Supporting information

ARS-TiO_2 photocatalyzed direct functionalization of sp2 C-H bonds toward thiocyanation and cyclization reactions under visible light

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Contents

1) Experimental information

General Information. TiO_2 (the mixture of anatase and rutile, specific surface area: 35-65 m^2g^{-1}, primary particle size: 21 nm) was purchased from Sigma-Aldrich. Unless otherwise noted, starting materials were purchased from Acros and Merck chemical companies and used without further purification. All the solvents dried according to standard methods. Elemental analysis was performed on a 2400 series PerkinElmer analyzer. Melting points were measured on a Buchi 510 apparatus in open capillary tubes and were uncorrected.^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ as solvent using Bruker Advance DPX FT 250 MHz and Bruker Ultrashield 400 MHz spectrometry, respectively, with TMS as an internal standard (multiplicity: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (J): in Hertz (Hz)). FT-IR spectra were obtained by a Shimadzu FT-IR 8300 spectrophotometer. The products purified by hand-made column chromatography: short columns of SiO_2 60 (230–400 mesh) in glass columns (1.0 –1.5 cm). The reactions were monitored by thin layer chromatography (TLC): silica gel PolyGram SIL G/UV 254 plates and visualized by UV lamp at 254 nm.

Preparation of ARS-TiO_2 photocatalyst.

At first, the TiO_2 powder was heated at 110 °C in air for 3 h to remove adsorbed water on the surface. Dyes-TiO_2 were prepared by a minor modified reported procedure1. Typically, three different molar concentration of ARS dye (0.1 mol/L, 0.2 mol/L and 0.4 mol/L) in ethanol were added to 1g of pre-heated nano TiO_2 (P25) and stirred at room temperature in the dark for 12 h. The solid was centrifuged and washed with ethanol five times and dried at 40 °C for 30 h on the vacuum oven and kept in the dark.

Synthesis of 2-phenylamino-thiazole (1)

2-phenylamino-thiazole derivatives were prepared in our laboratory using a modified procedure[2]. Typically, a mixture of 0.704 g (4 mmol) of acetophenone, 0.304 g (4 mmol) of thiourea, and 1.269 g (5 mmol) of diiodine were mixed and stirred at 120 ^{0}C for overnight without solvent. Then, 15 mL of cold water was added to reaction mixture and after filtration the precipitate washed with diethyl ether (15 mL twice). The filtrate was dissolved in boiling water, then, filtered again while it is hot. The solution was cooled down to room temperature and neutralized with aqueous sodium hydroxide solution (PH = 8). The crude product was filtered and purified by flash column chromatography with petroleum ether/ethyl acetate as eluent to afford target products.

Synthesis of 2-phenylamino-oxazole (4)

Thiourea (50.0 mmol, 3.0 g, 10 eq.) and 2-bromoacetophenone (5.0 mmol, 0.99 g) were dissolved in CH_3CN (40 ml) in a round-bottom flask, the mixture was stirred under reflux for overnight. The

reaction mixture was cooled down, the solvent was removed and the residue purified on silica gel using mixture of ethyl acetate/hexane (3:7).

Synthesis of 2-phenylimidazo[1,2-a]pyridine (6)

2-Aminopyridine (3.0 mmol, 0.28g) and 2-bromoacetophenone (3.0 mmol, 0.6 g) were dissolved in EtOH (10 ml) in a round-bottom flask and $NaHCO_3$ (4.5 mmol, 0.38 g, 1.5 eq.) was added, the mixture was stirred at rt °C for 6 hour and then dried under vacuum. A solution of PE:EA (50:1, 10 mL) was added, the mixture was filtered under reduced pressure, and the residue was washed with PE (10 mL×1). Then, the crude was purified using column chromatography on SiO_2 with PE:EA (7:3) to afford target compound.

General procedure for thiocynation reactions

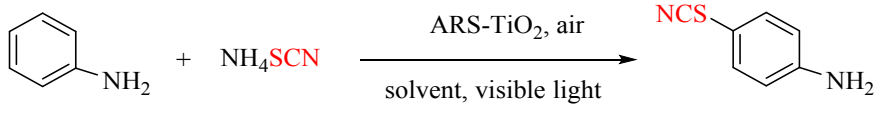
A mixture of aromatic compounds and (1 mmol) and ammonium thiocyanate (3 mmol) in THF or CH_3CN (6 mL) placed in 10 mL round bottom flask, ARS-TiO_2 (7.0 mg, 0.97 μmol g^{-1}, containing ~ 58×10^{-10} mol ARS) was added and the reaction was irradiated by 15 W blue LED Lamp (λ > 440 nm, distance app. 4.0 cm) in open air condition. The reaction was stirred for appropriate time at ambient temperature (28 °C) and monitored by TLC. After completion, the reaction mixture was centrifuged to separate the catalyst, then, the reaction was diluted with EtOAc (15mL) and washed with brine. The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure to obtain the crude. Final product purification was done through silica gel column chromatography using petroleum ether/ethyl acetate.

The box used for the reactions

Figure S1. The box containing 15 W blue LED lamp (λ > 440 nm).

Screening solvent, light and photocatalyst amount for thiocyanation reaction of aniline

Table S1. Optimization of the reaction conditions [a]



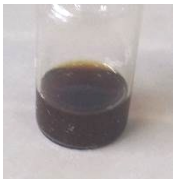
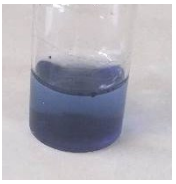
14a **2** **15a**

Entry	Solvent	Light	Yield of 7a [%][b]
	THF	15 W Blue LED	37
2	EtOH	15 W Blue LED	NR
3	$CHCl_3$	15 W Blue LED	8
4	EtOAC	15 W Blue LED	13
5	DMF	15 W Blue LED	trace
6	CH_3CN	15 W Blue LED	85
7	CH_3CN	15 W Green LED	62
8	CH_3CN	15 W Red LED	39
9	CH_3CN	Dark	13
10	CH_3CN	15 W Blue LED	65[c], 84[d]
11	CH_3CN	15 W Blue LED	85[e]

[a]*Reaction conditions*: A mixture of **14a** (1 mmol), **2** (3 mmol) and photocatalyst (7 mg, 0.48 μmol g−1), solvent (6 mL), 15 W LED lamp in air for 20 h at room temperature. [b] ^1H NMR yield using 1,3,5-trimethoxybenzene as internal standard. [c] 0.007 g ARS-TiO_2 0.97 μmol g^{-1}. [d] 0.007 g ARS-TiO_2 1.68 μmol g−1. [e]After 20h.

H_2O_2 test after completion of the reaction.

H_2O_2 starch−iodine test at the end of reaction (optimized reaction condition toward synthesis of **3a**).

 1	 2	 3	 4	 5	 6
H_2O_2 Indicator (KI/starch)	Reaction mixture at t = 0 h	Reaction mixture at t = 24 h	Addition of 1 to 3	Addition of 1 to H_2O_2 (30 wt. % in H_2O)	Addition of 1 to 2

2) Characterization

Photocatalyst characterizations.

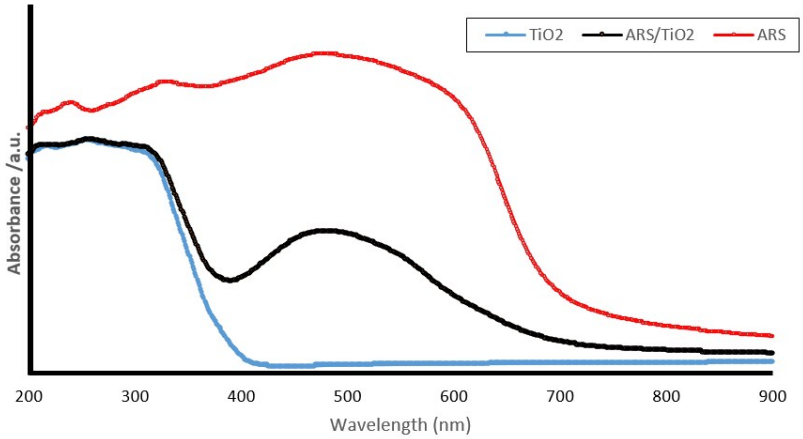


Fig. S2. Diffuse reflectance spectra of ARS, ARS-TiO_2 and TiO_2 powders.

Characterization of photocatalyst after reusability test

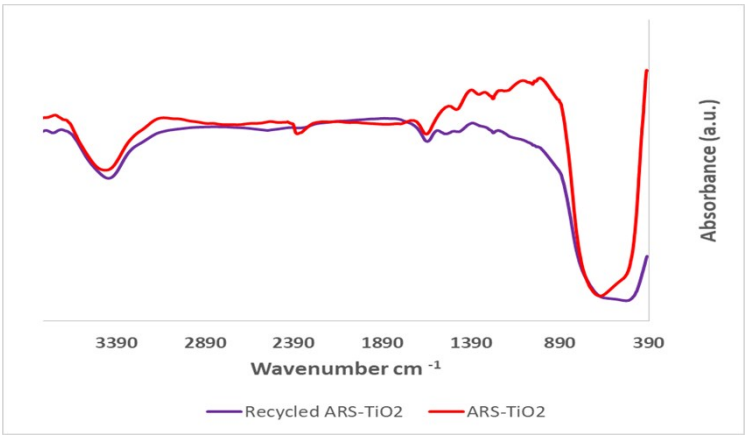


Figure S3. FT-IR spectra of ARS-TiO_2 before and after recycling

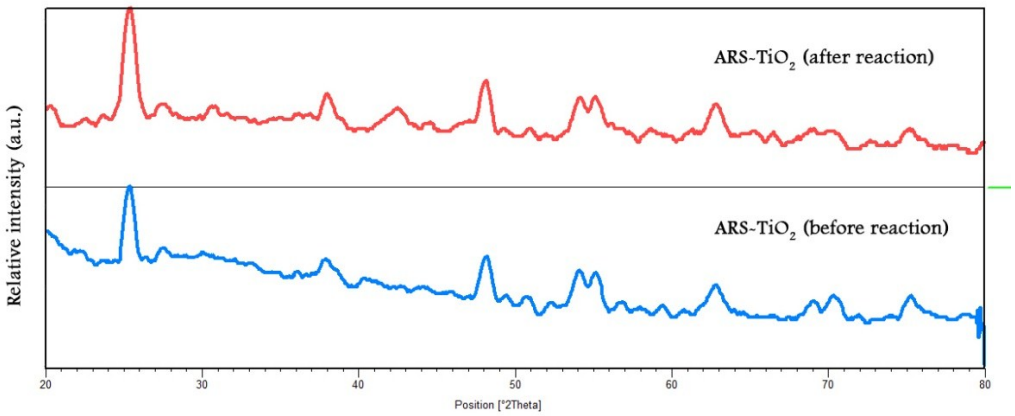
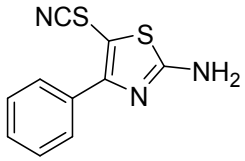


Figure S4. XRD spectra of ARS-TiO_2 before and after recycling

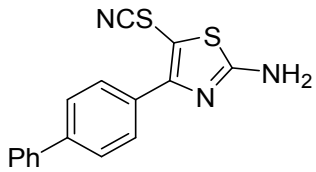
Characterization of compounds

4-Phenyl-5-thiocyanatothiazol-2-amine (3a)



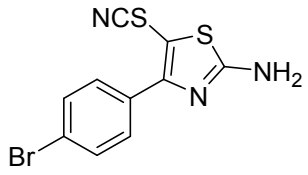
White solid. mp = 187-189 °C (lit. 185.1-185.5 °C) [3]. IR (KBr), ῡ(cm^{-1}); 3387, 3286, 3098, 2150, 1641, 1518, 1339, 1086, 831, 715, 603. ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm); 7.42-7.51 (m, 3H), 7.72-7.76 (m, 2H), 7.88 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 92.0, 112.6, 128.8, 129.2, 129.5, 133.3, 159.1, 171.3. $C_{10}H_7N_3S_2$: Calcd. C, 51.48; H, 3.02; N, 18.01; S, 27.48; Found. C, 51.37; H, 3.09; N, 17.76; S, 27.28.

4-([1,1'-Biphenyl]-4-yl)-5-thiocyanatothiazol-2-amine (3b)



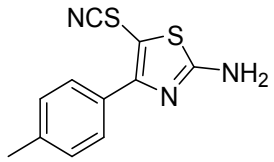
White solid. mp = 186-189 °C (lit. 183-185 °C) [4]. IR (KBr), ῡ(cm^{-1}); 3361, 3052, 2939, 2375, 2152, 1619, 1527, 1328, 1223, 1078, 844, 768, 695. ^{1}H NMR (250 MHz, DMSO-d_6) δ(ppm); 7.43-7.59 (m, 3H), 7.80-7.89 (m, 4H), 7.94-7.97 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 91.6, 112.1, 126.5, 126.7, 127.8, 129.0, 129.3, 131.9, 139.2, 140.5, 158.0, 170.7. $C_{16}H_{11}N_3S_2$: Calcd. C, 62.11; H, 3.58; N, 13.58; S, 20.72; Found. C, 62.19; H, 3.52; N, 13.49; S, 20.47.

4-(4-Bromophenyl)-5-thiocyanatothiazol-2-amine (3c)



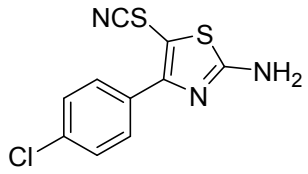
White solid. mp = 198-200 °C (lit. 274.8-275.3 °C) [3]. IR (KBr), ῡ(cm^{-1}); 3387, 3286, 3098, 2150, 1641, 1518, 1339, 1086, 831, 715, 603. ^{1}H NMR (250 MHz, DMSO-d_6) δ(ppm); 7.65-7.73 (m, 4H), 7.90 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 92.8, 112.4, 122.9, 131.2, 131.8, 132.5, 157.6, 171.3. $C_{10}H_6BrN_3S_2$: Calcd. C, 38.47; H, 1.94; N, 13.46; S, 20.54; Found. C, 38.32; H, 1.99; N, 13.25; S, 20.32.

5-Thiocyanato-4-(*p*-tolyl) thiazol-2-amine (3d)



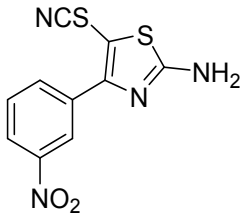
White solid. mp = 170-173 °C (lit. 178.4-178.9 °C) [3]. IR (KBr), ῡ(cm^{-1}); 3389, 3291, 3089, 2155, 1639, 1520, 1332, 1188, 1085, 820, 717, 602.^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm); 2.34 (s, 3H), 7.27 (d, *J* = 7.5Hz, 2H), 7.65 (d, *J* = 7.5Hz, 2H), 7.86 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 21.3, 91.2, 112.6, 129.1, 129.4, 130.5, 139.2, 159.2, 171.2. $C_{11}H_9N_3S_2$: Calcd. C, 53.42; H, 3.67; N, 16.99; S, 25.92; Found. C, 53.38; H, 3.58; N, 16.75; S, 25.61.

4-(4-Chlorophenyl)-5-thiocyanatothiazol-2-amine (3e)



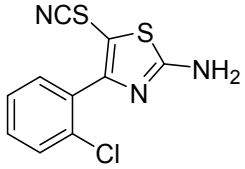
White solid. mp = 191-193 °C (lit. 266.6-267.8 °C) [3].IR (KBr), ῡ(cm^{-1}); 3376, 3301, 3088, 2157, 1643 , 1530, 1327, 1029, 836, 721, 604. ^{1}H NMR (250 MHz, DMSO-d_6) δ(ppm); 7.54 (d, *J* = 10Hz, 2H), 7.77 (d, *J* = 7.5Hz, 2H), 7.90 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 92.87, 112.5, 128.9, 131.0, 132.2, 134.2, 157.6, 171.3. $C_{10}H_6ClN_3S_2$: Calcd. C, 44.86; H, 2.26; N, 15.69; S, 23.95; Found. C, 44.92; H, 2.23; N, 15.44; S, 23.81.

4-(3-Nitrophenyl)-5-thiocyanatothiazol-2-amine (3f)



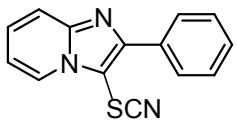
White solid. mp = 180-183 °C (lit. 183.7-184.2 °C) [3]. IR (KBr), ῡ(cm^{-1}); 3404, 3287, 2365, 2152 , 1647, 1514, 1350, 1262, 1095, 817, 747, 697. ^{1}H NMR (250 MHz, DMSO-d_6) δ(ppm); 7.76-7.82 (m, 1H), 7.99 (s, 2H), 8.24-8.30 (m, 2H), 8.61 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 94.23, 111.84, 123.29, 123.63, 130.13, 134.22, 134.75, 147.68, 155.34, 170.99. $C_{10}H_6N_4O_2S_2$: Calcd. C, 43.16; H, 2.17; N, 20.13; S, 23.04; Found. C, 43.09; H, 2.12; N, 19.93; S, 22.86.

4-(2-Chlorophenyl)-5-thiocyanatothiazol-2-amine (3g)



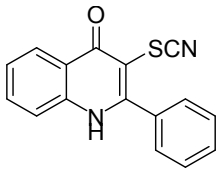
White solid. mp = 190-191 °C. IR (KBr), ῡ(cm^{-1}); 3396, 3289, 2159 ,1626, 1326, 1177, 1073, 841, 773, 699. ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm); 7.42-7.50(m, 2H), 7.72-7.76(m, 2H), 7.87(s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 92.1, 112.7, 128.5, 128.9, 129.0, 129.2, 129.6, 133.1, 159.2, 171.3. $C_{10}H_6ClN_3S_2$: Calcd. C, 44.86; H, 2.26; N, 15.69; S, 23.95; Found. C, 44.87; H, 2.22; N, 15.49; S, 23.78.

2-phenyl-3-thiocyanatoimidazo[1,2-a]pyridine (7)



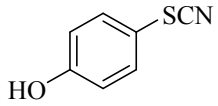
White solid, mp 119-121 °C (lit. 121-122 °C)[5]. IR (KBr), ῡ(cm^{-1}): 3075, 2143, 1641, 1484, 1461, 1433 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm); 8.45 (d, J = 6.8 Hz, 1H), 8.06 (d, J = 7.1 Hz, 2H), 7.77 (d, J = 9.0 Hz, 1H), 7.58 – 7.42 (m, 4H), 7.13 (t, J = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm); 153.11, 147.98, 131.97, 129.46, 128.82, 128.74, 127.98, 124.39, 118.29, 114.41, 108.07, 94.71. $C_{14}H_9N_3S$: Calcd. C, 66.91; H, 3.61; N, 16.72; S, 12.76 ; Found. C, 67.11; H, 3.87; N, 17.17; S, 11.93.

2-phenyl-3-thiocyanatoquinolin-4(1H)-one (11)



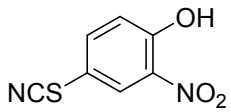
White solid, mp 175-177 °C (lit. 176-178 °C)[6]. IR (KBr), ῡ(cm^{-1}): 3448, 2152, 1619. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.51 (t, J= 7.31 Hz, 1H), 7.63-7.64 (m, 5H), 7.69 (d, J=8.1Hz, 1H), 7.81 (t, J= 7.39 Hz, 1H), 8.19 (d, J=8.1 Hz, 1H), 12.57 (s,1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 101.8, 111.2, 119.7, 125.2, 126.3, 126.8, 129.3, 129.7, 131.3, 134.2, 133.9, 139.1, 157.1, 174.3.

4-thiocyanatophenol (13a)



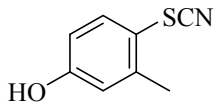
Brown solid. mp = 50-52 °C (lit. 51-53 °C)[7] IR (KBr), ῡ(cm^{-1}): 3368, 2265, 1556, 1509, 1305. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 6.82 (dd, *J* = 8.9 Hz, 2H), 7.39 (dd, *J* = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm) 112.07, 113.48, 117.46, 134.22, 157.92. C_7H_5NOS: Calcd. C,55.61; H, 3.33; N, 9.26; S, 21.21; Found. C, 55.98; H, 4.02; N, 8.83; S, 21.78.

2-nitro-4-thiocyanatophenol (13b)



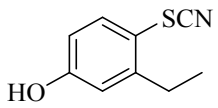
Yellow solid. mp = 94-97 °C , IR (KBr), ῡ(cm^{-1}): 3393, 2856, 2150, 1652, 1465, 1282. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.23 (d, J = 8.9 Hz, 1H), 7.72 (dd, J = 8.9, 2.2 Hz, 1H), 8.30 (d, J = 2.2 Hz, 1H), 10.65 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 110.68, 113.89, 120.47, 121.60, 137.64, 140.22, 163.16, 195.46. $C_7H_4N_2O_3S$: Calcd. C,42.86; H, 2.06; N, 14.28; S, 16.34; Found. C, 42.18; H, 2.32; N, 14.94; S, 17.03.

3-methyl-4-thiocyanatophenol (13c)



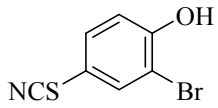
Yellow solid. mp = 76-78 °C, (lit. 75-78 °C) [8] IR (KBr), ῡ(cm^{-1}): 3350, 2159, 1577, 1234. 1H NMR (250 MHz, CDCl3) δ (ppm) 2.41 (s, 3H), 5.43 (s, 1H), 6.64 (dd, J = 8.5, 2.7 Hz, 1H), 6.72 (d, J = 2.8 Hz, 1H), δ 7.41 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 20.95, 111.55, 113.15, 114.87, 118.85, 136.03, 143.33, 158.16. C_8H_7NOS: Calcd. C,58.16; H, 4.27; N, 8.48; S, 19.41; Found. C, 58.87; H, 4.91; N, 9.03; S, 19.03.

3-ethyl-4-thiocyanatophenol (13e)



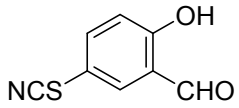
Yellow solid. mp = 75-77 °C, (lit. 75-78°C) [9] IR (KBr), ῡ(cm^{-1}): 3350, 2159, 1577, 1234. 1H NMR (250 MHz, CDCl3) δ (ppm) 1.18-1.20 (m, 3H), 2.76 (q, J = 7.7 Hz 2H), 5.35 (s, 1H), 6.65 (dd, J = 8.9, 2.87 Hz, 1H), 6.74 (d, J = 2.7 Hz, 1H), 7.44 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm) 13.31, 26.47, 111.39, 114.05, 115.94, 129.99, 135.29, 157.35. C_9H_9NOS: Calcd. C,60.31; H, 5.06; N, 7.81; S, 17.89; Found. C, 61.06; H, 4.93; N, 7.11; S, 17.24.

2-bromo-4-thiocyanatophenol (13f)



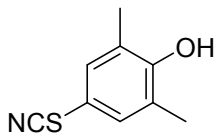
White solid. mp = 93-95 °C, (lit. 95-97°C) [9] IR (KBr), ῡ(cm^{-1}): 3448, 3092, 2363, 2159, 1529, 859. 1H NMR (250 MHz, CDCl3) δ (ppm) 5.89 (s, 1H), 7.01 (d, J = 8.5 Hz, 1H), 7.38 (dd, J = 8.5, 2.2 Hz, 1H), 7.65 (d, J = 2.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm) 111.03, 111.45, 117.79, 114.98, 154.51, 135.63, 133.23. C_7H_4BrNOS: Calcd. C,36.54; H, 1.75; N, 6.09; S, 13.93; Found. C, 37.04; H, 2.05; N, 6.01; S, 13.24.

2-hydroxy-5-thiocyanatobenzaldehyde (13g)



White solid. mp = 92-94 °C, (lit. 94-96°C) [7] IR (KBr), ῡ(cm^{-1}): 3393, 2856, 2150, 1652, 1465, 1282. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.09 (d, J = 8.8 Hz, 1H), 7.68 (dd, J =7.6, 2.5 Hz, 1H), 7.79 (d, J = 2.4 Hz, 1H), 9.85 (s, 1H), 11.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 110.68, 113.89, 120.47, 121.60, 137.64, 140.22, 163.16, 195.46. $C_8H_8NO_2S$: Calcd. C,53.62; H, 2.81; N, 7.82; S, 17.82; Found. C, 57.06; H, 3.12; N, 7.32; S, 17.16.

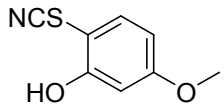
2,6-dimethyl-4-thiocyanatophenol (13h)



White solid. mp = 129- 131 °C, (lit. 131-133°C) [9] IR (KBr), ῡ(cm^{-1}):3351, 2157, 1584, 1311. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.19 (s, 6H), 4.96 (s, 1H), 7.14 (s, 2H). ^{13}C NMR (100 MHz,

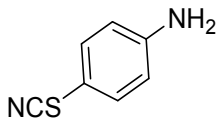
CDCl3) δ (ppm) 15.88, 112.19, 112.65, 124.26, 125.48, 132.51. C_9H_9NOS: Calcd. C,60.31; H, 5.06; N, 7.81; S, 17.89; Found. C, 60.89; H, 5.63; N, 7.28; S, 17.13.

5-methoxy-2-thiocyanatophenol (13i)



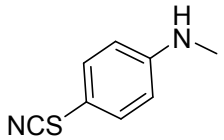
Yellow solid. mp = 72-74 °C, (lit. 75-78°C) [9] IR (KBr), ῡ(cm^{-1}): 3350, 2159, 1577, 1234. ^{1}H NMR (250 MHz, CDCl3) δ (ppm) 3.83 (s, 3H), 5.34 (s, 1H), 6.39 (m, 2H), 7.32 (dd, J = 7.1, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm) 56.21, 100.16, 108.77, 128.82, 130.98, 134.15, 159.59. $C_8H_7NO_2S$: Calcd. C,53.03; H, 3.89; N, 7.73; S, 17.69; Found. C, 53.79; H, 4.09; N, 7.19; S, 17.13.

4-Thiocyanatoaniline (15a)



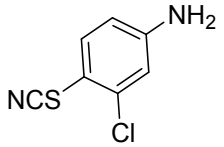
White solid. mp = 52-53 °C (lit. 49–51°C) [10]. IR (KBr), ῡ(cm^{-1}); 3419, 3348, 3233, 2918, 2147, 1622, 1595, 1496, 1384, 1301, 1179, 822, 628, 521. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 3.80 (s, br, 2H), 6.68 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 109.6, 112.4, 116.1, 134.5, 148.8. $C_7H_6N_2S$: Calcd. C, 55.98; H, 4.03; N, 18.65; S, 21.35; Found. C, 55.85; H, 3.97; N, 18.38; S, 21.11.

***N*-Methyl-4-thiocyanatoaniline (15b)**



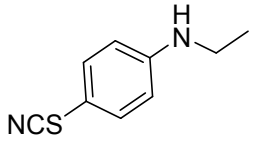
Yellow liquid [11]. IR (neat), ῡ(cm^{-1}); 3401, 2927, 2360, 2149, 1594, 1513, 1333, 1274, 1183, 819, 527.[1] H-NMR (250 MHz, $CDCl_3$) δ(ppm); 2.63 (s, 3H), 3.32 (s, br, 1H), 6.50 (d, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 30.26, 107.45, 112.71, 113.38, 134.78, 151.11.

3-Chloro-4-thiocyanatoaniline (15c)



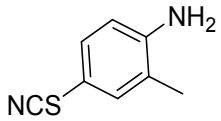
Yellow solid. mp = 59-62 °C(lit. 63-64 °C) [12]. IR (KBr), ῡ(cm^{-1}); 3430, 3340, 3214, 2149, 1634, 1593, 1476, 1384, 1302, 1240, 1020, 814, 668. ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm); 4.00 (brs, 2H), 7.45-6.55 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 108.7, 111.0, 114.5, 116.1, 135.3, 137.7, 149.9. $C_7H_5ClN_2S$: Calcd. C, 45.54; H, 2.73; N, 15.17; S, 17.36; Found. C, 45.44; H, 2.65; N, 15.06; S, 17.00.

***N*-Ethyl-4-thiocyanatoaniline (15d)**



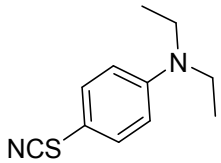
Yellow solid. mp = 53-55 °C (lit. 54-56 °C) [13]. IR (KBr), ῡ(cm^{-1}); 3402, 2971, 2151, 1597, 1512, 1332, 1177, 816. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 1.26 (t, *J* = 7.5 Hz, 3H), 3.16 (q, *J* = 7.5 Hz, 2H), 3.90 (s, br, 1H), 6.63 (d, *J* = 9.25 Hz, 2H), 7.39 (d, *J* =10 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 14.5, 38.0, 107.3, 112.6, 113.6, 134.8, 150.2. $C_9H_{10}N_2S$: Calcd. C, 60.64; H, 5.65; N, 15.72; S, 17.99; Found. C, 60.50; H, 5.56; N, 15.54; S, 17.67.

2-Methyl-4-thiocyanatoaniline (15e)



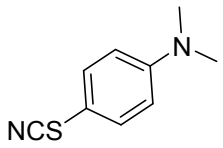
White solid. mp = 62-65 °C (lit. 65-66 °C) [11]. IR (KBr), ῡ(cm^{-1}); 3445, 3364, 3245, 2922, 2150 , 1629, 1491, 1299, 1153, 816, 718, 565. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 2.16 (s, 3H), 3.91 (s, br, 2H), 6.66(d, *J* = 7.5Hz, 1H), 7.24(m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 17.2, 109.3, 112.6, 115.7, 123.9, 132.1, 135.1, 147.1. $C_8H_8N_2S$: Calcd. C, 58.51; H, 4.91; N, 17.06; S, 19.52; Found. C, 58.42; H, 4.78; N, 16.73; S, 19.20.

***N, N*-Diethyl-4-thiocyanatoaniline (15f)**



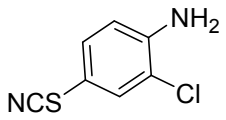
White solid. mp = 74-75 °C (lit. 72-73 °C) [14].IR (KBr), ῡ(cm^{-1}); 2973, 2151, 1591, 1507, 1403, 1355, 1270, 1196, 1077, 810, 741. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 1.17(t, *J* = 7.5 Hz, 6H), 3.36 (q, *J* = 7.5 Hz, 4H), 6.57 (d, *J* = 7.5Hz, 2H), 7.37 (d, *J* =7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 12.3, 44.4, 104.9, 112.5, 112.9, 135.0, 149.2. $C_{11}H_{14}N_{2S}$: Calcd. C, 64.04; H, 6.84; N, 13.58; S, 15.54; Found. C, 63.92; H, 6.74; N, 13.40; S, 15.32.

***N,N*-Dimethyl-4-thiocyanatoaniline (15g)**



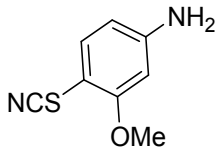
White solid. mp = 72–74 °C (lit. 72–74 °C) [10]. IR (KBr), ῡ(cm^{-1}); 3427, 2913, 2143, 1593, 1509, 1373, 1230, 1073, 807, 512. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 3.00 (s, 6H), 6.67 (d, *J* = 10 Hz, 2H), 7.42 (d, *J* = 10 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 40.17, 106.4, 112.6, 113.1, 134.5, 151.7. $C_9H_{10}N_2S$: Calcd. C, 60.64; H, 5.65; N, 15.72; S, 17.99; Found. C, 60.56; H, 5.52; N, 15.47; S, 17.73.

2-Chloro-4-thiocyanatoaniline (15h)



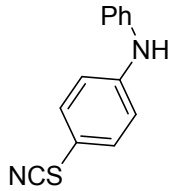
Yellow solid. mp = 58-60 °C (lit. 60–61 °C) [15]. IR (KBr), ῡ(cm^{-1}); 3441, 3369, 3185, 2149, 1618, 1489, 1322, 1257, 822, 723, 570. ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm); 4.30 (brs, 2H), 7.48-6.74 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 109.8, 111.8, 116.4, 119.6, 132.6, 133.8, 145.4. $C_7H_5ClN_2S$: Calcd. C, 45.54; H, 2.73; N, 15.17; S, 17.36; Found. C, 45.43; H, 2.68; N, 15.01; S, 17.05.

3-Methoxy-4-thiocyanatoaniline (15i)



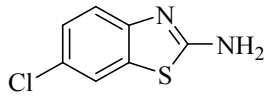
Yellow solid. mp = 99-100 °C (lit. 99–100 °C) [15]. IR (KBr), ῡ(cm^{-1}); 3446, 3371, 3224, 2918, 2148, 1628, 1595, 1471, 1335, 1215, 1020, 825, 638. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 3.88 (s, 3H), 6.26 (m, 2H), 7.29 (d, *J* = 10Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 55.98, 97.85, 98.54, 108.03, 112.16, 135.34, 150.82, 159.72. $C_8H_8N_2OS$: Calcd. C, 53.32; H, 4.47; N, 15.54; S, 17.79; Found. C, 53.15; H, 4.34; N, 15.27; S, 17.52.

N-phenyl-4-thiocyanatoaniline (15j)



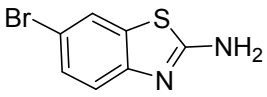
White solid, mp 57–59 °C (lit. 58–60 °C)[16]. IR (KBr), ῡ(cm^{-1}); 3356, 3032, 2171, 1483, 733. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (s, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 111.41 , 112.12 , 117.15 , 120.15 , 123.10 , 129.58 , 134.08 , 140.98 , 146.18. $C_{13}H_{10}N_2S$: Calcd. C, 69.00; H, 4.45; N, 12.38; S, 14.17; Found. C, 69.89; H, 4.93; N, 11.87; S, 13.87.

6-chlorobenzo[d]thiazol-2-amine (17a)



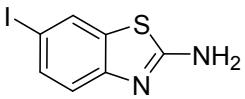
Yellow solid. mp = 211-213 °C (lit. 214-215 °C)[17]. IR (KBr), ῡ(cm^{-1}); 3456, 3270, 3078, 1678, 1532, 1444, 1109, 860, 762. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 5.48 (br s, 2H), 7.27 (d, *J* = 8.6 Hz 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 118.91, 119.72, 127.84, 128.38, 135.63, 154.52, 169.32. $C_8H_8N_2OS$: Calcd. C, 45.54; H, 2.73; N, 15.17; S, 17.36; Found. C, 46.09; H, 2.98; N, 15.28; S, 17.12.

6-bromobenzo[d]thiazol-2-amine (17b)



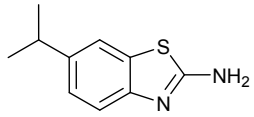
Yellow solid, mp = 211-213 °C. (lit. 214-215 °C)[17]. IR (KBr), ῡ(cm-1); 3423, 3301, 3070, 2946, 1728, 1609, 1543, 1436. ^{1}H NMR (400 MHz, DMSO) δ 7.16 (d, *J* = 8.5 Hz, 1H), 7.22 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.44 (s, 2H), 7.68 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 112.56 , 119.39 , 123.32 , 128.52 , 133.50 , 152.42 , 167.49. $C_7H_5BrN_2S$: Calcd. C, 36.70; H, 2.20; N, 12.23; S, 13.99; Found. C, 36.15; H, 2.07; N, 12.85; S, 14.29.

6-iodobenzo[d]thiazol-2-amine (17c)



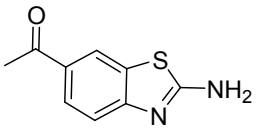
Solid. IR (KBr), ῡ(cm-1); 3398, 3335, 3045, 1783, 1629, 1521, 1396. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm); 7.19 (s, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 6.53 (d, *J* = 8.6 Hz, 1H), 3.64 (s, 2H).

6-isopropylbenzo[d]thiazol-2-amine (17d)



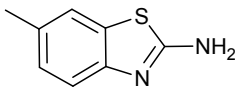
Green solid, mp = 122-124 °C (lit. 121-122 °C)[17].IR (KBr), ῡ(cm-1); 3454, 3103, 2947, 1643, 1558, 1474, 817. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (d, *J* = 7.0 Hz, 6H), 2.80 – 2.95 (m, 1H), 5.22 (s, 2H), 7.11 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.19 (s, 1H), 7.39 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 24.29 , 29.71 , 34.03 , 118.39 , 118.89 , 124.86 , 131.94 , 151.44 , 165.60. $C_{10}H_{12}N_2S$: Calcd. C, 62.47; H, 6.29; N, 14.57; S, 16.67 ; Found. C, 63.09; H, 6.56; N, 15.15; S, 17.32.

