Supporting Information

Modular Synthesis of Fluorinated 2*H*-Thiophenes via [4+1] Cyclization of Enaminothiones

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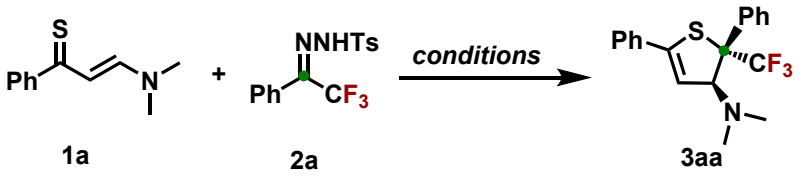
1. General methods:

All reactions were carried out in flame or oven-dried glassware under argon atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel 60 (230 – 400 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining with base solution of potassium permanganate and molybdate. NMR spectra were recorded at RT on 300 or 400 MHz Bruker spectrometers. The residual solvent signals were taken as the reference (0.00 ppm for ^{1}H NMR spectra and 77.0 ppm for ^{13}C NMR spectra in $CDCl_3$). Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, q = quartet and br = broad signal. HRMS (ESI) spectra were recorded on a Waters Q-Tof premier TM mass spectrometer.

2. Optimized reaction conditions:

Table S1 Optimized reaction conditions[a]



Entry	Metal Catalyst	Base	Solvent	temp	Yield (%)
1	CuI	^{t}BuOK	DCM	80	31
2	CuBr	^{t}BuOK	DCM	80	28
3	CuCl	^{t}BuOK	DCM	80	36
4	CuF_2	^{t}BuOK	DCM	80	29
5	CuCl	^{t}BuOK	MeOH	80	38
6	CuCl	^{t}BuOK	IPA	80	37
7	CuCl	^{t}BuOK	Tol.	80	39
8	CuCl	NaOH	Tol.	80	45
9	CuCl	K_2CO_3	Tol.	80	51
10	CuCl	K_2CO_3	Tol.	90	58
11	CuCl	K_2CO_3	Tol.	100	41
12	CuSCN	^{t}BuOK	DCE	80	10
13	CuSCN	^{t}BuOK	DCM	80	12
14	CuSCN	^{t}BuOK	PhCH3	80	14
15	CuSCN	^{t}BuOK	PhCl	80	13
16	CuSCN	^{t}BuOK	THF	80	27
17	CuSCN	^{t}BuOK	MeOH	80	19

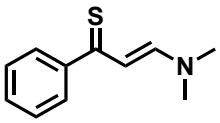
[a]If there is no otherwise noted, the reaction is performed as follows: **1a** (0.20 mmol, 1.0 equiv.), **2a** (0.48 mmol, 2.4 equiv.), metal catalyst (1.0 mol %) and base (0.50 mmol, 2.5 equiv.) were mixed with 2.0 mL solvent in sealed tube under argon atmosphere, and the obtained mixture was stirred at 90 °C until **1a** was consumed completely. [b] Isolated yield. [c]Metal catalyst-loading: 10 mol %. Oct = octanoate, TFA = trifluoroacetic acid, esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DIPEA = N,N-diisopropylethylamine. Tol. = toluene, THF = tetrahydrofuran, ACN = acetonitrile, DCM = dichloromethane.

3. General procedure and spectral data

3.1 General procedure for the synthesis of enaminothione and their spectral data[1]:

To a stirred solution of Lawesson's reagent (1 mmol, 0.5 equiv.) in DCM (20 ml), the enaminone (2 mmol, 1.0 equiv.) was added. The reaction mixture was stired at room temperature until complete conversion monitored by TLC (30-60 min), and then the solvent was removed under reduced pressure to afford a yellow or brown residue that was purified by flash column chromatography. The desired enaminothiones were obtained.

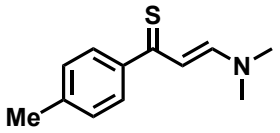
(*E*)-3-(Dimethylamino)-1-phenylprop-2-ene-1-thione (1a):



The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 102 - 104 ºC. Yield: 92% (351.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 10.4 Hz, 1H), 7.81 (s, 2H), 7.45 – 7.27 (m, 3H), 6.52 (d, J = 10.6 Hz, 1H), 3.25 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.3, 157.8, 148.3, 130.3, 128.0, 127.3, 111.3, 46.3, 38.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{14}NS$: 192.0847. Found: 192.0840.

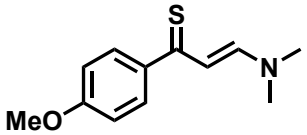
[1] R. Shabana, J. B. Rasmussen, S. O. Olesen and S.-O. Lawesson, *Tetrahedron*, 1980, **36**, 3047-3051.

(*E*)-3-(Dimethylamino)-1-(p-tolyl) prop-2-ene-1-thione (1b):



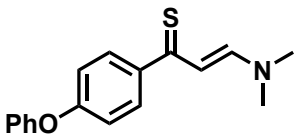
The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 122 - 124 ºC. Yield: 81% (332.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.75 (s, 2H), 7.12 (d, J = 7.9 Hz, 2H), 6.53 (d, J = 9.4 Hz, 1H), 3.23 (s, 3H), 2.99 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.7, 157.7, 145.4, 140.7, 128.6, 127.5, 110.8, 46.2, 38.5, 21.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{16}NS$: 206.1004. Found: 206.1003.

(*E*)-3-(Dimethylamino)-1-(4-methoxyphenyl) prop-2-ene-1-thione (1c):



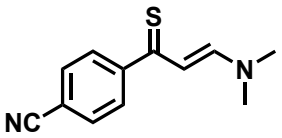
The title compound was prepared according to the general procedure. The product was obtained as faint yellow solid, Mp. 96 - 98 ºC. Yield: 85% (362.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.86 (s, 2H), 6.88 – 6.81 (m, 2H), 6.55 (d, J = 16.5 Hz, 1H), 3.83 (s, 3H), 3.24 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 140.6, 129.4, 113.1, 55.6, 46.2, 38.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{16}NOS$: 222.0953. Found: 222.0946.

(*E*)-3-(Dimethylamino)-1-(4-phenoxyphenyl)prop-2-ene-1-thione (1d):



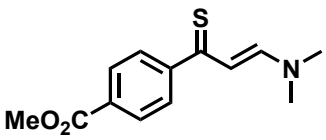
The title compound was prepared according to the general procedure (EA/PE = 1/1.5, R_f = 0.1). The product was obtained as red solid, Mp. 125 – 127 ºC. Yield: 60% (339.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.86 (s, 2H), 7.38 – 7.33 (m, 2H), 7.18 – 7.10 (m, 1H), 7.08 – 7.03 (m, 2H), 6.97 – 6.90 (m, 2H), 6.56 (d, J = 11.0 Hz, 1H), 3.28(s, 3H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 129.8, 129.1, 123.7, 119.4, 117.4, 46.1, 38.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{17}NOS$: 284.1109. Found: 284.1104.

(*E*)-4-(3-(Dimethylamino) prop-2-enethioyl) benzonitrile (1e):



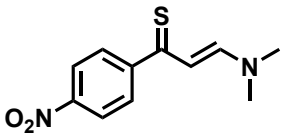
The title compound was prepared according to the general procedure, The product was obtained as red solid, Mp. 99 - 102 ºC. Yield: 83% (359.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 11.4 Hz, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.62 – 7.58 (m, 2H), 6.49 (d, J = 11.4 Hz, 1H), 3.33 (s, 3H), 3.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.1, 158.3, 152.0 131.9, 127.6, 119.0, 112.9, 111.6, 46.7, 38.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}N_2S$: 217.0799. Found: 217.0794.

Methyl (*E*)-4-(3-(dimethylamino)prop-2-enethioyl)benzoate(1f):



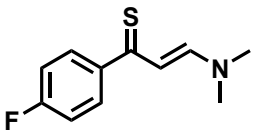
The title compound was prepared according to the general procedure, The product was obtained as faint yellow solid, Mp. 96 - 98 ºC. Yield: 73% (363.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 11.4 Hz, 1H), 8.07 – 7.95 (m, 2H), 7.90 – 7.78 (m, 2H), 6.48 (d, J = 11.4 Hz, 1H), 3.93 (s, 3H), 3.33 (s, 3H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 157.4, 129.2, 126.9, 111.5, 99.9, 52.2, 46.3, 38.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{16}NOS$: 250.0902. Found: 250.0909.

(*E*)-3-(Dimethylamino)-1-(4-nitrophenyl)prop-2-ene-1-thione (1g):



The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 122 - 123 ºC. Yield: 60% (283.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 11.3 Hz, 1H), 8.07 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 6.45 (d, J = 11.3 Hz, 1H), 3.29 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 158.0, 153.4, 147.8, 127.5, 122.9, 111.7, 46.4, 38.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}N_2O_2S$: 237.0698. Found: 237.0700.

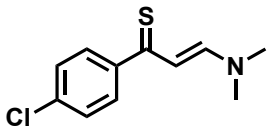
(*E*)-3-(Dimethylamino)-1-(4-fluorophenyl) prop-2-ene-1-thione (1h):



The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 99 - 100 ºC. Yield: 91% (380.9 mg); ^{1}H NMR (400 MHz,

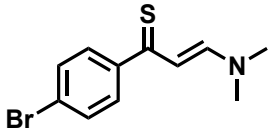
$CDCl_3$) δ 8.38 (s, 1H), 7.83 (s, 2H), 7.00 – 6.95 (m, 2H), 6.58 – 6.37 (m, 1H), 3.25(s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.9, 165.5, 158.1, 144.3, 129.5 (d, J = 6.9 Hz), 114.8 (d, J = 21.5 Hz), 110.8, 46.4, 38.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.00; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}FNS$: 210.0753. Found: 210.0746.

(*E*)-1-(4-Chlorophenyl)-3-(dimethylamino) prop-2-ene-1-thione (1i):



The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 113 - 114 ºC. Yield: 88% (397.3 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 10.9 Hz, 1H), 7.85 – 7.65 (m, 2H), 7.37 – 7.16 (m, 2H), 6.47 (d, J = 10.9 Hz, 1H), 3.25 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 158.2, 146.4, 136.2, 128.7, 128.1, 110.9, 46.5, 38.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}ClNS$: 226.0457. Found: 226.0451.

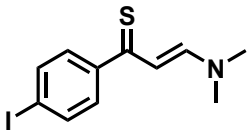
(*E*)-1-(4-Bromophenyl)-3-(dimethylamino) prop-2-ene-1-thione (1j):



The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 110 - 111 ºC. Yield: 91% (491.7 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 10.7 Hz, 1H), 7.76 – 7.63 (m, 2H), 7.46 – 7.39 (m, 2H), 6.48 (d, J = 11.0 Hz, 1H), 3.27 (s, 3H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7,

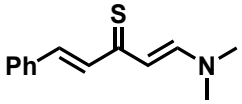
158.2, 146.9, 131.0, 128.5, 124.7, 110.9, 46.5, 38.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}BrNS$: 269.9952. Found: 269.9944.

(*E*)-3-(Dimethylamino)-1-(4-iodophenyl) prop-2-ene-1-thione (1k):



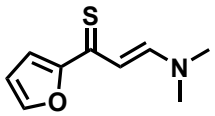
The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 139 - 140 ºC. Yield: 81% (513.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 10.5 Hz, 1H), 7.75 – 7.62 (m, 2H), 7.55 (d, J = 6.4 Hz, 2H), 6.48 (d, J = 10.9 Hz, 1H), 3.29 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.3, 158.1, 147.5, 137.0, 129.0, 110.9, 97.0, 46.5, 38.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}INS$: 317.9813. Found: 317.9807.

(1*E*, 4*E*)-1-(Dimethylamino)-5-phenylpenta-1, 4-diene-3-thione (1l):



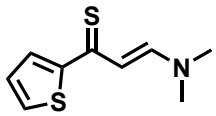
The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 105 - 107 ºC. Yield: 80% (347.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.80 (d, J = 15.4 Hz, 1H), 7.59 (d, J = 7.6 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.29 – 7.22 (m, 1H), 6.34 (d, J = 11.7 Hz, 1H), 3.27 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 144.0, 136.2, 136.0, 128.4, 79.8, 79.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{16}NS$: 218.1003. Found: 218.0998.

(*E*)-3-(Dimethylamino)-1-(furan-2-yl)prop-2-ene-1-thione (1m):



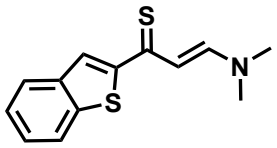
The title compound was prepared according to the general procedure (EA/PE = 1/1.5, R_f = 0.1). The product was obtained as red solid, Mp. 90 – 92 ºC. Yield: 60% (218.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 11.8 Hz, 1H), 7.52 (dd, J_1 = 1.7 Hz, J_2 = 0.8 Hz, 1H), 7.39(dd, J_1 = 3.5 Hz, J_2 = 0.8 Hz, 1H), 6.80 (d, J = 11.7 Hz, 1H), 6.48 (dd, J_1 = 3.5 Hz, J_2 = 1.7 Hz, 1H), 3.30 (s, 3H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 159.1, 157.6, 144.2, 116.0, 113.0, 107.3, 46.1, 38.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{12}NOS$: 182.0640. Found: 182.0634.

(*E*)-3-(Dimethylamino)-1-(thiophen-2-yl) prop-2-ene-1-thione (1n):



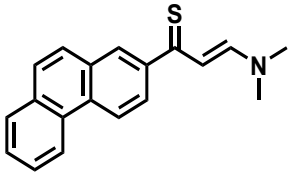
The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 129 - 131 ºC. Yield: 84% (331.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 11.5 Hz, 1H), 7.61 (dd, J_1 = 1.0 Hz, J_2 = 3.8 Hz, 1H), 7.49 (dd, J_1 = 1.2 Hz, J_2 = 5.2 Hz, 1H), 7.07 (dd, J_1 = 3.8 Hz, J_2 = 5.1 Hz, 1H), 6.62 (d, J = 11.5 Hz, 1H), 3.26 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 157.9, 154.7, 132.9, 128.1, 125.4, 108.0, 46.3, 38.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{12}NS_2$: 198.0411. Found: 198.0414.

(*E*)-1-(Benzo[b]thiophen-2-yl)-3-(dimethylamino)prop-2-ene-1-thione(1o):



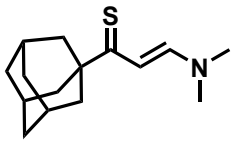
The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 195 - 197 ºC. Yield: 60% (296.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 11.5 Hz, 1H), 7.86 (s, 1H), 7.83 – 7.75 (m, 2H), 7.40 – 7.28 (m, 2H), 6.77 (d, J = 11.7 Hz, 1H), 3.28 (s, 3H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 157.5, 142.9, 139.9, 125.9, 125.4, 124.5, 122.3, 121.6, 46.2, 38.4, 29.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{14}NS_2$: 248.0568. Found: 248.0562.

(*E*)-3-(Dimethylamino)-1-(phenanthren-2-yl)prop-2-ene-1-thione(1p):



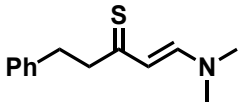
The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 169 - 170 ºC. Yield: 84% (489.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 8.0 Hz, 1H), 8.62 (d, J = 8.7 Hz, 1H), 8.55 – 8.30 (m, 2H), 8.18 (s, 1H), 7.89 – 7.87 (m, 1H), 7.83 – 7.71 (m, 2H), 7.69 – 7.56 (m, 2H), 6.73 (d, J = 11.2 Hz, 1H), 3.22 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.9, 157.9, 145.8, 132.6, 131.7, 131.5, 130.1, 128.8, 127.7, 127.5, 127.3, 127.2, 126.9, 126.1, 123.2, 122.4, 111.4, 46.3, 38.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}NS$: 292.1160. Found: 292.1153.

(*E*)-1-(Adamantan-1-yl)-3-(dimethylamino) prop-2-ene-1-thione (1q):



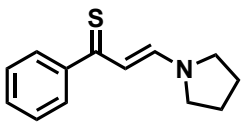
The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 144 - 146 ºC. Yield: 73% (364.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 11.4 Hz, 1H), 6.27 (d, J = 11.4 Hz, 1H), 3.21 (s, 3H), 2.97 (s, 3H), 2.04 (s, 3H), 2.01 – 1.94 (m, 6H), 1.69 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 108.7, 48.7, 43.2, 38.3, 36.9, 29.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{24}NS$: 250.1630. Found: 250.1627.

(*E*)-1-(Dimethylamino)-5-phenylpent-1-ene-3-thione (1r):



The title compound was prepared according to the general procedure. The product was obtained as red oil. Yield: 42% (182.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 10.8 Hz, 1H), 7.32 – 7.20 (m, 4H), 7.15 – 7.09 (m, 1H), 5.97 (d, J = 11.4 Hz, 1H), 3.14 (s, 3H), 3.00 (s, 3H), 2.92 – 2.75 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 223.0, 156.9, 141.4, 128.2, 128.0, 125.5, 111.8, 53.3, 45.7, 37.9, 36.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{18}NS$: 220.1160. Found:.220.1160.

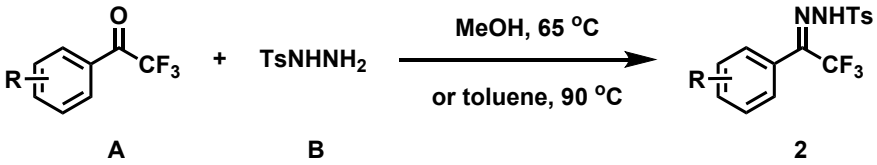
(*E*)-1-Phenyl-3-(pyrrolidin-1-yl) prop-2-ene-1-thione (1s):



The title compound was prepared according to the general procedure. The product was

obtained as red solid, Mp. 121 - 123 ºC. Yield: 78% (339.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 10.9 Hz, 1H), 7.84 (d, J = 7.3 Hz, 2H), 7.41 – 7.30 (m, 3H), 6.51 (d, J = 11.2 Hz, 1H), 3.72 (t, J = 6.0 Hz, 2H), 3.40 (t, J = 6.6 Hz, 2H), 2.14 – 1.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.1, 153.3, 148.1, 129.9, 127.7, 127.1, 112.1, 53.4, 48.2, 24.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{16}NS$: 218.1003. Found: 218.0998.

3.2 General procedure for hydrazones and their spectral data[2]:



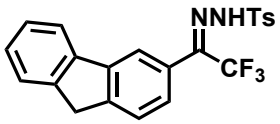
A **B** **2**

To a round bottom flask surmounted with a reflux condenser was added N-tosylhydrazide **B** (5.0 mmol, 1.0 equiv.) and the minimum quantity of solvent (either methanol or toluene according to individual substrates) needed to dissolve the hydrazide at reflux (approximately 1.5 M). Subsequently the reaction was cooled to room temperature and trifluoroacetophenone **A** (5.0 mmol, 1.0 equiv.) was added in one portion. The reaction mixture was then stirred at 65 °C (MeOH) or 90 °C (Toluene) over 4-16 h (monitor by TLC). The solution was cooled down to 0 °C, at which point the product precipitated out of solution in most cases (precipitation can be induced by addition of pentane). The precipitate was collected by vacuum filtration and washed with pentane, in which case it was used without further purification. If no precipitation occurred, the solvent was removed under reduced pressure and the residue used in the

[2] X. Liang, P. Guo, W. Yang, M. Li, C. Jiang, W. Sun, T.-P. Loh and Y. Jiang, *Chem. Commun.,* 2020, **56**, 2043-2046.

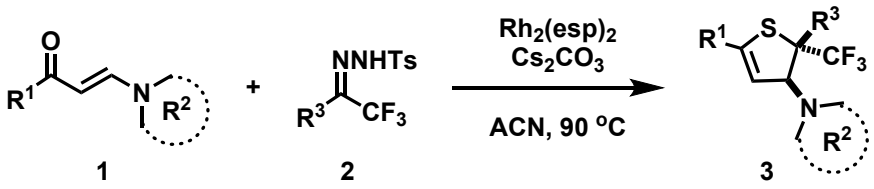
next step without further purification.

***N'*-(1-(9*H*-fluoren-3-yl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (2h):**



The title compound was prepared according to the general procedure (EA/PE = 1/1.5, R_f = 0.4). The product was obtained as yellow solid, Mp. 82 – 85 ℃. Yield: 86% (1853.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 1H), 7.93 – 7.88 (m, 1H), 7.89 – 7.80 (m, 3H), 7.63 – 7.57 (m, 1H), 7.47 – 7.32 (m, 5H), 7.29 – 7.21 (m, 1H), 3.95 (s, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.9, 144.7, 143.6, 140.0, 134.5, 129.8, 128.2, 128.0, 127.2, 126.8, 125.2, 124.7, 122.8, 121.1, 120.6, 36.9, 21.7; ^{19}F NMR (376 MHz, CDCl3) δ -67.95; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{22}H_{18}F_3N_2O_2S$: 431.1041. Found: 431.1047. The spectroscopic properties of the other compounds were consistent with literature data[2].

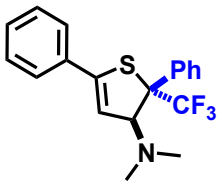
3.3 General procedure for 2-CF_3-2*H*-thiophenes and their spectral data:



A mixture of **1** (0.2 mmol, 1.0 equiv.), **2** (0.48 mmol, 2.4 equiv.), $Rh_2(esp)_2$ (0.002 mmol, 1 mol%), Cs_2CO_3 (0.5 mmol, 2.5 equiv.) and acetonitrile (4 mL) was sealed in a Schlenk tube under Argon protection at 90 °C and the mixture was stirred for 20 h or

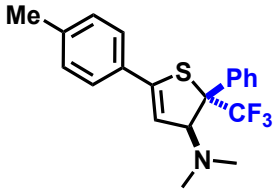
until the **1** was consumed completely. Then the reaction mixture was filetered by diatomite and concentrated under reduced pressure and purified by column chromatography (EA/PE = 1:20) to give the desired product **3**.

(2*S*,3*S*)-*N*,*N*-Dimethyl-2,5-diphenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3aa):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.5). The product was obtained as yellow solid, Mp. 131 – 133 ºC. Yield: 91% (63.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 4H), 7.42 – 7.33 (m, 6H), 6.14 (d, J = 3.2 Hz, 1H), 4.59 (d, J = 3.2 Hz, 1H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 132.9, 132.2, 131.1 (q, J = 1.4 Hz), 128.9, 128.6, 128.3, 128.2, 126.8, 126.6, 113.8, 73.3 (q, J = 1.5 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.25; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{19}F_3NS$: 350.1190. Found: 350.1181.

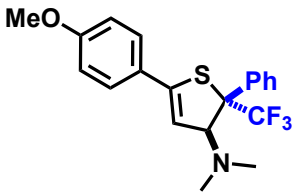
(2*S*,3*S*)-*N*,*N*-Dimethyl-2-phenyl-5-(p-tolyl)-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ab):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow solid, Mp. 95 – 96 ºC. Yield: 82% (59.7

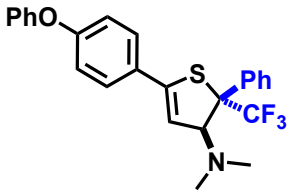
mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H), 7.50 – 7.44 (m, 2H), 7.37 – 7.32 (m, 3H), 7.22 – 7.17 (m, 2H), 6.09 (d, J = 3.1 Hz, 1H), 4.57 (d, J = 3.1 Hz, 1H), 2.38 (s, 3H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 132.3, 131.1 (q, J = 1.6 Hz), 130.1, 129.3, 128.6, 128.0, 126.8, 126.5, 112.9, 73.2 (q, J = 1.3 Hz), 21.3; ^{19}F NMR (376 MHz, CDCl3) δ -75.22; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{20}H_{21}F_3NS$: 364.1347. Found: 364.1341.

(2*S*,3*S*)-5-(4-Methoxyphenyl)-*N*,*N*-dimethyl-2-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ac):



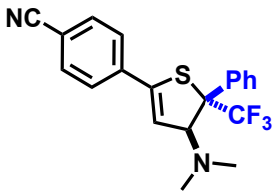
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.5). The product was obtained as red solid, Mp. 90 – 92 ºC. Yield: 93% (70.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 2H), 7.54 – 7.49 (m, 2H), 7.36 – 7.30 (m, 3H), 6.94 – 6.90 (m, 2H), 6.01 (d, J = 3.1 Hz, 1H), 4.56 (d, J = 3.1 Hz, 1H), 3.84 (s, 3H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 141.3, 132.3, 131.1(q, J = 1.6 Hz), 128.0, 127.9, 126.8, 125.6, 114.0, 111.9, 73.3 (q, J = 1.5 Hz), 55.4; ^{19}F NMR (376 MHz, CDCl3) δ -75.12; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{20}H_{21}F_3NOS$: 380.1296. Found: 380.1292.

(2*S*,3*S*)-*N*,*N*-Dimethyl-5-(4-phenoxyphenyl)-2-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ad):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as red solid, Mp. 123 – 133 ºC. Yield: 85% (75.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 4H), 7.39 – 7.32 (m, 5H), 7.19 – 7.13 (m, 1H), 7.06 – 7.00 (m, 4H), 6.07 (d, J = 3.1 Hz, 1H), 4.58 (d, J = 3.1 Hz, 1H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 156.6, 141.0, 132.1, 131.1 (q, J = 1.3 Hz), 129.9, 128.1, 128.1, 128.1, 127.9, 126.8, 123.7, 119.2, 118.6, 113.0, 73.2 (q, J = 1.5 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.27; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{25}H_{23}F_3NOS$: 442.1452. Found: 442.1447.

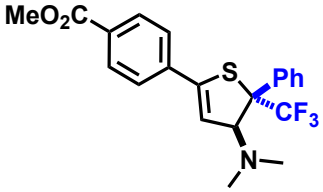
4-((4*S*,5*S*)-4-(Dimethylamino)-5-phenyl-5-(trifluoromethyl)-4,5-dihydrothiophen-2-yl)benzonitrile (3ae):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.4). The product was obtained as yellow solid, Mp. 105 – 106 ºC. Yield: 49% (36.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 4H), 7.55 – 7.53 (m, 2H), 7.38 – 7.33 (m, 3H), 6.27 (d, J = 3.2 Hz, 1H), 4.61 (d, J = 3.2 Hz, 1H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 137.2, 132.4, 131.6, 131.0 (q, J = 1.3 Hz), 127.2, 126.9, 118.5, 117.7, 112.3 , 73.2 (q, J = 1.4 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.40;

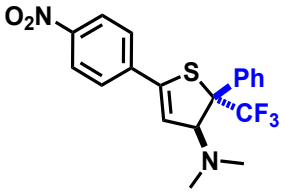
HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{20}H_{18}F_3N_2S$: 375.1143. Found: 375.1141.

4-Methyl-((4*S*,5*S*)-4-(dimethylamino)-5-phenyl-5-(trifluoromethyl)-4,5-dihydrothiophen-2-yl)benzoate (3af):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow solid, Mp. 131 – 133 ºC. Yield: 53% (42.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.05 (m, 2H), 7.65 – 7.56 (m, 4H), 7.55 – 7.26 (m, 3H), 6.26 (d, J = 1.2 Hz, 1H), 4.60 (d, J = 1.6 Hz, 1H), 3.94 (s, 3H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 140.9, 137.1, 131.9, 131.1 (q, J = 1.3 Hz), 130.2, 129.9, 128.2, 126.9, 126.5, 116.4, 73.2 (q, J = 1.4 Hz), 52.3; ^{19}F NMR (376 MHz, CDCl3) δ -75.43; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{21}H_{21}F_3NO_2S$: 408.1245. Found: 408.1250.

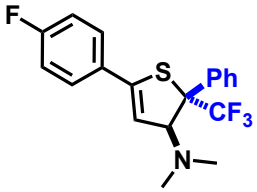
(2*S*,3*S*)-*N*,*N*-Dimethyl-5-(4-nitrophenyl)-2-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ag):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.4). The product was obtained as yellow solid, Mp. 128 – 129 ºC. Yield: 27%

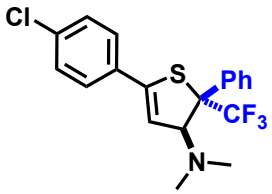
(21.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.24 (m, 2H), 7.74 – 7.71 (m, 2H), 7.56 – 7.54 (m, 2H), 7.39 – 7.33 (m, 3H), 6.32 (d, J = 3.2 Hz, 1H), 4.63 (d, J = 3.2 Hz, 1H), 2.17 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 139.9, 139.0, 131.6, 130.9 (q, J = 1.3 Hz), 128.3, 127.3, 127.0, 123.9, 118.6, 73.4 (q, J = 1.3 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.38; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}F_3N_2O_2S$: 395.1041. Found:395.1036.

(2*S*,3*S*)-5-(4-Fluorophenyl)-*N*,*N*-dimethyl-2-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ah):



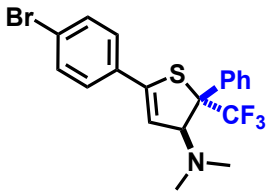
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.5). The product was obtained as yellow solid, Mp. 97 – 99 ºC. Yield: 71% (52.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 4H), 7.37 – 7.32 (m, 3H), 7.11 – 7.05 (m, 2H), 6.06 (d, J = 3.1 Hz, 1H), 4.58 (d, J = 3.1 Hz, 1H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, J = 249.3 Hz), 161.8, 140.7, 132.1, 131.1 (q, J = 1.3 Hz), 129.2 (d, J = 3.4 Hz), 128.4 (d, J = 8.2 Hz), 128.2, 126.9, 125.4, 115.6 (d, J = 21.6 Hz), 113.8, 73.3 (q, J = 1.4 Hz), 70.4; ^{19}F NMR (376 MHz, CDCl3) δ -75.32, -111.88; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}F_4NS$: 368.1096. Found: 368.1100.

(2*S*,3*S*)-5-(4-Chlorophenyl)-*N*,*N*-dimethyl-2-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ai):



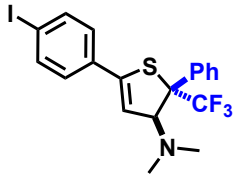
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow solid, Mp. 100 – 102 ºC. Yield: 78% (59.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 2H), 7.53 – 7.50 (m, 2H), 7.39 – 7.32 (m, 5H), 6.12 (d, J = 2.8 Hz, 1H), 4.59 (d, J = 3.2 Hz, 1H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 134.8, 131.4, 131.6 (q, J = 1.5 Hz), 128.8, 128.2, 127.8, 126.9, 114.6, 73.3 (q, J = 1.1 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.34; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}ClF_3NS$: 384.0801. Found: 384.0797.

(2*S*,3*S*)-5-(4-Bromophenyl)-*N*,*N*-dimethyl-2-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3aj):



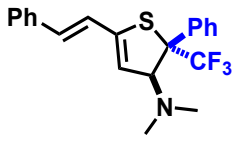
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow solid, Mp. 101 – 103 ºC. Yield: 84% (71.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 4H), 7.46 – 7.43 (m, 2H), 7.38 – 7.32 (m, 3H), 6.14 (d, J = 3.2 Hz, 1H), 4.58 (d, J = 3.2 Hz, 1H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 132.0, 131.9, 131.7, 131.1 (q, J = 1.4 Hz), 128.2, 128.1, 126.9, 122.9, 114.7, 73.3 (q, J = 1.7 Hz) ; ^{19}F NMR (376 MHz, CDCl3) δ -75.32; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}BrF_3NS$: 428.0295. Found: 428.0290.

(2*S*,3*S*)-5-(4-Iodophenyl)-N,N-dimethyl-2-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ak):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow solid, Mp. 101 – 103 ºC. Yield: 85% (80.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.70 (d, J = 8.4 Hz, 2H), 7.55 – 7.53 (d, J = 6.8 Hz, 2H), 7.34 – 7.29 (m, 5H), 6.13 (d, J = 2.8 Hz, 1H), 4.56 (d, J = 2.8 Hz, 1H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 137.7, 132.4, 131.9, 131.1 (q, J = 1.1 Hz), 128.2, 128.1, 126.9, 114.8, 94.6, 73.2 (q, J = 1.1 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.28; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}F_3INS$: 476.0157. Found: 476.0158.

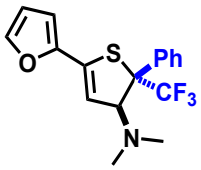
(2*S*,3*S*)-*N*,*N*-Dimethyl-2-phenyl-5-((*E*)-styryl)-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3al):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.5). The product was obtained as yellow solid, Mp. 121– 122 ºC. Yield: 58% (43.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H), 7.49 – 7.43 (m, 2H), 7.39 – 7.32 (m, 5H), 7.31 – 7.26 (m, 1H), 7.02 (d, J = 15.9 Hz, 1H), 6.69 (d, J = 15.9

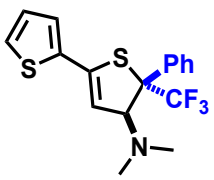
Hz, 1H), 5.90 (d, J = 3.2 Hz, 1H), 4.51 (d, J = 3.2 Hz, 1H), 2.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 136.3, 133.9, 131.1 (q, J = 1.6 Hz), 128.7, 128.3, 128.1, 126.9, 126.7, 121.5, 119.1,72.6 (q, J = 1.2 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.14; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{21}H_{21}F_3NS$: 376.1347. Found: 376.1348.

(2*S*,3*S*)-5-(Furan-2-yl)-*N*,*N*-dimethyl-2-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3am):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.5). The product was obtained as yellow solid, Mp. 62 – 64 ºC. Yield: 85% (57.8mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.50 (m, 2H), 7.50 – 7.45 (m, 1H), 7.40 – 7.26 (m, 3H), 6.70 – 6.38 (m, 2H), 6.15 (d, J = 3.2 Hz, 1H), 4.58 (s, 1H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 131.0 (q, J = 1.1 Hz), 128.2, 126.9, 112.8, 111.6, 109.3, 99.9, 73.1 (q, J = 1.7 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.15; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{17}F_3NOS$: 340.0983. Found: 340.0977.

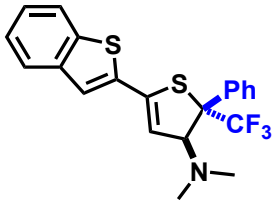
(4*S*,5*S*)-*N*,*N*-Dimethyl-5-phenyl-5-(trifluoromethyl)-4,5-dihydro-[2,2'-bithiophen]-4-amine (3an):



The title compound was prepared according to the general procedure (EA/PE = 1/20,

R_f = 0.5). The product was obtained as yellow solid, Mp. 84 – 86 ºC. Yield: 85% (60.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.48 (m, 2H), 7.42 – 7.32 (m, 4H), 7.18 – 7.14 (m, 1H), 7.08– 7.00 (m, 1H), 6.03 (d, J = 3.2 Hz, 1H), 4.55 (s, 1H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 134.7, 132.0 131.1 (q, J = 1.4 Hz), 128.2, 127.6,126.9, 126.7, 125.9,113.8, 99.9, 73.2 (q, J = 1.4 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.15; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_{17}H_{17}F_3NS_2$: 356.0755. Found: 356.0747.

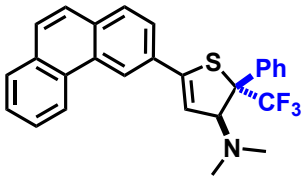
(2*S*,3*S*)-5-(Benzo[b]thiophen-2-yl)-*N*,*N*-dimethyl-2-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ao):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.5). The product was obtained as yellow solid, Mp. 97–99 ºC. Yield: 73% (59.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.75 (m, 2H), 7.58–7.56 (m, 2H), 7.39–7.35 (m, 6H), 6.15 (d, J = 3.2 Hz, 1H), 4.60 (d, J = 3.2 Hz, 1H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 139.3, 135.6, 135.2, 131.9, 131.0 (q, J = 1.6 Hz), 128.2, 126.9, 125.4, 124.8, 124.0, 123.8, 122.1, 116.5, 73.2 (q, J = 1.8 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.14; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_{21}H_{19}F_3NS_2$: 406.0911. Found:406.0906.

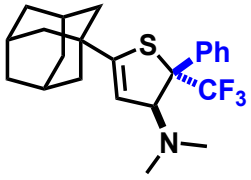
(2*S*,3*S*)-*N*,*N*-Dimethyl-5-(phenanthren-2-yl)-2-phenyl-2-(trifluoromethyl)-2,3-

dihydrothiophen-3-amine (3ap):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow solid, Mp. 168 – 170 ºC. Yield: 75% (67.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.78 – 8.76 (d, J = 8.4 Hz, 1H), 7.93 – 7.84 (m, 3H), 7.80 – 7.62 (m, 6H), 7.41 – 7.38 (m, 3H), 6.35 (d, J = 2.8 Hz, 1H), 4.69 (d, J = 3.2 Hz, 1H), 2.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 132.3, 132.3, 131.2 (q, J =1.6 Hz), 130.9, 130.2, 130.1, 128.8, 128.7, 128.1, 127.8, 127.0,126.9, 126.8, 126.4, 124.5, 122.8, 121.3, 114.5,114.5, 73.4 (q, J = 1.2 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.13; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{27}H_{23}F_3NS$: 450.1503. Found:450.1504.

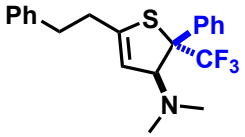
(2*S*,3*S*)-5-((3*S*,5*S*,7*S*)-Adamantan-1-yl)-*N*,*N*-dimethyl-2-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3aq):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.5). The product was obtained as yellow solid, Mp. 85 – 87 ºC. Yield: 58% (47.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.45 – 7.26 (s, 3H), 5.38 (d, J = 2.8 Hz, 1H), 4.36 (d, J = 2.8 Hz, 1H), 2.05 – 1.70 (m, 21H); ^{13}C NMR (100 MHz,

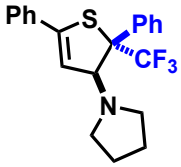
$CDCl_3$) δ155.2, 132.7, 131.2 (q, J = 1.5 Hz), 127.8, 126.7, 108.7, 72.2 (q, J = 1.4 Hz), 42.5, 36.8, 36.7, 28.4; ^{19}F NMR (376 MHz, CDCl3) δ -75.30; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{23}H_{29}F_3NS$: 408.1973. Found: 408.1979.

(2S,3S)-*N*,*N*-Dimethyl-5-phenethyl-2-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ar):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.4). The product was obtained as red oil. Yield: 35% (26.5 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 2H), 7.36 – 7.15 (m, 8H), 5.44 (d, J = 3.2 Hz, 1H), 4.35 (d, J = 3.2 Hz, 1H), 2.97 – 2.87 (m, 2H), 2.77 – 2.67 (m, 2H), 1.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 131.1 (q, J = 1.4 Hz), 128.4, 128.4, 127.9, 126.7, 126.1, 113.6, 72.8 (q, J = 1.1 Hz), 34.8, 32.6; ^{19}F NMR (376 MHz, CDCl3) δ -75.25; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{21}H_{23}F_3NS$: 378.1503. Found: 378.1497.

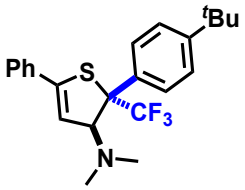
1-((2*S*,3*S*)-2,5-Diphenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-yl)pyrrolidine (3as):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.4). The product was obtained as yellow oil. Yield: 70% (52.7 mg); ^1H NMR (400

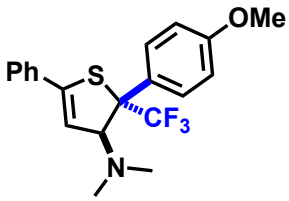
MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 4H), 7.42 – 7.27 (m, 6H), 6.10 (d, J = 3.2 Hz, 1H), 4.90 (d, J = 3.2 Hz, 1H), 2.65 – 2.64 (m, 2H), 2.37 – 2.34 (m, 2H), 1.54 – 1.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 133.0, 132.6, 130.9 (q, J = 1.4 Hz), 128.9, 128.6, 128.0, 126.6, 126.5, 113.9, 69.1 (q, J = 1.2 Hz), 24.0; ^{19}F NMR (376 MHz, CDCl3) δ -74.90; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{21}H_{20}F_3NS$: 376.1347. Found: 376.1350.

(2*S*,3*S*)-2-(4-(Tert-butyl)phenyl)-N,N-dimethyl-5-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine(3ba):



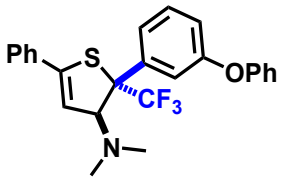
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow solid, Mp. 92 – 93 ºC. Yield: 96% (77.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H), 7.53 – 7.45 (m, 2H), 7.44 – 7.30 (m, 5H), 6.14 (d, J = 3.0 Hz, 1H), 4.58 (d, J = 2.5 Hz, 1H), 2.15 (s, 6H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 133.0 130.6 (q, J = 1.6 Hz), 128.9, 128.6, 126.6, 123.8, 114.0, 112.9, 105.1, 73.2 (q, J = 1.1 Hz), 34.5, 31.3; ^{19}F NMR (376 MHz, CDCl3) δ -75.33; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{23}H_{27}F_3NS$: 406.1816. Found: 406.1809.

(2*S*,3*S*)-2-(4-Methoxyphenyl)-*N*,*N*-dimethyl-5-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ca):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.4). The product was obtained as yellow solid, Mp. 88 – 90 ºC. Yield: 74% (56.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.54 – 7.49 (m, 2H), 7.37 – 7.30 (m, 3H), 6.94 – 6.89 (m, 2H), 6.01 (d, J = 3.2 Hz, 1H), 4.56 (d, J = 3.2 Hz, 1H), 3.84 (s, 3H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 141.3, 132.3, 131.1 (q, J = 1.6 Hz), 128.0, 127.9, 126.8, 125.6, 113.9, 111.9, 73.3 (q, J = 1.6 Hz), 55.4; ^{19}F NMR (376 MHz, CDCl3) δ -75.60; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{20}H_{21}F_3NOS$: 380.1296. Found: 380.1292.

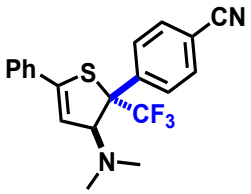
(2*S*,3*S*)-*N*,*N*-Dimethyl-2-(3-phenoxyphenyl)-5-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3da):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow oil. Yield: 85% (75.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.41 – 7.28 (m, 8H), 7.10 – 6.96 (m, 4H), 6.10 (d, J = 3.2 Hz, 1H), 4.50 (d, J = 3.2 Hz, 1H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5,155.1,141.8,134.0 (q, J = 1.0 Hz), 132.8, 129.6, 129.0, 128.6, 128.2, 126.6, 126.2, 123.0, 122.9, 119.3, 118.1, 113.7, 73.3 (q, J = 1.5 Hz); ^{19}F NMR (376 MHz, CDCl3) δ

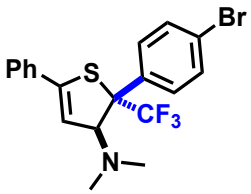
-75.16; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{25}H_{23}F_3NOS$: 442.1452. Found: 442.1447.

4-((2*S*,3*S*)-3-(Dimethylamino)-5-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-2-yl)benzonitrile (3ea):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow solid, Mp. 103 – 105 ºC. Yield: 28% (21.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 4H), 7.58 – 7.55 (m, 2H), 7.44 – 7.38 (m, 3H), 6.13 (d, J = 2.8 Hz, 1H), 4.61 (s, 1H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 137.6, 132.5, 132.0 (q, J = 1.3 Hz), 130.5, 129.2, 128.7, 126.6, 118.6, 113.5, 112.1, 73.6 (q, J = 1.2 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -74.88; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{20}H_{18}F_3N_2S$: 375.1143. Found: 375.1138.

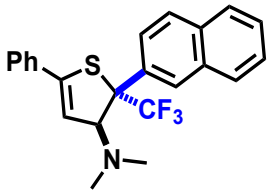
(2*S*,3*S*)-2-(4-Bromophenyl)-*N*,*N*-dimethyl-5-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3fa):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow oil. Yield: 83% (71.1 mg); ^{1}H NMR (400

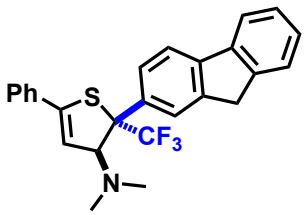
MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.51 – 7.44 (m, 4H), 7.43 – 7.36 (m, 3H), 6.13 (d, J = 3.2 Hz, 1H), 4.55 (d, J = 3.2 Hz, 1H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 132.8 (q, J = 1.5 Hz), 132.7, 131.3, 130.0, 129.1, 128.6, 126.6, 122.7, 113.7, 73.3 (q, J = 1.5 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -75.34; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}BrF_3NS$: 428.0295. Found: 428.0286.

(2*S*,3*S*)-N,N-dimethyl-2-(naphthalen-2-yl)-5-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ga)



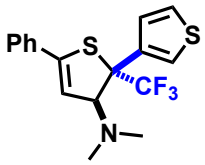
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow solid, Mp. 122 – 123 ºC. Yield: 92% (73.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.06 (m, 1H), 7.92 – 7.83 (m, 2H), 7.81 – 7.77 (m, 1H), 7.72 – 7.66 (m, 1H), 7.64 – 7.60 (m, 2H), 7.56 – 7.48 (m, 2H), 7.46 – 7.34 (m, 3H), 6.19 (d, J = 3.2 Hz, 1H), 4.69 (d, J = 3.2 Hz, 1H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 132.9, 132.7, 132.3, 130.4 (q, J = 1.1 Hz), 132.2, 129.0, 128.9, 128.9, 128.8, 128.6, 128.3, 127.3, 126.6, 126.6, 125.8, 125.5, 113.9, 73.3 (q, J = 1.3 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -74.83; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{23}H_{21}F_3NS$: 400.1347. Found: 400.1342.

(2*S*,3*S*)-2-(9*H*-Fluoren-2-yl)-*N*,*N*-dimethyl-5-phenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-amine (3ha):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow solid, Mp. 165 – 166 ºC. Yield: 45% (39.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J =7.5 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.64 – 7.58 (m, 3H), 7.57 – 7.53 (m, 1H), 7.44 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 6.15 (d, J = 3.2 Hz, 1H), 4.63 (d, J = 3.2 Hz, 1H), 3.94 (s, 2H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 141.9, 141.7, 141.5, 141.2, 133.0, 130.6, 129.9 (q, J = 1.5 Hz), 128.9, 128.6, 127.7, 126.9, 126.8, 126.6, 125.0, 120.1, 118.1, 114.0, 73.4 (q, J = 1.3 Hz), 37.0; ^{19}F NMR (376 MHz, CDCl3) δ -75.07; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{26}H_{23}F_3NS$: 438.1503. Found: 438.1495.

(2*S*,3*S*)-*N*,*N*-Dimethyl-5-phenyl-2-(trifluoromethyl)-2,3-dihydro-[2,3'-bithiophen]-3-amine (3ia)



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.6). The product was obtained as yellow solid, Mp. 74 – 76 ºC. Yield: 65% (46.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 3H), 7.45 – 7.33 (m, 3H), 7.31 – 7.26 (m, 2H), 6.09 (s, 1H), 4.58 (s, 1H), 2.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 132.9,130.0, 129.0, 128.6,126.6, 123.6, 114.1, 99.9, 74.5 (q, J = 1.6 Hz); ^{19}F

NMR (376 MHz, CDCl3) δ -75.42; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{17}F_3NS_2$: 356.0755. Found: 356.0748.

3.4 Derivative products and their spectral data

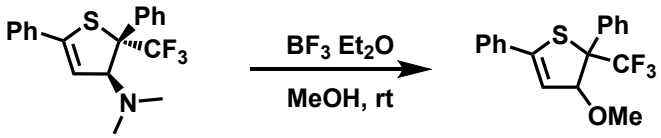
Large-scale reaction of 3aa：

A mixture of **1a** (10.0 mmol, 1.0 equiv.), **2a** (24.0 mmol, 2.4 equiv.), $Rh_2(esp)_2$ (0.1 mmol, 1 mol%), Cs_2CO_3 (25.0 mmol, 2.5 equiv.) and acetonitrile (50 mL) was sealed in a Schlenk tube under Argon protection at 90 °C and the mixture was stirred until the **1a** was consumed completely. Then the reaction mixture was filetered by diatomite and concentrated under reduced pressure and purified by column chromatography (EA/PE = 1:20) to give the desired product **3aa** (2.86g, 82%).

Large-scale reaction of 5a:

A mixture of enaminothione **1a** (10.0 mmol, 1.0 equiv.), **4** ($BrCF_2COOEt$, 20.0 mmol, 2.0 equiv.), $^nPr_3N$ (30.0 mmol, 3.0 equiv.), anhydrous THF (100 mL) was sealed in a Schlenk tube under nitrogen protection at 80 °C and the mixture was stirred until the enaminothione **1a** was consumed completely. The crude product was filtered through a short pad of Celite, and the filtrate was concentrated under vacuum and purified by flash chromatography (eluent: 20% v/v ethyl acetate in petroleum ether) to afford products **5a** (1.93g, 80%).

3-Methoxy-2,5-diphenyl-2-(trifluoromethyl)-2,3-dihydrothiophene (4)[3]:



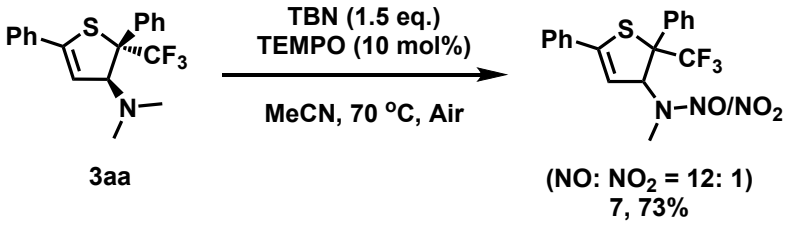
3aa **6, 78%**

A flame-dried round-bottomed flask was charged with **3aa** (0.2 mmol, 1.0 equiv.) and MeOH (2 mL), then cooled to 0 °C. $BF_3.Et_2O$ (0.2 mmol, 1.0 equiv.) was added dropwise and the mixture was stirred at room temperature until the **3aa** was consumed completely. The layers were separated and the aqueous layer was extracted with DCM (2 × 5 mL). The combined organic layers were washed with brine (10 mL), then dried (Na_2SO_4). After removal of the solvent, the residue was subjected to column chromatography (PE:EtOAc = 19:1) to give **6** (52.3 mg, 78% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 4H), 7.45 – 7.35 (m, 6H), 6.12 (d, J = 3.2 Hz, 1H), 5.26 (d, J = 3.2 Hz, 1H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 130.3 (q, J = 1.5 Hz), 129.5, 128.7, 128.6, 128.4, 128.2, 127.6, 126.8, 115.0, 99.9, 85.8, 54.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{16}F_3OS$: 337.0874. Found: 337.0860.

***N*-(2,5-diphenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-yl)-*N*-methylnitrous amide & *N*-(2,5-diphenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-yl)-*N*-methylnitramide (5)[4]:**

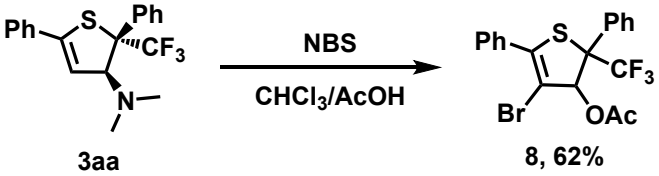
[3] M. Ikeda, T. Matsuzawa, T. Morita, T. Hosoya and S. Yoshida, *Chem. Eur. J.,* 2020, **26**, 12333–12337.

[4] X. Jia, P. Li, Y. Shao, Y. Yuan, H. Ji, W. Hou, X. Liu and X. Zhang, *Green Chem*., 2017, **19**, 5568−5574.



A tube was charged with 2*H*-thiophen **3aa** (0.4 mmol, 1.0 equiv.), TBN (0.6 mmol, 1.5 equiv.), TEMPO (0.04 mmol, 10 mol%), CH_3CN (5 mL) was added subsequently and the reaction mixture was stirred at 70 °C until the starting material was fully consumed (24 h). The product was obtained as brown oil. Yield: 73% (106.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 755 (m, 2H), 7.49– 7.40 (m, 5H), 7.37 – 7.29 (m, 3H), 7.19 (d, J = 3.6 Hz, 0.07H) & 6.88 (d, J = 3.6 Hz, 0.93H), 6.06 (d, J = 3.6 Hz, 0.93H) & 5.67 (d, J = 3.6 Hz, 0.07H), 3.25 (s, 0.21H) & 2.39 (s, 2.79H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 131.5, 130.1, 130.0 (q, J = 1.3 Hz), 129.1, 128.8, 128.1, 126.8, 72.3, 28.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.74, 75.28; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{16}F_2N_2OS$: 365.0935. Found: 365.0930. Calcd for $C_{18}H_{16}F_3N_2O_2S$: 381.0885. Found: 381.0877.

