Base-dependent divergent α-cyanation and pyridylation of tertiary amines with cyanoaromatics

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Supporting Information

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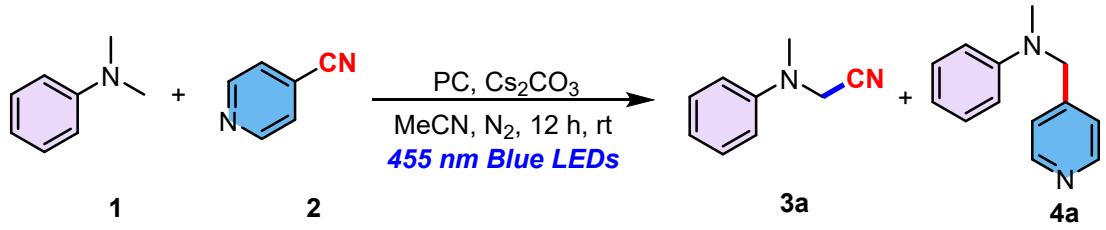
1. General Information

All the solvents involved in the reaction were dried by standard methods. The reagents were purchased from chemical reagent suppliers, such as Anergy, Bidet, etc, and were used without further purification. All products were separated by silica gel (200-300 mesh) column chromatography with petroleum ether (PE) (60-90°C) and ethyl acetate (EA). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 500 spectrometer or Bruker AVANCE NEO 400MHz at ambient temperature with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. High resolution mass spectrometry (HRMS) data were recorded by Agilent LC 1200 / MS QTOF6520. Melting points were measured by WRS-1B type melting point apparatus and are uncorrected.

2. Experimental Section

2.1 Screening of reaction conditions

Table S1. Screening of reaction conditions for photocatalysts.[a]

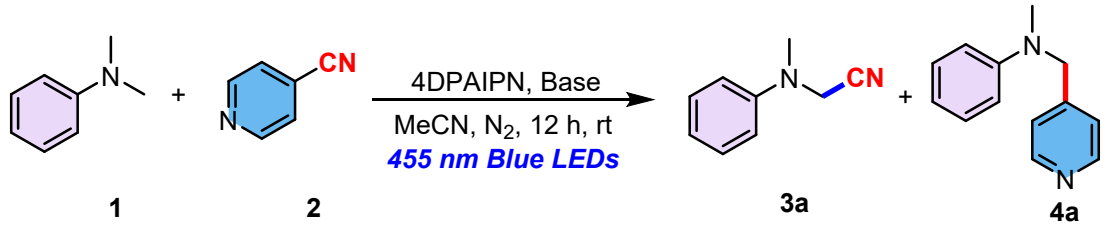


1 2 3a 4a

Entry	Photocatalyst	Yield of 3a (%)[b]	Yield of 4a (%)[b]
1	4CzIPN	42	39
2	4DPAIPN	64	16
3	Mes-Acr-$Me^{+}ClO_4^{-}$	19	23
4	4CzTPN	24	trace
5	*fac*-$Ir(ppy)_3$	trace	21
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	12	15
7	$[Ir(ppy)_2(dtbbpy)]PF_6$	15	18
8	$Ru(bpy)_3Cl_2$	trace	trace
9	4DPAIPN (1 mol%)	49	34
10	4DPAIPN (5 mol%)	62	15
11	-	trace	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), PC (3 mol%), Cs_2CO_3 (2.0 equiv.), MeCN (2 mL), 455 nm LEDs (10 W), N_2, rt, 12 h. [b] Isolated yields.

Table S2. Screening of reaction conditions for base.[a]



1 2 3a 4a

Entry	Base	Yield of 3a (%)[b]	Yield of 4a (%)[b]
1	Cs_2CO_3	64	16
2	CsCl	41	32
3	CH_3COOCs	36	30
4	K_2CO_3	trace	17
5	Na_2CO_3	trace	trace
6	KOH	20	trace
7	K_3PO_4	NR	NR
8	*t*-BuOK	12	19
9	Et_3N	23	trace
10	DABCO	trace	85
11	DBU	NR	NR
12	Cs_2CO_3 (1.0 equiv.)	42	46
13	Cs_2CO_3 (3.0 equiv.)	65	12
14	-	NR	NR

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), 4DPAIPN (3 mol%), Base (2.0 equiv.), MeCN (2 mL), 455 nm LEDs (10 W), N_2, rt, 12 h. [b] Isolated yields.

Table S3. Screening of reaction conditions for solvents.

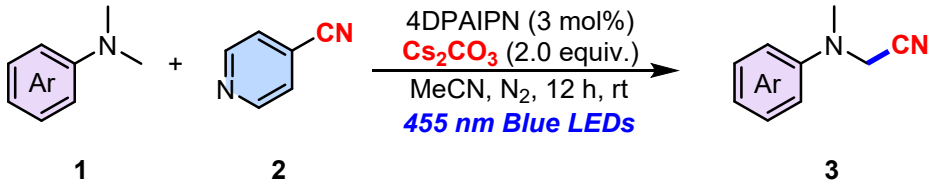
1 2 3a 4a

Entry	Solvent	Yield of 3a (%)[b]	Yield of 4a (%)[b]
1	MeCN	64	16
2	DCE	31	33
3	THF	21	32

4	DMSO	NR	NR
5	DMF	trace	trace
6	DMA	8	14
7	1,4-dioxane	22	12
8	NMP	NR	NR
9	PhCl	NR	NR

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), 4DPAIPN (3 mol%), Cs_2CO_3 (2.0 equiv.), Solvent (2 mL), 455 nm LEDs (10 W), N_2, rt, 12 h. [b] Isolated yields.

2.2 General procedure for synthesis of 3.



1 **2** **3**

The mixture of *N,N*-dimethylaniline **1** (0.2 mmol), 4-cyanopyridine **2** (0.3mmol), 4DPAIPN (3 mol%), Cs_2CO_3 (2.0 equiv.) and MeCN (2 mL) was added to a Schlenk tube. The tube was evacuated and backfilled with nitrogen (repeated five times). The reaction mixture was irradiated with 10 Blue LEDs at ambient temperature for 12 h. After concentrating on the solvent, the product was purified by flash chromatography with PE: EtOAc = 15: 1 to give the product **3**.

2.3 General procedure for synthesis of 4.

1 **2** **4**

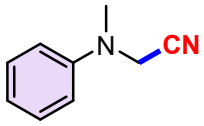
The mixture of *N,N*-dimethylaniline **1** (0.2 mmol), 4-cyanopyridine **2** (0.3mmol), 4DPAIPN (3 mol%), DABCO (2.0 equiv.) and MeCN (2 mL) was added to a Schlenk tube. The tube was evacuated and backfilled with nitrogen (repeated five times). The reaction mixture was irradiated with 10 Blue LEDs at ambient temperature for 12 h. After concentrating on the solvent, the product was purified by flash chromatography with PE: EtOAc = 1:2 to give the product **4**.

2.4 Fluorescence Quenching Experiment.

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solution of 5×10^{-5} M 4DPAIPN in degassed dry MeCN at room temperature. The solution was irradiated at 440 nm and the fluorescence was measured from 450 nm to 700 nm. Data was collected on an Agilent Technologices F-4600 spectrofluorometer at 25 °C. Parameters: data interval = 1 nm, scan rate = 645 nm/min, Averaging time = 0.1 sec. The samples were measured in Jingke ES quartz cuvettes (chamber volume = 2.5 mL, H × W × D = 56 nm × 12.5 nm × 12.5 nm).

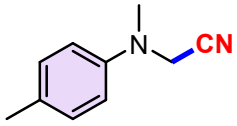
Characterization of Products

2-(Methyl(phenyl)amino)acetonitrile (3a)[1]



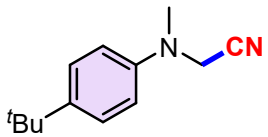
64% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 2H), 4.18 (s, 2H), 3.02 (s, 3H).

2-(Methyl(*p*-tolyl)amino)acetonitrile (3b)



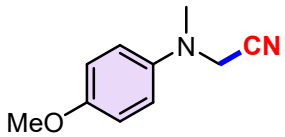
59% yield as a colorless oil. R_f = 0.5 (PE: EA =15: 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.14 (s, 2H), 2.97 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.71, 130.01, 129.95, 115.50, 115.49, 42.88, 39.51, 20.41; HRMS (ESI+): Calculated for $C_{10}H_{12}N_2H$: $[M + H]^+$ 161.1073, Found 161.1078.

2-((4-(*Tert*-butyl)phenyl)(methyl)amino)acetonitrile (3c) [2]



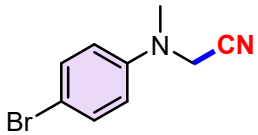
60% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.16 (s, 2H), 3.00 (s, 3H), 1.31 (s, 9H).

2-((4-Methoxyphenyl)(methyl)amino)acetonitrile (3d) [3]



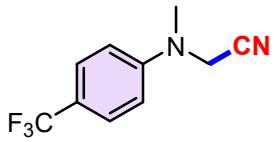
62% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, *J* = 1.6 Hz, 4H), 4.09 (s, 2H), 3.78 (s, 3H), 2.93 (s, 3H).

2-((4-Bromophenyl)(methyl)amino)acetonitrile (3e) [1]



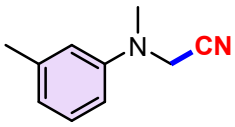
57% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 9.1 Hz, 2H), 6.73 (d, *J* = 9.1 Hz, 2H), 4.15 (s, 2H), 2.99 (s, 3H).

2-(Methyl(4-(trifluoromethyl)phenyl)amino)acetonitrile (3f) [2]



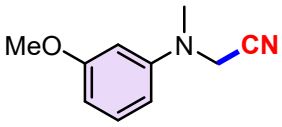
65% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.24 (s, 2H), 3.10 (s, 3H).

2-(Methyl(*m*-tolyl)amino)acetonitrile (3g) [1]



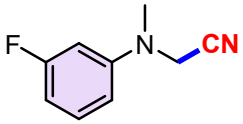
55% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 9.0, 7.5 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.70 (dd, *J* = 4.2, 1.8 Hz, 2H), 4.17 (s, 2H), 3.00 (s, 3H), 2.35 (s, 3H).

2-((3-Methoxyphenyl)(methyl)amino)acetonitrile (3h)



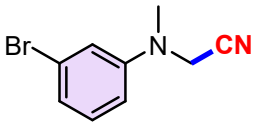
63% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.3 Hz, 1H), 6.48 (dt, *J* = 8.4, 2.5 Hz, 2H), 6.40 (d, *J* = 2.5 Hz, 1H), 4.18 (s, 2H), 3.81 (s, 3H), 3.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.76, 149.14, 130.28, 115.48, 107.52, 104.75, 101.72, 55.28, 42.24, 39.30; HRMS (ESI+): Calculated for $C_{10}H_{12}N_2OH$: $[M + H]^+$ 177.1023, Found 177.1018.

2-((3-Fluorophenyl)(methyl)amino)acetonitrile (3i)



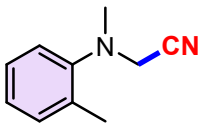
56% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (td, *J* = 8.2, 6.7 Hz, 1H), 6.61 (ddd, *J* = 8.3, 5.4, 2.3 Hz, 2H), 6.56 – 6.51 (m, 1H), 4.17 (s, 2H), 3.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.84 (d, *J* = 244.3 Hz), 148.35 (d, *J* = 9.9 Hz), 129.64 (d, *J* = 10.0 Hz), 114.18, 108.87 (d, *J* = 2.6 Hz), 105.54 (d, *J* = 21.4 Hz), 100.86 (d, *J* = 26.1 Hz), 40.87, 38.20; HRMS (ESI+): Calculated for $C_9H_9FN_2H$: $[M + H]^+$ 165.0823, Found 165.0827.

2-((3-Bromophenyl)(methyl)amino)acetonitrile (3j)



58% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.1 Hz, 1H), 7.04 (ddd, *J* = 7.9, 1.8, 0.9 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.77 (dt, *J* = 8.4, 1.6 Hz, 1H), 4.18 (s, 2H), 3.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.92, 130.74, 123.58, 122.96, 117.62, 115.16, 113.07, 41.94, 39.23; HRMS (ESI+): Calculated for $C_9H_9BrN_2H$: $[M + H]^+$ 225.0022, Found 225.0024.

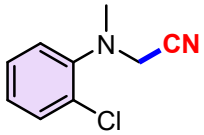
2-(Methyl(*o*-tolyl)amino)acetonitrile (3k)



50% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m,

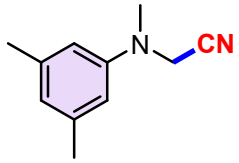
3H), 7.11 – 7.04 (m, 1H), 3.86 (s, 2H), 2.86 (s, 3H), 2.30 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.51, 132.85, 131.37, 126.92, 125.01, 120.71, 115.69, 45.09, 41.03, 17.81; HRMS (ESI+): Calculated for $C_{10}H_{12}N_2H$: $[M + H]^+$ 161.1073, Found 161.1078.

2-((2-Chlorophenyl)(methyl)amino)acetonitrile (3l) [3]



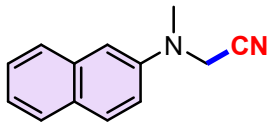
43% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.10 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.03 – 6.99 (m, 1H), 4.23 (s, 2H), 2.73 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.65, 131.46, 127.01, 126.14, 125.11, 120.81, 114.90, 45.17, 41.14.

2-((3,5-Dimethylphenyl)(methyl)amino)acetonitrile (3m)



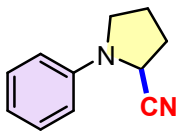
56% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 – 6.57 (m, 1H), 6.50 (d, *J* = 1.3 Hz, 2H), 4.16 (s, 2H), 2.99 (s, 3H), 2.31 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.93, 139.12, 122.25, 115.63, 112.97, 42.46, 39.33, 21.70; HRMS (ESI+): Calculated for $C_{11}H_{14}N_2H$: $[M + H]^+$ 175.1230, Found 175.1238.

2-(Methyl(naphthalen-2-yl)amino)acetonitrile (3n) [2]



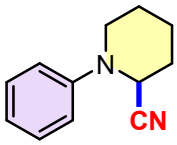
51% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.71 (m, 3H), 7.46 (s, 1H), 7.35 (s, 1H), 7.18 (d, *J* = 9.0 Hz, 1H), 7.15 (s, 1H), 4.26 (s, 2H), 3.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.63, 134.41, 129.43, 128.54, 127.54, 126.87, 126.72, 123.89, 117.24, 115.49, 110.30, 42.61, 39.48; HRMS (ESI+): Calculated for $C_{13}H_{12}N_2H$: $[M + H]^+$ 197.1073, Found 197.1078.

1-Phenylpyrrolidine-2-carbonitrile (3o) [4]



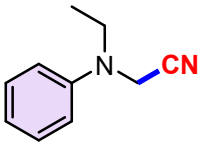
54% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 6.84 (d, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 2H), 4.44 (dd, *J* = 7.3, 1.8 Hz, 1H), 3.47 (td, *J* = 8.3, 2.8 Hz, 1H), 3.38 (dd, *J* = 8.6, 7.1 Hz, 1H), 2.45 – 2.38 (m, 1H), 2.34 – 2.16 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.22, 129.51, 119.34, 118.24, 112.72, 49.12, 47.50, 31.58, 24.00.

1-Phenylpiperidine-2-carbonitrile (3p) [1]



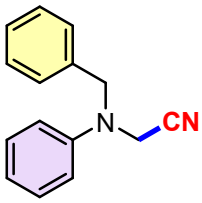
50% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.8, 7.2 Hz, 2H), 7.05 – 6.98 (m, 3H), 4.63 (t, *J* = 3.6 Hz, 1H), 3.50 – 3.44 (m, 1H), 3.04 (td, *J* = 12.0, 2.8 Hz, 1H), 2.09 – 1.96 (m, 2H), 1.91 – 1.82 (m, 2H), 1.76 – 1.65 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.72, 128.33, 121.14, 117.27, 116.17, 51.00, 45.53, 28.20, 24.08, 19.15.

2-(Ethyl(phenyl)amino)acetonitrile (3q)



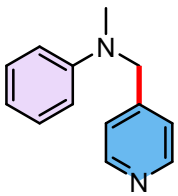
56% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 2H), 6.95 – 6.82 (m, 3H), 4.15 (s, 2H), 3.45 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.82, 129.57, 119.83, 116.44, 114.89, 46.31, 39.55, 12.26; HRMS (ESI+): Calculated for $C_{10}H_{12}N_2H$: $[M + H]^+$ 161.1073, Found 161.1078.

2-(Benzyl(phenyl)amino)acetonitrile (3r)



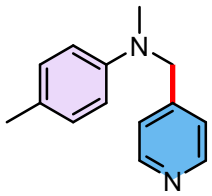
57% yield as a colorless oil. R_f = 0.5 (PE: EA = 15: 1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (td, *J* = 10.2, 8.9, 7.2 Hz, 7H), 6.97 (dd, *J* = 8.4, 2.3 Hz, 3H), 4.52 (s, 2H), 4.08 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.97, 136.83, 129.61, 128.95, 127.90, 127.66, 120.74, 115.83, 115.65, 55.76, 39.54; HRMS (ESI+): Calculated for $C_{15}H_{14}N_2H$: $[M + H]^+$ 223.1230, Found 223.1232.

***N*-Methyl-*N*-(pyridin-4-ylmethyl)aniline (4a)** [5]



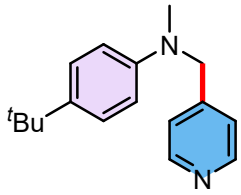
85% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.49 (m, 2H), 7.27 – 7.20 (m, 2H), 7.20 – 7.14 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 2H), 4.52 (s, 2H), 3.05 (s, 3H).

***N*,4-Dimethyl-*N*-(pyridin-4-ylmethyl)aniline (4b)**



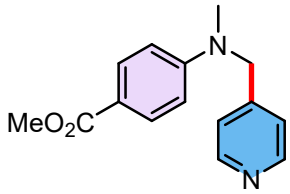
81% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 2H), 7.19 (d, *J* = 5.0 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 4.48 (s, 2H), 3.01 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.43, 147.13, 129.85, 129.77, 126.55, 122.18, 112.69, 56.35, 39.12, 20.25; HRMS (ESI+): Calculated for $C_{14}H_{16}N_2H$: $[M + H]^+$ 213.1386, Found 213.1382.

4-(*tert*-Butyl)-*N*-methyl-*N*-(pyridin-4-ylmethyl)aniline (4c)



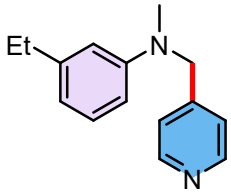
88% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.9 Hz, 2H), 7.29 – 7.19 (m, 4H), 6.66 (d, *J* = 8.7 Hz, 2H), 4.48 (s, 2H), 3.02 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.41, 149.35, 147.02, 140.01, 126.11, 122.12, 112.21, 56.34, 39.01, 33.80, 31.51; HRMS (ESI+): Calculated for $C_{17}H_{22}N_2H$: $[M + H]^+$ 255.1856, Found 255.1858.

Methyl 4-(methyl(pyridin-4-ylmethyl)amino)benzoate (4d)



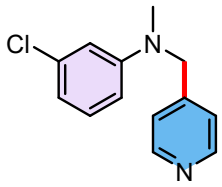
84% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 2H), 7.90 (d, *J* = 7.3 Hz, 2H), 7.17 (d, *J* = 5.0 Hz, 2H), 6.65 (d, *J* = 7.4 Hz, 2H), 4.63 (s, 2H), 3.85 (d, *J* = 1.5 Hz, 3H), 3.15 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.17, 152.14, 149.19, 131.52, 118.41, 110.99, 55.39, 51.61, 39.06; HRMS (ESI+): Calculated for $C_{15}H_{16}N_2O_2H$: $[M + H]^+$ 257.1285, Found 257.1284.

3-Ethyl-*N*-methyl-*N*-(pyridin-4-ylmethyl)aniline (4e)



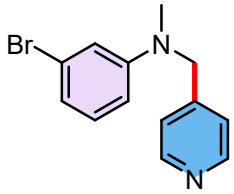
86% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 2H), 7.22 (d, *J* = 4.9 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.66 – 6.59 (m, 1H), 6.57 – 6.47 (m, 2H), 4.52 (s, 2H), 3.04 (s, 3H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.73, 149.31, 149.24, 145.55, 129.27, 122.17, 117.02, 112.03, 109.91, 56.13, 38.95, 29.31, 15.68; HRMS (ESI+): Calculated for $C_{15}H_{18}N_2H$: $[M + H]^+$ 227.1543, Found 227.1547.

3-Chloro-*N*-methyl-*N*-(pyridin-4-ylmethyl)aniline (4f)



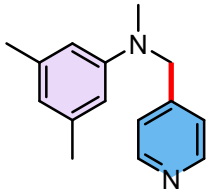
85% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.4 Hz, 2H), 7.17 – 7.08 (m, 3H), 6.73 – 6.65 (m, 2H), 6.53 (ddd, *J* = 8.5, 2.6, 0.8 Hz, 1H), 4.52 (s, 2H), 3.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.14, 148.81, 147.11, 134.25, 129.22, 120.74, 116.03, 111.12, 109.39, 54.67, 37.93; HRMS (ESI+): Calculated for $C_{13}H_{13}ClN_2H$: $[M + H]^+$ 233.0846, Found 233.0833.

3-Bromo-*N*-methyl-*N*-(pyridin-4-ylmethyl)aniline (4g)



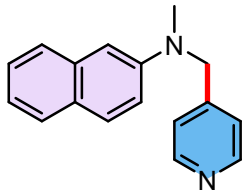
85% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 2H), 7.16 (d, *J* = 5.0 Hz, 2H), 7.08 – 7.02 (m, 1H), 6.89 – 6.81 (m, 2H), 6.57 (ddd, *J* = 8.5, 2.6, 0.8 Hz, 1H), 4.52 (s, 2H), 3.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.26, 149.54, 148.52, 130.55, 123.62, 121.87, 120.02, 115.01, 110.86, 55.69, 38.97. HRMS (ESI+): Calculated for $C_{13}H_{13}BrN_2H$: $[M + H]^+$ 277.0335, Found 277.0331.

***N*,3,5-Trimethyl-*N*-(pyridin-4-ylmethyl)aniline (4h)**



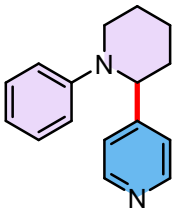
88% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.1 Hz, 2H), 7.19 (d, *J* = 6.0 Hz, 2H), 6.43 (s, 1H), 6.34 (s, 2H), 4.50 (s, 2H), 3.01 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.39, 149.26, 149.17, 138.99, 122.14, 119.38, 110.36, 56.05, 38.90, 21.77; HRMS (ESI+): Calculated for $C_{15}H_{18}N_2H$: $[M + H]^+$ 227.1543, Found 227.1547.

