Supporting Information

Copper-Promoted Cross Coupling of Nitroarenes with 4-Alkyl-1,4-dihydropyridines using a Peroxide-Driven Radical Reductive Strategy

Hui-Min Jiang,[a] Jing-Hao Qin,[a] Qing Sun,[a] Dong Zhang,[a] Jin-Peng Jiang,[a] Xuan-Hui Ouyang,*[a] Ren-Jie Song,*[a] and Jin-Heng Li*[a,b,c]

[a] Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, China

[b] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

[c] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 475004, China

E-mail: xuanhuiouyang@163.com

E-mail: srj0731@hnu.edu.cn

E-mail: jhli@hnu.edu.cn

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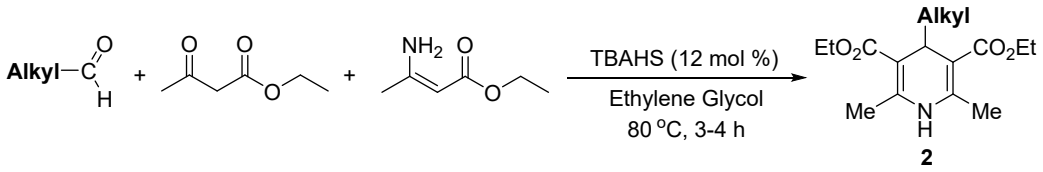
(A) General Experimental Procedures

(a) General Information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 500 MHz advance spectrometer at room temperature in $CDCl_3$ using TMS as internal standard. Low-resolution mass spectra (LRMS) data were measured on GCMS-QP2010 Ultra or LC-MS: HPLC (Dionex Ultimate 3000) and MS (Thermo Scientific ISQ EC). High-resolution mass spectra (HRMS) was recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting Points were recorded on Hanon MP100 Apparatus. Unless otherwise noted, all reactions were carried out using standard Schlenk techniques, and all starting materials and solvents were commercially available and were used without further purification. 1,4-Dihydropyridnes **2a-2p** were prepared according to literature procedures.[1] Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA).

Attention: Dicumyl peroxide (DCP) are prone to explosion at high temperatures. After the reaction sealed at room temperature, the increasing of temperature must be carried out under safety precautions. It is strictly forbidden to put the Schlenk tube directly into the 130 °C oil bath.[2]

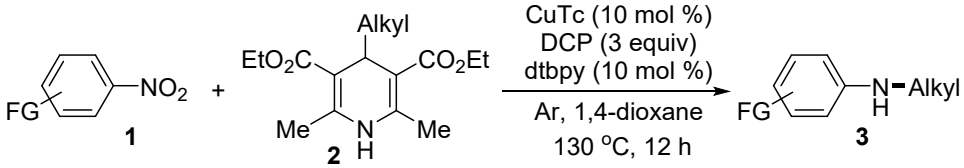
(b) Synthesis of 1,4-dihydropyridnes 2a-2p:[1]



To a round-bottom flask charged with ethyl 3-aminocrotonate (1.0 equiv) was added ethylene glycol (2.5 M) under argon. Next, ethyl acetoacetate (1.0 equiv) was added followed by the aldehyde (1.0 equiv). Finally, tetrabutylammonium hydrogen sulfate (TBASH, 12 mol %) was added in one portion. The flask was closed with a septum and heated at 100 °C for 3-4 h. At this time, the reaction was cooled to rt and diluted with EtOAc. The solution was poured into a separatory funnel containing

brine and extracted three times with EtOAc. The solution was added to brine and separated using ethyl acetate. The organic layers were combined, dried (Na_2SO_4) and concentrated in vacuo. The crude material was purified by silica gel column chromatography (hexane/ethyl acetate) to furnish the desired 4-alkyl-1,4-dihydropyridine (**2a-2p**).[1]

(c) Typical experimental procedure:



To a Schlenk tube were added substrates nitrobenzene **1** (0.2 mmol), 4-alkyl-1,4-dihydropyridines **2** (0.6 mmol), CuTc (10 mol %), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 10 mol %) DCP (3 equiv) and 1,4-dioxane (2 mL), the tube was then charged with argon. The mixture was stirred at 130 °C until complete consumption of starting material as monitored by TLC and/or GC-MS analysis (about 12 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **3**.

(d) Experimental Procedure for the 1 mmol Scale:

To a Schlenk tube were added CuTc (0.1 mmol; 10 mol %), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 0.1 mmol; 10 mol %), nitrobenzene **1a** (1.0 mmol), **2a** (3.0 mmol; 3.0 equiv) and 1,4-dioxane (10 mL). The tube was then charged with argon. The mixture was stirred at 130 °C until complete consumption of starting material as monitored by TLC and/or GC-MS analysis (about 24 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue

was purified by silica gel column chromatography (hexane/ethyl acetate = 50:1, R_f = 0.7) to afford the desired products **3aa** in 72% isolated yield (126 mg).

(d) Mechanistic studies

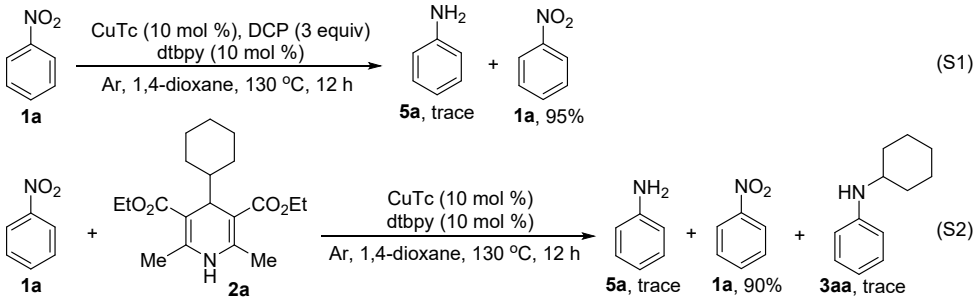


Figure S1. The acquisition of possible intermediates.

4-Cyclohexyl-1,4-dihydropyridine (**2a**) failed to reduce the nitroarene to the possible intermediates (Figure S1, S1). Only trace amount of aniline (**5a**) was observed by GC-MS under standard reaction conditions, and more than 95% of nitrobenzene is recycled. Simultaneously, the reaction could not proceed without peroxide, and more than 90% of nitrobenzene is recycled, thus shows that nitrobenzene cannot be converted in the absence of alkyl radicals. 4-Cyclohexyl-1,4-dihydropyridine (**2a**) could not be used as a reducing agent to reduce nitrobenzene (Figure S1, S2). Alkyl radicals are the key to the initiation of the reaction.

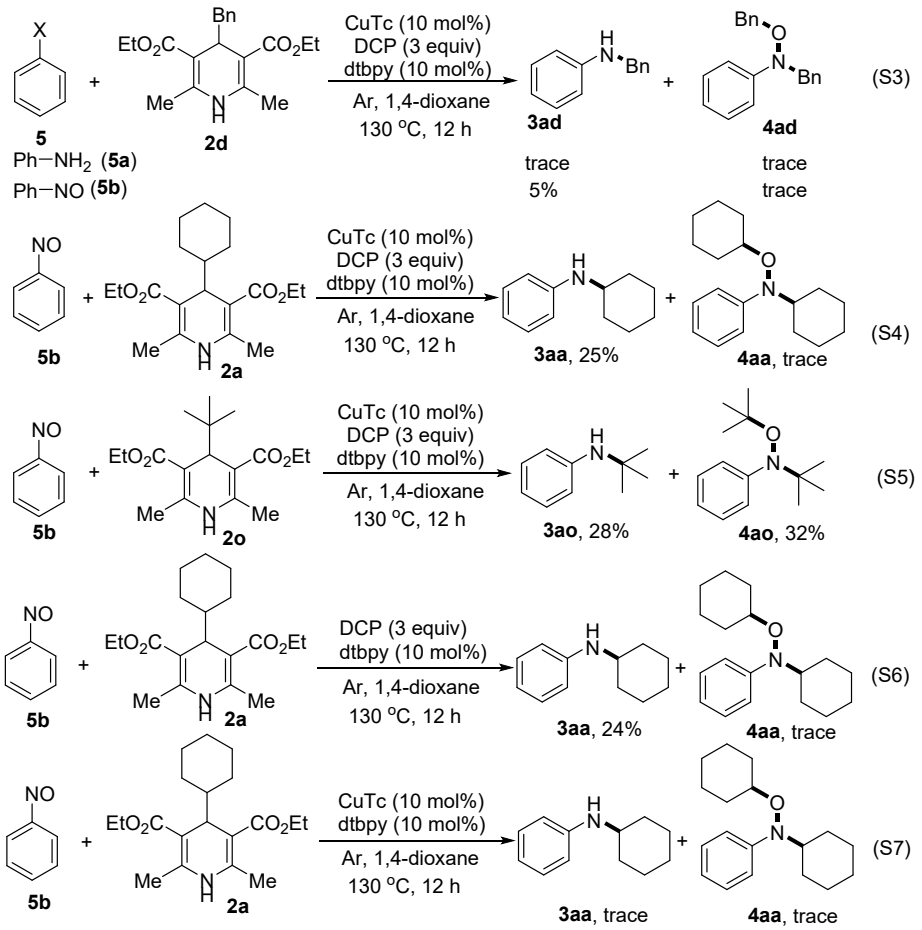


Figure S2. The reaction of different types of alkyl radical precursors with possible intermediates.

Some nitrogen intermediates of nitrobenzene were tested under standard conditions. Using nitrosobenzene (**5b**) react with the benzyl radical precursor (**2d**) to obtain the *N*-alkylated product (**3ad)** in a poor yield, and the *N,O*-alkylated aniline (**4ad**) was not detected (Figure S2, S3), indicating that nitrosobenzene (**5b**) has poor reactivity with benzyl radical in the presence of 4-benzyl-1,4-dihydropyridine (**2d**). Using 4-cyclohexyl-1,4-dihydropyridine (**2a**) and 4-*tert*-butyl-1,4-dihydropyridine (**2o**) as the radical precursor obtain the desired *N*-alkylated anilines (**3aa** and **3ao**) in 25% and 28% yields, respectively, in the presence of nitrosobenzene, thus implicating nitrosobenzene is a possible intermediate for the reductive reaction (Figure S2, S4-S5). At least nitrobenzene could be converted to nitrosobenzene under standard reaction conditions. Meanwhile, using 4-*tert*-butyl-1,4-dihydropyridine (**2o**) as a radical precursor provided the *N,O*-alkylated product (**4ao**) in 32% yield, which derived from

the reaction of two *tert*-butyl radical with nitrosobenzene (Figure S2, S5). Obviously, the tertiary alkyl radical is more reactive with nitrosobenzene (**5b**) than the primary and secondary alkyl radical. This result may also be the reason why Bara's work is limited to secondary and tertiary *N*-alkylbenzenamines.[3]

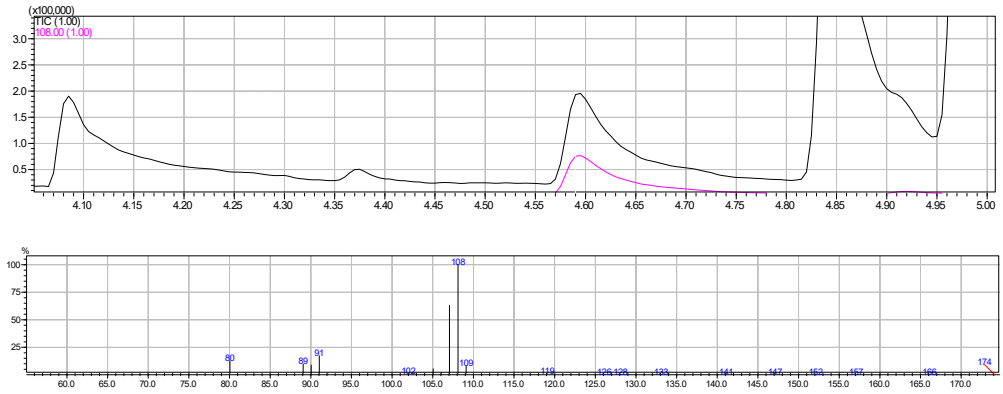
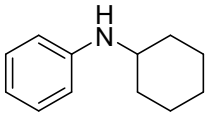


Figure S3. Benzyl alcohol was detected by GC-MS.

[MS Spectrum]			89.05	6498	9.18
# of Peaks	260		90.05	6229	8.80
Raw Spectrum	4.590 (scan : 119)		91.05	12100	17.09
Background	4.570 (scan : 115)		92.10	1086	1.53
Base Peak	m/z 108.10 (Inten : 70,798)		93.10	85	0.12
Event#	1		98.10	20	0.03
m/z	Absolute Intensity	Relative Intensity	99.10	3	0.00
80.05	9013	12.73	103.00	30	0.04
81.05	612	0.86	104.05	131	0.19
82.00	45	0.06	105.05	3289	4.65
84.00	60	0.08	106.05	946	1.34
85.00	303	0.43	107.05	44644	63.06
86.00	440	0.62	**108.10**	**70798**	**100.00**
87.05	240	0.34	109.10	5419	7.65
88.05	52	0.07	110.10	288	0.41

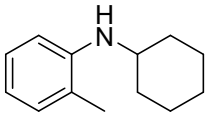
(B) Analytical data

***N*-cyclohexylaniline (3aa):**



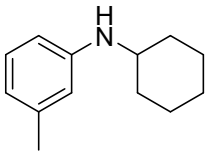
29.4 mg, 84% yield; R_f = 0.7 (PE:EA = 50:1); Colorless Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (t, *J* = 8.0 Hz, 2H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 3.48 (s, 1H), 3.28 - 3.21 (m, 1H), 2.08 - 2.03 (m, 2H), 1.79 - 1.73 (m, 2H), 1.67 - 1.62 (m, 1H), 1.40 - 1.33 (m, 2H), 1.23 - 1.10 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 129.2, 116.8, 113.1, 51.7, 33.5, 25.9, 25.0. LRMS (EI, 70eV) *m/z* (%): 175 (M^+, 35), 132 (100), 118 (20), 93 (16); HRMS (ESI) for $C_{12}H_{16}N$ $[M+H]^+$ calcd. 176.1434, found. 176.1431

***N*-cyclohexyl-2-methylaniline (3ba):**



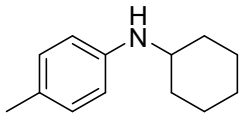
26.4 mg, 70% yield; R_f = 0.7 (PE:EA = 50:1); Colorless Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.63 - 6.58 (m, 2H), 3.33 (s, 1H), 3.34 - 3.27 (m, 1H), 2.11 (s, 3H), 2.10 - 2.05 (m, 2H), 1.79-1.73 (m, 2H), 1.67-1.63 (m, 1H), 1.41 - 1.34 (m, 2H), 1.27 - 1.17 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 130.2, 127.0, 121.5, 116.2, 110.1, 51.4, 33.6, 25.9, 25.0, 17.5; LRMS (EI, 70eV) *m/z* (%): 189 (M^+, 55), 146 (100), 131 (16), 91 (12); HRMS (ESI) for $C_{13}H_{19}N$ $[M+H]^+$ calcd. 190.1590, found. 190.1591.

***N*-cyclohexyl-3-methylaniline (3ca):**



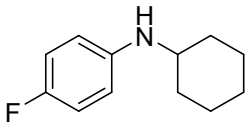
27.2 mg, 72% yield; R_f = 0.6 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (t, *J* = 8.0 Hz, 1H), 6.48 (d, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 7.0 Hz, 2H), 3.25 (s, 1H), 3.26 - 3.20 (m, 1H), 2.26 (s, 3H), 2.07-2.02 (m, 2H), 1.77-1.72 (m, 2H), 1.66 - 1.61 (m, 1H), 1.39-1.31 (m, 2H), 1.24 - 1.10 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 138.9, 129.1, 117.7, 113.8, 110.2, 51.6, 33.5, 25.9, 25.0, 21.6; LRMS (EI, 70eV) *m/z* (%): 189 (M^+, 55), 146 (100), 131 (15), 118 (38); HRMS (ESI) for $C_{13}H_{19}N$ $[M+H]^+$ calcd. 190.1590, found. 190.1592.

***N*-cyclohexyl-4-methylaniline (3da):**



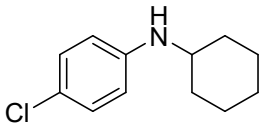
26.1 mg, 69% yield; R_f = 0.5 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 8.5 Hz, 2H), 3.24-3.17 (m, 1H), 3.18 (s, 1H), 2.22 (s, 3H), 2.07-2.01 (m, 2H), 1.78-1.71 (m, 2H), 1.66 - 1.61 (m, 1H), 1.39 - 1.31 (m, 2H), 1.24 - 1.09 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 129.7, 126.0, 113.4, 52.0, 33.5, 25.9, 25.0, 20.3; LRMS (EI, 70eV) *m/z* (%): 189 (M^+, 57), 146 (100), 133 (15), 106 (15); HRMS (ESI) for $C_{13}H_{19}N$ $[M+H]^+$ calcd. 190.1590, found. 190.1590.

***N*-cyclohexyl-4-fluoroaniline (3ea):**



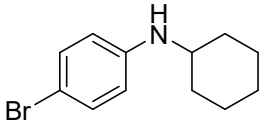
28.6 mg, 74% yield; R_f = 0.4 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 - 6.82 (m, 2H), 6.54 - 6.49 (m, 2H), 3.3 (s, 1H), 3.19 - 3.13 (m, 1H), 2.05 - 2.00 (m, 2H), 1.77 - 1.72 (m, 2H), 1.67 - 1.61 (m, 1H), 1.38 - 1.30 (m, 2H), 1.24 - 1.08 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, (d, $^1J_{FC}$ = 232.9 Hz), 143.7 (d, $^4J_{FC}$ = 2.3 Hz), 115.6 (d, $^2J_{FC}$ = 22.1 Hz), 114.0 (d, $^3J_{FC}$ = 7.3 Hz), 52.4, 33.4, 25.8, 24.9; ^{19}F NMR (500 MHz, $CDCl_3$) δ -128.6; LRMS (EI, 70eV) *m/z* (%): 193 (M^+, 55), 150 (100), 137 (17), 111 (22); HRMS (ESI) for $C_{12}H_{16}NF$ $[M+H]^+$ calcd. 194.1340, found. 194.1341.

4-chloro-*N*-cyclohexylaniline (3fa):



33.8 mg, 81% yield; R_f = 0.5 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 9.0Hz, 2H), 6.49 (d, *J* = 9.0 Hz, 2H), 3.51 (s, 1H), 3.21 - 3.16 (m, 1H), 2.04 - 2.00 (m, 2H), 1.78 - 1.72 (m, 2H), 1.66 - 1.61 (m, 1H), 1.38 - 1.30 (m, 2H), 1.24 - 1.09 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 129.0, 121.1, 114.1, 51.7, 33.2, 25.8, 24.9; LRMS (EI, 70eV) *m/z* (%): 211 (M^++2, 22), 209 (M^+, 65), 166 (100), 153 (18), 130 (30); HRMS (ESI) for $C_{12}H_{16}N^{35}Cl$ $[M+H]^+$ calcd. 210.1044, found. 210.1046.

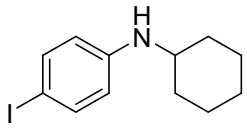
4-bromo-*N*-cyclohexylaniline (3ga):



42.0 mg, 83% yield; R_f = 0.5 (PE:EA = 50:1); Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 9.0 Hz, 2H), 6.44 (d, *J* = 9.0 Hz, 2H), 3.53 (s, 1H), 3.22 - 3.16 (m, 1H), 2.04 -

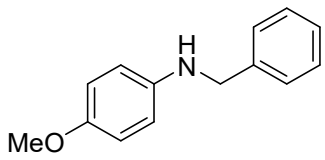
2.00 (m, 2H), 1.77 - 1.72 (m, 2H), 1.66 - 1.62 (m, 1H), 1.37 - 1.30 (m, 2H), 1.24 - 1.10 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 131.8, 114.6, 108.1, 51.6, 33.2, 25.8, 24.9; LRMS (EI, 70eV) *m/z* (%): 255 (M^++2, 66),253 (M^+, 67), 210 (100), 197 (20), 130 (81); HRMS (ESI) for $C_{12}H_{16}N^{80}Br$ $[M+H]^+$ calcd. 254.0539, found. 254.0540.

***N*-cyclohexyl-4-iodoaniline (3ha):**



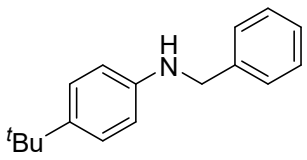
47.5 mg, 79% yield; R_f = 0.5 (PE:EA = 50:1); Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 9.0 Hz, 2H), 6.35 (d, *J* = 9.0 Hz, 2H), 3.55 (s, 1H), 3.22 - 3.16 (m, 1H), 2.04 - 2.00 (m, 2H), 1.77 - 1.72 (m, 2H), 1.66 - 1.61 (m, 1H), 1.38 - 1.30 (m, 2H), 1.23 - 1.09 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 137.7, 115.2, 76.9, 51.5, 33.2, 25.8, 24.9; LRMS (EI, 70eV) *m/z* (%): 301 (M^+, 100), 258 (92), 219 (18), 130 (54); HRMS (ESI) for $C_{12}H_{16}NI$ $[M+H]^+$ calcd. 302.0400, found. 302.0402.

***N*-benzyl-4-methoxyaniline (3ia):**



13.2 mg, 31% yield; R_f = 0.4 (PE:EA = 10:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.0 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.0 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 2H), 6.60 (d, *J* = 9.0 Hz, 2H), 4.28 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 142.4, 139.6, 128.6, 127.5, 127.1, 114.9, 114.1, 55.8, 49.2; LRMS (EI, 70eV) *m/z* (%): 213 (M^+, 100), 198 (15), 122 (85), 91 (78); HRMS (ESI) for $C_{14}H_{15}NO$ $[M+H]^+$ calcd. 214.1226, found. 214.1226.

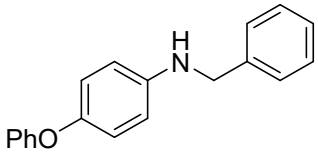
***N*-benzyl-4-(*tert*-butyl)aniline (3ja):**



33.5 mg, 70% yield; R_f = 0.4 (PE:EA = 30:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.0 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.20 (d, *J* = 9.0 Hz, 2H), 6.60 (d, *J* = 9.0 Hz, 2H), 4.30 (s, 2H), 3.92 (s, 1H), 1.27 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 140.3, 139.6, 128.6, 127.5, 127.1, 126.0, 112.5, 48.6, 33.8, 31.5; LRMS (EI, 70eV) *m/z* (%): 239 (M^+, 39), 224 (100),

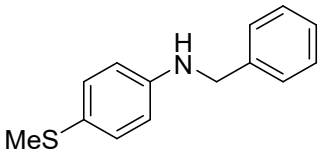
146 (60), 91 (60); HRMS (ESI) for $C_{17}H_{21}N$ $[M+H]^+$ calcd. 240.1747, found. 240.1748.

***N*-benzyl-4-phenoxyaniline (3ka):**



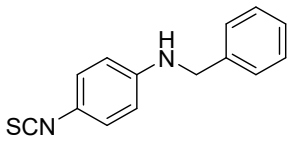
39.6 mg, 72% yield; R_f = 0.5 (PE:EA = 10:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 - 7.32 (m, 4H), 7.30 - 7.24 (m, 3H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 9.0 Hz, 2H), 4.30 (s, 2H), 3.95 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 147.7, 144.8, 139.3, 129.4, 128.6, 127.5, 127.3, 121.9, 121.2, 117.1, 113.8, 48.9; LRMS (EI, 70eV) *m/z* (%): 275 (M^+, 100), 184 (84), 129 (27), 91 (50); HRMS (ESI) for $C_{19}H_{17}NO$ $[M+H]^+$ calcd. 276.1383, found. 276.1381.

***N*-benzyl-4-(methylthio)aniline (3la):**



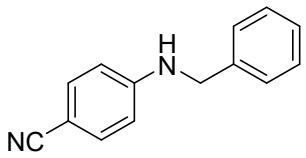
18.3 mg, 40% yield; R_f = 0.4 (PE:EA = 10:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 - 7.32 (m, 4H), 7.29 - 7.26 (m, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 8.5 Hz, 2H). 4.31 (s, 2H), 4.06 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 139.1, 131.4, 128.6, 127.4, 127.3, 124.4, 113.4, 48.2, 19.1. LRMS (EI, 70eV) *m/z* (%): 229 (M^+, 100), 214 (70), 138 (75), 91 (80); HRMS (ESI) for $C_{14}H_{15}NS$ $[M+H]^+$ calcd. 230.0998, found. 230.0997.

***N*-benzyl-4-isothiocyanatoaniline (3ma):**



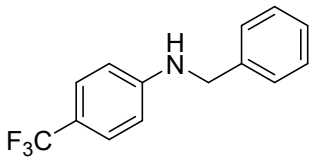
19.2 mg, 40% yield; R_f = 0.4 (PE:EA = 10:1); Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 - 7.32 (m, 4H), 7.31 - 7.27 (m, 1H), 7.04 (d, *J* = 9.0 Hz, 2H), 6.53 (d, *J* = 9.0 Hz, 2H), 4.32 (s, 2H), 4.25 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 138.5, 128.7, 127.5, 127.3, 126.9, 119.9, 113.0, 48.0. LRMS (EI, 70eV) *m/z* (%): 240 (M^+, 65), 149 (8), 122 (15), 91 (100); HRMS (ESI) for $C_{14}H_{12}N_2S$ $[M+H]^+$ calcd. 241.0794, found. 241.0794.

4-(benzylamino)benzonitrile (3na):



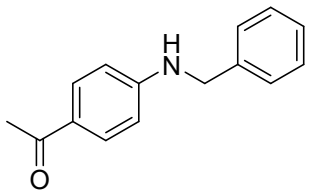
29.1 mg, 70% yield; R_f = 0.4 (PE:EA = 5:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.38 - 7.27 (m, 5H), 6.58 (d, *J* = 8.5 Hz, 2H), 4.65 (s, 1H), 4.37 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 137.7, 133.6, 128.8, 127.6, 127.2, 120.3, 112.3, 98.9, 47.4; LRMS (EI, 70eV) *m/z* (%): 208 (M^+, 31), 129 (5), 102 (6), 91 (100); HRMS (ESI) for $C_{14}H_{12}N_2$ $[M+H]^+$ calcd. 209.1073, found. 209.1075.

***N*-benzyl-4-(trifluoromethyl)aniline (3oa):**



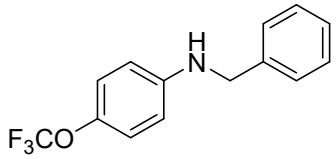
36.1 mg, 72% yield; R_f = 0.4 (PE:EA = 20:1); White Solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.37 - 7.32 (m, 4H), 7.31 - 7.27 (m, 1H), 6.63 (d, *J* = 8.5 Hz, 2H), 4.39 (s, 1H), 4.37 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 138.4, 128.8, 127.5, 127.3, 126.6 (q, $^4J_{FC}$ = 3.75 Hz), 111.9, 47.8. ^{19}F NMR (500 MHz, $CDCl_3$) δ -61.02. LRMS (EI, 70eV) *m/z* (%): 251 (M^+, 50), 174 (7), 145 (9), 91 (100); HRMS (ESI) for $C_{14}H_{12}F_3N$ $[M+H]^+$ calcd. 252.0995, found. 252.0993.

1-(4-(benzylamino)phenyl)ethan-1-one (3pa):



27.9 mg, 69% yield; R_f = 0.4 (PE:EA = 5:1); Yellow Solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.0 Hz, 2H), 7.37 - 7.32 (m, 4H), 7.31 - 7.27 (m, 1H), 6.59 (d, *J* = 9.0 Hz, 2H), 4.66 (s, 1H), 4.39 (s, 2H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.3, 151.9, 138.2, 130.7, 128.7, 127.5, 127.3, 126.9, 111.6, 47.5, 25.9; LRMS (EI, 70eV) *m/z* (%): 225 (M^+, 62), 210 (57), 148 (5), 91 (100); HRMS (ESI) for $C_{15}H_{15}NO$ $[M+H]^+$ calcd. 226.1226, found. 226.1226.

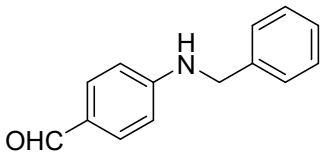
***N*-benzyl-4-(trifluoromethoxy)aniline (3qa):**



39.5 mg, 74% yield; R_f = 0.5 (PE:EA = 10:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 - 7.32 (m, 4H), 7.31 - 7.26 (m, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 8.5 Hz, 2H), 4.30 (s, 2H), 4.10 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 140.5 (q, $^4J_{FC}$ = 1.9 Hz), 138.8, 128.7, 127.4, 127.4, 122.4, 120.7 (q, $^1J_{FC}$ = 253.4 Hz), 113.0,

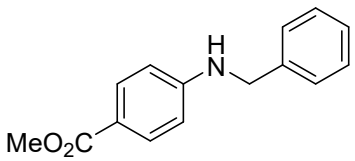
48.4; ^{19}F NMR (500 MHz, $CDCl_3$) δ -58.45; LRMS (EI, 70eV) *m/z* (%): 267 (M^+, 54), 190 (7), 95 (4), 91 (100); HRMS (ESI) for $C_{14}H_{12}F_3NO$ $[M+H]^+$ calcd. 268.0944, found. 268.0945.

4-(Benzylamino)benzaldehyde (3ra):



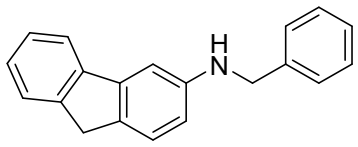
30.8 mg, 73% yield; R_f = 0.4 (PE:EA = 5:1); Yellow Solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.37 - 7.27 (m, 5H), 6.63 (d, *J* = 8.5 Hz, 2H), 4.90 (s, 1H), 4.40 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 153.1, 137.9, 128.7, 127.6, 127.3, 126.6, 111.9, 47.4. LRMS (EI, 70eV) *m/z* (%): 211 (M^+, 55), 180 (2), 134 (5), 91 (100); HRMS (ESI) for $C_{14}H_{13}NO$ $[M+H]^+$ calcd. 212.1070, found. 212.1071.

Methyl 4-(benzylamino)benzoate (3sa):



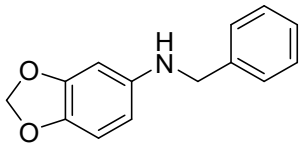
41.0 mg, 85% yield; R_f = 0.4 (PE:EA = 5:1); White Solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.0 Hz, 2H), 7.38 - 7.32 (m, 4H), 7.32 - 7.27 (m, 1H), 6.59 (d, *J* = 9.0 Hz, 2H), 4.50 (s, 1H), 4.39 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 151.7, 138.3, 131.5, 128.8, 127.5, 127.4, 118.7, 111.6, 51.5, 47.7; LRMS (EI, 70eV) *m/z* (%): 241 (M^+, 58), 210 (14), 164 (5), 91 (100); HRMS (ESI) for $C_{15}H_{15}NO_2$ $[M+H]^+$ calcd. 242.1176, found. 242.1174.

***N*-benzyl-9*H*-fluoren-3-amine (3ta):**



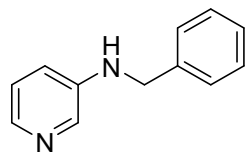
16.3 mg, 30% yield; R_f = 0.4 (PE:EA = 20:1); Yellow Solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 - 7.27 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.82 (s, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 4.38 (s, 2H), 4.11 (s, 1H), 3.79 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 145.2, 142.3, 142.2, 139.4, 132.1, 128.6, 127.5, 127.3, 126.6, 124.8, 124.6, 120.6, 118.4, 111.9, 109.2, 48.6, 36.9; LRMS (EI, 70eV) *m/z* (%): 271 (M^+, 97), 180 (100), 153 (25), 91 (25); HRMS (ESI) for $C_{20}H_{17}N$ $[M+H]^+$ calcd. 272.1434, found. 272.1436.

***N*-benzylbenzo[*d*][1,3]dioxol-5-amine (3ua):**



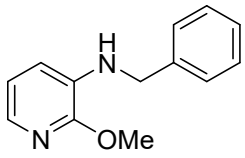
12.7 mg, 28% yield; R_f = 0.4 (PE:EA = 10:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 - 7.32 (m, 4H), 7.29 - 7.26 (m, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 6.26 (s, 1H), 6.07 (d, *J* = 8.5 Hz, 1H), 5.84 (s, 2H), 4.26 (s, 2H), 3.83 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 143.9, 139.7, 139.3, 128.6, 127.5, 127.2, 108.6, 104.4, 100.5, 95.9, 49.2; LRMS (EI, 70eV) *m/z* (%): 227 (M^+, 100), 150 (8), 136 (85), 91 (75); HRMS (ESI) for $C_{14}H_{13}NO_2$ $[M+H]^+$ calcd. 228.1019, found. 228.1018.

***N*-benzylpyridin-3-amine (3va):**



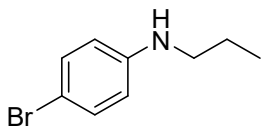
28.3 mg, 77% yield; R_f = 0.4 (PE:EA = 1:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.97 (d, *J* = 4.5 Hz, 1H), 7.38 - 7.32 (m, 4H), 7.31 - 7.27 (m, 1H), 7.06 (t, *J* = 6.5 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.34 (s, 2H), 4.16 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 138.9, 138.5, 136.2, 128.7, 127.5, 127.4, 123.7, 118.5, 47.8; LRMS (EI, 70eV) *m/z* (%): 184 (M^+, 5), 181 (50), 152 (15), 91 (100); HRMS (ESI) for $C_{12}H_{12}N_2$ $[M+H]^+$ calcd. 185.1073, found. 185.1073.

***N*-benzyl-2-methoxypyridin-3-amine (3wa):**



30.8 mg, 72% yield; R_f = 0.4 (PE:EA = 10:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 5.0 Hz, 1H), 7.37 - 7.31 (m, 4H), 7.29 - 7.25 (m, 1H), 6.71 (t, *J* = 6.0 Hz, 1H), 6.67 (d, *J* = 6.5 Hz, 1H), 4.60 (s, 1H), 4.32 (s, 2H), 3.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 138.7, 132.9, 132.8, 128.6, 127.4, 127.3, 117.3, 114.8, 53.2, 47.5; LRMS (EI, 70eV) *m/z* (%): 214 (M^+, 24), 184 (40), 123 (5), 91 (100); HRMS (ESI) for $C_{13}H_{14}N_2O$ $[M+H]^+$ calcd. 215.1179, found. 215.1180.

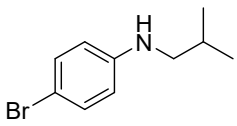
4-bromo-*N*-propylaniline (3gb):



29.1 mg, 69% yield; R_f = 0.5 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 9.0 Hz, 2H), 6.47 (d, *J* = 9.0 Hz, 2H), 3.64 (s, 1H), 3.03 (t, *J* = 7.0 Hz, 2H), 1.65 - 1.59 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 131.8, 114.2,

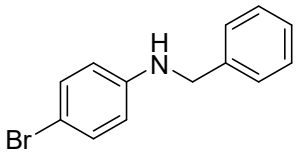
108.5, 45.7, 22.5, 11.5; LRMS (EI, 70eV) *m/z* (%): 213 (M^+, 35), 184 (100), 155 (5), 105 (38); HRMS (ESI) for $C_9H_{12}BrN$ $[M+H]^+$ calcd. 214.0226, found. 214.0224.