4-Bromo-2,5-diphenyl-2-(trifluoromethyl)-2,3-dihydrothiophen-3-yl acetate (6)[5]:



2*H*-thiophen **3aa** (0.2 mmol, 1.0 equiv.) and NBS (0.24 mmol, 1.2equiv.) were dissolved into CH_3COOH (4 mL) stirred at 55 °C for 12 h. After reaction, saturated

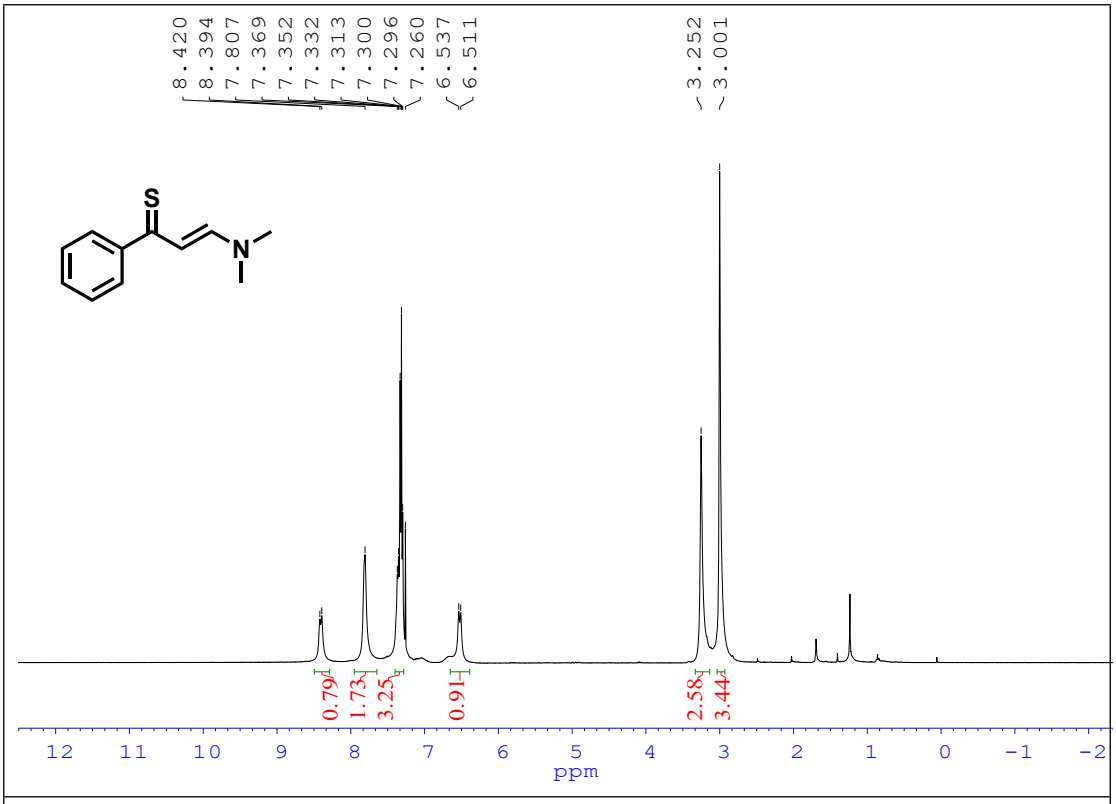
[5] M. Shi, Y. He, Y. Sun, D. Fang, J. Miao, M. U. Ali, T. Wang, Y. Wang, T. Zhang and H. Meng, *Org. Elect*., 2020, **84**, 105793–105803.

sodium bicarbonate (5 mL) was added to react with excess CH_3COOH and then retracted with DCM. The organic phase was dried, evaporated, was purified by column chromatography to give the product was obtained as a yellow oil (54.8 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H), 7.60 – 7.52 (m, 2H), 7.46 – 7.39 (m, 6H), 4.57 (s, 1H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 133.0, 132.1, 131.6, 129.9, 129.5, 128.7, 128.7, 128.5, 127.9, 104.3, 73,4, 29.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.47; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{15}BrF_3O_2S$: 442.9928. Found: 442.9916.

