Supporting Information

for

Direct Thiocyanation of Ketene Dithioacetals under Transition-metal-free Conditions

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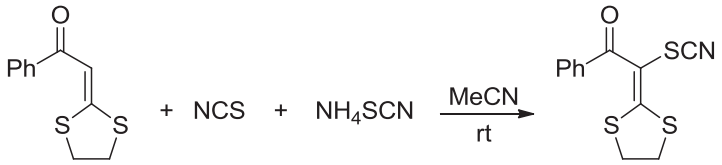
1. General Methods

All commercially available reagents were used without further purification unless otherwise stated. All solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC). Column chromatography purifications were carried out using silica gel GF254. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian instrument (300 MHz, 75 MHz and 282 MHz, respectively). Data are presented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet) and coupling constant in Hertz (Hz). HRMS (ESI) was measured with a maXis 4G mass spectrometer.

Starting materials **1a-1u** were prepared according to the previous reported procedures.[1] All other reagents were commercially available.

2. General procedure for the synthesis of 2-6

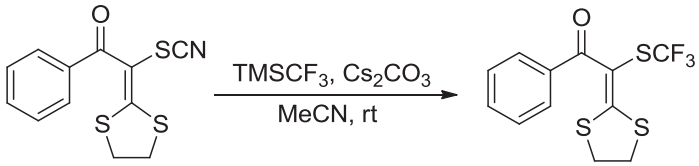
2.1 General procedure for the synthesis of 2a



1a **2a**

To a well-stirred solution of *N*-chlorosuccinimide (NCS) (0.4 mmol, 53.2 mg) in MeCN (2 ml) was added ammonium thiocyanate (0.4 mmol, 30.4 mg) at room temperature. The reaction was sealed and stirred at room temperature for 5 min. Then 2-(1,3-dithiolan-2-ylidene)-1-phenylethanone **1a** (0.2 mmol, 44.4 mg) was added to the reaction mixture under air. After stirring at room temperature for 24 h, the mixture was quenched with water and extracted with DCM. The organic layer was dried over Na_2SO_4, concentrated in vacuo and purified by column chromatography (petroleum ether/ EtOAc = 5:1) to afford product **2a**.

2.2 General procedure for the synthesis of 3a[2]

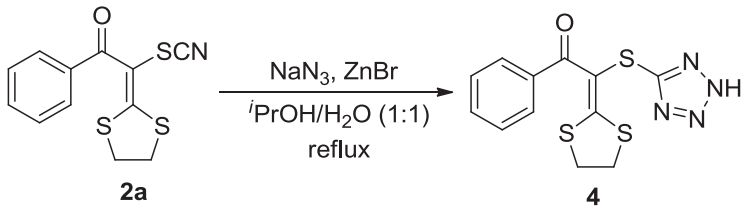


2a **3a**

In a 25 mL round-bottom flask, a mixture of **2a** (55.8 mg, 0.2 mmol) and Cs_2CO_3 (65.2 mg, 0.2 mmol) was dissolved in MeCN (1.6 mL) and cooled to 0 °C. Then trifluoromethyltrimethylsilane (56.8 mg, 0.4 mmol) was added at once via syringe and the mixture was stirred at room temperature for 8 h. The resulting mixture was filtered

through a short pad of celite and extracted with DCM. The resulting organic solution was washed with water (10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ EtOAc= 5:1), yielding the corresponding trifluoromethyl thioethers **3a** as yellow solid (38.9 mg, 60% yield.).

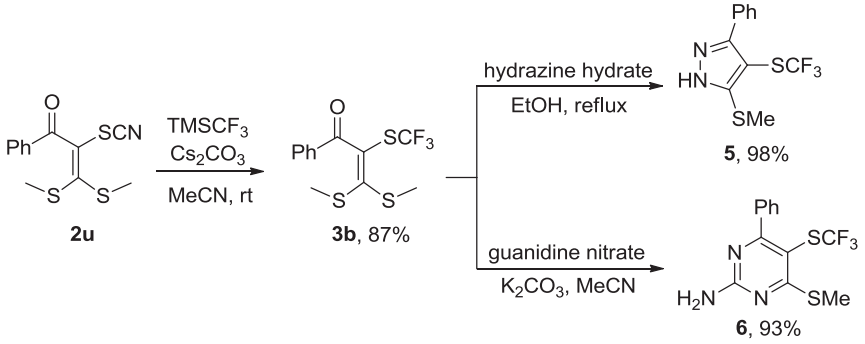
2.3 General procedure for the synthesis of 4[2]



2a **4**

A mixture of **2a** (83.7 mg, 0.3 mmol), NaN_3 (48.7 mg, 7.5 mmol) and $ZnBr_2$ (66.5 mg, 0.3 mmol) in $^{i}PrOH/H_2O$ (1:1, 6 mL) was heated to reflux until complete consumption of the starting material (6 h). After cooling to room temperature, the reaction mixture was acidified with 10% HCl and diluted with EtOAc (3 mL). The aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with H_2O (2 × 10 mL) and brine (10 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel column to give pure **4** as yellow liquid (91.0 mg, 94% yield).

2.4 Reaction of 3b with Hydrazine or Guanidine[3] **for the preparation of 5 or 6**

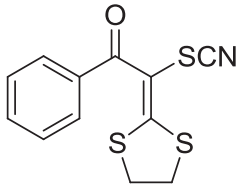


(1) Hydrazine hydrate (80%, 46.9 mg, 0.75 mmol) was added to **3b** (162.0 mg, 0.5 mmol) in ethanol (5 mL). The mixture was refluxed for 1.5 h. After the reaction was completed by TLC monitoring, the reaction mixture was cooled to room temperature, and all the volatiles were removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2, washed with water and brine and dried over anhydrous Na_2SO_4. The filtrate was evaporated to afford crude product. The crude product was washed by Et_2O to afford pure product **5** as a white solid (142.1 mg, 98% yield.)

(2) A mixture of **3b** (162.0 mg, 0.5 mmol), guanidine nitrate (61.0 mg, 0.5 mmol), and K_2CO_3 (137.9 mg, 1.0 mmol) in MeCN (5 mL) was stirred in 100 ^{o}C oil bath for 10 h. After the reaction was completed by TLC monitoring, the reaction mixture was cooled to room temperature, poured into ice cold water, and extracted with ethyl

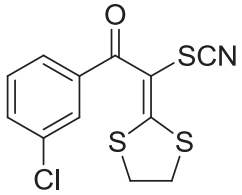
acetate. The organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to gain crude product. Afterwards the crude product was washed by Et_2O to afford pure product **6** as a white solid (148.0 mg, 93% yield.).

3. Characterization of Products



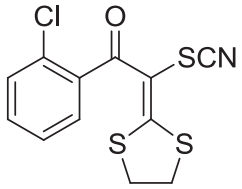
2a

2-(1,3-dithiolan-2-ylidene)-1-phenyl-2-thiocyanatoethanone:
53.2 mg, Yield: 95%. Yellow solid. M.p. 109-110 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 2H), 7.59 – 7.42 (m, 3H), 3.74 – 3.65 (m, 2H), 3.61 – 3.53 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 189.84, 186.10, 137.81, 131.35, 128.08, 128.00, 109.67, 100.67, 41.30, 36.45.
HRMS (ESI): $C_{12}H_{10}NOS_3$ $[M+H]^+$ Calcd: 279.9919, Found: 279.9913.



2b

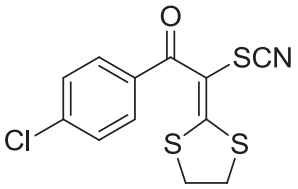
1-(3-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethanone:
58.7 mg, Yield: 94%. Yellow solid. M.p. 105-106 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (t, *J* = 1.7 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.41 (t, *J* = 7.7 Hz, 1H), 3.75 – 3.68 (m, 2H), 3.62 – 3.55 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 188.40, 187.43, 139.58, 134.30, 131.30, 129.47, 128.07, 126.00, 109.45, 100.35, 99.91, 41.46, 36.54.
HRMS (ESI): $C_{12}H_9ClNOS_3$ $[M+H]^+$ Calcd: 313.9529, Found: 313.9522.



2c

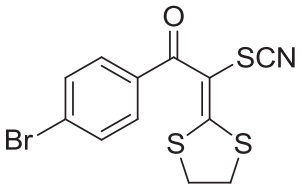
1-(2-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethanone:
61.0 mg, Yield: 97%. Yellow solid. M.p. 175-176 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 4H), 3.78 – 3.69 (m, 2H), 3.57 (dd, J = 7.6, 5.5 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 188.49, 186.60, 138.42, 130.91, 130.24, 129.34, 127.89, 127.10, 109.51, 101.84, 41.59, 36.44.
HRMS (ESI): $C_{12}H_9ClNOS_3$ $[M+H]^+$ Calcd: 313.9529, Found: 313.9525.



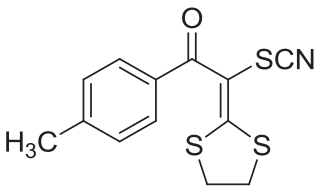
2d

1-(4-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethanone:
50.9 mg, Yield: 81%. Yellow solid. M.p. 155-156 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 2H), 7.48 – 7.40 (m, 2H), 3.74 – 3.66 (m, 2H), 3.62 – 3.54 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 188.63, 186.93, 137.61, 136.19, 129.58, 128.44, 109.51, 100.40, 41.40, 36.52.
HRMS (ESI): $C_{12}H_9ClNOS_3$ $[M+H]^+$ Calcd: 313.9529, Found: 313.9526.



2e

1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethanone:
62.9 mg, Yield: 88%. Yellow solid. M.p. 173-174 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.56 – 7.50 (m, 2H), 3.75 – 3.66 (m, 2H), 3.62 – 3.53 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 188.75, 187.06, 136.65, 131.40, 129.68, 126.09, 109.52, 100.37, 41.41, 36.52.
HRMS (ESI): $C_{12}H_9BrNOS_3$ $[M+H]^+$ Calcd: 357.9024, Found: 357.9020.



2f

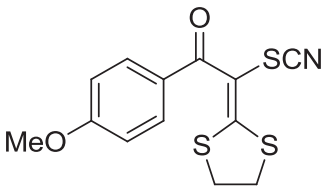
2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(p-tolyl)ethanone:

52.4 mg, Yield: 89%. Yellow solid. M.p. 165-166 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.66 (dd, *J* = 7.3, 5.2 Hz, 2H), 3.55 (dd, *J* = 7.3, 5.1 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.66, 185.25, 142.16, 134.92, 128.78, 128.37, 109.70, 100.82, 41.22, 36.48, 21.58.

HRMS (ESI): $C_{13}H_{12}NOS_3$ $[M+H]^+$ Calcd: 294.0076, Found: 294.0079



2g

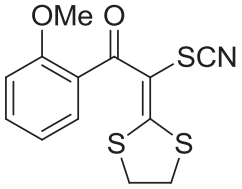
2-(1,3-dithiolan-2-ylidene)-1-(4-methoxyphenyl)-2-thiocyanatoethanone:

49.8 mg, Yield: 80%. Yellow solid. M.p. 122-123 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.63 (m, 2H), 7.74 – 7.67 (m, 2H), 7.03 – 6.90 (m, 2H), 6.99 – 6.93 (m, 2H), 3.87 (s, 3H), 3.87 (s, 3H), 3.68 – 3.61 (m, 2H), 3.71 – 3.49 (m, 4H), 3.59 – 3.51 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.56, 184.44, 162.38, 130.81, 129.84, 113.36, 109.72, 100.65, 55.38, 41.10, 36.49.

HRMS (ESI): $C_{13}H_{12}NO_2S_3$ $[M+H]^+$ Calcd: 310.0025, Found: 310.0020.



2h

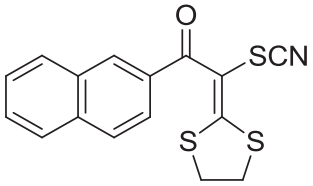
2-(1,3-dithiolan-2-ylidene)-1-(2-methoxyphenyl)-2-thiocyanatoethanone:

35.6 mg, Yield: 58%. Yellow solid. M.p. 92-93 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 1H), 7.36 (dd, J = 7.5, 1.6 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H), 3.68 (dd, J = 7.5, 5.3 Hz, 2H), 3.59 – 3.50 (m, 2H).

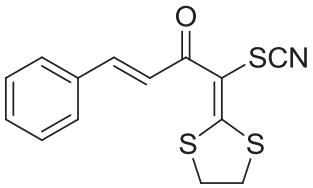
^{13}C NMR (75 MHz, $CDCl_3$) δ 189.50, 182.87, 156.03, 132.12, 129.08, 128.31, 121.02, 110.38, 103.62, 55.48, 41.15, 36.40.

HRMS (ESI): $C_{13}H_{12}NO_2S_3$ $[M+H]^+$ Calcd: 310.0025, Found: 310.0022.



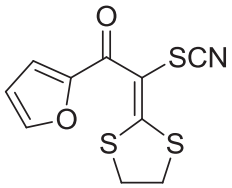
2i

2-(1,3-dithiolan-2-ylidene)-1-(naphthalen-2-yl)-2-thiocyanatoethanone:
43.9 mg, Yield: 67%. Yellow solid. M.p. 140-141 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.92 (dd, J = 18.1, 9.3 Hz, 3H), 7.71 (dd, J = 8.4, 1.6 Hz, 1H), 7.63 – 7.50 (m, 2H), 3.66 (dd, J = 7.4, 5.2 Hz, 2H), 3.60 – 3.50 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 189.76, 185.93, 135.07, 134.50, 132.12, 129.07, 128.98, 127.94, 127.89, 127.74, 126.75, 124.57, 109.74, 100.93, 41.30, 36.49.
HRMS (ESI): $C_{16}H_{12}NOS_3[M+H]^+$ Calcd: 330.0076, Found: 330.0070.



2j

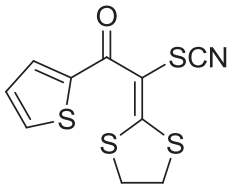
(E)-1-(1,3-dithiolan-2-ylidene)-4-phenyl-1-thiocyanatobut-3-en-2-one:
56.1 mg, Yield: 92%. Yellow solid. M.p. 167-168 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.69 (m, 2H), 7.64 (dd, J = 6.5, 2.9 Hz, 2H), 7.50 – 7.36 (m, 3H), 3.67 (dd, J = 7.6, 5.5 Hz, 2H), 3.52 (dd, J = 7.5, 5.5 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 185.03, 182.89, 145.50, 134.74, 130.68, 128.92, 128.64, 120.43, 109.41, 101.87, 41.57, 36.25.
HRMS (ESI): $C_{14}H_{12}NOS_3[M+H]^+$ Calcd: 306.0076, Found: 306.0071.



2k

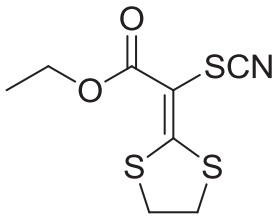
2-(1,3-dithiolan-2-ylidene)-1-(furan-2-yl)-2-thiocyanatoethanone:
42.4 mg, Yield: 79%. Yellow solid. M.p. 158-159 °C.
^{1}H NMR (300 MHz, DMSO) δ 8.04 (d, J = 1.1 Hz, 1H), 7.57 (d, J = 3.6 Hz, 1H), 6.76 (dd, J = 3.6, 1.6 Hz, 1H), 3.75 – 3.67 (m, 2H), 3.66 – 3.58 (m, 2H).
^{13}C NMR (75 MHz, DMSO) δ 186.37, 173.97, 150.30, 147.62, 119.78, 112.58, 111.22, 99.01, 41.15, 36.19.

HRMS (ESI): $C_{10}H8NO_2S_3$ $[M+H]^+$ Calcd: 269.9712, Found: 269.9708.



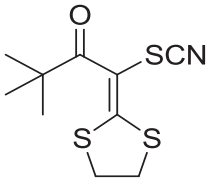
2l

2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(thiophen-2-yl)ethanone:
34.6 mg, Yield: 61%. Yellow solid. M.p. 182-183 °C.
^{1}H NMR (300 MHz, DMSO) δ 8.11 – 8.05 (m, 1H), 8.04 – 7.98 (m, 1H), 7.26 (dd, J = 4.8, 4.0 Hz, 1H), 3.76 – 3.68 (m, 2H), 3.68 – 3.59 (m, 2H).
^{13}C NMR (75 MHz, DMSO) δ 186.72, 178.47, 141.31, 134.77, 134.09, 128.29, 111.17, 99.75, 41.26, 36.32.
HRMS (ESI): $C_{10}H_8NOS_4$ $[M+H]^+$ Calcd: 285.9483, Found: 285.9478.



2m

ethyl 2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoacetate:
43.4 mg, Yield: 88%. Yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30 (q, J = 7.1 Hz, 2H), 3.72 – 3.64 (m, 2H), 3.57 – 3.49 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 182.03, 163.46, 109.72, 93.72, 62.16, 41.39, 37.16, 14.21.
HRMS (ESI): $C_8H_9NNaO_2S_3$ $[M+Na]^+$ Calcd: 269.9688, Found: 269.9681.

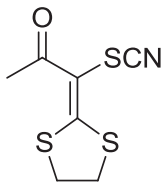


2n

ethyl 2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoacetate:
48.1 mg, Yield: 93%. Yellow solid. M.p. 108-109 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.64 – 3.55 (m, 2H), 3.54 – 3.43 (m, 2H), 1.40 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 198.80, 187.09, 109.72, 99.58, 43.22, 41.14, 35.82,

27.29.

HRMS (ESI): $C_{10}H_{14}NOS_3$ $[M+H]^+$ Calcd: 260.0232, Found: 260.0229.



2o

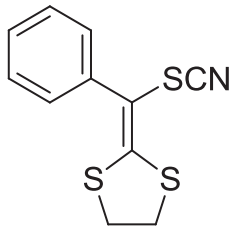
1-(1,3-dithiolan-2-ylidene)-1-thiocyanatopropan-2-one:

39.4 mg, Yield: 91%. Yellow solid. M.p. 141-142 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.65 (dd, *J* = 7.8, 5.7 Hz, 2H), 3.49 (dd, *J* = 7.6, 5.5 Hz, 2H), 2.55 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.10, 183.71, 109.45, 101.38, 41.58, 36.16, 27.65.

HRMS (ESI): $C_7H_8NOS_3$ $[M+H]^+$ Calcd: 217.9763, Found: 217.9756.



2p

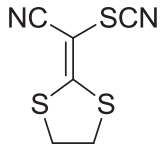
2-(phenyl(thiocyanato)methylene)-1,3-dithiolane:

30.6 mg, Yield: 61%. Yellow solid. M.p. 52-53 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (dt, J = 3.4, 2.0 Hz, 2H), 7.43 – 7.28 (m, 3H), 3.57 – 3.50 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.59, 138.87, 128.56, 128.43, 109.99, 102.55, 40.21, 38.55.

HRMS (ESI): $C_{11}H_9NNaS_3$ $[M+Na]^+$ Calcd: 273.9789, Found: 273.9783.



2q

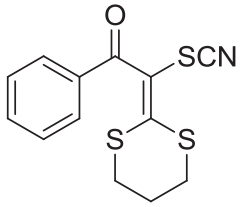
2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoacetonitrile:

17.8 mg, Yield: 45%. Yellow solid. M.p. 86-87 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.87 – 3.79 (m, 2H), 3.79 – 3.70 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 185.26, 115.91, 107.51, 72.93, 41.28, 40.20.

HRMS (ESI): $C_6H_4N_2NaS_3$ $[M+Na]^+$ Calcd: 222.9429, Found: 222.9422.



2r

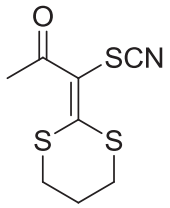
2-(1,3-dithian-2-ylidene)-1-phenyl-2-thiocyanatoethanone:

47.7 mg, Yield: 81%. Yellow solid. M.p. 93-94 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 7.1 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.3 Hz, 2H), 3.18 (t, J = 7.0 Hz, 2H), 2.95 (t, J = 7.0 Hz, 2H), 2.31 (p, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.21, 175.44, 137.62, 132.33, 128.79, 128.30, 109.52, 109.18, 30.68, 30.23, 23.62.

HRMS (ESI): $C_{13}H_{12}NOS_3$ $[M+H]^+$ Calcd: 294.0076, Found: 294.0071.



2s

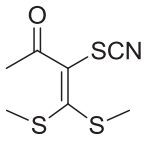
1-(1,3-dithian-2-ylidene)-1-thiocyanatopropan-2-one:

37.7 mg, Yield: 82%. Yellow solid. M.p. 105-106 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.13 (t, J = 7.1 Hz, 2H), 2.95 (t, J = 6.8 Hz, 2H), 2.55 (s, 3H), 2.32 (p, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.99, 179.67, 109.84, 109.74, 31.12, 30.59, 29.23, 23.53.

HRMS (ESI): $C_8H_9NNaOS_3$ $[M+Na]^+$ Calcd: 253.9738, Found: 253.9735.



2t

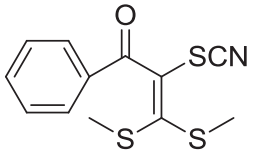
4,4-bis(methylthio)-3-thiocyanatobut-3-en-2-one:

25.7 mg, Yield: 59%. Yellow solid. M.p. 33-34 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.59 (s, 3H), 2.55 (s, 3H), 2.46 (s, 3H).

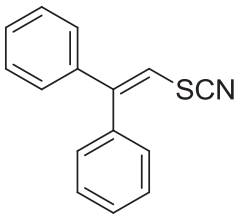
^{13}C NMR (75 MHz, $CDCl_3$) ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.89, 159.14, 121.00, 109.44, 30.07, 19.50, 18.53.

HRMS (ESI): $C_7H_{10}NOS_3$ $[M+Na]^+$ Calcd: 219.9919, Found: 219.9913.



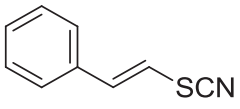
2u

3,3-bis(methylthio)-1-phenyl-2-thiocyanatoprop-2-en-1-one:
39.8 mg, Yield: 71%. Yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (dd, J = 5.2, 3.4 Hz, 2H), 7.68 – 7.60 (m, 1H), 7.51 (dd, J = 10.4, 4.6 Hz, 2H), 2.50 (s, 3H), 2.18 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 189.21, 175.44, 137.62, 132.33, 128.79, 128.30, 109.52, 109.18, 30.68, 30.23, 23.62.
HRMS (ESI): $C_{12}H_{12}NOS_3[M+H]^+$ Calcd: 282.0076, Found: 282.0069.



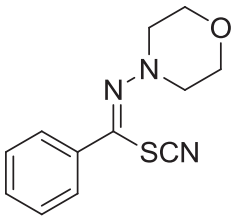
2v

(2-thiocyanatoethene-1,1-diyl)dibenzene:
35.7 mg, Yield: 75%. Pale yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 3H), 7.36 – 7.27 (m, 3H), 7.25 – 7.14 (m, 4H), 6.60 (s, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 148.39, 139.20, 136.74, 129.21, 129.17, 129.04, 128.95, 128.66, 127.38, 111.31, 111.22.
HRMS (ESI): $C_{15}H_{12}NS[M+H]^+$ Calcd: 238.0685, Found: 238.0691.



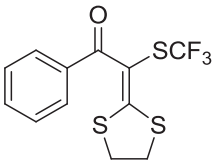
2w

(E)-(2-thiocyanatovinyl)benzene:
8.1mg, Yield: 25%. Pale yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (s, 5H), 7.00 (d, *J* = 15.1 Hz, 1H), 6.48 (d, *J* = 15.1 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 138.36, 134.41, 129.39, 128.99, 126.72, 109.77.
HRMS (ESI): $C_9H_{11}N_2S[M+NH_4]^+$ Calcd: 179.0637, Found: 179.0640.



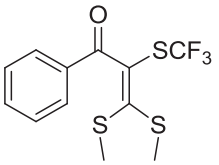
2x

cyanic (*Z*)-*N*-morpholinobenzimidic thioanhydride:
34.8 mg, Yield: 70%. Yellow solid. M.p. 91-92 °C.
^{1}H NMR (300 MHz, DMSO) δ 8.19 – 8.10 (m, 2H), 7.70 – 7.62 (m, 1H), 7.62 – 7.53 (m, 2H), 4.14 (d, *J* = 4.4 Hz, 4H), 3.84 (d, *J* = 11.6 Hz, 2H), 3.05 (s, 2H).
^{13}C NMR (75 MHz, DMSO) δ 198.21, 176.40, 132.98, 128.92, 128.62, 127.85, 62.49, 59.76.
HRMS (ESI): $C_{12}H_{14}N_3OS$ $[M+H]^+$ Calcd: 248.0852, Found: 248.0857.



3a

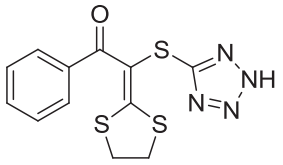
2-(1,3-dithiolan-2-ylidene)-1-phenyl-2-((trifluoromethyl)thio)ethanone:
38.9 mg, Yield: 60%. Yellow solid. M.p. 77-78 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.52 – 7.44 (m, 1H), 7.40 (ddd, J = 6.7, 4.5, 1.5 Hz, 2H), 3.67 – 3.60 (m, 2H), 3.52 – 3.45 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 191.75, 187.14, 138.22, 131.01, 130.73, 128.71, 127.73, 103.71, 41.12, 35.94.
^{19}F NMR (282 MHz, CDCl3) δ -43.6.
HRMS (ESI): $C_{12}H_{10}F_3OS_3$ $[M+H]^+$ Calcd: 322.9840, Found: 322.9835.



3b

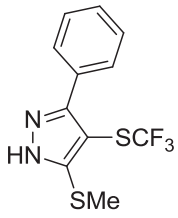
3,3-bis(methylthio)-1-phenyl-2-((trifluoromethyl)thio)prop-2-en-1-one:
56.6 mg, Yield: 87%. Yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.62 – 7.54 (m, 1H), 7.53 – 7.44 (m, 2H), 2.52 (s, 3H), 2.21 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 191.79, 158.35, 135.95, 133.40, 129.26, 128.65, 121.81, 77.47, 77.04, 76.62, 18.74, 17.18.
^{19}F NMR (282 MHz, $CDCl_3$) δ -39.4.

HRMS (ESI): $C_{12}H_{12}F_3OS_3$ $[M+H]^+$ Calcd: 324.9997, Found: 324.9995.



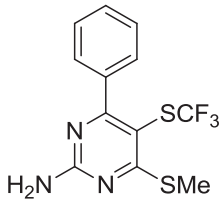
4

2-((2H-tetrazol-5-yl)thio)-2-(1,3-dithiolan-2-ylidene)-1-phenylethanone:
91.0 mg, Yield: 94%. Yellow liquid.
^{1}H NMR (300 MHz, DMSO) δ 7.56 – 7.49 (m, 2H), 7.48 – 7.29 (m, 3H), 3.69 (t, J = 6.6 Hz, 2H), 3.50 (t, J = 6.6 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 190.21, 184.58, 154.09, 138.93, 130.72, 127.83, 127.61, 104.76, 41.32, 35.95.
HRMS (ESI): $C_{12}H_{11}N_4OS_3$ $[M+H]^+$ Calcd: 323.0089, Found: 323.0080.



5

5-(methylthio)-3-phenyl-4-((trifluoromethyl)thio)-1H-pyrazole:
142.1 mg, Yield: 98%. Yellow solid. M.p. 172-173 °C.
^{1}H NMR (300 MHz, DMSO) δ 7.75 (d, *J* = 6.9 Hz, 2H), 7.59 – 7.39 (m, 3H), 2.51 (s, *J* = 8.1 Hz, 3H).
^{13}C NMR (75 MHz, DMSO) δ 135.25, 131.12, 129.39, 128.71, 127.77, 127.17, 127.00, 122.87.
^{19}F NMR (282 MHz, DMSO) δ -43.5.
HRMS (ESI): $C_{11}H_{10}F_3N_2S_2$ $[M+H]^+$ Calcd: 291.0232, Found: 291.0246.



6

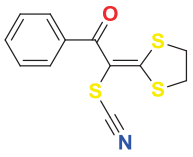
4-(methylthio)-6-phenyl-5-((trifluoromethyl)thio)pyrimidin-2-amine:
148.0 mg, Yield: 93%. Yellow solid. M.p. 185-186 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.38 (m, 5H), 2.47 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 180.08, 171.95, 161.62, 137.62, 130.75, 129.32, 128.93, 127.94, 126.60, 102.61, 14.24.

^{19}F NMR (282 MHz, $CDCl_3$) δ -42.7.
HRMS (ESI): $C_{12}H_{11}F_3N_3S_2$ $[M+H]^+$ Calcd: 318.0341, Found: 318.0337.

