Supplementary Information

A cascade process for direct converting nitriles (RCN) to cyanamide (RNHCN) via SO_2F_2-activated Tiemann rearrangement

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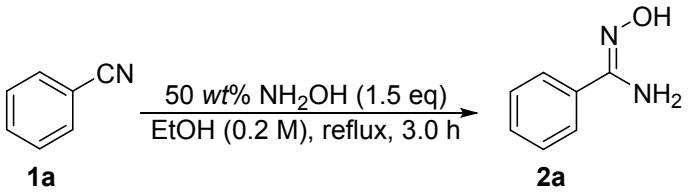
I. General Information

Reactions, unless otherwise stated, were carried out with magnetic stirring under an air or SO_2F_2 atmosphere in oven-dried glassware. Reagents were used as received without further purification, unless otherwise noted. All reaction solvents prior to use were distilled according to standard laboratory methods. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV light (254 or365 nm). Flash column chromatography was performed employing silica gel (200−300 mesh) at an increased pressure.^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance Ⅲ HD 500 and 126 MHz NMR spectrometer in $CDCl_3$ or DMSO-d_6, respectively. Chemical shifts δ are reported in parts per million (ppm) relative to a residual undeuterated solvent as an internal reference (^{1}H δ 7.26 for $CDCl_3$, δ 2.50 for DMSO-d_6; ^{13}C δ 77.16 for $CDCl_3$, δ 39.52 for DMSO-d_6). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad signal. High-resolution mass spectrometry was performed on an Agilent 6210 TOF-MS equipped with an ESI source of HR-MS System ESI spectrometer. Analytical and spectral data of all those known compounds are exactly matching with the reported values.

II. General procedure for the synthesis of benzamidoxime **2a**[1]



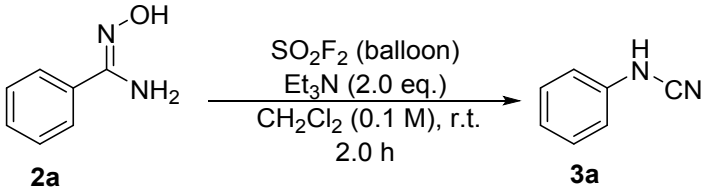
1a **2a**

To the solution of benzonitrile **1a** (1.0 g, 10 mmol) in EtOH (50 mL, 0.2 M) was added 50 *wt*% aqueous hydroxylamine solution (1.0 g, 15 mmol, 1.5equiv). The mixture was stirred at reflux temperature for 3 h under nitrogen. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and the residue was purified by recrystallization to give benzamidoxime **2a** (white solid, 1.12 g, 8.10 mmol, 81%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.65 (s, 1H), 7.76–7.63 (m, 2H), 7.38 (p, J = 3.7 Hz, 3H), 5.82 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 150.86, 133.38, 128.88, 128.10, 125.40; HRMS [ESI] calcd for $C_7H_9N_2O$ $[M+H]^+$: 137.0709, found: 137.0715.

Reference

1 C.-C. Lin, T.-H. Hsieh, P.-Y. Liao, Z.-Y. Liao, C.-W. Chang, Y.-C. Shih, W.-H. Yeh, T.-C. Chien, *Org. Lett.*, 2014, **16**, 892.

III. General procedure for converting benzamidoxime **2a** to *N*-phenylcyanamide **3a** with SO_2F_2

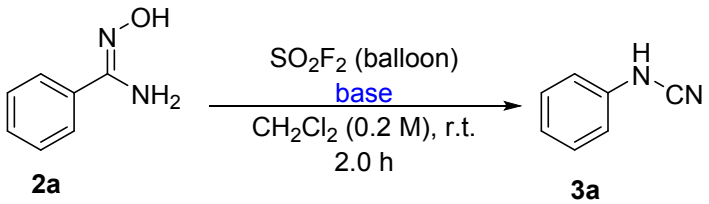


2a **3a**

Benzamidoxime **2a** (68.0 mg, 0.5 mmol), CH_2Cl_2 (5.0 mL, 0.1 M) and Et_3N (140 uL, 1.0 mmol) were added into a 35 mL Schlenk flask equipped with magnetic stirrer and rubber stopper. Then the SO_2F_2 gas was introduced into the stirring reaction mixture by slow bubbling through a SO_2F_2 balloon, and the reaction mixture was stirred at room temperature for 2.0 h. After the reaction, the mixture was concentrated under reduced pressure and the residue was purified by flashcolumn chromatography on silica gel (200-300 mesh) with hexane and ethyl acetate (Hex / EtOAc = 4 :1, Rf = 0.20) to give *N*-phenylcyanamide **3a** (yellow solid, 56.6 mg, 0.48 mmol, 96% isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.34–7.28 (m, 2H), 7.08–6.88 (m, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 135.84, 129.79, 128.95, 116.74, 111.09; HRMS [ESI] calcd for $C_7H_5N_2$ $[M-H]^-$: 117.0458, found: 117.0458.

IV. Screening the optimized reaction conditions

Table S1. Screening the bases.[a]

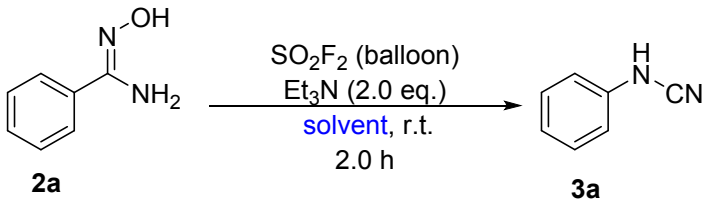


2a **3a**

Entry	Base (eq.)	Yield (%)[b]
1	DBU (2.0)	47
2	DIPEA (2.0)	73
3	**Et_3N (2.0)**	**94**
4[c]	K_2CO_3 (2.0)	7
5[c]	Na_2CO_3 (2.0)	>1
6[c]	*t*-BuONa (2.0)	13
7	Et_3N (1.5)	66
8	Et_3N (3.0)	93
9	-	nr

[a] Reaction conditions: benzamidoxime **2a** (0.5 mmol), base, CH_2Cl_2 (2.5 mL, 0.2 M), and SO_2F_2 balloon, room temperature, 2.0 h. [b] Isolated yield. [c] 5.0 h.

Table S2. Screening the solvents.[a]

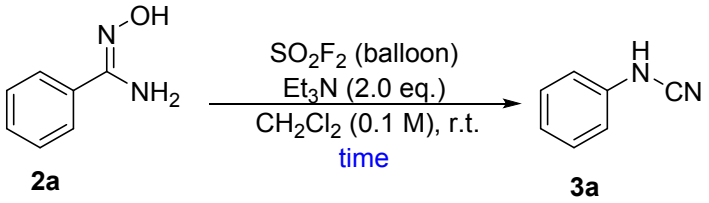


2a **3a**

Entry	Solvent	Yield (%)[b]
1	CH_2Cl_2	94
2	CH_3CN	49
3	EtOAc	85
4	DMF	22
5	DMSO	62
6	THF	30
7	CH_3OH	15
8[c]	**CH_2Cl_2**	**96**
9[d]	CH_2Cl_2	90

[a] Reaction conditions: benzamidoxime **2a** (0.5 mmol), Et_3N (1.0 mmol, 2.0 eq.), solvent (2.5 mL, 0.2 M), and SO_2F_2 balloon, room temperature, 2.0 h. [b] Isolated yield. [c] 5.0 mL of CH_2Cl_2 (0.1 M). [d] 10 mL of CH_2Cl_2 (0.05M).

Table S3. Screening the reaction time.[a]

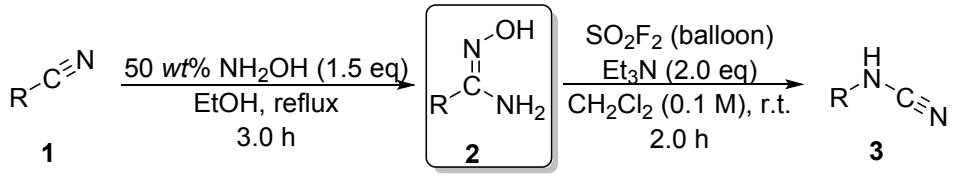


2a **3a**

Entry	Time (h)	Yield (%)[b]
1	**2.0**	**96**
2	3.0	95
3	1.5	94
4	1.0	86
5	0.5	43

[a] Reaction conditions: benzamidoxime **2a** (0.5 mmol), Et_3N (1.0 mmol, 2.0 eq.), CH_2Cl_2 (5.0 mL, 0.1 M), and SO_2F_2 balloon, room temperature, 2.0 h. [b] Isolated yield.

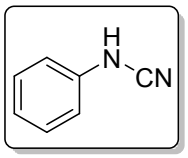
V. General procedure for the one-pot synthesis of cyanamides **3** from nitriles **1** and characterization datas of cyanamides **3**



Nitrile **1** (1.0 mmol, 1.0 eq.), 50 *wt*% aqueous hydroxylamine solution (0.1 g, 1.5 mmol, 1.5 eq.) and EtOH (10 mL, 0.1 M) were added into an oven-dried reactiontube (50 mL) equipped with a stirring bar, and the reactionmixture reacted at reflux temperature for 3.0 h. The reaction was monitored by TLC. After the nitrile was completely consumed, the reaction mixture was concentrated under reduced pressure to give the crude amidoxime **2**.The crude amidoxime **2** (without any purification), CH_2Cl_2 (10 mL, 0.1 M) and Et_3N (280 uL, 2.0 mmol, 2.0 eq.) were added into a 50 mL Schlenk flask equipped with magnetic stirrer and rubber stopper. Then the SO_2F_2 gas was introduced into the stirring reaction mixture by slow bubbling through a SO_2F_2 balloon, and the reaction mixture was stirred at room temperature for 2.0 h. After the reaction, the mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (300-400 mesh) with hexane and ethyl acetate to give cyanamide **3**.

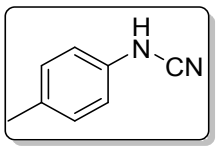
Characterization datas

N-phenylcyanamide (3a)



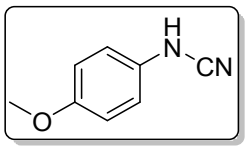
Yellow solid, 112.0 mg, 95% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.34–7.28 (m, 2H), 7.08–6.88 (m, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 135.84, 129.79, 128.95, 116.74, 111.09; HRMS [ESI] calcd for $C_7H_5N_2$ $[M-H]^-$: 117.0458, found: 117.0458.

N-(4-Methylphenyl)cyanamide (3b)



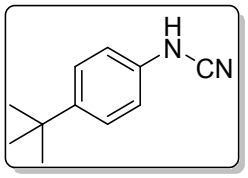
Yellow solid, 113.5 mg, 86% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.15 (d, J = 8.1 Hz, 2H), 6.98–6.87 (m, 2H), 6.38 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 134.60, 133.32, 130.24, 115.37, 111.53, 20.64; HRMS [ESI] calcd for $C_8H_8N_2Na$ $[M+Na]^+$: 155.0580, found: 155.0586.

N-(4-Methoxyphenyl)cyanamide (3c)



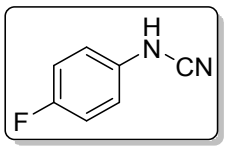
Brown solid, 115.4 mg, 78% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.01–6.94 (m, 2H), 6.92–6.85 (m, 2H), 6.72 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 156.04, 130.34, 116.87, 115.04, 112.27, 55.64; HRMS [ESI] calcd for $C_8H_7N_2O$ $[M-H]^-$: 147.0564, found: 147.0560.

N-(4-*tert*-Butylphenyl)cyanamide (3d)



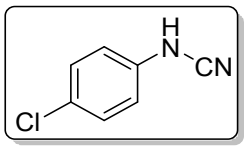
Yellow solid, 148.0 mg, 85% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.42–7.33 (m, 2H), 7.07 (s, 1H), 6.99 (d,*J* = 8.6 Hz, 2H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 146.61, 134.66, 126.53, 115.17, 111.99, 34.26, 31.32; HRMS [ESI] calcd for $C_{11}H_{13}N_2$ [M-H]$^-$: 173.1084, found: 173.1076.

N-(4-Fluorophenyl)cyanamide (3e)



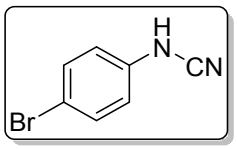
White solid, 118.3 mg, 87% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.09–7.02 (m, 2H), 7.02–6.97 (m, 2H), 6.75 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 133.23, 116.95, 116.89, 116.66, 116.47, 111.45; HRMS [ESI] calcd for $C_7H_4FN_2$ [M-H]$^-$: 135.0364, found: 135.0365.

N-(4-Chlorophenyl)cyanamide (3f)



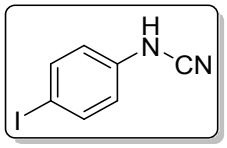
White solid, 129.7 mg, 85% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.58–7.51 (m, 3H), 7.49 (d, *J* = 2.9 Hz, 1H), 7.19 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 129.61, 129.50, 128.93, 128.80, 126.81; HRMS [ESI] calcd for $C_7H_4ClN_2$ [M-H]$^-$: 151.0068, found: 151.0064.

N-(4-Bromophenyl)cyanamide (3g)



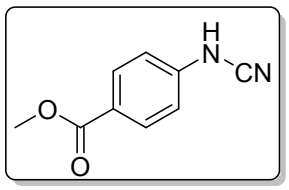
White solid, 176.4 mg, 90% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.48–7.41 (m, 2H), 7.21 (s, 1H), 6.94–6.89 (m, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 136.42, 132.68, 117.12, 116.23, 111.10; HRMS [ESI] calcd for $C_7H_4BrN_2$ [M-H]$^-$: 194.9563, found: 194.9558.

N-(4-Iodophenyl)cyanamide (3h)



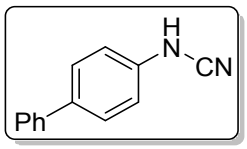
White solid, 205.0 mg, 84% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.69–7.61 (m, 2H), 6.84–6.77 (m, 2H), 6.68 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 138.64, 137.11, 117.44, 110.57, 86.39; HRMS [ESI] calcd for $C_7H_4IN_2$ [M-H]$^-$: 242.9425, found: 242.9433.

Methyl 4-cyanamidobenzoate (3i)



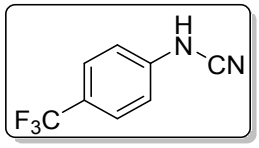
Yellow solid, 114.2 mg, 82% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.13 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 3.96 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 171.21, 137.17, 133.28, 129.93, 127.43, 114.92, 53.44; HRMS [ESI] calcd for $C_9H_7N_2O_2$ [M-H]$^-$: 175.0513, found: 175.0517.

N-([1,1'-Biphenyl]-4-yl)cyanamide (3j)



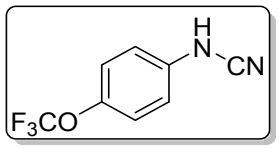
Yellow solid, 182.4 mg, 94% isolated yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.26 (s, 1H), 7.71–7.65 (m, 2H), 7.64–7.59 (m, 2H), 7.45 (t, J = 7.7 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.10–7.02 (m, 2H); ^{13}C NMR (126 MHz, DMSO- d_6): δ 139.39, 138.06, 134.52, 128.89, 127.99, 127.06, 126.19, 115.44, 111.95; HRMS [ESI] calcd for $C_{13}H_9N_2$ [M-H]$^-$: 193.0771, found: 193.0771.

N-(4-Trifluoromethylphenyl)cyanamide (3k)



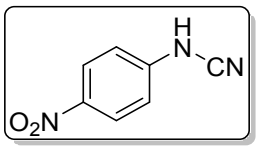
White solid, 161.8 mg, 87% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.61 (d, J = 8.6 Hz, 2H), 7.31 (s, 1H), 7.13 (d, J = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 140.41, 127.21, 127.19, 127.16, 127.12, 115.41, 110.41; HRMS [ESI] calcd for $C_8H_4F_3N_2$ [M-H]$^-$: 185.0332, found: 185.0334.

N-(4-Trifluoromethoxyphenyl)cyanamide (3l)



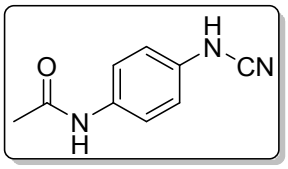
White solid, 181.8 mg, 90% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.36 (s, 1H), 7.21 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 2.2 Hz, 1H), 7.04 (d, J = 2.2 Hz, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 172.10, 145.04, 136.10, 122.72, 121.48, 119.44, 116.55, 111.18; HRMS [ESI] calcd for $C_8H_4F_3N_2O$ [M-H]$^-$: 201.0281, found: 201.0275.

N-(4-Nitrophenyl)cyanamide (3m)



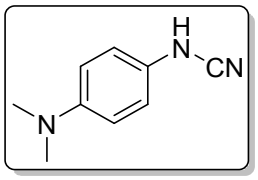
Yellow solid, 109.2 mg, 67% isolated yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.32–8.28 (m, 2H), 8.15–8.05 (m, 2H), 7.71 (s, 1H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 166.16, 149.04, 139.98, 128.88, 123.38; HRMS [ESI] calcd for $C_7H_4N_3O_2$ [M-H]$^-$: 162.0309, found: 162.0310.

N-(4-Cyanamidophenyl)acetamide (3n)



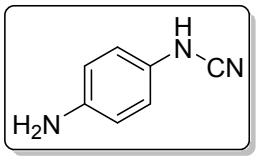
Yellow solid, 119.0 mg, 68% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.66 (d, J = 8.7 Hz, 2H), 7.62 (s, 2H), 7.61 (s, 1H), 7.53 (s, 1H), 2.23 (s, 3H); ^{13}C NMR (126 MHz, Chloroform- *d*): δ 171.17, 141.95, 133.30, 126.20, 119.42, 60.40, 53.43; HRMS [ESI] calcd for $C_9H_7N_3O$ [M-H]$^-$: 174.0564, found: 174.0558.

N-(4-Dimethylaminophenyl)cyanamide (3o)



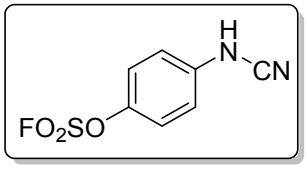
Yellow solid, 135.2 mg, 84% isolated yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.83 (d, J = 8.9 Hz, 2H), 6.74 (d, J = 9.0 Hz, 2H), 2.83 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 146.82, 128.19, 116.07, 113.96, 113.20, 40.63; HRMS [ESI] calcd for $C_9H_{10}N_3$ [M-H]$^-$: 160.0880, found: 160.0876.

N-(4-Aminophenyl)cyanamide (3p)



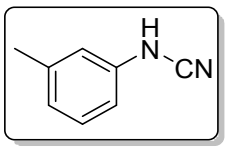
Brown solid, 107.7 mg, 81% isolated yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.44 (s, 1H), 6.69–6.64 (m, 2H), 6.58–6.53 (m, 2H), 4.85 (s, 2H); ^{13}C NMR (126 MHz, DMSO- d_6): δ 144.39, 127.36, 116.24, 114.96, 113.47; HRMS [ESI] calcd for $C_7H_6N_3$ [M-H]$^-$: 132.0567, found: 132.0566.

4-Cyanamidophenyl sulfurofluoridate (3q)



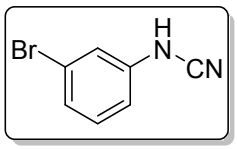
Yellow liquid, 162.0 mg, 75% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.36 (d, J = 8.7 Hz, 2H), 7.15–7.10 (m, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 145.63, 137.66, 122.59, 116.82; HRMS [ESI] calcd for $C_7H_4FN_2O_3S$ [M-H]$^-$: 215.1905, found: 215.2017.

N-(*m*-Tolyl)cyanamide (3r)



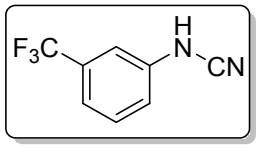
Yellow solid, 114.8 mg, 87% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.22 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 7.5 Hz, 1H), 6.87–6.81 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, Chloroform- *d*): δ 139.94, 137.19, 129.51, 124.39, 115.97, 112.52, 111.67, 21.35;HRMS [ESI] calcd for $C_8H_7N_2$ [M-H]$^-$: 131.0615, found: 131.0611.

N-(3-Bromophenyl)cyanamide (3s)



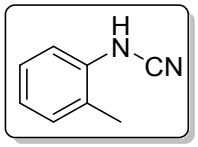
White solid, 174.4 mg, 89% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.23 (q, J = 7.7 Hz, 3H), 6.98 (dt, J = 6.9, 2.1 Hz, 1H), 6.64 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 138.52, 131.10, 126.91, 123.46, 118.59, 114.08, 110.36; HRMS [ESI] calcd for $C_7H_4BrN_2$ [M-H]$^-$: 194.9563, found: 194.9570.

N-(3-Trifluoromethylphenyl)cyanamide (3t)



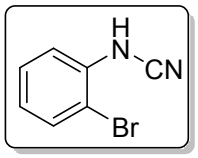
White solid, 163.7 mg, 88% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.49 (t, J = 7.9 Hz, 1H), 7.44 (s, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.26–7.22 (m, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 138.00, 132.48, 132.22, 131.96, 130.49, 124.59, 122.42, 120.48, 118.61, 112.36, 110.73; HRMS [ESI] calcd for $C_8H_4F_3N_2$ [M-H]$^-$: 185.0332, found: 185.0334.

N-(*o*-Tolyl)cyanamide (3u)



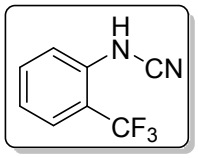
Yellow solid, 114.8 mg, 87% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.29–7.20 (m, 2H), 7.17 (d, J = 7.5 Hz, 1H), 7.03 (td, J = 7.4, 1.1 Hz, 1H), 6.44 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 135.56, 131.00, 127.49, 124.28, 123.68, 115.46, 111.76, 17.01; HRMS [ESI] calcd for $C_8H_7N_2$ [M-H]$^-$: 131.0615, found: 131.0621.

N-(2-Bromophenyl)cyanamide (3v)



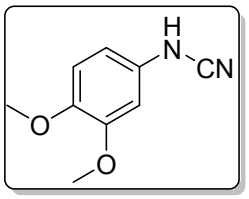
White solid, 176.4 mg, 90% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.59–7.50 (m, 1H), 7.41–7.34 (m, 1H), 7.31 (dd, J = 8.1, 1.4 Hz, 1H), 6.99 (td, J = 7.9, 1.5 Hz, 1H), 6.51 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 135.22, 132.87, 131.59, 129.07, 124.74, 116.05, 109.76; HRMS [ESI] calcd for $C_7H_4BrN_2$ [M-H]$^-$: 194.9563, found: 194.9573.

N-(2-Trifluoromethylphenyl)cyanamide (3w)



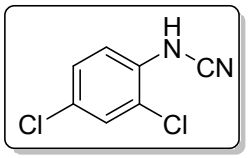
White solid, 145.1 mg, 78% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.66–7.57 (m, 2H), 7.46 (d, J = 8.5 Hz, 1H), 7.22 (t, J = 7.7 Hz, 1H), 6.51 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 135.11, 133.82, 127.02, 126.98, 126.95, 126.90, 124.87, 123.62, 122.70, 117.24, 109.32; HRMS [ESI] calcd for $C_8H_4F_3N_2$ [M-H]$^-$: 185.0332, found: 185.0338.

N-(3,4-Dimethoxyphenyl)cyanamide (3x)



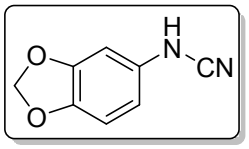
Whitesolid, 147.6 mg, 83% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.83 (d, J = 8.6 Hz, 1H), 6.61 (d, J = 2.7 Hz, 1H), 6.55 (dd, J = 8.5, 2.6 Hz, 1H), 6.10 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 150.15, 145.67, 130.73, 112.40, 111.57, 107.16, 100.42, 56.40, 56.09; HRMS [ESI] calcd for $C_9H_9N_2O_2$ [M-H]$^-$: 177.067, found: 177.0661.

N-(2,4-Dichlorophenyl)cyanamide (3y)



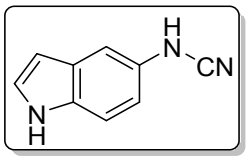
White solid, 135.8 mg, 73% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.39 (d, J = 2.2 Hz, 1H), 7.30 (dd, J = 8.7, 2.2 Hz, 1H), 7.22 (d, J = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 171.23, 133.12, 129.47, 128.95, 128.51, 127.77, 116.90; HRMS [ESI] calcd for $C_7H_3Cl_2N_2$ [M-H]$^-$: 184.9679, found: 184.9680.

N-(Benzo[d][1,3]dioxol-5-yl)cyanamide (3z)



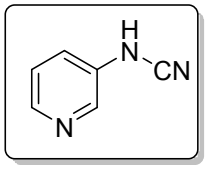
Yellow solid, 147.4 mg, 91% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.75 (d, J = 8.3 Hz, 1H), 6.58 (d, J = 2.3 Hz, 1H), 6.53 (d, J = 16.6 Hz, 1H), 6.47 (dd, J = 8.3, 2.4 Hz, 1H), 5.97 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 148.71, 144.12, 131.66, 108.72, 108.05, 101.60, 98.16, 53.43; HRMS [ESI] calcd for $C_8H_5N_2O_2$ [M-H]$^-$: 161.0357, found: 161.0349.

N-(1*H*-Indol-5-yl)cyanamide (3aa)



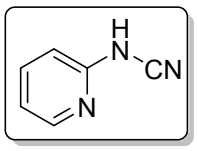
Yellow solid, 120.9 mg, 77% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.24 (s, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 1.9 Hz, 1H), 7.26 (d, J = 2.7 Hz, 1H), 6.90 (dd, J = 8.6, 2.2 Hz, 1H), 6.51 (s, 1H), 5.80 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 132.88, 130.03, 128.56, 125.95, 112.16, 112.08, 111.41, 106.97, 102.41; HRMS [ESI] calcd for $C_9H_6N_3$ [M-H]$^-$: 156.0567, found: 156.0567.

N-(Pyridin-3-yl)cyanamide (3ab)



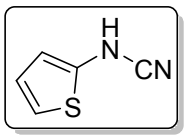
Yellow liquid, 90.5 mg, 87% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.86–7.60 (m, 1H), 7.17–6.82 (m, 3H), 6.78–6.64 (m, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 143.38, 127.65, 126.27, 119.25, 118.73, 114.64; HRMS [ESI] calcd for $C_6H_4N_3$ [M-H]$^-$: 118.0411, found: 118.0412.