***N*-Methyl-*N*-(pyridin-4-ylmethyl)naphthalen-2-amine (4i)**



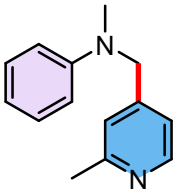
75% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.8 Hz, 2H), 7.70 (d, *J* = 9.1 Hz, 2H), 7.63 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.38 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.25 – 7.16 (m, 3H), 7.09 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.94 (d, *J* = 2.6 Hz, 1H), 4.63 (s, 2H), 3.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.78, 148.70, 147.09, 134.91, 129.15, 127.51, 127.05, 126.49, 126.22, 122.45, 122.05, 115.81, 106.48, 56.07, 39.10; HRMS (ESI+): Calculated for $C_{17}H_{16}N_2H$: $[M + H]^+$ 249.1386, Found 249.1384.

4-(1-Phenylpiperidin-2-yl)pyridine (4j) [5]



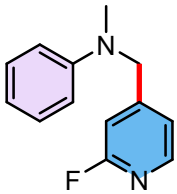
68% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 – 8.74 (m, 1H), 8.47 – 8.38 (m, 2H), 7.59 – 7.48 (m, 1H), 7.24 – 7.10 (m, 4H), 6.91 – 6.84 (m, 2H), 6.83 – 6.77 (m, 1H), 4.45 (dd, *J* = 7.3, 4.2 Hz, 1H), 3.42 – 3.34 (m, 1H), 3.20 (ddd, *J* = 12.3, 6.8, 5.1 Hz, 1H), 2.01 – 1.96 (m, 1H), 1.91 – 1.83 (m, 1H), 1.81 – 1.72 (m, 2H), 1.70 – 1.61 (m, 1H), 1.60 – 1.50 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.12, 151.40, 150.82, 149.77, 129.00, 125.29, 122.57, 120.46, 119.18, 60.49, 51.26, 33.33, 25.55, 22.14; HRMS (ESI+): Calculated for $C_{16}H_{18}N_2H$: $[M + H]^+$ 239.1543, Found 239.1548.

_N_-Methyl-_N_-((2-methylpyridin-4-yl)methyl)aniline (4k)



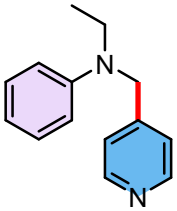
81% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.1 Hz, 1H), 7.22 (dd, *J* = 8.8, 7.3 Hz, 2H), 7.03 (d, *J* = 1.5 Hz, 1H), 6.98 – 6.95 (m, 1H), 6.74 (s, 1H), 6.71 – 6.68 (m, 2H), 4.47 (s, 2H), 3.03 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.65, 149.33, 149.26, 149.05, 129.30, 121.25, 119.03, 117.09, 112.35, 56.05, 38.89, 24.46; HRMS (ESI+): Calculated for $C_{14}H_{16}N_2H$: $[M + H]^+$ 213.1386, Found 213.1388.

_N_-((2-Fluoropyridin-4-yl)methyl)-_N_-methylaniline (4l)



72% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 5.1 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.05 (dq, *J* = 5.3, 1.2 Hz, 1H), 6.80 (q, *J* = 2.2, 1.6 Hz, 1H), 6.78 – 6.74 (m, 1H), 6.71 – 6.66 (m, 2H), 4.53 (s, 2H), 3.05 (d, *J* = 4.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.41 (d, *J* = 238.9 Hz), 155.16 (d, *J* = 7.4 Hz), 148.98, 147.82 (d, *J* = 15.2 Hz), 129.39, 119.56 (d, *J* = 3.9 Hz), 117.49, 112.43, 107.33 (d, *J* = 38.0 Hz), 55.92 (d, *J* = 3.2 Hz), 39.00; HRMS (ESI+): Calculated for $C_{13}H_{13}FN_2H$: $[M + H]^+$ 217.1136, Found 217.1134.

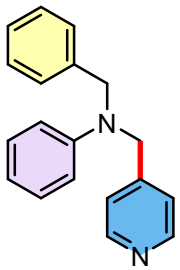
_N_-ethyl-_N_-(pyridin-4-ylmethyl)aniline (4m)



67% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.2 Hz, 2H), 7.19 (dd, *J* = 10.3, 5.9 Hz, 4H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 2H), 4.50 (s, 2H), 3.49 (q, *J* = 7.0 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.98,

148.96, 147.88, 129.39, 121.77, 116.67, 112.16, 53.34, 45.63, 12.28; HRMS (ESI+): Calculated for $C_{14}H_{16}N_2H$: $[M + H]^+$ 213.1386, Found 213.1384.

_N_-benzyl-_N_-(pyridin-4-ylmethyl)aniline (4n)



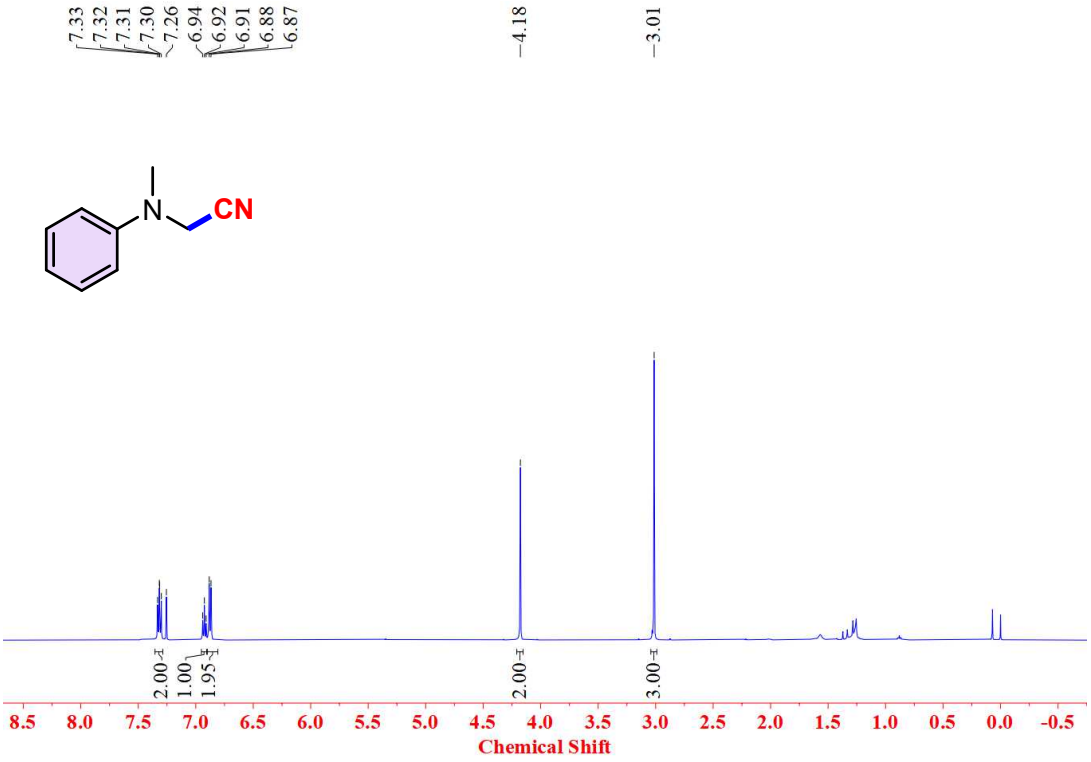
61% yield as a colorless oil. R_f = 0.5 (PE: EA =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.48 (m, 2H), 7.33 (d, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 11.0 Hz, 3H), 7.18 (d, *J* = 7.7 Hz, 4H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 2H), 4.67 (s, 2H), 4.62 (s, 2H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.02, 148.63, 148.30, 138.05, 129.40, 128.78, 127.17, 126.69, 121.88, 117.42, 112.52, 54.58, 53.49; HRMS (ESI+): Calculated for $C_{19}H_{18}N_2H$: $[M + H]^+$ 275.1543, Found 275.1547.

3. References

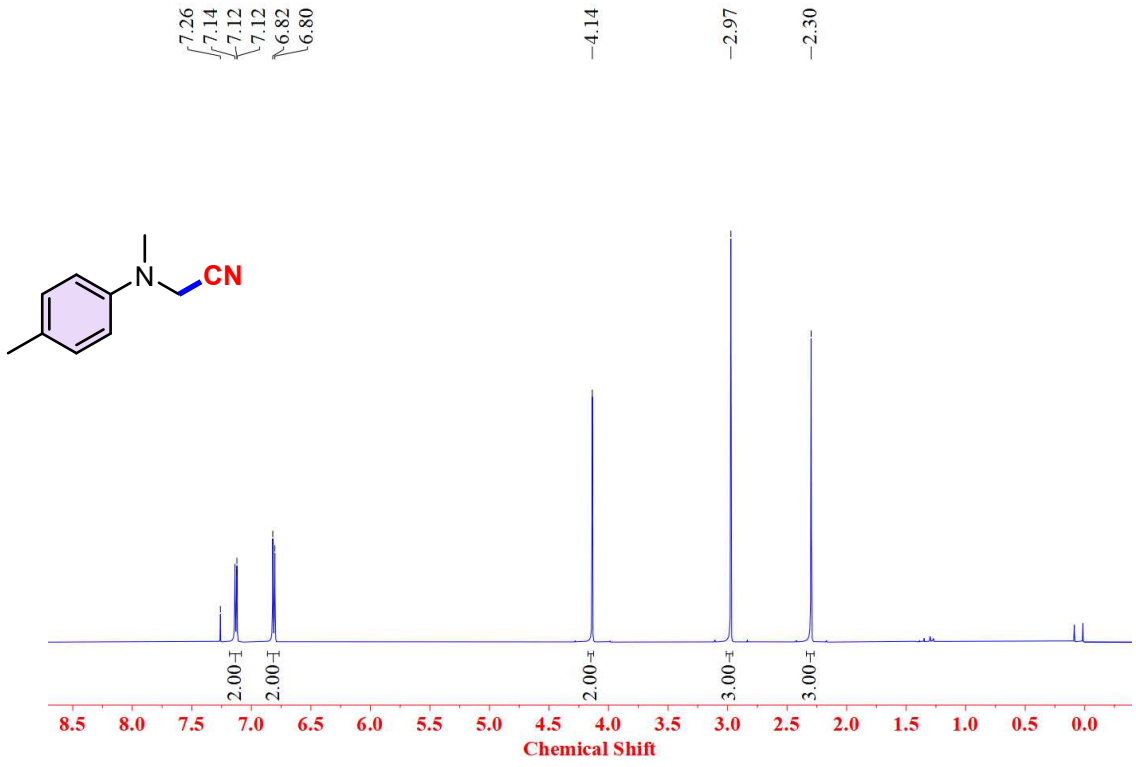
1. F. M. Moghaddam, R. Pourkaveh and M. Heidarian, *Catal. Commun.*, 2021, **149**, 106211.
2. B. Yusan, A. Amuti, X. J. Xu and A. Wusiman, *Eur. J. Org. Chem.*, 2024, **27**, e202400144.
3. W. Song, X. Chen, W. Kan, Y. Piao, C. Wang, L. Wang, F. Li, P. Chen and Z. Wang, *Appl. Catal. A Gen.*, 2025, **698**, 120248.
4. O. Yilmaz, C. Dengiz and M. H. Emmert, *J. Org. Chem.*, 2021, **86**, 2489–2498.
5. M. Benítez, M. L. Buil, M. A. Esteruelas, A. M. López, C. Martín-Escura and E. Oñate, *Inorg. Chem.*, 2024, **63**, 6346–6361