1-(2-aminobenzo[d]thiazol-6-yl)ethan-1-one (17e)



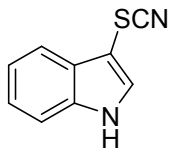
White solid. IR (KBr), ῡ(cm-1); 3444, 3113, 2992, 1724, 1633, 1534, 1479, 988. ^{1}H NMR (400 MHz, DMSO) δ 3.23 (s, 3H), 4.83 (s, 2H), 6.60 (d, *J* = 8.7 Hz, 1H), 7.29 (s, 1H), 7.51 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 29.05 , 111.30 , 113.26 , 121.03 , 124.54, 129.79 , 148.67 , 159.74 , 170.42. $C_9H_8N_2OS$: Calcd. C, 56.23; H, 4.19; N, 14.57; S, 16.68; Found. C, 55.93; H, 4.47; N, 14.16; S, 17.02.

6-methylbenzo[d]thiazol-2-amine (17f)



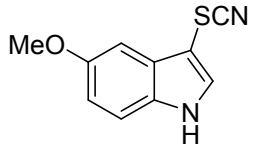
Yellow solid, mp = 128-130 °C (lit. 129-130 °C)[17]. IR (KBr), ῡ(cm-1); 3404, 3279, 3079, 2307, 1671, 1519, 1483, 1134, 823. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 5.25 (s, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.19 (s, 1H), 7.34 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.26, 118.86, 120.98, 127.19, 129.29, 132.17, 149.81, 165.12. $C_8H_8N_2S$: Calcd. C, 58.51; H, 4.91; N, 17.06; S, 19.52; Found. C, 59.03; H, 5.08; N, 17.32; S, 19.86.

3-Thiocyanato-*1H*-indole (19a)



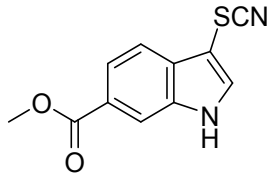
White solid, mp = 71–73 °C (lit. 72−74 °C) [18]. IR (KBr), ῡ(cm^{-1}); 3345, 2161, 1455, 1419, 1235, 736, 670, 592; ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 7.15-7.62 (m, 4H), 7.92 (s,1H), 11.97 (br,s,1H). ^{13}C NMR (62.5 MHz, DMSO-d_6) δ(ppm); 89.2, 112.2, 112.7, 117.6, 121.0, 122.8, 127.3, 133.1, 136.2. $C_9H_6N_2S$: Calcd. C, 62.05; H, 3.47; N, 16.08; S, 18.40; Found. C, 61.98; H, 3.32; N, 15.92; S, 18.27.

5-Methoxy-3-thiocyanato-*1H*-indole (19b)



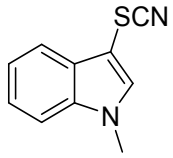
White solid. mp = 121−124 °C (lit. 123−125 °C) [18]. IR (KBr), ῡ(cm^{-1}); 3292, 3135, 2154, 1485, 1455, 1291, 1240, 1201, 1165, 1018, 920, 803, 709, 623, 580. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 3.89 (s, 3H), 6.92 (d, *J* = 10 Hz, 1H), 7.17 (s, 1H), 7.26 (d, *J* = 10 Hz, 1H), 7.40 (s, 1H), 8.78 (s, br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 55.8, 89.0, 99.5, 112.8, 113.6, 114.2, 128.7, 131.6, 133.9, 155.4. $C_{10}H_8N_2OS$: Calcd. C, 58.81; H, 3.95; N, 13.72; S, 15.70; Found. C, 58.74; H, 3.86; N, 13.53; S, 15.49.

Methyl 3-thiocyanato-1H-indole-6-carboxylate (19c)



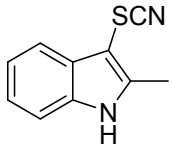
White solid. mp = 196-198 °C. IR (KBr), ῡ(cm^{-1}); 3292, 3150, 2944, 2153, 1695, 1429, 1313, 1233, 1111, 1084, 835, 770, 593, 525. ^{1}H-NMR (250 MHz, DMSO-d_6) δ(ppm); 3.68 (s, 3H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 10 Hz, 1H), 7.96 (s, 1H), 8.02 (s, 1H), 12.17 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 52.5, 90.9, 112.6, 115.1, 118.3, 122.0, 124.5, 131.4, 136.1, 137.0, 167.1. $C_{11}H_8N_2O_2S$: Calad. C, 56.89; H, 3.47; N, 12.06; S, 13.80; Found. C, 56.80; H, 3.38; N, 11.83; S, 13.56.

1-Methyl-3-thiocyanato-*1H*-indole (19d)



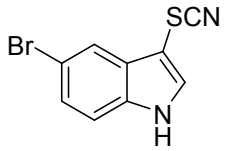
White solid, mp = 75−77 °C (lit. 76−78 °C)[18]. IR (KBr), ῡ(cm^{-1}); 2946, 2924, 2151, 1611, 1515, 1243, 757, 662, 542. ^{1}H-NMR (250 MHz, DMSO-d_6) δ(ppm); 3.35 (s, 3H), 7.24-7.36 (m, 2H), 7.58 (d, J = 7.5, 1H), 7.66 (d, J = 7.5, 1H), 7.97 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 33.6, 88.5, 111.6, 112.7, 118.3, 121.7, 123.4, 128.2, 137.0, 137.4. $C_{10}H_8N_2S$. Calcd. C, 63.80; H, 4.28; N, 14.88; S, 17.03; Found. C, 63.72; H, 4.16; N, 14.70; S, 16.76.

2-Methyl-3-thiocyanato-*1H*-indole (19e)



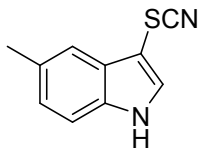
White solid, mp = 98-100 °C (lit. 99-101 °C) [19]. IR (KBr), ῡ(cm^{-1}); 3328, 2154, 1407, 1297, 1233, 742, 657, 617. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 2.52 (s,3H), 7.15-7.19 (m,2H), 7.41 (t,1H), 7.54 (t,1H), 11.96 (s,1H,NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 12.1, 87.1, 112.3, 112.6, 117.5, 121.3, 122.6, 128.7, 135.8, 143.5. $C_{10}H_8N_2S$: Calcd. C, 63.80; H, 4.28; N, 14.88; S, 17.03; Found. C, 63.73; H, 4.15; N, 14.64; S, 16.87.

5-Bromo-3-thiocyanato-*1H*-indole (19f)



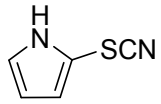
White solid. mp = 132−136 °C (lit. 138−141°C) [18]. IR (KBr), ῡ(cm^{-1}); 3341, 3109, 2150, 1460, 1408, 1237, 1214, 1108, 797, 655, 605, 565. ^{1}H-NMR (250 MHz, DMSO-d_6) δ(ppm); 7.37 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 10 Hz, 1H), 7.79 (s, 1H), 8.04 (s, 1H), 12.18 (s, 1H). ^{13}C NMR (62.5 MHz, DMSO-d_6) δ(ppm); 89.7, 112.5, 114.2, 115.3, 120.4, 126.0, 129.6, 135.0, 135.5. $C_9H_5BrN_2S$: Calcd. C, 42.71; H, 1.99; N, 11.07; S, 12.67; Found. C, 42.63; H, 1.92; N, 12.89; S, 12.44.

5-Methyl-3-thiocyanato-*1H*-indole (19g)



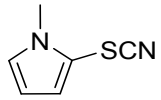
White solid. mp = 87−90 °C (lit. 88−90 °C) [18]. IR (KBr), ῡ(cm^{-1}); 3325, 3287, 2156, 1430, 1242, 1101, 795, 669, 607, 569. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 2.51 (s, 3H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 10 Hz, 1H), 7.44 (s, 1H), 7.59 (s, 1H), 8.61 (s, br, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ(ppm); 21.5, 91.4, 111.7, 112.1, 118.2, 125.5, 127.9, 130.9, 131.5, 134.3. $C_{10}H_8N_2S$: Calcd. C, 63.80; H, 4.28; N, 14.88; S, 17.03; Found. C, 63.70; H, 4.17; N, 14.71; S, 16.74.

2-Thiocyanato-*1H*-pyrrole (19h)



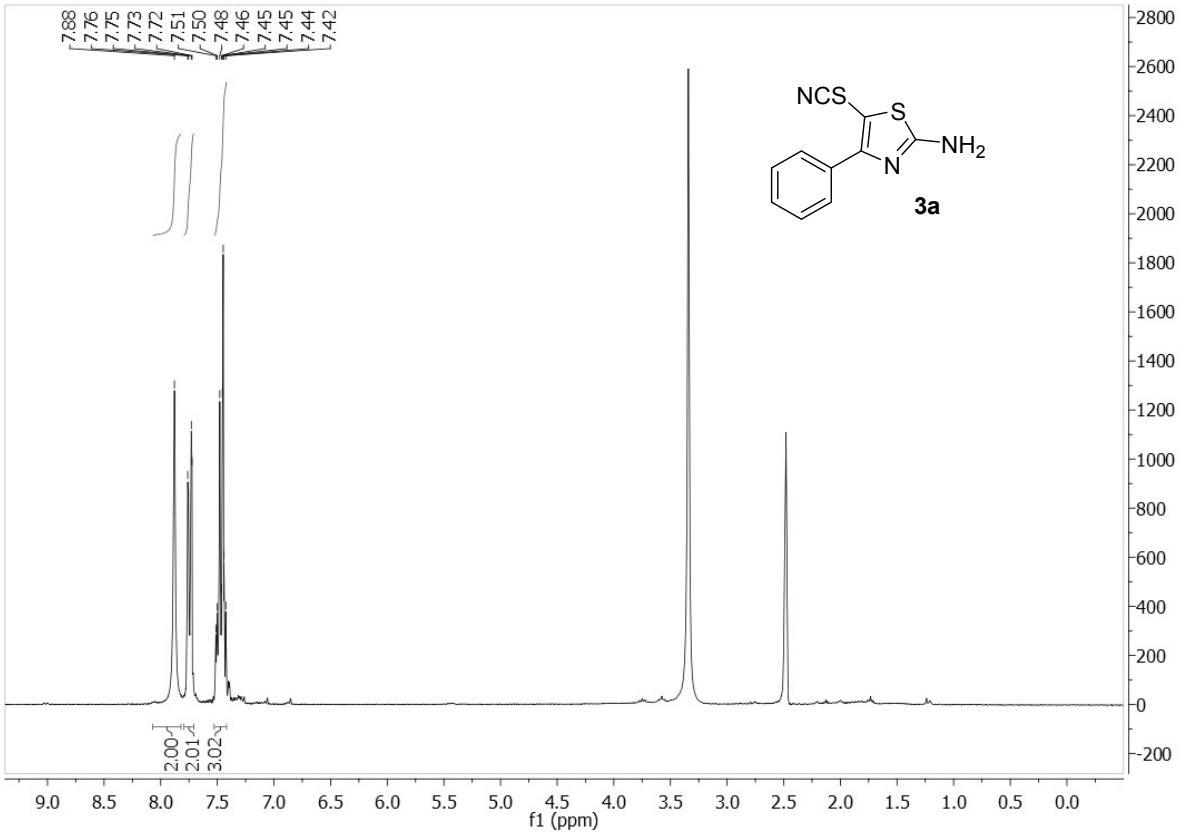
Pink liquid. IR (neat), ῡ(cm^{-1}); 3676, 2159, 1708, 1422, 1365, 1227, 1122, 1029, 737. ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm): 6.30 (s, 1H), 6.66 (s, 1H), 7.01 (s, 1H), 8.67 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 102.95, 110.98, 111.29, 120.21, 124.46.

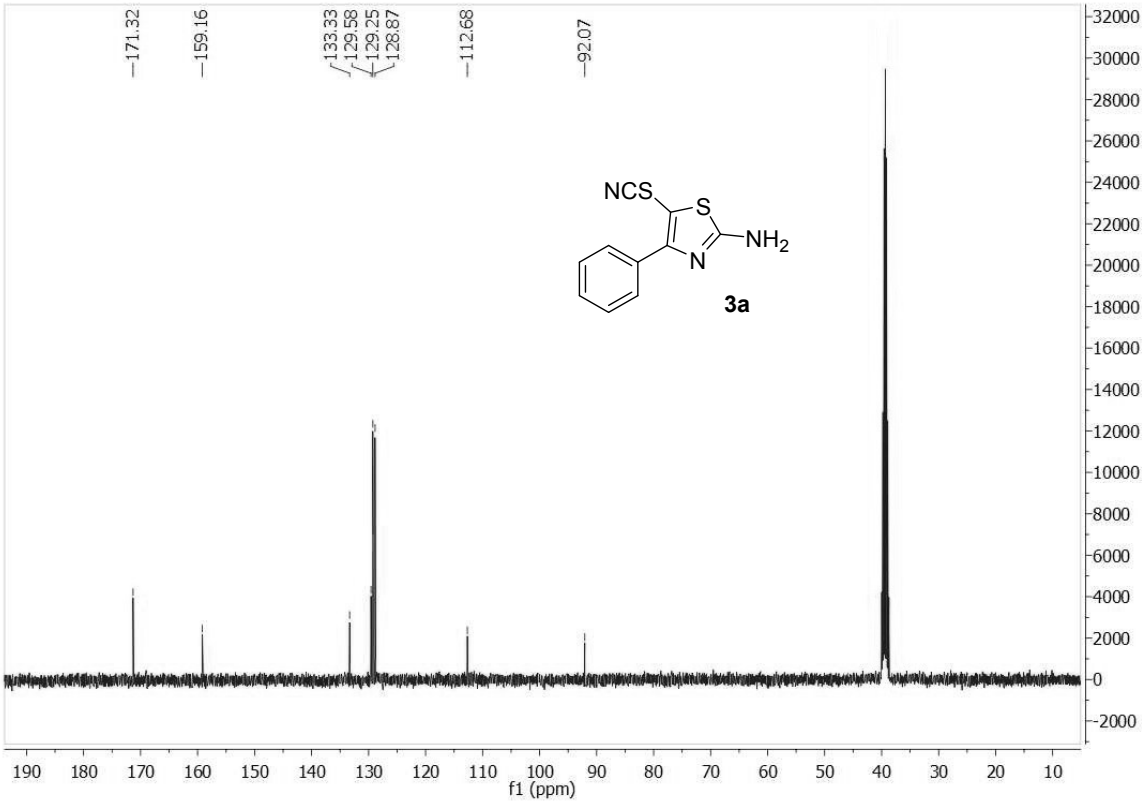
1-Methyl-2-thiocyanato-*1H*-pyrrole (19i)

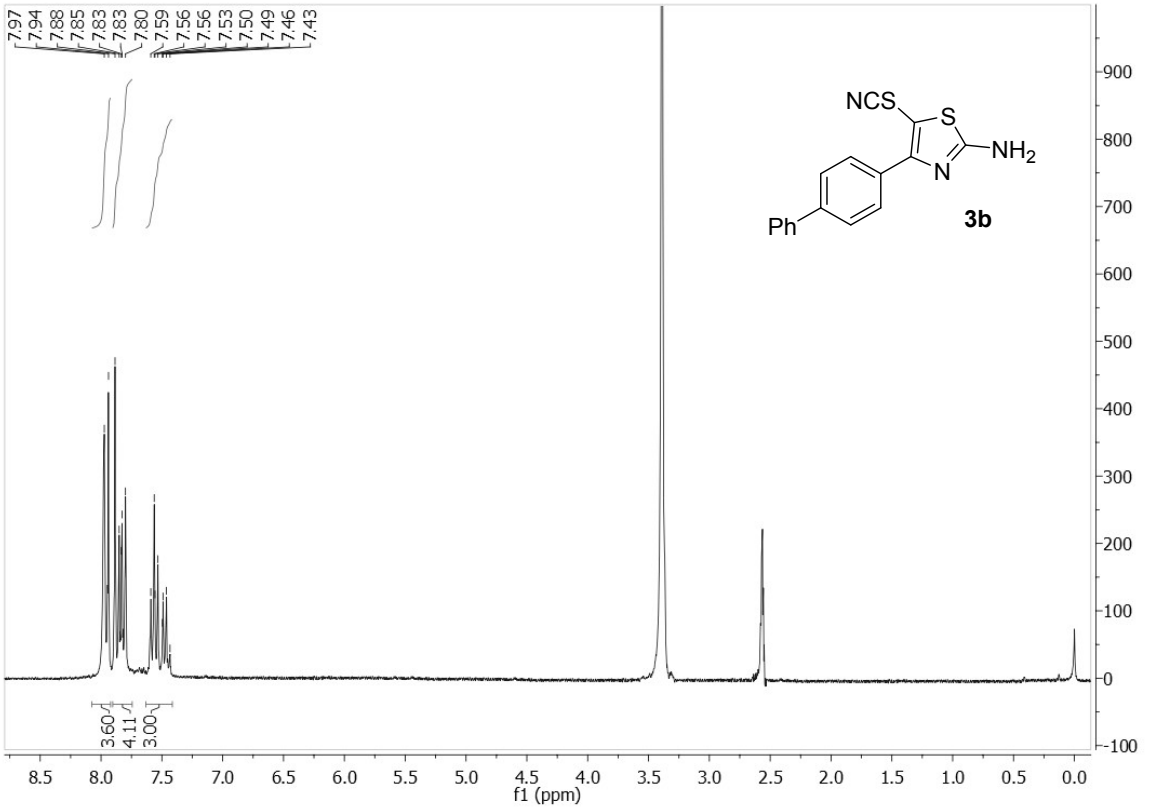


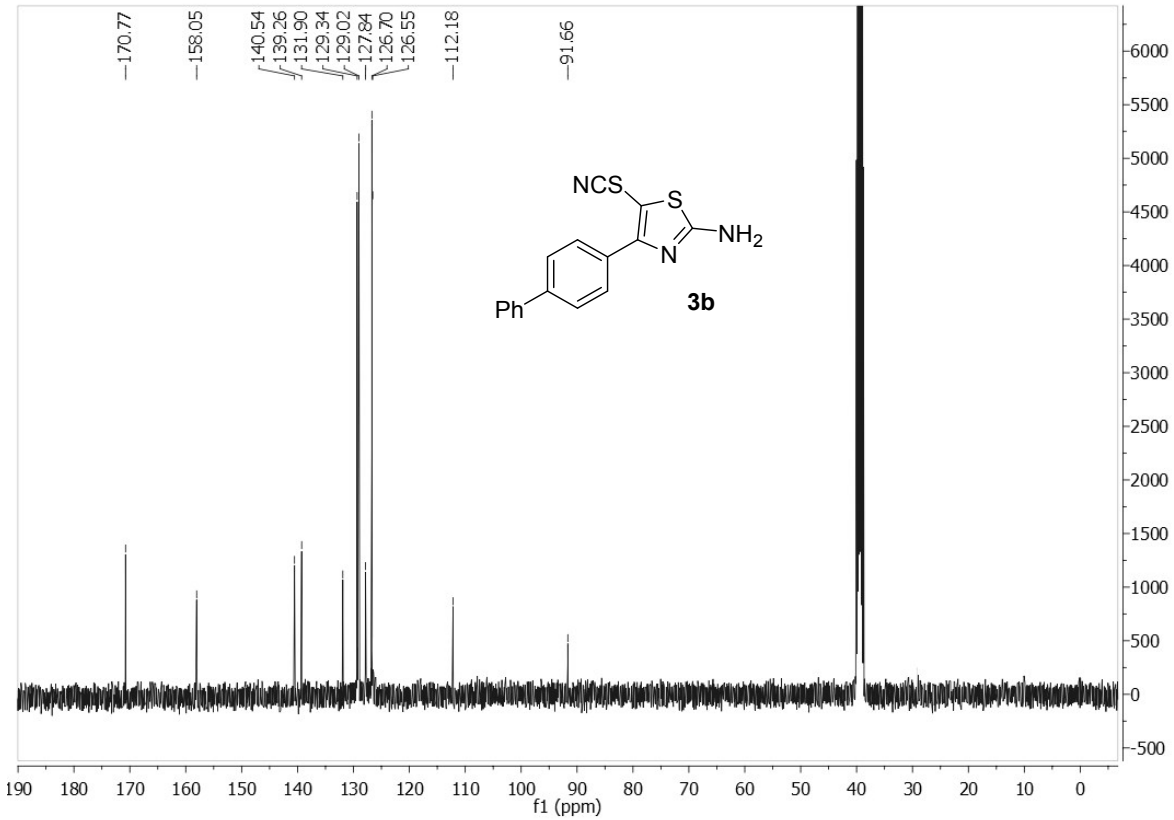
Brown liquid. IR (neat), ῡ(cm^{-1}); 3459, 3120, 2156, 1600, 1464, 1329, 1293, 1120, 1089, 805, 729. ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm): 3.78(s, 3H), 6.18 (s, 1H), 6.62 (s, 1H), 6.91 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 34.60, 109.63, 110.26, 120.13, 120.87, 128.46.

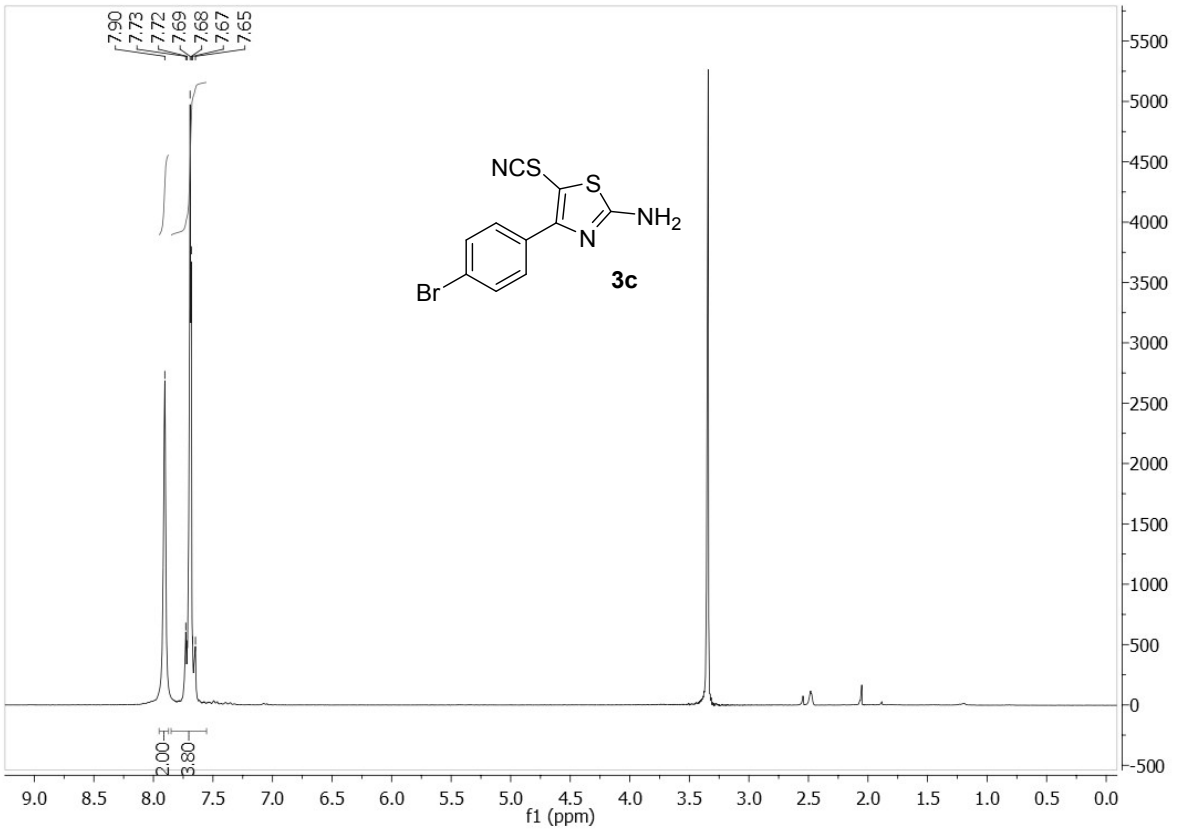
3) ^{1}H and ^{13}C NMR Spectra of Products

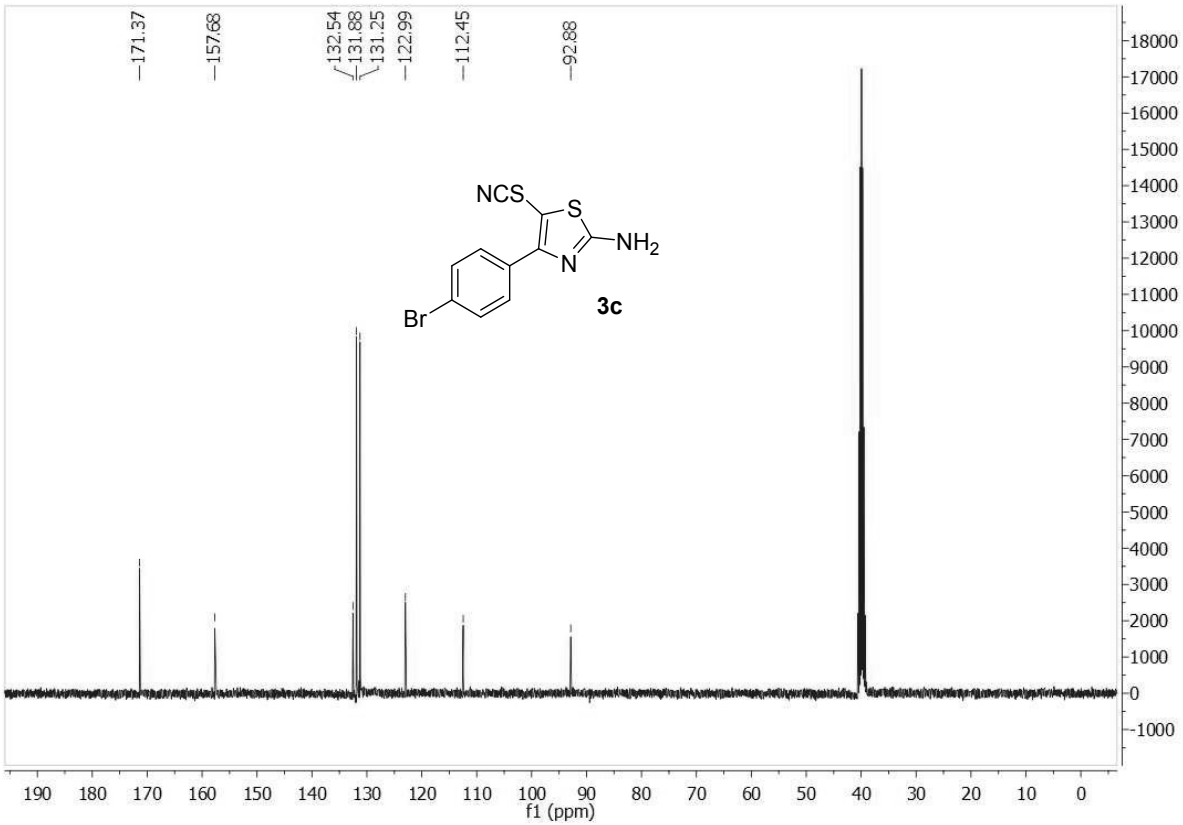


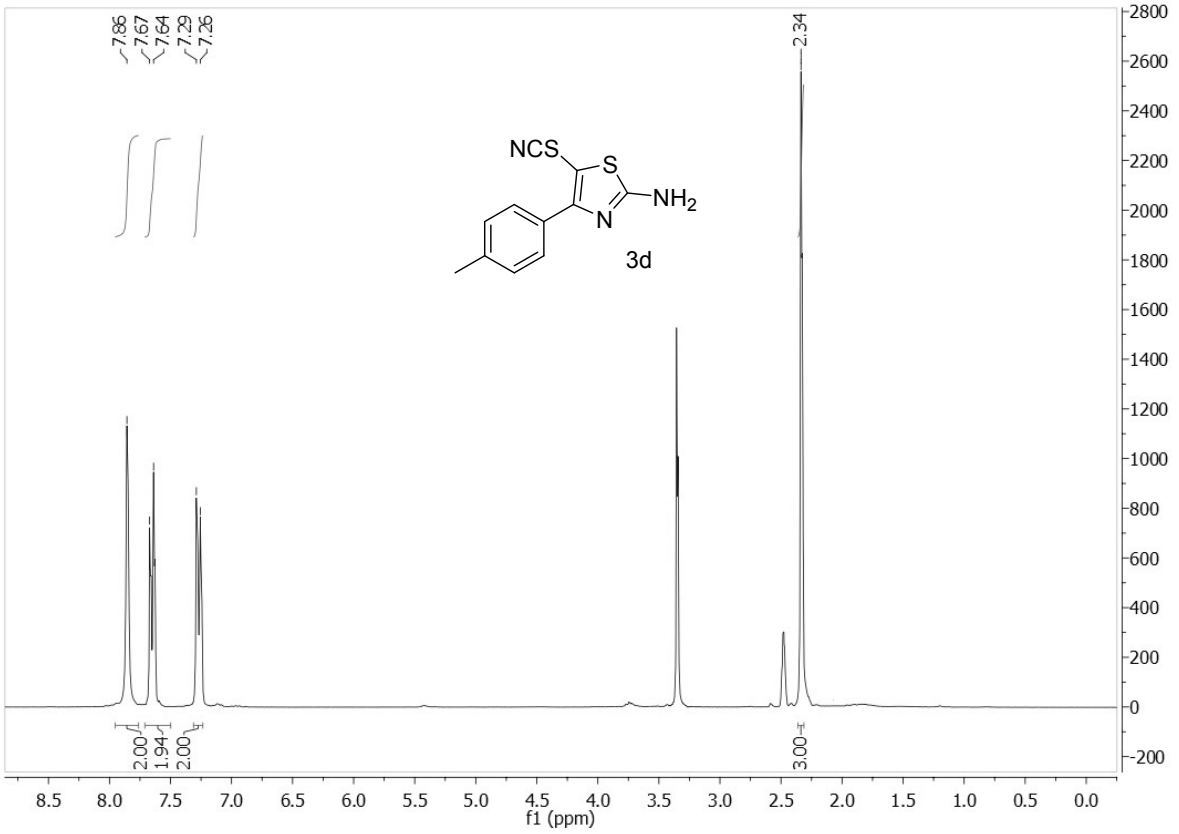


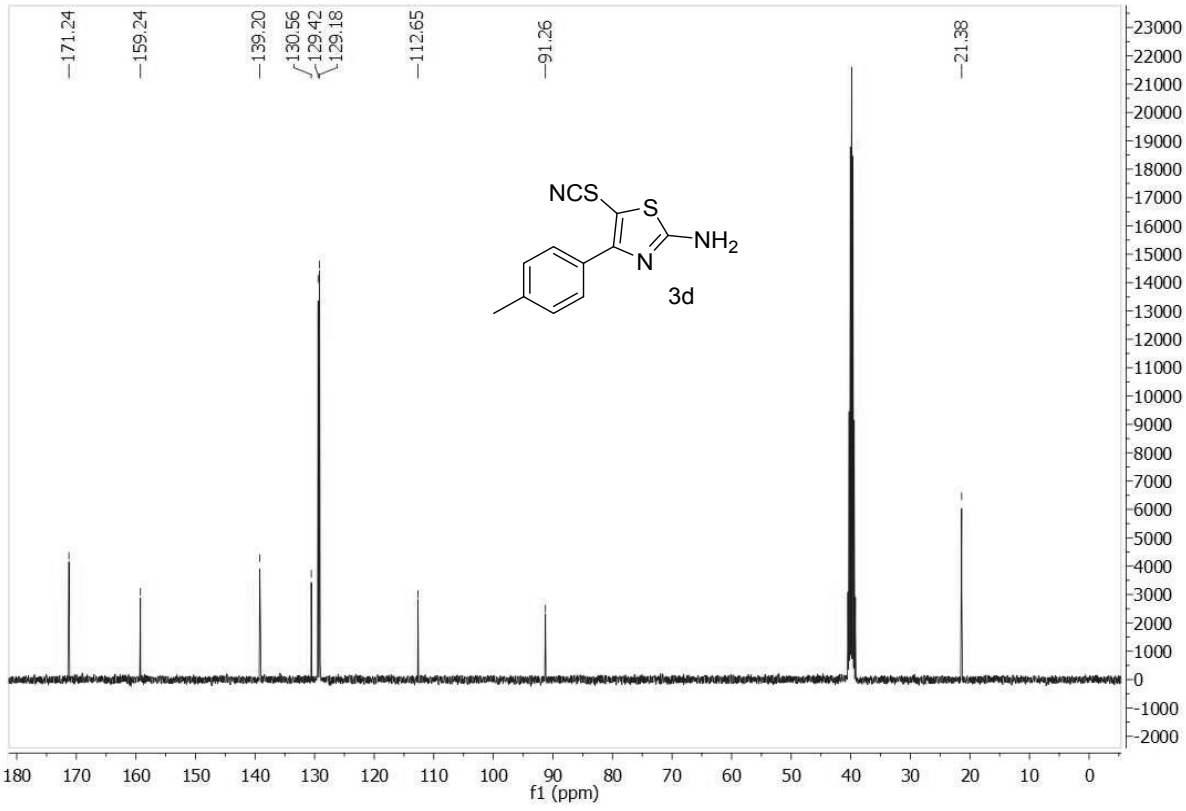

7.97
7.94
7.88
7.85
7.83
7.83
7.80
7.59
7.56
7.56
7.53
7.50
7.49
7.46
7.43
3.60
4.11
3.00
NCS
S
NH2
N
Ph
3b
f1 (ppm)

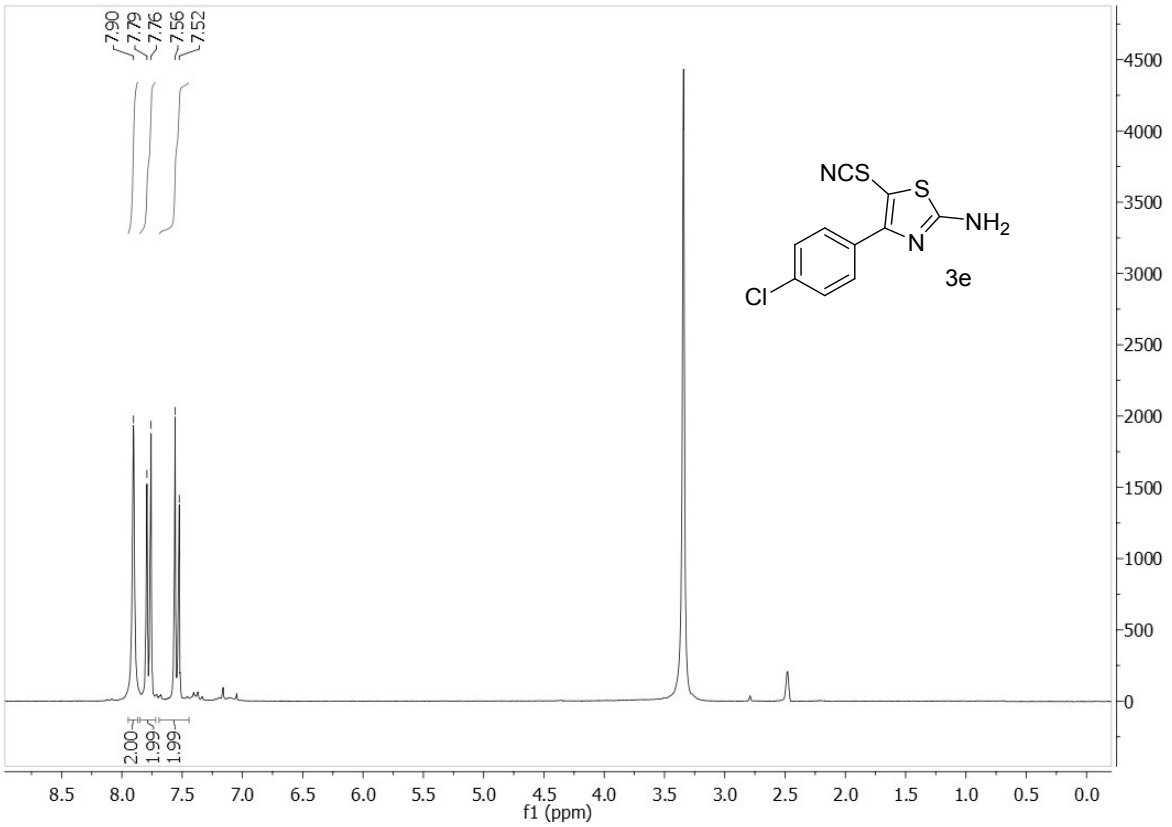

170.77
158.05
140.54
139.26
131.90
129.34
129.02
127.84
126.70
126.55
112.18
91.66
NCS
S
NH2
N
Ph
3b
f1 (ppm)


