Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

A Pincer Ligand Enabled Ruthenium Catalyzed Highly Selective N-Monomethylation of Nitroarenes with Methanol as the C1 Source

Shaochun Zhang,[a] Jessica Juweriah Ibrahim,[a,b] and Yong Yang[a]*

[a]Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, PR China

[b]University of Chinese Academy of Sciences, Beijing 100049, PR China

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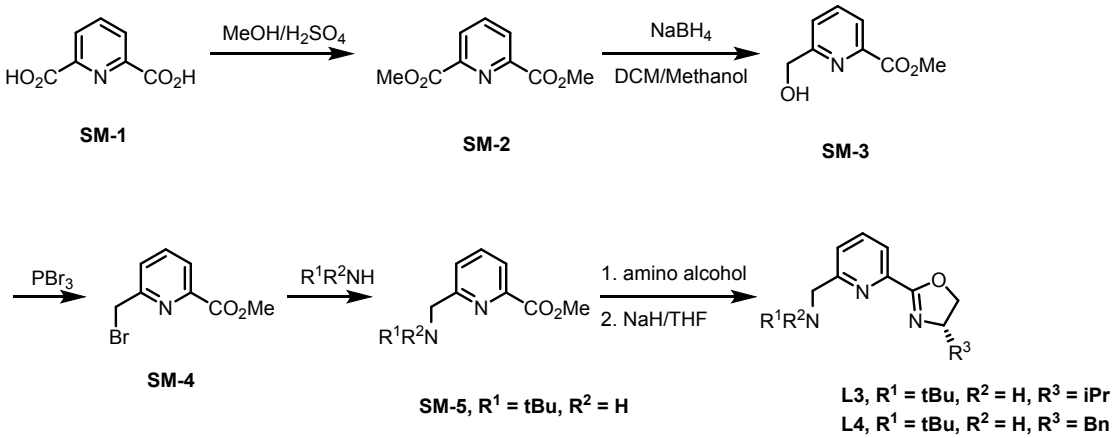
Corresponding author: Y. Yang (*yangyong@qibebt.ac.cn*)

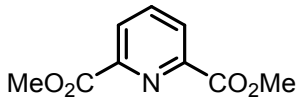
1. General Considerations

Unless otherwise noted, all reagents were purchased commercially from Sigma-Aldrich, J&K, Aladdin or Alfa Aesar and used as received without further purification. All operations were carried out in nitrogen atmosphere using glovebox and Schlenk techniques unless otherwise specified. Anhydrous tetrahydrofuran (THF), ether, 1,4-dioxane and toluene were used freshly distilled by sodium and benzophenone. Anhydrous dichloromethane and hexane were purchased from J&K as sure-sealed solvents and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as the visualizing agent. Column chromatography was carried out on silica gel (200-300 mesh) by elution with appropriate solvents. Gas chromatography analysis was performed on an Agilent HP-7890 instrument with a flame ionization detector (FID) and an HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thicknesses) using nitrogen as the carrier gas. Gas chromatography-mass spectrometry analysis was carried out on a SHIMADZU AOC-20i instrument with HP-5MS capillary column using helium carrier gas. NMR spectra were from a Bruker DRX-400, or DRX-600, instrument and calibrated using residual non-deuterated solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm) as an internal reference. Data for ^1H NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constan (s) in Hz, integration). Data for ^{13}C NMR were reported in terms of chemical shift (δ, ppm). High resolution mass spectra (HRMS) were recorded on an Agilent 6210 Series 1969A ESI-TOF (time of flight) mass spectrometer using ESI (electrospray ionization).

2. Ligand synthesis

The synthesis of **L1 (API)**, **L2 (DEt-API)** ligands were reported in our previously results[1], and the ligand **L5 (PyBox-Me)** and **L6 (PyBox-H)** were synthesized according to literature[2], the **APO** ligands were synthesized as follow:

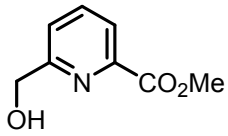




dimethyl pyridine-2,6-dicarboxylate (sm-2)[3]

Pyridine-2,6-dicarboxylic acid (**sm-1**, 20g, 0.12 mol) and methanol 100 mL was added in a round bottle, then heated the mixture to reflux for 24 hours. Allow the reaction solution to room temperature, neutralized with saturated sodium carbonate, extracted with DCM. The organic phase was dried with anhydrous Na_2SO_4, then evaporated under reduced pressure to give the product as white solid (20.4 g, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 7.8 Hz, 2H), 8.01 (t, J = 7.8 Hz, 1H), 4.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.06, 148.22, 138.39, 128.05, 53.21.

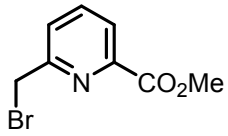


methyl 6-(hydroxymethyl)picolinate (sm-3)[4]

Cooled the mixture of dimethyl pyridine-2,6-dicarboxylate (**sm-2**, 10 g, 51.0 mmol), methanol 140 mL and dichloromethane 60 mL to 0 °C, $NaBH_4$ (1.95 g, 51.0 mmol) was added in three portions during half an hour, then kept the reaction stirring for 2

additional hours, removed the solvent under reduced pressure, the residue was re-dissolved in DCM, washed with brine twice, dried with anhydrous Na_2SO_4, then evaporated the solvent and purified the residue by gel column chromatography (PE/EA = 2/3 to 1/2) to give the product as white solid (5.90 g, 69%).

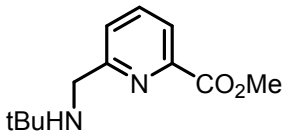
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.83 (t, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.45, 160.41, 146.81, 137.72, 124.05, 123.73, 64.56, 52.83.



methyl 6-(bromomethyl)picolinate (sm-4)[4]

Methyl 6-(hydroxymethyl)picolinate (**sm-3**, 2.0 g, 12 mmol) was dissolved in 100 mL chloroform, after the solution was cooled to 0 to 4 °C, then phosphorus tribromide (1.14 mL, 12 mmol) was added dropwise during 10 min. The reaction mixture was stirred for additional 4 h at room temperature and then neutralized with aqueous saturated K_2CO_3. After extracted the mixture with CH_2Cl_2 (100 mL × 3), the organic phase was washed with brine, dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure, leading to pure compound **sm-4** as white solid (2.51 g, 91%).

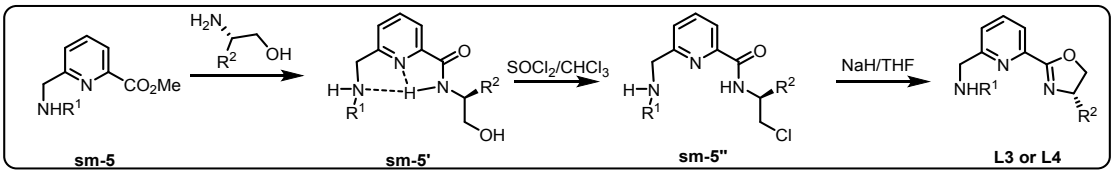
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.84 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 4.62 (s, 2H), 3.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.26, 157.34, 147.55, 138.11, 127.04, 124.37, 53.01, 33.08.

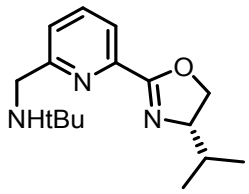


methyl 6-((tert-butylamino)methyl)picolinate (sm-5a)

The bromide compound **sm-4** (5.2 g, 22.6 mmol) was added in a round bottle, then 12 mL tert-butylamine (113.2 mmol, 5 equiv.) was added and stirred for 10 min at room temperature, CH_2Cl_2 80 mL was added to the mixture and the organic phase was washed with brine, dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure, leading to pure compound **sm-5a** as colorless oil (4.3 g, 86%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 4.00 (s, 2H), 3.95 (s, 3H), 3.43 (bs, 1H), 1.19 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.72, 160.66, 147.03, 137.43, 125.88, 123.44, 52.77, 51.54, 48.19, 28.71.



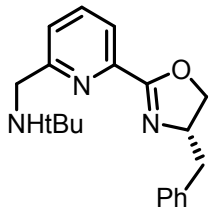


***t*Bu-APO-iPr Ligand (L3).**

Compound **sm-5** (1.334 g, 6.0 mmol) and L-Valinol (742 mg, 7.2 mmol) was added in a 10 mL Schlenk tube, heated to 120 °C (oil bath) for 2.5 h. After cooled to room temperature, the reaction mixture was kept in high vacuum overnight to remove excess L-Valinol leading the compound **sm-5a'** as yellow oil. Without further purification, the compound **sm-5a'** was dissolved in 40 mL chloroform, after added thionyl chloride (2.18 mL, 30.0mmol), the reaction mixture was heated reflux for 2 h. The solvent was removed under reduced pressure, then the residue was re-dissolved in dichloromethane, removed the solvent under reduced pressure and dried under high vacuum overnight to afford **5a''** as yellow solid. The chloride compound **5a''** was dissolved in 20mL THF, the solution was added in a suspension of NaH (60%, 480 mg, 12.0 mmol)/40 mL THF. Until the starting material was completely consumed, the mixture was passed though celite pad, and the filtrate was collected and evaporated under reduced pressure, then the residue was purified by silica gel column chromatography (CH_2Cl_2/methanol = 20/1 to 5/1) to afford the *t*Bu-APO-iPr (**L3**) as yellow solid 1.36 g in 82% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 4.50 (t, *J* = 9.0 Hz, 1H), 4.21 (t, *J* = 8.3 Hz, 1H), 4.15 (dd, *J* = 8.5,

7.0 Hz, 1H), 4.11 (s, 2H), 1.88 (dq, J = 13.2, 6.5 Hz, 1H), 1.30 (s, 9H), 1.04 (d, J = 6.7 Hz, 3H), 0.94 (d, J = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.60, 145.94, 137.41, 124.49, 122.61, 72.77, 70.85, 47.78, 32.77, 28.28, 19.09, 18.21. HRMS (ESI): Catal. For: $C_{16}H_{26}N_3O^+$ $[M+H]^+$: 276.2070, found: 276.2076.



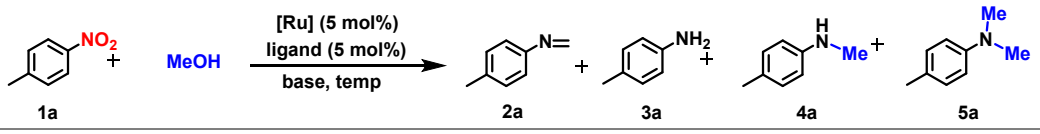
***t*Bu-APO-Bn Ligand (L4).**

The synthesis procedure was according to **L3**, afford the *t*Bu-APO-Bn (**6b**) as yellow solid in 73% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.61 – 7.58 (m, 1H), 7.35 – 7.30 (m, 2H), 7.28 – 7.22 (m, 3H), 4.67 (dt, J = 15.1, 7.7 Hz, 1H), 4.52 (t, J = 9.0 Hz, 1H), 4.35 – 4.20 (m, 3H), 3.11 (dd, J = 13.8, 6.7 Hz, 1H), 2.87 (dd, J = 13.8, 7.8 Hz, 1H), 2.07 (bs. 1H), 1.51 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.01, 152.08, 145.07, 138.51, 137.50, 129.24, 128.61, 126.74, 125.57, 123.47, 72.99, 67.43, 57.50, 45.24, 41.56, 25.91. HRMS (ESI): Catal. For: $C_{20}H_{26}N_3O^+$ $[M+H]^+$: 324.2070, found: 324.2072.

3. Optimization details for N-Monomethylating of Nitroarenes.

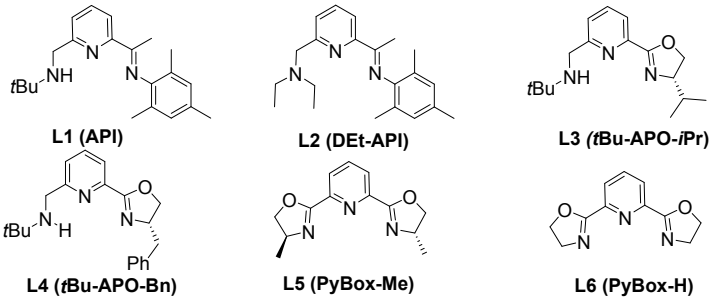
Table S1. Screening of Metal Salts.

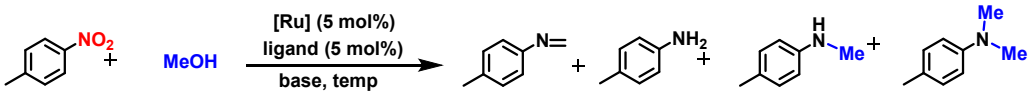


Entry	[Ru] (mol %)	Ligand (mol %)	Base (equiv)	T [°C]	t [h]	Conv. [%]	**2a** [%]	**3a** [%]	**4a** [%]	**5a** [%]
1	$RuH(CO)(PPh_3)_3Cl$ (5)	L1(5)	NaOMe (1.0)	110	10	16.0	0	92.5	7.5	0
2	$RuCl_3.3H_2O$ (5)	L1(5)	NaOMe (1.0)	110	10	11.2	0	55.4	44.6	0
3	**$[RuCl_2(cymene)_2]_2$ (5)**	**L1(5)**	**NaOMe (1.0)**	**110**	**10**	**27.4**	**20.4**	**15.0**	**64.6**	**0**
4	$RuH_2(CO)(PPh_3)_3$ (5)	L1(5)	NaOMe (1.0)	110	10	26.9	0	81.4	15.6	0

Reaction conditions: 1-methyl-4-nitrobenzene (**1a**) (0.2 mmol), NaOMe (0.2 mmol) [Ru] (5 mol%), **L1** (5 mol%) and methanol (2 mL), sealed tube, under nitrogen; conversion and selectivity were detected by GC-FID using mesitylene as an internal standard.

Table S2. Screening of Ligands.



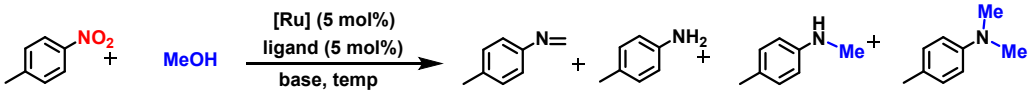


1a 2a 3a 4a 5a

Entry	[Ru] (mol %)	Ligand (mol %)	Base (equiv)	*T* [°C]	t [h]	Conv. [%]	**2a** [%]	**3a** [%]	**4a** [%]	**5a** [%]
1	**$[RuCl_2(cymene)_2]_2$ (5)**	**API (5)**	**NaOMe (1.0)**	**150**	**10**	**100**	**4.1**	**22.8**	**73.1**	**0**
2	$[RuCl_2(cymene)_2]_2$ (5)	*t*Bu-APO-iPr (5)	NaOMe (1.0)	150	10	40.0	7.6	59.4	33.0	0
3	$[RuCl_2(cymene)_2]_2$ (5)	*t*Bu-APO-Bn (5)	NaOMe (1.0)	150	10	26.8	4.8	65.1	30.1	0
4	$[RuCl_2(cymene)_2]_2$ (5)	PyBox-H(5)	NaOMe (1.0)	150	10	12.4	6.7	73.5	19.8	0
5	$[RuCl_2(cymene)_2]_2$ (5)	PyBox-Me(5)	NaOMe (1.0)	150	10	37.6	5.4	48.5	46.1	0
6	$[RuCl_2(cymene)_2]_2$ (5)	DEt-NNN (5)	NaOMe (1.0)	150	10	47.2	14.7	38.4	46.9	0

Reaction conditions: 1-methyl-4-nitrobenzene (**1a**) (0.2 mmol), NaOMe (0.2 mmol) $[RuCl_2(cymene)_2Cl_2]_2$ (2.5 mol%), ligand (5 mol%) and methanol (2 mL), sealed tube, under nitrogen; conversion and selectivity were detected by GC-FID using mesitylene as an internal standard.

Table S3. Screening of the Amount of Base.



1a 2a 3a 4a 5a

Entry	[Ru] (mol %)	Ligand (mol %)	Base (equiv)	*T* [°C]	t [h]	Conv. [%]	**2a** [%]	**3a** [%]	**4a** [%]	**5a** [%]
1	$[RuCl_2(cymene)_2]_2$ (5)	API (5)	Cs2CO3(0.5)	120	24	86	16.9	24.4	58.7	0
2	$[RuCl_2(cymene)_2]_2$ (5)	API (5)	Cs2CO3(1.2)	120	24	100	0	17.0	83.0	0
3	$[RuCl_2(cymene)_2]_2$ (5)	API (5)	Cs2CO3(1.5)	120	24	100	0	13.5	86.5	0
4	**$[RuCl_2(cymene)_2]_2$ (5)**	**API (5)**	**Cs2CO3(1.2)**	**120**	**36**	**100**	**0**	**9.1**	**90.9**	**0**
5	$[RuCl_2(cymene)_2]_2$ (5)	API (5)	Cs2CO3(1.5)	120	36	100	0	9.3	90.7	0

Reaction conditions: [a]*p*-nitrotoluene (0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), **L1** (5 mol %), methanol 2.0 mL. [b]conversion and selectivity determined by GC-FID.

4 Procedure for Synthesis of N-Monomethylated Amines.

In a nitrogen filled oven-dried tube, nitro compound (0.4 mmol), Cs_2CO_3 (0.48 mmol, 1.2 eq), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), ligand (**L1** (**API**), 5 mol %) were added, after methanol 2.0 mL was injected by syringe, the tube was sealed with Teflon screw cap. Then the tube was placed in a preheated oil bath at 120 °C for 36 h. Then the reaction solution was cooled at room temperature, filtered through a small plug of silica and added mesitylene as internal standard for GC analysis. The desired N-monomethylated amines were purified by column chromatography using petroleum ether-ethyl acetate (PE-EA) as eluent.

5 Proceduce for Scope of Alcohols.

In a nitrogen filled oven-dried tube, 4-methyl-nitrobenzene (0.4 mmol), Cs_2CO_3 (0.48 mmol, 1.2 eq), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), ligand (**L1** (**API**), 5 mol %) were added, after alcohol 2.0 mL was injected by syringe (for cyclohexanol, using cyclohexanol-toluene mixture as solvent (2 mL/2 mL); for (4-methoxyphenyl)methanol, using toluene (2 mL) as solvent), the tube was sealed with Teflon screw cap. Then the tube was placed in a preheated oil bath at 120 °C for 36 h. Then the reaction solution was cooled at room temperature, filtered through a small plug of silica and added mesitylene as internal standard for GC analysis. The desired N-alkylated amines were purified by column chromatography using petroleum ether-ethyl acetate (PE-EA) as eluent.

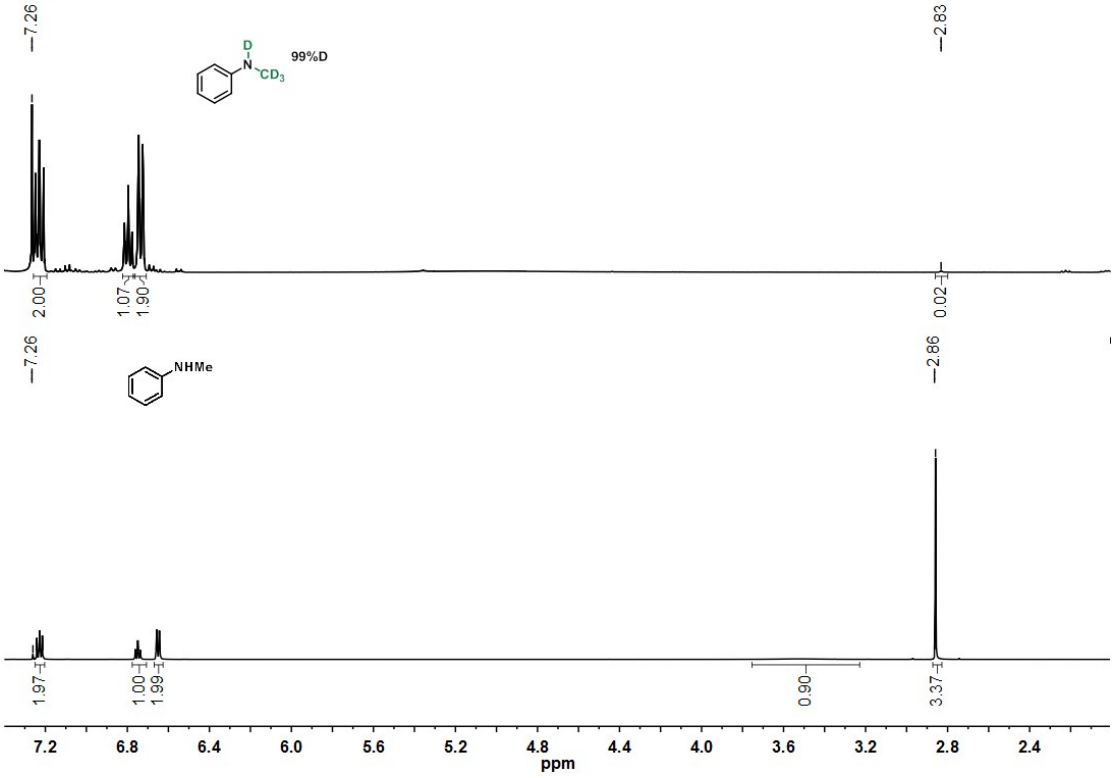
6 Deuterium-labeling Experiment and Control Experiments.

A Deutrium-labeling Experiment.

In a nitrogen filled oven-dried tube, nitrobenzene (0.4 mmol), Cs_2CO_3 (0.48 mmol, 1.2 eq), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), ligand (**L1** (**API**), 5 mol %) were added, after CD_3OD 2.0 mL was injected by syringe, the tube was sealed with Teflon screw cap. Then the tube was placed in a preheated oil bath at 120 °C for 36 h. After the reaction completed, the reaction solution was cooled at room temperature,

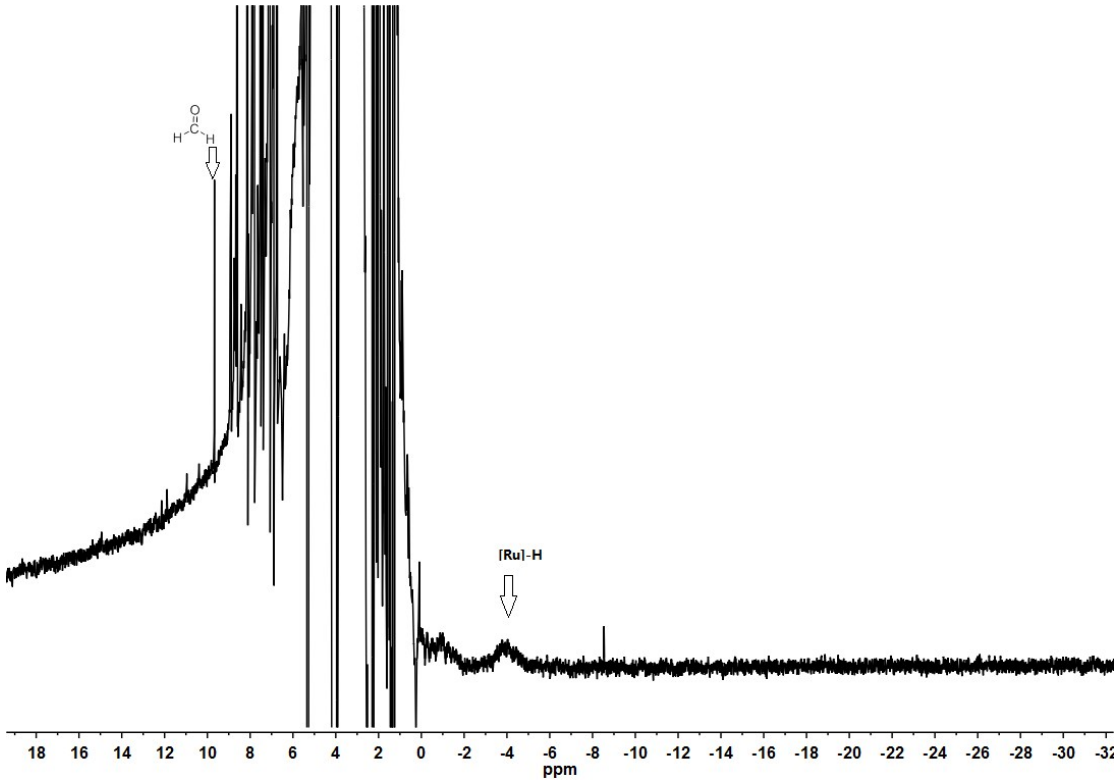
filtered through a small plug of silica and added mesitylene as internal standard for GC analysis (conversion > 99%; selectivity **[D]-4a/[D]-3a** = 92/8).

The desired N-monomethylated amines **[D]-4a** were purified by column chromatography using petroleum ether-ethyl acetate (PE-EA = 20/1) as eluent.



B Characterization of [Ru]-H Signal.

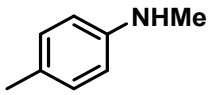
In a J-Young NMR tube, $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg) and **L1** (6.5 mg) NaOMe (1.1 mg) was dissolved in 0.6 mL methanol. After the solution was heated to 70 °C for 2 h, a capillary tube filled with CD_2Cl_2 was put in NMR tube using as an internal standard for ^1H NMR detection.



^{1}H NMR (600 MHz, CD_2Cl_2)

Figure S1. In-situ generation of Rh-H species

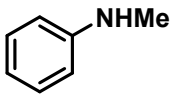
7 Characterization of N-Monomethylated Amines.



N,4-dimethylaniline (4a)[5].

The reaction was carried out according to the general procedure with 1-methyl-4-nitrobenzene (**1a**). Purification by column chromatography on silica gel (PE/EA = 20/1) affords **4a** as colorless oil (41 mg, 85%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (d, J = 8.1 Hz, 2H), 6.64 – 6.56 (m, 2H), 3.44 (bs, 1H), 2.86 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.20, 129.76, 126.54, 112.71, 31.16, 20.45.

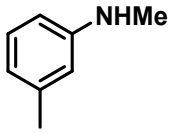


N-methylaniline (4b)[6].

The reaction was carried out according to the general procedure with nitrobenzene (**1b**) at 135 ^{o}C. Purification by column chromatography on silica gel (PE/EA = 20/1) affords

4b as colorless oil (34 mg, 79%).

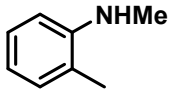
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 6.75 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.65 (dd, *J* = 8.6, 1.0 Hz, 2H), 3.52 (bs, 1H), 2.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.34, 129.25, 117.34, 112.50, 30.79.



N,3-dimethylaniline (4c)[7]

The reaction was carried out according to the general procedure with 1-methyl-3-nitrobenzene (**1c**). Purification by column chromatography on silica gel (PE/EA = 20/1) affords **4c** as colorless oil (40 mg, 83%).

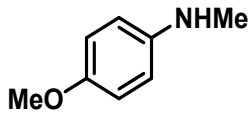
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 7.5 Hz, 1H), 6.49 – 6.45 (m, 2H), 3.60 (bs, 1H), 2.85 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.40, 139.02, 129.13, 118.31, 113.27, 109.73, 30.85, 21.68.



N,2-dimethylaniline (4d)[6]

The reaction was carried out according to the general procedure with 1-methyl-2-nitrobenzene (**1d**) at 135 °C. Purification by column chromatography on silica gel (PE/EA = 20/1) affords **4d** as yellow oil (39.5 mg, 82%).

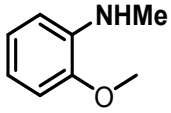
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.57 (t, *J* = 7.8 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 3.43 (bs, 1H), 2.77 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.33, 130.02, 127.31, 122.02, 116.98, 109.26, 30.88, 17.49.