N-(Pyridin-2-yl)cyanamide (3ac)



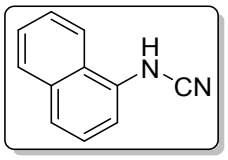
Yellow liquid, 95.2 mg, 80% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.76–7.68 (m, 1H), 7.64 (ddd, J = 8.9, 7.0, 1.8 Hz, 1H), 7.12 (d, J = 8.9 Hz, 1H), 6.68–6.55 (m, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 160.31, 142.12, 136.49, 118.48, 117.57, 111.56; HRMS [ESI] calcd for $C_6H_4N_3$ [M-H]$^-$: 118.0411, found: 118.0409.

***N*-(Thiophen-2-yl)cyanamide (3ad)**



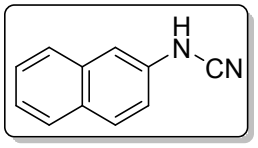
Brown liquid, 64.5 mg, 52% isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.52–7.47 (m, 1H), 7.08–7.02 (m, 1H), 6.96–6.84 (m, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 161.40, 155.11, 129.95, 128.25, 110.79; HRMS [ESI] calcd for $C_5H_3N_2S$ [M-H]$^-$: 123.0022, found: 123.0023.

***N*-(Naphthalen-1-yl)cyanamide (3ae)**



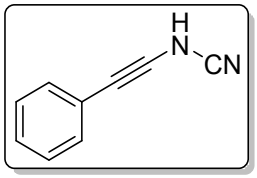
Yellow solid, 105.8 mg, 63% isolated yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.23 (s, 1H), 8.11–8.06 (m, 1H), 7.99–7.93 (m, 1H), 7.66 (d, J = 8.2 Hz, 1H), 7.63–7.56 (m, 2H), 7.52 (t, J = 7.9 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H); ^{13}C NMR (126 MHz, DMSO- d_6): δ 134.34, 133.86, 128.38, 126.70, 126.15, 126.01, 123.22, 123.16, 120.98, 112.63, 111.15; HRMS [ESI] calcd for $C_{11}H_7N_2$ [M-H]$^-$: 167.0615, found: 167.0615.

N-(Naphthalen-2-yl)cyanamide (3af)



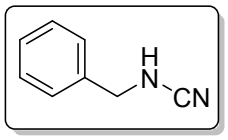
Yellow solid, 141.1 mg, 84% isolated yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.37 (s, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.86 (d, J = 8.9 Hz, 2H), 7.49 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.43–7.36 (m, 2H), 7.20 (dd, J = 8.8, 2.4 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 136.42, 133.65, 129.87, 129.33, 127.69, 126.99, 126.62, 124.44, 116.27, 112.05, 110.02; HRMS [ESI] calcd for $C_{11}H_7N_2$ [M-H]$^-$: 167.0615, found: 167.0616.

N-(Phenylethynyl)cyanamide (3ag)



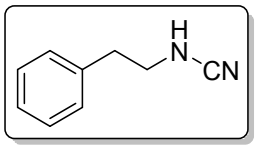
Yellow solid, 103.6 mg, 73% isolated yield. ^{1}H NMR (500 MHz, Chloroform-d): δ 7.72 (dd, J = 6.7, 3.0 Hz, 2H), 7.47–7.37 (m, 3H), 4.82 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-d): δ 169.11, 163.82, 129.67, 128.66, 126.52, 78.02; HRMS [ESI] calcd for $C_9H_5N_2$ [M-H]$^-$: 141.0531, found: 141.0530.

N-Benzylcyanamide (3ah)



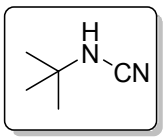
Yellow liquid, 84.5 mg, 64 % isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.45–7.31 (m, 5H), 4.21 (d, J = 5.5 Hz, 2H), 4.15 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 136.18, 128.95, 128.49, 127.82, 116.01, 50.22; HRMS [ESI] calcd for $C_8H_7N_2$ [M-H]$^-$: 131.0615, found: 131.0610.

N-Phenethylcyanamide (3ai)



Yellow liquid, 89.2 mg, 61 % isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.35 (t, J = 7.4 Hz, 2H), 7.30–7.25 (m, 1H), 7.22 (d, J = 7.1 Hz, 2H), 3.74 (s, 1H), 3.41–3.27 (m, 2H), 2.92 (t, J = 7.0 Hz, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 137.21, 128.84, 128.81, 126.99, 115.87, 47.39, 35.87; HRMS [ESI] calcd for $C_9H_9N_2$ [M-H]$^-$: 145.0771, found: 145.077.

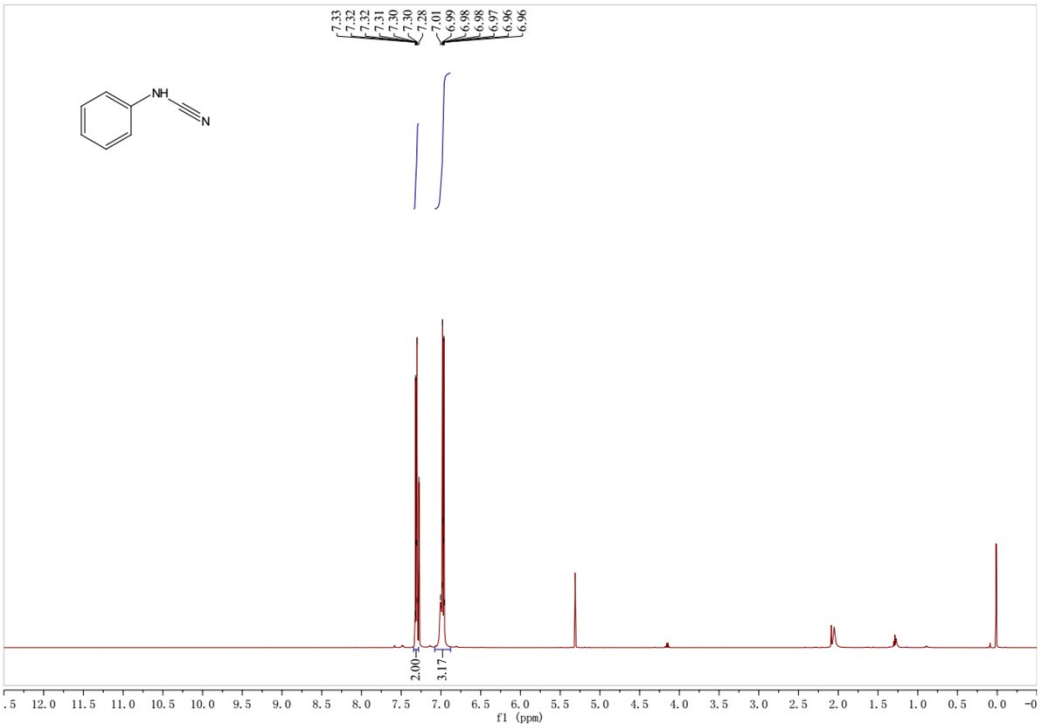
N-(*tert*-Butyl)cyanamide (3aj)

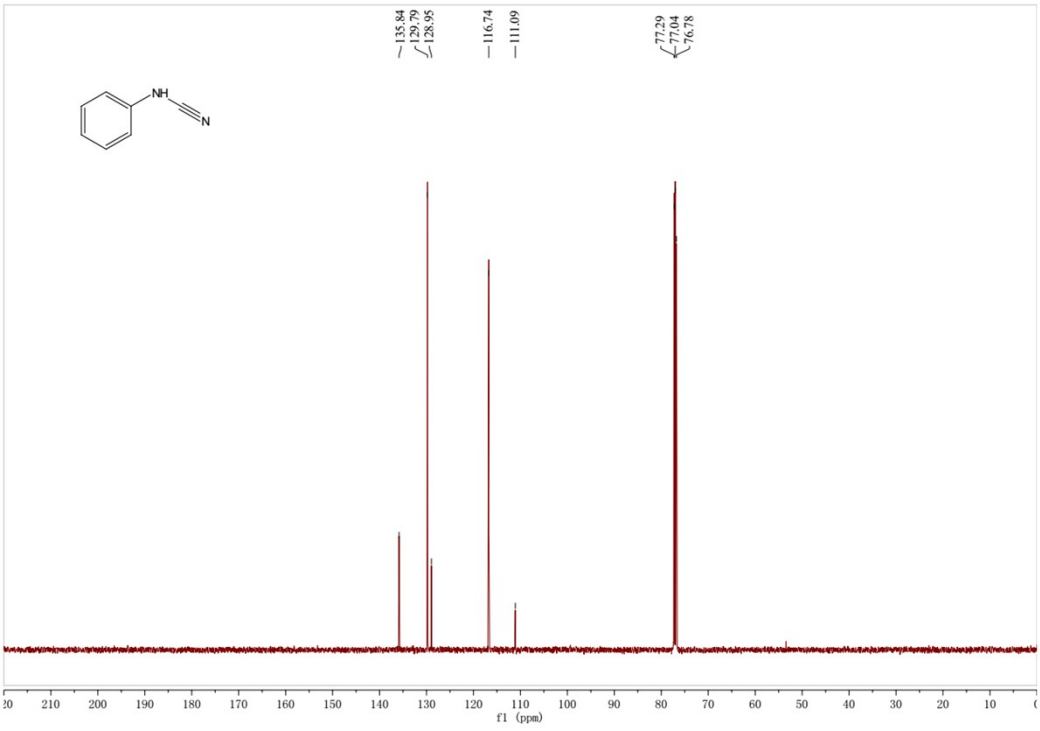


Yellow liquid, 82.4 mg, 84 % isolated yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 4.54 (s, 1H), 1.25 (s, 9H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ 115.24, 53.10, 28.94; HRMS [ESI] calcd for $C_5H_{11}N_2$ [M+H]$^+$: 99.0844, found: 99.0843.

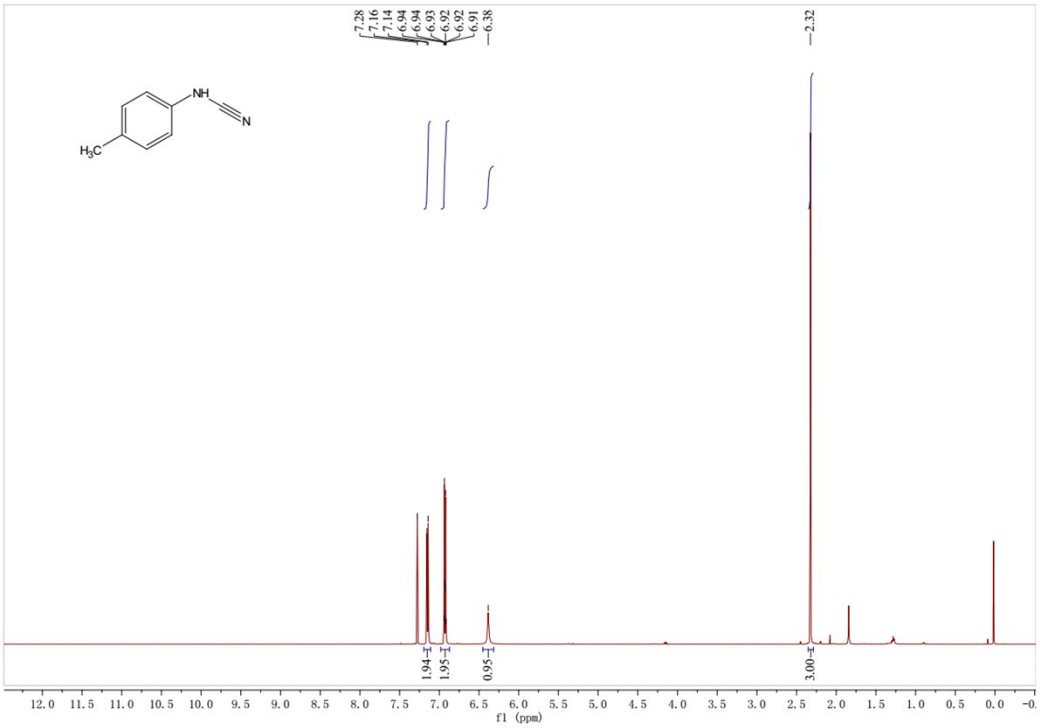
VI. Reproductions of ^{1}H NMR and ^{13}C NMR spectra

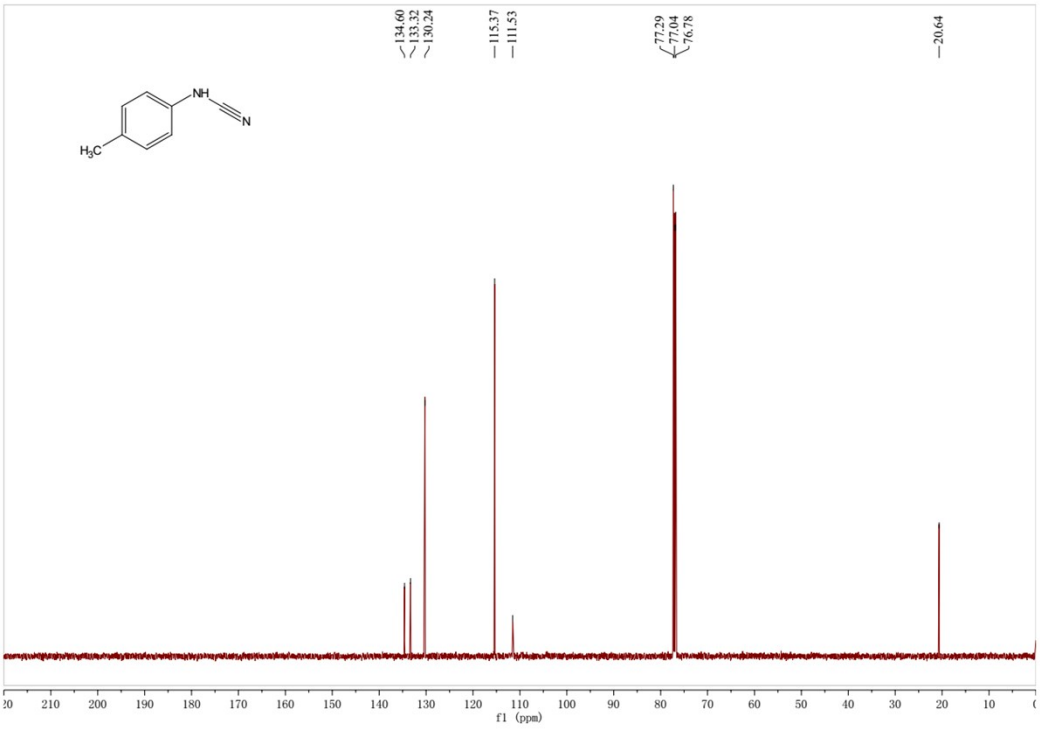
N-phenylcyanamide (3a)



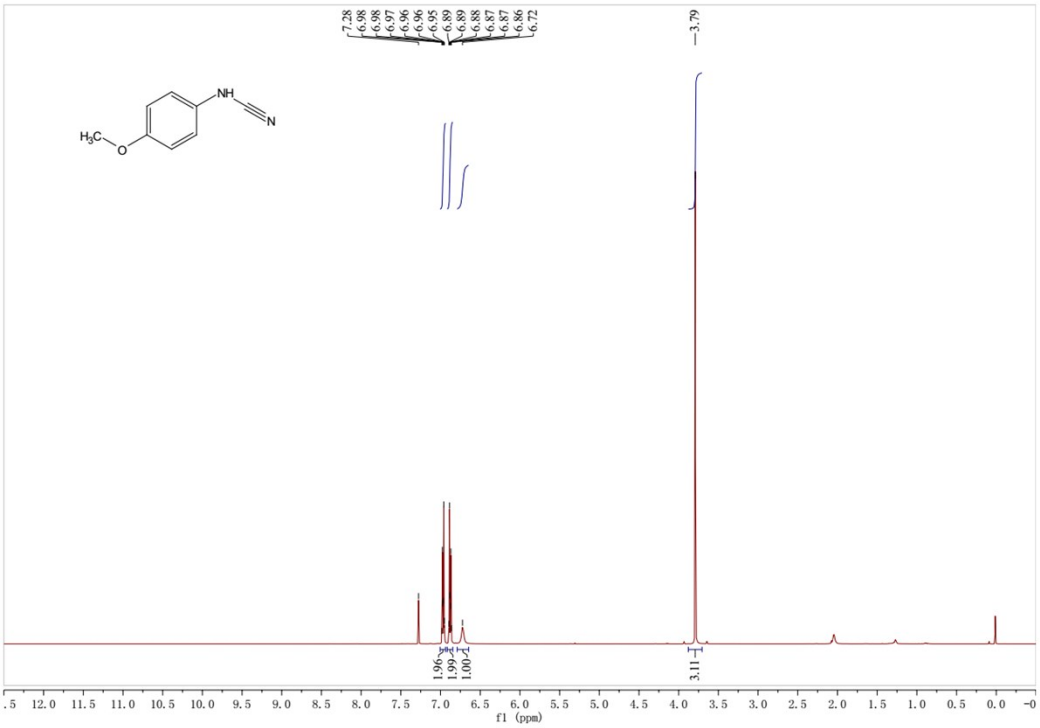


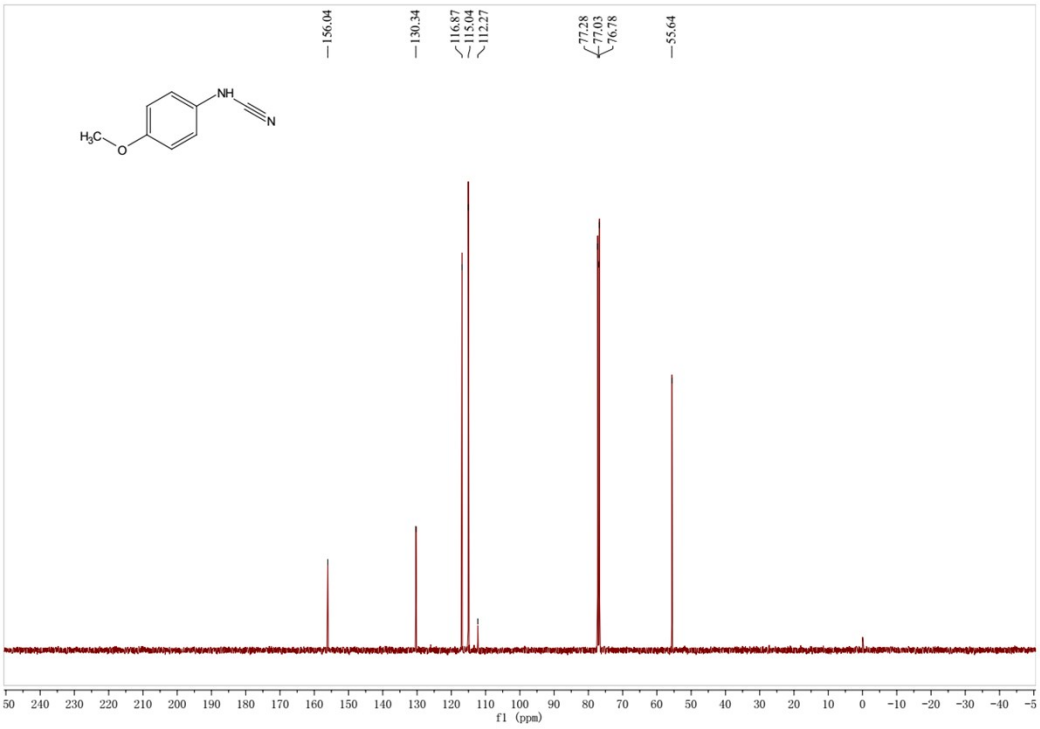
N-(4-Methylphenyl)cyanamide (3b)



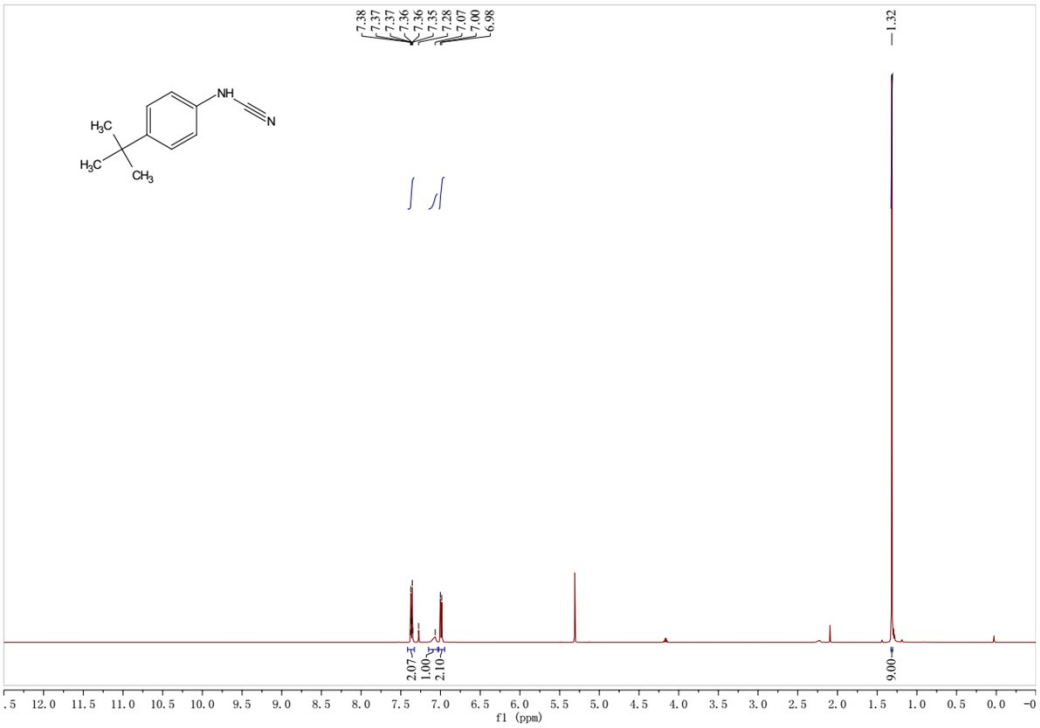


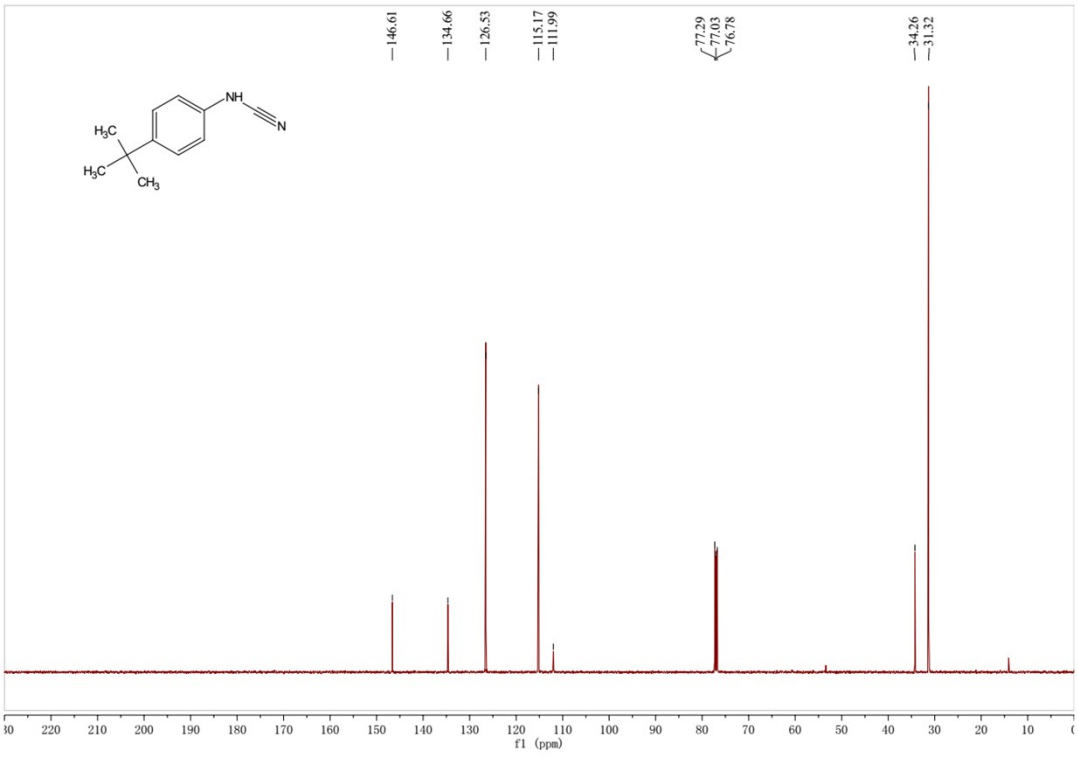
N-(4-Methoxyphenyl)cyanamide (3c)