4-bromo-*N*-isopentylaniline (3gc):



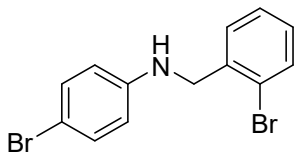
28.1 mg, 62% yield; R_f = 0.5 (PE:EA = 50:1); Yellow Oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 9.0 Hz, 2H), 6.46 (d, *J* = 9.0 Hz, 2H), 3.72 (s, 1H), 2.89 (d, *J* = 7.0 Hz, 2H), 1.90 - 1.82 (m, 1H), 0.97 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 131.8, 114.1, 108.3, 51.7, 27.9, 20.4; LRMS (EI, 70eV) *m/z* (%): 227 (M^+, 26), 184 (100), 155 (4), 105 (30); HRMS (ESI) for $C_{10}H_{14}BrN$ $[M+H]^+$ calcd. 228.0382, found. 228.0382.

***N*-benzyl-4-bromoaniline (3gd):**



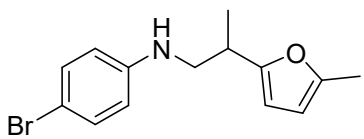
47.5 mg, 91% yield; R_f = 0.4 (PE:EA = 50:1); Yellow Oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.5 Hz, 4H), 7.29 - 7.26 (m, 1H), 7.23 (d, *J* = 9.0 Hz, 2H), 6.49 (d, *J* = 9.0 Hz, 2H), 4.29 (s, 2H), 4.07 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 138.8, 131.9, 128.7, 127.3, 127.3, 114.4, 109.1, 48.2; LRMS (EI, 70eV) *m/z* (%): 261 (M^+, 25), 184 (4), 130 (2), 91 (100); HRMS (ESI) for $C_{13}H_{12}BrN$ $[M+H]^+$ calcd. 262.0226, found. 262.0224.

4-bromo-*N*-(2-bromobenzyl)aniline (3ge):



55.1 mg, 82% yield; R_f = 0.4 (PE:EA = 50:1); Yellow Oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.28 - 7.25 (m, 1H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.47 (d, *J* = 9.0 Hz, 2H), 4.37 (s, 2H), 4.23 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 137.6, 132.9, 131.9, 129.0, 128.8, 127.5, 123.2, 114.5, 109.3, 48.3; LRMS (EI, 70eV) *m/z* (%): 341 (M^+, 70), 181 (60), 169 (100), 90 (41); HRMS (ESI) for $C_{13}H_{11}Br_2N$ $[M+H]^+$ calcd. 339.9331, found. 339.9333.

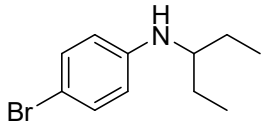
4-bromo-*N*-(2-(5-methylfuran-2-yl)propyl)aniline (3gf):



40.3 mg, 72% yield; R_f = 0.2 (PE:EA = 20:1); Yellow Oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 9.0 Hz, 2H), 6.47 (d, *J* = 9.0 Hz, 2H), 5.93 (d, *J* = 3.0 Hz, 1H),

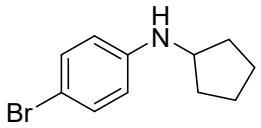
5.86 (d, *J* = 2.0 Hz, 1H), 3.80 (s, 1H), 3.27 - 3.18 (m, 2H), 3.10 - 3.02 (m, 1H), 2.26 (s, 3H), 1.29 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 151.0, 147.1, 131.8, 114.4, 108.7, 105.8, 105.7, 48.85, 32.9, 16.9, 13.5; LRMS (EI, 70eV) *m/z* (%): 293 (M^+, 15), 184 (100), 110 (40), 105 (35); HRMS (ESI) for $C_{14}H_{16}BrNO$ $[M+H]^+$ calcd. 279.0253, found. 279.0253.

4-bromo-*N*-(pentan-3-yl)aniline (3gg):



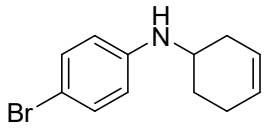
32.9 mg, 68% yield; R_f = 0.7 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 9.0 Hz, 2H), 6.44 (d, *J* = 9.0 Hz, 2H), 3.45 (s, 1H), 3.19 - 3.14 (m, 1H), 1.60 - 1.54 (m, 2H), 1.48 - 1.42 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 131.9, 114.4, 107.8, 55.5, 26.7, 10.1; LRMS (EI, 70eV) *m/z* (%): 241 (M^+, 22), 212 (100), 133 (42), 118 (23); HRMS (ESI) for $C_{11}H_{16}BrN$ $[M+H]^+$ calcd. 242.0539, found. 242.0541.

4-bromo-*N*-cyclopentylaniline (3gh):



37.5 mg, 78% yield; R_f = 0.4 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 9.0 Hz, 2H), 6.45 (d, *J* = 9.0 Hz, 2H), 3.74 - 3.69 (m, 1H), 3.63 (s, 1H), 2.03 - 1.96 (m, 2H), 1.74 - 1.67 (m, 2H), 1.64 - 1.57 (m, 2H), 1.47 - 1.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 131.7, 114.6, 108.3, 54.6, 33.4, 24.0; LRMS (EI, 70eV) *m/z* (%): 239 (M^+, 80), 210 (98), 197 (50), 130 (100); HRMS (ESI) for $C_{11}H_{14}BrN$ $[M+H]^+$ calcd. 240.0382, found. 240.0381.

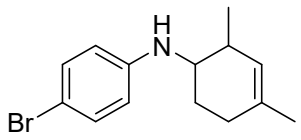
4-bromo-*N*-(cyclohex-3-en-1-yl)aniline (3gi):



39.2 mg, 79% yield; R_f = 0.4 (PE:EA = 50:1); Yellow Oil;^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 9.0 Hz, 2H), 6.48 (d, *J* = 9.0 Hz, 2H), 5.74 - 5.68 (m, 1H), 5.66 - 5.61 (m, 1H), 3.65 (s, 1H), 3.59 - 3.54 (m, 1H), 2.50 - 2.43 (m, 1H), 2.17 - 2.12 (m, 2H), 1.99 - 1.88 (m, 2H), 1.59 - 1.53 (m, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 131.9, 127.0, 124.5, 114.7, 108.43, 47.9, 32.1, 27.8, 23.7; LRMS (EI, 70eV) *m/z* (%):251 (M^+, 30), 197 (100), 117 (30), 91 (20); HRMS (ESI) for $C_{12}H_{14}BrN$ $[M+H]^+$ calcd. 252.0382, found.

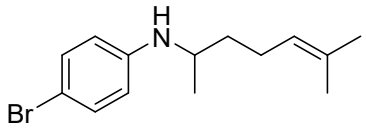
252.0384.

4-bromo-*N*-(2,4-dimethylcyclohex-3-en-1-yl)aniline (3gj):



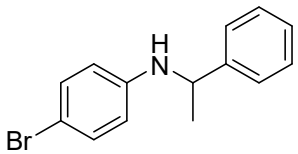
22.3 mg, 40% yield; R_f = 0.6 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 9.0 Hz, 2H), 6.46 (d, *J* = 9.0 Hz, 2H), 5.22 (d, *J* = 1.5 Hz, 1H), 3.59 (s, 1H), 3.17 - 3.04 (m, 1H), 2.12 - 2.05 (m, 1H), 2.02 - 1.92 (m, 3H), 1.68 (s, 3H), 1.54 - 1.48 (m, 1H), 1.06 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 133.3, 131.9, 125.5, 114.5, 108.1, 77.2, 54.3, 37.0, 28.2, 26.2, 23.4, 20.0; LRMS (EI, 70eV) *m/z* (%): 279 (M^+, 20), 197 (100), 117 (25), 91 (24); HRMS (ESI) for $C_{14}H_{18}BrN$ $[M+H]^+$ calcd. 280.0695, found. 280.0695.

4-bromo-*N*-(6-methylhept-5-en-2-yl)aniline (3gk):



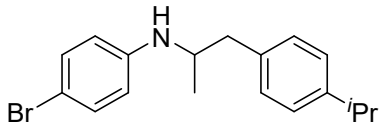
45.6 mg, 81% yield; R_f = 0.7 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 9.0 Hz, 2H), 6.45 (d, *J* = 9.0 Hz, 2H), 5.10 (t, *J* = 7.0 Hz, 1H), 3.44 (s, 1H), 3.42 - 3.37 (m, 1H), 2.10 - 2.01 (m, 2H), 1.69 (s, 3H), 1.58 (s, 3H), 1.56 - 1.53 (m, 1H), 1.49 - 1.43 (m, 1H), 1.16 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 131.9, 129.0, 123.7, 114.6, 108.1, 48.1, 36.9, 25.7, 24.6, 20.6, 17.6; LRMS (EI, 70eV) *m/z* (%): 281 (M^+, 20), 198 (100), 119 (40), 95 (42); HRMS (ESI) for $C_{14}H_{20}BrN$ $[M+H]^+$ calcd. 282.0852, found. 282.0853.

4-bromo-*N*-(1-phenylethyl)aniline (3gl):



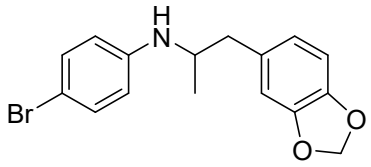
48.9 mg, 88% yield; R_f = 0.6 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 - 7.28 (m, 4H), 7.23 - 7.20 (m, 1H), 7.14 (d, *J* = 9.0 Hz, 2H), 6.36 (d, *J* = 9.0 Hz, 2H), 4.45 - 4.39 (m, 1H), 4.05 (s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 144.5, 131.7, 128.7, 127.0, 125.7, 114.8, 108.8, 53.4, 24.9; LRMS (EI, 70eV) *m/z* (%): 275 (M^+, 22), 260 (30), 171 (22), 105 (100); HRMS (ESI) for $C_{14}H_{14}BrN$ $[M+H]^+$ calcd. 276.0382, found. 276.0382.

4-bromo-*N*-(1-(4-isopropylphenyl)propan-2-yl)aniline (3gm):



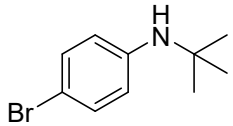
53.0 mg, 80% yield; R_f = 0.5 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 9.0 Hz, 2H), 3.72 - 3.66 (m, 1H), 3.55 (s, 1H), 2.89 - 2.82 (m, 2H), 2.70 - 2.65 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 6H), 1.14 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 146.2, 135.3, 131.9, 129.3, 126.4, 114.8, 108.5, 49.3, 41.6, 33.7, 24.0, 20.1; LRMS (EI, 70eV) *m/z* (%): 331 (M^+, 7), 198 (100), 119 (30), 91 (10); HRMS (ESI) for $C_{18}H_{22}BrN$ $[M+H]^+$ calcd. 332.1008, found. 332.1010.

***N*-(1-(benzo[*d*][1,3]dioxol-5-yl)propan-2-yl)-4-bromoaniline (3gn):**



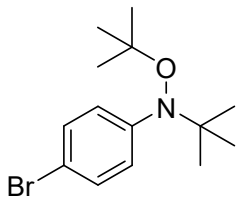
42.3 mg, 63% yield; R_f = 0.3 (PE:EA = 20:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 9.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.64 (s, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 9.0 Hz, 2H), 5.92 (s, 2H), 3.68 - 3.61 (m, 1H), 3.53 (s, 1H), 2.81 - 2.75 (m, 1H), 2.65 - 2.60 (m, 1H), 1.13 (d, *J* = 6.5 Hz, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 146.1, 146.0, 132.0, 131.8, 122.3, 114.8, 109.7, 108.6, 108.1, 100.8, 49.5, 41.7, 20.0; LRMS (EI, 70eV) *m/z* (%): 333 (M^+, 7), 198 (100), 136 (22), 119 (40); HRMS (ESI) for $C_{16}H_{16}BrNO_2$ $[M+H]^+$ calcd. 334.0437, found. 334.0436.

4-bromo-*N*-(*tert*-butyl)aniline (3go):



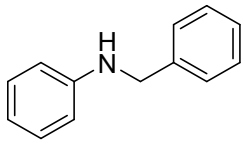
33.6 mg, 33% yield; R_f = 0.4 (PE:EA = 30:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.61 (d, *J* = 8.5 Hz, 2H), 1.32 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 131.6, 118.6, 110.0, 51.5, 29.9; LRMS (EI, 70eV) *m/z* (%): 227 (M^+, 39), 112 (97), 170 (100), 98 (55); HRMS (ESI) for $C_{10}H_{14}BrN$ $[M+H]^+$ calcd. 228.0382, found. 228.0383.

***N*-(4-bromophenyl)-*N,O*-di-tert-butylhydroxylamine (4go):**



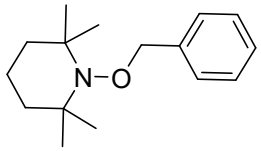
62.1 mg, 50% yield; R_f = 0.4 (PE:EA = 30:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.23 - 7.01 (m, 2H), 1.06 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 127.6, 117.5, 78.3, 59.5, 28.1, 26.7; LRMS (EI, 70eV) *m/z* (%): 301 (M^++2, 1), 299 (M^+, 1), 243 (31), 187 (100), 170 (9); HRMS (ESI) for $C_{14}H_{22}BrNO$ $[M+H]^+$ calcd. 300.0958, found. 300.0958.

***N*-benzylaniline (3ad):**



28.7 mg, 78% yield; R_f = 0.4 (PE:EA = 50:1); Yellow Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 - 7.32 (m, 4H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 2H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.33 (s, 2H), 4.03 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 139.4, 129.2, 128.6, 127.5, 127.2, 117.5, 112.8, 48.3; LRMS (EI, 70eV) *m/z* (%): 183 (M^+, 59), 106 (20), 91 (100), 83 (2); HRMS (ESI) for $C_{13}H_{13}N$ $[M+H]^+$ calcd. 184.1121, found. 184.1121.

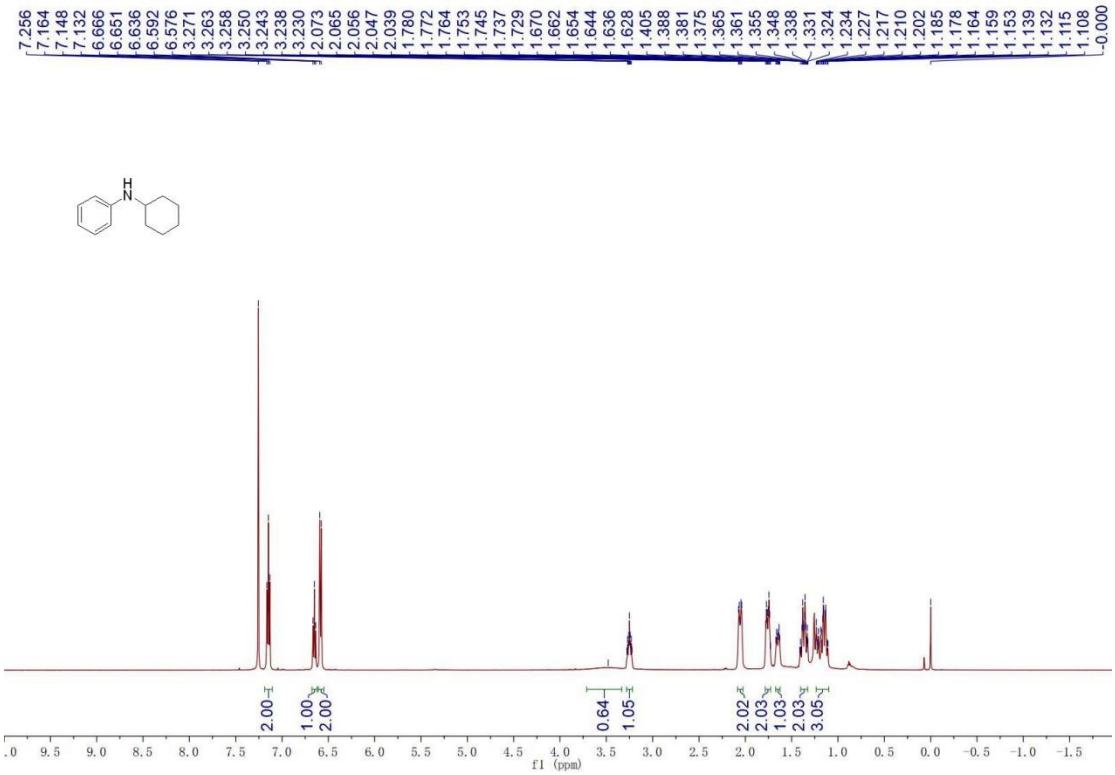
1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (6a):



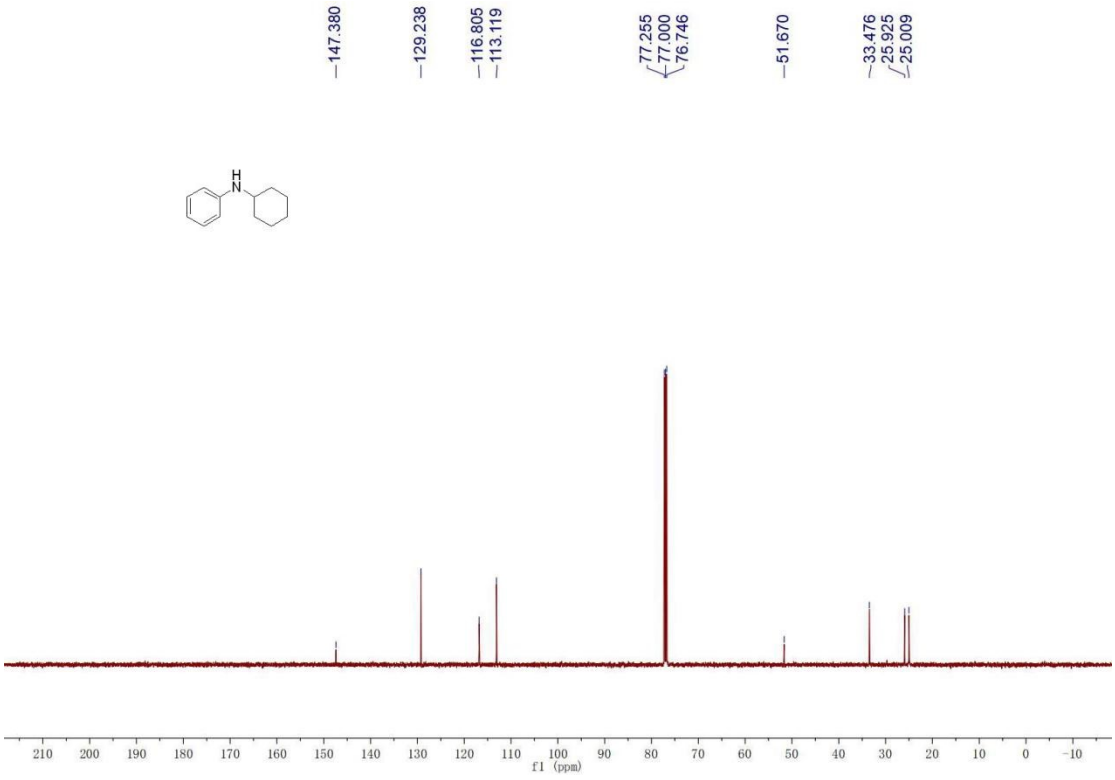
48.9 mg, 33% yield; R_f = 0.6 (PE:EA = 30:1); Colorless Oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 - 7.31 (m, 4H), 7.27 (t, *J* = 7.0 Hz, 1H), 4.83 (s, 2H), 1.64 - 1.47 (m, 5H), 1.37 - 1.32 (m, 1H), 1.26 (s, 6H), 1.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 128.2, 127.4, 127.3, 78.7, 60.0, 39.7, 33.1, 20.3, 17.1; HRMS (ESI) for $C_{16}H_{25}NO$ $[M+H]^+$ calcd. 248.2009, found. 248.2007.

(C) Spectra

***N*-cyclohexylaniline (3aa):**

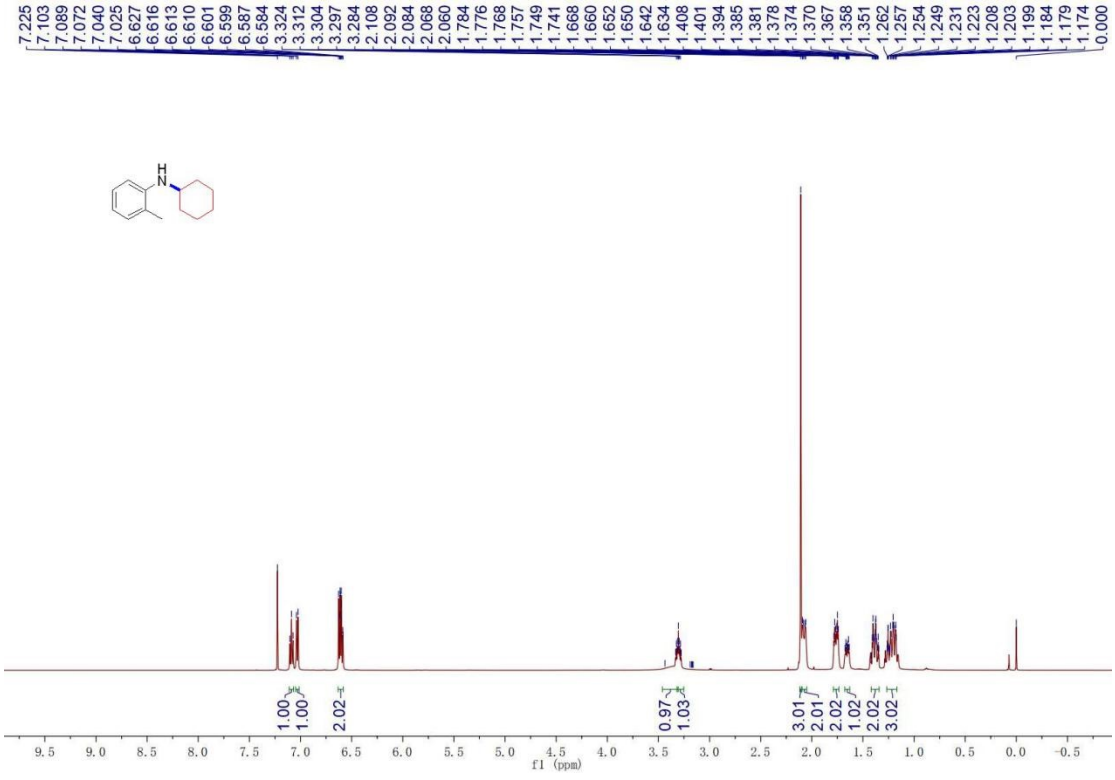


^{1}H NMR (500 MHz, $CDCl_3$)

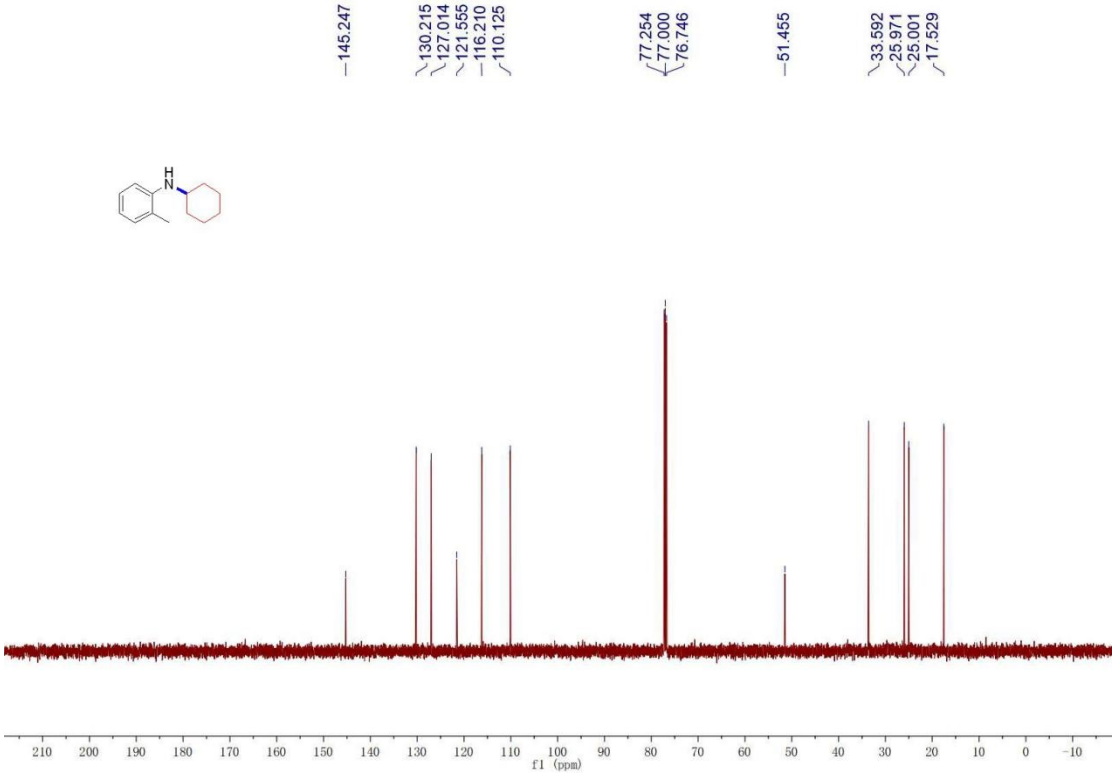


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-cyclohexyl-2-methylaniline (3ba):**

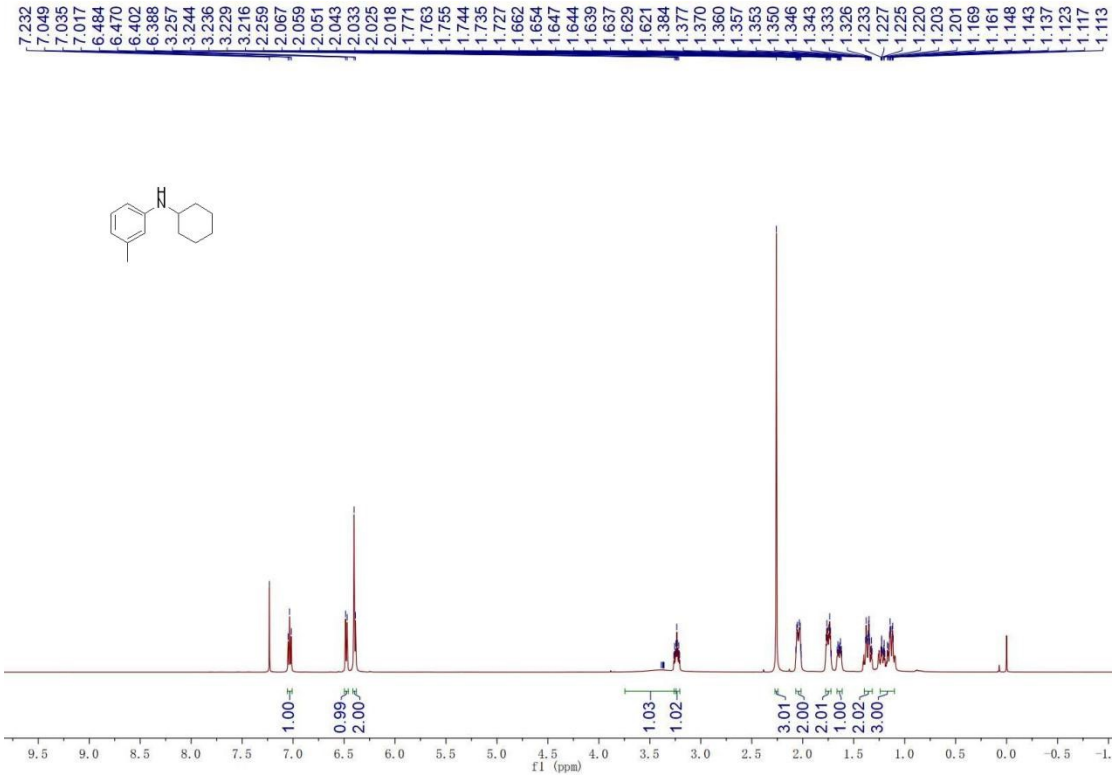


^{1}H NMR (500 MHz, $CDCl_3$)

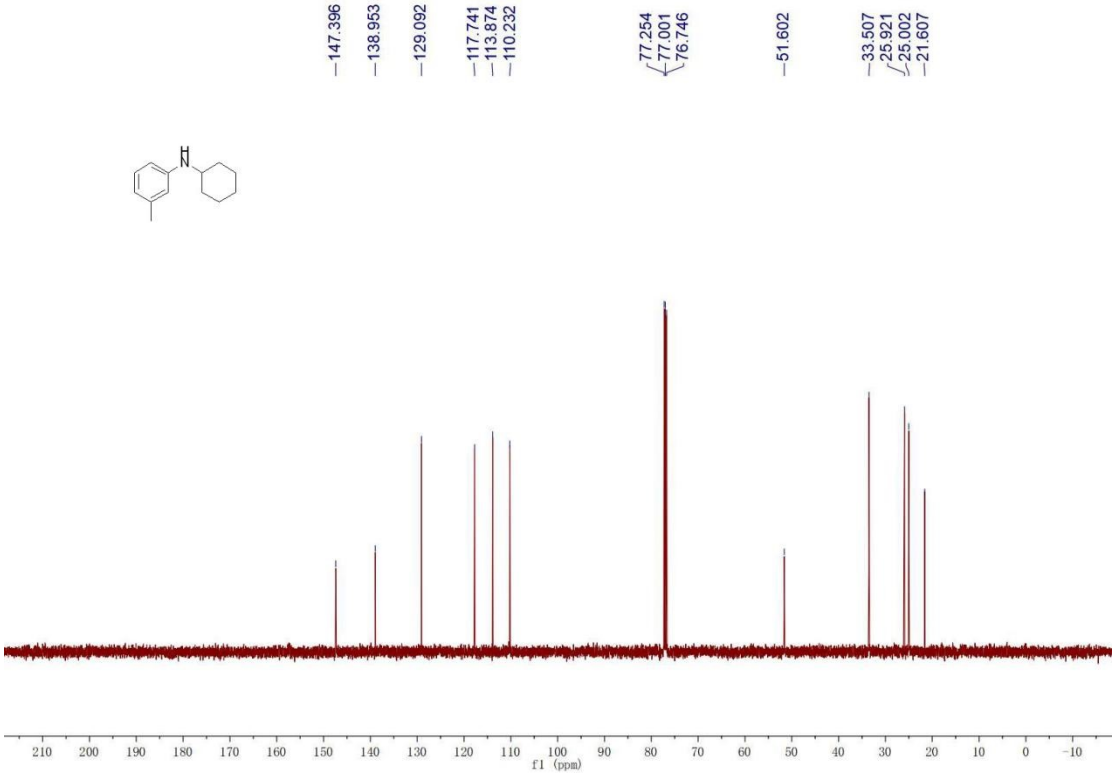


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-cyclohexyl-3-methylaniline (3ca):**

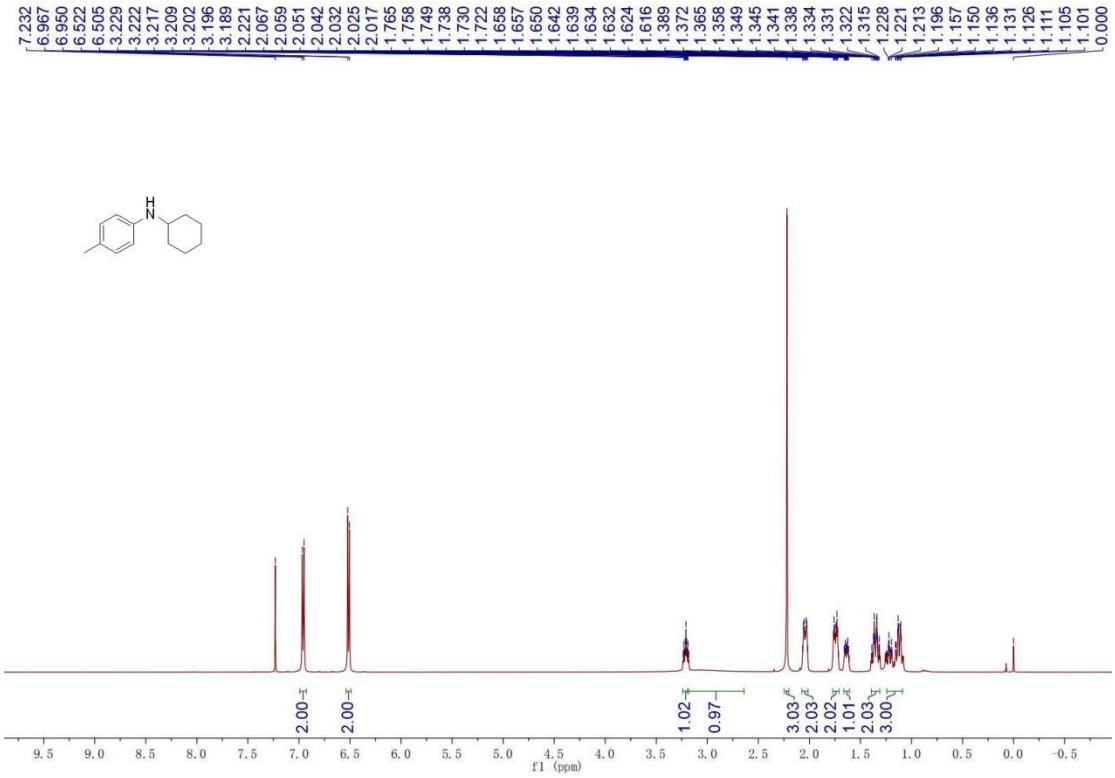


^{1}H NMR (500 MHz, $CDCl_3$)

