Supporting Information

Iron(III)-catalyzed mono-, di- and tricyanomethylation of primary amines with diazoacetonitrile: Construction of *α*-amino acetonitriles and asymmetric *α*-amino succinonitriles

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I. General Information

All reactions were carried out under an inert atmosphere (N_2) unless otherwise stated, with oven-dried glassware using standard techniques. All reagents with the exception of diazoacetonitrile (**1a**) and 2,2'-(phenylazanediyl)diacetonitrile (**3a'**) were purchased from reagent suppliers. Unless otherwise noted, all solvents and chemicals were reagent grade. Column chromatography was performed by using 200−300 mesh silica gel. Yields are based on the pure products isolated. The diazoacetonitrile was prepared according to the reported method. All ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer with tetramethylsilane (TMS) as internal reference in δ scale downfield from TMS. Coupling constants (*J*) were reported in hertz (Hz). The following abbreviations are used: s = singlet; d = doublet; and m = multiplet. High−resolution mass spectrometry (HR−MS) electrospray ionization (ESI) mass spectra were recorded on an Agilent 1290/6545 UPLC−TOF/MS spectrometer. GC−MS and HPLC−MS analyses were conducted on an Agilent 8890−7000 and an Agilent 1290/6545 UPLC−TOF/MS apparatus, respectively.

II. General Procedures

Procedure for the Synthesis of Diazoacetonitrile 1a[S1]

Aminoacetonitrile hydrochloride (4.63 g, 50 mmol) was dissolved in water (10 mL) in a 100 mL round-bottomed flask immersed in an ice-water bath, and then CH_2Cl_2 (20 mL) was added. The mixture was stirred vigorously, and $NaNO_2$ (3.45 g, 50 mmol) was added over 10 min. After stirring for another 1 h, the mixture was extracted with CH_2Cl_2 (50 mL), and the organic layer was washed with brine and dried over Na_2SO_4. Removing the solvent at 0 ^{o}C under vacuum and giving the N_2CHCN as a yellow liquid (1.98 g, 59%), and then it is formulated into a 1 mmol/mL acetonitrile solution to storage and use.

General Procedure of the 2a−2s

A 0.5 mmol amount of amines and 3.52 mg (1 mol%) of (TPP)Fe(III)Cl were placed into a reaction flask and dissolved in 4 mL of DCM at 25 ^{o}C under N_2. A solution of 52.25 mg (0.75 mmol) of diazoacetonitrile in 1 mL of DCM was added by syringe in one aliquot to the reaction mixture with vigorous stirring. After 20 min, the solvent was removed *in vacuo*. The residue was

separated through column chromatography using EtOAc/petroleum ether as eluting, and then the desired target product was obtained upon evaporation of the solvent.

General Procedure of the 3a−3p

A 0.5 mmol amount of aniline and 3.52 mg (1 mol%) of (TPP)Fe(III)Cl were placed into a reaction flask and dissolved in 2 mL of acetonitrile at 25 ^{o}C under N_2. A solution of 134 mg (2 mmol) of diazoacetonitrile in 0.5 mL of DCM was added by syringe in one aliquot to the reaction mixture with vigorous stirring. After 20 min, the solvent was removed *in vacuo*. The residue was separated through column chromatography using EtOAc/petroleum ether as eluting, and then the desired target product was obtained upon evaporation of the solvent.

General Procedure of the 5a−5r

A 0.5 mmol amount of amines and 3.52 mg (1 mol%) of (TPP)Fe(III)Cl were placed into a reaction flask and dissolved in 4 mL of DCM at 25 ^{o}C under N_2. A solution of 52.25 mg (0.75 mmol) of diazoacetonitrile in 1 mL of DCM was added by syringe in one aliquot to the reaction mixture until completion of the reaction (follow by TLC). Then 9 mg (3 mol%) of PcFe(III)Cl was added into the reaction flask, Another solution of 167.5 mg (2.5 mmol) of diazoacetonitrile in 1 mL of DCM was added by syringe in one aliquot to the reaction mixture with vigorous stirring. After 20 min, the solvent was removed *in vacuo*. The residue was separated through column chromatography using EtOAc/petroleum ether as eluting, and then the desired target product was obtained upon evaporation of the solvent.

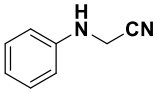
Procedure for the Synthesis of 2,2'-(Phenylazanediyl)diacetonitrile (3a')

A 0.5 mmol amount of aniline and 3.52 mg (1 mol%) of (TPP)Fe(III)Cl were placed into a reaction flask and dissolved in 4 mL of DCM at 25 ^{o}C under N_2. A solution of 134 mg (2 mmol) of diazoacetonitrile in 1 mL of DCM was added by syringe in one aliquot to the reaction mixture with vigorous stirring. After 20 min, the solvent was removed *in vacuo*. The residue was separated through column chromatography using EtOAc/petroleum ether as eluting, and then the desired target product was obtained upon evaporation of the solvent.

III. Characterization Data of the Diazoacetonitrile (1a)

Diazoacetonitrile (N_2CHCN): a yellow liquid, 1.98 g, yield: 59%. ^1H NMR (400 MHz, CD_3CN): δ 4.76 (s), The ^1H NMR spectral data are in good agreement with the literature data.[S1]

IV. Characterization Data of the Products 2a−2s, 3a−3p, 5a−5r and 3a'

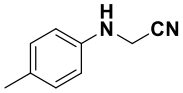


(phenylamino)acetonitrile (**2a**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 63mg, Yield: 95%.

^1H NMR (400 MHz, $CDCl_3$): δ 7.27-7.22 (m, 2 H), 6.88-6.85 (m, 1 H), 6.68-6.66 (m, 2 H), 3.99 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.19, 119.98, 117.30, 113.65, 32.61.

These spectroscopic data are in good agreement with the literature data.[S2]

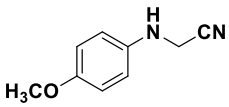


2-(p-tolylamino)acetonitrile (**2b**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 60 mg, Yield: 82%.

^1H NMR (400 MHz, $CDCl_3$): δ 7.07-7.05 (m, 2 H), 6.63-6.59 (m, 2 H), 4.02-3.87 (m, 3 H), 2.27 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.78, 130.10, 129.46, 117.27, 117.27, 113.89, 33.04, 20.49.

These spectroscopic data are in good agreement with the literature data.[S2]



2-((4-methoxyphenyl)amino)acetonitrile (**2c**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 67 mg, Yield: 83%.

^1H NMR (400 MHz, $CDCl_3$): δ 6.86-6.82 (m, 2 H), 6.69-6.65 (m, 2 H), 4.01 (s, 2 H), 3.83-3.76 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.89, 139.00, 117.38, 115.44, 115.08, 55.71, 33.75.

These spectroscopic data are in good agreement with the literature data.[S2]

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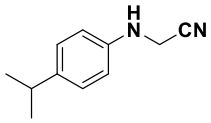
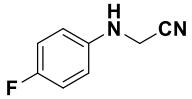


2-((4-isopropylphenyl)amino)acetonitrile (**2d)**: a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 76.5 mg, Yield: 88%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.10 (m, 2 H), 6.66-6.62 (m, 2 H), 4.01-3.91 (m, 3 H), 2.87-2.80 (m, 1 H), 1.22-1.20 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.08, 140.64, 127.49, 117.38, 113.80, 33.28, 32.96, 24.20.

These spectroscopic data are in good agreement with the literature data.[S3]



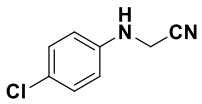
2-((4-fluorophenyl)amino)acetonitrile (**2e**): a light yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (20/1, v/v), 57 mg, Yield: 76%;

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99-6.93 (m, 2 H), 6.66-6.61 (m, 2 H), 4.03 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.38, 156.02, 141.40, 141.37, 117.13, 116.27, 116.04, 114.95, 114.87, 33.28.

^{19}F NMR (376 MHz, $CDCl_3$): δ -124.67-(-124.71) (m).

These spectroscopic data are in good agreement with the literature data.[S2]

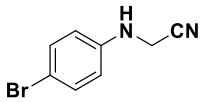


2-((chlorophenyl)amino)acetonitrile (**2f**): a light yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 76 mg, Yield: 92%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.17 (m, 2 H), 6.62-6.58 (m, 2 H), 4.12-4.00 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.75, 129.48, 124.74, 116.96, 114.81, 32.67.

These spectroscopic data are in good agreement with the literature data.[S2]

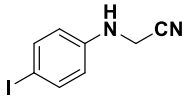


2-((4-bromophenyl)amino)acetonitrile (**2g**): a light yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (20/1, v/v), 98mg, Yield: 94%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.32 (m, 2 H), 6.58-6.54 (m, 2 H), 4.11-4.03 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.14, 132.37, 116.80, 115.25, 111.97, 32.59.

These spectroscopic data are in good agreement with the literature data.[S2]

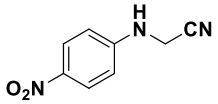


2-((4-iodophenyl)amino)acetonitrile (**2h**): a light yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 105 mg, Yield: 82%.

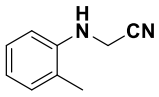
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.44 (m, 2 H), 6.43-6.40 (m, 2 H), 3.99 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.69, 138.25, 116.58, 115.75, 81.58, 32.46.

These spectroscopic data are in good agreement with the literature data.[S2]



((4-nitrophenyl)amino)acetonitrile (**2i**): Not detected.

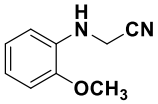


2-(*o*-tolylamino)acetonitrile (**2j**): a white solid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (20/1, v/v), 64 mg, Yield: 88%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.16 (m,1 H), 7.10-7.08 (m, 1 H), 6.82-6.78 (m, 1 H), 6.66-6.64 (m, 1 H), 4.04-4.02 (m, 2 H), 3.89 (s, 1 H), 2.10 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.27, 130.72, 127.38, 123.53, 119.60, 117.51, 117.47, 110.44, 32.45, 17.37.

These spectroscopic data are in good agreement with the literature data.[S2]

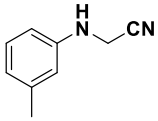


((2-methoxyphenyl)amino)acetonitrile (**2k**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 73 mg, Yield: 90%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95-6.90 (m, 1 H), 6.85-6.80 (m, 2 H), 6.69-6.67 (m, 1 H), 4.57 (s, 1 H), 4.07 (s 2 H), 3.82 (s, 3 H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.54, 135.06, 121.32, 119.43, 117.14, 110.86, 110.09, 55.58, 32.36.

These spectroscopic data are in good agreement with the literature data.[S4]

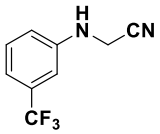


(*m*-tolylamino)acetonitrile **(2l)**: a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 69 mg, Yield: 95%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.11 (m, 1 H), 6.70-6.78 (m,1 H), 6.49-6.46 (m, 2 H), 3.97-3.94 (m, 3 H), 2.30 (s, 3 H);

^{13}CNMR (100 MHz, $CDCl_3$): δ 145.23, 139.54, 129.48, 120.93, 117.37, 114.45, 110.77, 32.64, 21.65.

These spectroscopic data are in good agreement with the literature data.[S2]



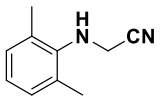
((3-(trifluoromethyl)phenyl)amino)acetonitrile (**2m**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (4/1, v/v), 84 mg, Yield: 84%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.32 (m, 1 H), 7.11-7.09 (m, 1 H), 6.89-6.88 (m, 1 H), 6.84-6.81 (m, 1 H), 4.34-4.09 (m, 3 H).

^{13}C NMR (100 MHz,$CDCl_3$): δ 145.45, 145.43, 132.00, 131.68, 130.15, 128.14, 125.44, 122,73, 120.02, 116.72, 116.69, 116.47, 116.42, 116.40, 116.35, 110.06, 110.02, 32.31.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.86-(-62.89) (m)

These spectroscopic data are in good agreement with the literature data.[S5]

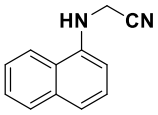


((2,6-dimethylphenyl)amino)acetonitrile (**2n**): a light yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 60mg, Yield: 75 %.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05-7.03 (m, 2 H), 6.95-6.91 (m, 1 H), 3.90 (s, 2 H), 3.42 (s, 1 H), 2.32 (s, 6 H).

^{13}C NMR (100 MHz,$CDCl_3$): δ 142.44, 130.87, 129.22, 124.26, 117.97, 36.16, 18.20.

These spectroscopic data are in good agreement with the literature data.[S2]

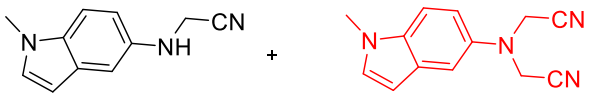


2-(naphthalen-1-ylamino)acetonitrile (**2o**): a light yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 77mg, Yield: 85%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.79 (m, 1 H), 7.69-7.67 (m, 1 H), 7.46-7.36 (m, 4 H), 6.67-6.63 (m, 1 H), 4.59 (s, 1 H), 4.13 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.45, 134.30, 128.85, 126.29, 126.24, 125.58, 123.89, 120.33, 120.30, 119.84, 117.16, 105.95, 32.70.

These spectroscopic data are in good agreement with the literature data.[S3]

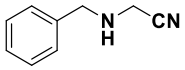


(**2p:2p'**)2-((1-methyl-1H-indol-5-yl)amino)acetonitrile:2,2'-((1-methyl-1H-indol-5-yl)azanediyl)diacetonitrile(1:1.5), a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (2/1, v/v), 95 mg, Yield: 93%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 2.0 Hz, 1 H), 7.31-7.29 (m, 1 H), 7.22-7.20 (m, 0.65 H), 7.09 (d, *J* = 3.1 Hz, 1 H), 7.01-6.96 (m, 1.65 H), 6.96 (d, *J* = 2.5 Hz, 1 H), 6.71-6.69 (m, 0.65 H), 6.46-6.45 (m, 1 H), 6.37 (m, 0.65 H), 4.17 (s, 4 H), 4.11 (s, 1 H), 3.78 (s, 3 H), 3.74 (s, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 139.49, 138.59, 134.52, 132.56, 130.48, 129.66, 129.21, 128.92, 117.70, 115.94, 115.20, 112.51, 112.07, 110.61, 110.42, 104.61, 101.18, 100.24, 43.06, 34.45, 33.16, 33.07.

HR-MS (ESI): Calcd. 225.1135 for $C_{13}H_{13}N_4^+[M+H]^+$, found: 225.1131 and Calcd. 186.1026 for $C_{11}H_{12}N_3^+[M+H]^+$, found: 186.1026.

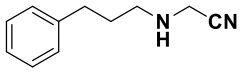


2-(benzylamino)acetonitrile (**2q**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 66 mg, Yield: 90%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.25 (m, 5 H), 3.91 (s, 2 H), 3.54 (s, 2 H), 1.70 (s, 1 H）

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.86, 128.69, 128.48, 127.73, 117.74, 52.35, 36.30.

These spectroscopic data are in good agreement with the literature data.[S3]

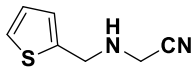


2-((3-phenylpropyl)amino)acetonitrile (**2r**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 61 mg, Yield: 70%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2 H), 7.21-7.16 (m, 3 H), 3.53 (s, 2 H), 2.72(t, *J* = 7.08 Hz, 2 H), 2.67 (t, *J* =7.32 Hz, 2 H), 1.84-1.77 (m, 2H), 1.35 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.67, 128.49, 128.44, 126.03, 117.97, 48.28, 37.33, 33.33, 31.11.

HR-MS (ESI): Calcd. 175.1230 for $C_{11}H_{15}N_2$ $[M+H]^+$, found: 175.1232.

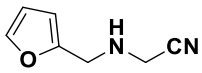


2-((thiophen-2-ylmethyl)amino)acetonitrile(**2s**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 50 mg, Yield: 66%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.26 (m, 1 H), 7.01-7.00 (m, 1 H), 6.98-6.96 (m, 1 H), 4.13 (s, 2 H), 3.59 (s, 2 H), 1.80 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.09, 126.85, 126.37, 125.58, 117.49, 46.95, 35.90.

HR-MS (ESI): Calcd. 153.0481 for $C_7H_9N_2S^+$$[M+H]^+$, found: 153.0485.

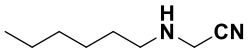


((furan-2-ylmethyl)amino)acetonitrile (**2t**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 43 mg, Yield: 64%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1 H), 6.34-6.28 (m, 2 H), 3.93 (s, 2 H), 3.58 (s, 2 H), 1.80 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.09, 126.85, 126.37, 125.58, 117.49, 46.95, 35.90.

HR-MS (ESI): Calcd. 137.0709 for $C_7H_9N_2O^+$$[M+H]^+$, found: 137.0710.

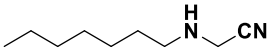


2-(hexylamino)acetonitrile (**2u**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 44 mg, Yield: 57%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.60 (s, 2 H), 2.73 (t, *J* = 7.08 Hz, 2 H), 1.52-1.46 (m, 2 H), 1.34 -1.30 (m, 6 H), 1.25 (s, 1 H), 0.91-0.88 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 117.93, 48.91, 37.36, 31.62, 29.43, 26.77, 22.57, 14.02.

HR-MS (ESI): Calcd. 141.1386 for $C_8H_{17}N_2$ $[M+H]^+$, found: 141.1389.

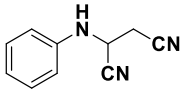


2-(heptylamino)acetonitrile (**2v**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (5/1, v/v), 50.5 mg, Yield: 60%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.59 (s, 2 H), 2.74-2.70 (m, 2 H), 1.53-1.48 (m, 2 H), 1.36-1.27 (m, 8 H), 0.90-0.86 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 117.96, 48.88, 37.33, 31.73, 29.45, 29.07, 27.03, 22.57, 14.04.

HR-MS (ESI): Calcd. 155.1543 for $C_9H_{19}N_2^+$ $[M+H]^+$, found: 155.1536.



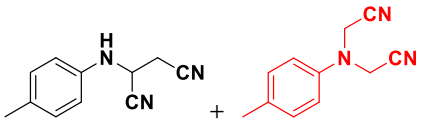
2-(phenylamino)succinonitrile (**3a**): a yellow solid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 67.5 mg, Yield: 79%, m.p. 119-120 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.24-7.20 (m, 2 H), 6.81-6.77 (m, 3 H), 6.47 (d, *J* = 10.04 Hz, 1 H), 5.11-5.05 (m, 1 H), 3.33-3.21 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 145.79, 129.71, 119.50, 119.07, 117.47, 114.37, 42.18, 21.90.

DEPT135: 129.71, 119.50, 114.37, 42.17, -21.90.

HR-MS (ESI): Calcd. 194.0689 for $C_{10}H_9N_3Na^+$ $[M+Na]^+$, found: 194.0680.

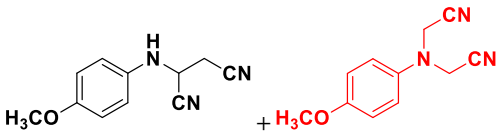


(**3b** : **3b'**): 2-(*p*-tolylamino)succinonitrile : 2,2'-(*p*-tolylazanediyl)diacetonitrile (1:1), a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (3/1, v/v), 47.5 mg, Yield: 60%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.15 (m, 2 H), 7.07-7.04 (m, 2 H), 6.87-6.84 (m, 2 H), 6.66-6.63 (m, 2 H), 4.54-4.46 (m, 1 H), 4.22-4.13 (m, 5 H), 2.93-2.91 (m, 2 H), 2.28 (d, *J* = 13.7 Hz 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.94, 141.26, 132.94, 130.88, 130.86, 130.29, 118.45, 117.39,117.18, 117.08, 115.40, 115.37, 115.20, 115.18, 43.38, 41.20, 22.72, 20.57.

HR-MS (ESI): Calcd. 208.0845 for $C_{11}H_{11}N_3Na^+$ $[M+Na]^+$, found: 208.0840.

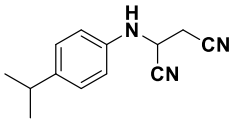


(**3c** : **3c'**) 2-((4-methoxyphenyl)amino)succinonitrile : 2,2'-((4-methoxyphenyl)azanediyl)diacetonitrile (1.2 : 1), a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (3/1, v/v), 30 mg, Yield: 30%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02-7.99 (m, 2.2 H), 6.91-6.83 (m, 4 H), 6.78-6.75 (m, 1.8 H), 4.48-4.43 (m, 1 H), 4.11-4.04 (m, 5 H), 3.80-3.76 (m, 6 H), 2.98 (d, *J* = 6.48 Hz 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.62, 155.02, 139.29, 137.09, 121.91, 120.79, 117.83, 117.31,115.14, 115.01, 114.92, 114.27, 55.65, 55.60, 44.56, 42.19, 22.90.

HR-MS (ESI): Calcd. 224.0794 for $C_{11}H_{11}N_3NaO^+$ $[M+Na]^+$, found: 224.0797.

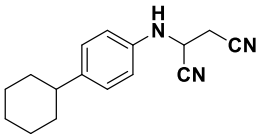


2-((4-isopropylphenyl)amino)succinonitrile (**3d**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using Petroleum ether/EtOAc (3/1, v/v), 49mg, Yield: 46%.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.11-7.07 (m, 2 H), 6.75-6.71 (m, 2 H), 6.28 (d, J = 10.28 Hz, 1 H), 5.06-4.99 (m, 1 H), 3.30-3.18 (m, 2 H), 2.84-2.73 (m, 1 H), 1.16 (d, J = 6.84 Hz, 6 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 143.71, 139.53, 127.43, 119.22, 117.48, 114.49, 42.46, 33.04, 24.59, 24.56, 21.93.

HR-MS (ESI): Calcd. 236.1158 for $C_{13}H_{15}N_3Na^+$[M+Na]$^+$, found: 236.1154.

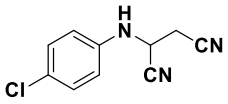


2-((2,3-dichlorophenyl)amino)succinonitrile (**3e**): a yellow solid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 73.5 mg, Yield: 58%, m.p. 117-118 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.08-7.05 (m, 2 H), 6.74-6.70 (m, 2 H), 6.28 (d, J = 10.16 Hz, 1 H), 5.05-4.99 (m, 1 H), 3.30-3.17 (m, 2 H), 2.41-2.35 (m, 1 H), 1.79-1.66 (m, 5 H), 1.40-1.22 (m, 5 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 143.72, 138.84, 127.78, 119.22, 117.48, 114.45, 43.40, 42.43, 34.70, 26.92, 26.12, 21.94.

HR-MS (ESI): Calcd. 276.1471 for $C_{16}H_{19}N_3Na^+$ [M+Na]$^+$, found: 276.1479.

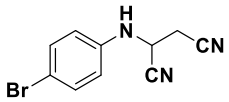


2-((4-chlorophenyl)amino)succinonitrile (**3f**): a yellow solid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 67 mg, Yield: 65%, m.p. 89-90 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.28-7.24 (m, 2 H), 6.84-6.80 (m, 2 H), 6.67 (d, J = 9.8 Hz, 1 H), 5.13-5.07 (m, 1 H), 3.34-3.22 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 144.77, 129.46, 123.03, 118.79, 117.37, 115.88, 42.21, 21.82.

HR-MS (ESI): Calcd. 228.0299 for $C_{10}H_8ClN_3Na^+$ $[M+Na]^+$, found: 228.0291.

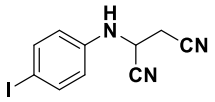


2-((4-bromophenyl)amino)succinonitrile (**3g**): a yellow solid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 84 mg, Yield: 68%, m.p. 98-99 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.40-7.36 (m, 2 H), 6.80-6.76 (m, 2 H), 6.69 (d, J = 9.8 Hz, 1 H), 5.12-5.06 (m, 1 H), 3.34-3.22 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 145.15, 132.30, 118.74, 117.35, 116.37, 110.61, 42.13, 21.83.

HR-MS (ESI): Calcd. 271.9706 for $C_{10}H_8BrN_3Na^+$ $[M+Na]^+$, found: 271.9708.

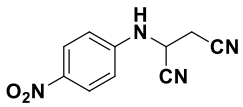


2-((4-isopropylphenyl)amino)succinonitrile (**3h**): a yellow solid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 111 mg, Yield: 75%, m.p. 117-118 ^{o}C.

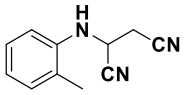
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.54-7.50 (m, 2 H), 6.69-6.65 (m, 3 H), 5.11-5.05 (m, 1 H), 3.33-3.21 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 145.61, 138.06, 118.74, 117.35, 116.90, 81.20, 41.98, 21.81.

HR-MS (ESI): Calcd. 319.9655 for $C_{10}H_8IN_3Na^+$ $[M+Na]^+$, found: 319.9647.



2-((4-nitrophenyl)amino)succinonitrile (**3i**): Not detected.

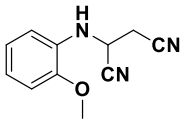


2-(o-tolylamino)succinonitrile (**3j**): a yellow solid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 65 mg, Yield: 70%, m.p. 149-150 ^oC.

^1H NMR (400 MHz, DMSO-d_6): δ 7.15-7.08 (m, 2 H), 6.82-6.73 (m, 2 H), 5.66 (d, *J* = 10.4 Hz, 1 H), 5.12-5.05 (m, 1 H), 3.37-3.35 (m, 2 H), 2.15 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 143.62, 130.89, 127.32, 124.54, 119.67, 119.21, 117.55, 112.23, 42.22, 21.81, 18.01.

HR-MS (ESI): Calcd. 208.0845 for $C_{11}H_{10}N_3Na^+$[M+Na]$^+$, found: 208.0838.

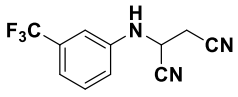


2-((2-methoxyphenyl)amino)succinonitrile (**3k**): a yellow solid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 57 mg, Yield: 57%, m.p. 108-109 ^oC.

^1H NMR (400 MHz, DMSO-d_6): δ 6.95-6.77 (m, 4 H), 5.87 (d, *J* = 10.88 Hz, 1 H), 5.15-5.08 (m, 1 H), 3.82 (s, 3 H), 3.38 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 147.91, 134.92, 121.40, 119.67, 119.09, 117.63, 112.38, 111.12, 55.93, 41.95, 21.53.

HR-MS (ESI): Calcd.224.0794 for $C_{11}H_{11}N_3NaO^+$ [M+Na]$^+$, found: 224.0790.



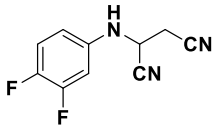
2-((3-(trifluoromethyl)phenyl)amino)succinonitrile (**3l**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 61 mg, Yield: 51%.

^1H NMR (400 MHz, DMSO-d_6): δ 7.47-7.43 (m, 1 H), 7.14-7.08 (m, 3 H), 7.00 (d, *J* = 9.64 Hz, 1 H), 5.30-5.25 (m, 1 H), 3.37-3.26 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 146.47, 131.06-130.12(m), 130.76, 128.78-120.66 (m), 118.68, 117.94, 117.31, 115.58-115.46 (m), 110.23-110.15 (m), 41.91, 21.83.

^{19}F NMR (376 MHz, DMSO-d_6): δ -61.36-(-61.40) (m).

HR-MS (ESI): Calcd. 240.0743 for $C_{11}H_9F_3N_3^+$ $[M+H]^+$, found: 240.0750.



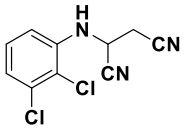
2-((3,4-difluorophenyl)amino)succinonitrile (**3m**): a yellow solid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 67 mg, Yield: 65%, m.p. 81-82 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.31-7.24 (m, 1 H), 6.92-6.86 (m, 1 H), 6.72 (d, *J* = 9.92 Hz, 1 H), 6.64-6.61 (m, 1 H), 5.13-5.07 (m, 1 H), 3.31-3.27 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 150.38 (dd, J = 996.84, 53.96 Hz,), 144.59 (d, *J* = 51.04 Hz), 143.33-143.22 (m), 142.25, (d, *J* = 51.04 Hz), 118.34 (d, *J* = 65.6 Hz), 117.99 (d, *J* = 552.68 Hz), 110.43-110.34 (m), 103.11 (d, *J* = 84.56 Hz), 112.23, 42.49, 21.81.

^{19}F NMR (376 MHz, DMSO-d_6): δ -137.43-(-137.49) (m), -151.37-(-151.43) (m).

HR-MS (ESI): Calcd. 230.0500 for $C_{10}H_7F_2N_3Na^+$ $[M+Na]^+$, found: 230.0490.

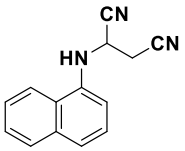


2-((2,3-dichlorophenyl)amino)succinonitrile (**3n**): a yellow solid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 74 mg, Yield: 62%, m.p. 132-133 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.32-7.28 (m, 1 H), 7.09-7.01 (m, 2 H), 6.54 (d, *J* = 10 Hz, 1 H), 5.33-5.27 (m, 1 H), 3.51-3.41 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 143.62, 132.77, 129.15, 120.74, 118.49, 118.03, 117.32, 112.17, 42.01, 21.45.

HR-MS (ESI): Calcd. 261.9909 for $C_{10}H_7Cl_2N_3Na^+$ $[M+Na]^+$, found: 261.9900.

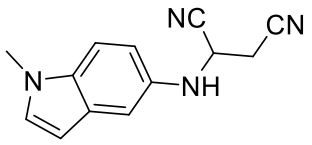


2-(naphthalen-1-ylamino)succinonitrile (**3o**): a yellow solid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 74 mg, Yield: 67%, m.p. 99-100 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.15-8.13 (m, 1 H), 7.88-7.85 (m, 1 H), 7.54-7.51 (m, 2 H), 7.45-7.39(m, 2 H), 6.88-6,84 (m, 2 H), 5.30-5.24 (m, 1 H), 3.49-3.47 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 141.14, 134.40, 128.71, 126.78, 126.66, 125.52, 124.15, 121.93, 119.75, 119.05, 117.57, 106.92, 42.34, 21.83.

HR-MS (ESI): Calcd. 244.0845 for $C_{14}H_{11}N_3Na^+$ $[M+Na]^+$, found: 244.0838.

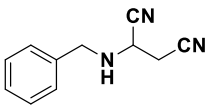


2-((1-methyl-1H-indol-5-yl)amino)succinonitrile (**3p**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (2/1, v/v), 56 mg, Yield: 50%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-6.94 (m, 5 H), 4.2 (s, 2 H), 3.80-3.72 (m, 5 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.82, 134.88, 129.04, 126.94, 116.56, 115.00, 111.24, 109.89, 103.15, 100.51, 43.01, 33.21, 14.41.

HR-MS (ESI): Calcd. 225.1135 for $C_{13}H_{13}N_4^+$$[M+H]^+$, found: 225.1133.

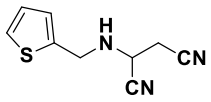


2-(benzylamino)succinonitrile (**3q**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 46 mg, Yield: 50%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.31(m, 6 H), 4.12-4.09 (m, 1 H), 3.89-3.78 (m, 2 H), 2.89-2.78 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.04, 128.86, 128.45, 128.08, 117.24, 115.06, 51.33, 45.57, 23.19.

HR-MS (ESI): Calcd. 208.0845 for $C_{11}H_{10}N_3Na^+[M+Na]^+$, found: 208.0856.

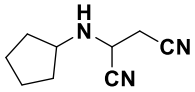


2-((thiophen-2-ylmethyl)amino)succinonitrile (**3r**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 23 mg, Yield: 30%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.31 (m, 1 H), 7.07-7.05 (m, 1 H), 7.01-6.99 (m, 1 H), 4.34-4.30 (m, 1 H), 4.18-4.14 (m, 1 H), 3.89 (t, J = 6.4 Hz, 1 H), 2.89-2.87(m, 2 H), 2.04(s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.13, 126.99, 126.76, 126.05, 116.99, 114.89, 46.16, 45.06, 23.19.

HR-MS (ESI): Calcd. 192.0590 for $C_9H_{10}N_3S^+[M+H]^+$, found: 192.0593.

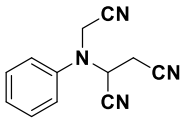


2-(cyclopentylamino)succinonitrile(**3s**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 29 mg, Yield: 31%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.75 (t,J = 6.4 Hz, 1 H), 3.32-3.25 (m, 1 H), 2.83-2.74 (m, 2 H), 1.90-1.84 (m, 1 H), 1.76-1.64 (m, 3 H), 1.57-1.50 (m, 2 H), 1.38-1.28 (m, 2 H), 1.22-1.18 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 117.97, 115.31, 57.92, 45.55, 33.63, 32.09, 23.85, 23.81, 23.69.

HR-MS (ESI): Calcd. 164.1182 for $C_9H_{14}N_3^+[M+H]^+$, found: 164.1180.



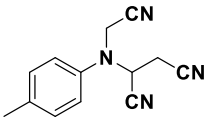
2-((cyanomethyl)(phenyl)amino)succinonitrile (**5a**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 97.5 mg, Yield: 93%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.44 (m, 2 H), 7.37-7.31 (m, 3 H), 4.68-4.65 (m, 1 H), 4.26-4.15 (m, 2 H), 2.96-2.85 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.48, 130.45, 127.48, 123.59, 114.91, 114.67, 114.27, 50.84, 41.60, 21.89.

DEPT135: 130.58, 127.49, 123.60, 50.84, -41.61, -21.89.

HR-MS (ESI): Calcd. 233.0798 for $C_{12}H_{10}N_4Na^+$ $[M+Na]^+$, found: 233.0803.

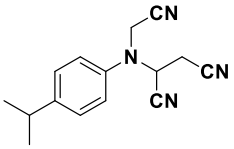


2-((cyanomethyl)(p-tolyl)amino)succinonitrile (**5b**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 99.5 mg, Yield: 89%.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.23-7.21 (m, 2 H), 7.12-7.10 (m, 2 H), 5.51-5.47 (m, 1 H), 4.71-4.54 (m, 2 H), 3.46-3.36 (m, 2 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 142.90, 132.60, 130.45, 118.67, 116.87, 116.85, 116.29, 48.88, 37.35, 20.87, 20.58.

HR-MS (ESI): Calcd. 247.0954 for $C_{13}H_{12}N_4Na^+$ $[M+Na]^+$, found: 247.0947.

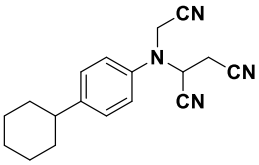


2-((cyanomethyl)(4-isopropylphenyl)amino)succinonitrile (**5c**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 101 mg, Yield: 80%.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.31-7.26 (m, 4 H), 4.62-4.58 (m, 1 H), 4.22-4.10 (m, 2 H), 2.96-2.86 (m, 3 H), 1.28-1.23 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.77, 140.95, 128.36, 124.31, 115.05, 114.87, 114.45, 51.06, 42.19, 33.70, 23.87, 21,92.

HR-MS (ESI): Calcd. 275.1267 for $C_{15}H_{16}N_4Na^+$ $[M+Na]^+$, found: 275.1259.

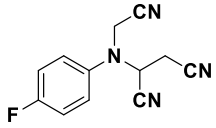


2-((cyanomethyl)(4-cyclohexylphenyl)amino)succinonitrile (**5d**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 117 mg, Yield: 80%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.24 (m, 4 H), 4.62-4.58 (m, 1 H), 4.22-4.10 (m, 2 H), 2.88-2.85 (m, 2 H), 2.54-2.49 (m, 1 H), 1.88-1.74 (m, 5 H), 1.44-1.27 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.94, 140.96, 128.71, 124.21, 115.06, 114.87, 114.45, 51.06, 44.04, 42.14, 34.34, 26.76, 26.02, 21,93.

HR-MS (ESI): Calcd. 315.1580 for $C_{18}H_{20}N_4Na^+$ $[M+Na]^+$, found: 315.1583.



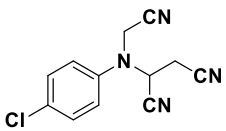
2-((cyanomethyl)(4-fluorophenyl)amino)succinonitrile (**5e**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 97 mg, Yield: 85%.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.28-7.26 (m, 4 H), 5.49-5.45 (m, 1 H), 4.72-4.56 (m, 2 H), 3.46-3.37 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 158.81 (d, J = 956.6Hz), 141.76 (d, J = 10.0Hz), 121.19 (d, J = 33.52), 121.23, 121,15, 116.82-116.74 (m), 116.78, 116.56, 116.18, 49.31, 37.79, 20.89.

^{19}F NMR (376 MHz, DMSO-d_6): δ -120.06.

HR-MS (ESI): Calcd. 251.0703 for $C_{12}H_9FN_4Na^+$ $[M+Na]^+$, found: 251.0705.

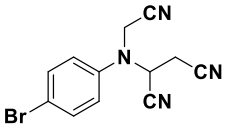


2-((4-chlorophenyl)(cyanomethyl)amino)succinonitrile (**5f**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 110 mg, Yield: 90%.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.49-7.45 (m, 2 H), 7.24-7.20 (m, 2 H), 5.66-5.62 (m, 1 H), 4.79-4.63 (m, 2 H), 3.51-3.49 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 144.10, 129.81, 126.91, 119.34, 116.73, 116.63, 116.05, 48.32, 36.83, 20.69.

HR-MS (ESI): Calcd. 267.0408 for $C_{12}H_9ClN_4Na^+$ $[M+Na]^+$, found: 267.0401.

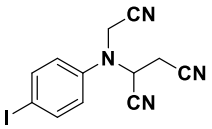


2-((4-bromophenyl)(cyanomethyl)amino)succinonitrile (**5g**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 129 mg, Yield: 90%.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.61-7.56 (m, 2 H), 7.18-7.14 (m, 2 H), 5.67-5.63 (m, 1 H), 4.79-4.64 (m, 2 H), 3.51-3.50 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 144.50, 132.69, 119.59, 116.72, 116.61, 116.03, 114,71, 48.19, 36.73, 20.67.

HR-MS (ESI): Calcd. 310.9903 for $C_{12}H_9BrN_4Na^+$ $[M+Na]^+$, found: 310.9894.

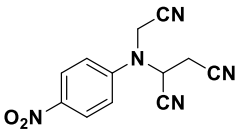


2-((cyanomethyl)(4-iodophenyl)amino)succinonitrile (**5h**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 117 mg, Yield: 70%.

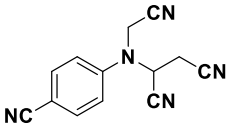
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.62 (m, 2 H), 6.93-6.89 (m, 2 H), 4.71-4.68 (m, 1 H), 4.12 (s, 2 H), 2.95-2.83 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.53, 139.29, 123.63, 115.33, 115.00, 114.94, 90.41, 50.07, 40.40, 21.69.

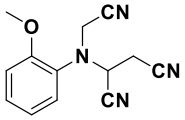
HR-MS (ESI): Calcd. 358.9764 for $C_{12}H_9IN_4Na^+$ $[M+Na]^+$, found: 358.9769.



2-((cyanomethyl)(4-nitrophenyl)amino)succinonitrile (**5i**): Not detected.



2-((cyanomethyl)(4-cyanophenyl)amino)succinonitrile (**5j**): Not detected.

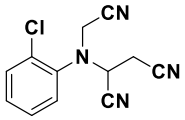


2-((cyanomethyl)(2-methoxyphenyl)amino)succinonitrile (**5k**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 48 mg, Yield: 40%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.29 (m, 2 H), 7.01-6.97 (m, 2H), 4.62-4.59 (m, 1 H), 4.24-4.13 (m, 2 H), 3.90 (s, 3 H), 2.98-2.84 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.70, 132.10, 129.40, 127.80, 121.53, 115.69, 115.30, 114.79, 112.47, 55.48, 51.04, 40.75, 22.32.

HR-MS (ESI): Calcd. 263.0903 for $C_{13}H_{13}N_4O^+$ $[M+H]^+$, found: 263.0897.

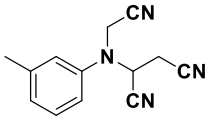


2-((2-chlorophenyl)(cyanomethyl)amino)succinonitrile (**5l**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 91 mg, Yield: 75%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.47 (m, 1 H), 7.35-7.32 (m, 1 H), 7.26-7.18 (m, 2 H), 4.64-4.61 (m, 1 H), 4.27-4.17 (m, 2 H), 3.04-2.92 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.26 (d, *J* = 993.1 Hz), 131.13 (d, *J* = 43.7 Hz), 129.62 (d, *J* = 33.5 Hz), 126.78, 125.66 (d, *J* = 14.6 Hz), 117.53 (d, *J* = 80.2 Hz), 115.00, 114.79, 114.44, 51.09 (d, *J* = 7.3 Hz), 41.15 (d, *J* = 11.6 Hz), 22.00.

HR-MS (ESI): Calcd. 267.0408 for $C_{12}H_9ClN_4Na^+$ $[M+Na]^+$, found: 267.0400.

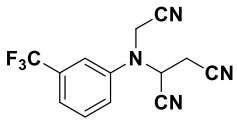


2-((cyanomethyl)(m-tolyl)amino)succinonitrile (**5m**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 96 mg, Yield: 86%.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.30-7.26 (m, 1 H), 7.03-6.97 (m, 2 H), 6.91-6.89 (m, 1 H), 5.62-5.58 (m, 1 H), 4.75-4.59 (m, 2 H), 3.54-3.43 (m, 2 H), 2.33 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 145.26, 139.48, 129.84, 123.68, 118.31, 116.87, 116.83, 116.27, 114.80 , 48.32, 36.75, 21.74, 20.80.

HR-MS (ESI): Calcd. 247.0954 for $C_{13}H_{12}N_4Na^+$$[M+Na]^+$, found: 247.0947.



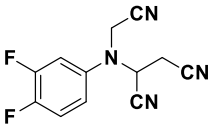
2-((cyanomethyl)(3-(trifluoromethyl)phenyl)amino)succinonitrile (**5n**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 115 mg, Yield: 83%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.47 (m, 4 H), 4.80-4.70 (m, 1 H), 4.31-4.22 (m, 2 H), 3.05-2.94 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.35, 133.09-130.73 (m), 125.31-121.96 (m), 119.17-119.13 (m), 114.55, 114.27, 114.03, 50.47, 40.54, 21.88.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.80-(-62.81) (m).

HR-MS (ESI): Calcd. 301.0672 for $C_{13}H_9F_3N_4Na^+$ $[M+Na]^+$, found: 301.0668.



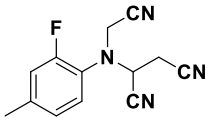
2-((cyanomethyl)(3,4-difluorophenyl)amino)succinonitrile (**5o**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 100 mg, Yield: 81%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.13 (m, 3 H), 4.64-4.60 (m, 1 H), 4.21-4.12 (m, 2 H), 2.99-2.86 (m, 2 H).

^{13}C NMR (100 MHz,$CDCl_3$): δ 152.10-148.20 (m), 139.89-139.78 (m), 120.66-120.56 (m), 118.97-118.78 (m), 114.65, 114.53, 114.33, 114,01 (d, *J* = 806.84Hz), 50.94, 41.85, 21.86.

^{19}F NMR (376 MHz, $CDCl_3$): δ -132.19-(-132.25) (m), -136.95-(-137.01) (m).

HR-MS (ESI): Calcd.269.0609 for $C_{12}H_8F_2N_4Na^+$ $[M+Na]^+$, found: 269.0603.



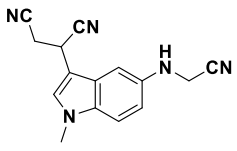
2-((cyanomethyl)(2-fluoro-4-methylphenyl)amino)succinonitrile (**5p**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 100.5 mg, Yield: 83%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 1 H), 7.04-7.00 (m, 2 H), 4.58-4.55 (m, 1 H), 4.23-4.12 (m, 2 H), 2.99-2.86 (m, 2 H), 2.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.31 (d, *J* = 991.64Hz), 140.90 (d, *J* = 32.08Hz), 127.94 (d, *J* = 45.2Hz), 126.95 (d, *J* = 7.28Hz), 126.21 (d, *J* = 13.12Hz), 117.94 (d, *J* = 80.2Hz),114.96, 114.80, 114.38, 51.23 (d, *J* = 7.28Hz), 41.61 (d, *J* = 10.2Hz), 22.00, 21.10 (d, *J* = 5.84Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -119.82.

HR-MS (ESI): Calcd. 265.0860 for $C_{13}H_{12}FN_4Na^+$$[M+Na]^+$, found: 265.0851.

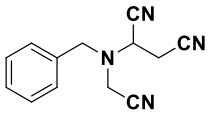


2-((3-(cyanomethyl)-1-methyl-1H-indol-5-yl)amino)succinonitrile (**5q**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (2/1, v/v), 112 mg, Yield: 85%.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.46-7.42 (m, 1 H), 7.33 (s, 1 H), 7.23-7.22 (m, 1 H), 7.06-7.02 (m, 1 H), 4.60-4.57 (m, 4 H), 4.00-3.95(m, 2 H), 3.72 (s, 3 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ 139.10, 133.14, 129.65, 127.36, 119.92, 117.50, 116.96, 113.04, 111.56, 105.44, 103.02, 41.33, 33.09, 19.88, 13.57.

HR-MS (ESI): Calcd. 264.1244 for $C_{15}H_{14}N_5^+[M+H]^+$, found: 264.1242.

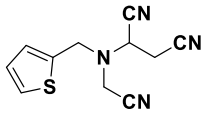


2-(benzyl(cyanomethyl)amino)succinonitrile (**5r**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 58 mg, Yield: 52%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.38 (m, 5 H), 4.18-4.06 (m, 2 H), 3.80-3.44 (m, 4 H), 2.98-2.95 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 133.89, 129.31, 129.04, 114.15, 113.89, 113.39, 55.48, 50.42, 39.88, 21.58.