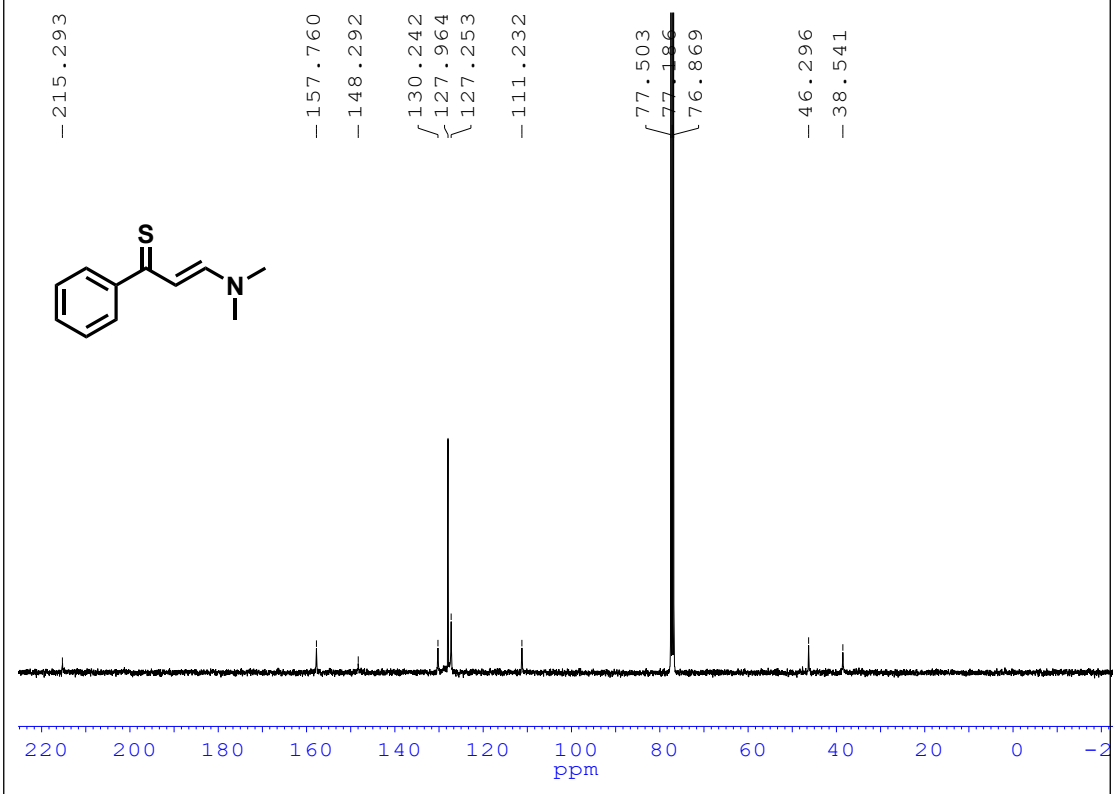
4. NMR Spectra

4.1 NMR spectra for enaminothiones

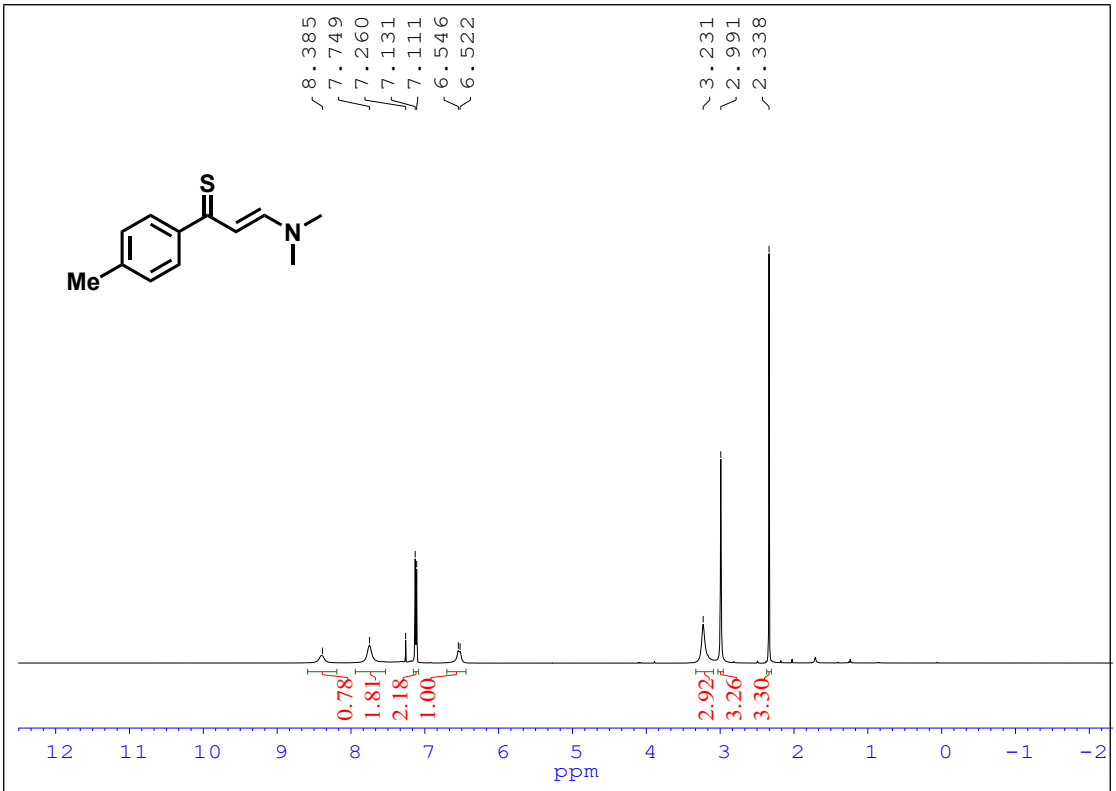
^1H NMR spectra of **1a**



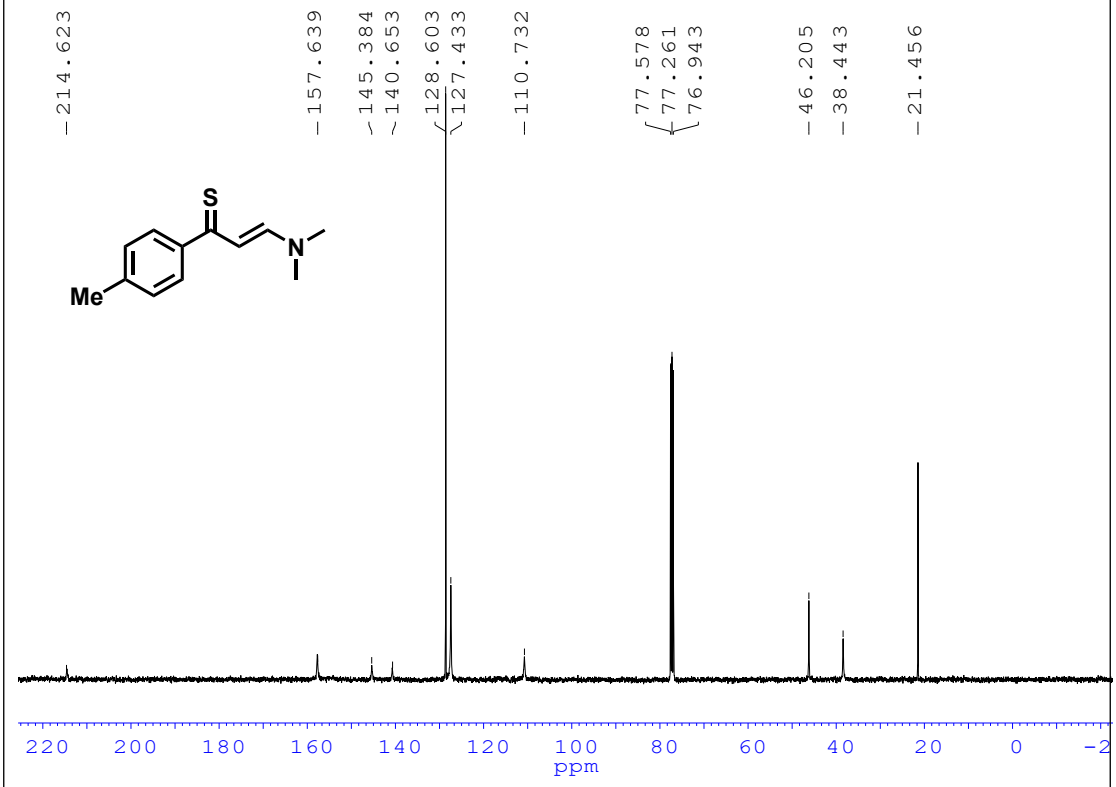
^{13}C NMR spectra of **1a**



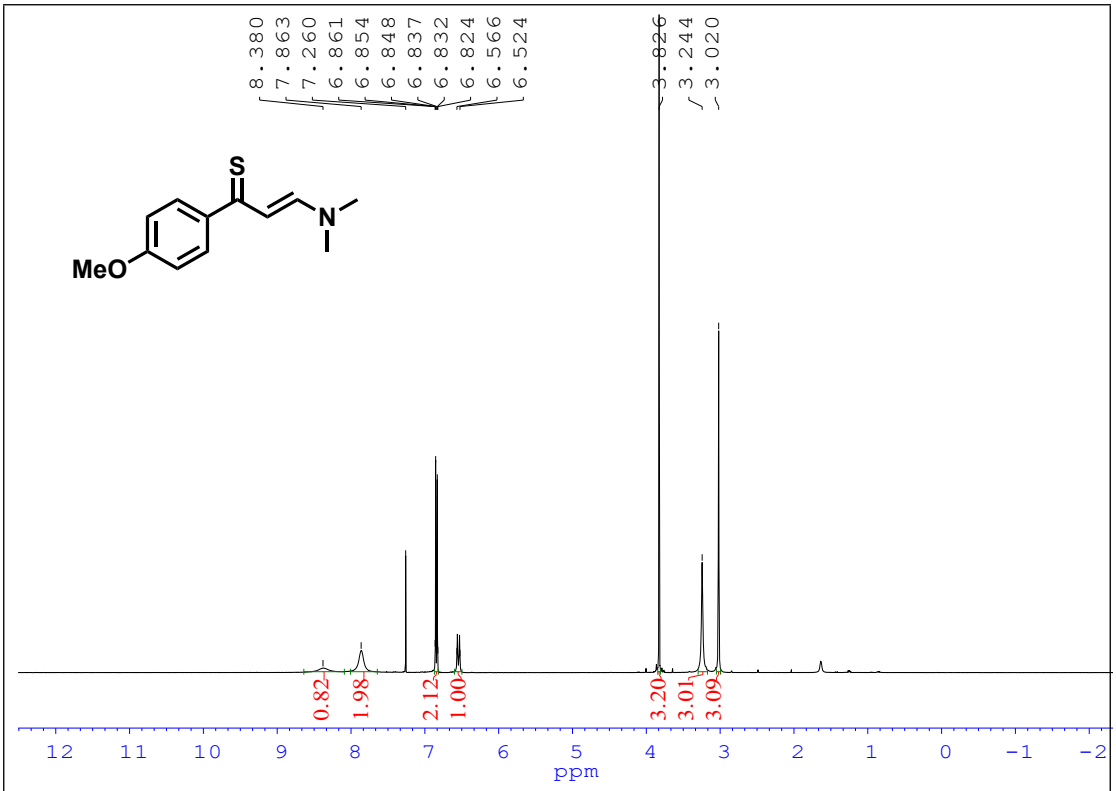
^{1}H NMR spectra of **1b**



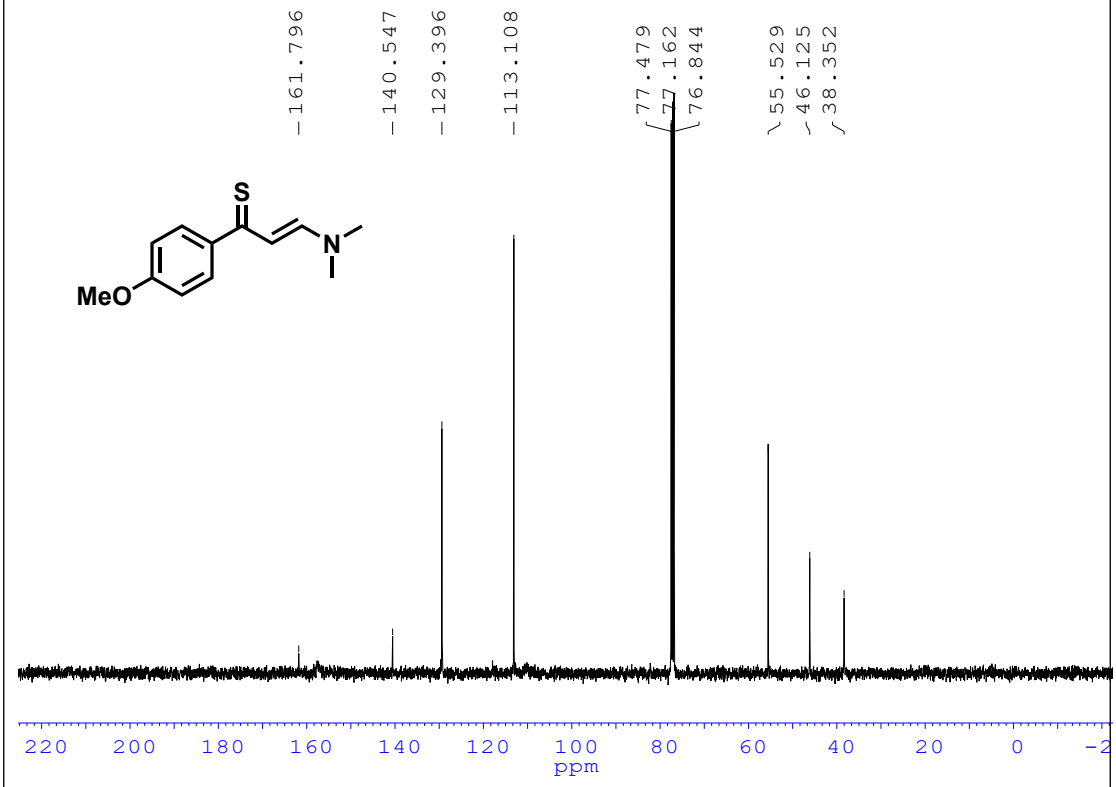
^{13}C NMR spectra of **1b**



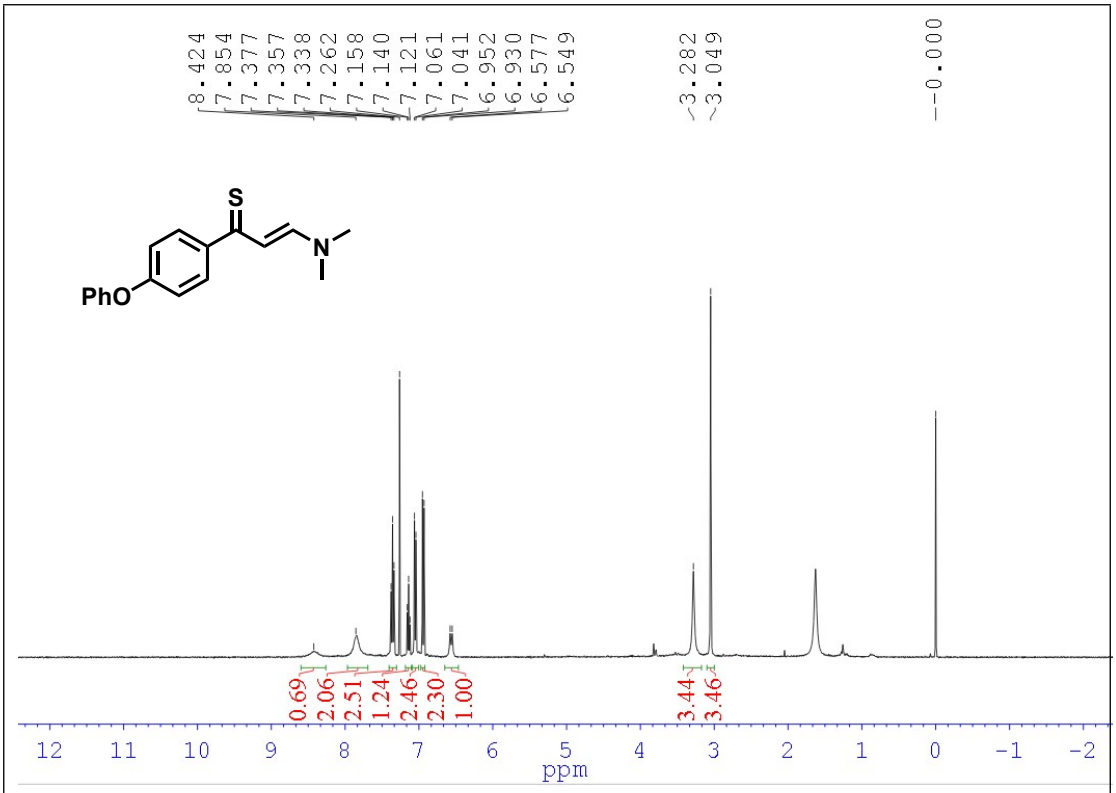
^{1}H NMR spectra of **1c**



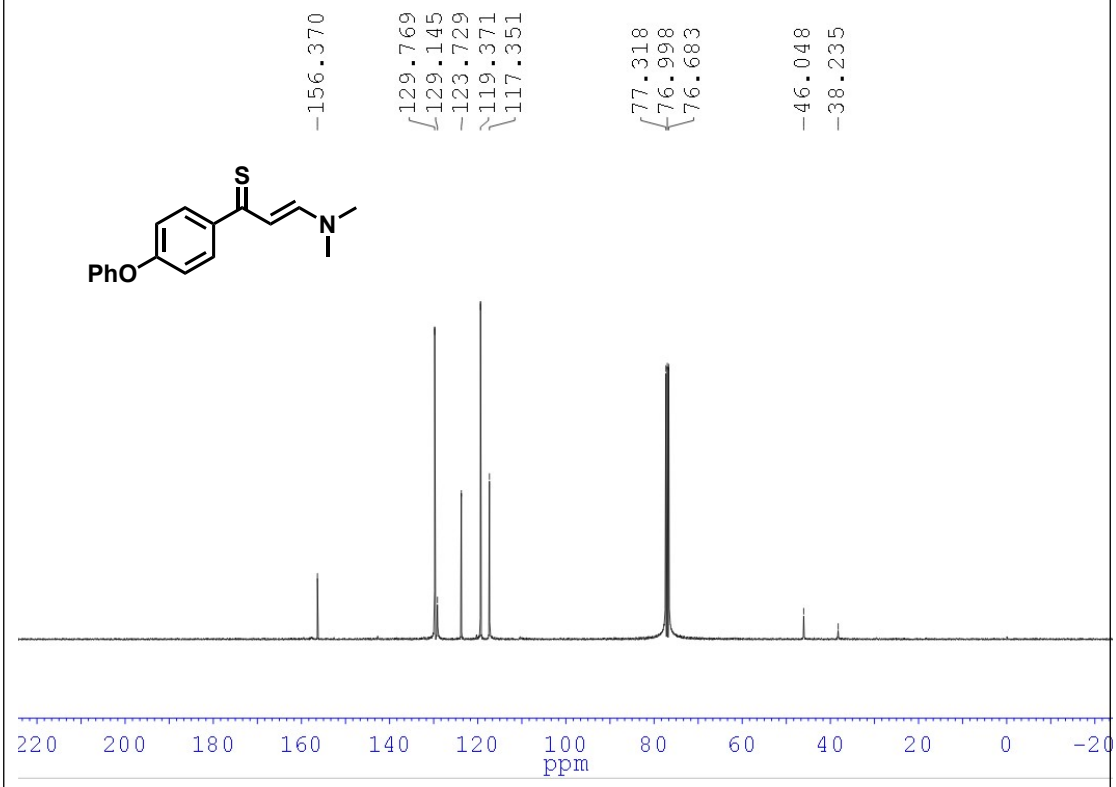
^{13}C NMR spectra of **1c**



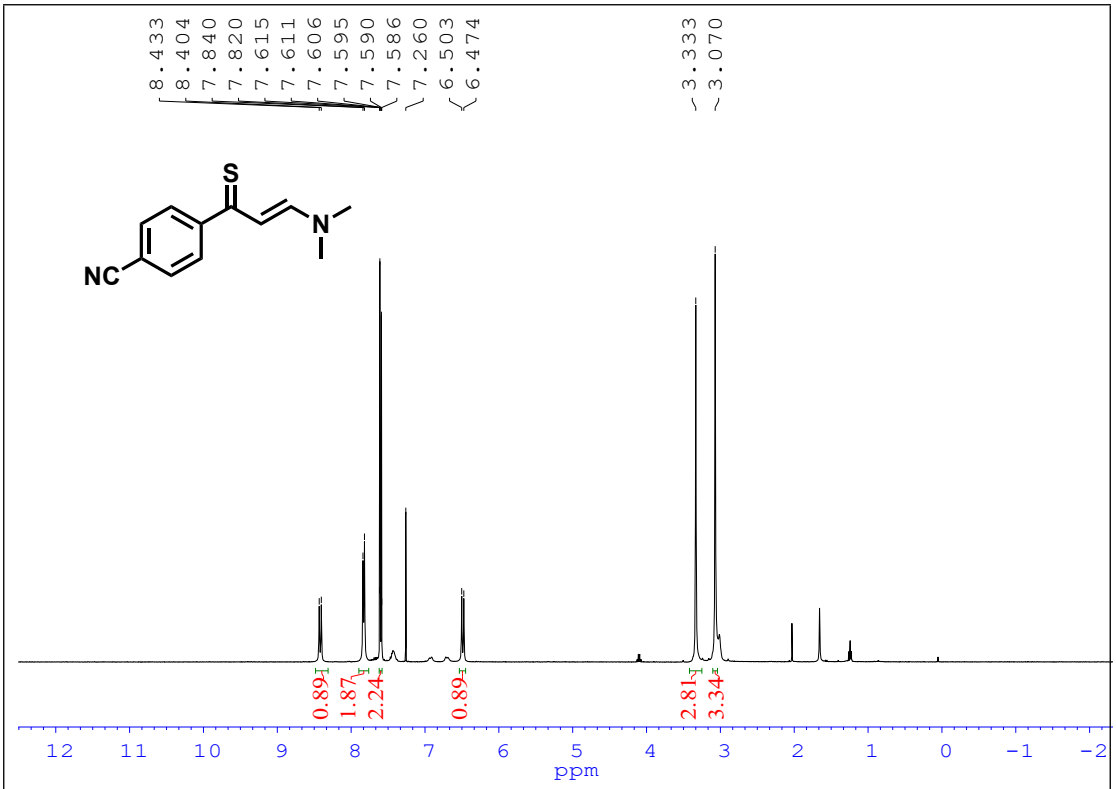
^{1}H NMR spectra of **1d**



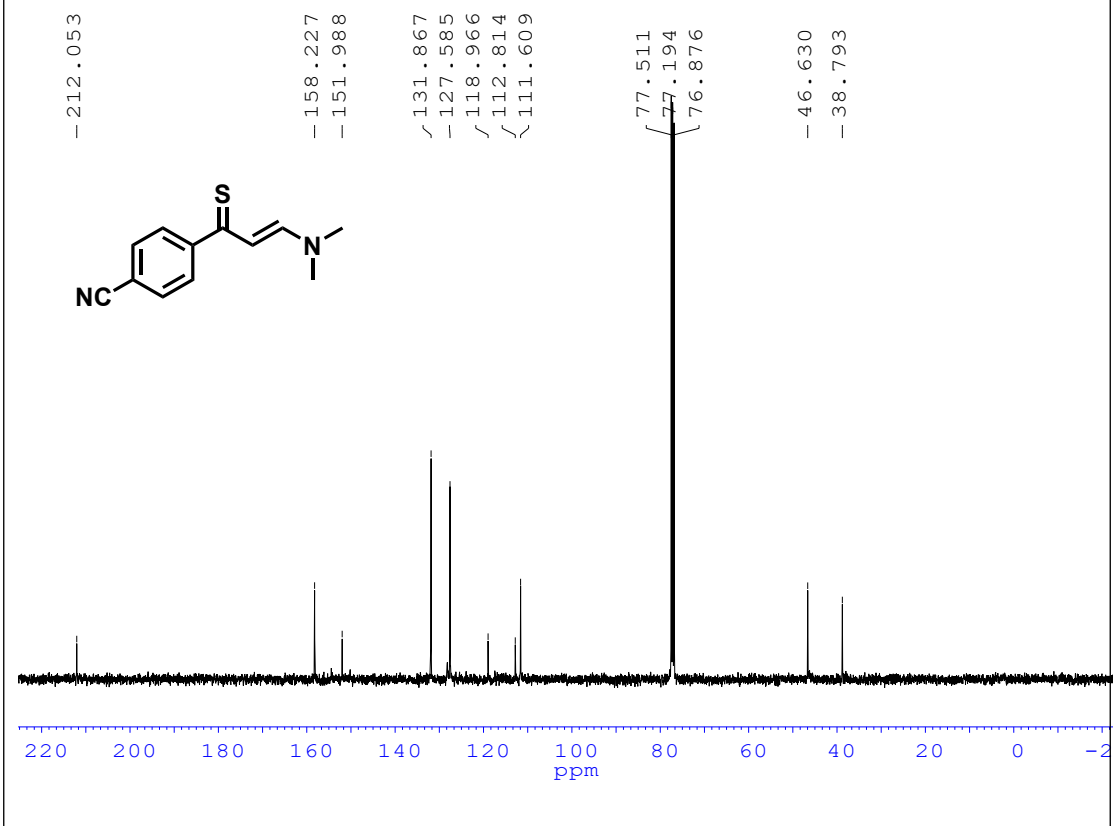
^{13}C NMR spectra of **1d**



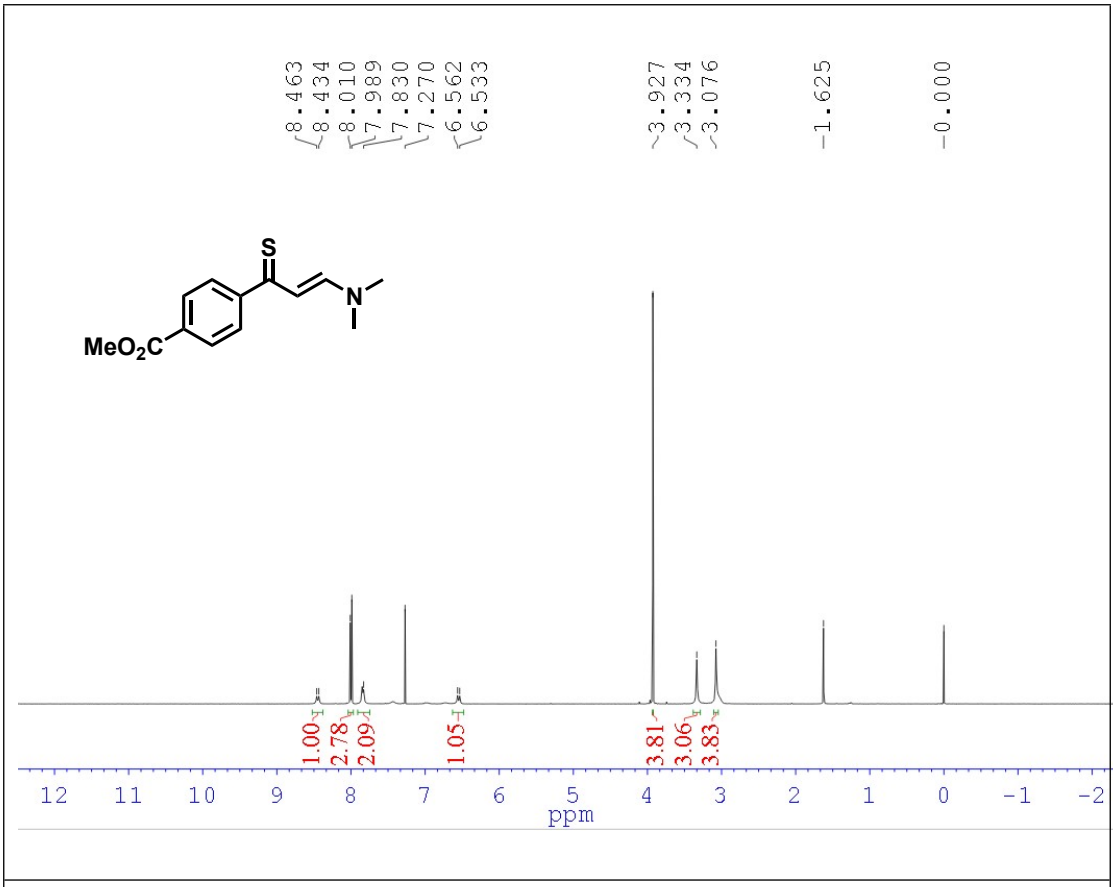
^{1}H NMR spectra of **1e**



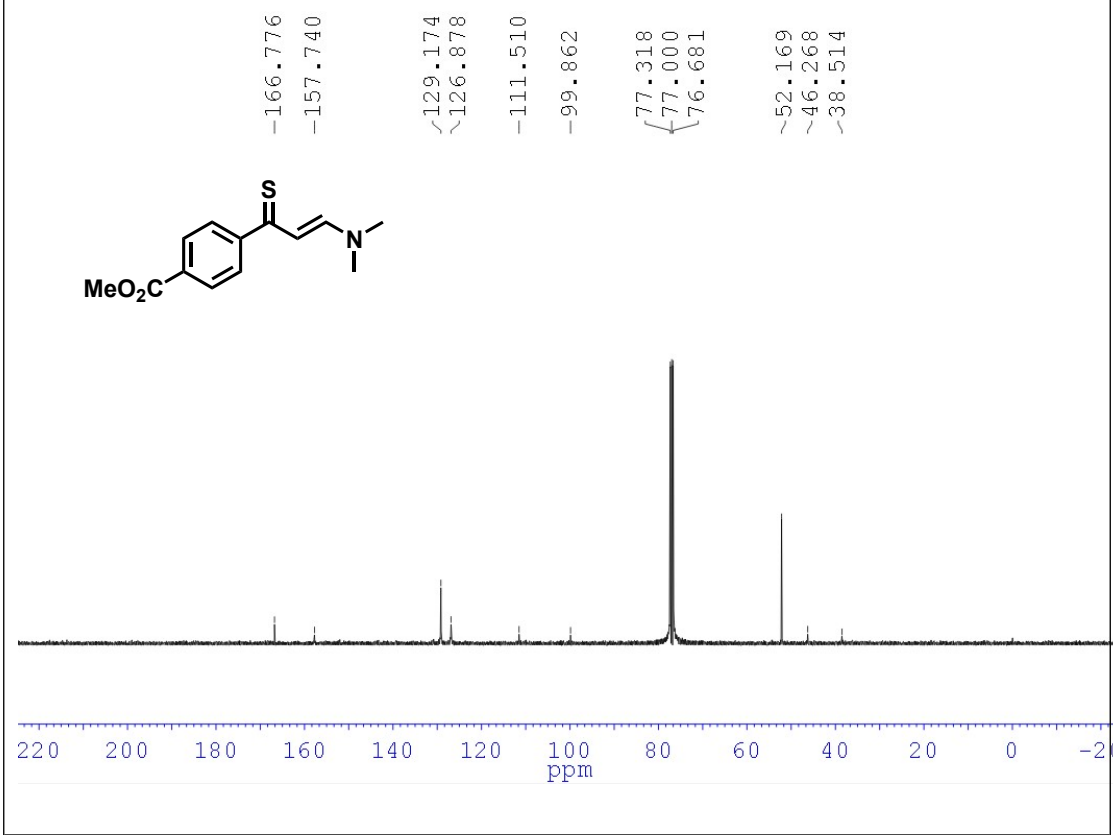
^{13}C NMR spectra of **1e**



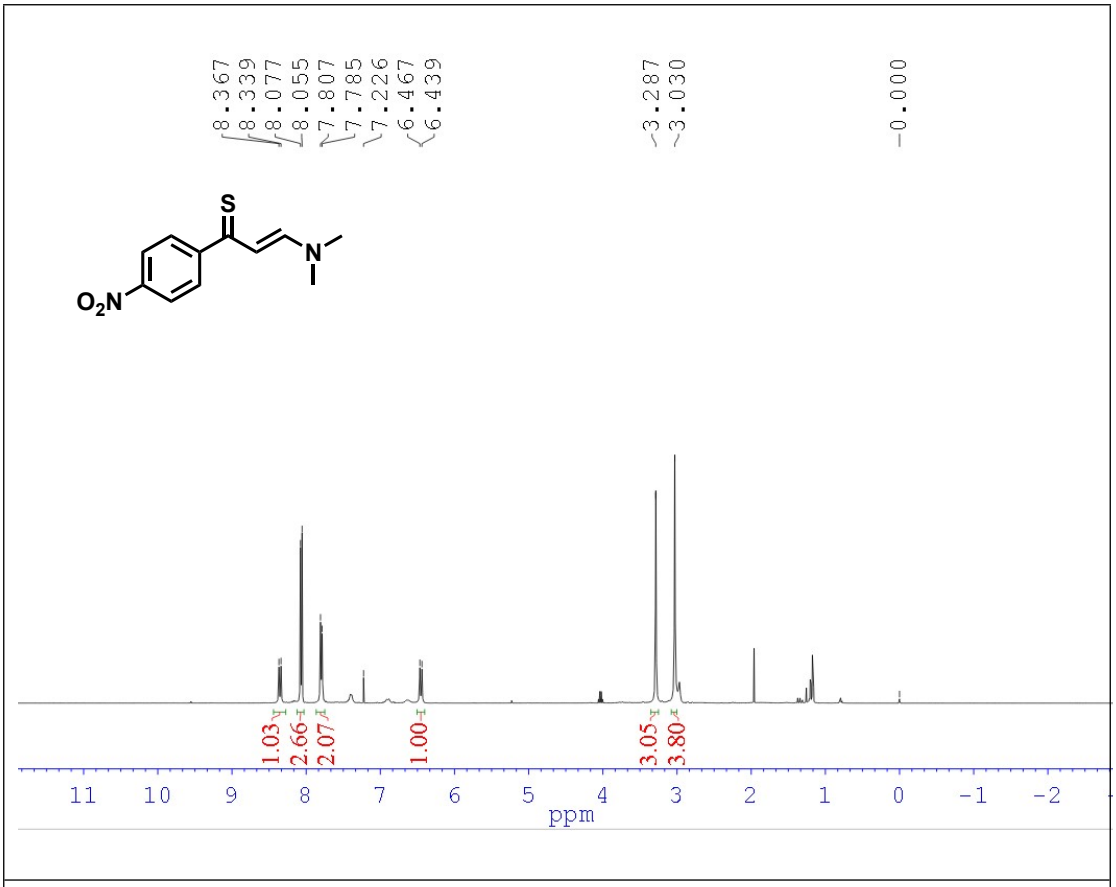
^{1}H NMR spectra of **1f**



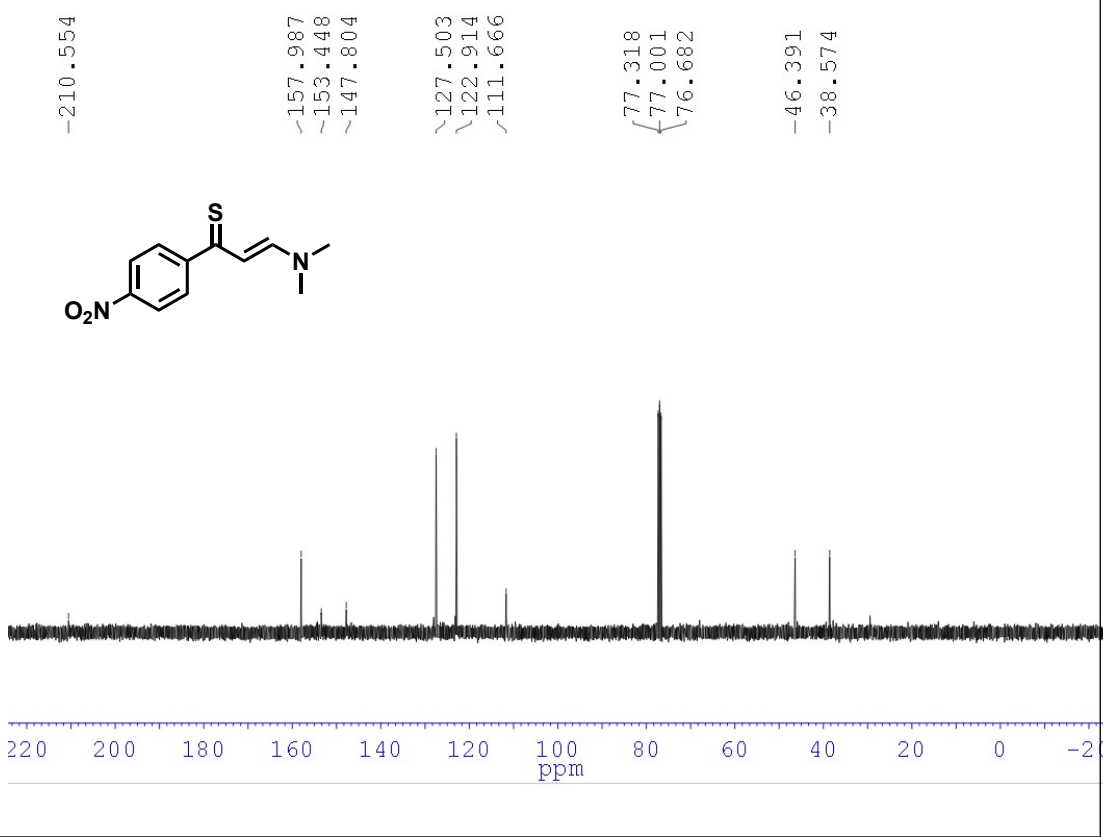
^{13}C NMR spectra of **1f**



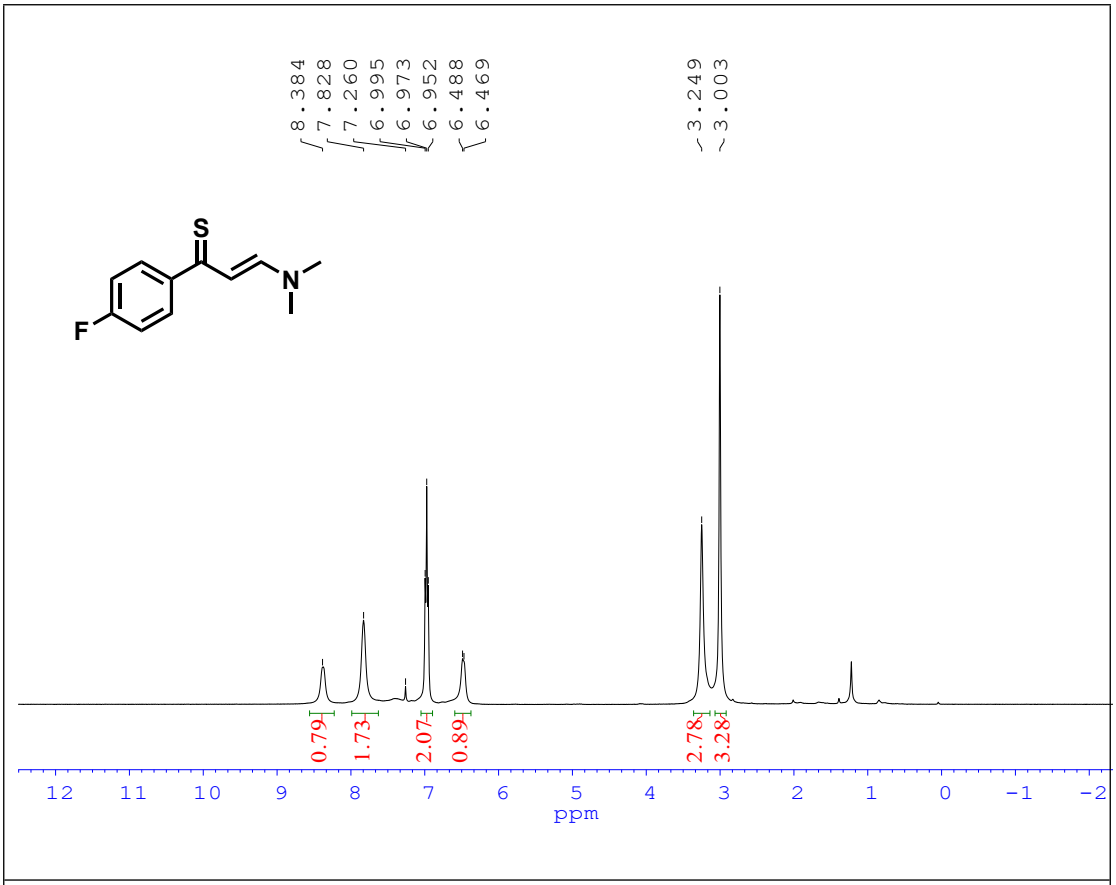
^{1}H NMR spectra of **1g**



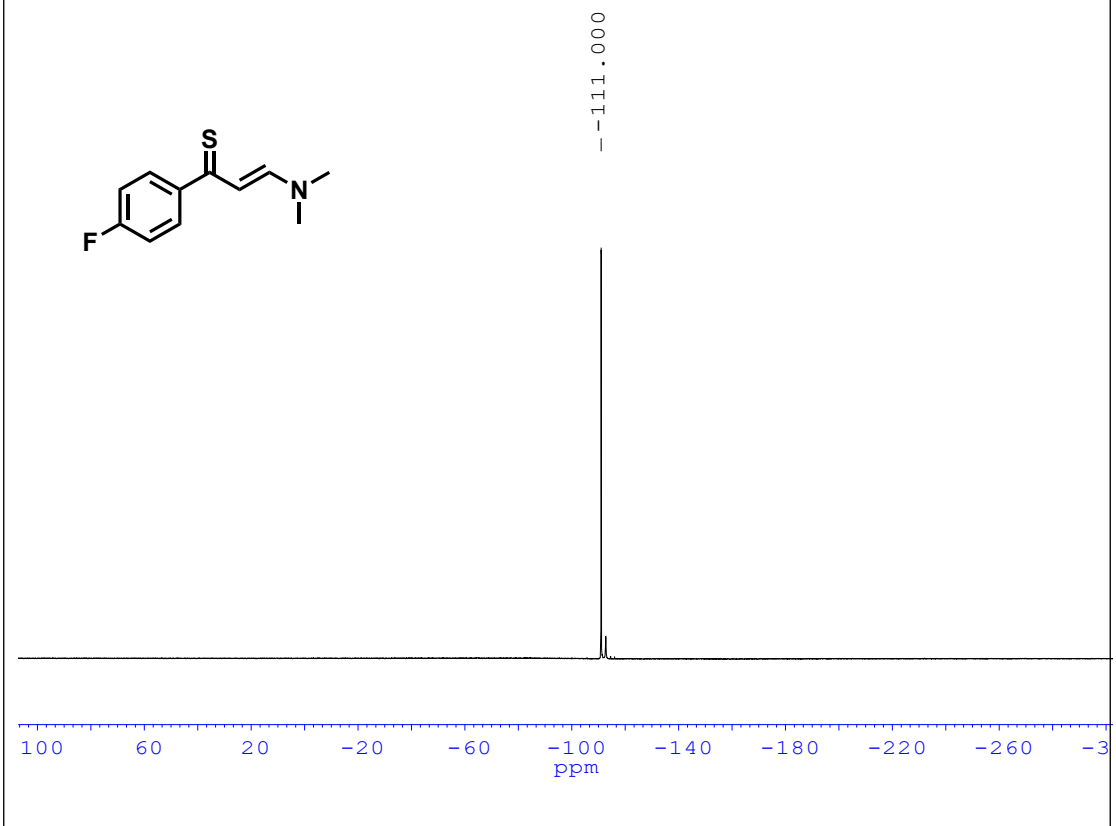
^{13}C NMR spectra of **1g**



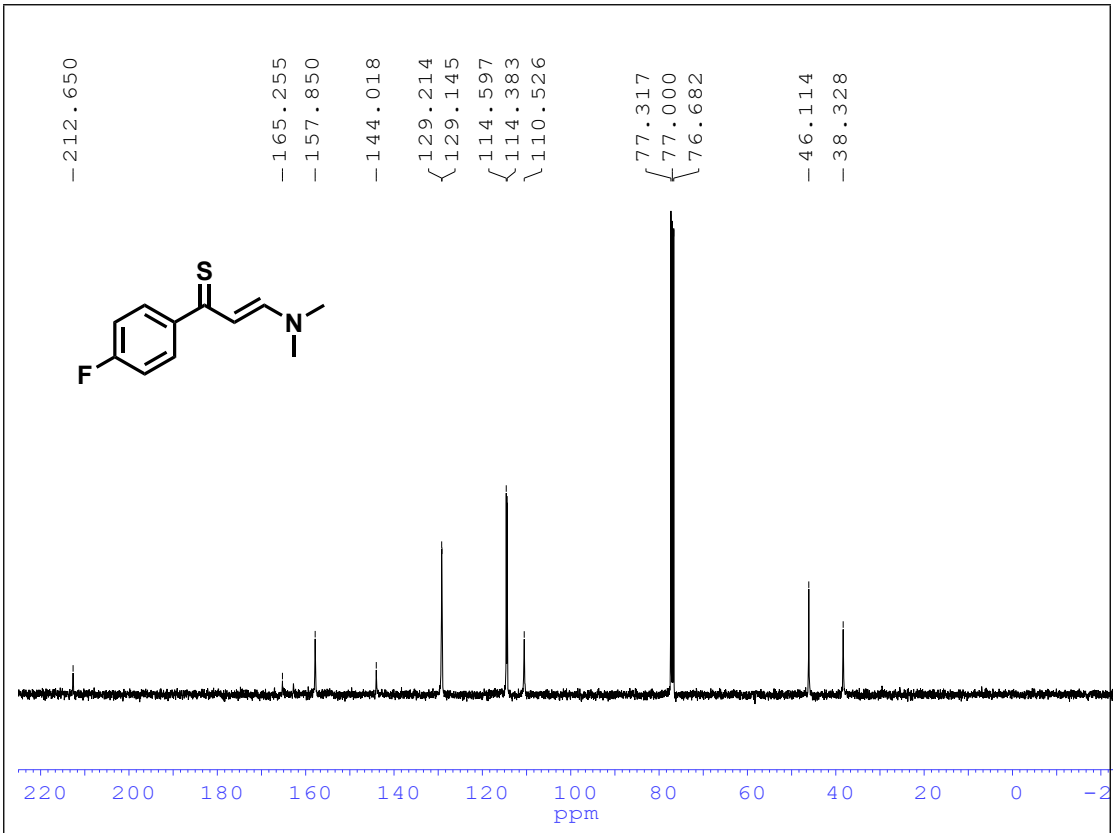
^{1}H NMR spectra of **1h**



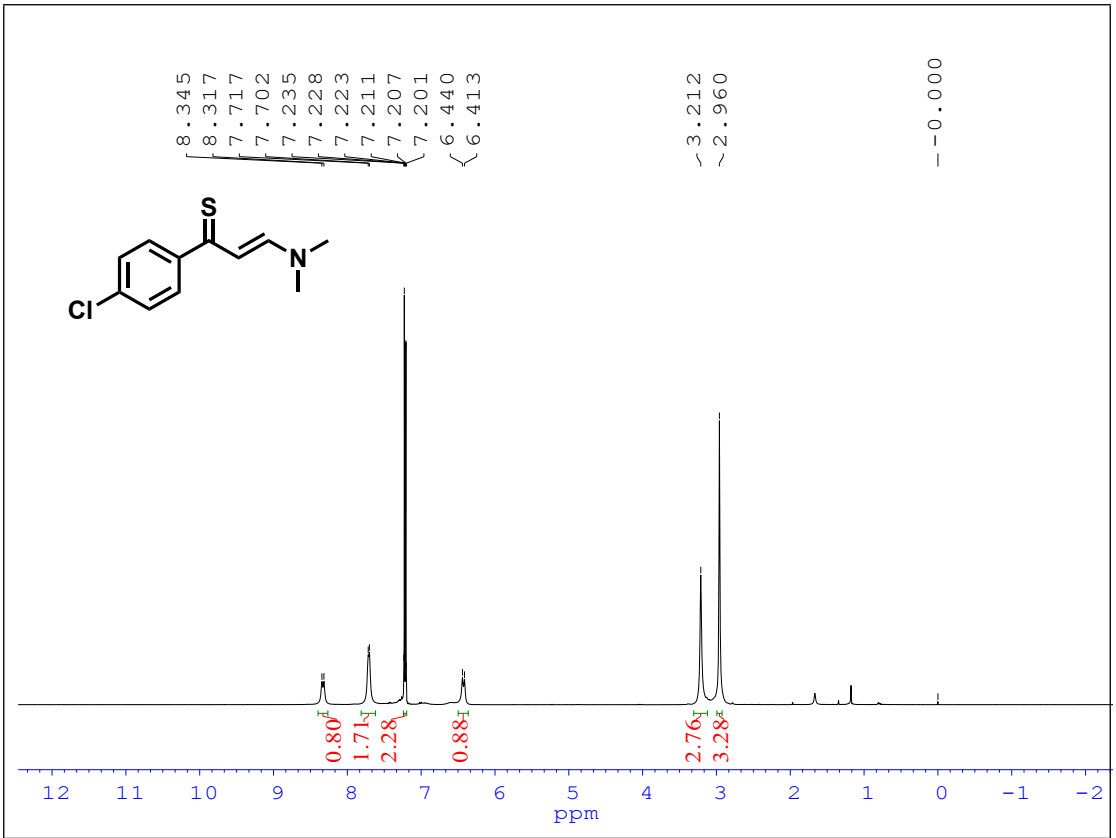
^{19}F NMR spectra of **1h**



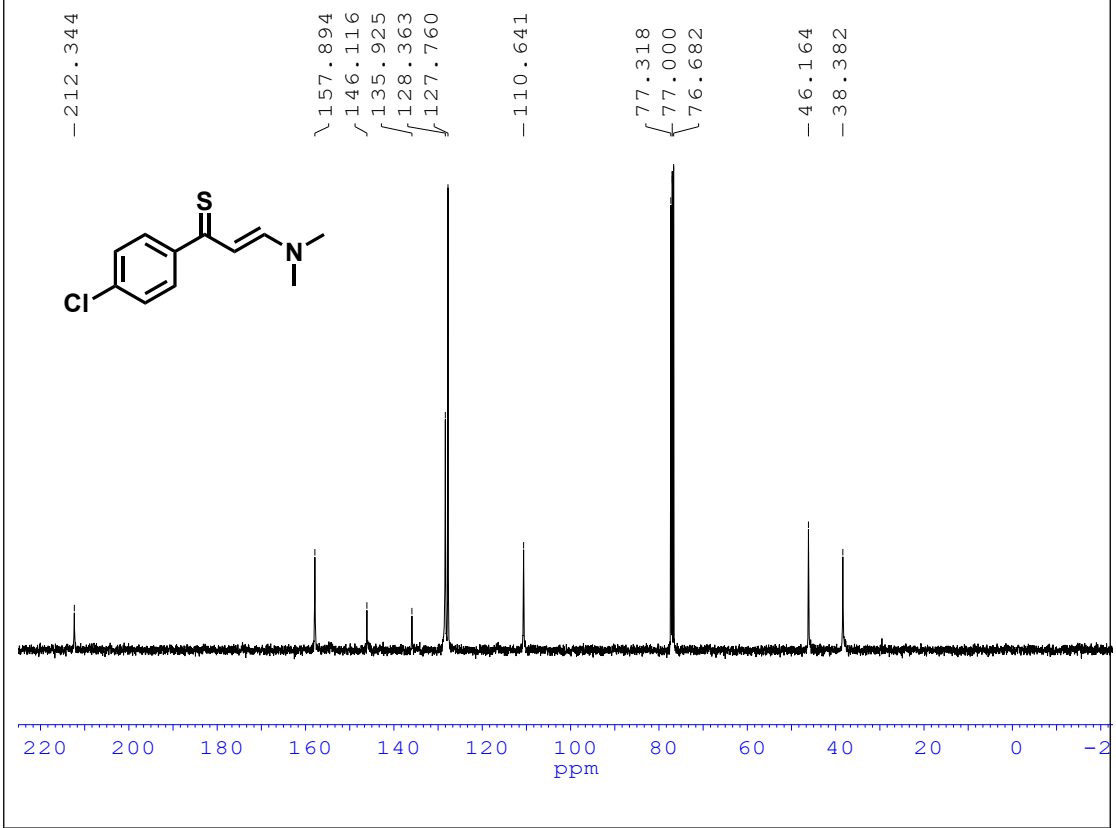
^{13}C NMR spectra of **1h**



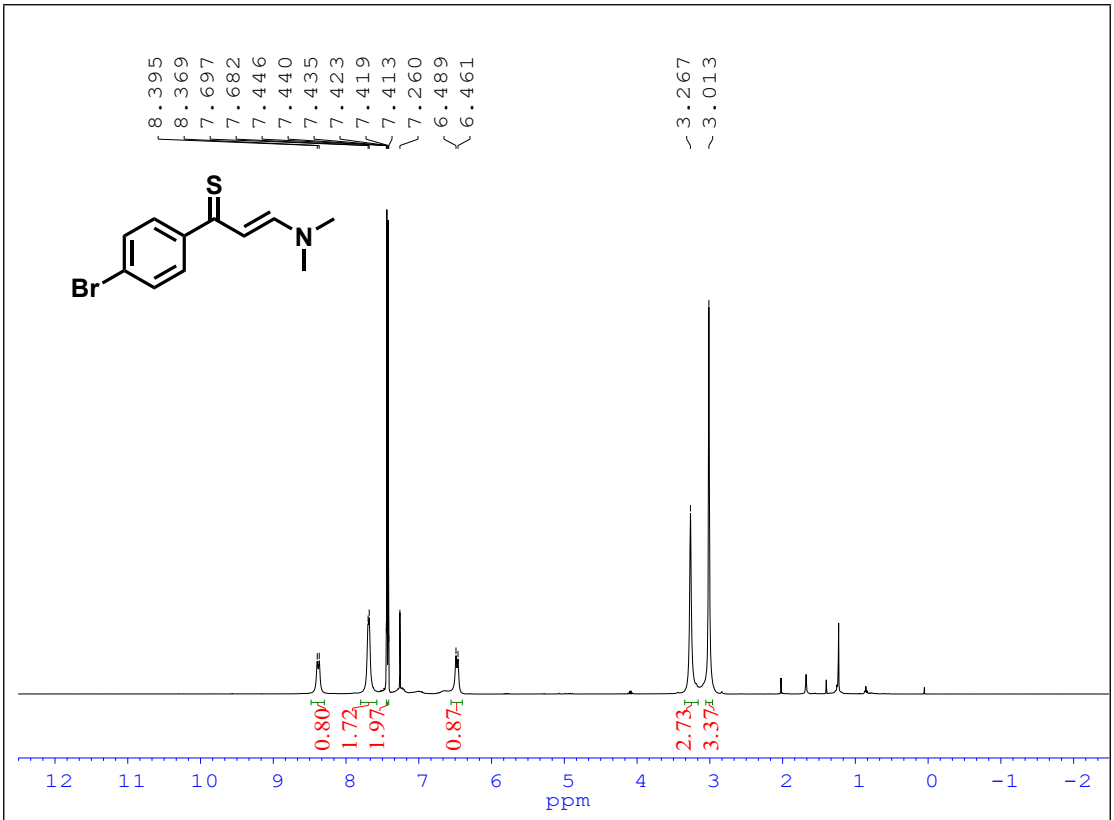
^{1}H NMR spectra of **1i**



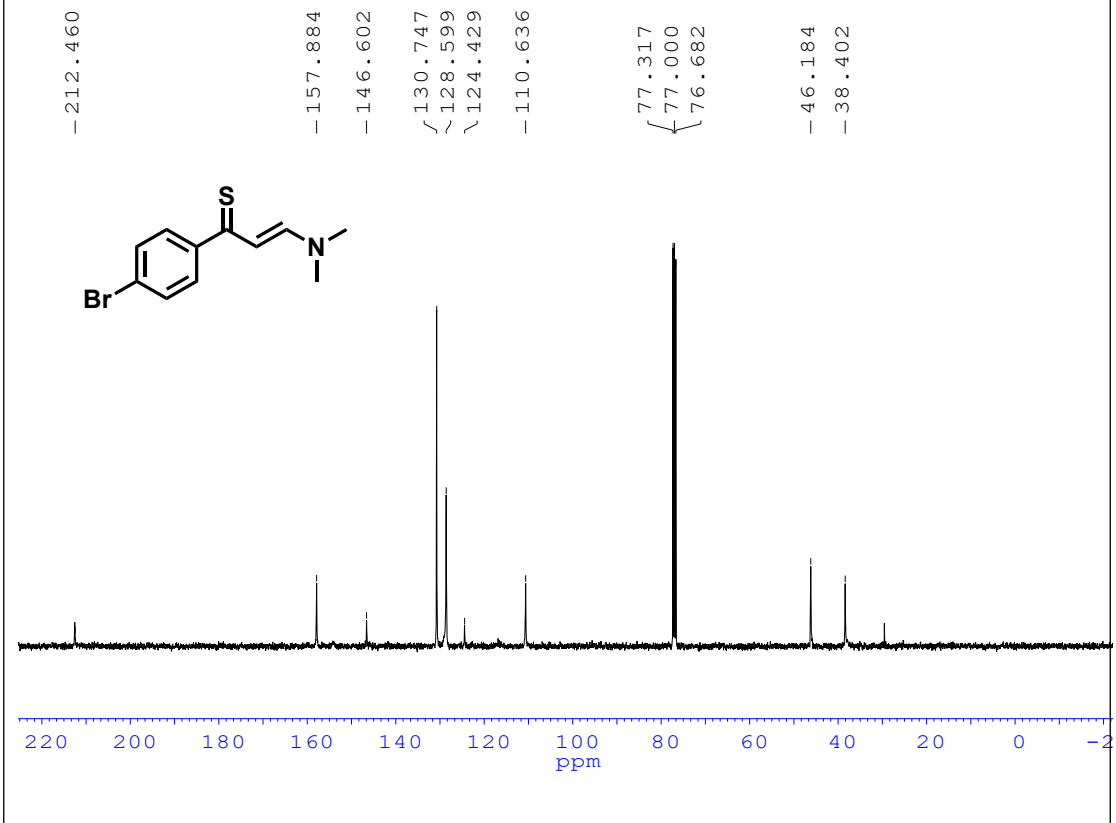
^{13}C NMR spectra of **1i**



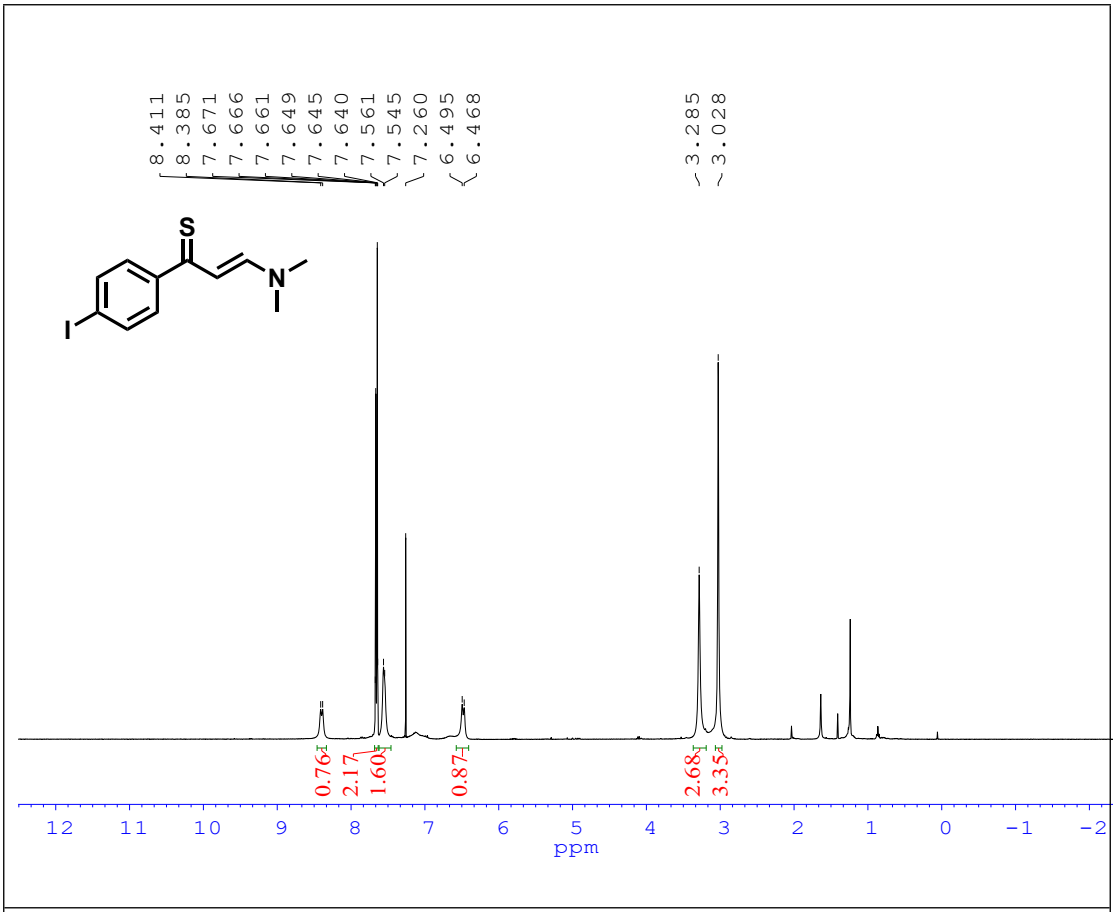
^{1}H NMR spectra of **1j**



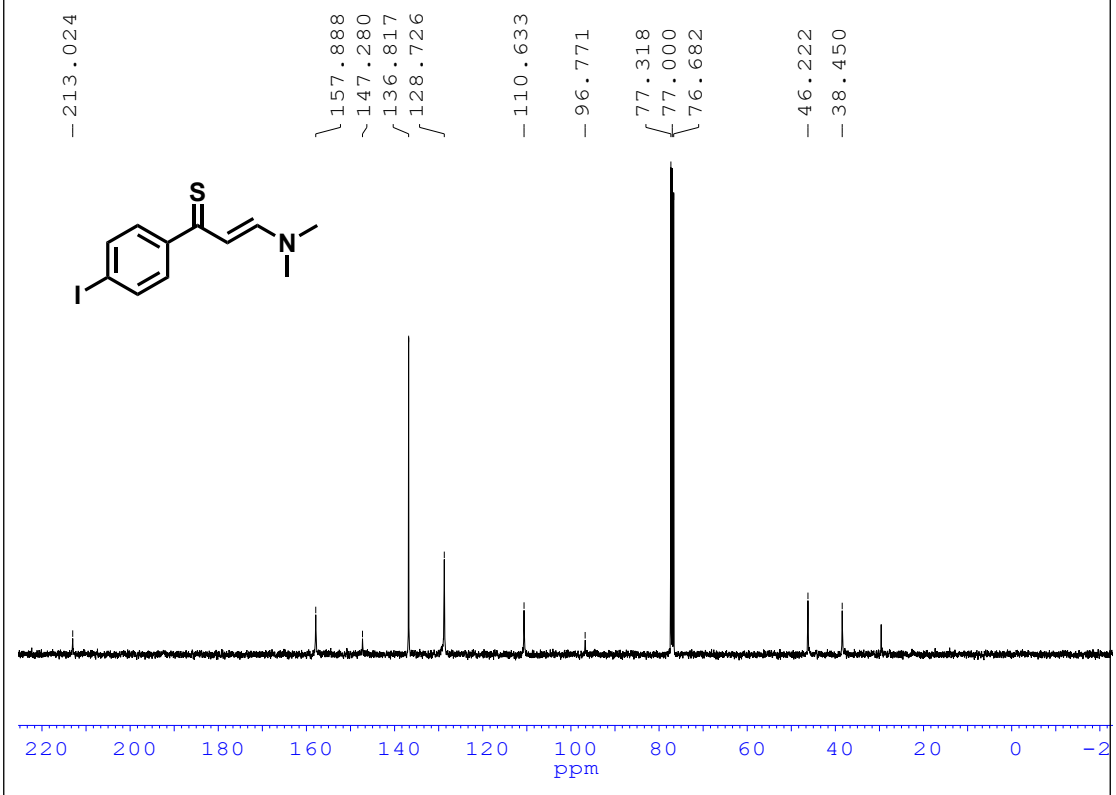
^{13}C NMR spectra of **1j**



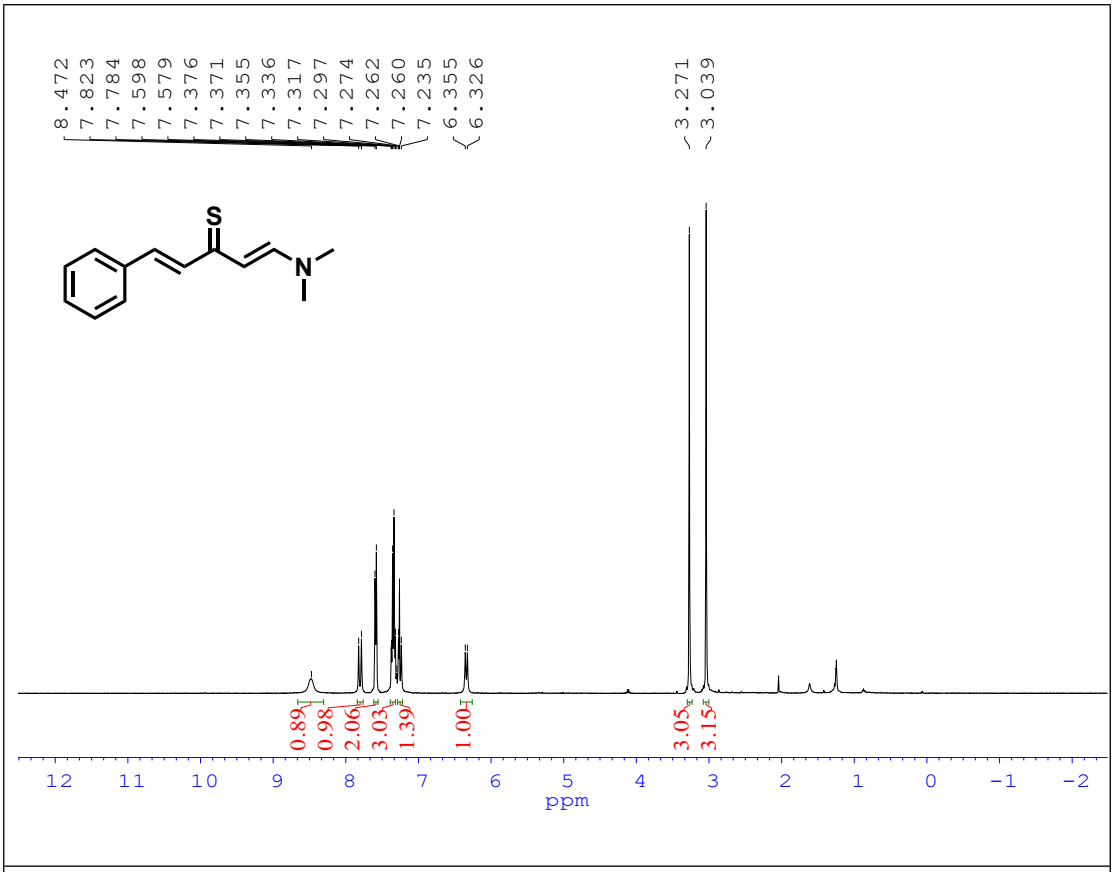
