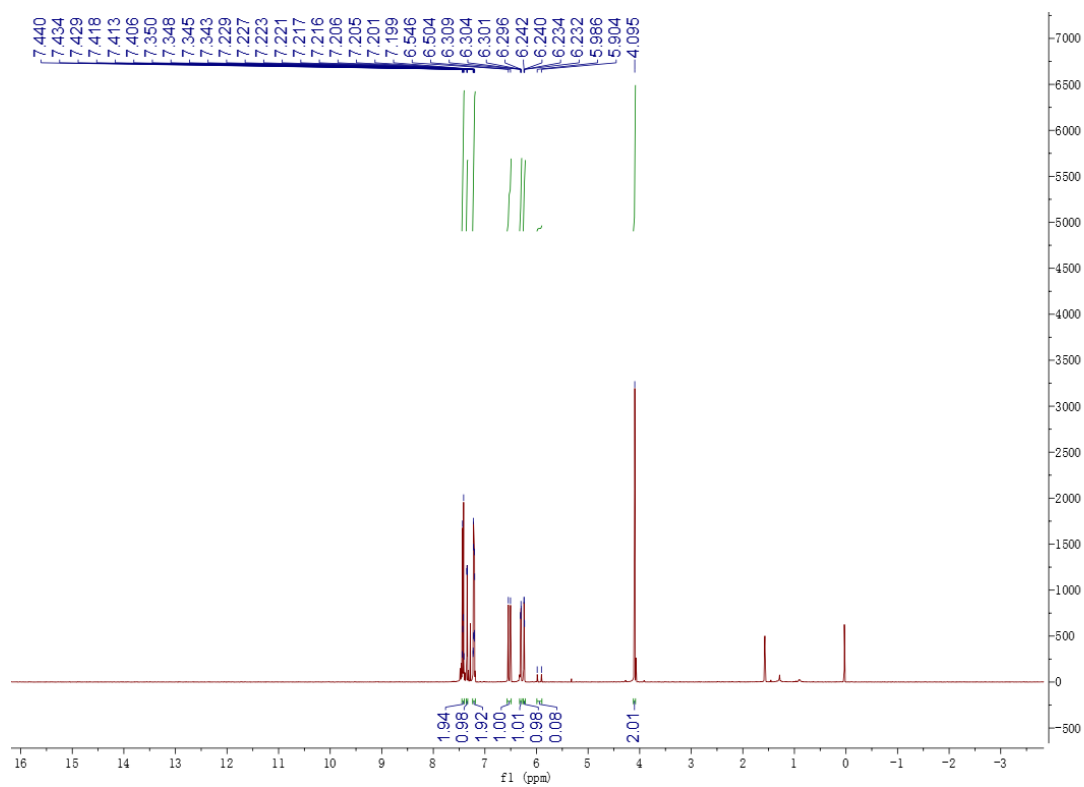
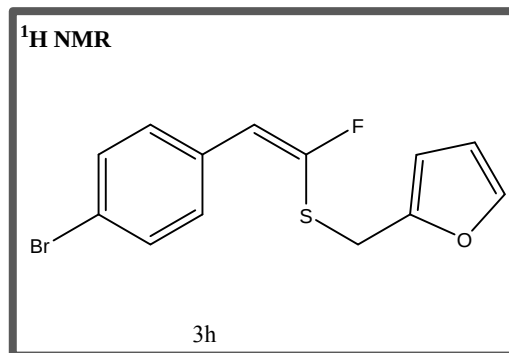




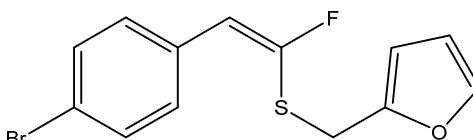




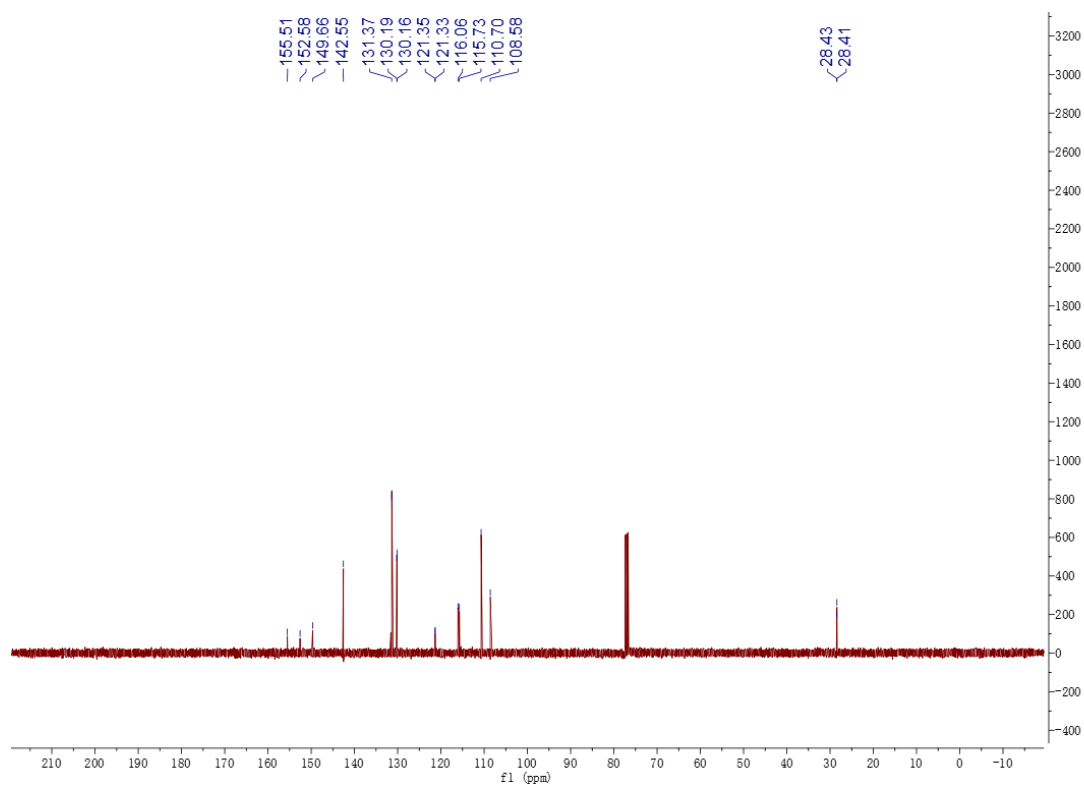


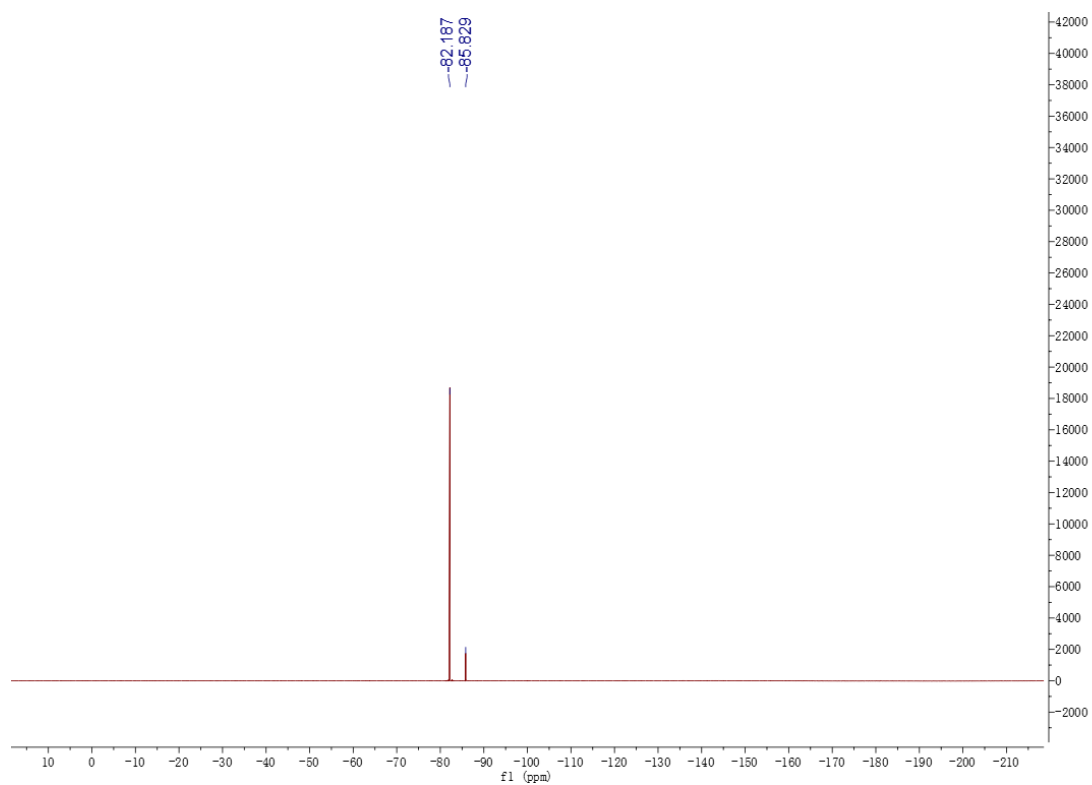
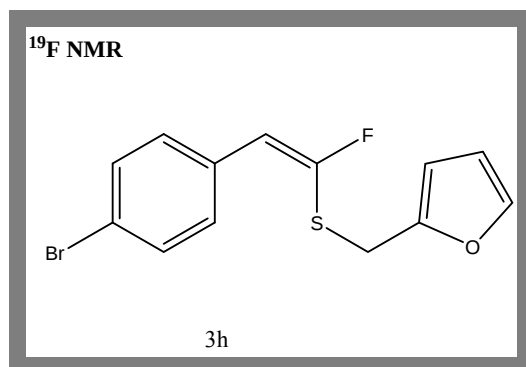


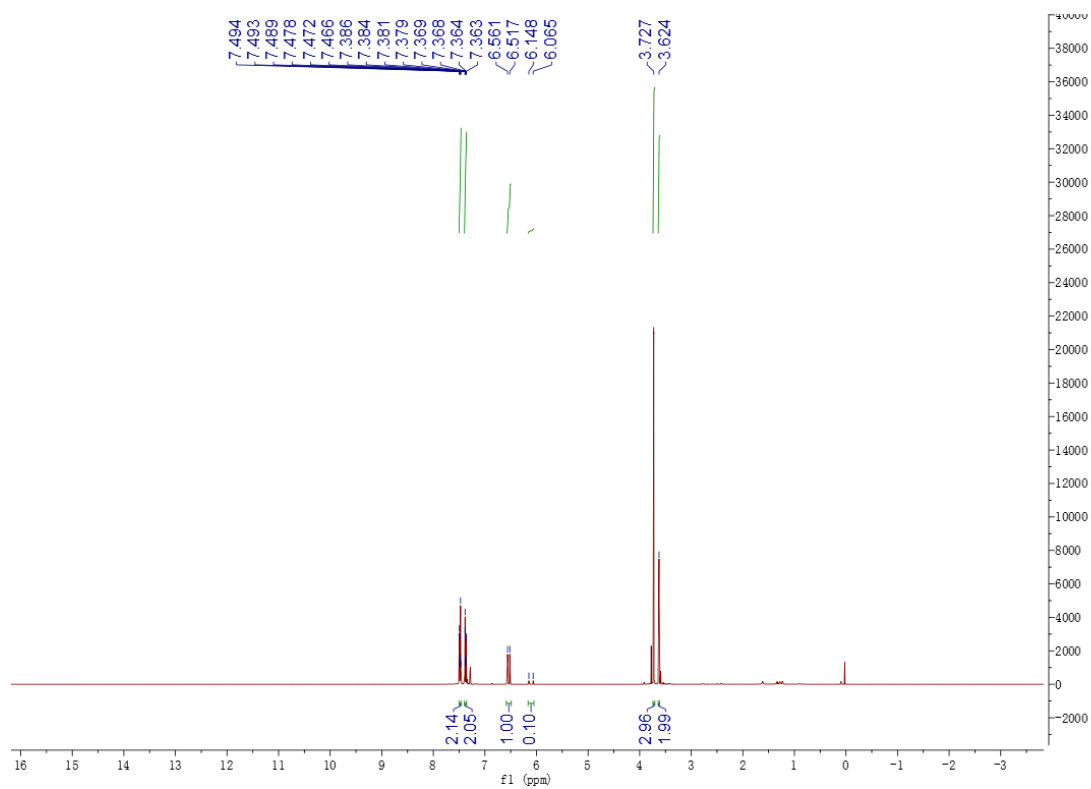
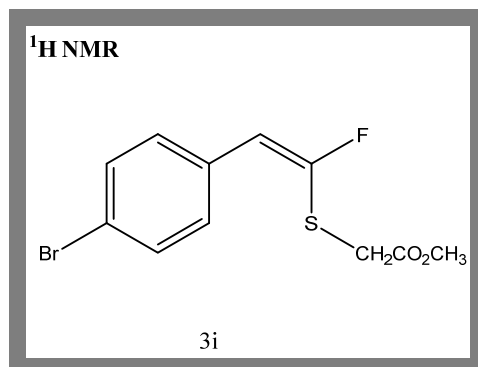
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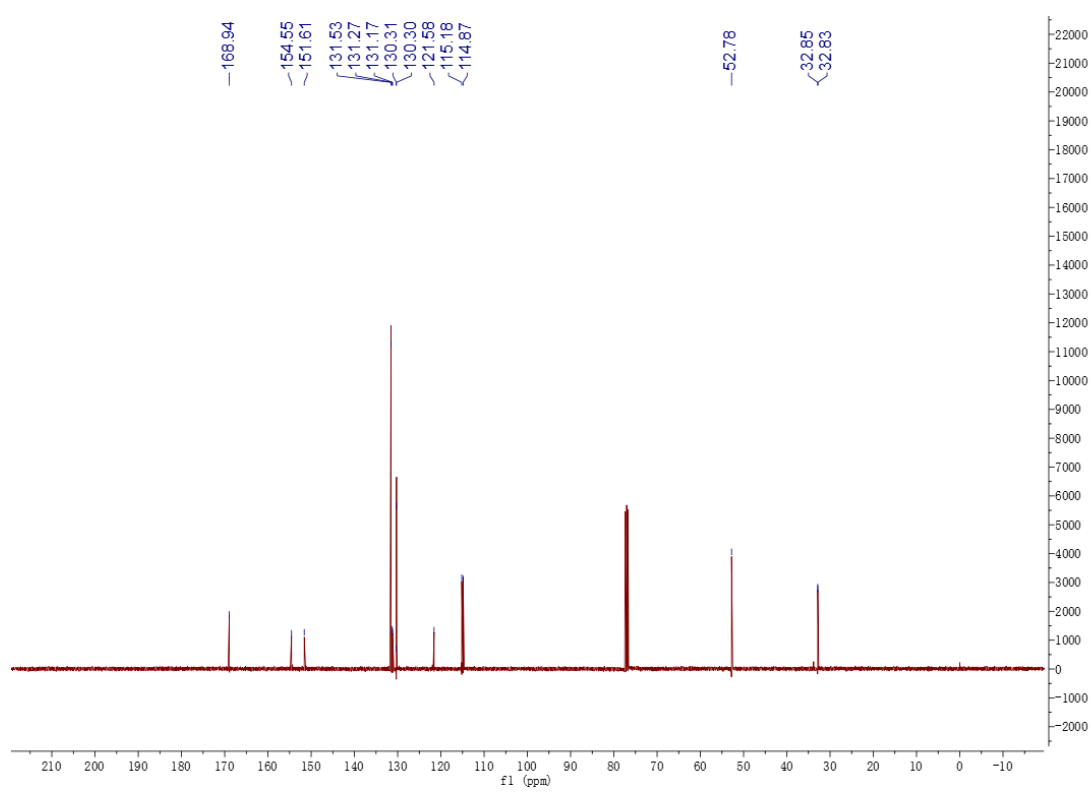
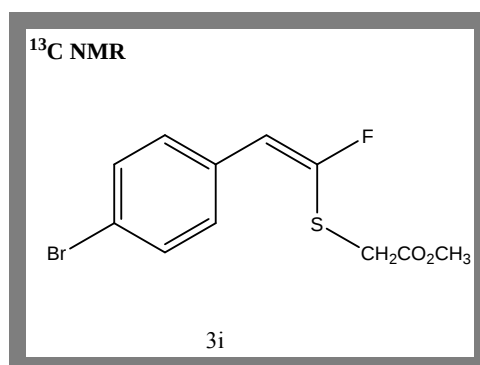


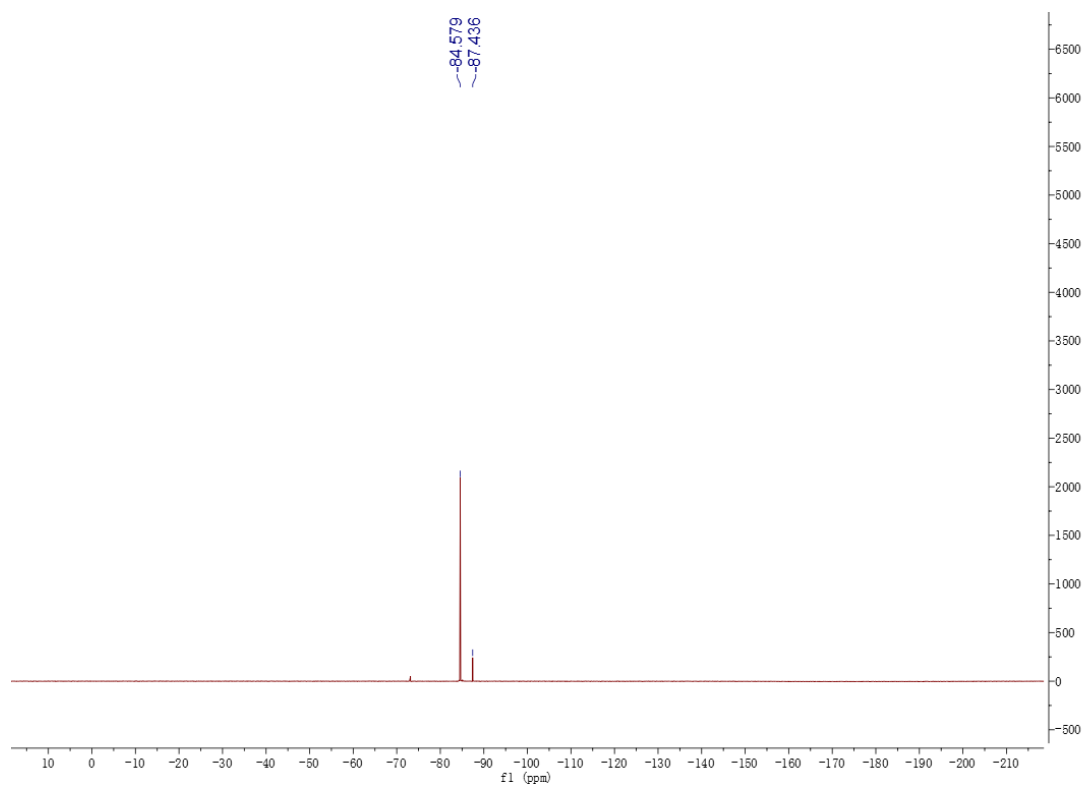
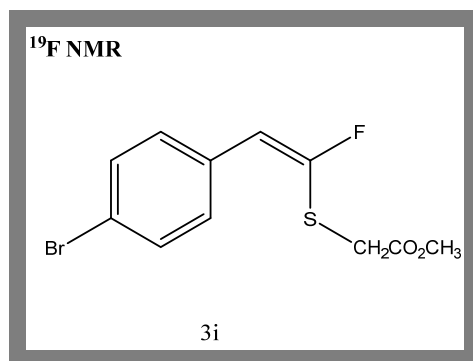
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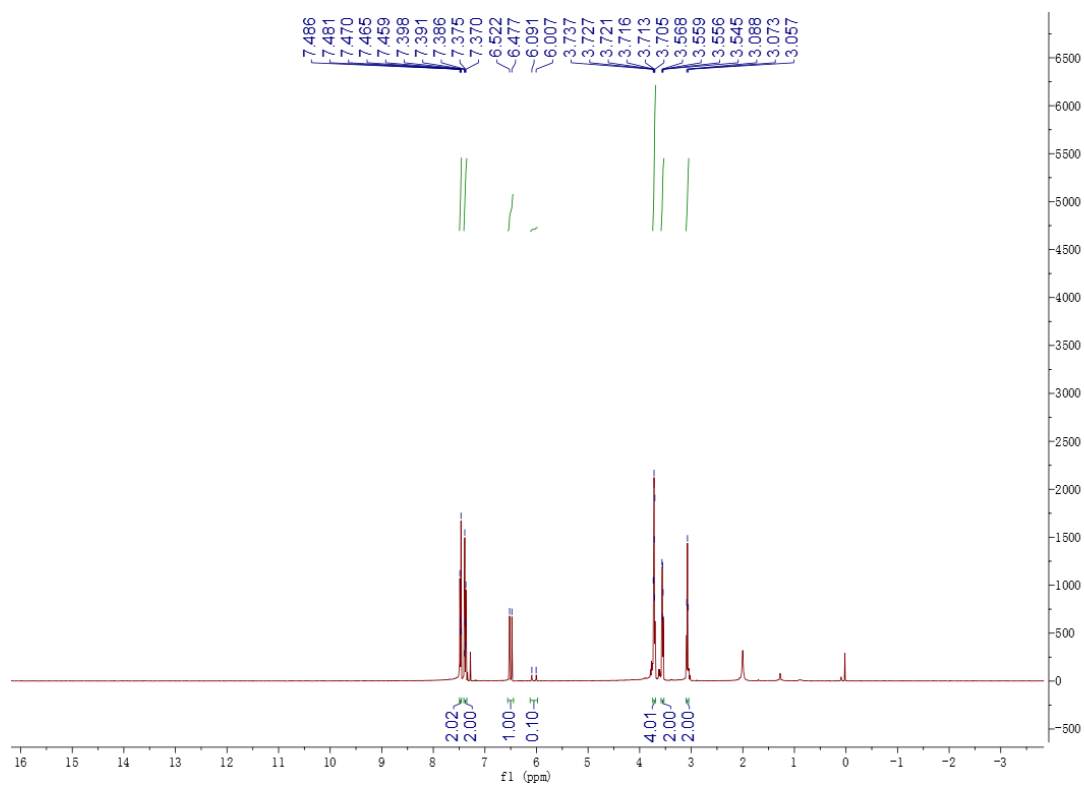
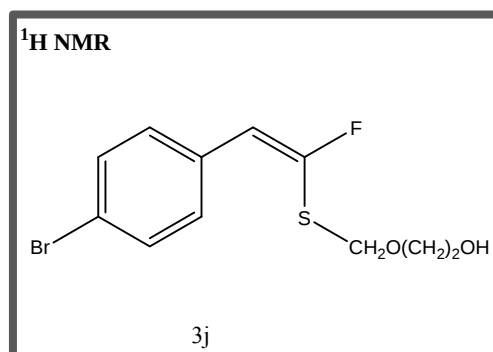


