Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Visible light aerobic thiocyanation of *N*-bearing aromatic and heteroaromatic compounds using Ag/TiO_2 nanotube photocatalyst.

Mona Hosseini-Sarvari*[†], Zeinab Hosseinpour[†], Mehdi Koohgard[†]

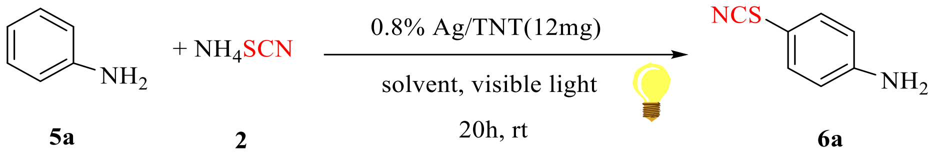
[†]Department of Chemistry, Shiraz University, Shiraz 7194684795, I.R. Iran

***Correspondence to: Mona Hosseini-Sarvari**

E-mail: Hossaini@shirazu.ac.ir

Contents

1 The effect of solvents on thiocyanation of aniline.



5a 2 6a

Scheme S1. Optimizations of different solvents on thiocyanation of aniline [a].

Entry	Solvent	Yield of **6a** [%][b]
1	THF	42
2	CH_3CN	78
3	EtOH	36
4	$CHCl_3$	Trace
5	EtOAC	64

[a] *Reaction conditions:* Aniline (1 mmol), ammonium thiocyanate (3 mmol), 0.8%Ag/TNT (12 mg), solvent (6.0 mL) , open to the air, under irradiation of 12 W CFL at room temperature, 20 h. [b]Isolated yield.

2 Optimizations of thiocyanation reaction conditions of 2-Amino-4-phenylthiazole

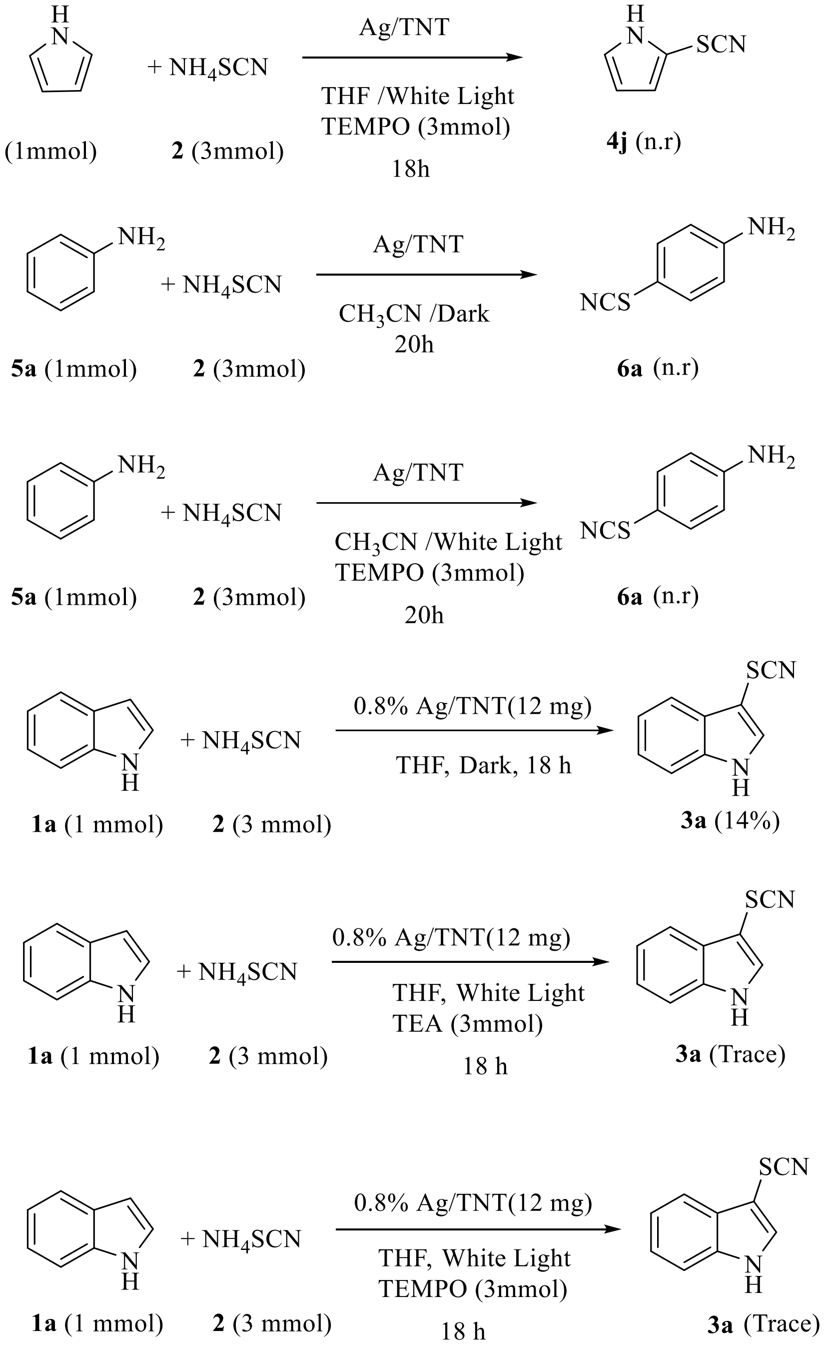
It is found that the best solvent for this model reaction is THF. Other organic solvents such as DMF, $CHCl_3$, and EtOH afforded product in lower yields or did not afford the desired product. The efficiency of reaction under blue LED was higher than other light sources and the amount of photocatalyst was determined to 6 mg (Scheme S2, entry 11[f]).

Scheme S2. Screening the thiocyanation reaction conditions of 2-Amino-4-phenylthiazole[a]

Entry	**Solvent**	**Light**	**Yield of 7a [%][b]**
1	THF	12 W CFL, White	79
2	CH_3CN	12 W CFL, White	38
3	EtOH	12 W CFL, White	0
4	$CHCl_3$	12 W CFL, White	Trace
5	EtOAC	12 W CFL, White	Trace
6	DMF	12 W CFL, White	0
7	THF	12 W CFL, White	80[C]
8	THF	12W, Green LED	64
9	THF	12W, Red LED	55
10	THF	Dark	28
11	THF	12W, Blue LED	0[d], 70[e], 87[f], 87[g]

[a]Reaction conditions: 4-phenylthiazol-2-amine (1 mmol), ammonium thiocyanate (3 mmol), 2%Ag/TNT ,Solvent (6.0 mL) , 0.8%Ag/TNT(6 mg), open to the air, irradiation under visible light at room temperature, 24 h. [b]Isolated yield. [c]Used 2.0%Ag/TNT. [d]0.8%Ag/TNT (0mg). [e]0.8%Ag/TNT (3 mg). [f]0.8%Ag/TNT (6 mg). [g]0.8%Ag/TNT (12mg)

3 Control experiments.



4 Indication of H_2O_2 after completing the reaction.

The presence of H_2O_2 at the end of reaction was approved by using H_2O_2 paper indicator (Reaction conditions: A mixture of **7a** (1 mmol), **2** (3 mmol), THF (6.0 mL), 0.8% Ag/TNT (6mg), open to air, at room temperature, under irradiation of 12 W blue LED, 24 h.) is shown in Figure S1(a,b) and also the presence of H_2O_2 was found in ^{1}HNMR spectrum (250 MHz, DMSO-d_6 δ(ppm); 9.76) that is shown in Figure S1(c).

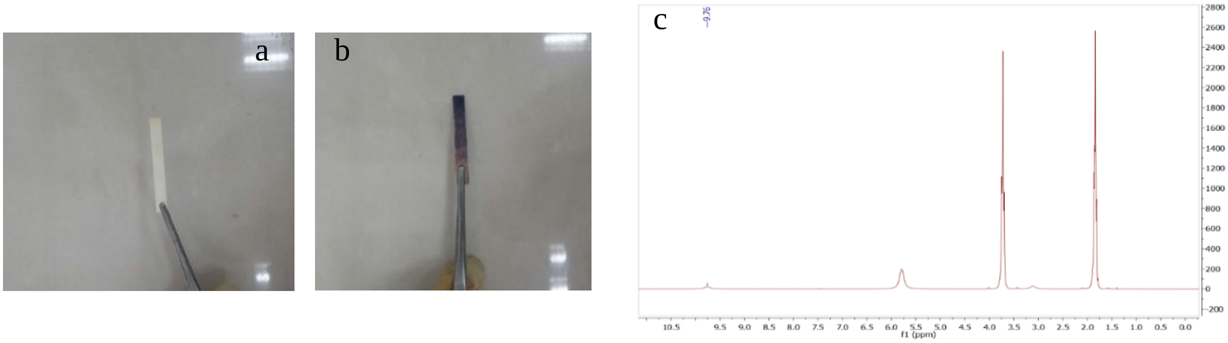


Figure S1. H_2O_2 test by paper (a) before and (b) after used. The presence of H_2O_2 after completion of the reaction by ^{1}HNMR spectrum (c).

5 Calculation of band Gap

Generally, the optical band gap of semiconductors can be obtained using two main method. To draw Tauc plot and calculation of band gap, absorption spectra and following equation can be applied [1].

Eq.1: $(\alpha h\nu)^{1/n} = A(h\nu - Eg)$

h: Planck's constant, ν: frequency of vibration
α: absorption (extinction) coefficient
Eg: band gap
A: proportionality constant
n: the value of the exponent ***n*** denotes the nature of the transition

Second method which is also capable of calculating the band gap is applying diffuse reflectance spectra and Kubelka-Munk equation [2].

In this study, first method estimated the band gap energy value of TNT and Ag/TNT photocatalyst which obtained from UV-Vis spectra of coresponding semiconductor [3, 4].Figure S2, depicts the plot of band-gap energy estimation of TNT and Ag/TNT samples obtained by Tauc's equation (2) [5].

Eq.2: $(\alpha h\nu)^{1/2} = A(h\nu - Eg)$

The calculated band-gap energy found to be 3.2 eV for rutile TNT and 3.0 eV for the Ag/TNT, respectively. Noticeably, the band-gap of TNT significantly reduced by loading of Ag nanoparticles on the surface of TNT [6].

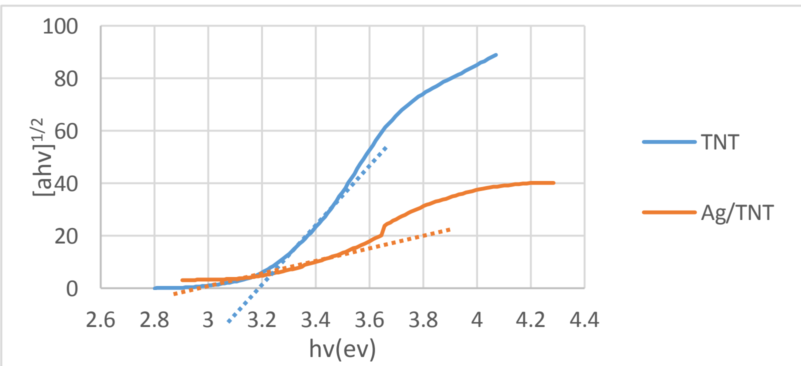


Figure S2. The plot for the band gap calculation of TNT and Ag/TNT deduced from $(\alpha h\nu)^{1/2} = A(h\nu - Eg)$ equation.

6 BET analysis of Ag/TNT

Table 1S. Specific surface area of Ag/TNT.

	BJH adsorption summary	BJH desorption summary	BET summary
Surface Area	187.318 m^2/g	221.096 m^2/g	166.006 m^2/g
Pore Volume	0.260 cc/g	0.270 cc/g	
Pore Diameter Dv (d)	3.891 nm	3.804 nm	

7 Experimental Section

7.1 General Methods

TiO_2 (P25, specific surface area: 50 m2g−1) was made from Degussa company. Other materials were made from Sigma-Aldrich and Merck companies. UV–vis diffuse reflectance spectrum was accomplished with a Shimadzu UV-2450 spectrophotometer. Measurement of melting points were investigated by a Buchi 510 device in open capillary tubes. We explored elemental analysis by a 2400 series PerkinElmer analyzer. We achieved ^1H NMR and ^{13}C NMR spectra by using $CDCl_3$ as solvent on Bruker Advance DPX FT 250 and Bruker Ultrashield 400 101 MHz spectrometry, respectively. We examined chemical shifts of ^1H NMR in parts per million (δ) related to TMS (0.00 ppm). (FT-IR) spectra were reported by a Shimadzu FT-IR 8300 spectrophotometer. Brunauer–Emmett–Teller (BET) surface area, Barret–Joyner–Halenda (BJH), pore volume and pore size repartition were obtained by a Micromeritics ASSP 2020 equipment. Thin layer chromatography (TLC) was prepared by silica gel PolyGram SIL G/UV 254 plates. The catalyst phase were characterized by X-ray diffraction (XRD) technique using Bruker D8-advance X-ray diffractometer with Cu Ka (λ = 1.54178 Å) radiation. We characterized size and images of nanoparticles by using transmission electron microscopy (TEM) that obtained by using a JEM-2100F, TEM at 200 kV and distribution and morphology of the nanotubes were obtained by JEOL, JSM-7610F Fe-SEM. The X-ray photoelectron spectroscopy (XPS) analysis was examined by using Thermo Scientifi, ESCALAB 250 Xi Mg X-ray resource.

7.2 General Procedure for the Preparation of TiO_2 -NTs

TiO_2 –NTs was prepared by modify hydrothermal method according to literatures. 0.5 g P25 was added into 25 mL of NaOH (10 M) solution, and the mixture refluxed for 24 h in an oil bath at 108 ˚C. After 2h milky white mixture cooled down and separated by centrifuge, the white product was washed with 1 M HCl and deionized water, until the mixture pH was lower than 7. Aafterward, TiO_2 -NTs was drained at room temperature and then calcined at 300 ˚C for 1 h [7].

7.3 General Procedure for the Preparation of Ag/TNT

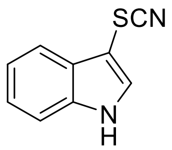
0.5g TiO_2-NTs were immersed into 250 mL $AgNO_3$ ethanol solution with a concentration of 0.25 mM and 0.50 mM then the mixture refluxed for 24 h at 83 ˚C. After 2 h the mixture cooled down at room temperature, the sample was centrifuged and washed with ethanol and deionized water for 4 times [8].

7.4 Typical Procedure for Thiocyanation

To a mixture of heterocyclic aromatic compounds (1 mmol), ammonium thiocyanat (3 mmol) in appropriate solvent, 0.8% Ag/TNT as catalyst was added and the mixture was irradiated by visible light (Irradiation light was under 12W compact fluorescent lamp (CFL), 12 W blue LED, 12 W green LED and 12 W red LED) and was open to air, at room temperature. The progress of the reactions was screened by TLC. After completion of the reactions, we separated catalyst from reaction solvent by centrifuging, and then 20 mL H_2O was added to reaction solvent and the mixture was extracted by CH_2Cl_2 in a decanter. The organic layer was further cleaned with distilled water (2×15 mL) and dried over Na_2SO_4. Then, the solvent was removed from mixture under reduced pressure and the resulting crude product was purified on silica gel column chromatography with petroleum ether/ethyl acetate (20:1) to give the desired thiocyanation products in good to excellent isolated yields. Furthermore, 2-Amino-4-phenylthiazole derivatives was purified by recrystallization in acetone.

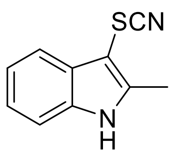
7.5 Physical and Spectral Data

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



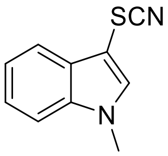
Yield 92 %, white solid, mp = 71–73 °C (lit. 72−74 °C) [9]. IR (KBr), ῡ(cm^{-1}); 3345(NH), 2161(SCN), 1455, 1419, 1235, 736, 670, 592; ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 7.15-7.62 (m, 4H), 7.92 (s,1H), 11.97 (br,s,1H). ^{13}C NMR (62.5 MHz, DMSO-d_6) δ(ppm); 89.2, 112.2, 112.7, 117.6, 121.0, 122.8, 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.

2-Methyl-3-thiocyanato-*1H*-indole (3b)



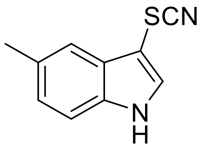
Yield 98%, white solid, mp = 98-100 °C (lit. 99-101 °C) [10]. IR (KBr), ῡ(cm^{-1}); 3328(NH), 2154(SCN), 1407, 1297, 1233, 742, 657, 617. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 2.52 (s,3H), 7.15-7.19 (m,2H), 7.41 (t,1H), 7.54 (t,1H), 11.96 (s,1H,NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 12.1, 87.1, 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.

1-Methyl-3-thiocyanato-*1H*-indole (3c)



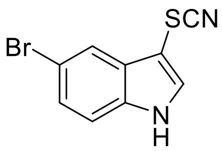
Yield 68 %, white solid, mp = 75−77 °C (lit. 76−78 °C)[9]. IR (KBr), ῡ(cm^{-1}); 2946, 2924, 2151 (SCN), 1611, 1515, 1243, 757, 662, 542. ^{1}H-NMR (250 MHz, DMSO-d_6) δ(ppm); 3.35 (s, 3H), 7.24-7.36 (m, 2H), 7.58 (d, *J* = 7.5, 1H), 7.66 (d, *J* = 7.5, 1H), 7.97 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) 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.

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



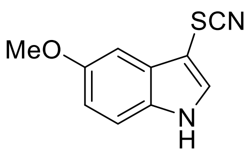
Yield 99 %, white solid. mp = 87−90 °C (lit. 88−90 °C) [9]. IR (KBr), ῡ(cm^{-1}); 3325(NH), 3287, 2156(SCN), 1430, 1242, 1101, 795, 669, 607, 569. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 2.51 (s, 3H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 10 Hz, 1H), 7.44 (s, 1H), 7.59 (s, 1H), 8.61 (s, br, 1H). ^{13}C 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.

5-Bromo-3-thiocyanato-*1H*-indole (3e)



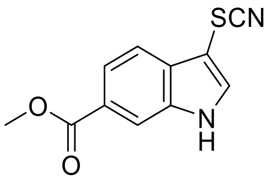
Yield 81 %, white solid. mp = 132−136 °C (lit. 138−141°C) [9]. IR (KBr), ῡ(cm^{-1}); 3341 (NH), 3109, 2150 (SCN), 1460, 1408, 1237, 1214, 1108, 797, 655, 605, 565. ^{1}H-NMR (250 MHz, DMSO-d_6) δ(ppm); 7.37 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 10 Hz, 1H), 7.79 (s, 1H), 8.04 (s, 1H), 12.18 (s, 1H). ^{13}C 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-Methoxy-3-thiocyanato-*1H*-indole (3f)



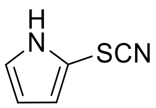
Yield 98 %, white solid. mp = 121−124 °C (lit. 123−125 °C) [9]. IR (KBr), ῦ(cm^{-1}); 3292 (NH), 3135, 2154 (SCN), 1485, 1455, 1291, 1240, 1201, 1165, 1018, 920, 803, 709, 623, 580. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 3.89 (s, 3H), 6.92 (d, *J* = 10 Hz, 1H), 7.17 (s, 1H), 7.26 (d, *J* = 10 Hz, 1H), 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 (3g)



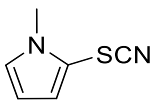
Yield 72 %, white solid. mp = 196-198 °C. IR (KBr), ῦ(cm^{-1}); 3292 (NH), 3150, 2944, 2153 (SCN), 1695, 1429, 1313, 1233, 1111, 1084, 835, 770, 593, 525. ^{1}H-NMR (250 MHz, DMSO-*d*$_6$) δ(ppm); 3.68 (s, 3H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 10 Hz, 1H), 7.96 (s, 1H), 8.02 (s, 1H), 12.17 (s, 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.

2-Thiocyanato-*1H*-pyrrole (4h)



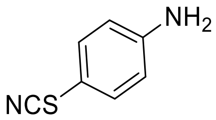
Yield 83%, pink liquid. IR (neat), ῦ(cm^{-1}); 3676 (NH), 2159 (SCN), 1708, 1422, 1365, 1227, 1122, 1029, 737. ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm): 6.30 (s, 1H), 6.66 (s, 1H), 7.01 (s, 1H), 8.67 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 102.95, 110.98, 111.29, 120.21, 124.46.

1-Methyl-2-thiocyanato-*1H*-pyrrole (4i)



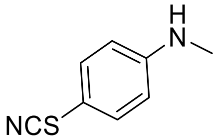
Yield 71%, brown liquid. IR (neat), ῦ(cm^{-1}); 3459, 3120, 2156 (SCN), 1600, 1464, 1329, 1293, 1120, 1089, 805, 729. ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm): 3.78(s, 3H), 6.18 (s, 1H), 6.62 (s, 1H), 6.91 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 34.60, 109.63, 110.26, 120.13, 120.87, 128.46.

4-Thiocyanatoaniline (6a)



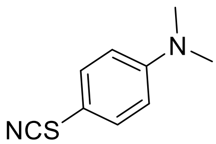
Yield 78%, white solid. mp = 52-53 °C (lit. 49–51°C) [11]. IR (KBr), ῡ(cm^{-1}); 3419, 3348 (NH_2), 3233, 2918, 2147 (SCN), 1622, 1595, 1496, 1384, 1301, 1179, 822, 628, 521. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 3.80 (s, br, 2H), 6.68 (d, J = 7.5 Hz, 2H), 7.36 (d, J = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 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 (6b)**



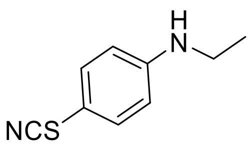
Yield 77%, yellow liquid [12]. IR (neat), ῡ(cm^{-1}); 3401(NH), 2927, 2360, 2149 (SCN), 1594, 1513, 1333, 1274, 1183, 819, 527. ^{1} H-NMR (250 MHz, DMSO-d_6) δ(ppm); 2.63 (s, 3H), 3.62 (s, br, 1H), 6.50 (d, J = 7.5 Hz, 2H), 6.91 (d, J = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 30.26, 107.45, 112.71, 113.38, 134.78, 151.11.

***N*,*N*-Dimethyl-4-thiocyanatoaniline (6c)**



Yield 45%, white solid. mp = 72–74 °C (lit. 72–74 °C) [11]. IR (KBr), ῡ(cm^{-1}); 3427, 2913, 2143 (SCN), 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.

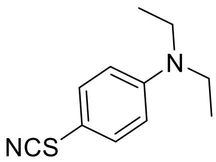
***N*-Ethyl-4-thiocyanatoaniline (6d)**



Yield 64%, yellow solid. mp = 53-55 °C (lit. 54-56 °C) [13]. IR (KBr), ῡ(cm^{-1}); 3402 (NH), 2971, 2151 (SCN), 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,

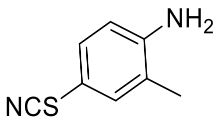
$CDCl_3$) δ(ppm); 14.5, 38.0, 107.3, 112.6, 113.6, 134.8, 150.2. $C_9H_{10}N_2S$: Calcd. C, 60.64; H, 5.65; N, 15.72; S, 17.99; Found. C, 60.50; H, 5.56; N, 15.54; S, 17.67.

