Supporting Information

Pd-Catalyzed Imine Synthesis from Nitroarenes via Fe-H_2O under Electromagnetic Mill

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Table of Contents

1. General Information

The starting materials were obtained from commercial suppliers and used as received. The ferromagnetic rod used is SUS304 stainless steel, which is purchased from Donghuan Feiada Metal Materials Co., Ltd. and then processed by ourselves. Solvents were purchased from commercial suppliers. Purifications of reactions products were carried out by flash chromatography using Merck silica gel (40-63 μm). All mechanochemical reactions were carried out using grinding vessels in a Magnetic grinding machine. The reaction bottles used were commercially available 10 mL pressure bottle. The grinding medium is customized ferromagnetic rods (3.5 * 0.5 mm). 1H NMR (400 MHz), 13C NMR (100 MHz) were measured on a Brucker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, δ) downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), etc. Splitting patterns that could not be interpreted or easily visualized are designated as multiple states (m). Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

About the magnetic grinding used: The magnetic grinding machine (Figures S1, S2) is self-developed and has not yet been put into commercial use, and the instrument consists of two parts, the working room (left blue part of the picture) and the console (right part of the picture). The left cavity is the main working part. In terms of working principle, four square magnets rotate around the cavity to form a rotating magnetic field, which drives the ferromagnetic rod to move. The magnetic field strength is about 0.2 T.

Figure S1. Magnetic abrasive equipment

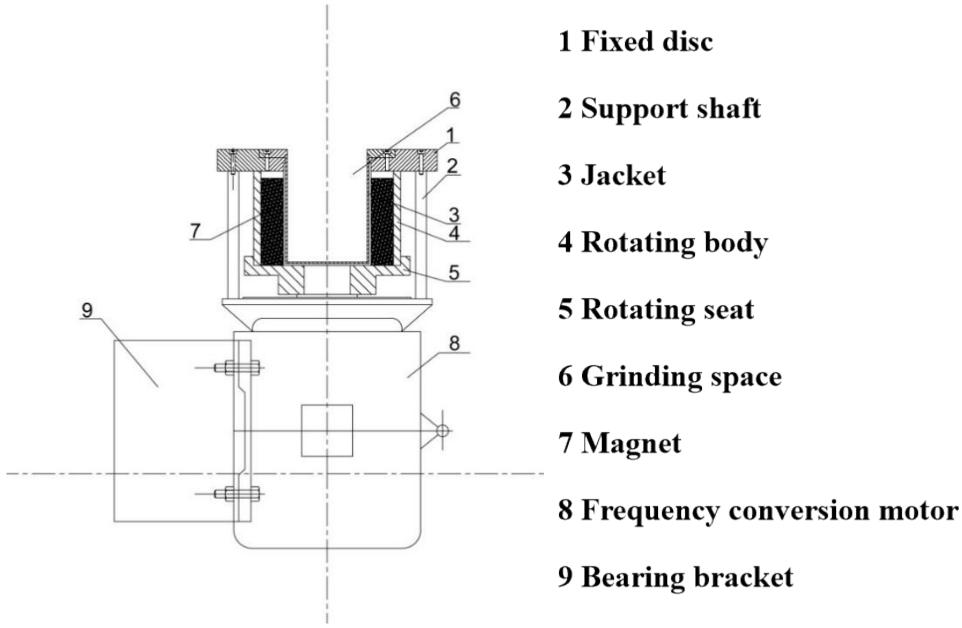
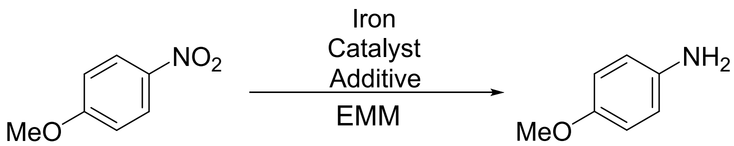


Figure S2. Plan view of magnetic ginding equipment

2. Condition Optimization

Table S1. Optimization of the nitro reduction reaction[a,c]



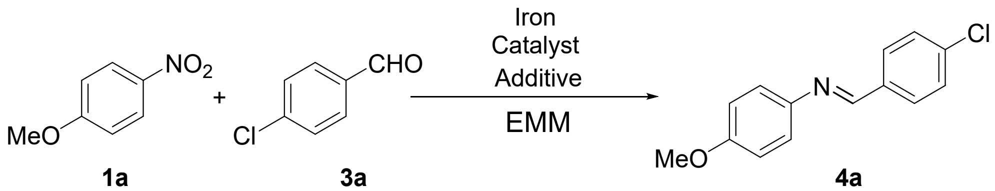
1a **2a**

Entry	Catalyst	Additive 1	Additive 2	Yield[b]/%
1	-	-	H_2O	44
2	-	K_3PO_4•$3H_2O$	-	20
3	$Pd(OAc)_2$ (2 mol%)	-	H_2O	39
4	**$Pd(OAc)_2$ (2 mol%)**	**K_3PO_4•$3H_2O$**	**-**	**60**
5	$Pd(OAc)_2$ (2 mol%)	K_3PO_4	H_2O	35
6	$Pd(OAc)_2$ (2 mol%)	K_3PO_4•$3H_2O$	1,4-Dioxane	60
7	$Pd(OAc)_2$ (5 mol%)	K_3PO_4•$3H_2O$	1,4-Dioxane	62
8	$PdCl_2$(dppf) (2 mol%)	K_3PO_4•$3H_2O$	-	30
9[c]	$Pd(OAc)_2$ (2 mol%)	K_2HPO_4	-	trace
10[c]	$Pd(OAc)_2$ (2 mol%)	$NaHCO_3$	-	N.D.

[a] Conditions: **1a** (1 mmol), Iron (3 mmol), Additive 1 (2 mmol), Additive 2 (0.1 mL), in a pressure-resistant bottles (10 mL) with SUS304 stainless steel rods (7 g), EMM at 50 Hz, 3 h. [b] Isolated yields. [c] Additive 1 (3 mmol).

As shown in Table S1, first focused on a mixture of **1a** and H_2O using iron as reductant to obtain the desired 4-methoxyaniline (**2a**) (entry 1), under 50 Hz in pressure-resistant bottles (10 mL) with SUS304 stainless steel rods of 0.3*5 mm. After using K_3PO_4•$3H_2O$ instead of water, although the yield of aromatic amine products is low, it produces fewer by-products (entry 2). Except for aromatic amines, only azoxy compounds that may be intermediates in the reaction pathway were detected.

Table S2. Optimization of the synthesis conditions of imines[a,c]

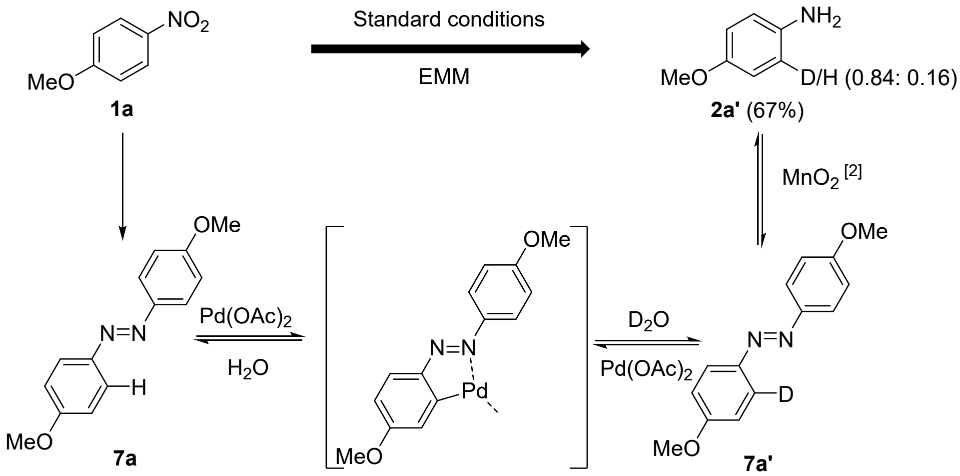


Entry	Catalyst / 2 mol%	Additive	Yield[b]/%
1	**$Pd(OAc)_2$**	**K_3PO_4•$3H_2O$**	**95**
2	$PdCl_2$(dppf)	K_3PO_4•$3H_2O$	82
3[c]	$PdCl_2$(dppf)	K_3PO_4•$3H_2O$	47
4	$Pd(OAc)_2$	K_3PO_4	N.D.
5	-	K_3PO_4•$3H_2O$	34

[a] Conditions: **1a** (1 mmol), **3a** (1.5 mmol), Iron (3 mmol), Catalyst (0.02 mmol), Additive (2 mmol), in a pressure-resistant bottles (10 mL) with SUS304 stainless steel rods (7 g), EMM at 50 Hz, 3 h. [b] Isolated yields. [c] The feed ratio of 1a to 3a is 1:1.

Subsequently, we investigated the reduction-condensation in one step using nitroarenes and aldehyde under the optimal conditions outlined in Table S1. To our delighted, the desired imine **4a** was obtained in 95% yield (entry 1, Table S2).

3. Deuteration Experiment

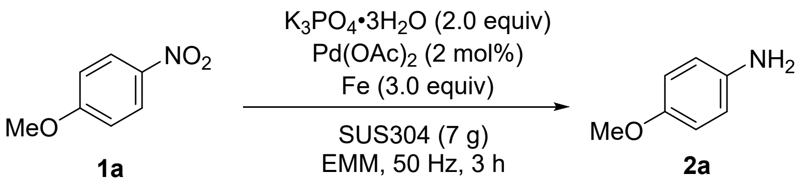


Scheme S1. Deuterium substitution experiment

To further investigate the reaction mechanism, several control experiments were conducted. When D_2O (6 equiv.) was added to the reaction system, it was observed that deuterium atom was installed on the benzene ring while it was detected in the amino group of **1a** which might be exchanged with H_2O during the work up (Scheme S1). According to the previous work,[1] it can be concluded that the interaction between the palladium catalyst and azoxy compounds or azo compounds via C-H bond activation results in the exchange of hydrogen on the benzene ring and hydrogen in water.

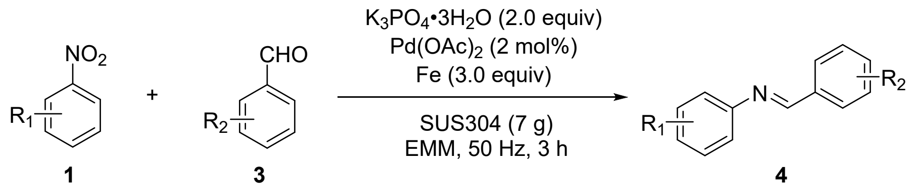
4. General Procedure for Synthesis

4.1 Procedure I: Reduction of Nitro Group



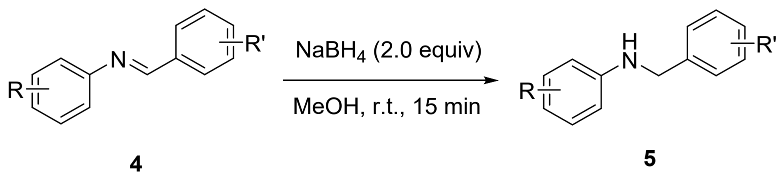
To a 10 mL pressure bottle, 1-methoxy-4-nitrobenzene (**1a**, 1.0 mmol), K_3PO_4•$3H_2O$ (2.0 equiv., 2.0 mmol), $Pd(OAc)_2$ (2 mol%, 0.02 mmol), Iron powder (3.0 equiv., 3 mmol), and SUS304 stainless steel (7 g, 0.3 × 5 mm) were added. Put it in magnetic grinder and adjust the frequency to 50 Hz. After 3 h, the mixture was dissolved in ethyl acetate. Then purified by flash chromatography (PE: EA = 5: 1) to give compound 4-methoxyaniline (**2a**, 73.95 mg, 60% yield).

4.2 Procedure II: Synthesis of Schiff Bases



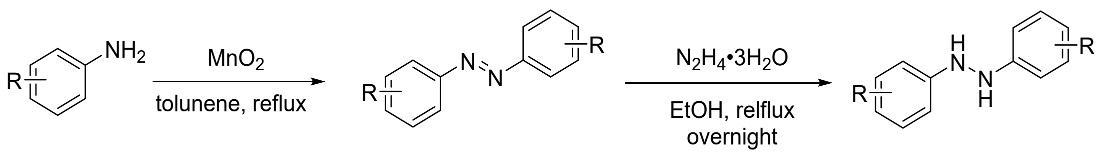
To a 10 mL pressure bottle, nitroaromatic hydrocarbon (1.0 mmol), aromatic aldehyde (1.5 equiv., 1.5 mmol), K_3PO_4•$3H_2O$ (2.0 equiv., 2 mmol), $Pd(OAc)_2$ (2 mol%, 0.02 mmol), Iron powder (3.0 equiv., 3 mmol), and SUS304 stainless steel (7 g, 0.3 × 5 mm) were added. Put it in magnetic grinder and adjust the frequency to 50 Hz. After 3 h, the mixture was dissolved in ethyl acetate. Then evaporated and purified by recrystallization to give compound Schiff base.

4.3 Procedure III: Reduction and transformation of Schiff bases



Crude products of Schiff base (**4**), $NaBH_4$ (2 equiv., 2 mmol) and MeOH (5 mL) were placed in 25 mL round-bottom flask. After stirring for 15 minutes, the mixture was dissolved in ethyl acetate. Then remove the inorganic salt from the mixture with water. The organic phase was combined, dried over Na_2SO_4, evaporated and purified by flash chromatography (PE: EA) to give compound **5**.

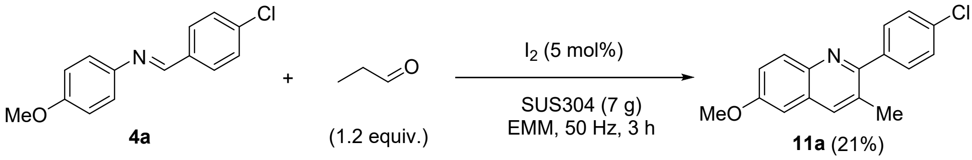
4.4 Procedure IV: Preparation of azobenzene (7a) and hydroazobenzene (8q) [1]



To a solution of amine (1.0 g) in toluene (60 mL), activated manganese (IV) oxide (10 equiv.) was added. The mixture was heated at reflux and monitored by TLC. Then, the reaction mixture was filtered and washed with toluene for three times. The filtrate was subjected to vacuum to afford the products which was directly used in the next step. Or the crude product mixture was purified by flash column chromatography (Hexane:EtOAc = 19:1) to obtain pure azobenzene compounds. The above crude product was dissolved in EtOH (50 mL), then hydrazine hydrate solution (25 mL, 88%) was added at room temperature. The reaction mixture was refluxed in a sealed tube for overnight and then poured into ice water. The formed precipitated was filtered and dried under vacuum. The crude product was crystallized from 95% EtOH to give the desired hydroazobenzene product.

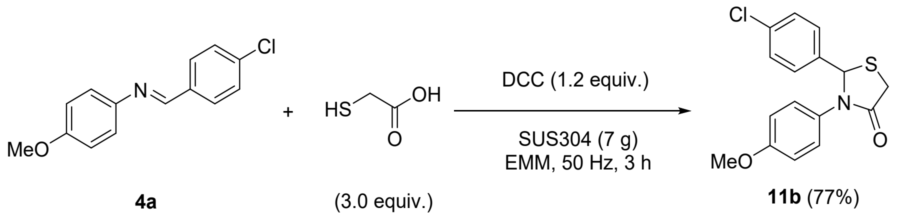
4.5 Procedure V: Synthesis procedures for application products (9a-9d)

9a: [3]



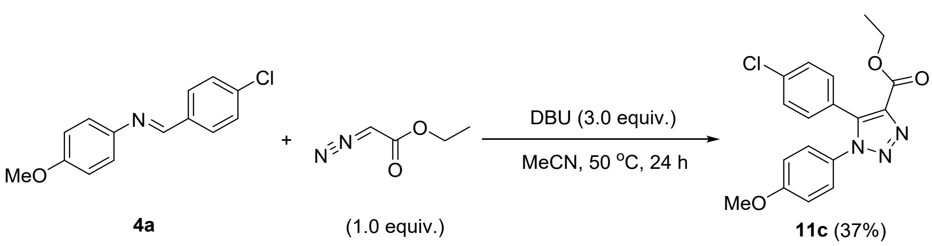
To a 10 mL pressure bottle, 1-(4-chlorophenyl)-*N*-(4-methoxyphenyl)methanimine (**4a**, 1.0 mmol), propionaldehyde (1.2 equiv., 1.2 mmol), I_2 (5 mol%, 0.05 mmol) and SUS304 stainless steel (7 g, 0.3 × 5 mm) were added. Put it in magnetic grinder and adjust the frequency to 50 Hz. After 3 h, the mixture was dissolved in ethyl acetate. Then purified by flash chromatography to give compound 2-(4-chlorophenyl)-6-methoxy-3-methylquinoline (**11a**) (59.58 mg, 21% yield).

9b: [4]



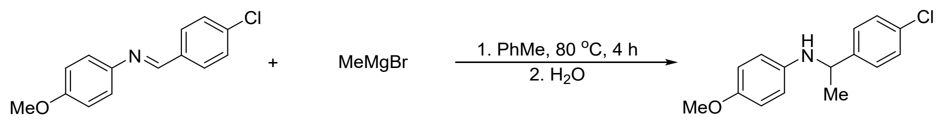
To a 10 mL pressure bottle, 1-(4-chlorophenyl)-*N*-(4-methoxyphenyl)methanimine (**4a**, 1.0 mmol), 2-mercaptoacetic acid (3.0 equiv., 3.0 mmol), DCC (1.2 equiv., 1.2 mmol) and SUS304 stainless steel (7 g, 0.3 × 5 mm) were added. Put it in magnetic grinder and adjust the frequency to 50 Hz. After 3 h, the mixture was dissolved in ethyl acetate. Then purified by flash chromatography to give compound 2-(4-chlorophenyl)-3-(4-methoxyphenyl)thiazolidin-4-one (**11b**) (246.25 mg, 77% yield).

9c: [5]



To a stirred solution of imine (1.2 mmol) in MeCN (2.5 mL) was added ethyl diazoacetate (1.0 mmol) at the specified temperature. The mixture was stirred for 2 min and then DBU (1.5 mmol) was added dropwise. Stirring was continued until the starting material disappeared completely upon inspection by TLC. The solvent was removed under reduced pressure, and the product was purified by flash column chromatography on silica gel (eluting with hexanes/ethyl acetate = 4:1 to 2:1) to give the corresponding 1,2,3-triazoles as a yellowish solid (11c, 132.38 mg, 37% yield). The solid was recrystal lized from hexanes/EtOAc.

9d: [6]

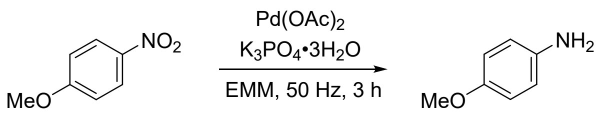


Add methylmagnesium bromide (2.0 mmol) dropwise to a toluene solution of imine (1.0 mmol) (25 mL) at -30 °C, stir the mixture for 30 minutes, then heat and stir at 80 °C for 4 hours, and quench with 1 mL of water. The solution is dried over anhydrous sodium sulfate and concentrated under pressure. Then purified by flash chromatography to give compound *N*-(1-(4-chlorophenyl)ethyl)-4-methoxyaniline (**11d**) (125.64 mg, 48% yield).

5. The Influence of Grinding Media on Experiments

In addition, we also studied the effect of the material and size of grinding media in grinder. The results show that the addition of iron powder plays an important role in the reaction system, and the size of the grinding medium had a great influence on the collision efficiency. Through the screening results, we selected 304 stainless steel of 0.3*5 mm (diameter 0.3 mm and length 5 mm) as the grinding medium (Table S3).

Table S3. Screening of grinding media *a*



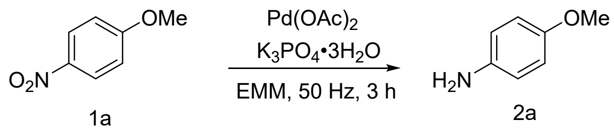
Entry	Weight of ferromagneticrod	Material of abrasive media	Frequency/Hz	diameter*length	Yield^{b}/%
1	7g	304 stainless steel & iron powder	50	0.2*3	44
2	7g	304 stainless steel & iron powder	50	0.3*5	60
3	7g	304 stainless steel & iron powder	50	1*5	20
4	7g	pure iron (99.9%) & iron powder	50	1*5	24
5	7g	pure nickel (99.95%)	50	1*5	NR

^{a} Conditions: 1 (1.0 mmol), base (2.0 mmol), Iron powder (3.0 mmol), in a pressure-resistant bottles (10 mL) with ferromagnetic rods (7 g), EMM at 50 Hz, 3 h. ^{b} Isolated yields.

6. Advantages of Electromagnetic Grinding

We also explore the comparison of the experimental methods of electromagnetic grinding, solvent reaction and ball milling. However, the reaction conditions of solvent and ball milling did not produce products, which further highlights the efficiency of electromagnetic grinding (Table S4).

Table S4. Comparison between Electromagnetic grinding and other reaction methods[a]



Entry	Reaction method	Addition	Solvent	T/°C	Yield[b]/%
1	EMM	304 stainless steel & iron powder	-	-	60
2	Mixing and stirring	agitator	-	100	NR
3	Mixing and stirring	agitator & iron powder	-	100	NR
4	Mixing and stirring	304 stainless steel & iron powder	1,4-dioxance	100	NR
5	ball milling	304 stainless steel & iron powder	-	-	NR
6	ball milling	agate	-	-	NR

[a] Conditions: 1 (1.0 mmol), base (2.0 mmol), Iron powder (3.0 mmol), ferromagnetic rods (7 g), EMM at 50 Hz, 3 h.
[b] Isolated yields.

7. Gas Chromatography Detection Experiment

In an argon atmosphere glove box, potassium phosphate trihydrate (2.0 equiv.) and 7 g for SUS304 stainless steel needles were added to a 20 mL ground reaction tube, sealed with a rubber stopper, and reinforced with sealing film and strapping. After the reaction is complete, extract the upper layer gas for gas chromatography analysis. The result is shown in Figure S3.

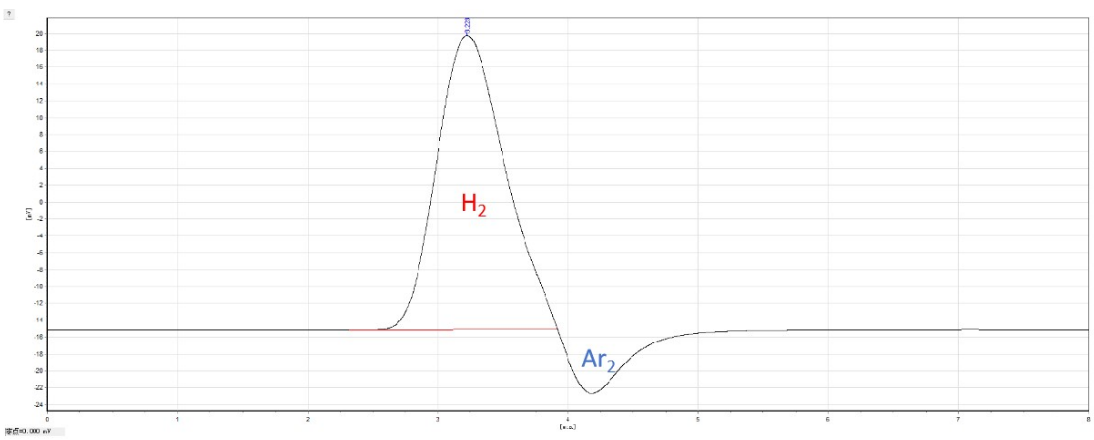


Figure S3. Gas chromatogram of the gas phase after reaction

8. XPS Spectrum Experiment of Iron Powder

The feeding and sampling in the experimental procedure were carried out in a glove box.

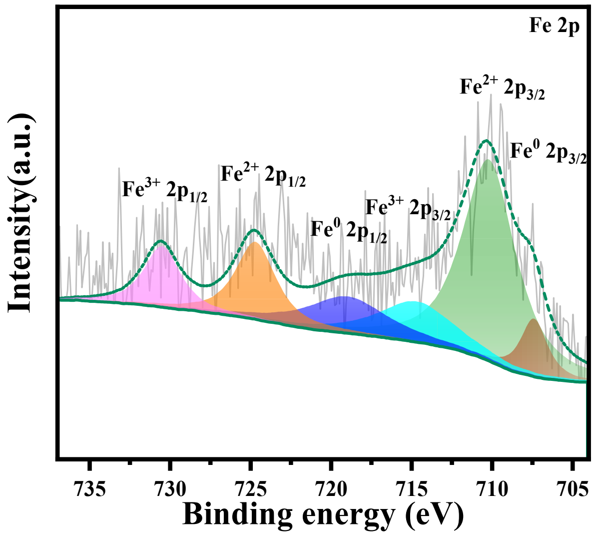
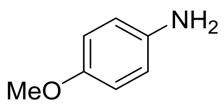


Figure S4. XPS pattern of the iron powder after reaction.

9. Analytical Data for the Products

2a 

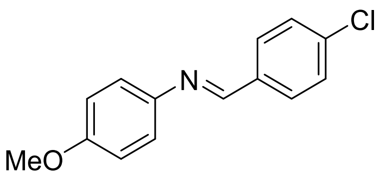
4-methoxyaniline [7]

C_7H_9NO. MW: 123.15 g·mol^{-1}. Colorless solid (73.89 mg, 60%). M.p. 46.3-47.8 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.75 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 9.2 Hz, 2H), 3.75 (s, 3H), 3.15 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 152.8, 139.8, 116.4, 114.8, 55.7.

MS(EI): m/z (%) 124 (7.43), 123 (90.20), 122 (3.07), 109 (8.06), 108 (100.00), 95 (2.80), 80 (43.96), 65 (8.25), 53 (20.72), 52 (12.82).

4a 

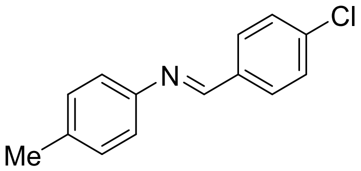
N-(4-chlorobenzylidene)-4-methoxyaniline [7]

$C_{14}H_{12}ClNO$. MW: 245.71 g·mol^{-1}. Yellow solid (233.42 mg, 95%). M.p. 124.2-126.4 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.44 (s, 1H), 7.84 (d, *J* =8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H) , 6.96 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 158.4, 156.5, 144.3, 136.8, 134.8, 129.6, 128.9, 122.2, 114.3, 55.4.

MS(EI): m/z (%) 247 (31.21), 245 (88.21), 230 (100.00), 201 (7.36), 167 (23.08), 139 (9.94), 122 (9.04), 107 (3.29), 92 (12.37), 77 (16.88).



4b

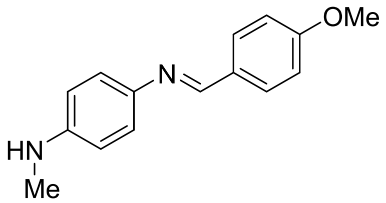
N-(4-chlorobenzylidene)-4-methoxyaniline [8]

$C_{14}H_{12}ClN$. MW: 229.71 g·mol^{-1}. Yellow solid (190.66 mg, 83%). M.p. 127.5-128.3 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.32 (s, 1H), 7.73 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8.4Hz, 2H), 7.10 (d, *J* = 8Hz, 2H), 7.04 (d, *J* = 8Hz, 2H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 158.0, 149.0, 137.1, 136.2, 134.9, 129.9, 129.1, 120.9, 21.1.

MS(EI): m/z (%) 231 (34.25), 230 (45.31), 229 (100.00), 228 (87.24), 214 (2.30), 165 (5.22), 118 (22.56), 91 (89.07), 65 (45.21), 51 (8.25).



4c

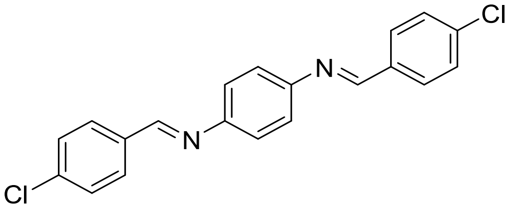
4-((4-methoxybenzylidene)amino)-*N*-methylaniline

$C_{15}H_{16}N_2O$. MW: 240.31 g·mol^{-1}. Yellow solid (204.26 mg, 85%). M.p. 74.8-76.0 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.43 (s, 1H), 7.83 (d, *J* =8.8 Hz, 2H), 7.20 (d, *J* =8.8 Hz, 2H), 6.97 (d, *J* =8.8 Hz, 2H), 6.64 (d, *J* =8.8 Hz, 2H), 3.86 (s, 3H), 2.86 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 161.6, 155.7, 147.9, 141.9, 129.9, 129.8, 122.2, 114.0, 112.7, 55.3, 30.9.

HRMS (ESI) Calcd for $C_{15}H_{16}N_2O+H^+$ 241.1335, Found 241.1333.



4d

N,*N'*-(1,4-phenylene)bis(1-(4-chlorophenyl)methanimine) [9]

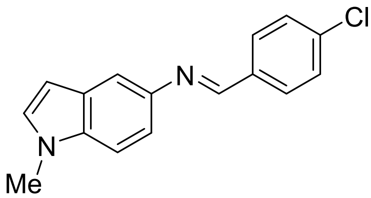
$C_{20}H_{14}Cl_2N_2$. MW: 353.25 g·mol^{-1}. Yellow Solid (308.03 mg, 87%). M.p. 199.6-200.2

°C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.47 (s, 2H), 7.86 (d, *J* = 8.8 Hz, 4H), 7.46 (d, *J* = 8.8 Hz, 4H), 7.28 (s, 4H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 158.2, 149.7, 137.4, 134.7, 129.9, 129.1, 121.9.

MS(EI): m/z (%) 354 (62.08), 353 (44.83), 352 (100.00), 351 (37.52), 241 (7.16), 214 (6.99), 176 (20.47), 152 (31.99), 127 (6.60), 102 (11.92).



4e

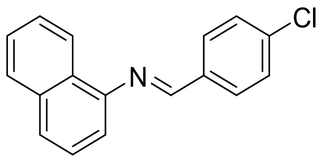
1-(4-chlorophenyl)-*N*-(1-methyl-1*H*-indol-5-yl)methanimine

$C_{16}H_{13}ClN_2$. MW: 268.74 g·mol^{-1}. Yellow solid (169.31 mg, 63%). M.p. 135.9-136.4 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.56 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 2 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.24-7.27 (m, 1H), 7.09 (d, *J* = 3.2 Hz, 1H), 6.52 (d, *J* = 3.2 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 156.4, 144.0, 136.6, 135.8, 135.2, 129.8, 129.6, 129.0, 128.9, 116.2, 112.5, 109.6, 101.4, 33.0.

HRMS (ESI) Calcd for $C_{16}H_{13}ClN_2+H^+$ 269.0840, Found 269.0827.



4f

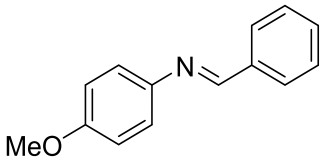
N-(4-chlorobenzylidene)naphthalene-1-amine [10]

$C_{17}H_{12}ClN$. MW: 265.74 g·mol^{-1}. Yellow solid (174.68 mg, 65%). M.p. 103.7-106.1 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.52 (s, 1H), 8.34-8.31 (m, 1H), 7.98-7.95 (m, 2H), 7.95-7.85 (m, 1H), 7.74 (d, *J* = 8 Hz, 1H),7.54-7.47 (m, 5H), 7.06 (dd, *J* = 7.2 Hz, 0.8 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 158.8, 148.9, 137.5, 14.9, 133.9, 130.1, 129.1, 128.7, 127.7, 126.5, 126.1, 126.0, 125.8, 123.8, 112.6.