4. Copies of ^{1}H and ^{13}C Spectra

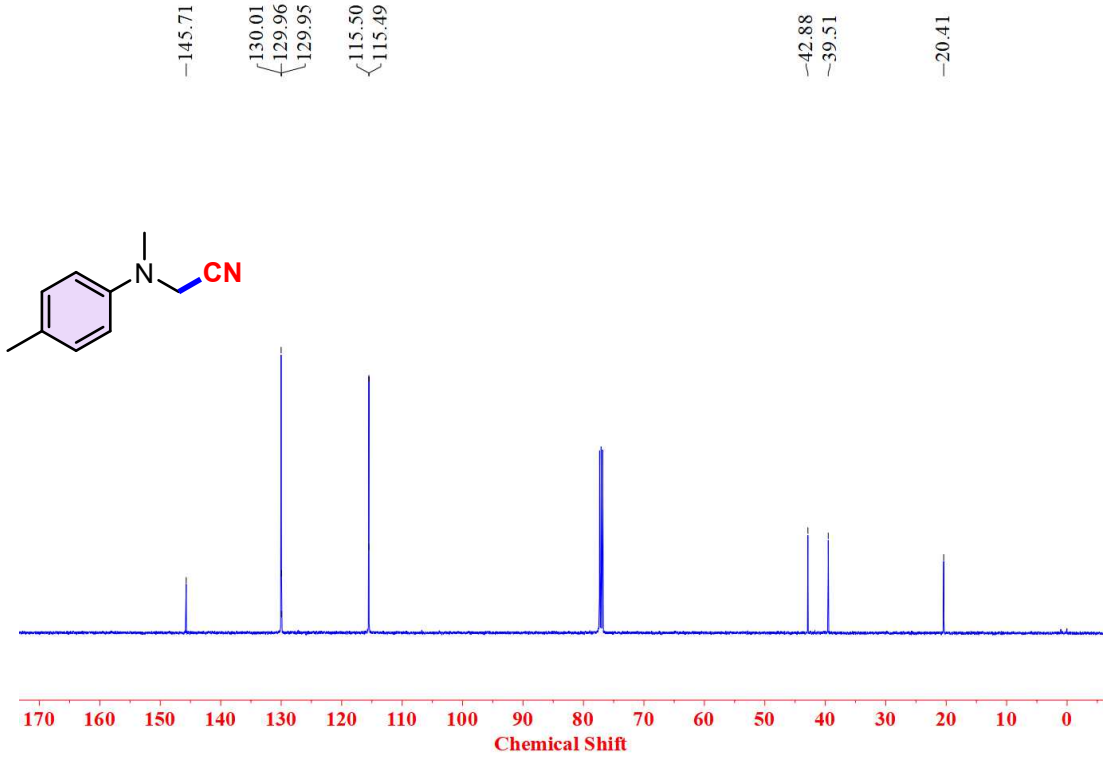
3a ^{1}H NMR



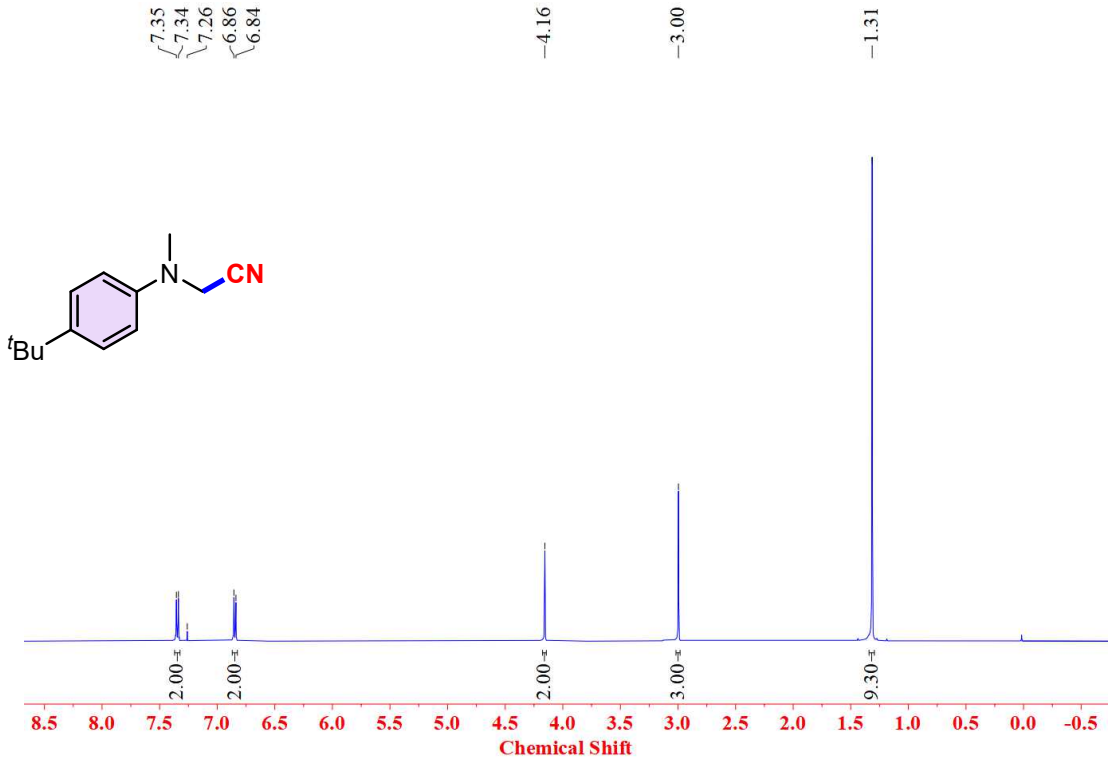
3b ^{1}H NMR



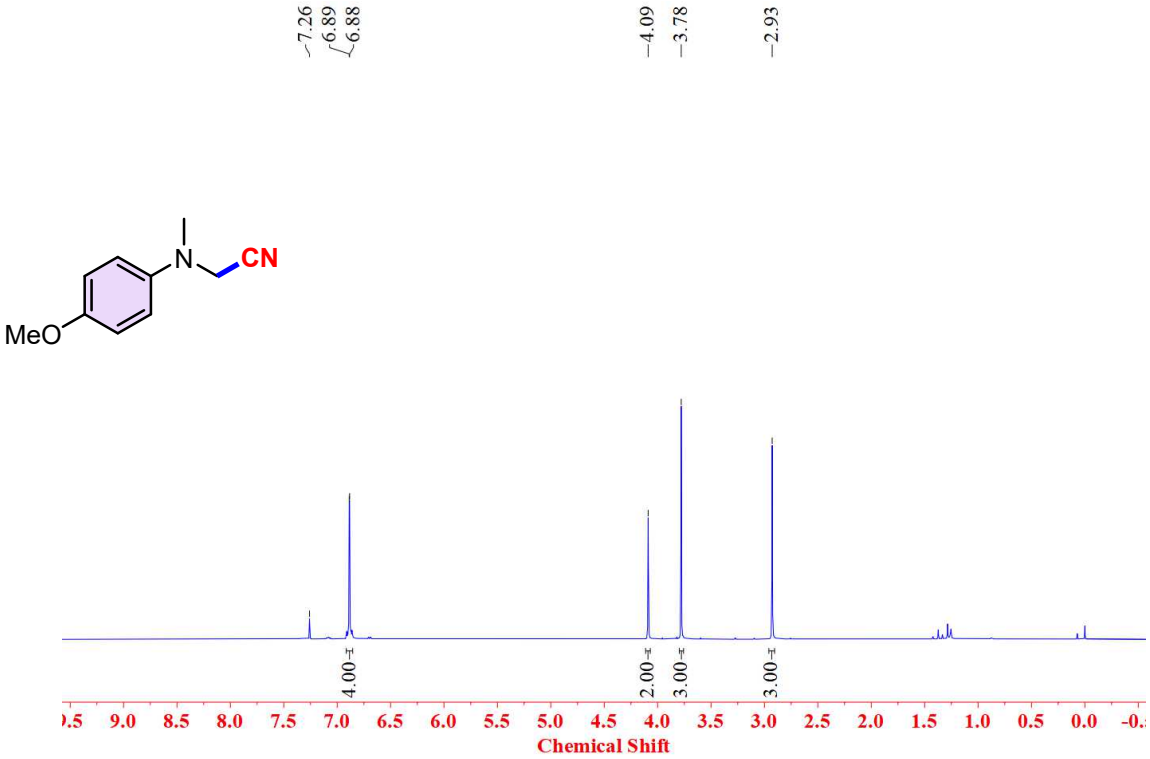
3b ^{13}C NMR



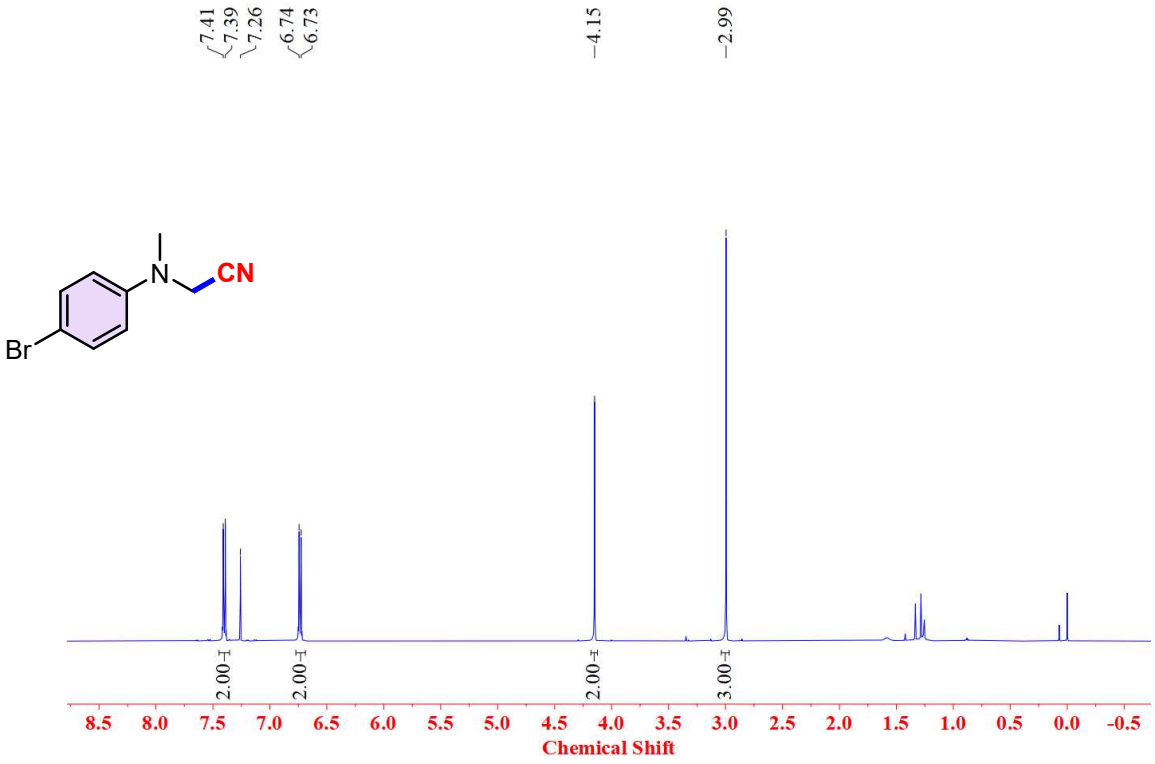
3c ^{1}H NMR



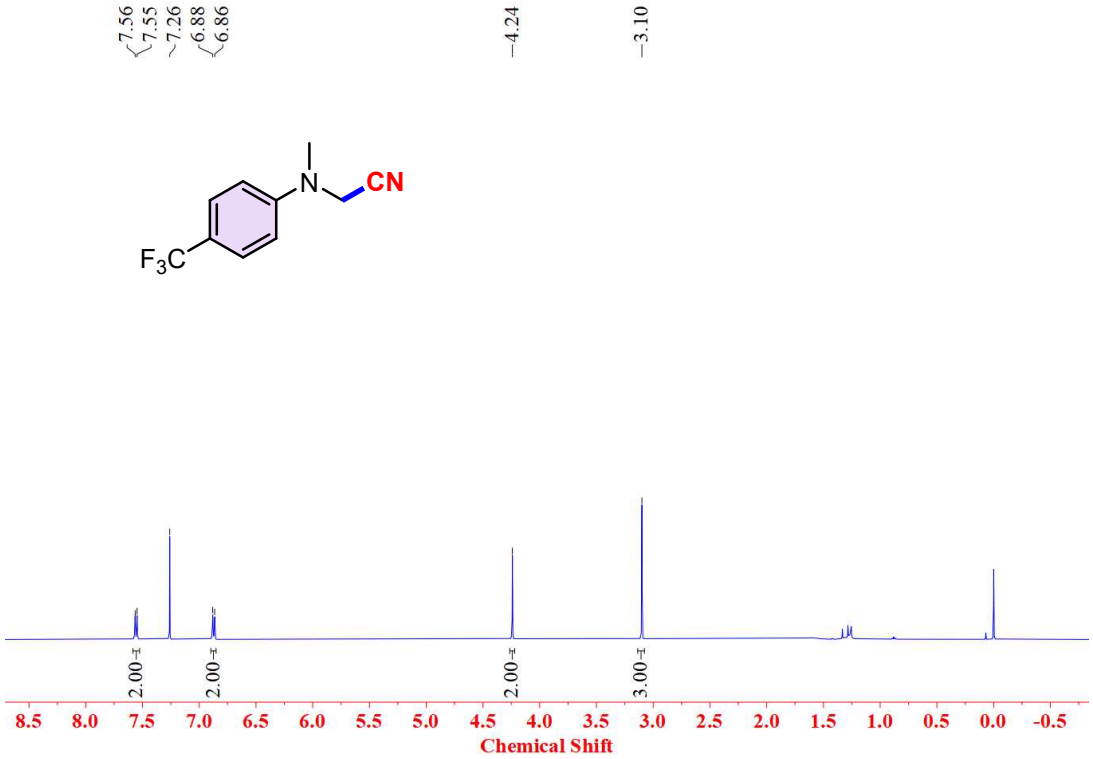
3d ^{1}H NMR



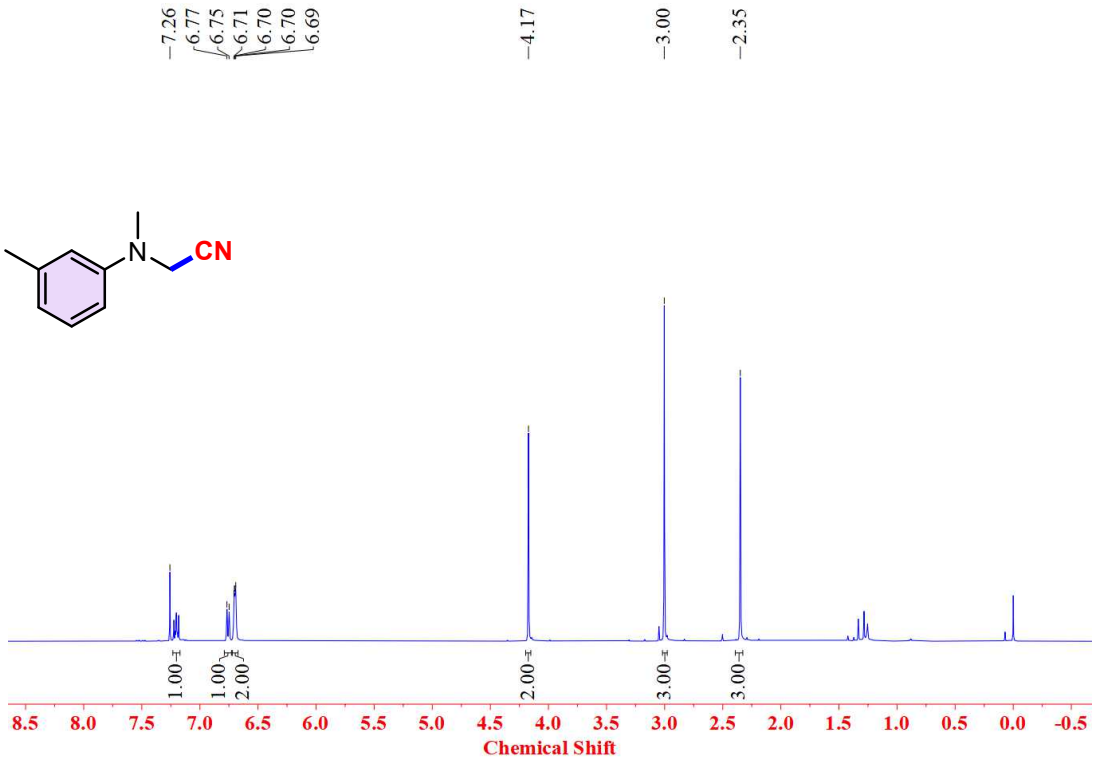
3e ^{1}H NMR



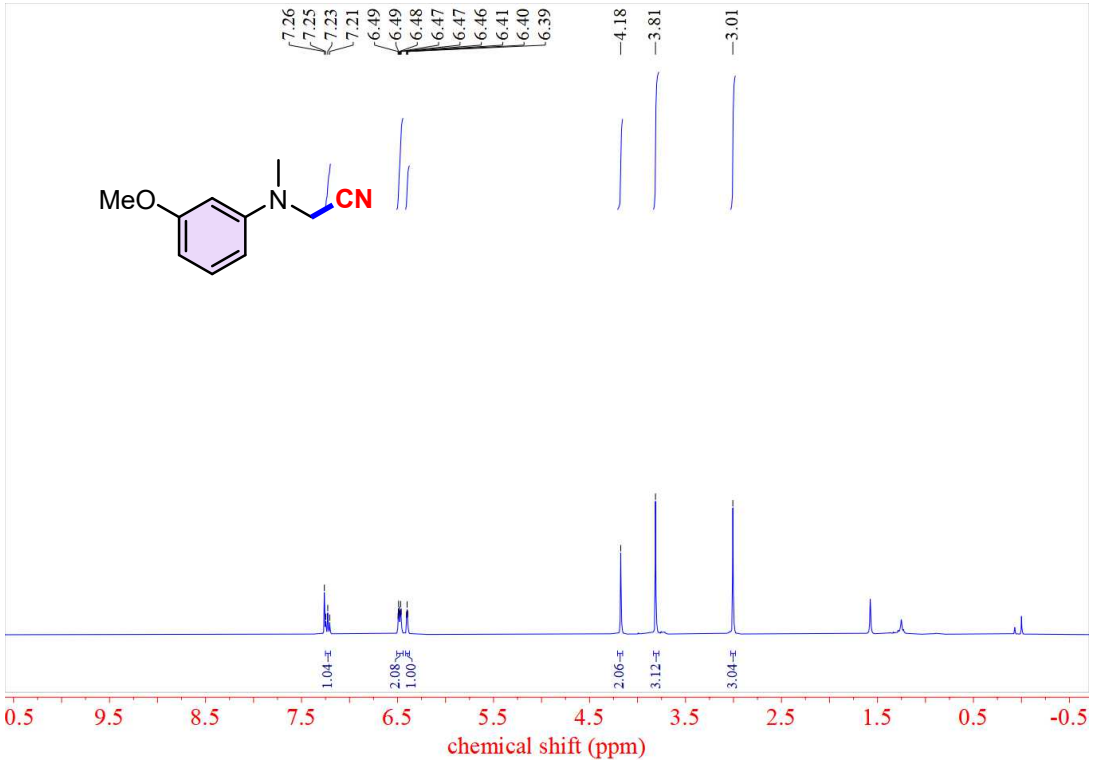
3f ^{1}H NMR



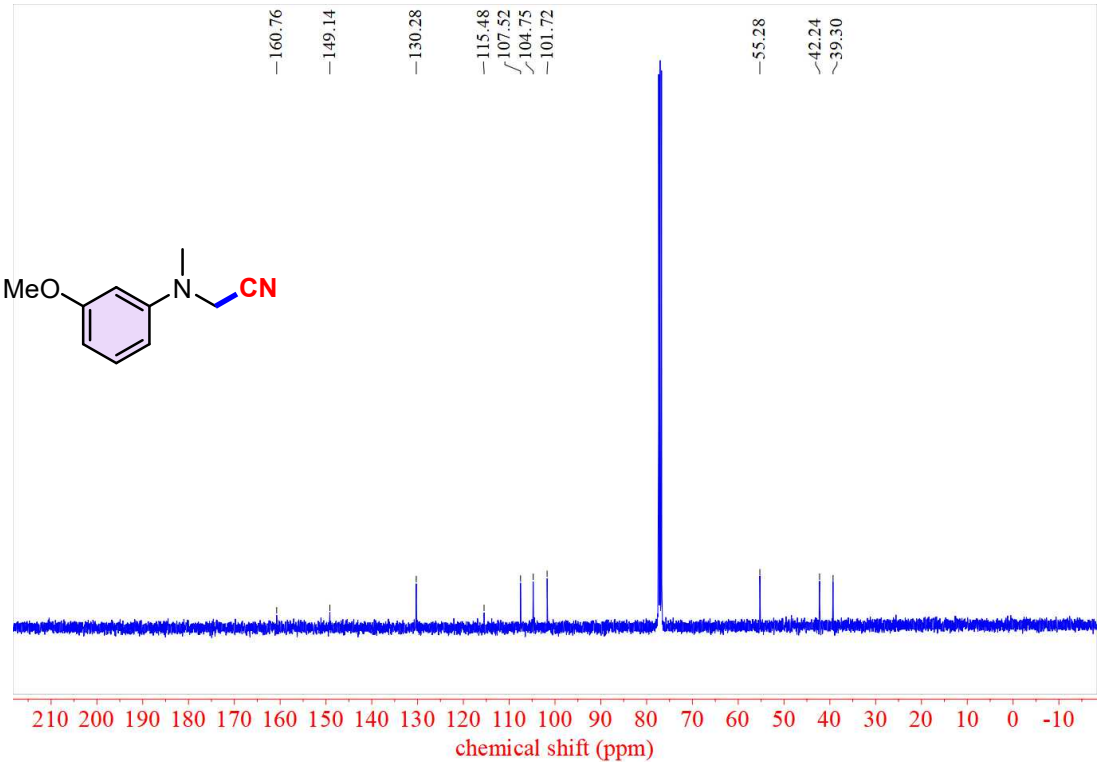
3g ^{1}H NMR



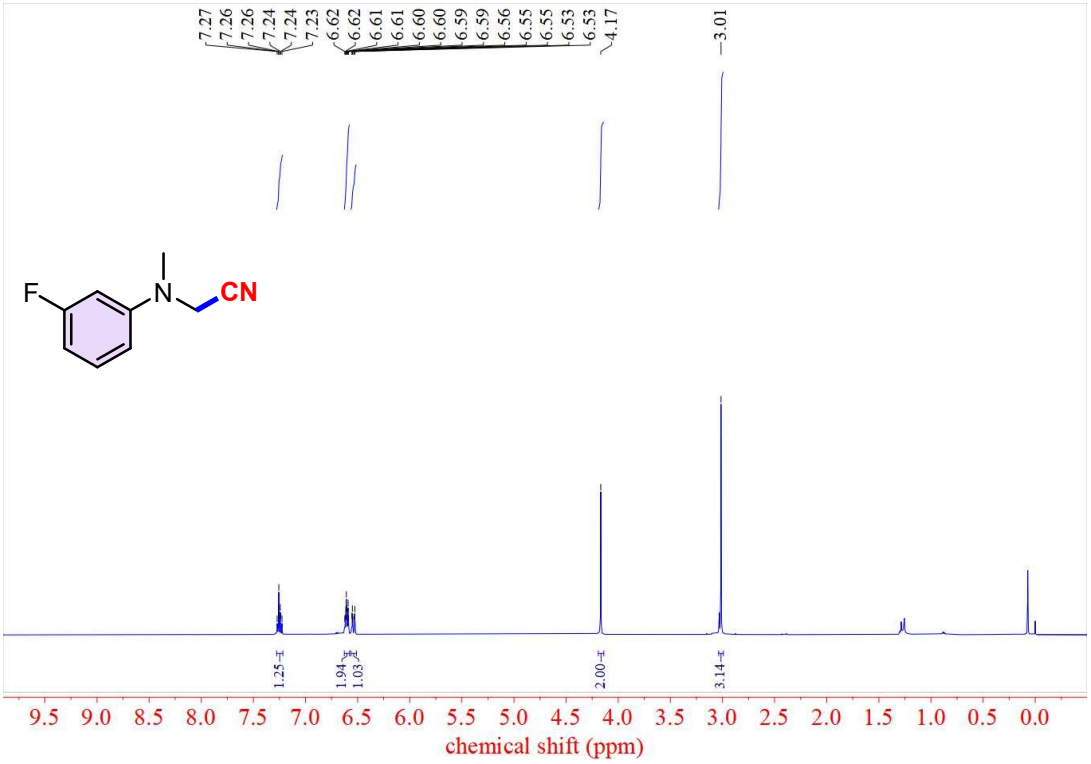
3h ^{1}H NMR



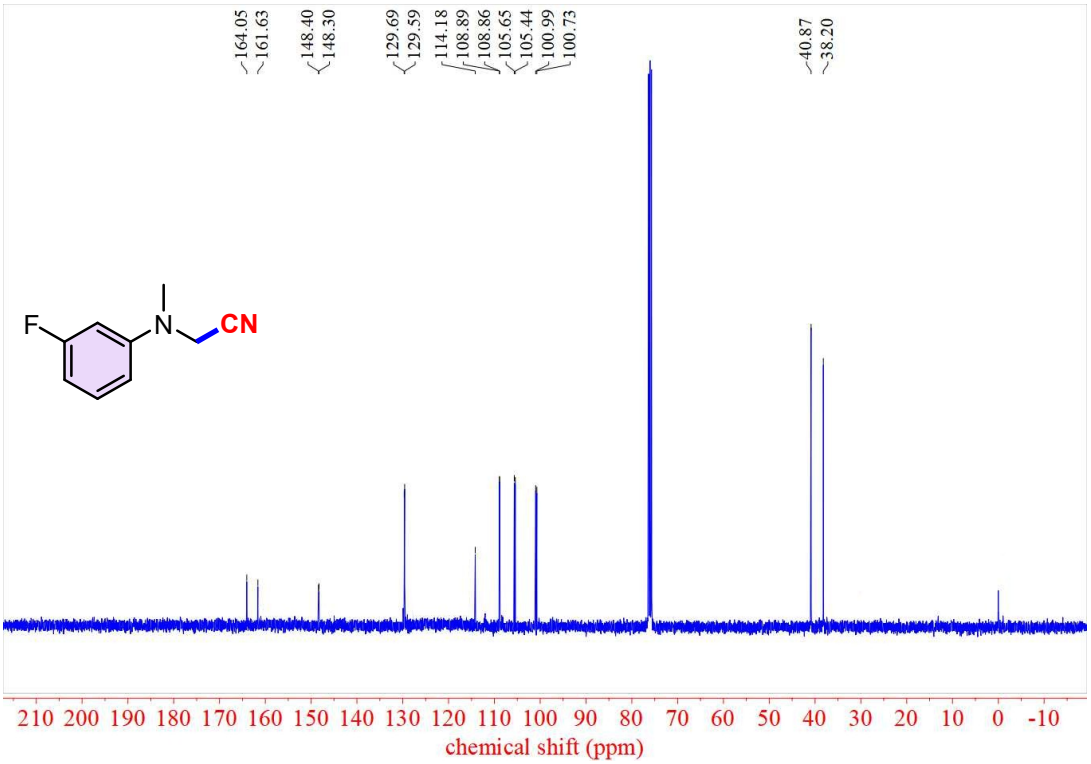
3h ^{13}C NMR



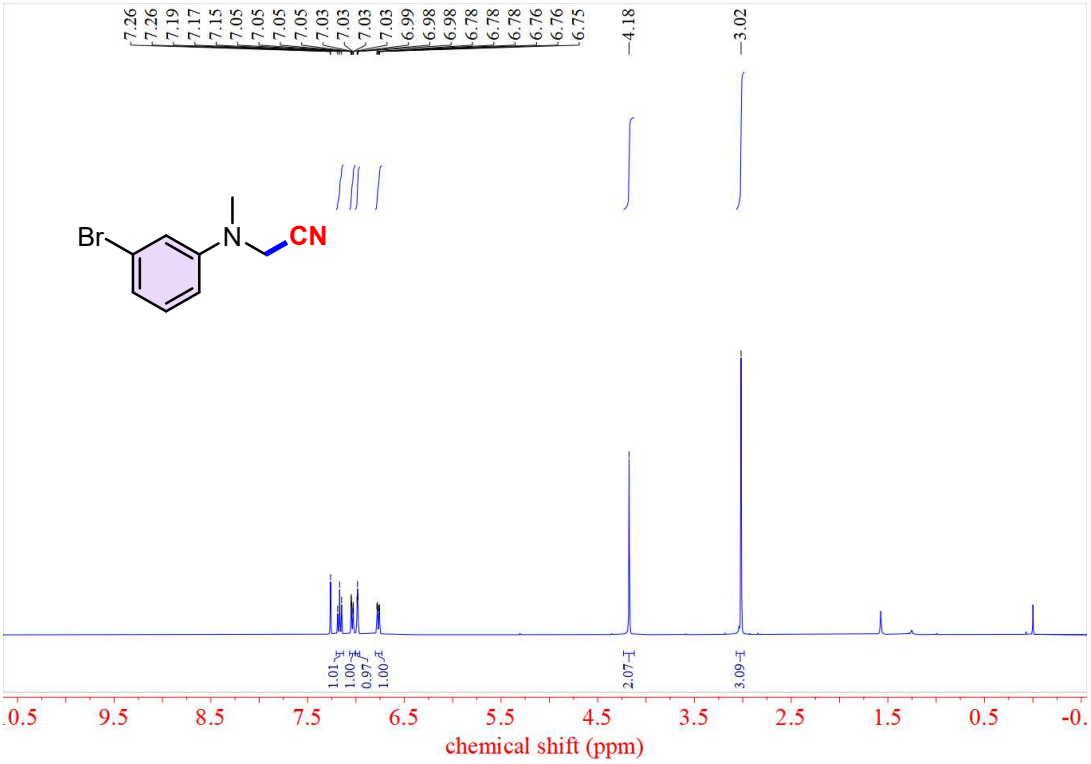
3i ^{1}H NMR



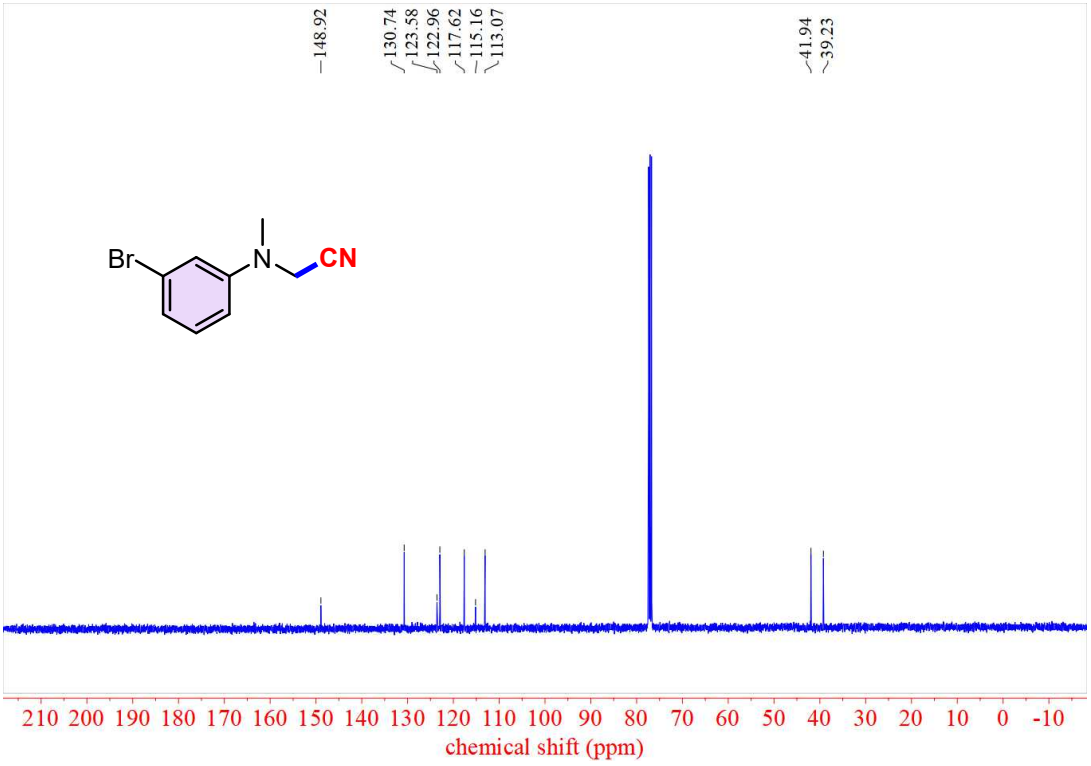
3i ^{13}C NMR



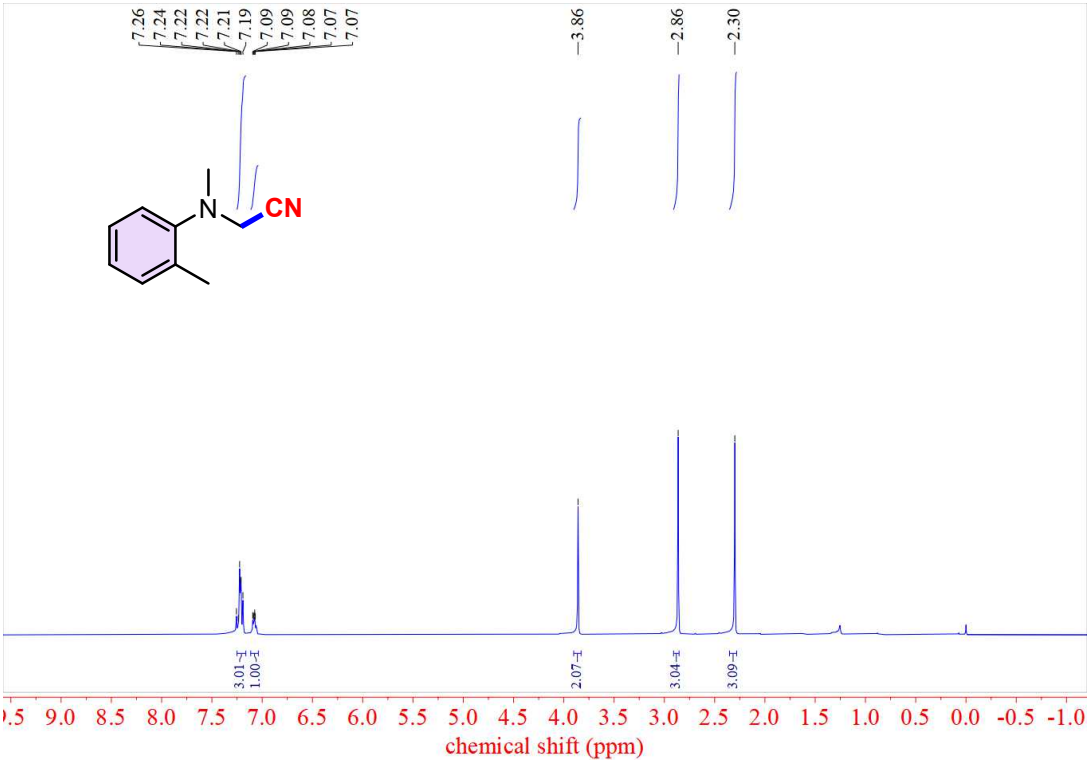
