Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

for

Copper-Catalyzed Cyanation of Arenes Using Benzyl Nitrile as a Cyanide Anion Surrogate

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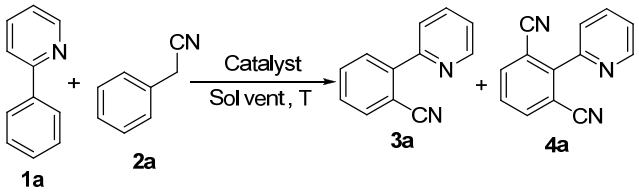
1. General experimental details

Melting points were recorded on a BÜCHI 535. NMR spectra were obtained on a Bruker AVANCE DMX500 spectrometer operating at 500 MHz or 400 MHz for ^{1}H-NMR, 125 MHz or 100 MHz for ^{13}C-NMR in $CDCl_3$. Chemicals were either purchased or purified by standard techniques without special instructions. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, m = multiple. Coupling constants J, were reported in hertz unit (Hz). Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and chemical shifts were reported in ppm referenced to the center line of a triplet at 77.36 ppm of $CDCl_3$.

Typical procedure for the reaction of 2-arylpyridine and benzyl cyanide: A 10 mL round-bottom flask was charged with 2-arylpyridine (0.5 mmol), benzyl cyanide (0.75 mmol), CuBr (0.6 mmol), and DMF (2 mL). The reaction mixture was stirred at 130 °C (oil bath) for 18 h. After cooling to room temperature, the resultant mixture was added to water (30 mL), extracted with DCM (3×5 mL), and dried over Na_2SO_4. The dichloromethane was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel to give the products.

2. Optimization of the reaction conditions

Table S1 Optimization of the reaction conditions [a]

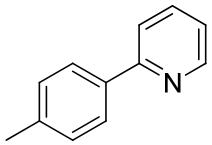


Entry	Catalyst (equiv)	**2a** (equiv)	Solvent	Time (h)	Temp (°C)	**3a**/Yield (%) [b]	**4a**/Yield (%) [b]	Recovery of **1a** (%)
1	CuI (1) + $Pd(OAc)_2$ (0.1)	1.5	DMF	12	130	30	41	0
2	CuBr (1) + $Pd(OAc)_2$ (0.1)	1.5	DMF	12	130	53	ND	40
3	CuCl (1) + $Pd(OAc)_2$ (0.1)	1.5	DMF	12	130	32	ND	50
4	CuBr (1)	1.5	DMF	18	130	80	ND	0
5	Cu_2O (1)	1.5	DMF	18	130	68	ND	0
6	CuOTf (1)	1.5	DMF	18	130	0	ND	>95
7	$Cu(OAc)_2$ (1)	1.5	DMF	18	130	0	ND	0
8	$CuBr_2$ (1)	1.5	DMF	18	130	<5	ND	>95
9	CuBr (0.5)	1.5	DMF	18	130	38	ND	51
10	CuBr (1.2)	1.5	DMF	18	130	83	ND	0
11	CuBr (1.5)	1.5	DMF	18	130	63	ND	0
12	CuBr (2)	1.5	DMF	18	130	31	ND	36
13	CuBr (1.2)	1.2	DMF	18	130	75	ND	0
14	CuBr (1.2)	2	DMF	18	130	58	ND	10
15	CuBr (1.2)	1.5	DMSO	18	130	55	ND	0
16	CuBr (1.2)	1.5	DME	18	130	<5	ND	>95
17	CuBr (1.2)	1.5	Toluene	18	reflux	34	ND	50
18	CuBr (1.2)	1.5	NMP	18	130	72	ND	0
19	CuBr (1.2)	1.5	DMF	24	130	61	ND	0
20	CuBr (1.2)	1.5	DMF	36	130	42	30	0
21	CuBr (1.2)	1.5	DMF	18	100	61	ND	<5
22	CuBr (1.2)	1.5	DMF	18	160	53	ND	0
23 [c]	CuBr (1.2)	1.5	DMF	18	130	<5	ND	>95
24 [d]	CuBr (1.2)	1.5	DMF	18	130	0	ND	>95
25 [e]	CuBr (1.2)	1.5	DMF	18	130	0	ND	>95
26 [f]	CuBr (1.2)	1.5	DMF	18	130	0	ND	>95
27 [g]	CuBr (1.2)	1.5	DMF	18	130	0	ND	>95
28 [h]	CuBr (1.2)	1.5	DMF	18	130	0	ND	>95

[a] Reaction conditions: 2-phenylpyridine **1a** (0.5 mmol), solvent (2 mL), air. [b] Isolated yield. [c] Under O_2. [d] Addition of DDQ (0.5 mmol). [e] Addition of *t*-BuOOH (0.5 mmol). [f] Under N_2. [g] Addition of 1,10-Phen (0.5 mmol). [h] Addition of K_2CO_3 (1 mmol).

2. Spectral data for substrates and products:

2-(p-tolyl)pyridine (1b)

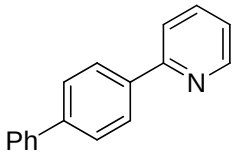


colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.7 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.63 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.13 (td, *J* = 5.9, 3.7 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.06, 149.27, 138.62, 136.40, 136.29, 129.23, 126.50, 121.53, 119.93, 21.00.

2-(1,1'-biphenyl-4-yl)pyridine (1c) [1]

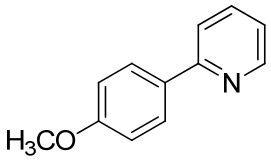


white solid, m.p. 142-143 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.7 Hz, 1H), 8.12 (d, *J* = 7.7 Hz, 2H), 7.77 (m, 4H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.26 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.01, 149.71, 141.70, 140.57, 138.26, 136.74, 128.82, 127.51, 127.44, 127.29, 127.09, 122.09, 120.41.

2-(4-methoxyphenyl)pyridine (1d)

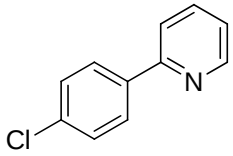


colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.4 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 2H), 7.67 (m, 2H), 7.17-6.99 (m, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.41, 157.03, 149.46, 136.56, 131.97, 128.09, 121.32, 119.69, 114.05, 55.25.

2-(4-chlorophenyl)pyridine (1e) [2]



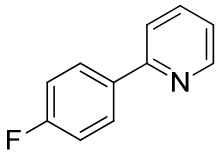
white solid, m.p. 44-45^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.4 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.78-7.73 (m, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.25 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.16, 149.72, 137.76, 136.87, 135.08, 128.91, 128.15, 122.36,

120.32.

2-(4-fluorophenyl)pyridine (1f) [3]

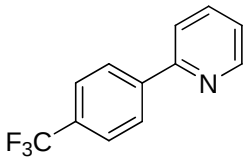


white solid, m.p. 39-41 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.5 Hz, 1H), 7.99 (dd, *J* = 8.0, 5.7 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.21 (m, 1H), 7.15 (t, *J* = 8.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (d, $J_{C\text{-}F}$ = 247 Hz), 156.3, 149.6, 136.7, 135.4 (d, $J_{C\text{-}F}$ = 3.4 Hz), 128.6 (d, $J_{C\text{-}F}$ = 8.7 Hz), 121.9, 120.1, 115.5 (d, $J_{C\text{-}F}$ = 21 Hz).

2-(4-(trifluoromethyl)phenyl)pyridine (1g) [3]

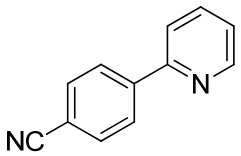


white solid, m.p.70-72 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.5 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.75 (m, 4H), 7.27 (dd, *J* = 8.4, 3.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 149.8, 142.6, 136.9, 130.6 (q, $J_{C\text{-}F}$ = 32 Hz), 127.1, 125.5, 124.1 (q, $J_{C\text{-}F}$ = 270 Hz), 122.9, 120.7.

4-(pyridin-2-yl)benzonitrile (1h)

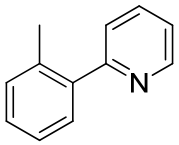


colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.5 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.80 (m, 4H), 7.33 (dd, *J* = 6.4, 5.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.09, 149.99, 143.39, 137.08, 132.51, 127.39, 123.32, 120.94, 118.80, 112.34.

2-(o-tolyl)pyridine (1i)



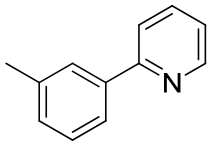
colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.4 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.25 (m, 4H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.06, 149.19, 140.44, 136.10, 135.74, 130.72, 129.61, 128.25,

125.86, 124.08, 121.60, 20.26.

2-(m-tolyl)pyridine (1j)

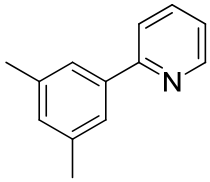


colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.7 Hz, 1H), 7.86 (s, 1H), 7.76 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.24 (m, 2H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.64, 149.60, 139.34, 138.46, 136.76, 129.75, 128.66, 127.67, 124.01, 122.05, 120.68, 21.55.

2-(3,5-dimethylphenyl)pyridine (1k)

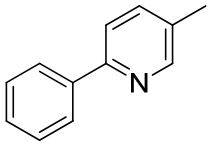


colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.7 Hz, 1H), 7.70 (d, *J* = 3.6 Hz, 2H), 7.64 (s, 2H), 7.19 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.07 (s, 1H), 2.41 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.06, 149.78, 143.55, 137.77, 136.66, 134.78, 130.59, 128.49, 124.53, 123.10, 118.20, 112.62, 20.05.

5-methyl-2-phenylpyridine (1l)

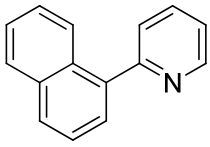


colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.00 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.49 (m, 3H), 7.40 (t, *J* = 7.3 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.48, 149.83, 139.17, 137.07, 131.35, 128.48, 128.38, 126.46, 119.77, 17.90.

2-(naphthalen-1-yl)pyridine (1m)

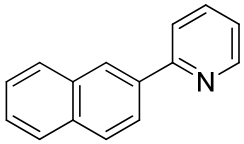


colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.7 Hz, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.81 (dd, *J* = 10.7, 4.6 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.60 (m, 2H), 7.53 (dd, *J* = 9.5,

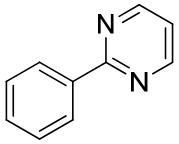
5.3 Hz, 2H), 7.33 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.04, 149.35, 138.33, 136.26, 133.77, 130.98, 128.75, 128.22, 127.34, 126.35, 125.73, 125.45, 125.16, 124.89, 121.87.

2-(naphthalen-2-yl)pyridine (1n)



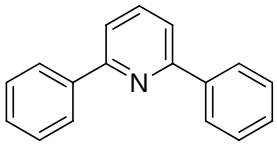
colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.6 Hz, 1H), 8.53 (s, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 7.97 (m, 2H), 7.90 (m, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.74 (m, 1H), 7.54 (m, 2H), 7.24 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.13, 149.65, 136.72, 136.54, 133.53, 133.41, 128.64, 128.38, 127.59, 126.44, 126.22, 124.46, 122.07, 120.70.

2-phenylpyrimidine (1o)



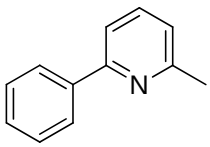
colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.8 Hz, 2H), 8.47 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.51 (m, 3H), 7.15 (t, *J* = 4.8 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.63, 157.16, 137.49, 130.72, 128.55, 128.07, 119.02.

2,6-diphenylpyridine (2s) [4]



white solid, m. P. 79-80 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 4H), 7.83 (m, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 4H), 7.49 (dd, *J* = 10.6, 3.8 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.75, 139.43, 137.48, 128.97, 128.68, 126.97, 118.62, 77.36, 77.04, 76.73.

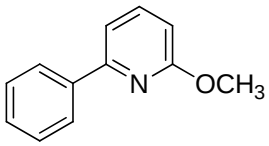
2-methyl-6-phenylpyridine (2t)



colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.3 Hz, 2H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.51 (m, 3H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 2.66 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.27, 156.88, 139.70, 136.82, 128.62, 126.94, 121.54, 117.56, 24.70.

2-methoxy-6-phenylpyridine (2u)

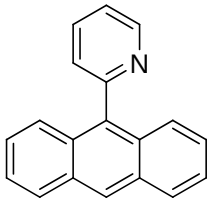


colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 2H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.44 (dd, *J* = 10.6, 3.8 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.70, 154.60, 139.13, 139.02, 128.81, 128.58, 126.66, 112.74, 109.21, 53.16.

2-(anthracen-9-yl)pyridine (2v) [3]

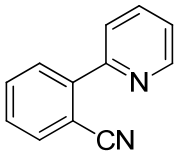


white solid, m. p. 165-167 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 4.8 Hz, 1H), 8.58 (s, 1H), 8.09 (d, J = 8.4 Hz, 2H), 7.92 (dd, J = 11.0, 4.2 Hz, 1H), 7.65 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 7.7 Hz, 1H), 7.46 (ddd, J = 22.9, 15.3, 7.2 Hz, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.13, 149.98, 136.20, 134.99, 131.29, 129.95, 128.41, 127.52, 126.74, 125.91, 125.81, 125.05, 122.28.

2-(pyridin-2-yl)benzonitrile (3a)

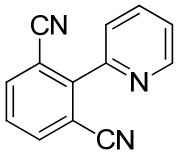


colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.7 Hz, 1H), 7.85-7.76 (m, 4H), 7.71-7.67 (dd, *J* = 8.0, 4.4 Hz, 1H), 7.50 (m, 1H), 7.37-7.34(m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.18, 149.86, 143.39, 136.80, 134.07, 132.79, 129.91, 128.71, 123.29, 123.18, 118.64, 110.98.

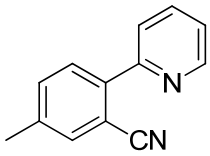
2-(pyridin-2-yl)isophthalonitrile (4)



white solid, m. p. 141-142 °C.

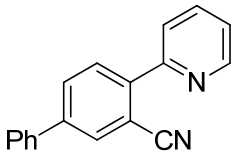
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 3.9 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 2H), 7.94 (td, *J* = 7.8, 1.4 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.66 (dd, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 7.1, 5.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.17, 150.31, 146.97, 137.31, 137.10, 129.34, 124.76, 124.57, 116.50, 114.20, 77.36, 77.11, 76.85.
HRMS (EI) Calcd. for [$C_{13}H_7N_3$] ($[M]^+$) : 205.0640, found: 205.0636.

5-methyl-2-(pyridin-2-yl)benzonitrile (3b) [4]



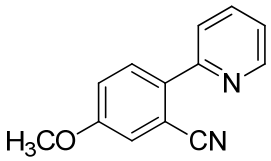
white solid, m. p. 61-62 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.4 Hz, 1H), 7.83 (dd, *J* = 10.8, 4.5 Hz, 1H), 7.76 (m, 2H), 7.61 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 6.6, 5.5 Hz, 1H), 2.44 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.16, 149.78, 140.61, 139.05, 136.75, 134.39, 133.72, 129.79, 123.05, 123.03, 118.88, 110.65, 20.82.

4-(pyridin-2-yl)-(1,1'-biphenyl)-3-carbonitrile (3c)



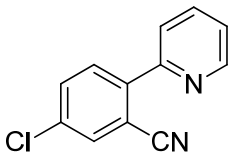
colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.03 (d, J = 1.4 Hz, 1H), 7.93 (q, J = 8.1 Hz, 2H), 7.86 (s, 2H), 7.64 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.4 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H), 7.38 (s, 1H)..
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.93, 150.00, 141.95, 138.36, 136.89, 132.64, 131.43, 130.49, 129.21, 128.58, 127.07, 123.38, 123.19, 118.84, 111.49.

5-methoxy-2-(pyridin-2-yl)benzonitrile (3d) [4]



white solid, m. p. 102-103 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.5 Hz, 1H), 7.80 (m, 3H), 7.31 (dd, *J* = 11.7, 5.6 Hz, 1H), 7.28 (d, *J* = 2.5 Hz, 1H), 7.22 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.89 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.61, 155.05, 149.85, 136.84, 136.10, 131.43, 122.93, 122.89, 119.47, 118.73, 118.56, 111.80, 55.82.

5-chloro-2-(pyridin-2-yl)benzonitrile (3e) [4]

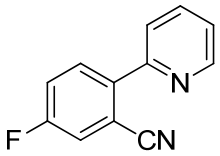


white solid, m. p. 166-167 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.7 Hz, 1H), 7.82 (m, 4H), 7.67 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.38 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.14, 150.10, 141.88, 137.03, 134.99, 133.66, 133.24, 131.36, 123.67, 123.14, 117.51, 112.46.

5-fluoro-2-(pyridin-2-yl)benzonitrile (3f) [4]

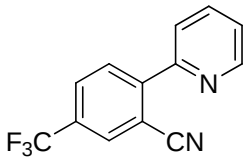


white solid, m. p. 130-131 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.4 Hz, 1H), 7.84 (dt, *J* = 7.6, 5.5 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.49 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.39 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, $J_{C\text{-}F}$ = 252 Hz), 154.1, 149.9, 139.8 (d, $J_{C\text{-}F}$ = 3.4 Hz), 136.9, 132.1 (d, $J_{C\text{-}F}$ = 8 Hz), 123.3, 123.0, 120.6 (d, $J_{C\text{-}F}$ = 25 Hz), 120.4 (d, $J_{C\text{-}F}$ = 22 Hz), 117.4, 112.3 (d, $J_{C\text{-}F}$ = 10 Hz).

2-(pyridin-2-yl)-5-(trifluoromethyl)benzonitrile (3g)



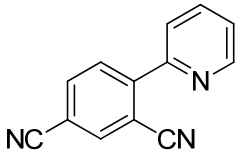
white solid, m. p. 58-59 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.7 Hz, 1H), 8.08 (s, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.90 (t, *J* = 7.2 Hz, 1H), 7.85 (d, *J* = 7.4 Hz, 1H), 7.44 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 150.3, 146.6, 137.1, 131.4 (q, $J_{C\text{-}F}$ = 26 Hz), 131.1 (q, $J_{C\text{-}F}$ = 3.4 Hz), 130.8, 129.5 (q, $J_{C\text{-}F}$ = 2.6 Hz), 124.1, 123.4, 123.0 (q, $J_{C\text{-}F}$ = 217 Hz), 117.4, 112.0.

HRMS (EI) Calcd. for [$C_{13}H_7N_2F_3$] ($[M]^+$) : 248.0561, found: 248.0561.

4-(pyridin-2-yl)isophthalonitrile (3h) [4]

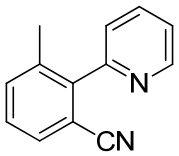


white solid, m. p. 155-156 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.07 (s, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.88 (m, 2H), 7.43 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.28, 150.39, 147.07, 137.52, 137.26, 135.82, 131.06, 124.49, 123.45, 116.75, 116.68, 113.33, 112.59.

3-methyl-2-(pyridin-2-yl)benzonitrile (3i)

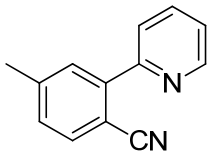


colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.4 Hz, 1H), 7.85 (td, *J* = 7.7, 1.7 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.39 (m, 3H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.06, 149.78, 143.55, 137.77, 136.66, 134.78, 130.59, 128.49, 124.53, 123.10, 118.20, 112.62, 20.05.

4-methyl-2-(pyridin-2-yl)benzonitrile (3j)

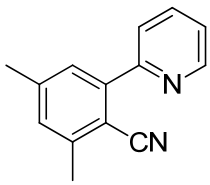


colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.80 (dd, *J* = 16.1, 7.8 Hz, 2H), 7.66 (dd, *J* = 18.5, 8.0 Hz, 3H), 7.48 (t, *J* = 7.6 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.19, 149.73, 143.74, 143.15, 136.68, 133.85, 130.57, 129.45, 123.17, 123.14, 118.87, 107.80, 21.68.

2,4-dimethyl-6-(pyridin-2-yl)benzonitrile (3k)

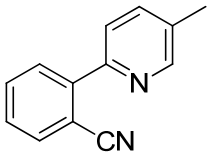


light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 3.3 Hz, 1H), 7.77 (m, 2H), 7.40 (s, 1H), 7.31 (m, 1H), 7.17 (s, 1H), 2.57 (t, *J* = 4.2 Hz, 3H), 2.40 (t, *J* = 4.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.81, 149.61, 143.78, 143.03, 143.01, 136.58, 130.75, 128.03, 123.32, 123.01, 117.73, 108.34, 21.54, 20.80.

2-(5-methylpyridin-2-yl)benzonitrile (3l)

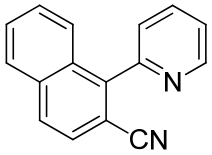


colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.75 (dd, *J* = 15.6, 7.8 Hz, 2H), 7.60 (dd, *J* = 18.4, 8.2 Hz, 3H), 7.42 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.46, 150.38, 143.52, 137.28, 134.04, 133.14, 132.79, 129.79, 128.44, 122.68, 118.84, 110.88, 18.27.

1-(pyridin-2-yl)-2-naphthonitrile (3m) [5]

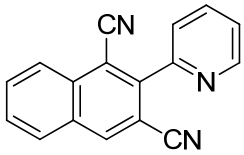


white solid, m. p. 156-157 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.5 Hz, 1H), 7.91 (m, 3H), 7.69 (m, 2H), 7.60 (dd, *J* = 14.4, 7.2 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.43 (dd, *J* = 7.5, 5.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.23, 149.96, 144.41, 136.72, 134.97, 131.10, 129.38, 128.73, 128.27, 127.87, 126.76, 126.67, 125.60, 123.47, 118.49, 109.69.

2-(pyridin-2-yl)naphthalene-1,3-dicarbonitrile (4b)



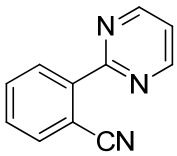
white solid, m. p. 201-202 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.4 Hz, 1H), 8.58 (s, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.95 (dt, *J* = 16.7, 7.7 Hz, 2H), 7.81 (dd, *J* = 14.9, 7.4 Hz, 2H), 7.52 (dd, *J* = 7.5, 5.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.93, 150.34, 144.20, 139.77, 137.08, 133.78, 132.22, 131.40, 129.51, 129.11, 126.14, 125.01, 124.63, 116.94, 115.56, 111.72, 110.57, 77.36, 77.11, 76.85.

HRMS (EI) Calcd. for [$C_{17}H_9N_3$] ($[M]^+$) : 255.0796, found: 255.0803.

2-(pyrimidin-2-yl)benzonitrile (3o) [5]

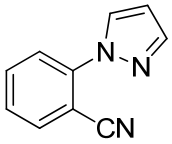


white solid, m. p. 136-137 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 4.0 Hz, 2H), 8.36 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.33 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.72, 157.29, 140.21, 134.98, 132.52, 130.36, 130.17, 120.11, 118.88, 111.70.

2-(1H-pyrazol-1-yl)benzonitrile (3p)



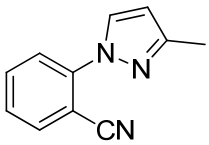
colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.4 Hz, 1H), 7.79 (m, 3H), 7.71 (td, *J* = 8.0, 1.1 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 6.55 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.17, 141.90, 134.39, 133.95, 129.46, 127.19, 124.17, 116.94,

108.42, 105.24.

2-(3-methyl-1H-pyrazol-1-yl)benzonitrile (3q)

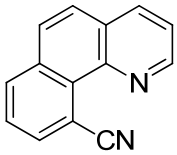


colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.3 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.75 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.68 (td, *J* = 8.2, 1.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 6.34 (d, *J* = 2.3 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.85, 142.13, 134.38, 134.00, 130.23, 126.70, 124.04, 117.23, 108.65, 104.62.

benzo[h]quinoline-10-carbonitrile (3r)



white solid, m. p. 132-133 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (m, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.12 (dd, *J* = 15.6, 7.7 Hz, 2H), 7.78 (q, *J* = 8.8 Hz, 2H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.61 (dd, *J* = 8.0, 4.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.41, 144.37, 136.19, 135.68, 133.98, 132.71, 130.63, 127.33, 127.19, 127.05, 126.90, 123.01, 120.81, 108.81.

4. References

1 I. M. Heilbron, D. H. Hey, A. Lambert. *J. Chem. Soc.*, 1940, 1279.

2 M. Li, R. Hua. *Tetrahedron Lett.*, 2009, **50**, 1478.

3 L. Ackermann, H. K. Potukuchi, A. R. Kapdi, C. Schulzke. *Chem. Eur. J.*, 2010, **16**, 3300.

4 J. Xu, G. Cheng, D. Su, Y. Liu, X. Wang, Y. Hu. *Chem. Eur. J.*, 2009, **15**, 13105.

5 J. Kim, S. Chang, *J. Am. Chem. Soc.*, 2010, **132,** 10272.

5. Detection of CN^- by indicator paper

Table S2 Detection of CN^- by indicator paper[a]

Entry	Benzyl Cyanide	[Cu]	Solvent	Air / N_2	Turn Red [b]
1		CuBr	DMF	air	Y
2		$CuBr_2$	DMF	air	N
3		CuBr	DMF	N_2	N
4		CuBr	DMF	air	Y
5		$CuBr_2$	DMF	air	N
6		CuBr	DMF	air	Y
7		--	DMF	air	Y
8		CuBr	DMF	air	Y
9		--	DMF	air	Y (deep red)

[a] Reaction conditions: The mixture was heated at 130 °C in DMF (2 mL) for 3 h before the test.

[b] CN^- was detected according to the published procedure ((a) J. Kim, J. Choi, K. Shin, Sukbok Chang, *J. Am. Chem. Soc*., 2012, **134**, 2528; (c) G, Zhang, X. Ren, J. Chen, M. Hu, J. Cheng, *Org. Lett*., 2011, **13**, 5004); "N" means negative result and "Y" means positive result.

6. GC-MS data and possible formation pathway for by-products

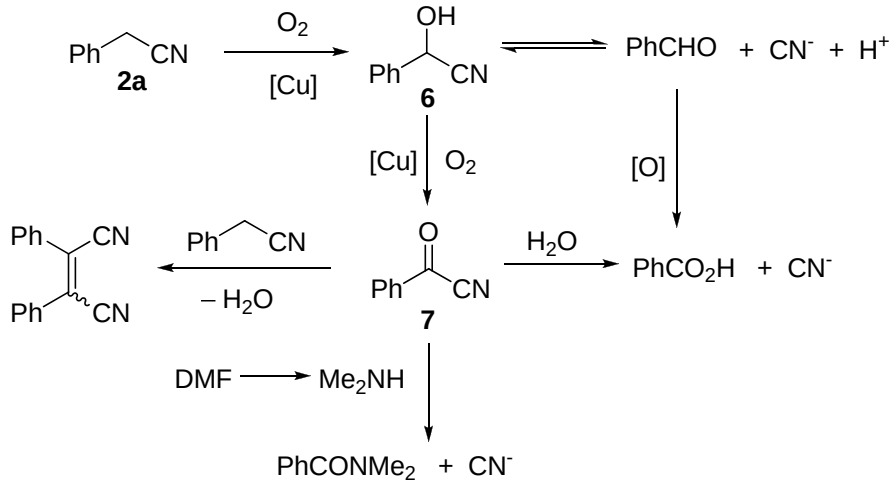
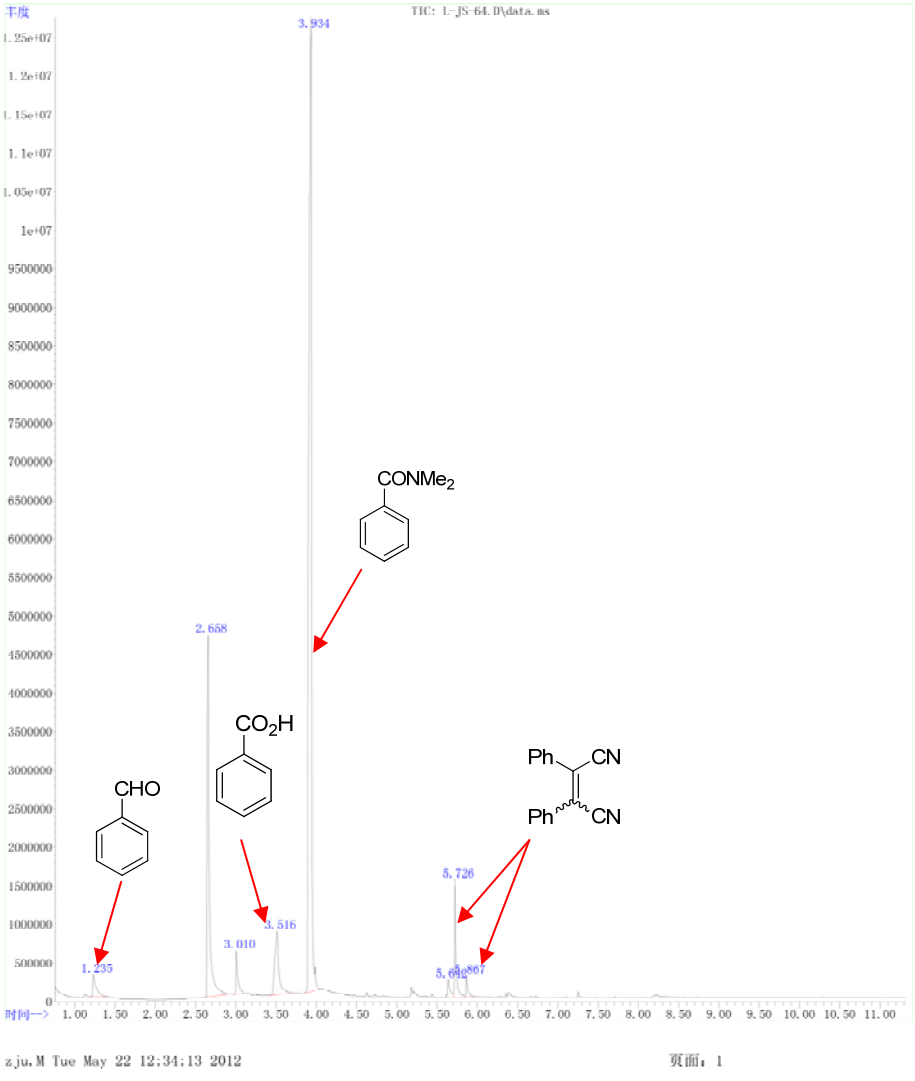
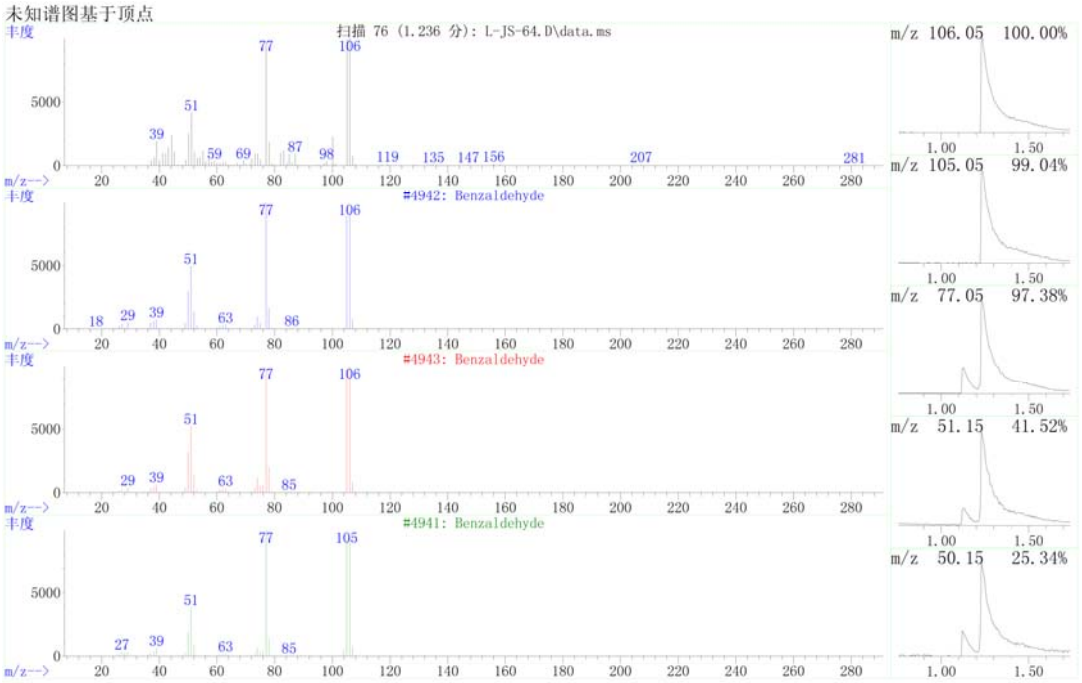