4-methoxy-N-methylaniline (4e)[7]

The reaction was carried out according to the general procedure with 1-methoxy-4-nitrobenzene (**1e**). Purification by column chromatography on silica gel (PE/EA = 10/1) affords **4e** as yellow oil (48.3 mg, 88%).

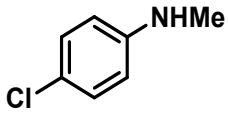
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H), 3.39 (bs, 1H), 2.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.38, 143.24, 114.94, 114.01, 55.87, 31.86.



2-methoxy-N-methylaniline (4f)[8].

The reaction was carried out according to the general procedure with 1-methoxy-2-nitrobenzene (**1f**) at 135 °C. Purification by column chromatography on silica gel (PE/EA = 10/1) affords **4f** as colorless oil (35.7 mg, 65%).

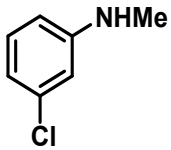
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (ddd, *J* = 7.6, 6.1, 1.4 Hz, 1H), 6.78 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.69 (td, *J* = 7.7, 1.5 Hz, 1H), 6.63 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.40 (bs, 1H), 3.85 (s, 3H), 2.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.99, 139.20, 121.37, 116.52, 109.57, 109.30, 55.43, 30.48.



4-chloro-N-methylaniline (4g)[5]

The reaction was carried out according to the general procedure with 1-chloro-4-nitrobenzene (**1g**). Purification by column chromatography on silica gel (PE/EA = 10/1) affords **4g** as yellow oil (39.6 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 3.73 (bs, 1H), 2.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.79, 129.03, 121.90, 113.54, 30.88.

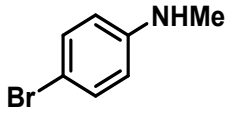


3-chloro-N-methylaniline (4h)[5]

The reaction was carried out according to the general procedure with 1-chloro-3-nitrobenzene (**1h**). Purification by column chromatography on silica gel (PE/EA = 10/1) affords **4h** as yellow oil (39.4 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 8.0 Hz, 1H), 6.71 – 6.67 (m, 1H), 6.59 (t, *J*

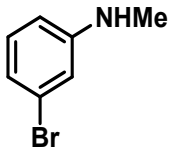
= 2.1 Hz, 1H), 6.49 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.80 (bs, 1H), 2.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.39, 135.05, 130.16, 117.08, 111.96, 110.92, 30.58.



4-bromo-N-methylaniline (4i)[5]

The reaction was carried out according to the general procedure with 1-bromo-4-nitrobenzene (**1i**). Purification by column chromatography on silica gel (PE/EA = 15/1) affords **4i** as yellow oil (42.3 mg, 57%).

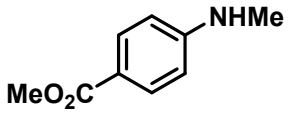
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 6.53 – 6.45 (m, 2H), 3.91 (bs, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.03, 131.91, 114.15, 109.10, 30.86.



3-bromo-N-methylaniline (4j)[9]

The reaction was carried out according to the general procedure with 1-bromo-3-nitrobenzene (**1j**). Purification by column chromatography on silica gel (PE/EA = 15/1) affords **4j** as yellow oil (38.0 mg, 51%).

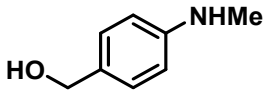
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (t, *J* = 8.0 Hz, 1H), 6.82 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.74 (t, *J* = 2.0 Hz, 1H), 6.52 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.80 (bs, 1H), 2.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.53, 130.45, 123.33, 119.98, 114.85, 111.31, 30.57.



methyl 4-(methylamino)benzoate (4k)[6]

The reaction was carried out according to the general procedure with methyl 4-nitrobenzoate (**1k**). Purification by column chromatography on silica gel (PE/EA = 5/1) affords **4k** as white solid (36.3 mg, 55%).

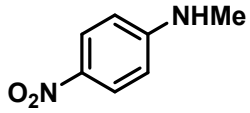
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 4.18 (bs, 1H), 3.85 (s, 2H), 2.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.42, 152.91, 131.55, 118.27, 111.12, 51.55, 30.19.



(4-(methylamino)phenyl)methanol (4l)[10][11]

The reaction was carried out according to the general procedure with (4-nitrophenyl)methanol (**1l**). Purification by column chromatography on silica gel (PE/EA = 2/1 to 1/1) affords **4l** as brown oil (40.0 mg, 73%).

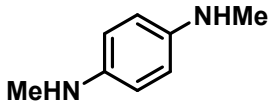
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 4.55 (s, 2H), 2.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.02, 129.73, 128.85, 112.49, 65.47, 30.84.



N-methyl-4-nitroaniline (4m')[7]

The reaction was carried out according to the general procedure with 4-nitroaniline (**1m**). Purification by column chromatography on silica gel (PE/EA = 4/1) affords N-methyl-4-nitroaniline (**4m'**) as yellow solid (38.4 mg, 63%).

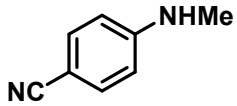
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.2 Hz, 2H), 6.53 (d, *J* = 9.2 Hz, 2H), 4.62 (bs, 1H), 2.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.17, 138.01, 126.42, 110.77, 30.19.



***N*^{1},*N*^{4}-dimethylbenzene-1,4-diamine (4m).**

The reaction was carried out according to the general procedure with 4-nitroaniline (**1m**) using 10 mol% [Ru] and 10 mol% API Ligand. Purification by column chromatography on silica gel (DCM/Acetone = 8/1) affords *N*^{1},*N*^{4}-dimethylbenzene-1,4-diamine (**4m**) as yellow solid (25.6 mg, 47%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.51 (s, 4H), 2.75 (s, 6H). (added one drop of hydrazine hydrate in NMR tube)



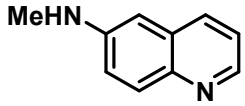
4-(methylamino)benzonitrile (4n)[6][7][9]**.**

The reaction was carried out according to the general procedure with 4-nitrobenzonitrile (**1n**). Purification by column chromatography on silica gel (PE/EA = 4/1) affords 4-methoxybenzonitrile (**4n'**) as white solid (37.5 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 6.97 – 6.93 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.86, 134.00, 119.24, 114.77, 104.00, 55.56.

The reaction carried out under general procedure using Na_2CO_3 instead of Cs_2CO_3. Purification by column chromatography on silica gel (PE/Acetone = 10/1) affords 4-(methylamino)benzonitrile (**4n**) as white solid (24.8 mg, 47%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 2H), 4.30 (bs, 1H), 2.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.18, 133.70, 120.53, 111.87, 98.66, 30.01.



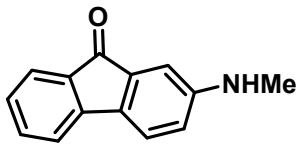
N-methylquinolin-6-amine (4o)[12]

The reaction was carried out according to the general procedure with 6-nitroquinoline (**1o**). Purification by column chromatography on silica gel (PE/EA = 2/1) affords 6-methoxyquinoline (**4o')** as white solid (46.8 mg, 74%).

^{1}H NMR (400 MHz, CDCl3) δ 8.70 (d, *J* = 4.2 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.36 (ddd, *J* = 8.5, 4.2, 0.7 Hz, 1H), 7.29 (d, *J* = 1.0 Hz, 2H), 4.08 (bs, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.82, 143.71, 137.95, 136.13, 128.44, 126.34, 123.79, 121.66, 121.12, 60.19.

The reaction carried out under general procedure using Na_2CO_3 instead of Cs_2CO_3. Purification by column chromatography on silica gel (PE/Acetone = 8/1) affords N-methylquinolin-6-amine (**4o**) as white solid (28.5 mg, 45%).

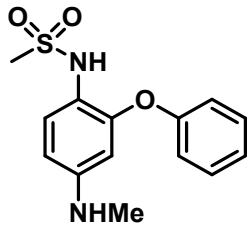
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 3.2 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.23 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.05 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.62 (d, *J* = 2.5 Hz, 1H), 4.03 (s, 1H), 2.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.43, 145.15, 134.57, 130.37, 129.94, 129.47, 121.81, 121.35, 102.20, 30.67.



2-(methylamino)-9H-fluoren-9-one (4p)[13].

The reaction was carried out according to the general procedure with 6-nitroquinoline (**1p**). Purification by column chromatography on silica gel (PE/EA = 3/1) affords **4p** as red solid (62.8 mg, 75%).

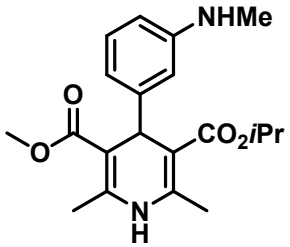
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.3 Hz, 1H), 7.35 (td, *J* = 7.4, 1.1 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.08 (td, *J* = 7.4, 0.8 Hz, 1H), 6.88 (d, *J* = 2.3 Hz, 1H), 6.60 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.03 (bs, 1H), 2.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.78, 150.23, 145.93, 135.90, 134.81, 134.07, 133.25, 126.96, 124.15, 121.33, 118.92, 116.98, 108.36, 30.82.



Nimesulide (4q)

The reaction was carried out according to the general procedure with **Nimesulide**. Purification by column chromatography on silica gel (PE/EA = 2/1) affords **N-Me Nimesulide** (**4q**) as yellow solid (90.0 mg, 77%).

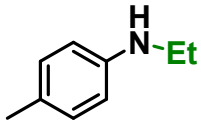
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3H), 7.17 – 7.12 (m, 1H), 7.02 – 6.97 (m, 2H), 6.36 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.32 (bs, 1H), 6.11 (d, *J* = 2.6 Hz, 1H), 3.71 (bs, 1H), 2.89 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.13, 150.62, 149.07, 130.10, 127.63, 124.03, 118.44, 116.75, 108.26, 102.19, 38.96, 30.74.



Nimodipine derivative (4r)

The reaction was carried out according to the general procedure with Nimodipine derivative (**3-isopropyl 5-methyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate**) (**1r**). Purification by column chromatography on silica gel (PE/EA = 1/1) affords **N-methylated Nimodipine derivative** (**4r**) as white solid (107.5 mg, 75%).

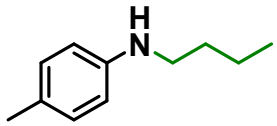
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (t, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.57 – 6.55 (m, 1H), 6.39 (dd, *J* = 7.9, 2.1 Hz, 1H), 6.16 (bs, 1H), 5.00 – 4.94 (m, 1H), 4.93 (s, 1H), 3.63 (s, 3H), 3.40 (bs, 1H), 2.75 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.40, 167.45, 148.98, 148.57, 144.58, 143.85, 128.71, 117.19, 112.70, 110.16, 104.31, 103.41, 67.02, 50.95, 39.42, 30.89, 22.17, 21.94, 19.41.



N-ethyl-4-methylaniline (6a)[14]

The reaction was carried out according to the general procedure with 1-methyl-4-nitrobenzene (**1a**) using ethanol instead of methanol. Purification by column chromatography on silica gel (PE/EA = 15/1) affords **6a** as colorless oil (46.0 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.1 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 3.15 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.83, 129.75, 126.86, 113.30, 39.13, 20.42, 14.85.

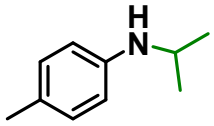


N-butyl-4-methylaniline (6b)[15]

The reaction was carried out according to the general procedure with 1-methyl-4-nitrobenzene (**1a**) using butanol instead of methanol. Purification by column chromatography on silica gel (PE/EA = 15/1) affords **6b** as colorless oil (54.3 mg, 83%).

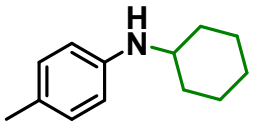
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.1 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 3.10

(t, J = 7.2 Hz, 2H), 3.14 – 3.06 (m, 2H), 2.24 (s, 3H), 1.66 – 1.55 (m, 2H), 1.48 – 1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.27, 129.77, 127.34, 113.72, 44.76, 31.40, 20.43, 20.29, 13.89.



N-isopropyl-4-methylaniline (6c)[16]

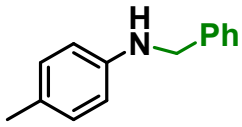
The reaction was carried out according to the general procedure with 1-methyl-4-nitrobenzene (**1a**) using isopropanol instead of methanol. Purification by column chromatography on silica gel (PE/EA = 15/1) affords **6c** as colorless oil (44.6 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.97 (d, J = 8.2 Hz, 2H), 6.52 (d, J = 8.3 Hz, 2H), 3.63 – 3.54 (m, 1H), 2.23 (s, 3H), 1.19 (d, J = 6.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.27, 129.77, 126.23, 113.56, 44.54, 30.73, 23.08.



N-cyclohexyl-4-methylaniline (6d)[17]

The reaction was carried out according to the general procedure with 1-methyl-4-nitrobenzene (**1a**) using cyclohexanol/toluene (1.5 mL/1.5 mL) instead of methanol. Purification by column chromatography on silica gel (PE/EA = 15/1) affords **6d** as yellow oil (58.3 mg, 77%).

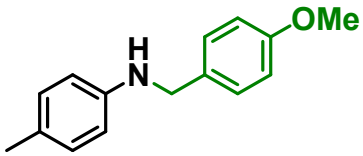
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, J = 8.1 Hz, 2H), 6.50 (d, J = 8.4 Hz, 2H), 3.21 – 3.18 (m, 1H), 2.21 (s, 3H), 2.06 – 1.99 (m, 2H), 1.77 – 1.70 (m, 2H), 1.65 – 1.60 (m, 1H), 1.39 – 1.28 (m, 2H), 1.25 – 1.17 (m, 1H), 1.15 – 1.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.22, 129.83, 126.10, 113.55, 52.10, 33.63, 26.10, 25.16, 20.46.



N-benzyl-4-methylaniline (6e)[14][15]

The reaction was carried out according to the general procedure with 1-methyl-4-nitrobenzene (**1a**) using benzyl alcohol instead of methanol. Purification by column

chromatography on silica gel (PE/EA = 15/1) affords **6e** as colorless oil (69.5 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 4H), 7.36 – 7.31 (m, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 4.37 (s, 2H), 3.92 (bs, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.98, 139.74, 129.84, 128.68, 127.60, 127.24, 126.84, 113.12, 48.73, 20.50.



N-(4-methoxybenzyl)-4-methylaniline (6f)[17]

The reaction was carried out according to the general procedure with 1-methyl-4-nitrobenzene (**1a**) using (4-methoxyphenyl)methanol (4 mmol, 10 eq)/toluene (2 mL) instead of methanol. Purification by column chromatography on silica gel (PE/EA = 10/1) affords **6f** as white solide (69.1 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 2H), 7.01 – 6.89 (m, 2H), 6.85 – 6.77 (m, 2H), 6.53 – 6.43 (m, 2H), 4.14 (s, 2H), 3.75 (bs, 1H), 3.70 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.96, 146.21, 131.86, 129.91, 128.93, 126.71, 114.14, 113.18, 55.38, 48.21, 20.61.

8. Reference:

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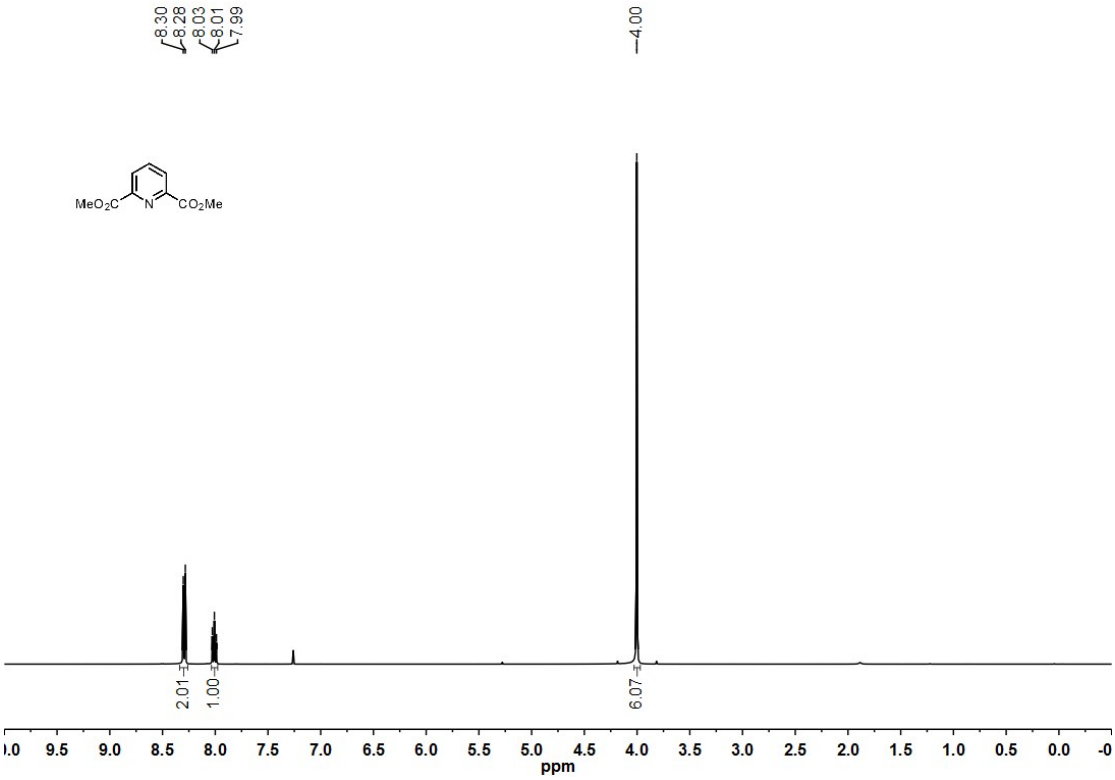
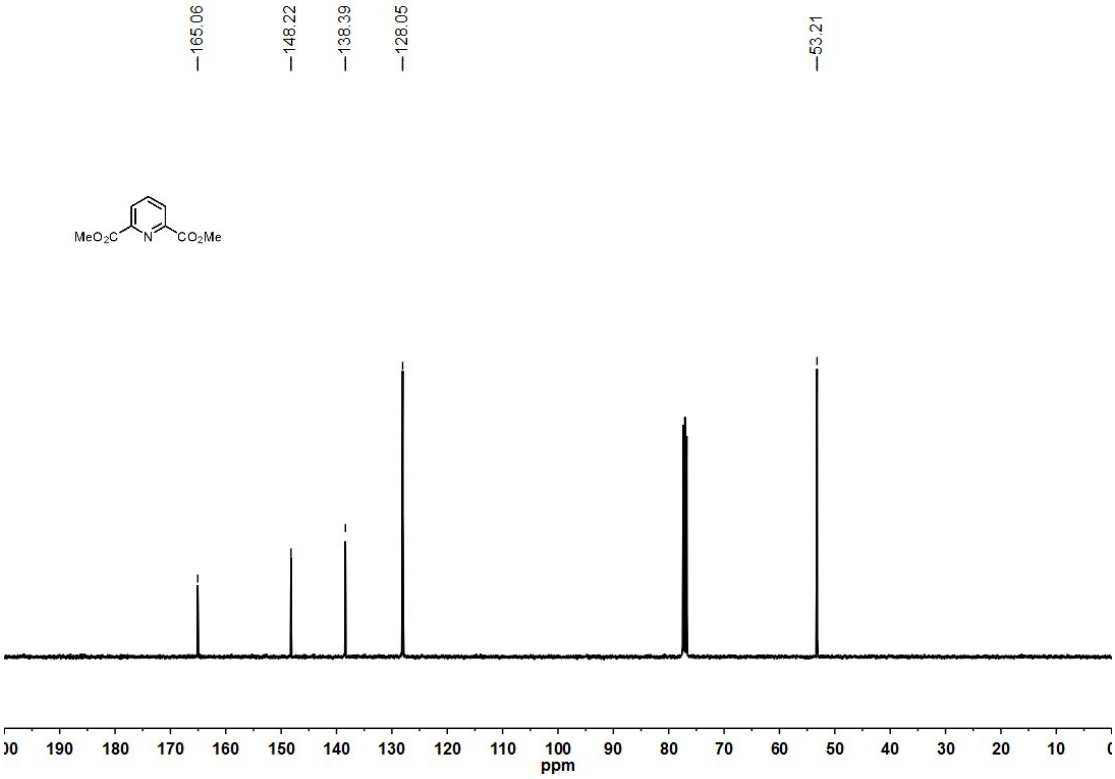
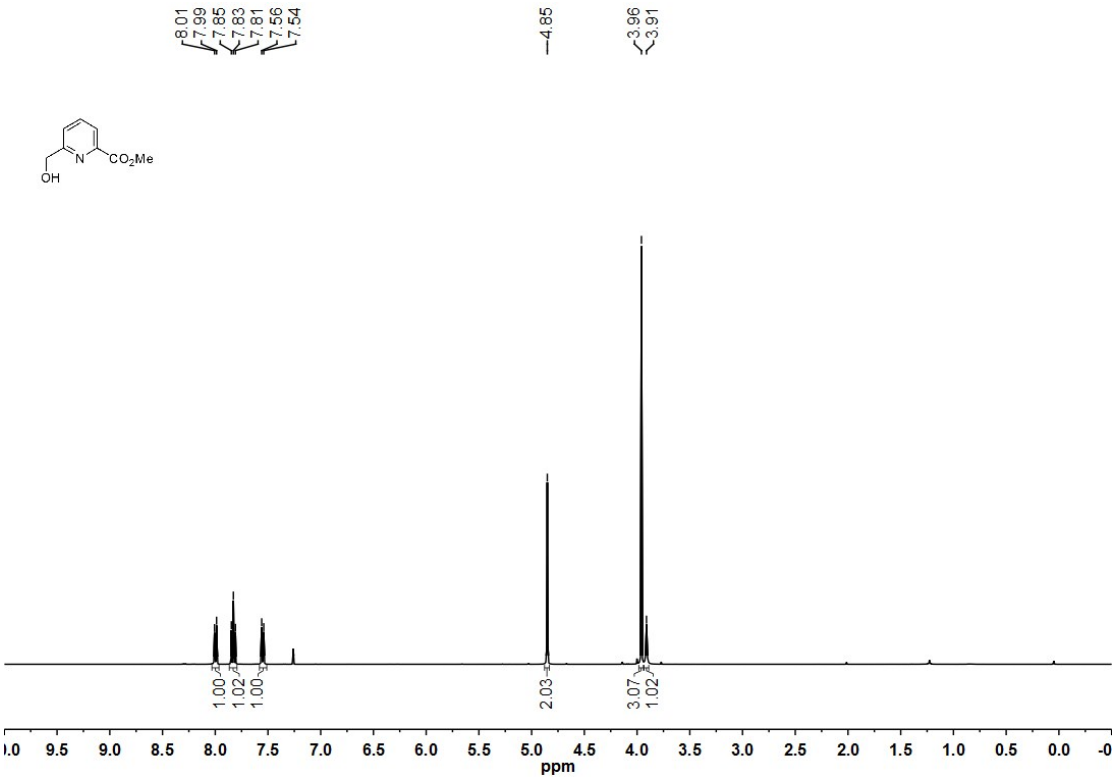
9 NMR Spectra



^{1}H NMR (400M, $CDCl_3$) spectrum of **sm-2**



^{13}C NMR (101 M, $CDCl_3$) spectrum of **sm-2**



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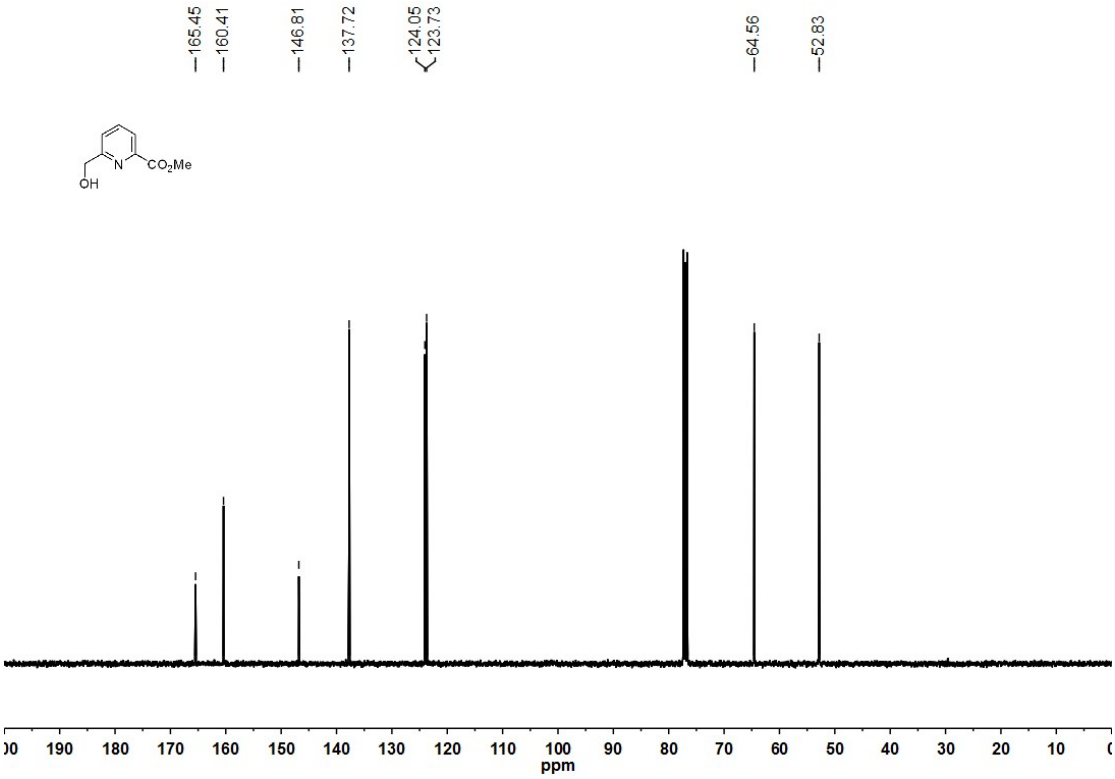
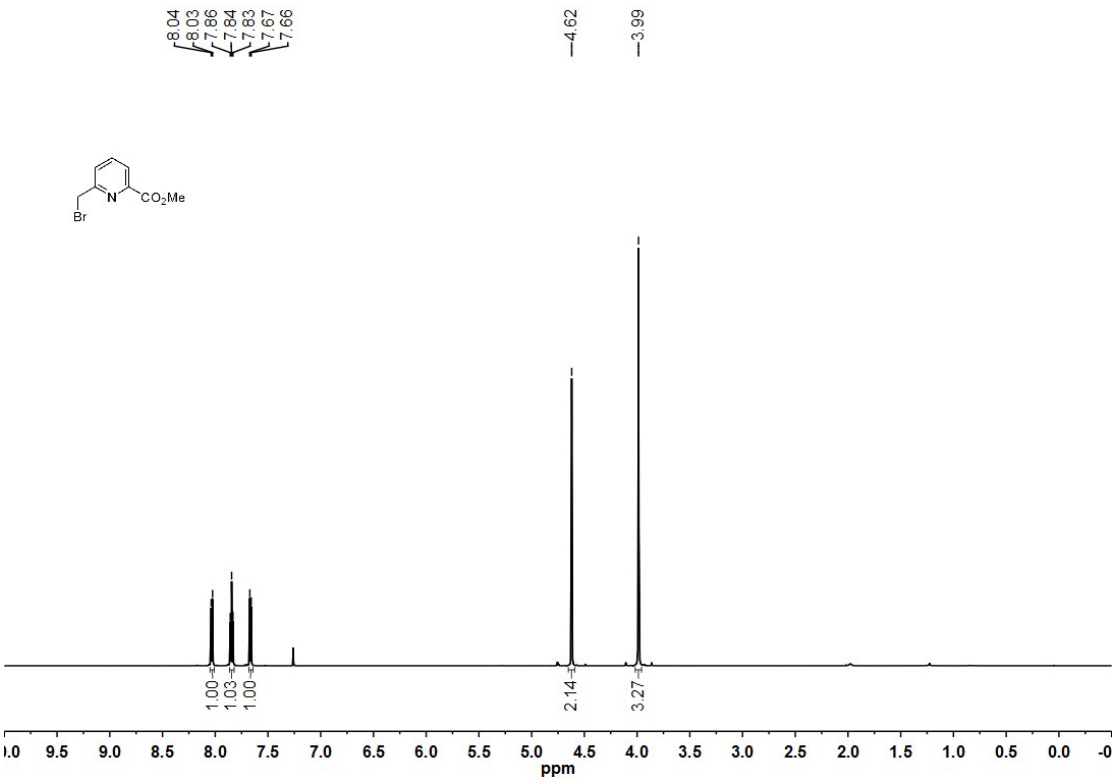
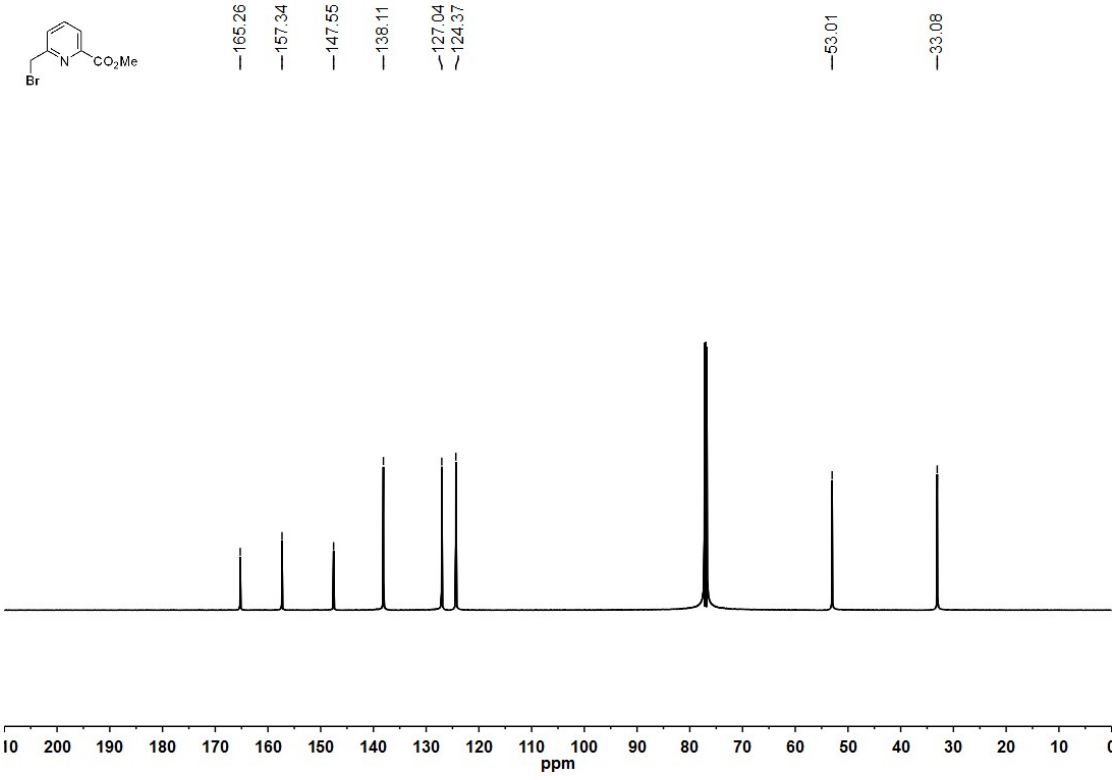