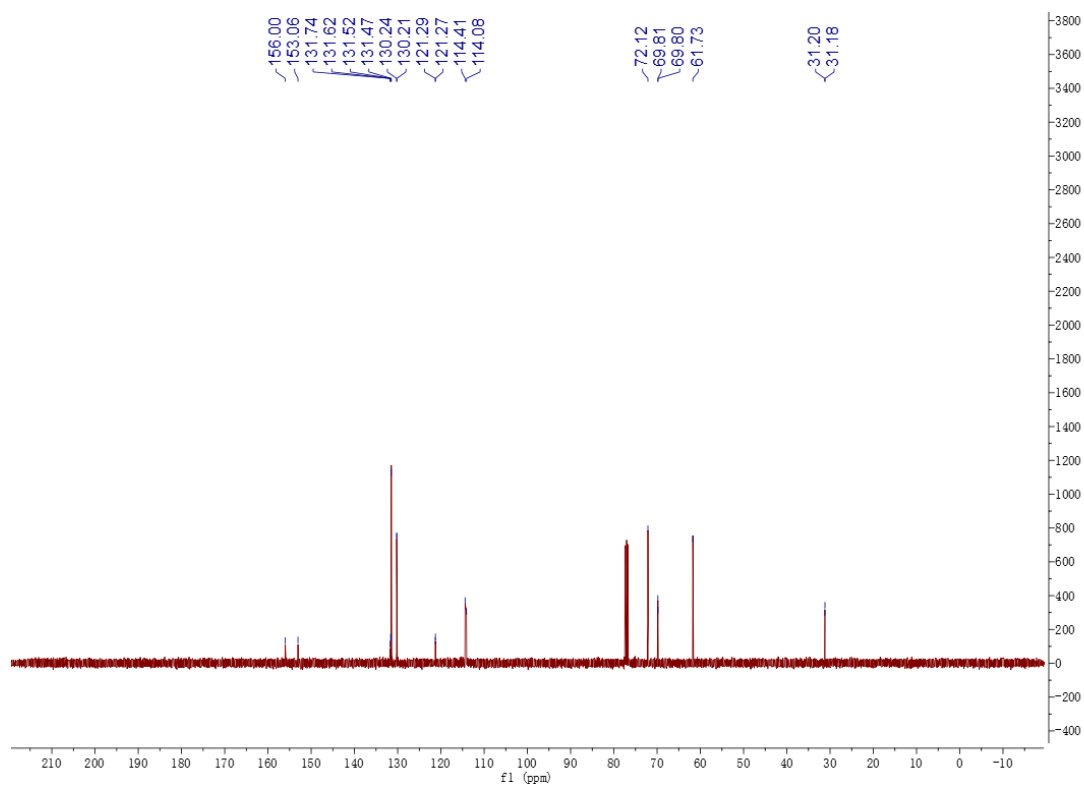
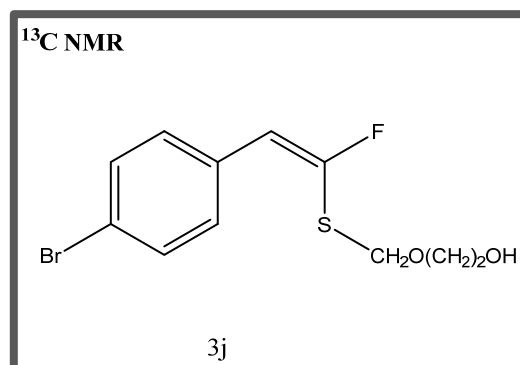




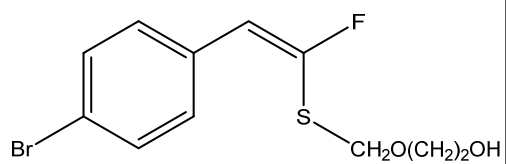




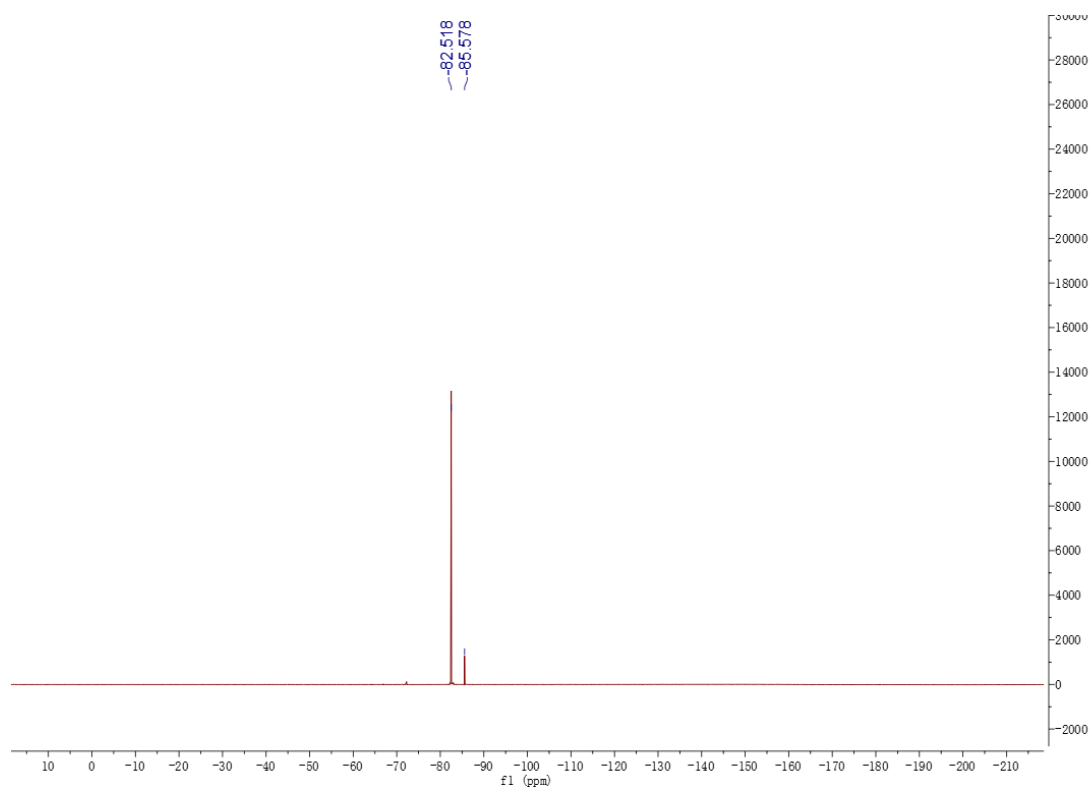


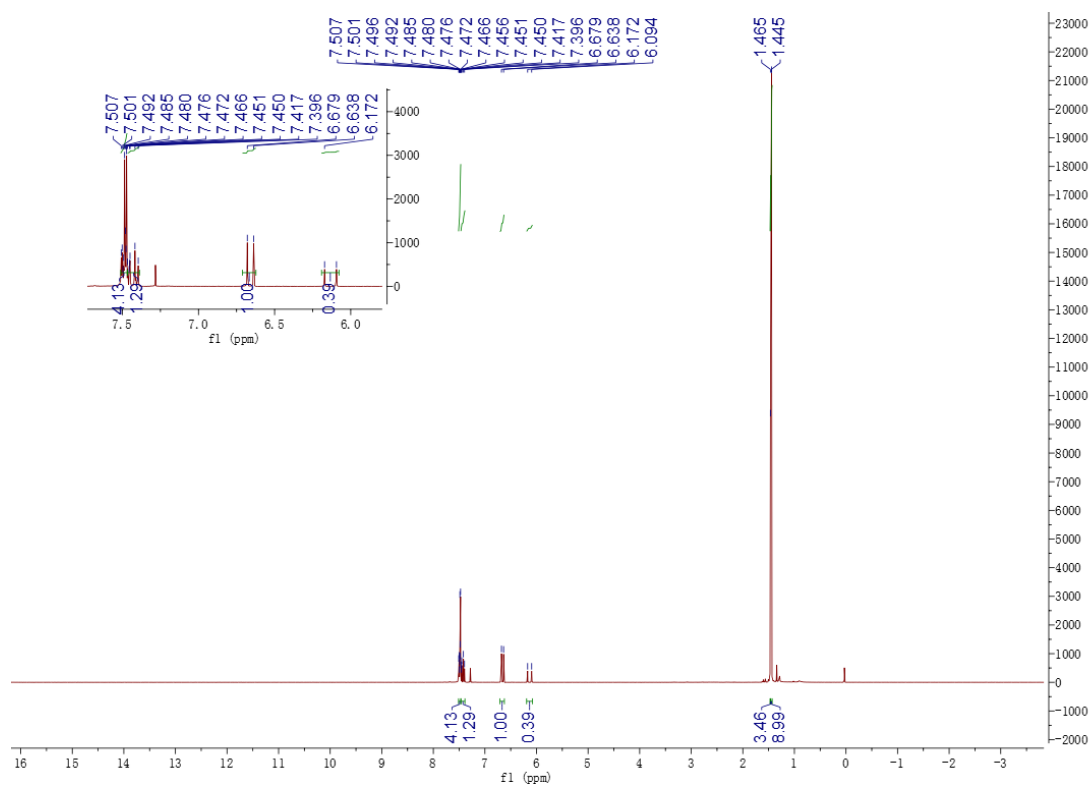
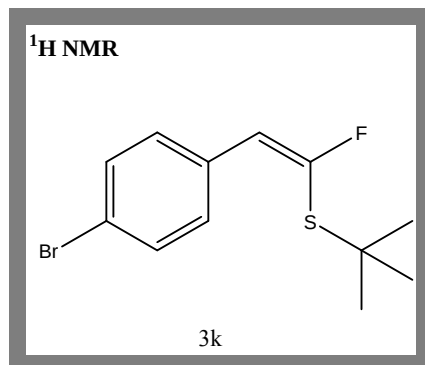


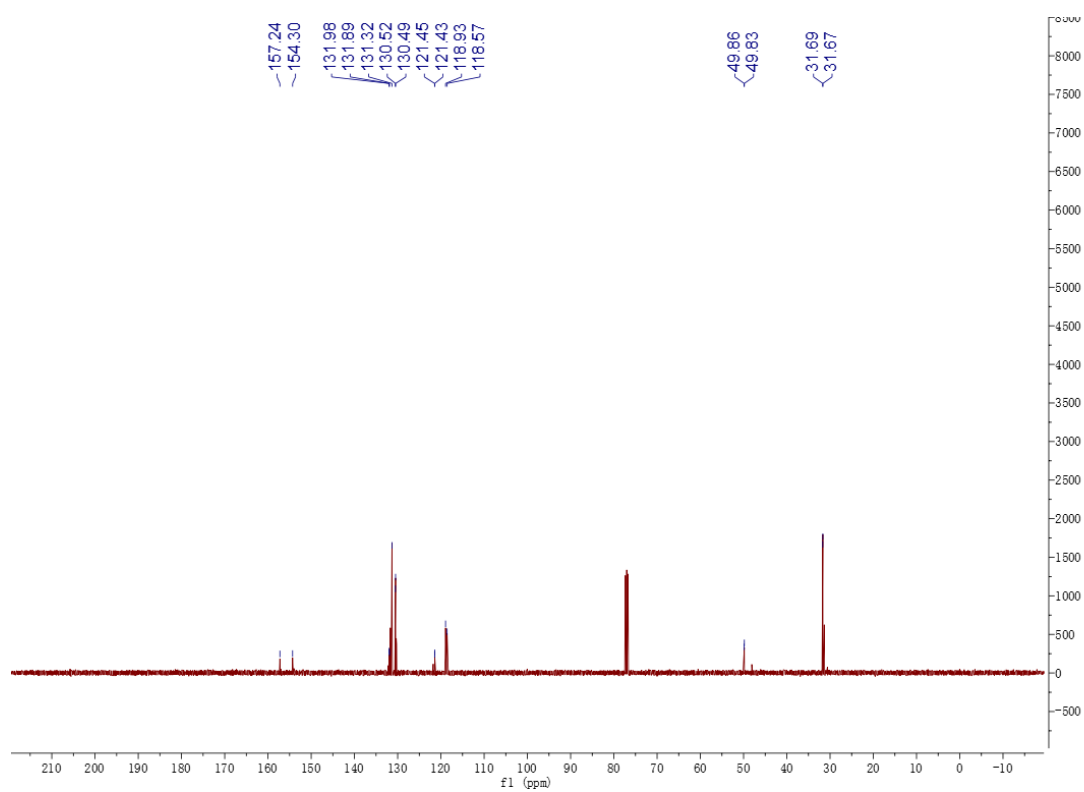
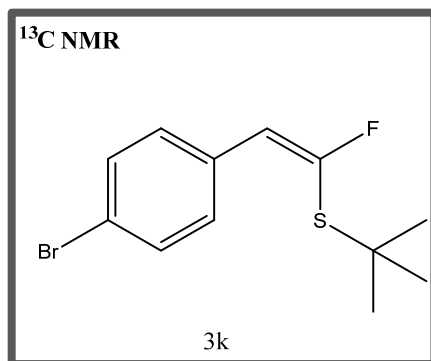
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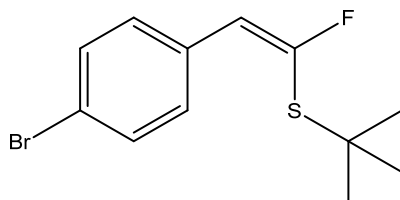
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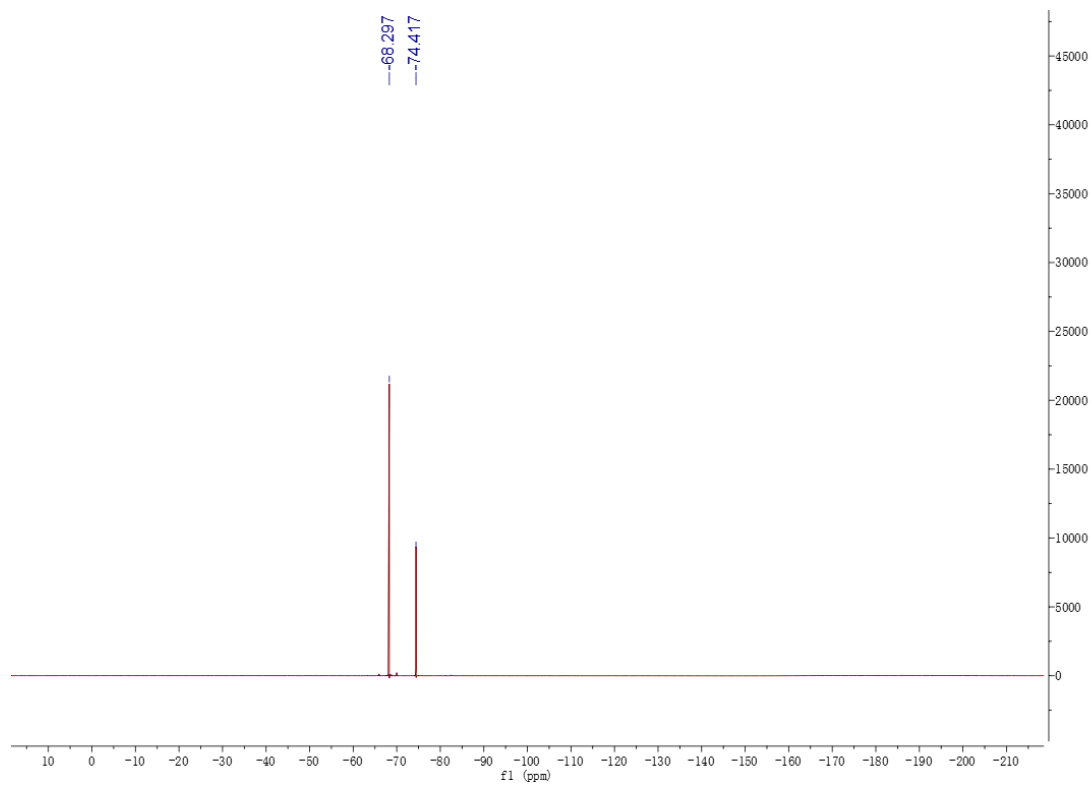


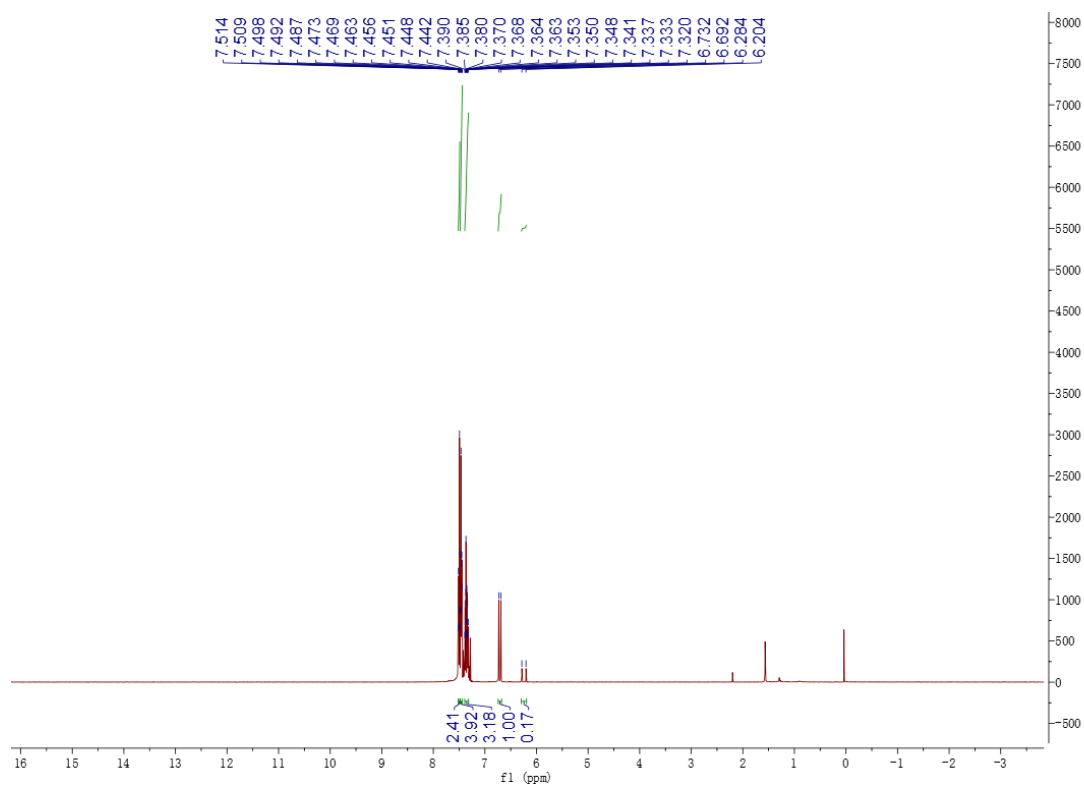
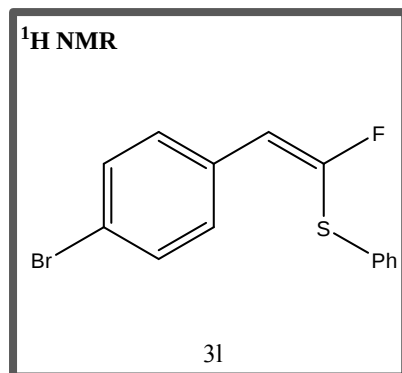