4. References

(1) Zhu, L.; Yu, H.; Guo, Q.; Chen, Q.; Xu, Z.; Wang, R. *Org. Lett.* **2015**, *17*, 1978.
(2) Liang, Z.; Wang, F.; Chen, P.; Liu, G. *Org. Lett.* **2015**, 17, 2438.
(3) Mao, Z.; Huang, F.; Yu, H.; Chen, J.; Yu, Z.; Xu, Z. *Chem. Eur. J.* **2014**, 20, 3439.

5. X-ray Structure of 2a



2a
CCDC 1483477

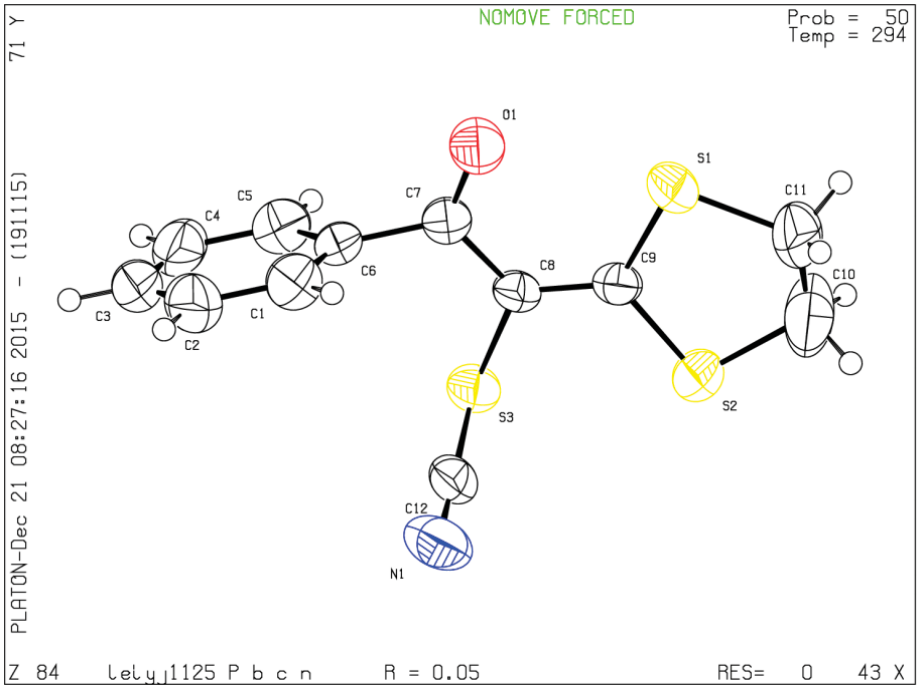
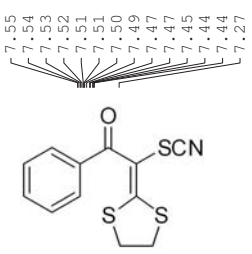
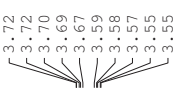


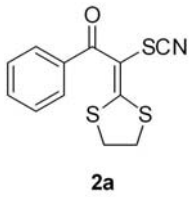
Table S1. Crystal data and structure refinement for **2a**.

Identification code	leiyj1125
Empirical formula	$C_{24}H_{18}N_2O_2S_6$
Formula weight	558.76
Temperature/K	294.06(10)
Crystal system	orthorhombic
Space group	Pbcn
a/Å	7.9629(3)
b/Å	16.9905(6)
c/Å	18.7808(5)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2540.93(15)
Z	4
ρ_{calc}g/cm^3	1.461
μ/mm^{-1}	0.564
F(000)	1152.0
Crystal size/mm^3	0.24 × 0.22 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.7 to 52.02
Index ranges	$-5 \le h \le 9$, $-13 \le k \le 20$, $-14 \le l \le 23$
Reflections collected	6634
Independent reflections	2499 [R_{int} = 0.0292, R_{sigma} = 0.0328]
Data/restraints/parameters	2499/0/154
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0483, wR_2 = 0.1140
Final R indexes [all data]	R_1 = 0.0698, wR_2 = 0.1315
Largest diff. peak/hole / e Å^{-3}	0.35/-0.42

6. Copies of NMR Spectra of Products

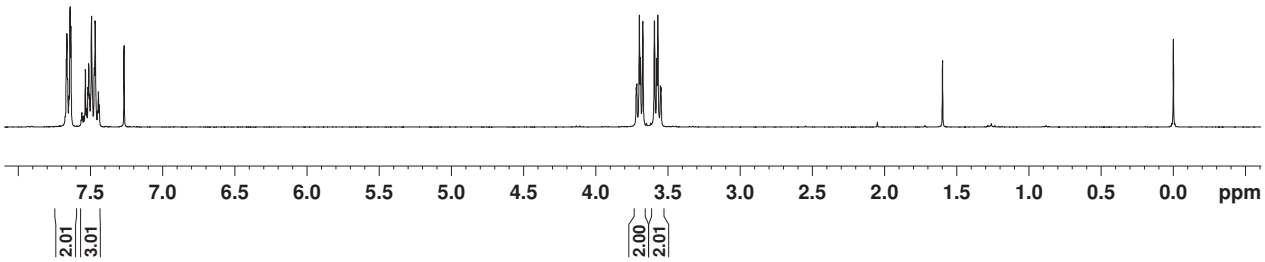


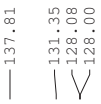


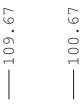


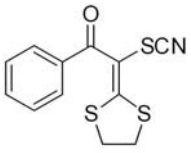
2a

^{1}H NMR (300 MHz, $CDCl_3$)



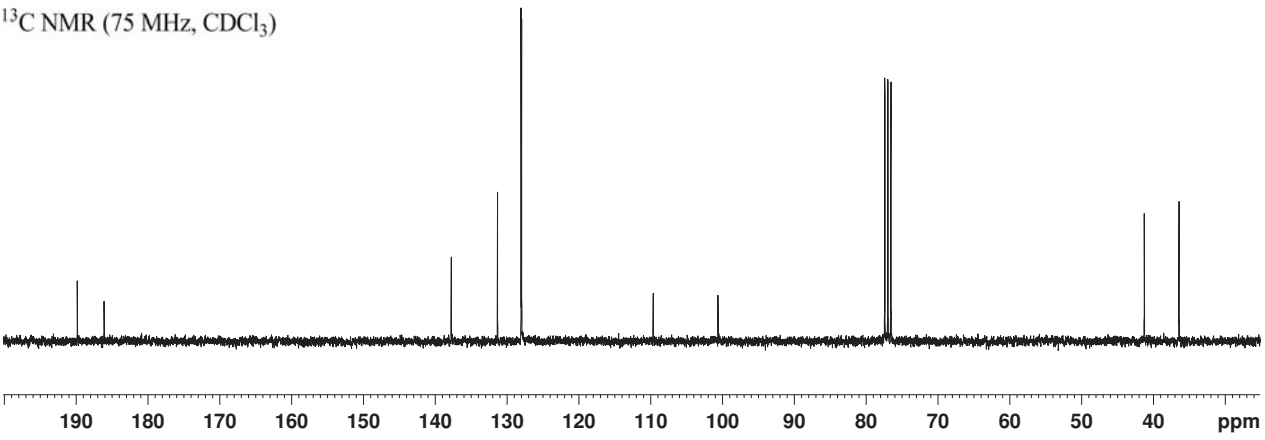


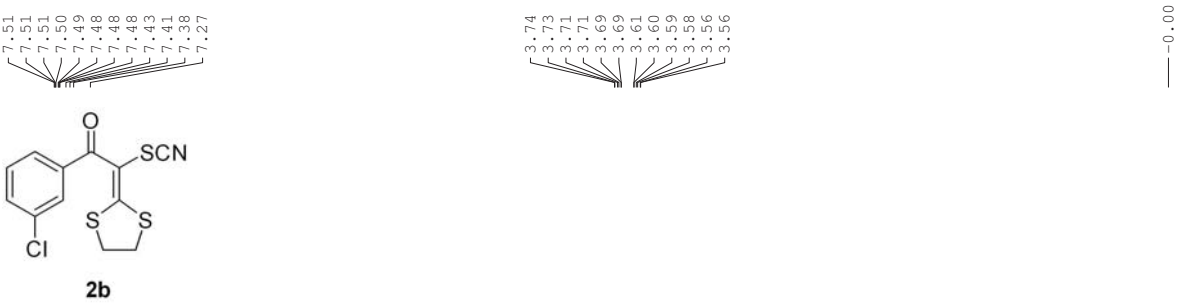




2a

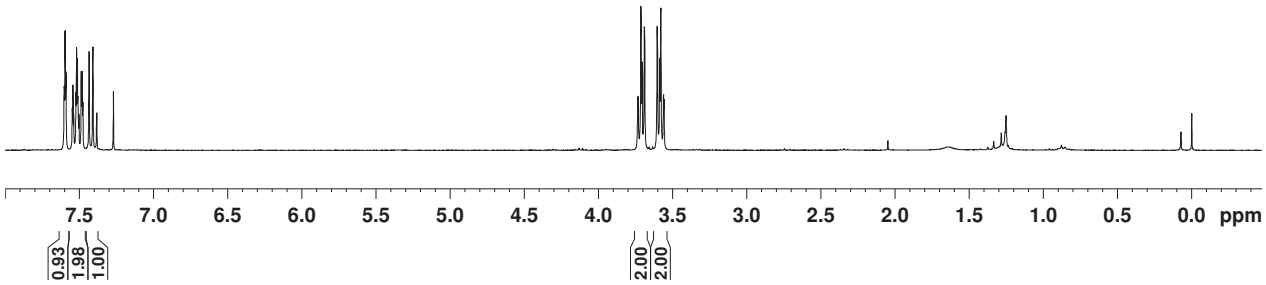
^{13}C NMR (75 MHz, $CDCl_3$)





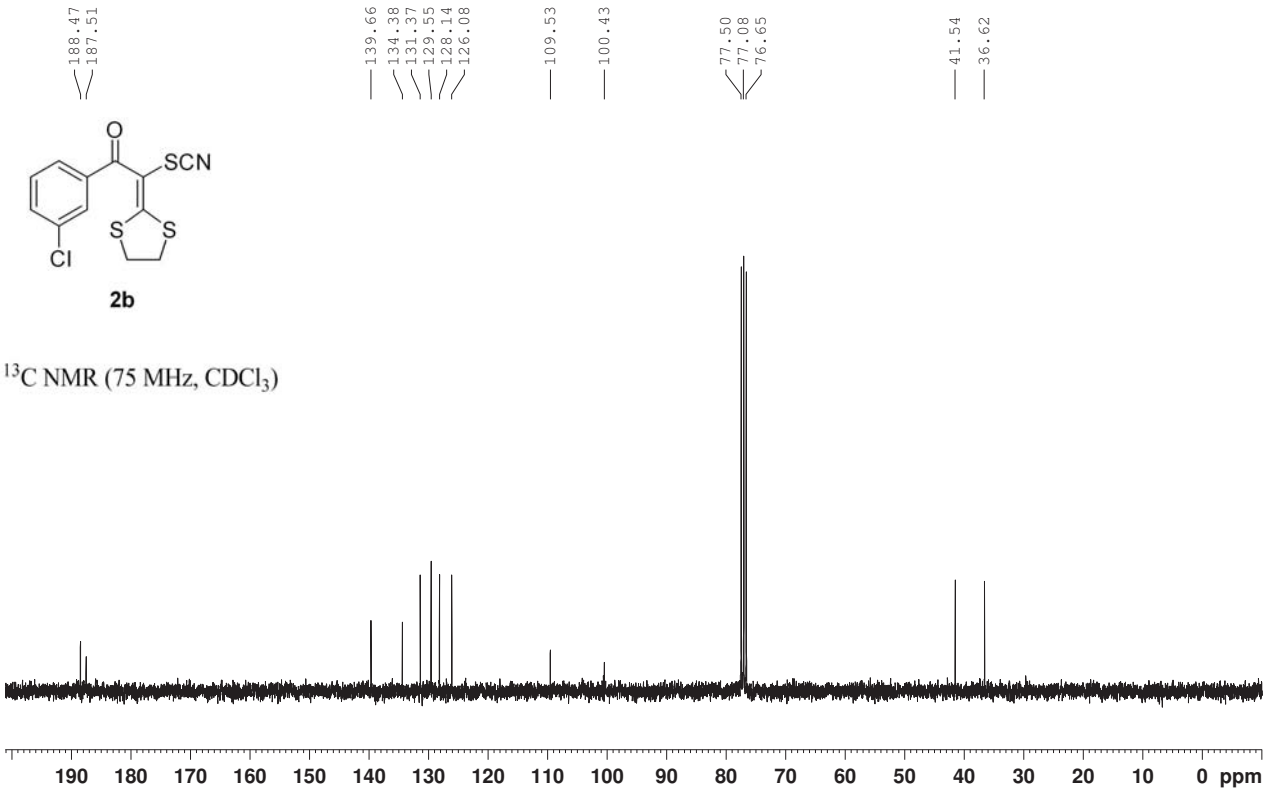
2b

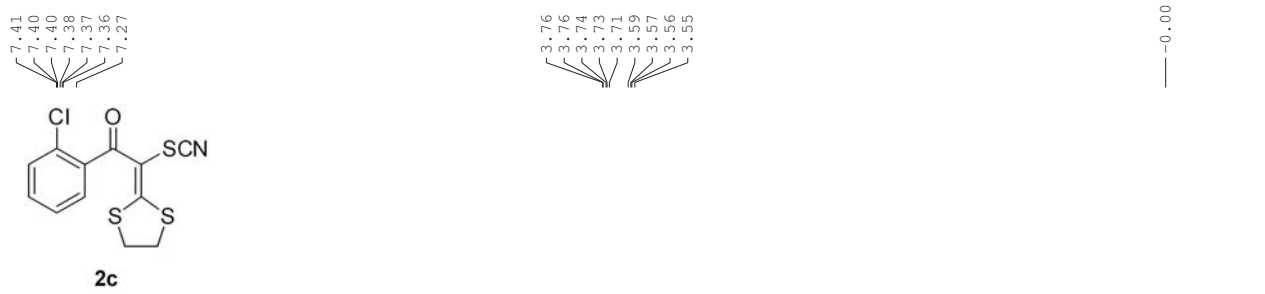
^{1}H NMR (300 MHz, $CDCl_3$)



2b

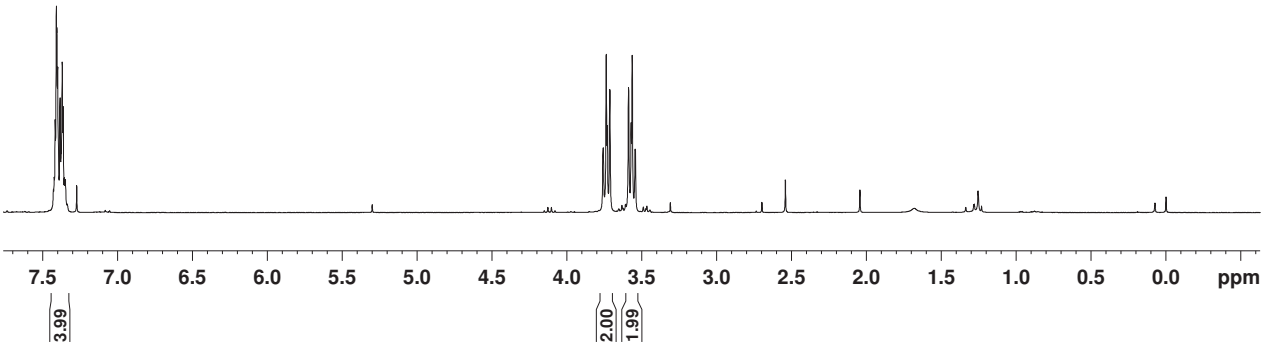
^{13}C NMR (75 MHz, $CDCl_3$)

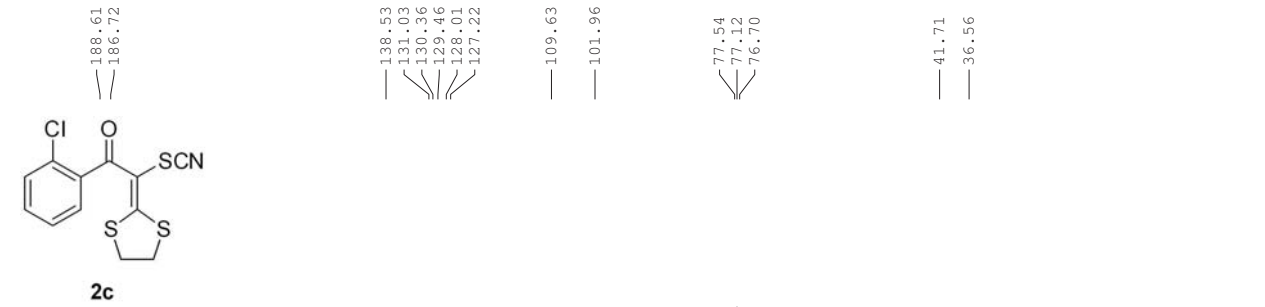




2c

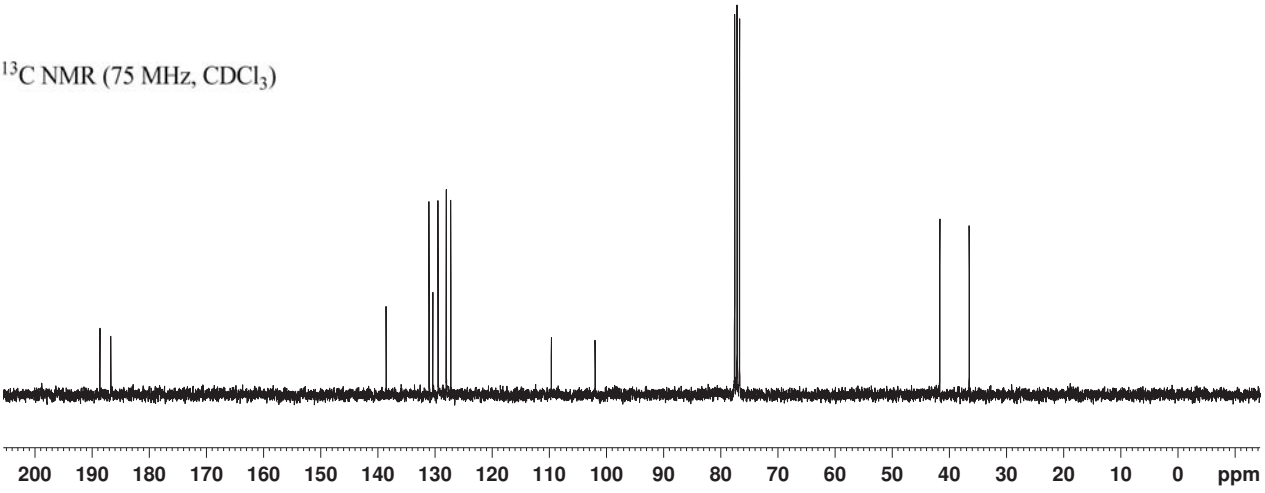
^{1}H NMR (300 MHz, $CDCl_3$)

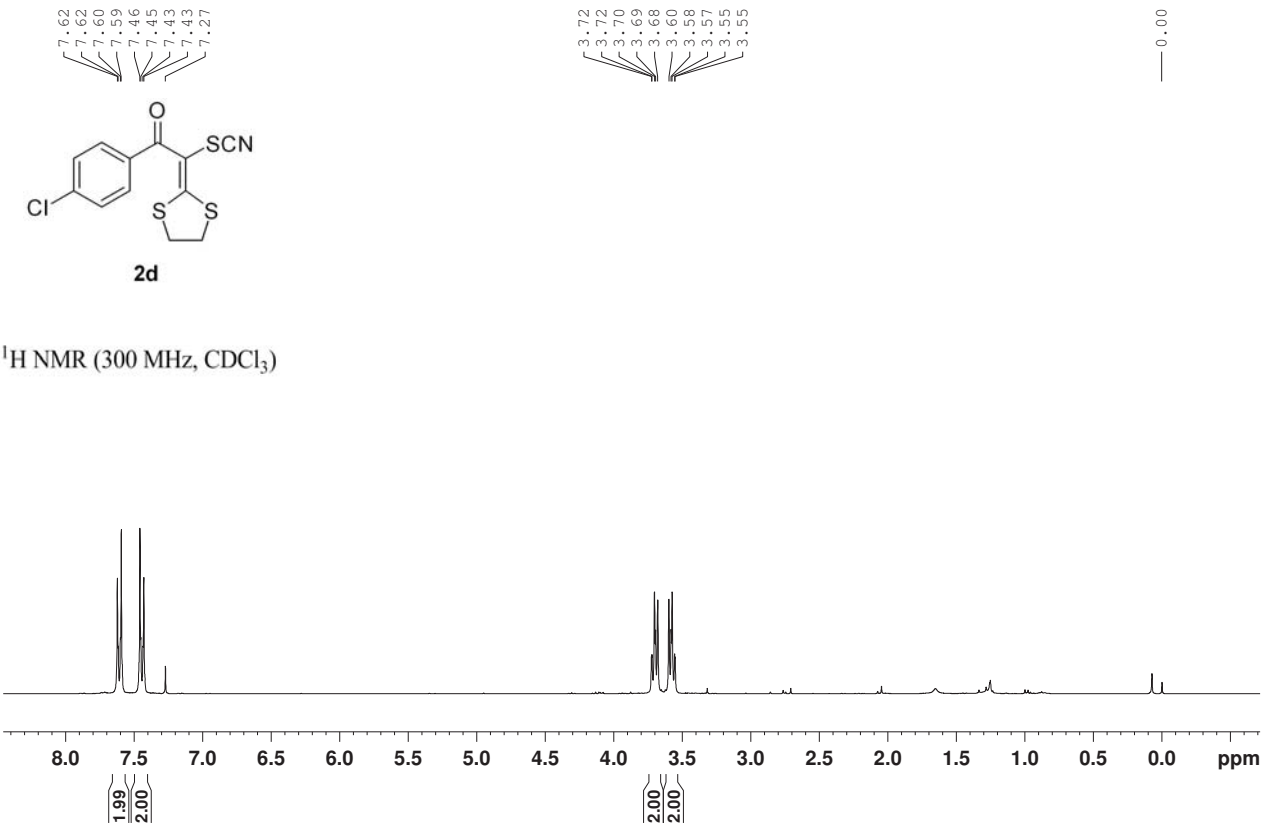




2c

^{13}C NMR (75 MHz, $CDCl_3$)

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7.62
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7.59
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7.45
7.43
7.43
7.27
3.72
3.72
3.70
3.69
3.68
3.60
3.58
3.57
3.55
3.55
0.00
O
SCN
Cl
S
S
2d
^{1}H NMR (300 MHz, $CDCl_3$)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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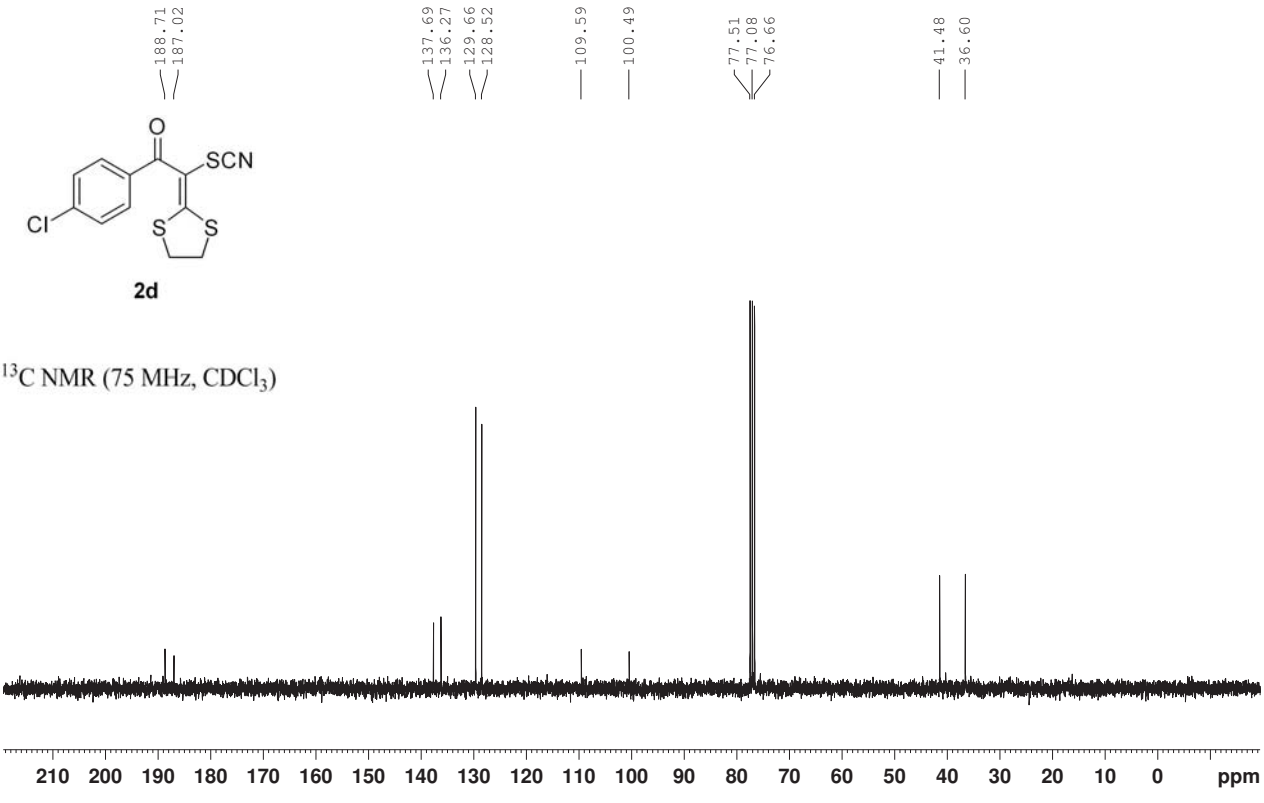
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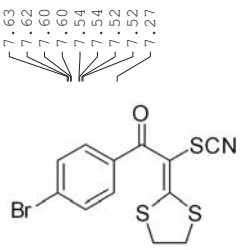
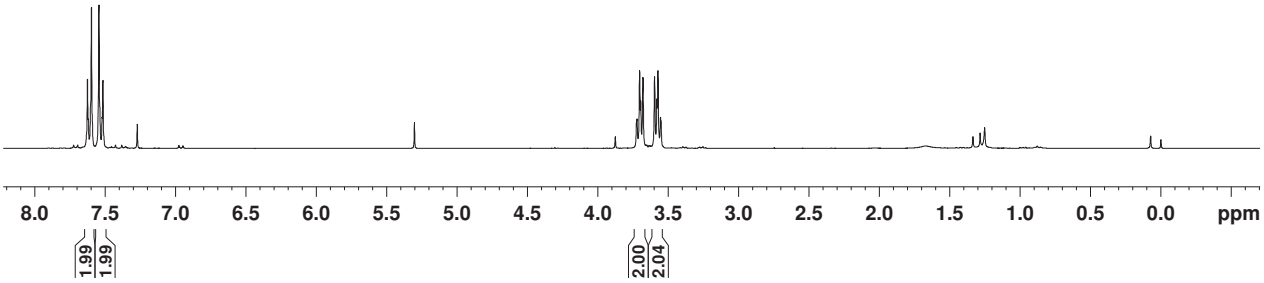
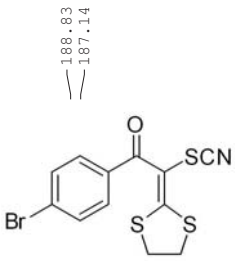
O
SCN
Cl
S
S
2d
^{13}C NMR (75 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



2e

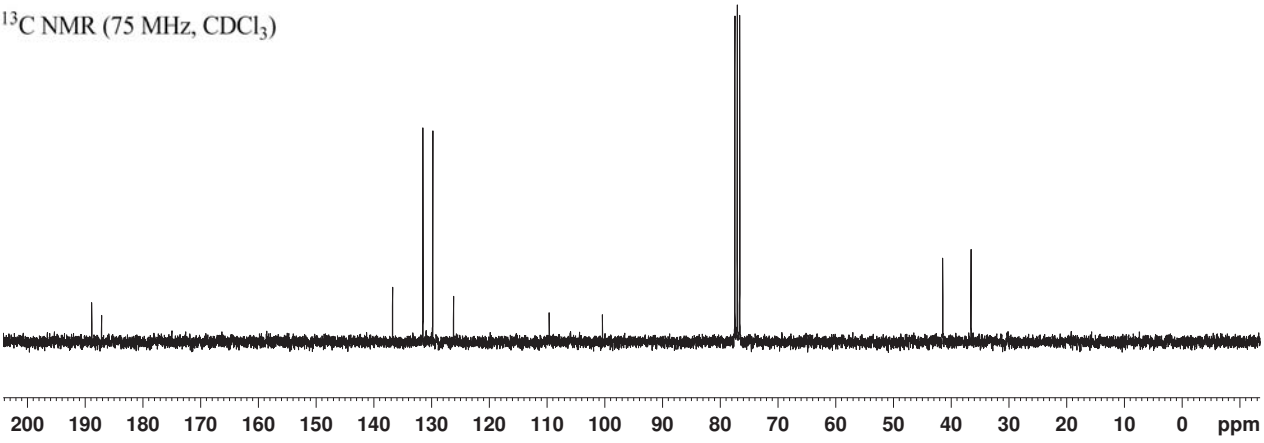
^{1}H NMR (300 MHz, $CDCl_3$)

