Supporting Information

Selectively electrochemical *para*-thiocyanation of aromatic amines under metal-, oxidant- and exogenous-electrolyte-free conditions

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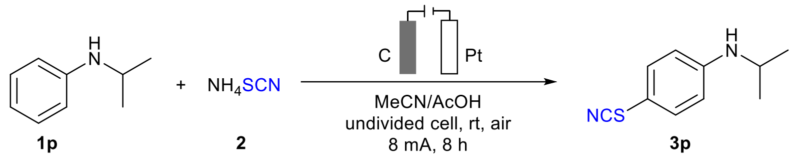
General information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. And all the solvents were used without any purification. The instrument for electrolysis is CHI-660E (made in China). The method employed is chronopotentiometry (CP). The anodic electrode was graphite rod (ϕ6 mm) and cathodic electrode was platinum plate (10 mm×10 mm×0.1 mm). Thin layer chromatography (TLC) was performed on glass plates coated with silica gel GF254 (Qingdao Jiyida silica gel reagent factory). Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 100MHz (^{13}C NMR), 376 MHz (^{19}F NMR). All chemical shifts are reported relative to tetramethylsilane and solvent peaks. And all ^{1}H, ^{13}C and ^{19}F NMR data spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Unknown compounds and were characterized by m.p., ^{1}H & ^{13}C NMR, and HRMS. All of the known compounds described in the paper were characterized by comparing their ^{1}H&^{13}C NMR to the previously reported data.

Experimental procedure

Optimization of the reaction conditions

Table S1. Optimization of Reaction Condition for secondary anilines [a]



Entry	Variation from standard conditions	Yield [%] [b]
1	none	58
2 [c]	0.2 mmol of **1p**	63
3	entry 2, 1.2 mmol of **2**	60
4	entry 2, 2.0 mmol of **2**	57
5	**entry 2, MeCN**	**87**
6	entry 5, 6.0 equiv of TFA	30
7	entry 5, 10 mA	84
8	entry 5, 12 mA	81
9	without electricity	n.d.

[a] Reaction conditions: **1p** (0.2 mmol), **2** (1.6 mmol), MeCN/AcOH (4.5/1.5 mL), air, graphite rod as the anode, platinum plate (10×10×0.1 mm^3) as the cathode, constant current of 8 mA, 8 h. [b] Isolated yields. [c] Constant current of 8 mA for 4 h.

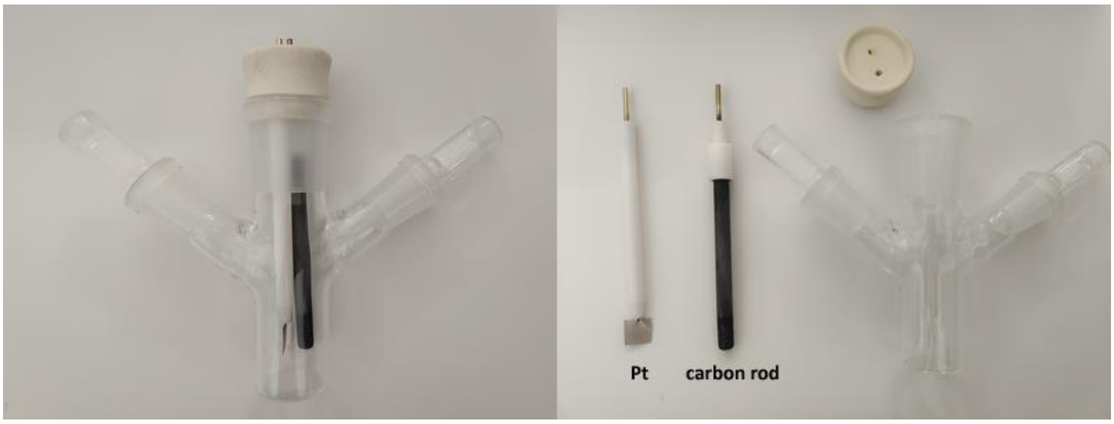
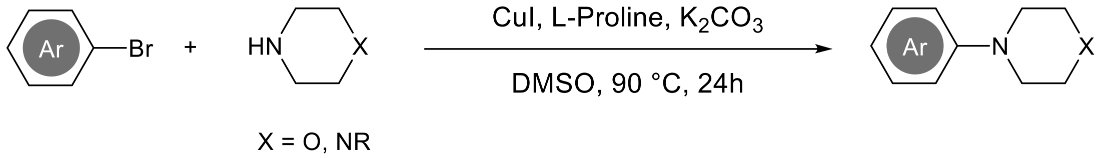


Figure S1 Electrolysis setup

General procedure for synthesis of (2h-2j) [1]



A mixture of aryl bromide (10 mmol), morpholines (20 mmol), K_2CO_3 (20 mmol), CuI (1.0 mmol and L-proline (2.0 mmol) in 10 mL of DMSO was heated at 90℃ and for 24 h. The cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The desired products were isolated by silica gel column chromatography (n-heptane/ethyl acetate mixtures).

General procedure for synthesis of 3a-3l'

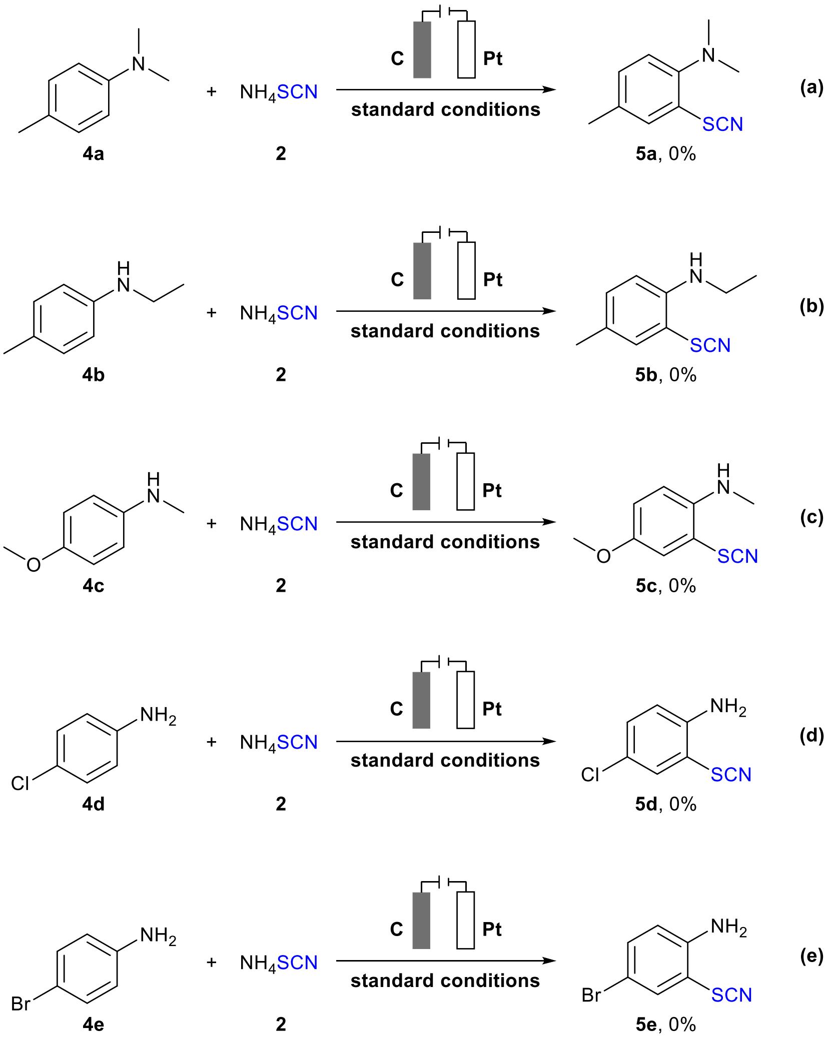
Tertiary amine derivatives **1** (0.4 mmol) and ammonium thiocyanate **2** (1.5 mmol) were combined and added into a dried undivided three-necked bottle (25.0 mL) equipped with stir bar. The bottle was equipped with graphite rod (ϕ6 mm, about 10.0 mm immersion depth in solution) as the anode and platinum plate (10 mm×10 mm×0.1 mm) as the cathode. MeCN/AcOH (4.5/1.5 mL) were injected into the tubes *via* syringes under air at room temperature. The reaction mixture was stirred and electrolyzed at a constant current of 12.0 mA for 6.5 h. After the reaction was completed, the solvent was removed with a rotary evaporator. The pure product **3a-3l'** was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

General procedure for synthesis of 3m-3zh

Secondary and primary amine derivatives **1** (0.2 mmol) and ammonium thiocyanate **2** (1.6 mmol) were combined and added into a dried undivided three-necked bottle (25.0 mL) equipped with stir bar. The bottle was equipped with graphite rod (ϕ6 mm, about 10.0 mm immersion depth in solution) as the anode and platinum plate (10 mm×10 mm×0.1 mm) as the cathode. MeCN (6.0 mL) were injected into the tubes via syringes under air at room temperature. The reaction mixture was stirred and electrolyzed at a constant current of 8.0 mA for 4 h. After the reaction was completed, the solvent was removed with a rotary evaporator. The pure product **3m-3zh** was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

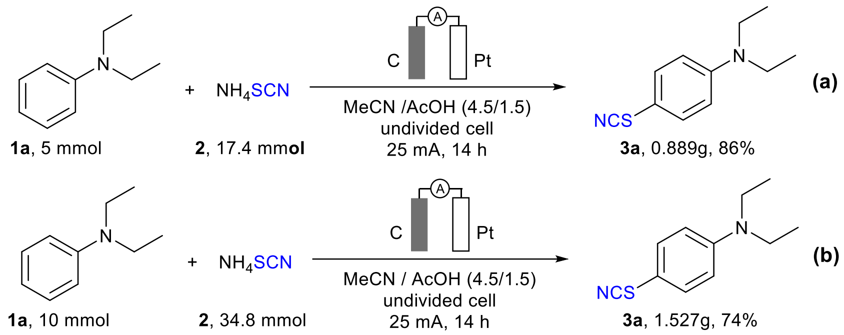
Procedure for gram scale synthesis of 3a

N,*N*-diethylaniline **1a** (5.0/10.0 mmol) and ammonium thiocyanate **2** (17.4/34.8 mmol) were combined and added into an dried undivided three-necked bottle (125/250 mL) equipped with stir bar. The bottle was equipped with graphite rod (ϕ6 mm, about 10.0 mm immersion depth in solution) as the anode and platinum plate (10 mm×10 mm×0.1 mm) as the cathode. The mixed solvent 70/140 mL (MeCN/AcOH=3/1) were joined into the beaker under air at room temperature. The reaction mixture was stirred and electrolyzed at a constant current of 25.0 mA for 14/28 h. After the reaction was completed, the solvent was removed with a rotary evaporator. The pure product **3a** (0.889g/1.527g, 86%/74%) was obtained by flash chromatography columns using petroleum ether and ethyl acetate as the eluent.

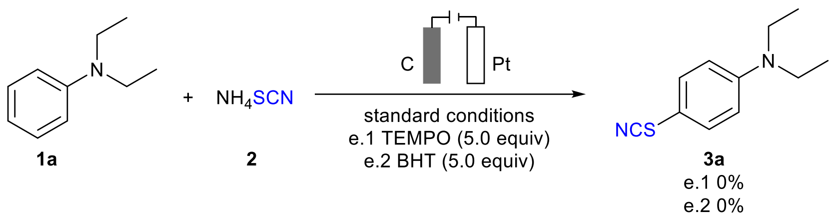


Scheme S1 Thiocyanation reaction of *para*-substituted anilines.

In any above reactions, the corresponding 2-thiocyanatoanilines could not be observed, which indicated that the electrochemical thiocyanation of anilines might be *para*-specific.



Scheme S2 Gram scale synthesis of *N*,*N*-diethyl-4-thiocyanatoaniline.



Scheme S3 Control experiments

Cyclic voltammograms

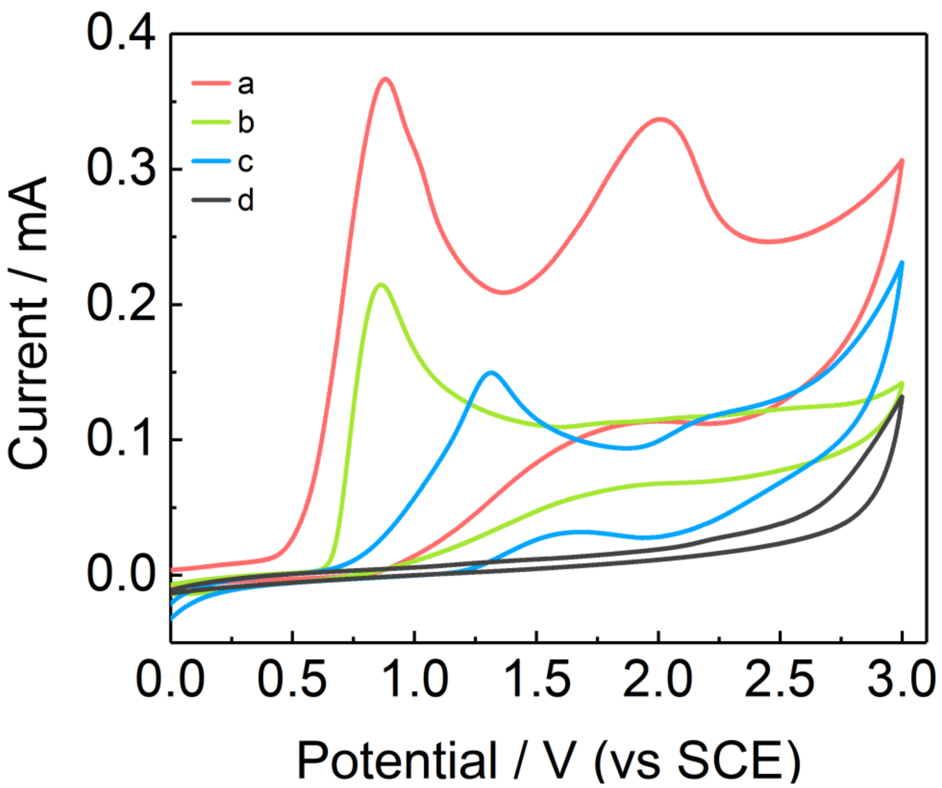


Figure S2. Cyclic voltammograms of 0.1 M $^{n}Bu_4NBF_4$ and related compounds in MeCN (20 mL) using glassy carbon working electrode, platinum plate and saturated calomel electrode as counter and reference electrode at 100 mV/s scan rate, (a) 0.2 mmol of **1a** and 0.75 mmol of **2**, (b) 0.2mmol of **1a**, (c) 0.2 mmol of **2**, (d) blank.

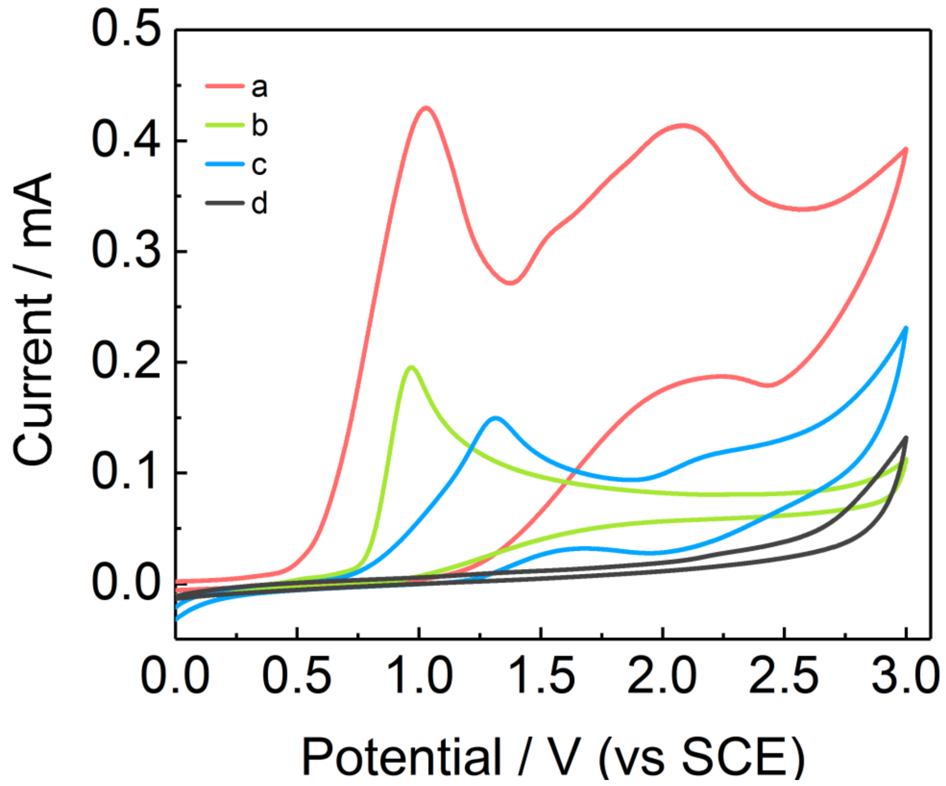


Figure S3. Cyclic voltammograms of 0.1 M $^{n}Bu_4NBF_4$ and related compounds in MeCN (20 mL) using glassy carbon working electrode, platinum plate and saturated calomel electrode as counter and reference electrode at 100 mV/s scan rate, (a) 0.2 mmol of **1p** and 1.6 mmol of **2**, (b) 0.2 mmol of **1p**, (c) 0.2 mmol of **2**, (d) blank.

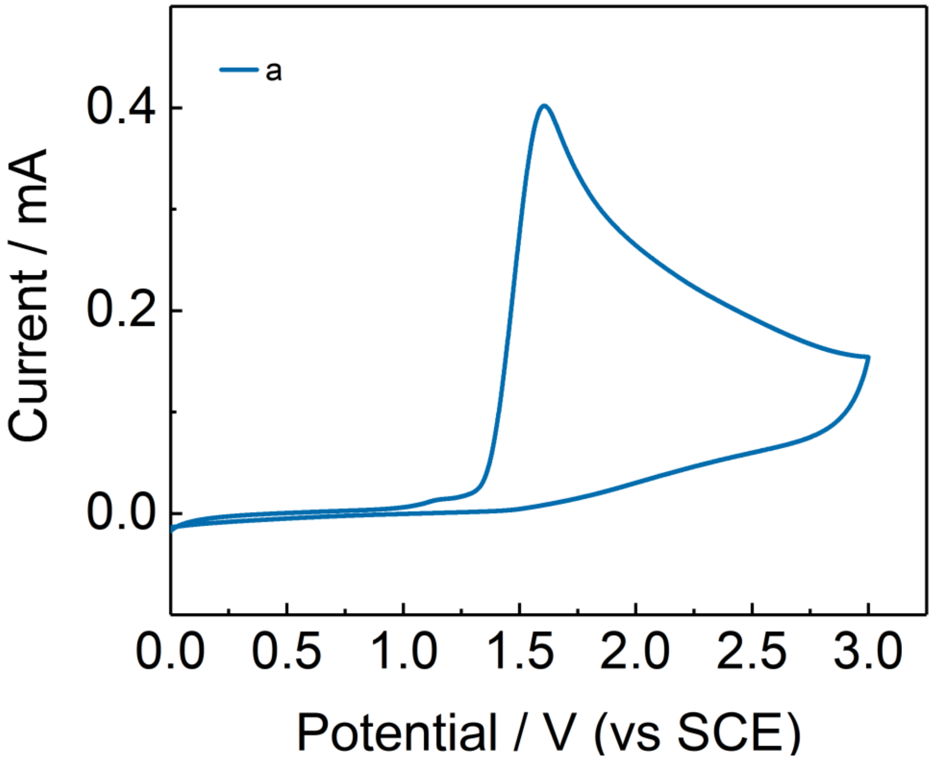


Figure S4. Cyclic voltammograms of 0.1 M $^{n}Bu_4NBF_4$ and related compounds in MeCN (20 mL) using glassy carbon working electrode, platinum plate and saturated calomel electrode as counter and reference electrode at 100 mV/s scan rate, (a) 0.2 mmol of **1zi**.

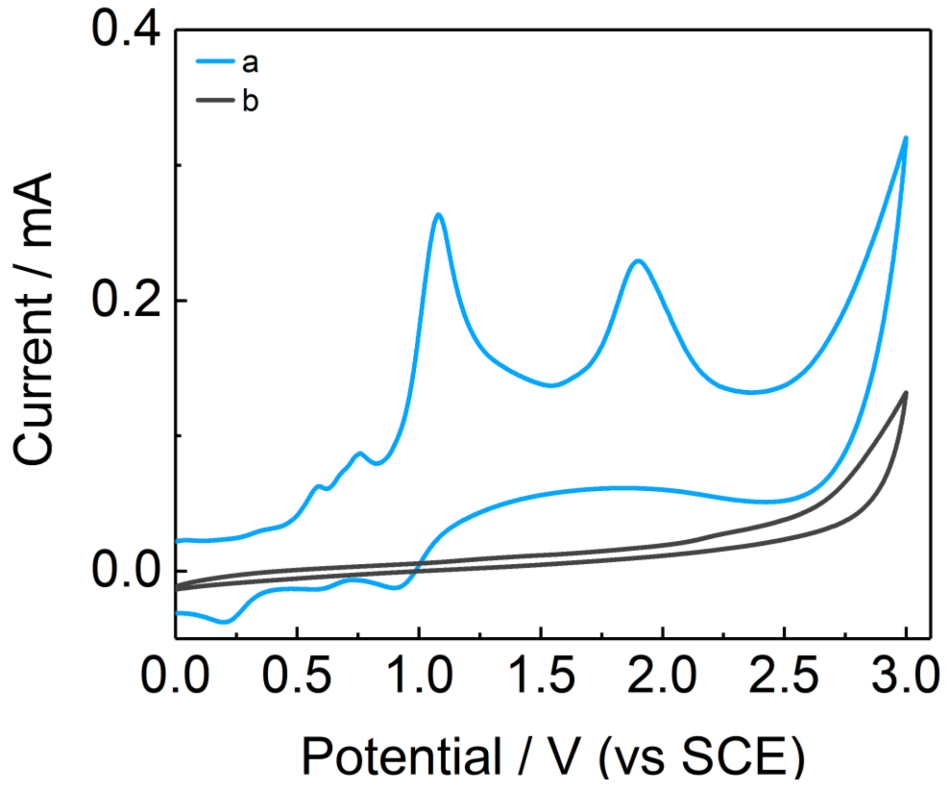
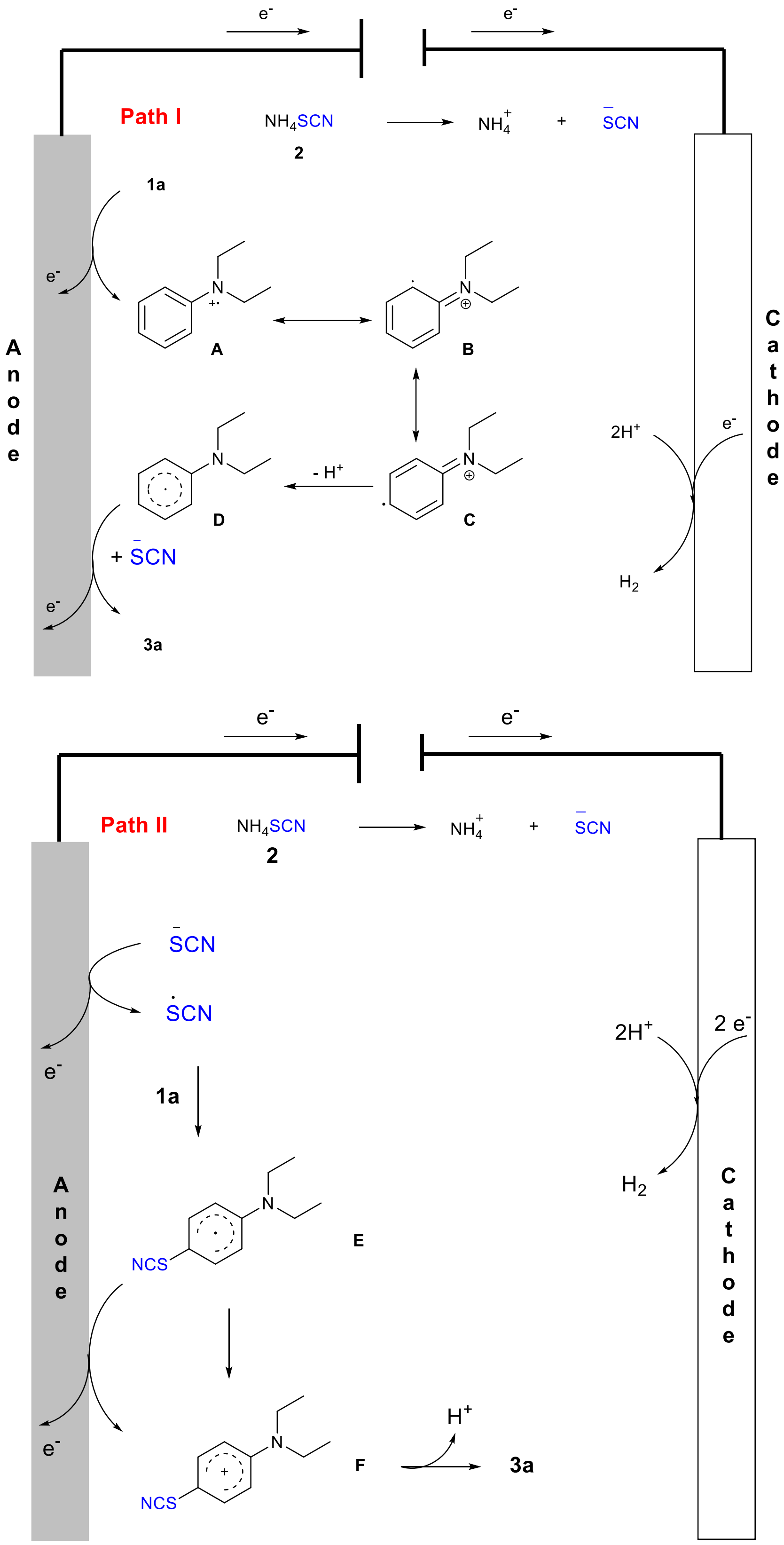


Figure S5. Cyclic voltammograms of 0.1 M ^{n}Bu$_4$NBF$_4$ and related compounds in MeCN (20 mL) using glassy carbon working electrode, platinum plate and saturated calomel electrode as counter and reference electrode at 100 mV/s scan rate, (a) 0.2 mmol of **3a**, (b) blank.



Scheme S4 Proposed reaction pathway.

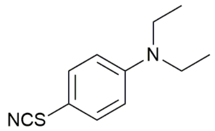
On the basic of the above experimental evidence, especially the CV experiments, and previous reports, we proposed a plausible mechanism for the electro-catalytic thiocyanation in Scheme S4 (Path I).

Firstly, substrate **1a** is oxidized at the anode to generate a radical cation specie **A**, and transformed into **B** subsequently. Next, the intermediate **B** isomerizes into **C** by electron transfer. Then, **C** is transformed into **D** though deprotonation. The resulting specie **D** reacts with SCN^- and then loses an electron at the anode to give the final product **3a**.

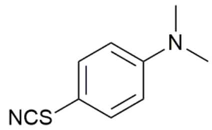
According to the viewpoint of resonance theory, the resonance structure in which two electron-deficient centers far away from each other should be the most stable. Thus, we also proposed the radical cation **C** might be more stable than intermediate **B**, which could be trapped by thiocyanate anion with difficulty and was less likely to generate *ortho*-thiocyanation product. In fact, a semblable phenomenon of para-regioselectivity was also widely reported in earlier studies, and it seems to be a common phenomenon in the reaction of aromatic amines involving a radical intermediate generated from a SEO process of amines.

Alternative, another proposed approach is initialized from the oxidation of SCN- (Path II). Since the substrate **1zi** having higher oxidation potential than NH_4SCN failed to work in this transformation, we speculate the reaction sequence involving intermediate **A** should be the major pathway.

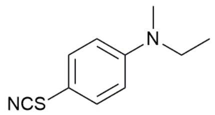
Detailed descriptions for products



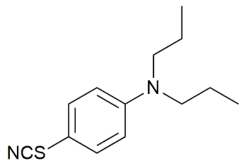
***N*,*N*-diethyl-4-thiocyanatoaniline (3a)**. [2] (The desired product was obtained as yellow liquid in 90% isolated, 72.3 mg). δ $_H$ (400 MHz, Chloroform-*d*) 7.37 (2 H, d, *J* 9.0), 6.62 (2 H, d, *J* 9.0), 3.35 (4 H, q, *J* 7.1), 1.16 (6 H, t, *J* 7.1); δ $_C$ (101 MHz, Chloroform-*d*) 149.32, 134.99, 112.82, 112.62, 104.97, 44.51, 12.39.



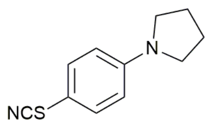
***N*,*N*-dimethyl-4-thiocyanatoaniline (3b)**. [2] (The desired product was obtained as light yellow solid in 89% isolated, 63.5 mg). δ $_H$ (400 MHz, Chloroform-*d*) 7.39 (2 H, d, *J* 8.4), 6.64 (2 H, d, *J* 8.4), 2.96 (6 H, s); δ $_C$ (101 MHz, Chloroform-*d*) 151.72, 134.46, 113.19, 112.63, 106.43, 40.14.



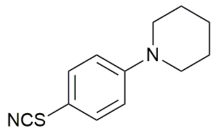
***N*-ethyl-*N*-methyl-4-thiocyanatoaniline (3c)**. (The desired product was obtained as yellow liquid in 85% isolated, 68.5 mg). δ $_H$ (400 MHz, Chloroform-*d*) 7.38 (2 H, d, *J* 8.1), 6.64 (2 H, d, *J* 8.2), 3.39 (2 H, q, *J* 7.0), 2.92 (3 H, s), 1.12 (3 H, t, *J* 7.1); δ $_C$ (101 MHz, Chloroform-*d*) 150.49, 134.71, 113.04, 112.70, 105.81, 46.62, 37.47, 11.28. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{13}N_2S^+$; 193.0799, found 193.0793.



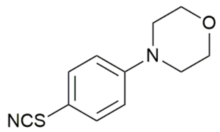
***N*,*N*-dipropyl-4-thiocyanatoaniline (3d)**. [3] (The desired product was obtained as yellow liquid in 86% isolated, 80.6 mg). δ $_H$ (400 MHz, Chloroform-*d*) 7.36 (2 H, d, *J* 9.1), 6.59 (2 H, d, *J* 9.1), 3.33 – 3.17 (4 H, m), 1.60 (4 H, h, *J* 7.4), 0.93 (6 H, t, *J* 7.4); δ $_C$ (101 MHz, Chloroform-*d*) δ 149.76, 134.90, 112.80, 112.72, 104.89, 52.79, 20.24, 11.39.



