Supporting information

Mono/Dual Amination of Phenols with Amines in Water

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1. General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR and ^{13}C-NMR. Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-500 and referenced to 7.26 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), used without further purification. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument.

2. Typical procedure for the synthesis of the corresponding products.

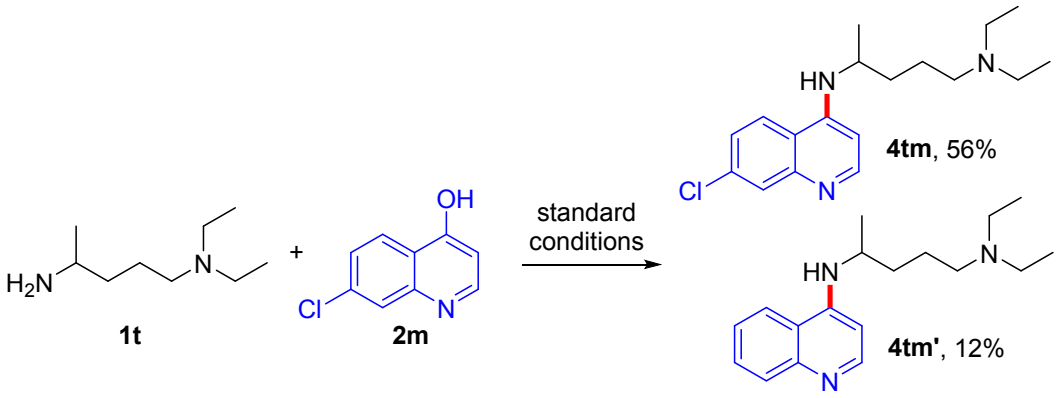
Mono Amination of Phenols with Amines: In a 25 mL Schlenk tube was combined Amines **1** (0.45 mmol), Phenols **2** (0.30 mmol), Pd/C (10 wt%, 5 mol% based on Pd content), HCO_2NH_4 (1 equiv) and $K_2S_2O_5$ (50 mol %) in H_2O (1.0 mL). The mixture was then stirred at 100 °C under oil-bath heating for 16 h under N_2 protection. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether (60-90 °C): ethyl acetate (20:1) to give the corresponding products **3aa-3oa**.

Dual Amination of Phenols with Amines: In a 25 mL Schlenk tube was combined Amines **1** (0.9 mmol), Phenols **2** (0.3 mmol), Pd/C (10 wt%, 5 mol% based on Pd content), HCO_2NH_4 (2 equiv) and $K_2S_2O_5$ (50 mol %) in water (1.0 mL) at 100 °C for 16 h under N_2 protection. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether (60-90 °C): ethyl acetate (10:1) to give the corresponding products **4ei-4sl**.

Synthesis of *N-phenethylnaphthalen-2-amine (**3ea**)*: In a 25 mL Schlenk tube was combined Phenylethylamine **1e** (1.2 mmol), 2-Naphthol **2a** (1 mmol), Pd/C (10 wt%, 5 mol% based on Pd content), HCO_2NH_4 (1 equiv) and $K_2S_2O_5$ (50 mol %) in H_2O (2.0 mL). The mixture was then stirred at 100 °C under oil-bath heating for 16 h under N_2 protection. Purification of the residue by column chromatography (30:1 petroleum ether: ethyl acetate) gave **3ea** as a yellow solid (150.7 mg, 61% yield).

3. The new synthetic method for the synthesis of chloroquine

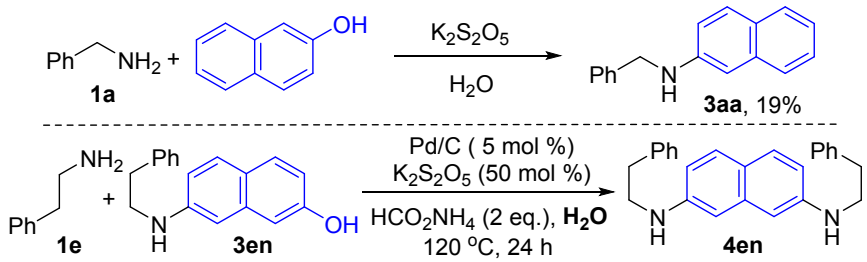
In a 25 mL Schlenk tube was combined 2-amino-5-diethylaminopentane **1t** (0.45 mmol), 7-chloroquinolin-4-ol **2m** (0.30 mmol), Pd/C (10 wt%, 5 mol% based on Pd content), HCO_2NH_4 (1 equiv) and $K_2S_2O_5$ (50 mol%) in H_2O (1.0 mL) N_2 protection. The mixture was then stirred at 120 °C under oil-bath heating for 16 h. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether: ethyl acetate (5:1) to give chloroquine **4tm** and dechlorinated product **4tm'**.



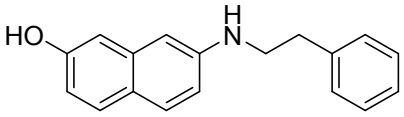
Scheme 1 The synthetic utility of the developed chemistry.

4. The control experiments

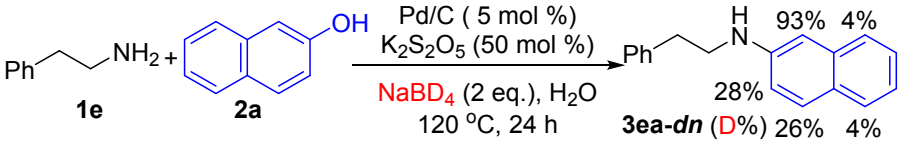
Under the same conditions using only $K_2S_2O_5$ and water, benzylamine and naphthol produced the expected product in low yield (19%), but the yield increased greatly to 73% when the hydrogen source was added (Manuscript, table 1, entry 13). These results indicate that the $K_2S_2O_5$ and hydrogen source jointly promoted the transformation of this reaction.

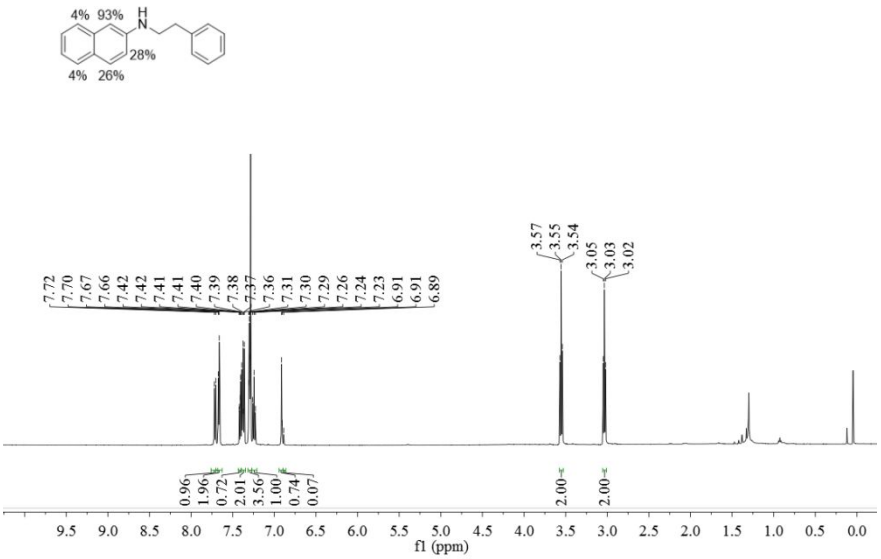


Scheme 2

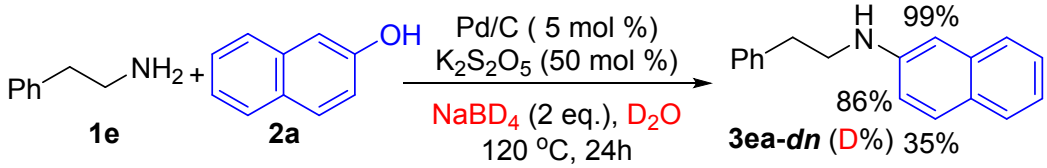


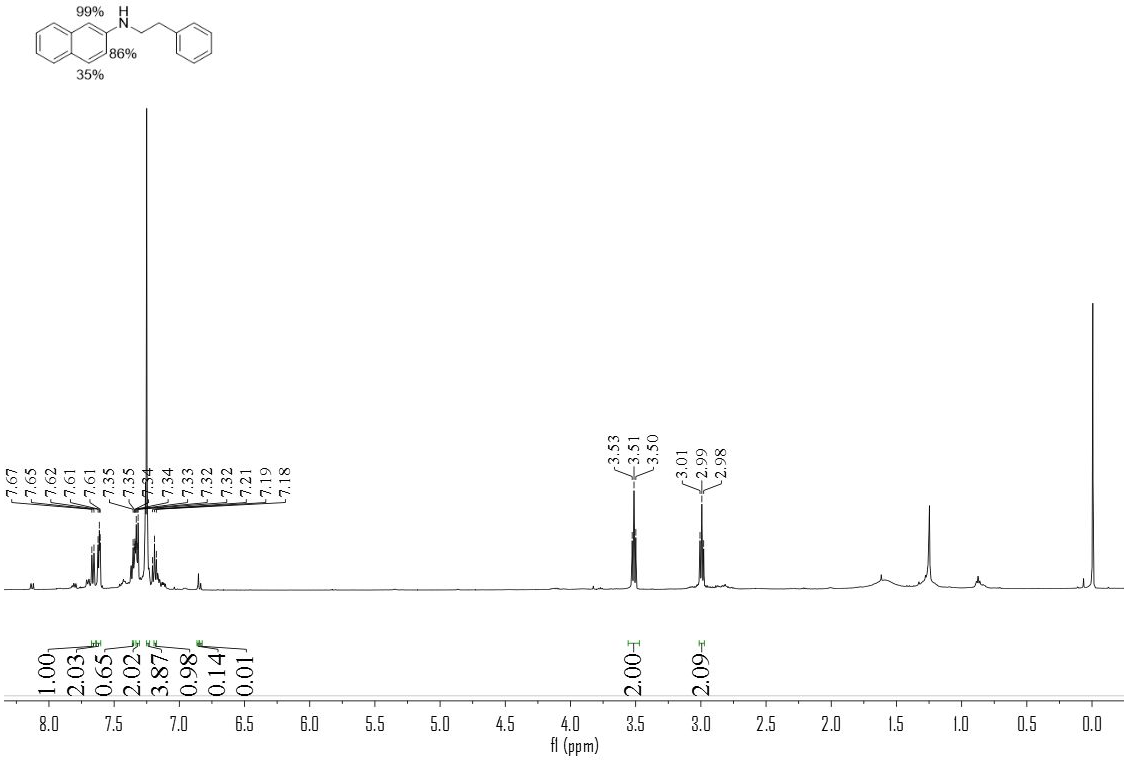
7-(phenethylamino)naphthalen-2-ol (3en). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.7 Hz, 1H), 7.44 (d, J = 8.7 Hz, 1H), 7.39 (t, J = 7.3 Hz, 2H), 7.31 (dd, J = 16.3, 6.9 Hz, 3H), 7.07 (d, J = 8.8 Hz, 1H), 7.04 (s, 1H), 6.90 (s, 1H), 6.86 (d, J = 8.7 Hz, 1H), 4.76 (s, 2H), 3.51 (t, J = 7.0 Hz, 2H), 3.00 (t, J = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.2, 143.6, 139.3, 130.3, 128.9, 128.8, 128.7, 127.8, 127.6, 126.6, 119.1, 118.4, 109.9, 106.3, 45.6, 35.2.





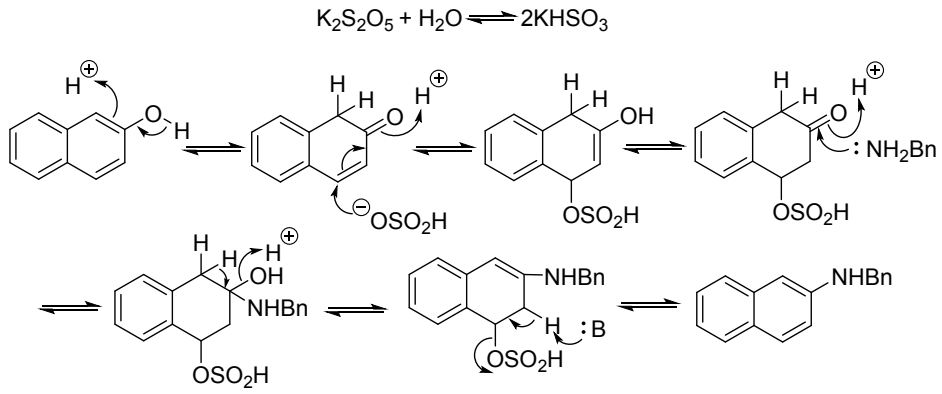
To better understand the mechanism, it may be better for the authors to examine the deuterium ratio with $NaBH_4$ as the hydride donor but in D_2O as the solvent. The product generated under the conditions of $NaBD_4$ and D_2O increases the ratio of deuteration on the naphthalene ring, suggesting that water has a promoting effect in this transformation or that proton-exchange process may occur in the presence of D_2O.





5. Plausible reaction pathways

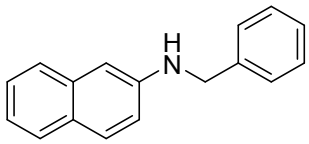
We believe that $K_2S_2O_5$ plays a key role in water, similar to the bucherer reaction pathway. The reaction proceeded via bisulfite adducts of the tautomeric keto or ketimine forms of the naphthols or naphthylamines, in accordance with Scheme 2.



Scheme 3

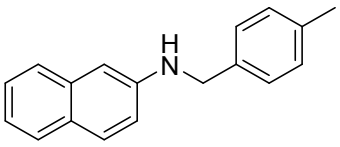
6. Analytical data of the obtained compounds

(1)



N-benzylnaphthalen-2-amine (3aa). Brown solid (52.5 mg, 75% yield), m.p: 132-133 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.43 – 7.37 (m, 3H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.25 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.96 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.89 (d, *J* = 2.2 Hz, 1H), 4.48 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 139.1, 135.2, 129.0, 128.8, 127.7, 127.7, 127.4, 126.4, 126.1, 122.2, 118.0, 104.8, 48.5. HRMS (ESI) m/z calcd for $C_{17}H_{16}N$ $[M+H]^+$: 234.1277; found 234.1270.

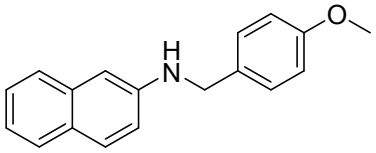
(2)



N-(4-methylbenzyl)naphthalen-2-amine (3ba). Yellow oil (60.1 mg, 81% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 30/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.66 (dd, *J* = 16.2, 8.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.27 – 7.18 (m, 3H), 6.96 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.91 (s, 1H), 4.43 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 137.1, 135.9, 135.2, 129.4, 129.0, 127.8, 127.7, 126.4, 126.1, 122.2, 118.0, 105.0, 48.3, 21.2.

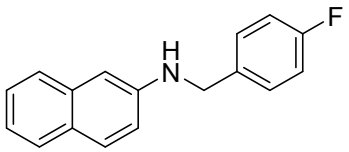
HRMS (ESI) m/z calcd for $C_{18}H_{18}N$ $[M+H]^+$: 248.1434; found 248.1421.

(3)



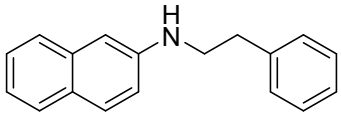
N-(4-methoxybenzyl)naphthalen-2-amine (3ca). Yellow solid (65.5 mg, 83% yield), m.p: 103-104.2 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.66 (dd, *J* = 14.4, 8.5 Hz, 2H), 7.39 (dd, *J* = 15.7, 7.8 Hz, 3H), 7.24 (t, *J* = 3.9 Hz, 1H), 6.98 – 6.89 (m, 4H), 4.39 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 145. 5, 135.1, 130.9, 129.1, 129.0, 127.7, 126.4, 126.1, 122.2, 118.1, 114.1, 105.1, 55.4, 48.1. HRMS (ESI) m/z calcd for $C_{18}H_{18}NO$ $[M+H]^+$: 264.1383; found 264.1385.

(4)



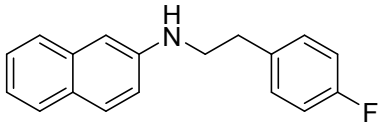
N-(4-fluorobenzyl)naphthalen-2-amine (3da). Brown solid (53.5 mg, 71% yield) , m.p: 86.4-87.6 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 30/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 17.1, 8.4 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.27 – 7.22 (m, 1H), 7.07 (t, *J* = 8.7 Hz, 2H), 6.96 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.87 (s, 1H), 4.44 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.1 Hz), 145.1, 135.0, 134.5, 129.3 (d, *J* = 8.0 Hz), 129.1, 127.8, 127.7, 126.3 (d, *J* = 46.0 Hz), 122.4, 118.0, 115.6, 115.5, 105.3, 47.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.30. HRMS (ESI) m/z calcd for $C_{17}H_{15}FN$ $[M+H]^+$: 252.1183; found 252.1176.

(5)



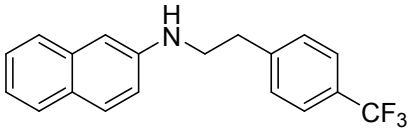
N-phenethylnaphthalen-2-amine (3ea). Yellow oil (56.3 mg, 76% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 30/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.69 (dd, *J* = 8.4, 3.7 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.35 – 7.27 (m, 4H), 6.95 – 6.89 (m, 2H), 3.57 (t, *J* = 7.0 Hz, 2H), 3.05 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 139.3, 135.3, 129.1, 128.9, 128.7, 127.7, 127.7, 126.6, 126.4, 126.0, 122.1, 118.2, 104.9, 45.2, 35.3. HRMS (ESI) m/z calcd for $C_{18}H_{18}N$ $[M+H]^+$: 248.1434; found 248.1423.

(6)



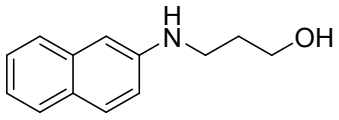
N-(4-fluorophenethyl)naphthalen-2-amine (3fa). Yellow oil (54.1 mg, 68% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 40/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 2H), 7.41 (dd, *J* = 7.9, 7.1 Hz, 1H), 7.27 – 7.20 (m, 3H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 6.7 Hz, 2H), 3.52 (t, *J* = 7.0 Hz, 2H), 2.99 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7 (d, *J* = 244.3 Hz), 145.5, 135.2, 134.9 (d, *J* = 3.0 Hz), 130.3 (d, *J* = 7.6 Hz), 129.1, 127.7, 127.6, 126.4, 126.0, 122.1, 118.1, 115.5 (d, *J* = 21.1 Hz), 104.7, 45.1, 34.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.62. HRMS (ESI) m/z calcd for $C_{18}H_{17}FN$ $[M+H]^+$: 266.1340; found 266.1351.

(7)



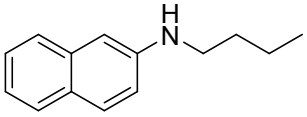
N-(4-(trifluoromethyl)phenethyl)naphthalen-2-amine (3ga). Yellow oil (33.4 mg, 53% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 30/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.6, 3.7 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 6.5 Hz, 2H), 7.45 – 7.37 (m, 3H), 7.26 (dd, *J* = 4.0, 2.8 Hz, 1H), 6.95 – 6.83 (m, 2H), 3.86 (s, 1H), 3.57 (t, *J* = 6.9 Hz, 2H), 3.07 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 143.5, 135.2, 129.2, 129.1, 127.7, 127.7, 126.5, 125.9, 125.6 (q, *J* = 3.6 Hz), 122.2, 118.0, 104.7, 44.7, 35.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.3. HRMS (ESI) m/z calcd for $C_{19}H_{17}F_3N$ $[M+H]^+$: 316.1308; found 316.1301.

(8)



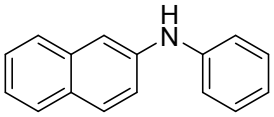
3-(naphthalen-2-ylamino)propan-1-ol (3ha). Yellow oil (51.3 mg, 85% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 4/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 25.1, 7.9 Hz, 3H), 7.40 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 7.27 – 7.22 (m, 1H), 6.94 – 6.87 (m, 2H), 3.88 – 3.84 (m, 2H), 3.40 (t, *J* = 6.5 Hz, 2H), 1.99 – 1.94 (m, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 145.9, 135.1, 129.0, 127.7, 126.4, 126.0, 122.1, 118.3, 104.9, 61.7, 42.1, 31.7. HRMS (ESI) m/z calcd for $C_{13}H_{15}NONa$ $[M+Na]^+$: 224.1046; found 224.1053.

(9)



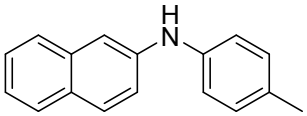
N-butylnaphthalen-2-amine (3ia). Yellow oil (48.4 mg, 81% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 40/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 23.5, 8.3 Hz, 3H), 7.39 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.22 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.84 (d, *J* = 2.3 Hz, 1H), 3.25 (t, *J* = 7.2 Hz, 2H), 1.70 (td, *J* = 7.2, 2.2 Hz, 2H), 1.51 (q, *J* = 7.5 Hz, 2H), 1.02 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 135.3, 128.9, 127.7, 127.5, 126.3, 125.9, 121.9, 118.1, 104.3, 43.8, 31.5, 20.4, 14.0. HRMS (ESI) m/z calcd for $C_{14}H_{18}N$ $[M+H]^+$: 200.1434; found 200.1439.

(10)



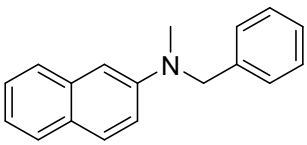
N-phenylnaphthalen-2-amine (3ja). Yellow solid (42.1 mg, 64% yield), m.p: 103-105 °C ; R_f = 0.4 (petroleum ether/ethyl acetate = 4/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.80 (m), 7.73 (d, *J* = 8.2 Hz), 7.55 – 7.48 (m), 7.44 – 7.36 (m), 7.30 – 7.27 (m), 7.24 (dd, *J* = 8.5, 1.0 Hz), 7.08 (dd, *J* = 10.6, 4.1 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 140.9, 134.7, 129.6, 129.3, 129.3, 127.8, 126.6, 126.6, 123.6, 121.5, 120.1, 118.3, 111.6. HRMS (ESI) m/z calcd for $C_{16}H_{13}NNa$ $[M+Na]^+$: 242.0940; found 242.0956.

(11)



N-(p-tolyl)naphthalen-2-amine (3ka). Yellow solid (48.3 mg, 69% yield), m.p: 101-103 °C ; R_f = 0.4 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 12.1, 5.1 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.45 (s, 1H), 7.42 – 7.36 (m, 1H), 7.27 – 7.22 (m, 3H), 7.19 (t, *J* = 5.1 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 140.1, 134.8, 131.5, 130.1, 129.3, 129.0, 127.8, 126.5, 126.5, 123.3, 119.7, 119.4, 110.4, 20.9. HRMS (ESI) m/z calcd for $C_{17}H_{16}N$ $[M+H]^+$: 234.1277; found 234.1277.

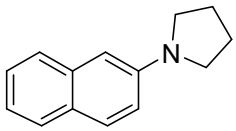
(12)



N-benzyl-N-methylnaphthalen-2-amine (3la). Yellow oil (45.2 mg, 61% yield); R_f

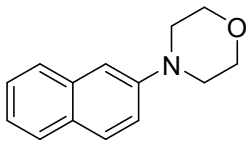
= 0.4 (petroleum ether/ethyl acetate = 30/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.33 – 7.28 (m, 3H), 7.27 – 7.18 (m, 2H), 7.00 (d, *J* = 2.1 Hz, 1H), 4.69 (s, 2H), 3.14 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 138.8, 135.1, 128.9, 128.6, 127.5, 127.0, 126.9, 126.9, 126.3, 126.2, 122.1, 116.2, 106.2, 56.8, 38.7. HRMS (ESI) m/z calcd for $C_{18}H_{18}N$ $[M+H]^+$: 248.1434; found 248.1431.

(13)



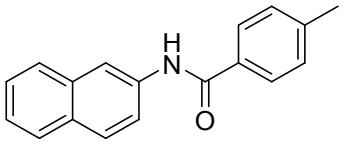
1-(naphthalen-2-yl)pyrrolidine (3ma). Yellow oil (34.3 mg, 58% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 40/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.6, 4.4 Hz), 7.73 (d, *J* = 8.2 Hz), 7.45 (ddd, *J* = 8.3, 6.7, 1.3 Hz), 7.26 (ddd, *J* = 8.1, 6.7, 1.2 Hz), 7.08 (dd, *J* = 9.0, 2.5 Hz), 6.85 (d, *J* = 2.5 Hz), 3.51 – 3.45 (m), 2.12 (dq, *J* = 6.7, 3.8, 3.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) 145.9, 135.3, 128.9, 127.7, 126.4, 126.2, 125.9, 121.3, 115.8, 104.8, 47.9, 25.6. HRMS (ESI) m/z calcd for $C_{14}H_{15}NNa$ $[M+ Na]^+$: 220.1097; found 220.1089.

(14)



4-(naphthalen-2-yl)morpholine (3na). Yellow oil (41.6 mg, 65% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 30/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 3H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.29 (dd, *J* = 9.0, 2.5 Hz,1H), 7.16 (d, *J* = 2.2 Hz, 1H), 3.95 (t, *J* = 1.1 Hz, 4H), 3.29 (t, *J* = 1.1 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 134.6, 128.9, 128.7, 127.5, 126.9, 126.4, 123.6, 119.0, 110.2, 67.0, 49.9. HRMS (ESI) m/z calcd for $C_{14}H_{15}NONa$ $[M+Na]^+$: 236.1046; found 236.1046.

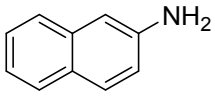
(15)



4-methyl-N-(naphthalen-2-yl)benzamide (3oa). Yellow solid (6.3 mg, 8% yield), m.p: 123-125 °C ; R_f = 0.4 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.33 (m, 1H), 8.13 (s, 1H), 7.84- 7.81 (m, 4H), 7.69 – 7.60 (m, 1H), 7.52 – 7.43 (m, 2H), 7.42 – 7.25 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 142.5, 135.5, 133.9, 132.0, 130.7, 129.5, 128.8, 127.8, 127.6, 127.1, 126.6, 125.1, 120.2, 117.0, 21.6. HRMS (ESI) m/z calcd for $C_{18}H_{15}NONa$ $[M+Na]^+$:

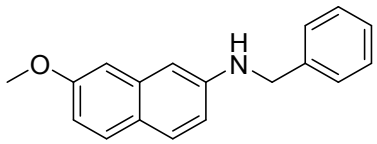
284.1046; found 284.1035.

(16)



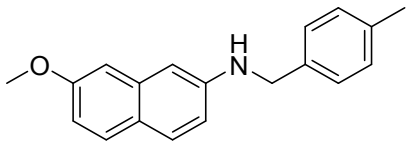
naphthalen-2-amine (3pa). Yellow solid (9.2 mg, 32% yield), m.p: 110-112 °C ; R_f = 0.4 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.62 (s, 1H), 7.40 (s, 1H), 7.28 (s, 1H), 7.00 (d, *J* = 15.8 Hz, 2H), 3.89 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 134.9, 129.2, 128.0, 127.7, 126.4, 125.8, 122.5, 118.3, 108.6. HRMS (ESI) m/z calcd for $C_{10}H_{10}N$ $[M+H]^+$: 144.0808; found 144.0821.

(17)



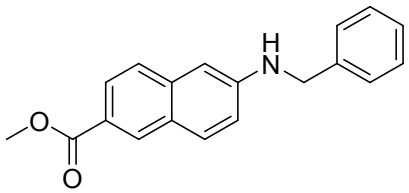
N-benzyl-7-methoxynaphthalen-2-amine (3ab). Yellow solid (60.8 mg, 77% yield), m.p: 179.6-181.3 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 20/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 9.0, 4.3 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.0 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.81 (d, *J* = 6.8 Hz, 2H), 4.47 (s, 2H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 145.9, 139.0, 136.4, 129.2, 128.8, 128.7, 127.7, 127.4, 123.1, 115.5, 114.6, 104.6, 55.2, 48.5. HRMS (ESI) m/z calcd for $C_{18}H_{18}NO$ $[M+H]^+$: 264.1383; found 264.1389.

(18)



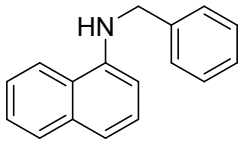
7-methoxy-N-(4-methylbenzyl)naphthalen-2-amine(3bb). Yellow oil (67.3 mg, 81% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 4/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.36 (dd, *J* = 8.1, 2.3 Hz, 2H), 7.24 (dd, *J* = 8.0, 2.3 Hz, 2H), 6.99 (t, *J* = 2.5 Hz, 2H), 6.86 – 6.77 (m, 2H), 4.43 (s, 2H), 3.93 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 146.2, 137.1, 136.5, 136.0, 129.4, 129.2, 128.8, 127.7, 123.0, 115.5, 114.6, 104.6, 104.4, 55.2, 48.3, 21.2. HRMS (ESI) m/z calcd for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539; found 278.1547.

(19)



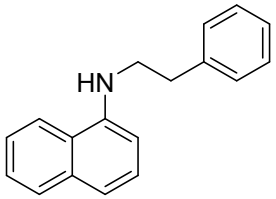
methyl 6-(benzylamino)-2-naphthoate (3ac). Yellow oil (46.3 mg, 53% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 4/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 – 8.43 (m, 1H), 8.00 – 7.92 (m, 1H), 7.78 – 7.72 (m, 1H), 7.63 – 7.58 (m, 1H), 7.54 – 7.25 (m, 5H), 6.98 (ddd, *J* = 9.1, 7.3, 2.7 Hz, 1H), 6.85 (dt, *J* = 8.1, 2.4 Hz,1H), 4.54 – 4.46 (m, 2H), 4.02 – 3.94 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 147.7, 138.5, 137.8, 131.1, 130.6, 128.8, 127.6, 127.6, 126.3, 126.0, 125.9, 123.3, 118.5, 104.1, 52.0, 48.1. HRMS (ESI) m/z calcd for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1332; found 292.1339.

(20)



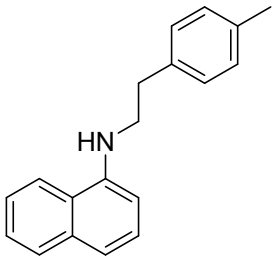
N-benzylnaphthalen-1-amine (3ad). Yellow solid (50.3 mg, 72% yield), m.p: 86.5-89.2 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 30/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 2H), 7.56 – 7.46 (m, 4H), 7.44 (dd, *J* = 11.0, 3.9 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.30 (dd, *J* = 15.3, 4.9 Hz, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 4.55 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 139.1, 134.3, 128.8, 128.8, 127.8, 127.5, 126.7, 125.8, 124.8, 123.4, 120.0, 117.7, 104.9, 48.7. HRMS (ESI) m/z calcd for $C_{17}H_{16}N$ $[M+H]^+$: 234.1227; found 234.1222.

(21)



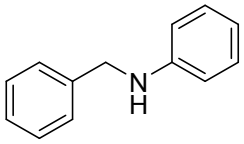
N-phenethylnaphthalen-1-amine (3ed). Yellow oil (51.9mg, 70% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 4/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.46 (dt, *J* = 14.1, 7.7 Hz, 2H), 7.39 (q, *J* = 7.4 Hz, 3H), 7.35 – 7.31 (m, 2H), 7.28 (t, *J* = 6.5 Hz, 2H), 6.71 (d, *J* = 7.5 Hz, 1H), 4.44 (s, 1H), 3.60 (t, *J* = 7.0 Hz, 2H), 3.12 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 139.3, 134.3, 128.9, 128.8, 128.7, 126.7, 126.6, 125.7, 124.7, 123.5, 119.8, 117.5, 104.5, 45.2, 35.4. HRMS (ESI) m/z calcd for $C_{18}H_{18}N$ $[M+H]^+$: 248.1434; found 248.1425.

(22)



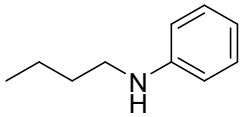
N-(4-methylphenethyl) naphthalen-1-amine (3fd). Yellow oil (58.7 mg, 75% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 40/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.37 (m, 3H), 7.29 (d, *J* = 5.3 Hz, 2H), 7.21 (dd, *J* = 17.6, 7.8 Hz, 4H), 6.72 (d, *J* = 7.4 Hz, 1H), 3.58 (t, *J* = 6.9 Hz, 2H), 3.08 (t, *J* = 6.9 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 136.1, 134.3, 129.5, 128.7, 128.7, 126.7, 125.8, 124.8, 123.5, 119.9, 117.6, 104.7, 45.4, 34.9, 21.1. HRMS (ESI) m/z calcd for $C_{19}H_{20}N$ $[M+H]^+$: 262.1590; found 262.1592.