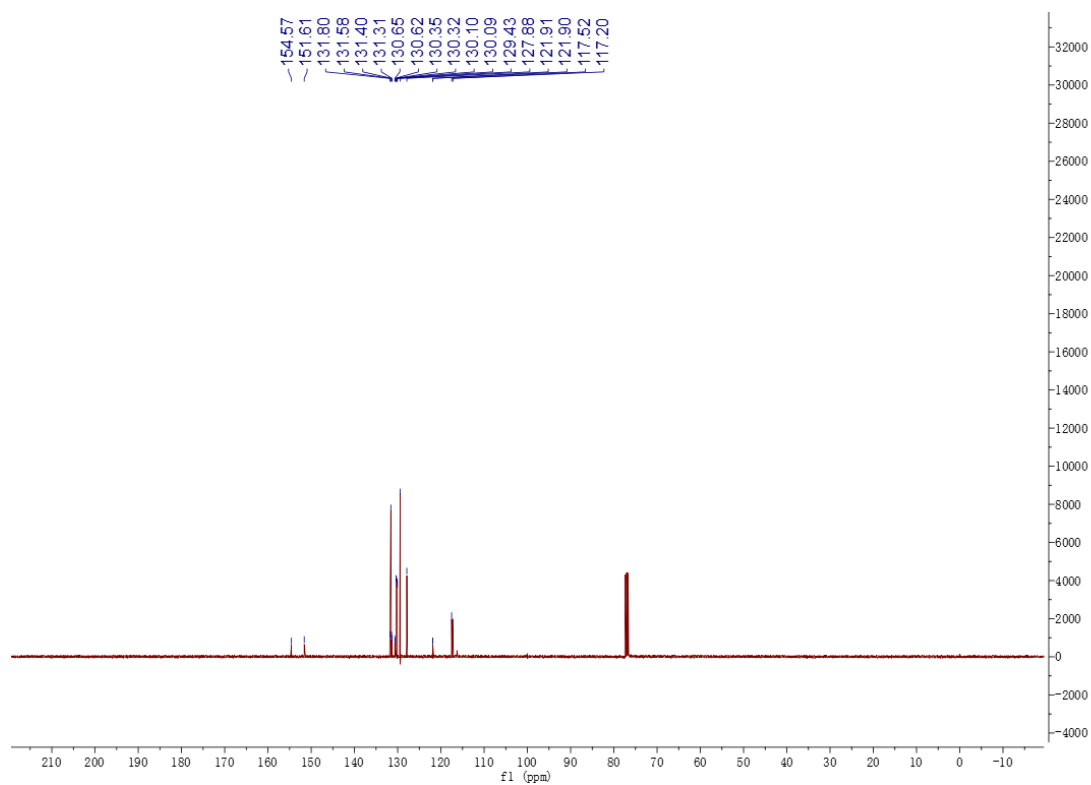
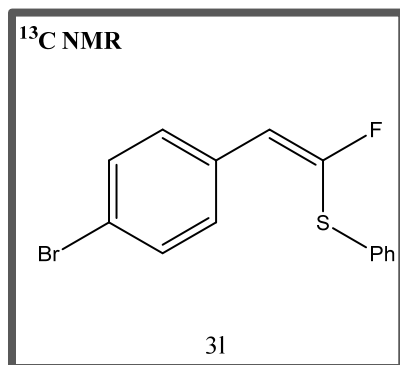
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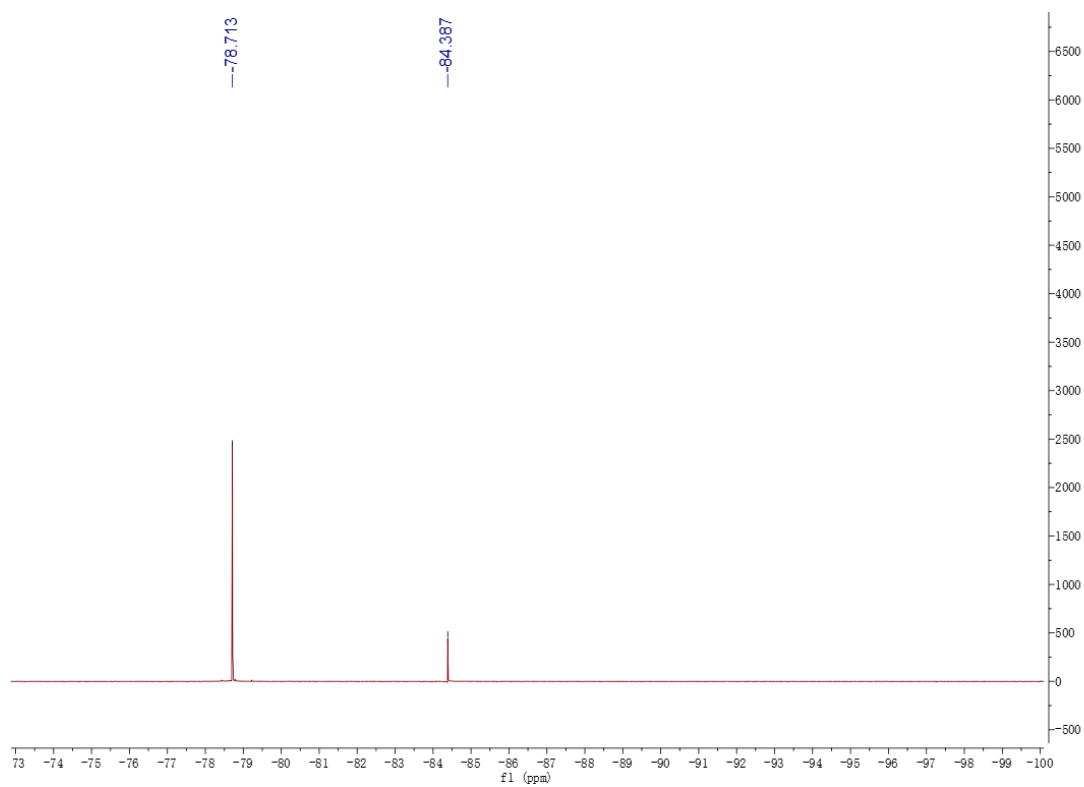
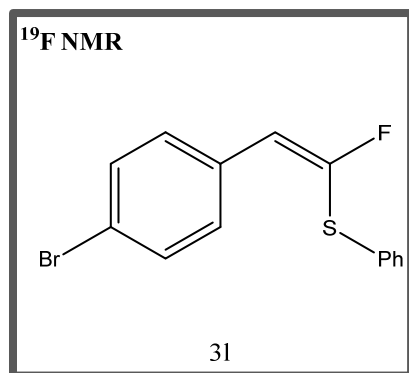


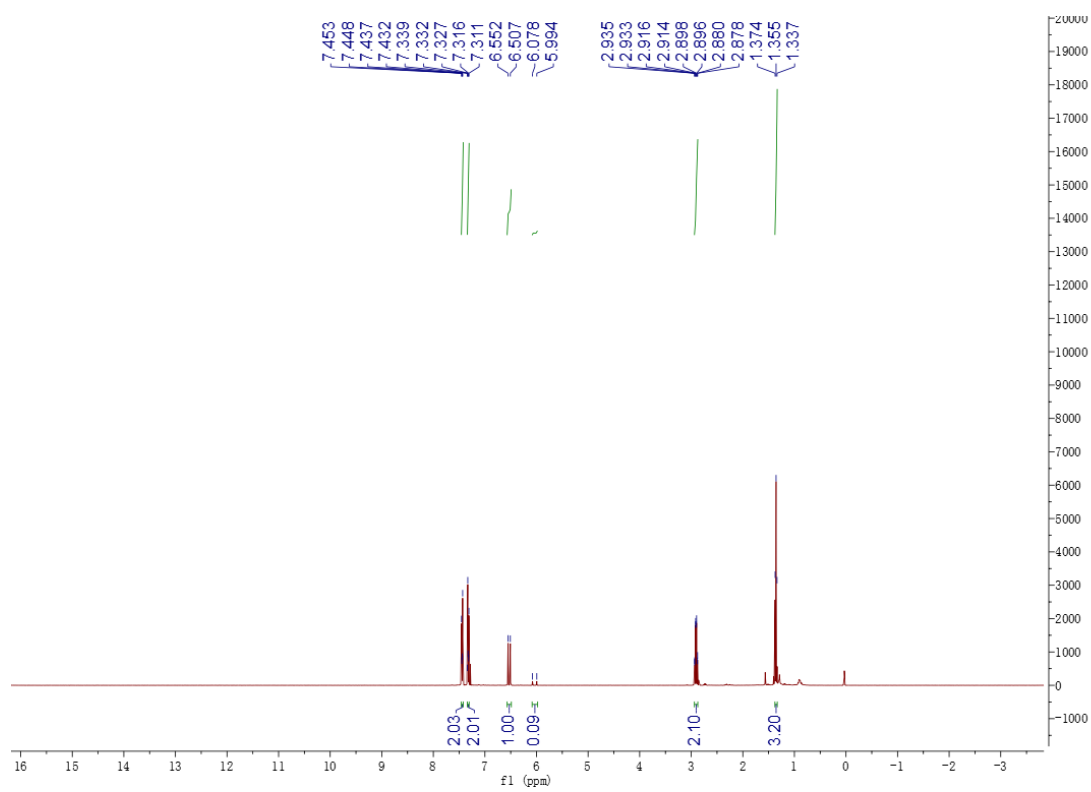
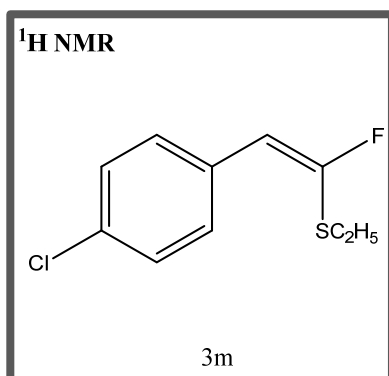
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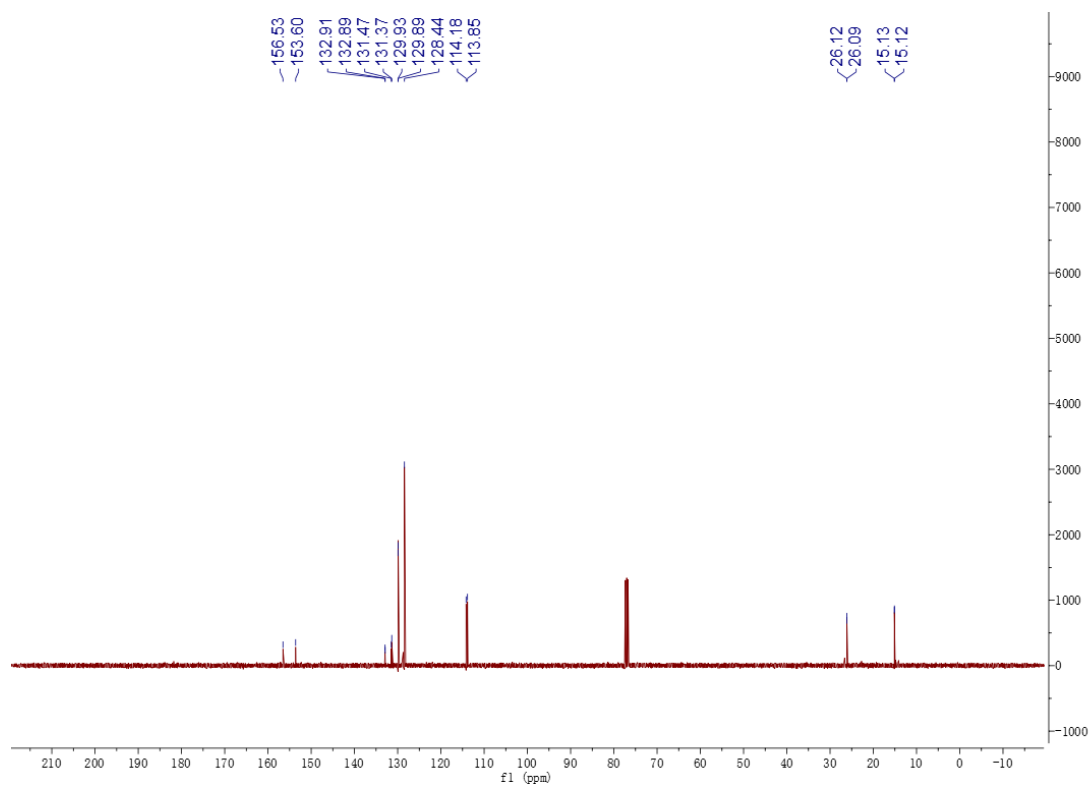
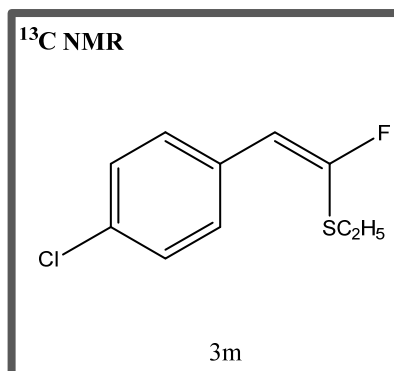


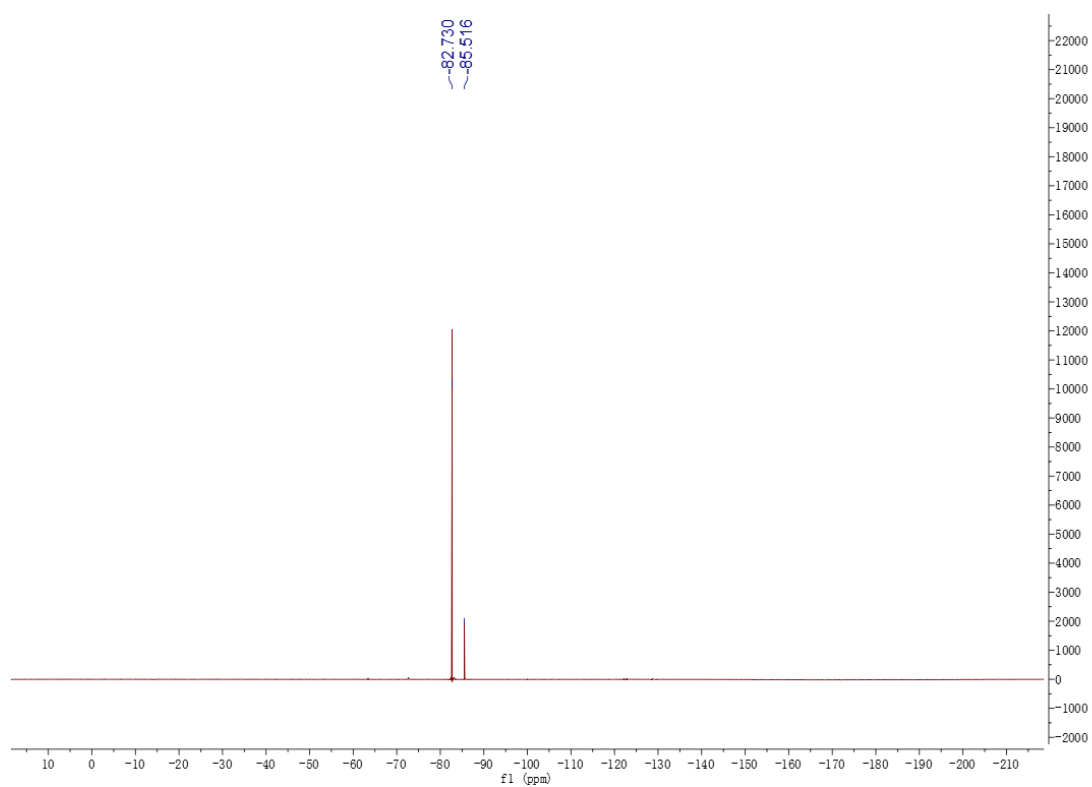
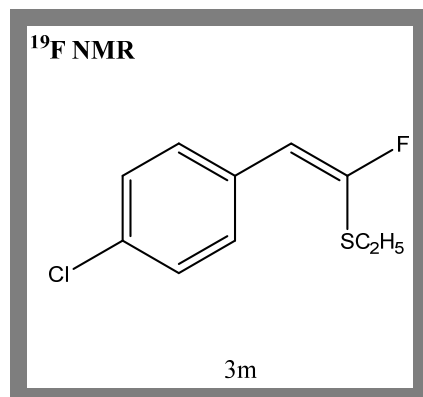


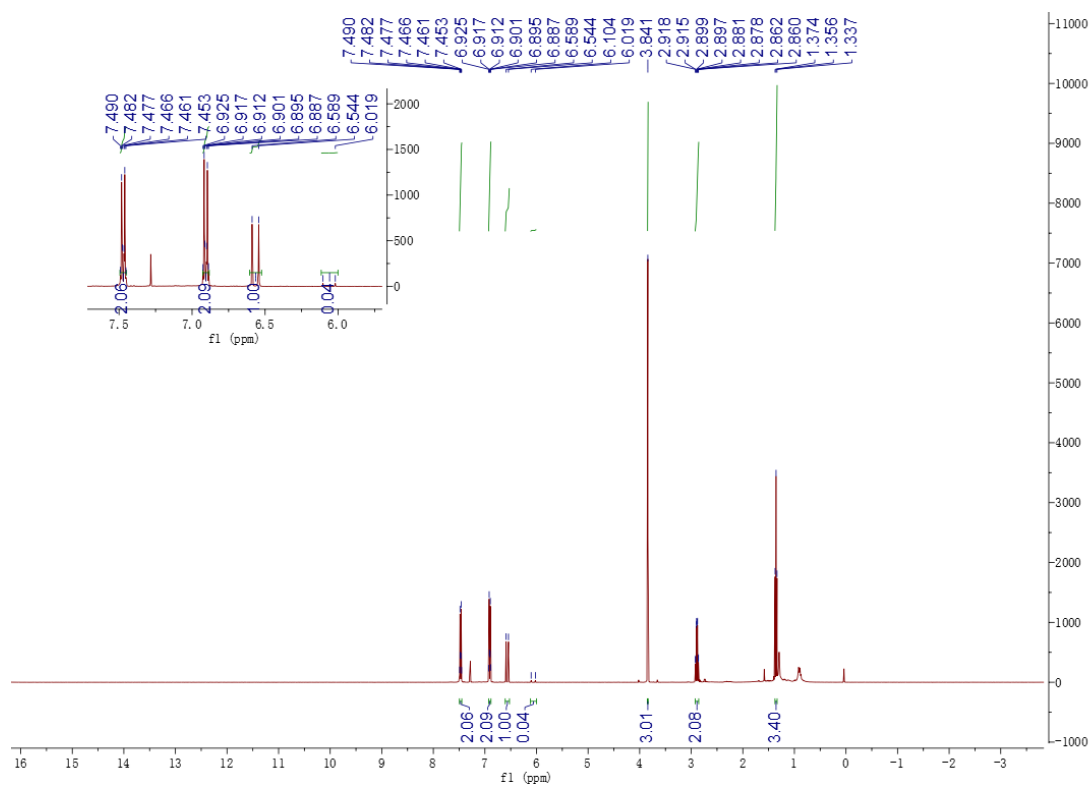
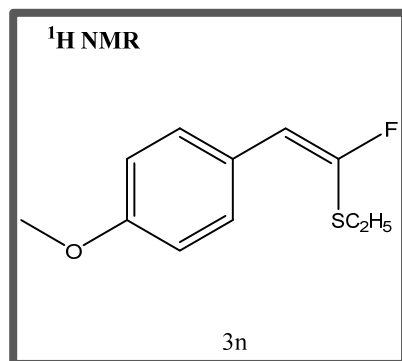