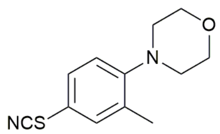
1-(4-thiocyanatophenyl)pyrrolidine (3e). [4] (The desired product was obtained as light yellow solid in 76% isolated, 62.1 mg). δ H (400 MHz, Chloroform-*d*) 7.39 (2 H, d, *J* 8.8), 6.51 (2 H, d, *J* 8.8), 3.27 (4 H, t, *J* 6.5), 2.10 – 1.94 (4 H, m); δ C (101 MHz, Chloroform-*d*) 149.25, 134.78, 112.94, 112.80, 105.27, 47.60, 25.51.



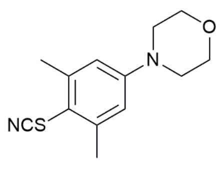
1-(4-thiocyanatophenyl)piperidine (3f). [3] (The desired product was obtained as colorless liquid in 80% isolated, 70.0 mg). δ H (400 MHz, Chloroform-*d*) 7.39 (2 H, d, *J* 9.0), 6.87 (2 H, d, *J* 9.0), 3.31 – 3.16 (4 H, m), 1.64 (6 H, dtd, *J* 16.4, 12.2, 11.4, 6.5); δ C (101 MHz, Chloroform-*d*) 153.02, 134.01, 116.45, 112.29, 108.98, 49.21, 25.40, 24.26.



4-(4-thiocyanatophenyl)morpholine (3g). [2] (The desired product was obtained as white solid in 87% isolated, 76.6 mg). δ H (400 MHz, Chloroform-*d*) 7.43 (2 H, d, *J* 8.9), 6.88 (2 H, d, *J* 8.9), 3.92 – 3.75 (4 H, m), 3.29 – 3.13 (4 H, m); δ C (101 MHz, Chloroform-*d*) 152.56, 133.71, 116.19, 111.92, 111.09, 66.57, 48.06.

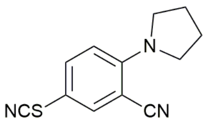


4-(2-methyl-4-thiocyanatophenyl)morpholine (3h). (The desired product was obtained as yellow liquid in 62% isolated, 58.1 mg). δ H (400 MHz, Chloroform-*d*) 7.35 (2 H, d, *J* 8.2), 7.02 (1 H, d, *J* 8.1), 3.93 – 3.77 (4 H, m), 3.00 – 2.84 (4 H, m), 2.32 (3 H, s); δ C (101 MHz, Chloroform-*d*) 153.12, 134.85, 134.07, 129.98, 120.51, 116.82, 111.41, 67.17, 51.89, 18.14. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}N_2OS^+$; 235.0905, found 235.0899.

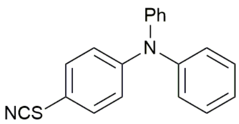


4-(3,5-dimethyl-4-thiocyanatophenyl)morpholine (3i). (The desired product was obtained as white solid in 78% isolated, 77.5 mg), m.p.:105.1– 105.7 °C. δ H (400 MHz, Chloroform-*d*) 6.67 (2 H, s), 3.93

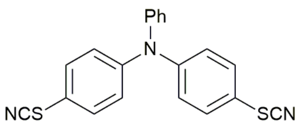
– 3.74 (4 H, m), 3.31 – 3.07 (4 H, m), 2.53 (6 H, s); δ C (101 MHz, Chloroform-*d*) 152.76, 144.03, 115.19, 111.45, 110.55, 66.65, 47.96, 22.51. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}N_2OS^+$; 249.1061, found 249.1057.



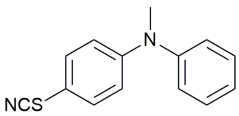
2-(pyrrolidin-1-yl)-5-thiocyanatobenzonitrile (3j). (The desired product was obtained as yellow liquid in 37% isolated, 33.9 mg). δ H (400 MHz, Chloroform-*d*) 7.64 (1 H, d, *J* 2.4), 7.48 (1 H, dd, *J* 9.2, 2.4), 6.67 (1 H, d, *J* 9.2), 3.64 (4 H, t, *J* 6.6), 2.15 – 1.96 (4 H, m); δ C (101 MHz, Chloroform-*d*) 150.53, 140.82, 137.71, 119.64, 116.31, 111.32, 106.91, 95.36, 50.10, 25.70. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}N_3S^+$; 230.0752, found 230.0747.



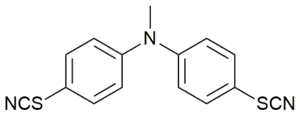
***N*,*N*-diphenyl-4-thiocyanatoaniline (3k)**. [3] (The desired product was obtained as light yellow liquid in 57% isolated, 68.9 mg). δ H (400 MHz, Chloroform-*d*) 7.34 (2 H, d, *J* 8.6), 7.28 (4 H, t, *J* 7.7), 7.09 (6 H, d, *J* 14.8), 7.01 (2 H, d, *J* 8.6); δ C (101 MHz, Chloroform-*d*) 150.03, 146.69, 133.13, 129.71, 125.53, 124.45, 122.80, 113.57, 111.60.



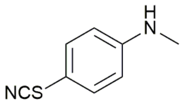
***N*-phenyl-4-thiocyanato-*N*-(4-thiocyanatophenyl)aniline (3k')**. [5] (The desired product was obtained as white solid in 38% isolated, 54.6 mg). δ H (400 MHz, Chloroform-*d*) 7.42 (4 H, d, *J* 8.2), 7.34 (2 H, t, *J* 7.6), 7.18 (1 H, t, *J* 7.4), 7.15 – 7.04 (6 H, m); δ C (101 MHz, Chloroform-*d*) 148.77, 145.86, 132.85, 130.06, 126.13, 125.52, 124.62, 116.40, 111.06.



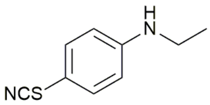
***N*-methyl-*N*-phenyl-4-thiocyanatoaniline (3l)**. [3] (The desired product was obtained as yellow liquid in 51% isolated, 49.0 mg). δ H (400 MHz, Chloroform-*d*) 7.37 (2 H, t, *J* 2.1), 7.35 (2 H, d, *J* 2.9), 7.19 – 7.14 (3 H, m), 6.82 – 6.78 (2 H, m), 3.30 (3 H, s); δ C (101 MHz, Chloroform-*d*) 150.84, 147.52, 133.89, 129.92, 125.44, 125.26, 116.63, 112.25, 109.55, 40.29.



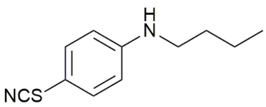
***N*-methyl-4-thiocyanato-*N*-(4-thiocyanatophenyl)aniline (3l')**. (The desired product was obtained as brown liquid in 33% isolated, 39.3 mg). δ H (400 MHz, Chloroform-*d*) 7.48 (4 H, d, *J* 8.7), 7.07 (4 H, d, *J* 8.7), 3.35 (3 H, s); δ C (101 MHz, Chloroform-*d*) 149.48, 133.16, 121.98, 115.24, 111.34, 40.22. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}N_3S_2^+$; 298.0472, found 298.0467.



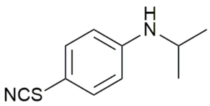
***N*-methyl-4-thiocyanatoaniline (3m)**. [6] (The desired product was obtained as yellow liquid in 81% isolated, 26.6 mg). δ H (400 MHz, Chloroform-*d*) 7.36 (2 H, d, *J* 8.3), 6.57 (2 H, d, *J* 8.3), 3.69 (1 H, s), 2.83 (3 H, s). δ C (101 MHz, Chloroform-*d*) 151.17, 134.69, 113.42, 112.67, 107.45, 30.25.



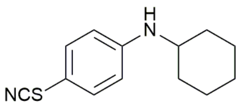
***N*-ethyl-4-thiocyanatoaniline (3n)**. [6] (The desired product was obtained as light yellow solid in 83% isolated, 29.6 mg). δ H (400 MHz, Chloroform-*d*) 7.35 (2 H, d, *J* 8.7), 6.56 (2 H, d, *J* 8.7), 3.96 (1 H, s), 3.15 (2 H, q, *J* 7.2), 1.25 (3 H, t, *J* 7.2); δ C (101 MHz, Chloroform-*d*) 150.29, 134.75, 113.67, 112.67, 107.31, 38.07, 14.55.



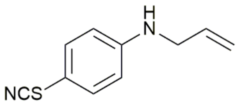
***N*-butyl-4-thiocyanatoaniline (3o)**. [3] (The desired product was obtained as yellow liquid in 80% isolated, 33.0 mg). δ H (400 MHz, Chloroform-*d*) 7.34 (2 H, d, *J* 8.7), 6.56 (2 H, d, *J* 8.7), 3.79 (1 H, s), 3.10 (2 H, t, *J* 7.1), 1.59 (2 H, p, *J* 7.2), 1.42 (2 H, h, *J* 7.3), 0.96 (3 H, t, *J* 7.3); δ C (101 MHz, Chloroform-*d*) 150.42, 134.77, 113.64, 112.68, 107.12, 43.21, 31.32, 20.23, 13.86.



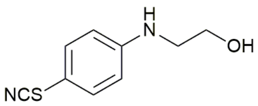
***N*-isopropyl-4-thiocyanatoaniline (3p)**. [6] (The desired product was obtained as yellow solid in 87% isolated, 33.5 mg). δ H (400 MHz, Chloroform-*d*) 7.34 (2 H, d, *J* 7.9), 6.54 (2 H, d, *J* 8.0), 3.89 (1 H, s), 3.61 (1 H, p, *J* 6.2), 1.21 (3 H, s), 1.20 (3 H, s); δ C (101 MHz, Chloroform-*d*) 149.46, 134.84, 114.06, 112.71, 106.88, 44.08, 22.69.



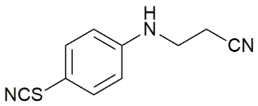
***N*-cyclohexyl-4-thiocyanatoaniline (3q)**. (The desired product was obtained as light yellow liquid in 78% isolated, 36.2 mg). δ H (400 MHz, Chloroform-*d*) 7.33 (2 H, d, *J* 8.6), 6.54 (2 H, d, *J* 8.6), 3.96 (1 H, s), 3.24 (1 H, ddd, *J* 13.7, 10.0, 3.6), 2.01 (2 H, d, *J* 9.9), 1.76 (2 H, dt, *J* 12.7, 3.5), 1.65 (1 H, d, *J* 12.7), 1.37 (2 H, q, *J* 12.1), 1.28 – 1.13 (3 H, m); δ C (101 MHz, Chloroform-*d*) 149.36, 134.88, 113.97, 112.70, 106.69, 51.42, 33.07, 25.77, 24.87. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}N_2S^+$; 233.1112, found 233.1106.



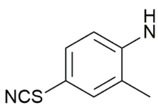
***N*-allyl-4-thiocyanatoaniline (3r)**. [3] (The desired product was obtained as light yellow liquid in 72% isolated, 27.4 mg). δ H (400 MHz, Chloroform-*d*) 7.34 (2 H, d, *J* 8.8), 6.58 (2 H, d, *J* 8.8), 5.88 (1 H, ddt, *J* 17.1, 10.3, 5.2), 5.34 – 5.13 (2 H, m), 4.26 (1 H, s), 3.76 (2 H, d, *J* 4.6); δ C (101 MHz, Chloroform-*d*) 150.04, 134.69, 134.26, 116.76, 114.00, 112.73, 107.68, 45.91.



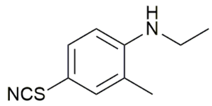
2-((4-thiocyanatophenyl)amino)ethan-1-ol (3s). [3] (The desired product was obtained as white solid in 80% isolated, 31.1 mg). δ H (400 MHz, Chloroform-*d*) 7.38 (2 H, d, *J* 8.7), 6.63 (2 H, d, *J* 8.7), 4.43 (1 H, s), 3.94 – 3.78 (2 H, m), 3.30 (2 H, t, *J* 5.1), 1.77 (1 H, s); δ C (101 MHz, Chloroform-*d*) 150.13, 134.70, 114.11, 112.55, 108.28, 60.99, 45.46.



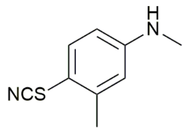
3-((4-thiocyanatophenyl)amino)propanenitrile (3t). (The desired product was obtained as brown liquid in 89% isolated, 36.2 mg). δ H (400 MHz, Chloroform-*d*) 7.39 (2 H, d, *J* 8.8), 6.61 (2 H, d, *J* 8.8), 4.52 (1 H, s), 3.50 (2 H, q, *J* 5.9), 2.63 (2 H, t, *J* 6.5); δ C (101 MHz, Chloroform-*d*) 148.50, 134.71, 118.03, 114.07, 112.48, 109.45, 39.27, 18.04. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{10}N_3S^+$; 204.0595, found 204.0590.



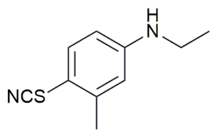
***N*,2-dimethyl-4-thiocyanatoaniline (3u)**. [3] (The desired product was obtained as white solid in 79% isolated, 28.1 mg). δ H (400 MHz, Chloroform-*d*) 7.34 (1 H, d, *J* 10.2), 7.24 (1 H, s), 6.55 (1 H, d, *J* 8.5), 3.92 (1 H, s), 2.89 (3 H, s), 2.10 (3 H, s); δ C (101 MHz, Chloroform-*d*) 149.23, 134.50, 132.85, 123.64, 112.81, 109.95, 106.97, 30.43, 17.18.



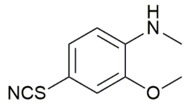
***N*-ethyl-2-methyl-4-thiocyanatoaniline (3v)**. [7] (The desired product was obtained as brown liquid in 83% isolated, 31.9 mg). δ H (400 MHz, Chloroform-*d*) 7.31 (1 H, d, *J* 8.5), 7.24 (1 H, s), 6.56 (1 H, d, *J* 8.5), 3.37 (1 H, s), 3.20 (2 H, q, *J* 7.1), 2.10 (3 H, s), 1.30 (3 H, t, *J* 7.1); δ C (101 MHz, Chloroform-*d*) 148.32, 134.65, 132.80, 123.50, 112.79, 110.43, 106.86, 38.18, 17.25, 14.68.



***N*,3-dimethyl-4-thiocyanatoaniline (3w)**. [3] (The desired product was obtained as light yellow liquid in 65% isolated, 23.2 mg). δ H (400 MHz, Chloroform-*d*) 7.38 (1 H, d, *J* 8.5), 6.49 (1 H, d, *J* 2.5), 6.41 (1 H, dd, *J* 8.5, 2.6), 4.04 (1 H, s), 2.83 (3 H, s), 2.47 (3 H, s); δ C (101 MHz, Chloroform-*d*) 151.69, 143.00, 136.39, 114.57, 112.24, 111.16, 107.29, 30.24, 21.18.

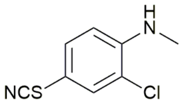


***N*-ethyl-3-methyl-4-thiocyanatoaniline (3x)**. [8] (The desired product was obtained as light yellow solid in 67% isolated, 25.8 mg). δ H (400 MHz, Chloroform-*d*) 7.34 (1 H, d, *J* 8.5), 6.47 (1 H, d, *J* 2.5), 6.39 (1 H, dd, *J* 8.5, 2.6), 3.95 (1 H, s), 3.12 (2 H, q, *J* 7.2), 2.45 (3 H, s), 1.23 (3 H, t, *J* 7.2); δ C (101 MHz, Chloroform-*d*) 150.90, 143.01, 136.45, 114.86, 112.41, 111.38, 106.85, 38.01, 21.20, 14.60.

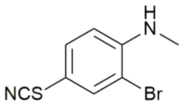


2-methoxy-*N*-methyl-4-thiocyanatoaniline (3y). (The desired product was obtained as yellow solid in 56% isolated, 21.8 mg), m.p.:74.2–75.2 °C. δ H (400 MHz, Chloroform-*d*) 7.11 (1 H, dd, *J* 8.3, 2.0), 6.90 (1 H, d, *J* 2.0), 6.50 (1 H, d, *J* 8.3), 4.58 (1 H, s), 3.85 (3 H, s), 2.86 (3 H, s); δ C (101 MHz, Chloroform-

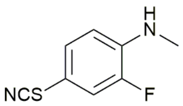
d) 147.27, 141.63, 127.72, 113.38, 112.73, 109.17, 106.17, 55.76, 29.86. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{11}N_2OS^+$; 195.0592, found 195.0587.



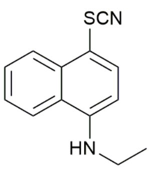
2-chloro-*N*-methyl-4-thiocyanatoaniline (3z). [9] (The desired product was obtained as light yellow liquid in 84% isolated, 33.4 mg). δ_H (400 MHz, Chloroform-*d*) 7.48 (1 H, s), 7.37 (1 H, d, *J* 8.6), 6.61 (1 H, d, *J* 8.6), 4.70 (1 H, s), 2.91 (3 H, s); δ_C (101 MHz, Chloroform-*d*) 146.90, 133.46, 133.39, 119.63, 111.90, 111.21, 107.52, 30.13.



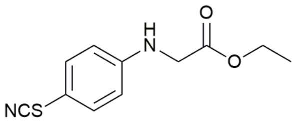
2-bromo-*N*-methyl-4-thiocyanatoaniline (3za). (The desired product was obtained as yellow liquid in 92% isolated, 44.7 mg). δ_H (400 MHz, Chloroform-*d*) 7.64 (1 H, d, *J* 2.2), 7.41 (1 H, dd, *J* 8.6, 2.2), 6.59 (1 H, d, *J* 8.6), 4.72 (1 H, s), 2.91 (3 H, d, *J* 5.0); δ_C (101 MHz, Chloroform-*d*) 147.82, 136.67, 134.03, 111.96, 111.18, 109.66, 107.93, 30.37. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_8N_2BrS^+$; 242.9591, found 242.9585.



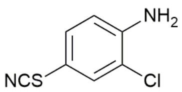
2-fluoro-*N*-methyl-4-thiocyanatoaniline (3zb). [3] (The desired product was obtained as yellow liquid in 75% isolated, 27.3 mg). δ_H (400 MHz, Chloroform-*d*) 7.28 – 7.24 (1 H, m), 7.21 (1 H, dd, *J* 10.9, 2.1), 6.65 (1 H, t, *J* 8.7), 4.30 (1 H, s), 2.90 (3 H, s); δ_C (101 MHz, Chloroform-*d*) 150.99 (d, *J* 243), 140.15 (d, *J* 12), 130.59 (d, *J* 3), 118.86(d, *J* 21), 111.92, 111.81(d, *J* 5), 106.74 (d, *J* 8), 29.79. δ_F (376 MHz, Chloroform-*d*) -134.04 (s, 1 F).



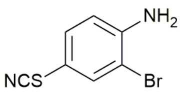
***N*-ethyl-4-thiocyanatonaphthalen-1-amine (3zc)**. (The desired product was obtained as brown solid in 68% isolated, 31.0 mg), m.p.:106.1–106.9 °C. δ_H (400 MHz, Chloroform-*d*) 8.32 (1 H, d, *J* 8.4), 7.78 (1 H, d, *J* 8.5), 7.73 (1 H, d, *J* 8.2), 7.63 (1 H, d, *J* 15.3), 7.48 (1 H, t, *J* 8.1), 6.48 (1 H, d, *J* 8.2), 4.72 (1 H, s), 3.29 (2 H, q, *J* 7.1), 1.38 (3 H, t, *J* 7.2); δ_C (101 MHz, Chloroform-*d*) δ 147.14, 136.99, 133.97, 127.96, 125.74, 125.55, 123.92, 120.56, 112.43, 104.12, 103.62, 38.40, 14.44. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}N_2S^+$; 229.0799, found 229.0796.



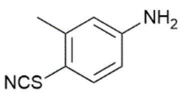
ethyl (4-thiocyanatophenyl)glycinate (3zd). [10] (The desired product was obtained as white solid in 89% isolated, 42,1 mg). δ_H (400 MHz, Chloroform-*d*) 7.36 (2 H, d, *J* 8.5), 6.57 (2 H, d, *J* 8.6), 4.75 (1 H, s), 4.24 (2 H, q, *J* 7.1), 3.88 (2 H, d, *J* 4.7), 1.29 (3 H, t, *J* 7.2); δ_C (101 MHz, Chloroform-*d*) 170.41, 148.98, 134.52, 114.06, 112.39, 108.92, 61.65, 45.18, 14.22.



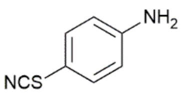
2-chloro-4-thiocyanatoaniline (3ze). [11] (The desired product was obtained as yellow liquid in 52% isolated, 19.2 mg). δ_H (400 MHz, Chloroform-*d*) 7.48 (1 H, d, *J* 2.2), 7.26 (1 H, dd, *J* 8.5, 2.2), 6.75 (1 H, d, *J* 8.5), 4.41 (2 H, s); δ_C (101 MHz, Chloroform-*d*) 145.42, 133.85, 132.67, 119.67, 116.46, 111.81, 109.86.



2-bromo-4-thiocyanatoaniline (3zf). [6] (The desired product was obtained as yellow liquid in 35% isolated, 16.0 mg). δ_H (400 MHz, Chloroform-*d*) 7.64 (1 H, d, *J* 1.9), 7.31 (1 H, dd, *J* 8.5, 2.0), 6.75 (1 H, d, *J* 8.5), 4.45 (2 H, s); δ_C (101 MHz, Chloroform-*d*) 146.54, 136.92, 133.29, 116.25, 111.79, 110.19, 109.22.



3-methyl-4-thiocyanatoaniline (3zg). [6] (The desired product was obtained as yellow solid in 78% isolated, 25.6 mg). δ_H (400 MHz, Chloroform-*d*) 7.28 (2 H, d, *J* 8.6), 6.60 (2 H, d, *J* 8.6), 4.07 (2 H, s); δ_C (101 MHz, Chloroform-*d*) 149.28, 134.60, 116.13, 112.96, 108.83.



4-thiocyanatoaniline (3zh). [2] (The desired product was obtained as white solid in 72% isolated, 21.6 mg). δ_H (400 MHz, Chloroform-*d*) 7.25 (1 H, d, *J* 8.4), 6.48 (1 H, d, *J* 2.5), 6.39 (1 H, dd, *J* 8.4, 2.6), 3.87 (2 H, s), 2.34 (3 H, s); δ_C (101 MHz, Chloroform-*d*) 149.60, 143.03, 136.31, 117.32, 113.78, 112.28, 108.86, 20.97.

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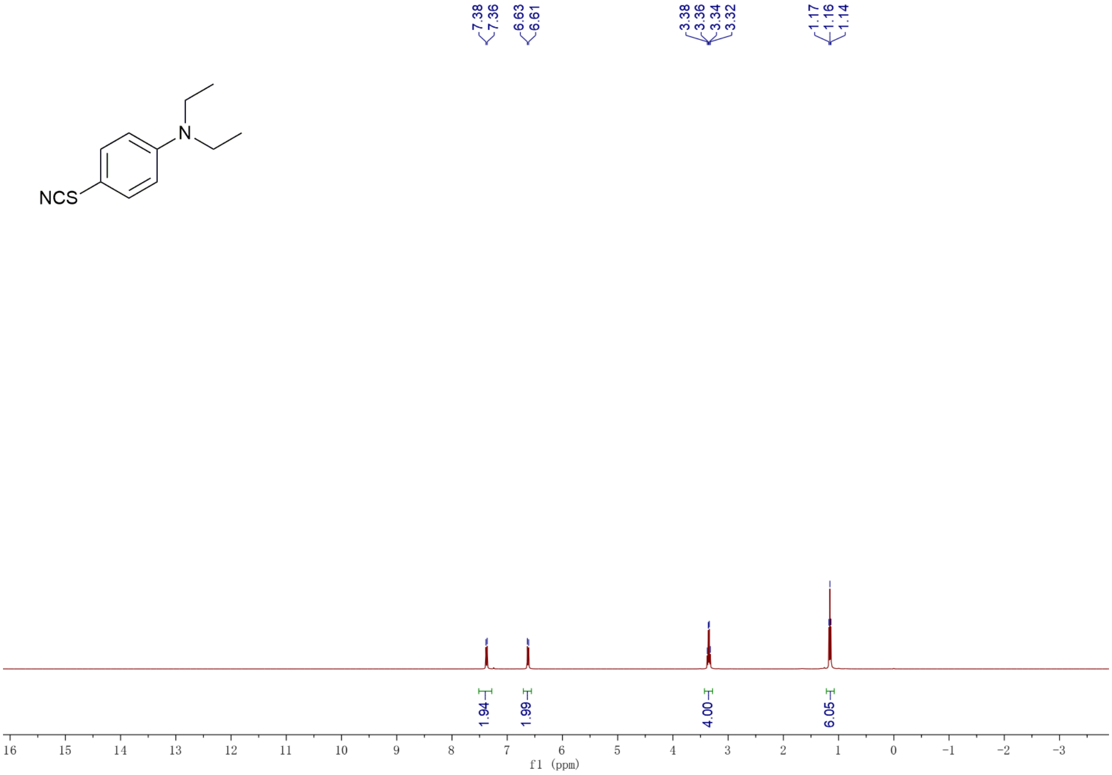
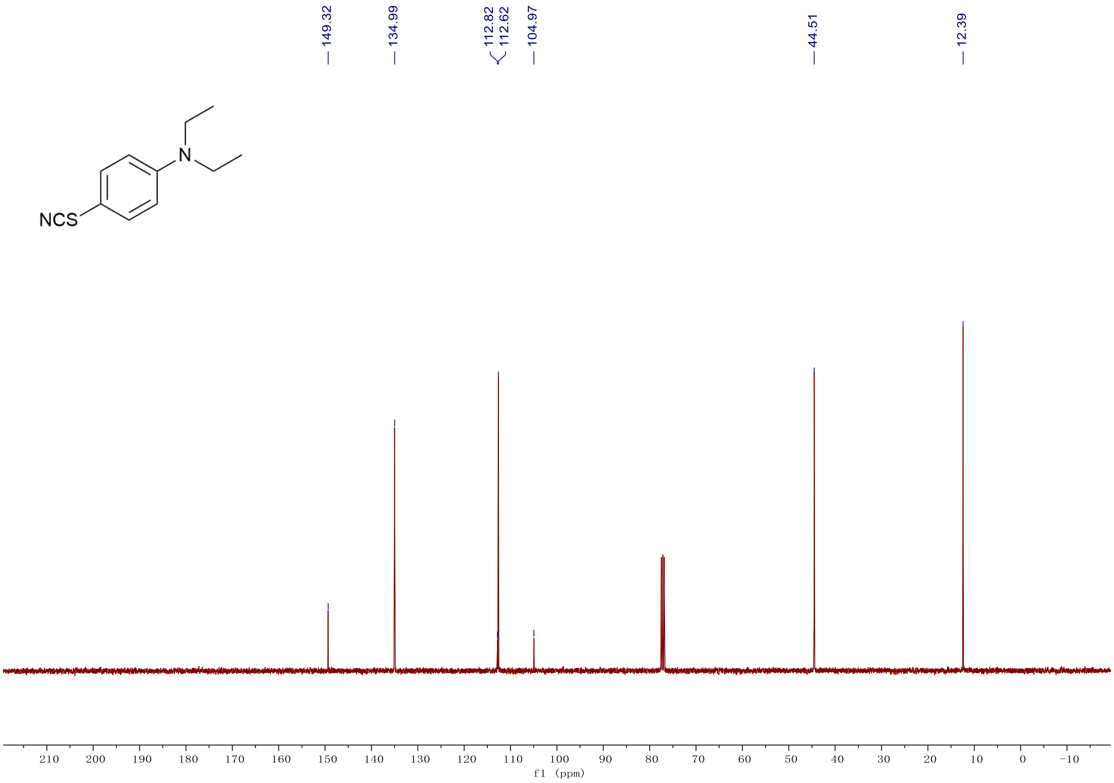
Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

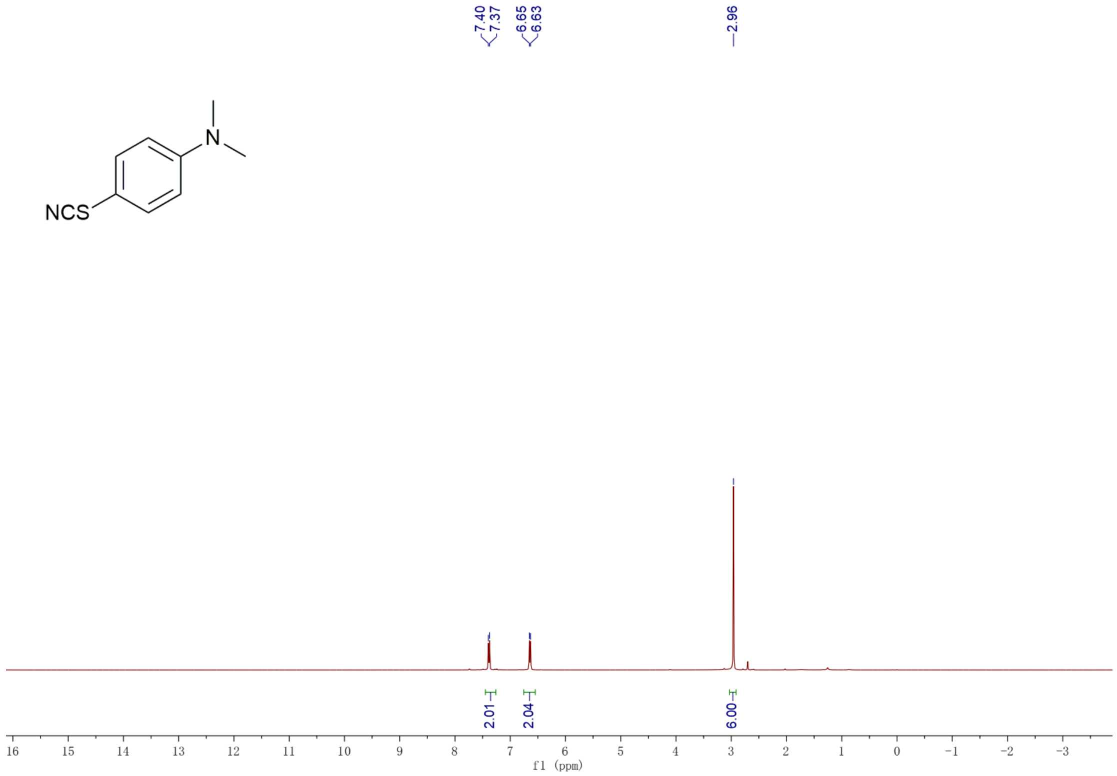
^{1}H NMR (400 MHz, CDCl$_3$) spectrum of 3a