Figure S1 GC-MS data for benzaldehyde, benzoic acid, *N*,*N*-dimethylbenzamide and *cis*- and *trans*-2,3-diphenylfumaronitrile as the by-products

(a) GC data for the reaction mixture



(b) MS data for benzaldehyde

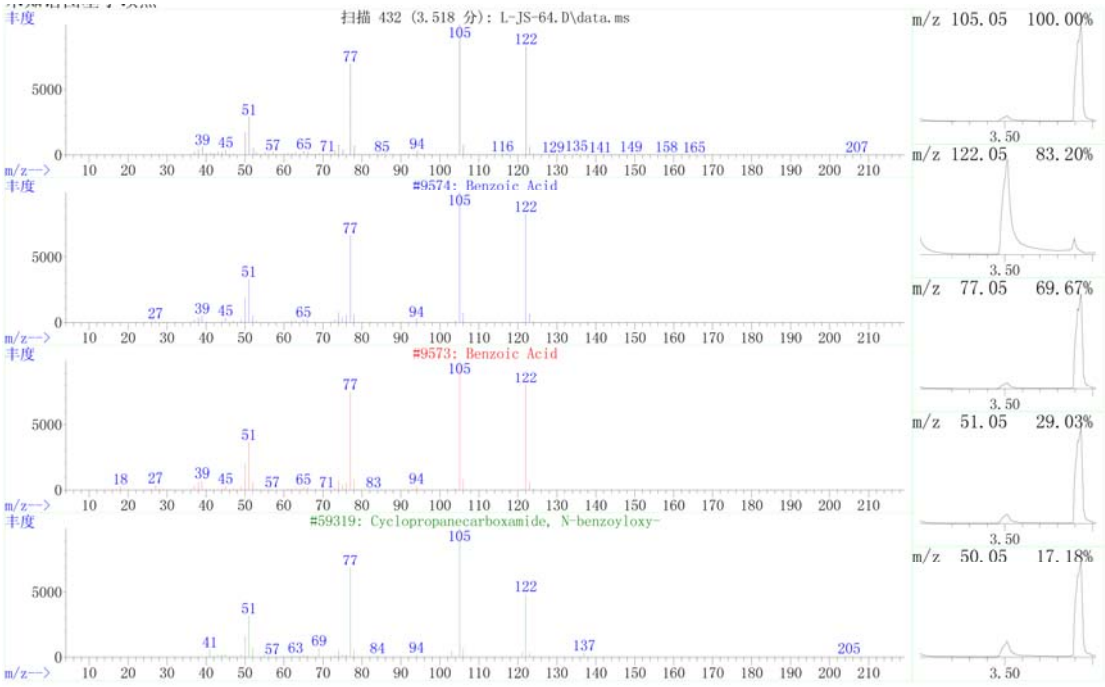


Data File: E:\PINGLU\Snapshot\L-JS-64.D
样品:

峰编号: 1 1.236 分钟处 面积: 8491365 面积 % 1.84

每个库中 3 个最匹配的记录。	Ref\#	CAS\#	定量
D:\Database\NIST02.L			
1 Benzaldehyde	4942	000100-52-7	96
2 Benzaldehyde	4943	000100-52-7	96
3 Benzaldehyde	4941	000100-52-7	94

(c) MS data for benzoic acid

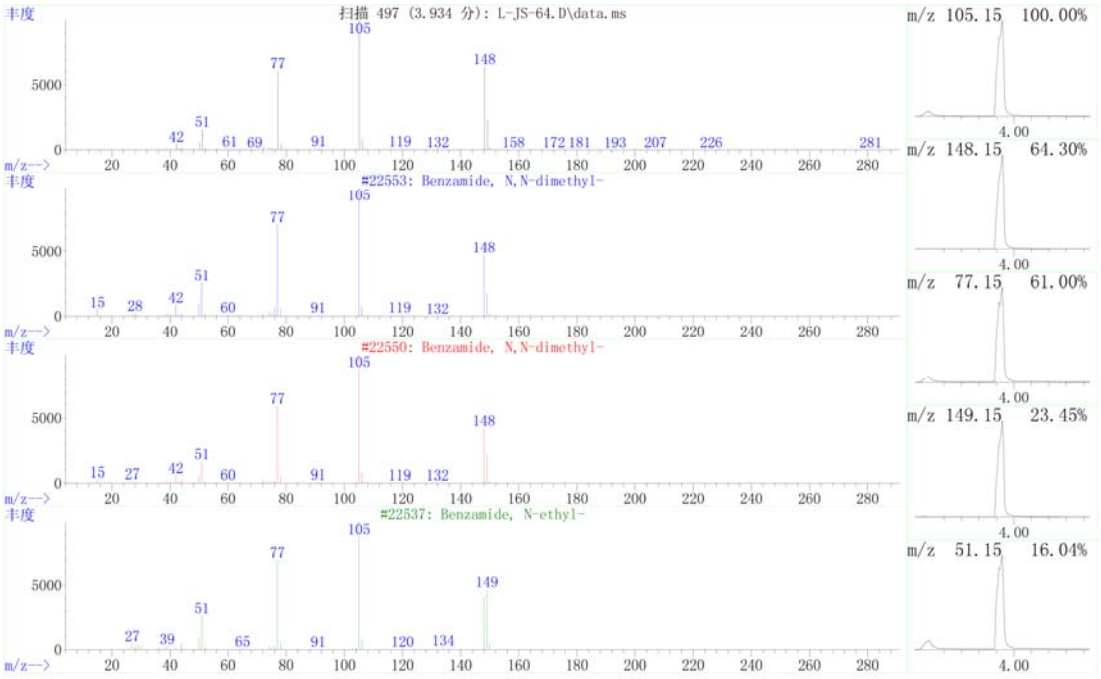


Data File: E:\PINGLU\Snapshot\L-JS-64.D
样品:

峰编号: 4 3.518 分钟处 面积: 28874503 面积 % 6.27

每个库中 3 个最匹配的记录。	Ref\#	CAS\#	定量
D:\Database\NIST02.L			
1 Benzoic Acid	9574	000065-85-0	94
2 Benzoic Acid	9573	000065-85-0	91
3 Cyclopropanecarboxamide, N-benzo...	59319	1000253-25-4	83

(d) MS data for *N*,*N*-dimethylbenzamide

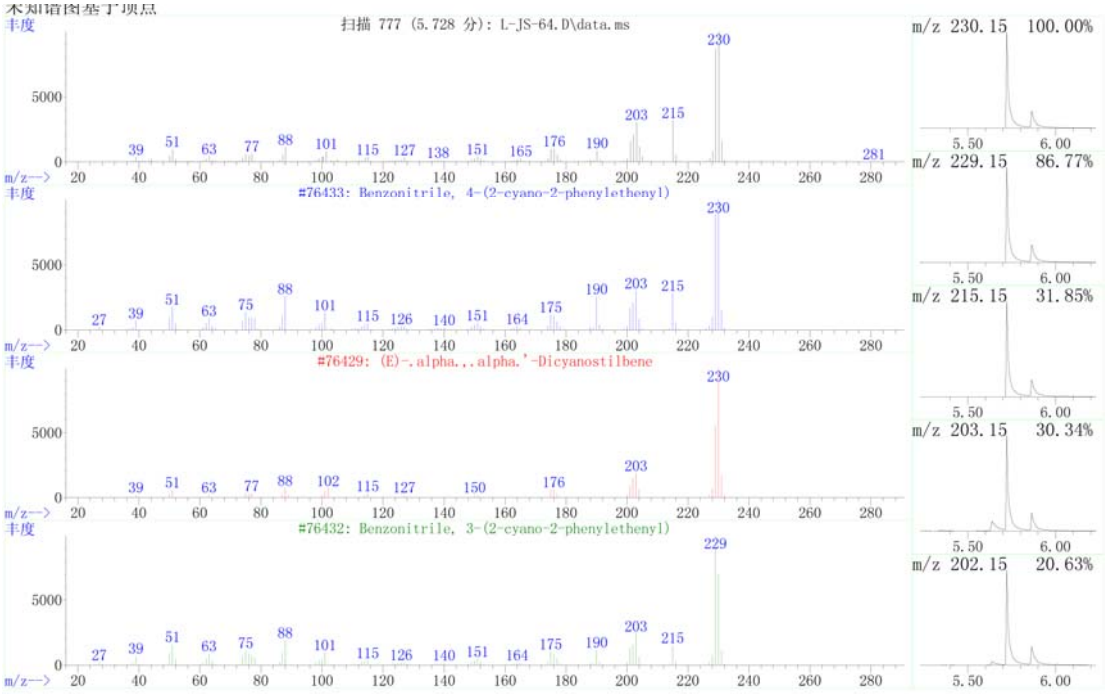


Data File: E:\PINGLU\Snapshot\L-JS-64.D
样品:

峰编号: 5 3.934 分钟处 面积: 299062012 面积 % 64.97

每个库中 3 个最匹配的记录。	Ref\#	CAS\#	定量
D:\Database\NIST02.L			
1 Benzamide, N,N-dimethyl-	22553	000611-74-5	91
2 Benzamide, N,N-dimethyl-	22550	000611-74-5	87
3 Benzamide, N-ethyl-	22537	000614-17-5	50

(e) MS data for *cis*- or *trans*-2,3-diphenylfumaronitrile

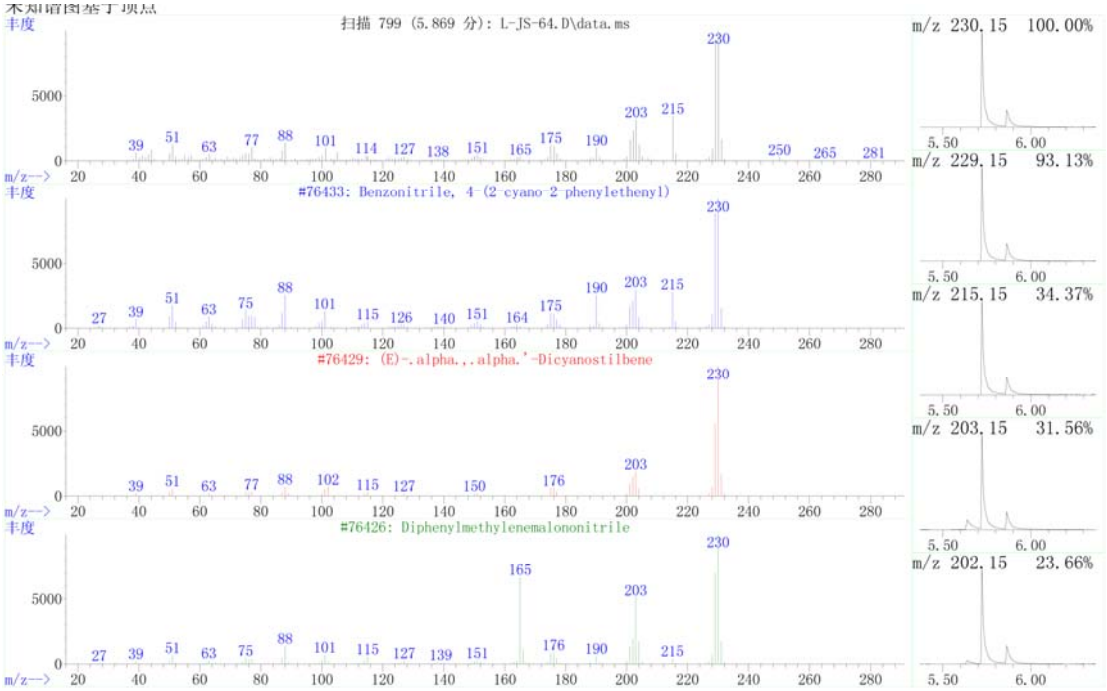


Data File: E:\PINGLU\Snapshot\L-JS-64.D
样品:

峰编号: 7 5.728 分钟处 面积: 17322148 面积 % 3.76

每个库中 3 个最匹配的记录。	Ref\#	CAS\#	定量
D:\Database\NIST02.L			
1 Benzonitrile, 4-(2-cyano-2-pheny...	76433	061469-58-7	95
2 (E)-.alpha.,.alpha.'-Dicyanostil...	76429	002450-55-7	92
3 Benzonitrile, 3-(2-cyano-2-pheny...	76432	147728-29-8	83

(f) MS data for *trans*- or *cis*-2,3-diphenylfumaronitrile



Data File: E:\PINGLU\Snapshot\L-JS-64.D
样品:

峰编号: 8 5.869 分钟处 面积: 4431735 面积 % 0.96

每个库中 3 个最匹配的记录。	Ref\#	CAS\#	定量
D:\Database\NIST02.L			
1 Benzonitrile, 4-(2-cyano-2-pheny...	76433	061469-58-7	96
2 (E)-.alpha.,.alpha.'-Dicyanostil...	76429	002450-55-7	95
3 Diphenylmethylenemalononitrile	76426	010394-96-4	90