***N, N*-Diethyl-4-thiocyanatoaniline (6e)**



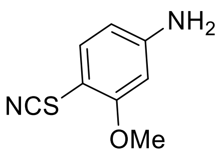
Yield 43%, white solid. mp = 74-75 °C (lit. 72-73 °C) [14].IR (KBr), ῦ(cm^{-1}); 2973, 2151 (SCN), 1591, 1507, 1403, 1355, 1270, 1196, 1077, 810, 741. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 1.17(t, J = 7.5 Hz, 6H), 3.36 (q, J = 7.5 Hz, 4H), 6.57 (d, J = 7.5Hz, 2H), 7.37 (d, J =7.5 Hz, 2H). ^{13}C NMR (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.

2-Methyl-4-thiocyanatoaniline (6f)



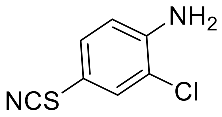
Yield 93 %, white solid. mp = 62-65 °C (lit. 65-66 °C) [12]. IR (KBr), ῦ(cm^{-1}); 3445 (NH), 3364, 3245, 2922, 2150 (SCN), 1629, 1491, 1299, 1153, 816, 718, 565. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 2.16 (s, 3H), 3.91 (s, br, 2H), 6.66(d, J = 7.5Hz, 1H), 7.24(m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 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.

3-Methoxy-4-thiocyanatoaniline (6g)



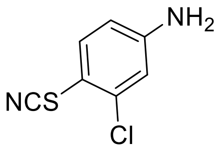
Yield 57 %, yellow solid. mp = 99-100 °C (lit. 99–100 °C) [15]. IR (KBr), ῦ(cm^{-1}); 3446 (NH), 3371, 3224, 2918, 2148 (SCN), 1628, 1595, 1471, 1335, 1215, 1020, 825, 638. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 3.88 (s, 3H), 6.26 (m, 2H), 7.29 (d, J = 10Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 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.

2-Chloro-4-thiocyanatoaniline (6h)



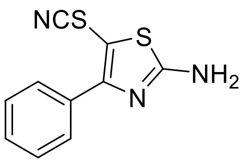
Yield 89%, yellow solid. mp = 58-60 °C (lit. 60–61 °C) [15]. IR (KBr), ῡ(cm^{-1}); 3441 (NH2), 3369, 3185, 2149 (SCN), 1618, 1489, 1322, 1257, 822, 723, 570. ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm); 4.30 (brs, 2H), 7.48-6.74 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 109.8, 111.8, 116.4, 119.6, 132.6, 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-Chloro-4-thiocyanatoaniline (6i)



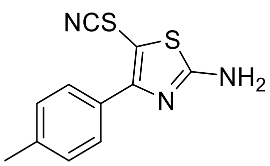
Yield 85%, yellow solid. mp = 59-62 °C(lit. 63-64 °C) [16]. IR (KBr), ῡ(cm^{-1}); 3430, 3340 (NH_2), 3214, 2149 (SCN), 1634, 1593, 1476, 1384, 1302, 1240, 1020, 814, 668. ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm); 4.00 (brs, 2H), 7.45-6.55 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm); 108.7, 111.0, 114.5, 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.

4-Phenyl-5-thiocyanatothiazol-2-amine (8a)



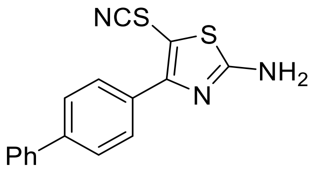
Yield 87%, white solid. mp = 187-189 °C (lit. 185.1-185.5 °C) [17]. IR (KBr), ῡ(cm^{-1}); 3387, 3286, 3098, 2150 (SCN), 1641 (C=N), 1518, 1339, 1086, 831, 715 (NH2), 603. ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm); 7.42-7.76 (m, 5H), 7.88 (brs, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 92.0, 112.6, 128.8, 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.

5-Thiocyanato-4-(*p*-tolyl) thiazol-2-amine (8b)



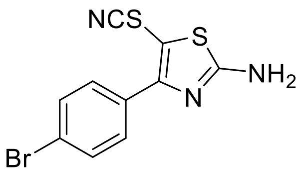
Yield 93%, white solid. mp = 170-173 °C (lit. 178.4-178.9 °C) [17]. IR (KBr), ῡ(cm^{-1}); 3389, 3291, 3089, 2155 (SCN), 1639 (C=N), 1520, 1332, 1188, 1085, 820, 717, 602. ^1H NMR (250 MHz, $CDCl_3$) δ(ppm); 2.34 (s, 3H), 7.27 (d, J = 7.5Hz, 2H), 7.65 (d, J = 7.5Hz, 2H), 7.86 (s, 2H). ^{13}C NMR (100 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-([1,1'-Biphenyl]-4-yl)-5-thiocyanatothiazol-2-amine (8c)



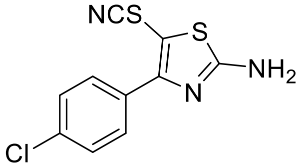
Yield 91%, white solid. mp = 186-189 °C (lit. 183-185 °C) [18]. IR (KBr), ῡ(cm^{-1}); 3361, 3052, 2939, 2375, 2152 (SCN), 1619 (C=N), 1527, 1328, 1223, 1078, 844, 768, 695. ^1H NMR (250 MHz, DMSO-d_6) δ(ppm); 7.43-7.59 (m, 3H), 7.79-7.97 (m, 8H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 91.6, 112.1, 126.5, 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 (8d)



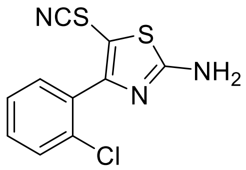
Yield 80%, white solid. mp = 198-200 °C (lit. 274.8-275.3 °C) [17]. IR (KBr), ῡ(cm^{-1}); 3387, 3286, 3098, 2150 (SCN), 1641 (C=N), 1518, 1339, 1086, 831, 715, 603. ^1H NMR (250 MHz, DMSO-d_6) δ(ppm); 7.65-7.73 (m, 4H), 7.90 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 92.8, 112.4, 122.9, 131.2, 131.8, 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.

4-(4-Chlorophenyl)-5-thiocyanatothiazol-2-amine (8e)



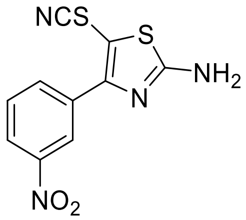
Yield 74%, white solid. mp = 191-193 °C (lit. 266.6-267.8 °C) [17].IR (KBr), ῡ(cm^{-1}); 3376, 3301, 3088, 2157(SCN), 1643 (C=N), 1530, 1327, 1029, 836, 721, 604. ^1H NMR (250 MHz, DMSO-d_6) δ(ppm); 7.54 (d, J = 10Hz, 2H), 7.77 (d, J = 7.5Hz, 2H), 7.90 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm); 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-(2-Chlorophenyl)-5-thiocyanatothiazol-2-amine (8f)



Yield 67%, white solid. mp = 190-191 °C. IR (KBr), ῡ(cm^{-1}); 3396, 3289, 2159 (SCN),1626 (C=N), 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.

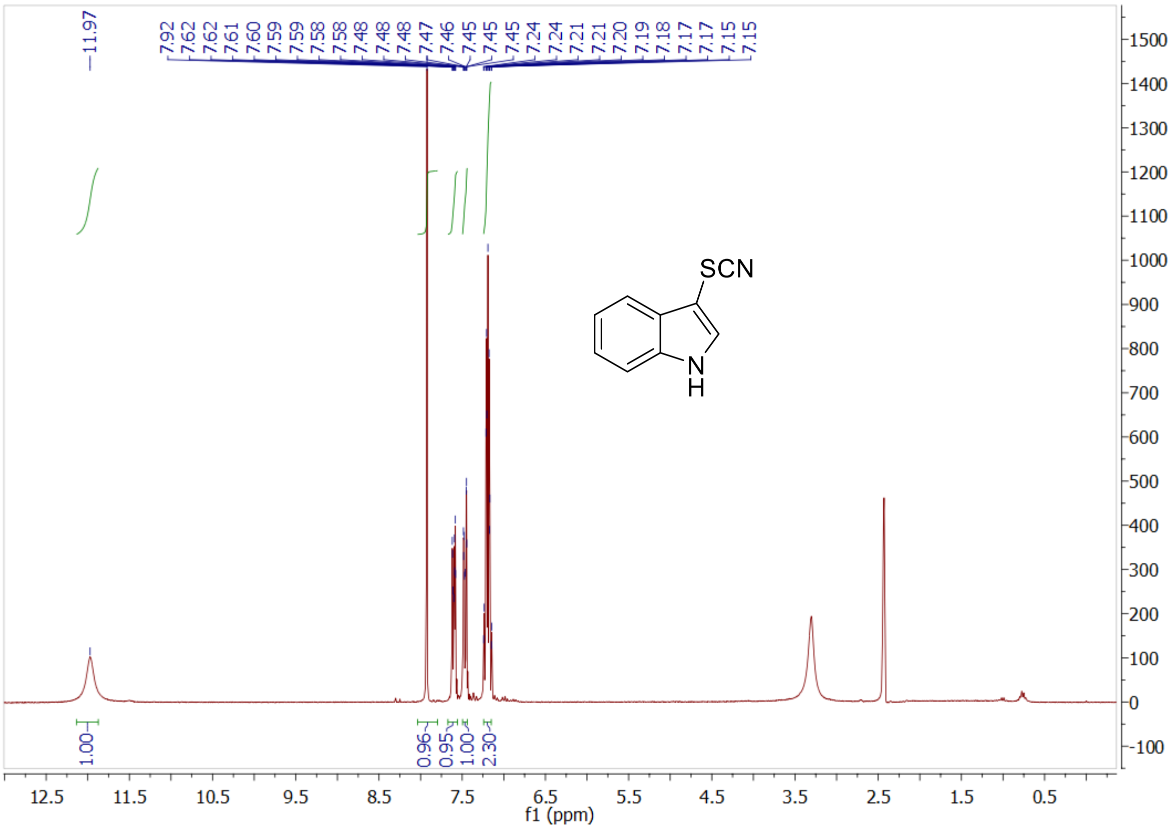
4-(3-Nitrophenyl)-5-thiocyanatothiazol-2-amine (8g)



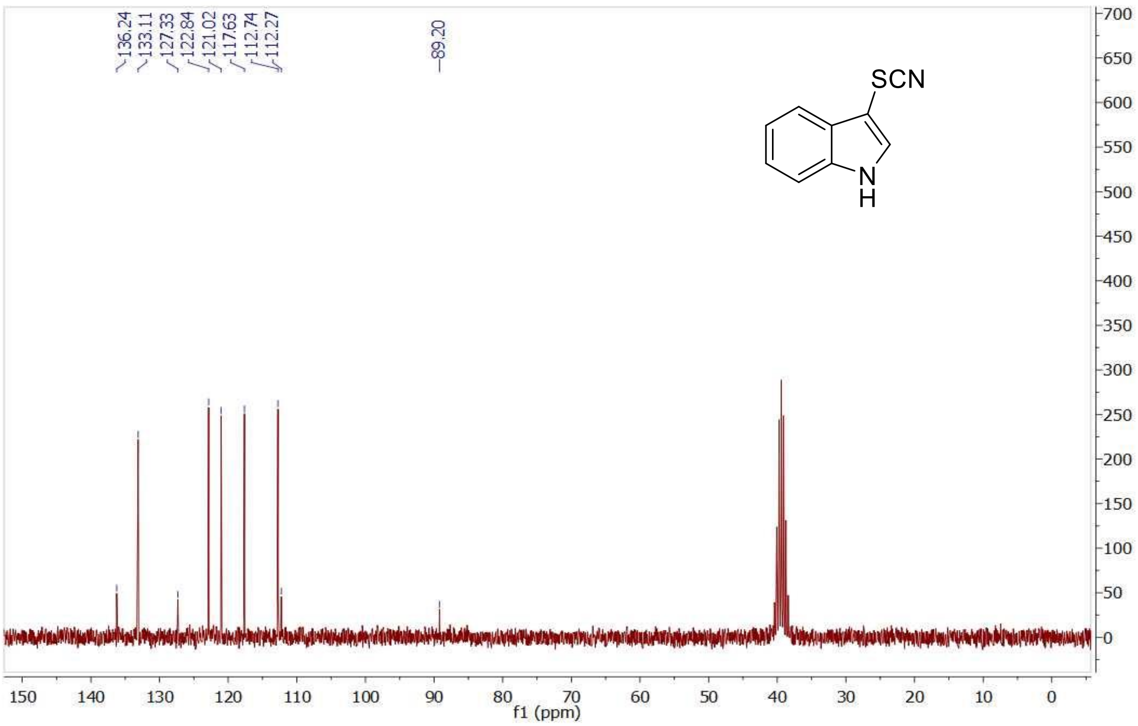
Yield 53%, white solid. mp = 180-183 °C (lit. 183.7-184.2 °C) [17]. IR (KBr), ῡ(cm^{-1}); 3404, 3287, 2365, 2152 (SCN), 1647 (C=N), 1514, 1350, 1262, 1095, 817, 747, 697. ^{1}H NMR (250 MHz, DMSO-*d$_6$*) δ(ppm); 7.76-7.82 (m, 1H), 7.99 (s, 2H), 8.24-8.30 (m, 2H), 8.61 (s, 1H). ^{13}C NMR (100 MHz, DMSO-*d$_6$*) 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.