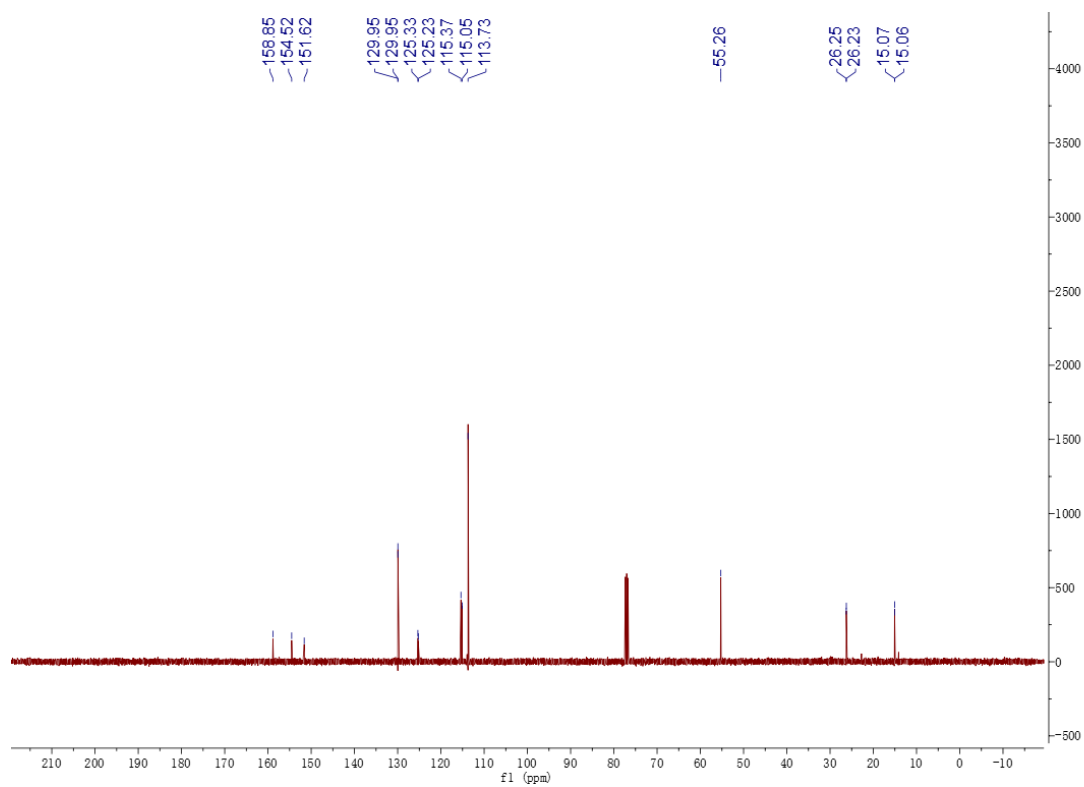
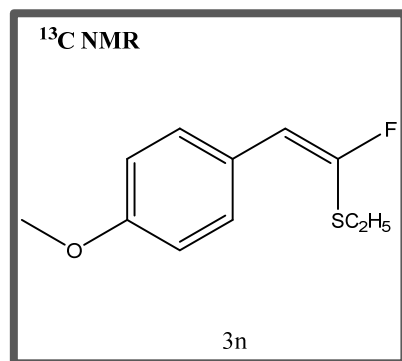


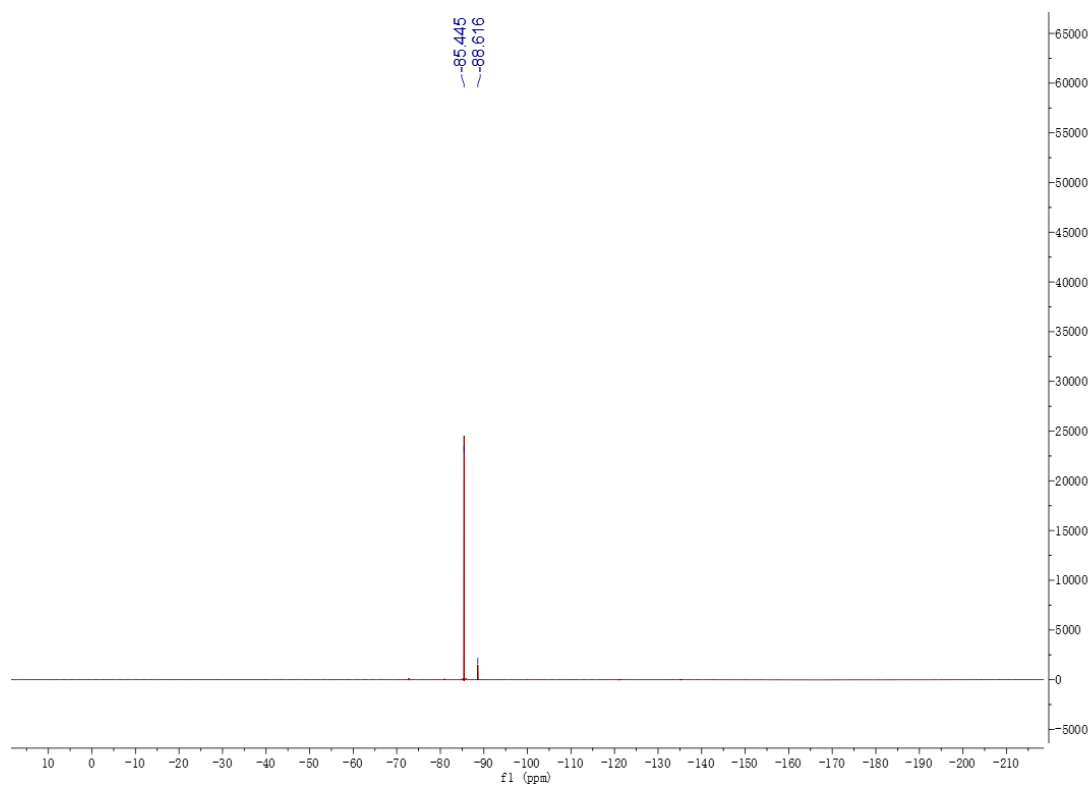
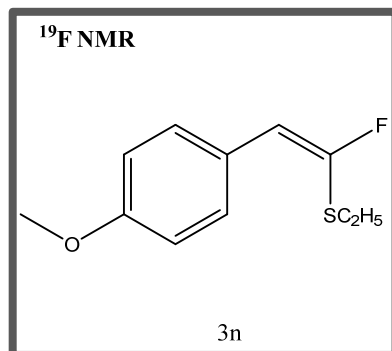


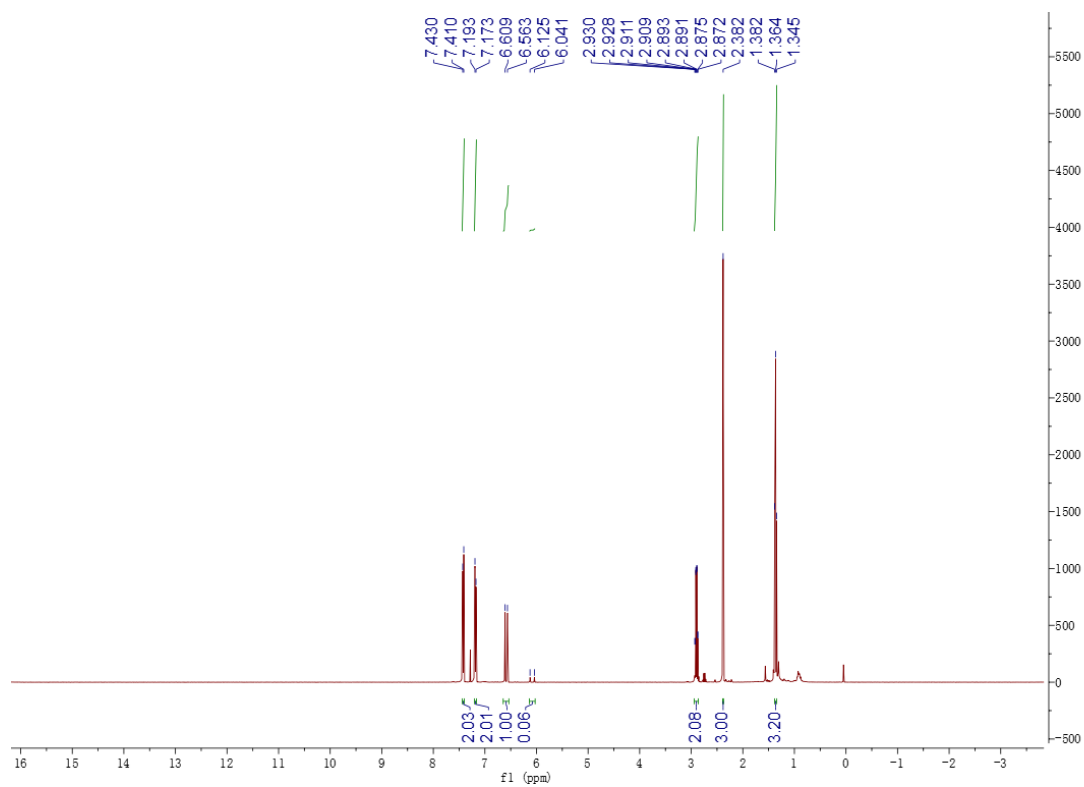
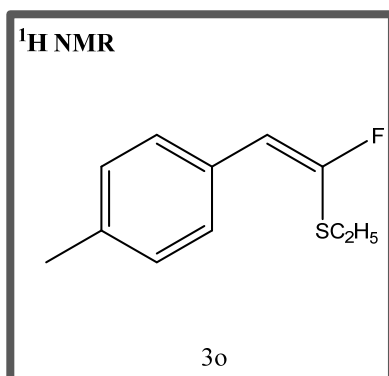


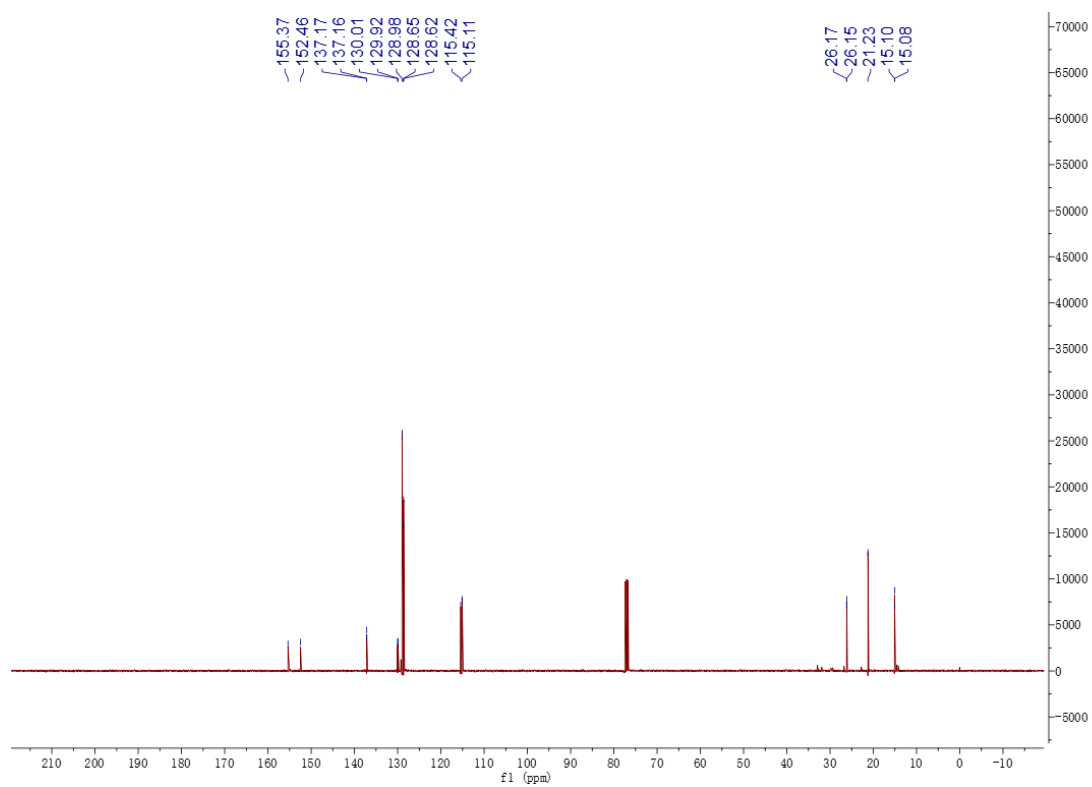
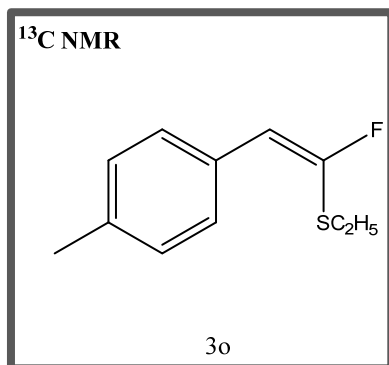


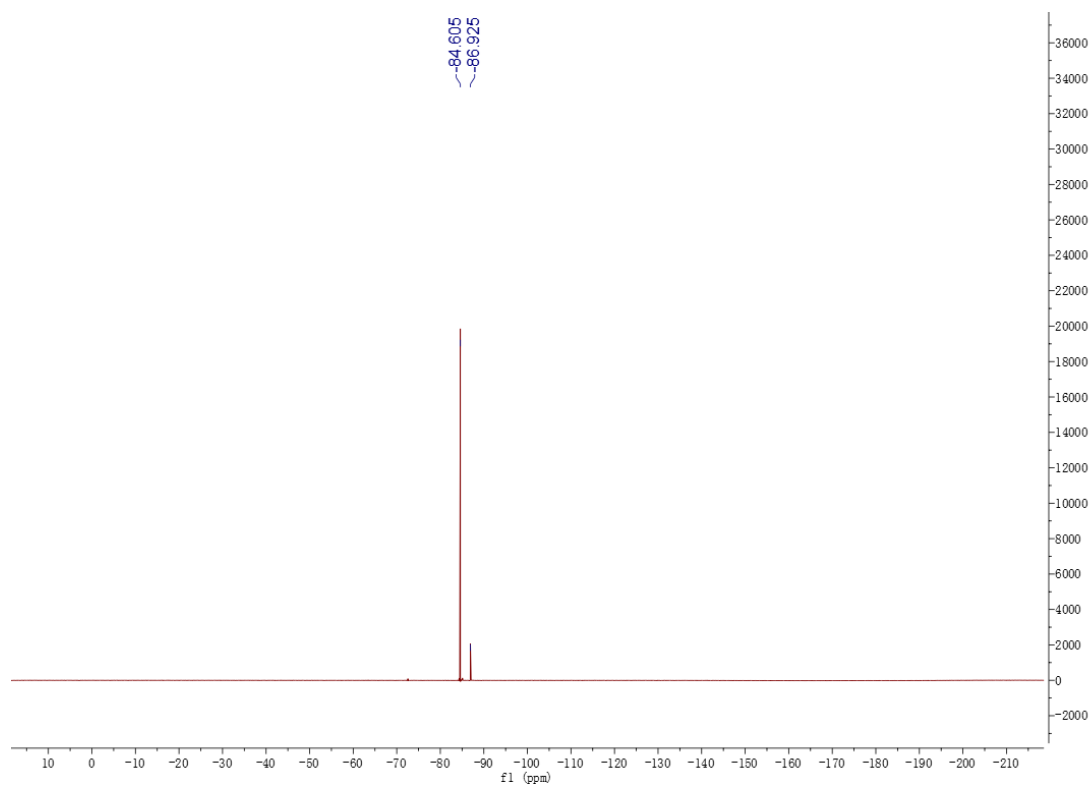
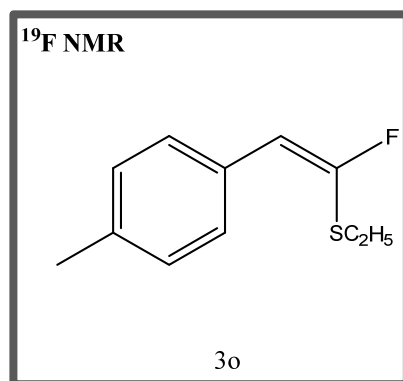


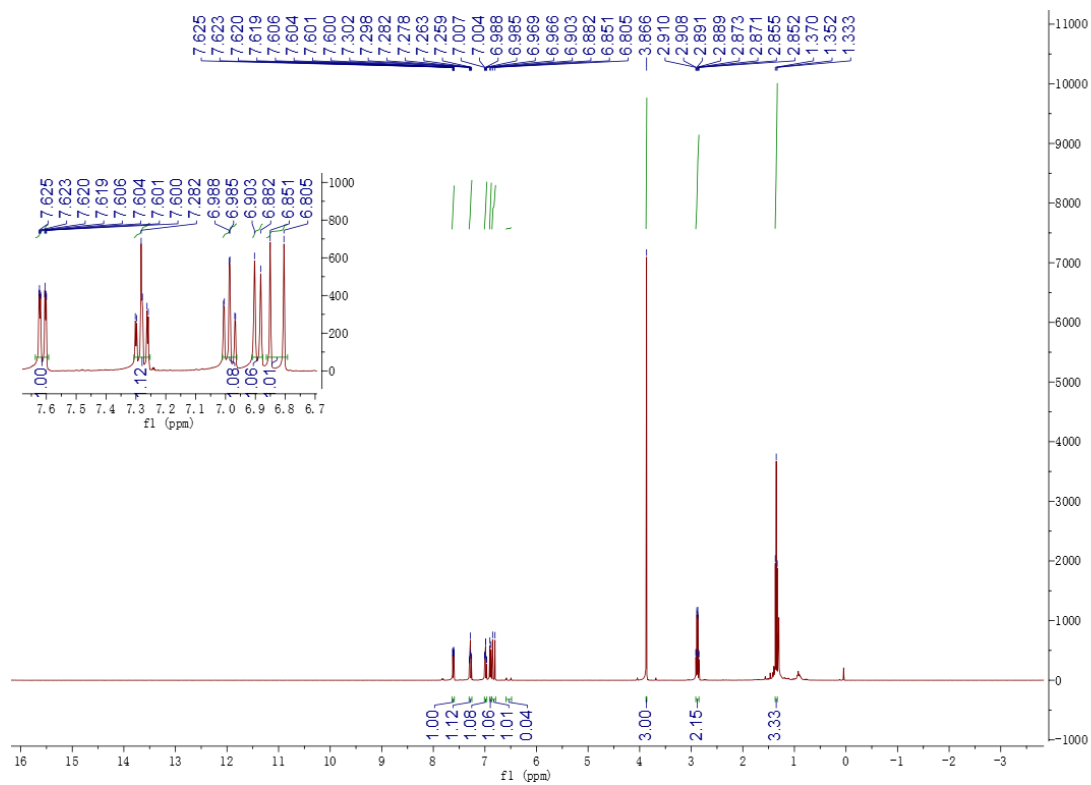
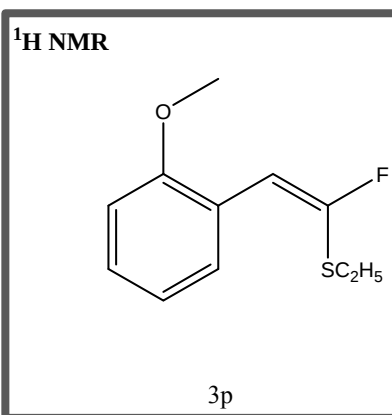


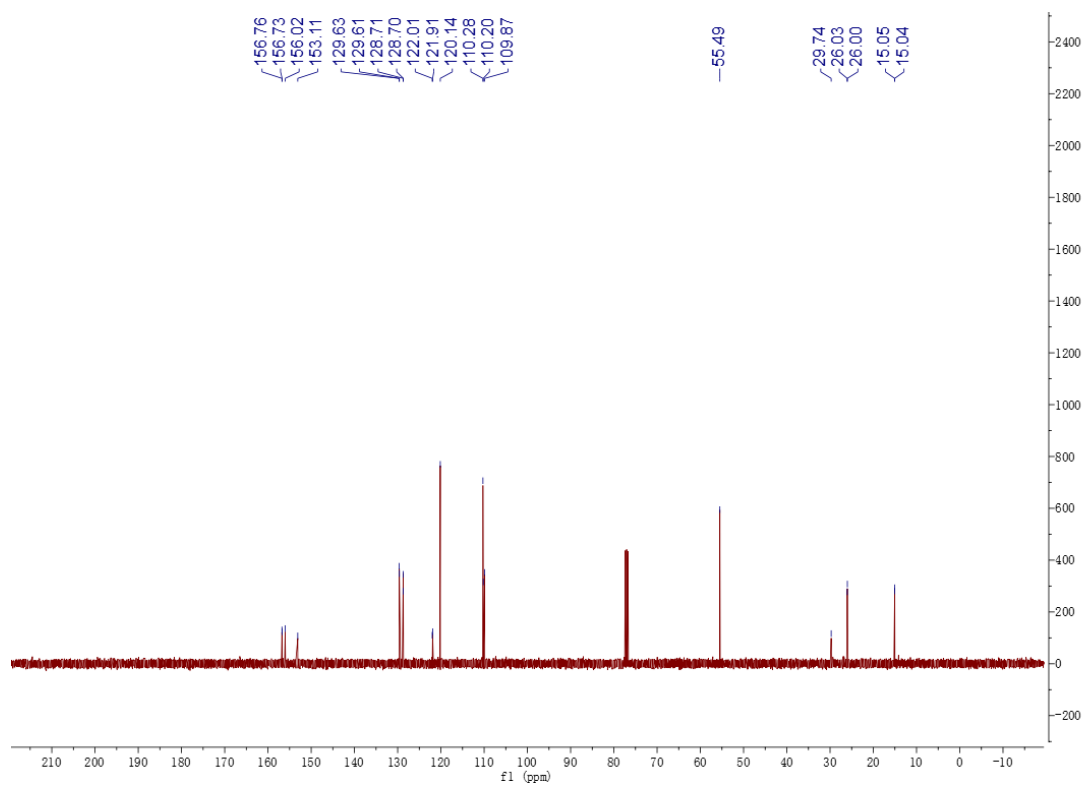
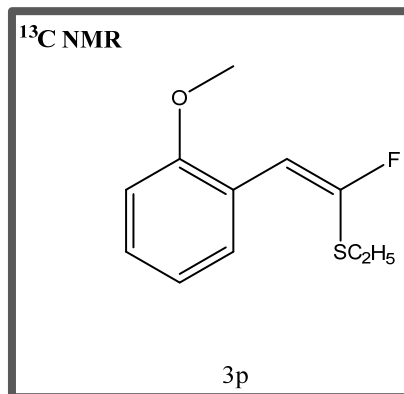