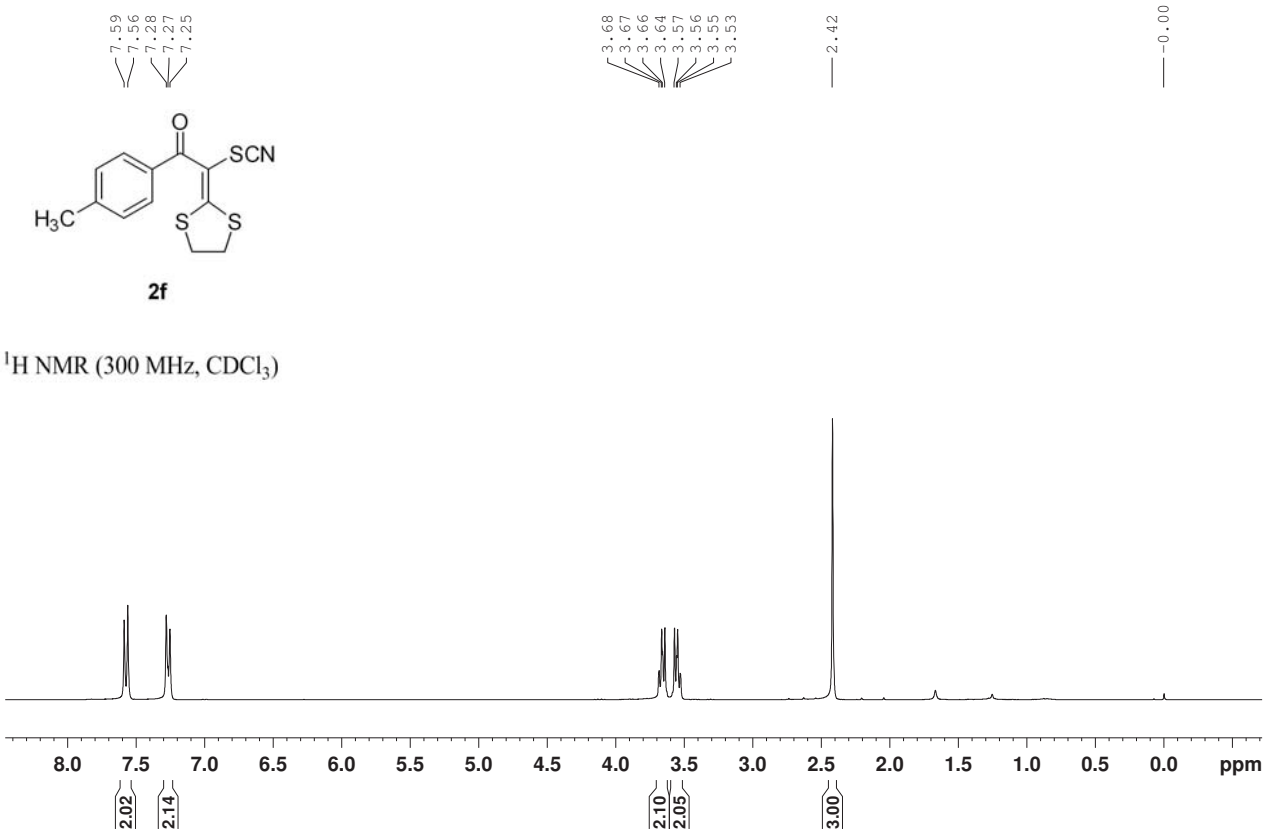


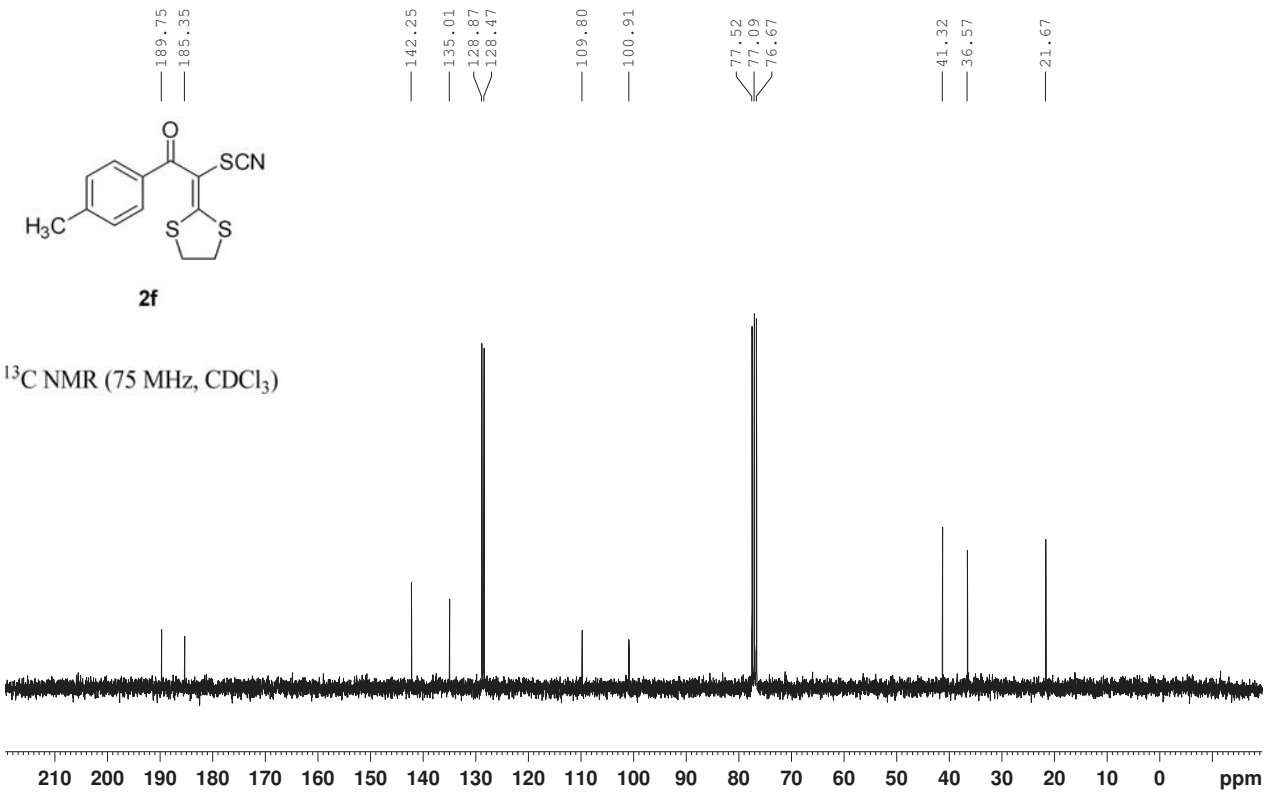


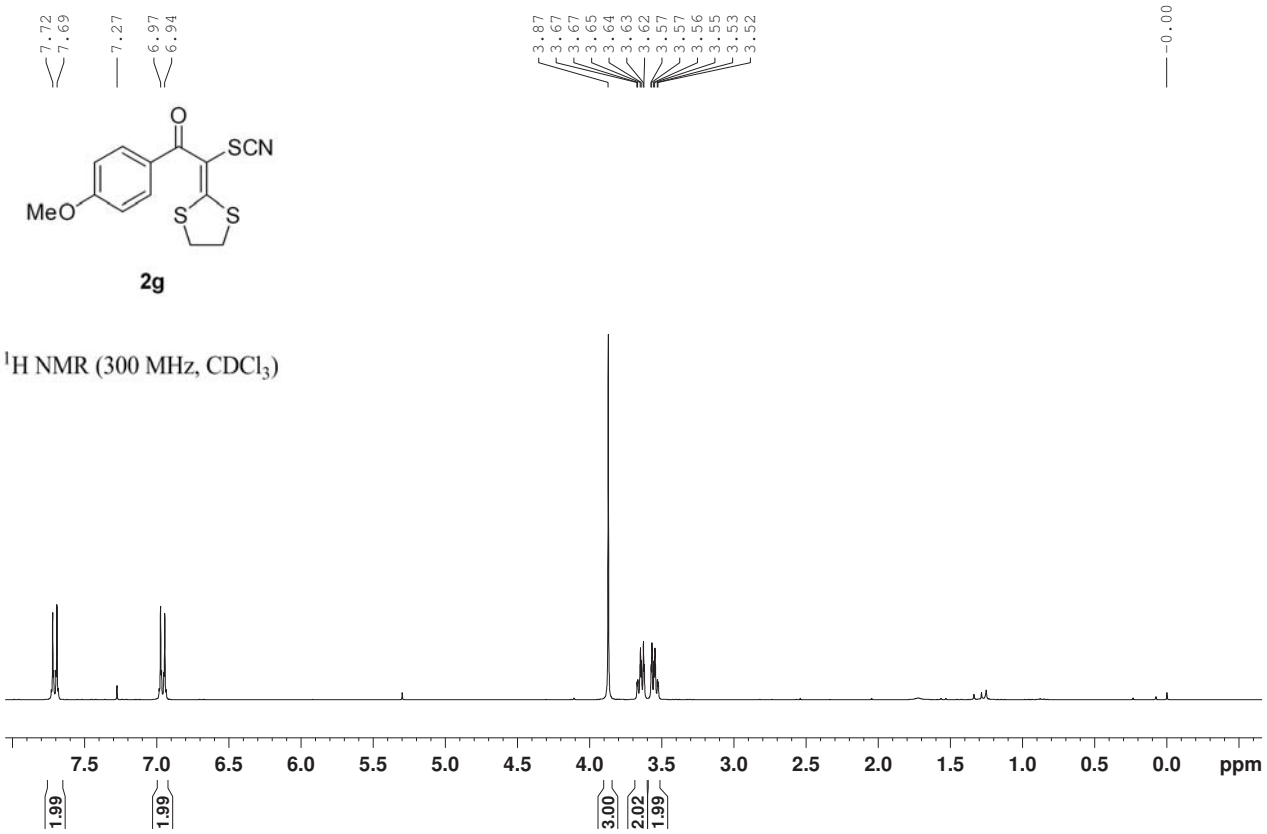
2e

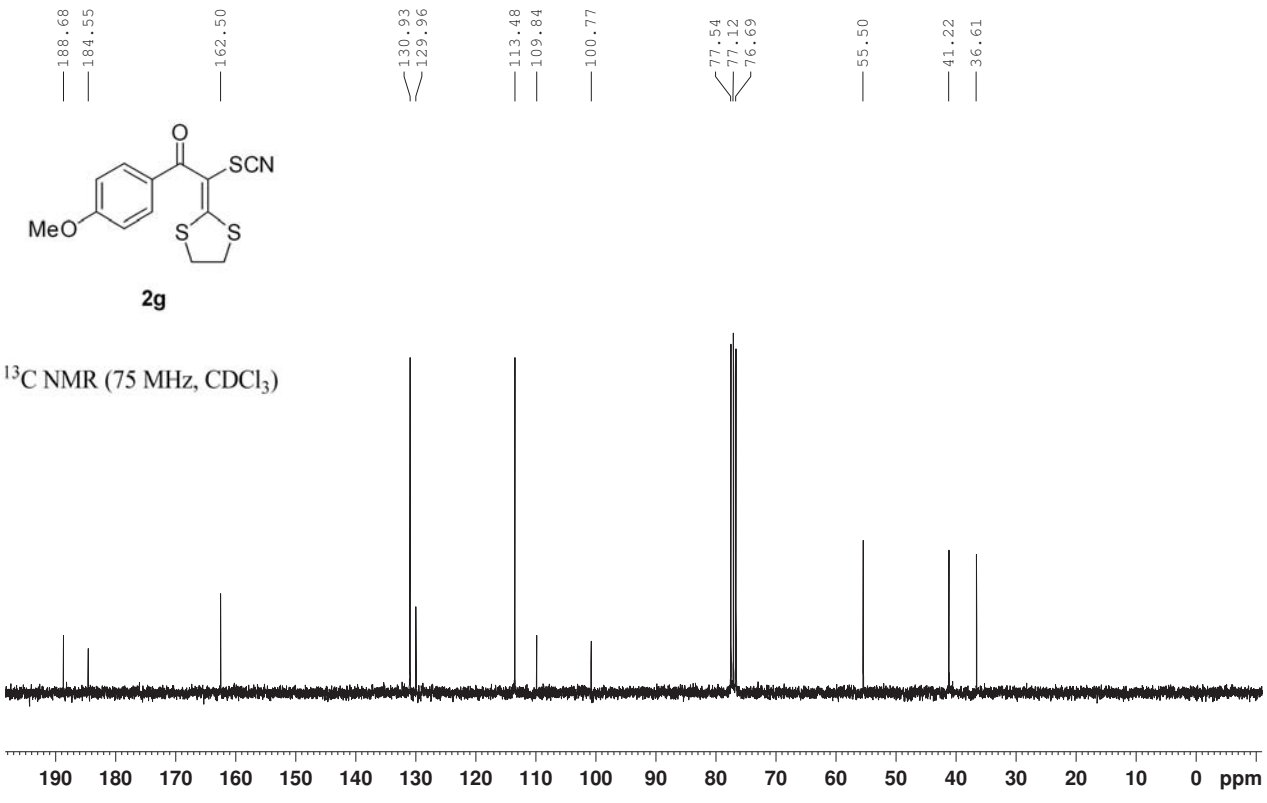
^{13}C NMR (75 MHz, $CDCl_3$)

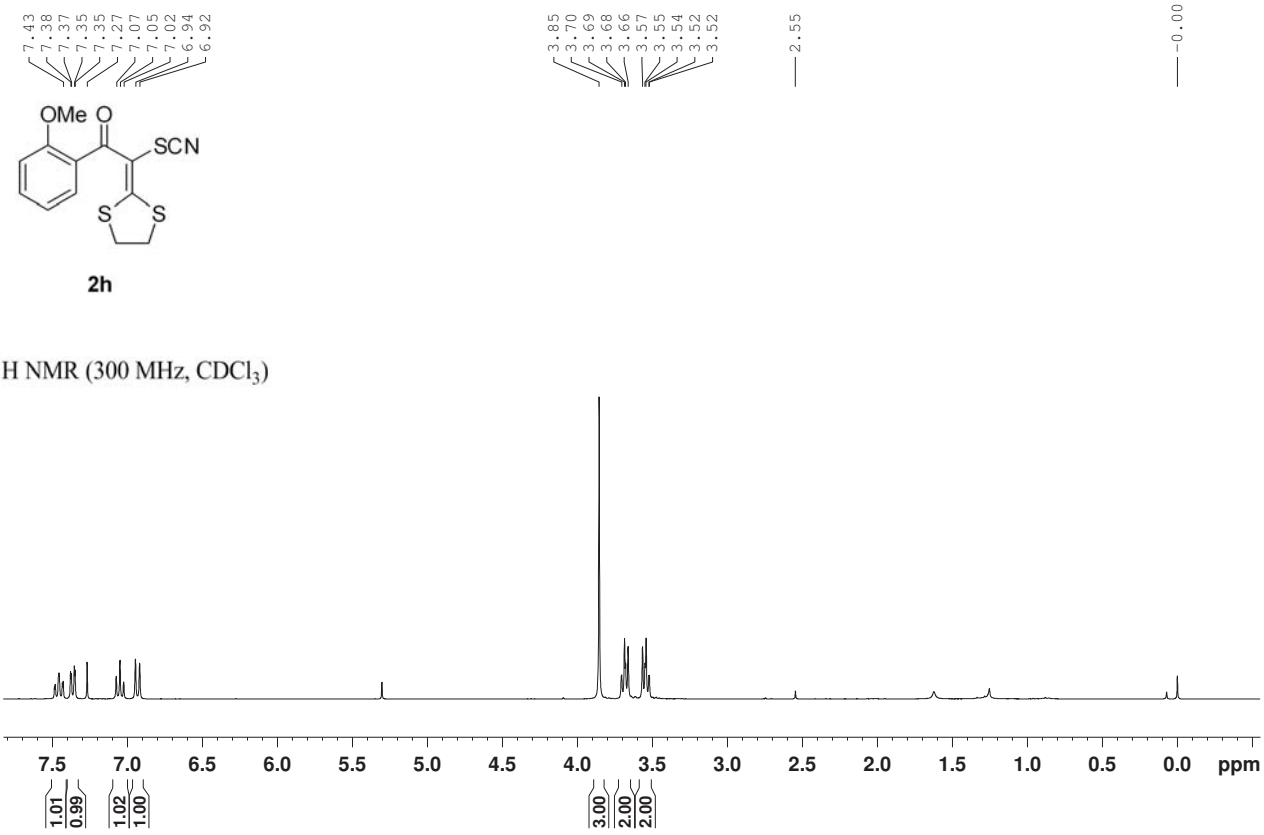


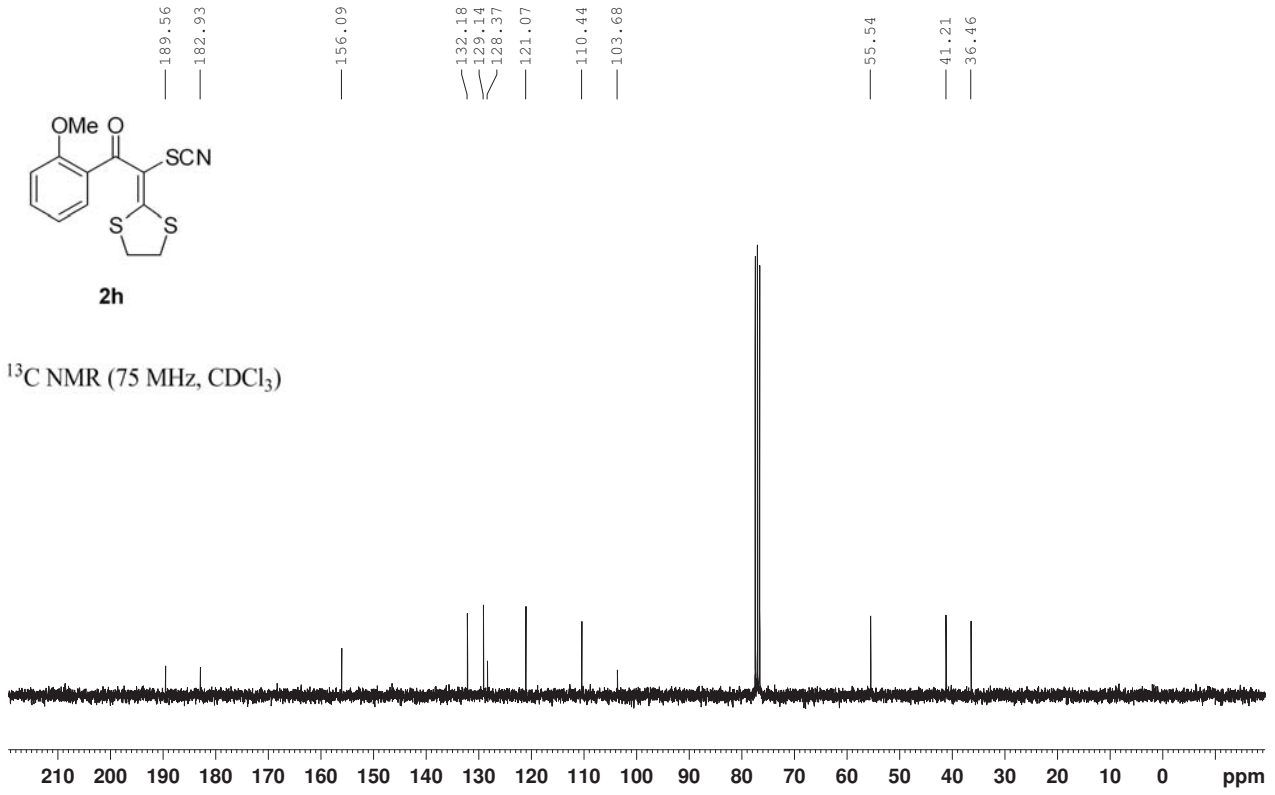

7.59
7.56
7.28
7.27
7.25
3.68
3.67
3.66
3.64
3.57
3.56
3.55
3.53
2.42
0.00
O
SCN
H3C
S
S
2f
1H NMR (300 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.02
2.14
2.10
2.05
3.00

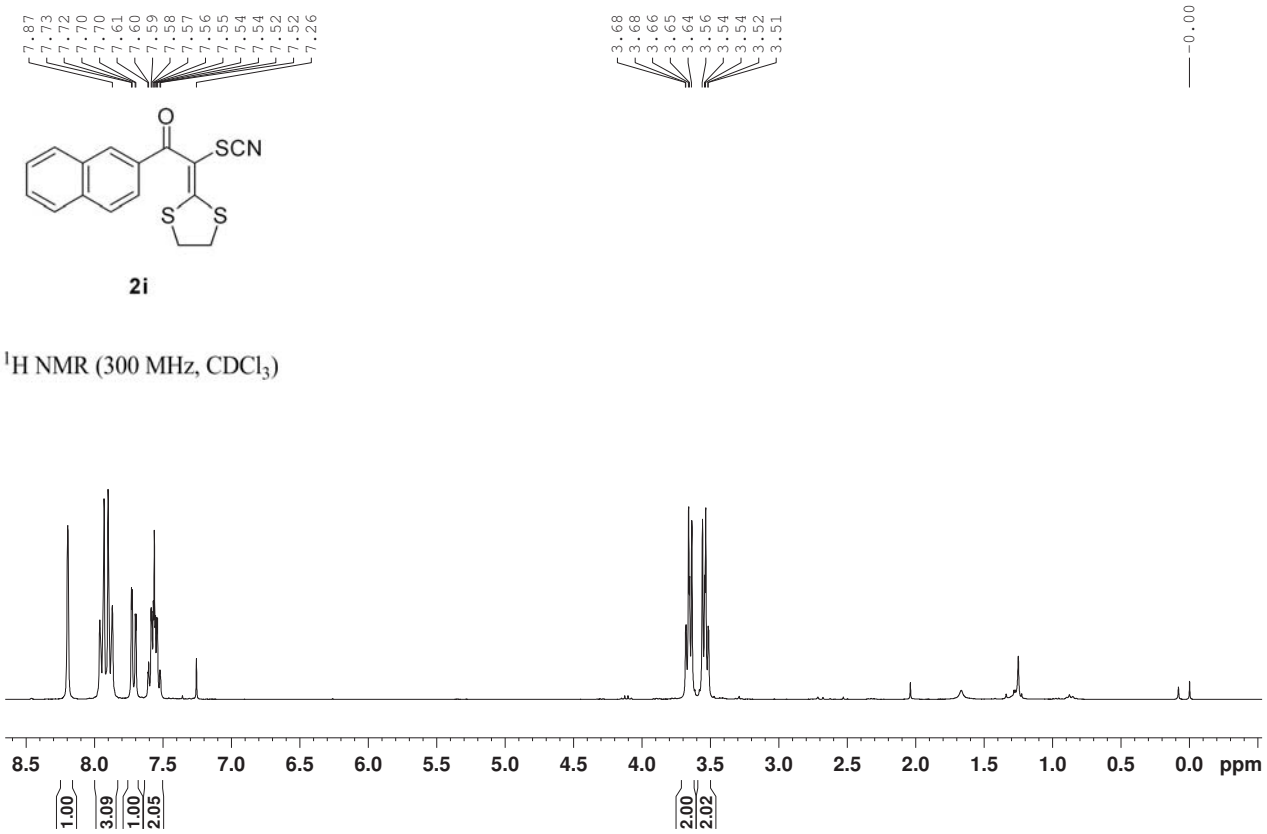

189.75
185.35
142.25
135.01
128.87
128.47
109.80
100.91
77.52
77.09
76.67
41.32
36.57
21.67
O
SCN
H3C
S
S
2f
13C NMR (75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

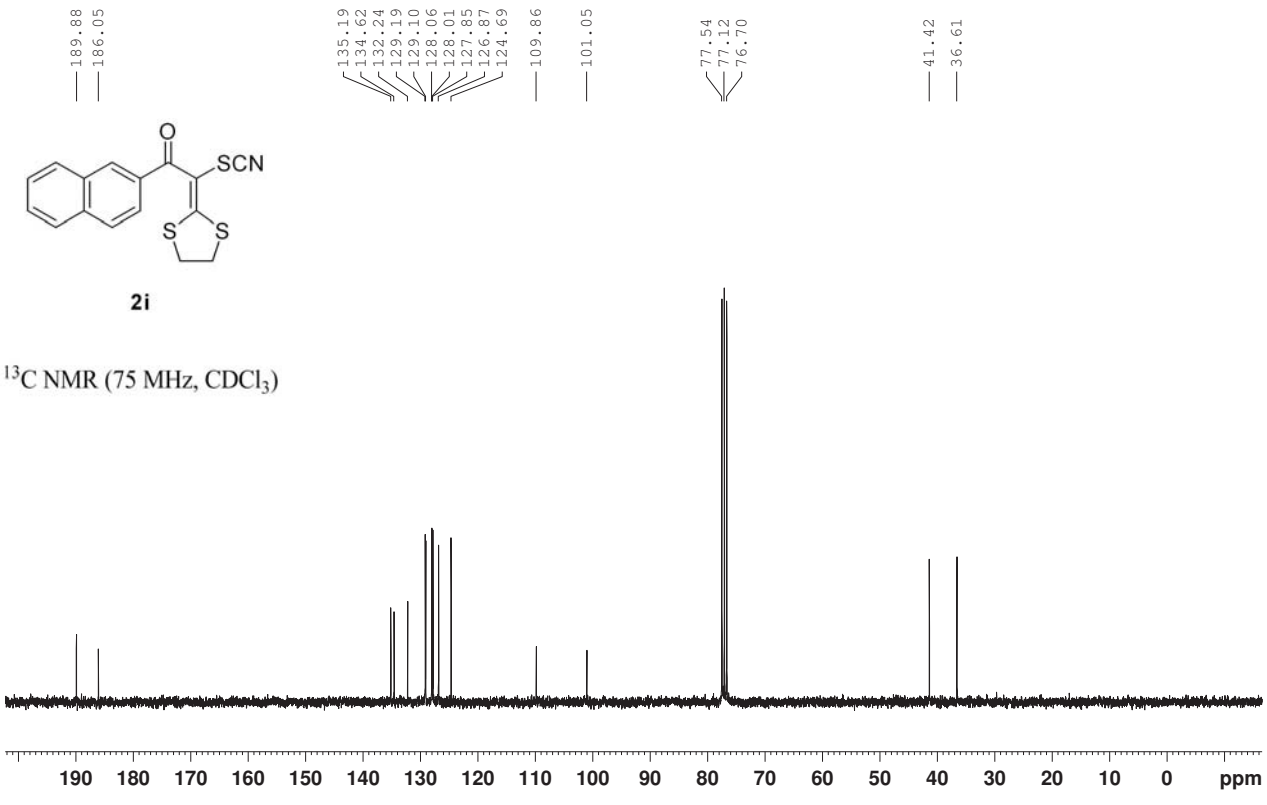

7.72
7.69
7.27
6.97
6.94
3.87
3.67
3.67
3.65
3.64
3.63
3.62
3.57
3.57
3.56
3.55
3.53
3.52
0.00
O
SCN
MeO
S
S
2g
^{1}H NMR (300 MHz, $CDCl_3$)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.99
1.99
3.00
2.02
1.99