[1]H-NMR, [13]C-NMR, IR spectra of some synthesized compounds

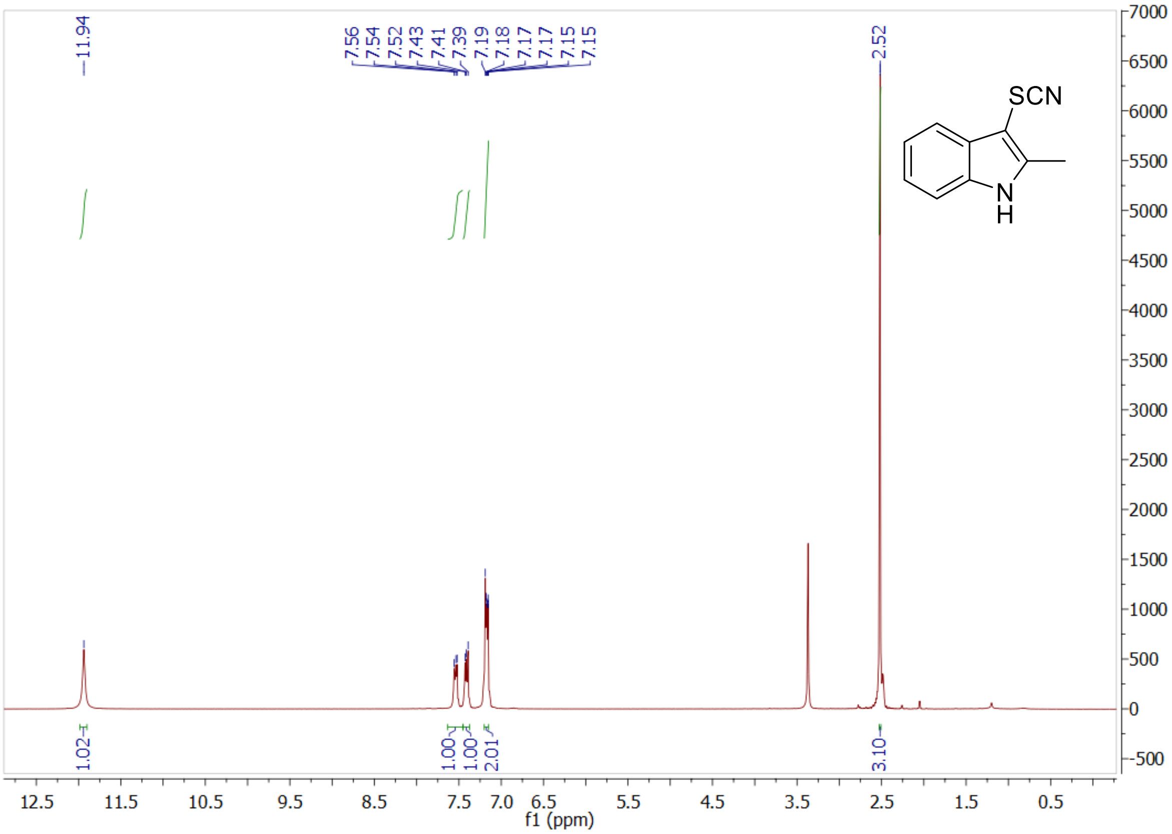
3a [1]H-NMR



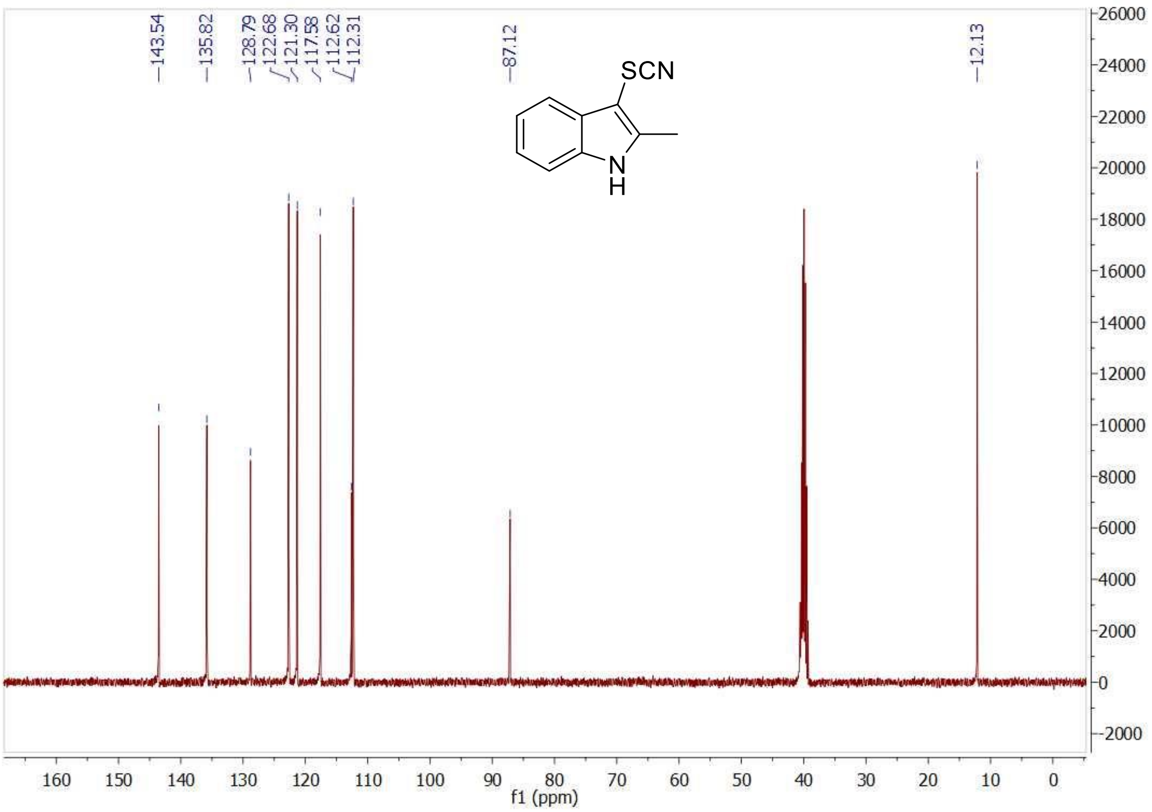
3a [13]C-NMR



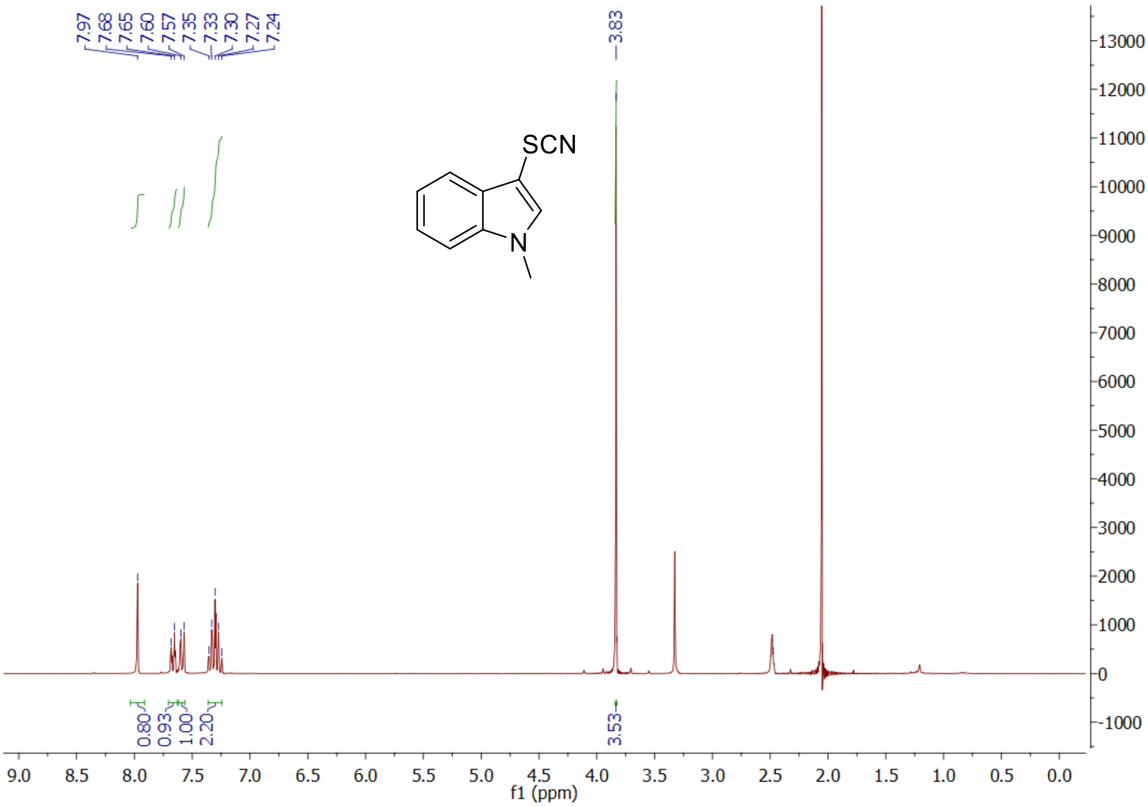
3b ¹H-NMR



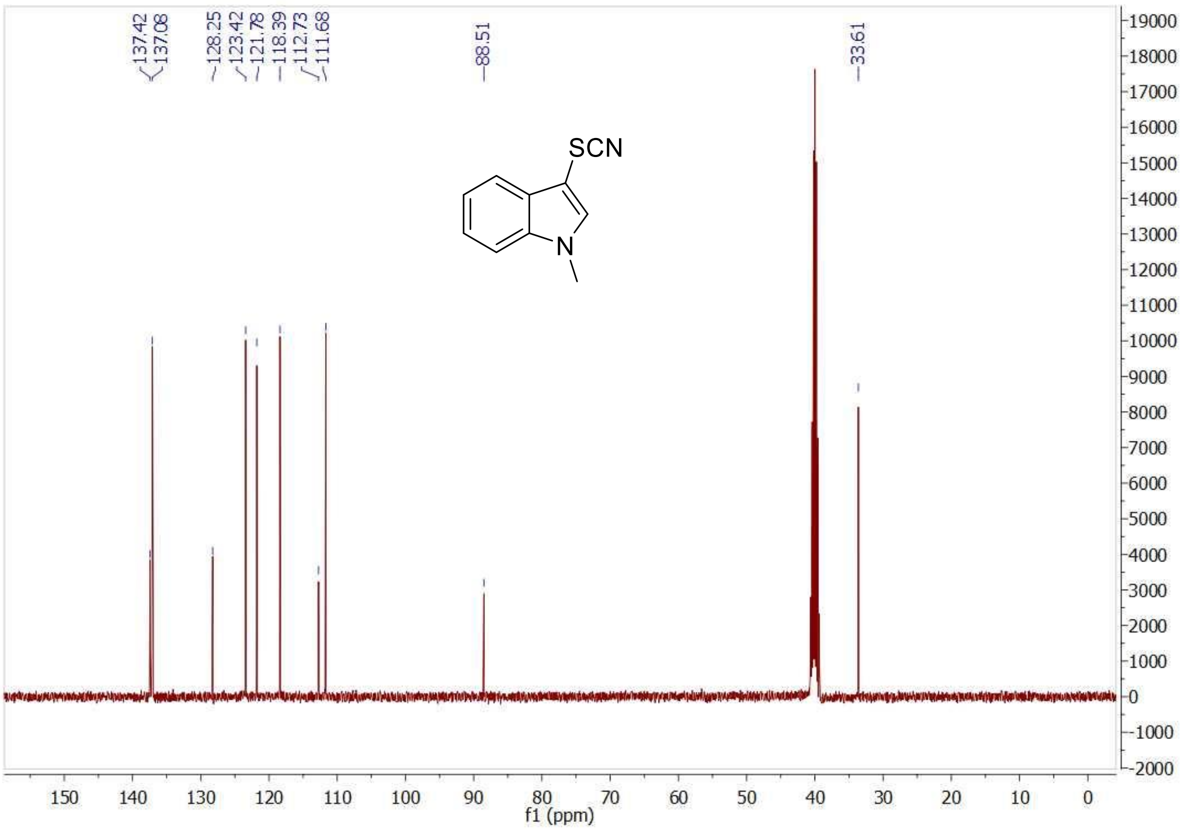
3b ¹³C-NMR



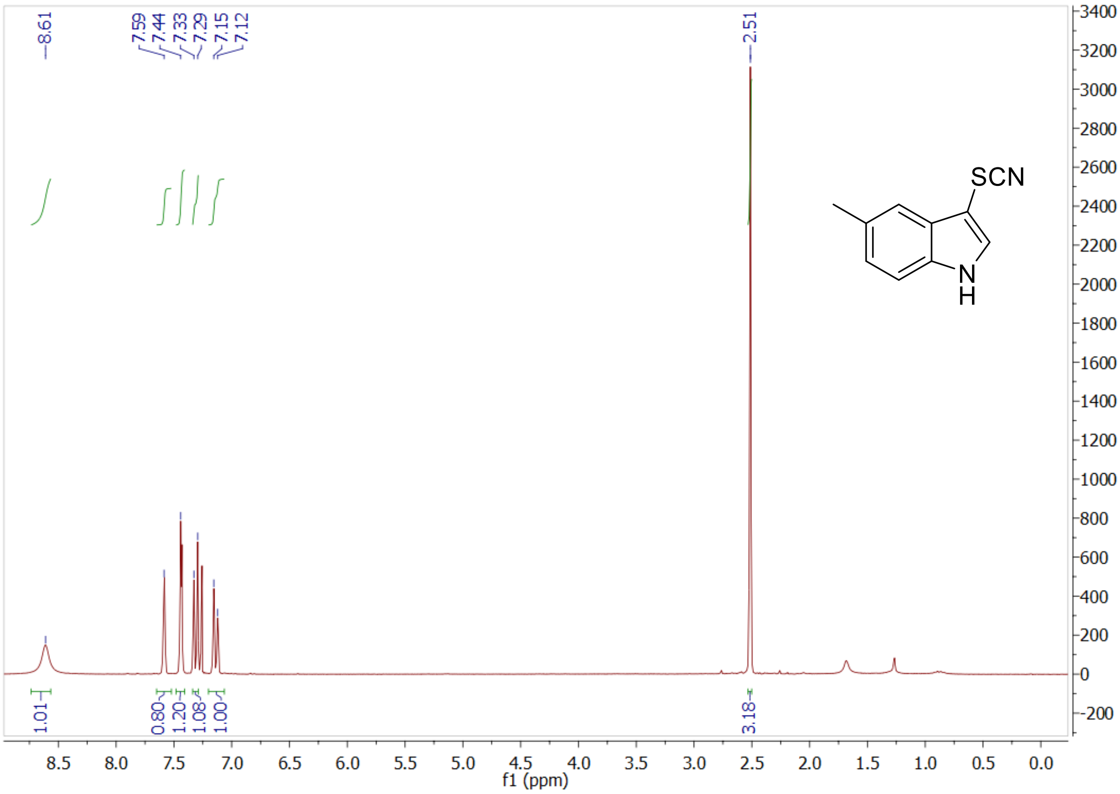
3c ^{1}H-NMR



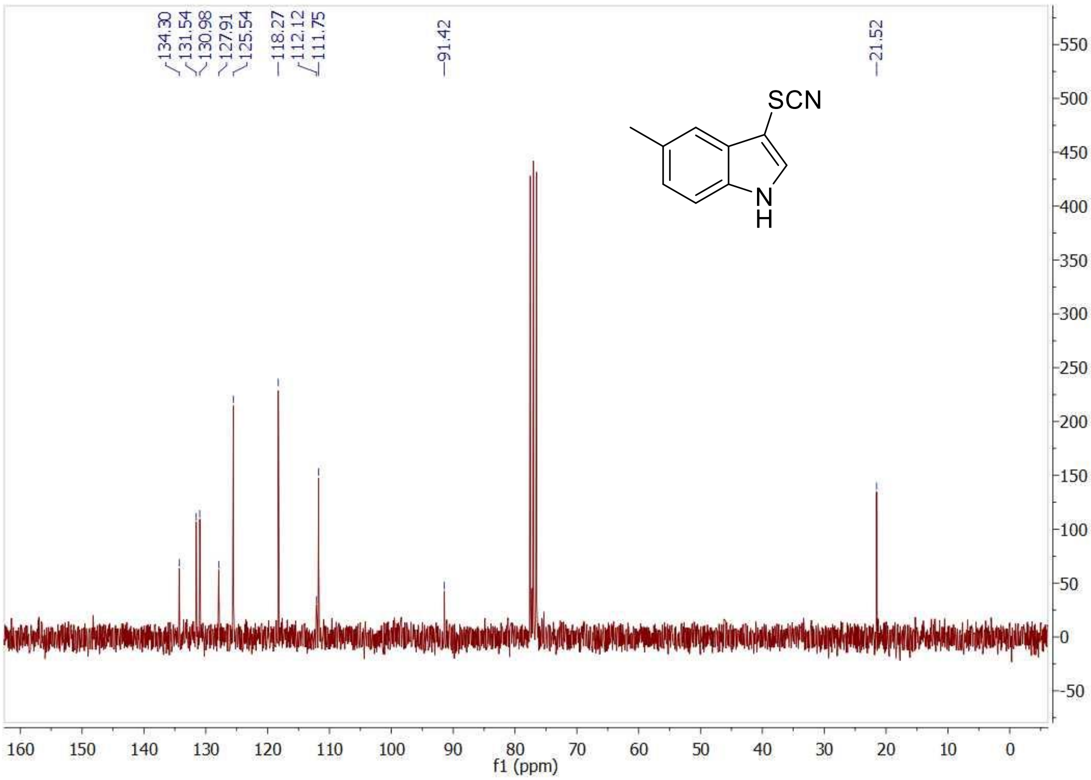
3c ^{13}C-NMR



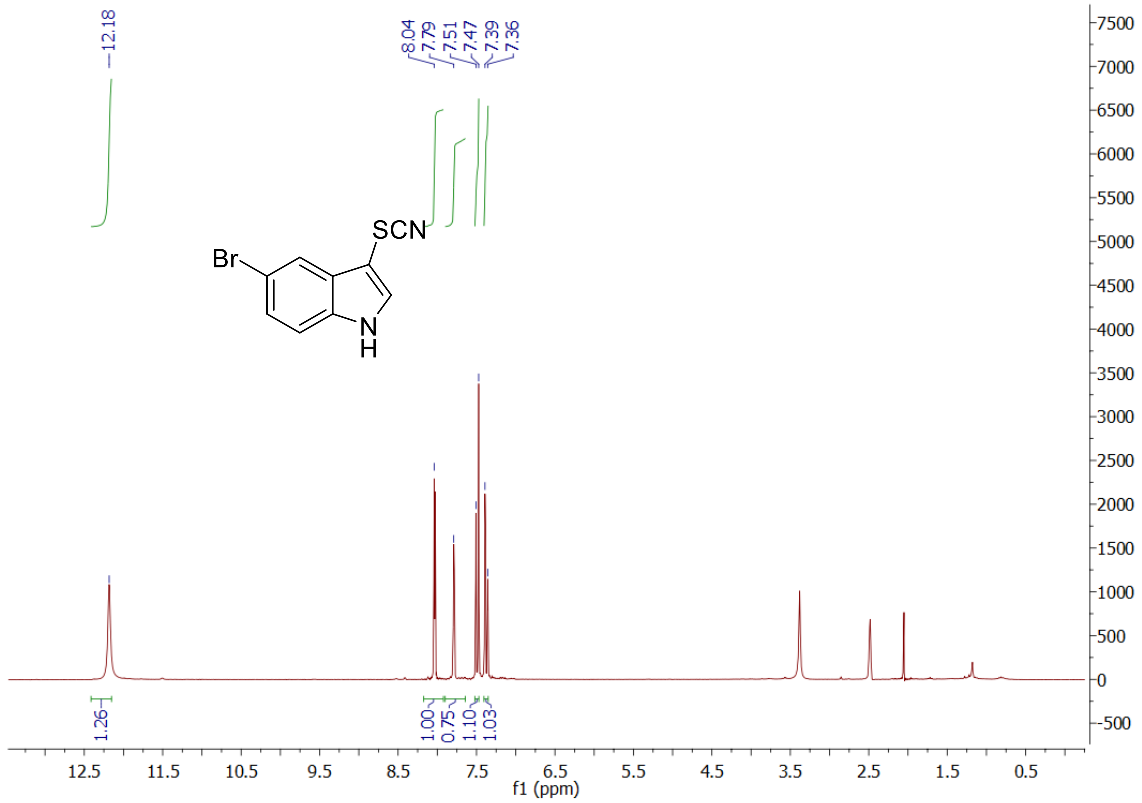
3d ^{1}H-NMR



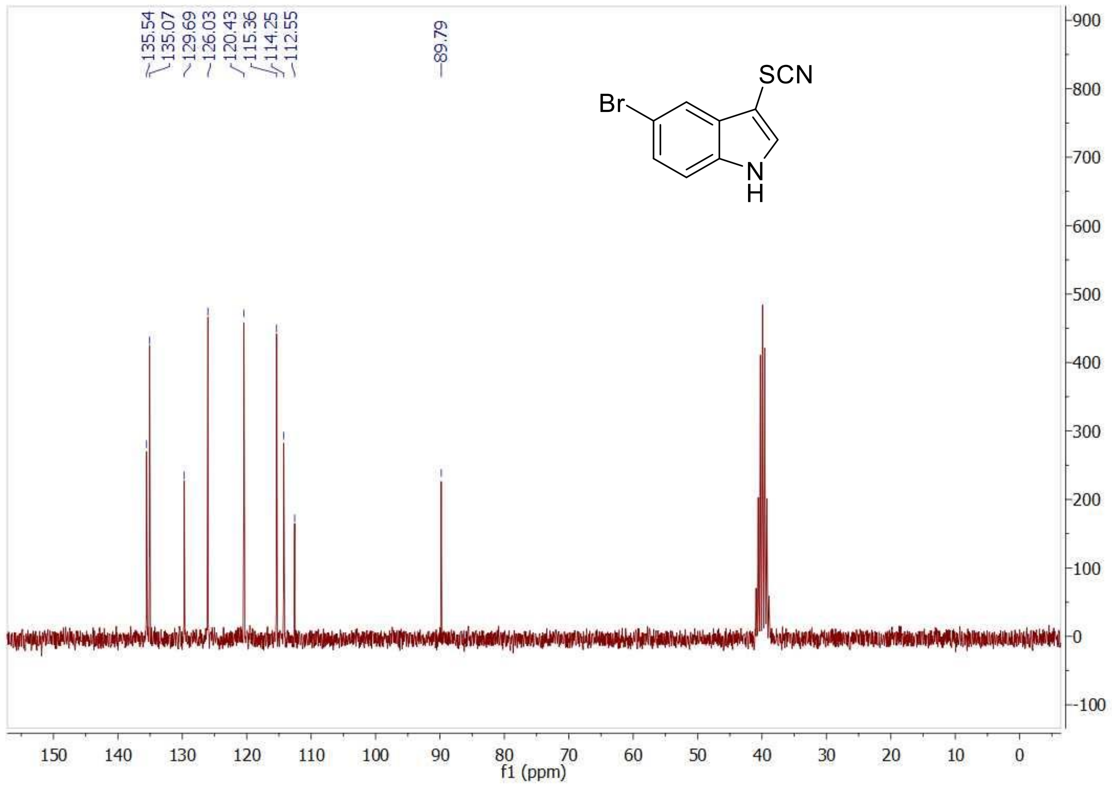
3d ^{13}C-NMR



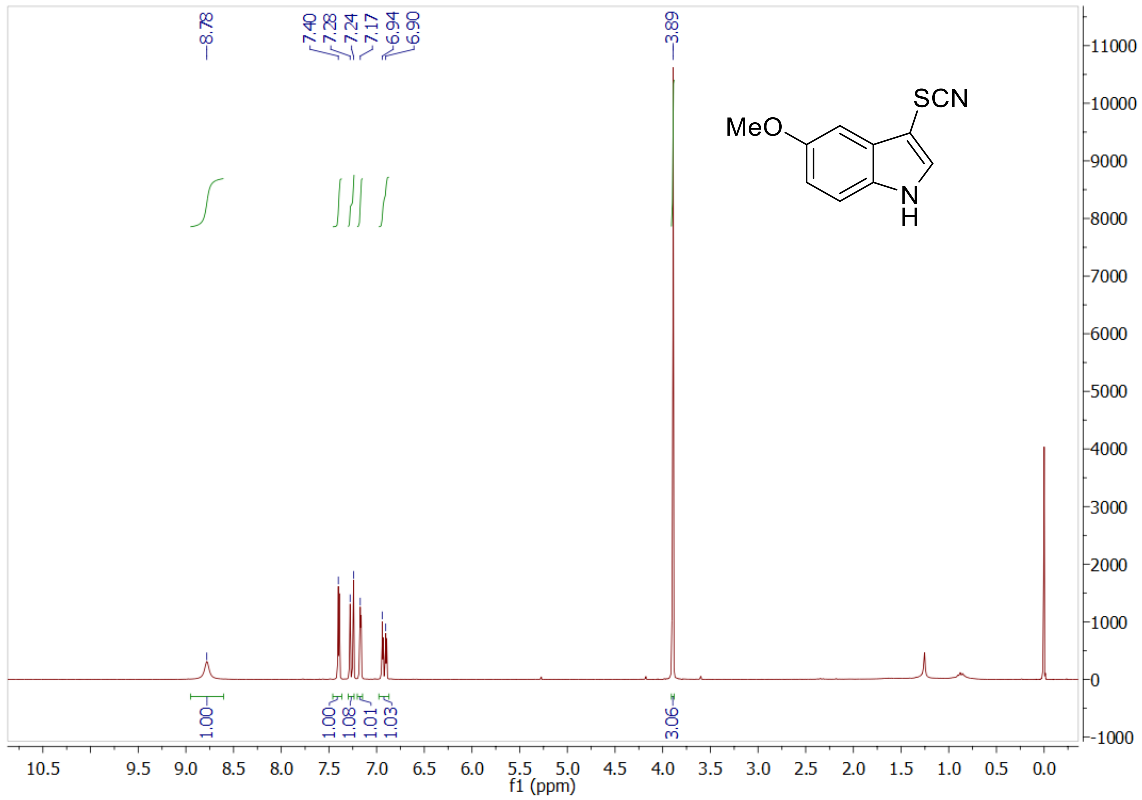
3e ^{1}H-NMR



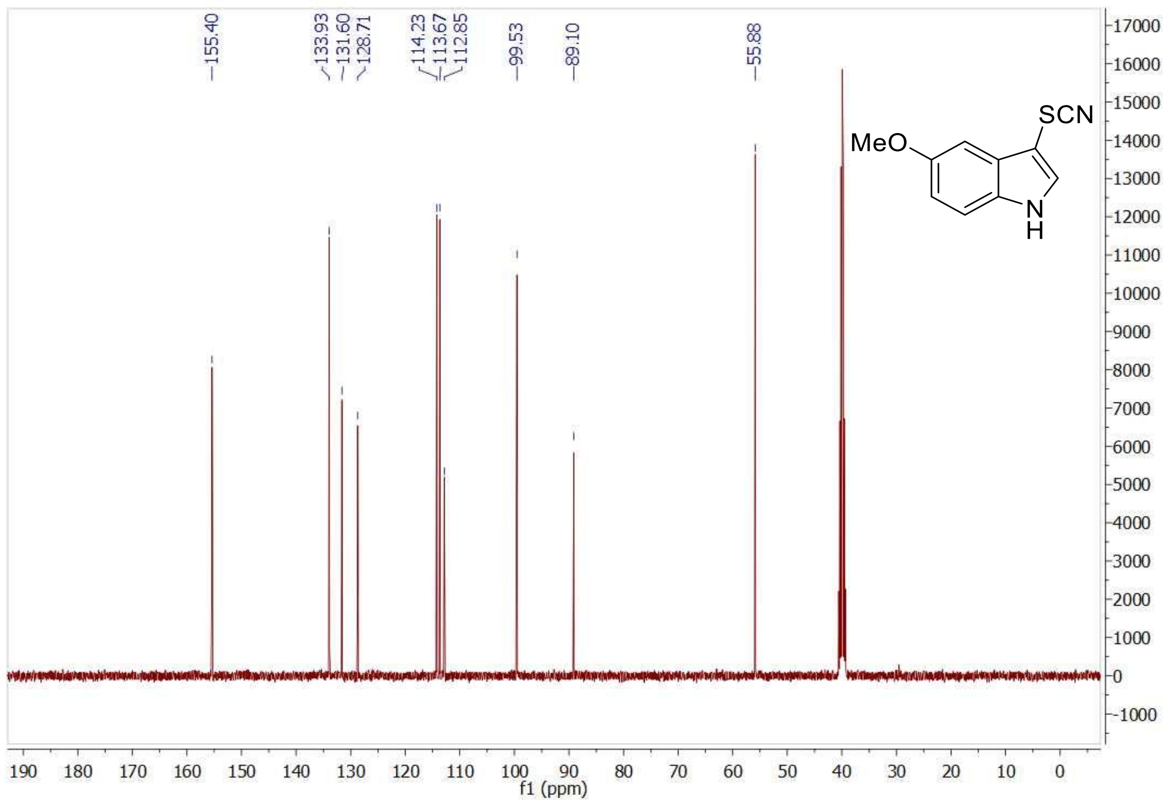
3e ^{13}C-NMR



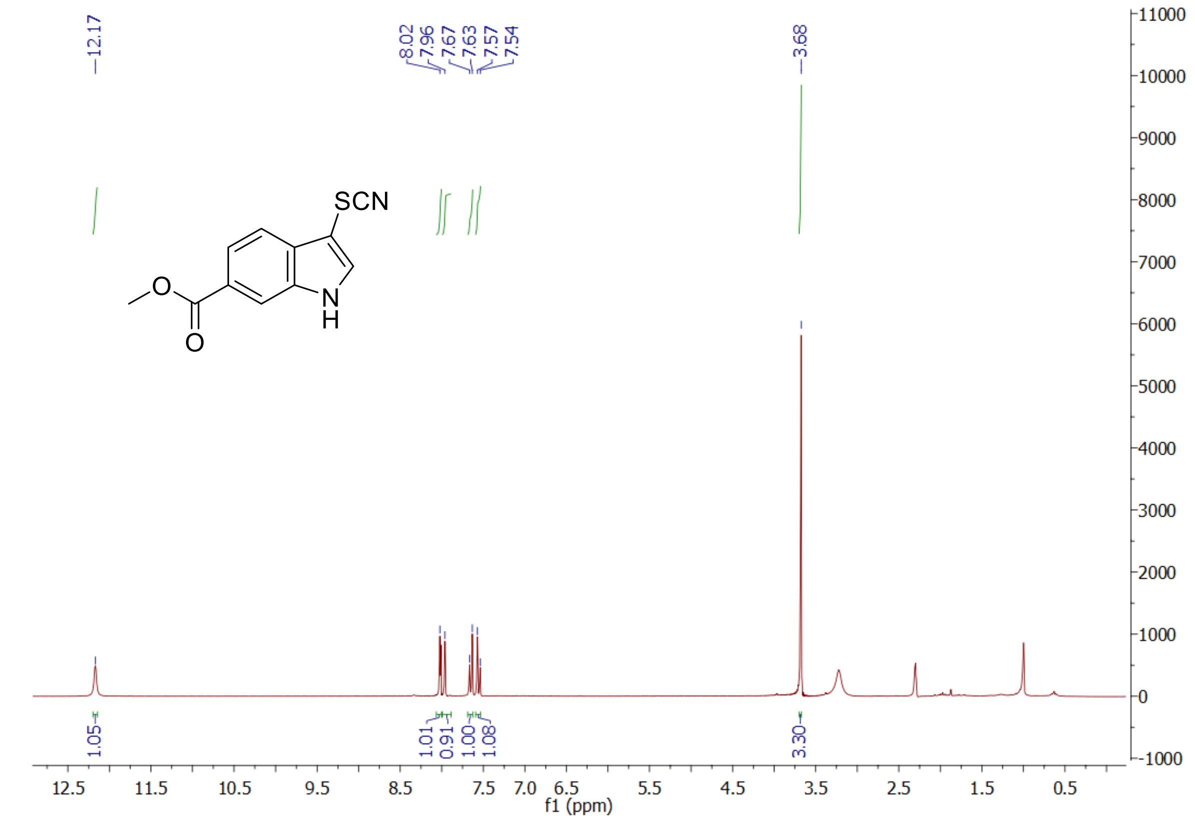
3f ^{1}H-NMR



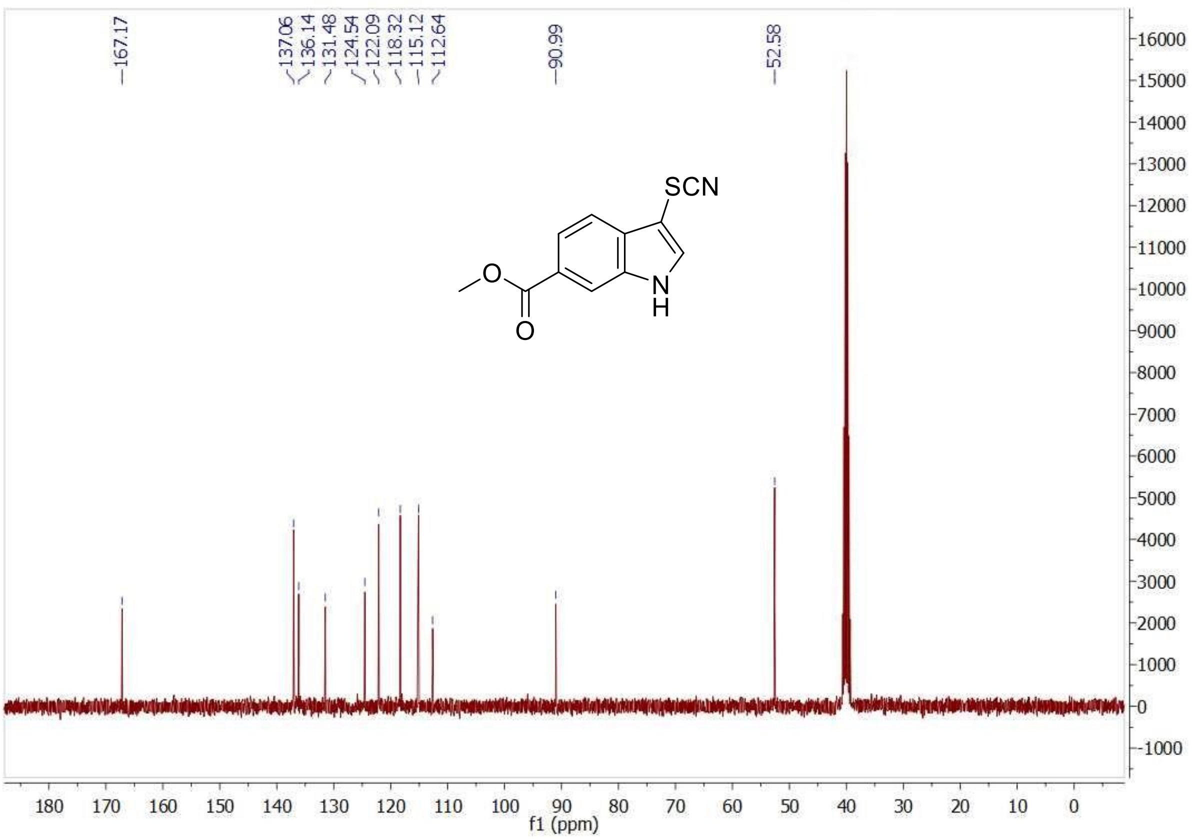
3f ^{13}C-NMR



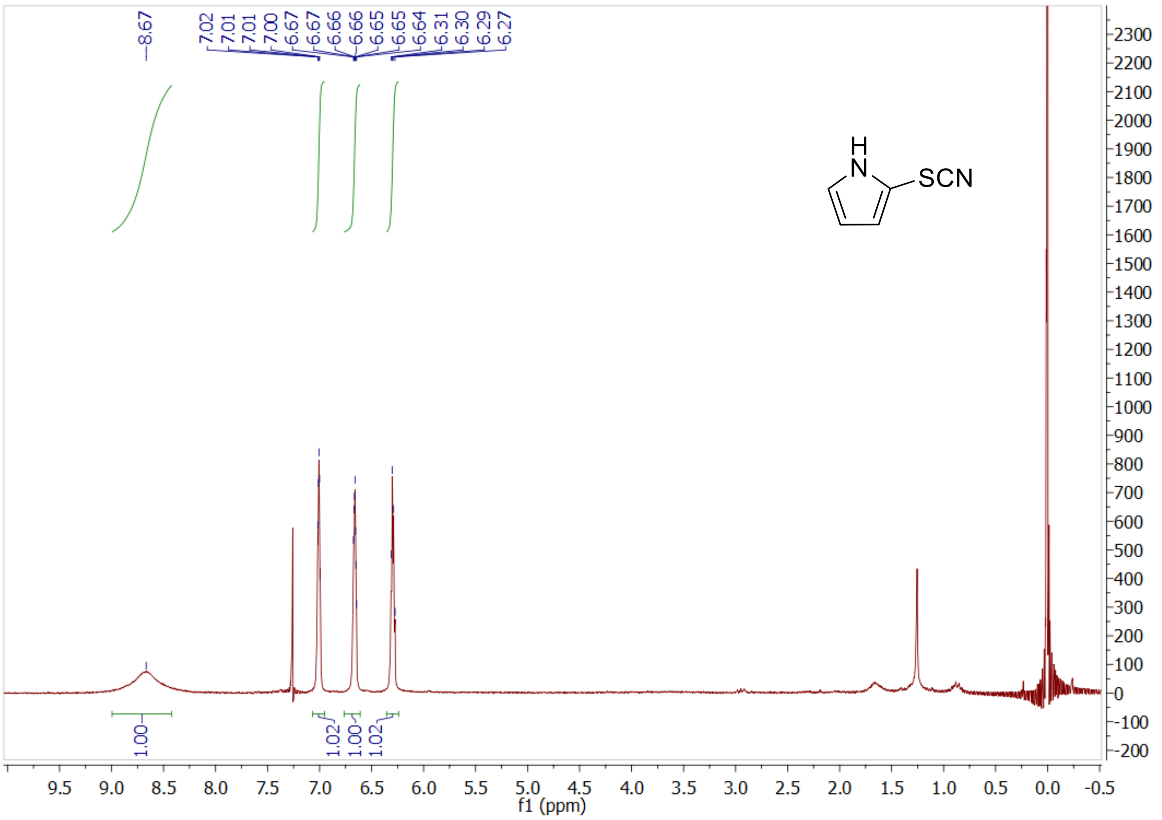
3g ¹H-NMR



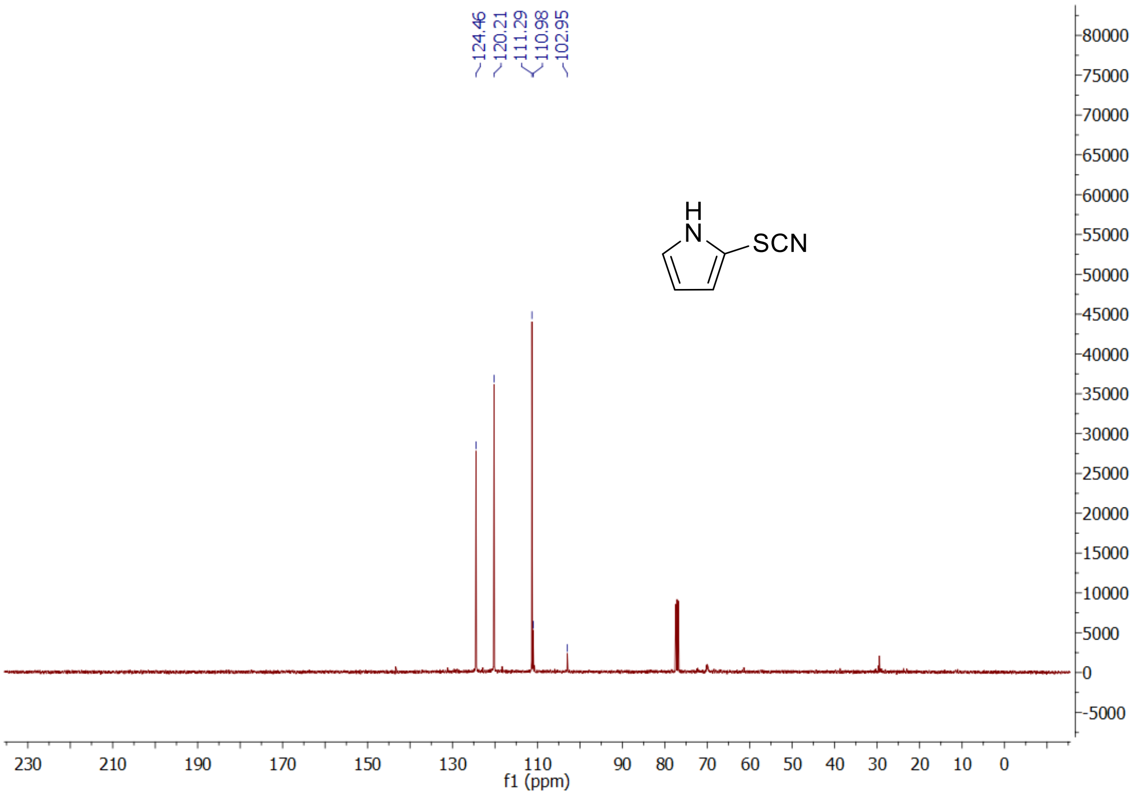
3g ¹³C-NMR



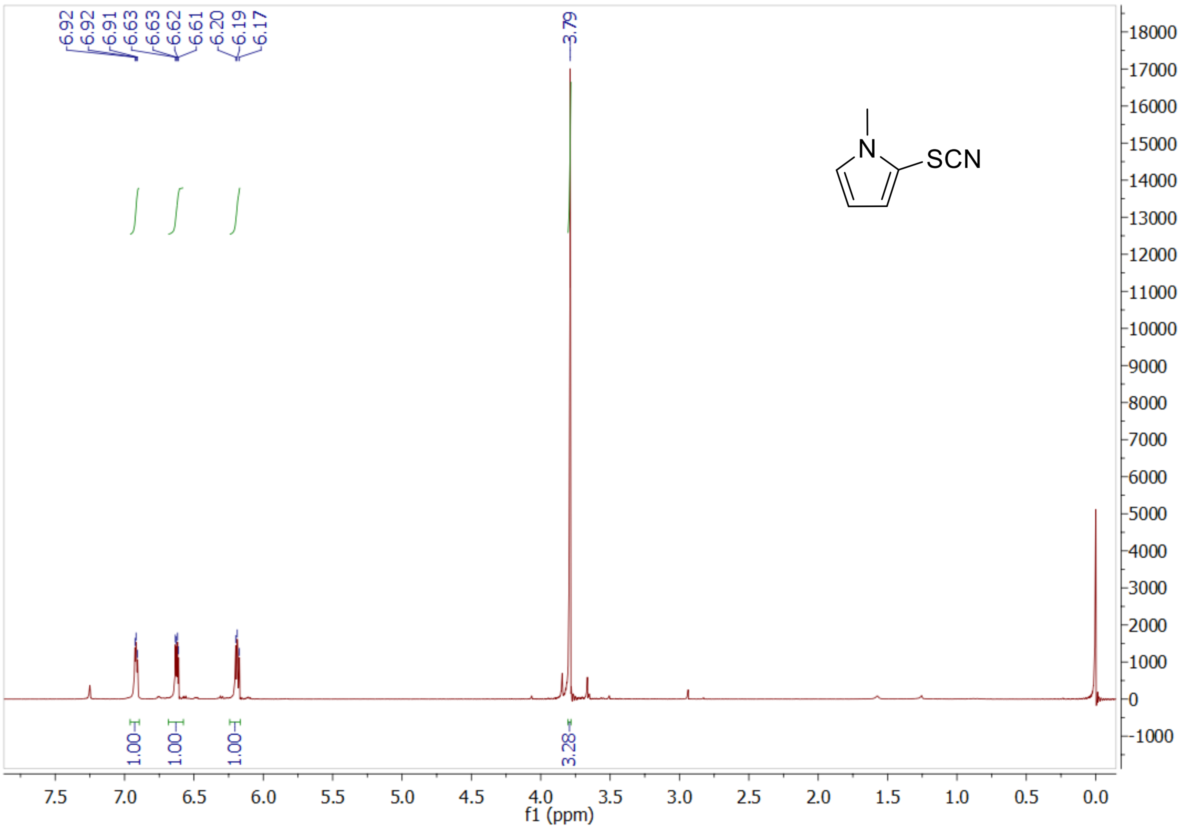
4h ¹H-NMR



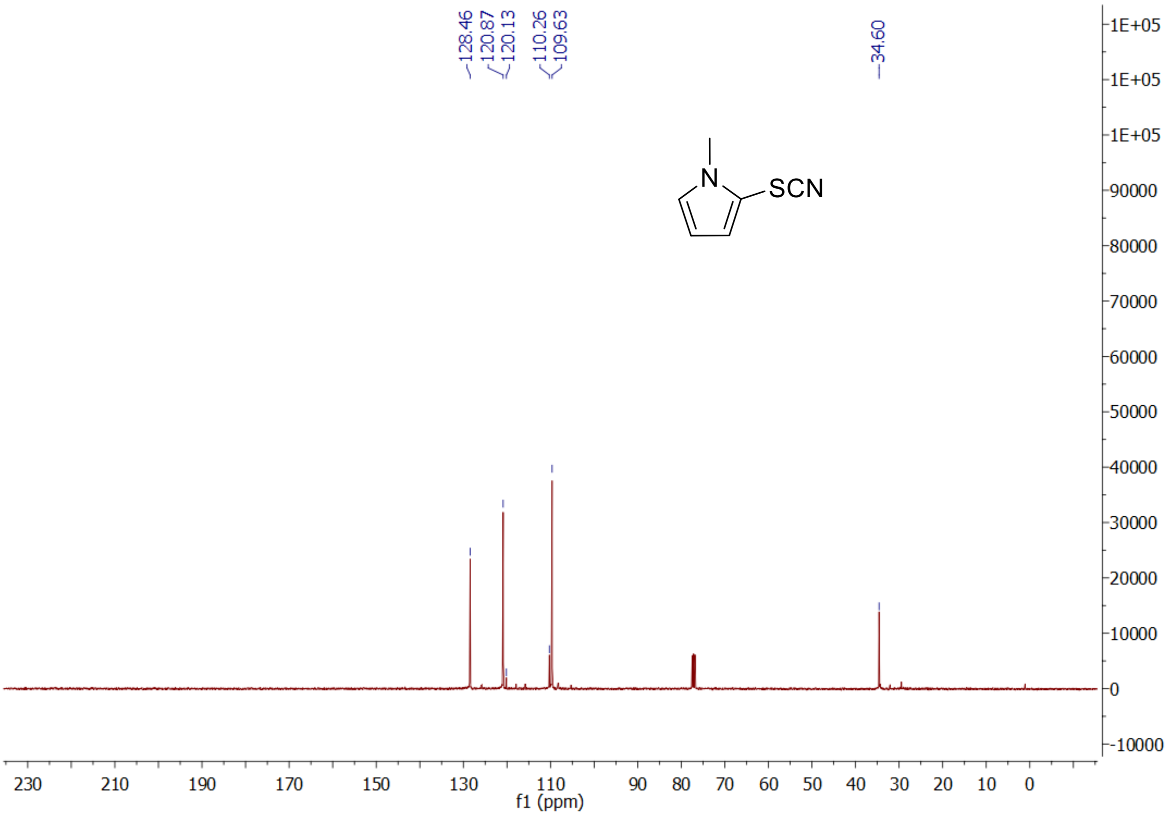
4h ¹³C-NMR



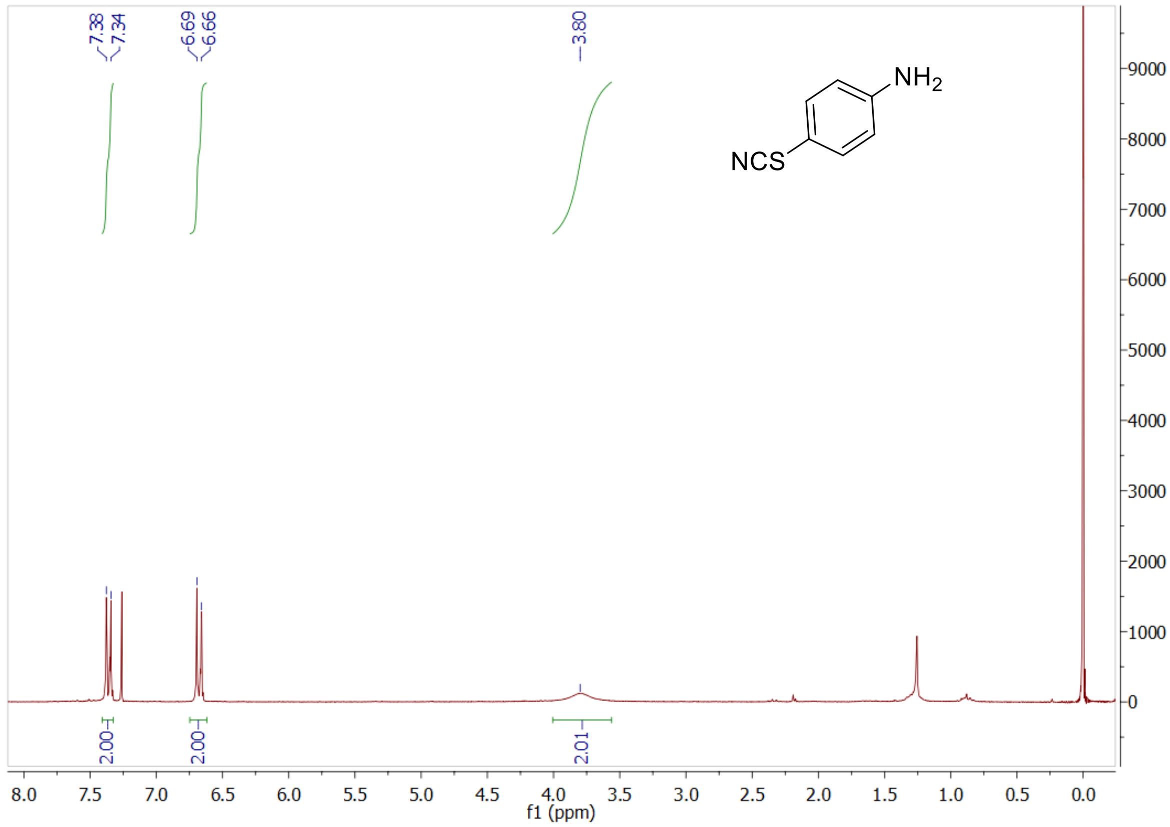
4i ¹H-NMR



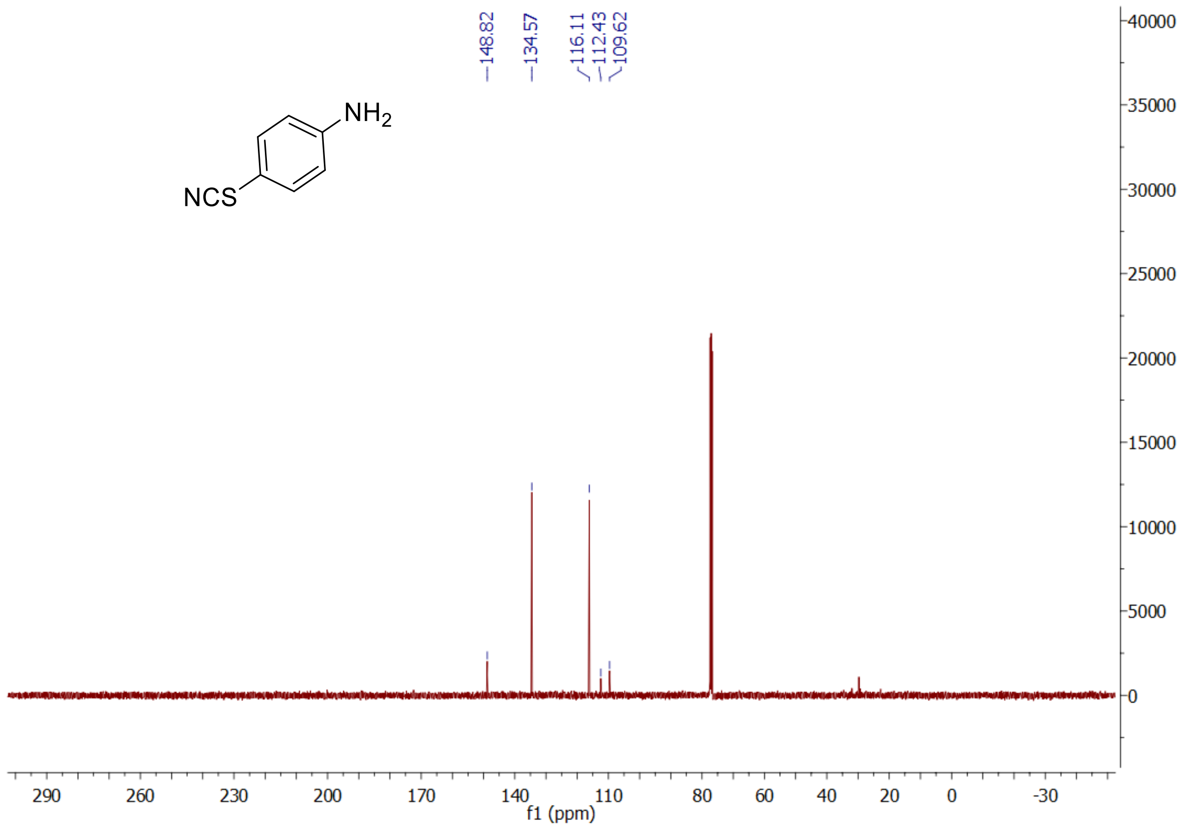
4i ¹³C-NMR