7.90
7.73
7.72
7.69
7.68
7.67
7.65
NCS
S
NH2
N
Br
3c
2.00
3.80
f1 (ppm)


171.37
157.68
132.54
131.88
131.25
122.99
112.45
92.88
NCS
S
NH2
N
Br
3c
f1 (ppm)


7.86
7.67
7.64
7.29
7.26
2.34
NCS
S
NH2
N
3d
2.00
1.94
2.00
3.00
f1 (ppm)


171.24
159.24
139.20
130.56
129.42
129.18
112.65
91.26
21.38
NCS
S
NH2
N
3d
f1 (ppm)


7.90
7.79
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7.56
7.52
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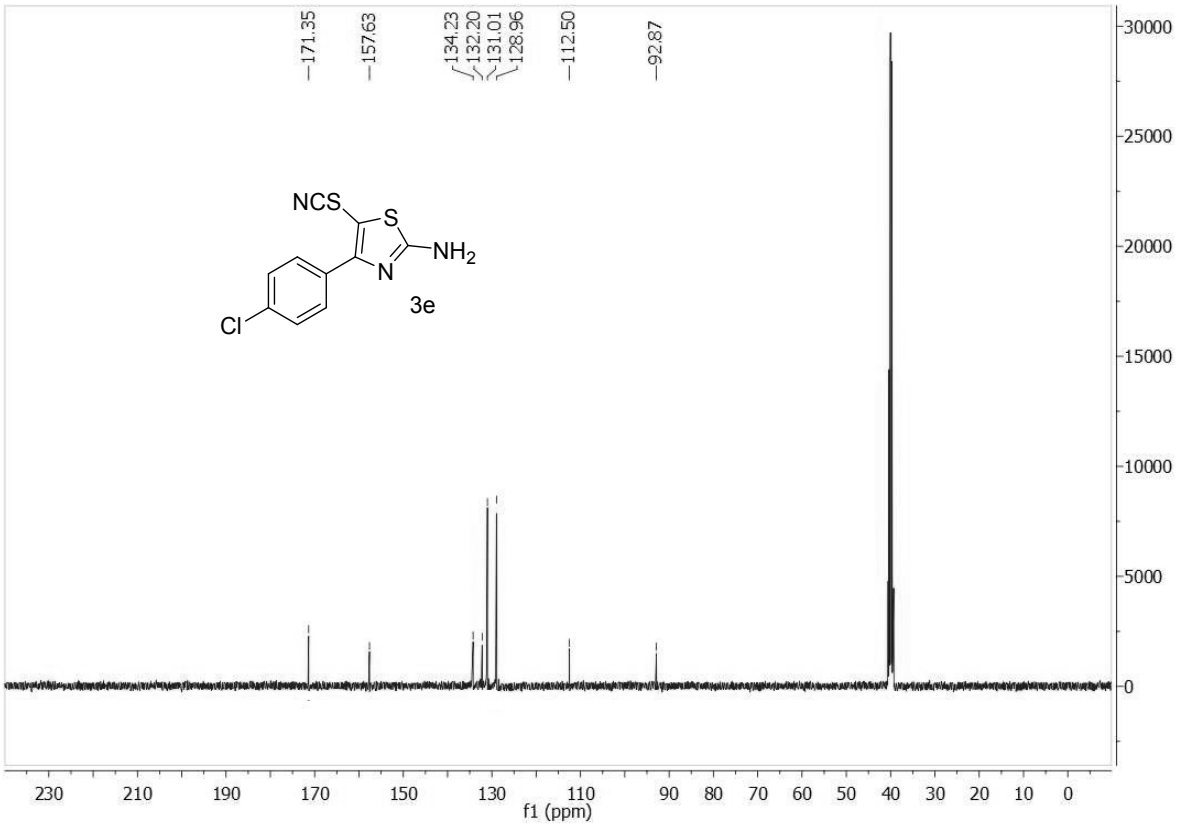
S
NH2
N
Cl
3e
2.00
1.99
1.99
f1 (ppm)


171.35
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131.01
128.96
112.50
92.87
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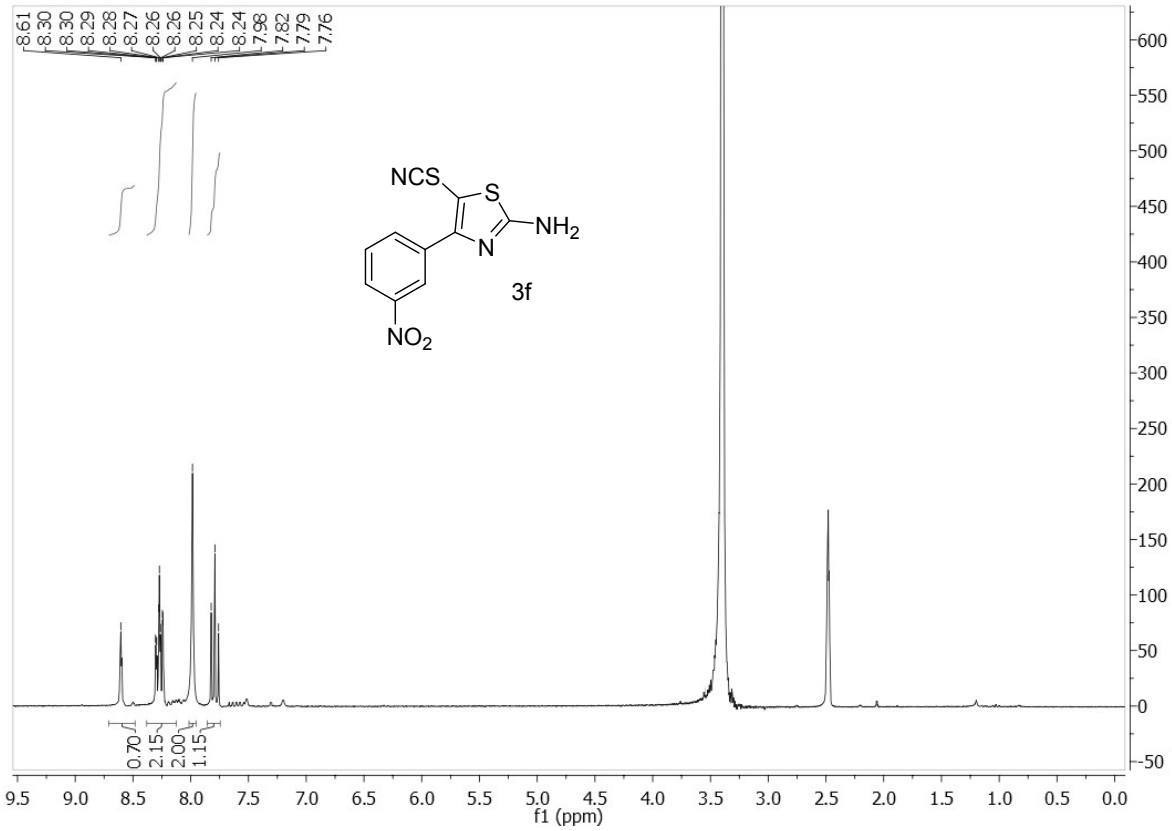
S
NH2
N
Cl
3e
f1 (ppm)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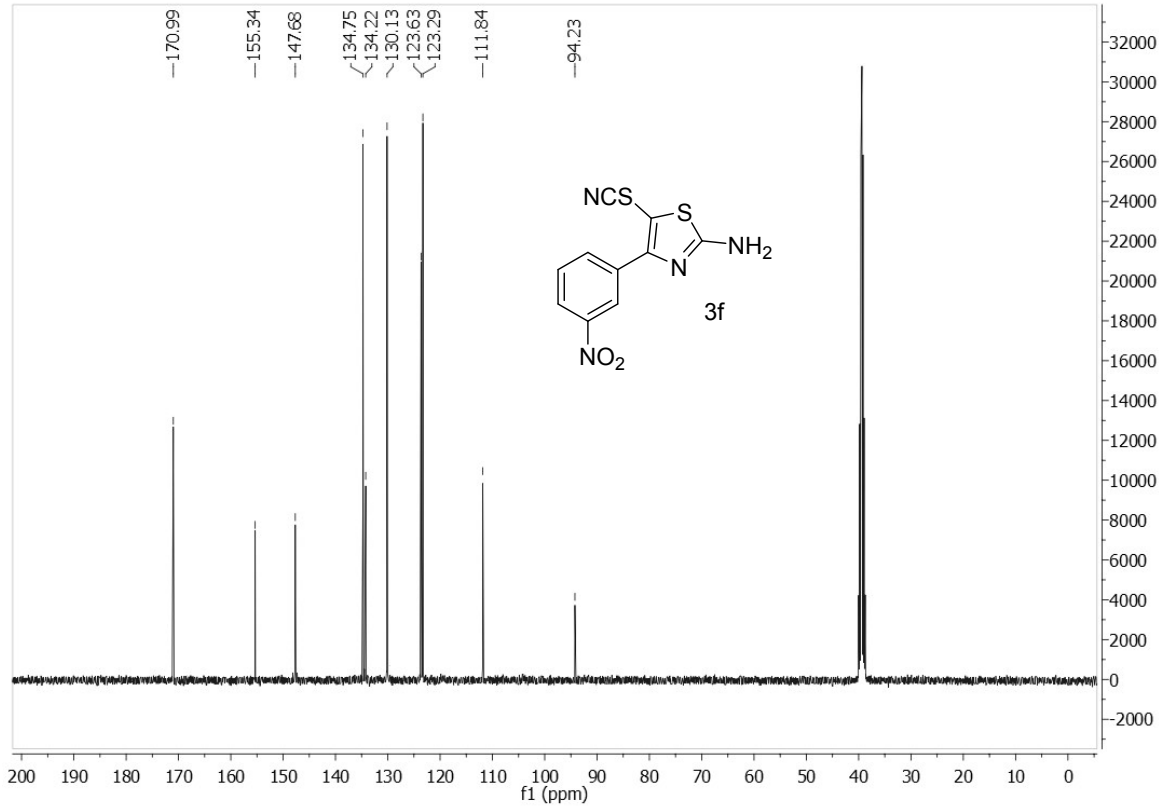
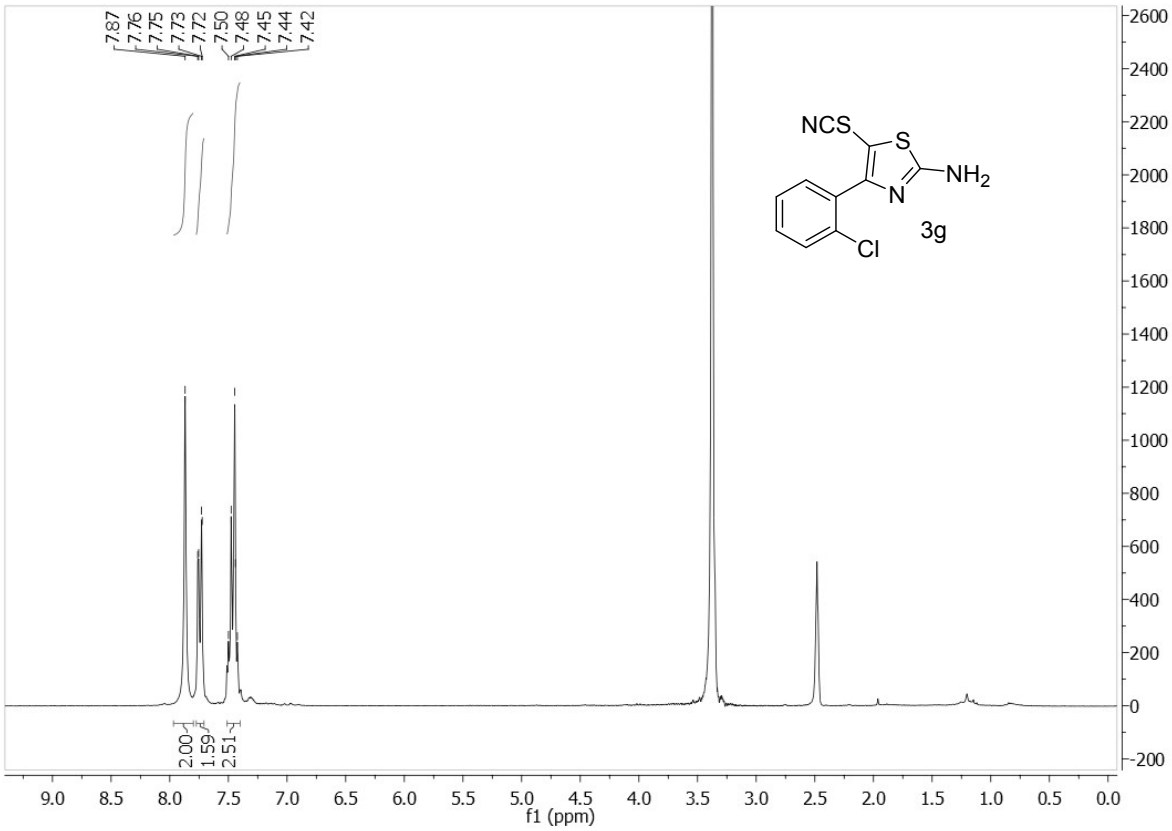
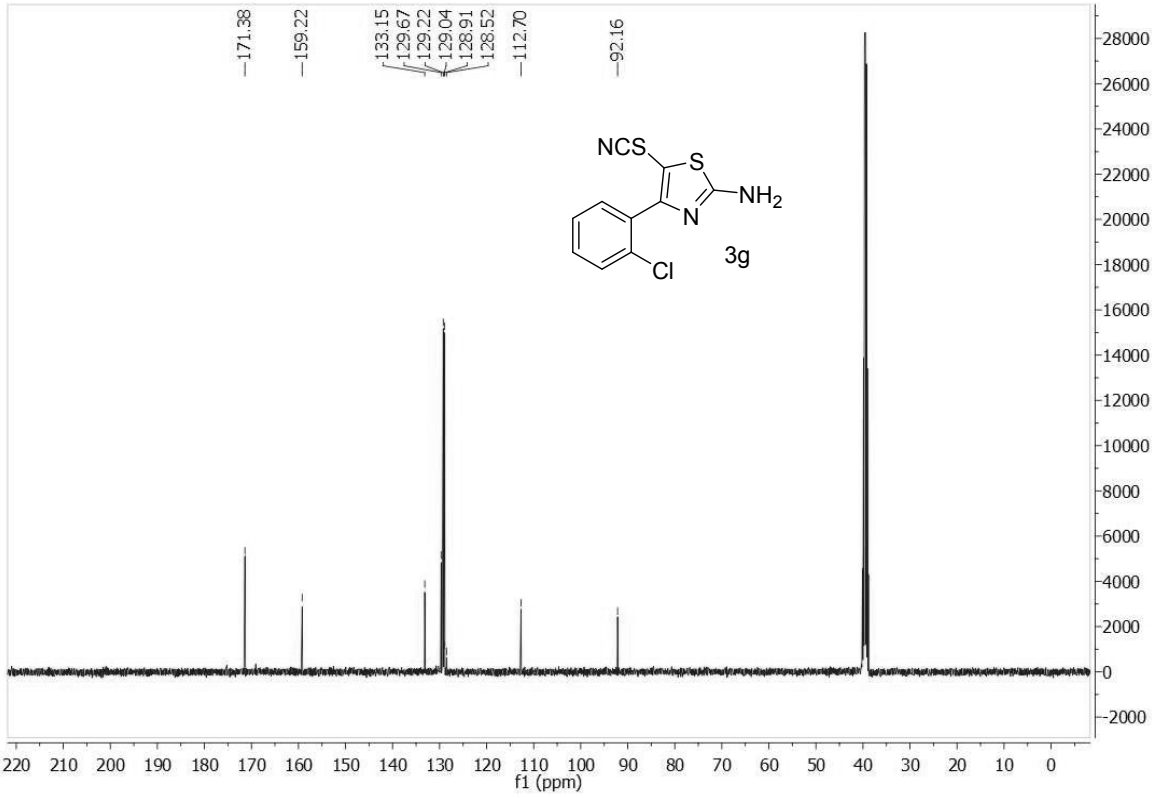
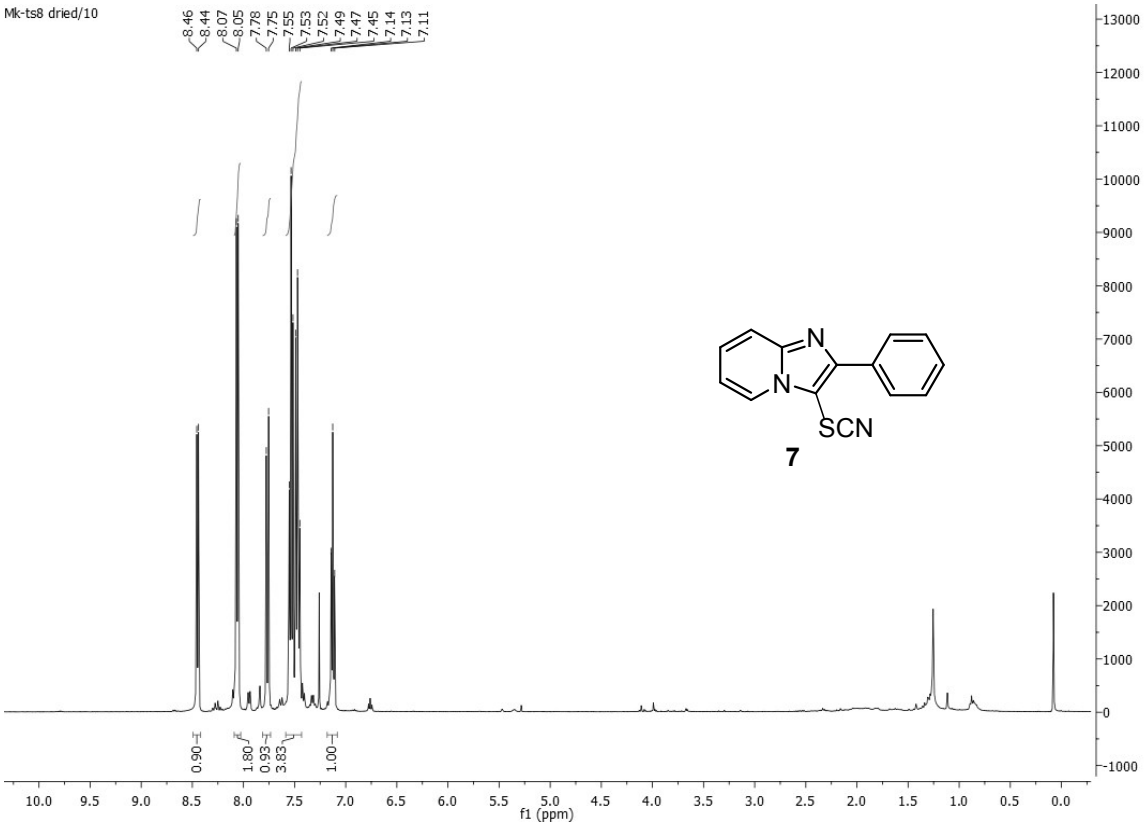
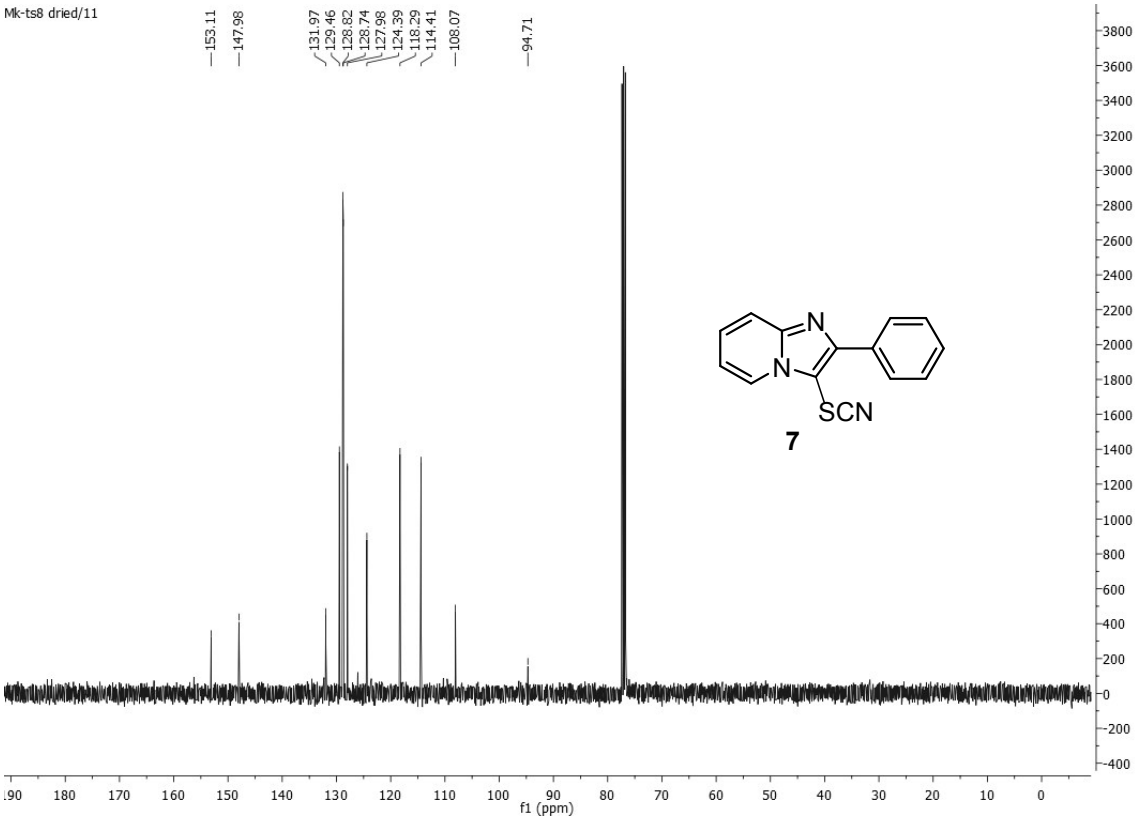
8.30
8.30
8.29
8.28
8.27
8.26
8.26
8.25
8.24
8.24
7.98
7.82
7.79
7.76
NCS
S
NH2
N
3f
NO2
0.70
2.15
2.00
1.15
f1 (ppm)

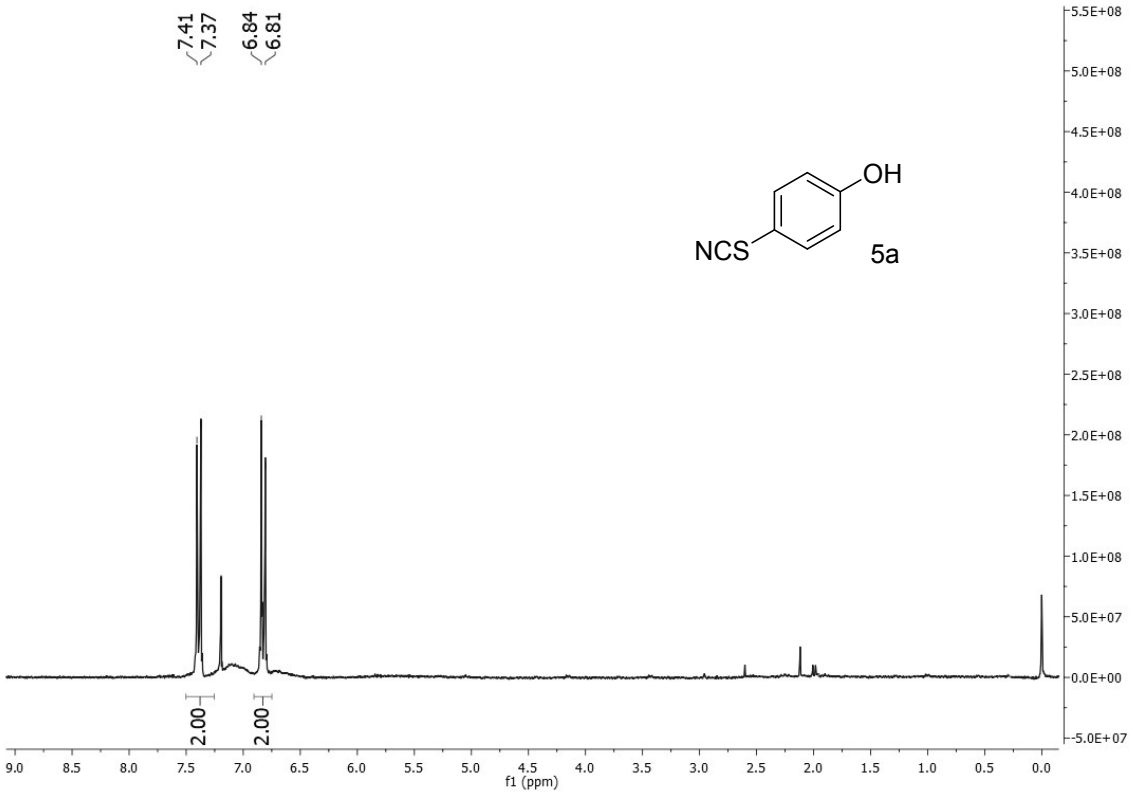

170.99
155.34
147.68
134.75
134.22
130.13
123.63
123.29
111.84
94.23
NCS
S
NH2
N
3f
NO2
f1 (ppm)


7.87
7.76
7.75
7.73
7.72
7.50
7.48
7.45
7.44
7.42
NCS
S
NH2
N
Cl
3g
2.00
1.59
2.51
f1 (ppm)


171.38
159.22
133.15
129.67
129.22
129.04
128.91
128.52
112.70
92.16
NCS
S
NH2
N
Cl
3g
f1 (ppm)


Mk-ts8 dried/10
8.46
8.44
8.07
8.05
7.78
7.75
7.55
7.53
7.52
7.49
7.47
7.45
7.14
7.13
7.11
0.90
1.80
0.93
3.83
1.00
f1 (ppm)
N
N
SCN
7


Mk-ts8 dried/11
153.11
147.98
131.97
129.46
128.82
128.74
127.98
124.39
118.29
114.41
108.07
94.71
f1 (ppm)
N
N
SCN
7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6.81
OH
NCS
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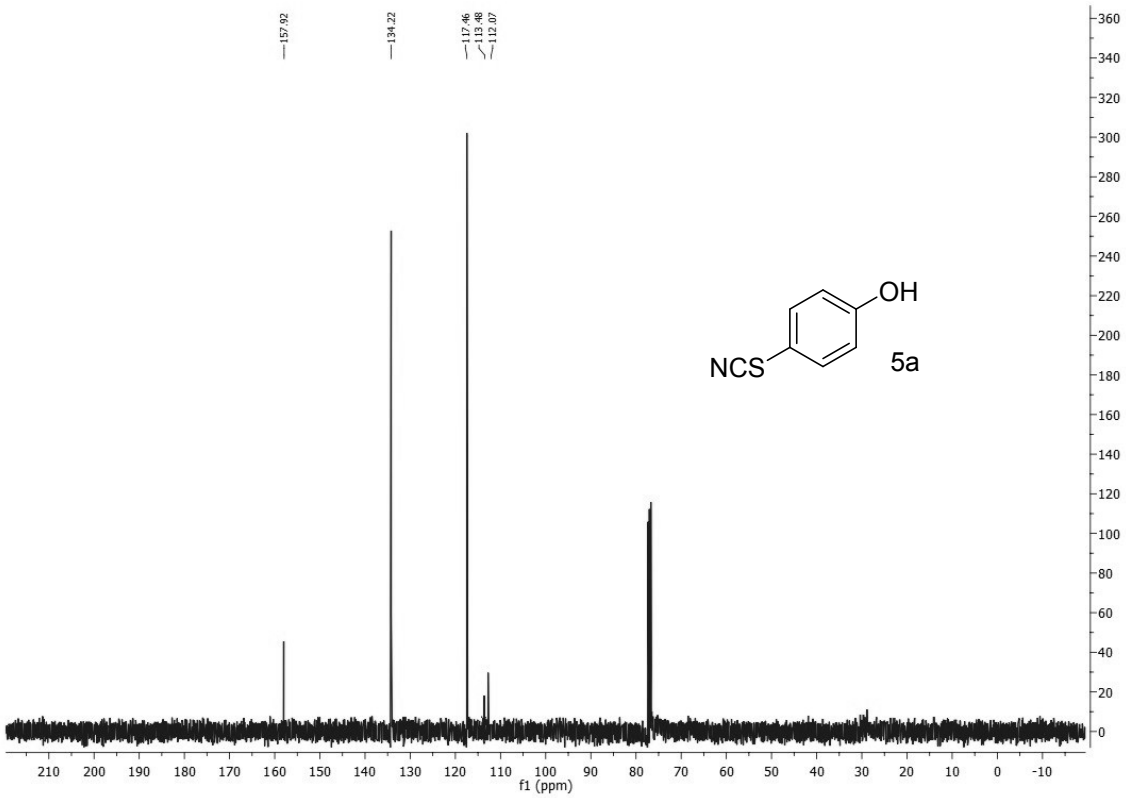
2.00
f1 (ppm)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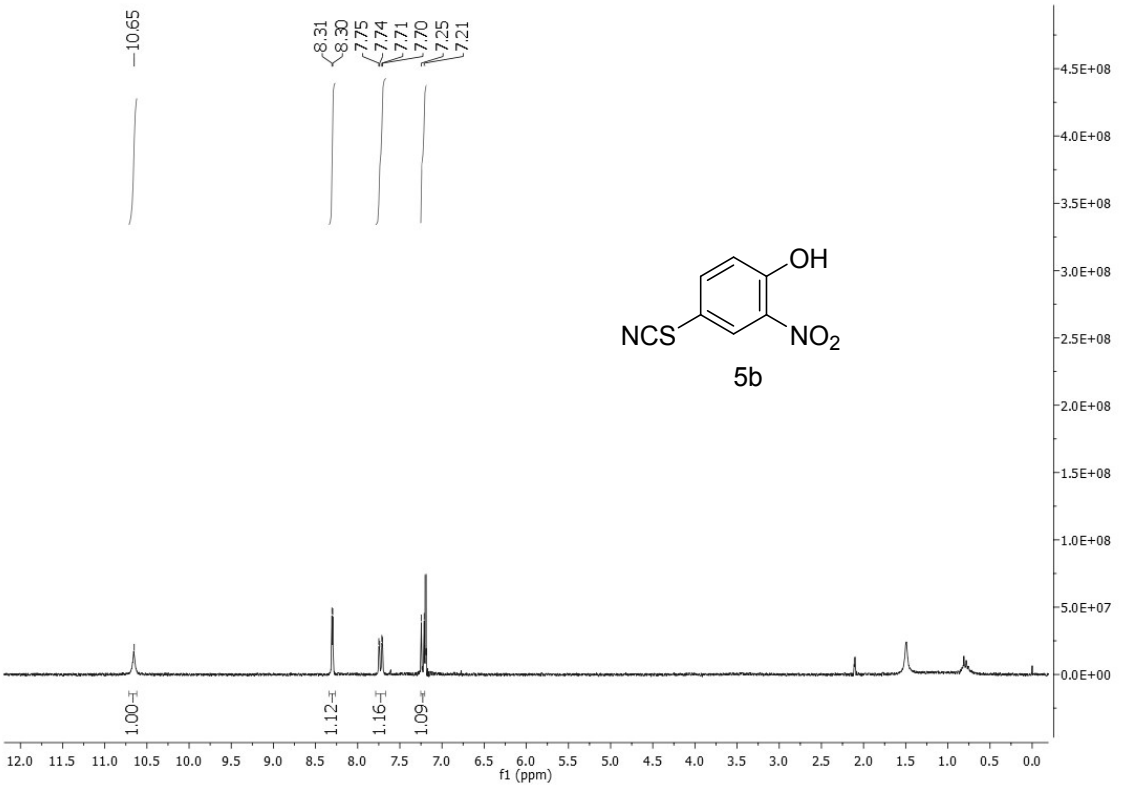
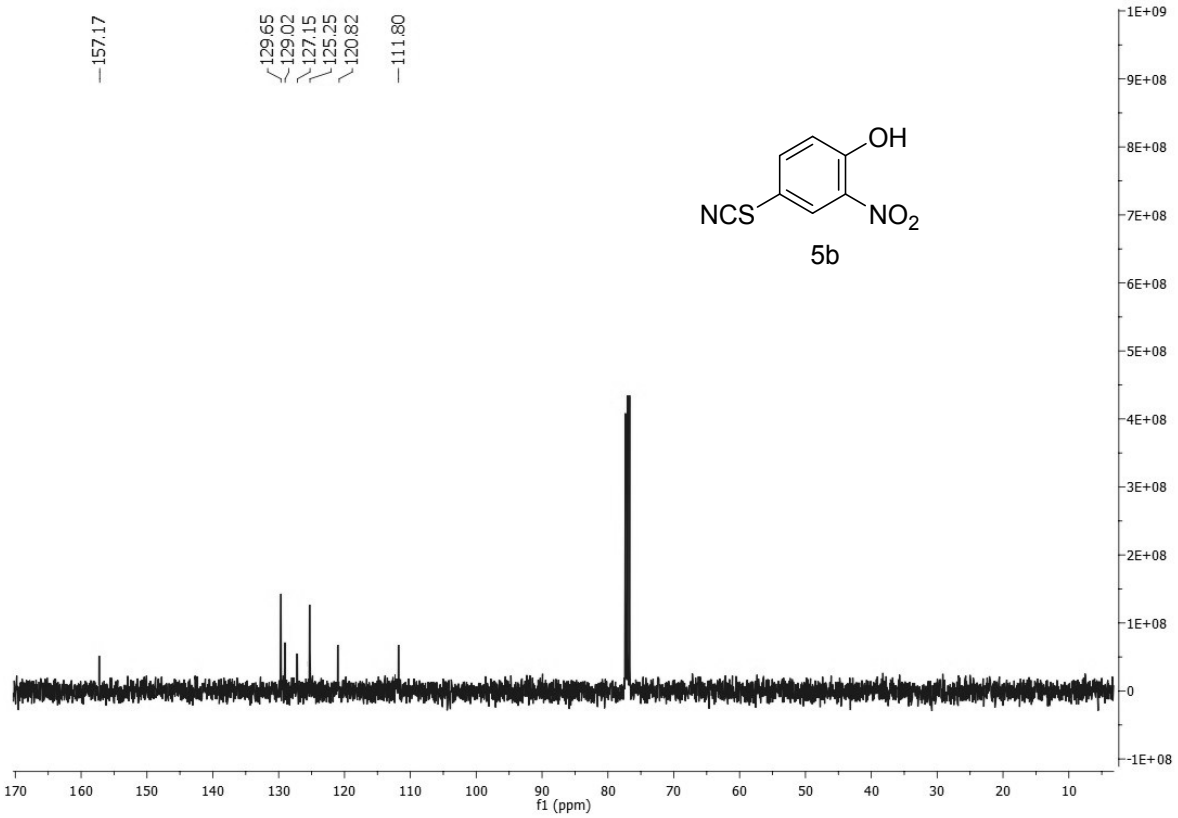
134.22
117.46
113.48
112.07
OH
NCS
5a
f1 (ppm)


10.65
8.31
8.30
7.75
7.74
7.71
7.70
7.25
7.21
OH
NCS
NO2
5b
1.00
1.12
1.16
1.09
f1 (ppm)