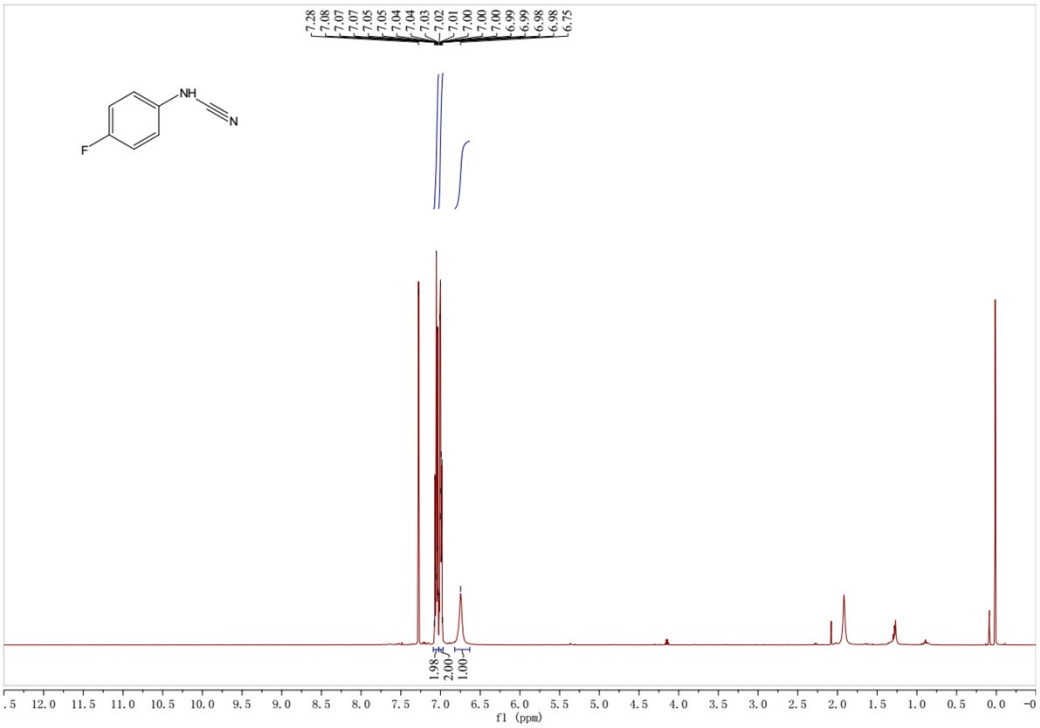


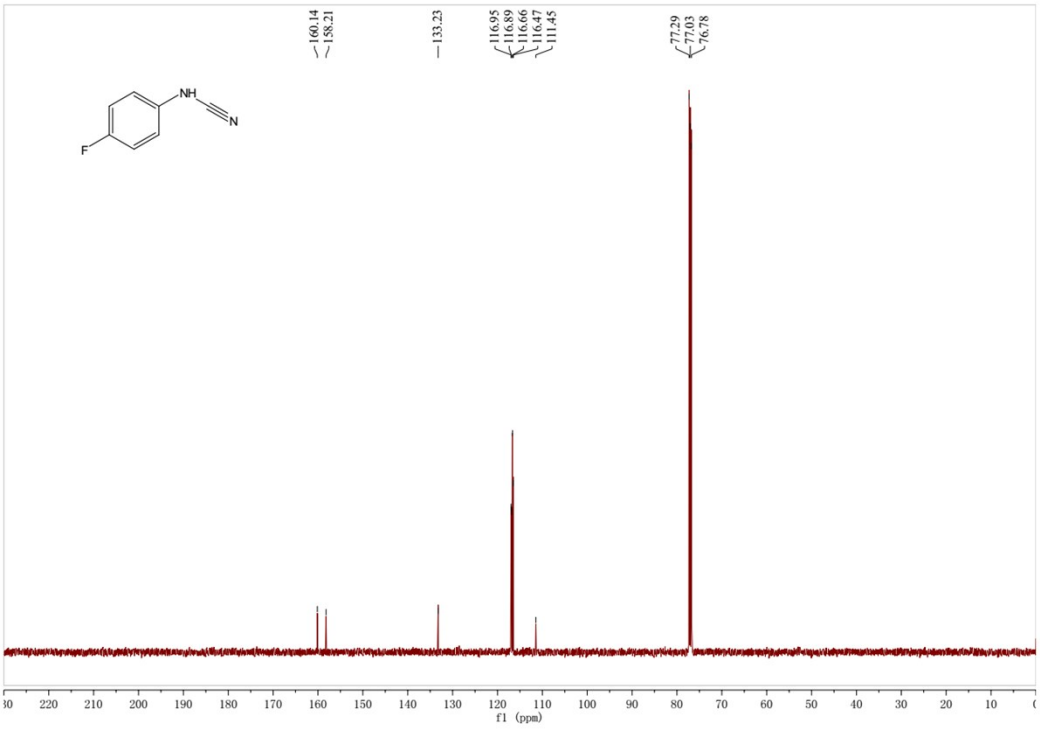
N-(4-*tert*-Butylphenyl)cyanamide (3d)



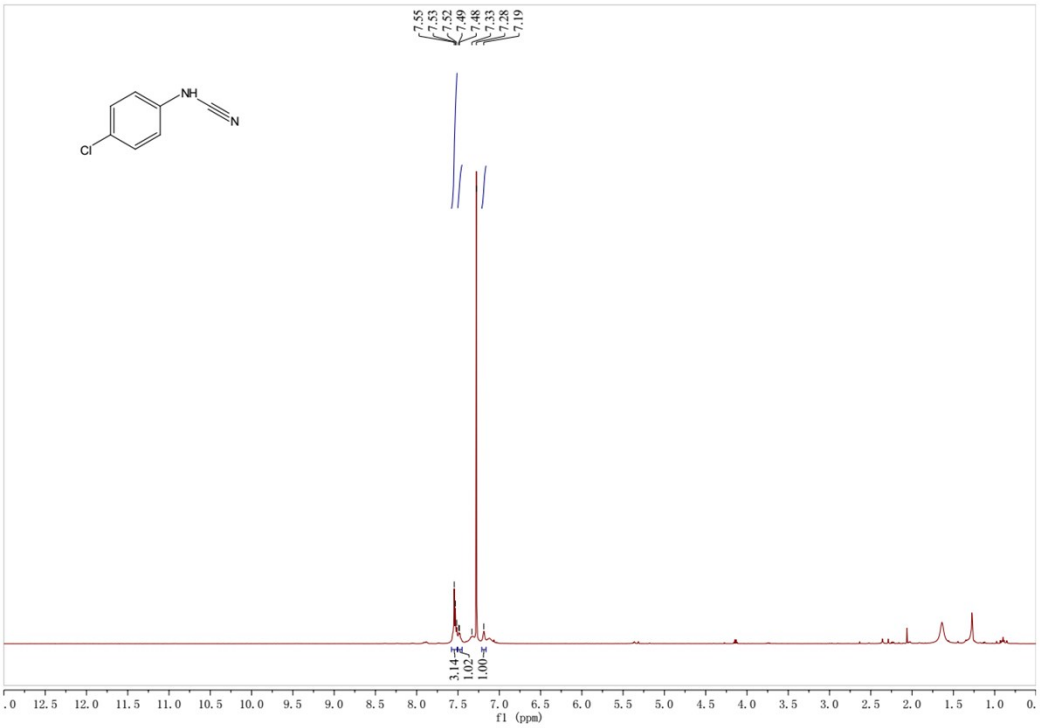


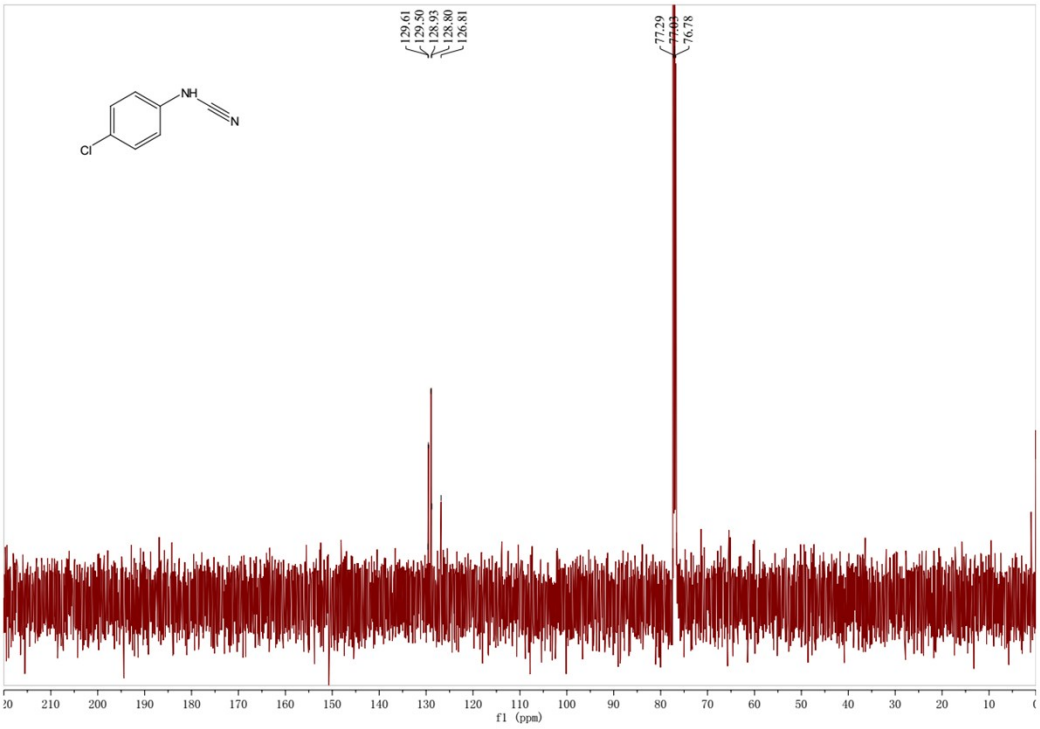
N-(4-Fluorophenyl)cyanamide (3e)



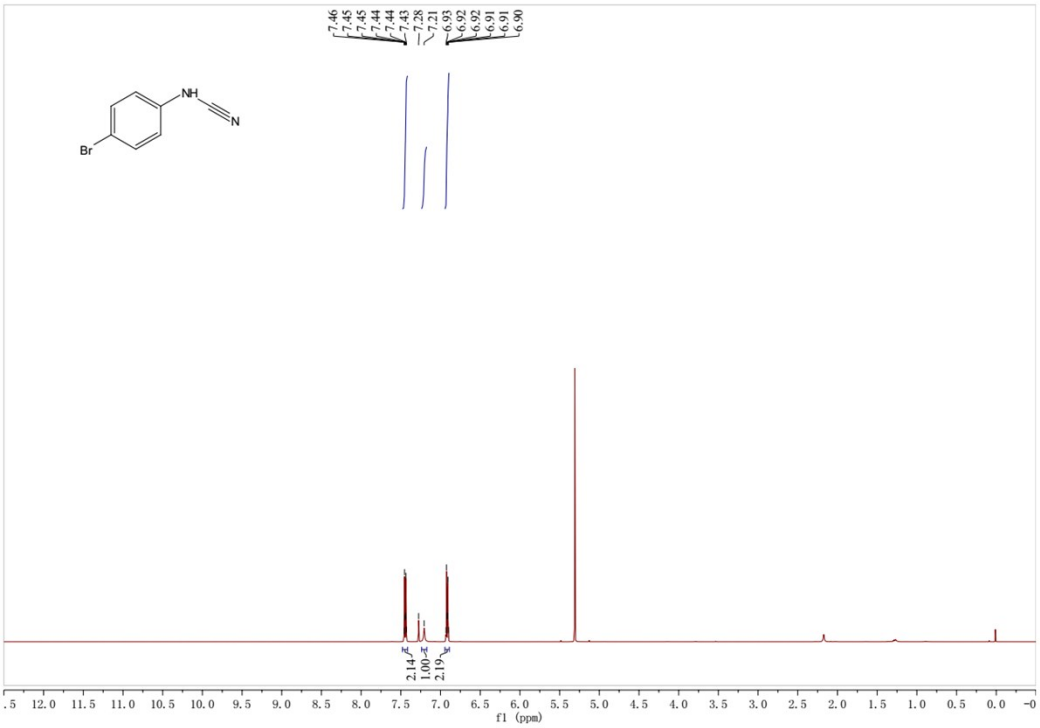


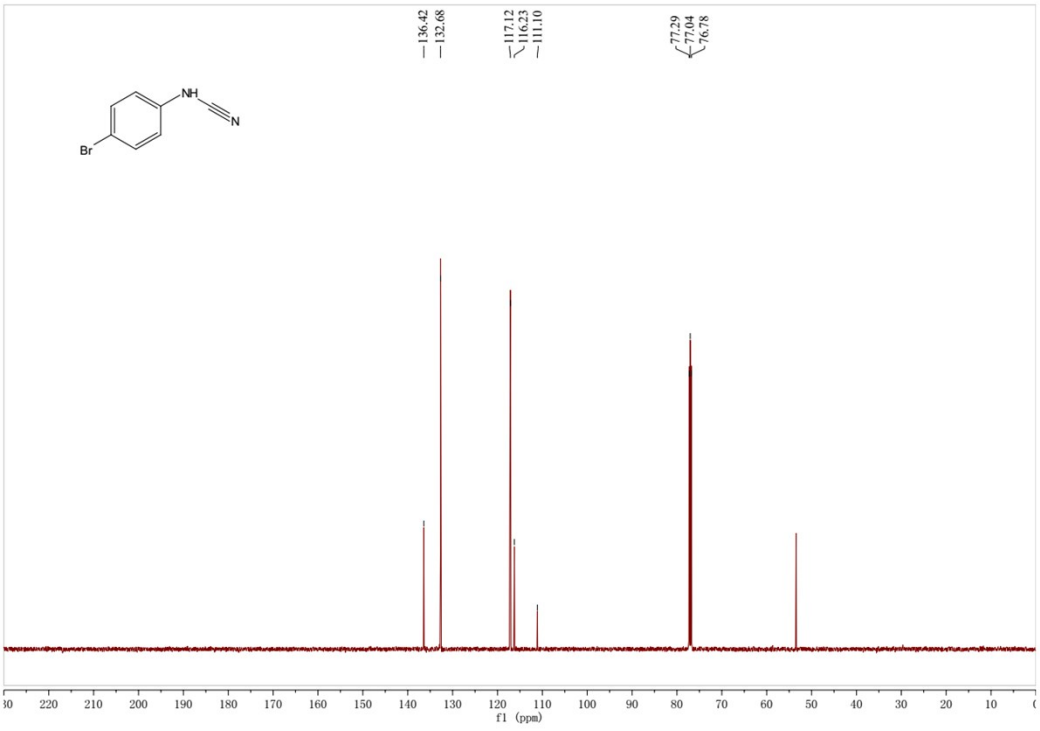
N-(4-Chlorophenyl)cyanamide (3f)



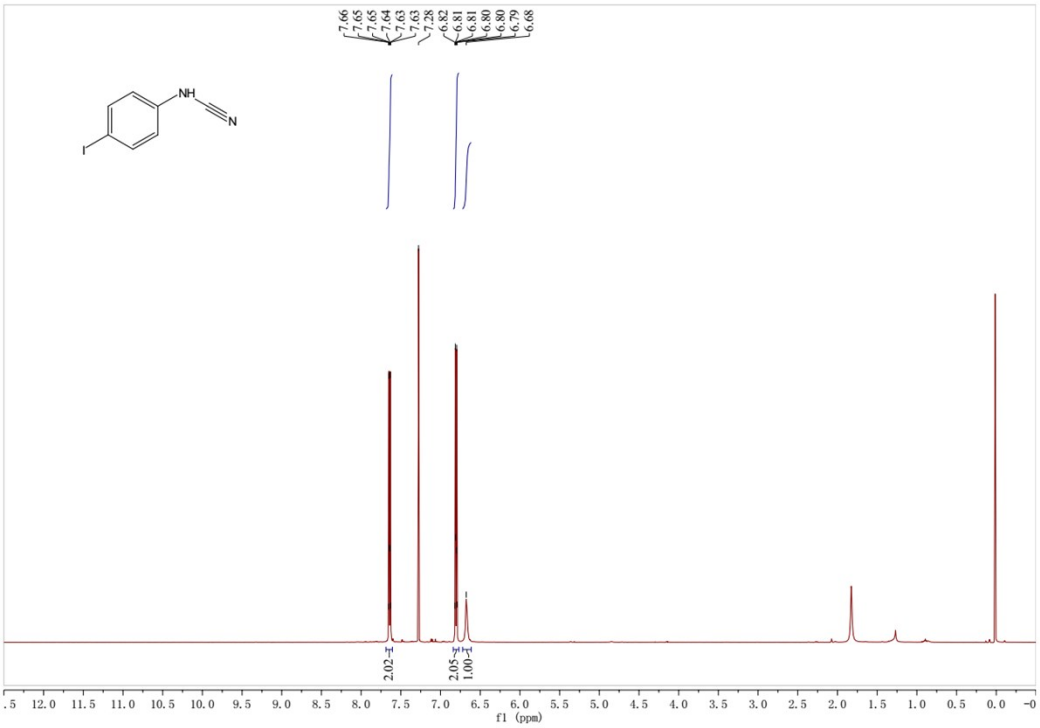


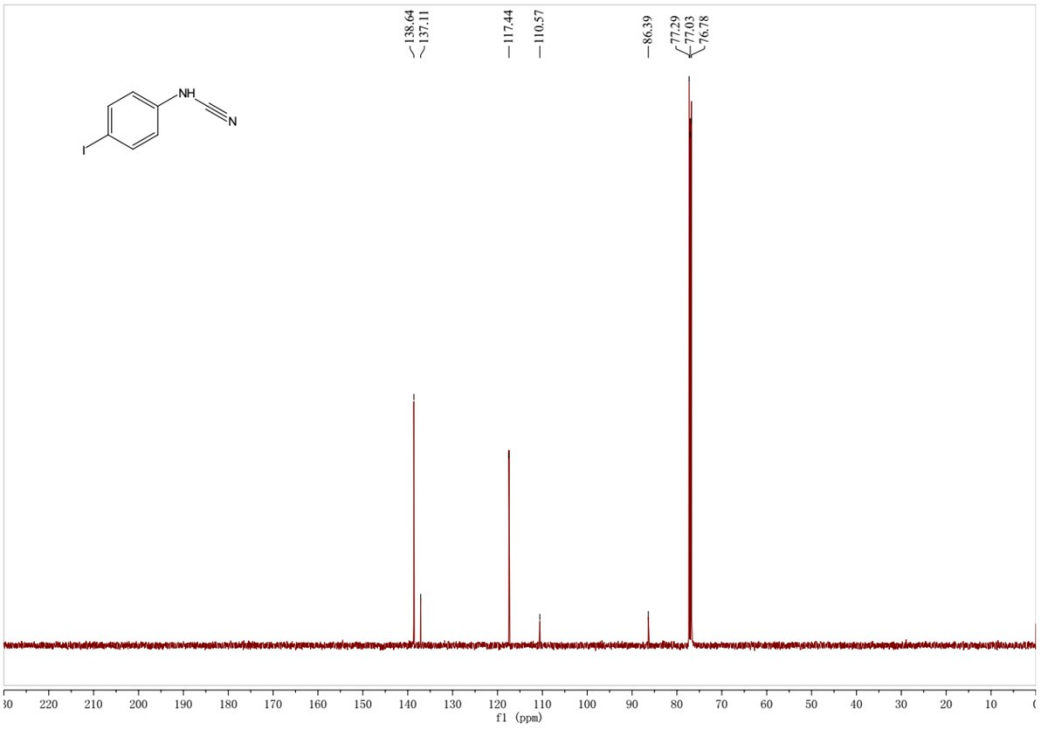
N-(4-Bromophenyl)cyanamide (3g)



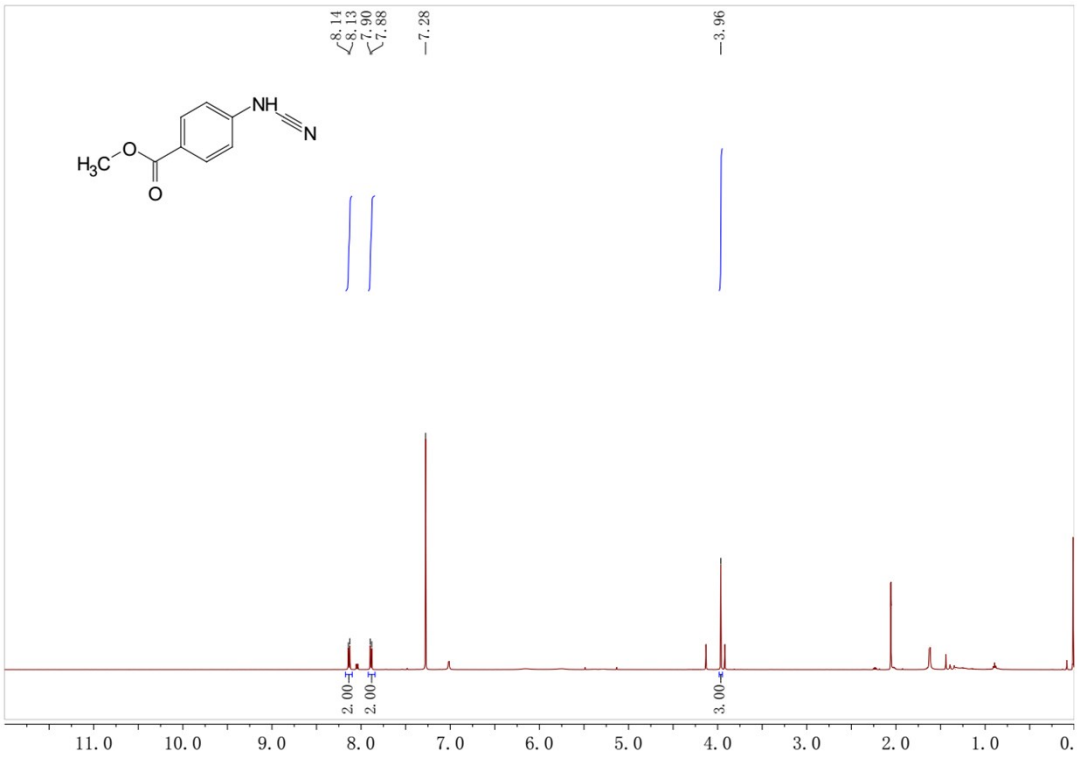


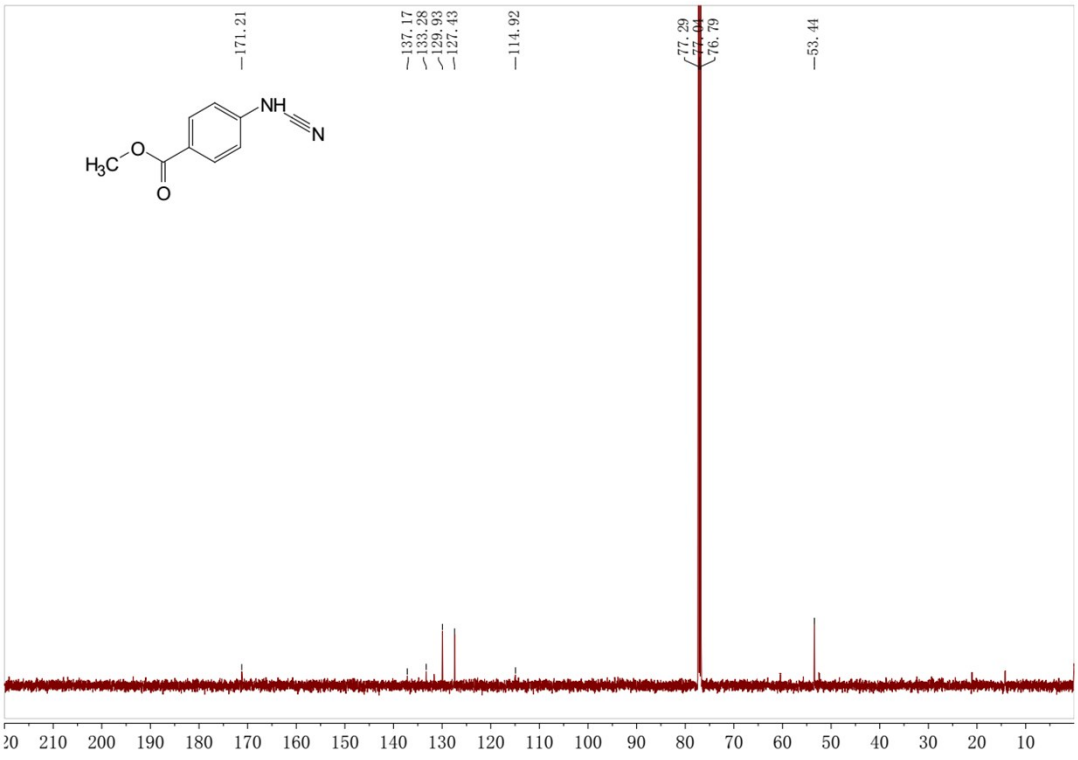
N-(4-Iodophenyl)cyanamide (3h)



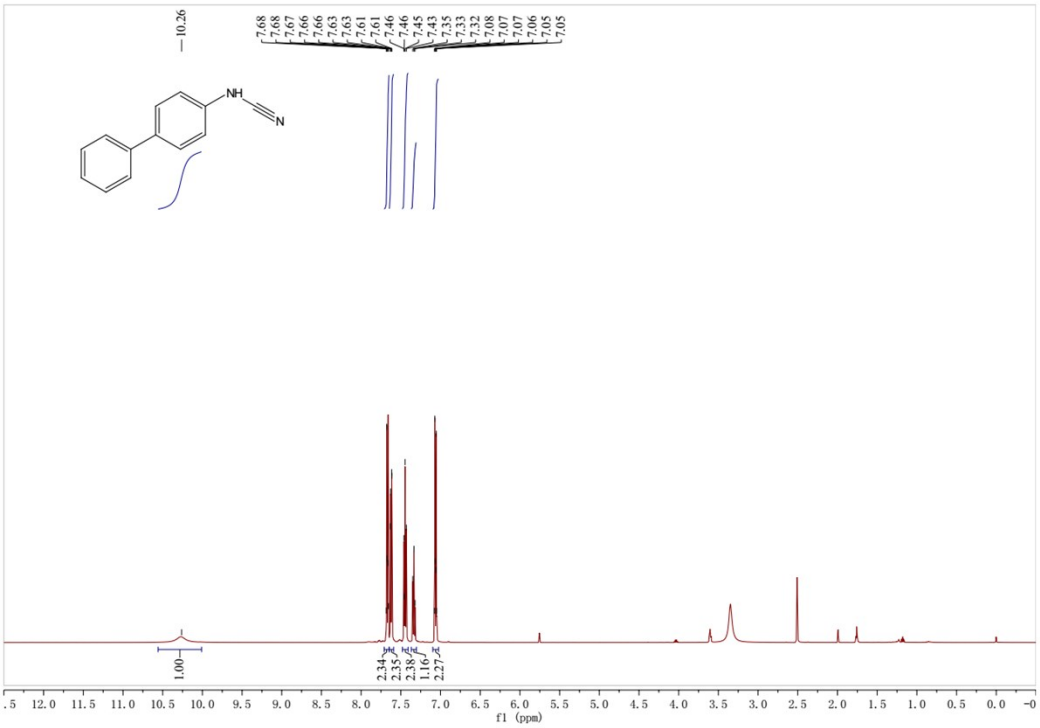


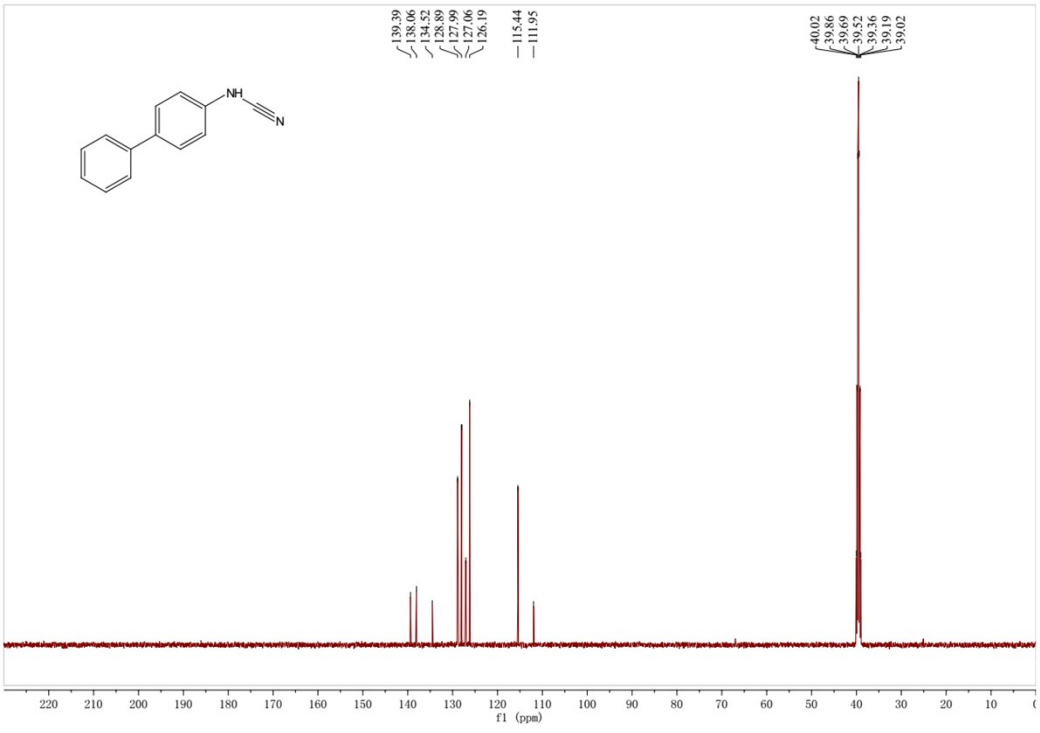
Methyl 4-cyanamidobenzoate (3i)