7. Kinetics Investigation Data

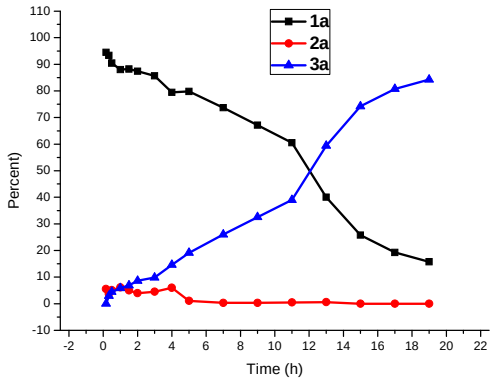


Figure S2 CuBr-catalyzed cyanation of **1a** with **2a**

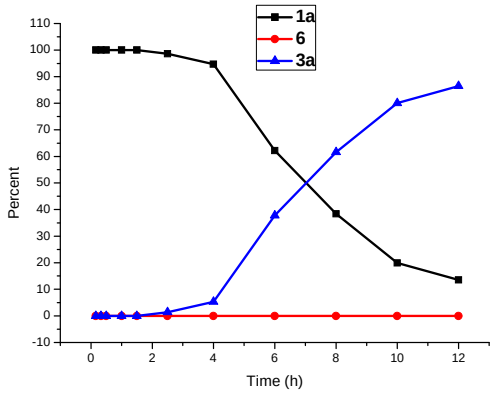


Figure S3 CuBr-catalyzed cyanation of **1a** with **6**

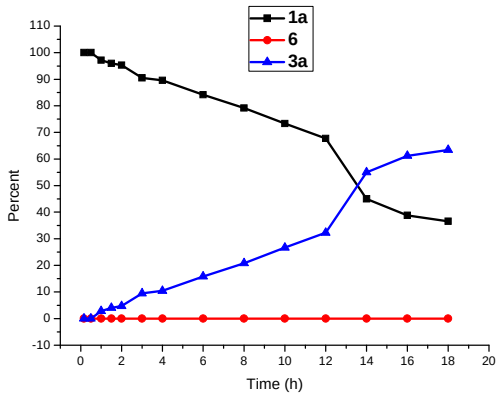


Figure S4 $Cu(OAc)_2$-catalyzed cyanation of **1a** with **6**

8. Copies of ^{1}H and ^{13}C NMR for substrates and products

Figure S5 ^{1}H-NMR spectrum of **1b**

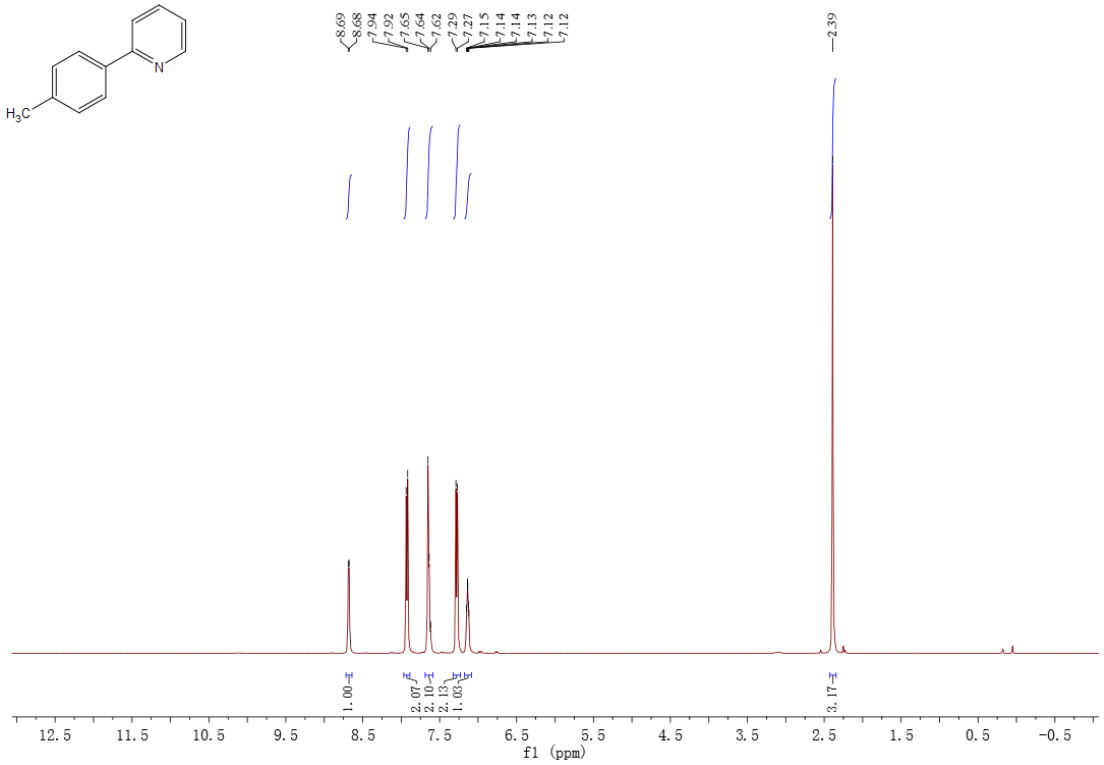


Figure S6 ^{13}C-NMR spectrum of **1b**

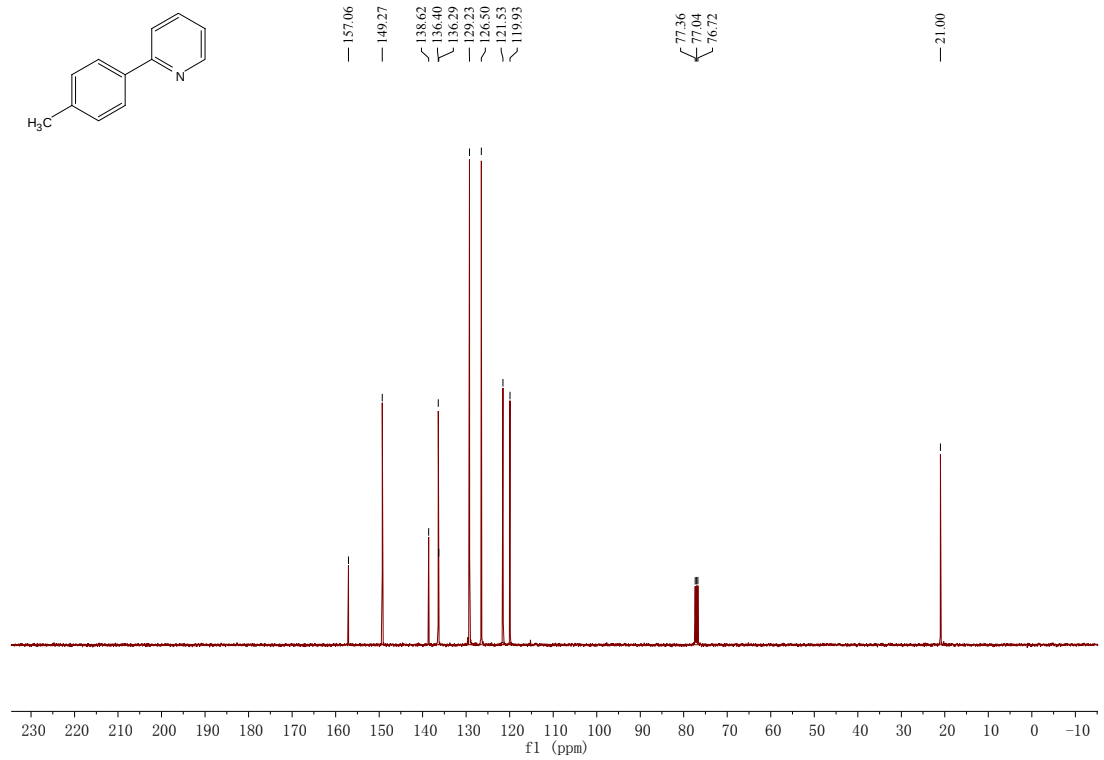


Figure S7 ^{1}H-NMR spectrum of **1c**

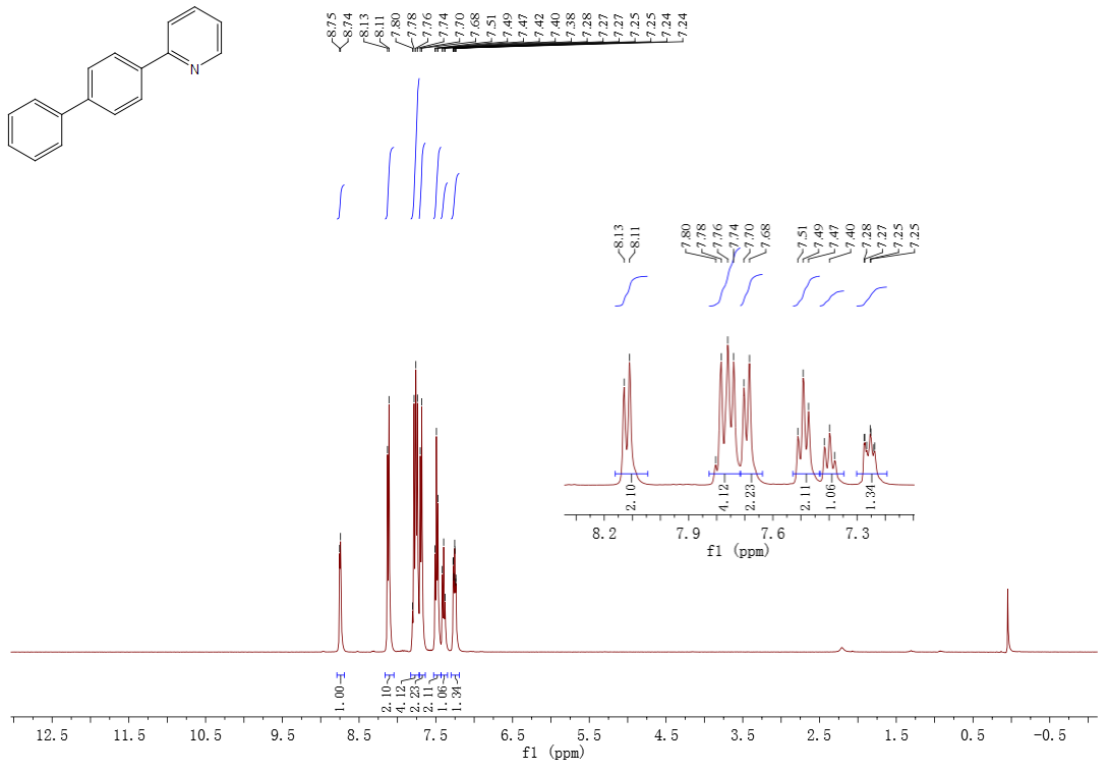


Figure S8 ^{13}C-NMR spectrum of **1c**

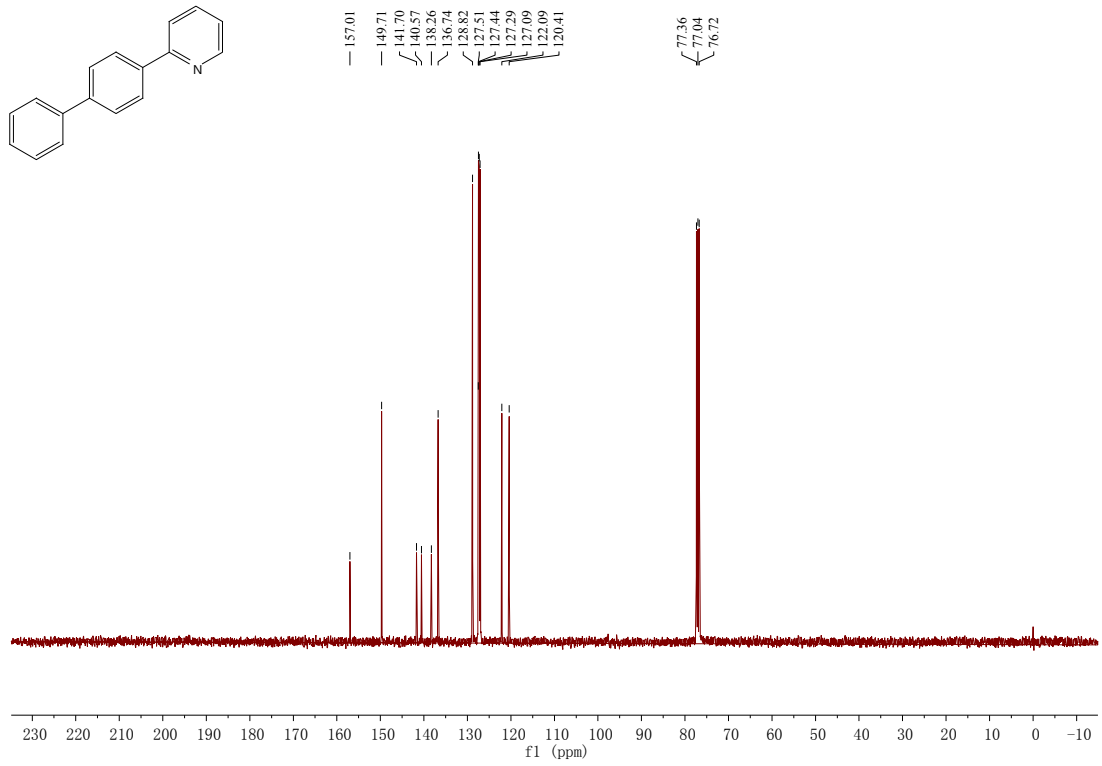


Figure S9 ^{1}H-NMR spectrum of **1d**

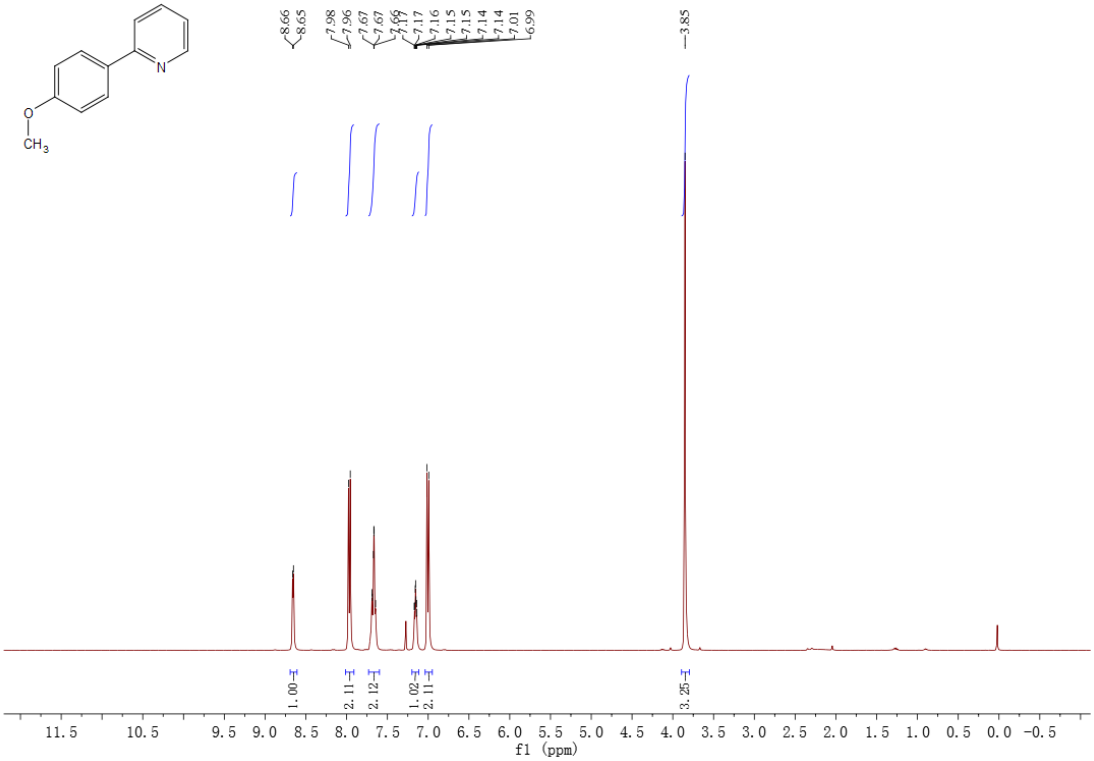


Figure S10 ^{13}C-NMR spectrum of **1d**

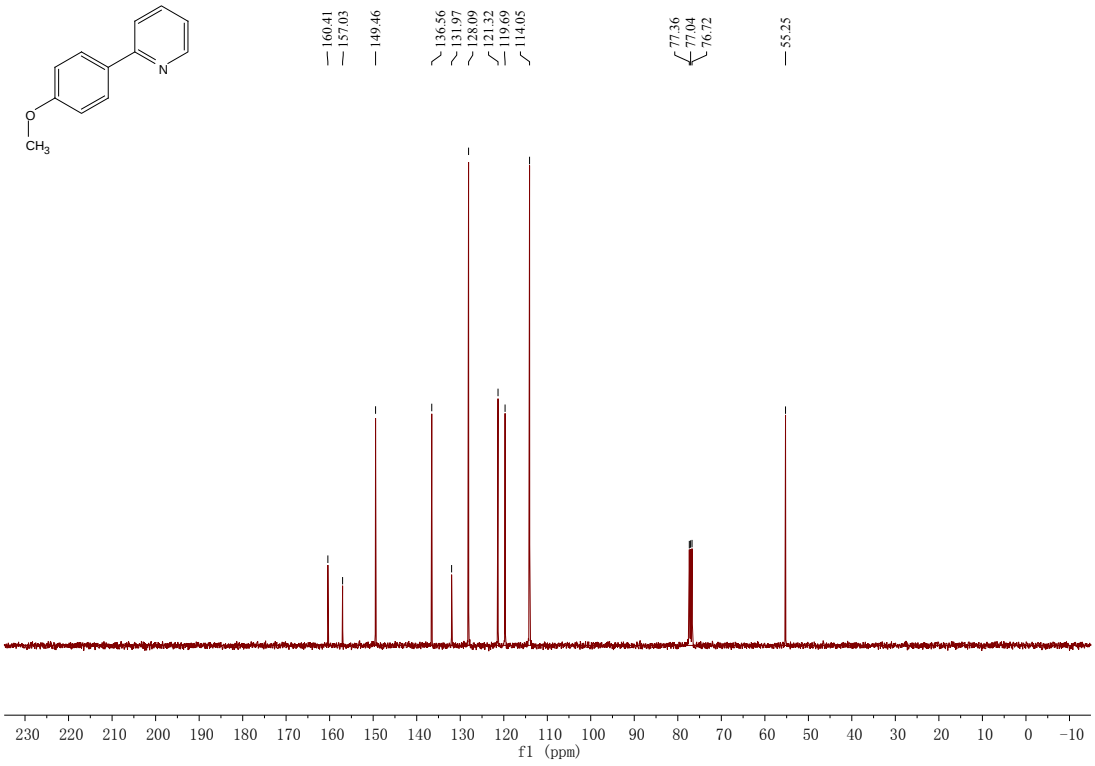


Figure S11 ^{1}H-NMR spectrum of **1e**

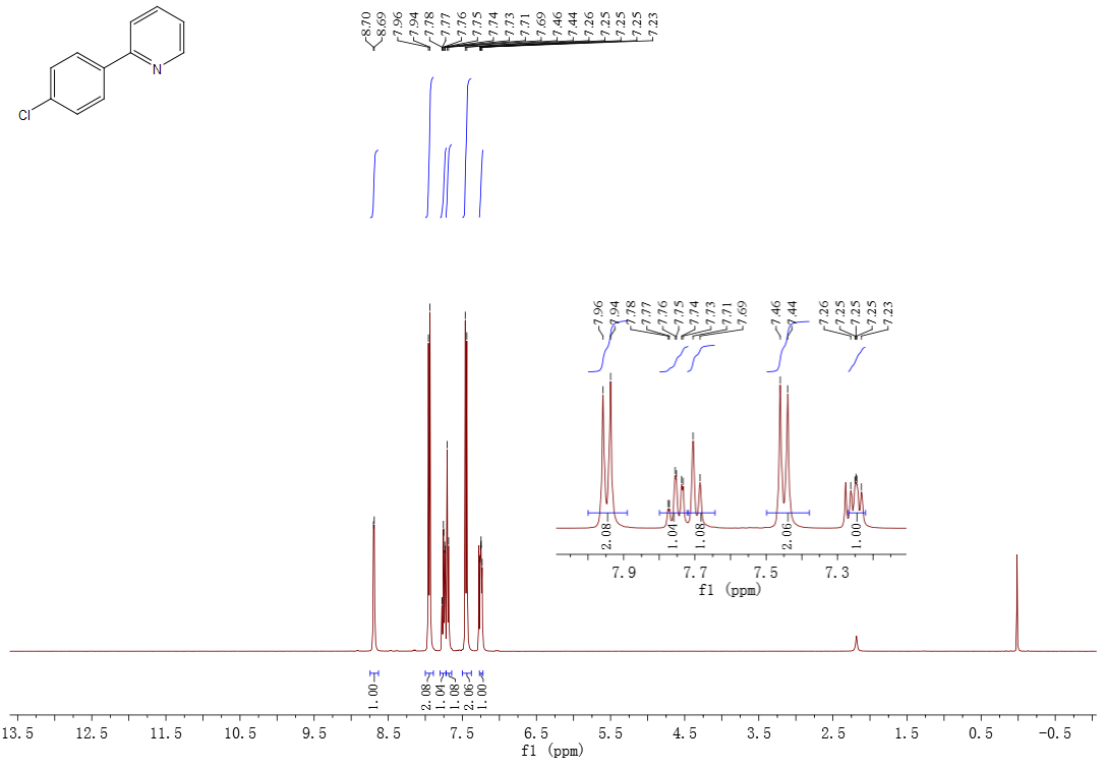


Figure S12 ^{13}C-NMR spectrum of **1e**

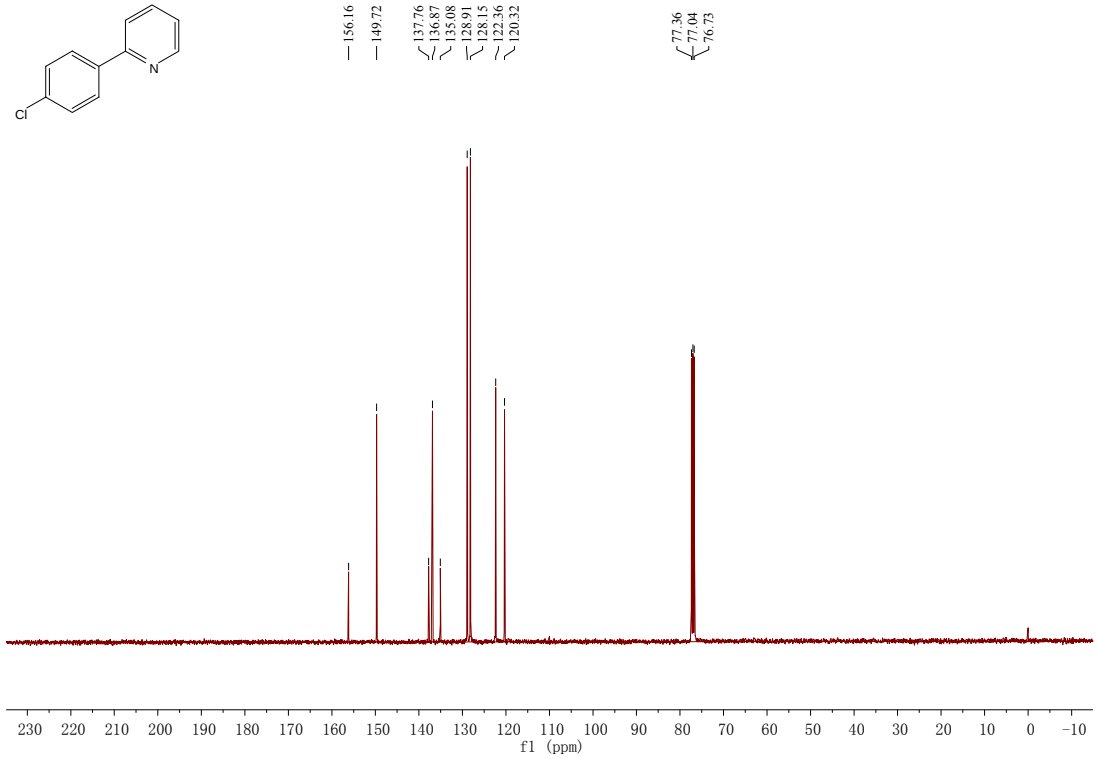