157.17
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129.02
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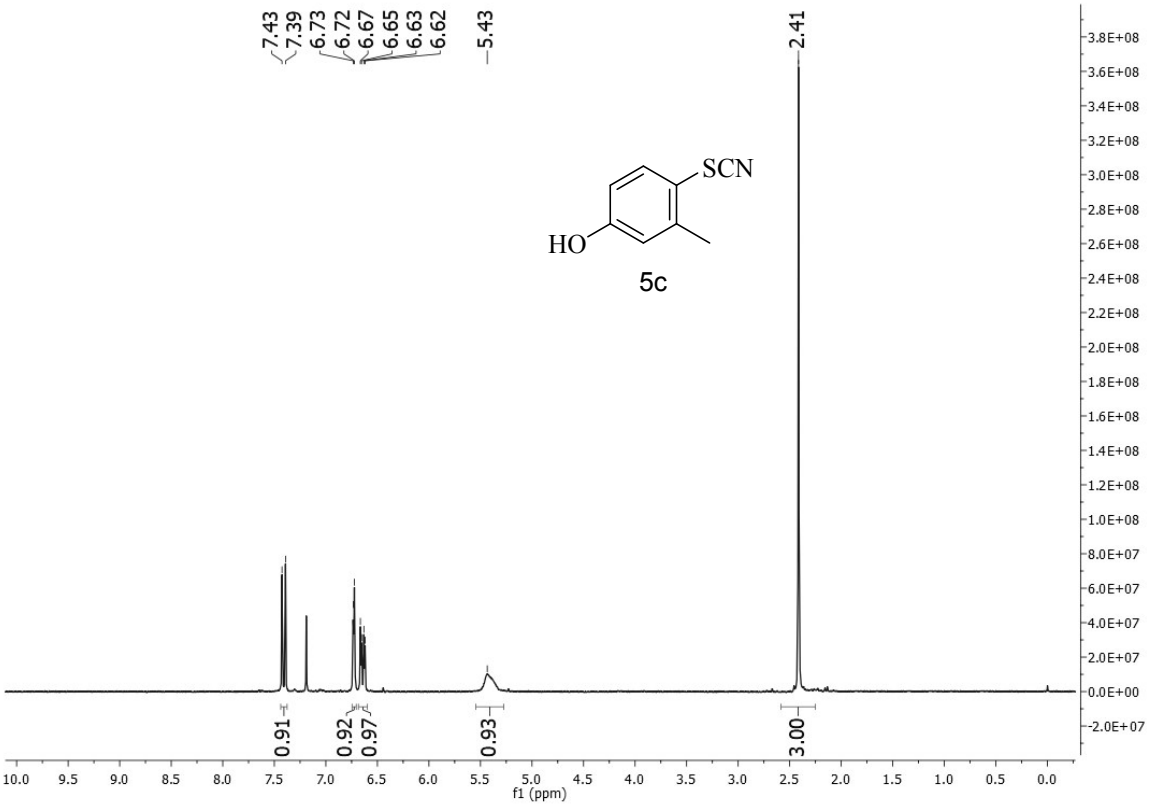
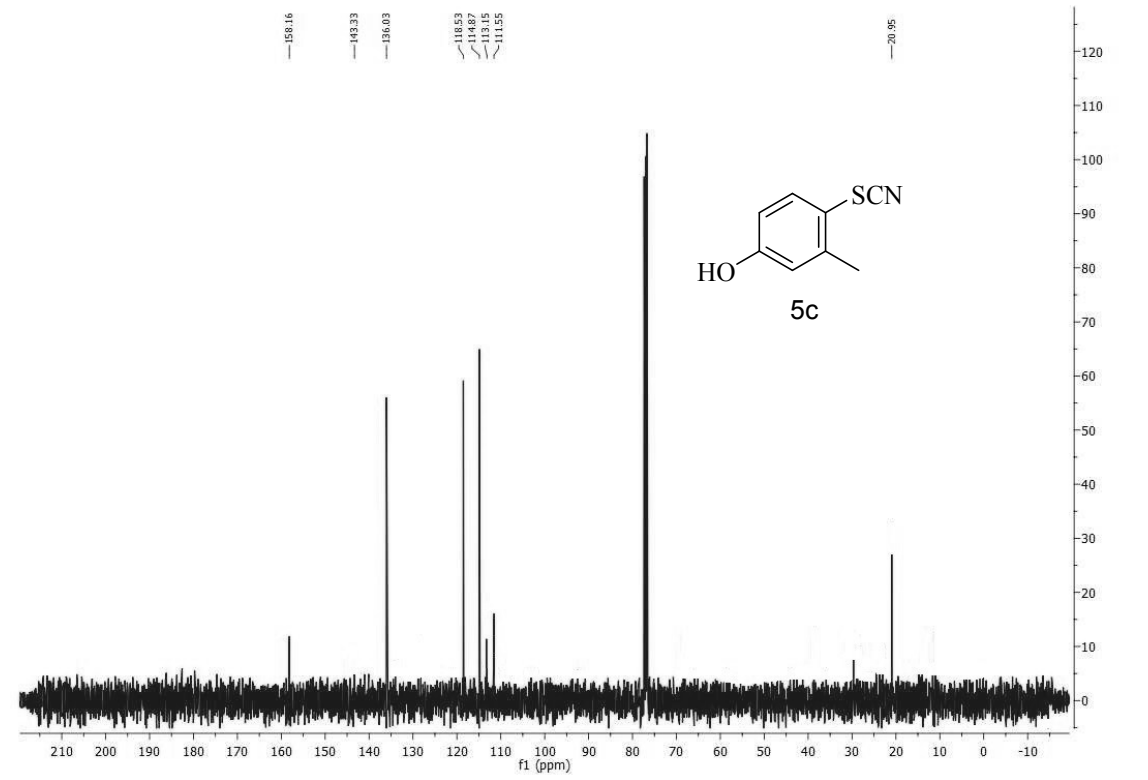
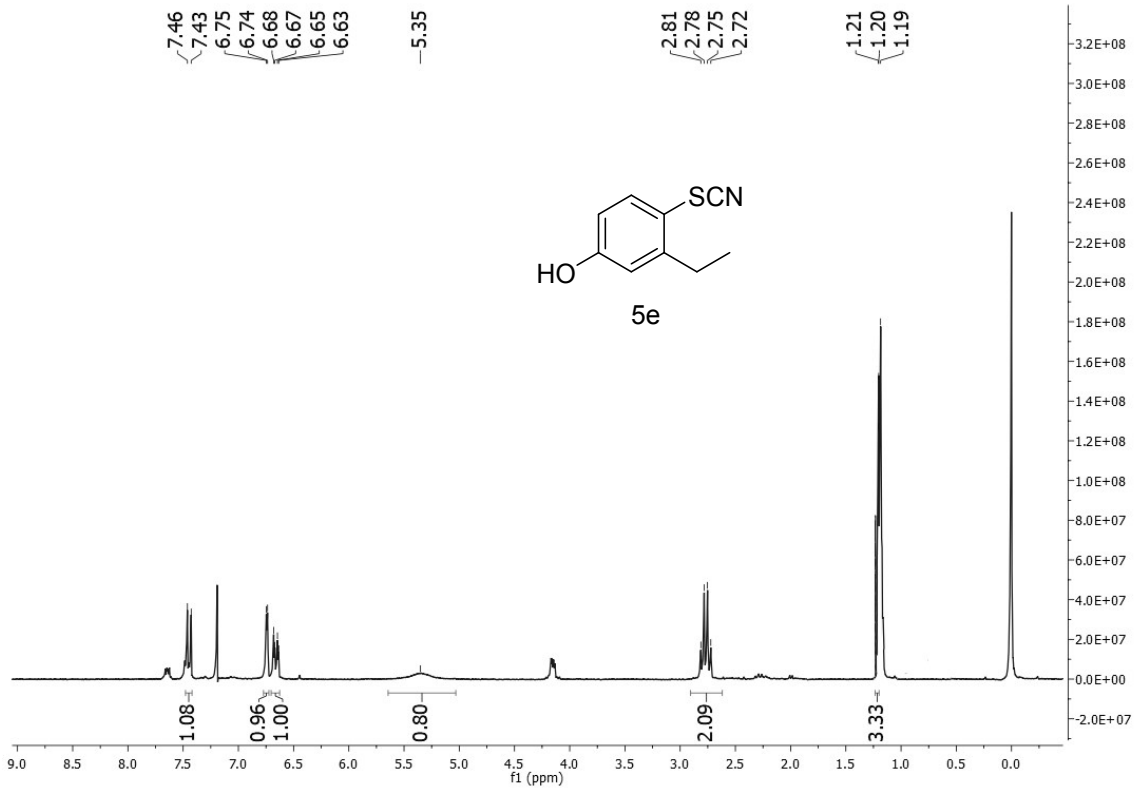
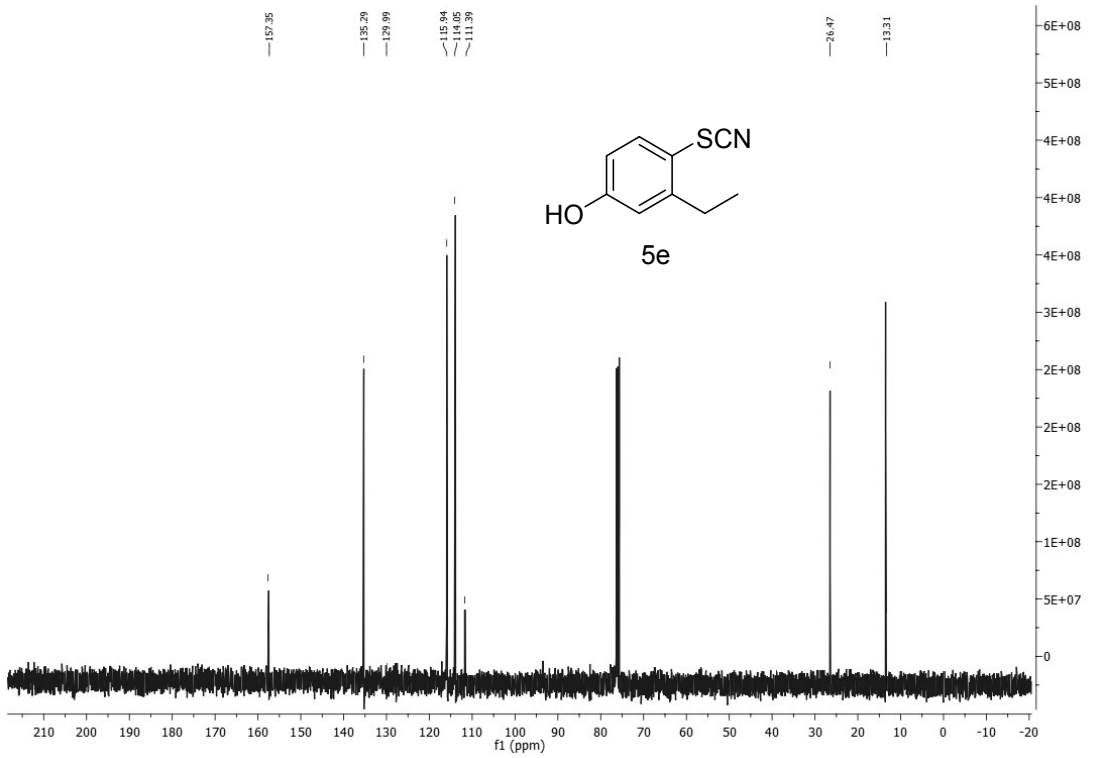
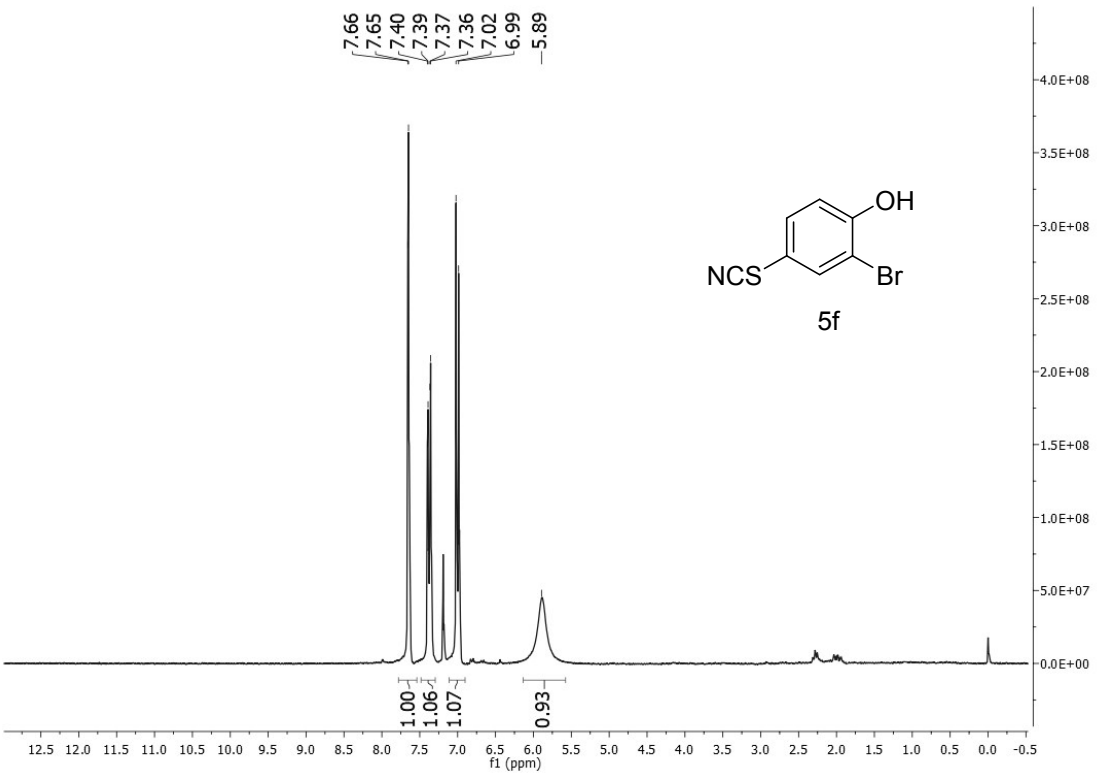
125.25
120.82
111.80
OH
NCS
NO2
5b
f1 (ppm)

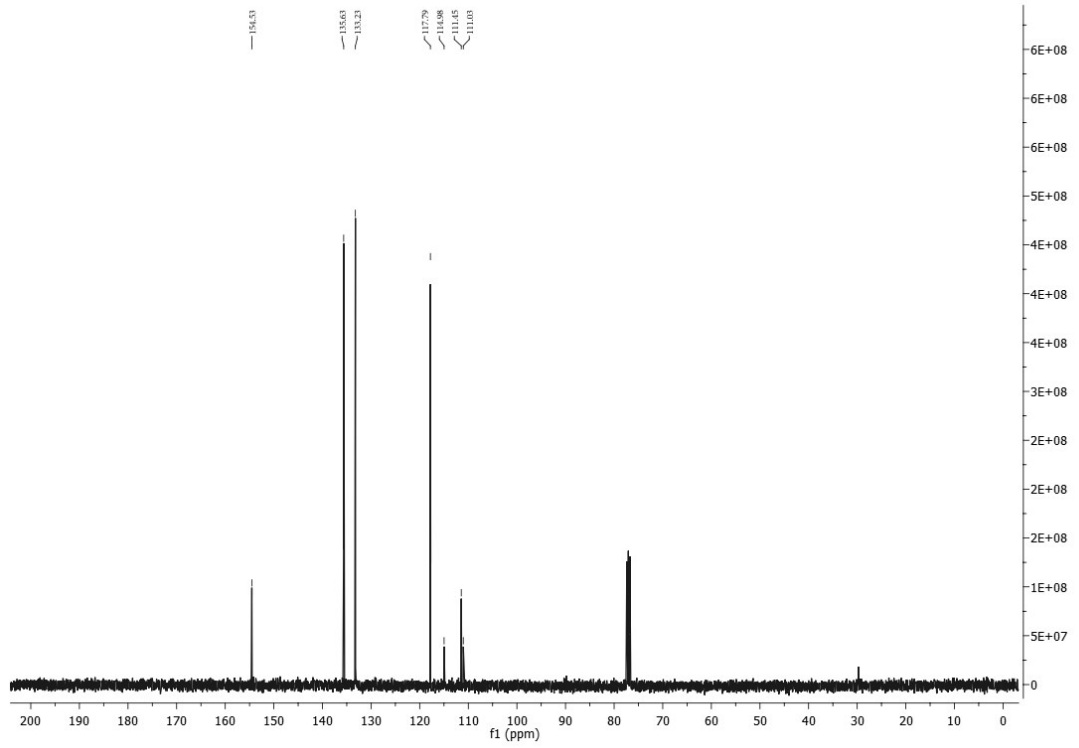

7.43
7.39
6.73
6.72
6.67
6.65
6.63
6.62
5.43
2.41
SCN
HO
5c
0.91
0.92
0.97
0.93
3.00
f1 (ppm)

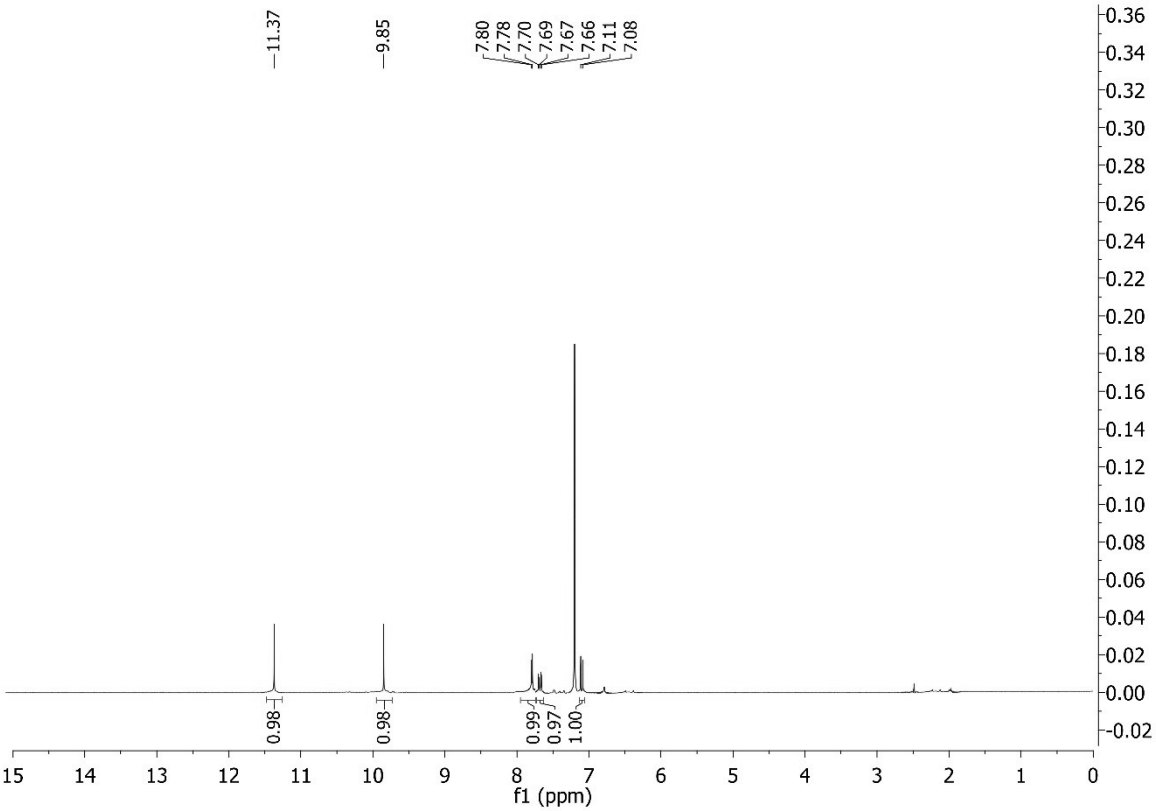

158.16
143.33
136.03
118.53
114.87
113.15
111.55
20.95
SCN
HO
5c
f1 (ppm)

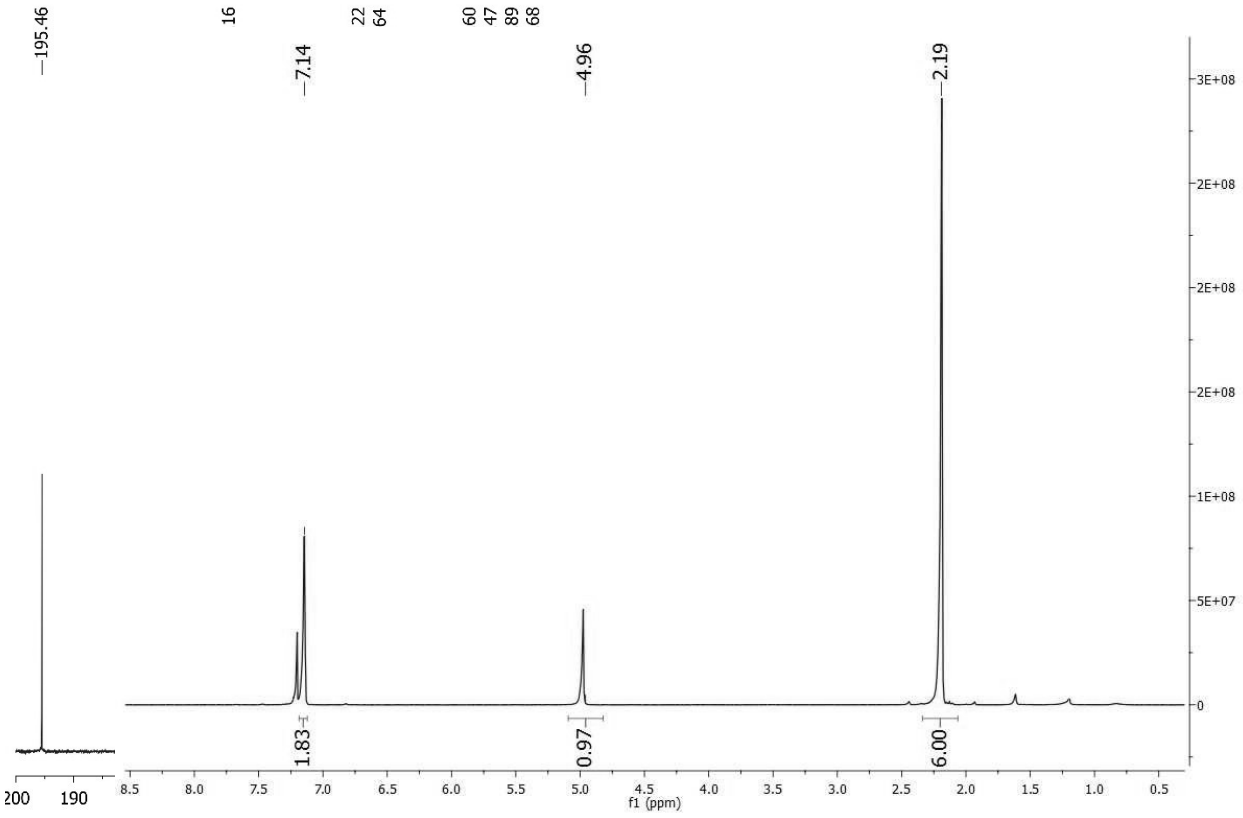

7.46
7.43
6.75
6.74
6.68
6.67
6.65
6.63
5.35
2.81
2.78
2.75
2.72
1.21
1.20
1.19
SCN
HO
5e
1.08
0.96
1.00
0.80
2.09
3.33
f1 (ppm)

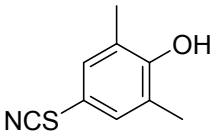

157.35
135.29
129.99
115.94
114.65
111.39
26.47
13.31
SCN
HO
5e
f1 (ppm)


7.66
7.65
7.40
7.39
7.37
7.36
7.02
6.99
5.89
OH
NCS
Br
5f
1.00
1.06
1.07
0.93
f1 (ppm)

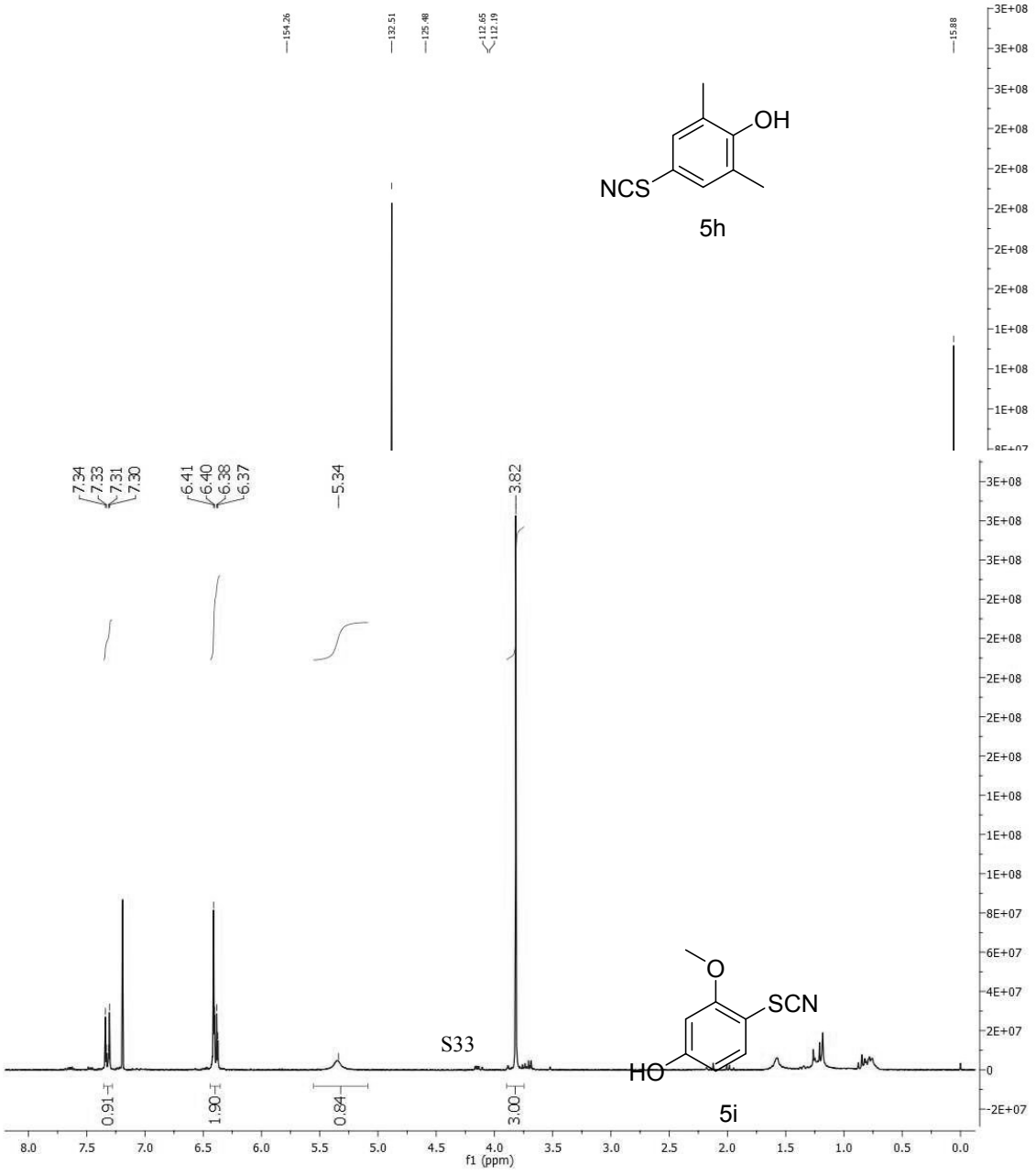

154.51
135.63
133.23
117.79
114.98
111.45
111.03
f1 (ppm)

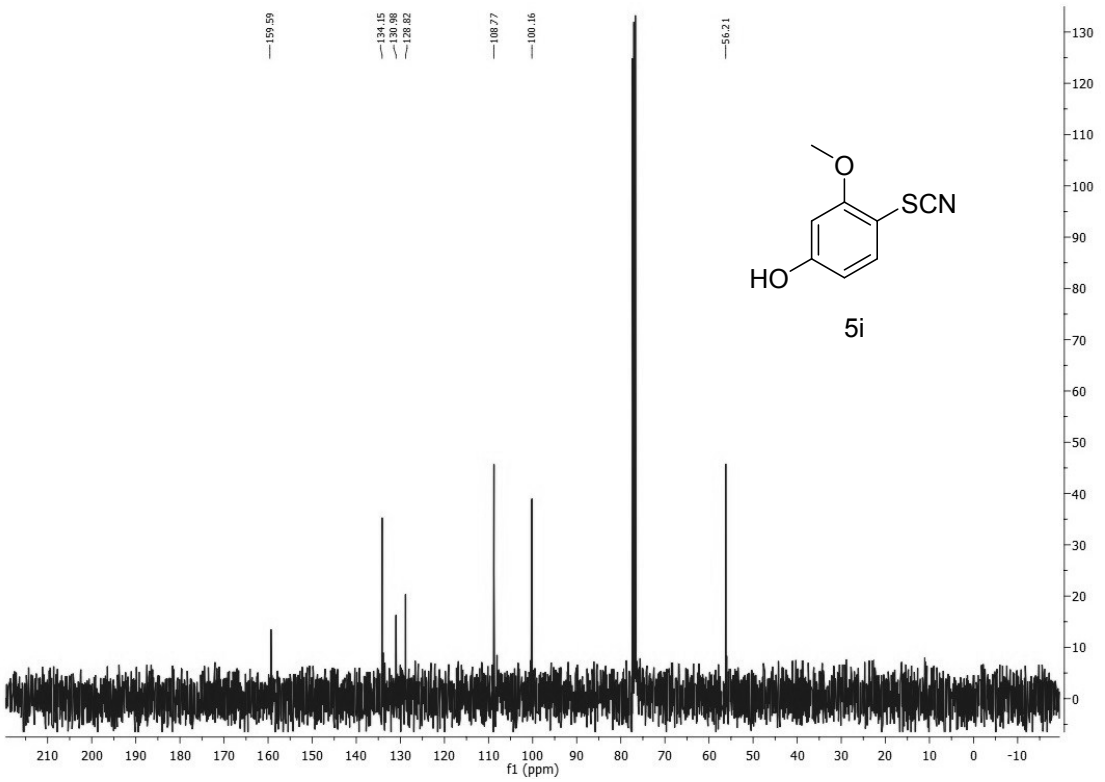

11.37
9.85
7.80
7.78
7.70
7.69
7.67
7.66
7.11
7.08
0.98
0.98
0.99
0.97
1.00
f1 (ppm)

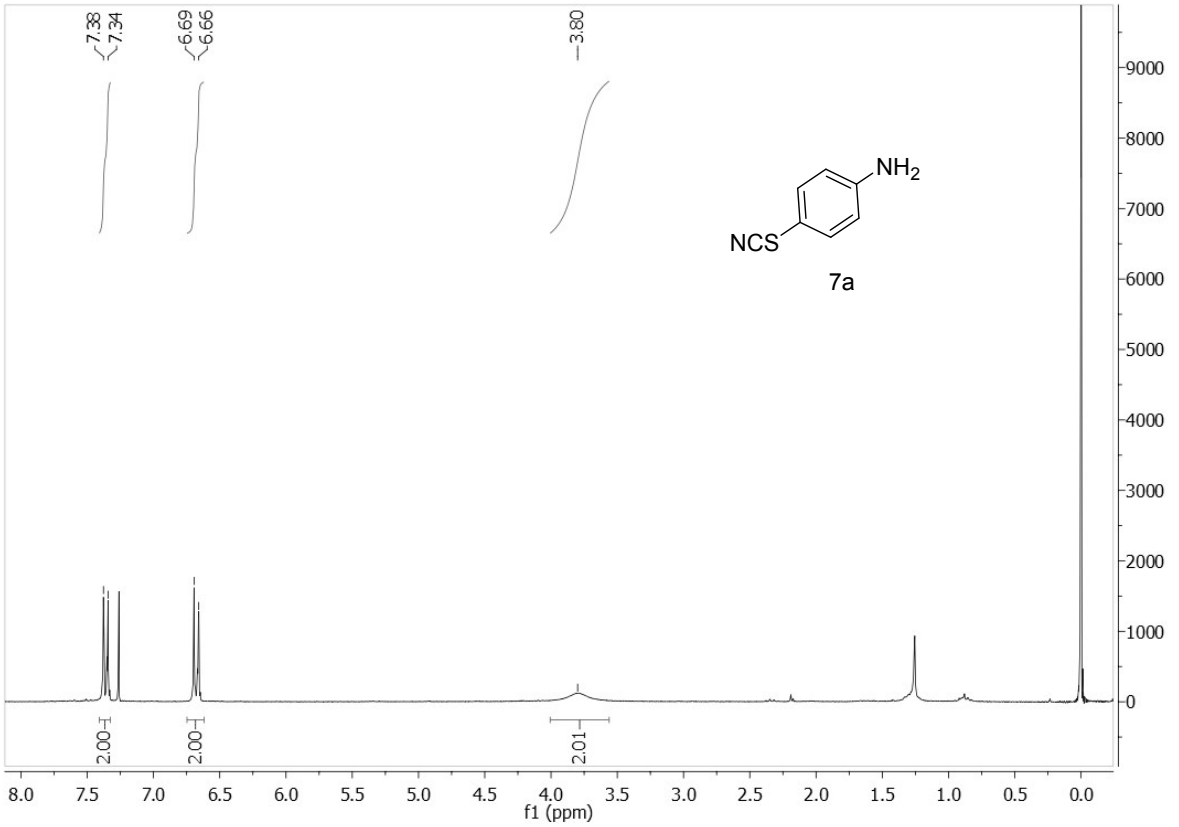

195.46
16
22
64
60
47
89
68
7.14
4.96
2.19
1.83
0.97
6.00
f1 (ppm)