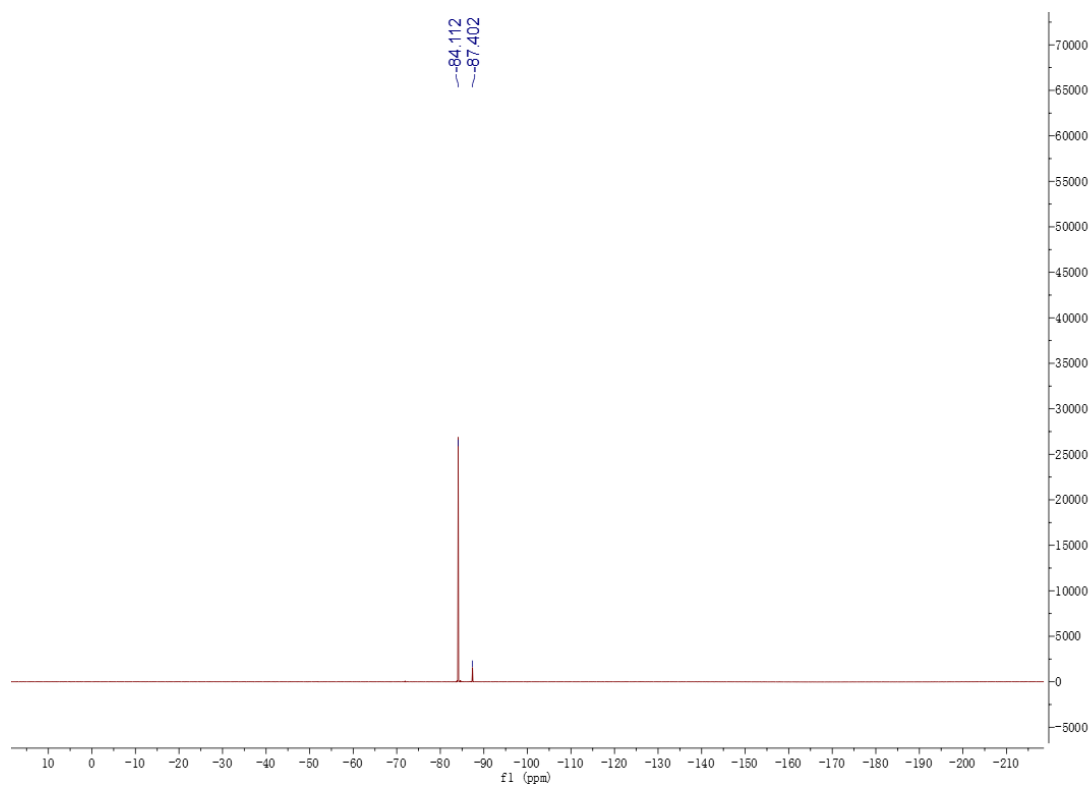
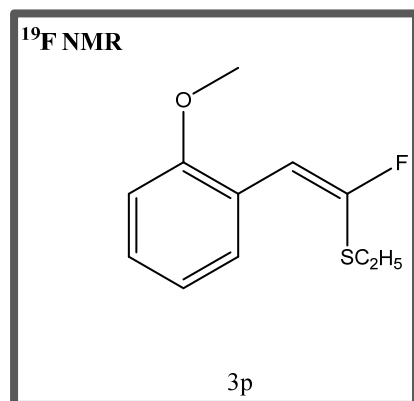


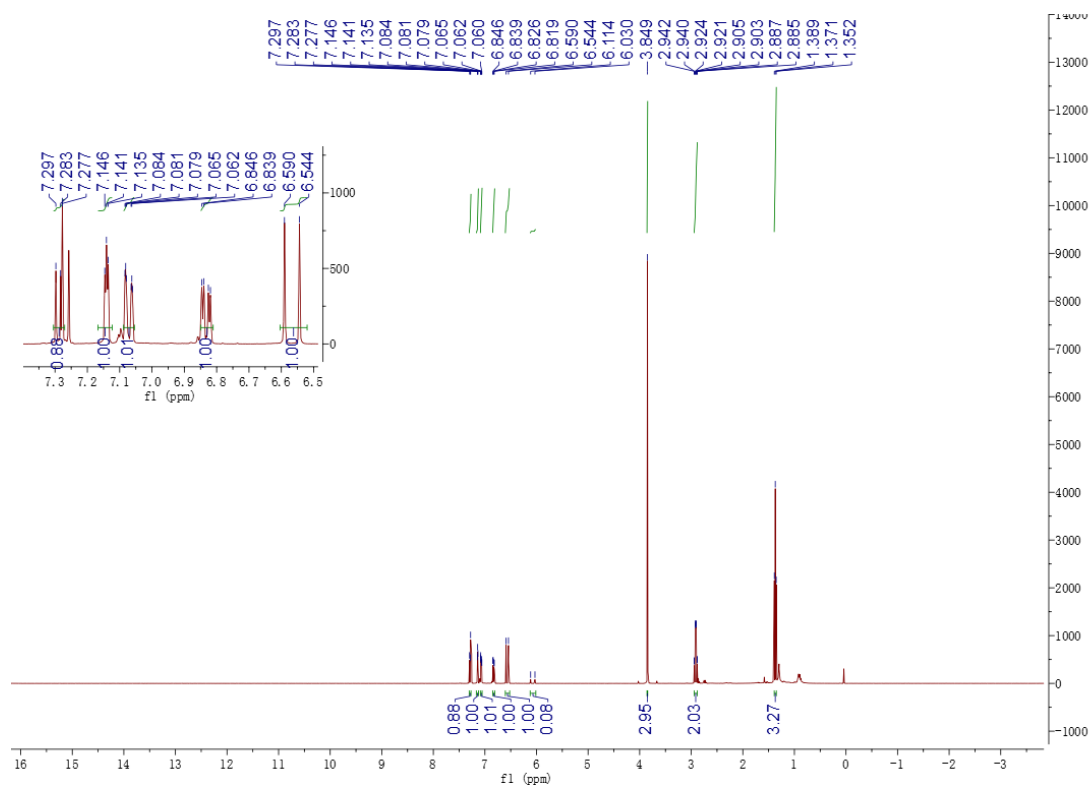
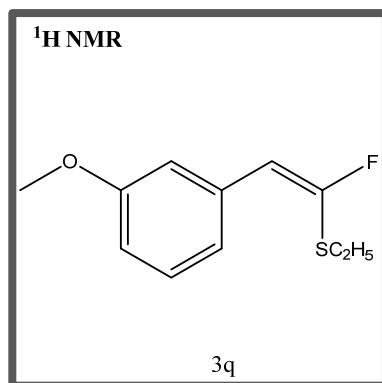


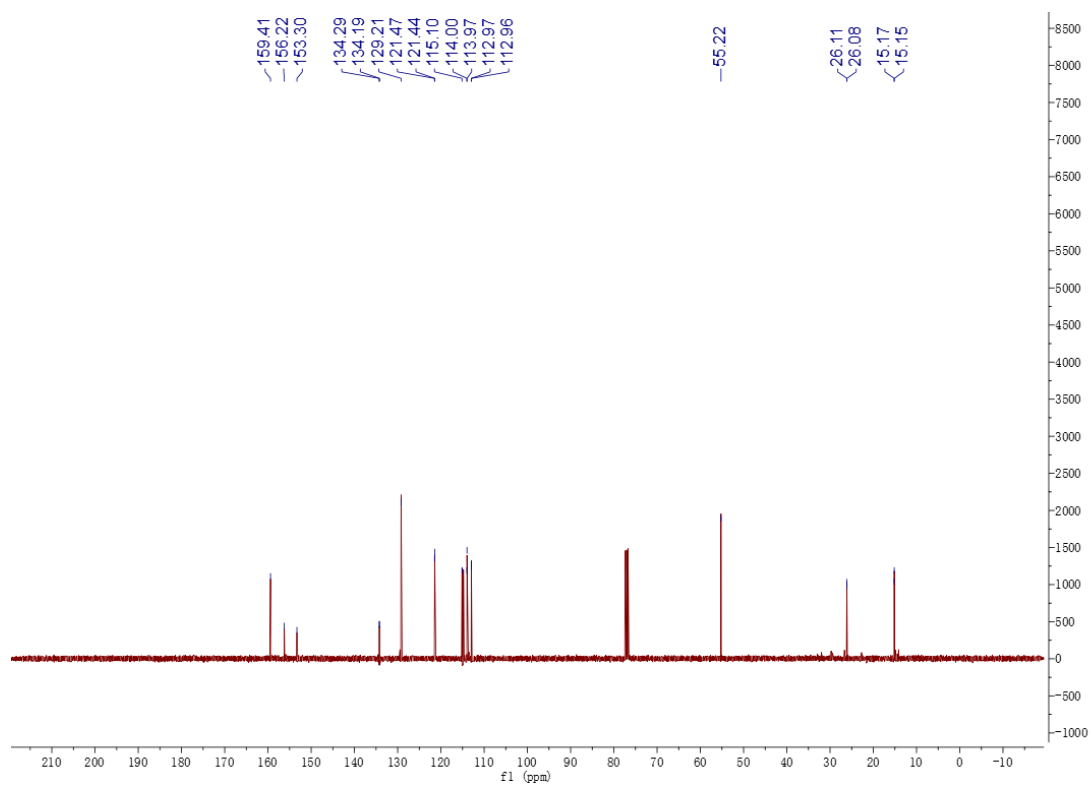
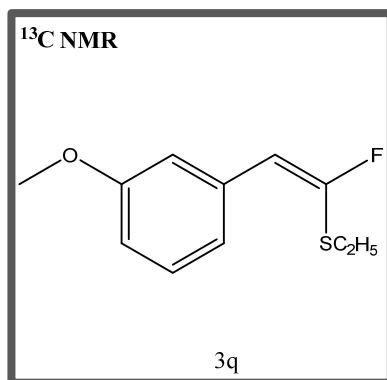


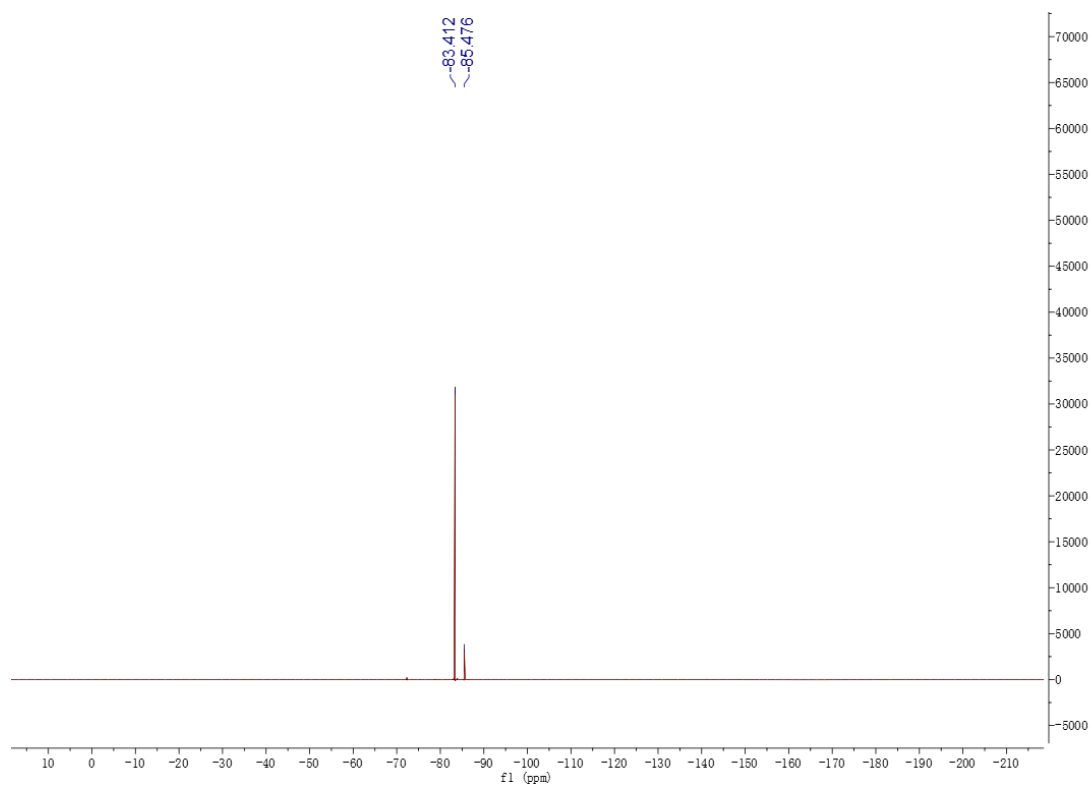
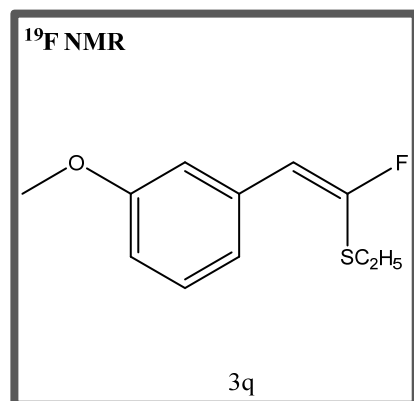


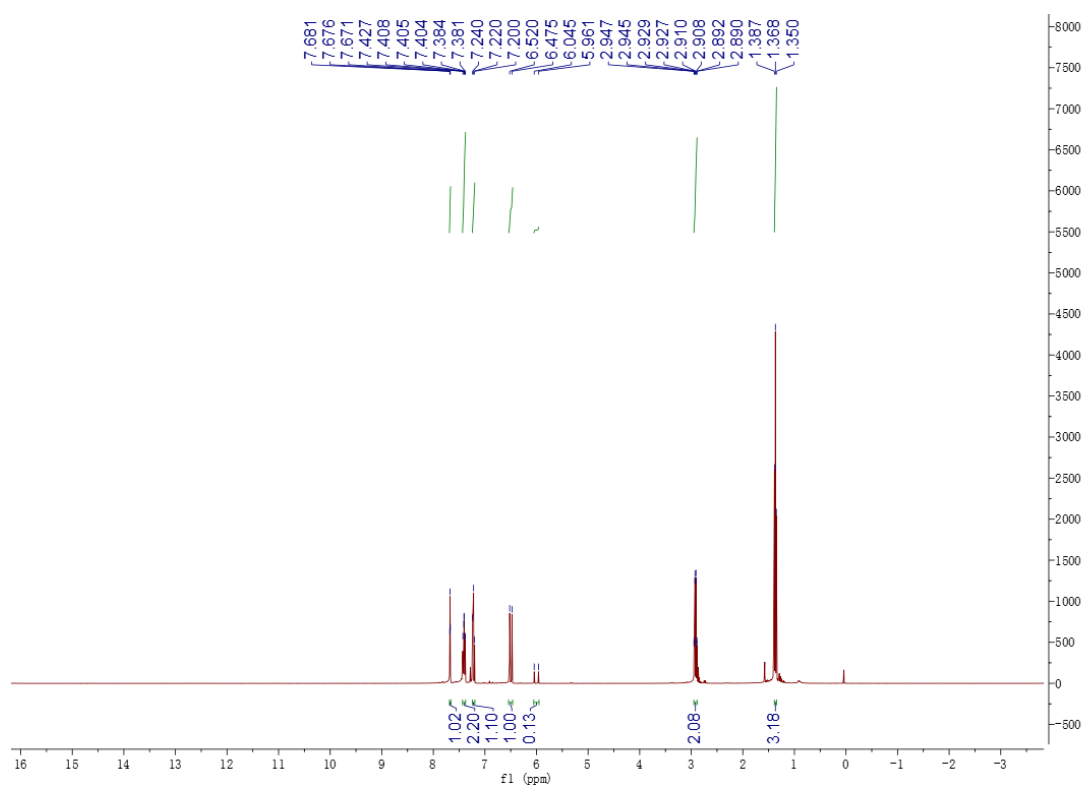
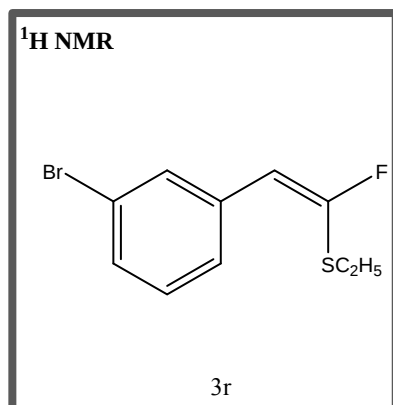


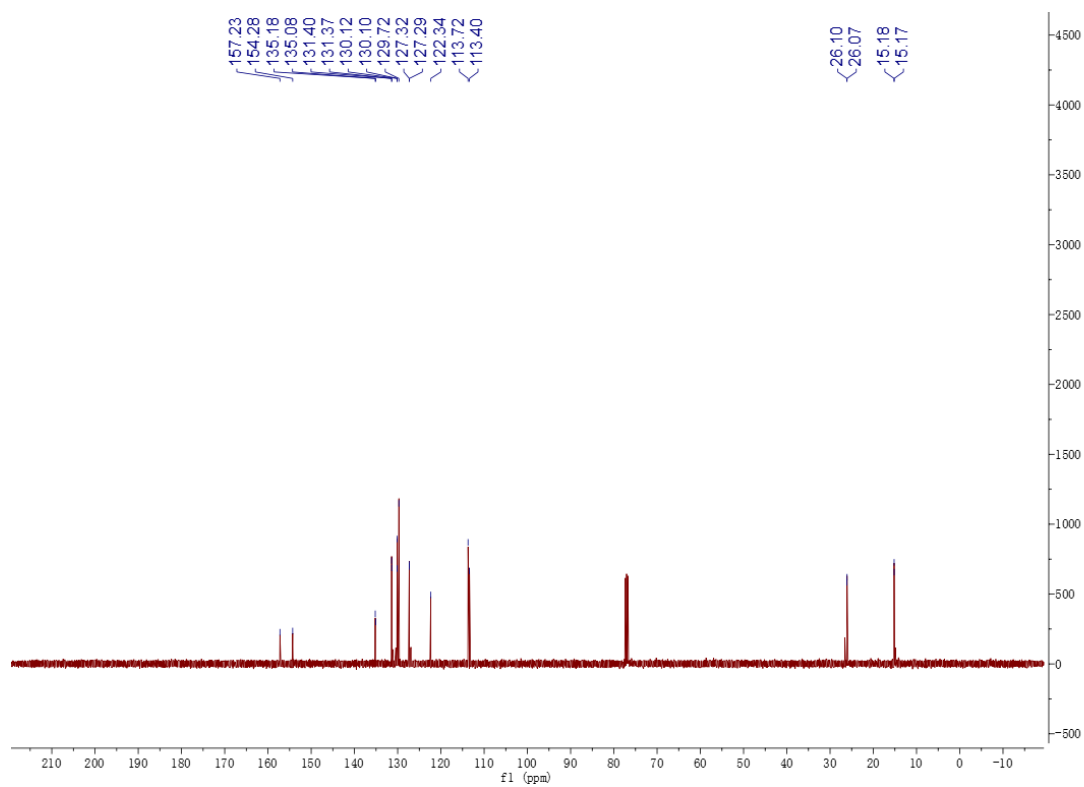
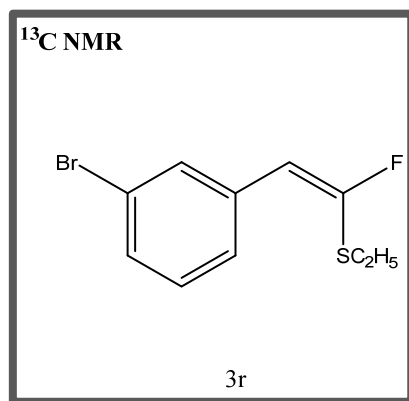