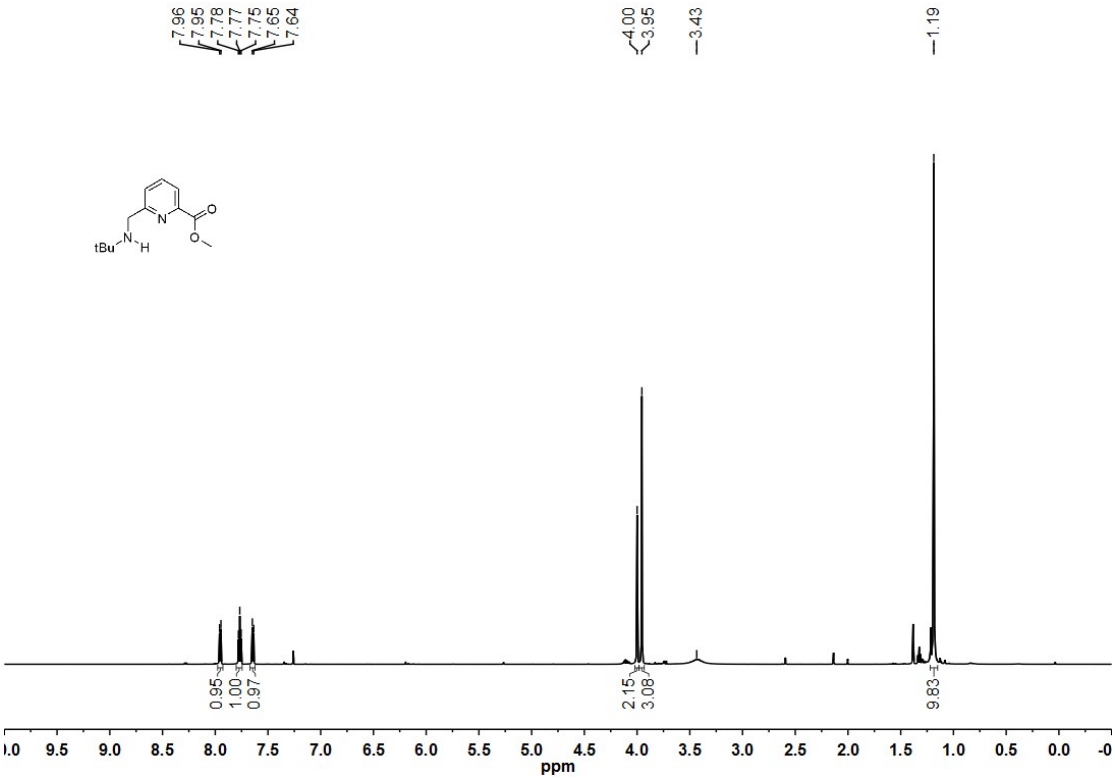
^{13}C NMR (101 M, $CDCl_3$) spectrum of **sm-3**



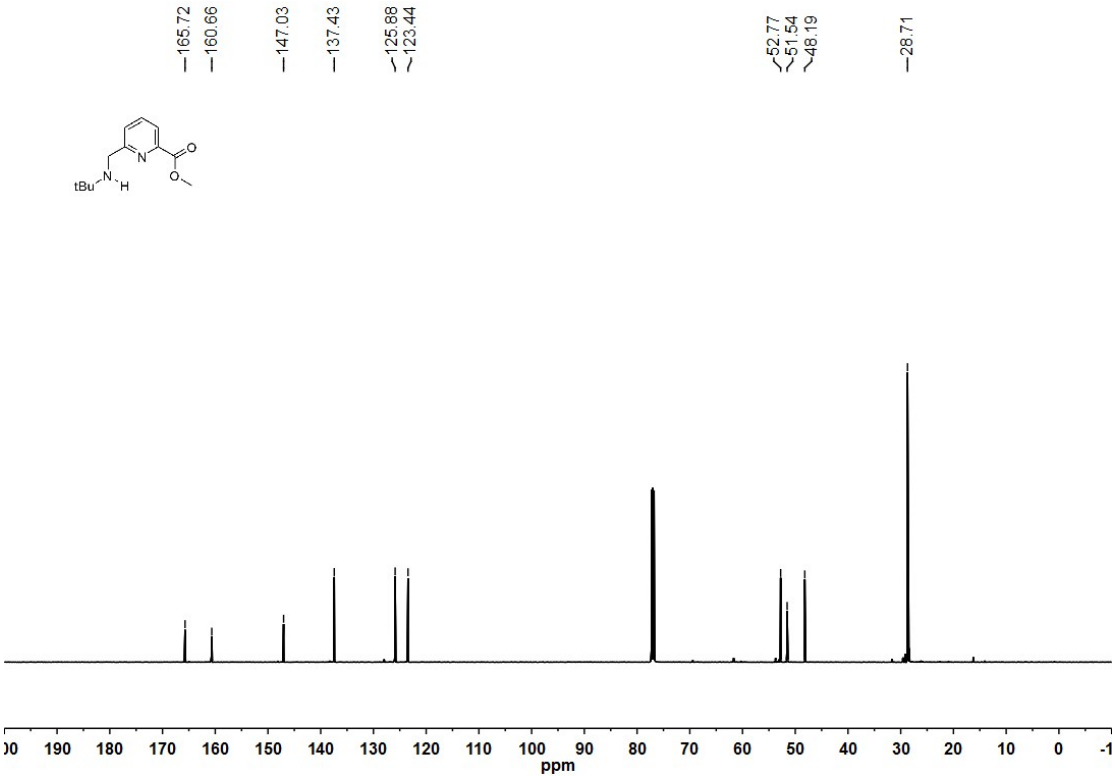
^{1}H NMR (600M, $CDCl_3$) spectrum of **sm-4**



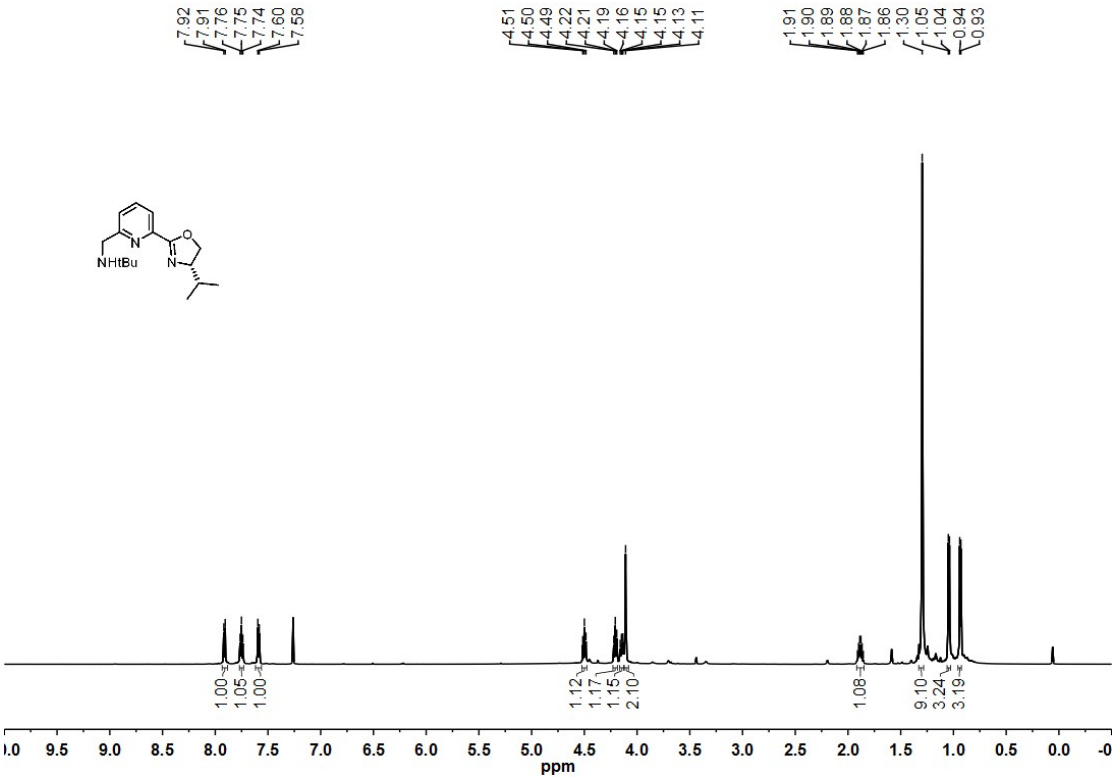
^{13}C NMR (151 M, $CDCl_3$) spectrum of **sm-4**



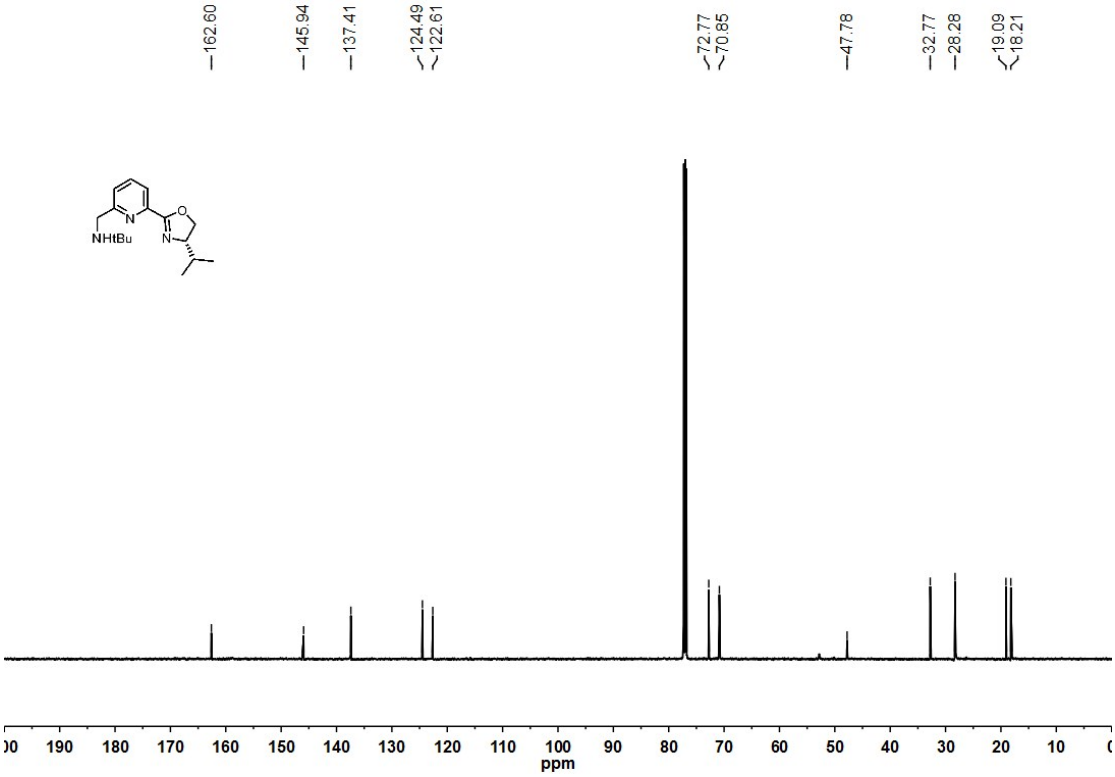
^{1}H NMR (600M, $CDCl_3$) spectrum of **sm-5**



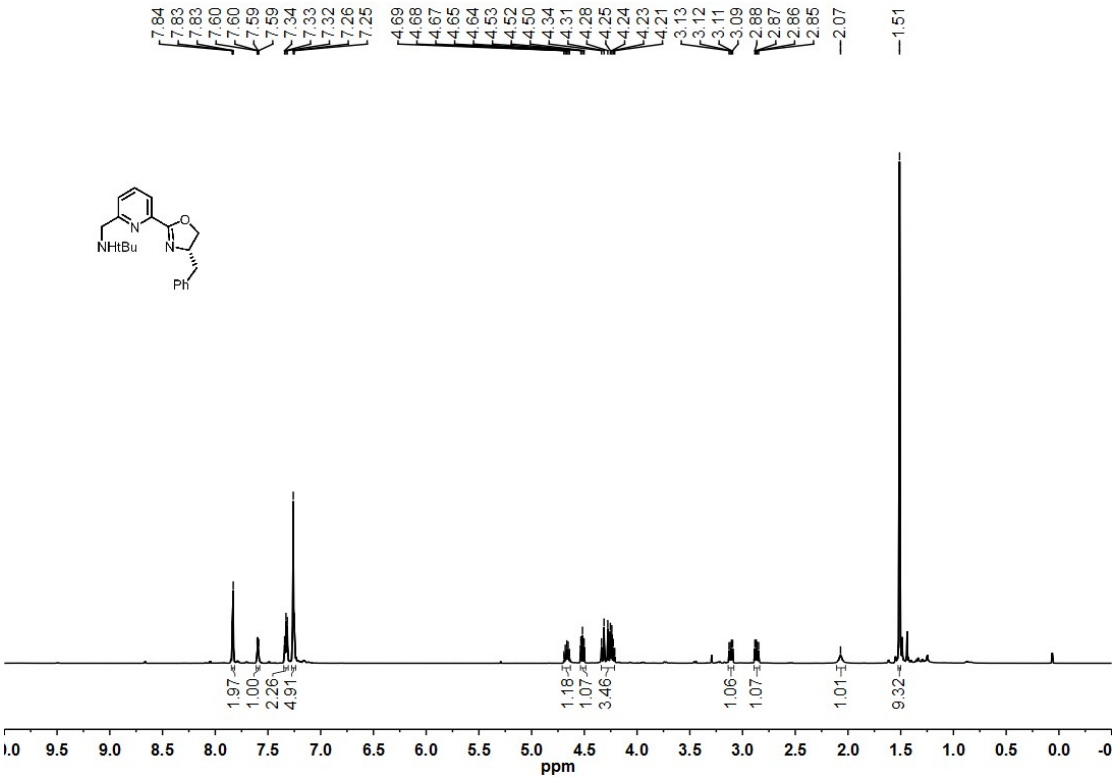
^{13}C NMR (151 M, $CDCl_3$) spectrum of **sm-5**



^{1}H NMR (600M, $CDCl_3$) spectrum of **sm-6a**



^{13}C NMR (151 M, $CDCl_3$) spectrum of **sm-6a**



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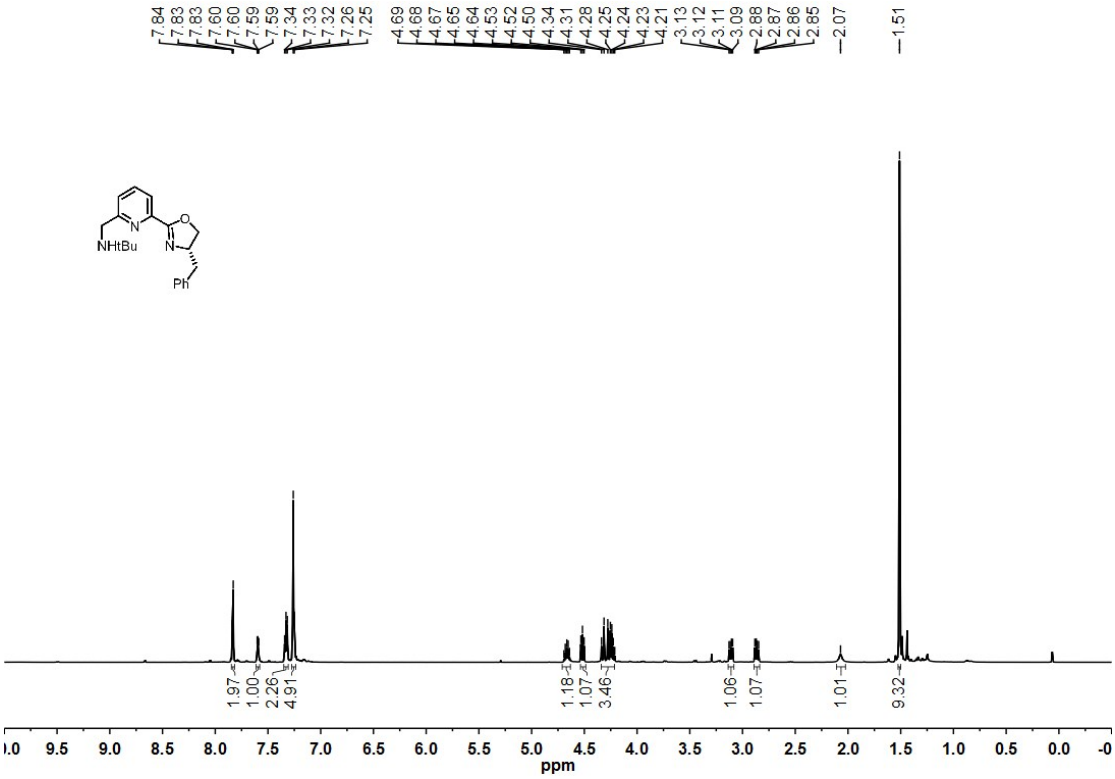

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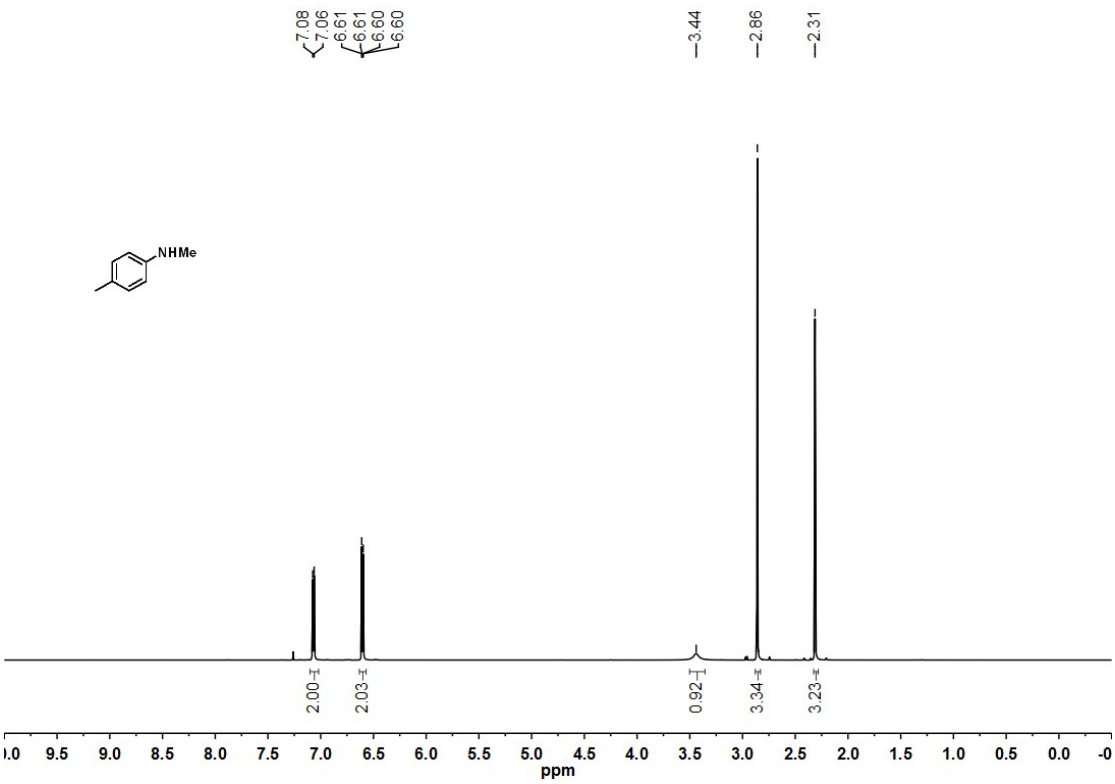
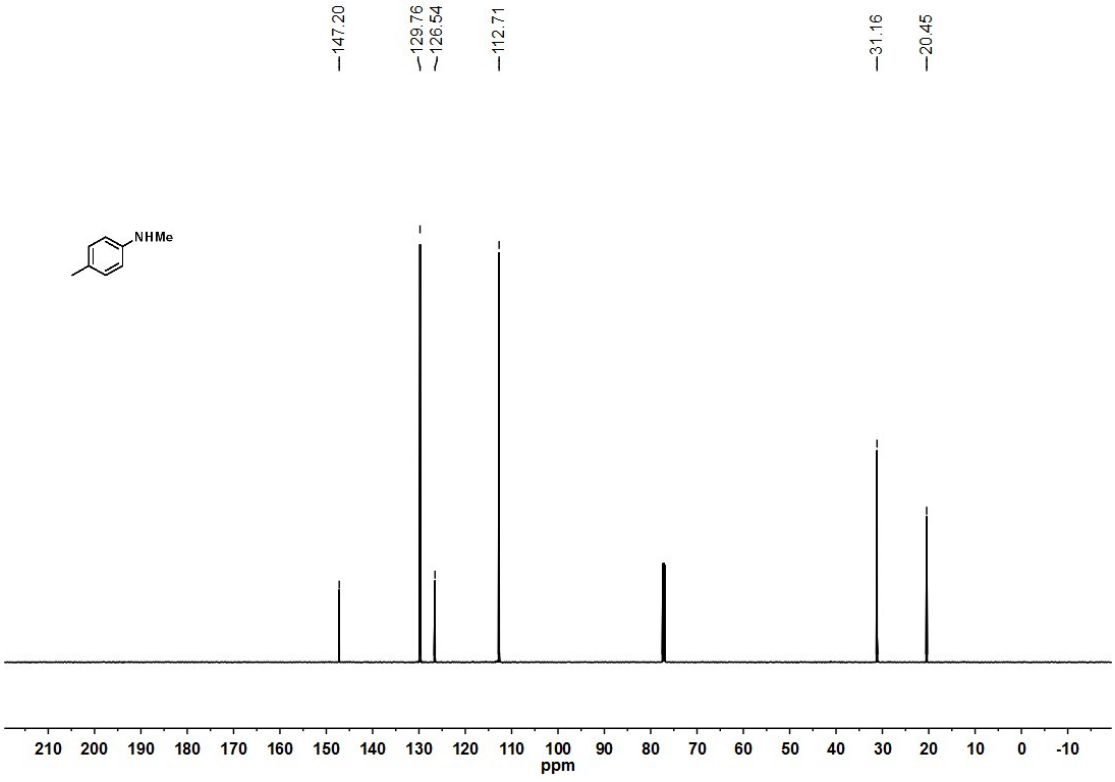
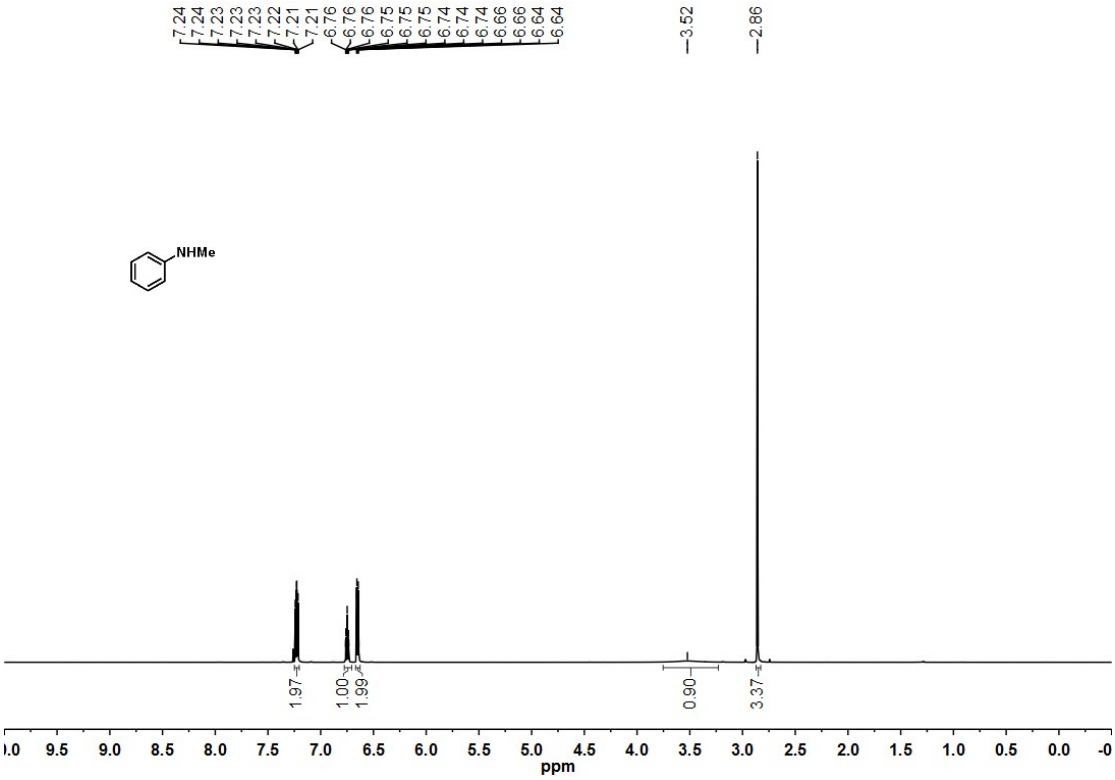