(23)



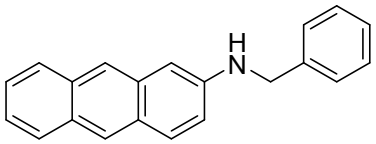
N-benzylaniline (3ae). Yellow oil (33.0 mg, 60% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 10/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 4H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 2H), 4.38 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 139.4, 129.3, 128.7, 127.6, 127.7, 117.7, 112.9, 48.4. HRMS (ESI) m/z calcd for $C_{13}H_{14}N$ $[M+H]^+$: 184.1121; found 184.1133.

(24)



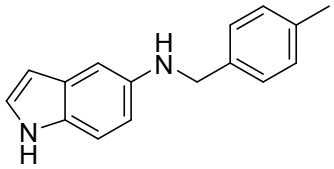
N-butylaniline (3ie). Yellow oil (13.7 mg, 46% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 2H), 3.17 – 3.13 (m, 2H), 1.68 – 1.61 (m, 2H), 1.51 – 1.43 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 129.2, 117.1, 112.7, 43.7, 31.7, 20.4, 13.9. HRMS (ESI) m/z calcd for $C_{10}H_{16}N$ $[M+H]^+$:150.1277; found 150.1268.

(25)



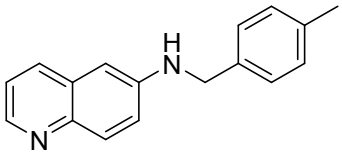
N-benzylanthracen-2-amine (3af). Yellow oil (49.2 mg, 58% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 8/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.12 (s, 1H), 7.98 – 7.80 (m, 3H), 7.54 – 7.32 (m, 7H), 7.14 – 6.87 (m, 2H), 4.48 (s, 2H), 4.25 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 138.98, 133.6, 132.5, 129.6, 129.5, 128.8, 128.3, 127.8, 127.5, 127.5, 127.5, 126.2, 125.3, 123.7, 122.8, 120.2, 101.8, 48.4. HRMS (ESI) m/z calcd for $C_{21}H_{18}N$ $[M+H]^+$: 284.1434; found 284.1430.

(26)



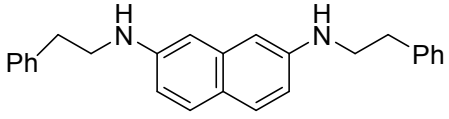
N-(4-methylbenzyl)-1H-indol-5-amine (3bg). Yellow oil (43.9mg, 62% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 10/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.15 – 7.13 (m, 1H), 6.96 (d, *J* = 2.1 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.44 – 6.40 (m, 1H), 4.35 (s, 2H), 2.37 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.9, 136.3, 130.5, 129.3, 128.7, 128.0, 124.6, 112.5, 111.7, 103.2, 101.9, 50.0, 21.2. HRMS (ESI) m/z calcd for $C_{16}H_{16}N_2Na$ $[M+Na]^+$: 259.1206; found 259.1198.

(27)



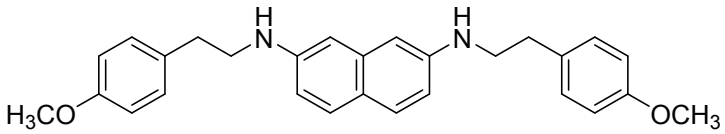
N-(4-methylbenzyl)quinolin-6-amine (3bh). Yellow oil (48.4mg, 65% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 10/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 6.4 Hz, 1H), 8.34 – 7.67 (m, 2H), 7.42 – 7.17 (m, 6H), 6.77 (d, *J* = 8.6 Hz, 1H), 4.44 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$)δ 146.4, 144.9, 135.4, 135.1, 130.4, 129.5, 129.1, 127.6, 126.3, 122.1, 121.5, 115.9, 103.1, 48.0, 21.1. HRMS (ESI) m/z calcd for $C_{17}H_{17}N_2$ $[M+H]^+$: 249.1386; found 249.1390.

(28)



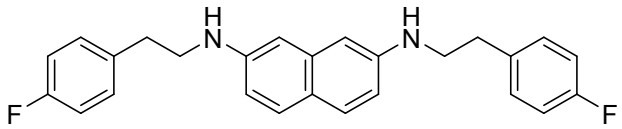
N^2,N^7-diphenethylnaphthalene-2,7-diamine (4ei). Yellow oil (79.1 mg, 72% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 30/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.34 (m, 4H), 7.30 – 7.27 (m, 6H), 6.71 (s, 2H), 6.61 (d, *J* = 8.6 Hz, 2H), 3.52 (t, *J* = 7.0 Hz, 4H), 3.01 (t, *J* = 7.0 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 139.4, 136.9, 128.9, 128.8, 128.6, 126.4, 121.7, 114.0, 103.5, 45.1, 35.4. HRMS (ESI) m/z calcd for $C_{26}H_{27}N_2$ $[M+H]^+$:367.2169; found 367.2167.

(29)



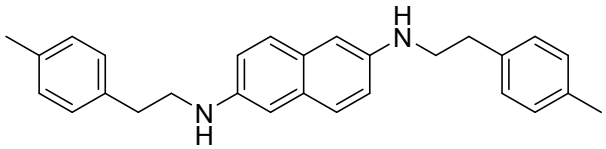
N^2,N^7-bis(4-methoxyphenethyl)naphthalene-2,7-diamine (4gi). Yellow oil (63.9 mg, 75% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 30/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.7 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.78 (s, 1H), 6.66 (dd, *J* = 8.7, 1.9 Hz, 1H), 3.87 (s, 3H), 3.52 (t, *J* = 7.0 Hz, 2H), 2.98 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 146.4, 137.1, 131.5, 129.9, 128.9, 121.7, 114.2, 114.1, 103.6, 55.4, 45.4, 34.5. HRMS (ESI) m/z calcd for $C_{28}H_{30}N_2O_2Na$ $[M+Na]^+$: 449.2200; found 449.2181.

(30)



N^2,N^7-bis(4-fluorophenethyl)naphthalene-2,7-diamine (4fi). Yellow oil (54.7 mg, 68% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.21 (m, 4H), 7.09 (dd, *J* = 10.7, 6.5 Hz, 4H), 6.78 (s, 2H), 6.67 (dd, *J* = 8.6, 1.9 Hz, 2H), 3.70 (s, 2H), 3.52 (t, *J* = 7.0 Hz, 4H), 2.99 (t, *J* = 7.0 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7 (d, *J* = 244.2 Hz), 146.2, 137.1, 135.2 (d, *J* = 2.9 Hz), 130.3 (d, *J* = 8.0 Hz), 128.9, 121.8, 115.5 (d, *J* = 21.1 Hz), 114.2, 103.6, 45.2, 34.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.6. HRMS (ESI) m/z calcd for $C_{26}H_{25}F_2N_2$ $[M+H]^+$:403.1980; found 403.1969.

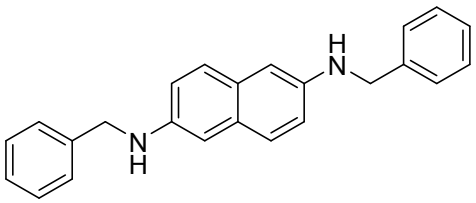
(31)



N^2,N^6-bis(4-methylphenethyl)naphthalene-2,6-diamine (4hj). Brown oil (52.8 mg, 67% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 30/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.21 (m, 8H), 6.78 (d, *J* = 1.8 Hz, 2H),

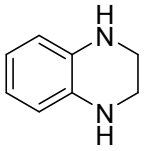
6.66 (dd, *J* = 8.3, 2.0 Hz, 2H), 3.55 (t, *J* = 6.7 Hz, 4H), 3.02 (t, *J* = 6.7 Hz, 4H), 2.44 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 137.0, 136.4, 136.0, 129.4, 128.8, 121.7, 114.2, 103.6, 45.3, 34.9, 21.2. HRMS (ESI) m/z calcd for $C_{28}H_{30}N_2Na$ $[M+Na]^+$: 417.2301; found 417.2280.

(32)



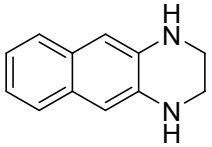
N^2,N^6-dibenzylnaphthalene-2,6-diamine (4aj). Brown oil (45.3 mg, 67% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 30/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 4H), 7.37 (t, *J* = 7.5 Hz, 4H), 7.32 (d, *J* = 7.3 Hz, 2H), 6.76 – 6.67 (m, 2H), 4.43 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 138.8, 136.6, 128.9, 128.7, 127.9, 127.4, 122.3, 114.4, 104.5, 48.8. HRMS (ESI) m/z calcd for $C_{24}H_{22}N_2Na$ $[M+Na]^+$: 361.1675; found 361.1664.

(33)



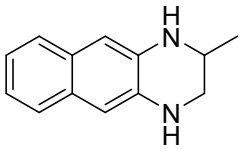
1,2,3,4-tetrahydroquinoxaline (4qk). Brown oil (9.7 mg, 36% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 (dd, *J* = 5.7, 3.4 Hz, 2H), 6.53 (dd, *J* = 5.7, 3.5 Hz, 2H), 3.45 (s, 4H), 3.08 (s, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 133.7, 118.8, 114.8, 41.4. HRMS (ESI) m/z calcd for $C_8H_{11}N_2$ $[M+H]^+$: 135.0917; found 135.0911.

(34)



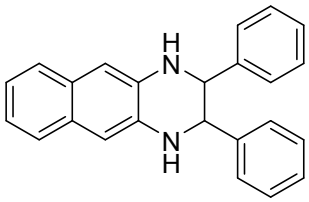
1,2,3,4-tetrahydrobenzo[g]quinoxaline (4ql). Brown oil (26.5 mg, 72% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.14 (dd, *J* = 6.2, 3.2 Hz, 2H), 6.81 (s, 2H), 3.51 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 129.0, 125.1, 122.5, 107.9, 41.1. HRMS (ESI) m/z calcd for $C_{12}H_{13}N_2$ $[M+H]^+$: 185.1073; found 185.1066.

(35)



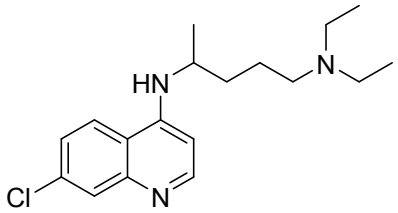
2-methyl-1,2,3,4-tetrahydrobenzo[g]quinoxaline (4rl). Brown oil (26.1 mg, 66% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.17 – 7.12 (m, 2H), 6.80 (d, *J* = 1.7 Hz, 2H), 3.64 (ddd, *J* = 8.6, 6.3, 3.0 Hz, 1H), 3.40 (dd, *J* = 10.6, 3.1 Hz, 1H), 3.15 (dd, *J* = 10.6, 8.5 Hz, 1H), 1.26 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 134.8, 129.0, 128.9, 125.2, 125.1, 122.5, 122.4, 107.6, 107.4, 47.9, 45.7, 19.9. HRMS (ESI) m/z calcd for $C_{13}H_{15}N_2$ $[M+H]^+$: 199.1230; found 199.1222.

(36)



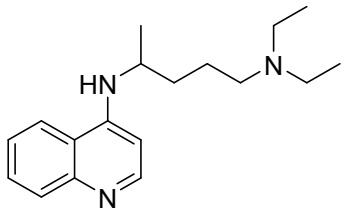
2,3-diphenyl-1,2,3,4-tetrahydrobenzo[g]quinoxaline (4sl). Brown oil (43.6 mg, 65% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.27 (dd, *J* = 5.7, 4.6 Hz, 6H), 7.21 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.14 (dd, *J* = 7.2, 1.8 Hz, 4H), 6.94 (s, 2H), 4.39 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 135.0, 128.9, 128.3, 128.1, 127.9, 125.3, 122.8, 107.6, 62.1. HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2$ $[M+H]^+$: 337.1699; found 337.1690.

(37)



Chloroquine (4tm). Yellow solid (53.6 mg, 56% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 8/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 4.9, 2.7 Hz, 1H), 7.89 (d, *J* = 2.2 Hz, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.27 (d, *J* = 1.7 Hz, 1H), 6.38 (dd, *J* = 4.8, 2.5 Hz, 1H), 5.41 (s, 1H), 3.66 (s, 1H), 2.48 (dd, *J* = 6.9, 3.1 Hz, 4H), 2.43 – 2.36 (m, 2H), 1.73 – 1.65 (m, 1H), 1.59 (dd, *J* = 18.7, 3.4 Hz, 3H), 1.26 (dt, *J* = 5.8, 4.1 Hz, 3H), 1.00 – 0.94 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 149.4, 149.1, 134.7, 128.7, 124.9, 121.4, 117.4, 99.3, 52.5, 48.3, 46.8, 34.5, 23.8, 20.1, 11.4. HRMS (ESI) m/z calcd for $C_{18}H_{27}ClN_3$ $[M+H]^+$: 320.1888; found 320.1881.

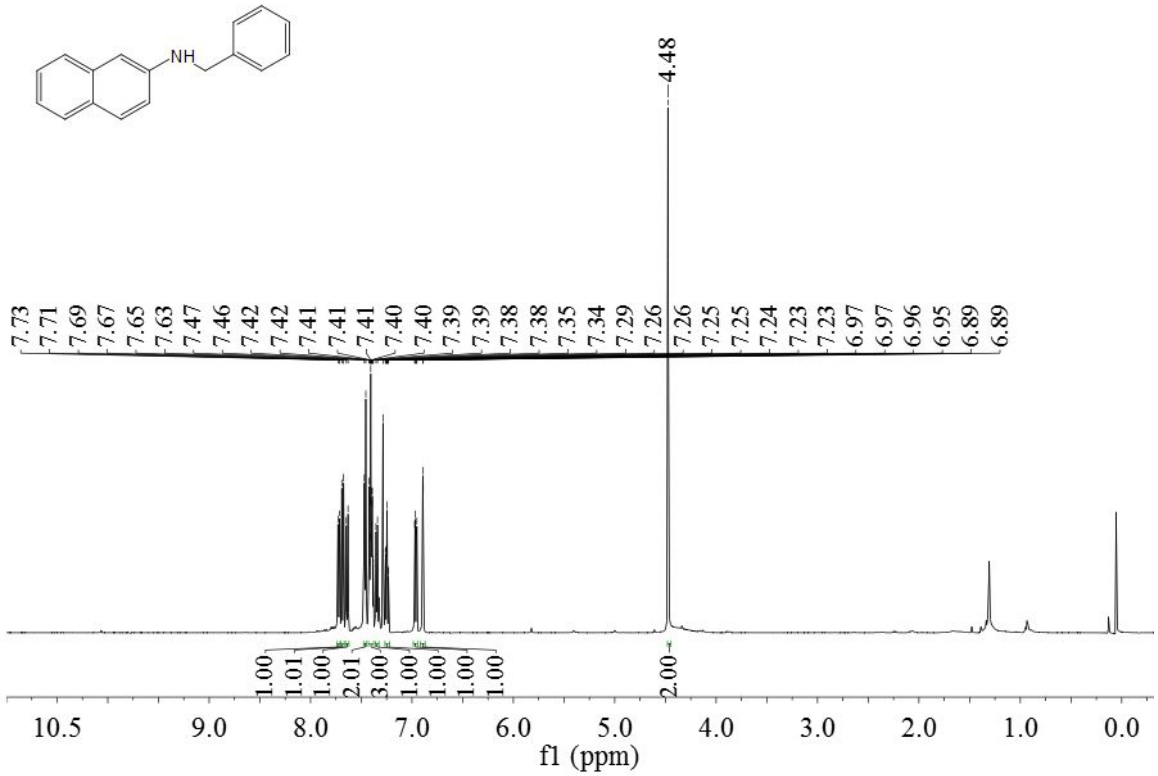
(38)



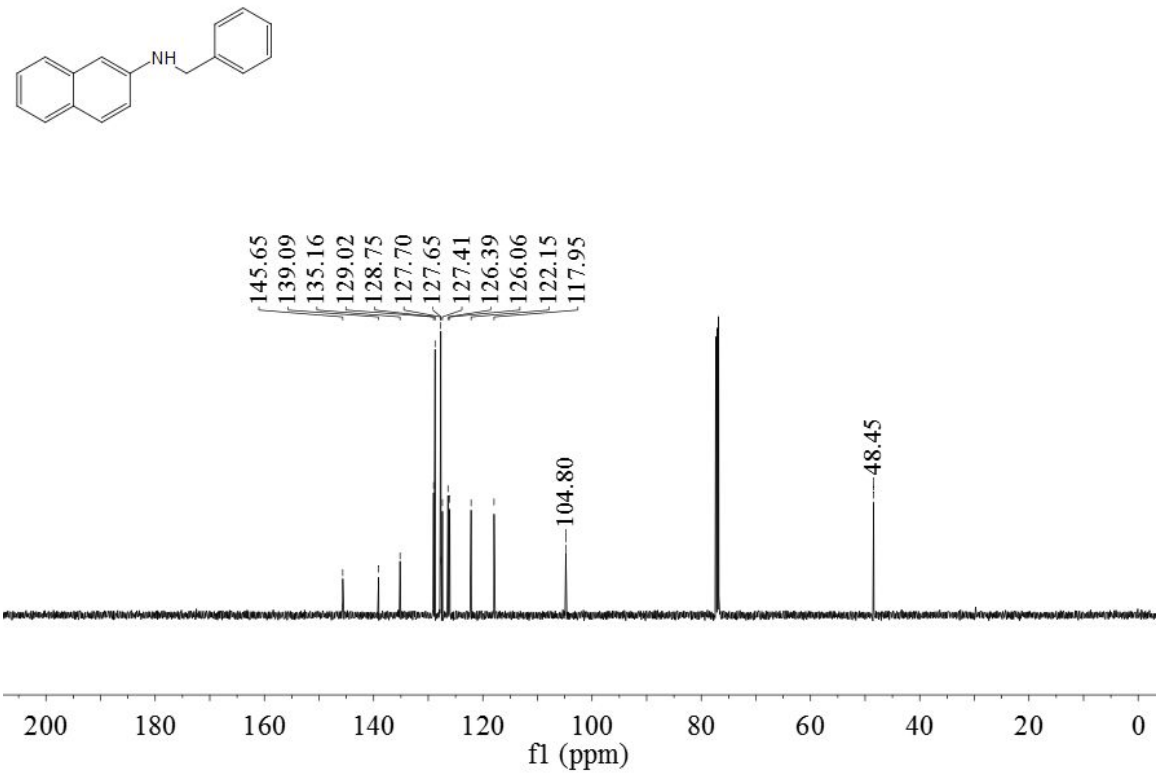
***N*^{1},*N*^{1}-diethyl-*N*^{4}-(quinolin-4-yl)pentane-1,4-diamine (4tm').** Yellow oil (10.3 mg, 12% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 8/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 8.1 Hz, 1H), 6.43 (d, *J* = 5.5 Hz, 1H), 5.37 (s, 1H), 3.77 – 3.72 (m, 1H), 2.61 (q, *J* = 7.2 Hz, 4H), 2.53 (t, *J* = 6.0 Hz, 2H), 1.72 – 1.64 (m, 4H), 1.33 (d, *J* = 6.3 Hz, 3H), 1.06 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 149.3, 148.0, 129.4, 129.2, 124.6, 119.8, 118.8, 98.8, 52.5, 48.3, 46.8, 34.3, 23.4, 20.3, 10.9. HRMS (ESI) m/z calcd for $C_{18}H_{28}N_3$ $[M+H]^+$: 286.2278; found 286.2277.

7. NMR spectra of products

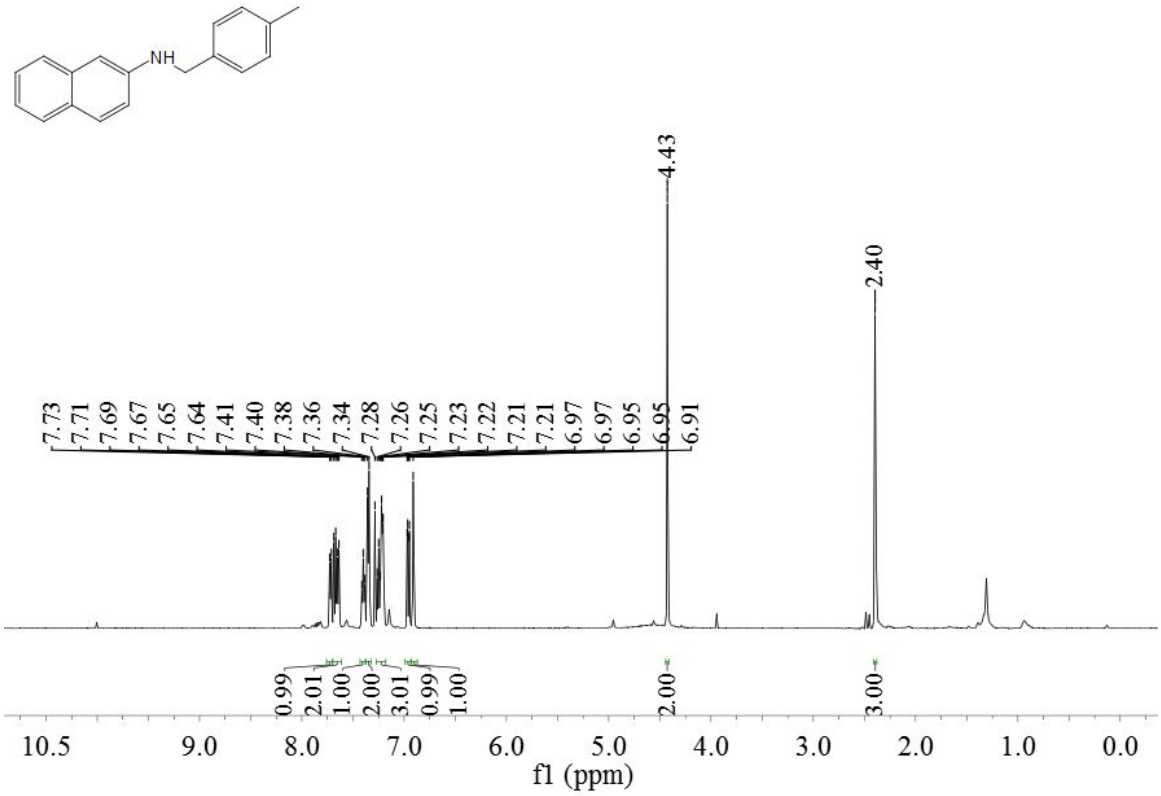
^{1}H NMR spectra of 3aa (500 MHz, $CDCl_3$)



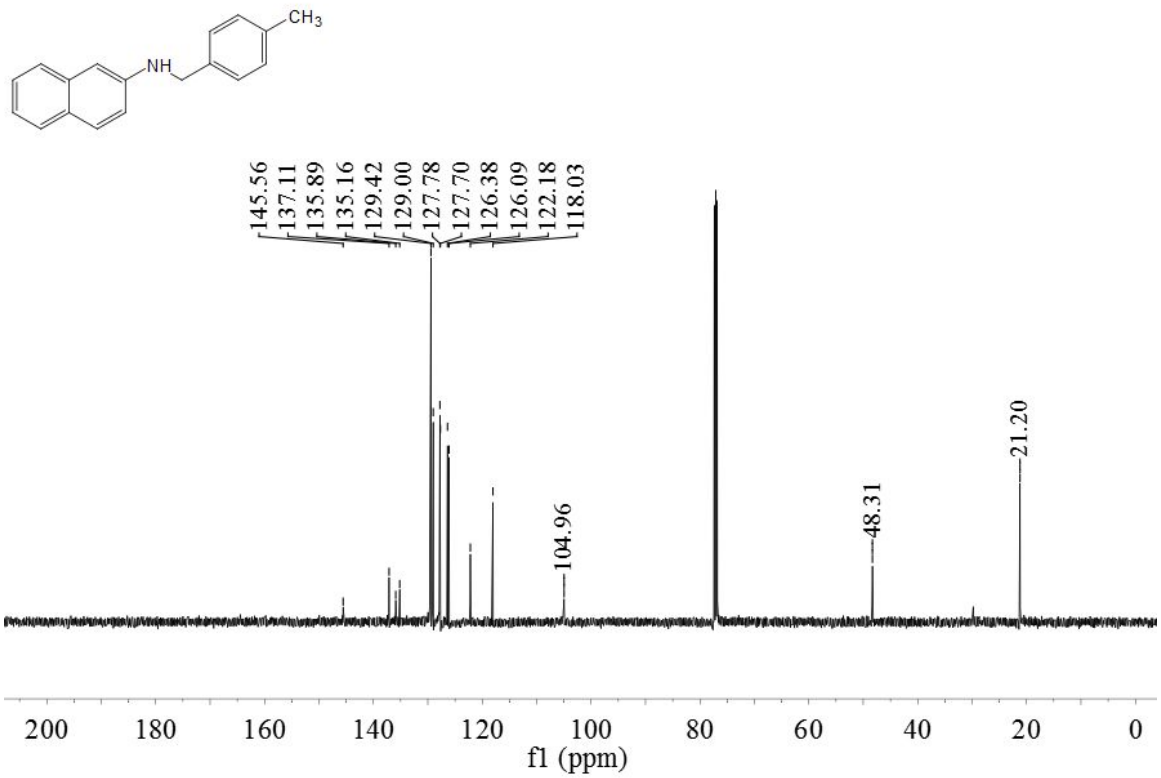
^{13}C NMR spectra of 3aa (126 MHz, $CDCl_3$)



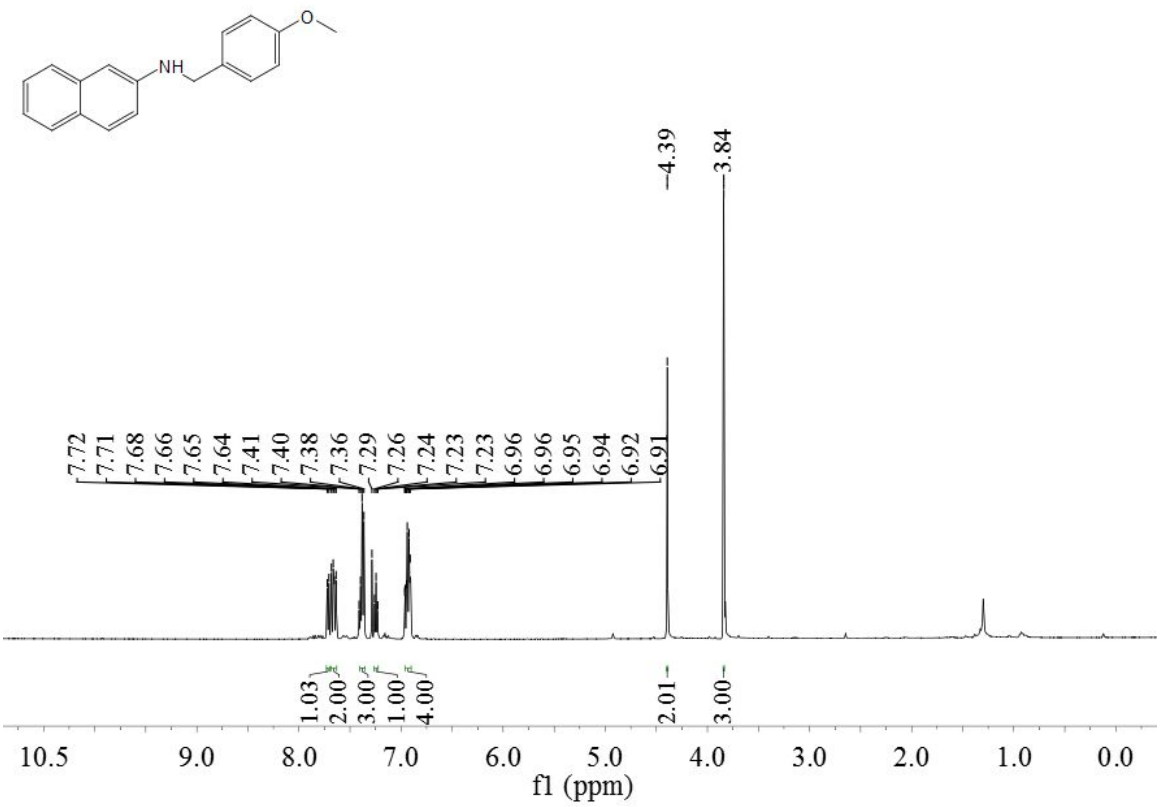
^{1}H NMR spectra of 3ba (500 MHz, $CDCl_3$)



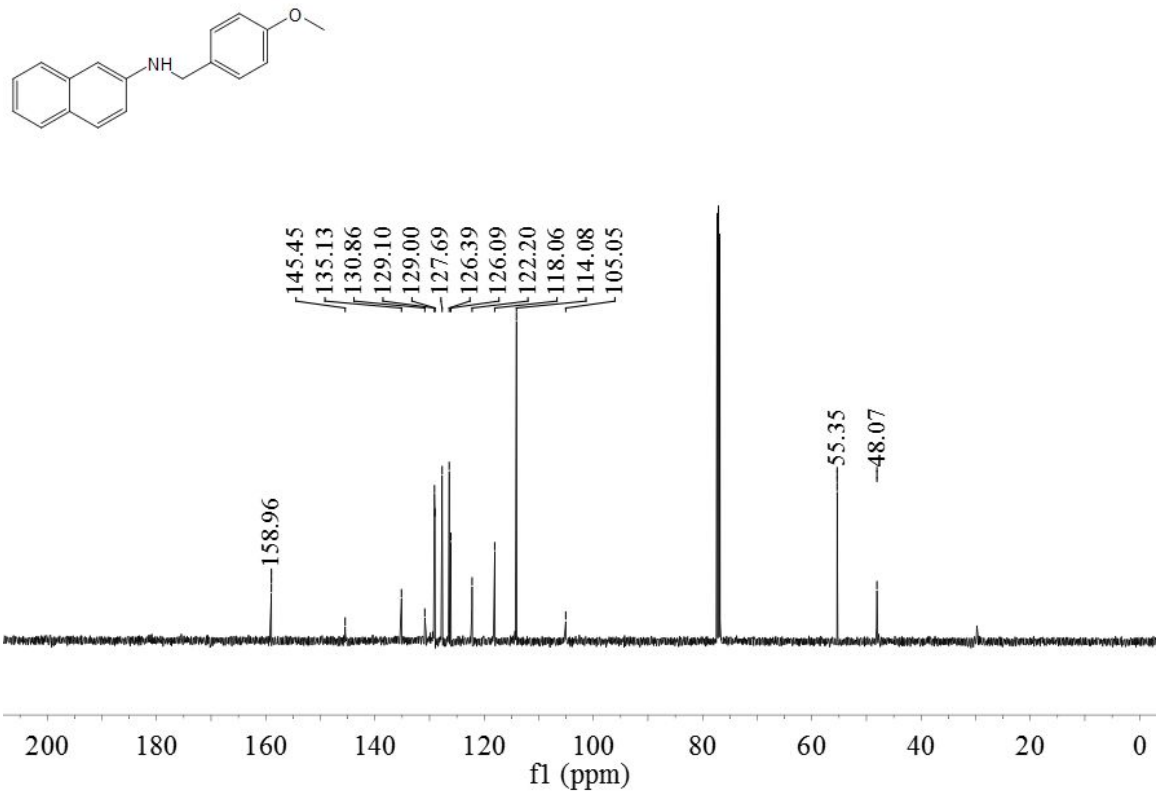
^{13}C NMR spectra of 3ba (126 MHz, $CDCl_3$)



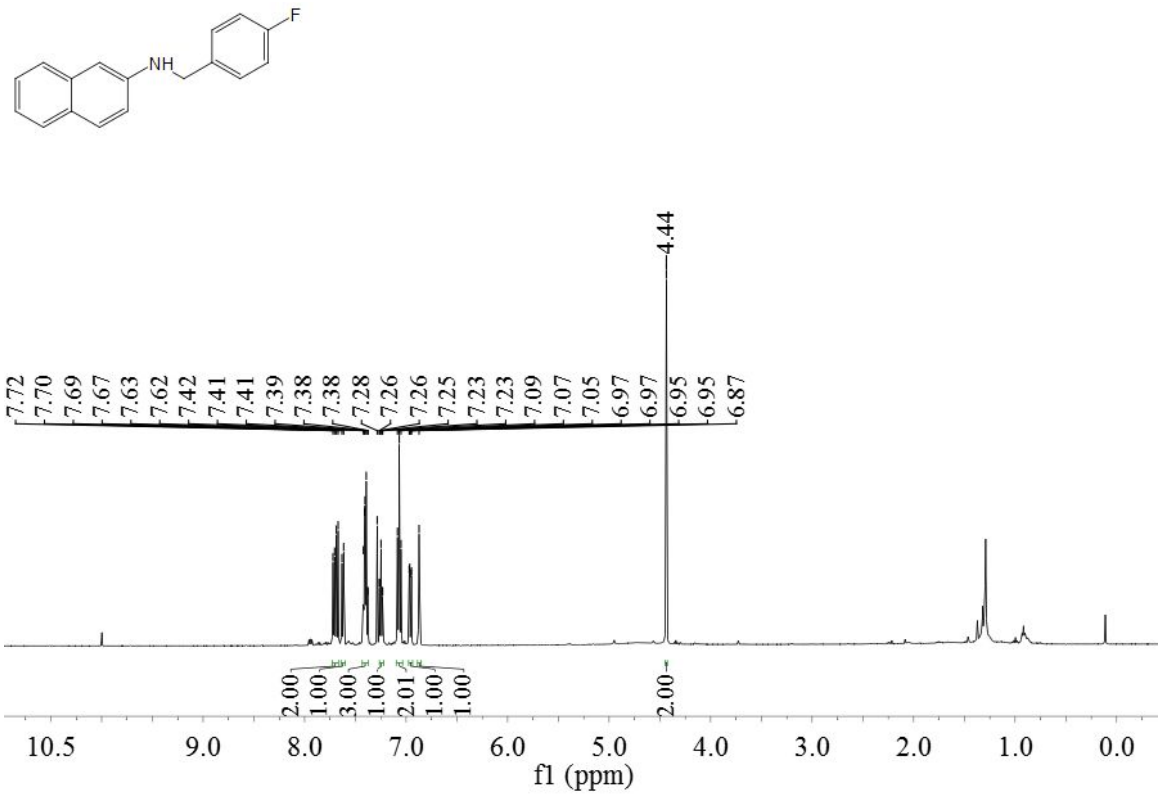
^{1}H NMR spectra of 3ca (500 MHz, $CDCl_3$)