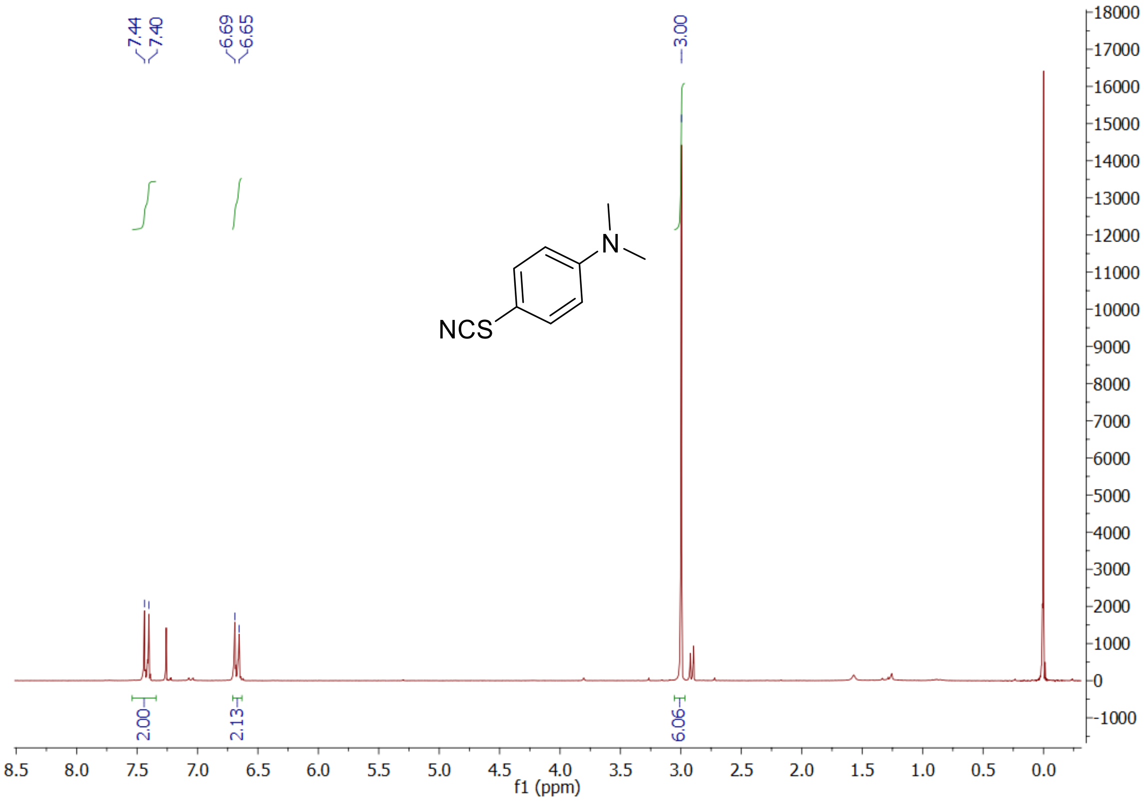
6a ^{1}H-NMR



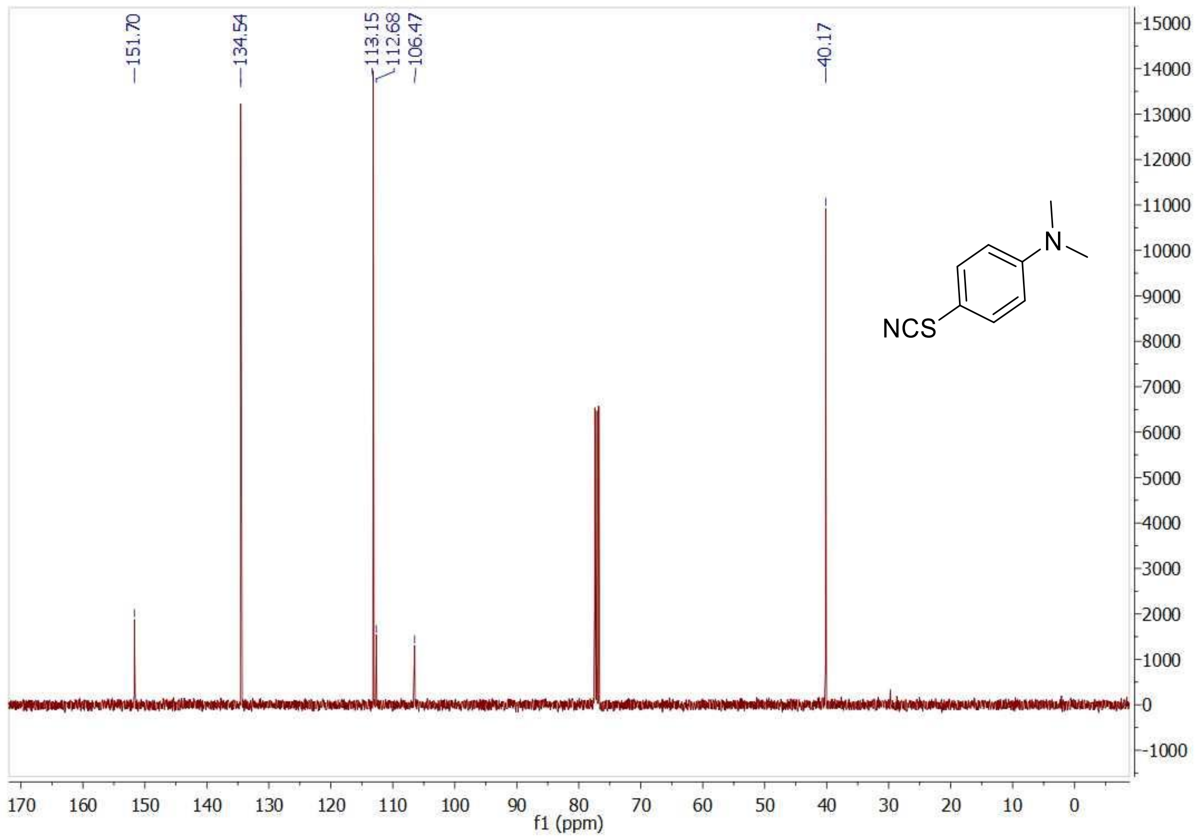
6a ^{13}C-NMR



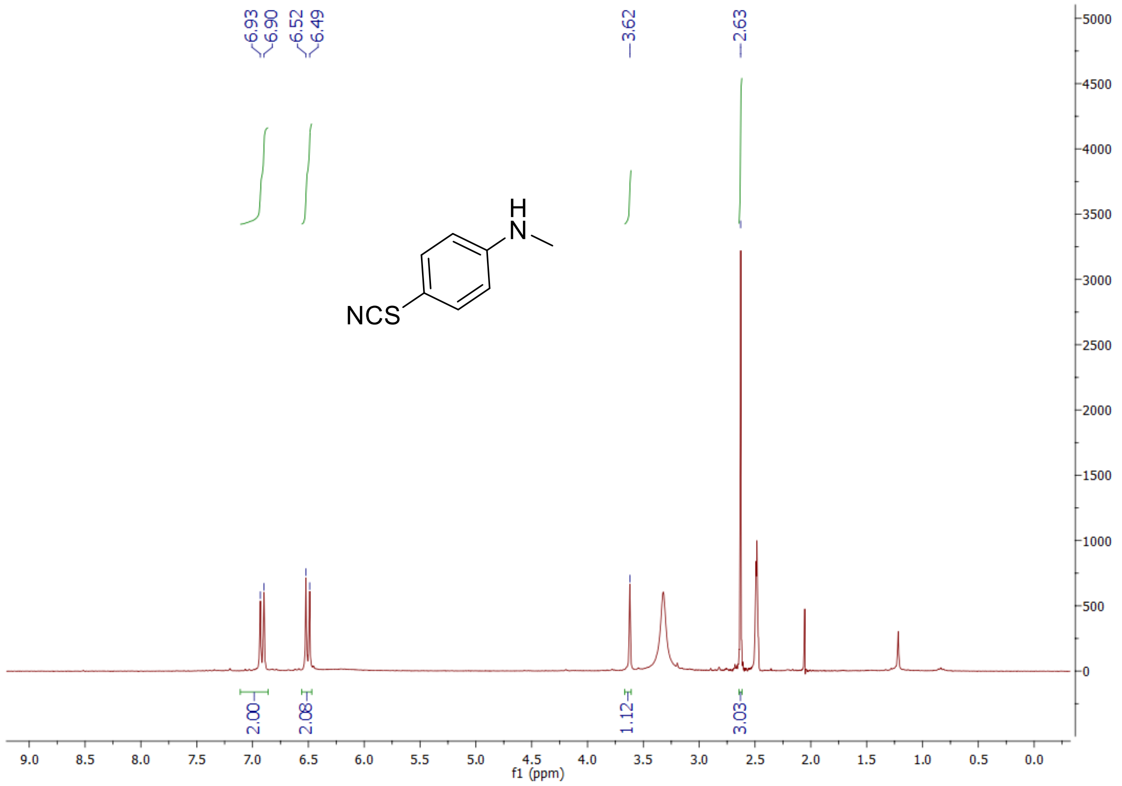
6c ^{1}H-NMR



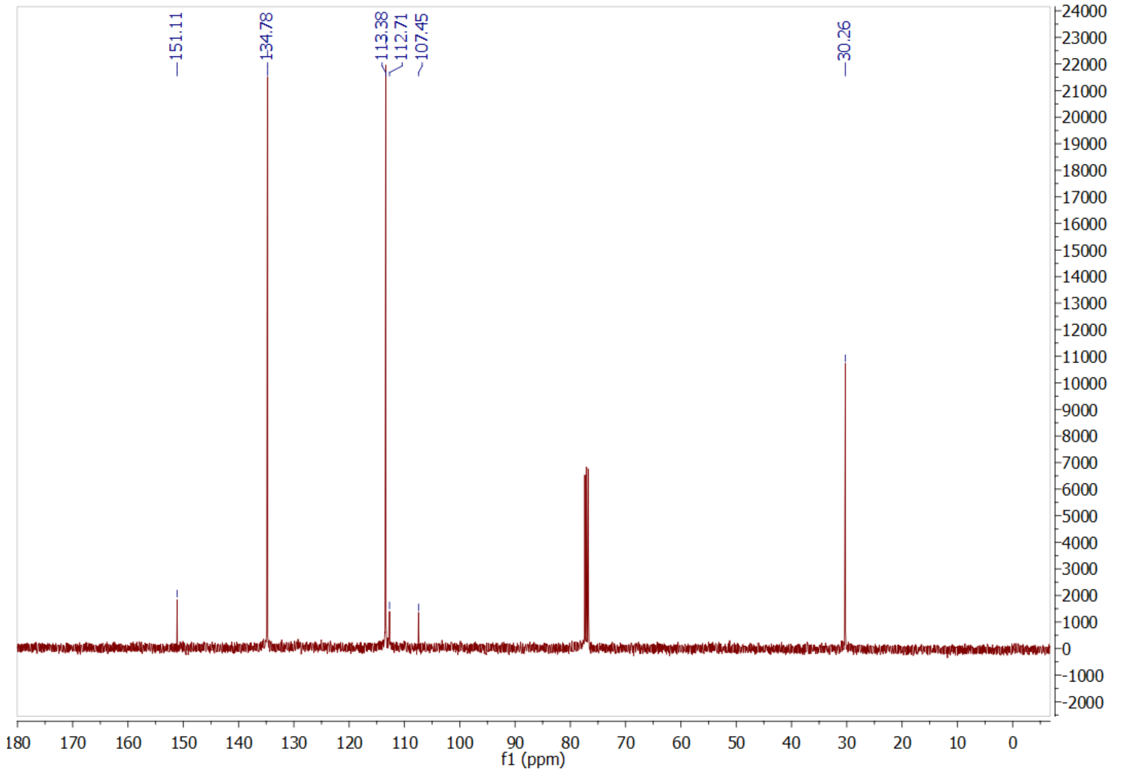
6c ^{13}C-NMR



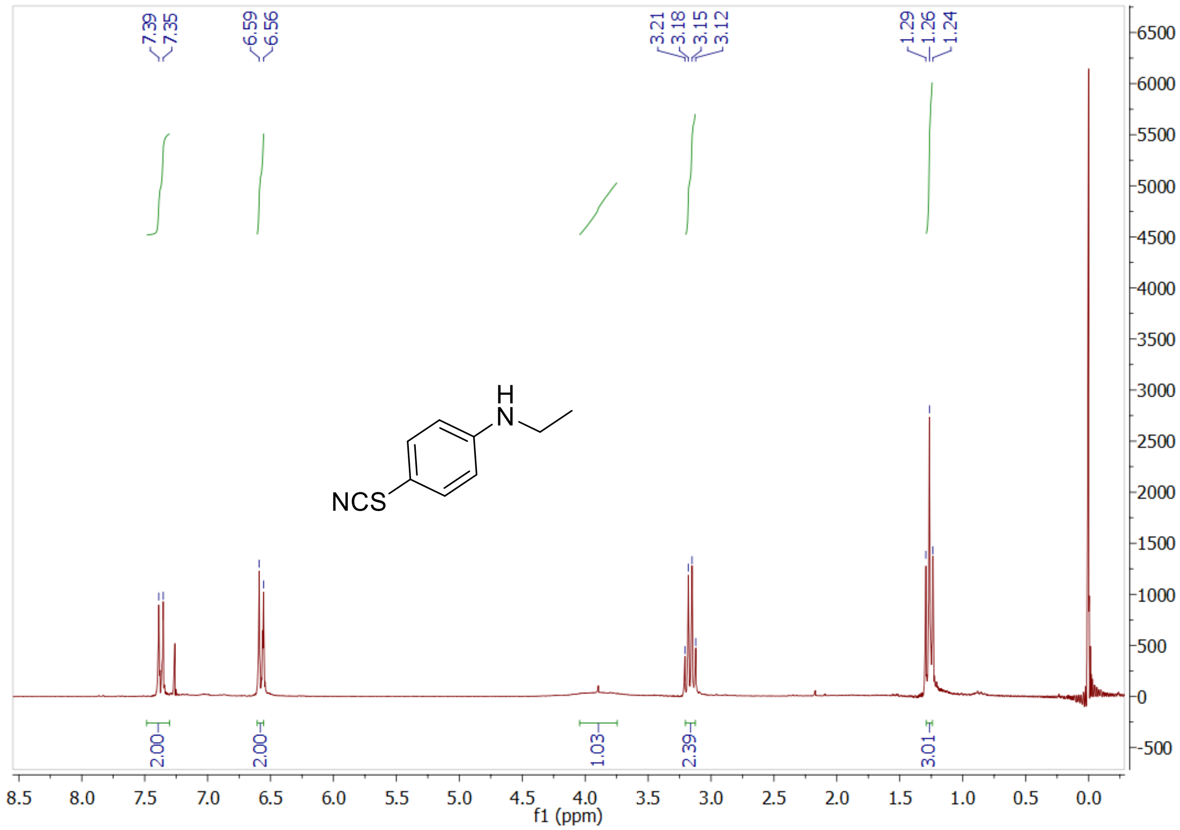
6b ^{1}H-NMR



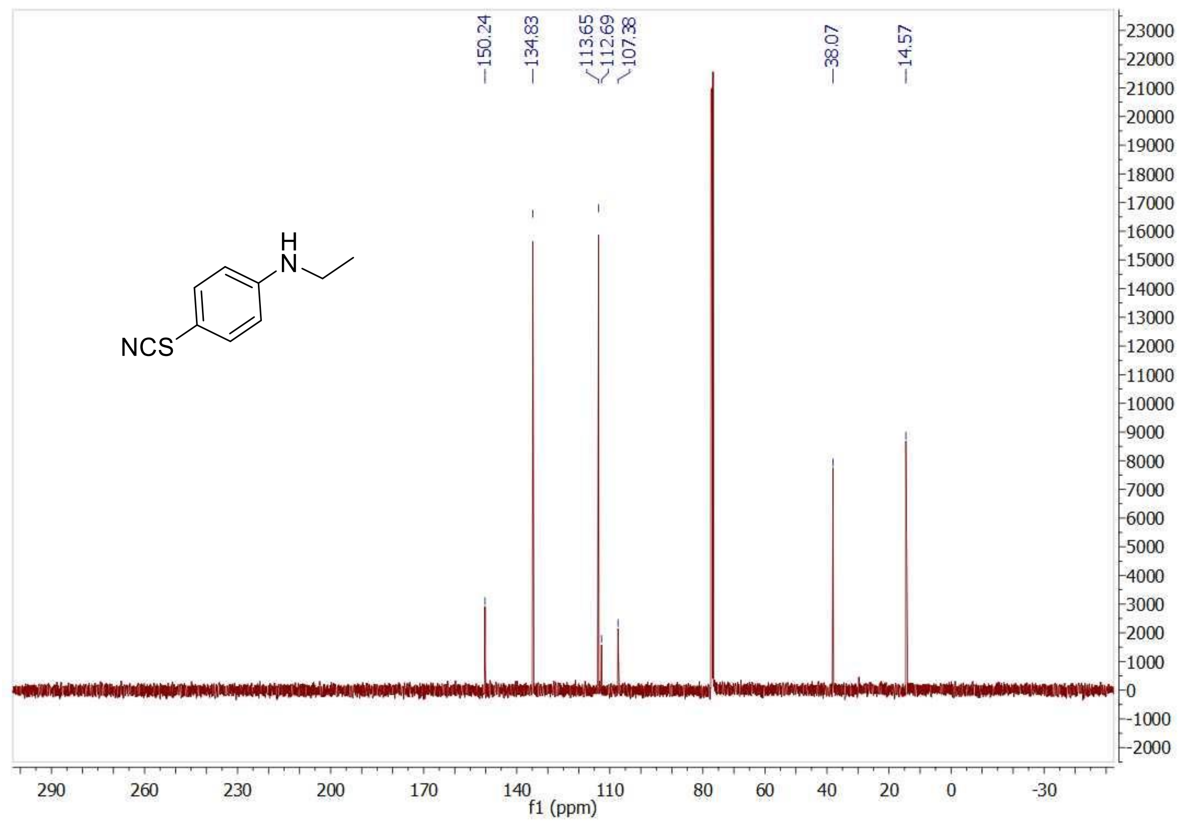
6b^{13}C-NMR



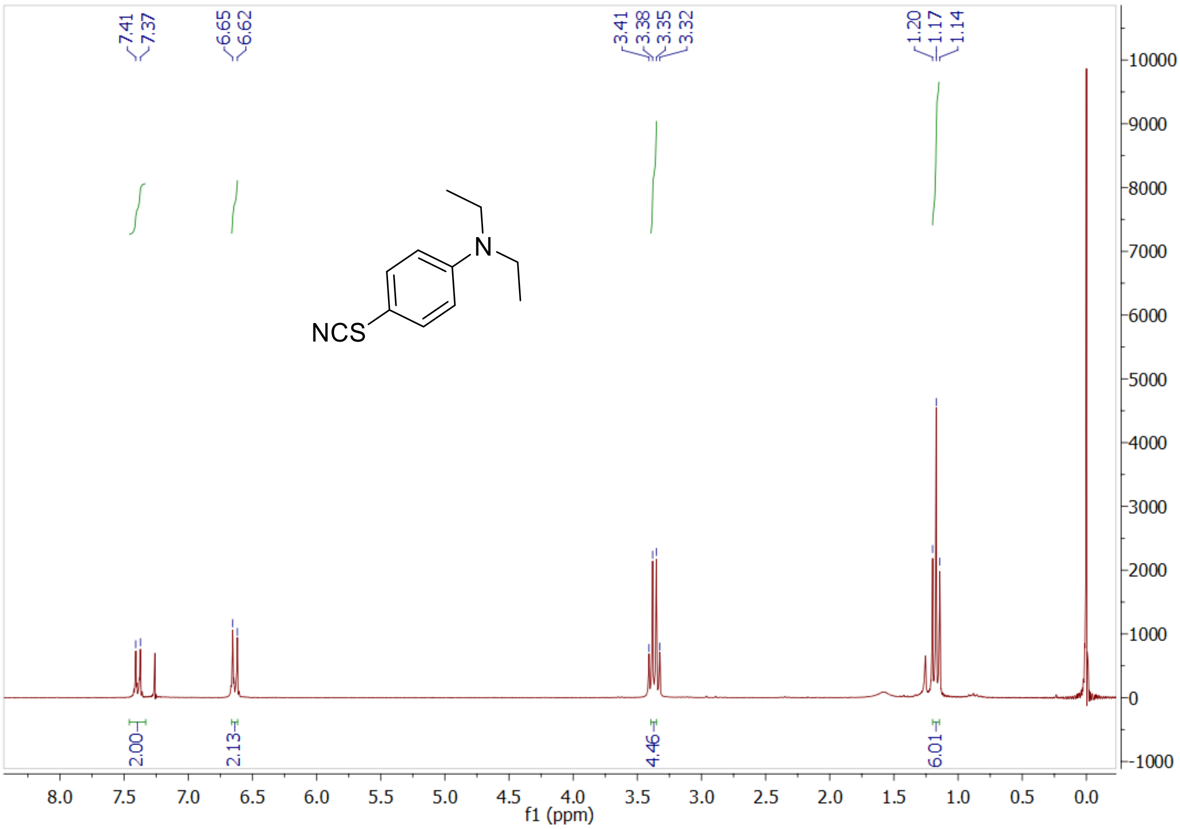
6d [1]H-NMR



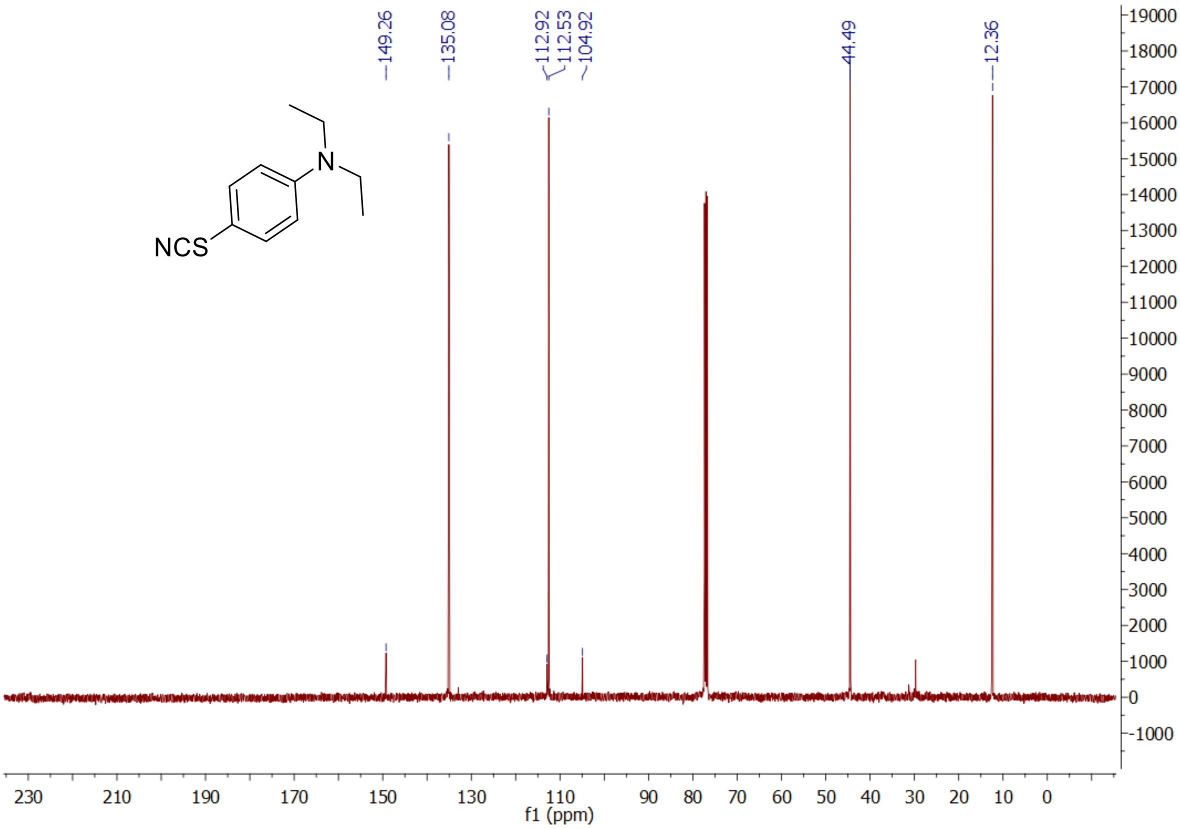
6d[13]C-NMR



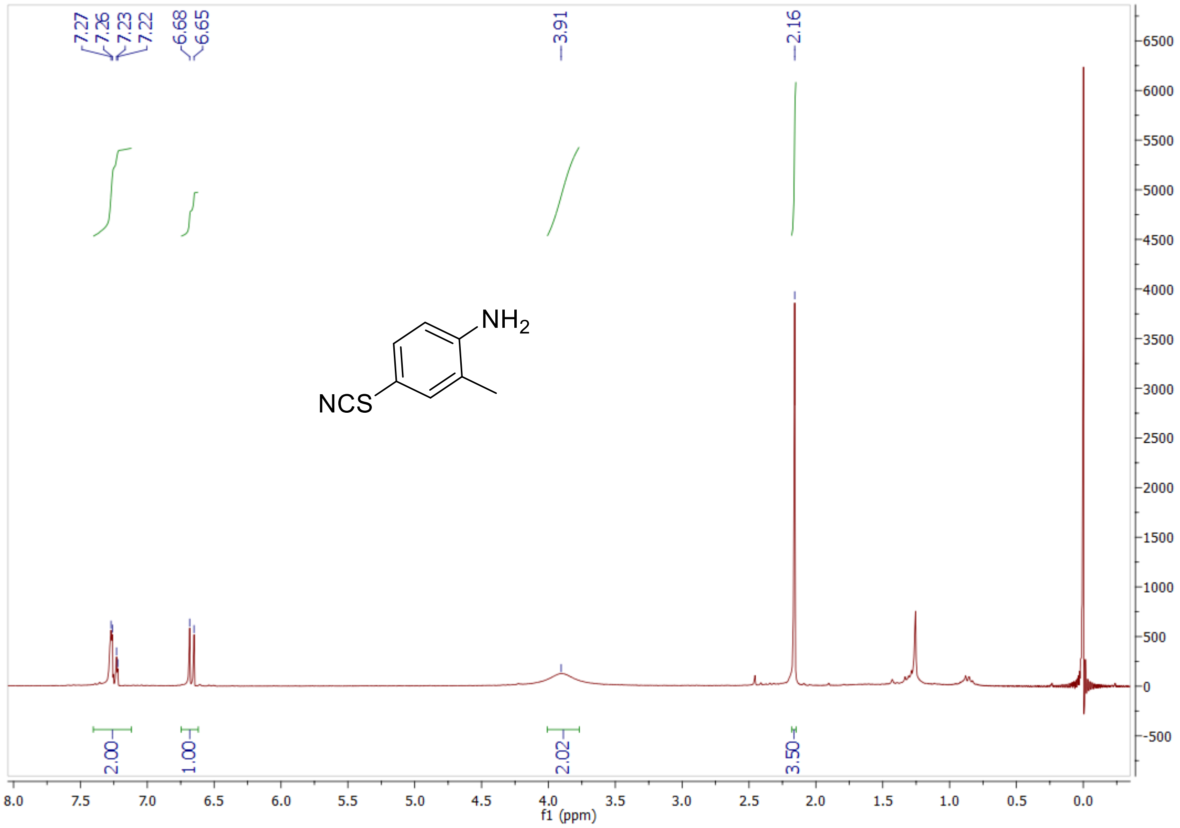
6e ^{1}H-NMR



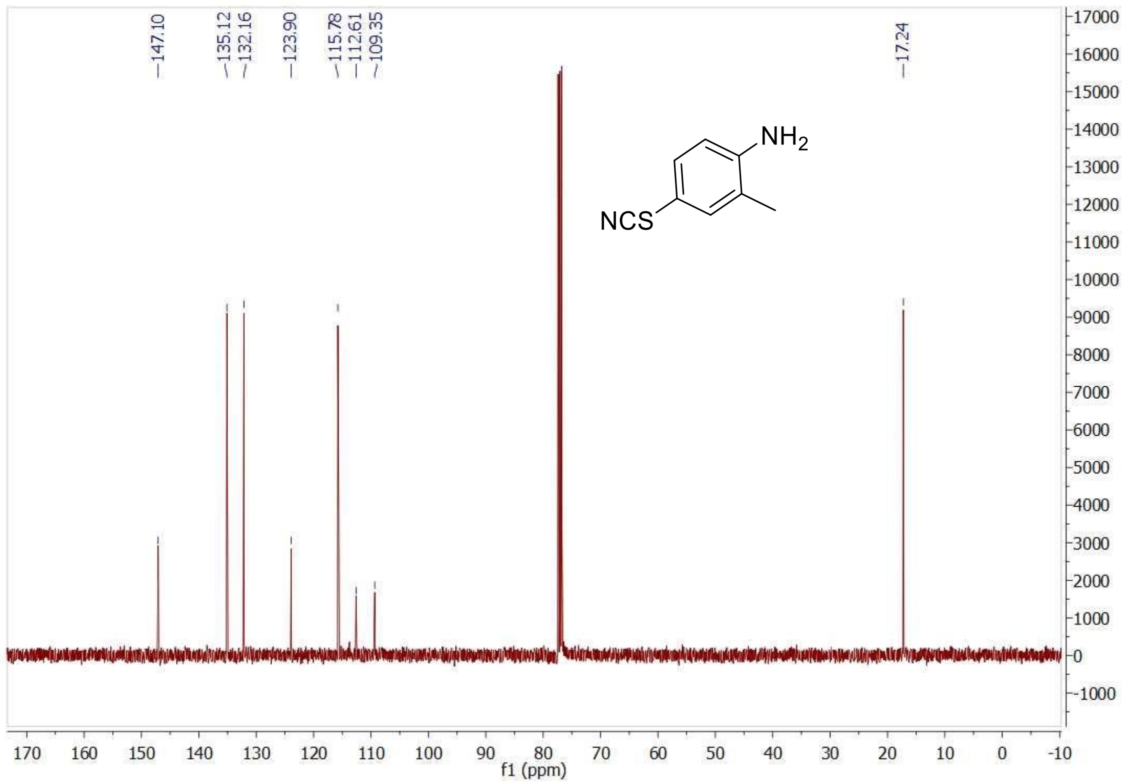
6e ^{13}C-NMR



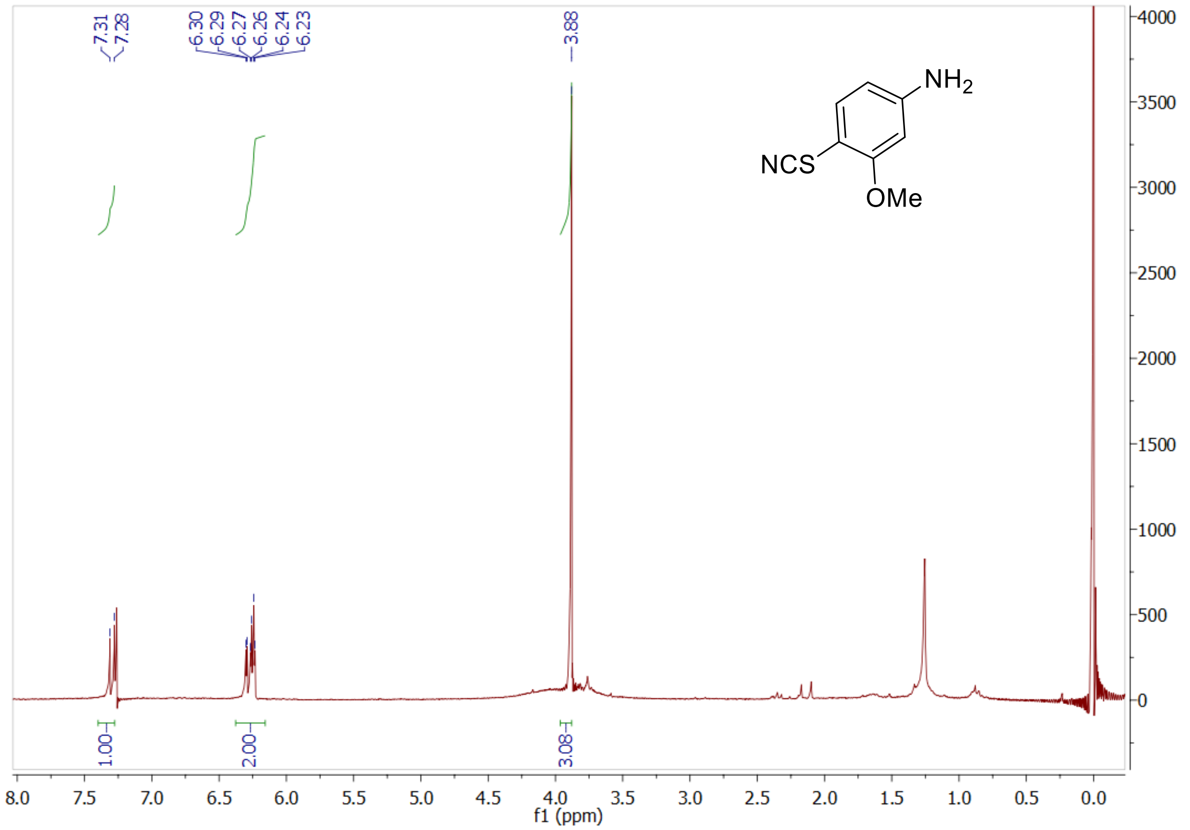
6f ^{1}H-NMR



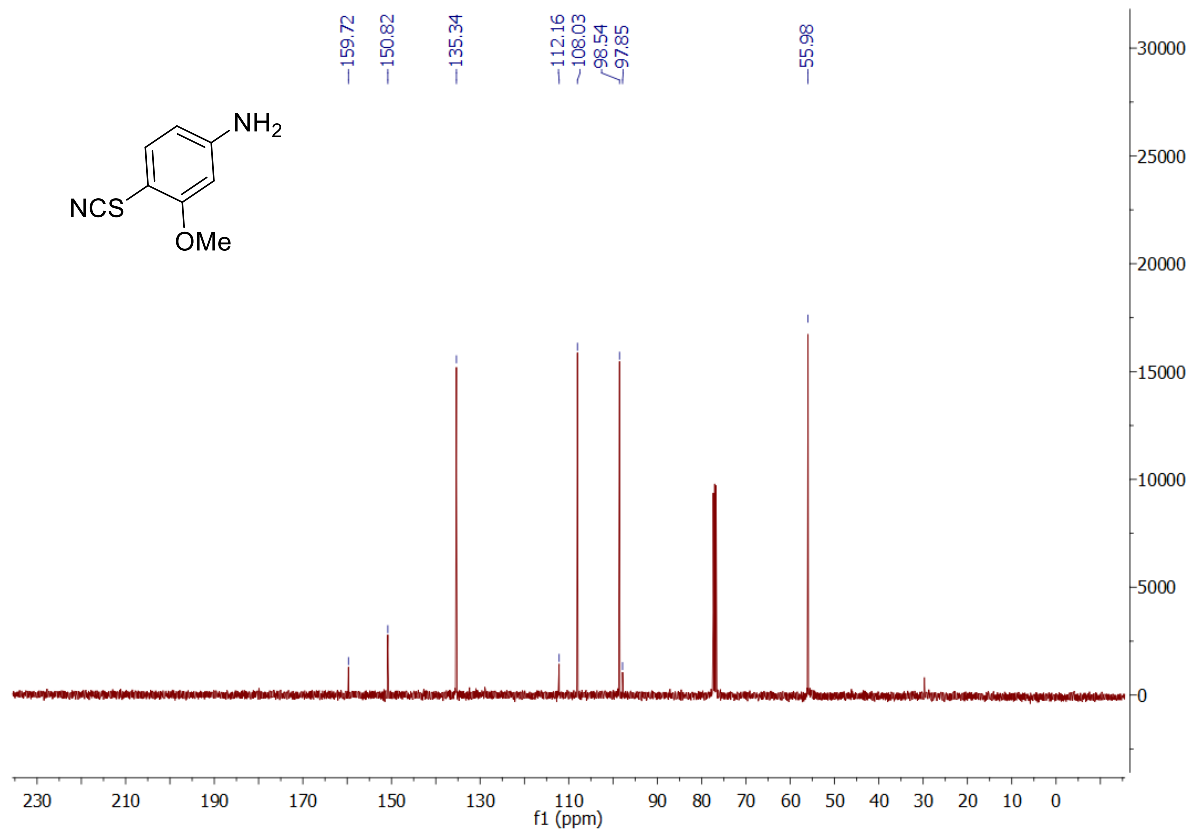
6f^{13}C-NMR



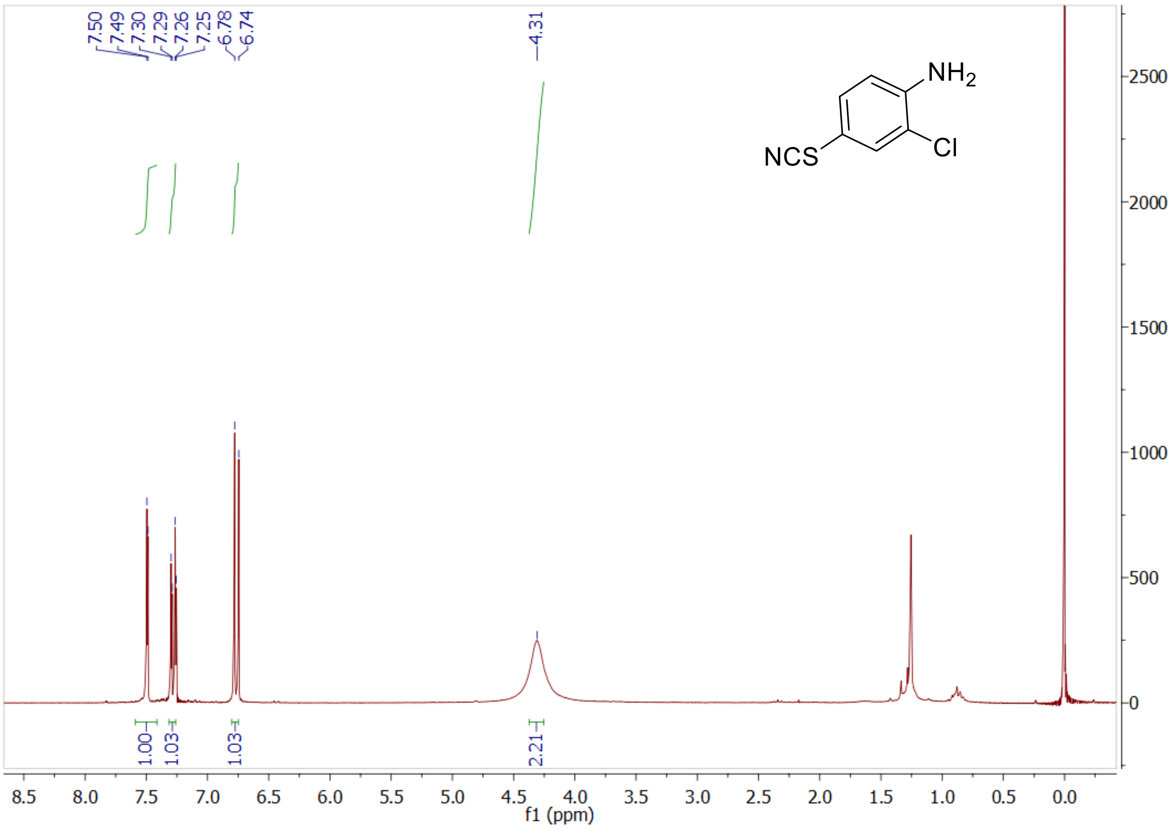
6g ¹H-NMR



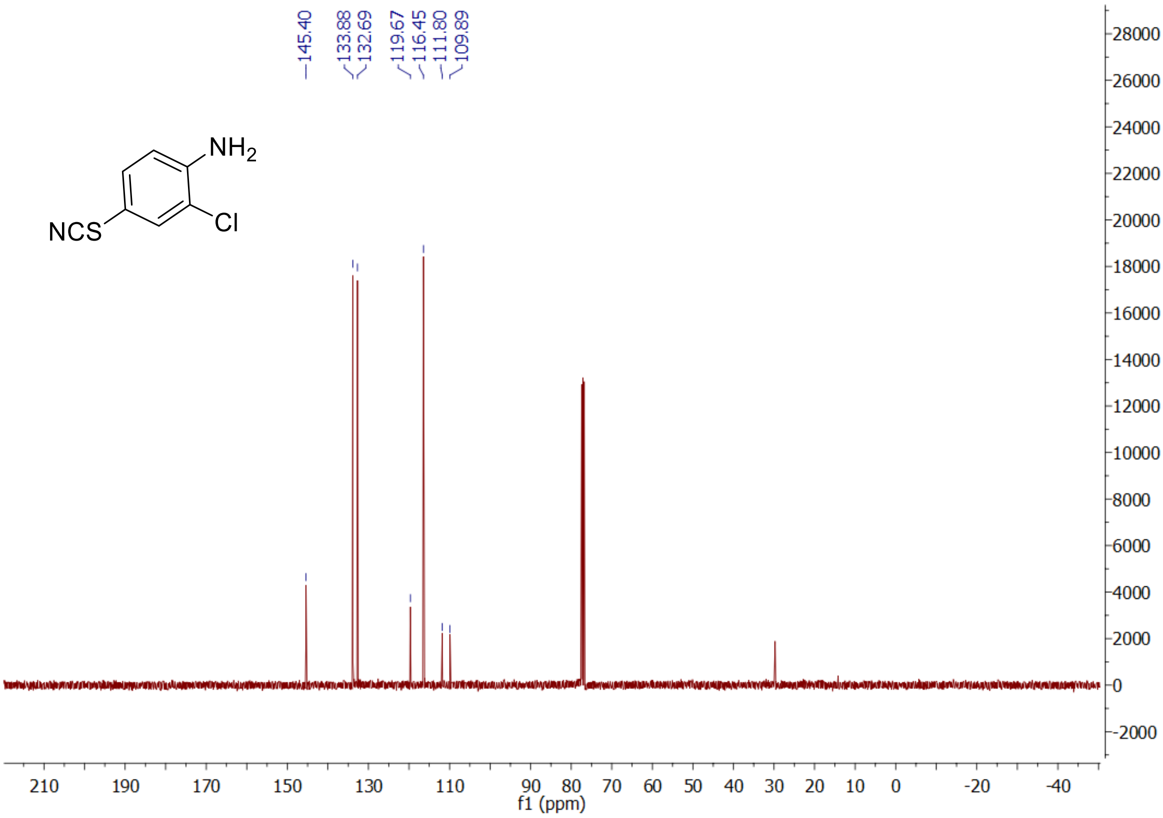
6g¹³C-NMR



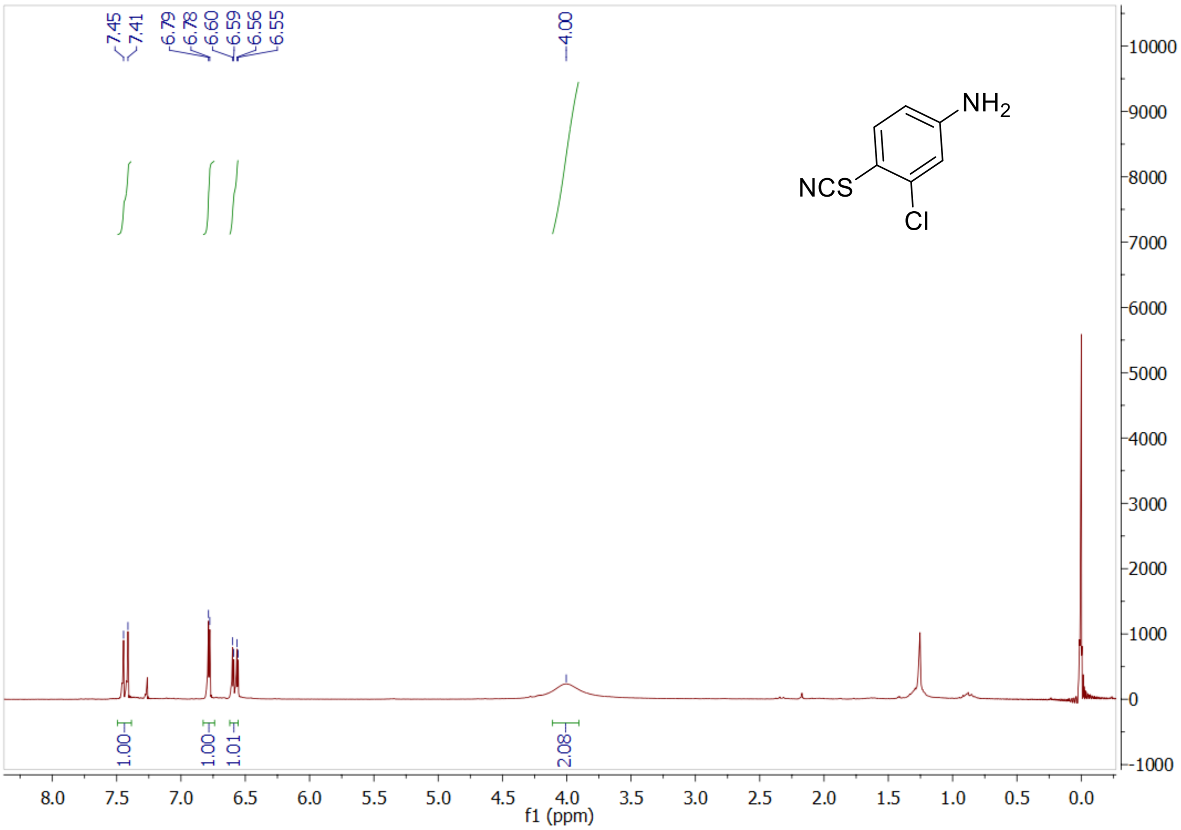
6h ^{1}H-NMR



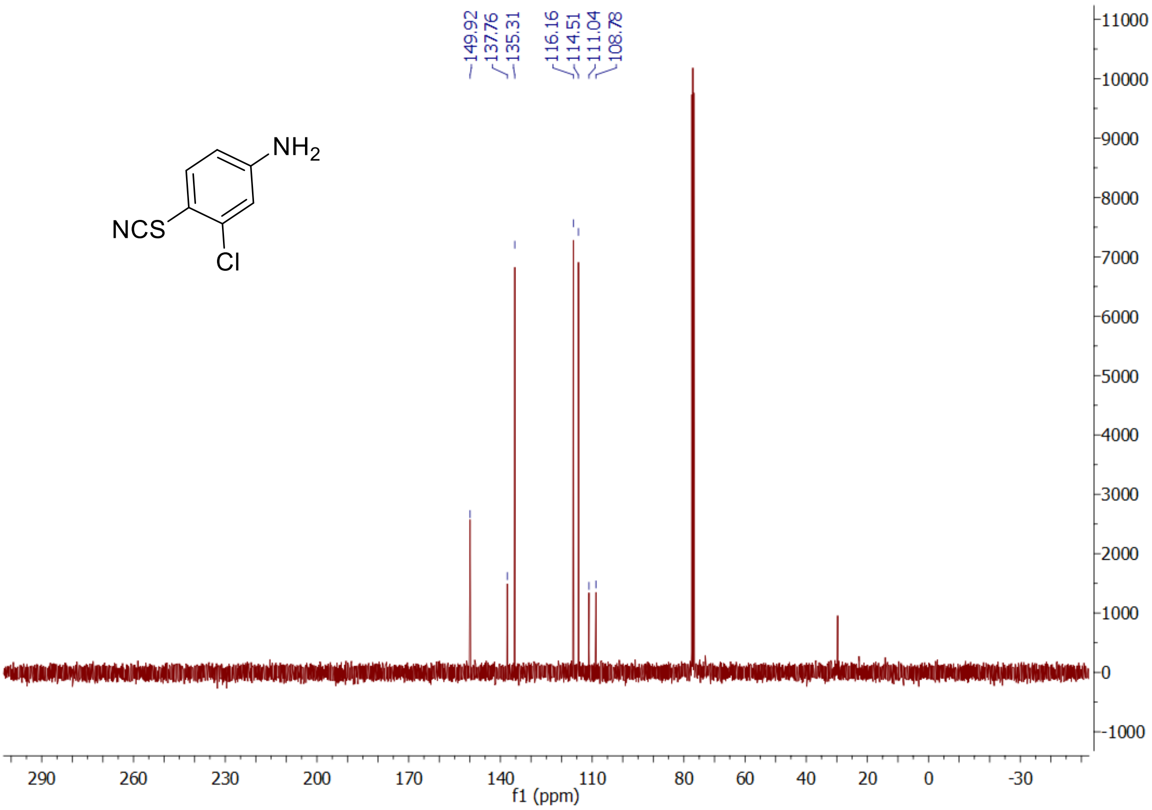
6h ^{13}C-NMR



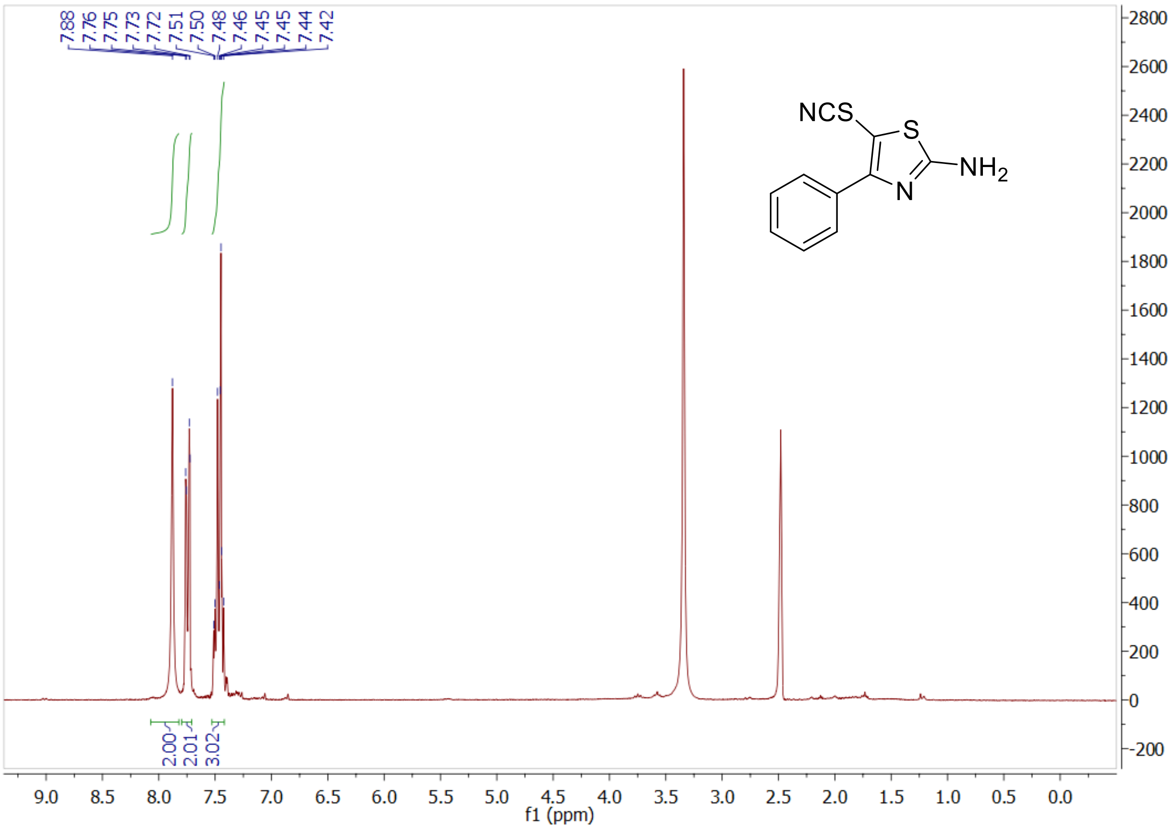
6i ^{1}H-NMR



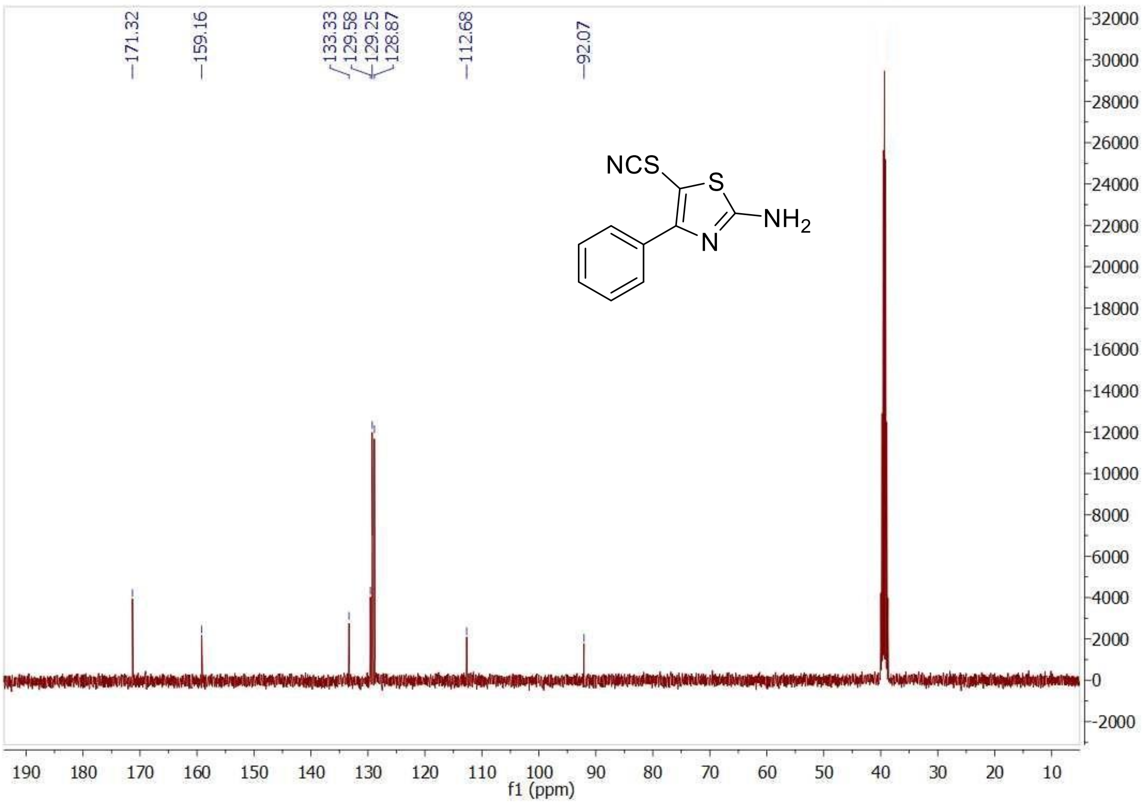
6i^{13}C-NMR



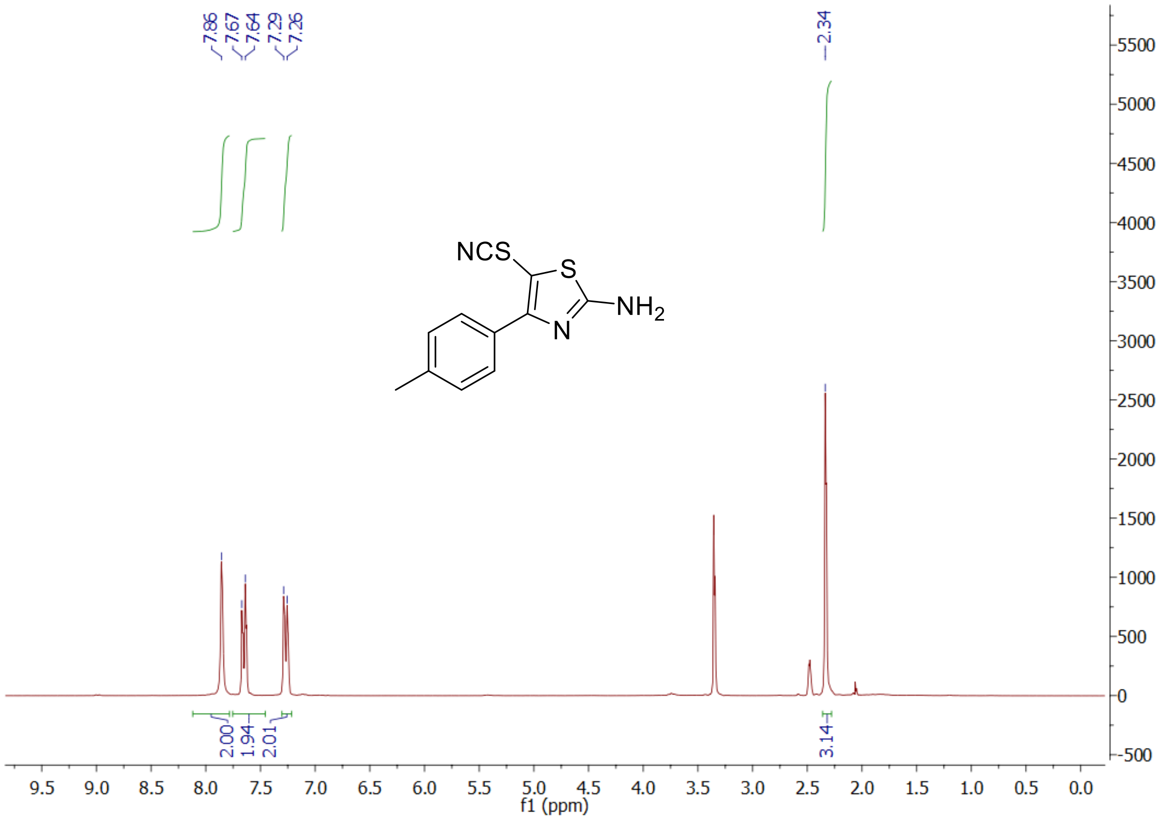
8a ^{1}H-NMR



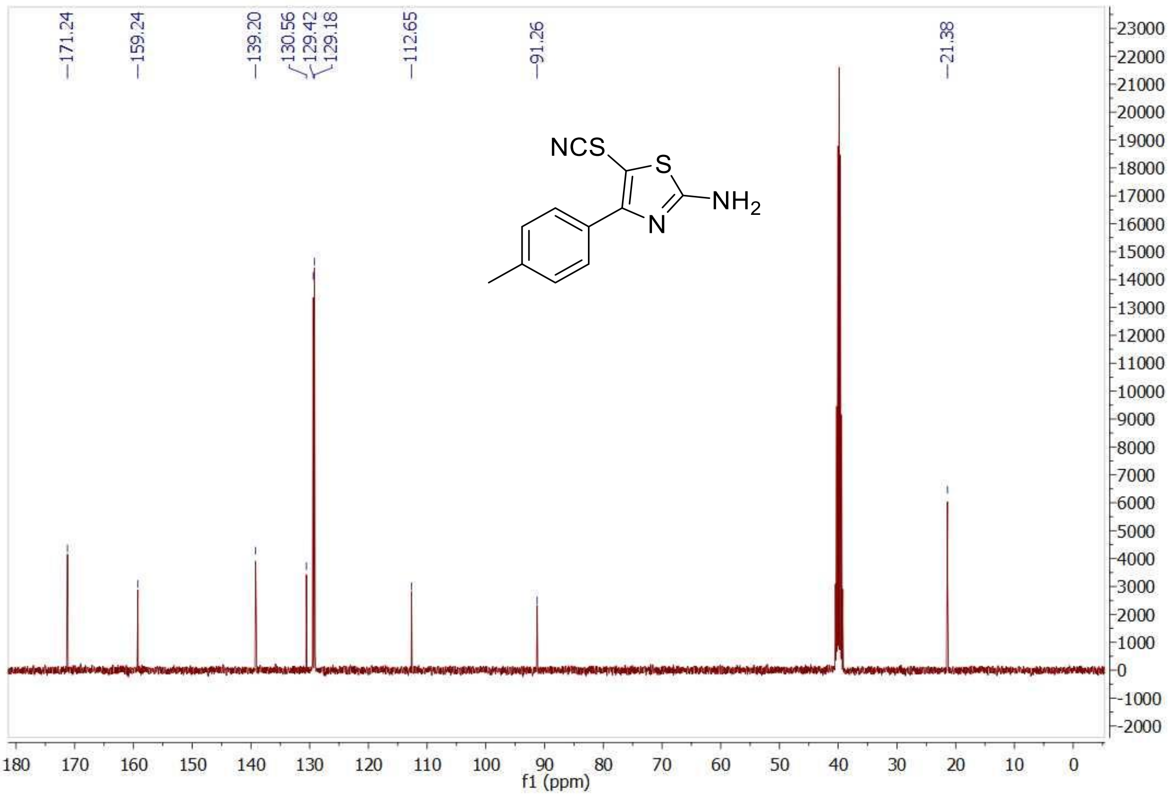