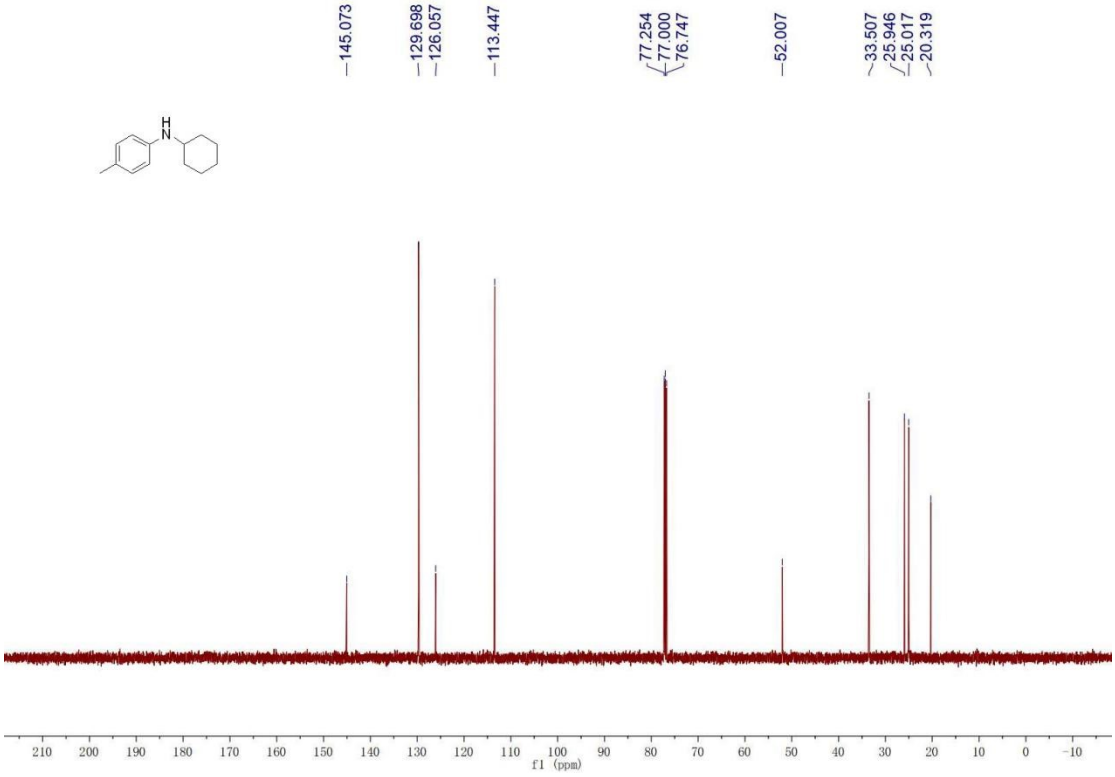


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-cyclohexyl-4-methylaniline (3da):**

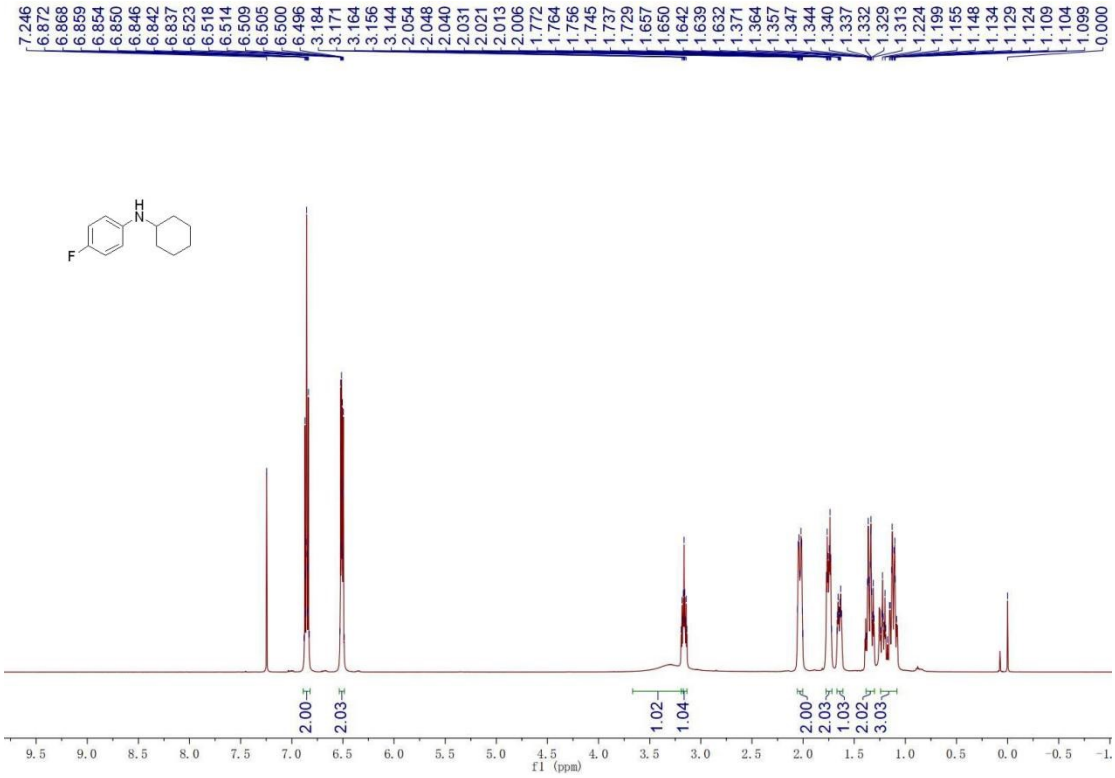


^{1}H NMR (500 MHz, $CDCl_3$)

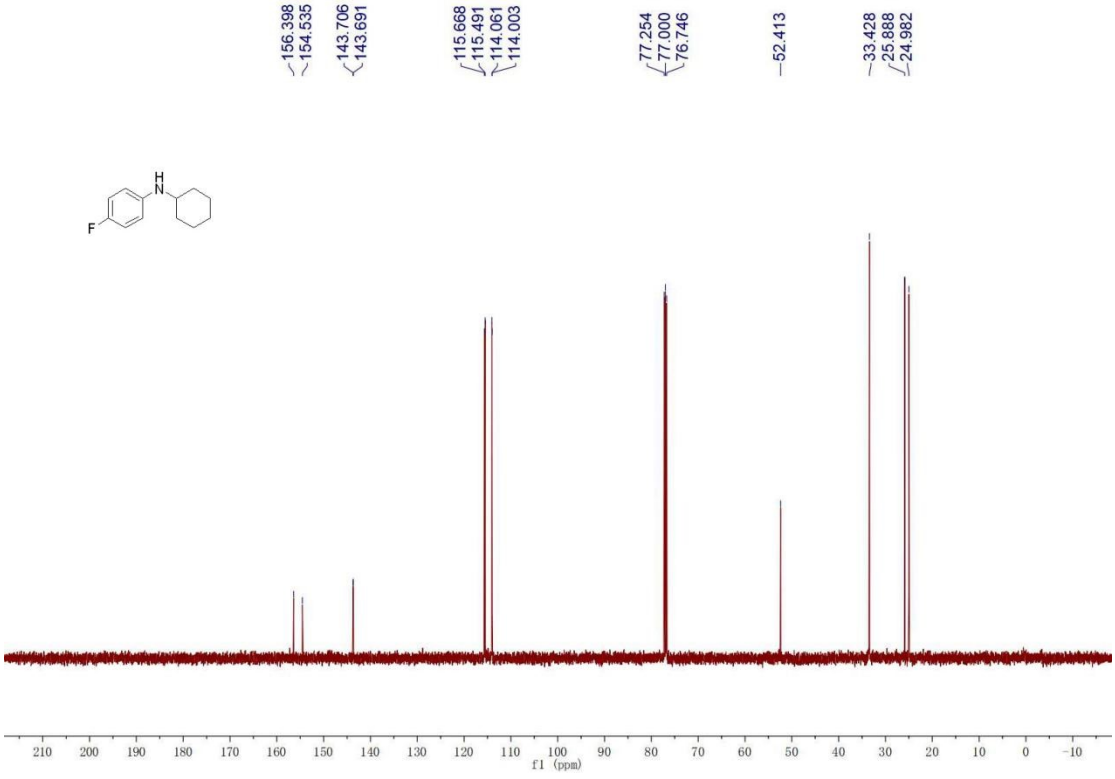


^{13}C NMR (125 MHz, $CDCl_3$)

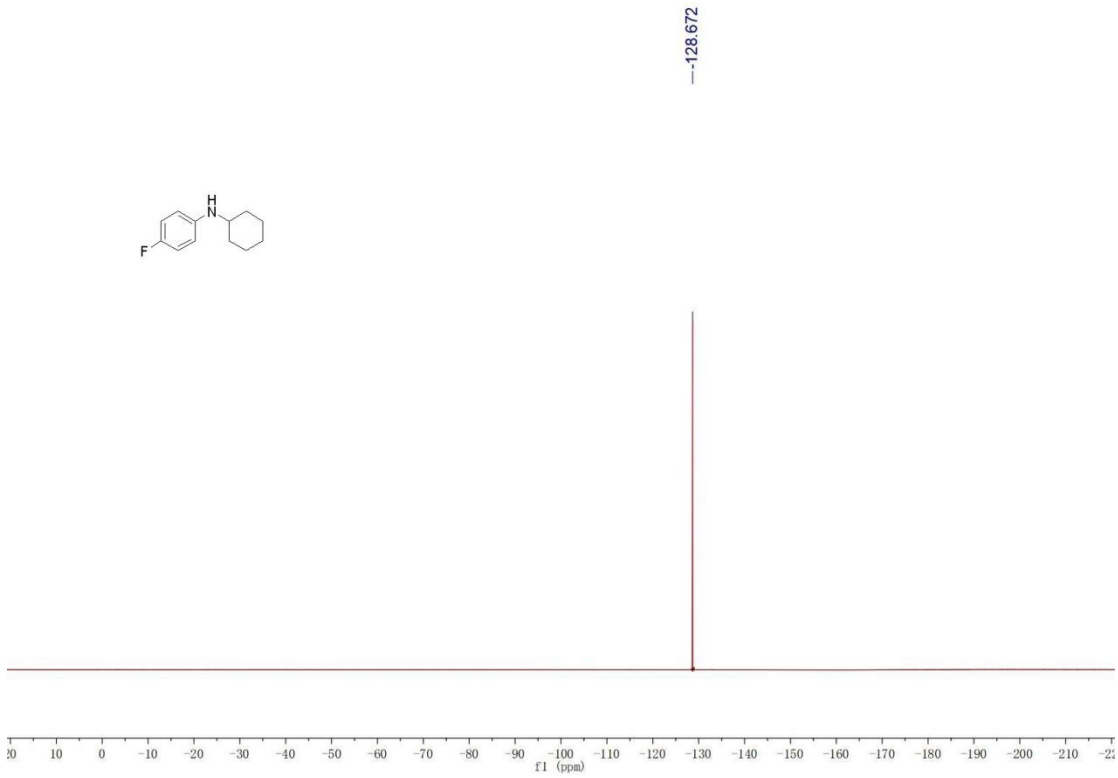
***N*-cyclohexyl-4-fluoroaniline (3ea):**



^{1}H NMR (500 MHz, $CDCl_3$)

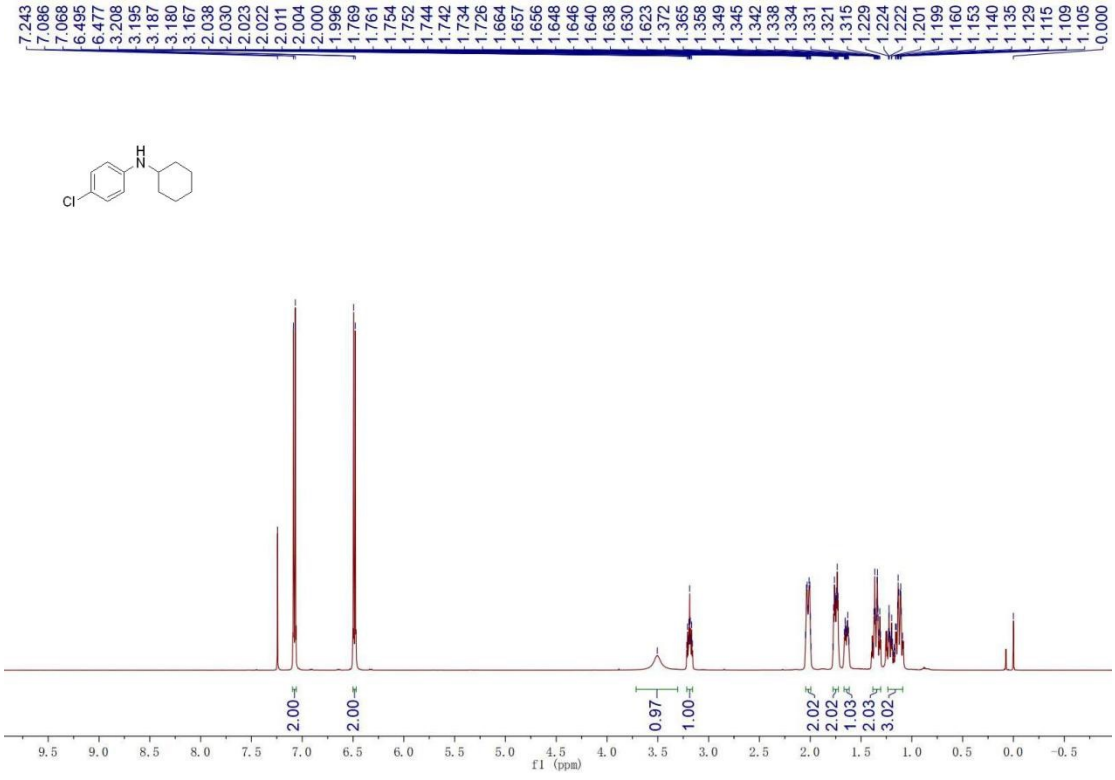


^{13}C NMR (125 MHz, $CDCl_3$)

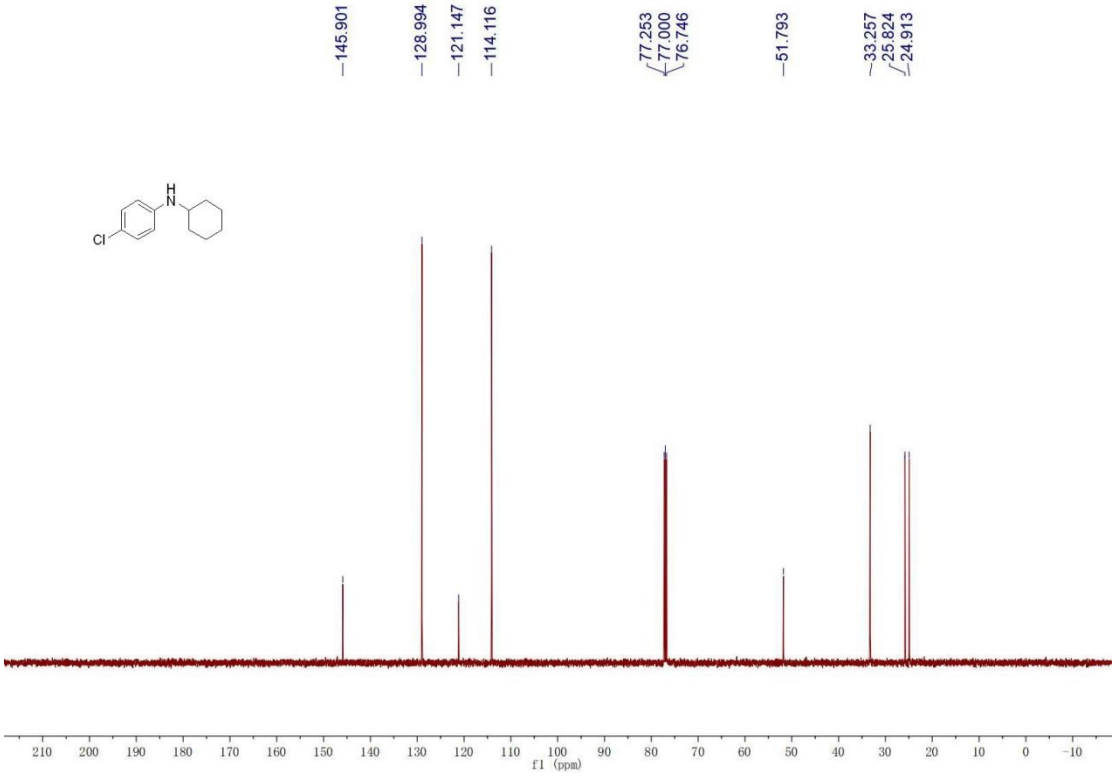


^{19}F NMR (471 MHz, $CDCl_3$)

4-chloro-*N*-cyclohexylaniline (3fa):

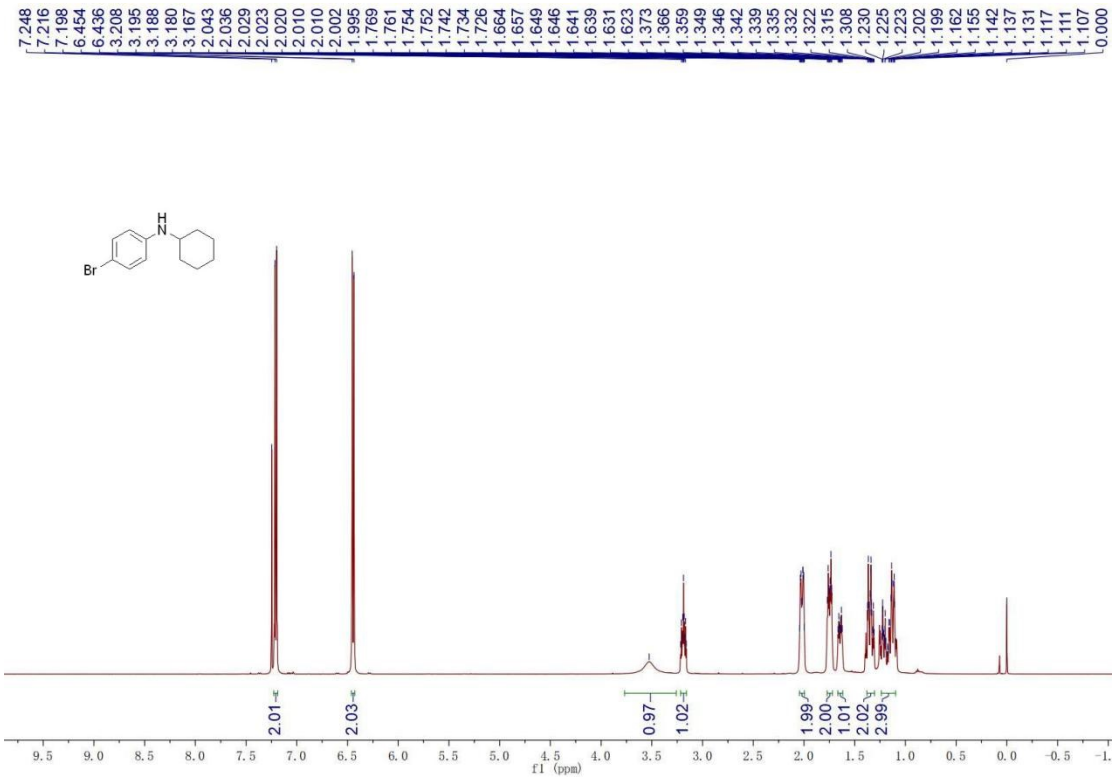


^{1}H NMR (500 MHz, $CDCl_3$)

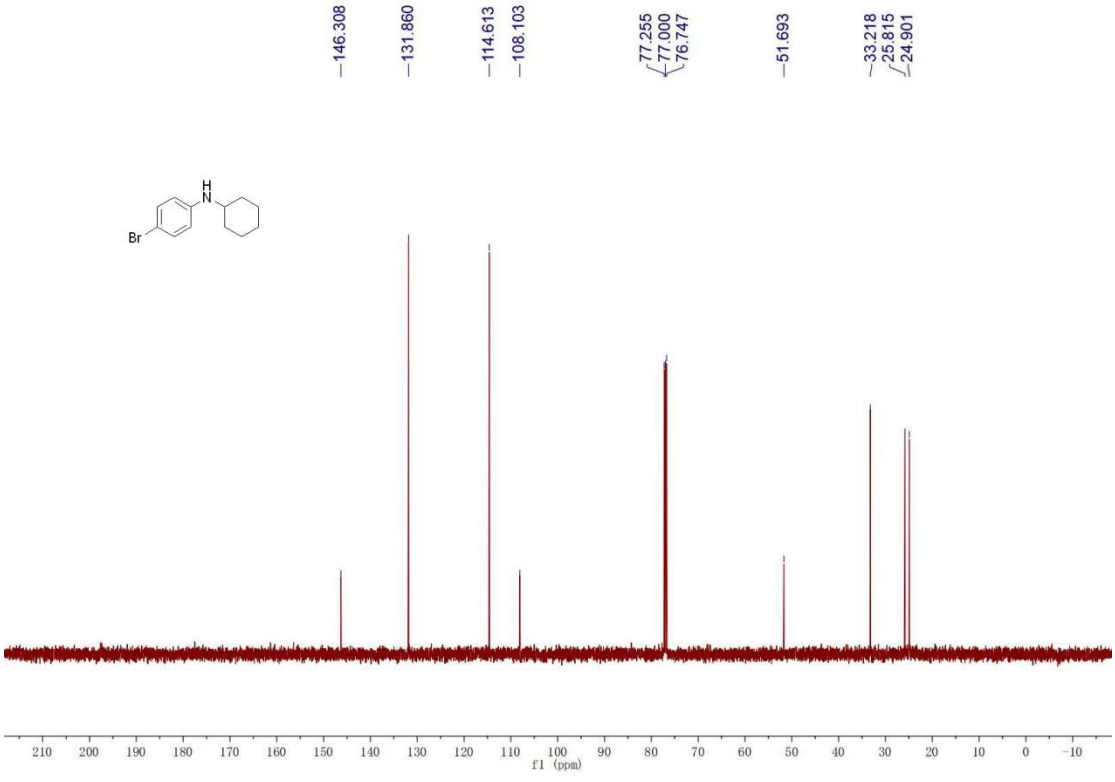


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-cyclohexylaniline (3ga):

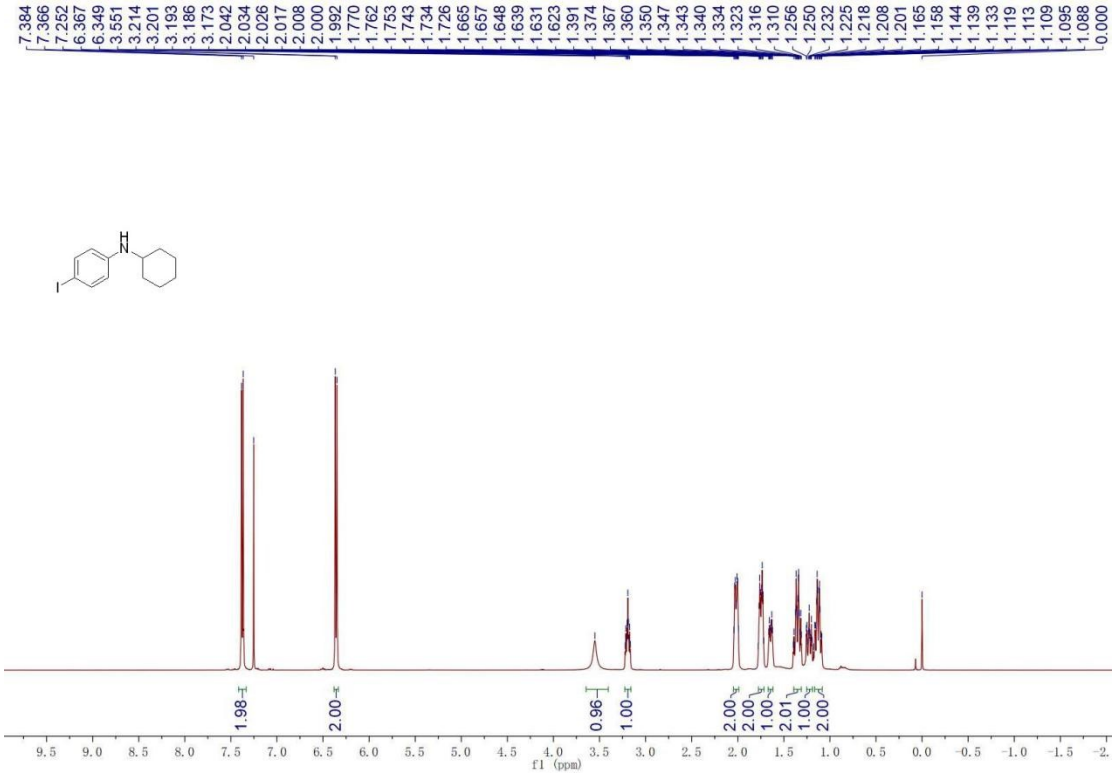


^{1}H NMR (500 MHz, $CDCl_3$)

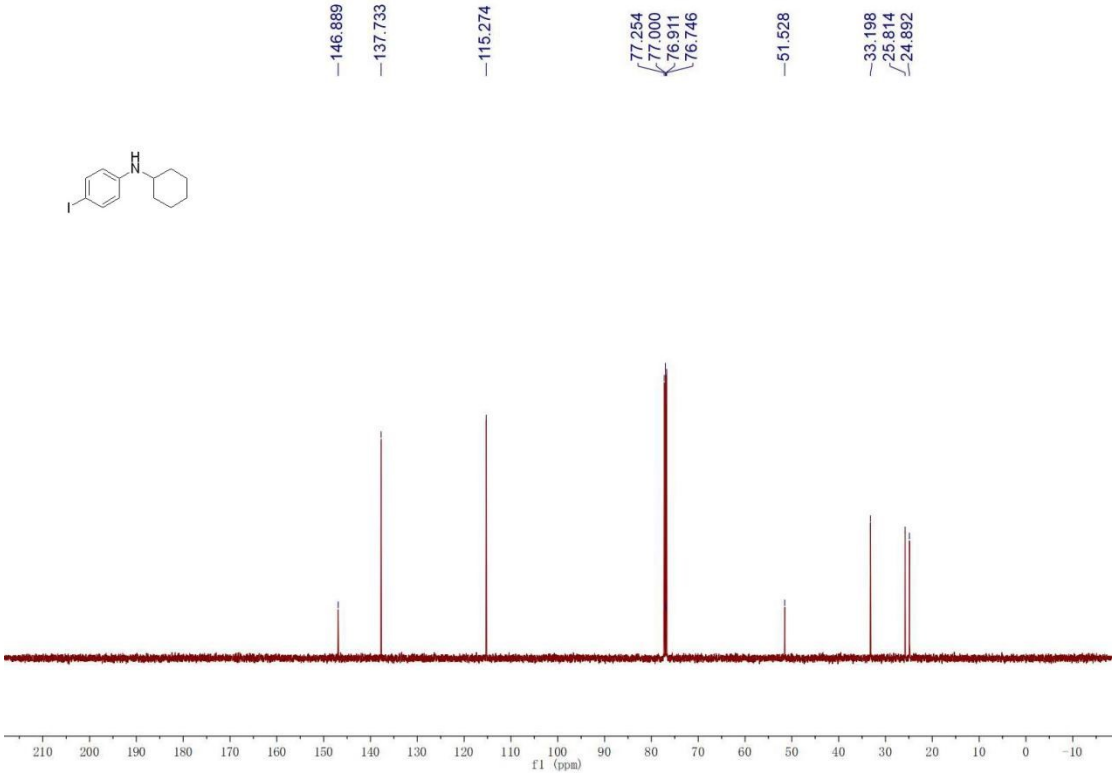


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-cyclohexyl-4-iodoaniline (3ha):**

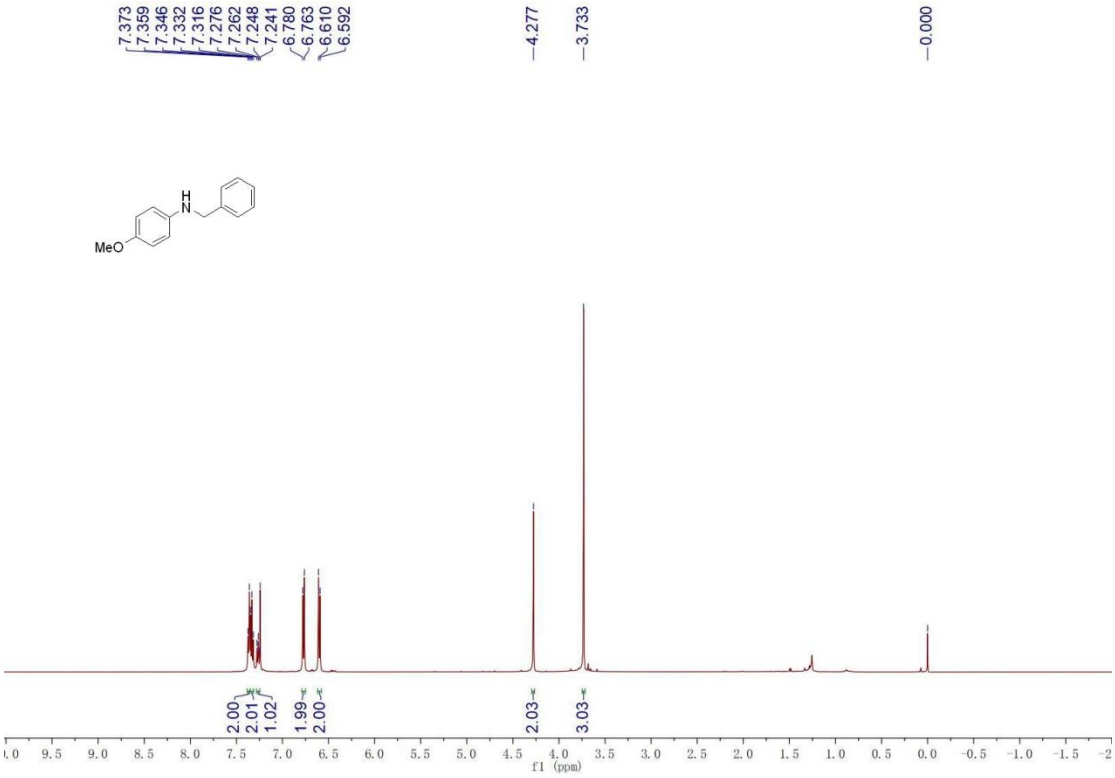


^{1}H NMR (500 MHz, $CDCl_3$)

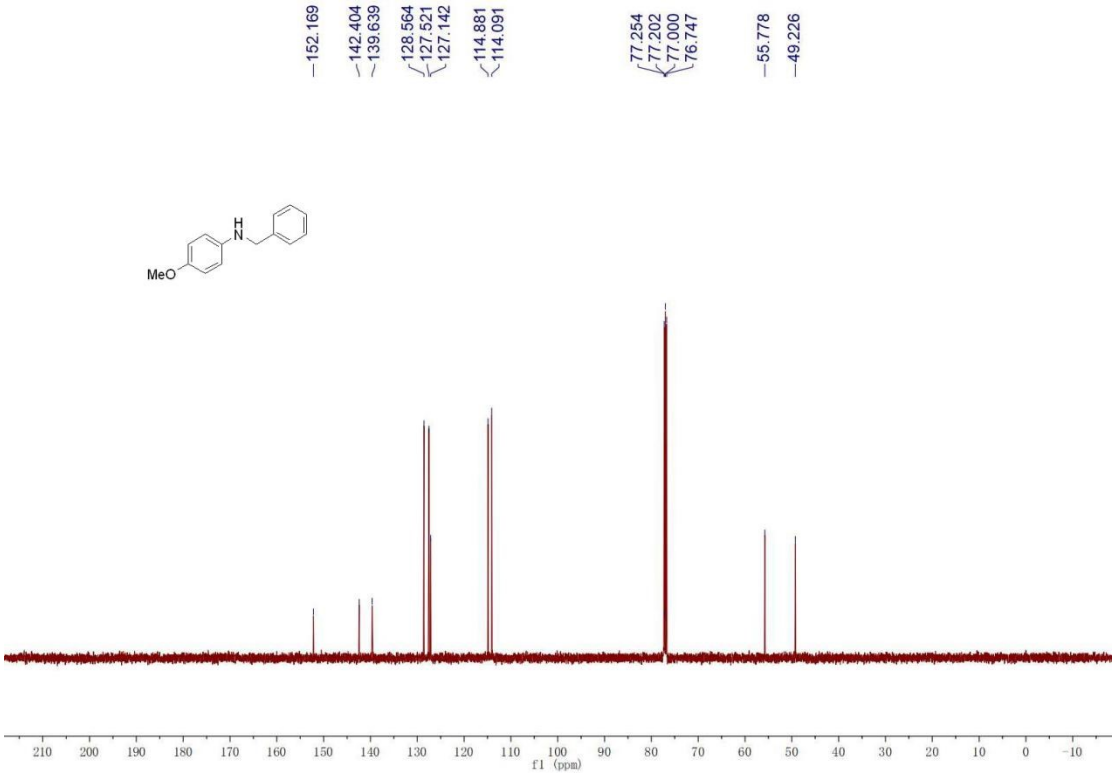


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-benzyl-4-methoxyaniline (3ia):**

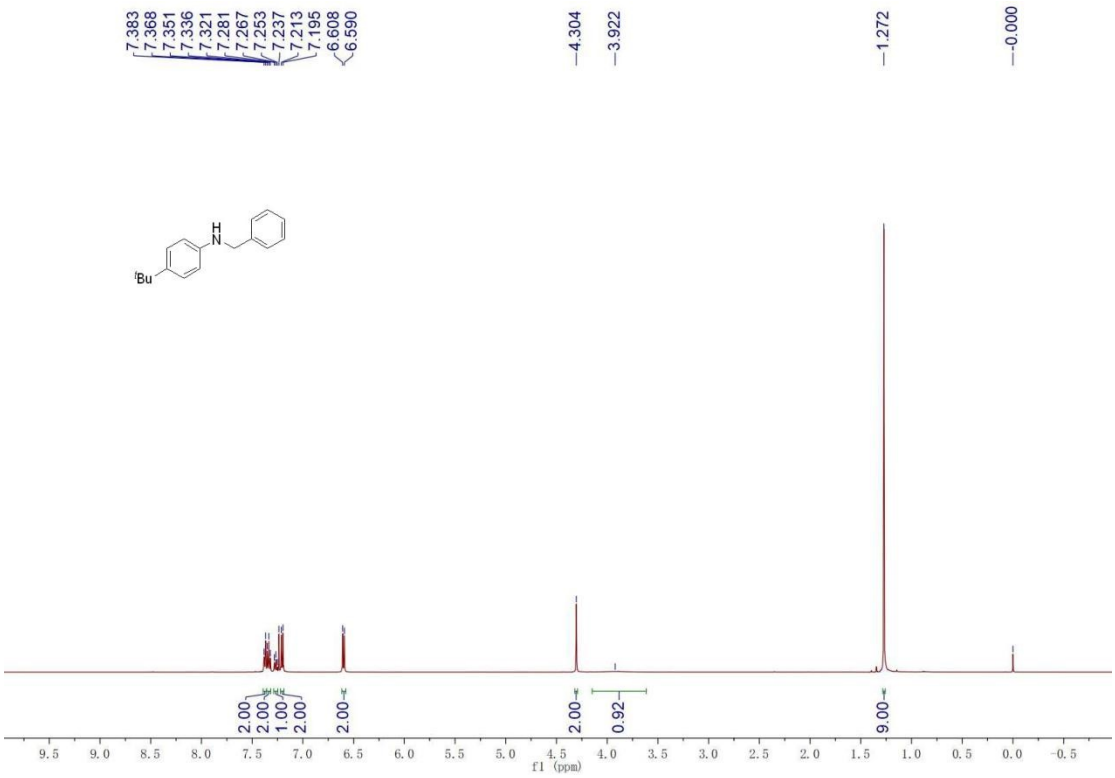


^{1}H NMR (500 MHz, $CDCl_3$)