MS(EI): m/z (%) 268 (7.44), 267 (32.79), 266 (44.56), 265 (100), 264 (72.5), 154 (35.11), 135 (16.37), 127 (97.45), 101 (18.62), 77 (27.67).



4g

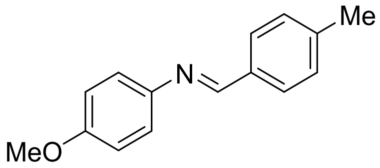
N-(4-methoxyphenyl)-1-phenylmethanimine [7]

$C_{14}H_{13}NO$. MW: 211.26 g·mol^{-1}. Yellow solid (194.36 mg, 92%). M.p. 67.1-68.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.40 (s, 1H), 7.82-7.79 (m, 2H), 7.39-7.37 (m, 3H), 7.18-7.14 (m, 2H), 6.87-6.83 (m, 2H), 3.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 158.4, 158.2, 144.8, 136.4, 131.0, 128.7, 128.5, 122.2, 114.3, 55.4.

MS(EI): m/z (%) 212 (14.83), 211 (88.12), 210 (13.74), 197 (14.73), 196 (100.00), 167 (27.15), 141 (13.82), 115 (11.37), 92 (10.48), 77 (16.91).

4h 

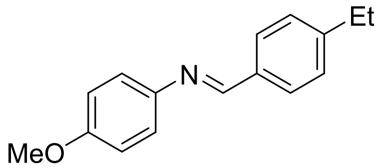
N-(4-methoxyphenyl)-1-(*p*-tolyl)methanimine [7]

$C_{15}H_{15}NO$. MW: 225.29 g·mol^{-1}. Yellow solid (205.39 mg, 91%). M.p. 87.5-88.6 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.44 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 158.5, 158.1, 145.1, 1415, 133.8, 129.5, 128.6, 122.1, 114.3, 55.5, 21.6.

MS(EI): m/z (%) 226 (15.15), 225 (80.56), 224 (13.94), 211 (15.25), 210 (100.00), 181 (8.94), 155 (10.11), 113 (7.32), 91 (11.73), 77 (15.66).

4i 

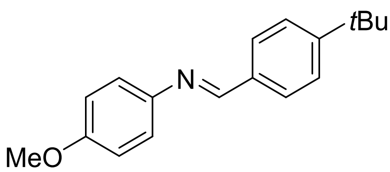
N-4-ethylbenzylidene-4-methoxyaniline [11]

$C_{16}H_{17}NO$. MW: 239.32 g·mol^{-1}. Yellow solid (214.91 mg, 90%). M.p. 56.8-58.4 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.45 (s, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H), 2.71 (q, J = 7.6 Hz, 2H),1.27 (t, J = 7.6 Hz, 3H).

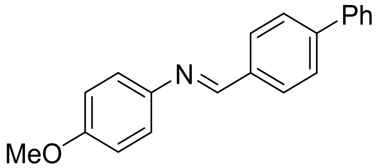
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 158.5, 158.1, 147.8, 145.1, 134.1, 128.6, 128.3, 122.1, 114.3, 55.5, 28.9, 15.4.

MS(EI): m/z (%) 239 (95.58), 224 (100.00), 197 (2.20), 180 (7.19), 167 (5.31), 134 (2.87), 112 (7.08), 91 (15.33), 77 (13.69), 64 (8.00).

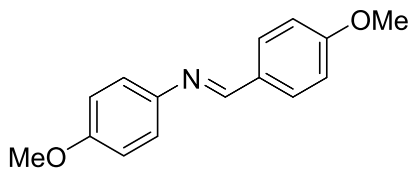
4j 

1-(4-(*tert*-butyl)phenyl)-*N*-(4-methoxyphenyl)methanimine [11]

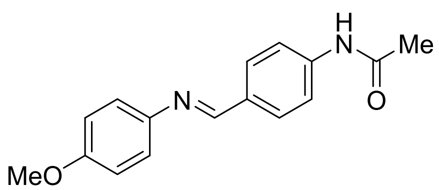
$C_{18}H_{21}NO$. MW: 267.37 g·mol^{-1}. Yellow solid (155.87 mg, 58%). M.p. 90.4-95.5 °C.
^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.46 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 1.36 (s, 9H).
^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 158.4, 158.1, 154.6, 145.2, 133.8, 128.4, 125.7, 122.1, 114.3, 55.5, 35.0, 31.2.
MS(EI): m/z (%) 268 (19.77), 267 (100.00), 266 (7.02), 252 (75.32), 237 (12.57), 134 (16.27), 126 (11.66), 112 (32.10), 91 (17.20), 77 (10.70).

4k


1-([1,1'-biphenyl]-4-yl)-*N*-(4-methoxyphenyl)methanimine [12]
$C_{20}H_{17}NO$. MW: 287.36 g·mol^{-1}. White solid (238.51 mg, 83%). M.p. 181.8-182.7 °C.
^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.56 (s, 1H), 8.00 (s, 2H), 7.71 (d, *J* = 19.2 Hz, 4H), 7.63-7.46 (m, 3H),7.29 (s, 2H), 6.99 (s, 2H), 3.87 (s, 3H)
^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 158.3, 157.9, 144.9, 143.7, 140.3, 135.3, 129.0, 128.9, 127.8, 127.4, 127.1, 122.2, 114.4, 55.5.
MS(EI): m/z (%) 288 (23,31), 287 (100.00), 286 (11.32), 273 (18.21), 272 (79.53), 243 (8.34), 217 (6.59), 165 (8.59), 144 (11.65), 77 (8.58).

4l


N,1-bis(4-methoxyphenyl)methanimine [7]
$C_{15}H_{15}NO_2$. MW: 241.29 g·mol^{-1}. Yellow solid (226.81 mg, 94%). M.p. 144.2-145.1 °C.
^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.43 (s, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* =8.8 Hz, 2H), 6.95 (d, *J* =8.8 Hz, 2H), 3.88 (s, 3H), 3.84 (s, 3H)
^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 161.9, 157.8, 157.7, 145.1, 130.1, 129.4, 122.0, 114.2, 114.0, 55.4, 55.3.
MS(EI): m/z (%) 241 (94.69), 226 (100.00), 171 (10.38), 155 (15.91), 154 (18.71), 121 (13.06), 92 (9.02), 77 (15.72), 64 (10.76), 51 (7.52).

4m


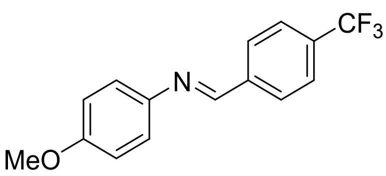
N-(4-(((4-methoxyphenyl)imino)methyl)phenyl)acetamide [13]

$C_{16}H_{16}N_2O_2$. MW: 268.32 g·mol^{-1}. White solid (193.19 mg, 72%). M.p. 180.7-181.4 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.42 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.72 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 9.2 Hz, 2H), 3.83 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 168.5, 158.1, 157.6, 144.8, 140.4, 132.3, 131.1, 129.5, 122.1, 119.4, 114.3, 55.5, 24.7.

MS(EI): m/z (%) 269 (17.95), 268 (100.00), 267 (6.33), 253 (31.30), 226 (24.77), 212 (16.46), 211 (69.08), 156 (9.81), 92 (25.09), 65 (18.17).



4n

N-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)methanimine [11]

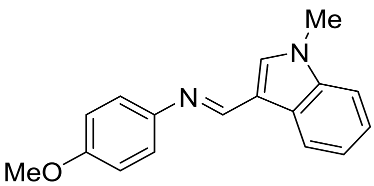
$C_{15}H_{12}F_3NO$. MW: 279.26 g·mol^{-1}. Yellow solid (114.50 mg, 41%). M.p. 119.9-120.8 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.52 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 9.2 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 158.8, 156.2, 144.0, 139.5, 132.3 (q, *J* = 32.3 Hz), 128.7, 125.6 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 270.9 Hz), 122.4, 114.4, 55.5.

^{19}F NMR (376 MHz, CDCl$_3$, δ ppm): δ-62.73.

MS(EI): m/z (%) 279 (91.01), 264 (100.00), 235 (12.79), 209 (4.47), 167 (12.93), 134 (7.89), 107 (4.77), 92 (10.54), 77 (13.25), 64 (11.52), 51 (3.64).



4o

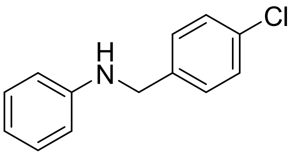
N-(4-methoxyphenyl)-1-(1-methyl-1*H*-indol-3-yl)methanimine [14]

$C_{17}H_{16}N_2O$. MW: 264.33 g·mol^{-1}. Yellow solid (163.88 mg, 62%). M.p. 103.5-105.5 °C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.65 (s, 1H), 8.46 (d, *J* = 7.2 Hz, 1H), 7.53 (s, 1H), 7.38-7.32 (m, 1H), 7.30 (d, *J* = 8 Hz, 2H), 7.25-7.21 (m, 2H), 6.93 (d, *J* = 8.8 Hz, 2H),3.85 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 157.3, 152.7, 146.5, 137.8, 133.8, 126.0, 123.2, 122.1, 121.8, 121.5, 115.0, 114.3, 109.5, 55.5, 33.3.

MS(EI): m/z (%) 265 (20.87), 264 (80.50), 250 (22.86), 249 (100.00), 207 (55.73), 131 (15.48), 97 (15.13), 85 (16.11), 71 (25.44), 57 (37.97).

5a 

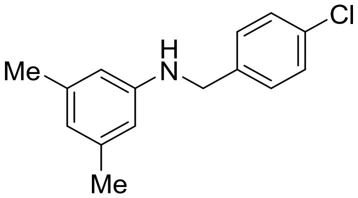
N-(4-chlorobenzyl)aniline [15]

$C_{13}H_{12}ClN$. MW: 217.70 g·mol^{-1}. Yellow- solid (148.1 mg, 68%). M.p. 47.6-48.5 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.23-7.28 (m, 4H), 7.14 (dd, *J* = 8.8 Hz, 7.2 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.56 (dd, *J* = 8.4 Hz, 1.2 Hz, 2H), 4.24 (s, 2H), 3.99 (s, 1H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 147.7, 137.9, 132.7, 129.2, 128.6, 128.7, 117.6, 112.8, 47.4.

MS(EI): m/z (%) 219 (10.63), 218 (6.08), 217 (29.43), 182 (7.50), 127 (33.61), 126 (8.68), 125 (100.00), 106 (10.59), 89 (16.01), 77 (17.06).

5b 

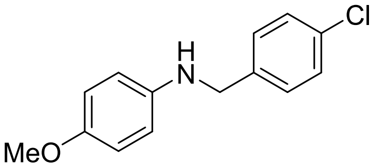
N-(4-chlorobenzyl)-3,5-dimethylaniline [16]

$C_{15}H_{16}ClN$. MW: 245.75 g·mol^{-1}. Yellow liquid (117.9 mg, 48%).

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.29 (s, 4H), 6.39 (s, 1H), 6.25 (s, 2H), 4.27 (s, 2H), 3.91 (s, 1H), 2.22 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 147.9, 139.0, 138.2, 132.7, 128.7, 119.8, 110.7, 47.6, 21.5.

MS(EI): m/z (%) 245 (51.13), 230 (3.71), 210 (14.45), 134 (20.06), 127 (33.58), 125 (100.00), 105 (8.32), 91 (11.44), 89 (16.40), 77 (13.36).

5c 

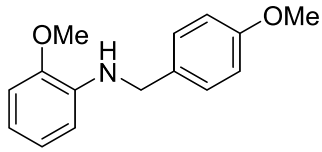
N-(4-chlorobenzyl)-4-methoxyaniline [16]

$C_{14}H_{14}ClNO$. MW: 247.72 g·mol^{-1}. Yellow solid (131 mg, 53%). M.p. 73.4-75.2 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.21 (s, 4H), 6.68 (d, *J* = 9.2 Hz, 2H), 6.48 (d, *J* = 9.2 Hz, 2H), 4.16 (s, 2H), 3.64 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 152.2, 142.0, 138.2, 132.7, 128.7, 114.8, 114.1, 55.7, 48.4.

MS(EI): m/z (%) 249 (11.16), 247 (31.01), 232 (3.62), 230 (6.08), 167 (2.53), 134 (2.26), 127 (13.90), 125 (42.19), 122 (100), 89 (10.99).



5d

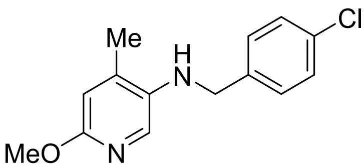
2-methoxy-*N*-(4-methoxybenzyl)aniline [17]

$C_{15}H_{17}NO_2$. MW: 243.31 g·mol^{-1}. Yellow solid (97.4 mg, 40%). M.p. 74.8-76.1 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.29 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.83 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 6.77 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.67 (td, *J* = 11.6 Hz, 1.6 Hz, 1H), 6.61 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 4.26 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 158.7, 146.7, 138.1, 131.5, 128.8, 121.2, 116.5, 113.9, 110.0, 109.3, 55.3, 55.2, 47.4.

MS(EI): m/z (%) 244 (2.75), 243 (14.08), 241 (1.21), 226 (0.76), 134 (1.52), 121 (100.00), 91 (4.17), 77 (7.44), 65 (4.14), 52 (2.18).



5e

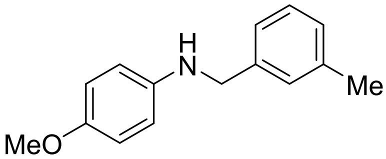
N-(4-chlorobenzyl)-6-methoxy-4-methylpyridin-3-amine

$C_{14}H_{15}ClN_2O$. MW: 262.74 g·mol^{-1}. Reddish brown liquid (126.1 mg, 48%).

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.39 (s, 1H), 7.31 (s, 4H), 6.53 (s, 1H), 4.30 (s, 2H), 3.83 (s, 3H), 3.49 (s, 1H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 157.4, 137.5, 137.3, 136.5, 133.0, 128.8, 127.6, 111.6, 53.0, 48.2, 17.3.

HRMS (ESI) Calcd for $C_{14}H_{15}ClN_2O+H^+$ 263.0946, Found 263.0945.



5f

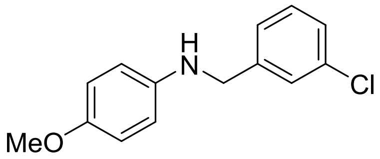
4-methoxy-*N*-(3-methylbenzyl)aniline [18]

$C_{15}H_{17}NO$. MW: 227.31 g·mol^{-1}. Reddish brown liquid (136.4 mg, 60%).

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.13-7.22 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 4.19 (s, 2H), 3.70 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 152.0, 142.4, 139.5, 138.1, 128.4, 128.2, 127.8, 124.5, 114.7, 114.0, 55.6, 49.1, 21.3.

MS(EI): m/z (%) 228 (10.41), 227 (63.83), 212 (5.39), 210 (8.21), 136 (7.60), 122 (78.45), 105 (100.00), 77 (17.80), 65 (6.15), 52 (3.69).



5g

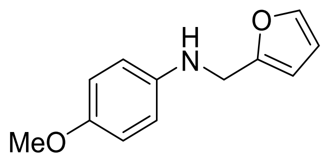
N-(3-chlorobenzyl)-4-methoxyaniline [19]

$C_{14}H_{14}ClNO$. MW: 247.72 g·mol^{-1}. Yellow liquid (161.0 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.35 (s, 1H), 7.23 (s, 3H), 6.76 (d, *J* = 6.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 4.25 (s, 2H), 3.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 152.2, 141.9, 134.4, 129.8, 127.4, 127.2, 125.4, 114.8, 114.1, 55.7, 48.6.

MS(EI): m/z (%) 249 (12.09), 247 (38.56), 232 (8.40), 230 (7.84), 167 (3.76), 136 (8.63), 127 (12.99), 125 (40.52), 122 (100.00), 95 (10.06).



5h

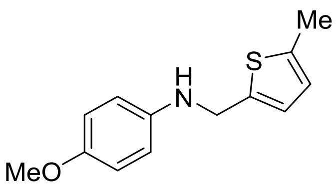
N-(furan-2-ylmethyl)-4-methoxyaniline [20]

$C_{12}H_{13}NO_2$. MW: 203.24 g·mol^{-1}. Yellow solid (107.7 mg, 53%). M.p. 45.3-46.9 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.32 (dd, *J* = 2 Hz, 0.8 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.33 (dd, *J* = 3.2 Hz, 2 Hz, 2H), 6.23 (dd, *J* = 3.2 Hz, 1.2 Hz, 2H), 4.28 (s, 2H), 3.76 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 152.9, 152.5, 141.8, 141.7, 114.7, 114.6, 110.2, 106.9, 55.6, 42.3.

MS(EI): m/z (%) 203 (51.25), 202 (27.52), 175 (5.25), 160 (4.93), 122 (99.32), 108 (8.99), 95 (20.17), 81 (100.00), 77 (6.76), 53 (36.56).



5i

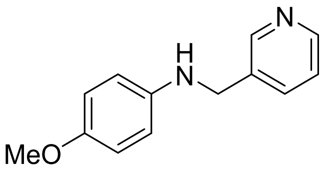
4-methoxy-*N*-((5-methylthiophen-2-yl)methyl)aniline [21]

$C_{13}H_{15}NOS$. MW: 233.33 g·mol^{-1}. Yellow liquid (168.0 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.75 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 3.6 Hz, 1H), 6.58 (d, *J* = 9.2 Hz, 2H), 6.57-6.52 (m, 1H), 4.31 (s, 2H), 3.69 (s, 3H), 3.62 (s, 1H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 152.3, 141.7, 140.6, 138.8, 124.7, 124.6, 114.6, 114.3, 55.5, 44.4, 15.2.

MS(EI): m/z (%) 233 (4.96), 232 (13.02), 231 (90.39), 216 (100.00), 187 (9.32), 173 (7.70), 116 (10.09), 97 (11.25), 77 (13.22), 64 (10.66).

5j 

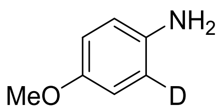
4-methoxy-*N*-(pyridin-3-ylmethyl)aniline [28]

$C_{13}H_{14}N_2O$. MW: 214.27 g • mol^{-1}. Yellow solid (126.87 mg, 59%). M.p. 56.4-59.4 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.60 (d, *J* = 2.4 Hz, 1H), 8.50 (dd, *J* = 4.8 Hz, 1.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.27-7.20 (m, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 9.2 Hz, 2H), 4.28 (s, 2H), 3.71 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 152.3, 149.0, 148.5, 141.7, 135.1, 123.4, 114.8, 114.1, 55.6, 46.5.

MS(EI): m/z (%) 215 (14.08), 214 (92.07), 199 (9.93), 169 (3.54), 136 (9.68), 122 (100.00), 95 (17.24), 92 (65), 65 (24.00), 52 (6.73).

2a' 

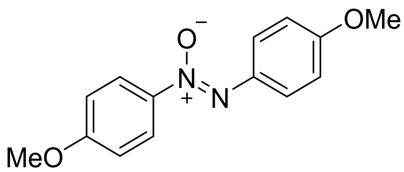
4-methoxybenzen-2-*d*-amine

C_7H_8DNO. MW: 124.16 g·mol^{-1}. Red brown solid (83.19 mg, 67%). M.p. 57.4-58.1 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 6.78-6.72 (m, 2H), 6.65 (d, *J* = 9.2 Hz, 1H), 3.75 (s, 3H), 3.44 (s, 2H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 152.6, 139.8 (t, *J* = 6.7 Hz), 116.3, 114.6 (d, *J* = 1.8 Hz), 114.5 (d, *J* = 1.8 Hz), 55.6.

MS(EI): m/z (%) 125 (51.78), 124 (97.34), 123 (75.20), 110 (62.6), 109 (100.00), 108 (90.91), 81 (63.58), 80 (49.92), 54 (29.67), 53 (34.08).

6a 

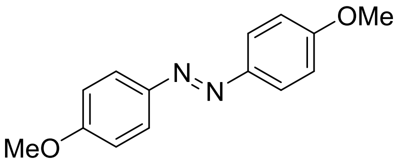
1,2-bis(4-methoxyphenyl)diazene 1-oxide [22]

$C_{14}H_{14}N_2O_3$. MW: 258.28 g·mol^{-1}. Yellow solid (56.8 mg, 44%). M.p. 116.4-118.7 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.26 (dd, J = 13.6 Hz, 9.2 Hz, 4H), 6.97 (dd, J = 9.2 Hz, 6.8 Hz, 4H), 3.89 (s, 3H), 3.88 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 161.8, 160.2, 138.0, 127.8, 123.8, 113.7, 113.6, 55.7, 55.5.

MS(EI): m/z (%) 259 (14.78), 258 (93.43), 215 (6.91), 135 (16.07), 122 (24.40), 121 (100.00), 107 (97.18), 92 (35.26), 77 (56.88), 64 (26.31).

7a 

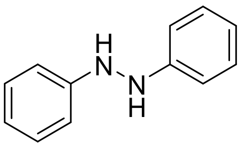
1,2-bis(4-methoxyphenyl)diazene [23]

$C_{14}H_{14}N_2O_2$. MW: 242.28 g·mol^{-1}. Yellow solid (42.6 mg, 35%). M.p. 163.8-165.0 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.89 (dt, *J* = 8.8 Hz, 3.2 Hz, 4H), 7.01 (dt, *J* = 8.8 Hz, 3.2 Hz, 4H), 3.88 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 161.5, 147.0, 124.3, 114.1, 54.9.

MS(EI): m/z (%) 243 (6.46), 242 (40.46), 135 (33.97), 128 (3.15), 121 (4.47), 108 (8.92), 107 (100.00), 92 (28.69), 77 (51.62), 64 (17.19).

8q 

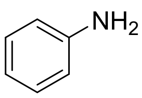
1,2-diphenylhydrazine [24]

$C_{12}H_{12}N_2$. MW: 184.24 g·mol^{-1}. Yellow solid (525.1 mg, 57%). M.p. 124.8-125.4 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.29-7.12 (m, 4H), 6.94-6.70 (m, 6H), 5.57 (s, 2H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 148.8, 129.3, 119.8, 112.3.

MS(EI): m/z (%) 185 (14.36), 184 (100.00), 183 (52.18), 182 (24.47), 181 (10.94), 169 (59.86), 105 (11.61), 91 (19.15), 77 (58.55), 51 (26.50).

2q 

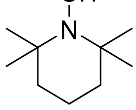
Aniline [7]

C_6H_7N. MW: 93.13 g·mol^{-1}. Light yellow liquid (63.3 mg, 68%).

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.17 (dd, *J* = 8.4 Hz, 7.2 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 7.2 Hz, 2H), 3.61 (s, 2H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 146.3, 129.2, 118.5. 115.1.

MS(EI): m/z (%) 94 (6.51), 93 (100.00), 92 (10.95), 77 (1.08), 67 (4.14), 66 (40.03), 65 (18.32), 63 (4.00), 52 (4.12), 51 (3.66).



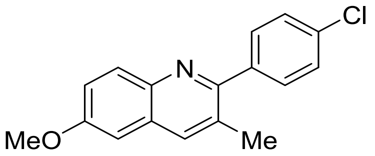
2,2,6,6-tetramethylpiperidin-1-ol (Unstable in the air) [25]

$C_9H_{19}NO$. MW: 157.26 g·mol^{-1}. solid (283.07 mg, 60%). M.p. 36.6-38.1 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 1.55 (s, 6H), 1.19 (s, 12H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 58.2, 38.3, 28.6, 15.9.

MS(EI): m/z (%) 157 (6.41), 143 (9.04), 142 (100.00), 126 (3.69), 110 (3.52), 109 (22.82), 86 (8.48), 74 (18.70), 69 (29.56), 55 (15.58).

9a 

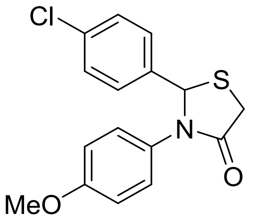
2-(4-chlorophenyl)-6-methoxy-3-methylquinoline [3]

$C_{17}H_{14}ClNO$. MW: 283.75 g·mol^{-1}. Brown solid (59.59 mg, 21%). M.p. 71.3-75.4 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.99 (d, *J* = 9.2 Hz, 1H), 7.88 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.32 (dd, *J* = 9.2 Hz, 2.8 Hz, 1H), 7.01 (d, *J* = 2.8 Hz, 1H), 3.91 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 157.8, 156.5, 142.6, 139.3, 135.8, 134.0, 130.6, 130.3, 129.1, 128.5, 128.4, 121.6, 104.1, 55.4, 20.5.

MS(EI): m/z (%) 285 (21.14), 284 (47.06), 283 (67.93), 282 (100.00), 267 (4.31), 239 (18.46), 204 (22.65), 176 (2.76), 124 (13.94), 102 (22.08).

9b 

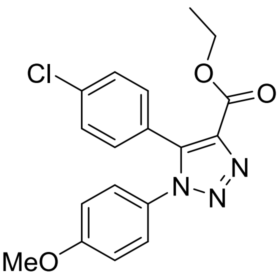
2-(4-chlorophenyl)-3-(4-methoxyphenyl)thiazolidin-4-one [26]

$C_{12}H_{14}ClNO_2S$. MW: 319.80 g·mol^{-1}. Yellow solid (246.25 mg, 77%). M.p. 163.9-165.0 ^{o}C.

^{1}H NMR (400 MHz, DMSO d-6, δ ppm): 7.42 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.42 (d, *J* = 1.6 Hz, 1H), 4.02 (dd, *J* = 15.6 Hz, 1.6 Hz, 1H), 3.87 (d, *J* = 15.2 Hz, 1H), 3.67 (s, 3H).

^{13}C NMR (100 MHz, DMSO d-6, δ ppm): 170.8, 158.0, 139.8, 133.4, 130.5, 129.6, 129.1, 127.7, 114.5, 63.4, 55.6, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 33.0.

MS(EI): m/z (%) 321 (17.85), 320 (9.64), 319 (47.79), 245 (10.18), 230 (21.40), 167 (8.57), 153 (100.00), 135 (94.52), 125 (12.61), 77 (11.00).

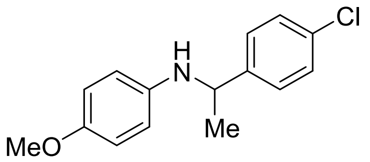
9c 

ethyl 5-(4-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxylate [5]

$C_{18}H_{16}ClN_3O_3$. MW: 357.79 g·mol^{-1}. Brown solid (132.38 mg, 37%). M.p. 119.1-120.7 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.36 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 9.2 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 4.38 (q, J = 7.2 Hz, 2H), 3.82 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 160.9, 160.3, 139.7, 136.7, 136.1, 131.6, 128.7, 128.3, 126.6, 124.2, 114.5, 61.3, 55.5, 14.2.
MS(EI): m/z (%) 359 (11.45), 358 (7.94), 357 (29.09), 329 (38.21), 314 (23.67), 300 (33.84), 283 (27.63), 256 (66.58), 150 (57.97), 123 (100.00).

9d



N-(1-(4-chlorophenyl)ethyl)-4-methoxyaniline [27]

$C_{15}H_{16}ClNO$. MW: 261.75 g·mol^{-1}. Yellow oil (125.64 mg, 48%).
^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.32-7.13 (m, 4H), 6.67 (d, J = 9.2 Hz, 2H), 6.40 (d, J = 9.2 Hz, 2H), 4.32 (q, J = 6.8 Hz, 1H), 3.64 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 151.8, 144.0, 141.1, 132.0, 128.5, 127.2, 114.6, 114.4, 55.4, 53.5, 24.9.
MS(EI): m/z (%) 263 (26.77), 262 (14.40), 261 (75.52), 246 (71.22), 141 (35.34), 139 (100.00), 123 (98.13), 122 (49.87), 103 (71.72), 77 (40.96).