^{1}H NMR spectra of **1k**



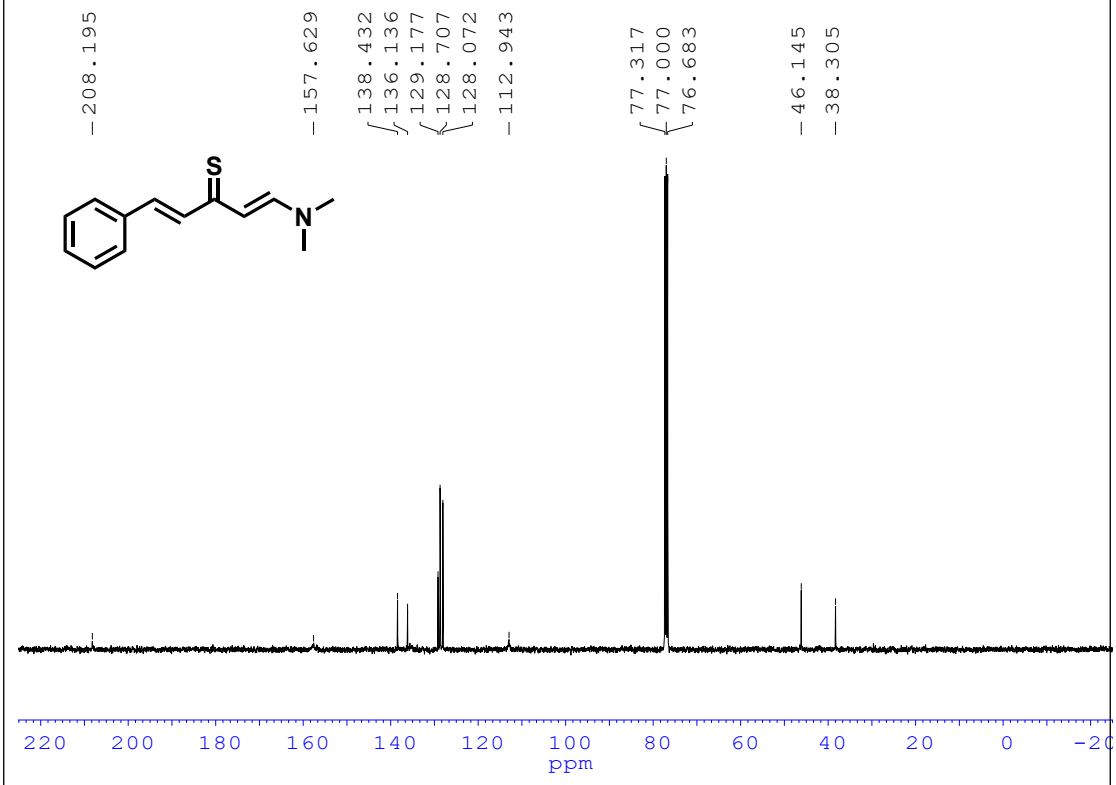
^{13}C NMR spectra of **1k**



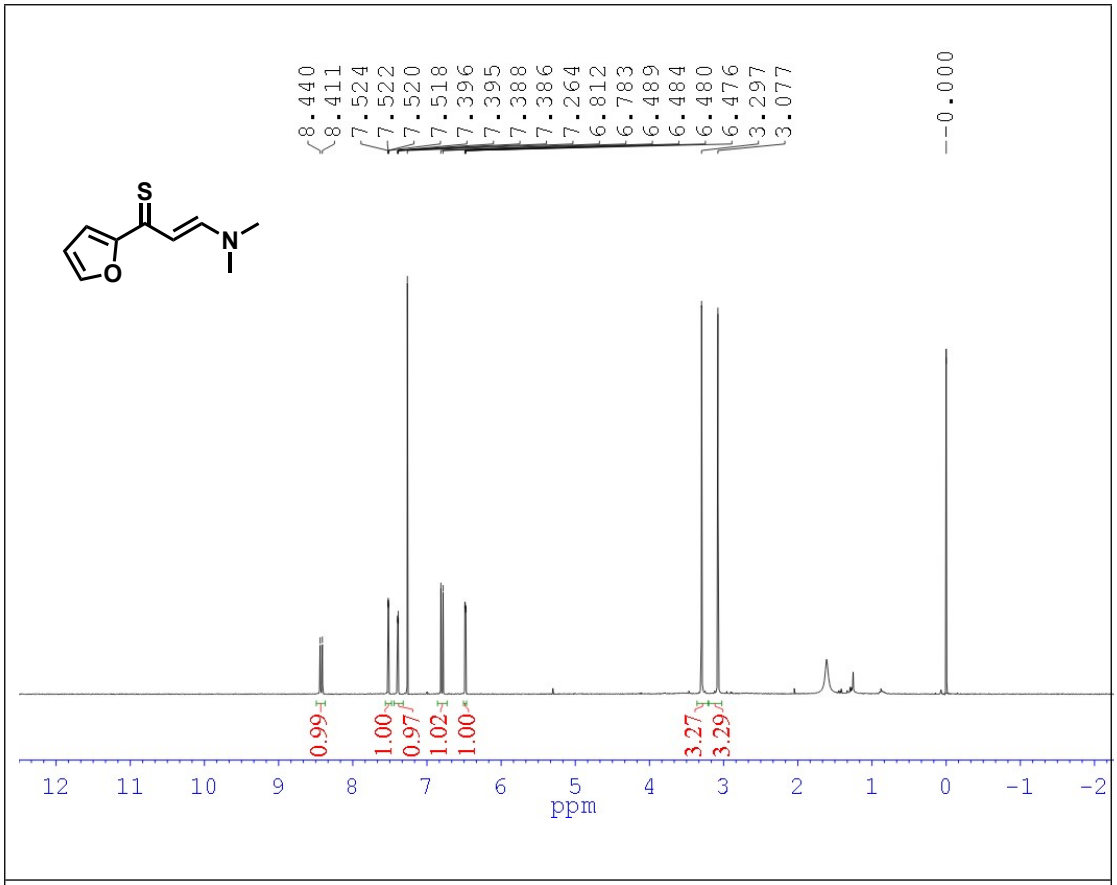
^{1}H NMR spectra of **1l**



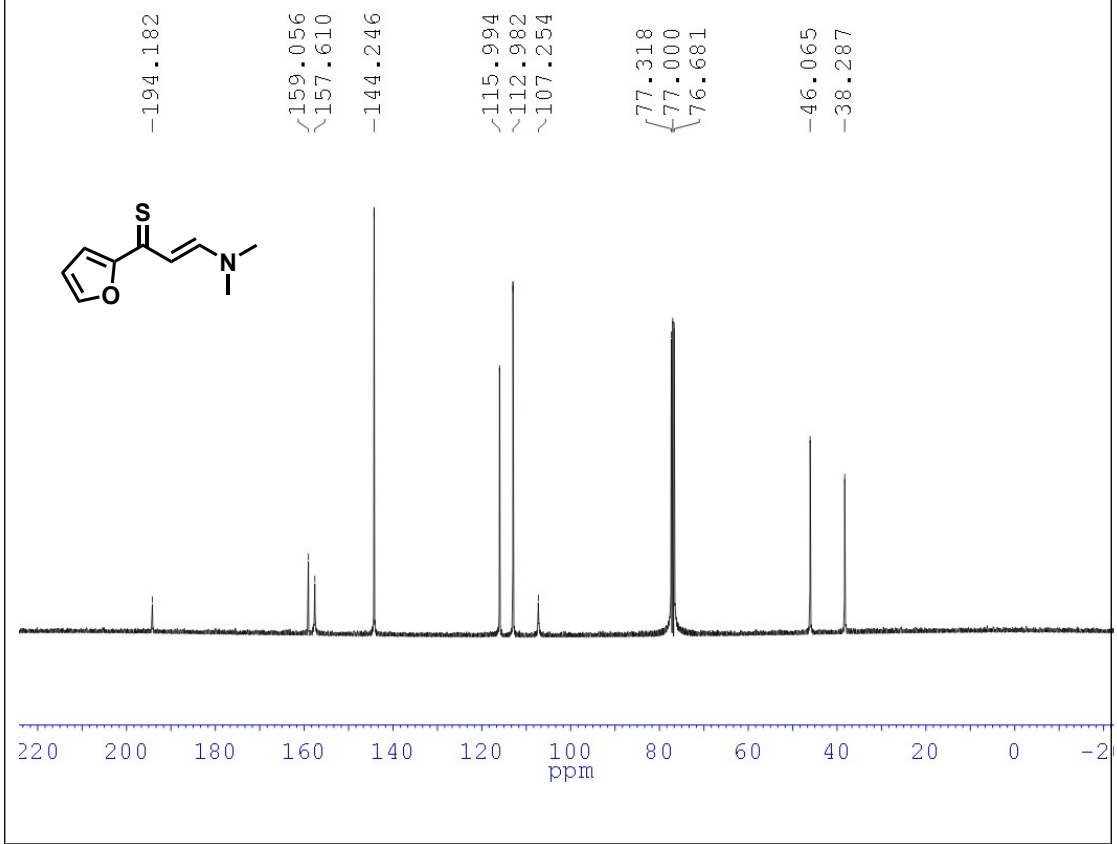
^{13}C NMR spectra of **1l**



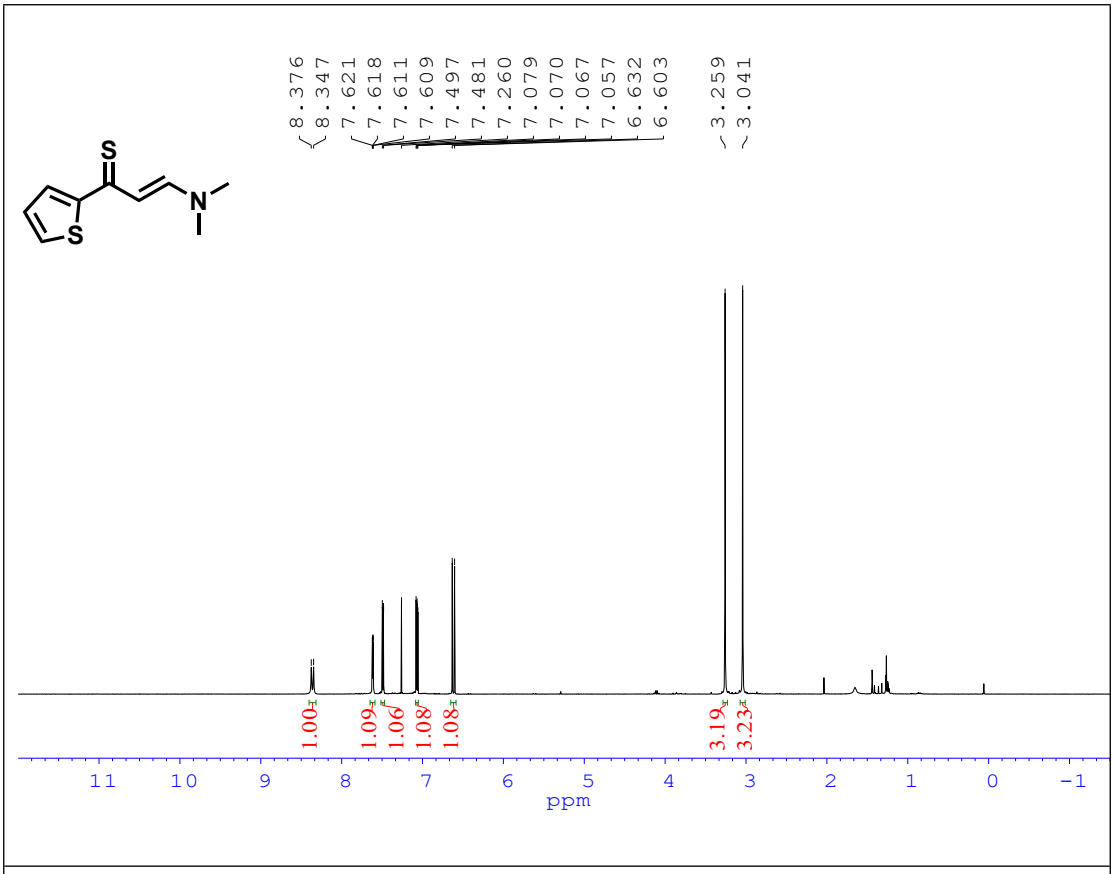
^{1}H NMR spectra of **1m**



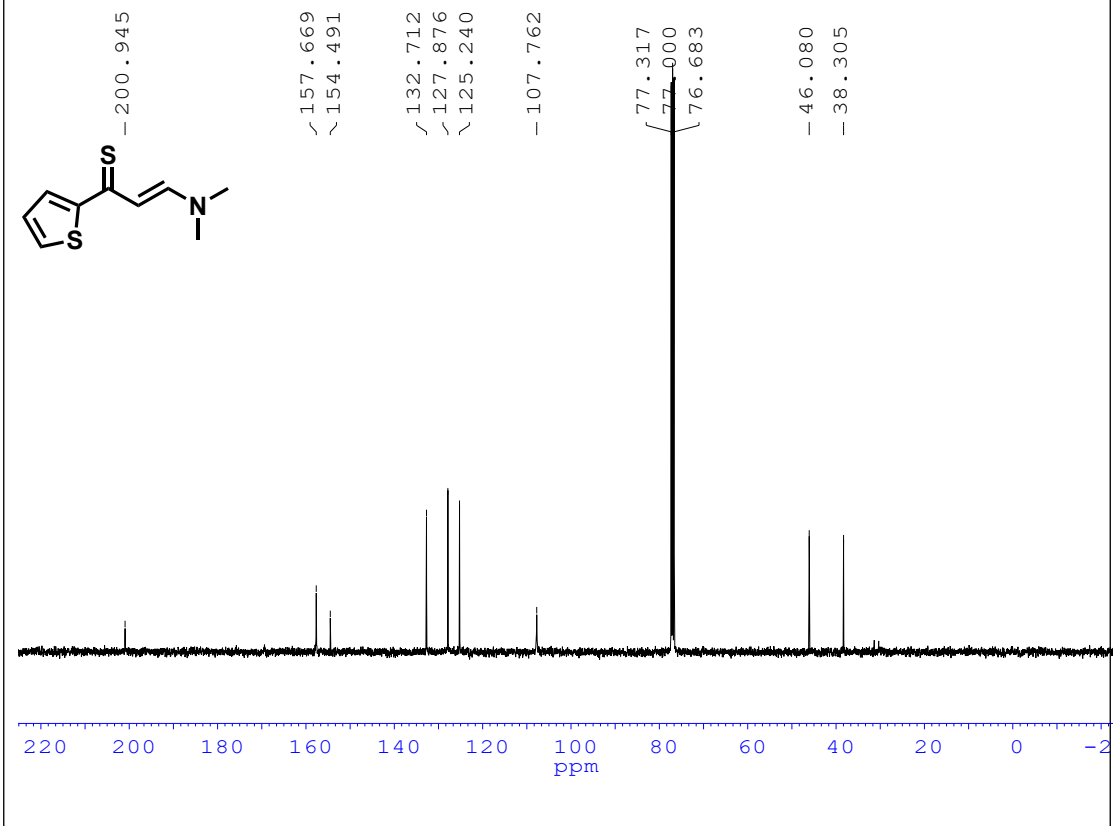
^{13}C NMR spectra of **1m**



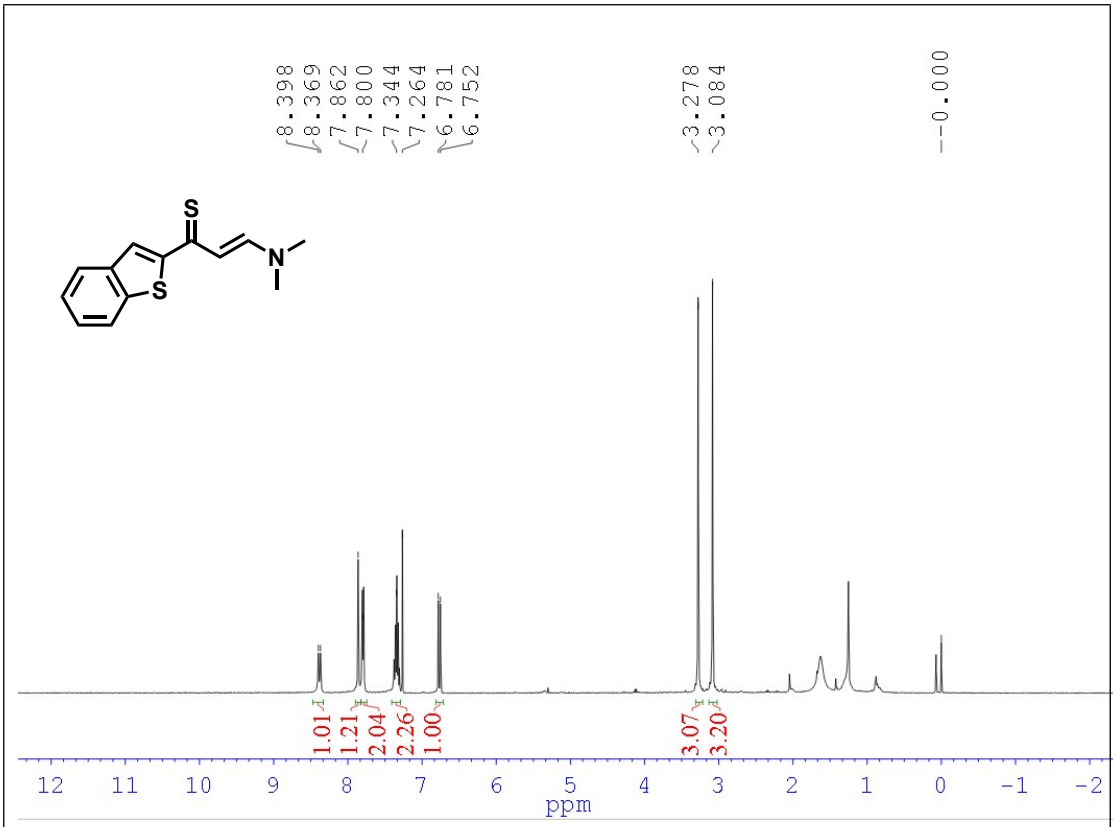
^{1}H NMR spectra of **1n**



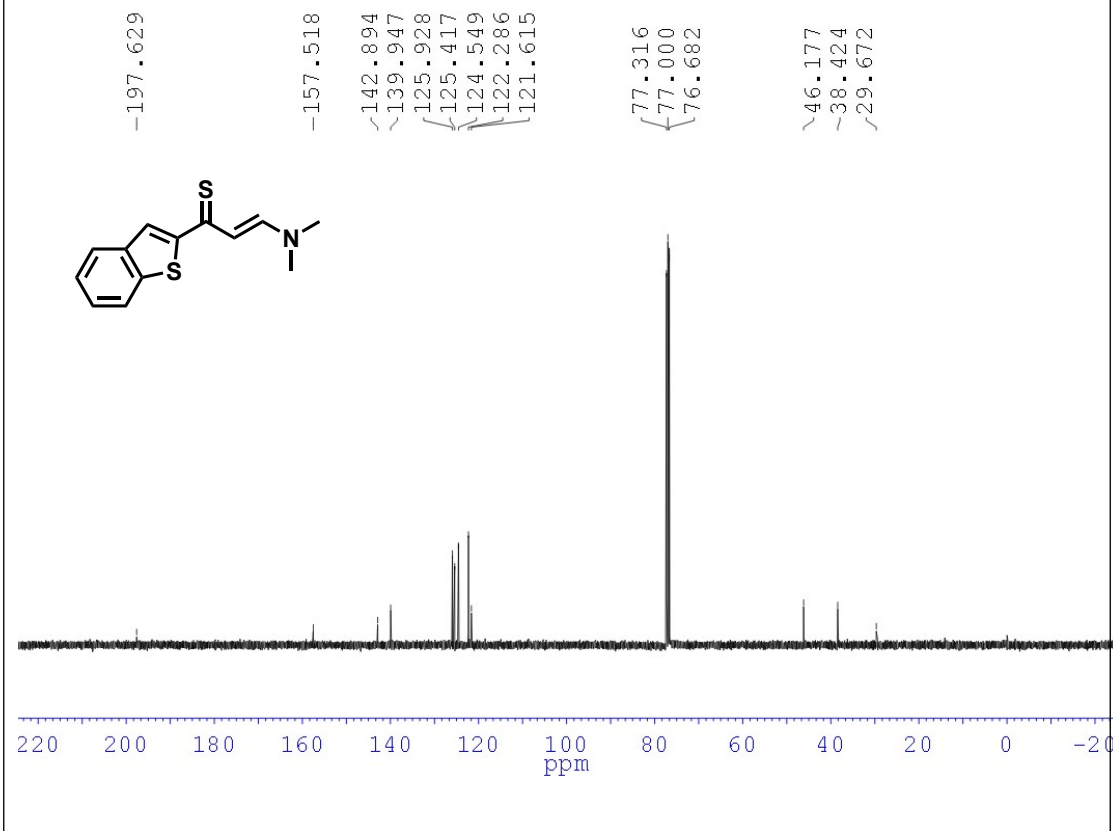
^{13}C NMR spectra of **1n**



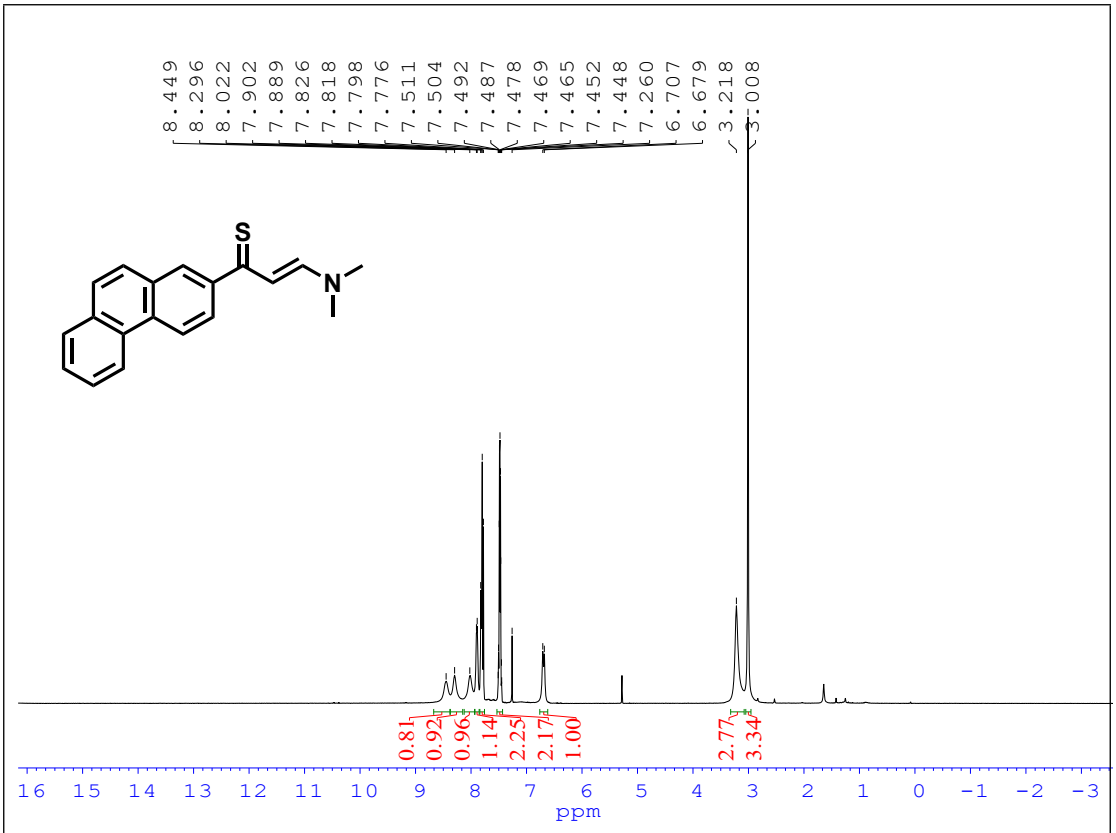
^{1}H NMR spectra of **1o**



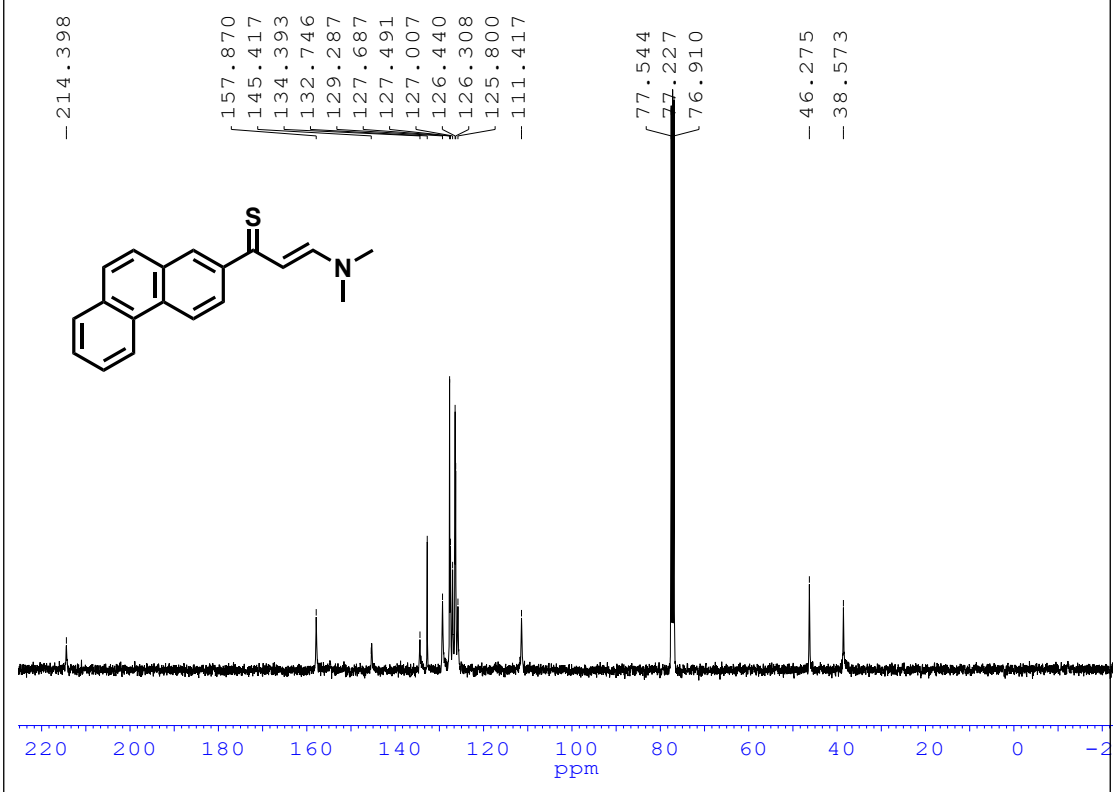
^{13}C NMR spectra of **1o**



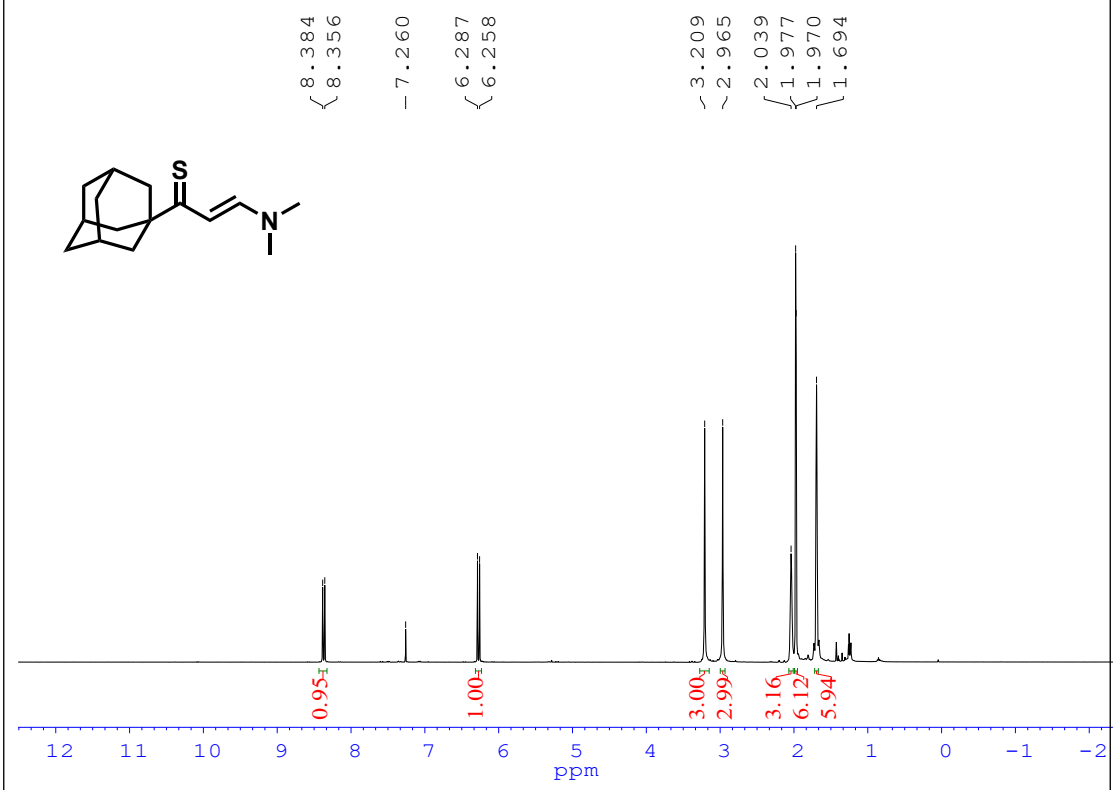
^{1}H NMR spectra of **1p**



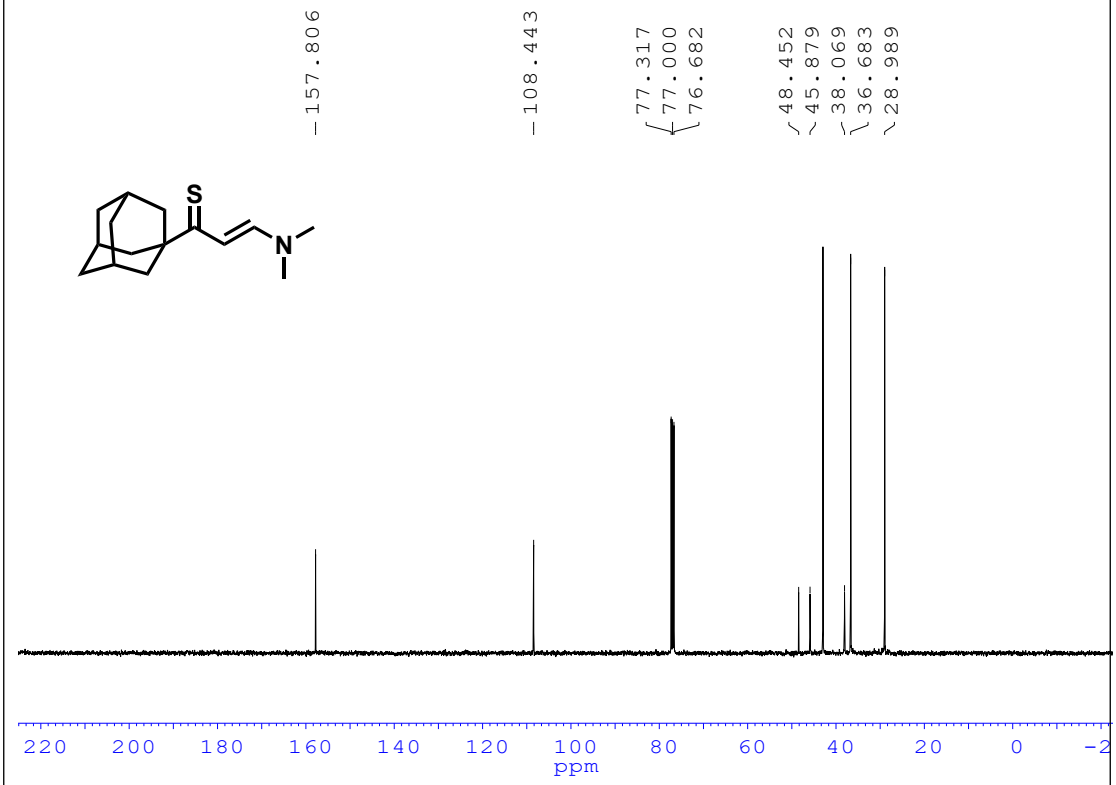
^{13}C NMR spectra of **1p**



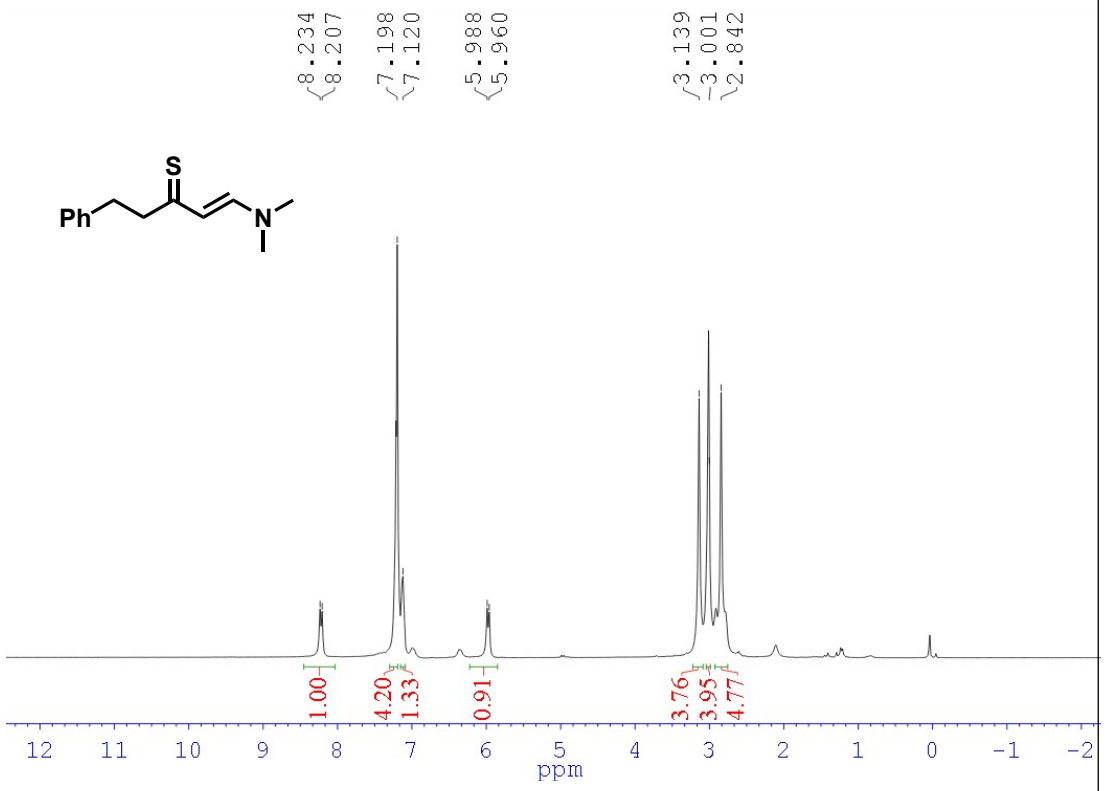
^{1}H NMR spectra of **1q**



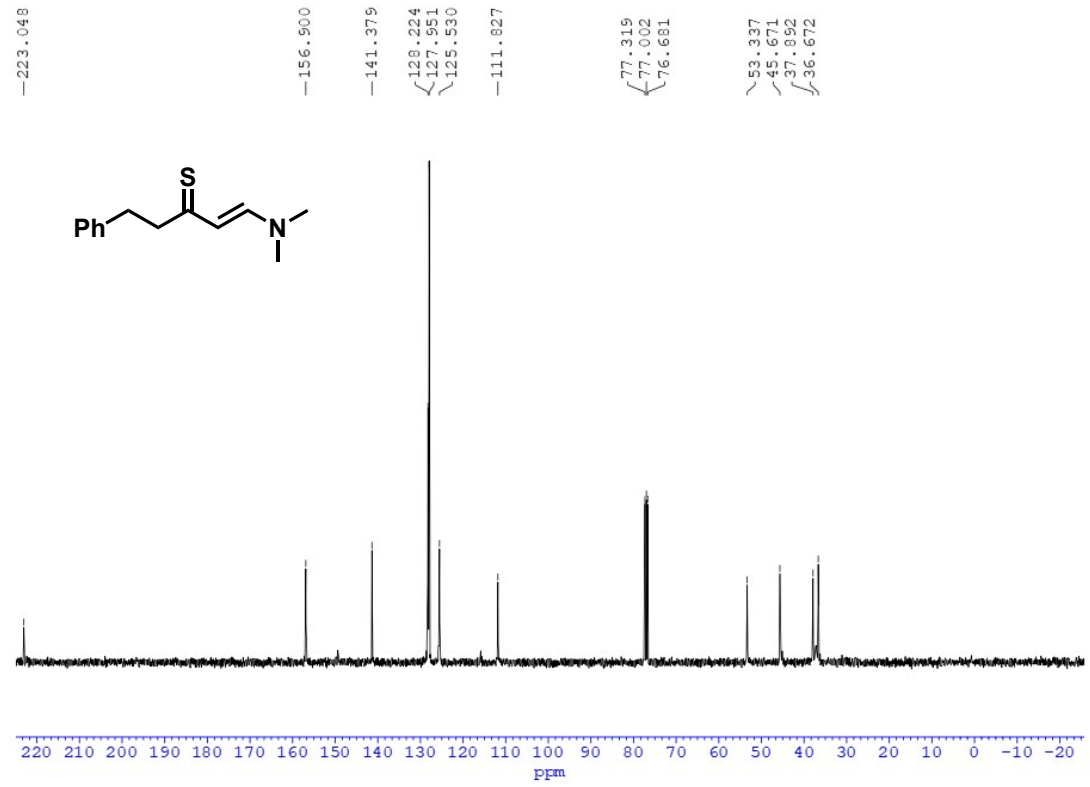
^{13}C NMR spectra of **1q**



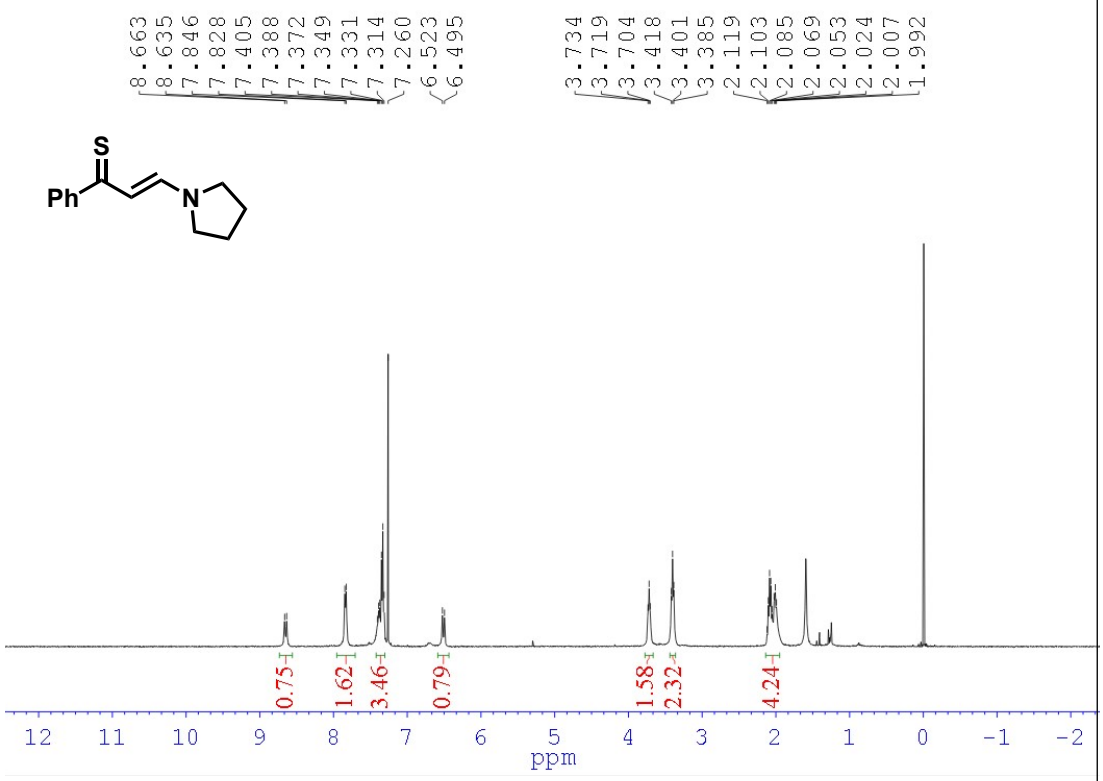
^{1}H NMR spectra of **1r**



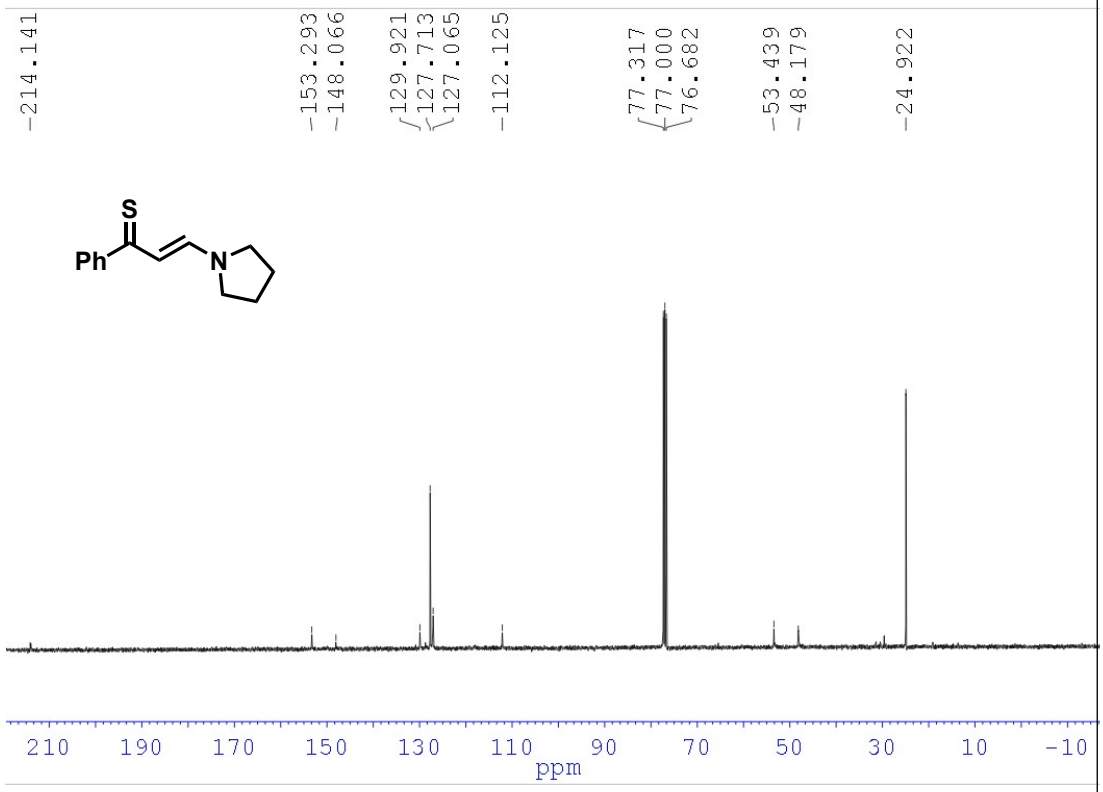
^{13}C NMR spectra of **1r**



^{1}H NMR spectra of **1s**

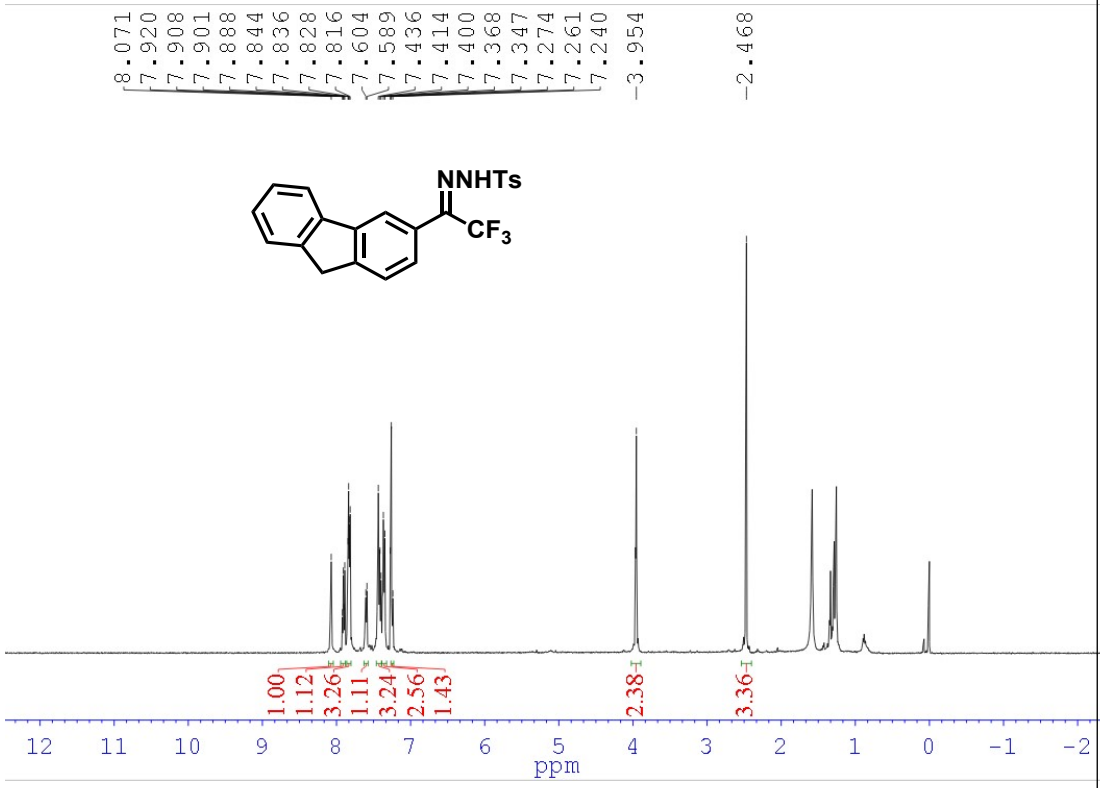


^{13}C NMR spectra of **1s**

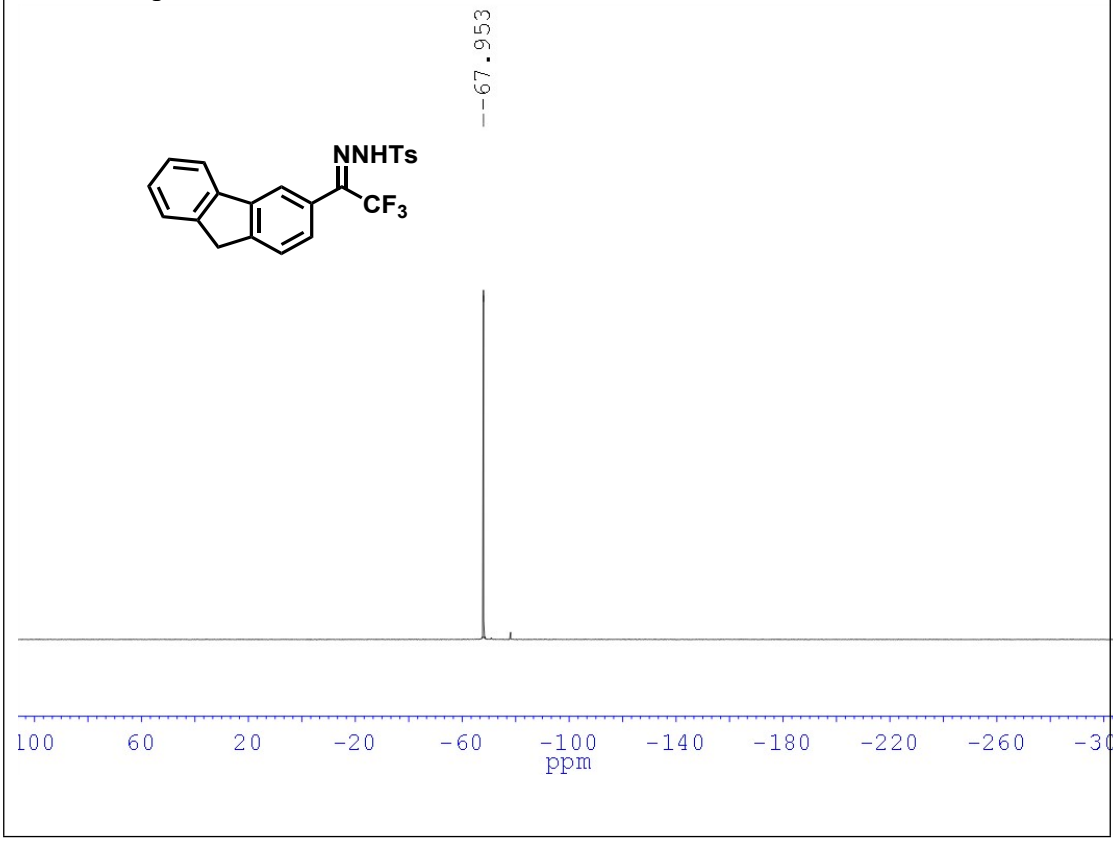


4.2 NMR spectra for hydrazones

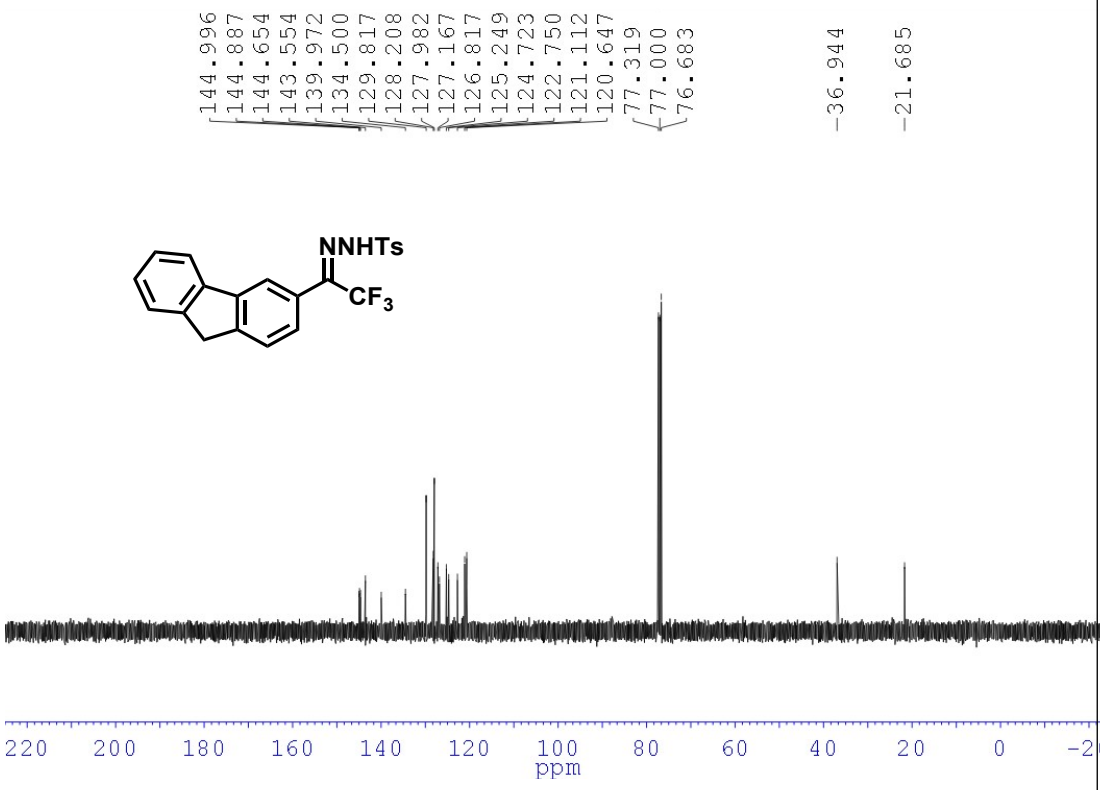
^{1}H NMR spectra of **2h**



^{1}H NMR spectra of **2h**

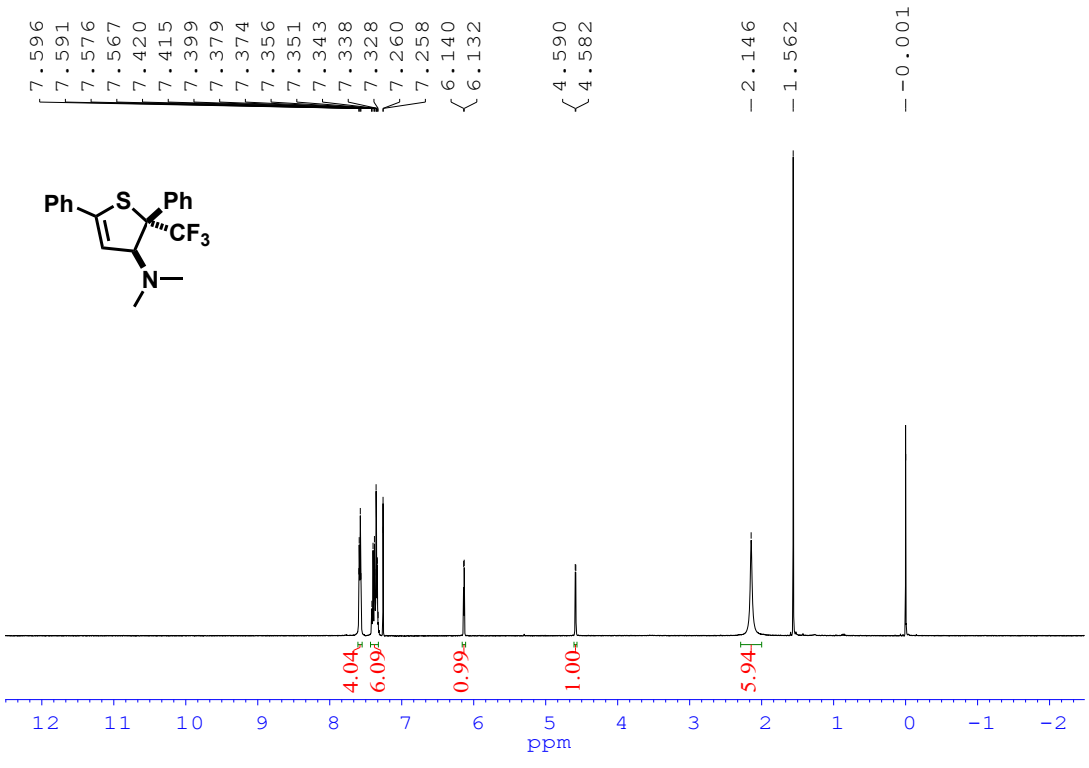


^{13}C NMR spectra of **2h**

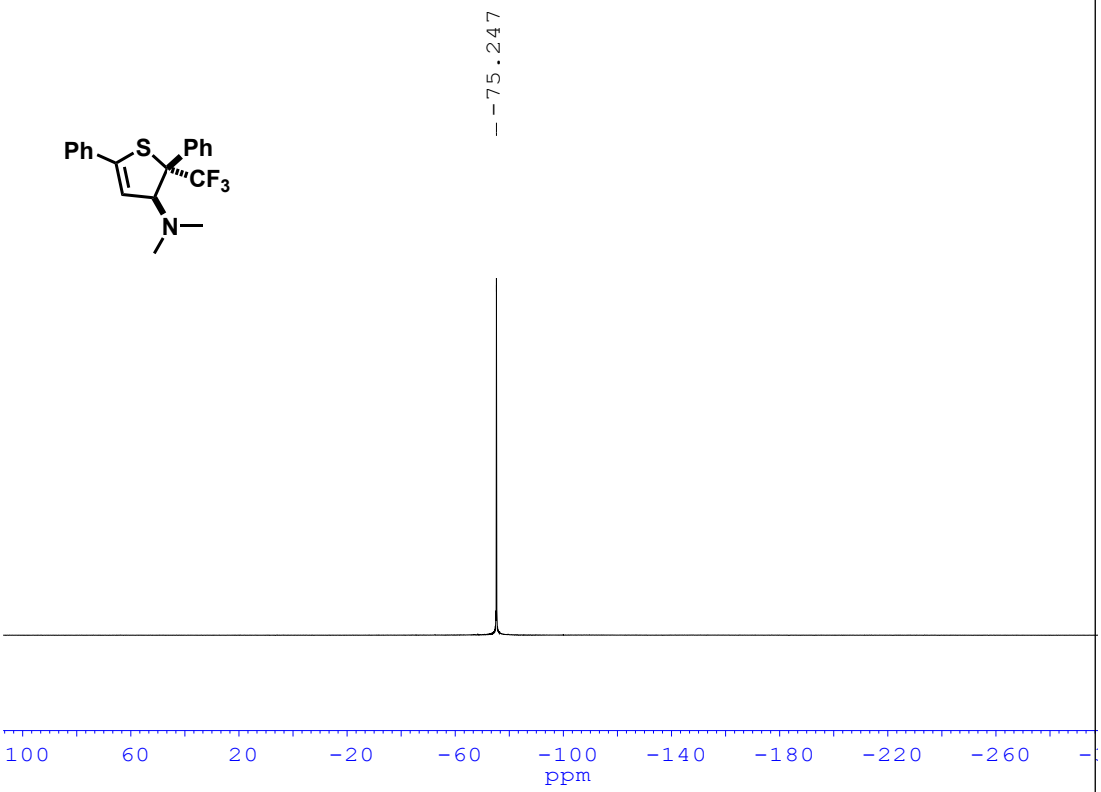


4.3 NMR spectra for 2-CF_3-2*H*-thiophenes

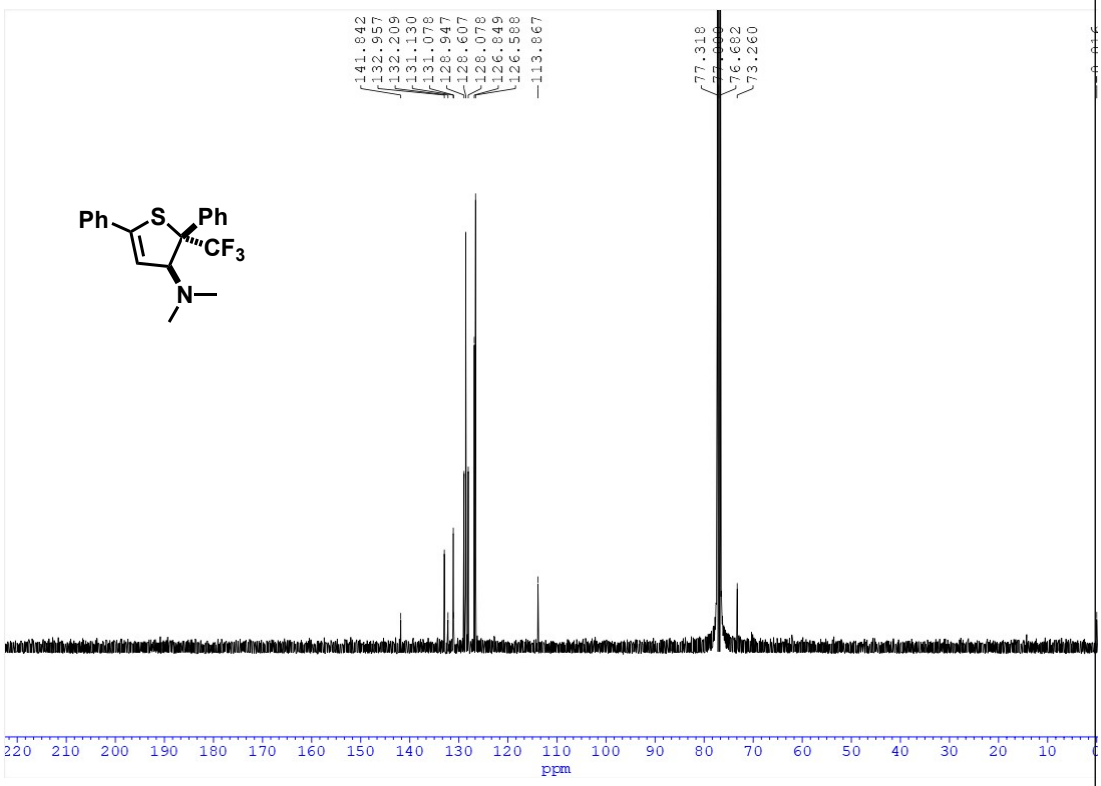
^{1}H NMR spectra of **3aa**