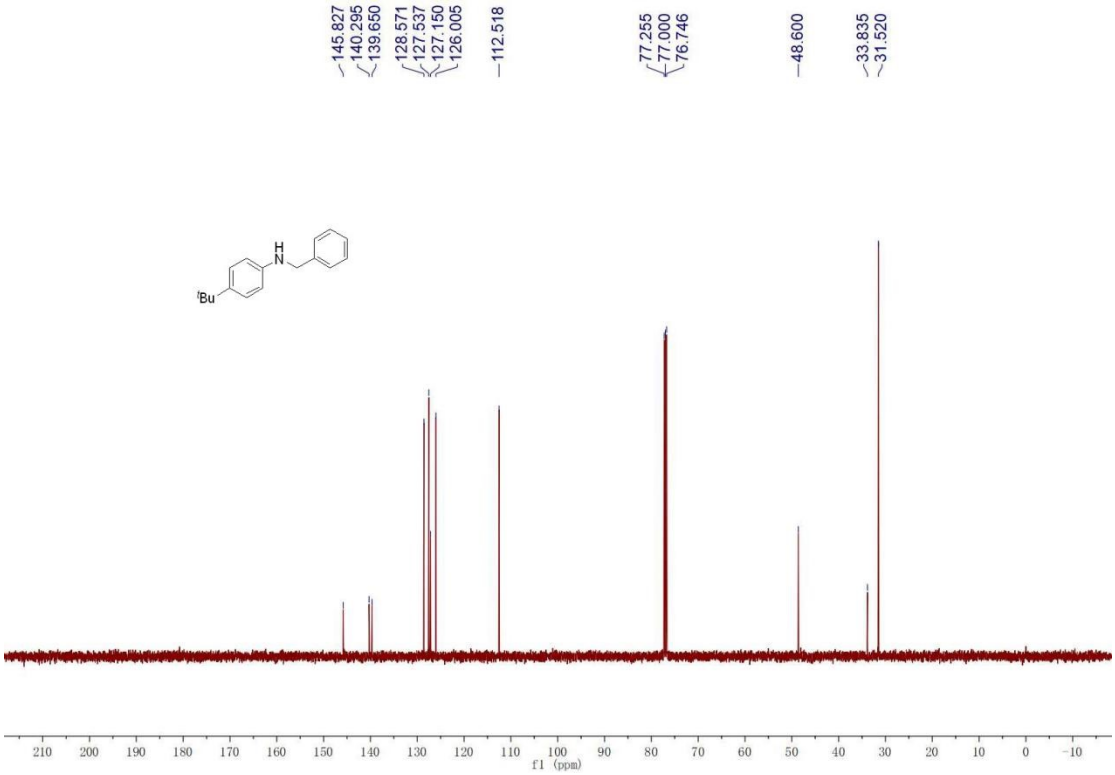


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-benzyl-4-(*tert*-butyl)aniline (3ja):**

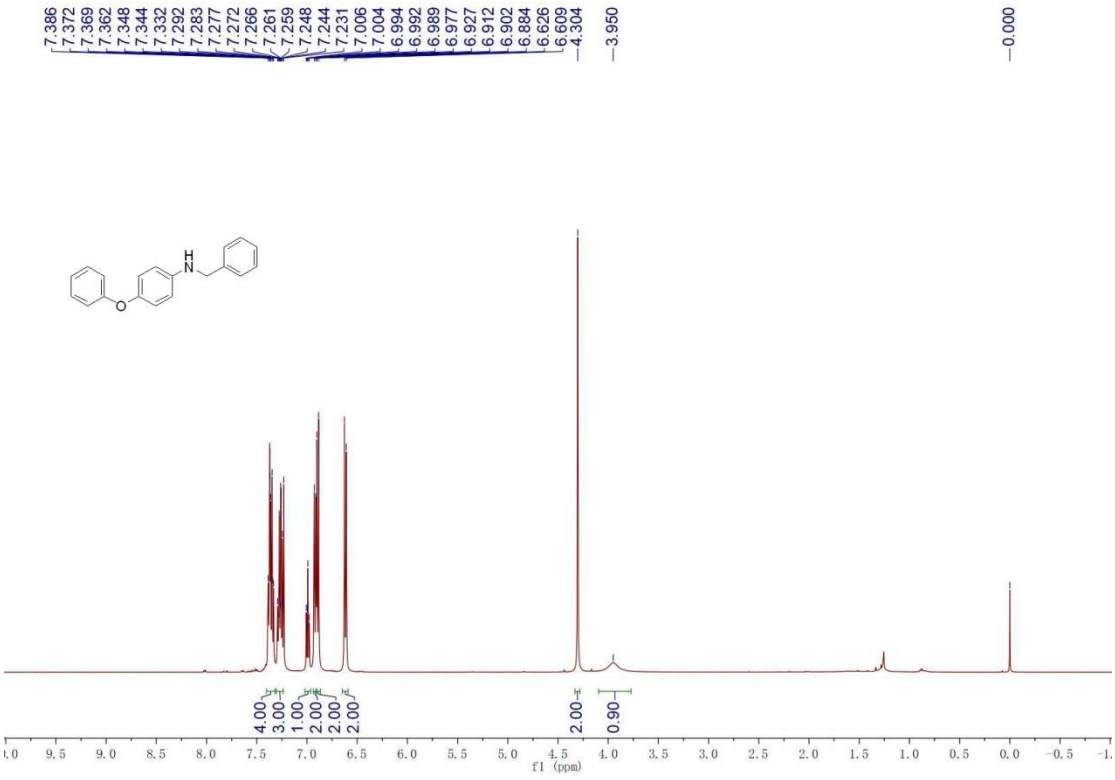


^{1}H NMR (500 MHz, $CDCl_3$)

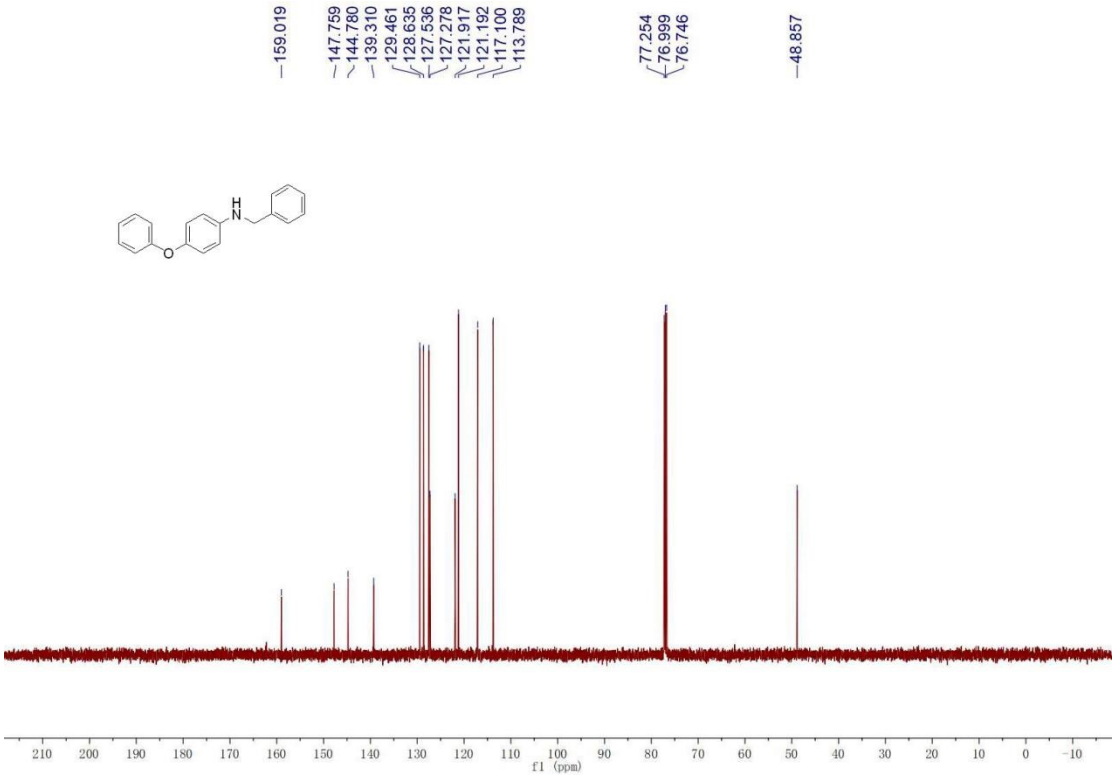


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-benzyl-4-phenoxyaniline (3ka):**

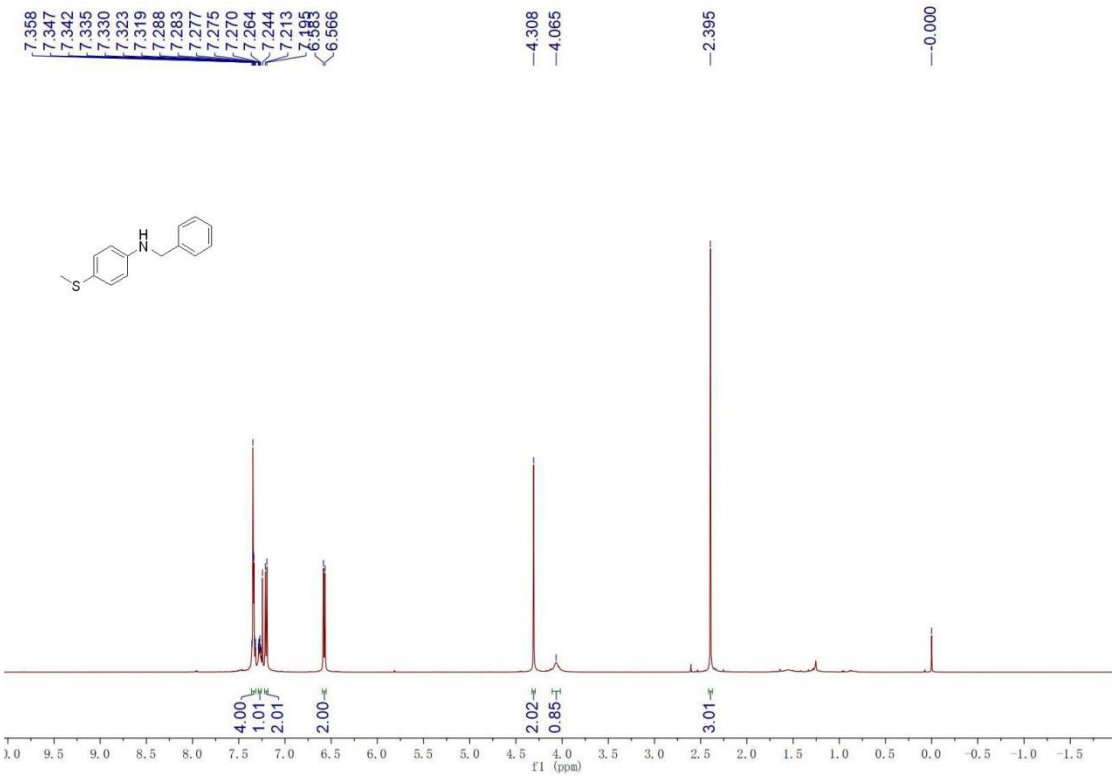


^{1}H NMR (500 MHz, $CDCl_3$)

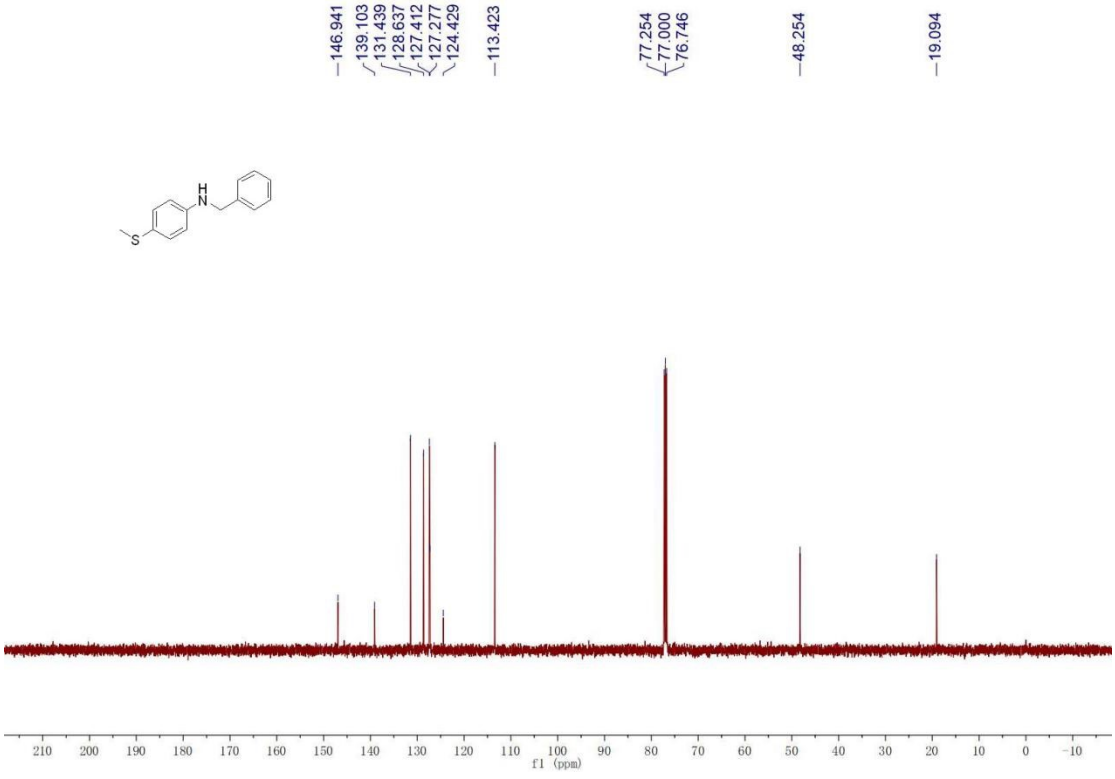


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-benzyl-4-(methylthio)aniline (3la):**

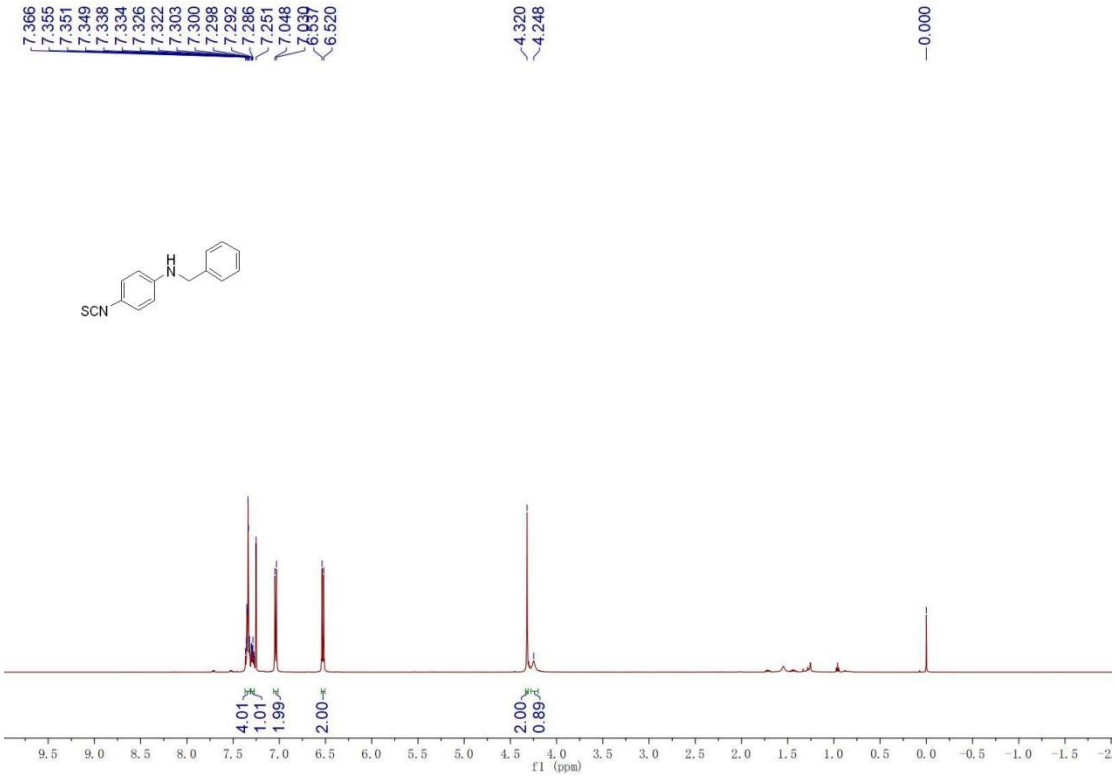


^{1}H NMR (500 MHz, $CDCl_3$)

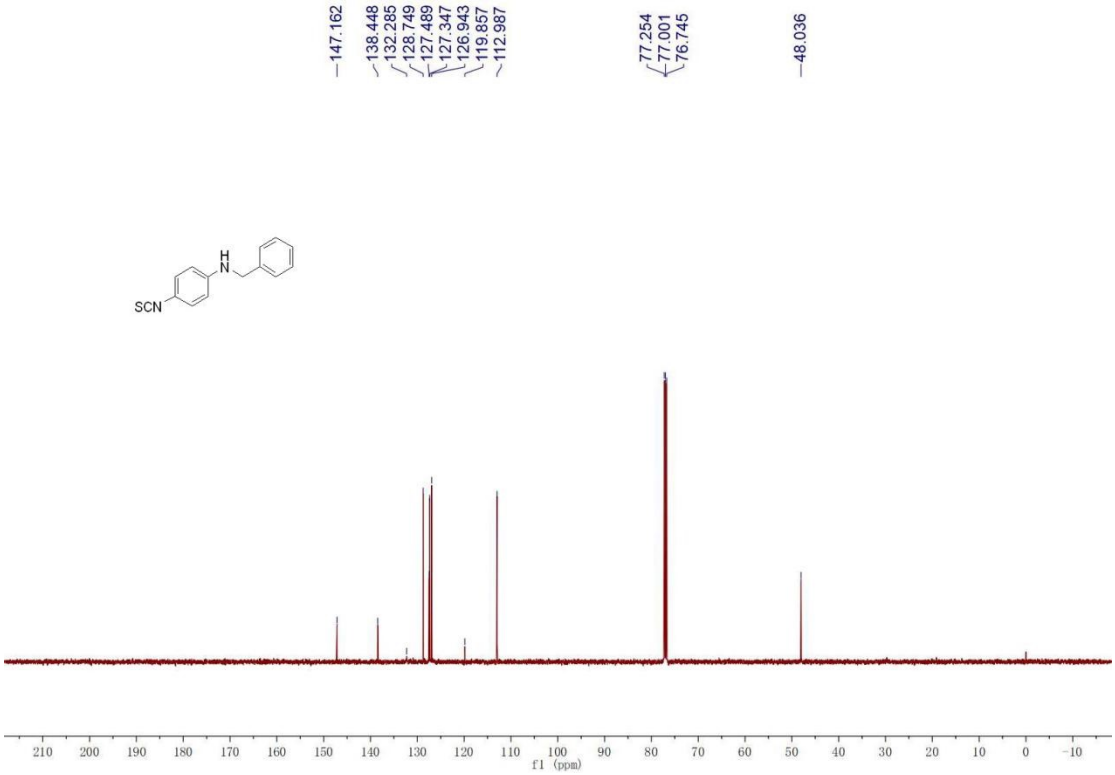


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-benzyl-4-isothiocyanatoaniline (3ma):**

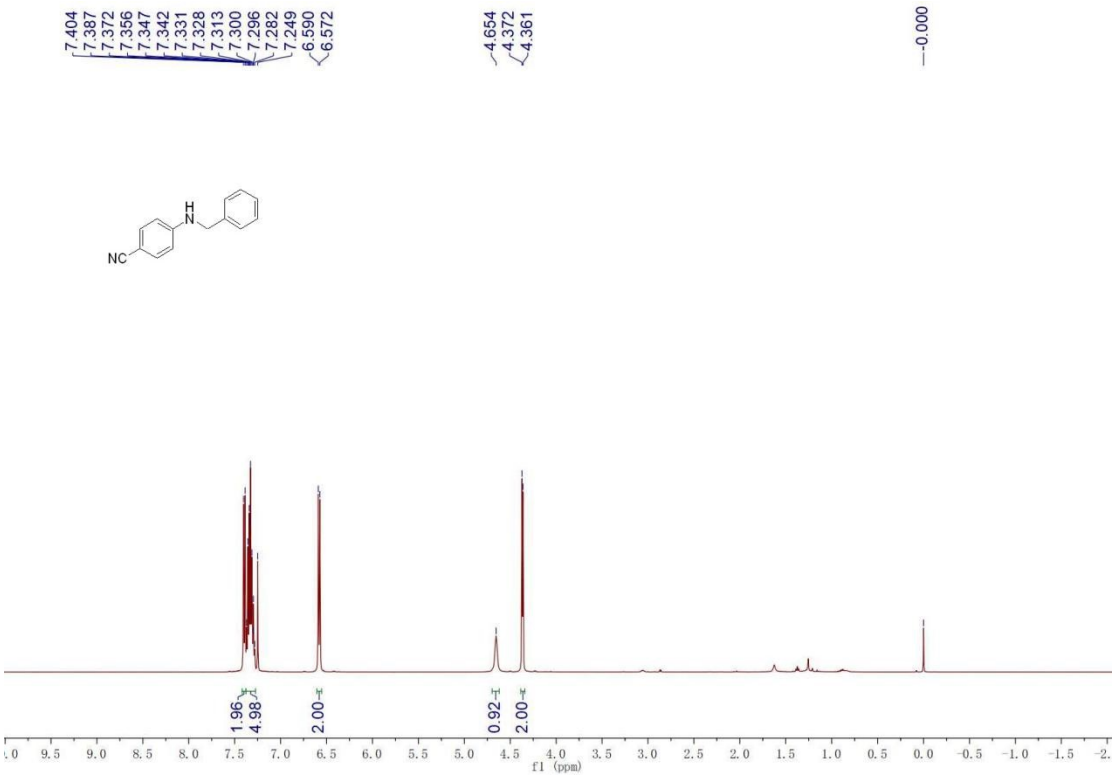


^{1}H NMR (500 MHz, $CDCl_3$)

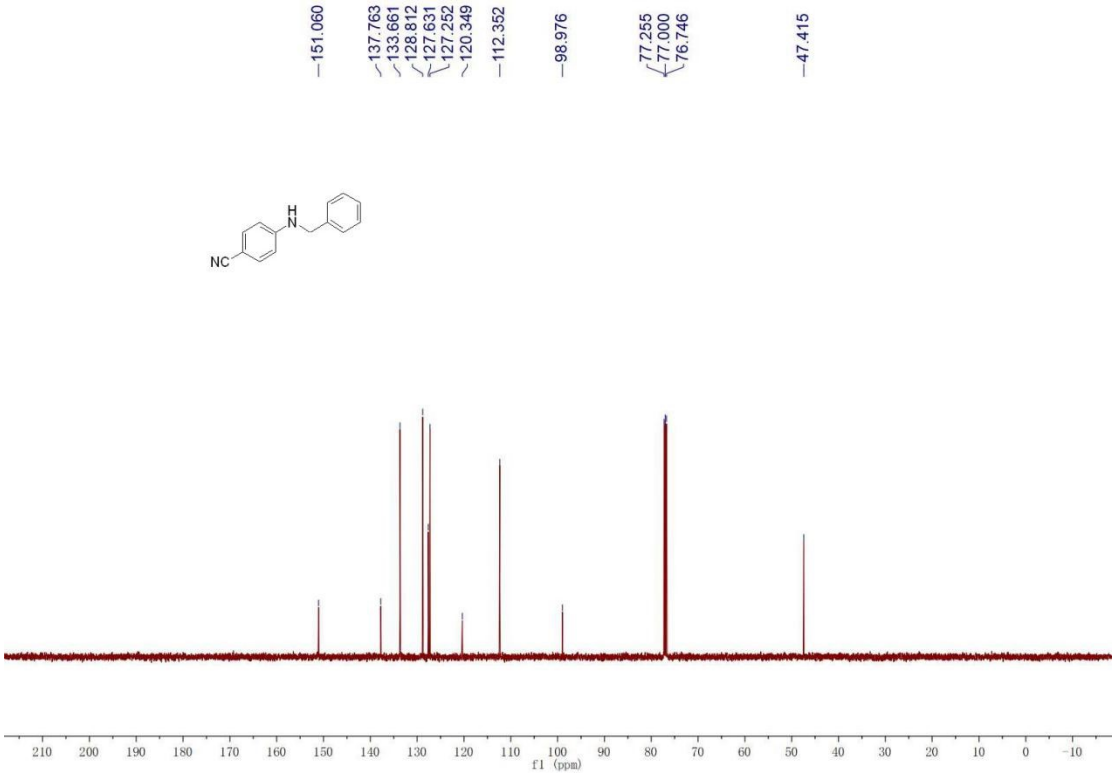


^{13}C NMR (125 MHz, $CDCl_3$)

4-(benzylamino)benzonitrile (3na):

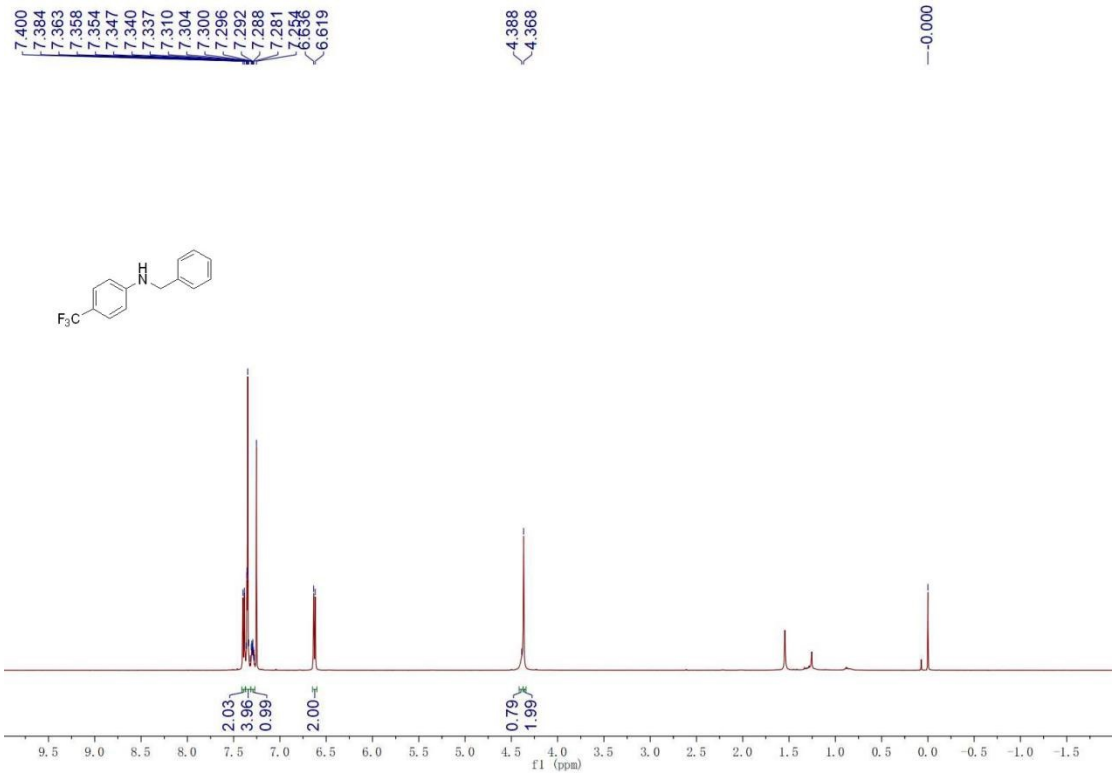


^{1}H NMR (500 MHz, $CDCl_3$)

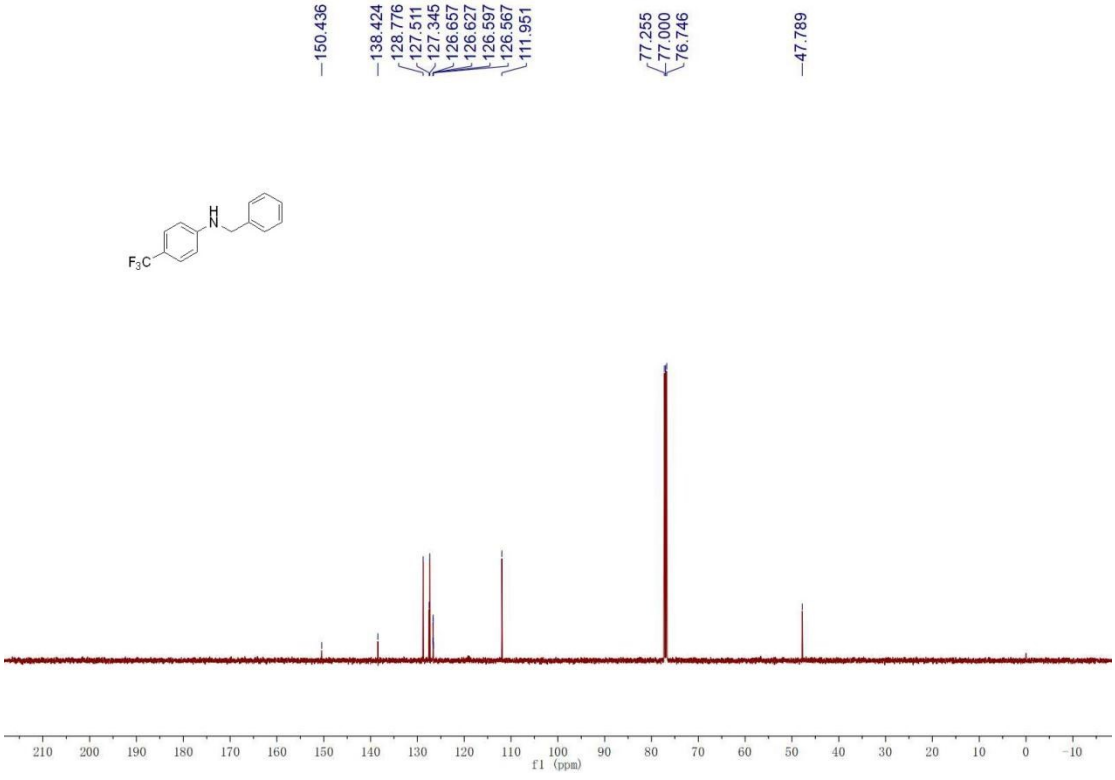


^{13}C NMR (125 MHz, $CDCl_3$)

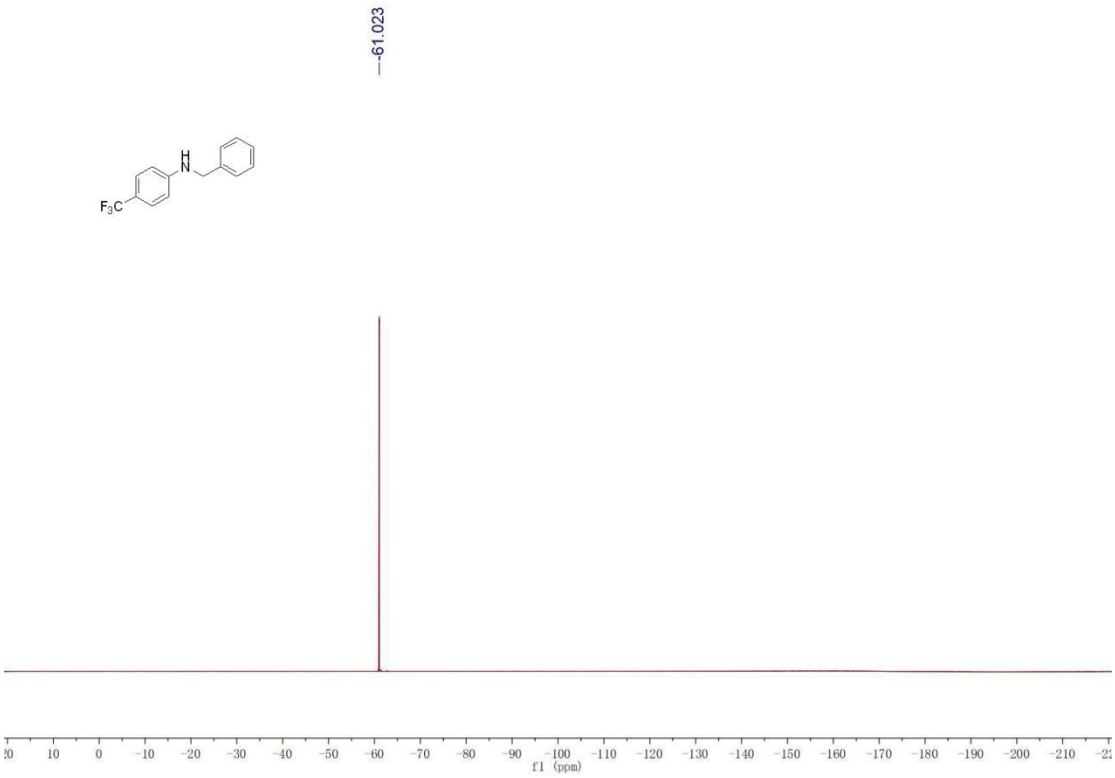
***N*-benzyl-4-(trifluoromethyl)aniline (3oa):**



^{1}H NMR (500 MHz, $CDCl_3$)

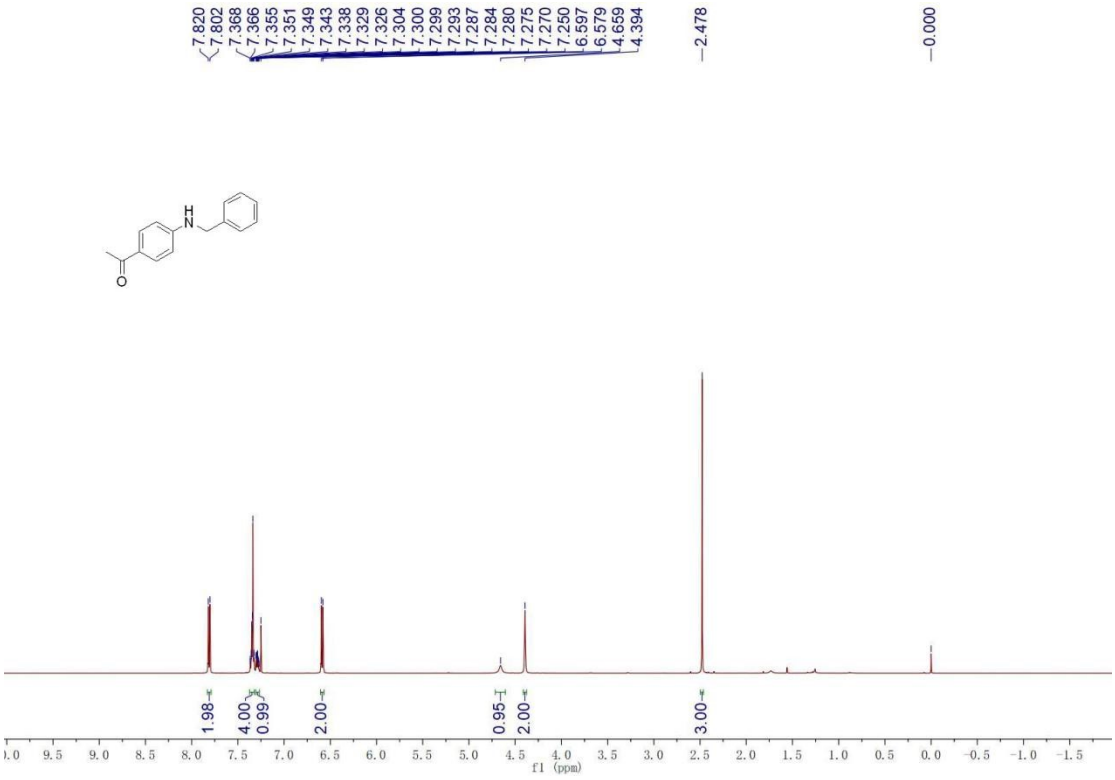


^{13}C NMR (125 MHz, $CDCl_3$)