3j ^{1}H NMR



3j ^{13}C NMR



3k ^{1}H NMR



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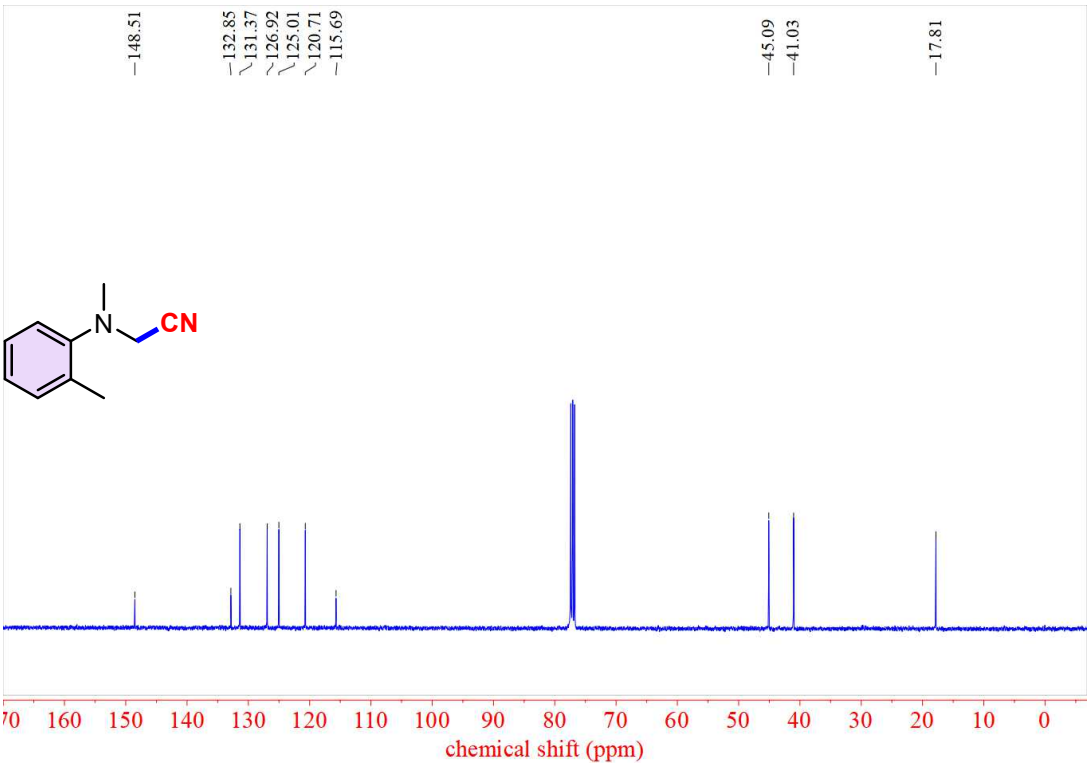

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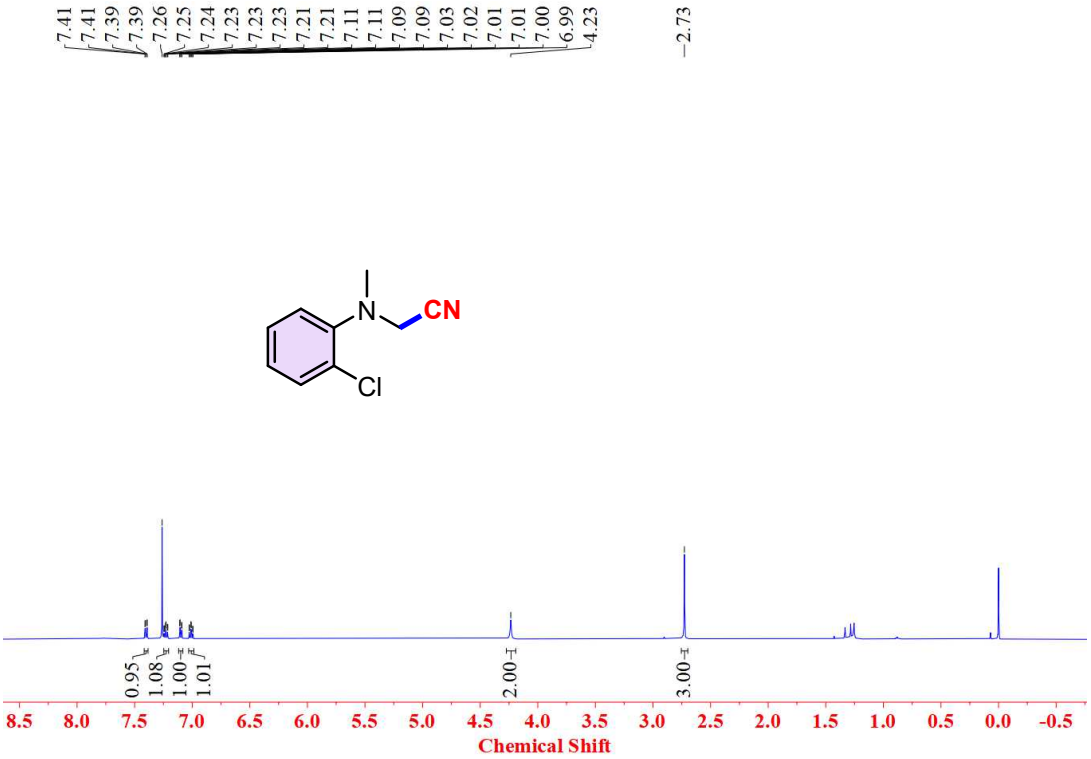

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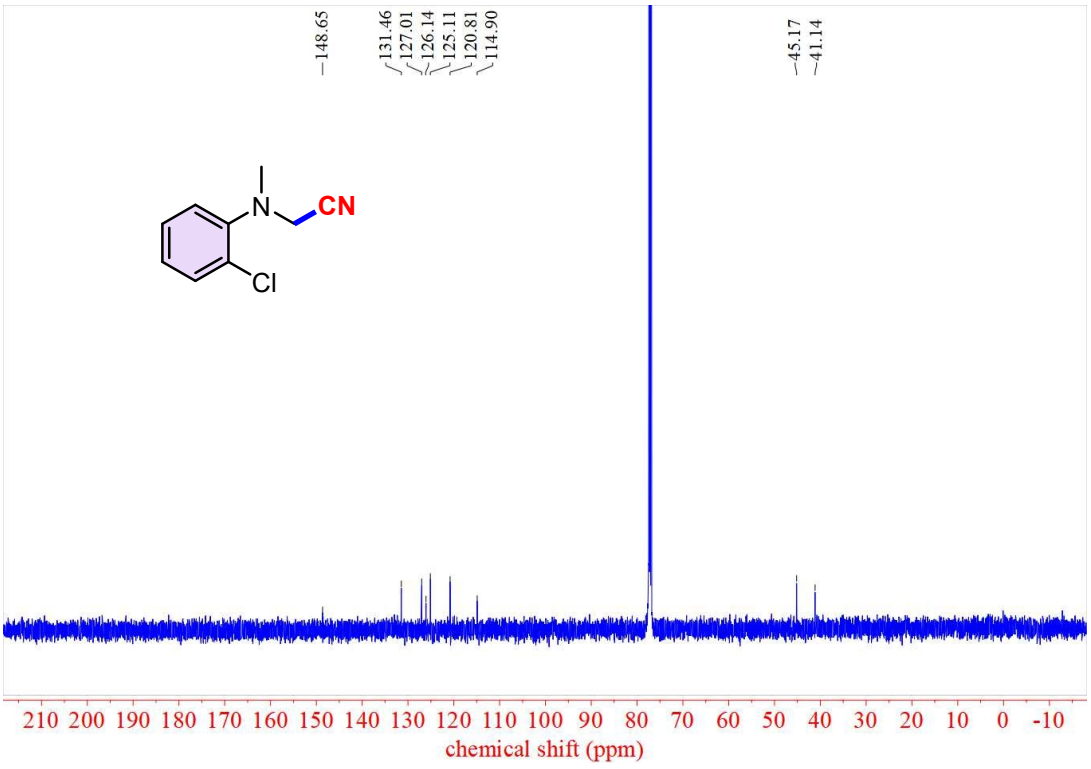
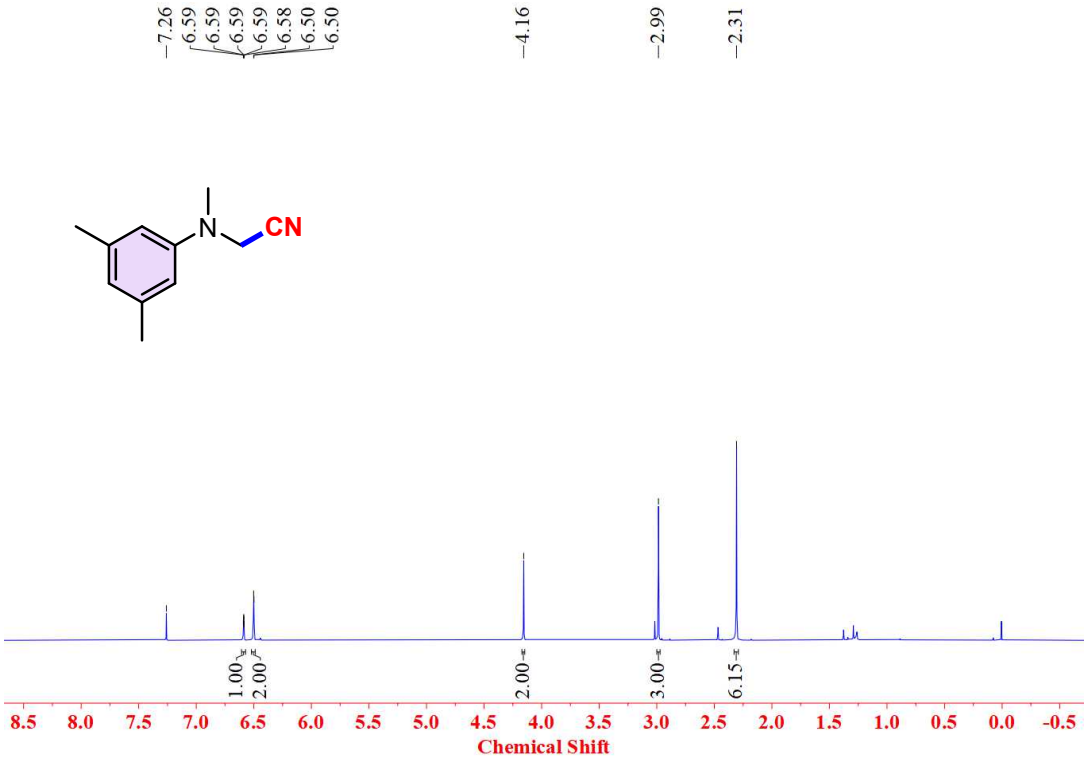


3m ^{1}H NMR



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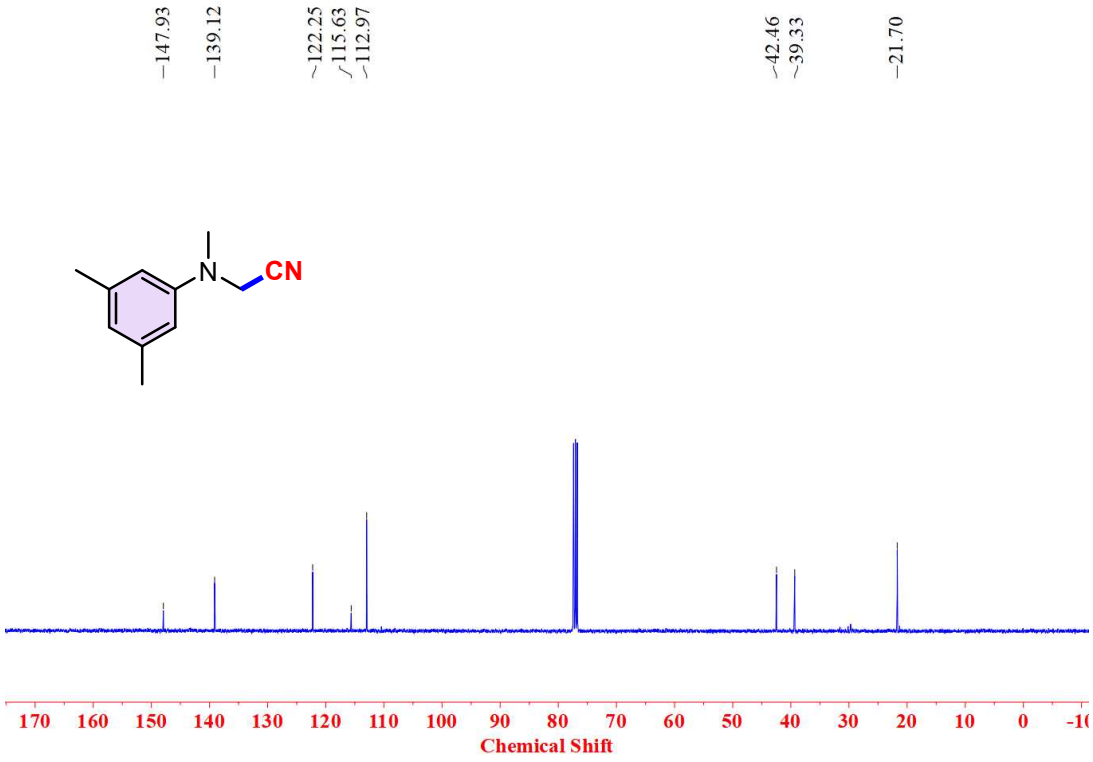

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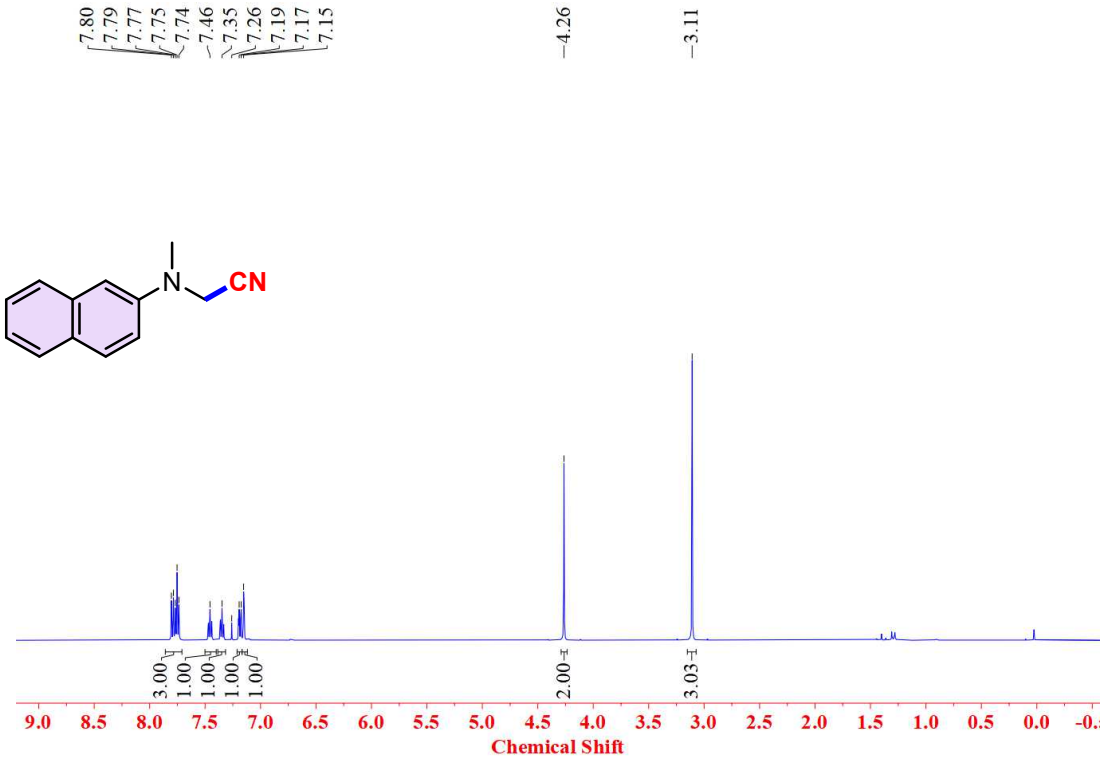

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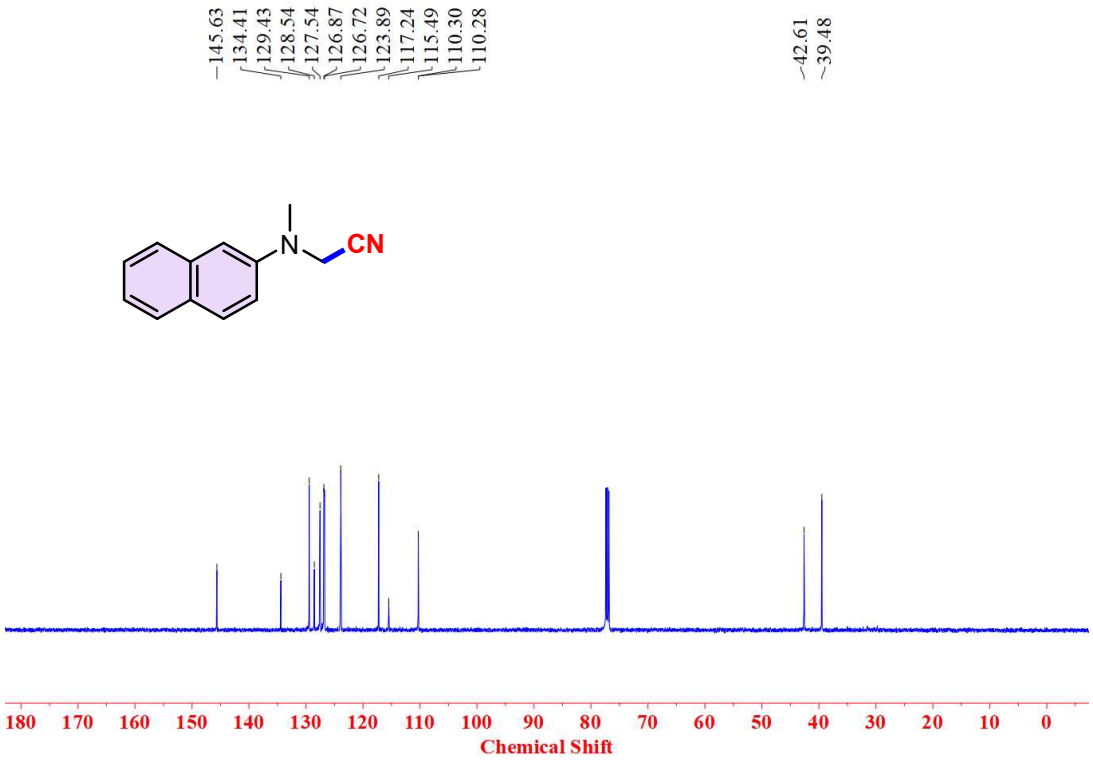

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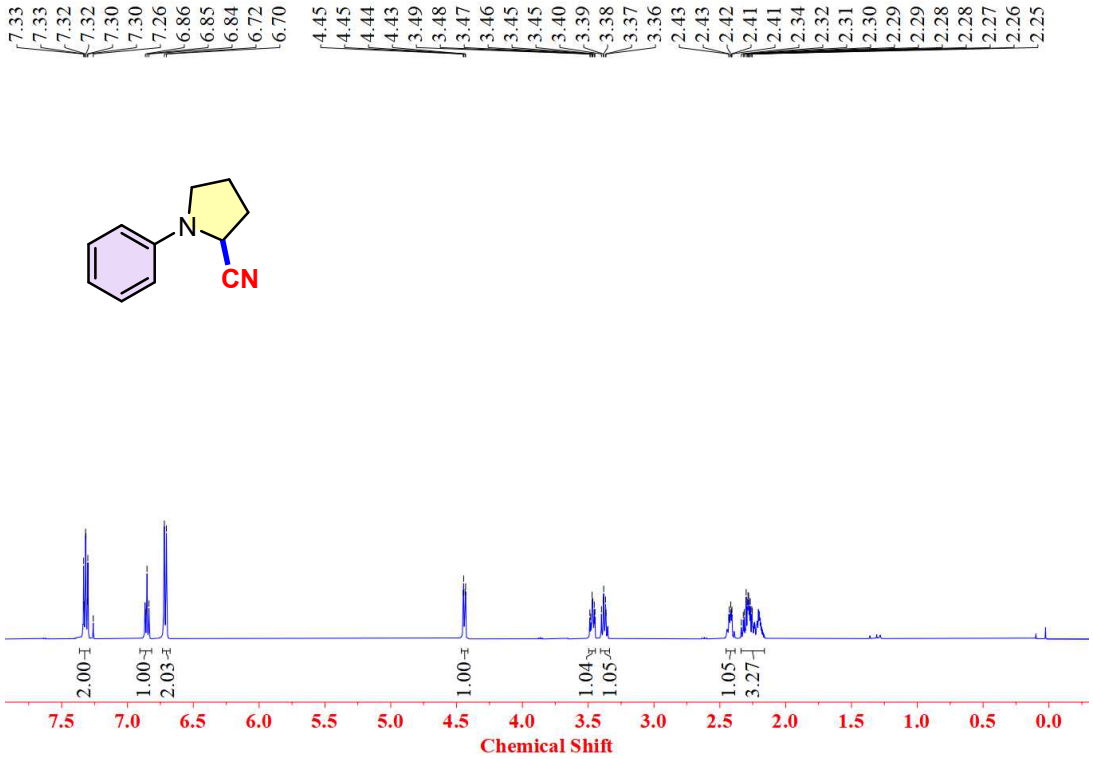