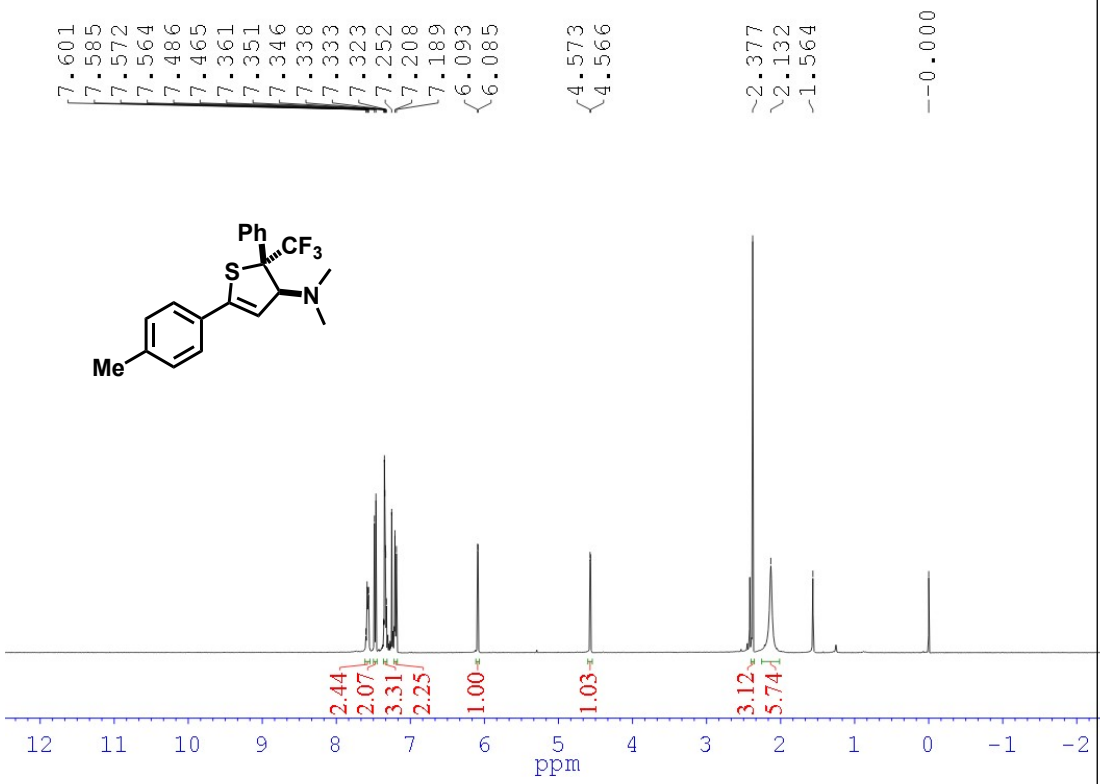
^{19}F NMR spectra of **3aa**



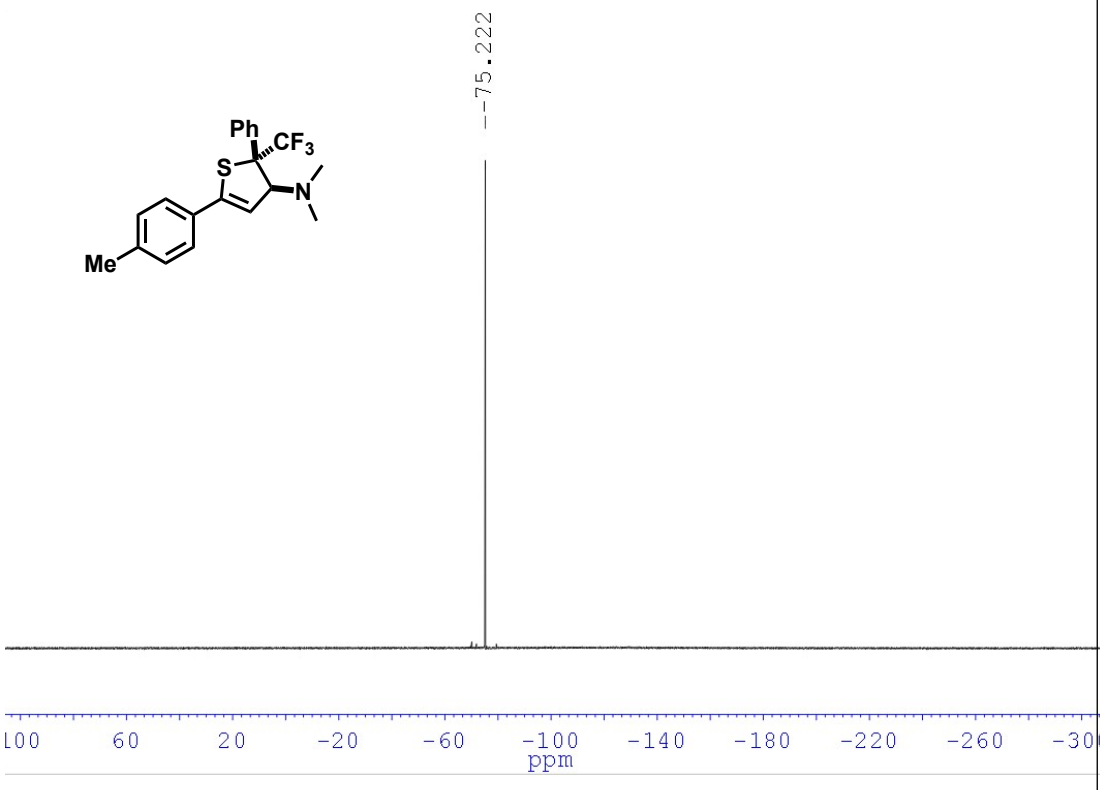
^{13}C NMR spectra of **3aa**



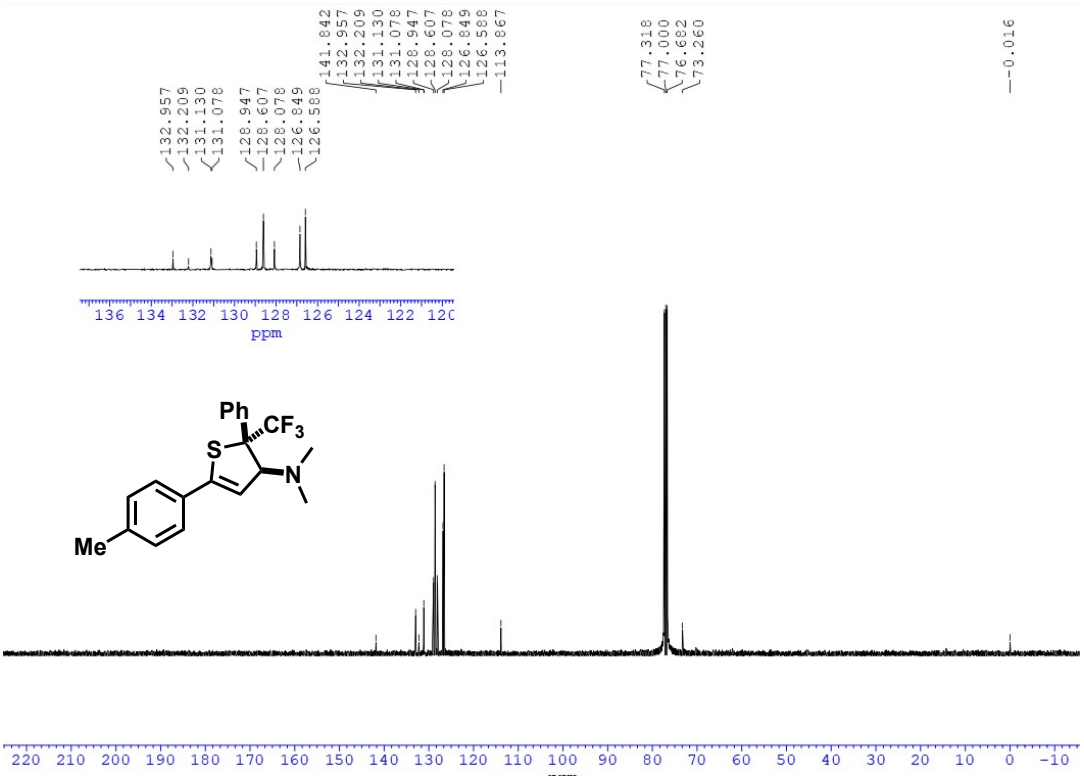
^{1}H NMR spectra of **3ab**



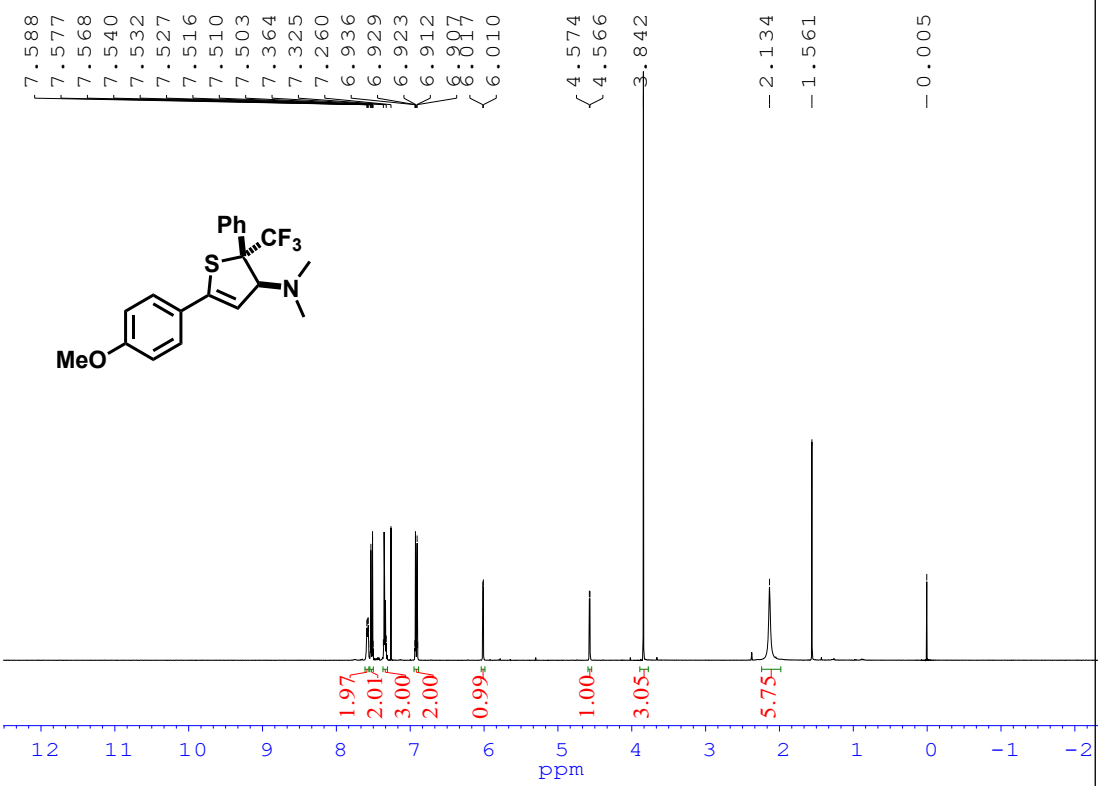
^{19}F NMR spectra of **3ab**



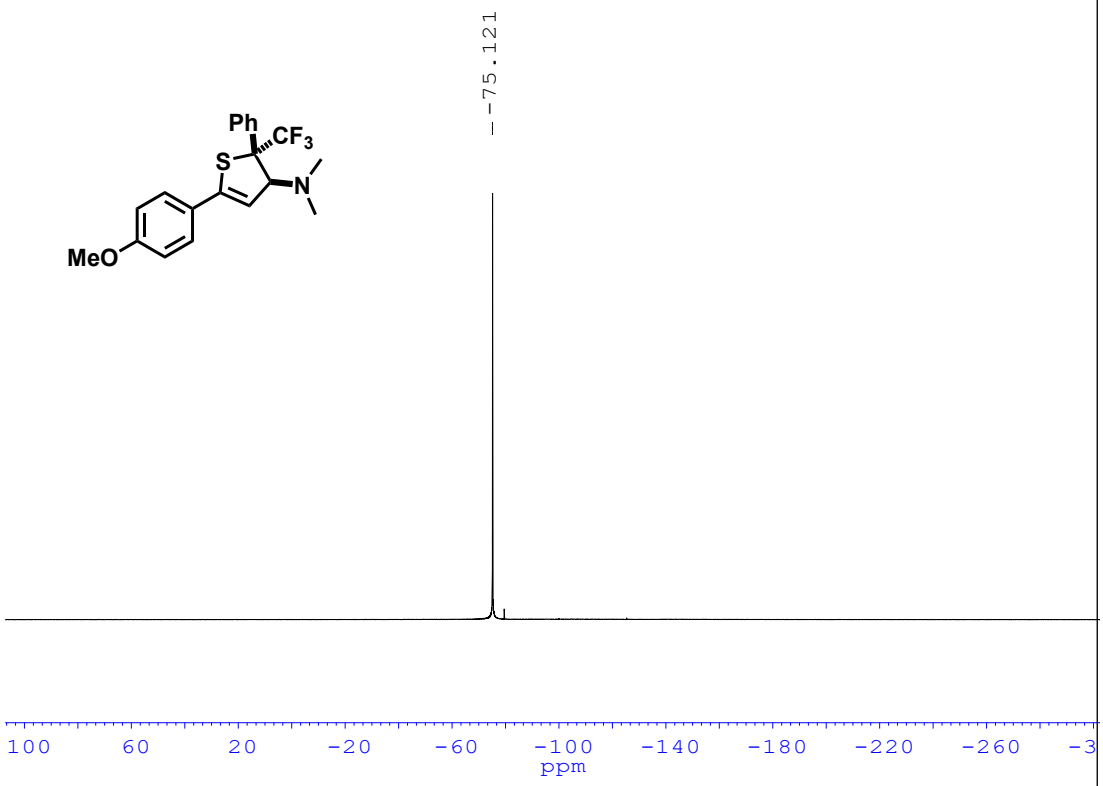
^{13}C NMR spectra of **3ab**



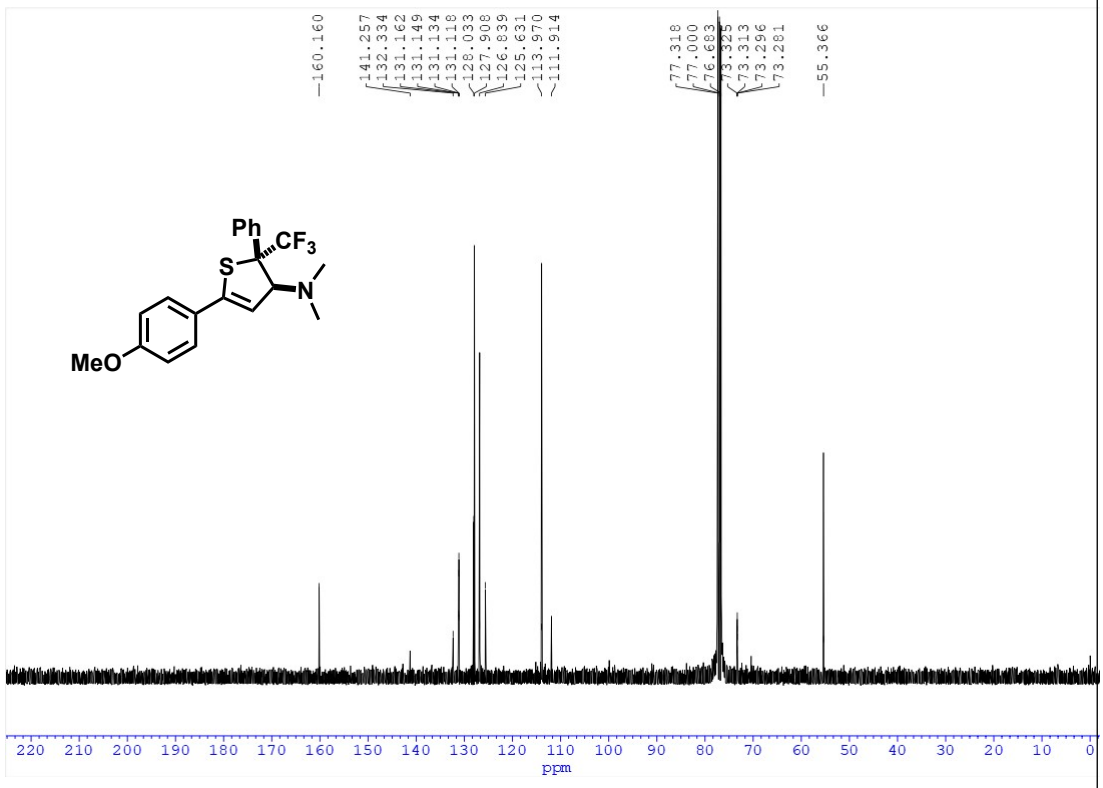
^{1}H NMR spectra of **3ac**



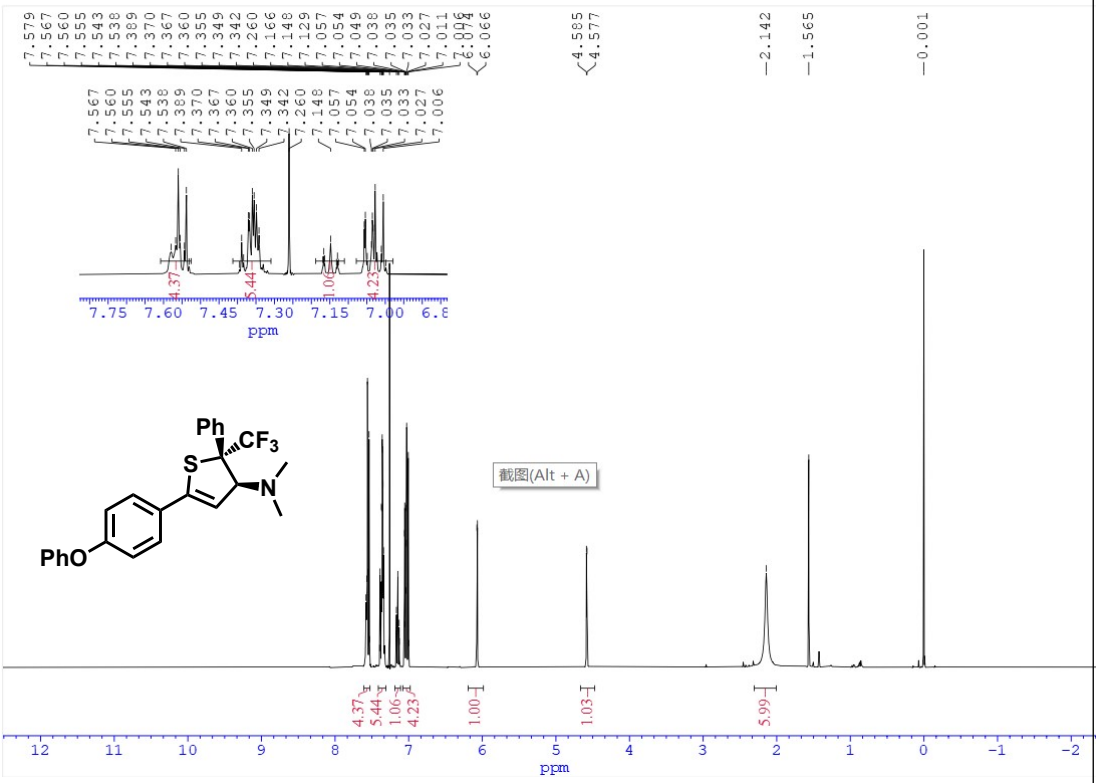
^{19}F NMR spectra of **3ac**



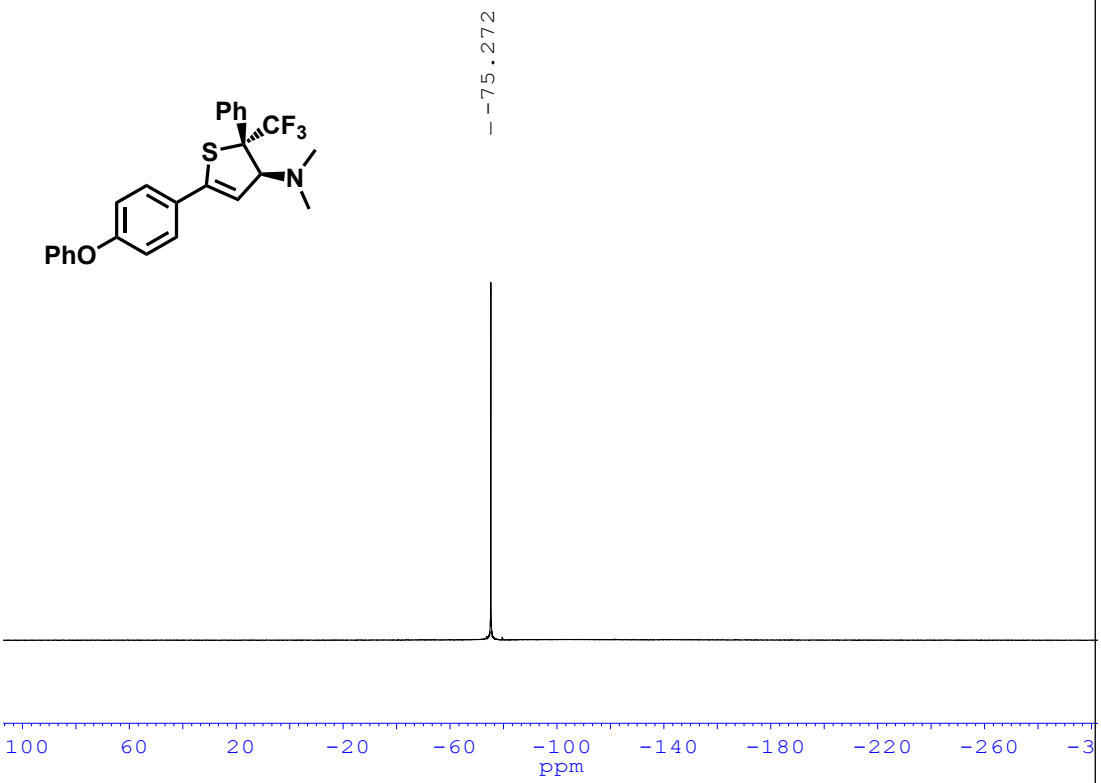
^{13}C NMR spectra of **3ac**



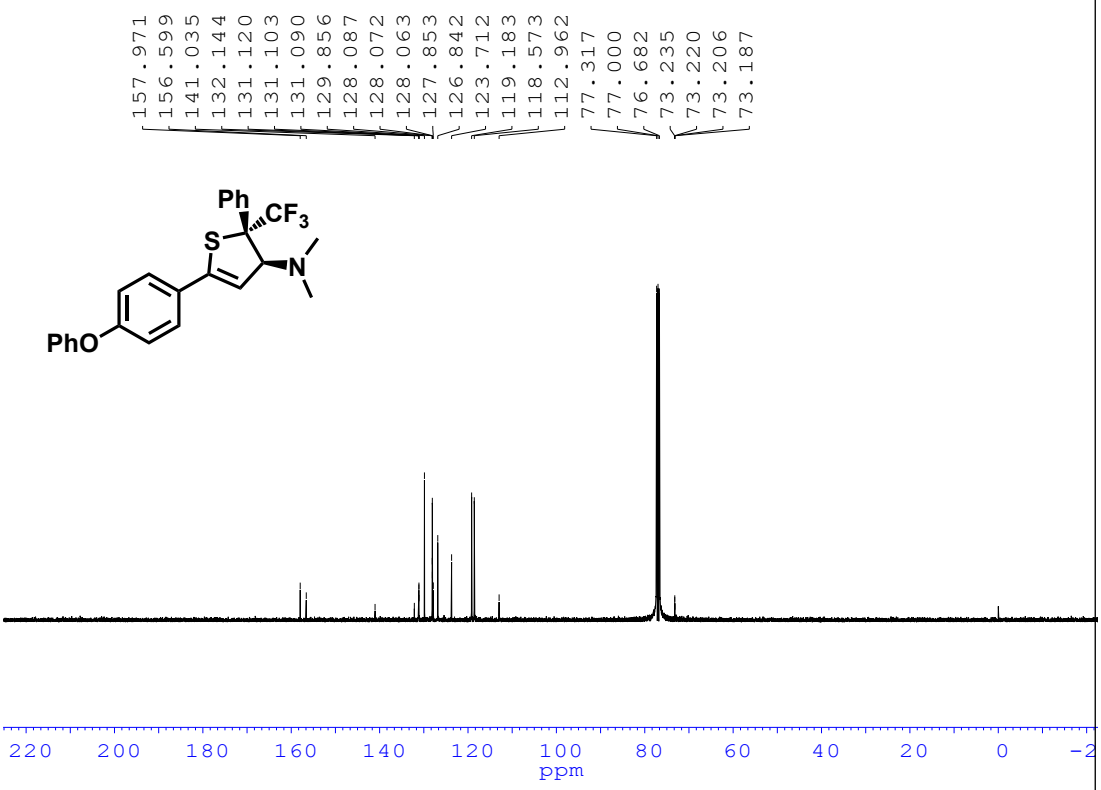
^{1}H NMR spectra of **3ad**



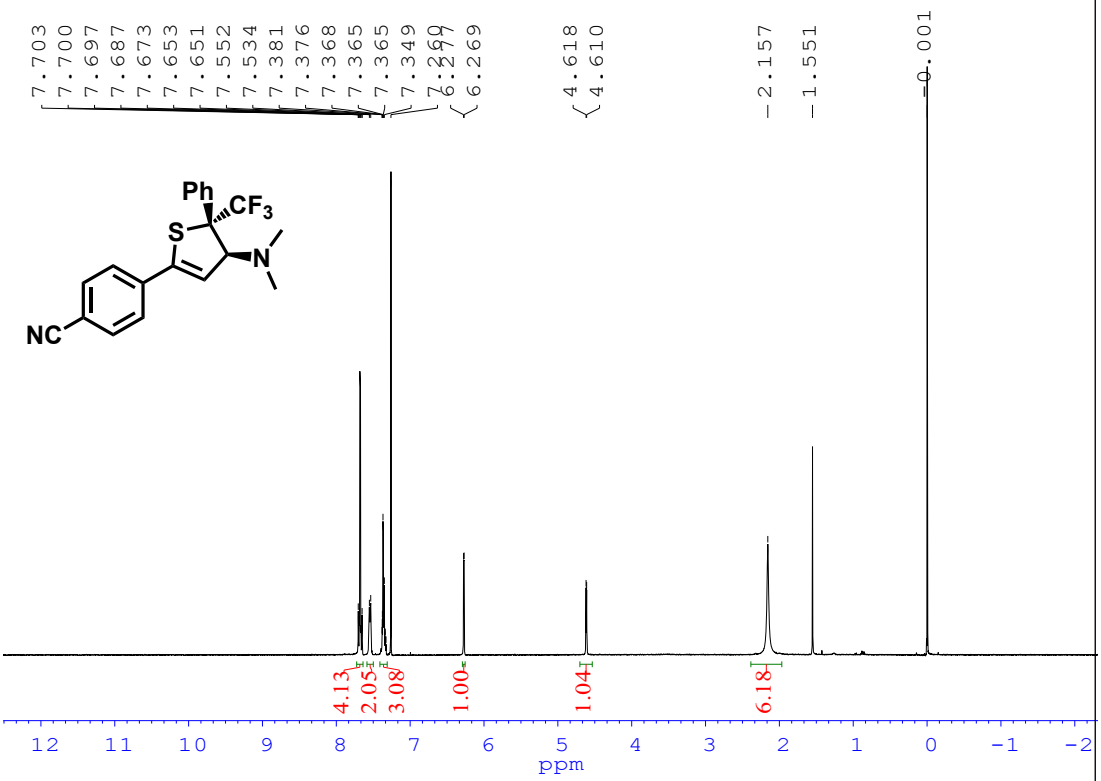
^{19}F NMR spectra of **3ad**



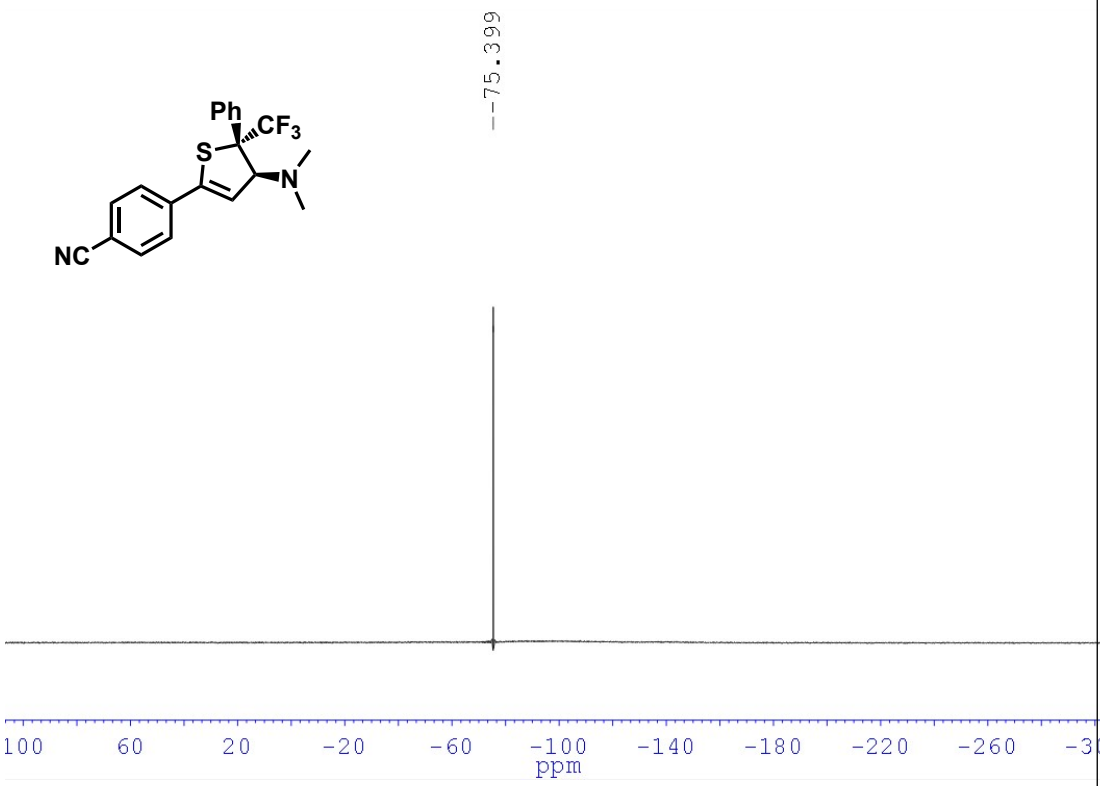
^{13}C NMR spectra of **3ad**



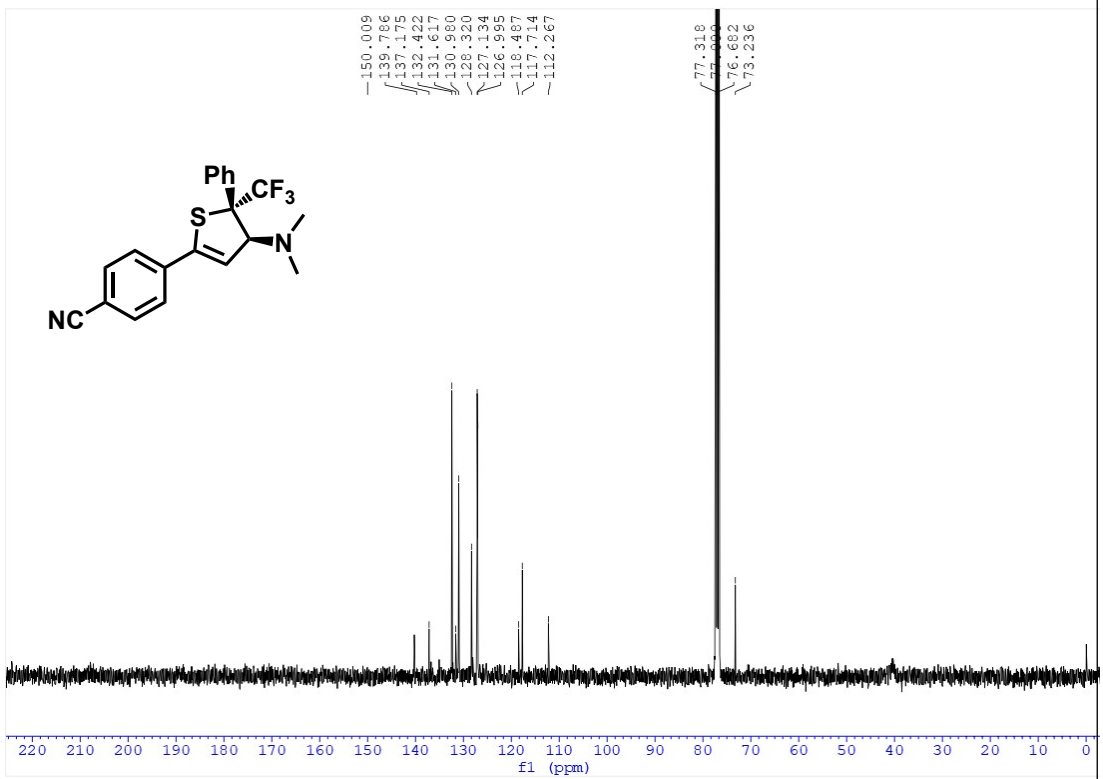
^{1}H NMR spectra of **3ae**



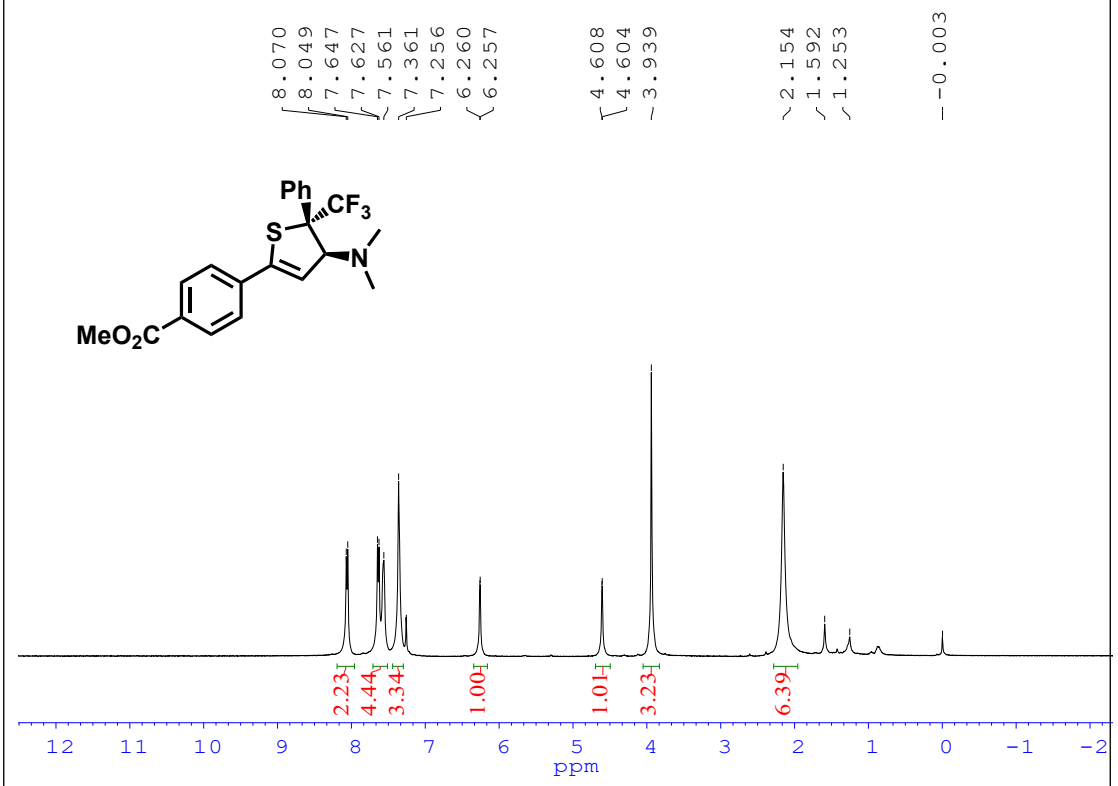
^{19}F NMR spectra of **3ae**



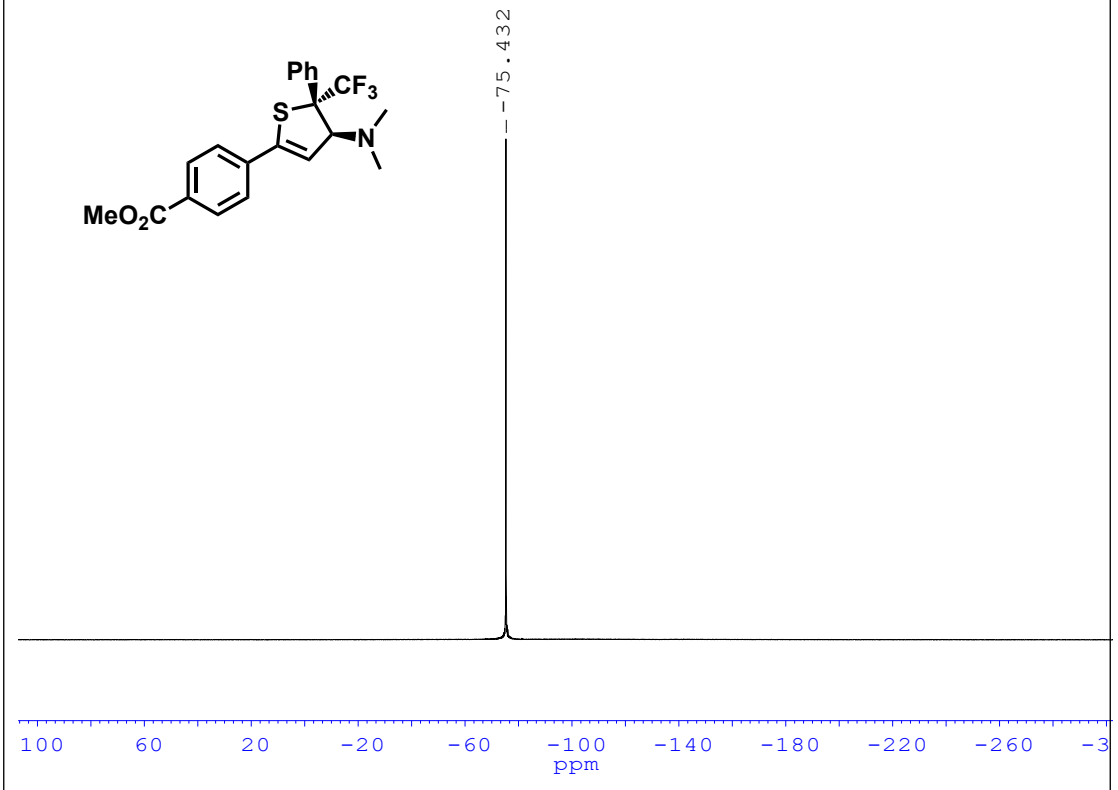
^{13}C NMR spectra of **3ae**



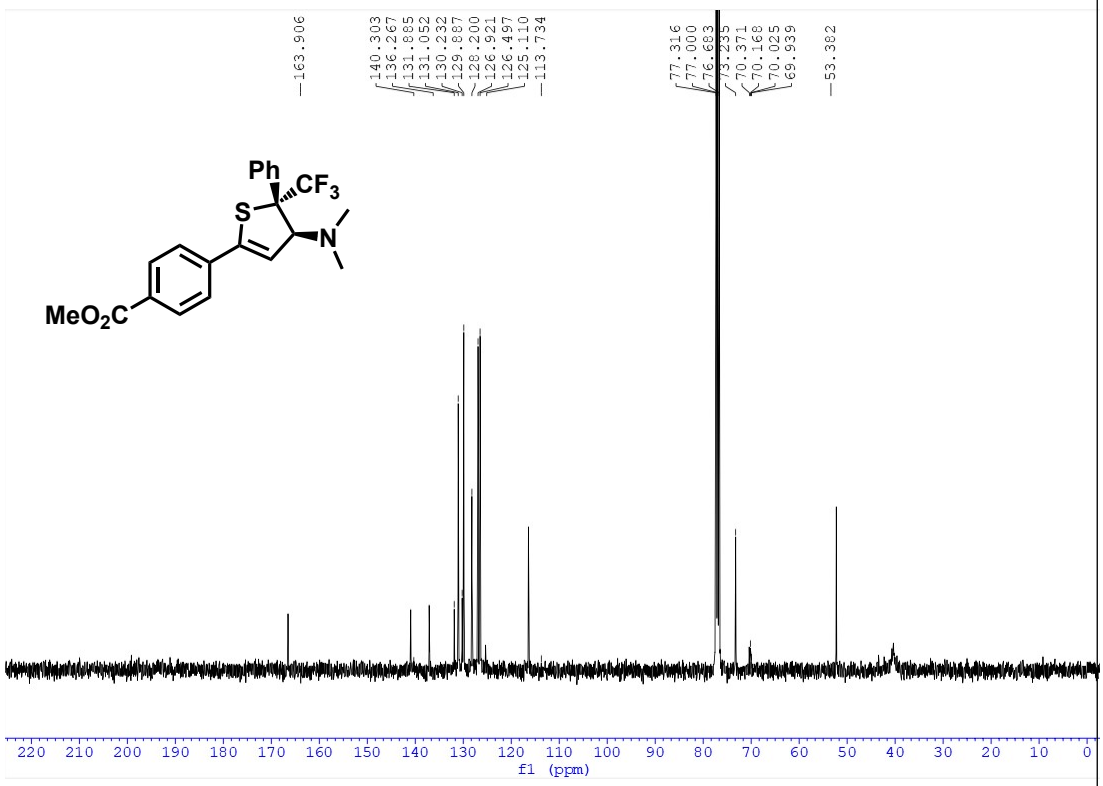
^{1}H NMR spectra of **3af**



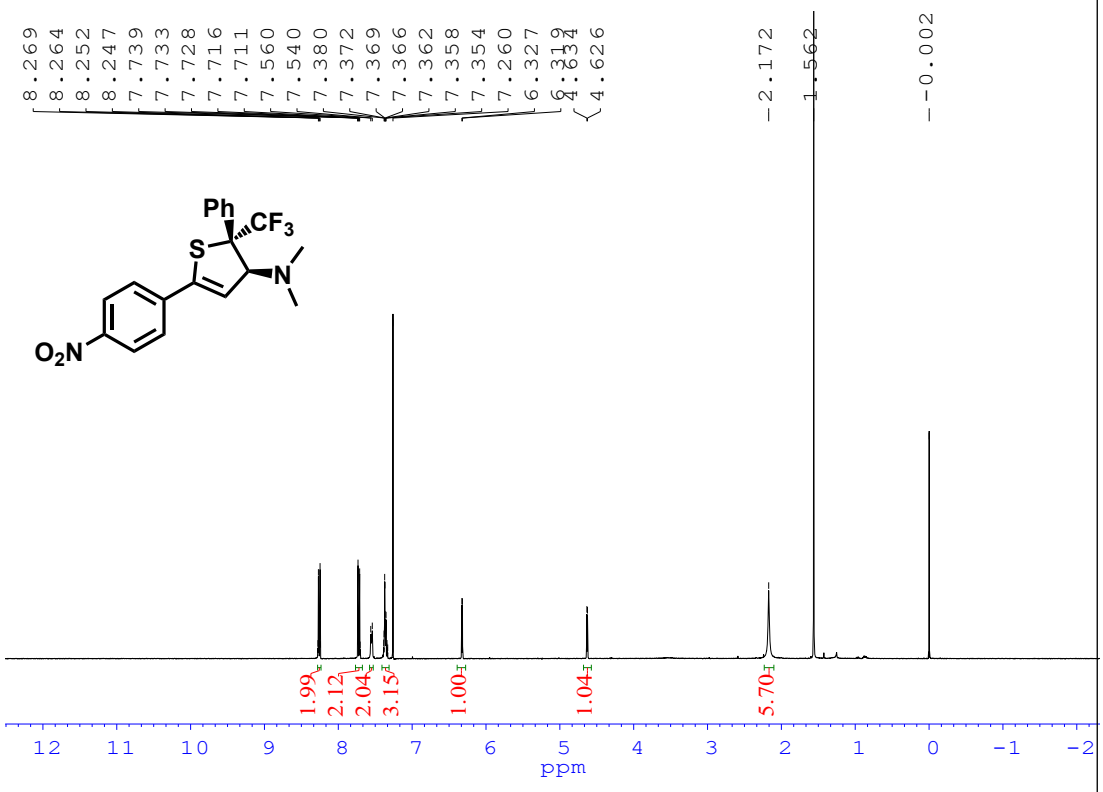
^{19}F NMR spectra of **3af**



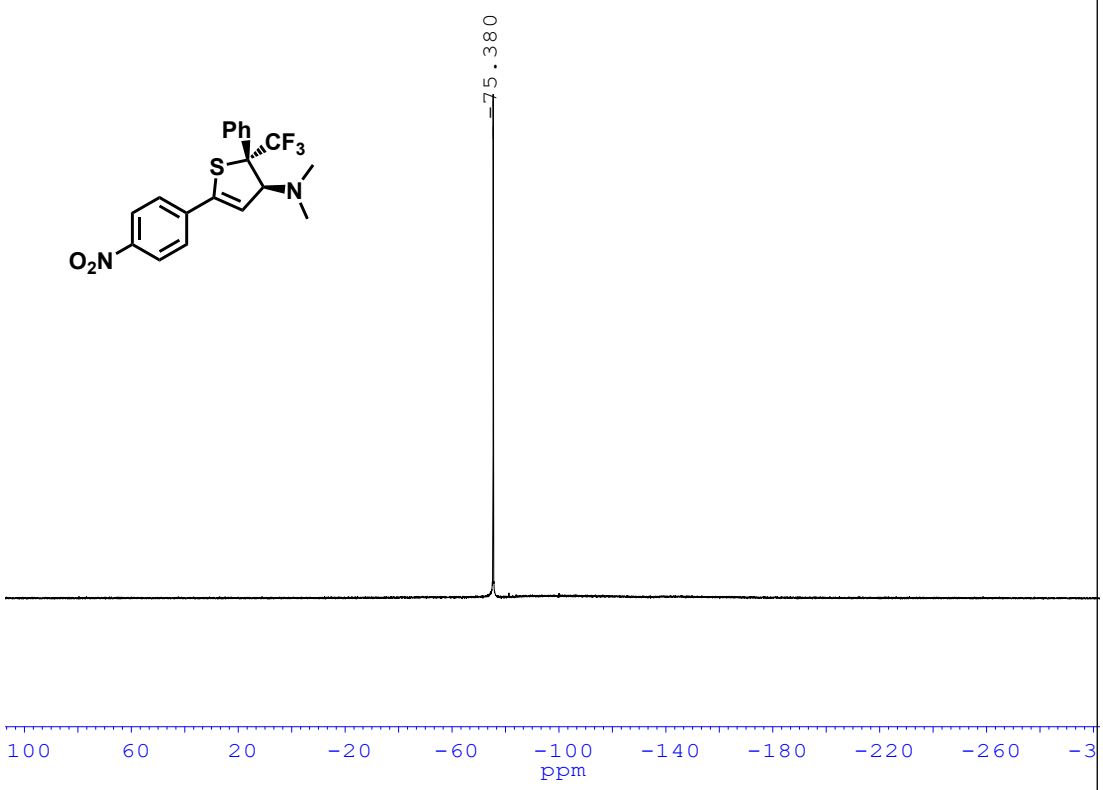
^{13}C NMR spectra of **3af**



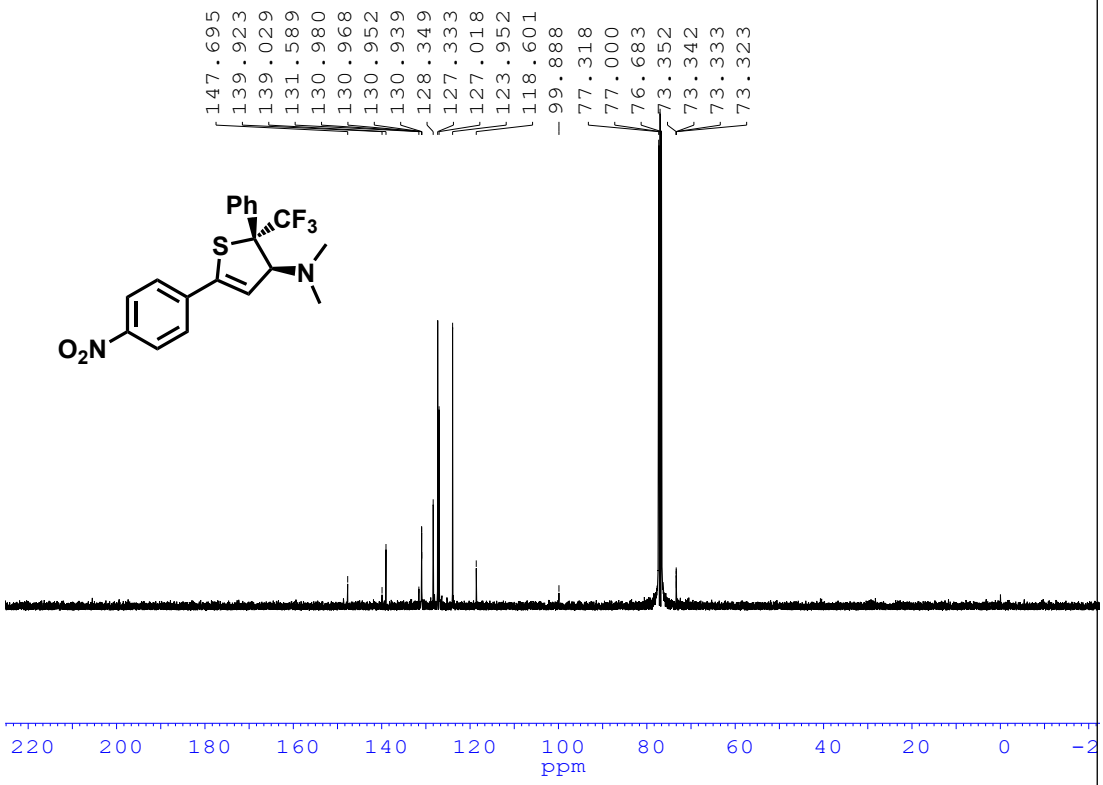
^{1}H NMR spectra of **3ag**



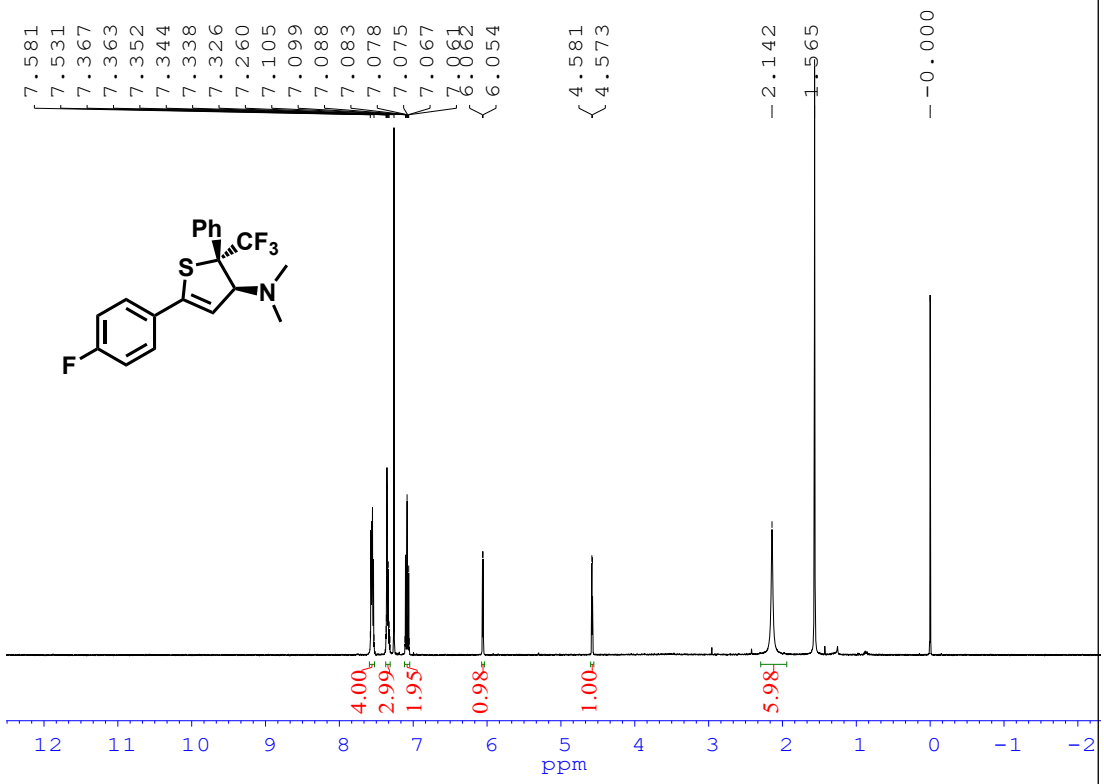
^{19}F NMR spectra of **3ag**



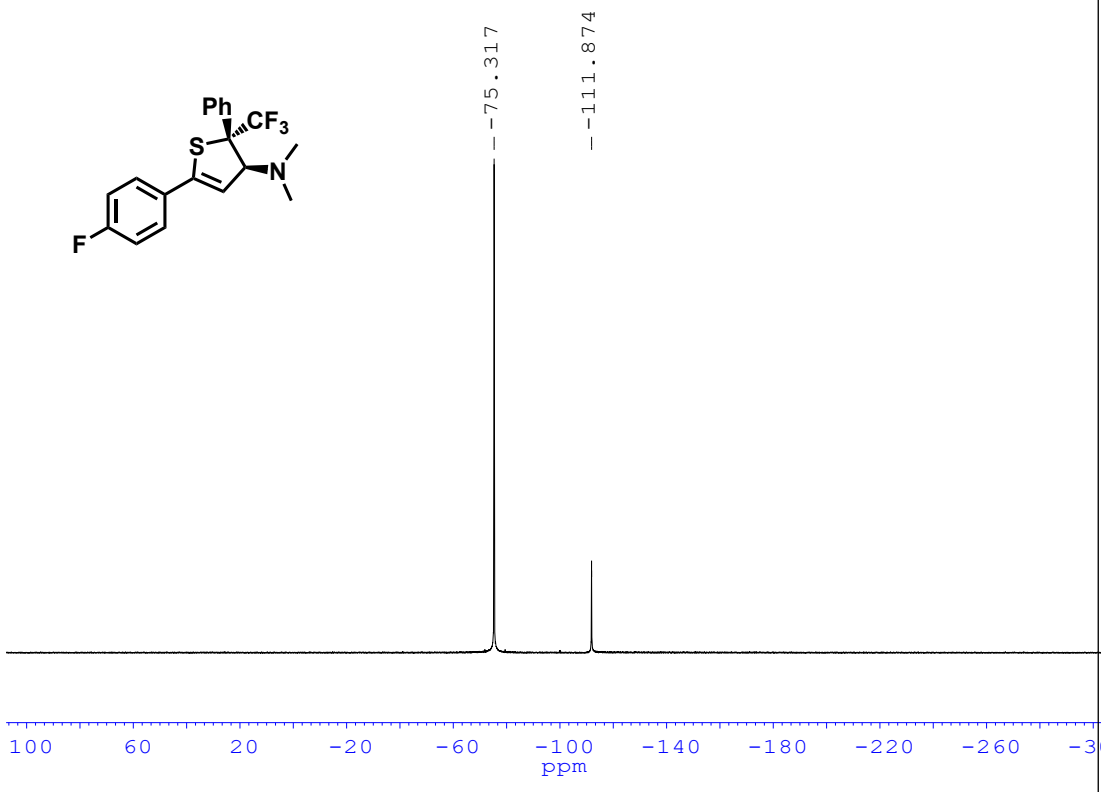
^{13}C NMR spectra of **3ag**



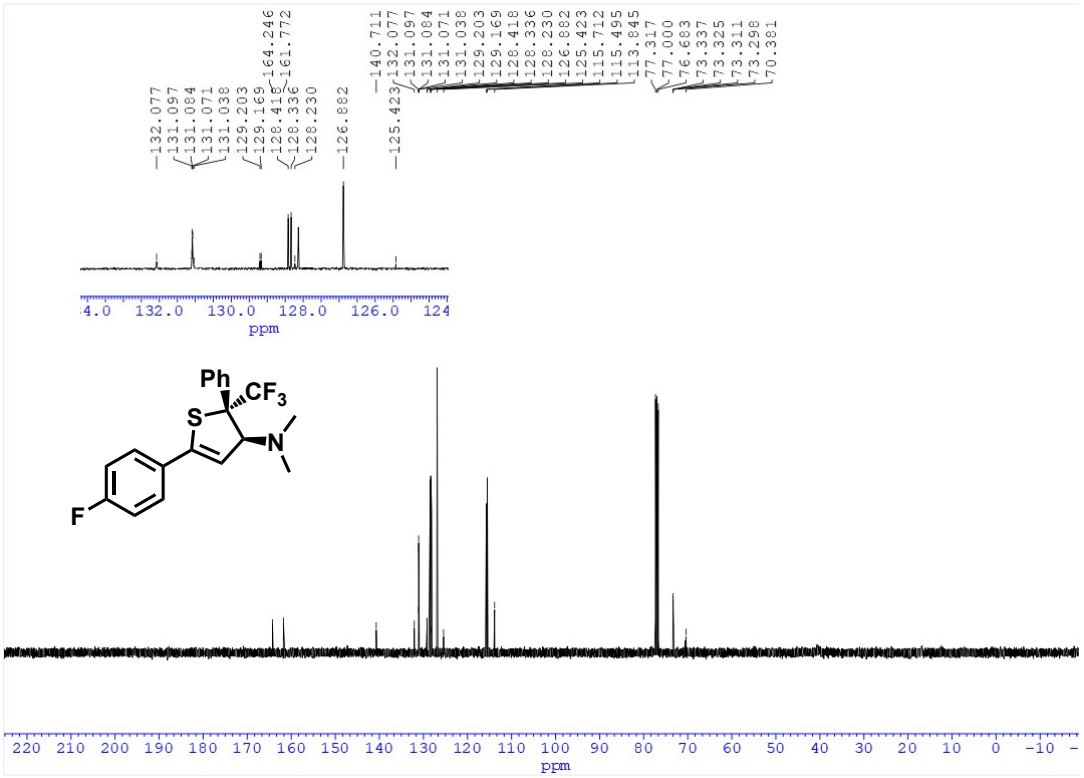
[1]H NMR spectra of **3ah**



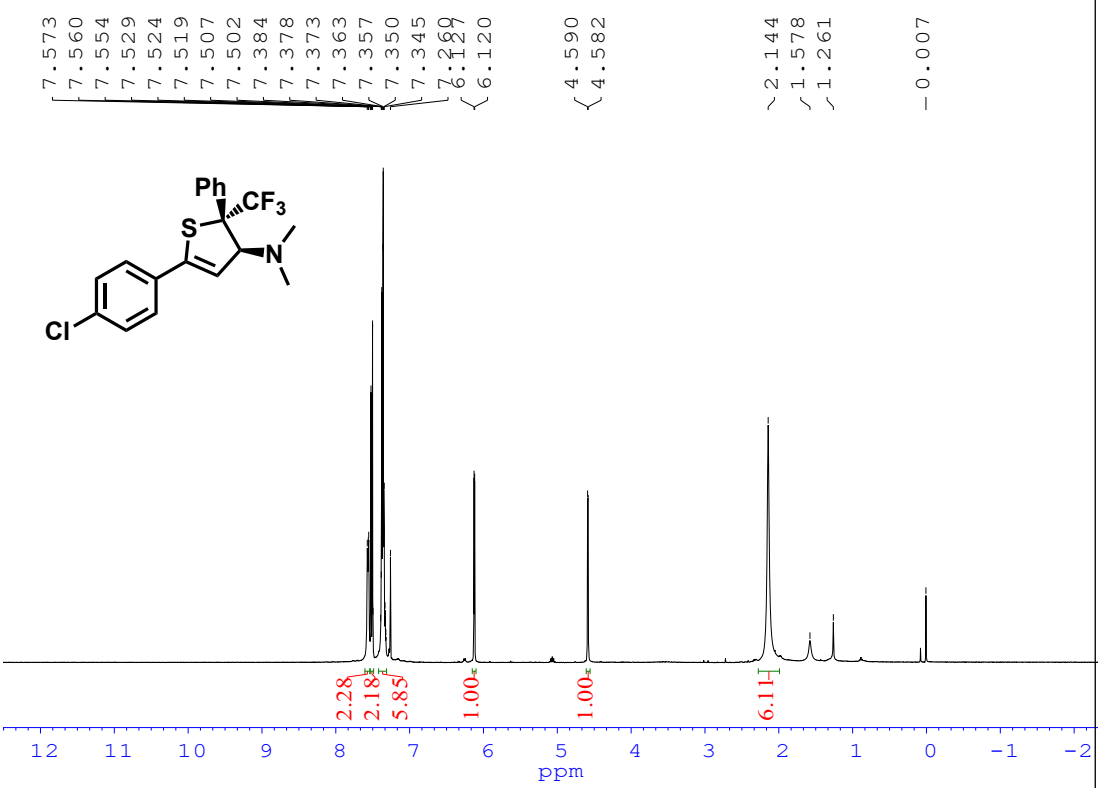
[19]F NMR spectra of **3ah**