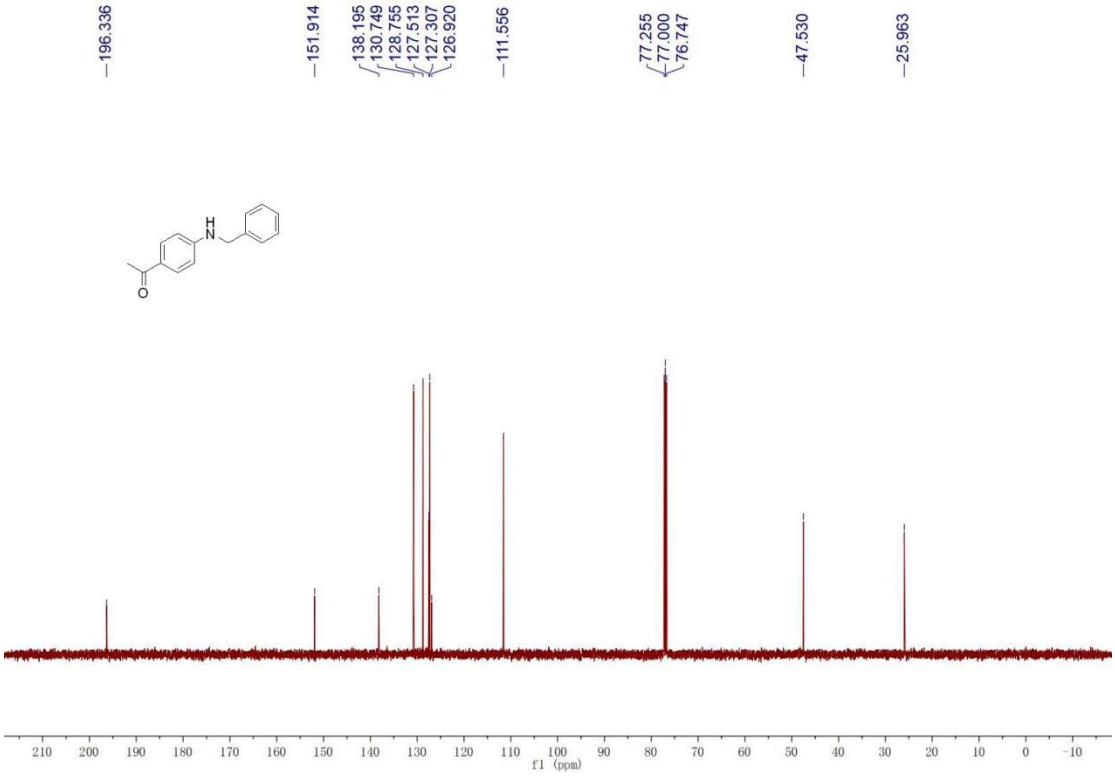


^{19}F NMR (471 MHz, $CDCl_3$)

1-(4-(benzylamino)phenyl)ethan-1-one (3pa):

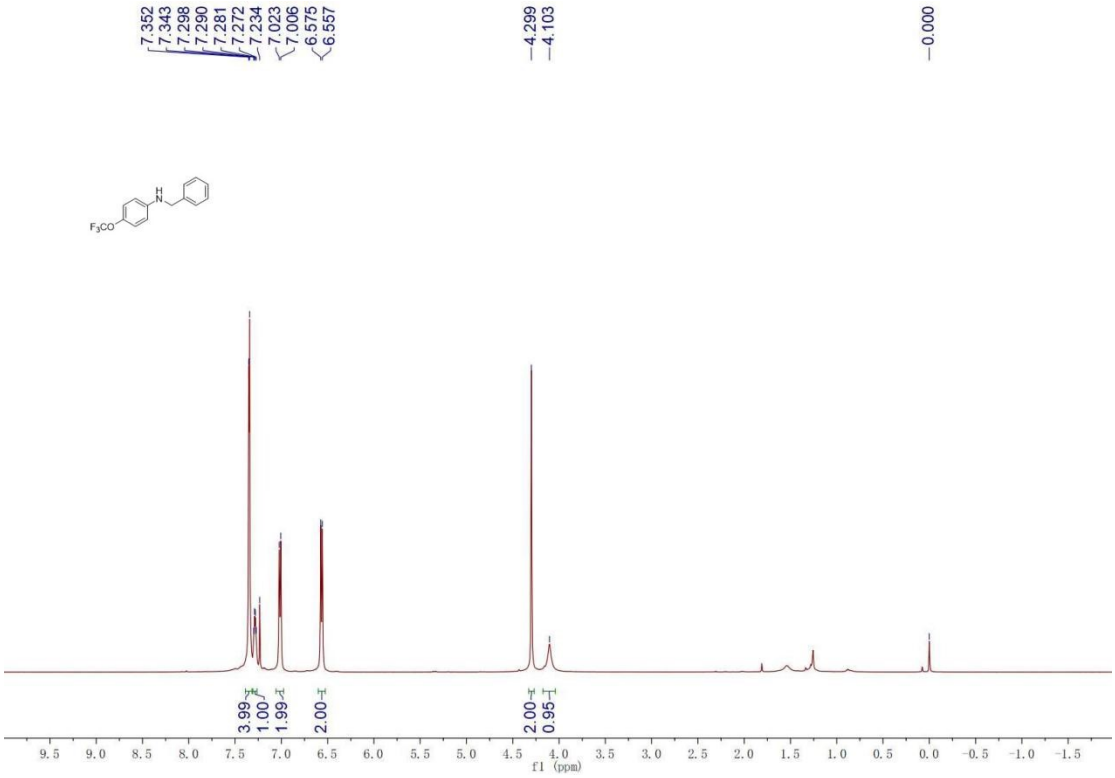


^{1}H NMR (500 MHz, $CDCl_3$)

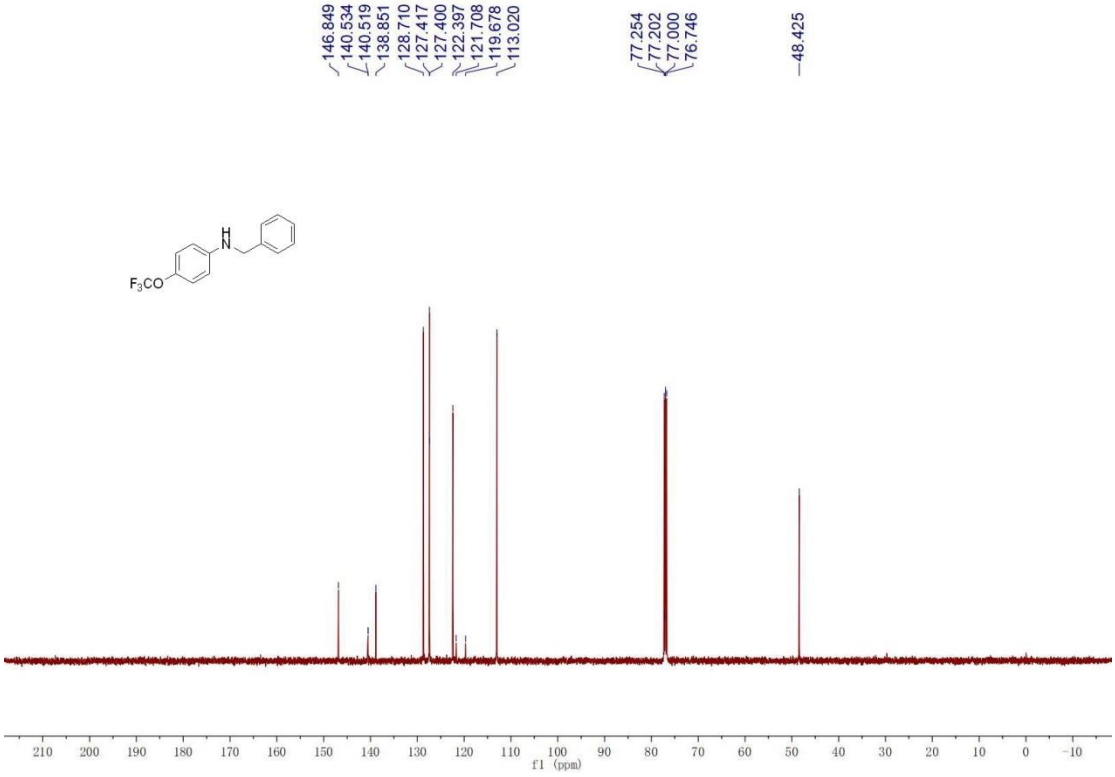


^{13}C NMR (125 MHz, $CDCl_3$)

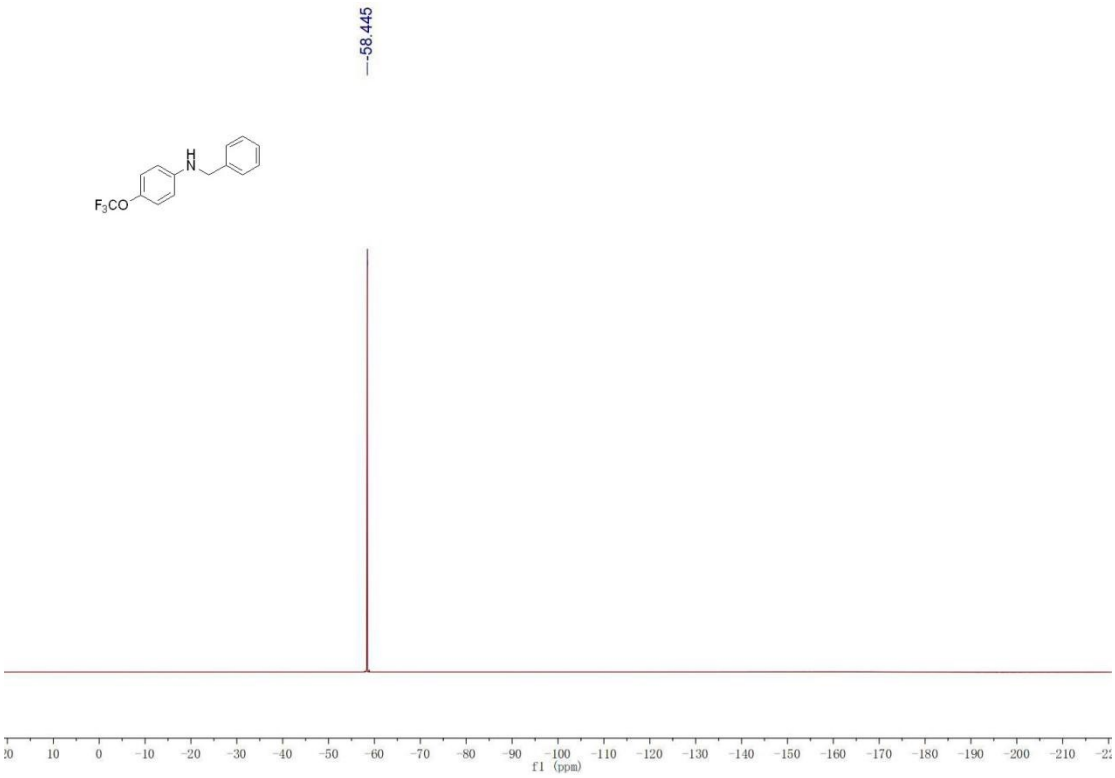
***N*-benzyl-4-(trifluoromethoxy)aniline (3qa):**



^{1}H NMR (500 MHz, $CDCl_3$)

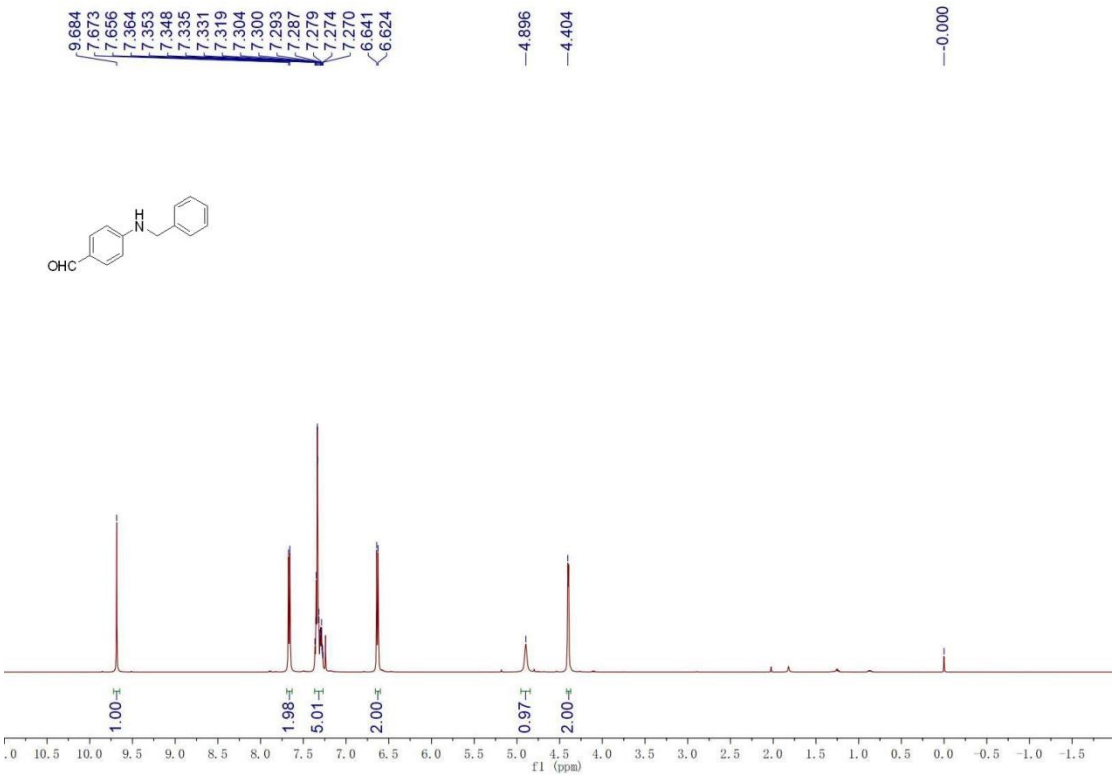


^{13}C NMR (125 MHz, $CDCl_3$)

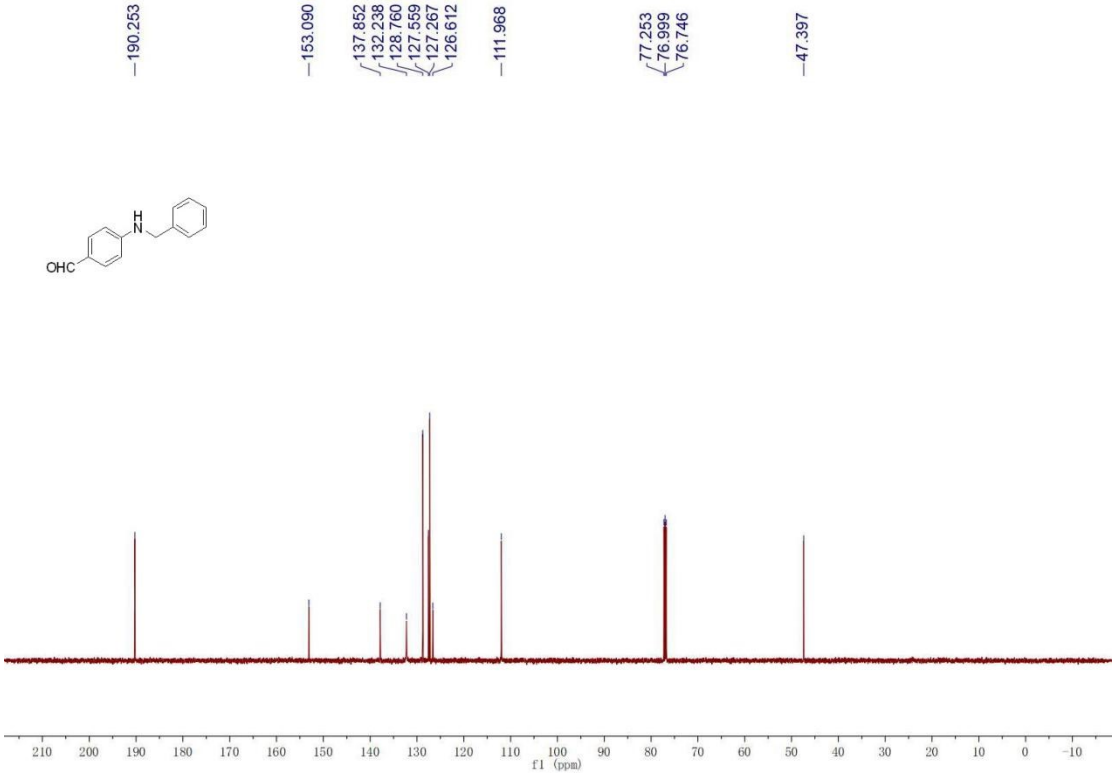


^{19}F NMR (471 MHz, $CDCl_3$)

4-(benzylamino)benzaldehyde (3ra):

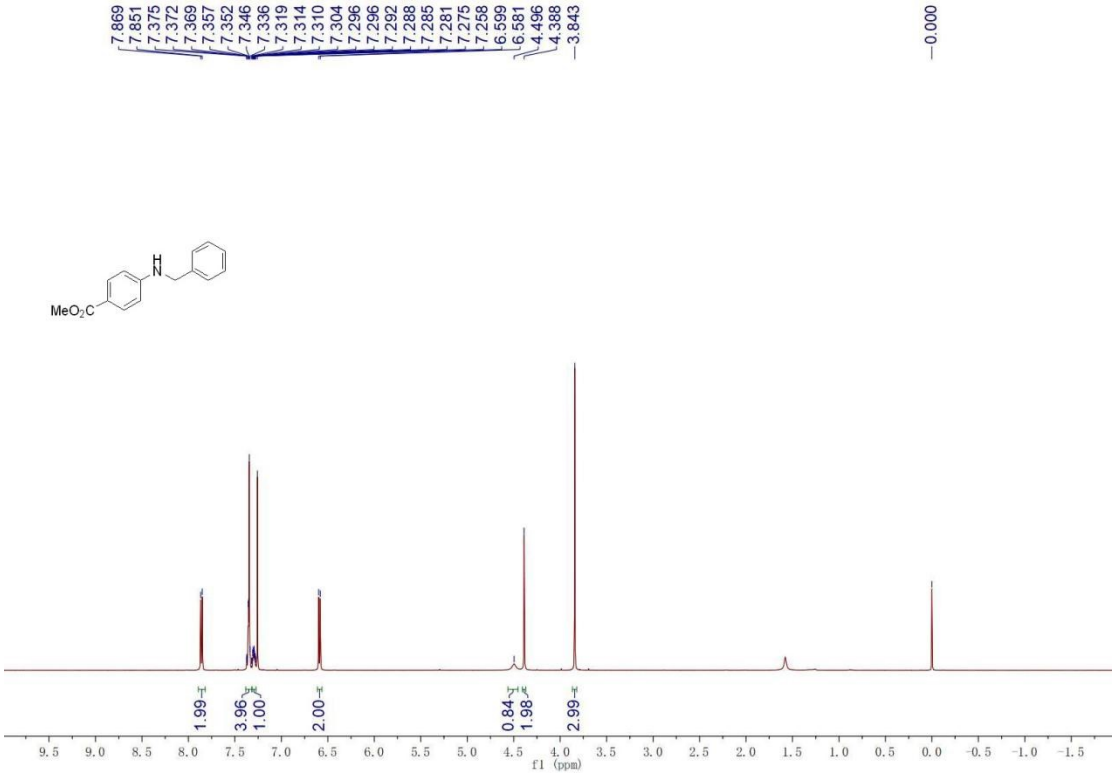


^{1}H NMR (500 MHz, $CDCl_3$)

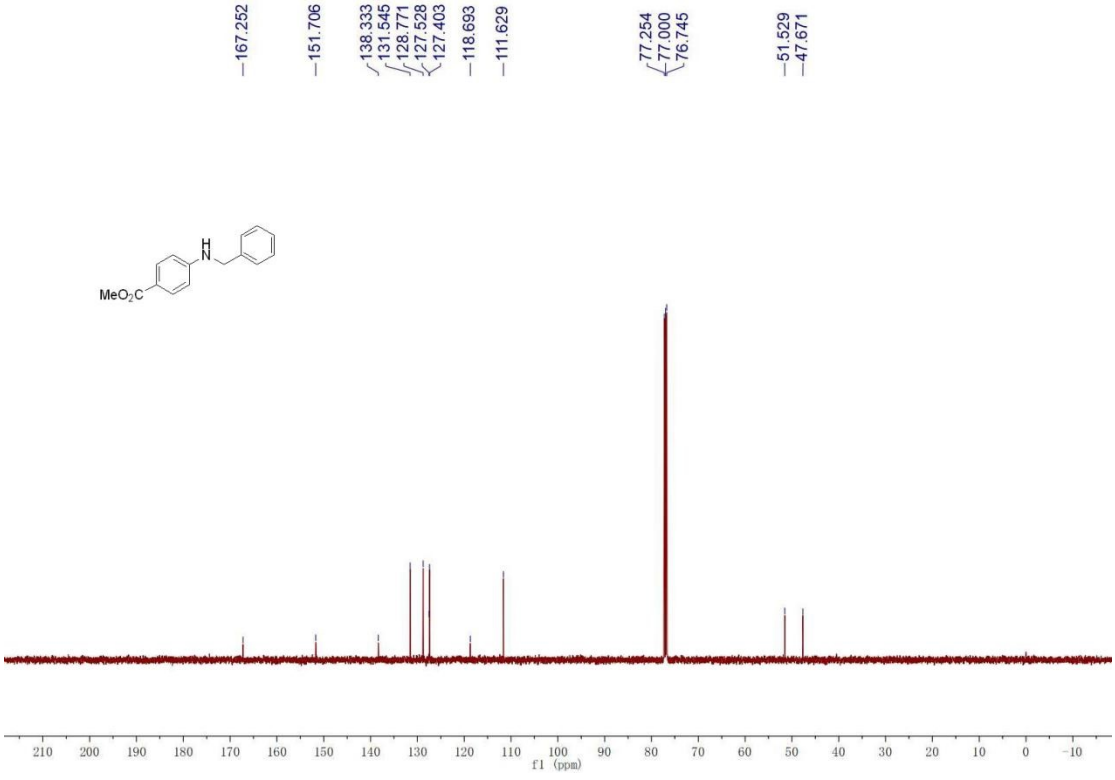


^{13}C NMR (125 MHz, $CDCl_3$)

methyl 4-(benzylamino)benzoate (3sa):

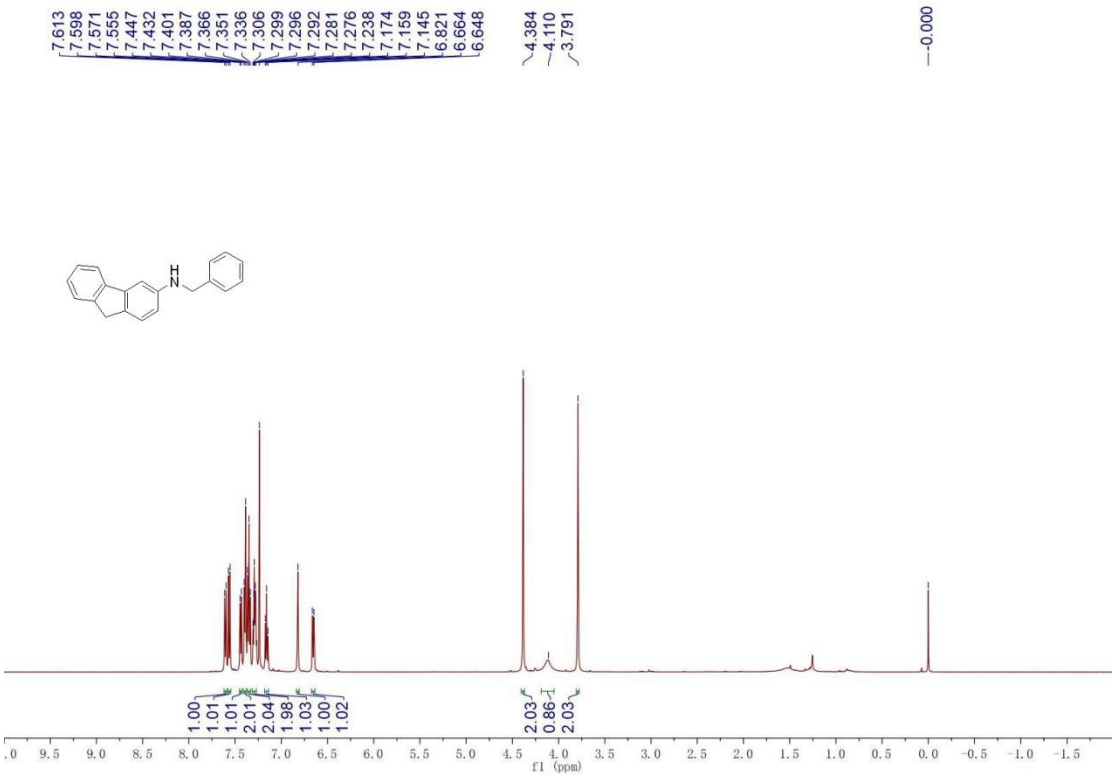


^{1}H NMR (500 MHz, $CDCl_3$)

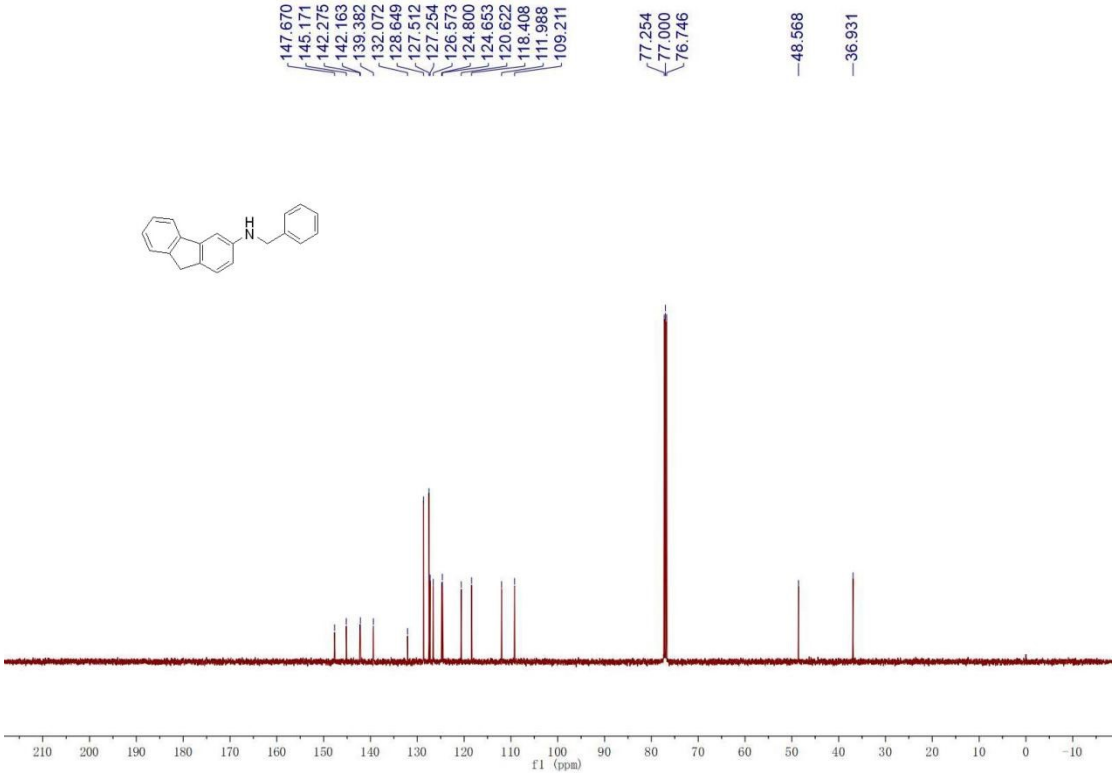


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-benzyl-9*H*-fluoren-3-amine (3ta):**

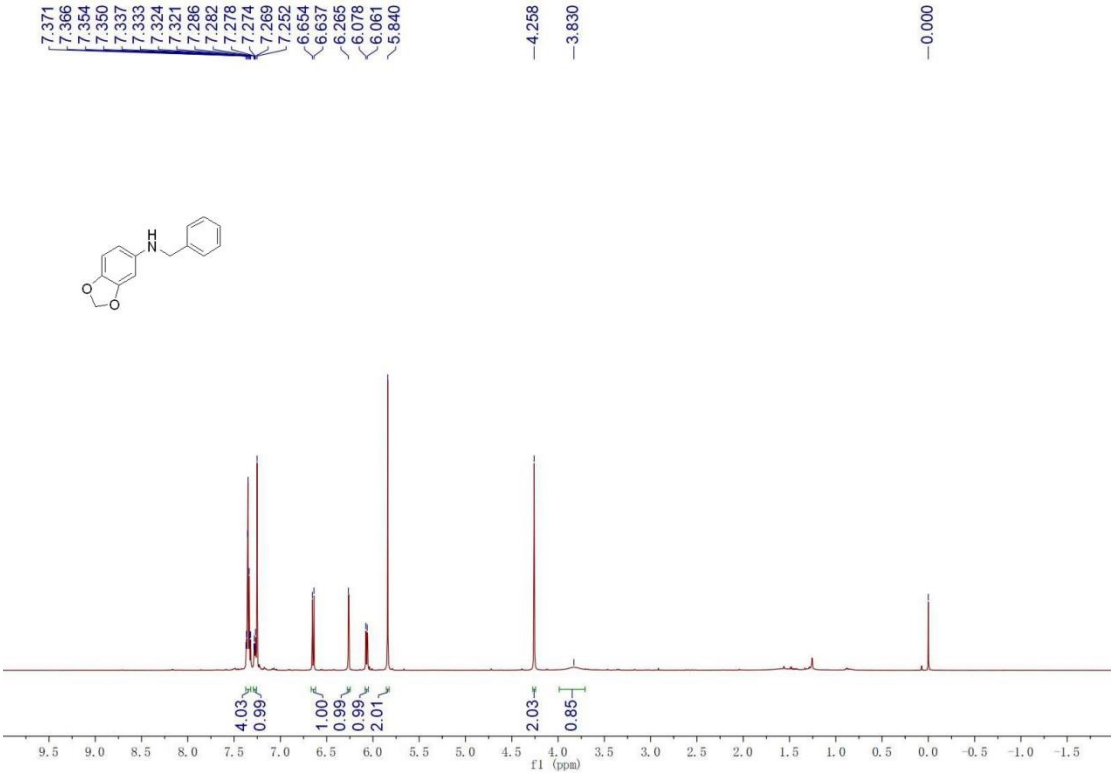


^{1}H NMR (500 MHz, $CDCl_3$)

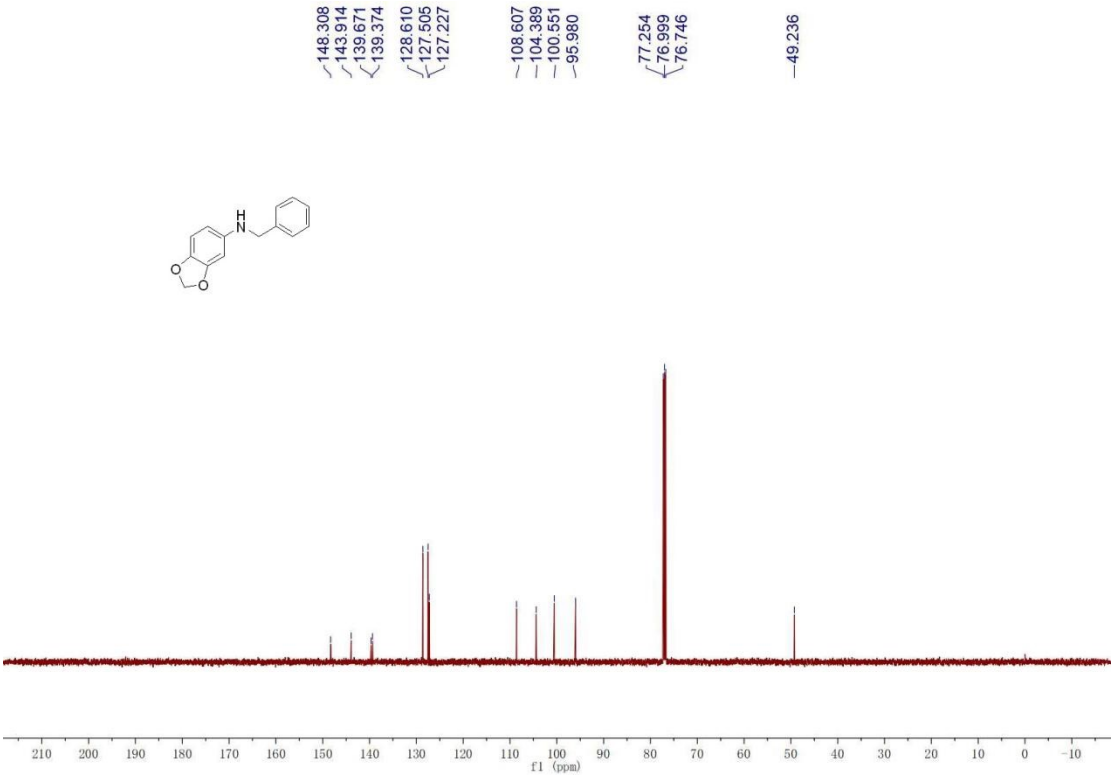


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-benzylbenzo[*d*][1,3]dioxol-5-amine (3ua):**