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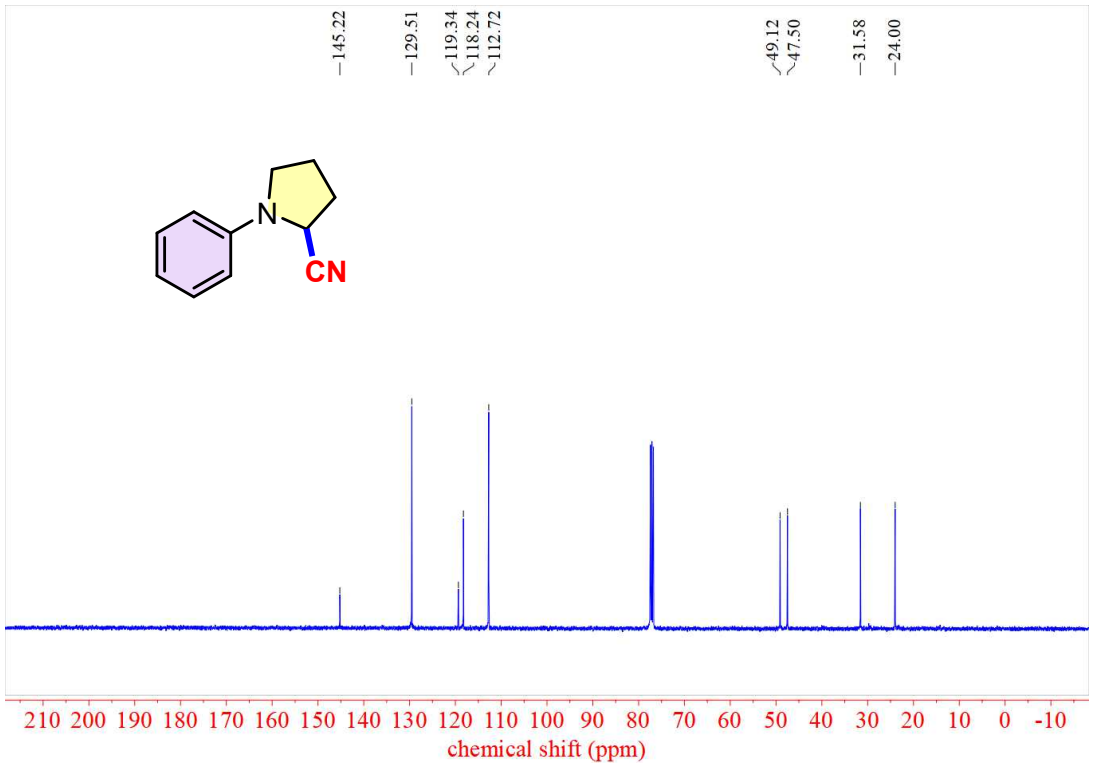
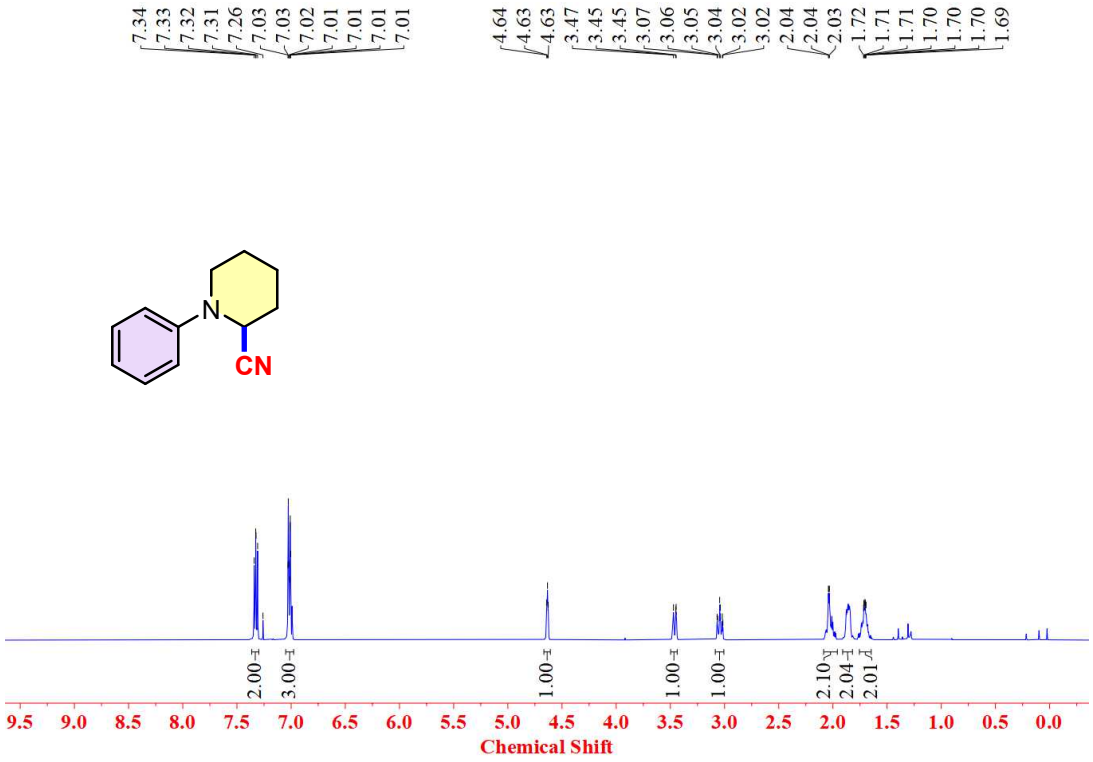


3p ^{1}H NMR



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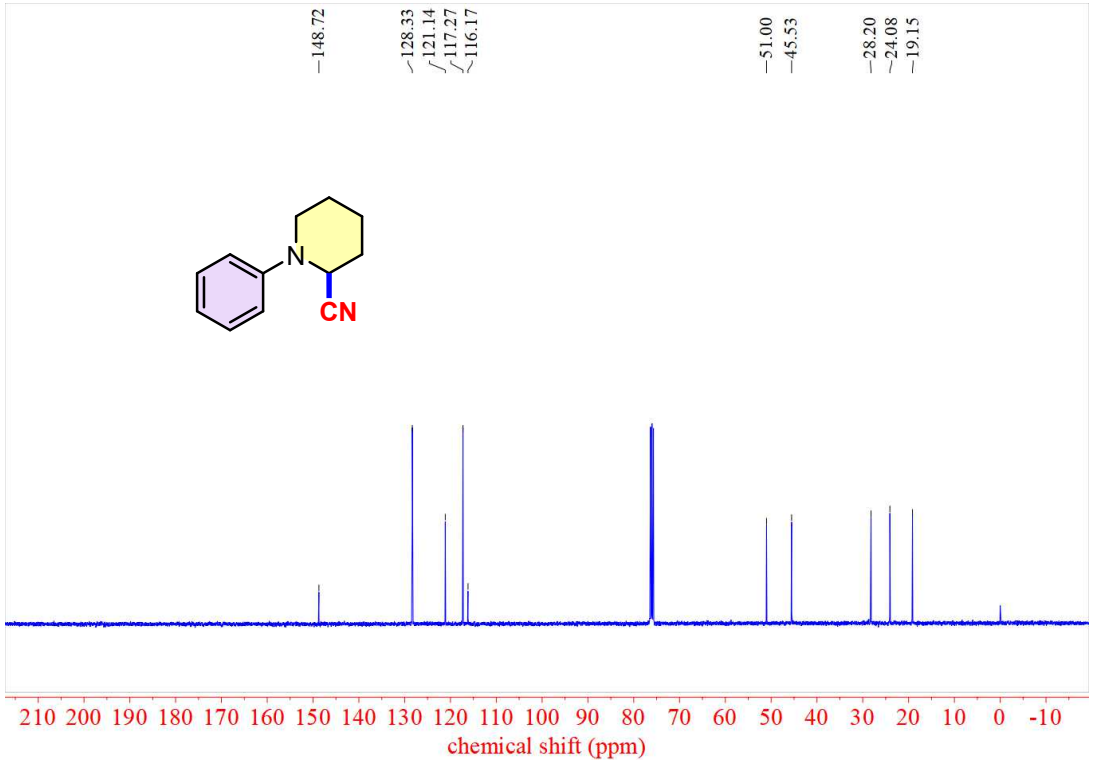

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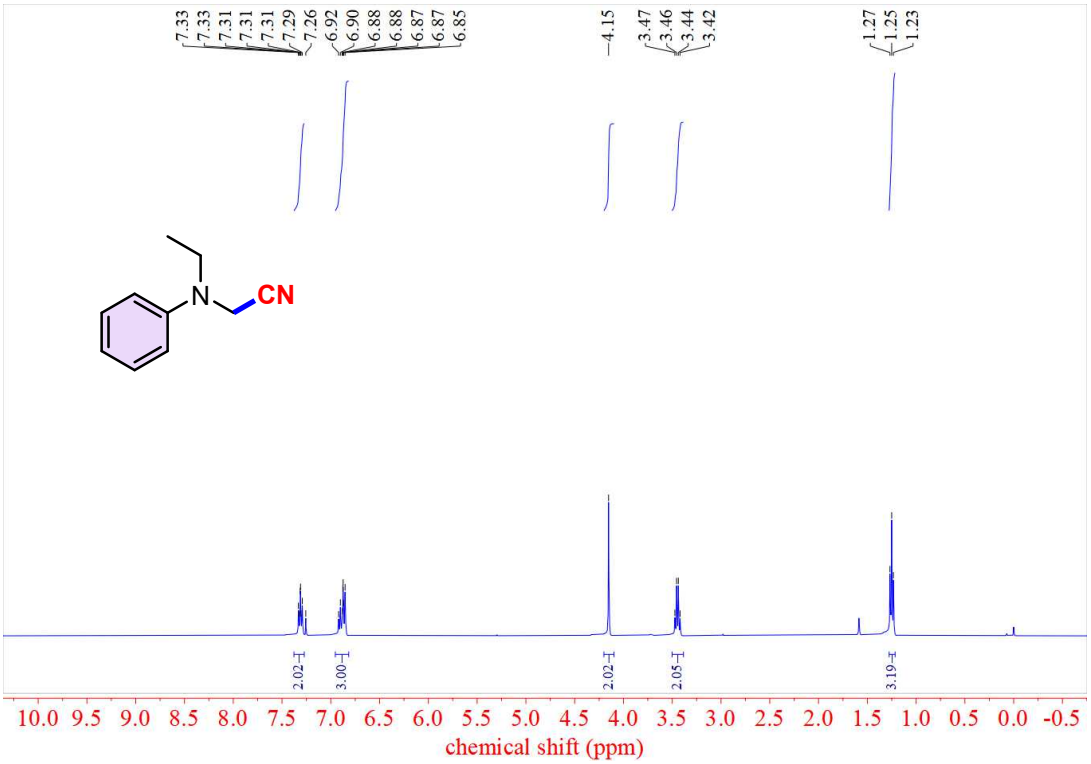
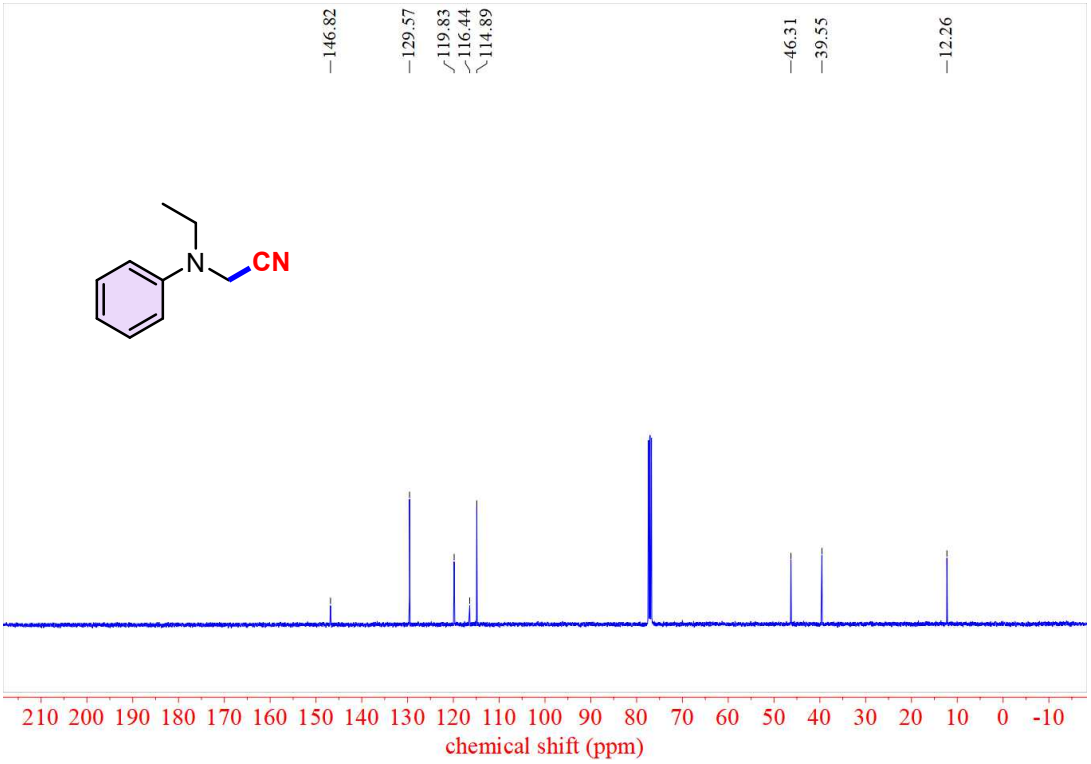
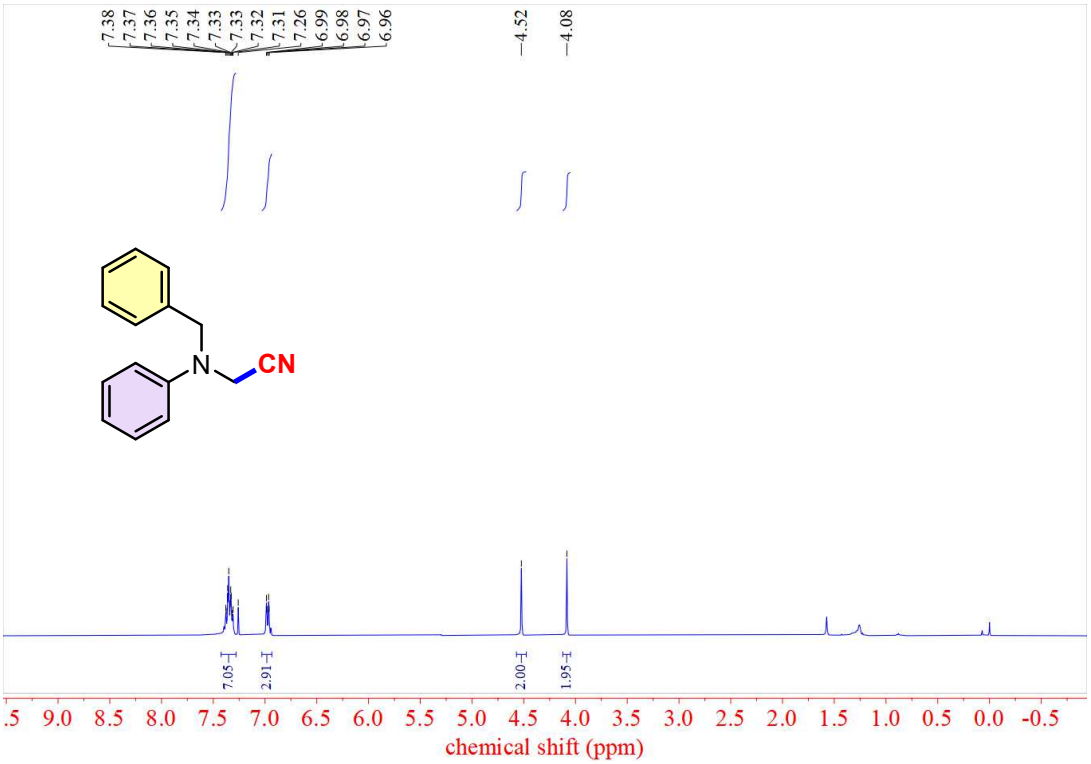


3q ^{13}C NMR



3r ^{1}H NMR



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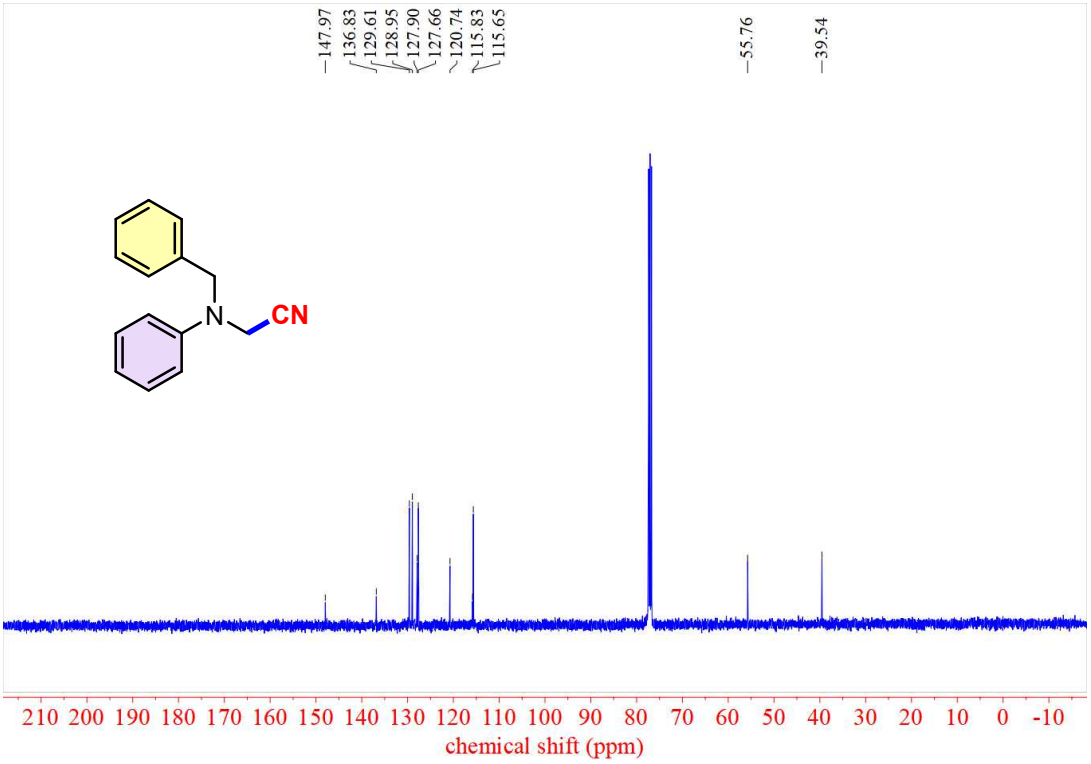
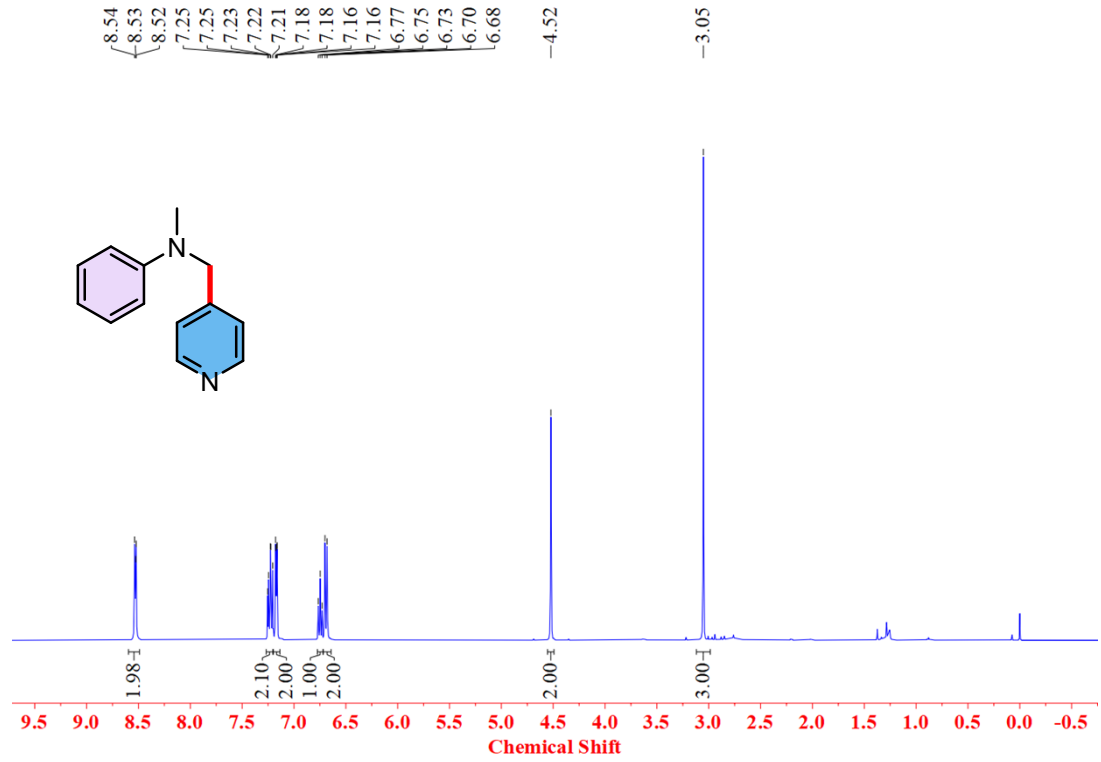


4a ^{1}H NMR



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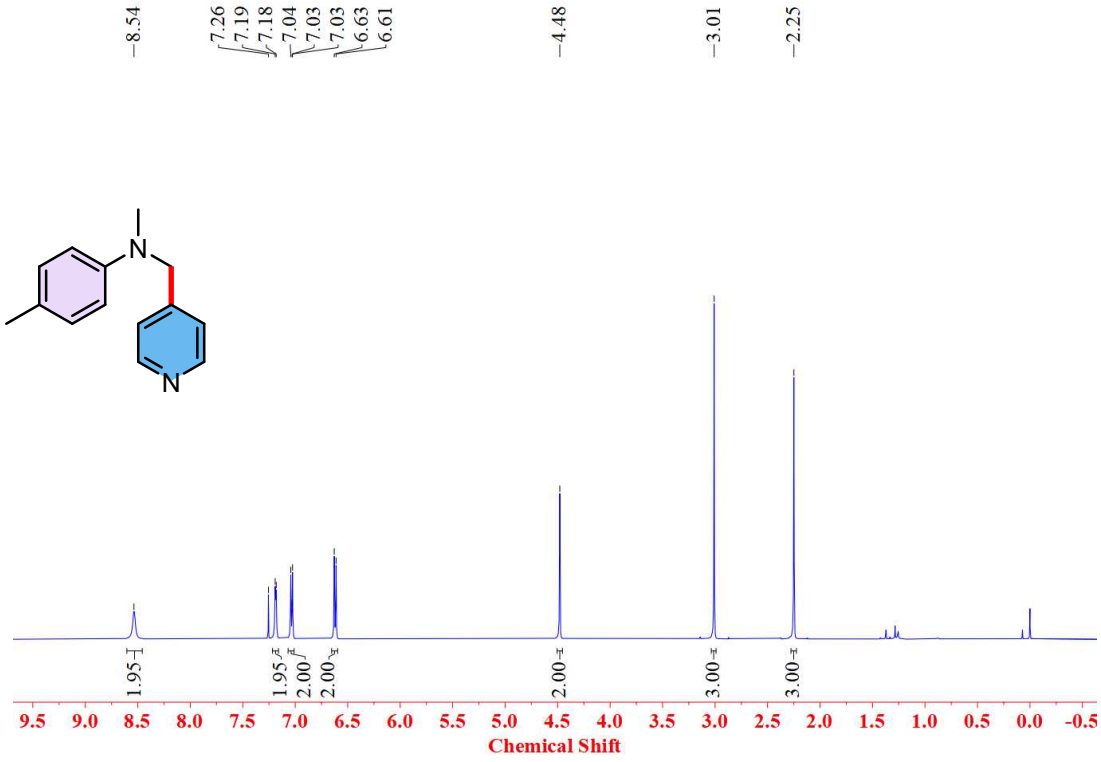