HR-MS (ESI): Calcd. 247.0954 for $C_{13}H_{12}N_4Na^+[M+Na]^+$, found: 247.0948.

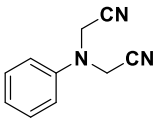


2-((cyanomethyl)(thiophen-2-ylmethyl)amino)succinonitrile (**5s**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (3/1, v/v), 64.5 mg, Yield: 56%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.37 (m, 1 H), 7.14-7.12 (m, 1 H), 7.04-7.00 (m, 1H), 4.23-4.18 (m, 2 H), 4.10-4.06(m, 1 H), 3.71-3.62 (m, 2 H), 2.97-2.95 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.70, 128.64, 127.58, 127.29, 114.17, 113.87, 113.34, 50.55, 49.99, 39.59, 21.65.

HR-MS (ESI): Calcd. 253.0518 for $C_{11}H_{10}N_4NaS^+[M+Na]^+$, found: 253.0509.



2,2'-(phenylazanediyl)diacetonitrile (**3a'**): a yellow liquid was obtained after column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-Hexane/EtOAc (5/1, v/v), 17 mg, Yield: 20%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.36 (m, 2 H), 7.13-7.09 (m, 1 H), 7.02-6.98 (m, 2 H), 4.25 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.47, 130.00, 123.46, 117.23, 114.62, 41.01.

HR-MS (ESI): Calcd. 194.0689 for $C_{10}H_9N_3Na^+[M+Na]^+$, found: 194.0683.

V. The Gram-Scale Synthesis of 2a, 3a and 5a

The Gram-Scale Synthesis of 2a

A 20 mmol amount of aniline, and 140 mg (1 mol%) of (TPP)Fe(III)Cl were placed into a three-necked flask and dissolved in 80 mL of DCM at 25 ^{o}C under N_2. A solution of 2.01 g (30 mmol) of diazoacetonitrile **1a** in 20 mL of DCM was added by syringe over 10 min to the reaction mixture. After 20 min, the solvent was removed in vacuo. The residue was separated through column chromatography using EtOAc/petroleum ether as eluting, and then the desired product **2a** of 2.376 g in 90% yield was obtained upon evaporation of the solvent.

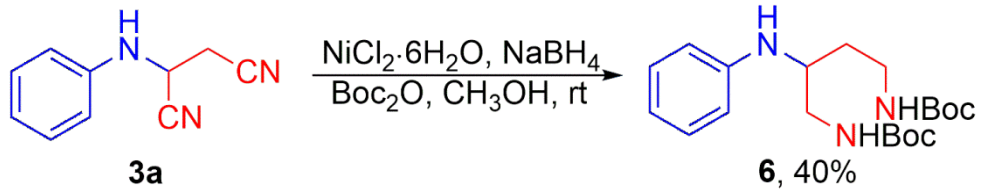
The Gram-Scale Synthesis of 3a

A 20 mmol amount of aniline, and 140 mg (1 mol%) of (TPP)Fe(III)Cl were placed into a three-necked flask and dissolved in 40 mL of acetonitrile at 25 ^{o}C under N_2. A solution of 2.01 g (80 mmol) of diazoacetonitrile **1a** in 10 mL of DCM was added by syringe over 10 min to the reaction mixture. After 20 min, the solvent was removed in vacuo. The residue was separated through column chromatography using EtOAc/petroleum ether as eluting, and then the desired product **3a** of 1.915 g in 56 % yield was obtained upon evaporation of the solvent.

The Gram-Scale Synthesis of 5a

A 20 mmol amount of amines and 140 mg (1 mol%) of (TPP)Fe(III)Cl were placed into a reaction flask and dissolved in 80 mL of DCM at 25 ^{o}C under N_2. A solution of 2.01 g (30 mmol) of diazoacetonitrile in 10 mL of DCM was added by syringe over 10 min to the reaction mixture until completion of the reaction (follow by TLC). Then 360 mg (3 mol%) of PcFe(III)Cl was added into the reaction flask, Another solution of 6.7 g (100 mmol) of diazoacetonitrile in 10 mL of DCM was added by syringe over 10 min to the reaction mixture with vigorous stirring. After about 20 min, the solvent was removed *in vacuo*. The residue was separated through column chromatography using EtOAc/petroleum ether as eluting, and then the desired product **5a** of 3.444 g in 82 % yield was obtained upon evaporation of the solvent.

VI. Procedure for Synthetic Transformation of 3a and Characterization Data of the Product 6



3a **6**, 40%

General procedure for the synthesis of 1,4-diamines:[S6] To a stirring solution of the hydrogenation product (0.2 mmol) in CH_3OH (3 mL) Boc_2O (0.8 mmol) and $NiCl_2$•$6H_2O$ (0.8 mmol) were first added, then $NaBH_4$ (3.2mmol) was added portionwise at 0 ^{o}C over 1 h. The mixture was stirred at room temperature until no starting material was detected by TLC and carefully quenched with H_2O. The aqueous layer was extracted with ethyl acetate, dried over $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 5/1, v/v) to afford the corresponding 1,4-diamines **6** (wax, 30 mg, 40%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18-7.14 (m, 2 H), 6.69 (t, *J* = 7.3 Hz, 1 H), 6.63-6.60 (m, 2 H), 4.82 (m, 2 H), 3.79-3.50 (m, 2 H), 3.31-3.13 (m, 4 H), 1.80-1.58 (m, 2 H), 1.44-1.42 (m, 18 H).

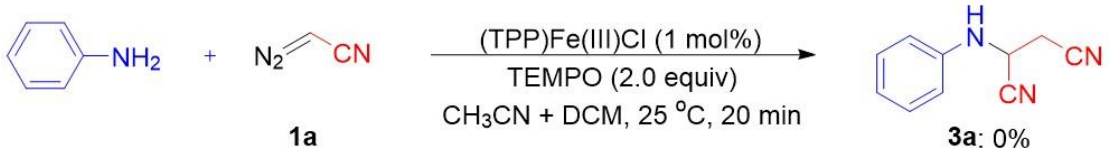
^{13}C NMR ($CDCl_3$, 101 MHz): δ 156.50, 156.06, 147.55, 129.44, 117.57, 113.17, 79.54, 79.36, 52.10, 44.32, 37.71, 33.46, 28.42, 28.38.

HR-MS (ESI): Calcd. 402.2363 for $C_{20}H_{33}N_3NaO_4^+$ $[M+Na]^+$ found:402.2364.

VII. The Control Experiments

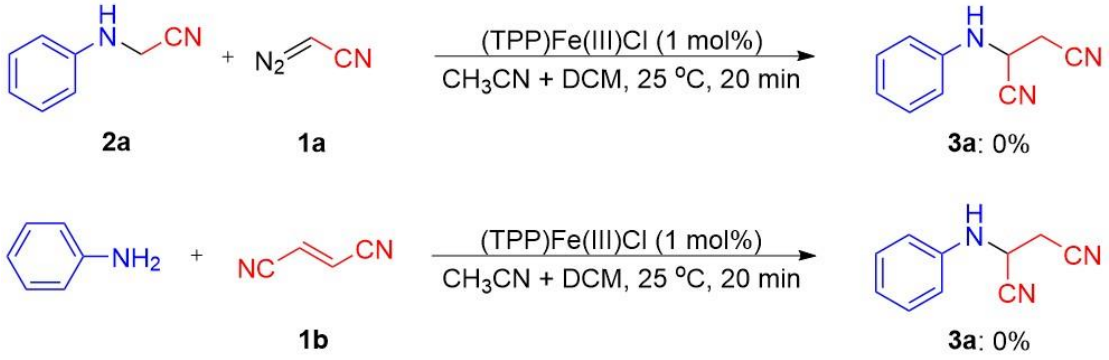
The Control Experiments of 3a

(a) Trapping of Radicals by TEMPO



A 0.5 mmol amount of aniline, TEMPO (156.3 mg, 1 mmol, 2.0 equiv.) and 3.5 mg (1 mol%) of (TPP)Fe(III)Cl were placed into a reaction flask and dissolved in 2 mL of acetonitrile at 25 ^{o}C under N_2. A solution of 67 mg (1 mmol) of diazoacetonitrile **1a** in 0.5 mL of DCM was added by syringe in one aliquot to the reaction mixture with vigorous stirring. After 20 min, The reaction solution was analyzed by GC-MS, but the product **3a** was not detected.

(b) Exclusion of Possible Intermediates



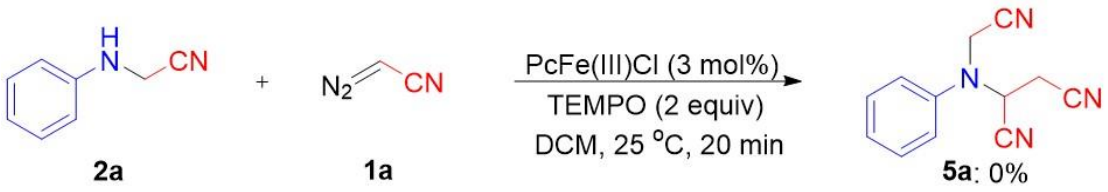
Reaction 1: A 0.5 mmol amount of **2a** and 3.5 mg (1 mol%) of (TPP)Fe(III)Cl were placed into a reaction flask and dissolved in 2 mL of acetonitrile at 25 ^{o}C under $N_{2,}$ A solution of 67 mg (1 mmol) of diazoacetonitrile **1a** in 0.5 mL of DCM was added by syringe in one aliquot to the reaction mixture with vigorous stirring. After 20 min, The reaction solution was analyzed by GC-MS, but the product **3a** was not detected.

Reaction 2: A 0.5 mmol amount of aniline and 3.5 mg (1 mol%) of (TPP)Fe(III)Cl were placed into a reaction flask and dissolved in 2 mL of acetonitrile at 25 ^{o}C under $N_{2,}$ A solution of fumaronitrile (1 mmol, 78 mg, 2.0 equiv.) in 0.5 mL of DCM was added by syringe in one aliquot

to the reaction mixture with vigorous stirring. After 20 min, The reaction solution was analyzed by GC-MS, but the product **3a** was not detected.

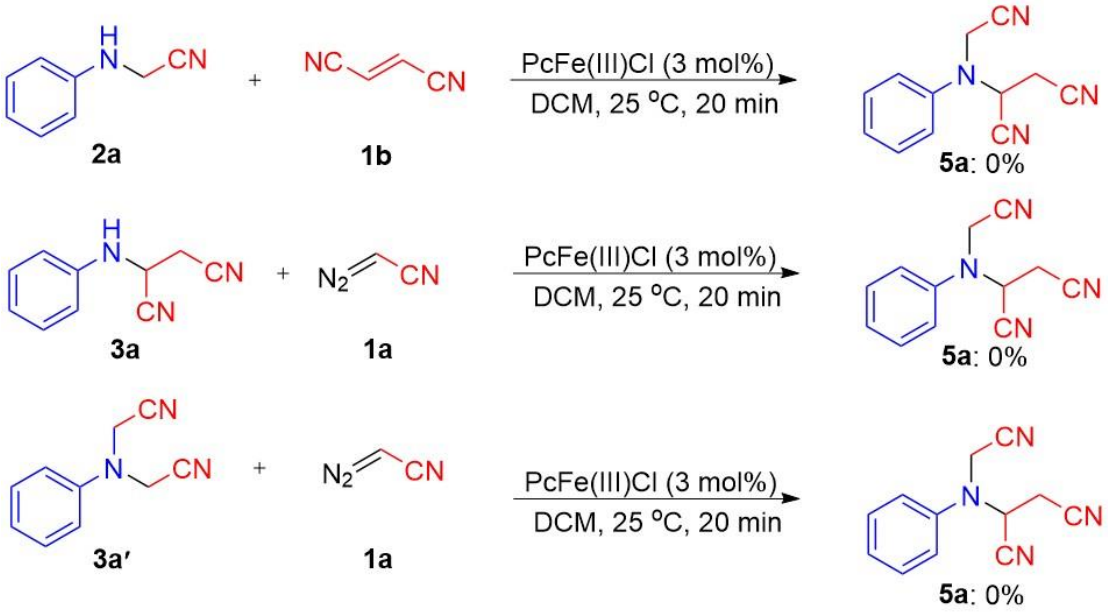
The Control Experiments of 5a

(a) Trapping of Radicals by TEMPO



A 0.5 mmol amount of **2a**, TEMPO (156.3 mg, 1 mmol, 2.0 equiv.) and 9 mg (3 mol%) of PcFe(III)Cl were placed into a reaction flask and dissolved in 4 mL of DCM at 25 ^{o}C under N_2. A solution of 167.5 mg (2.5 mmol) of diazoacetonitrile **1a** in 1 mL of DCM was added by syringe in one aliquot to the reaction mixture with vigorous stirring. After 20 min, The reaction solution was analyzed by GC-MS, but the product **5a** was not detected.

(b) Exclusion of Possible Intermediates



Reaction 1: A 0.5 mmol amount of **2a** and 9.0 mg (3 mol%) of PcFe(III)Cl were placed into a reaction flask and dissolved in 4 mL of DCM at 25 ^{o}C under N_2, A solution of (2.5 mmol) of fumaronitrile **1b** in 1 mL of DCM was added by syringe in one aliquot to the reaction mixture

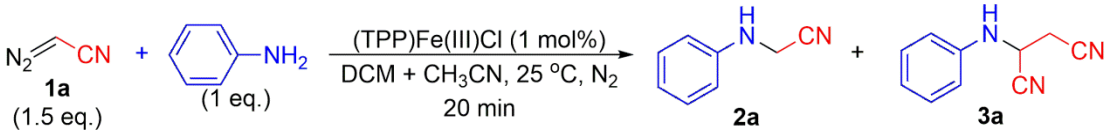
with vigorous stirring. After 20 min, The reaction solution was analyzed by GC-MS, but the product **5a** was not detected.

Reaction 2: A 0.5 mmol amount of **3a** and 9.0 mg (3 mol%) of PcFe(III)Cl were placed into a reaction flask and dissolved in 4 mL of DCM at 25 ^{o}C under N_2, A solution of 167.5 mg (2.5 mmol) of diazoacetonitrile **1a** in 1 mL of DCM was added by syringe in one aliquot to the reaction mixture with vigorous stirring. After 20 min, The reaction solution was analyzed by GC-MS, but the product **5a** was not detected.

Reaction 3: A 0.5 mmol amount of **3a**' and 9.0 mg (3 mol%) of PcFe(III)Cl were placed into a reaction flask and dissolved in 4 mL of DCM at 25 ^{o}C under N_2, A solution of 167.5 mg (2.5 mmol) of diazoacetonitrile **1a** in 1 mL of DCM was added by syringe in one aliquot to the reaction mixture with vigorous stirring. After 20 min, The reaction solution was analyzed by GC-MS, but the product **5a** was not detected.

VIII. Solvent Effect on the Mono- and Dicyanomethylation Reaction

Table S1 Solvent effect to the mono- and dicyanomethylation reaction



Entry	Solvent	Volume ratio of acetonitrile in solvent	Yield of **2a** (%)	Yield of **3a** (%)
1	DCM (4 mL) + MeCN (1 mL)	0.2	74	12
2	DCM (3 mL) + MeCN (2 mL)	0.4	50	43
3	DCM (2.5 mL) + MeCN (2.5 mL)	0.5	21	56
4	DCM (2 mL) + MeCN (3 mL)	0.6	7	63
5	DCM (1.5 mL) + MeCN (3.5 mL)	0.7	28	7
6	DCM (1 mL) + MeCN (4 mL)	0.8	42	33

IX. References

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S4. F. Yan, Z. Huang, C.-X. Du, J.-F. Bai and Y. Li, Iron-Catalyzed Reductive Strecker Reaction, *J. Catal.*, 2021, **395**, 188−194.

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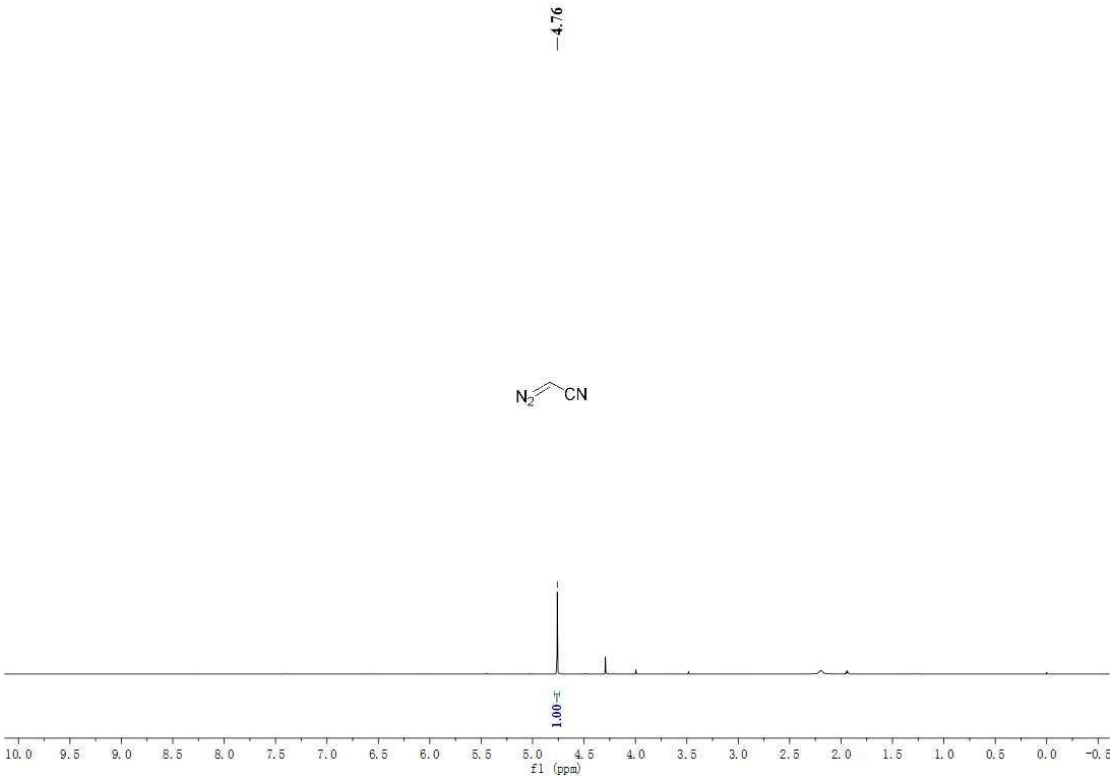
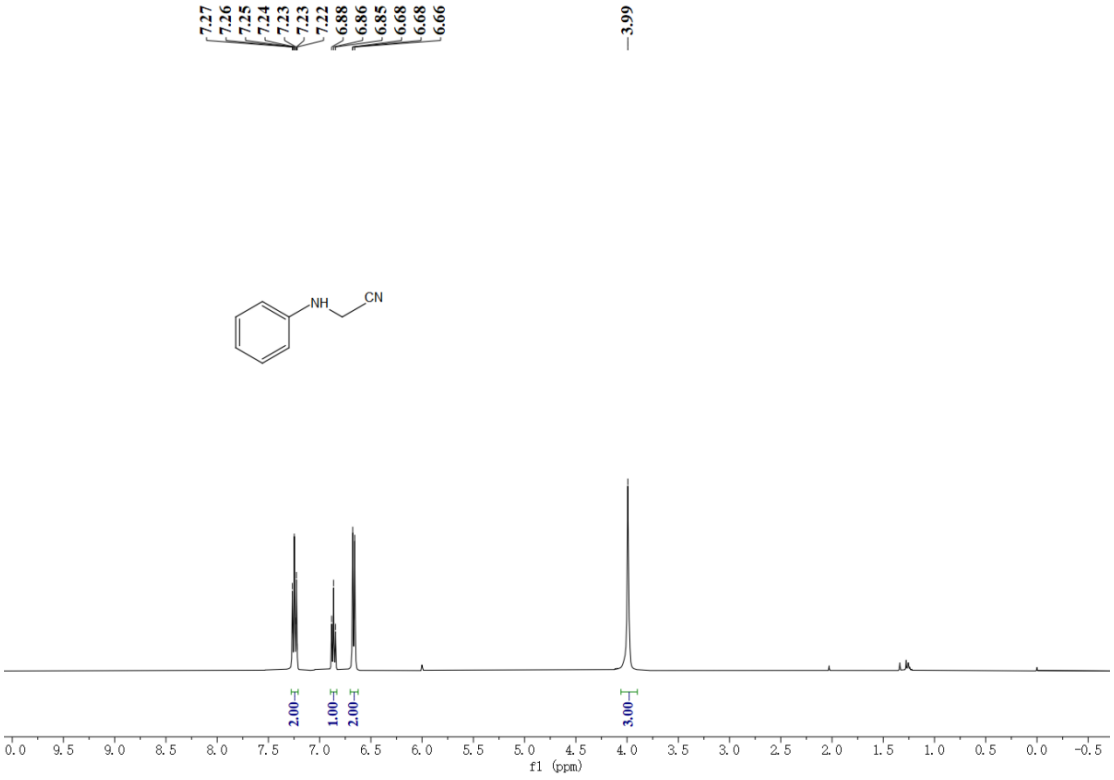
S6. M. Li, D. Kong, G. Zi and G, Hou. Rh-Catalyzed Asymmetric Hydrogenation of 1,2-Dicyanoalkenes. *J. Org. Chem.*, 2017, **82**, 680–687.

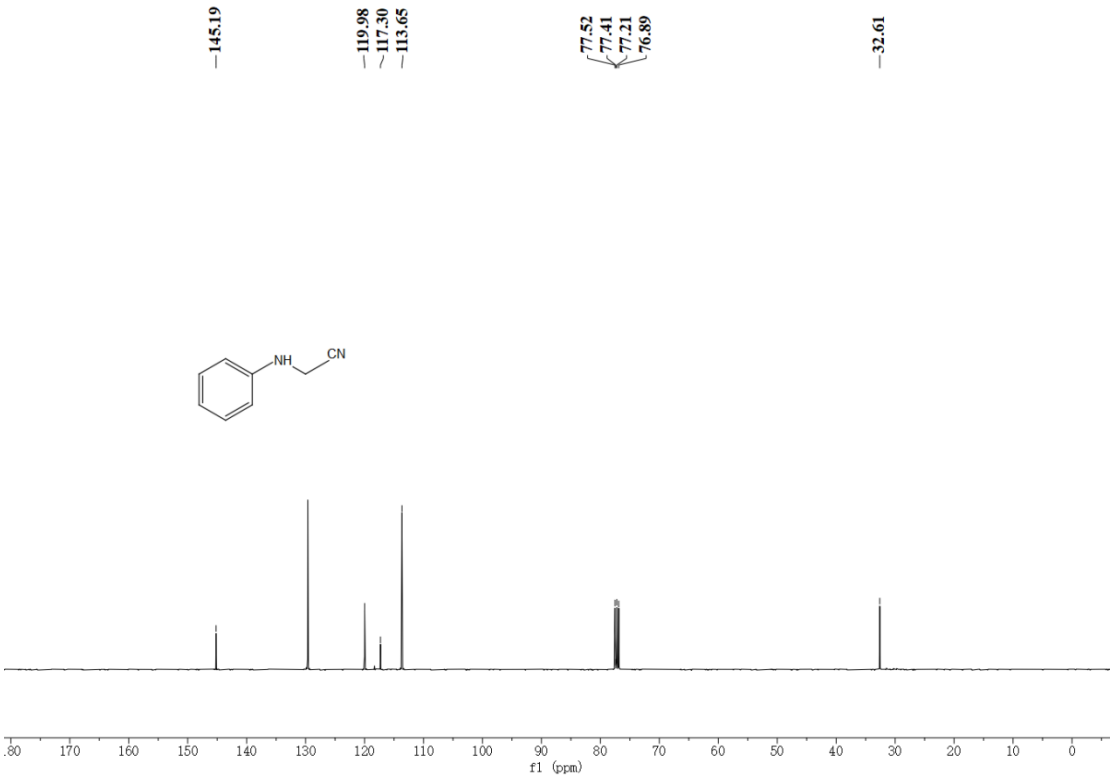
X. NMR Spectra

^{1}H NMR of the diazoacetonitrile **1a**

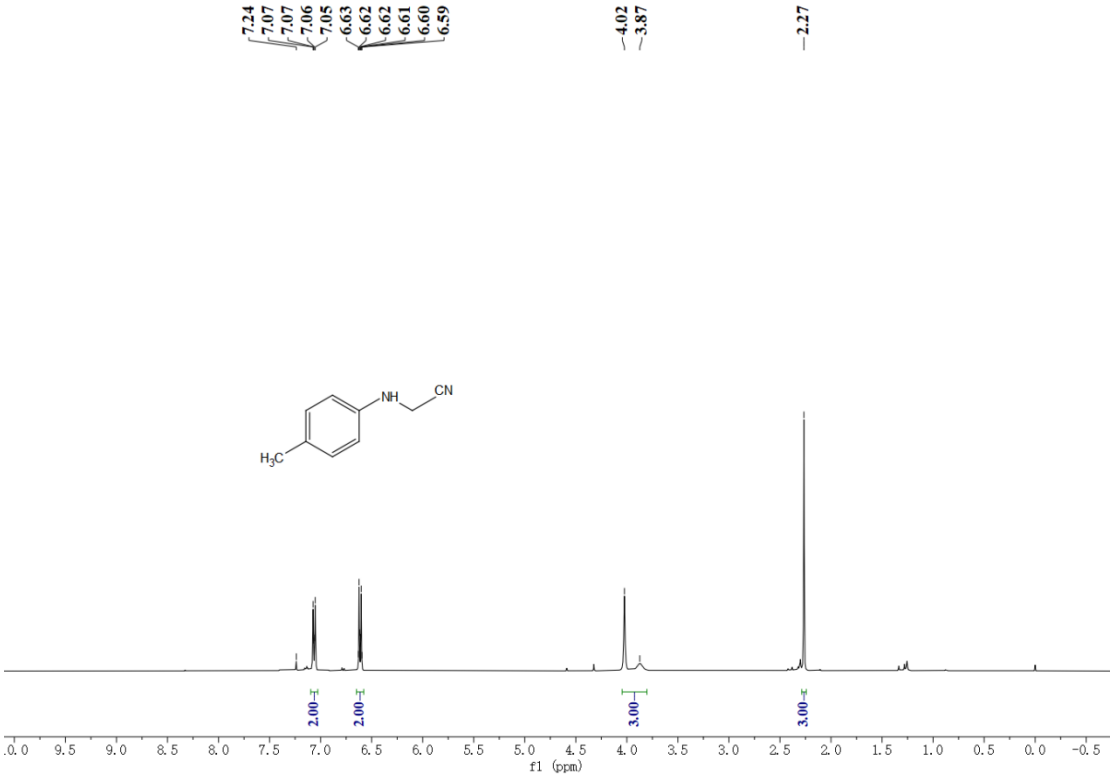


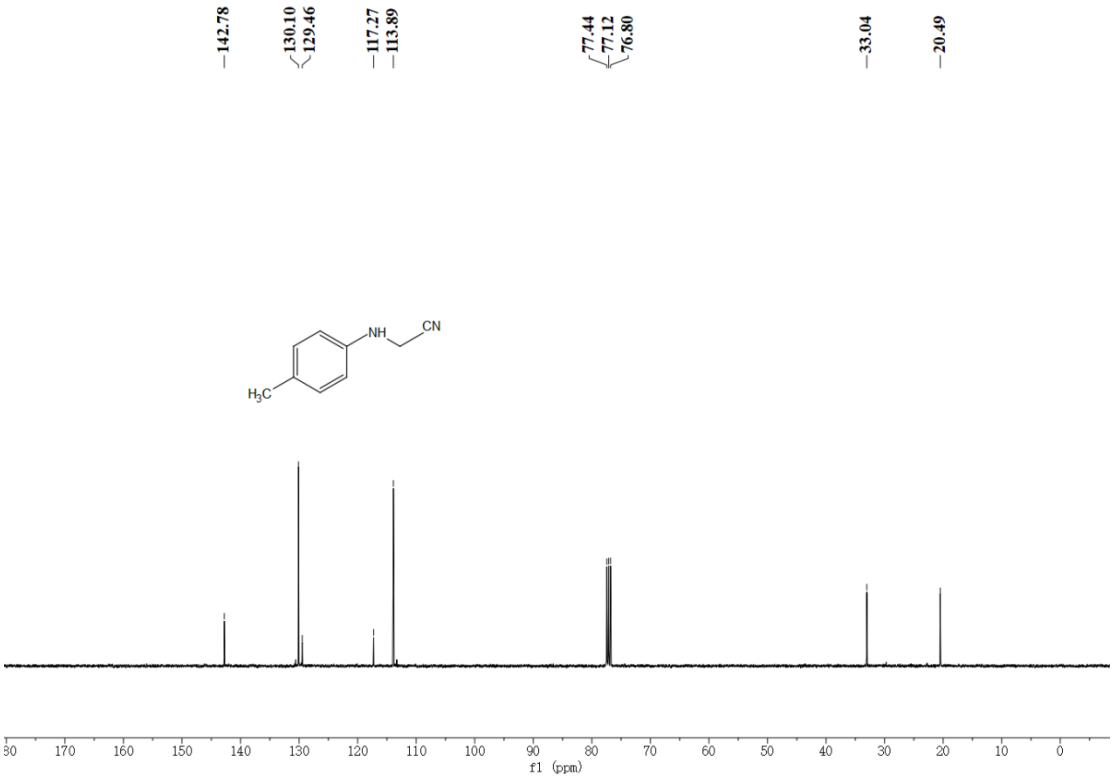
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2a**



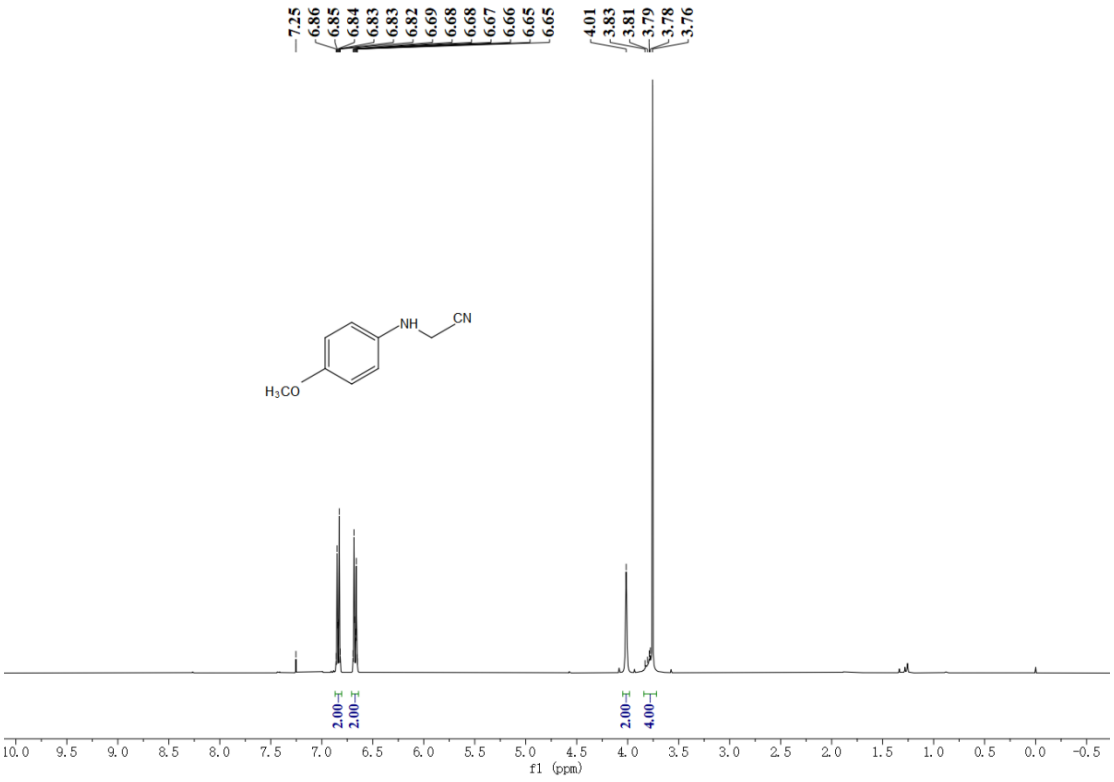


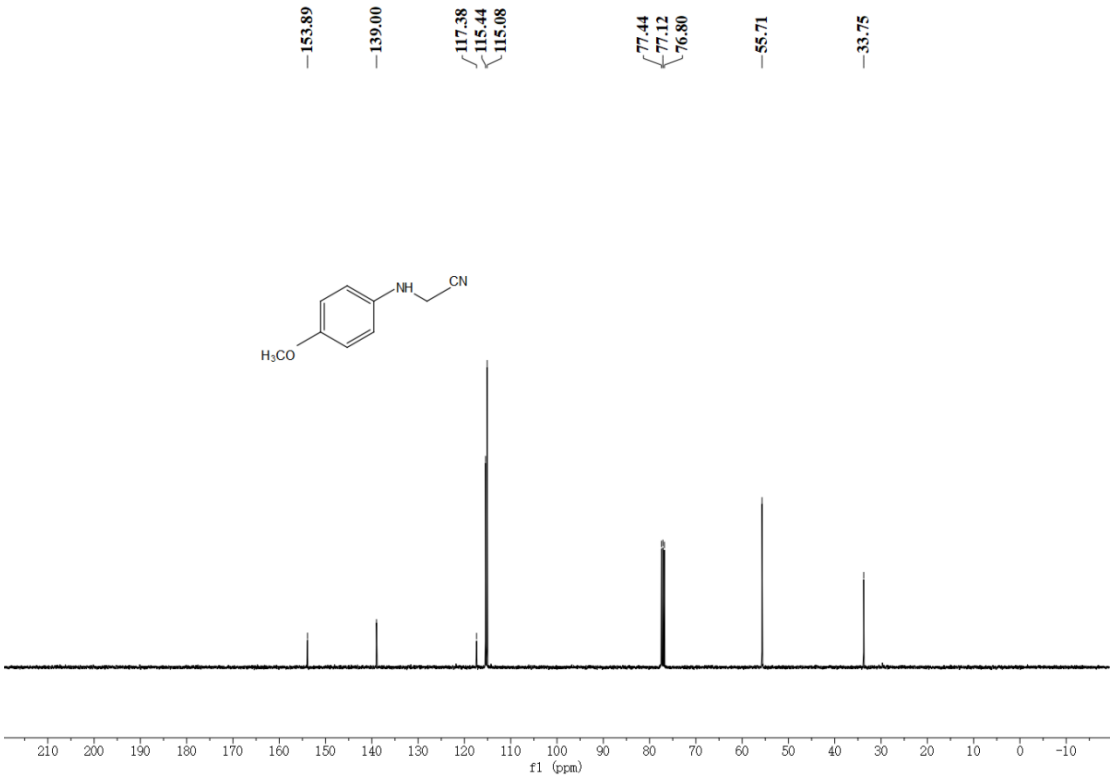
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2b**



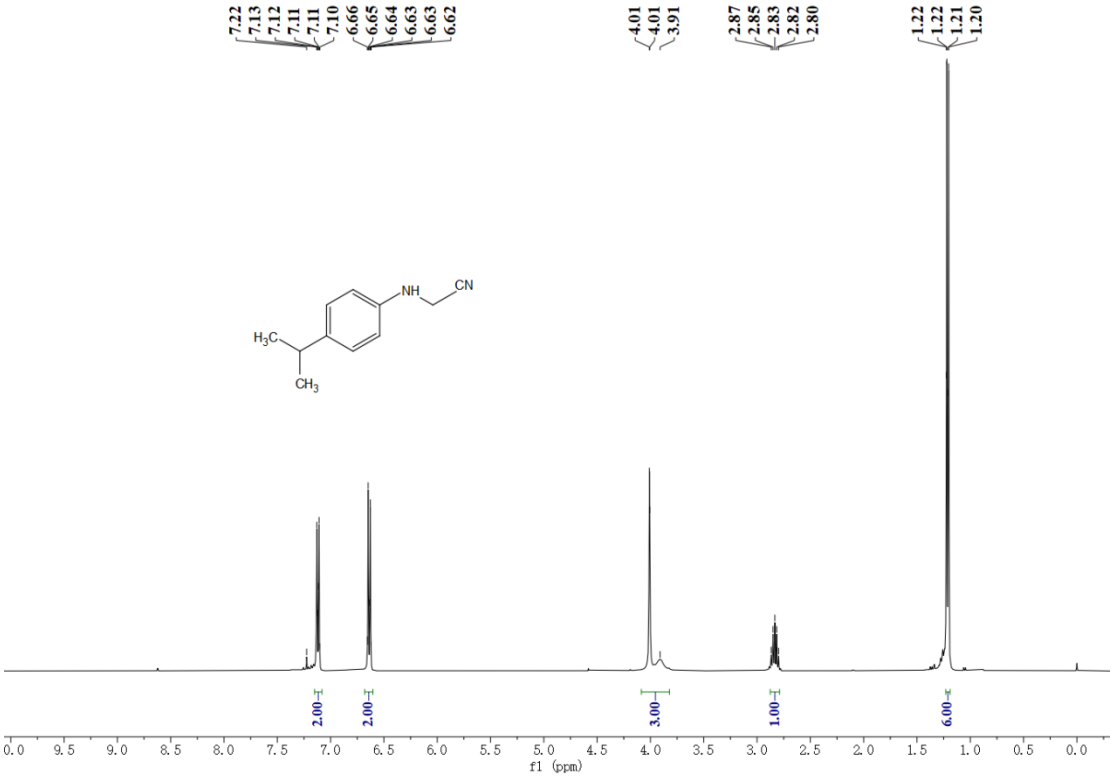


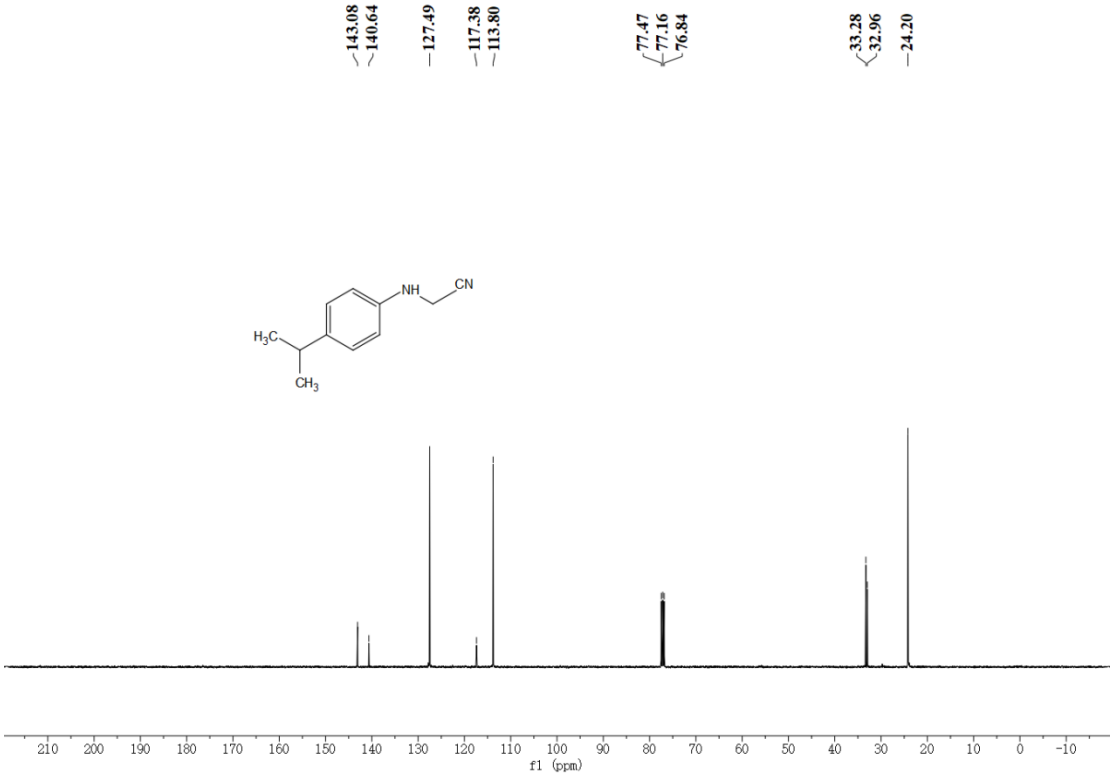
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2c**



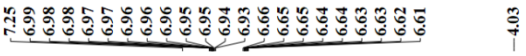


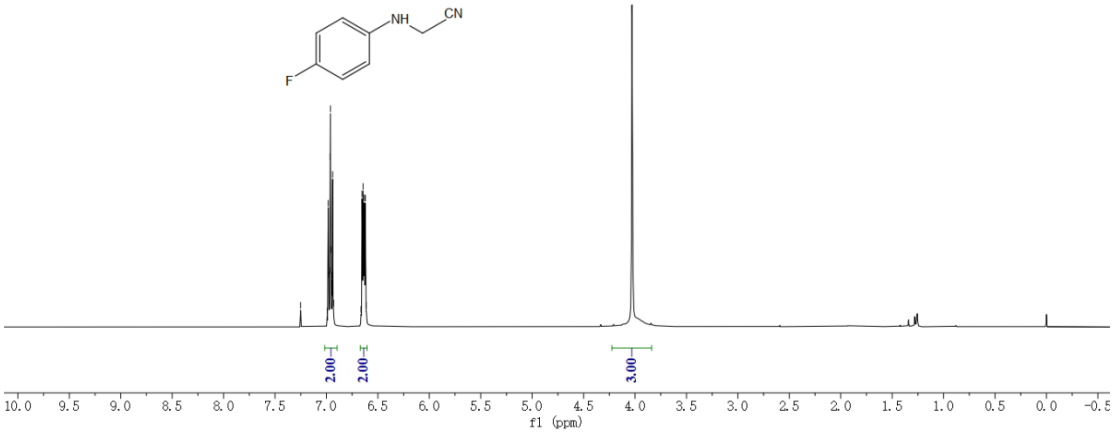
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2d**

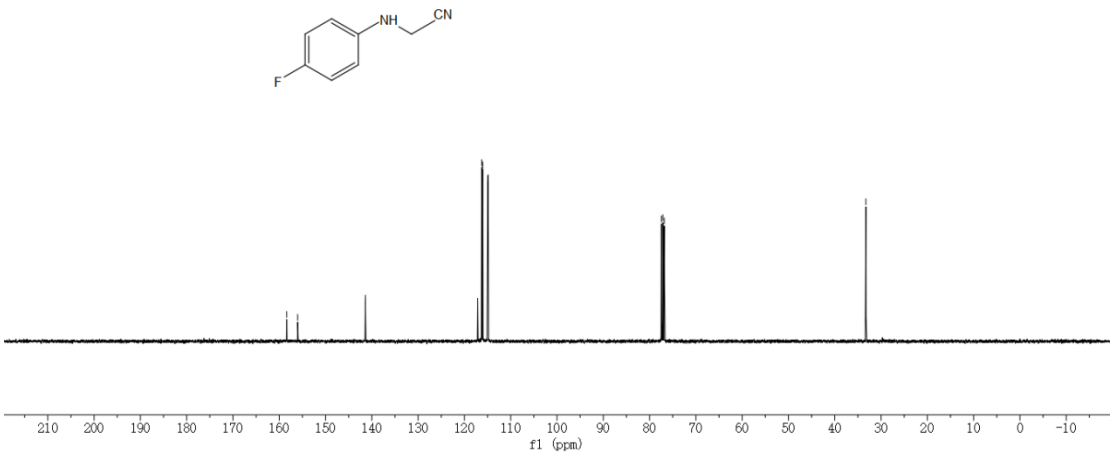


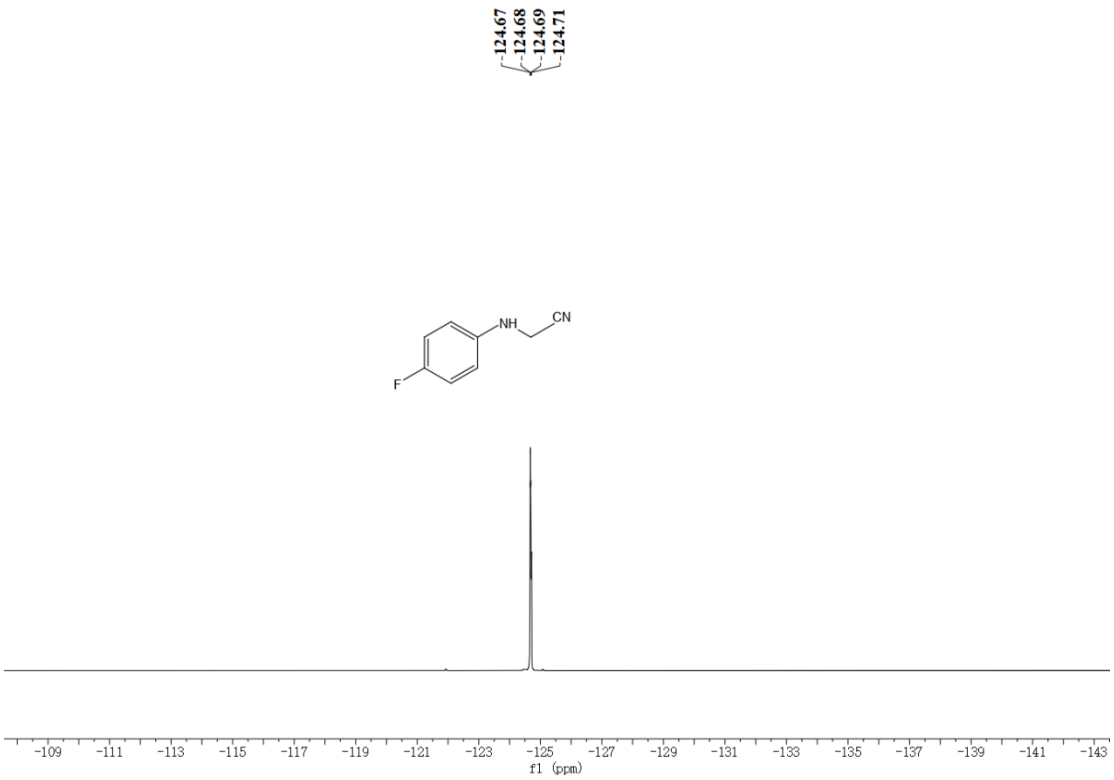


^{1}H NMR (400 MHz, $CDCl_3$) , ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra for **2e**