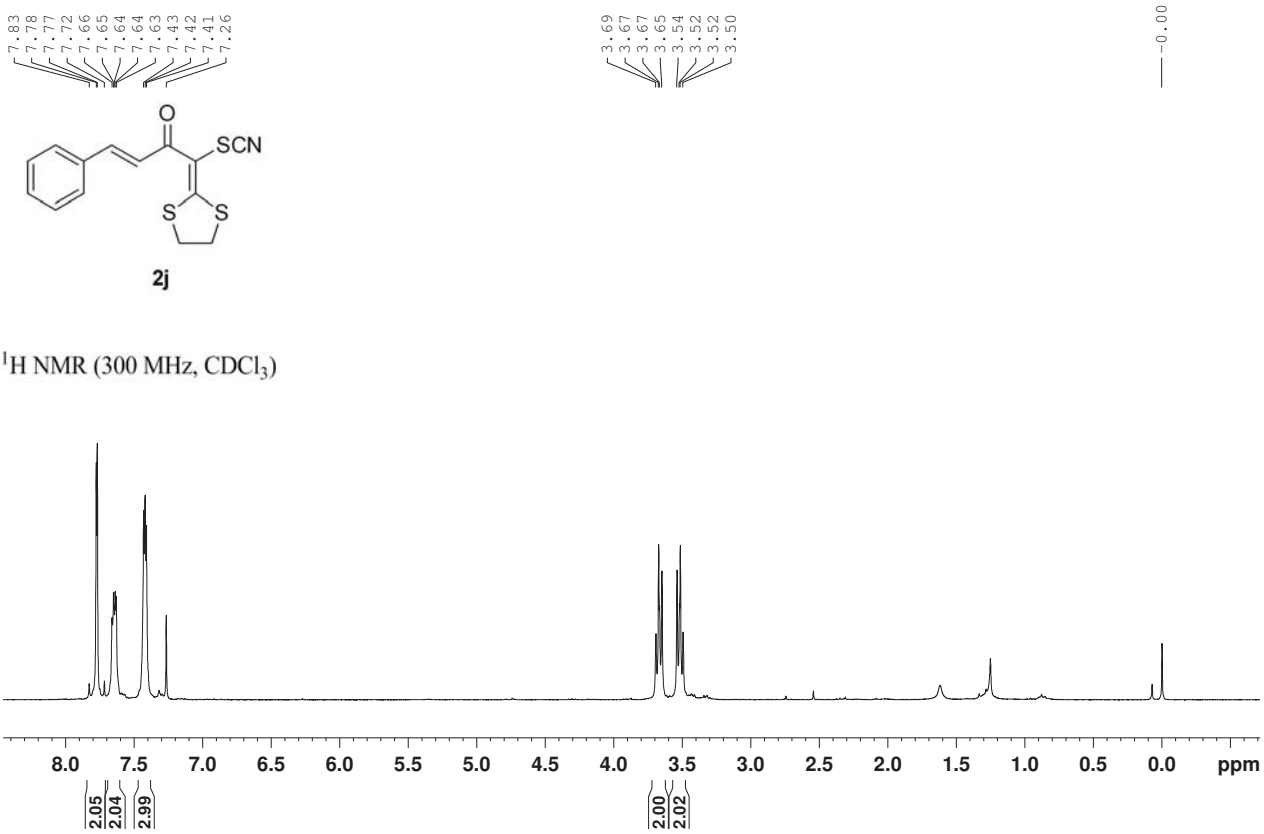

188.68
184.55
162.50
130.93
129.96
113.48
109.84
100.77
77.54
77.12
76.69
55.50
41.22
36.61
O
SCN
MeO
S
S
2g
^{13}C NMR (75 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

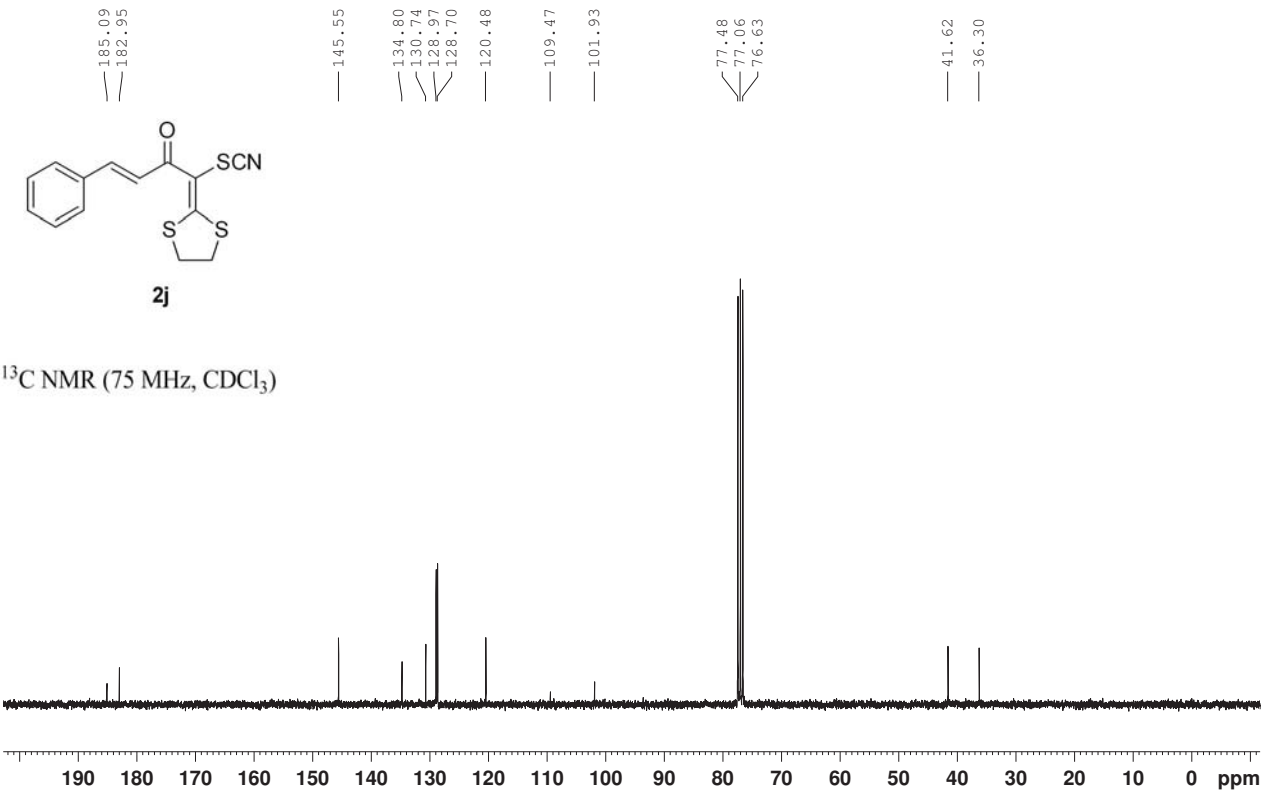

7.43
7.38
7.37
7.35
7.35
7.27
7.07
7.05
7.02
6.94
6.92
3.85
3.70
3.69
3.68
3.66
3.57
3.55
3.54
3.52
3.52
2.55
0.00
OMe
O
SCN
S
S
2h
^{1}H NMR (300 MHz, $CDCl_3$)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
0.99
1.02
1.00
3.00
2.00
2.00

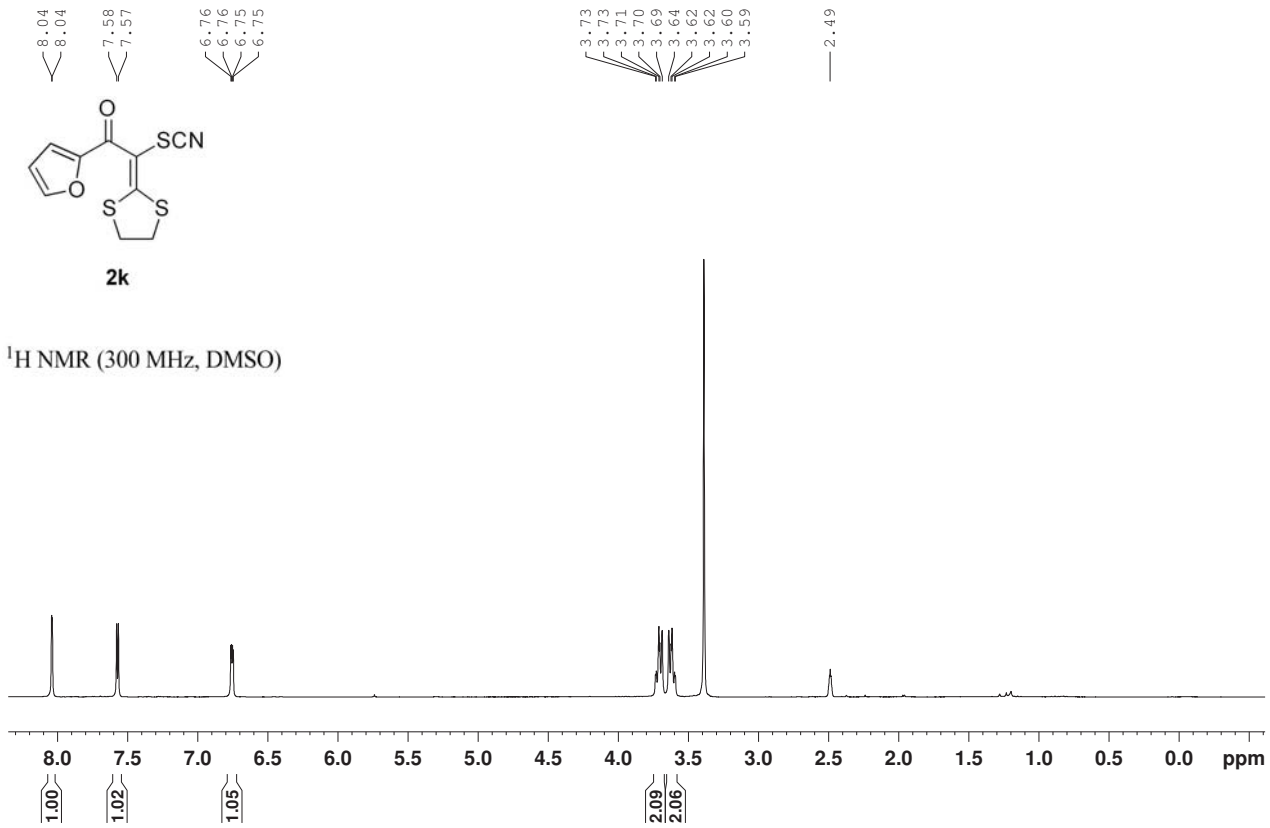

189.56
182.93
156.09
132.18
129.14
128.37
121.07
110.44
103.68
55.54
41.21
36.46
OMe
O
SCN
S
S
2h
^{13}C NMR (75 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

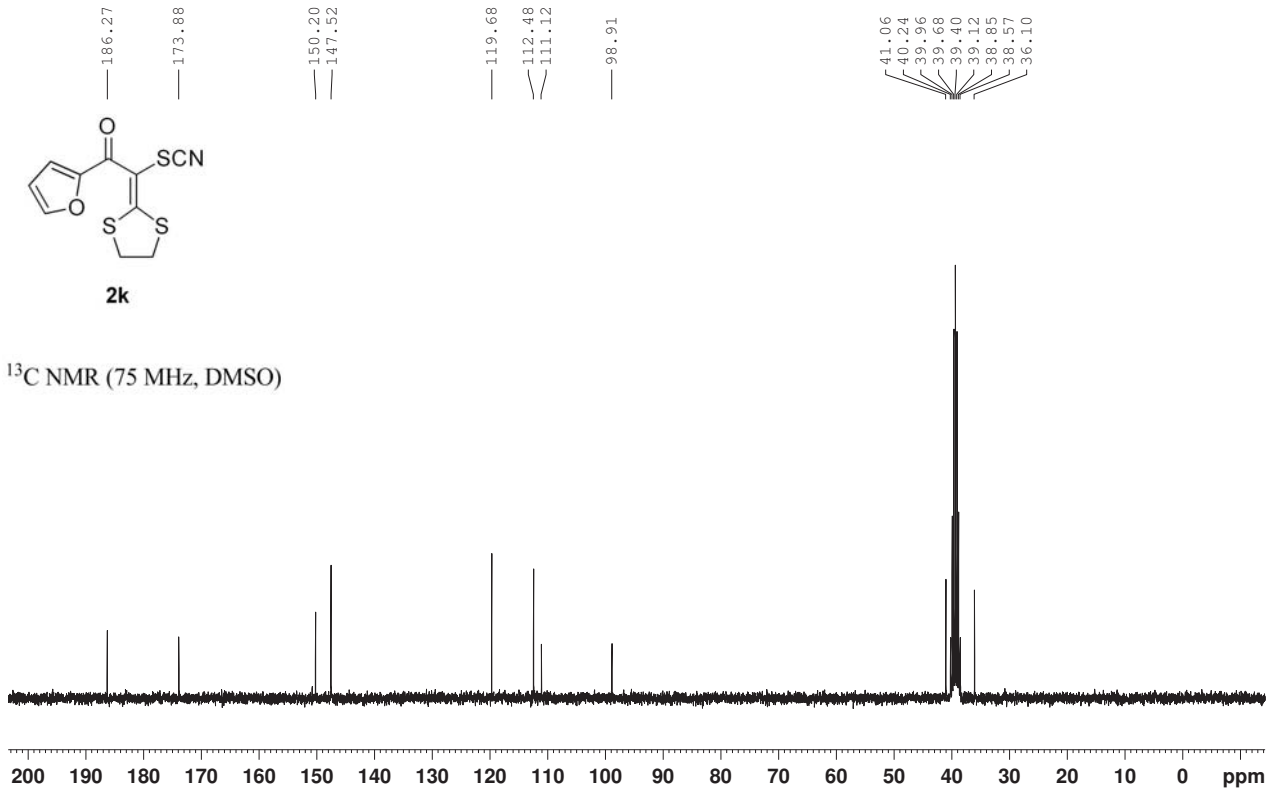

7.87
7.73
7.72
7.70
7.70
7.61
7.60
7.59
7.58
7.57
7.56
7.55
7.54
7.54
7.52
7.52
7.26
3.68
3.68
3.66
3.65
3.64
3.56
3.54
3.54
3.52
3.51
0.00
O
SCN
S
S
2i
1H NMR (300 MHz, CDCl3)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
3.09
1.00
2.05
2.00
2.02

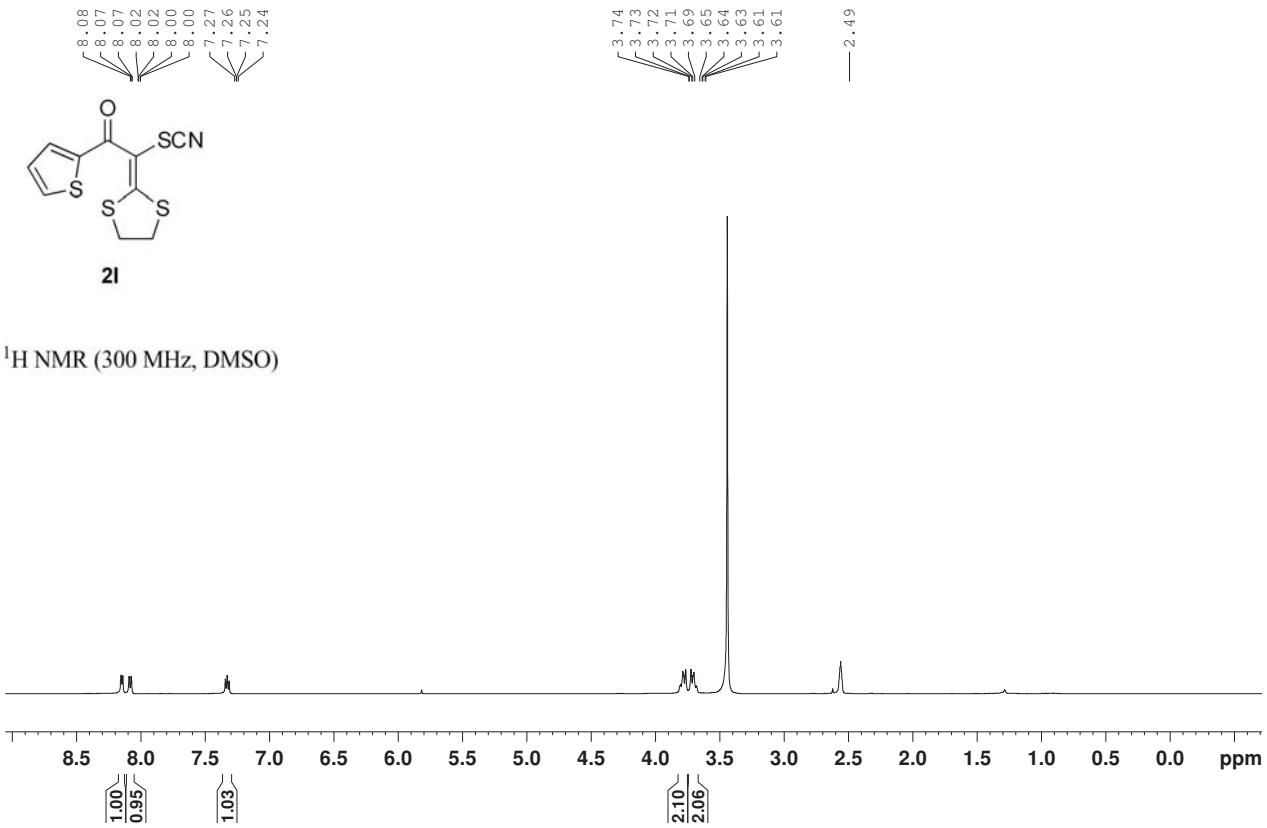

189.88
186.05
135.19
134.62
132.24
129.19
129.10
128.06
128.01
127.85
126.87
124.69
109.86
101.05
77.54
77.12
76.70
41.42
36.61
O
SCN
S
S
2i
13C NMR (75 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

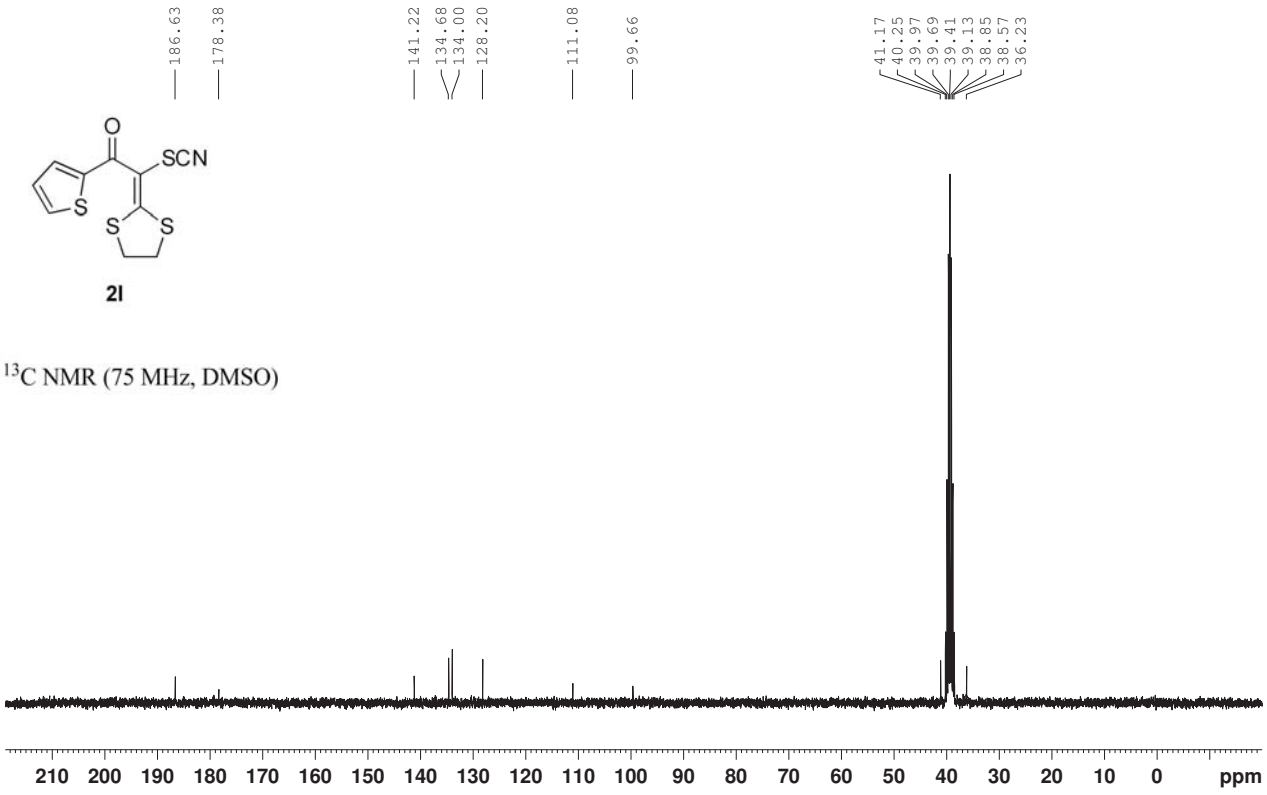

7.83
7.78
7.77
7.72
7.66
7.65
7.64
7.64
7.63
7.43
7.42
7.41
7.26
3.69
3.67
3.67
3.65
3.54
3.52
3.52
3.50
0.00
O
SCN
S
S
2j
1H NMR (300 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.05
2.04
2.99
2.00
2.02

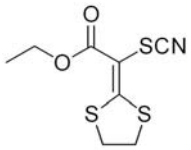

185.09
182.95
145.55
134.80
130.74
128.97
128.70
120.48
109.47
101.93
77.48
77.06
76.63
41.62
36.30
O
SCN
S
S
2j
13C NMR (75 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.04
8.04
7.58
7.57
6.76
6.76
6.75
6.75
3.73
3.73
3.71
3.70
3.69
3.64
3.62
3.62
3.60
3.59
2.49
O
SCN
O
S
S
2k
1H NMR (300 MHz, DMSO)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.02
1.05
2.09
2.06


186.27
173.88
150.20
147.52
119.68
112.48
111.12
98.91
41.06
40.24
39.96
39.68
39.40
39.12
38.85
38.57
36.10
O
SCN
O
S
S
2k
13C NMR (75 MHz, DMSO)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

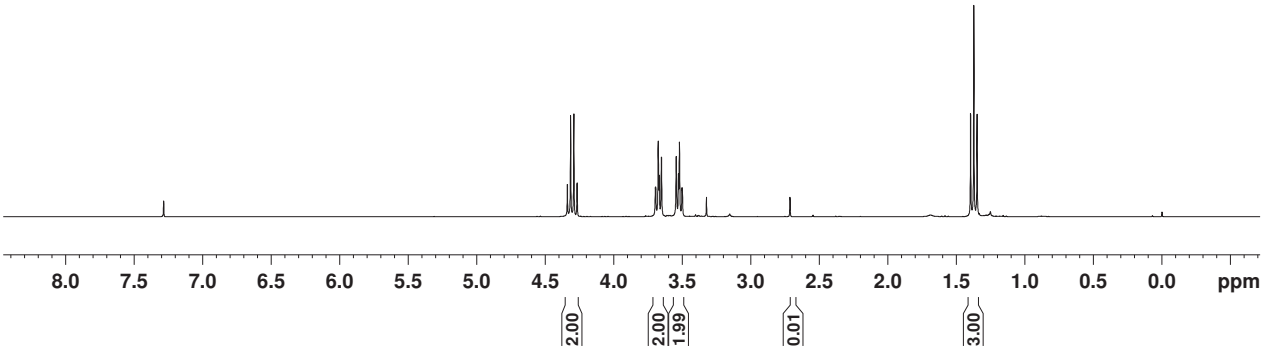

8.08
8.07
8.07
8.02
8.02
8.00
8.00
7.27
7.26
7.25
7.24
3.74
3.73
3.72
3.71
3.69
3.65
3.64
3.63
3.61
3.61
2.49
O
SCN
S
S
S
2l
1H NMR (300 MHz, DMSO)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
0.95
1.03
2.10
2.06

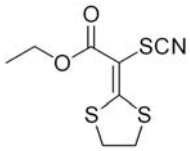

186.63
178.38
141.22
134.68
134.00
128.20
111.08
99.66
41.17
40.25
39.97
39.69
39.41
39.13
38.85
38.57
36.23
O
SCN
S
S
S
2l
13C NMR (75 MHz, DMSO)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



2m

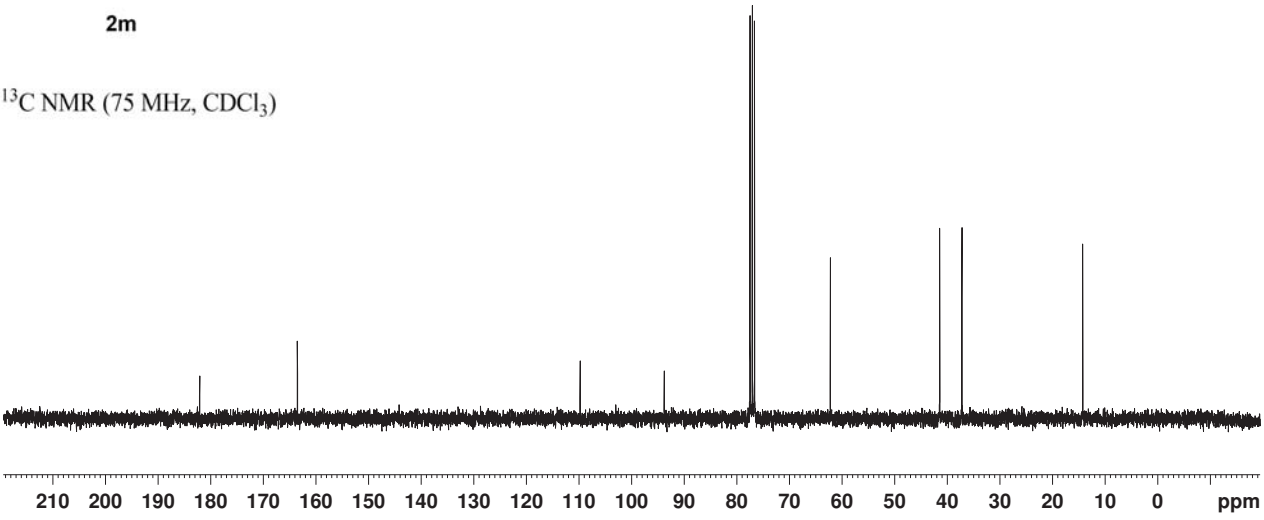
^{1}H NMR (300 MHz, $CDCl_3$)