8a^{13}C-NMR



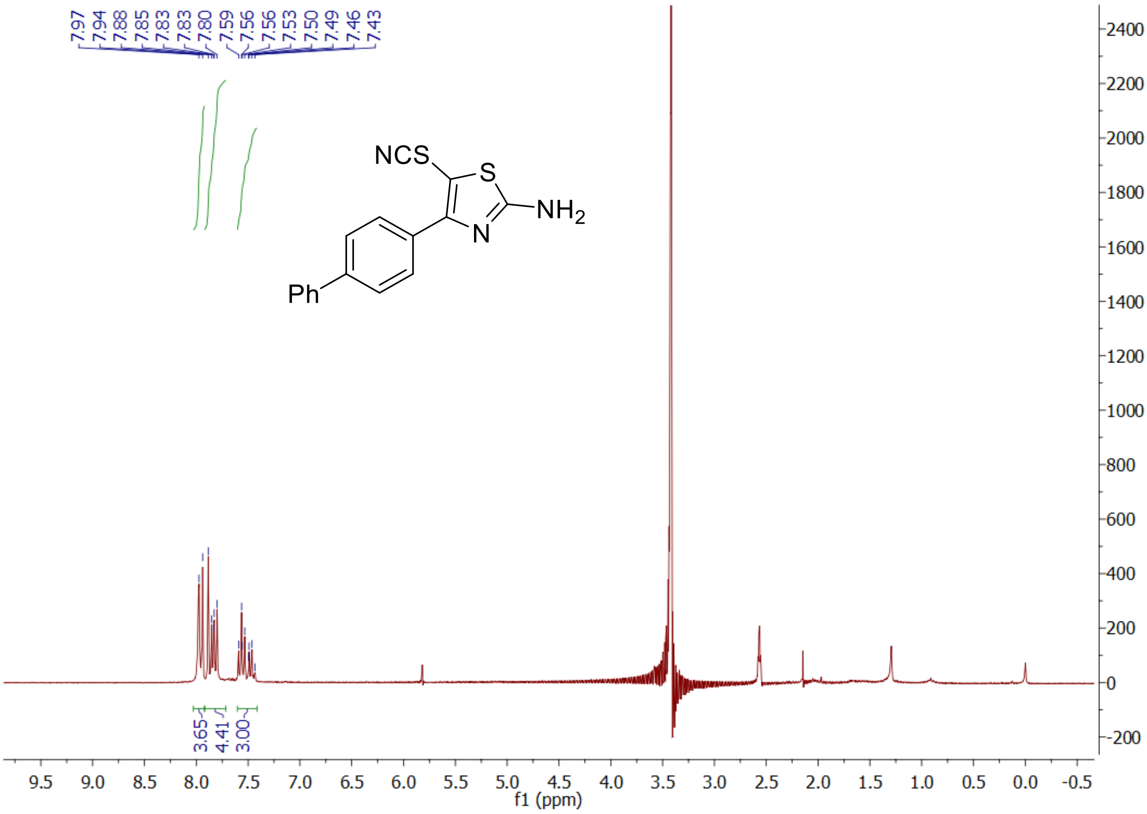
8b ¹H-NMR



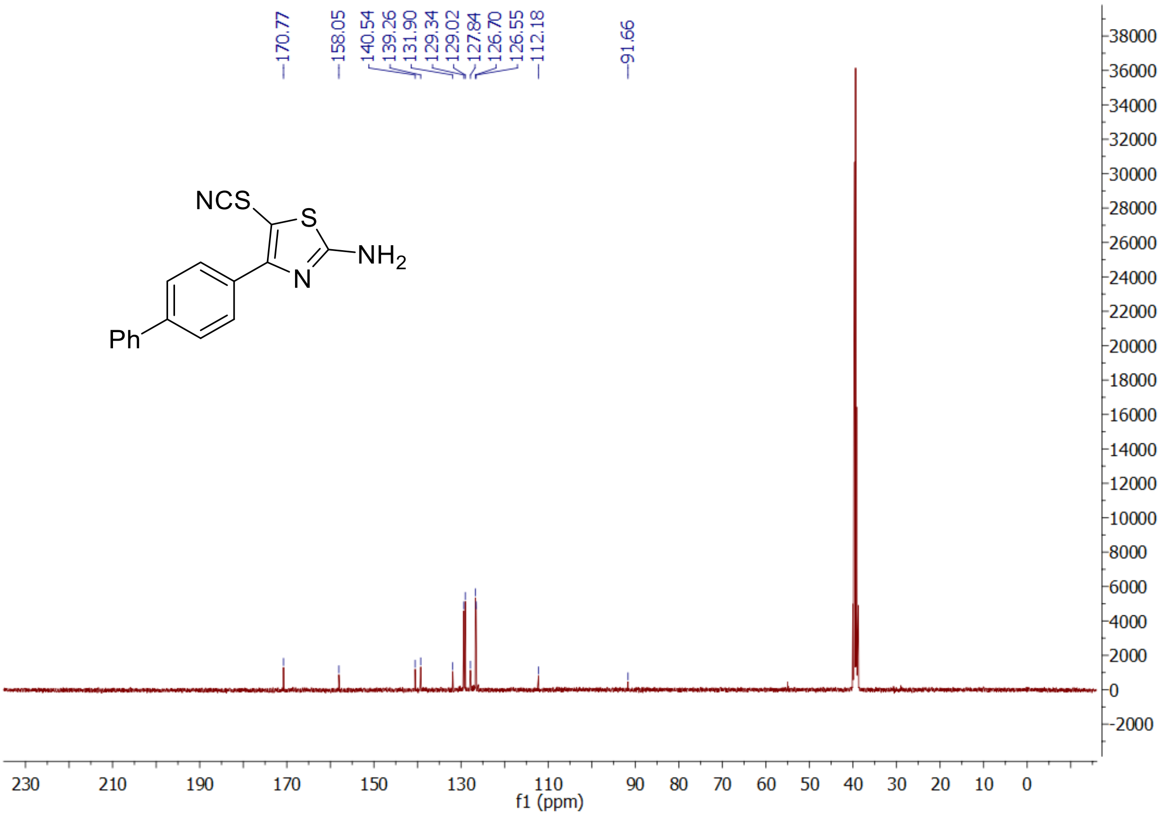
8b¹³C-NMR



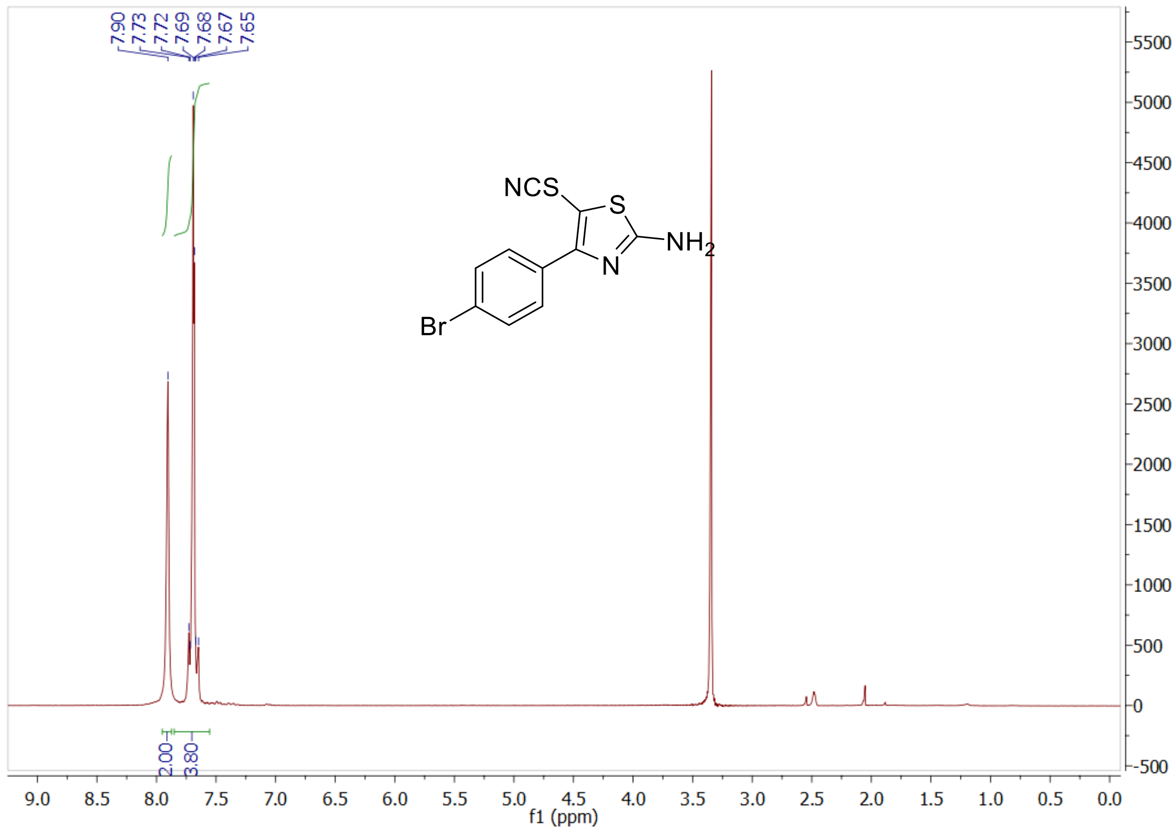
8c ¹H-NMR



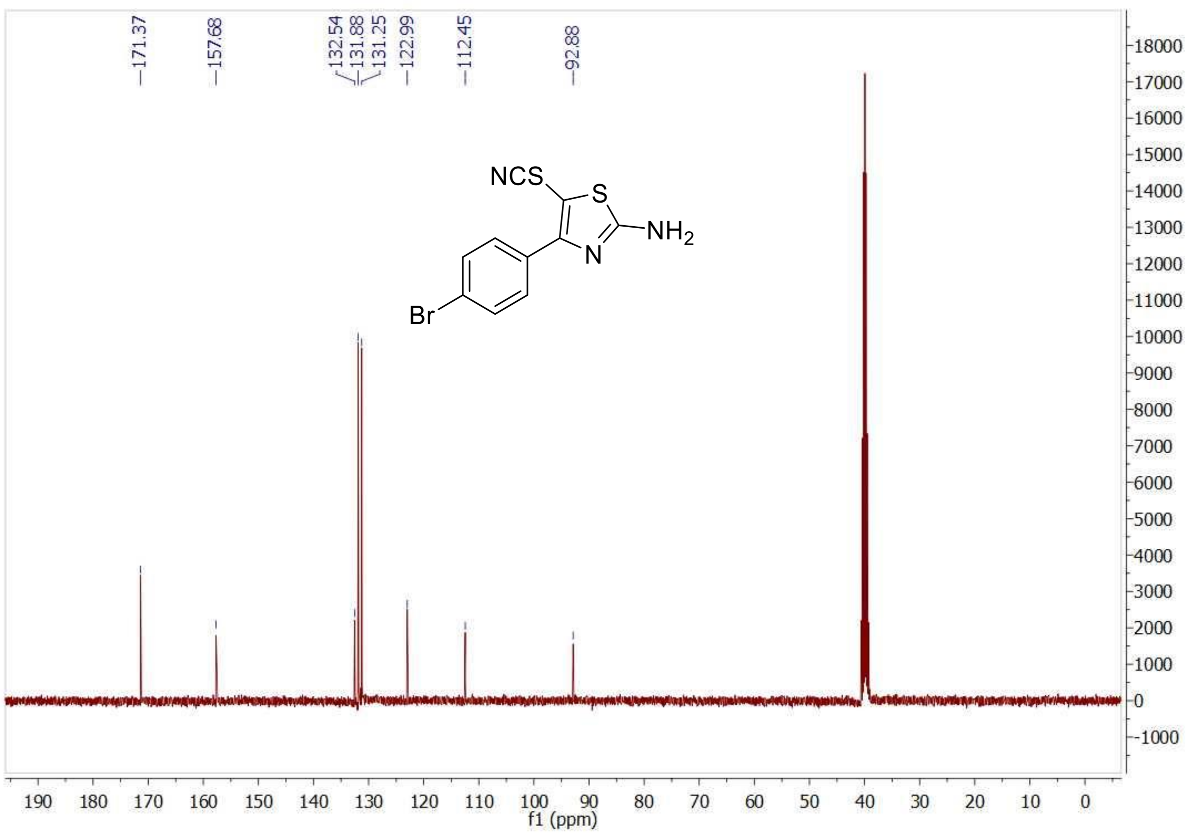
8c ¹³C-NMR



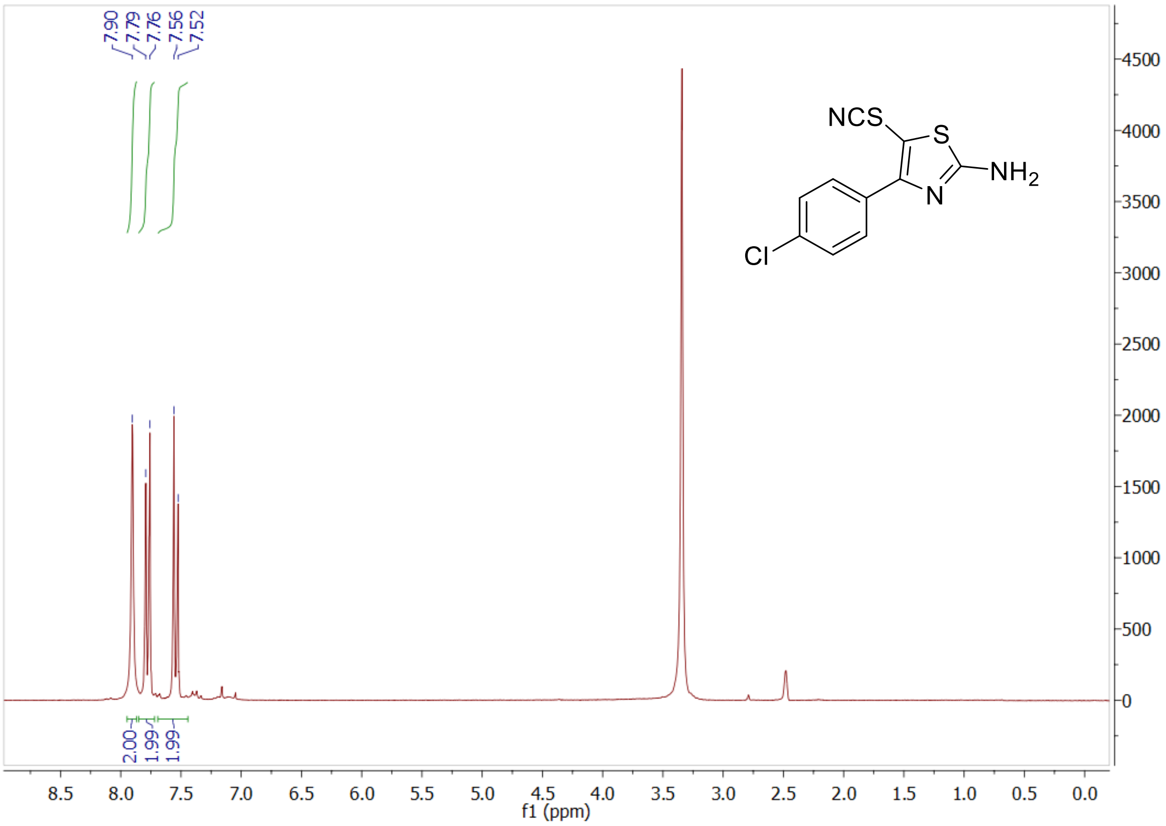
8d ¹H-NMR



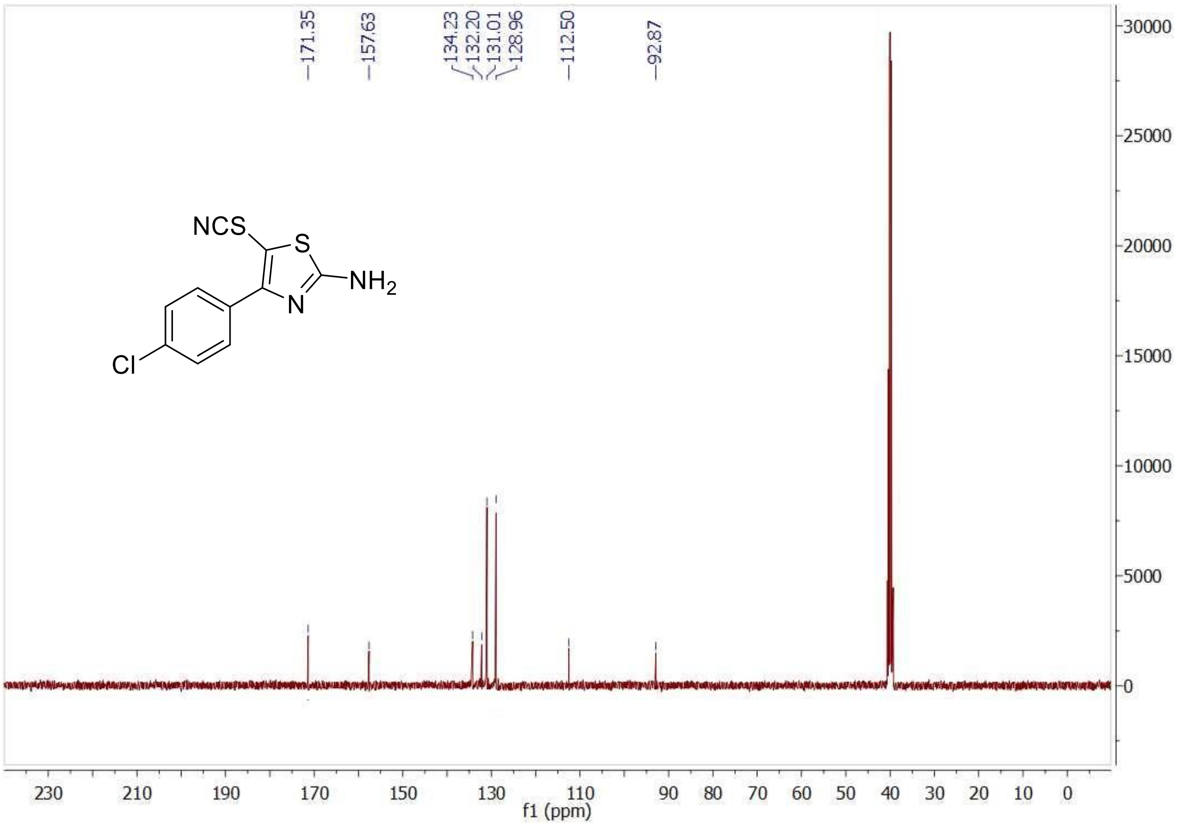
8d¹³C-NMR



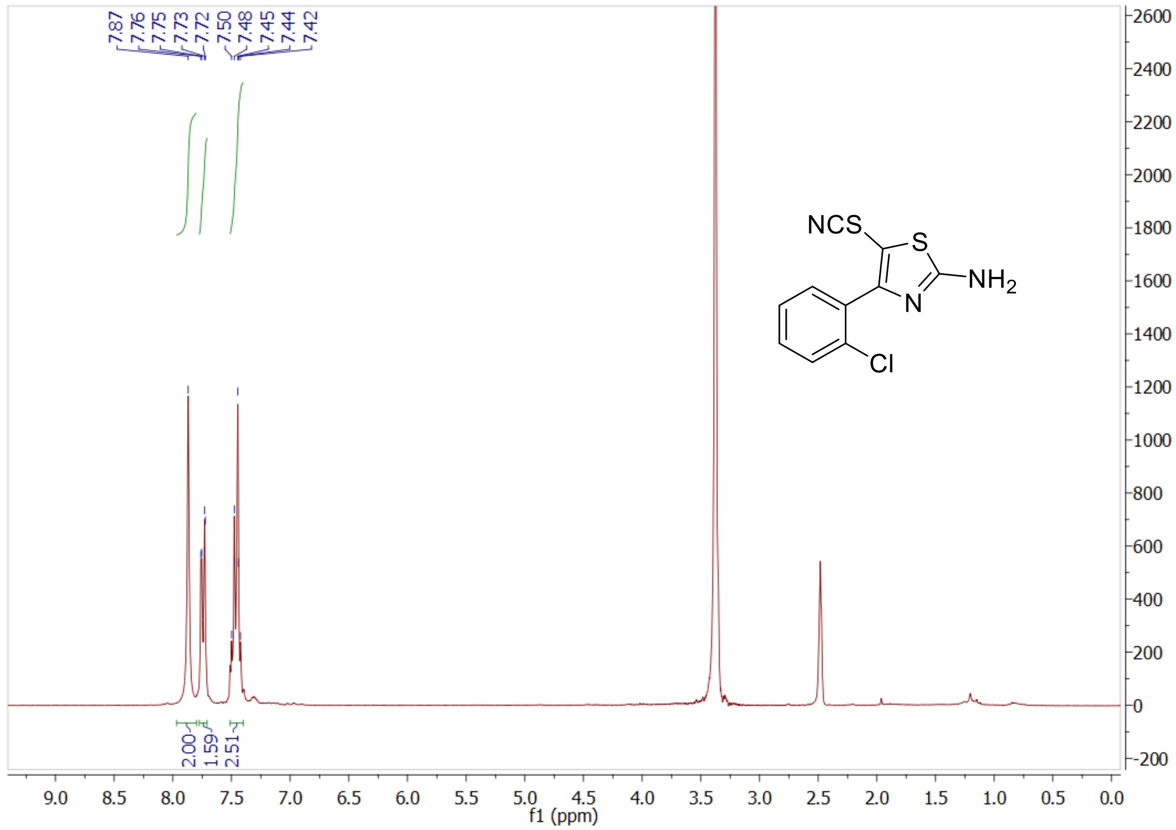
8e ¹H-NMR



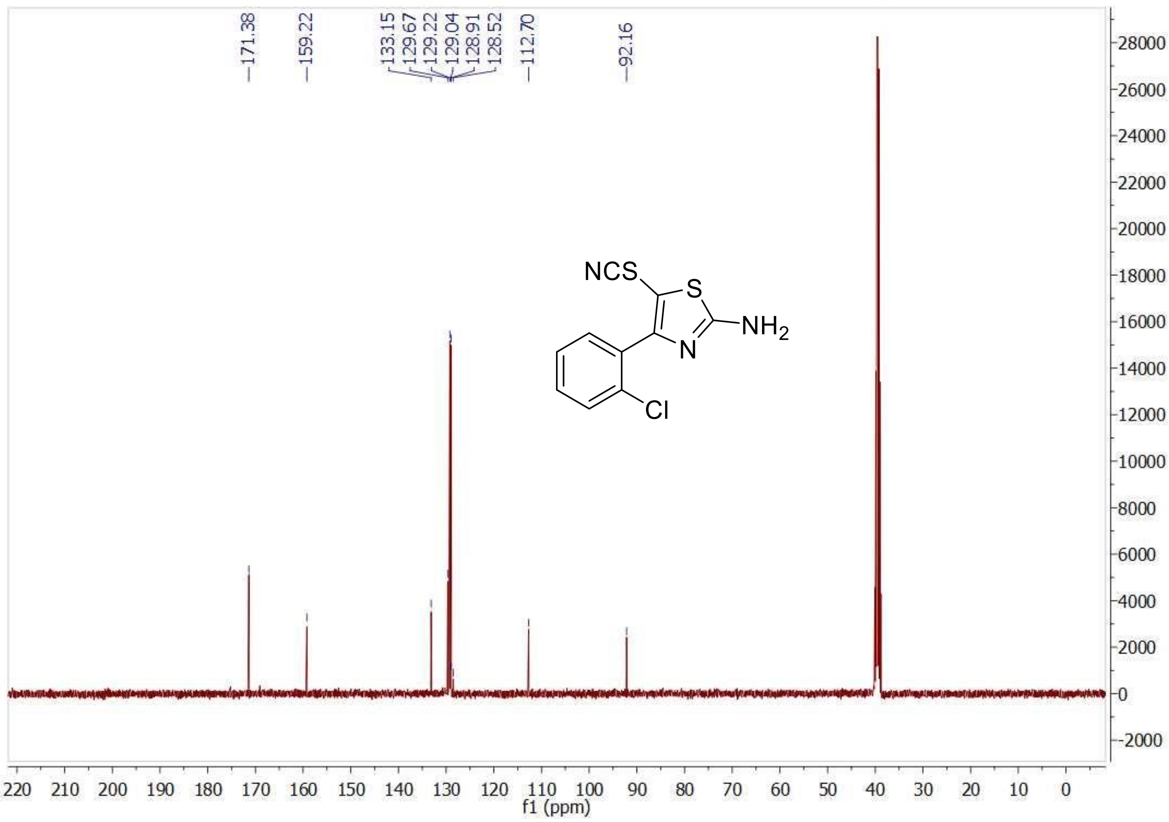
8e¹³C-NMR



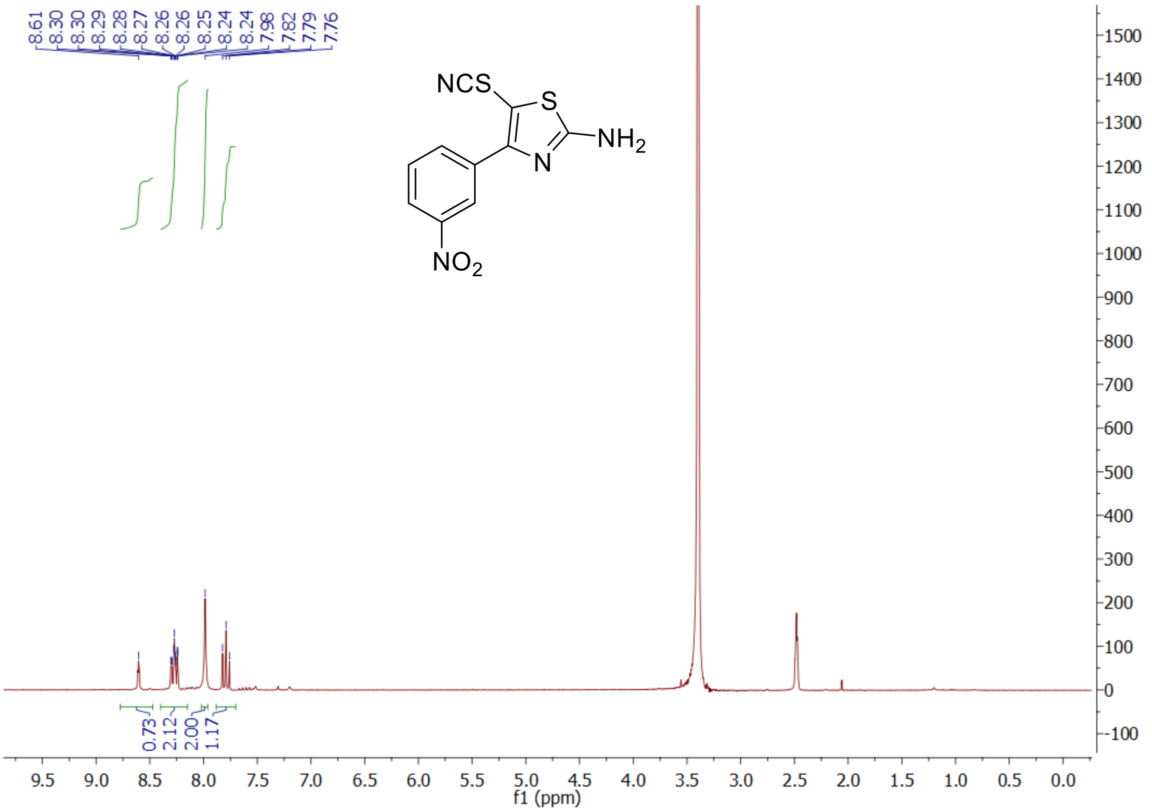
8f ¹H-NMR



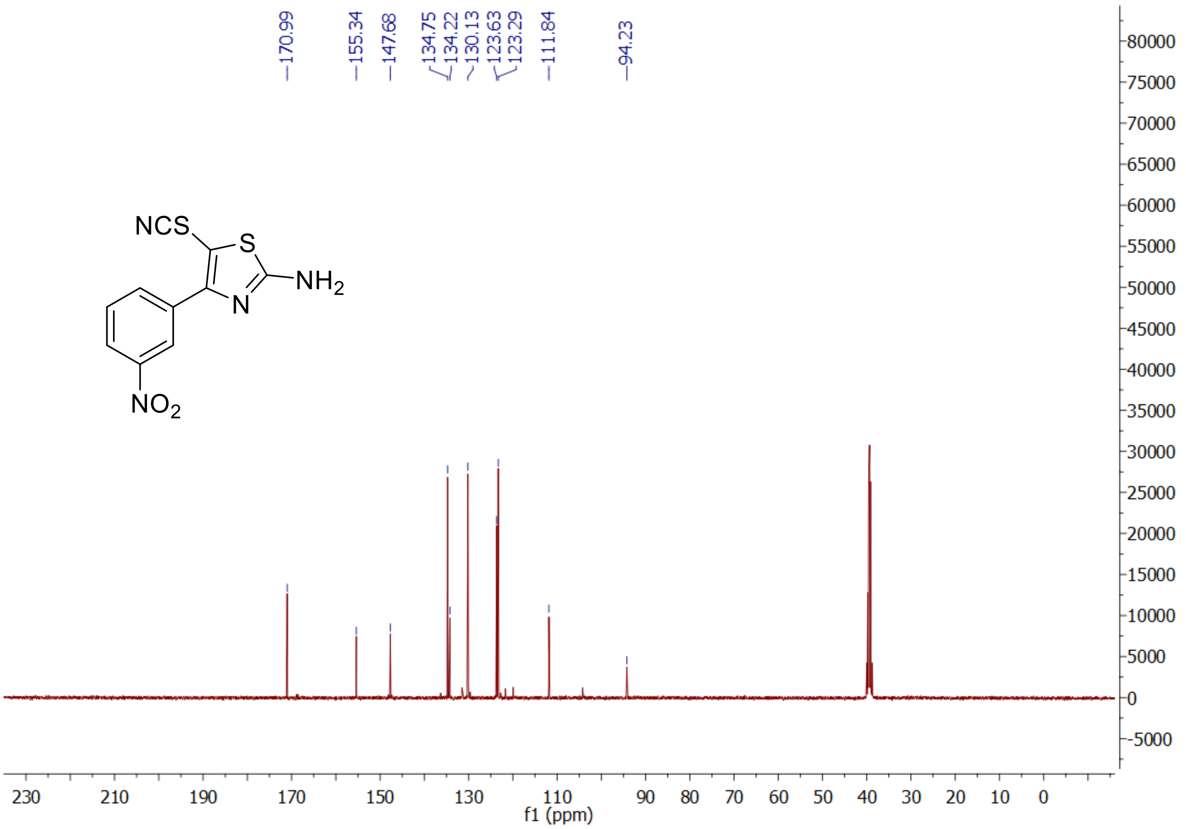
8f ¹³C-NMR



8g ¹H-NMR



8g ¹³C-NMR



8 Reference

1. Hassanien, A.S. and A.A. Akl, *Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films.* Superlattices and Microstructures, 2016. **89**: p. 153-169.
2. Chaudhary, D., N. Khare, and V.D. Vankar, *Ag nanoparticles loaded TiO2/MWCNT ternary nanocomposite: A visible-light-driven photocatalyst with enhanced photocatalytic performance and stability.* Ceramics International, 2016. **42**(14): p. 15861-15867.