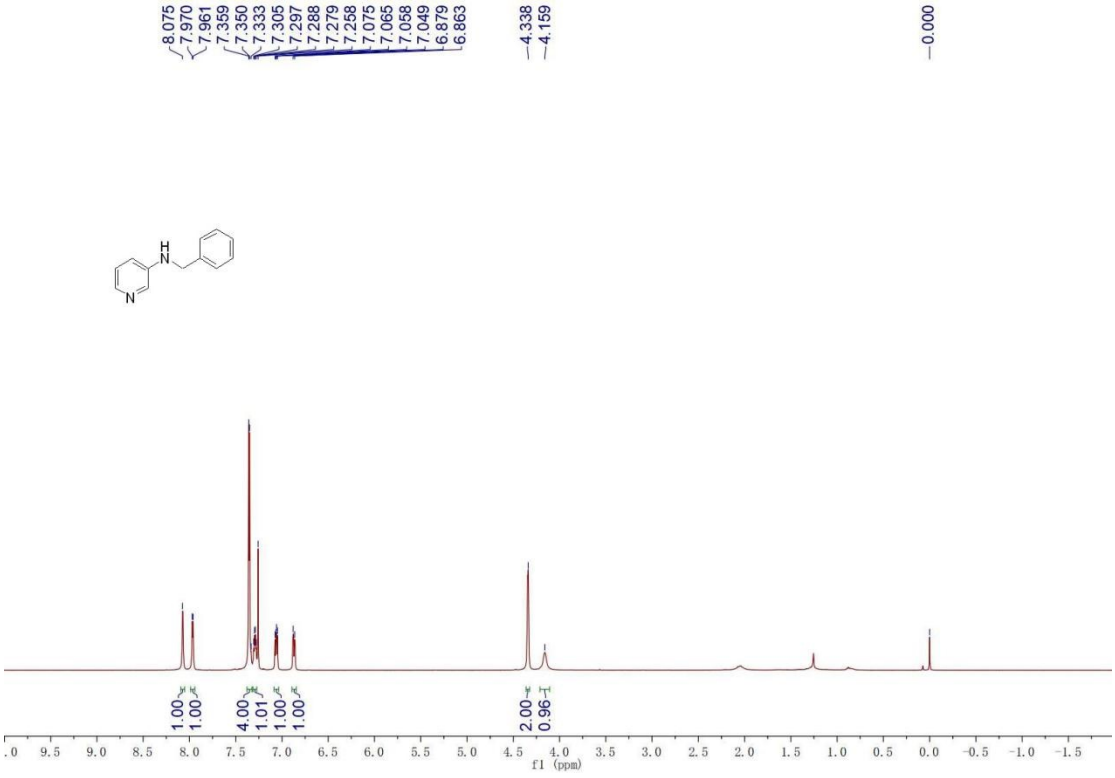


^{1}H NMR (500 MHz, $CDCl_3$)

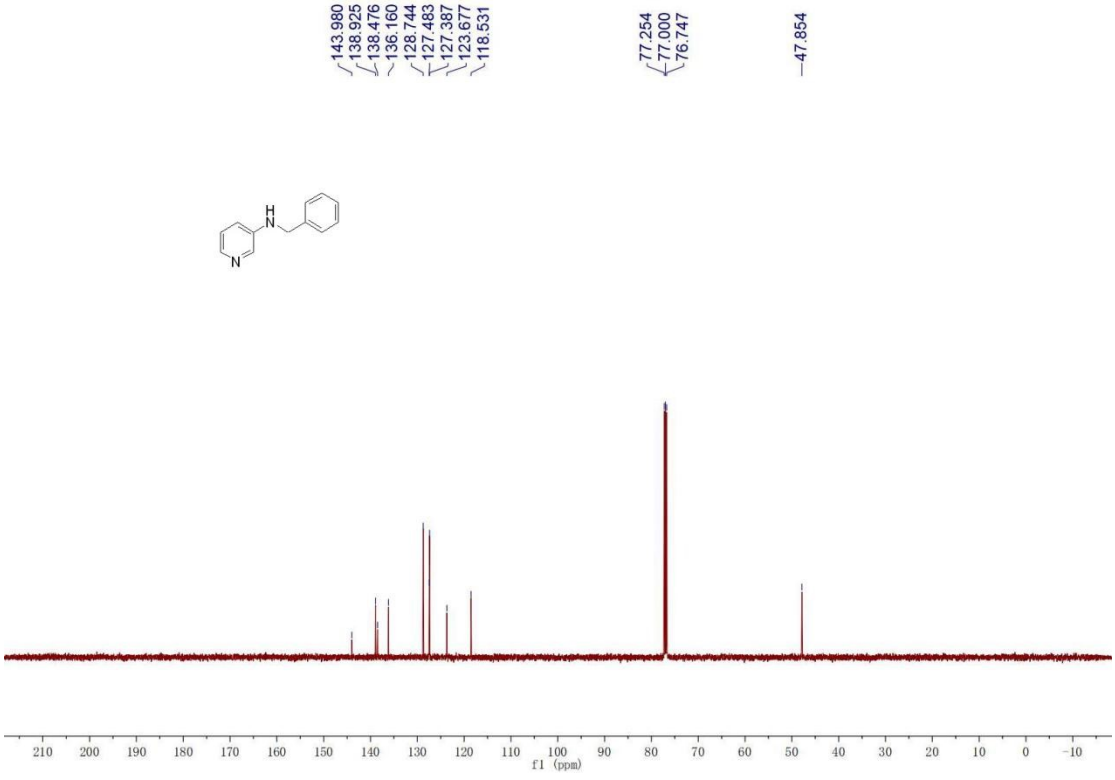


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-benzylpyridin-3-amine (3va):**

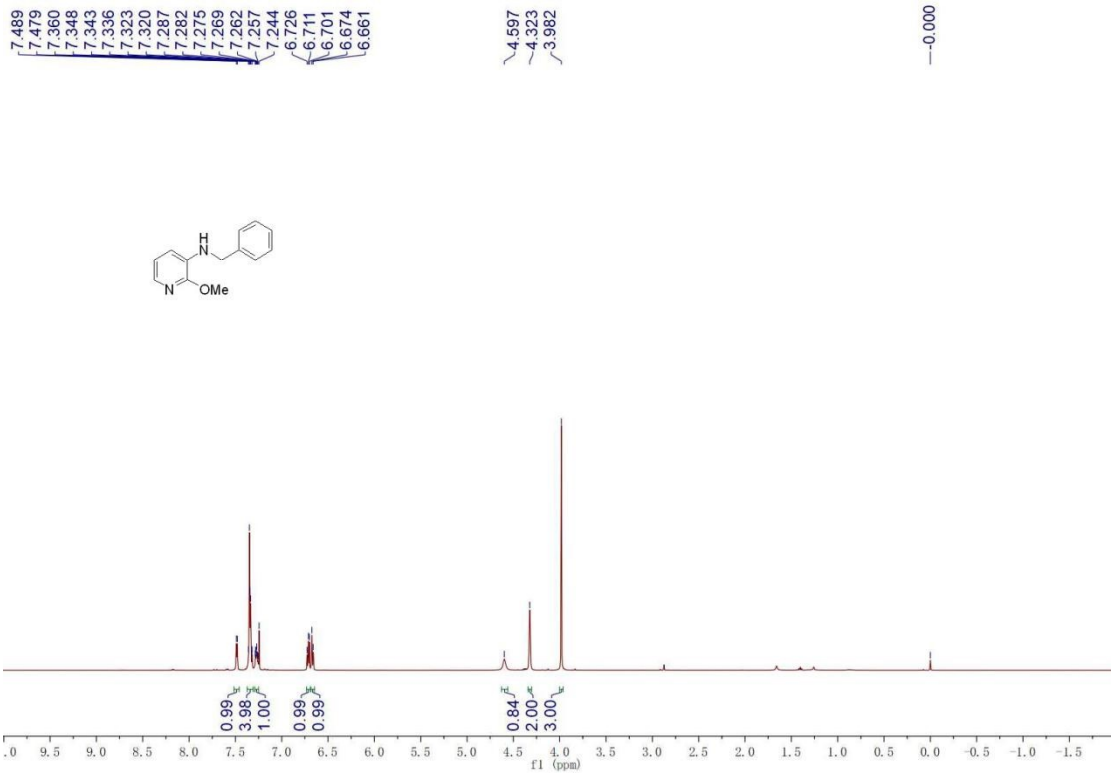


^{1}H NMR (500 MHz, $CDCl_3$)

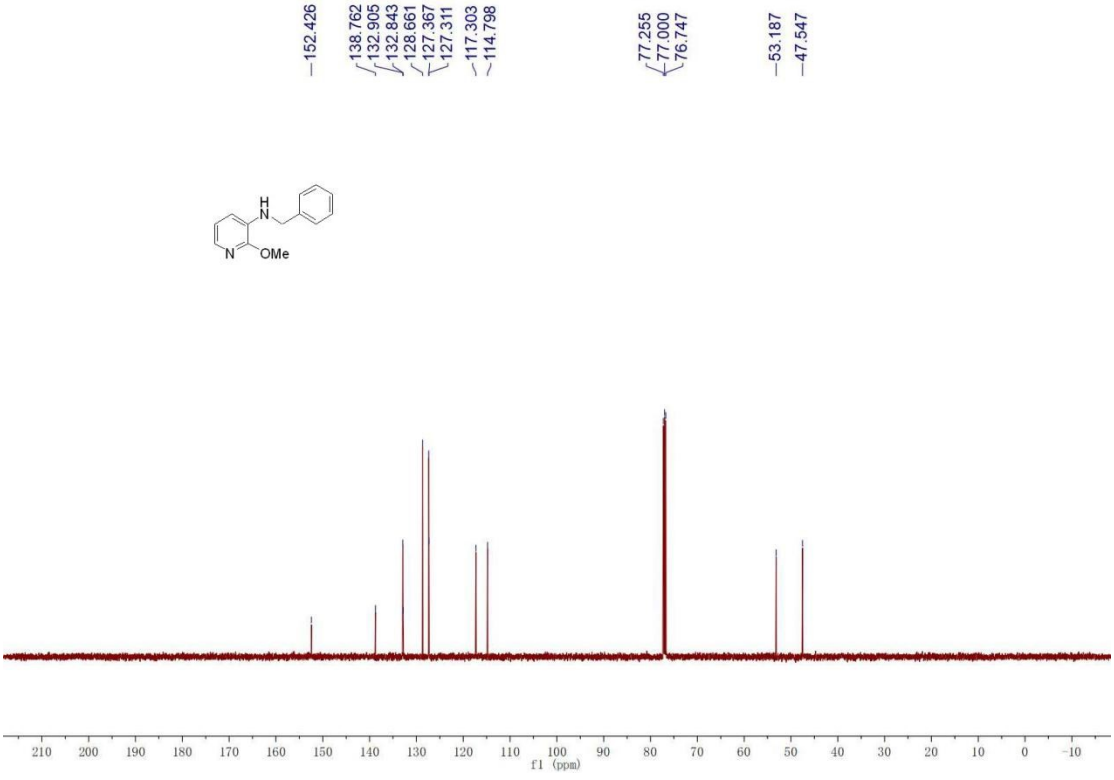


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-benzyl-2-methoxypyridin-3-amine (3wa):**

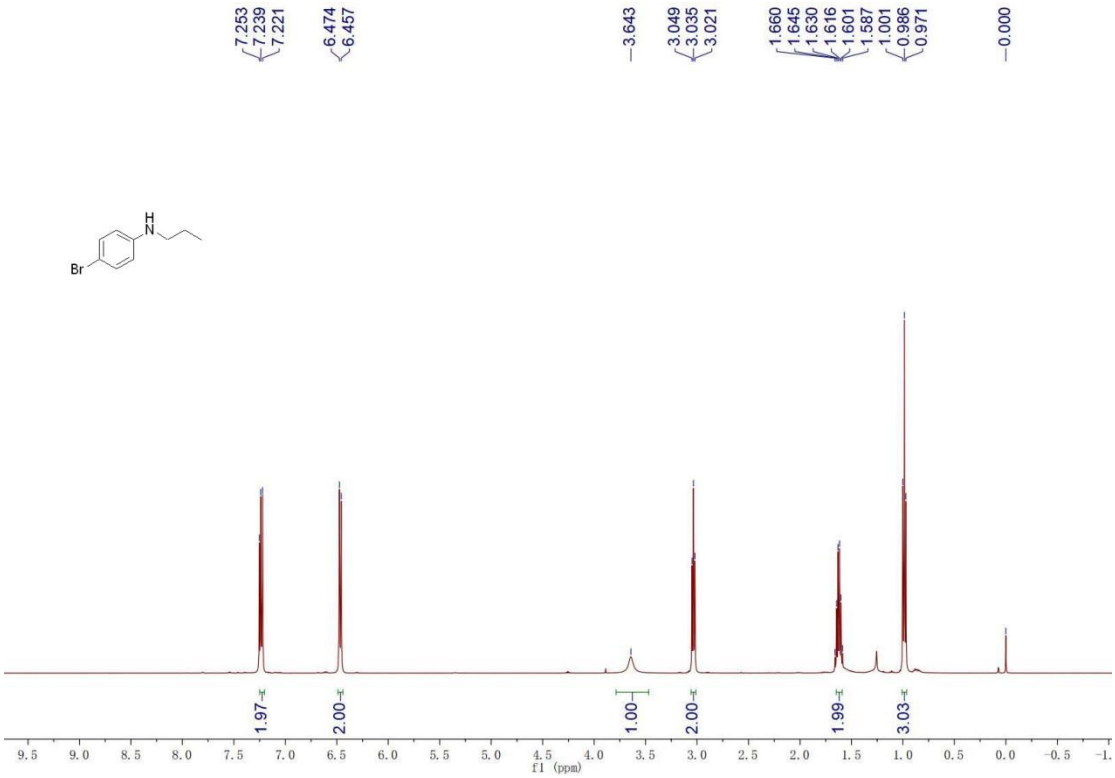


^{1}H NMR (500 MHz, $CDCl_3$)

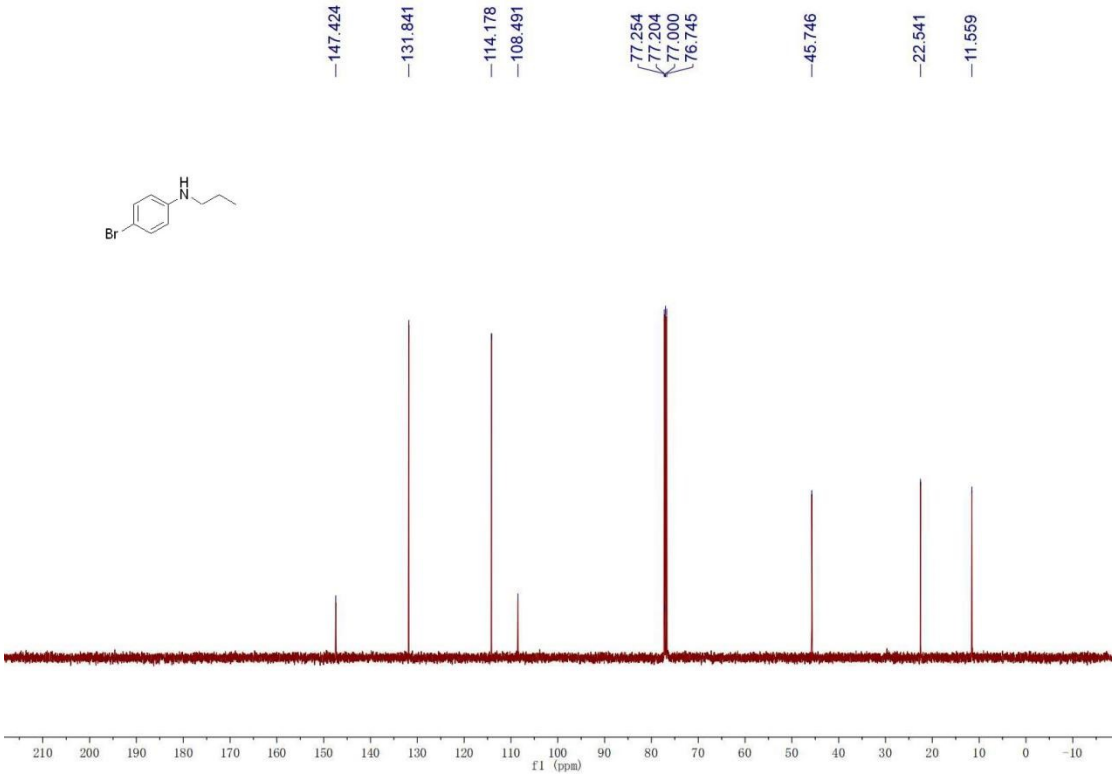


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-propylaniline (3gb):

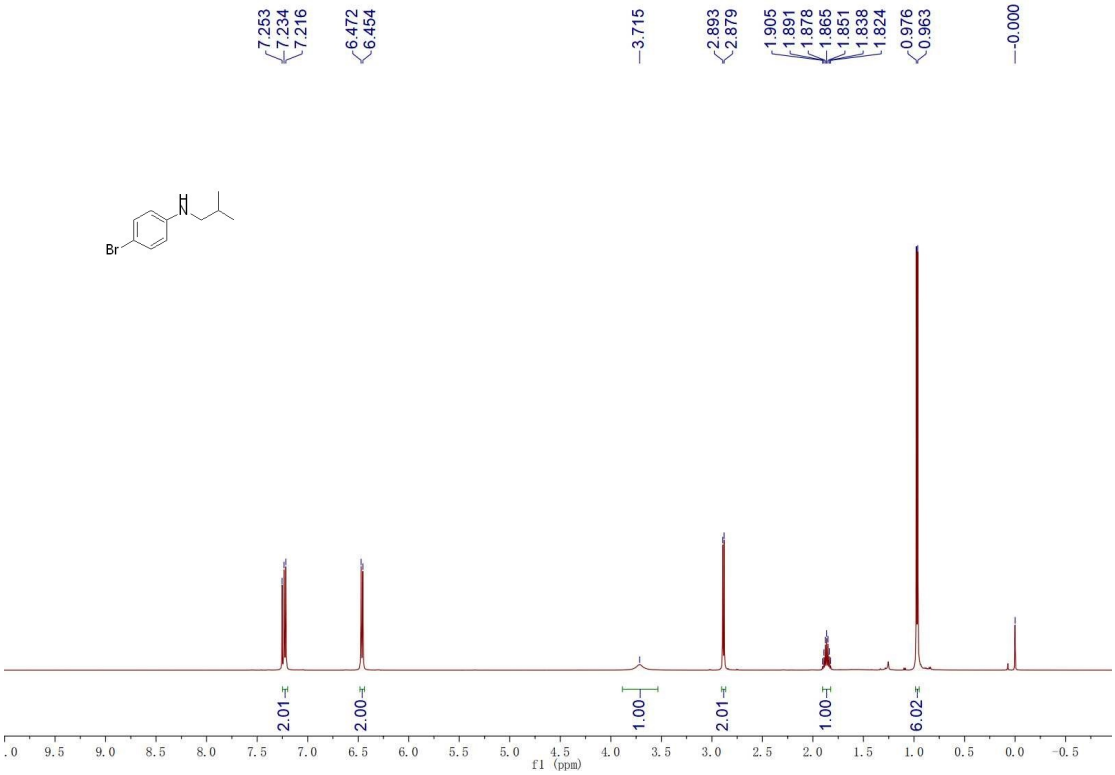


^{1}H NMR (500 MHz, $CDCl_3$)

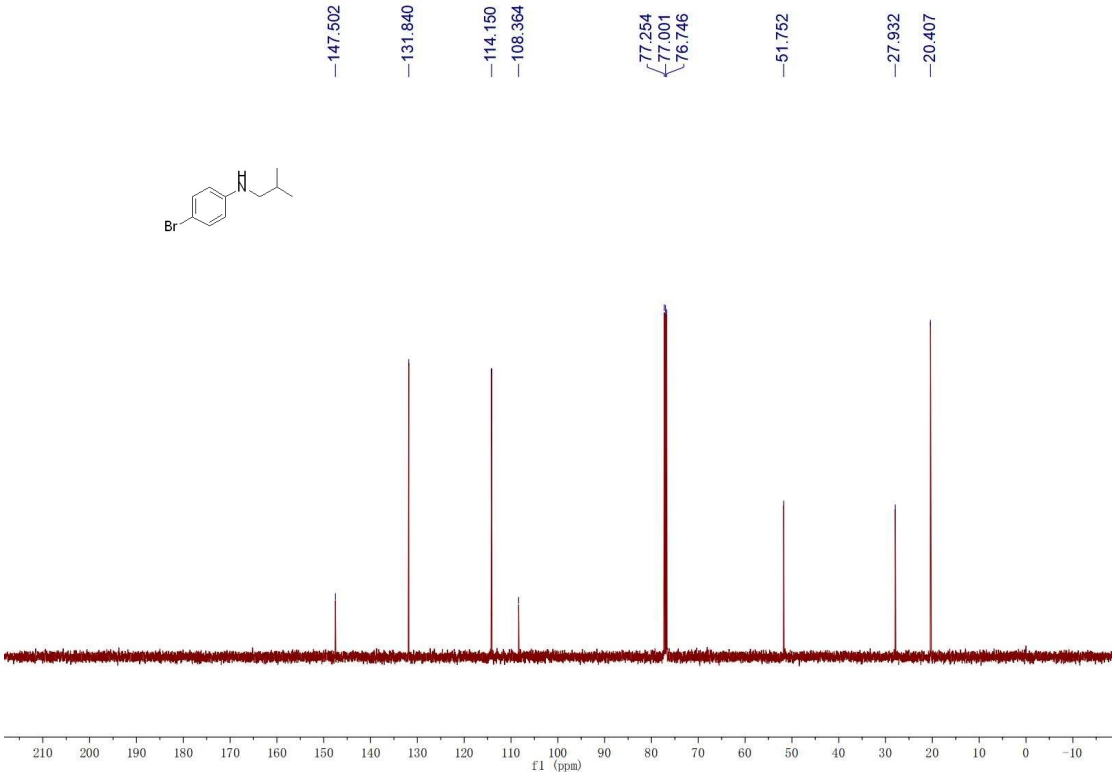


^{13}C NMR (125 MHz, $CDCl_3$)

5-bromo-*N*-isopentylaniline (3gc):

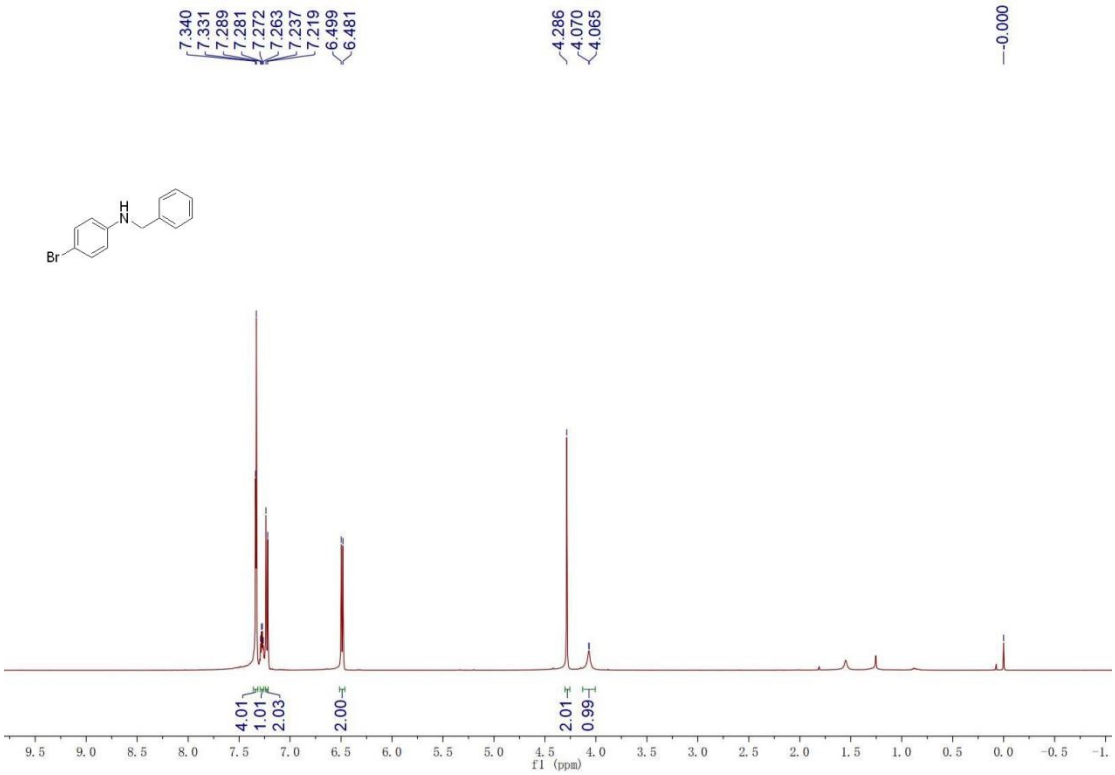


^{1}H NMR (500 MHz, $CDCl_3$)

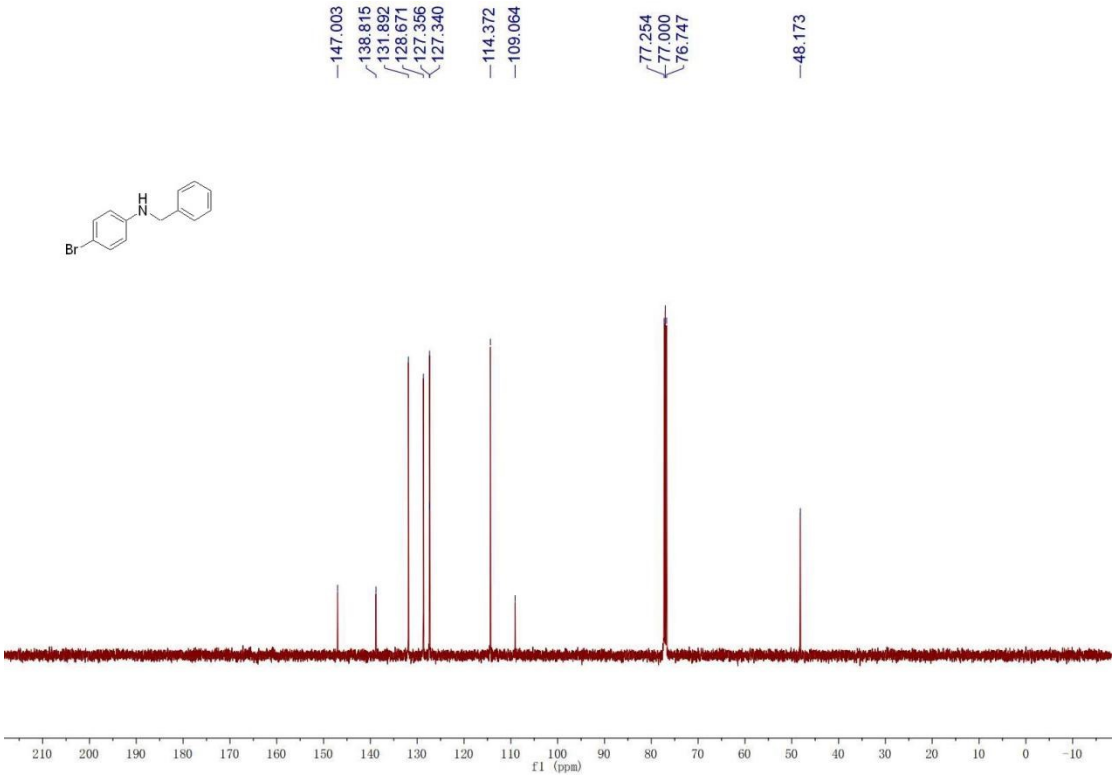


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-benzyl-4-bromoaniline (3gd):**

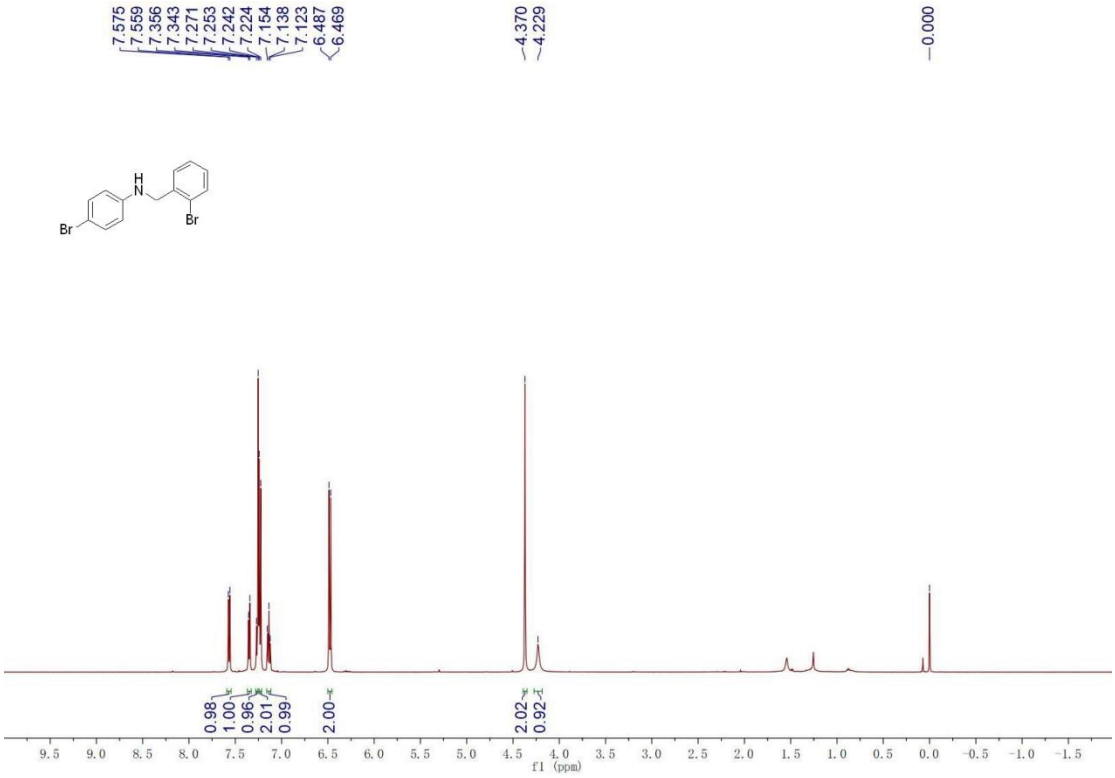


^{1}H NMR (500 MHz, $CDCl_3$)

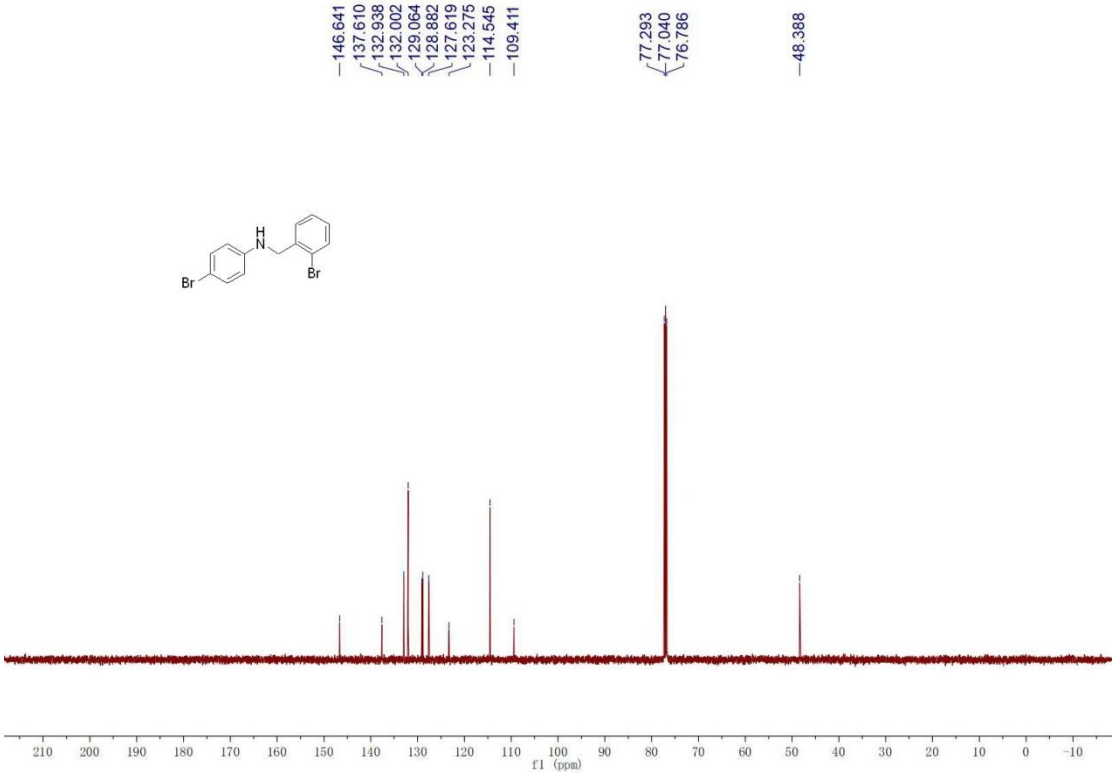


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-(2-bromobenzyl)aniline (3ge):

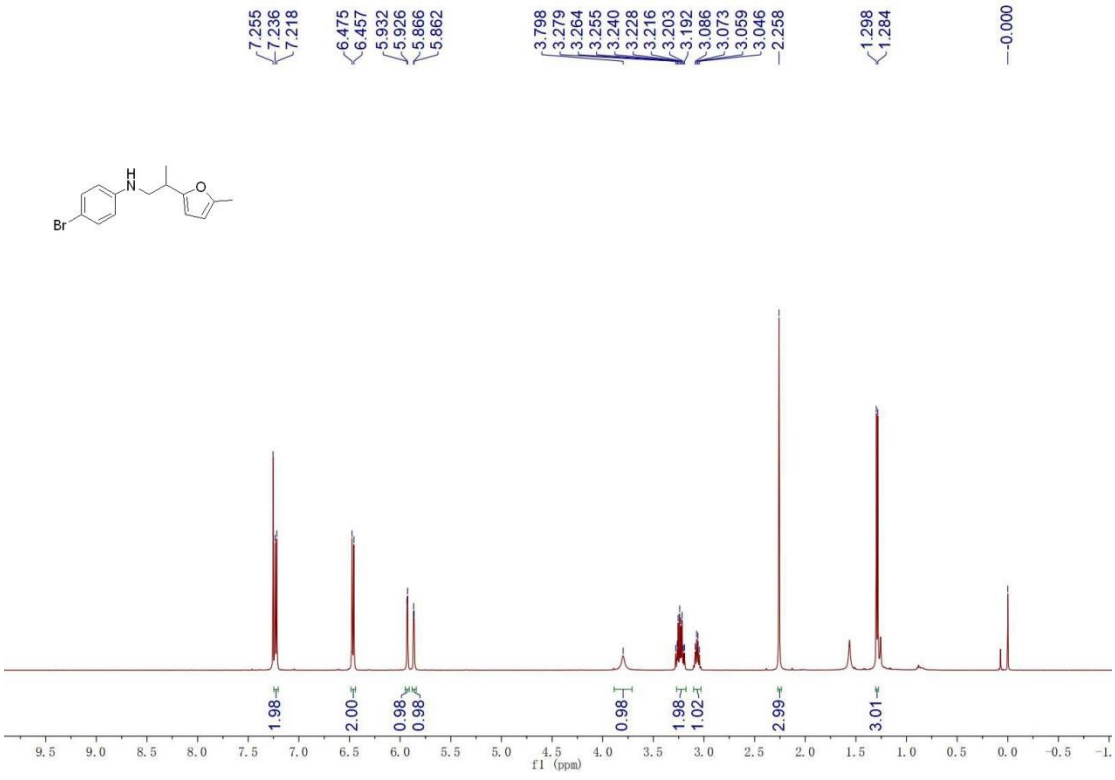


^{1}H NMR (500 MHz, $CDCl_3$)