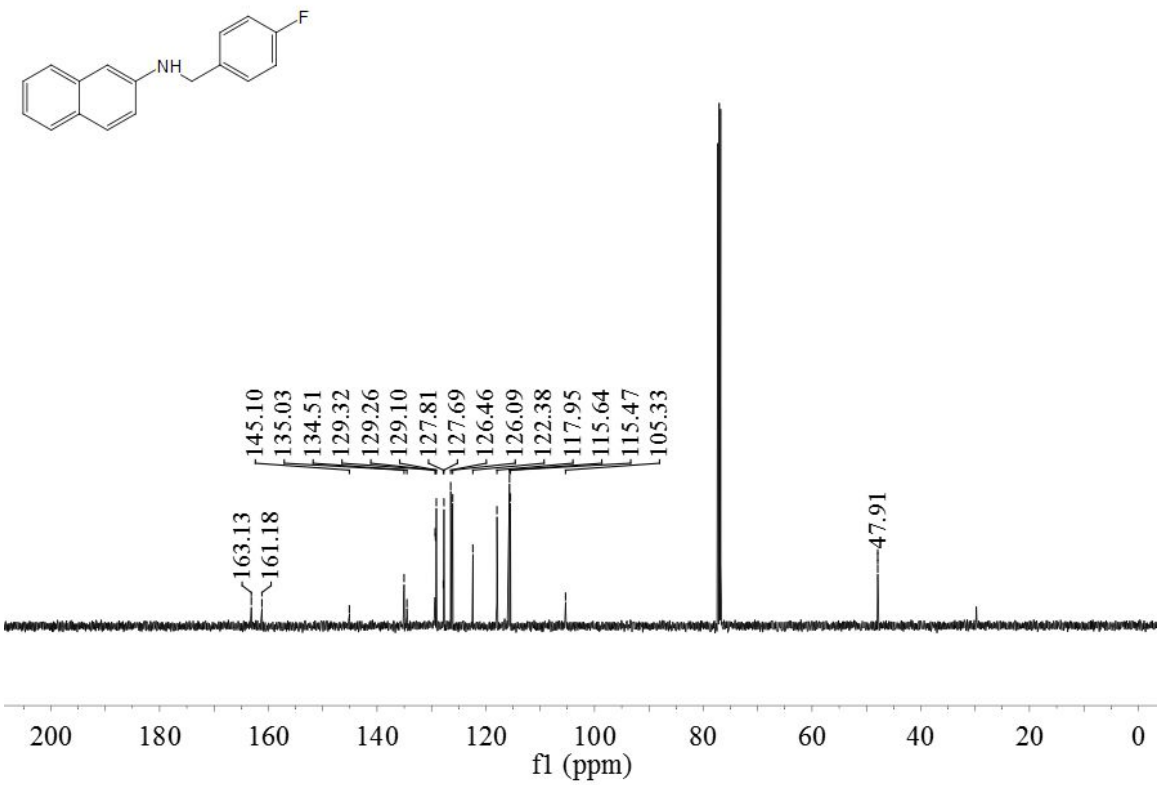
^{13}C NMR spectra of 3ca (126 MHz, $CDCl_3$)



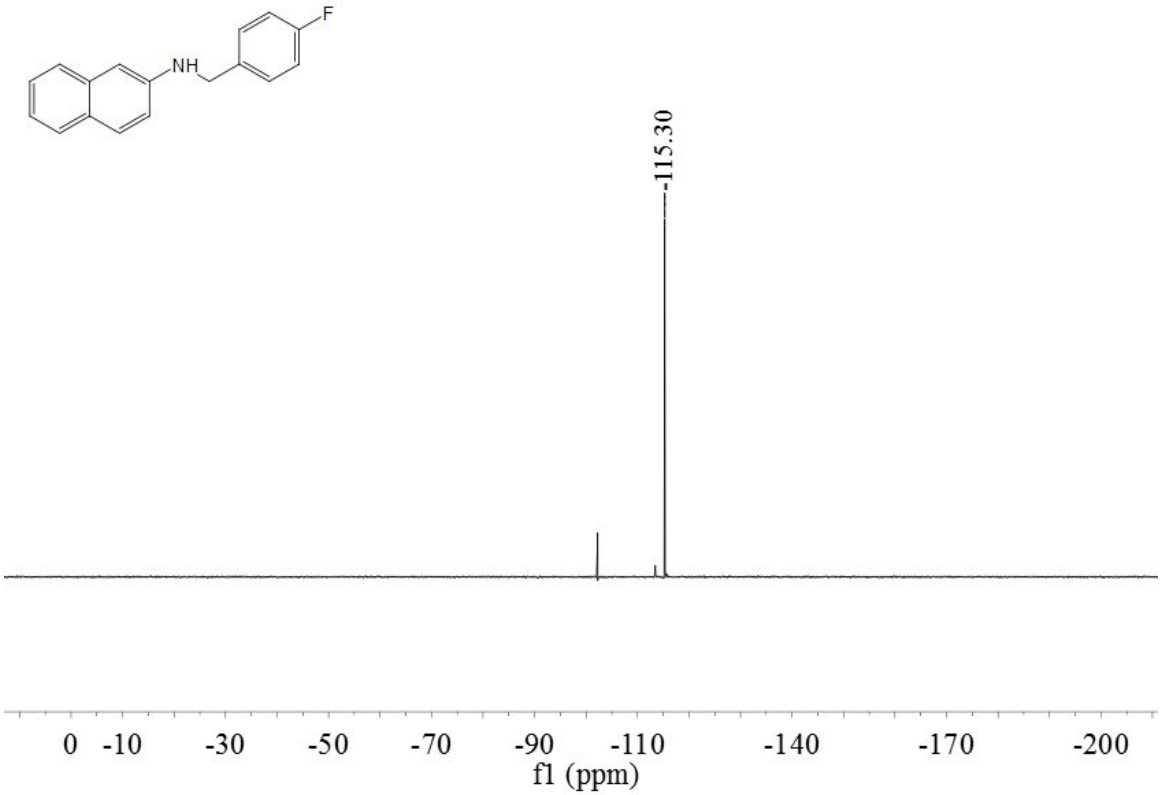
^{1}H NMR spectra of 3da (500 MHz, $CDCl_3$)



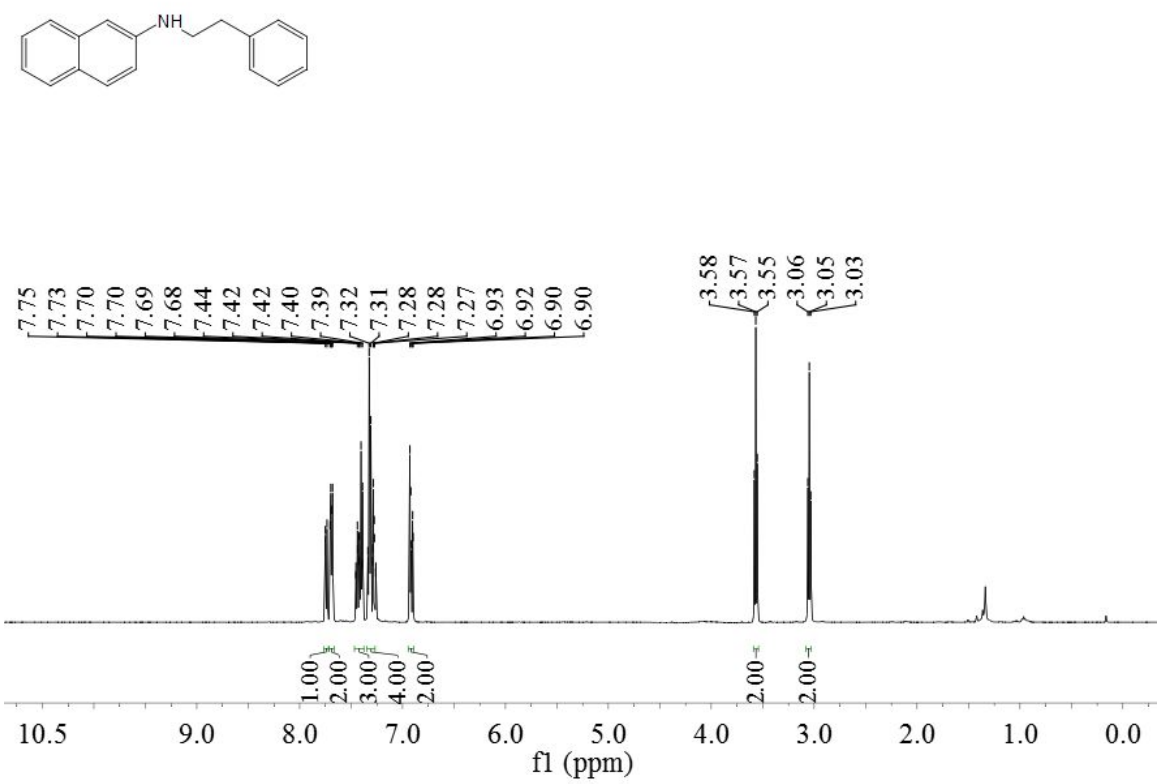
^{13}C NMR spectra of 3da (126 MHz, $CDCl_3$)



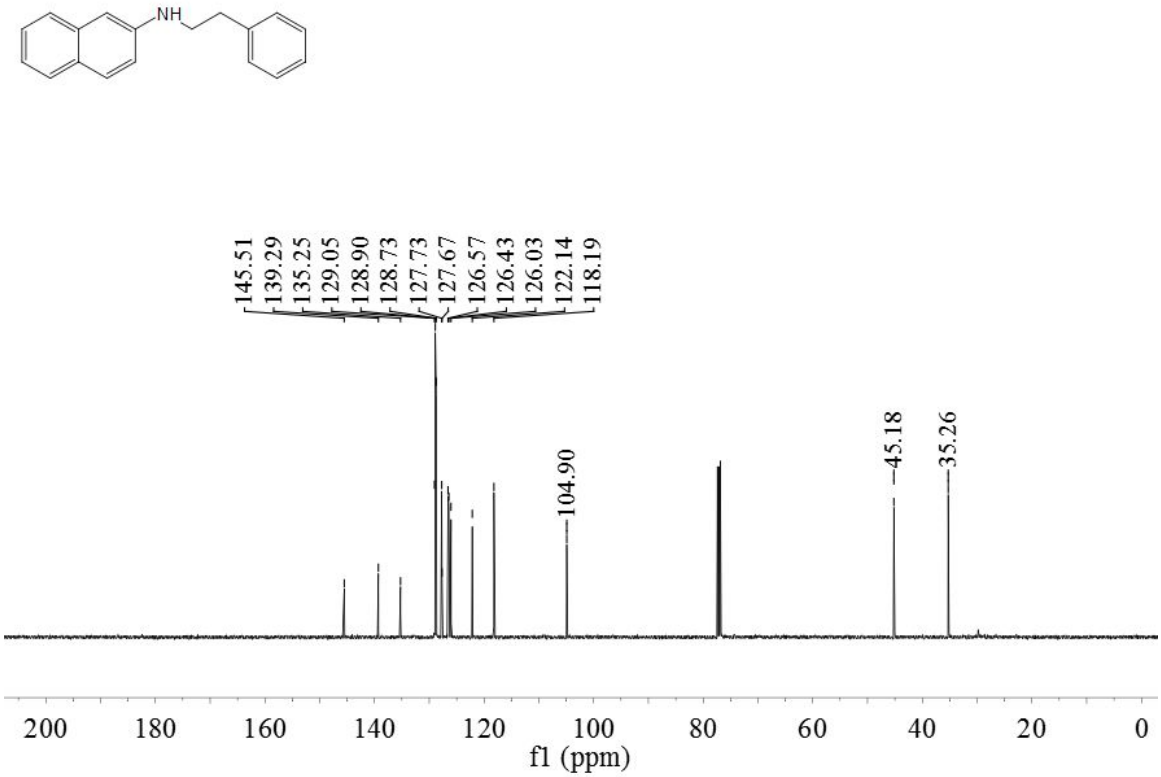
^{19}F NMR spectra of 3da (471 MHz, $CDCl_3$)



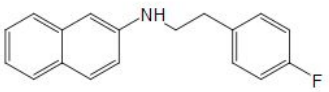
^{1}H NMR spectra of 3ea (500 MHz, $CDCl_3$)

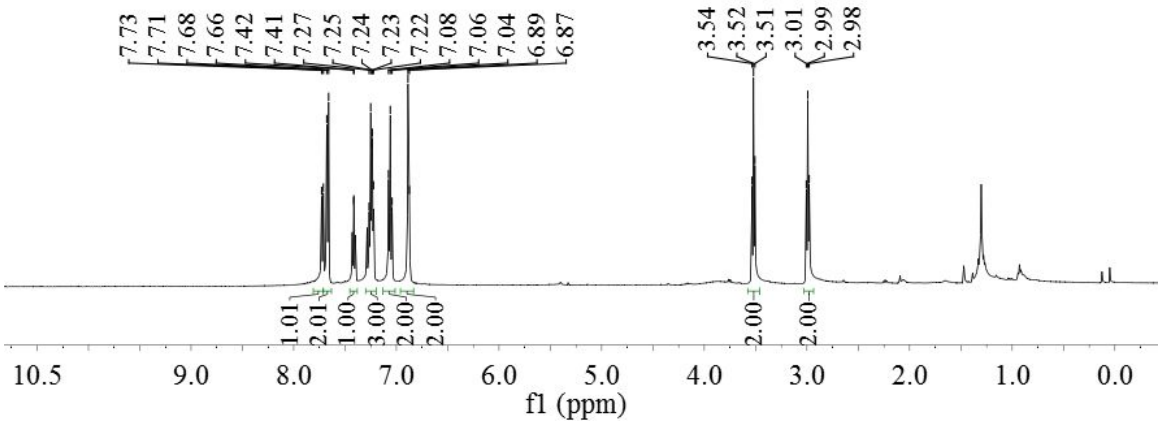


^{13}C NMR spectra of 3ea (126 MHz, $CDCl_3$)

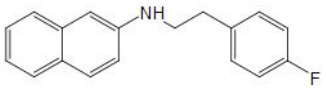


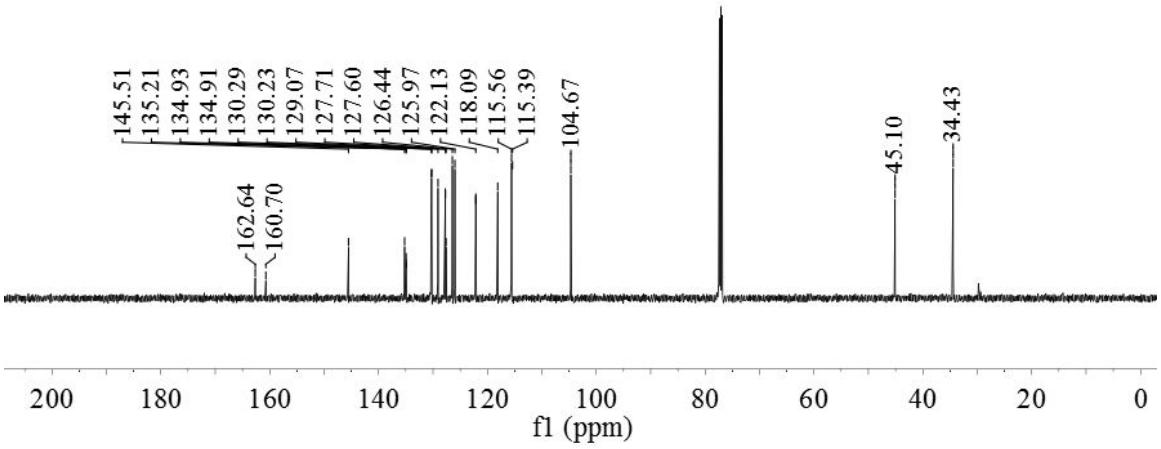
^{1}H NMR spectra of 3fa (500 MHz, $CDCl_3$)



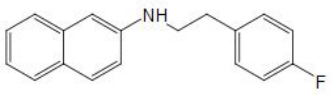


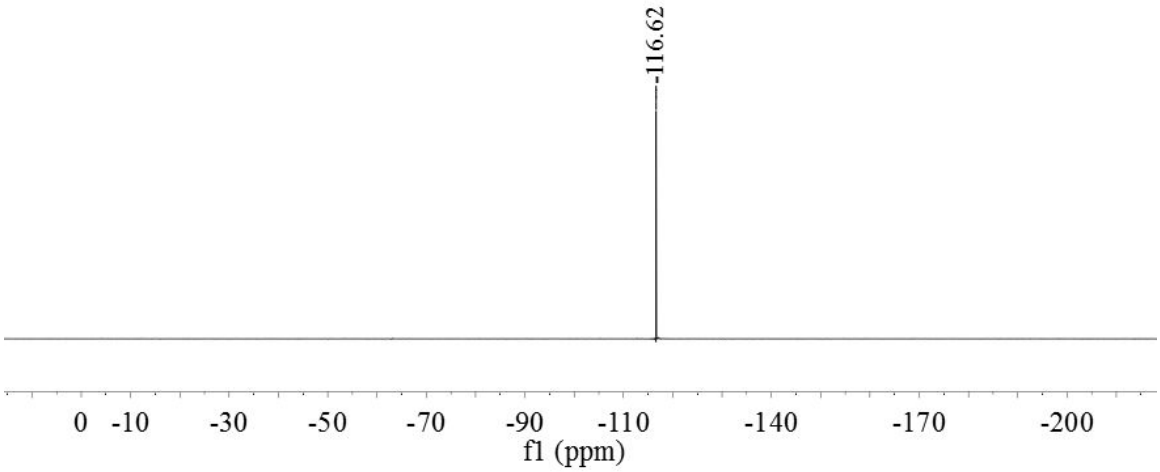
^{13}C NMR spectra of 3fa (126 MHz, $CDCl_3$)



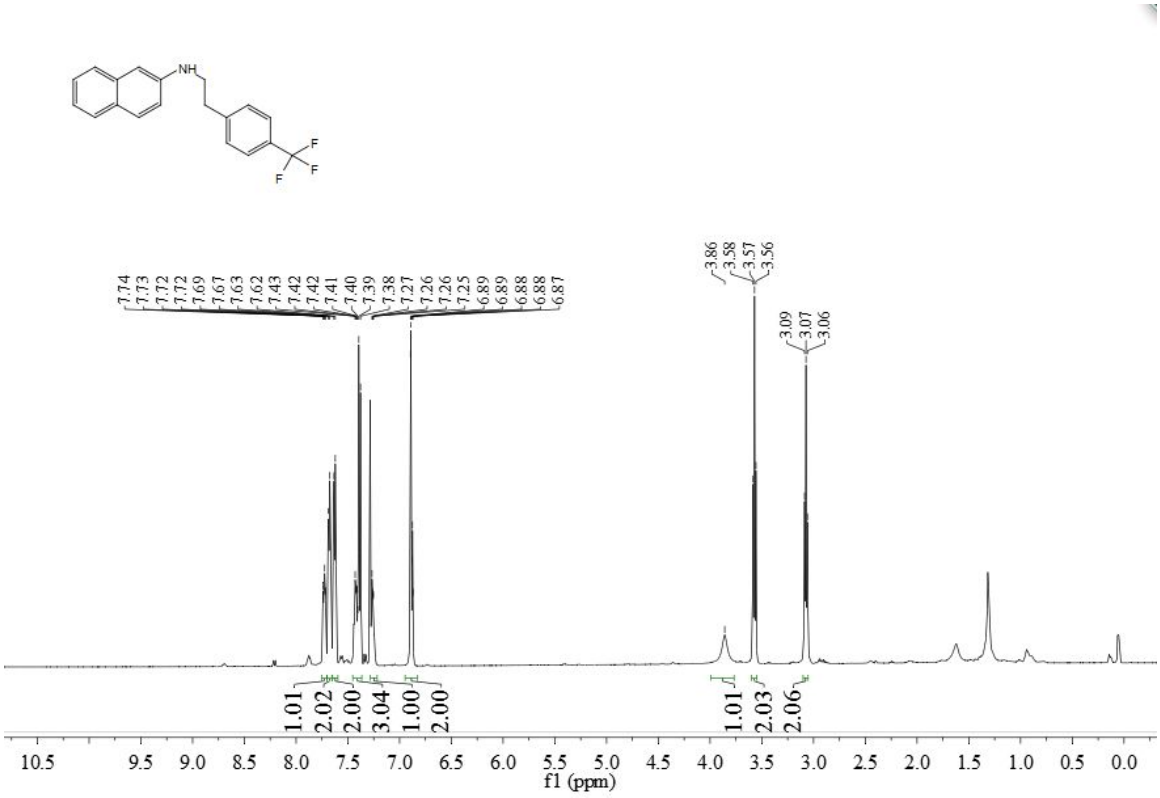


^{19}F NMR spectra of 3fa (471 MHz, $CDCl_3$)

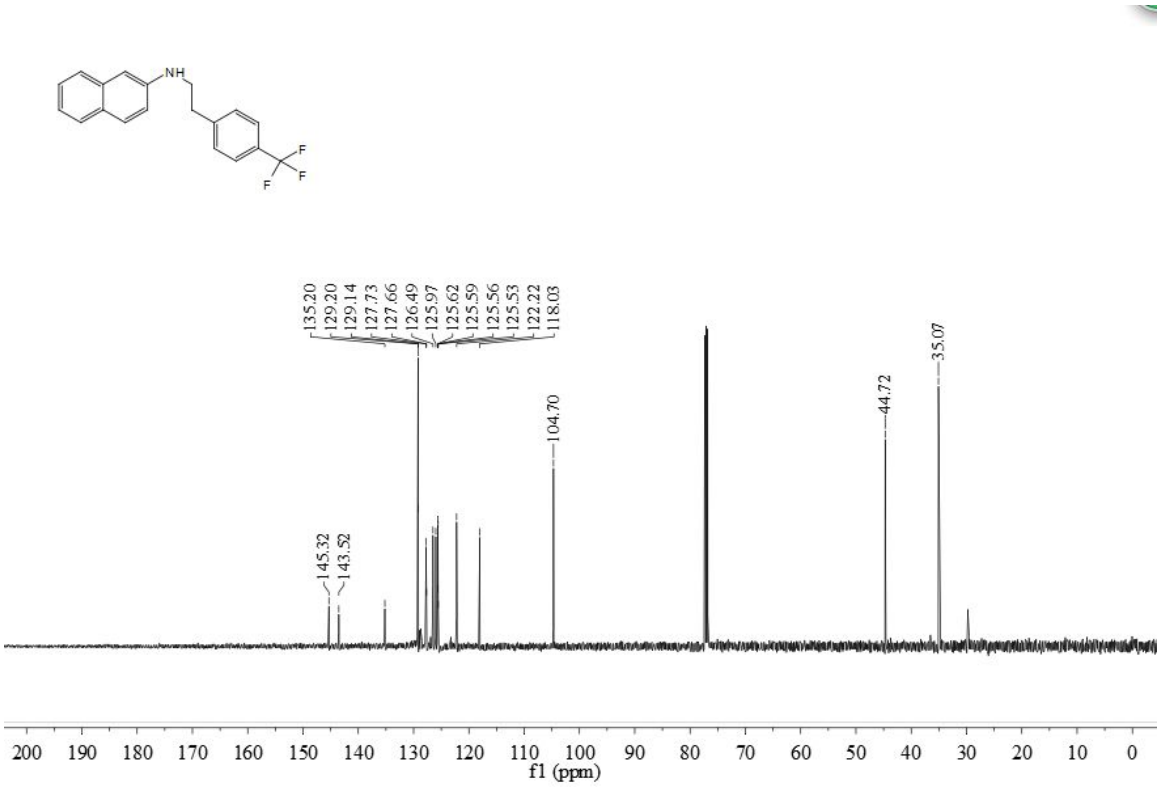




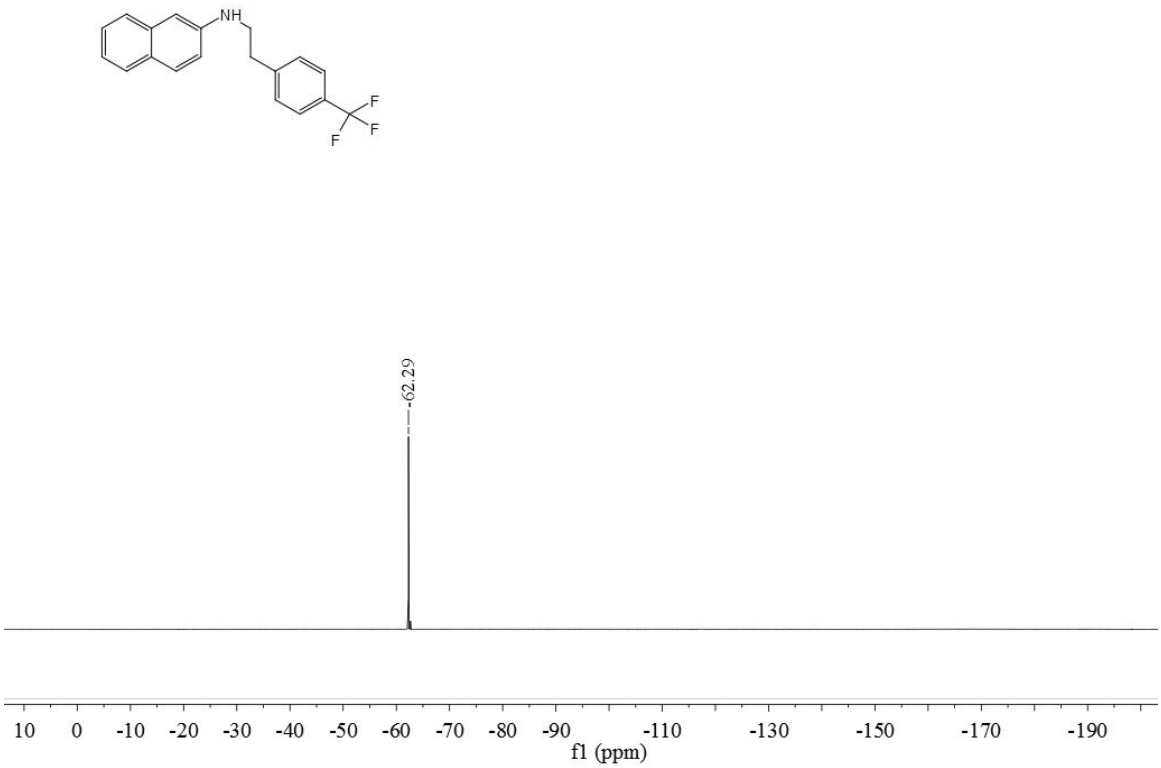
^{1}H NMR spectra of 3ga (500 MHz, $CDCl_3$)



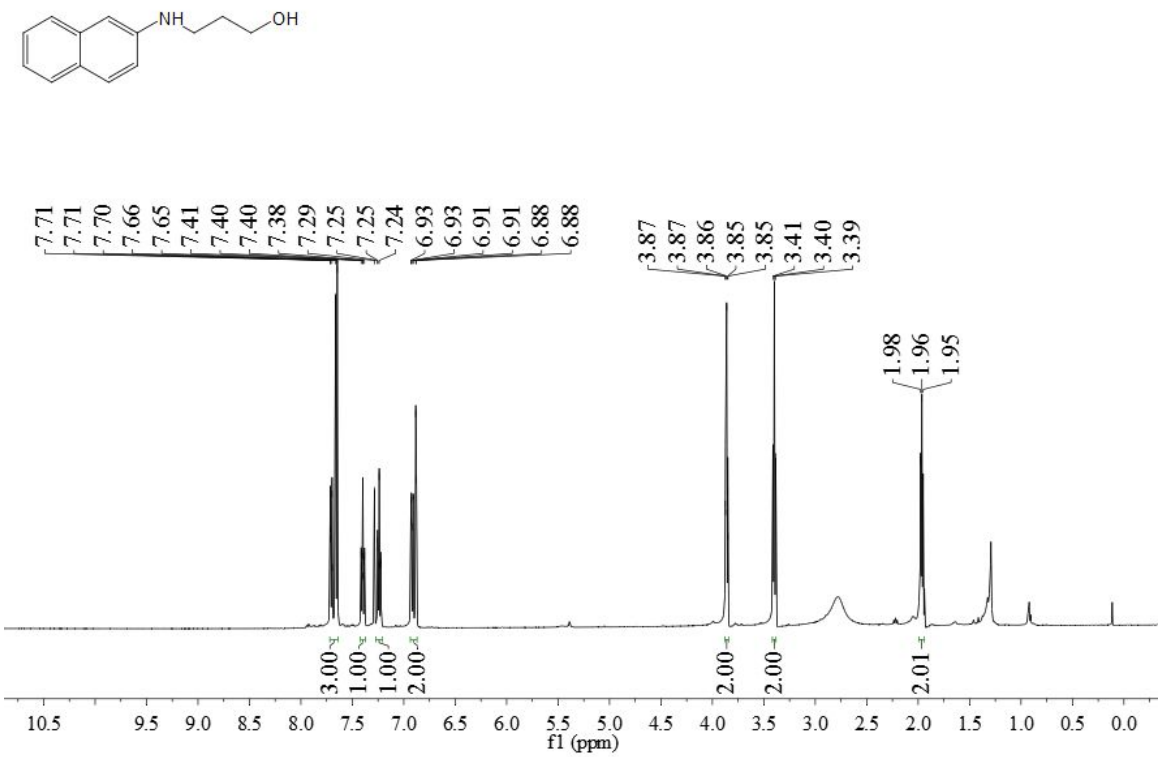
^{13}C NMR spectra of 3ga (126 MHz, $CDCl_3$)



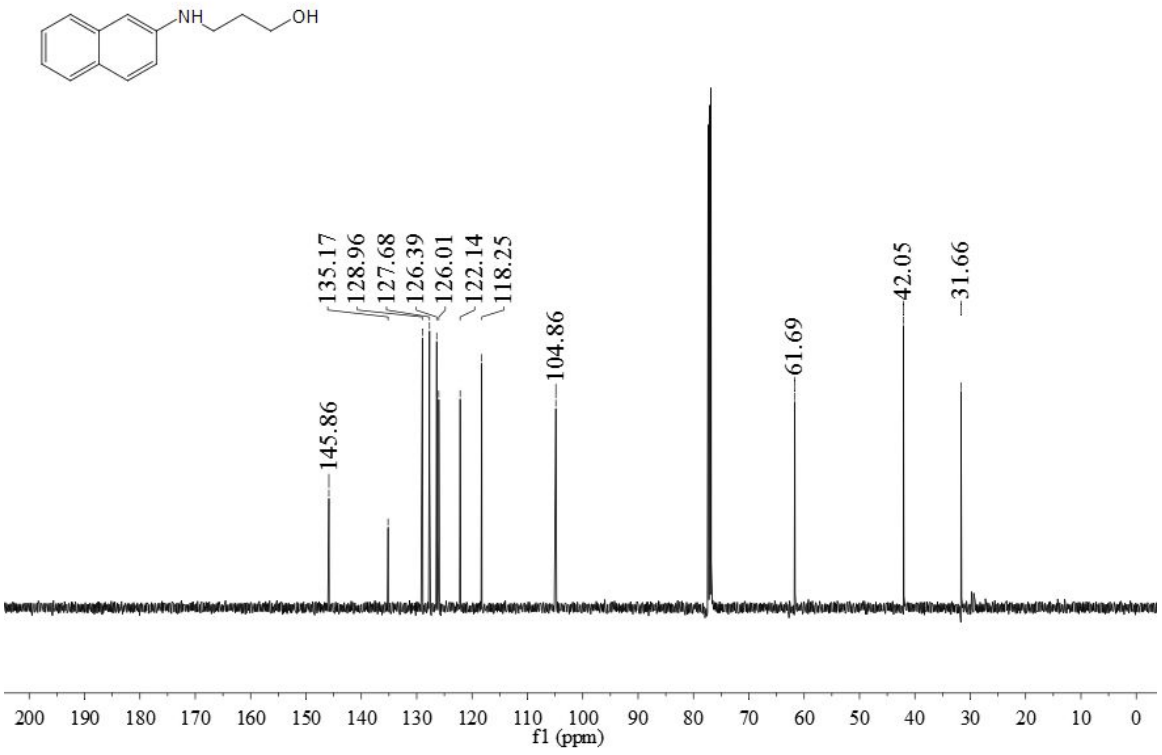
^{19}F NMR spectra of 3ga (471 MHz, $CDCl_3$)