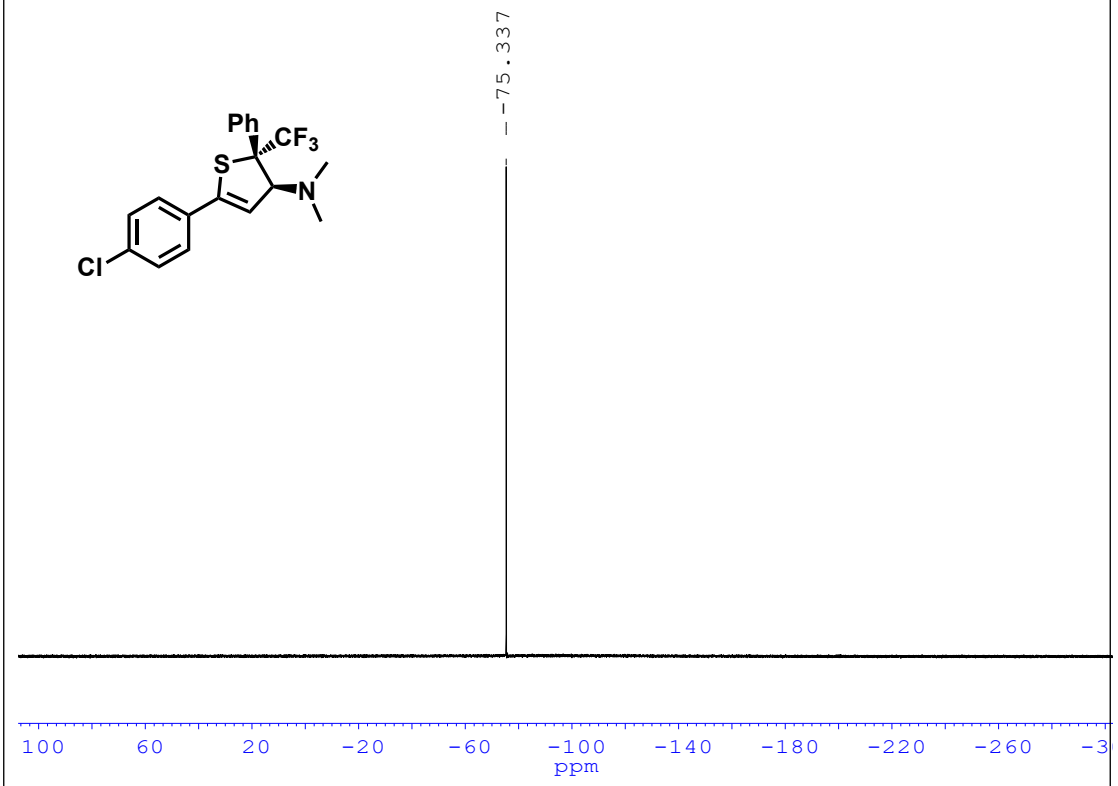
^{13}C NMR spectra of **3ah**



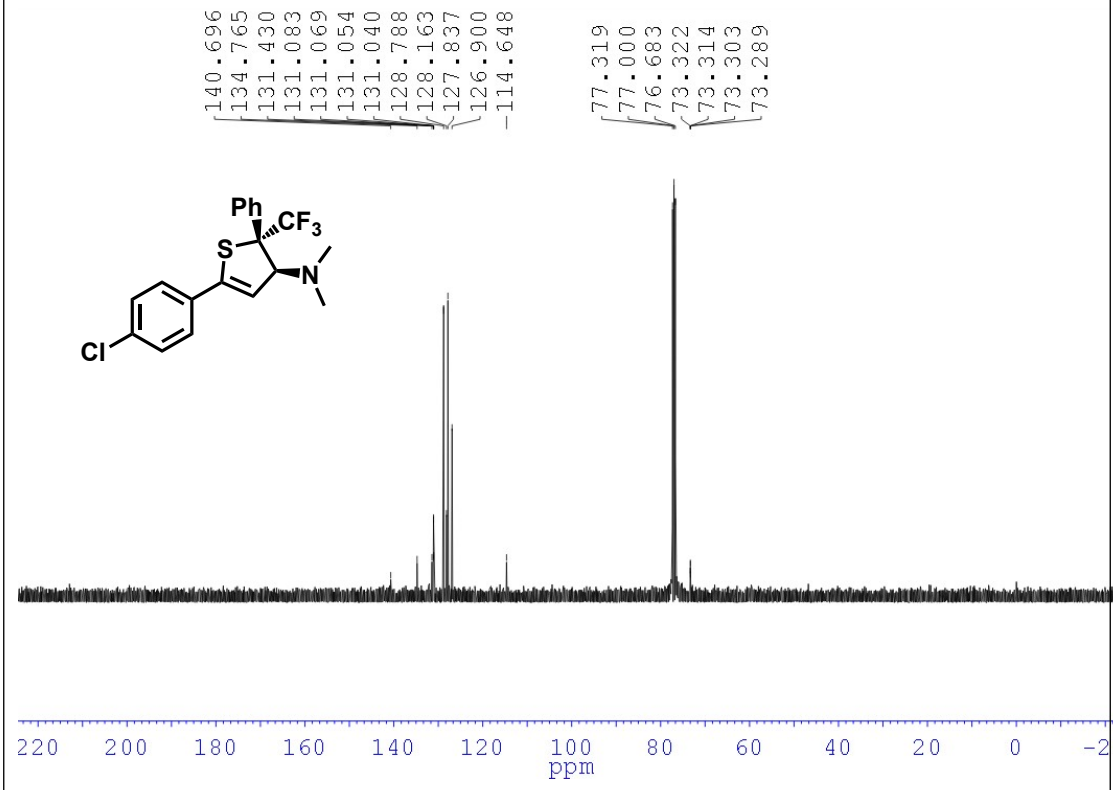
^{1}H NMR spectra of **3ai**



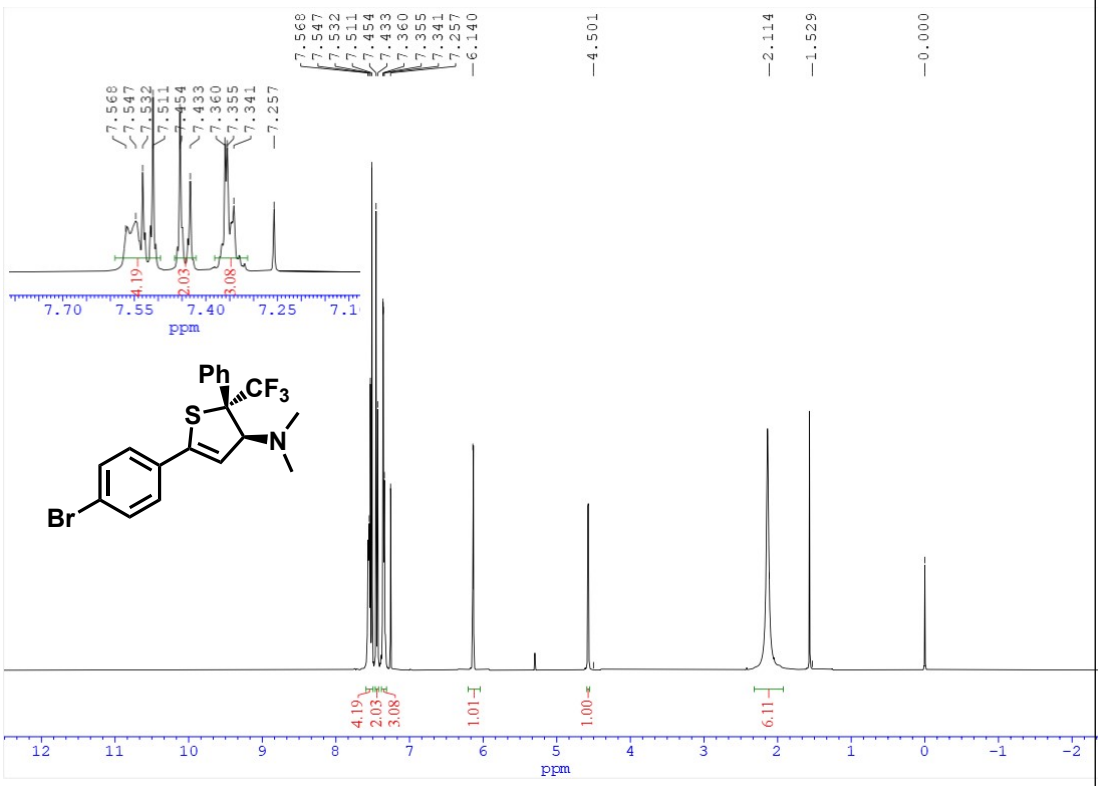
^{19}F NMR spectra of **3ai**



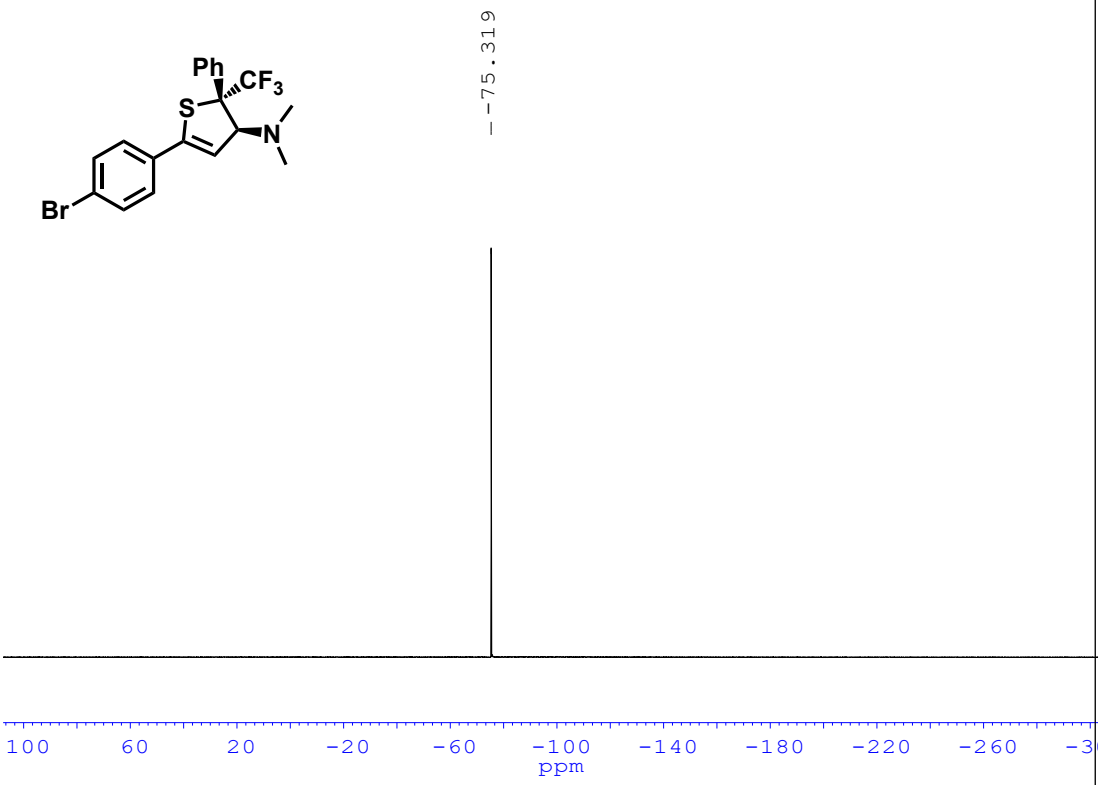
^{13}C NMR spectra of **3ai**



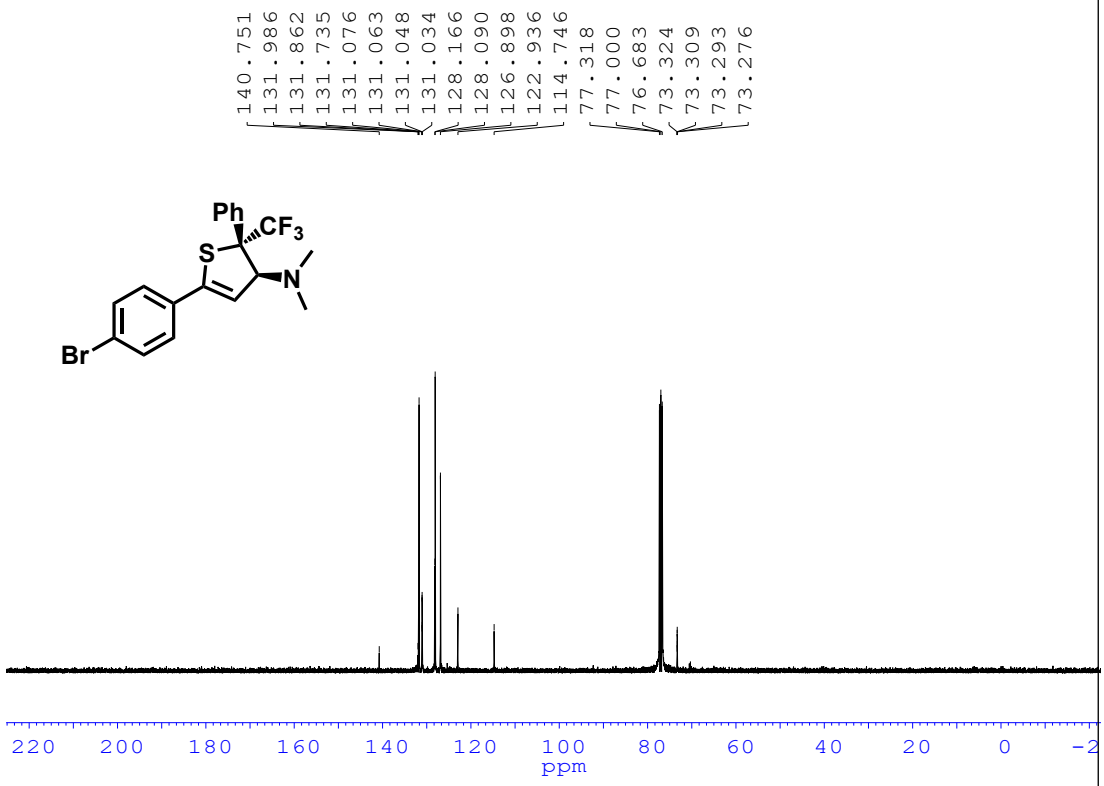
^{1}H NMR spectra of **3aj**



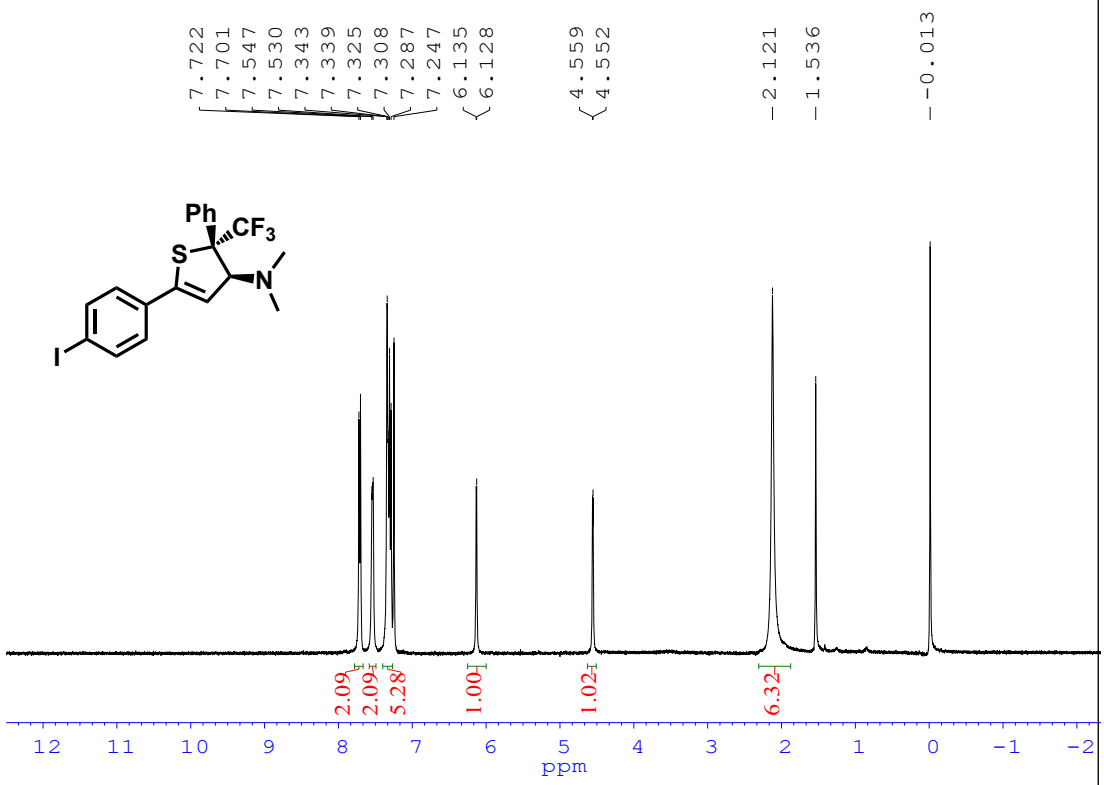
^{19}F NMR spectra of **3aj**



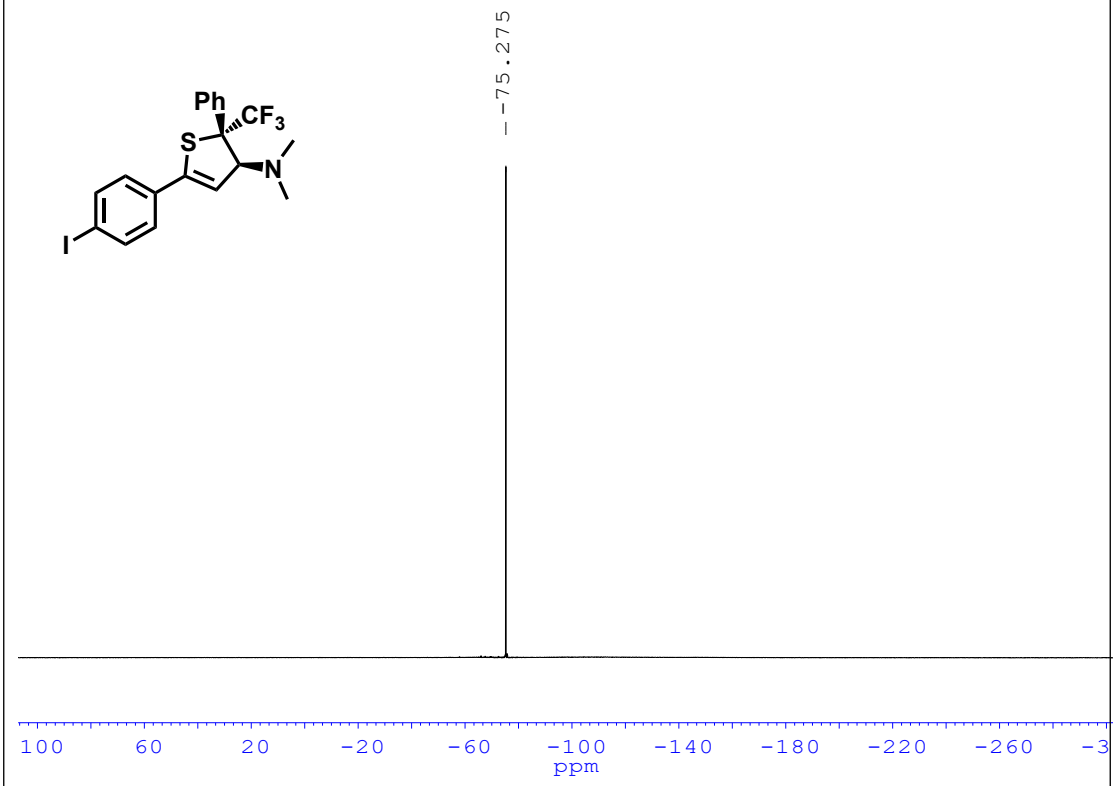
^{13}C NMR spectra of **3aj**



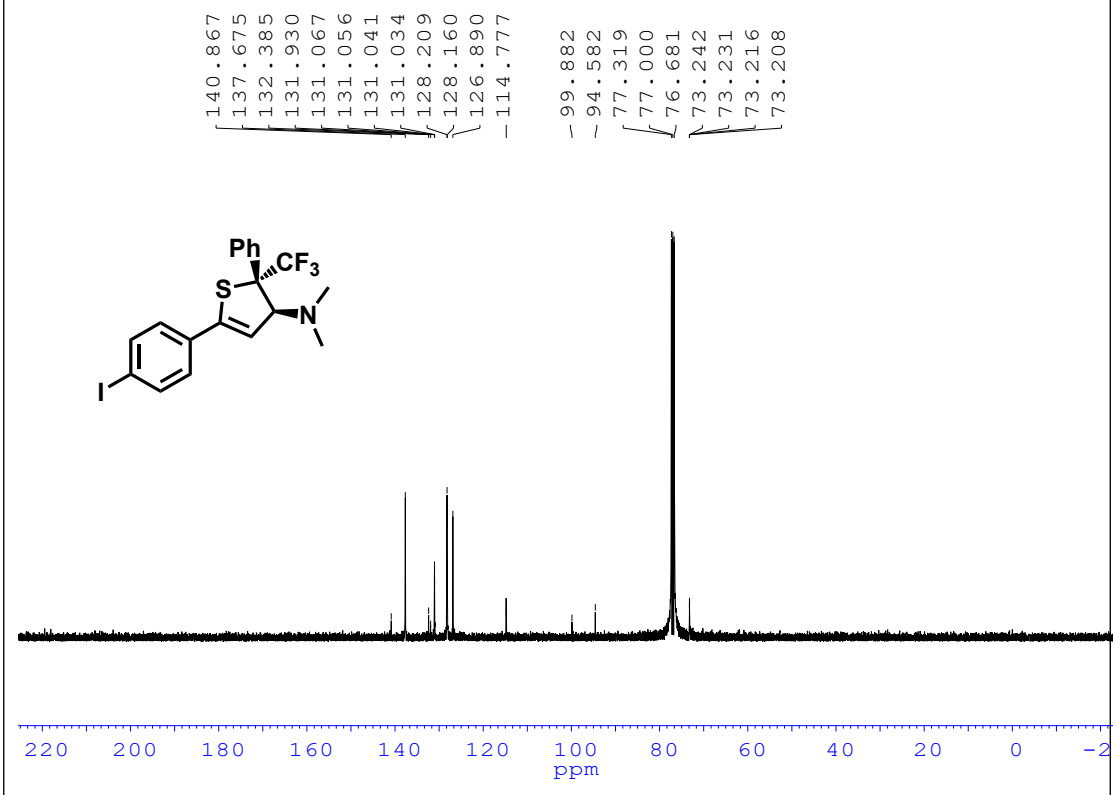
^{1}H NMR spectra of **3ak**



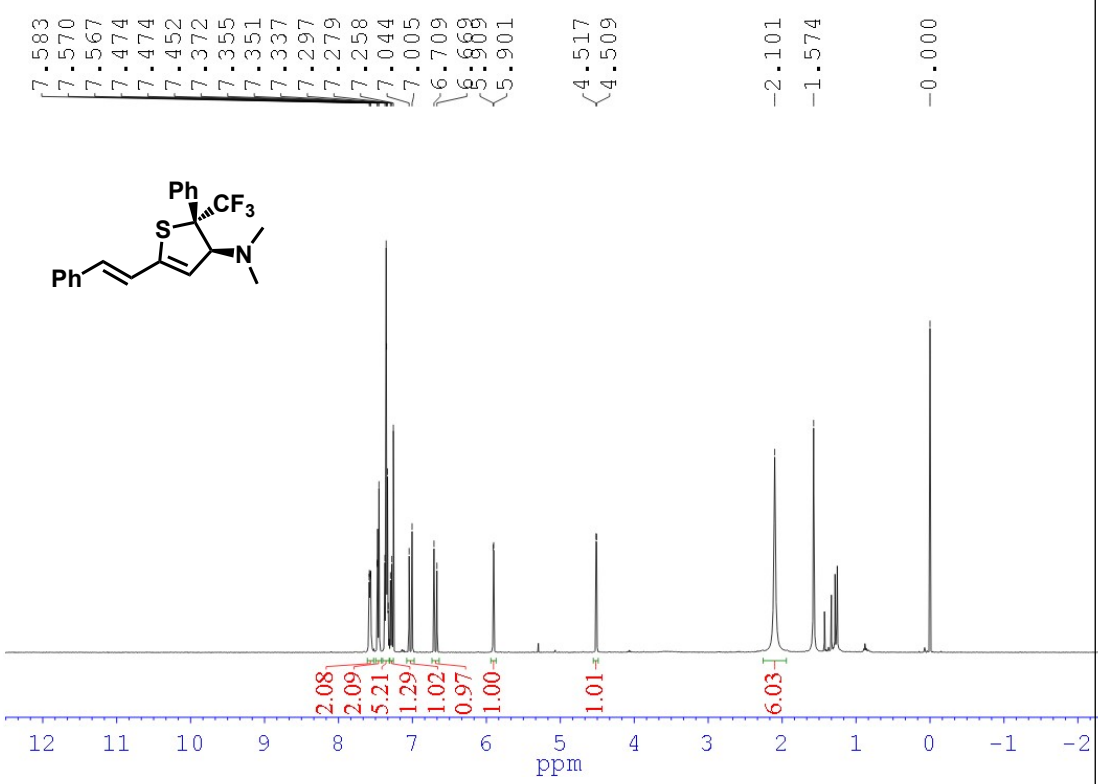
^{19}F NMR spectra of **3ak**



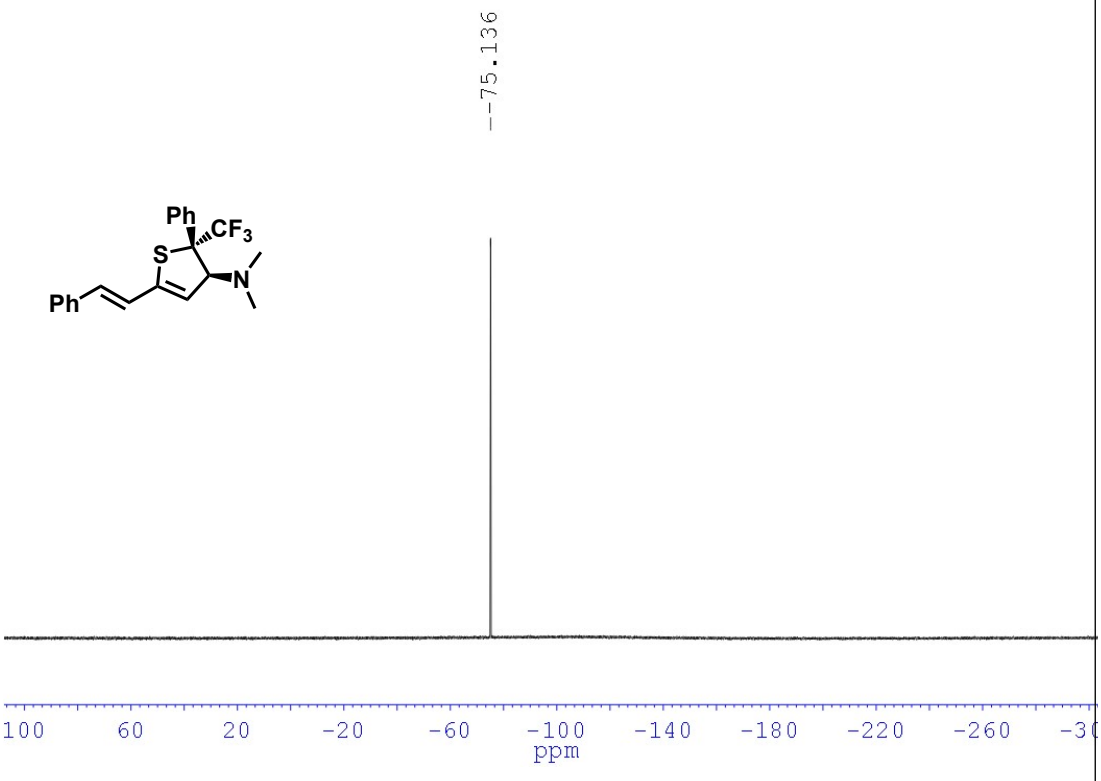
^{13}C NMR spectra of **3ak**



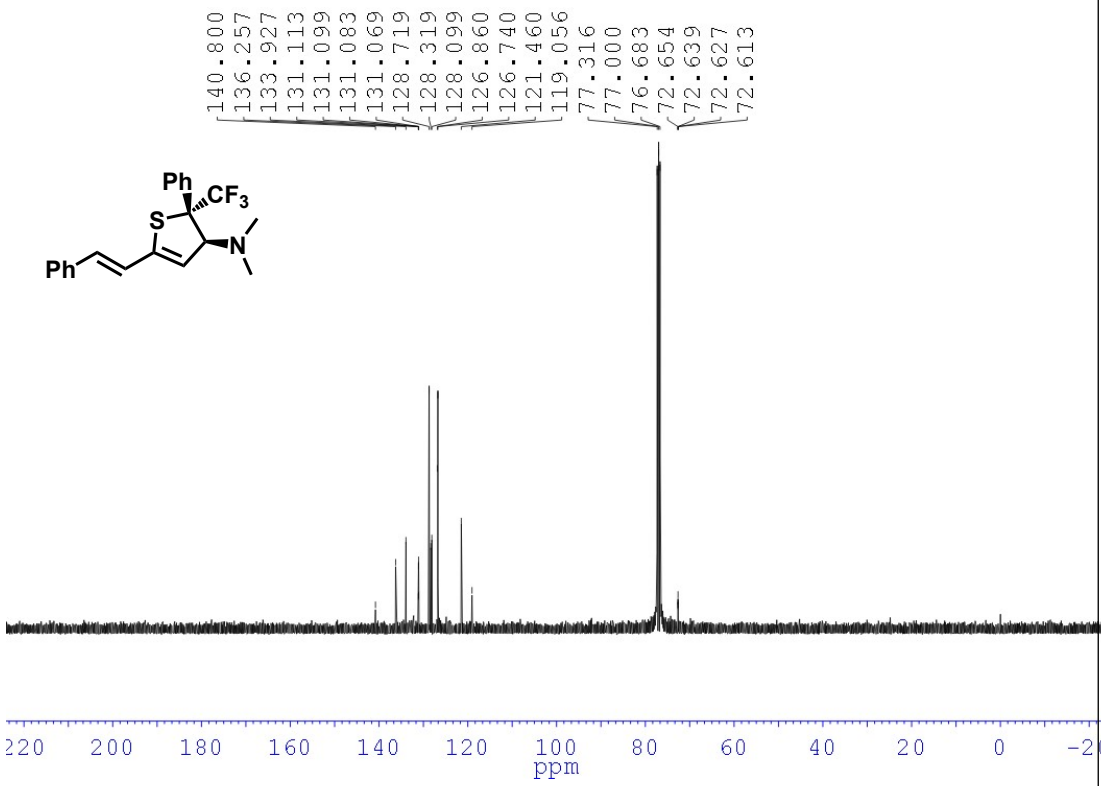
^{1}H NMR spectra of **3al**



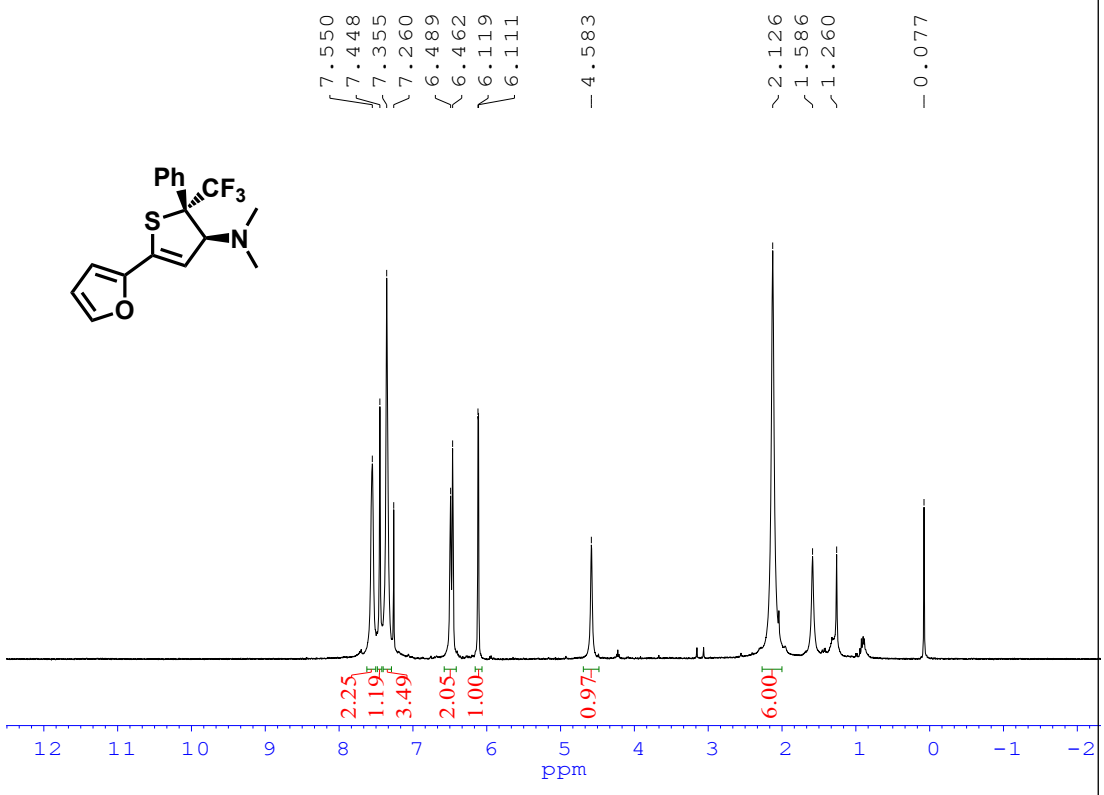
^{19}F NMR spectra of **3al**



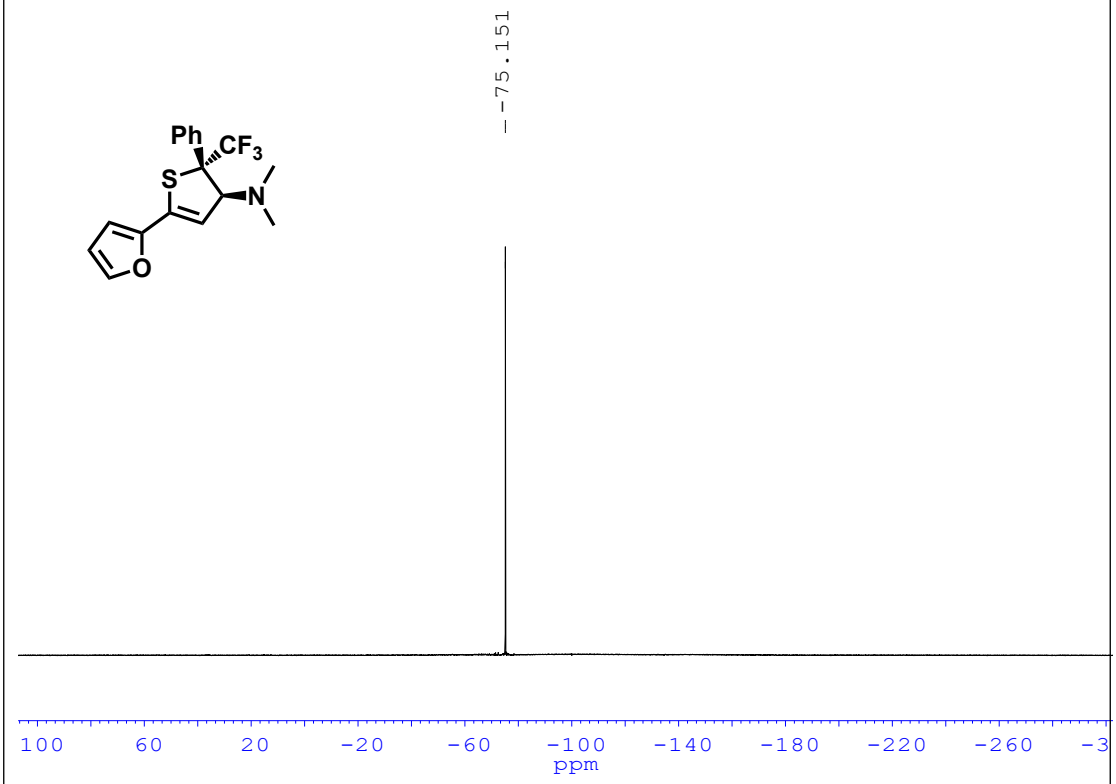
^{13}C NMR spectra of **3al**



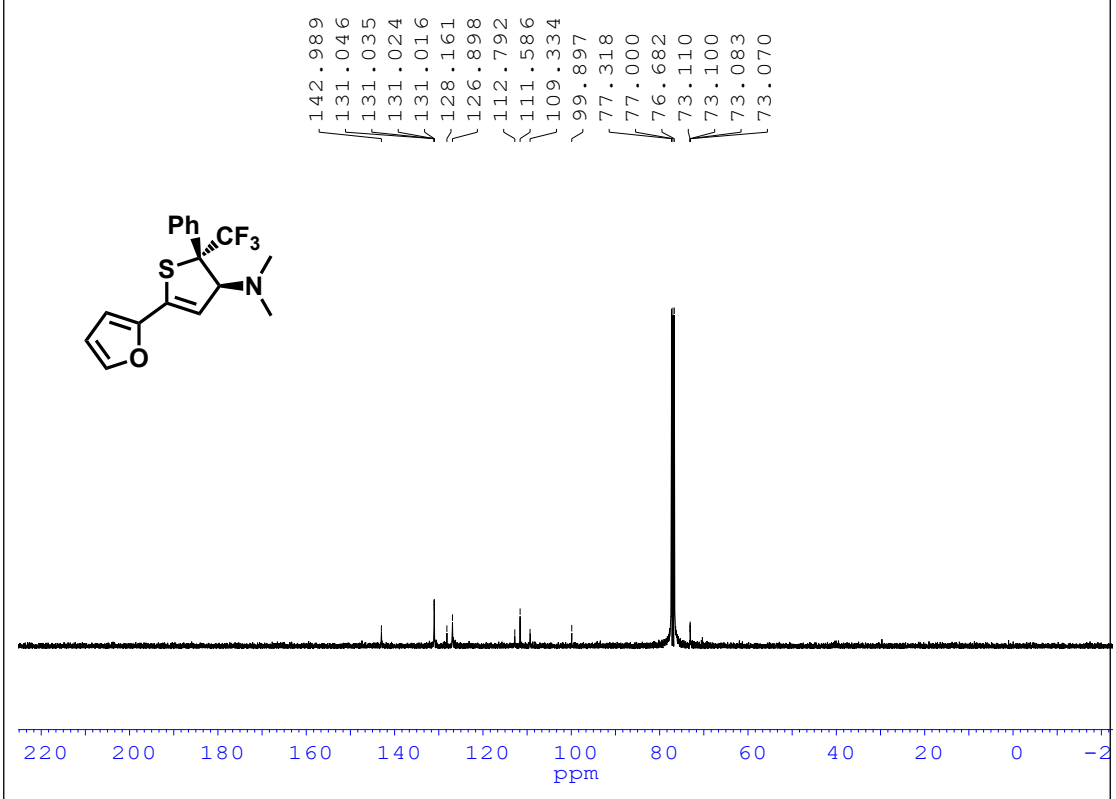
^{1}H NMR spectra of **3am**



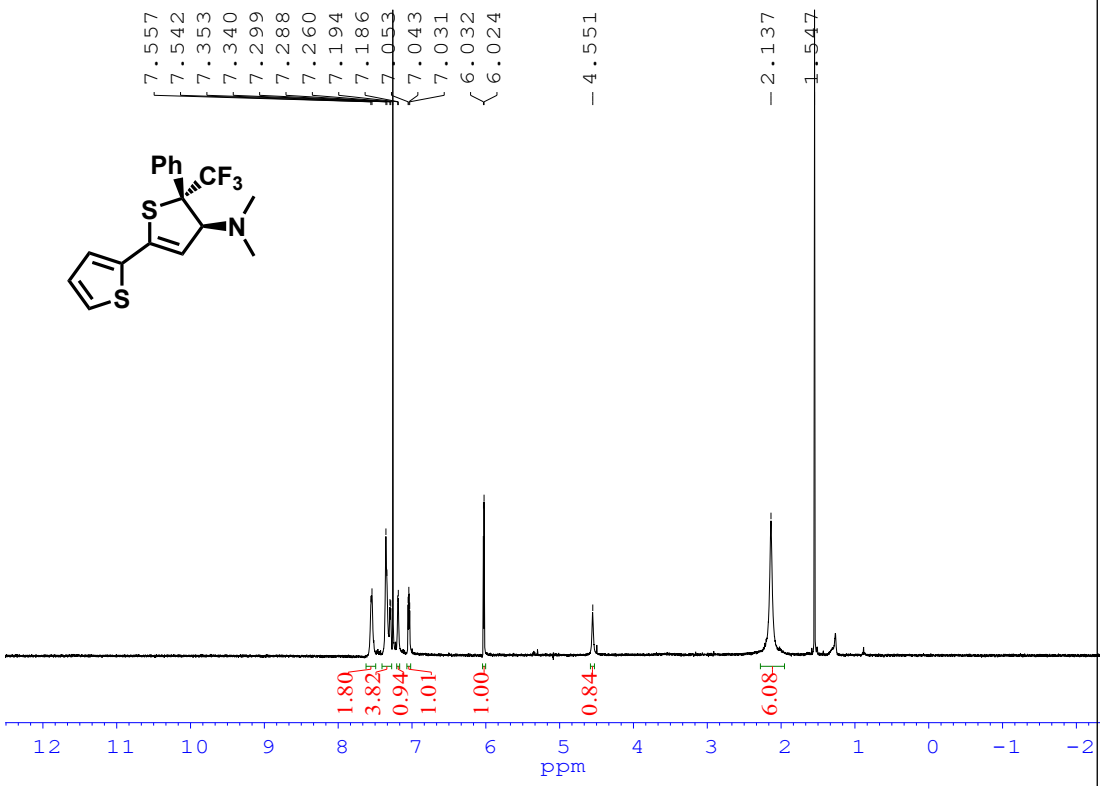
^{19}F NMR spectra of **3am**



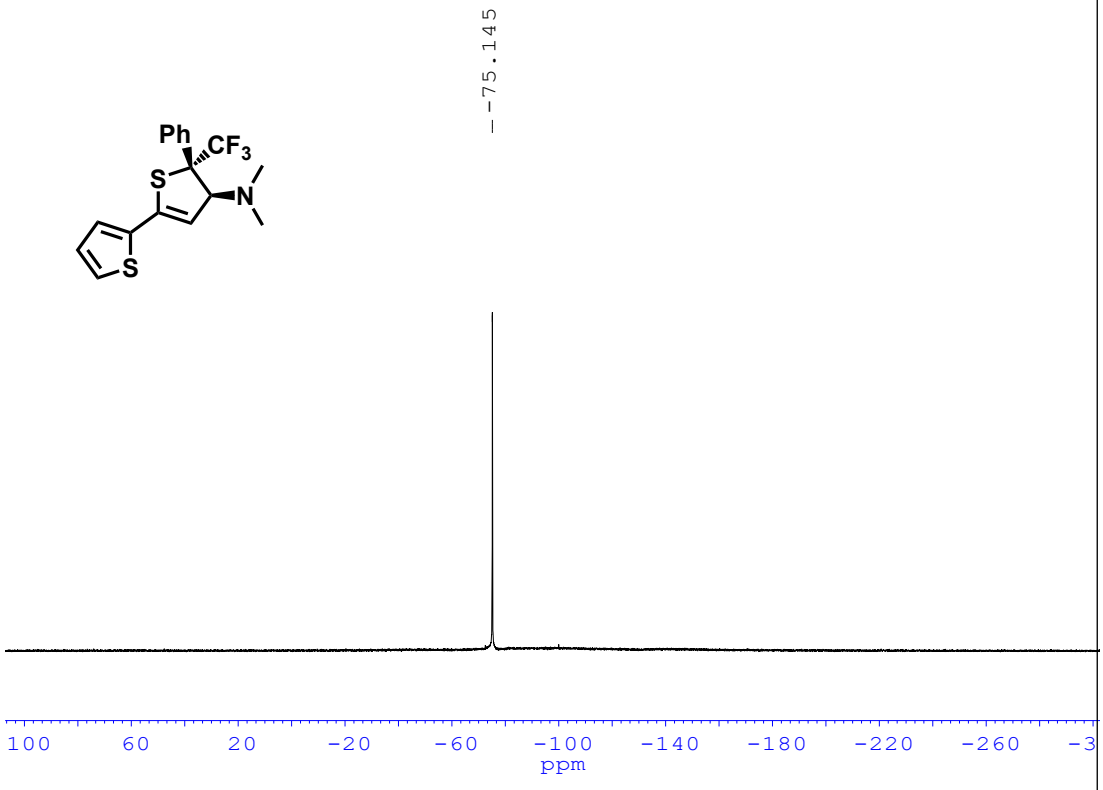
^{13}C NMR spectra of **3am**



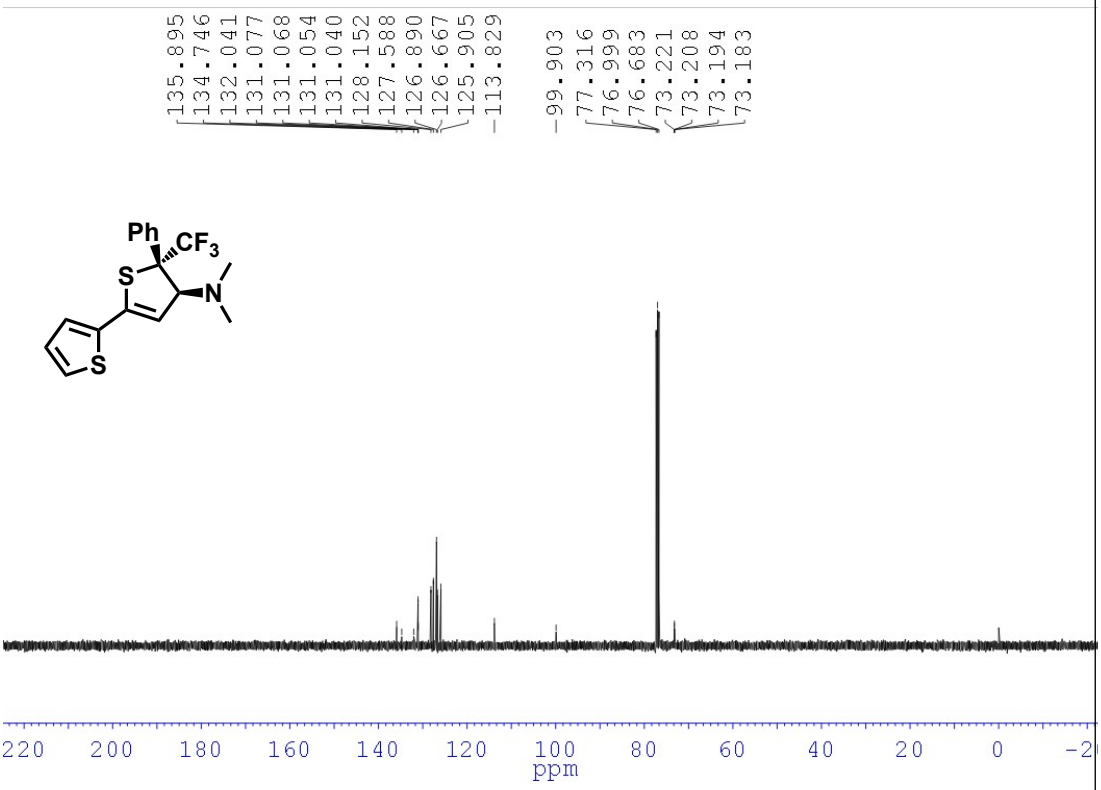
^{1}H NMR spectra of **3an**



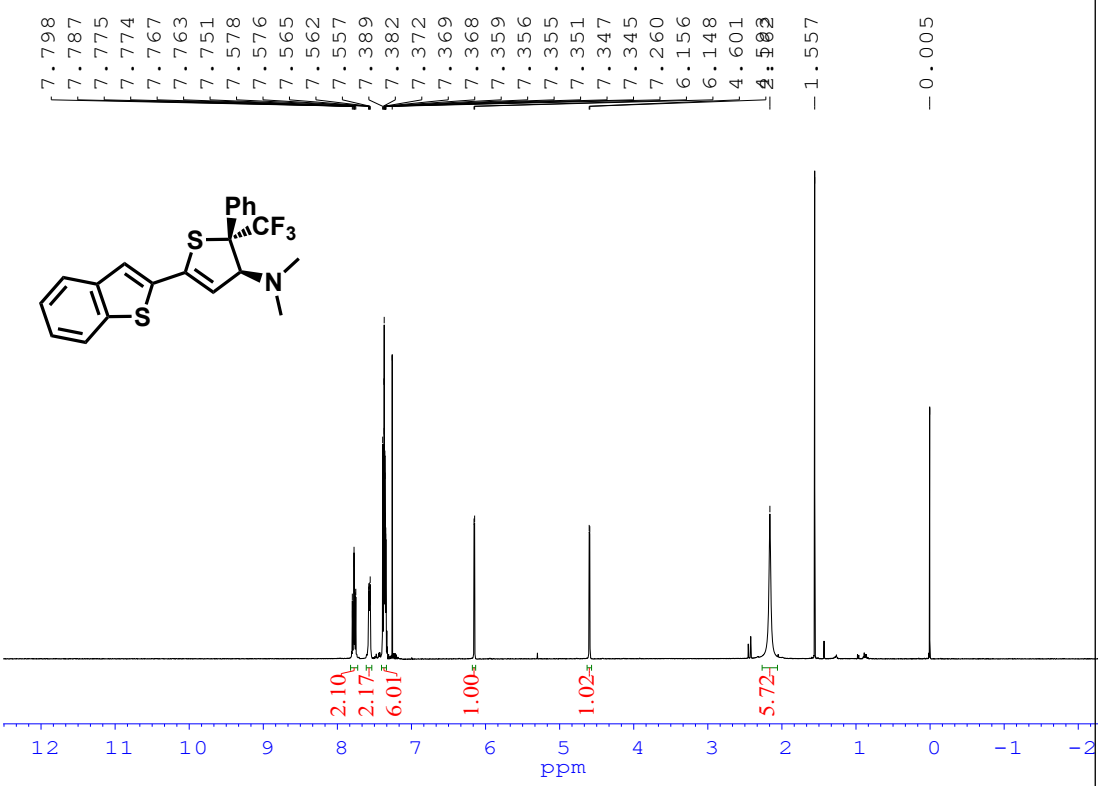
^{19}F NMR spectra of **3an**



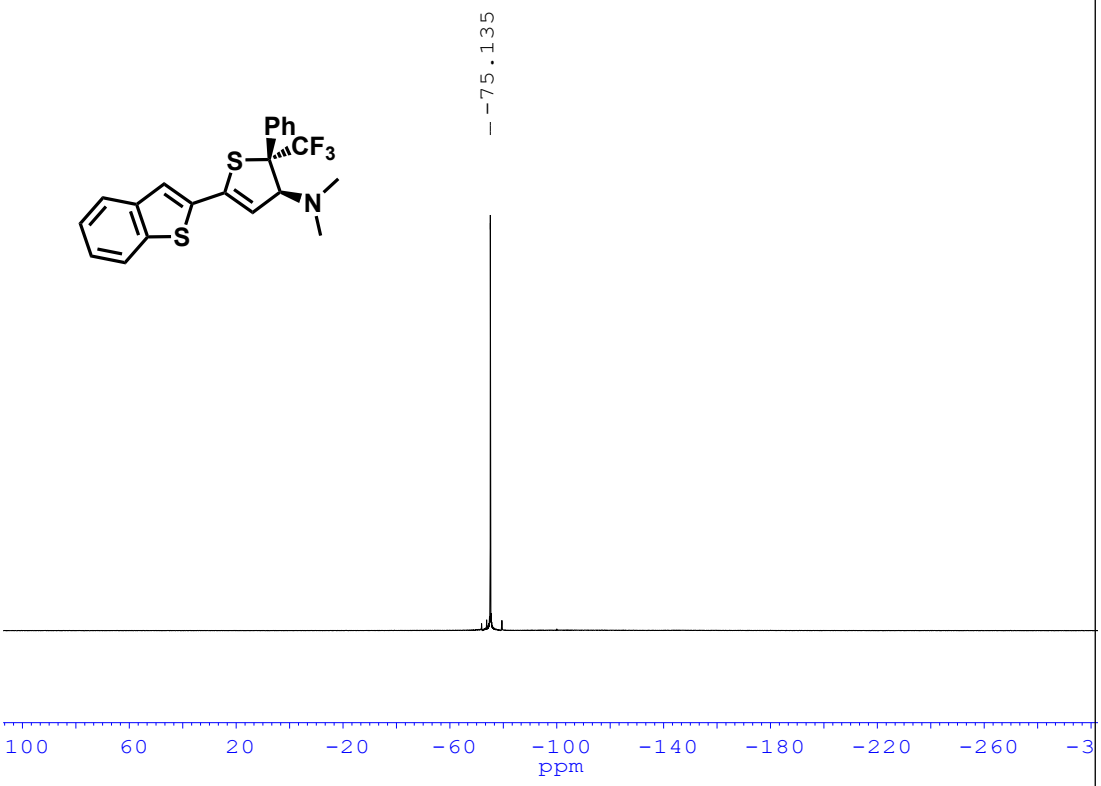
^{13}C NMR spectra of **3an**



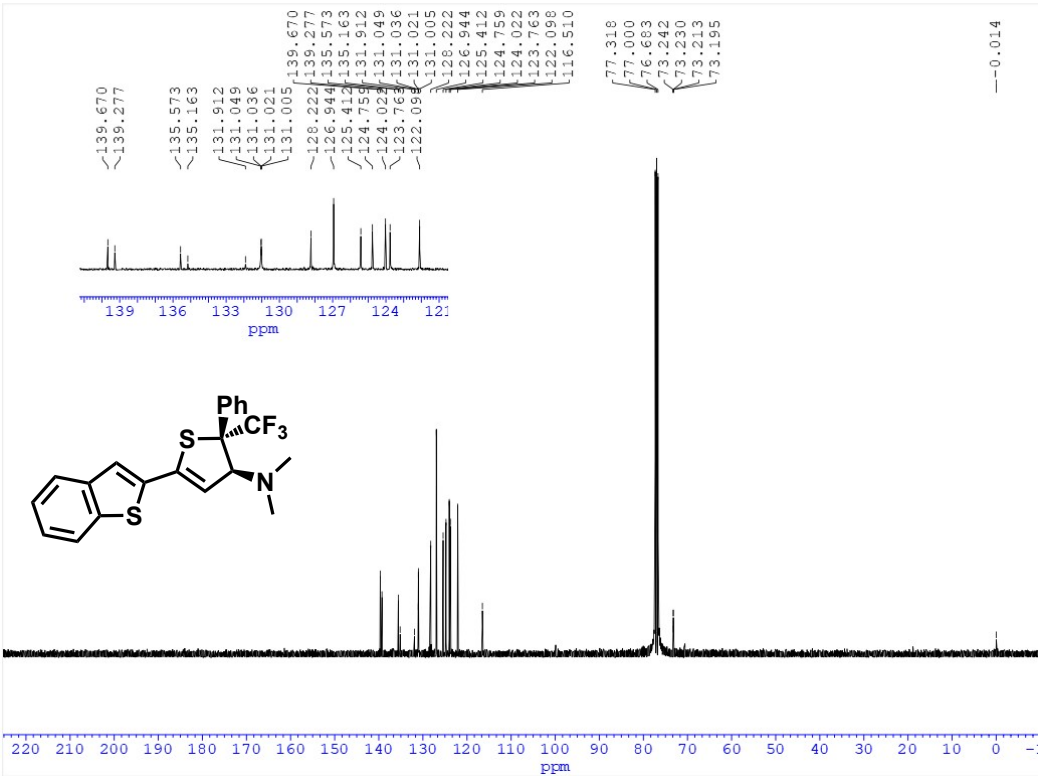
^{1}H NMR spectra of **3ao**



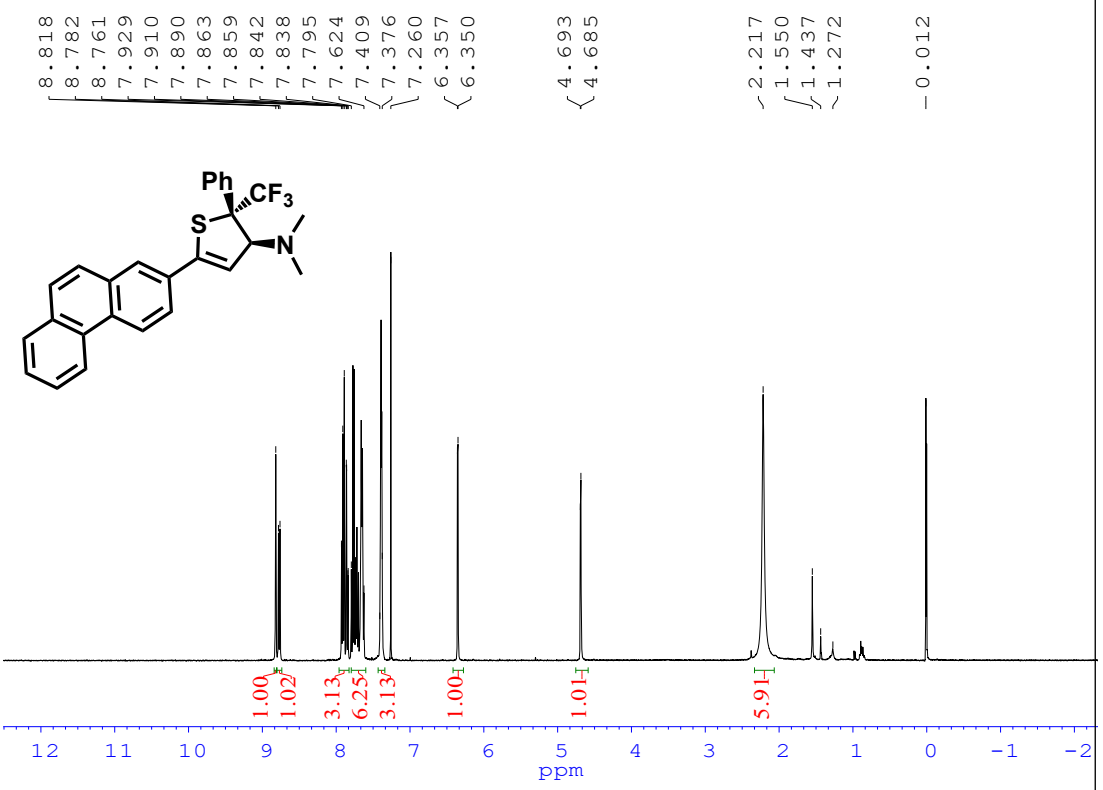
^{19}F NMR spectra of **3ao**



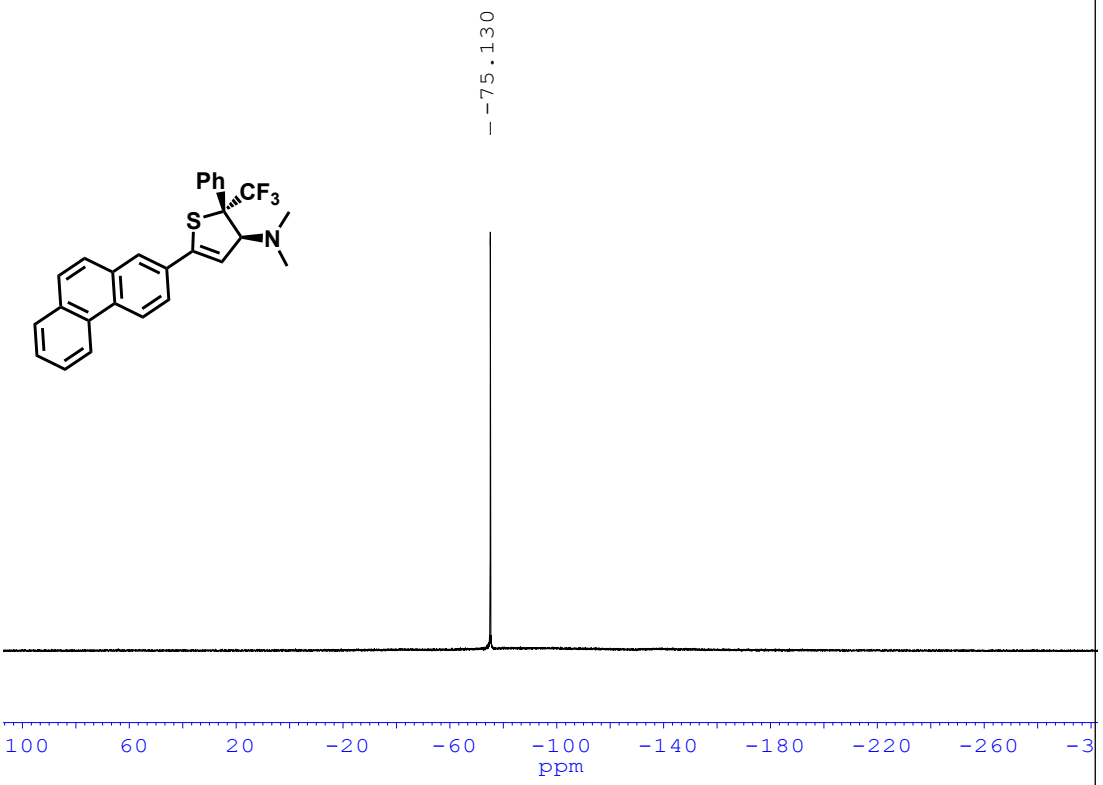
^{13}C NMR spectra of **3ao**



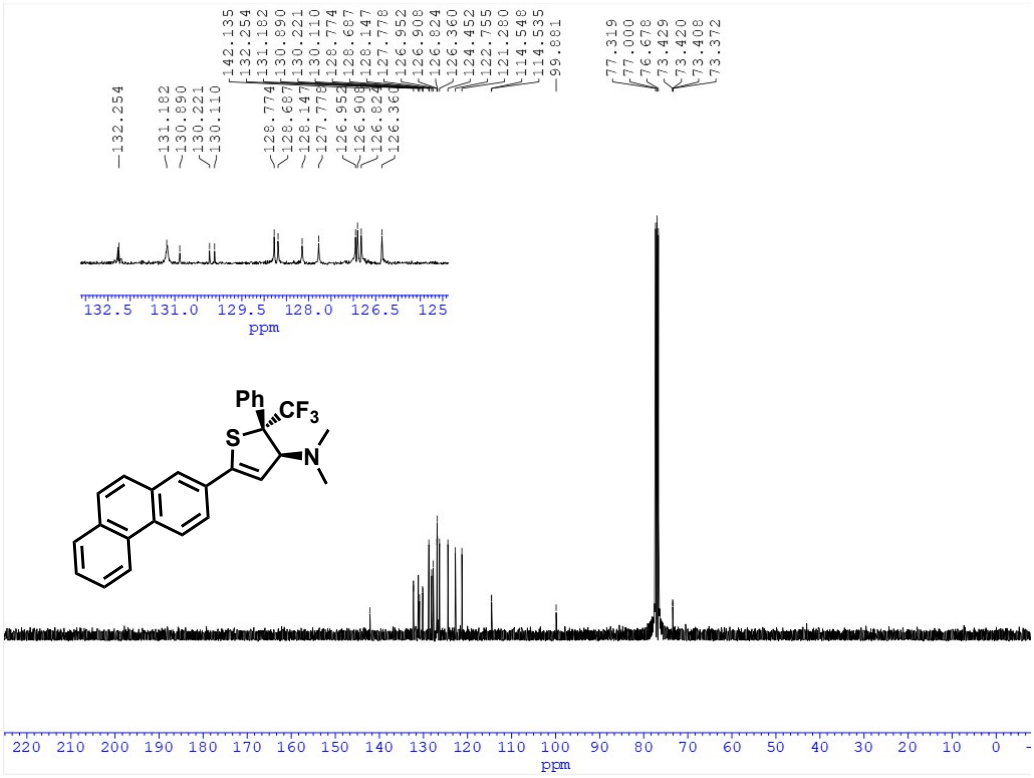