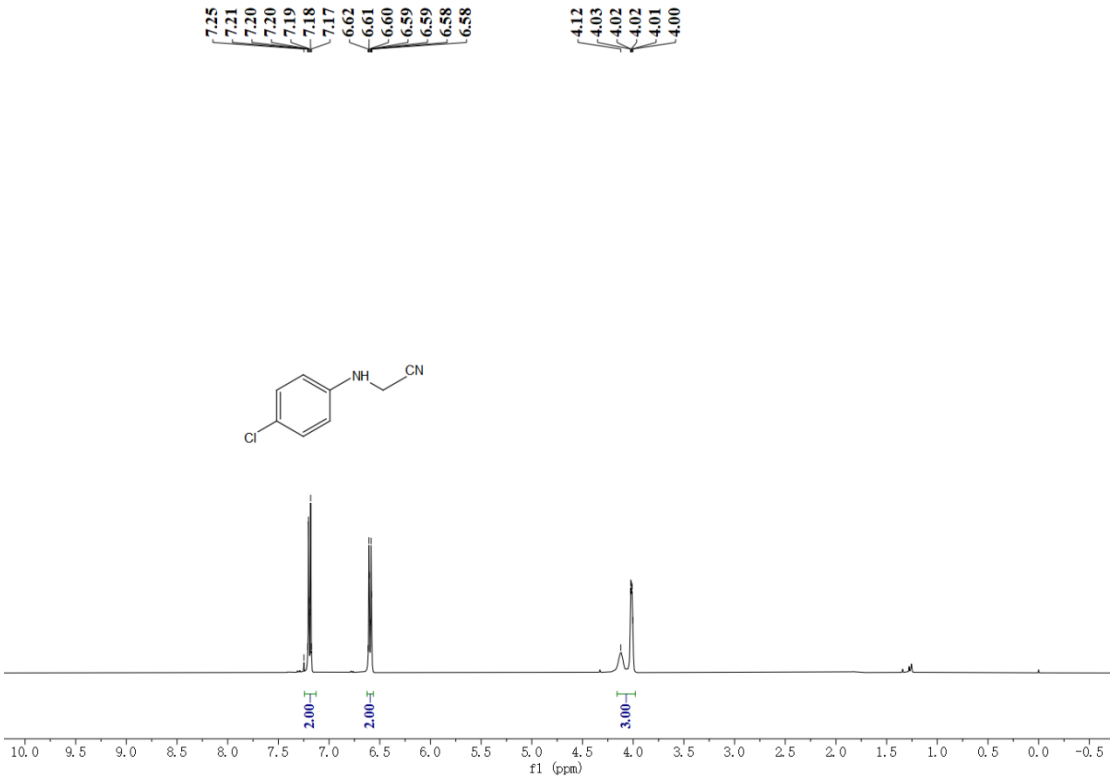


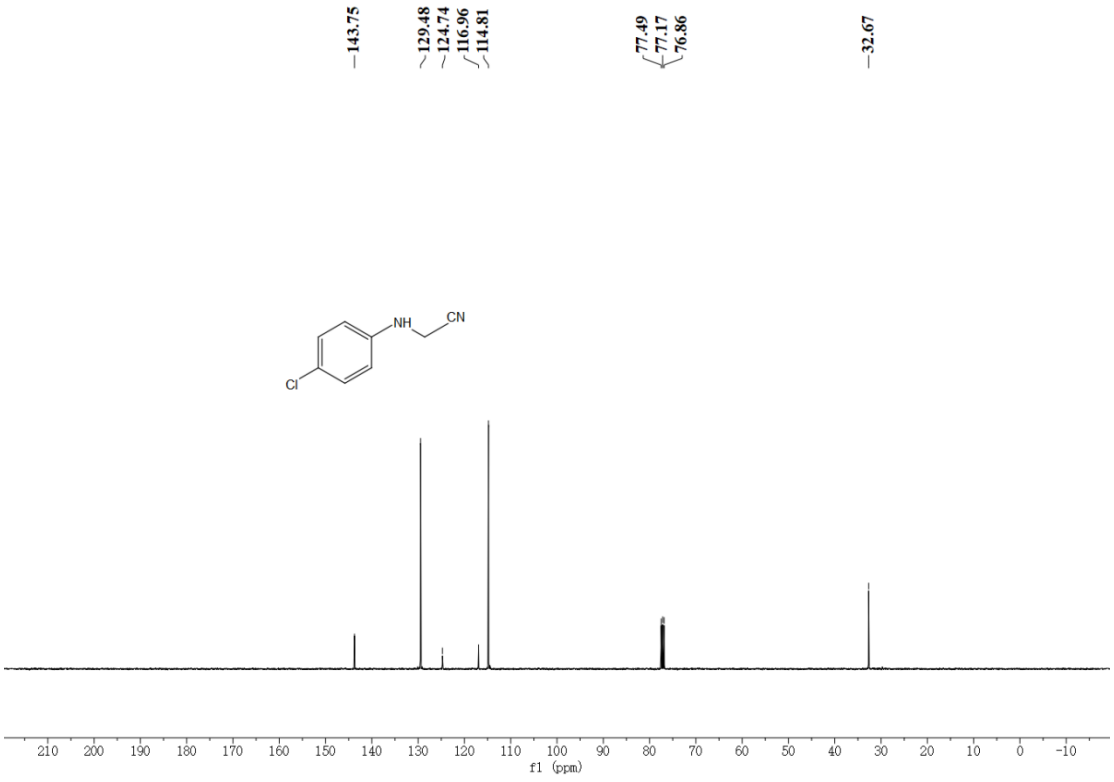




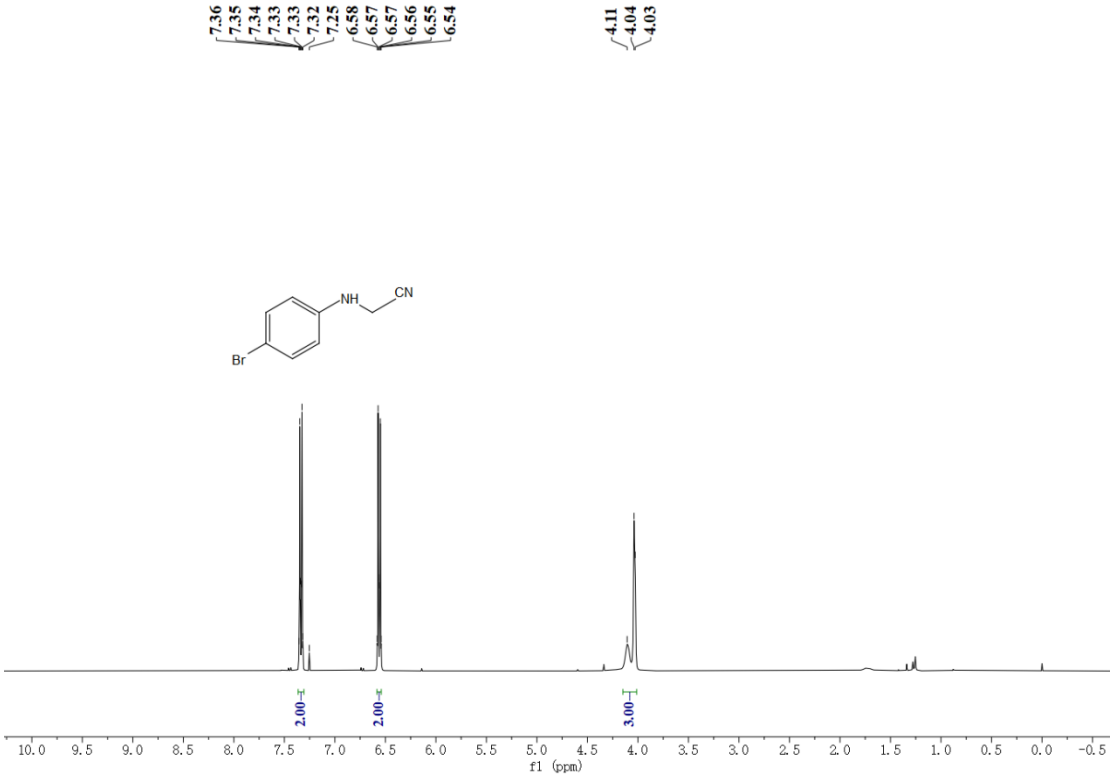

124.67
124.68
124.69
124.71
NH
CN
F
-109
-111
-113
-115
-117
-119
-121
-123
-125
-127
-129
-131
-133
-135
-137
-139
-141
-143
f1 (ppm)

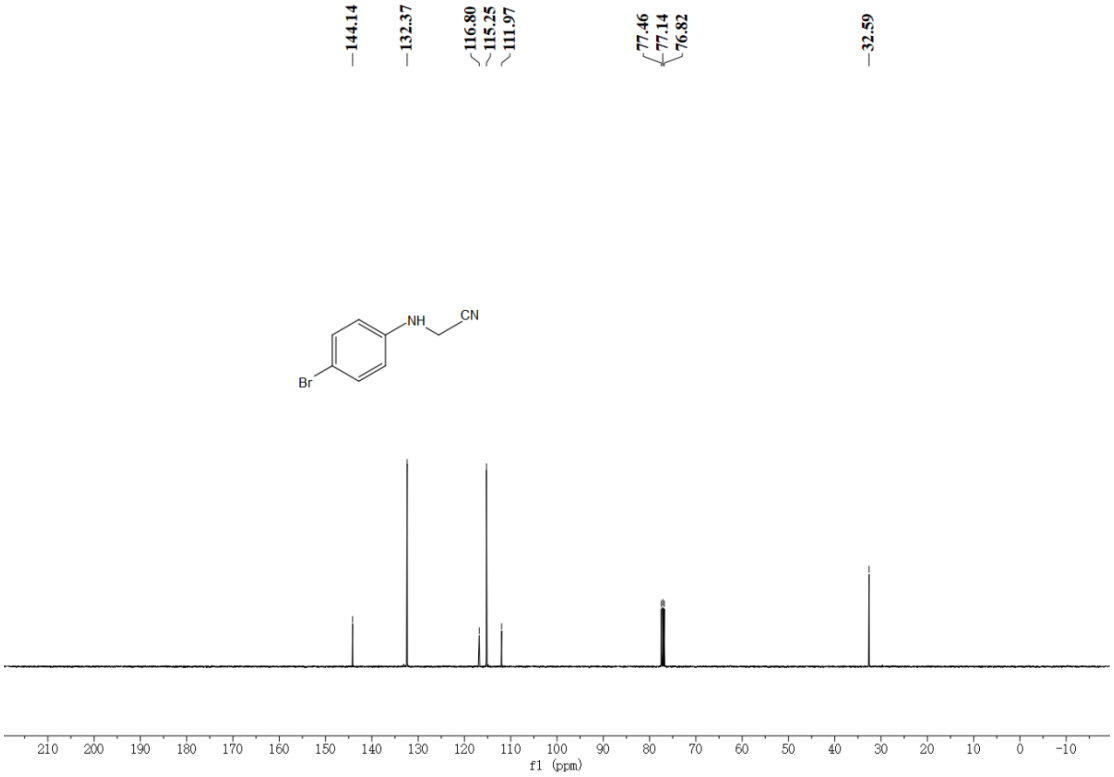
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2f**



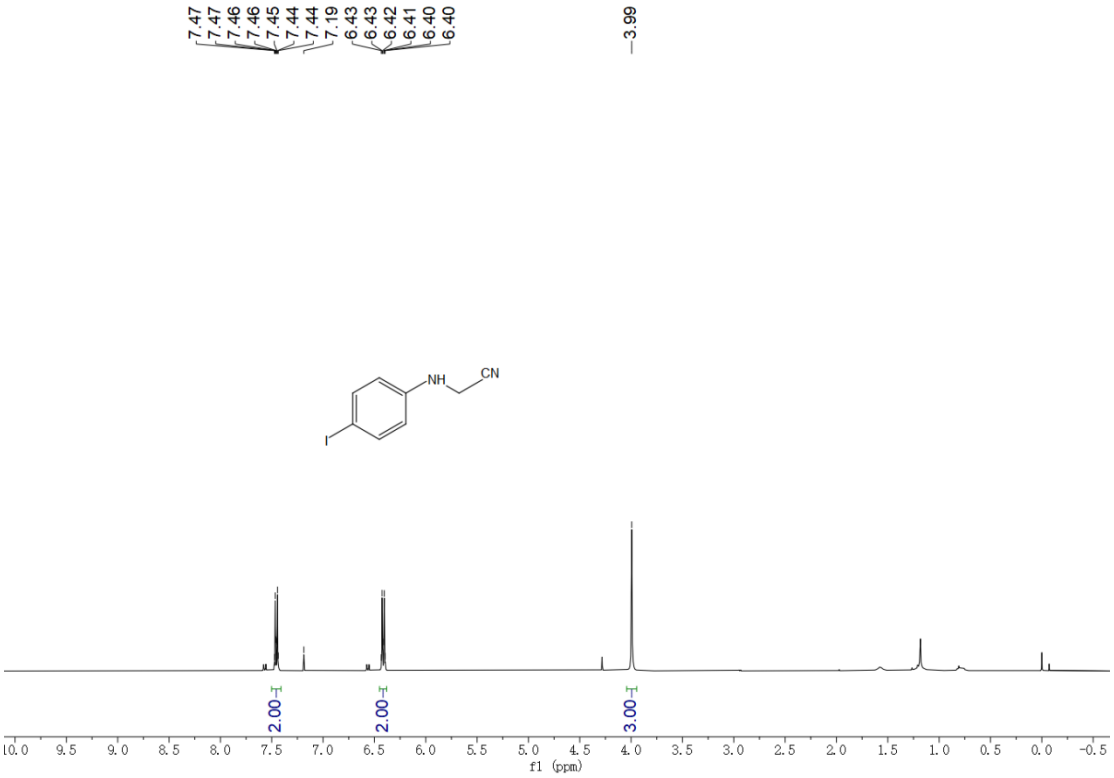


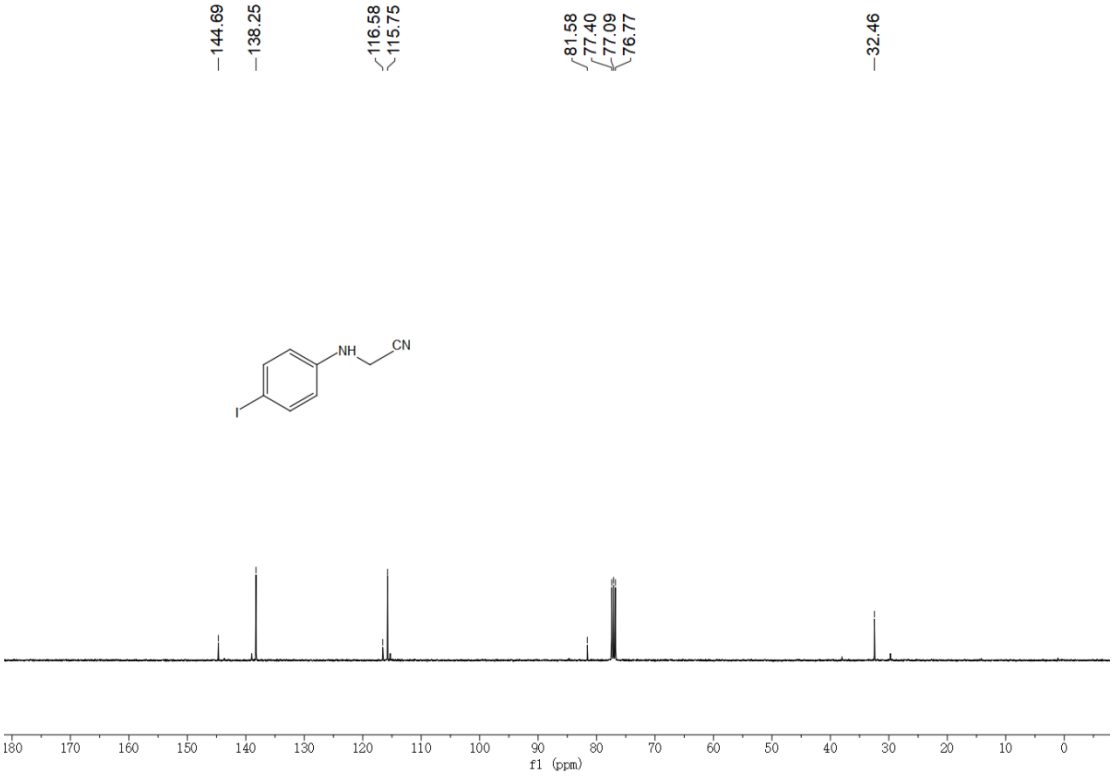
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2g**



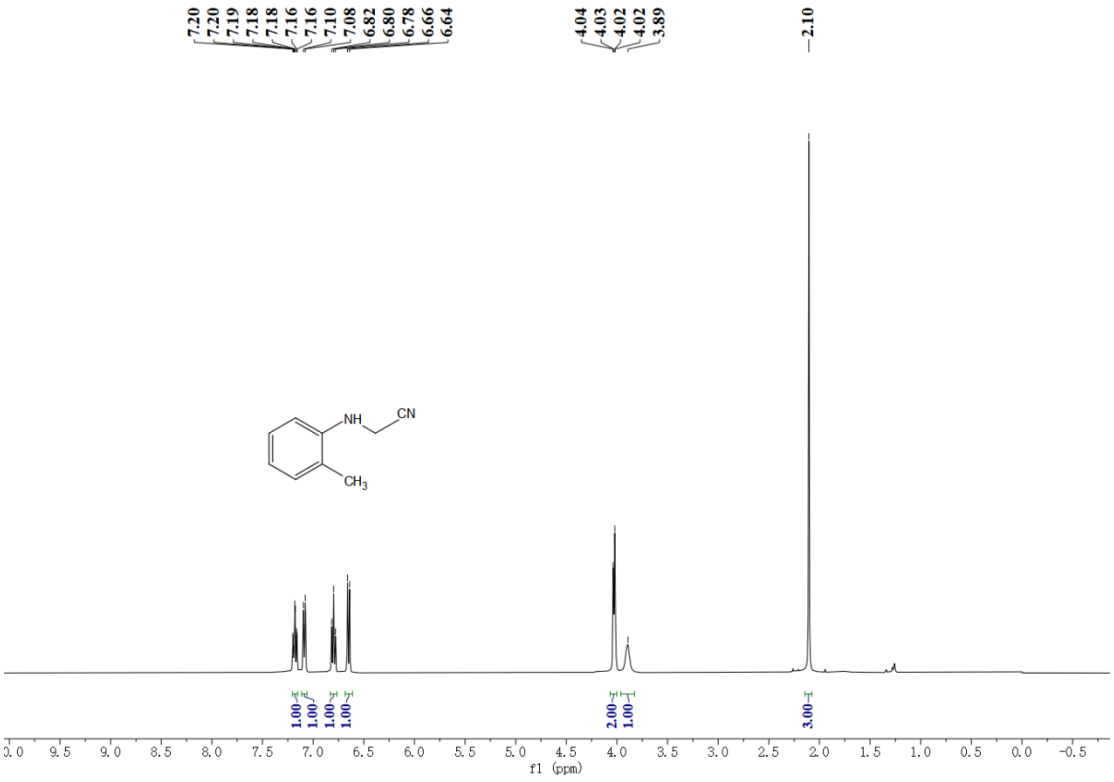


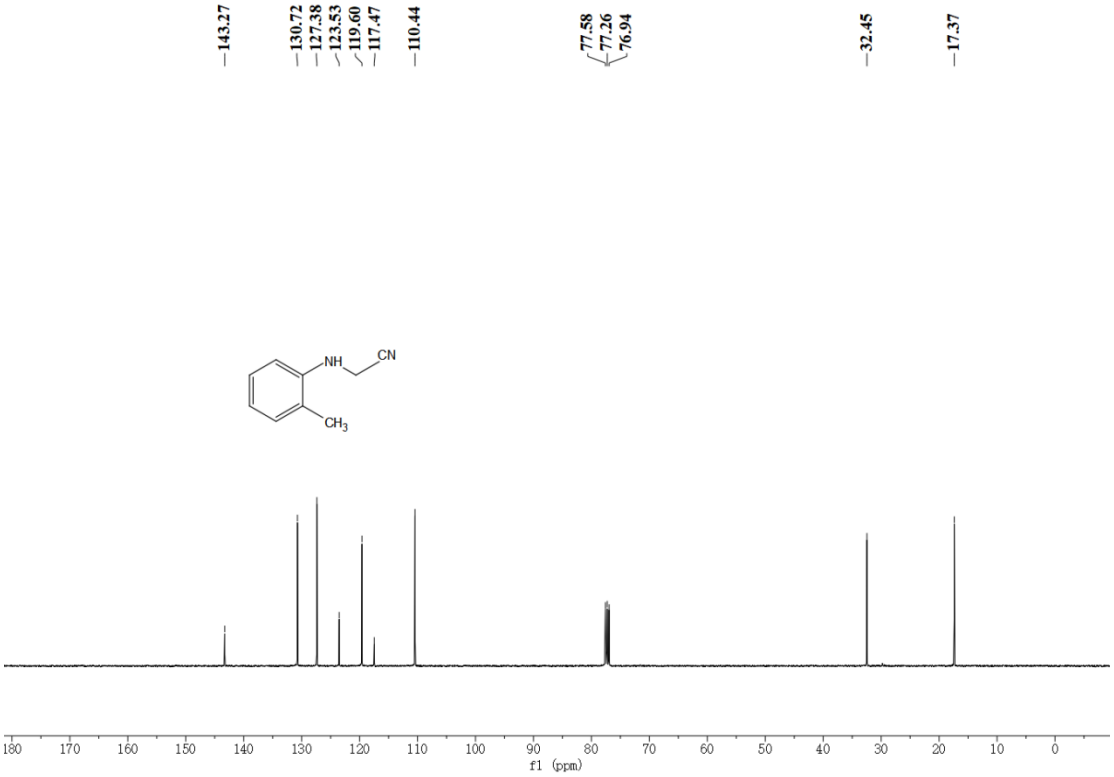
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2h**



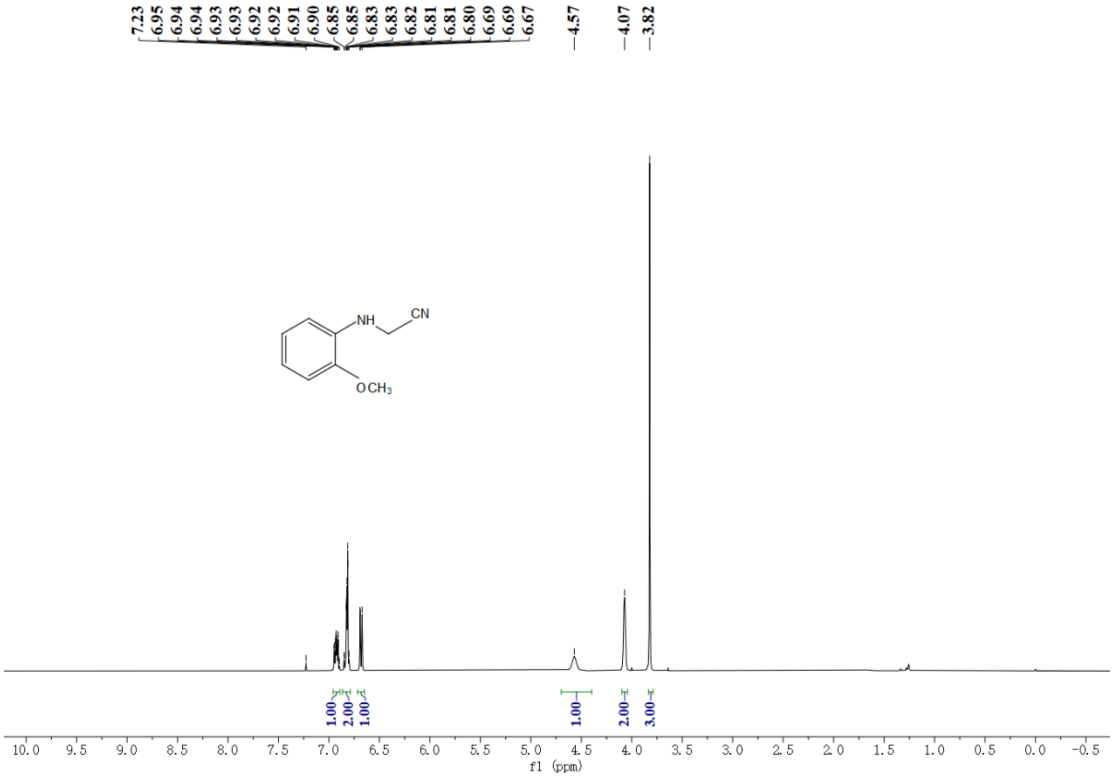


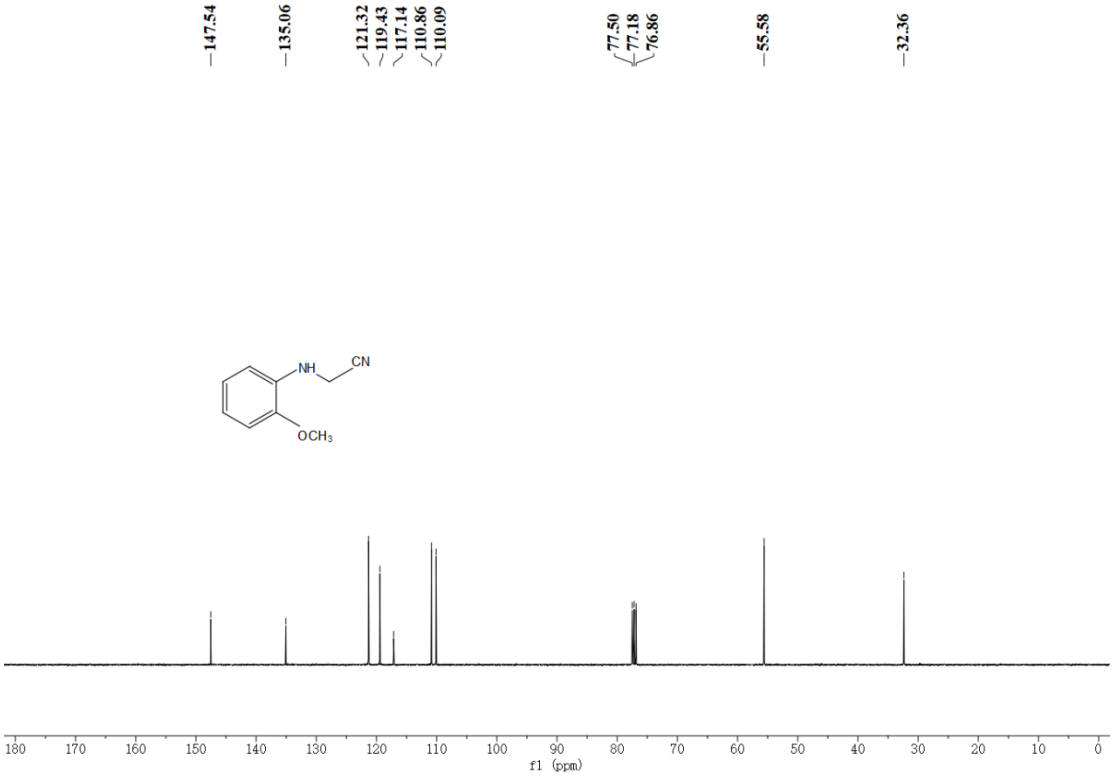
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2j**





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2k**





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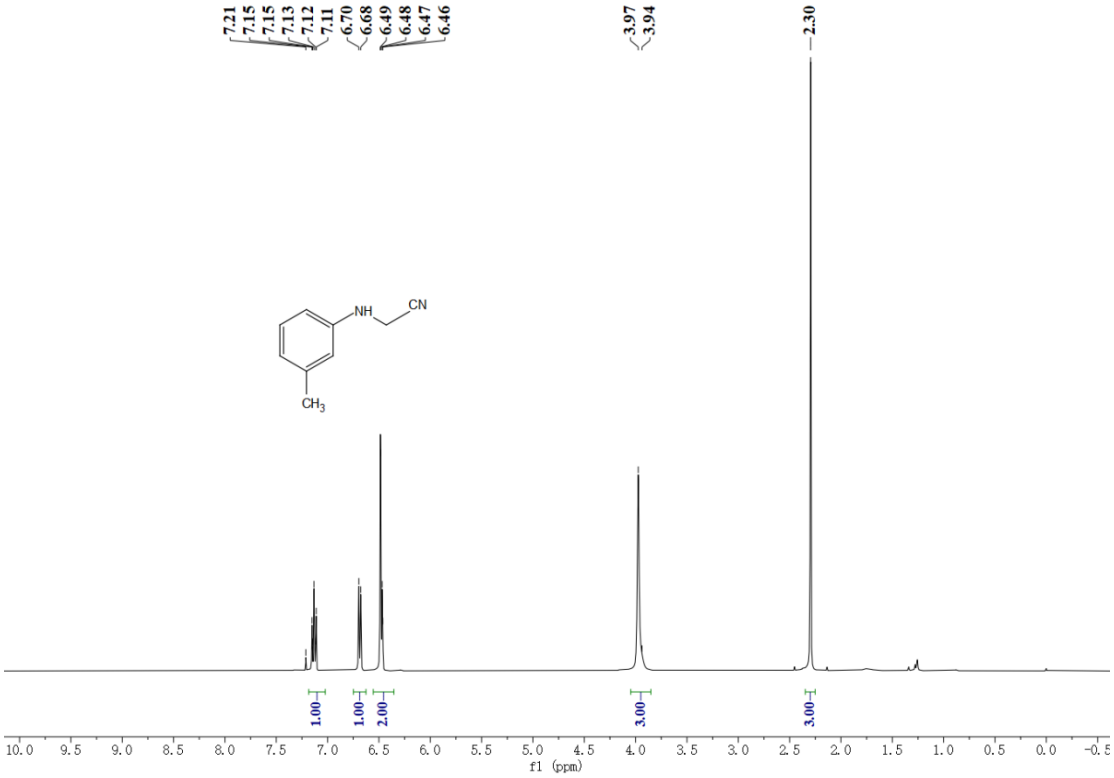
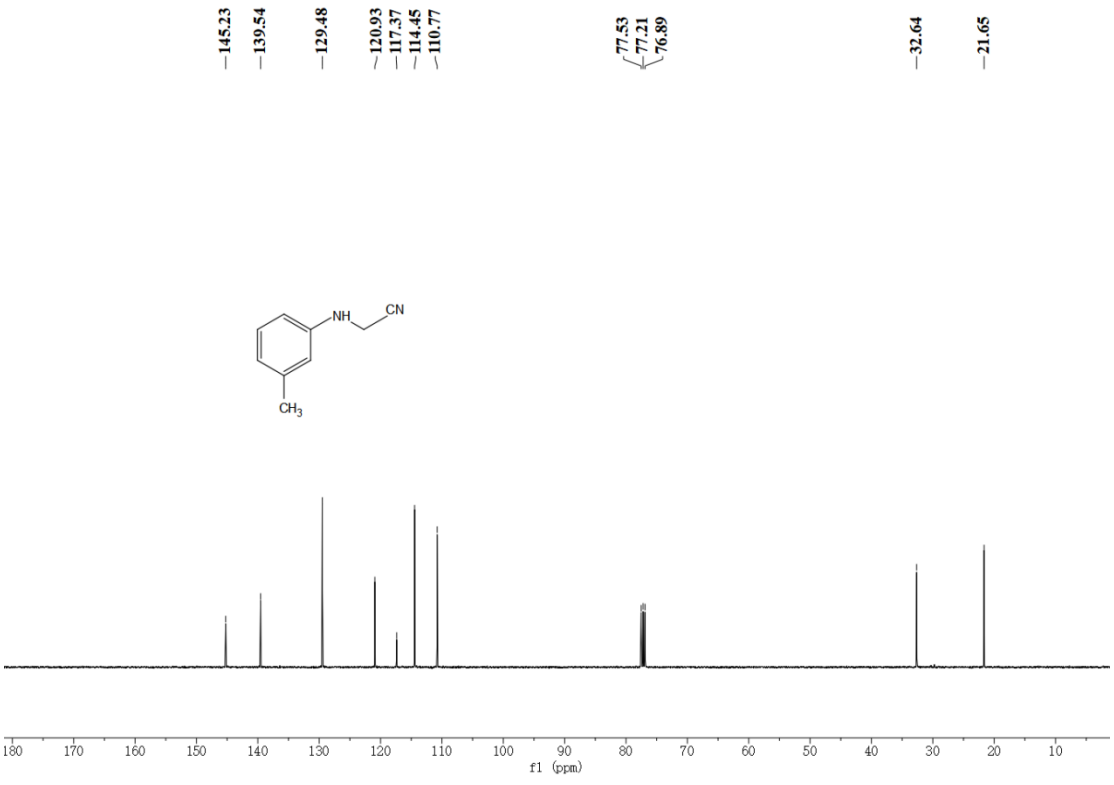
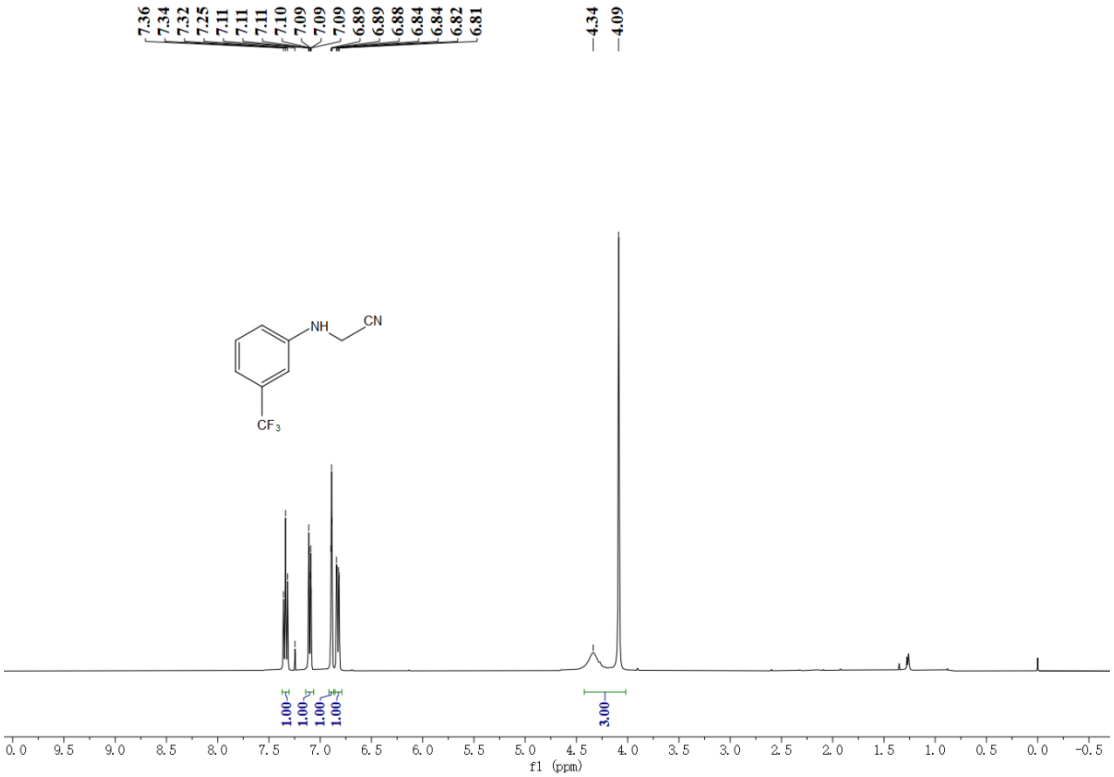
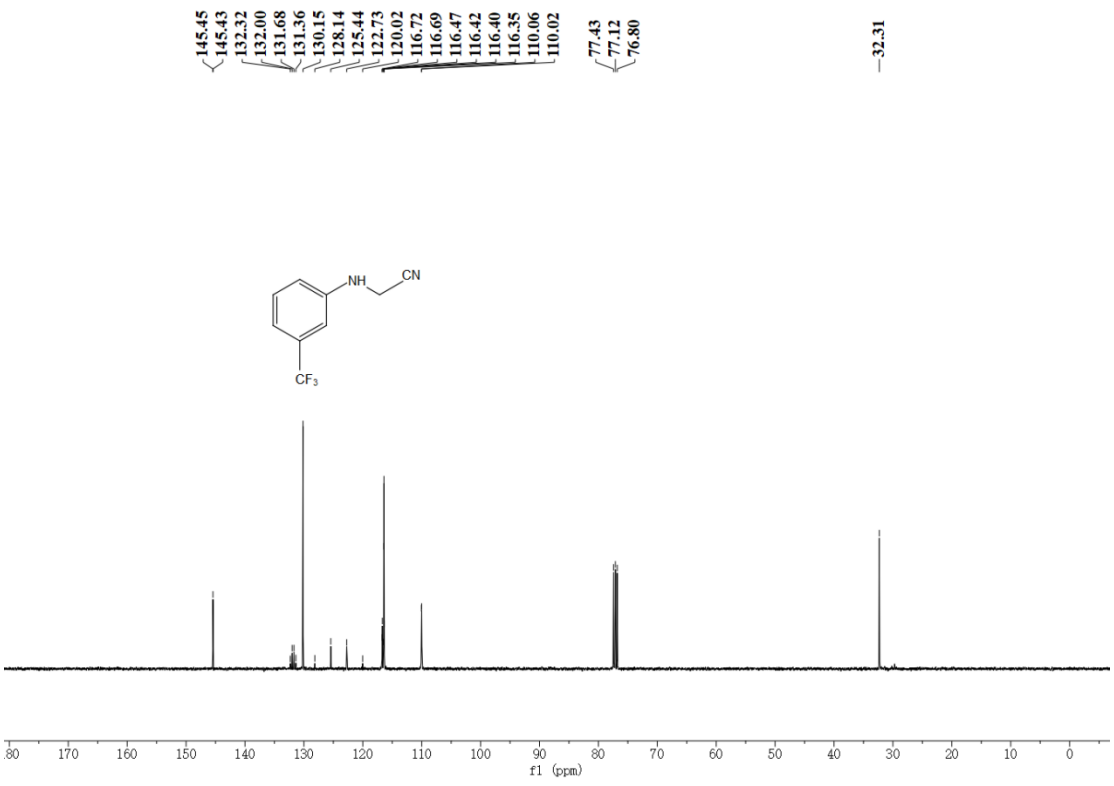
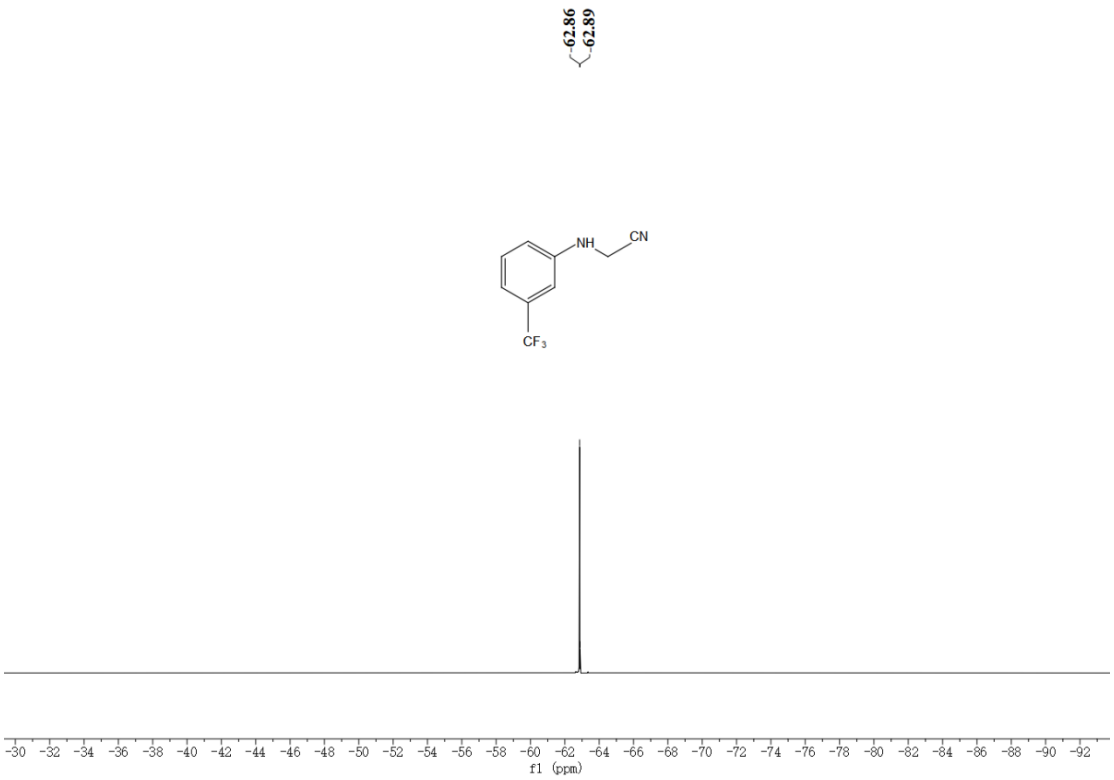




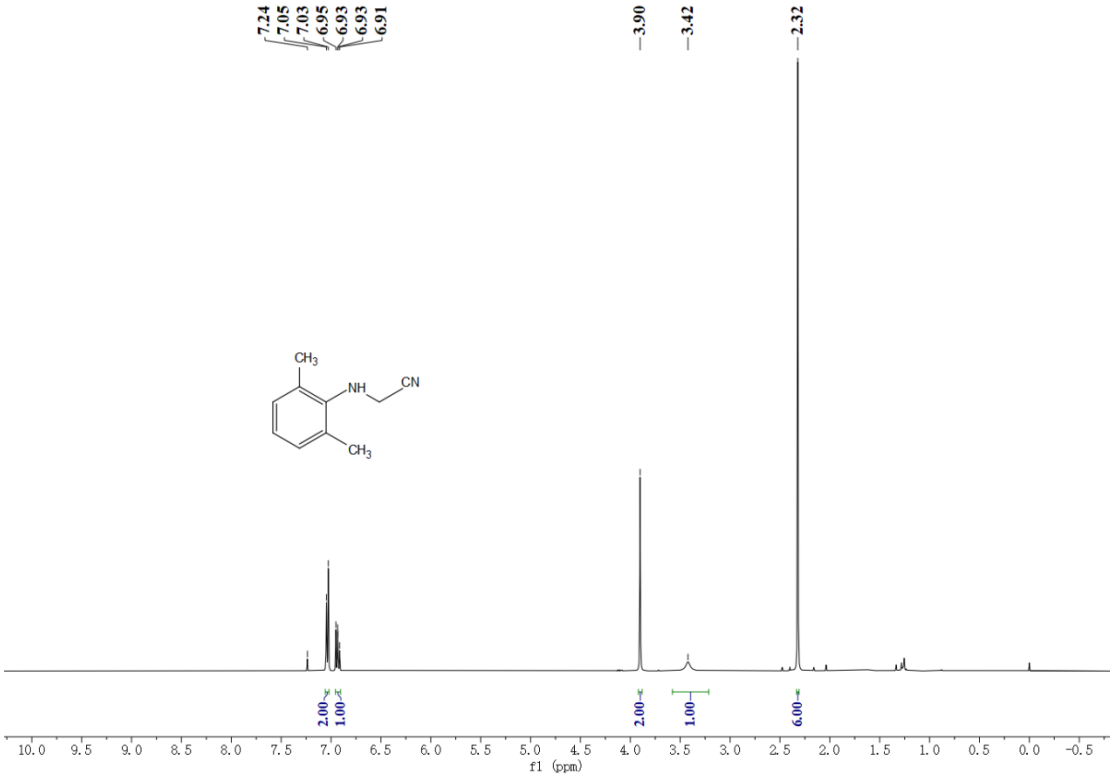
^{1}H NMR (400 MHz, $CDCl_3$) , ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra for **2m**