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11. NMR Spectra

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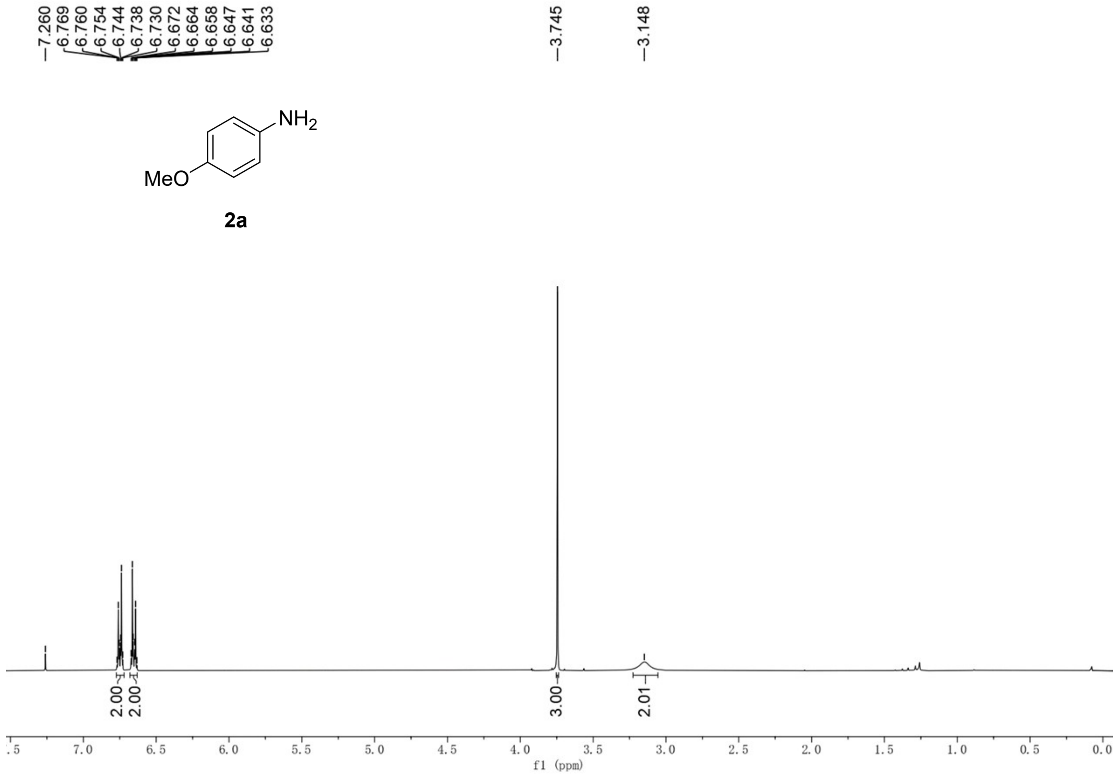

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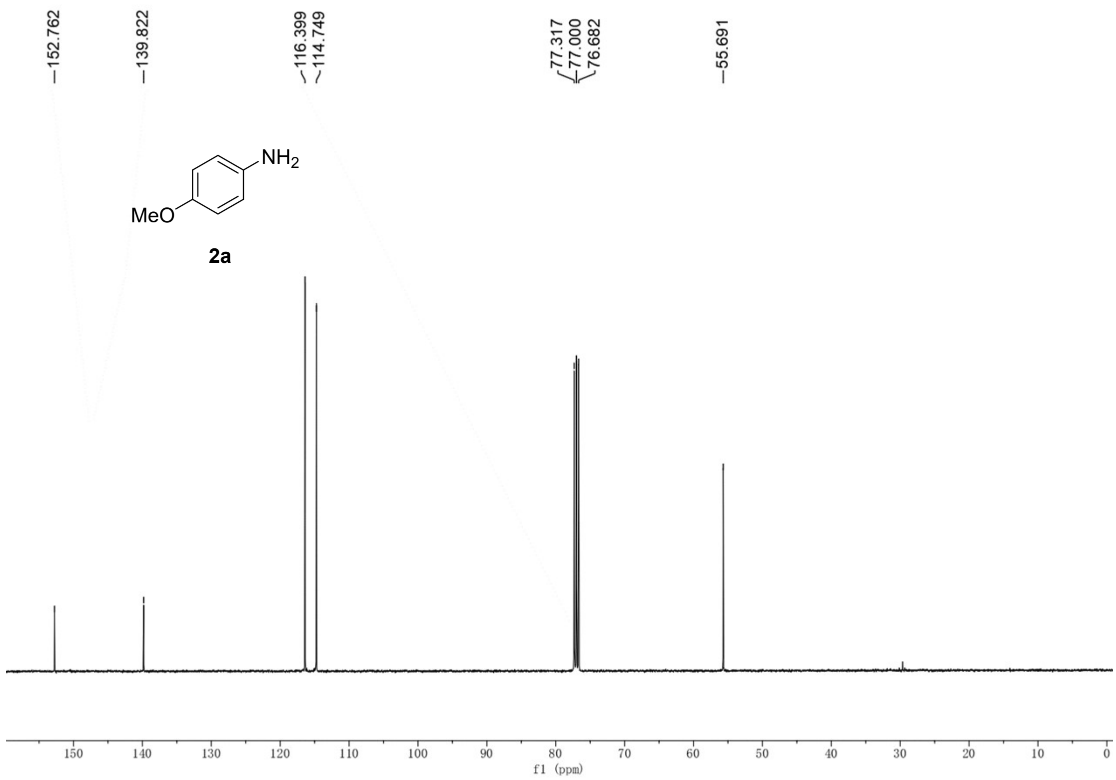

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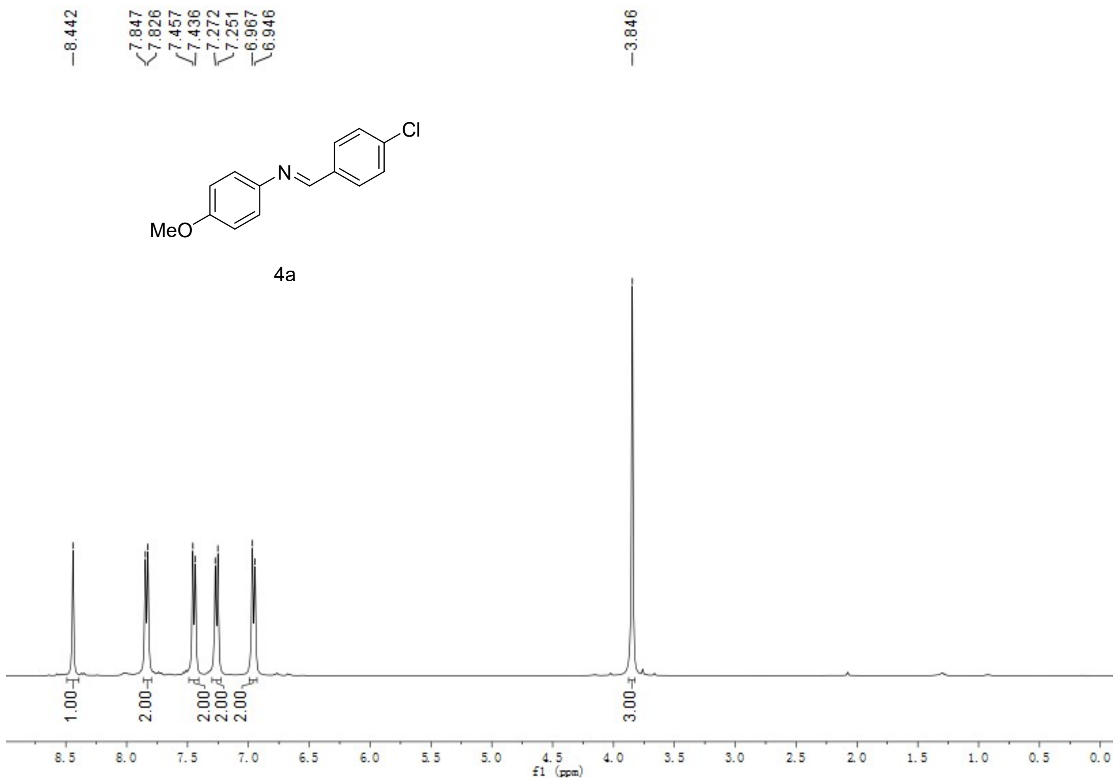

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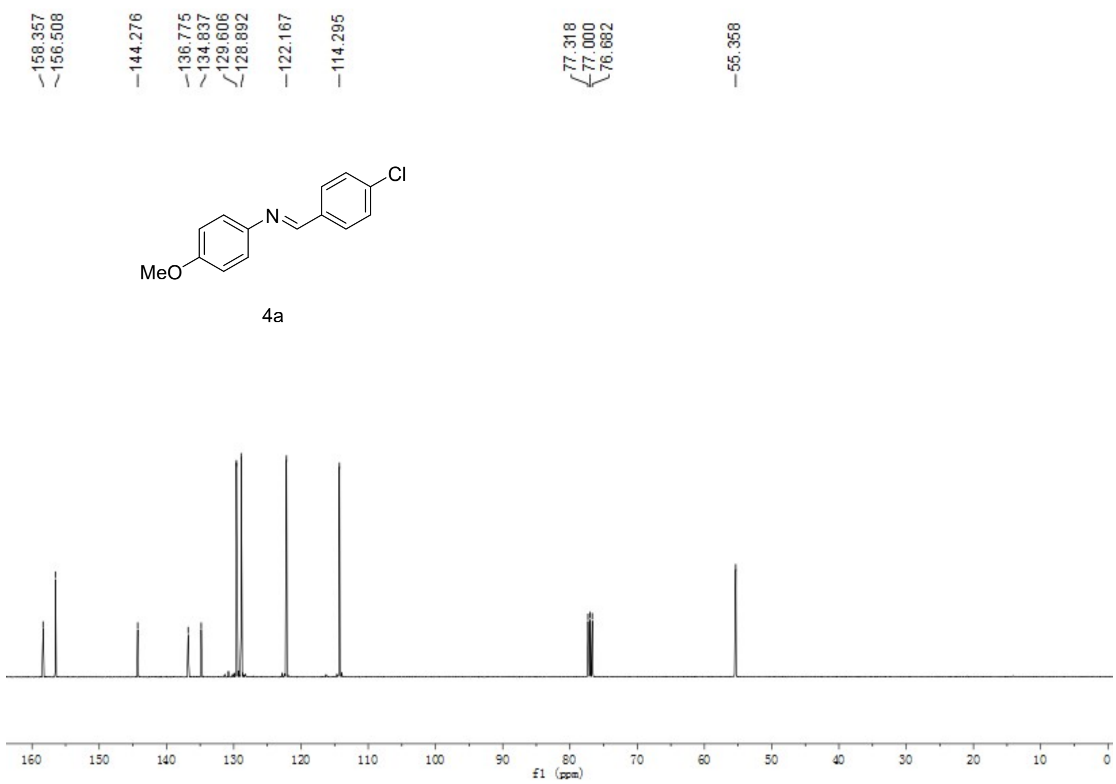

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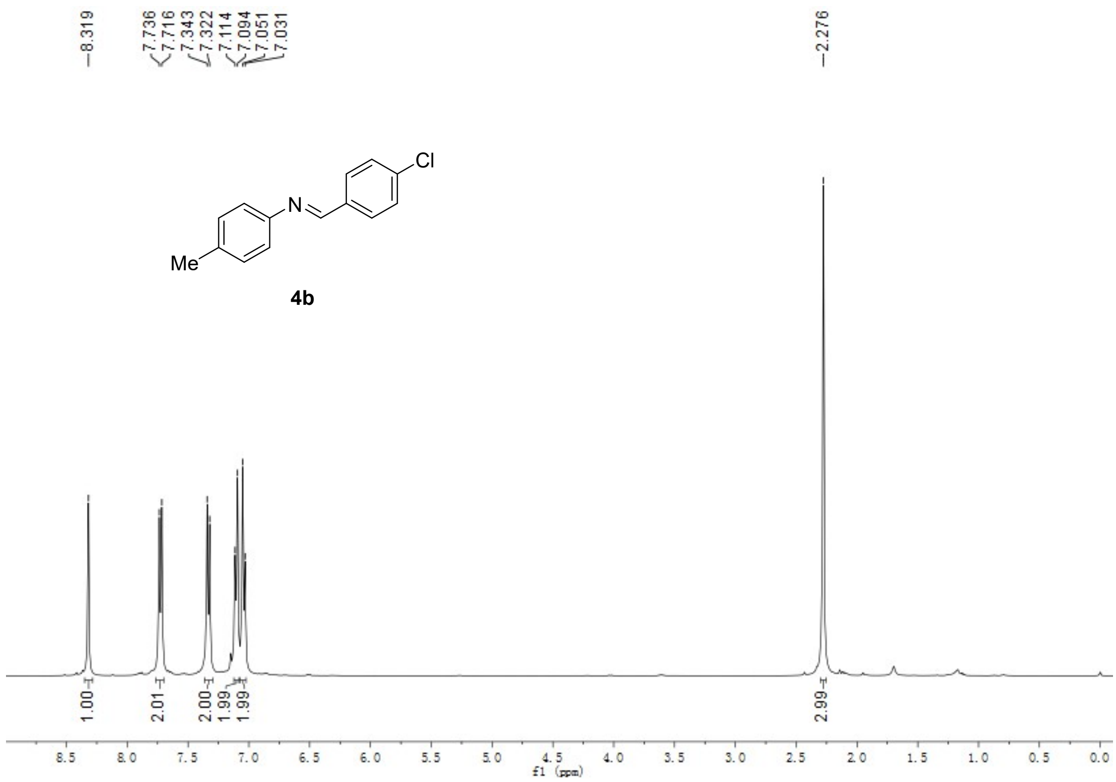

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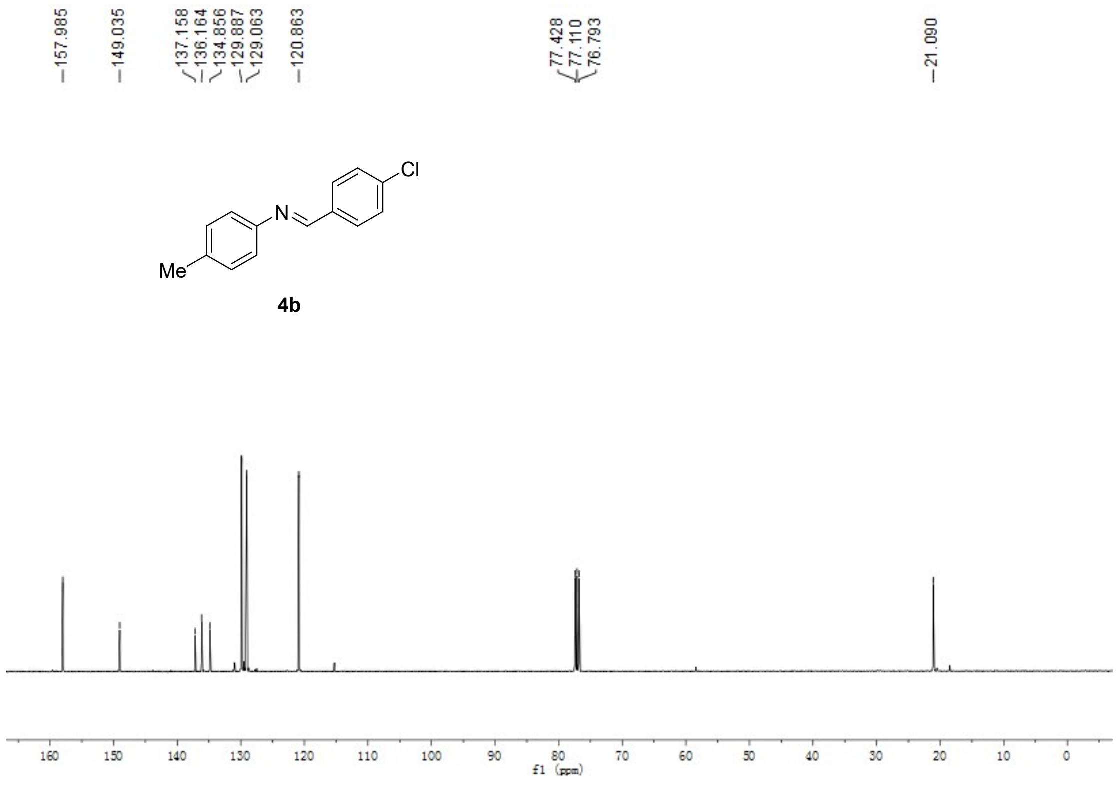

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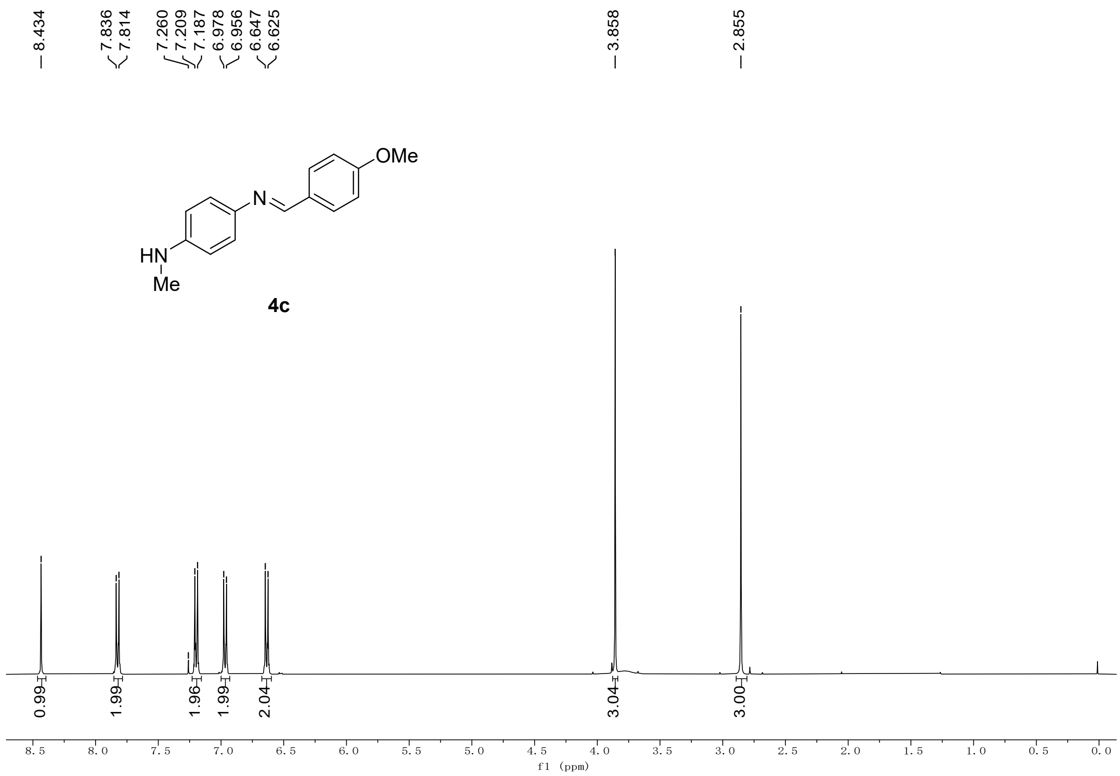

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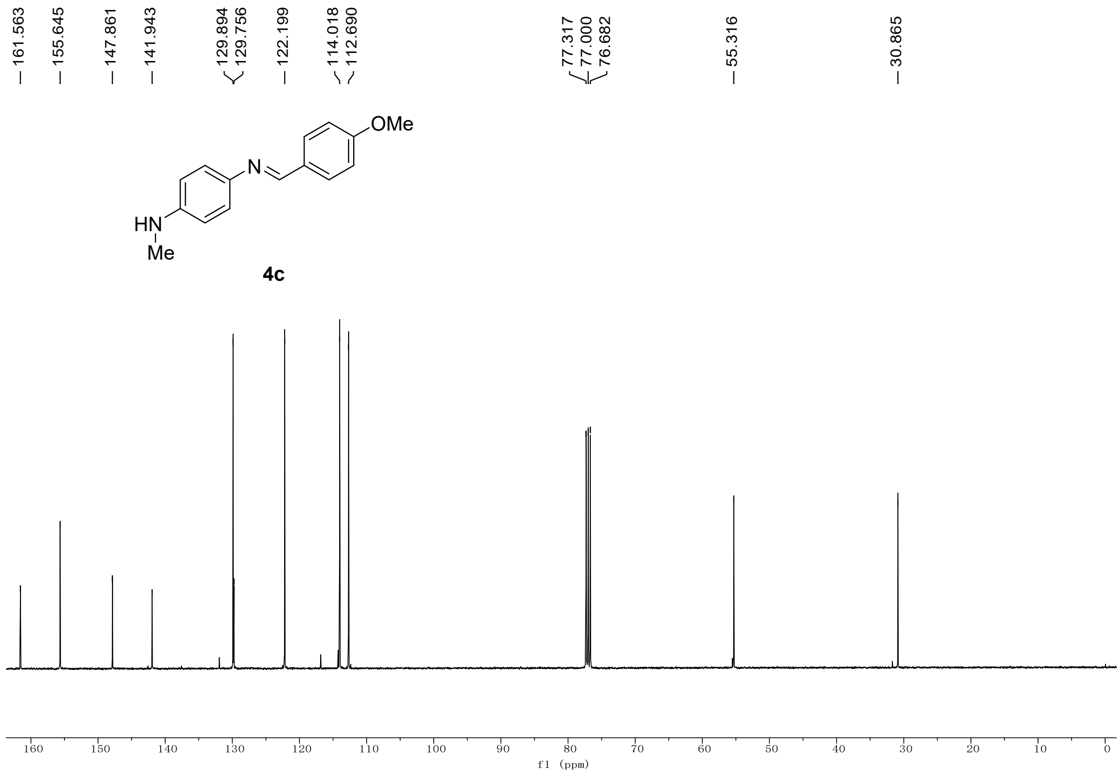

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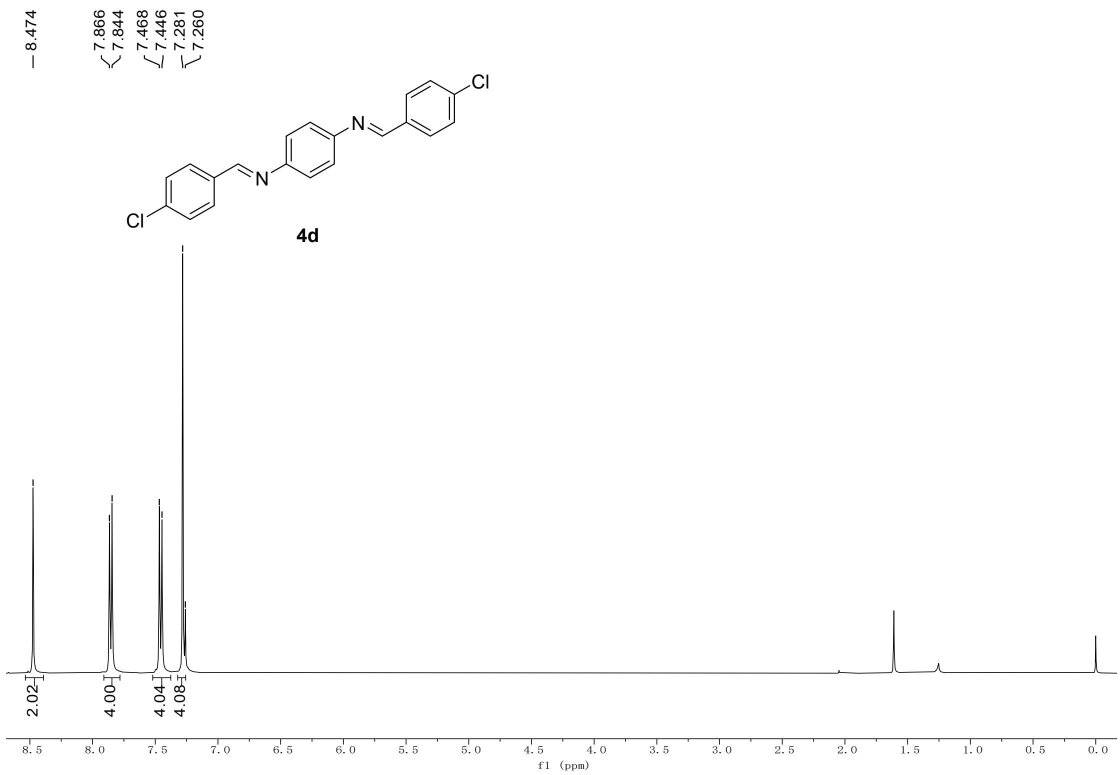

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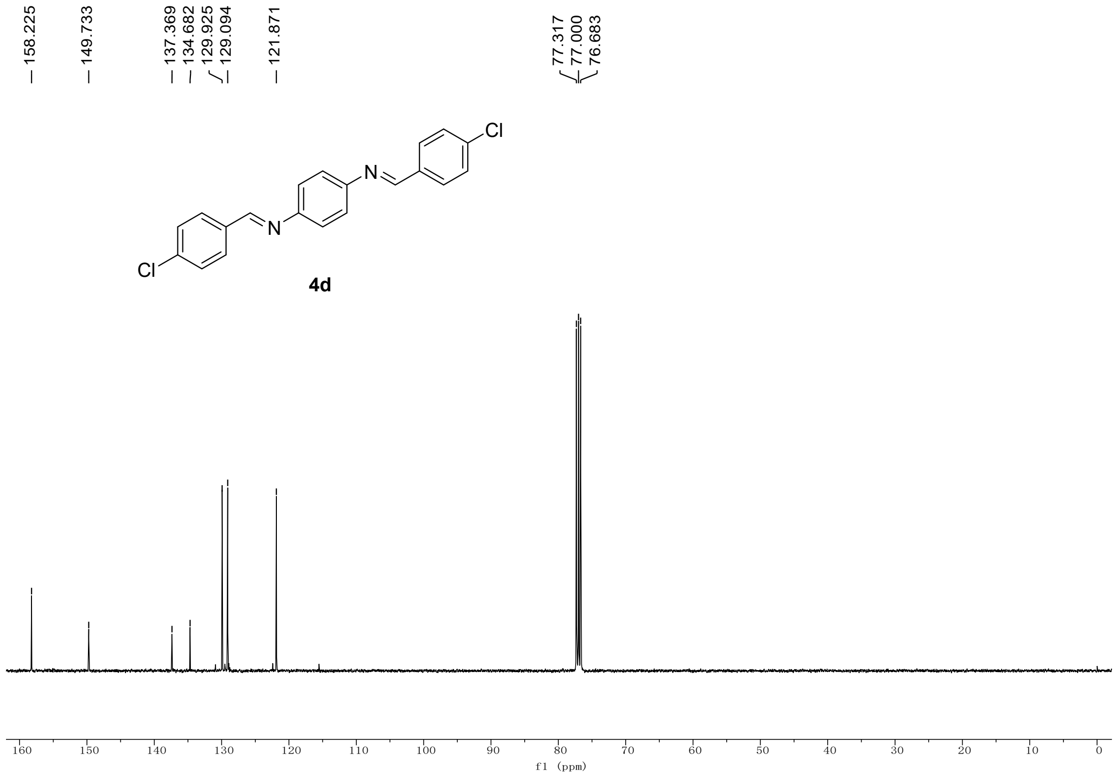

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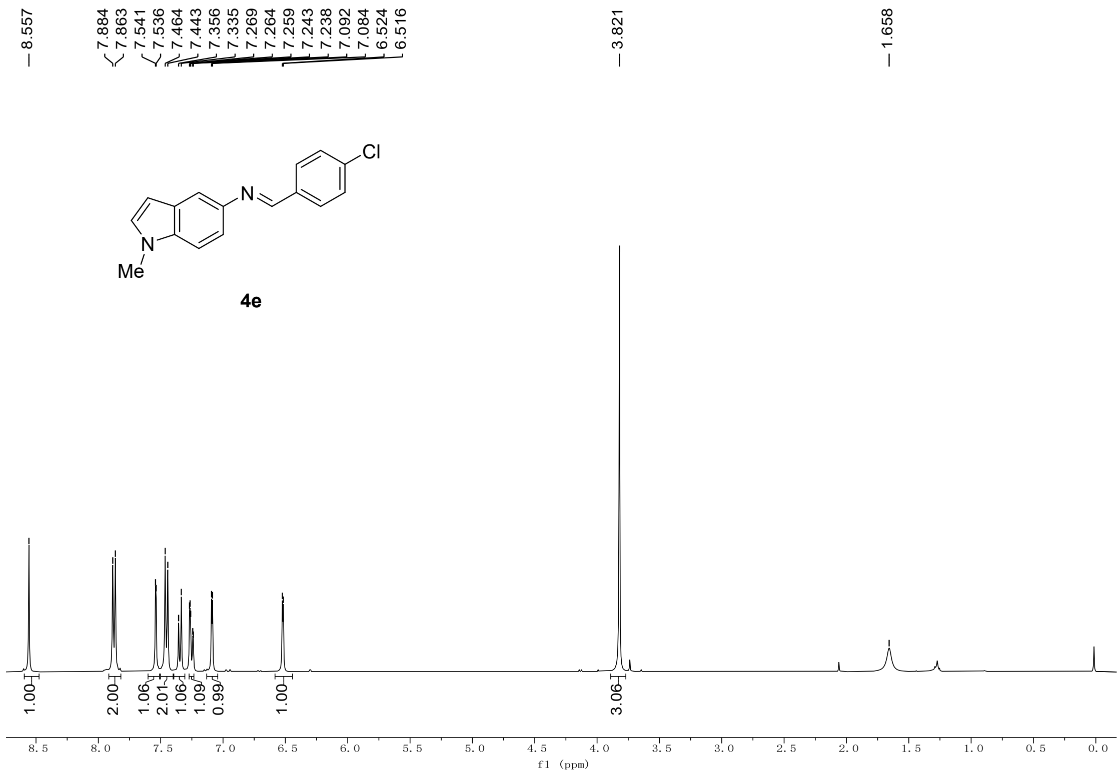

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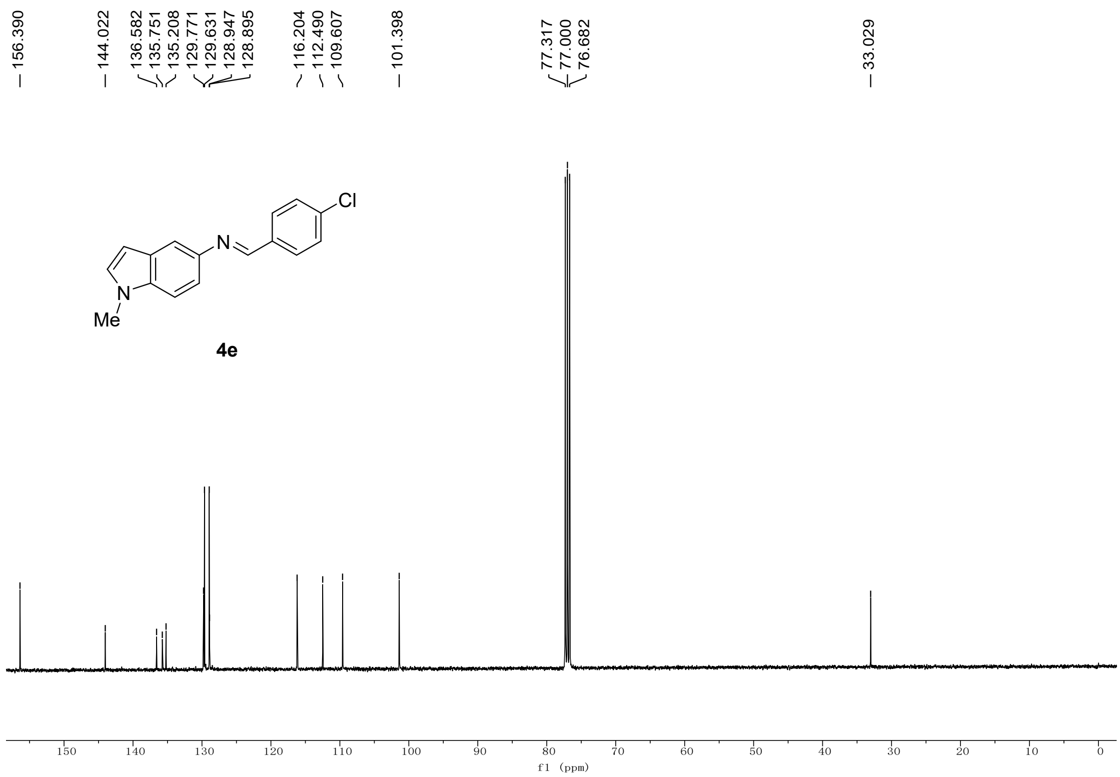

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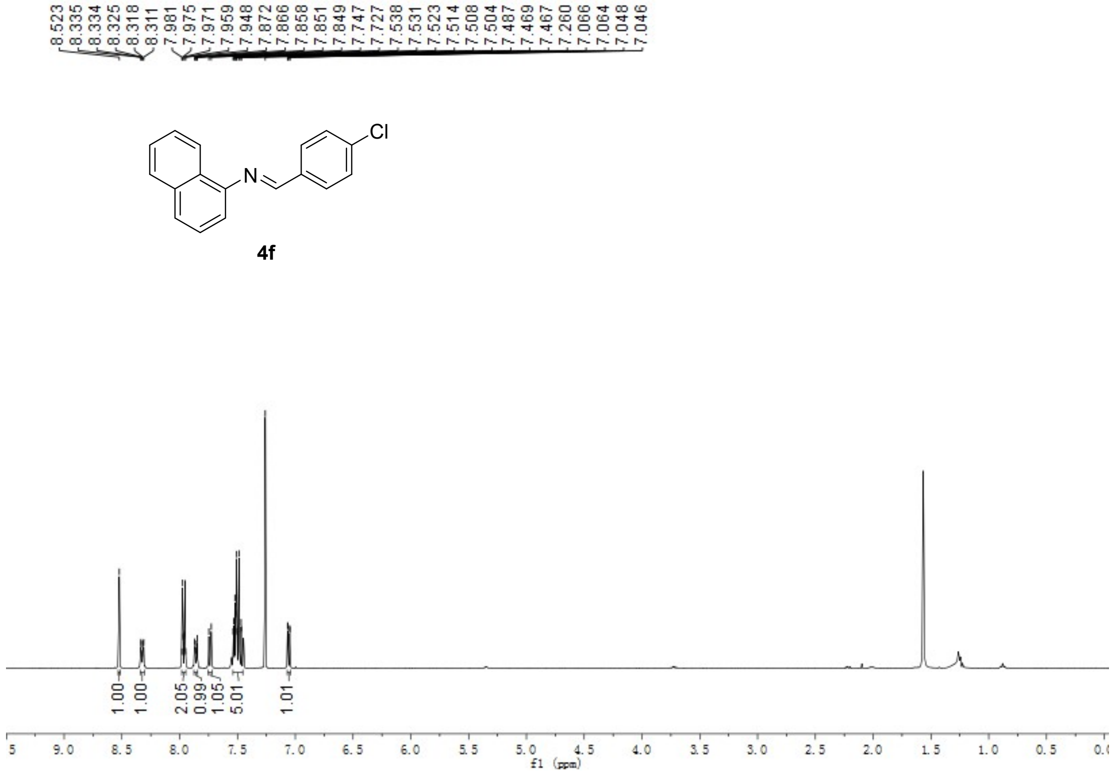