^{1}H NMR spectra of **3ap**



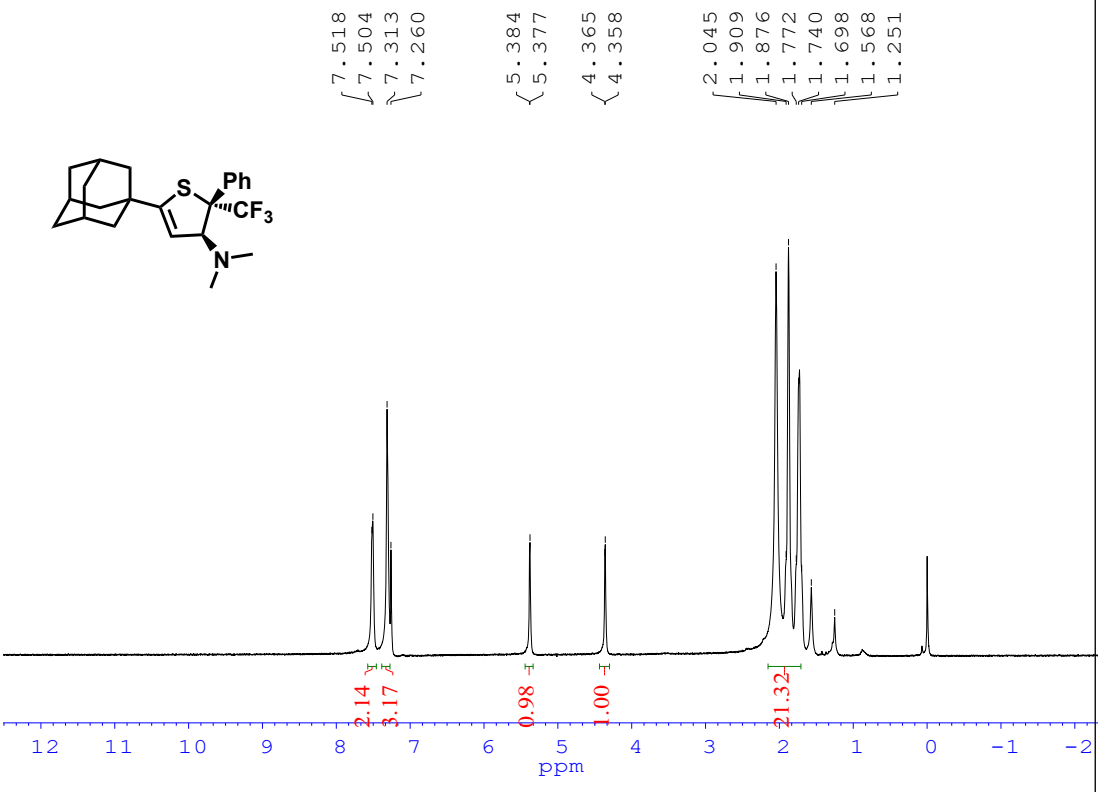
^{19}F NMR spectra of **3ap**



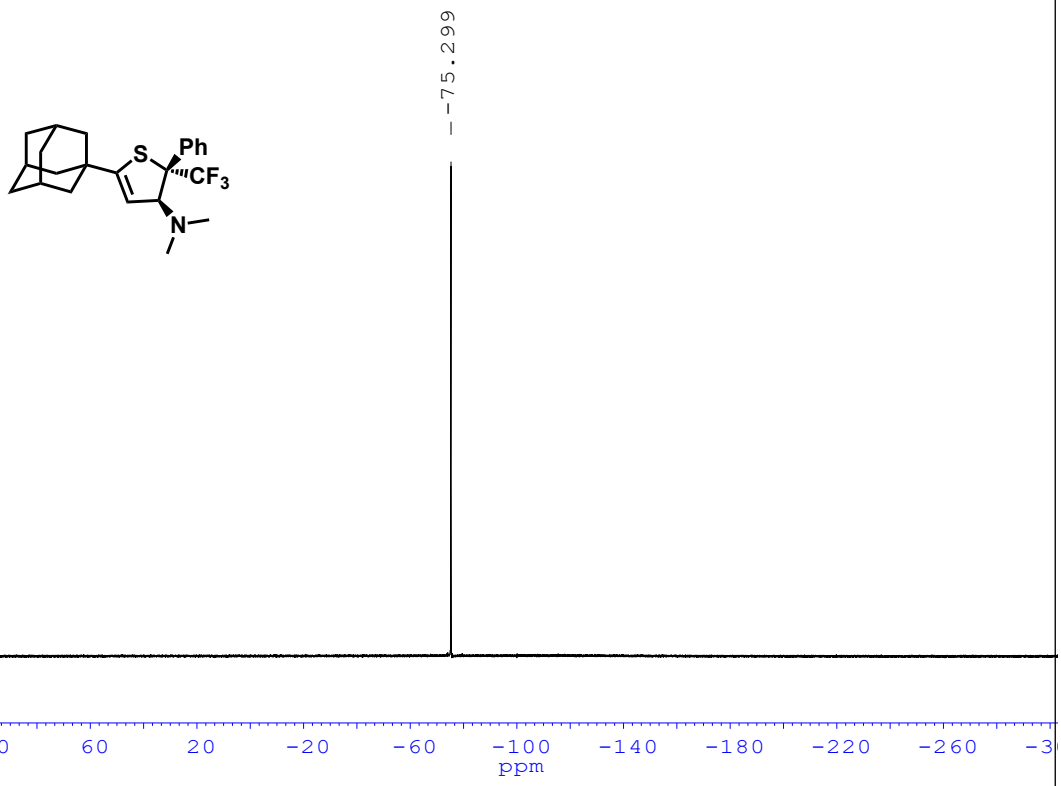
^{13}C NMR spectra of **3ap**



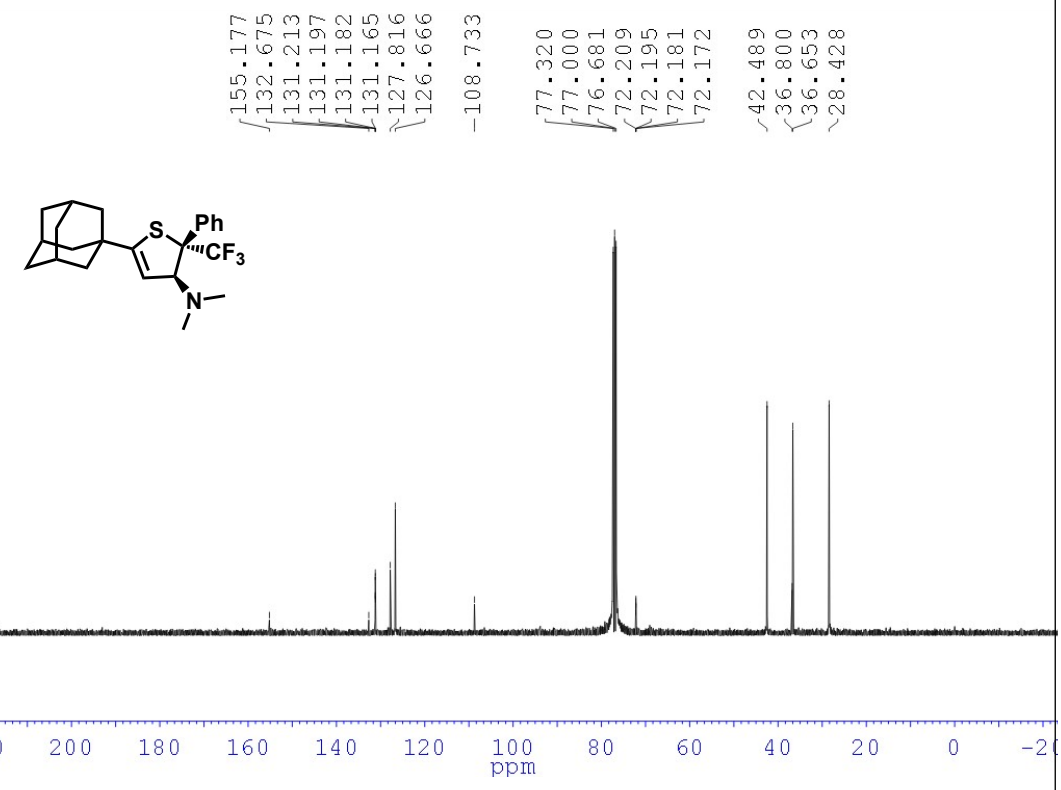
^{1}H NMR spectra of **3aq**



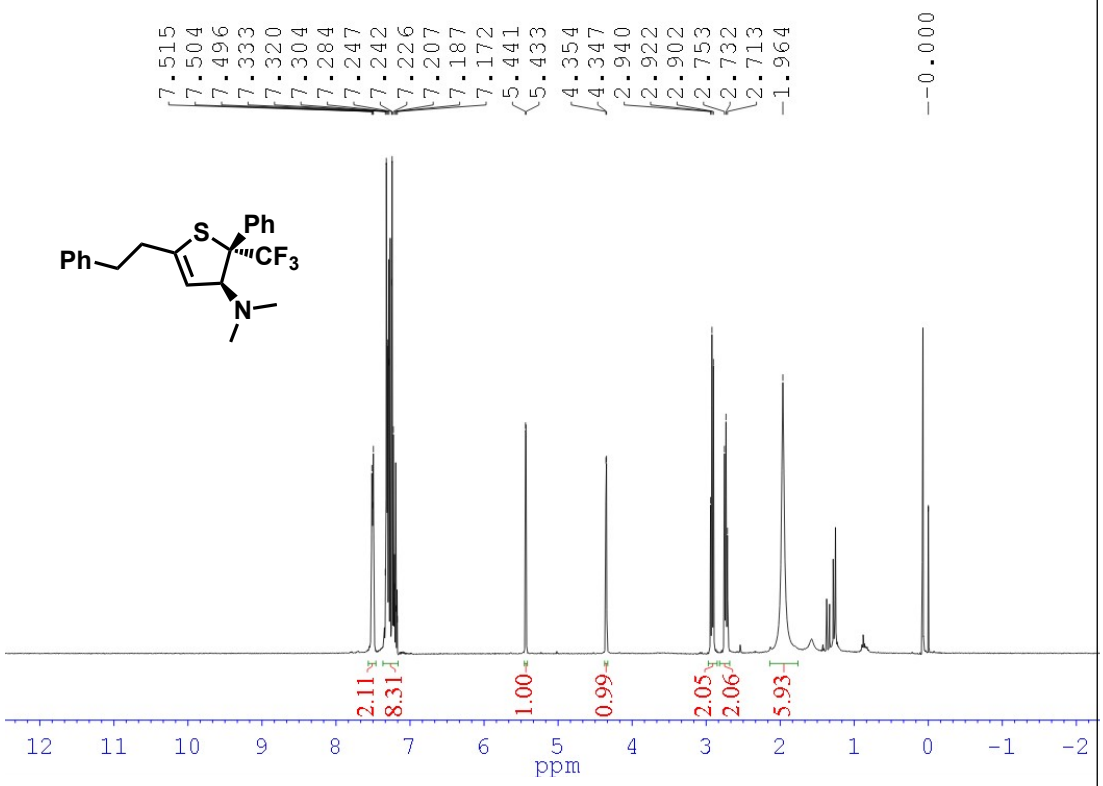
^{19}F NMR spectra of **3aq**



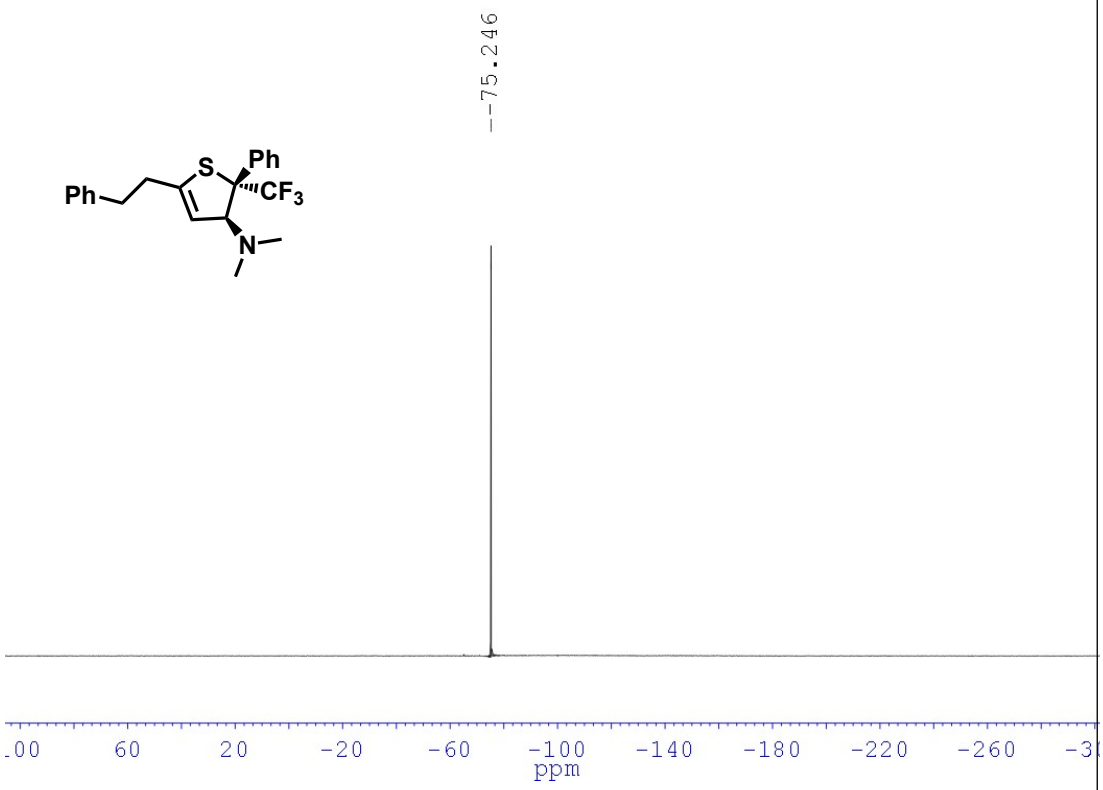
^{13}C NMR spectra of **3aq**



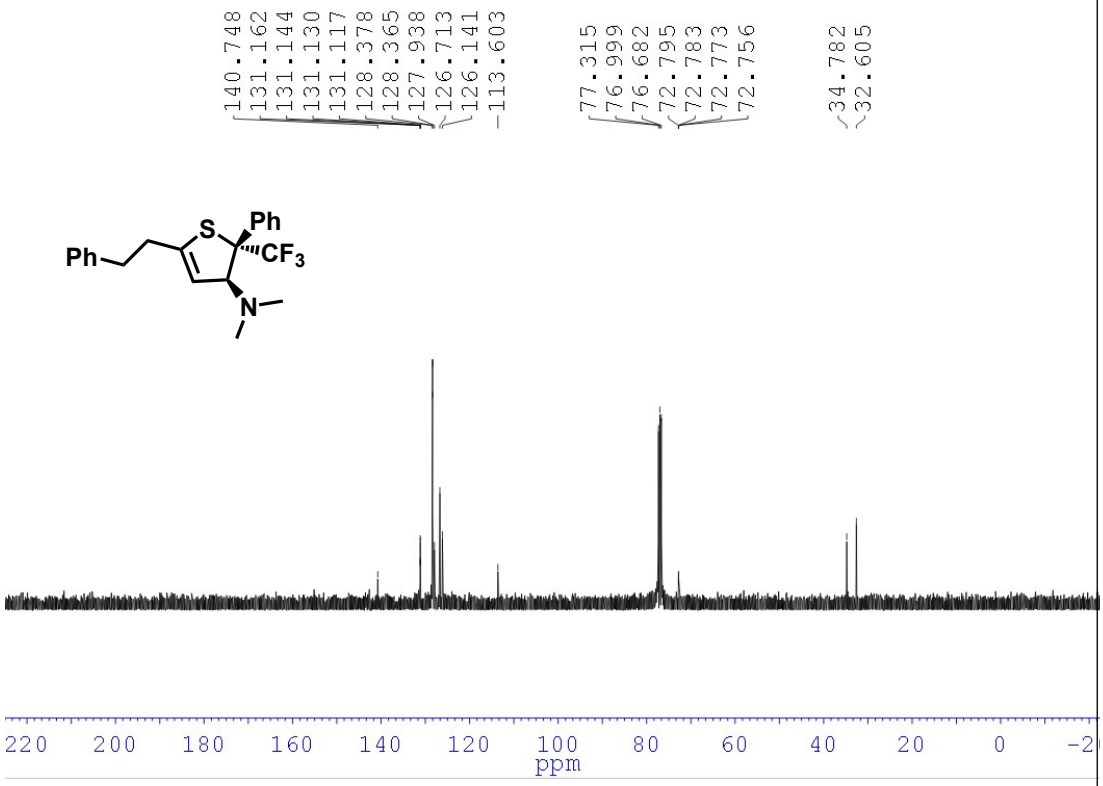
^{1}H NMR spectra of **3ar**



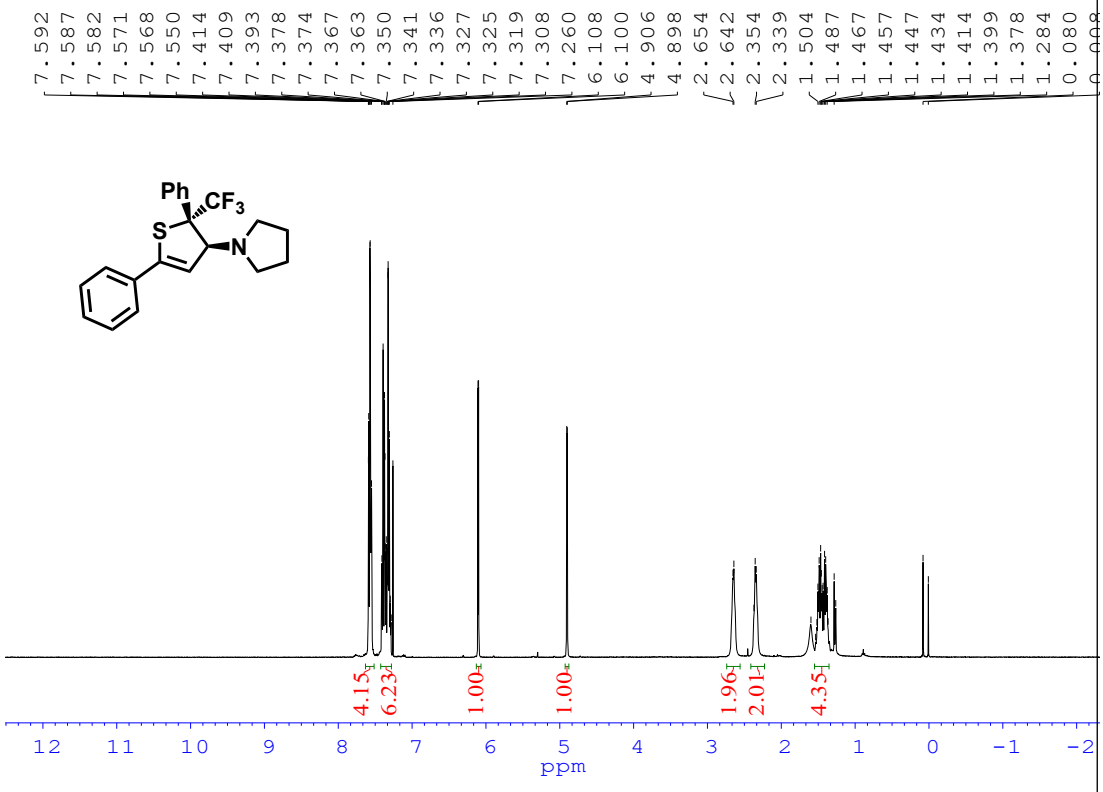
^{19}F NMR spectra of **3ar**



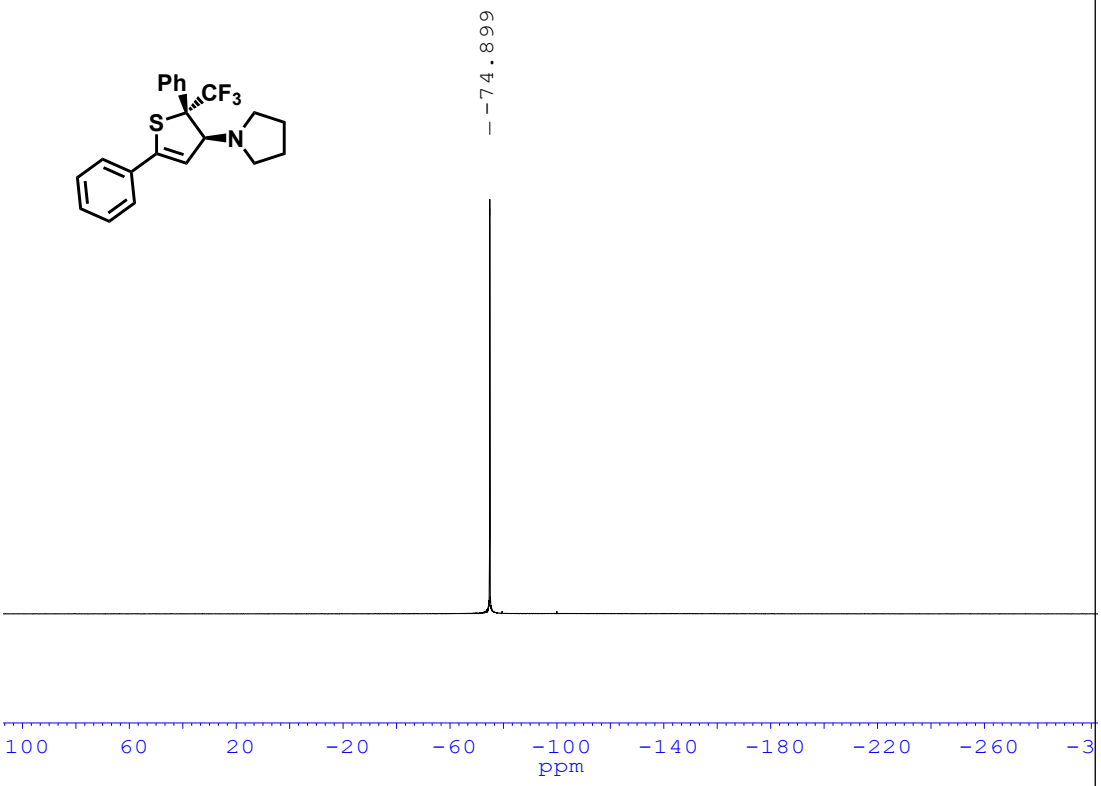
^{13}C NMR spectra of **3ar**



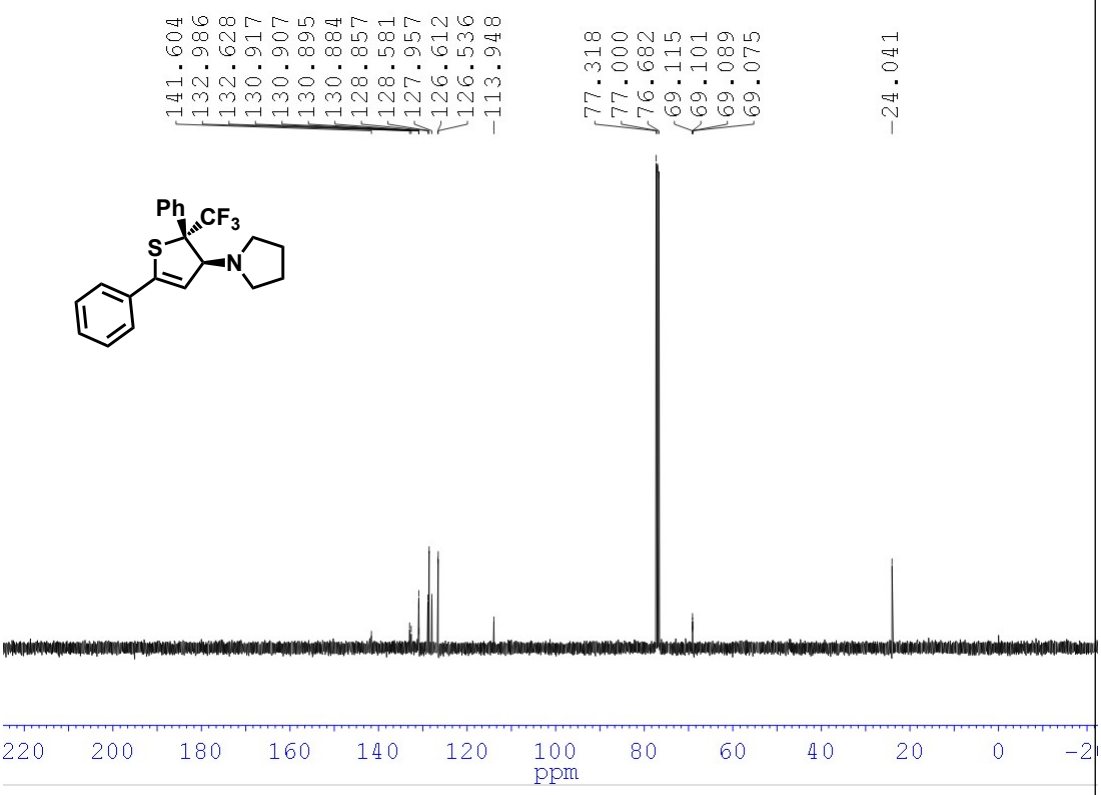
^{1}H NMR spectra of **3as**



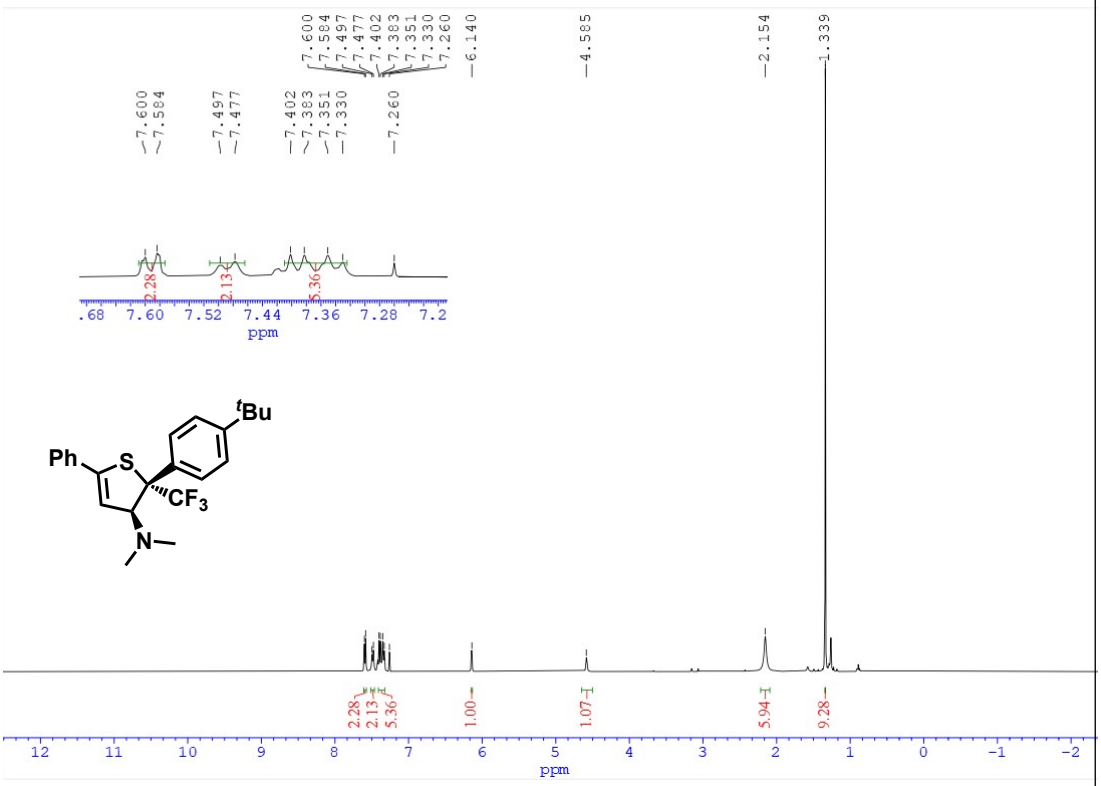
^{19}F NMR spectra of **3as**



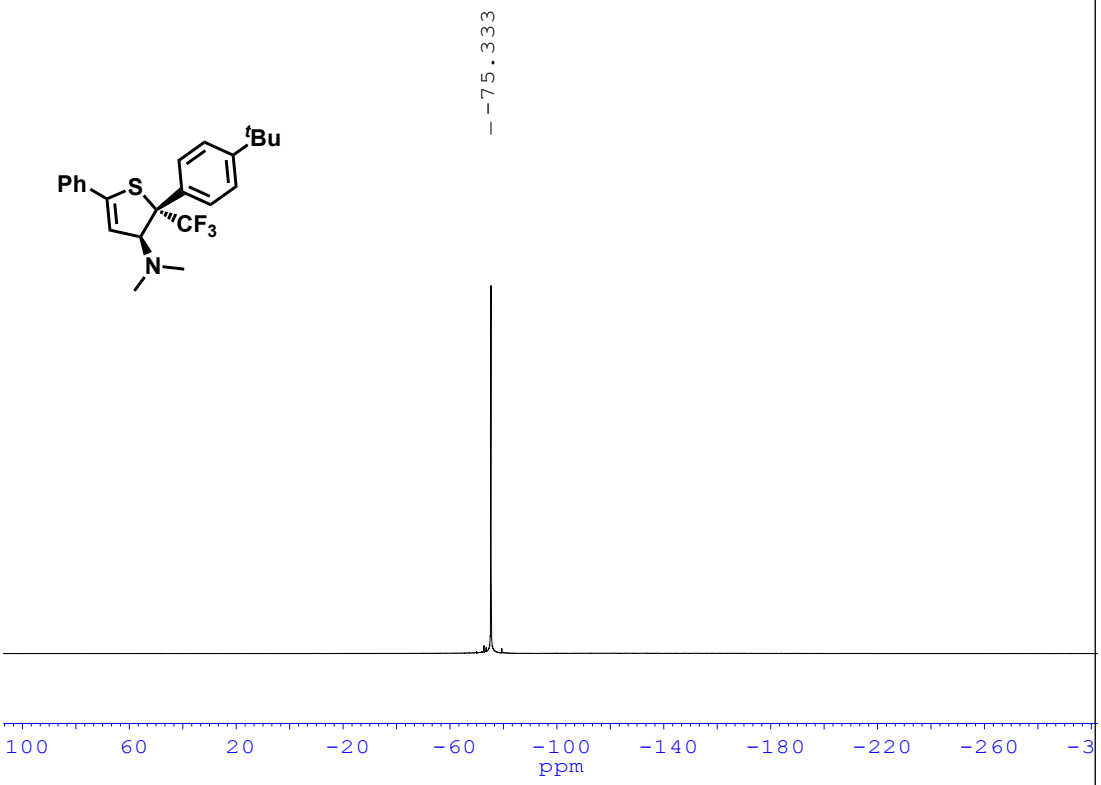
^{13}C NMR spectra of **3as**



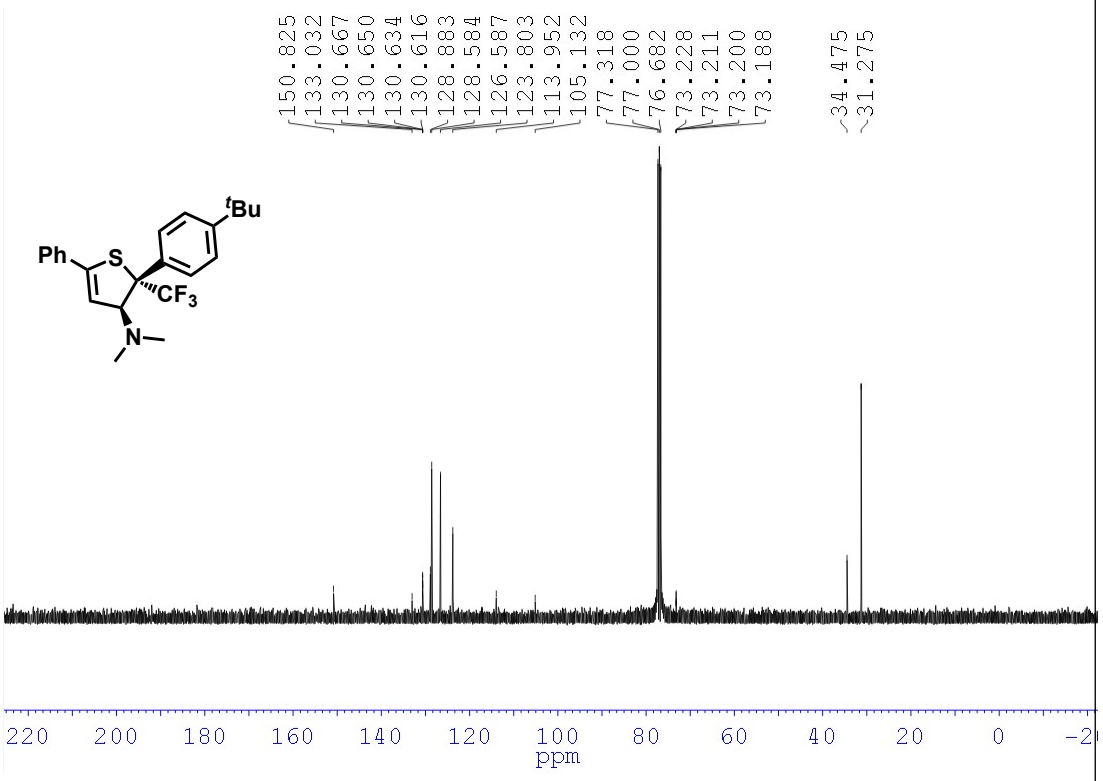
^{1}H NMR spectra of **3ba**



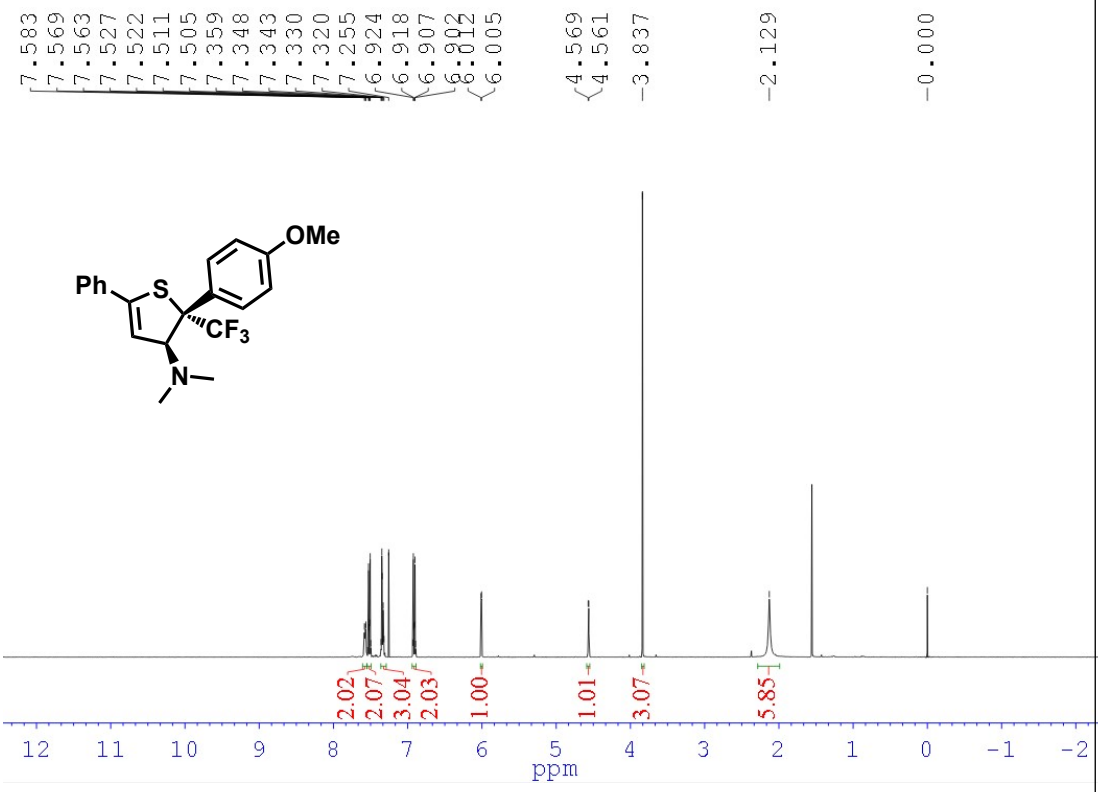
^{19}F NMR spectra of **3ba**



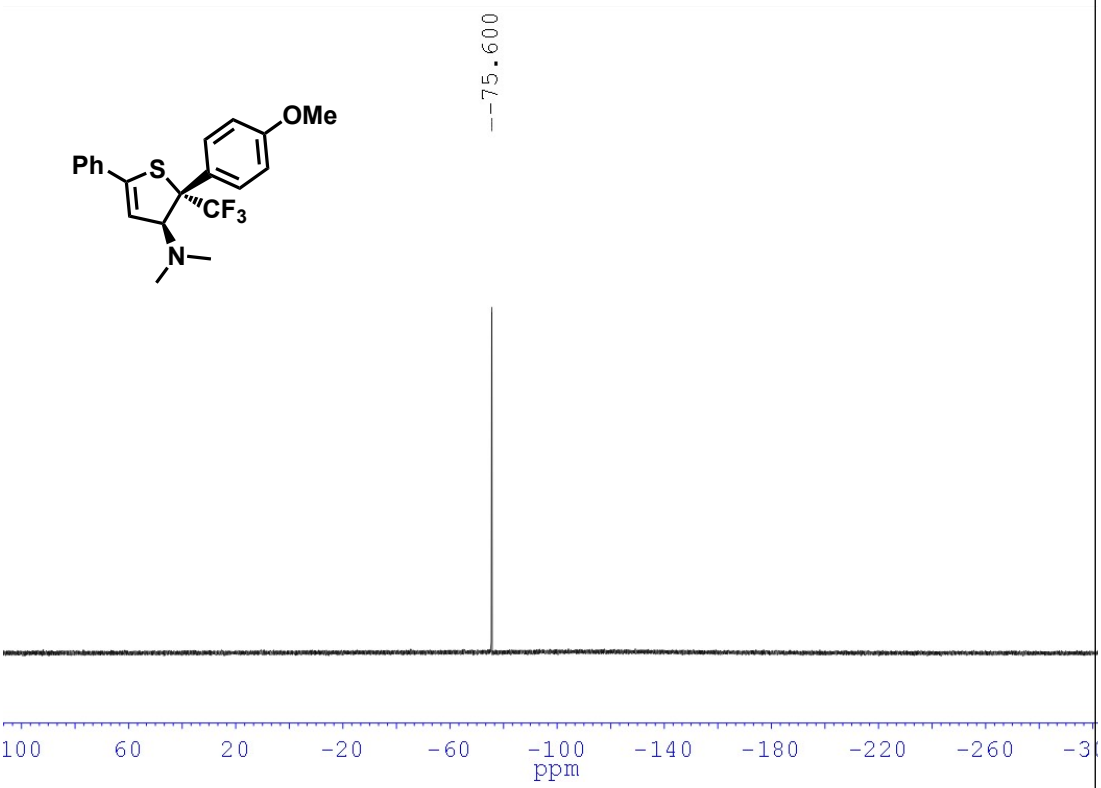
^{13}C NMR spectra of **3ba**



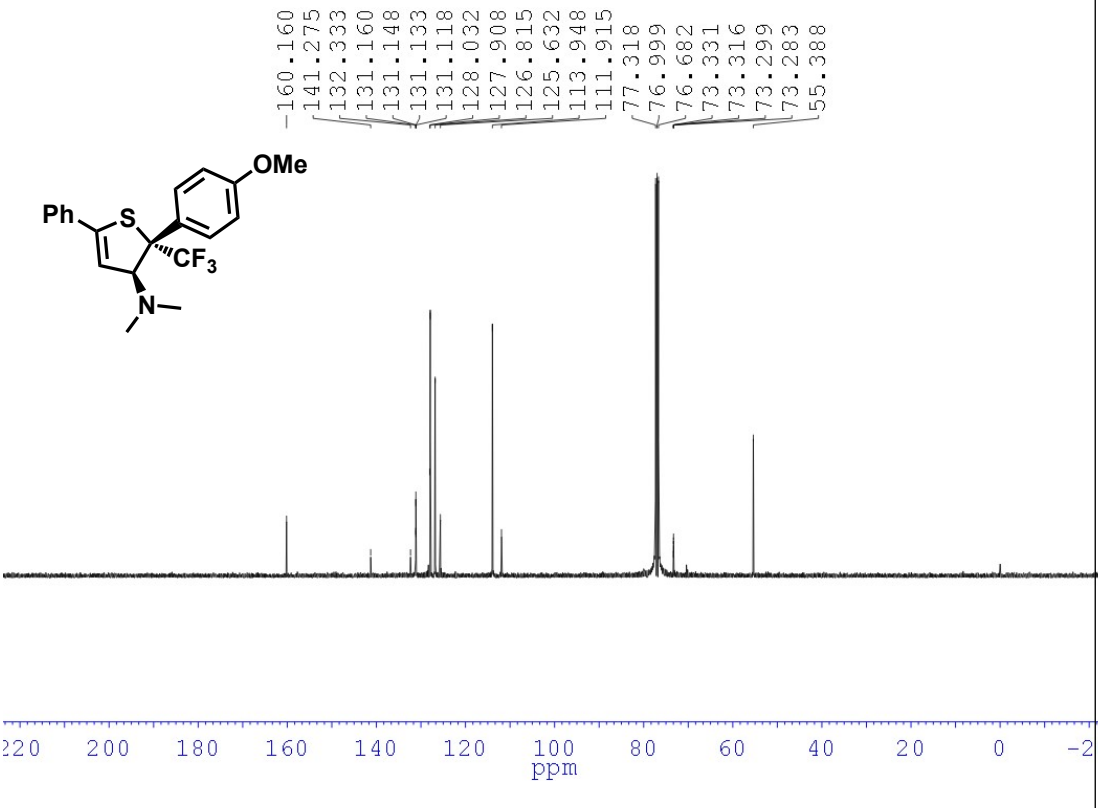
^{1}H NMR spectra of **3ca**



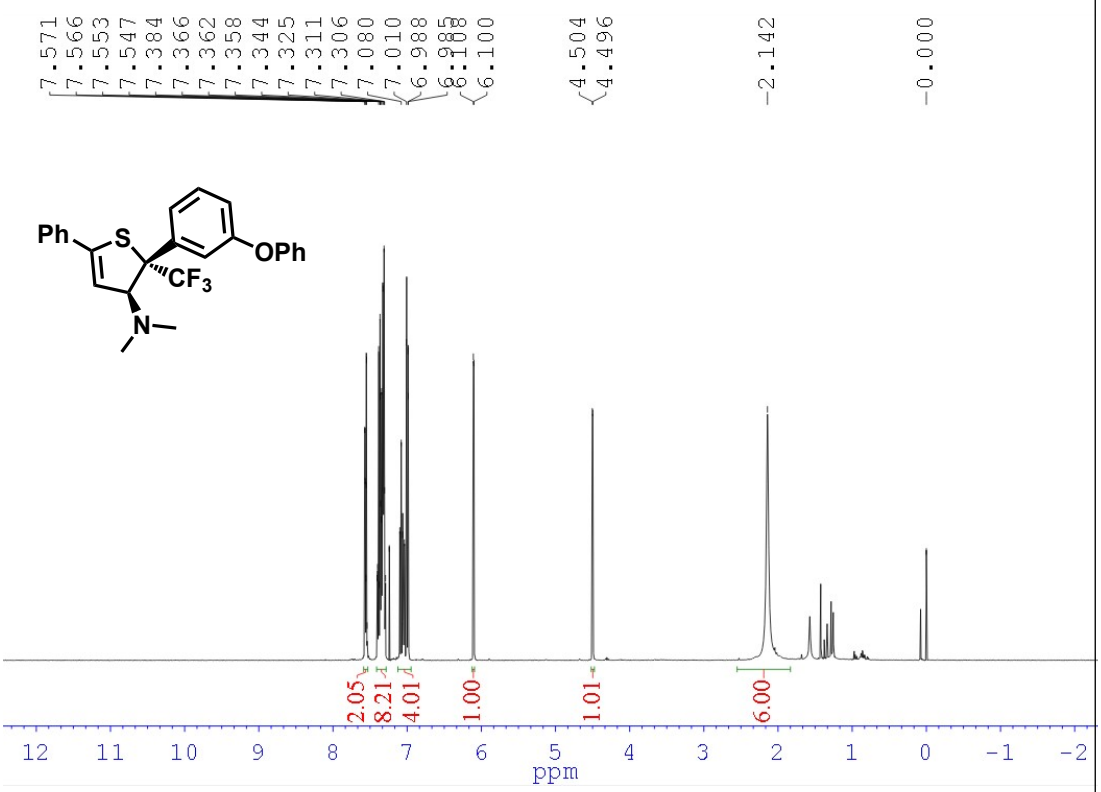
^{19}F NMR spectra of **3ca**



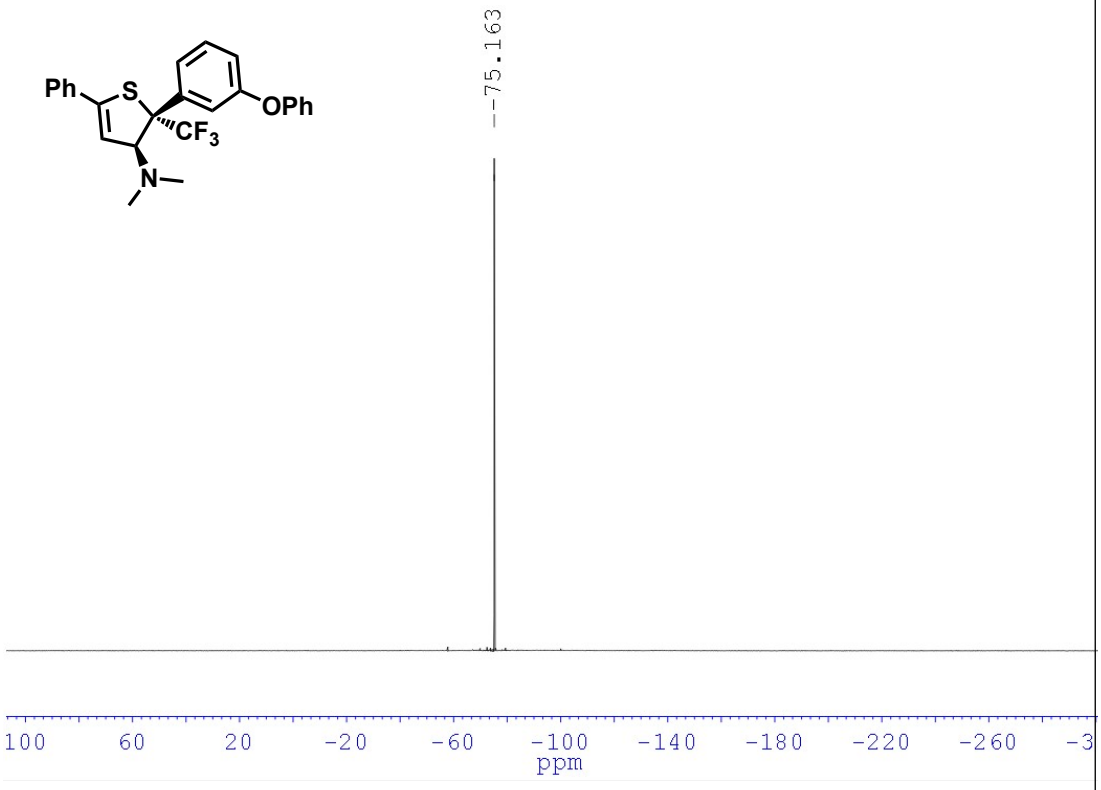
^{13}C NMR spectra of **3ca**



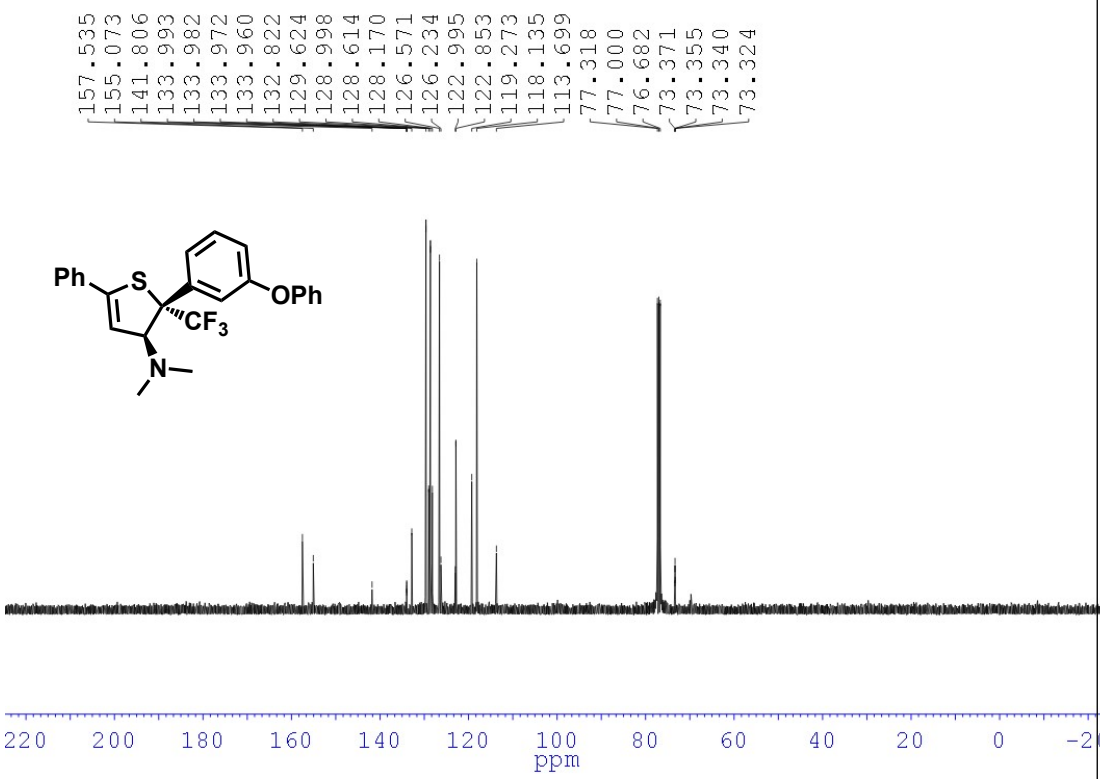
^{1}H NMR spectra of **3da**



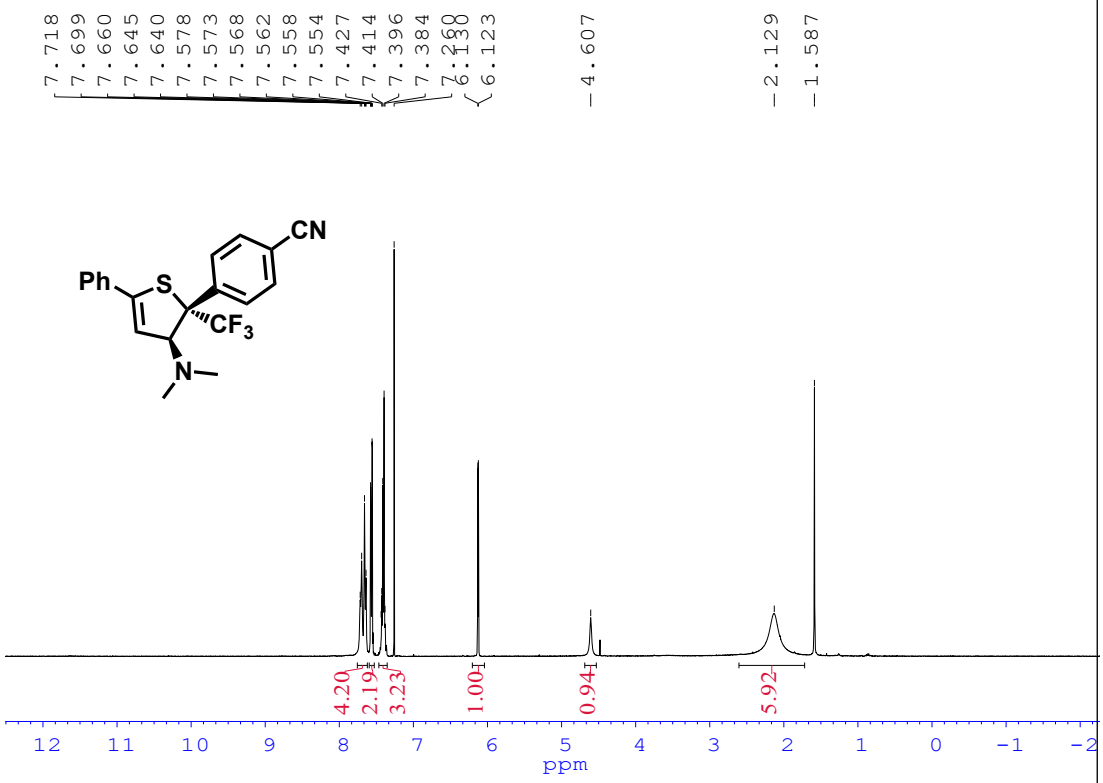
^{19}F NMR spectra of **3da**



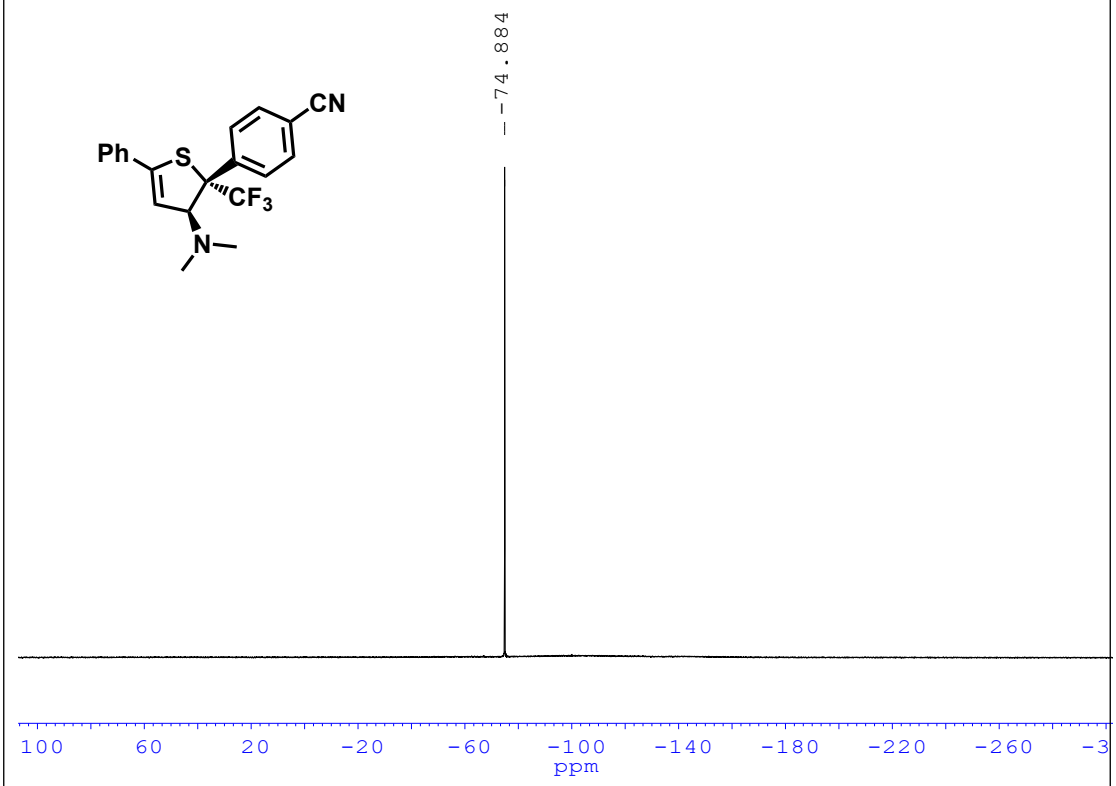
^{13}C NMR spectra of **3da**



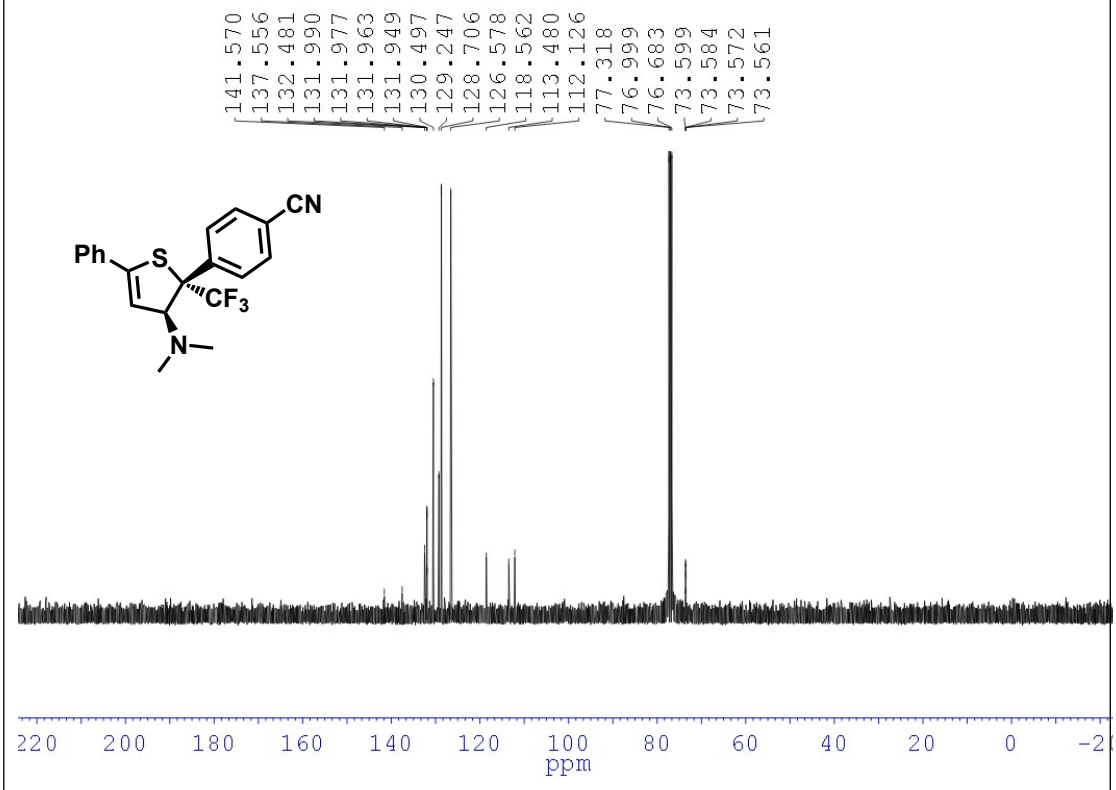
^{1}H NMR spectra of **3ea**



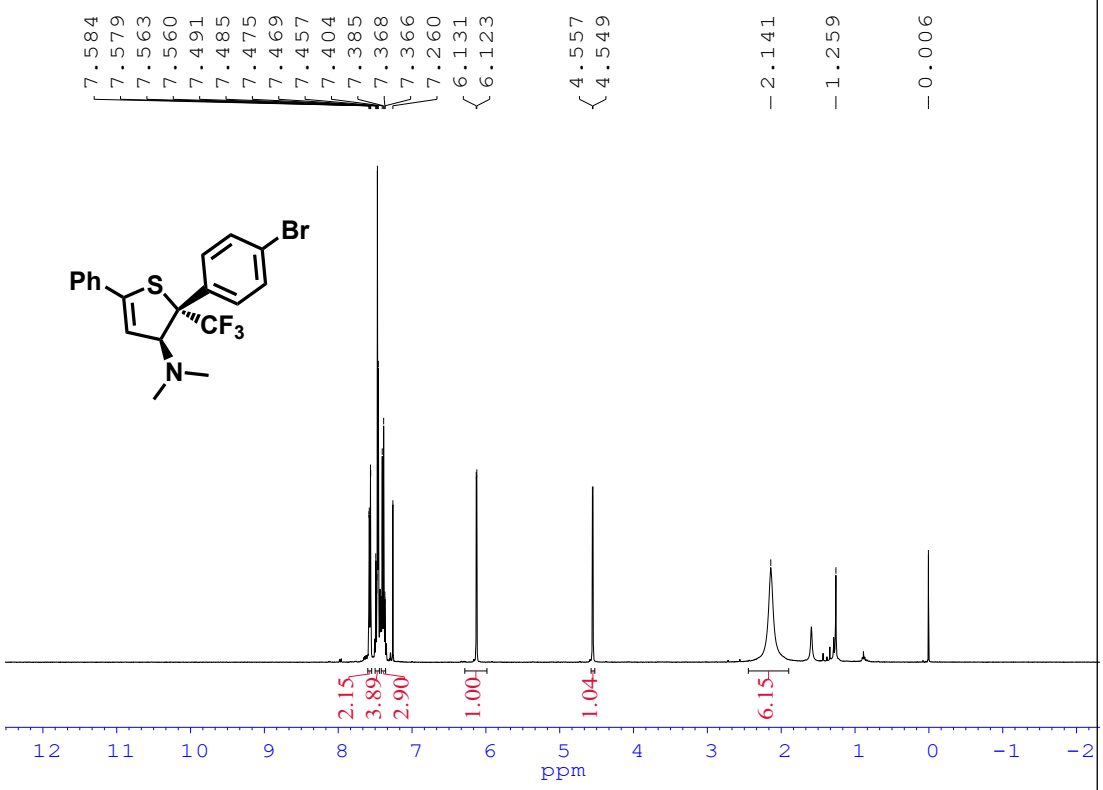