^{13}C NMR (100 MHz, CDCl$_3$) spectrum of 3a



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3b



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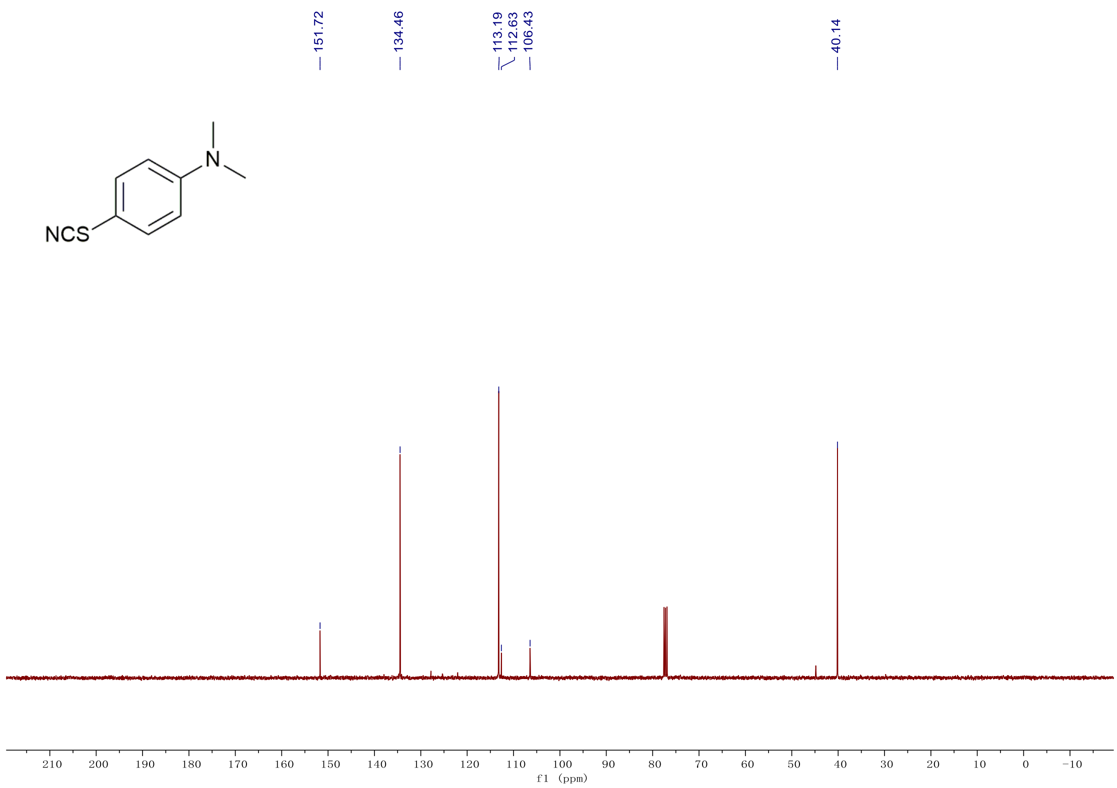

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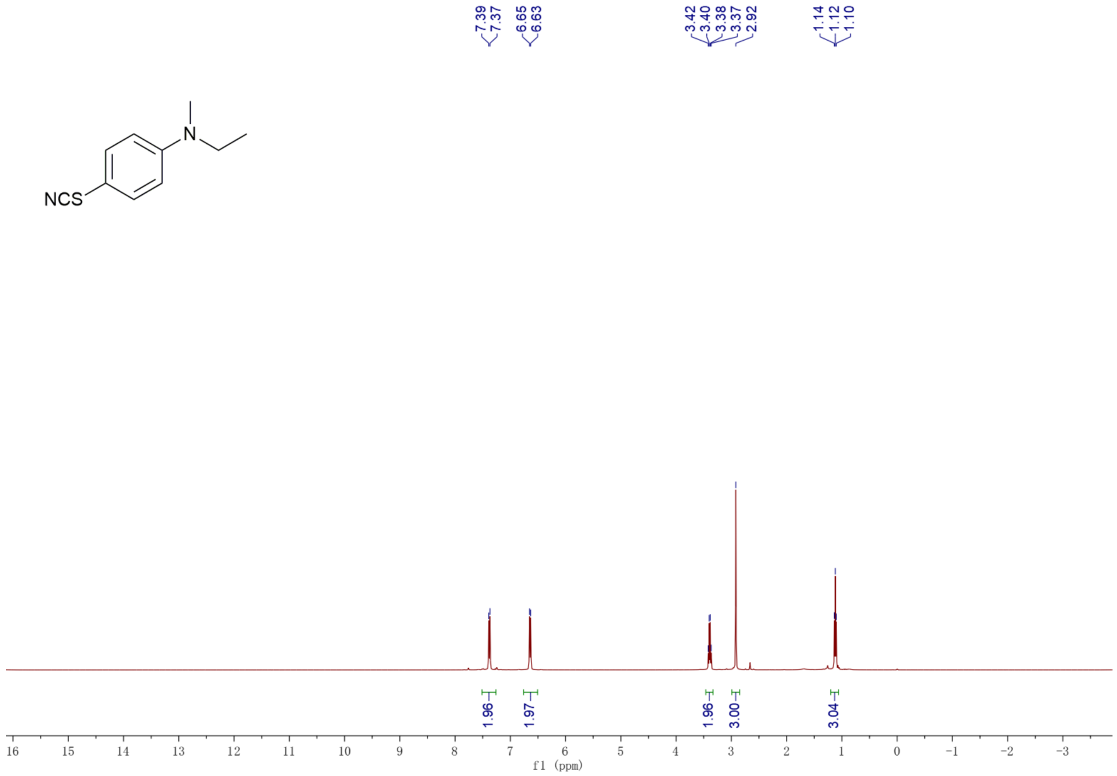

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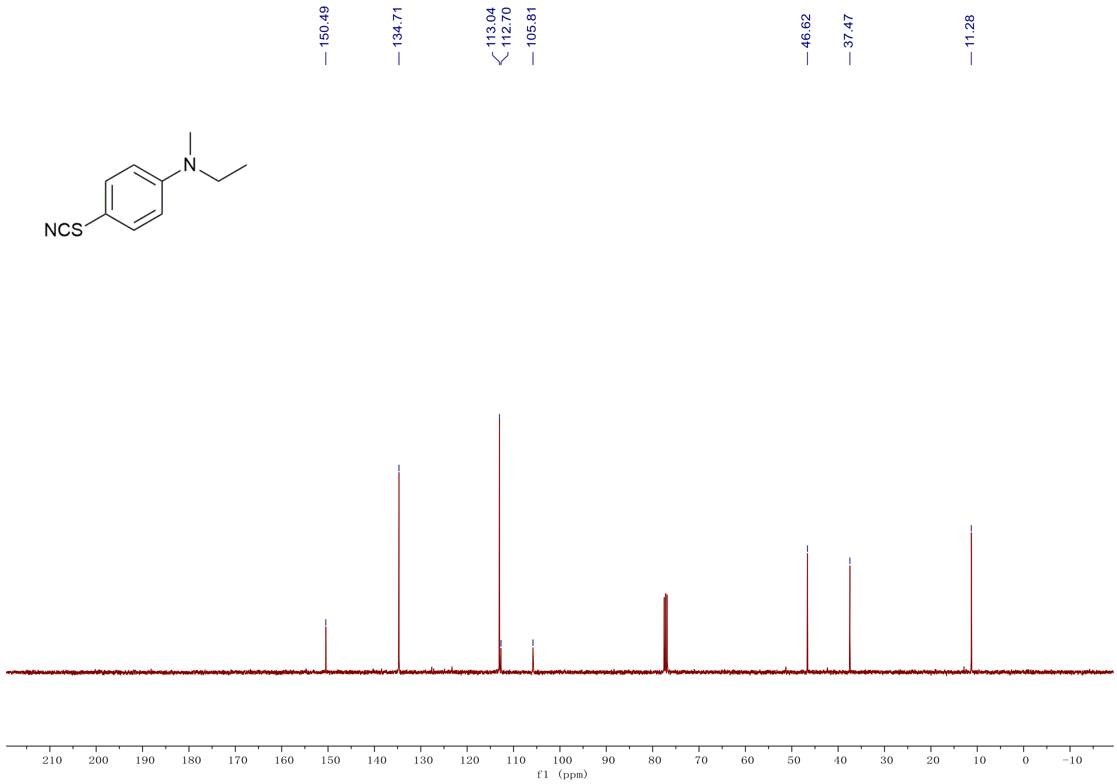

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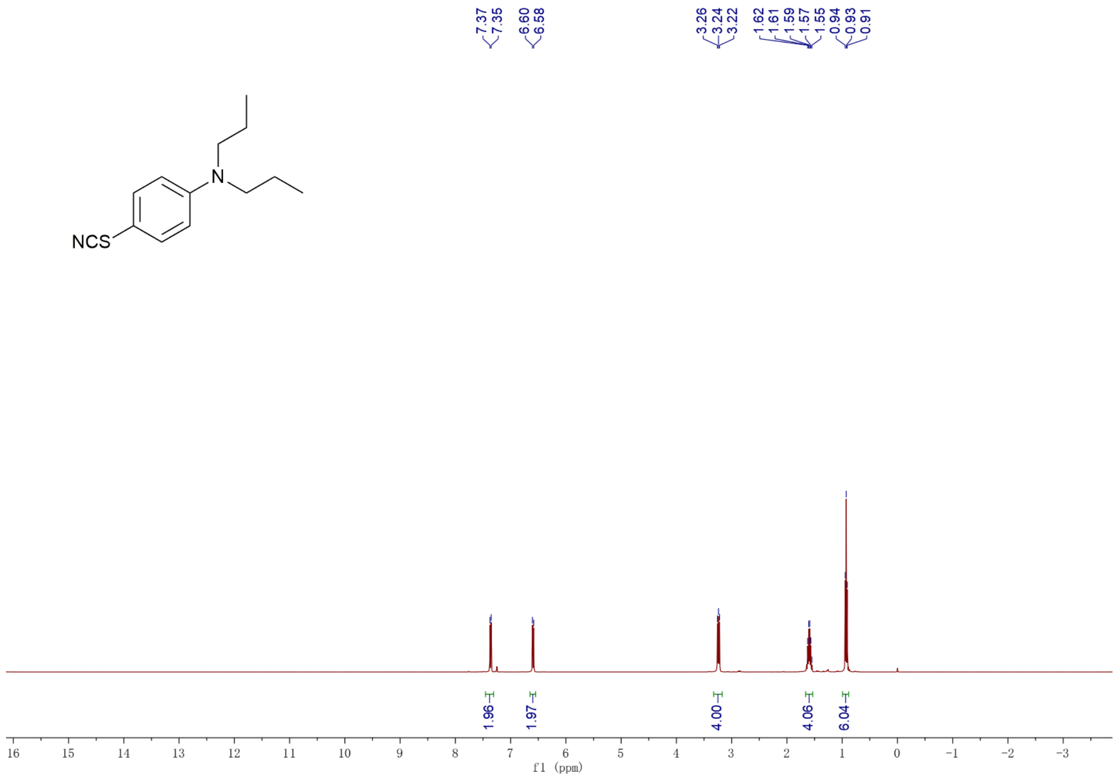

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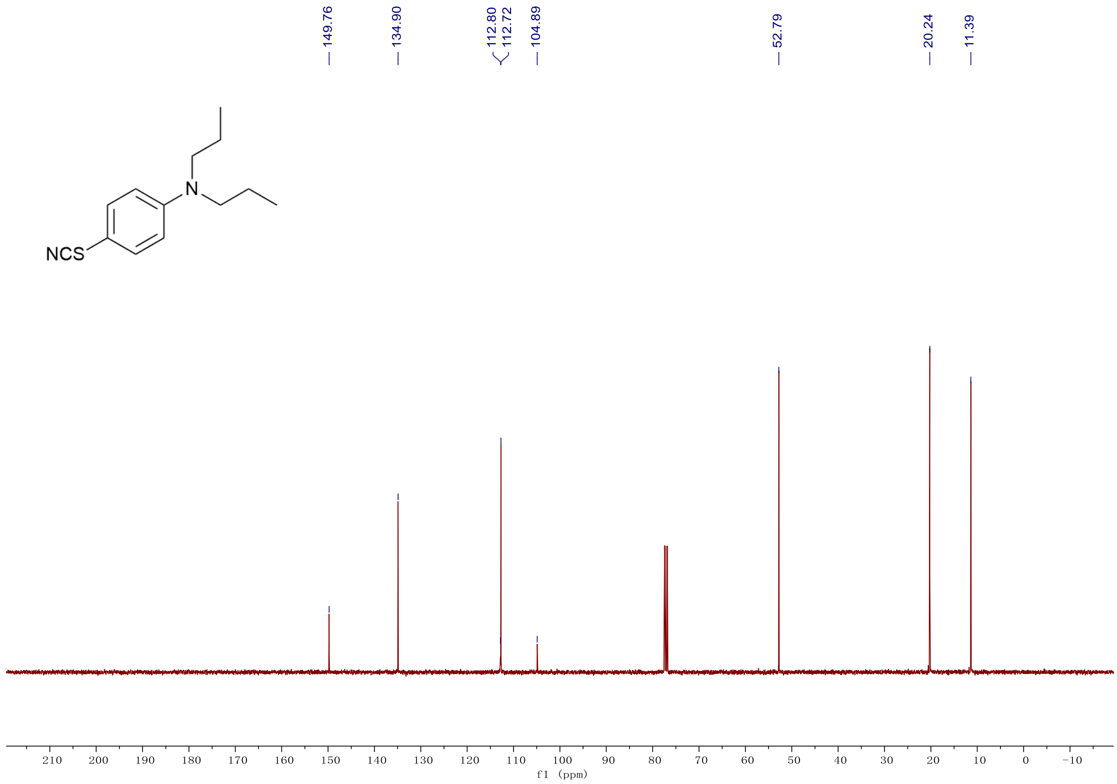

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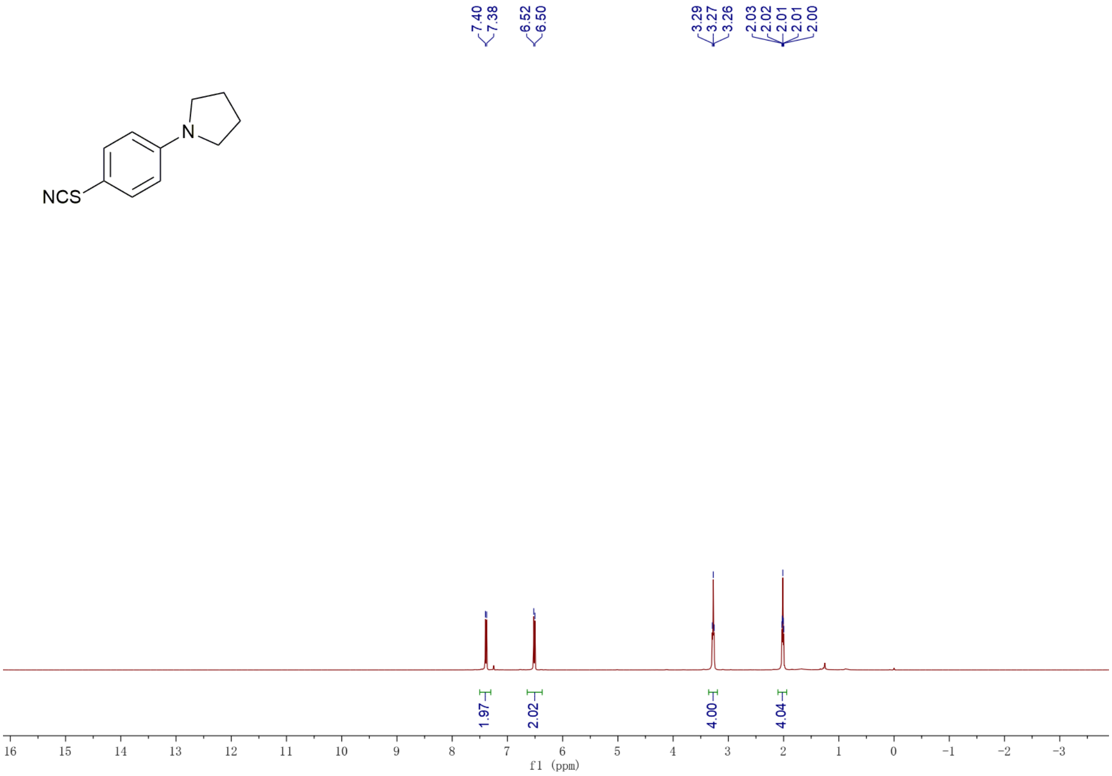

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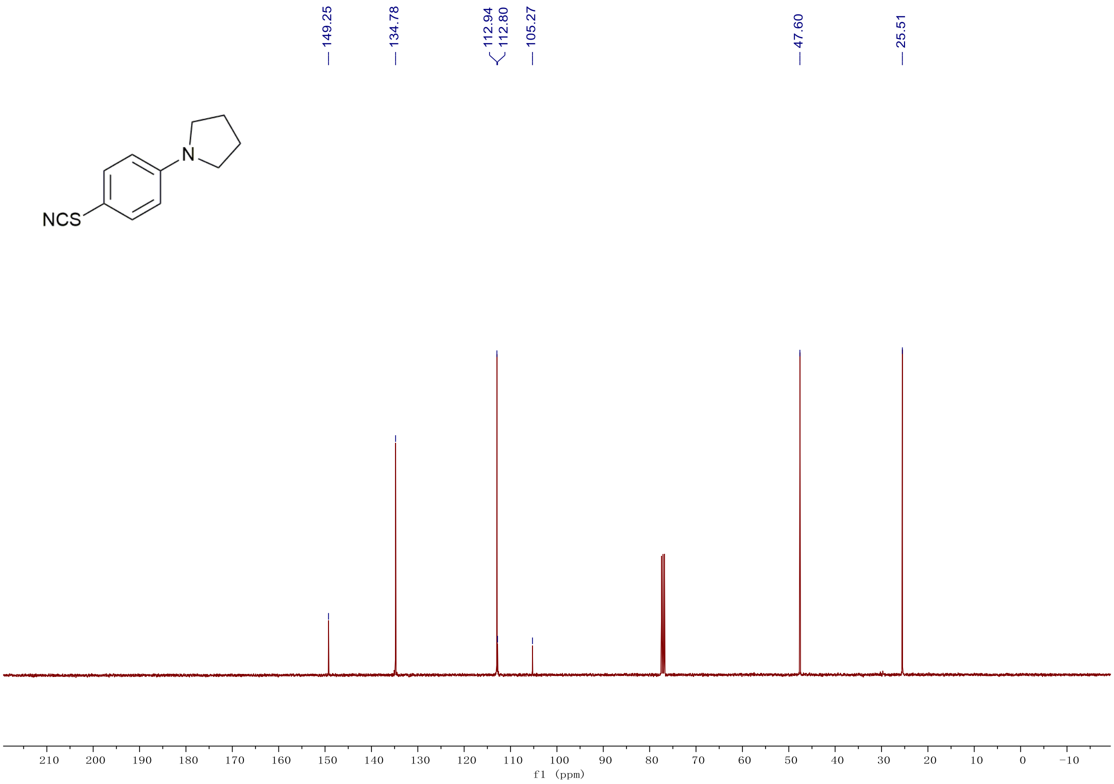

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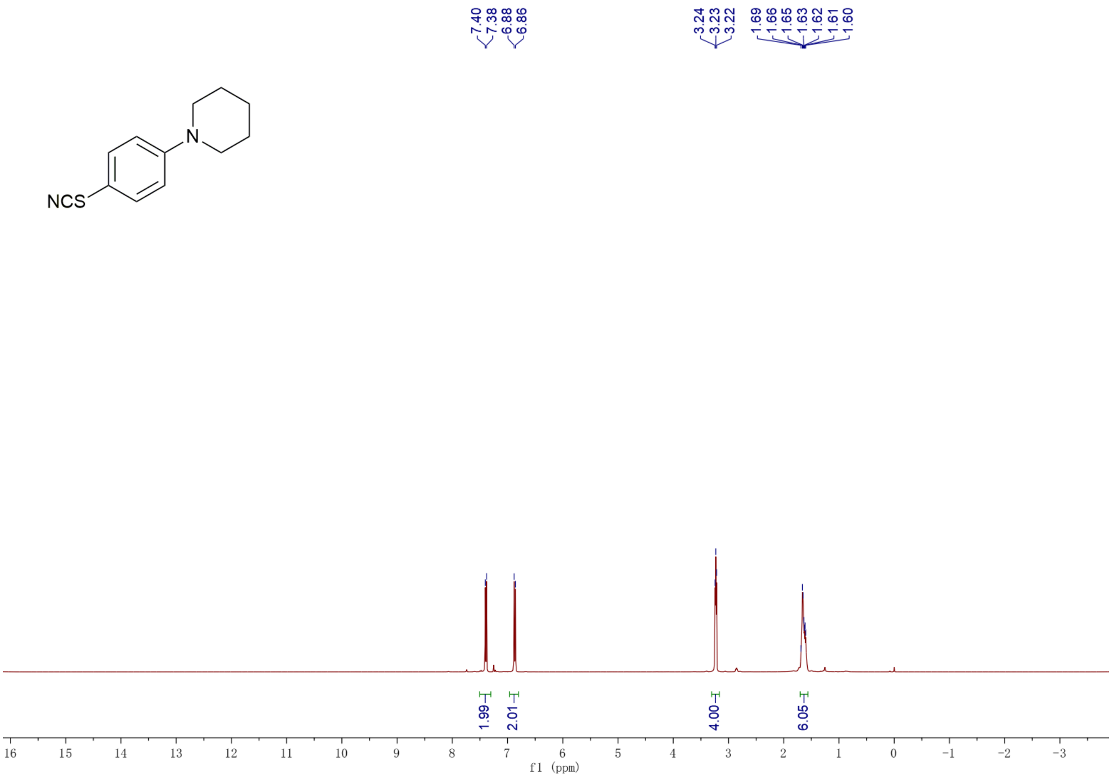
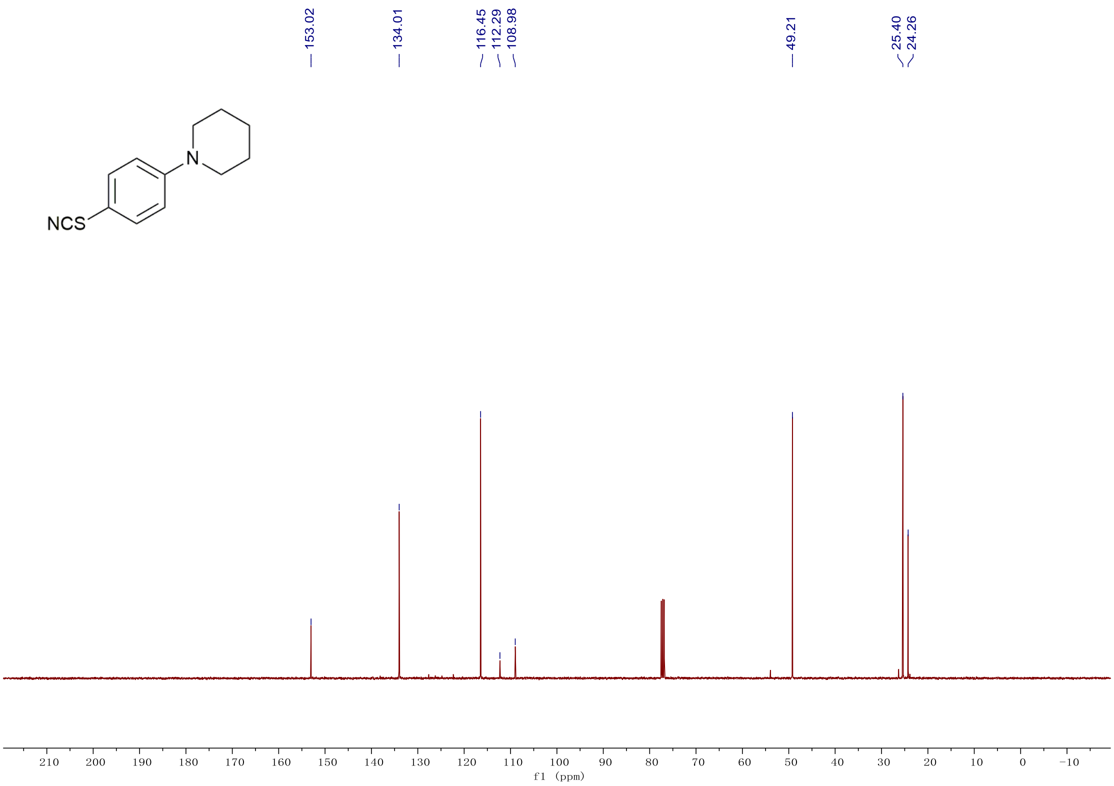
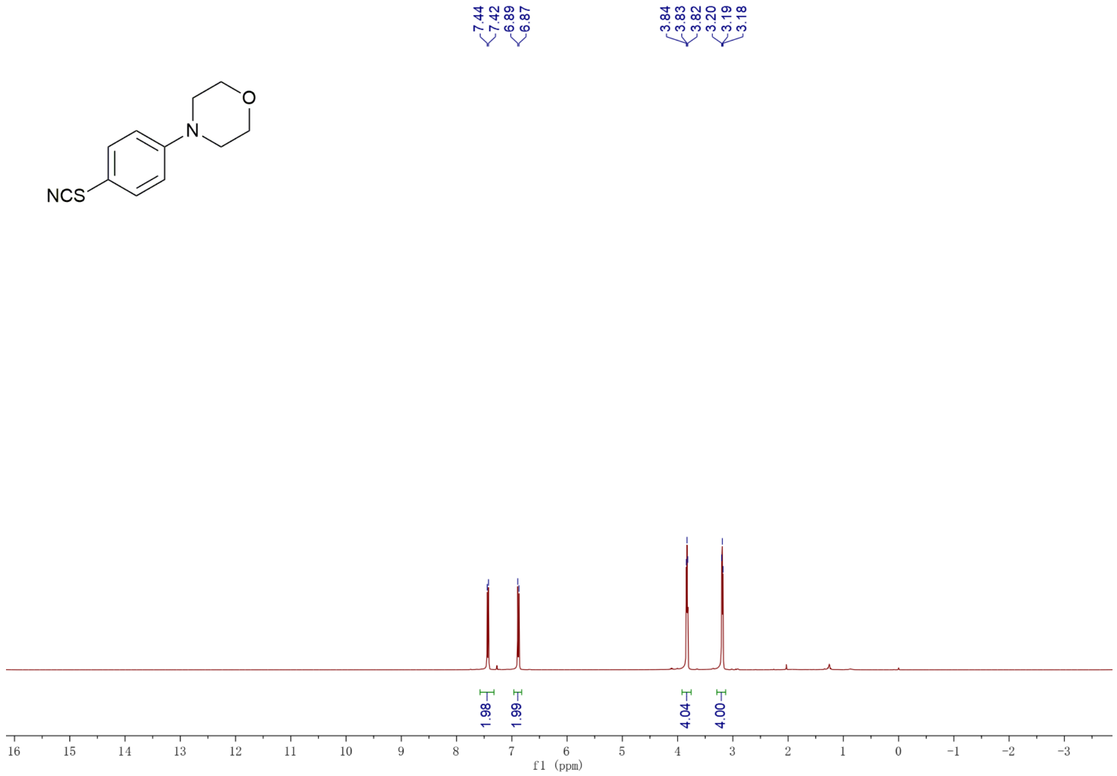


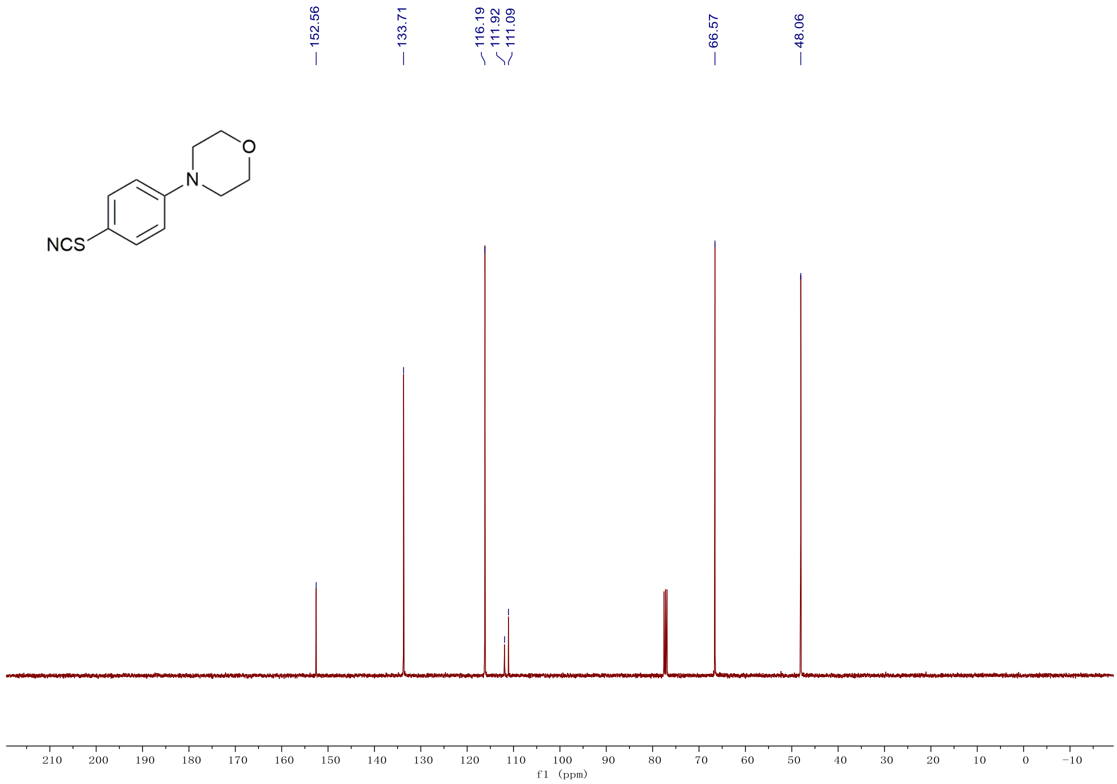
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3f