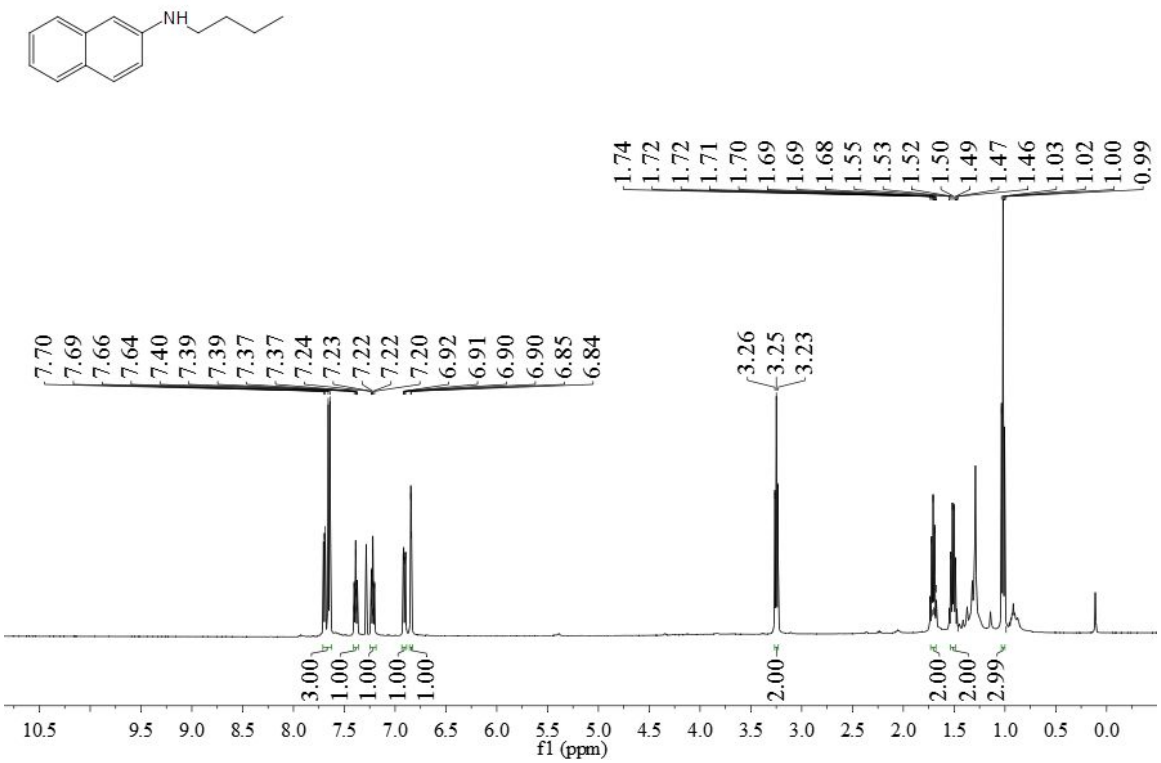
^{1}H NMR spectra of 3ha (500 MHz, $CDCl_3$)



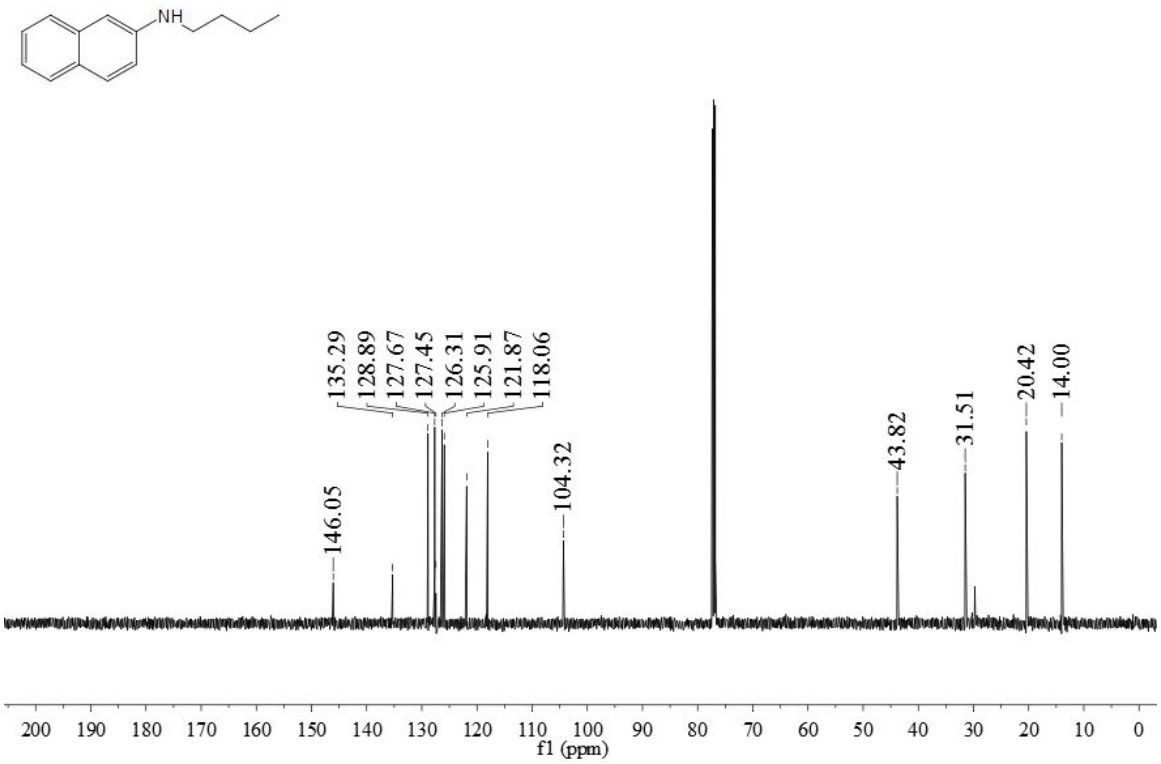
^{13}C NMR spectra of 3ha (126 MHz, $CDCl_3$)



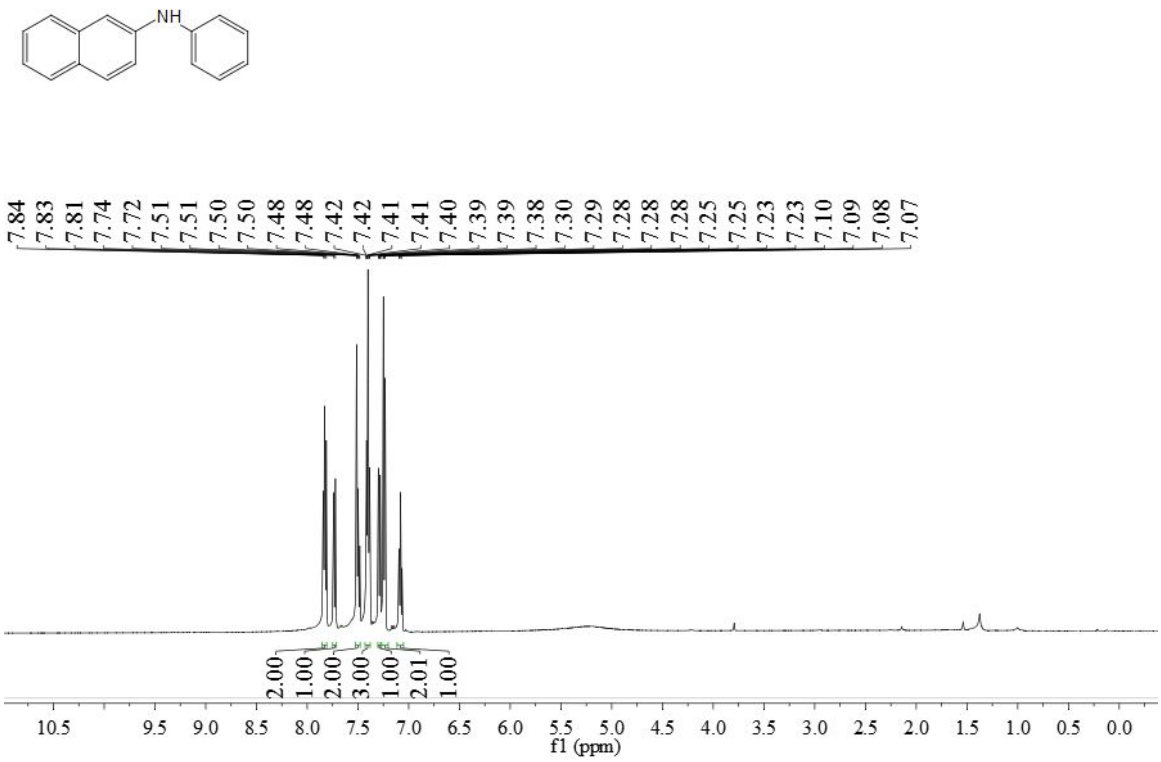
^{1}H NMR spectra of 3ia (500 MHz, $CDCl_3$)



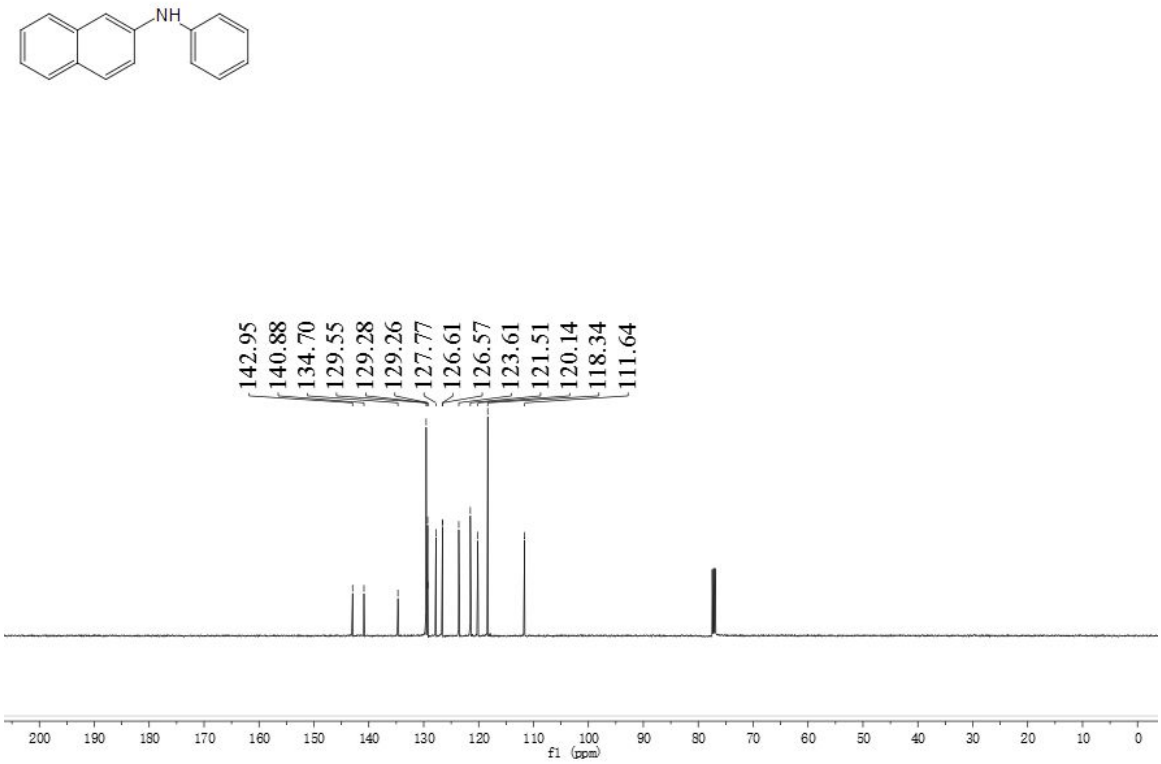
^{13}C NMR spectra of 3ia (126 MHz, $CDCl_3$)



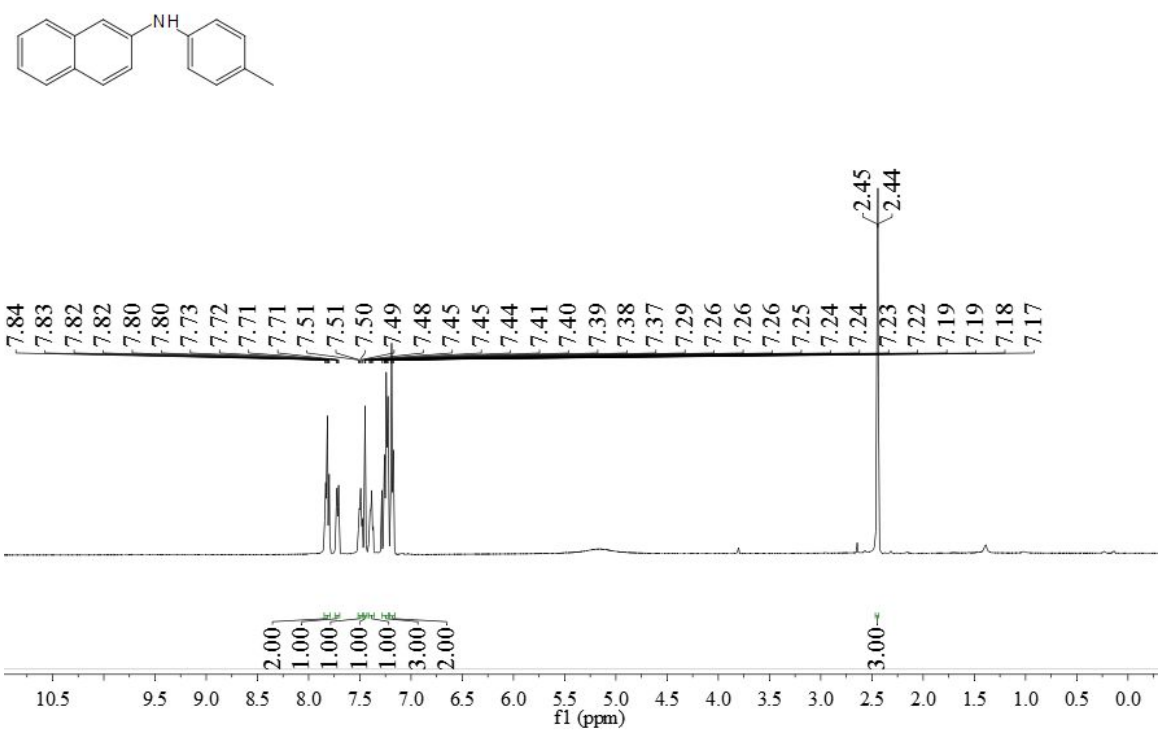
^{1}H NMR spectra of 3ja (500 MHz, $CDCl_3$)



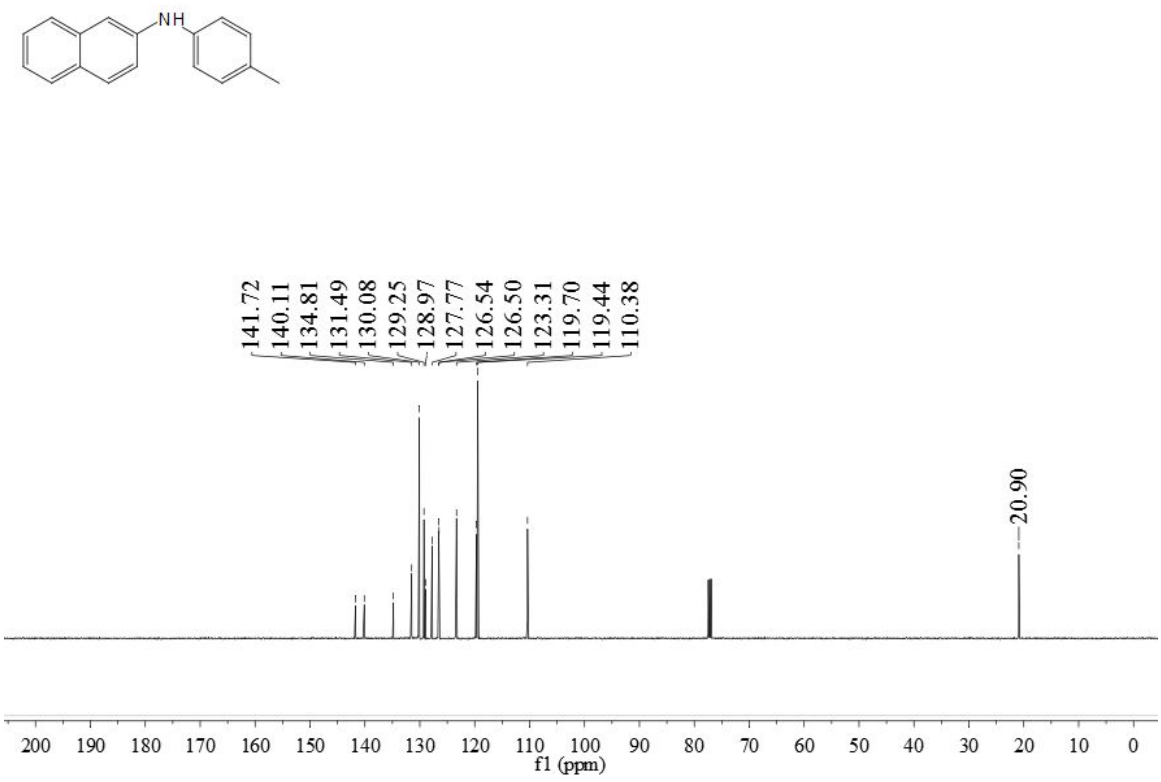
^{13}C NMR spectra of 3ja (126 MHz, $CDCl_3$)



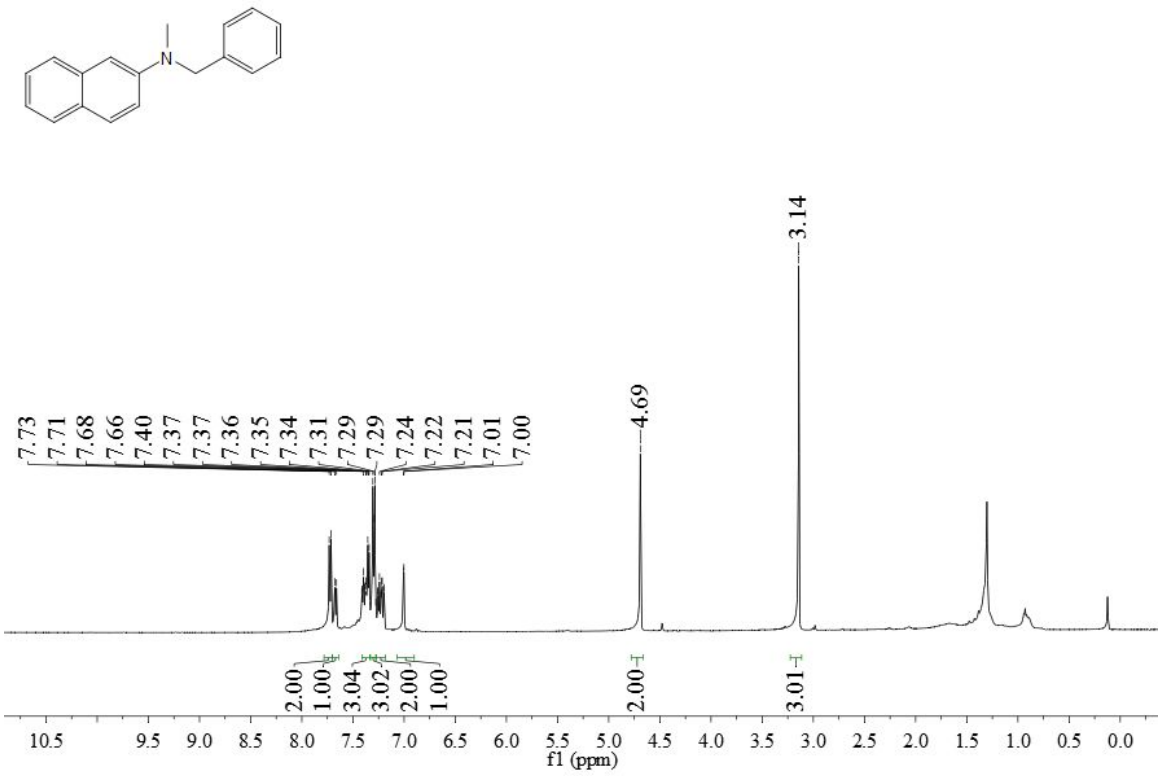
^{1}H NMR spectra of 3ka (500 MHz, $CDCl_3$)



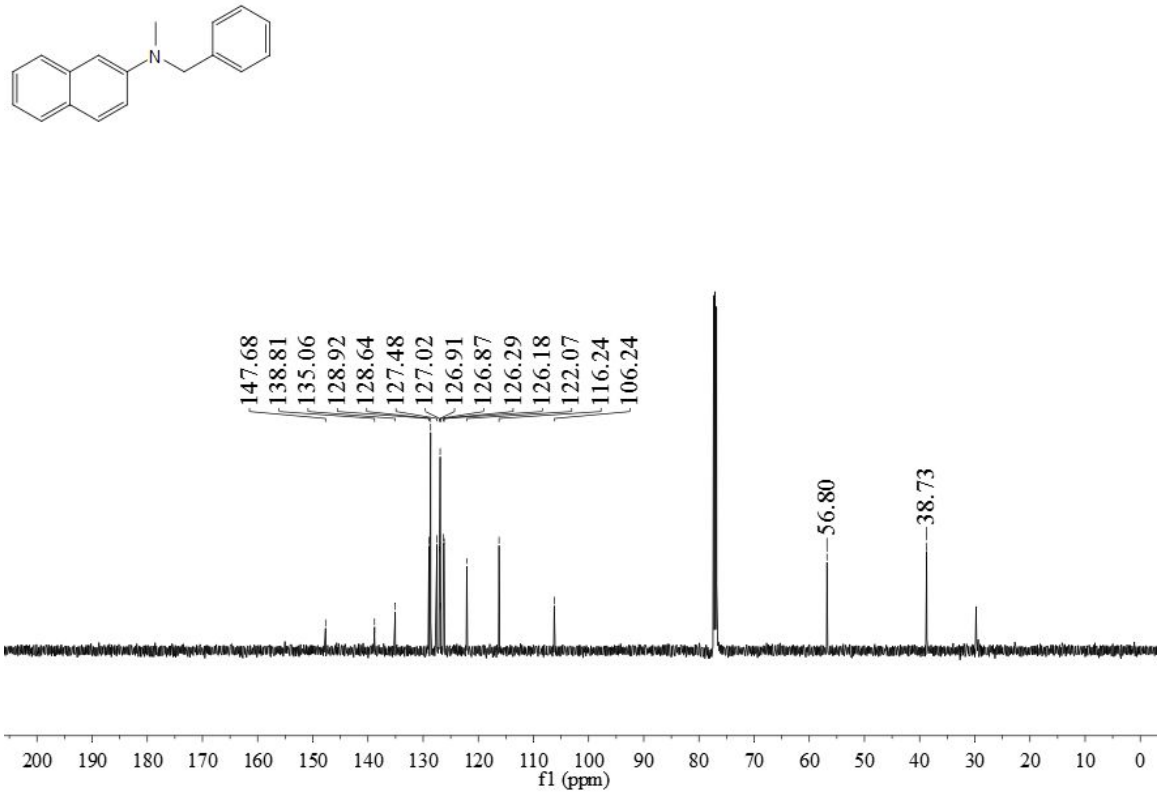
^{13}C NMR spectra of 3ka (126 MHz, $CDCl_3$)



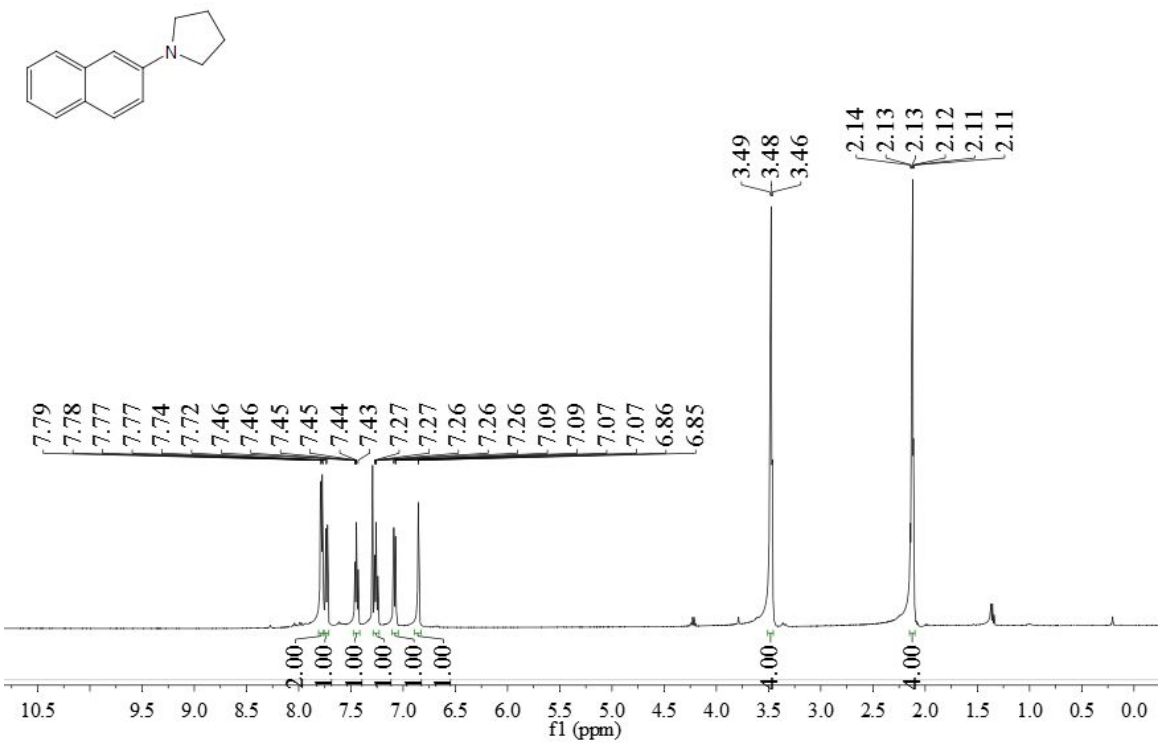
^{1}H NMR spectra of 3la (500 MHz, $CDCl_3$)



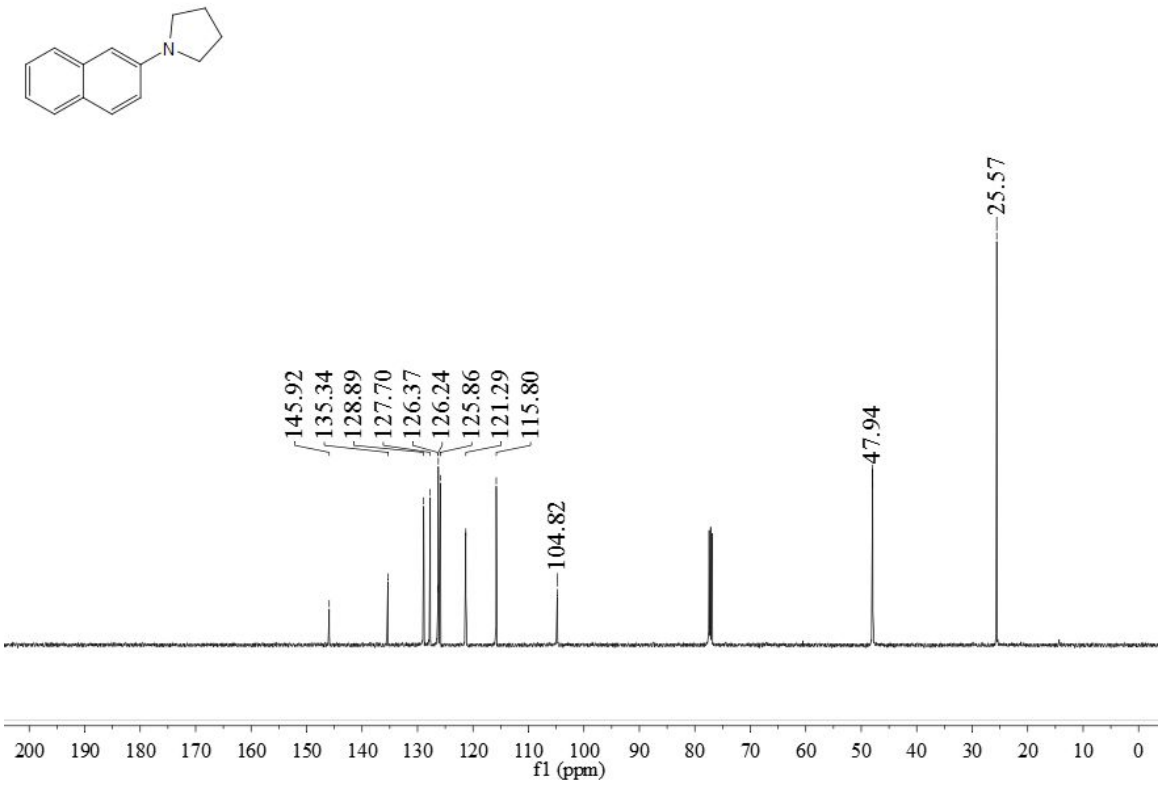
^{13}C NMR spectra of 3la (126 MHz, $CDCl_3$)



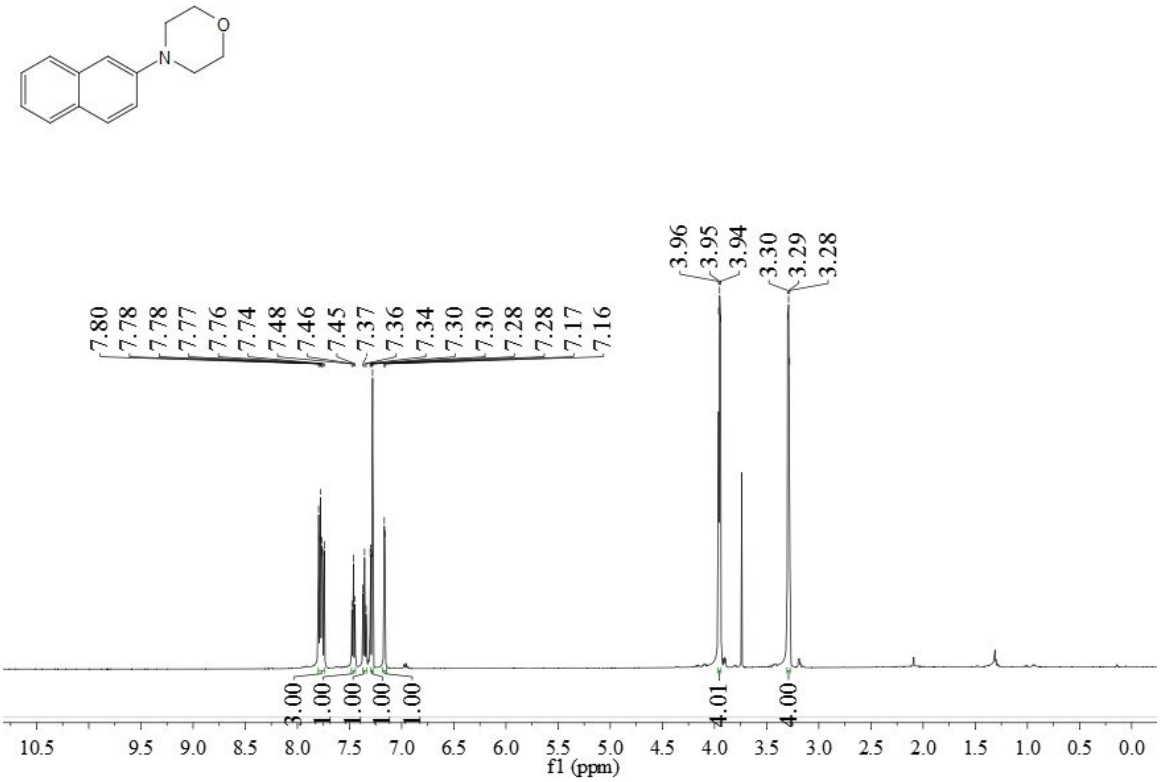
^{1}H NMR spectra of 3ma (500 MHz, $CDCl_3$)