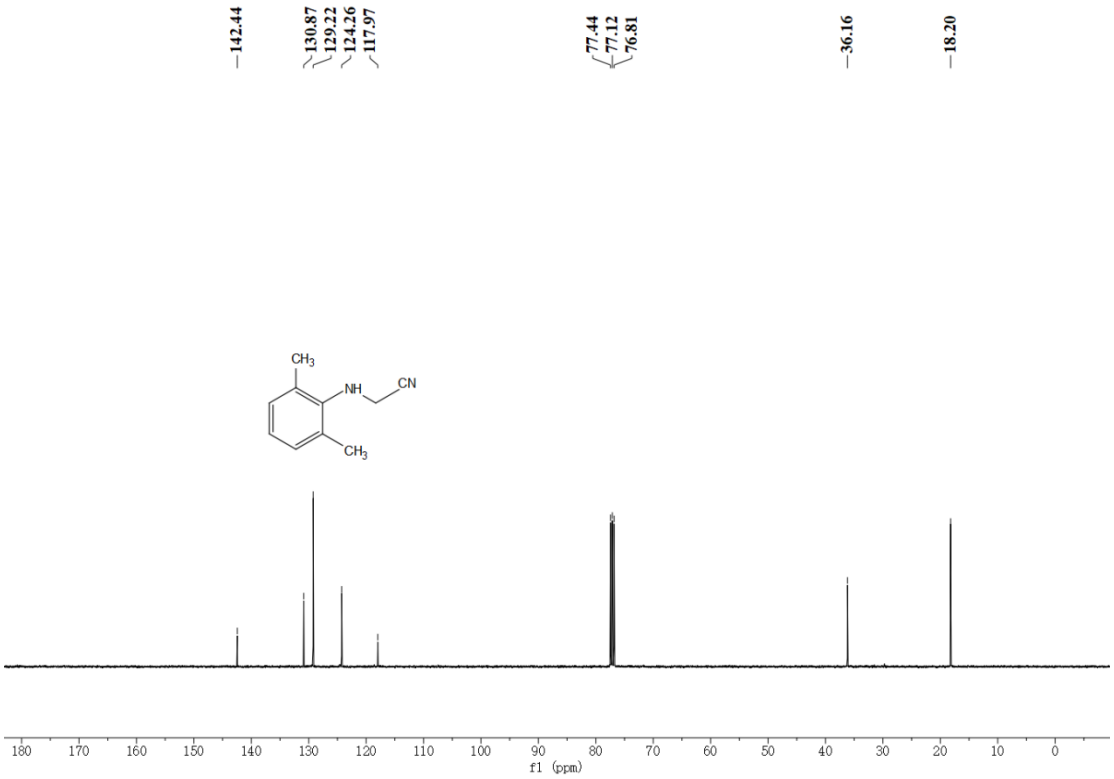




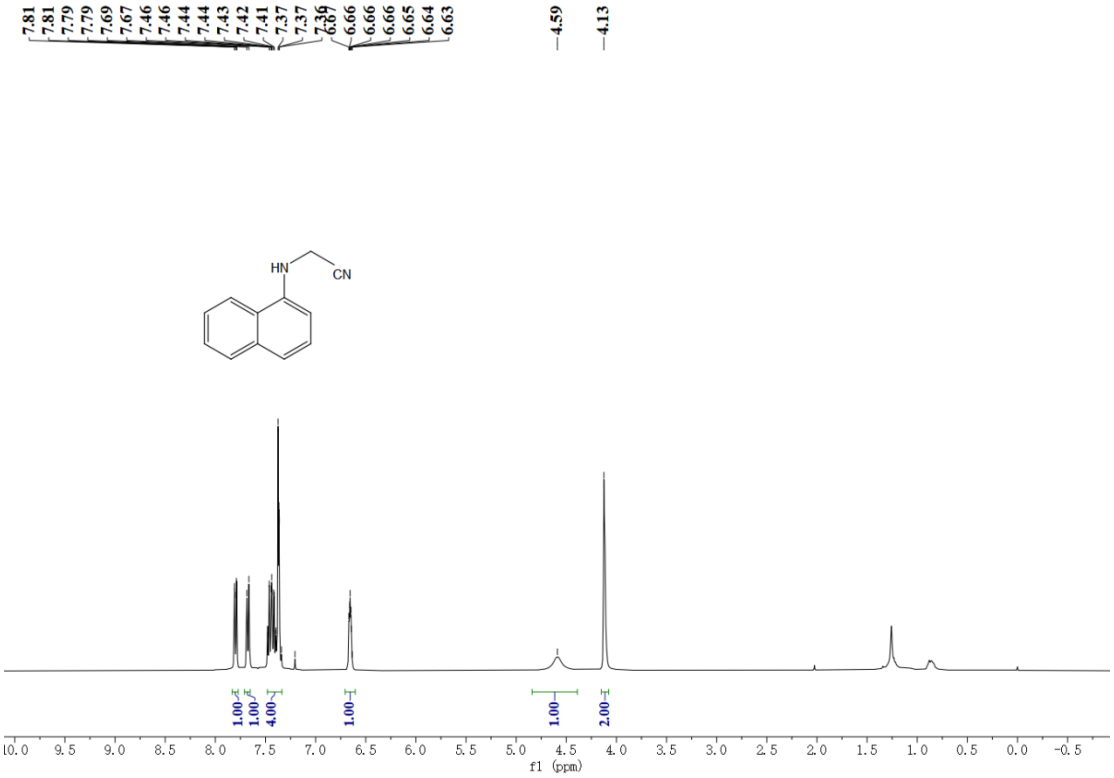

-62.86
-62.89
NH
CN
CF3
-30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92
f1 (ppm)

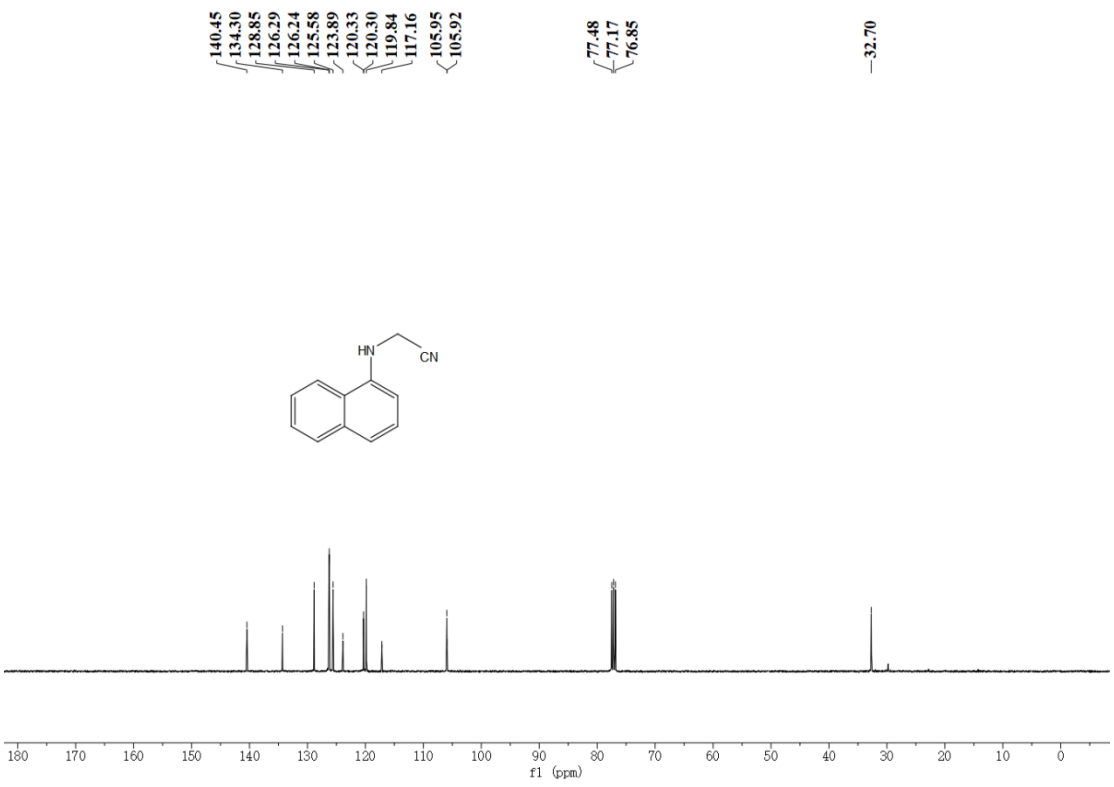
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **2n**



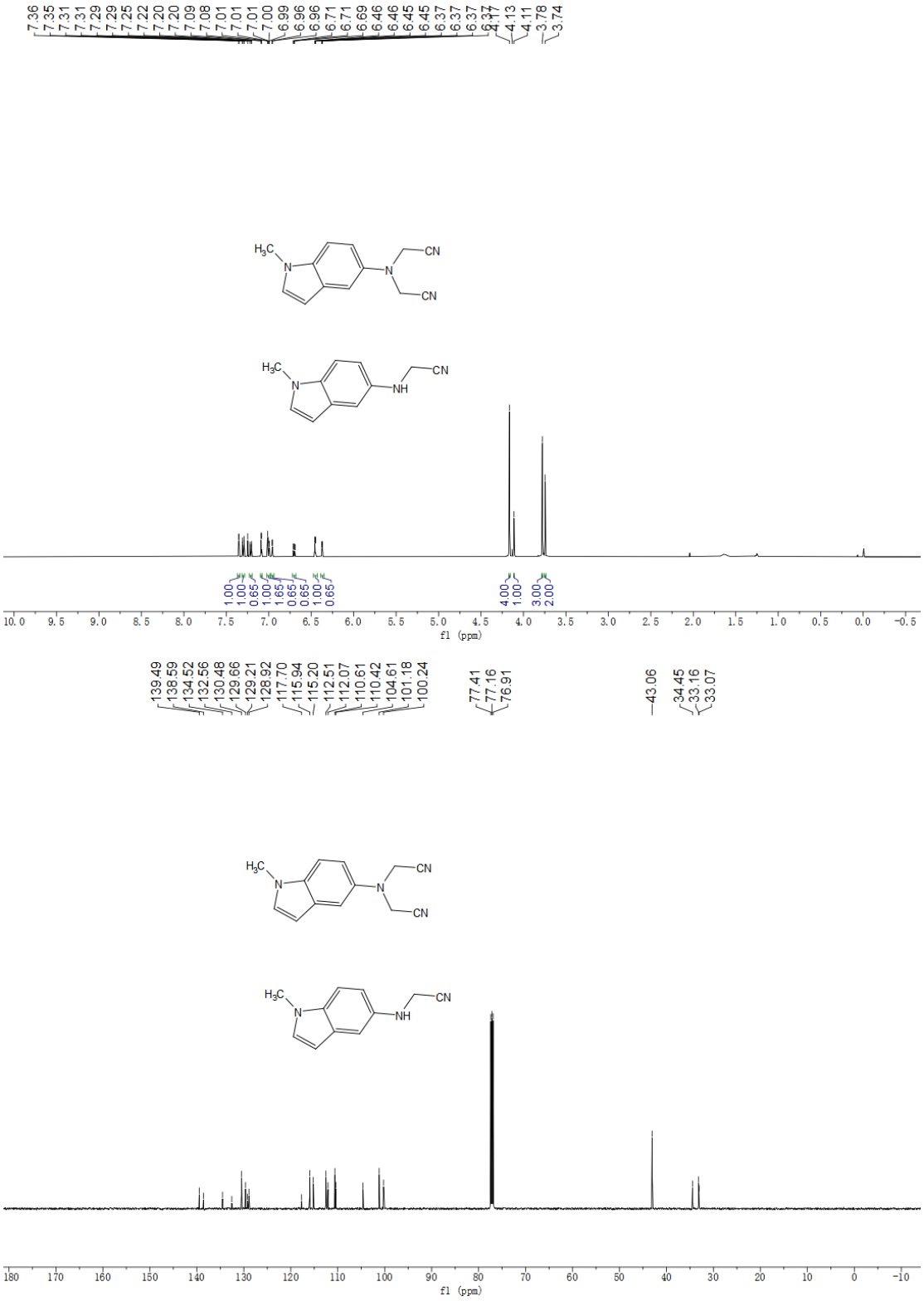


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **2o**

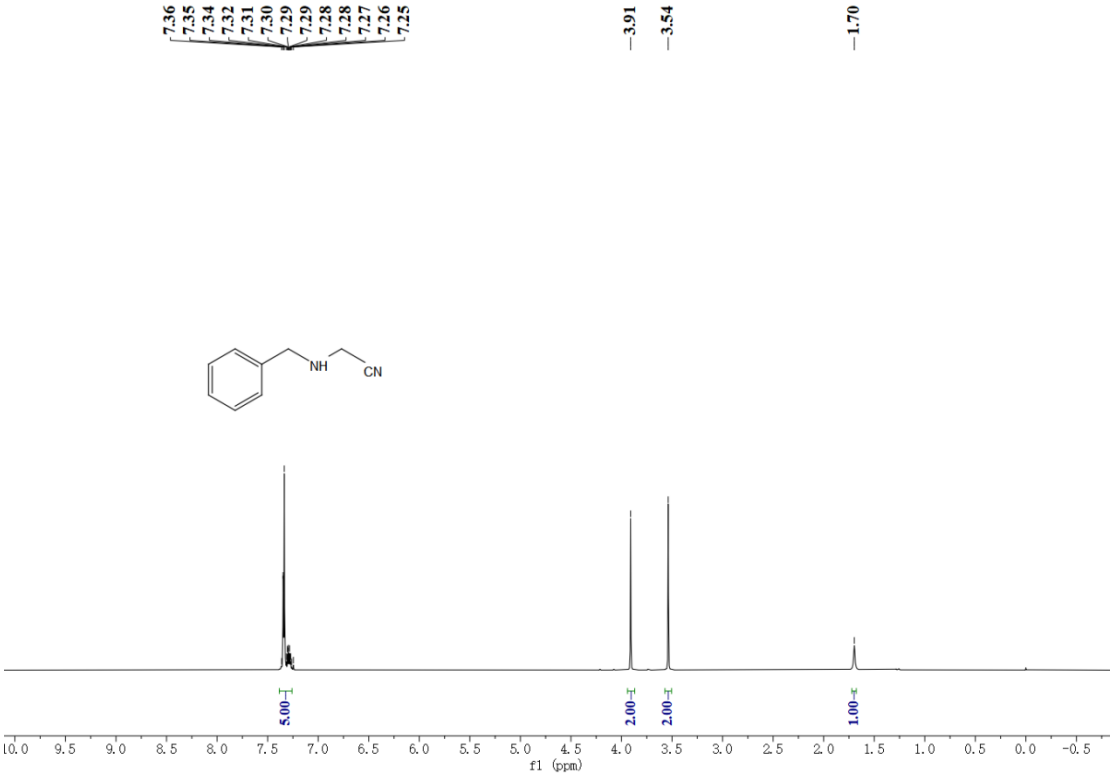


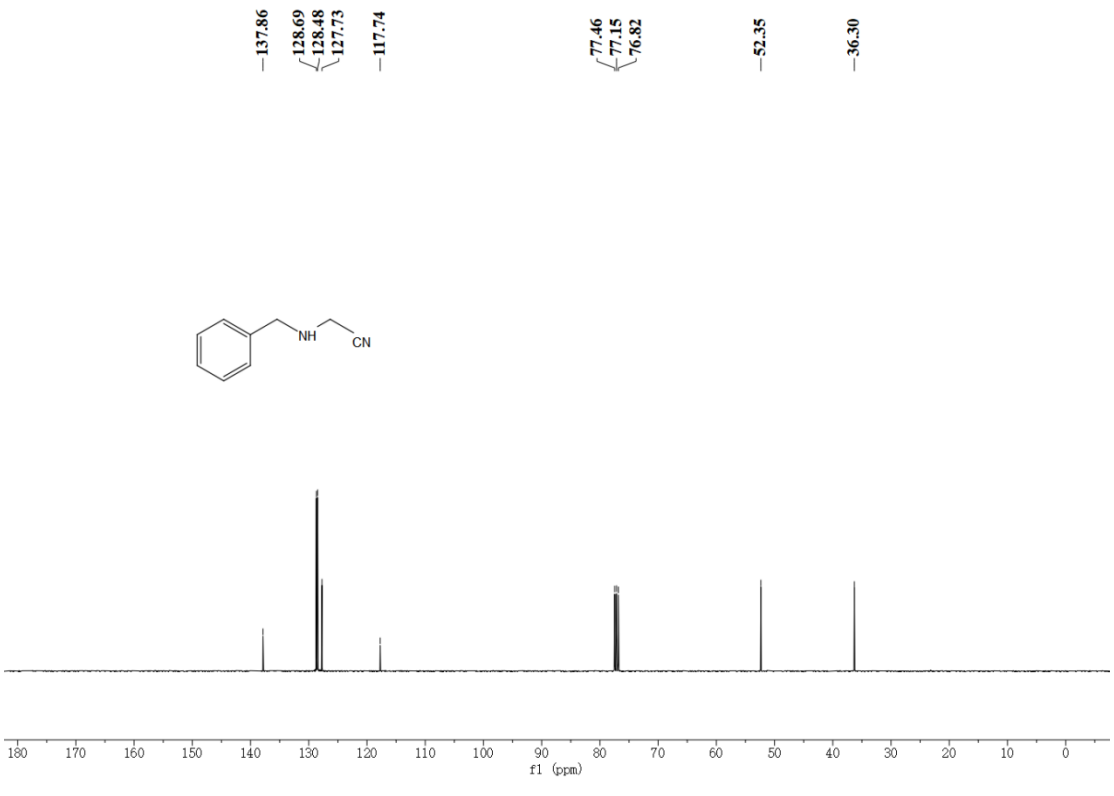


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) for **2p**

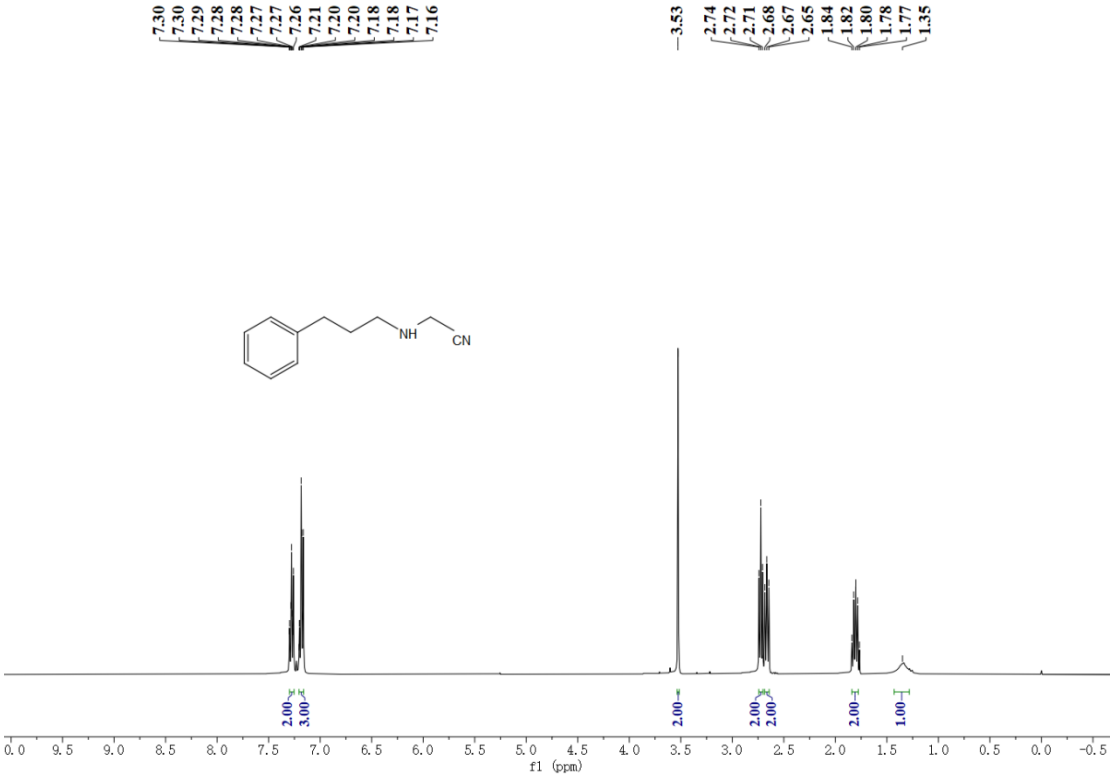


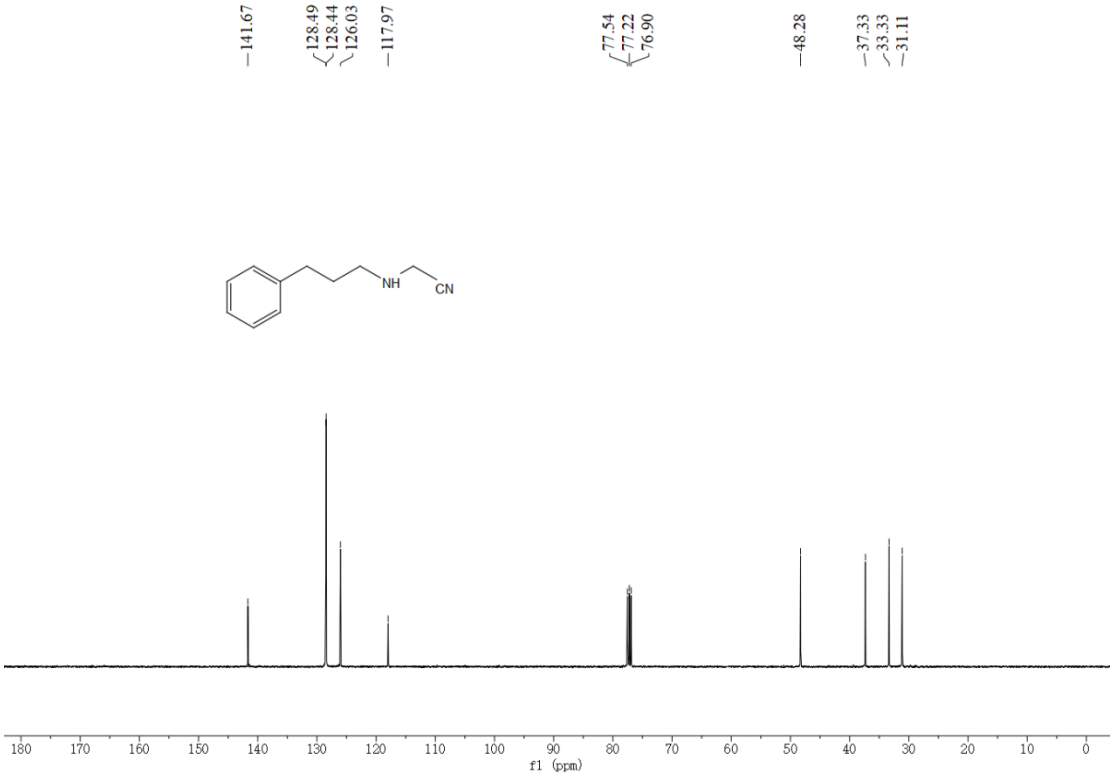
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **2q**



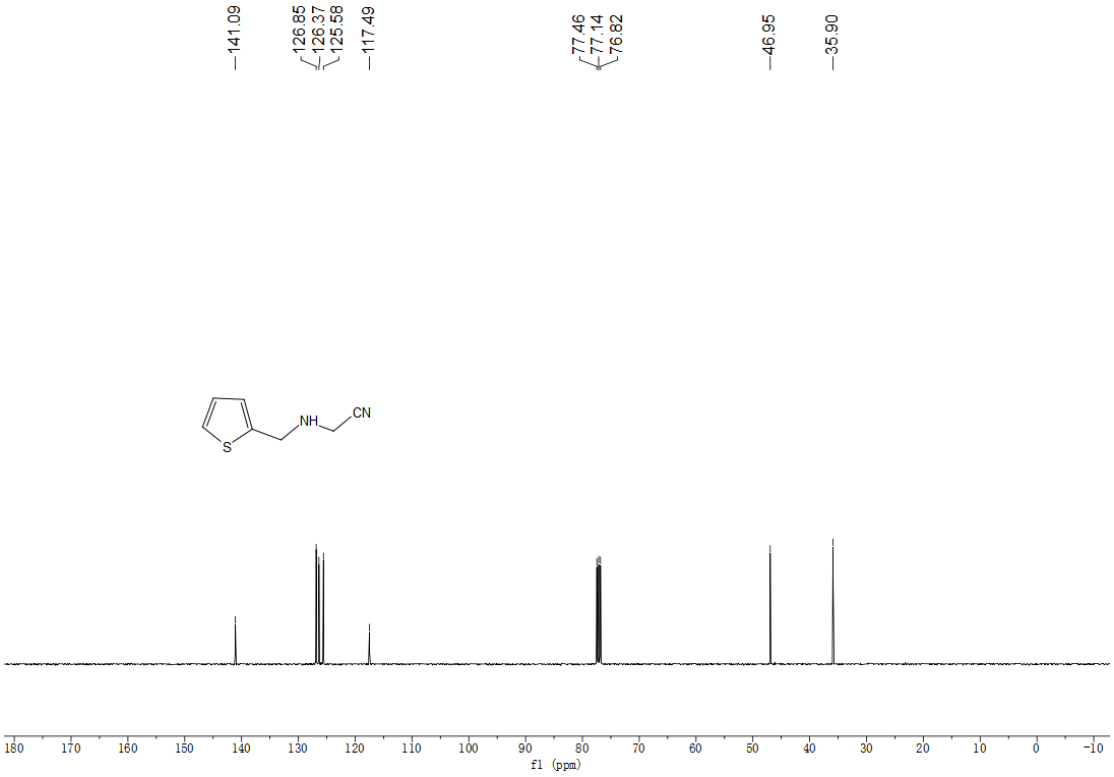


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2r**

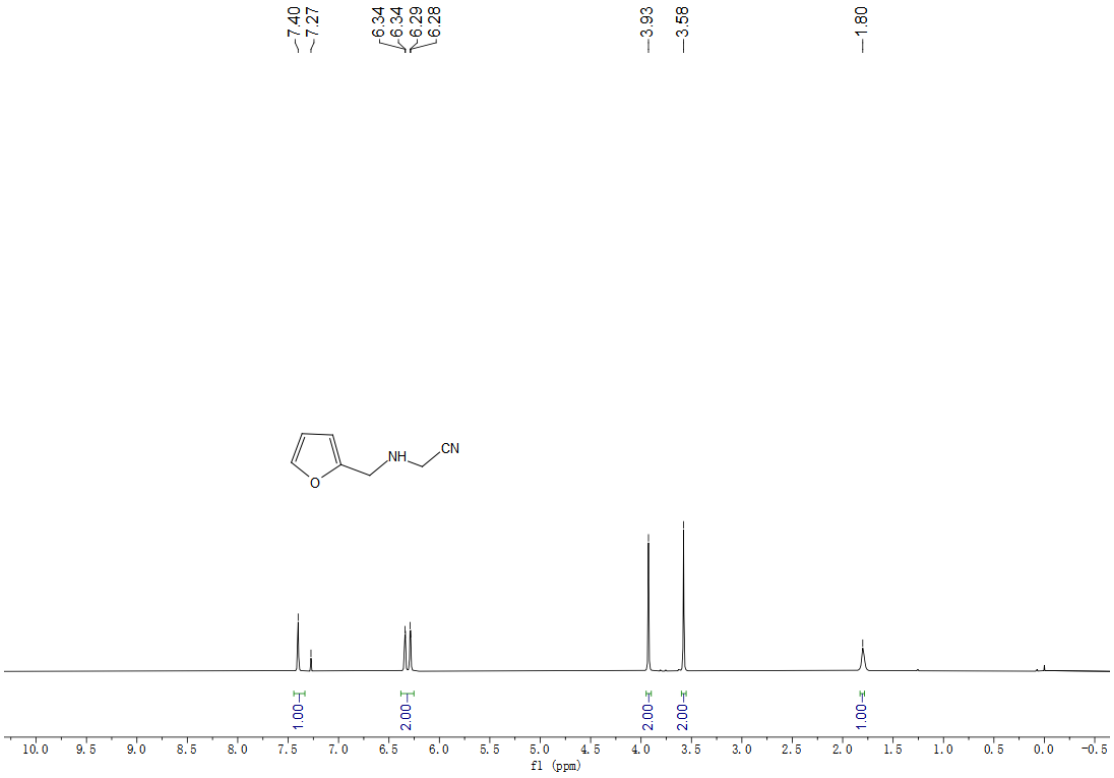


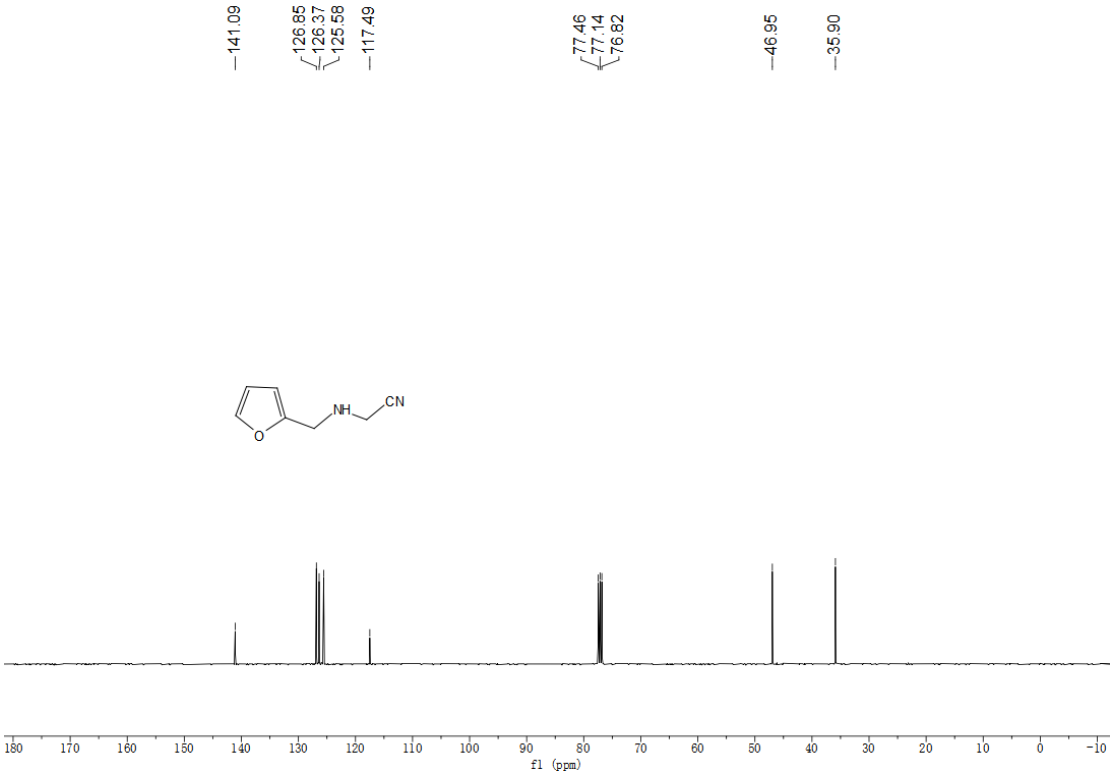


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2s**

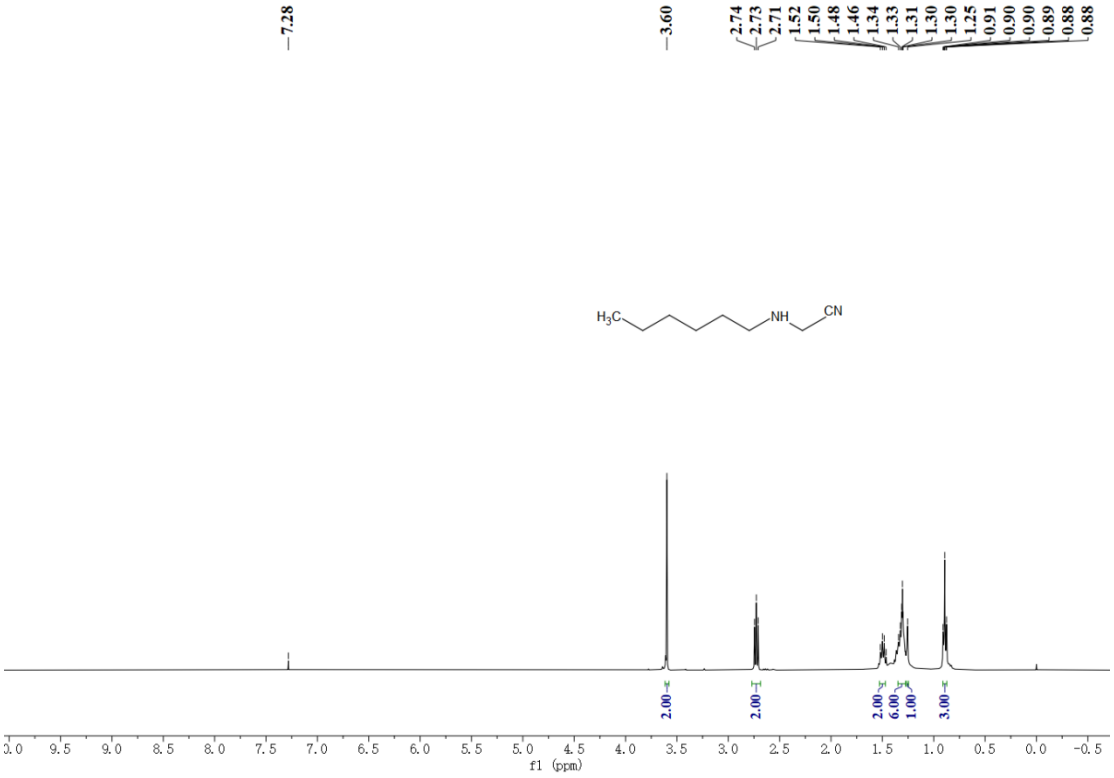


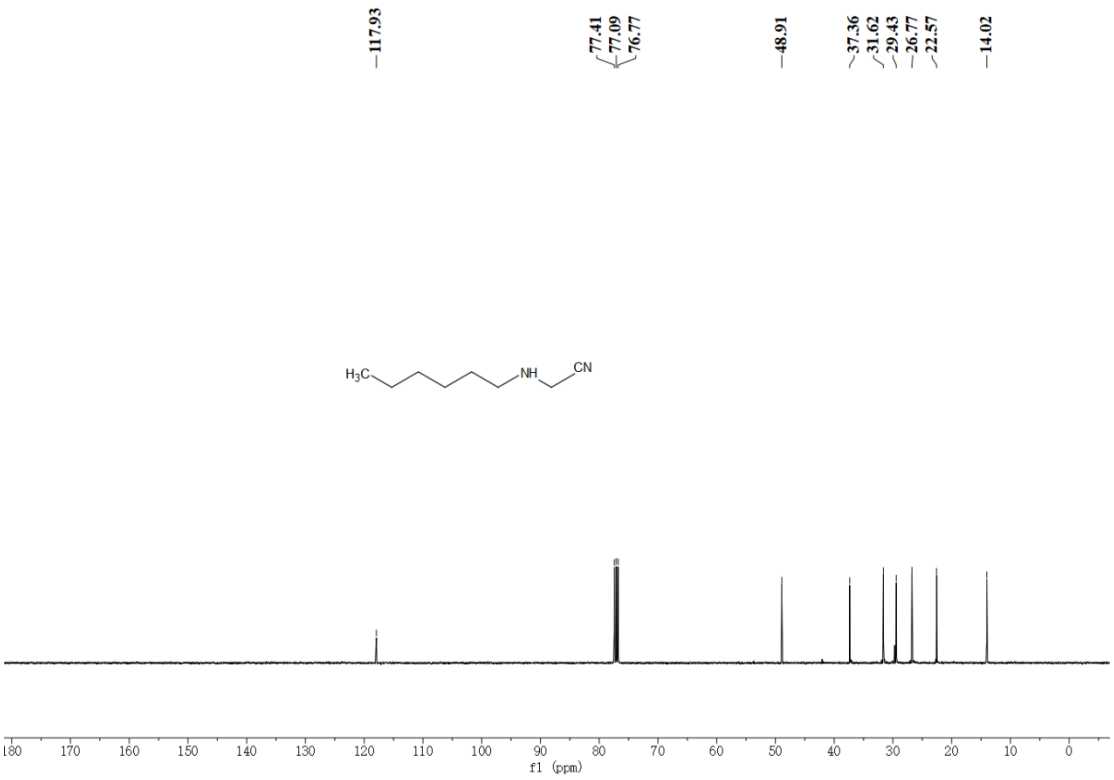
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2t**



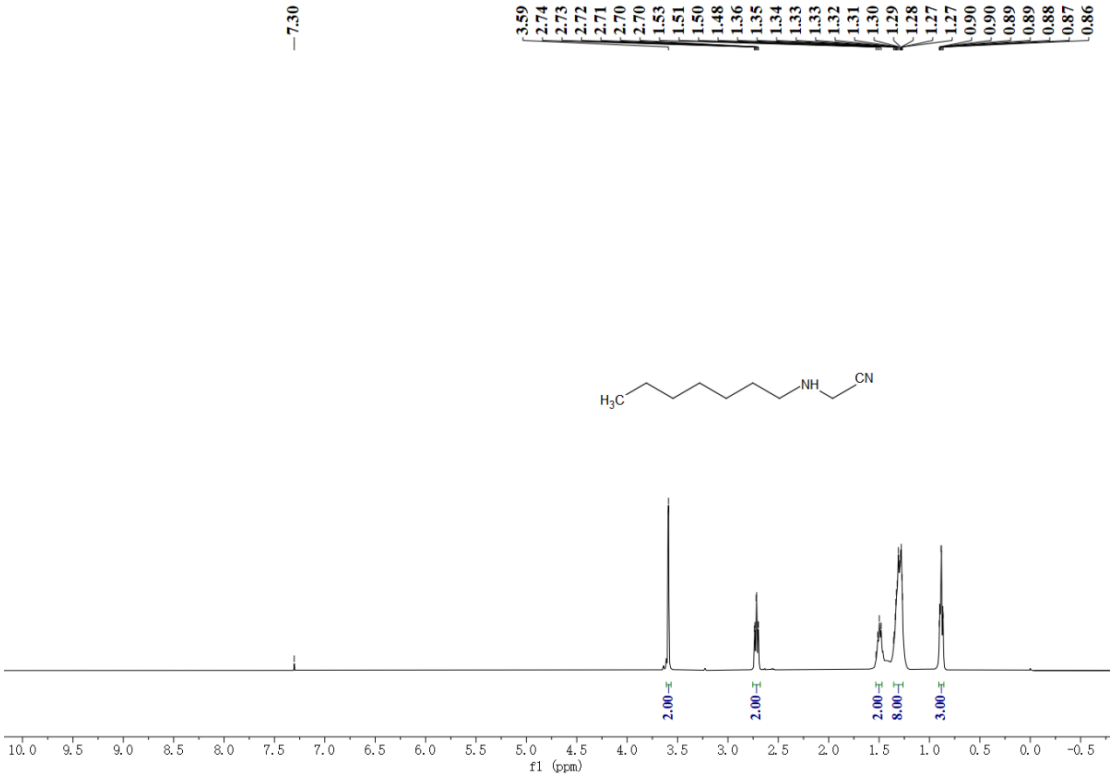


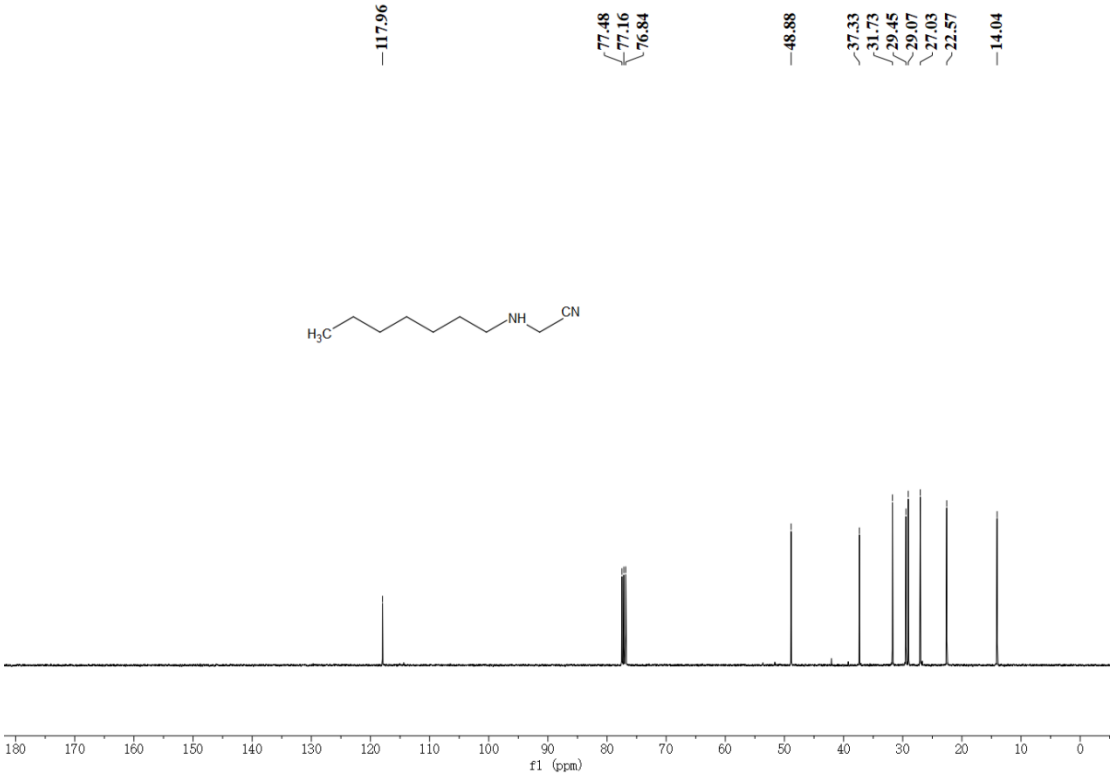
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2u**



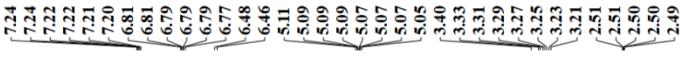


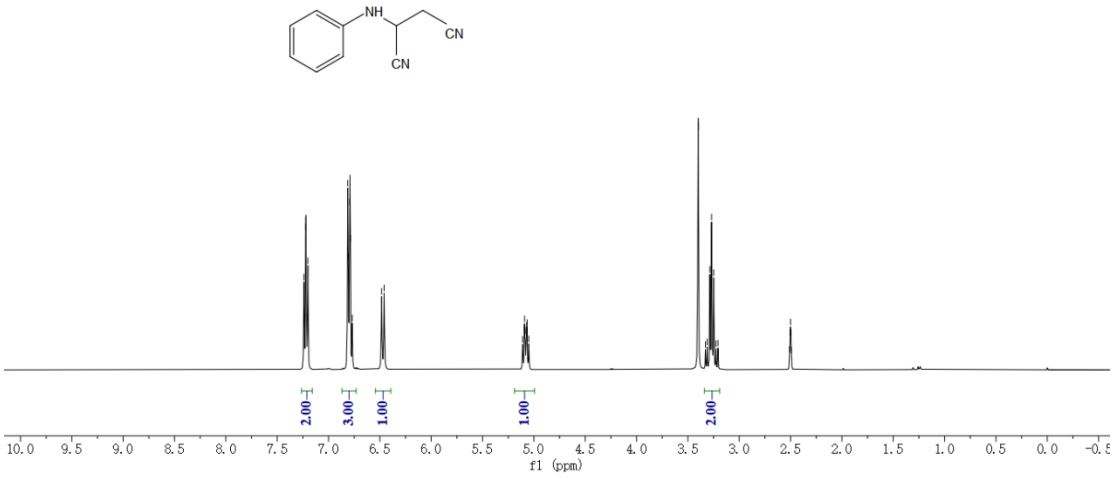
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **2v**