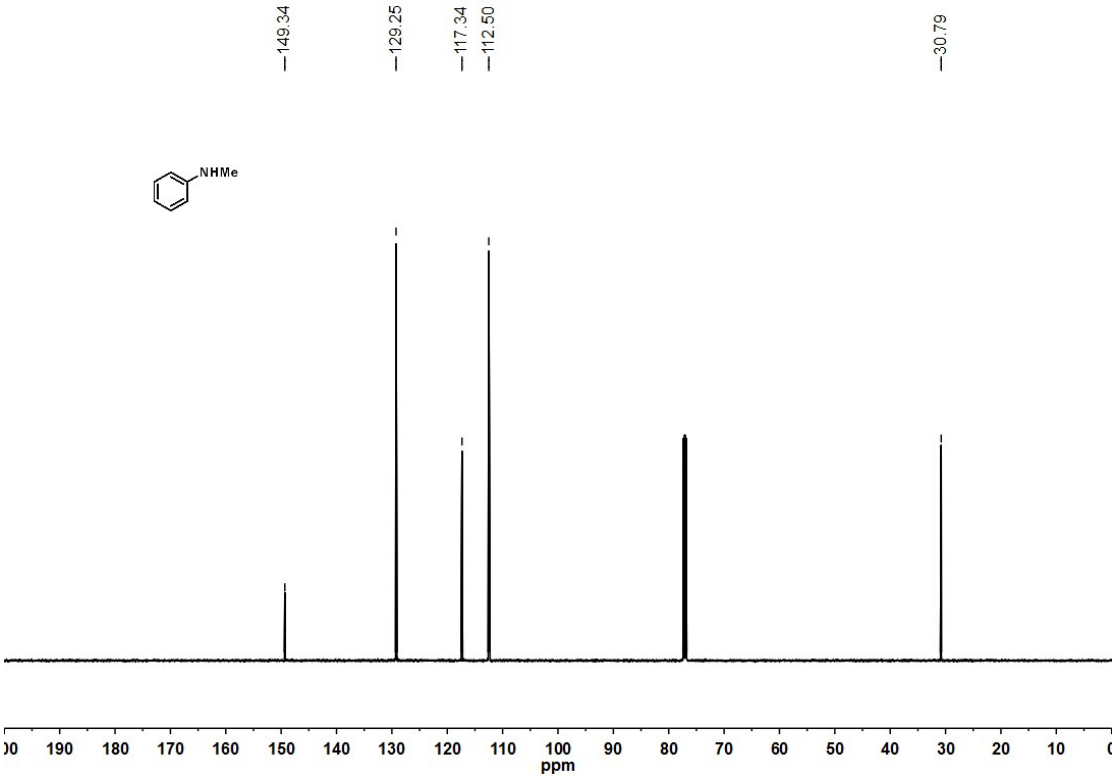
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4a**



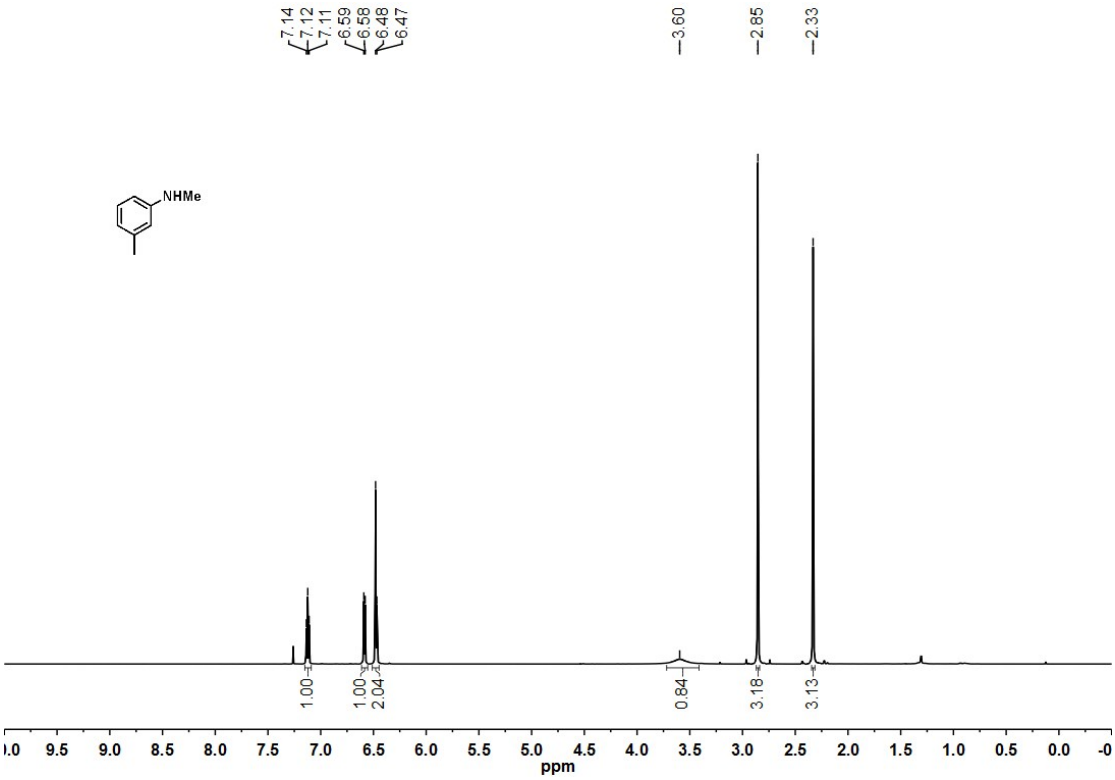
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4a**



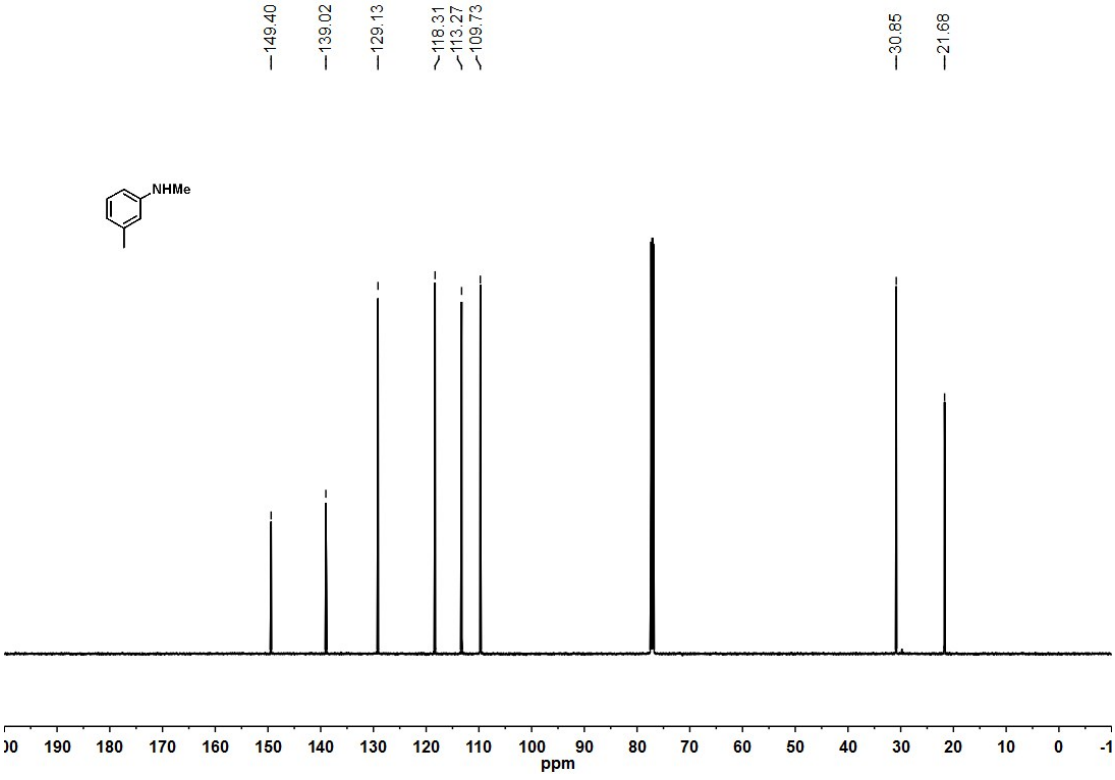
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4b**



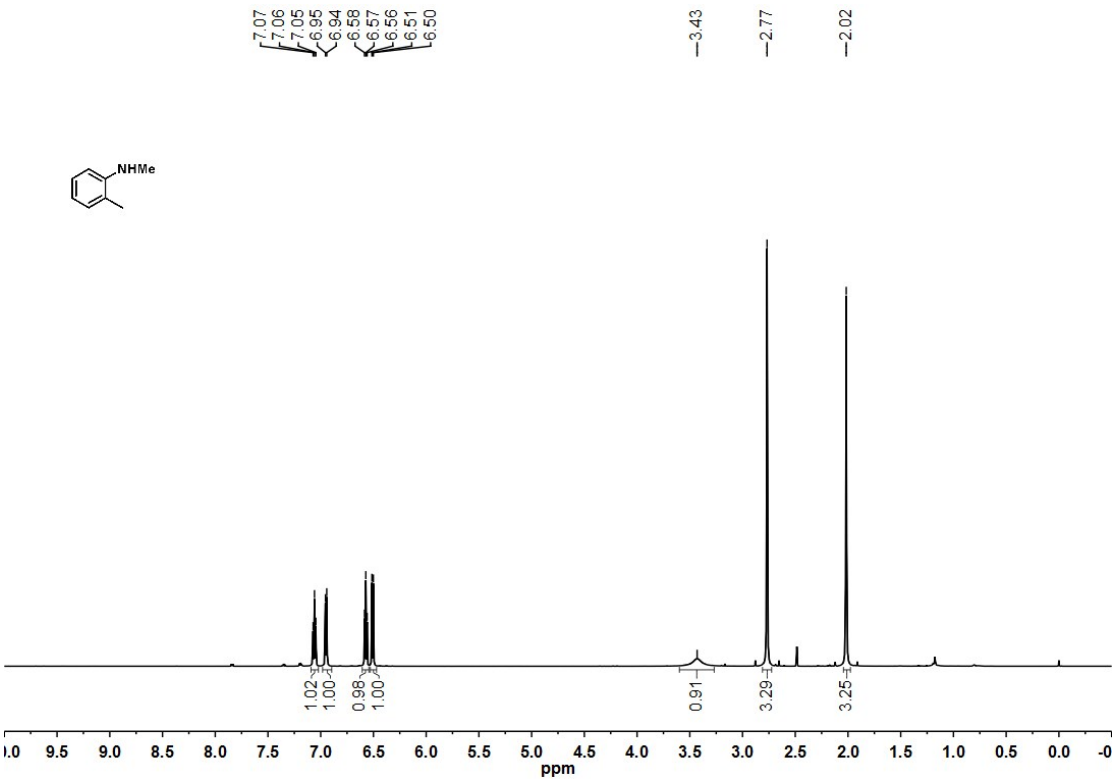
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4b**



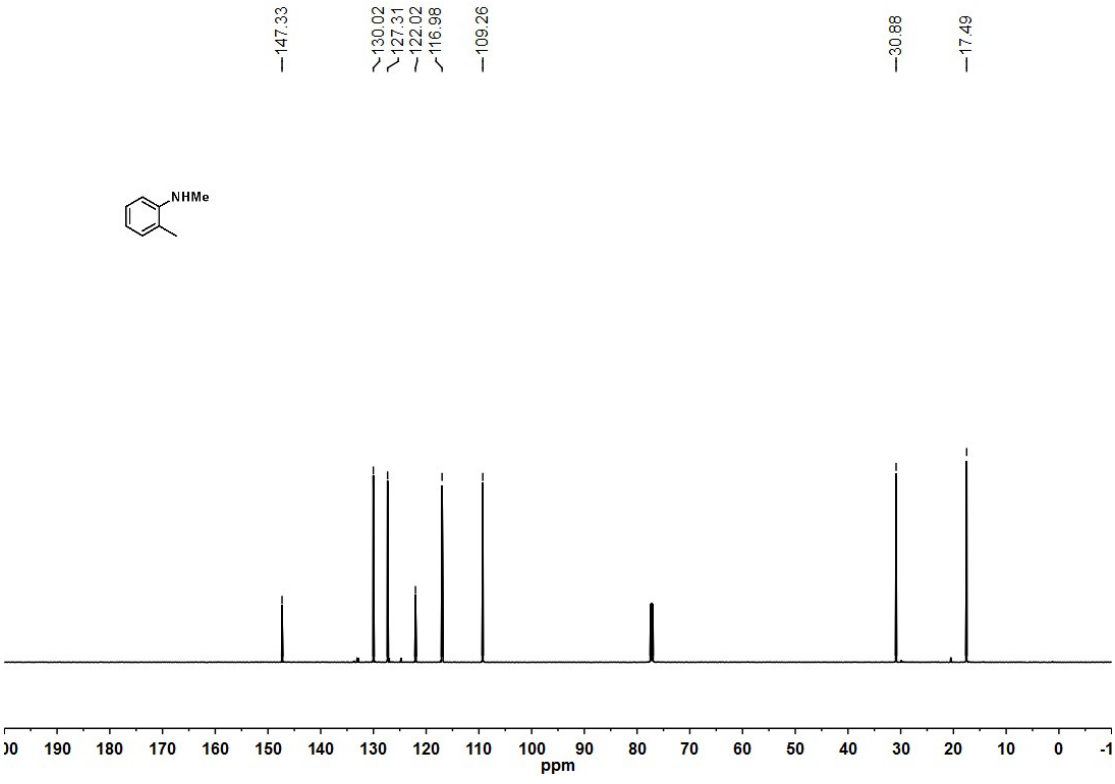
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4c**



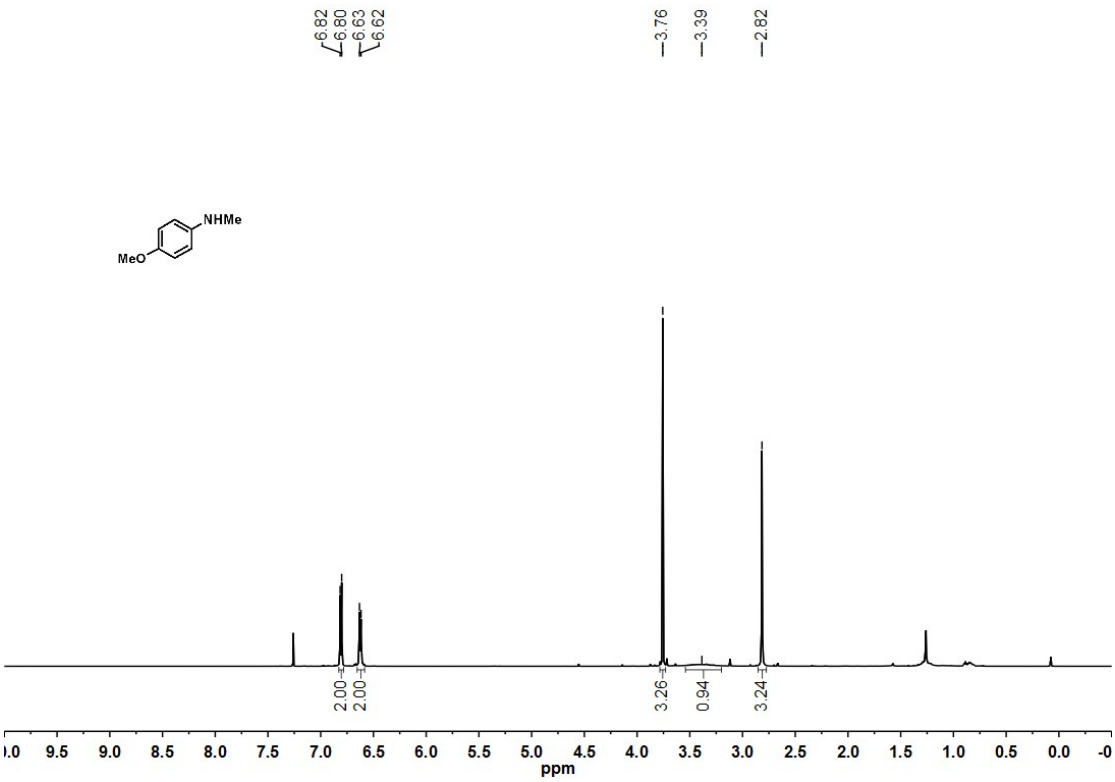
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4c**



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4d**



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4d**



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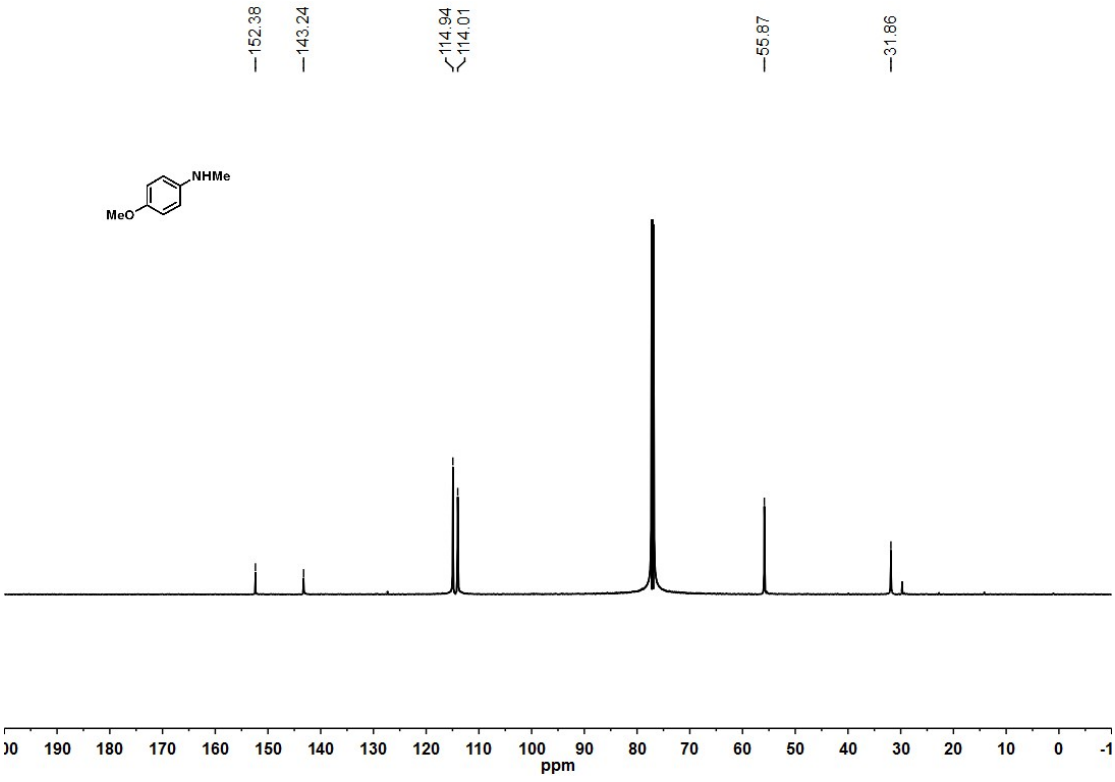

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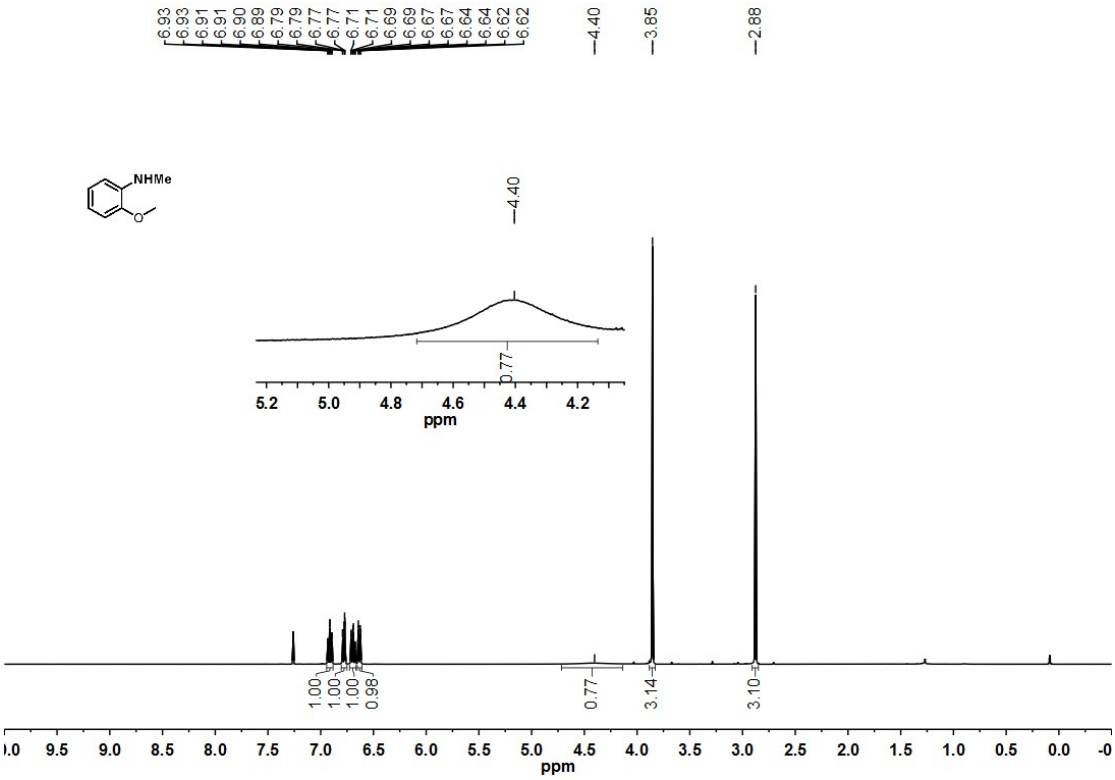
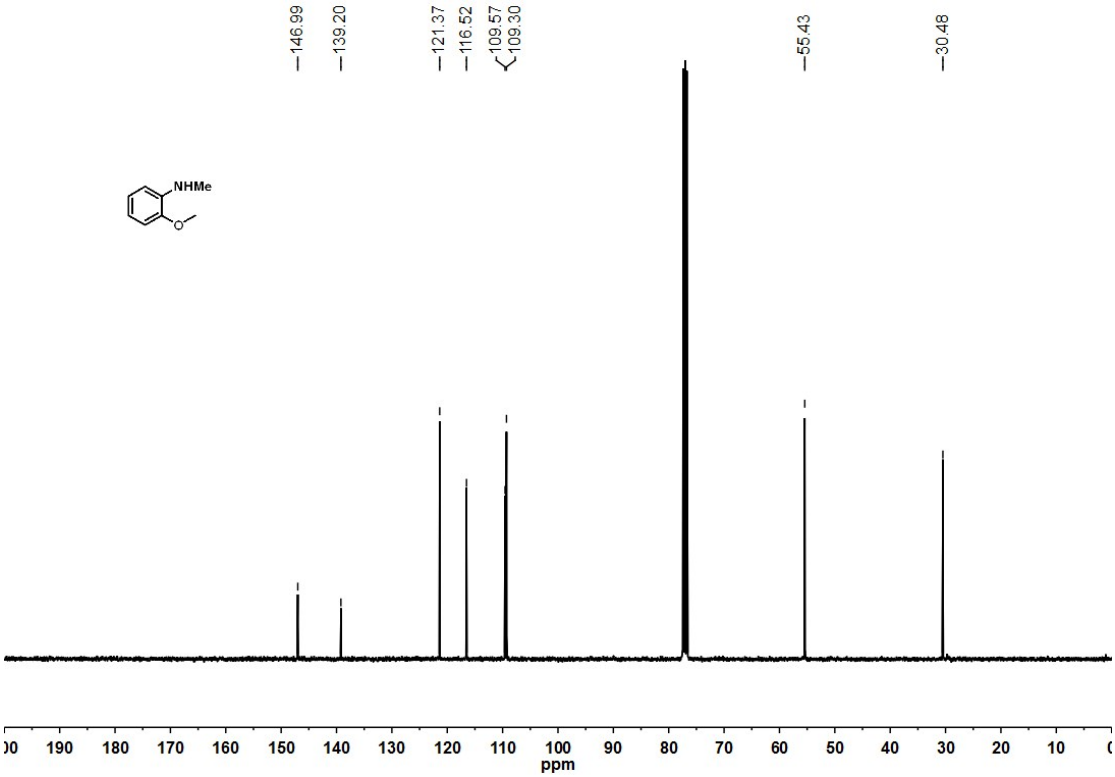