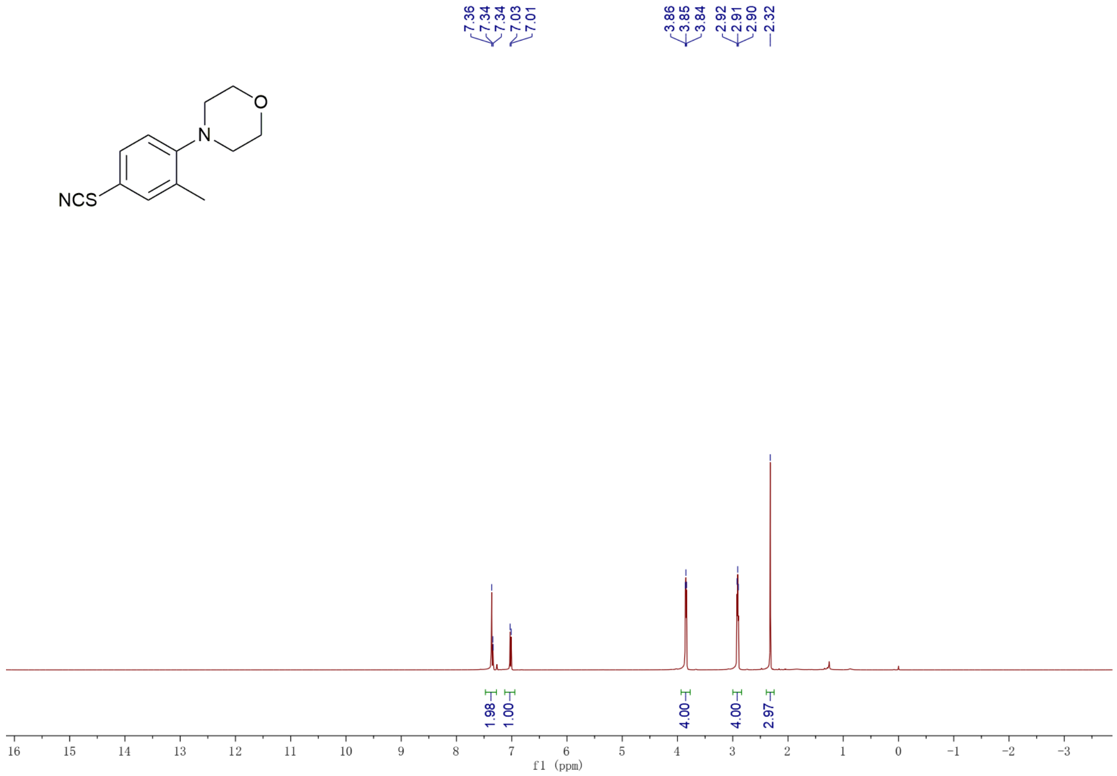
^1H NMR (400 MHz, $CDCl_3$) spectrum of 3g



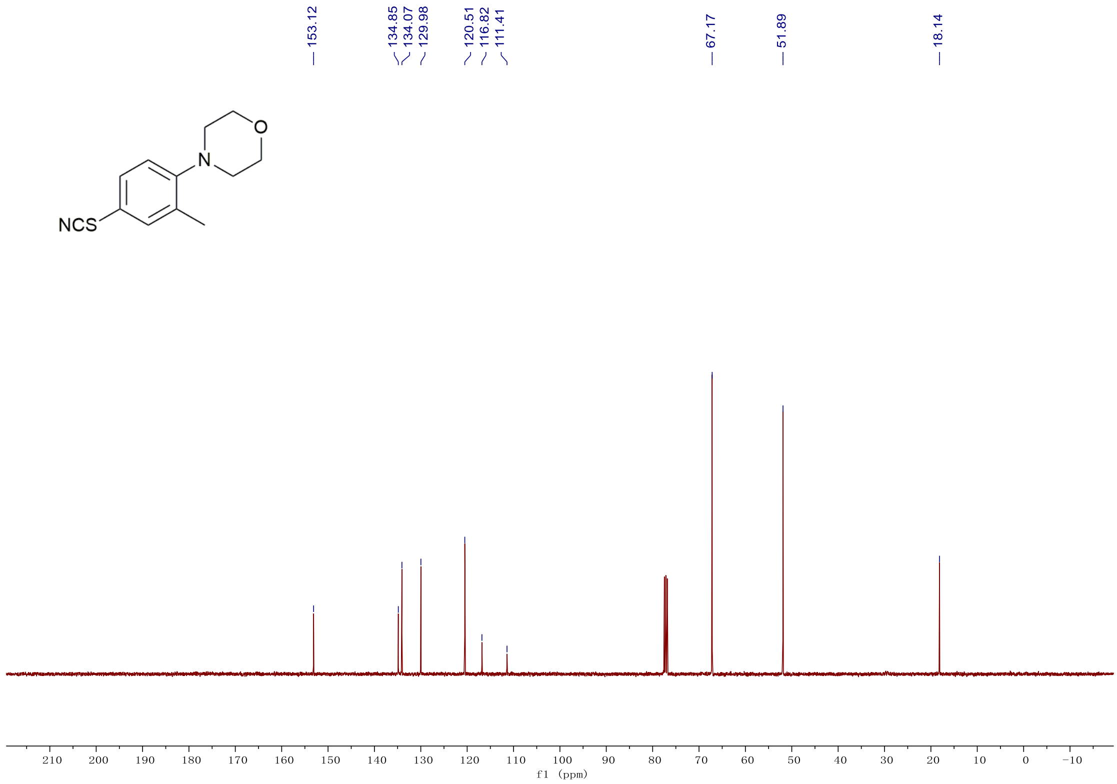
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3g



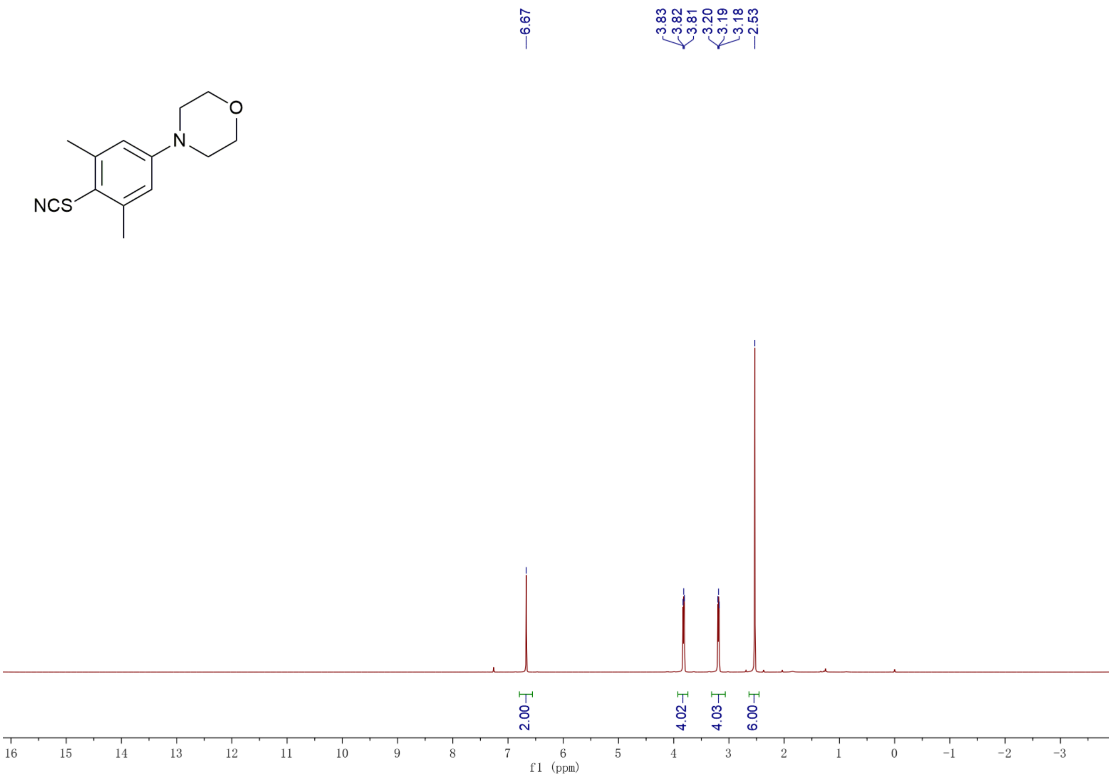
¹H NMR (400 MHz, $CDCl_3$) spectrum of 3h



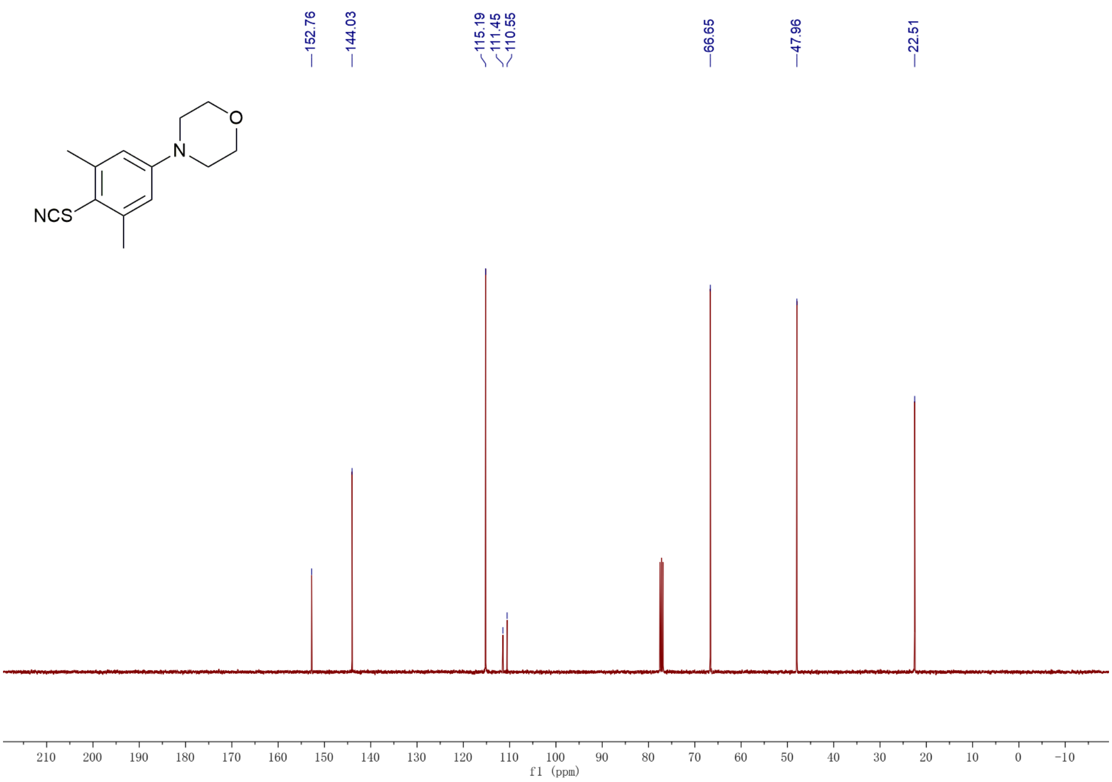
¹³C NMR (100 MHz, $CDCl_3$) spectrum of 3h



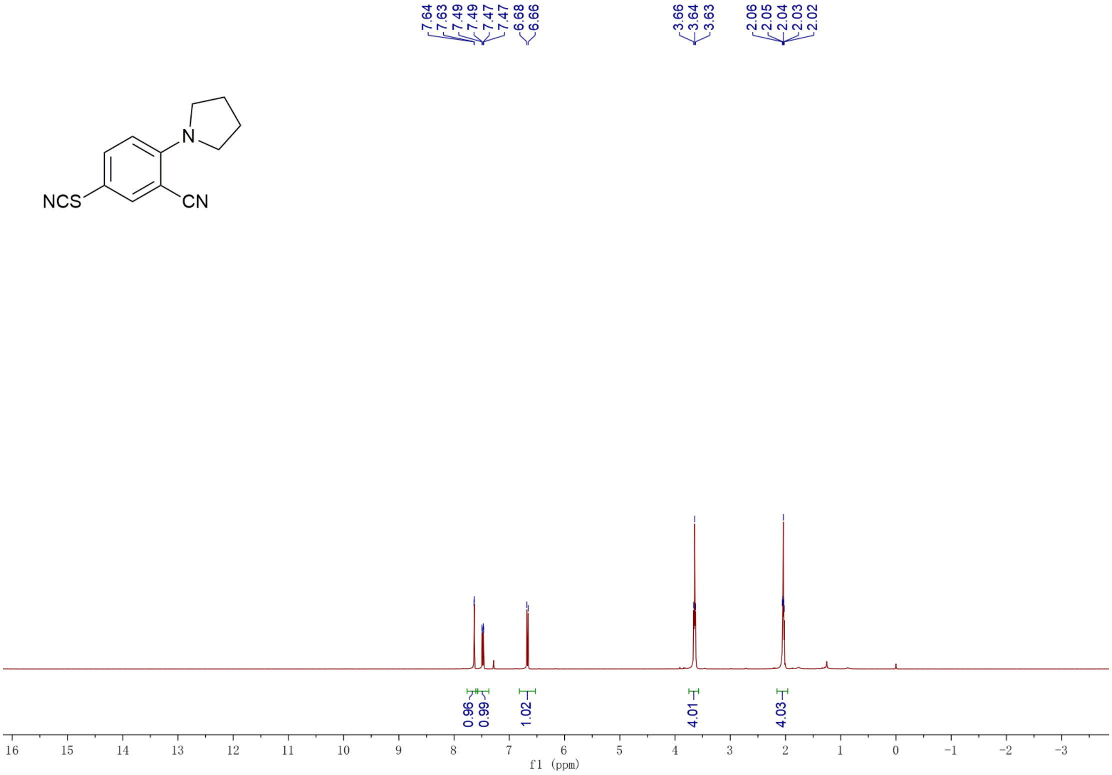
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3i



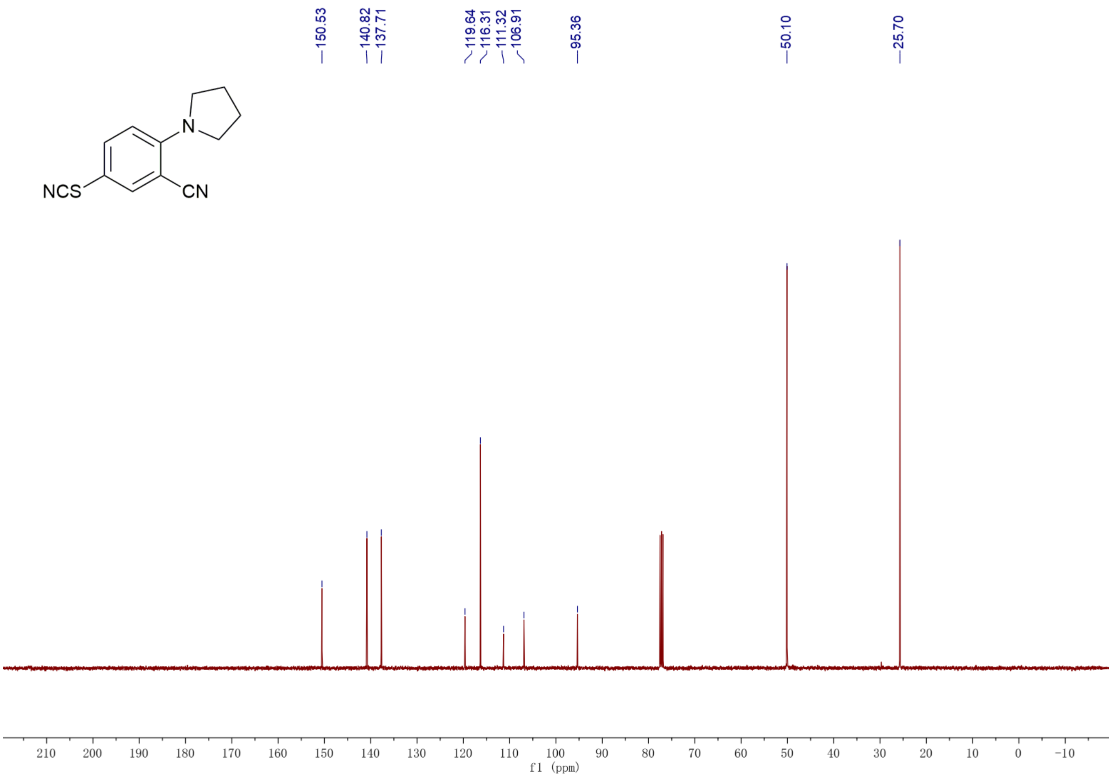
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3i



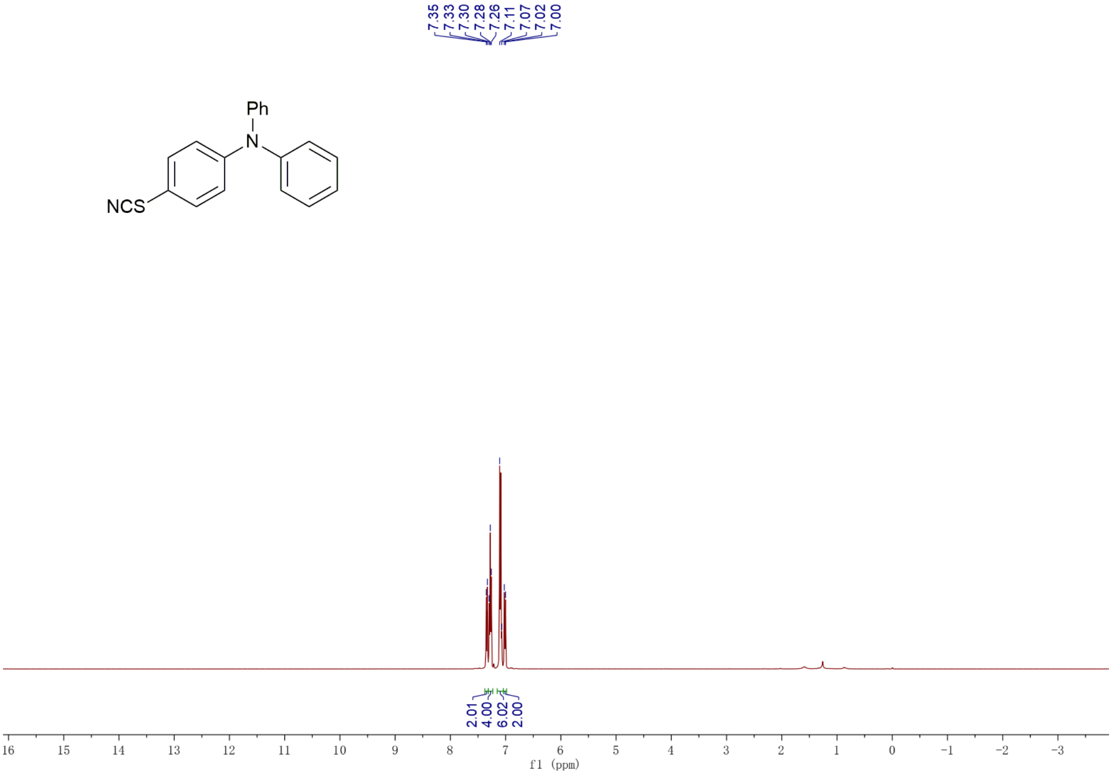
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3j



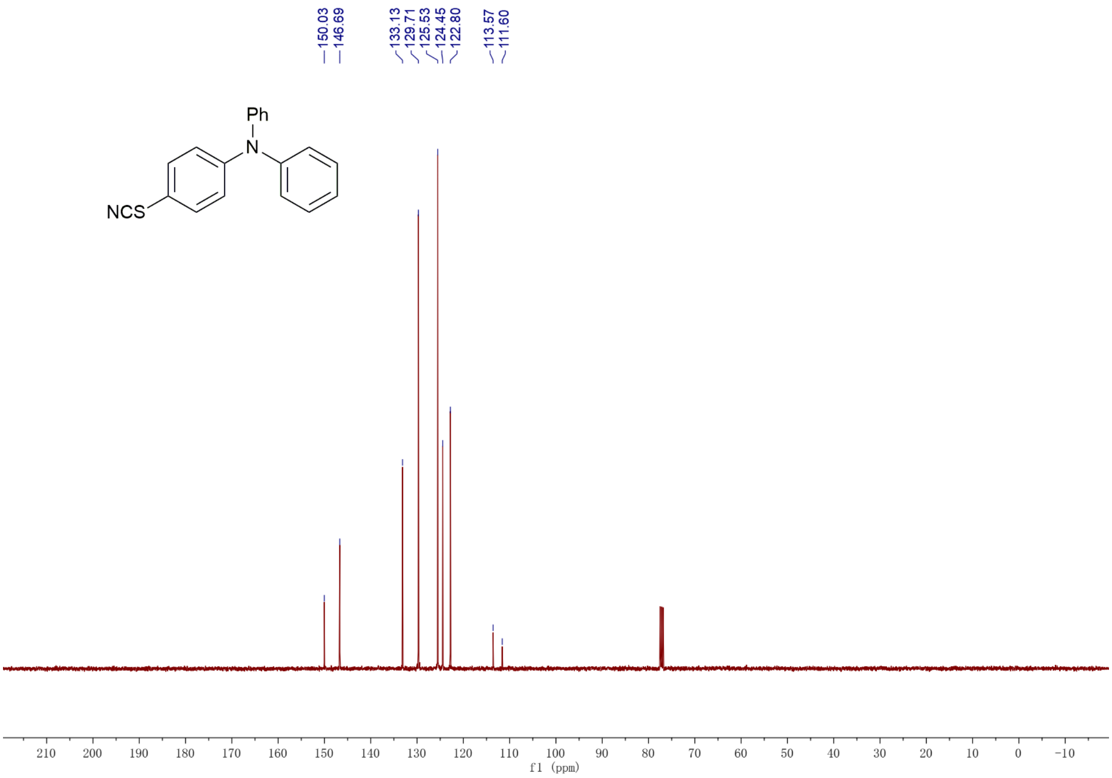
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3j



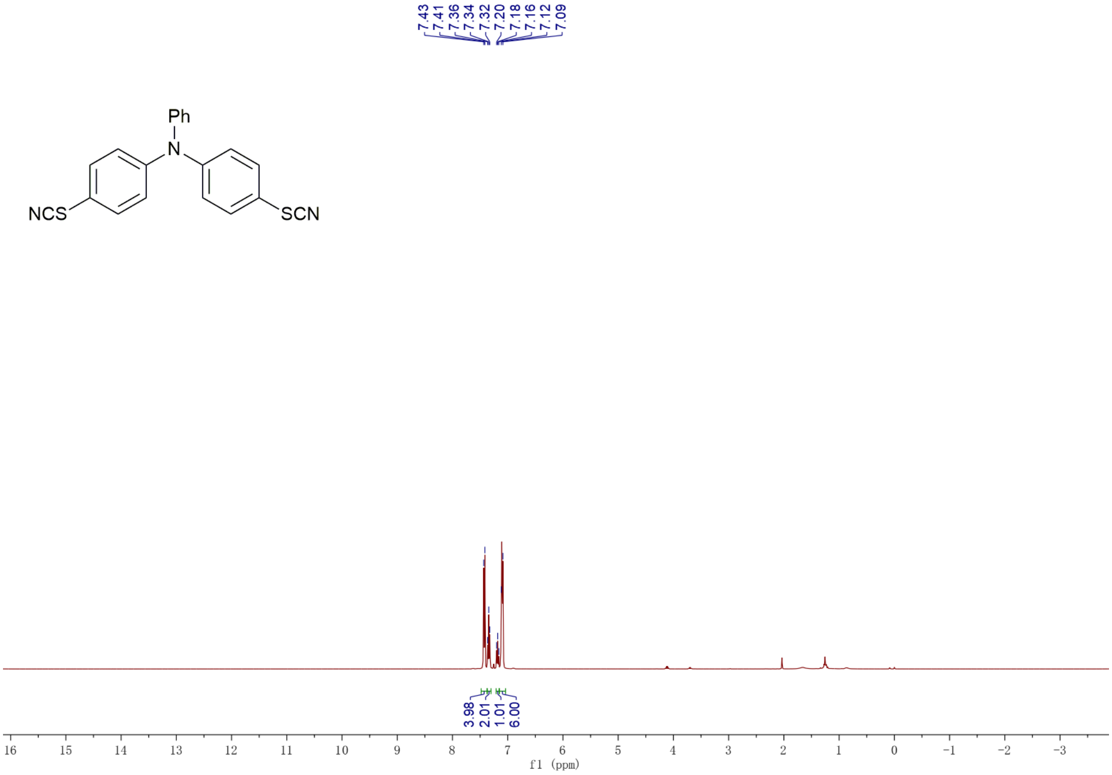
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3k



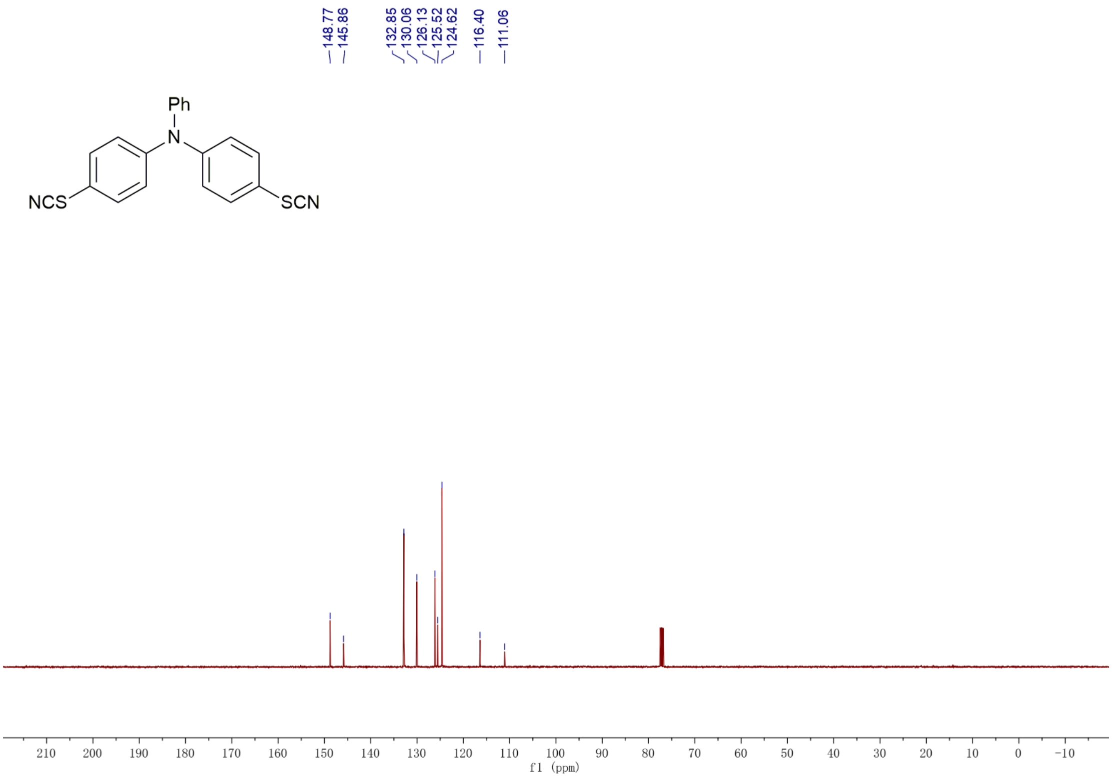
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3k



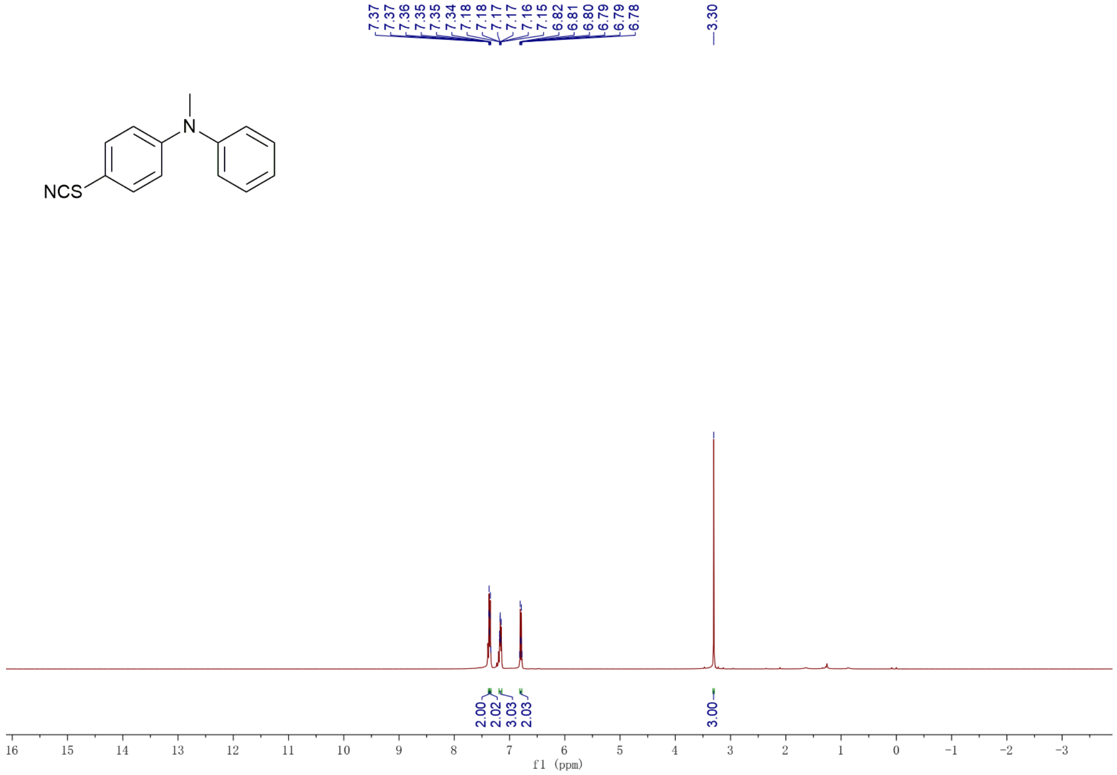
^1H NMR (400 MHz, $CDCl_3$) spectrum of 3k’



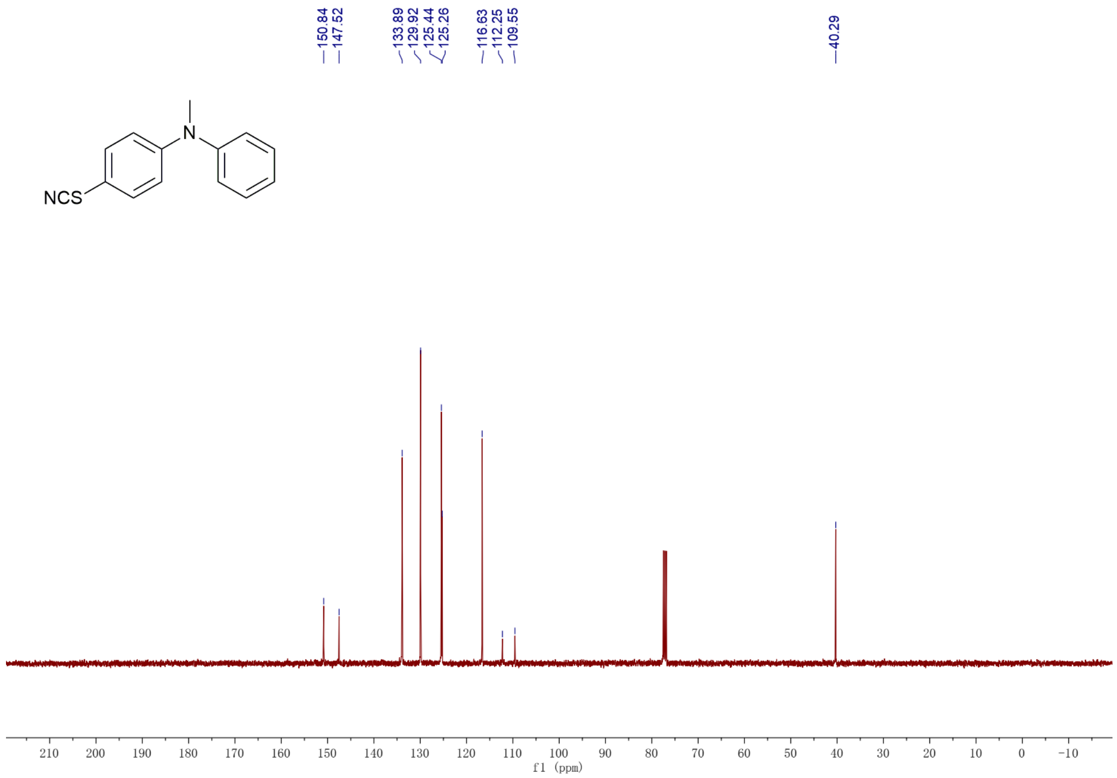
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3k’