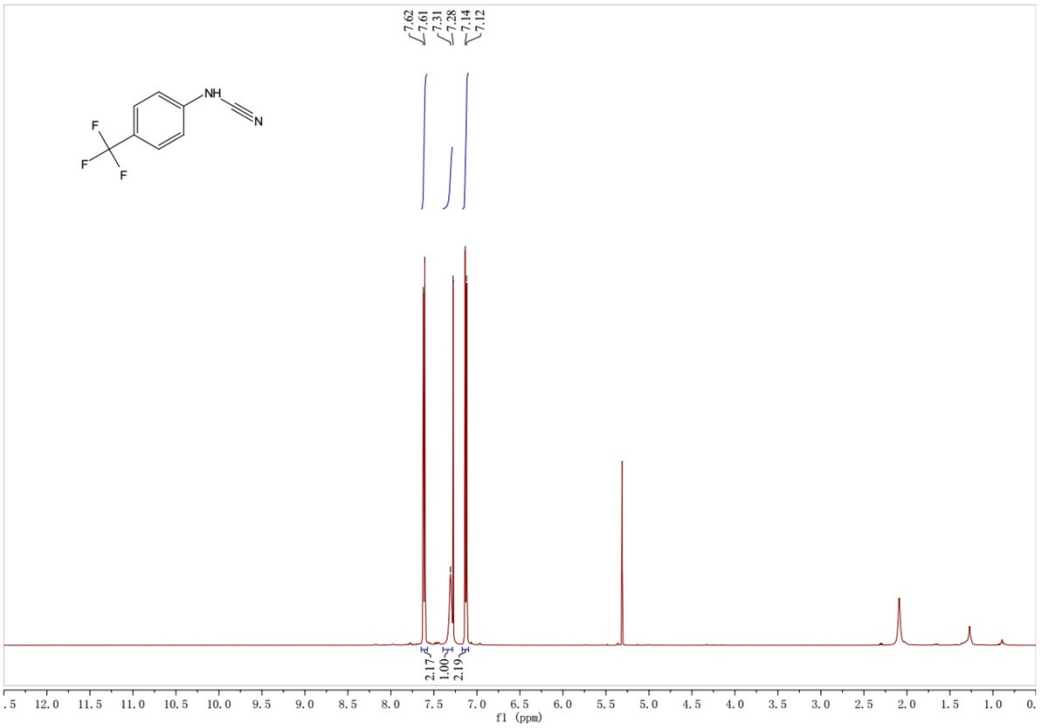


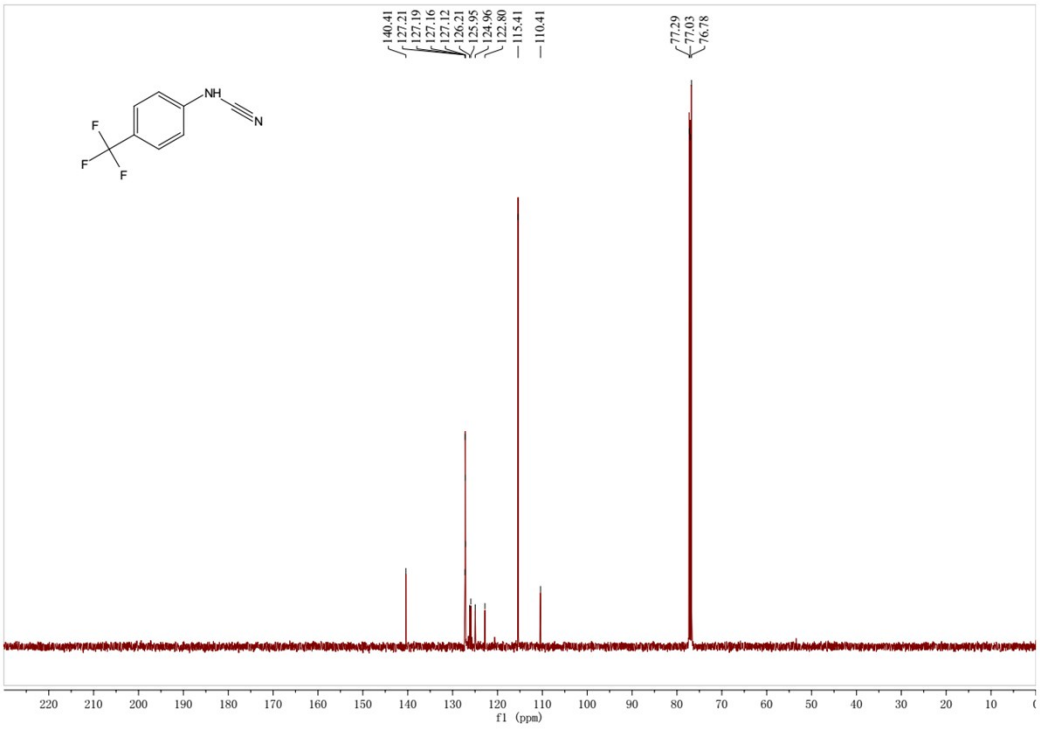
N-([1,1'-biphenyl]-4-yl)cyanamide (3j)



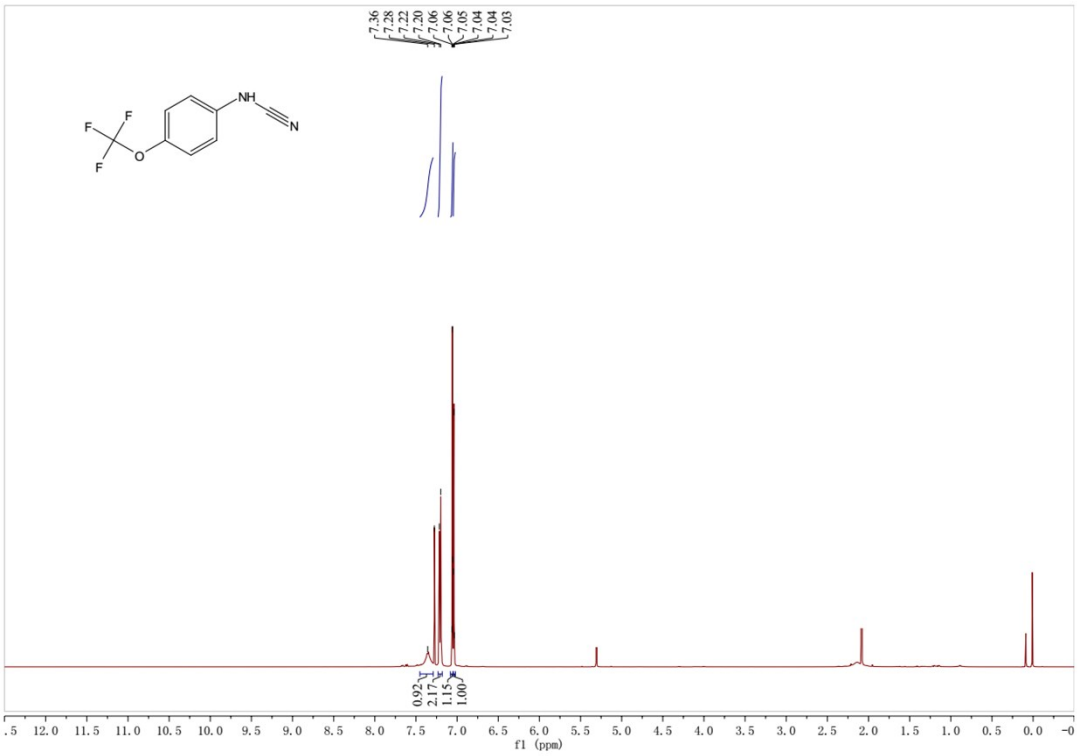


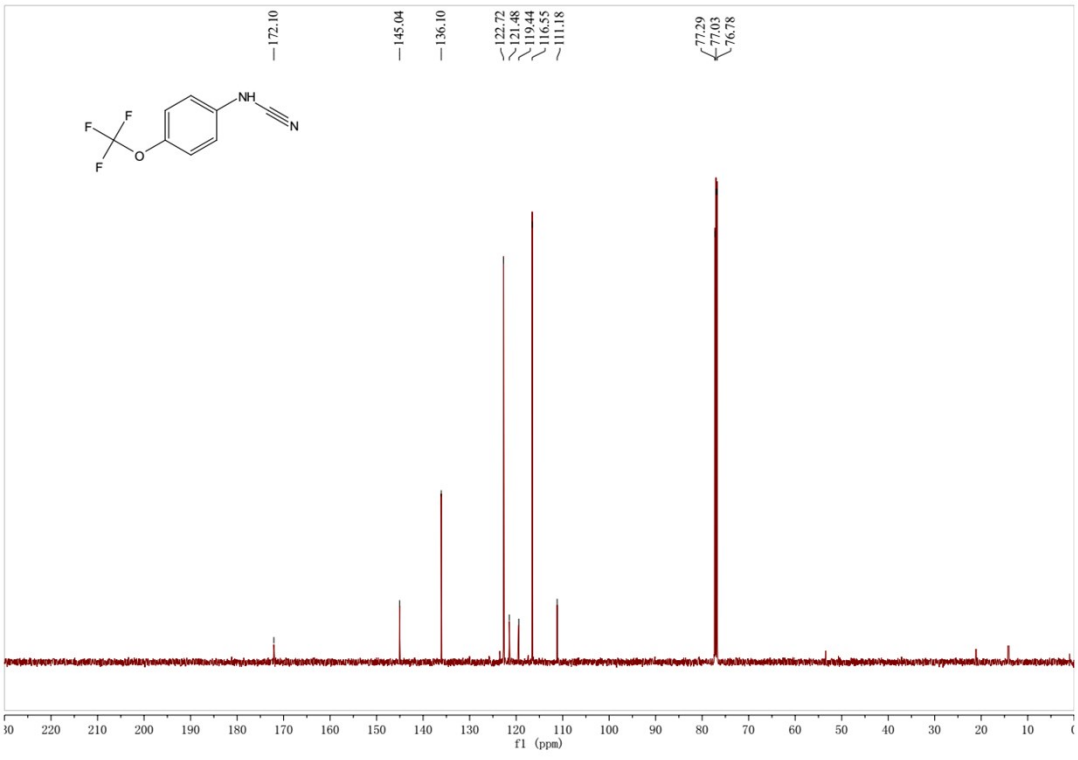
N-(4-Trifluoromethylphenyl)cyanamide (3k)



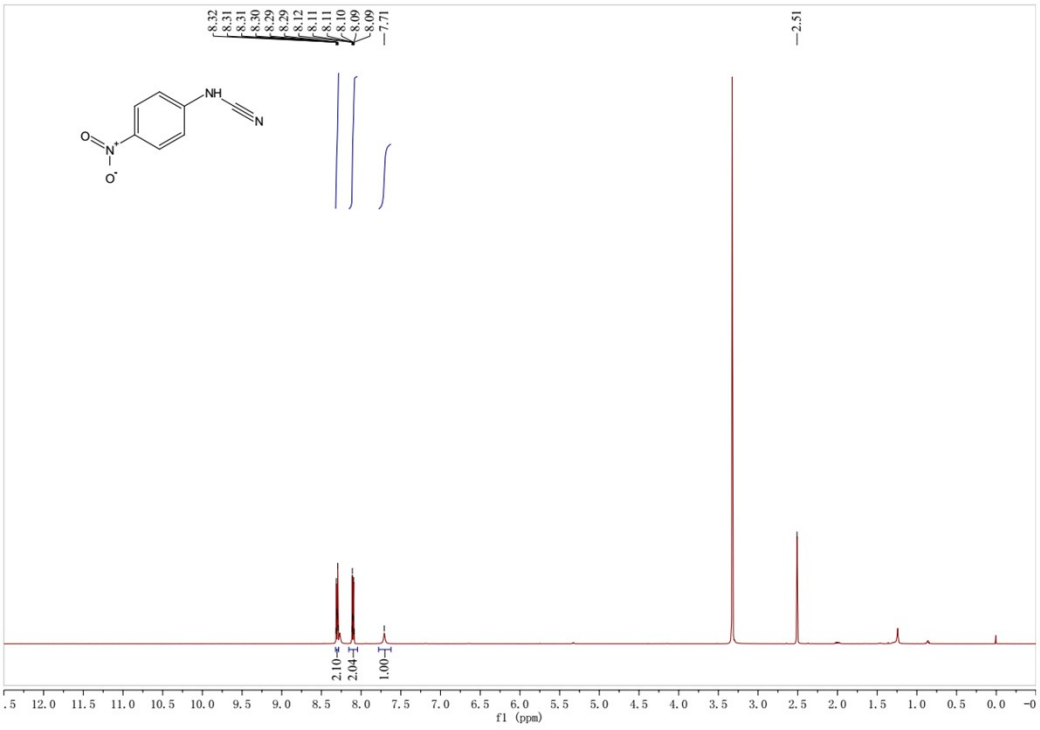


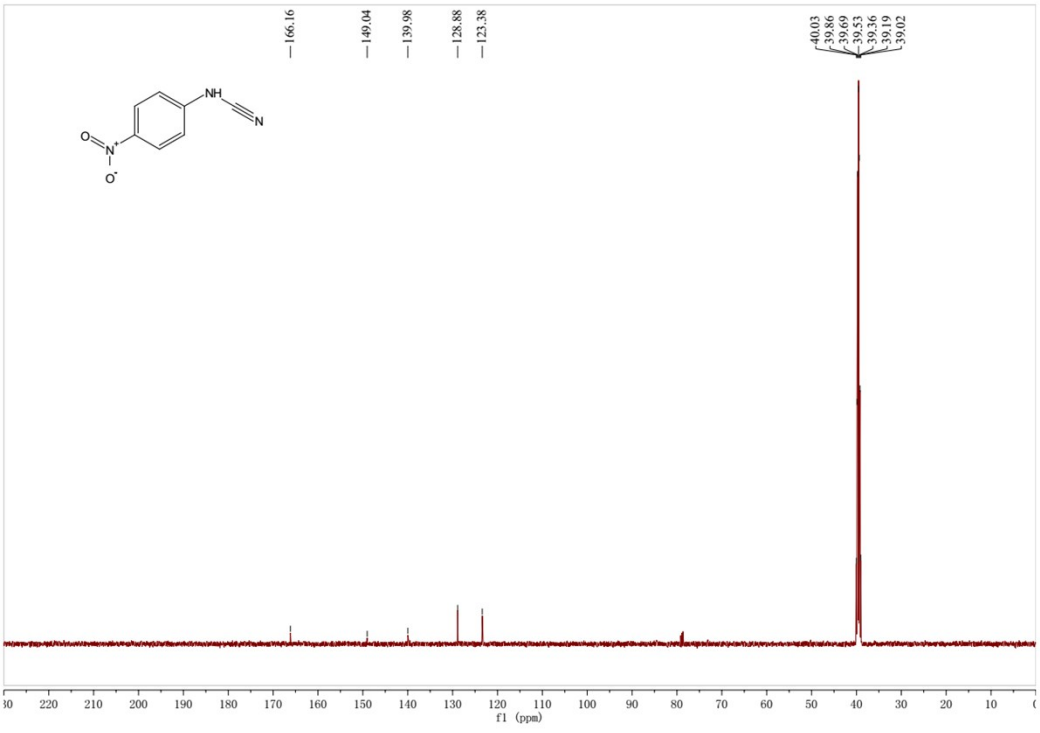
N-(4-Trifluoromethoxyphenyl)cyanamide (3l)



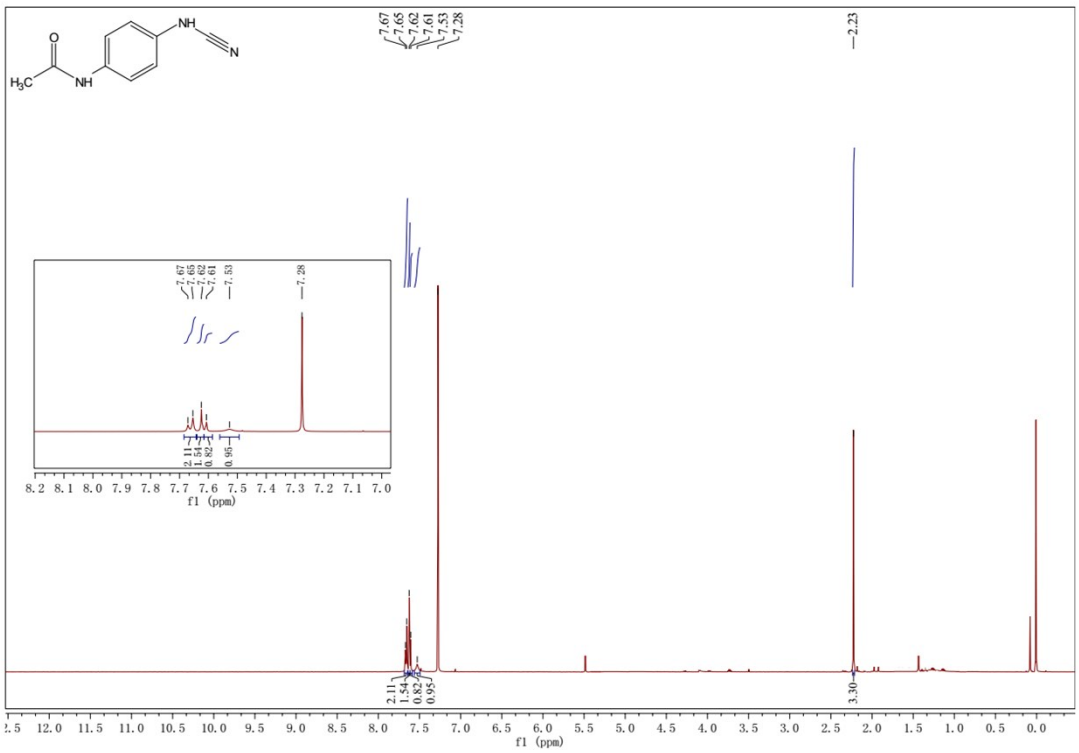


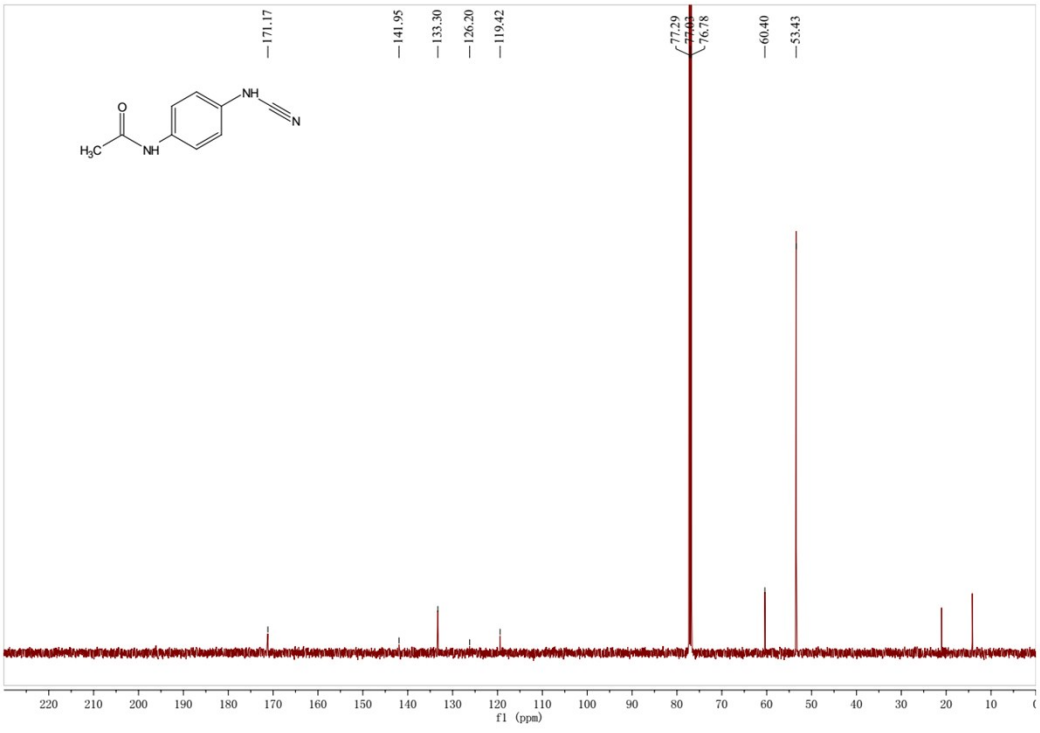
N-(4-Nitrophenyl)cyanamide (3m)



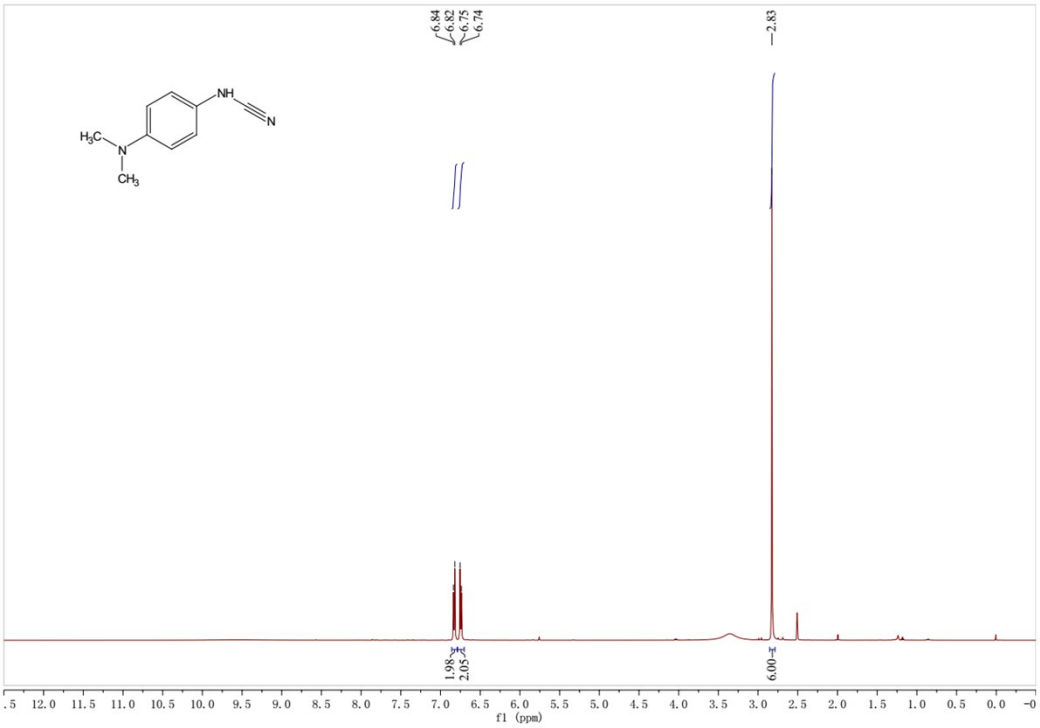


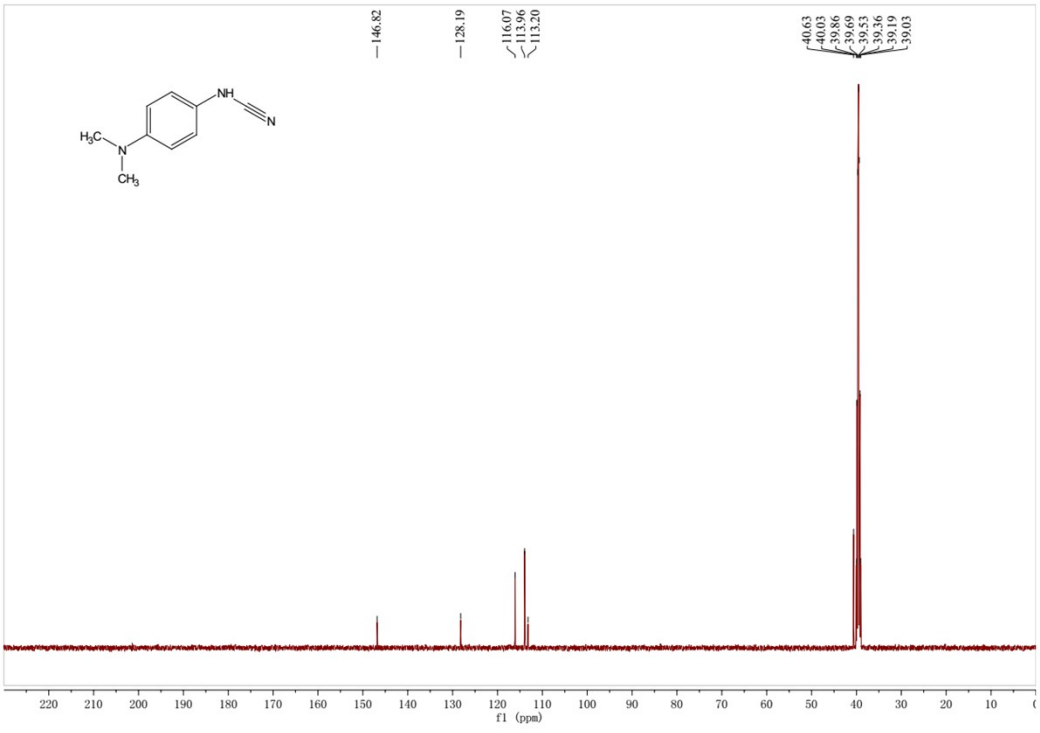
N-(4-Cyanamidophenyl)acetamide (3n)