^{1}H NMR (400 M, $CDCl_3$) spectrum of **4f**



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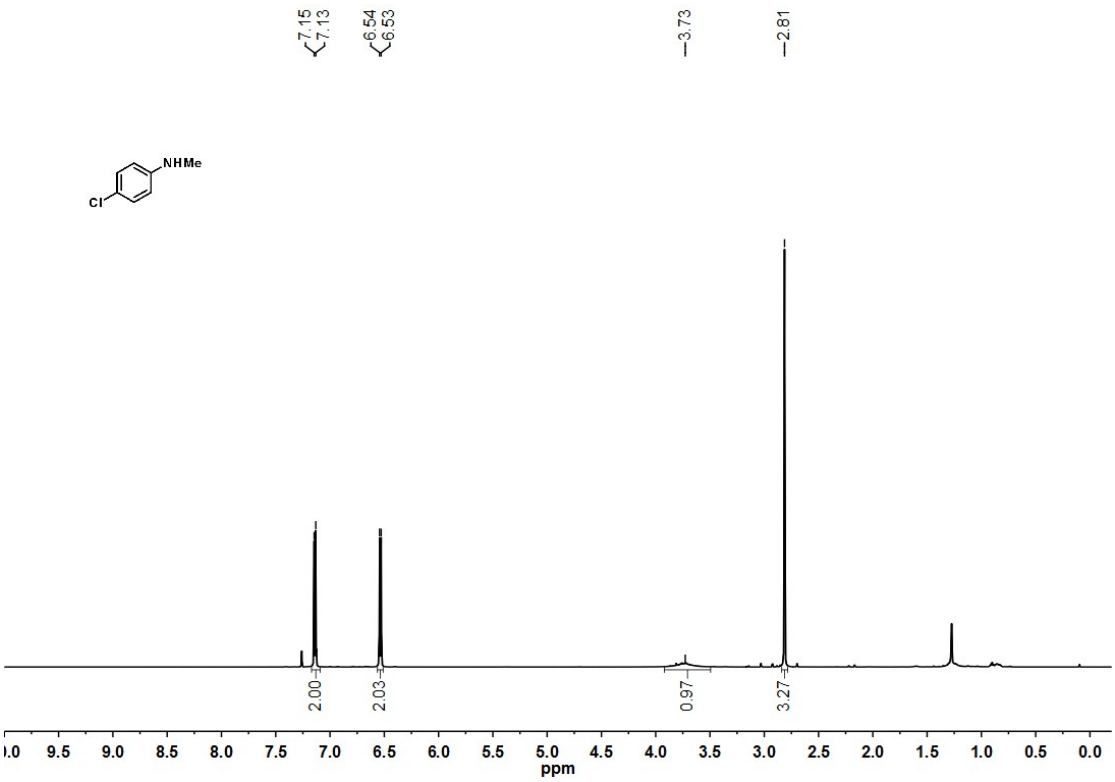
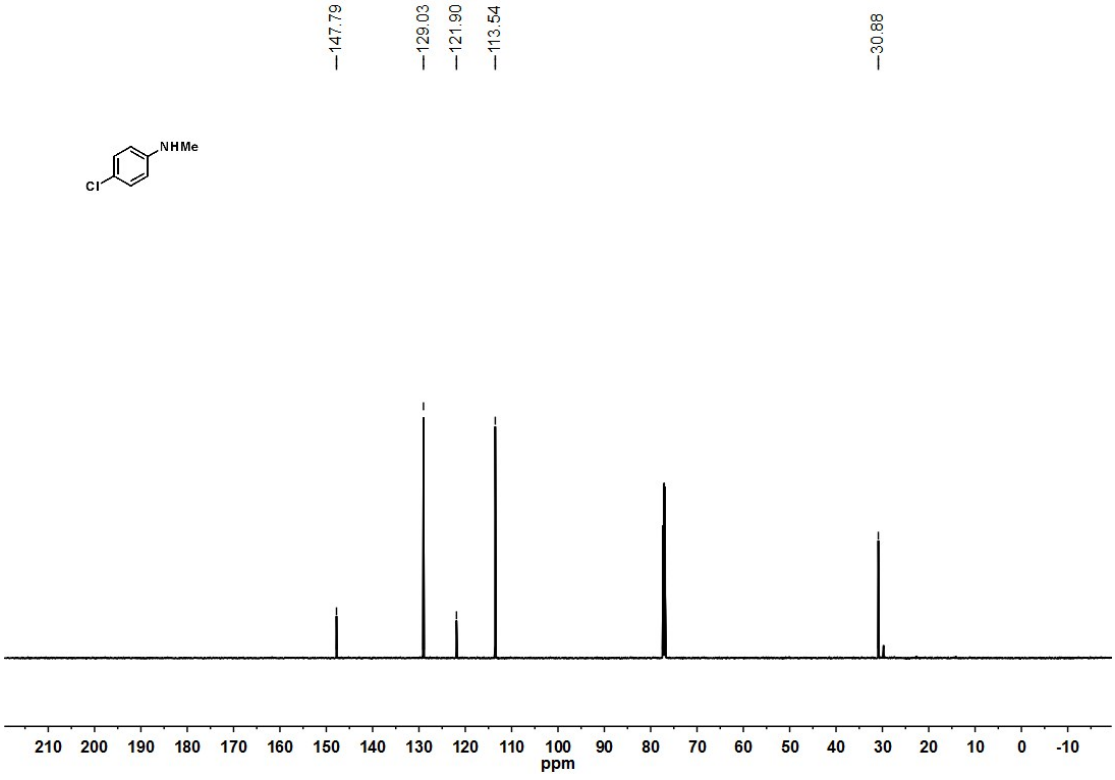
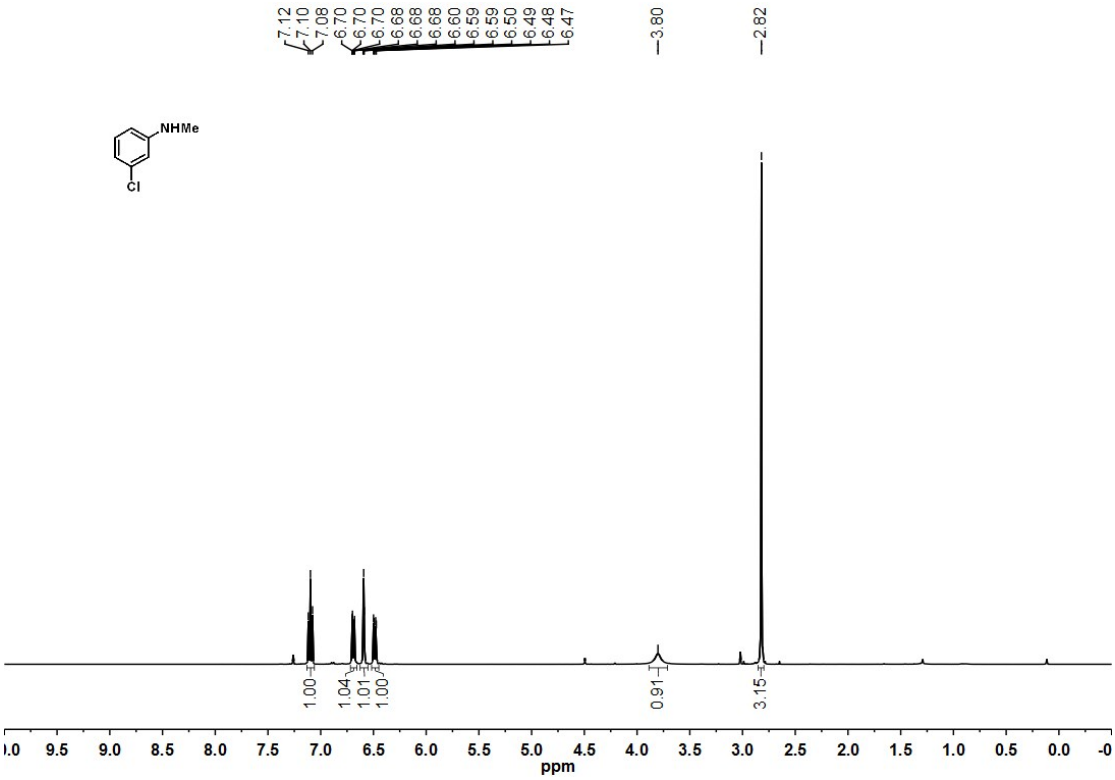


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4g**



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4g**



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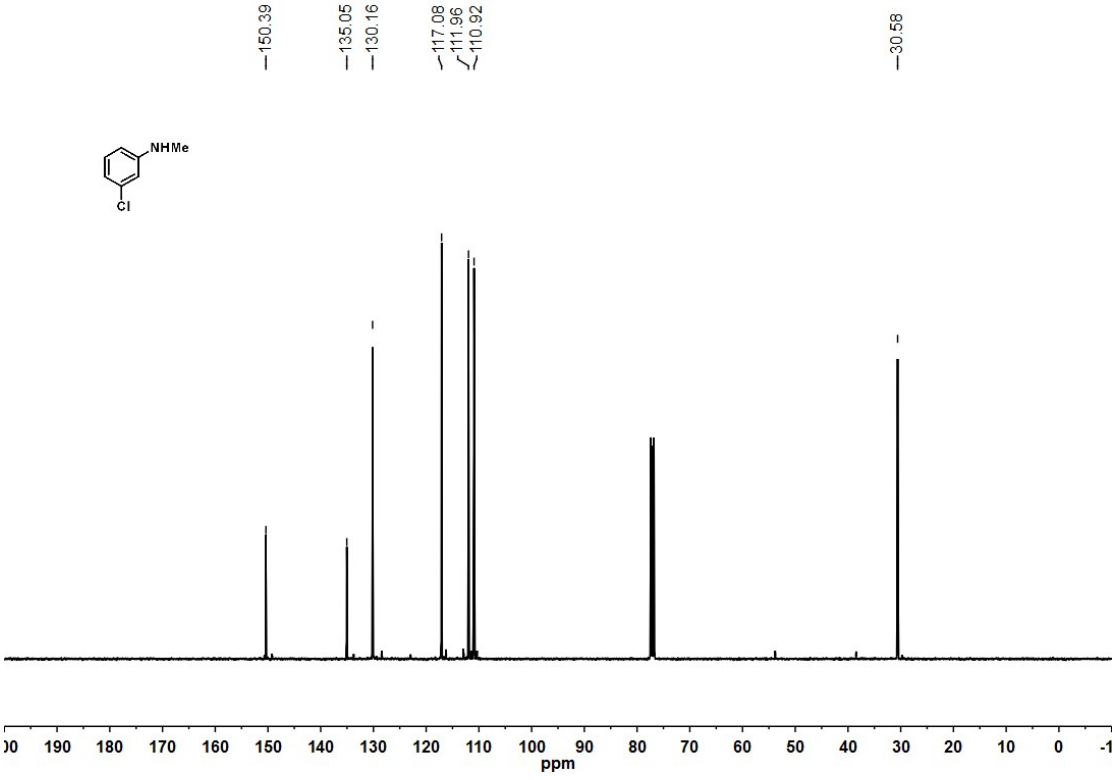

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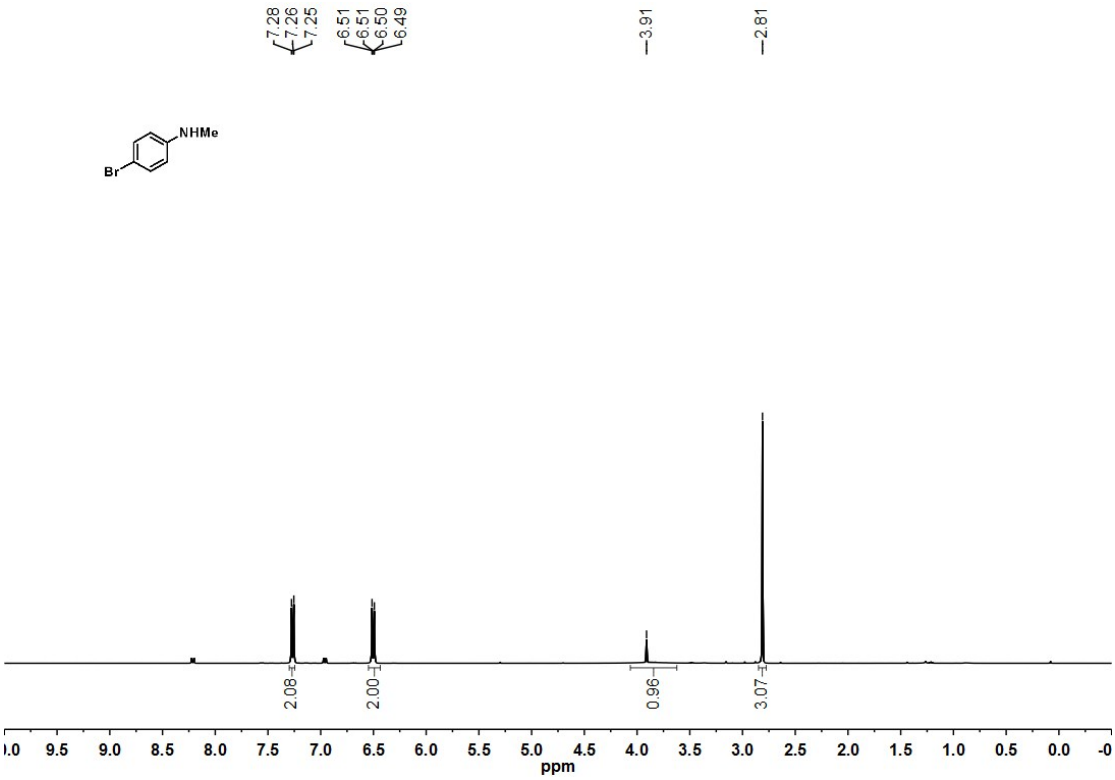
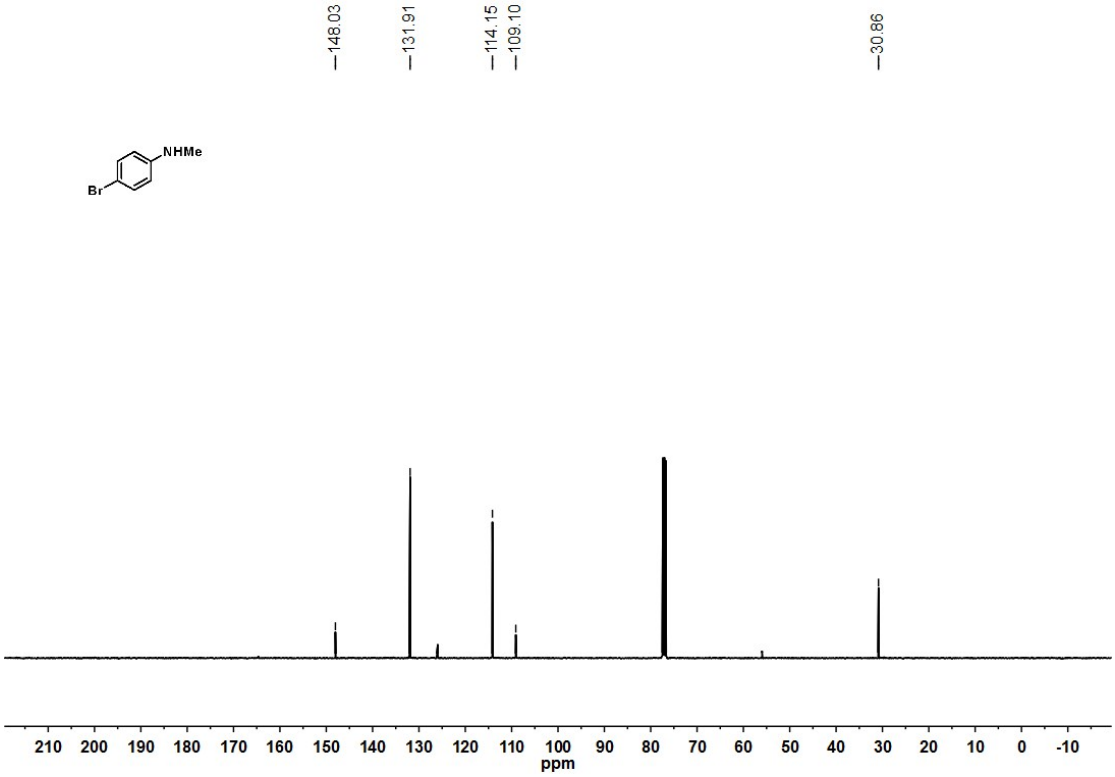


^{1}H NMR (400 M, $CDCl_3$) spectrum of **4i**



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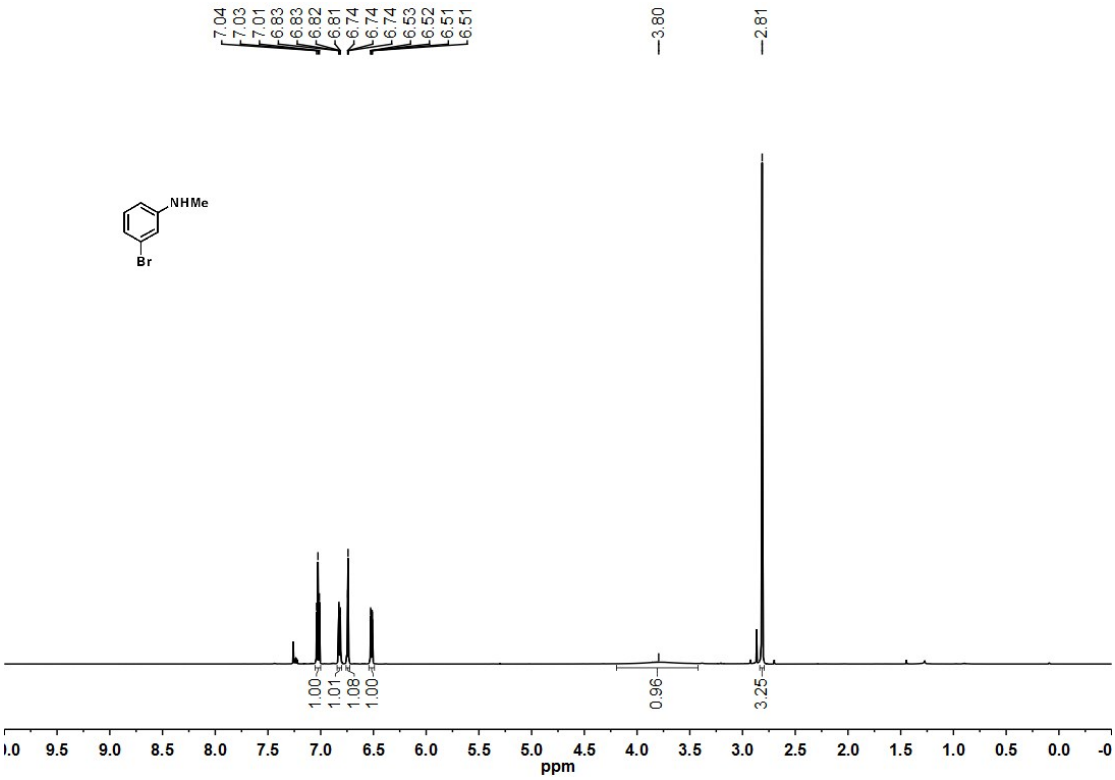
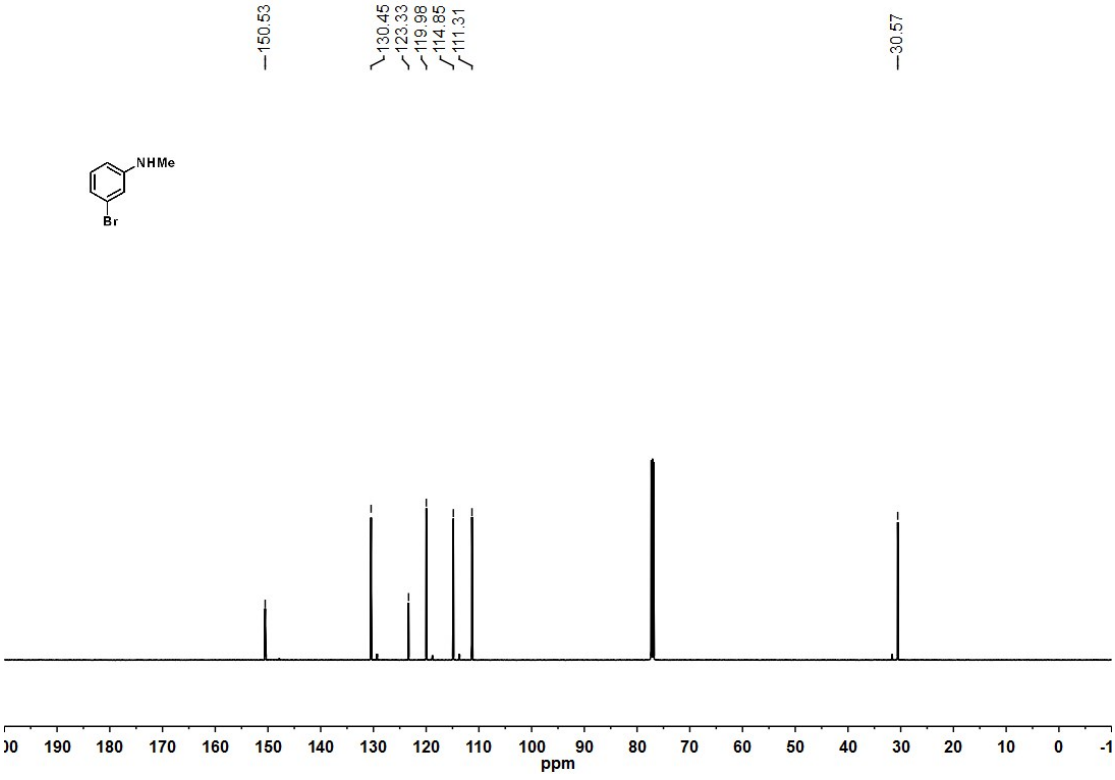
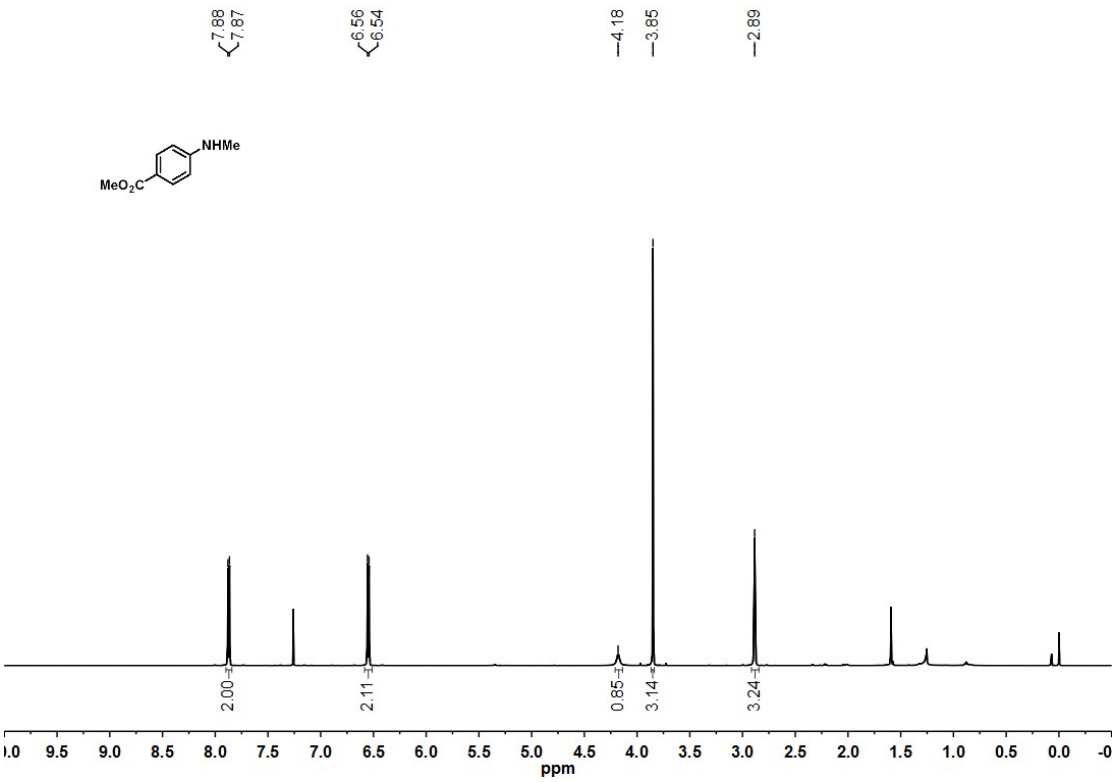


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4j**



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4j**



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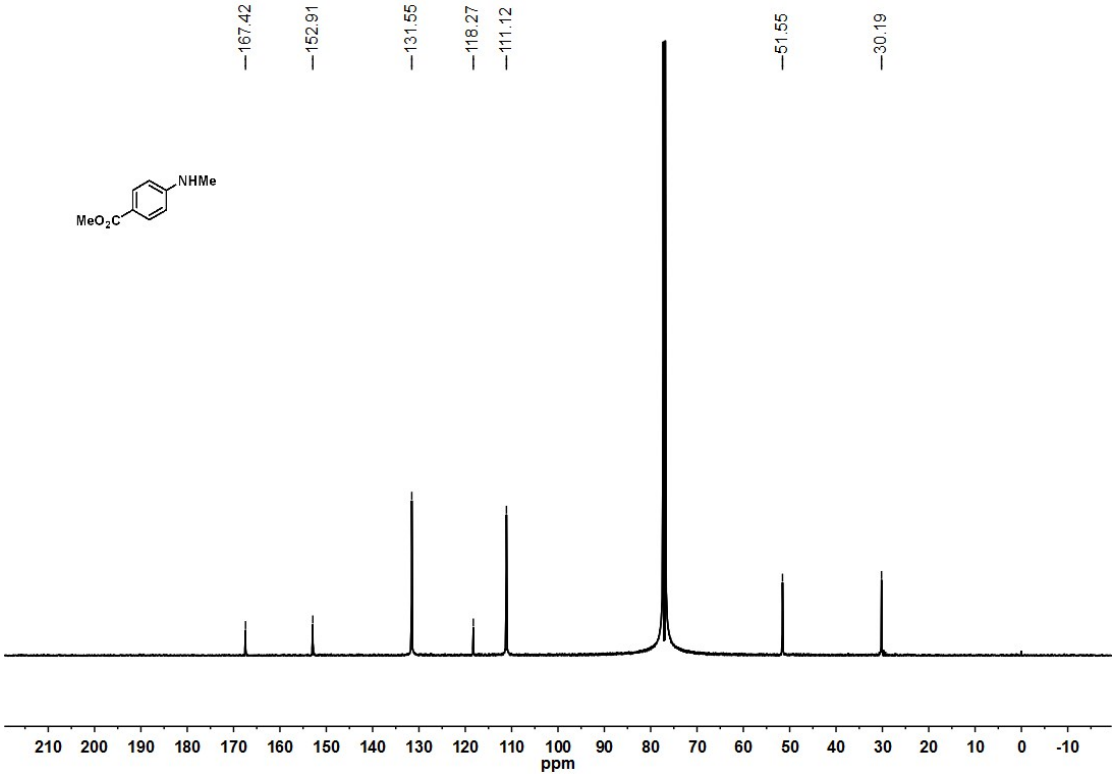

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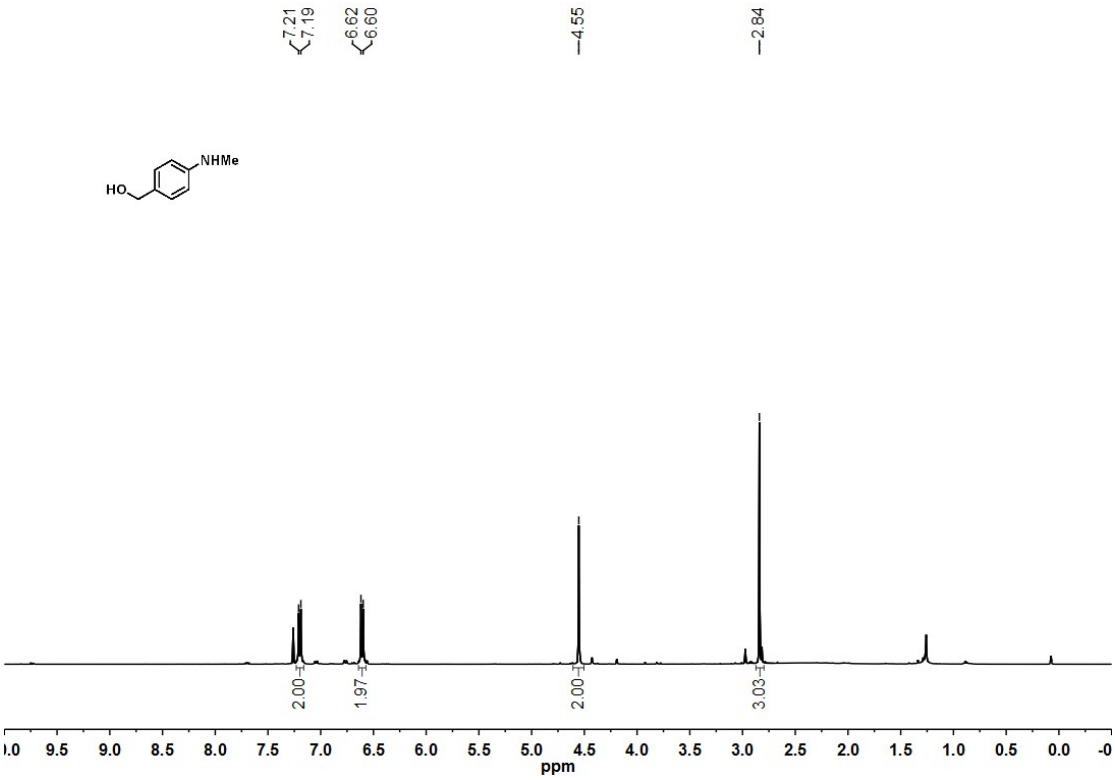