Figure S13 ^{1}H-NMR spectrum of **1f**

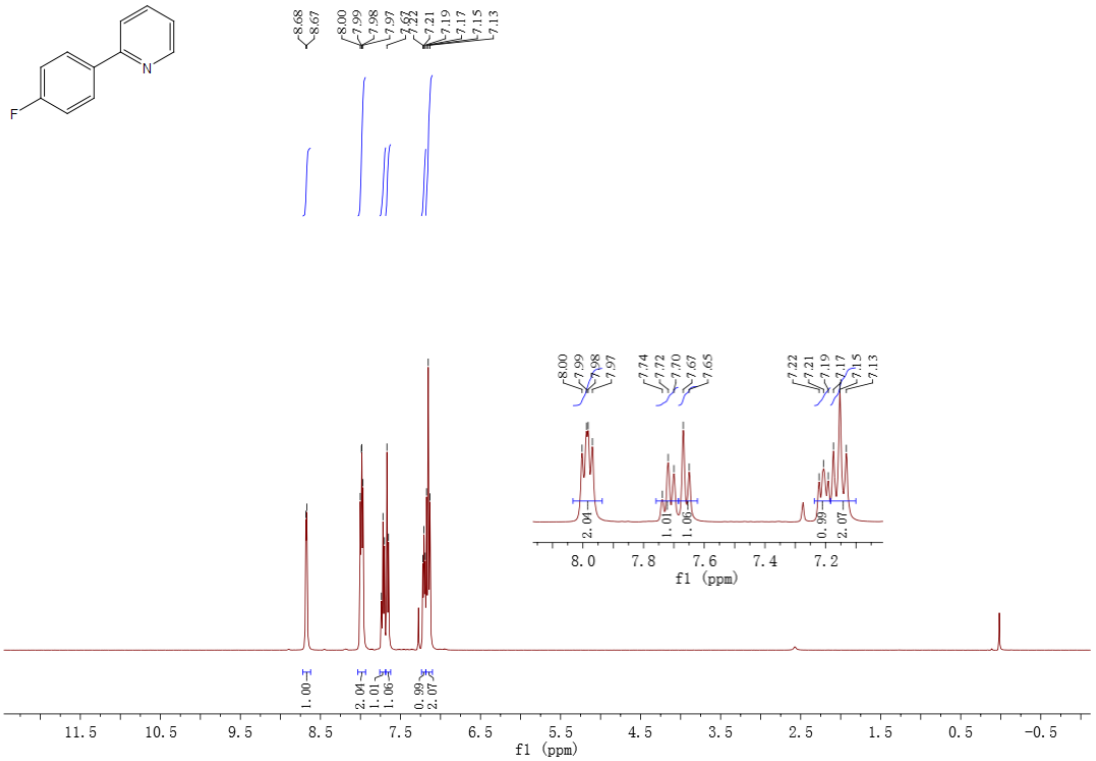


Figure S14 ^{13}C-NMR spectrum of **1f**

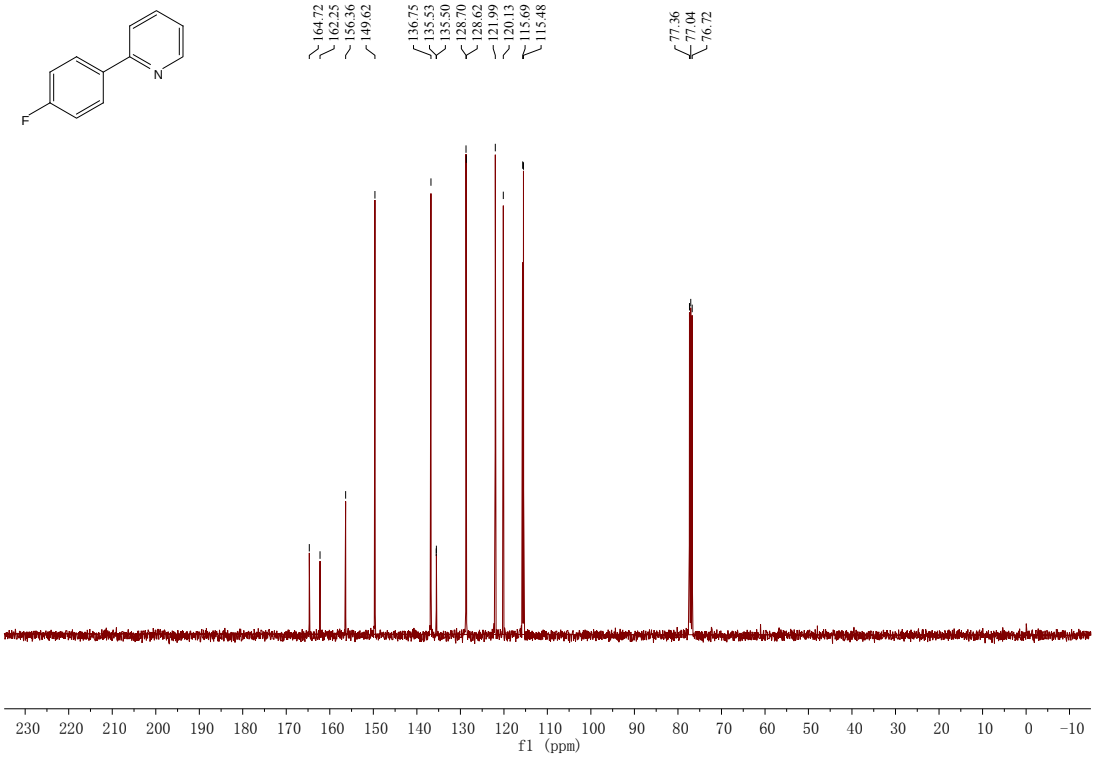


Figure S15 ^{1}H-NMR spectrum of **1g**

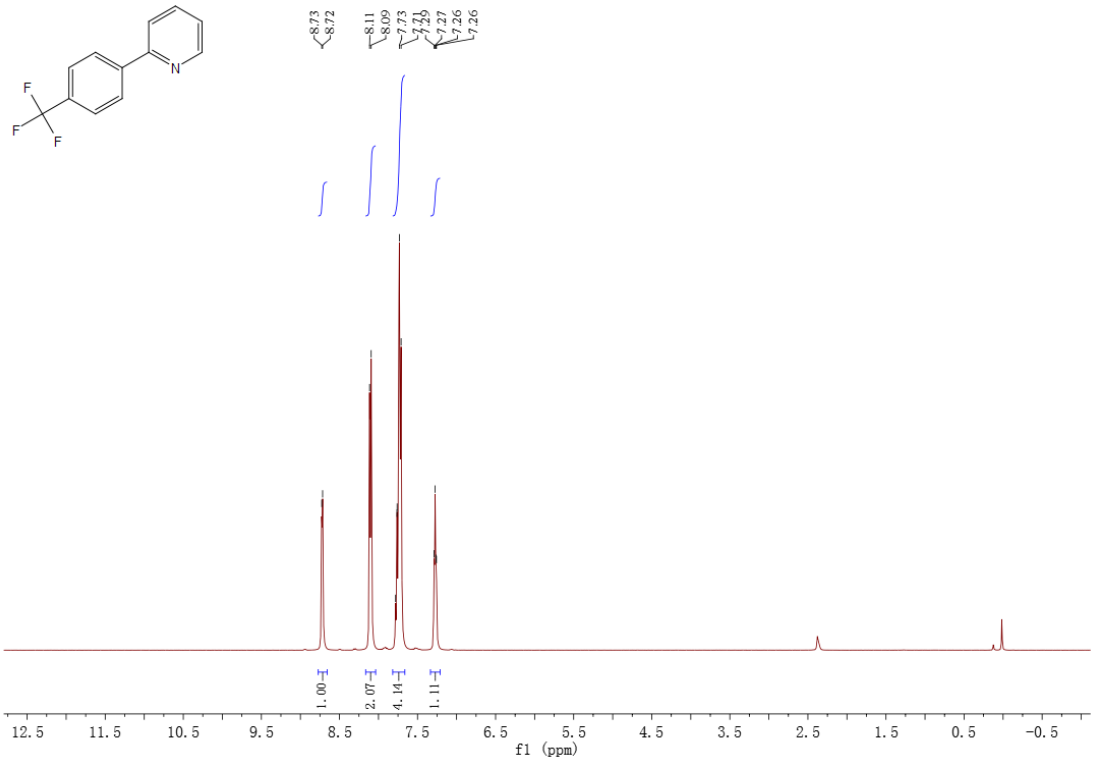


Figure S16 ^{13}C-NMR spectrum of **1g**

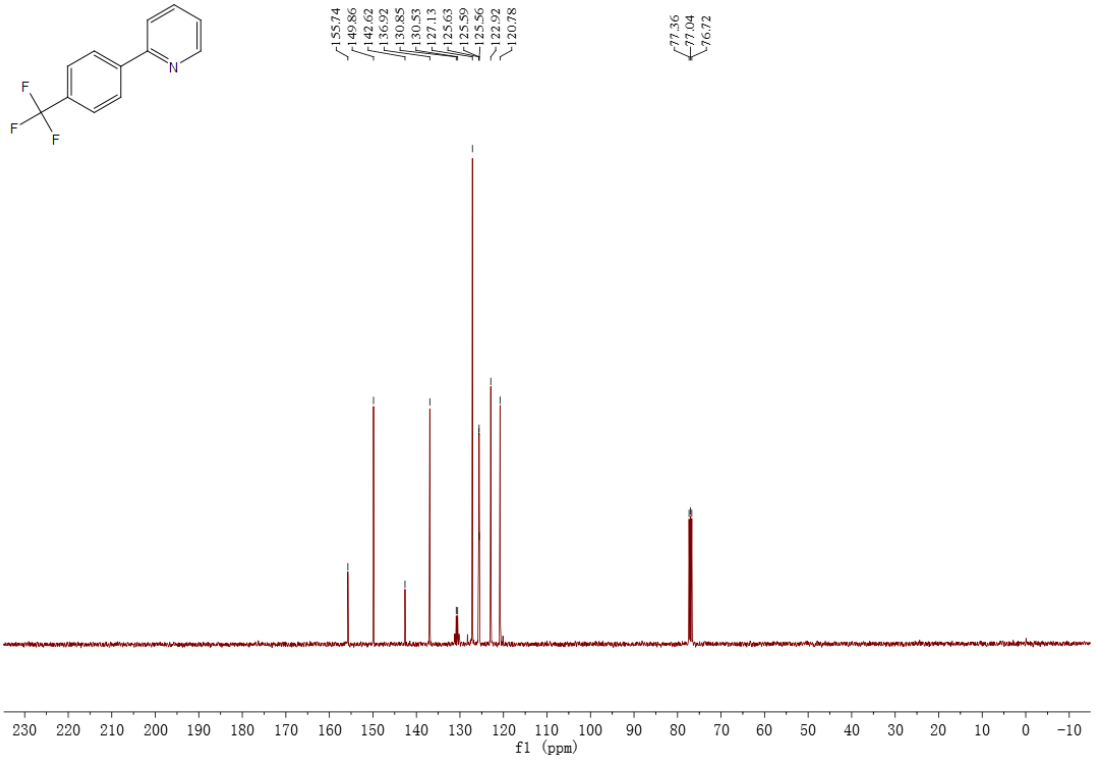


Figure S17 ^{1}H-NMR spectrum of **1h**

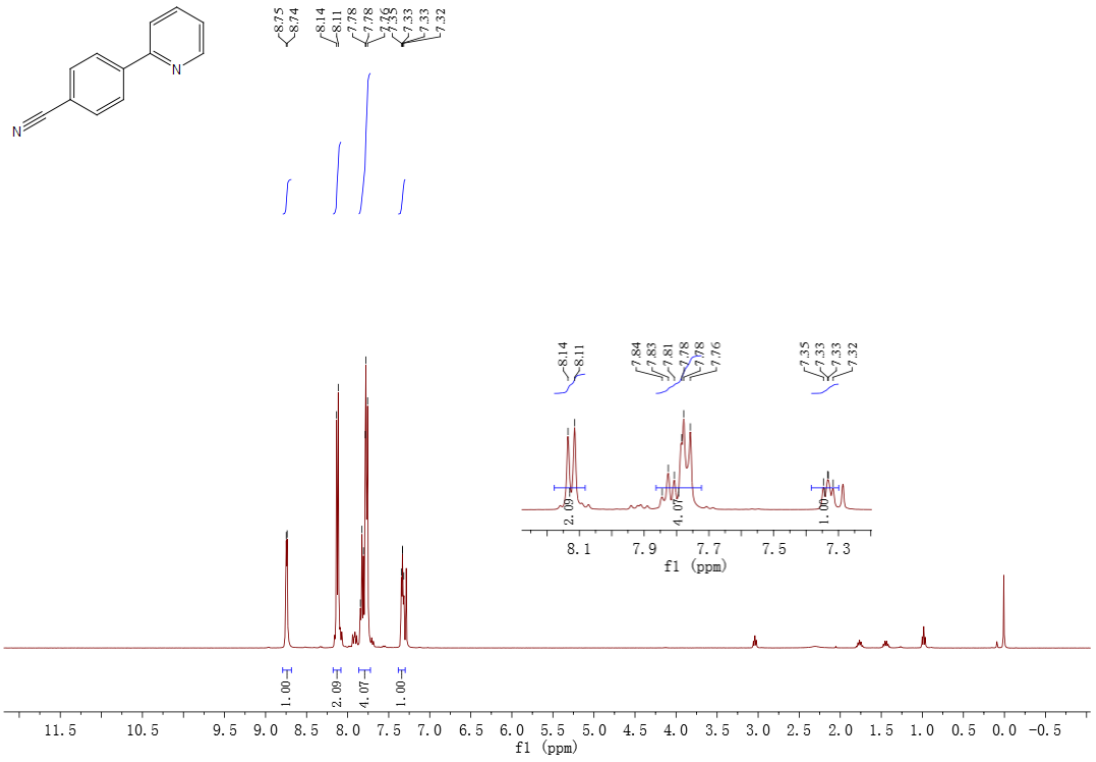


Figure S18 ^{13}C-NMR spectrum of **1h**

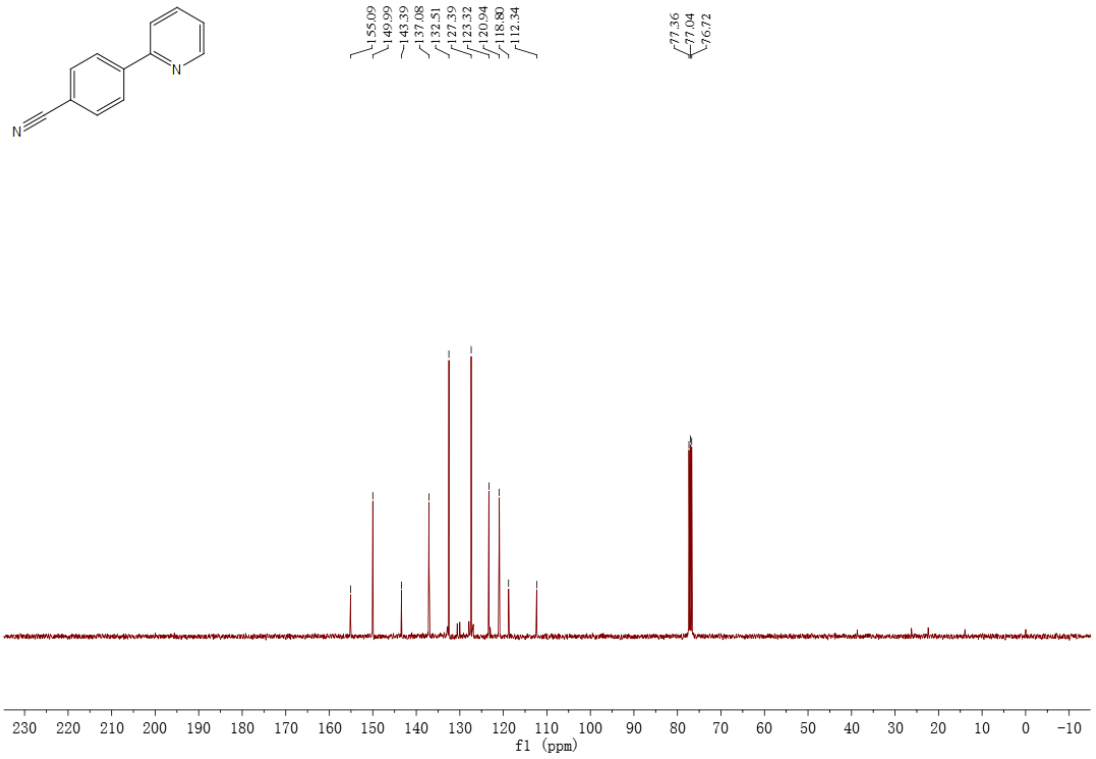


Figure S19 ^{1}H-NMR spectrum of **1i**

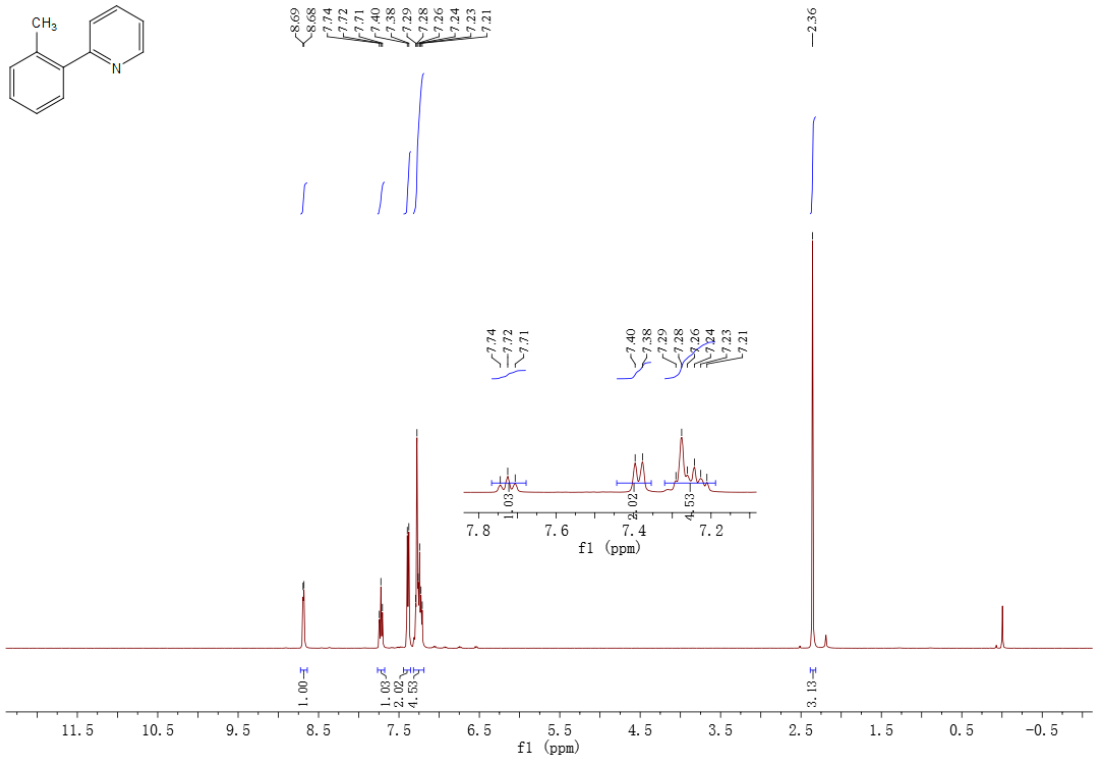


Figure S20 ^{13}C-NMR spectrum of **1i**

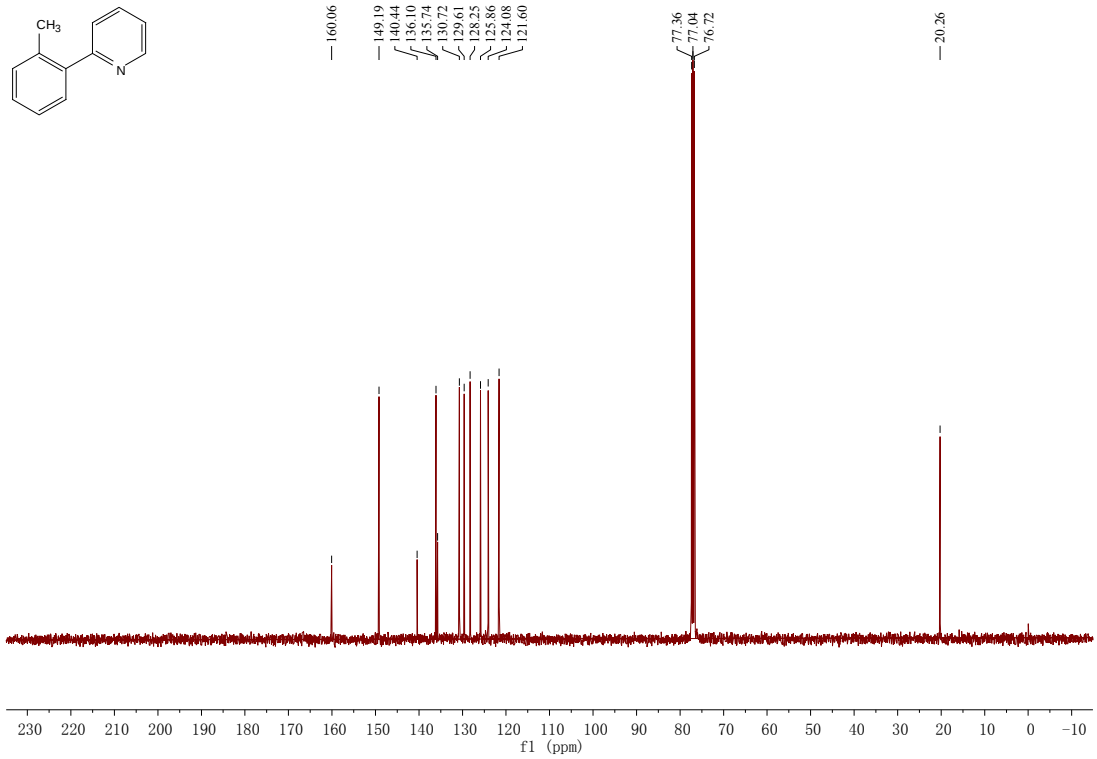


Figure S21 ^{1}H-NMR spectrum of **1j**

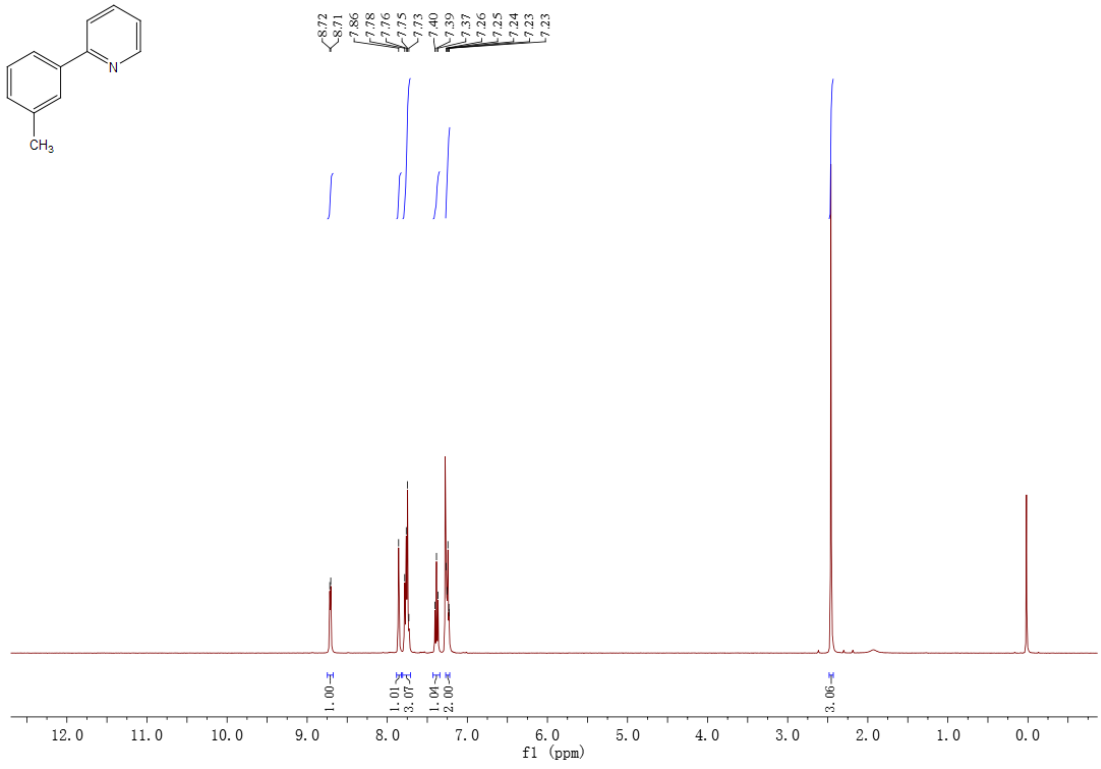


Figure S22 ^{13}C-NMR spectrum of **1j**

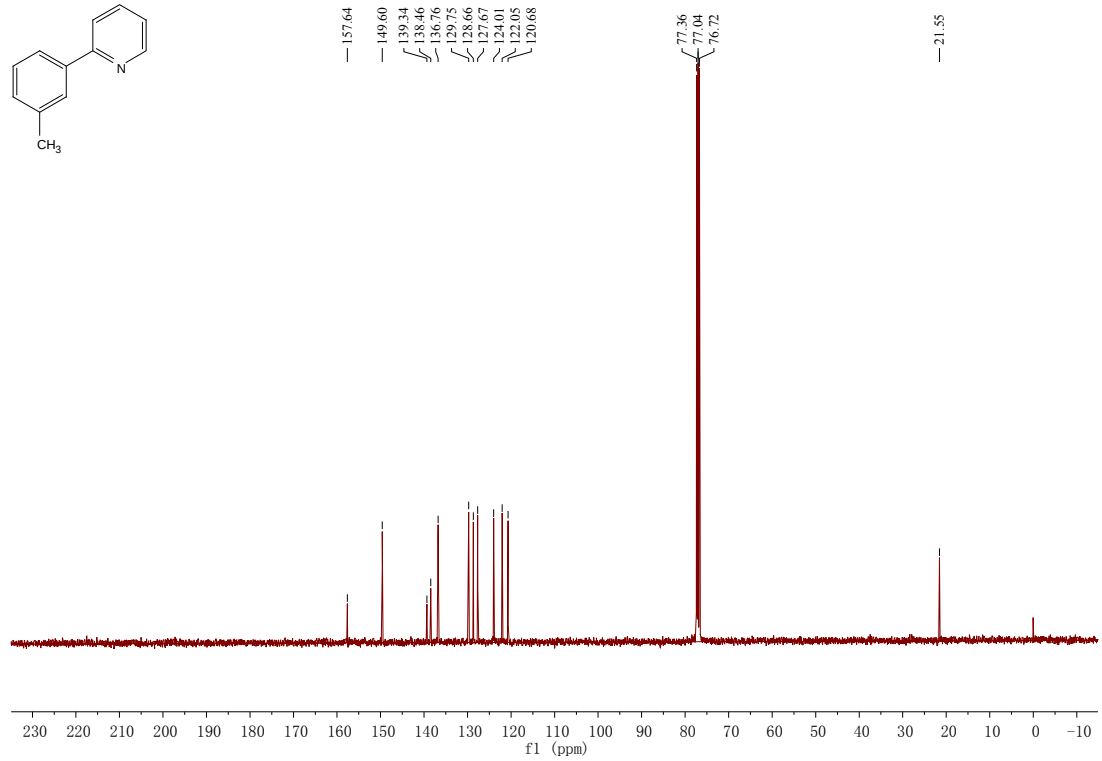


Figure S23 ^{1}H-NMR spectrum of **1k**

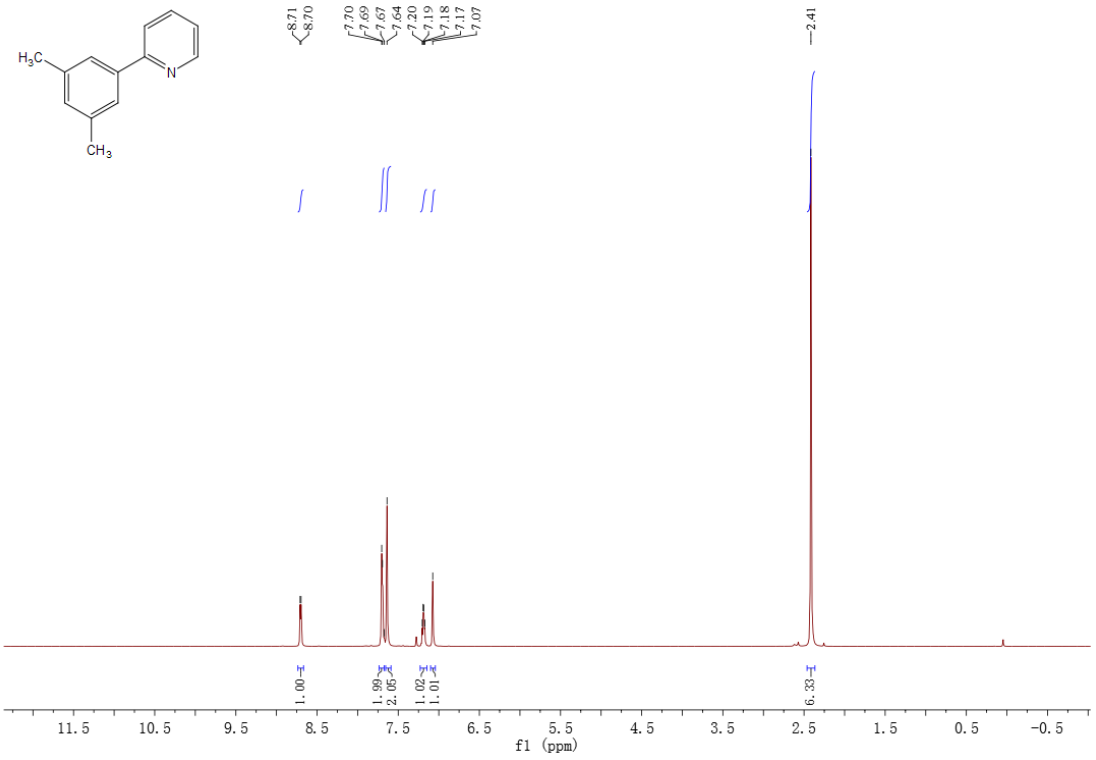


Figure S24 ^{13}C-NMR spectrum of **1k**

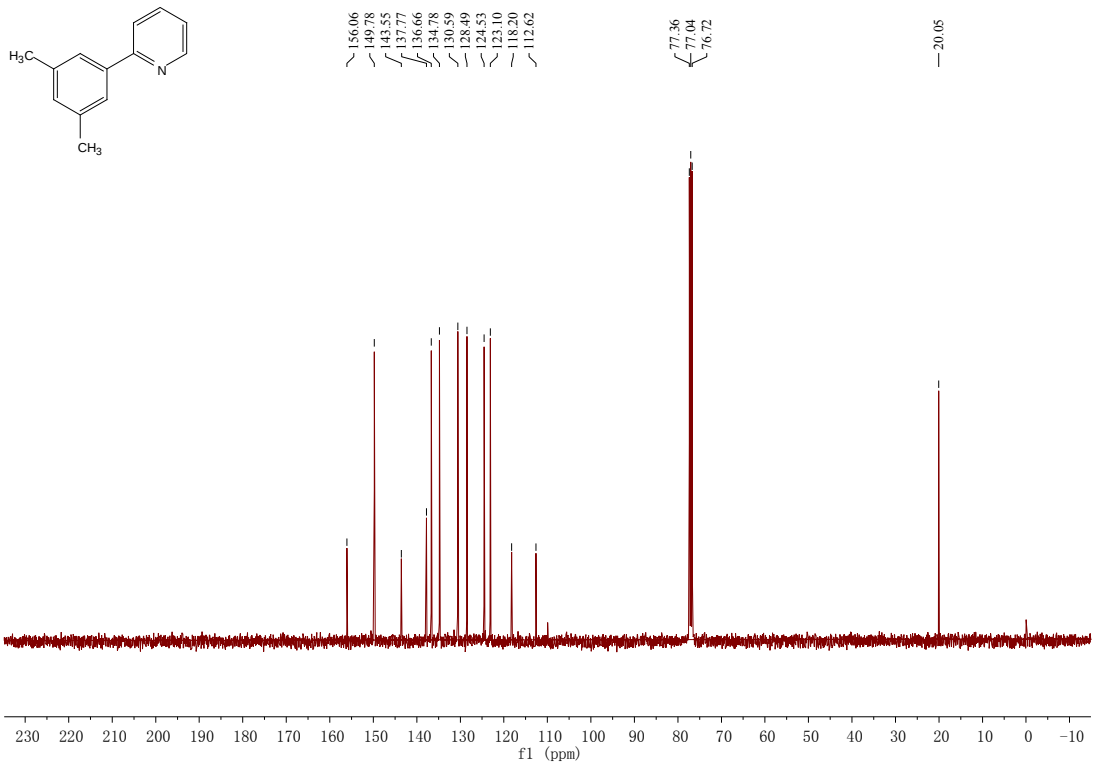


Figure S25 ^{1}H-NMR spectrum of **1l**

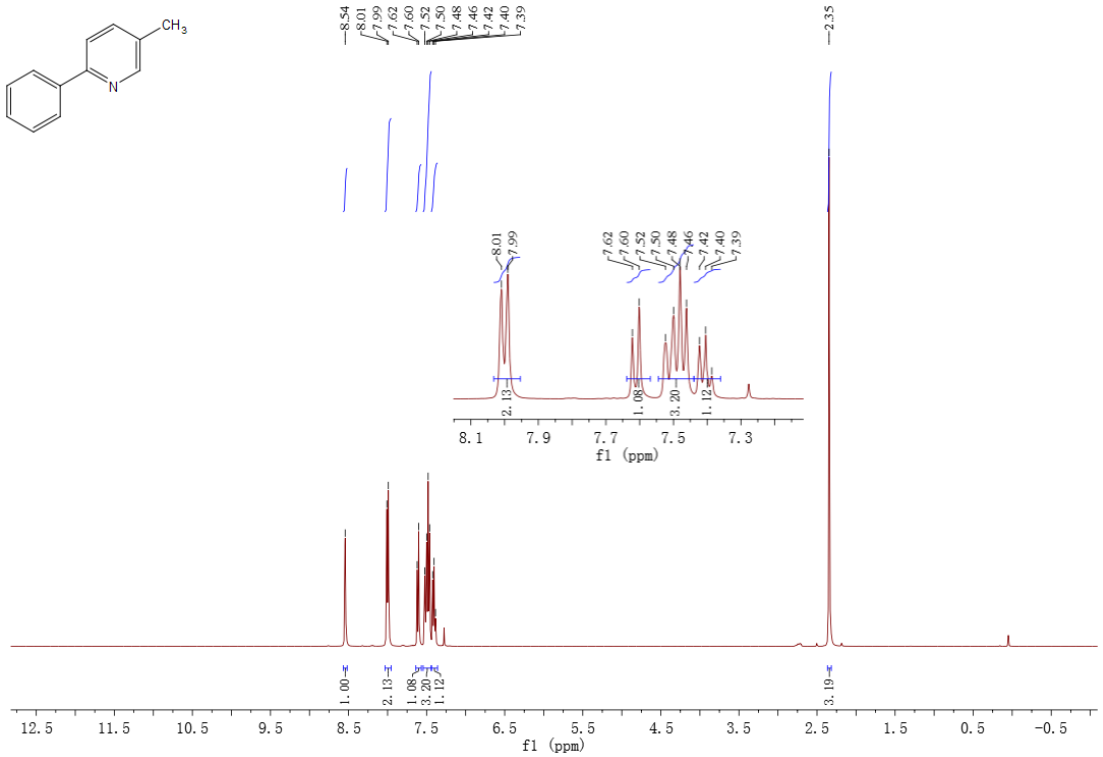