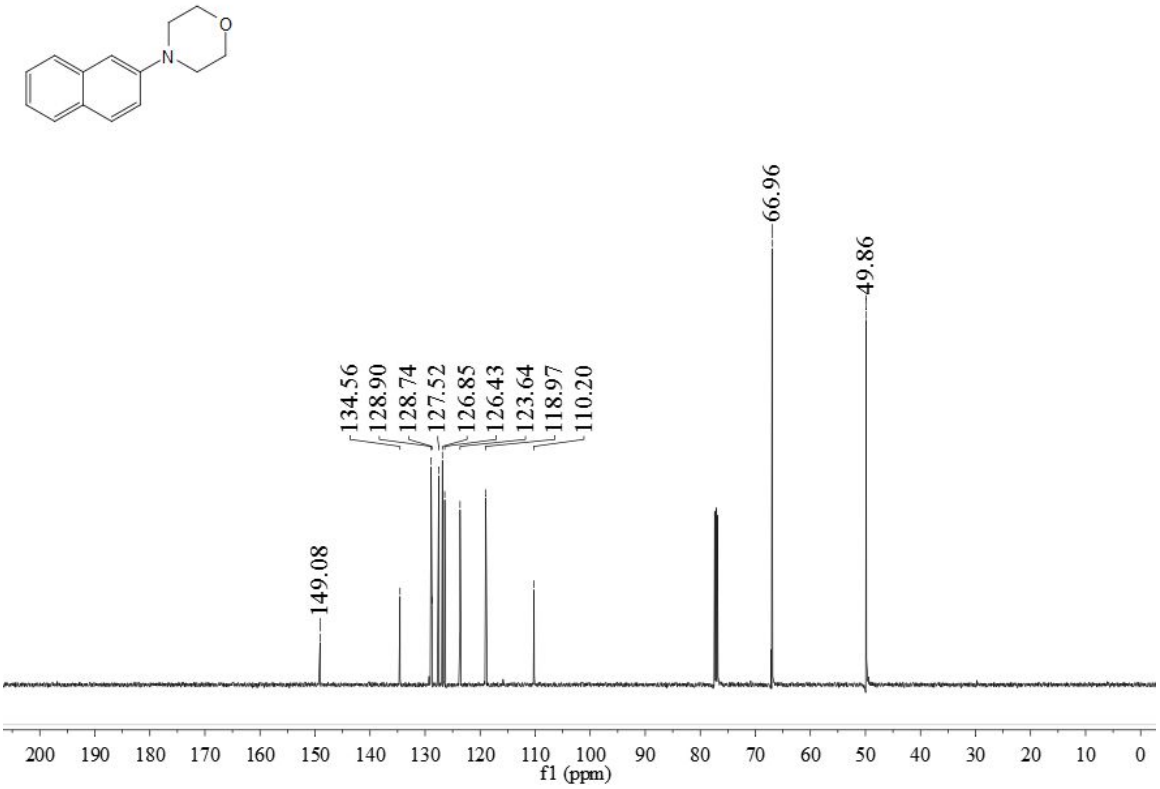
^{13}C NMR spectra of 3ma (126 MHz, $CDCl_3$)



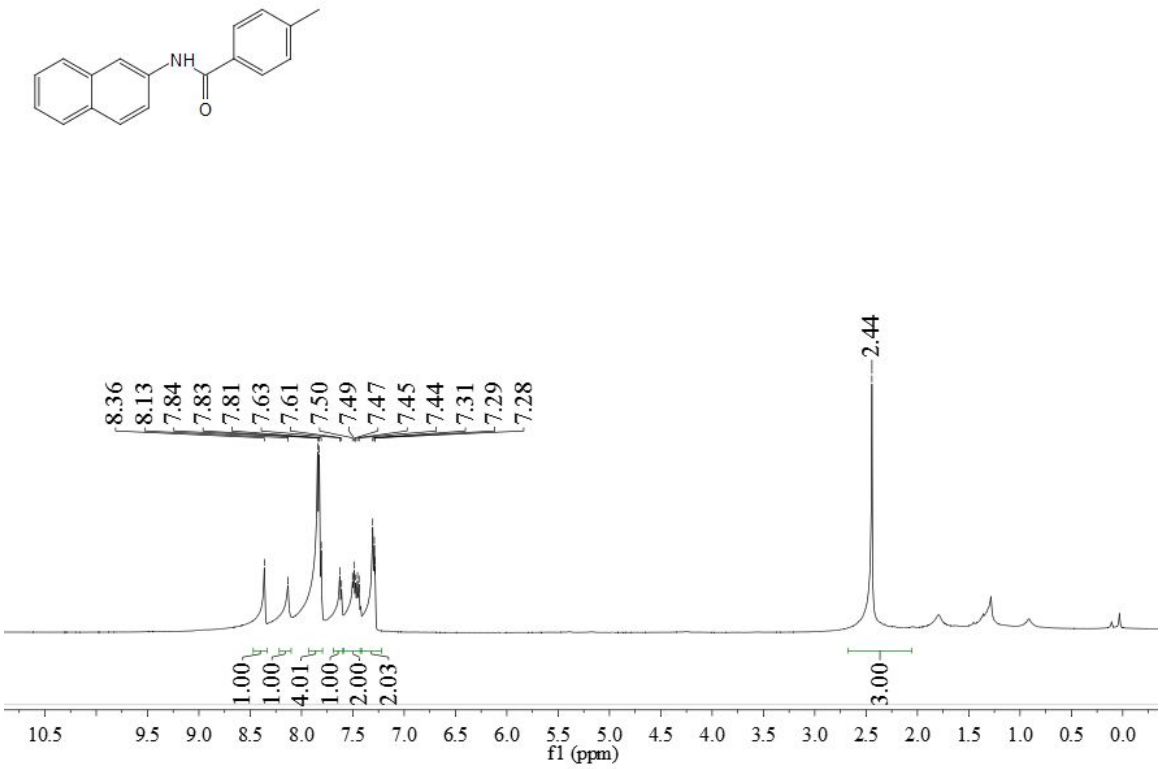
^{1}H NMR spectra of 3na (500 MHz, $CDCl_3$)



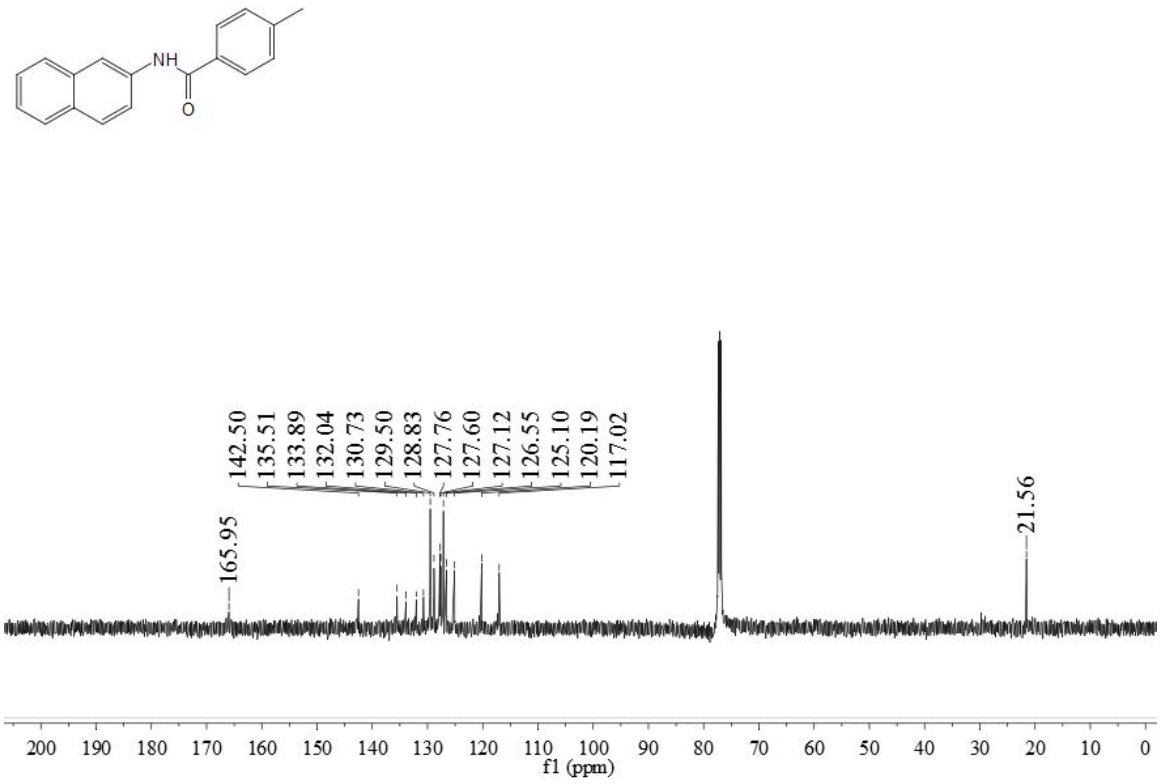
^{13}C NMR spectra of 3na (126 MHz, $CDCl_3$)



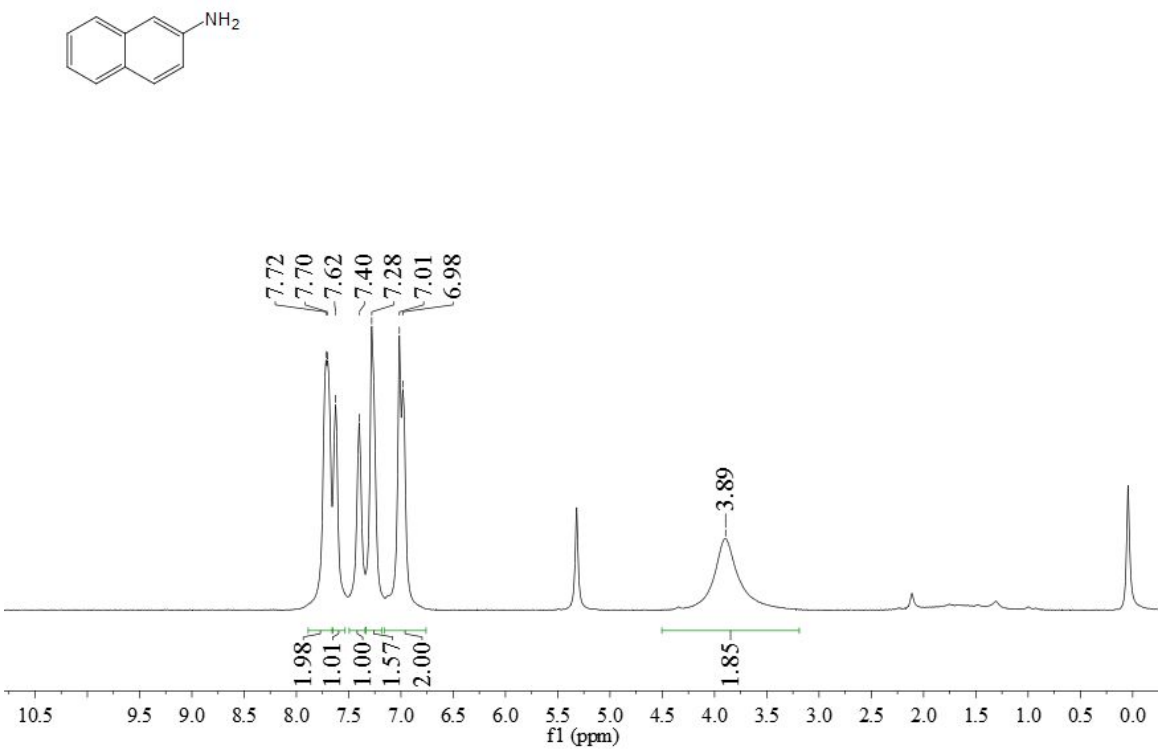
^{1}H NMR spectra of 3oa (500 MHz, $CDCl_3$)



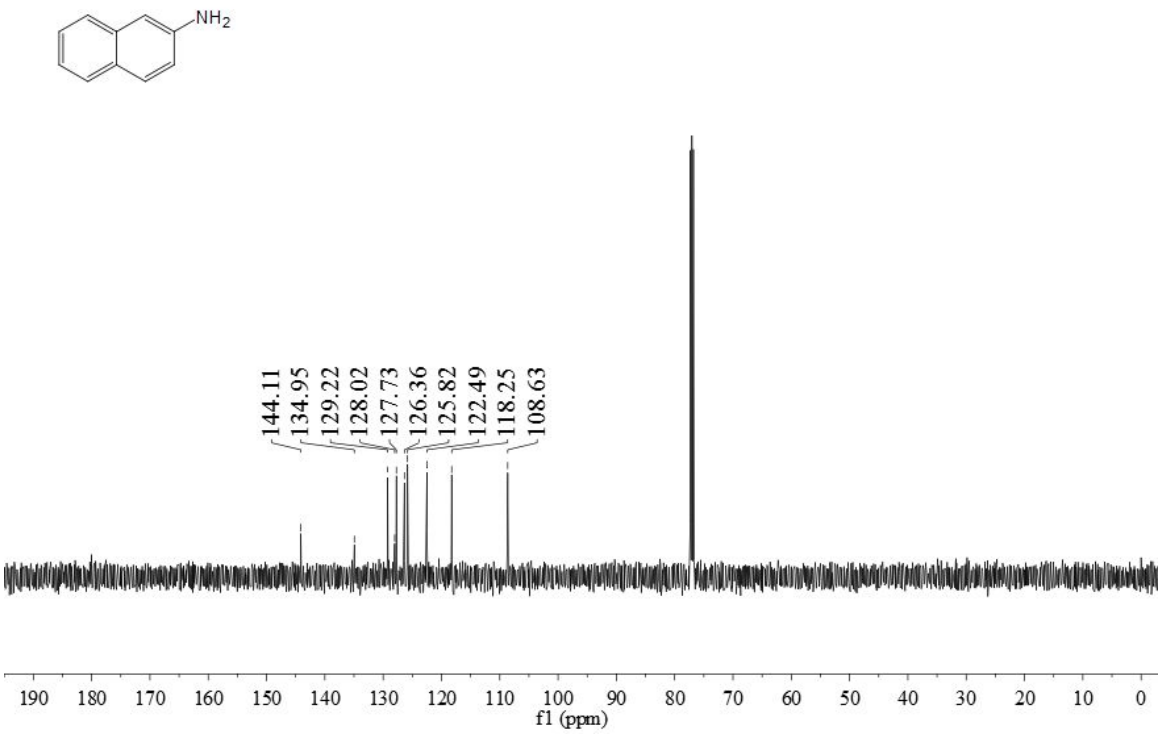
^{13}C NMR spectra of 3oa (126 MHz, $CDCl_3$)



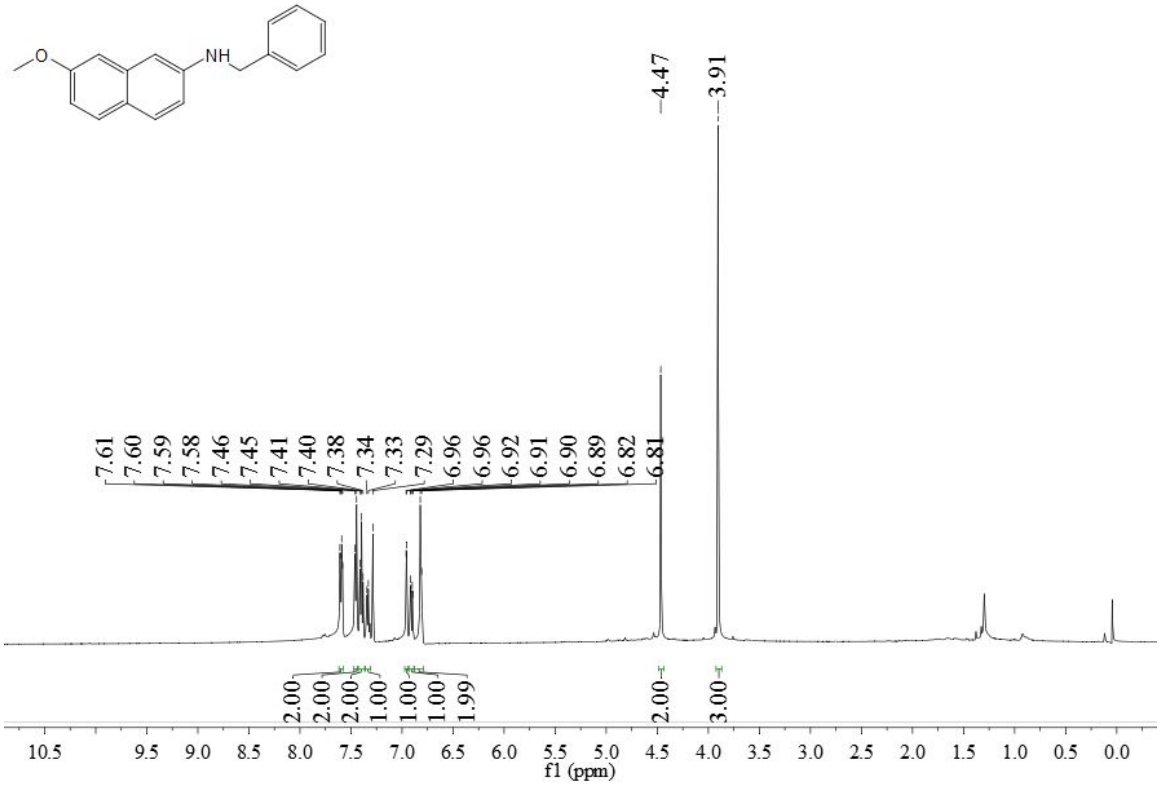
^{1}H NMR spectra of 3pa (500 MHz, $CDCl_3$)



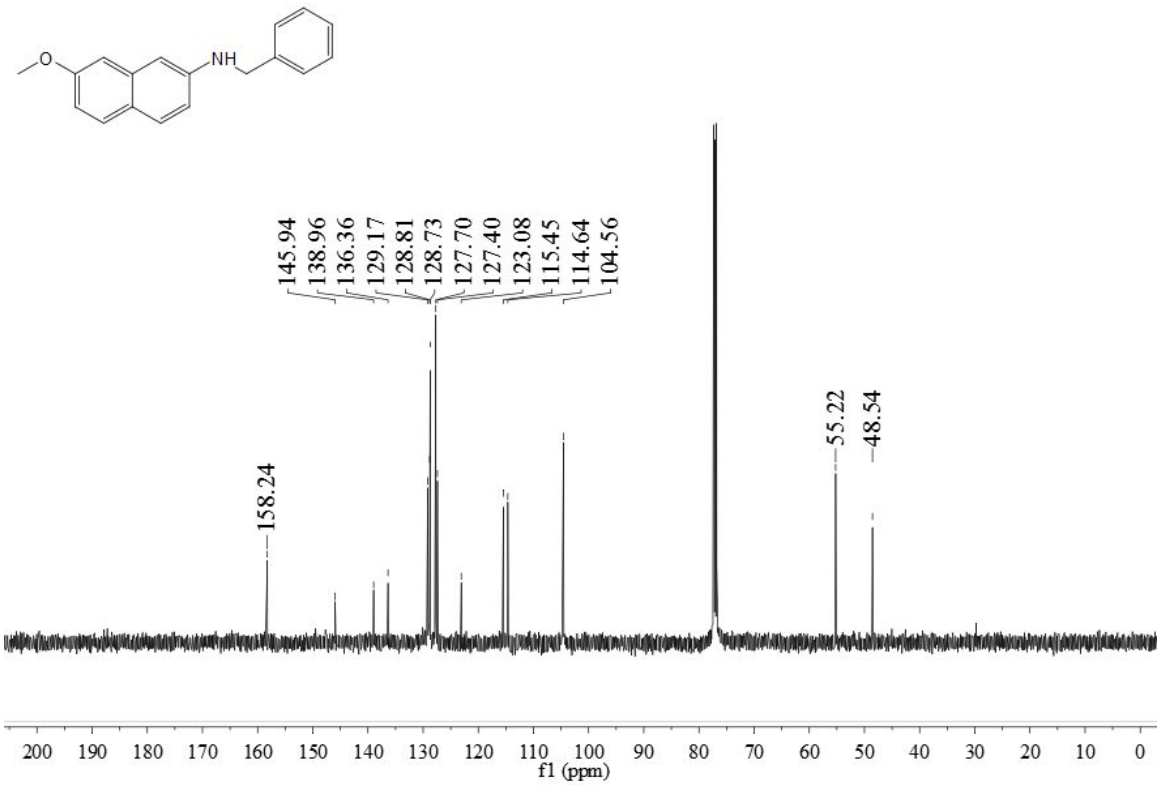
^{13}C NMR spectra of 3pa (126 MHz, $CDCl_3$)



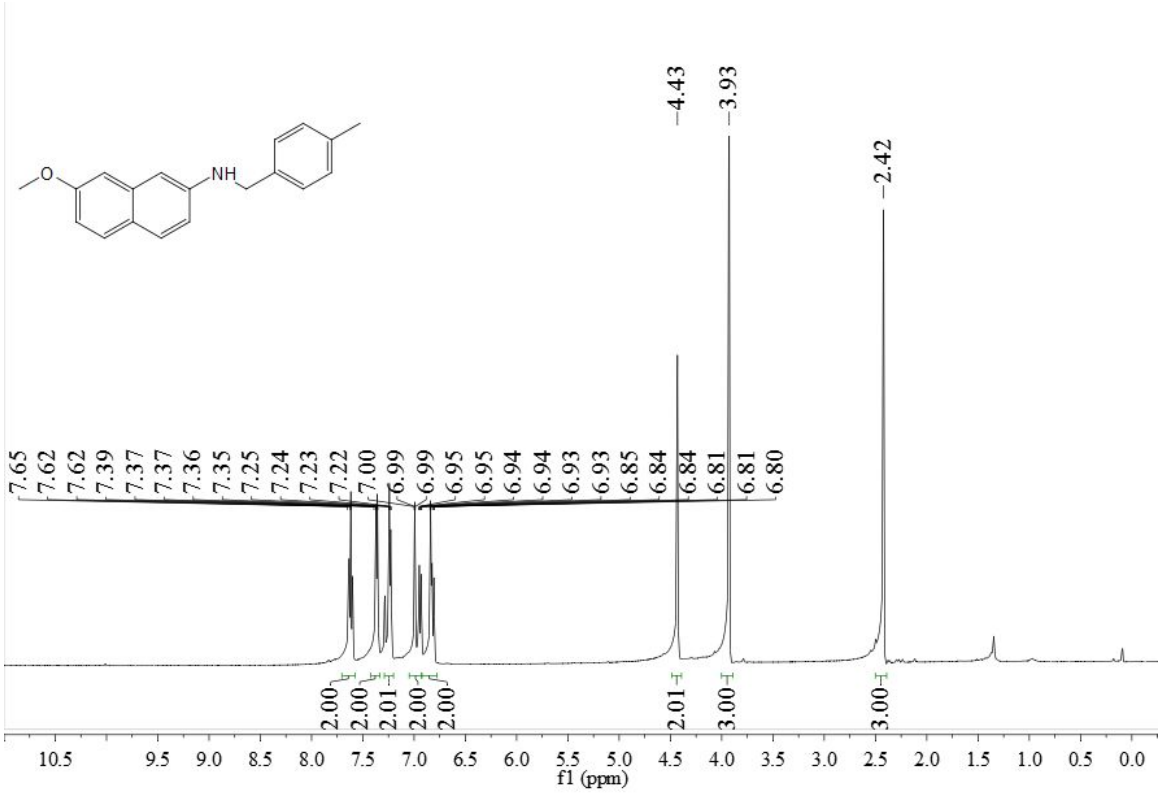
^{1}H NMR spectra of 3ab (500 MHz, $CDCl_3$)



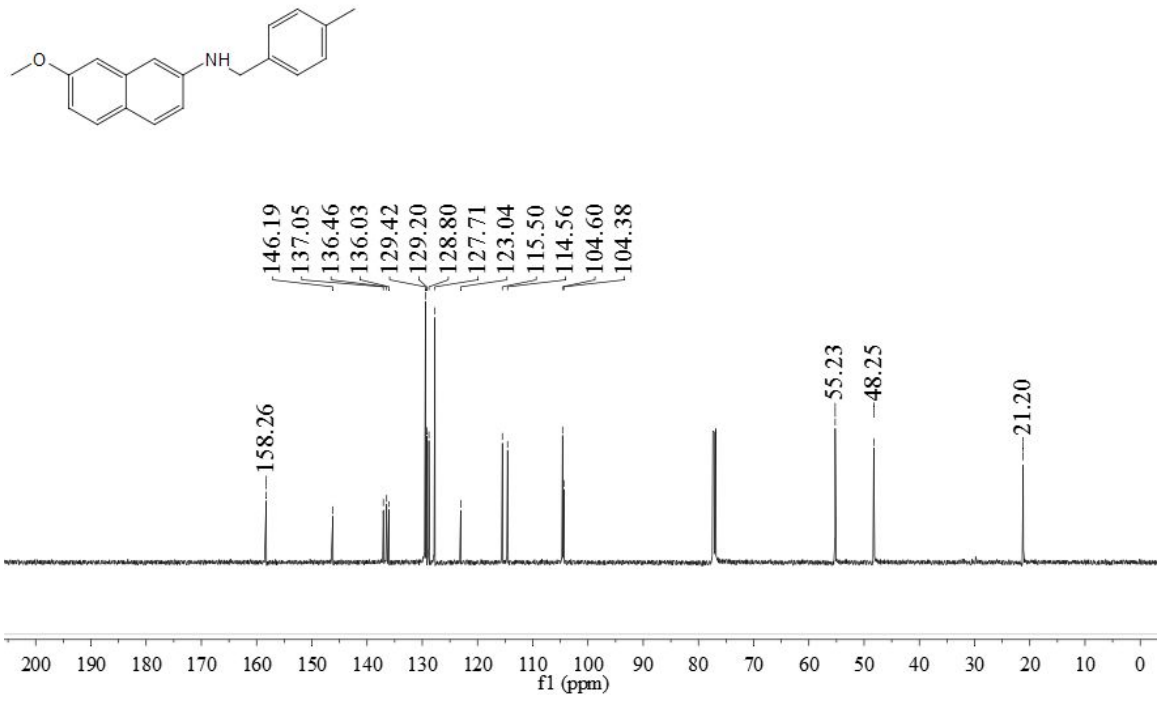
^{13}C NMR spectra of 3ab (126 MHz, $CDCl_3$)



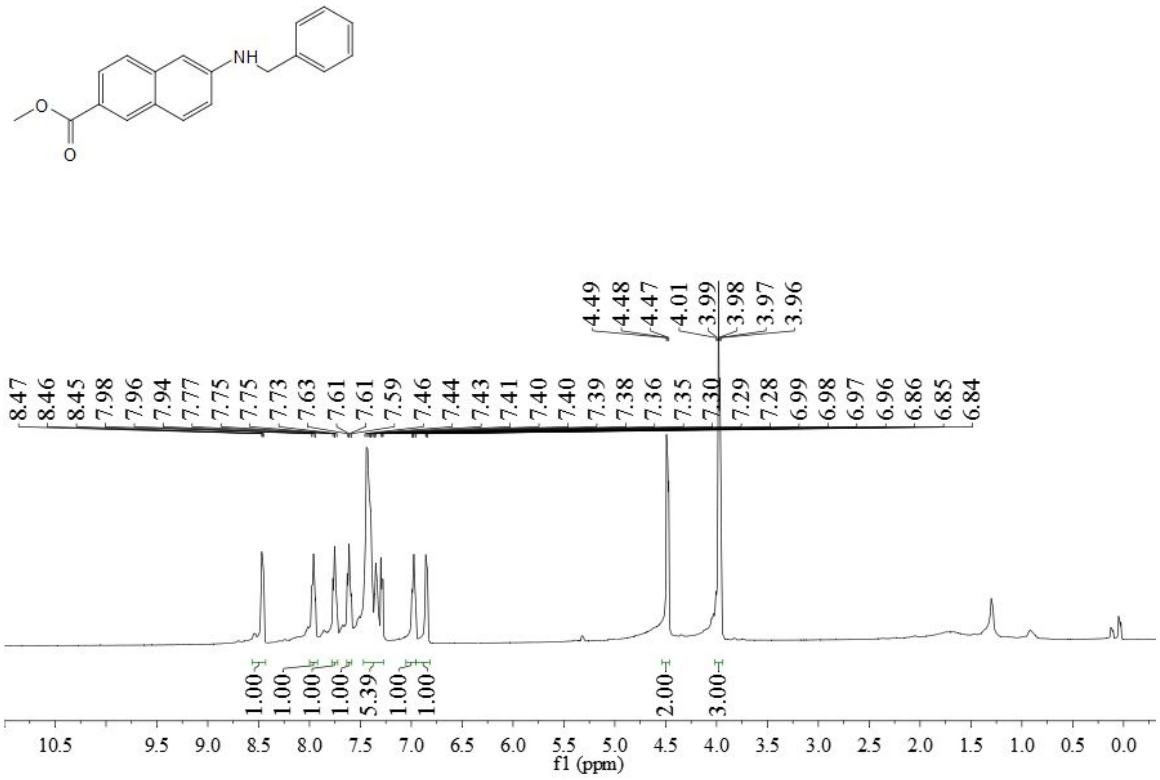
^{1}H NMR spectra of 3bb (500 MHz, $CDCl_3$)



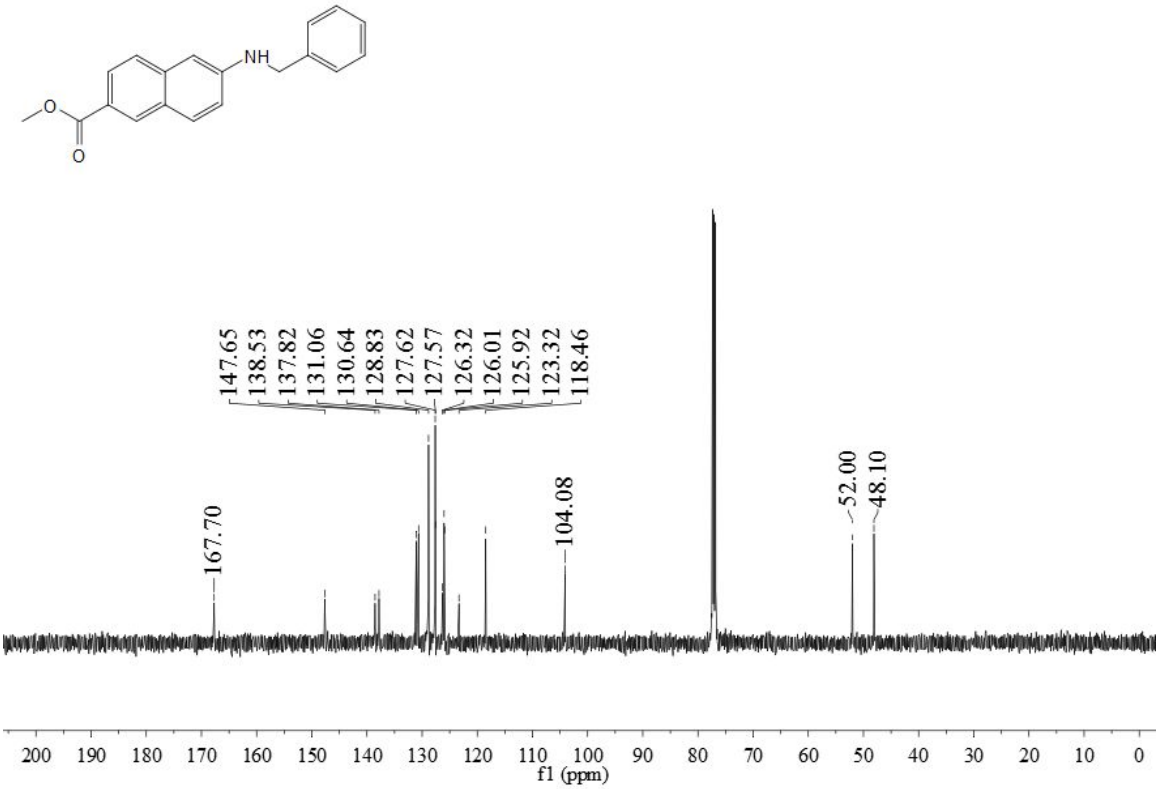
^{13}C NMR spectra of 3bb (126 MHz, $CDCl_3$)