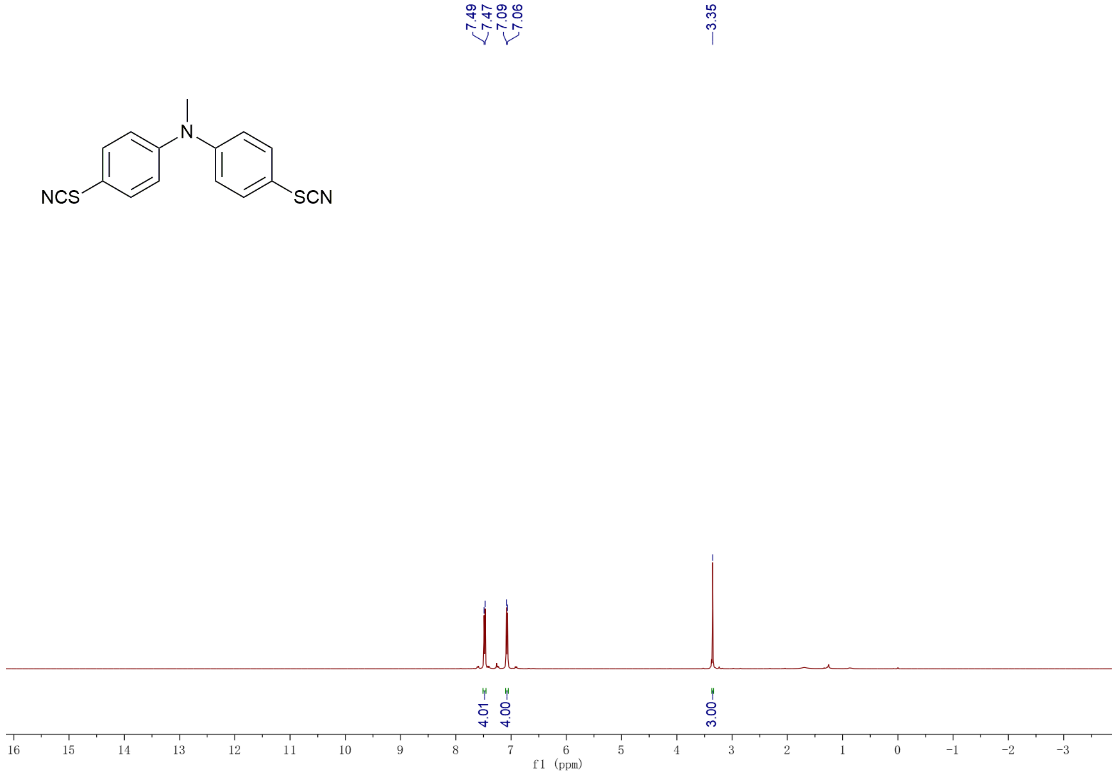
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3l



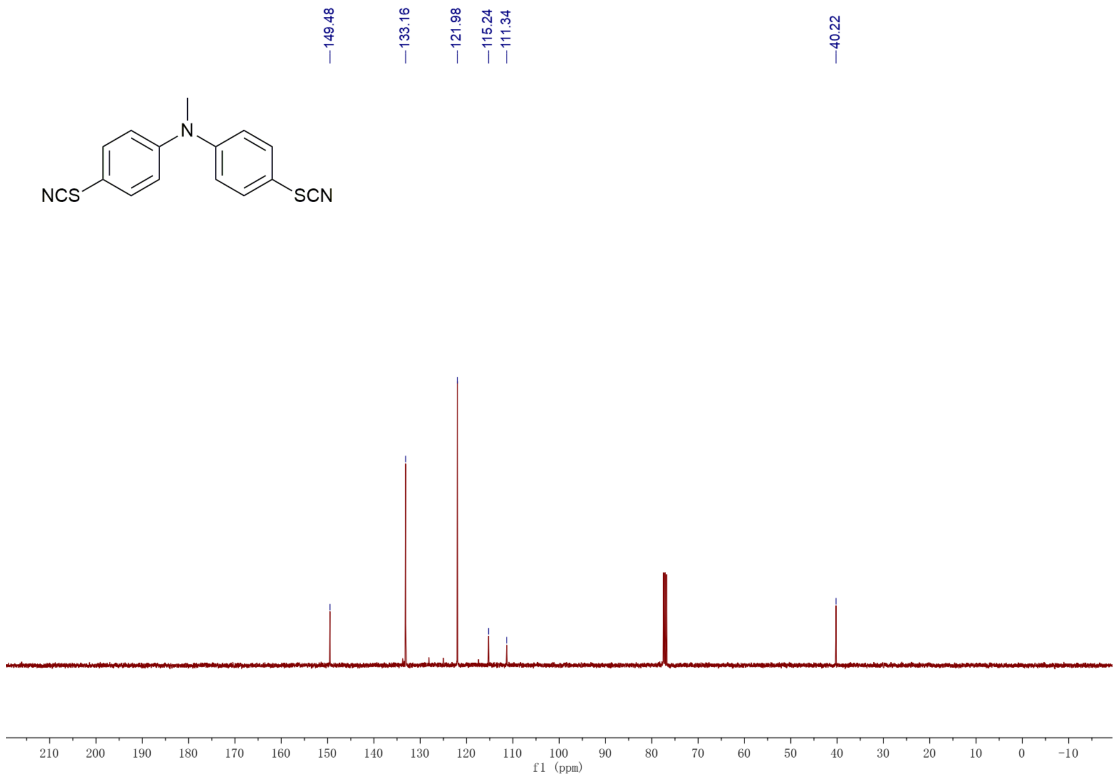
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3l



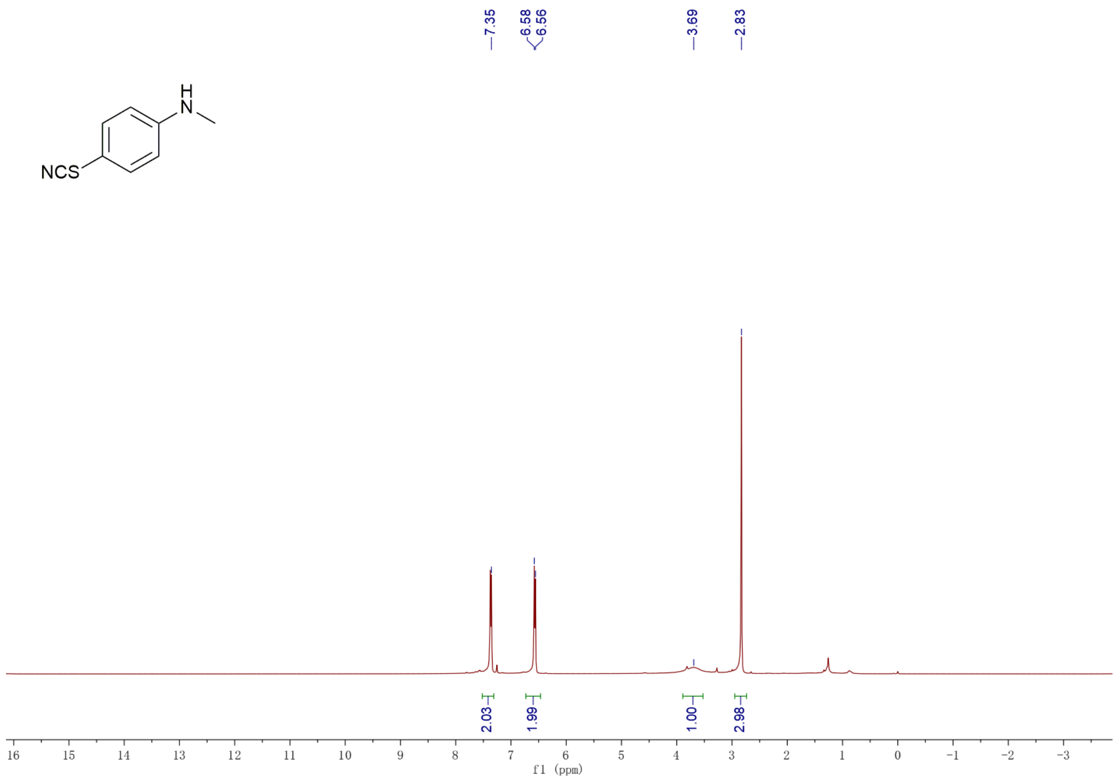
[1]H NMR (400 MHz, CDCl$_3$) spectrum of 3l’



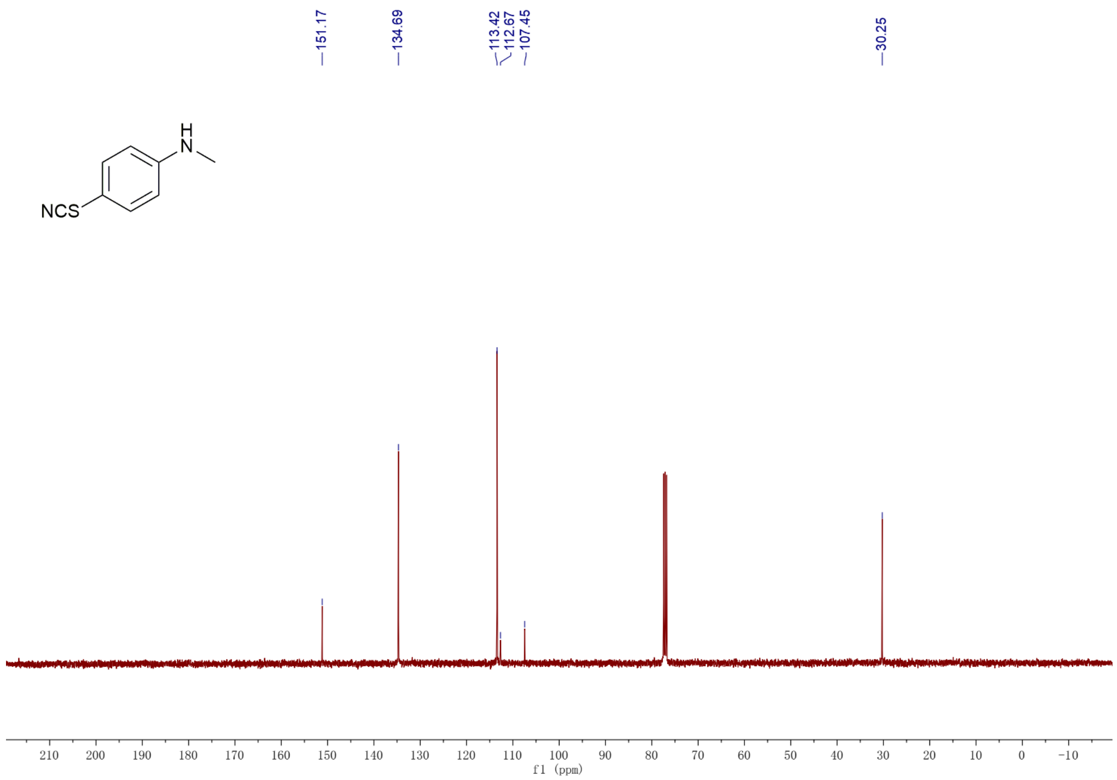
[13]C NMR (100 MHz, CDCl$_3$) spectrum of 3l’



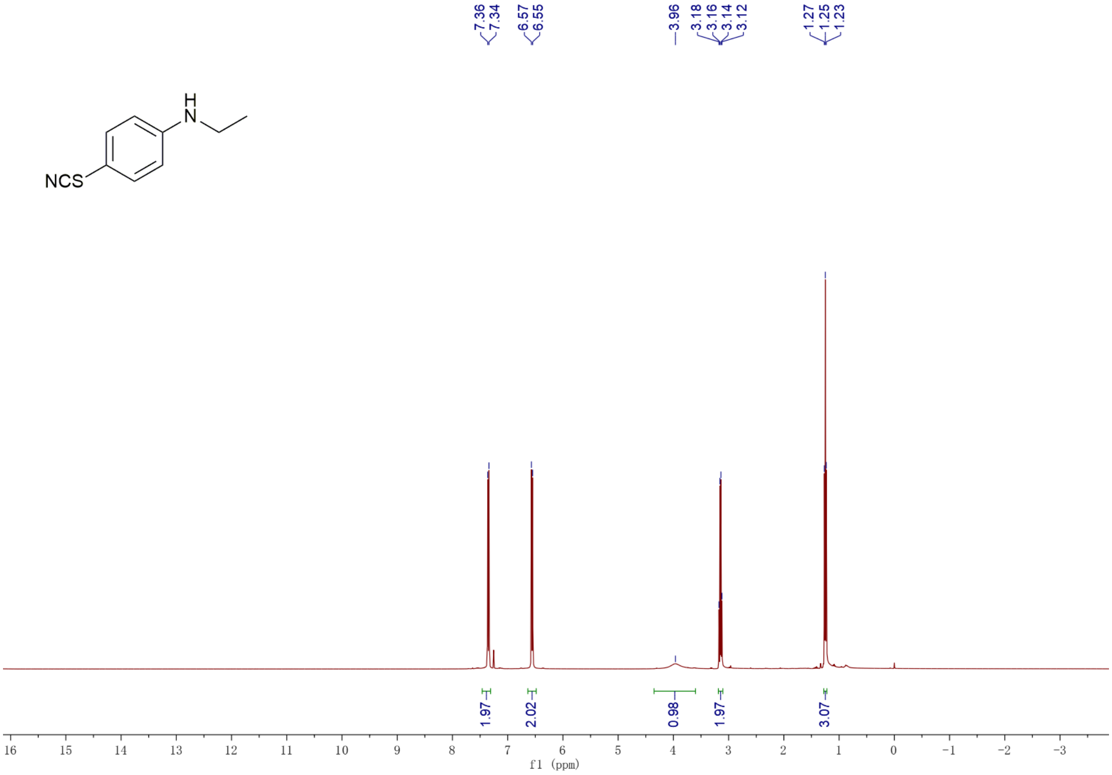
[1]H NMR (400 MHz, $CDCl_3$) spectrum of 3m



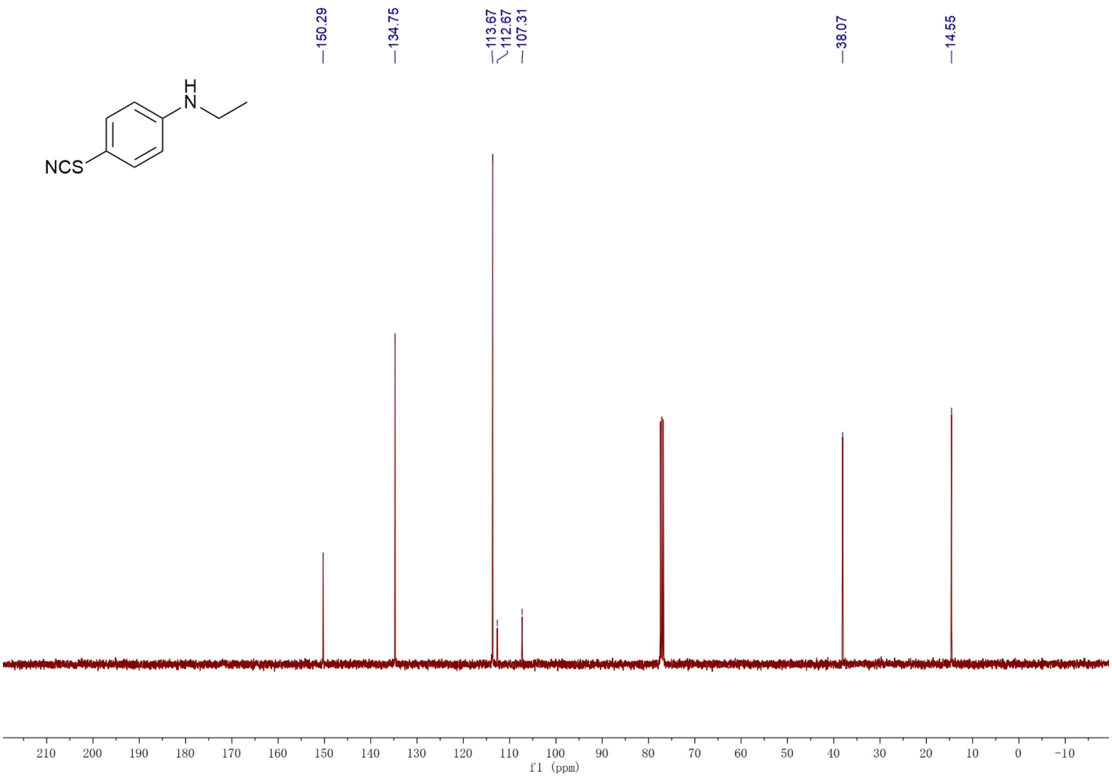
[13]C NMR (100 MHz, $CDCl_3$) spectrum of 3m



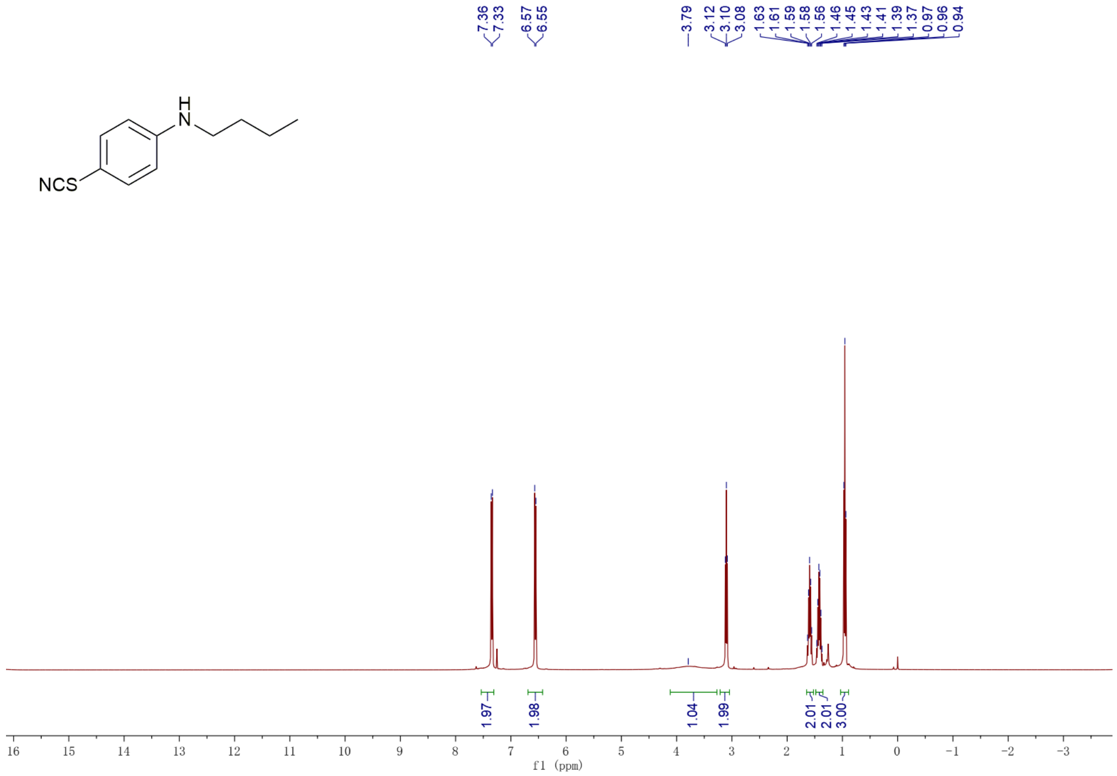
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3n



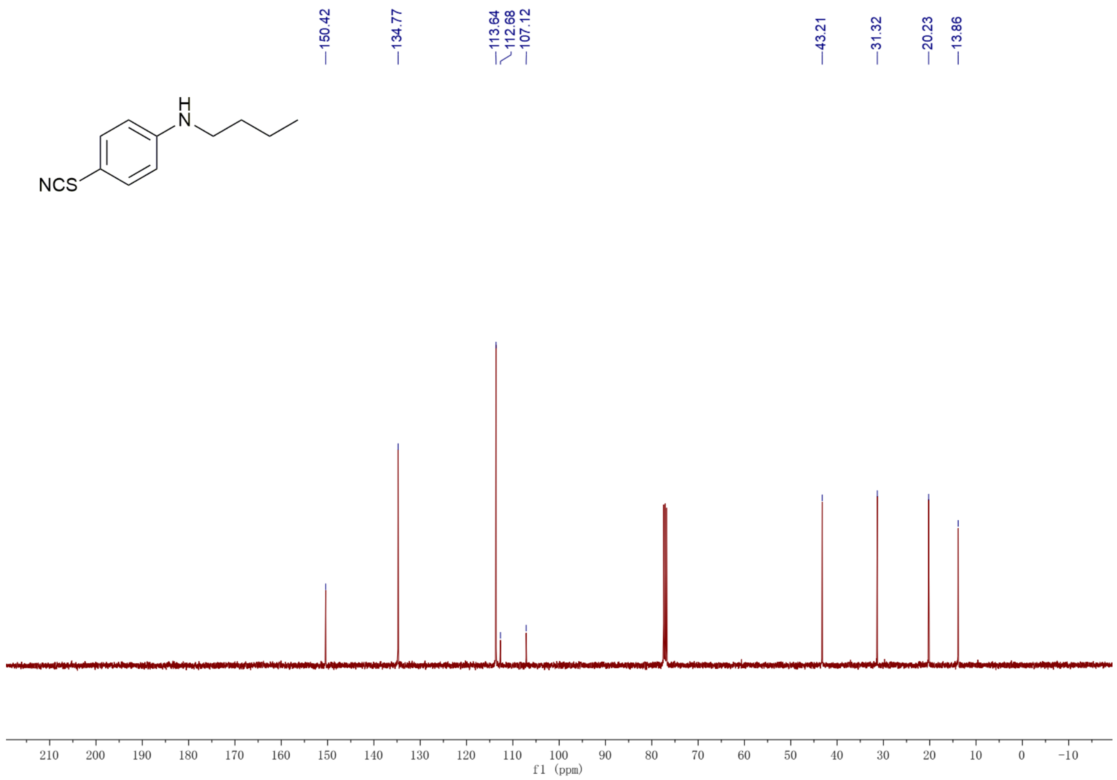
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3n



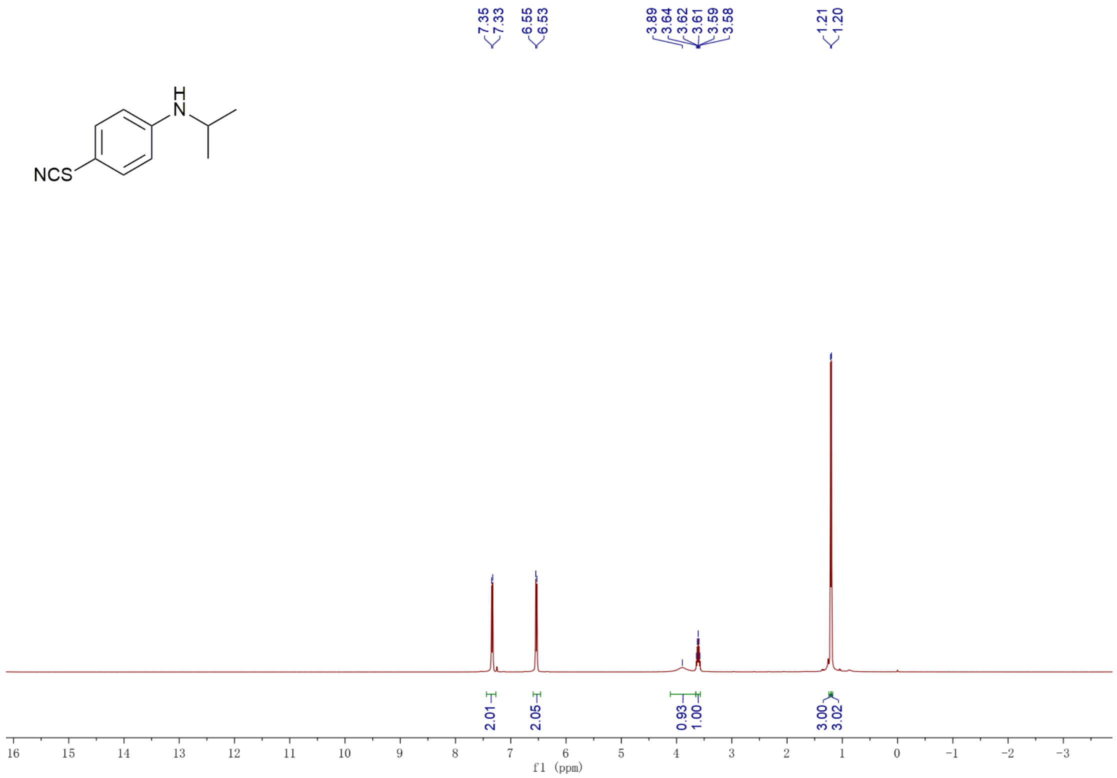
[1]H NMR (400 MHz, CDCl$_3$) spectrum of 3o



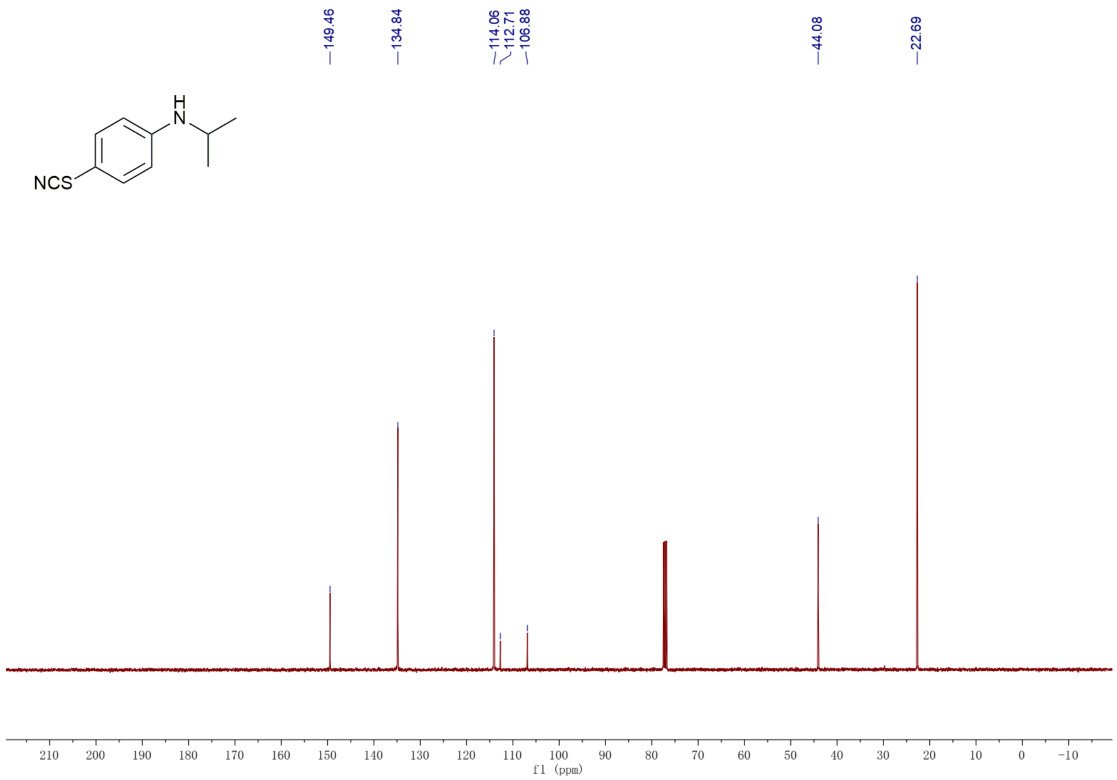
[13]C NMR (100 MHz, CDCl$_3$) spectrum of 3o



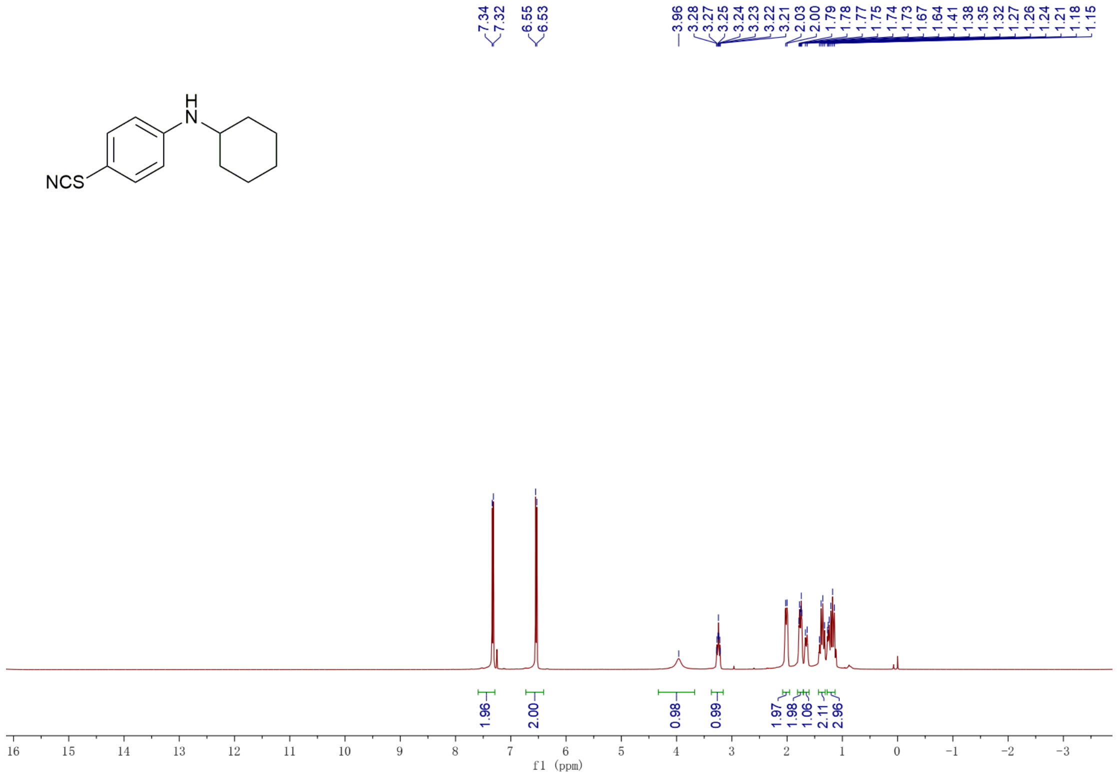
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3p