Figure S26 ^{13}C-NMR spectrum of **1l**

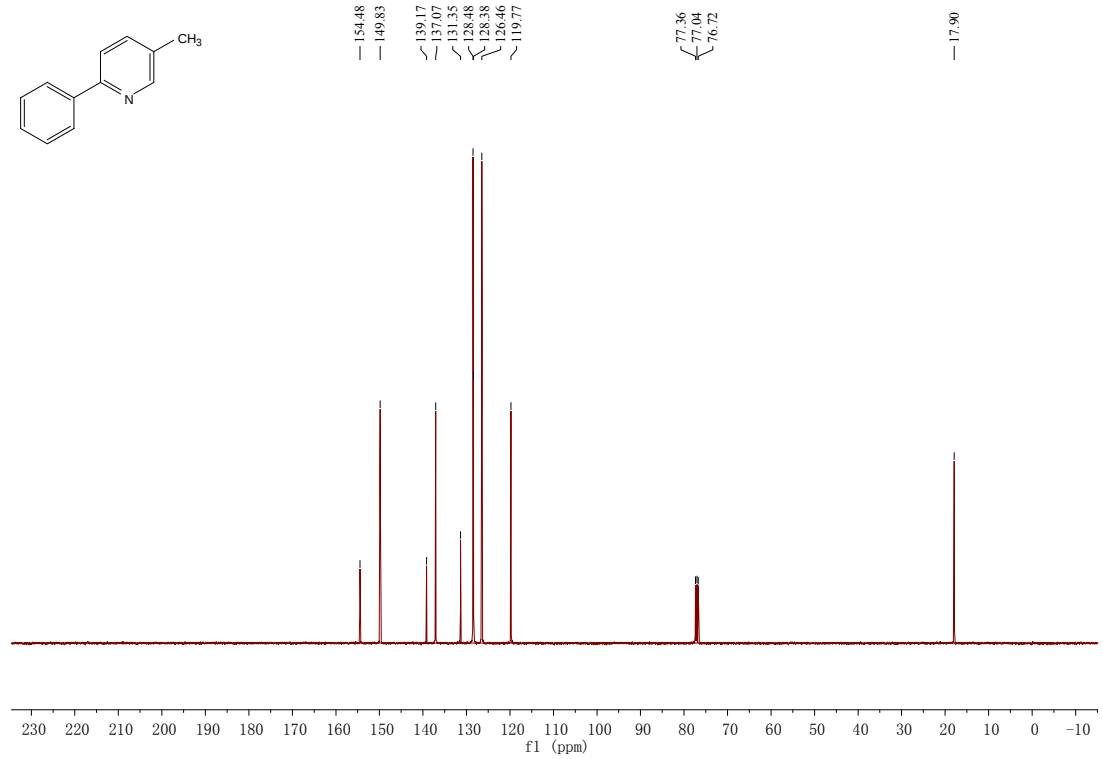


Figure S27 ^{1}H-NMR spectrum of **1m**

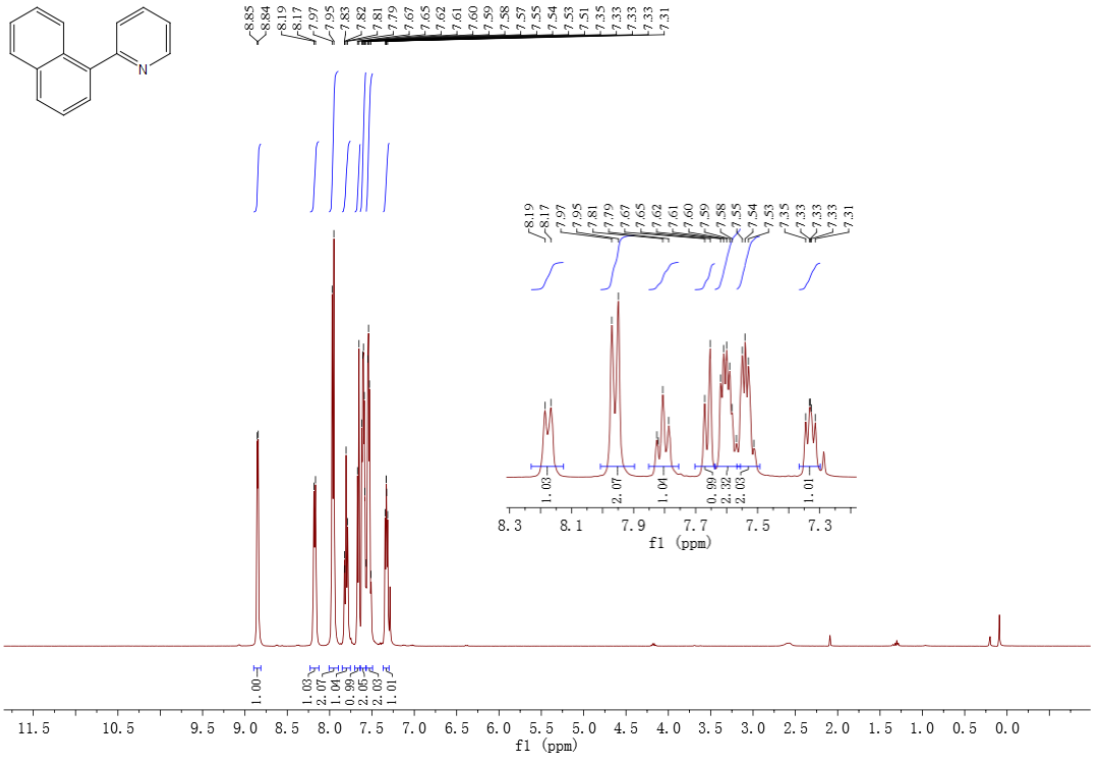


Figure S28 ^{13}C-NMR spectrum of **1m**

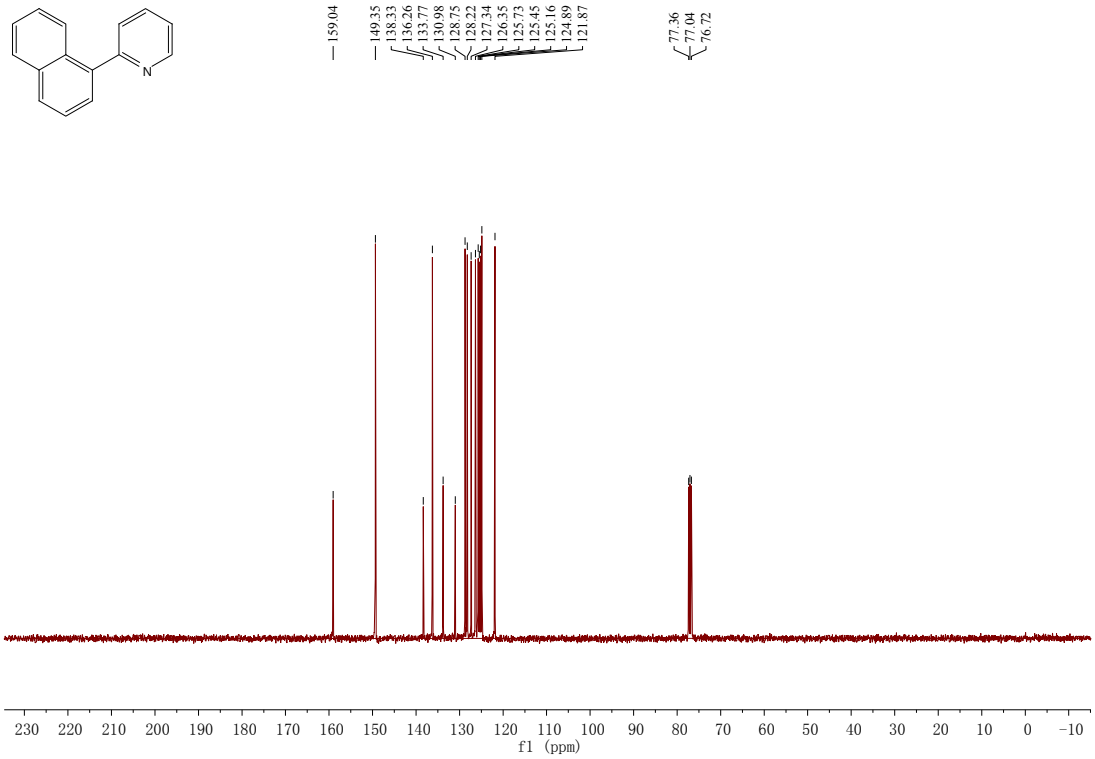


Figure S29 ^{1}H-NMR spectrum of **1n**

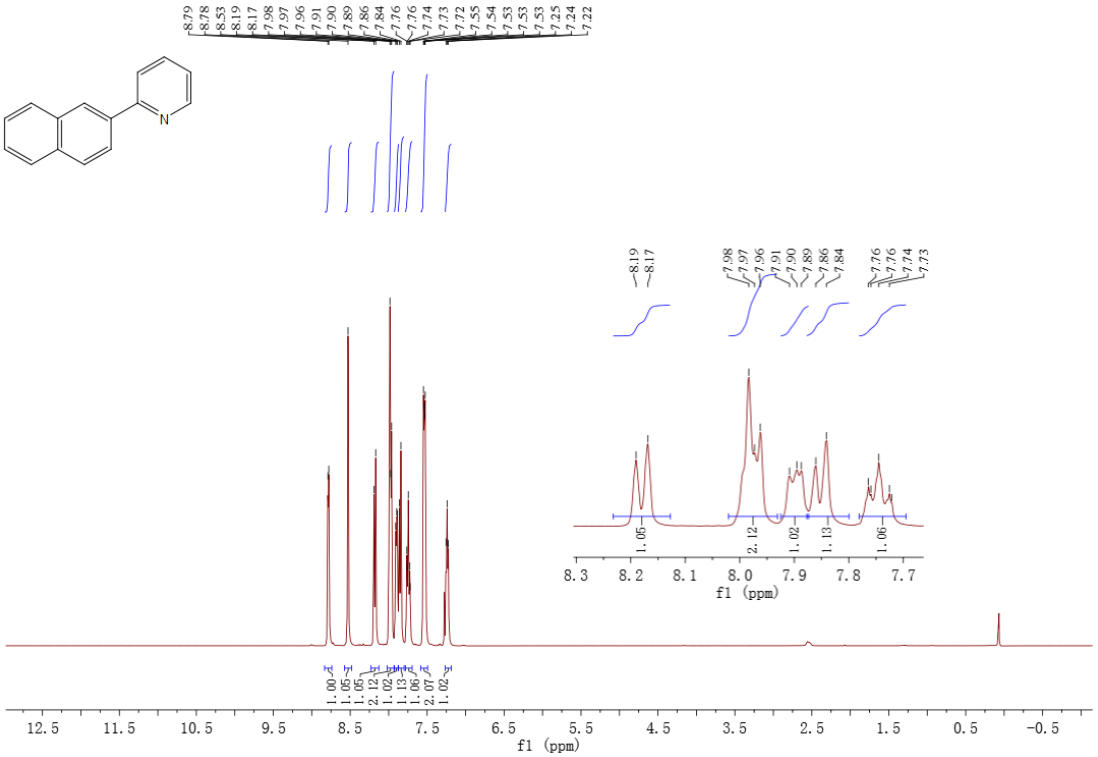


Figure S30 ^{13}C-NMR spectrum of **1n**

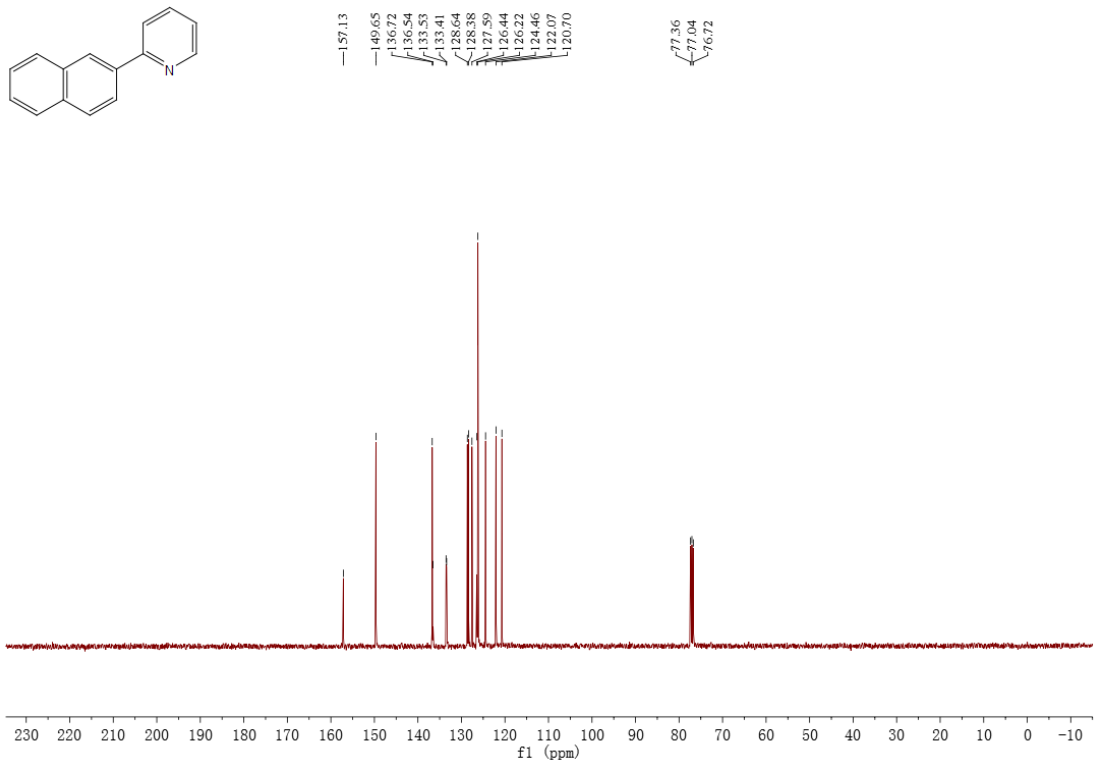


Figure S31 ^{1}H-NMR spectrum of **1o**

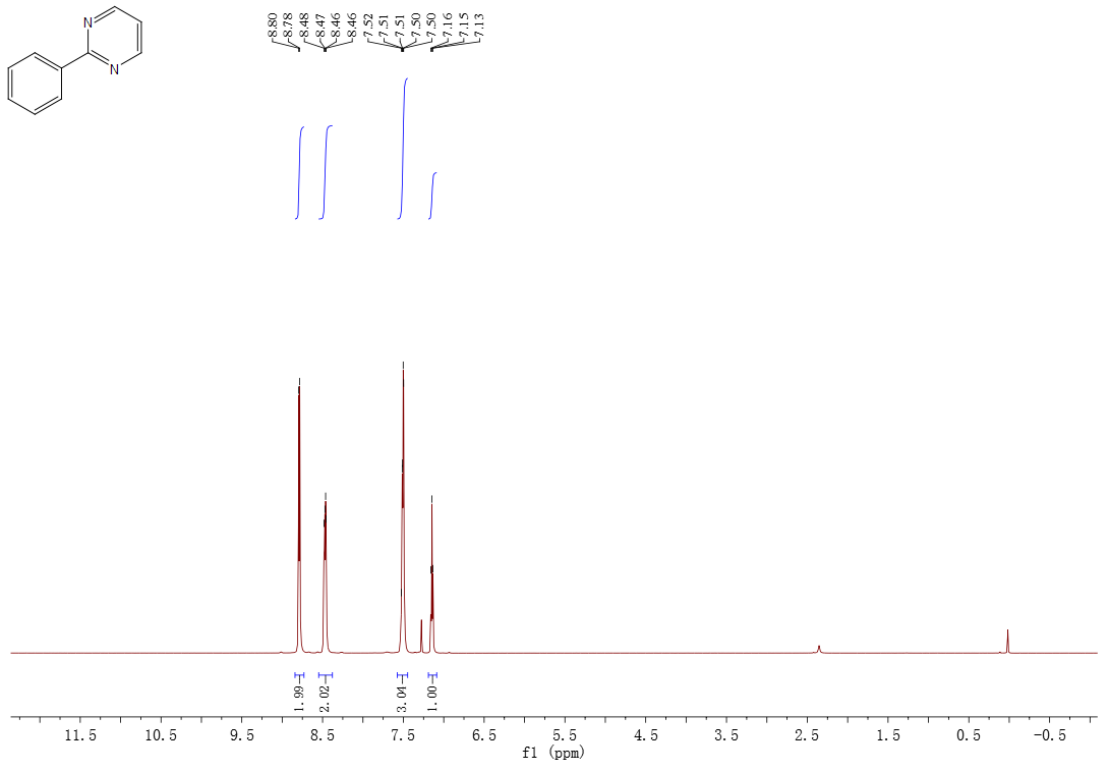


Figure S32 ^{13}C-NMR spectrum of **1o**

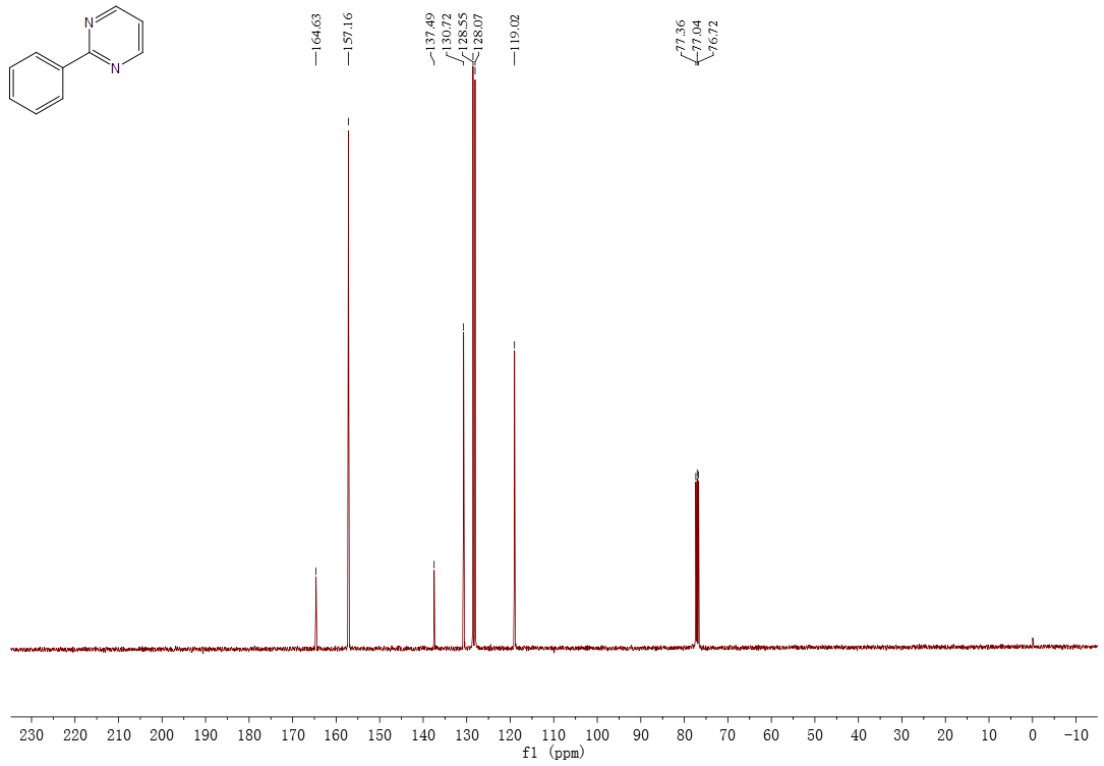


Figure S33 ^{1}H-NMR spectrum of **1s**

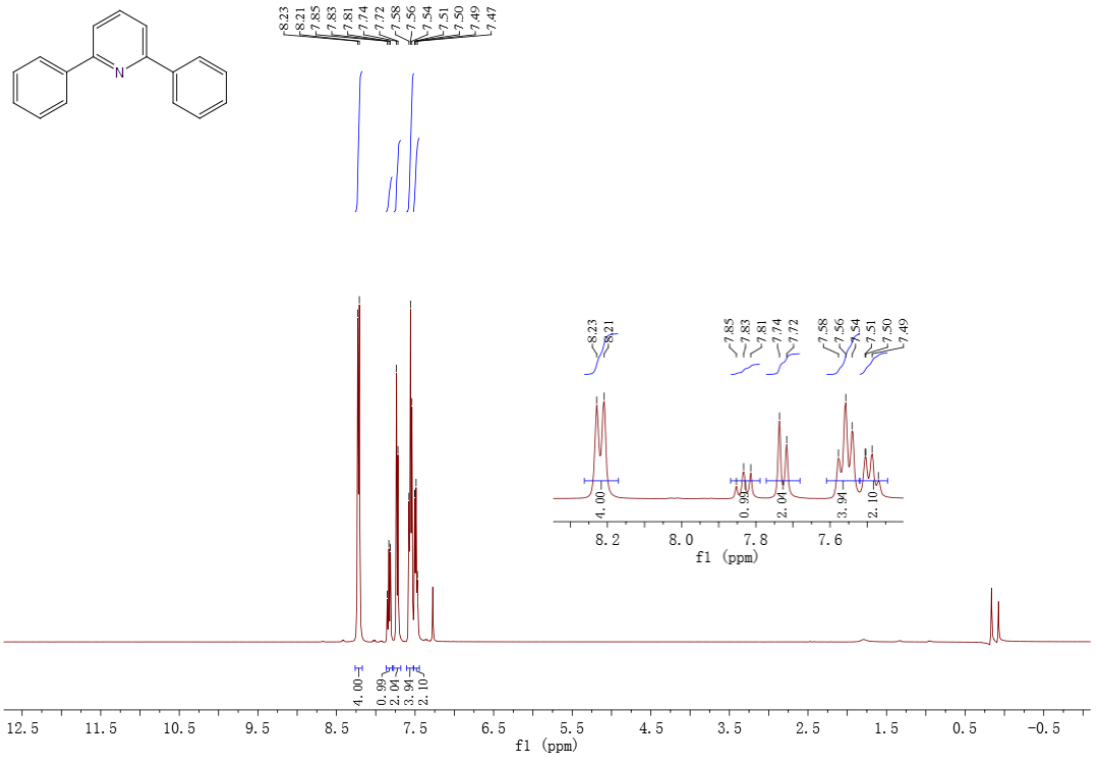


Figure S34 ^{13}C-NMR spectrum of **1s**

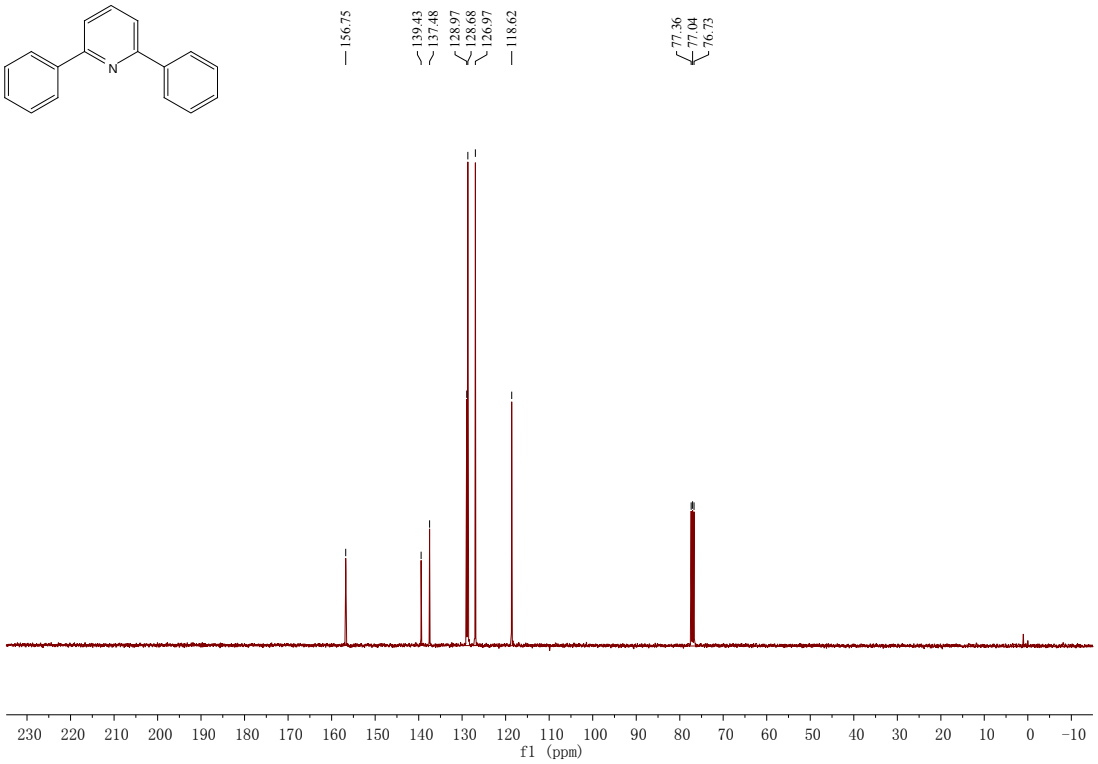


Figure S35 ^{1}H-NMR spectrum of **1t**

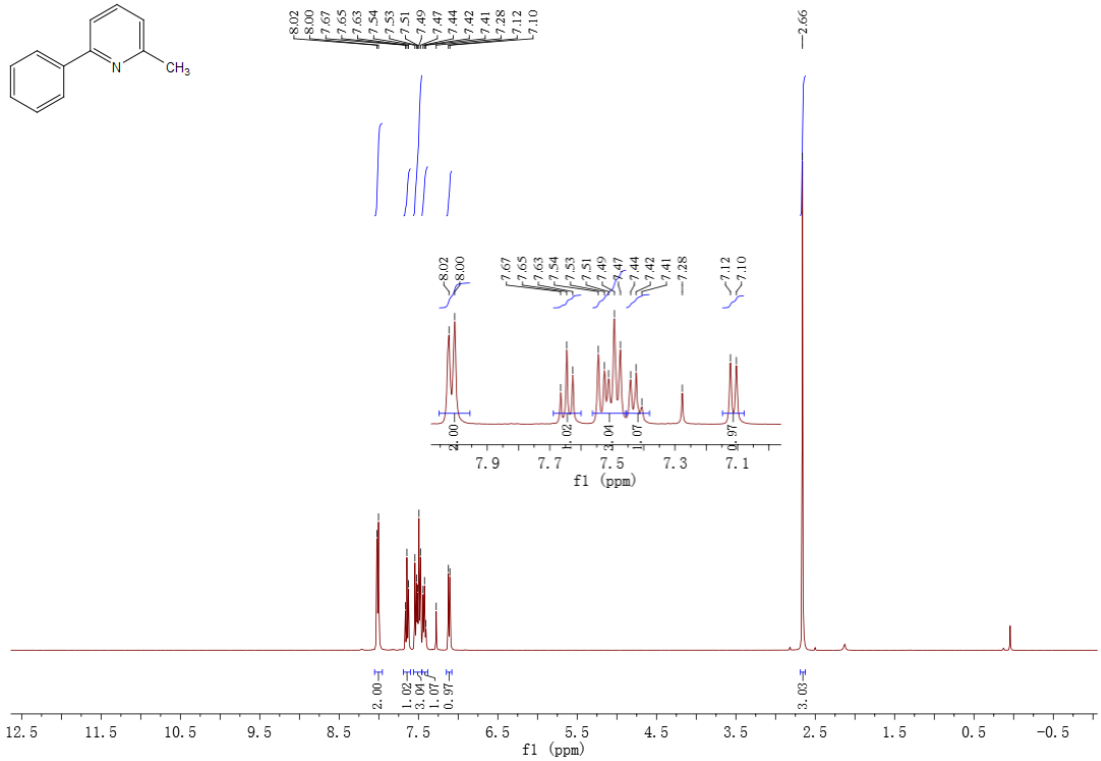


Figure S36 ^{13}C-NMR spectrum of **1t**

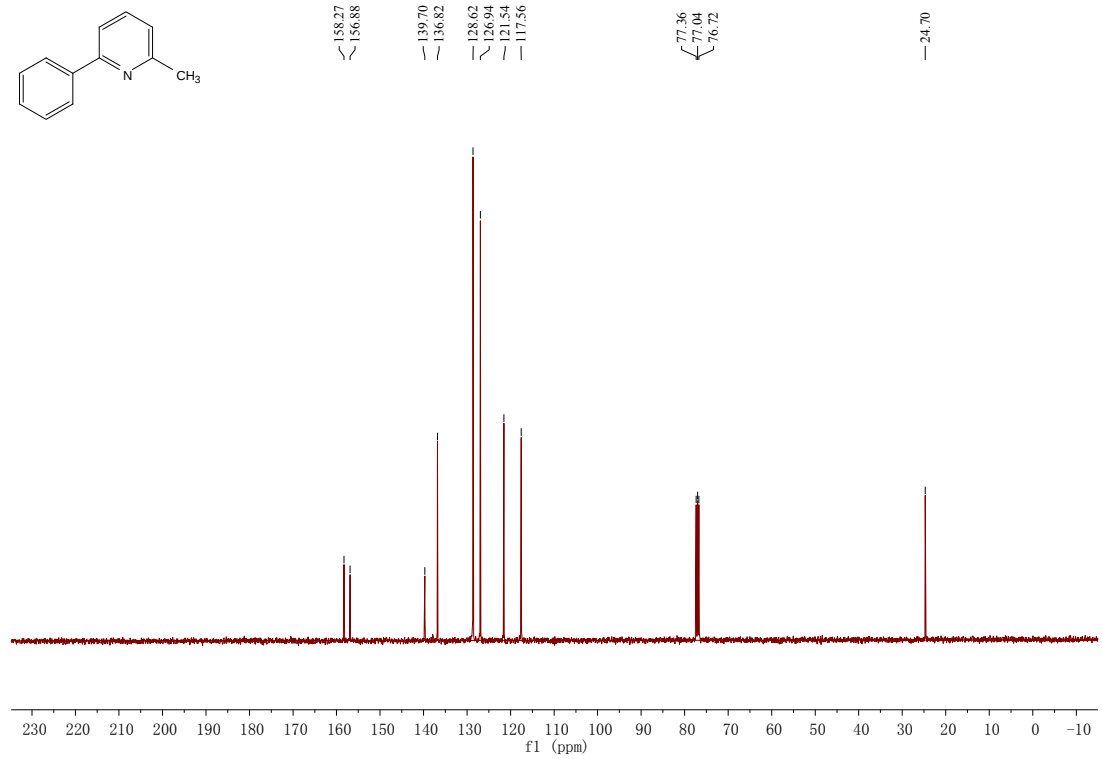


Figure S37 ^{1}H-NMR spectrum of **1u**

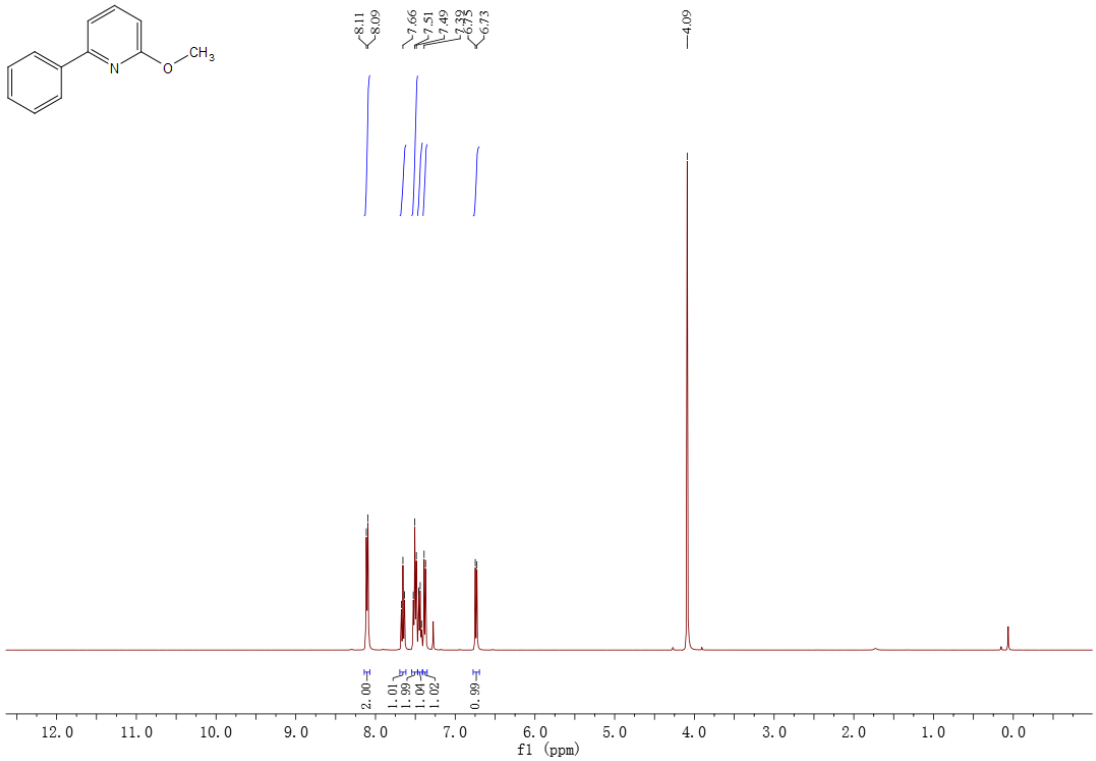


Figure S38 ^{13}C-NMR spectrum of **1u**

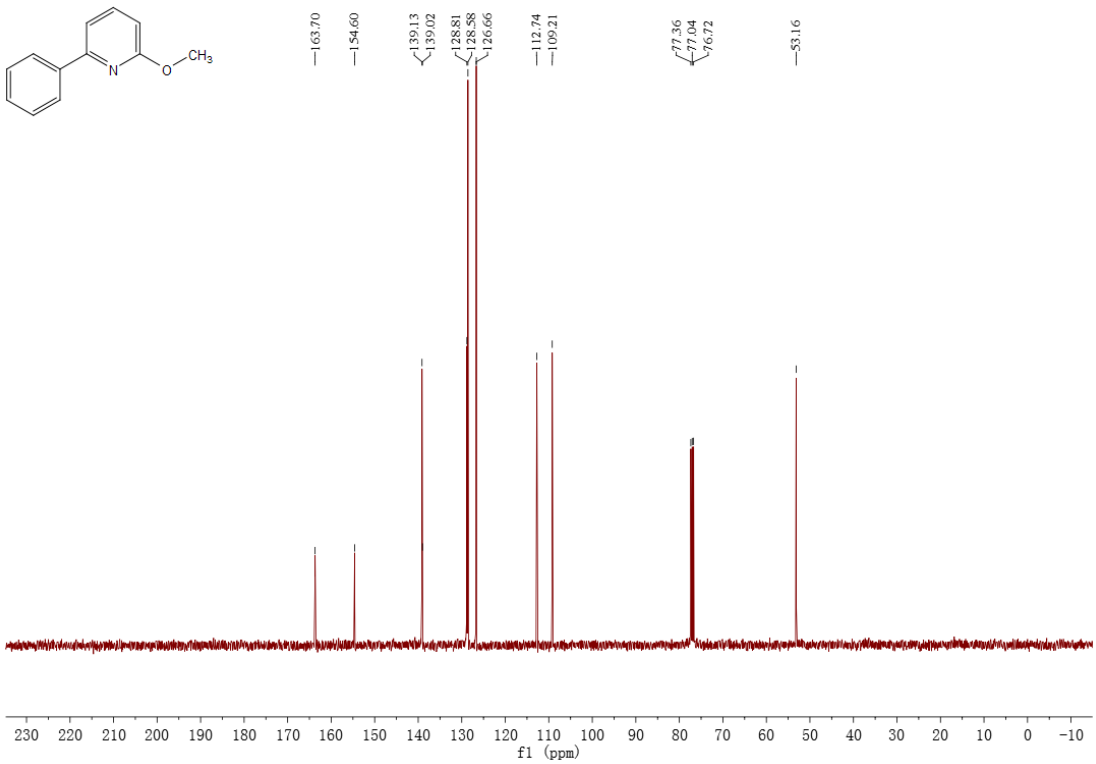