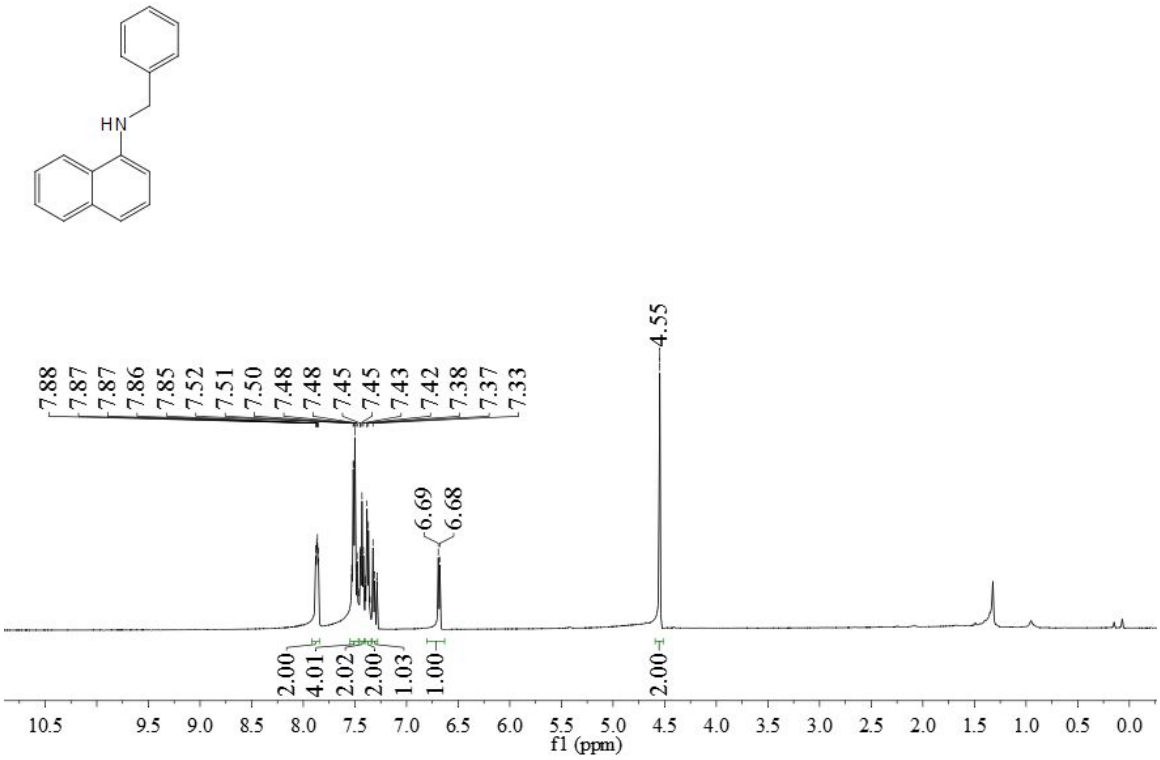
^{1}H NMR spectra of 3ac (500 MHz, $CDCl_3$)



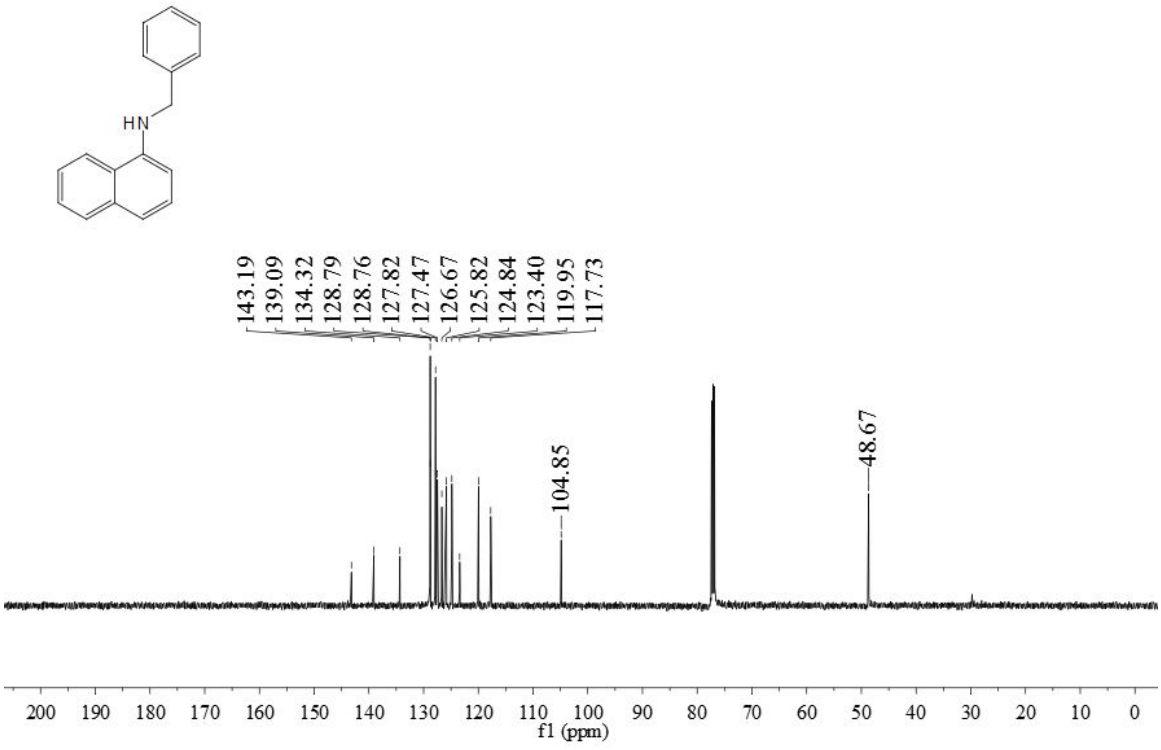
^{13}C NMR spectra of 3ac (126 MHz, $CDCl_3$)



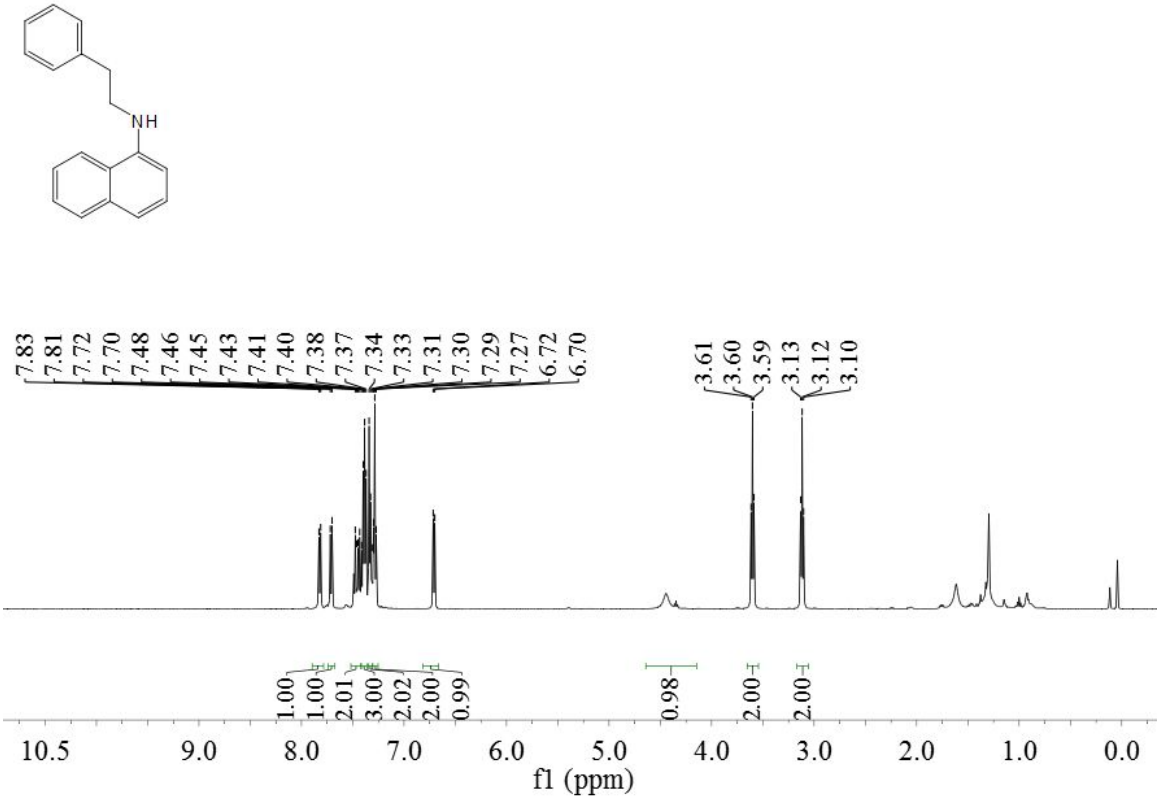
^{1}H NMR spectra of 3ad (500 MHz, $CDCl_3$)



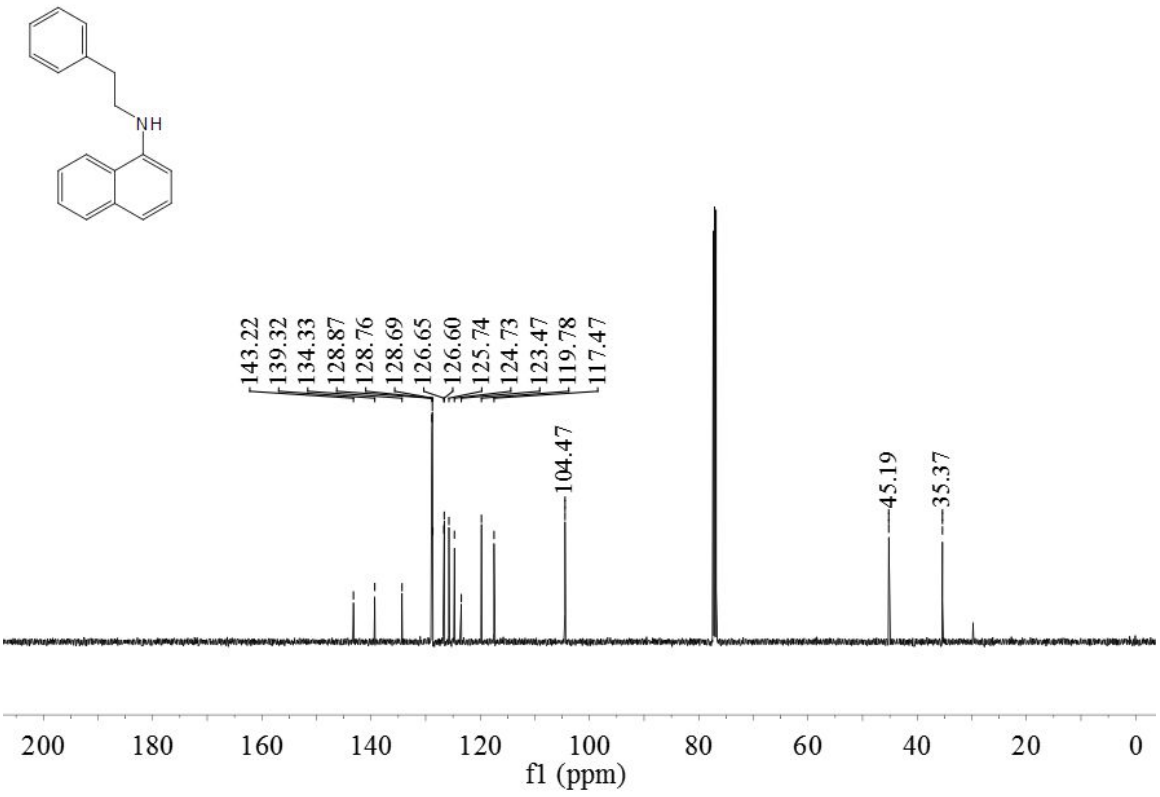
^{13}C NMR spectra of 3ad (126 MHz, $CDCl_3$)



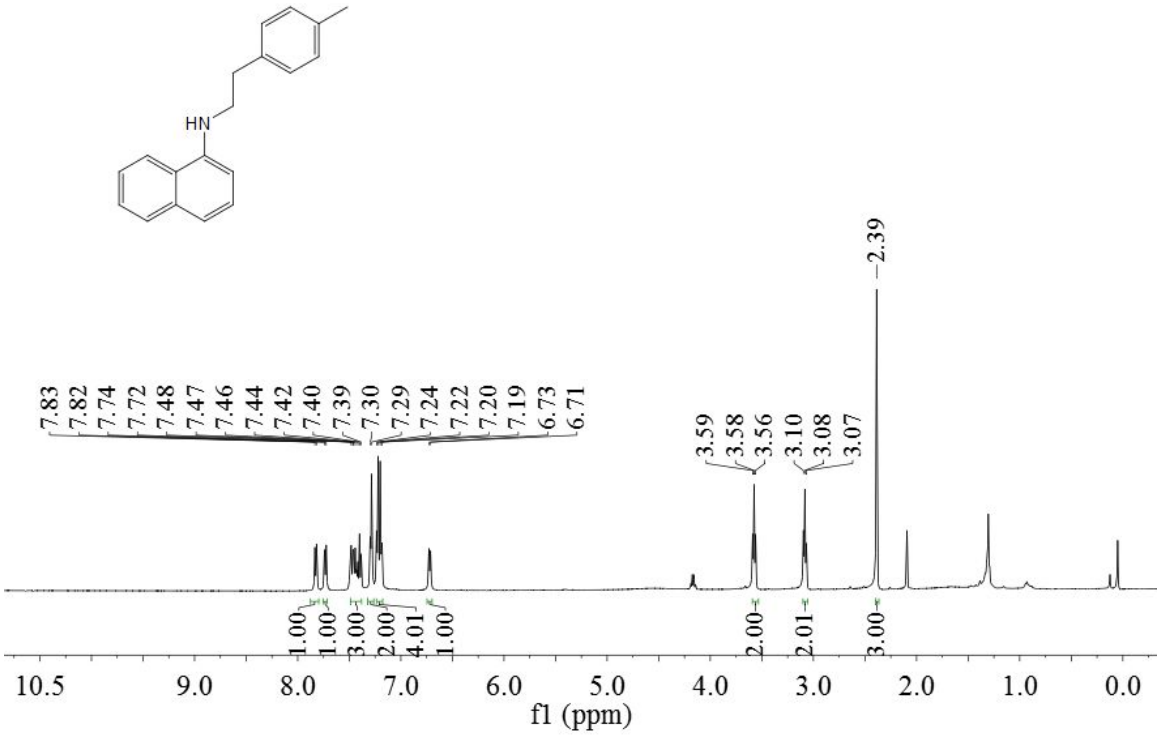
^{1}H NMR spectra of 3ed (500 MHz, $CDCl_3$)



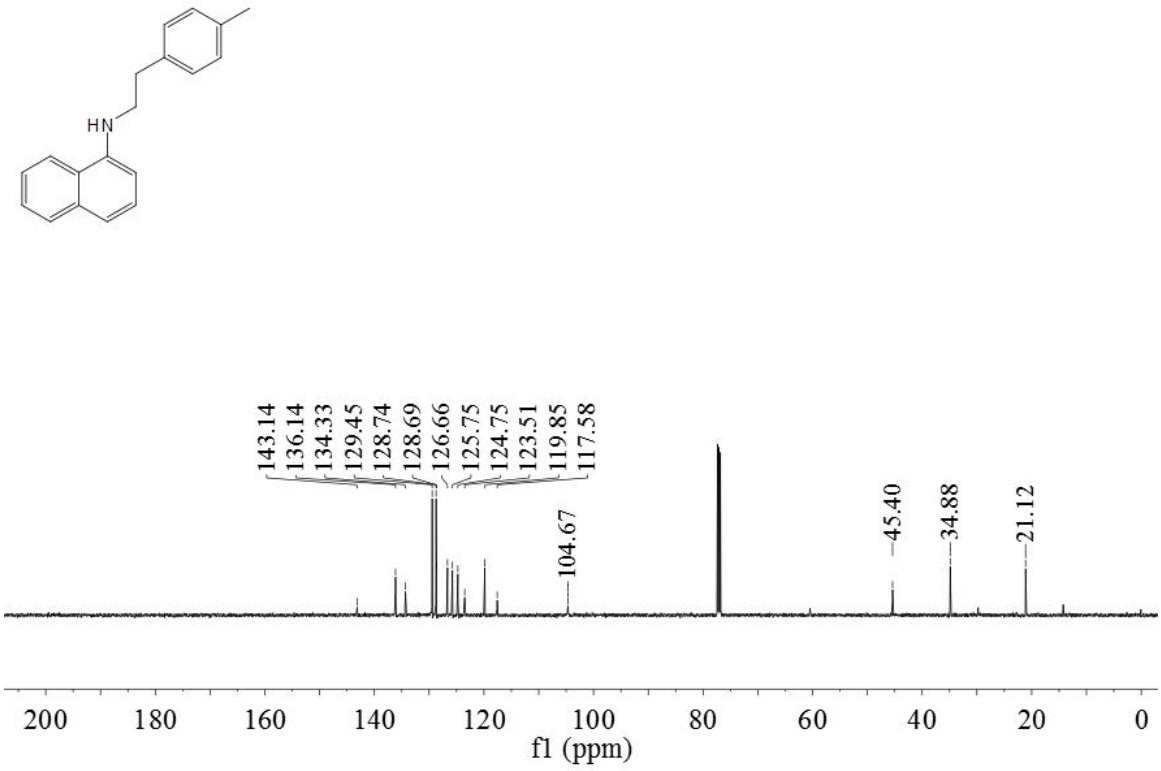
^{13}C NMR spectra of 3ed (126 MHz, $CDCl_3$)



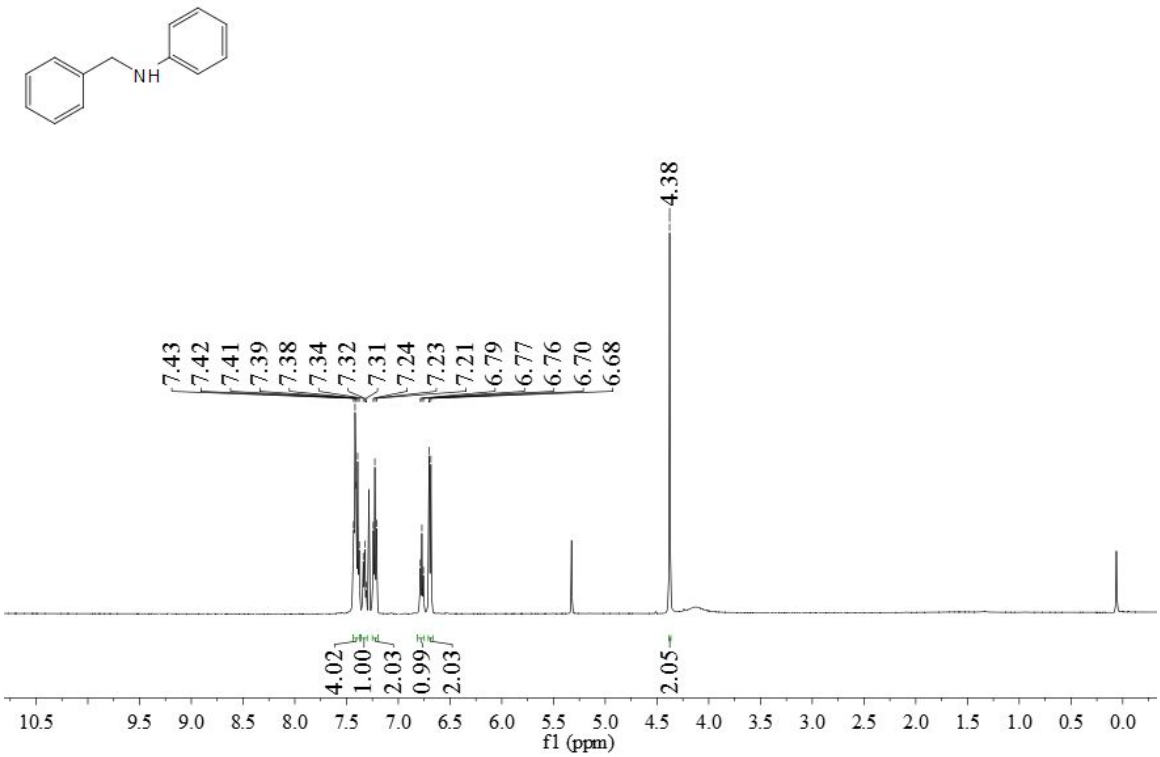
^{1}H NMR spectra of 3fd (500 MHz, $CDCl_3$)



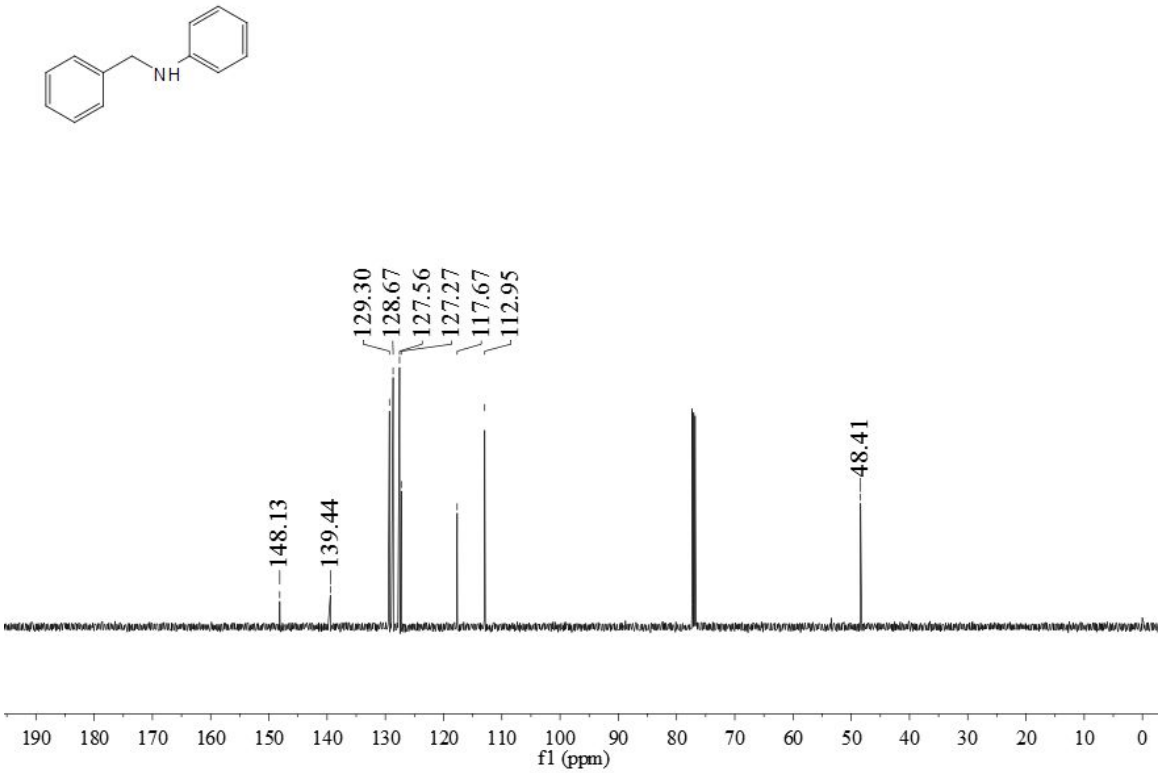
^{13}C NMR spectra of 3fd (126 MHz, $CDCl_3$)



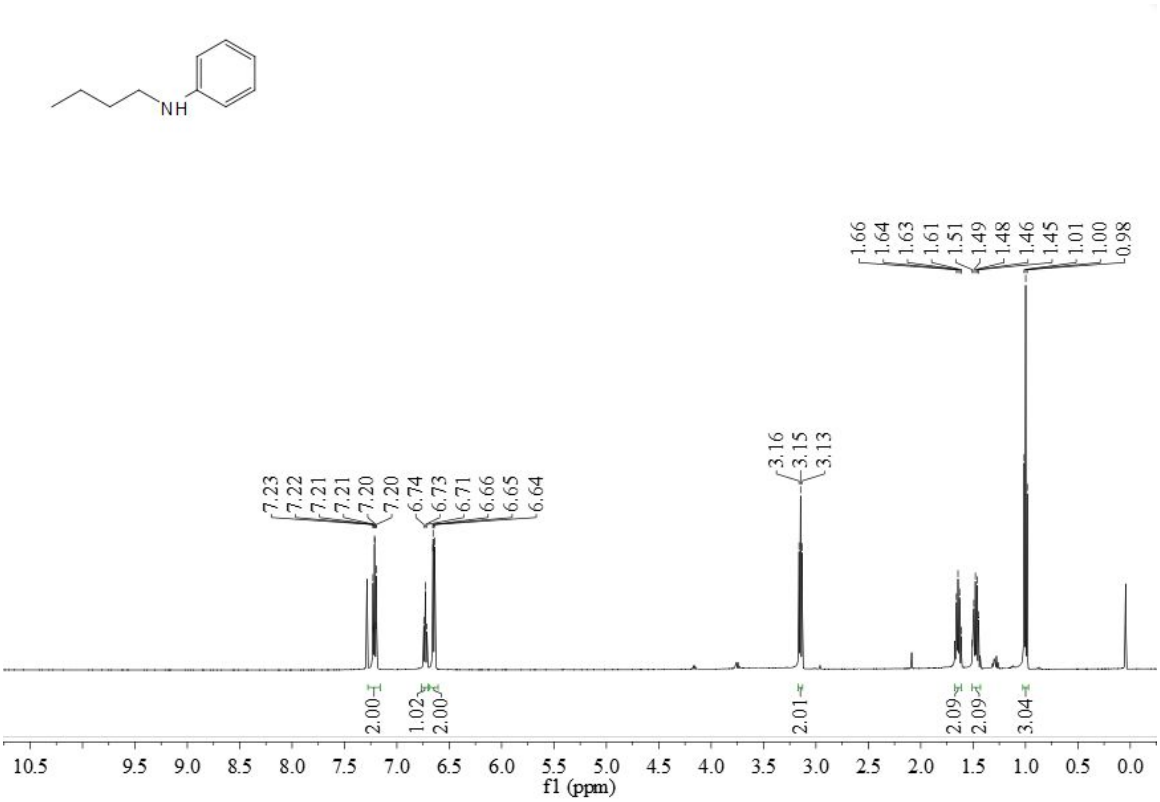
^{1}H NMR spectra of 3ae (500 MHz, $CDCl_3$)



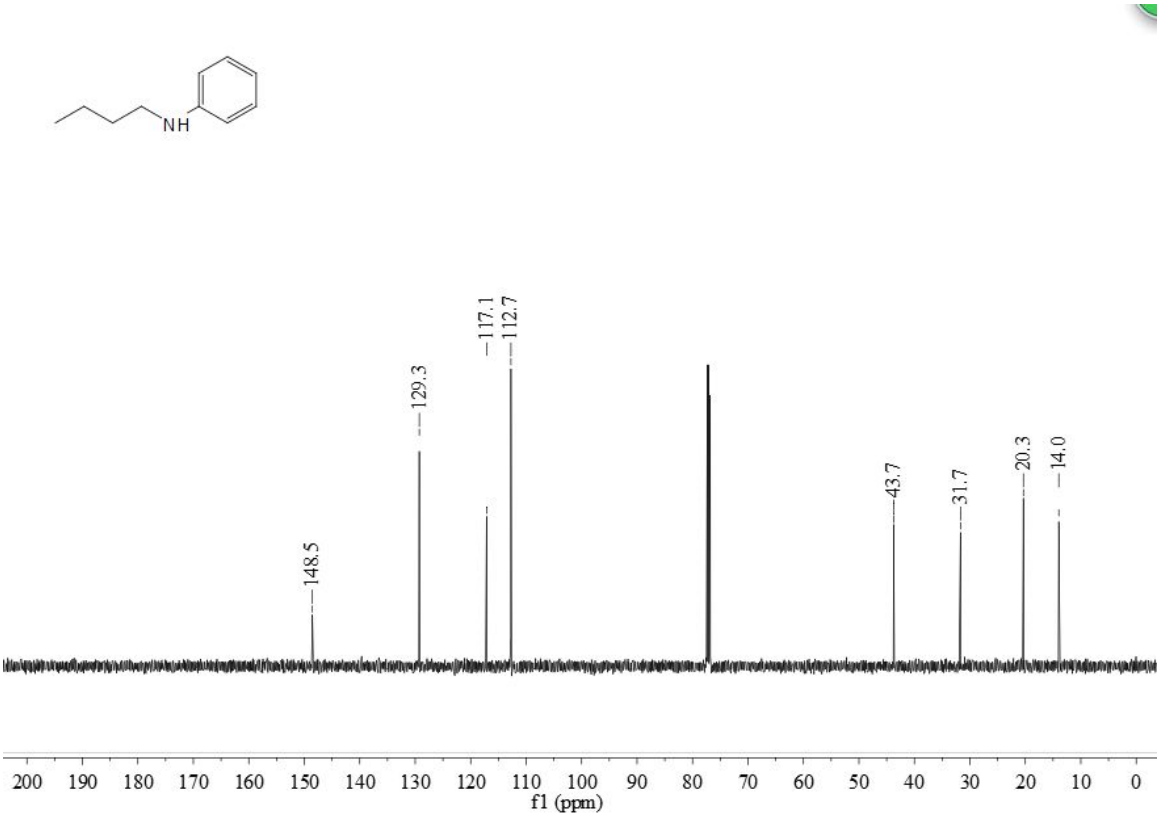
^{13}C NMR spectra of 3ae (126 MHz, $CDCl_3$)



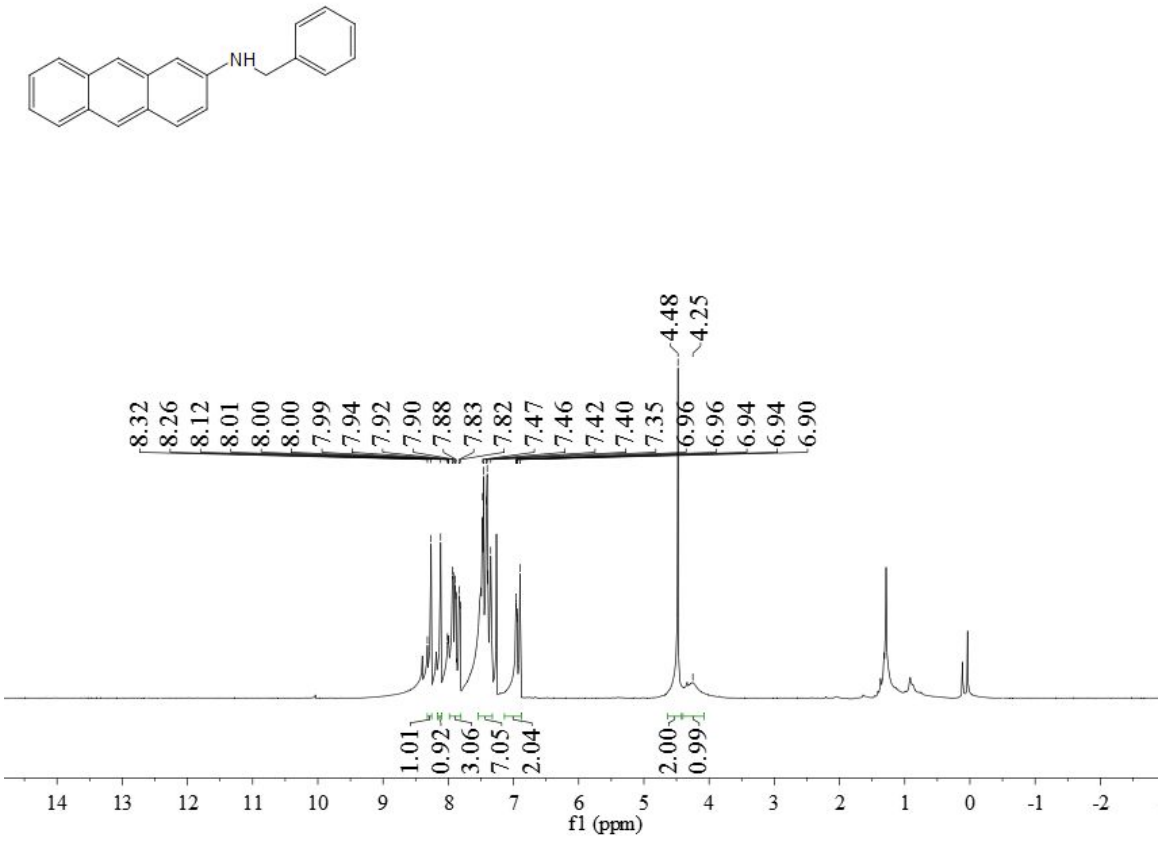
^{1}H NMR spectra of 3ie (500 MHz, $CDCl_3$)