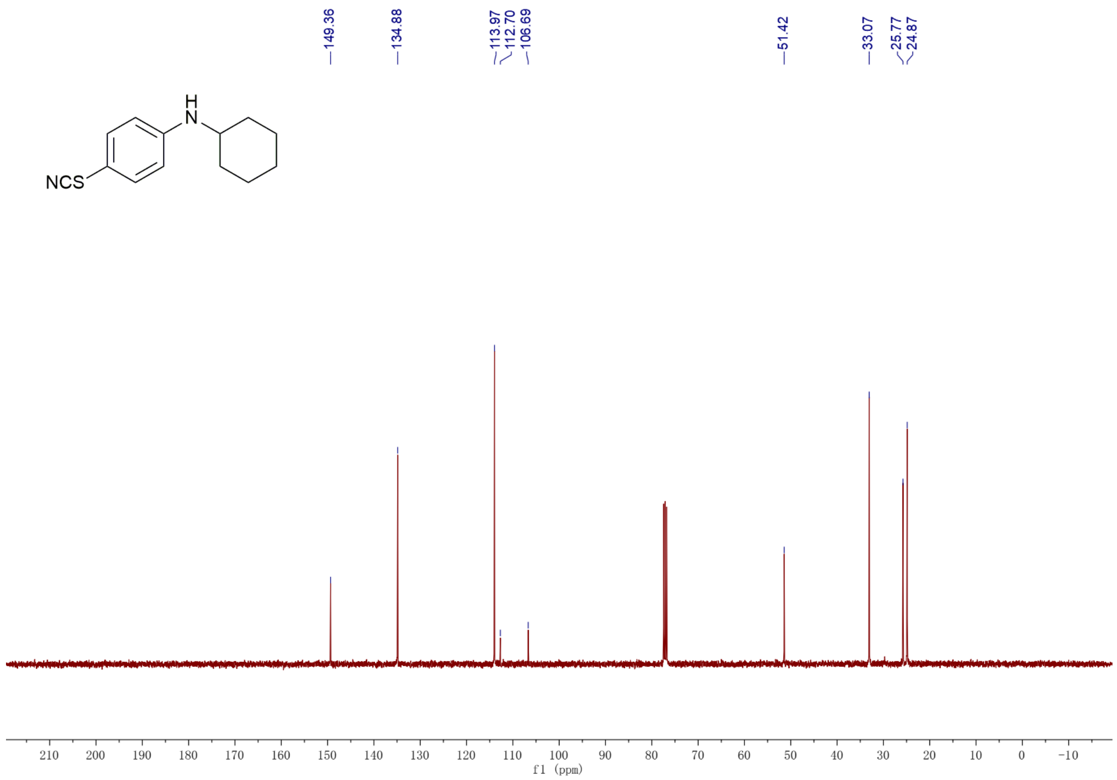
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3p



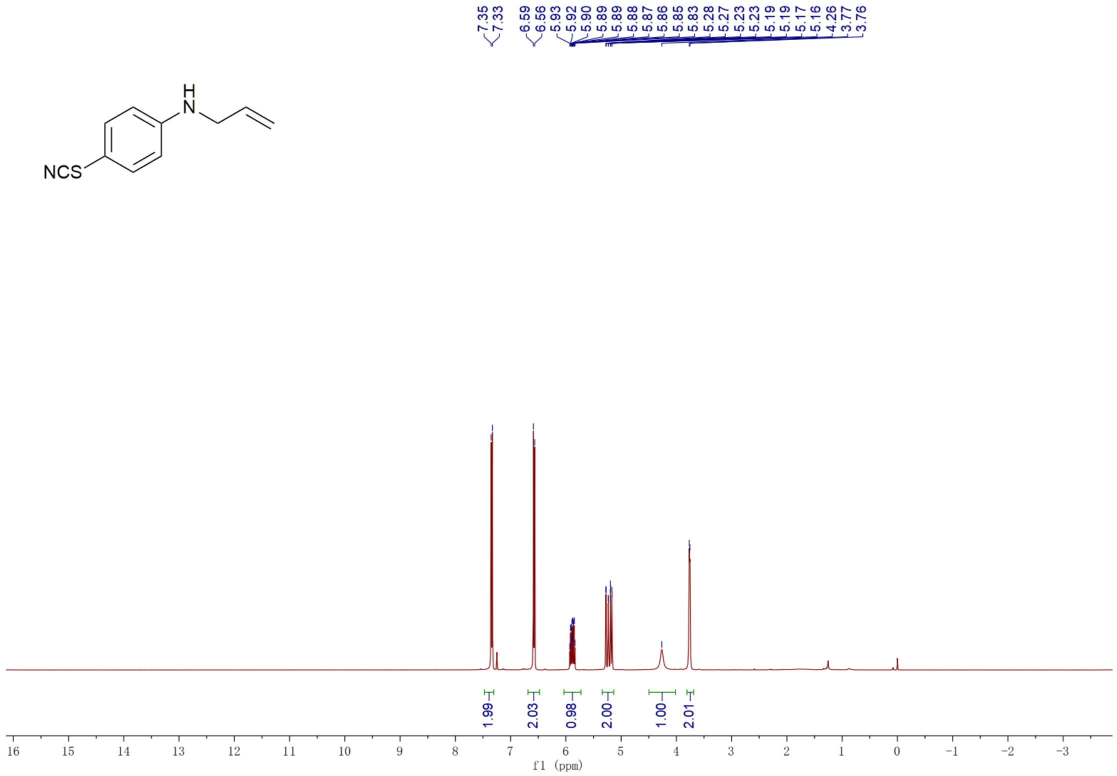
[1]H NMR (400 MHz, $CDCl_3$) spectrum of 3q



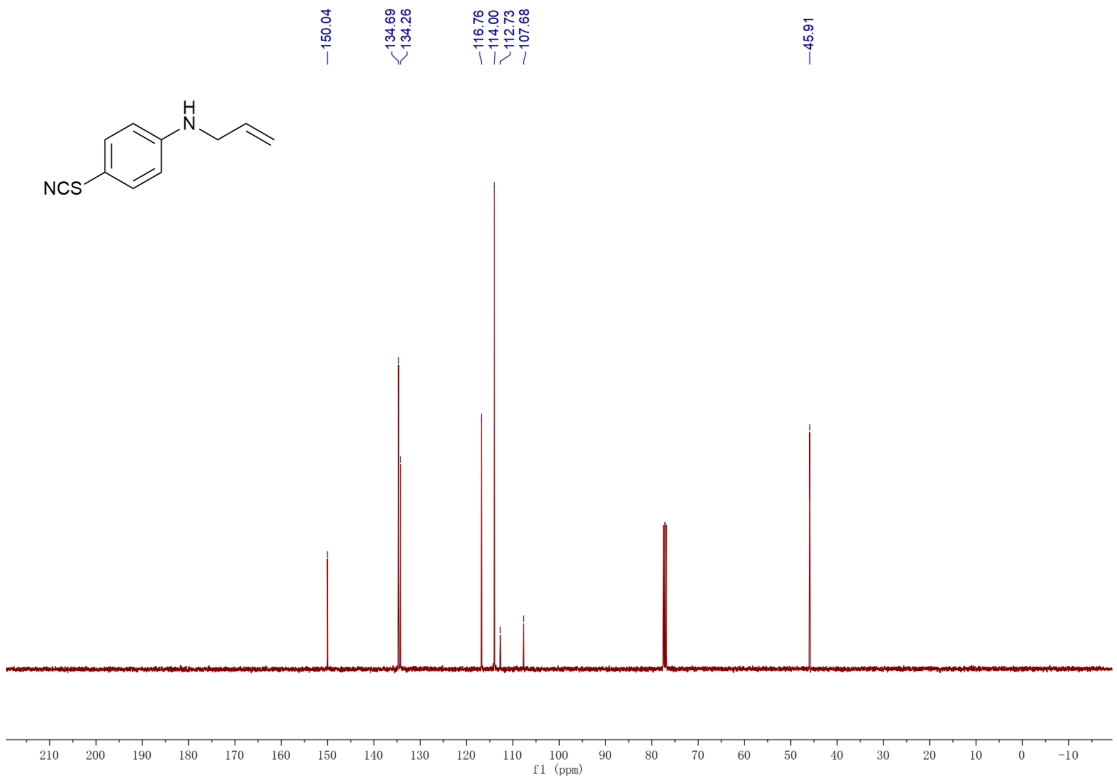
[13]C NMR (100 MHz, $CDCl_3$) spectrum of 3q



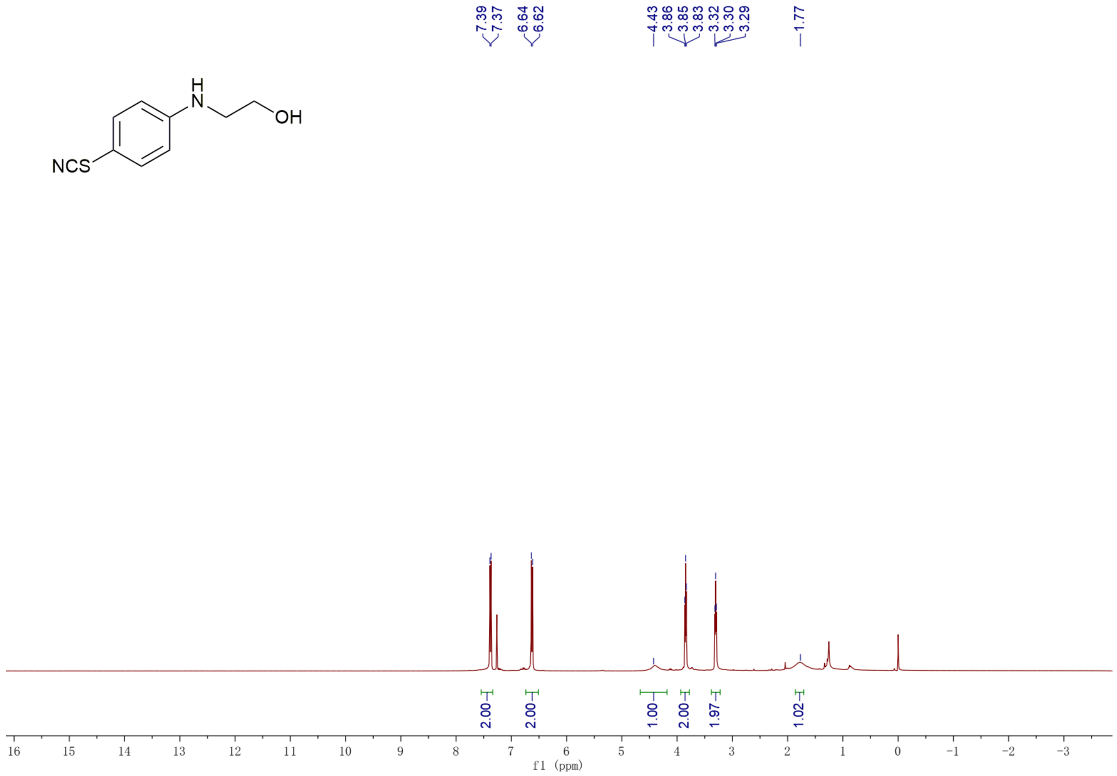
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3r



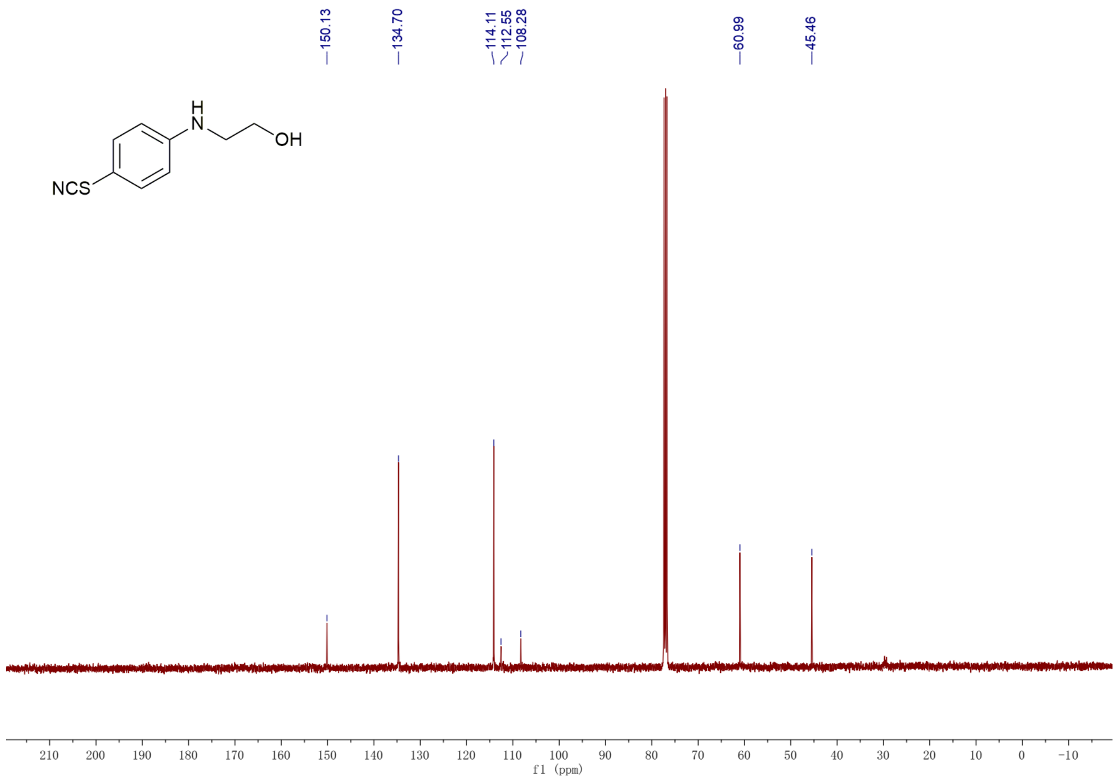
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3r



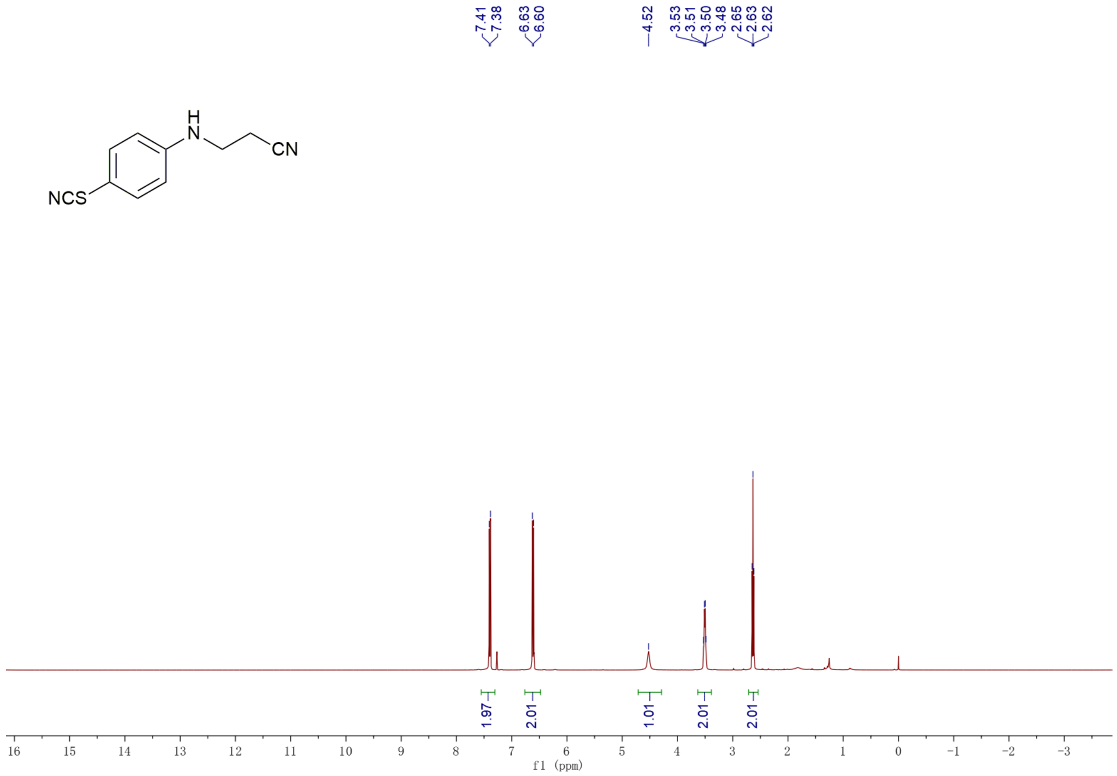
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3s



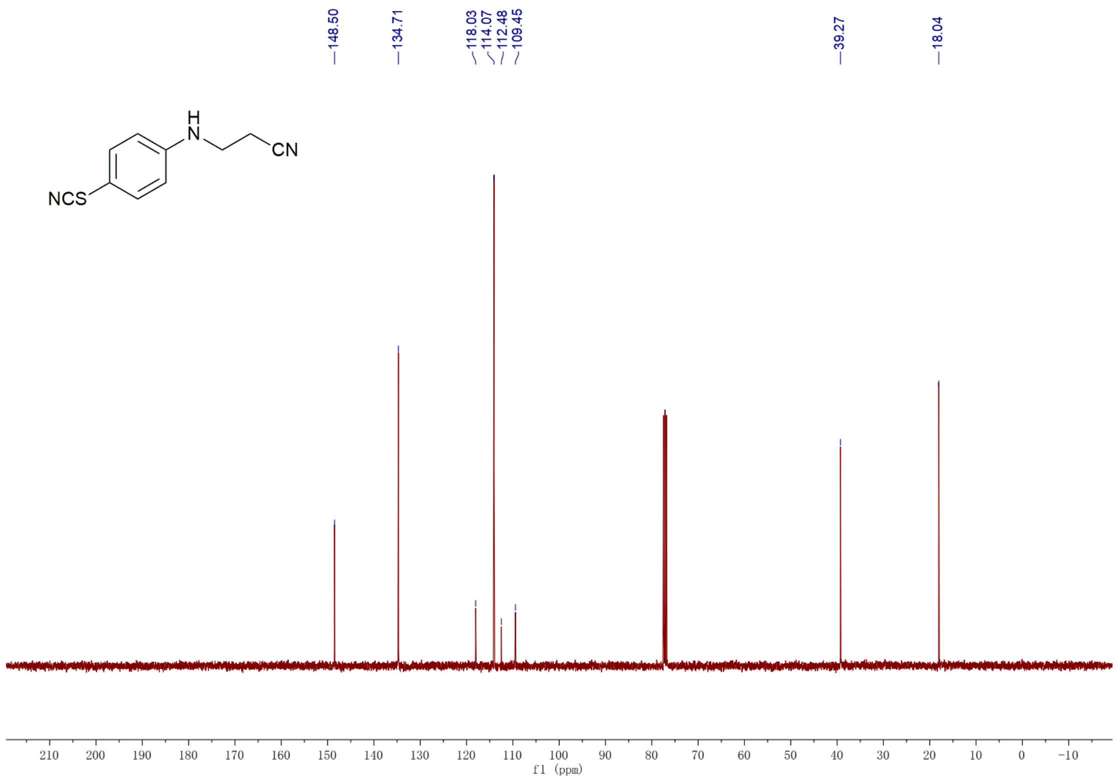
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3s



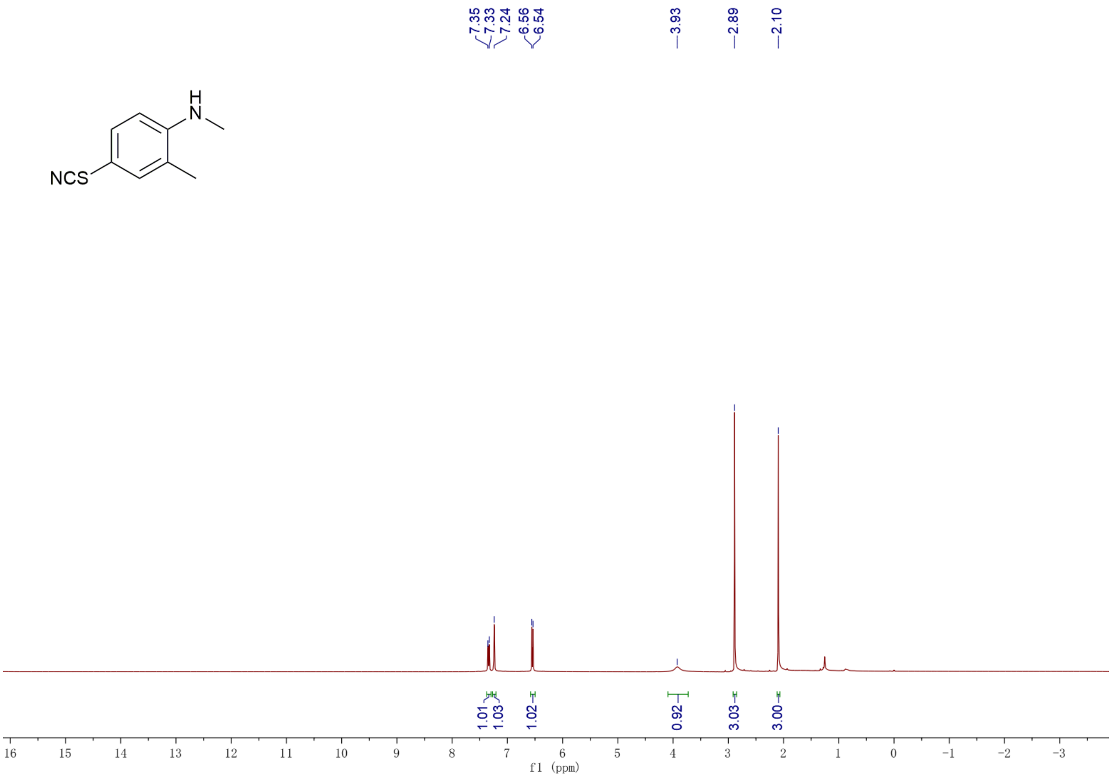
[1]H NMR (400 MHz, $CDCl_3$) spectrum of 3t



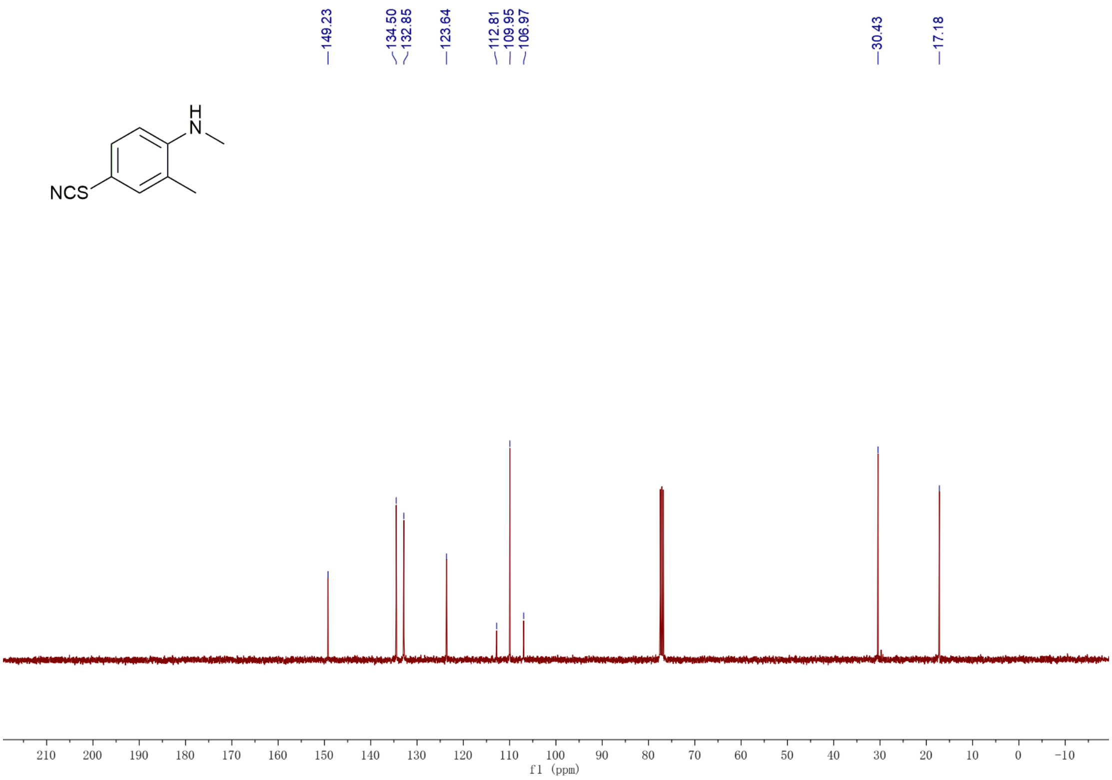
[13]C NMR (100 MHz, $CDCl_3$) spectrum of 3t



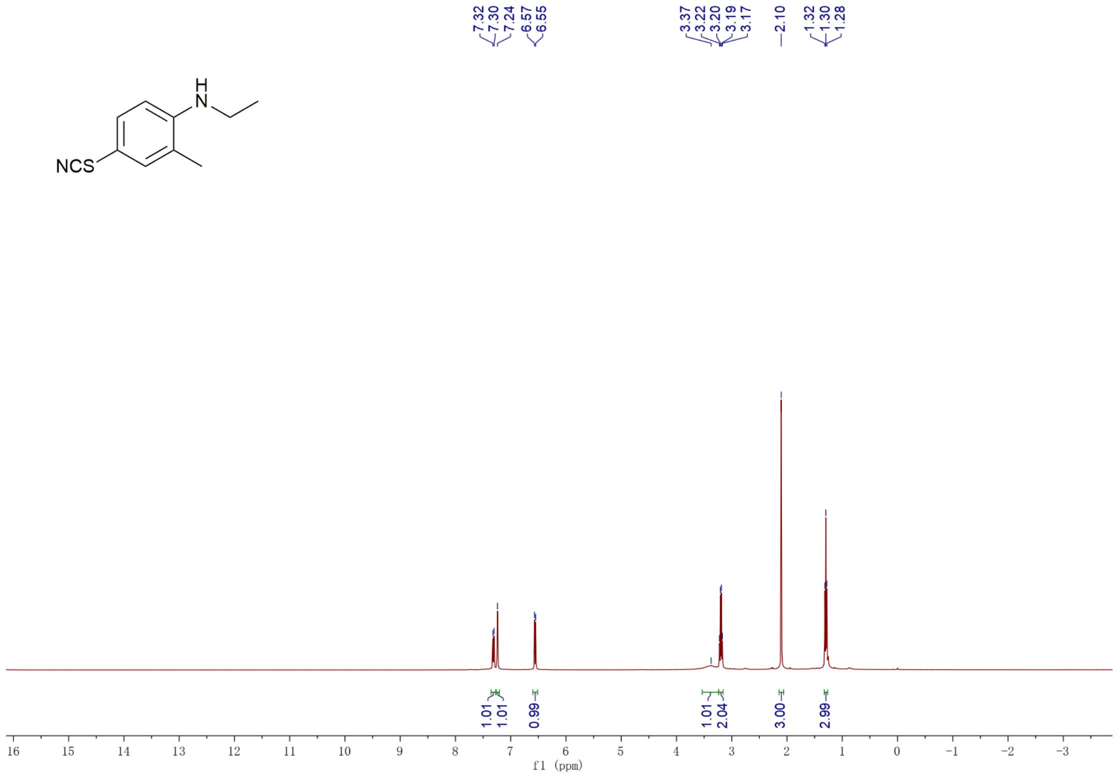
^1H NMR (400 MHz, $CDCl_3$) spectrum of 3u



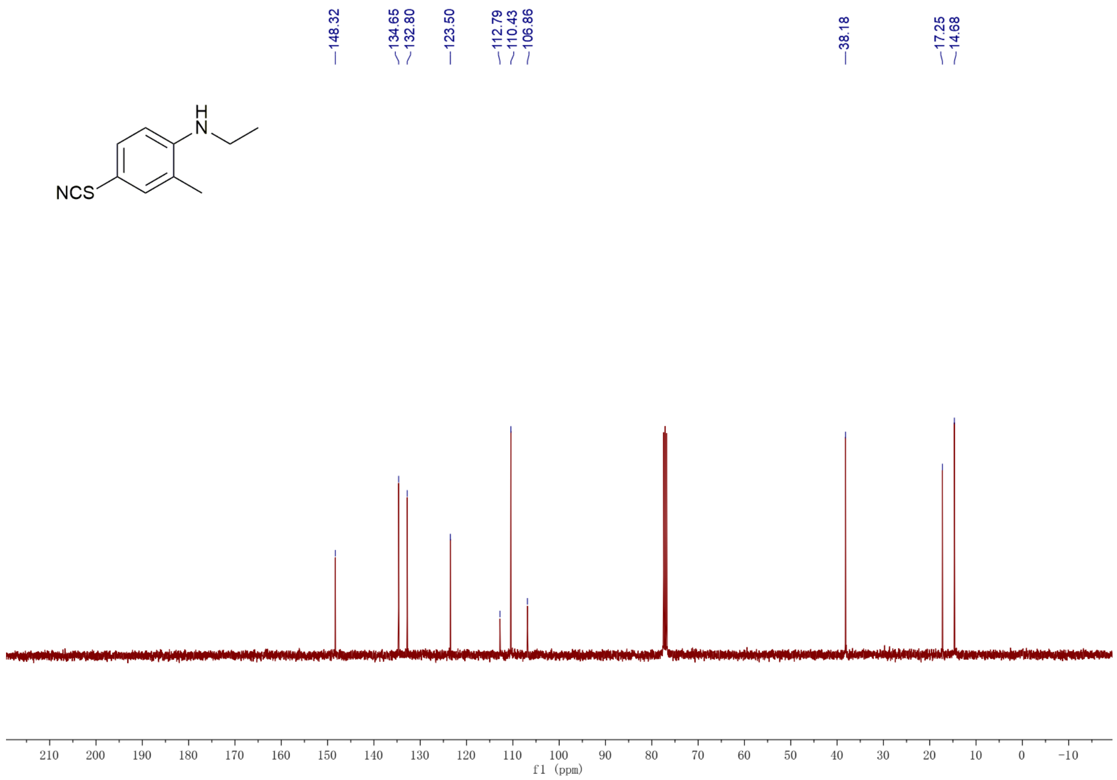
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3u