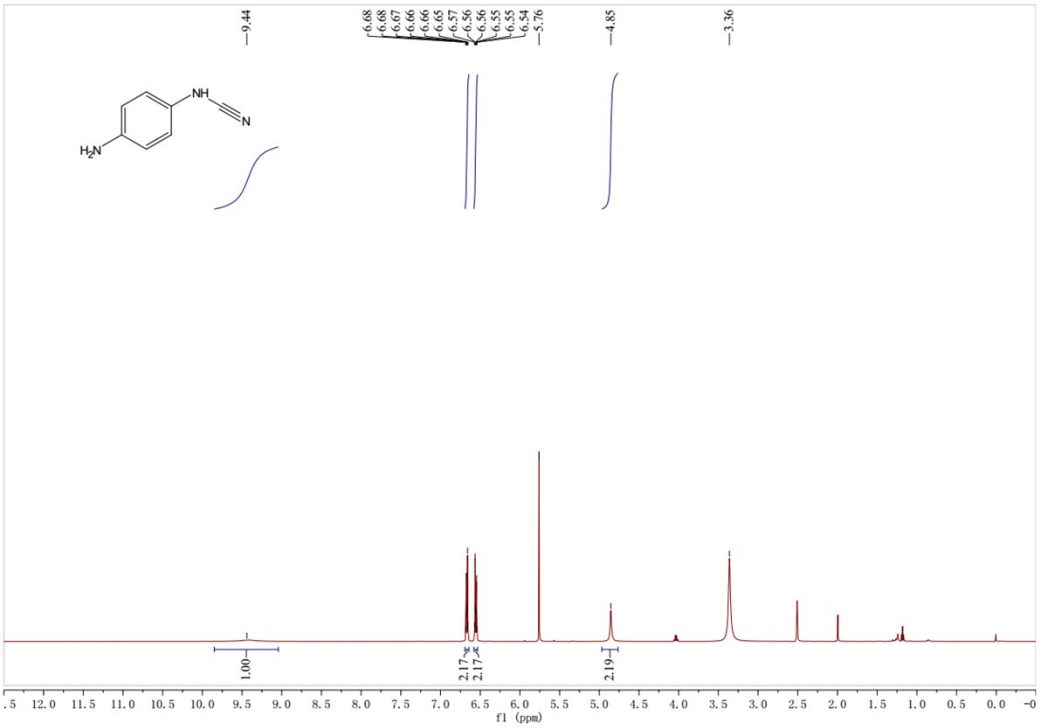


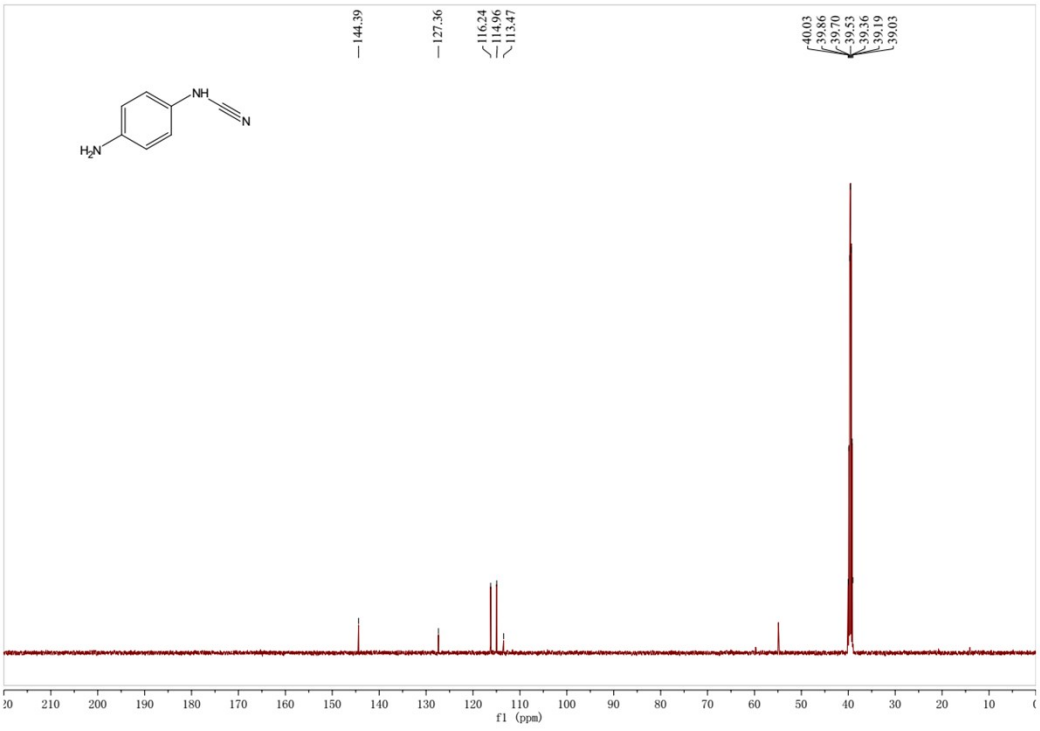
N-(4-Dimethylaminophenyl)cyanamide (3o)



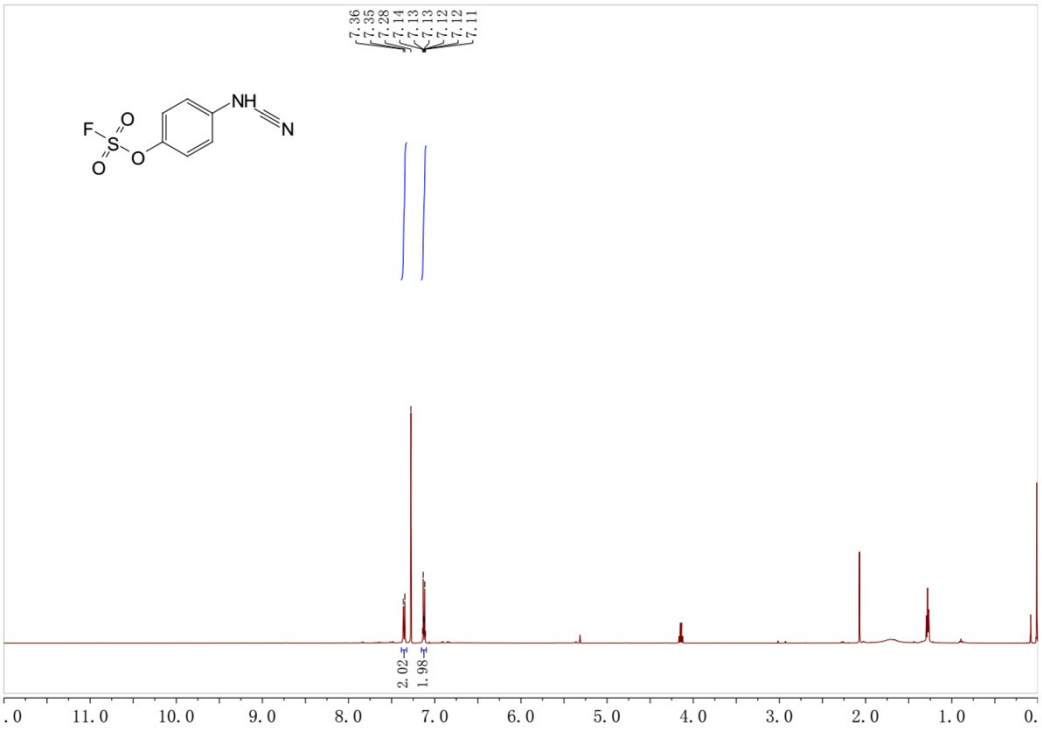


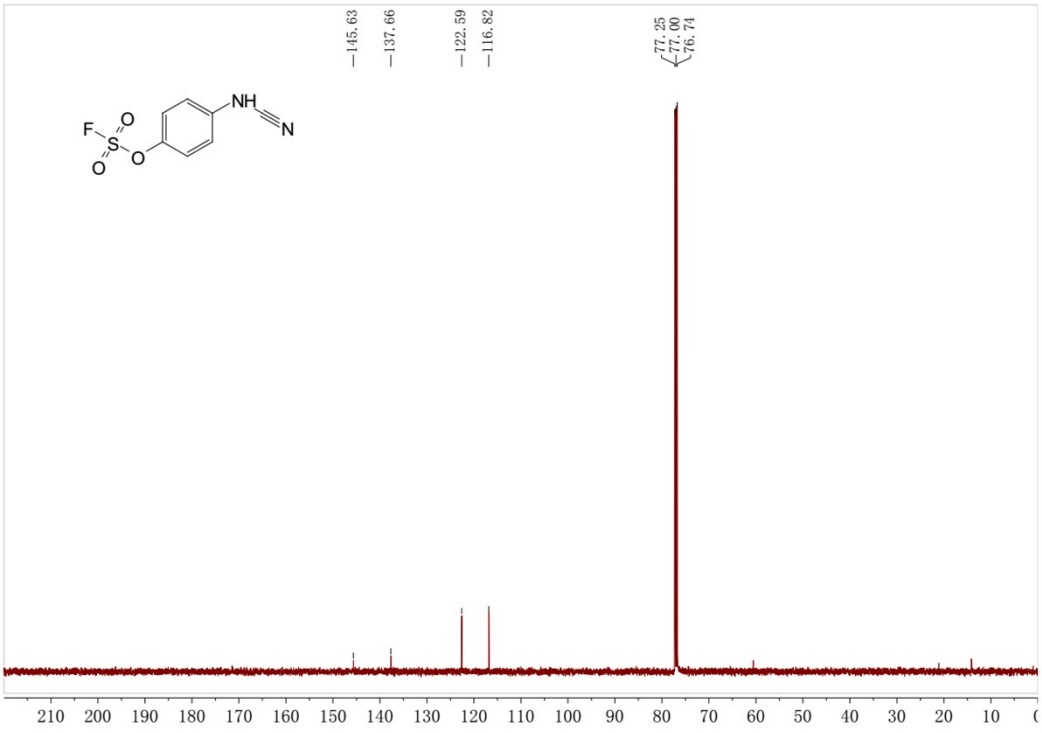
N-(4-Aminophenyl)cyanamide (3p)



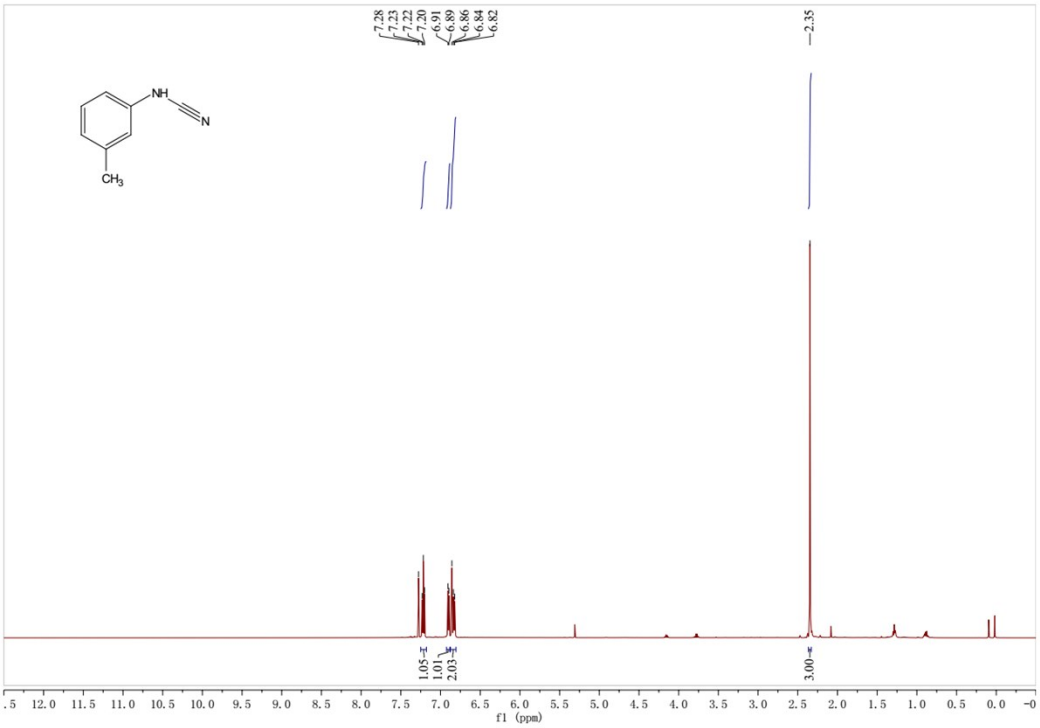


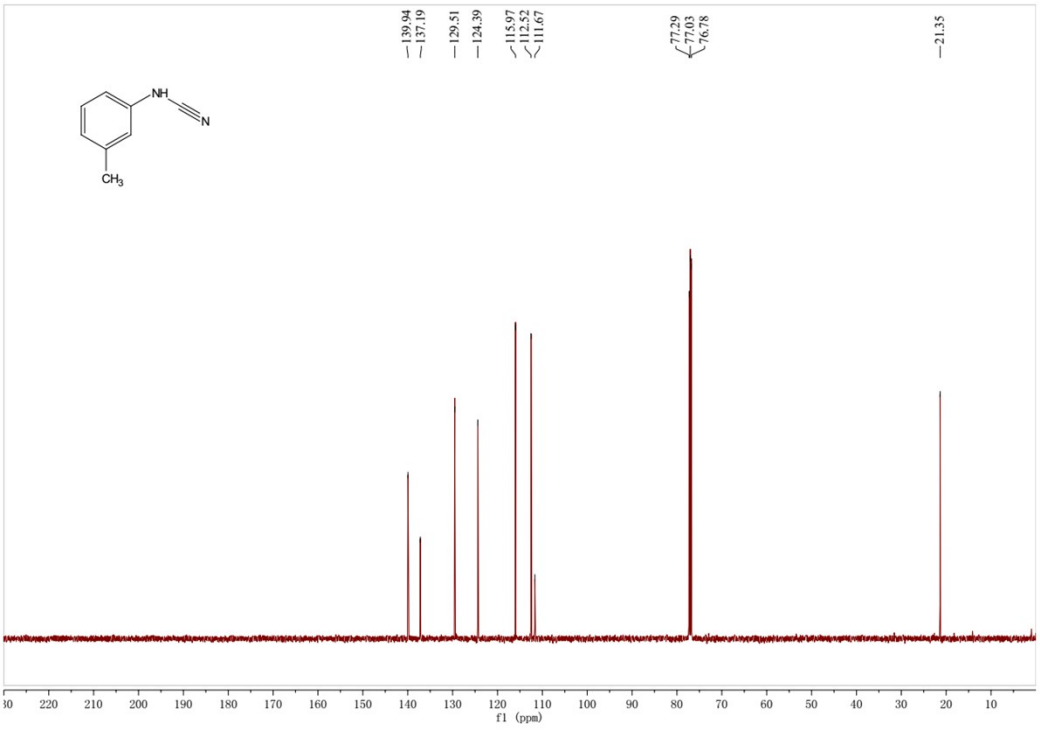
4-Cyanamidophenyl sulfurofluoridate (3q)



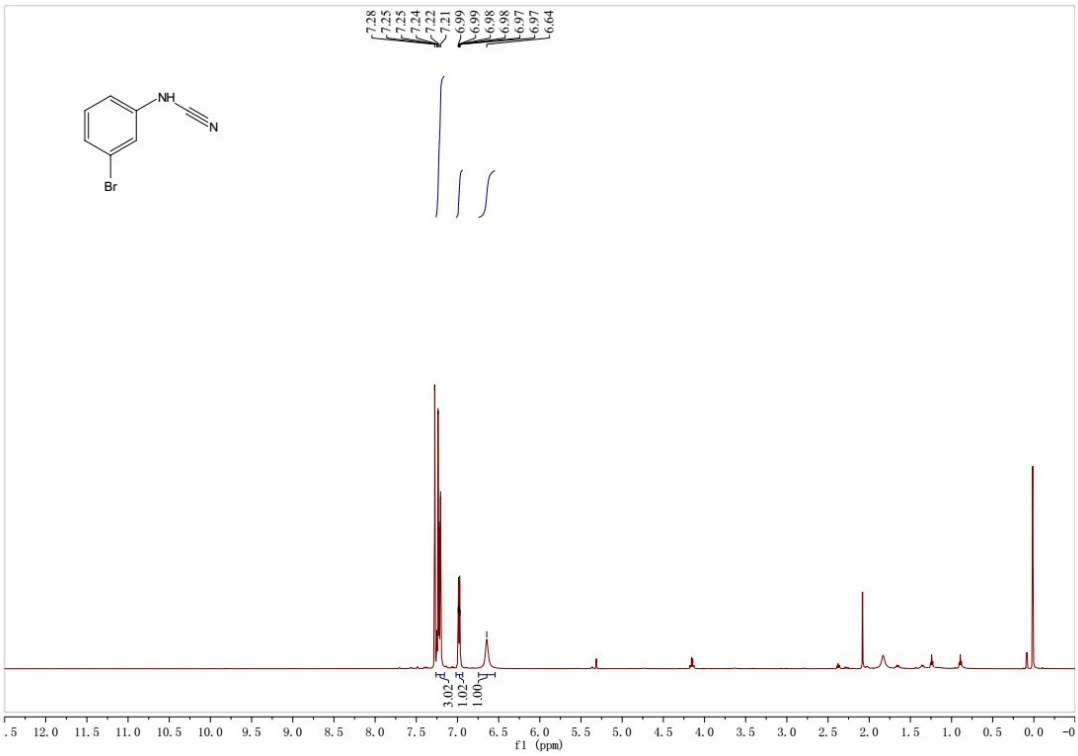


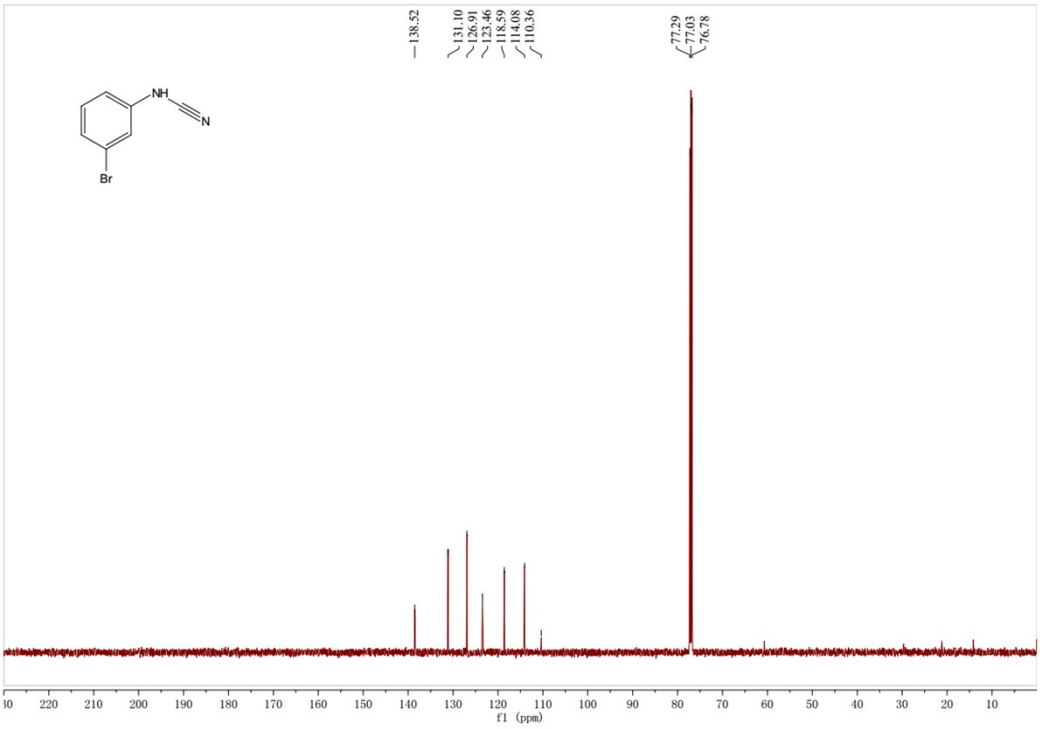
N-(*m*-Tolyl)cyanamide (3r)



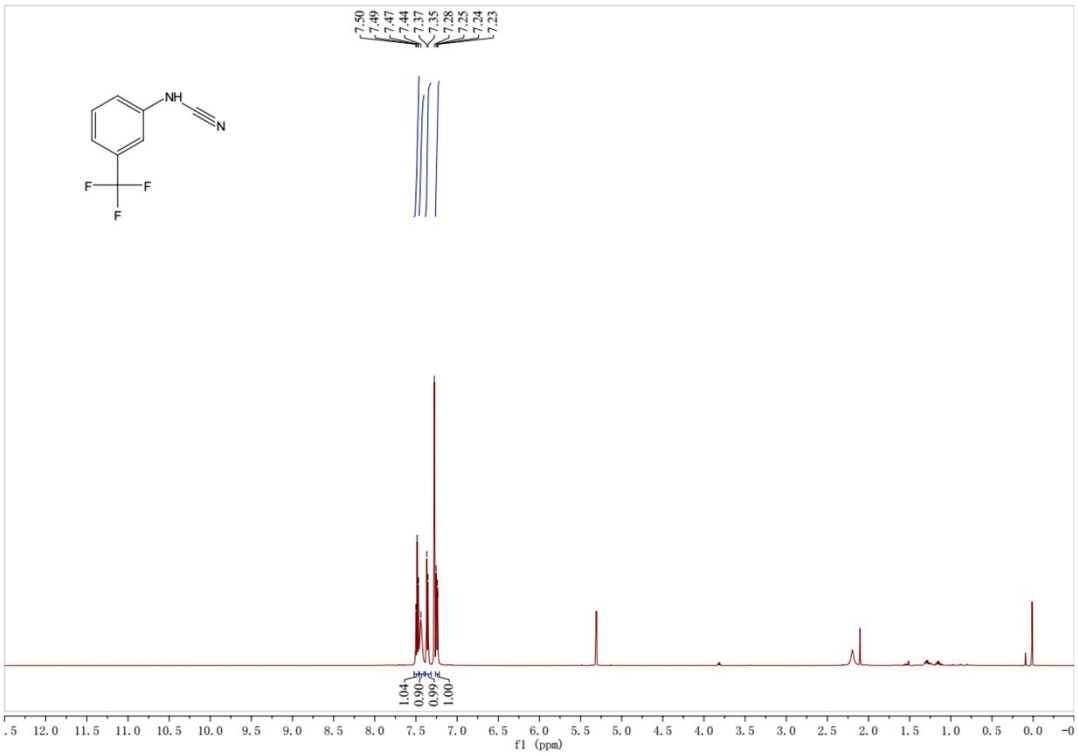


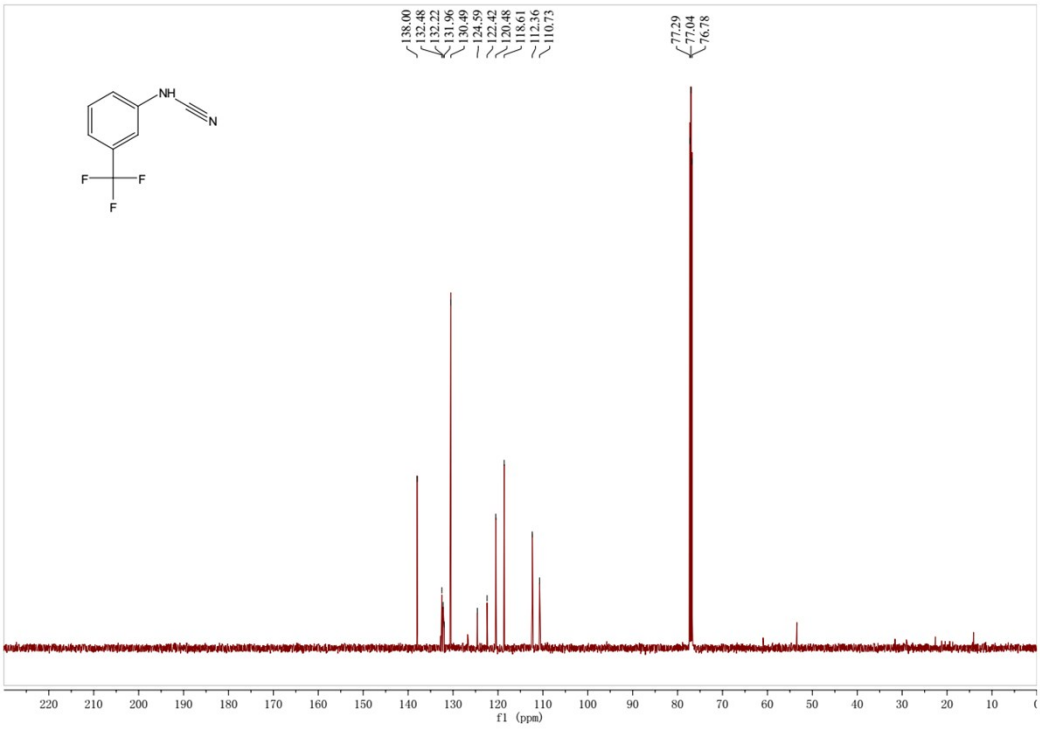
N-(3-Bromophenyl)cyanamide (3s)