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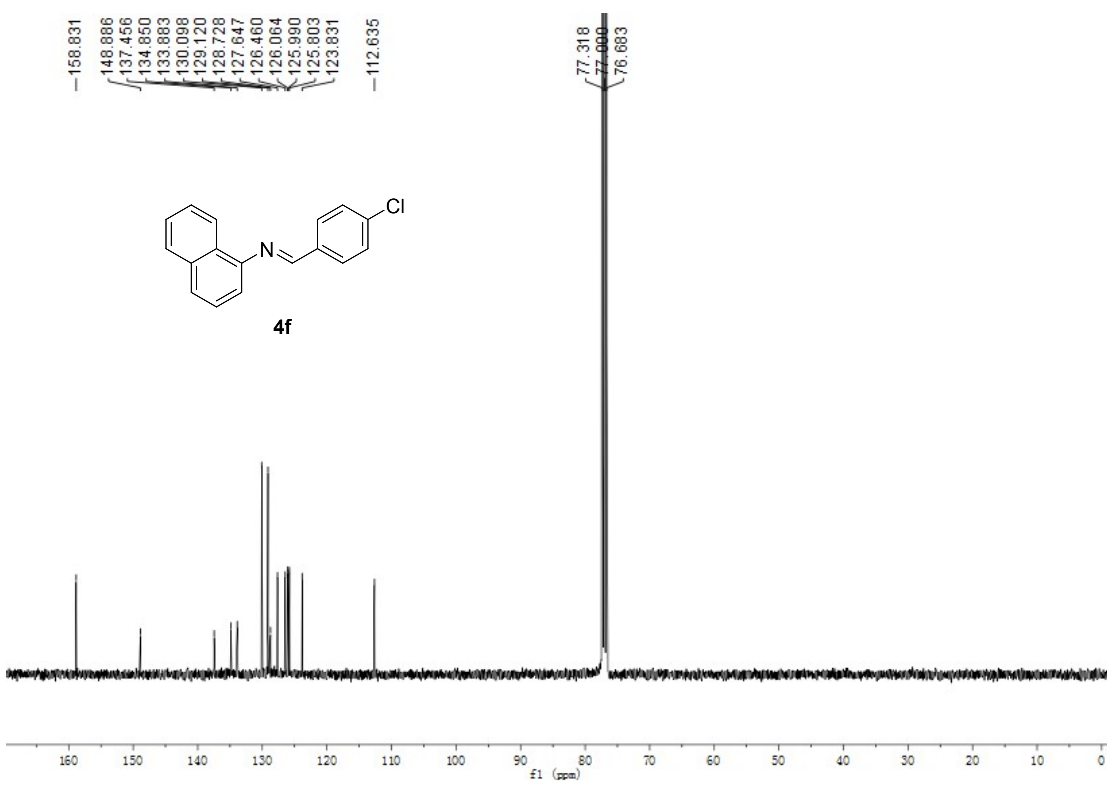
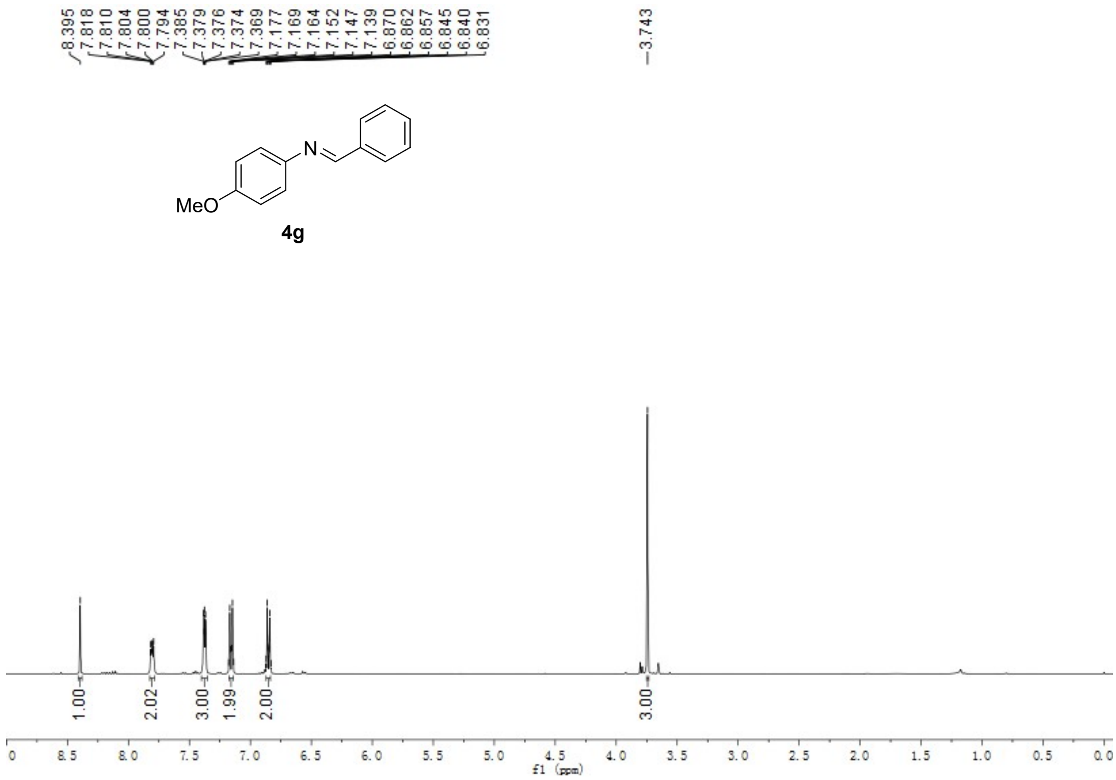


^{1}H NMR (400 MHz, $CDCl_3$)



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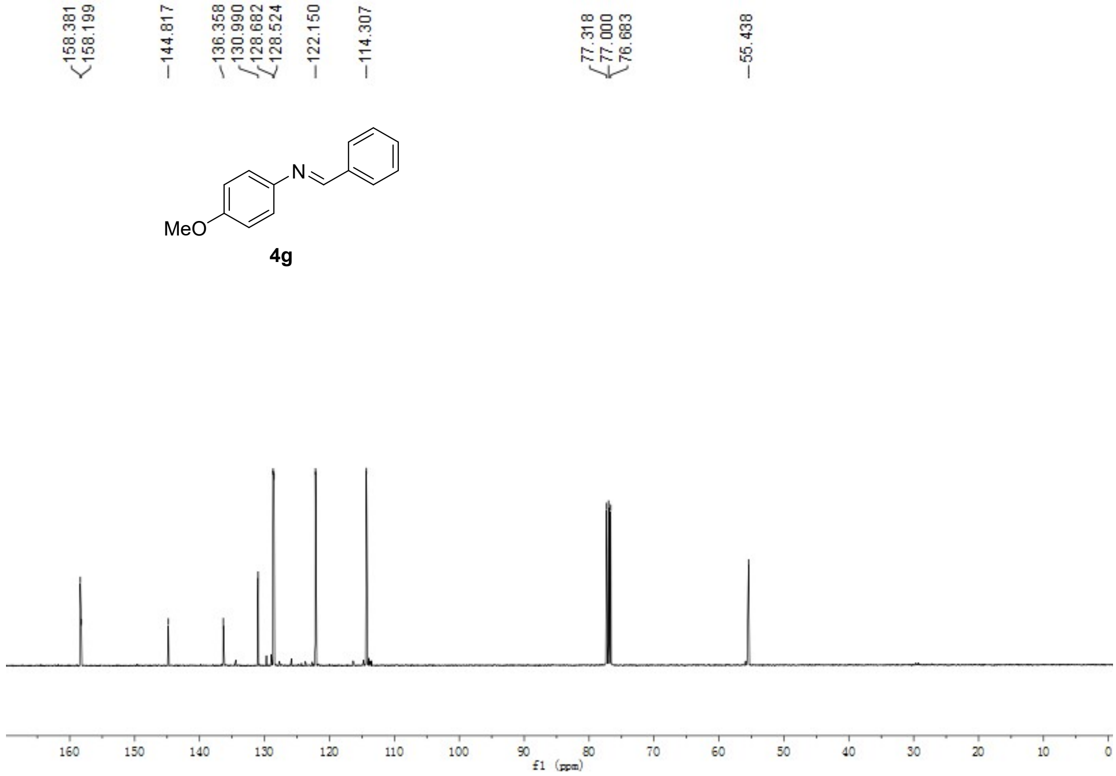

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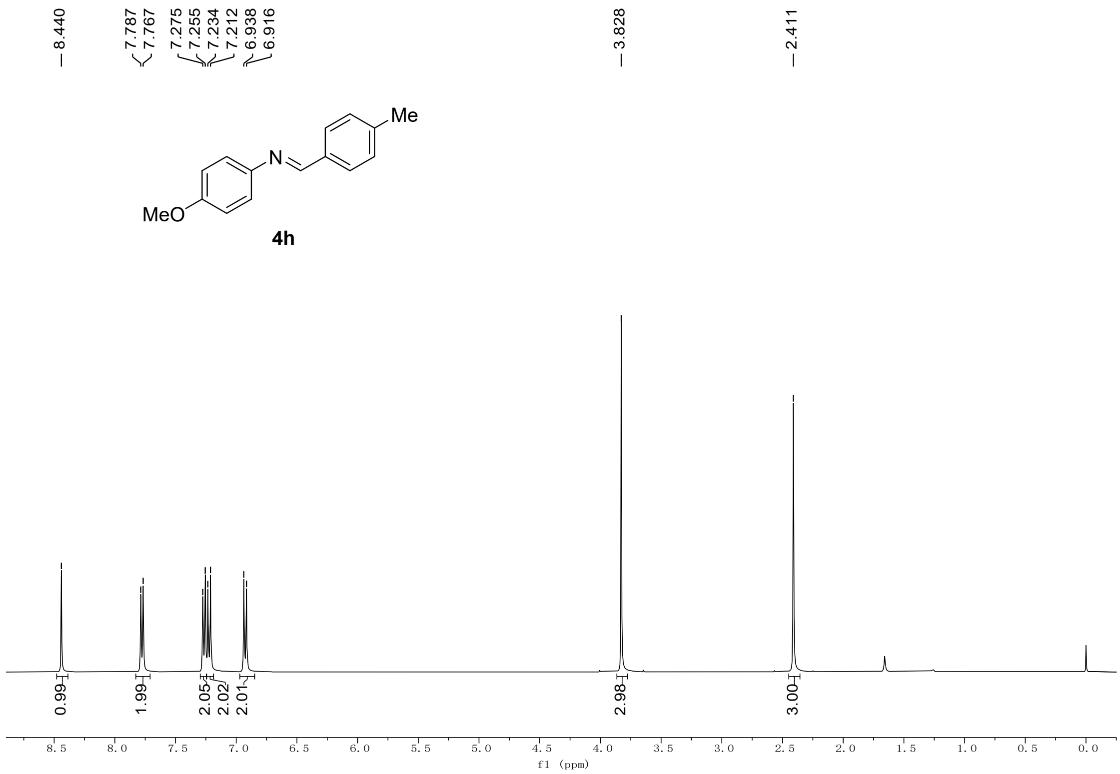

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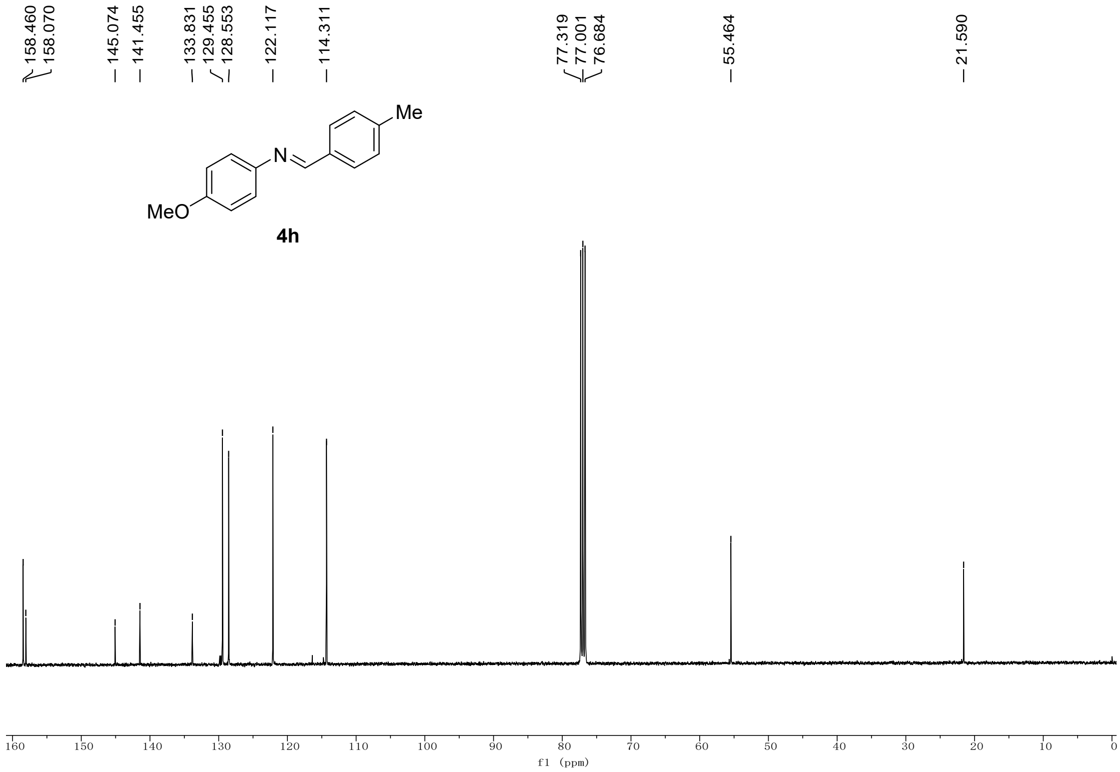

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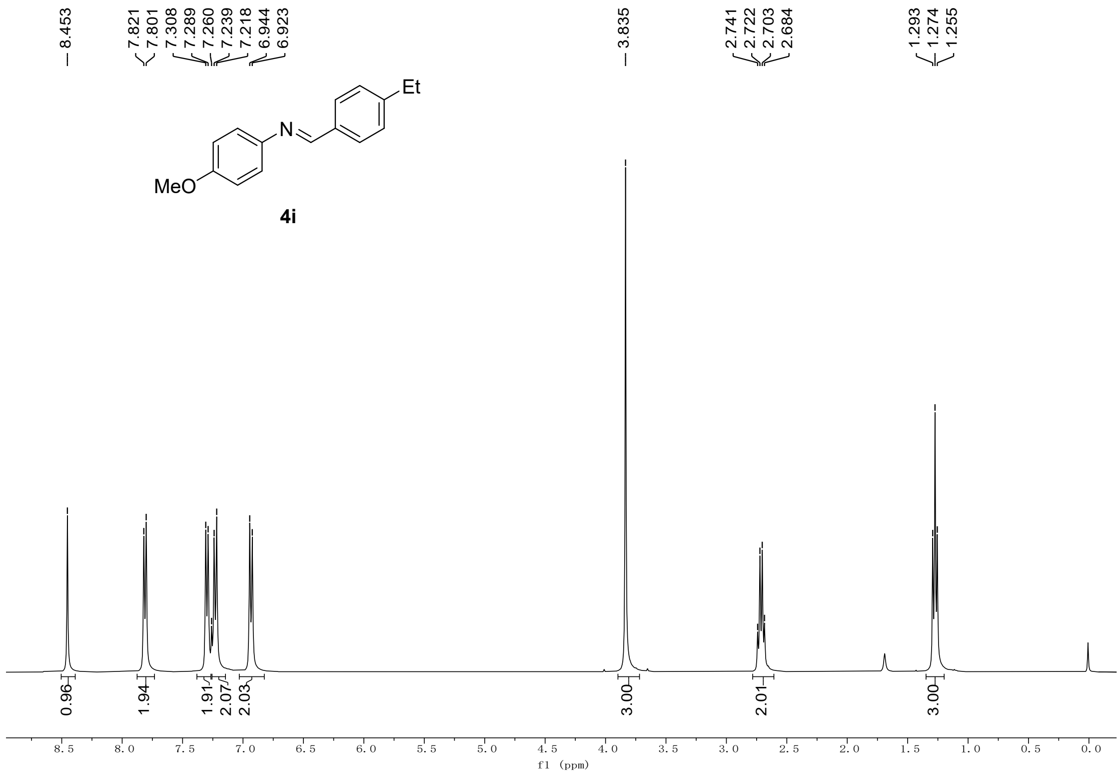
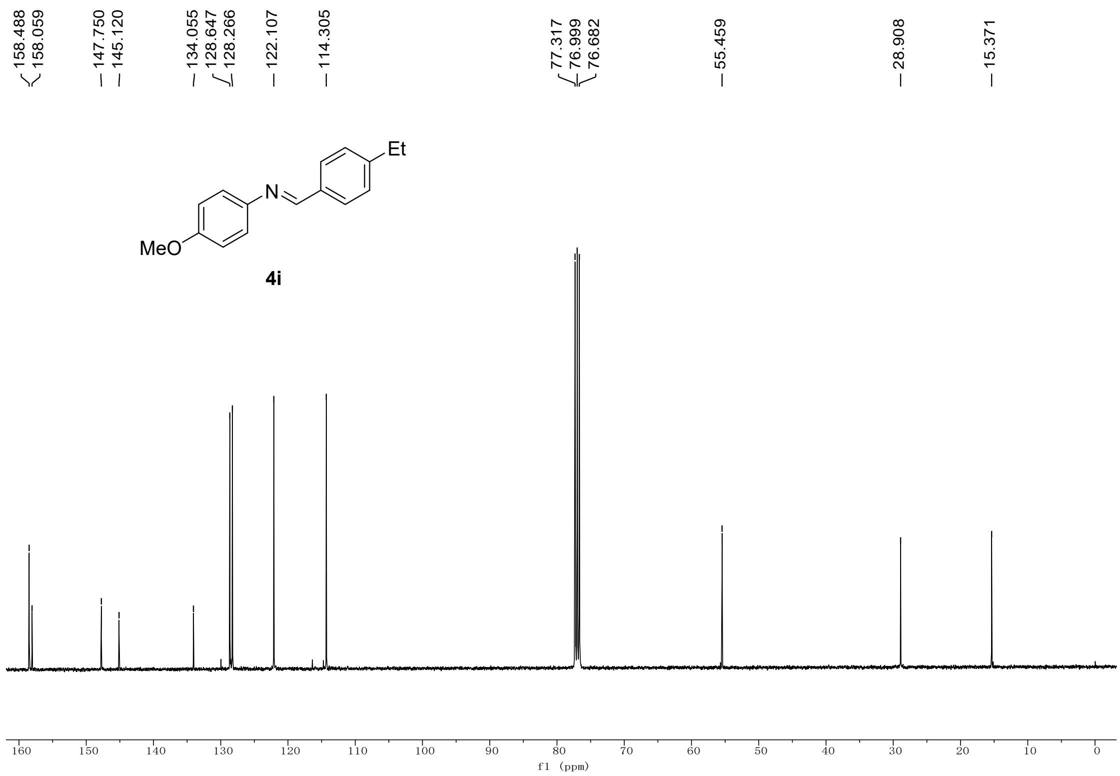
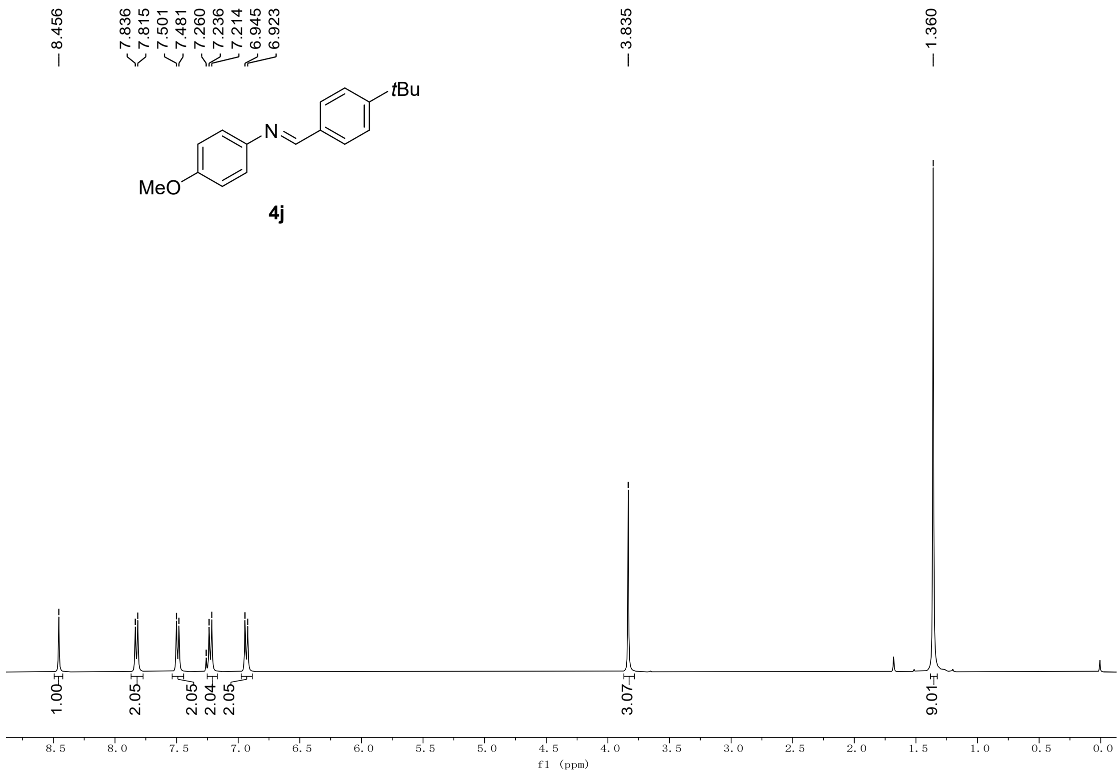


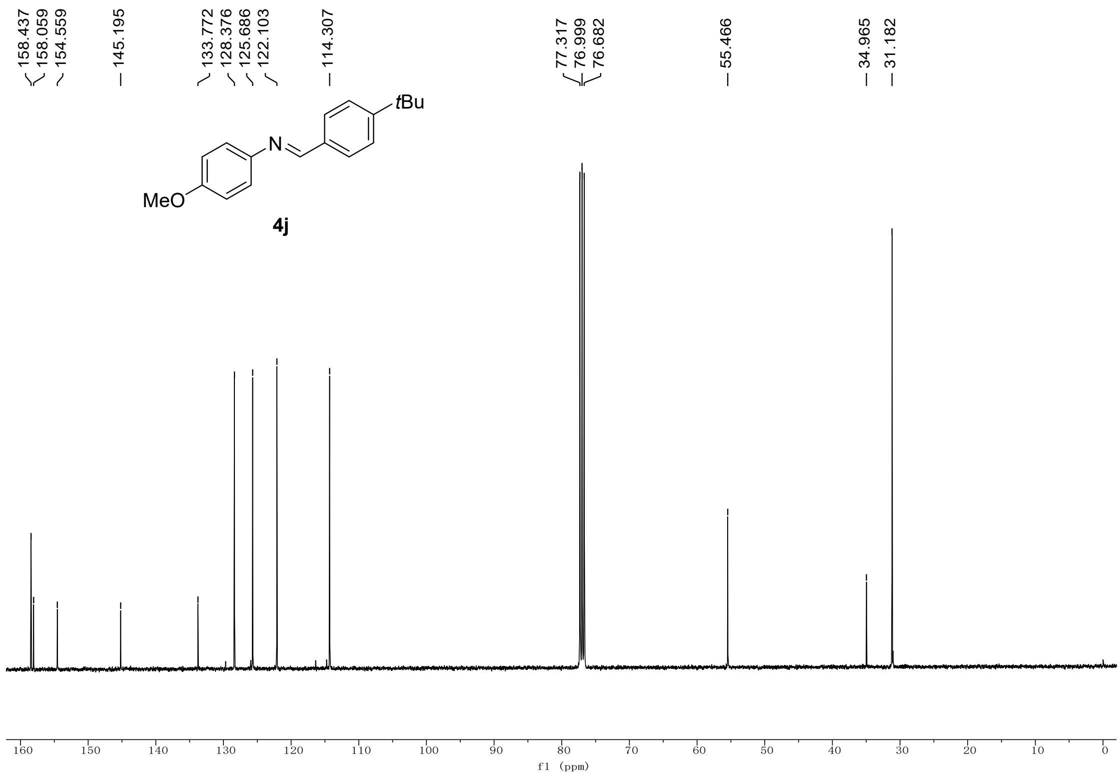
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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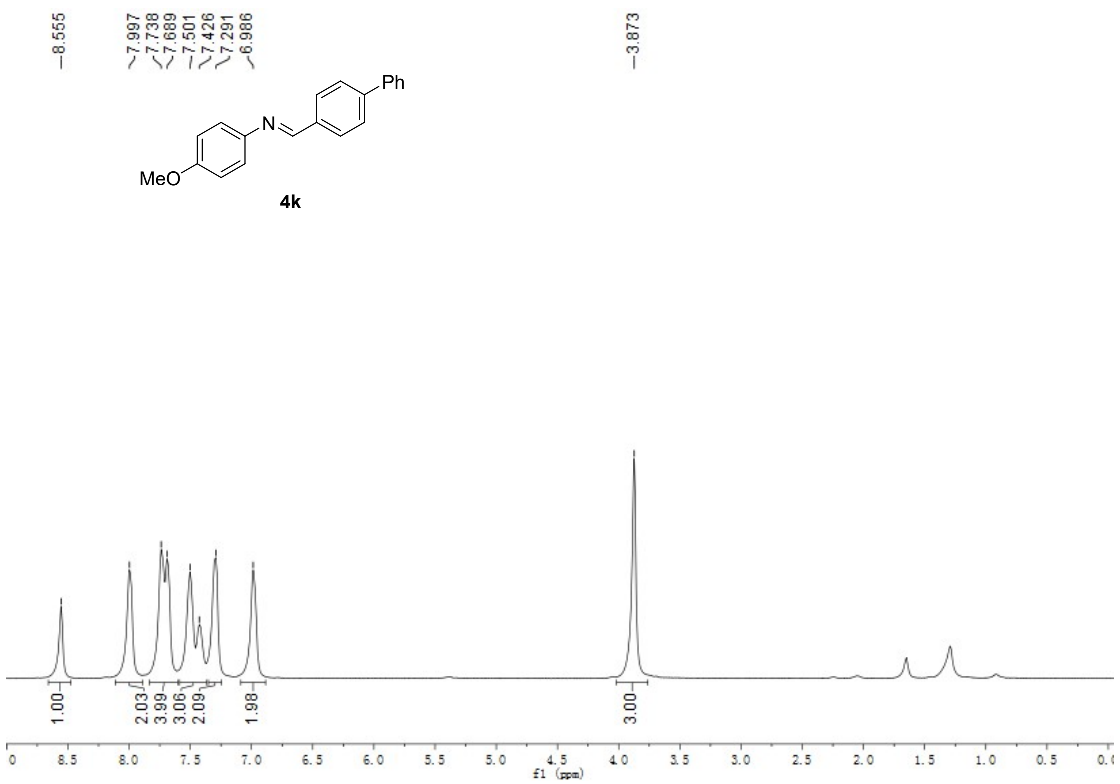
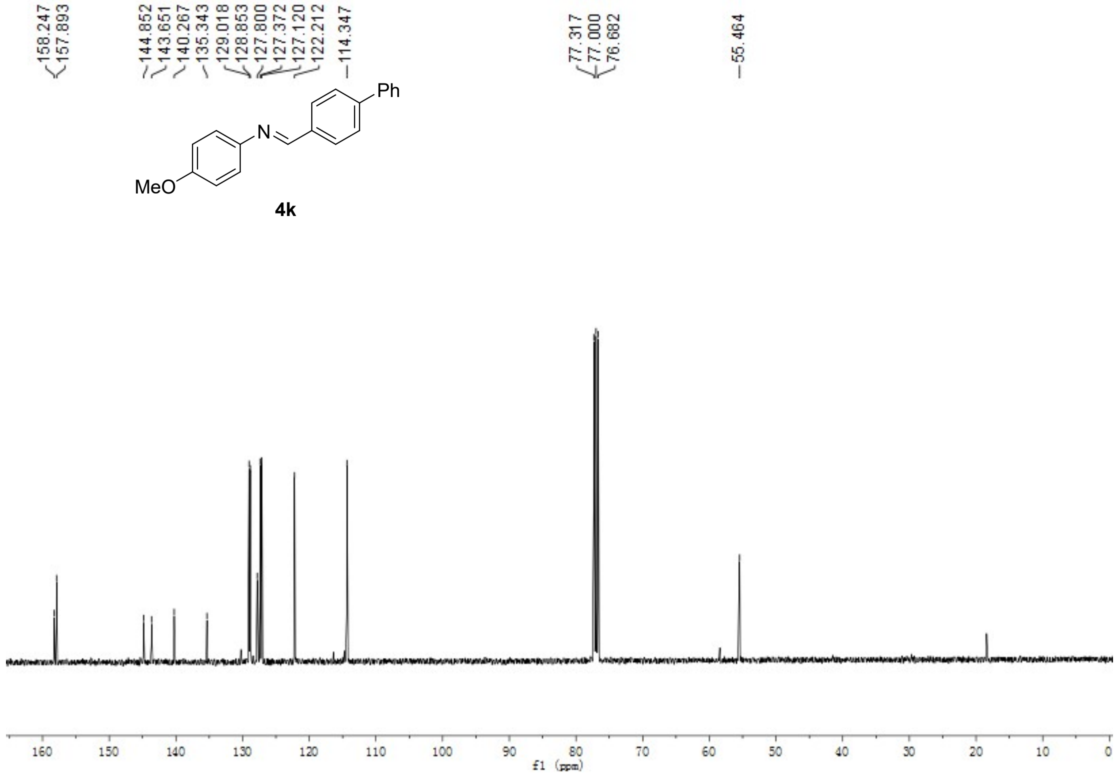
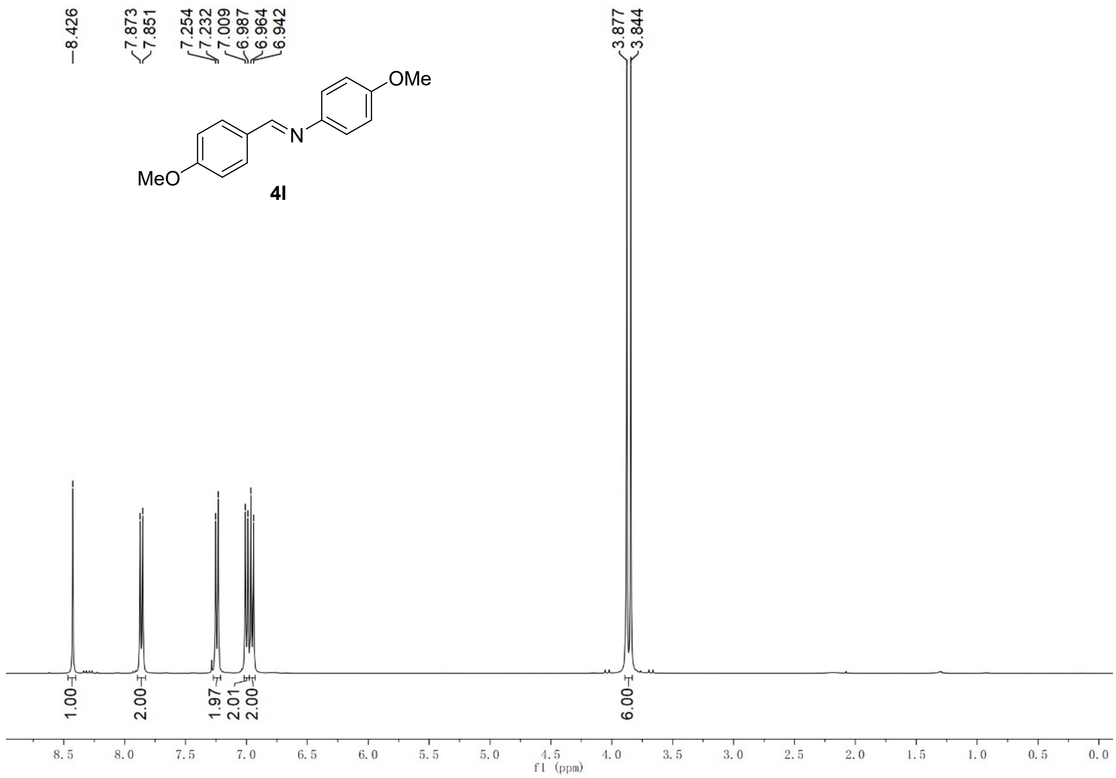