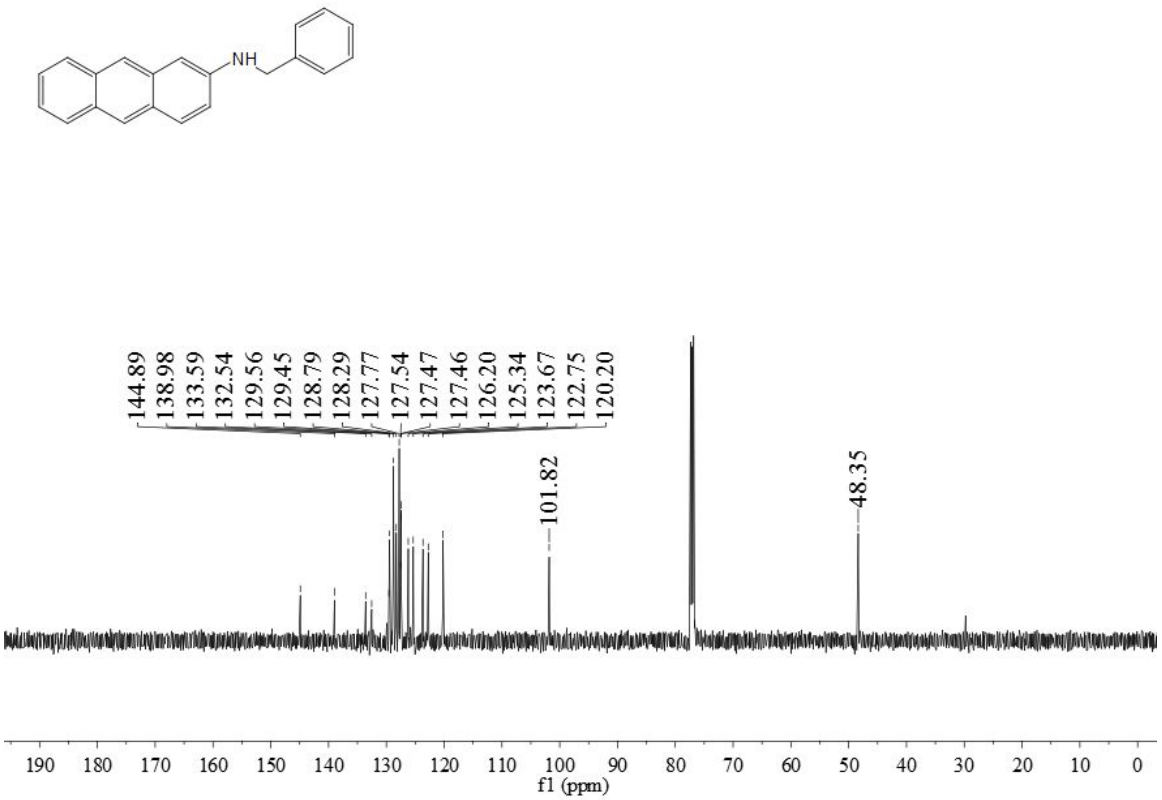
^{13}C NMR spectra of 3ie (126 MHz, $CDCl_3$)



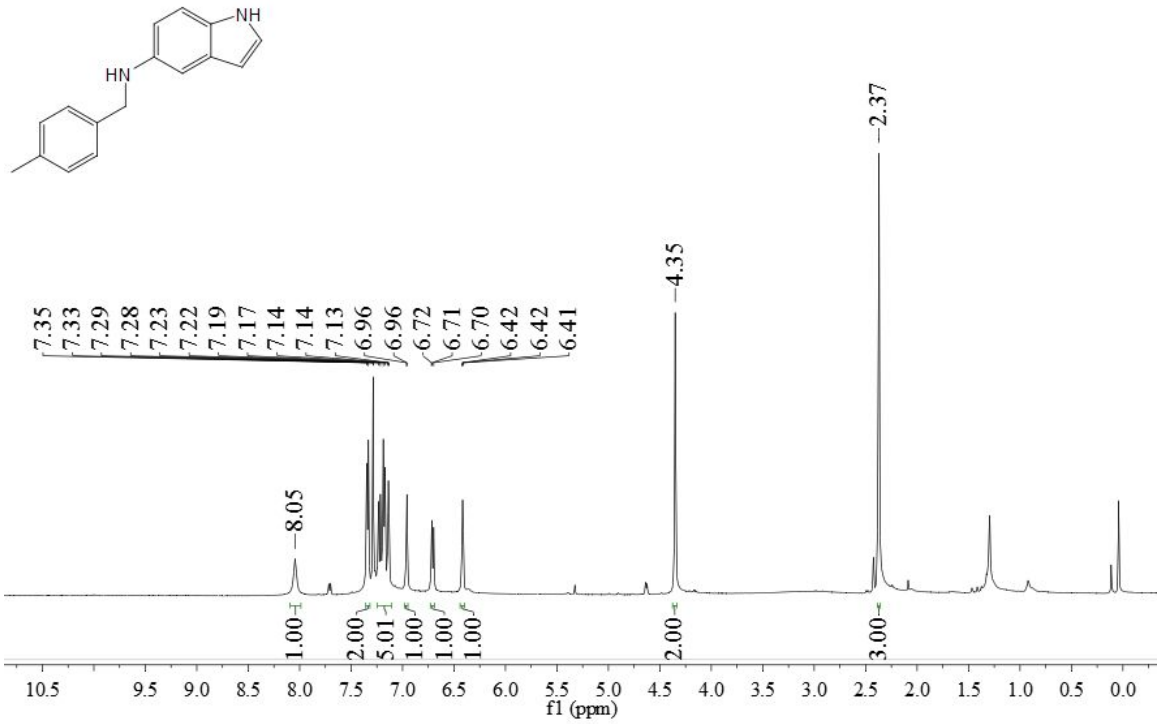
^{1}H NMR spectra of 3af (500 MHz, $CDCl_3$)



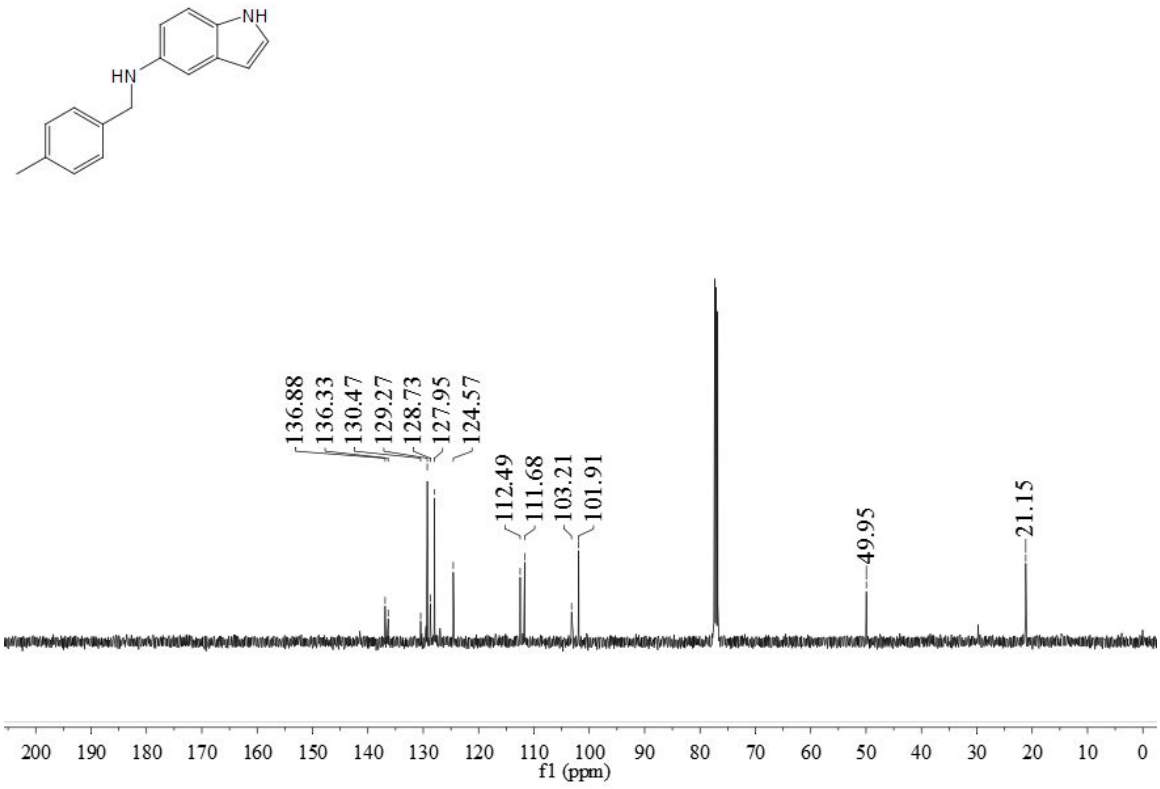
^{13}C NMR spectra of 3af (126 MHz, $CDCl_3$)



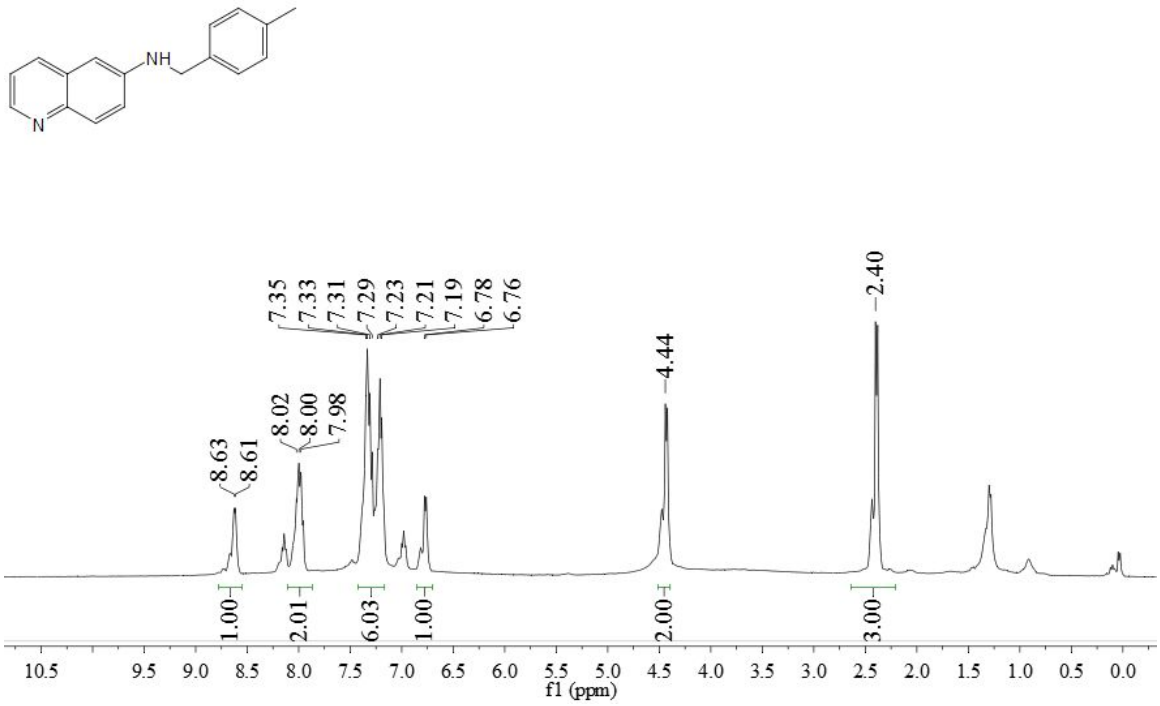
^{1}H NMR spectra of 3bg (500 MHz, $CDCl_3$)



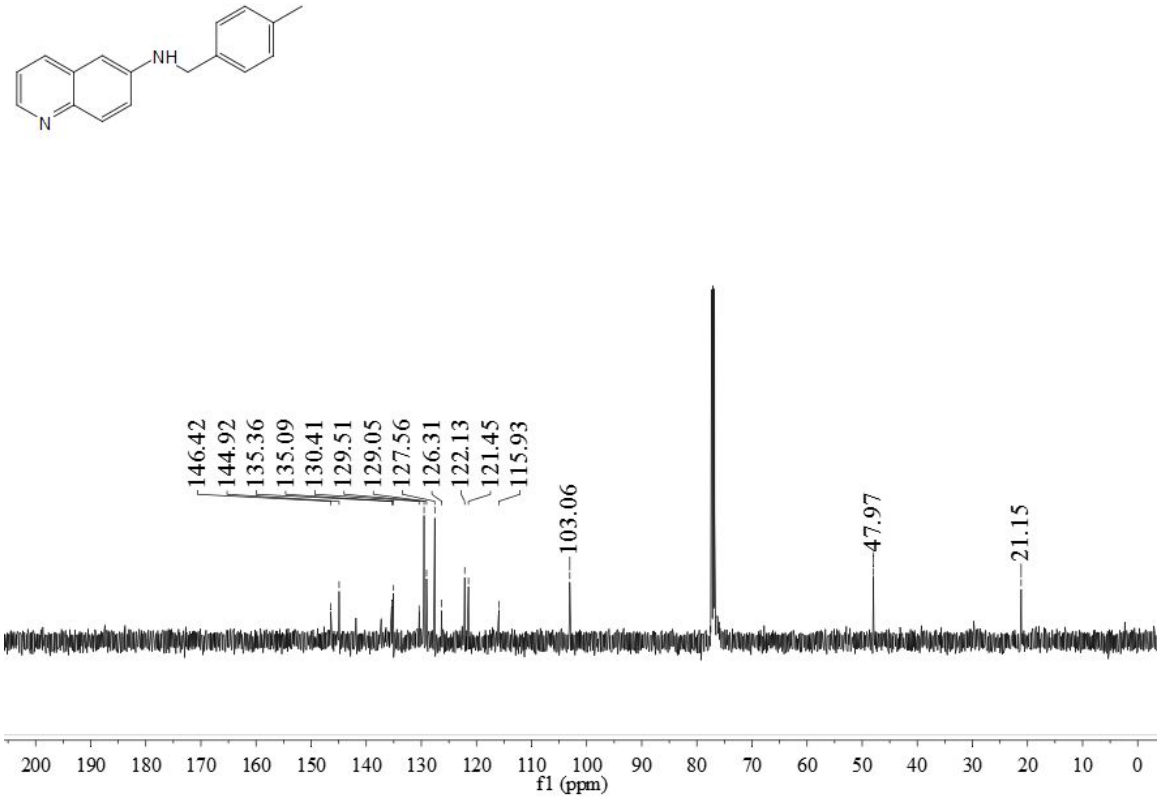
^{13}C NMR spectra of 3bg (126 MHz, $CDCl_3$)



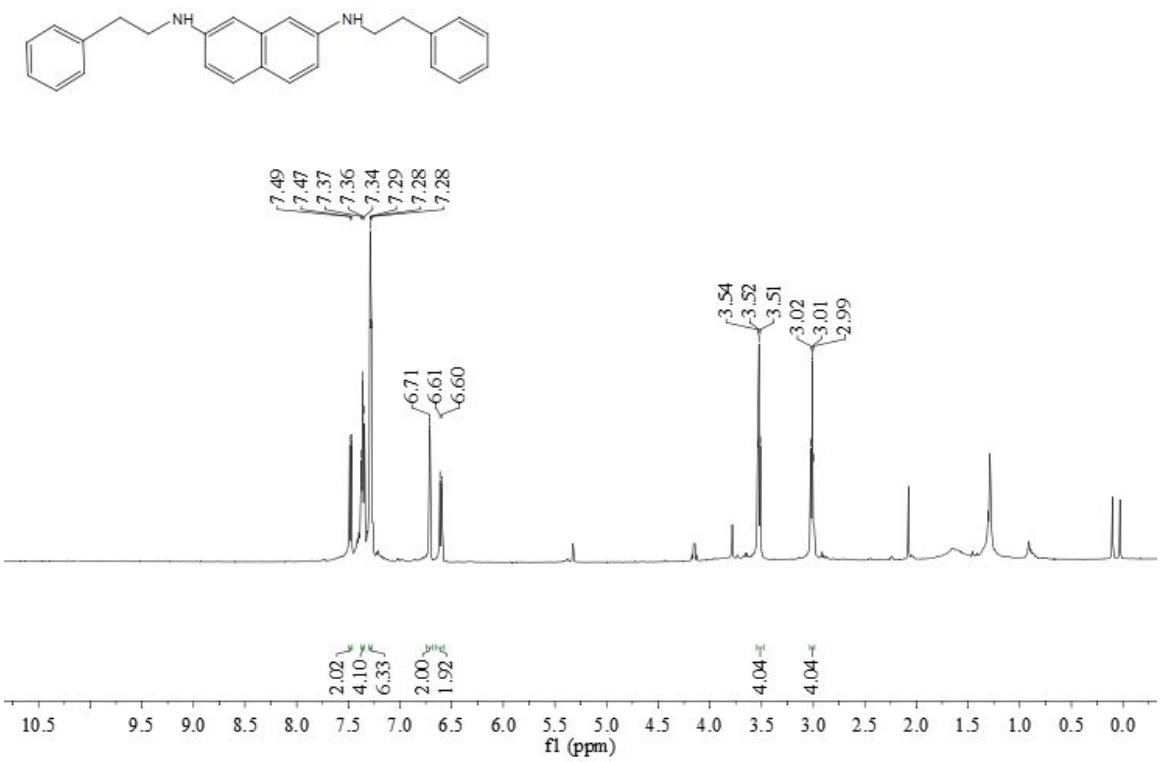
^{1}H NMR spectra of 3bh (500 MHz, $CDCl_3$)



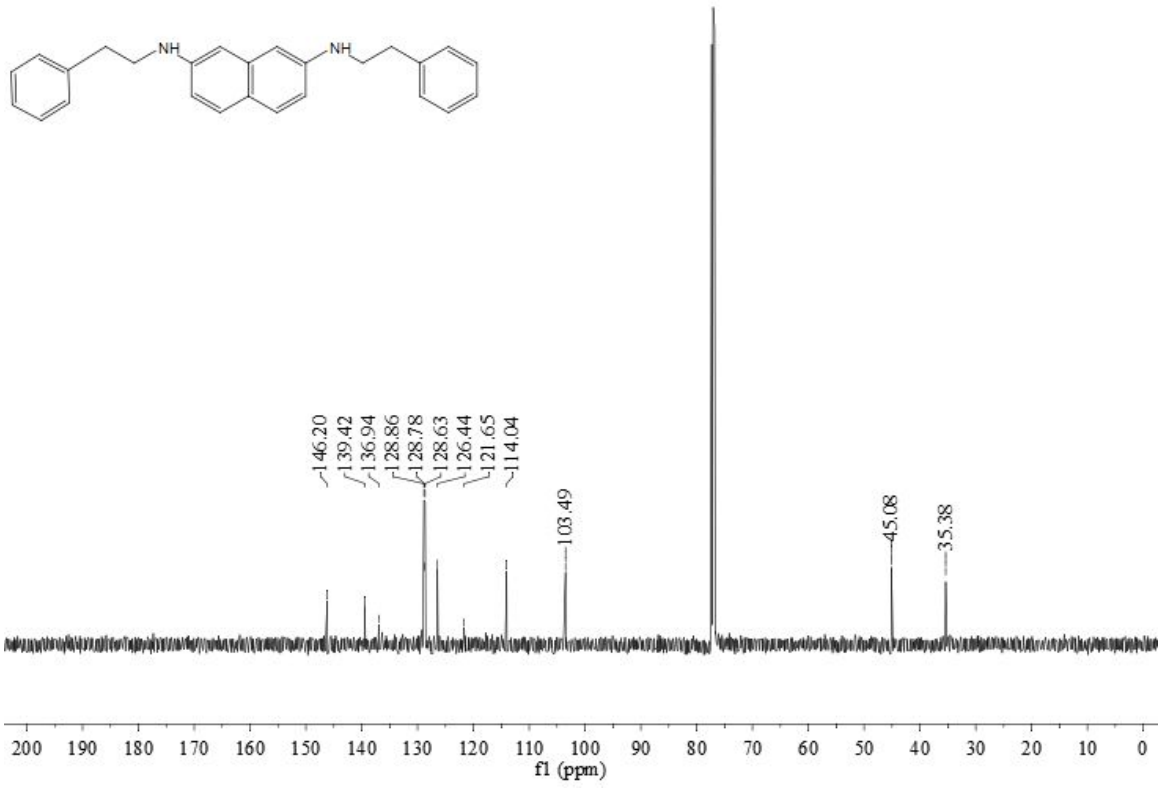
^{13}C NMR spectra of 3bh (126 MHz, $CDCl_3$)



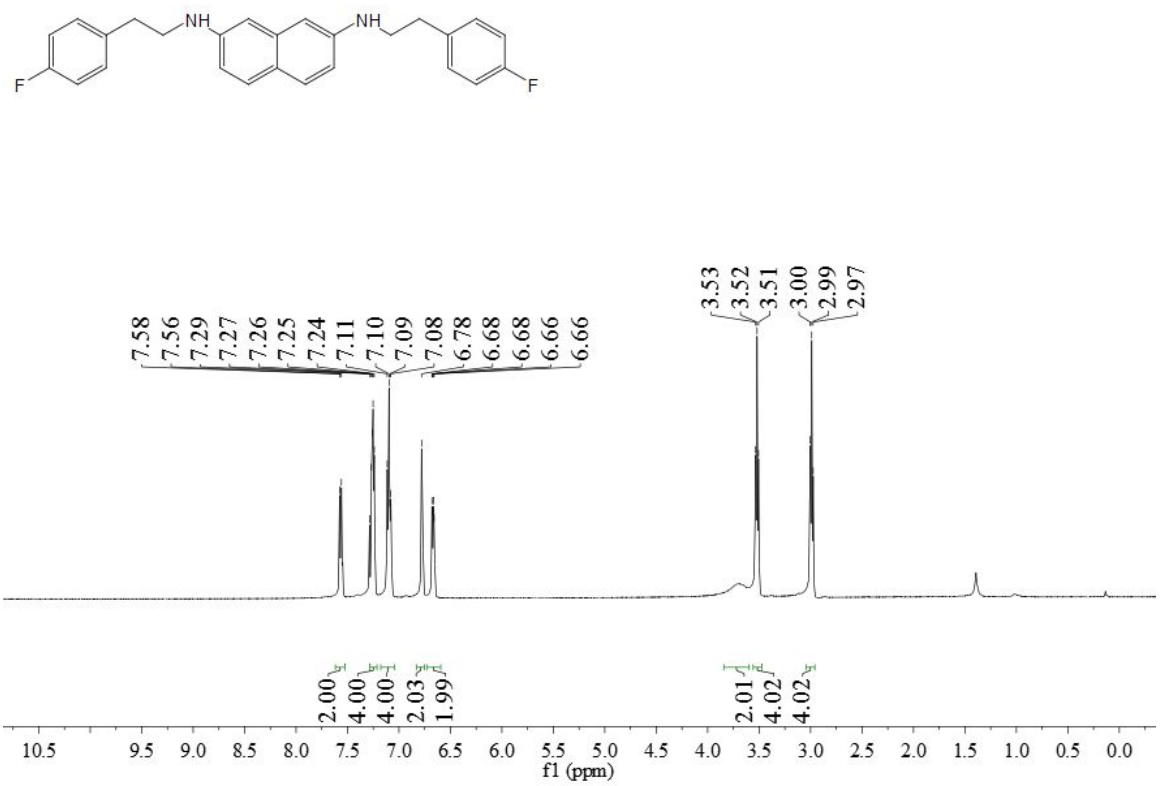
^{1}H NMR spectra of 4ei (500 MHz, $CDCl_3$)



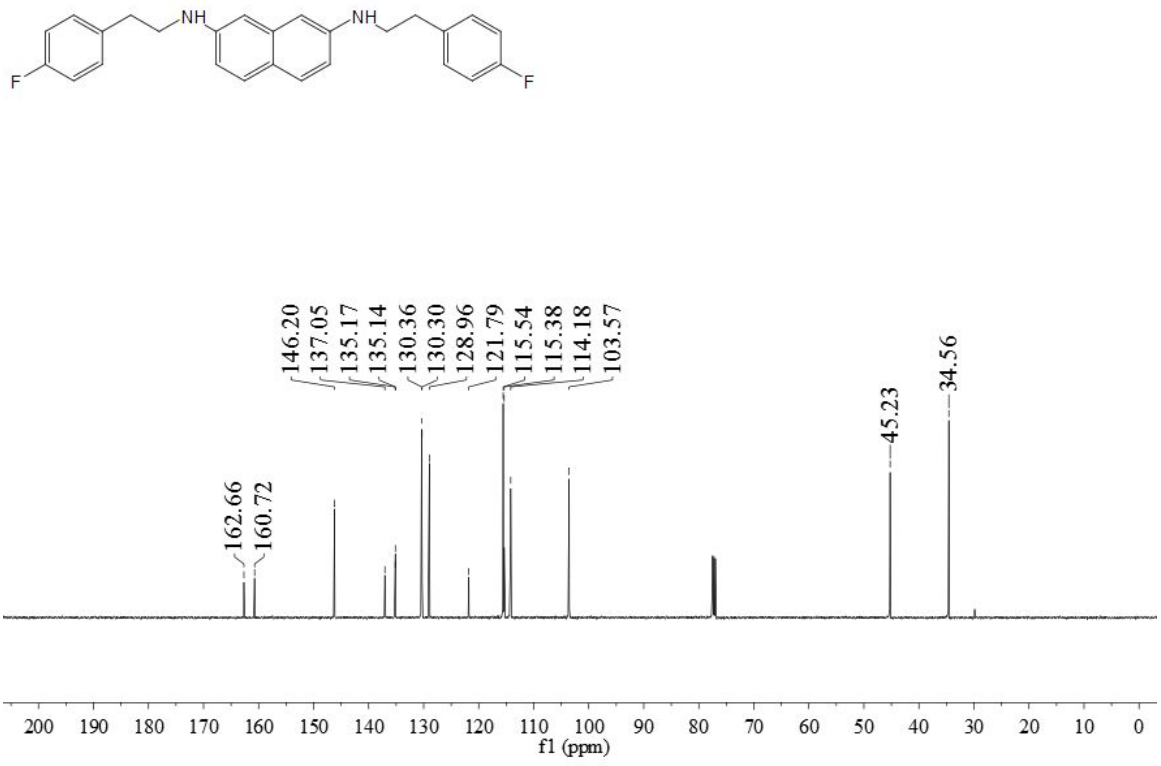
^{13}C NMR spectra of 4ei (126 MHz, $CDCl_3$)



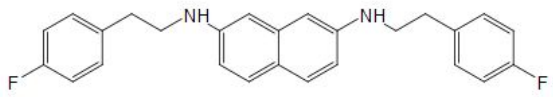
^{1}H NMR spectra of 4fi (500MHz, $CDCl_3$)

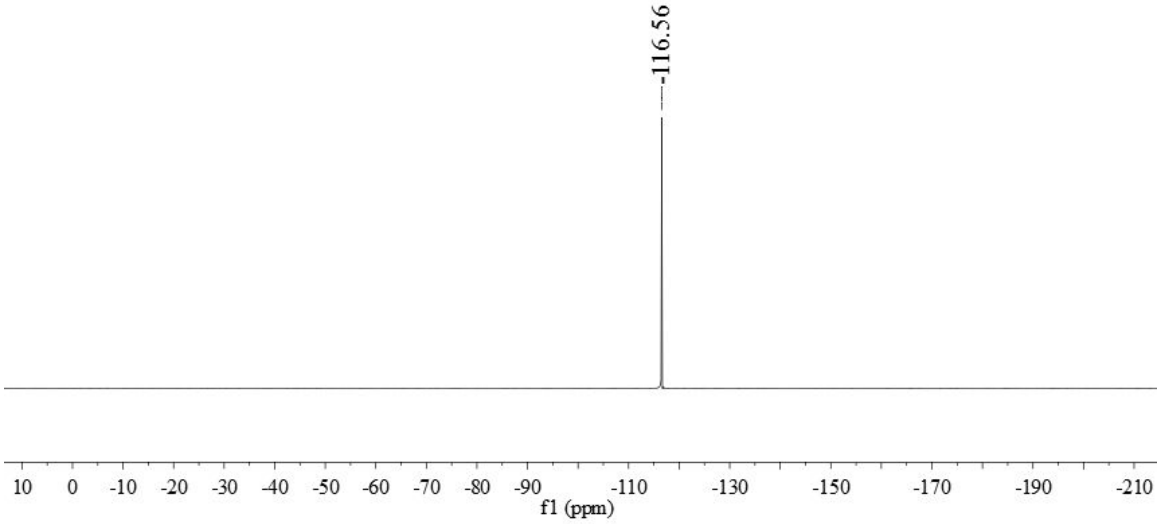


^{13}C NMR spectra of 4fi (126 MHz, $CDCl_3$)

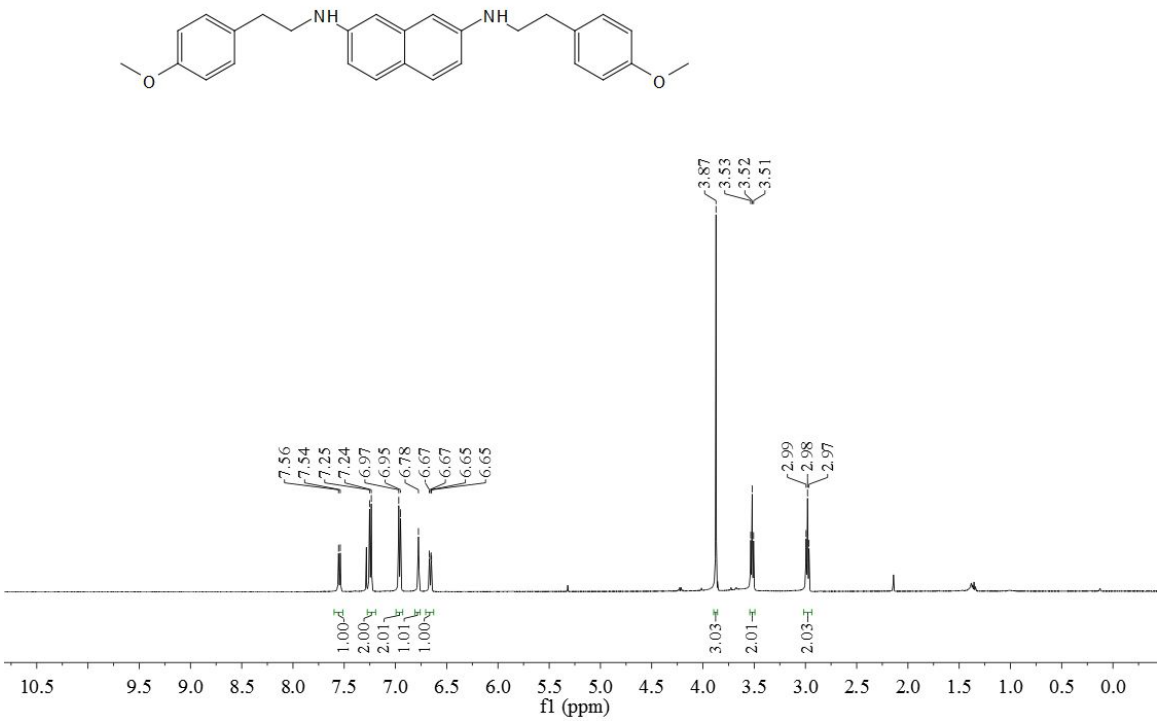


^{19}F NMR spectra of 4fi (471 MHz, $CDCl_3$)



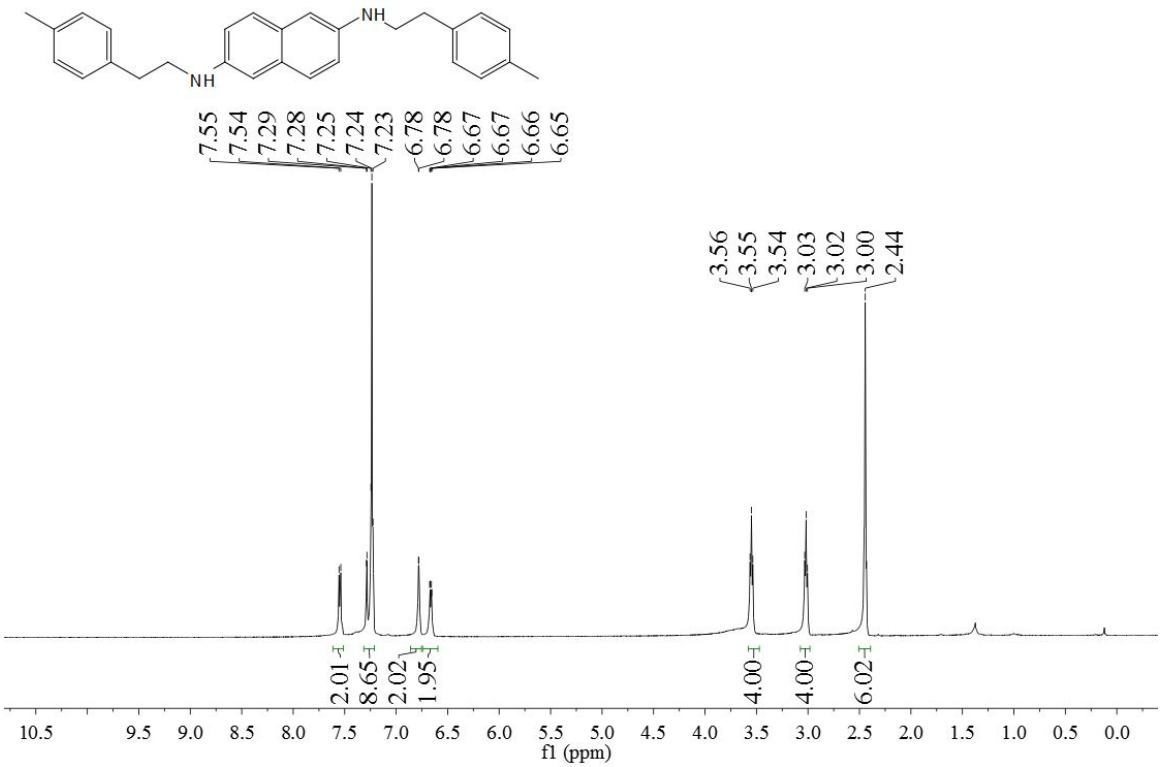


^{1}H NMR spectra of 4gi (500MHz, $CDCl_3$)