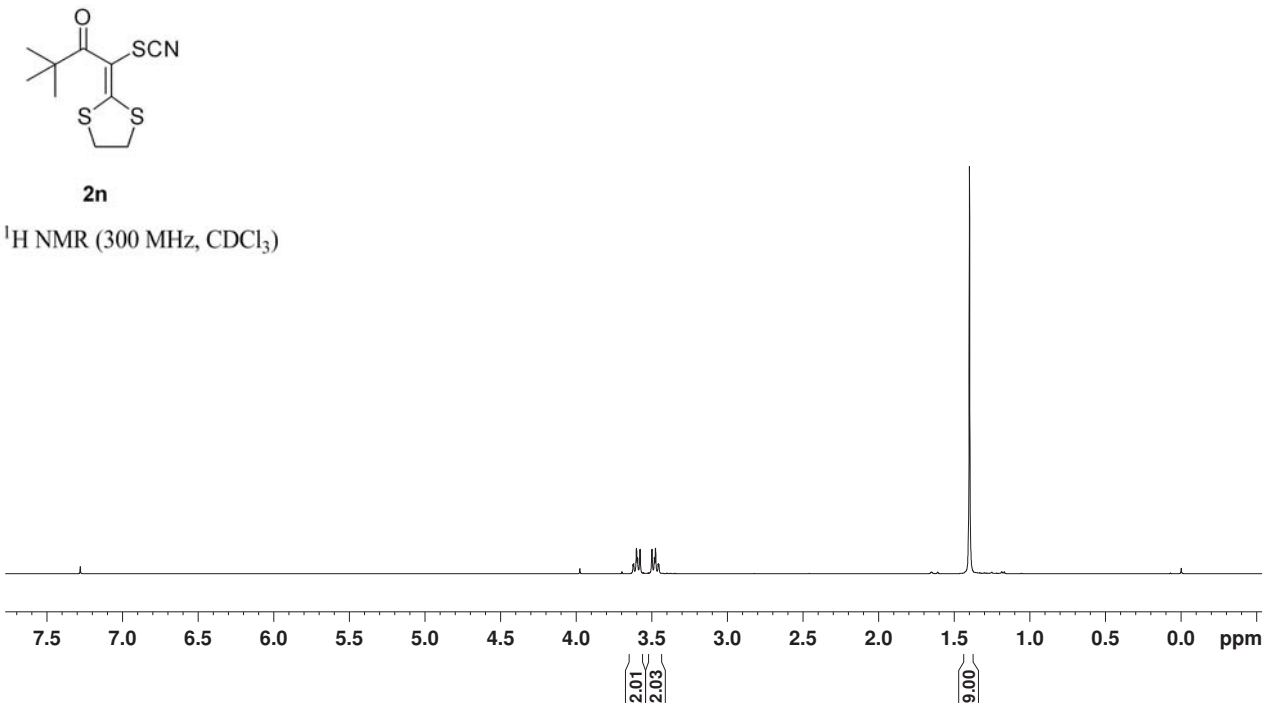




2m

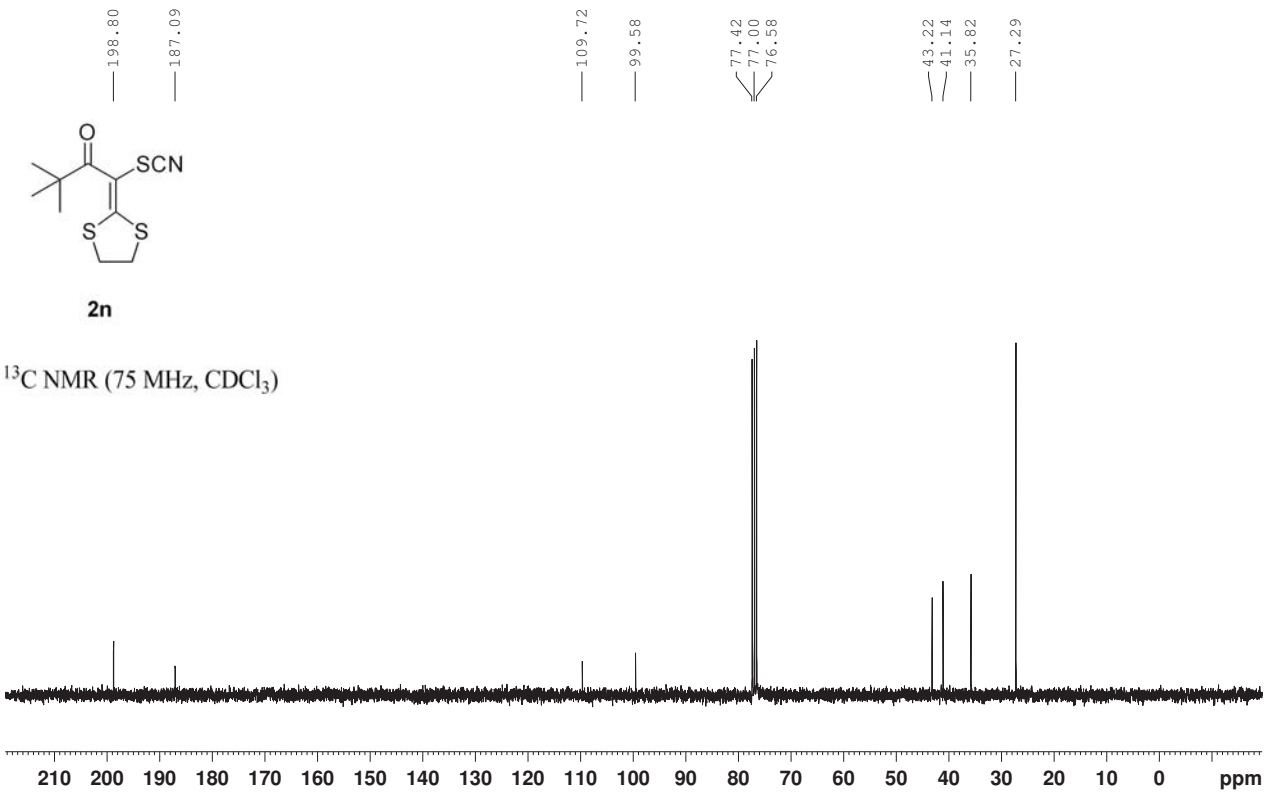
^{13}C NMR (75 MHz, $CDCl_3$)





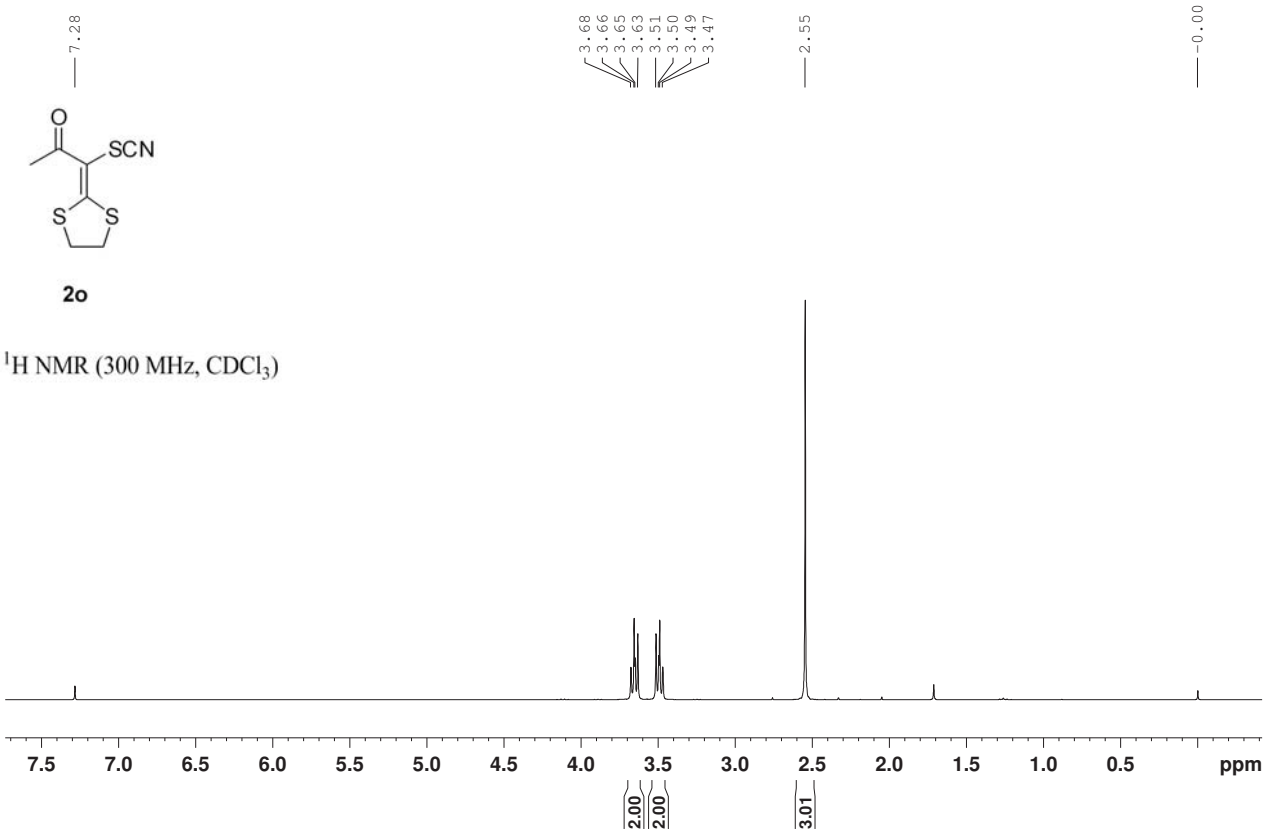
2n

^{1}H NMR (300 MHz, $CDCl_3$)



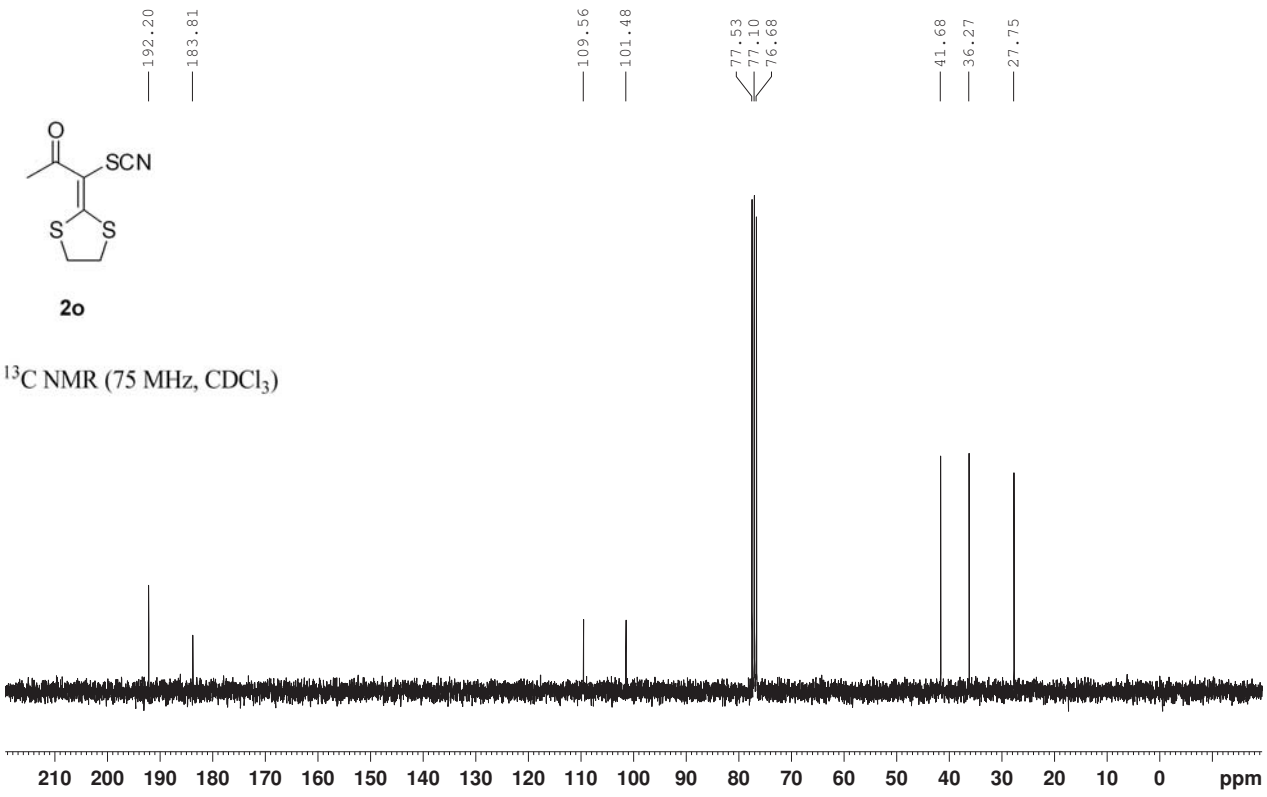
2n

^{13}C NMR (75 MHz, $CDCl_3$)



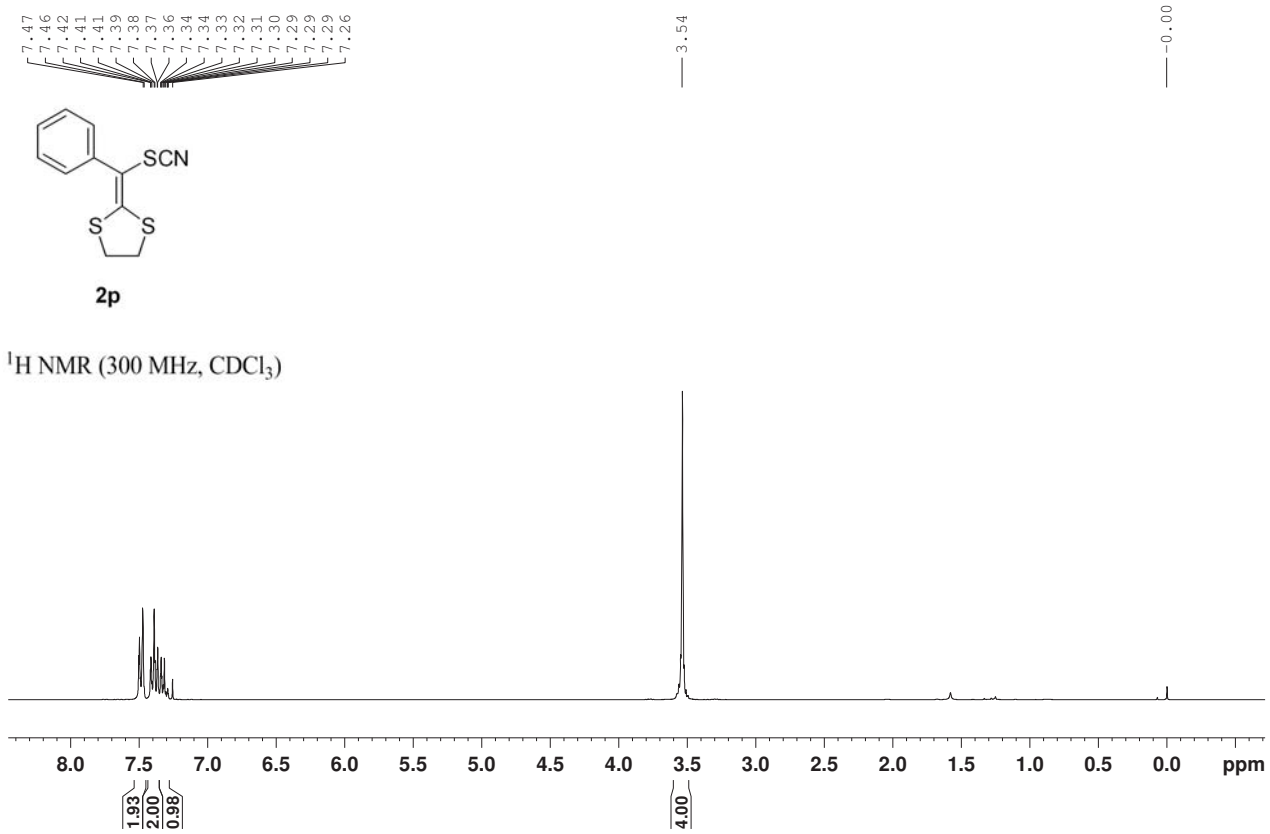
2o

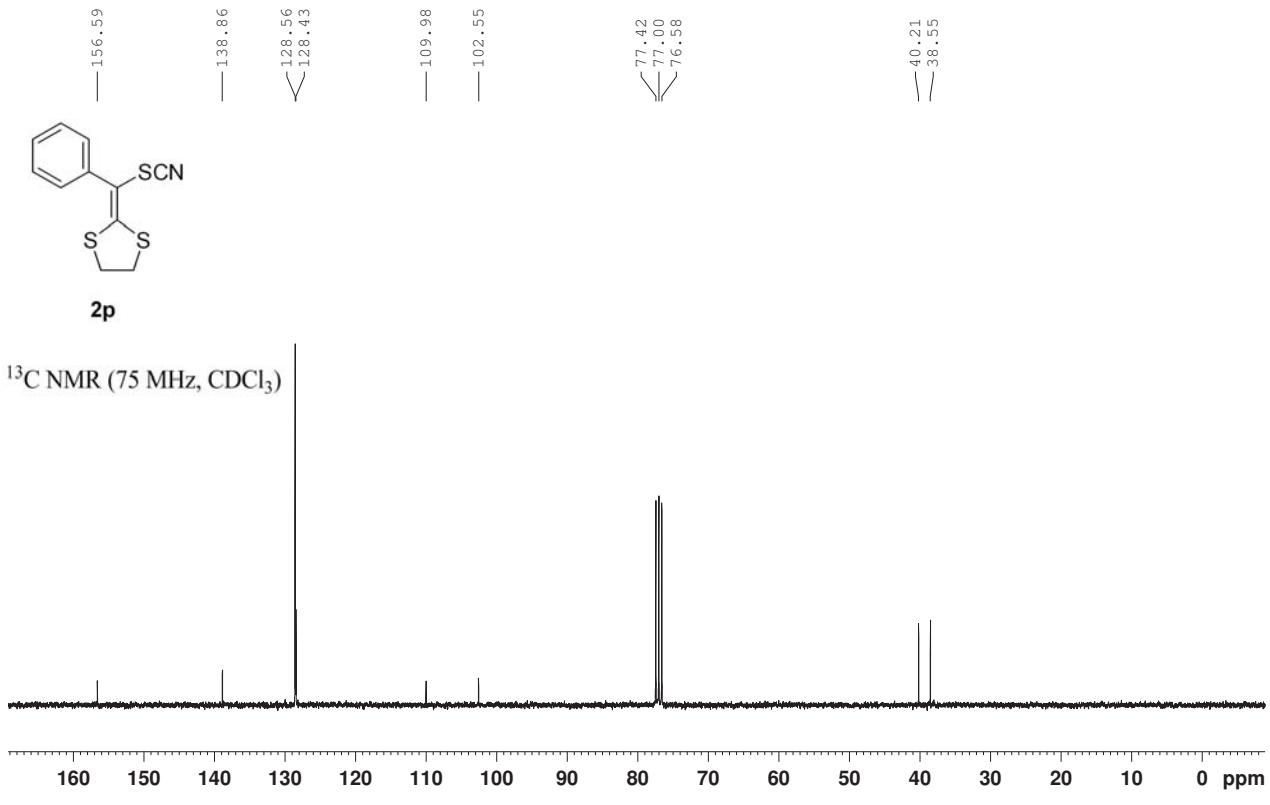
^{1}H NMR (300 MHz, $CDCl_3$)

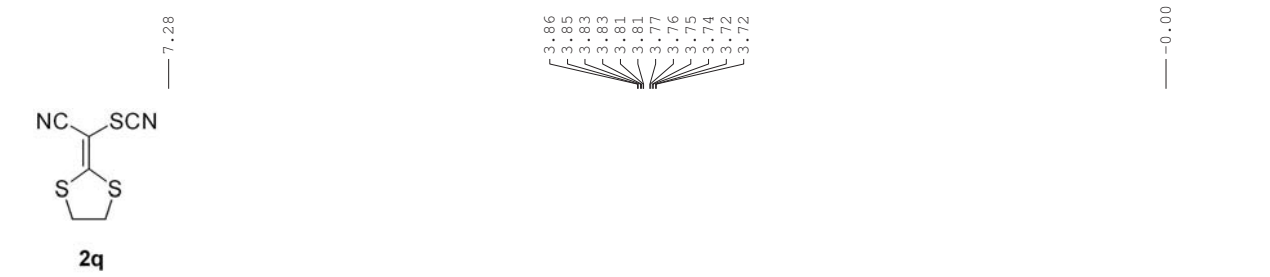


2o

^{13}C NMR (75 MHz, $CDCl_3$)

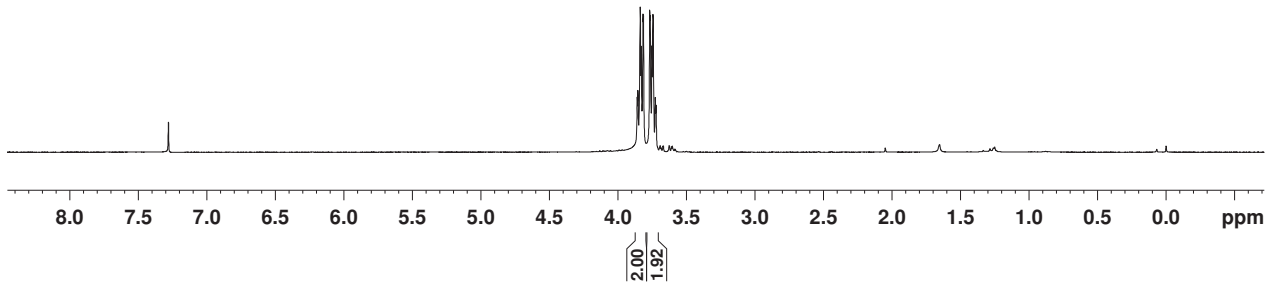

7.47
7.46
7.42
7.41
7.41
7.39
7.38
7.37
7.36
7.34
7.34
7.33
7.32
7.31
7.30
7.29
7.29
7.29
7.26
3.54
0.00
SCN
S
S
2p
1H NMR (300 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.93
2.00
0.98
4.00

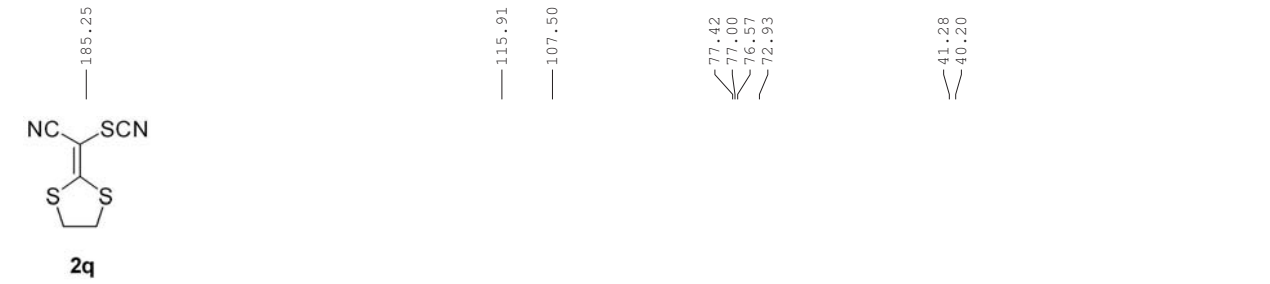

156.59
138.86
128.56
128.43
109.98
102.55
77.42
77.00
76.58
40.21
38.55
SCN
S
S
2p
13C NMR (75 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



2q

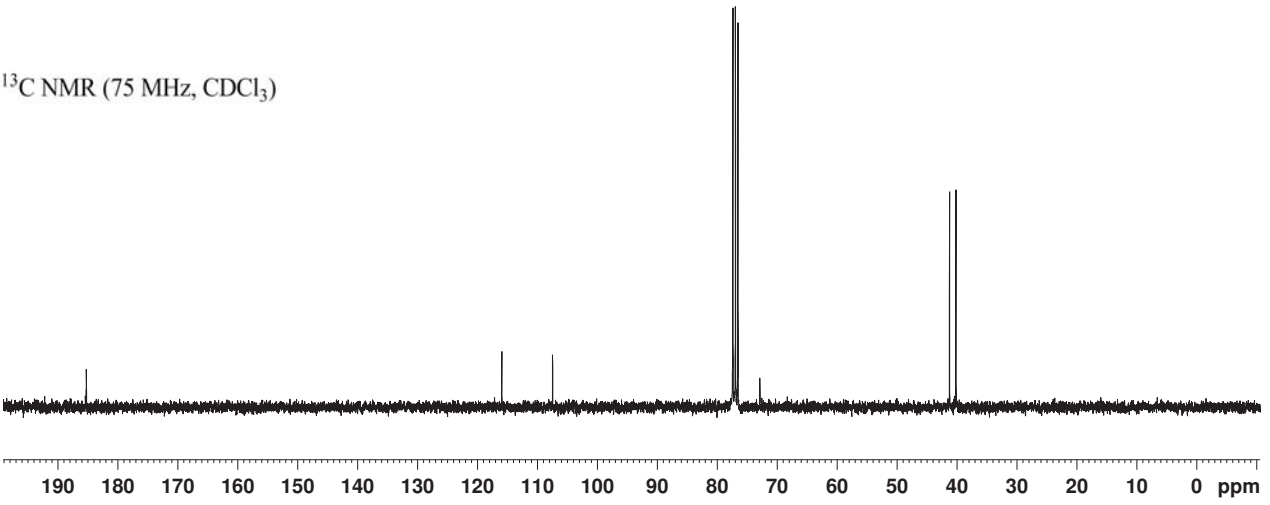
^{1}H NMR (300 MHz, $CDCl_3$)

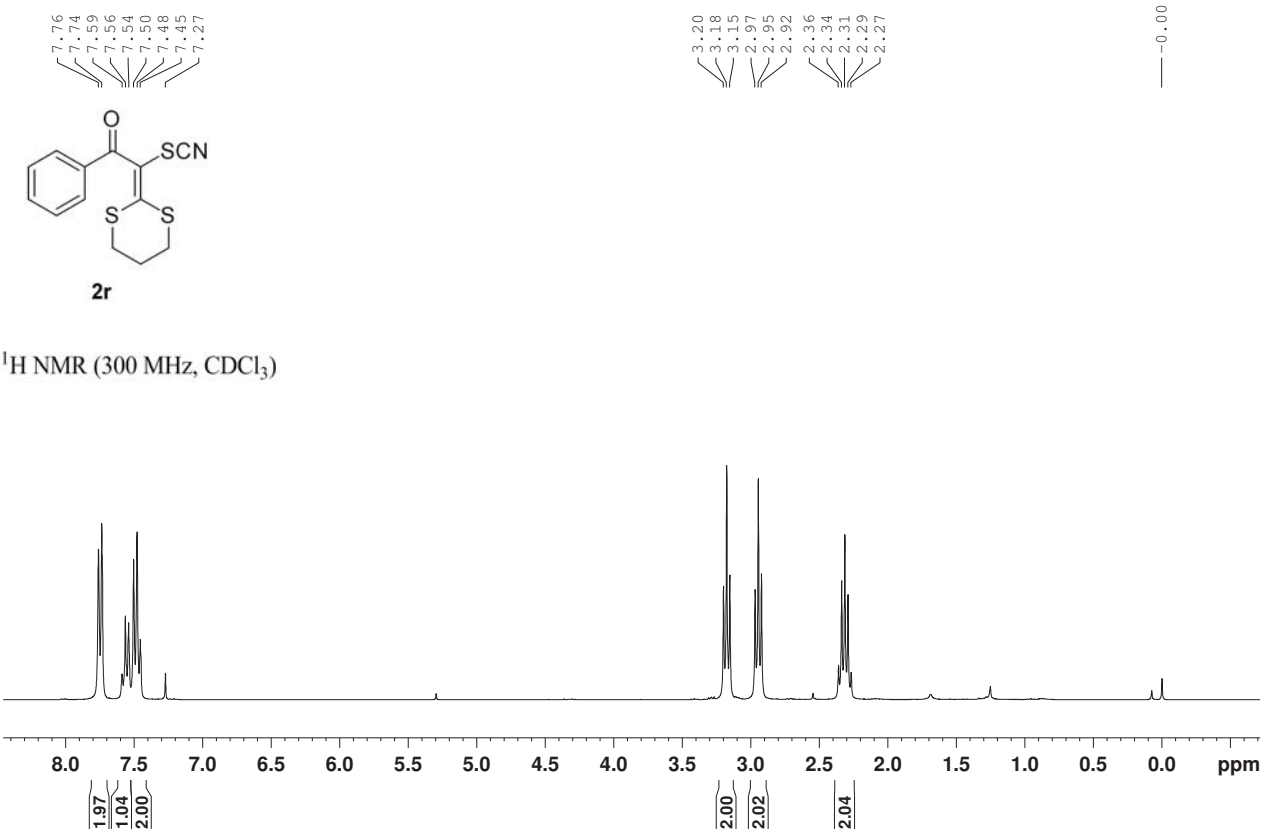


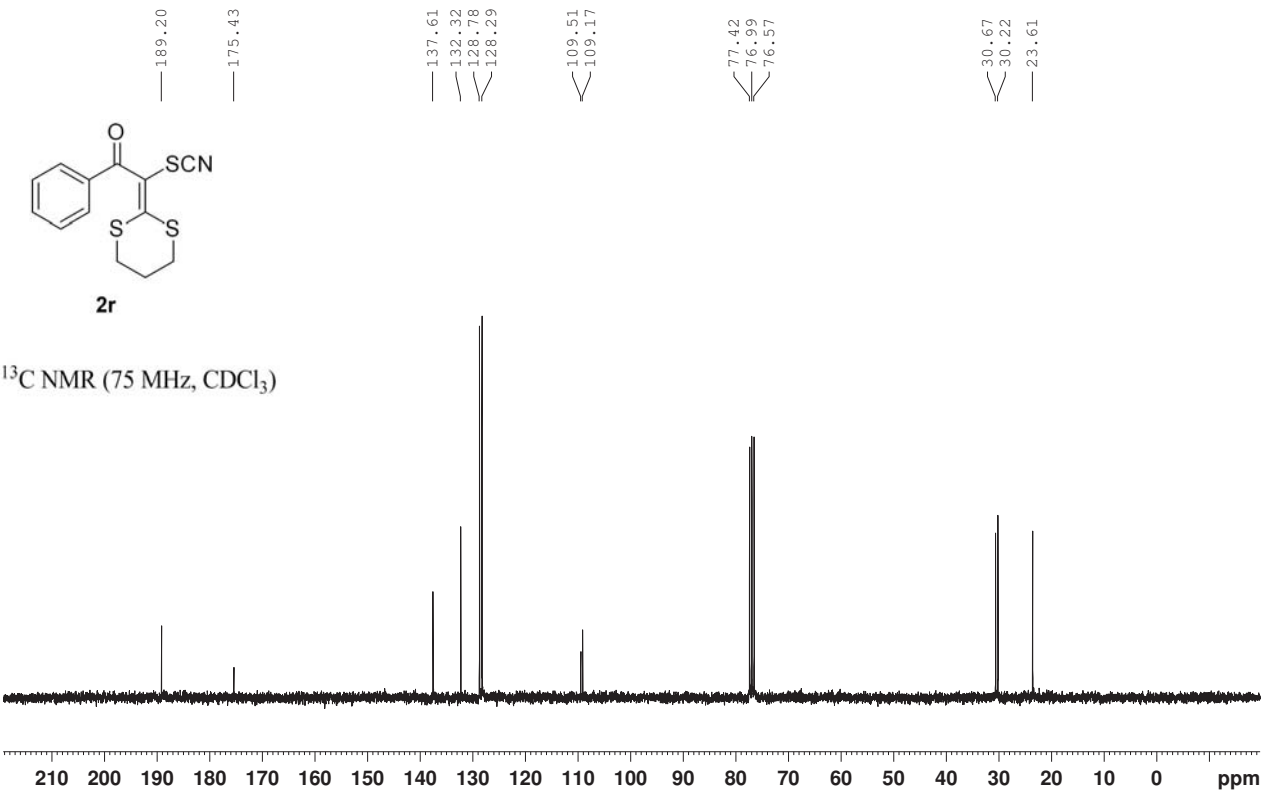


2q

^{13}C NMR (75 MHz, $CDCl_3$)