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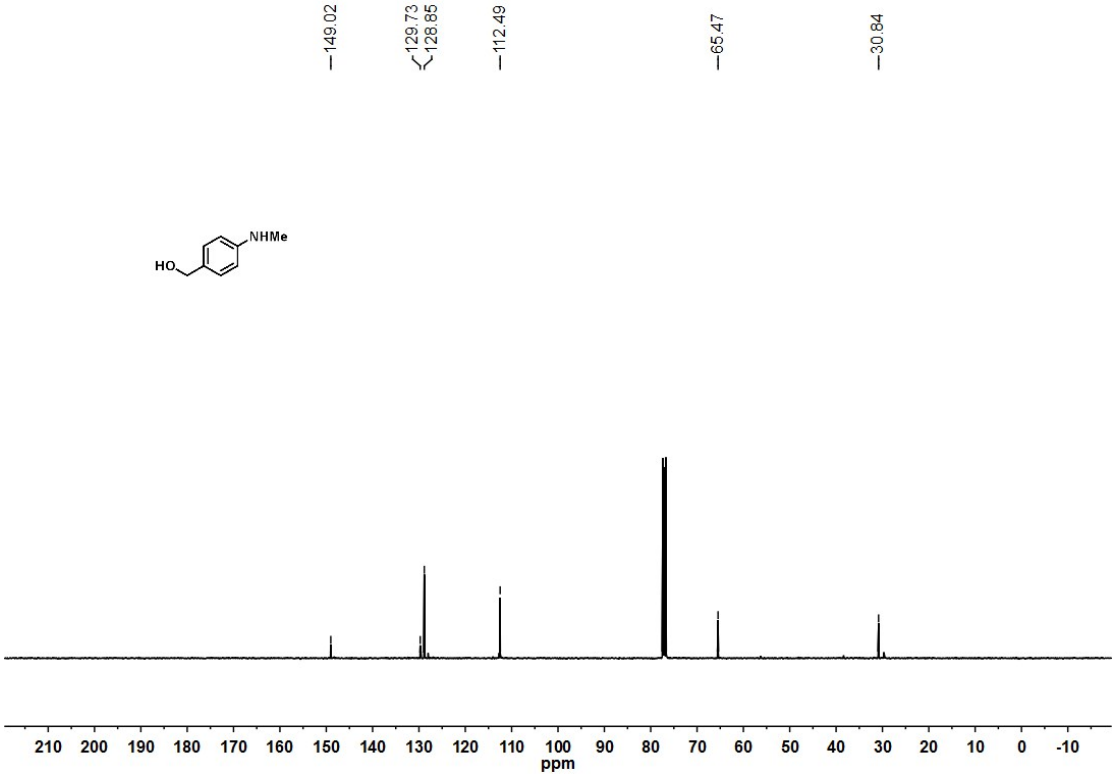

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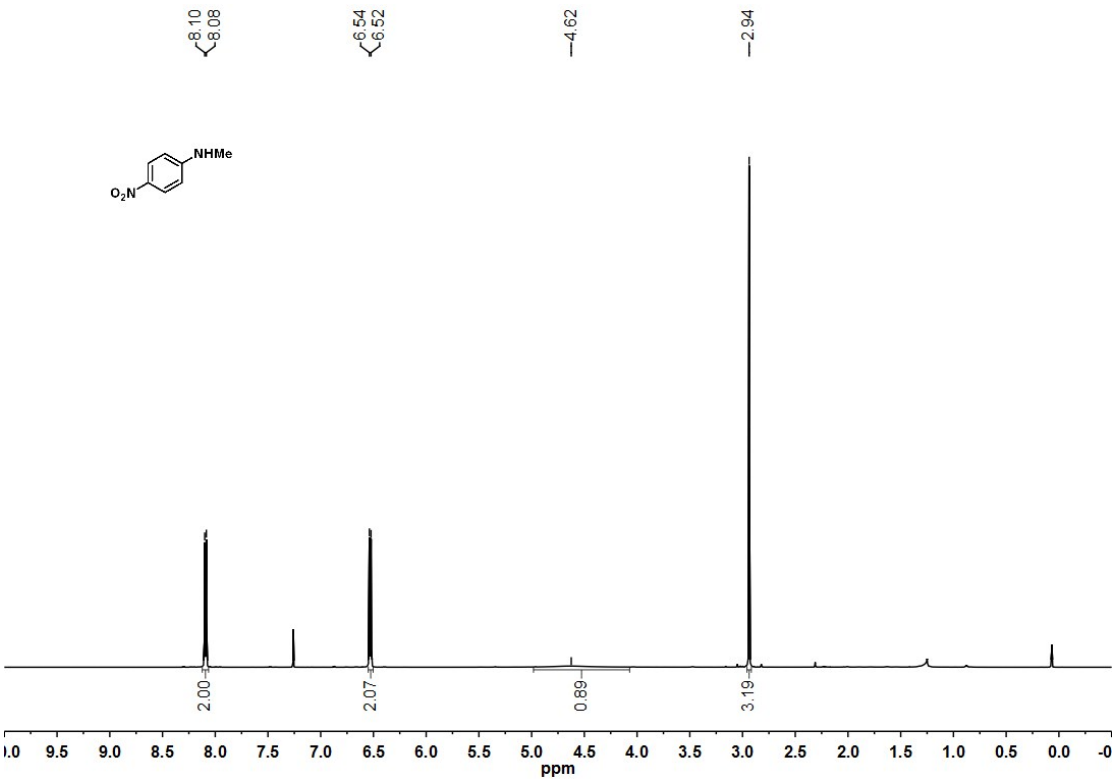

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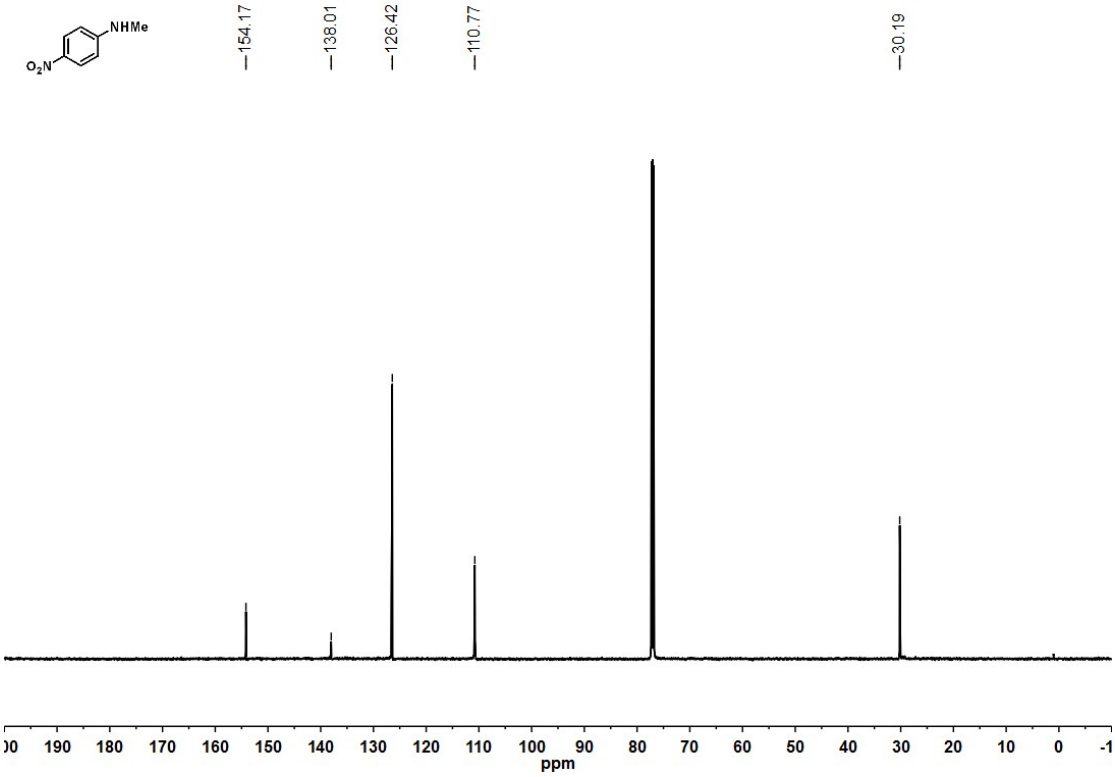
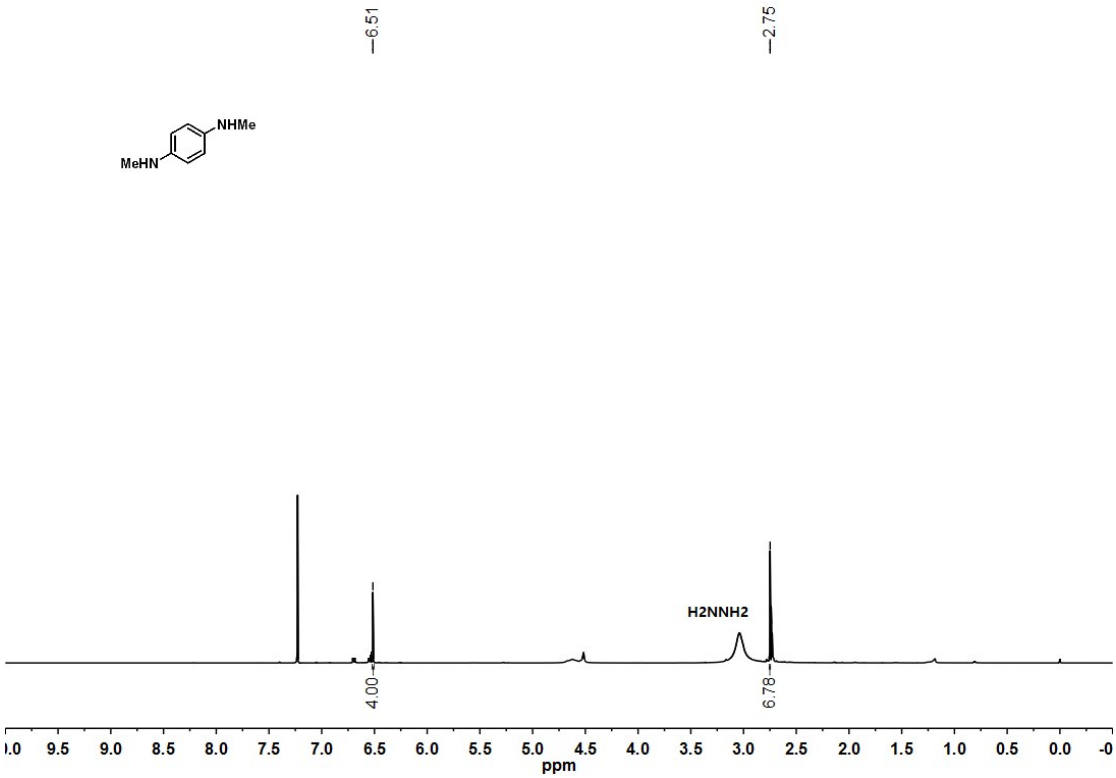
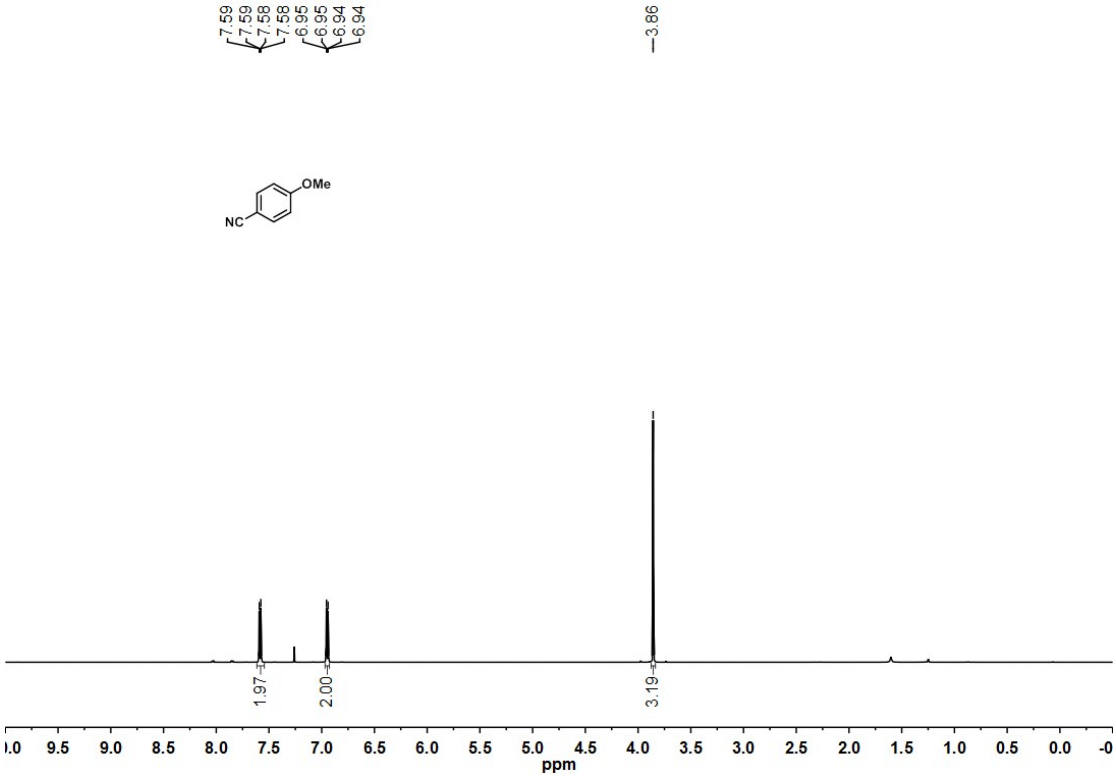


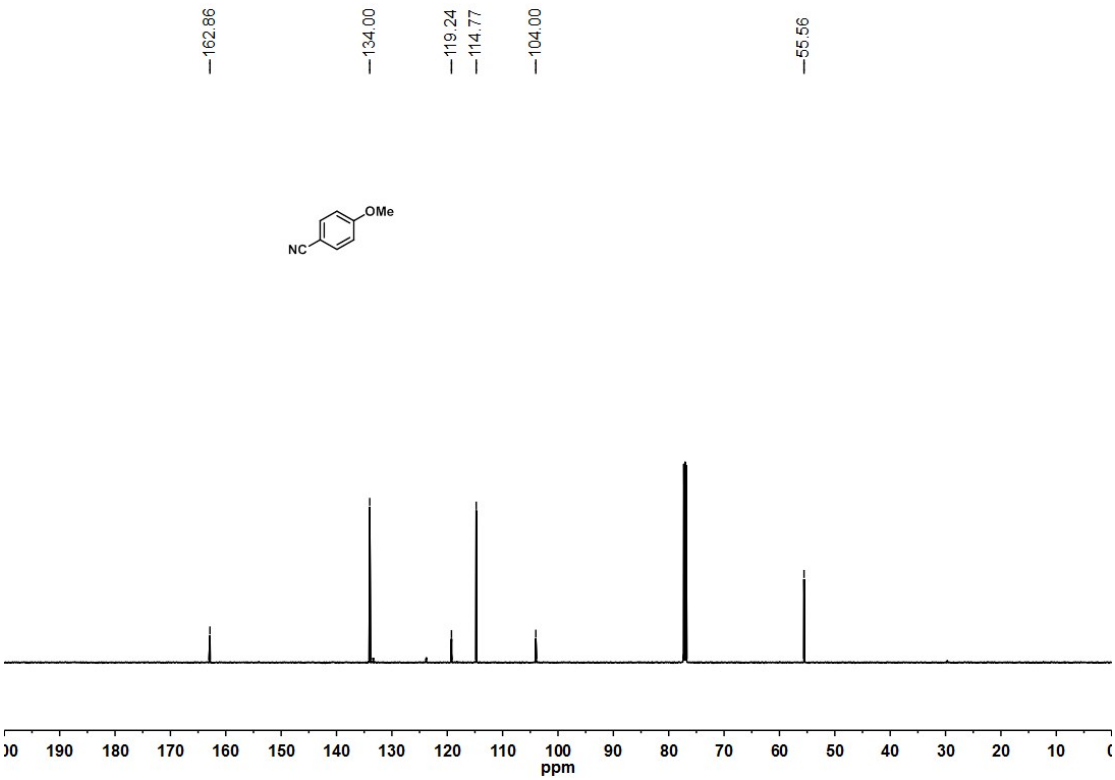
^{13}C NMR (151 M, $CDCl_3$) spectrum of **4m'**



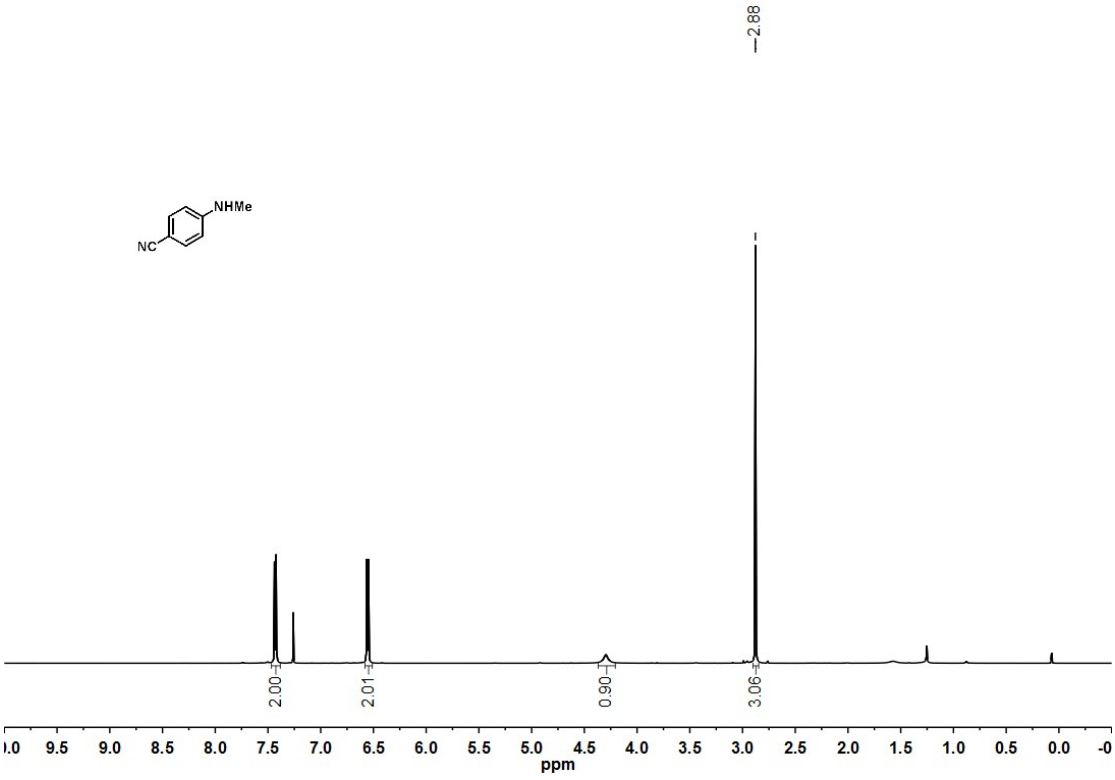
^{1}H NMR (600 MHz, $CDCl_3$ – one drop hydrazine hydrate) spectrum of **4m**



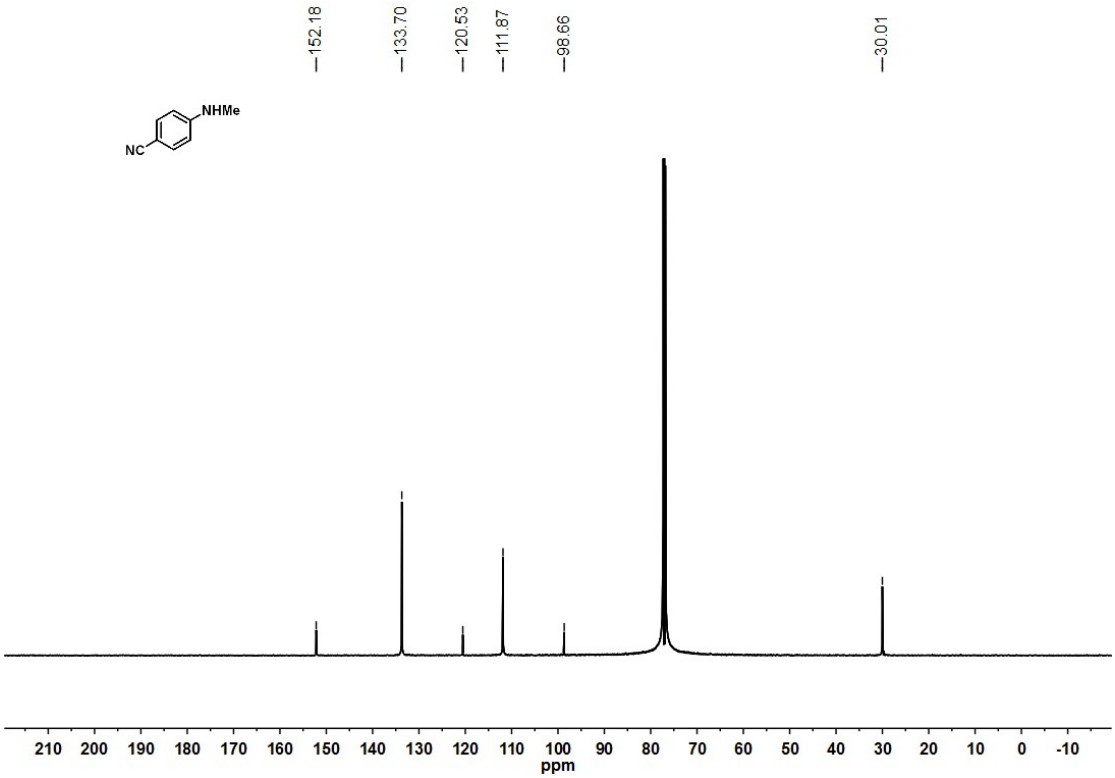
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4n'**



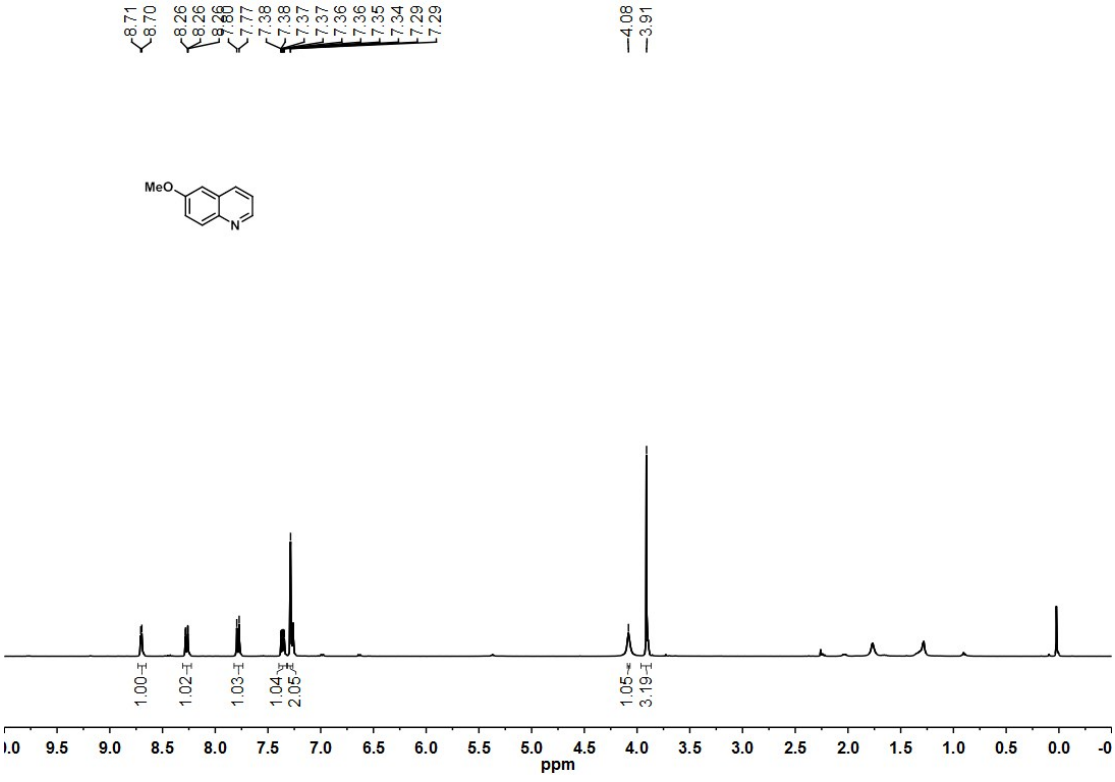
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4n'**



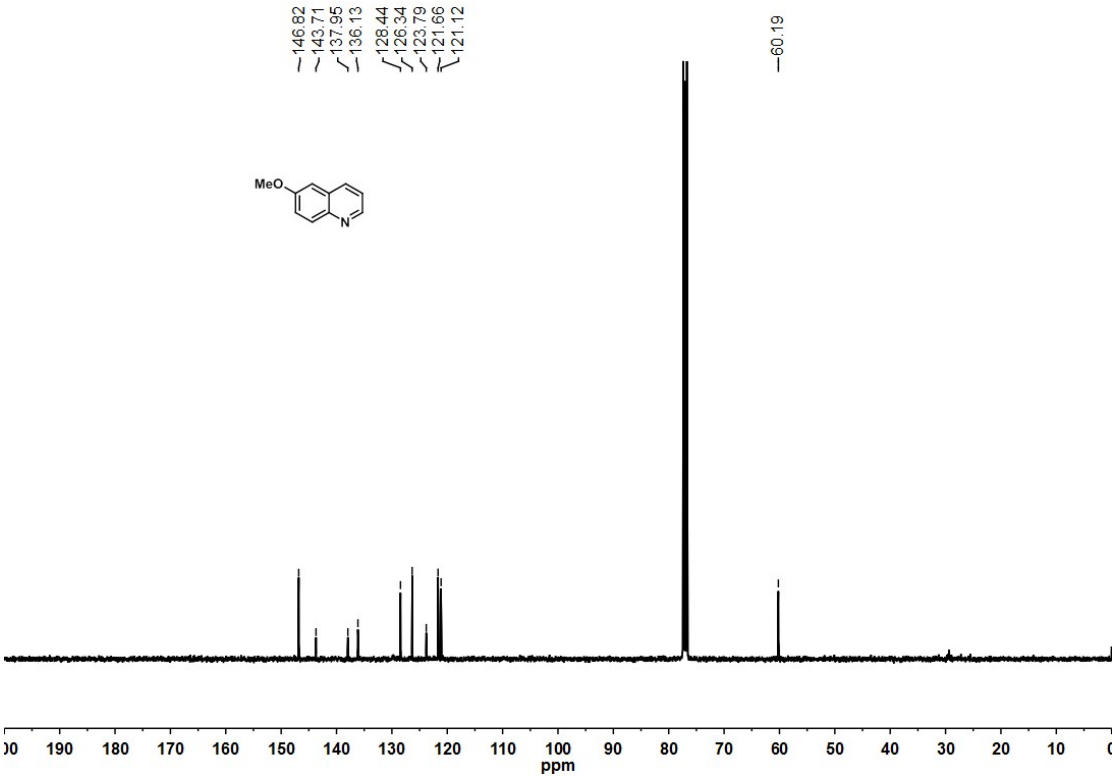
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4n**