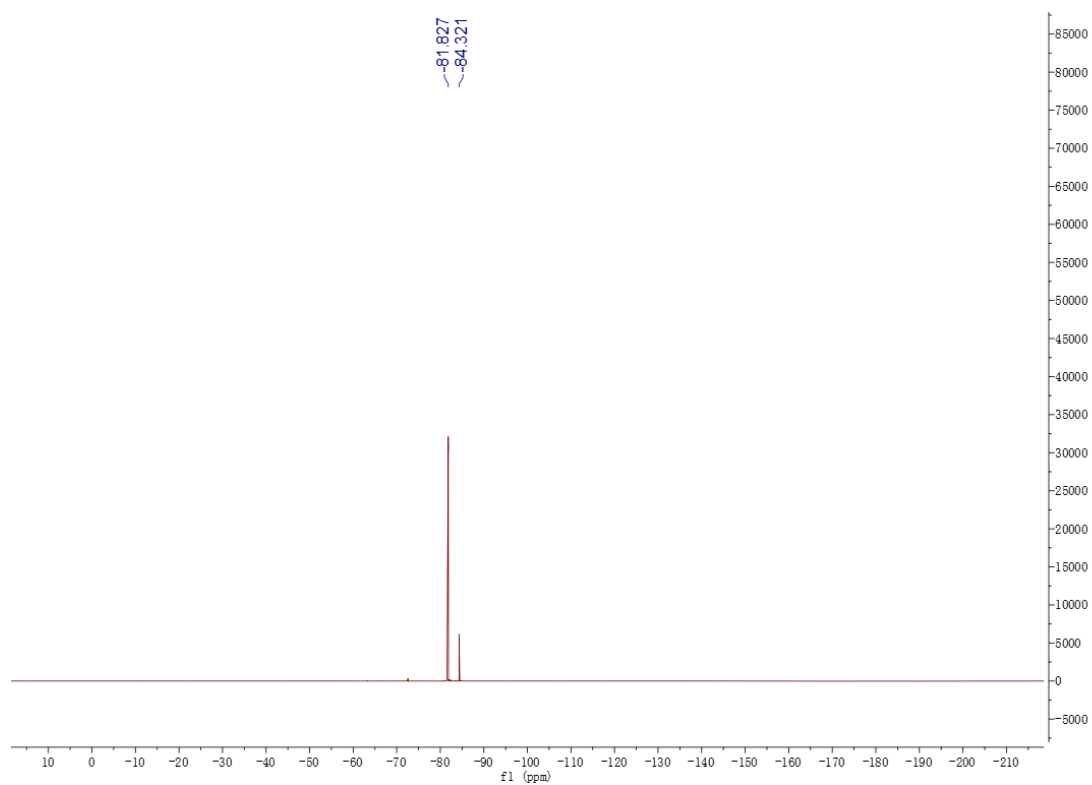
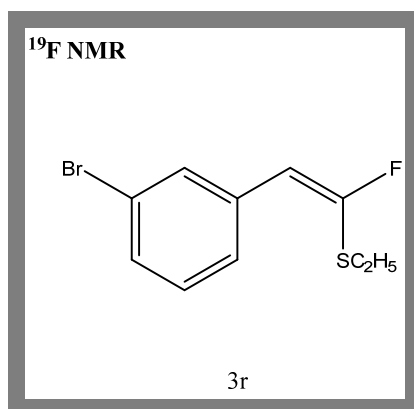


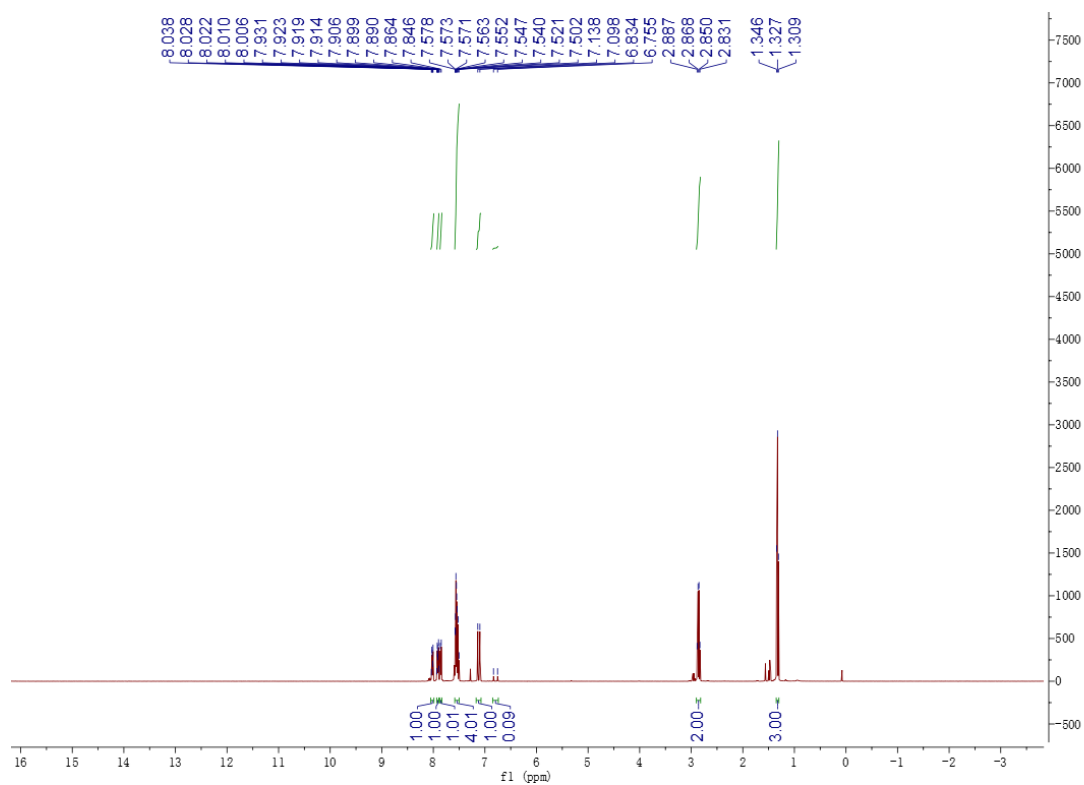
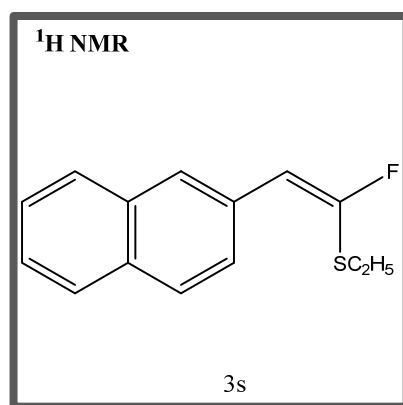


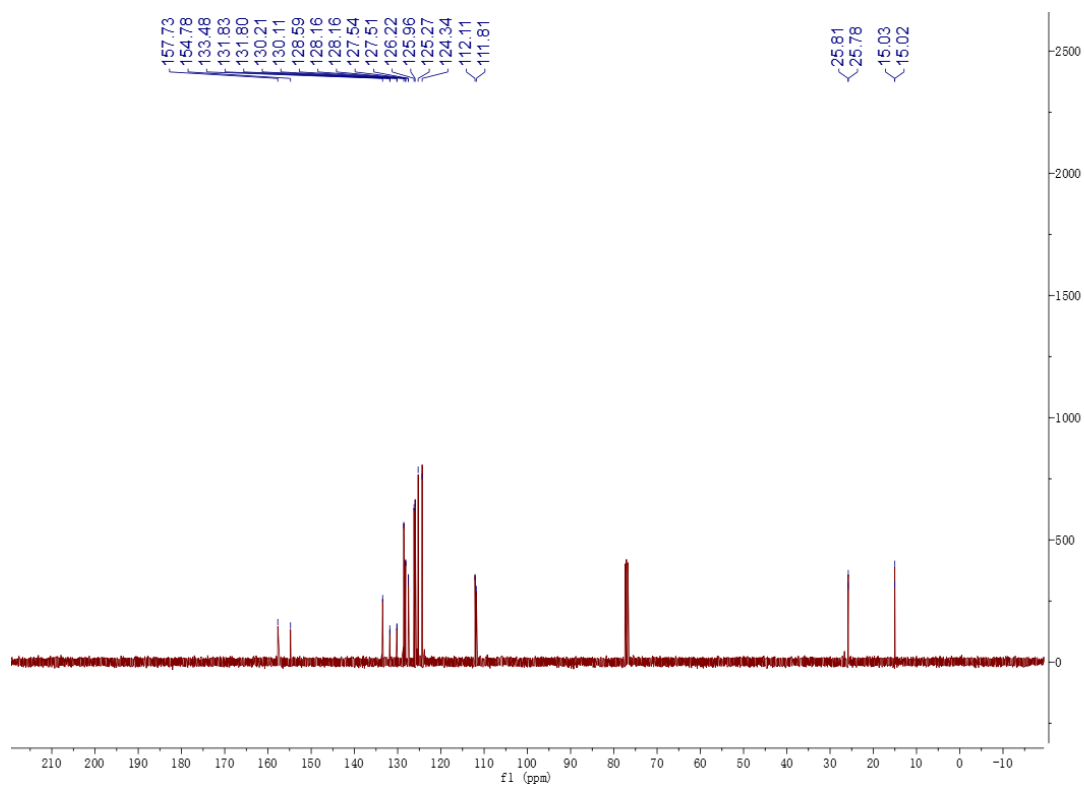
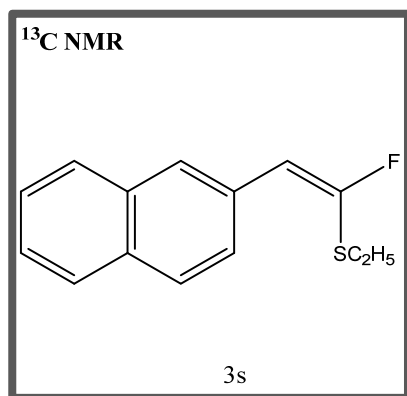


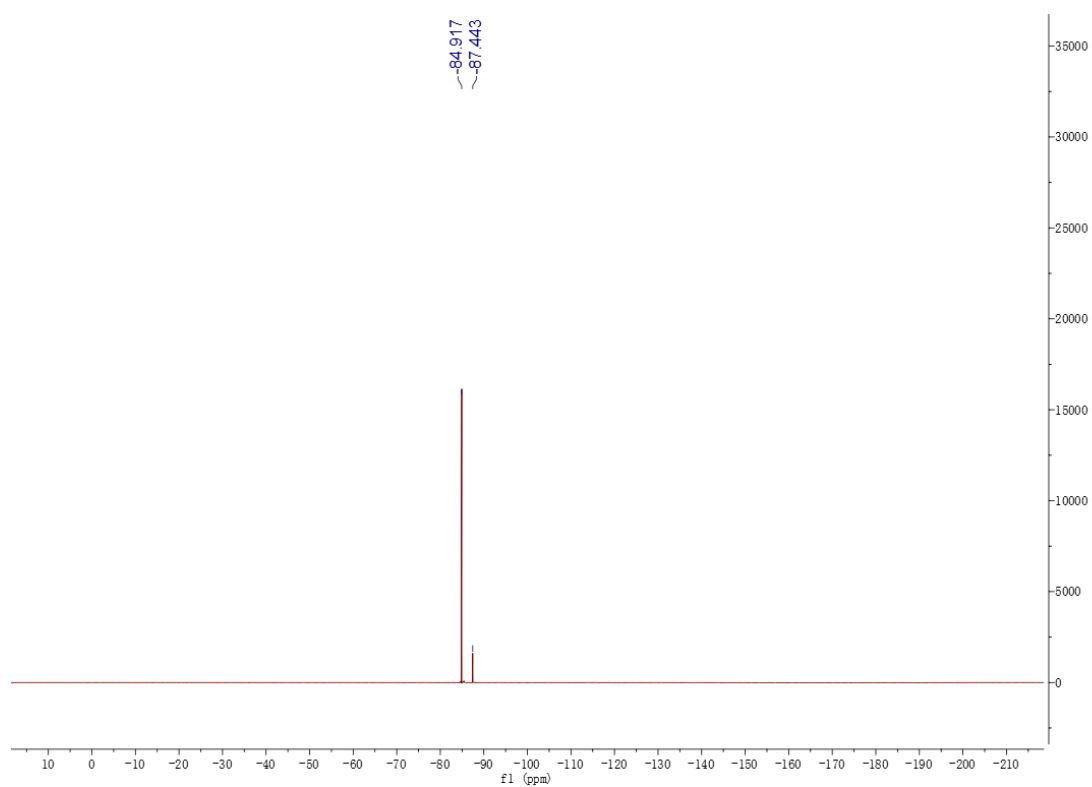
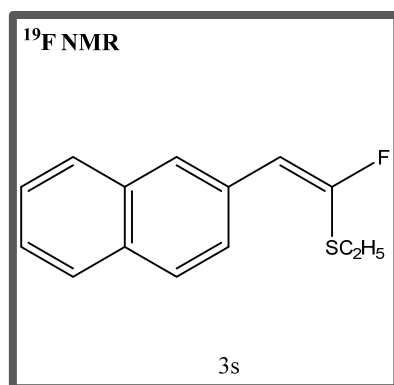


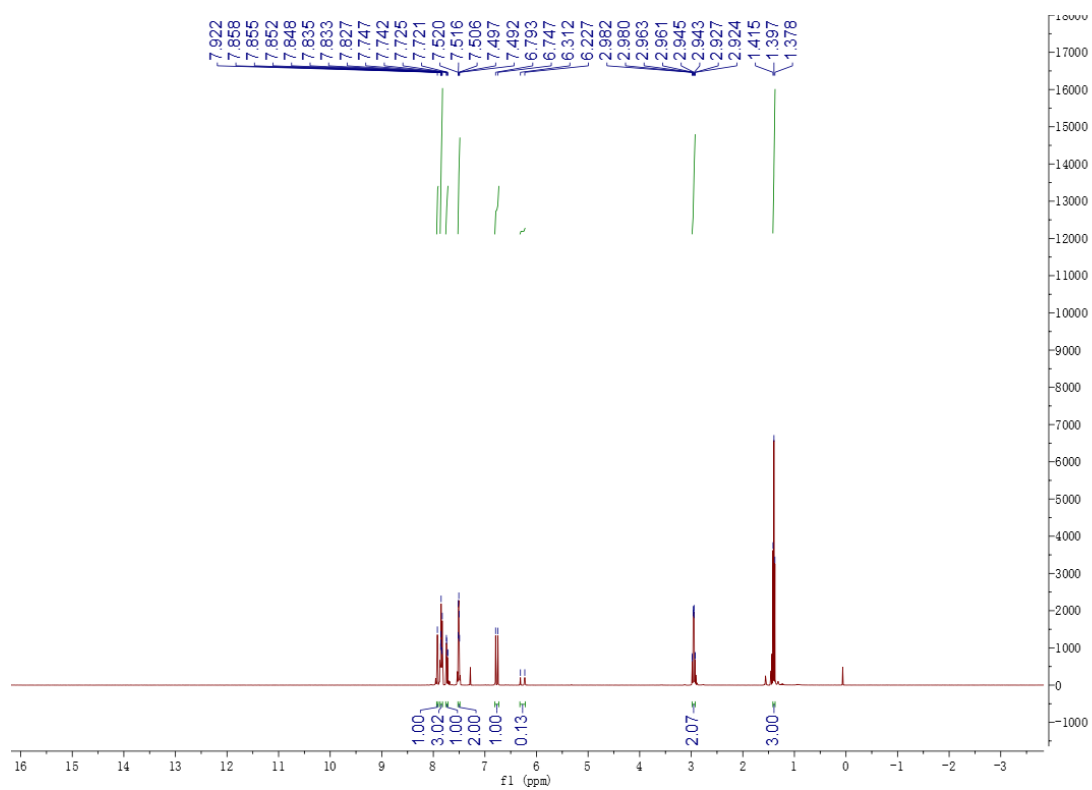
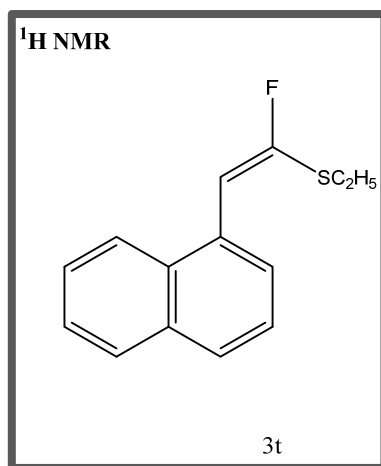


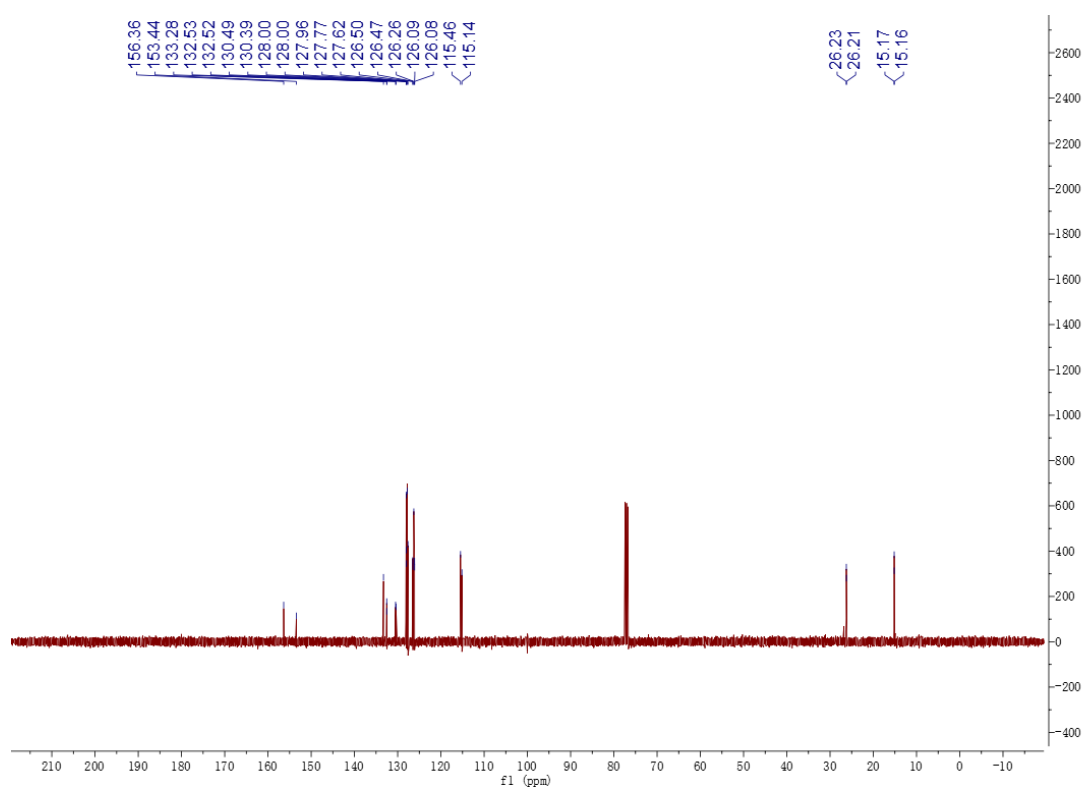
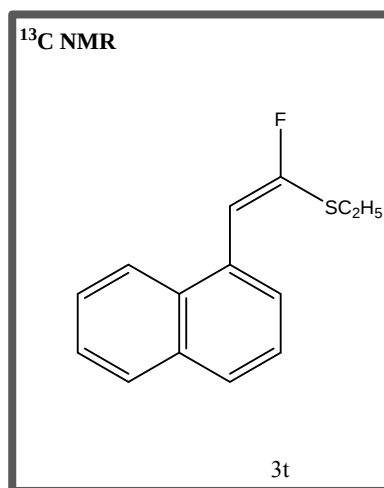