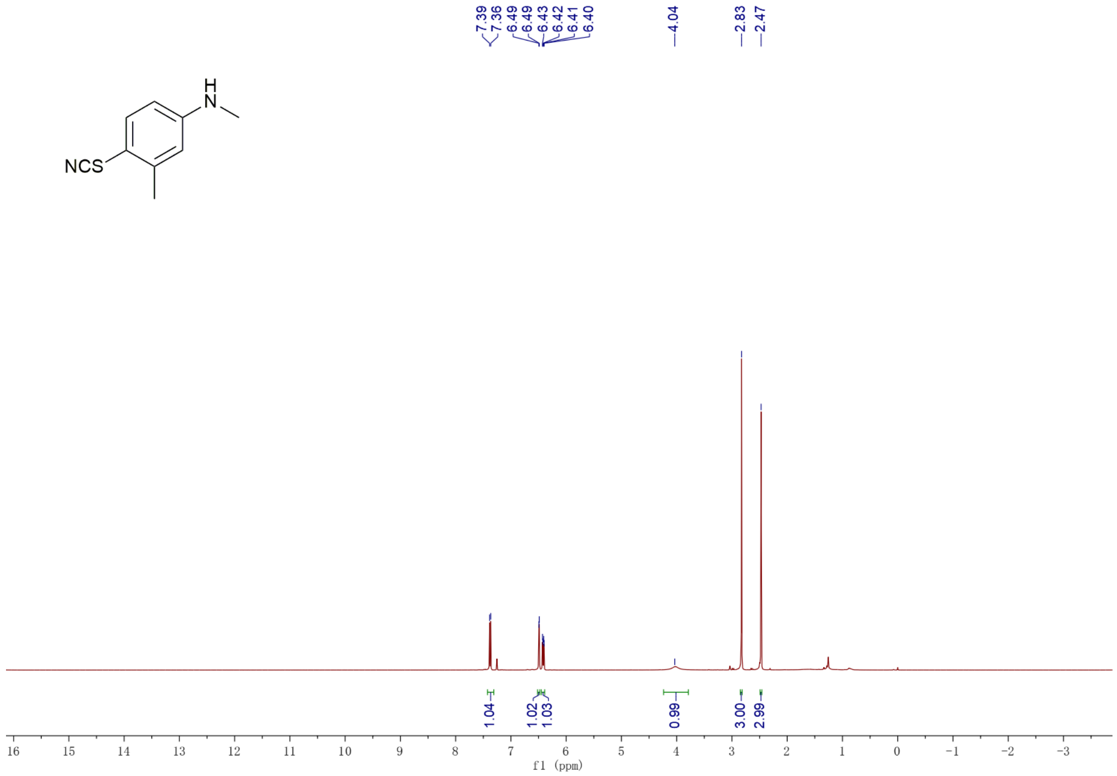
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3v



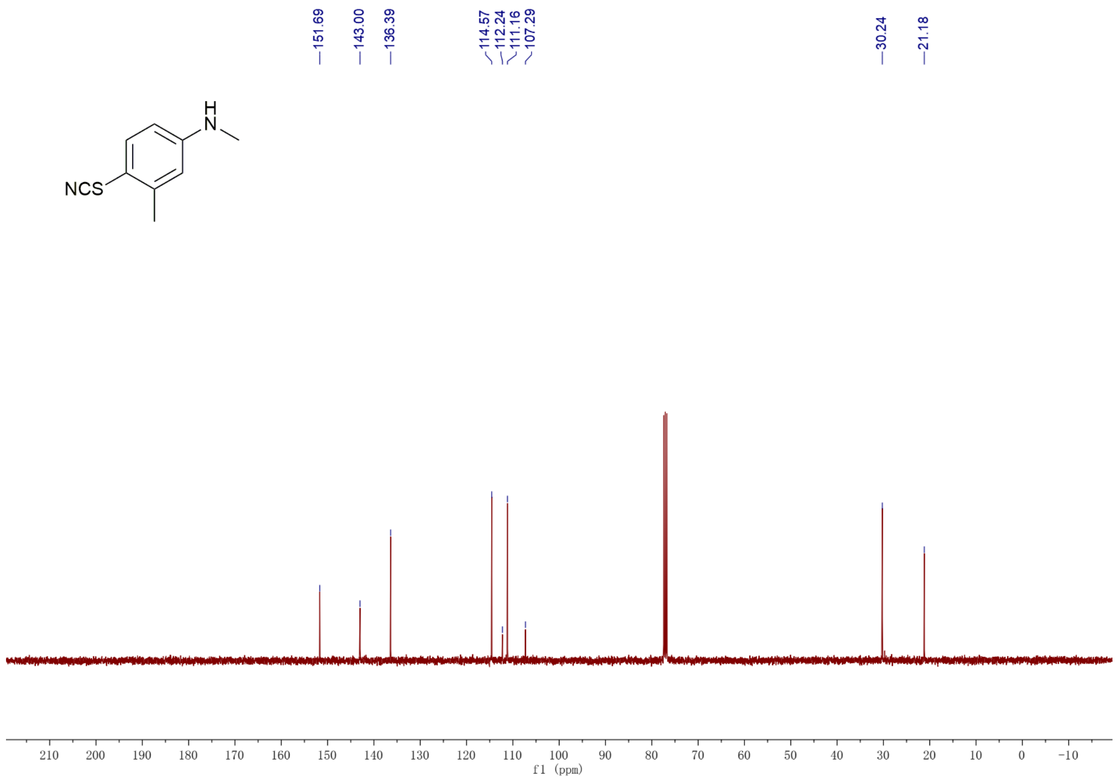
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3v



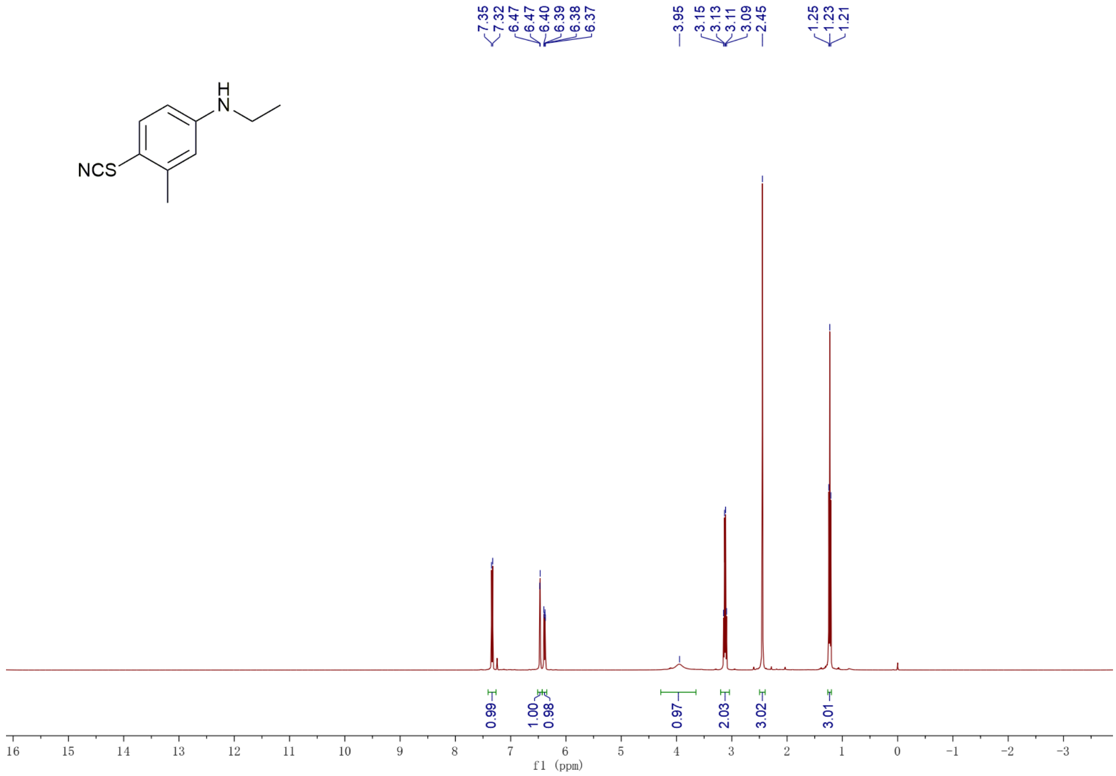
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3w



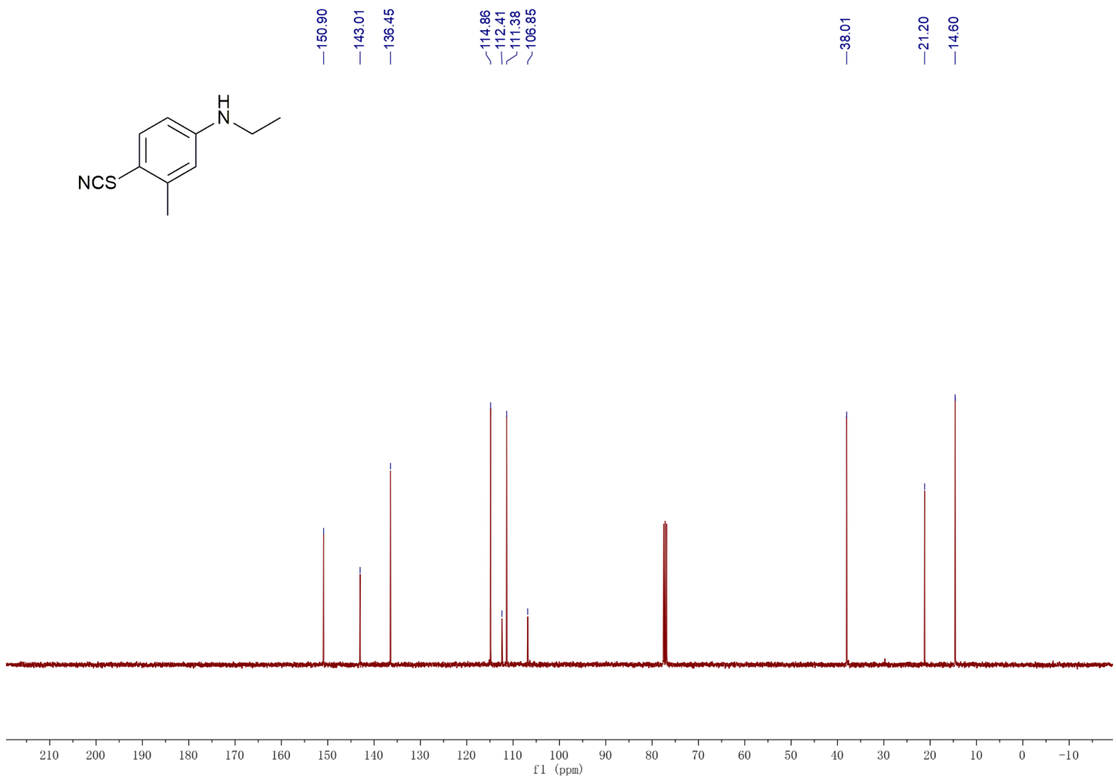
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3w



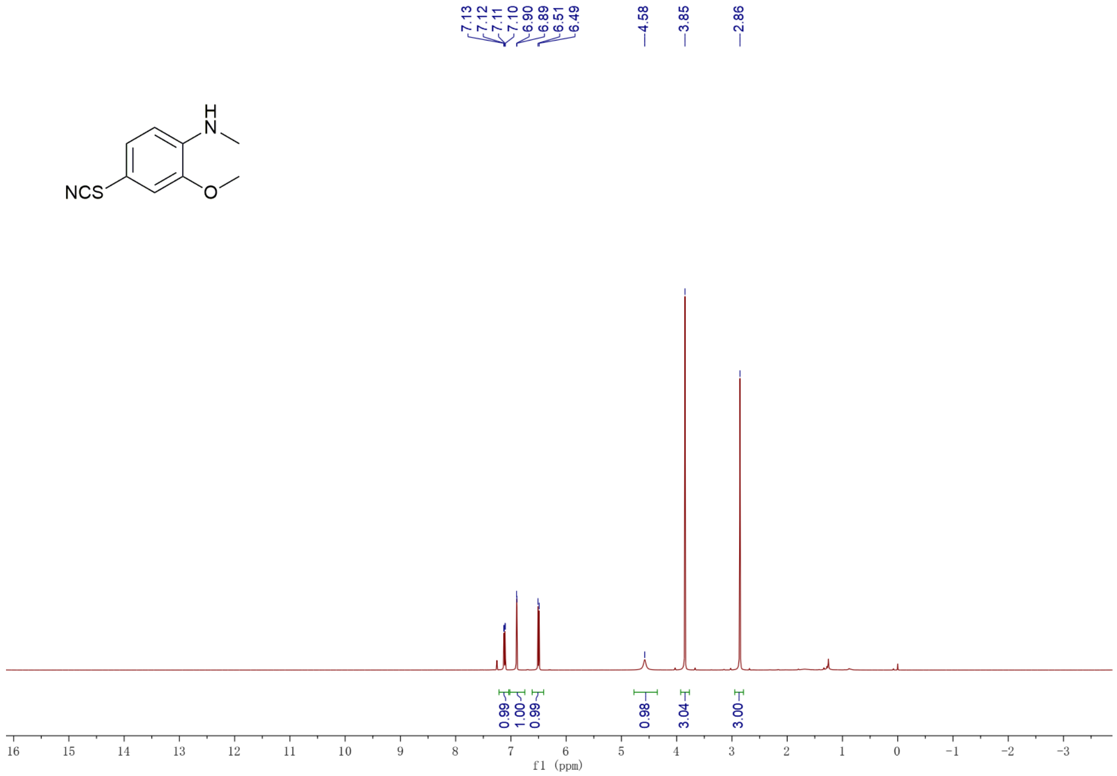
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3x



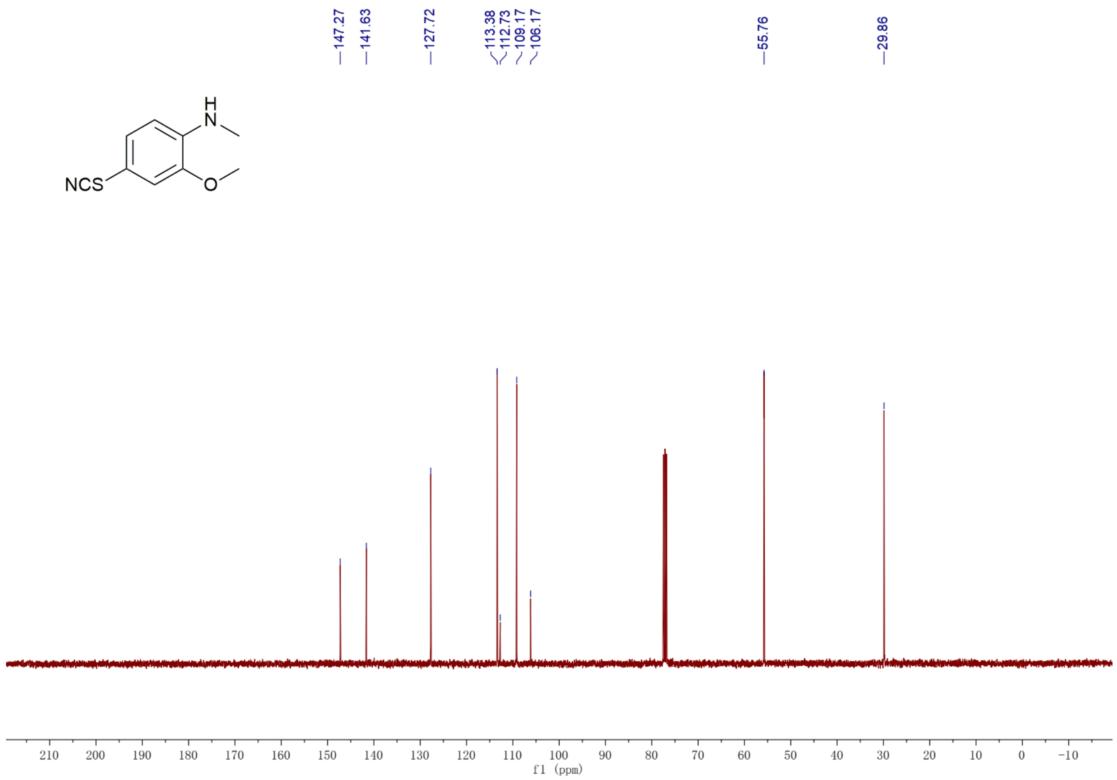
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3x



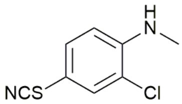
^1H NMR (400 MHz, $CDCl_3$) spectrum of 3y

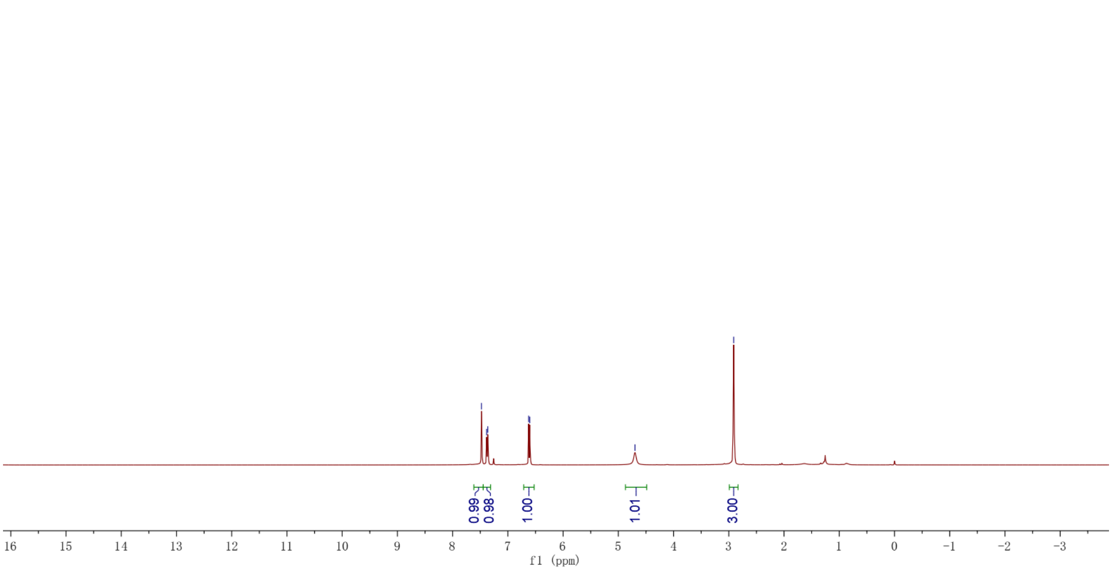


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3y

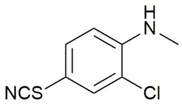


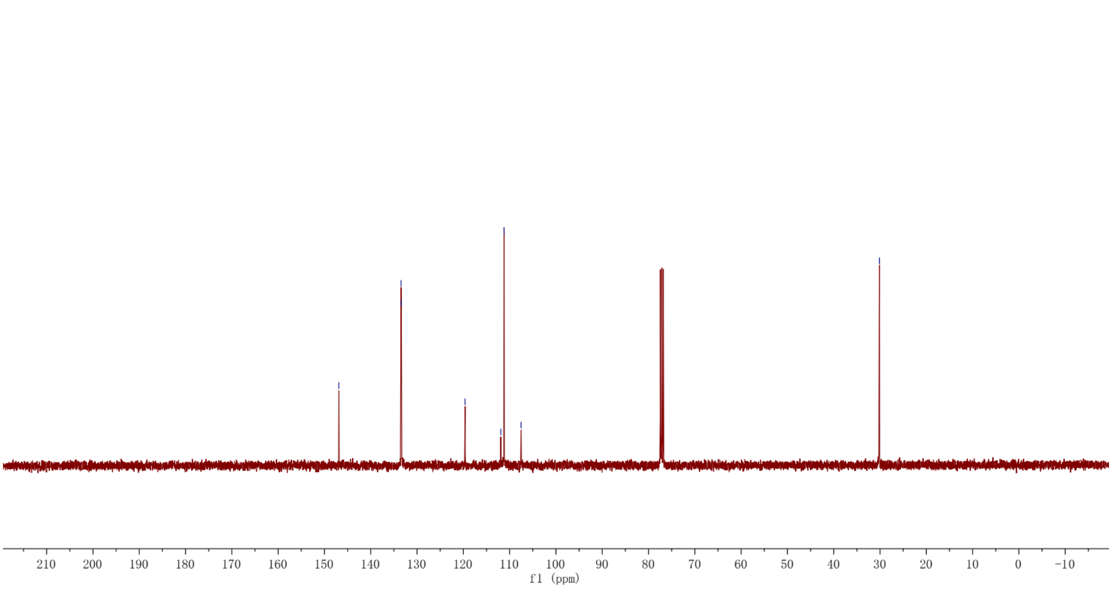
[1]H NMR (400 MHz, $CDCl_3$) spectrum of 3z



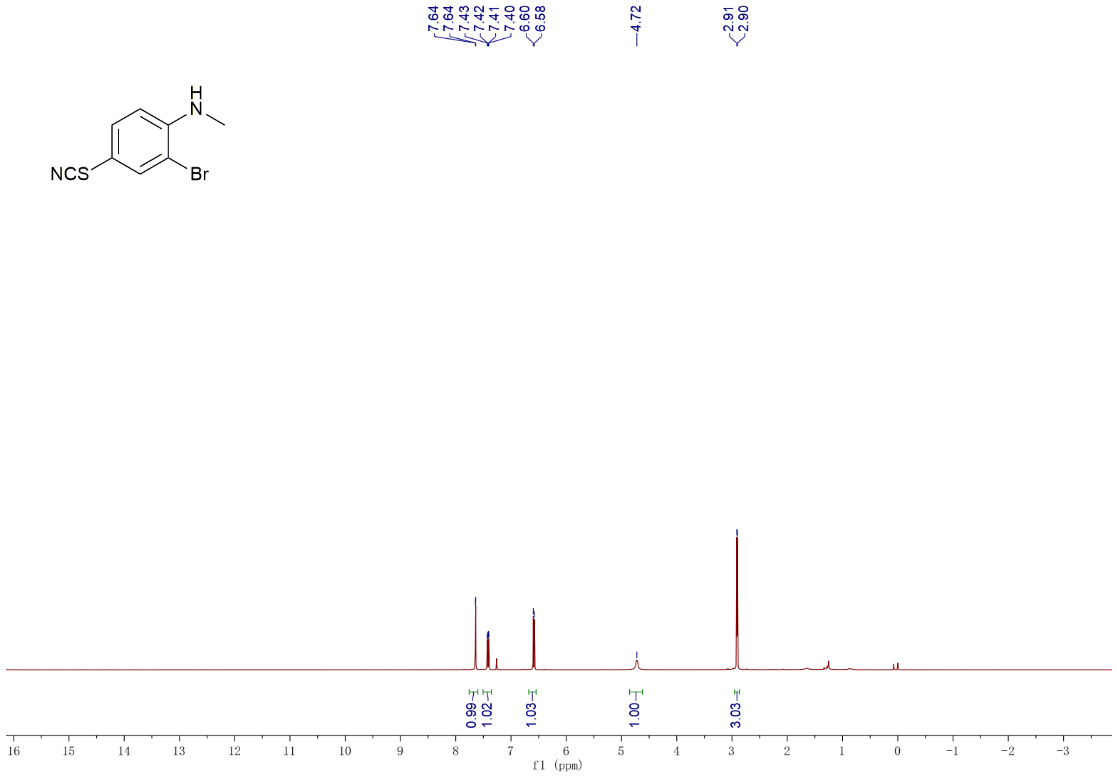


[13]C NMR (100 MHz, $CDCl_3$) spectrum of 3z

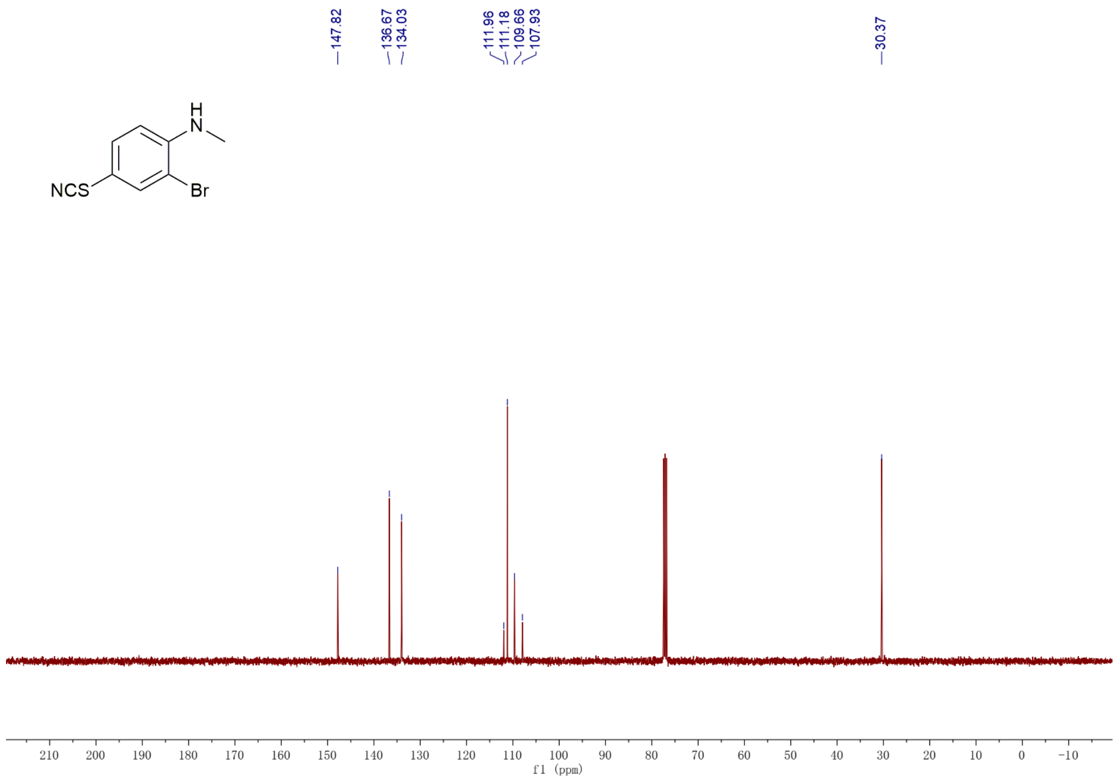




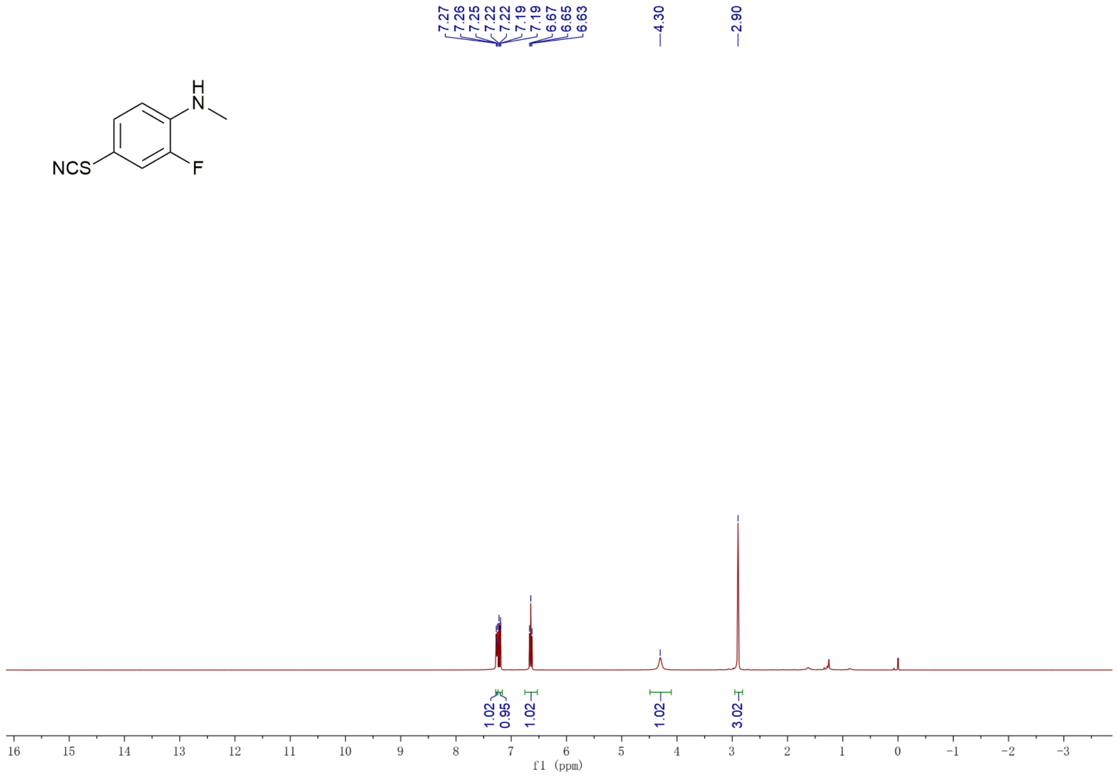
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3za



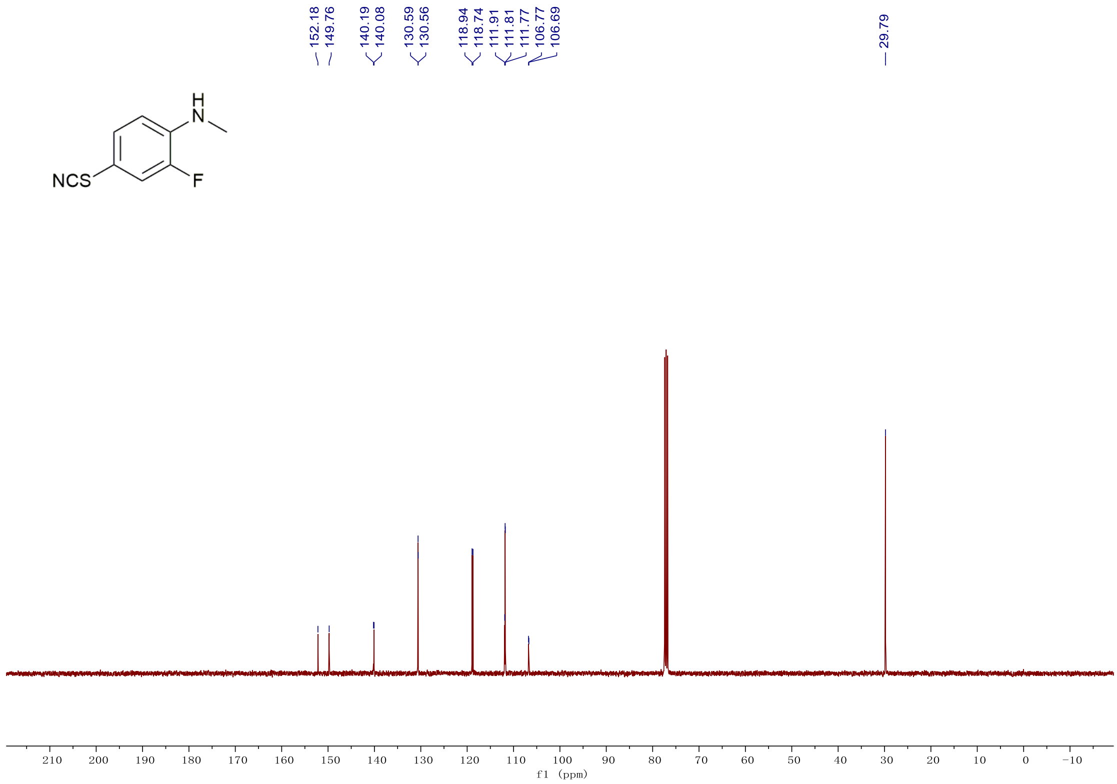
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3za