^{19}F NMR spectra of **3ea**



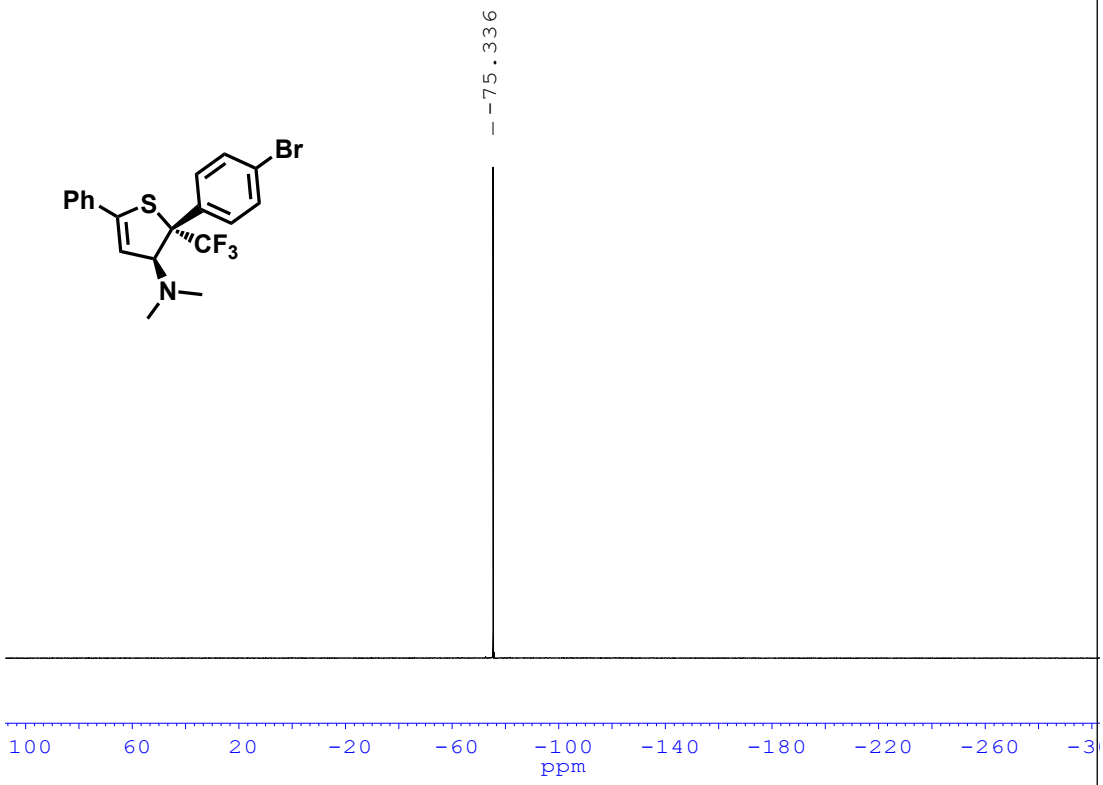
^{13}C NMR spectra of **3ea**



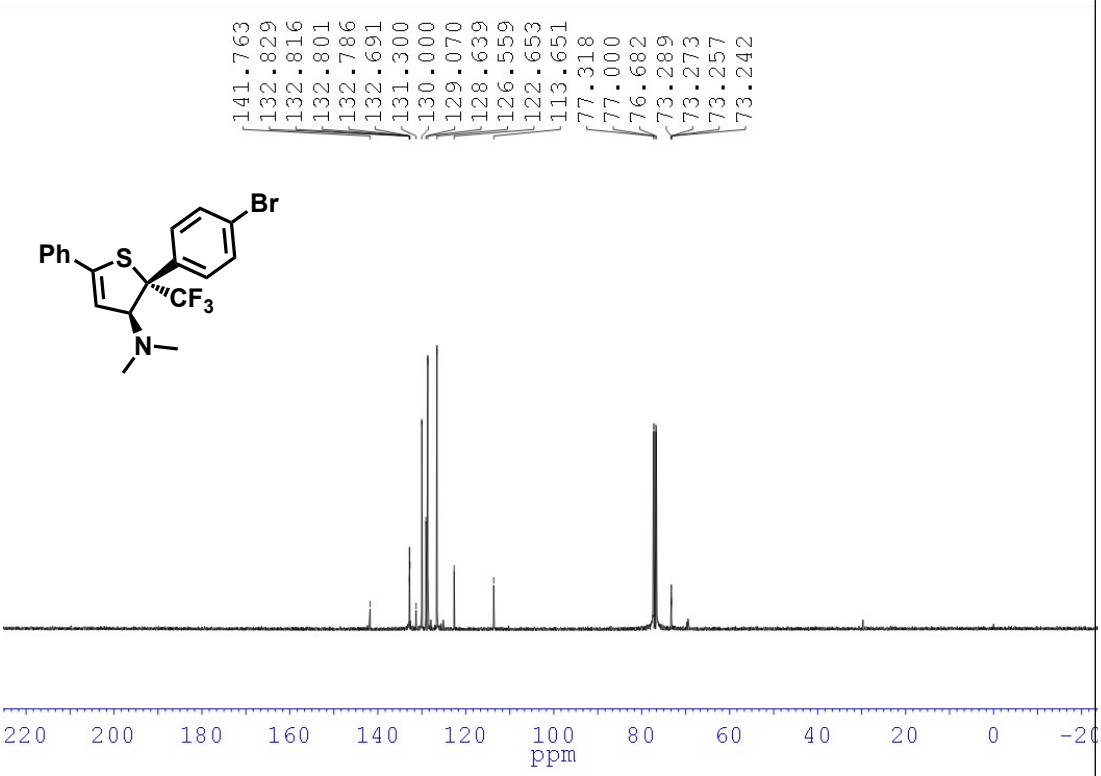
^{1}H NMR spectra of **3fa**



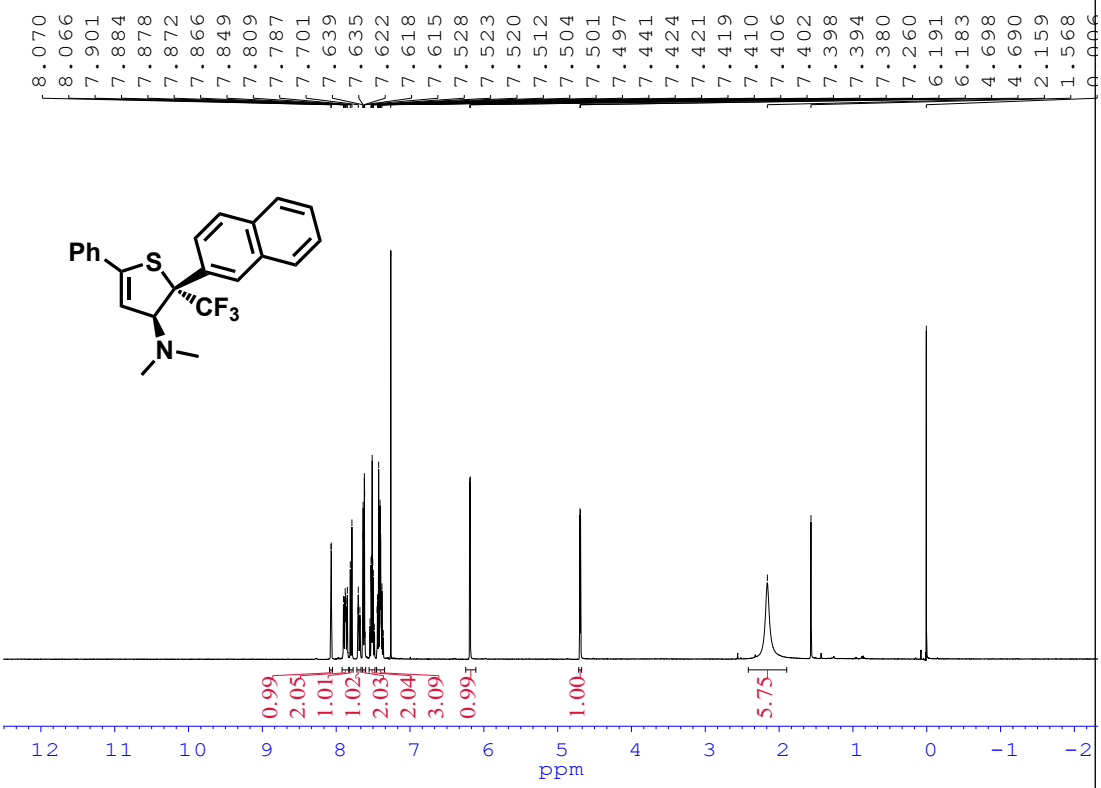
^{19}F NMR spectra of **3fa**



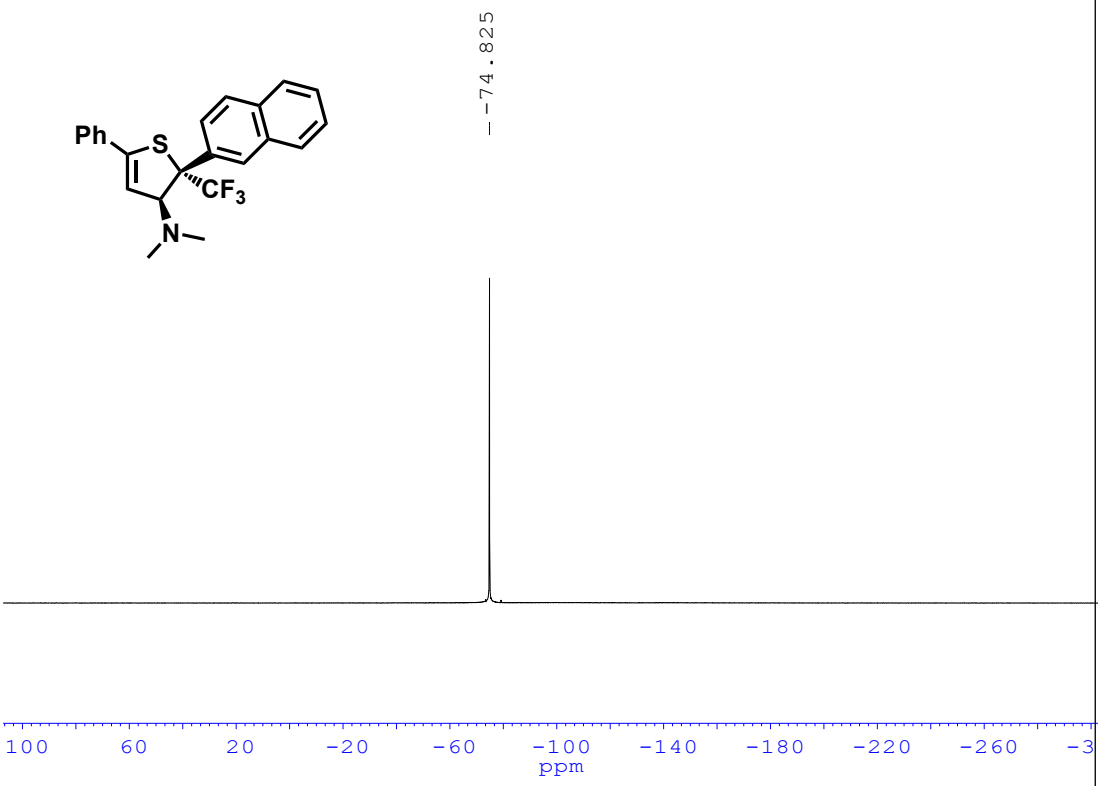
^{13}C NMR spectra of **3fa**



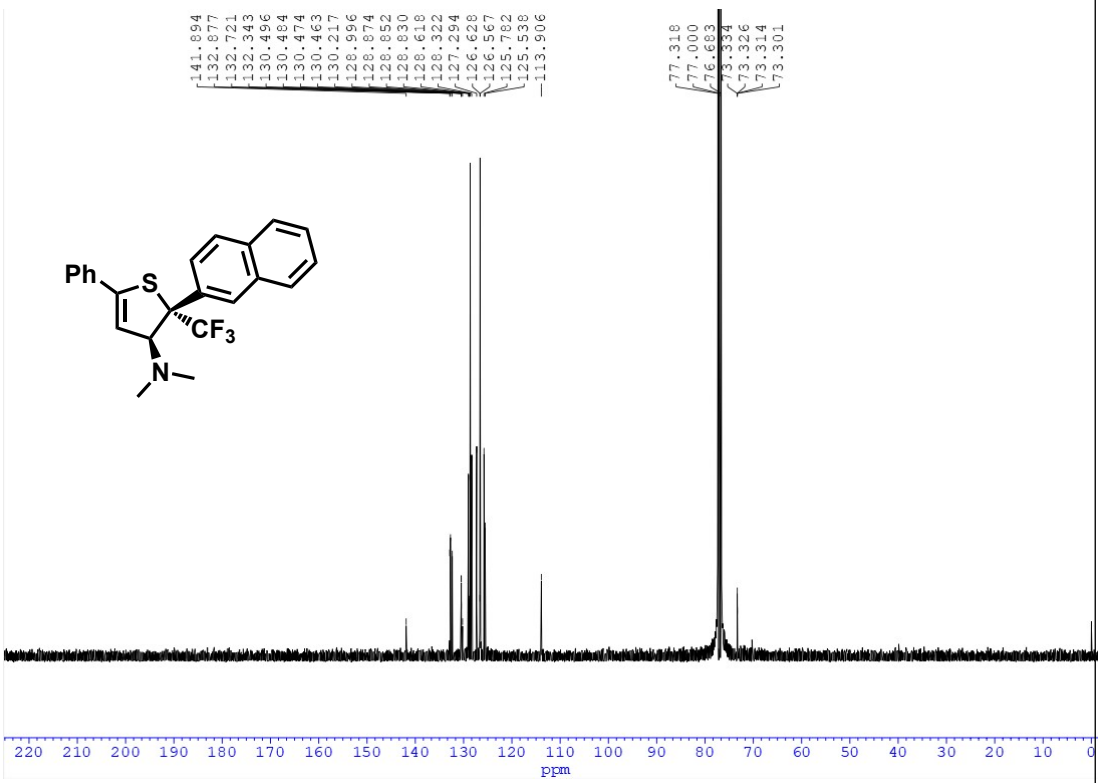
^{1}H NMR spectra of **3ga**



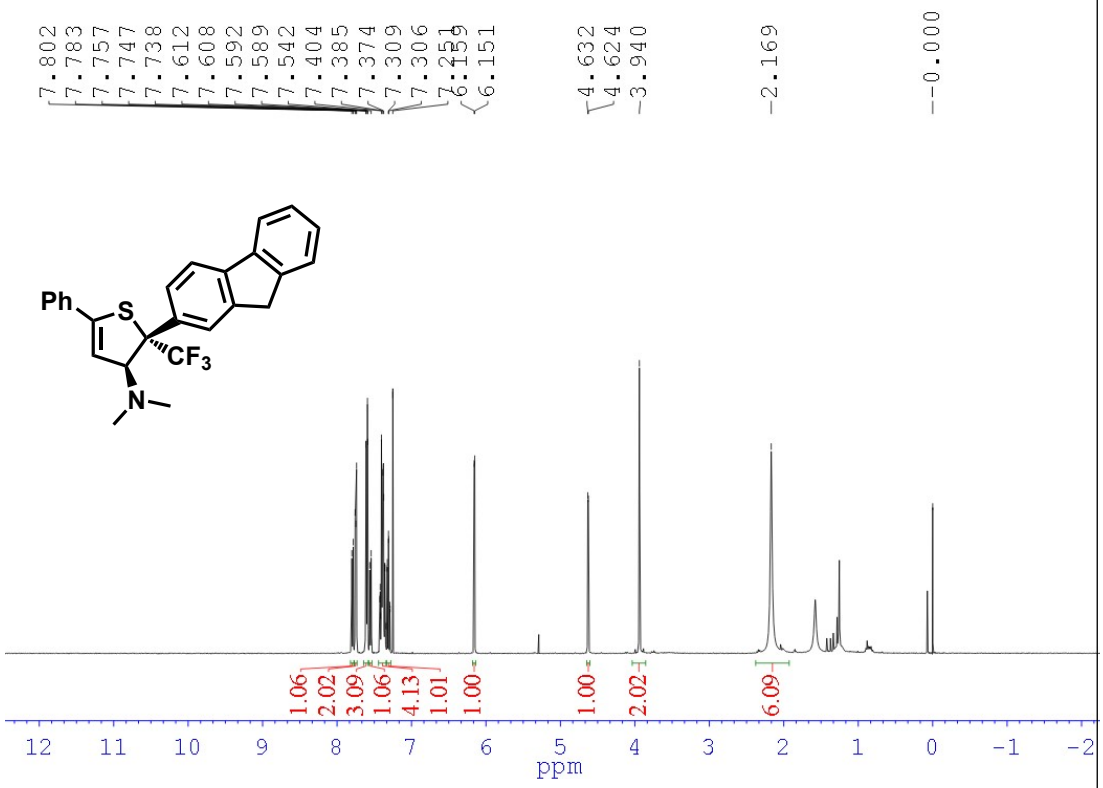
^{19}F NMR spectra of **3ga**



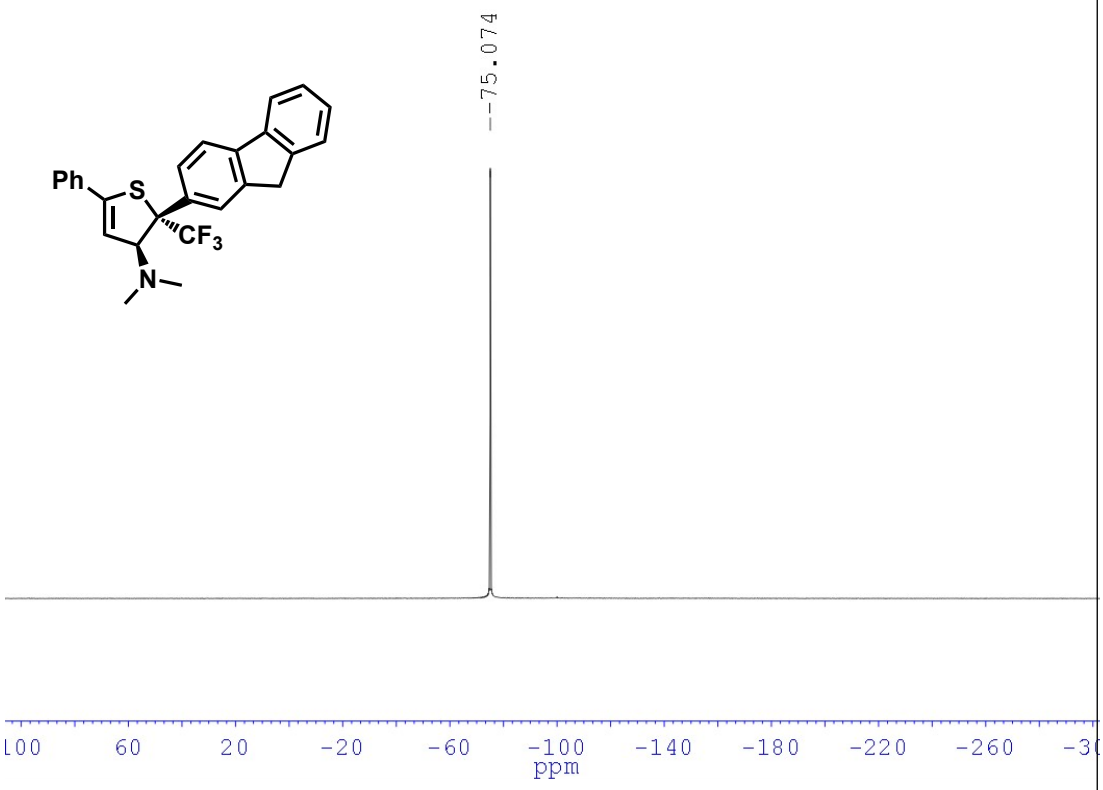
^{13}C NMR spectra of **3ga**



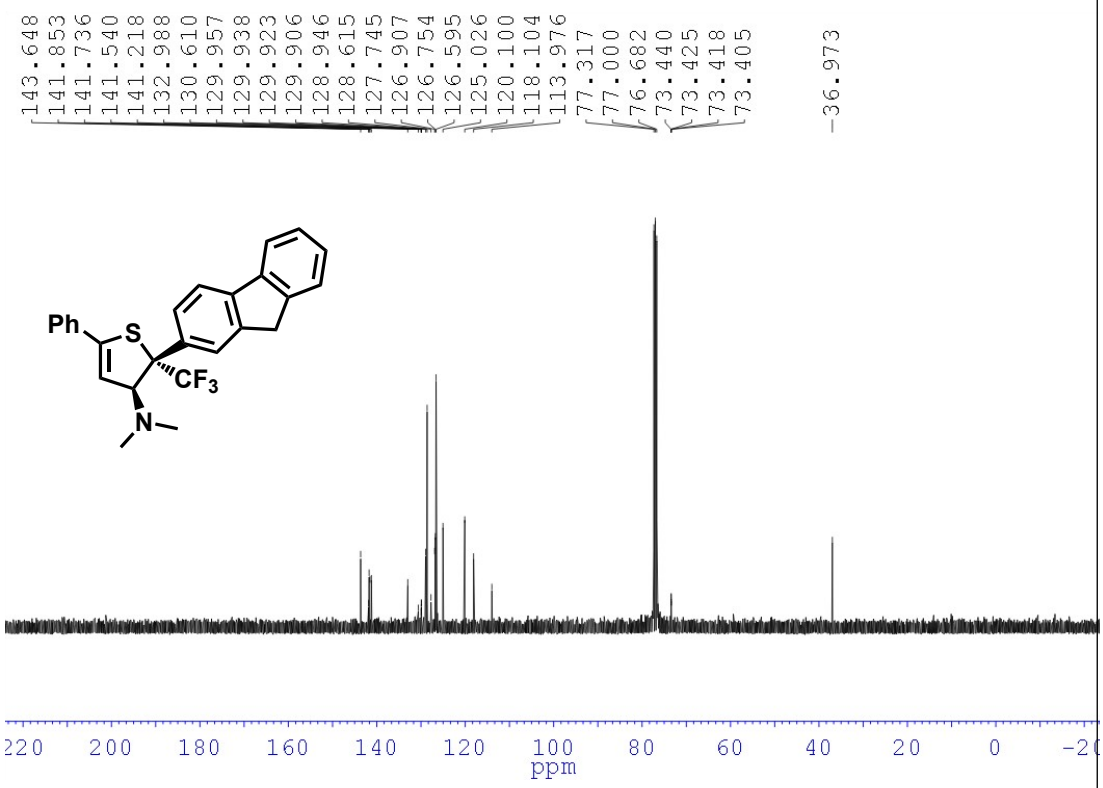
^{1}H NMR spectra of **3ha**



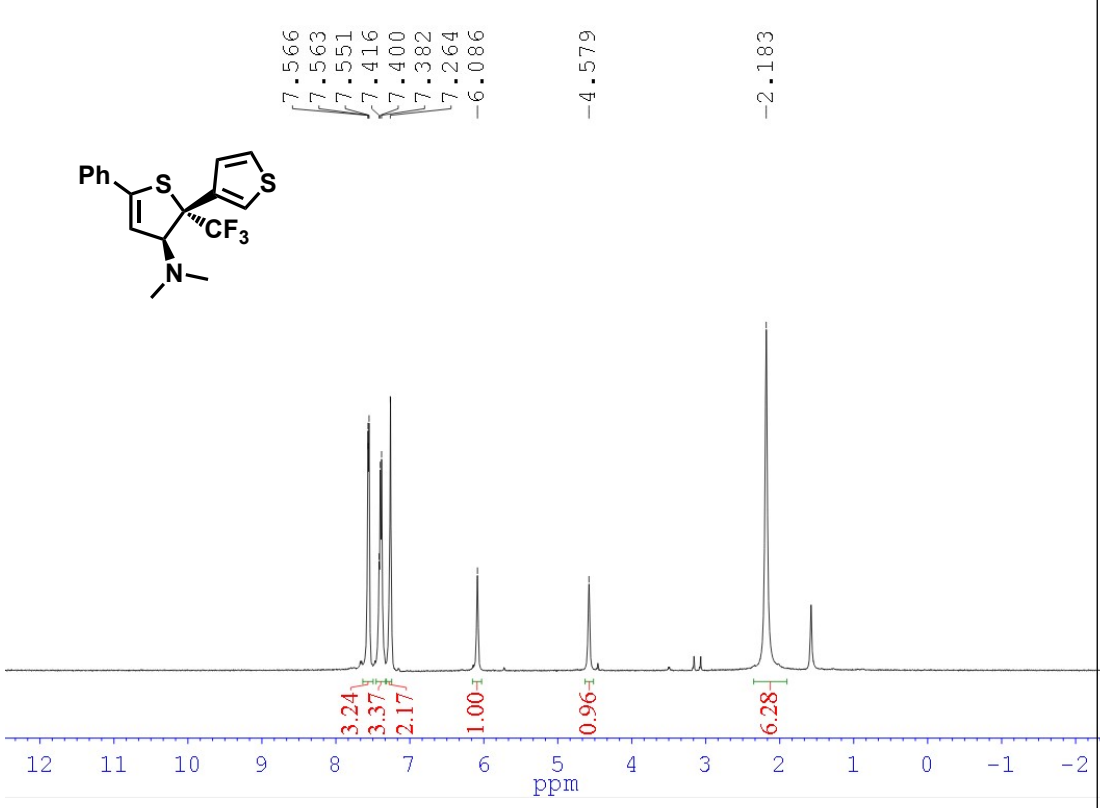
^{19}F NMR spectra of **3ha**



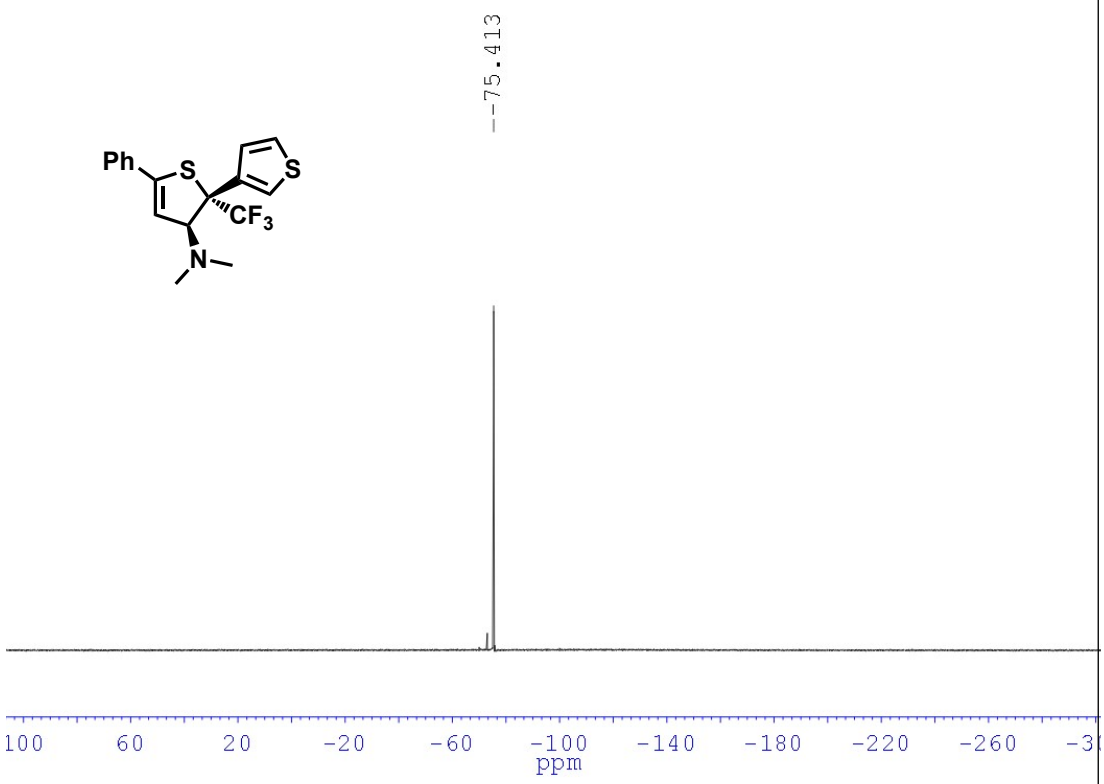
^{13}C NMR spectra of **3ha**



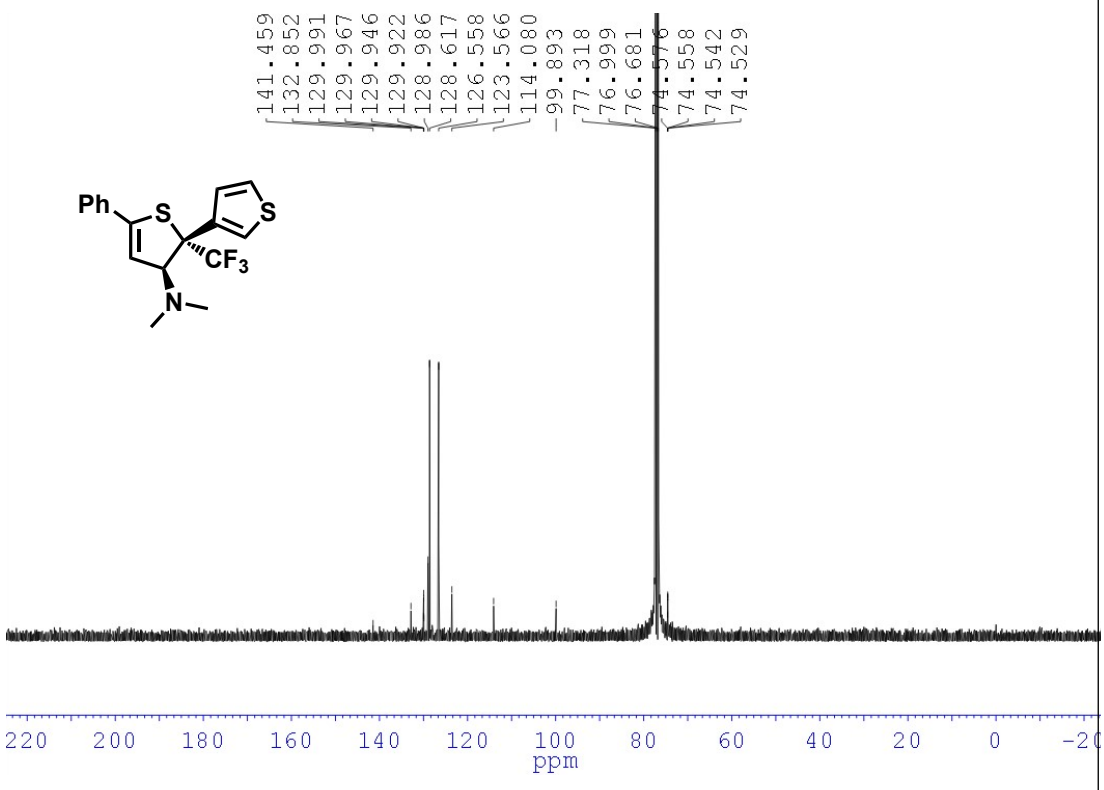
^{1}H NMR spectra of **3ia**



^{19}F NMR spectra of **3ia**

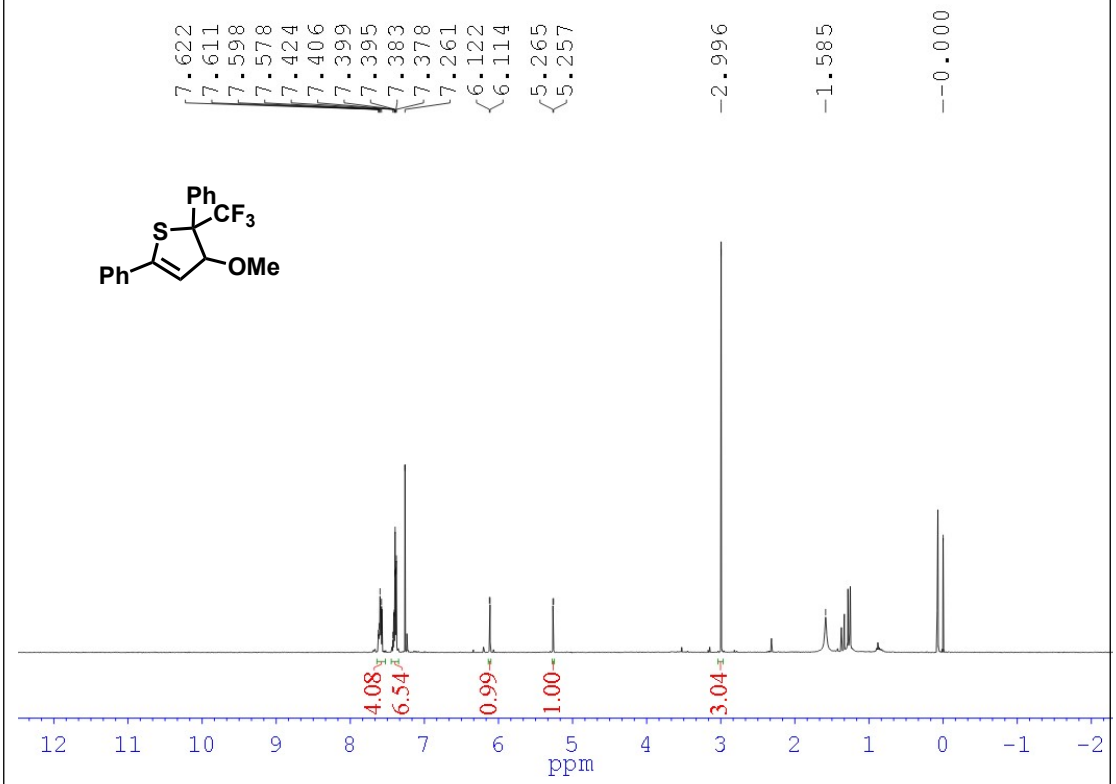


^{13}C NMR spectra of **3ia**

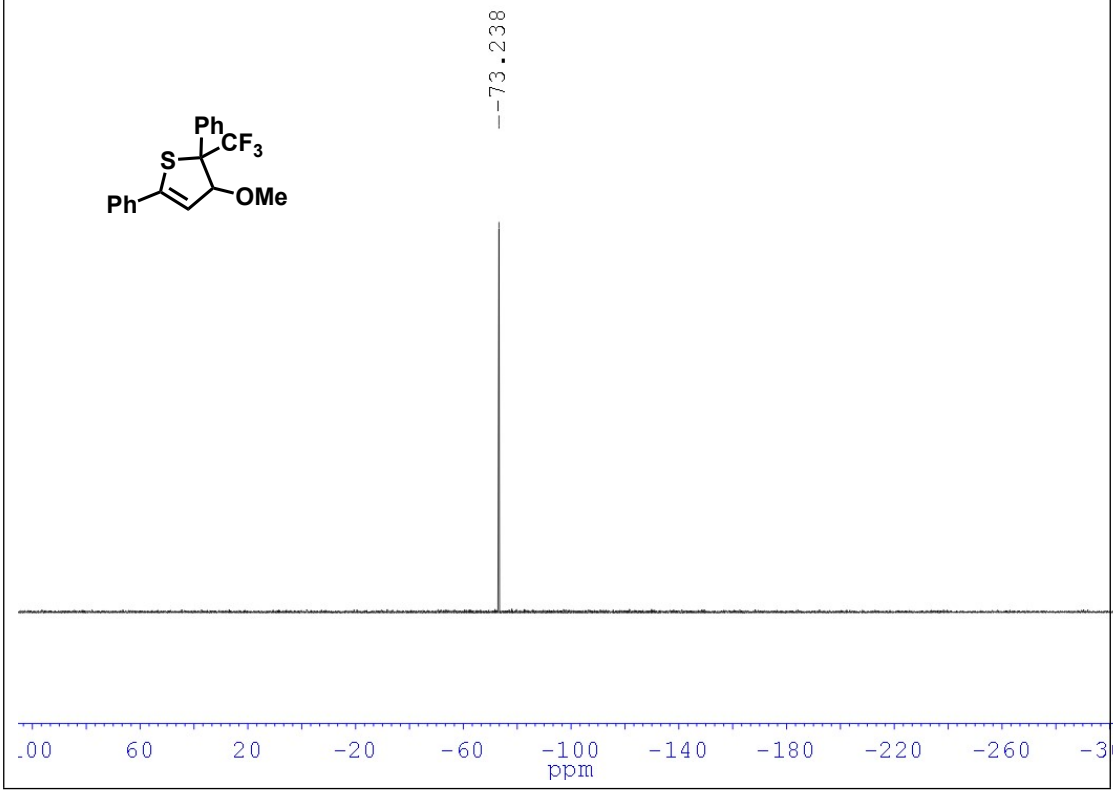


4.4 NMR spectra for derivative products:

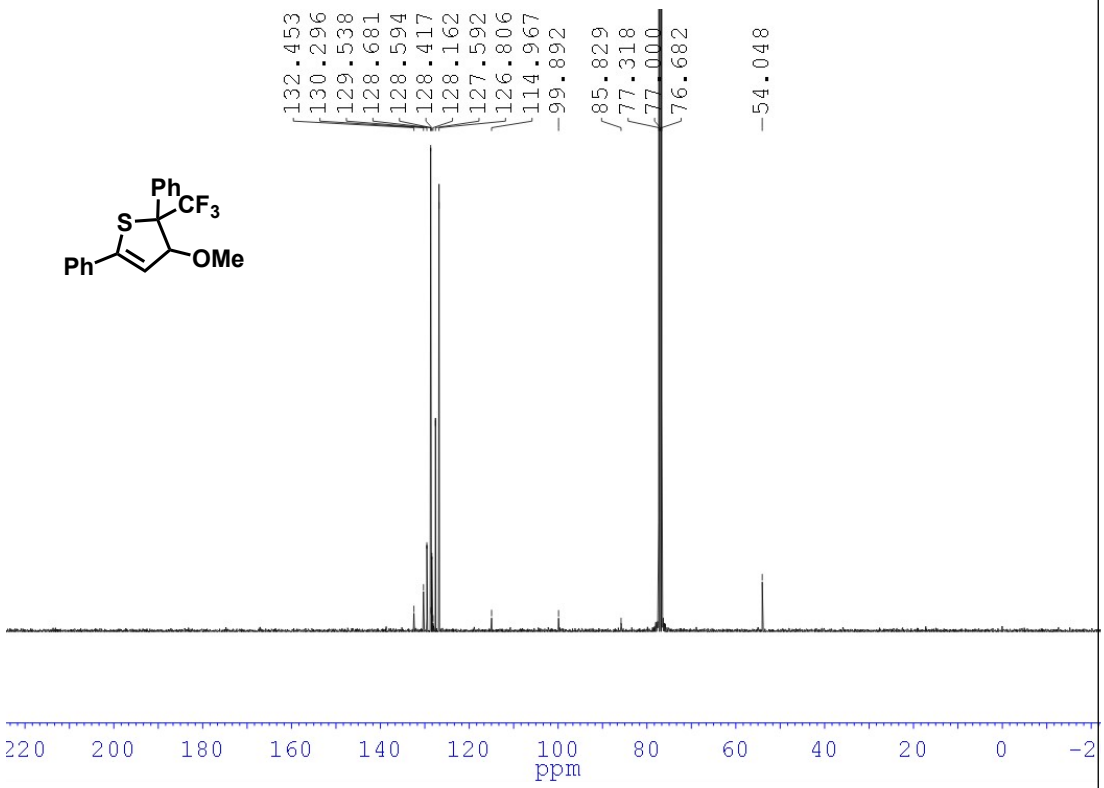
^{1}H NMR spectra of **4**



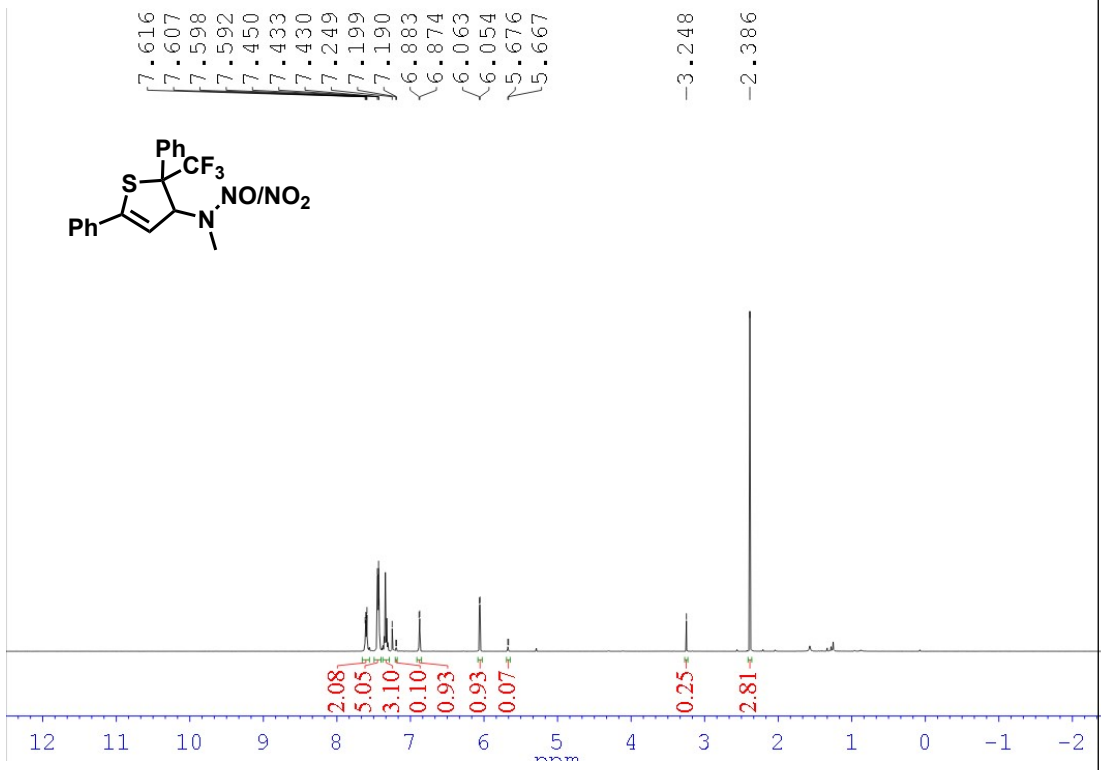
^{19}F NMR spectra of **4**



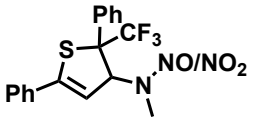
^{13}C NMR spectra of **4**

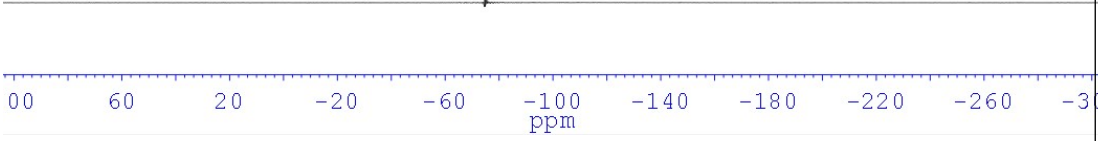


^{1}H NMR spectra of **5**

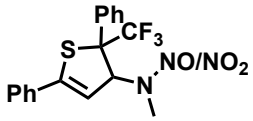


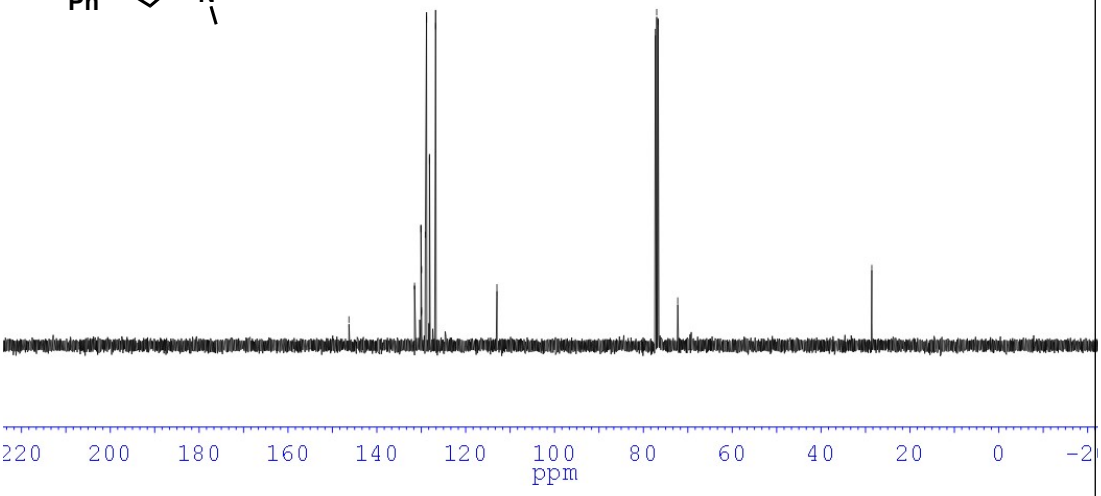
^{19}F NMR spectra of **5**



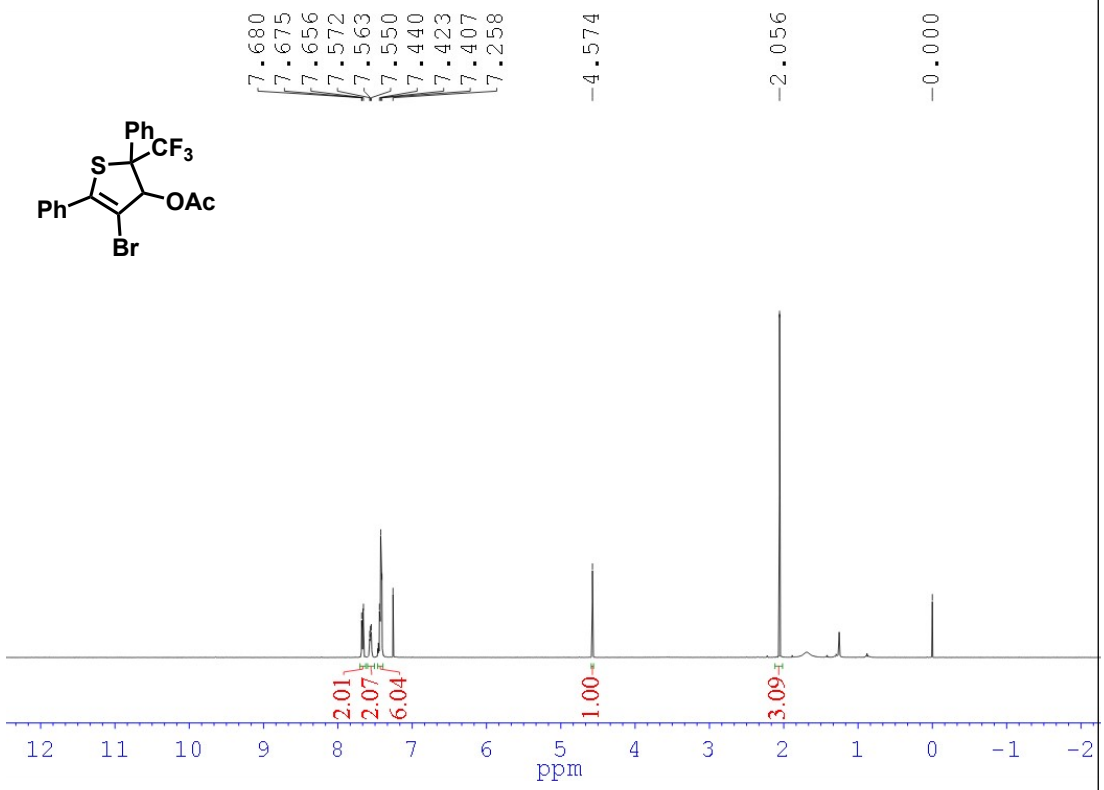


^{13}C NMR spectra of **5**

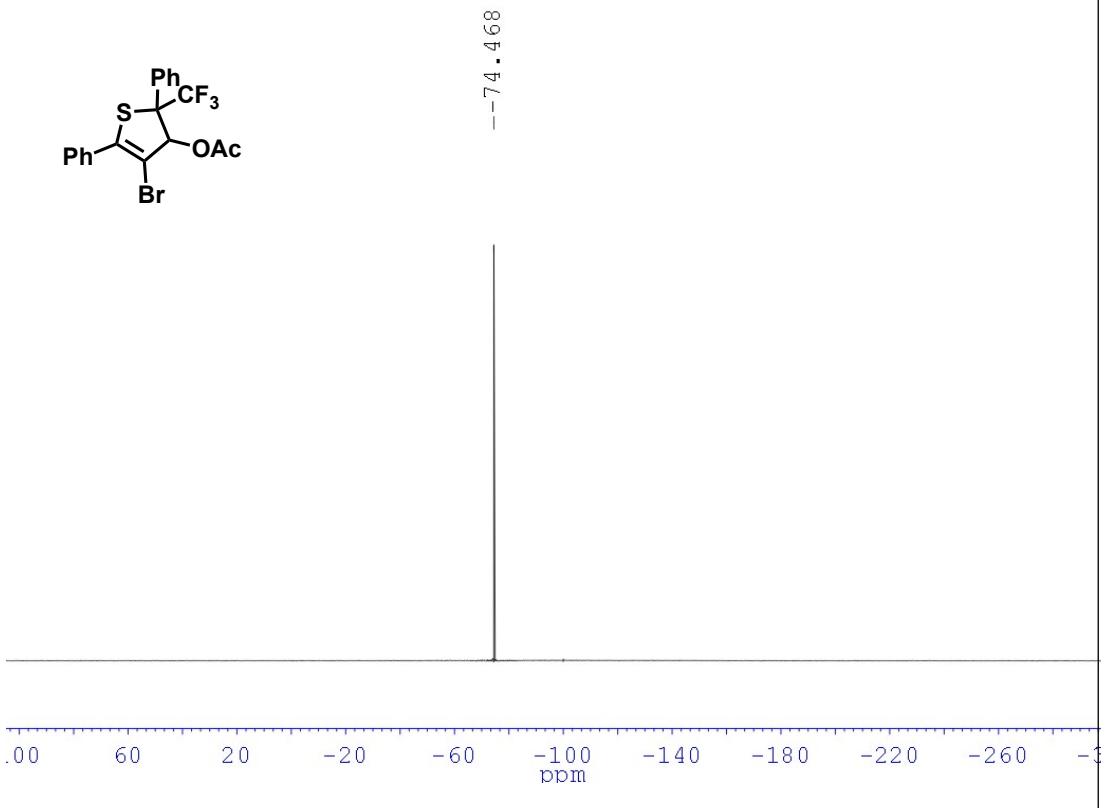




^{1}H NMR spectra of **6**



^{19}F NMR spectra of **6**



^{13}C NMR spectra of **6**