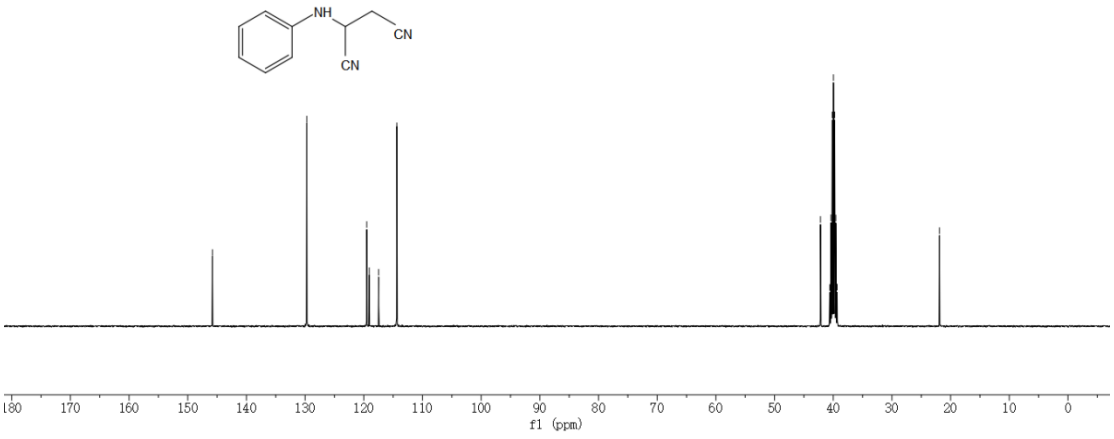


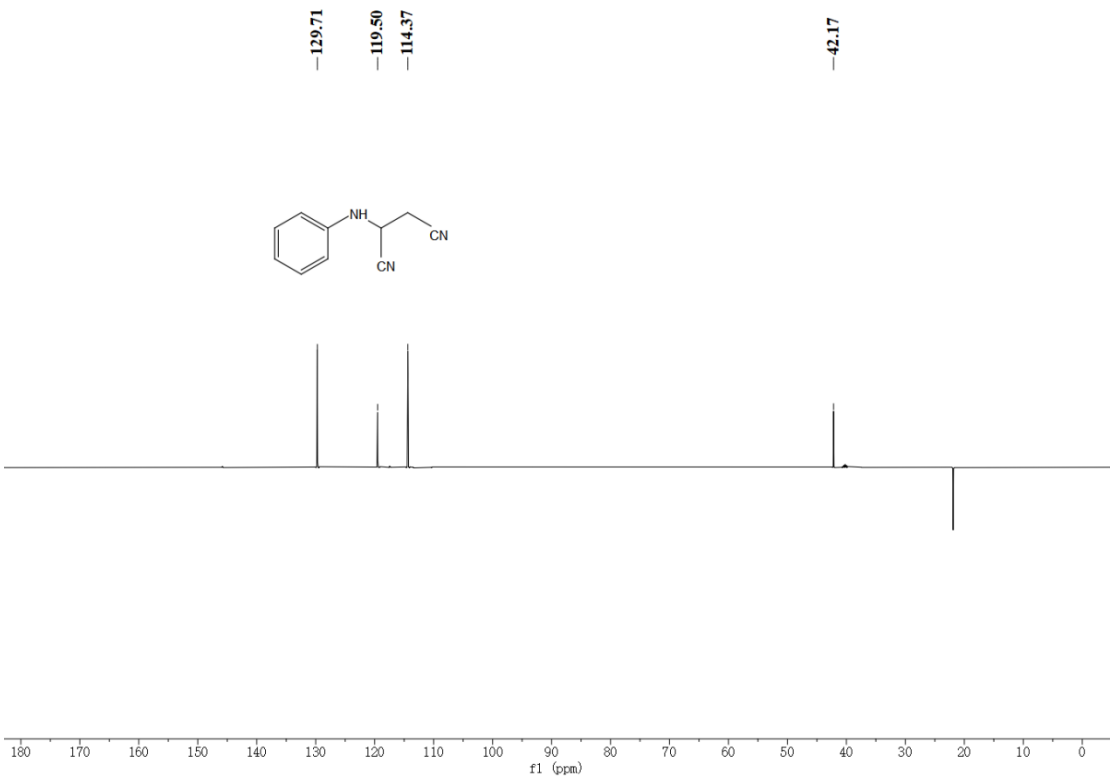


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **3a**

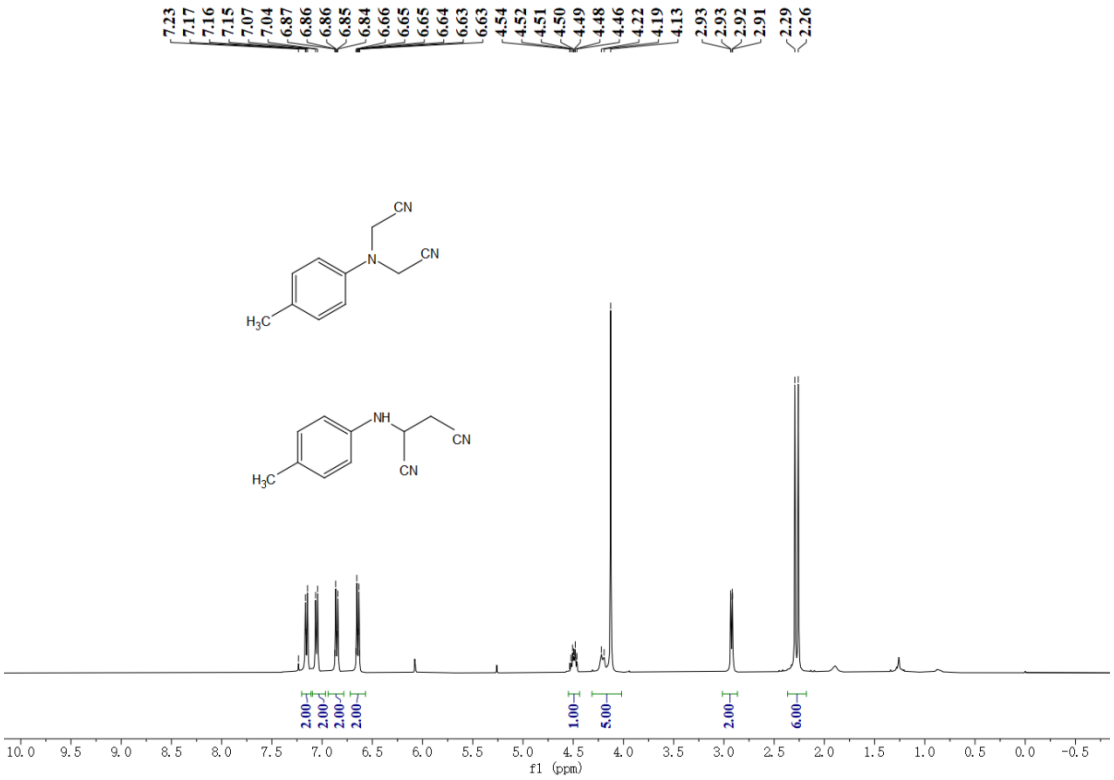


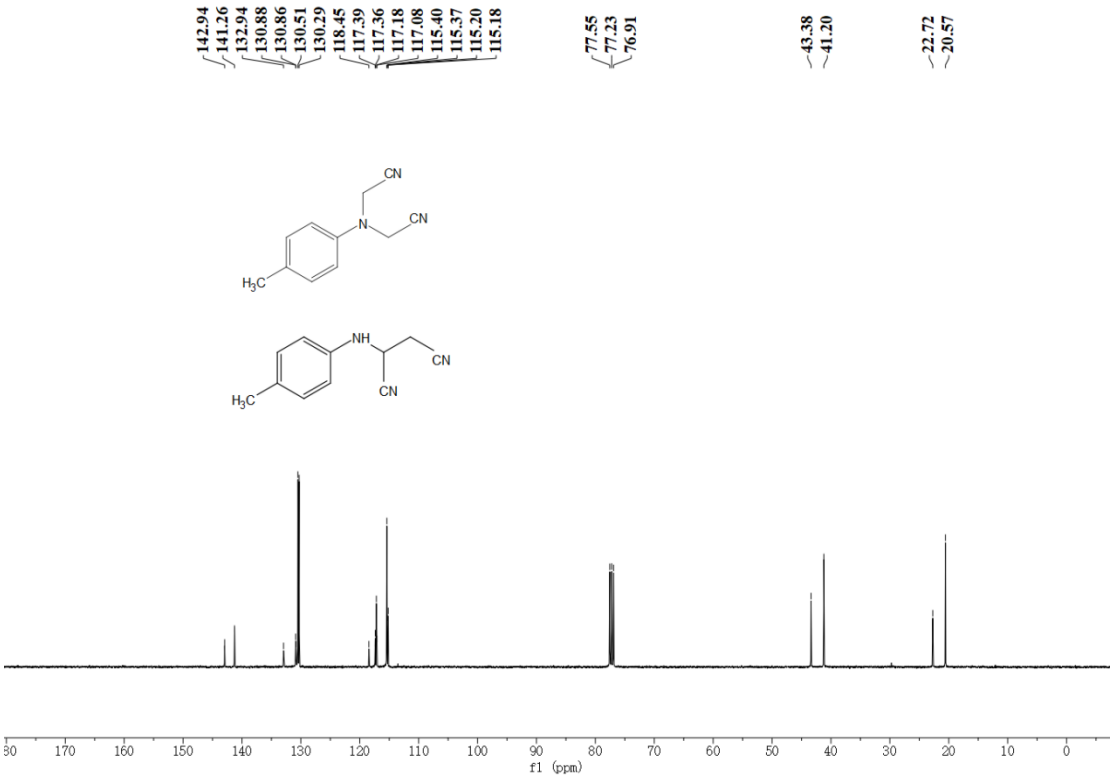




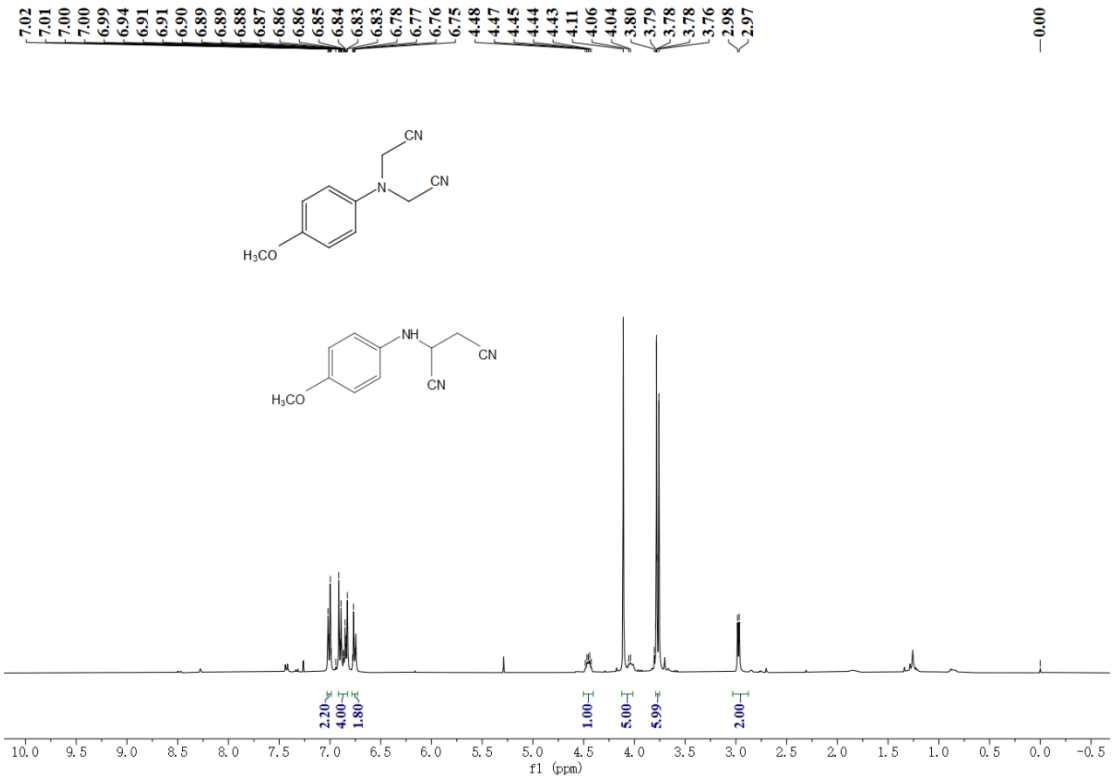

129.71
119.50
114.37
42.17
NH
CN
CN
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

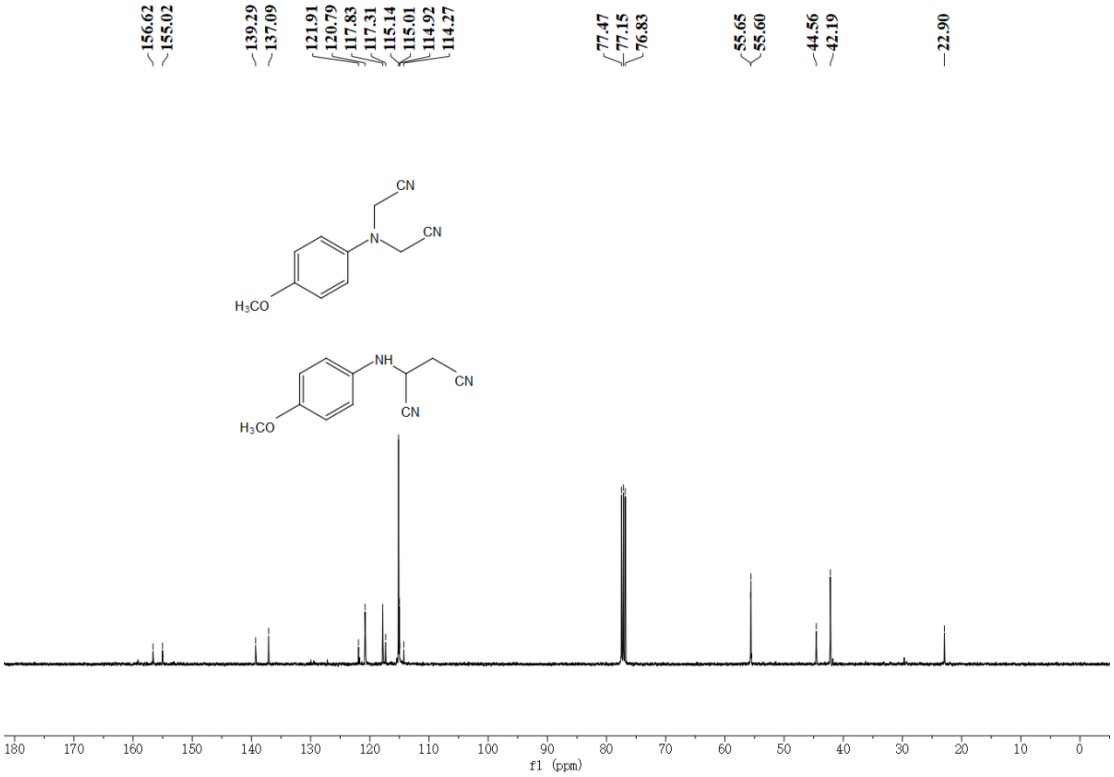
^{1}H NMR (400 MHz, $CDCl_{3)}$ and ^{13}C NMR (100 MHz, $CDCl_{3}$) for **3b**



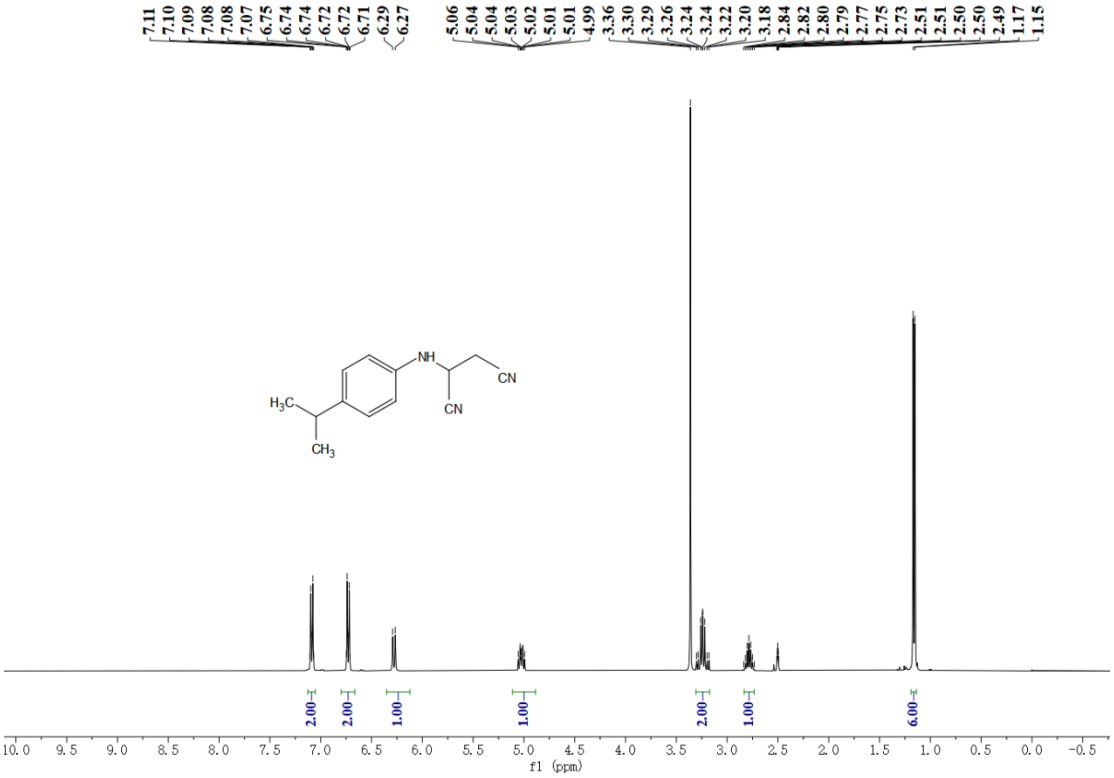


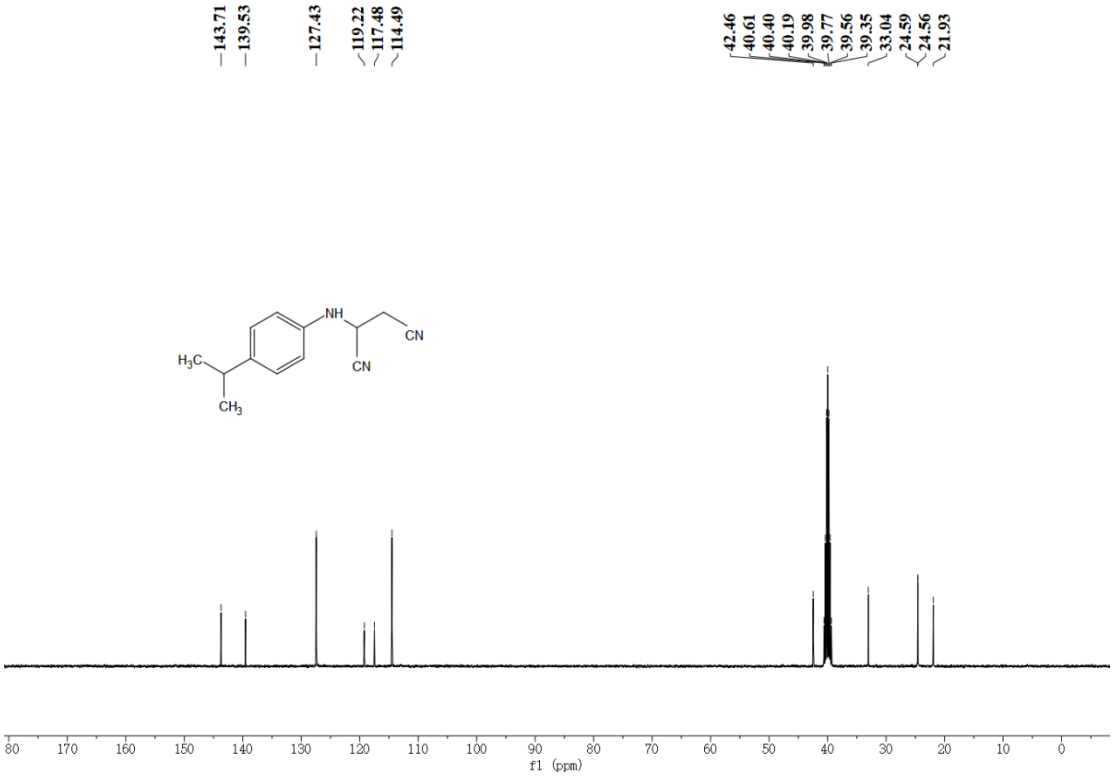
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **3c**



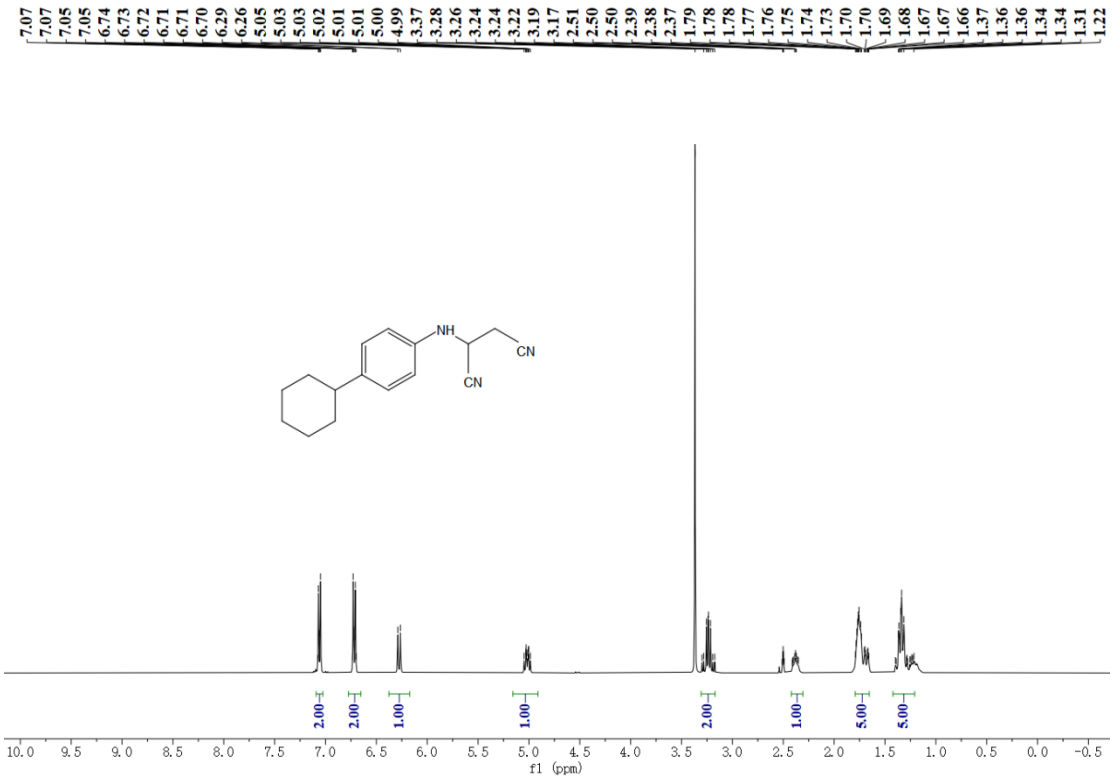


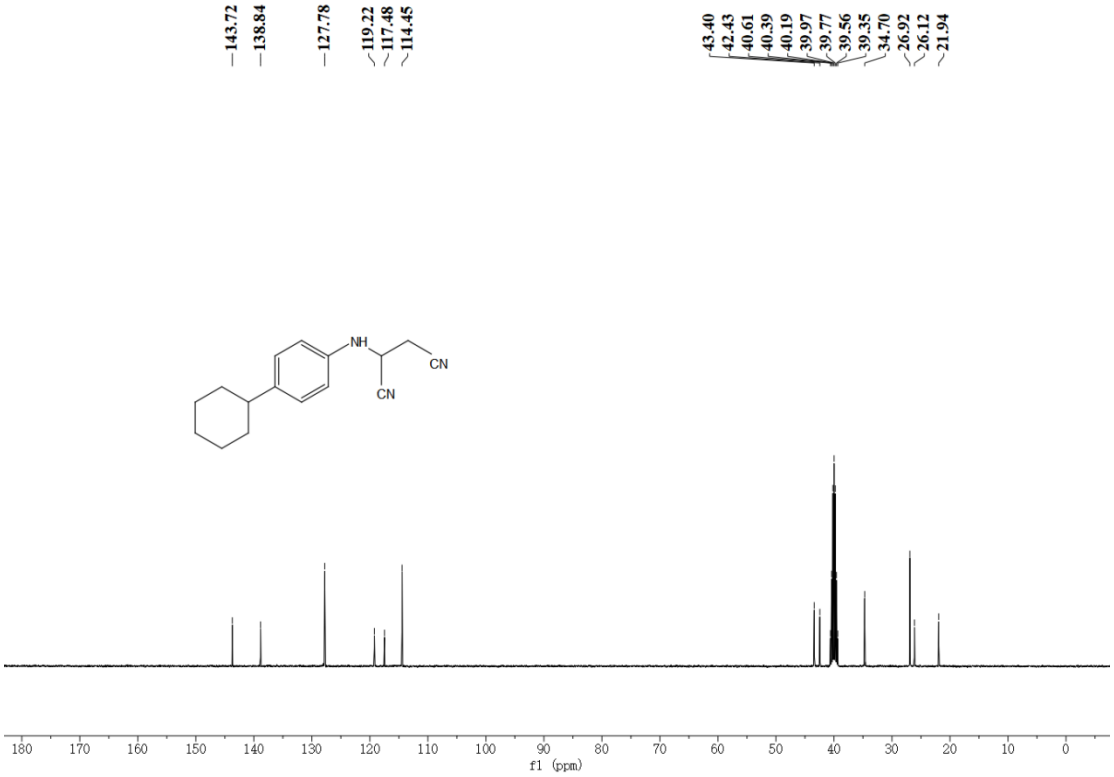
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **3d**



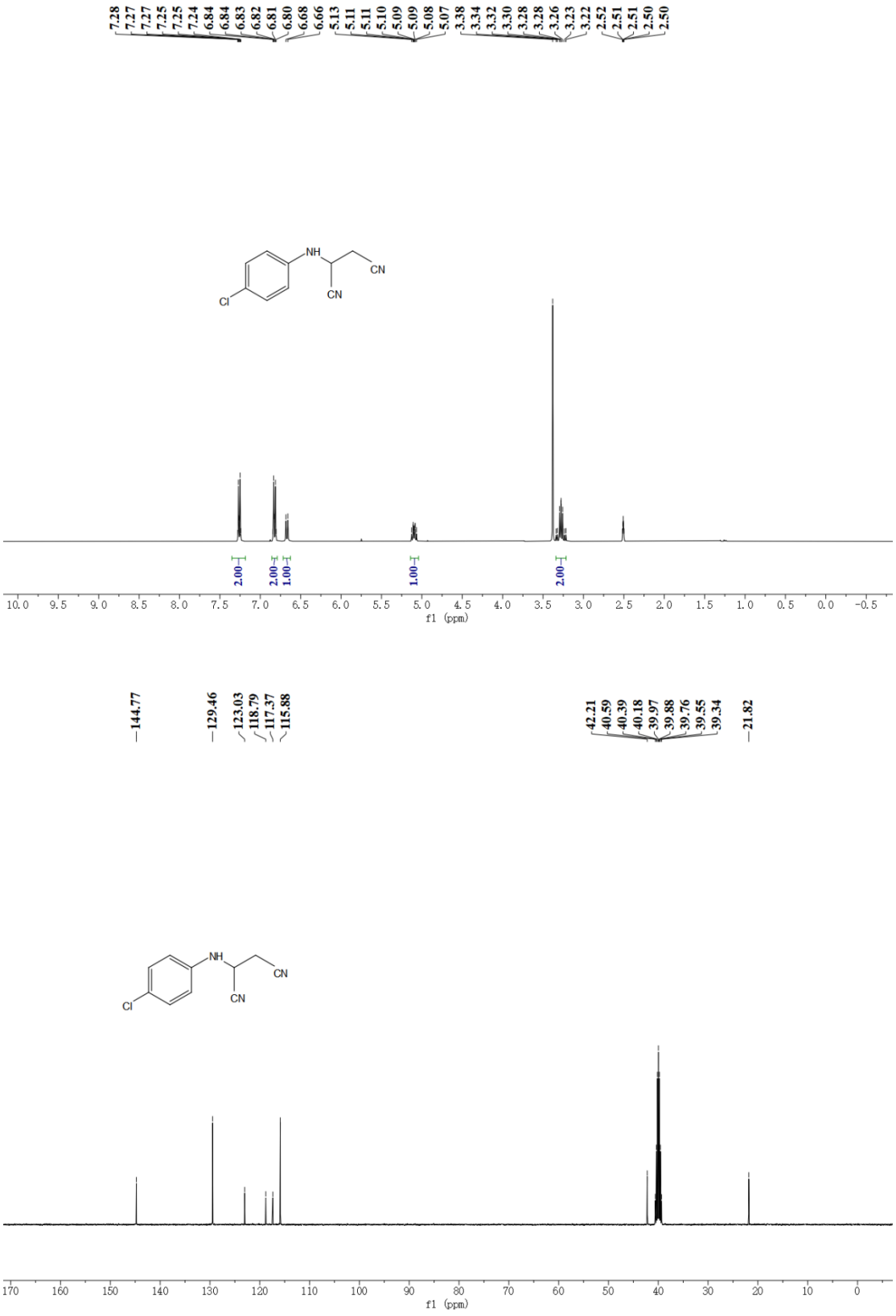


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **3e**

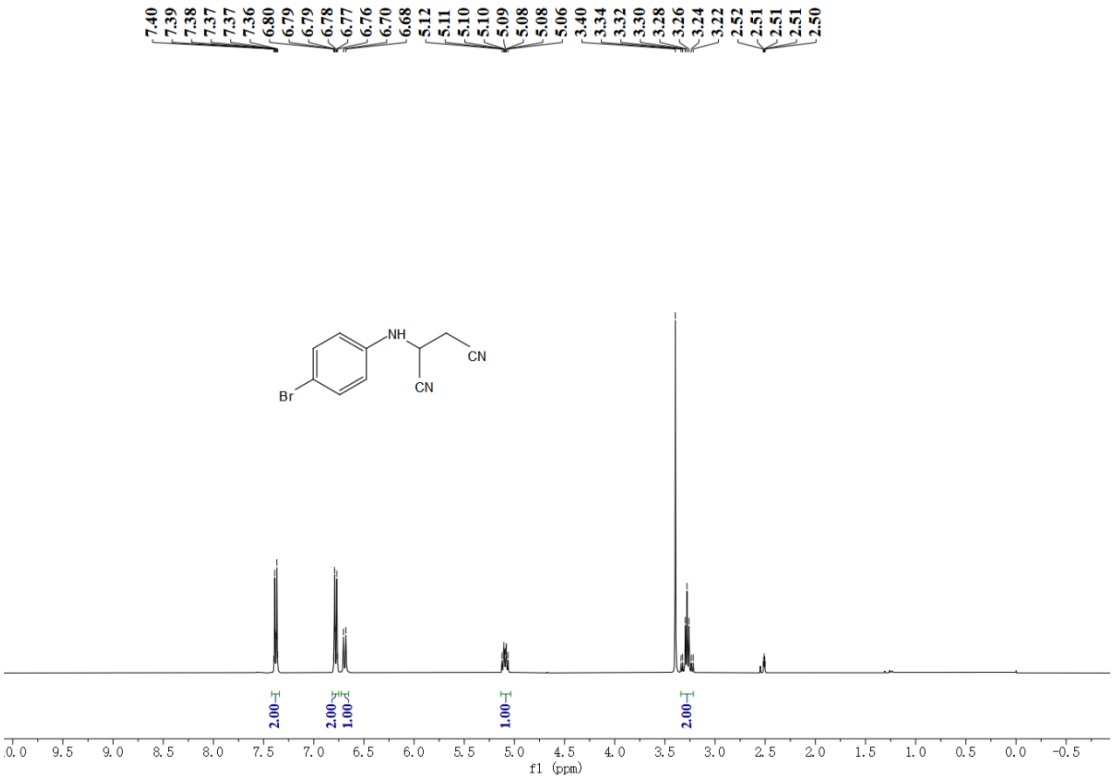


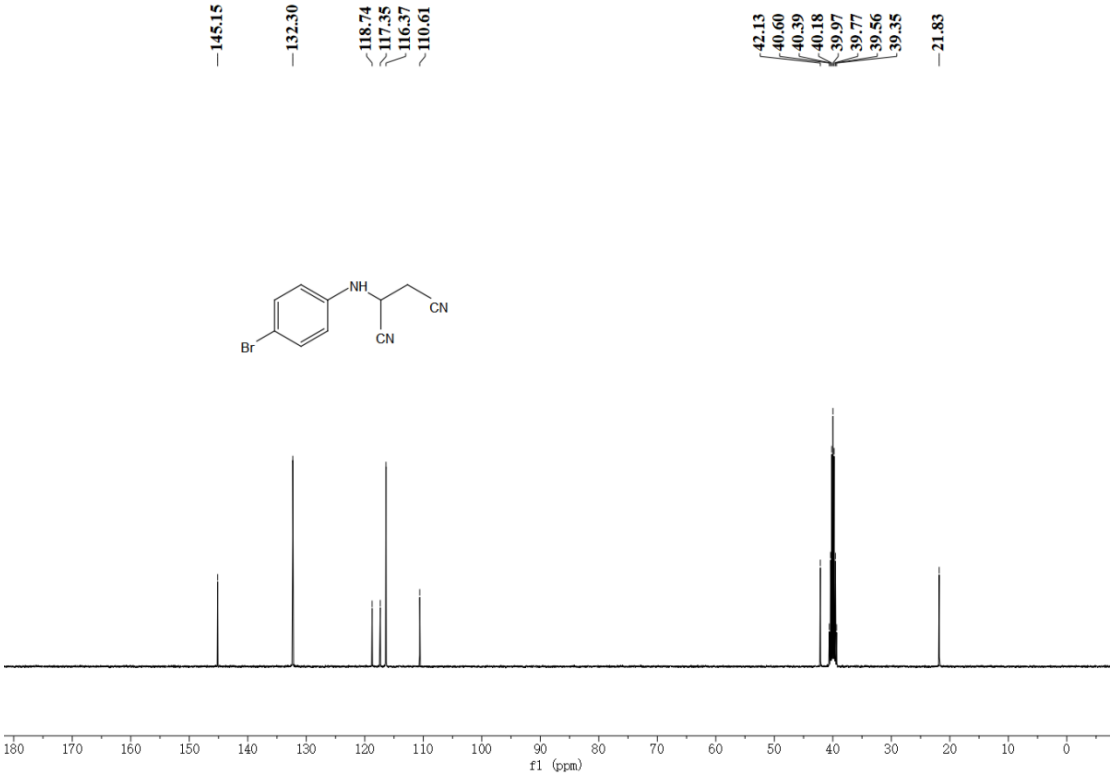


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **3f**

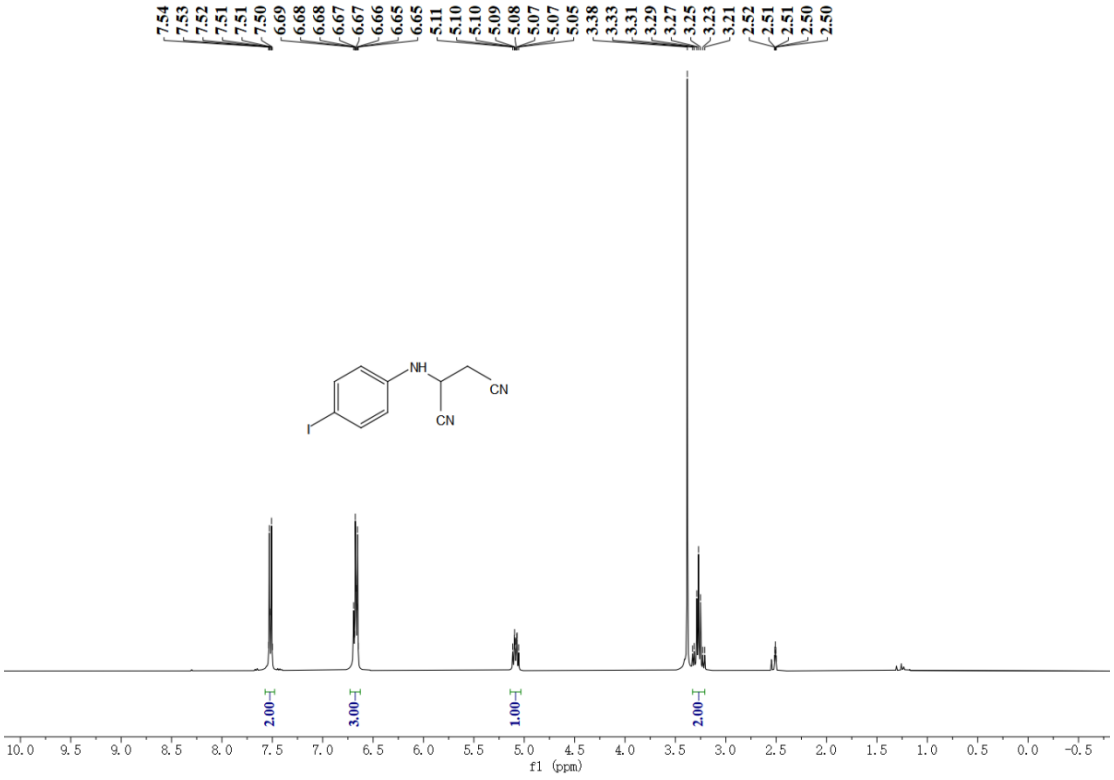


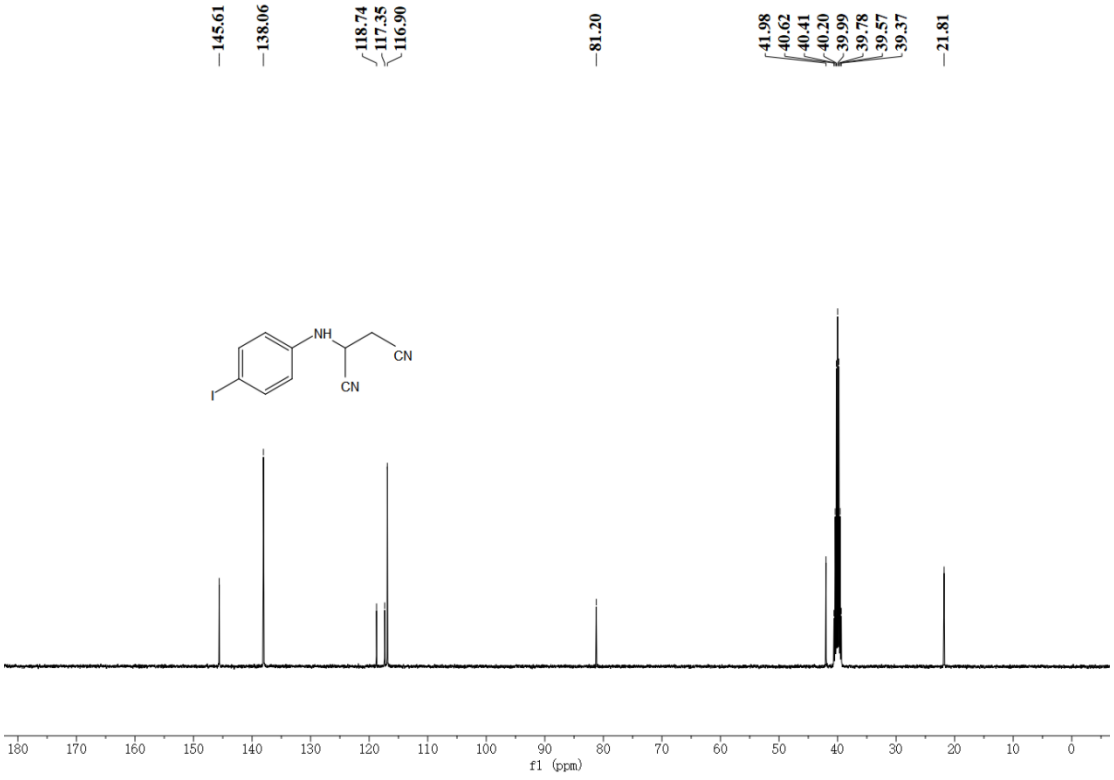
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **3g**



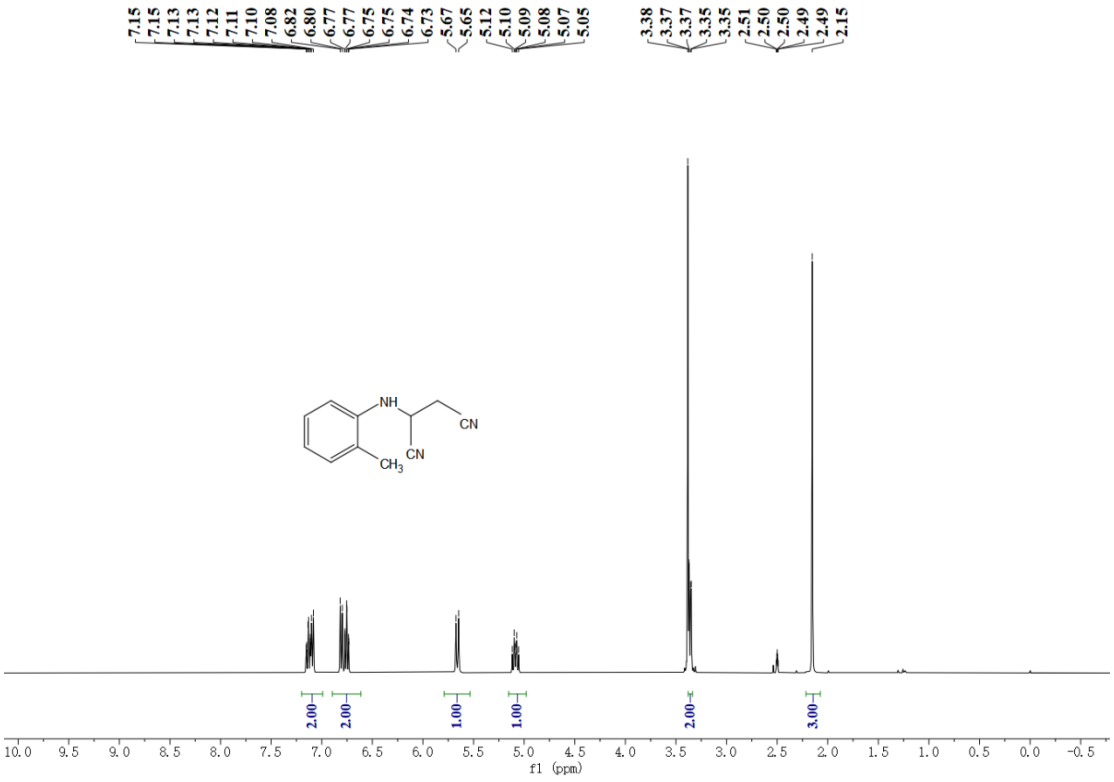


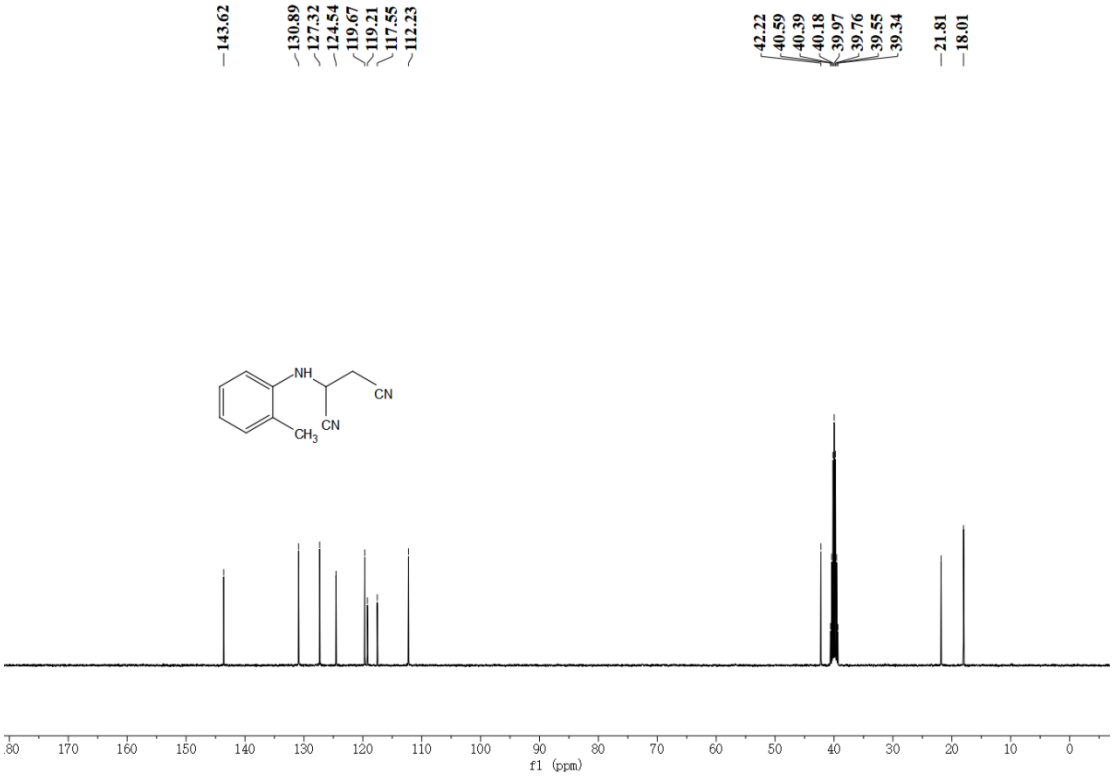
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **3h**