3. López, R. and R. Gómez, *Band-gap energy estimation from diffuse reflectance measurements on sol–gel and commercial TiO2: a comparative study.* Journal of sol-gel science and technology, 2012. **61**(1): p. 1-7.
4. Tauc, J., R. Grigorovici, and A. Vancu, *Optical Properties and Electronic Structure of Amorphous Germanium.* physica status solidi (b), 1966. **15**(2): p. 627-637.
5. Butler, M., *Photoelectrolysis and physical properties of the semiconducting electrode WO2.* Journal of Applied Physics, 1977. **48**(5): p. 1914-1920.
6. Chaudhary, D., N. Khare, and V. Vankar, *Ag nanoparticles loaded TiO2/MWCNT ternary nanocomposite: a visible-light-driven photocatalyst with enhanced photocatalytic performance and stability.* Ceramics International, 2016. **42**(14): p. 15861-15867.
7. Guo, G., et al., *Synthesis and photocatalytic applications of Ag/TiO 2-nanotubes.* Talanta, 2009. **79**(3): p. 570-575.
8. Zhong, J., Q. Wang, and Y. Yu, *Solvothermal preparation of Ag nanoparticles sensitized TiO 2 nanotube arrays with enhanced photoelectrochemical performance.* Journal of Alloys and Compounds, 2015. **620**: p. 168-171.