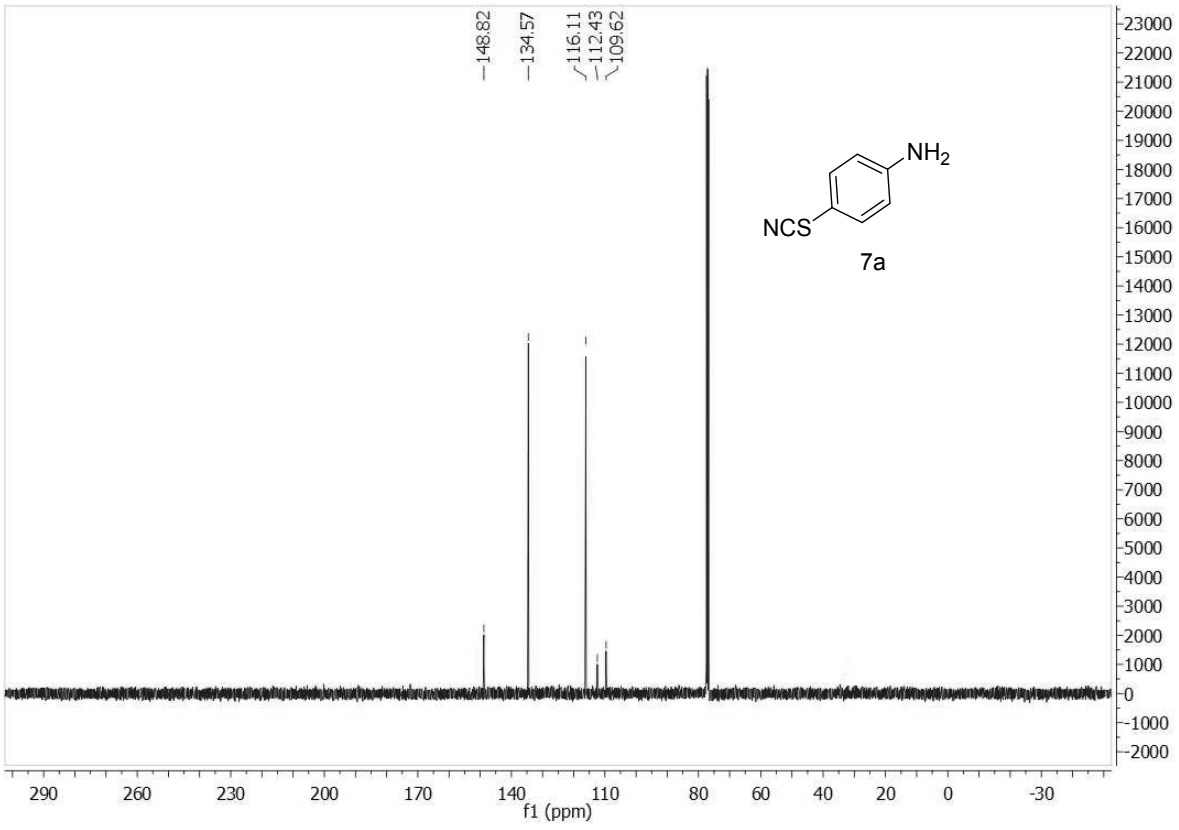

OH
NCS

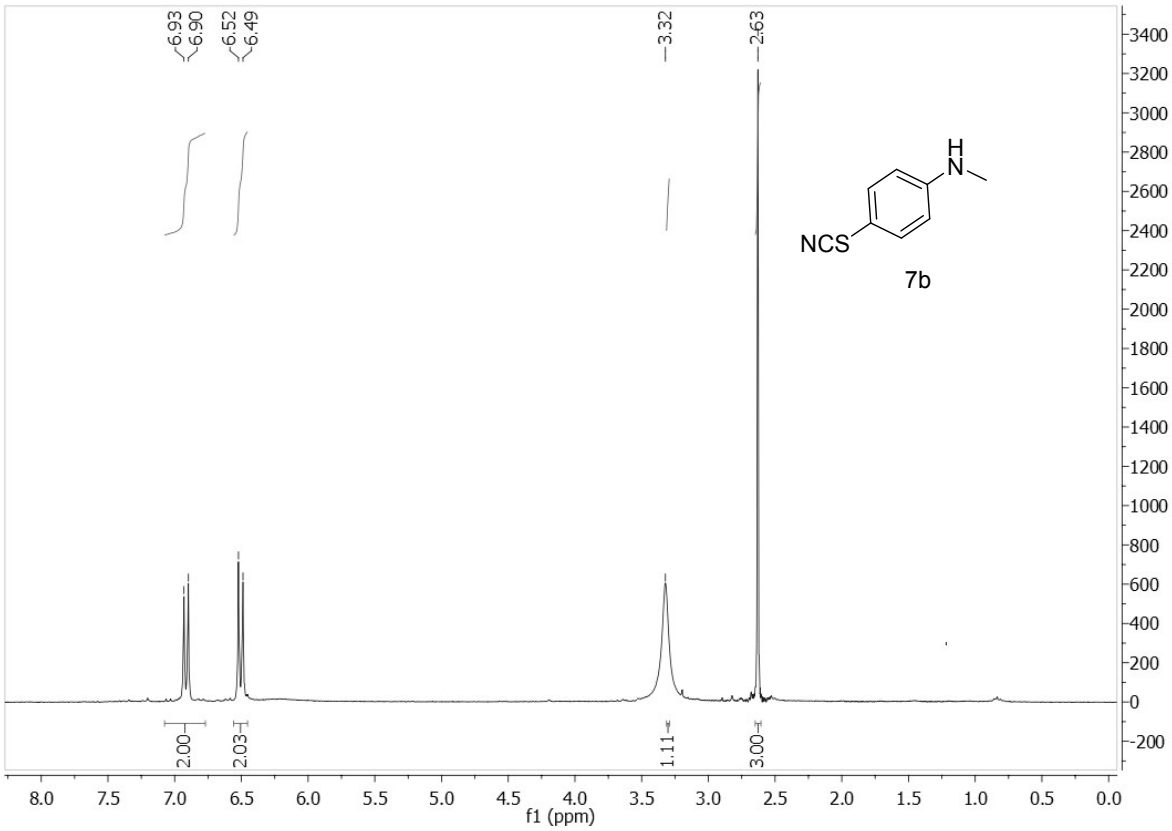
5h

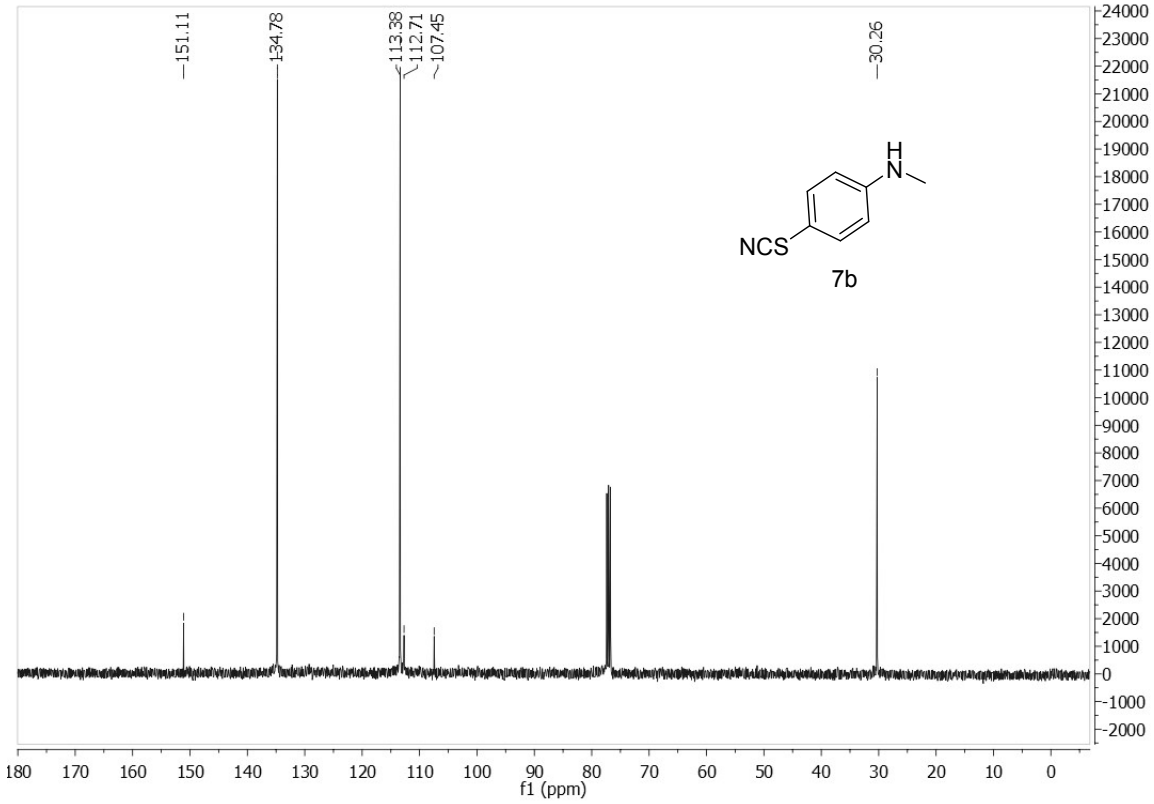

154.26
132.51
125.48
112.65
112.19
15.88
7.34
7.33
7.31
7.30
6.41
6.40
6.38
6.37
5.34
3.82
0.91
1.90
0.84
3.00
f1 (ppm)
OH
NCS
5h
O
SCN
HO
5i

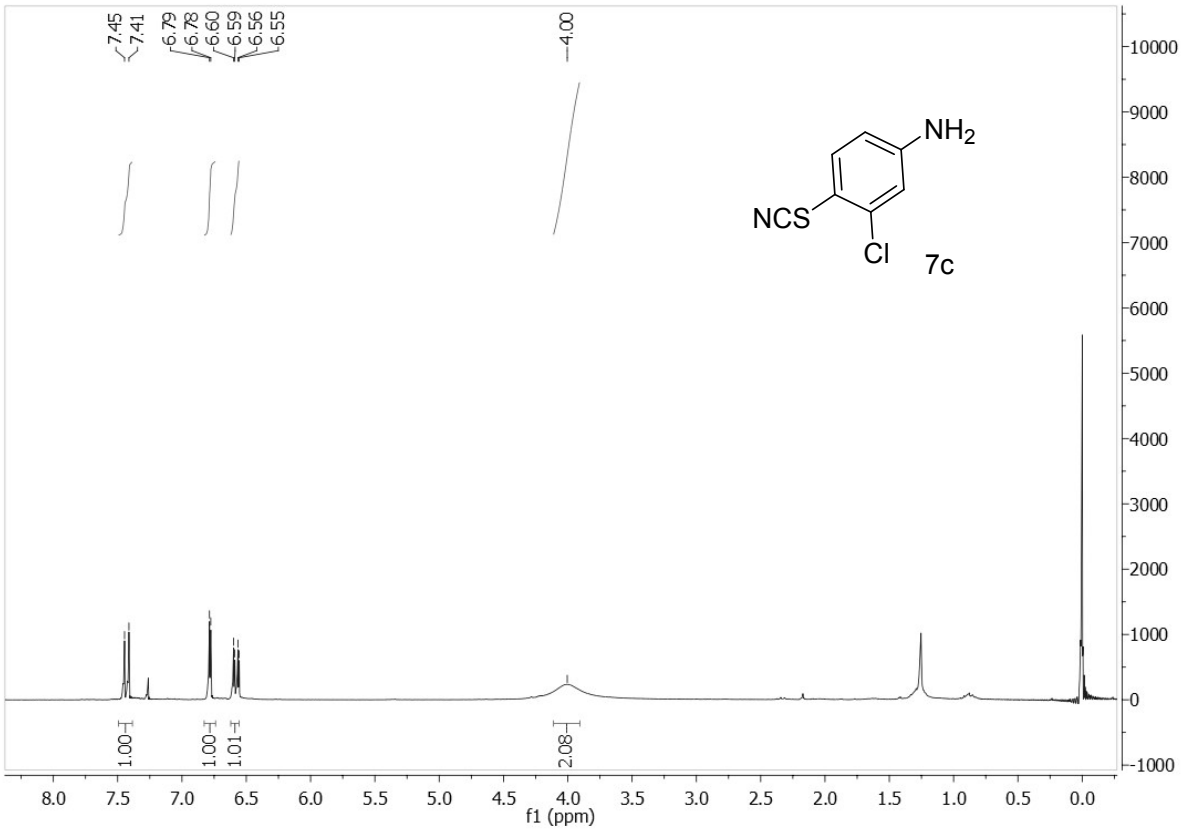

159.59
134.15
130.98
128.82
108.77
100.16
56.21
O
SCN
HO
5i
f1 (ppm)

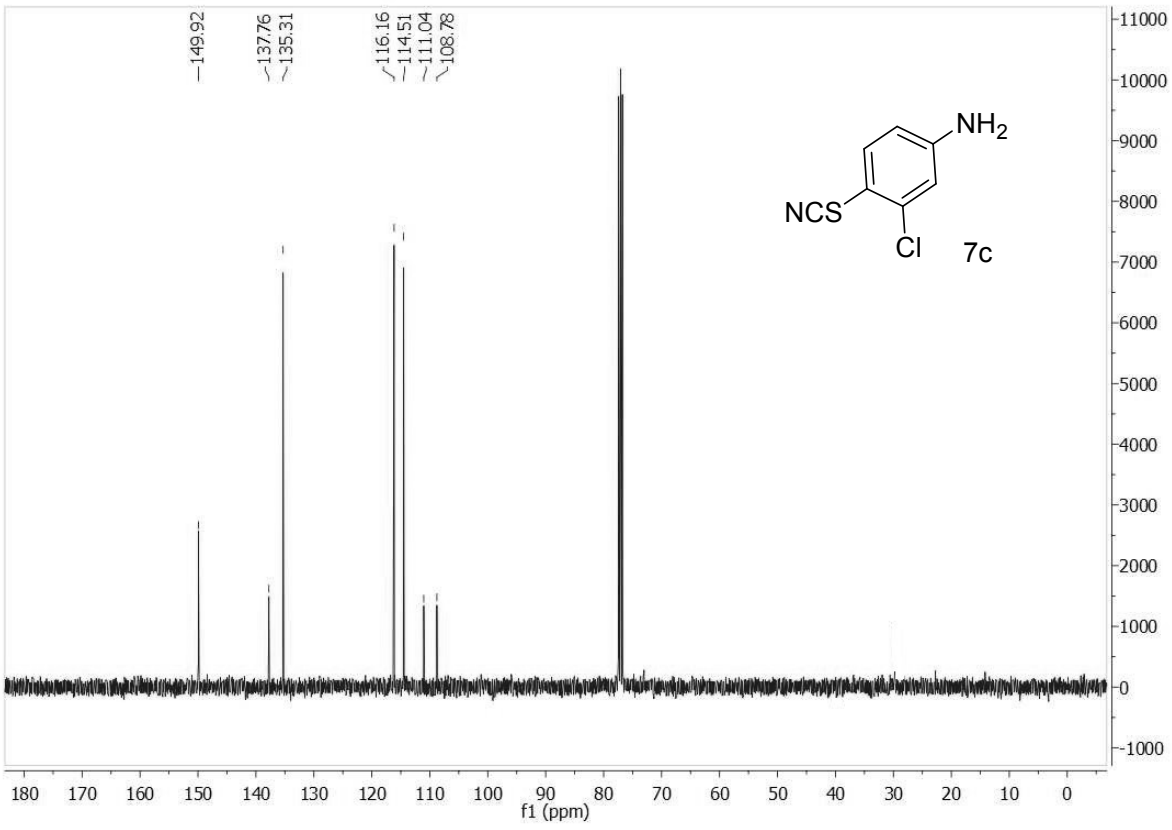

7.38
7.34
6.69
6.66
3.80
NH2
NCS
7a
2.00
2.00
2.01
f1 (ppm)

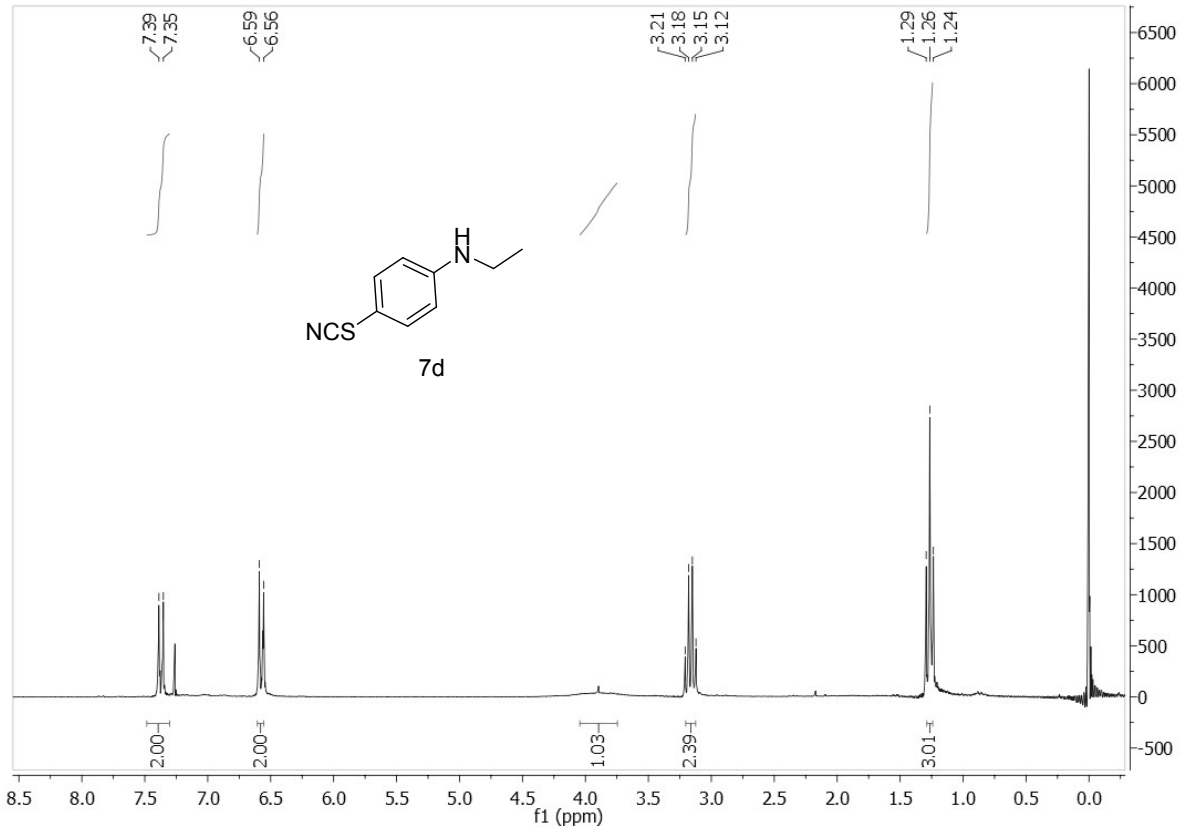

148.82
134.57
116.11
112.43
109.62
NH2
NCS
7a
f1 (ppm)

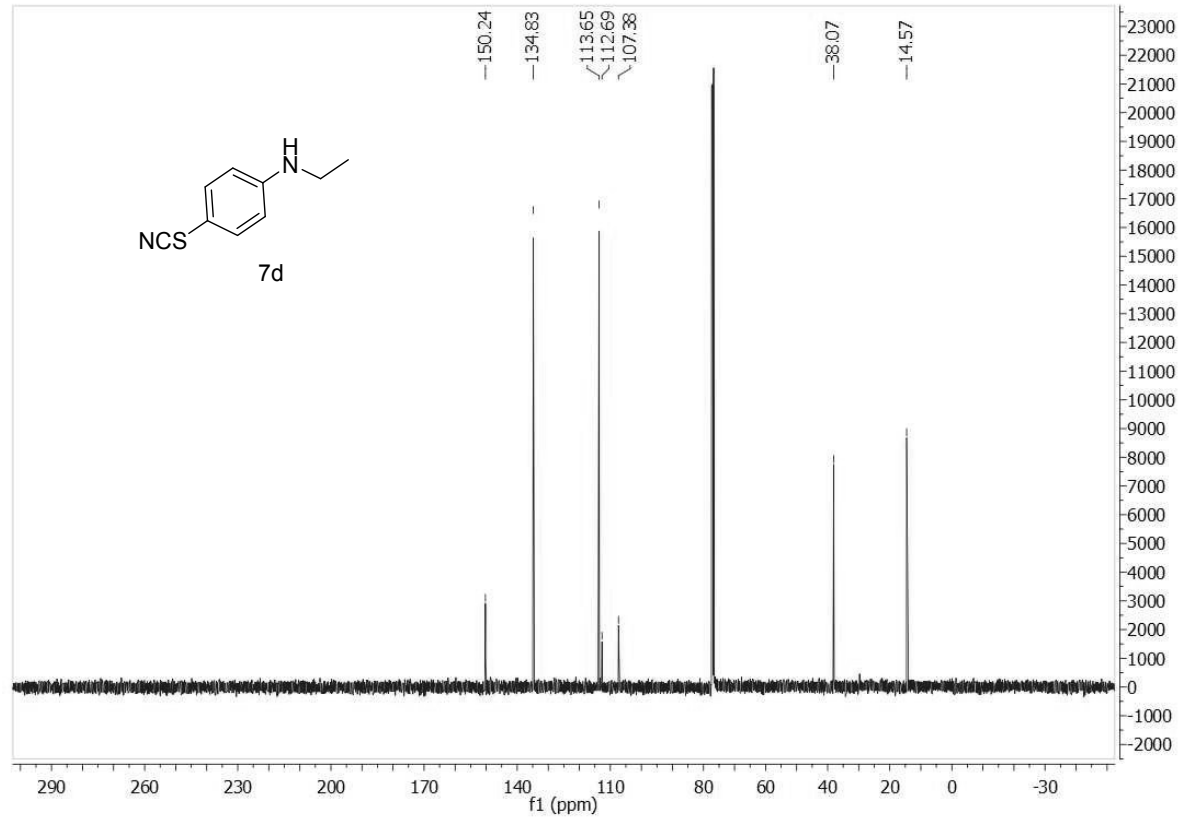

6.93
6.90
6.52
6.49
3.32
2.63
2.00
2.03
1.11
3.00
NCS
H
N
7b
f1 (ppm)

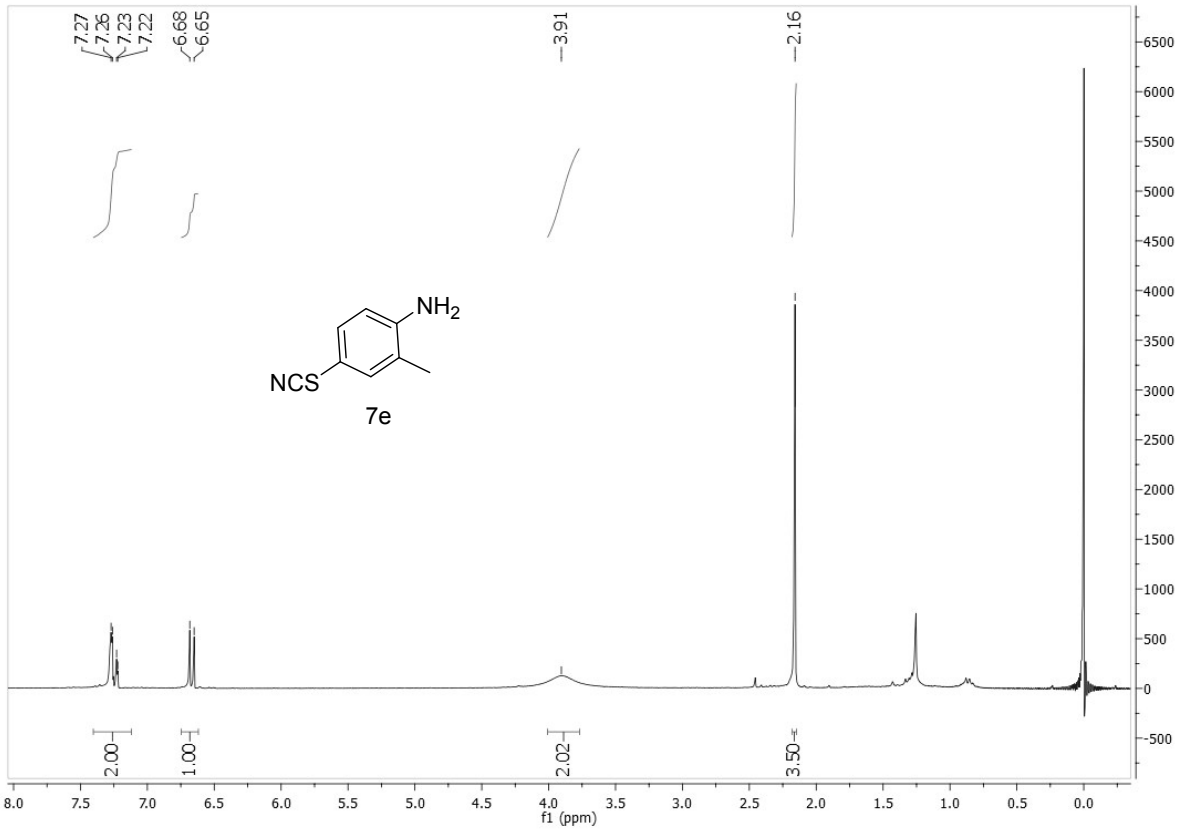

151.11
134.78
113.38
112.71
107.45
30.26
NCS
H
N
7b
f1 (ppm)

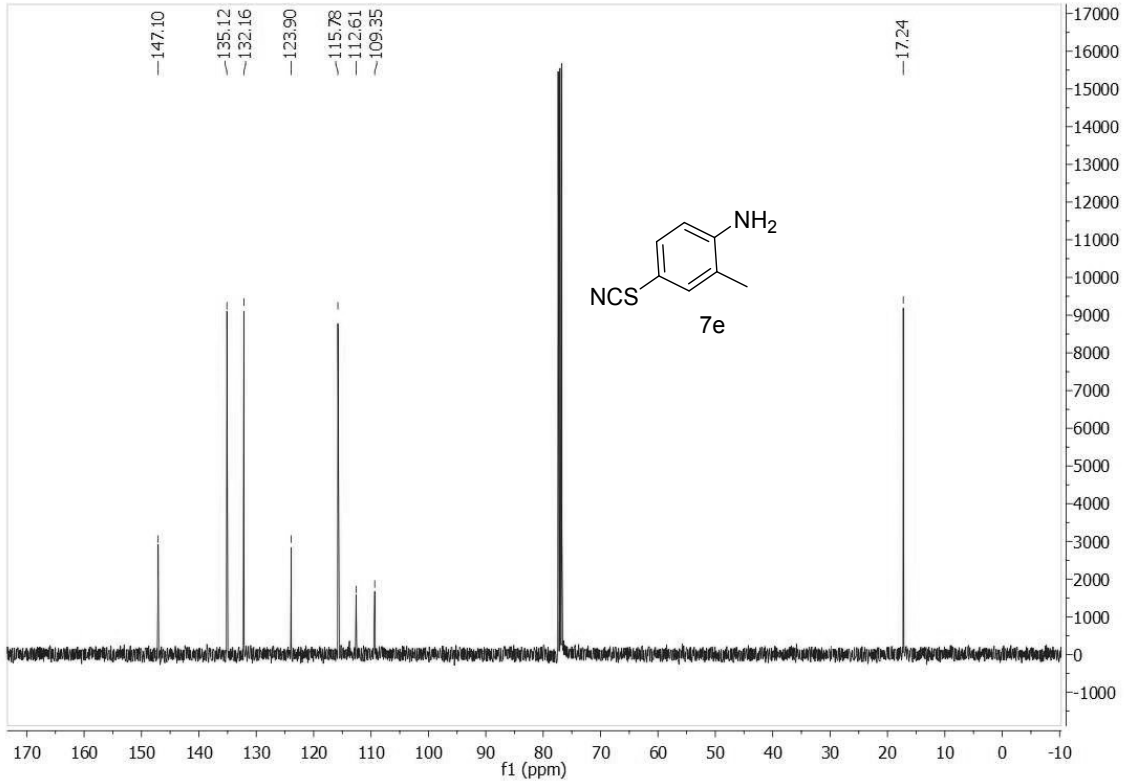

7.45
7.41
6.79
6.78
6.60
6.59
6.56
6.55
4.00
NH2
NCS
Cl
7c
1.00
1.00
1.01
2.08
f1 (ppm)

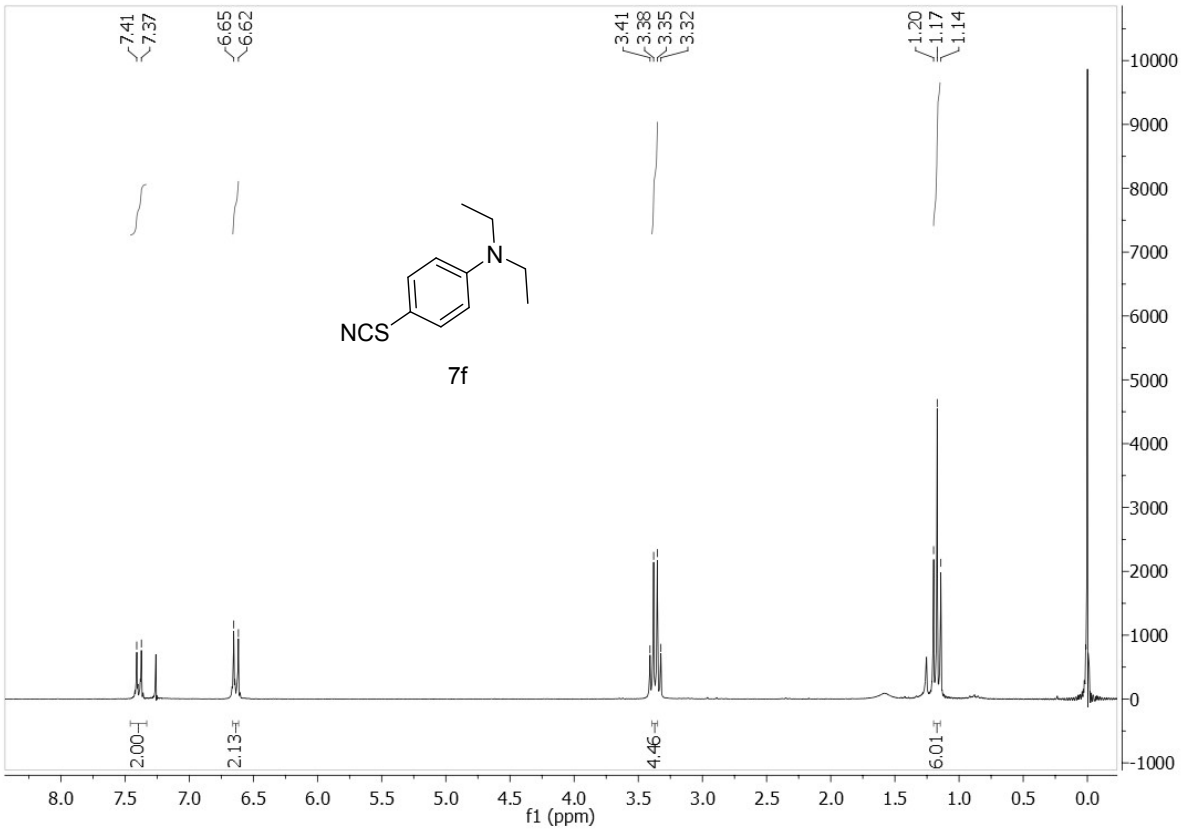

149.92
137.76
135.31
116.16
114.51
111.04
108.78
NH2
NCS
Cl
7c
f1 (ppm)

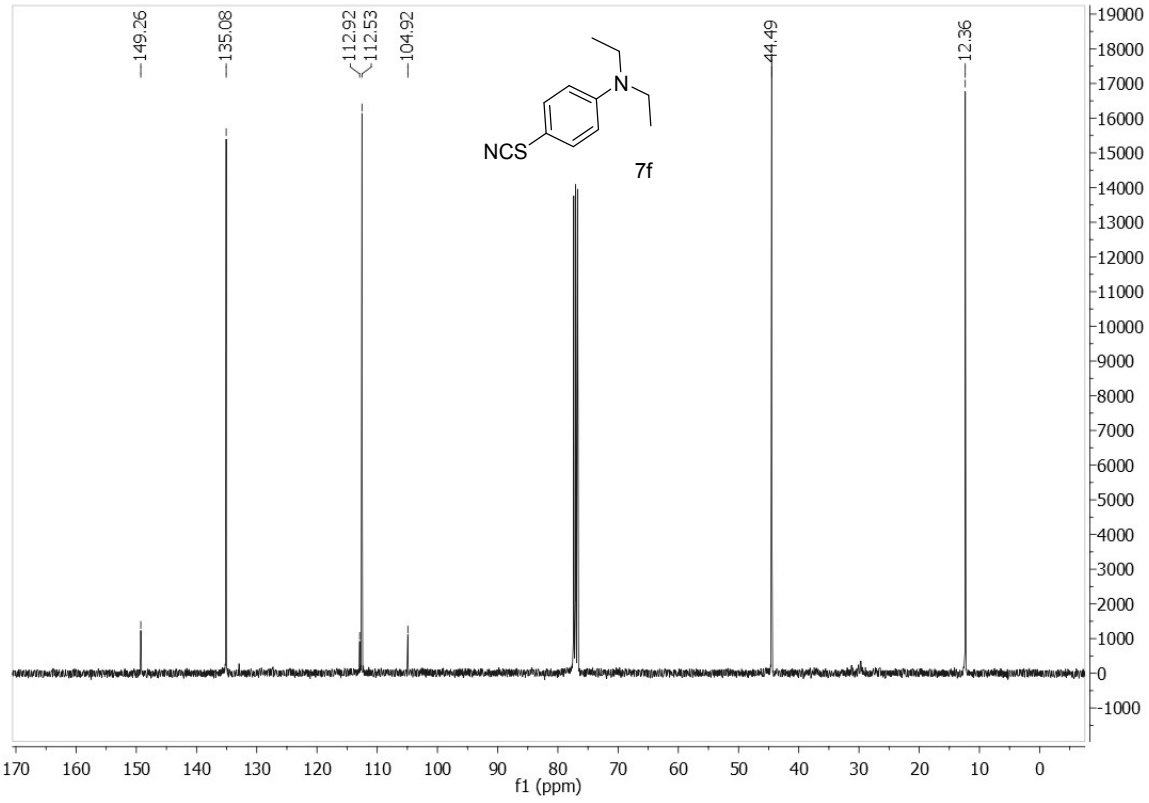

7.39
7.35
6.59
6.56
3.21
3.18
3.15
3.12
1.29
1.26
1.24
NCS
H
N
7d
2.00
2.00
1.03
2.39
3.01
f1 (ppm)

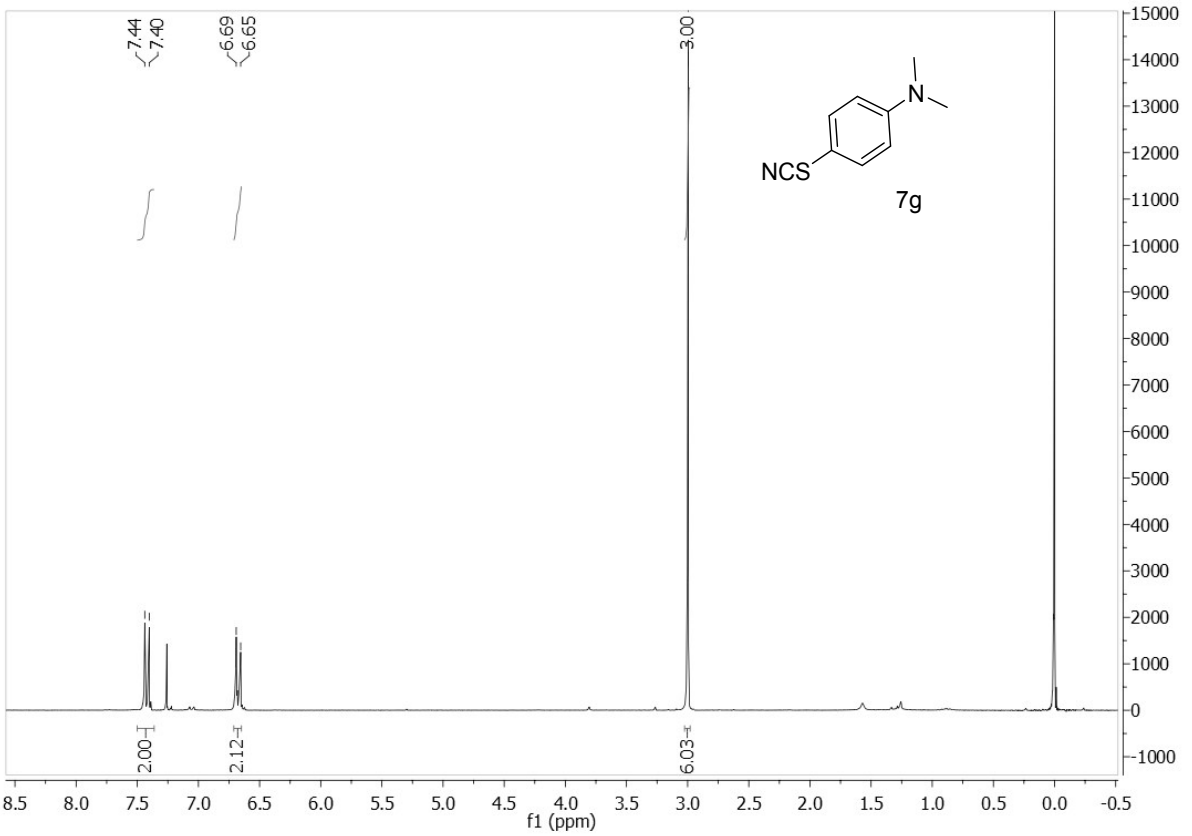

150.24
134.83
113.65
112.69
107.38
38.07
14.57
NCS
H
N
7d
f1 (ppm)

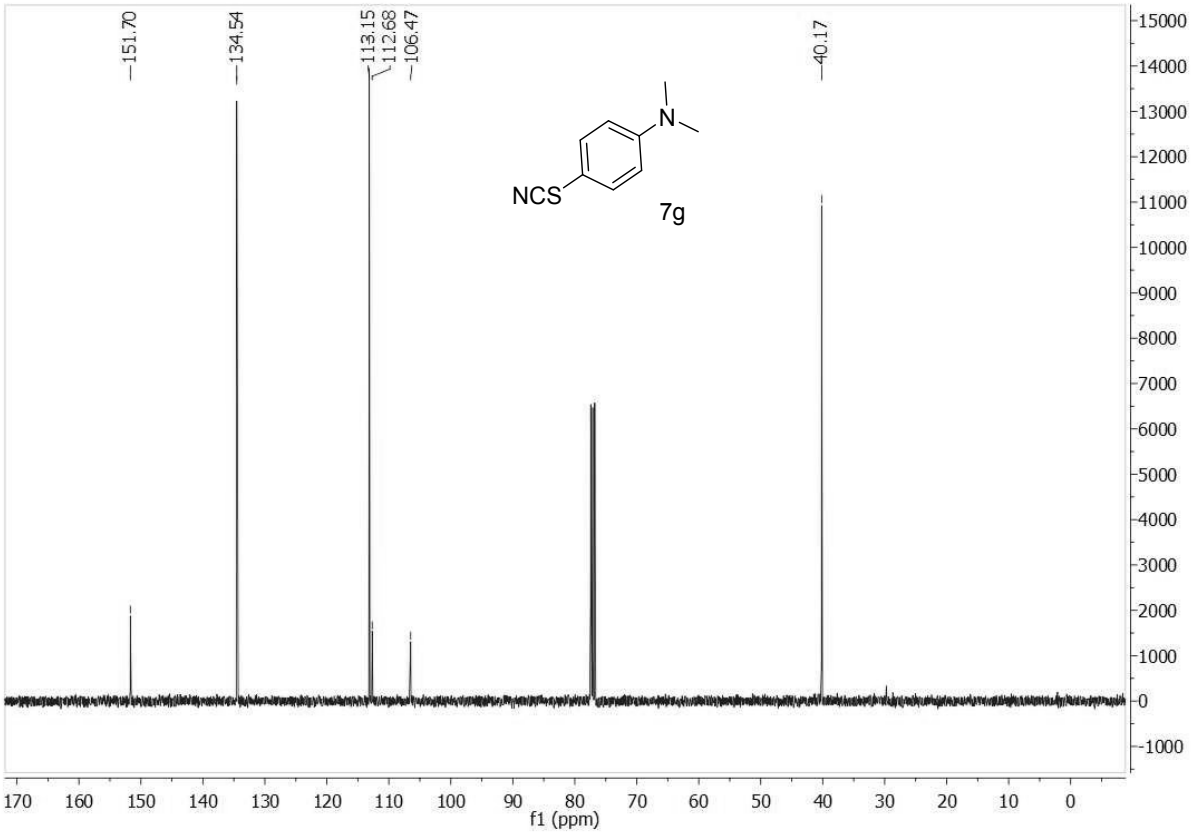

7.27
7.26
7.23
7.22
6.68
6.65
3.91
2.16
NH2
NCS
7e
2.00
1.00
2.02
3.50
f1 (ppm)