Figure S39 ^{1}H-NMR spectrum of **1v**

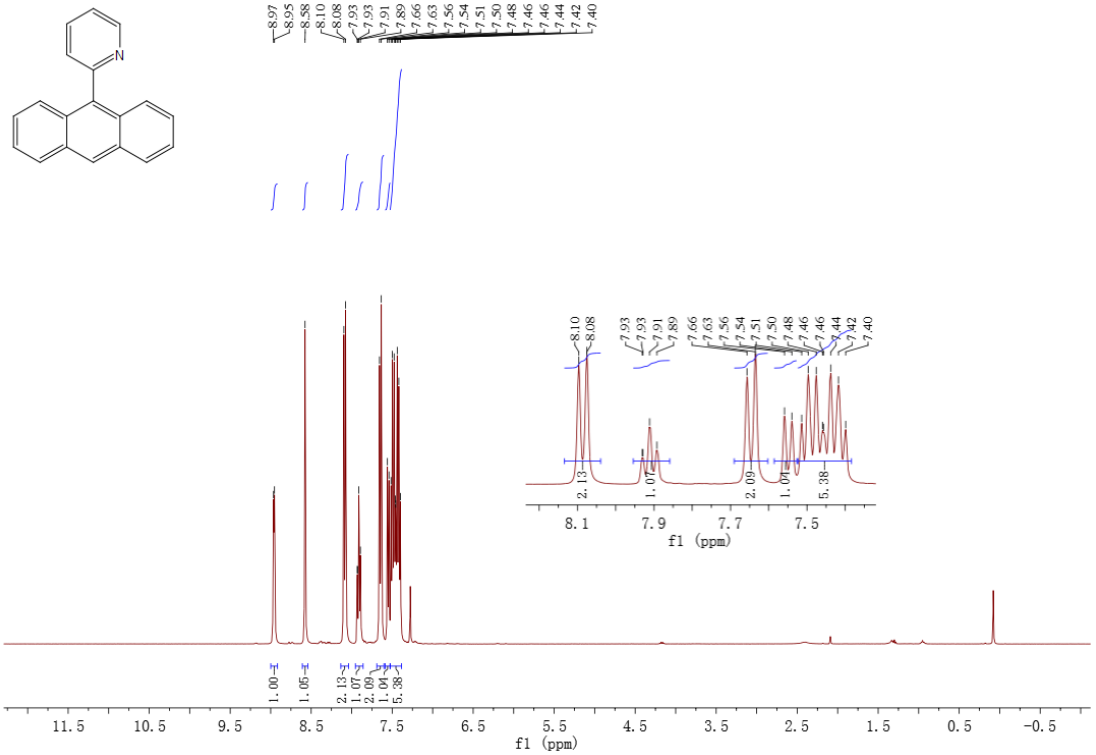


Figure S40 ^{13}C-NMR spectrum of **1v**

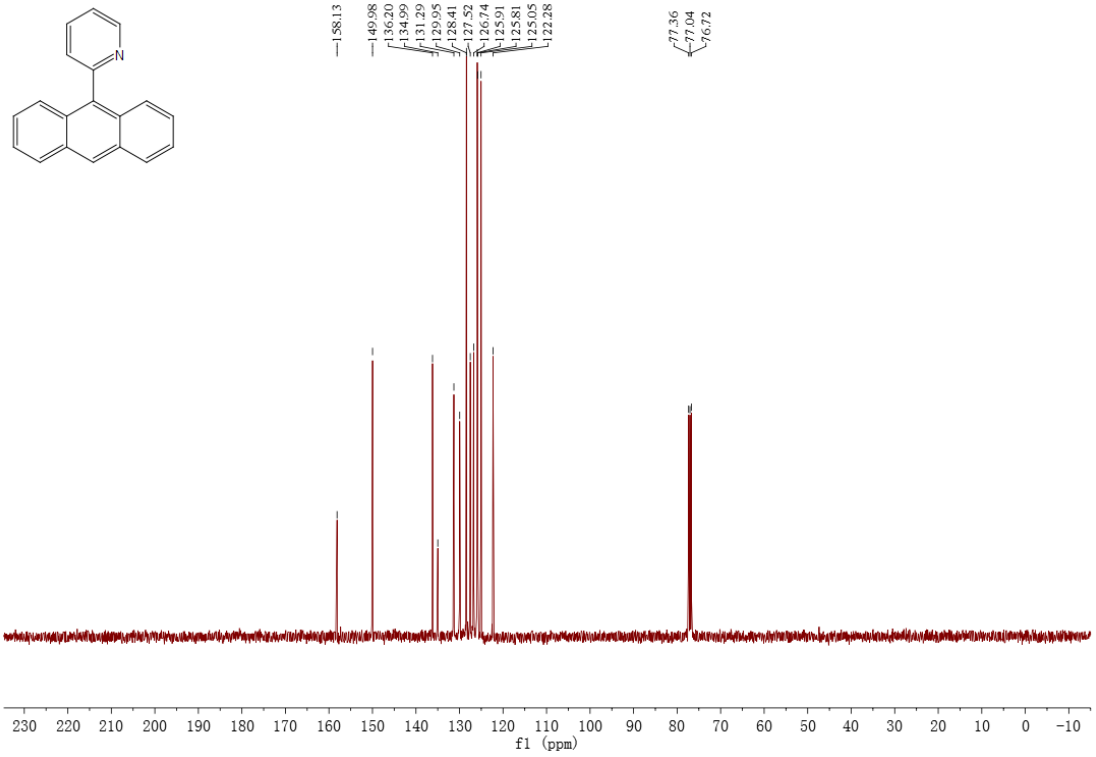


Figure S41 ^{1}H-NMR spectrum of **3a**

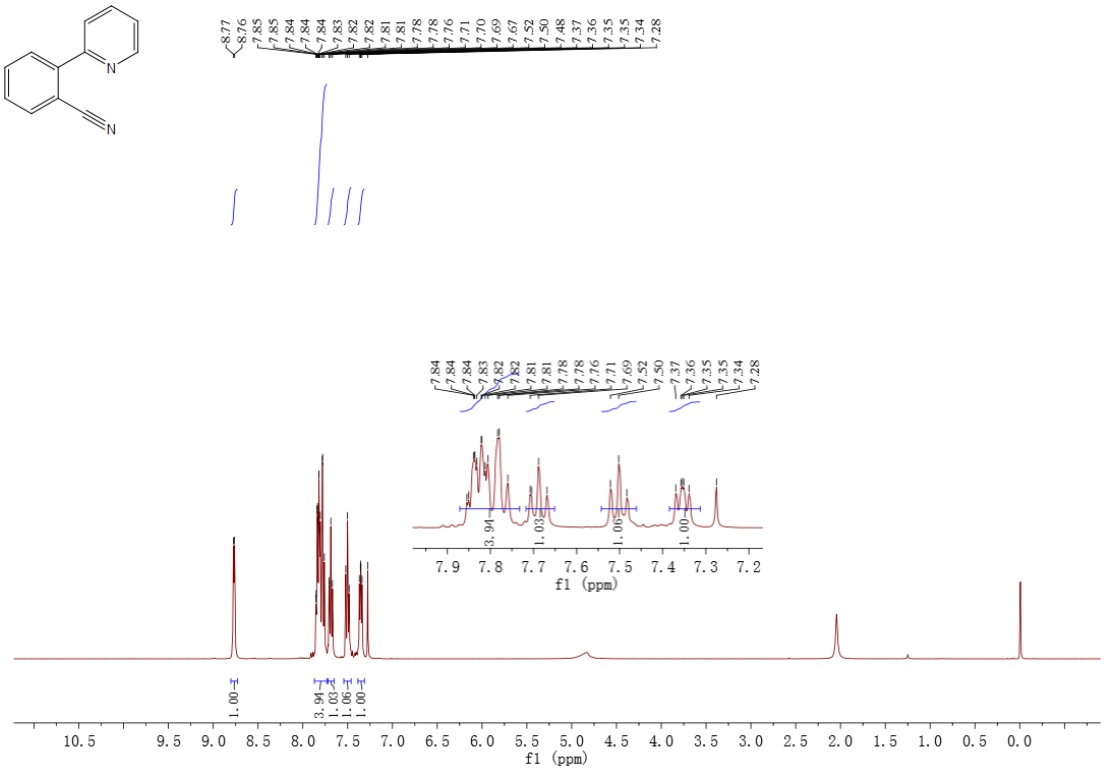


Figure S42 ^{13}C-NMR spectrum of **3a**

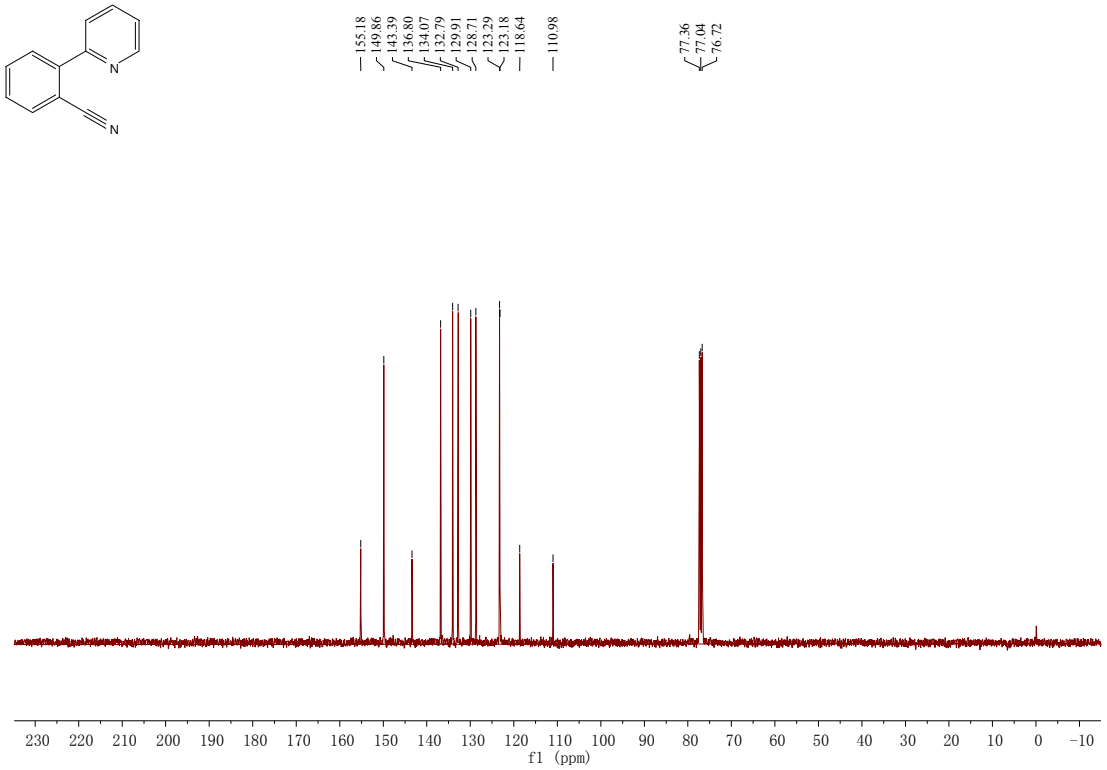


Figure S43 ^{1}H-NMR spectrum of **3b**

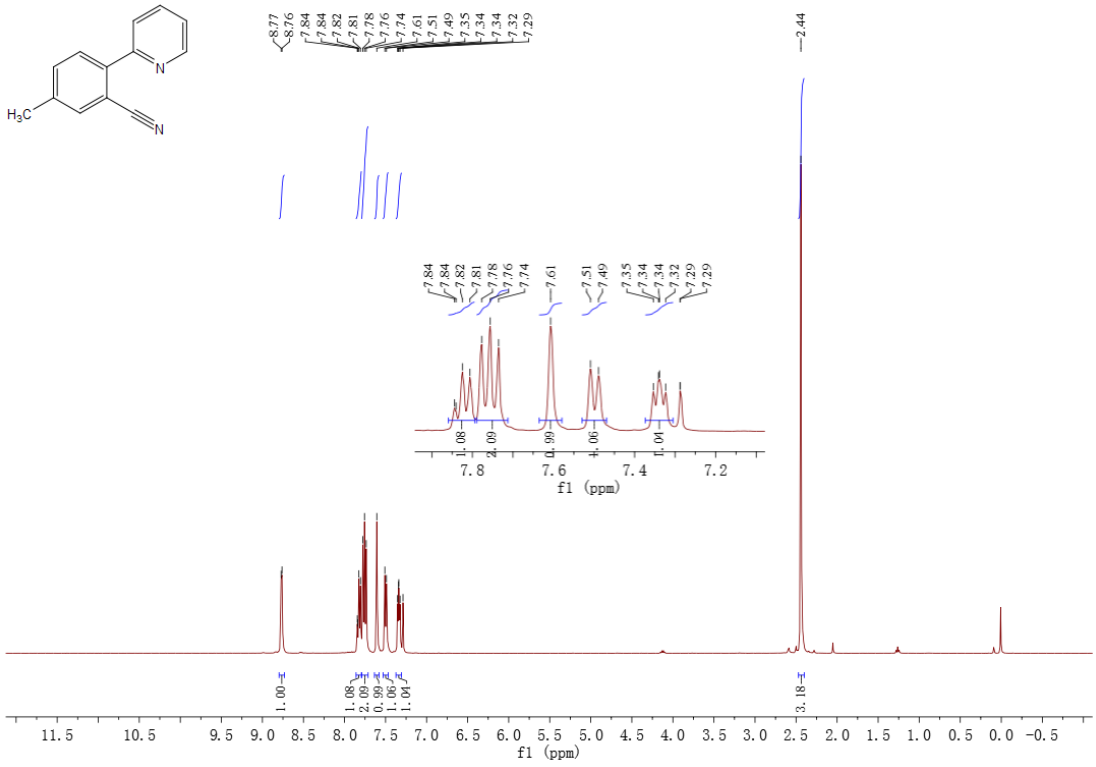


Figure S44 ^{13}C-NMR spectrum of **3b**

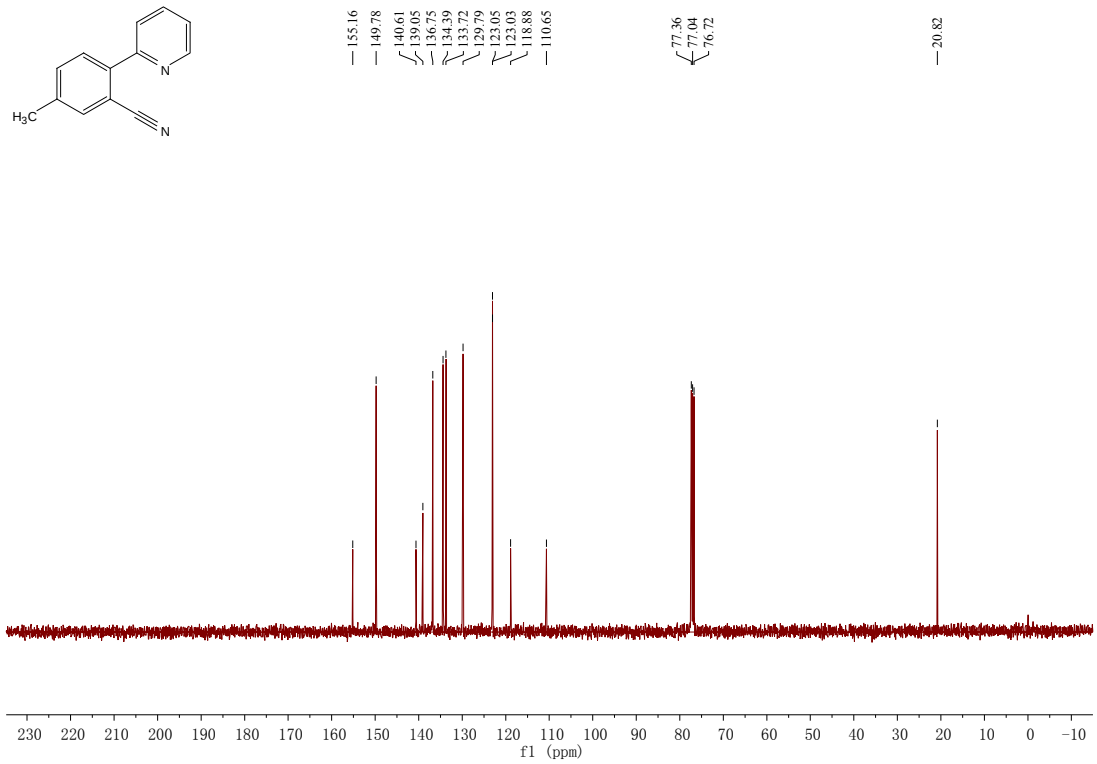


Figure S45 ^{1}H-NMR spectrum of **3c**

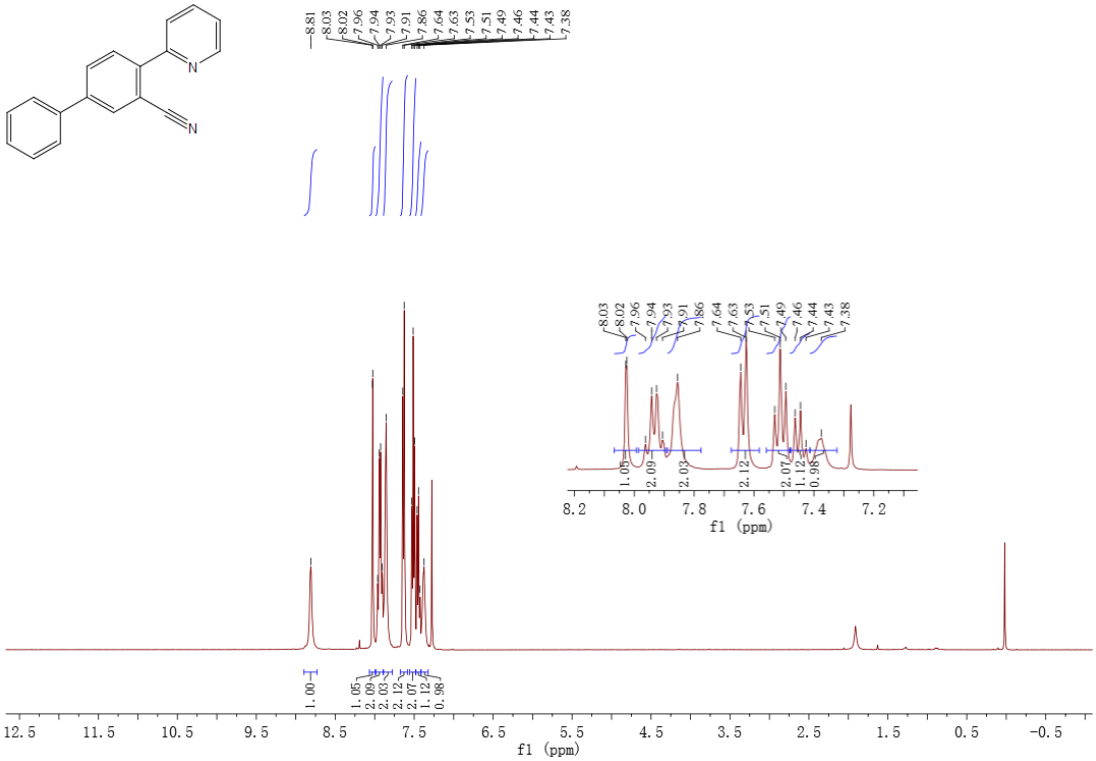


Figure S46 ^{13}C-NMR spectrum of **3c**

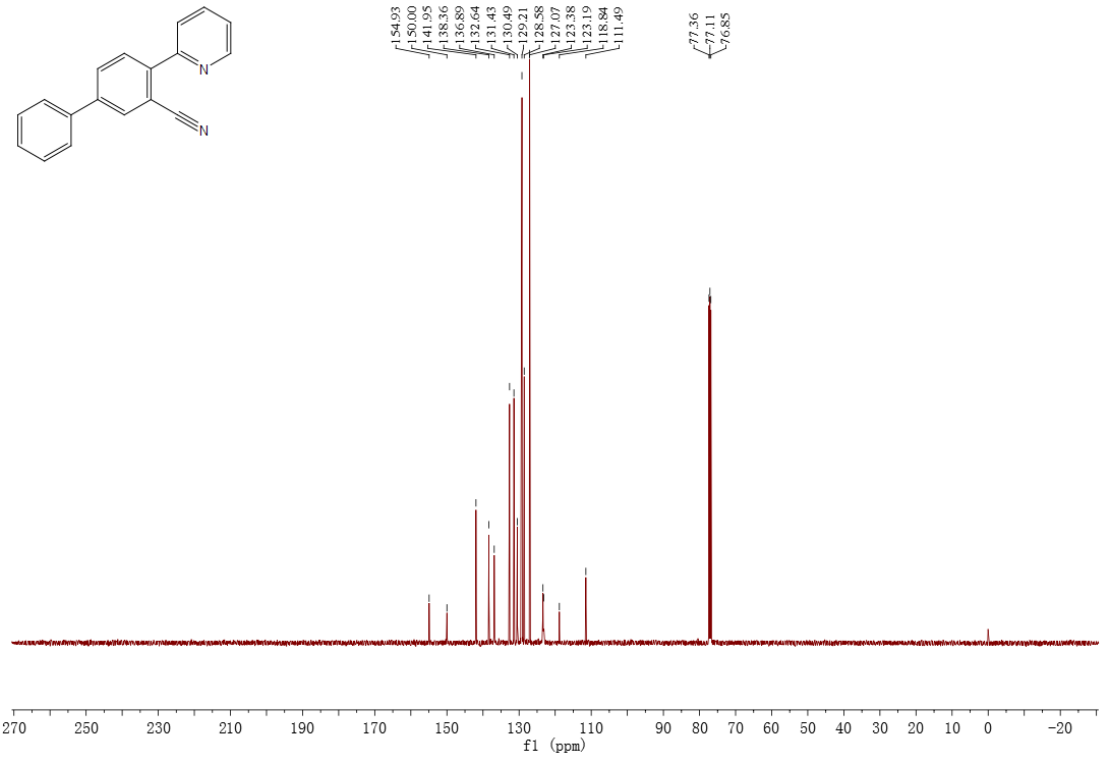


Figure S47 ^{1}H-NMR spectrum of **3d**

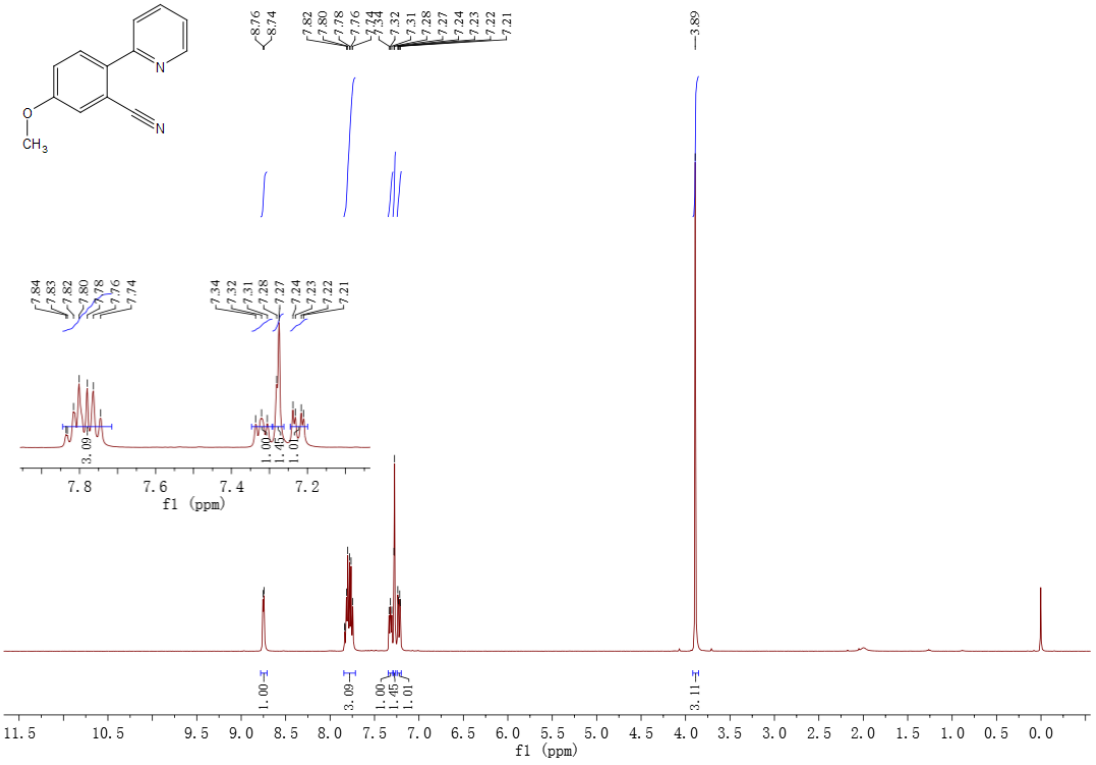


Figure S48 ^{13}C-NMR spectrum of **3d**

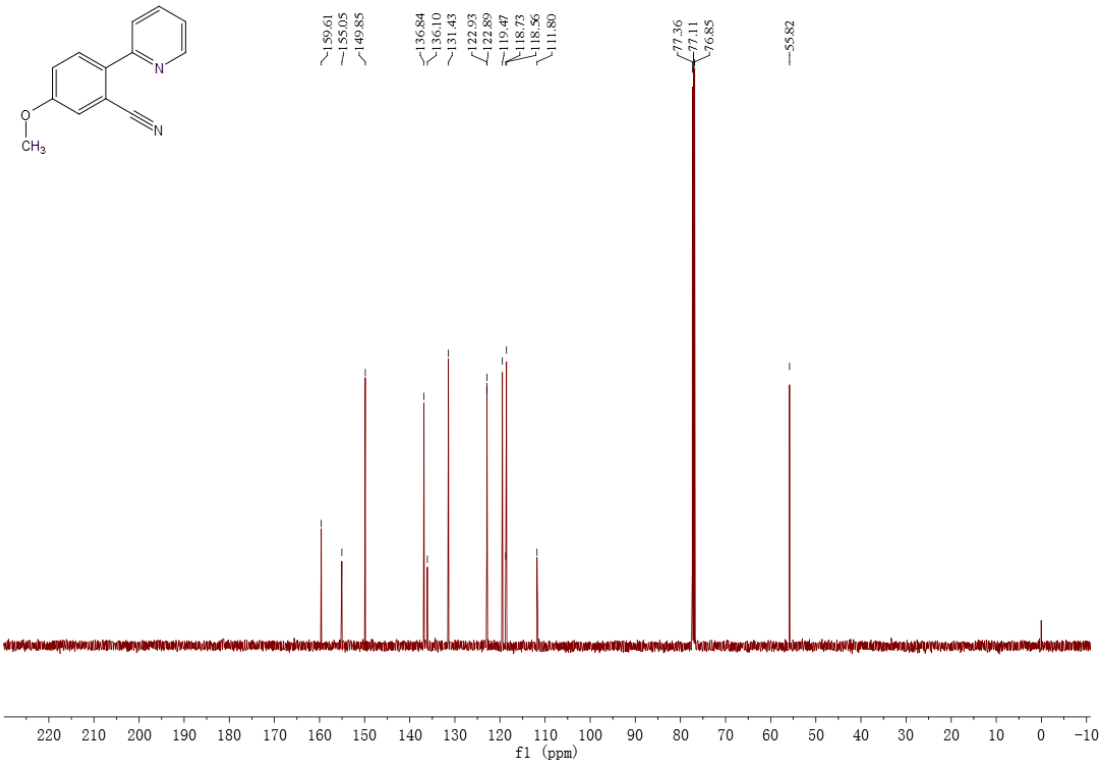


Figure S49 ^{1}H-NMR spectrum of **3e**

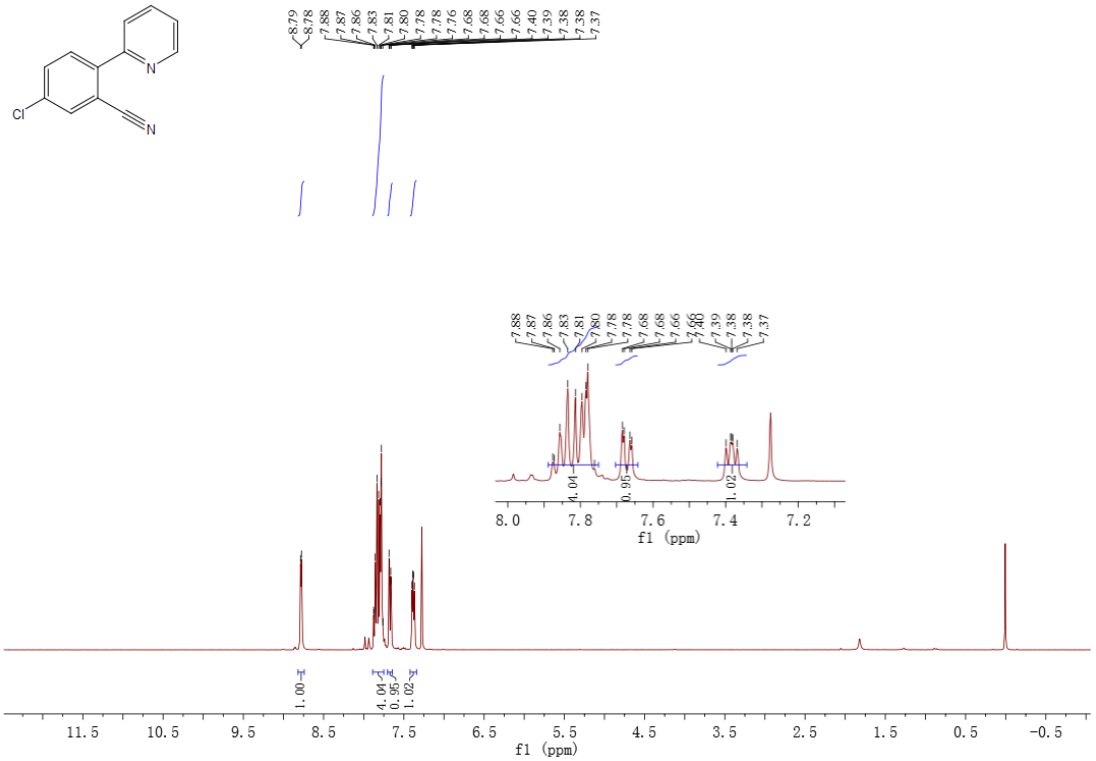


Figure S50 ^{13}C-NMR spectrum of **3e**

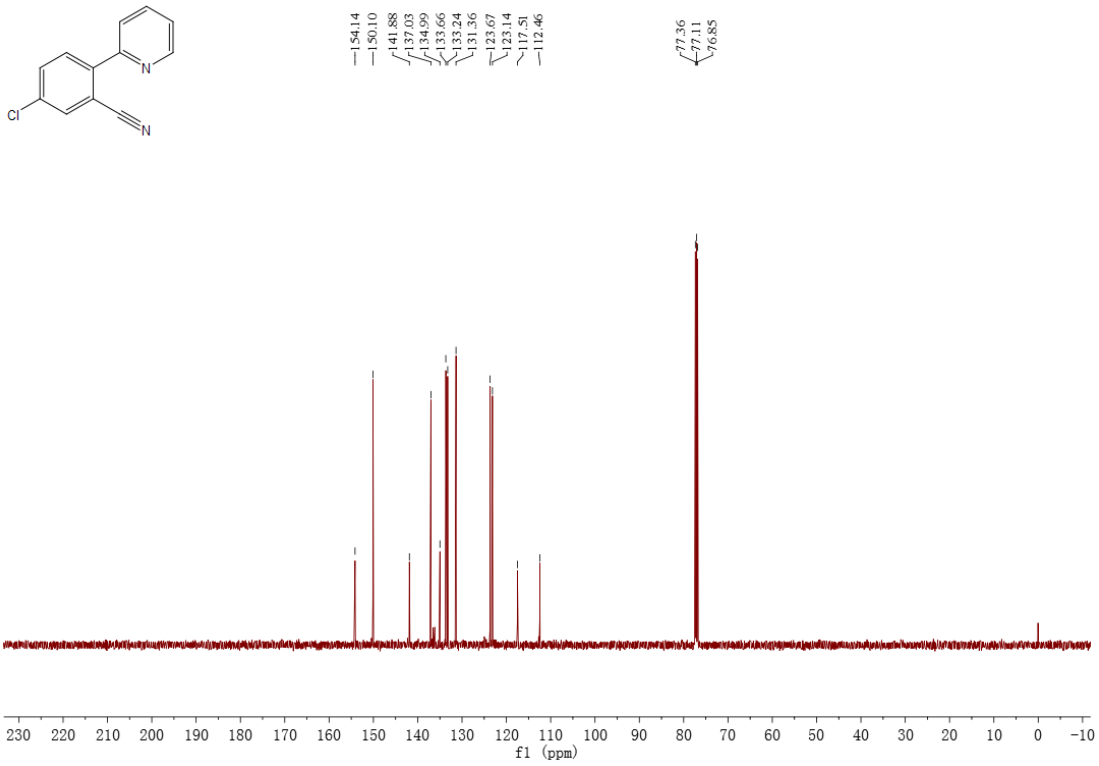


Figure S51 ^{1}H-NMR spectrum of **3f**

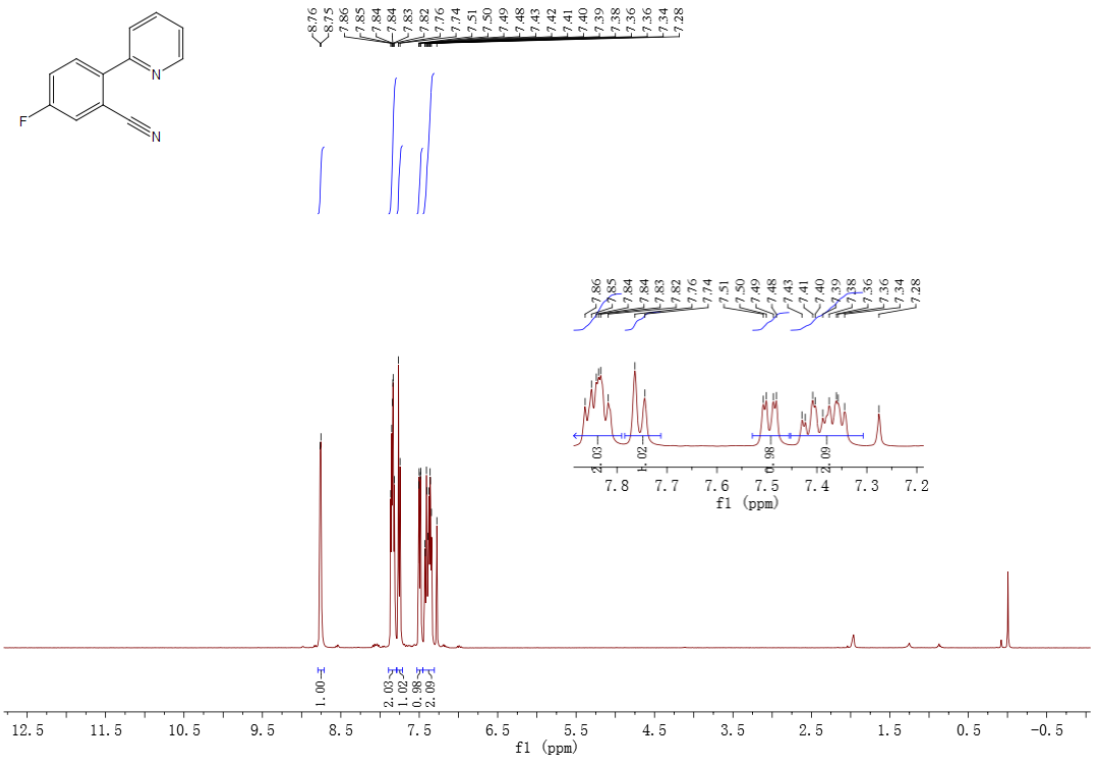