9. Fan, W., et al., *A visible-light-promoted aerobic metal-free C-3 thiocyanation of indoles.* J Org Chem, 2014. **79**(21): p. 10588-92.
10. Fotouhi, L. and K. Nikoofar, *Electrochemical thiocyanation of nitrogen-containing aromatic and heteroaromatic compounds.* Tetrahedron Letters, 2013. **54**(23): p. 2903-2905.
11. Yadav, J., et al., *Iodine/MeOH: a novel and efficient reagent system for thiocyanation of aromatics and heteroaromatics.* Tetrahedron letters, 2004. **45**(14): p. 2951-2954.
12. Pan, X.-Q., et al., *Mn (OAc) 3-promoted regioselective free radical thiocyanation of indoles and anilines.* Tetrahedron Letters, 2009. **50**(3): p. 347-349.
13. Khalili, D., *Graphene oxide: a promising carbocatalyst for the regioselective thiocyanation of aromatic amines, phenols, anisols and enolizable ketones by hydrogen peroxide/KSCN in water.* New Journal of Chemistry, 2016. **40**(3): p. 2547-2553.
14. Sajjadifar, S., et al., *1-Methyl-3-(2-(Sulfooxy) Ethyl)-1H-Imidazol-3-Ium Thiocyanate as A Novel, Green, and Efficient BrØNsted Acidic Ionic Liquid-Promoted Regioselective Thiocyanation of Aromatic and Heteroaromatic Compounds at Room Temperature.* Phosphorus, Sulfur, and Silicon and the Related Elements, 2014. **189**(3): p. 333-342.
15. Memarian, H.R., I. Mohammadpoor-Baltork, and K. Nikoofar, *Ultrasound-assisted thiocyanation of aromatic and heteroaromatic compounds using ammonium thiocyanate and DDQ.* Ultrasonics sonochemistry, 2008. **15**(4): p. 456-462.
16. Kil, K.-E., et al., *Synthesis and evaluation of N-(methylthiophenyl) picolinamide derivatives as PET radioligands for metabotropic glutamate receptor subtype 4.* Bioorganic & medicinal chemistry letters, 2016. **26**(1): p. 133-139.
17. Chen, B., et al., *Selective Access to 4-Substituted 2-Aminothiazoles and 4-Substituted 5-Thiocyano-2-aminothiazoles from Vinyl Azides and Potassium Thiocyanate Switched by Palladium and Iron Catalysts.* Organic letters, 2015. **17**(19): p. 4698-4701.

18. Hebade, M.J., et al., *A rapid, mild, and efficient method for C-5 iodination/thiocyanation of 2-aminothiazoles.* Phosphorus, Sulfur, and Silicon and the Related Elements, 2016. **191**(8): p. 1155-1159.