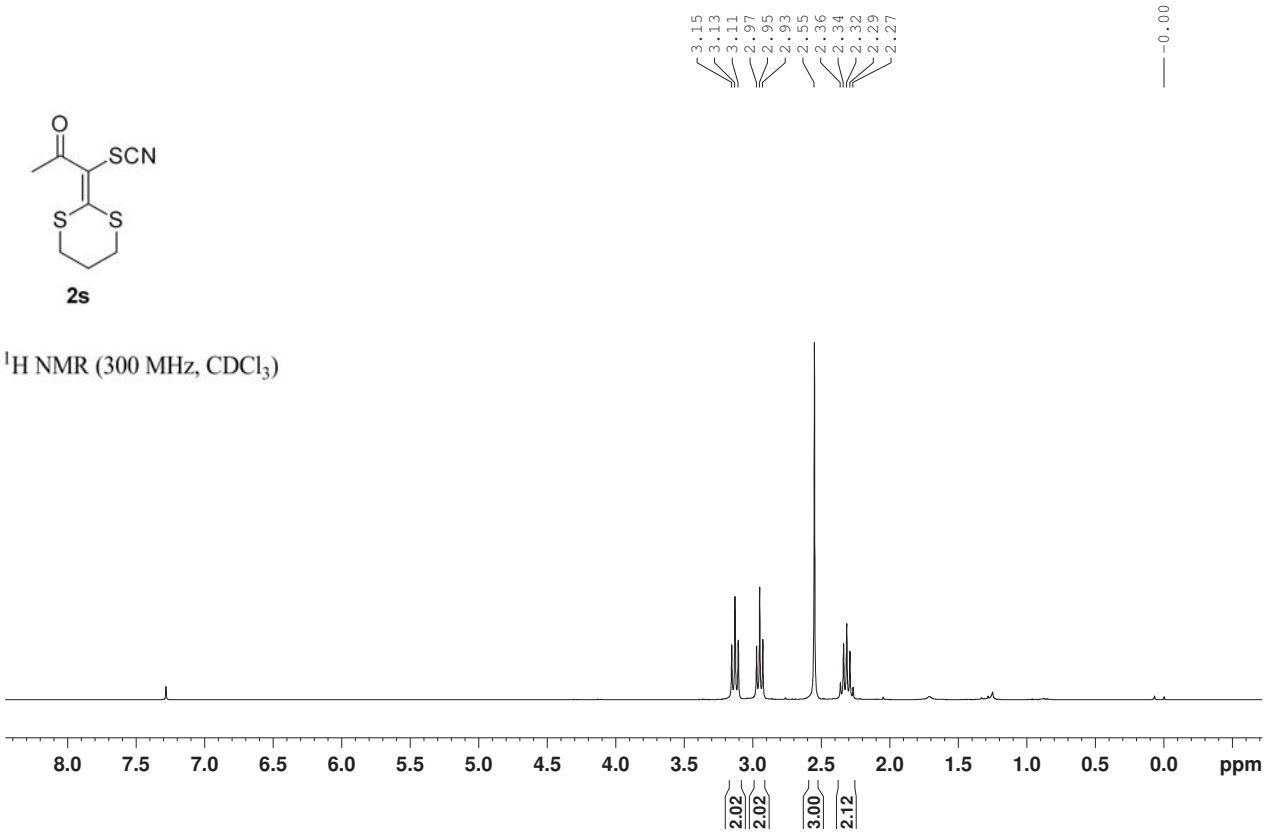



7.76
7.74
7.59
7.56
7.54
7.50
7.48
7.45
7.27
3.20
3.18
3.15
2.97
2.95
2.92
2.36
2.34
2.31
2.29
2.27
0.00
O
SCN
S
S
2r
1H NMR (300 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.97
1.04
2.00
2.00
2.02
2.04


189.20
175.43
137.61
132.32
128.78
128.29
109.51
109.17
77.42
76.99
76.57
30.67
30.22
23.61
O
SCN
S
S
2r
13C NMR (75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

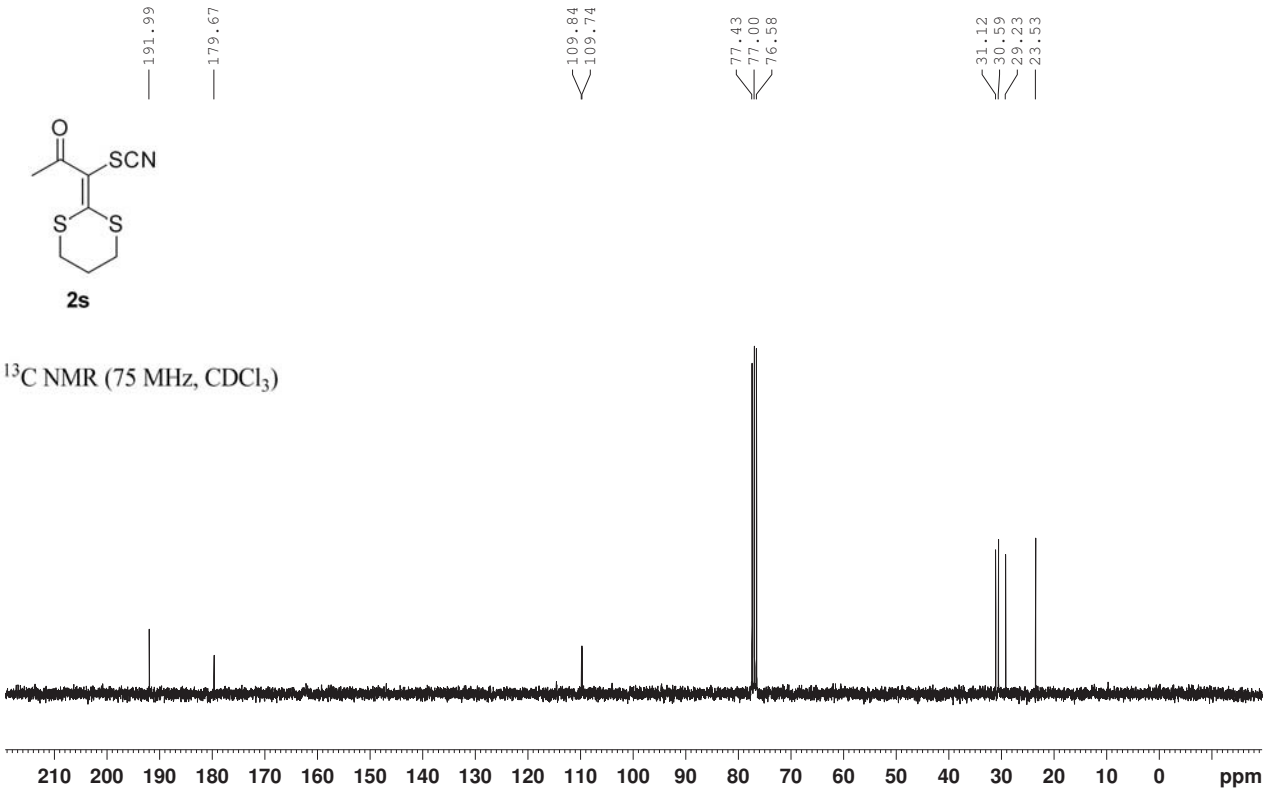
2s

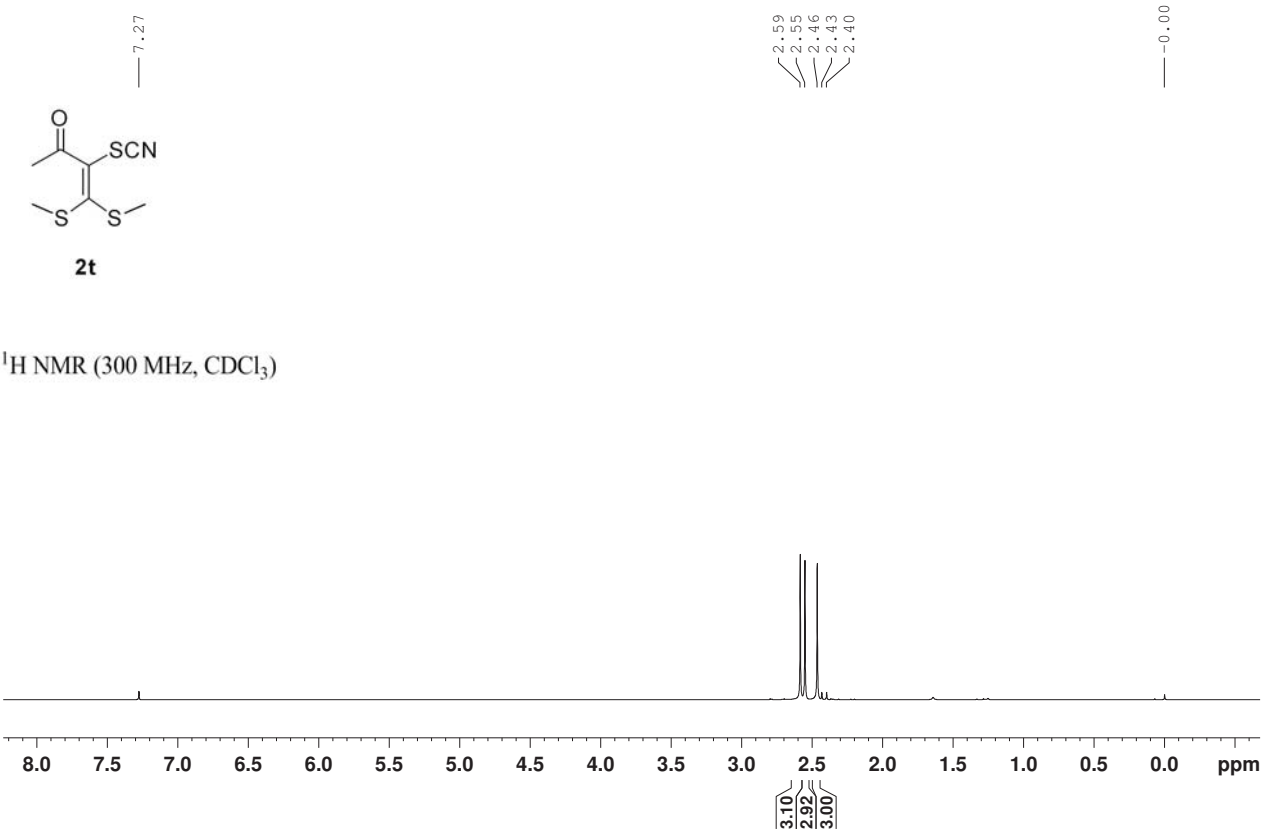
^{1}H NMR (300 MHz, $CDCl_3$)



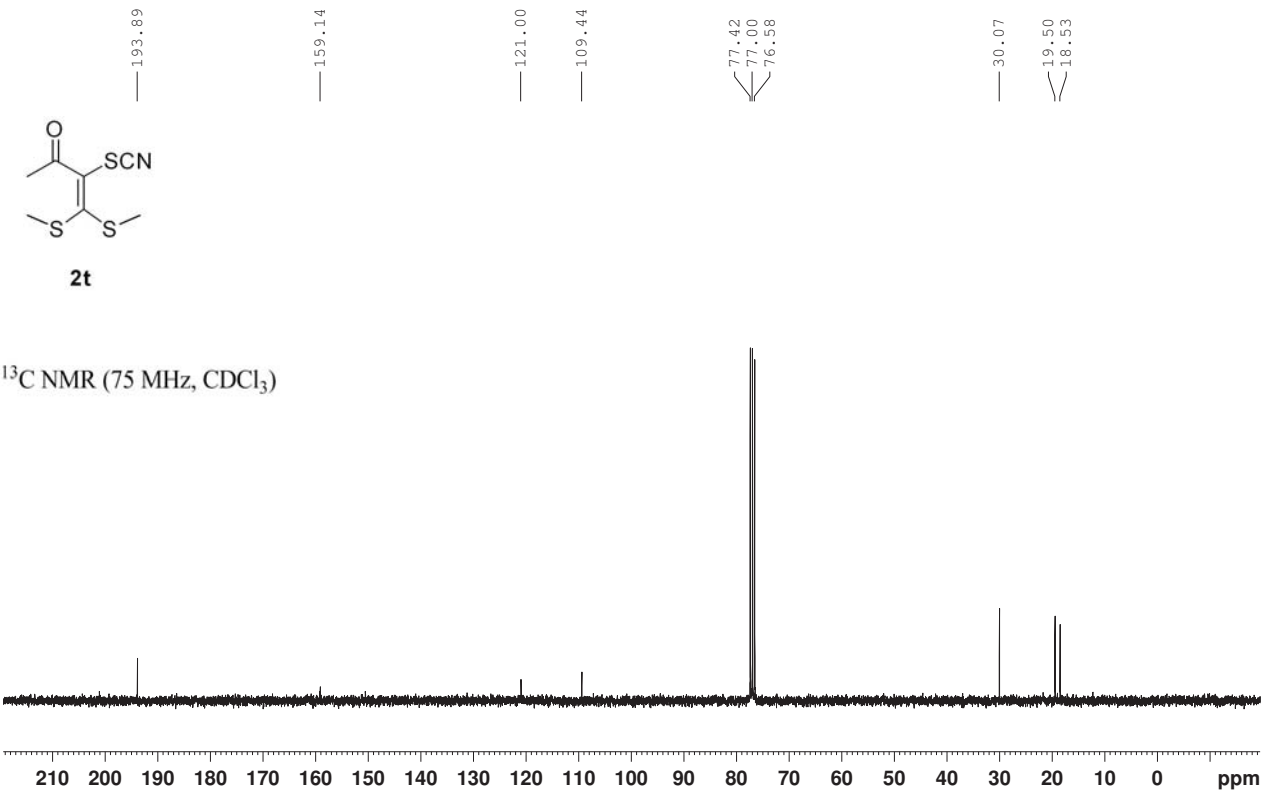
2s

^{13}C NMR (75 MHz, $CDCl_3$)

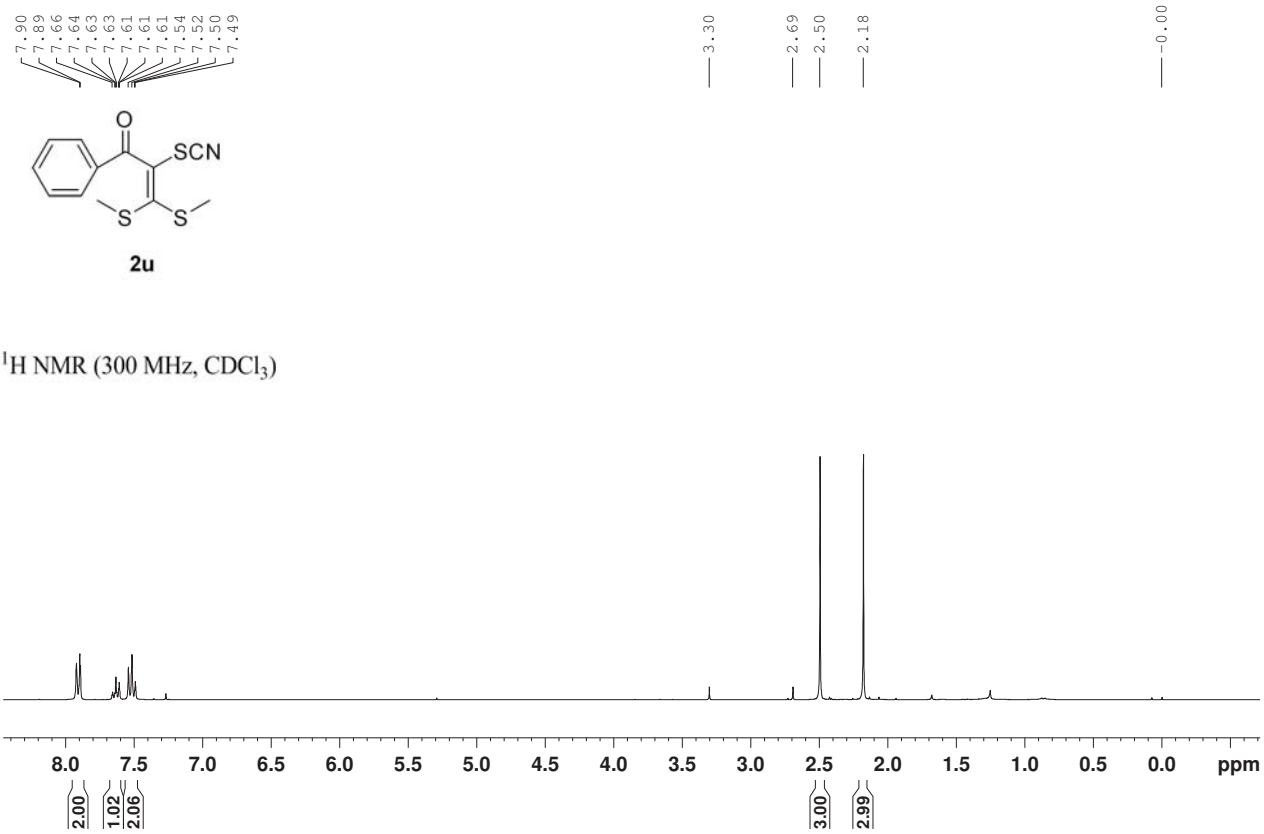


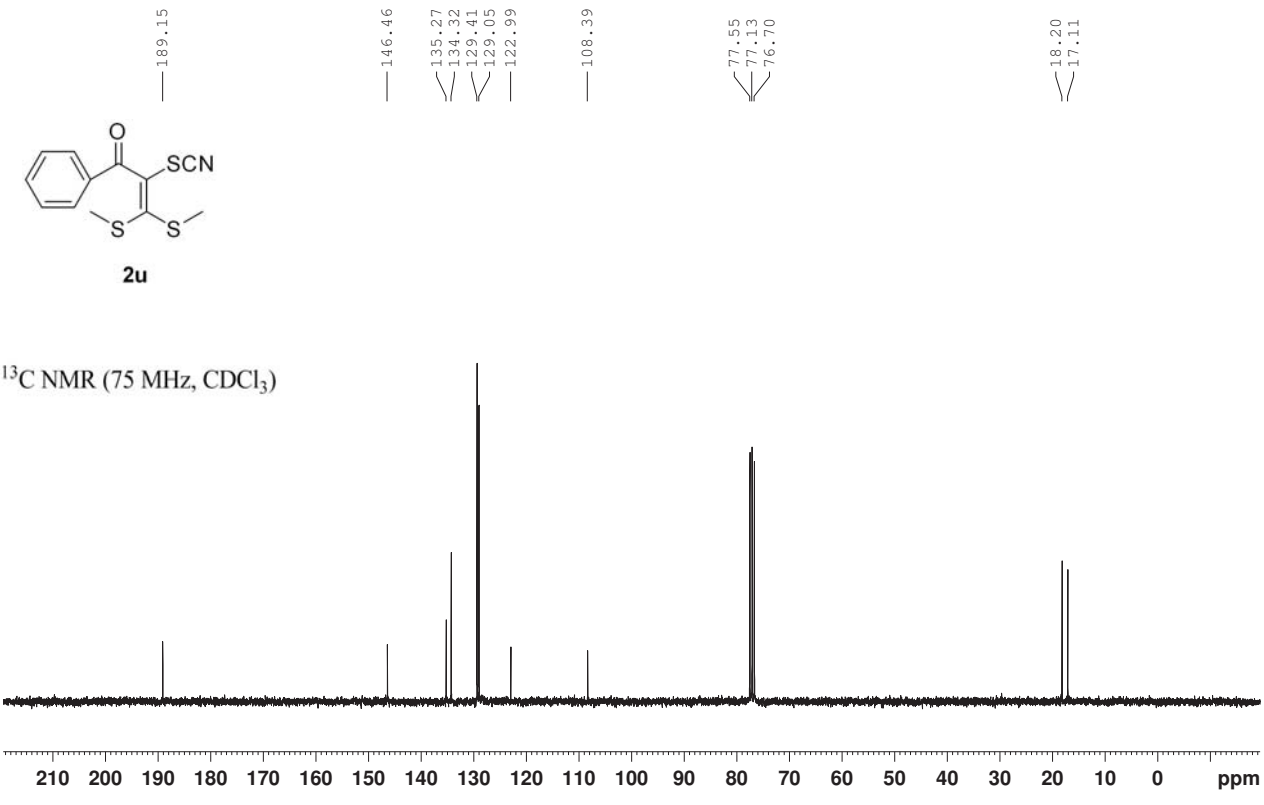


^{1}H NMR (300 MHz, $CDCl_3$)



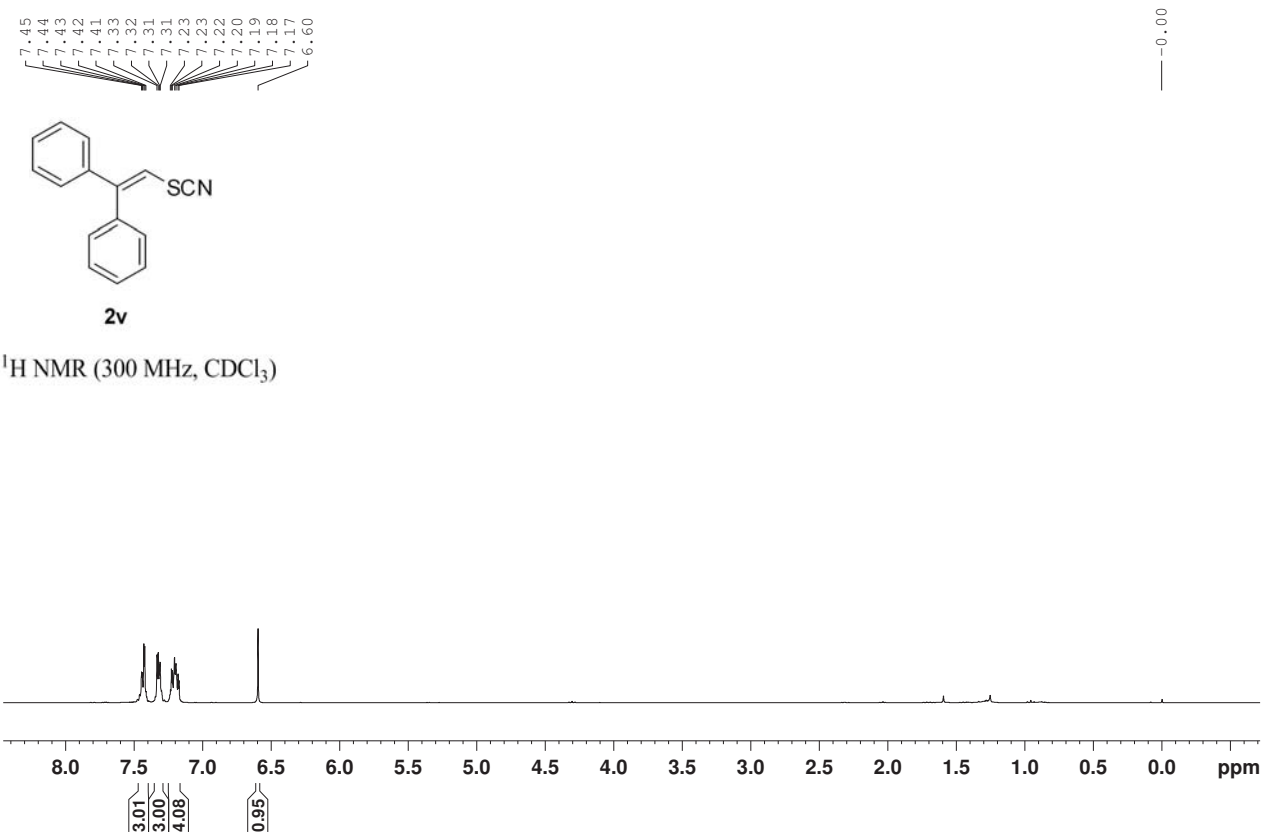
^{13}C NMR (75 MHz, $CDCl_3$)

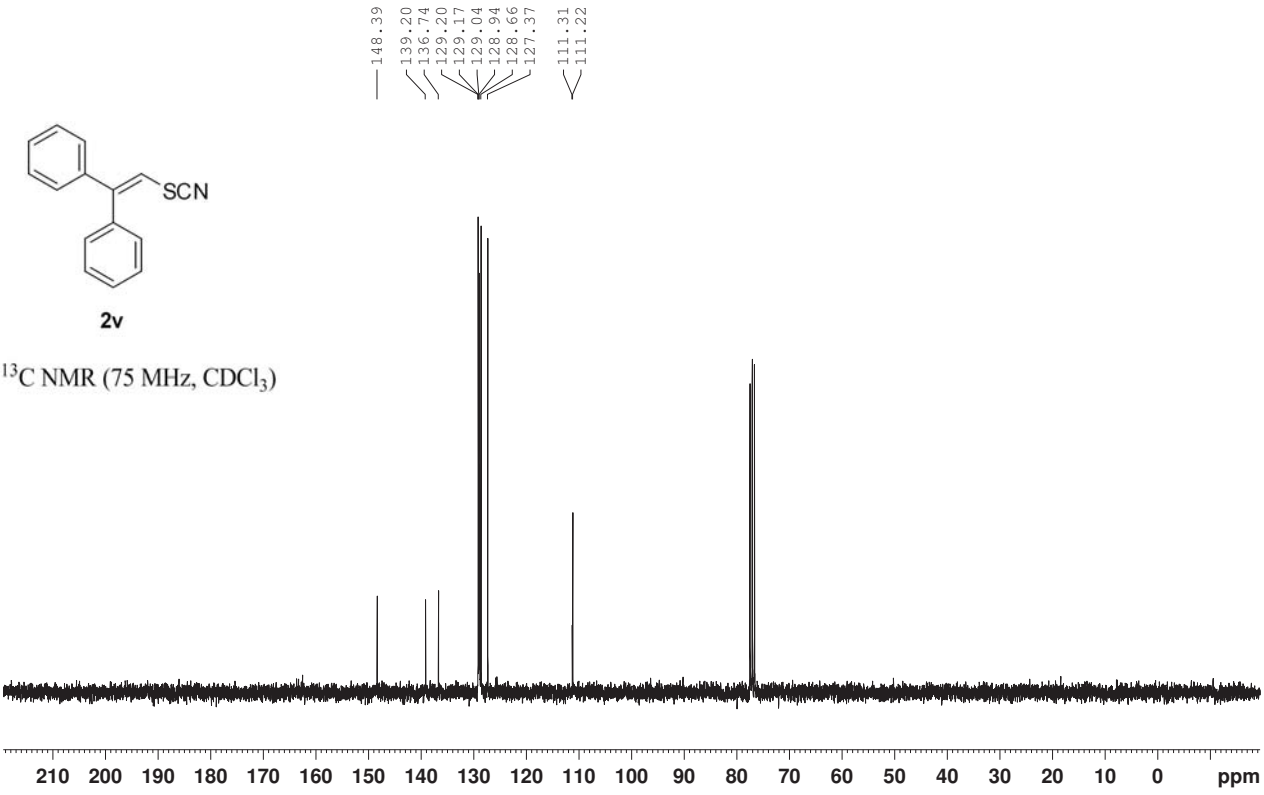

7.90
7.89
7.66
7.64
7.63
7.63
7.61
7.61
7.61
7.54
7.52
7.50
7.49
3.30
2.69
2.50
2.18
0.00
O
SCN
S
S
2u
1H NMR (300 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
1.02
2.06
3.00
2.99


189.15
146.46
135.27
134.32
129.41
129.05
122.99
108.39
77.55
77.13
76.70
18.20
17.11
O
SCN
S
S
2u
13C NMR (75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

2v

^{1}H NMR (300 MHz, $CDCl_3$)