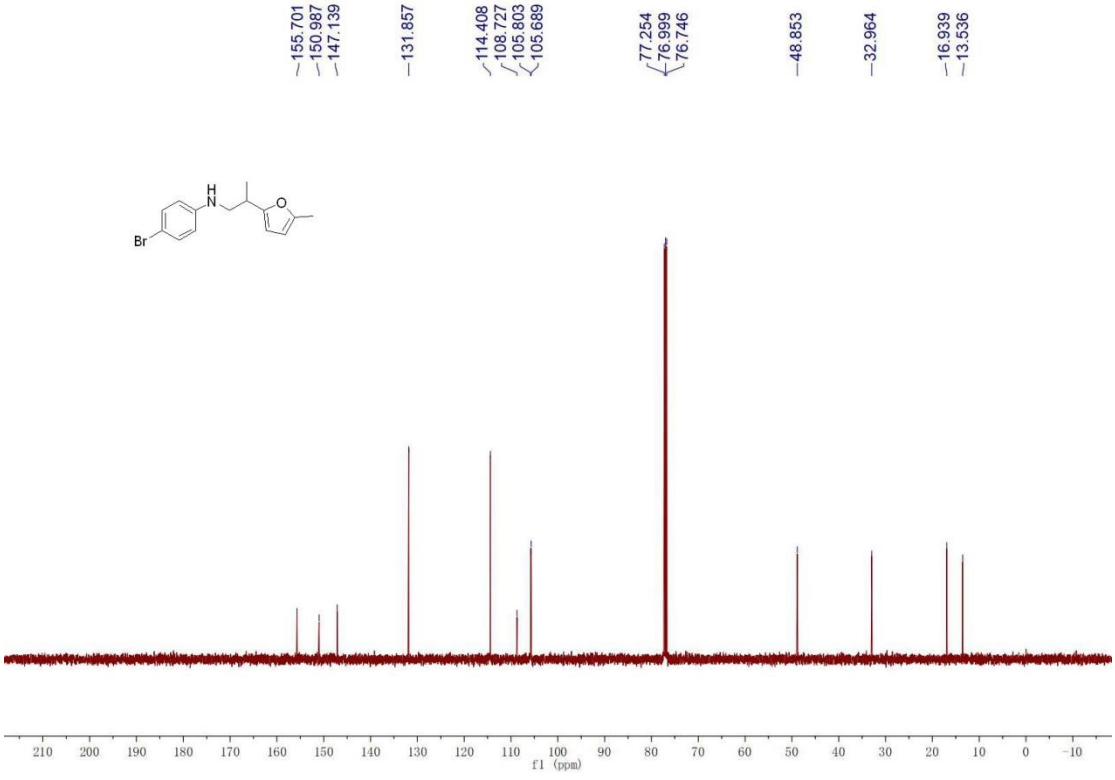


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-(2-(5-methylfuran-2-yl)propyl)aniline (3gf):

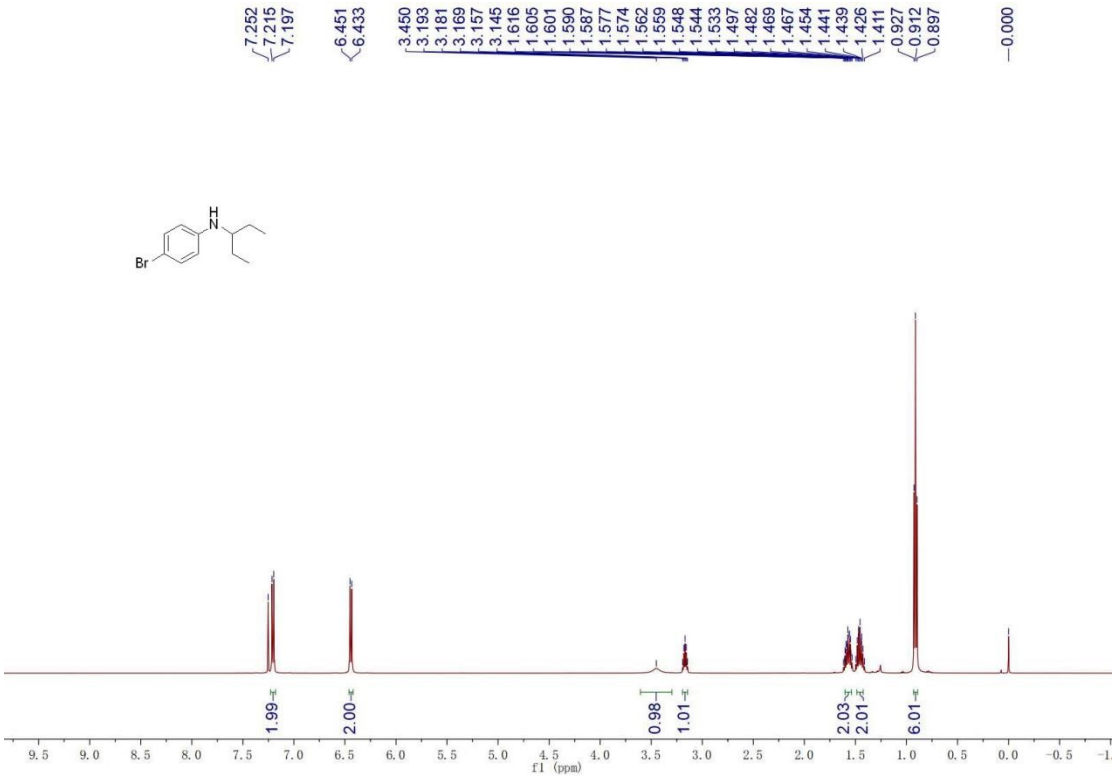


^{1}H NMR (500 MHz, $CDCl_3$)

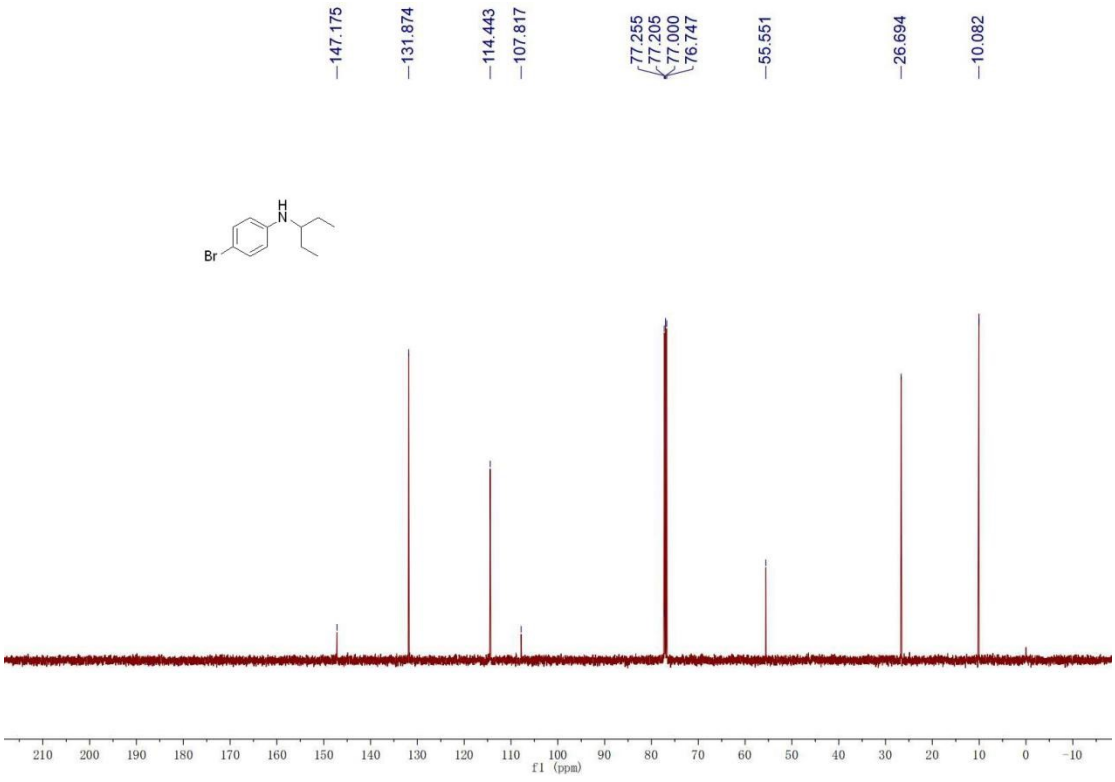


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-(pentan-3-yl)aniline (3gg):

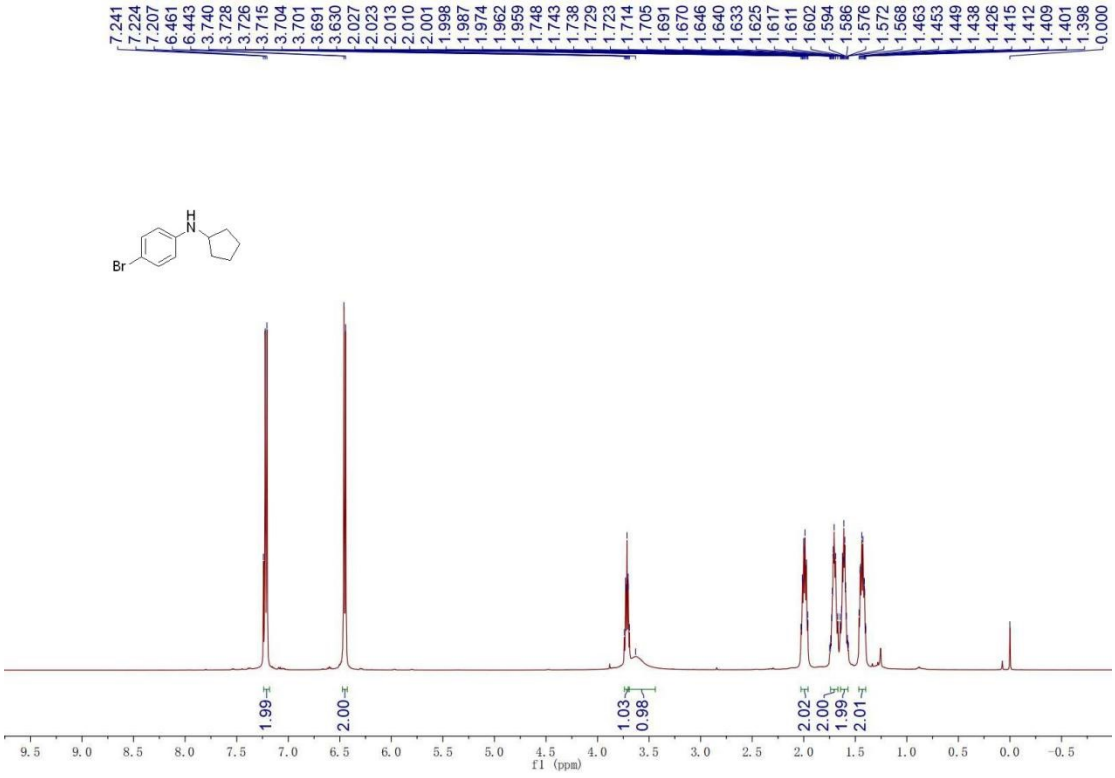


^{1}H NMR (500 MHz, $CDCl_3$)

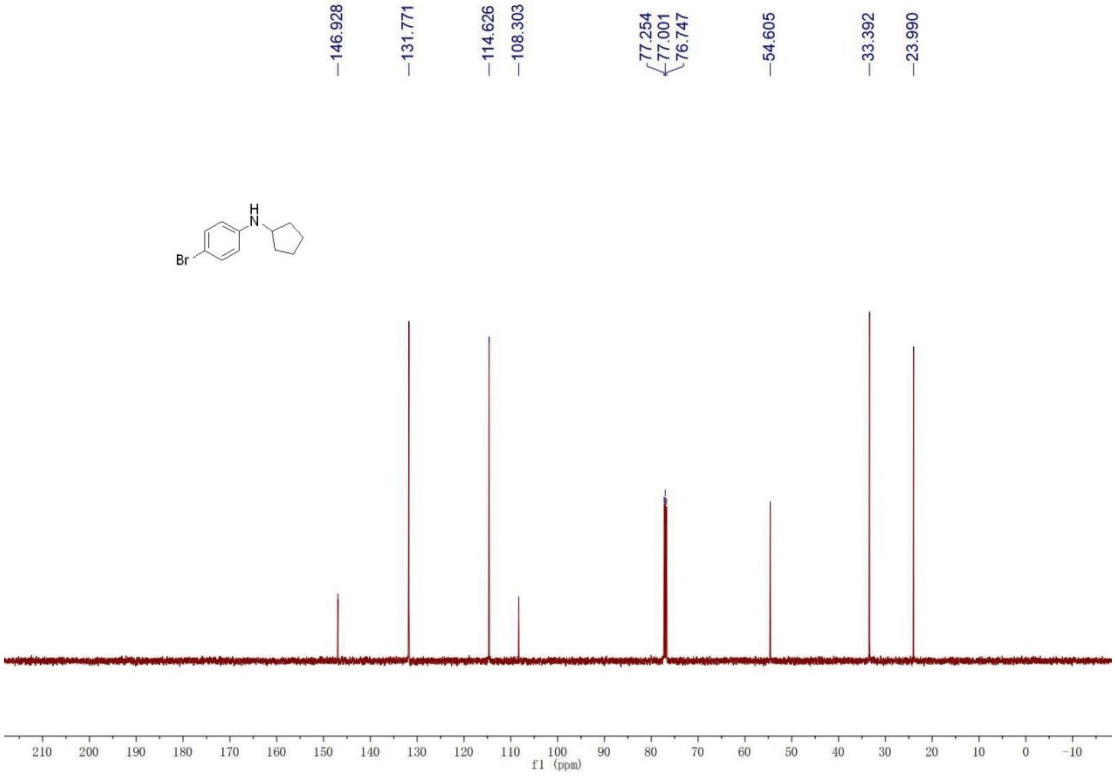


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-cyclopentylaniline (3gh):

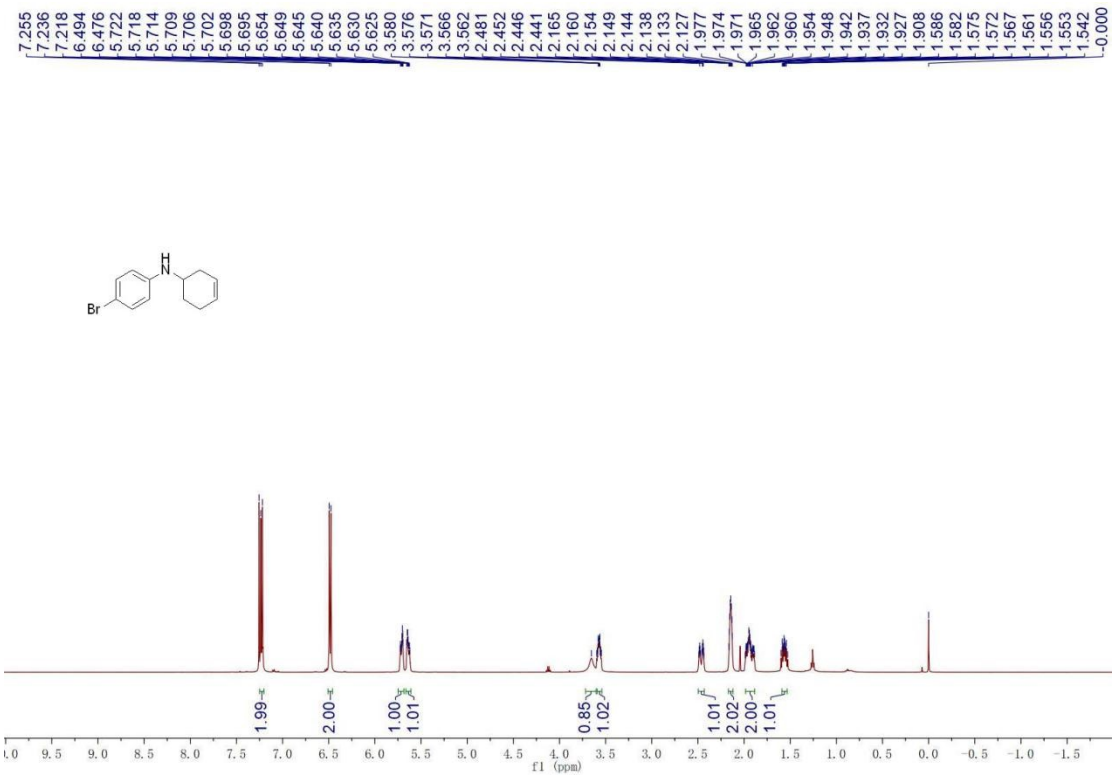


^{1}H NMR (500 MHz, $CDCl_3$)

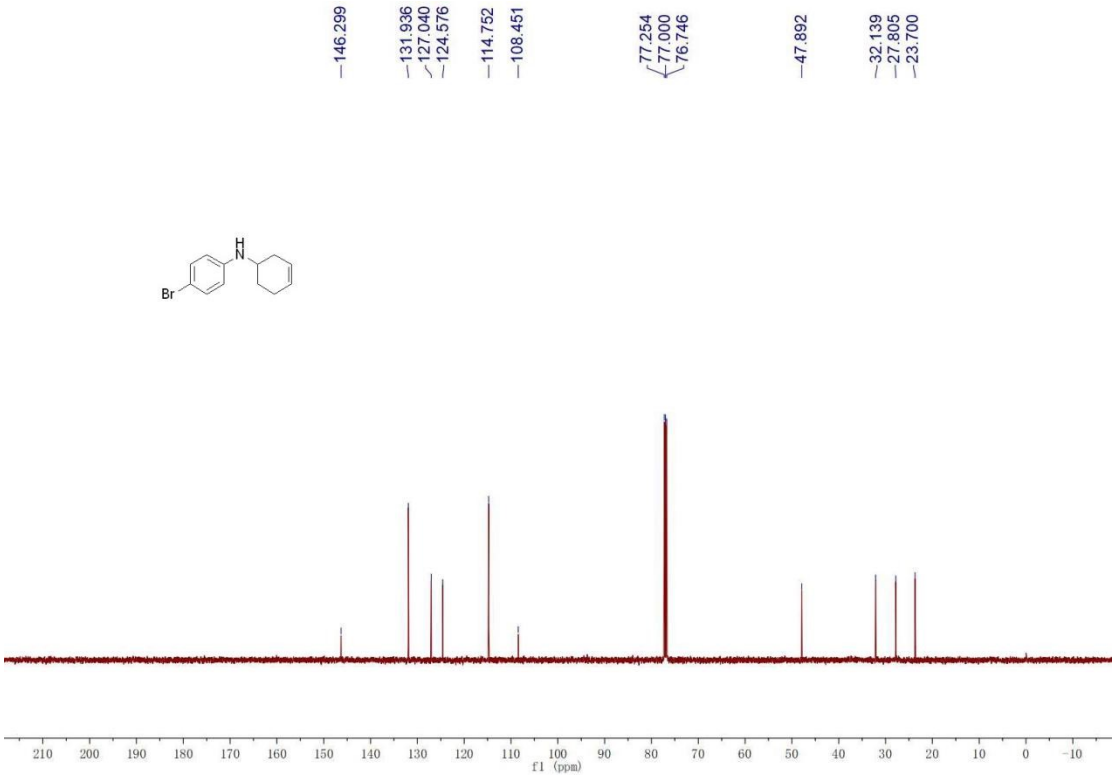


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-(cyclohex-3-en-1-yl)aniline (3gi):

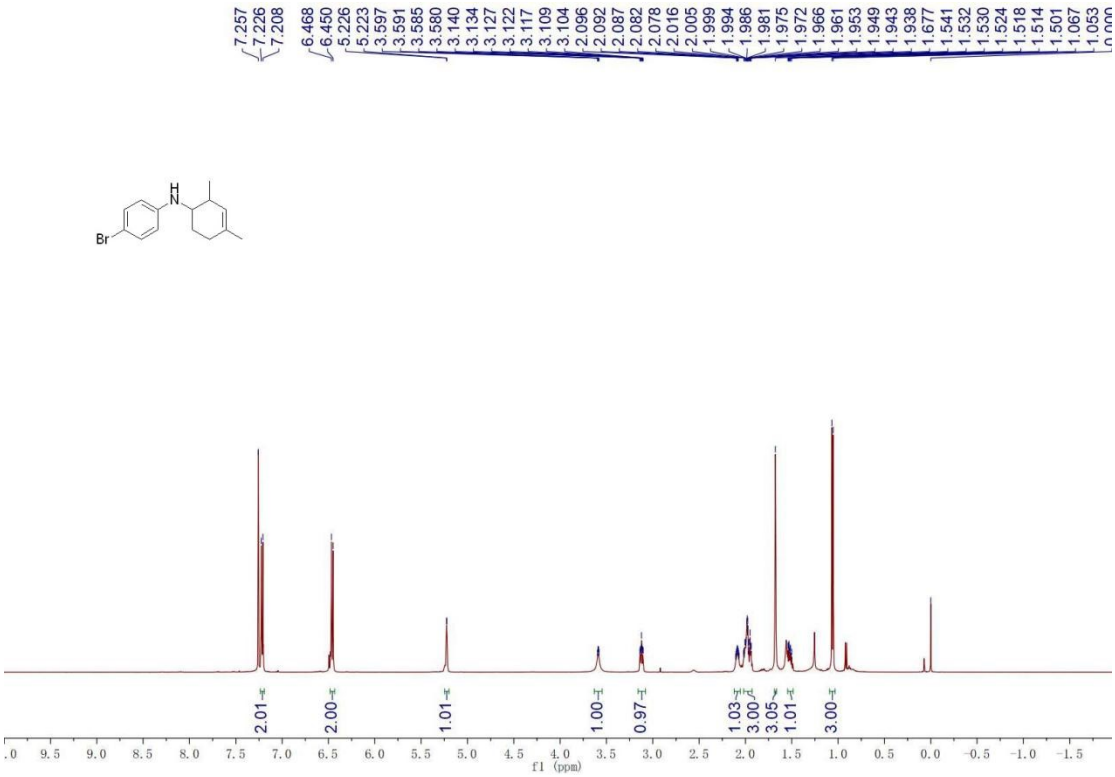


^{1}H NMR (500 MHz, $CDCl_3$)

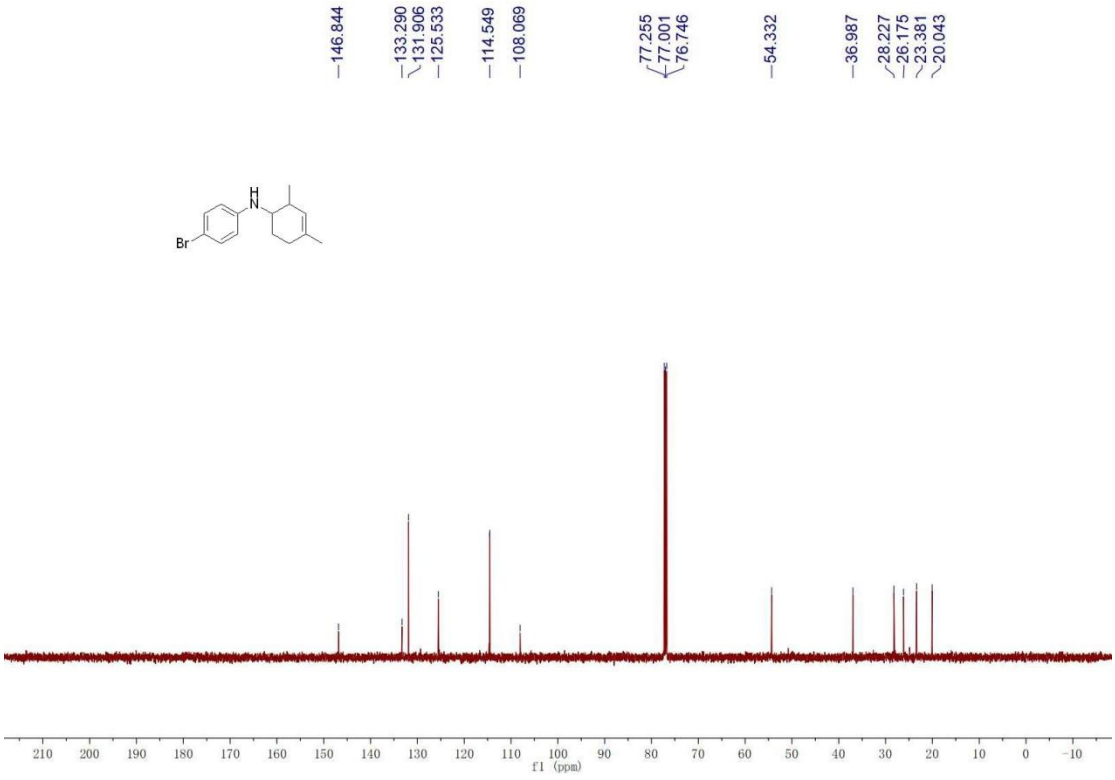


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-(2,4-dimethylcyclohex-3-en-1-yl)aniline (3gj):

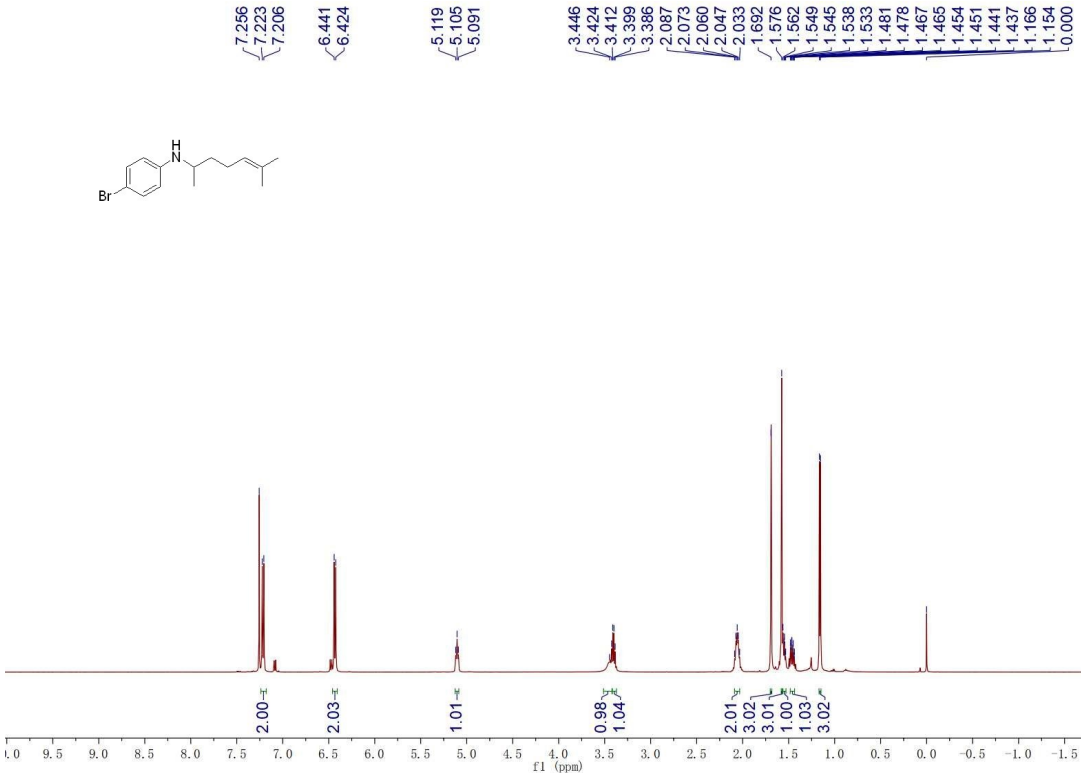


^{1}H NMR (500 MHz, $CDCl_3$)

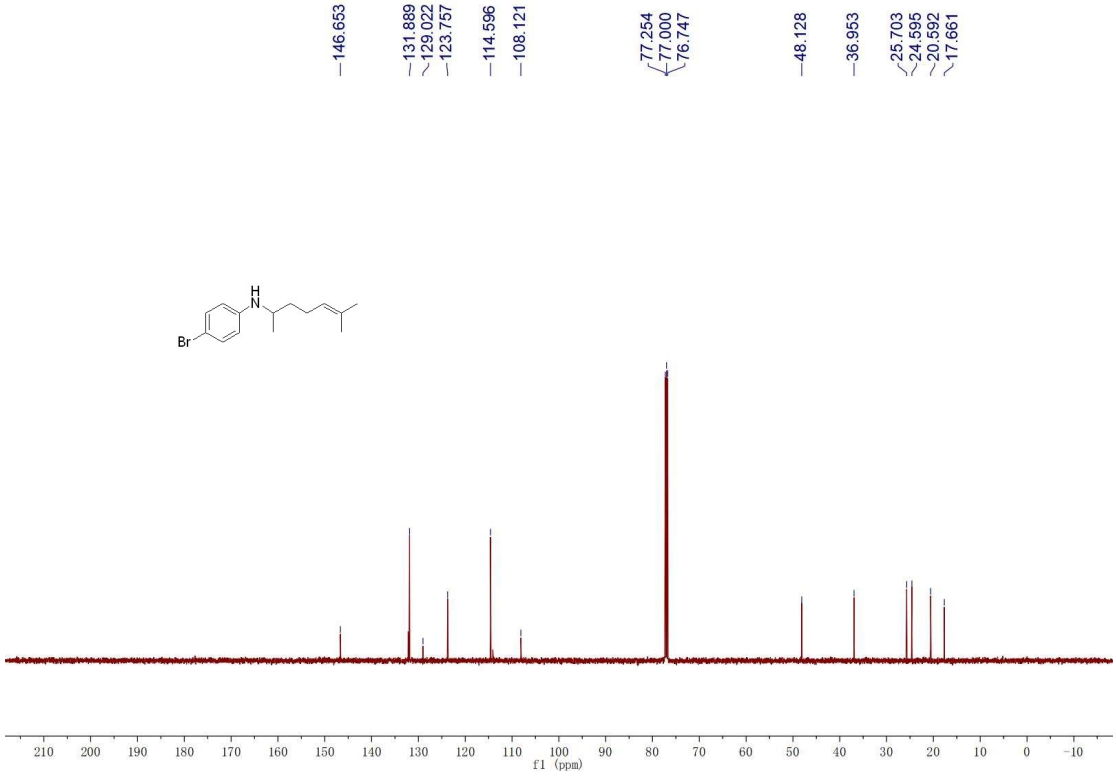


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-(6-methylhept-5-en-2-yl)aniline (3gk):

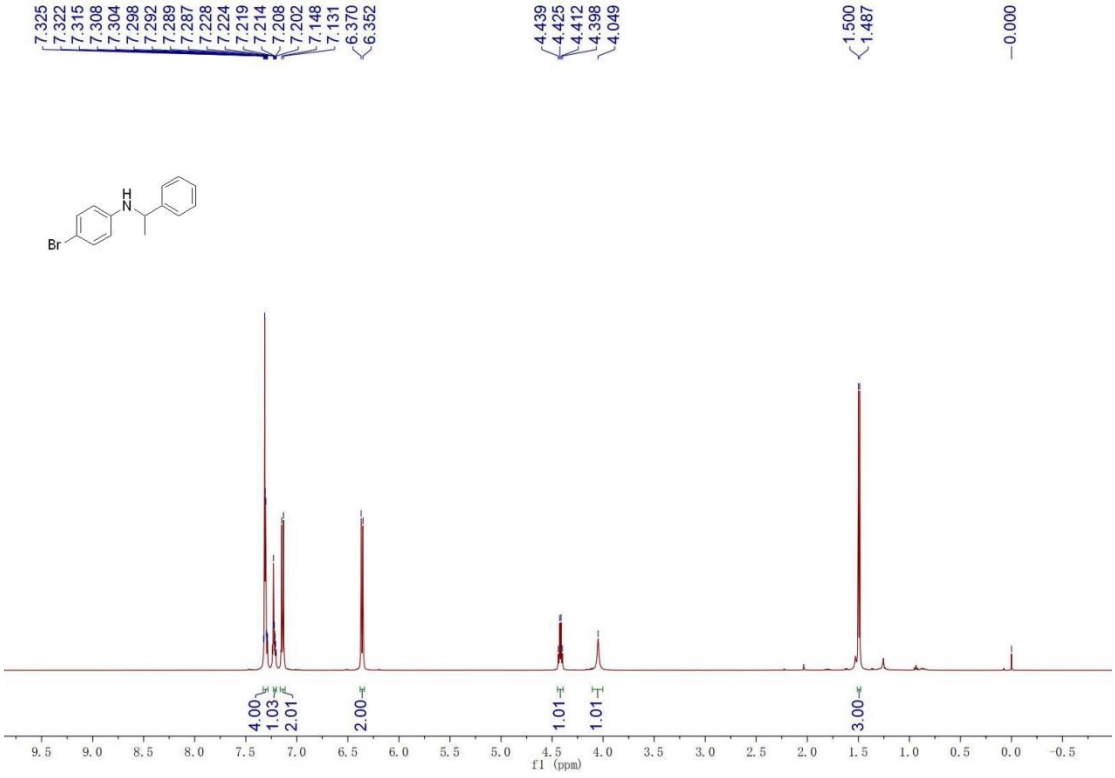


^{1}H NMR (500 MHz, $CDCl_3$)