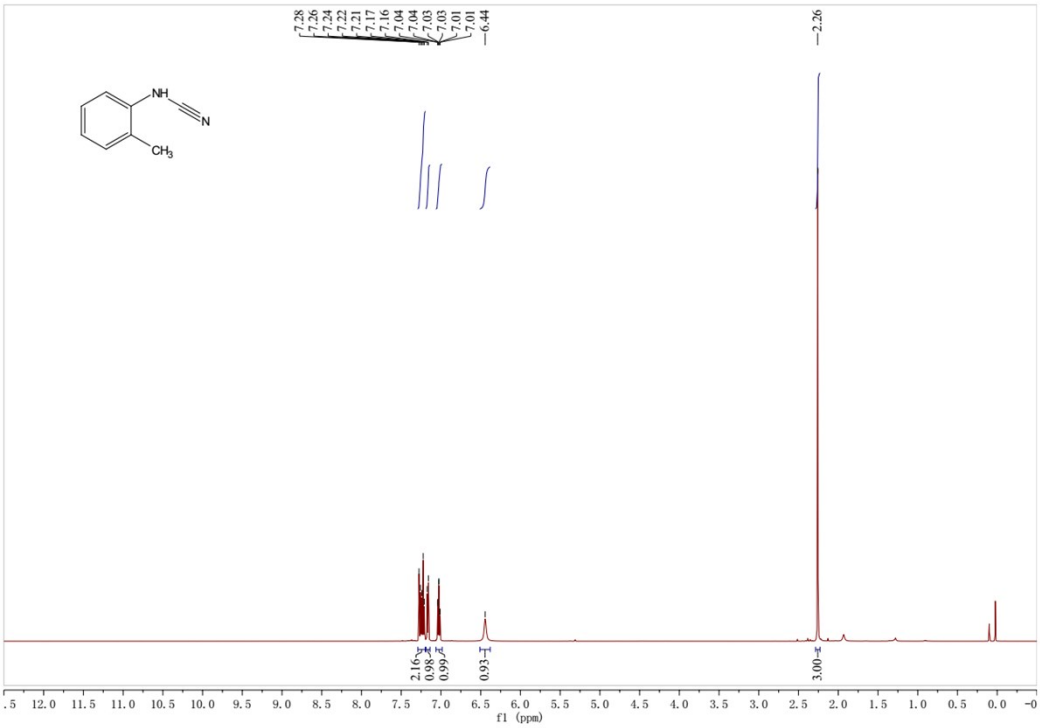


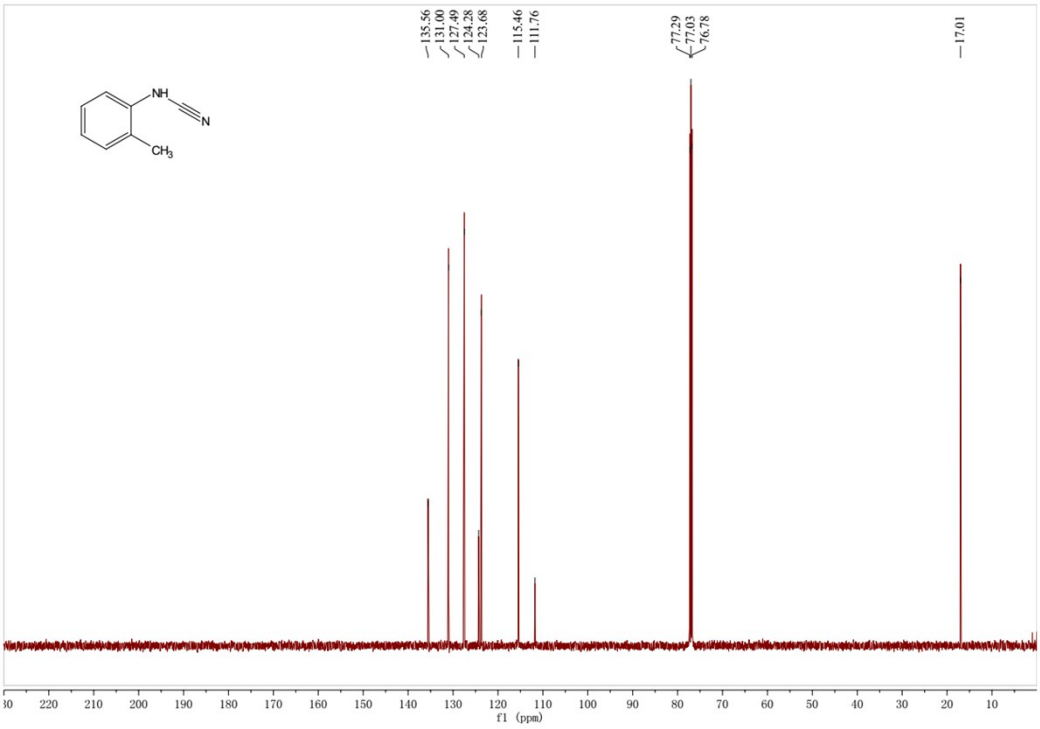
N-(3-Trifluoromethylphenyl)cyanamide (3t)



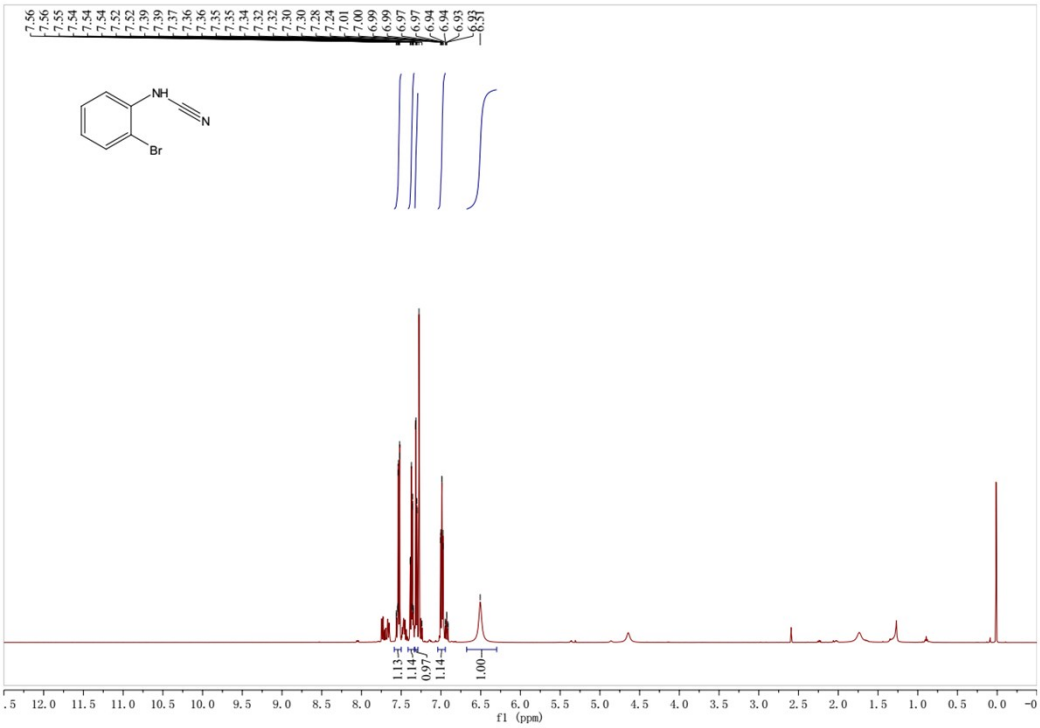


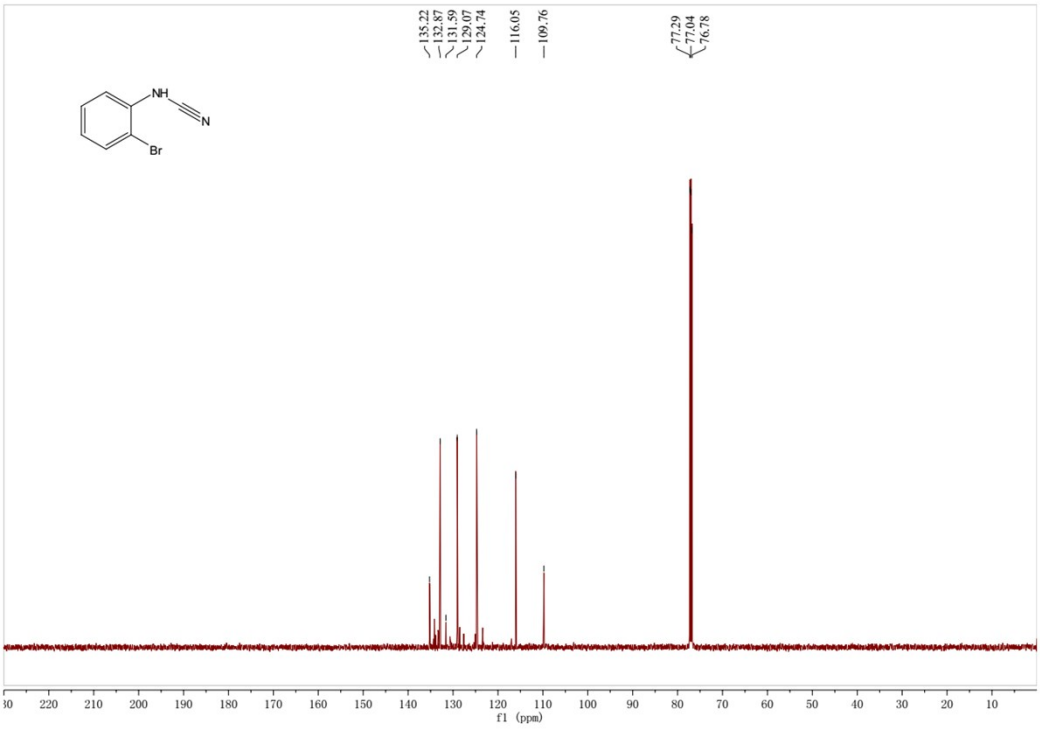
N-(*o*-Tolyl)cyanamide (3u)



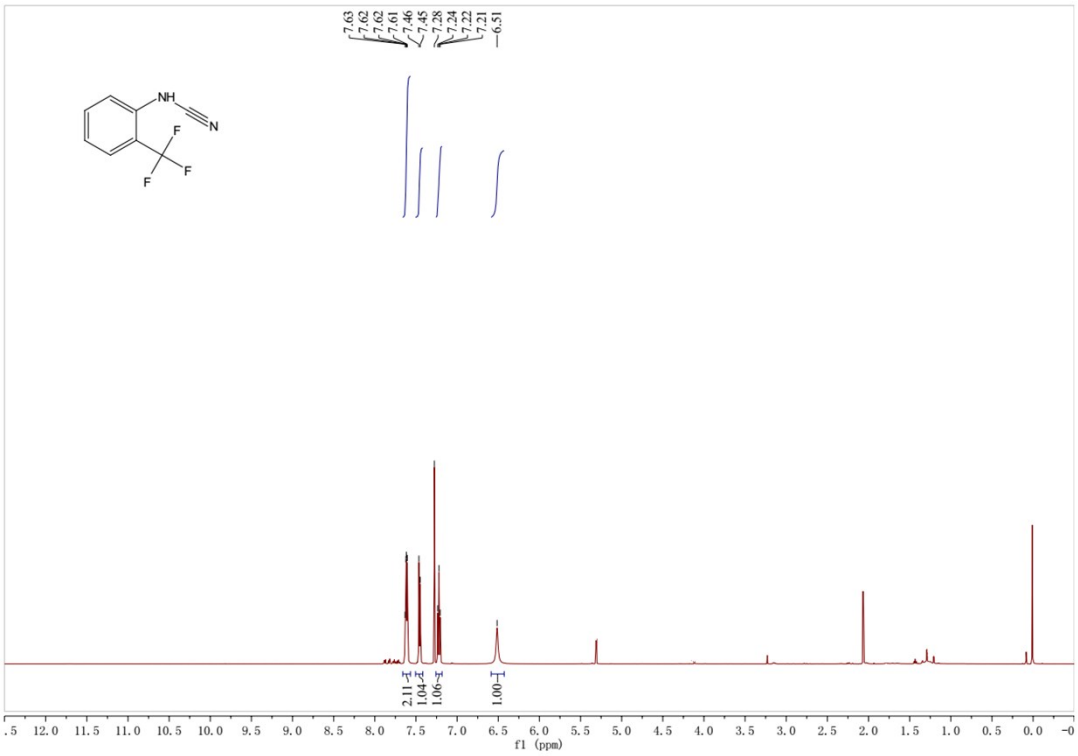


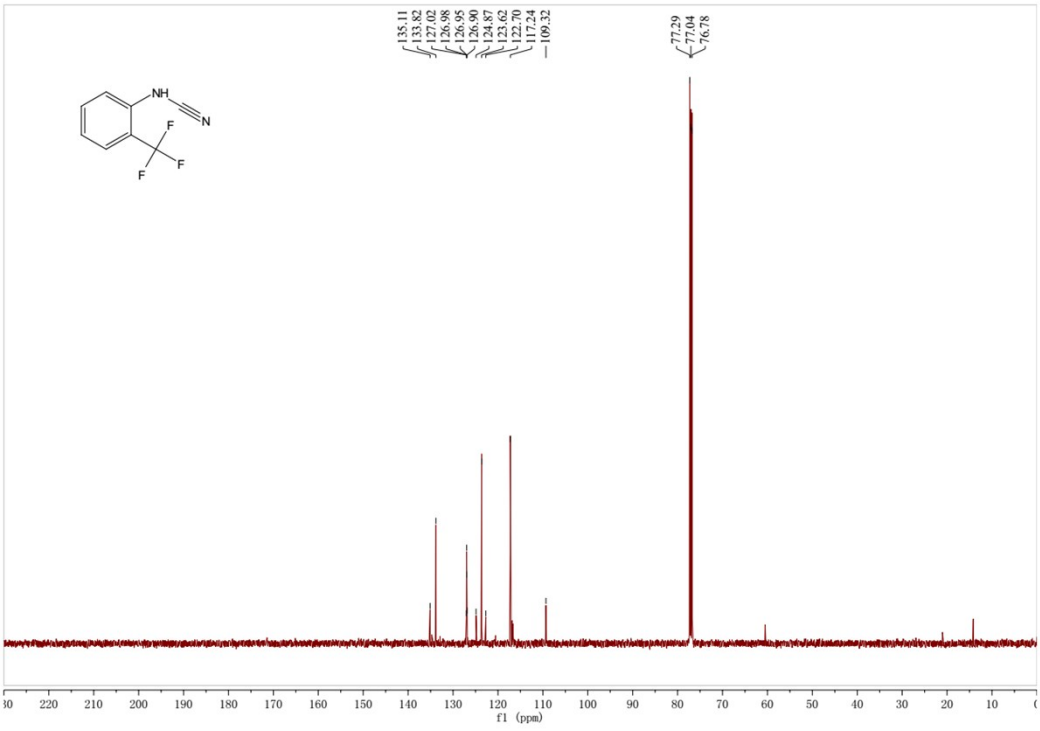
N-(2-Bromophenyl)cyanamide (3v)



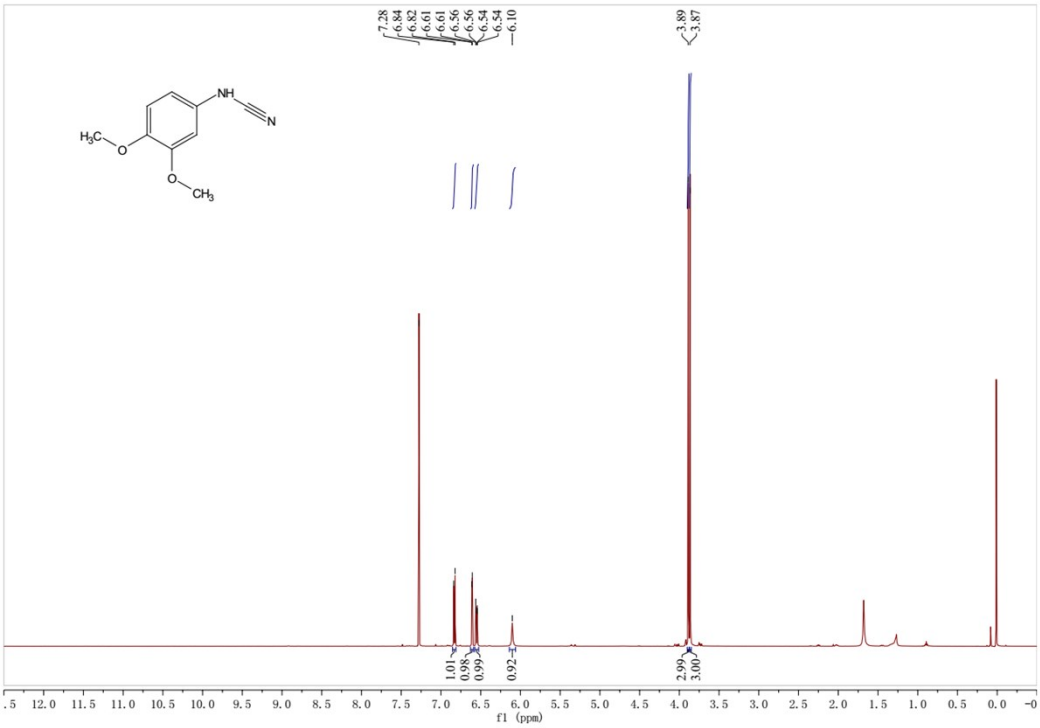


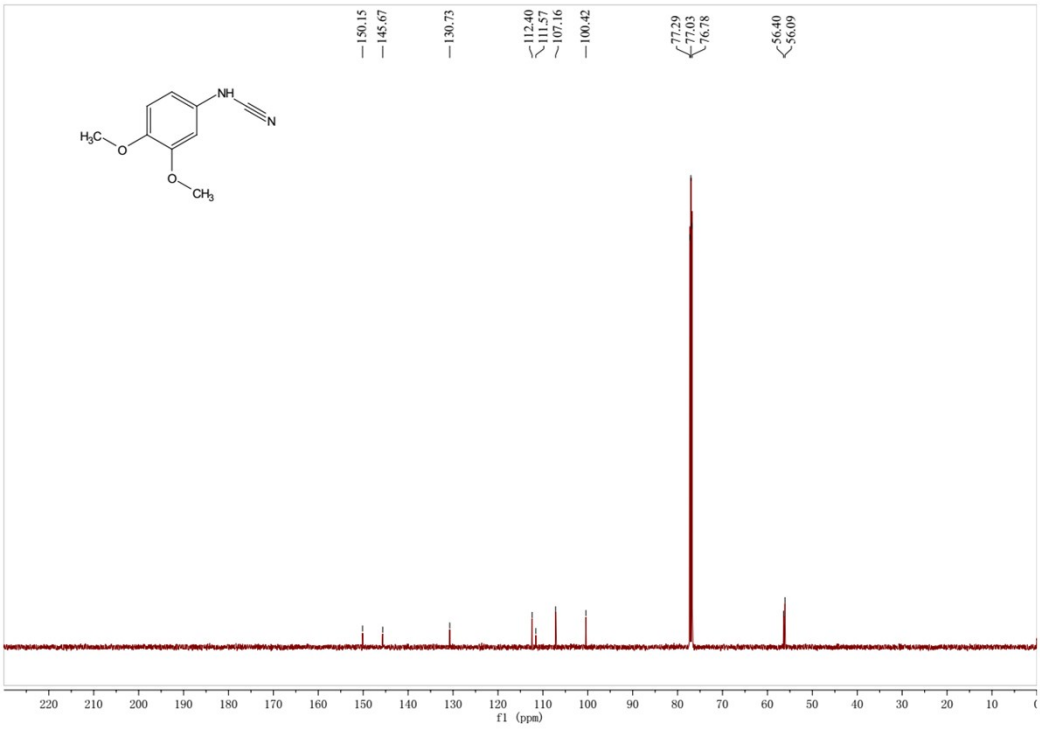
N-(2-Trifluoromethylphenyl)cyanamide (3w)



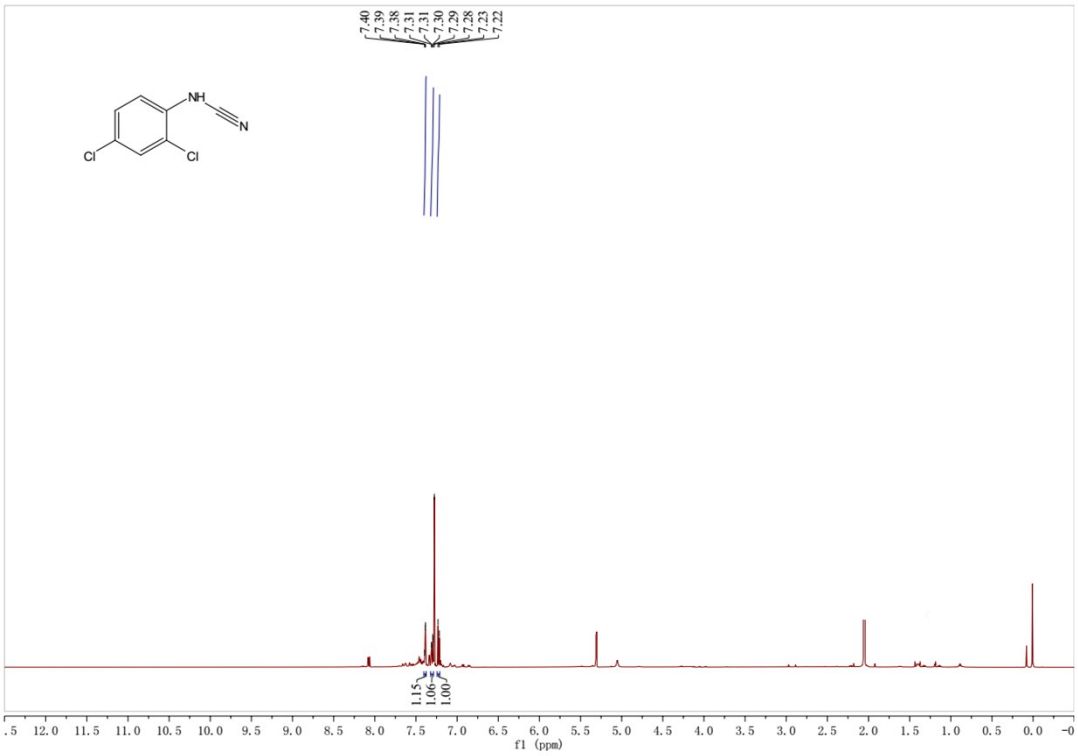


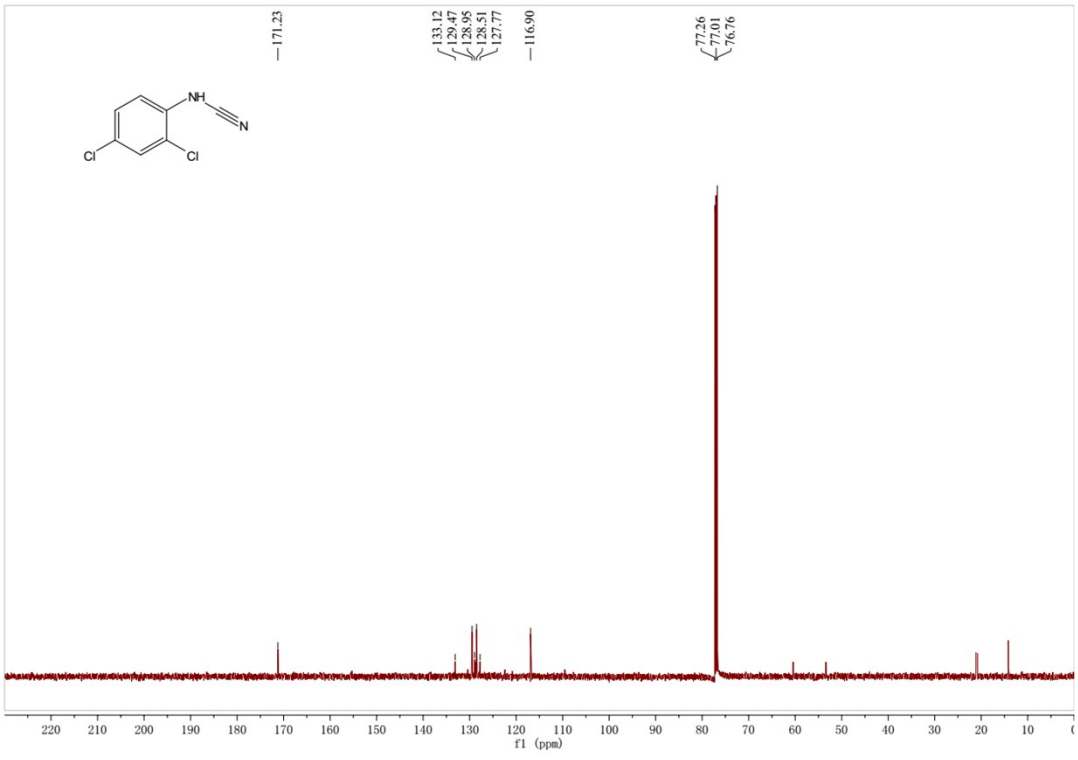
N-(3,4-Dimethoxyphenyl)cyanamide (3x)



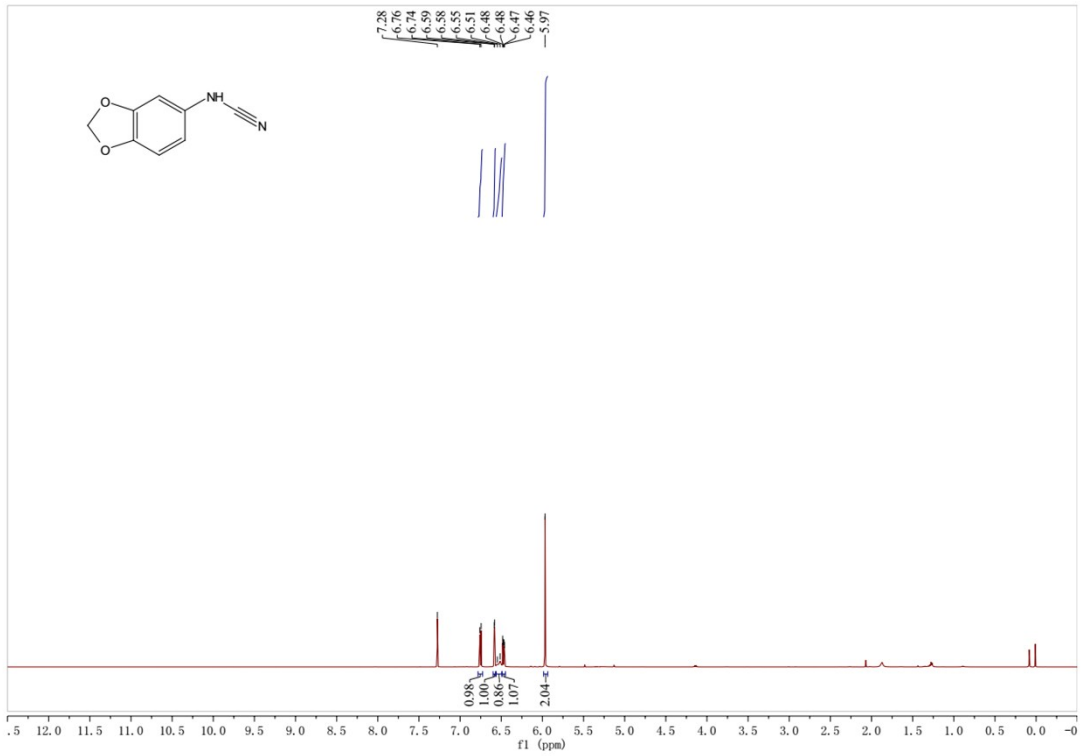


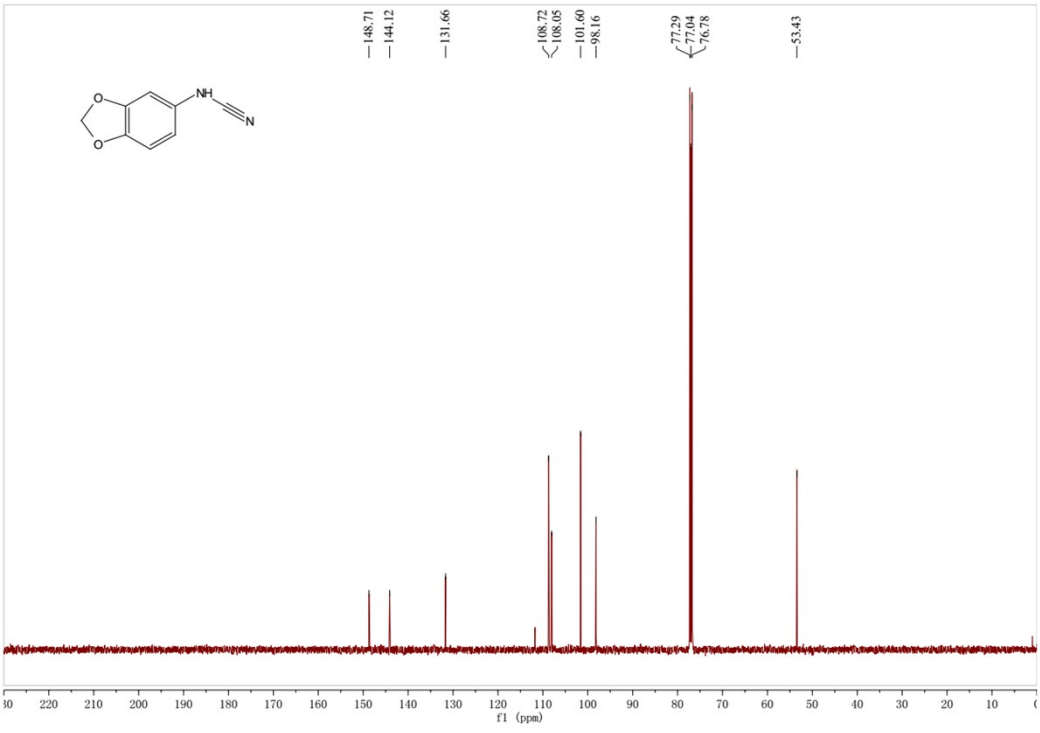
N-(2,4-Dichlorophenyl)cyanamide (3y)