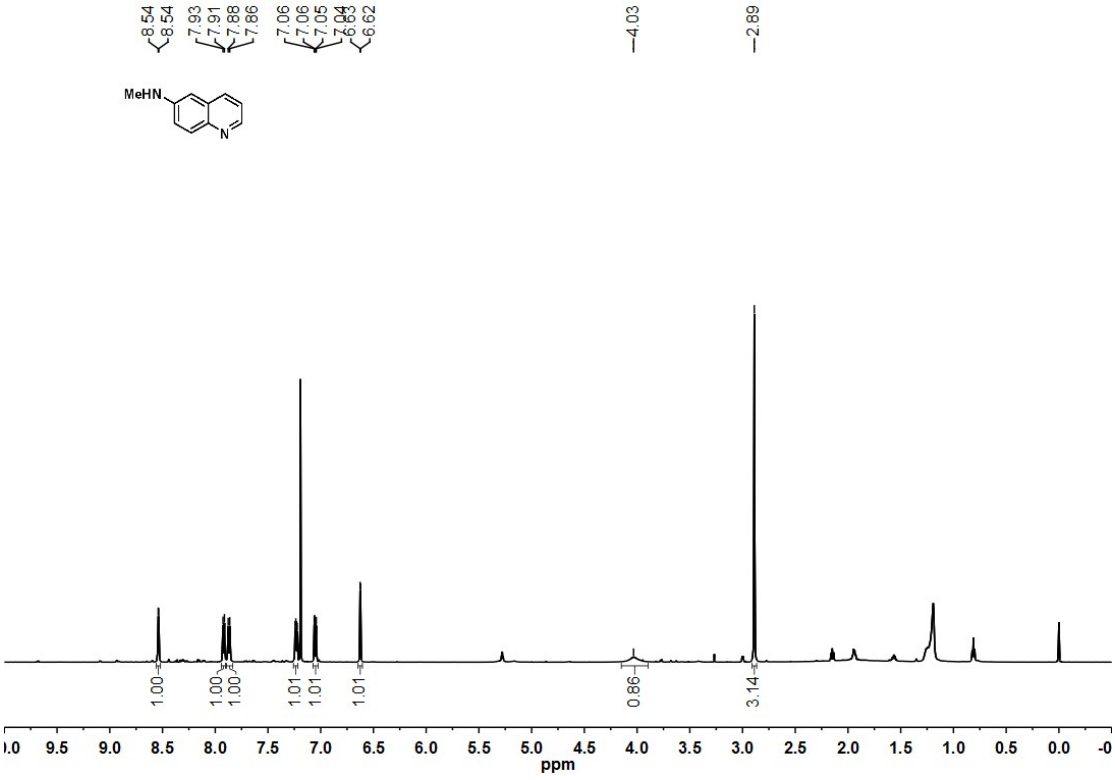
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4n**



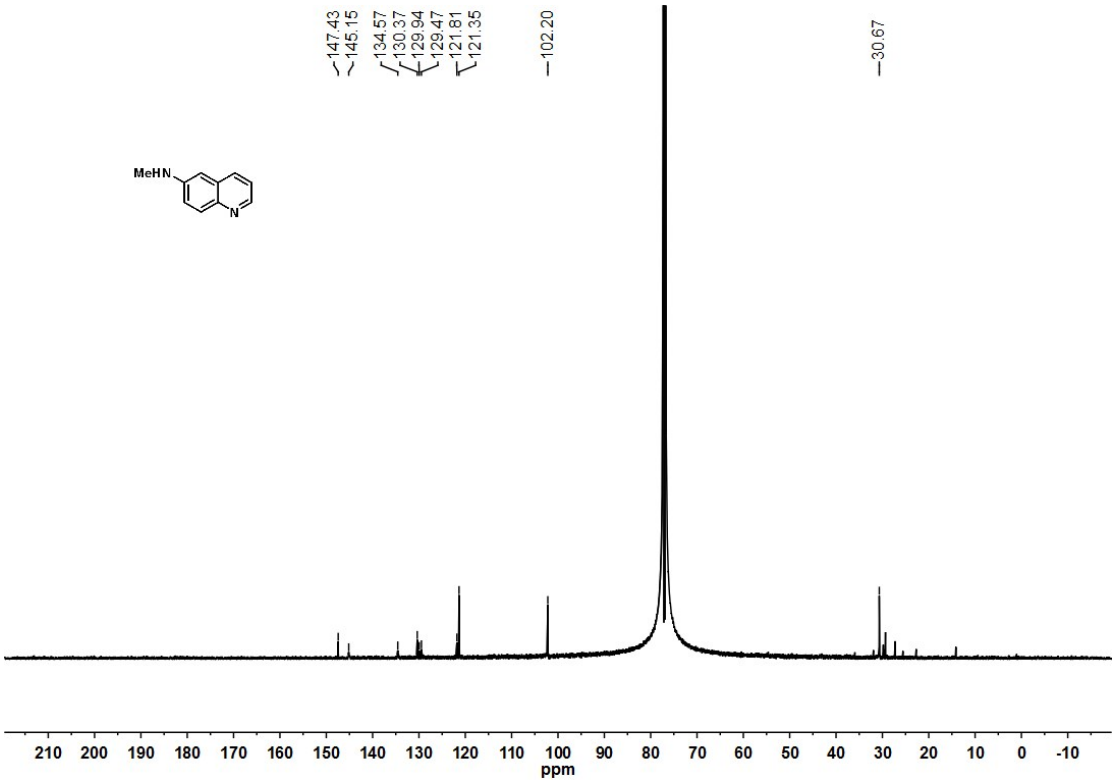
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4o'**



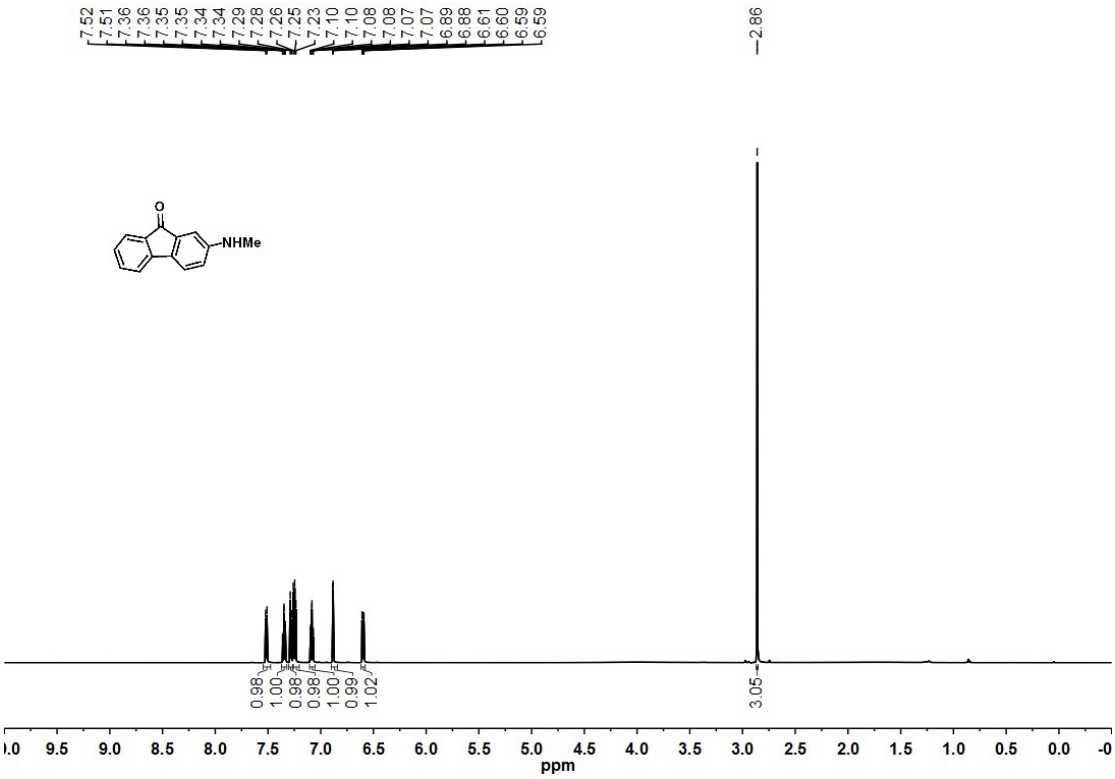
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4o'**



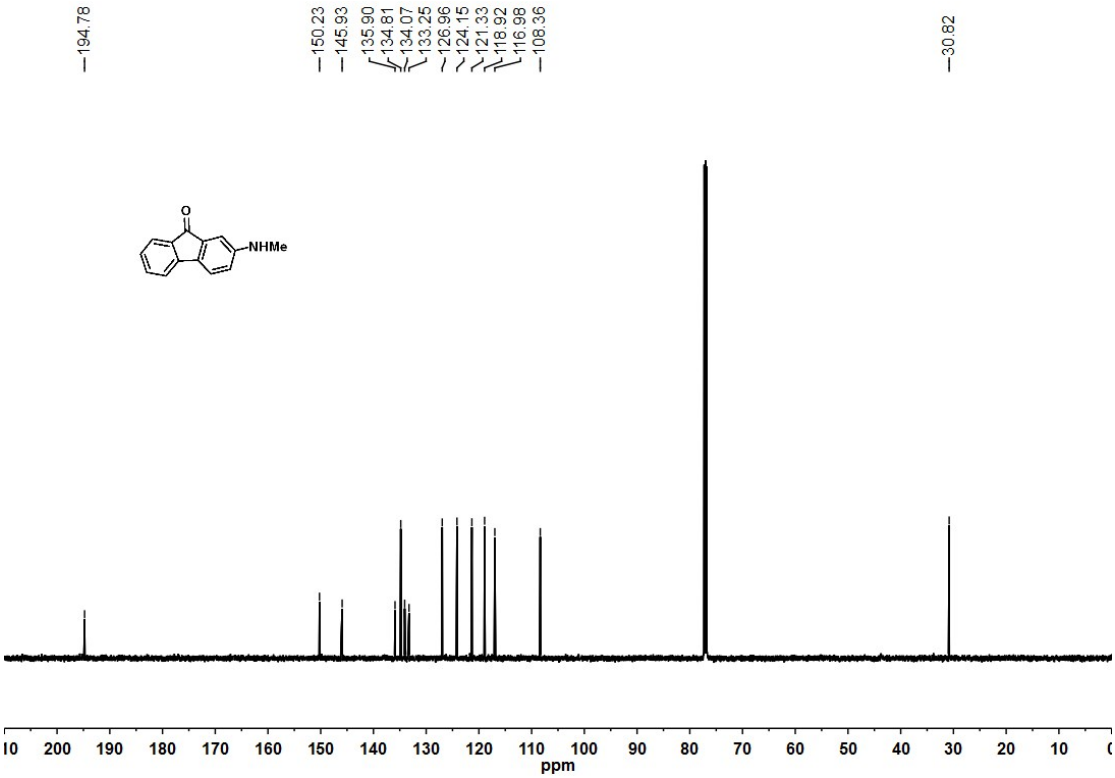
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4o**



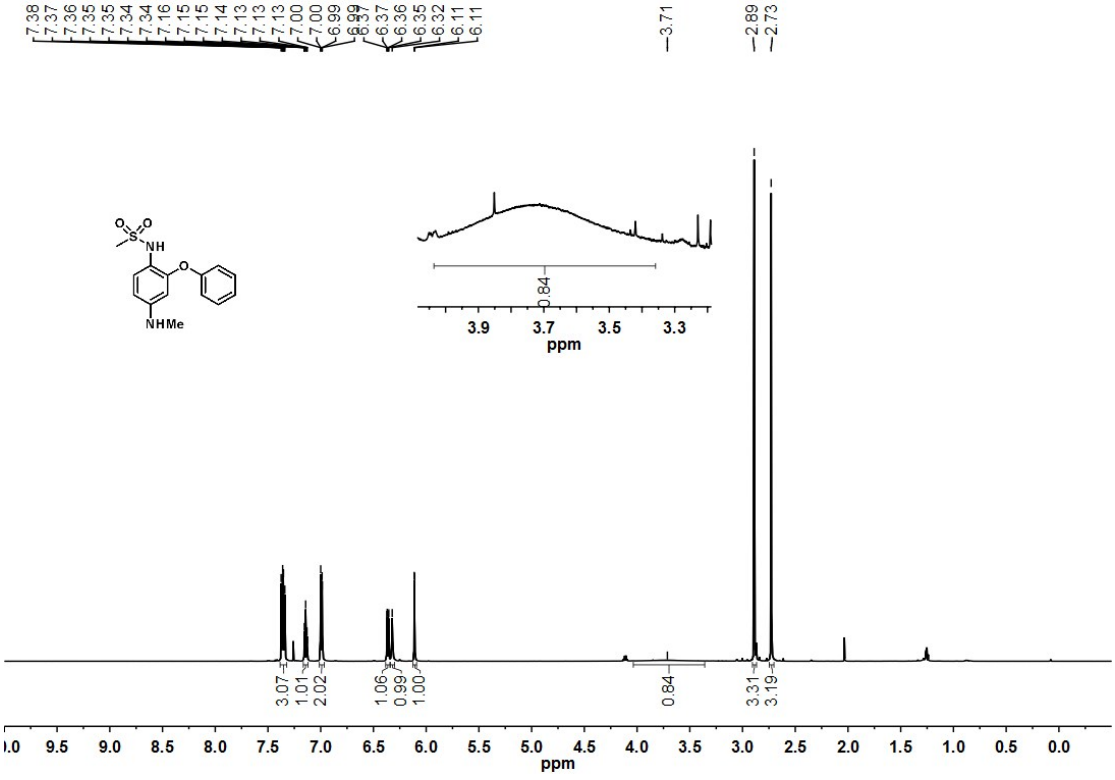
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4o**



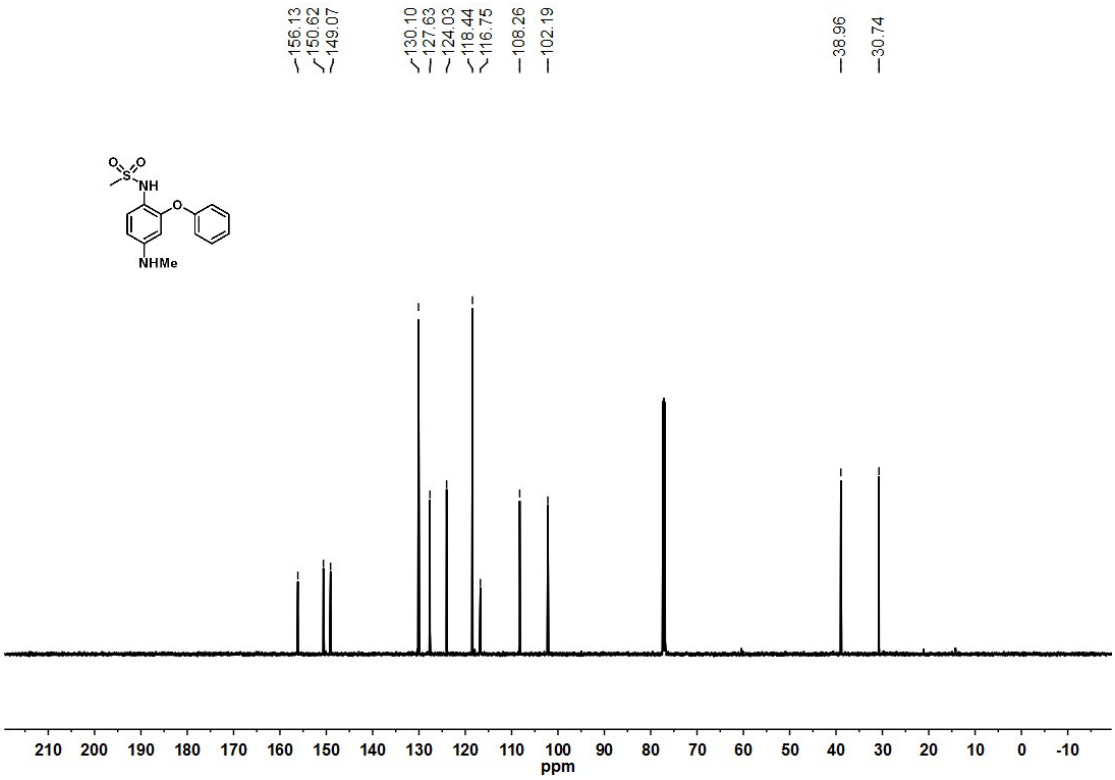
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4p**



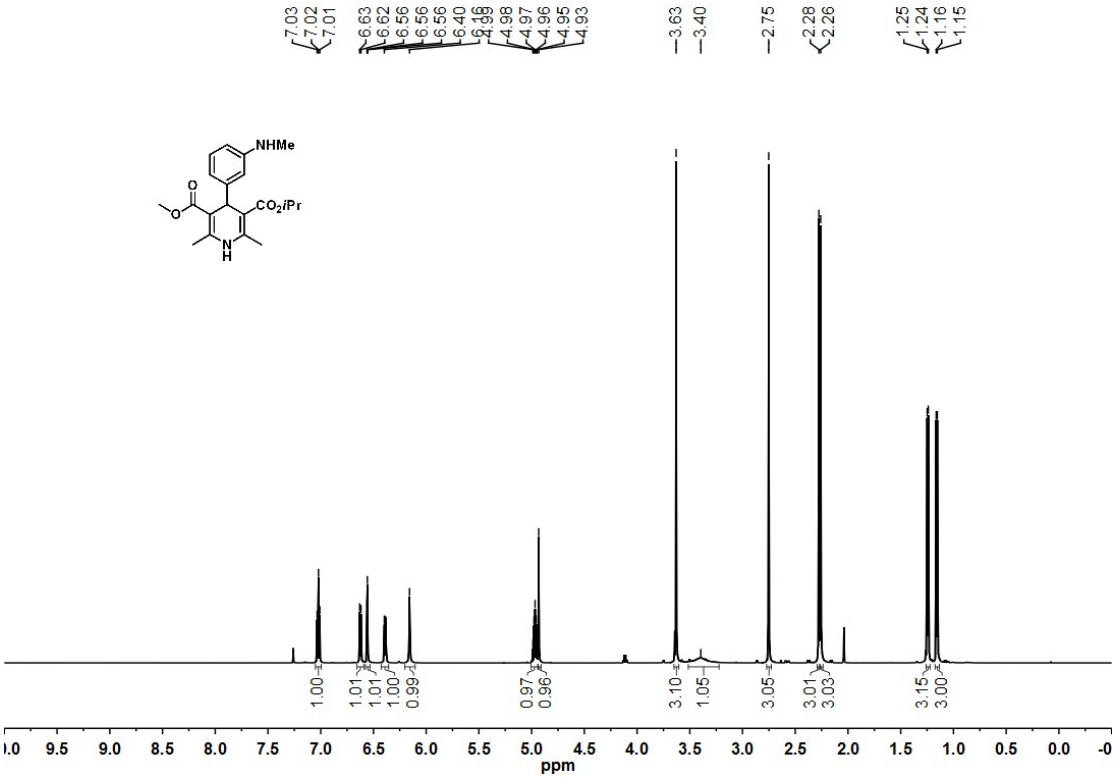
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4p**



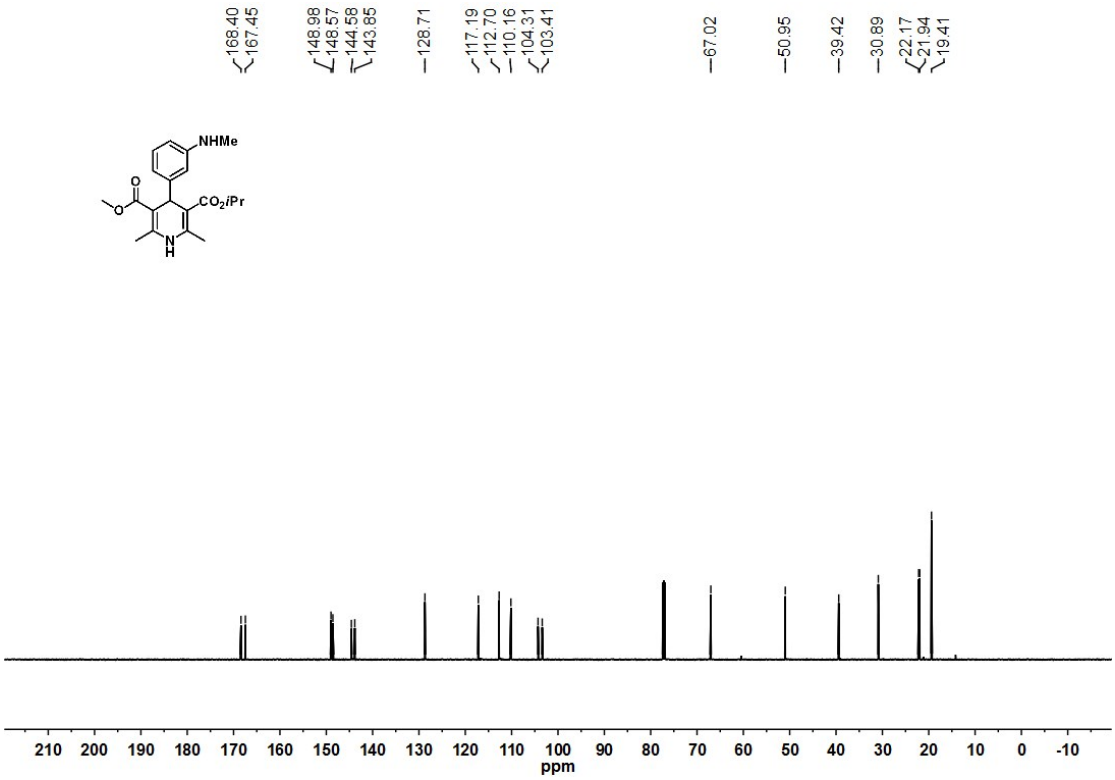
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4q**



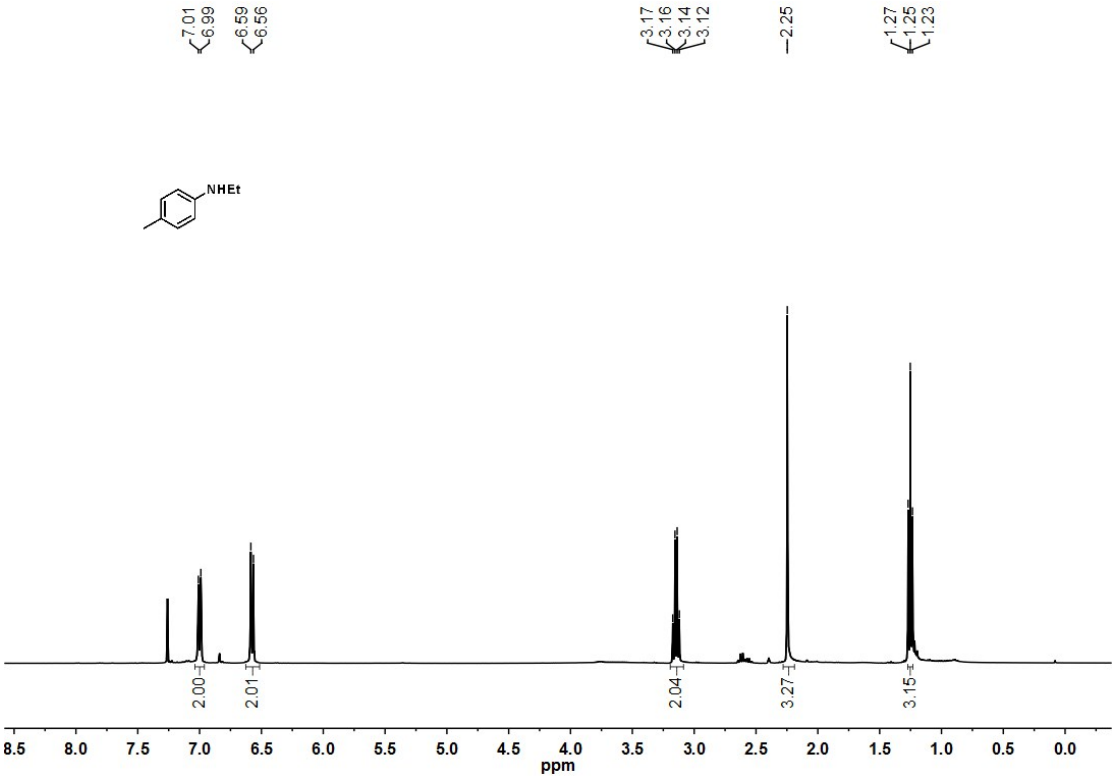
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4q**



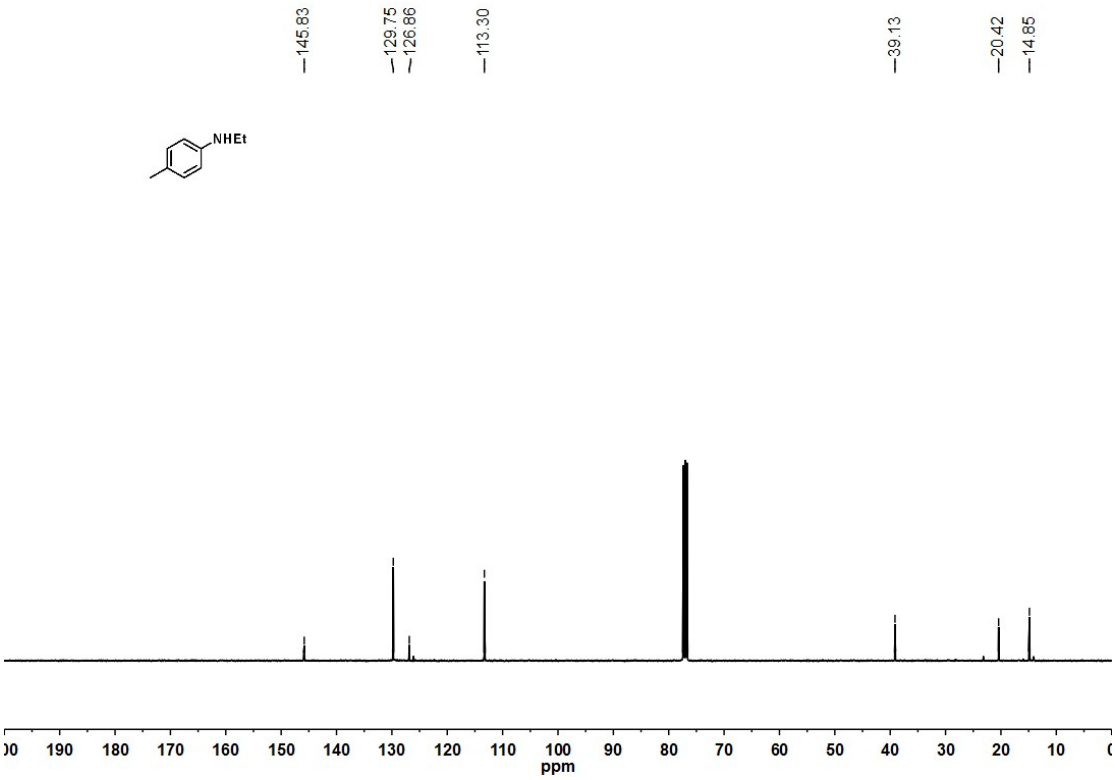
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4r**