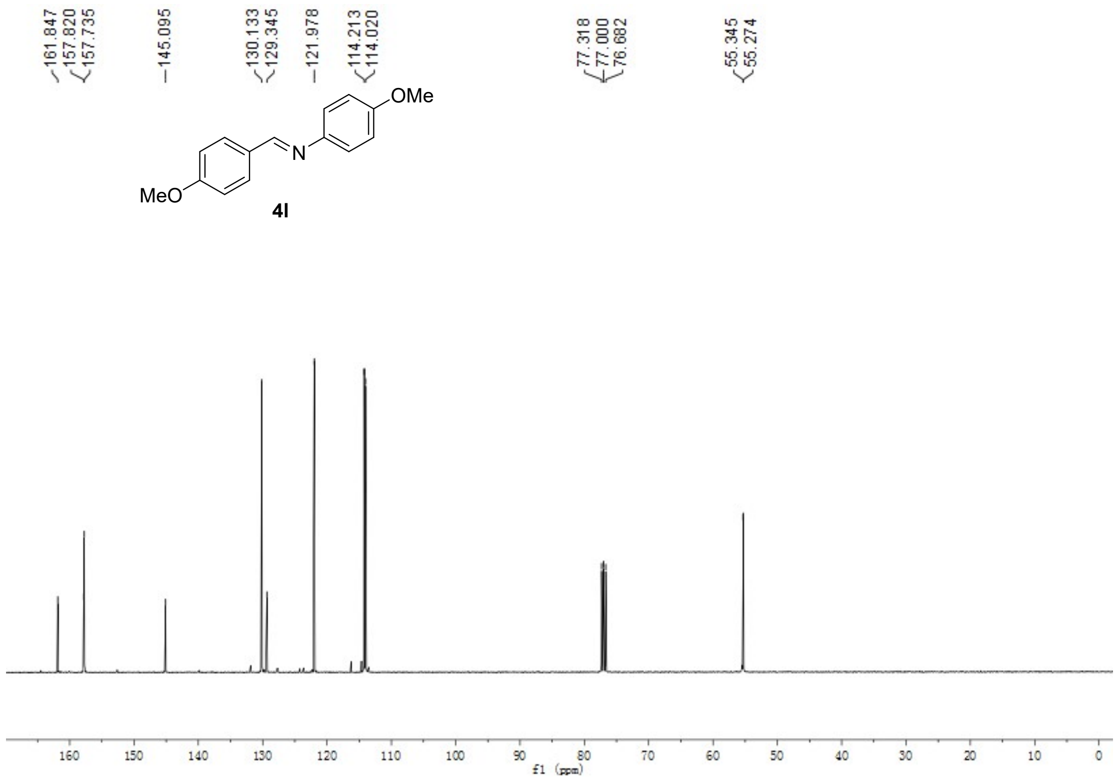
^{13}C NMR (100 MHz, CDCl$_3$)



^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (100 MHz, CDCl$_3$)



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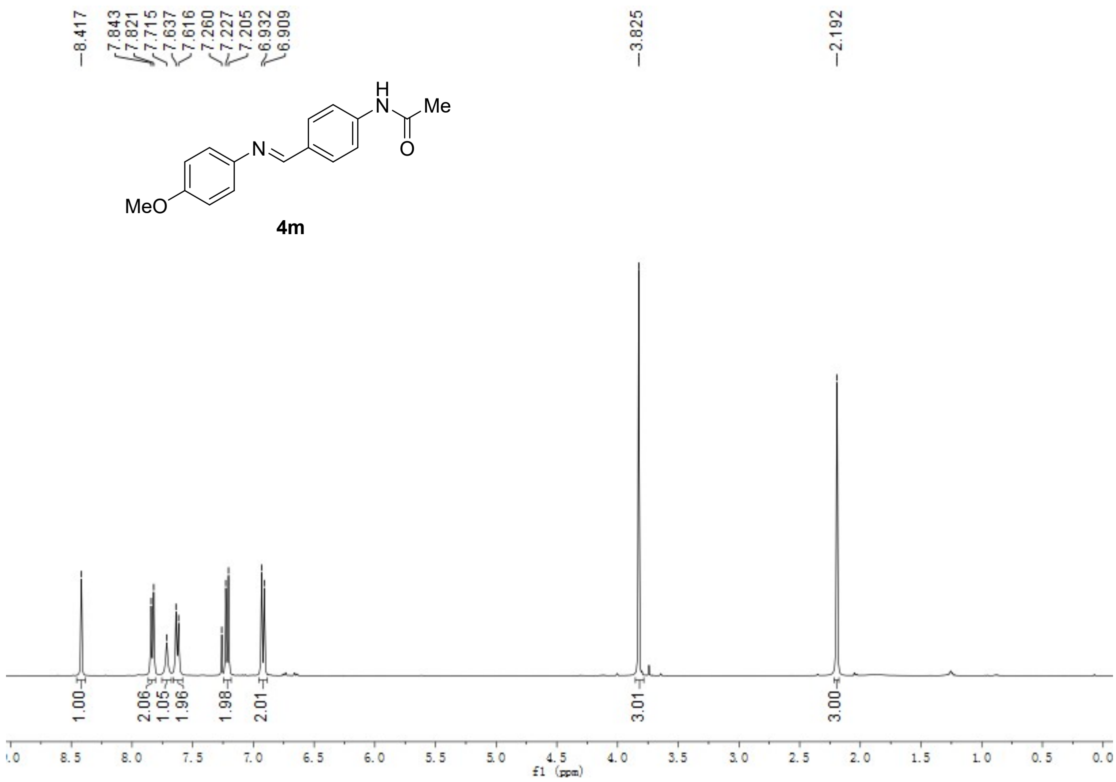
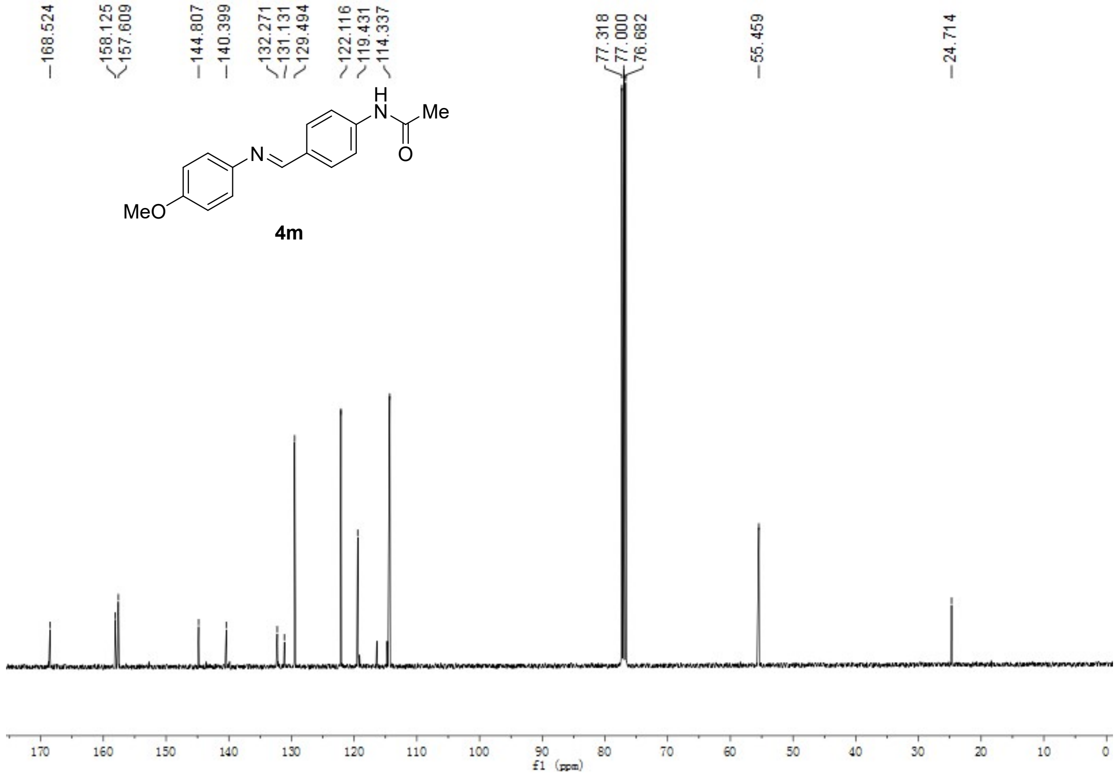
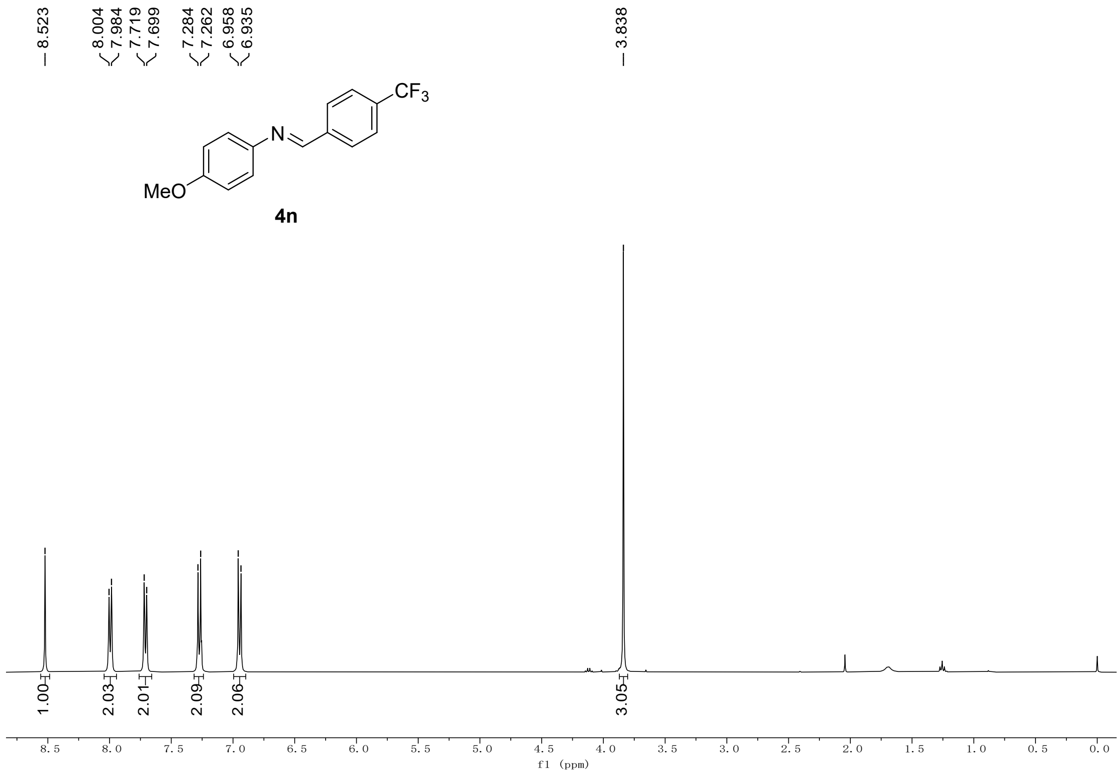


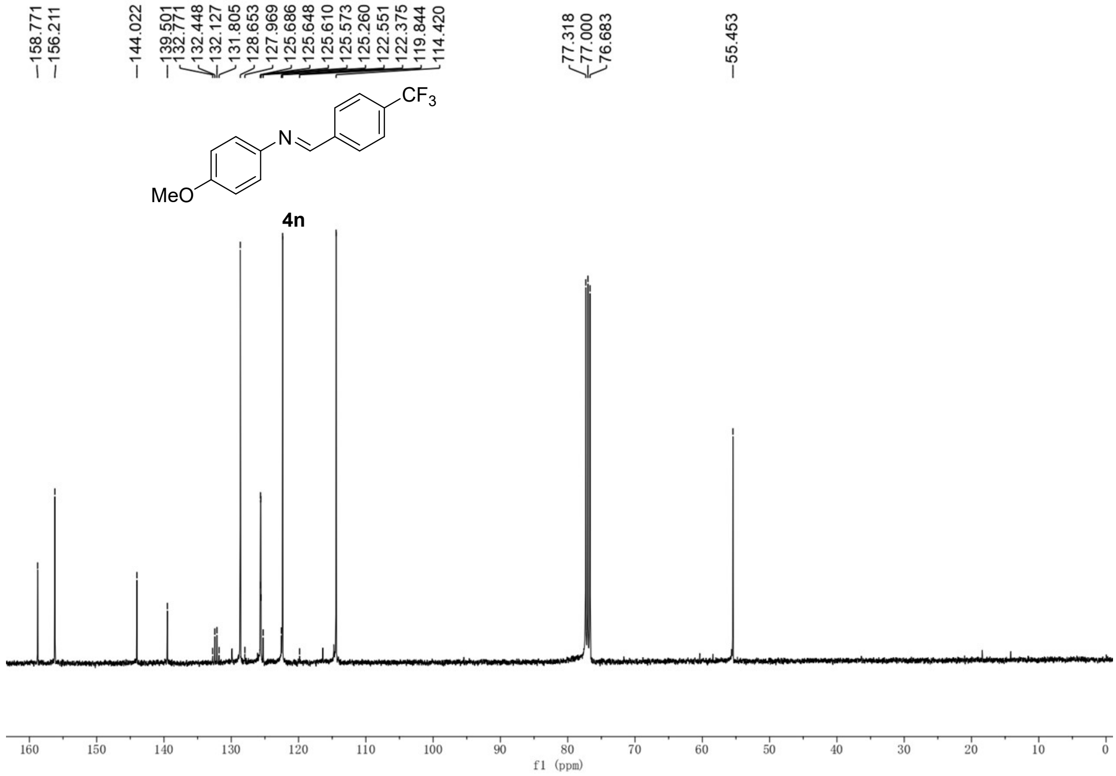
^{13}C NMR (100 MHz, $CDCl_3$)



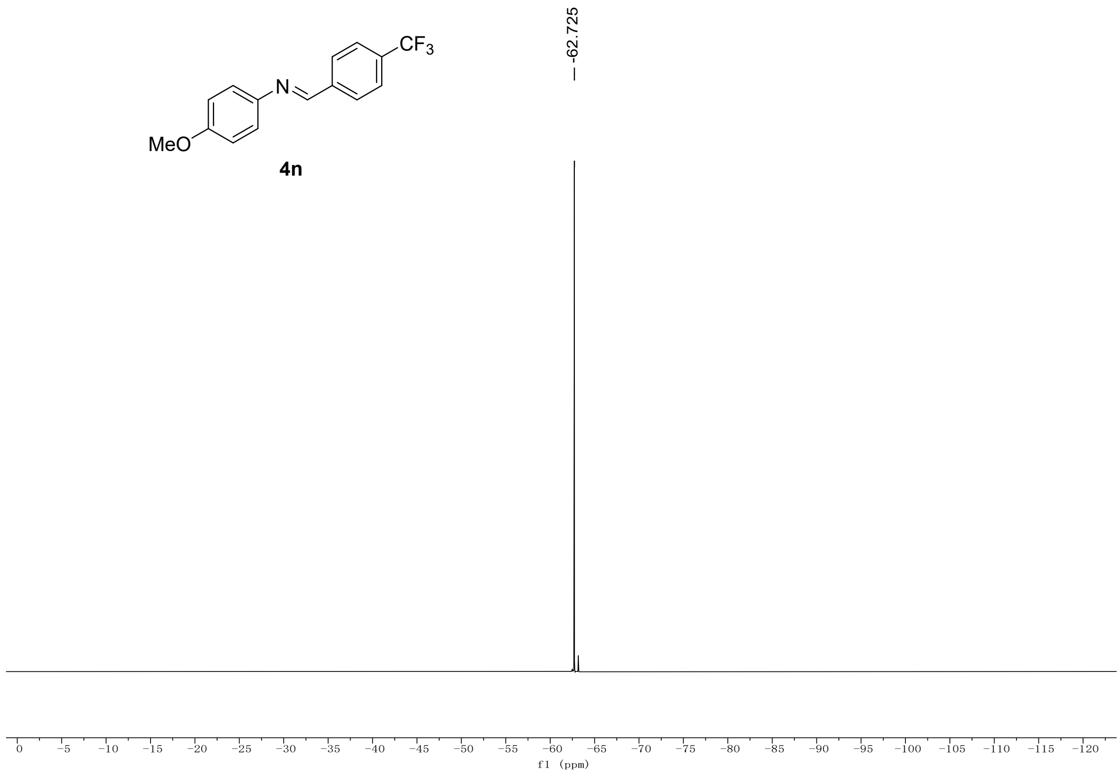
^{1}H NMR (400 MHz, $CDCl_3$)



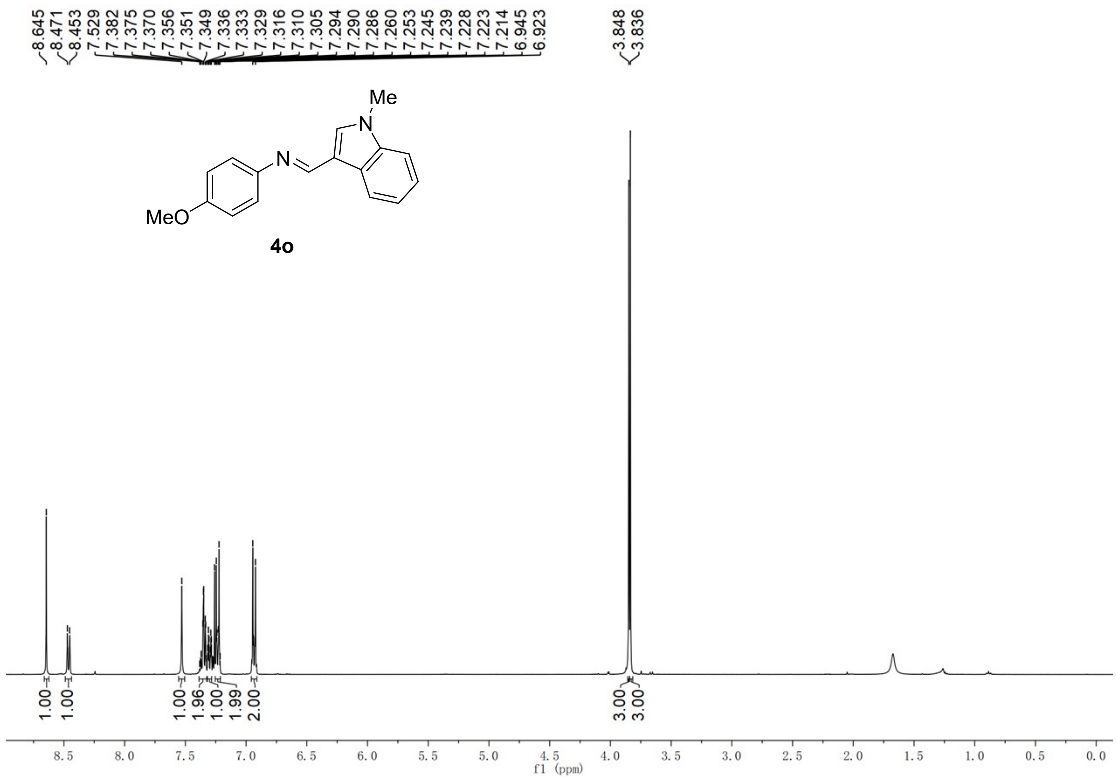
^{13}C NMR (100 MHz, $CDCl_3$)



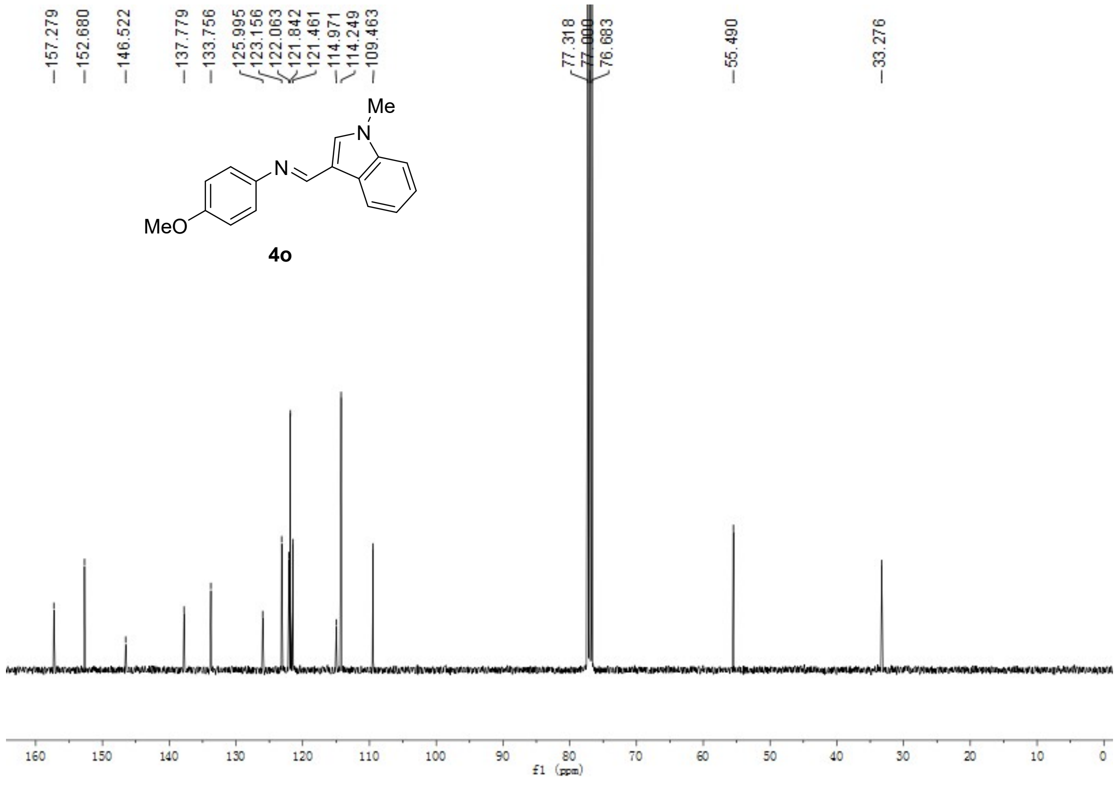
^{19}F NMR (376 MHz, $CDCl_3$)



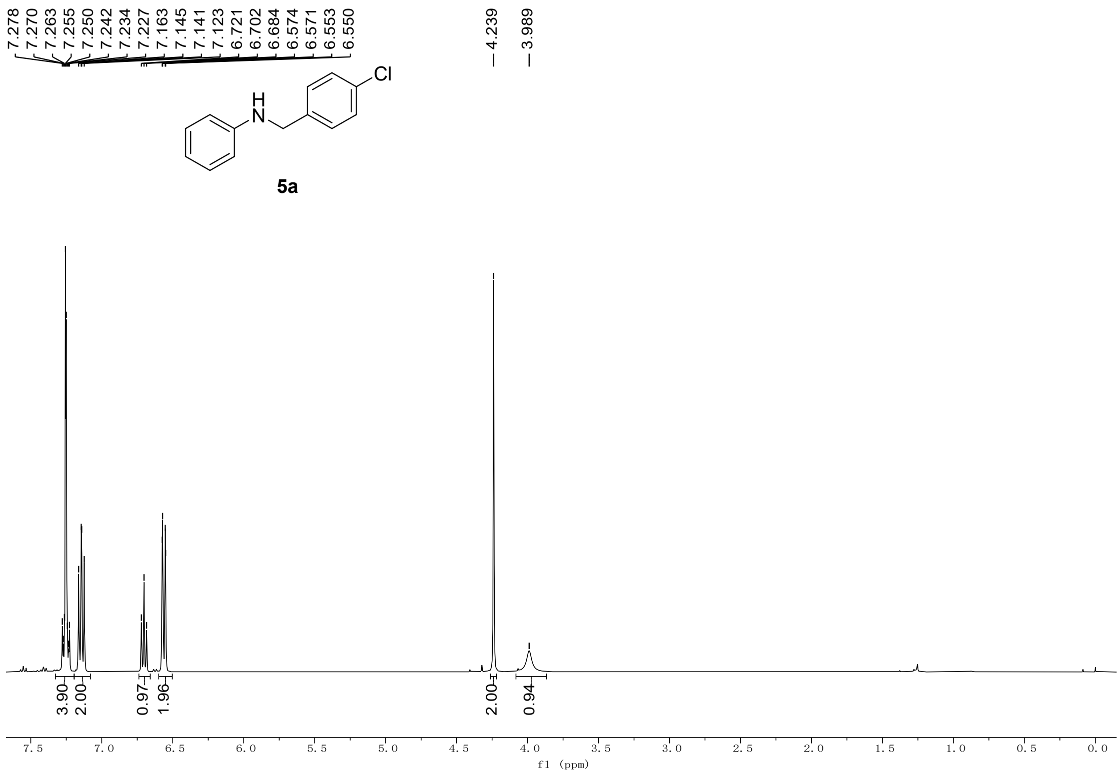
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

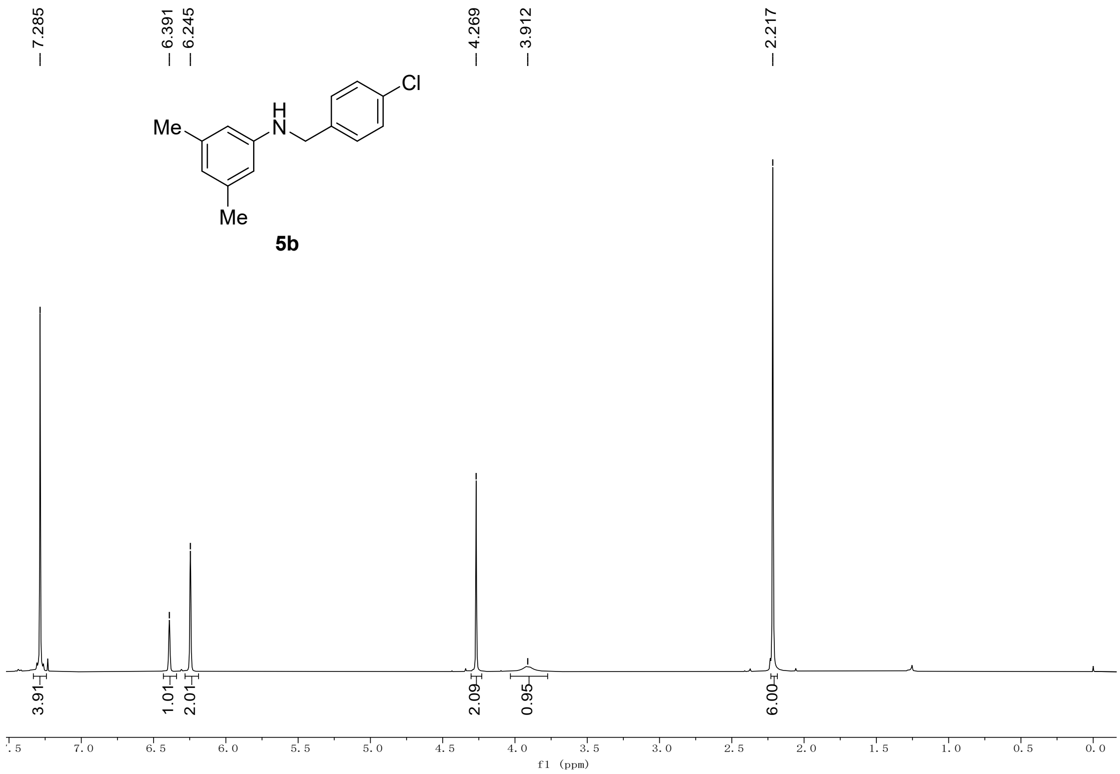


^{1}H NMR (400 MHz, $CDCl_3$)

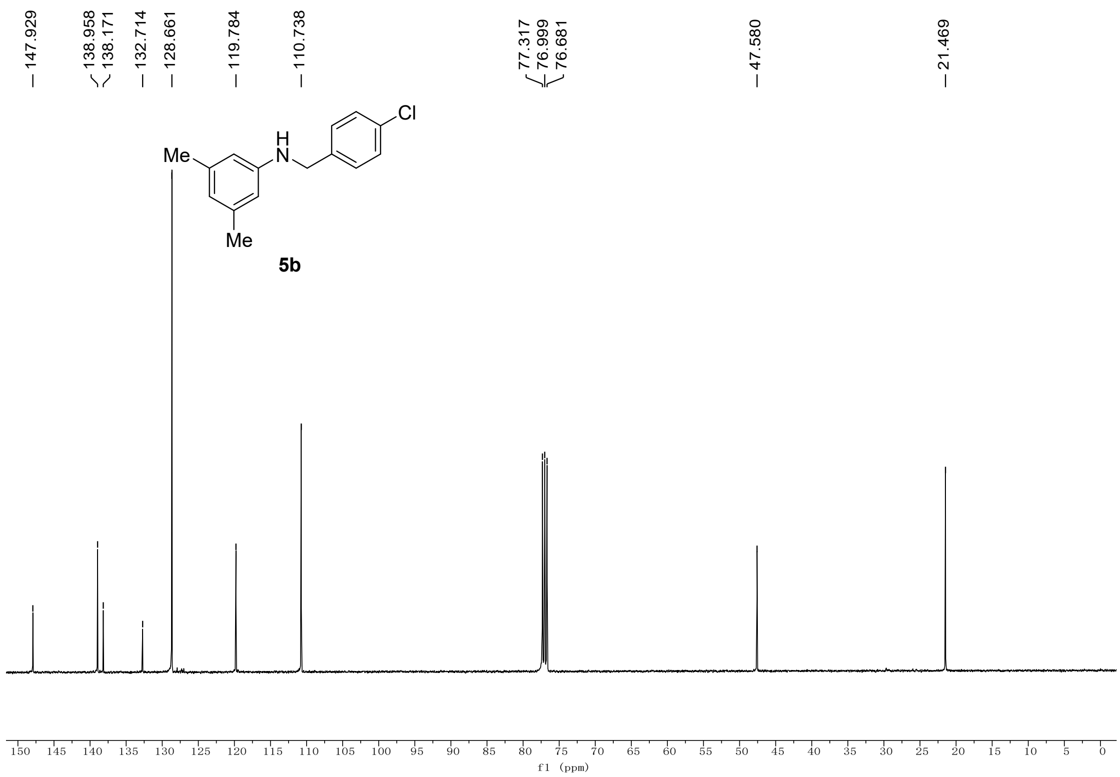


^{13}C NMR (100 MHz, $CDCl_3$)