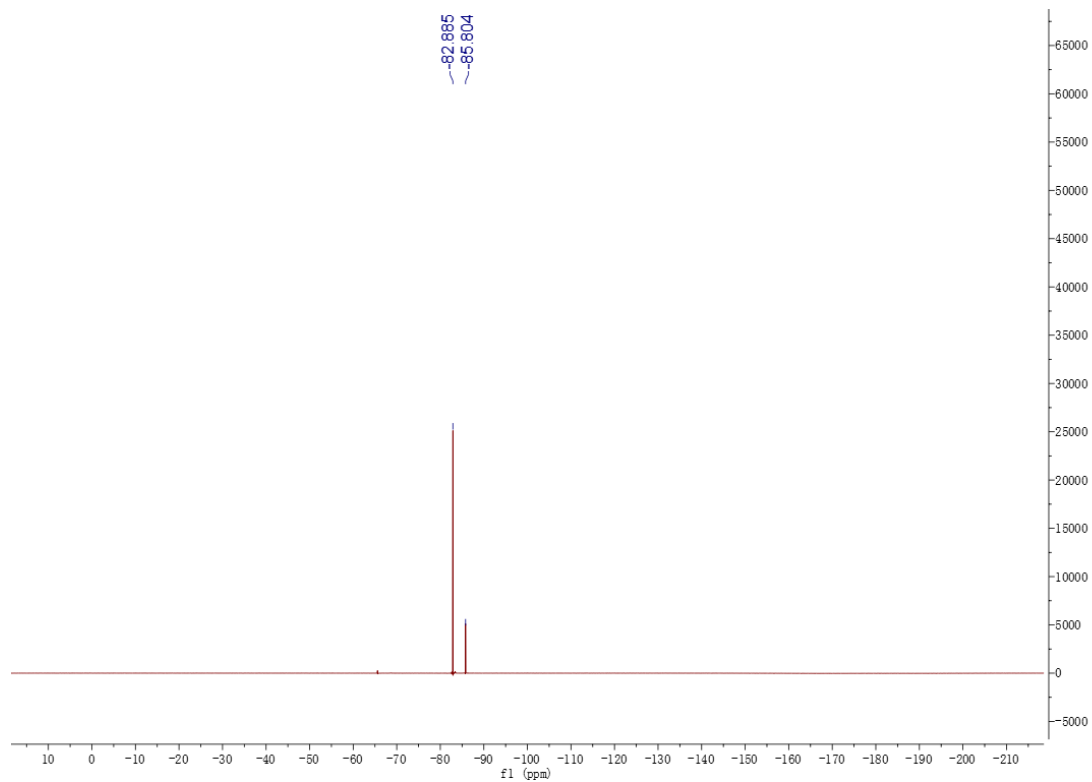
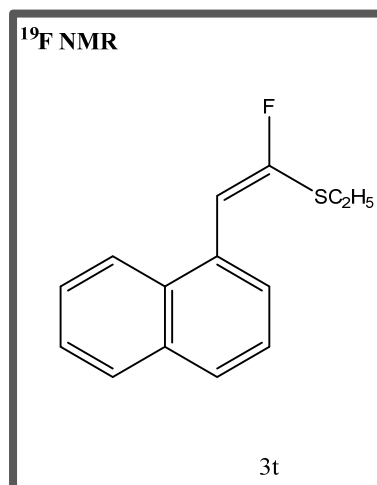


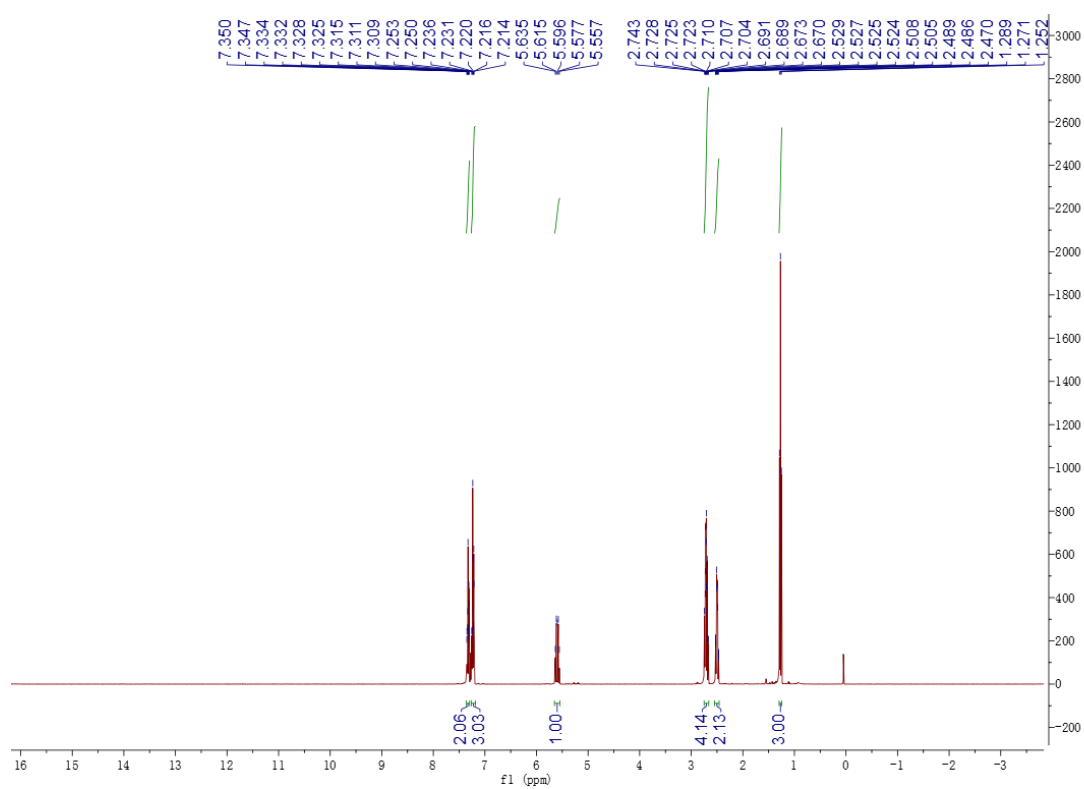
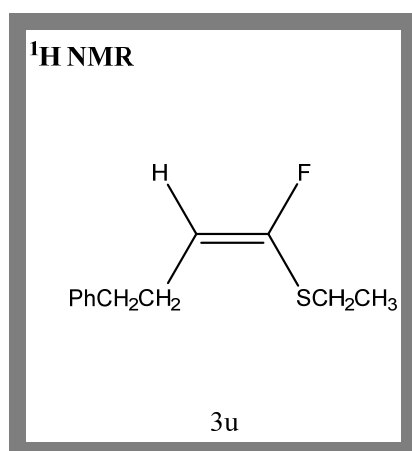


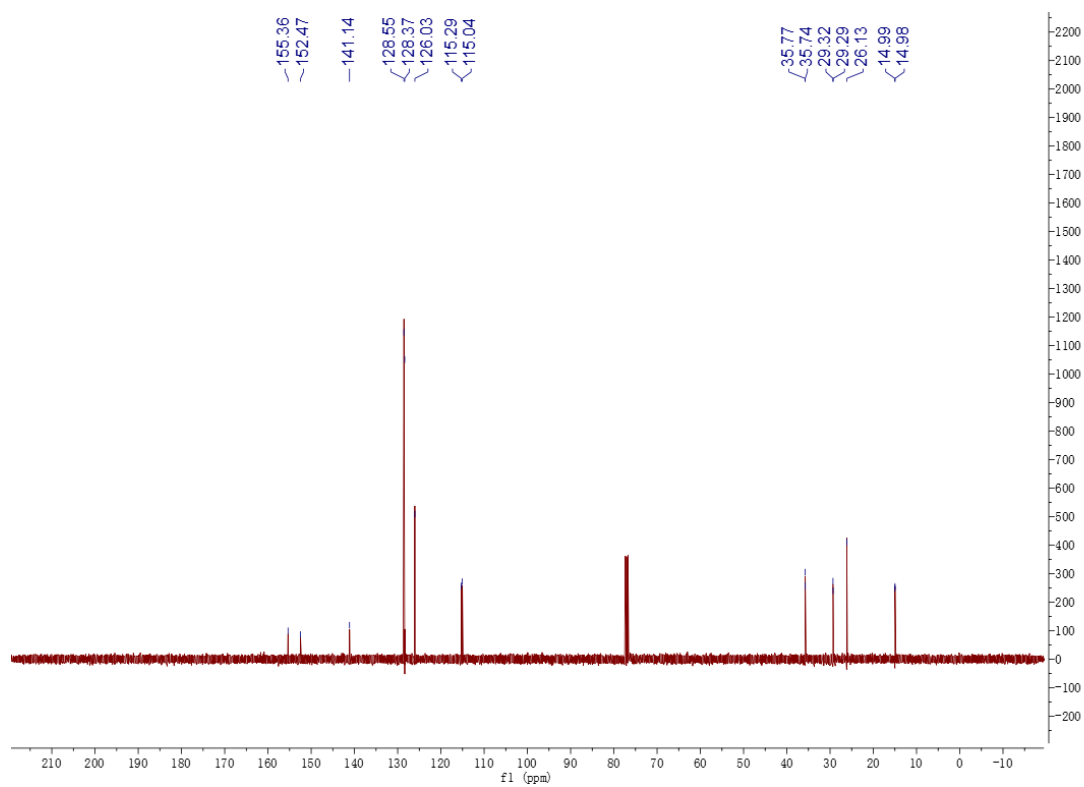
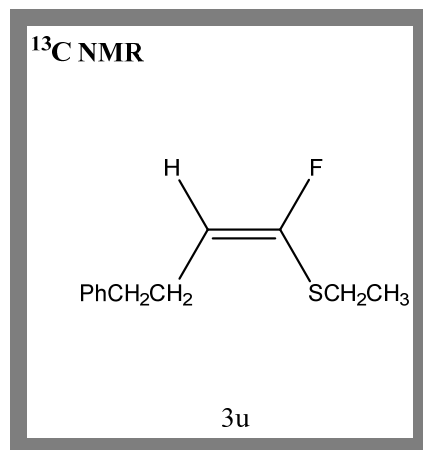


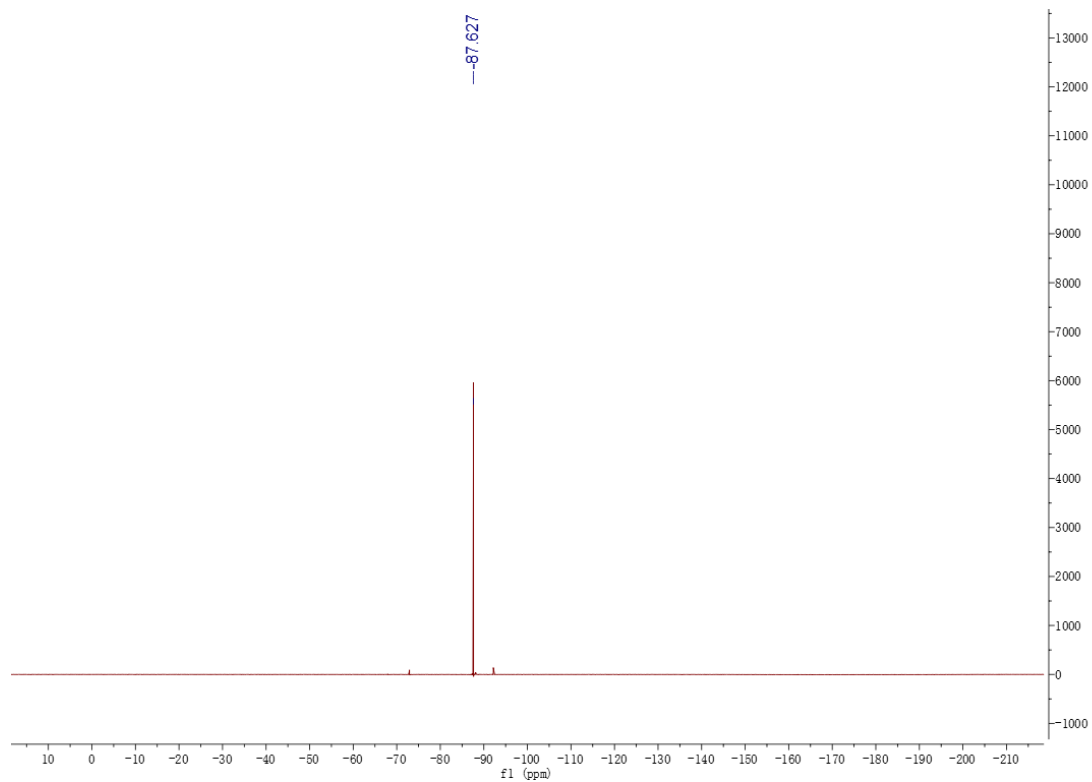
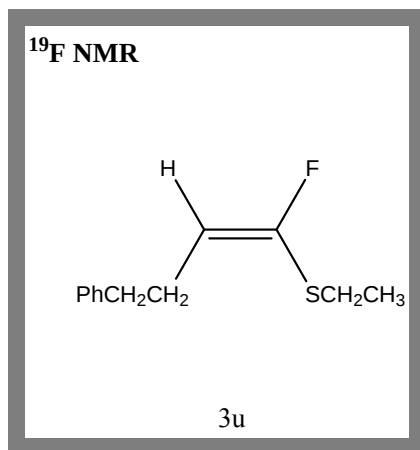


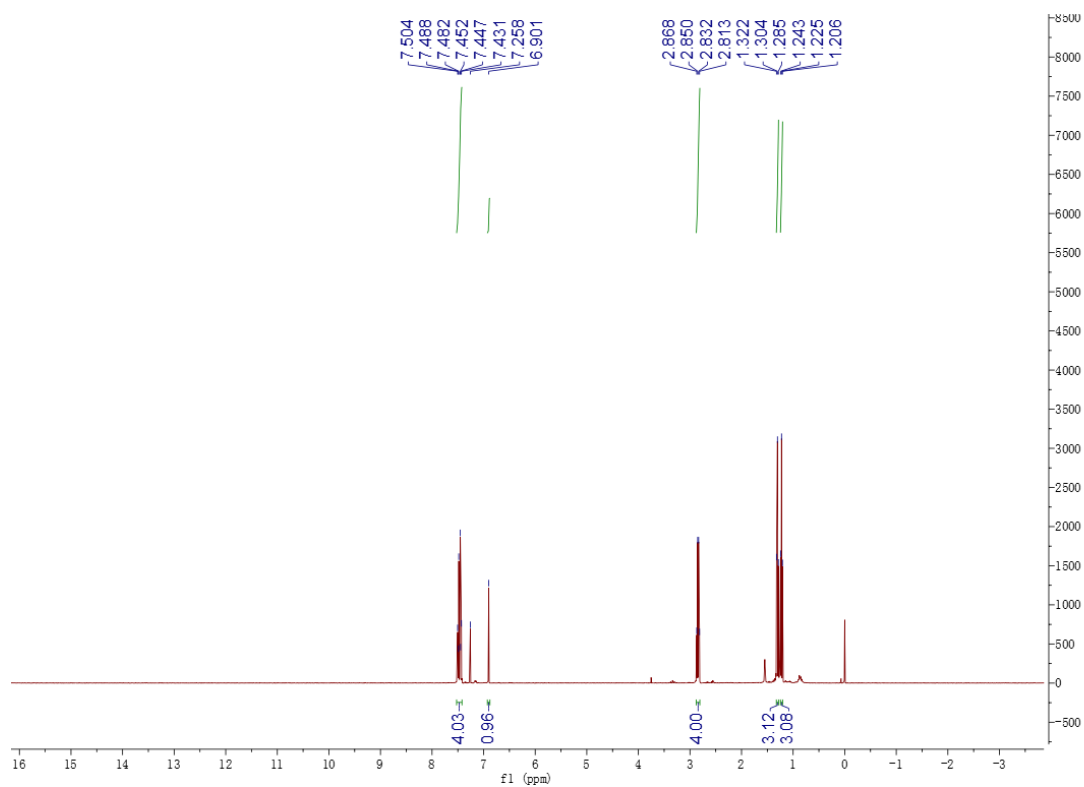
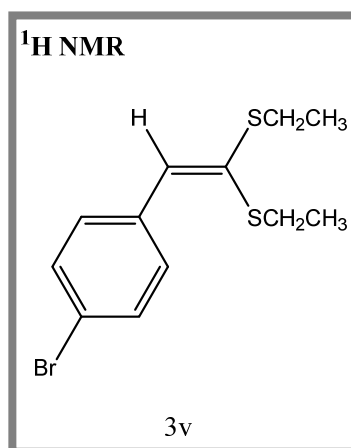


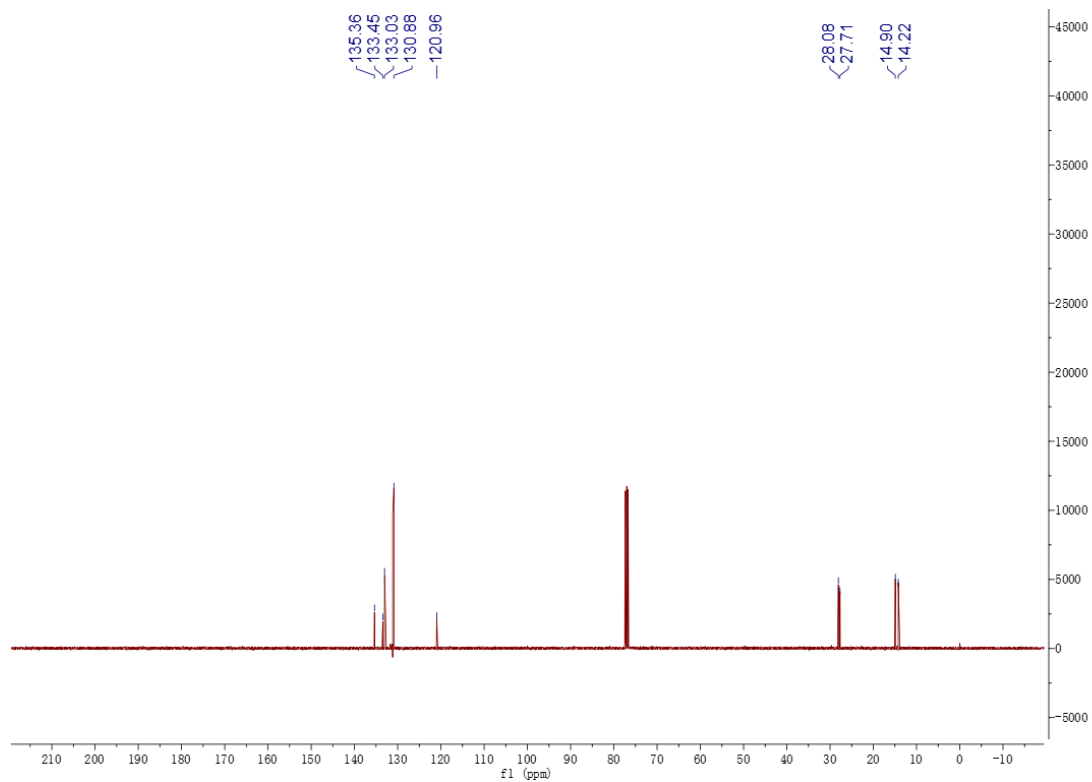
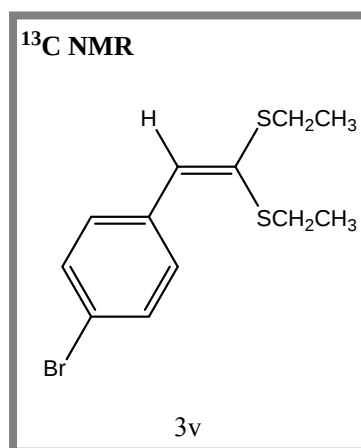


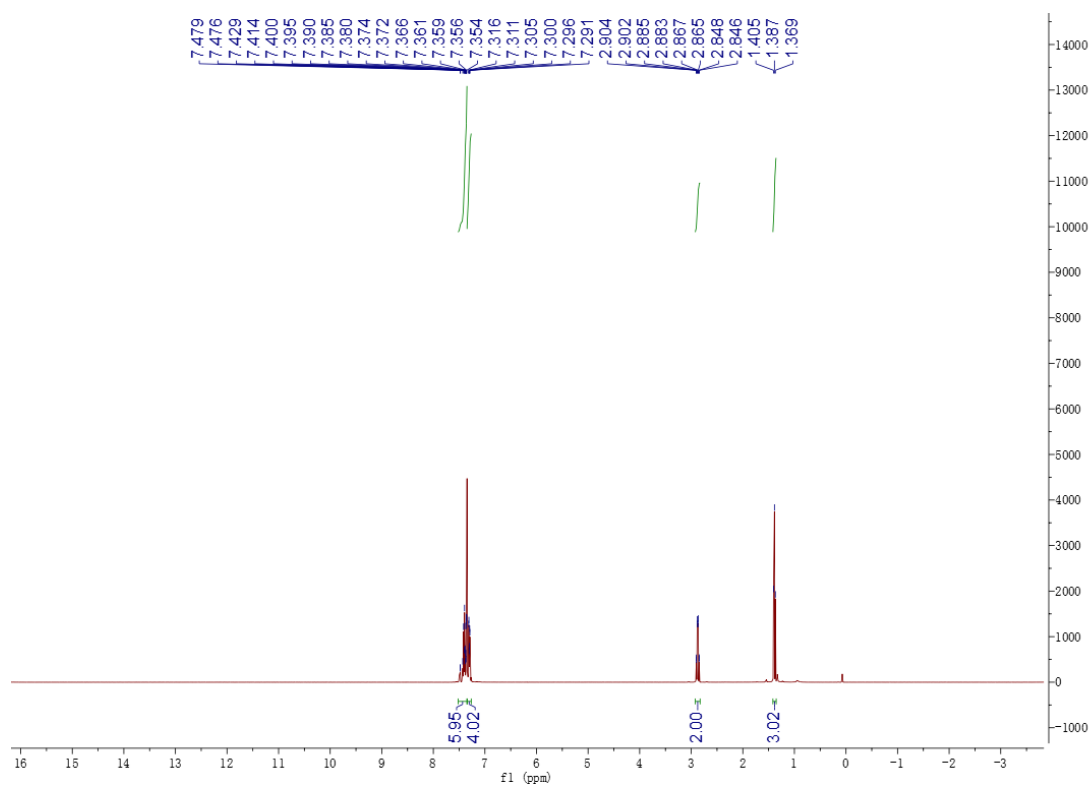
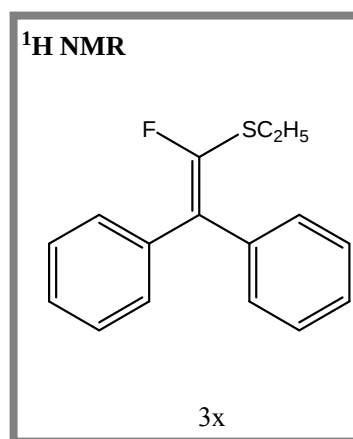