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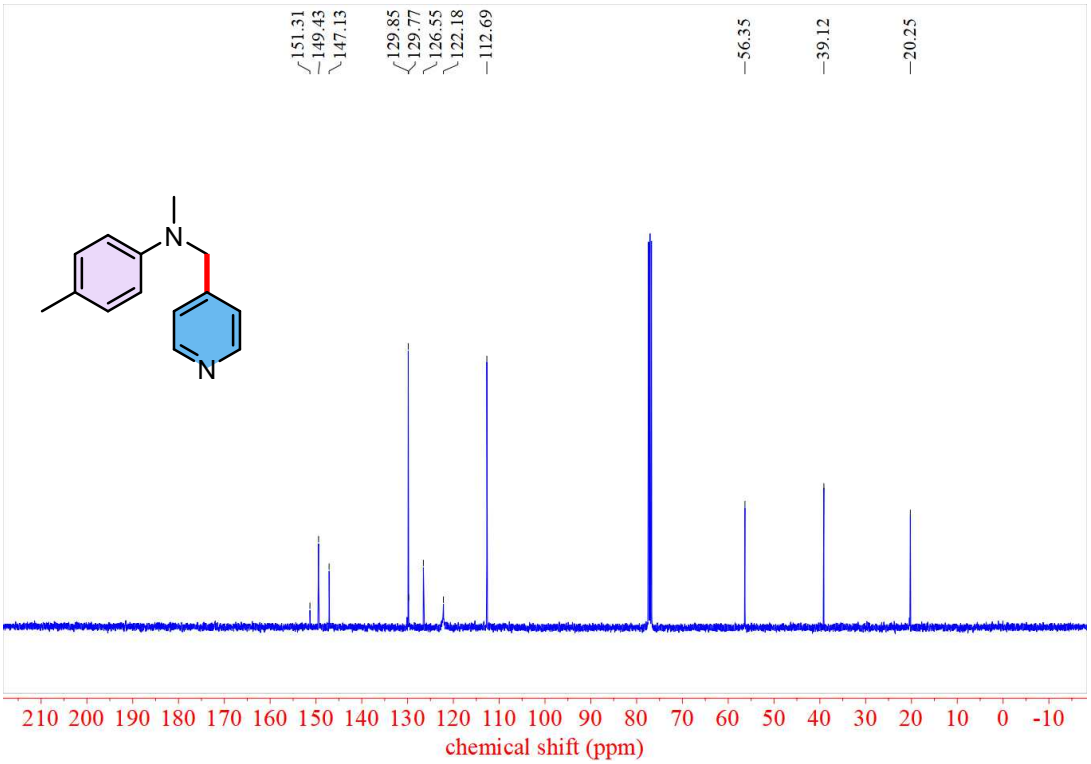
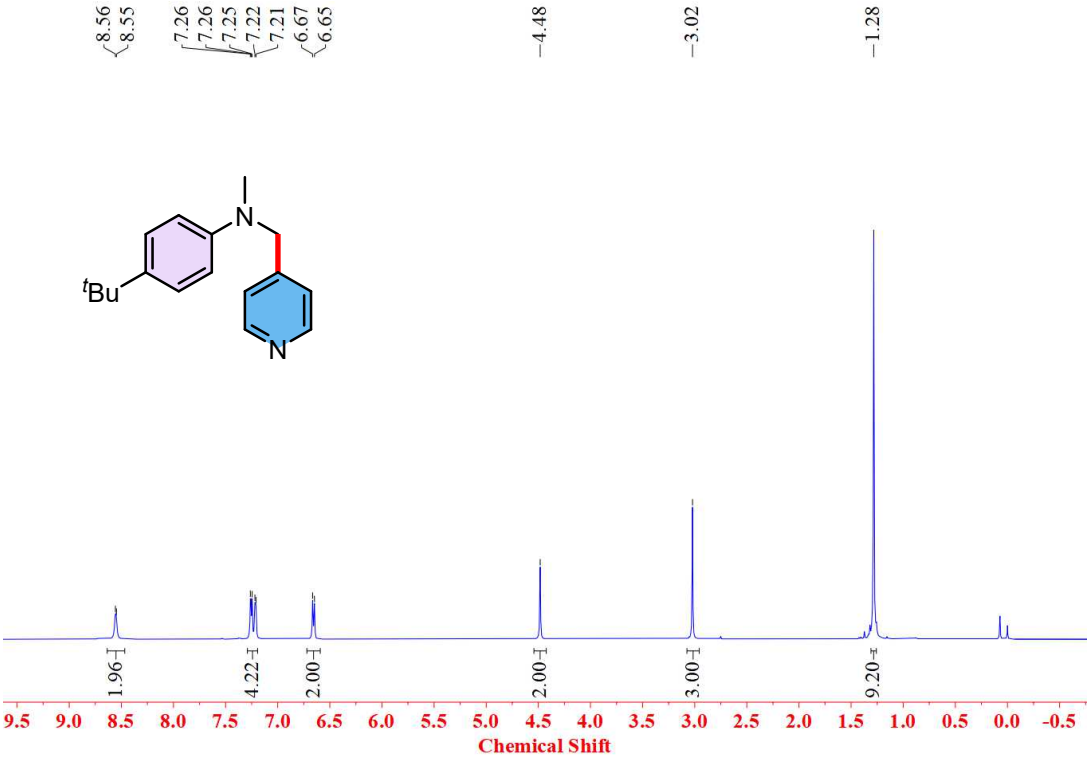


4c ^{1}H NMR



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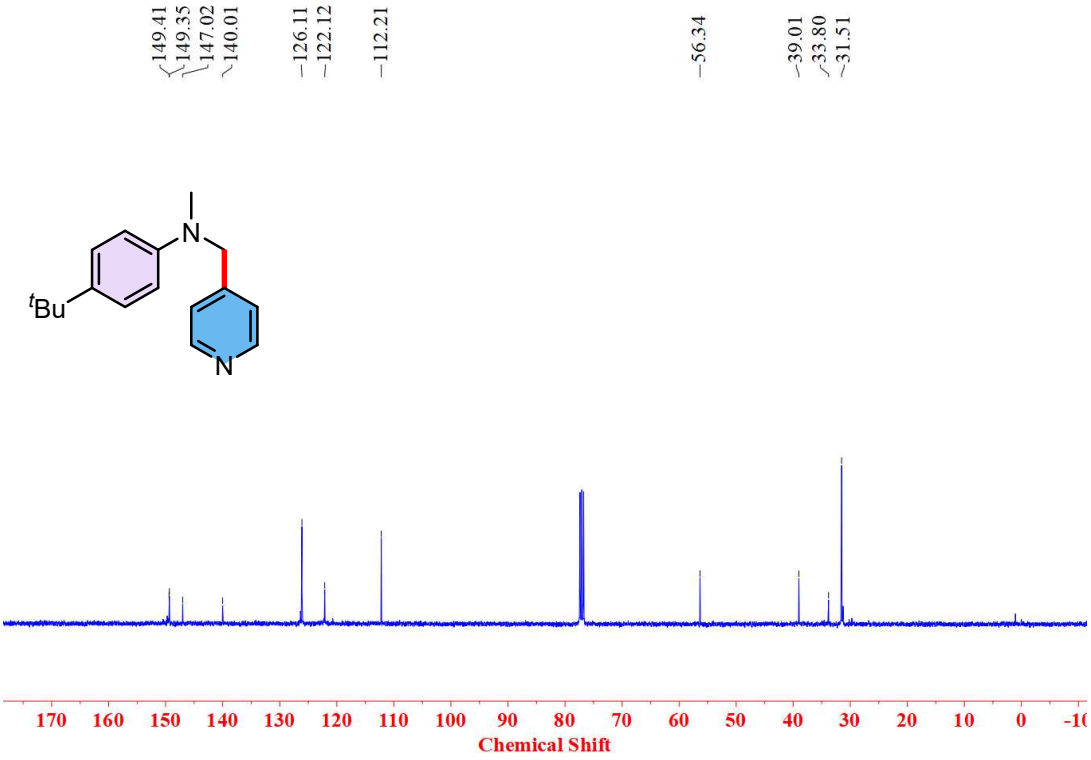
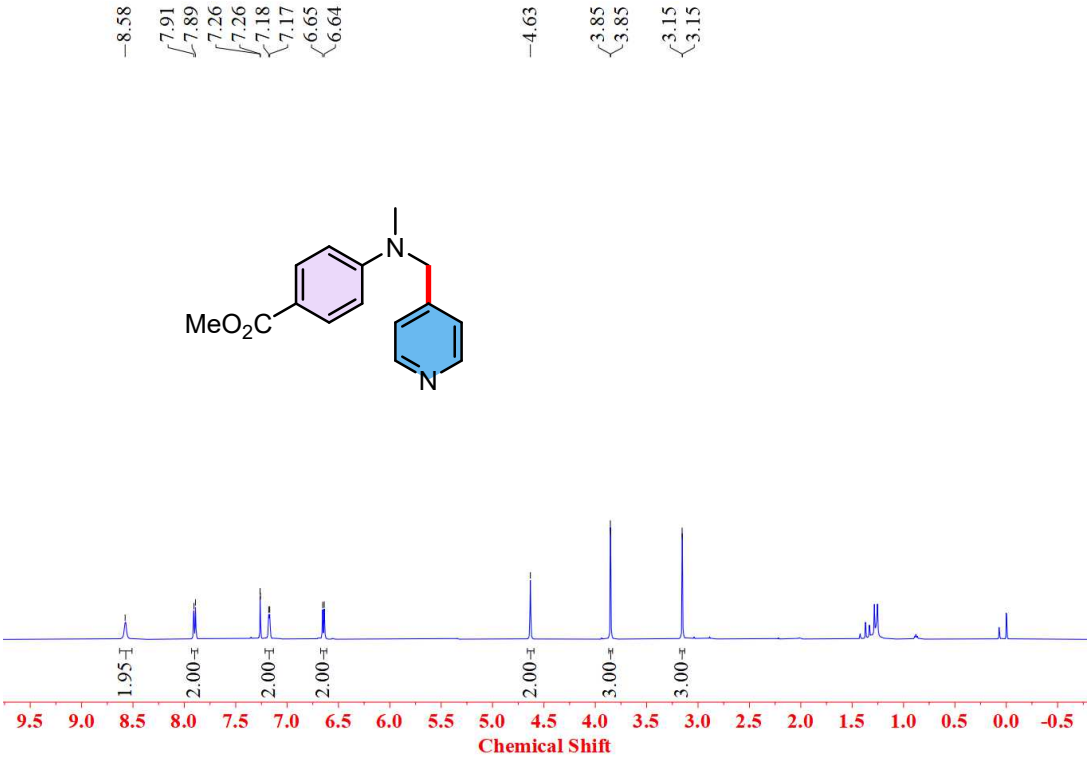


4d ^{1}H NMR



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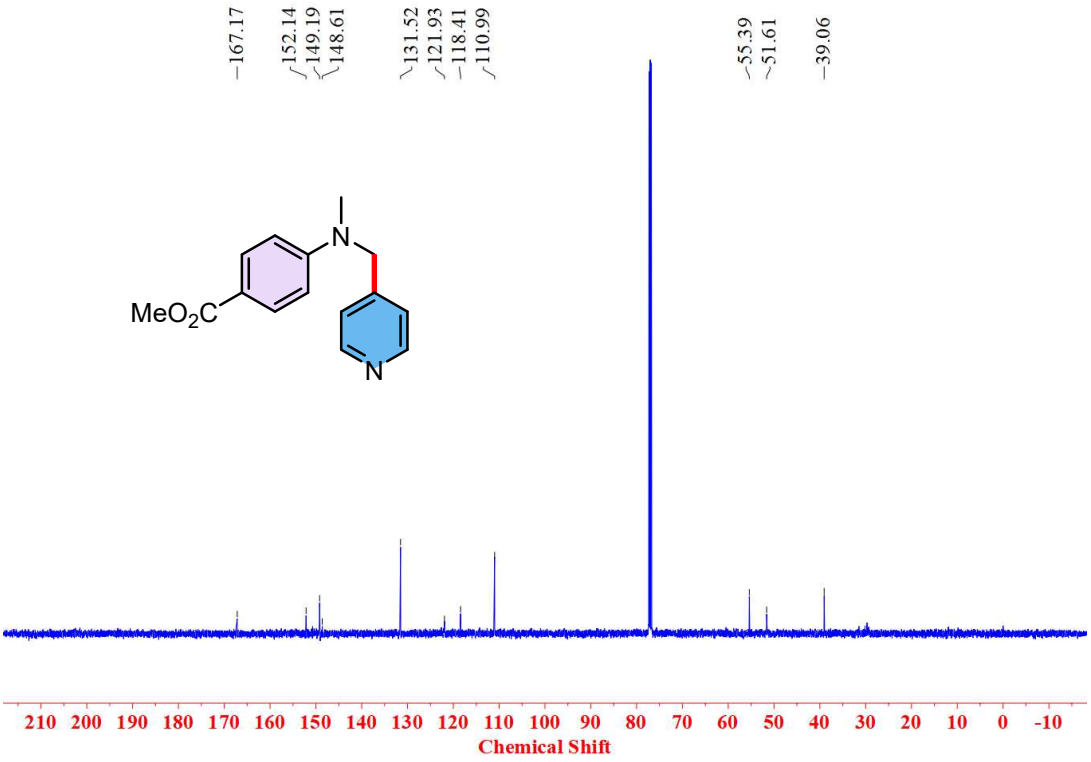

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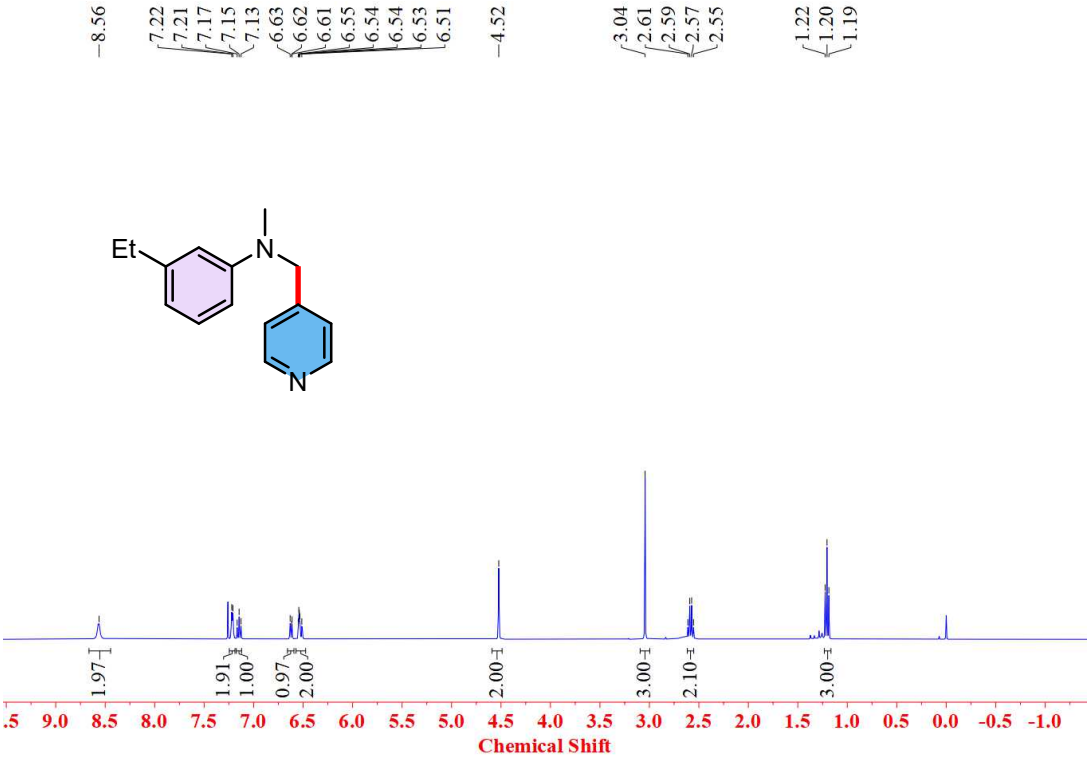

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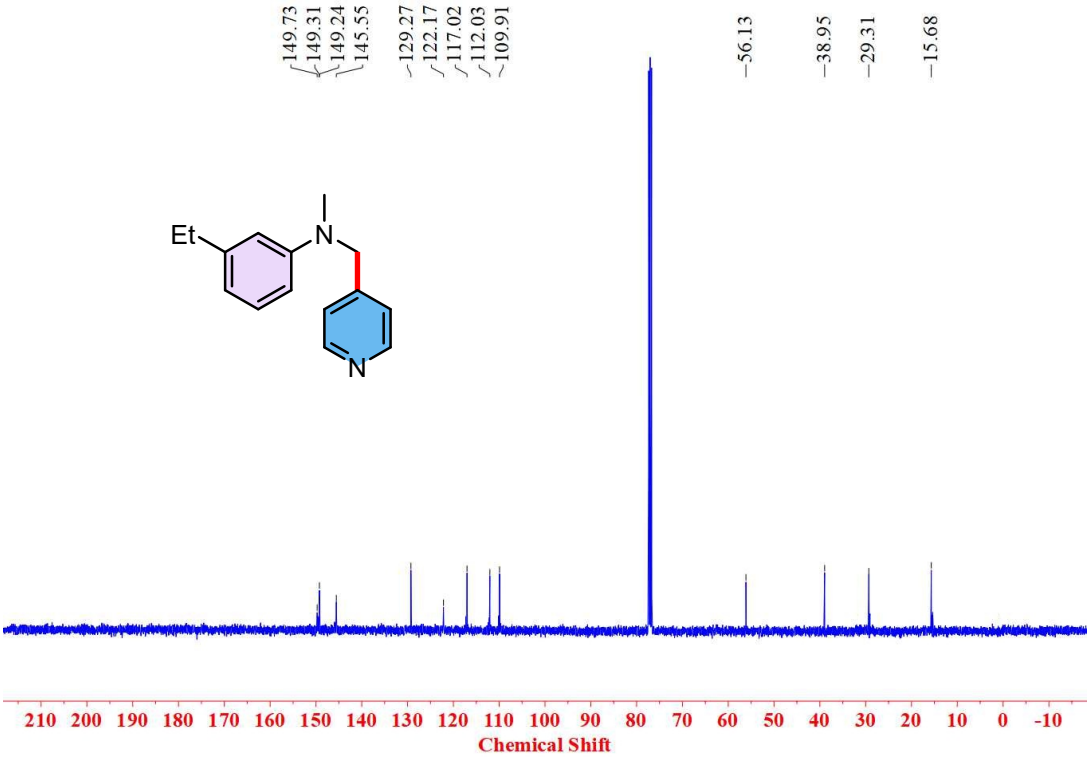

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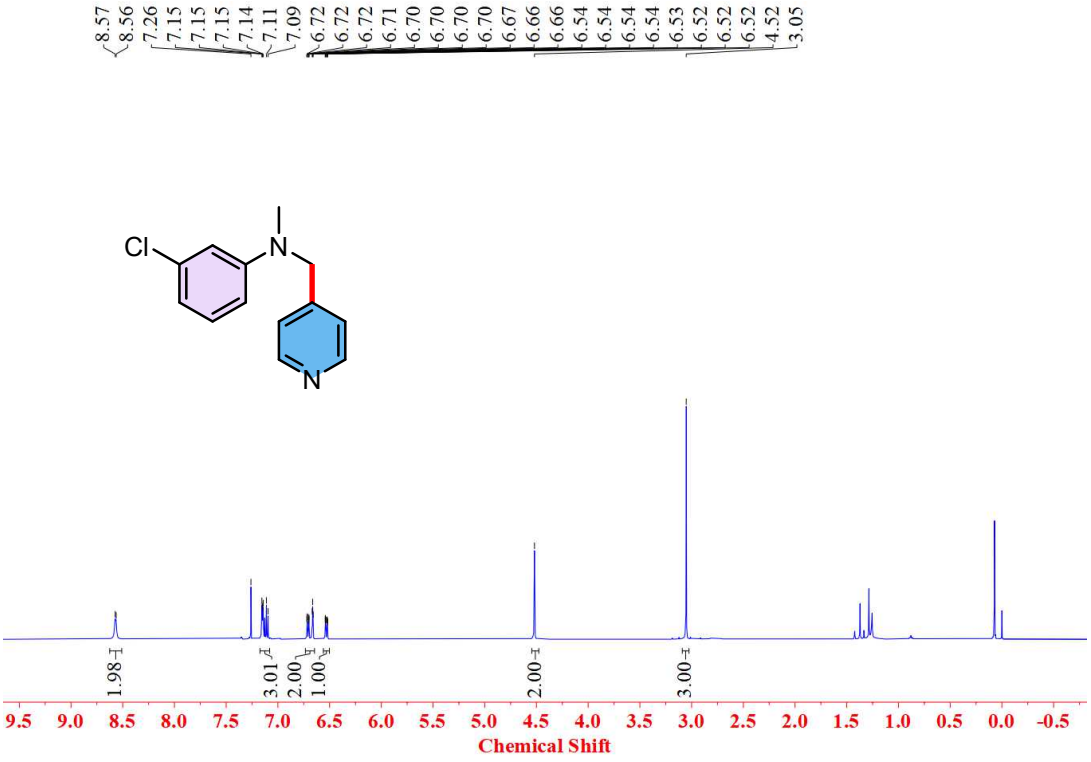