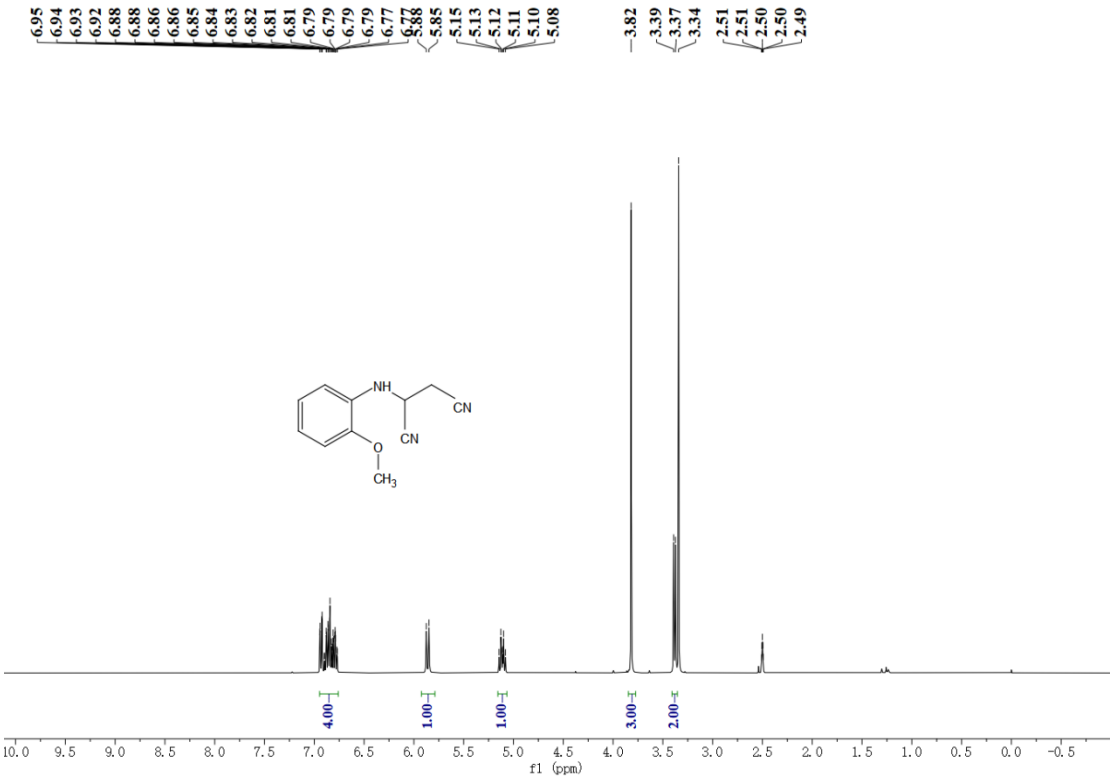


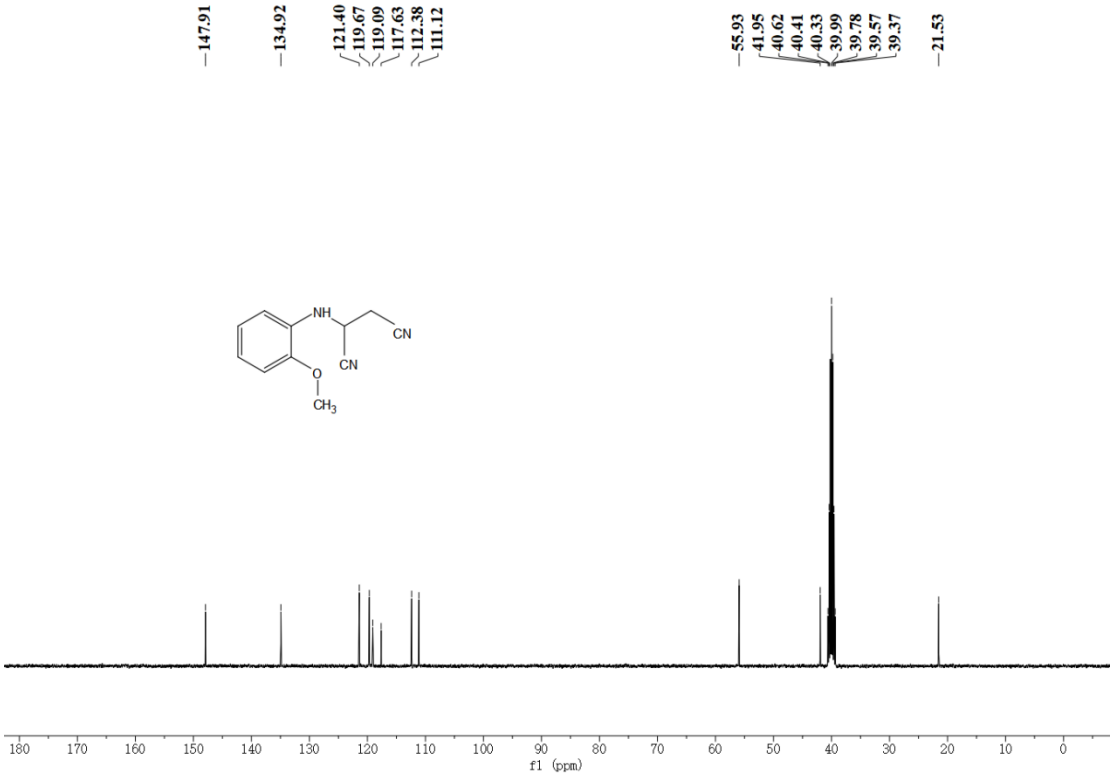
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **3j**



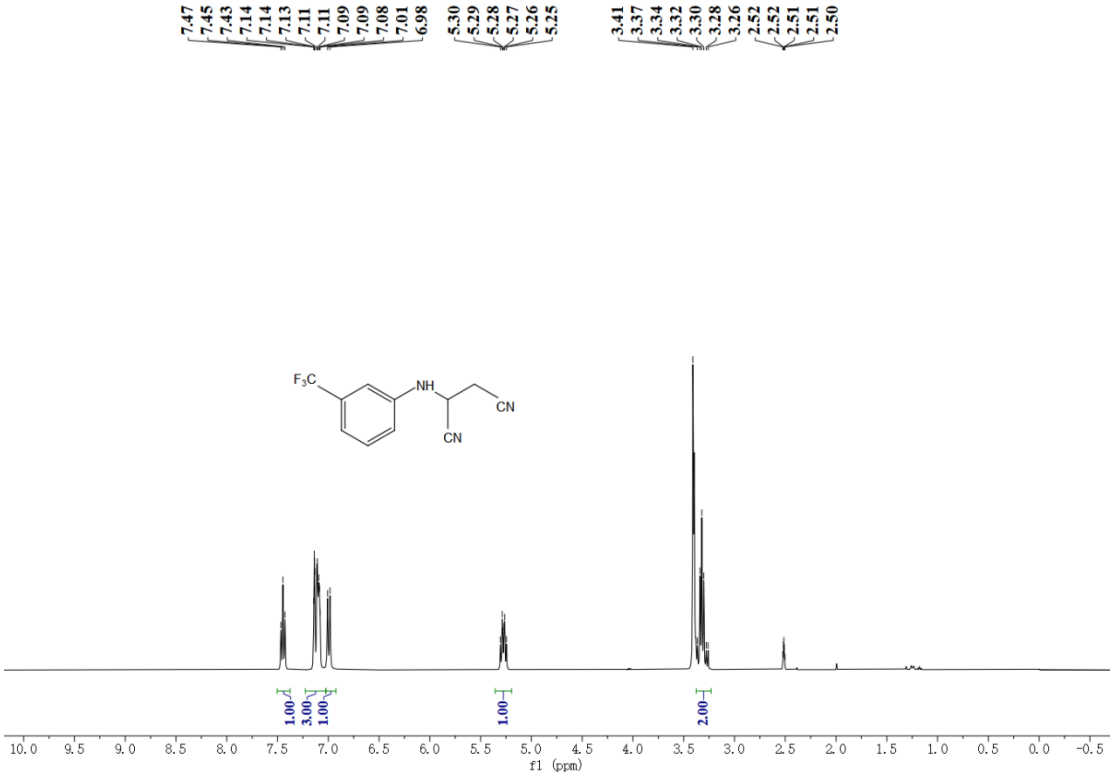


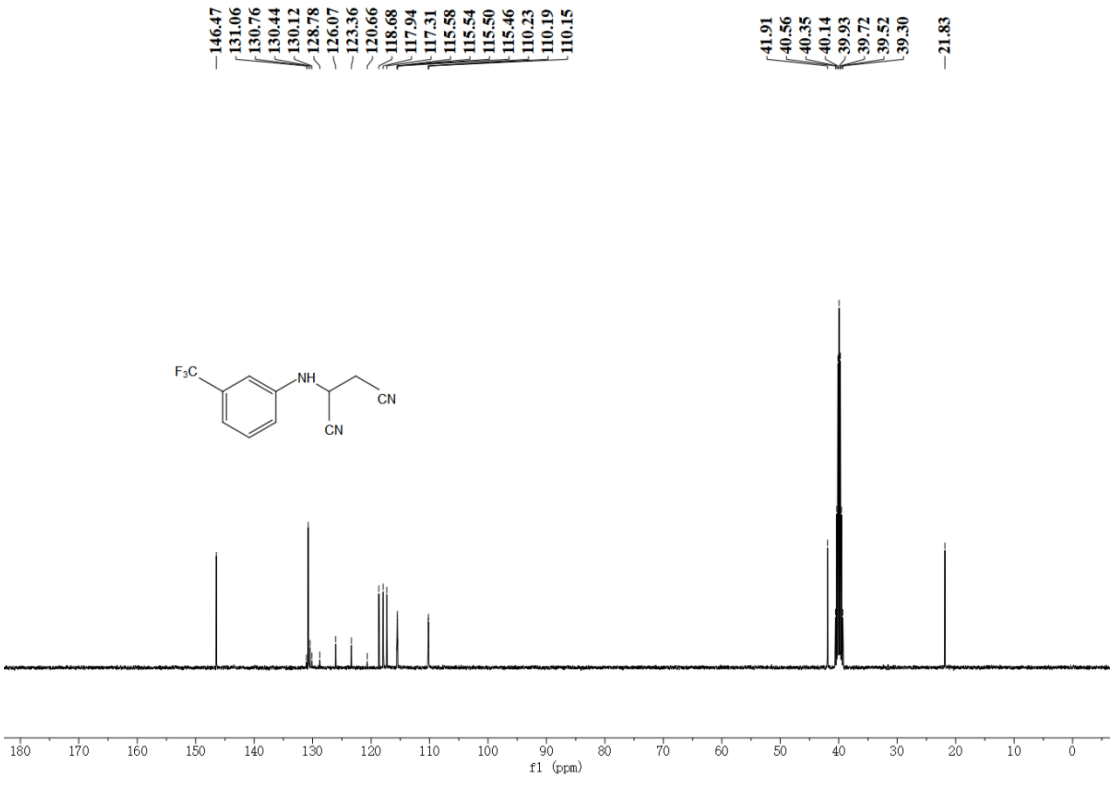
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **3k**

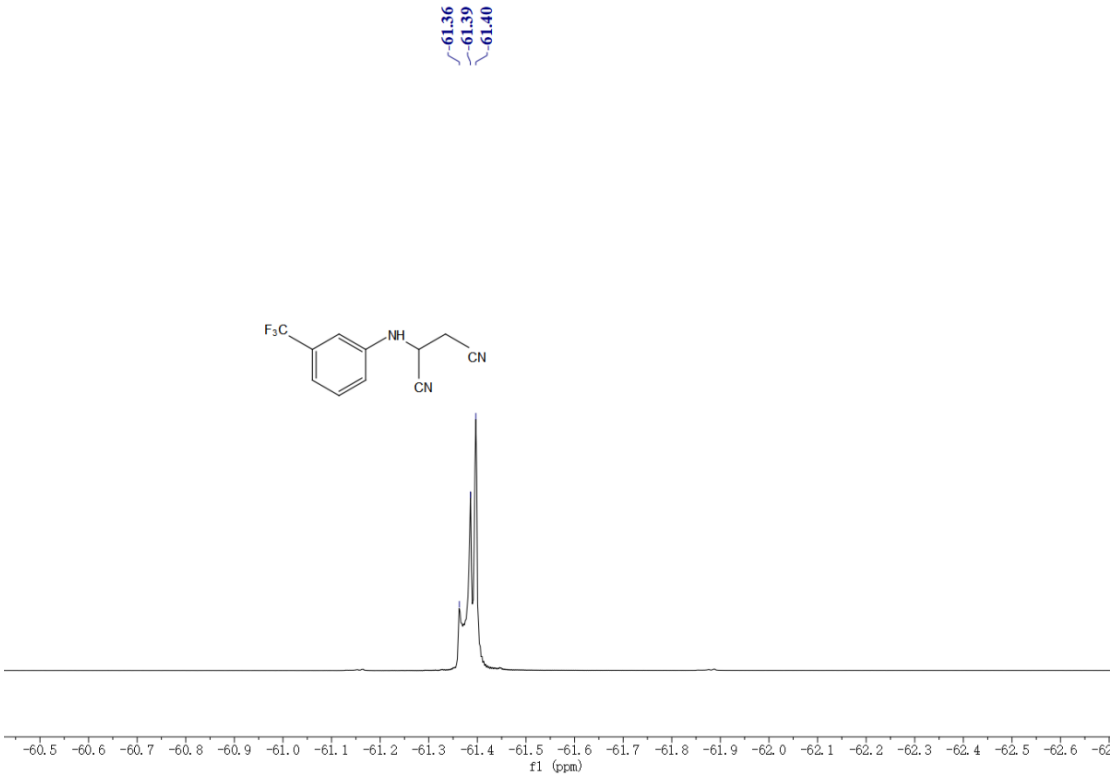




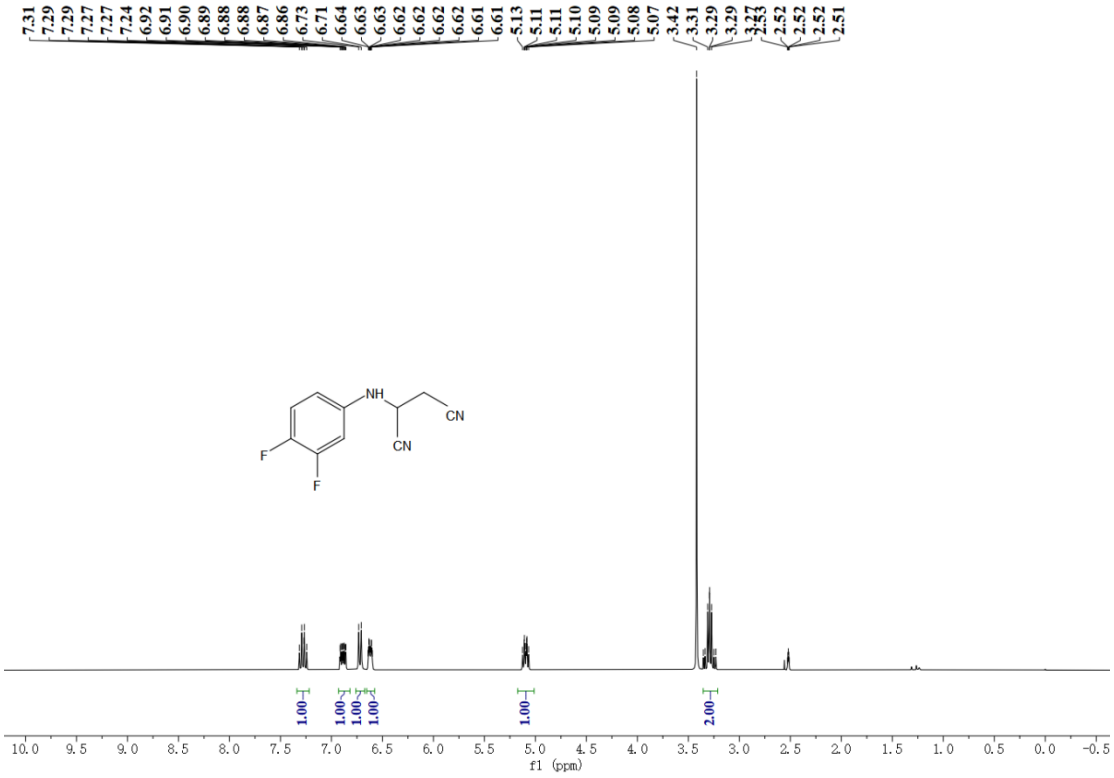
^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (100 MHz, DMSO-d_6) and ^{19}F(376 MHz, DMSO-d_6) for **3l**

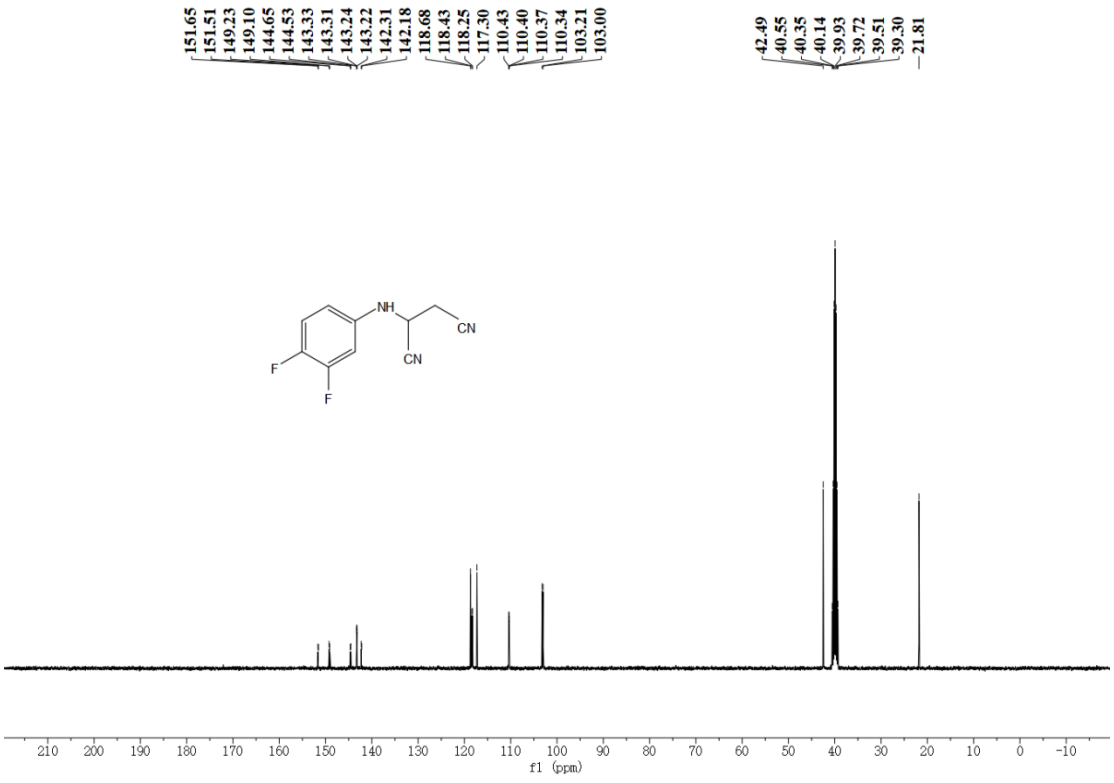


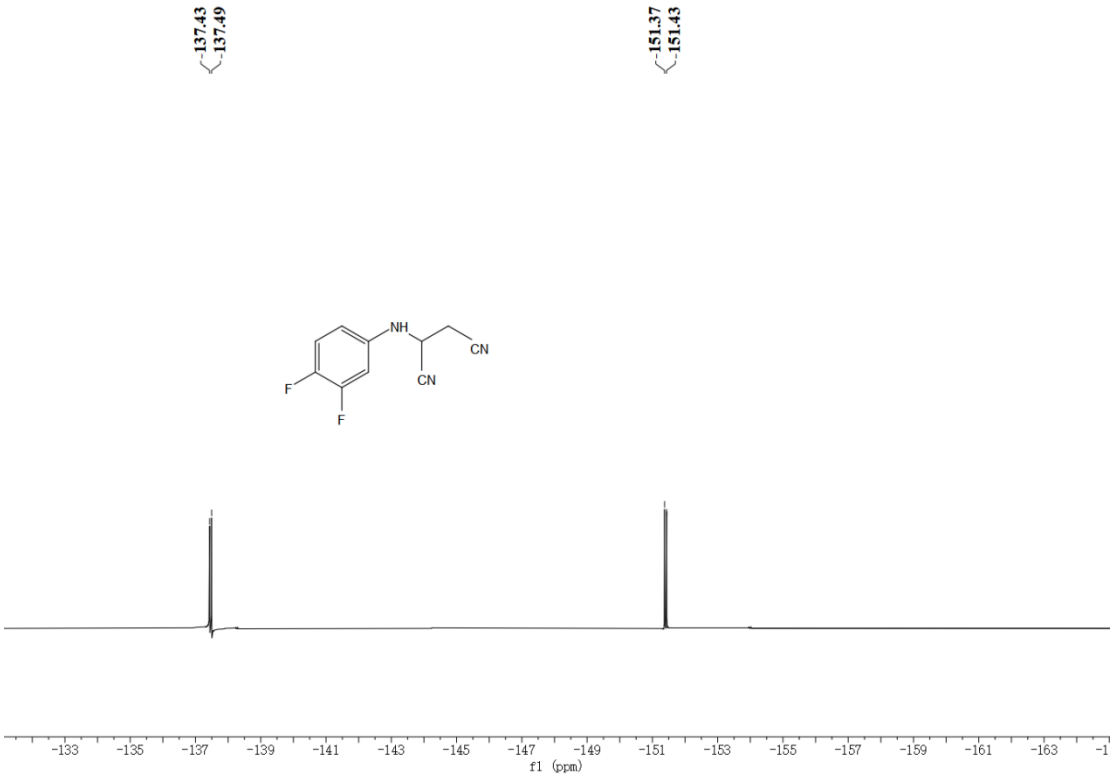



-61.36
-61.39
-61.40
F3C
NH
CN
CN
-60.5 -60.6 -60.7 -60.8 -60.9 -61.0 -61.1 -61.2 -61.3 -61.4 -61.5 -61.6 -61.7 -61.8 -61.9 -62.0 -62.1 -62.2 -62.3 -62.4 -62.5 -62.6
f1 (ppm)

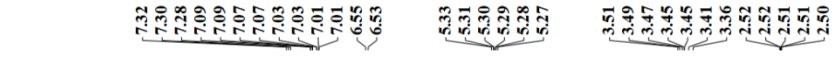
^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (100 MHz, DMSO-d_6) and ^{19}F(376 MHz, DMSO-d_6) for **3m**

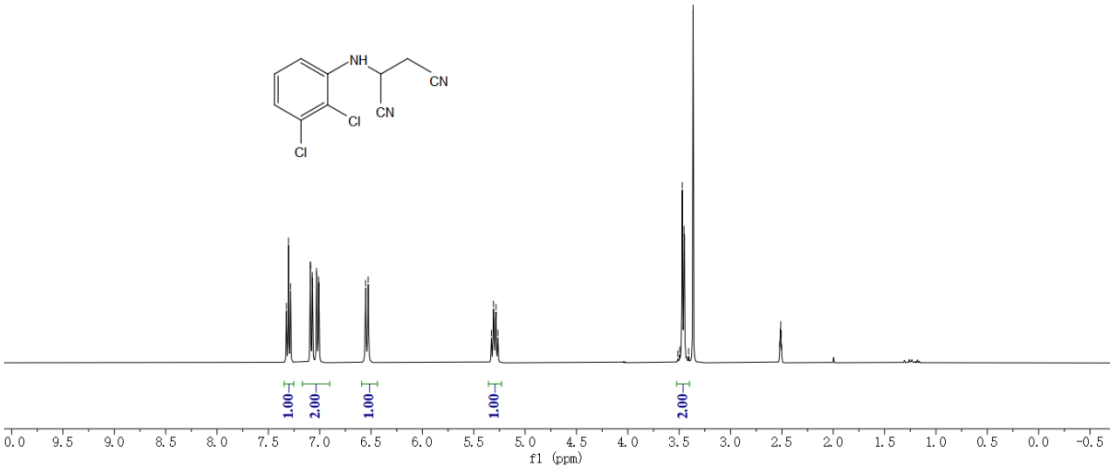


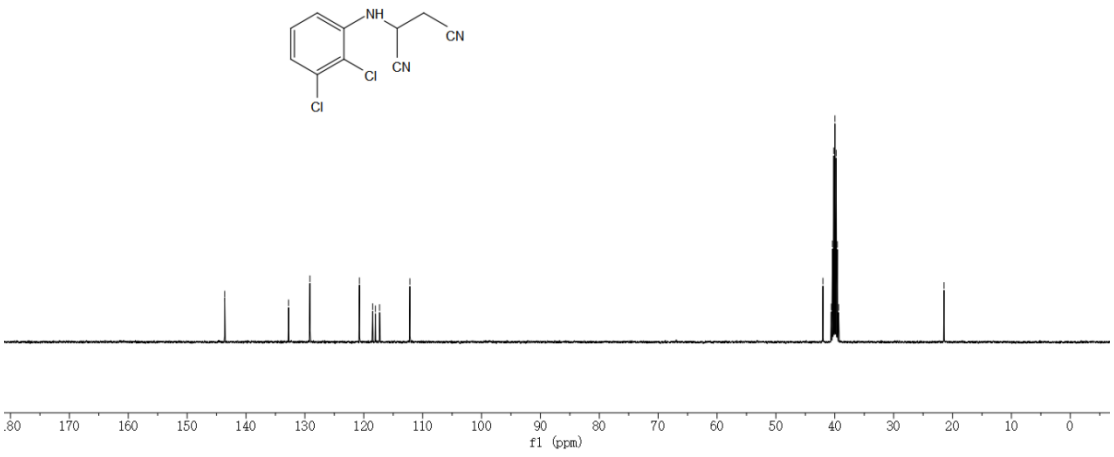



137.43
137.49
151.37
151.43
NH
CN
CN
F
F
-133
-135
-137
-139
-141
-143
-145
-147
-149
-151
-153
-155
-157
-159
-161
-163
f1 (ppm)

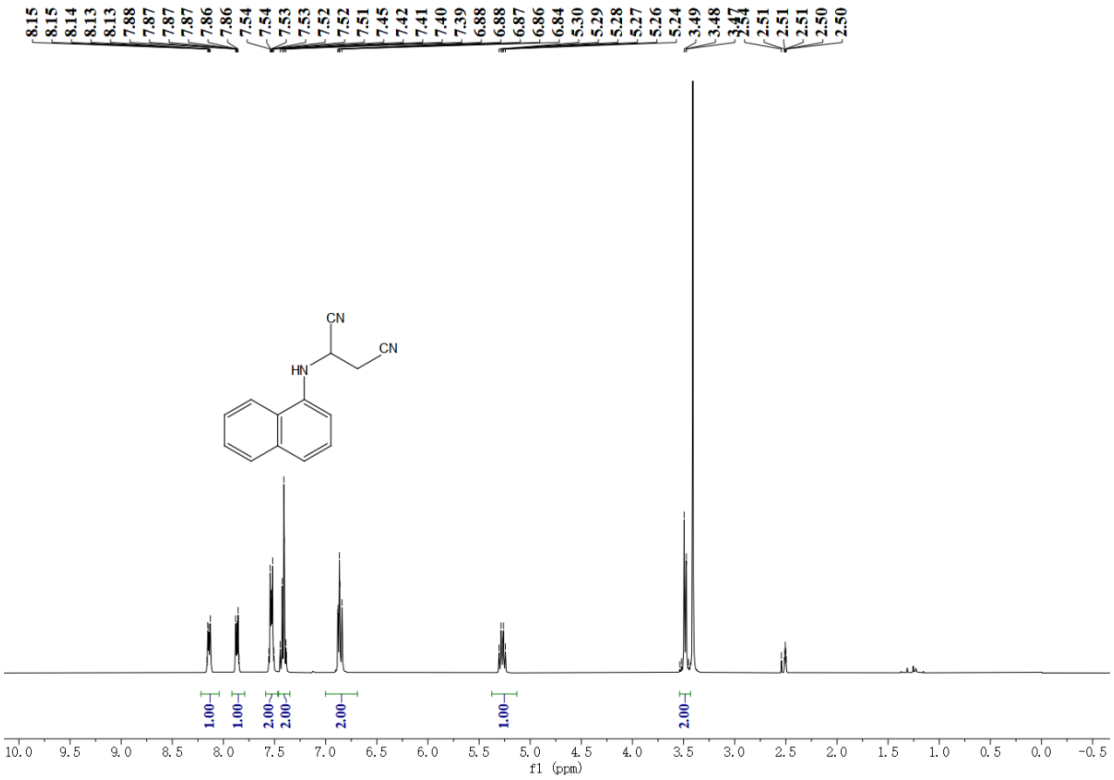
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **3n**

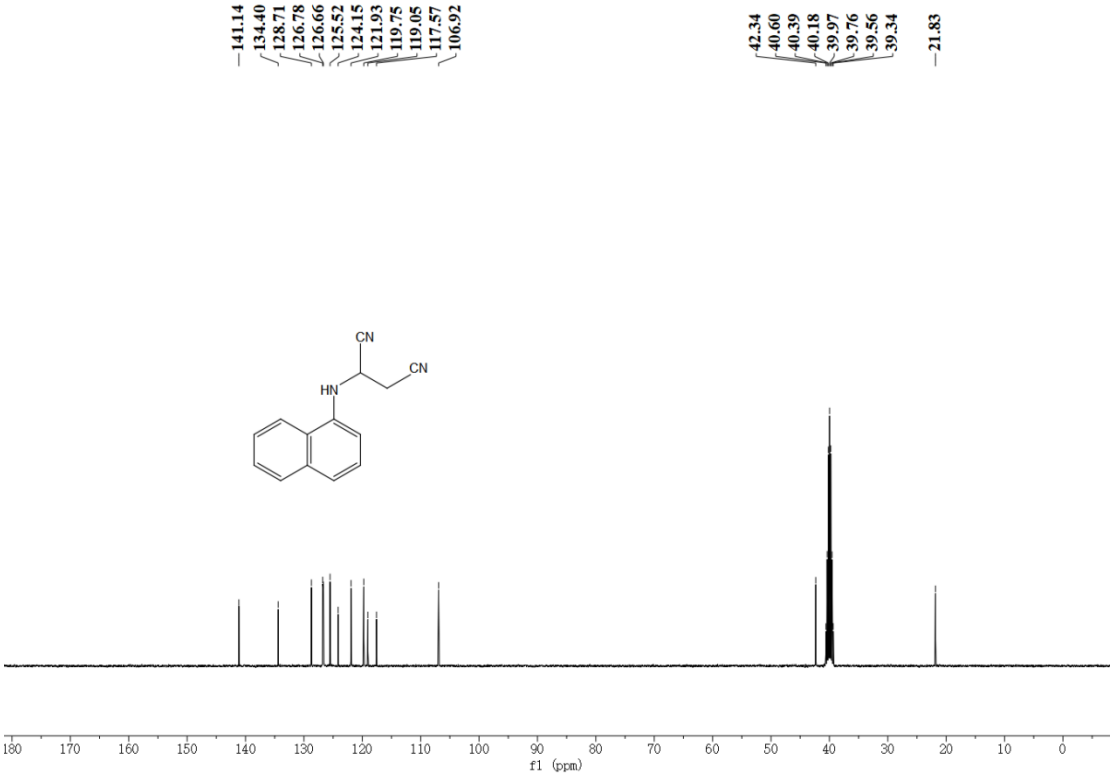




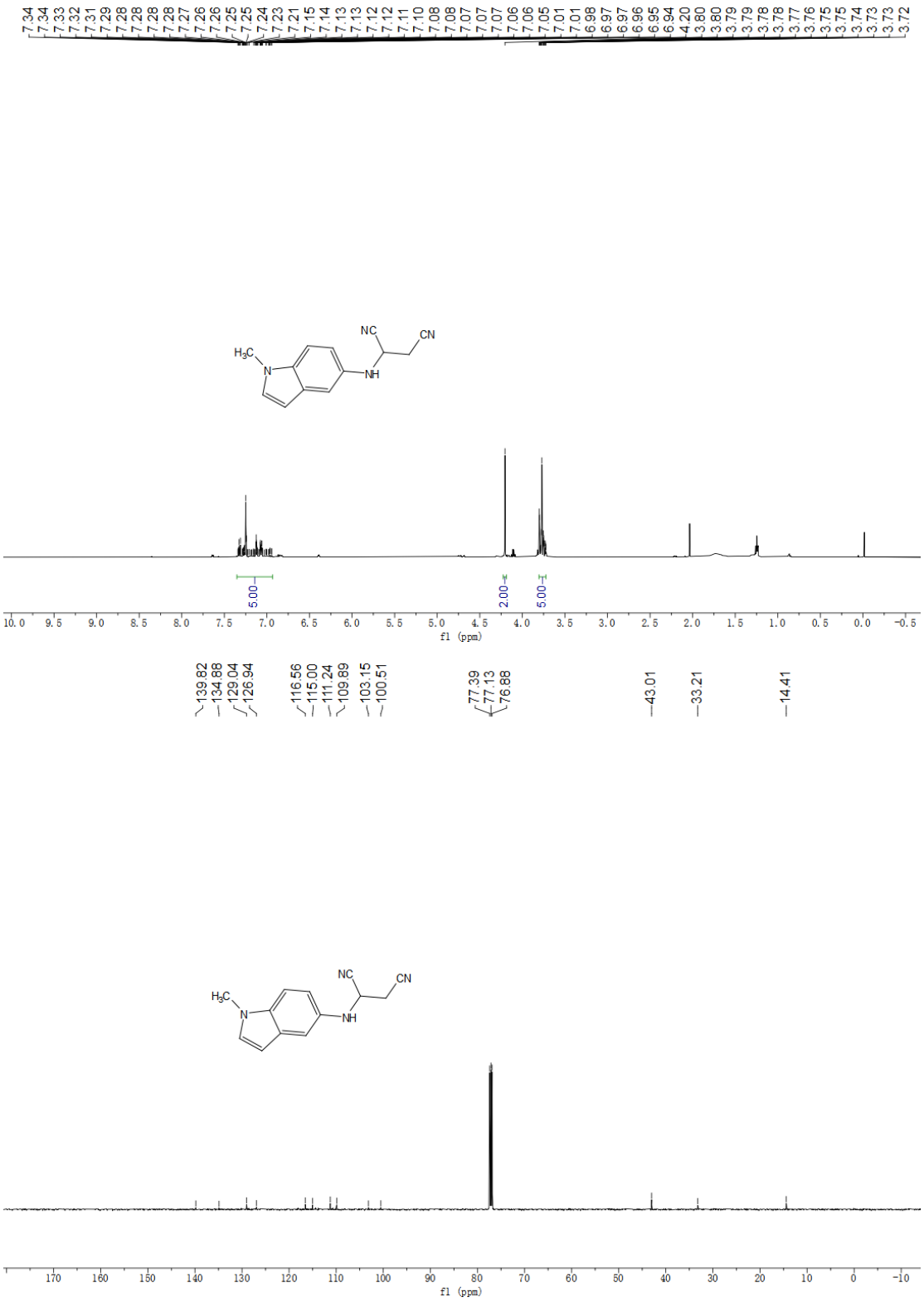


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **3o**

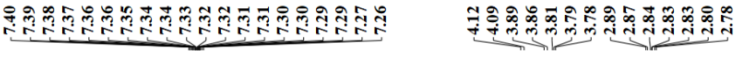


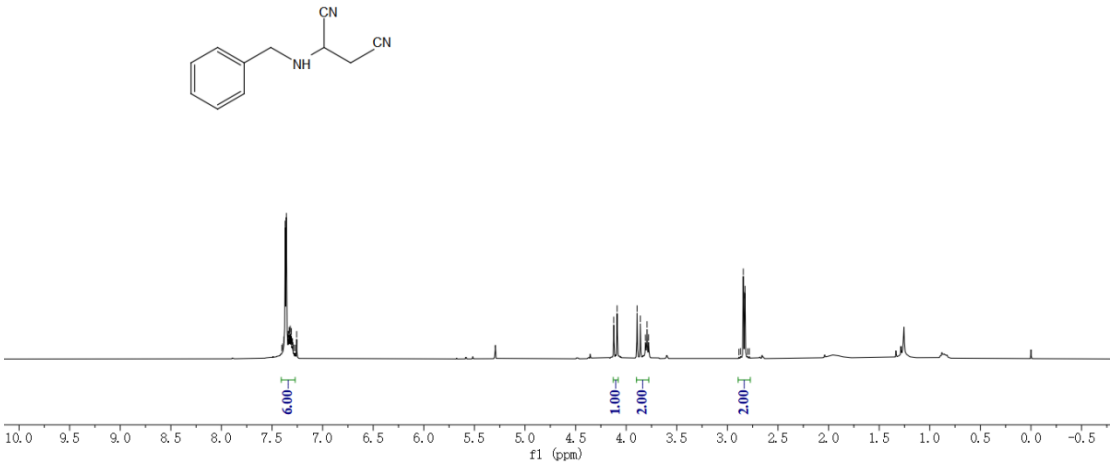


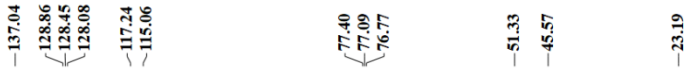
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) for **3p**

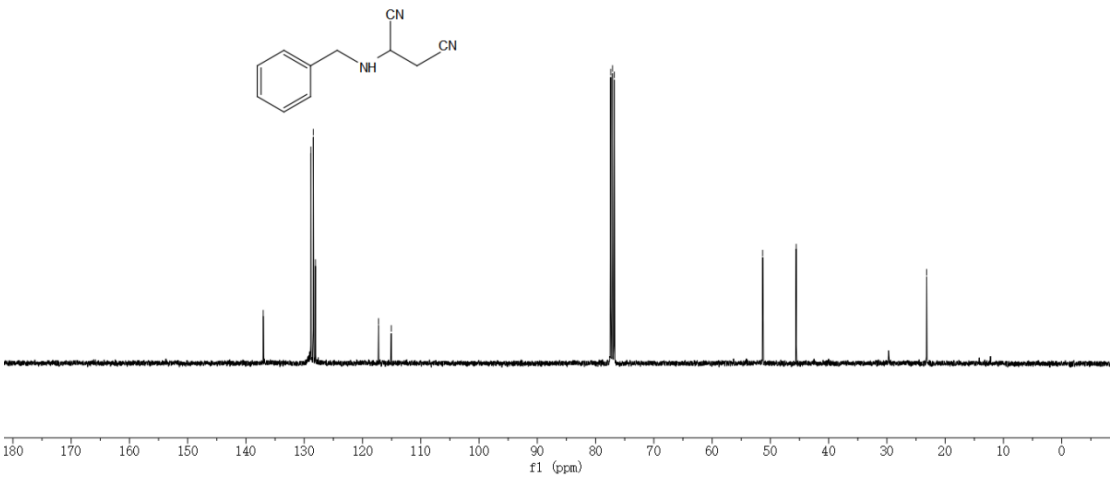


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **3q**

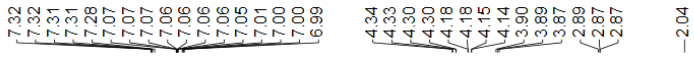


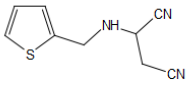


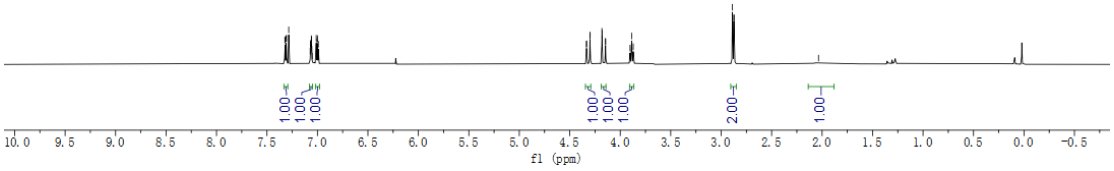


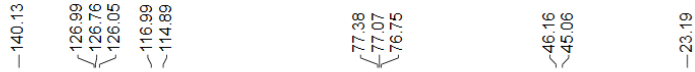


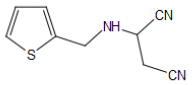
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **3r**

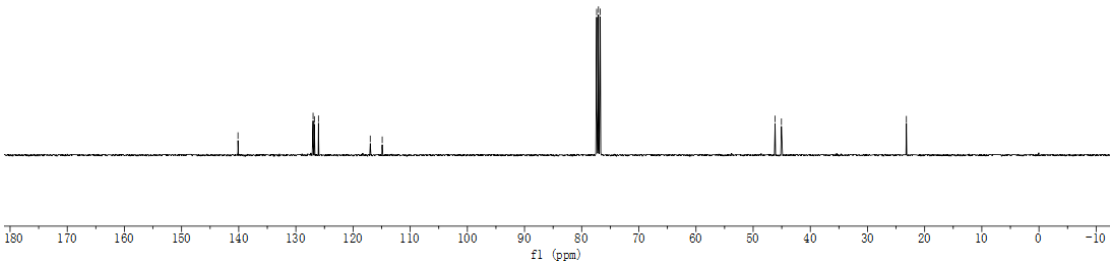




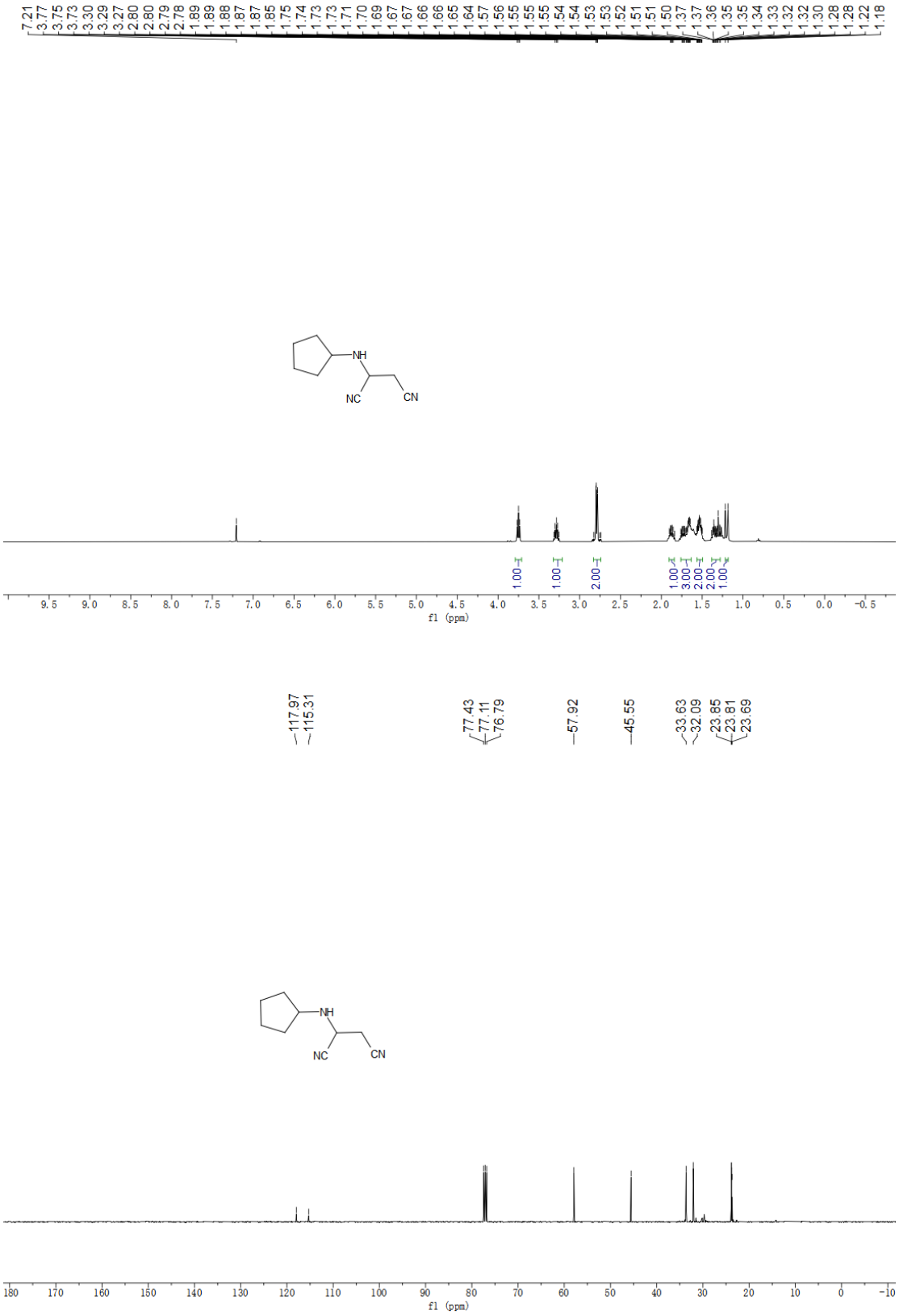




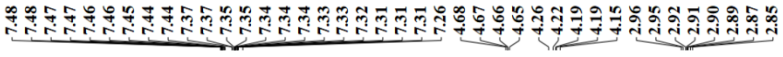


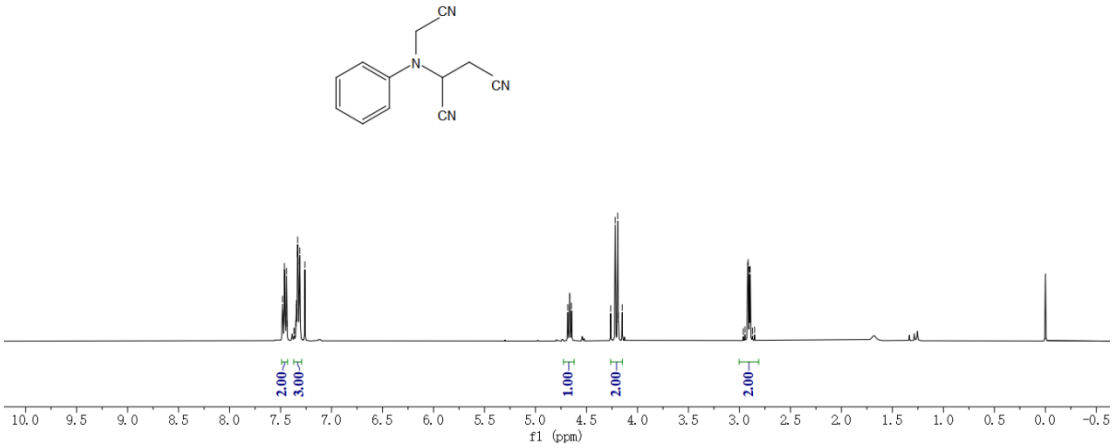


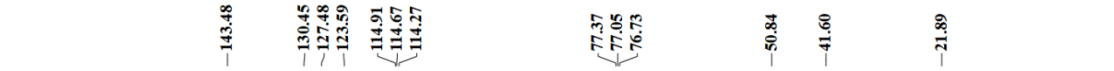
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **3s**