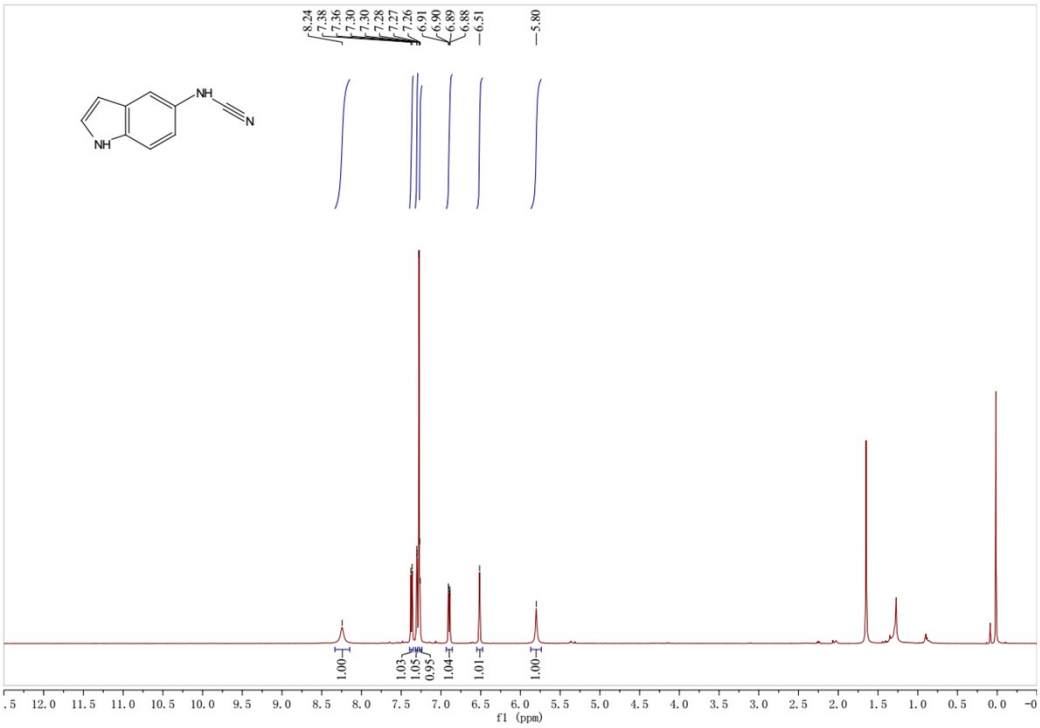


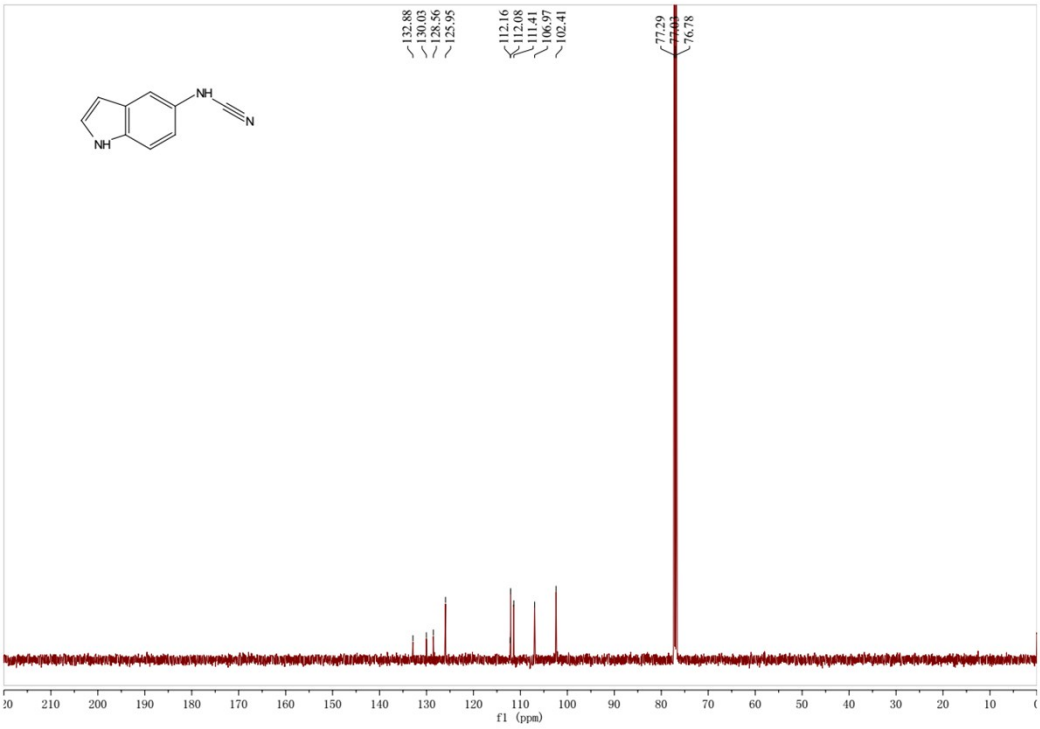
N-(Benzo[d][1,3]dioxol-5-yl)cyanamide (3z)



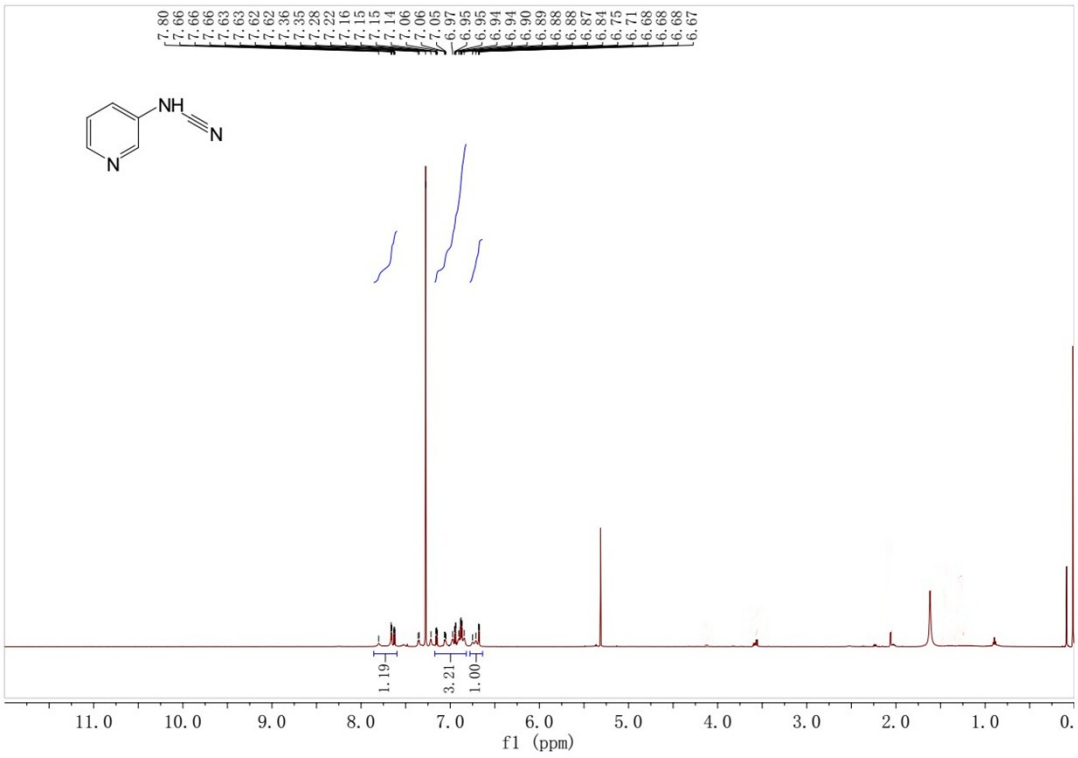


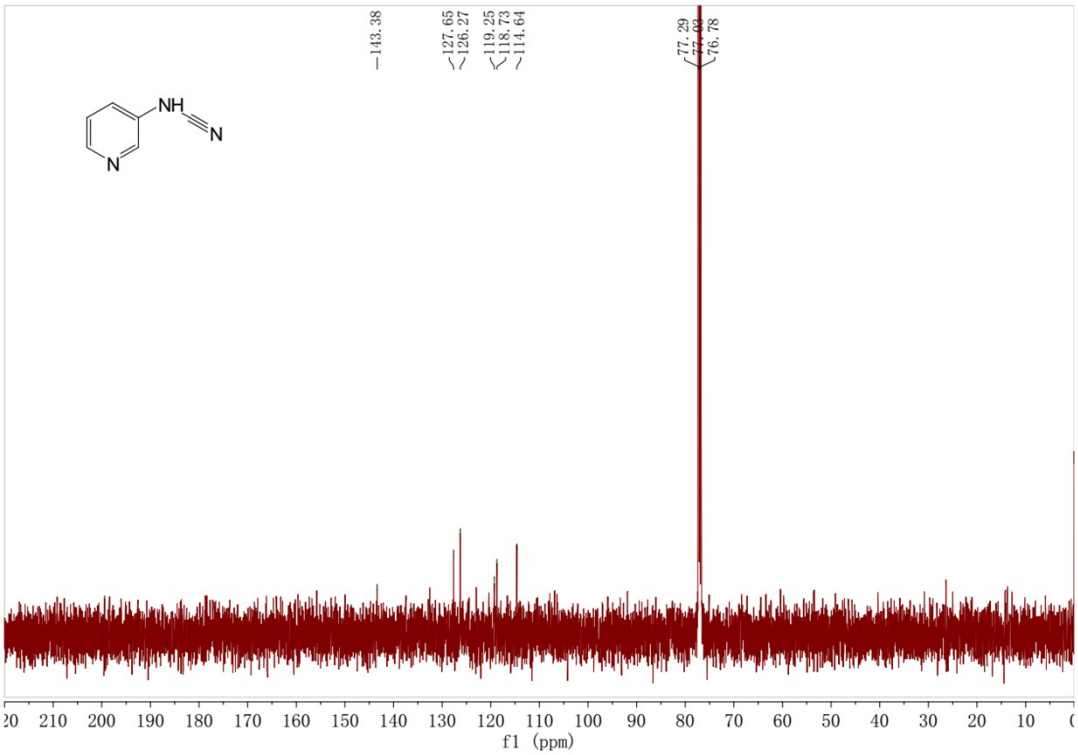
N-(1*H*-Indol-5-yl)cyanamide (3aa)



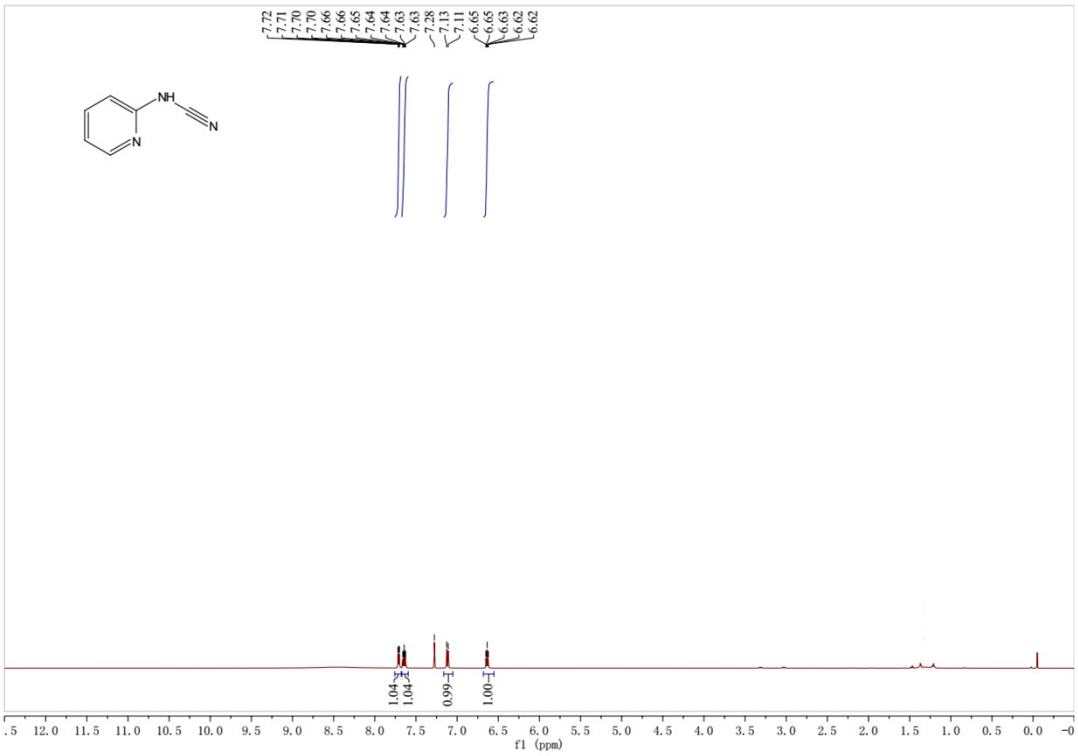


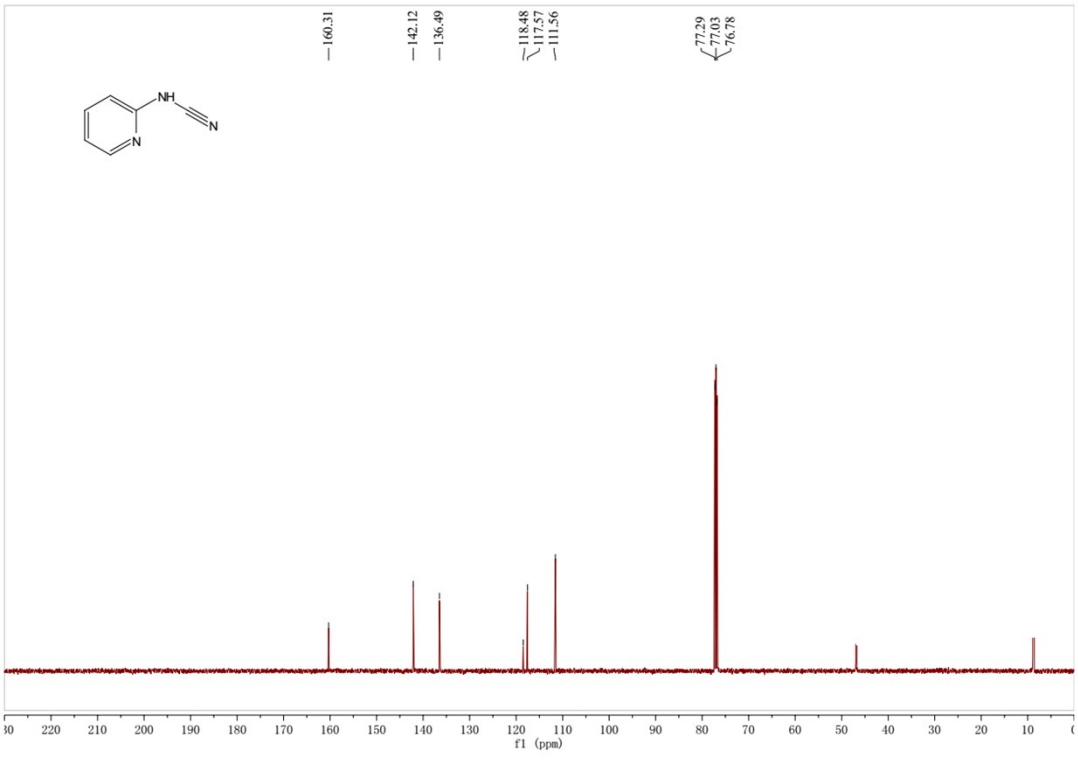
N-(Pyridin-3-yl)cyanamide (3ab)



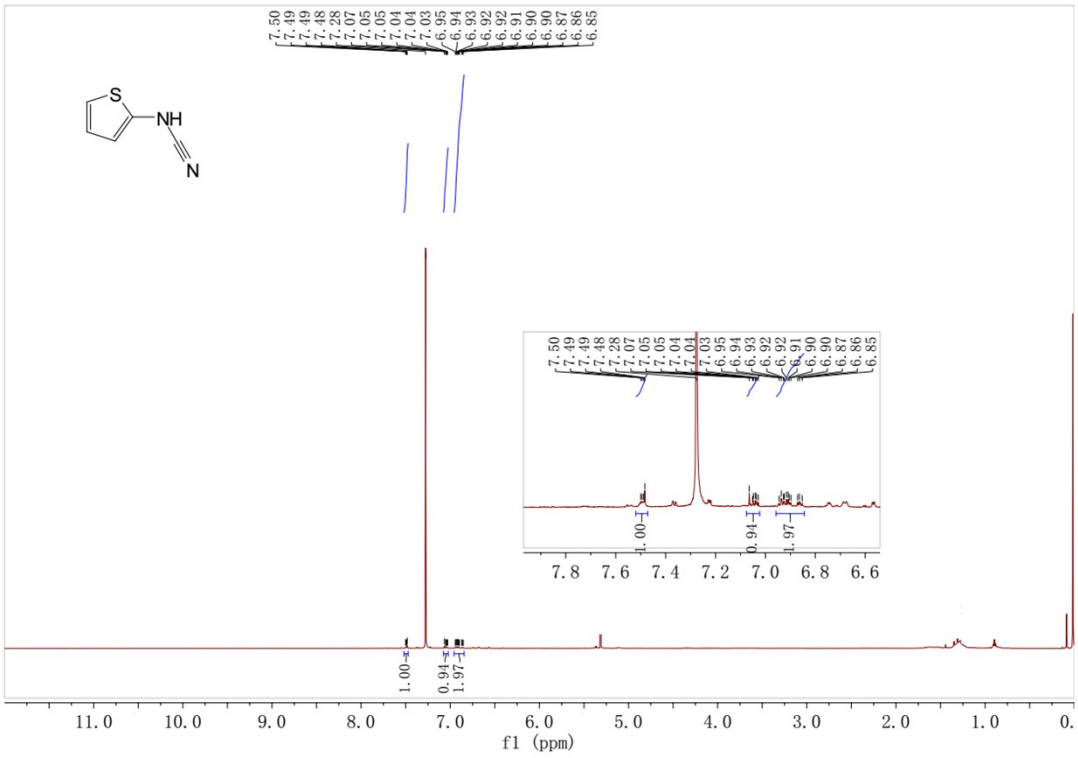


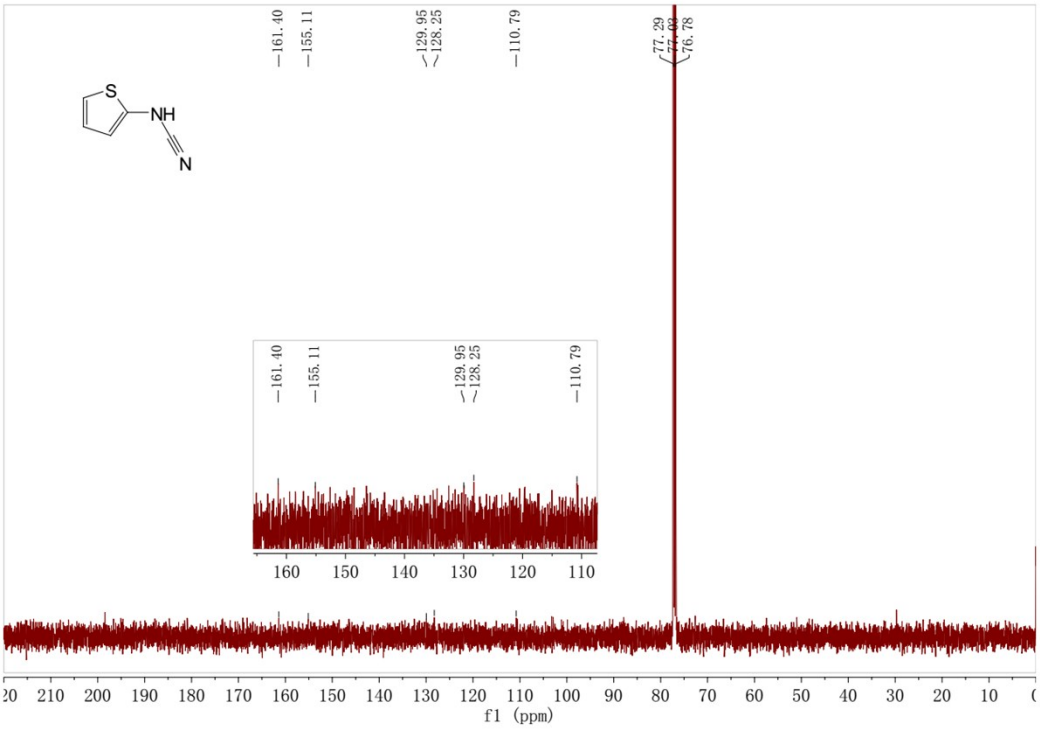
N-(Pyridin-2-yl)cyanamide (3ac)



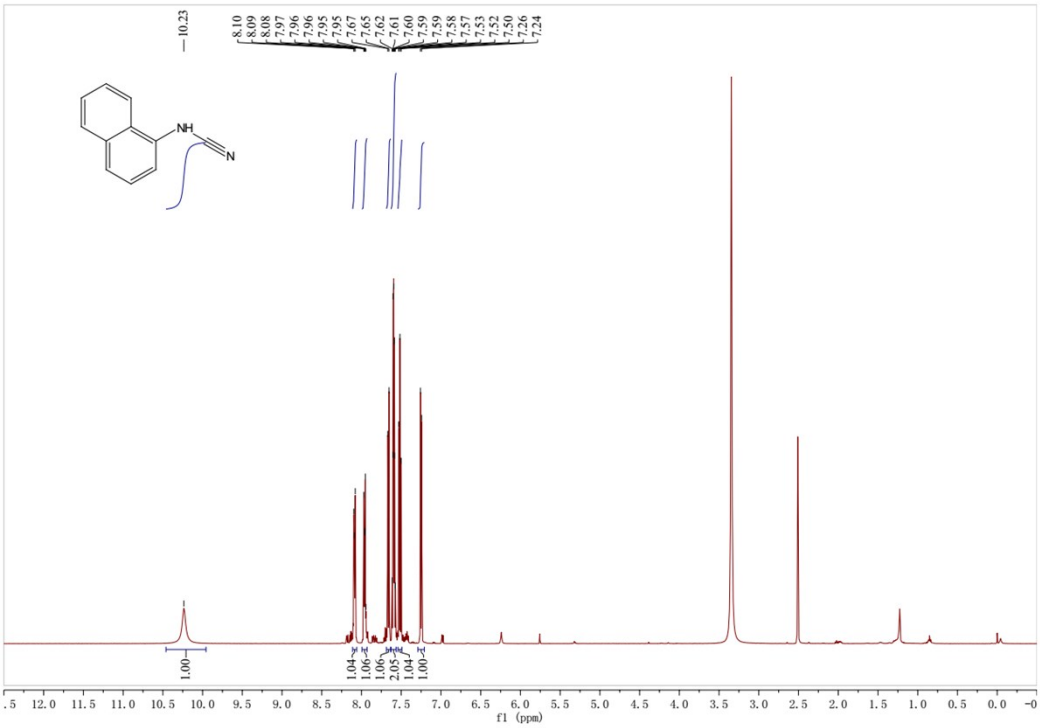


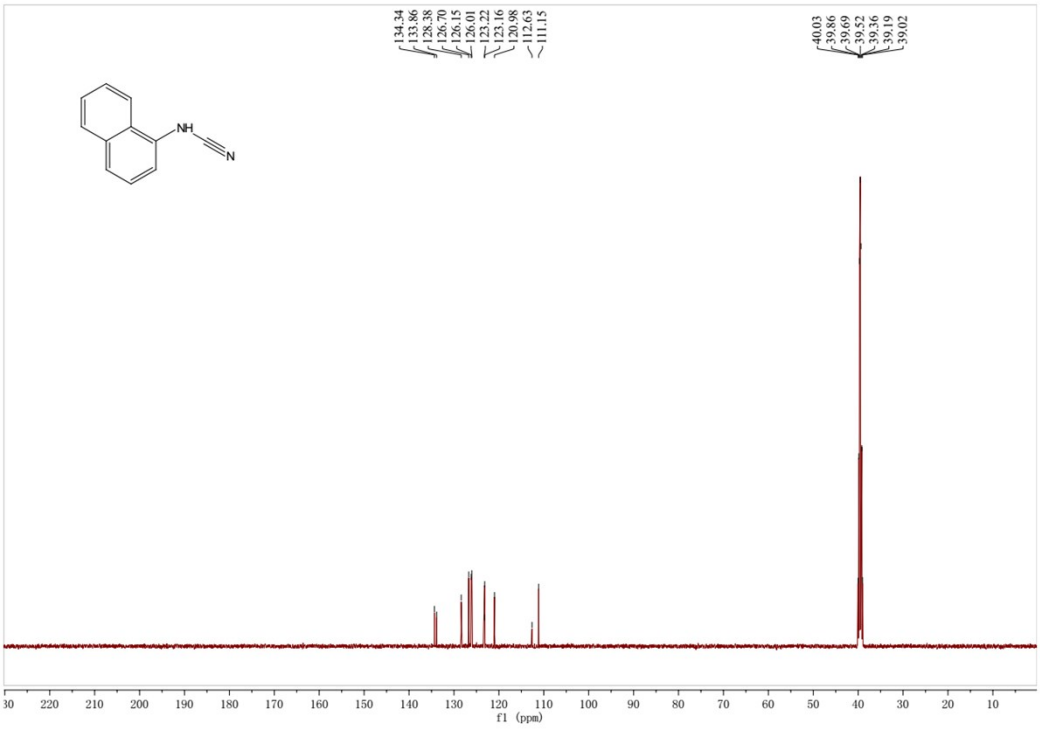
N-(Thiophen-2-yl)cyanamide (3ad)