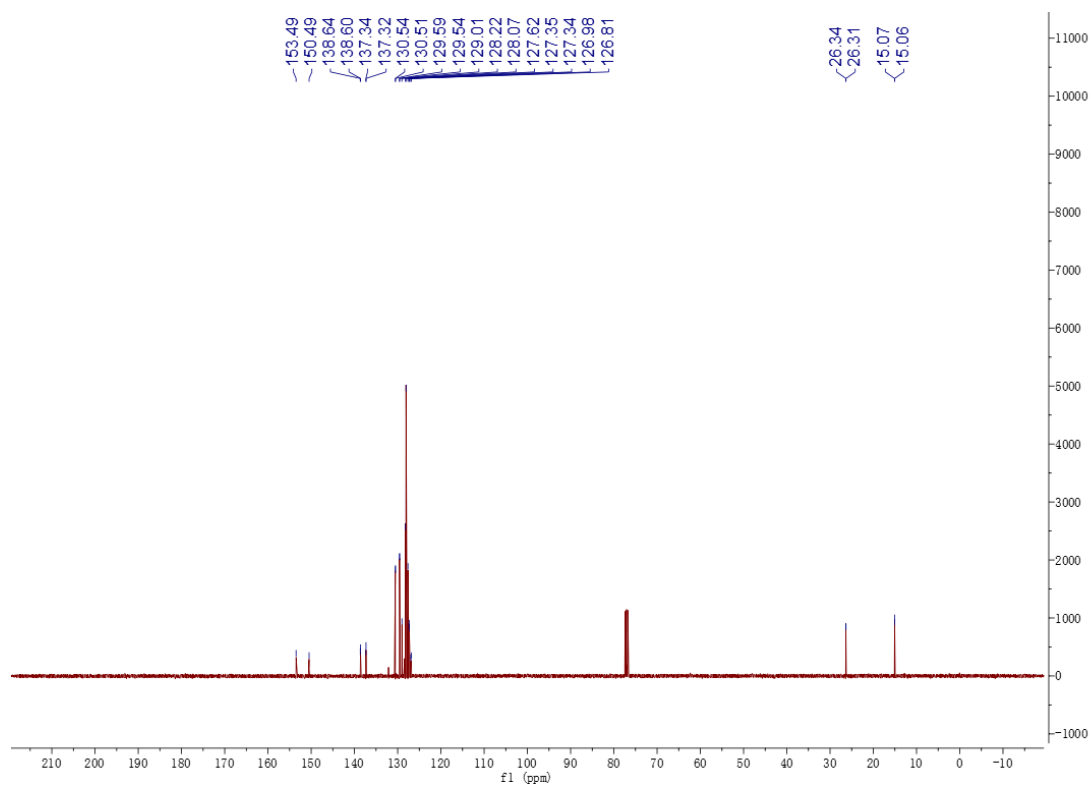
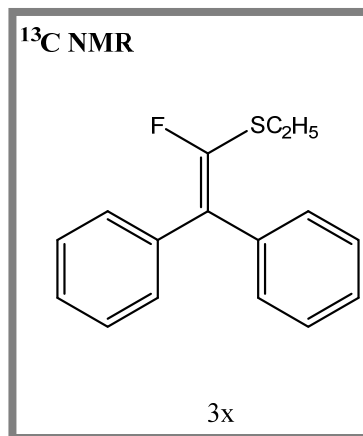


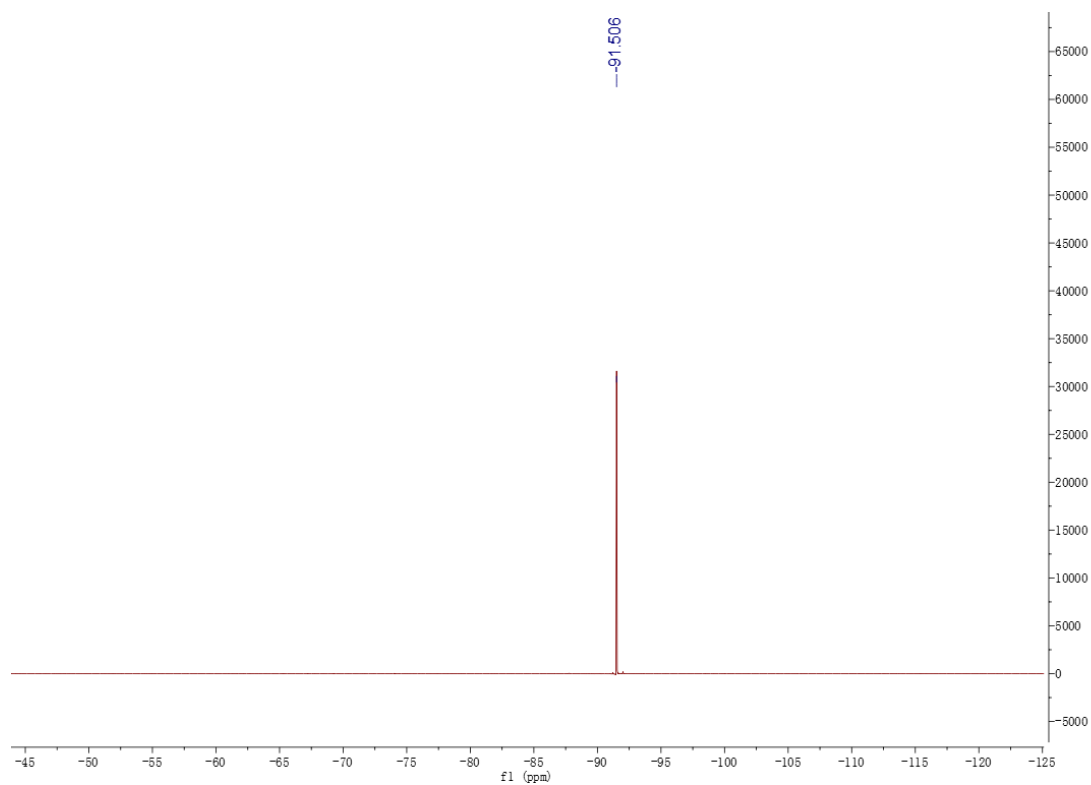
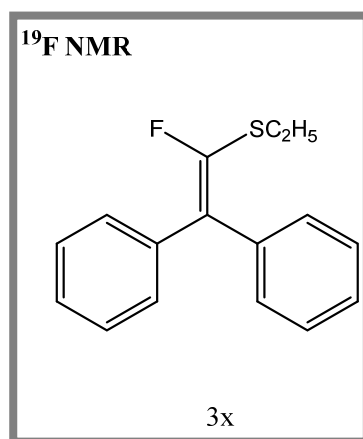


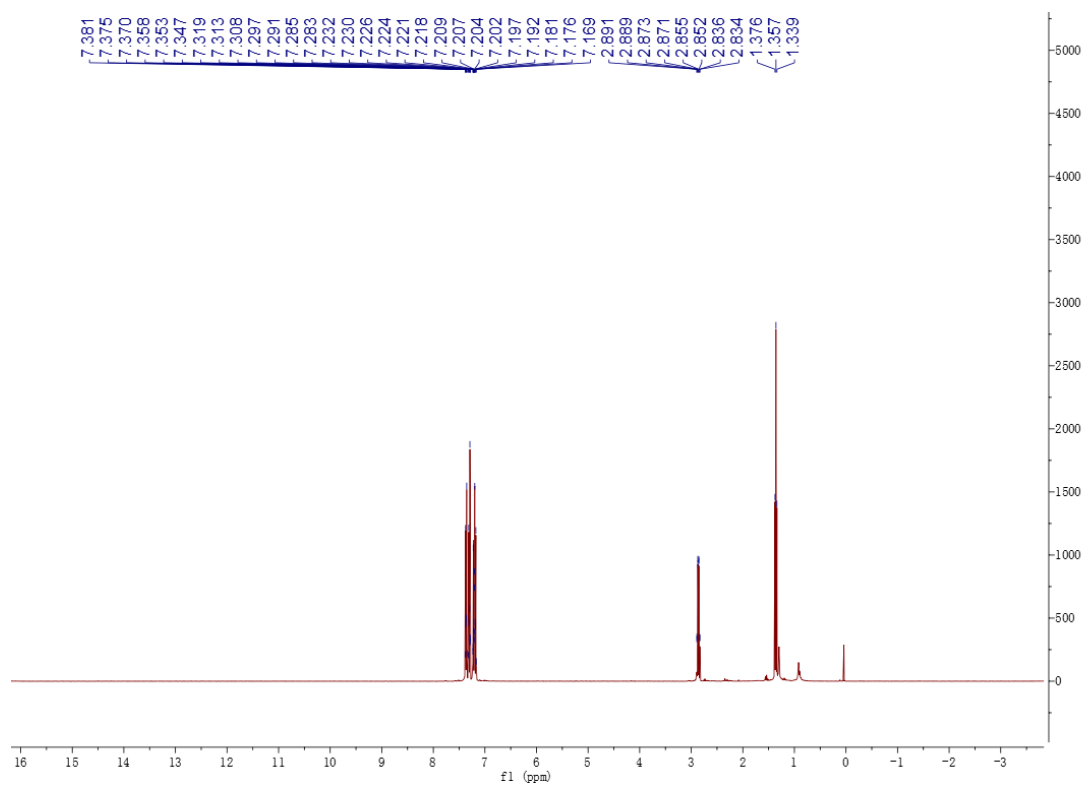
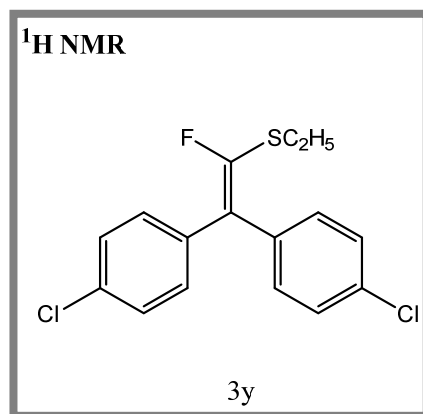


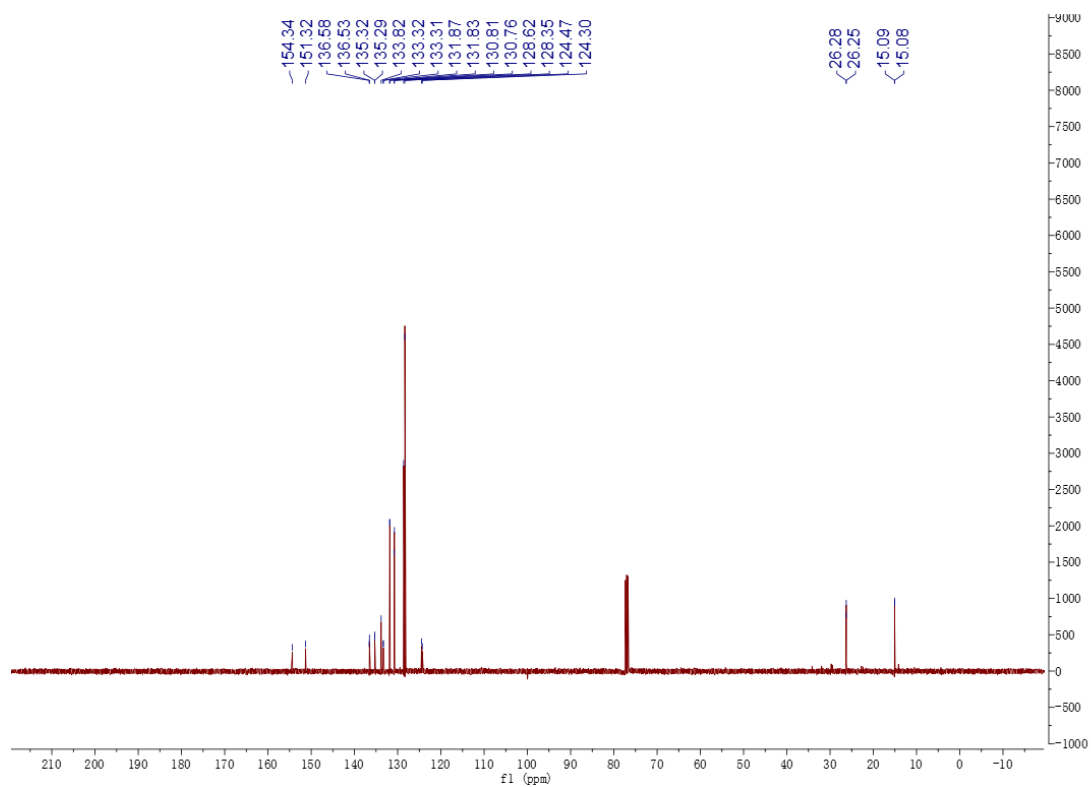
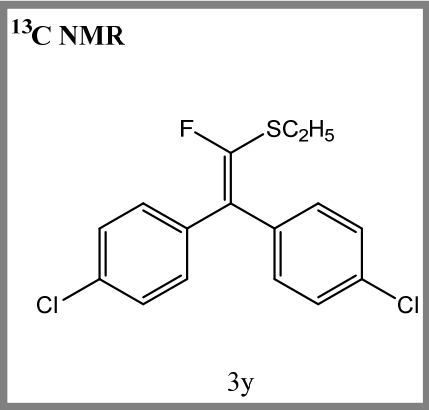




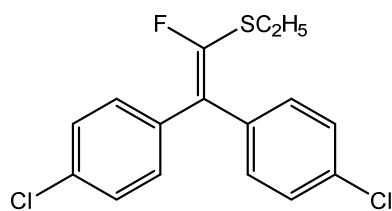




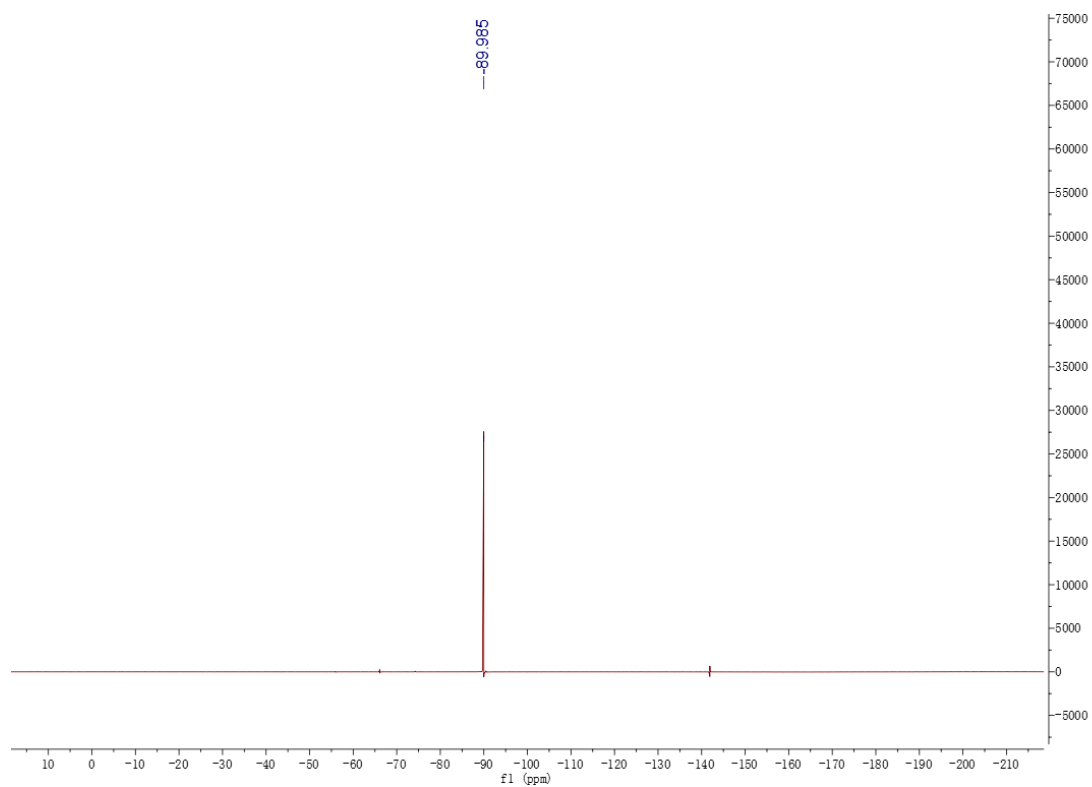


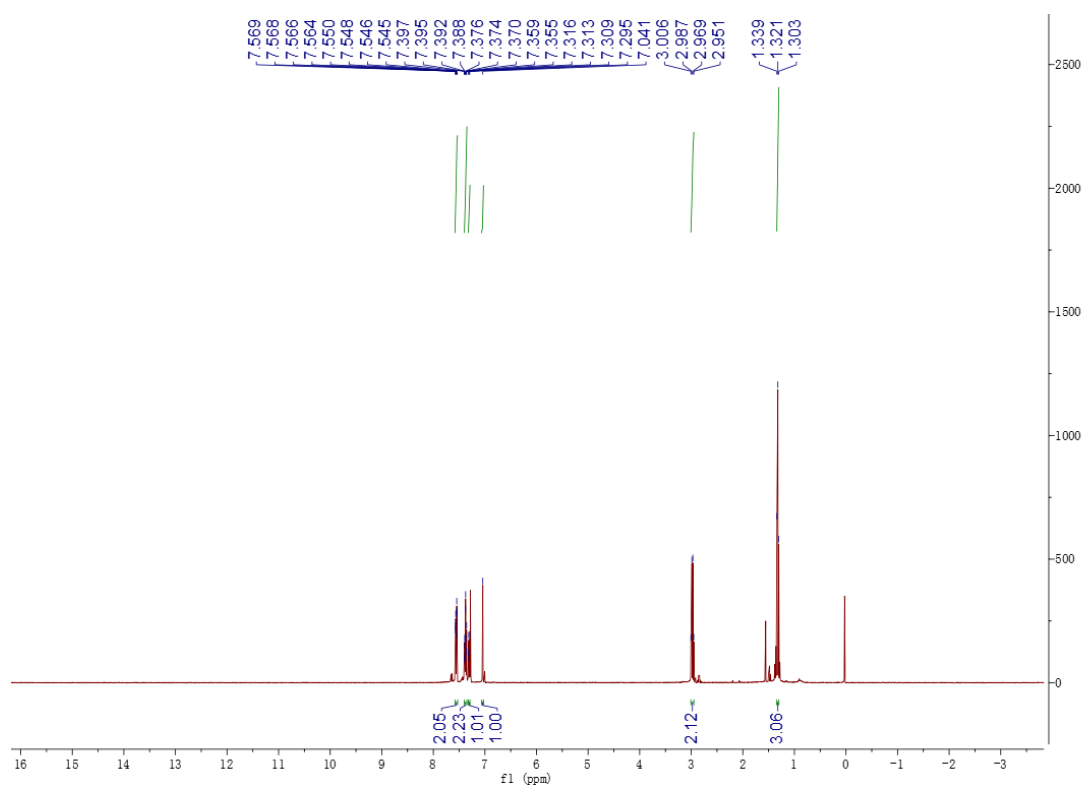
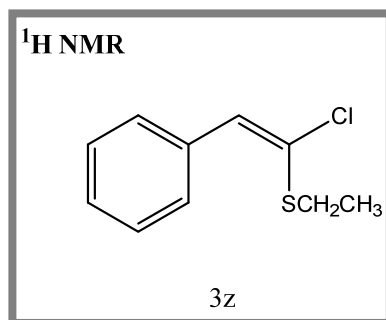


^{19}F NMR

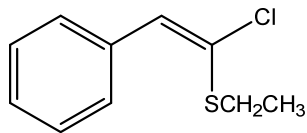


3y





¹³C NMR



3z