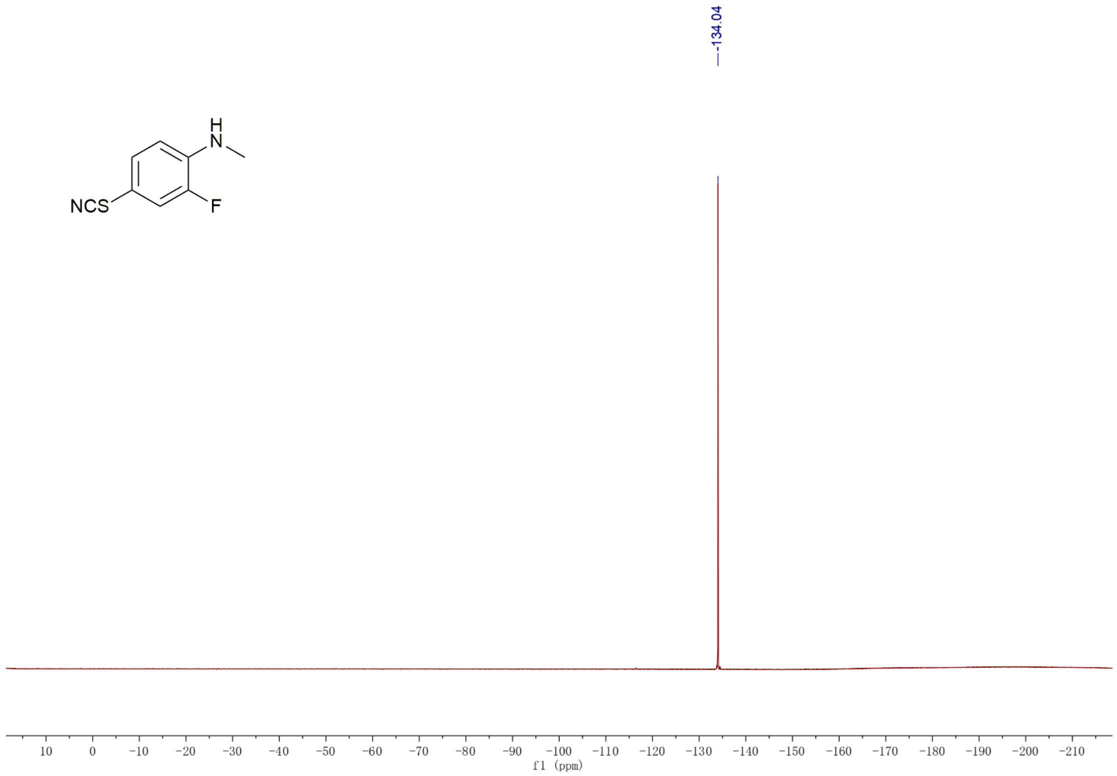
[1]H NMR (400 MHz, $CDCl_3$) spectrum of 3zb



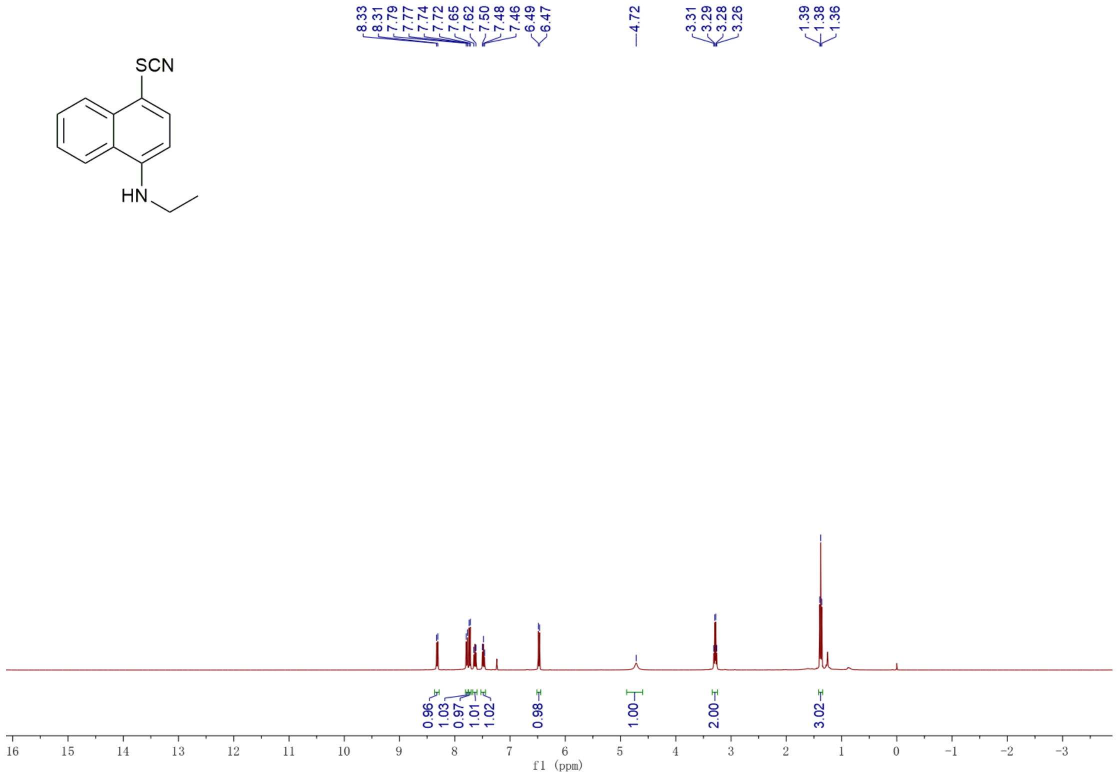
[13]C NMR (100 MHz, $CDCl_3$) spectrum of 3zb



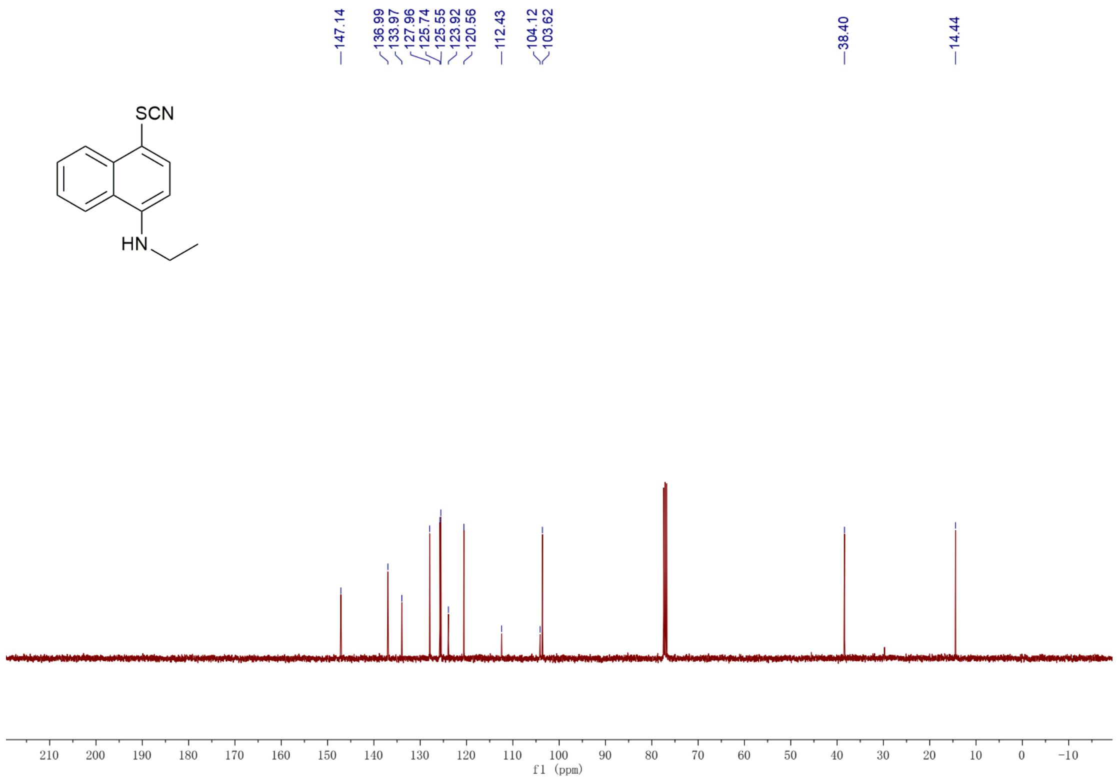
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3zb



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3zc

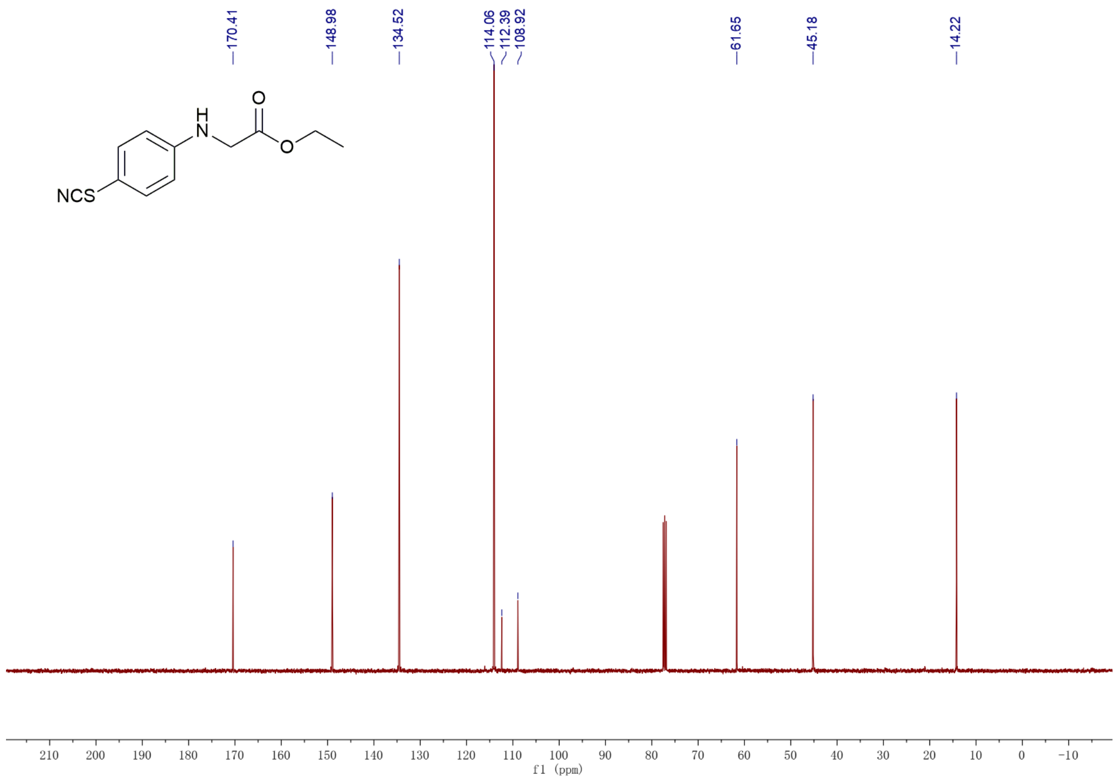


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3zc

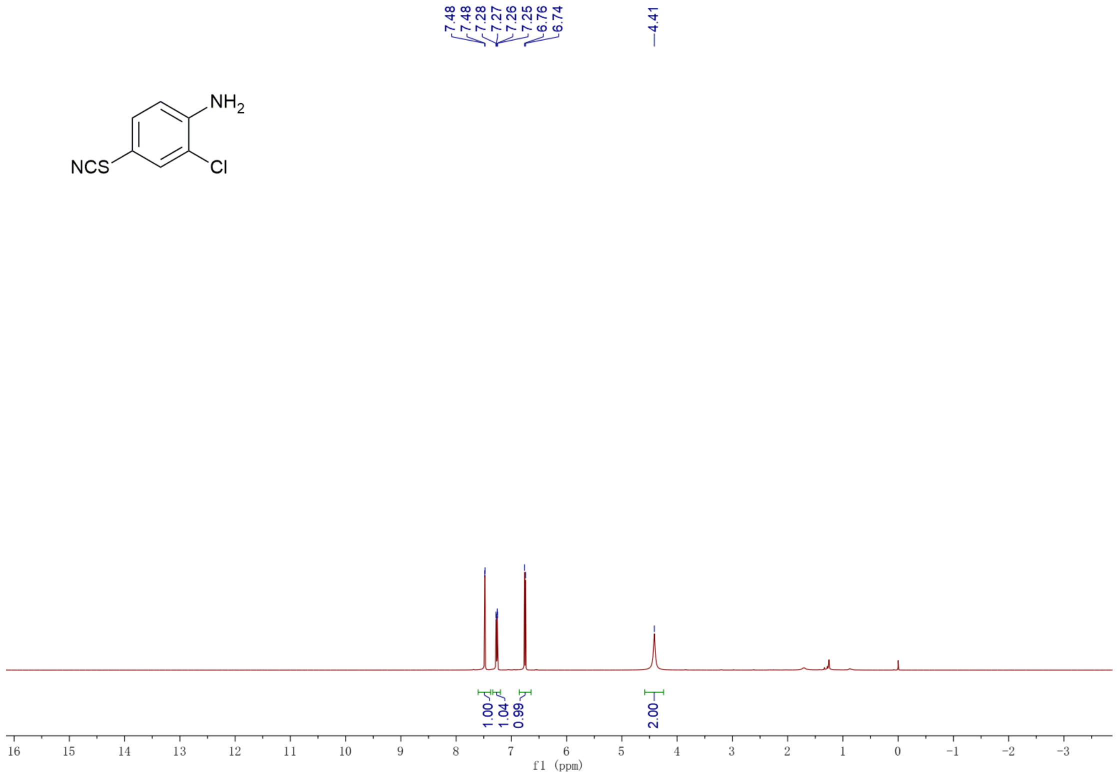


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3zd

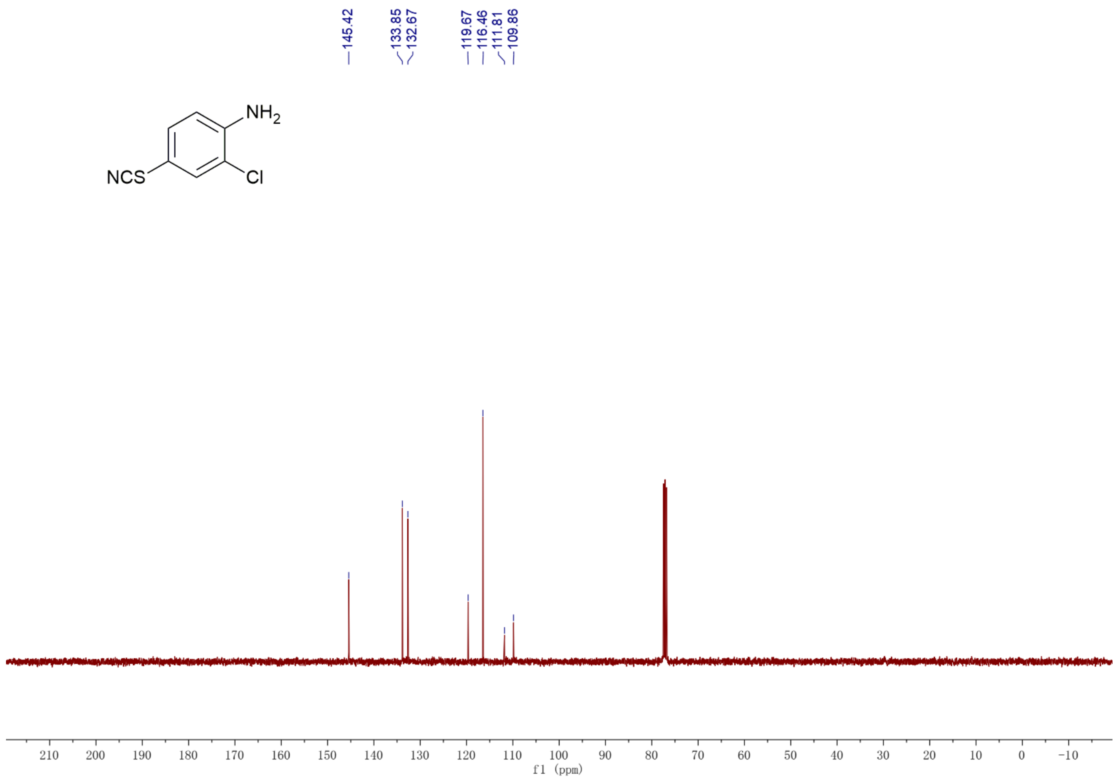
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3zd



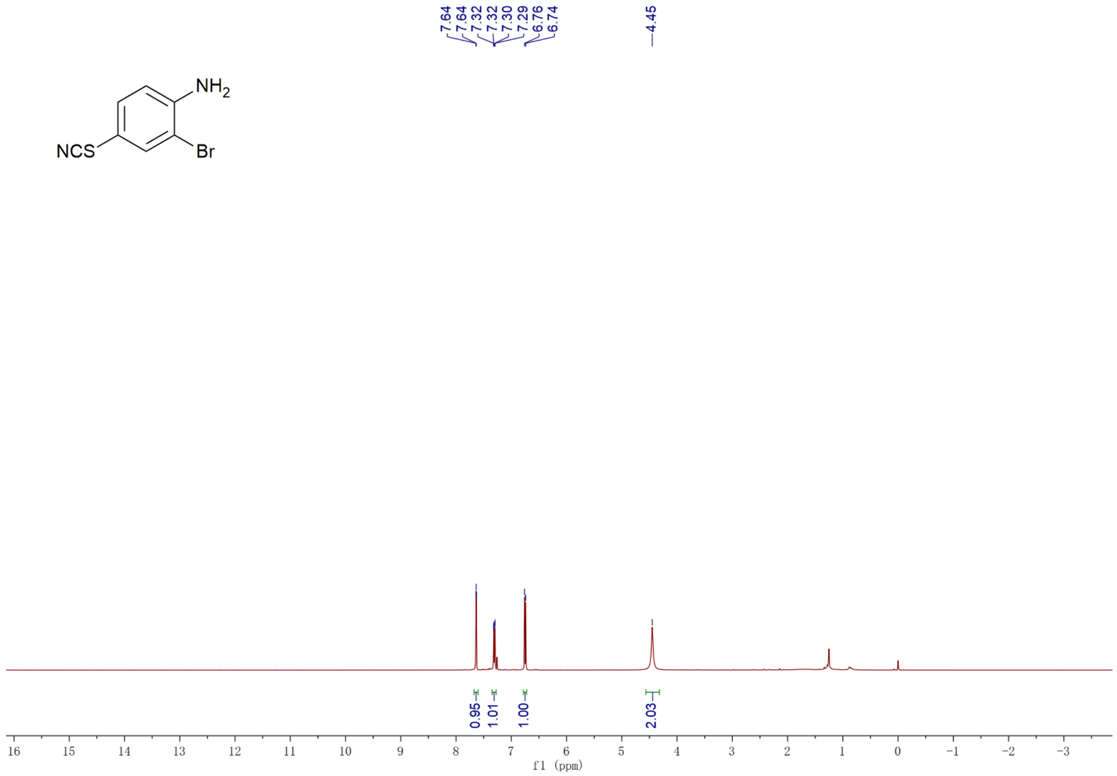
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ze



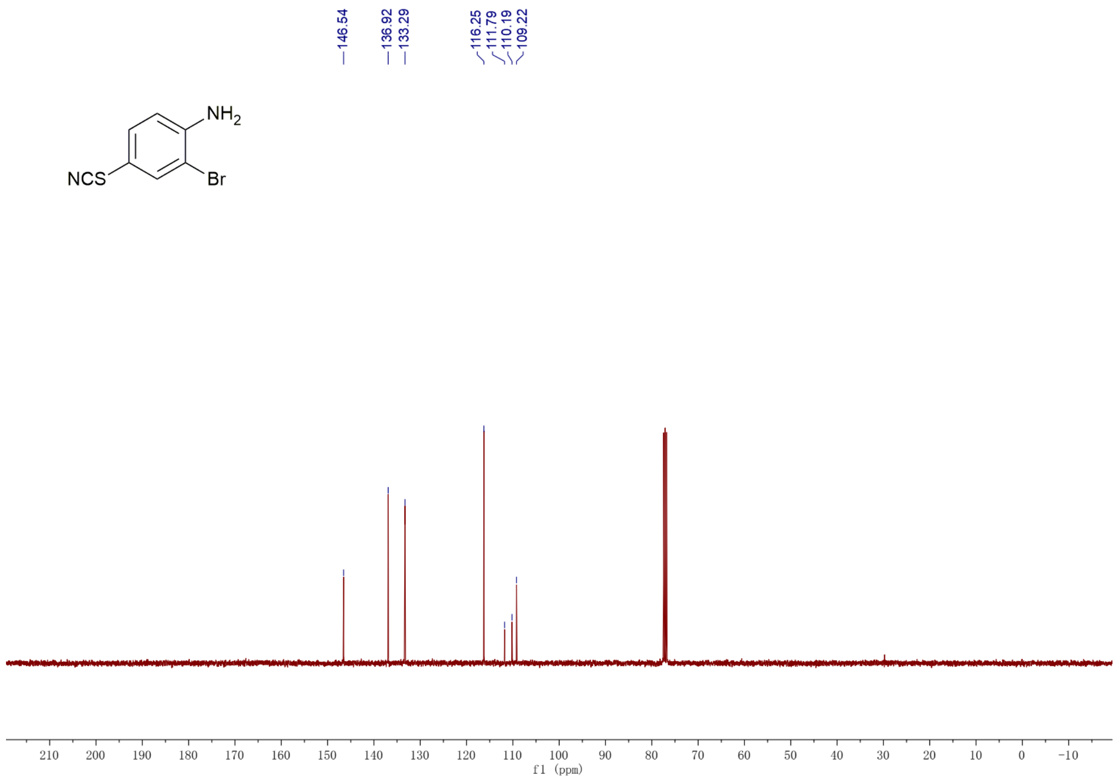
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ze



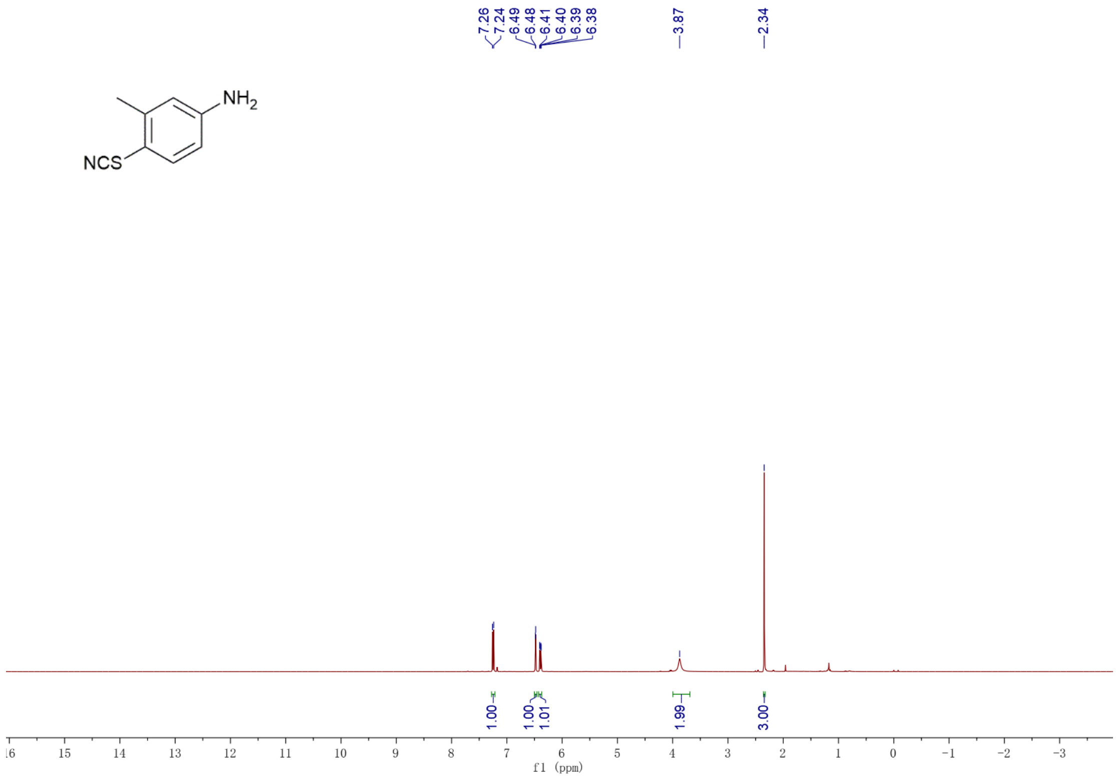
^1H NMR (400 MHz, $CDCl_3$) spectrum of 3zf



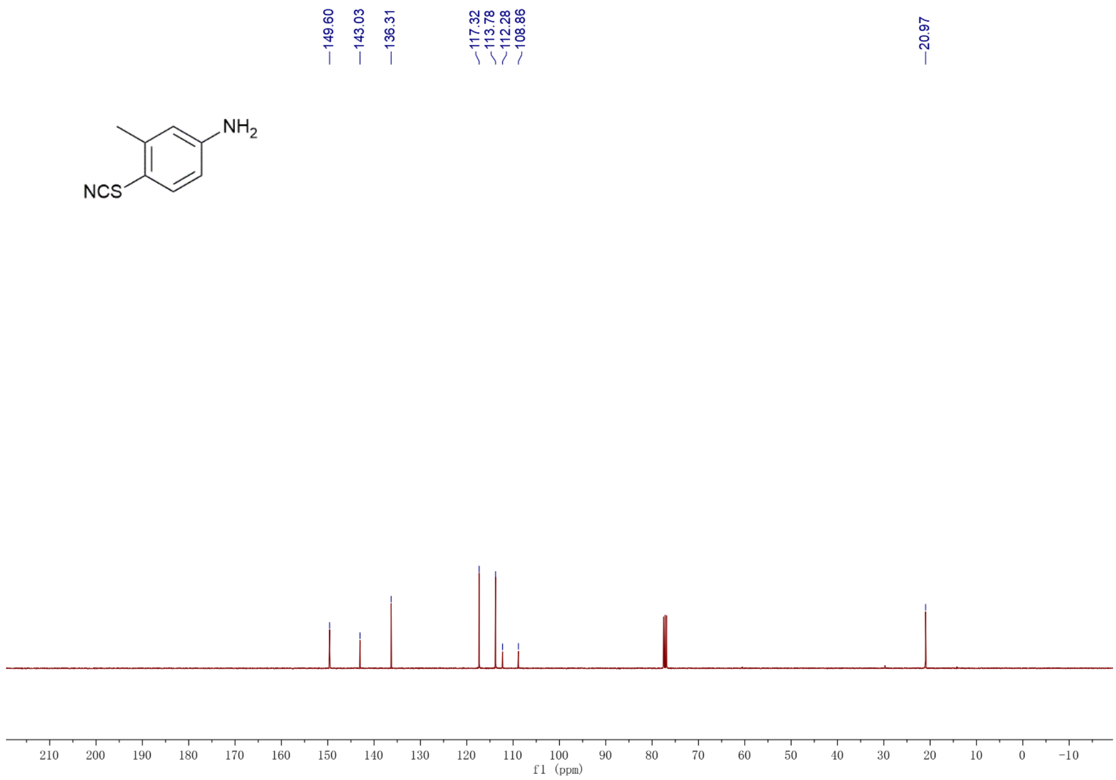
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3zf



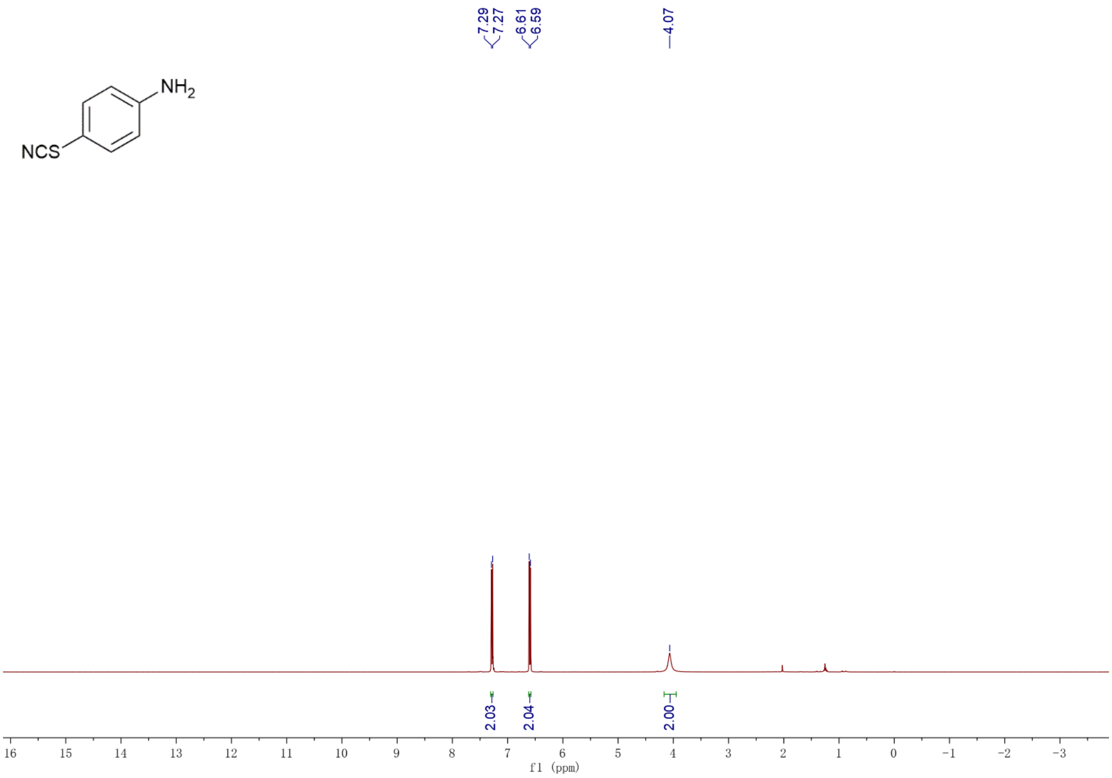
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3zg



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3zg



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3zh



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3zh