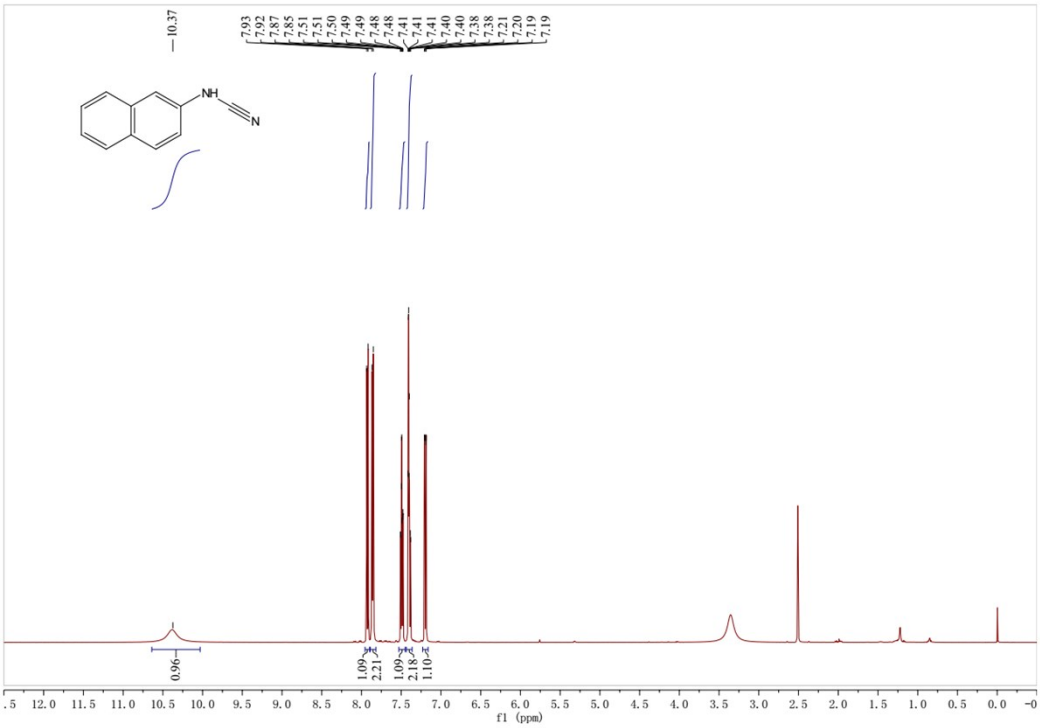


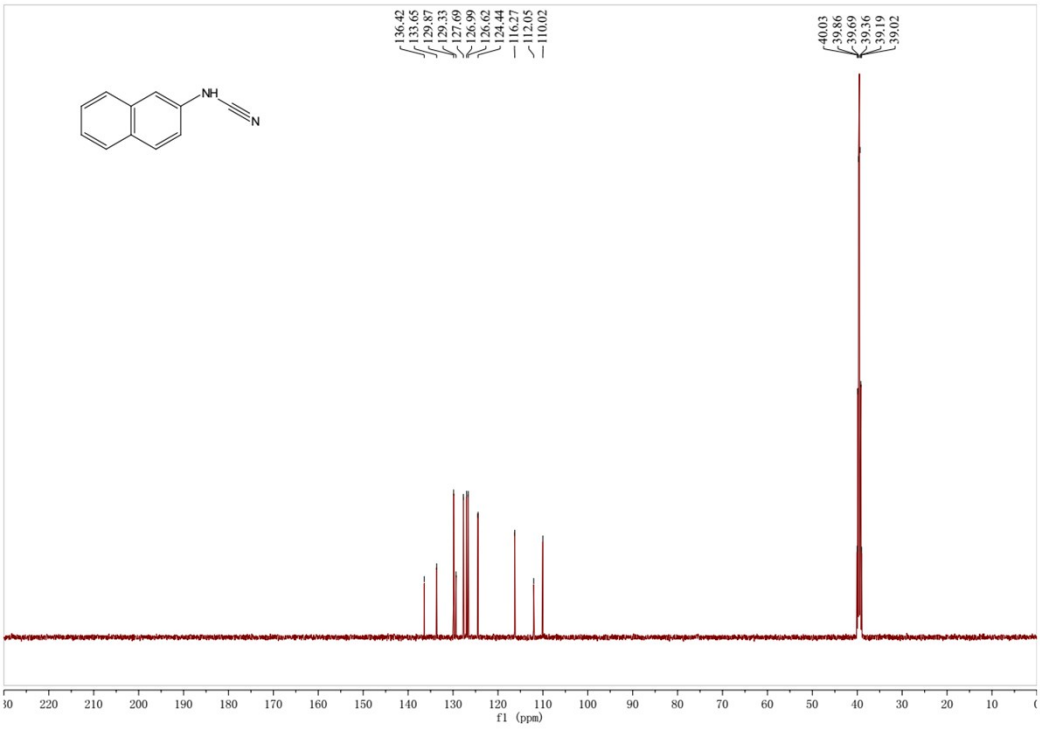
N-(Naphthalen-1-yl)cyanamide (3ae)



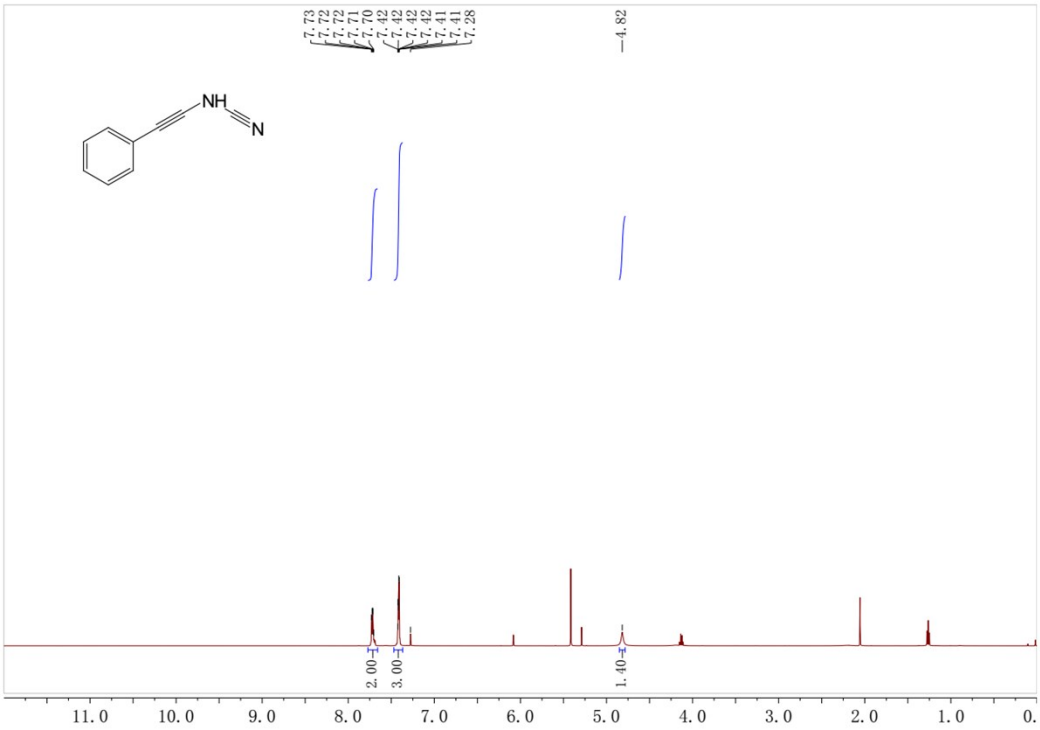


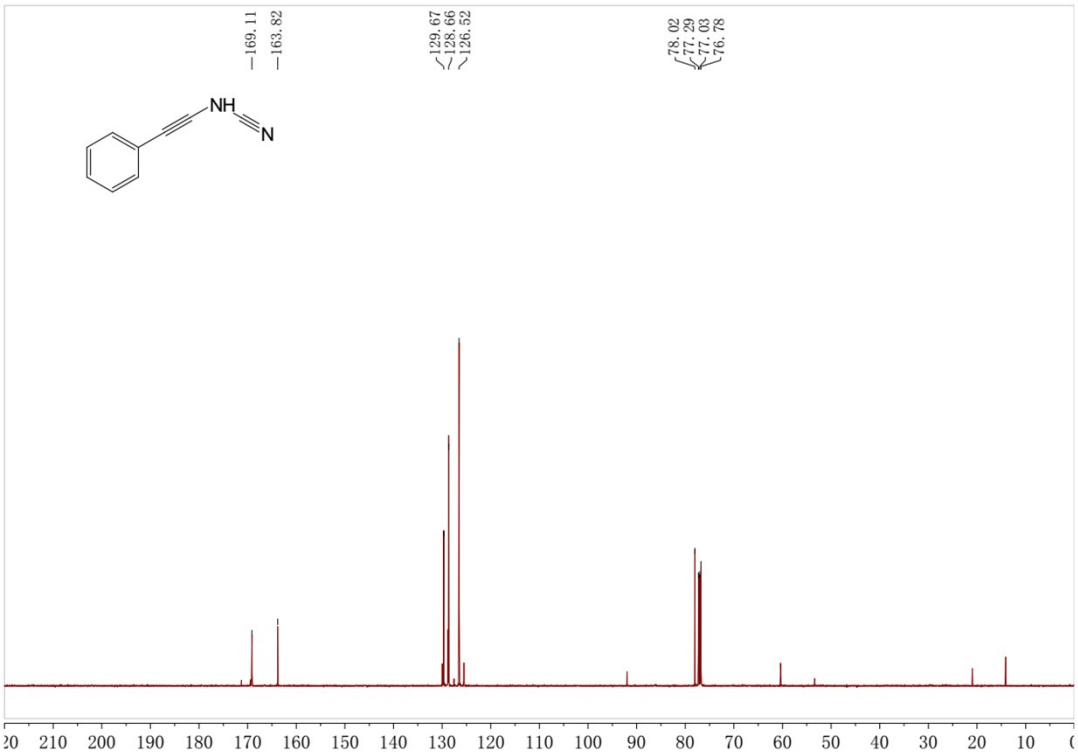
N-(Naphthalen-2-yl)cyanamide (3af)



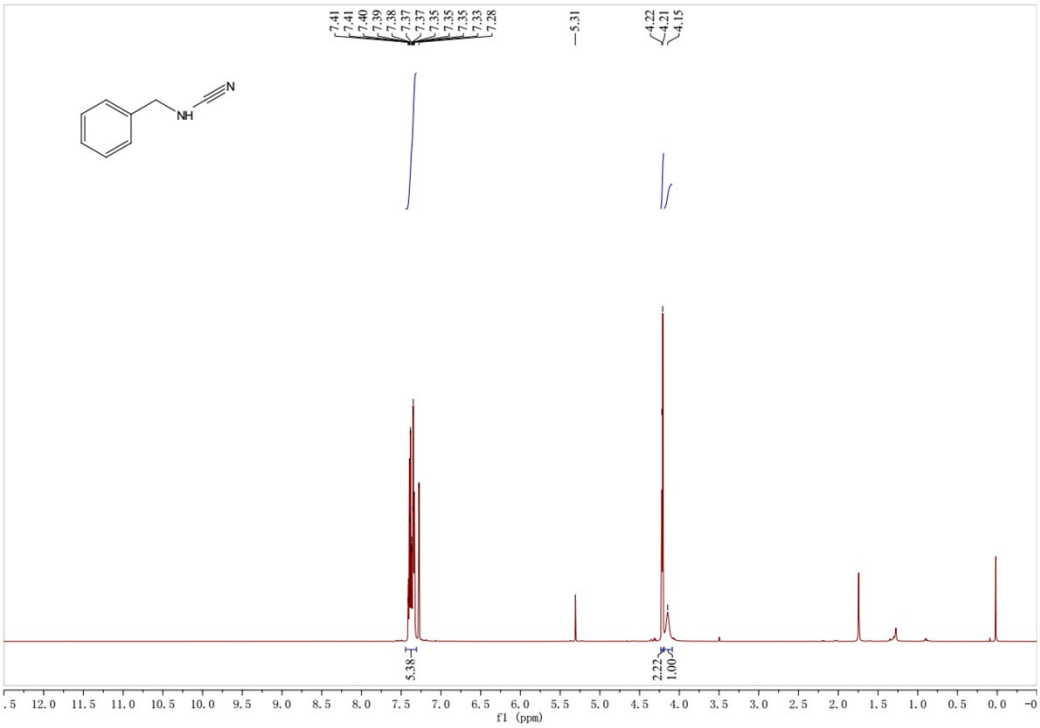


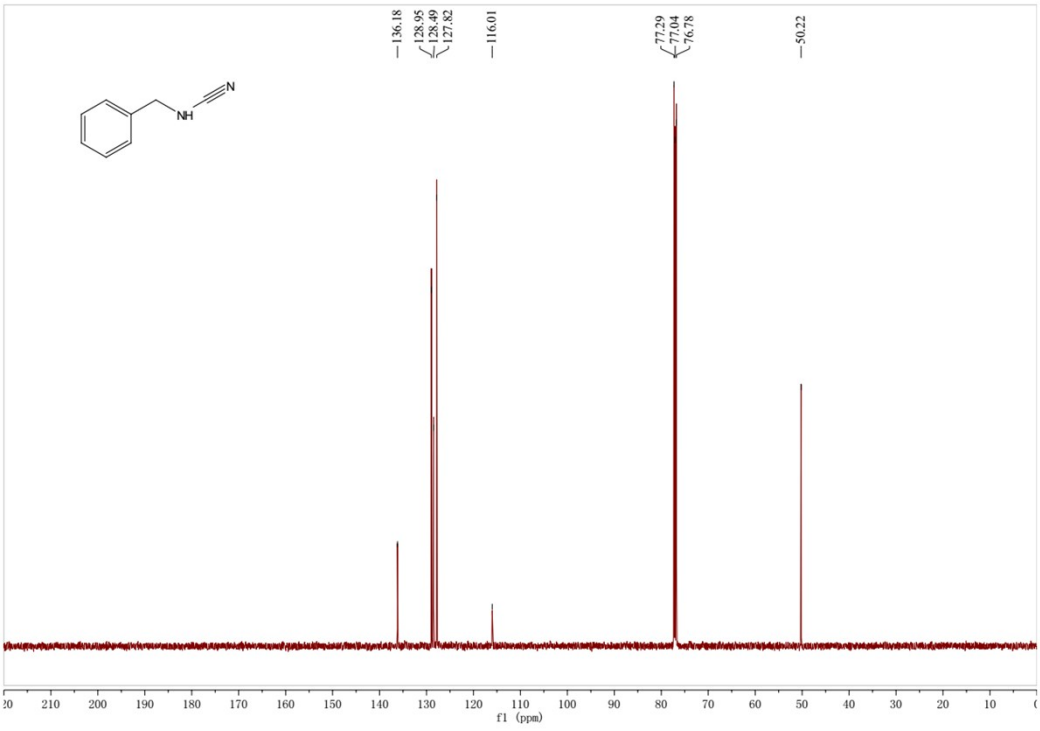
N-(Phenylethynyl)cyanamide (3ag)



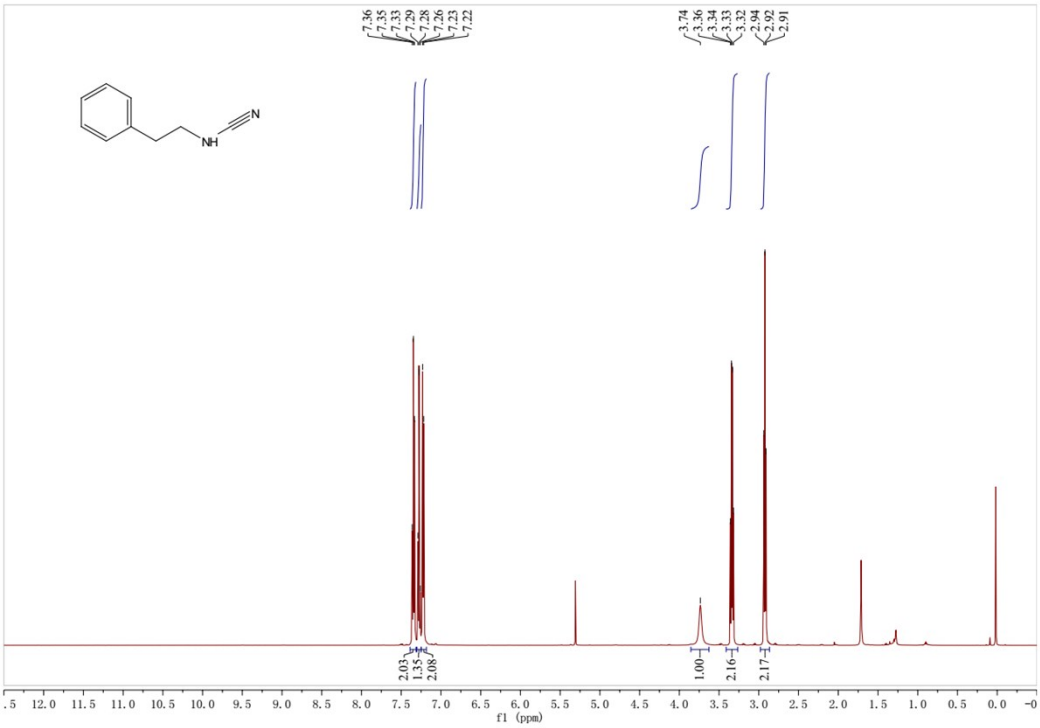


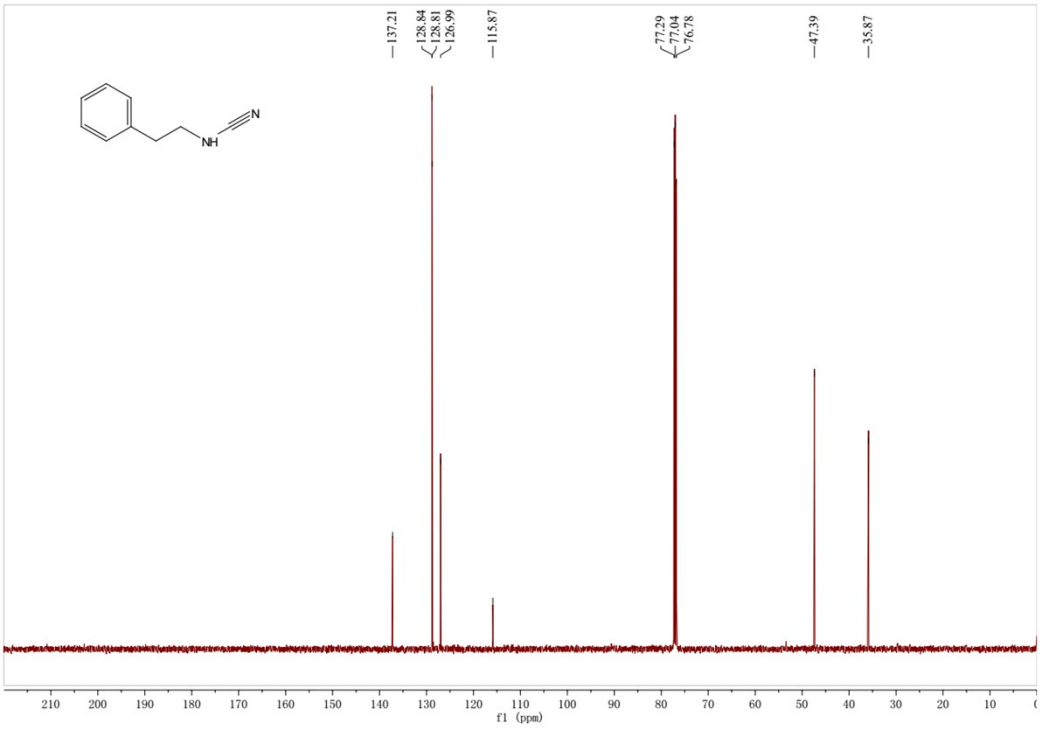
N-Benzylcyanamide (3ah)



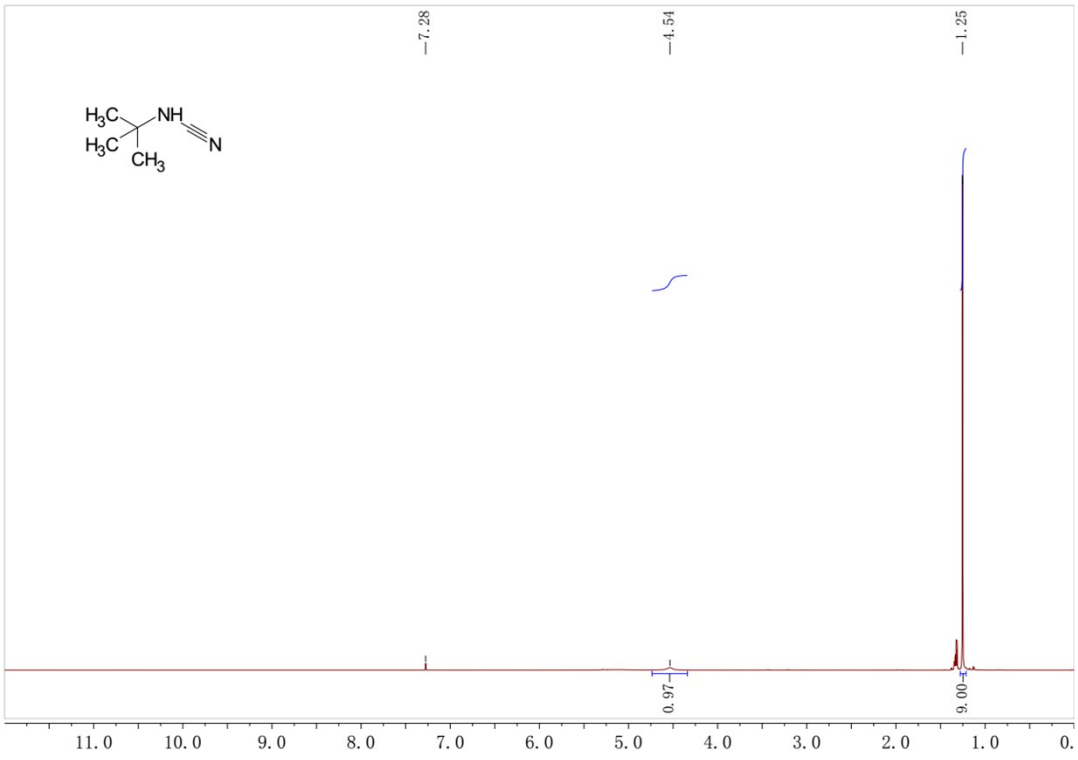


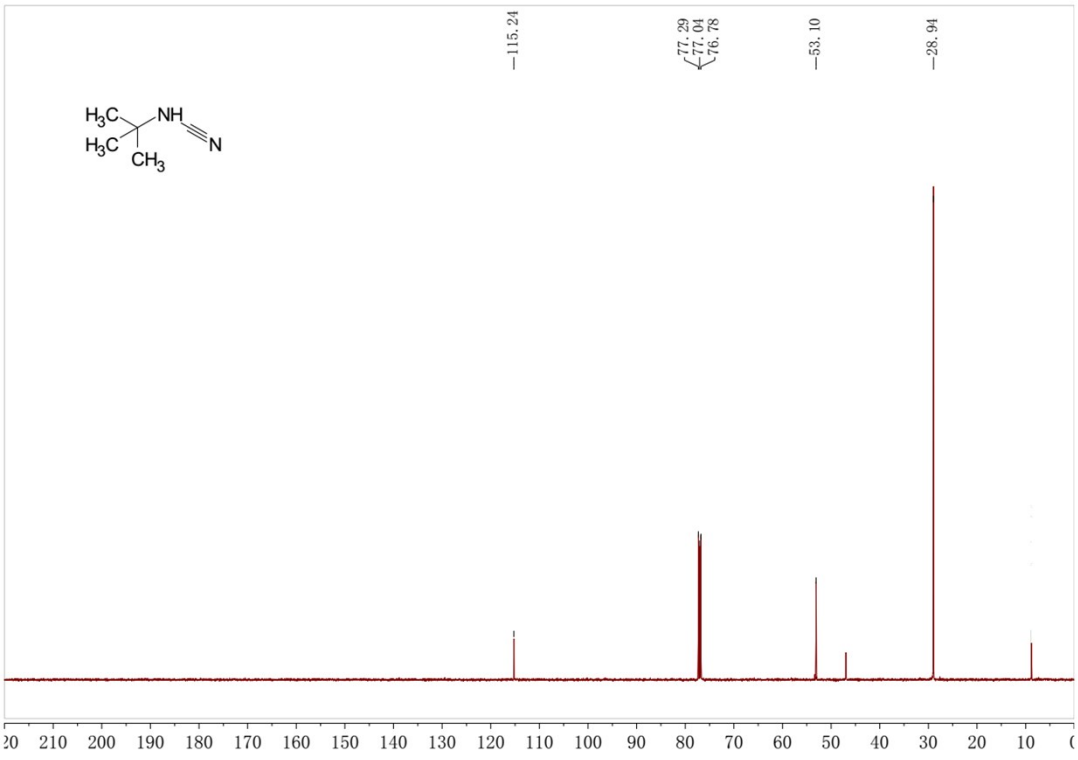
N-Phenethylcyanamide (3ai)





N-(*tert*-Butyl)cyanamide (3aj)


7.28
4.54
1.25
0.97
9.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


115.24
77.29
77.04
76.78
53.10
28.94