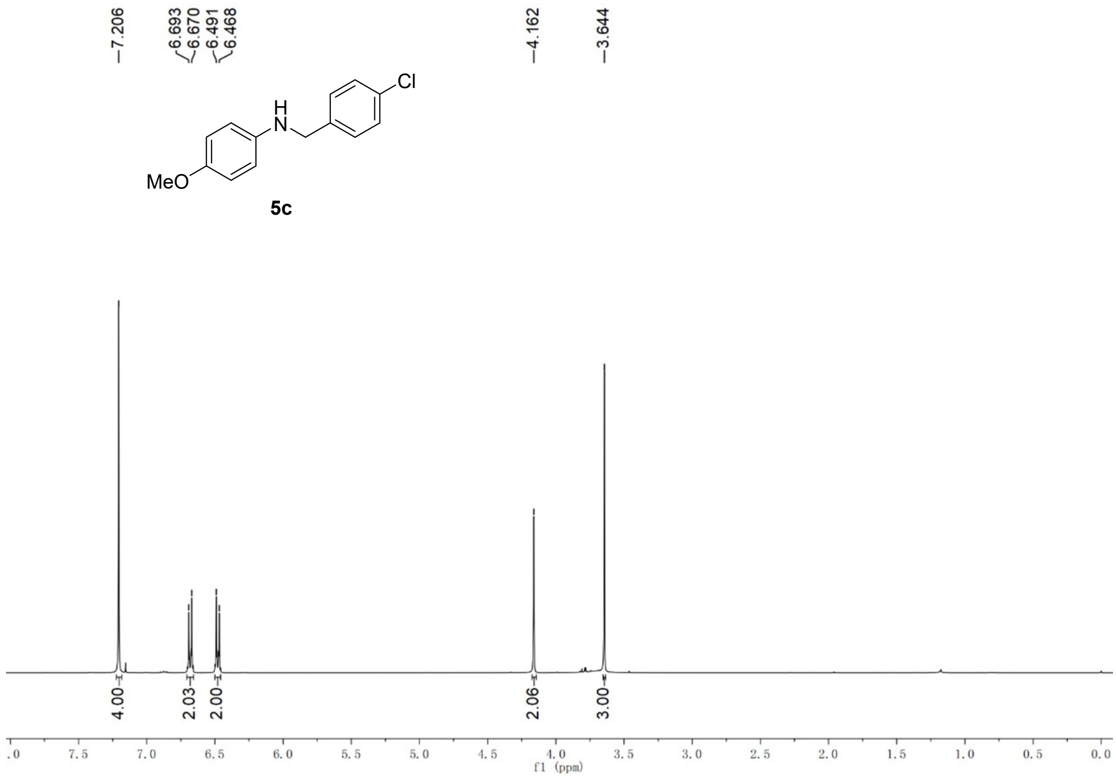
^{1}H NMR (400 MHz, $CDCl_3$)



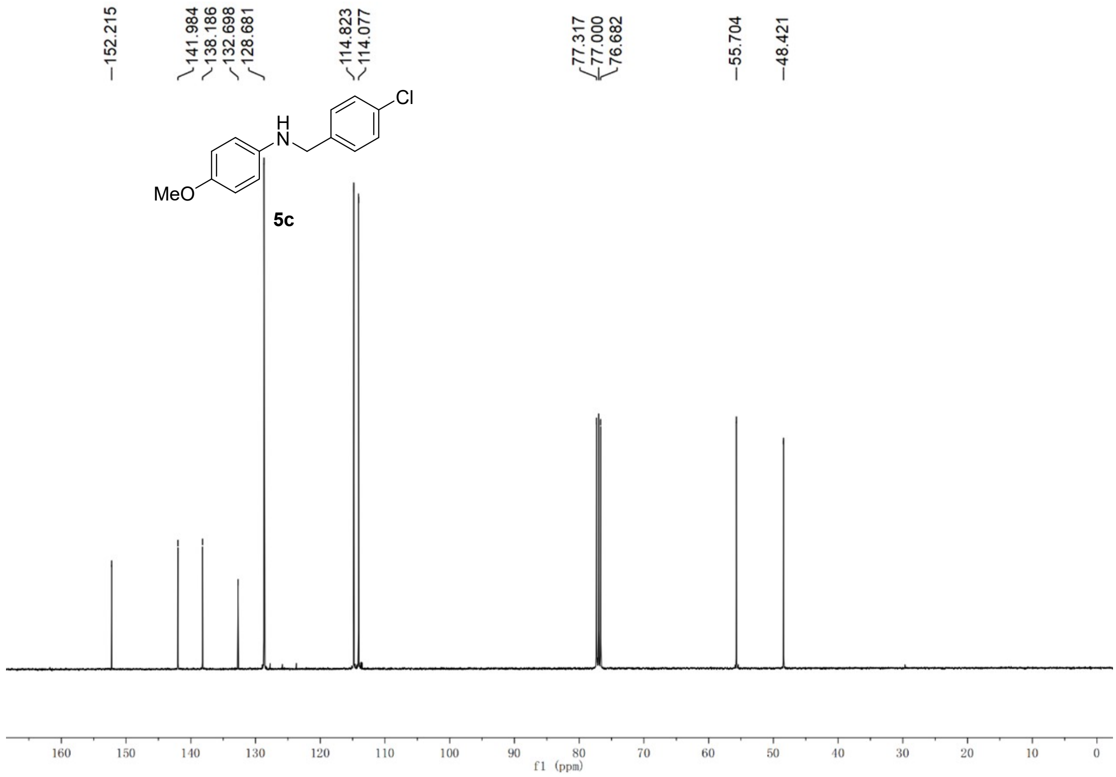
^{13}C NMR (100 MHz, $CDCl_3$)



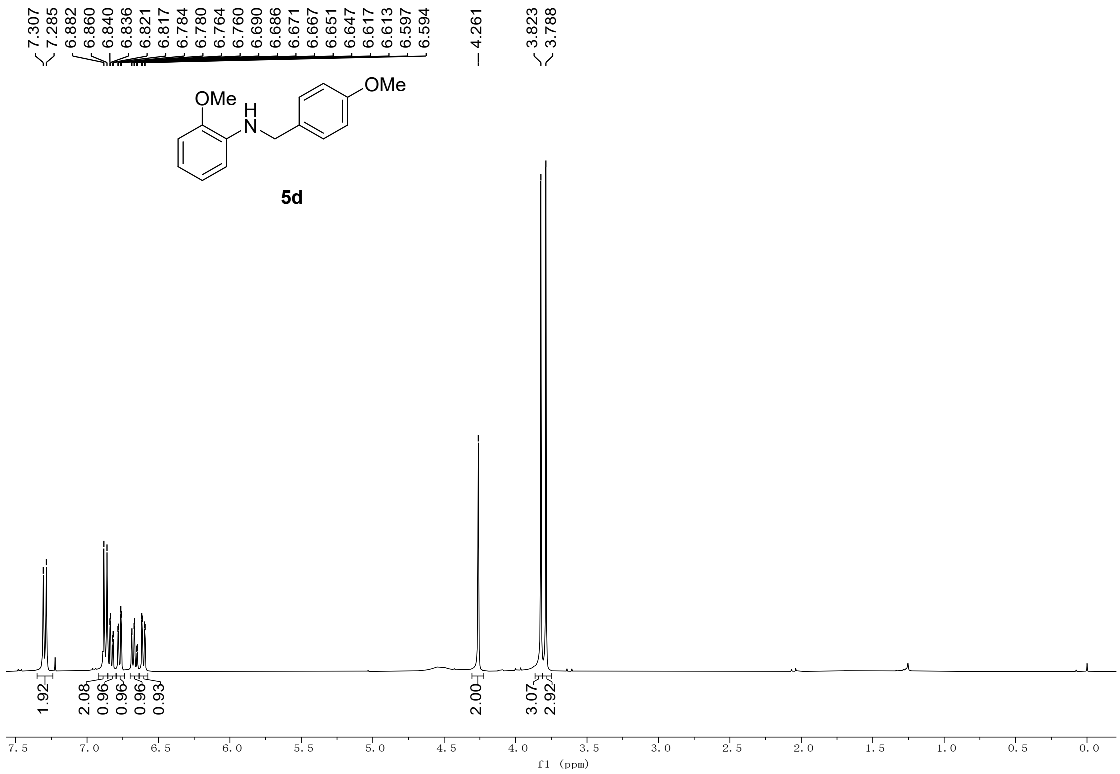
^1H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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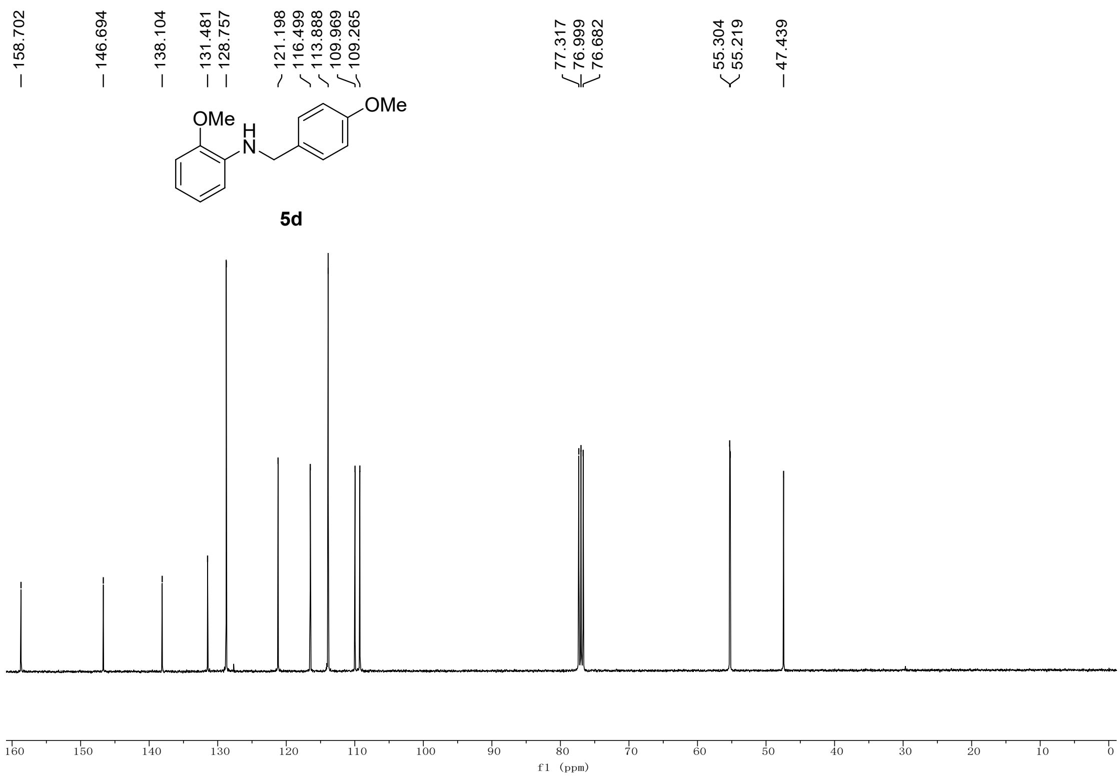

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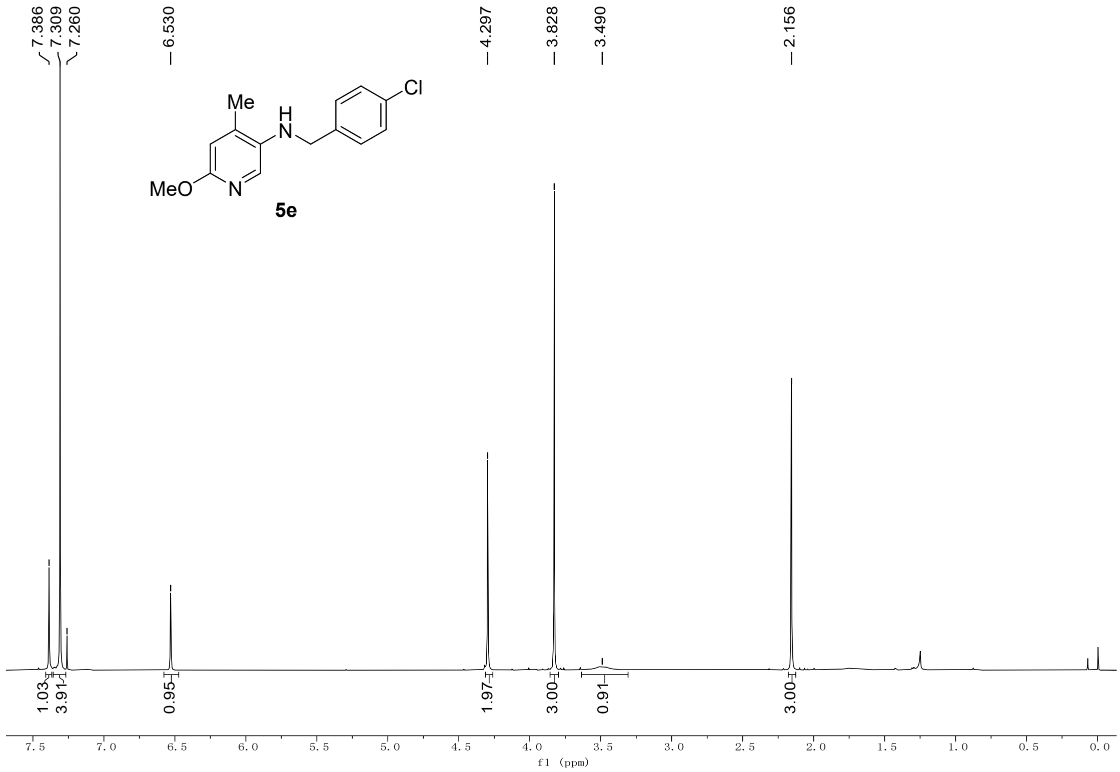

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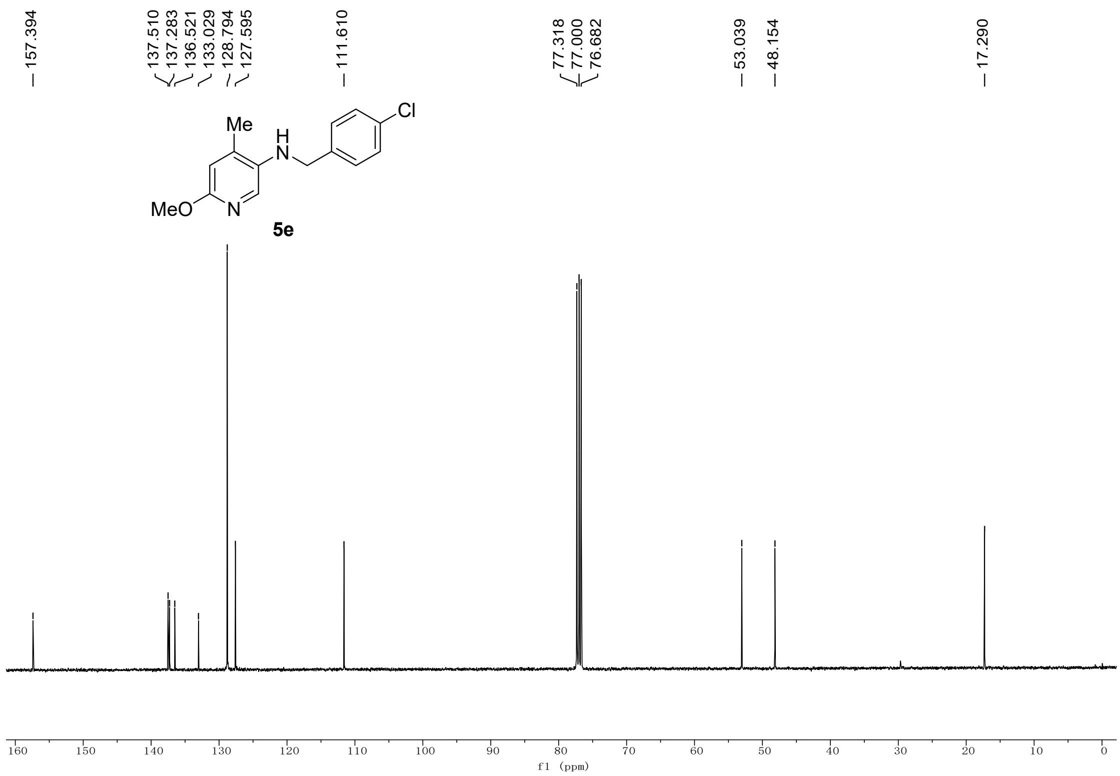

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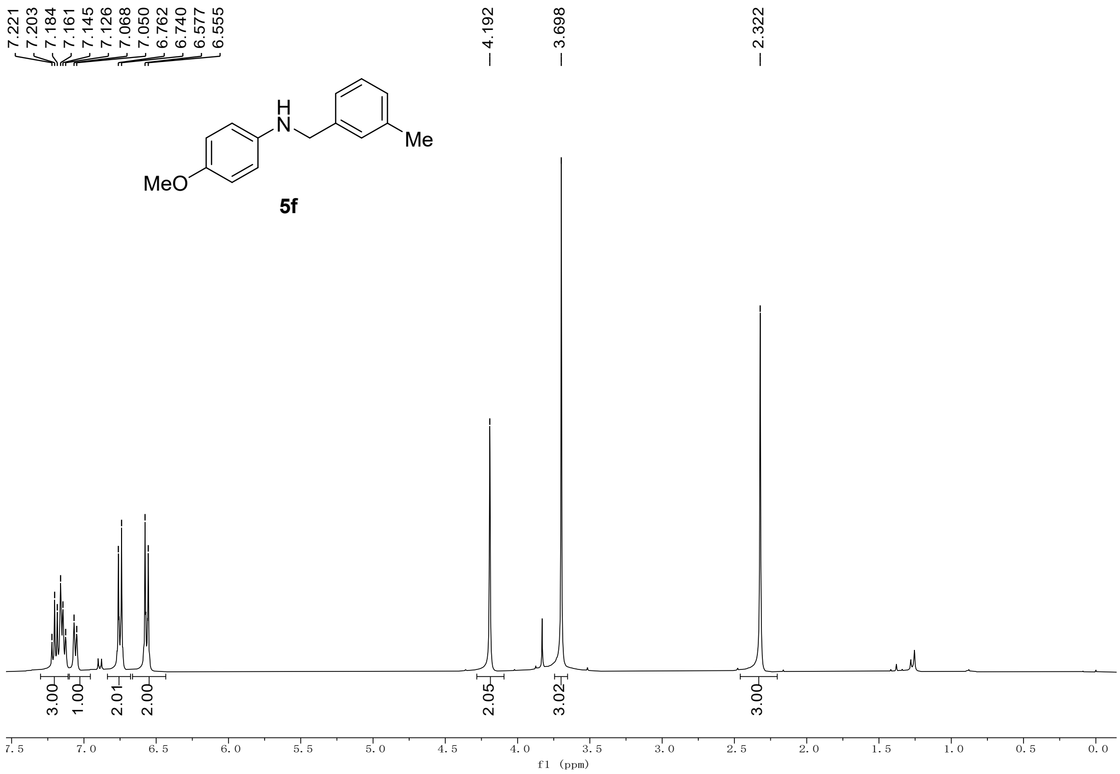

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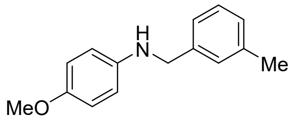

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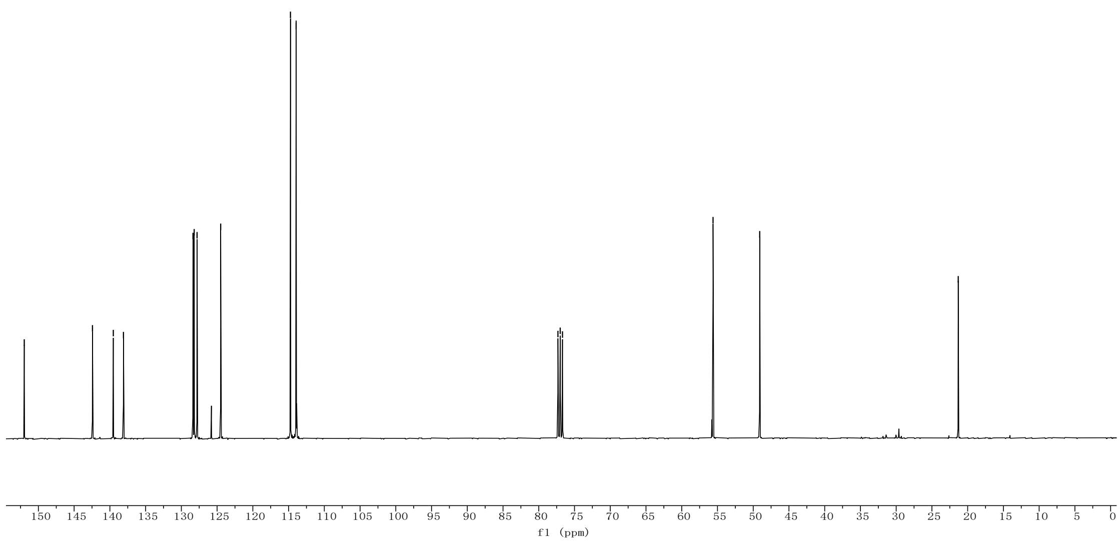

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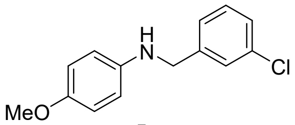

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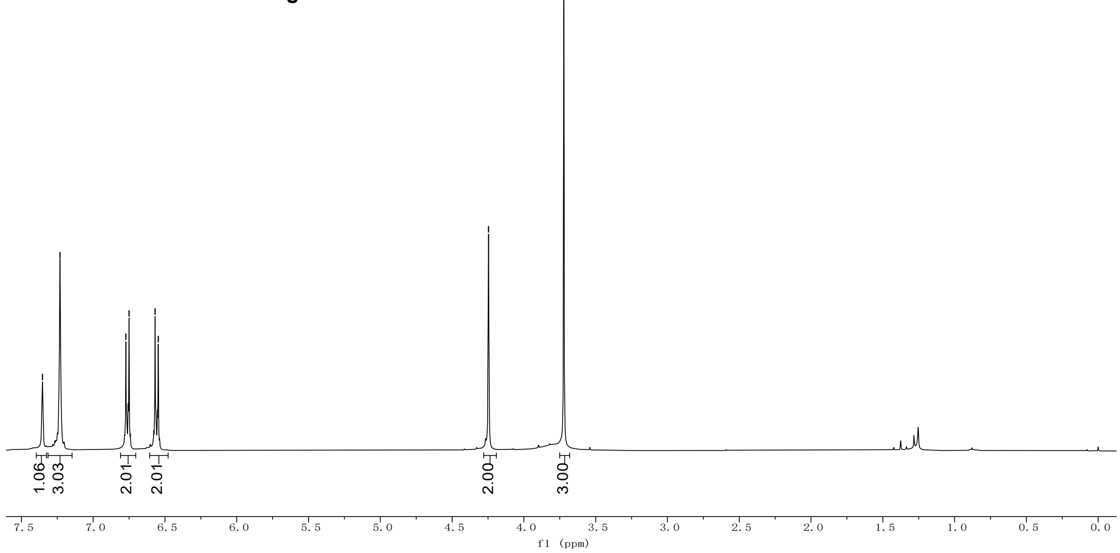
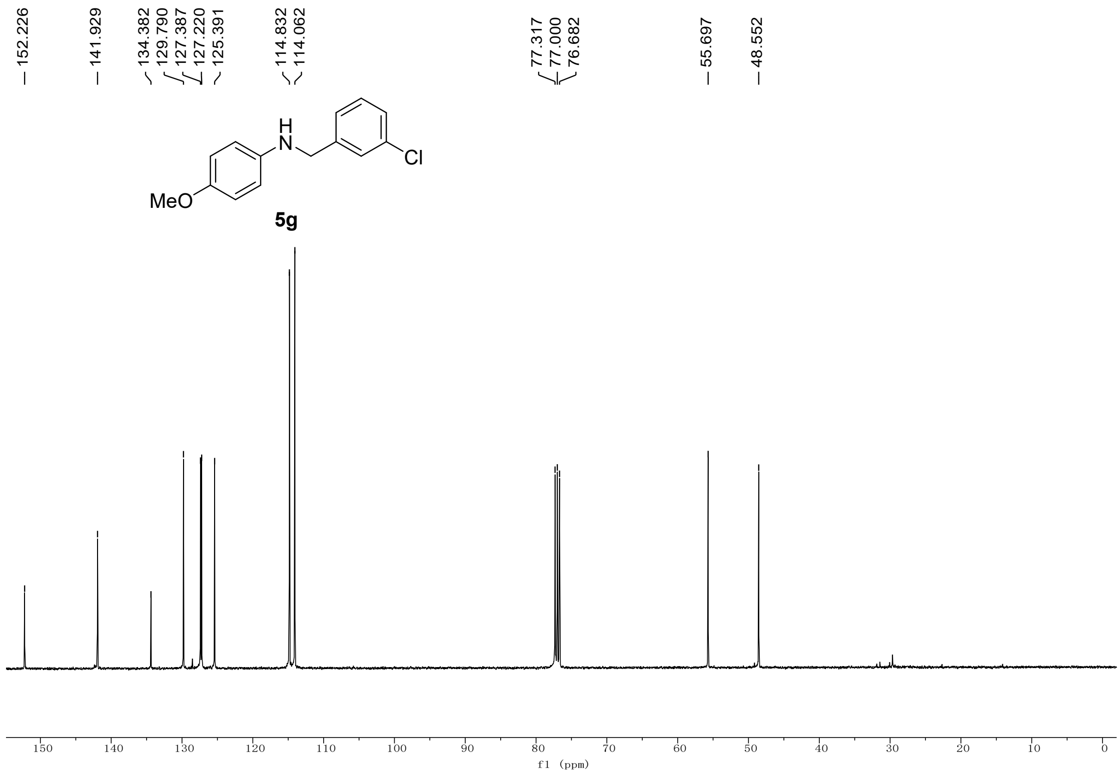
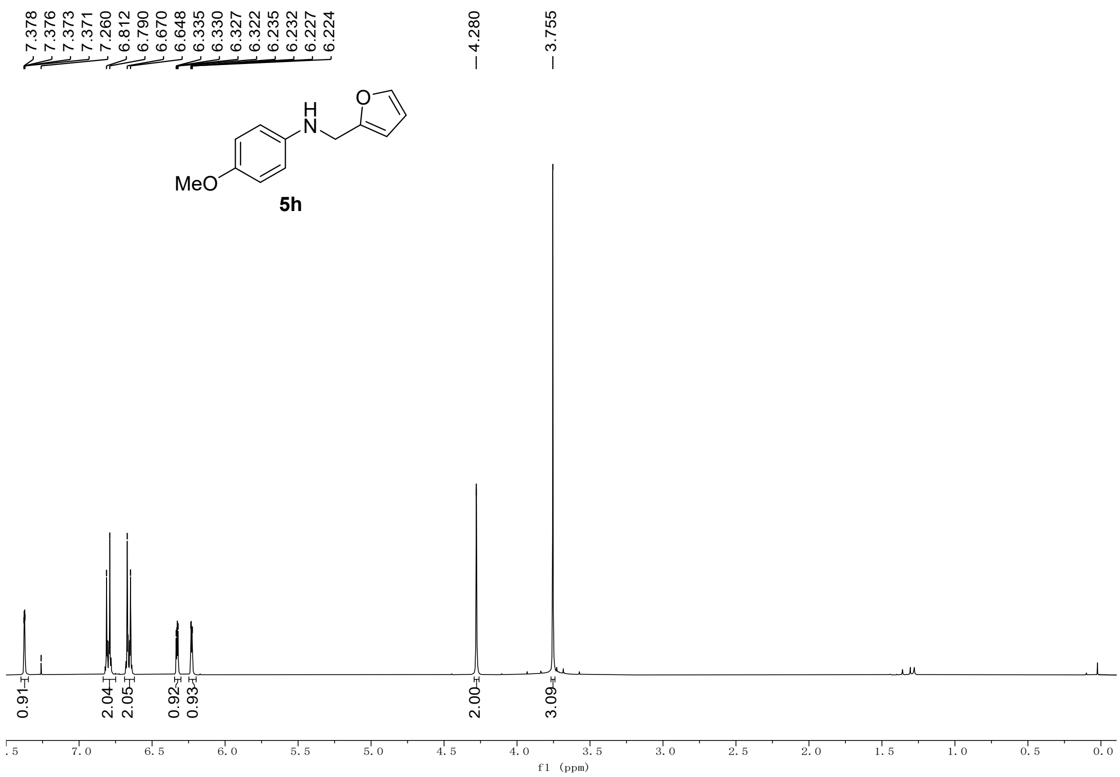


^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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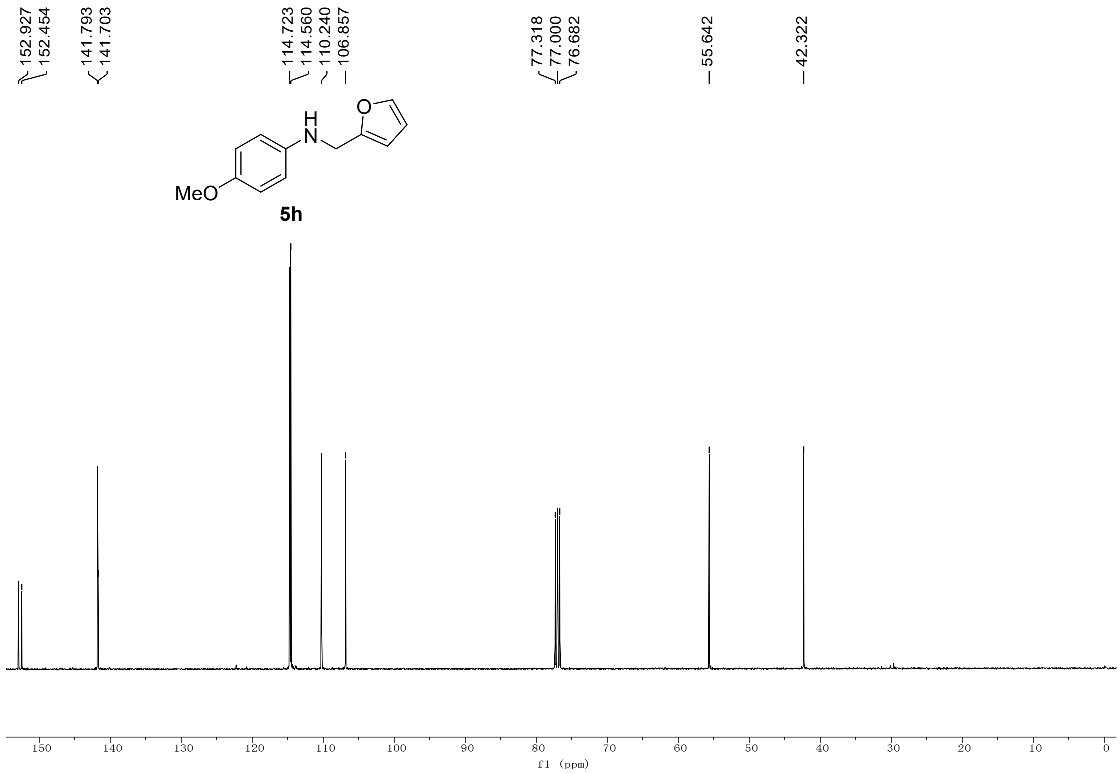