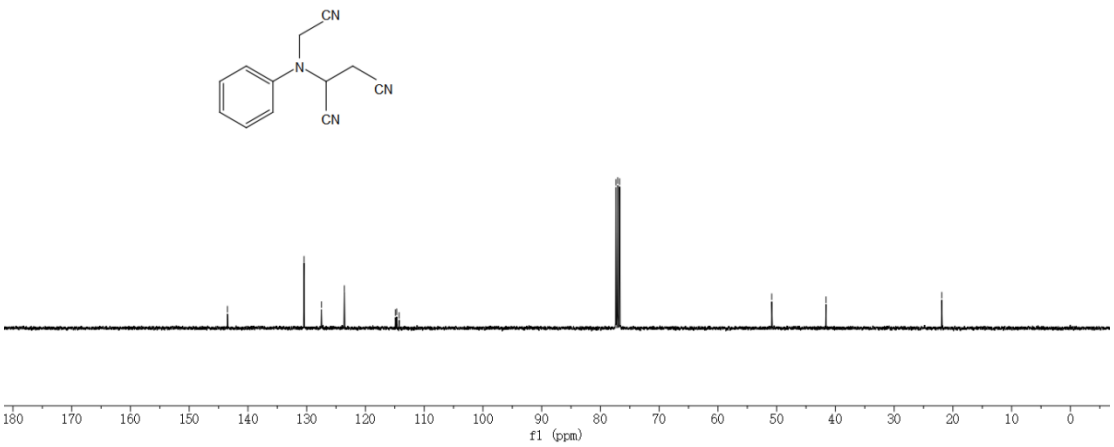


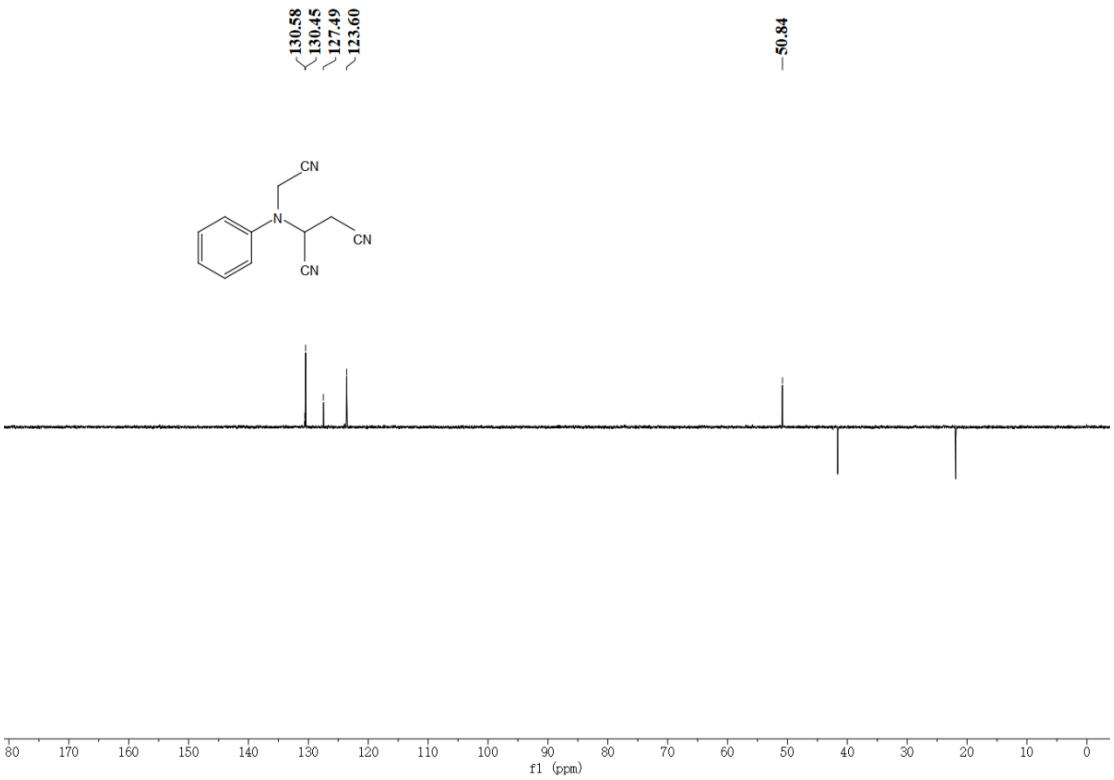
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **5a**



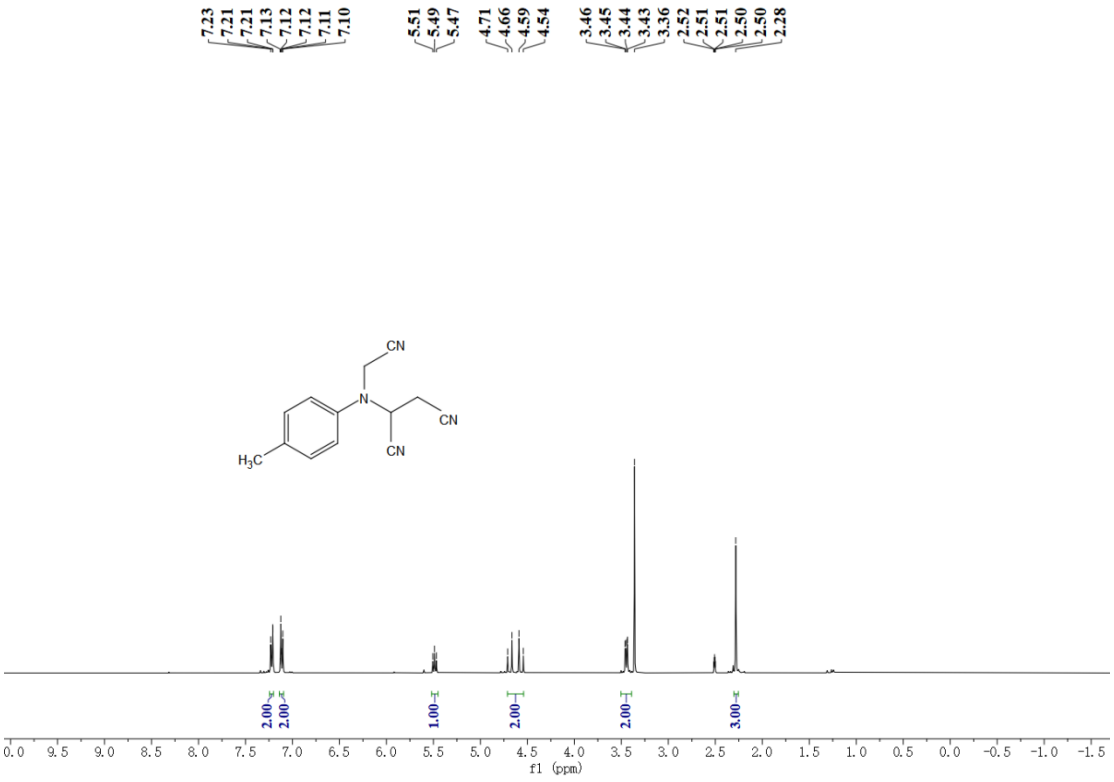


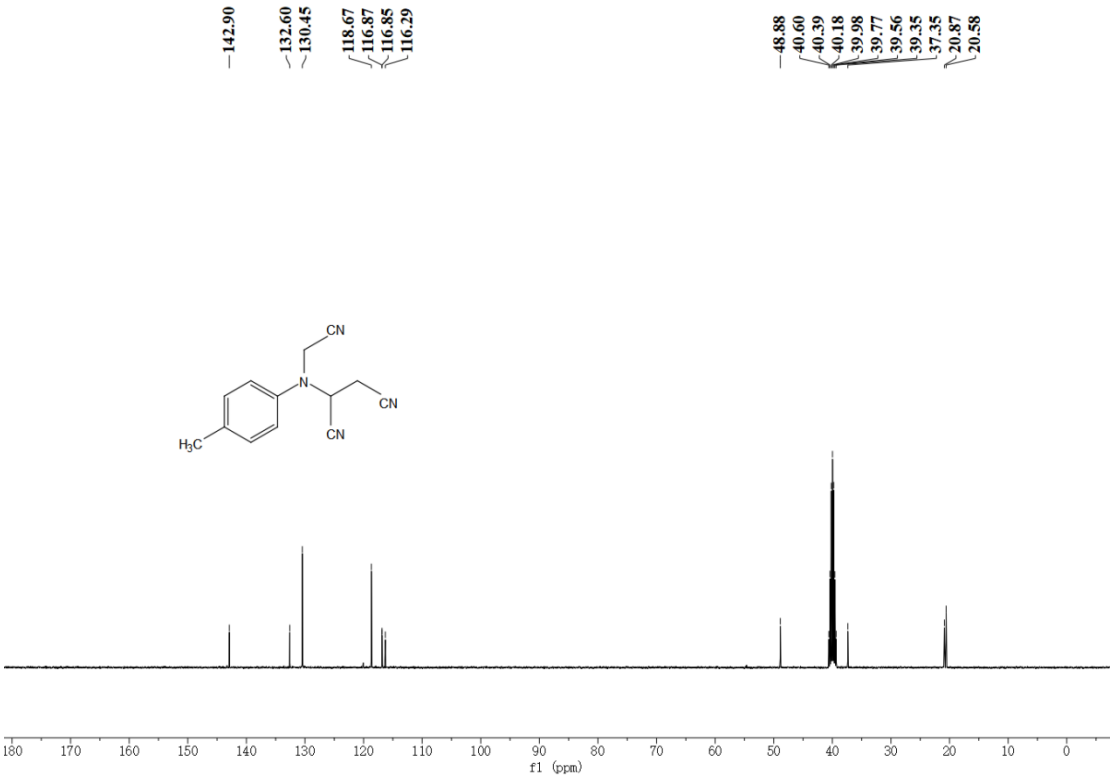




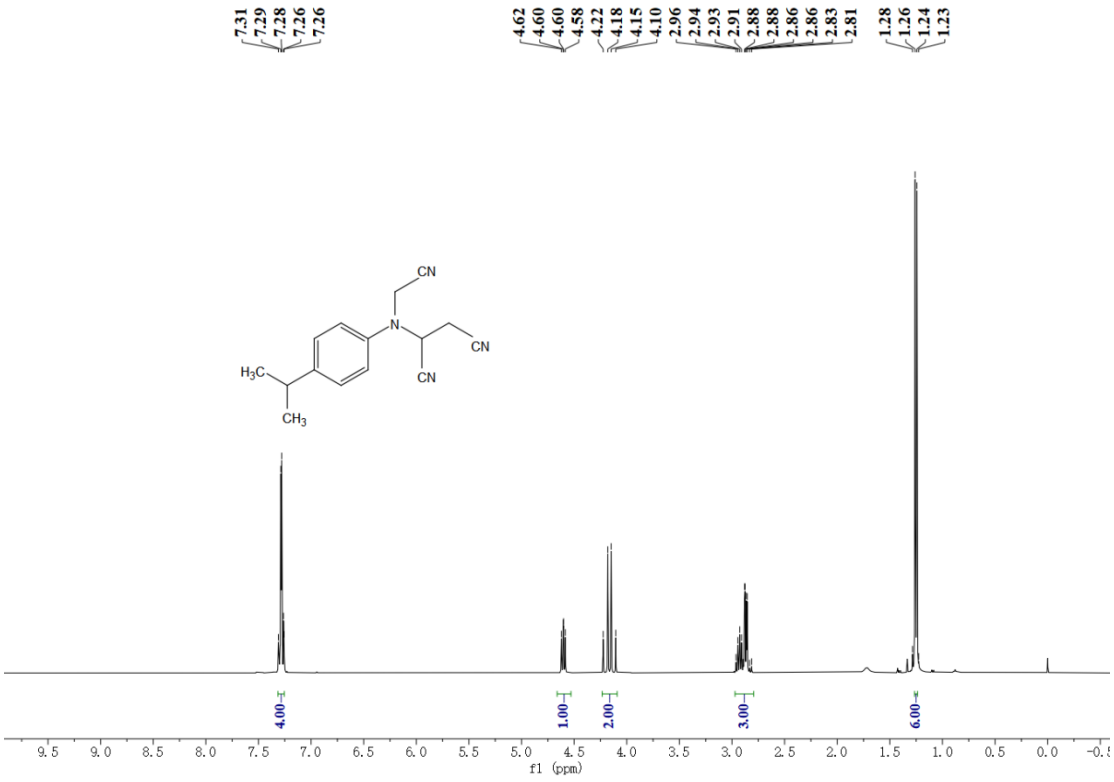

130.58
130.45
127.49
123.60
50.84
CN
N
CN
CN
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

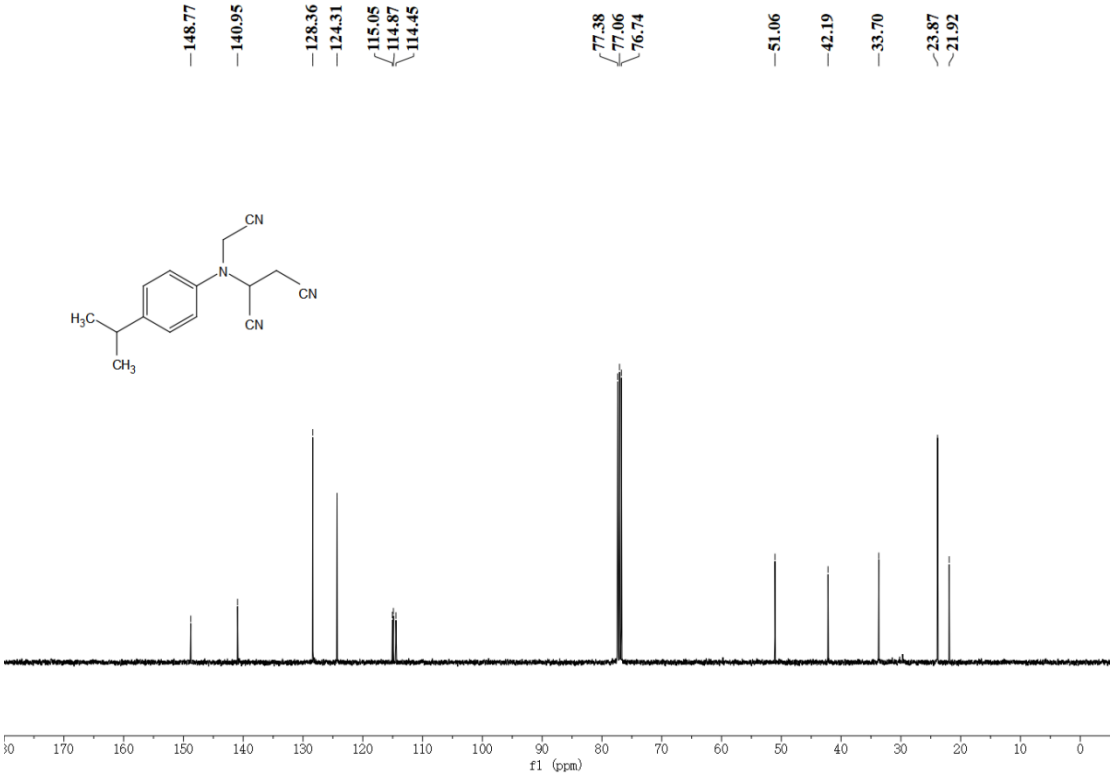
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **5b**



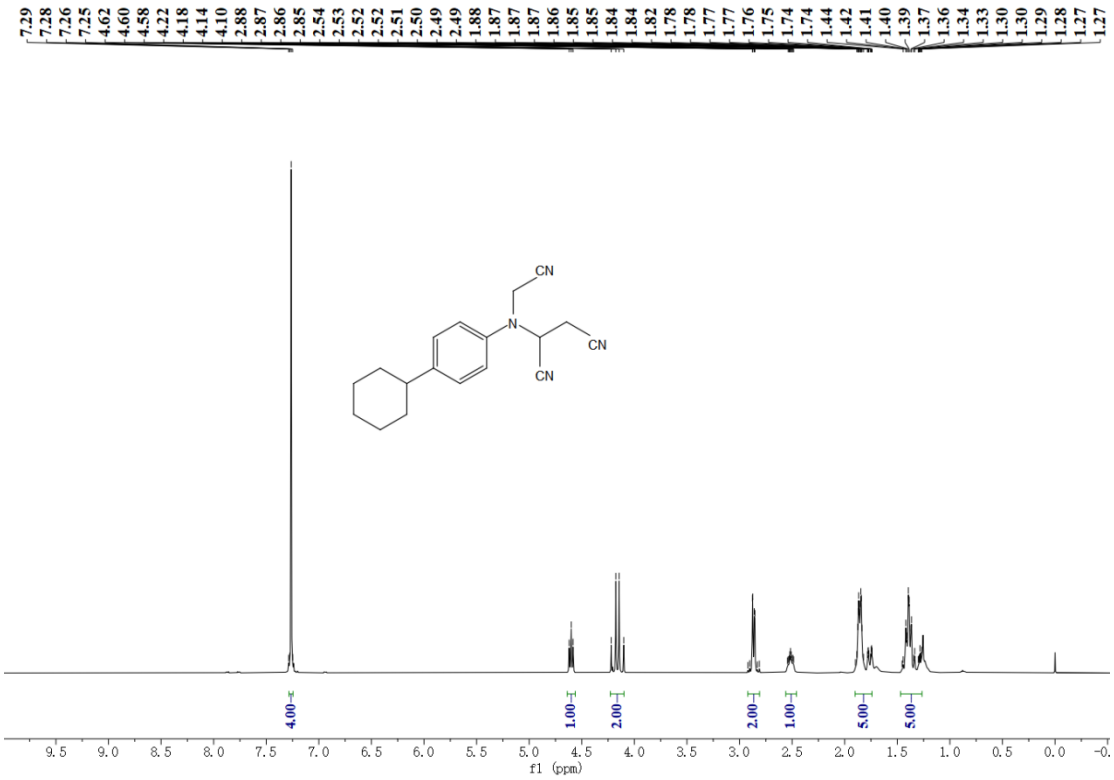


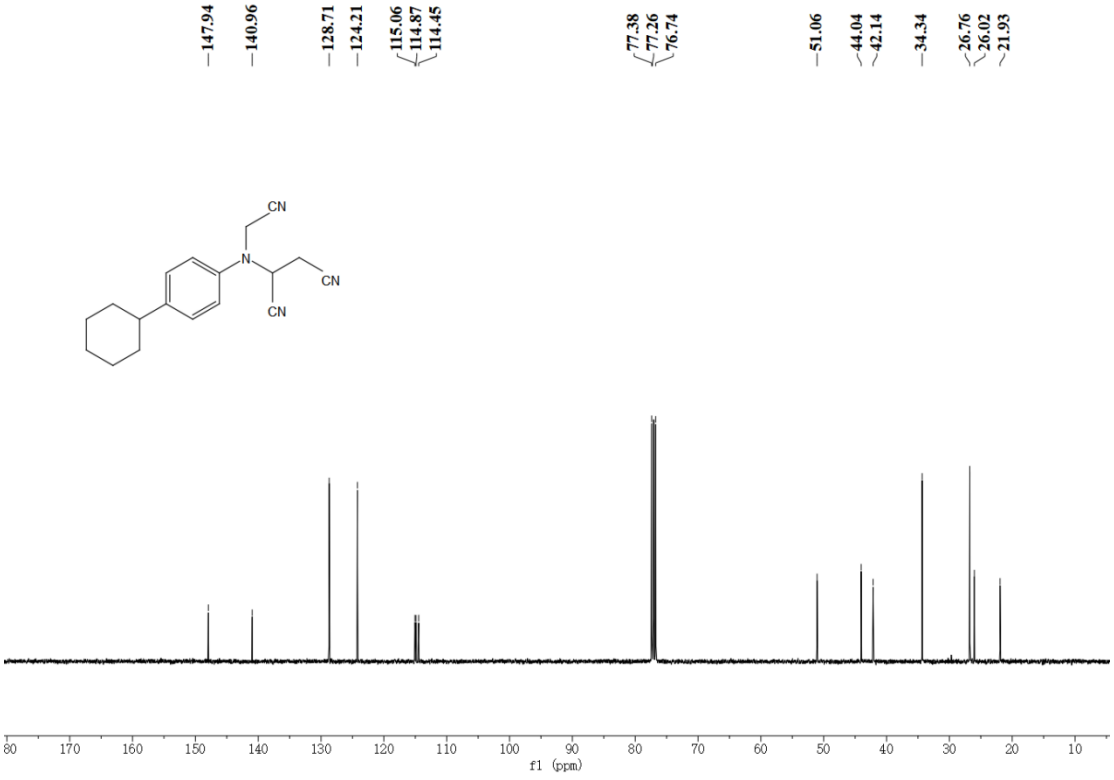
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **5c**



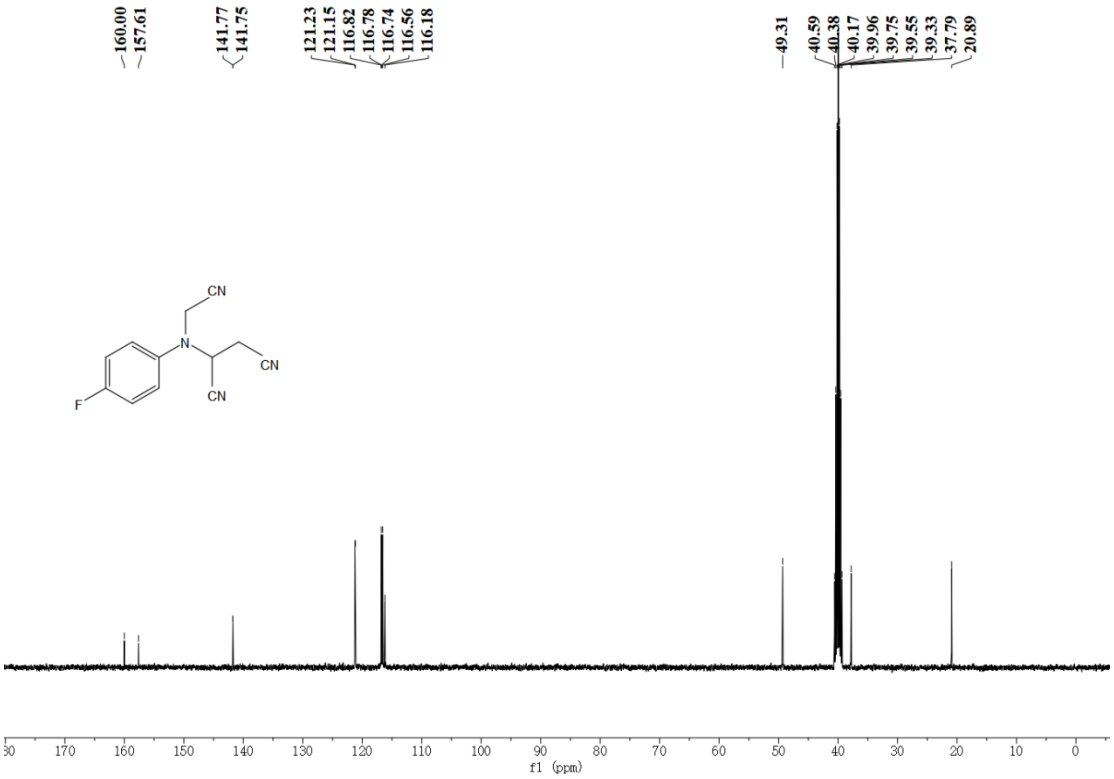


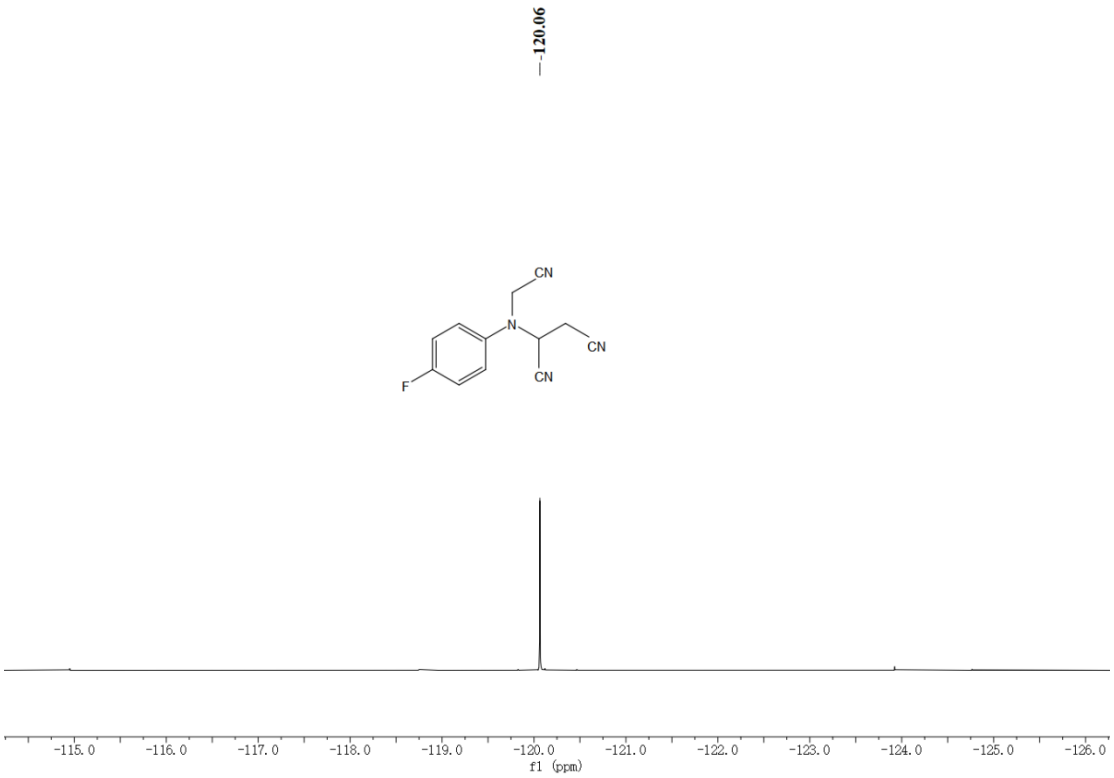
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **5d**



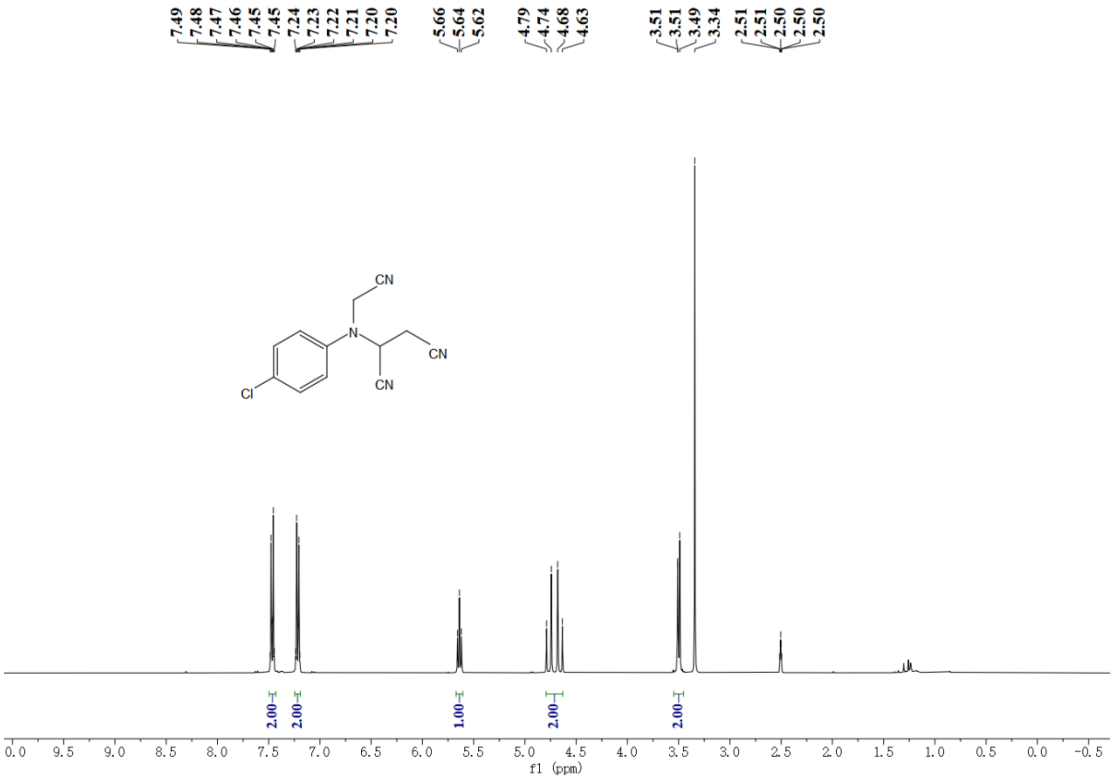


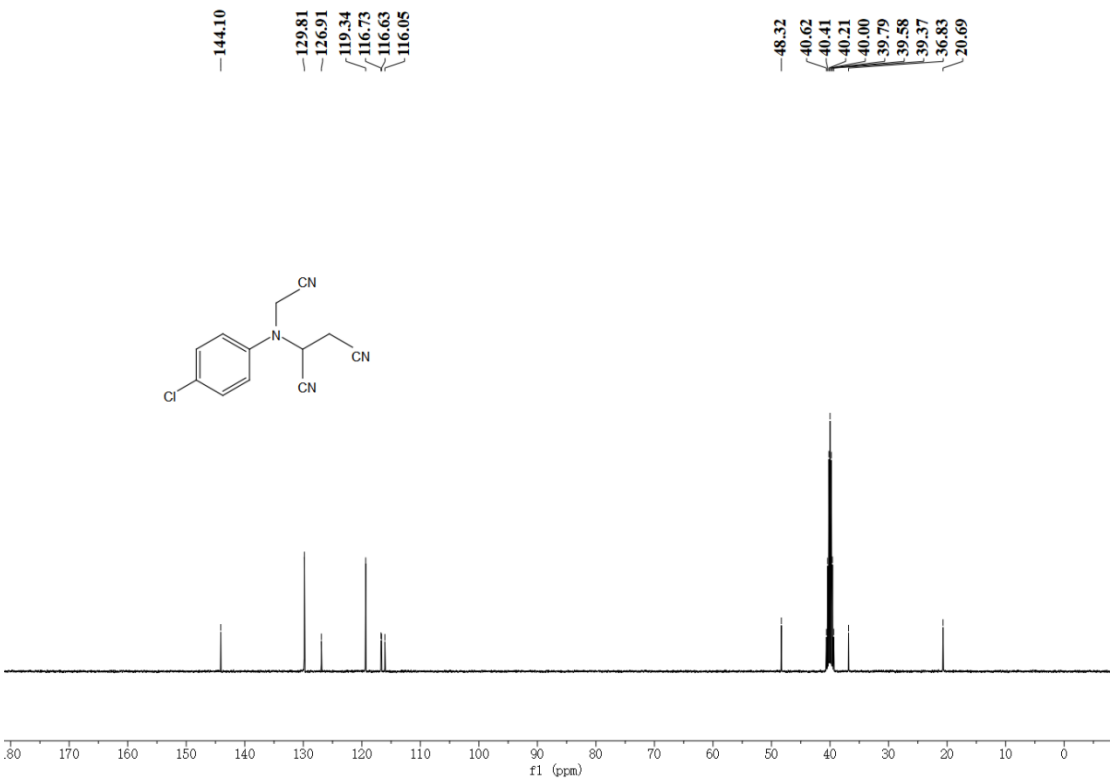
^{1}H NMR (400 MHz, DMSO-d_6, ^{13}C NMR (100 MHz, DMSO-d_6) and ^{19}F NMR (376 MHz, DMSO-d_6) spectra for **5e**



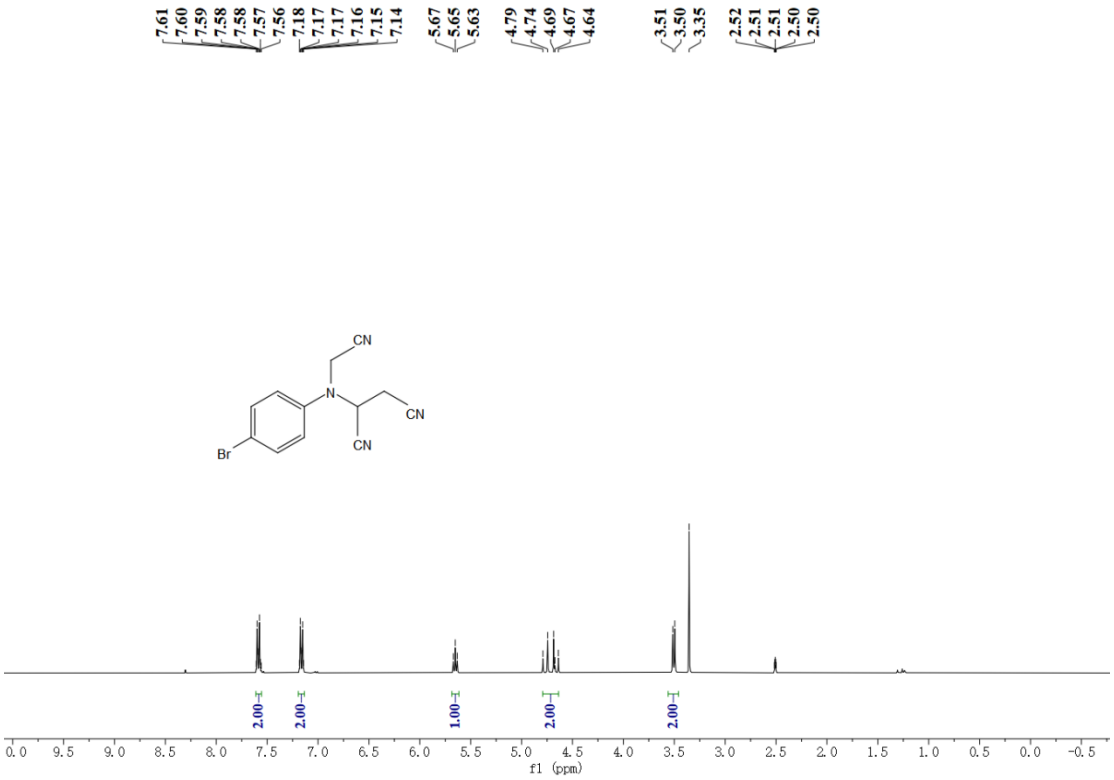

-120.06
CN
N
CN
CN
F
-115.0
-116.0
-117.0
-118.0
-119.0
-120.0
-121.0
-122.0
-123.0
-124.0
-125.0
-126.0
f1 (ppm)

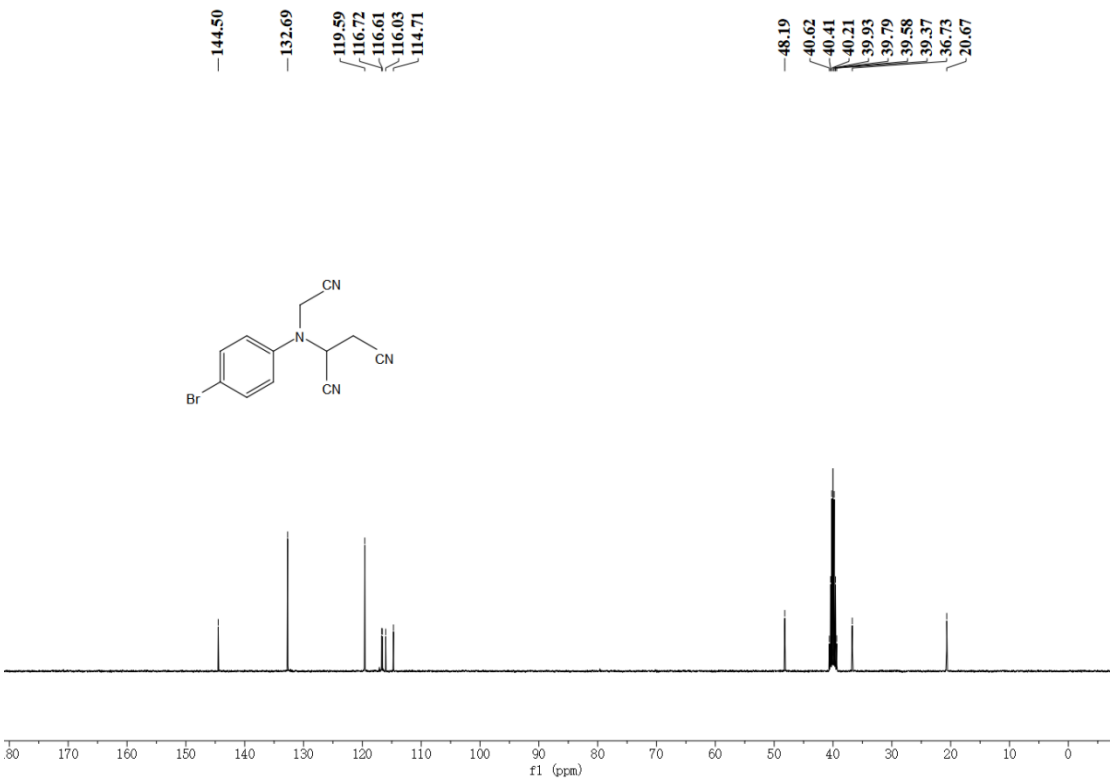
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **5f**



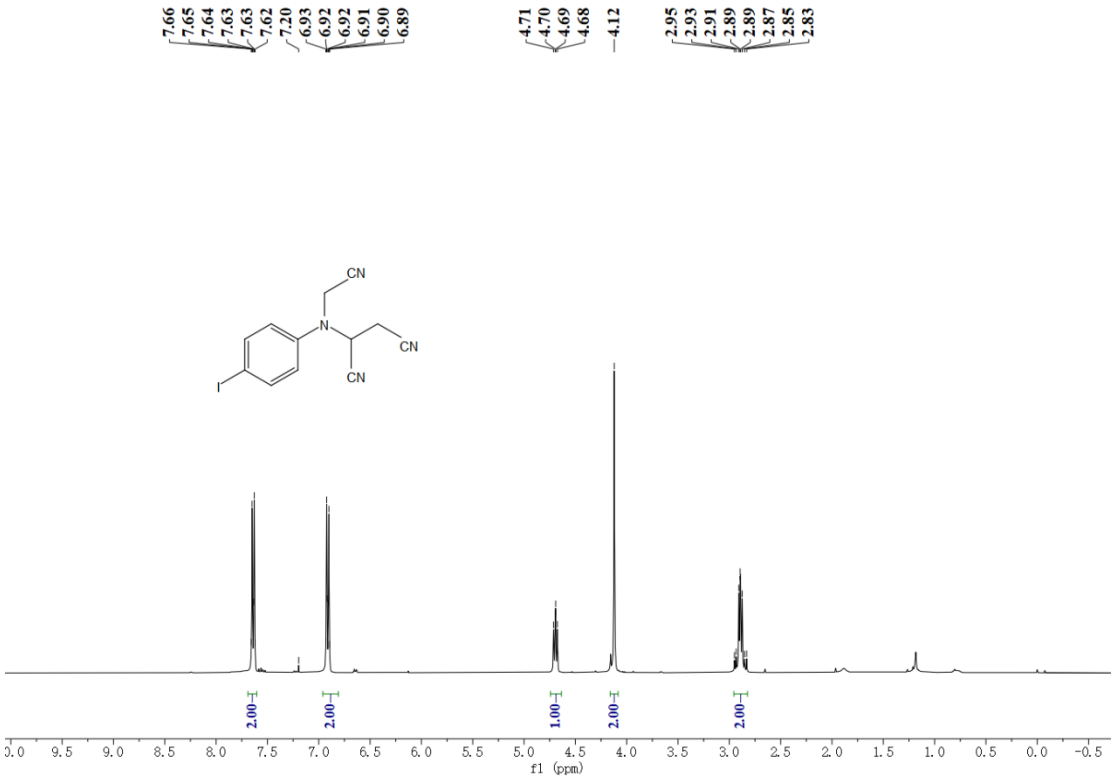


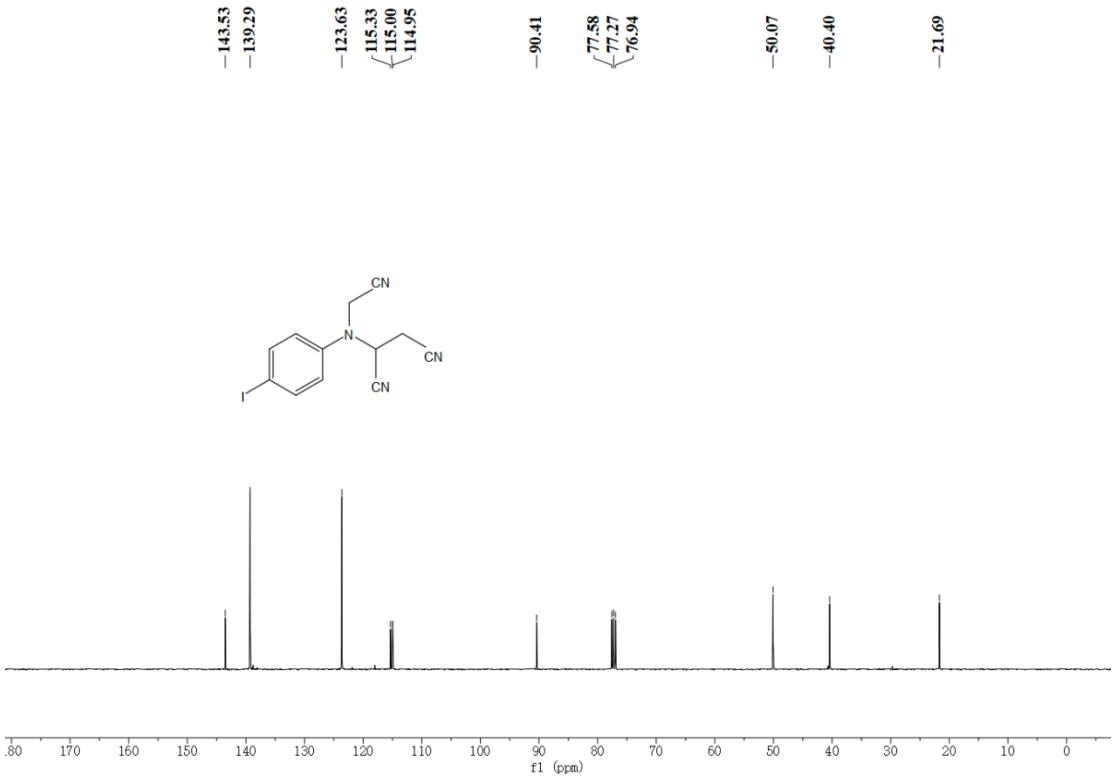
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **5g**



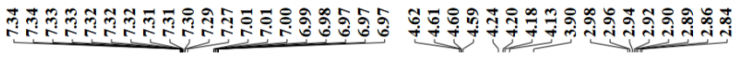


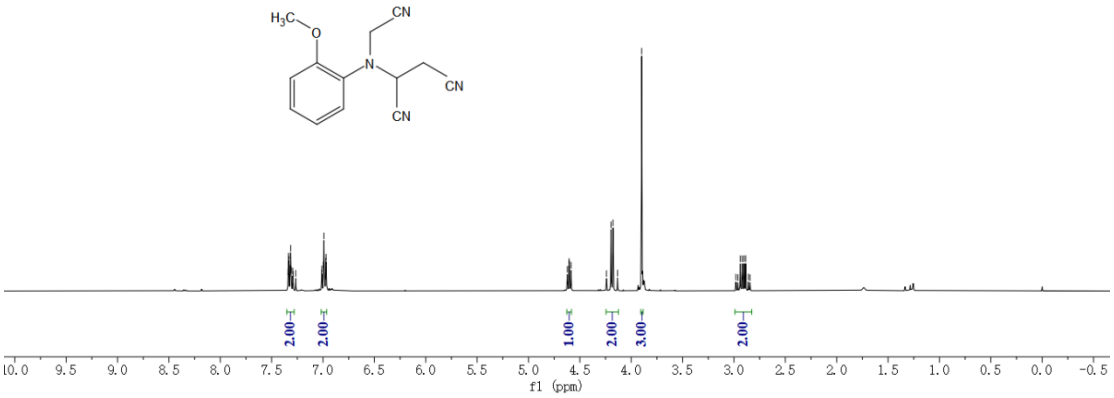
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **5h**