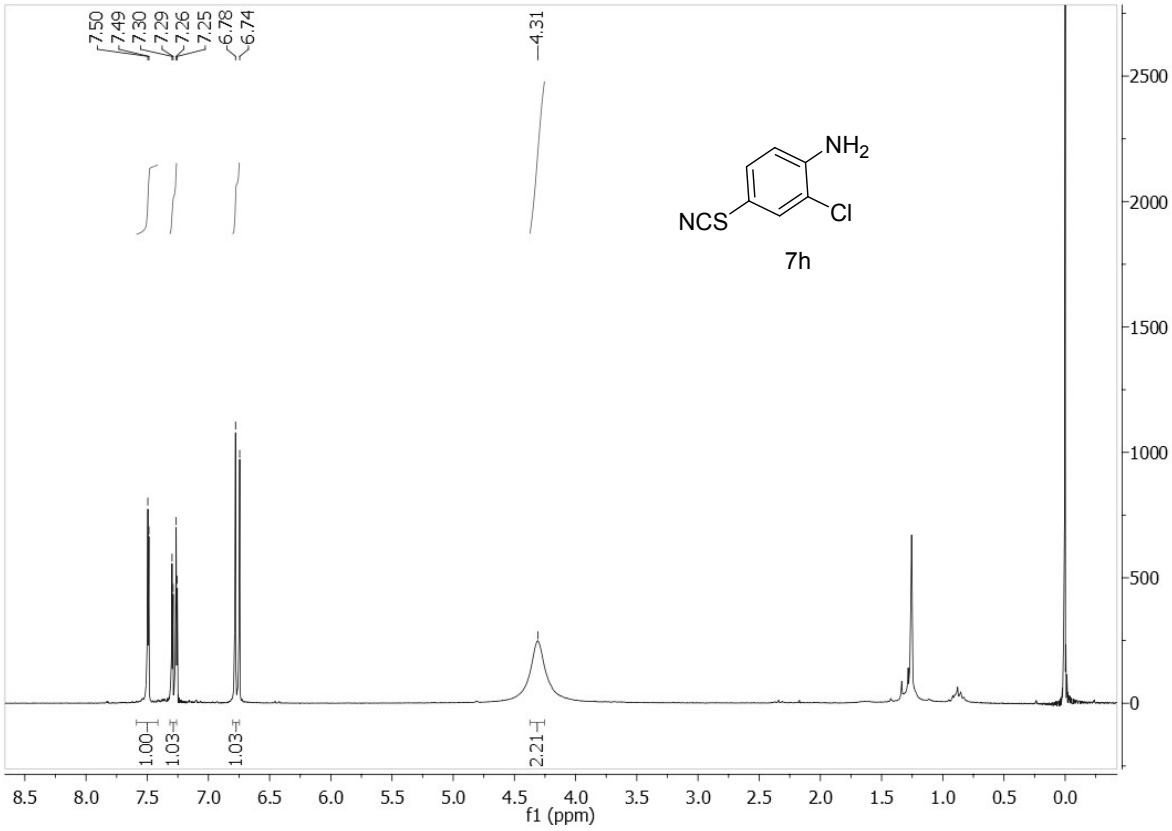

147.10
135.12
132.16
123.90
115.78
112.61
109.35
17.24
NH2
NCS
7e
f1 (ppm)

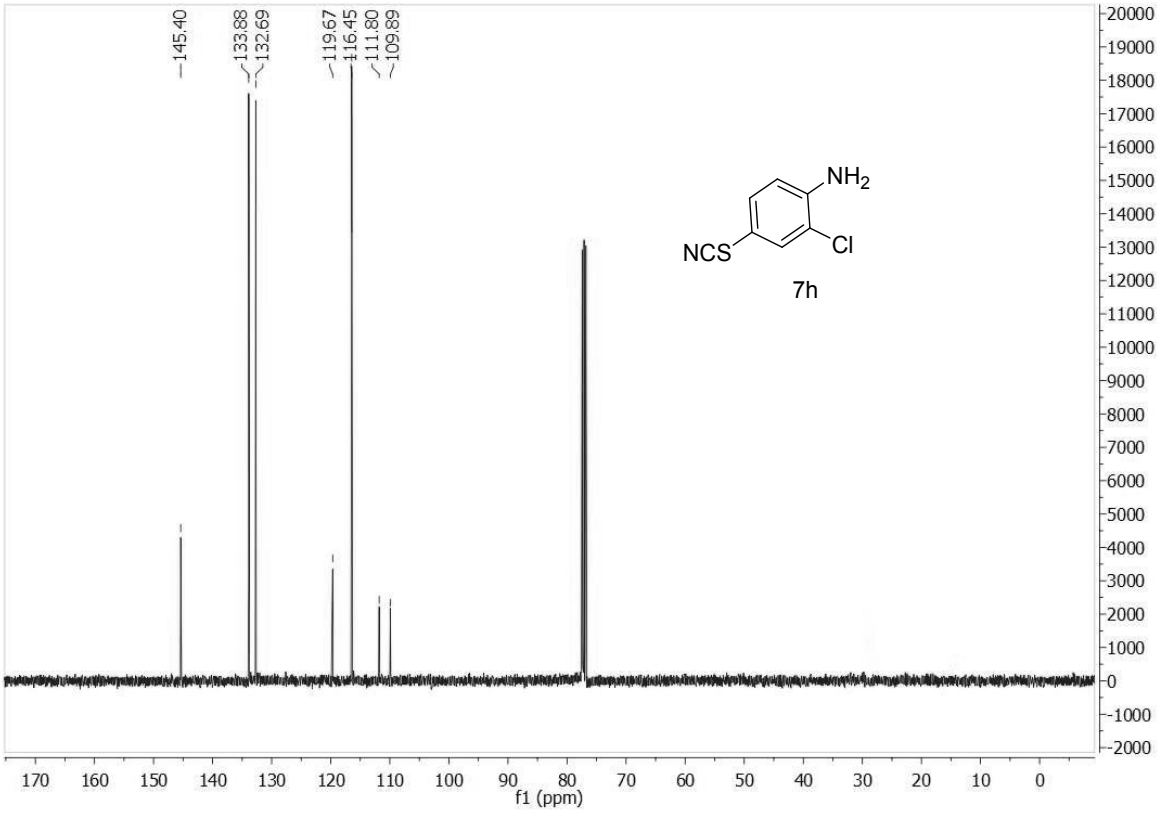

7.41
7.37
6.65
6.62
3.41
3.38
3.35
3.32
1.20
1.17
1.14
NCS
N
7f
2.00
2.13
4.46
6.01
f1 (ppm)

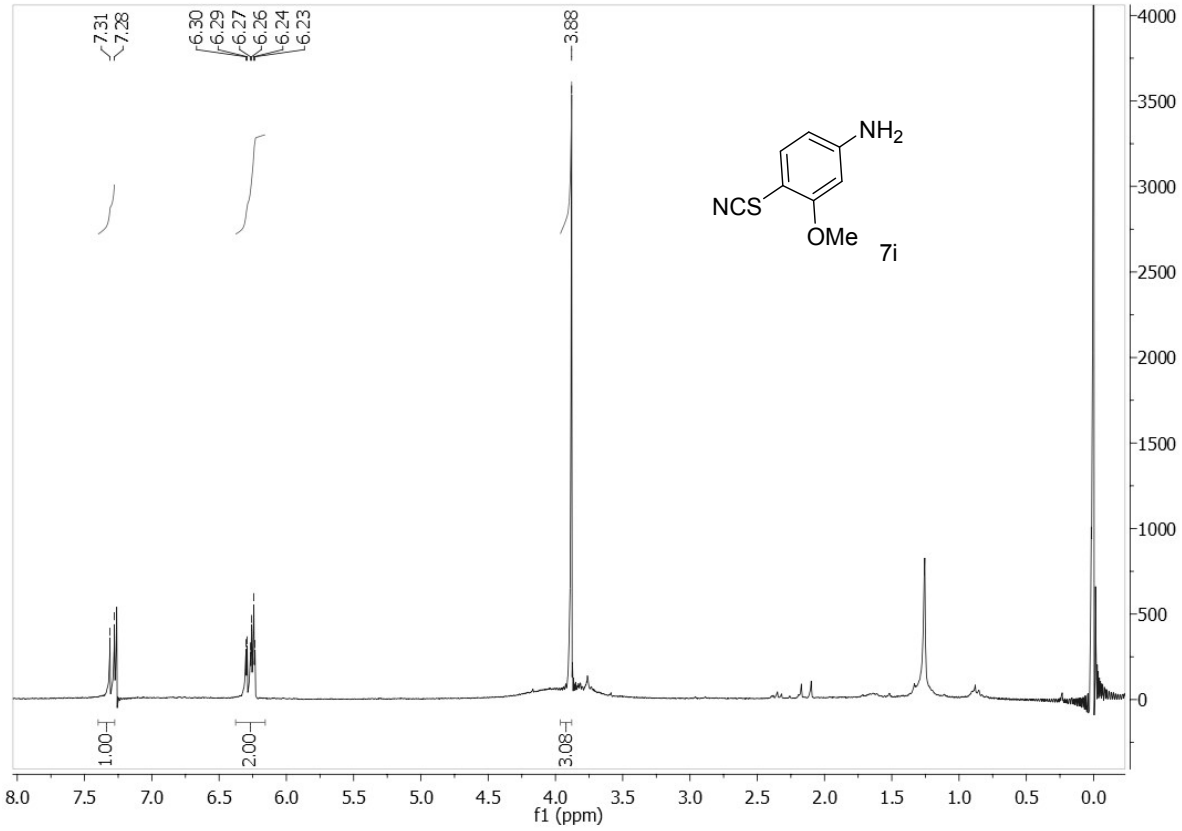

149.26
135.08
112.92
112.53
104.92
44.49
12.36
NCS
N
7f
f1 (ppm)

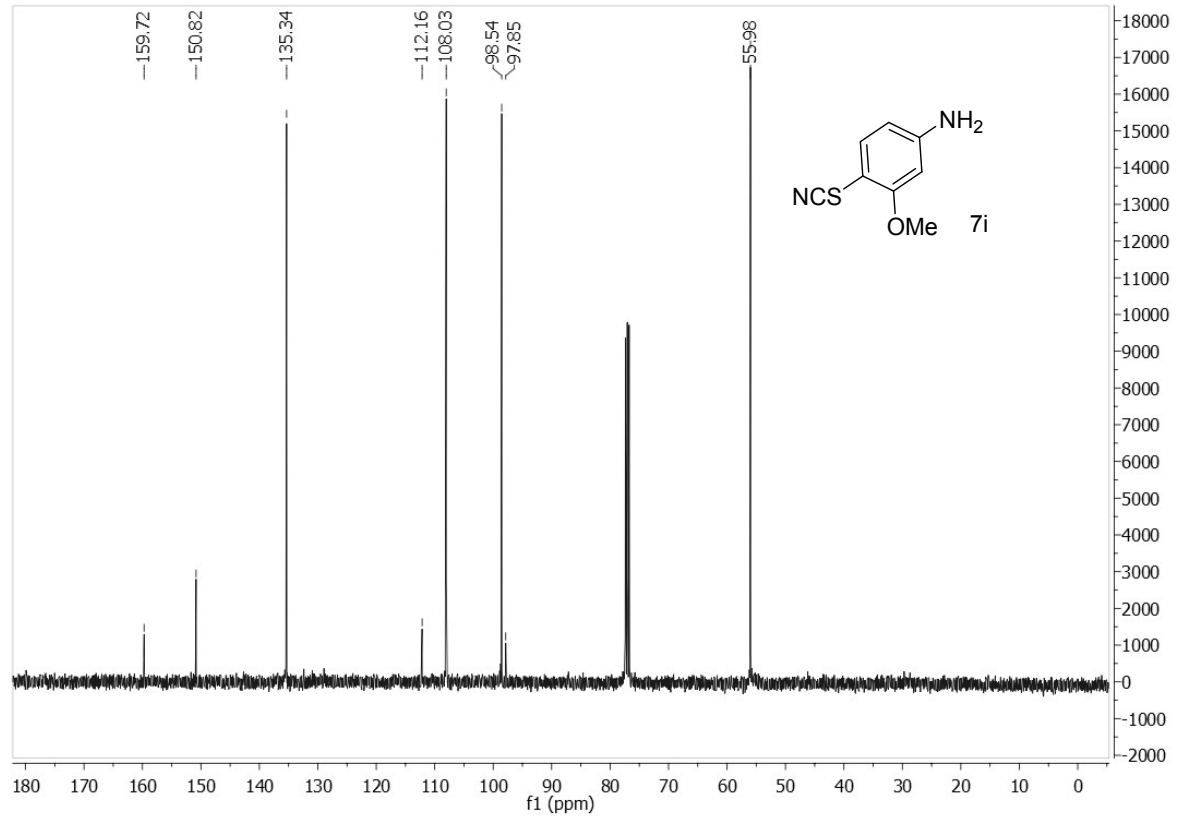

7.44
7.40
6.69
6.65
3.00
2.00
2.12
6.03
NCS
N
7g
f1 (ppm)

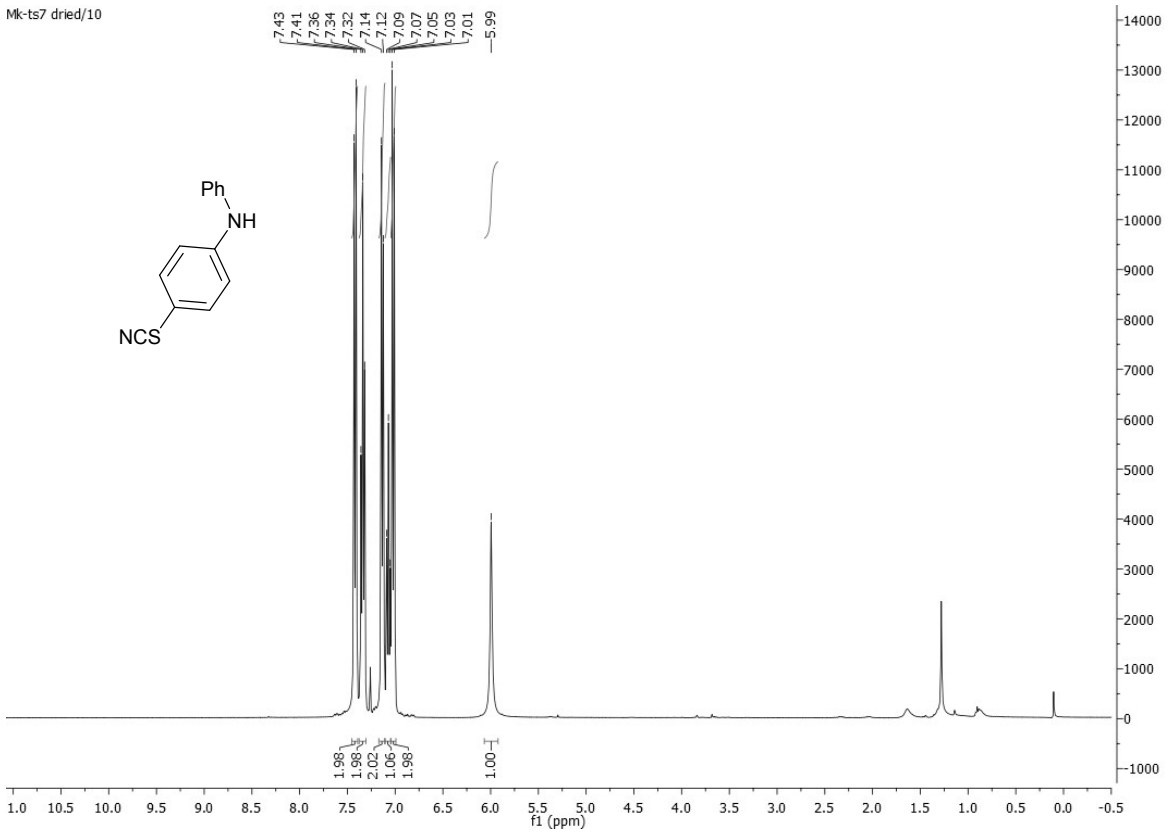

151.70
134.54
113.15
112.68
106.47
40.17
NCS
N
7g
f1 (ppm)

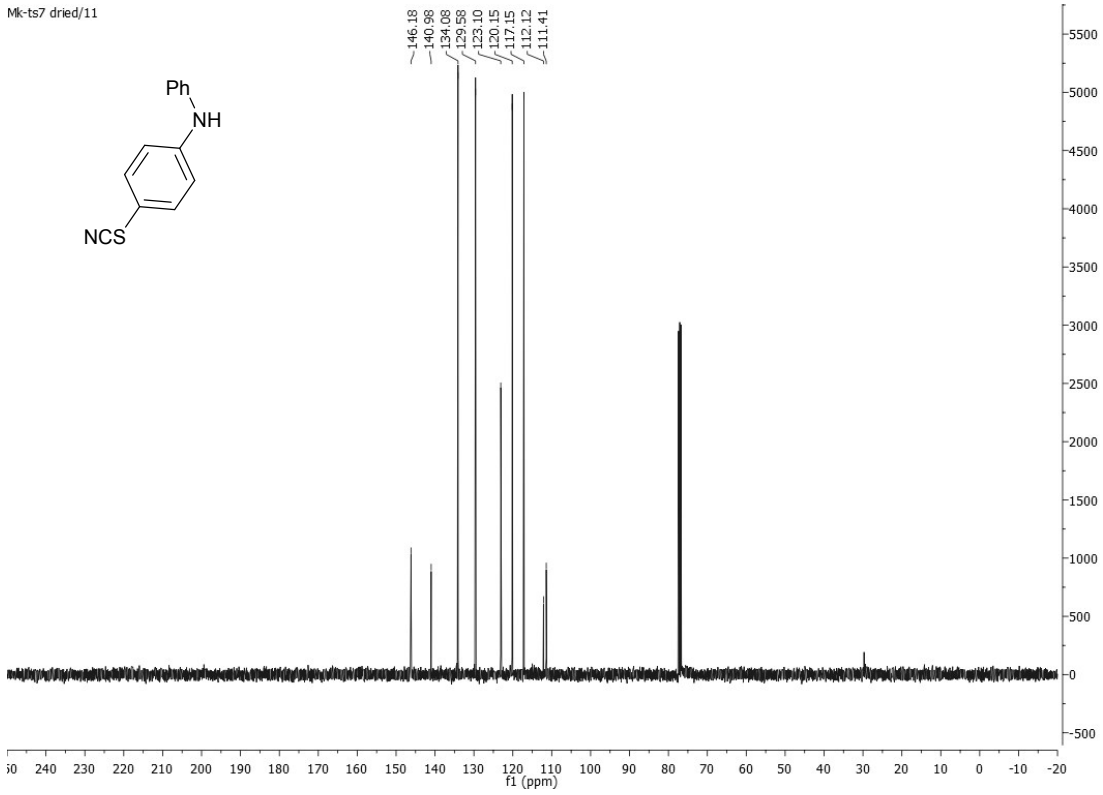

7.50
7.49
7.30
7.29
7.26
7.25
6.78
6.74
4.31
NH2
NCS
Cl
7h
1.00
1.03
1.03
2.21
f1 (ppm)

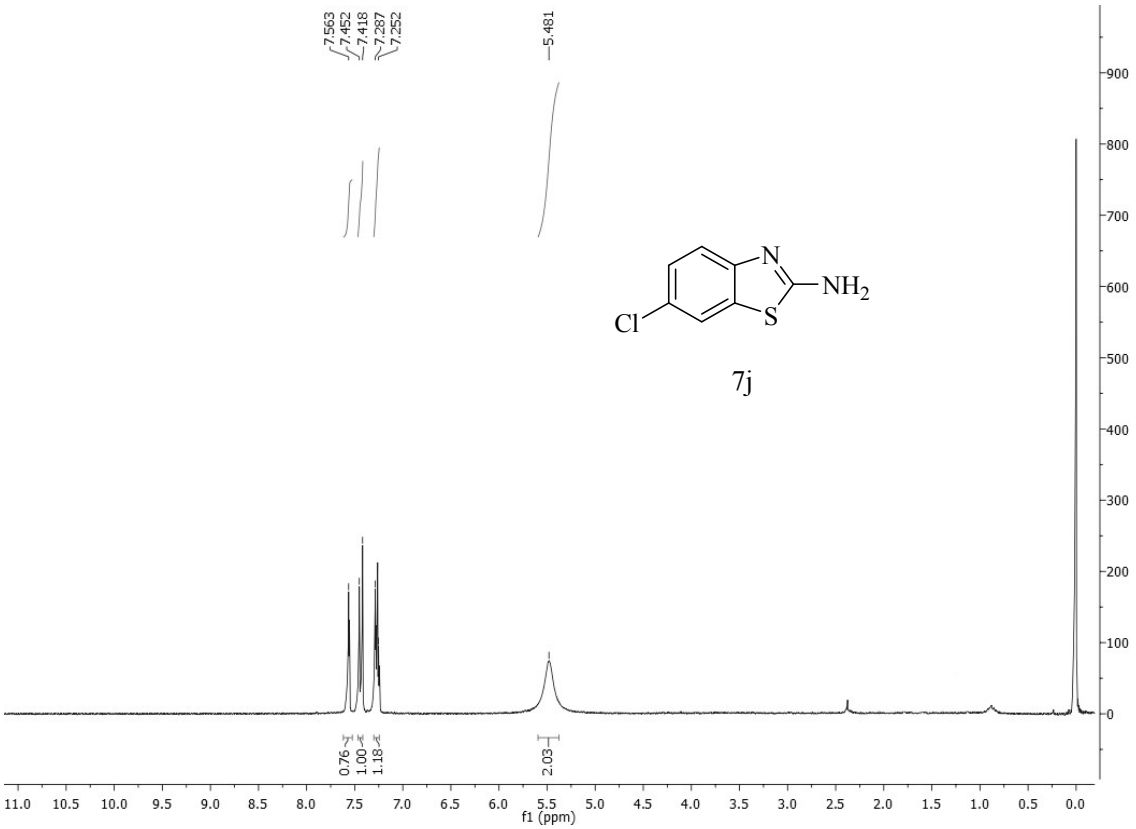

145.40
133.88
132.69
119.67
116.45
111.80
109.89
NH2
NCS
Cl
7h
f1 (ppm)


7.31
7.28
6.30
6.29
6.27
6.26
6.24
6.23
3.88
NH2
NCS
OMe
7i
1.00
2.00
3.08
f1 (ppm)

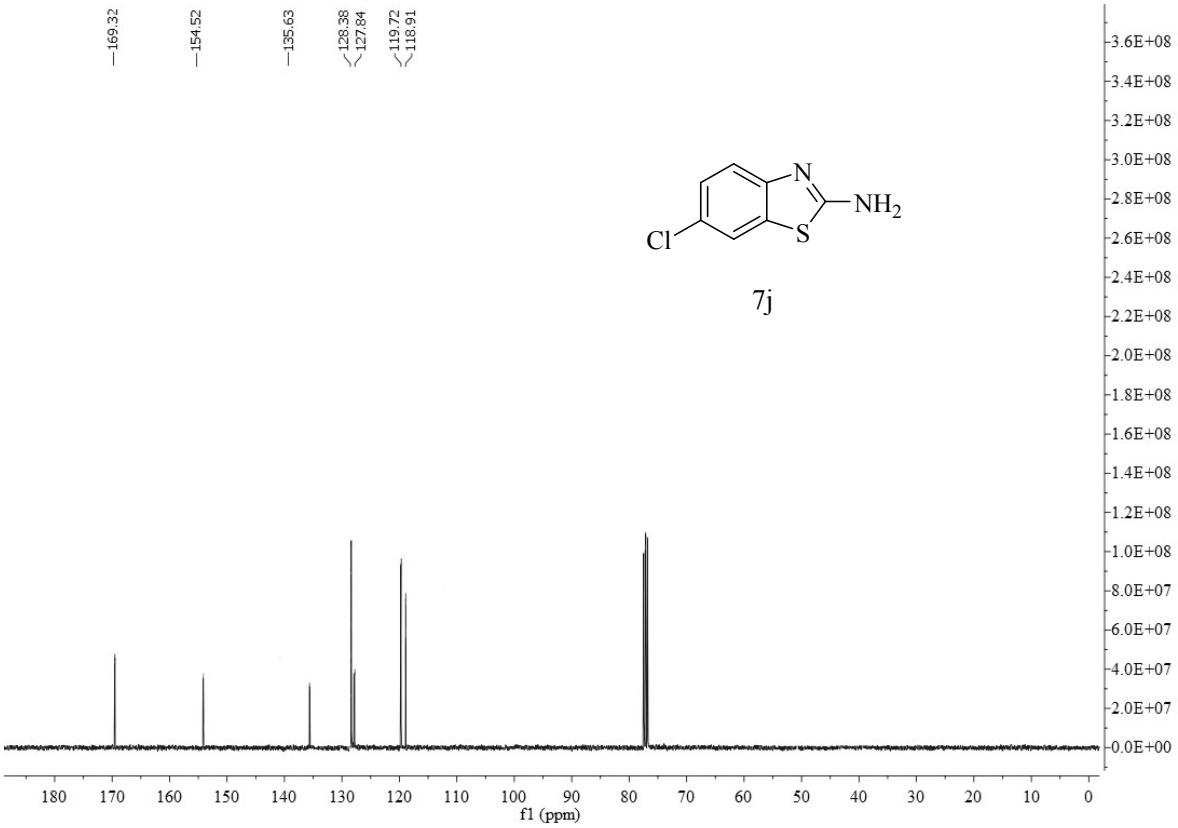

159.72
150.82
135.34
112.16
108.03
98.54
97.85
55.98
NH2
NCS
OMe
7i
f1 (ppm)


Mk-ts7 dried/10
7.43
7.41
7.36
7.34
7.32
7.14
7.12
7.09
7.07
7.05
7.03
7.01
5.99
Ph
NH
NCS
1.98
1.98
2.02
1.06
1.98
1.00
f1 (ppm)

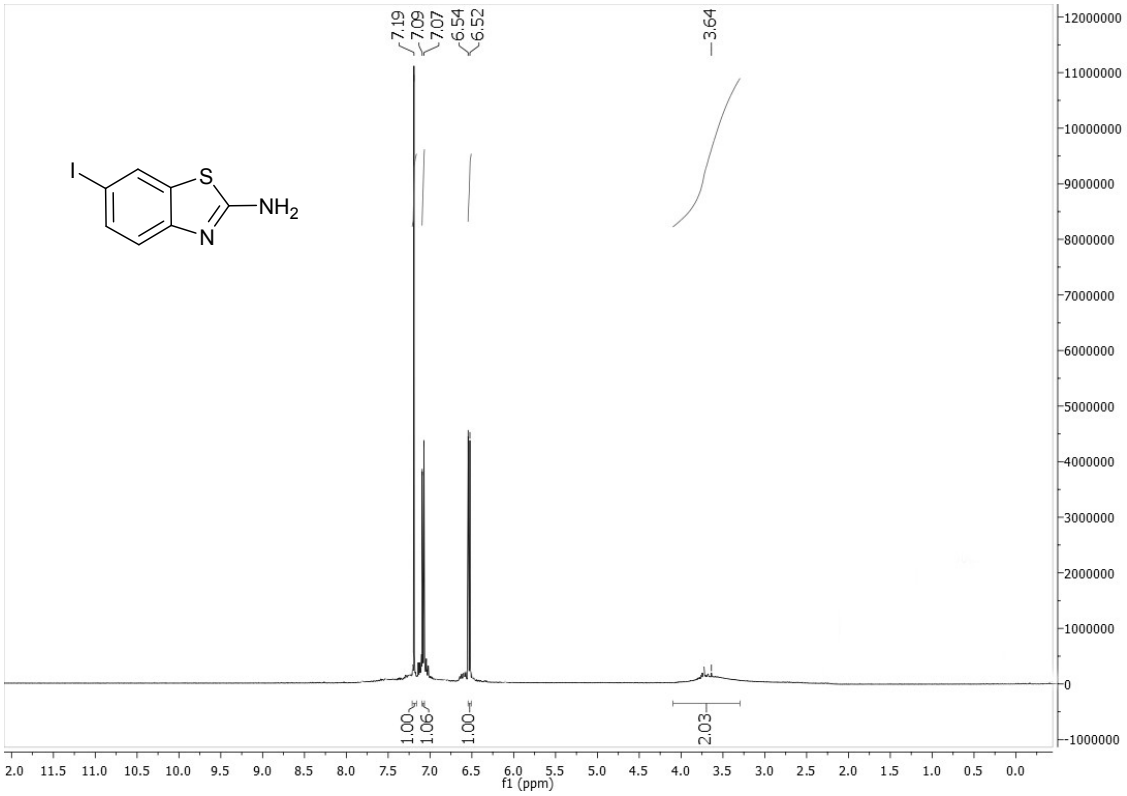

Mk-ts7 dried/11
146.18
140.98
134.08
129.58
123.10
120.15
117.15
112.12
111.41
Ph
NH
NCS
f1 (ppm)

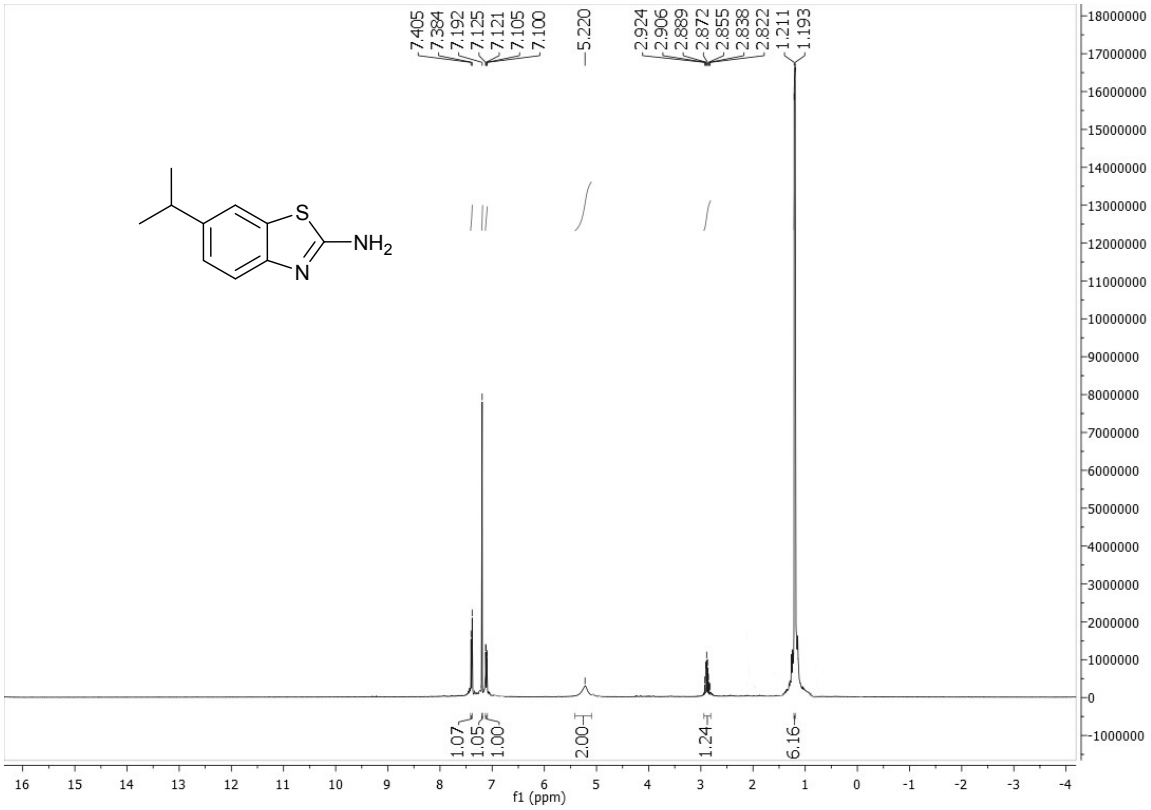

7.563
7.452
7.418
7.287
7.252
5.481
N
NH2
Cl
S
0.76
1.00
1.18
2.03
f1 (ppm)

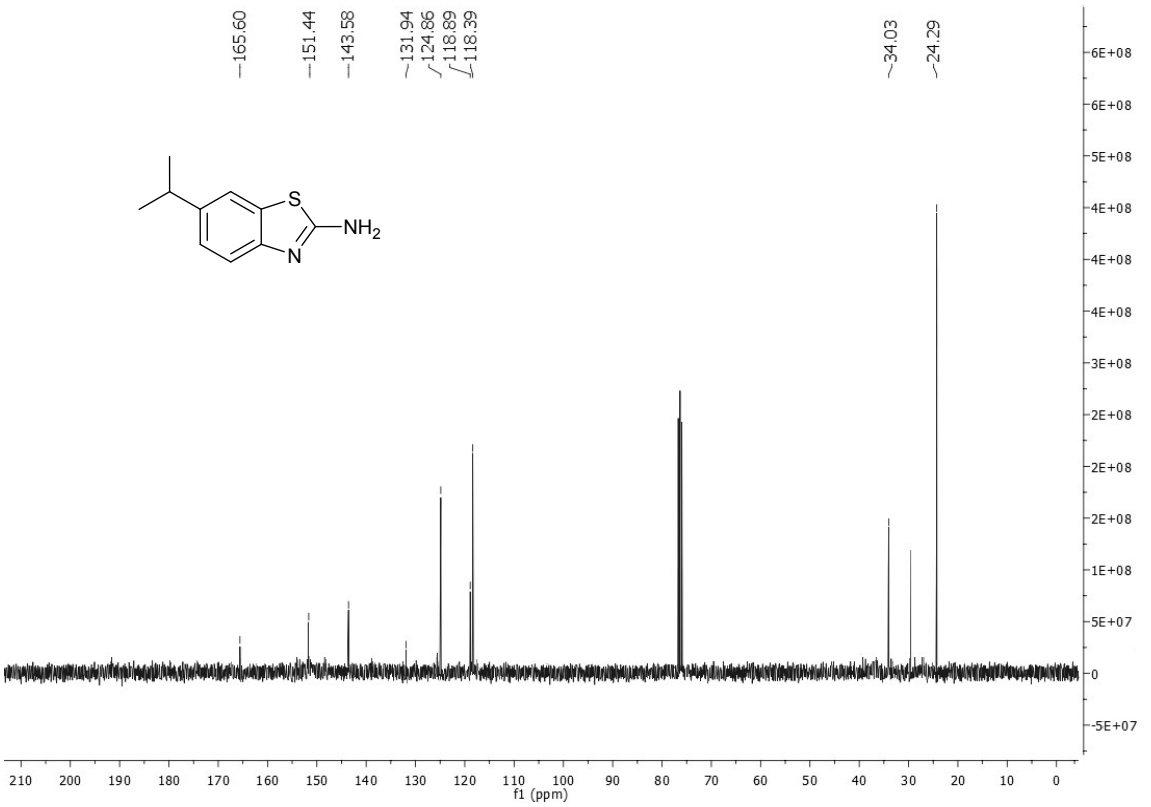
7j

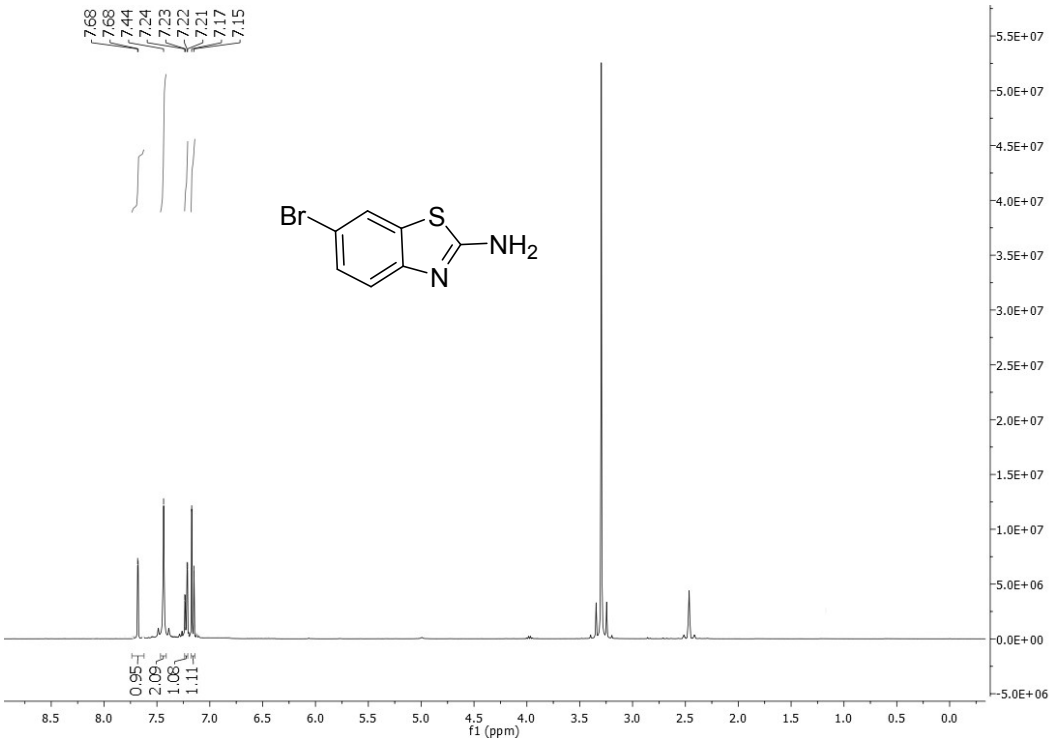

169.32
154.52
135.63
128.38
127.84
119.72
118.91
N
NH2
Cl
S
f1 (ppm)