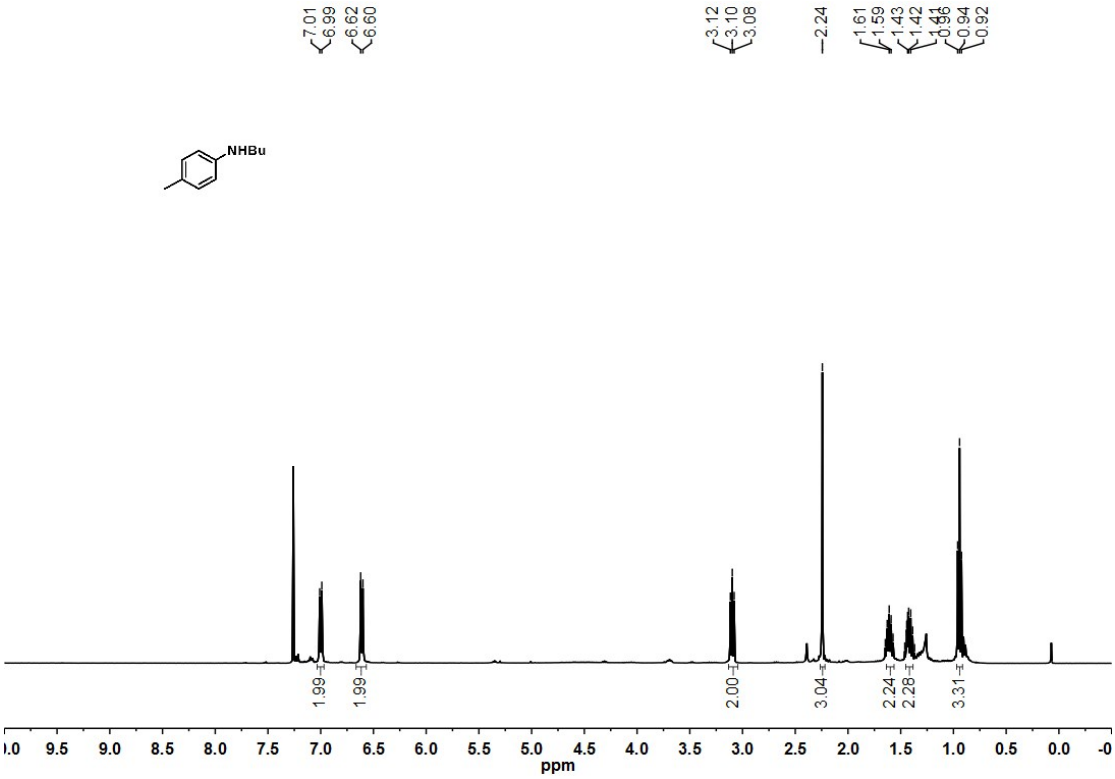
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4r**



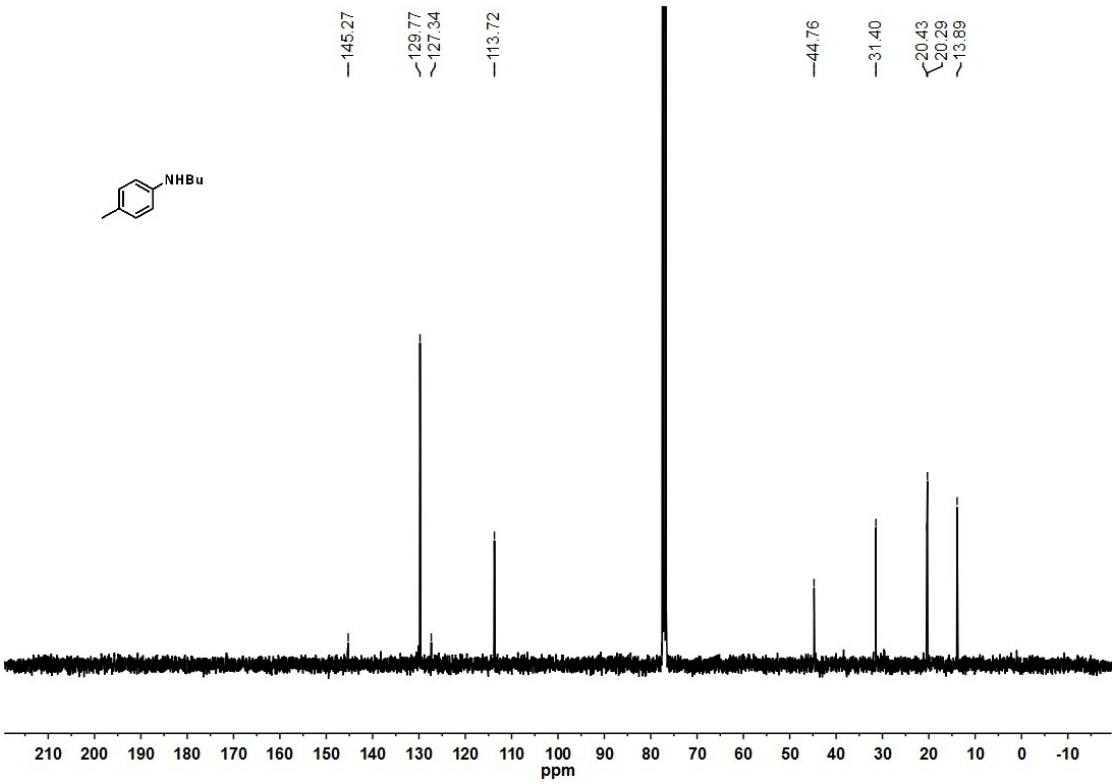
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6a**



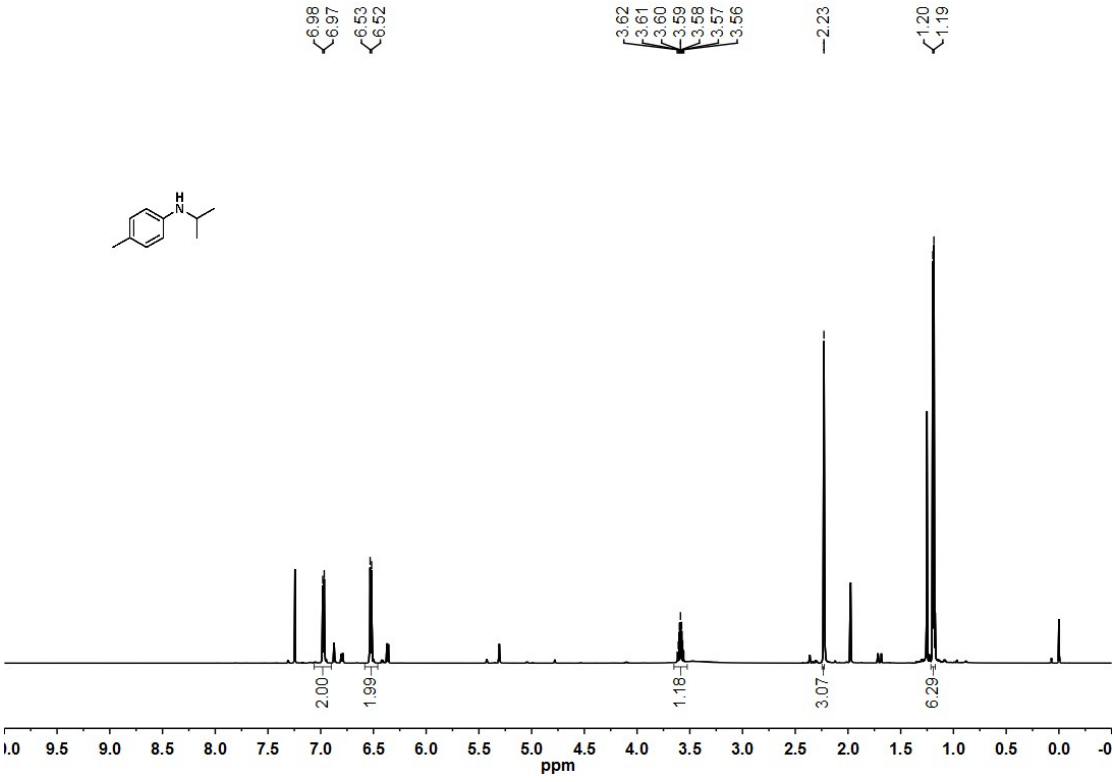
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **6a**



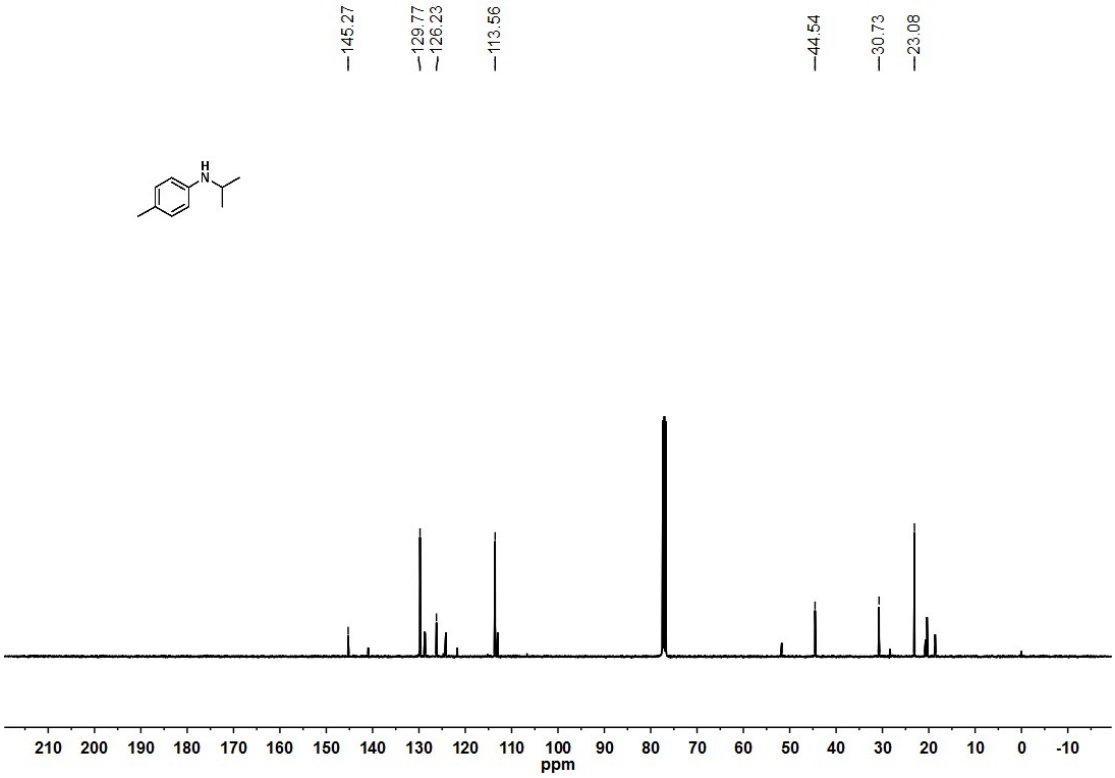
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6b**



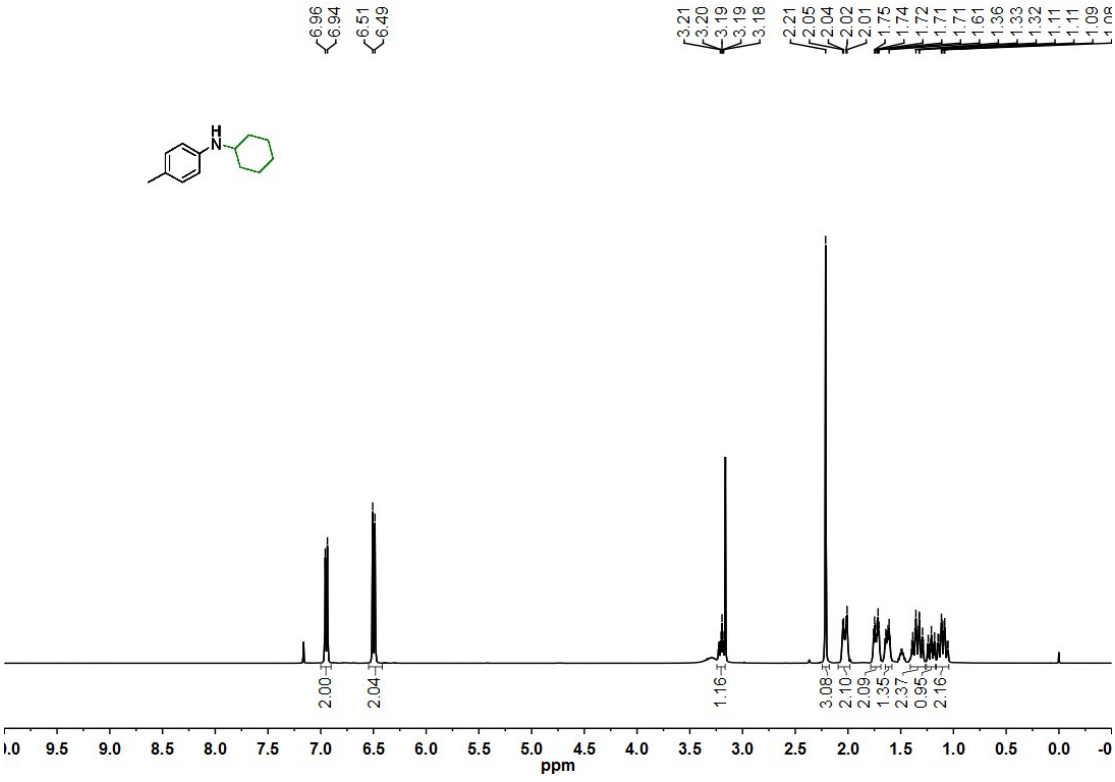
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **6b**



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6c**

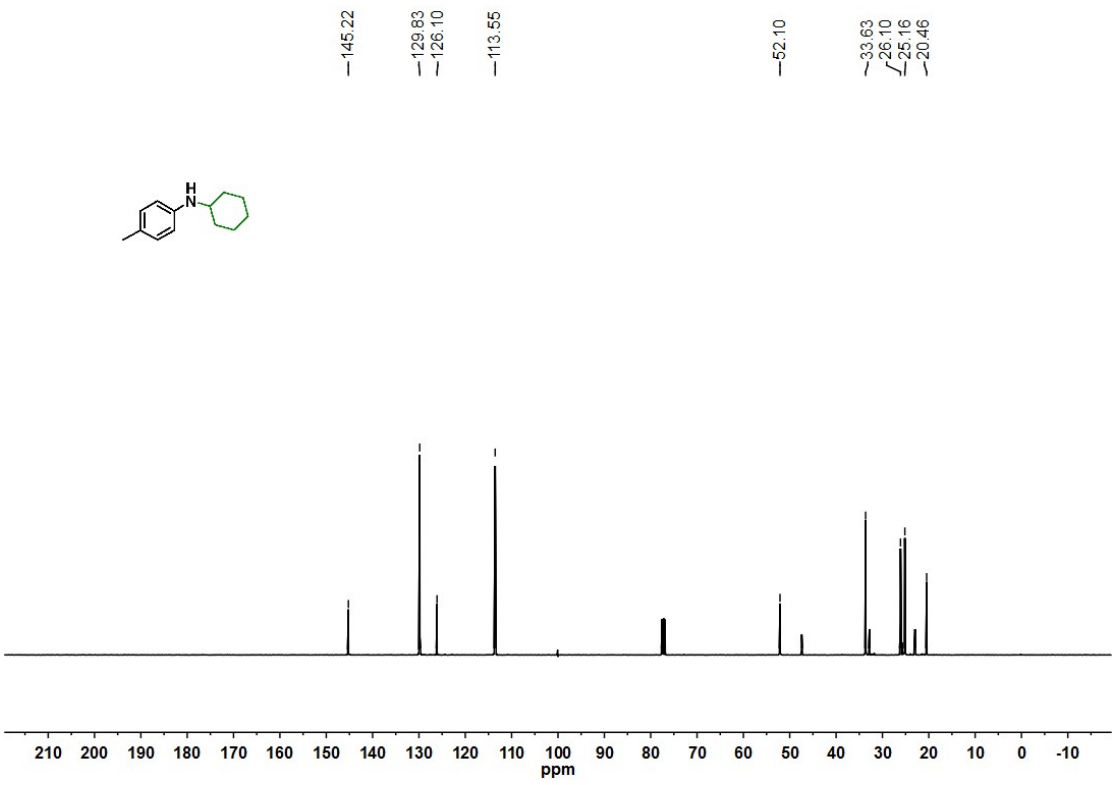


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **6c**

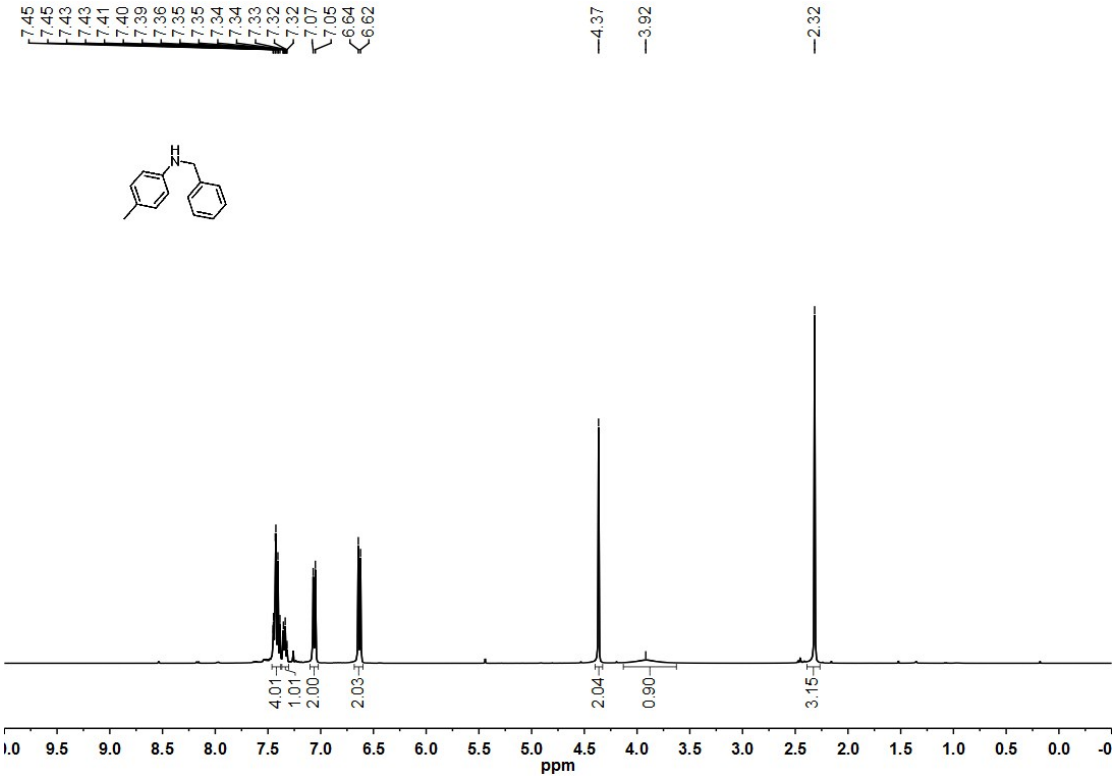


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6d**

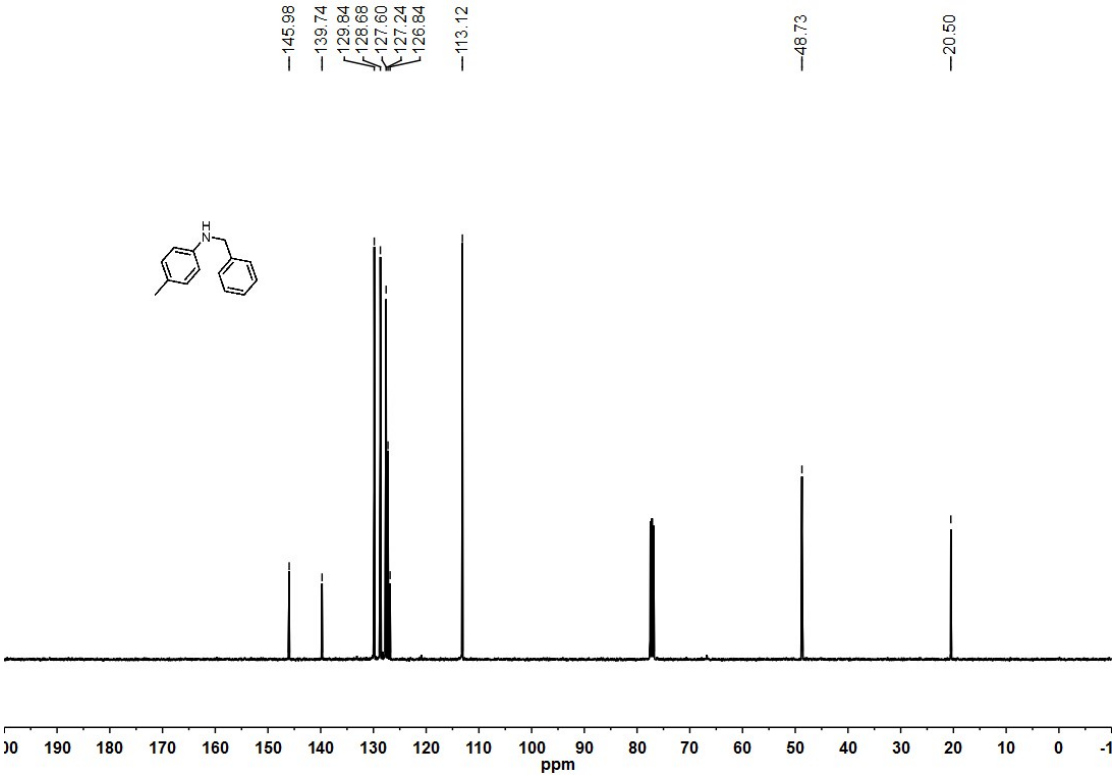
^{13}C NMR (101 MHz, CDCl



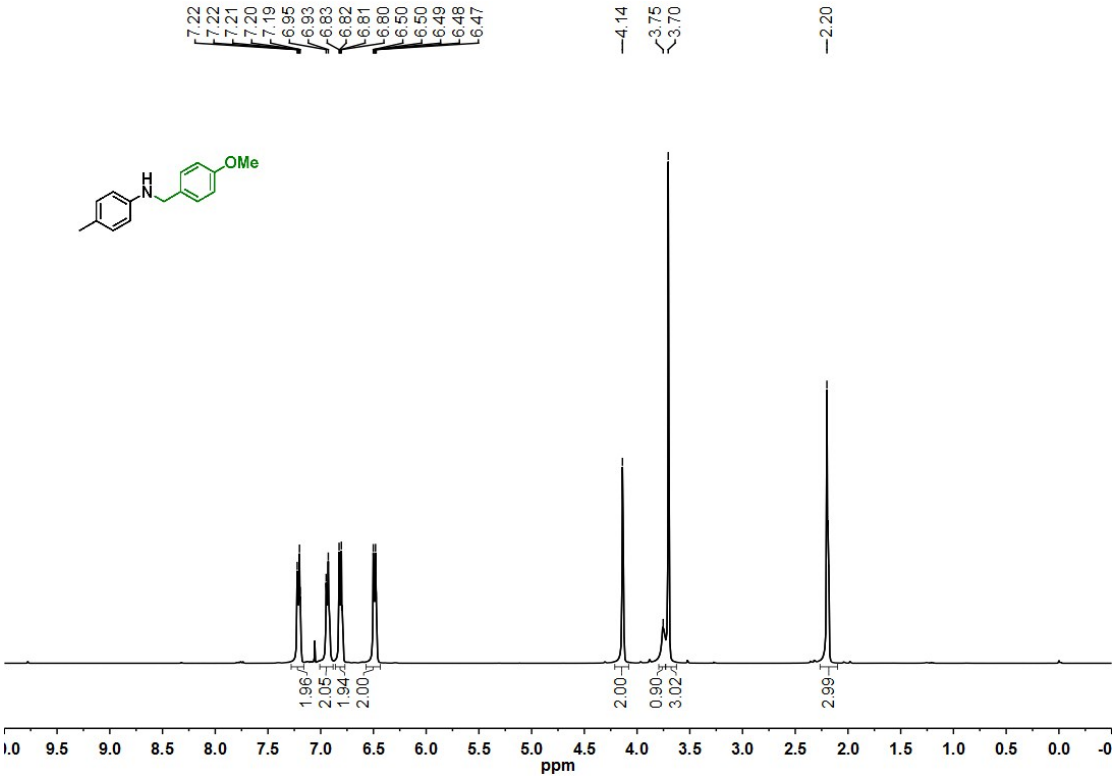
$_3$) spectrum of **6d**



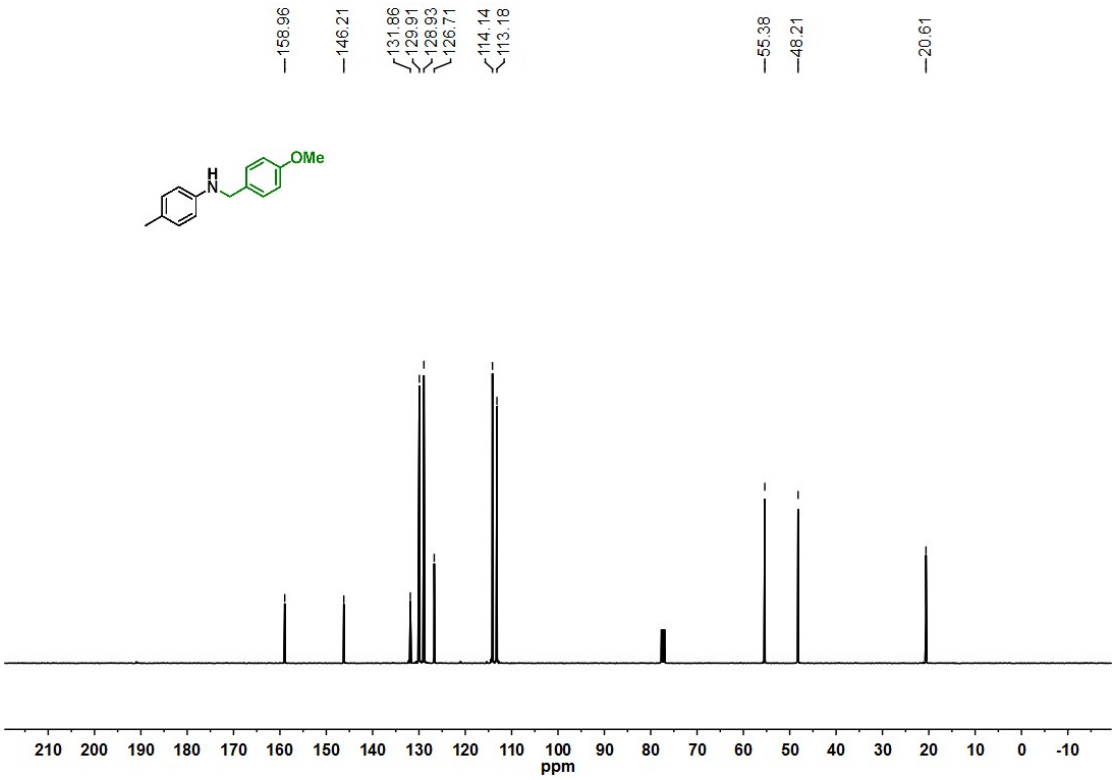
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6e**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **6e**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6f**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **6f**