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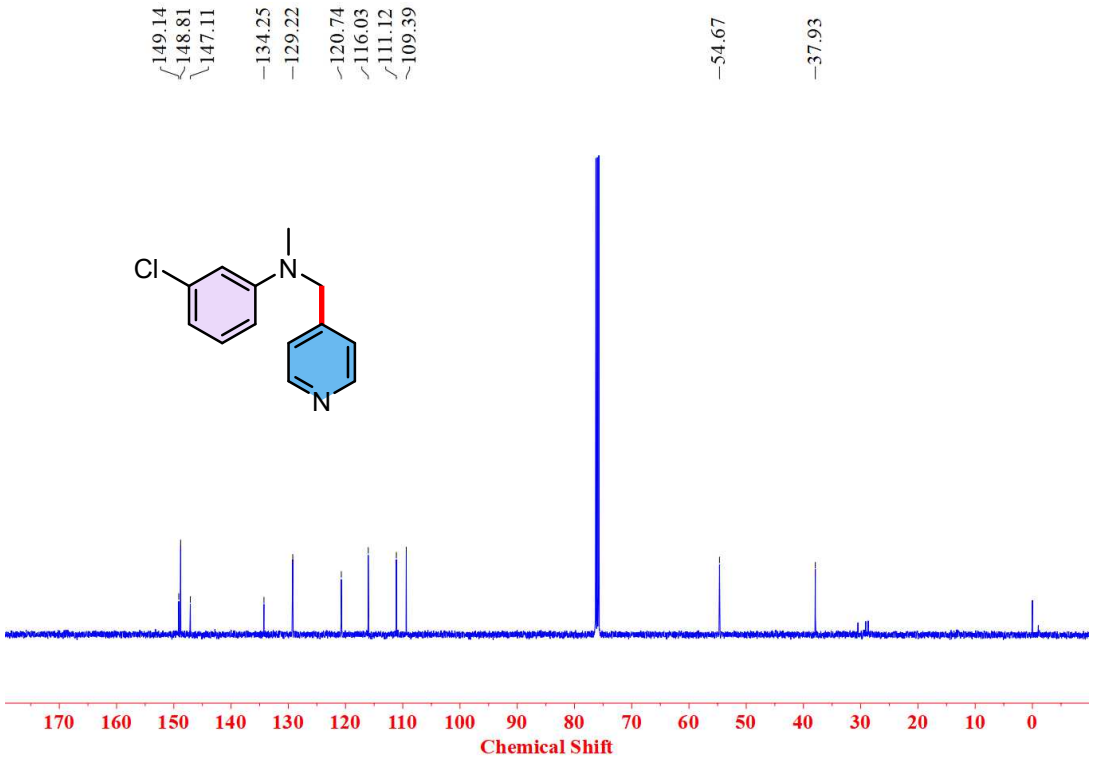

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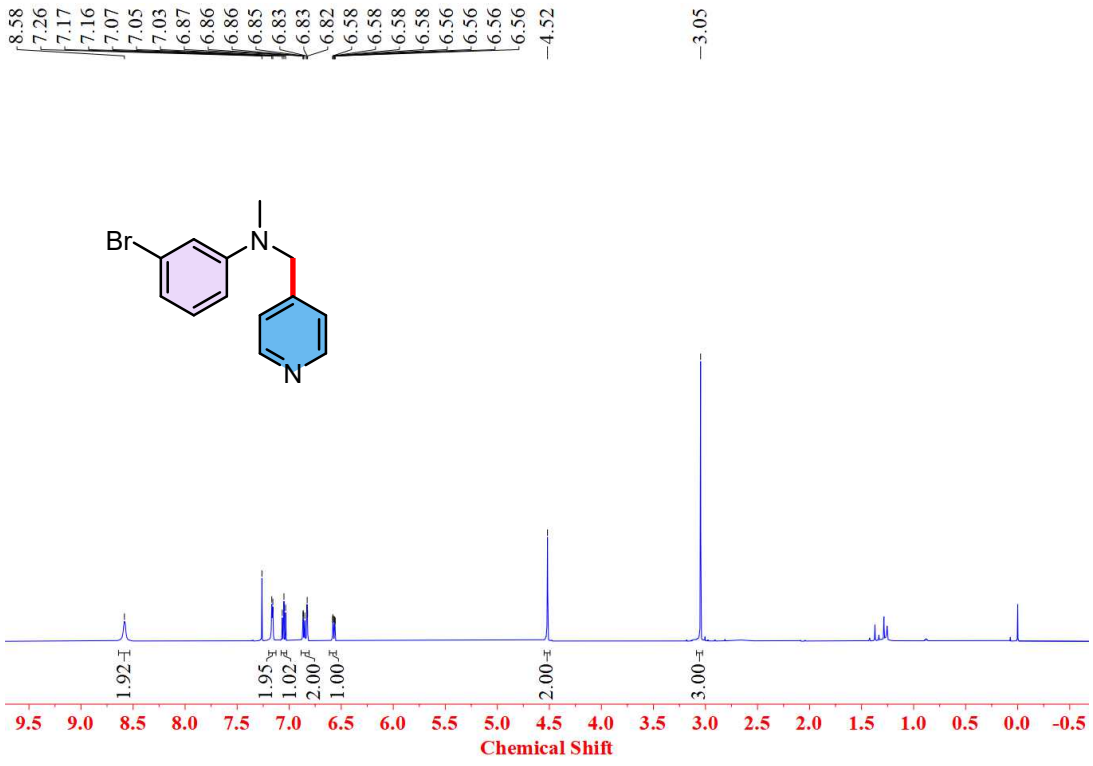

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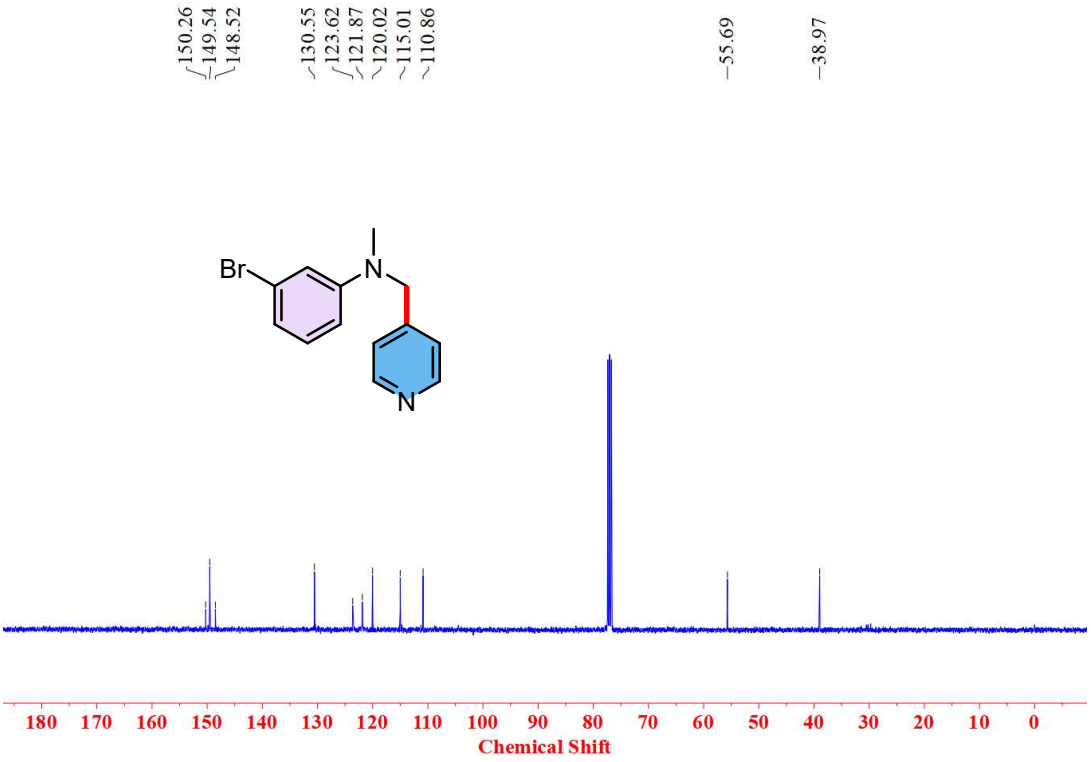

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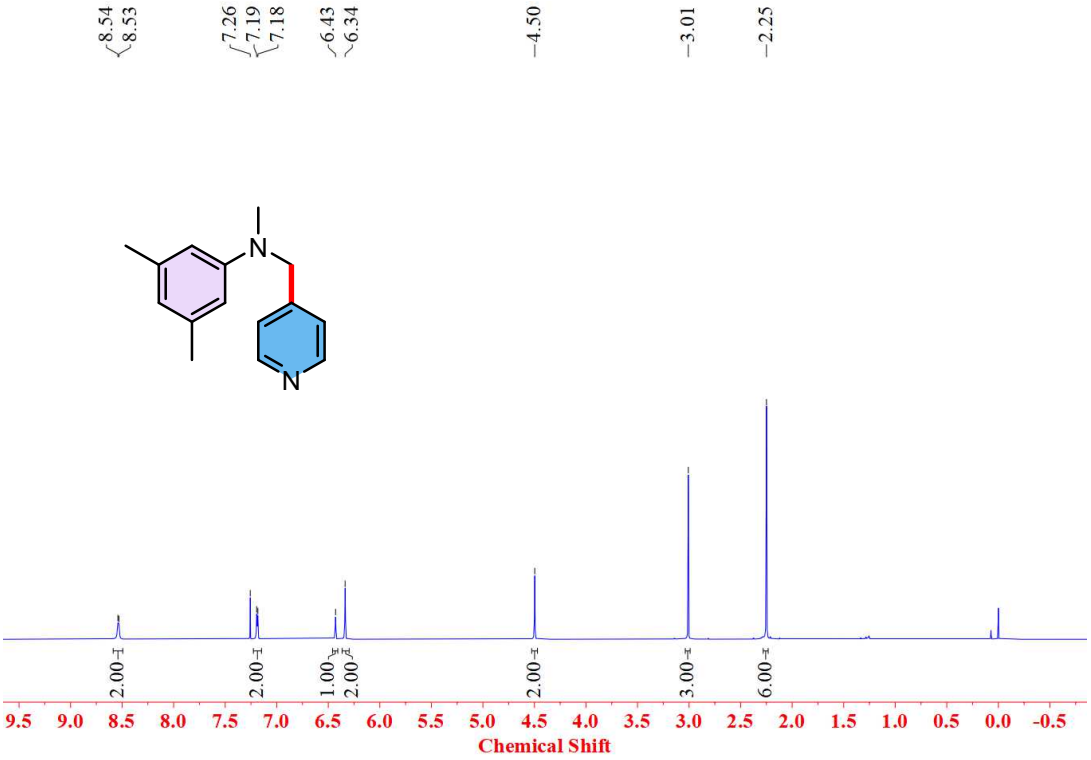

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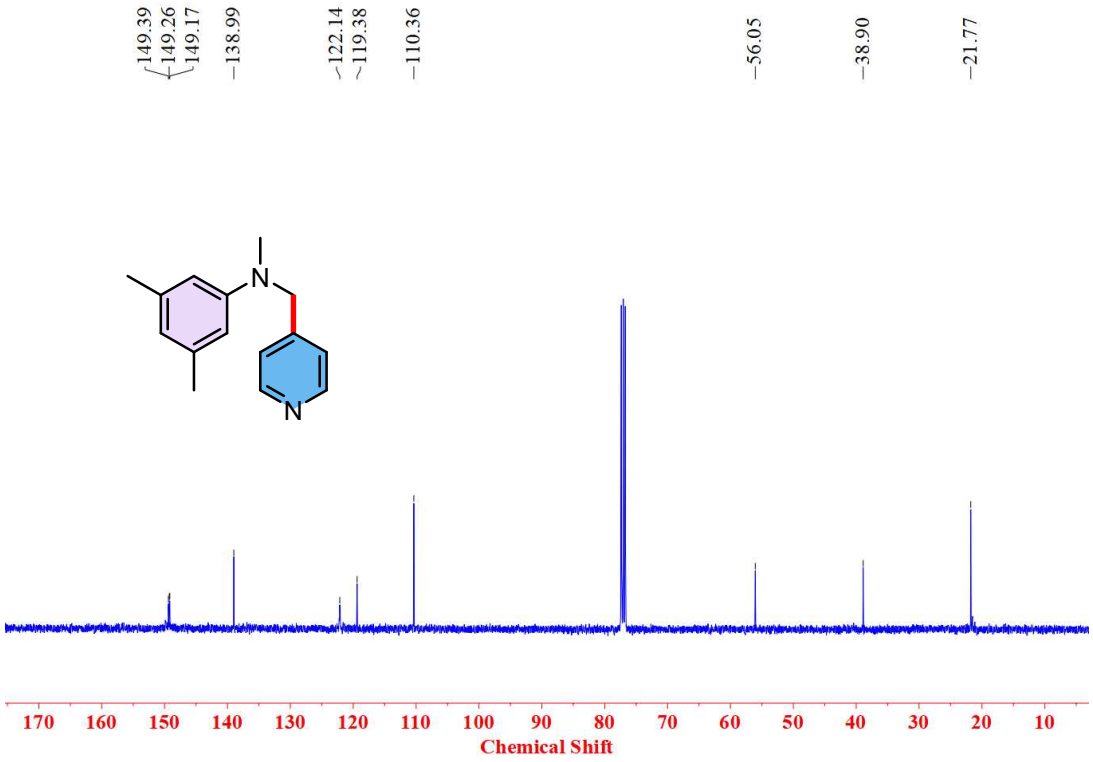

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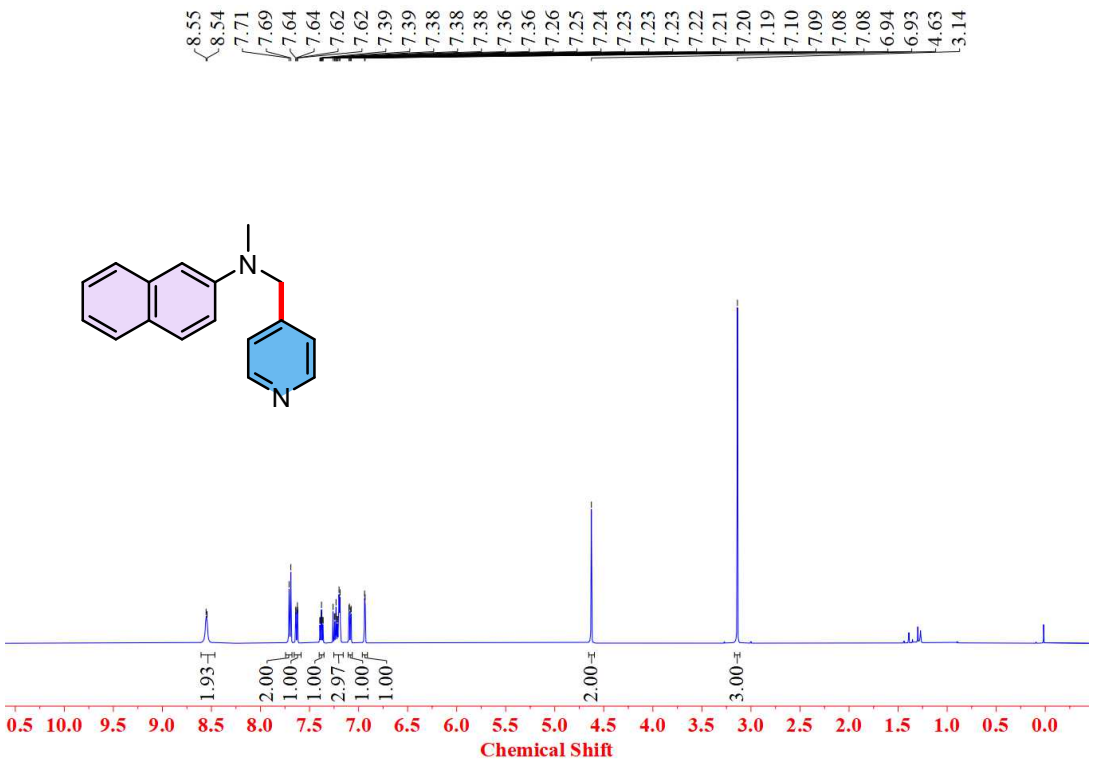

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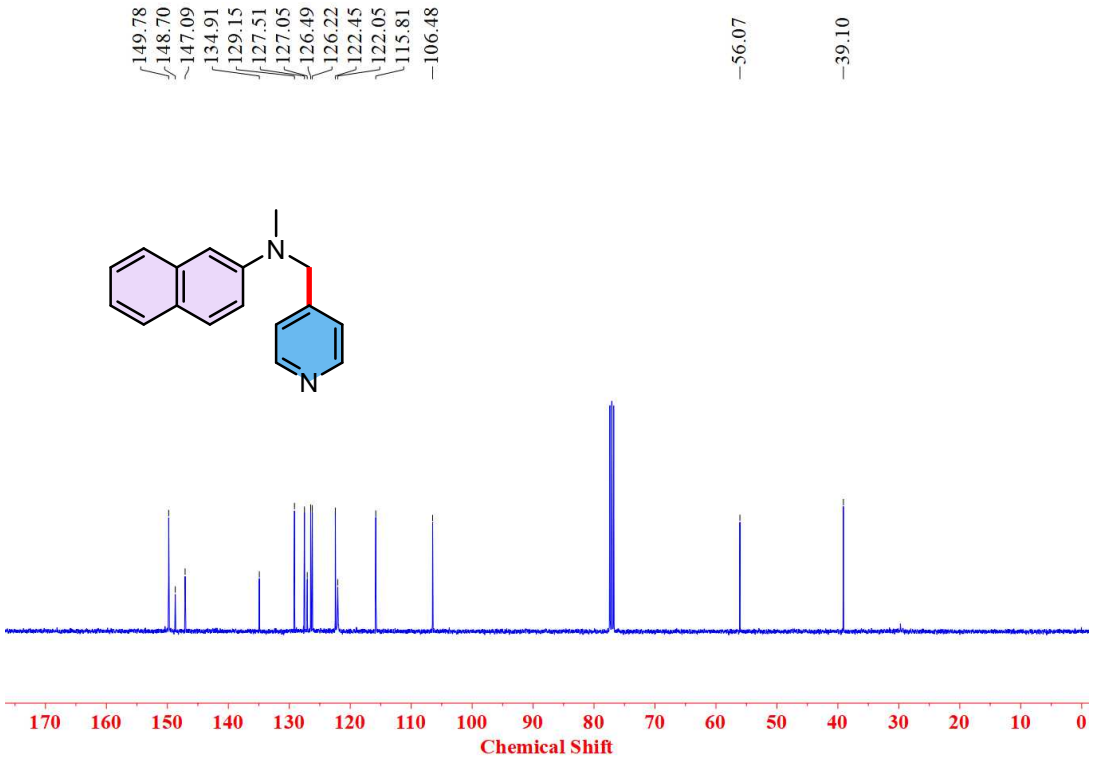

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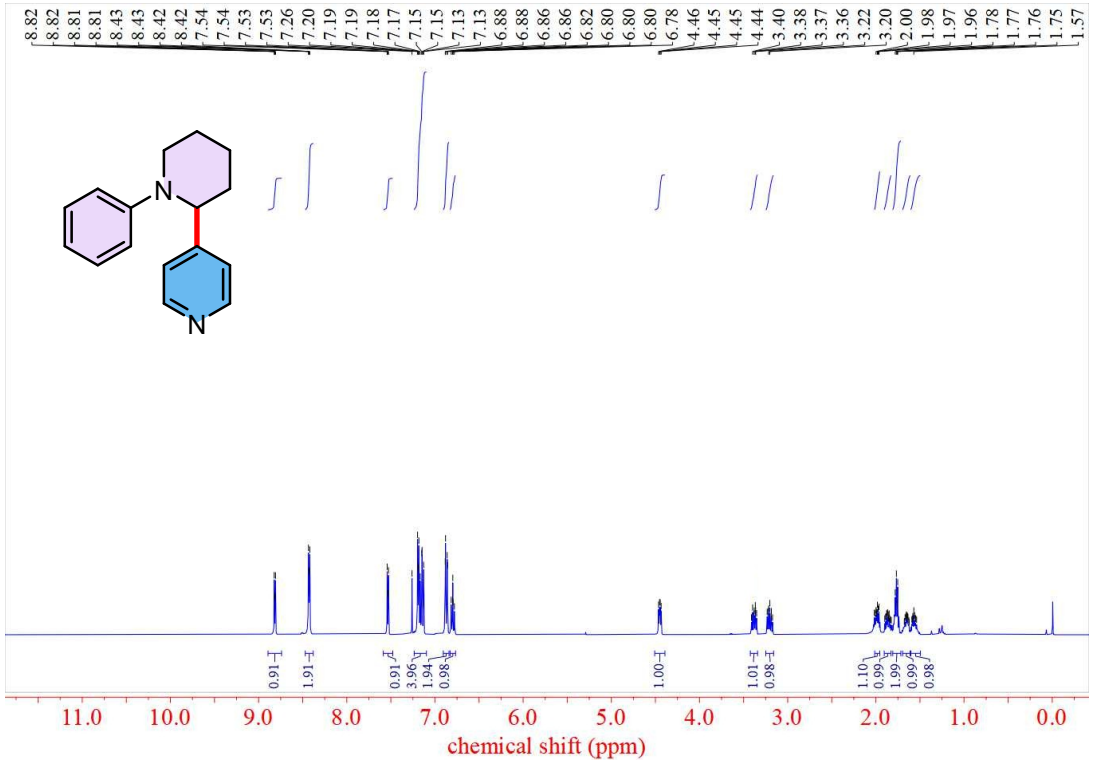

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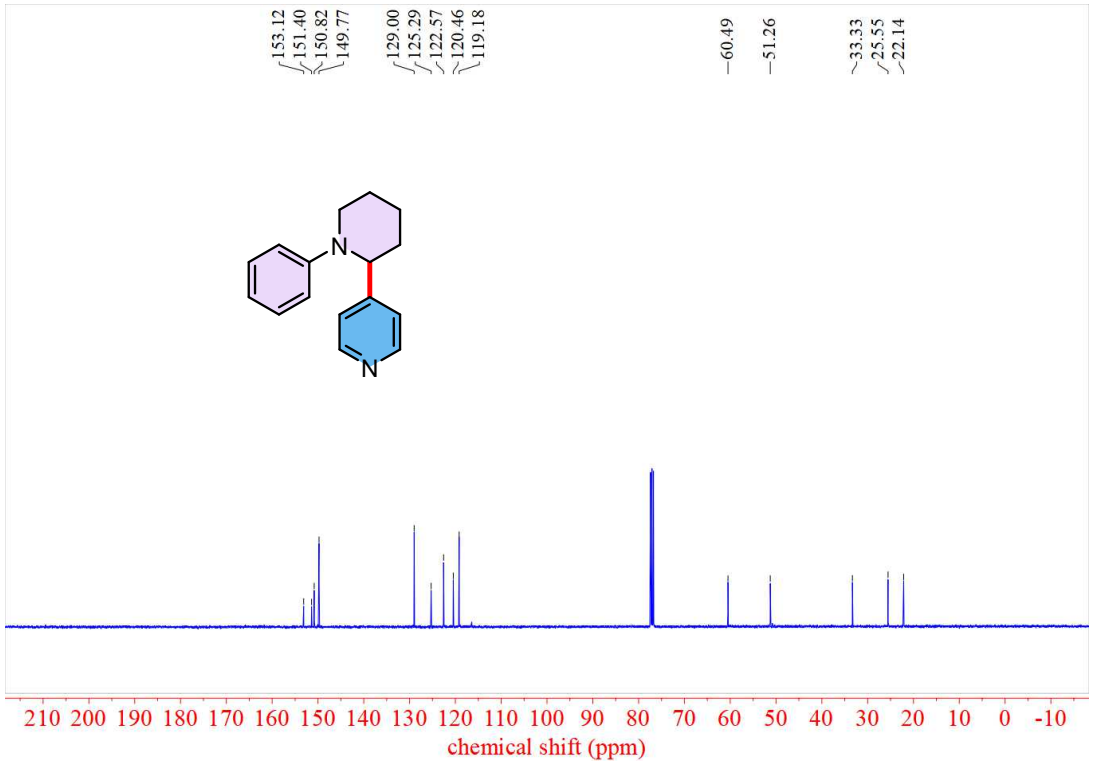