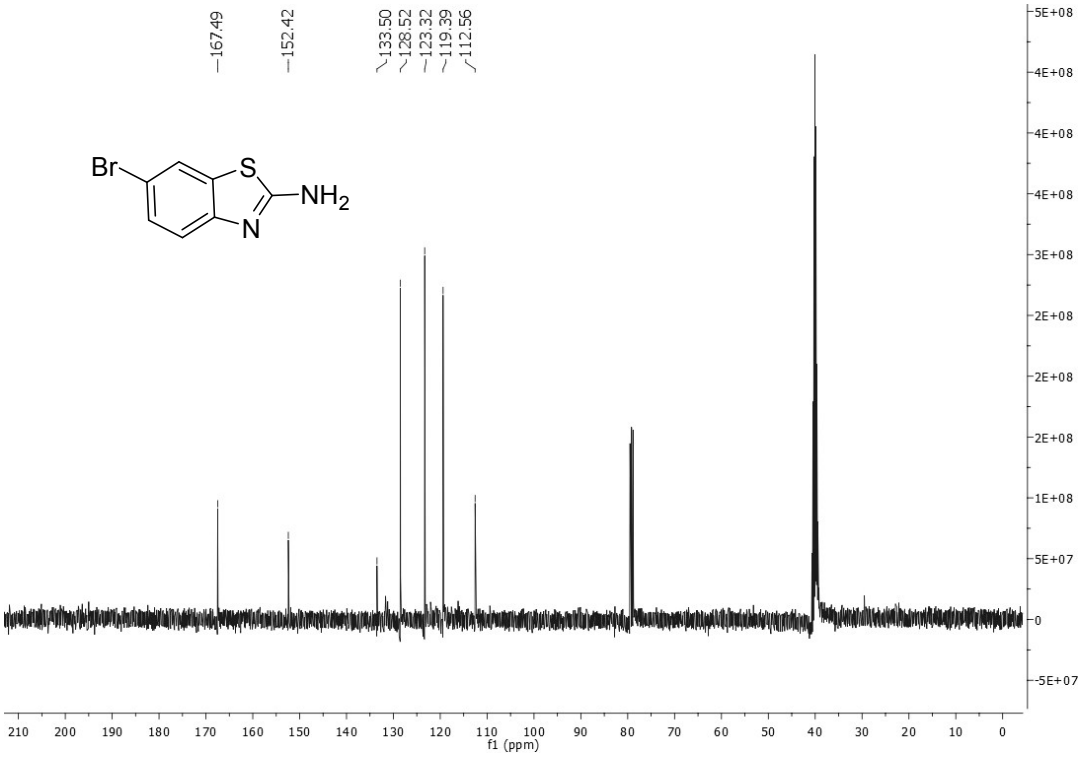
7j

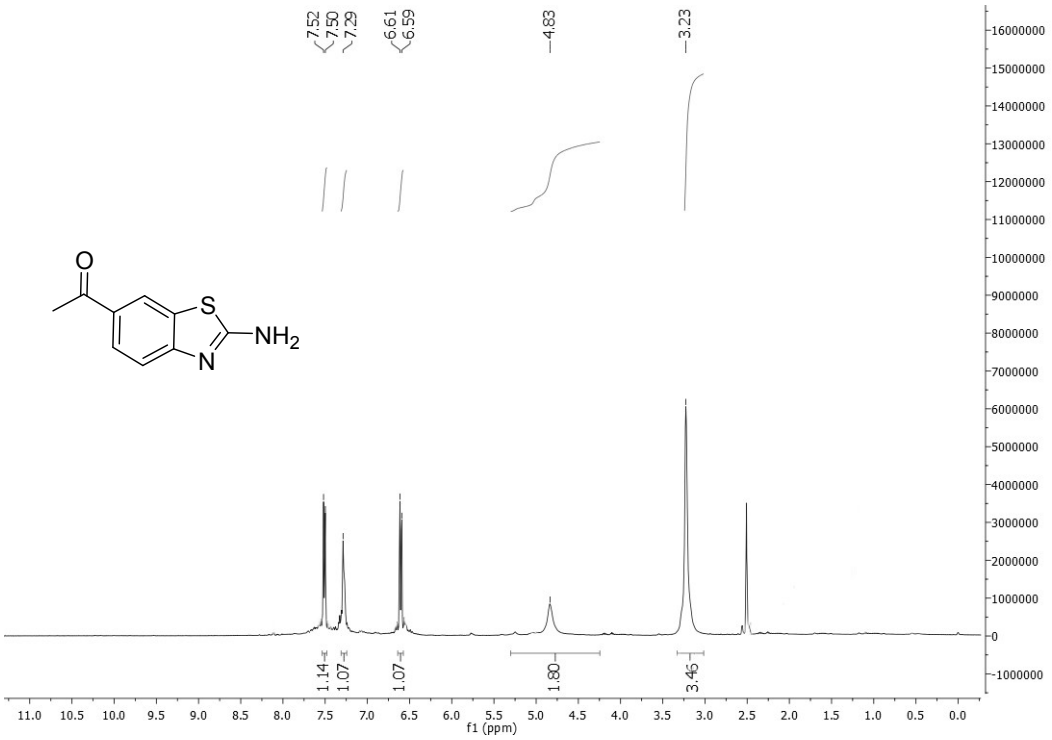

7.19
7.09
7.07
6.54
6.52
3.64
I
S
NH2
N
1.00
1.06
1.00
2.03
f1 (ppm)

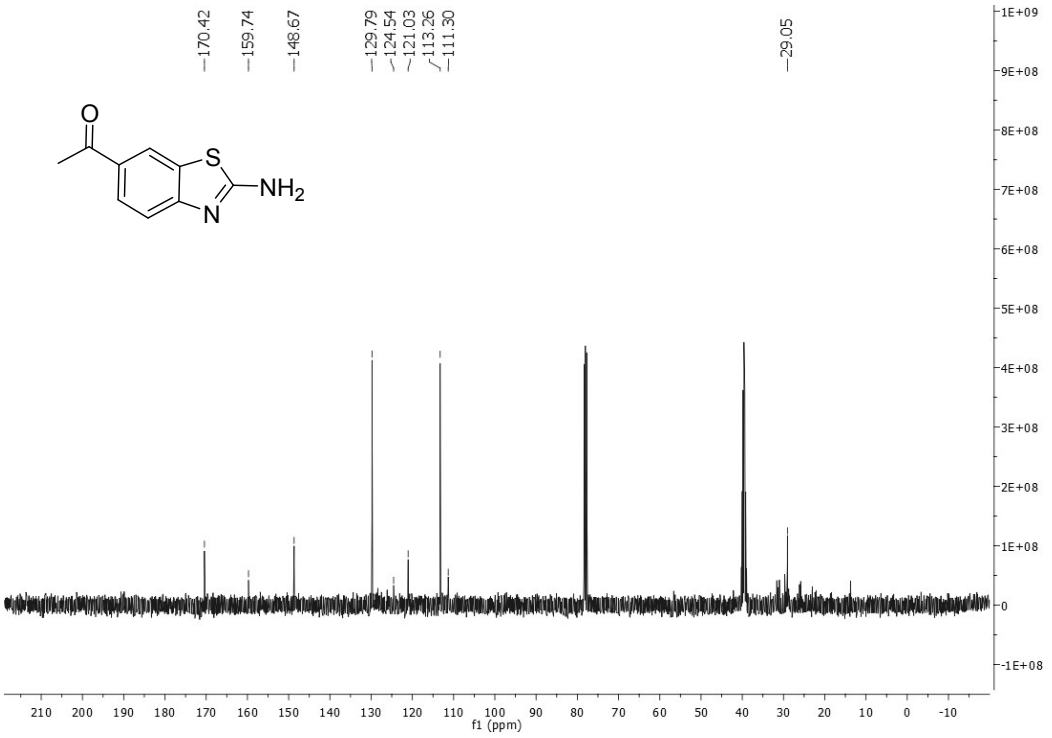

7.405
7.384
7.192
7.125
7.121
7.105
7.100
5.220
2.924
2.906
2.889
2.872
2.855
2.838
2.822
1.211
1.193
S
NH2
N
1.07
1.05
1.00
2.00
1.24
6.16
f1 (ppm)

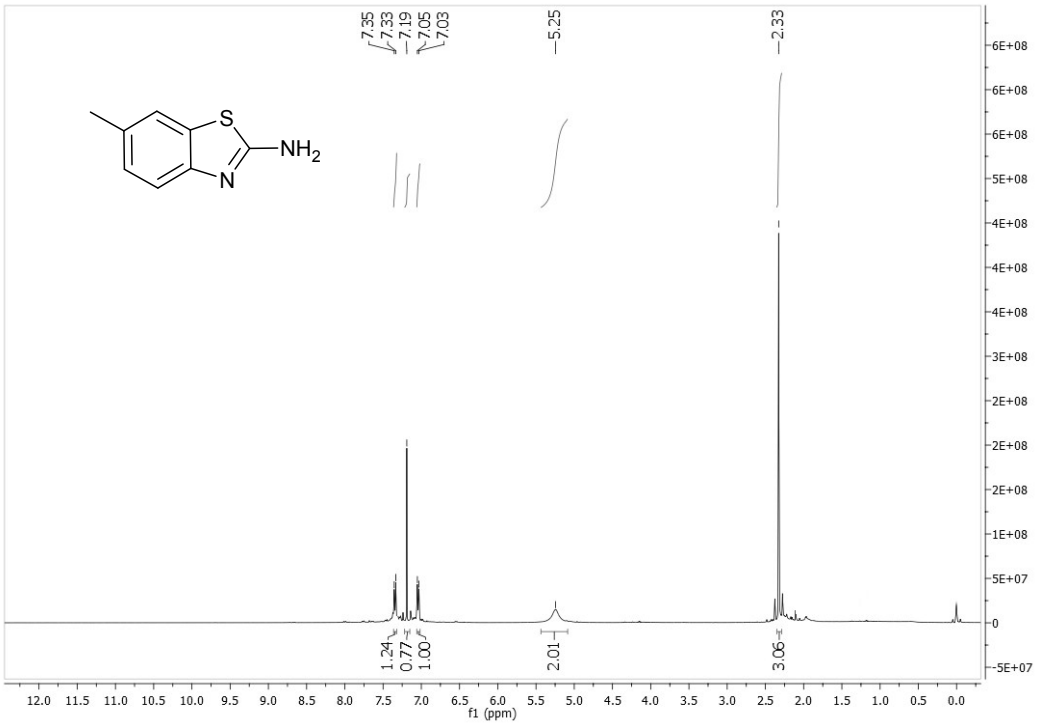

165.60
151.44
143.58
131.94
124.86
118.89
118.39
34.03
24.29
S
NH2
N
f1 (ppm)

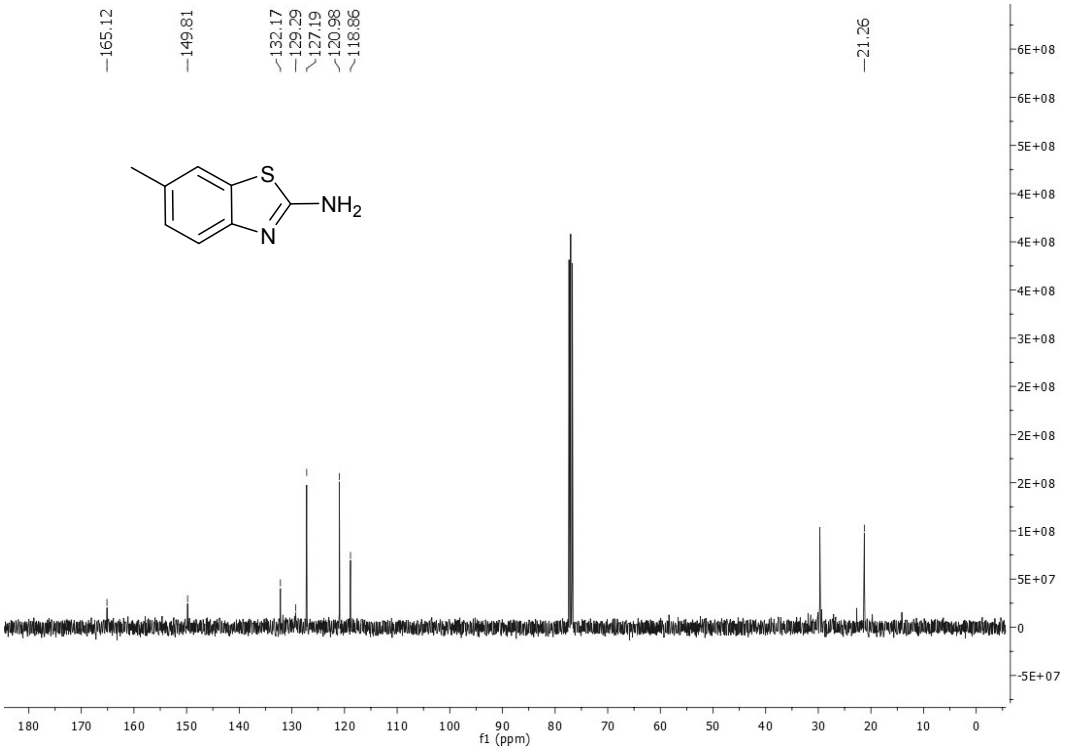

7.68
7.68
7.44
7.24
7.23
7.22
7.21
7.17
7.15
Br
S
NH2
N
0.95
2.09
1.08
1.11
f1 (ppm)

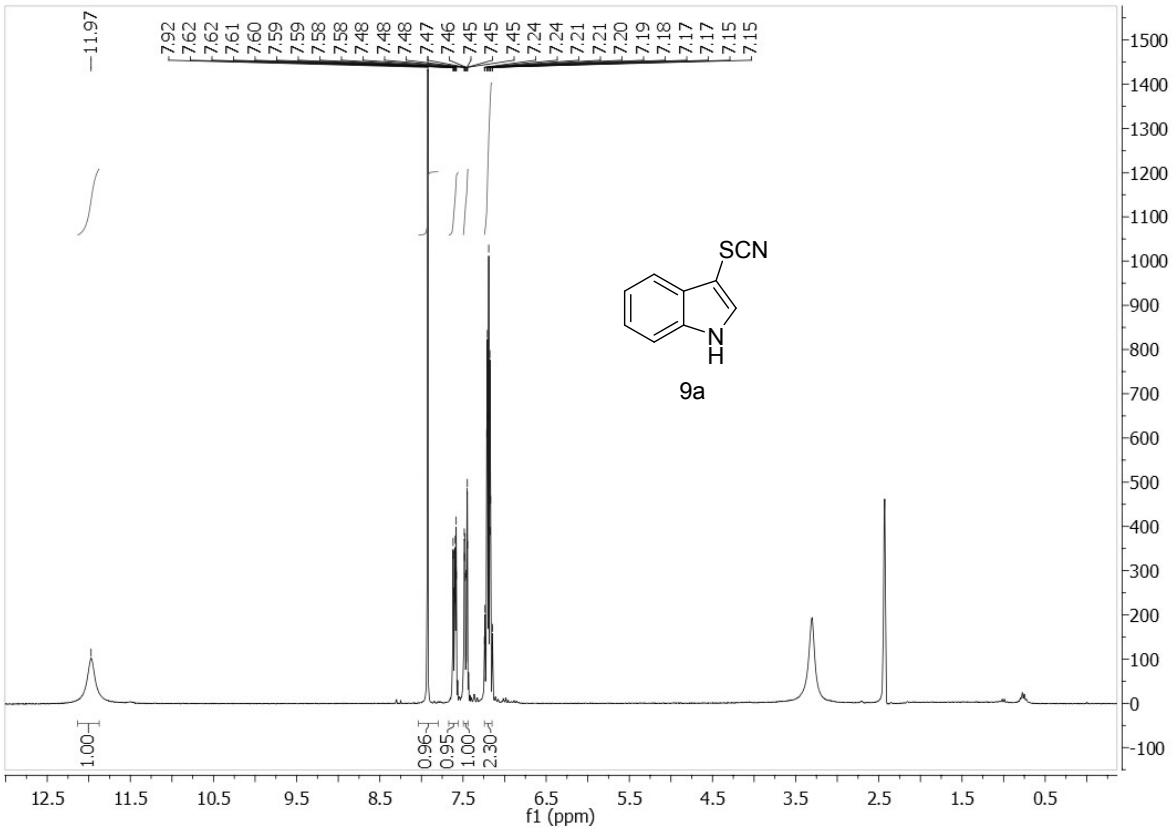

167.49
152.42
133.50
128.52
123.32
119.39
112.56
Br
S
NH2
N
f1 (ppm)

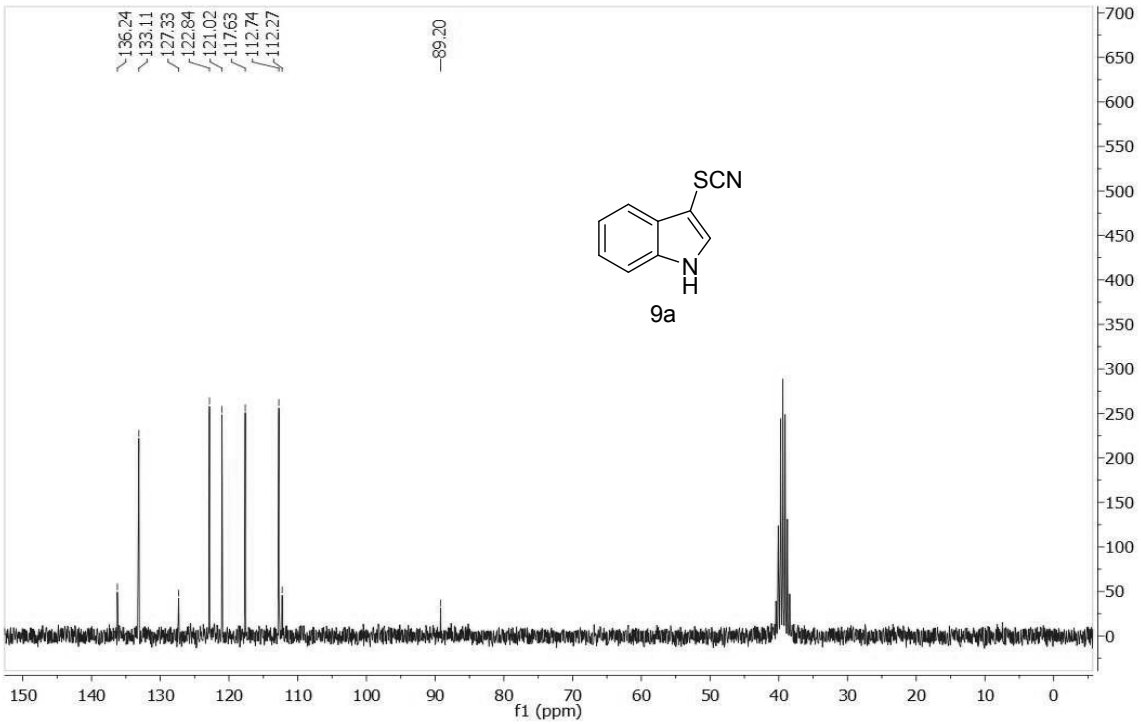

7.52
7.50
7.29
6.61
6.59
4.83
3.23
O
S
NH2
N
1.14
1.07
1.07
1.80
3.45
f1 (ppm)

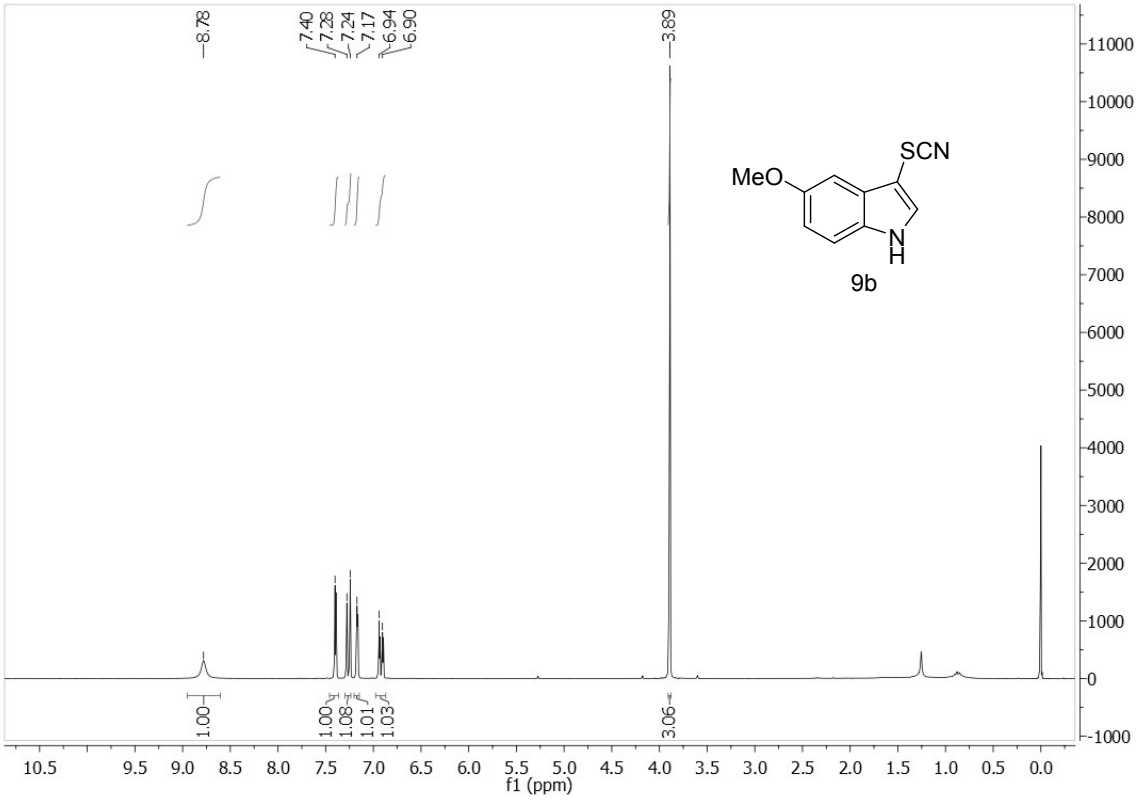

170.42
159.74
148.67
129.79
124.54
121.03
113.26
111.30
29.05
O
S
NH2
N
f1 (ppm)

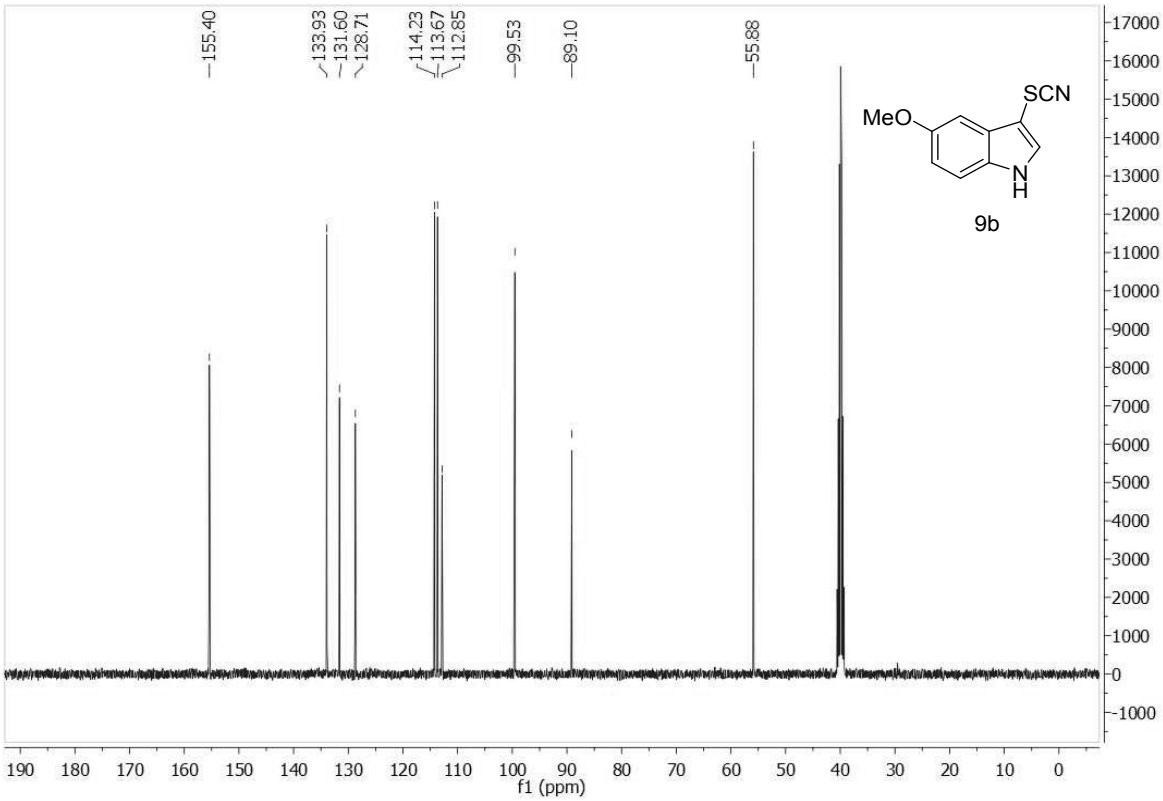

7.35
7.33
7.19
7.05
7.03
5.25
2.33
S
NH2
N
1.24
0.77
1.00
2.01
3.06
f1 (ppm)

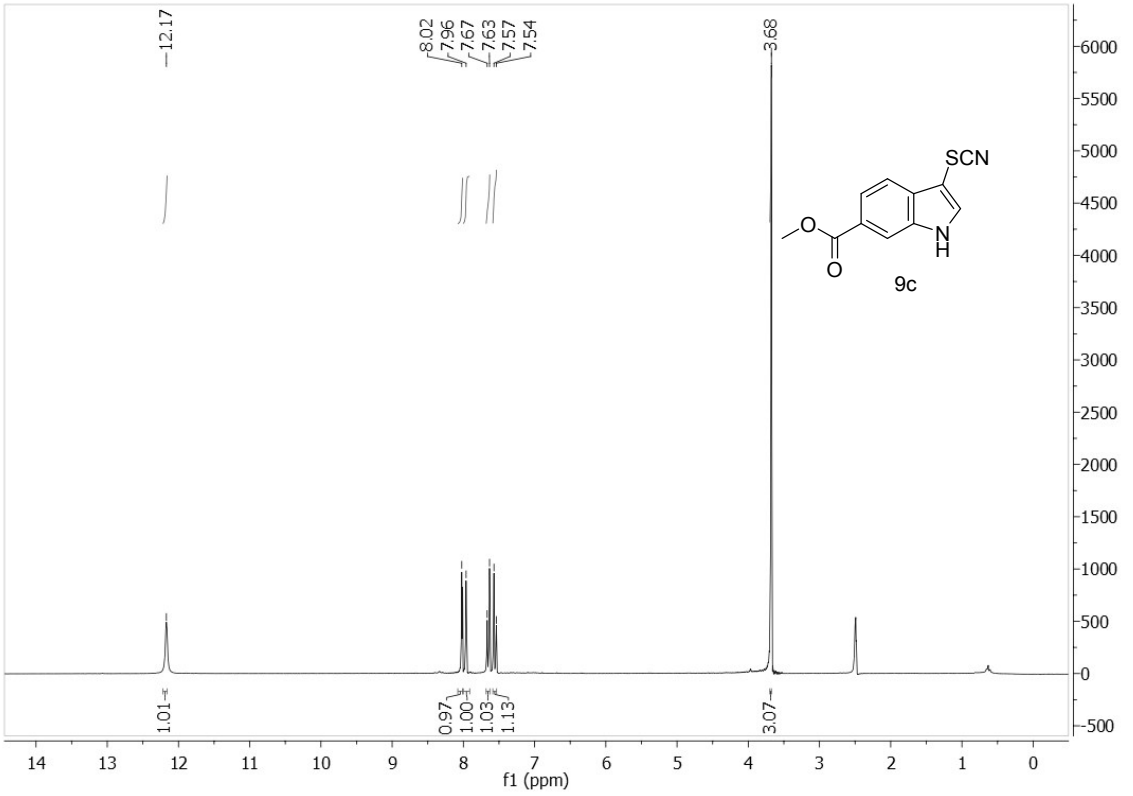

165.12
149.81
132.17
129.29
127.19
120.98
118.86
21.26
S
NH2
N
f1 (ppm)

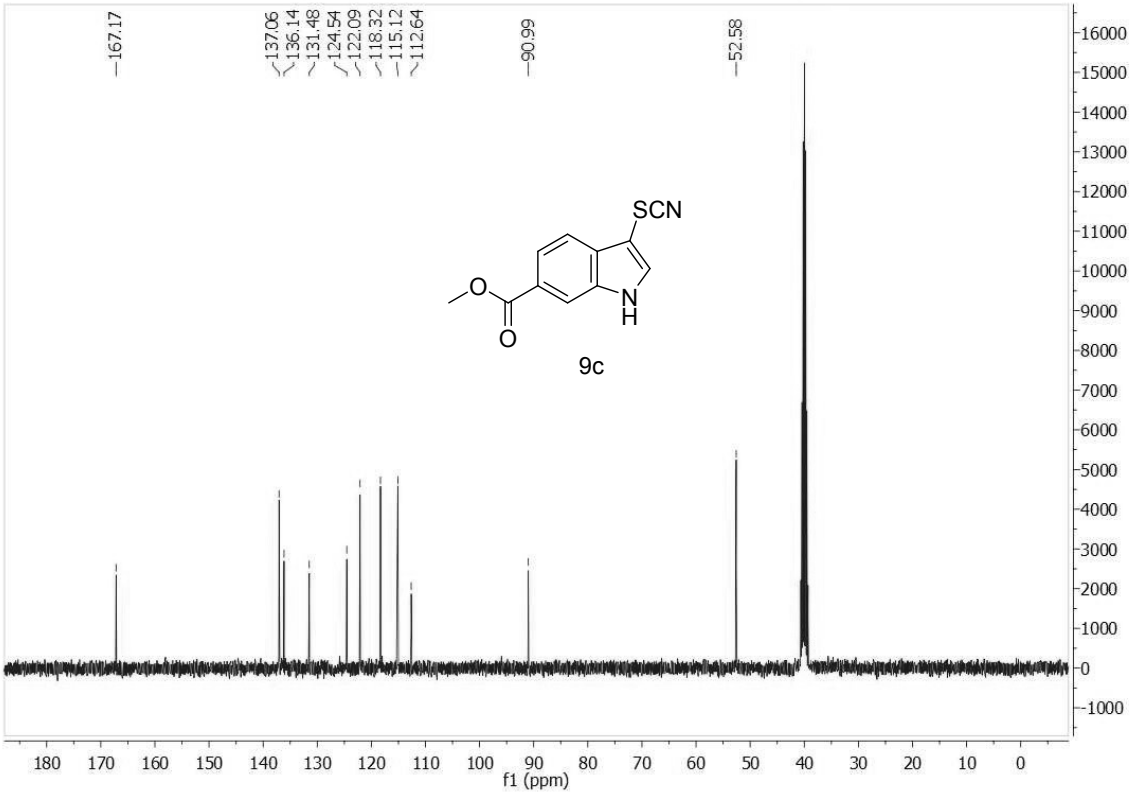

11.97
7.92
7.62
7.62
7.61
7.60
7.59
7.59
7.58
7.58
7.48
7.48
7.48
7.47
7.46
7.45
7.45
7.45
7.24
7.24
7.21
7.21
7.20
7.19
7.18
7.17
7.17
7.15
7.15
SCN
N
H
9a
1.00
0.96
0.95
1.00
2.30
f1 (ppm)

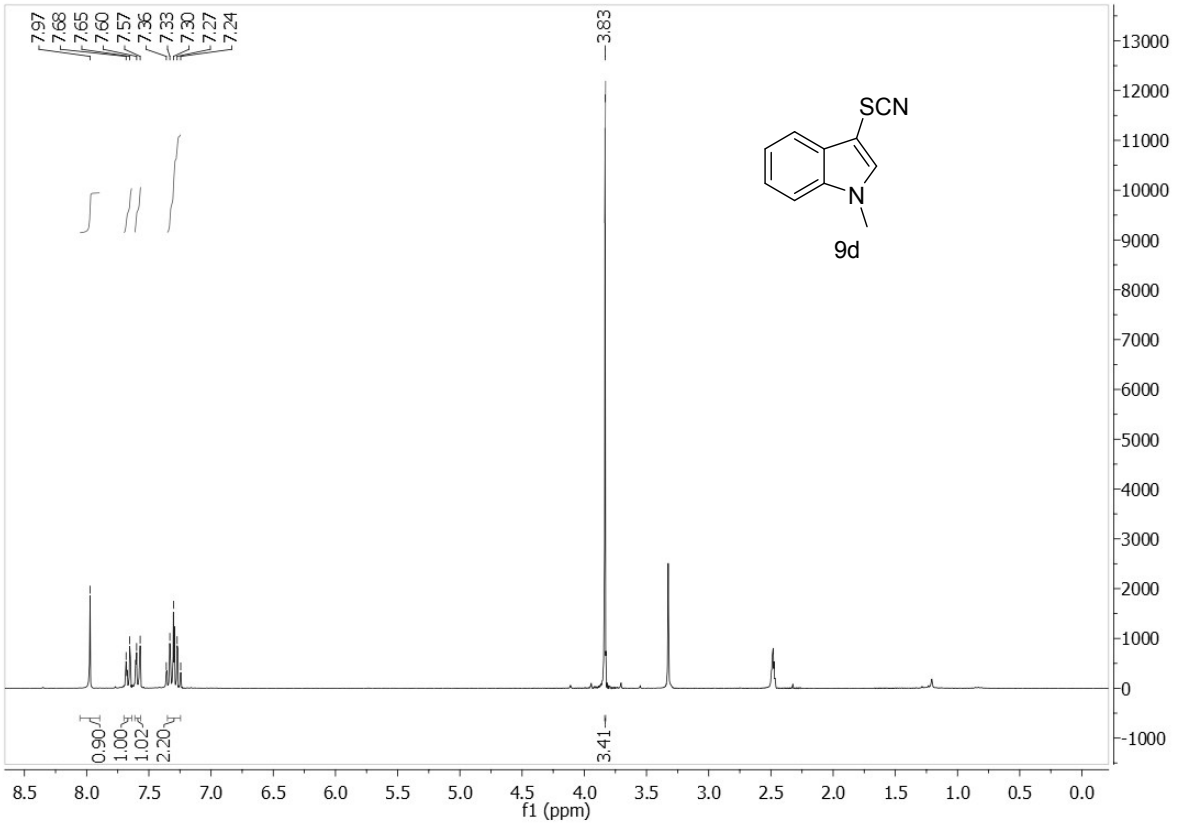

136.24
133.11
127.33
122.84
121.02
117.63
112.74
112.27
89.20
SCN
N
H
9a
f1 (ppm)