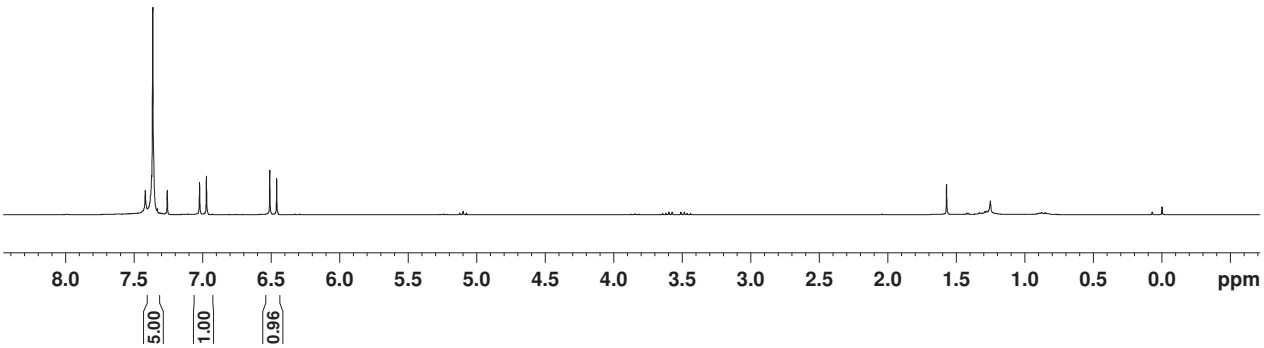


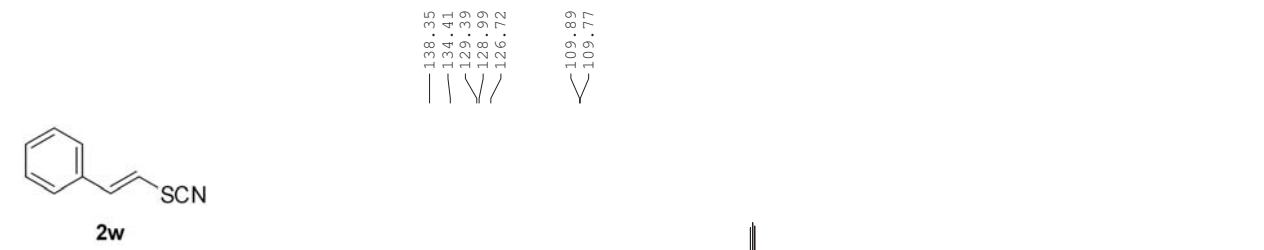
2v

^{13}C NMR (75 MHz, $CDCl_3$)

2w

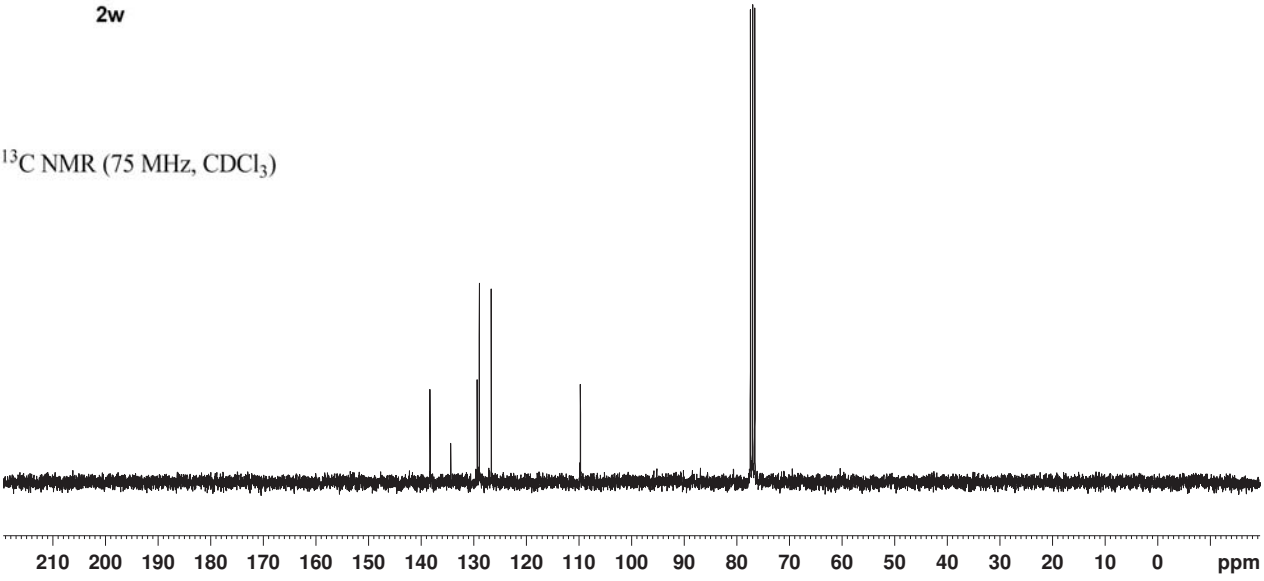
^{1}H NMR (300 MHz, $CDCl_3$)

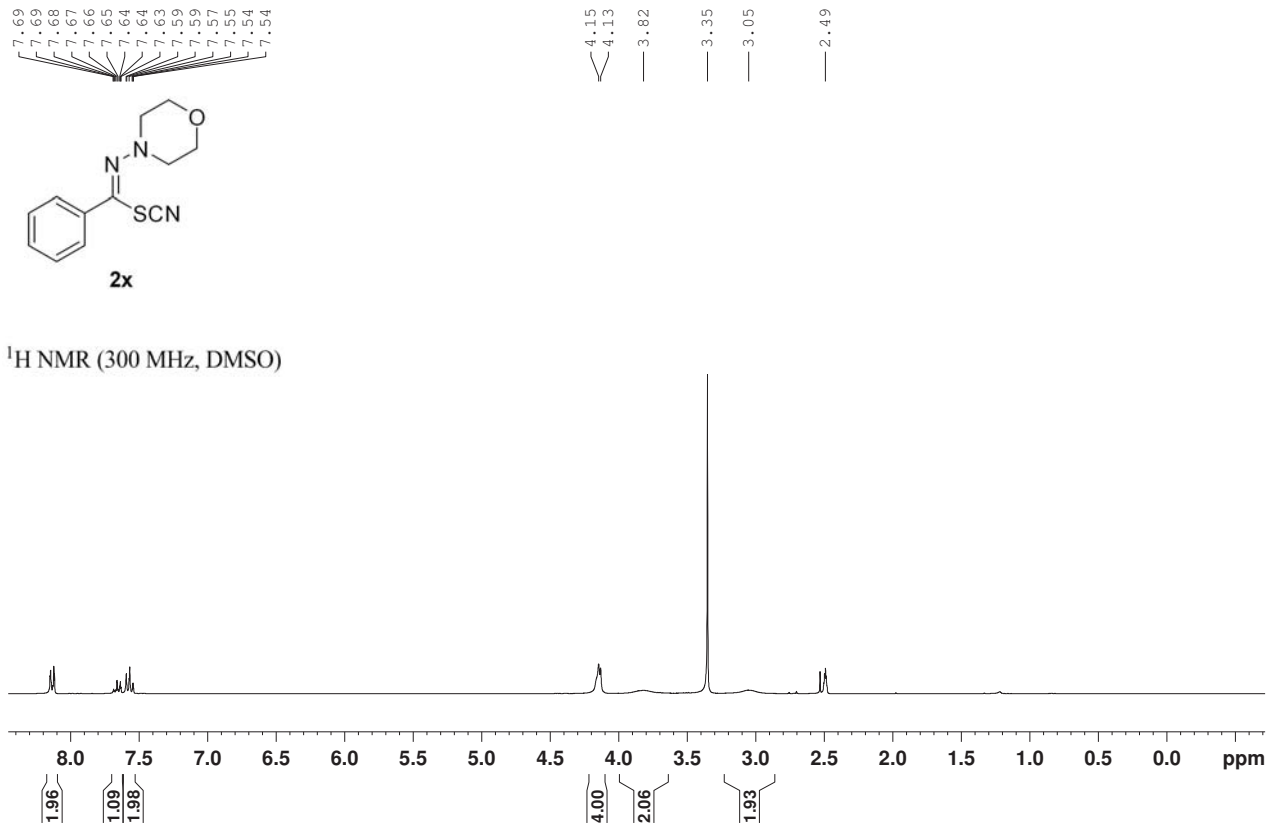


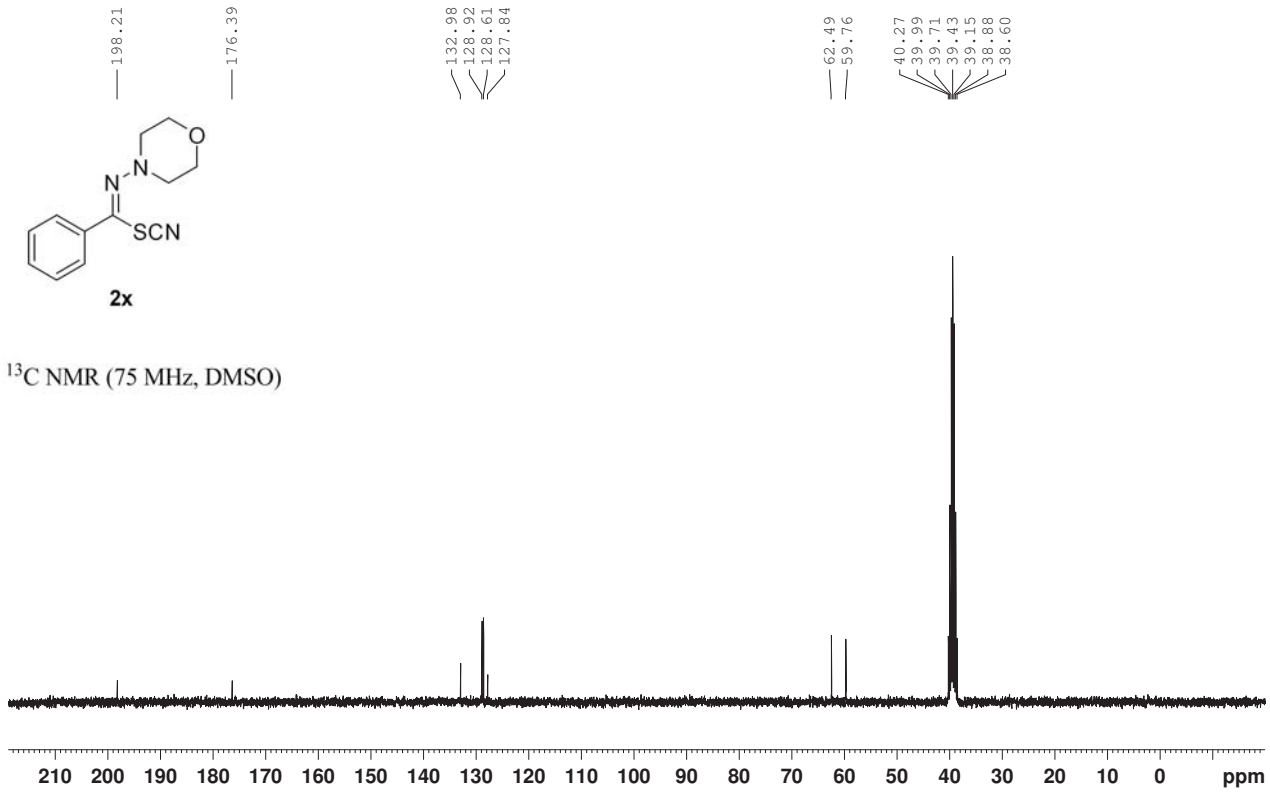


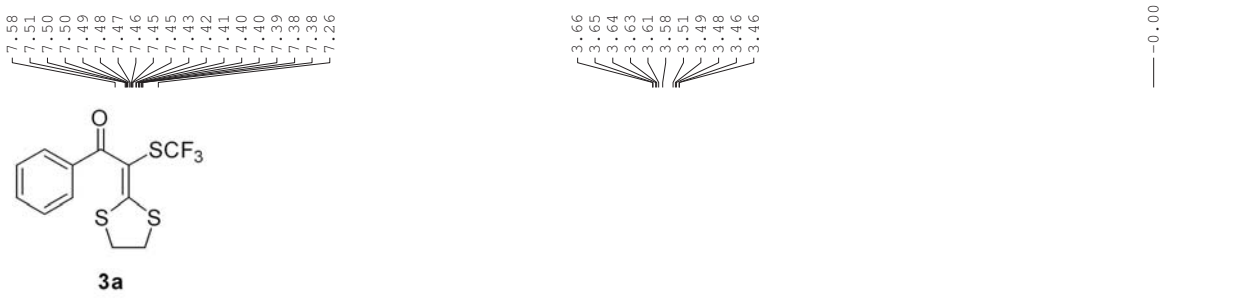
2w

^{13}C NMR (75 MHz, $CDCl_3$)



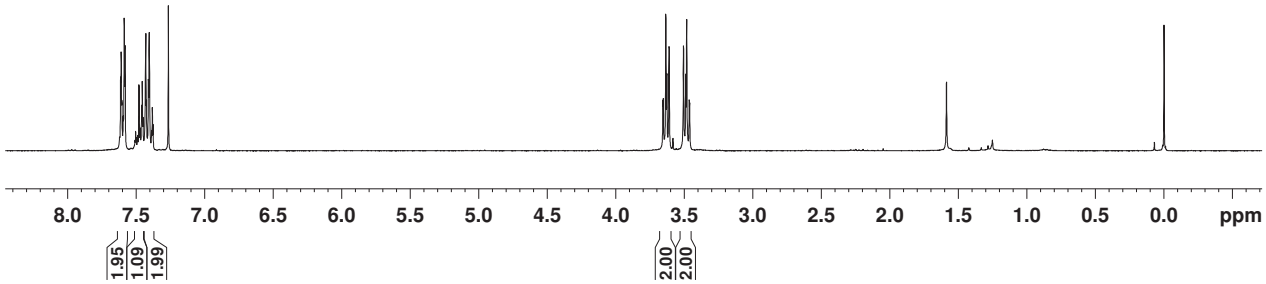

7.69
7.69
7.68
7.67
7.66
7.65
7.64
7.64
7.63
7.59
7.59
7.57
7.55
7.54
7.54
4.15
4.13
3.82
3.35
3.05
2.49
O
N
N
SCN
2x
1H NMR (300 MHz, DMSO)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.96
1.09
1.98
4.00
2.06
1.93

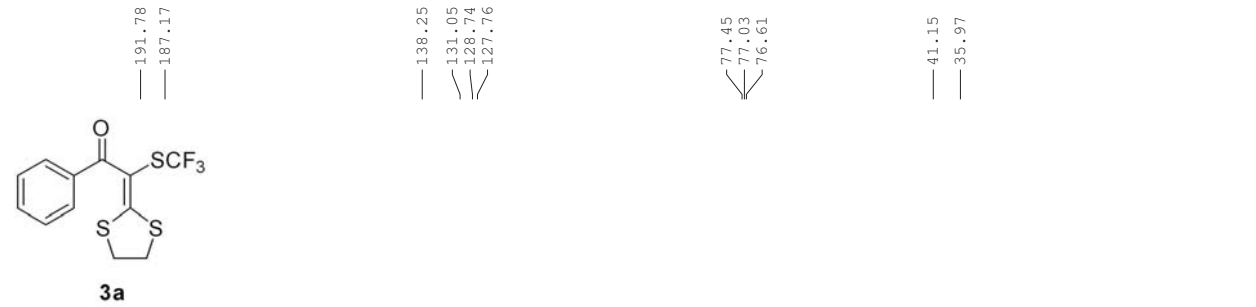

198.21
176.39
132.98
128.92
128.61
127.84
62.49
59.76
40.27
39.99
39.71
39.43
39.15
38.88
38.60
O
N
N
SCN
2x
13C NMR (75 MHz, DMSO)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



3a

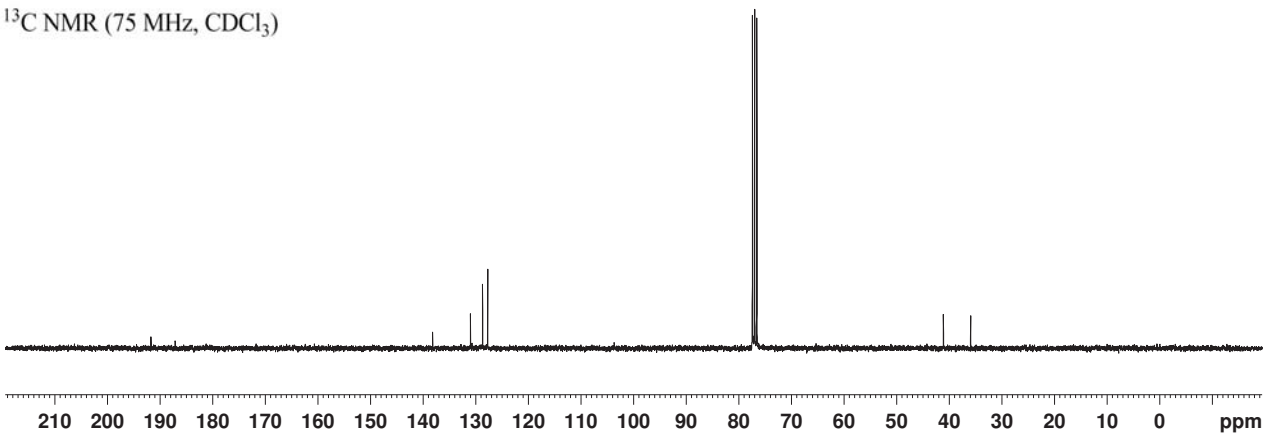
^{1}H NMR (300 MHz, $CDCl_3$)

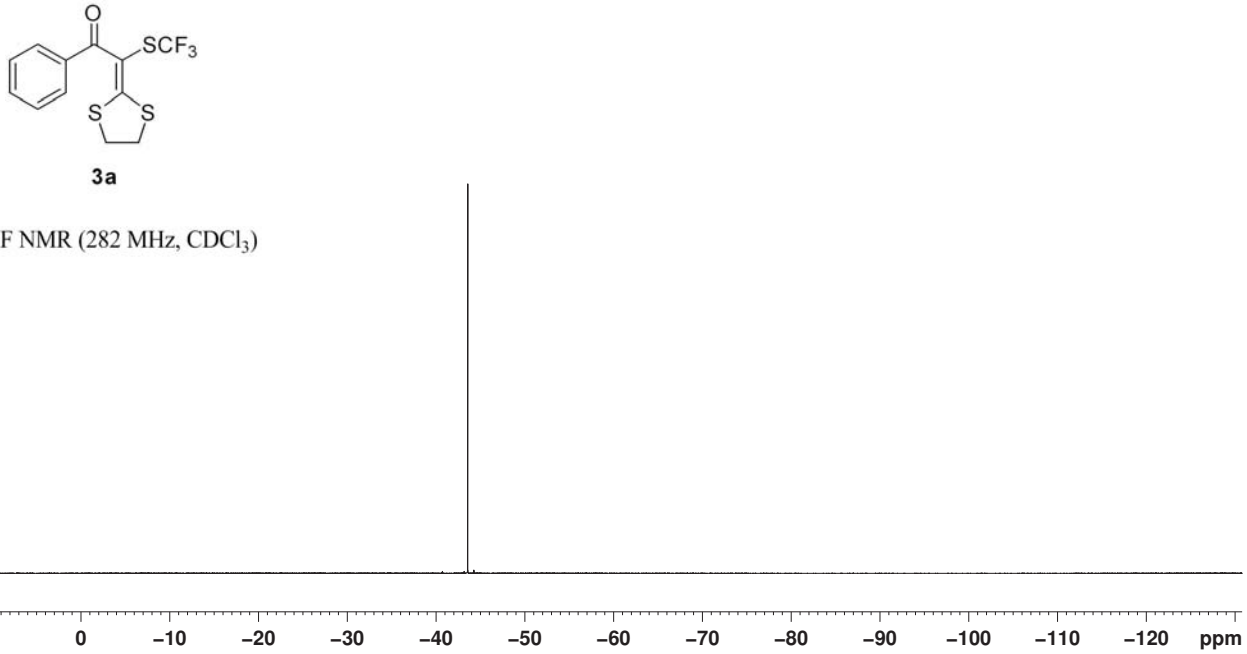




3a

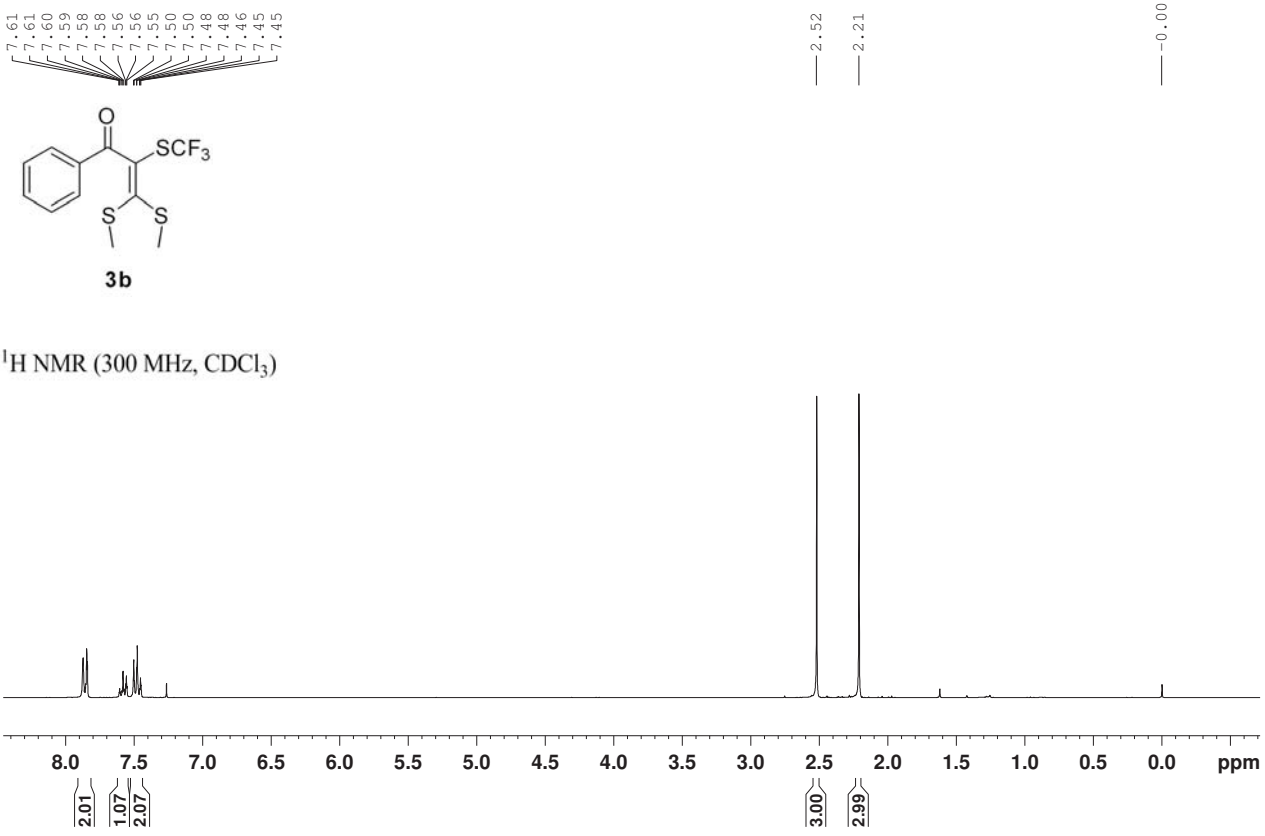
^{13}C NMR (75 MHz, $CDCl_3$)





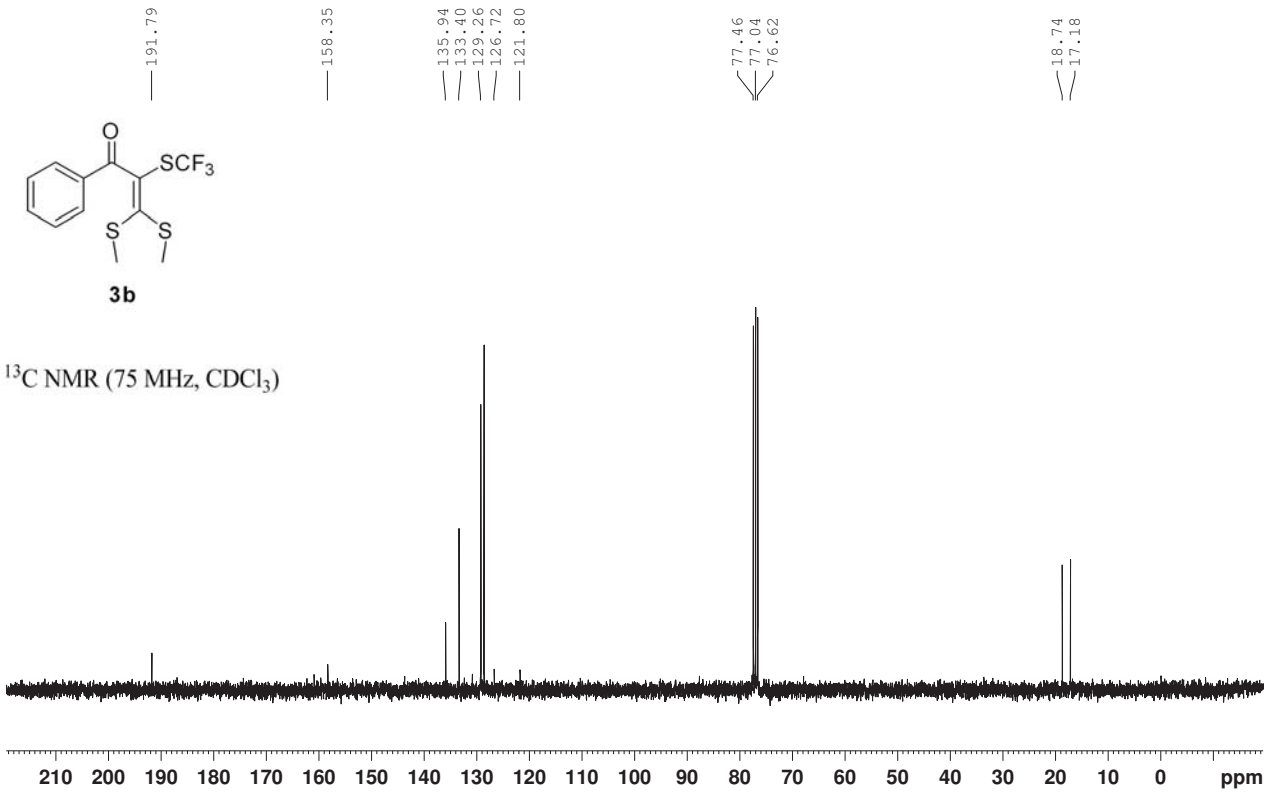
3a

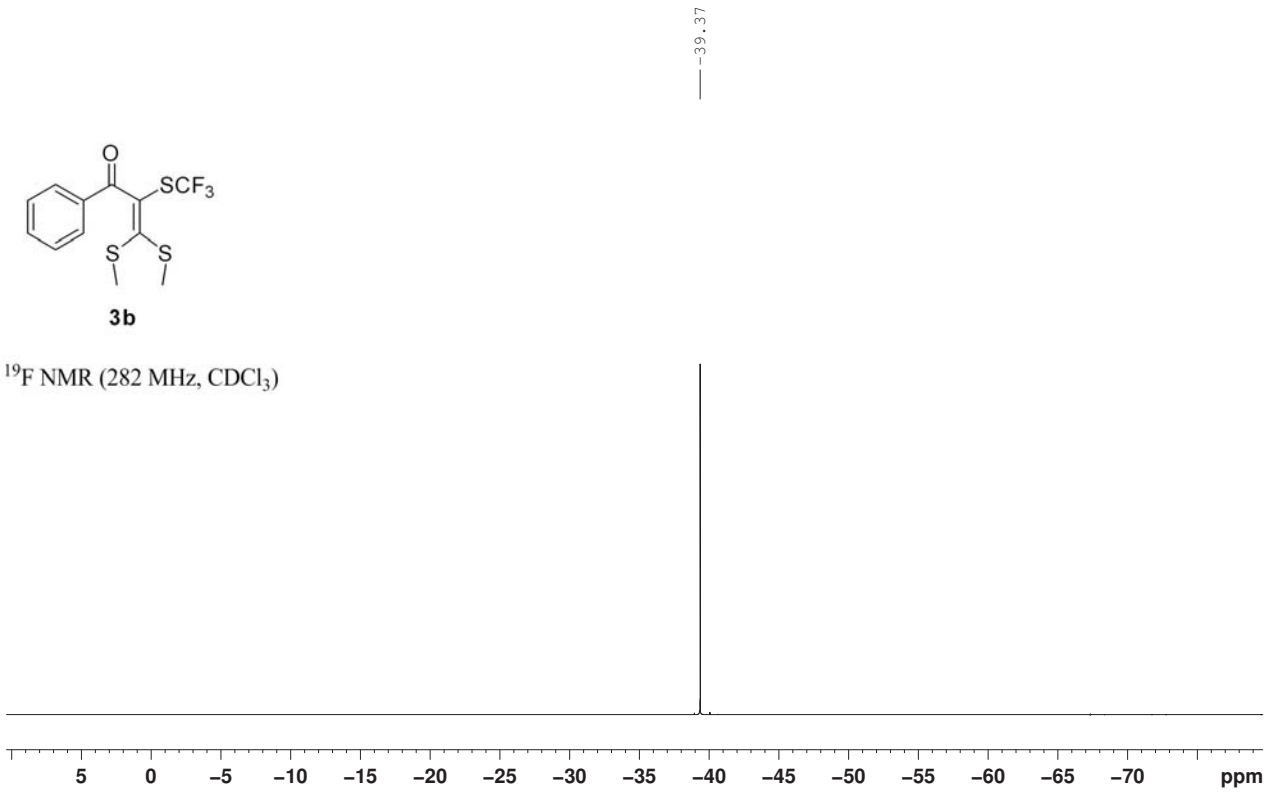
^{19}F NMR (282 MHz, $CDCl_3$)