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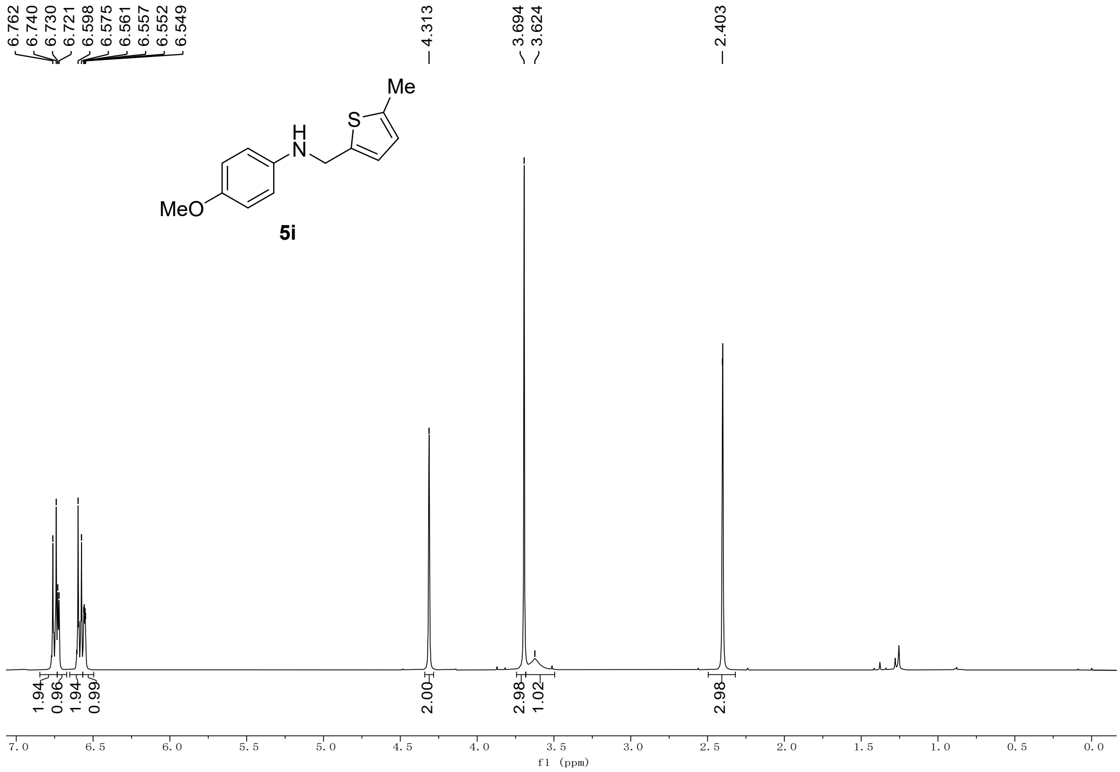

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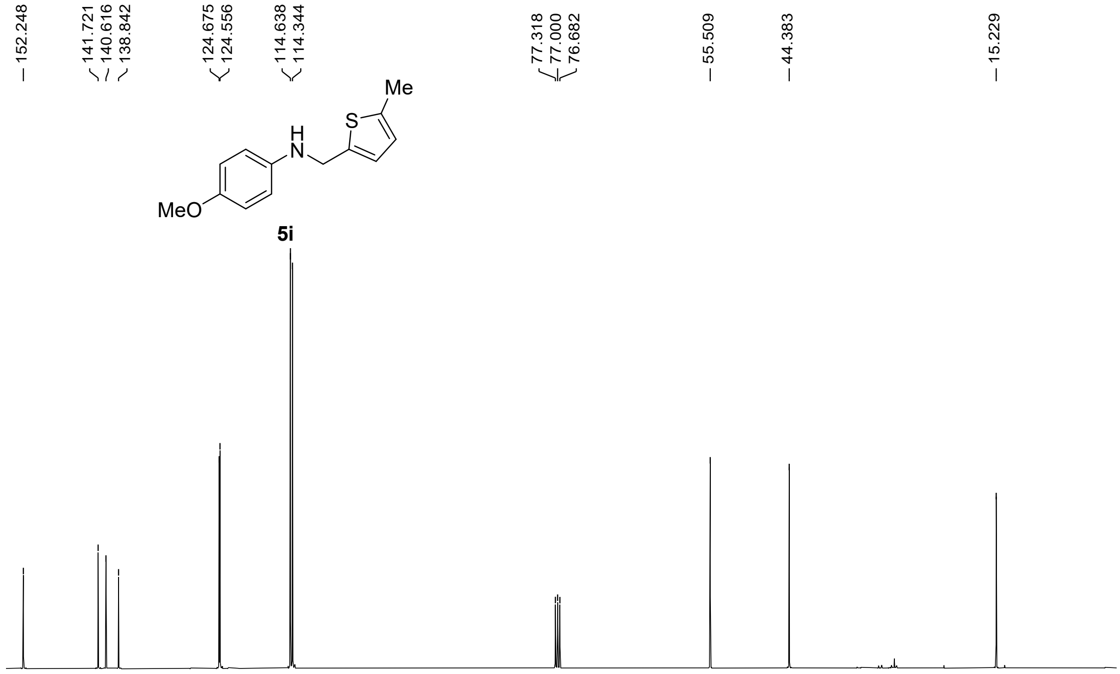

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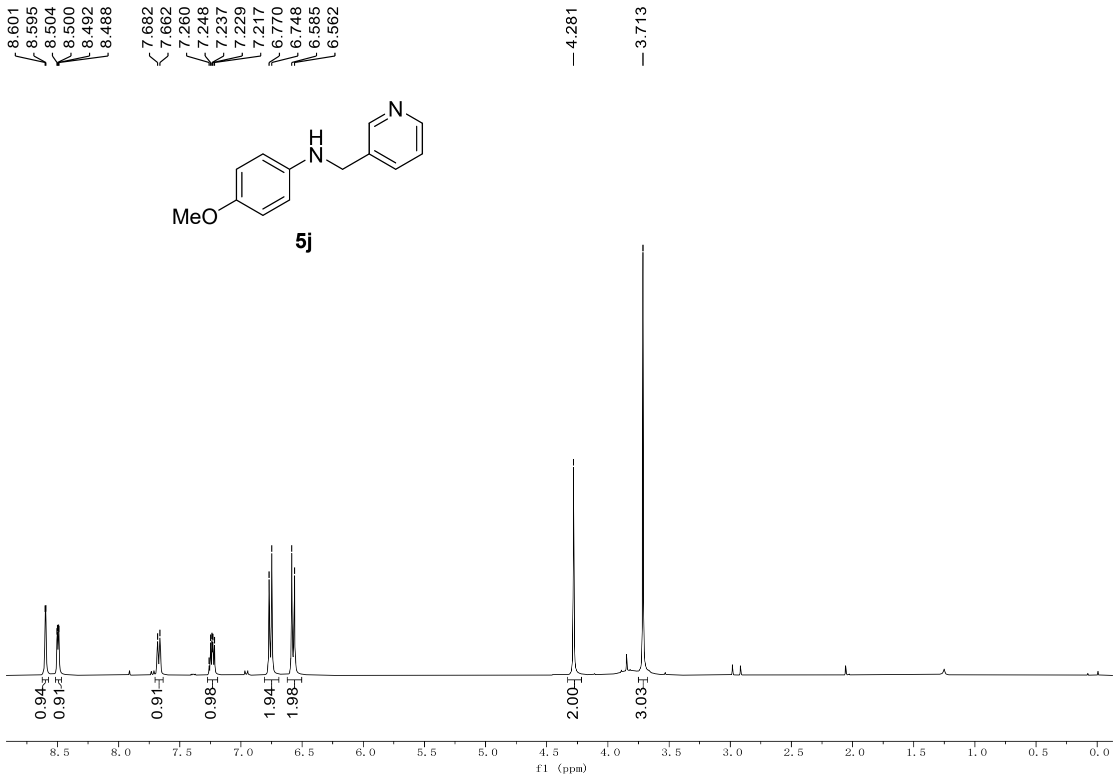

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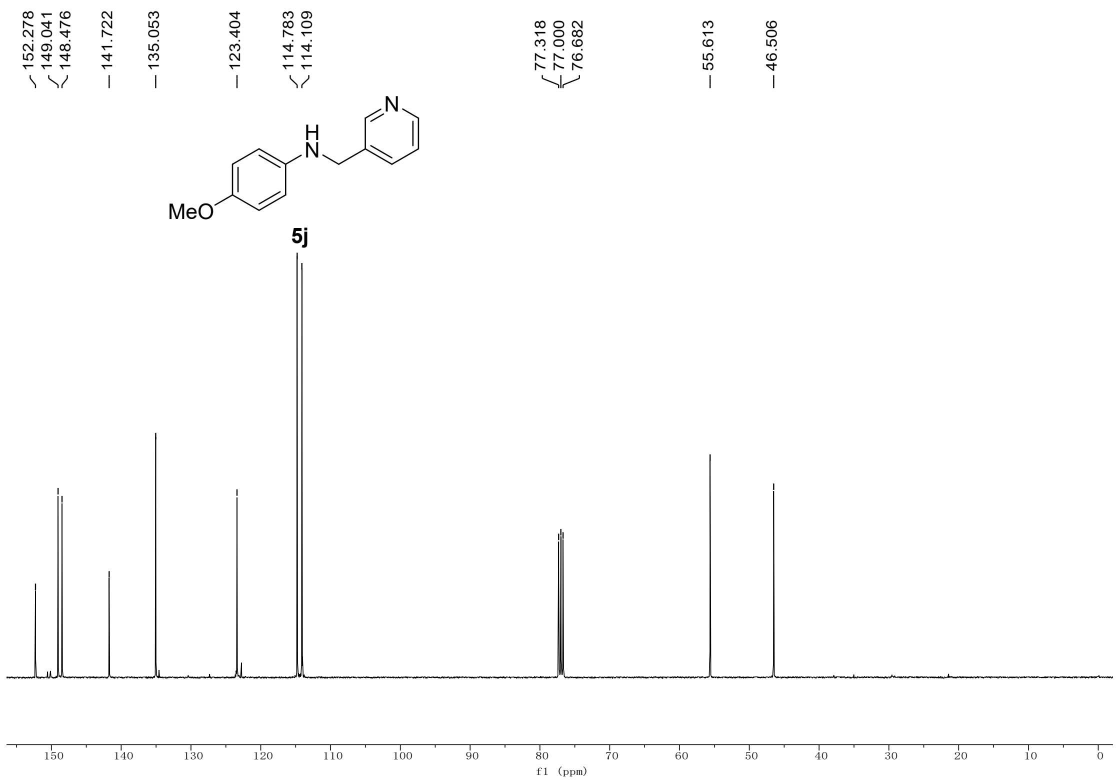

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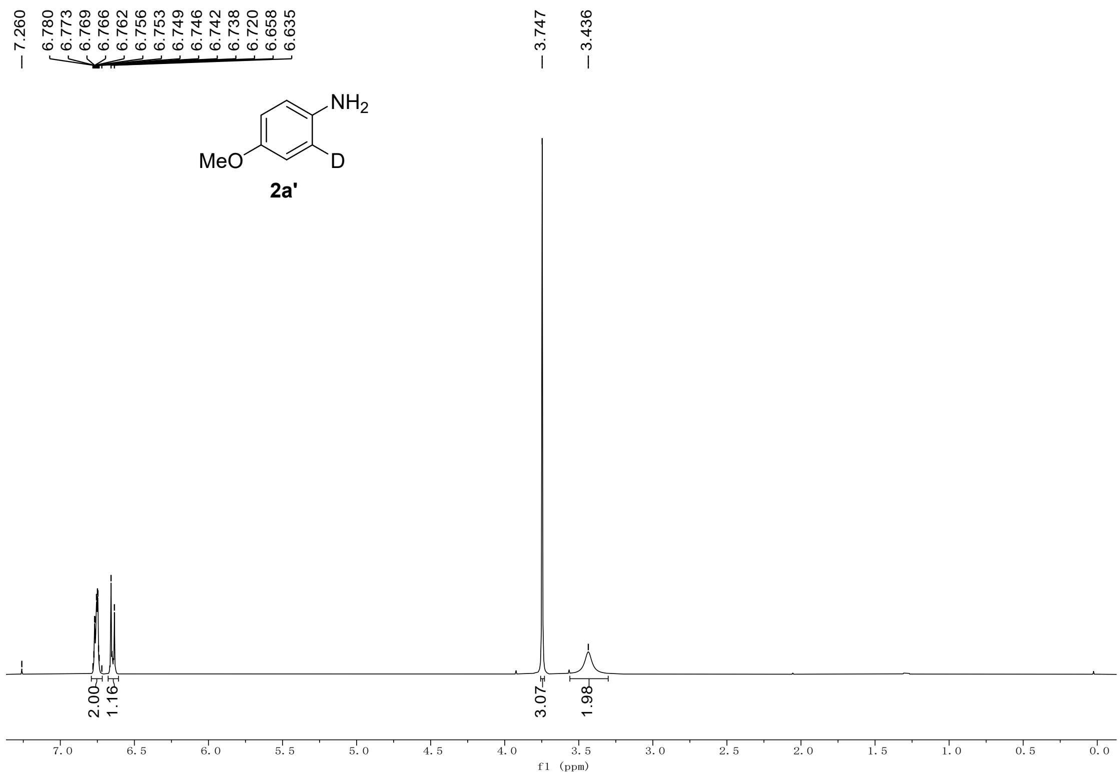

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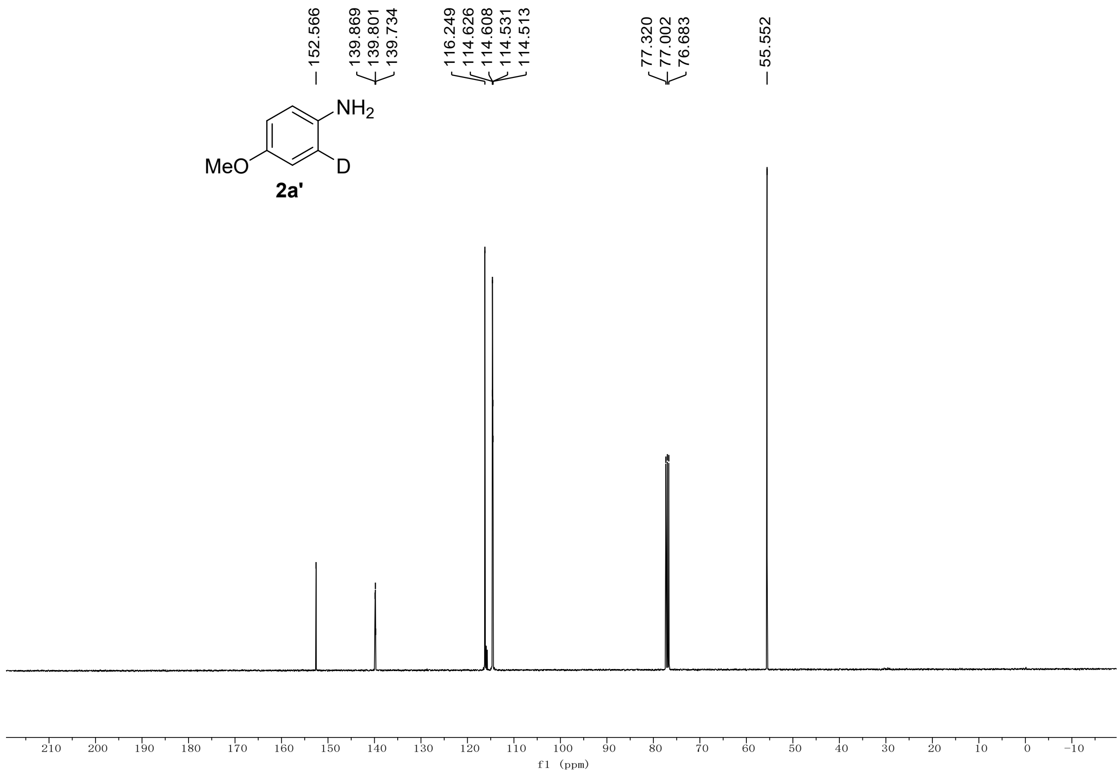

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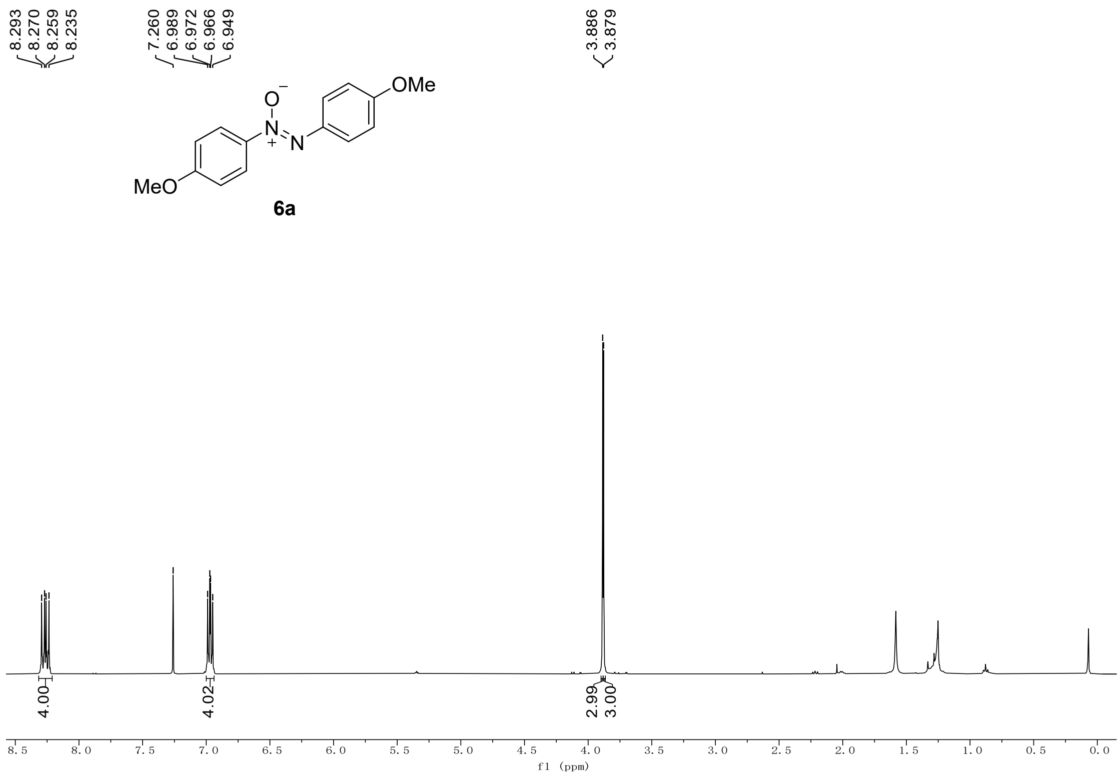

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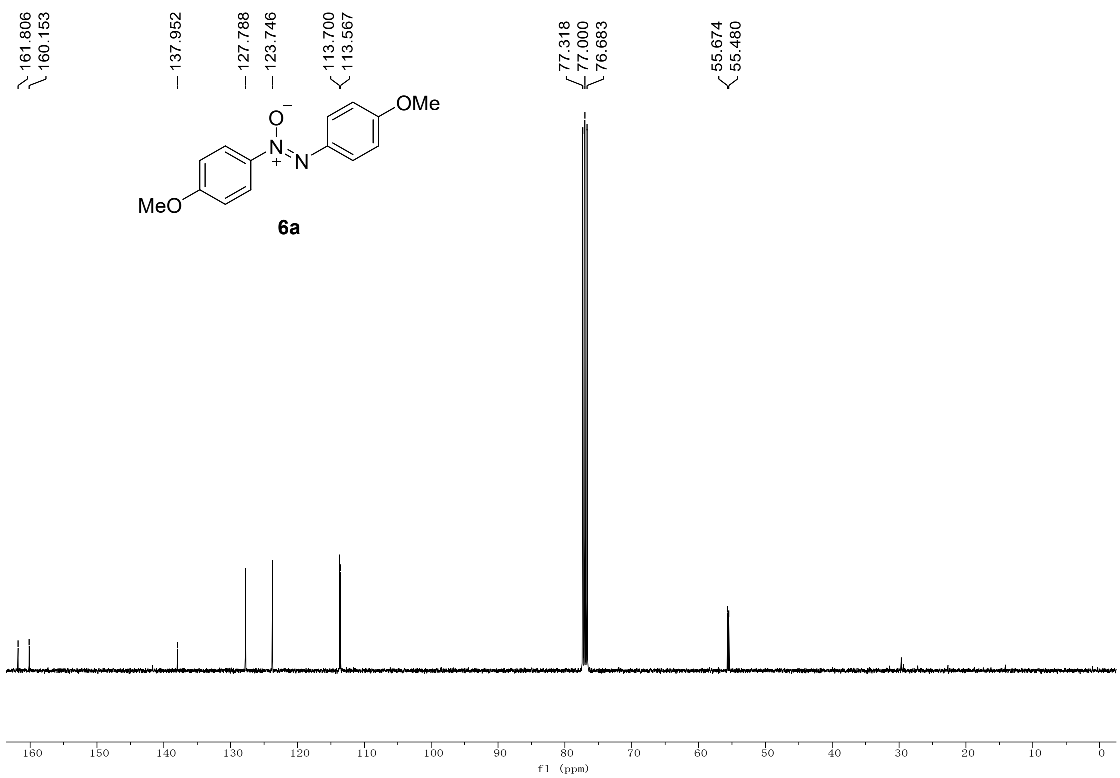

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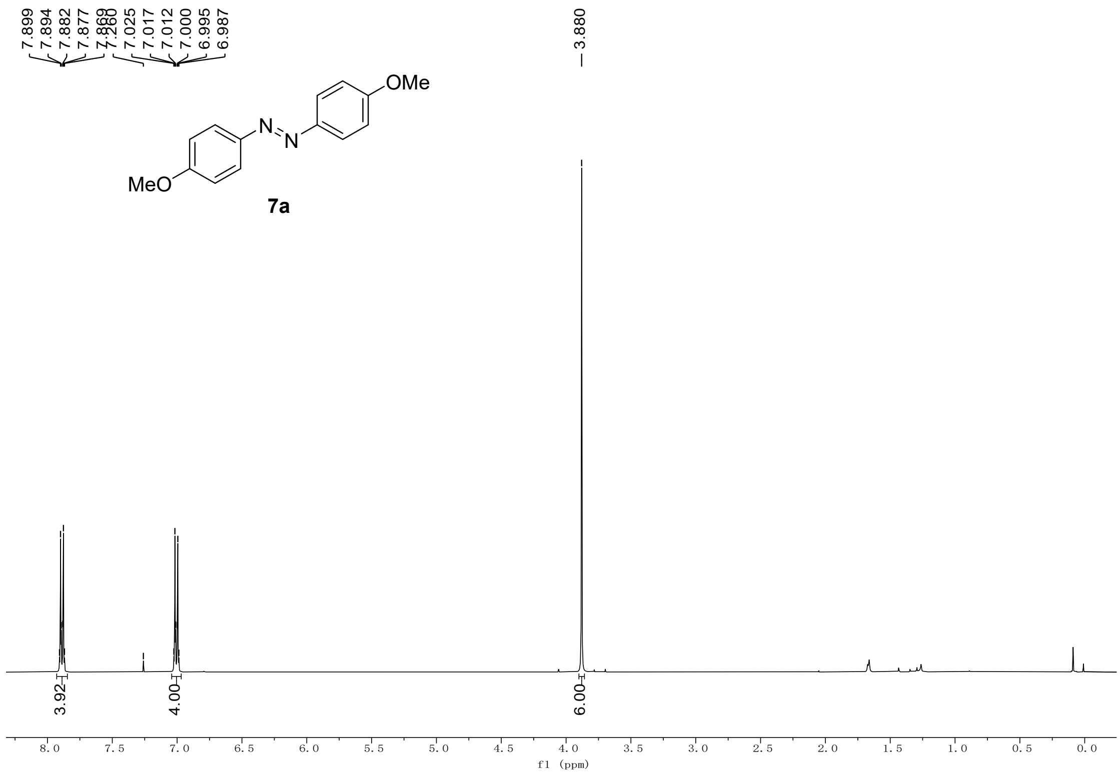

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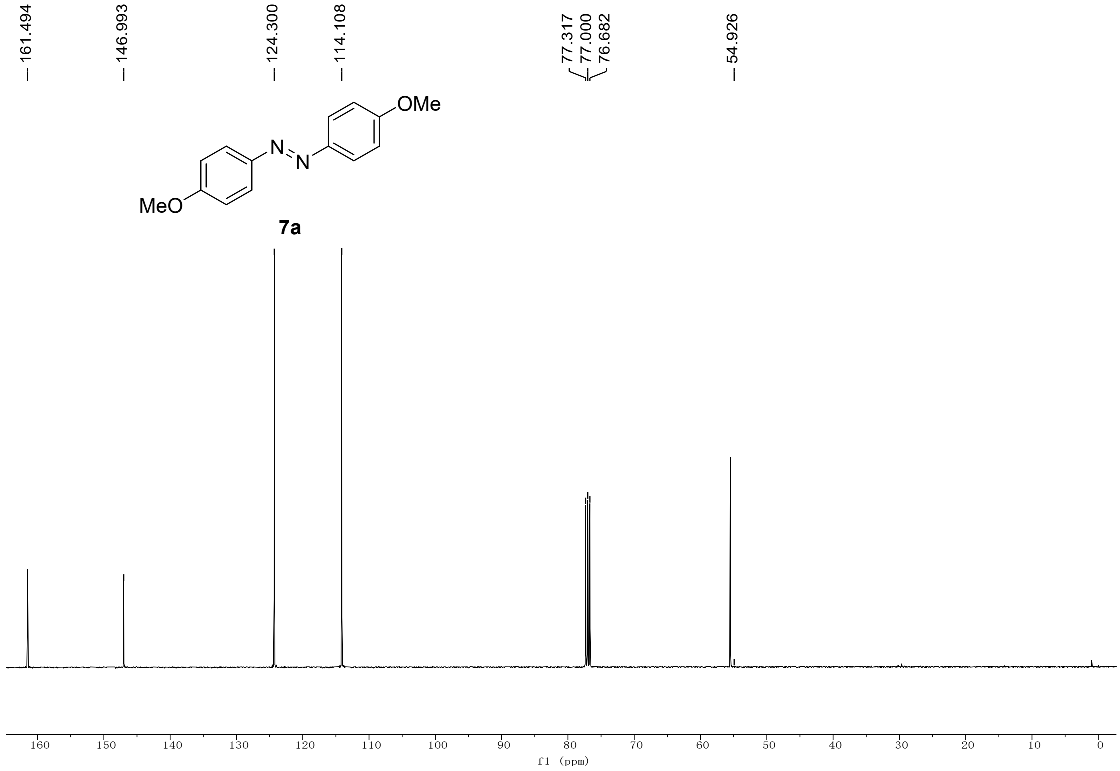

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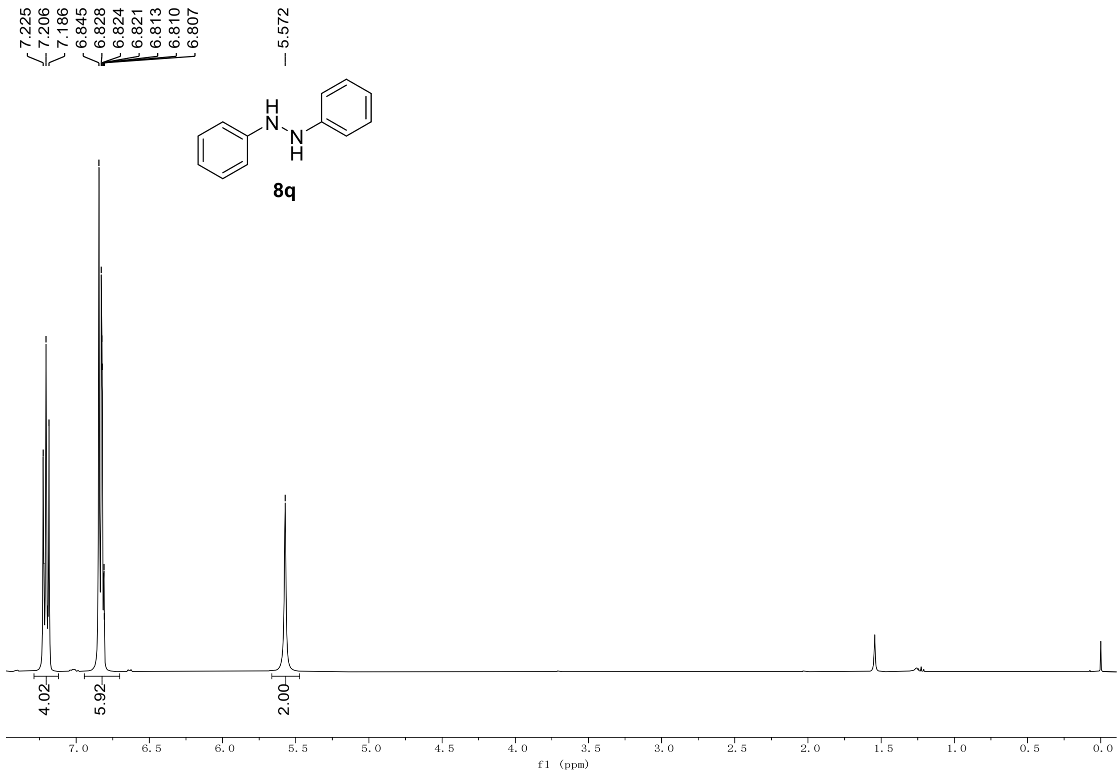

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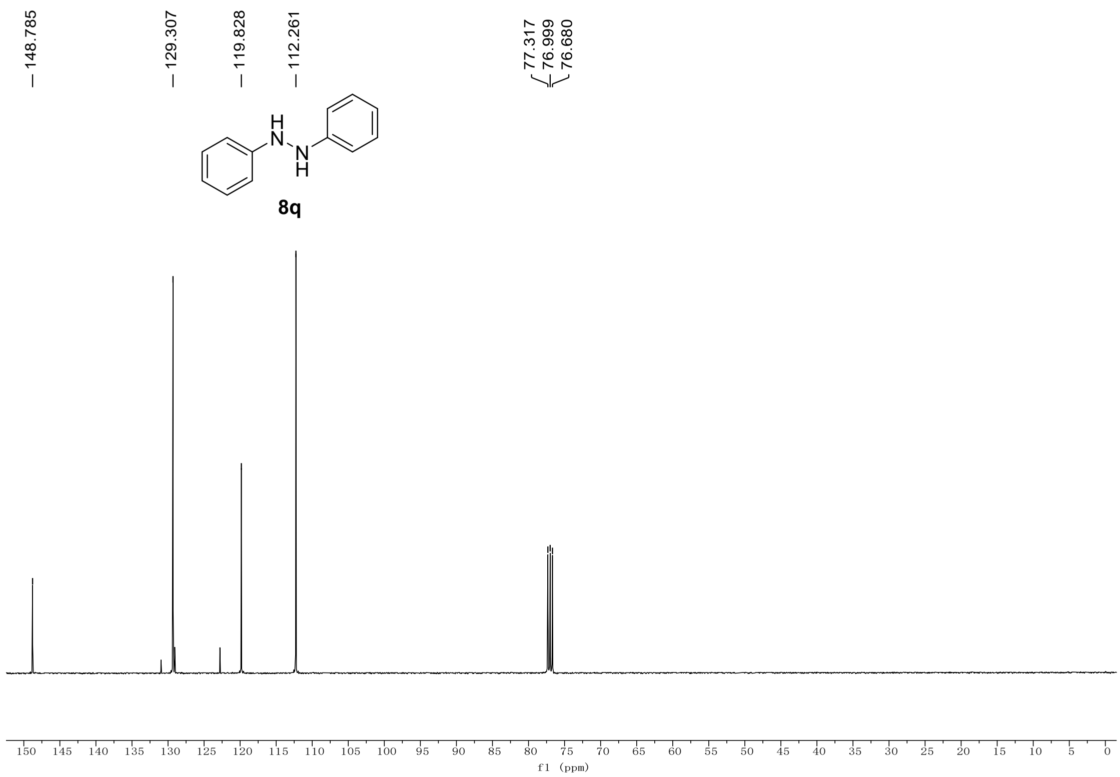