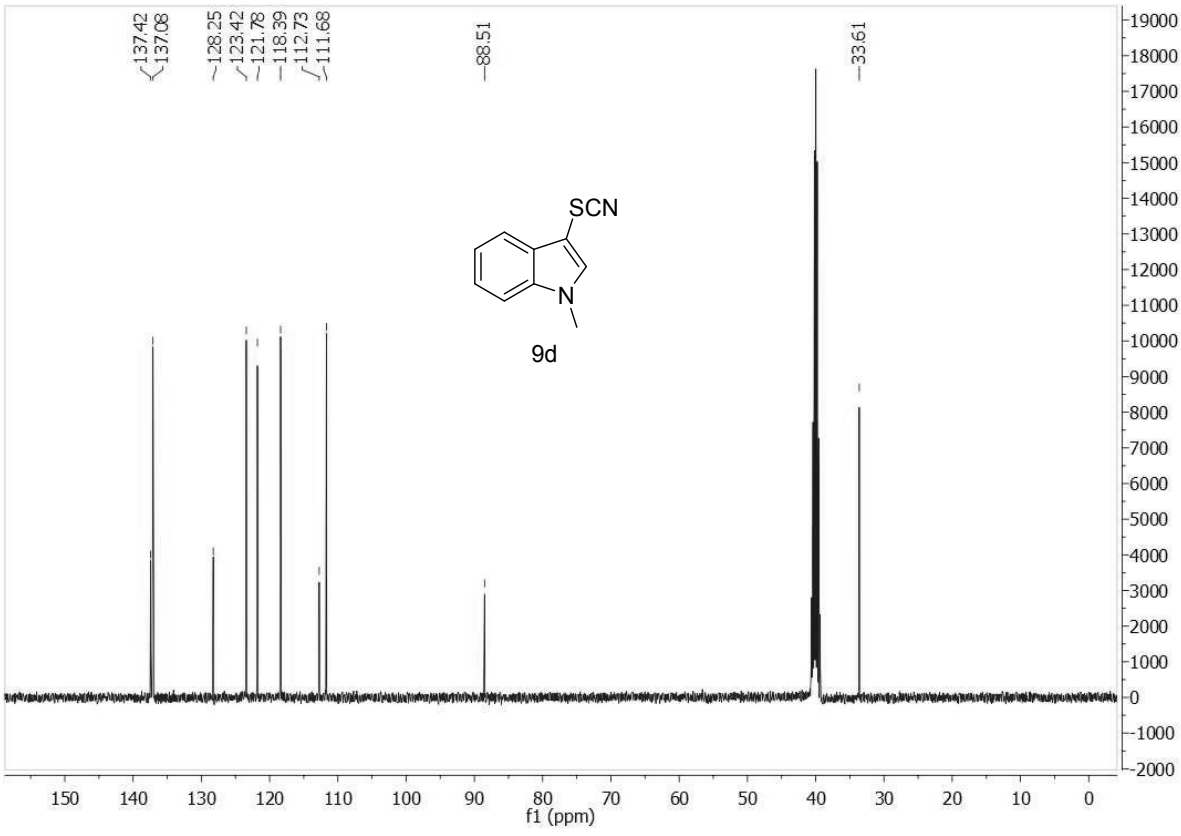

8.78
7.40
7.28
7.24
7.17
6.94
6.90
3.89
SCN
MeO
N
H
9b
1.00
1.00
1.08
1.01
1.03
3.06
f1 (ppm)

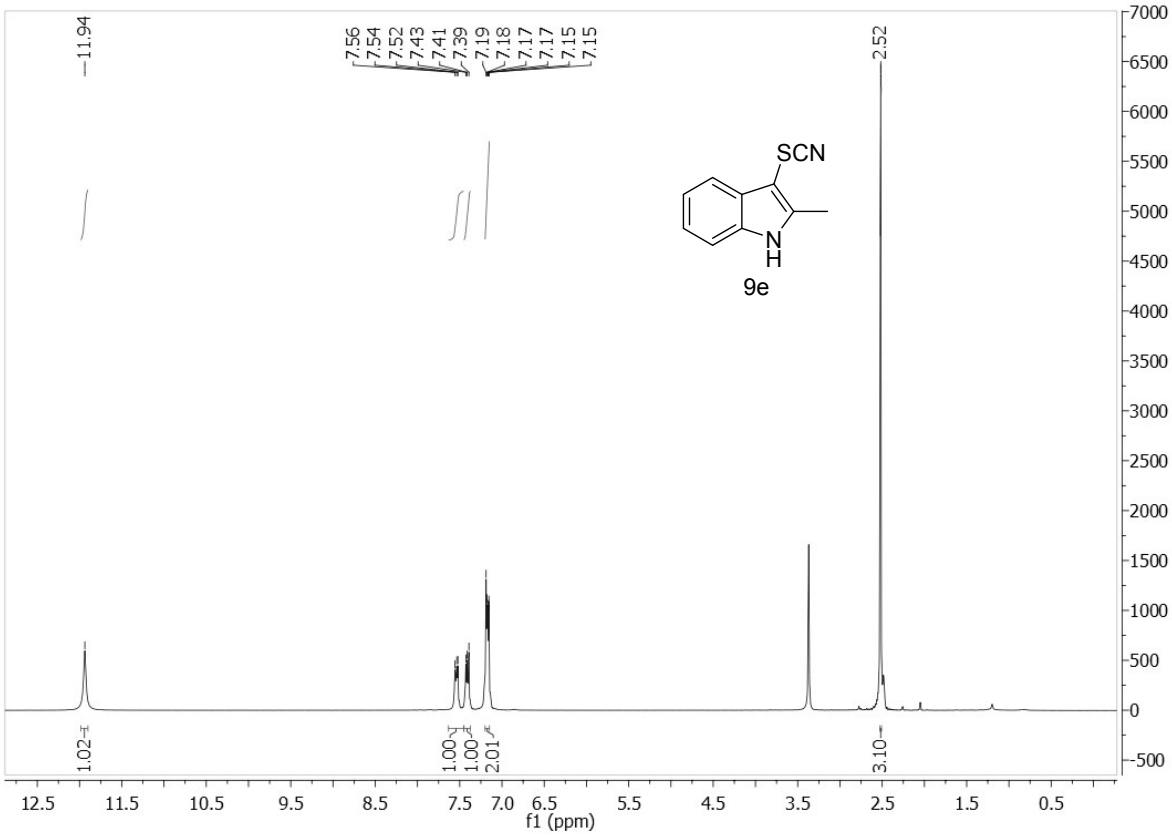

155.40
133.93
131.60
128.71
114.23
113.67
112.85
99.53
89.10
55.88
SCN
MeO
N
H
9b
f1 (ppm)

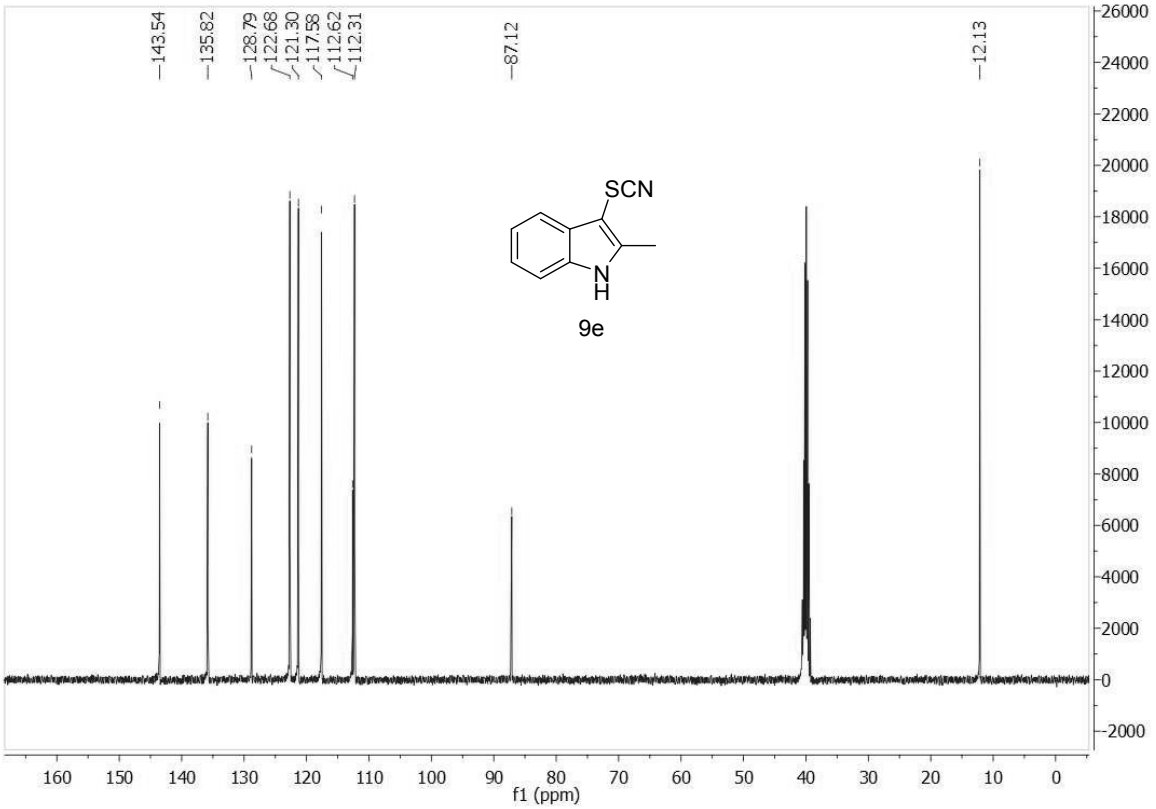

12.17
8.02
7.96
7.67
7.63
7.57
7.54
3.68
SCN
O
O
N
H
9c
1.01
0.97
1.00
1.03
1.13
3.07
f1 (ppm)

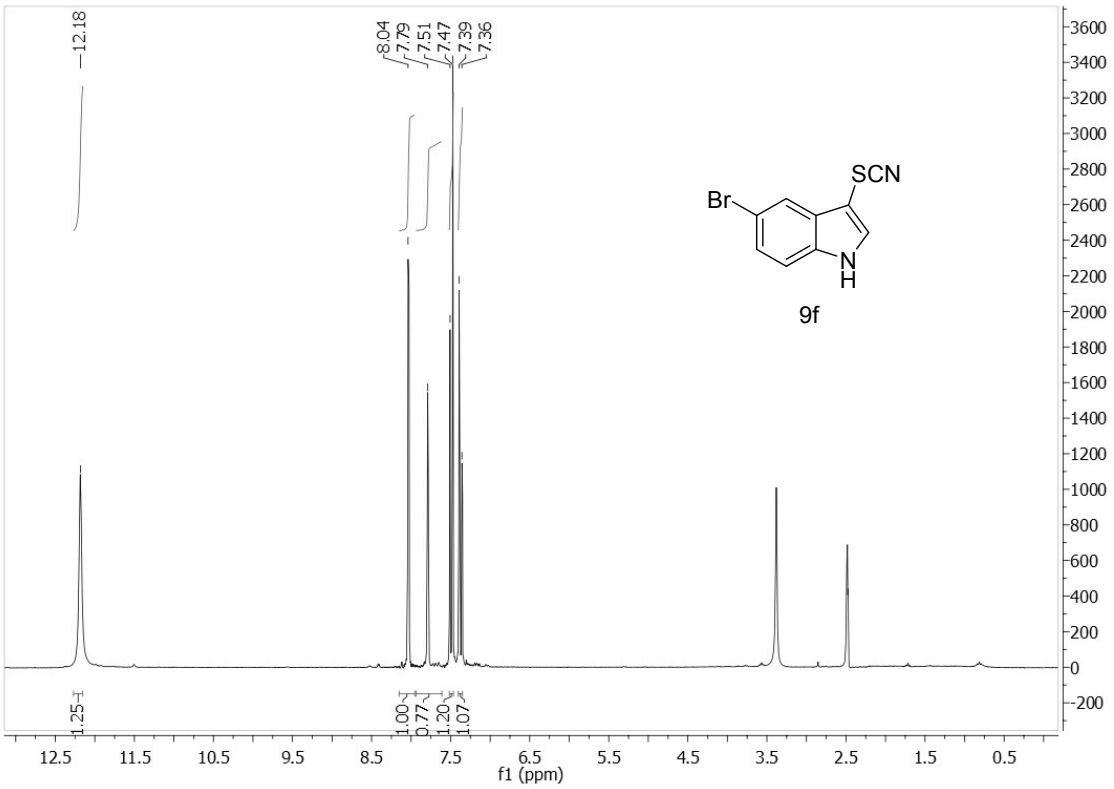

167.17
137.06
136.14
131.48
124.54
122.09
118.32
115.12
112.64
90.99
52.58
SCN
O
O
N
H
9c
f1 (ppm)

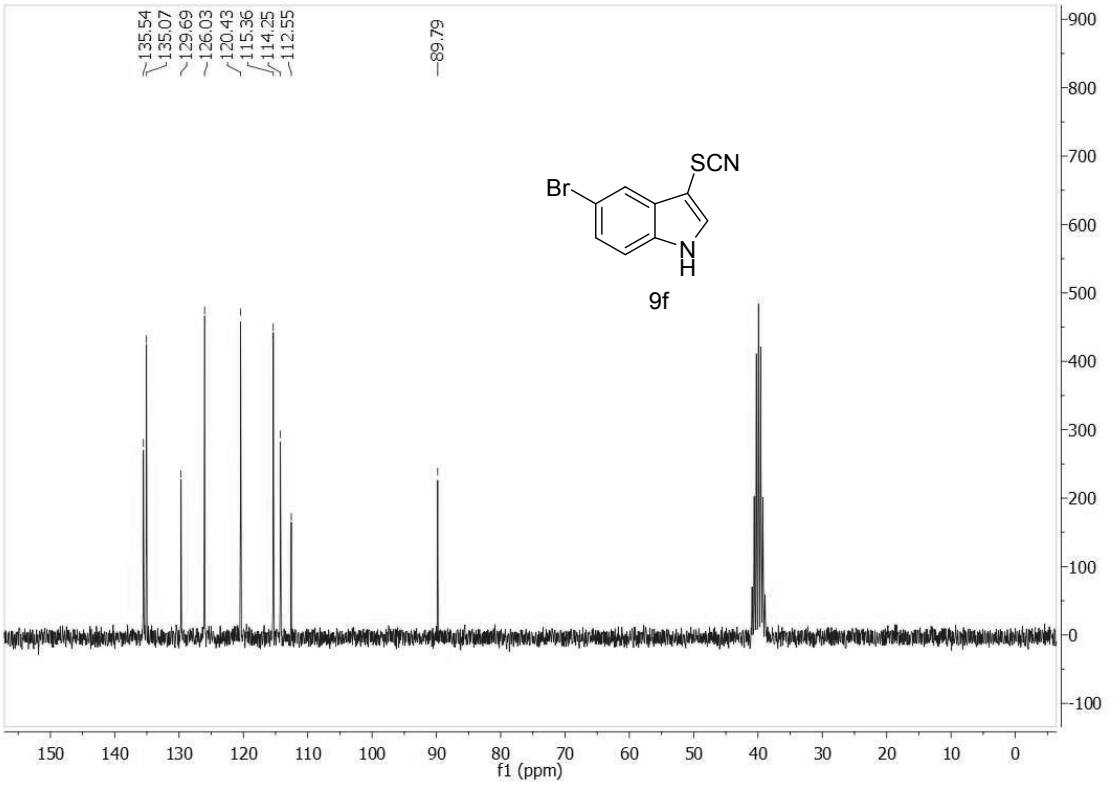

7.97
7.68
7.65
7.60
7.57
7.36
7.33
7.30
7.27
7.24
3.83
SCN
N
9d
0.90
1.00
1.02
2.20
3.41
f1 (ppm)

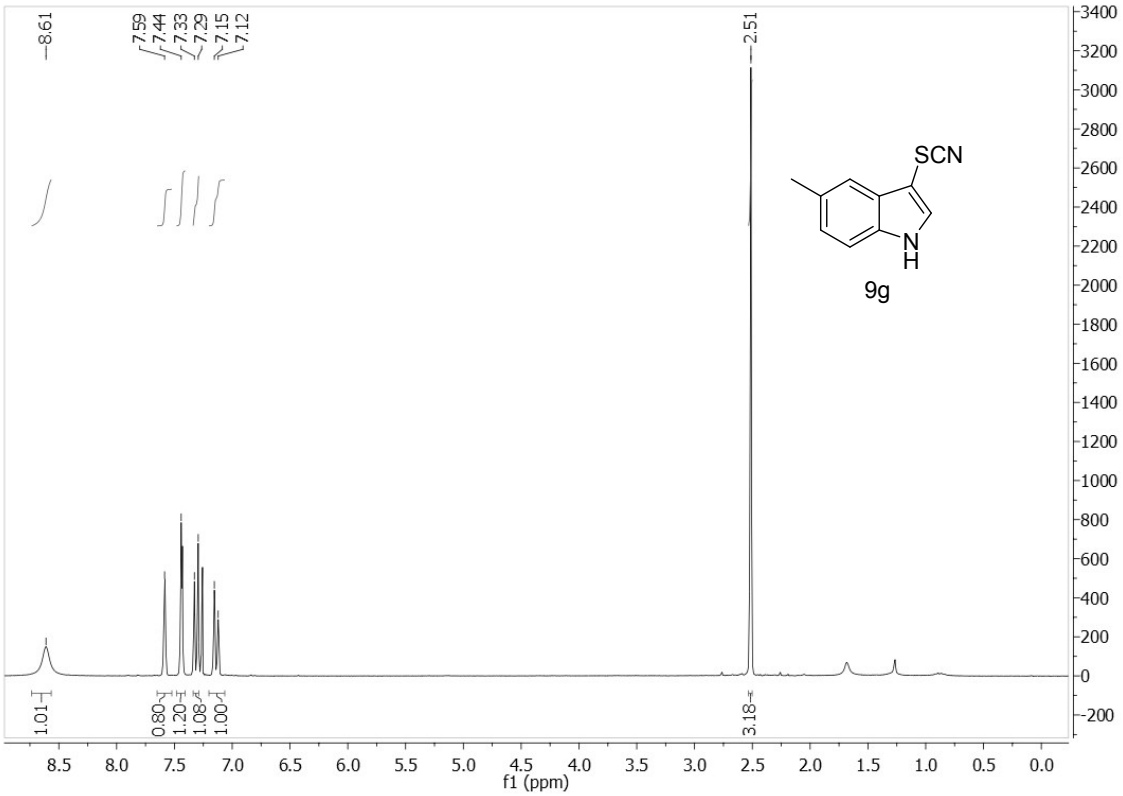

137.42
137.08
128.25
123.42
121.78
118.39
112.73
111.68
88.51
33.61
SCN
N
9d
f1 (ppm)

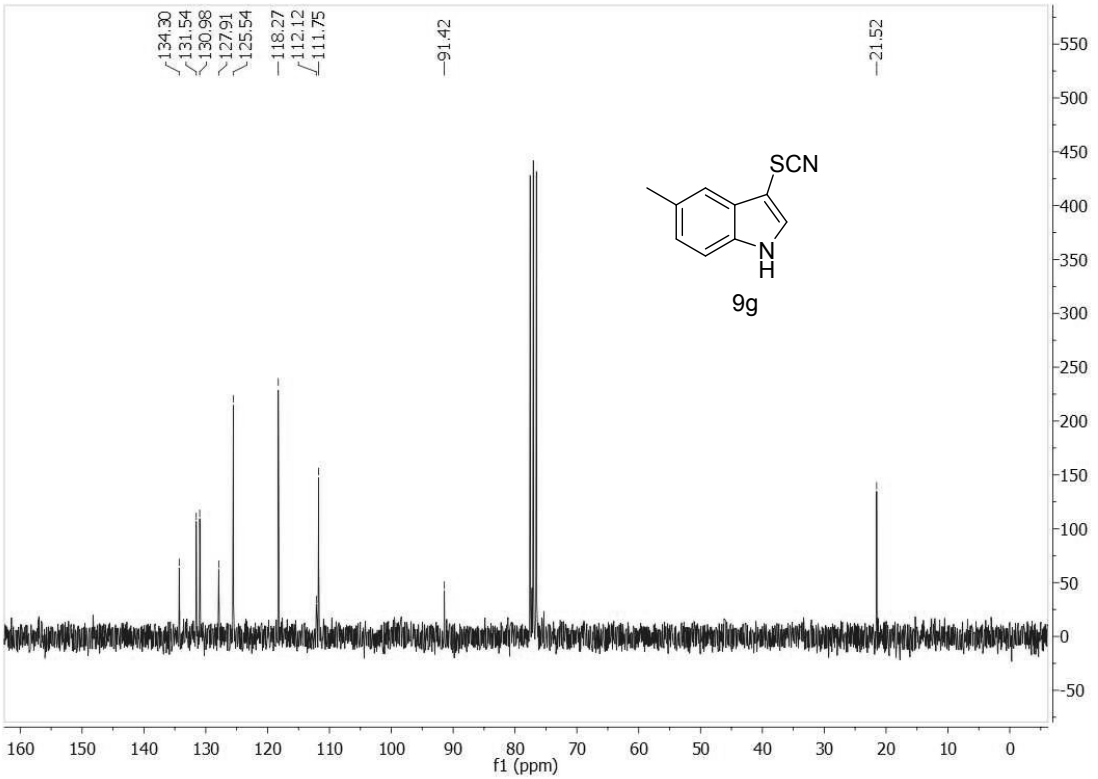

11.94
7.56
7.54
7.52
7.43
7.41
7.39
7.19
7.18
7.17
7.17
7.15
7.15
2.52
SCN
N
H
9e
1.02
1.00
1.00
2.01
3.10
f1 (ppm)

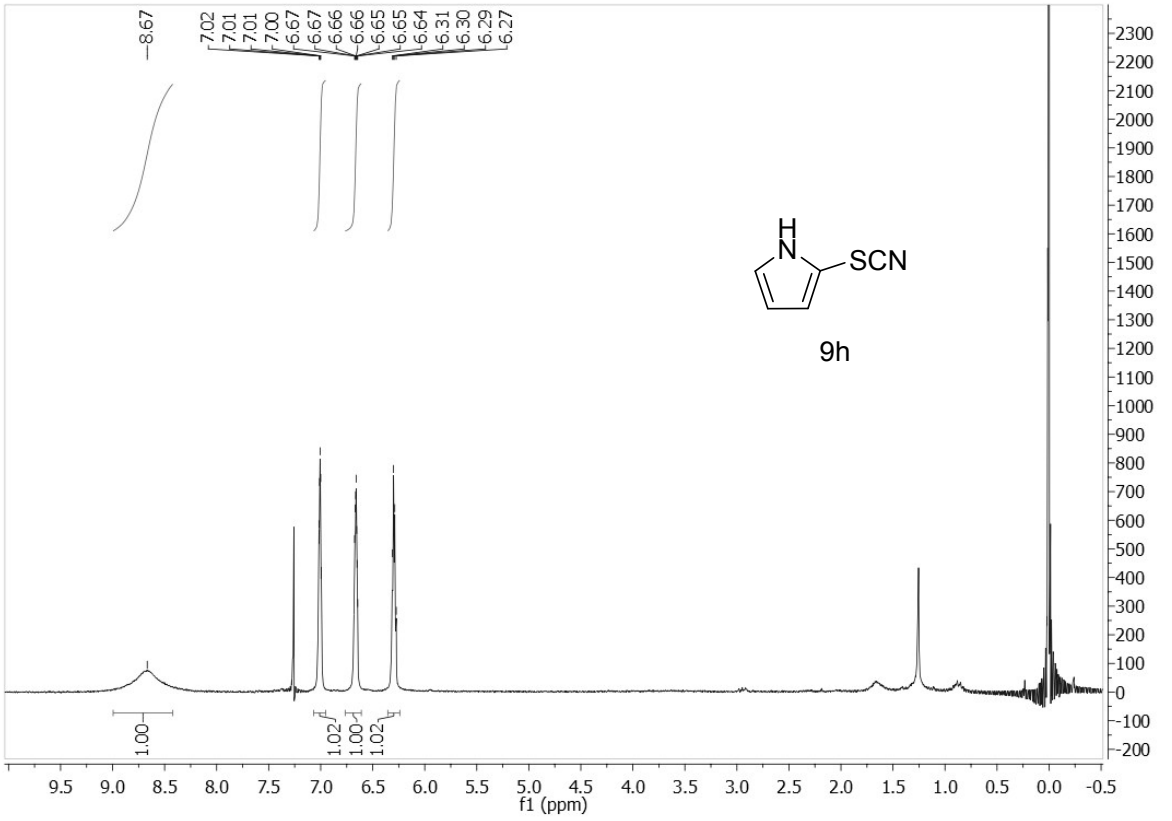

143.54
135.82
128.79
122.68
121.30
117.58
112.62
112.31
87.12
12.13
SCN
N
H
9e
f1 (ppm)

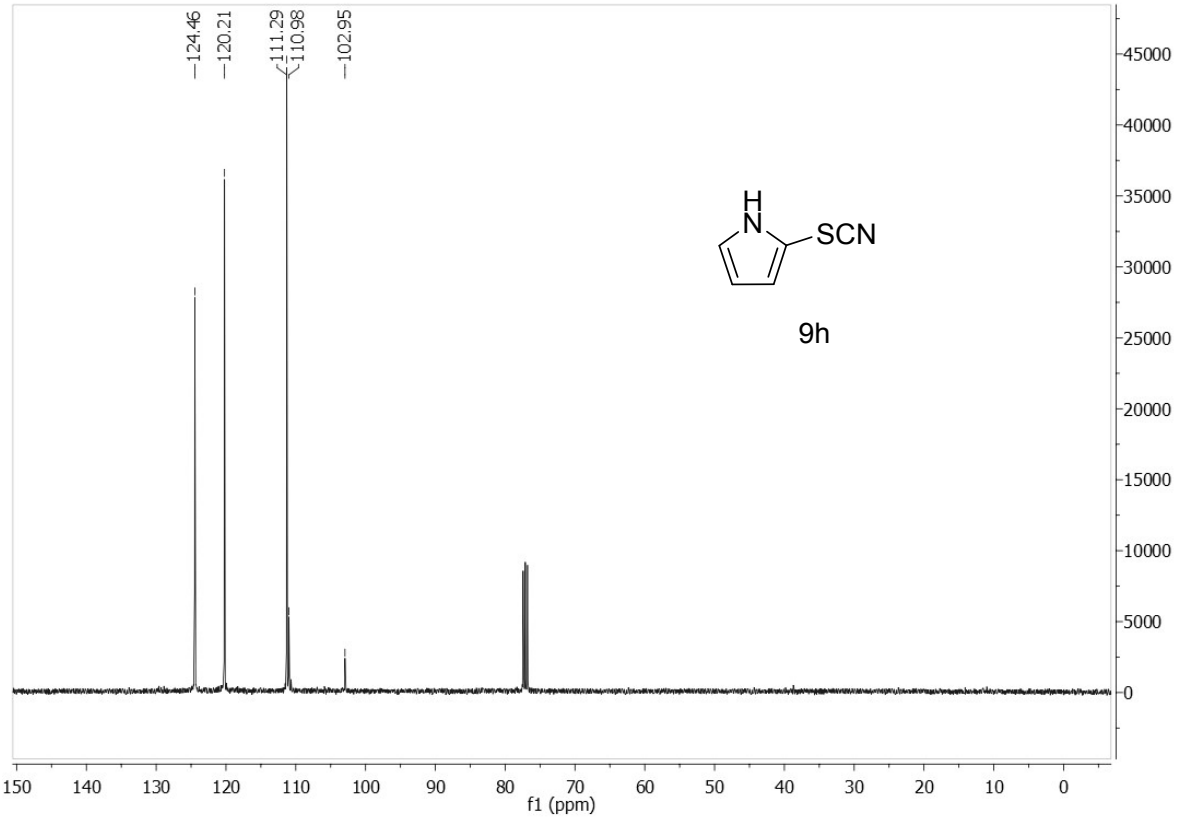

12.18
8.04
7.79
7.51
7.47
7.39
7.36
SCN
Br
N
H
9f
1.25
1.00
0.77
1.20
1.07
f1 (ppm)

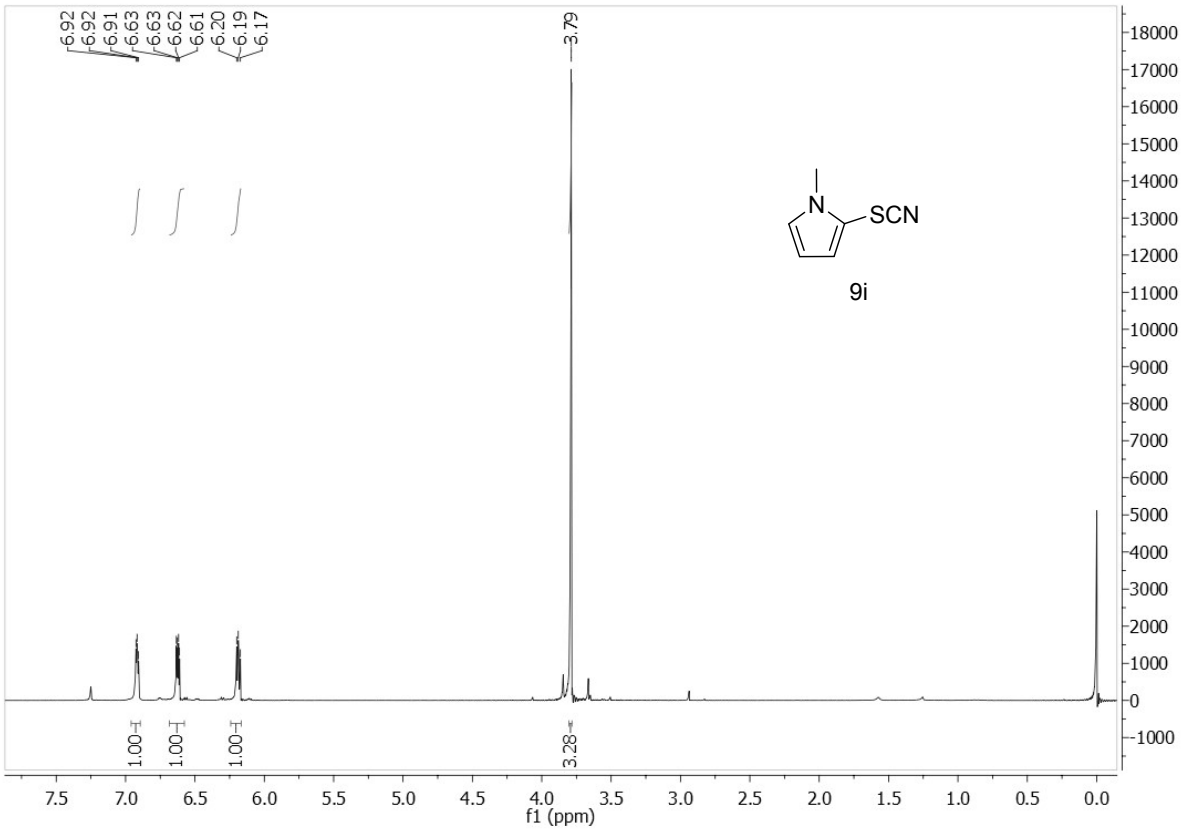

135.54
135.07
129.69
126.03
120.43
115.36
114.25
112.55
89.79
SCN
Br
N
H
9f
f1 (ppm)

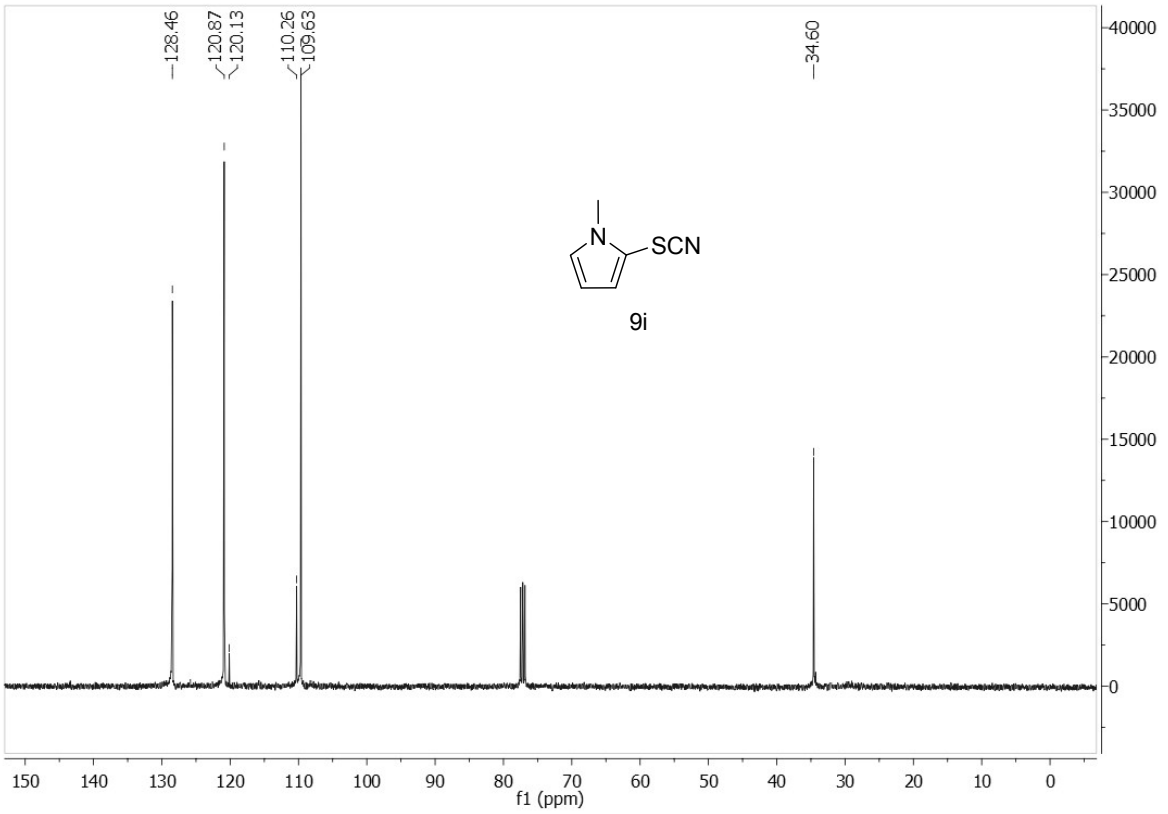

8.61
7.59
7.44
7.33
7.29
7.15
7.12
2.51
SCN
N
H
9g
1.01
0.80
1.20
1.08
1.00
3.18
f1 (ppm)


134.30
131.54
130.98
127.91
125.54
118.27
112.12
111.75
91.42
21.52
SCN
N
H
9g
f1 (ppm)


8.67
7.02
7.01
7.01
7.00
6.67
6.67
6.66
6.66
6.65
6.65
6.64
6.31
6.30
6.29
6.27
1.00
1.02
1.00
1.02
SCN
9h
f1 (ppm)


124.46
120.21
111.29
110.98
102.95
SCN
9h
f1 (ppm)


6.92
6.92
6.91
6.63
6.63
6.62
6.61
6.20
6.19
6.17
3.79
1.00
1.00
1.00
3.28
N
SCN
9i
f1 (ppm)


128.46
120.87
120.13
110.26
109.63
34.60
N
SCN
9i
f1 (ppm)

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