Figure S52 ^{13}C-NMR spectrum of **3f**

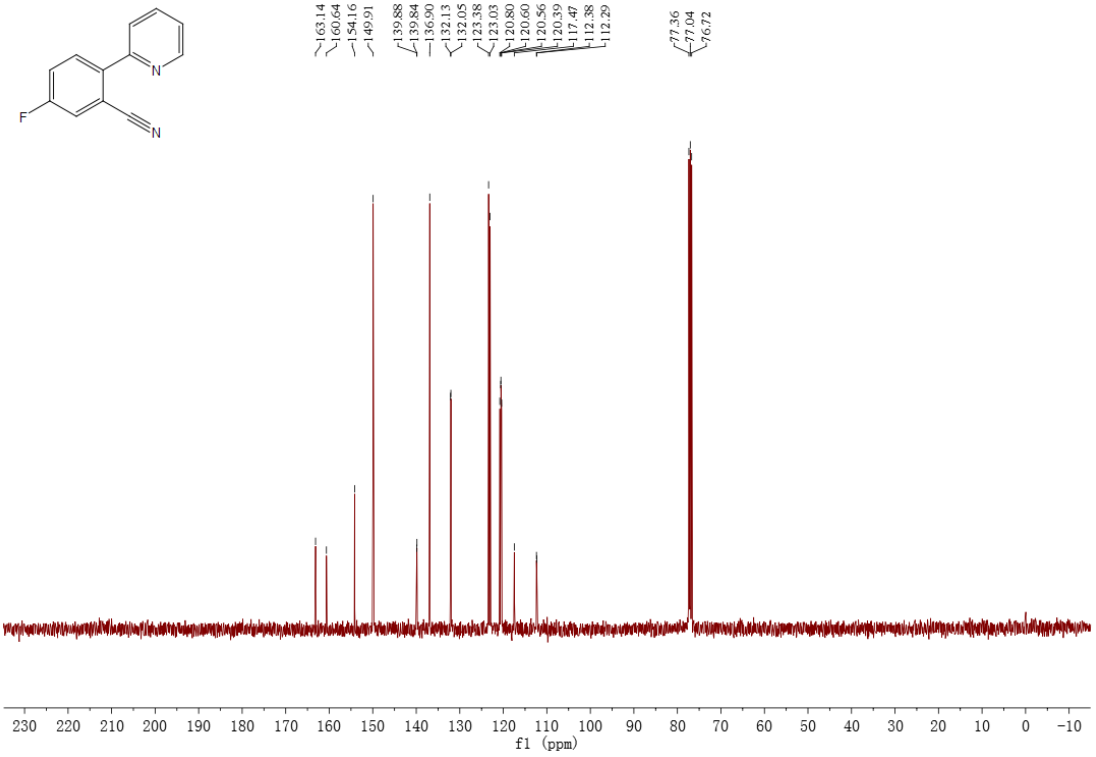


Figure S53 ^{1}H-NMR spectrum of **3g**

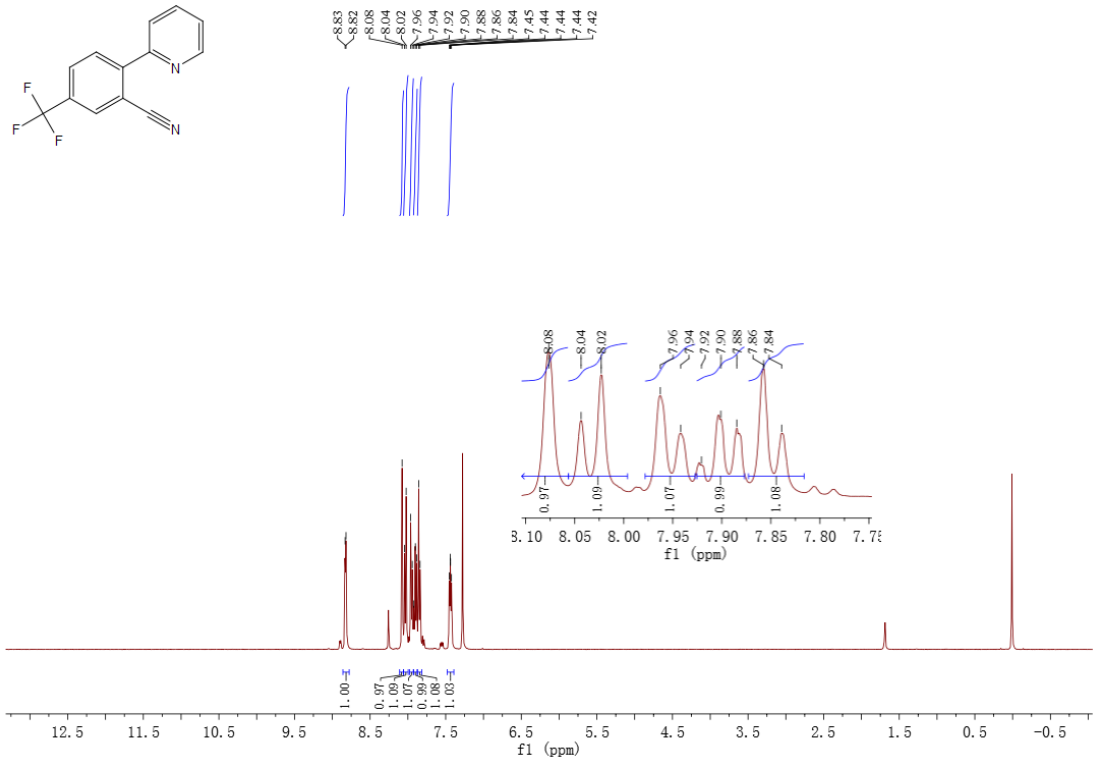


Figure S54 ^{13}C-NMR spectrum of **3g**

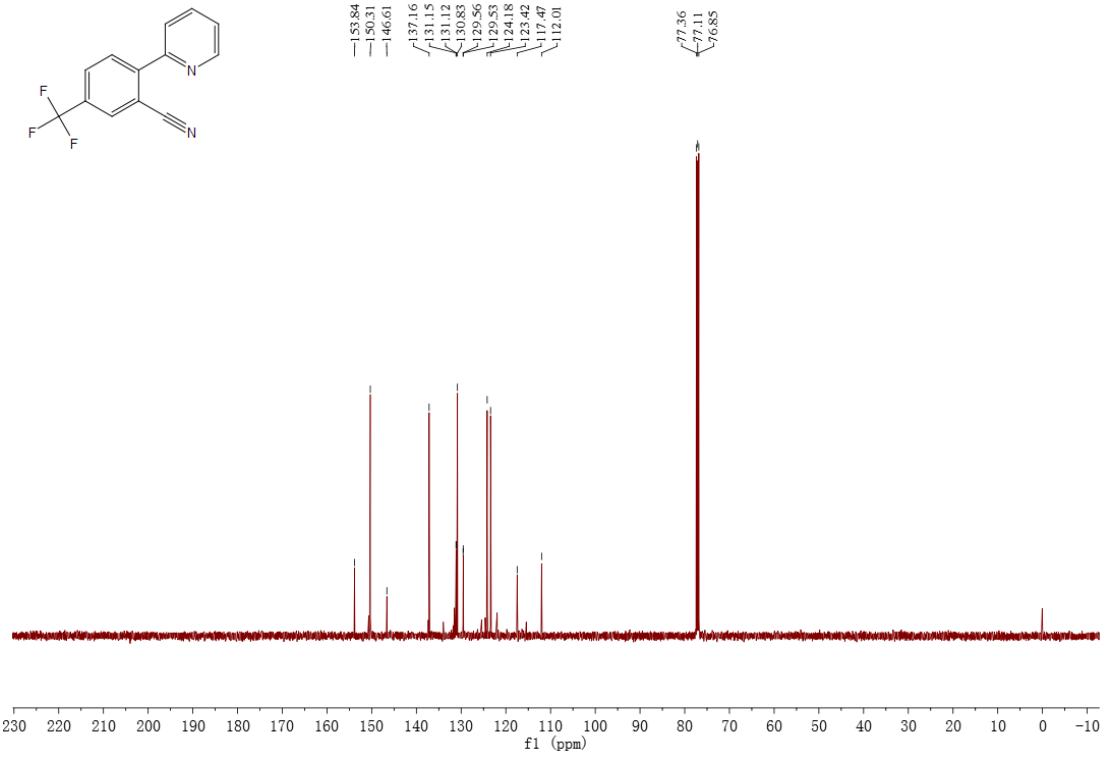


Figure S55 ^{1}H-NMR spectrum of **3h**

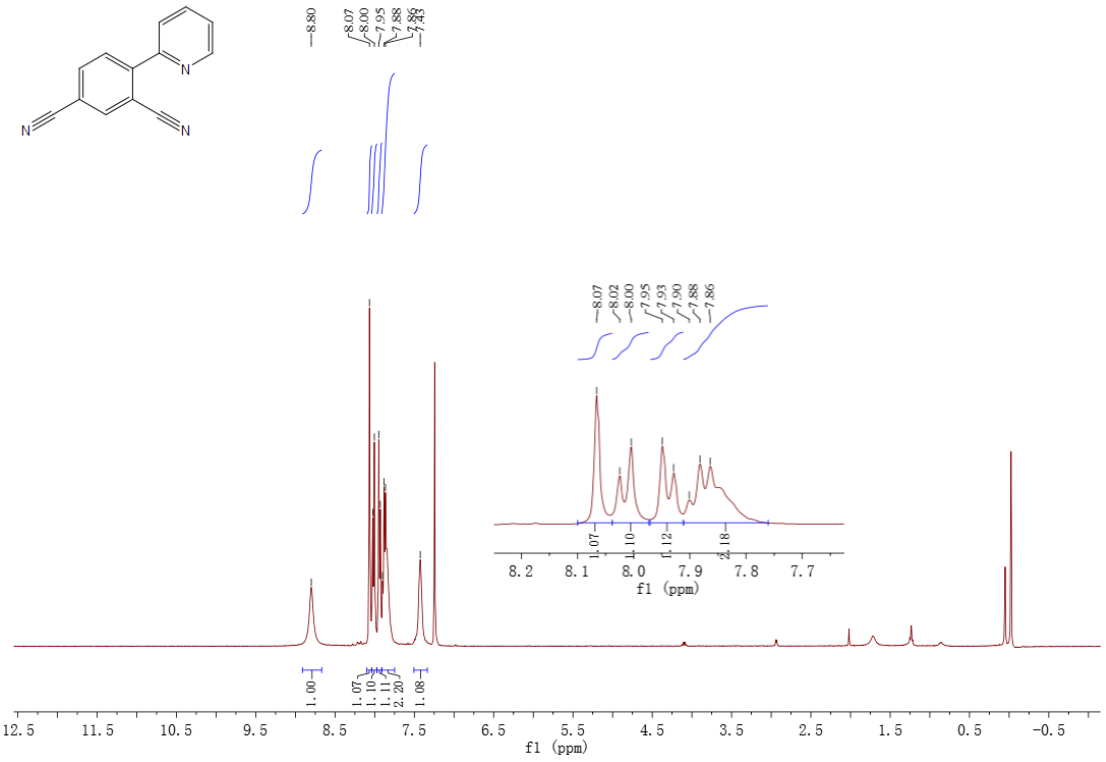


Figure S56 ^{13}C-NMR spectrum of **3h**

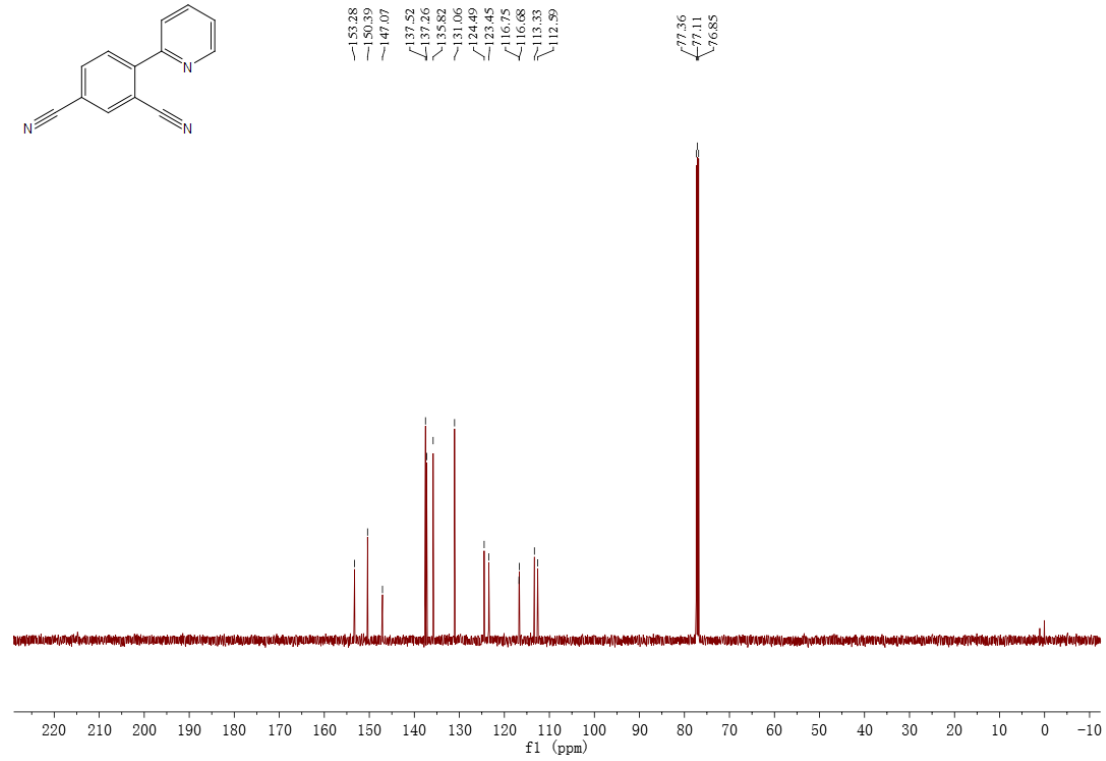


Figure S57 ^{1}H-NMR spectrum of **3i**

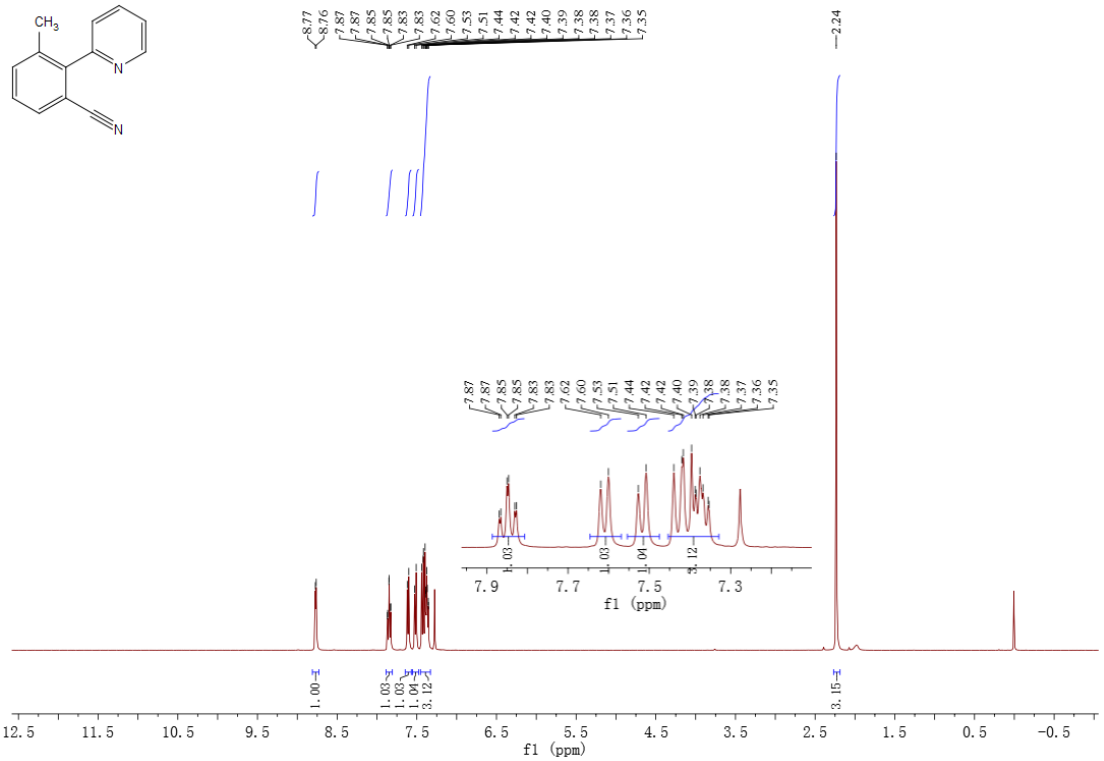


Figure S58 ^{13}C-NMR spectrum of **3i**

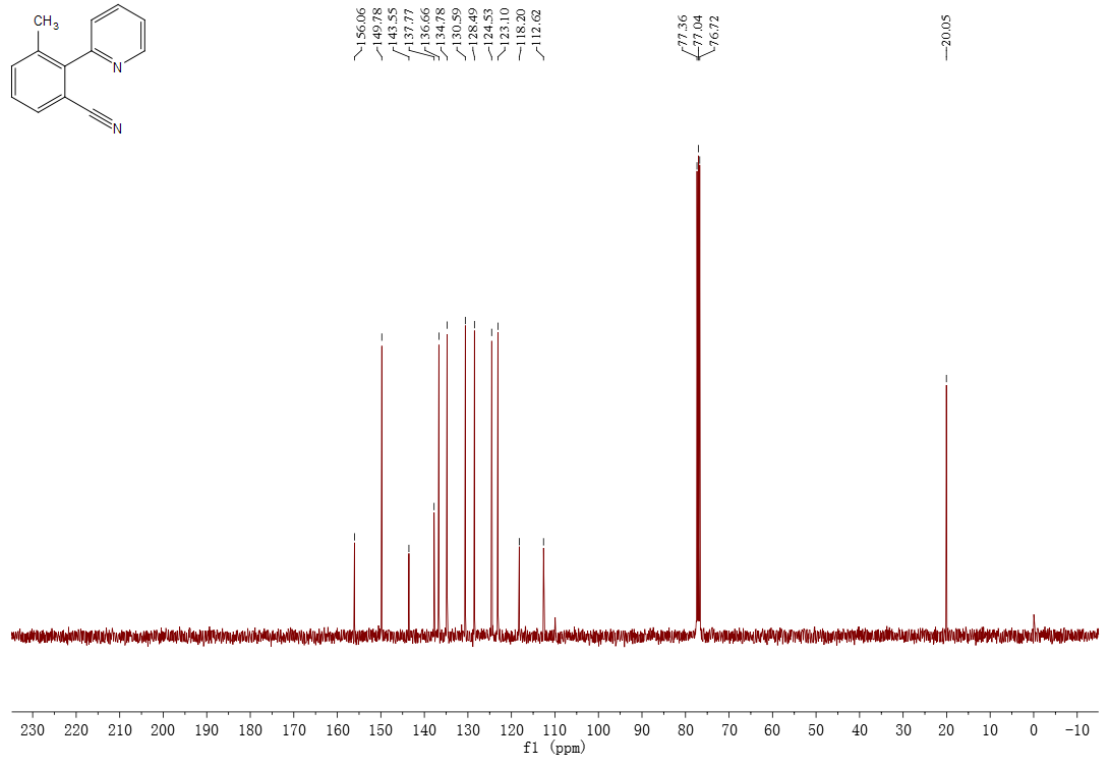


Figure S59 ^{1}H-NMR spectrum of **3j**

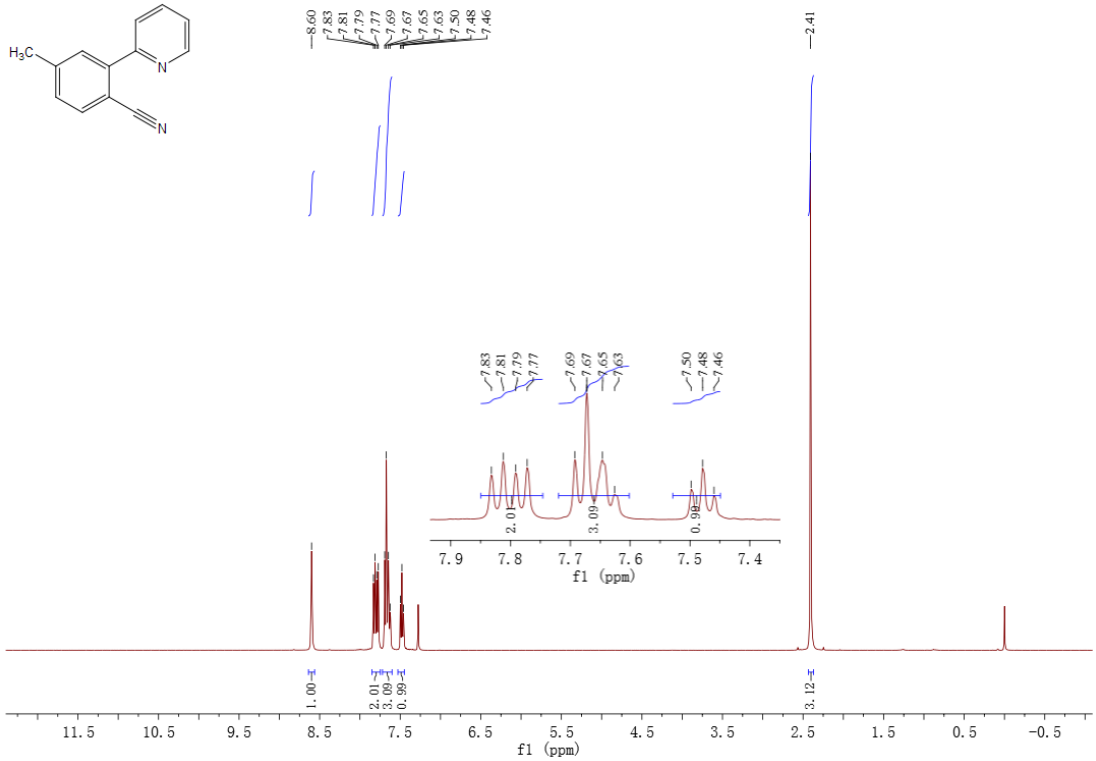


Figure S60 ^{13}C-NMR spectrum of **3j**

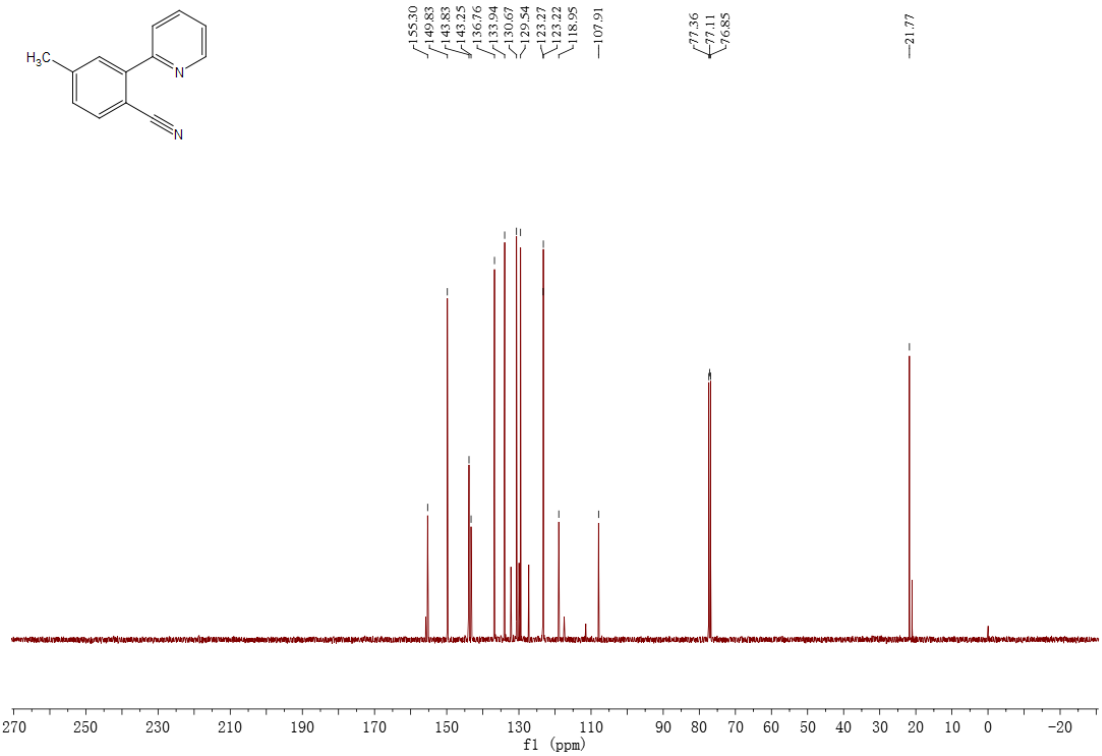


Figure S61 ^{1}H-NMR spectrum of **3k**

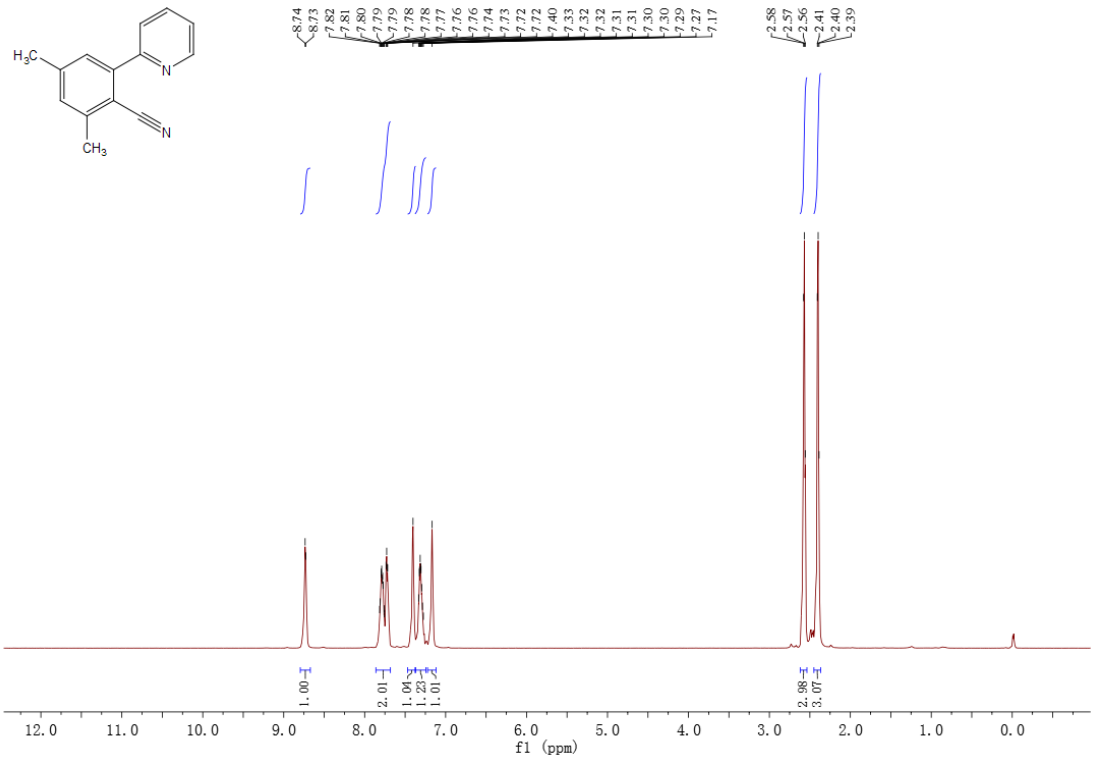


Figure S62 ^{13}C-NMR spectrum of **3k**

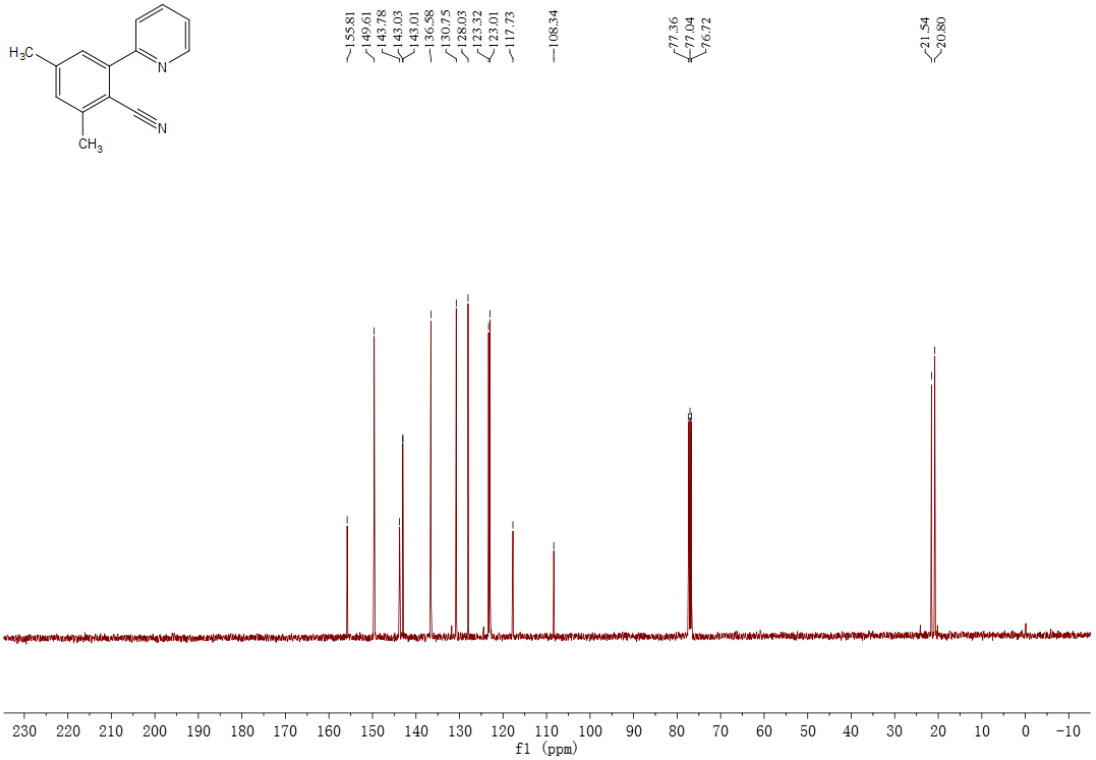


Figure S63 ^{1}H-NMR spectrum of **3l**

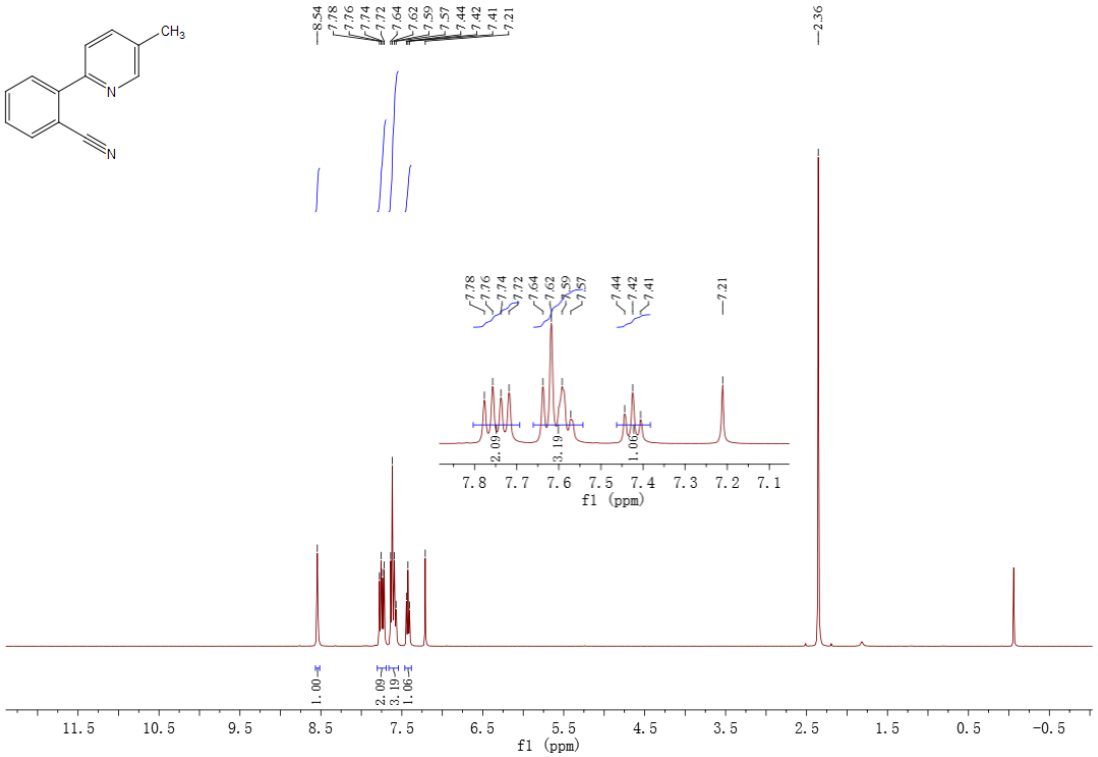


Figure S64 ^{13}C-NMR spectrum of **3l**