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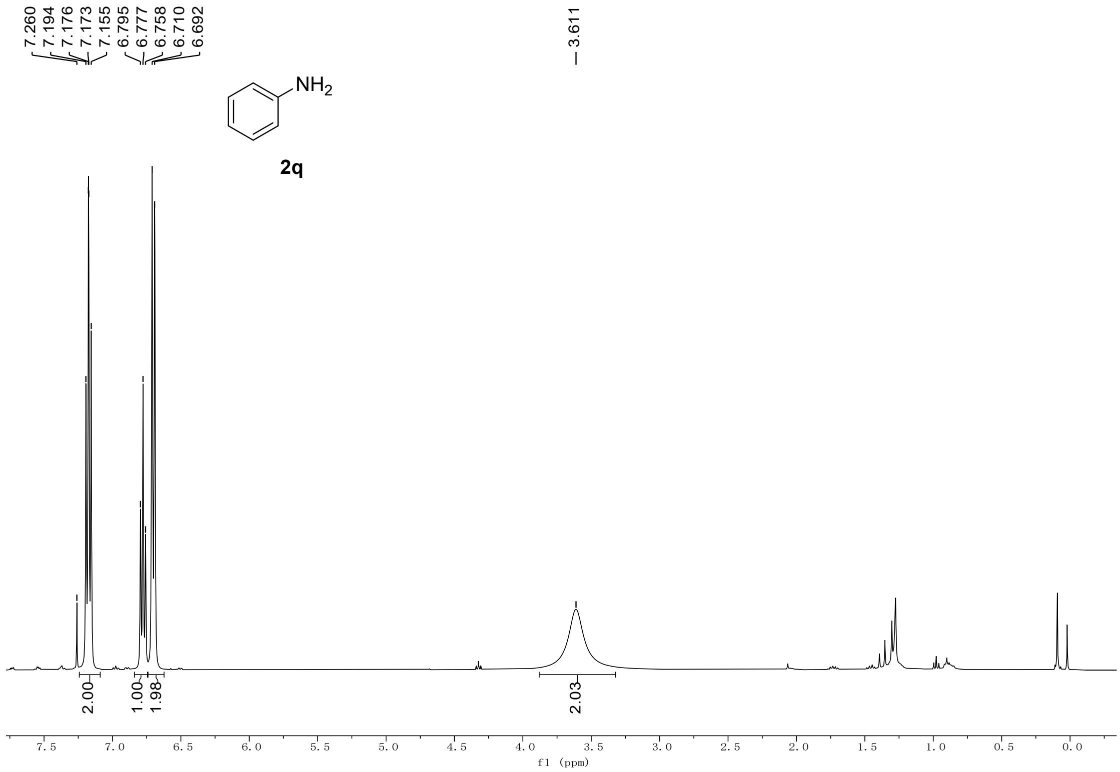

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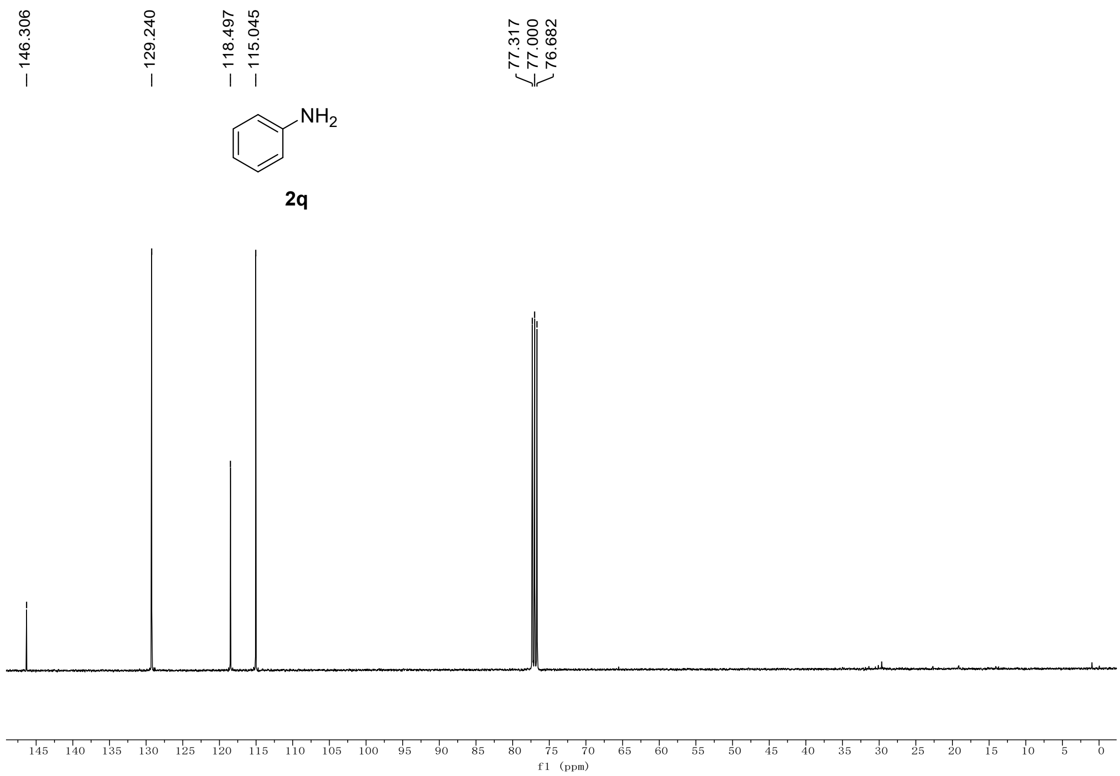
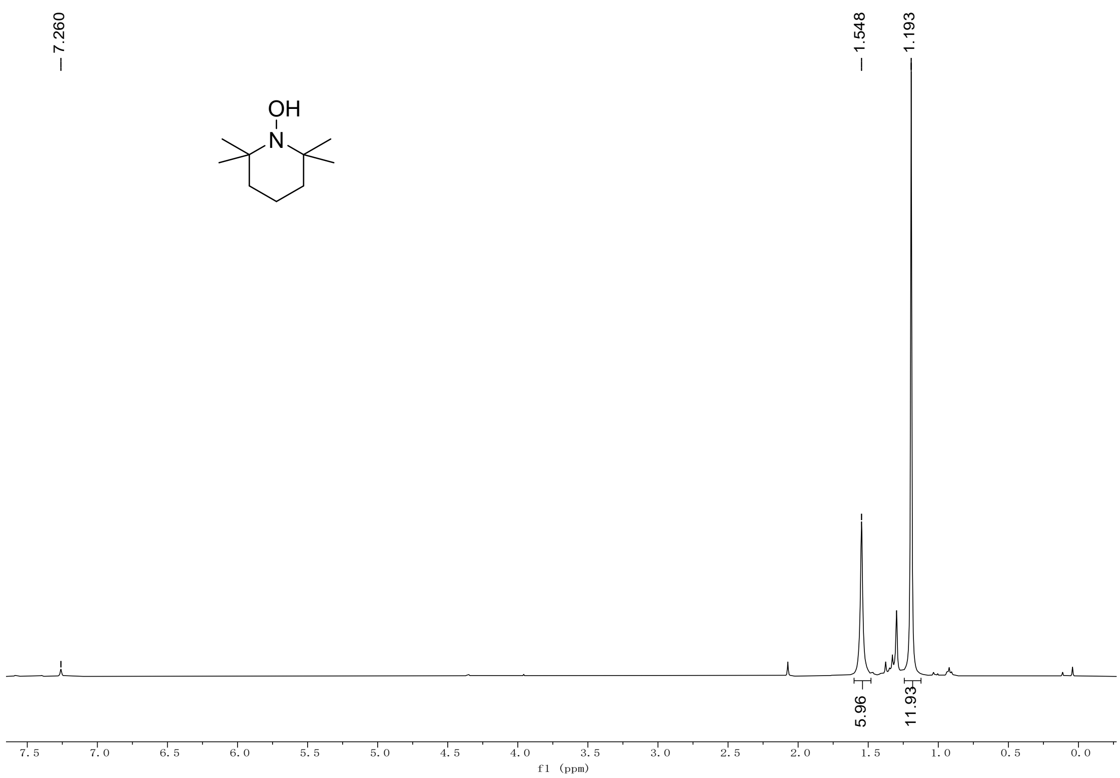
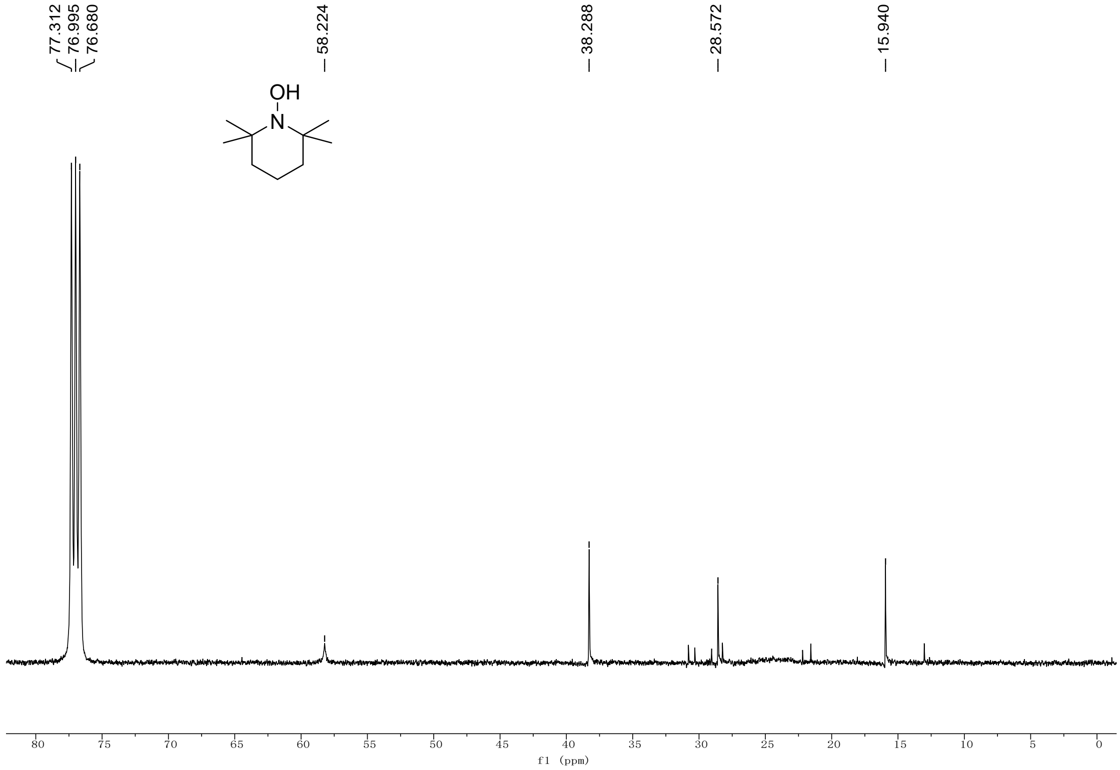


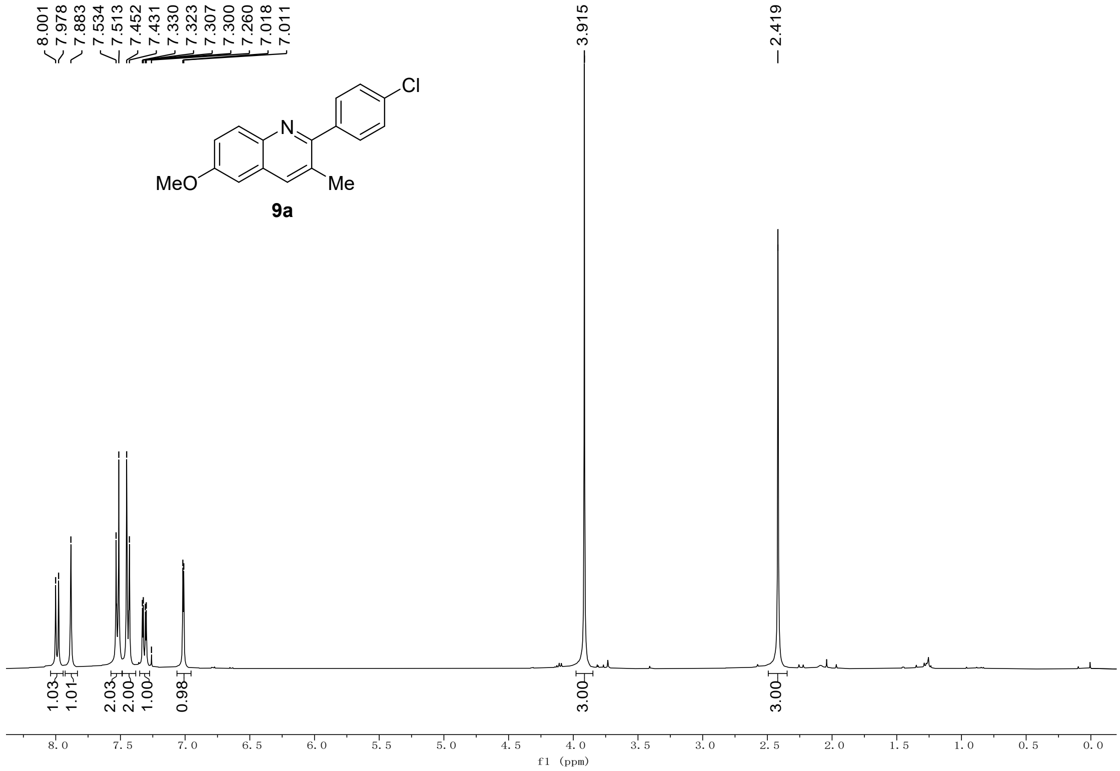
^{1}H NMR (400 MHz, $CDCl_3$)



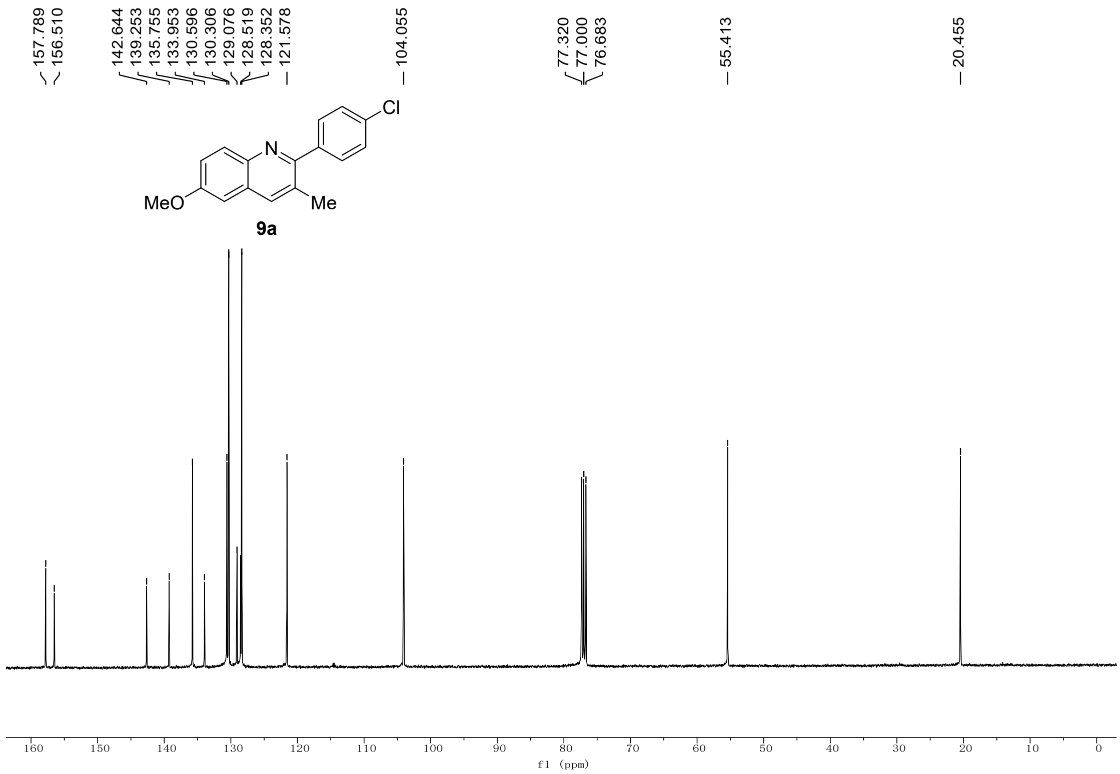
^{13}C NMR (100 MHz, CDCl$_3$)



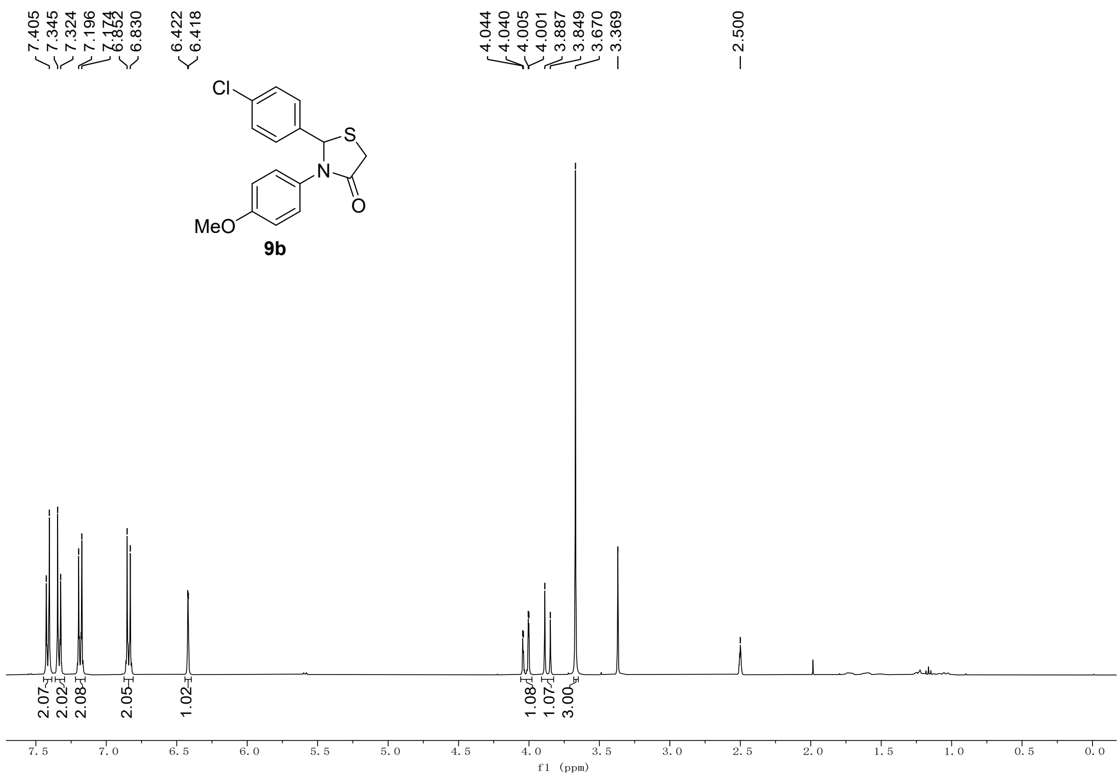
^{1}H NMR (400 MHz, CDCl$_3$)



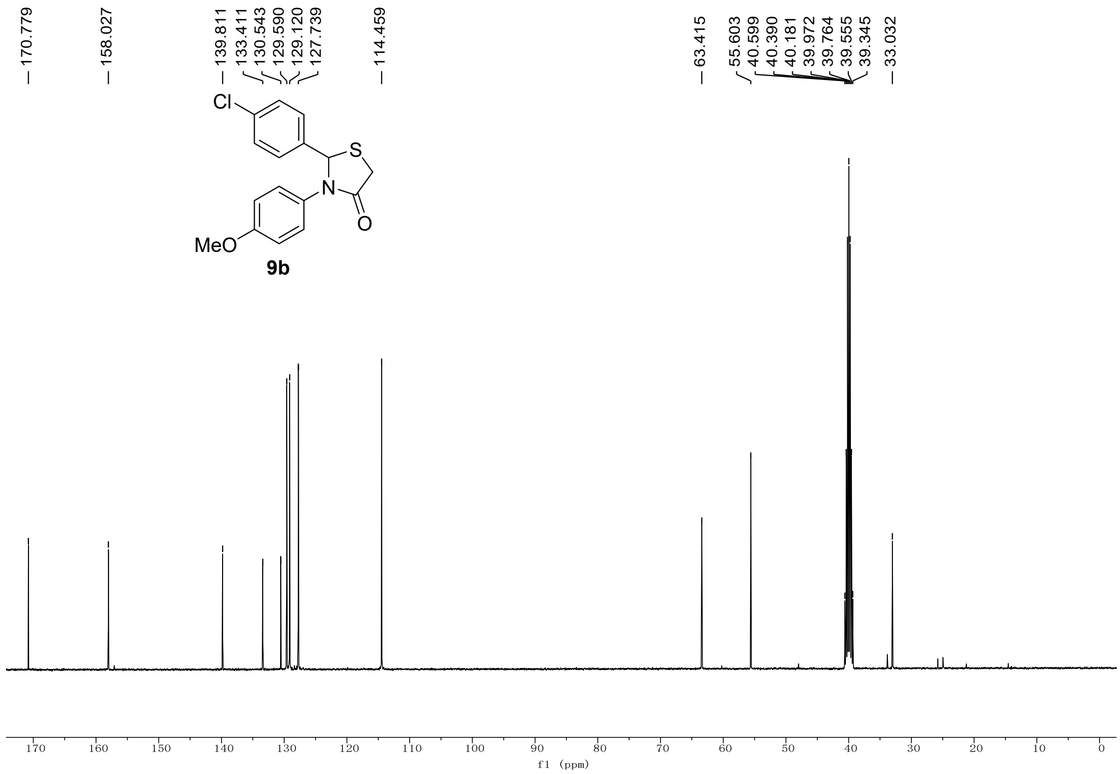
^{13}C NMR (100 MHz, $CDCl_3$)



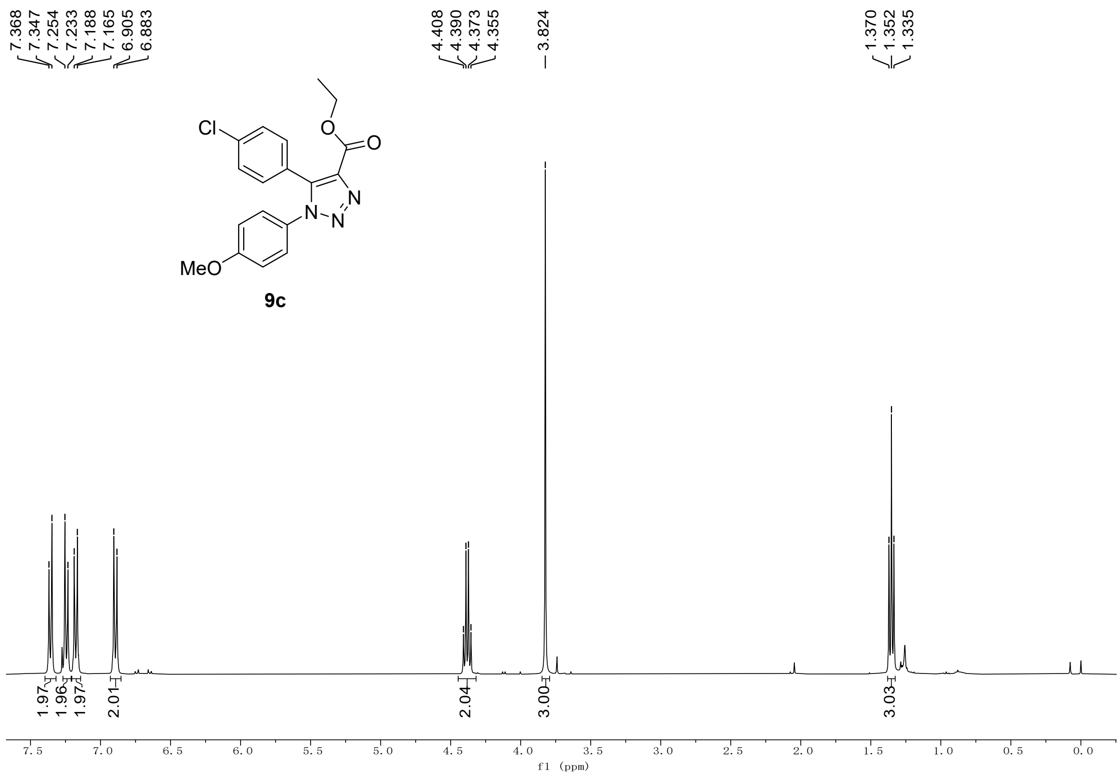
^{1}H NMR (400 MHz, DMSO)



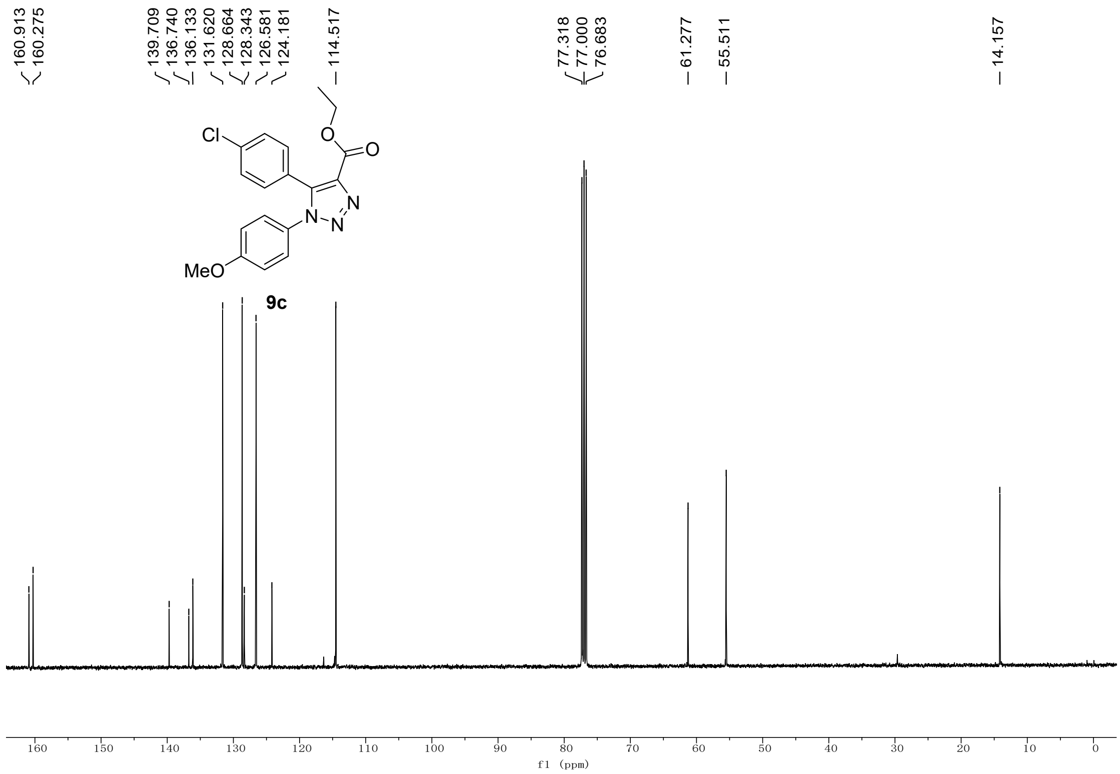
^{13}C NMR (100 MHz, DMSO)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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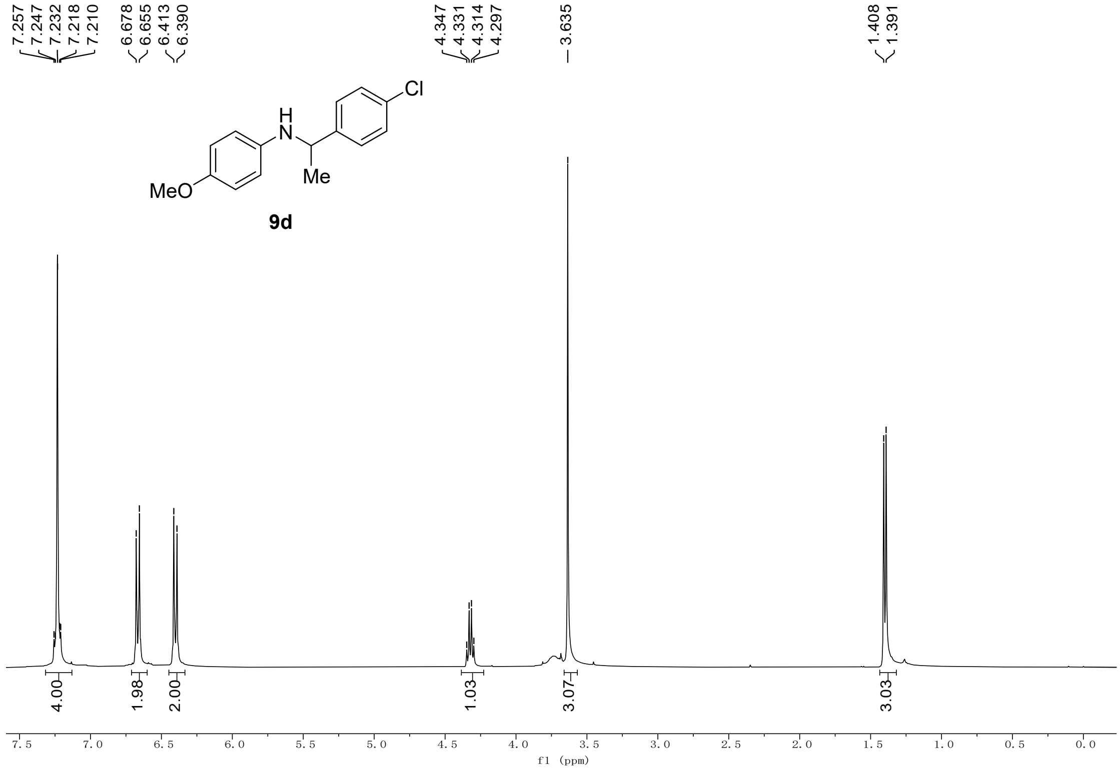

^{13}C NMR (100 MHz, $CDCl_3$)