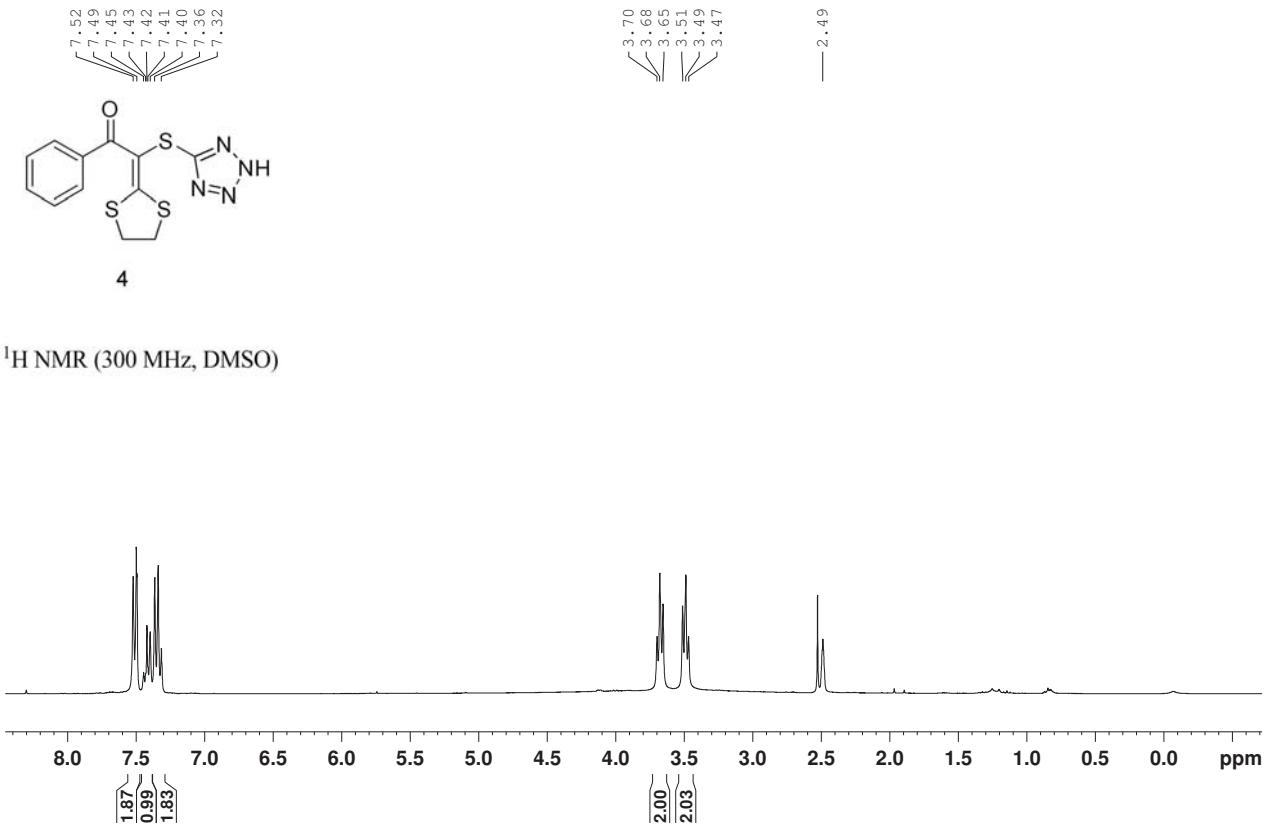


3b

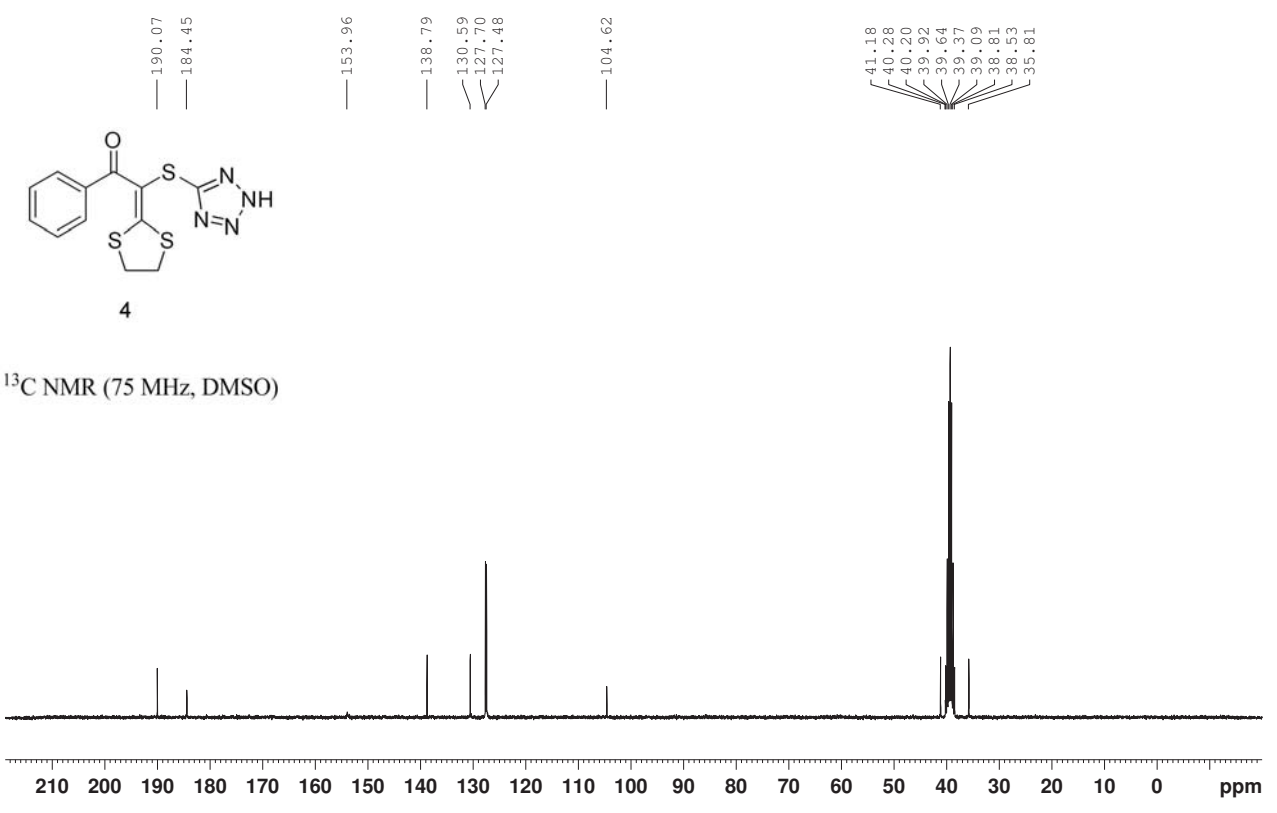
^{1}H NMR (300 MHz, $CDCl_3$)


191.79
158.35
135.94
133.40
129.26
126.72
121.80
77.46
77.04
76.62
18.74
17.18
O
SCF3
S
S
3b
13C NMR (75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

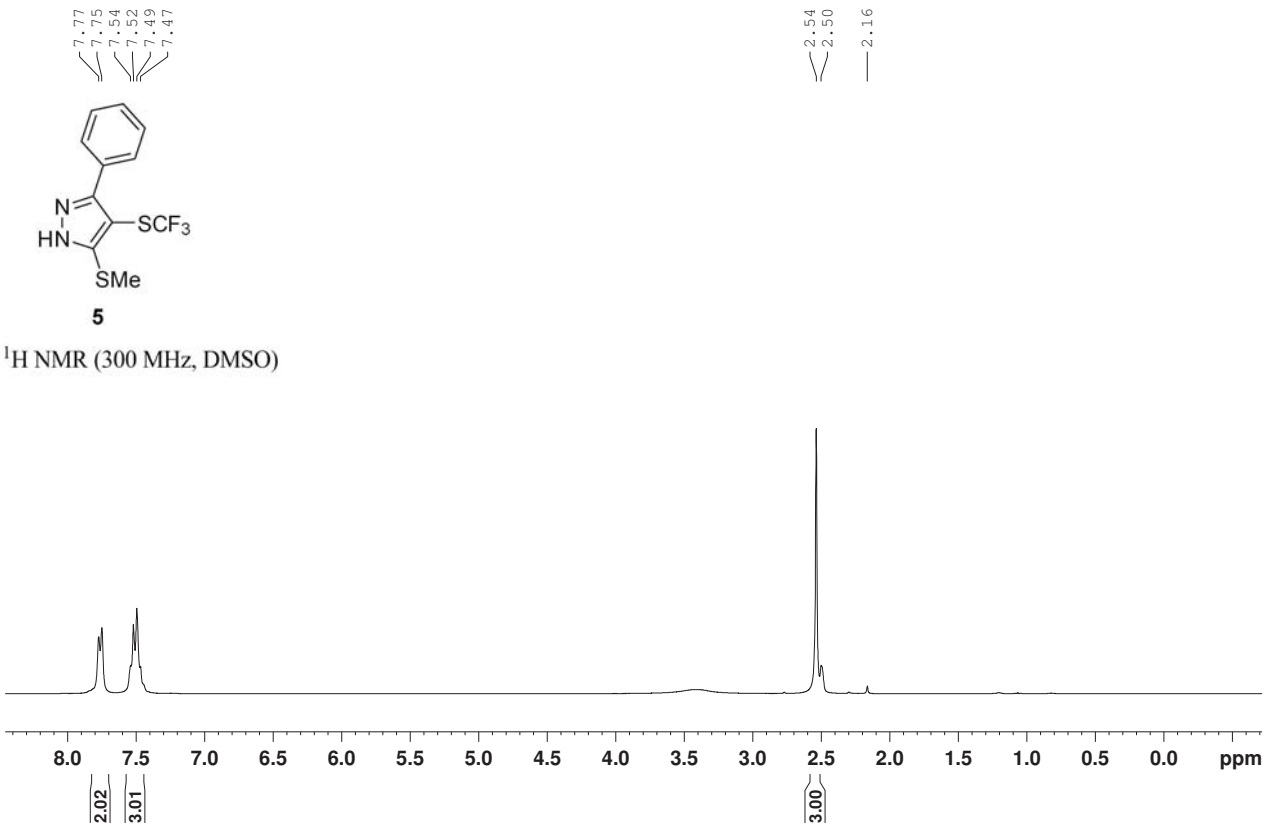

-39.37
O
SCF3
S
S
3b
19F NMR (282 MHz, CDCl3)
5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 −60 −65 −70 ppm



^{1}H NMR (300 MHz, DMSO)

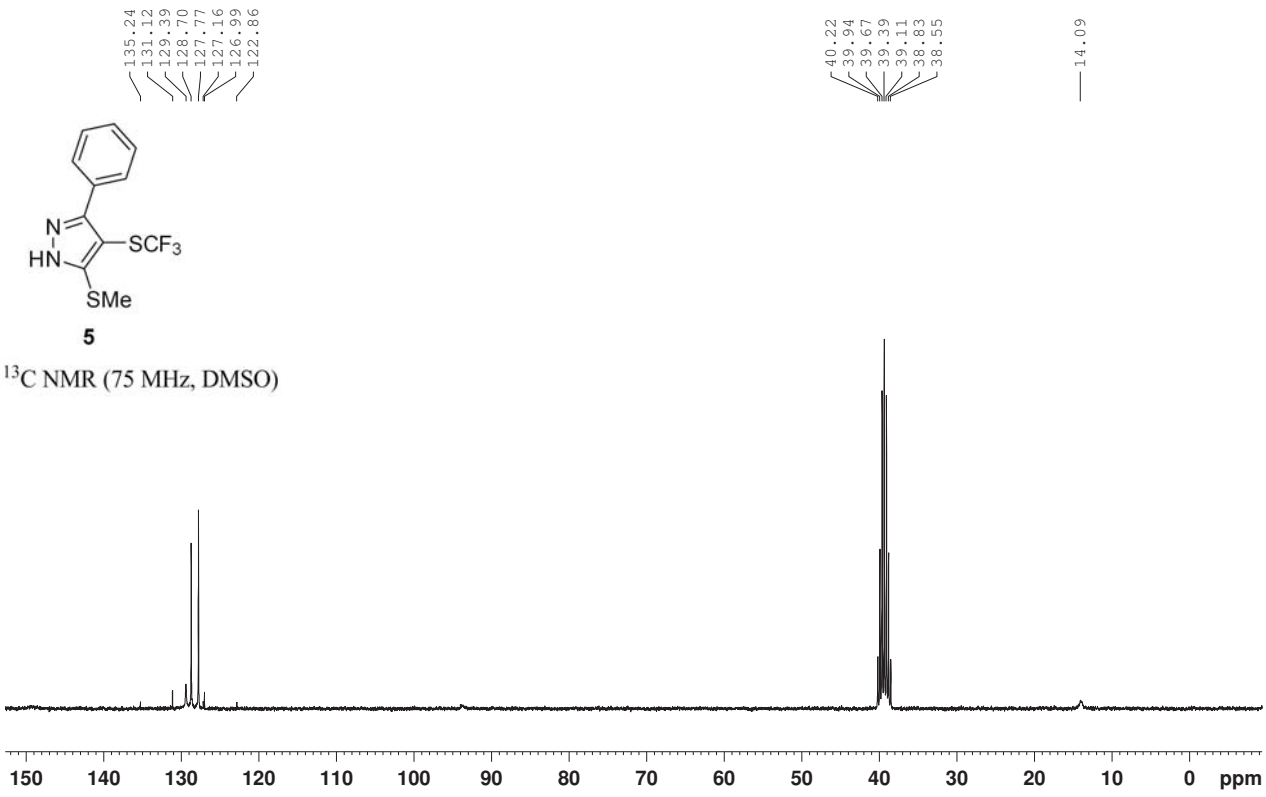


^{13}C NMR (75 MHz, DMSO)



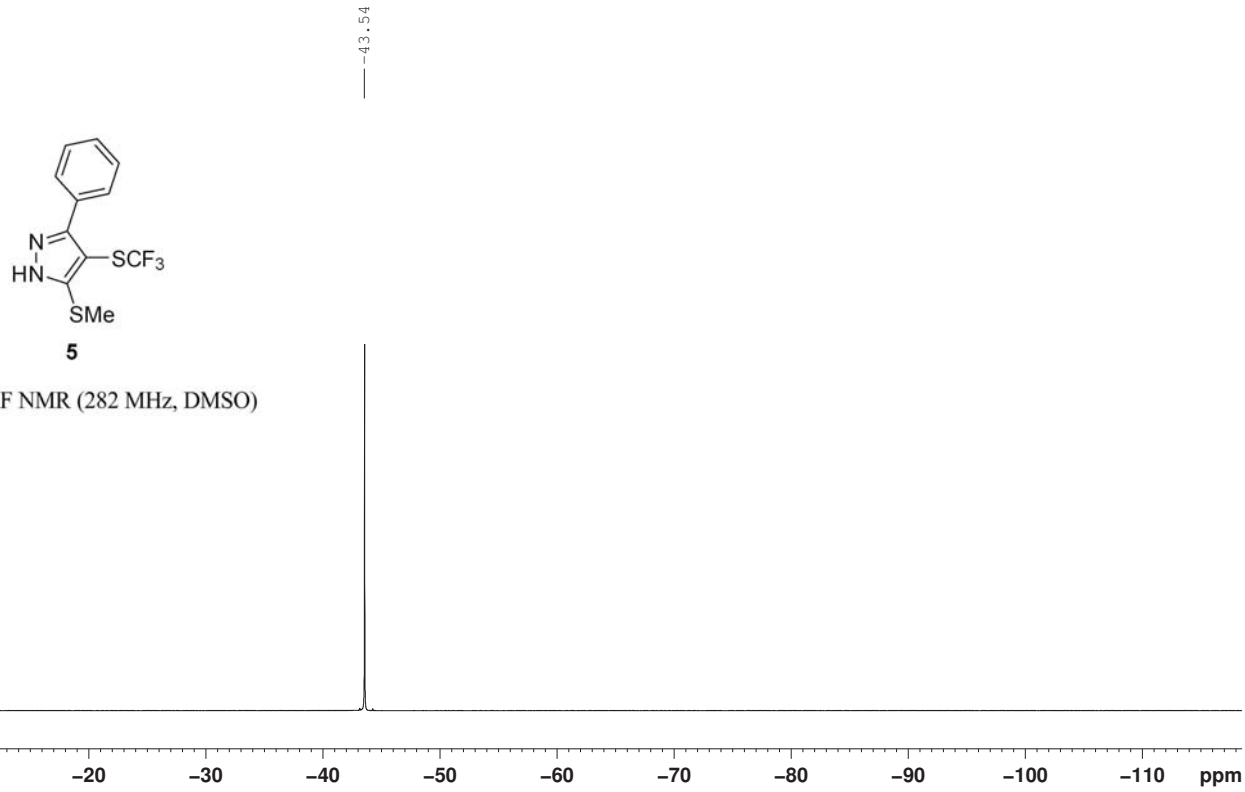
5

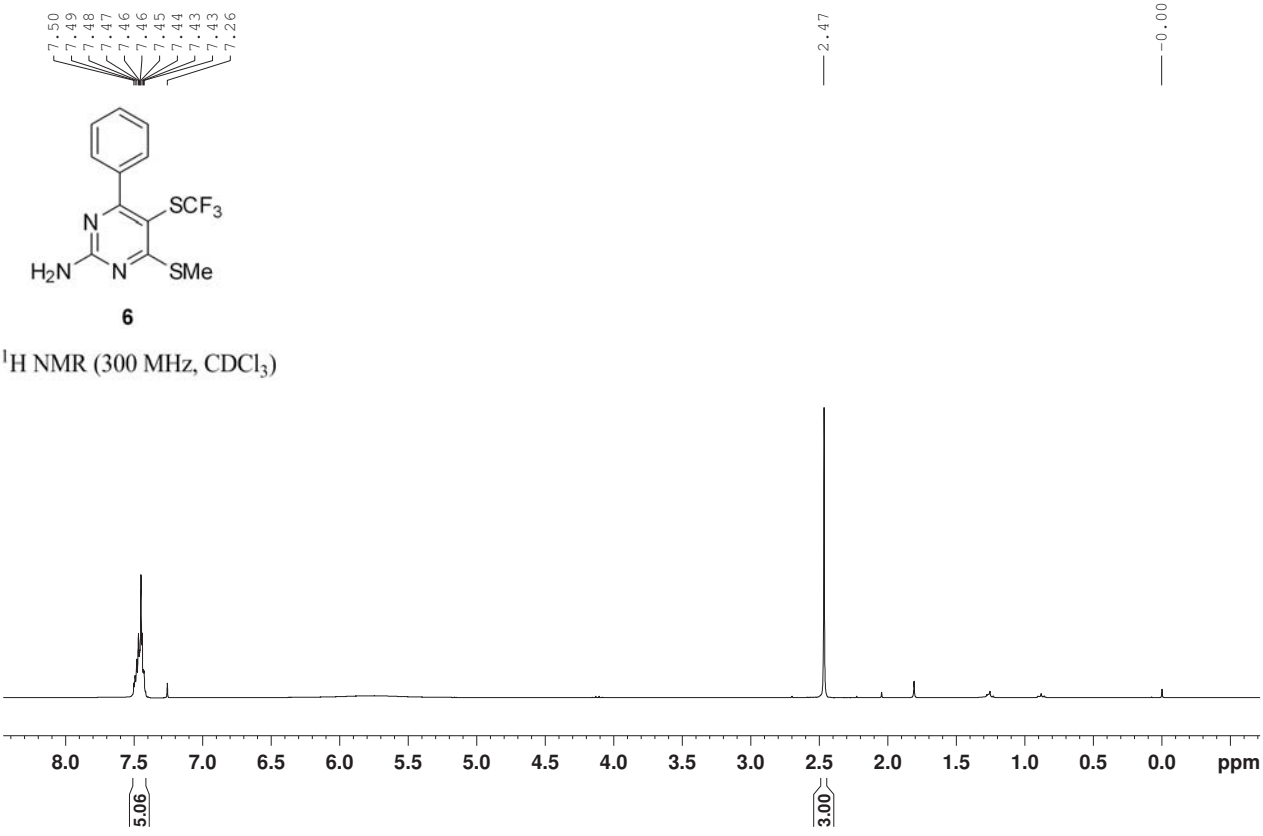
^{1}H NMR (300 MHz, DMSO)

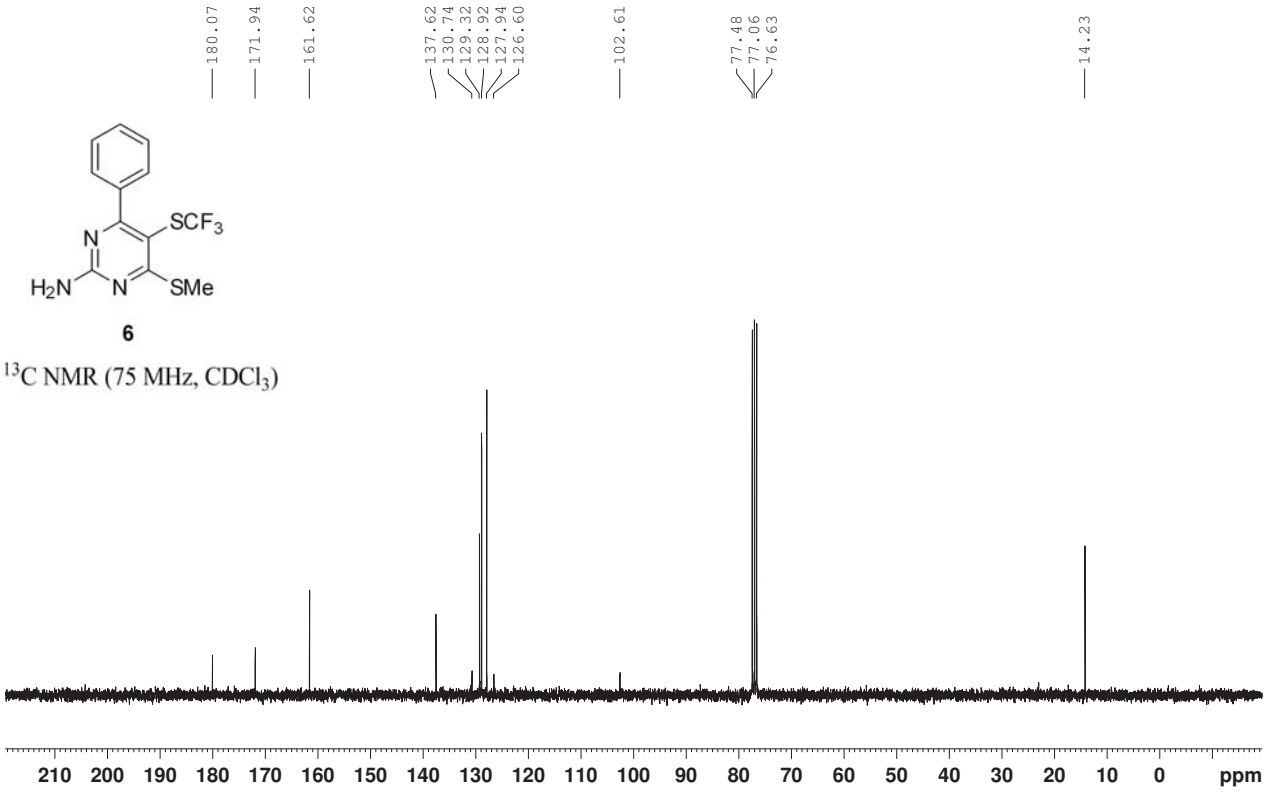


5

^{13}C NMR (75 MHz, DMSO)

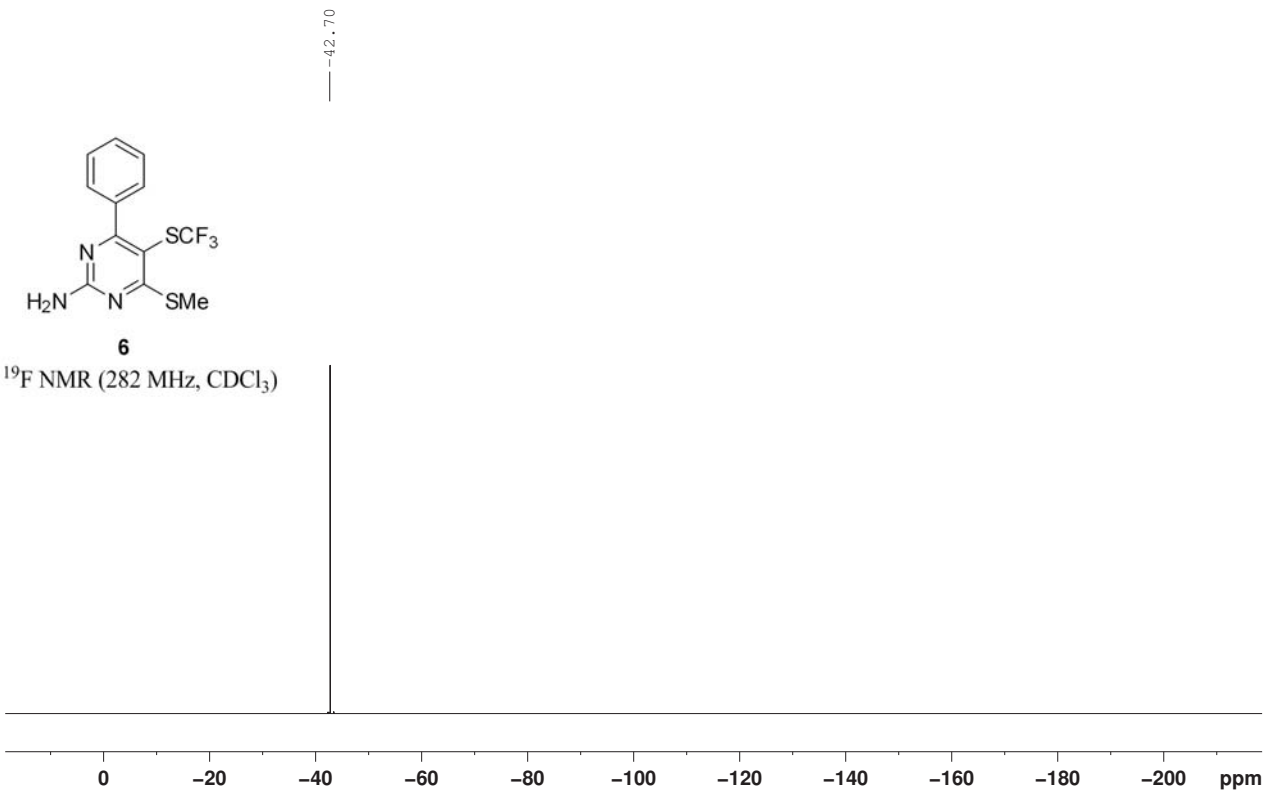

-43.54
N
HN
SCF3
SMe
5
19F NMR (282 MHz, DMSO)
–20
–30
–40
–50
–60
–70
–80
–90
–100
–110
ppm


7.50
7.49
7.48
7.47
7.46
7.46
7.45
7.44
7.43
7.43
7.26
2.47
0.00
SCF3
N
H2N
N
SMe
6
1H NMR (300 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.06
3.00



6

^{13}C NMR (75 MHz, $CDCl_3$)



6

^{19}F NMR (282 MHz, $CDCl_3$)