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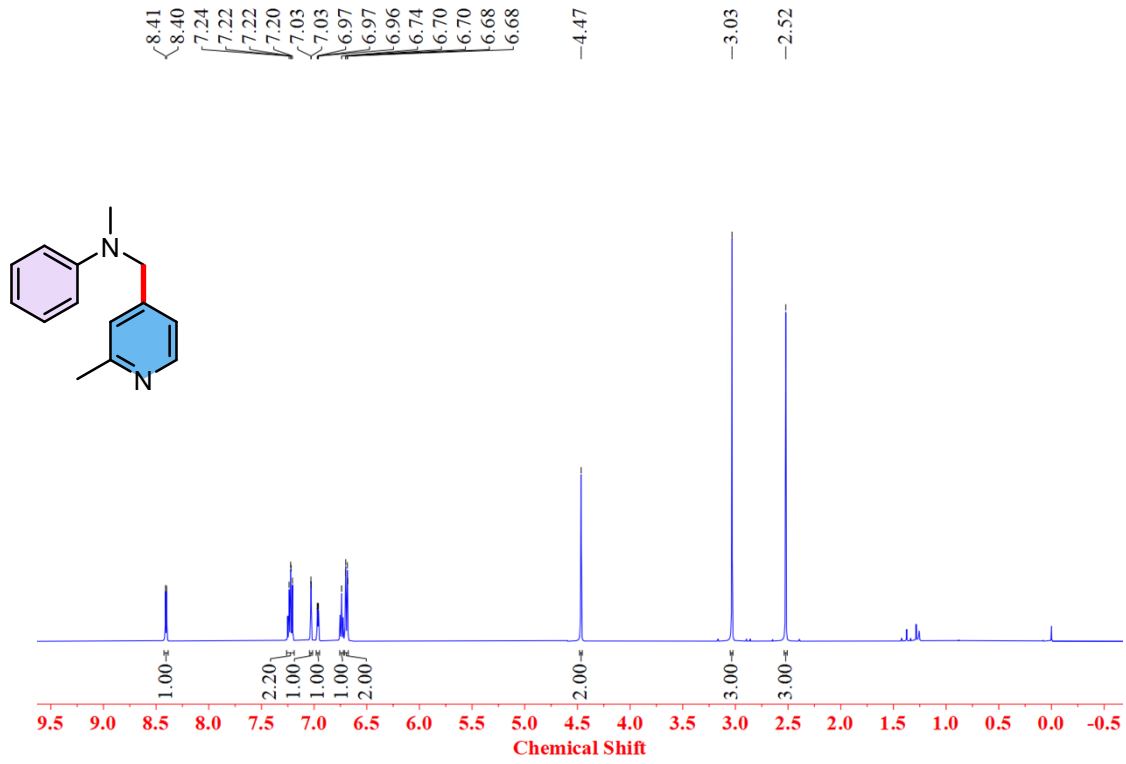

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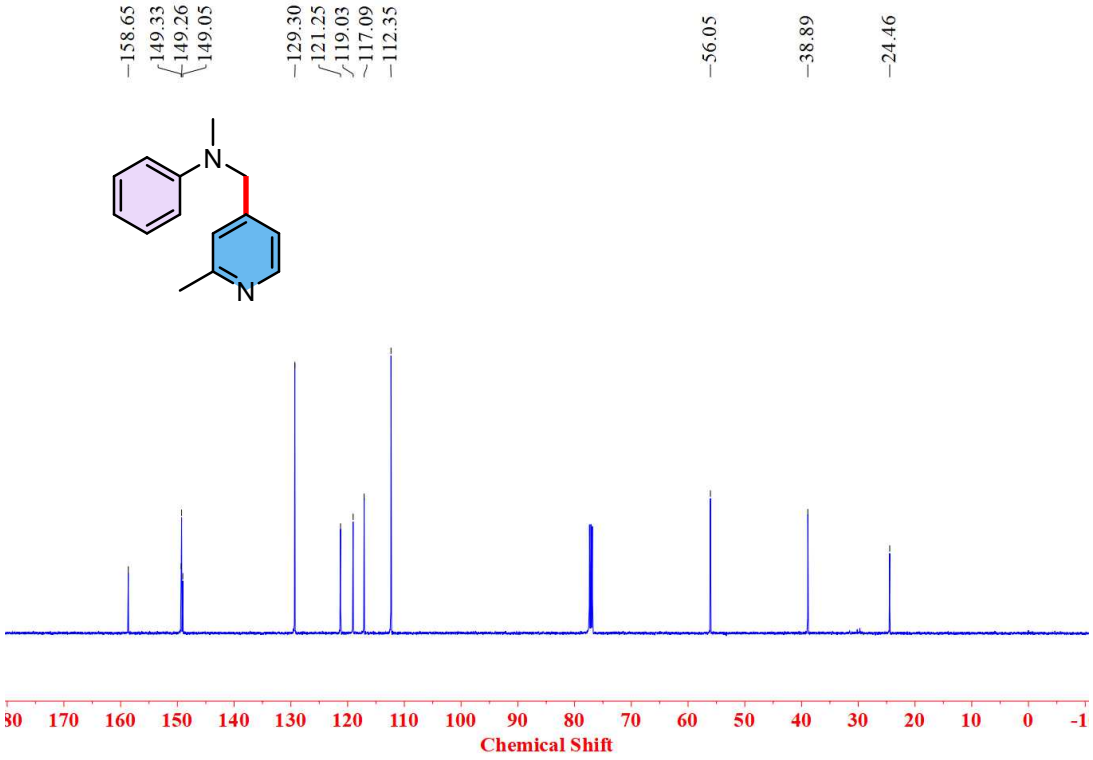

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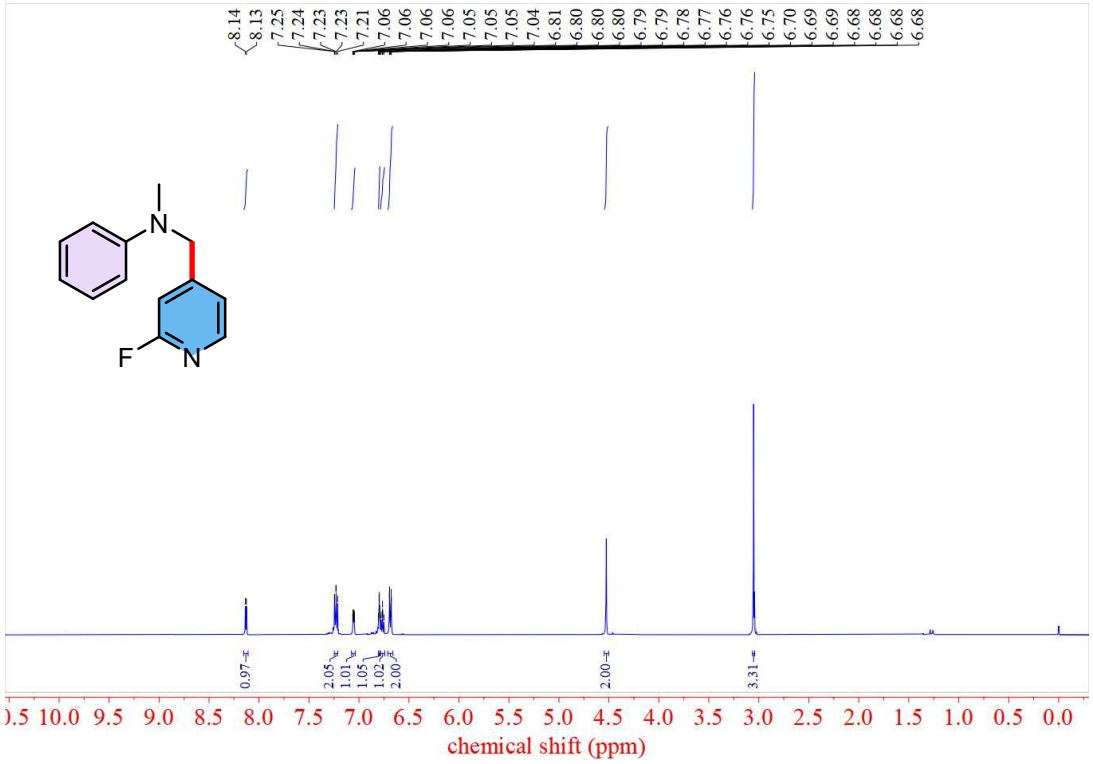
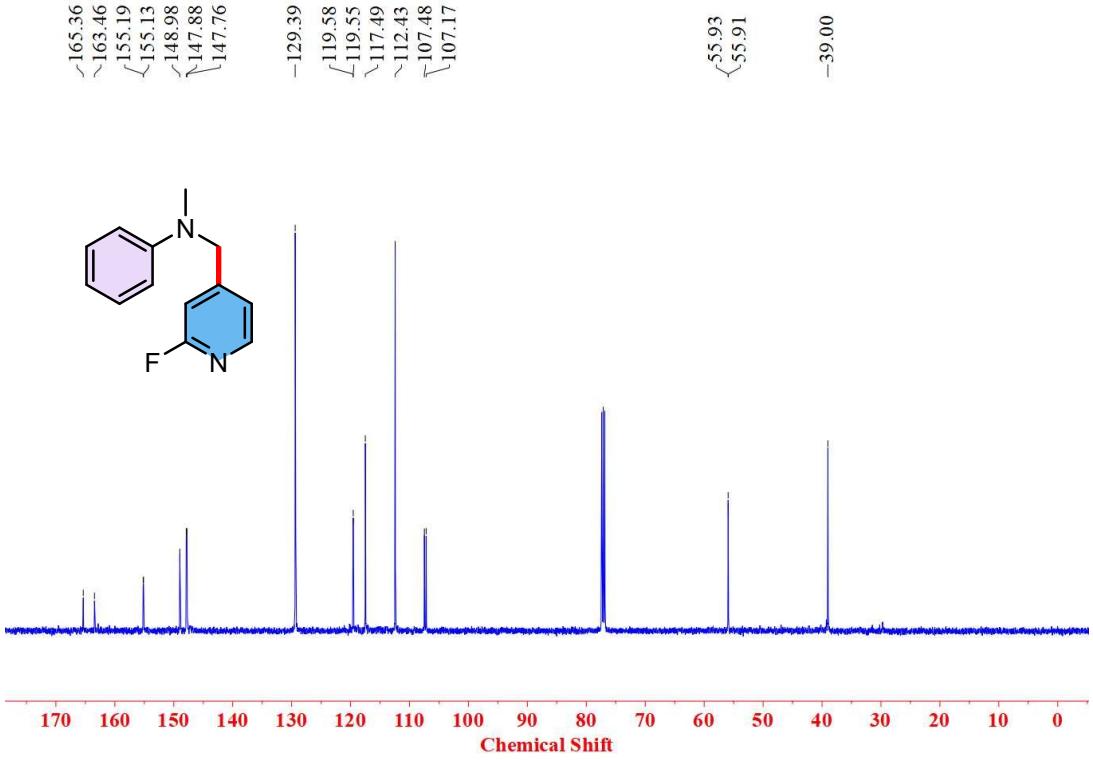


4l ^{13}C NMR



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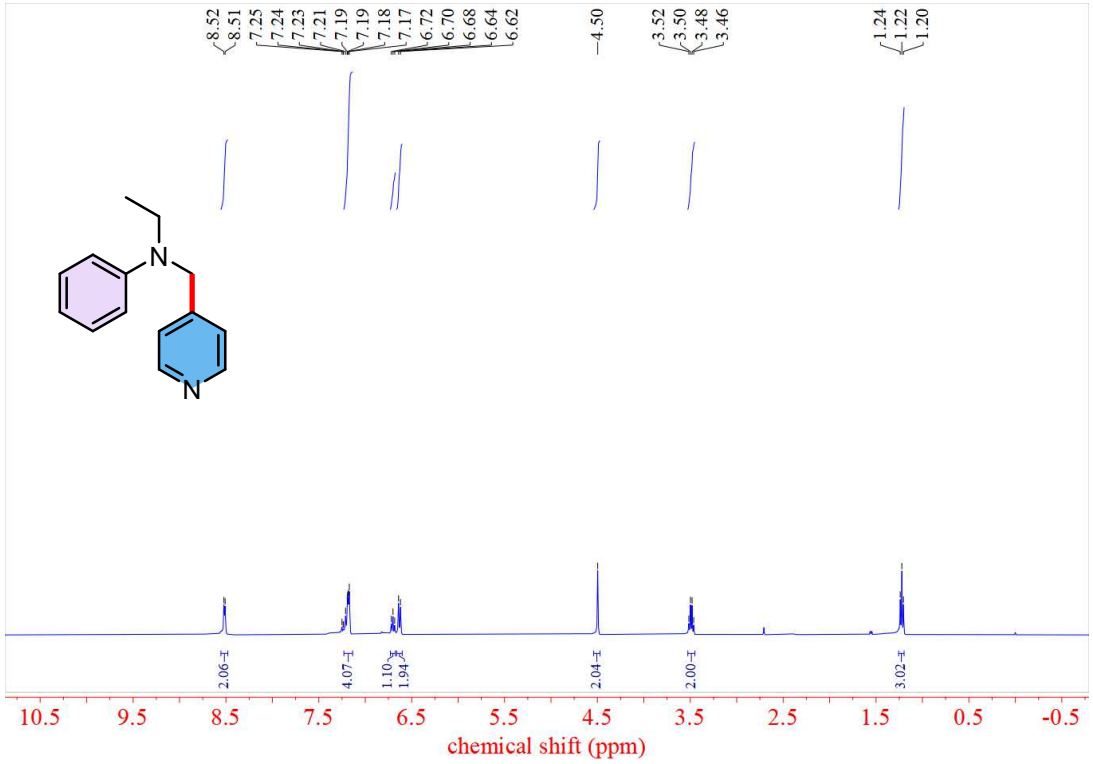
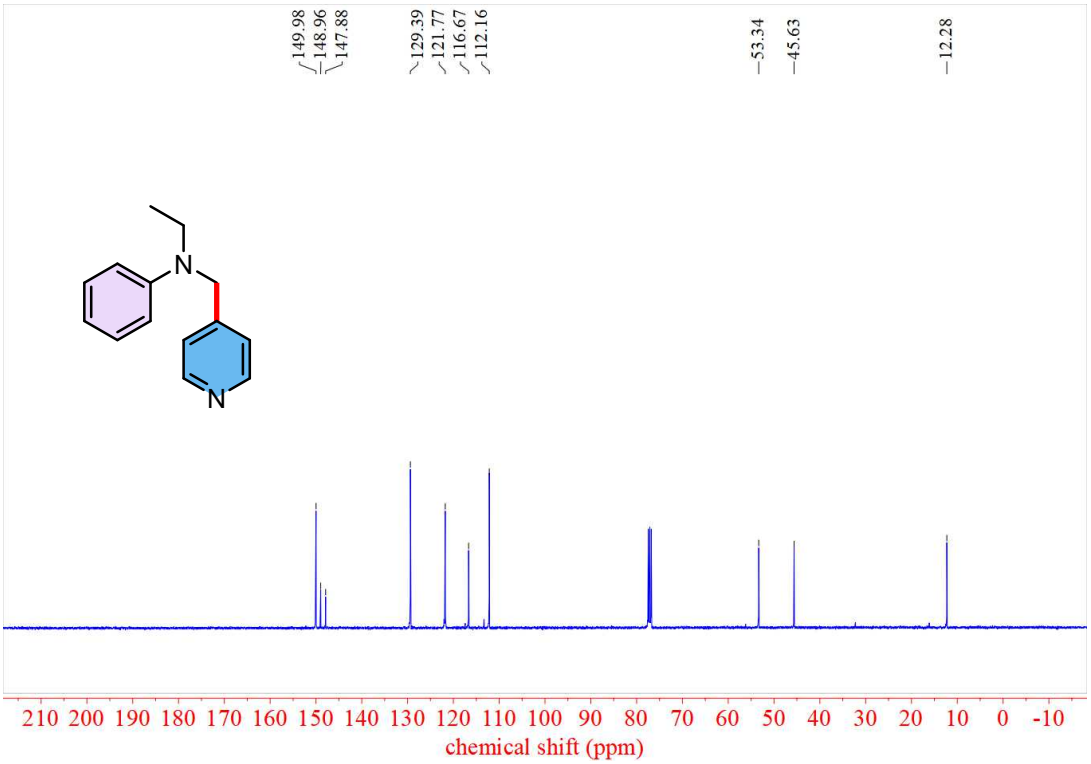


4m ^{13}C NMR



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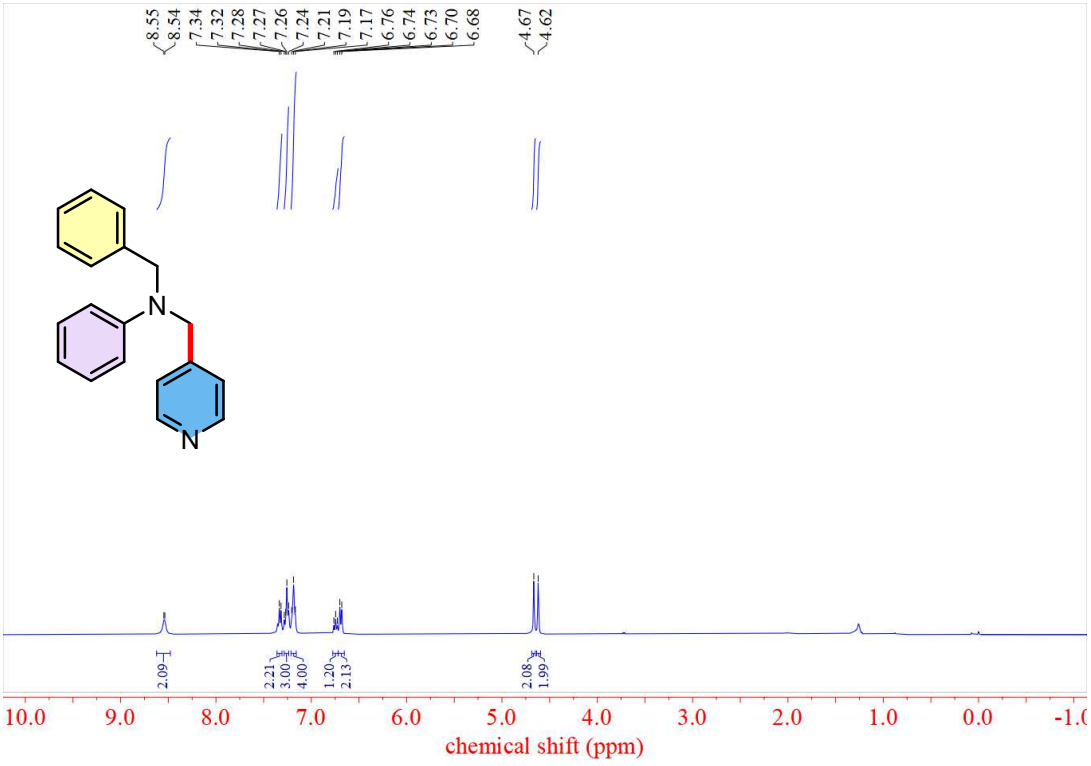

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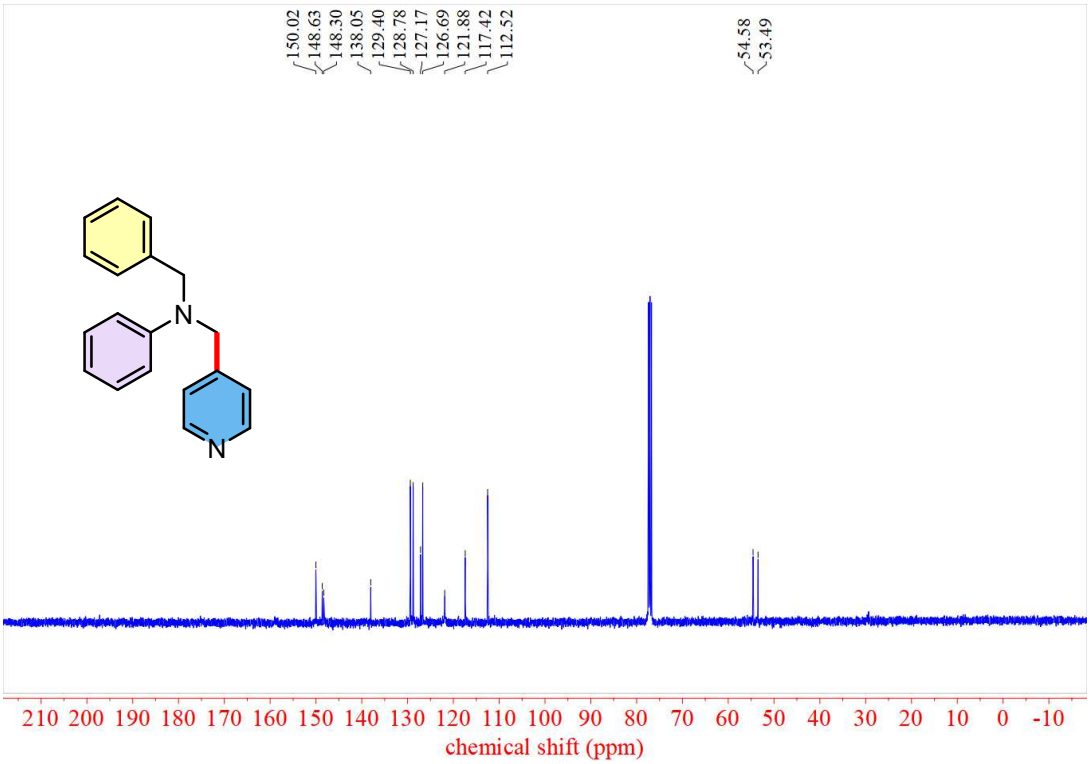
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N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
chemical shift (ppm)