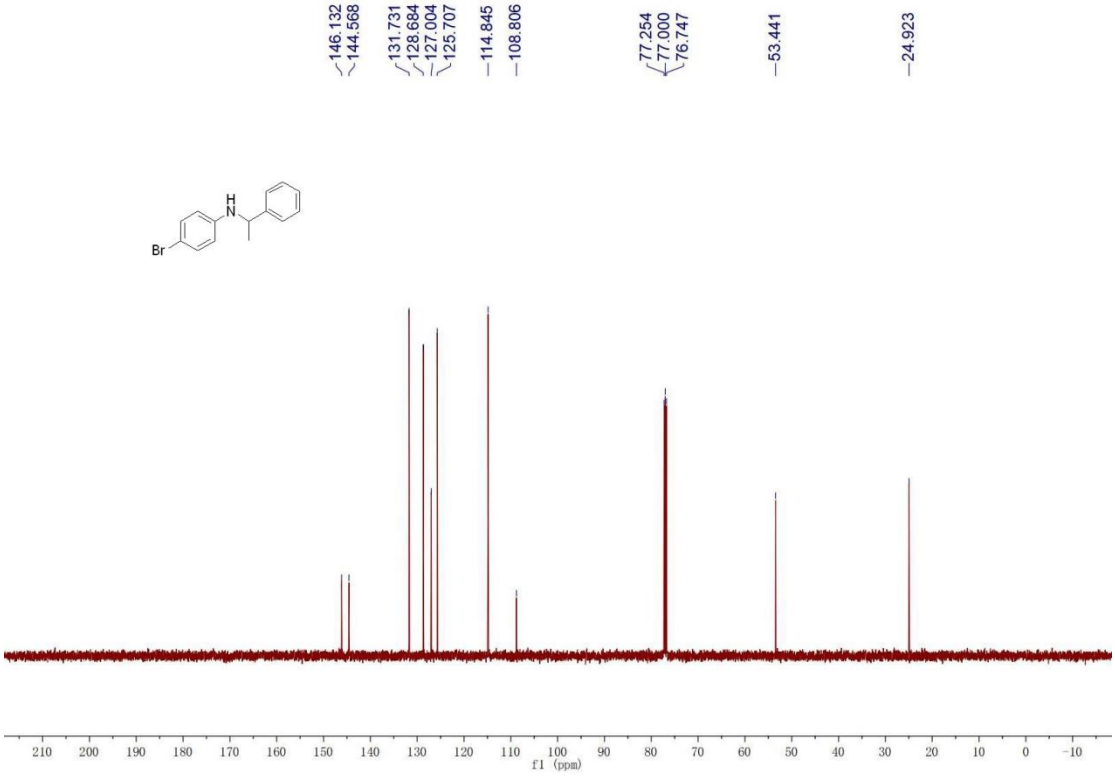


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-(1-phenylethyl)aniline (3gl):

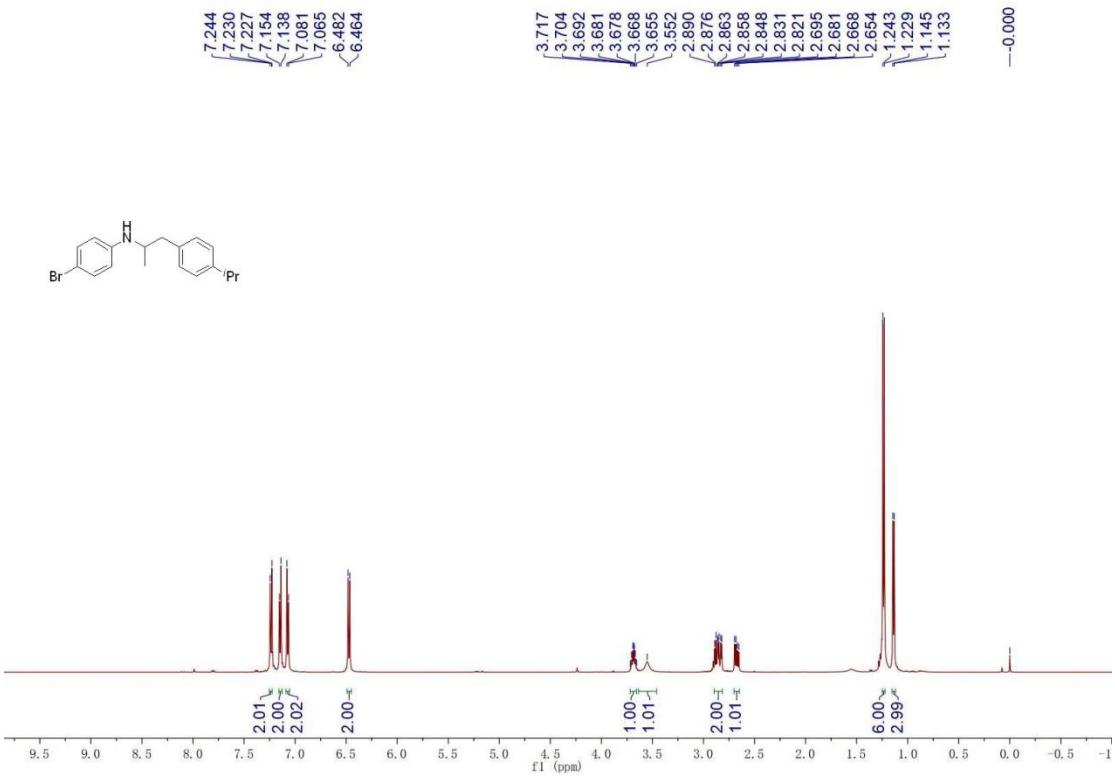


^{1}H NMR (500 MHz, $CDCl_3$)

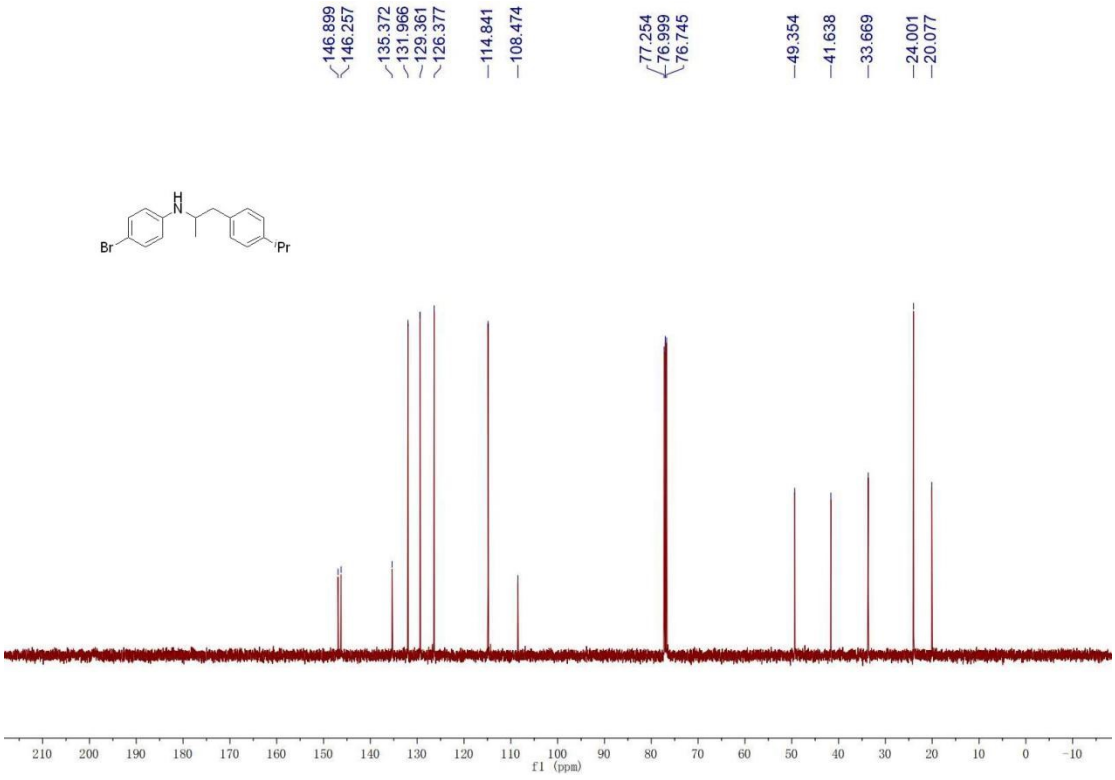


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-(1-(4-isopropylphenyl)propan-2-yl)aniline (3gm):

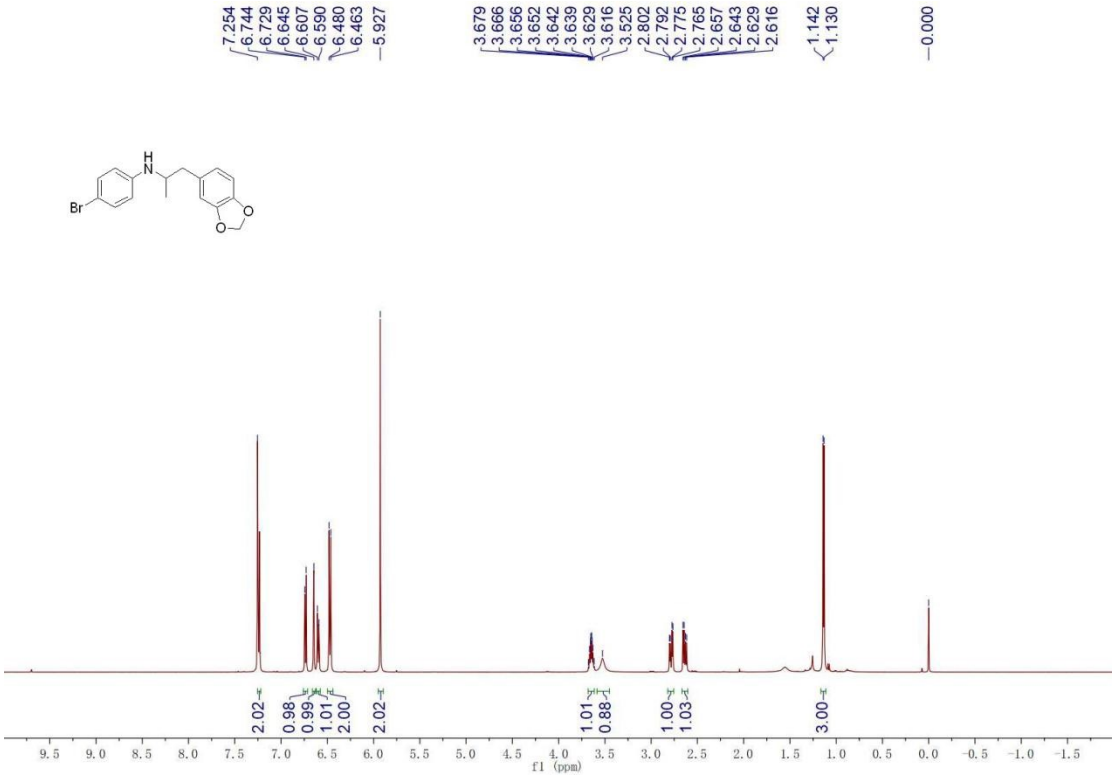


^{1}H NMR (500 MHz, $CDCl_3$)

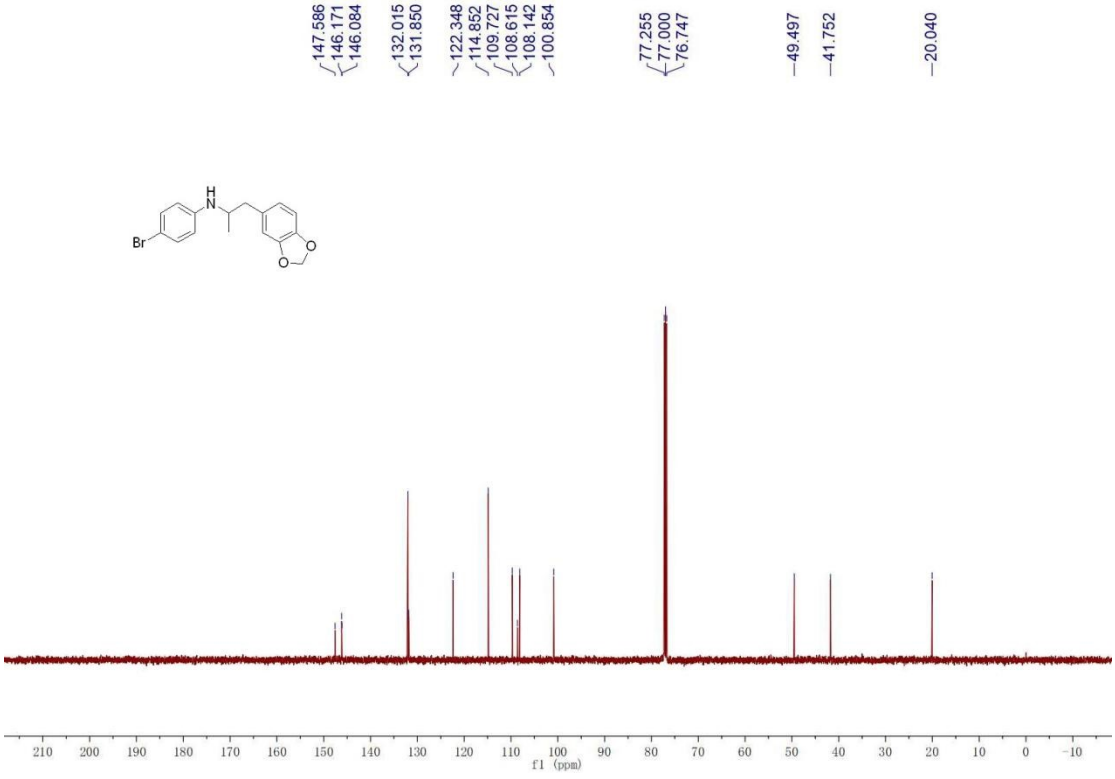


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-(1-(benzo[*d*][1,3]dioxol-5-yl)propan-2-yl)-4-bromoaniline (3gn):**

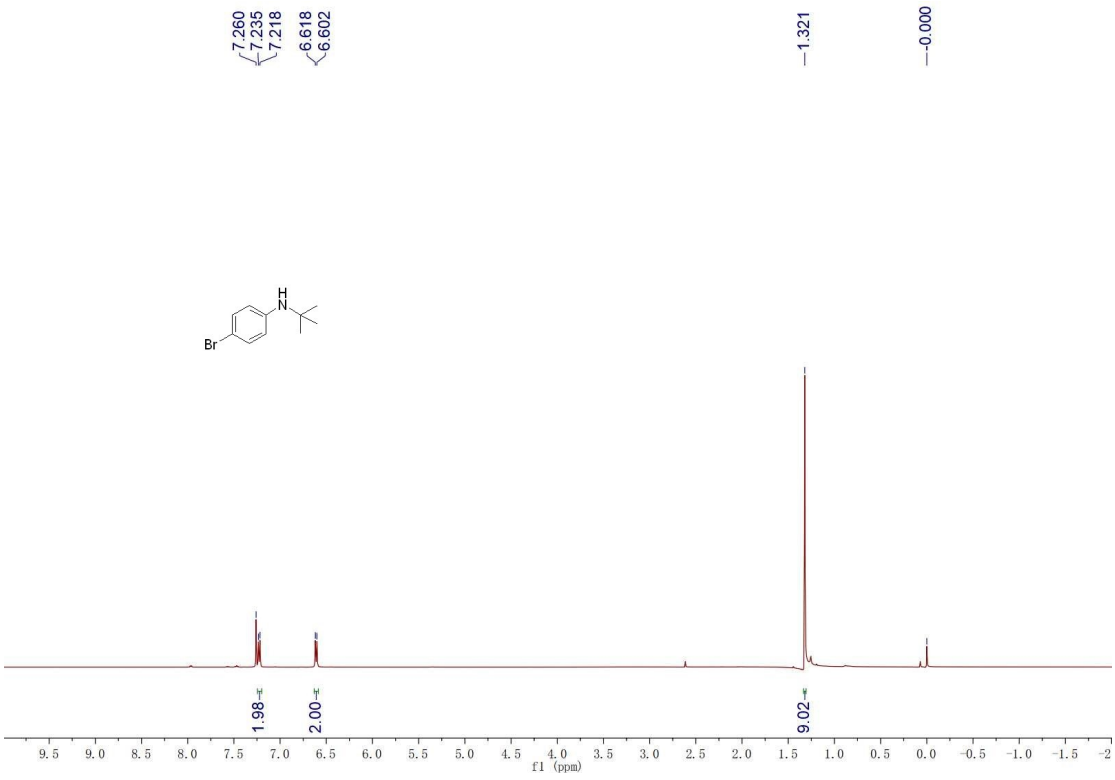


^{1}H NMR (500 MHz, $CDCl_3$)

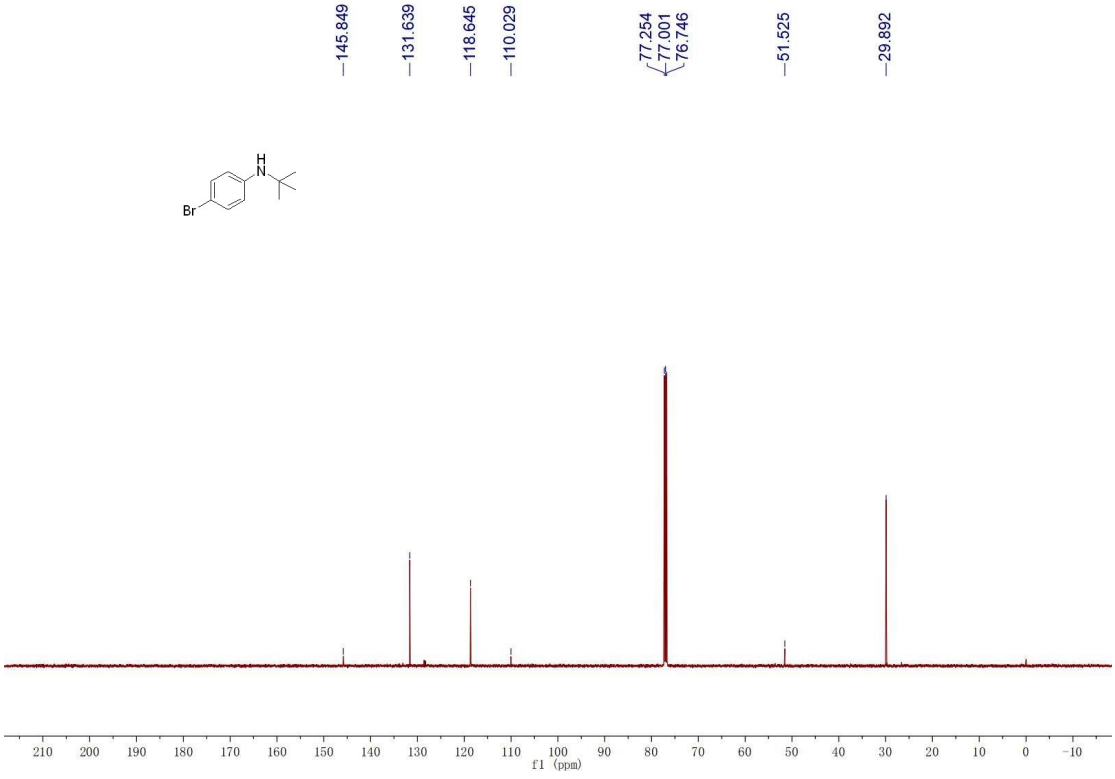


^{13}C NMR (125 MHz, $CDCl_3$)

4-bromo-*N*-(*tert*-butyl)aniline (3go):

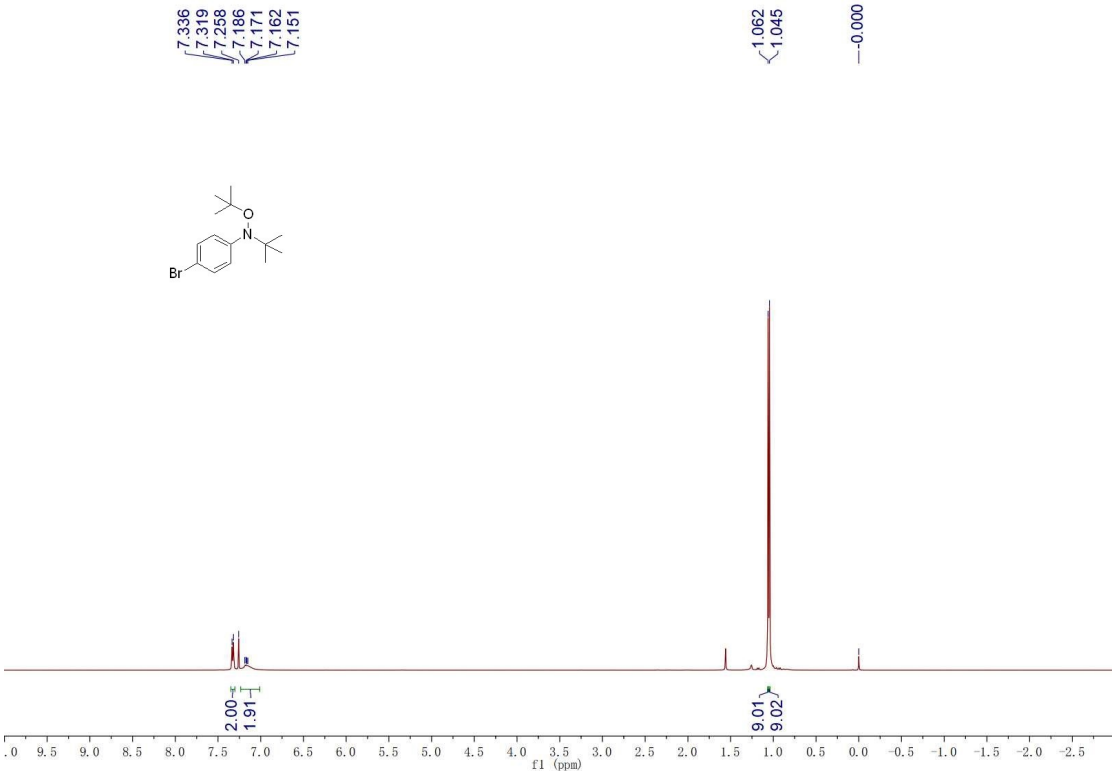


^{1}H NMR (500 MHz, $CDCl_3$)

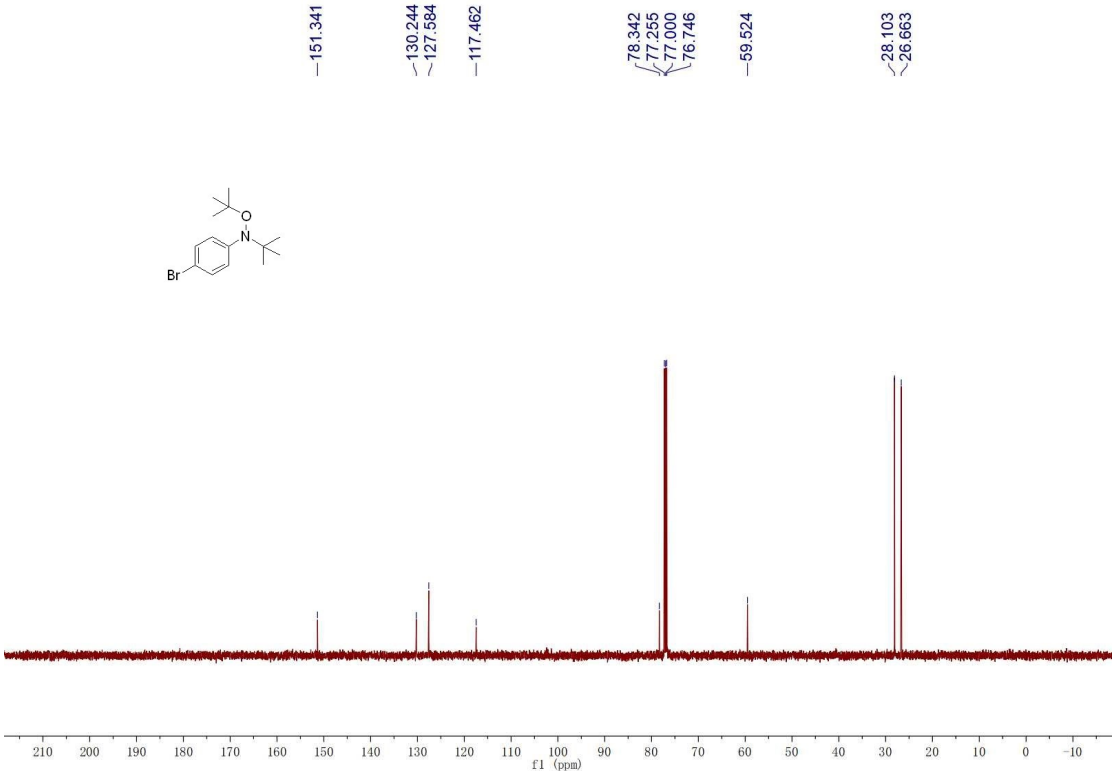


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-(4-bromophenyl)-*N,O*-di-tert-butylhydroxylamine (4go):**

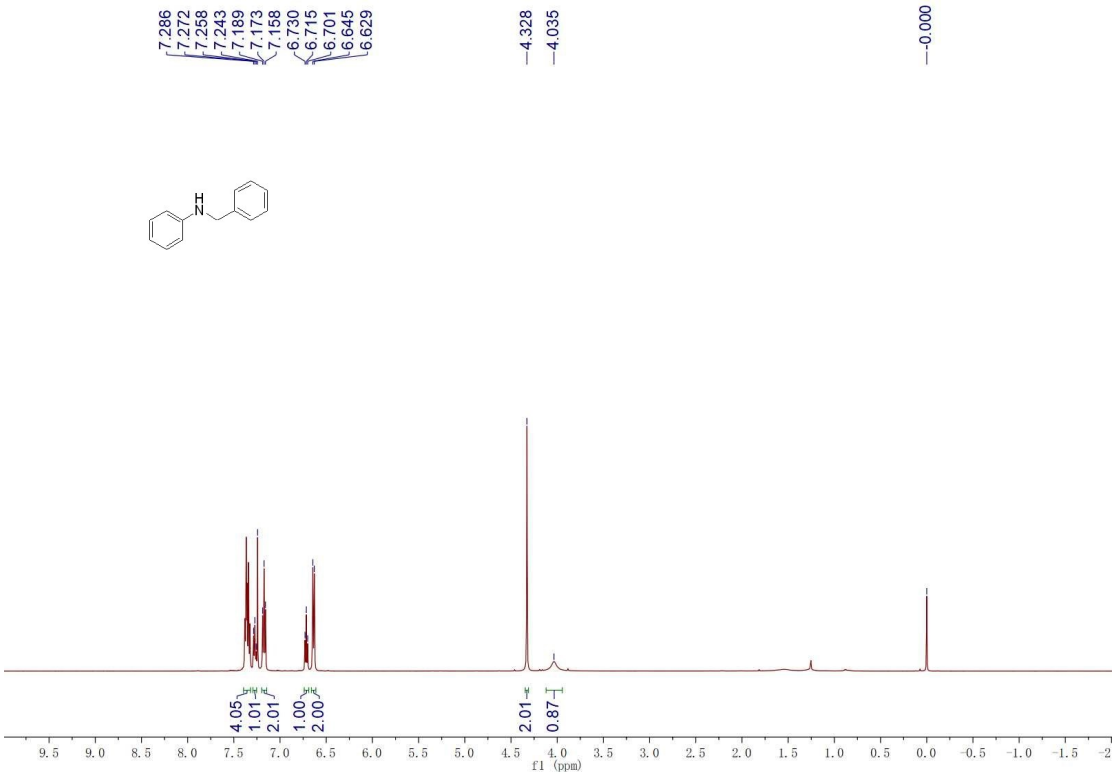


^{1}H NMR (500 MHz, $CDCl_3$)

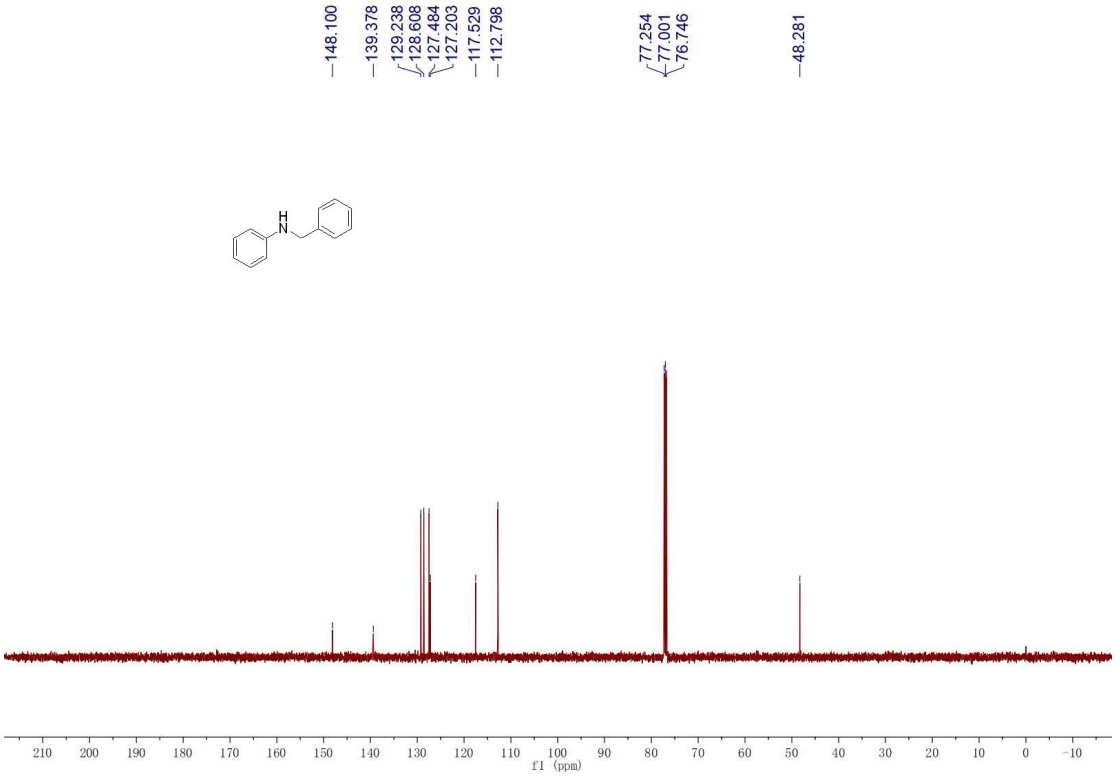


^{13}C NMR (125 MHz, $CDCl_3$)

***N*-benzylaniline (3ad):**

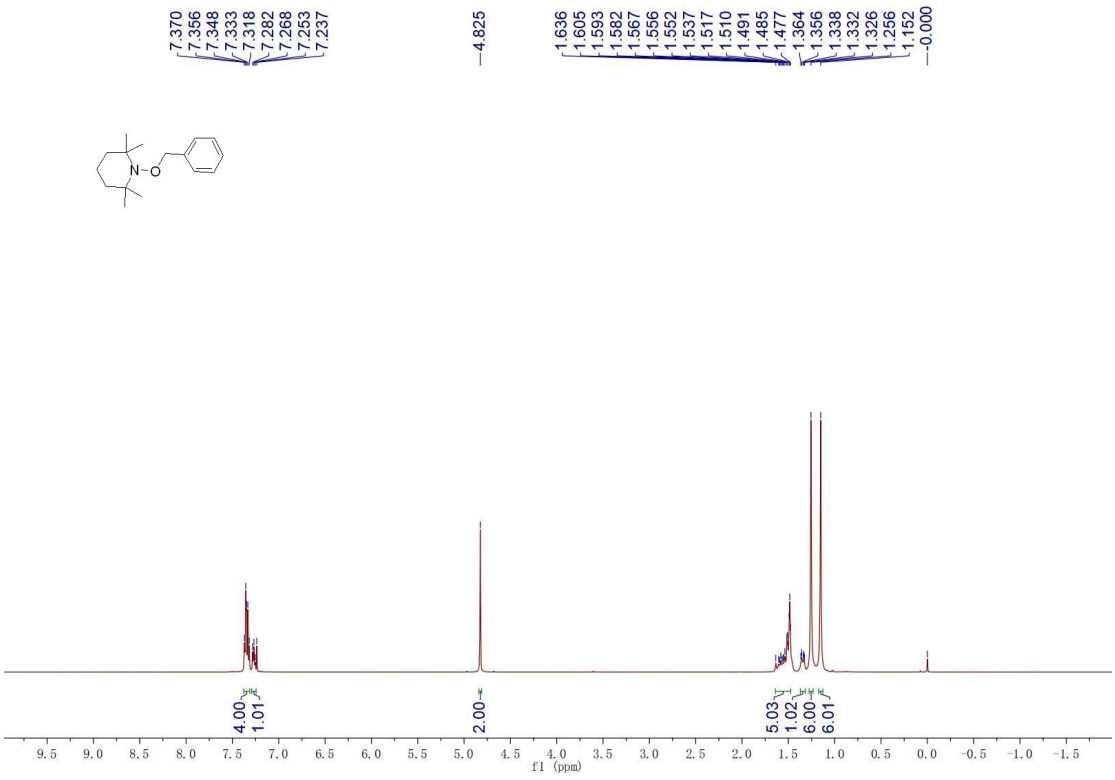


^{1}H NMR (500 MHz, $CDCl_3$)

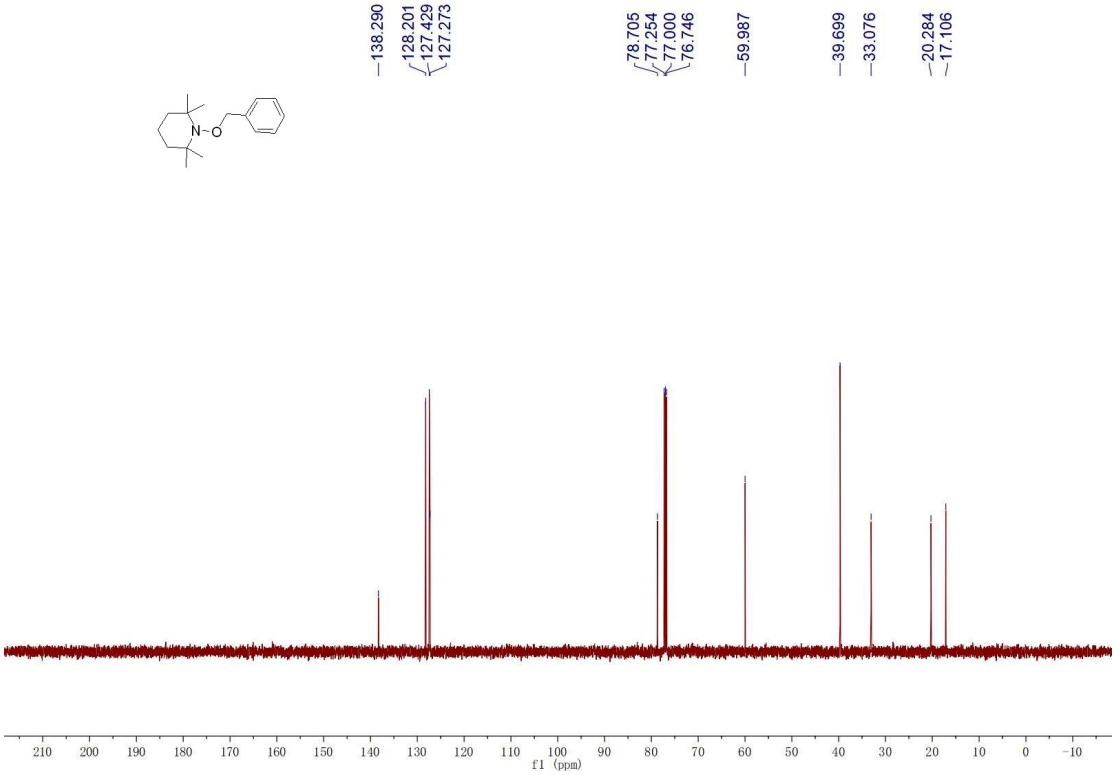


^{13}C NMR (125 MHz, $CDCl_3$)

1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (6a):



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

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