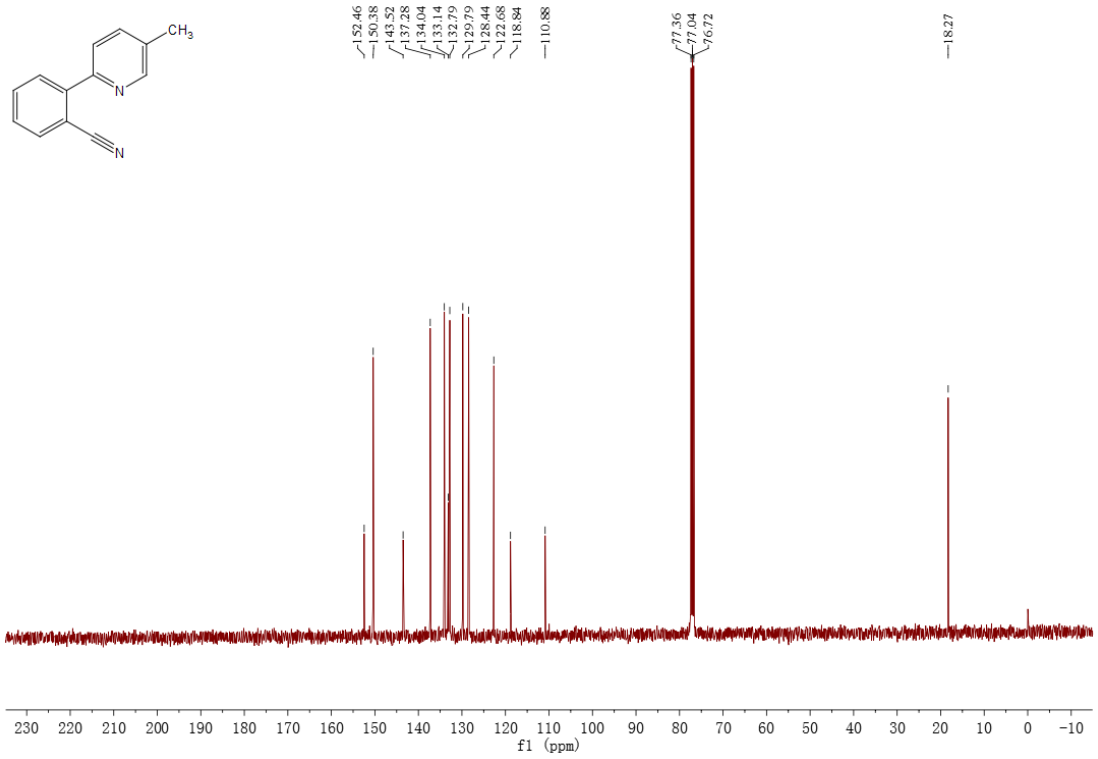


Figure S65 ^{1}H-NMR spectrum of **3m**

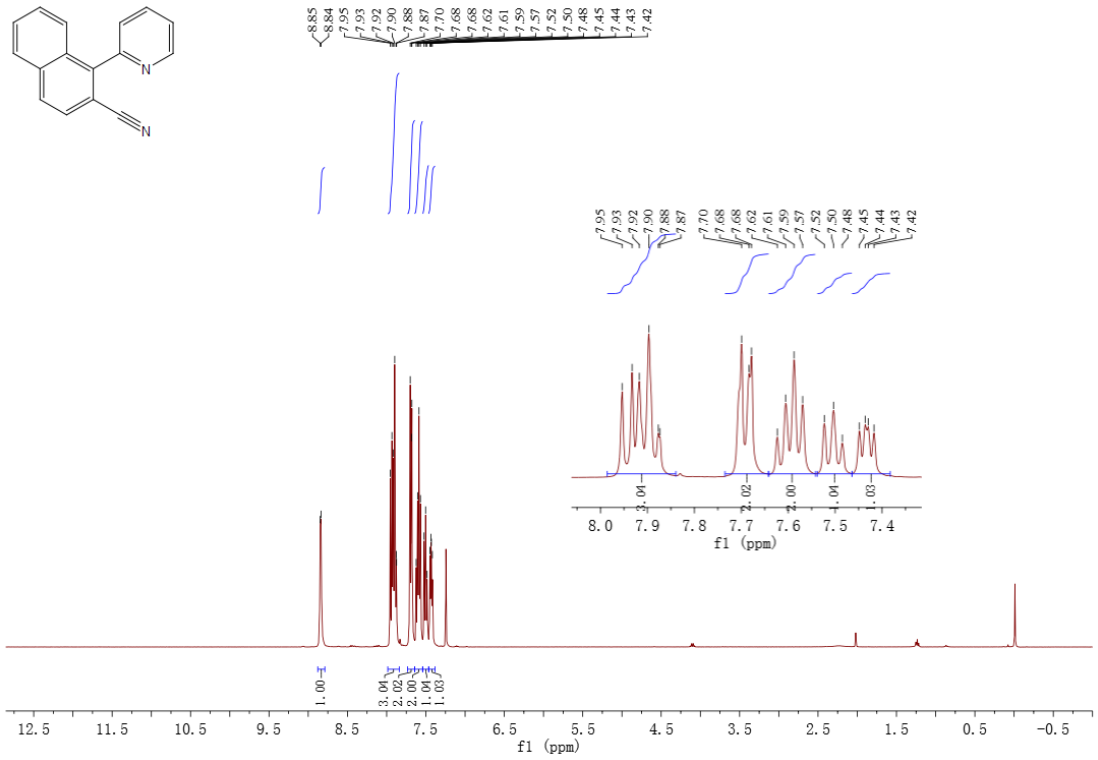


Figure S66 ^{13}C-NMR spectrum of **3m**

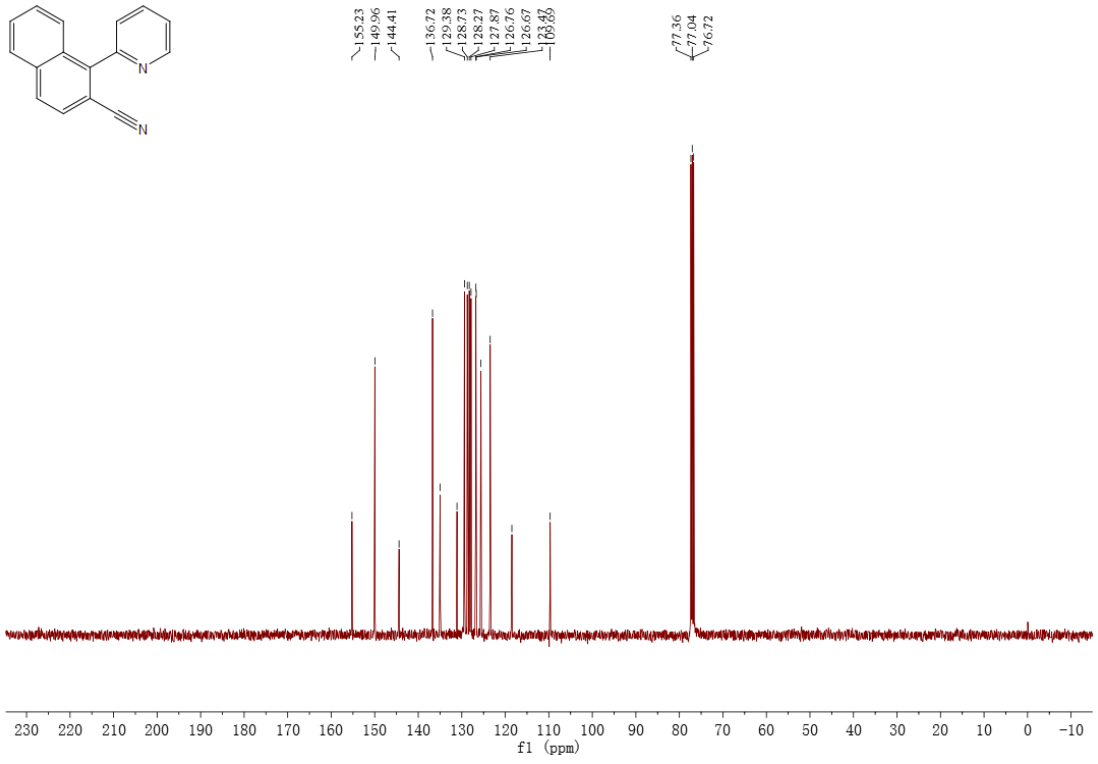


Figure S67 ^{1}H-NMR spectrum of **3na+3nb**

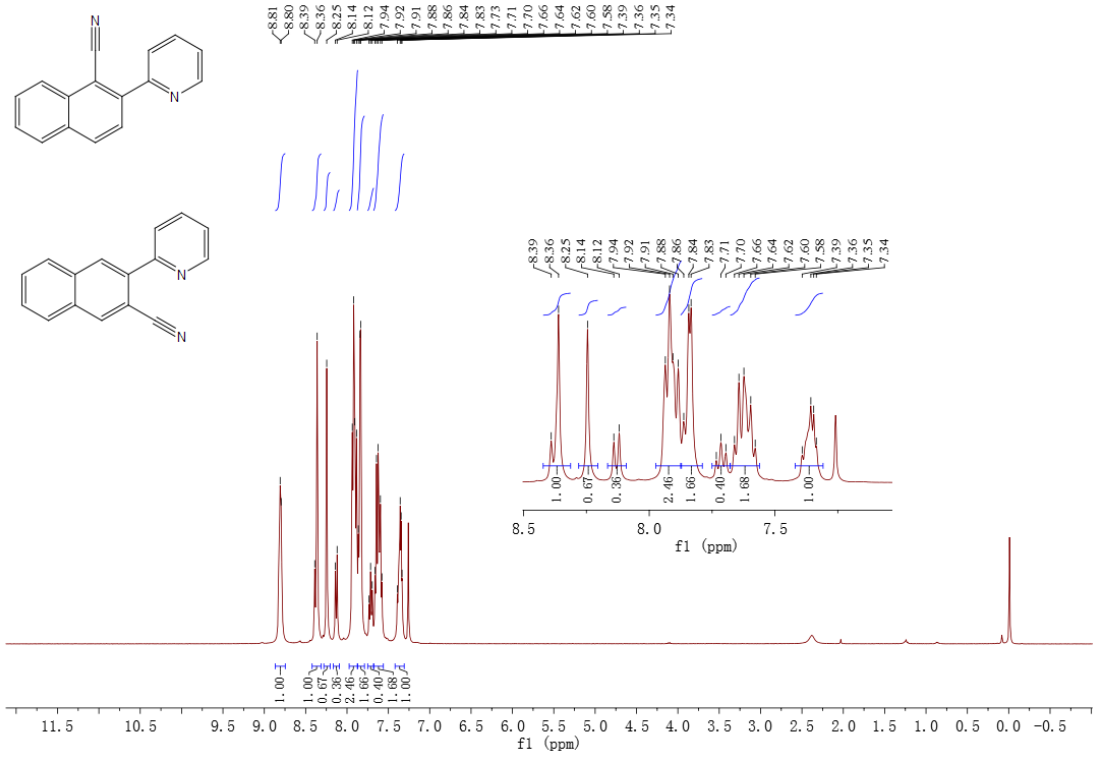


Figure S68 ^{1}H-NMR spectrum of **4b**

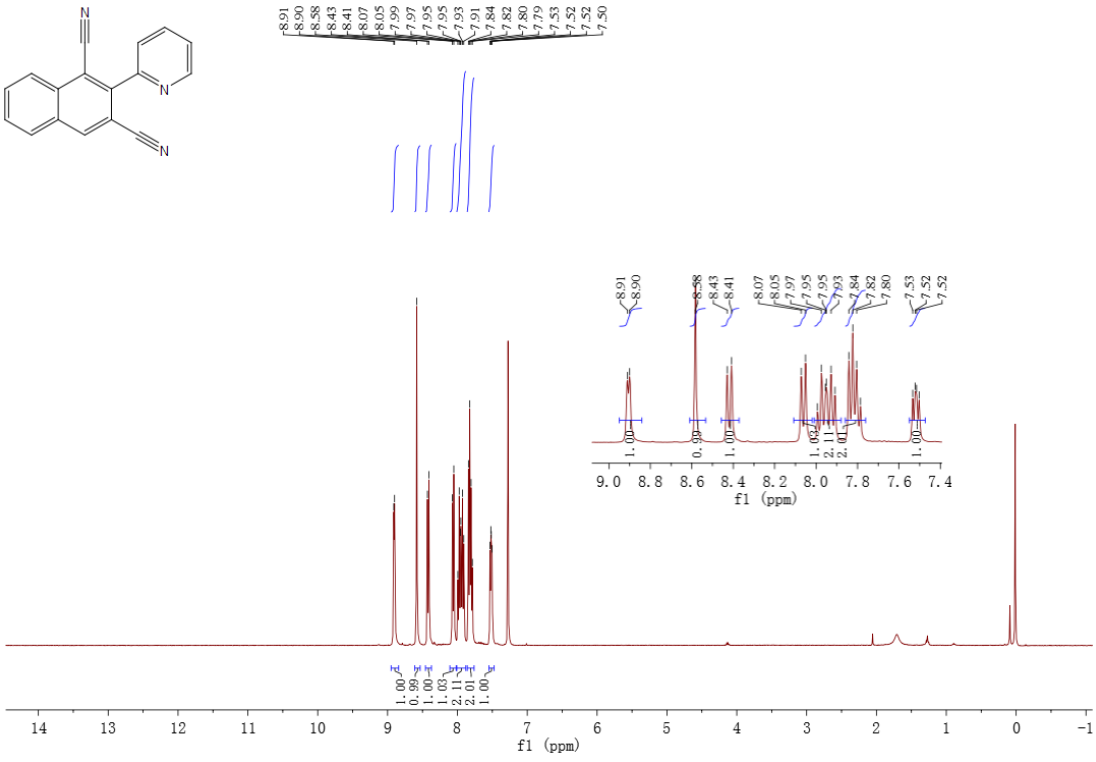


Figure S69 ^{13}C-NMR spectrum of **3nc**

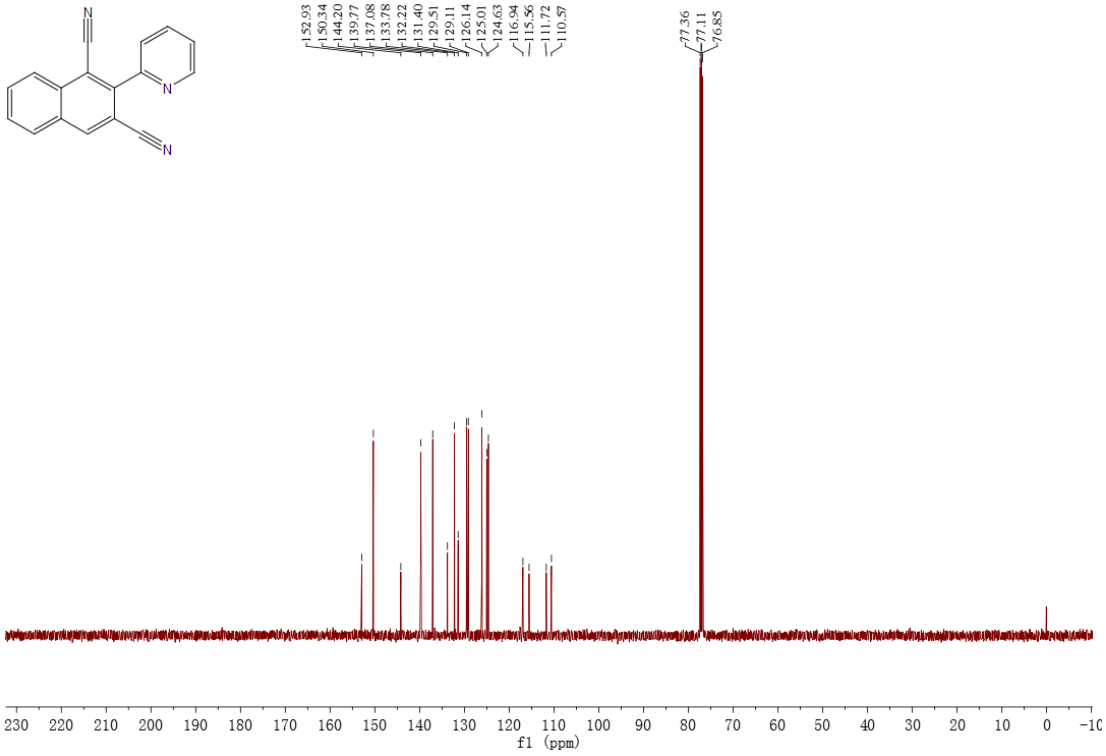


Figure S70 ^{1}H-NMR spectrum of **3o**

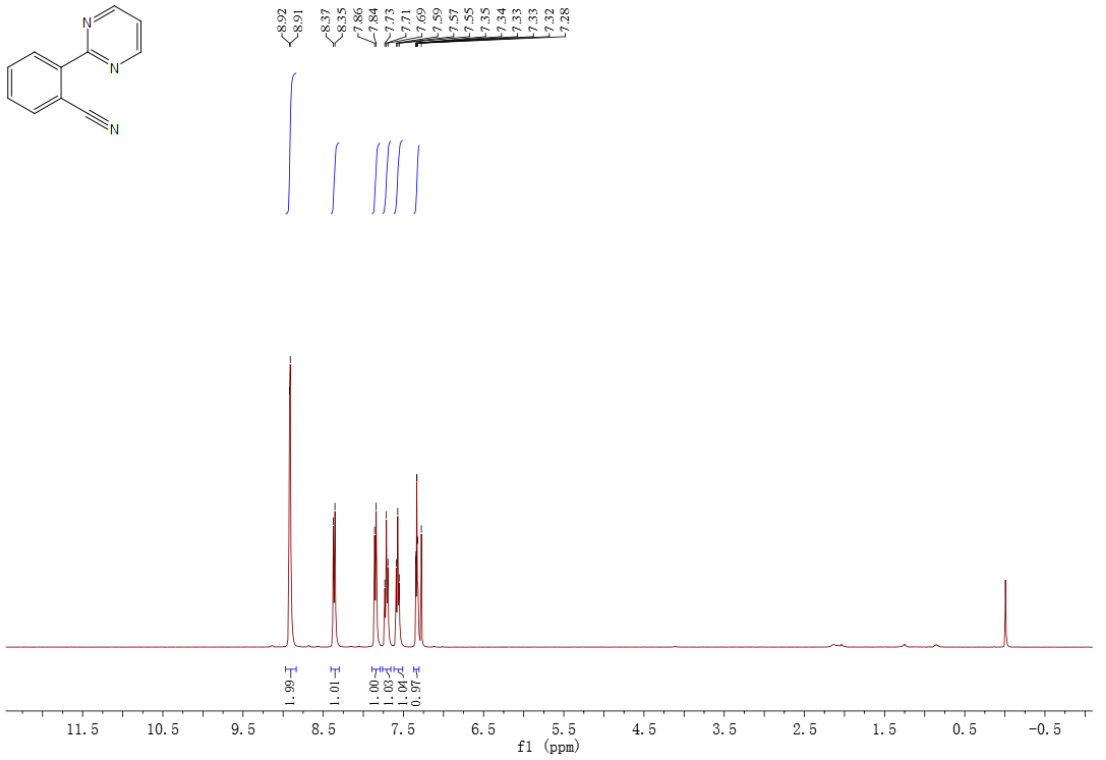


Figure S71 ^{13}C-NMR spectrum of **3o**

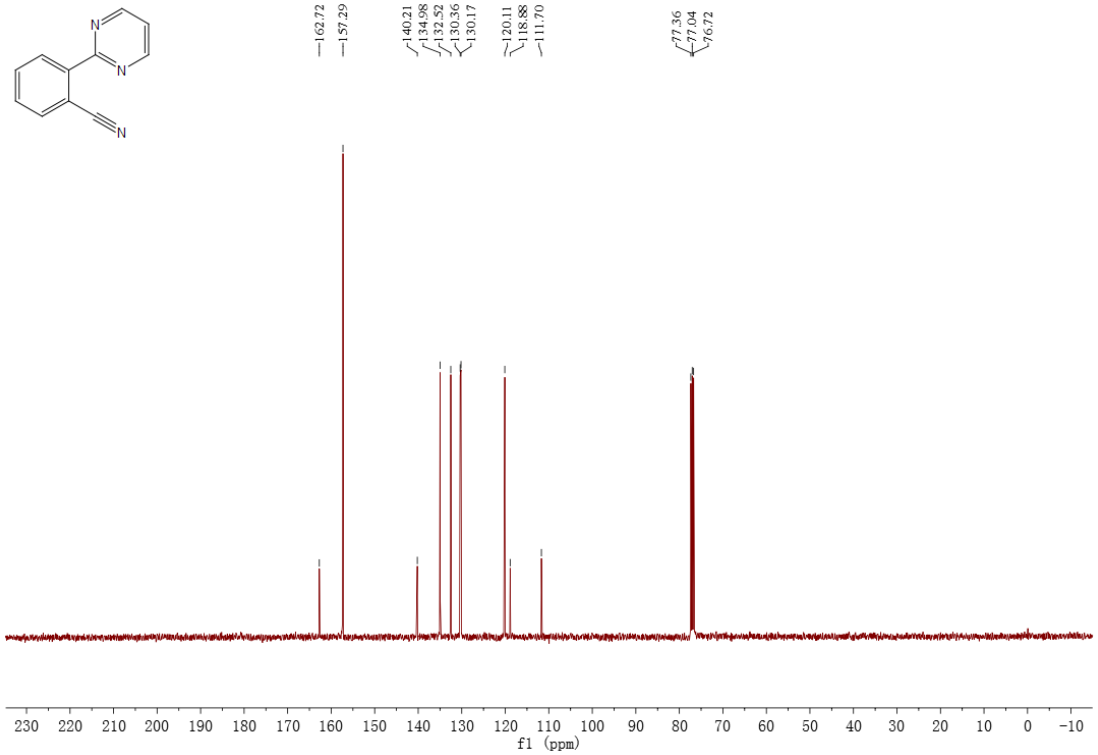


Figure S72 ^{1}H-NMR spectrum of **3p**

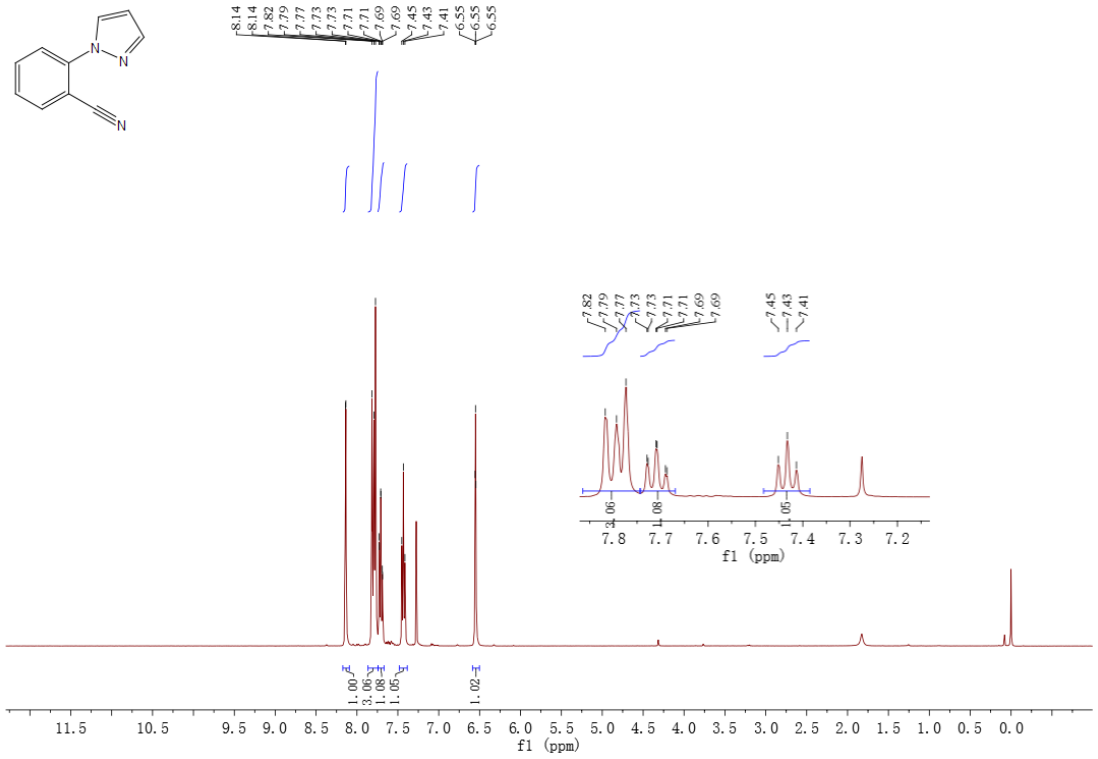


Figure S73 ^{13}C-NMR spectrum of **3p**

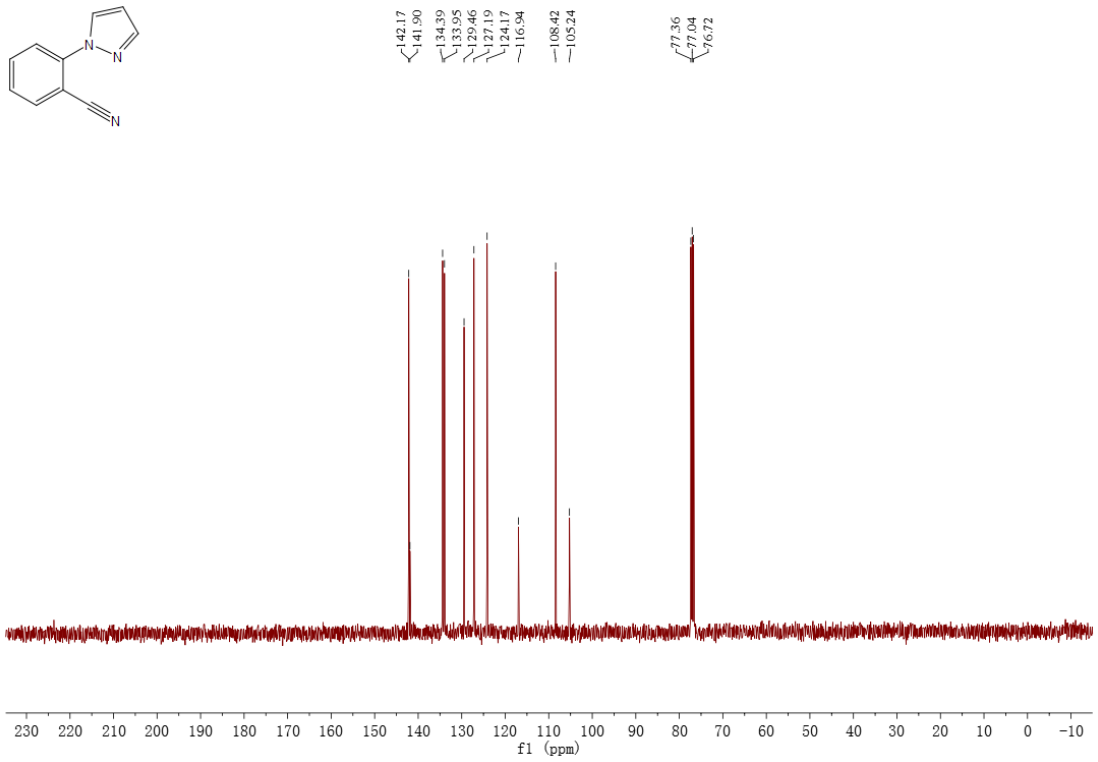


Figure S74 ^{1}H-NMR spectrum of **3q**

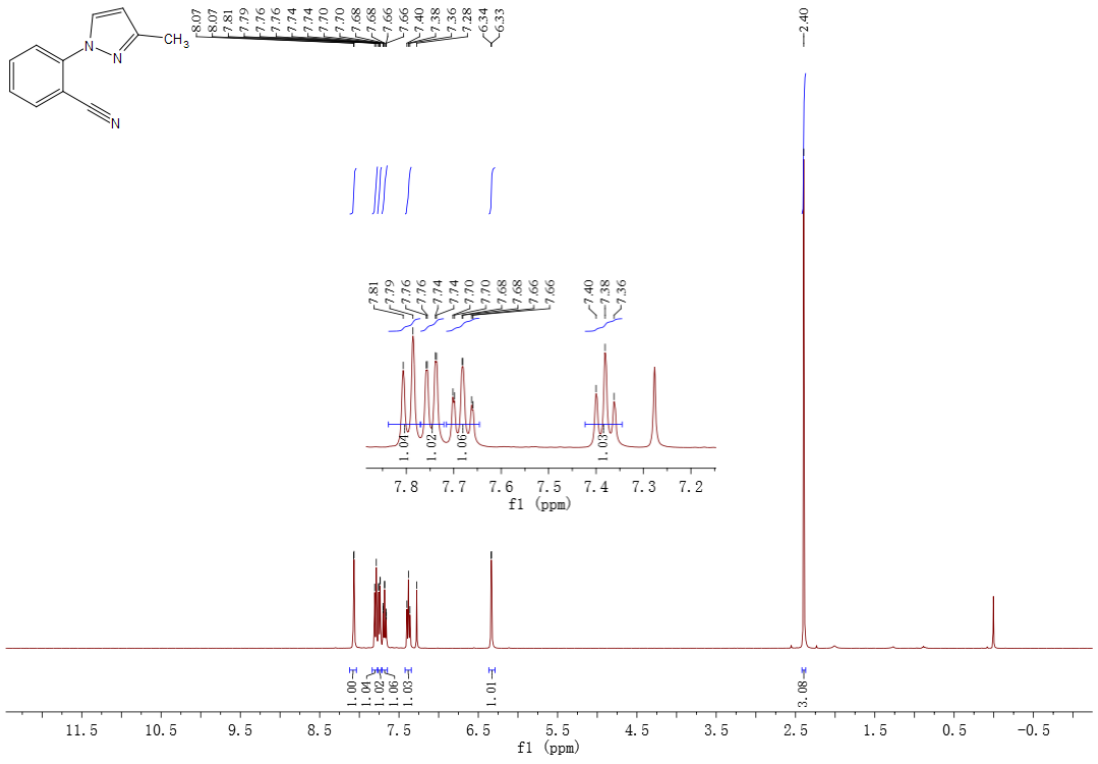


Figure S75 ^{13}C-NMR spectrum of **3q**

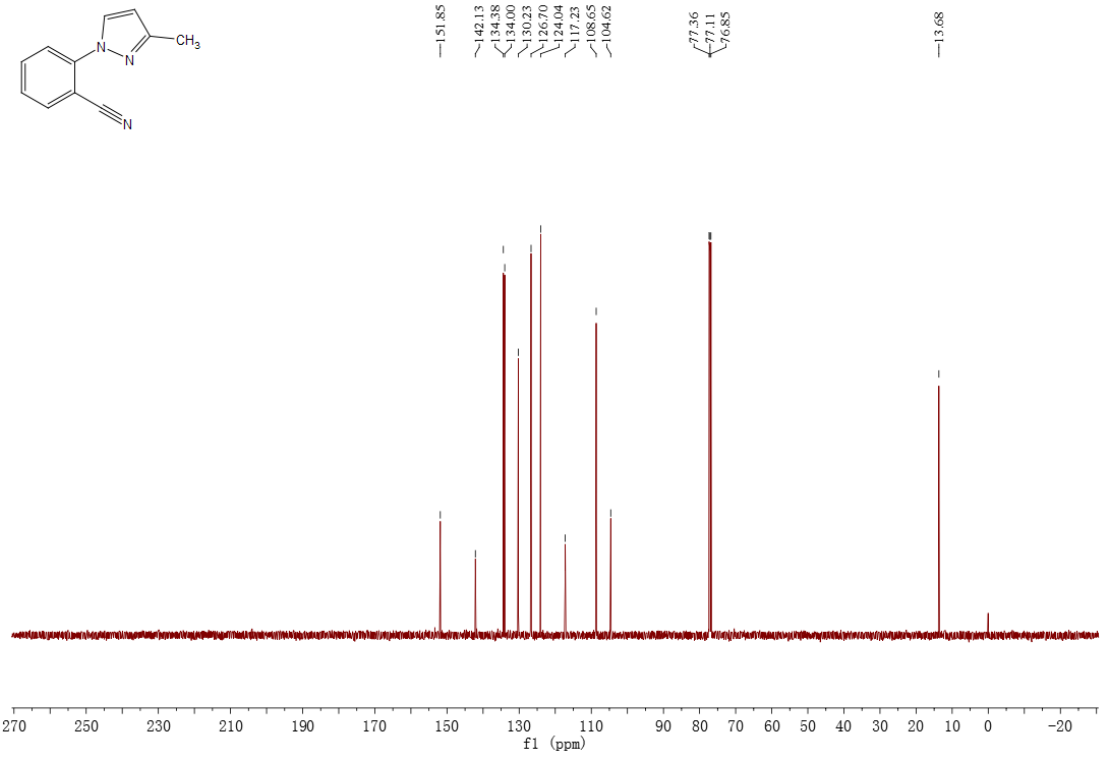


Figure S76 ^{1}H-NMR spectrum of **3r**

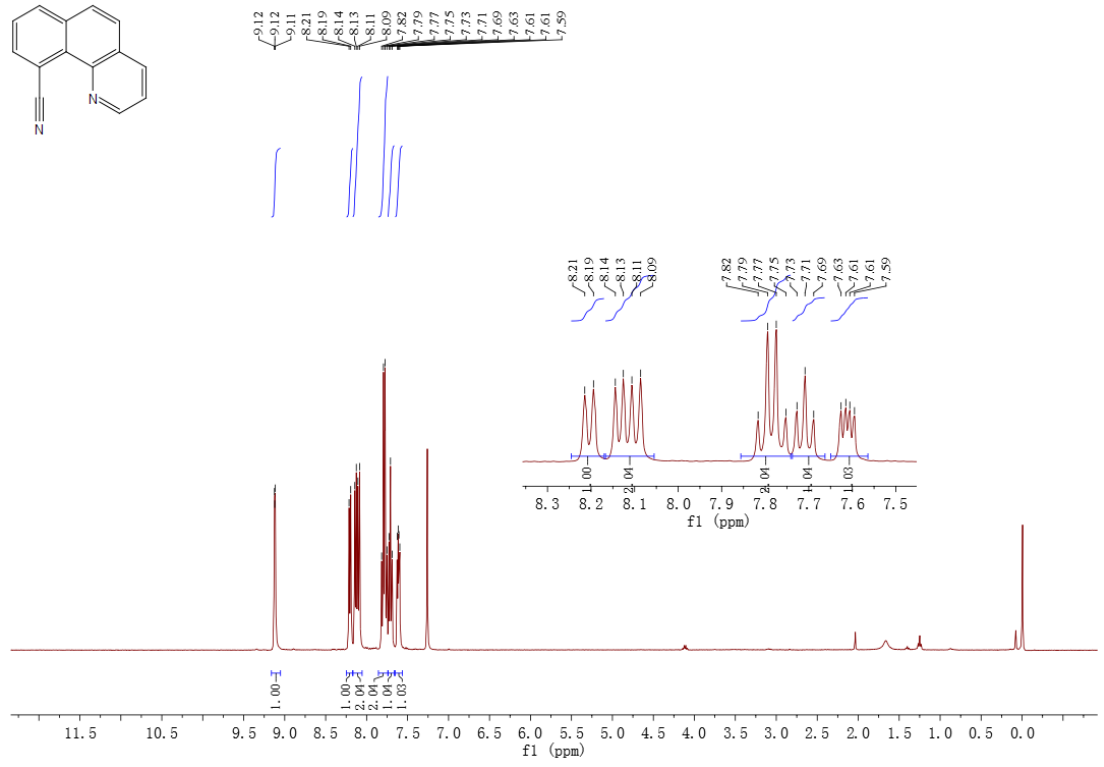


Figure S77 ^{13}C-NMR spectrum of **3r**