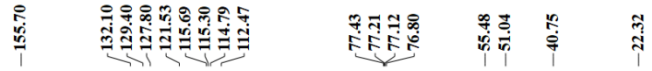


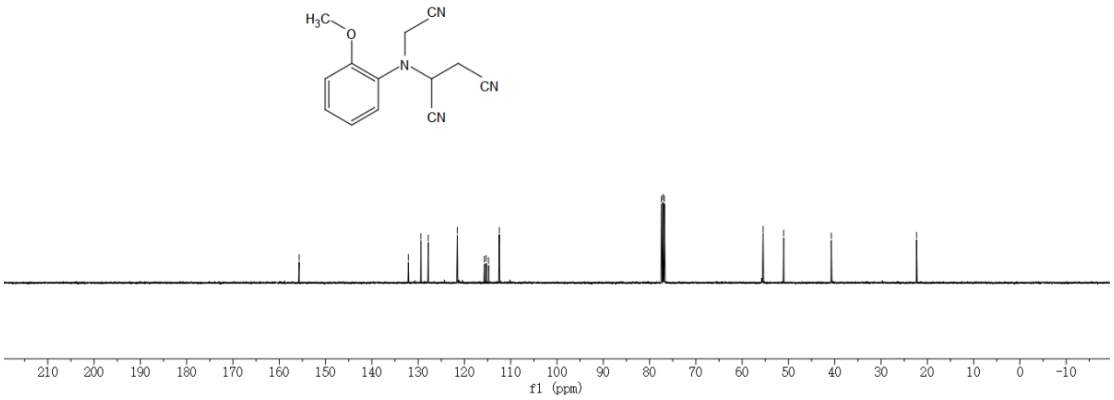


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **5k**

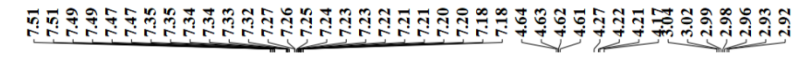


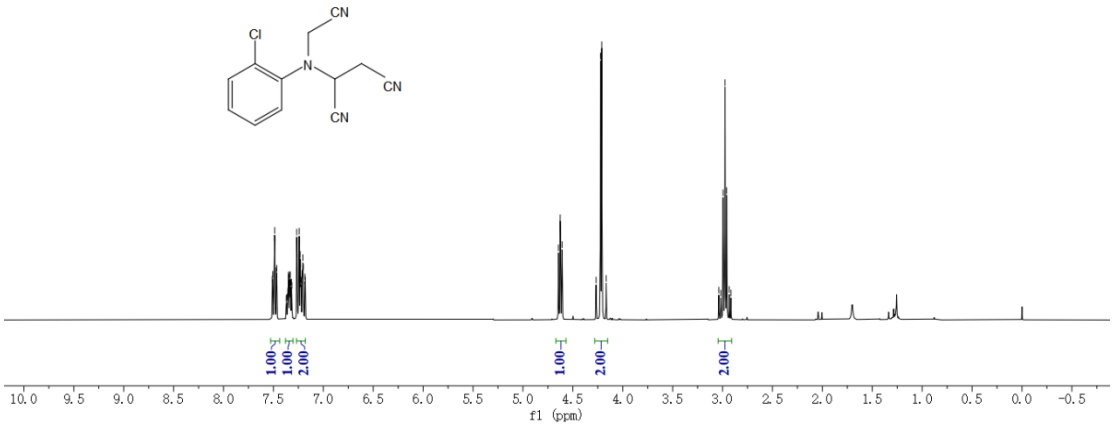


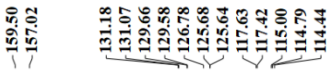


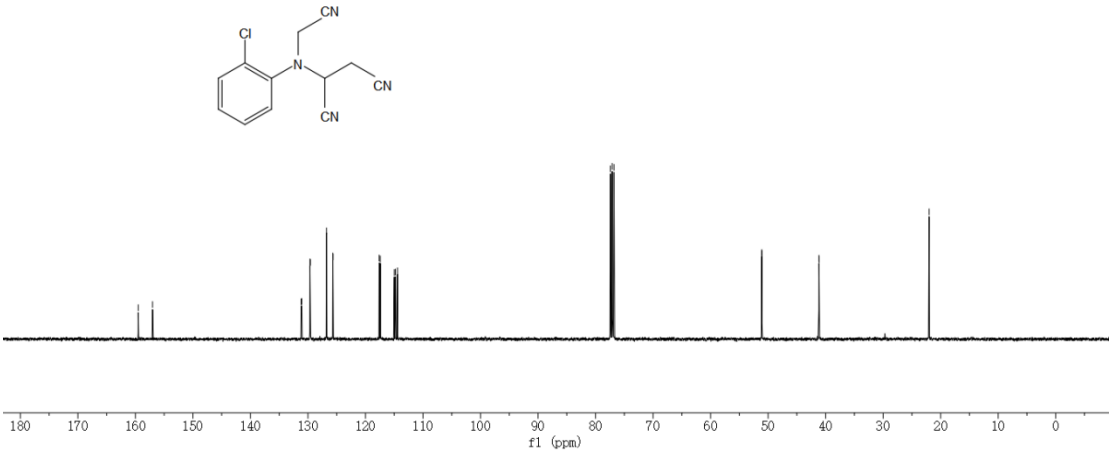


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for **5l**

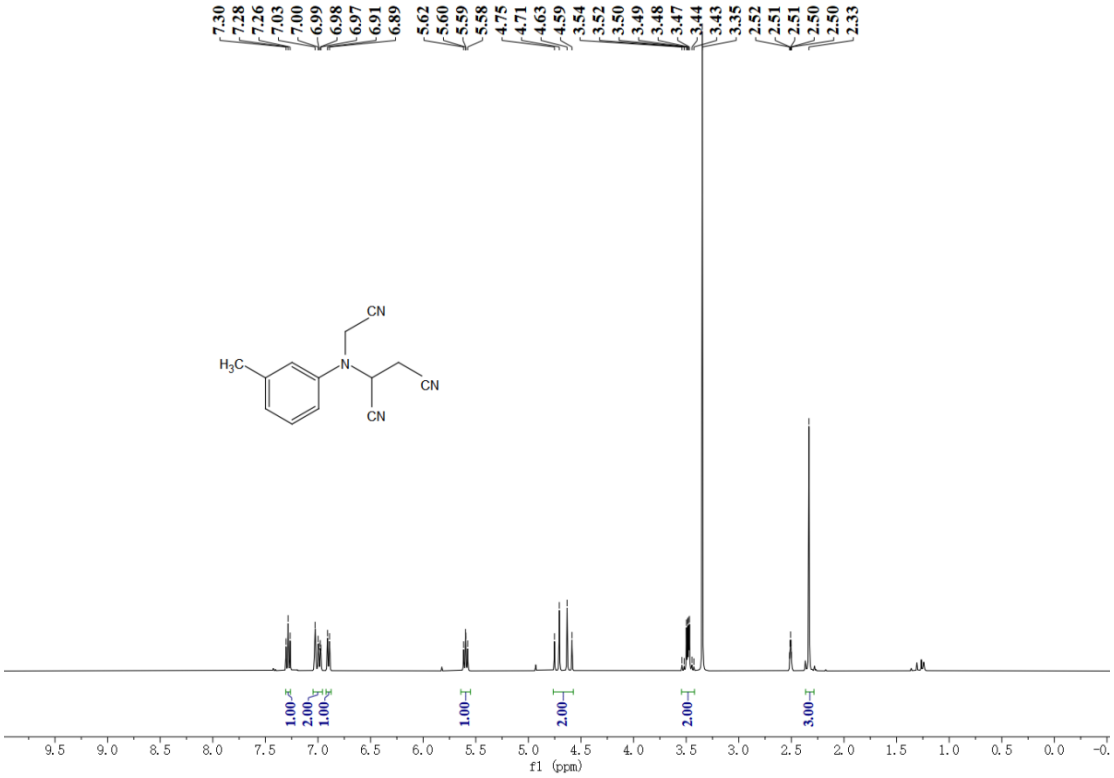


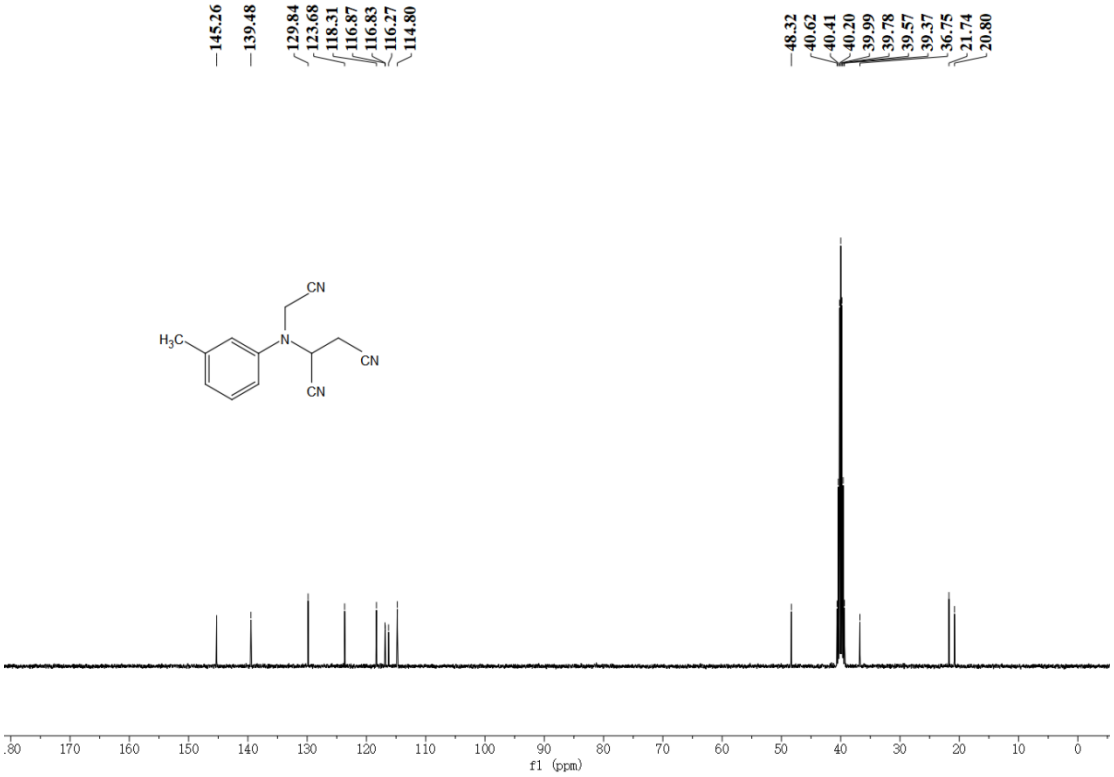




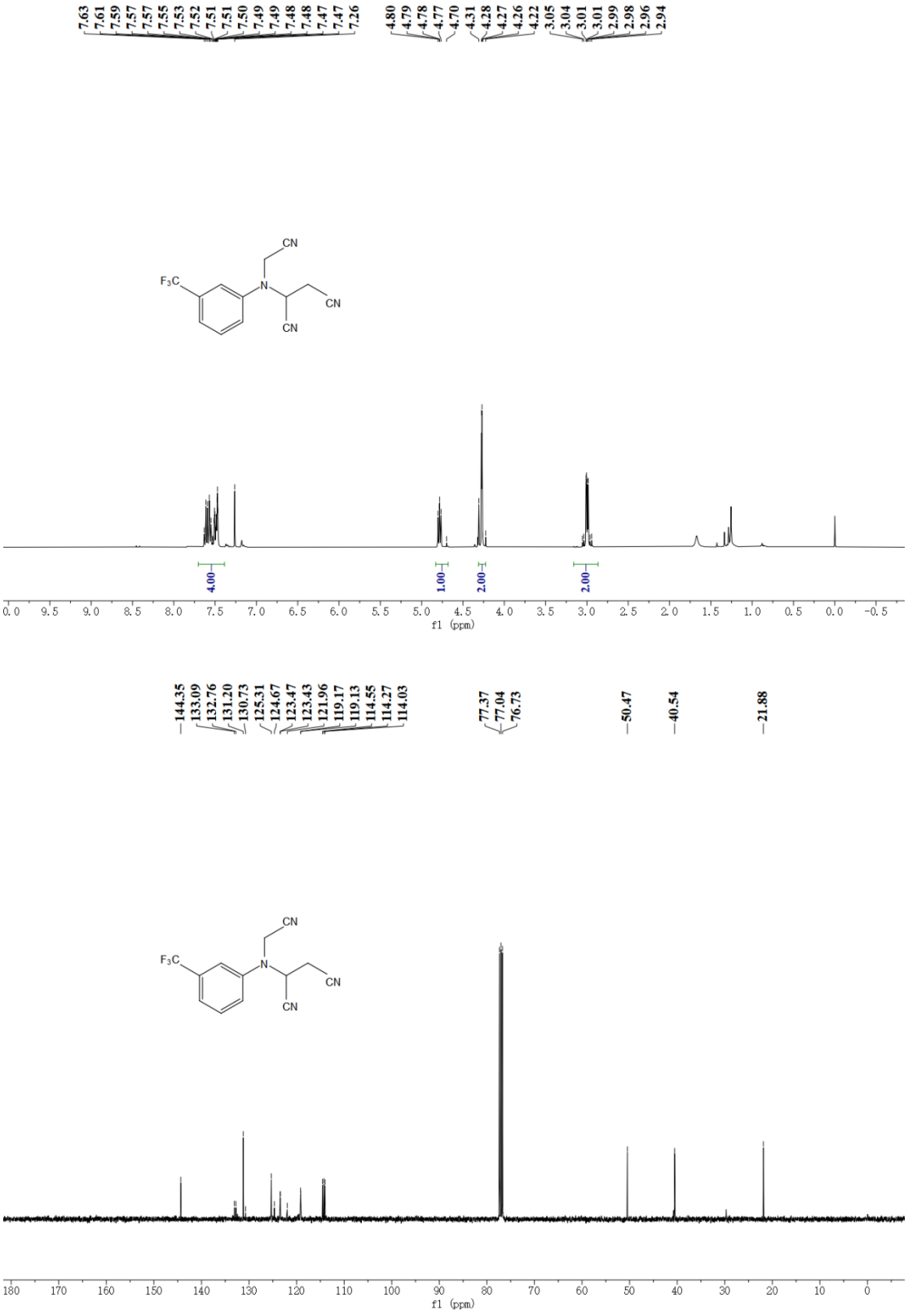


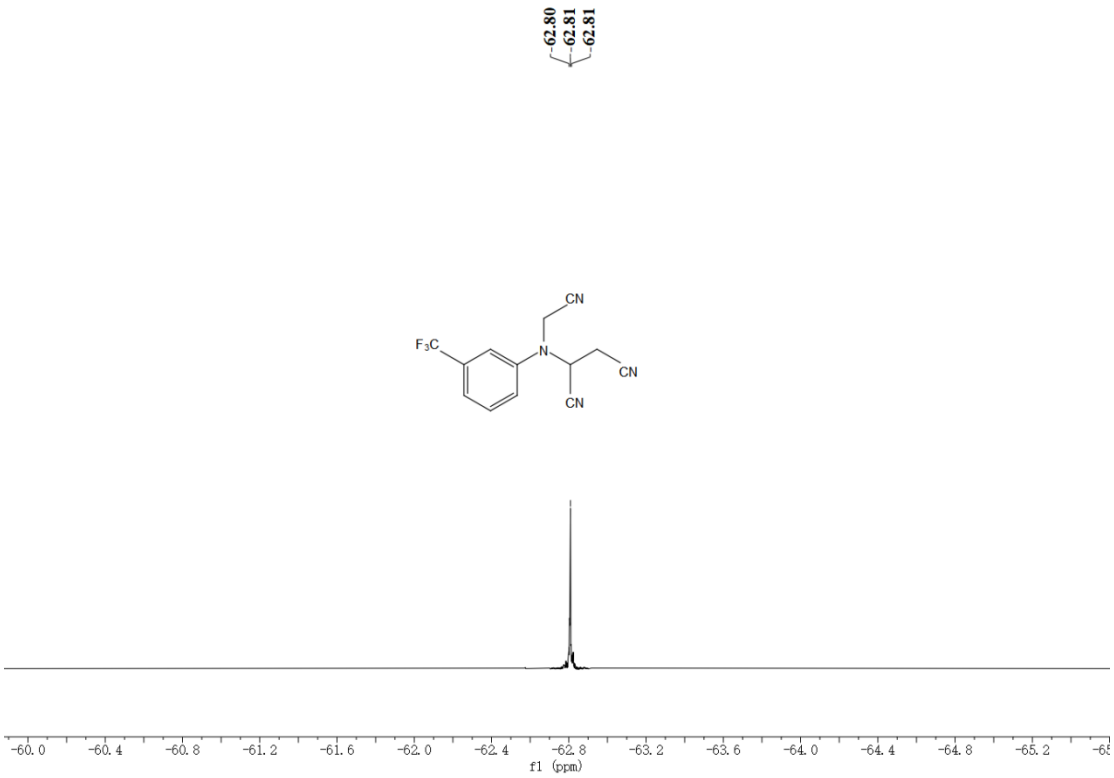
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO-d_6) for **5m**



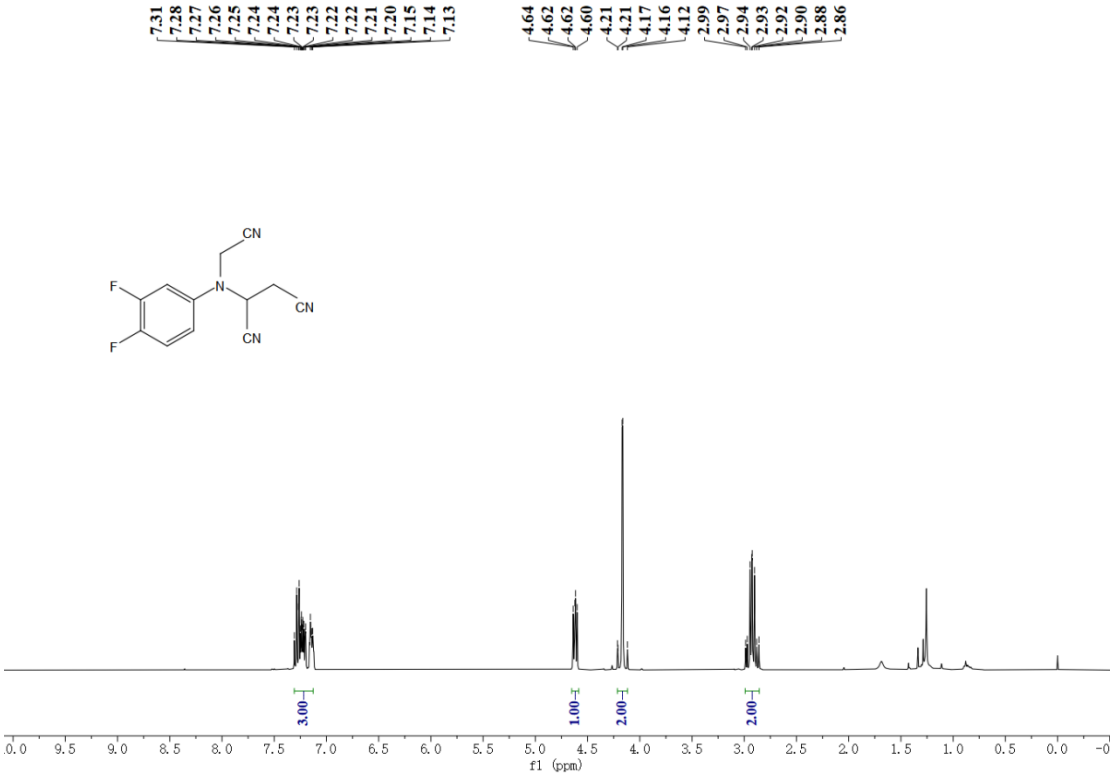


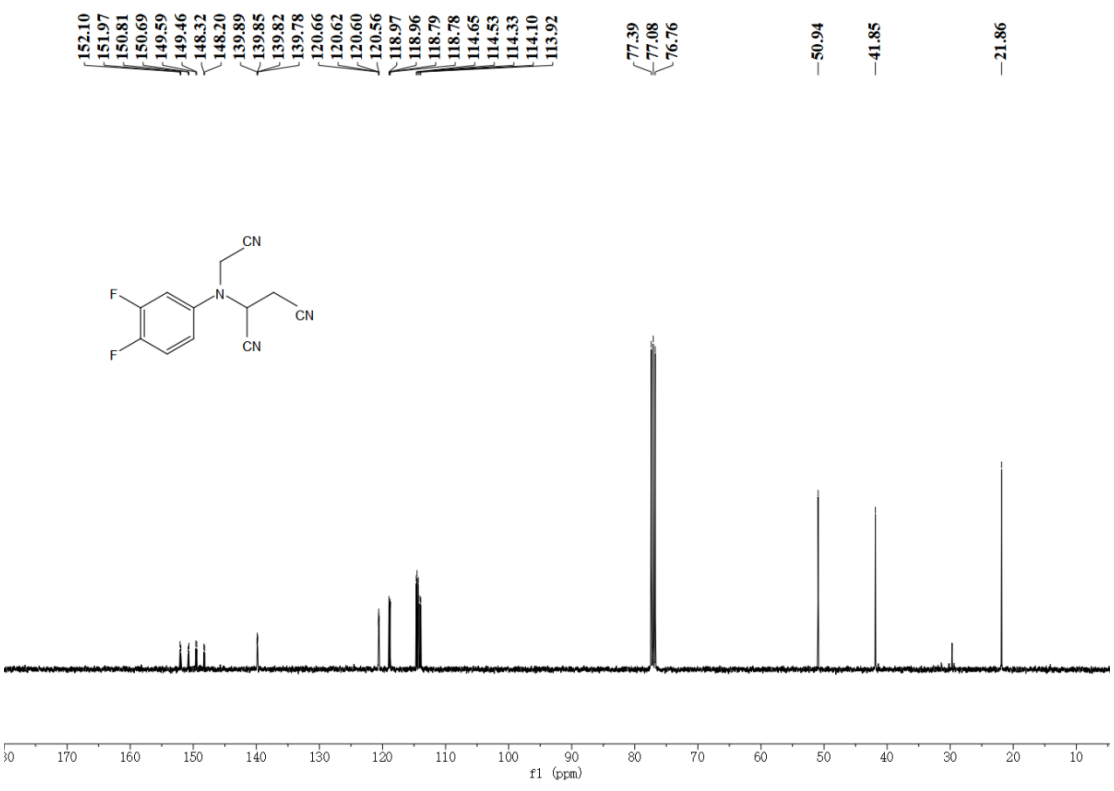
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra for **5n**

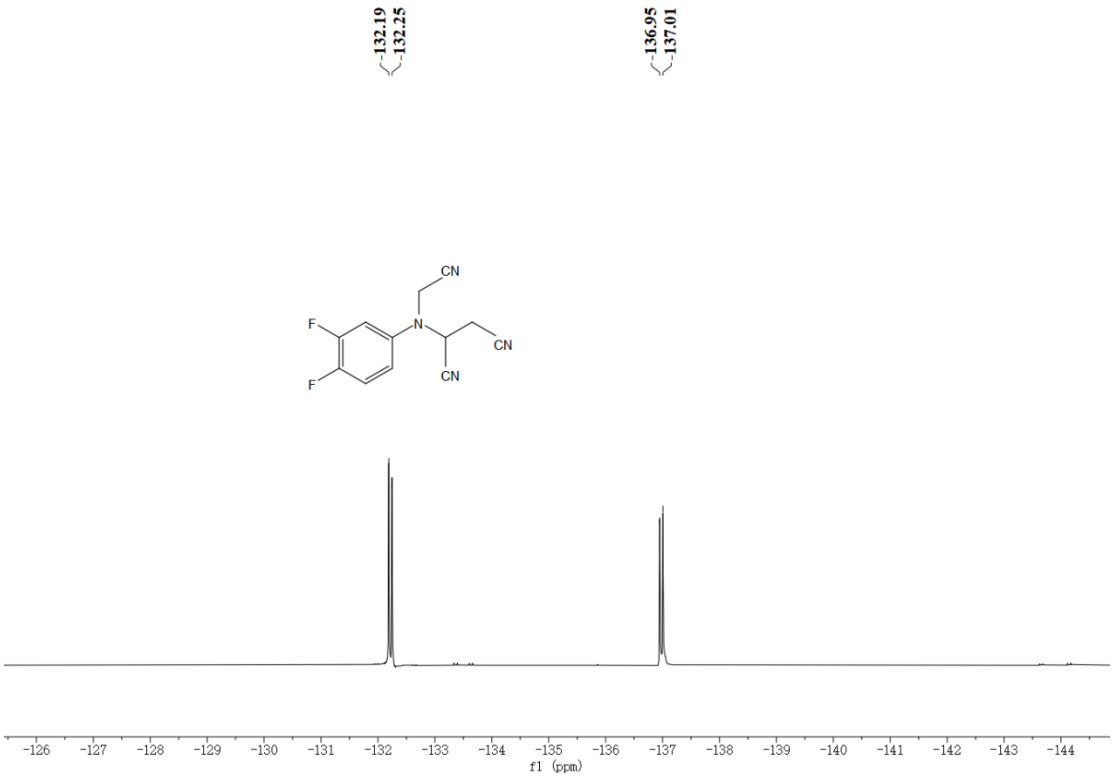



-62.80
-62.81
-62.81
CN
F3C
N
CN
CN
-60.0
-60.4
-60.8
-61.2
-61.6
-62.0
-62.4
-62.8
-63.2
-63.6
-64.0
-64.4
-64.8
-65.2
f1 (ppm)

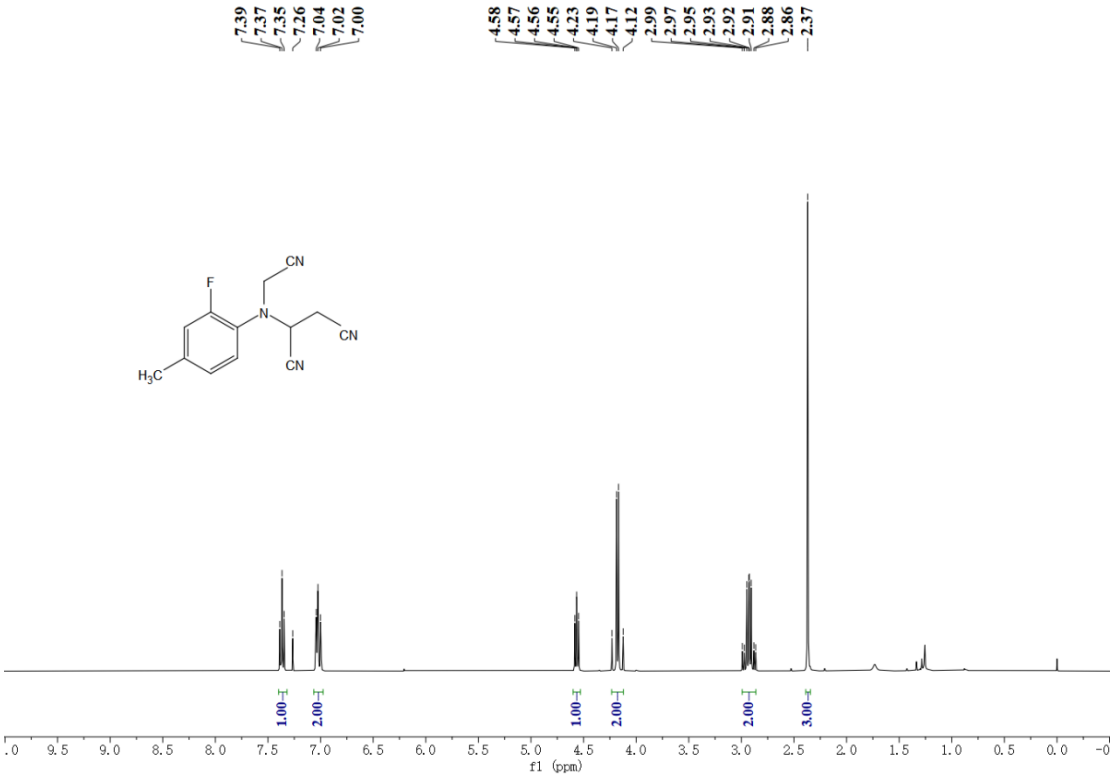
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra for **5o**

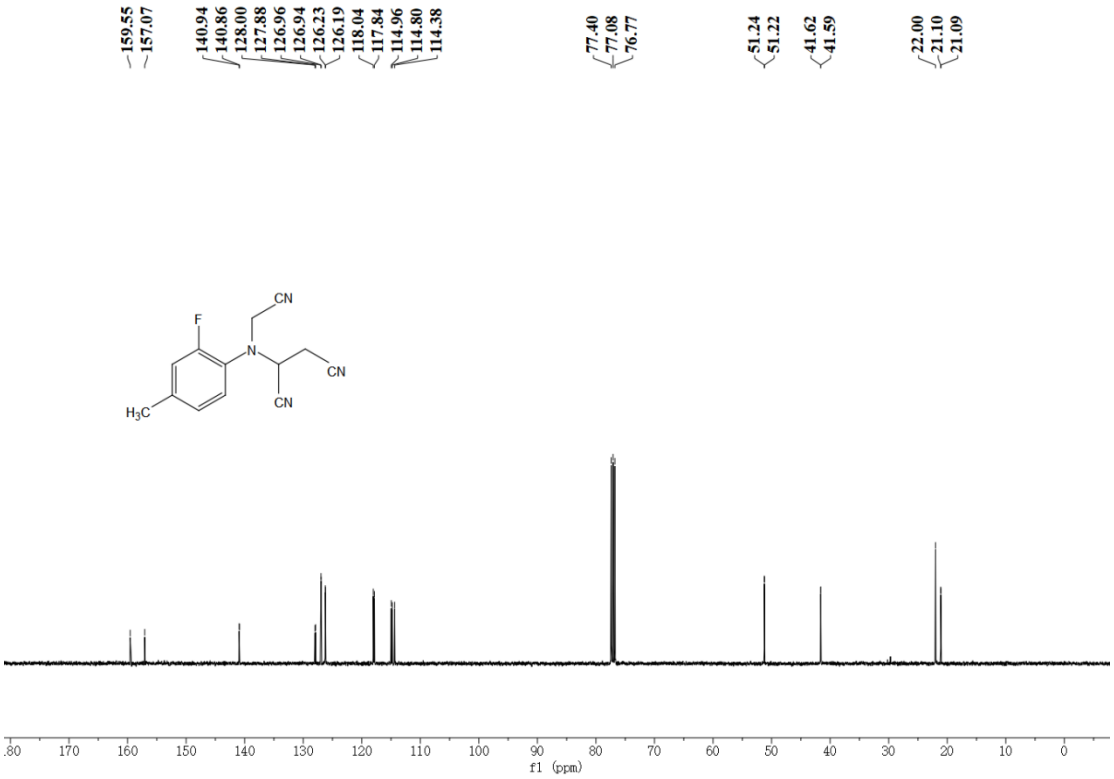


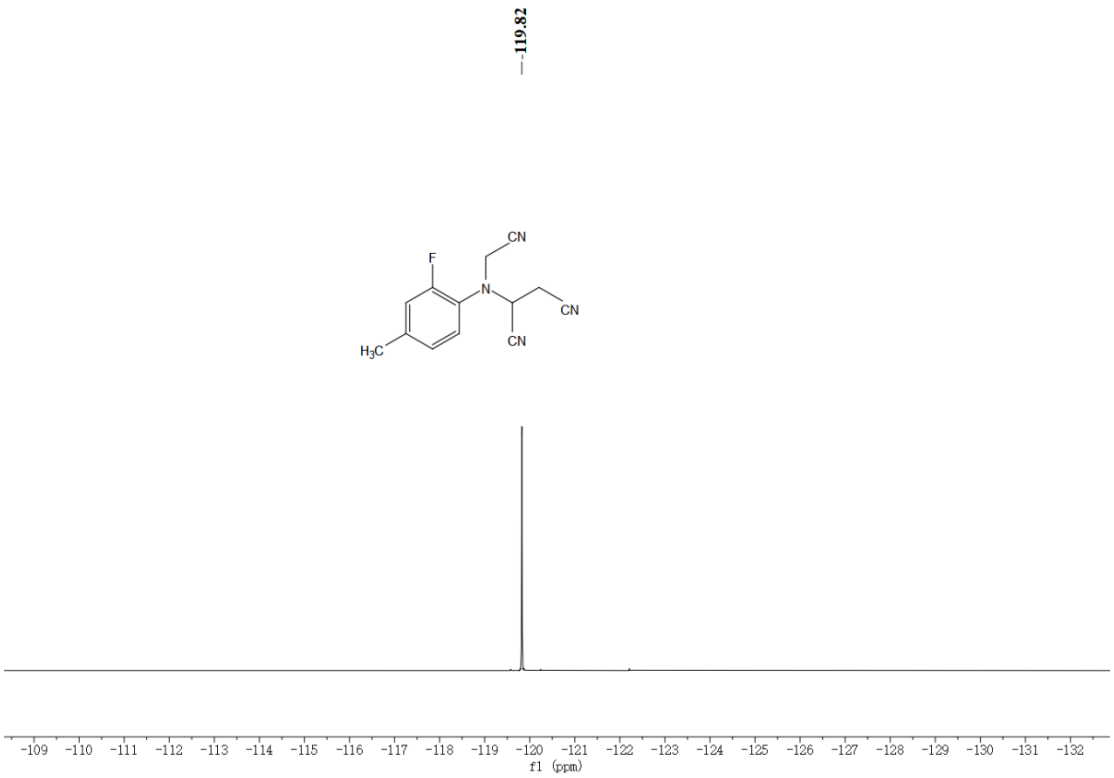



-132.19
-132.25
-136.95
-137.01
CN
F
N
CN
CN
F
-126
-127
-128
-129
-130
-131
-132
-133
-134
-135
-136
-137
-138
-139
-140
-141
-142
-143
-144
f1 (ppm)

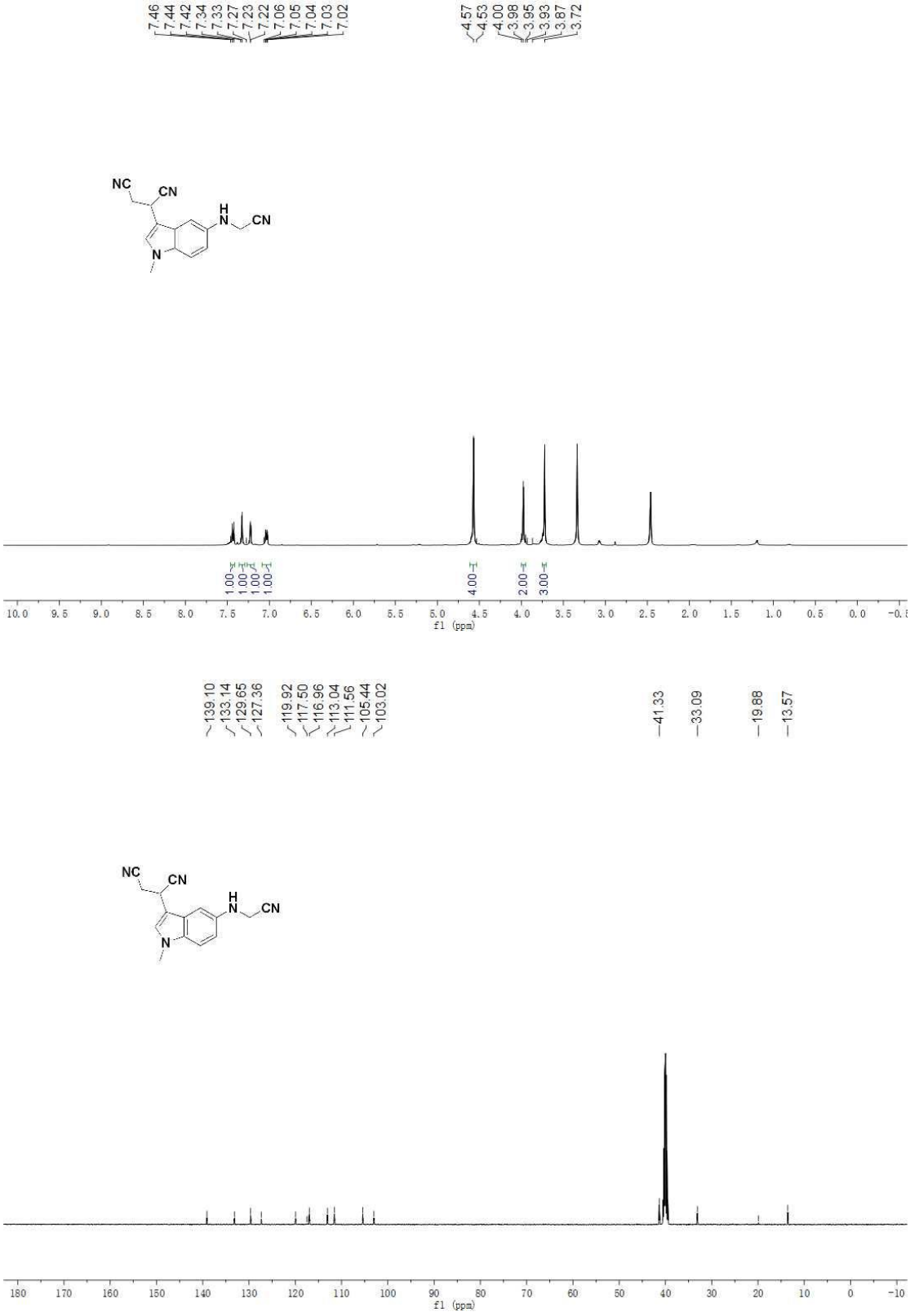
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra for **5p**



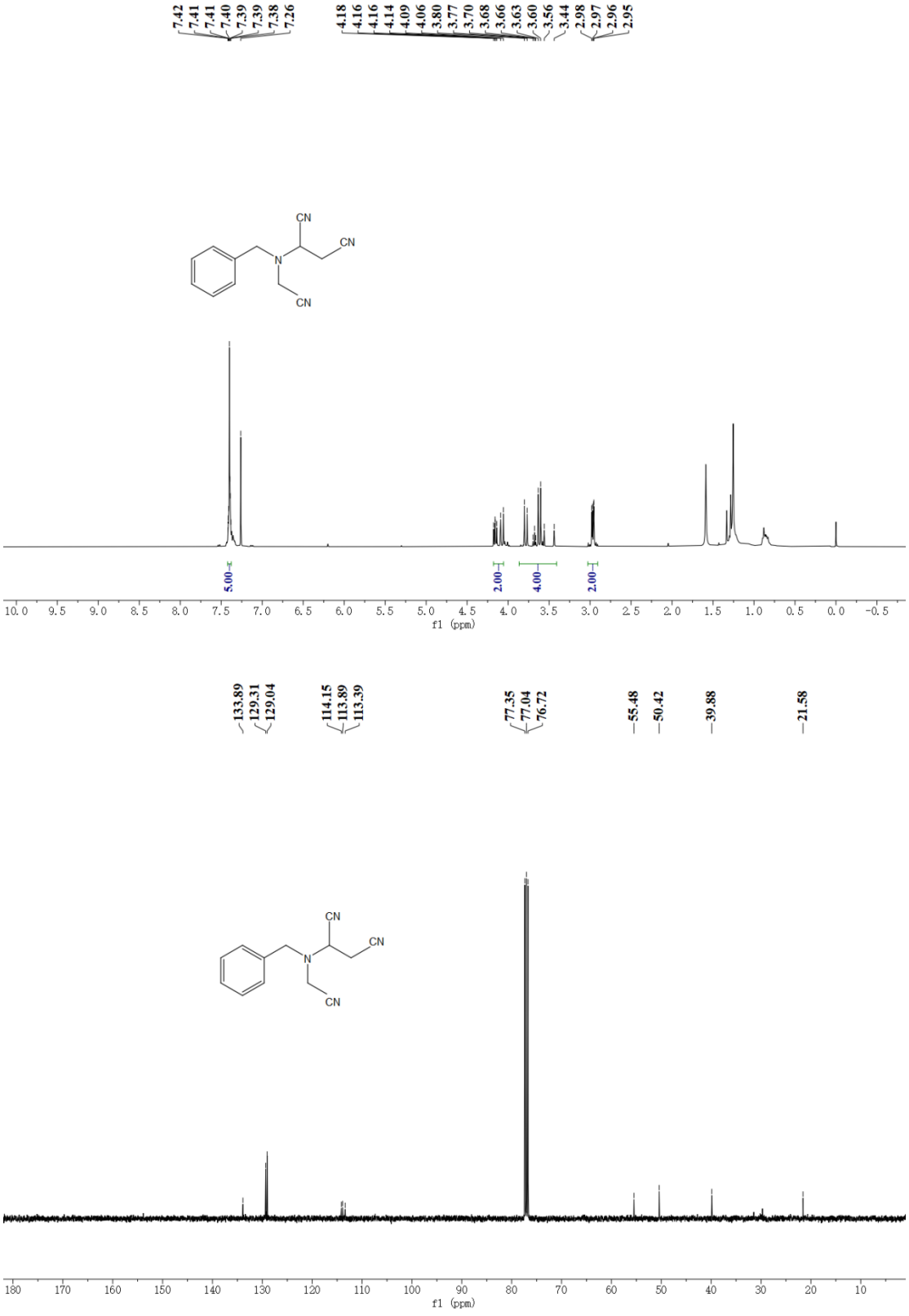



-119.82
CN
F
N
CN
CN
H3C
-109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126 -127 -128 -129 -130 -131 -132
f1 (ppm)

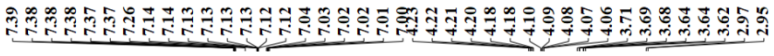
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (126 MHz, DMSO-d_6) spectra for **5q**

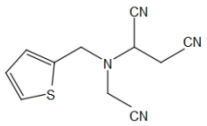


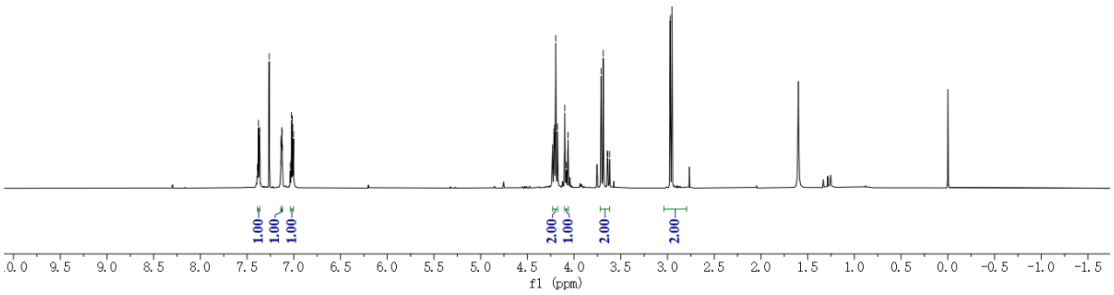
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and spectra for **5r**

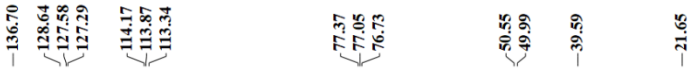


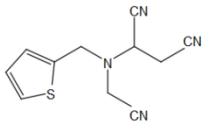
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **5s**



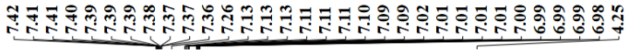


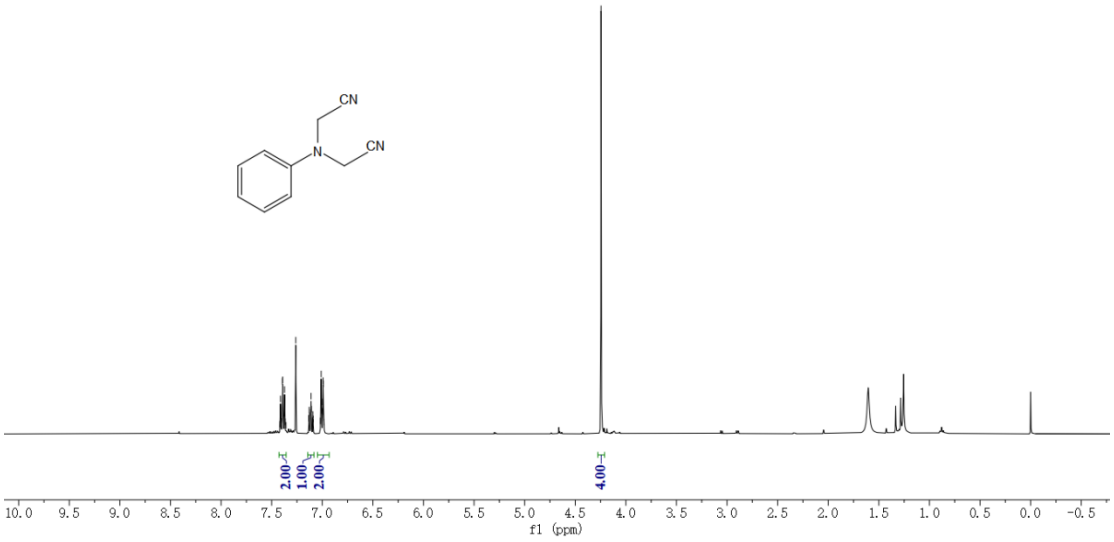


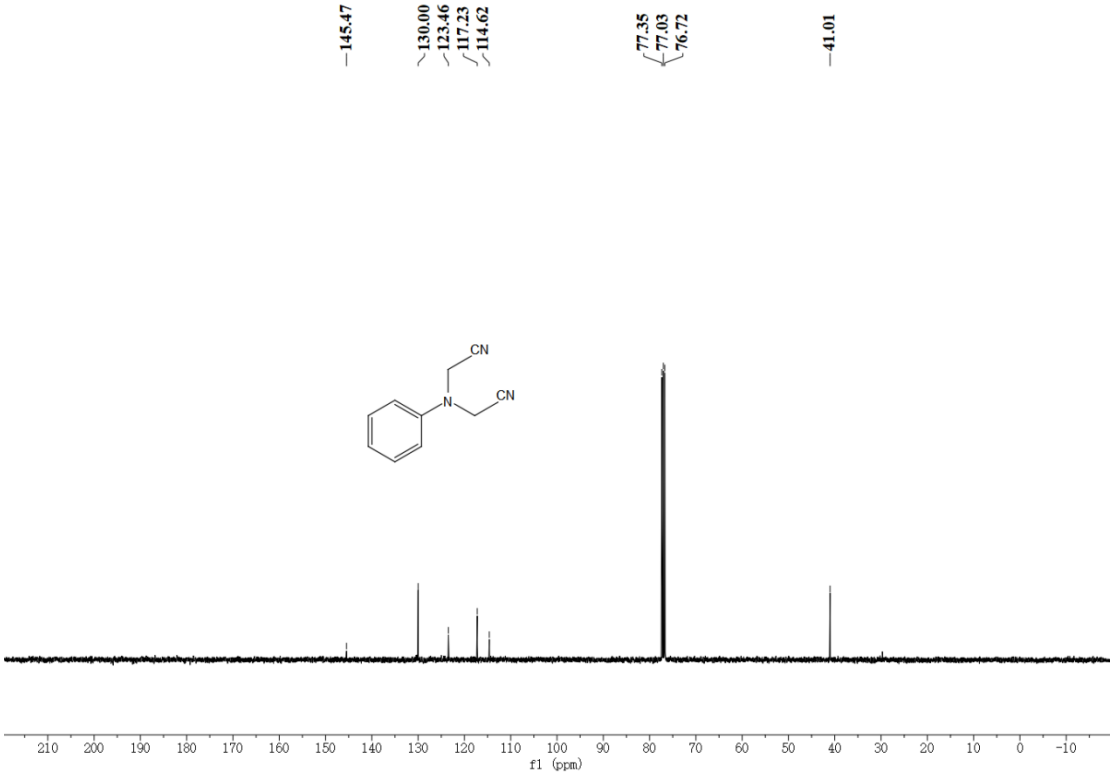




^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **3a'**







^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for **6**