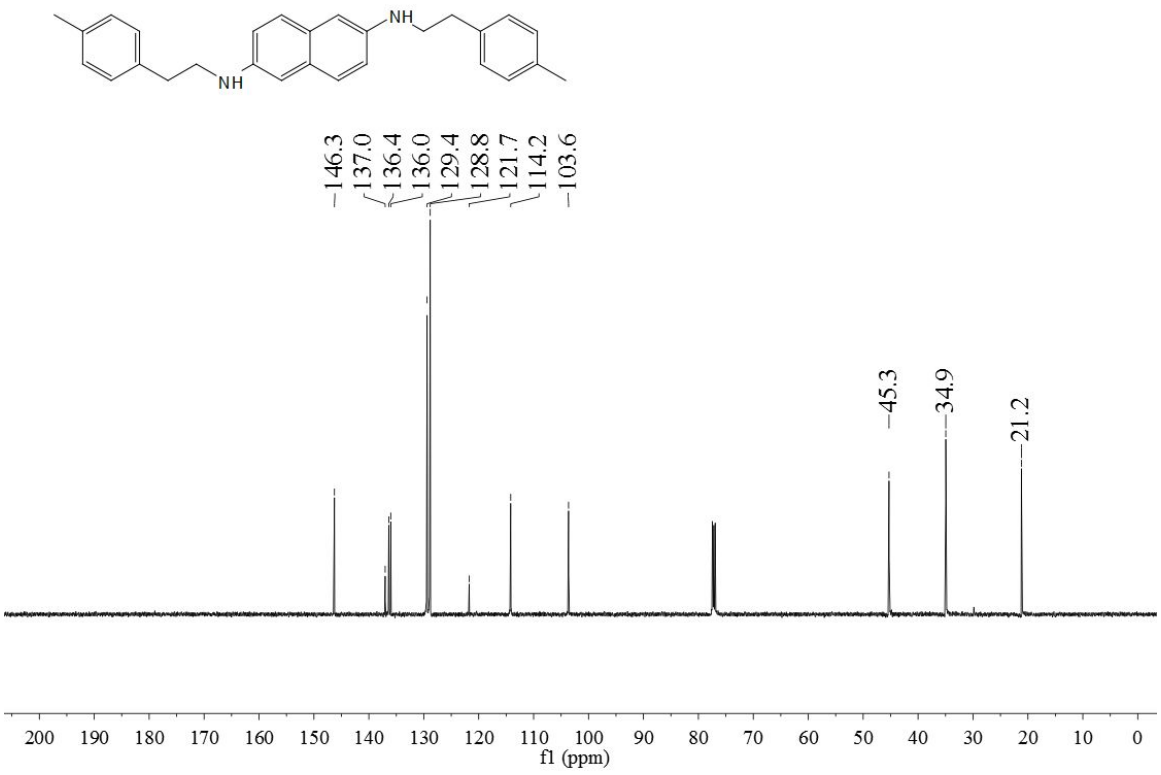


^{13}C NMR spectra of 4gi (126 MHz, $CDCl_3$)

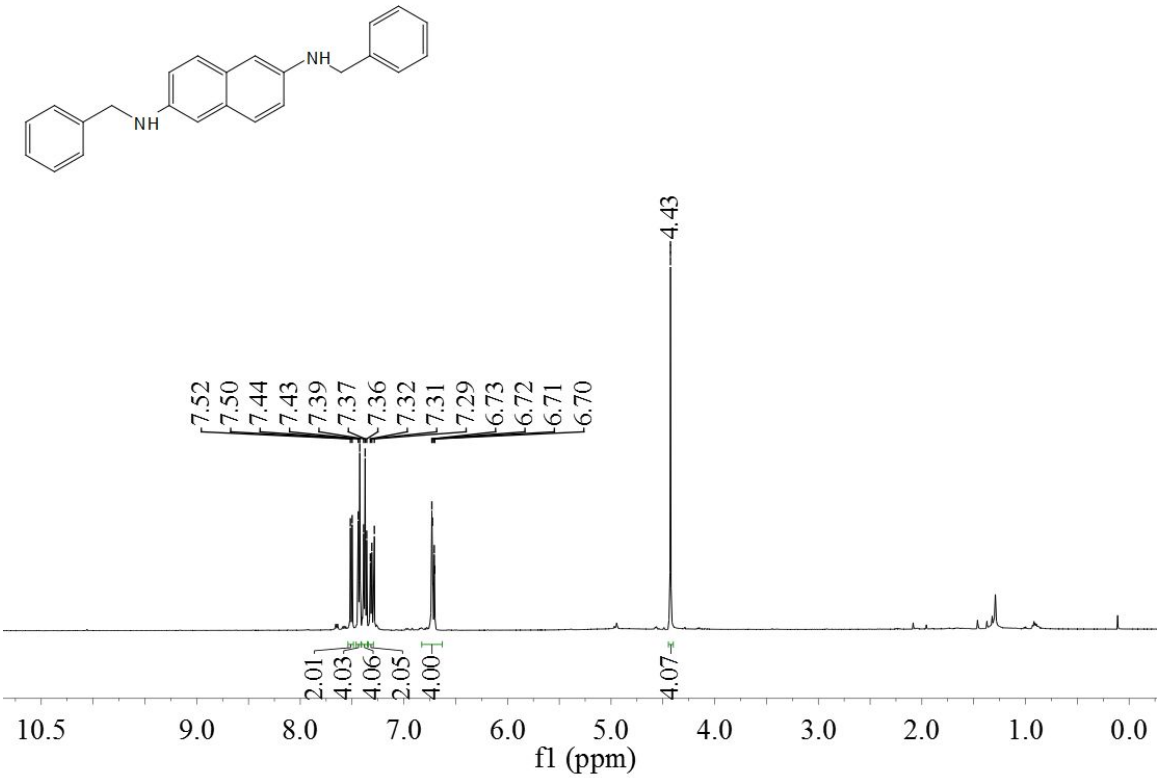
^{1}H NMR spectra of 4hj (500MHz, $CDCl_3$)



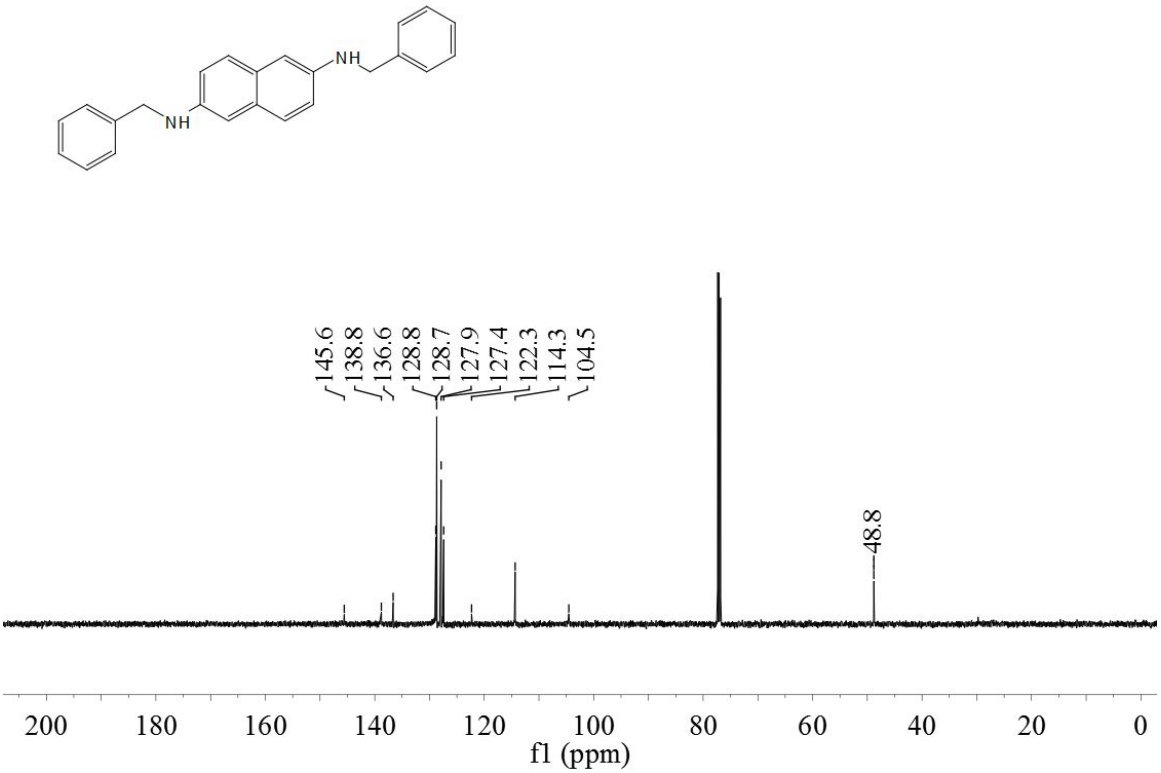
^{13}C NMR spectra of 4hj (126 MHz, $CDCl_3$)



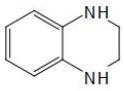
^{1}H NMR spectra of 4aj (500MHz, $CDCl_3$)

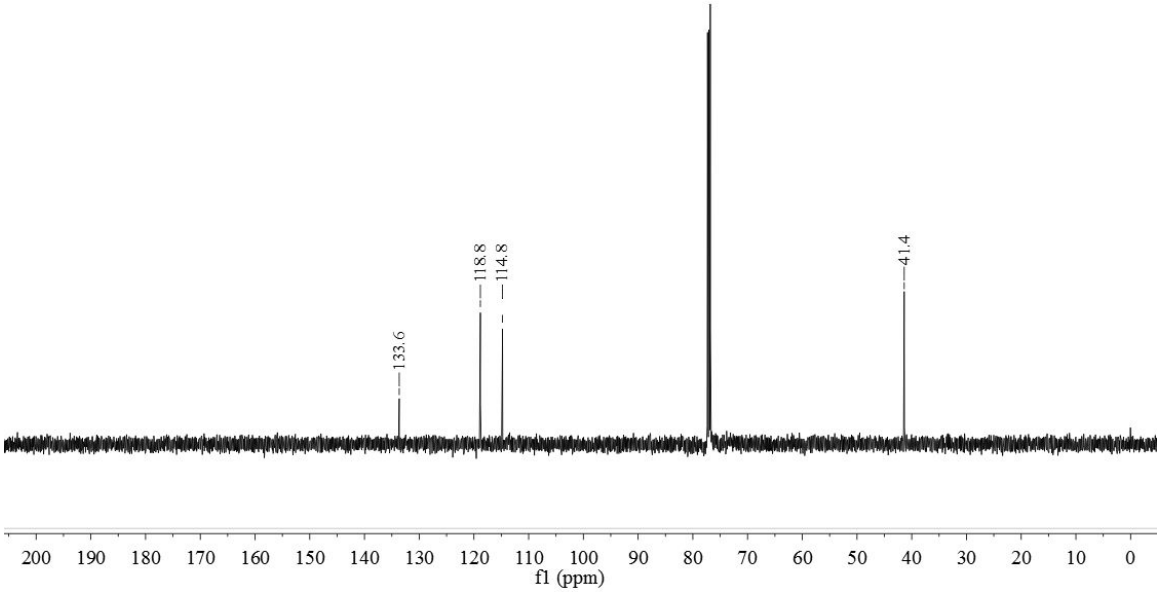


^{13}C NMR spectra of 4aj (126 MHz, $CDCl_3$)

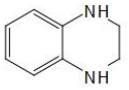


^{1}H NMR spectra of 4qk (500MHz, $CDCl_3$)

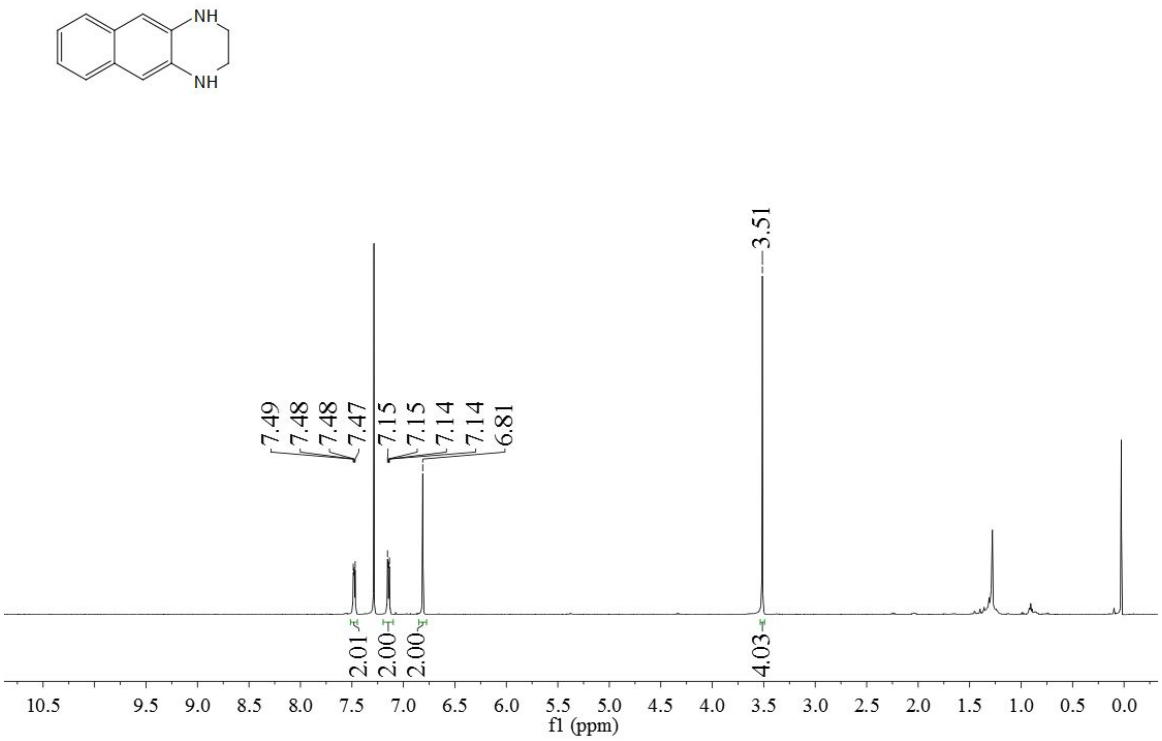




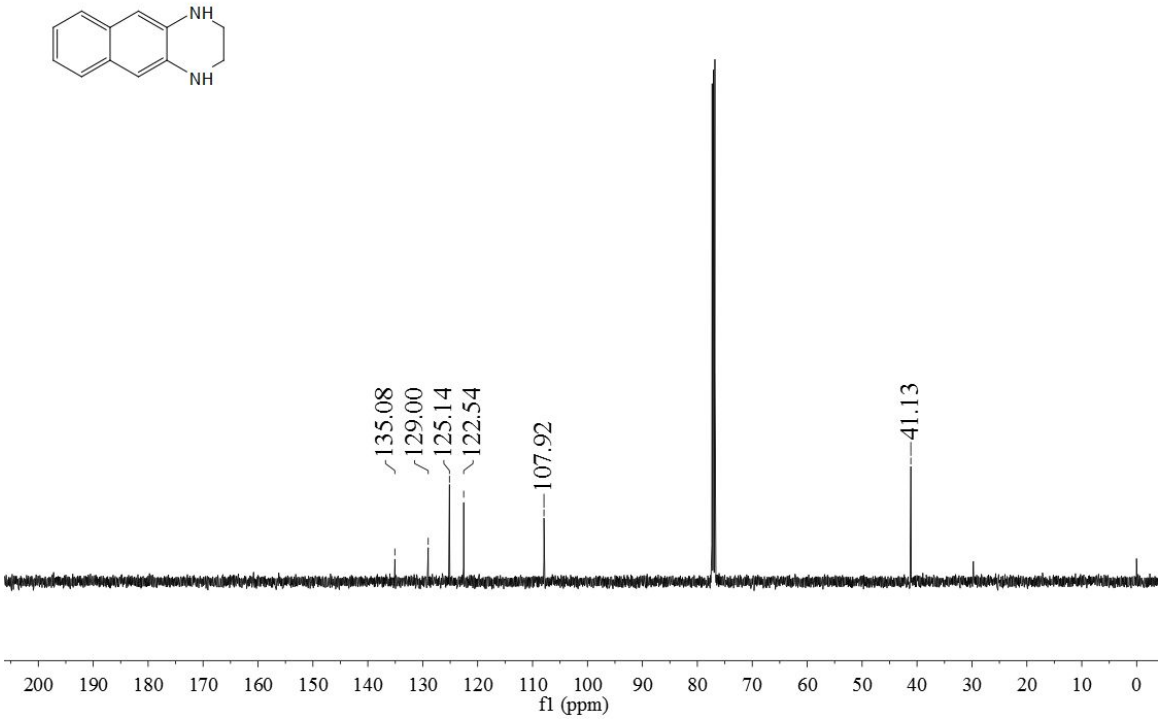
^{13}C NMR spectra of 4qk (126 MHz, $CDCl_3$)



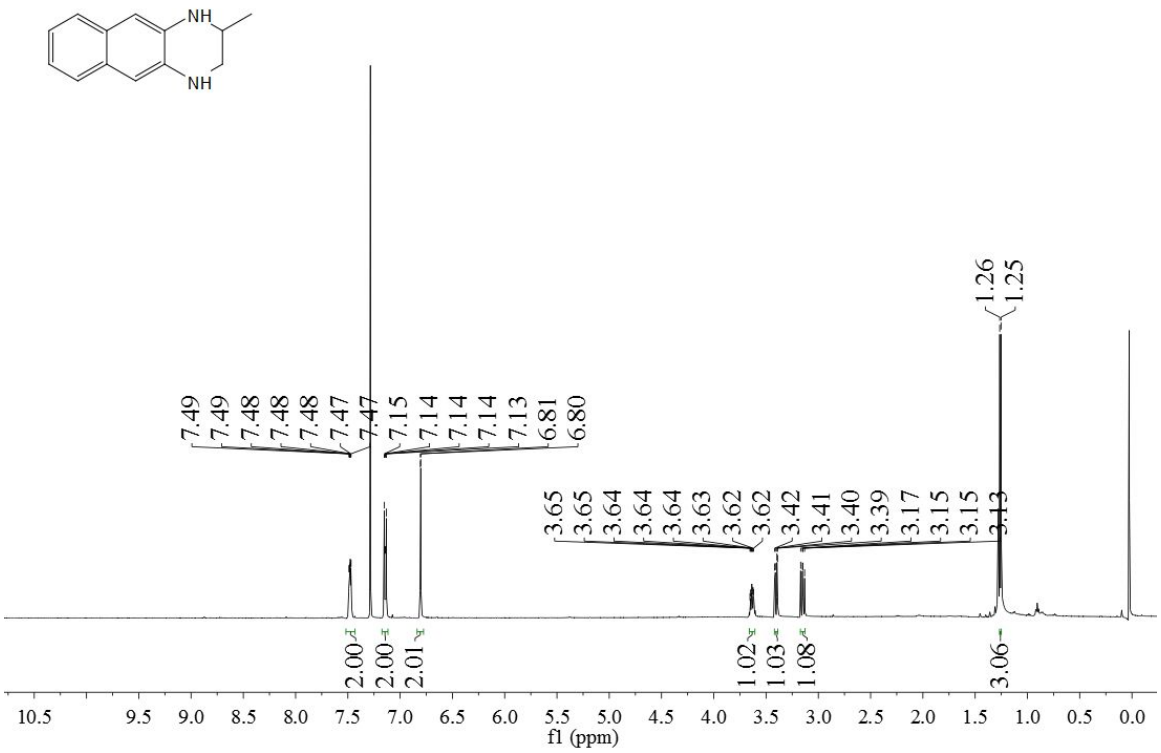
^{1}H NMR spectra of 4ql (500MHz, $CDCl_3$)



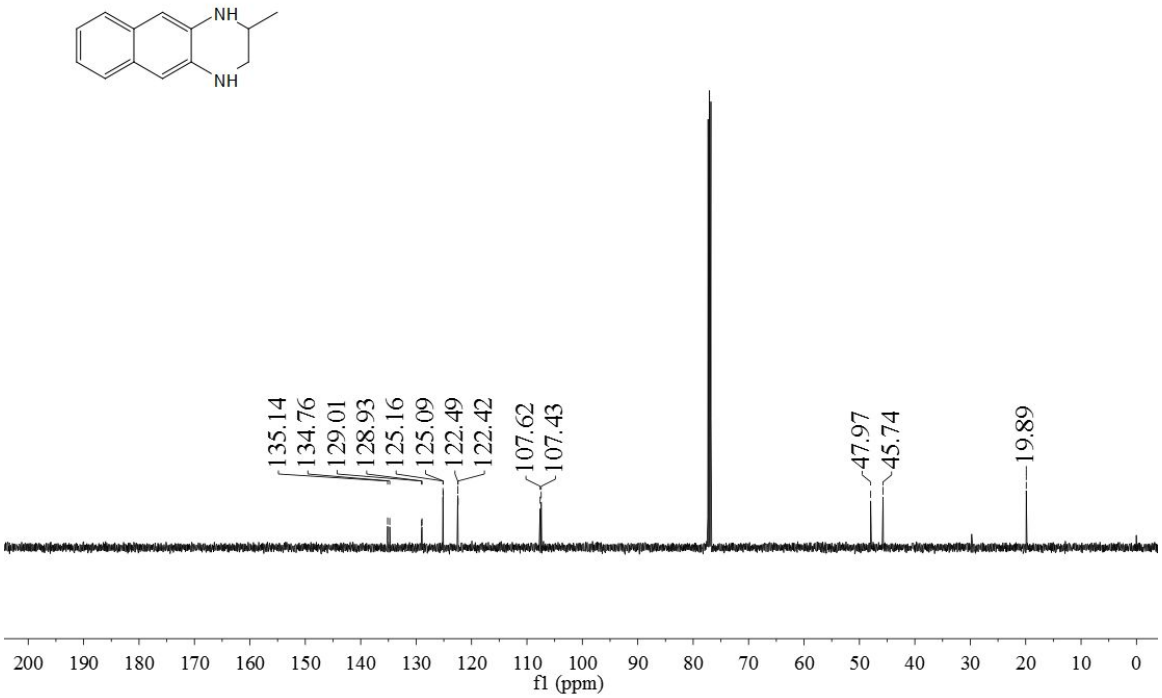
^{13}C NMR spectra of 4ql (126 MHz, $CDCl_3$)



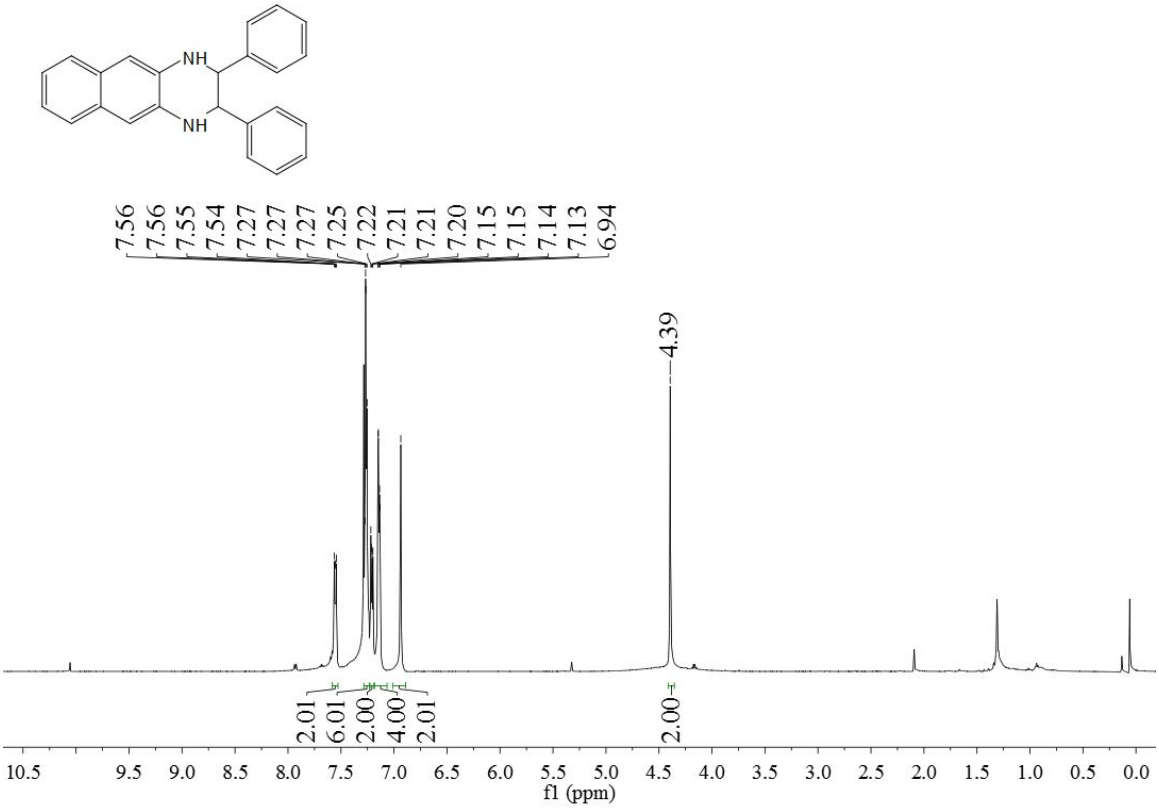
^{1}H NMR spectra of 4rl (500MHz, $CDCl_3$)



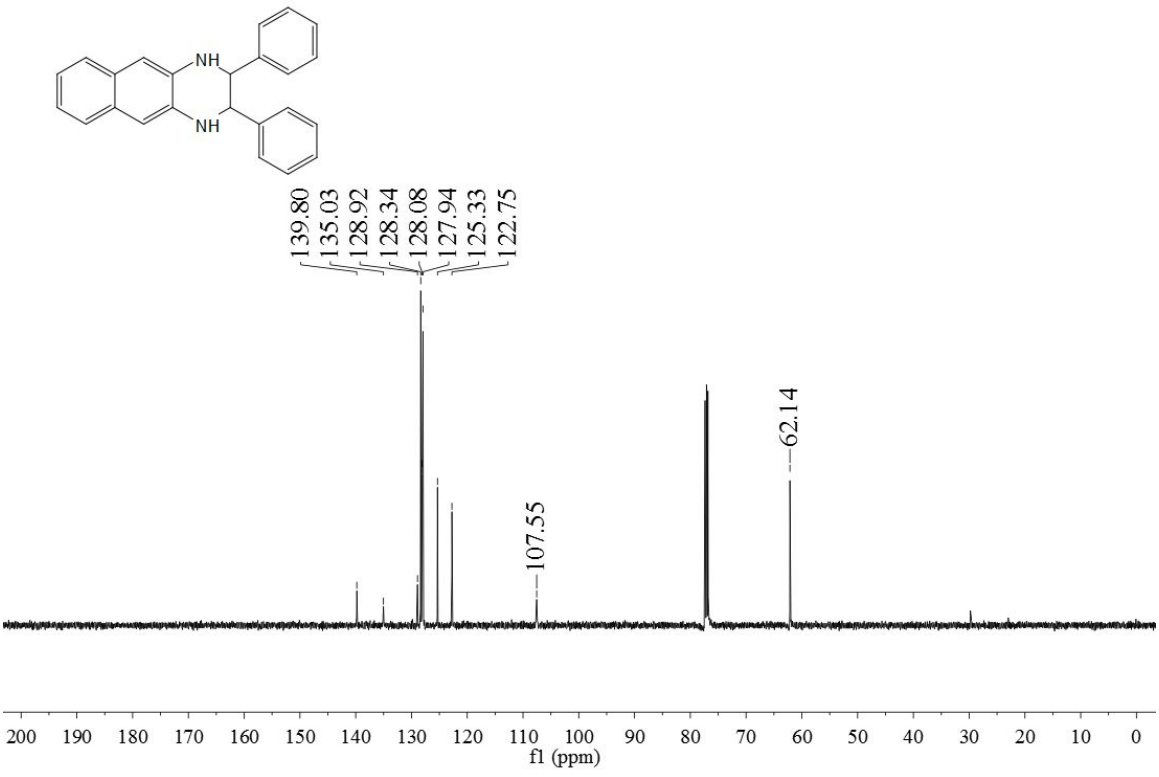
^{13}C NMR spectra of 4rl (126 MHz, $CDCl_3$)



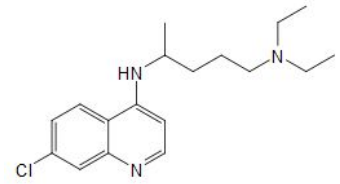
^{1}H NMR spectra of 4sl (500MHz, $CDCl_3$)

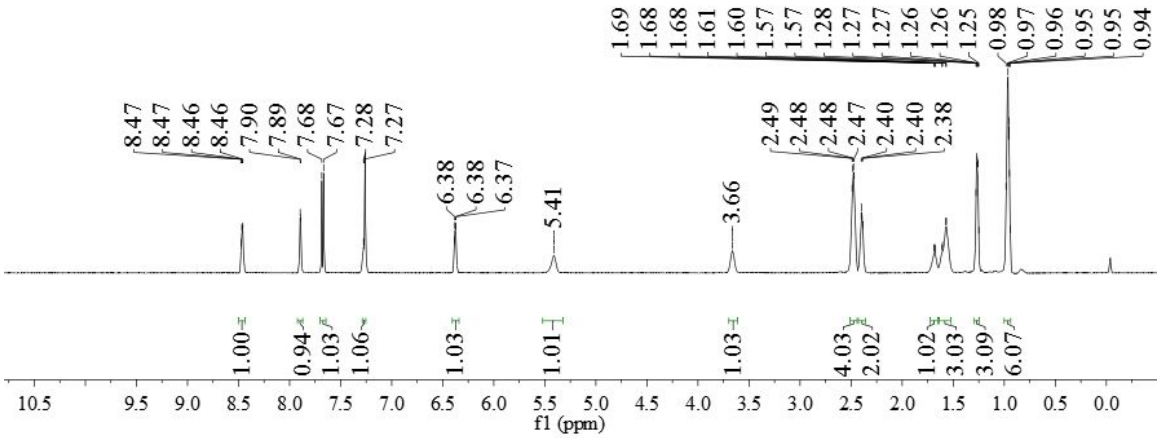


^{13}C NMR spectra of 4sl (126 MHz, $CDCl_3$)

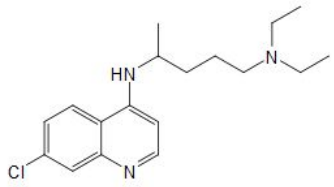


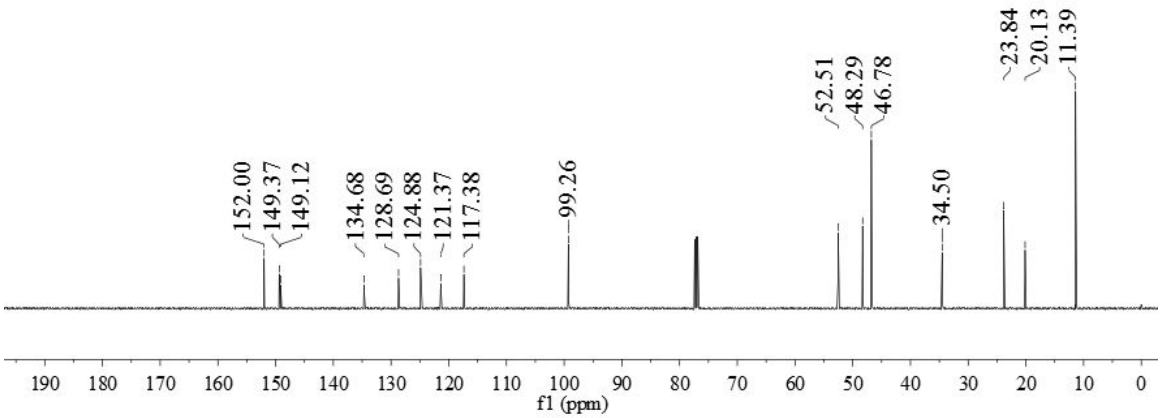
^{1}H NMR spectra of 4tm (500MHz, $CDCl_3$)



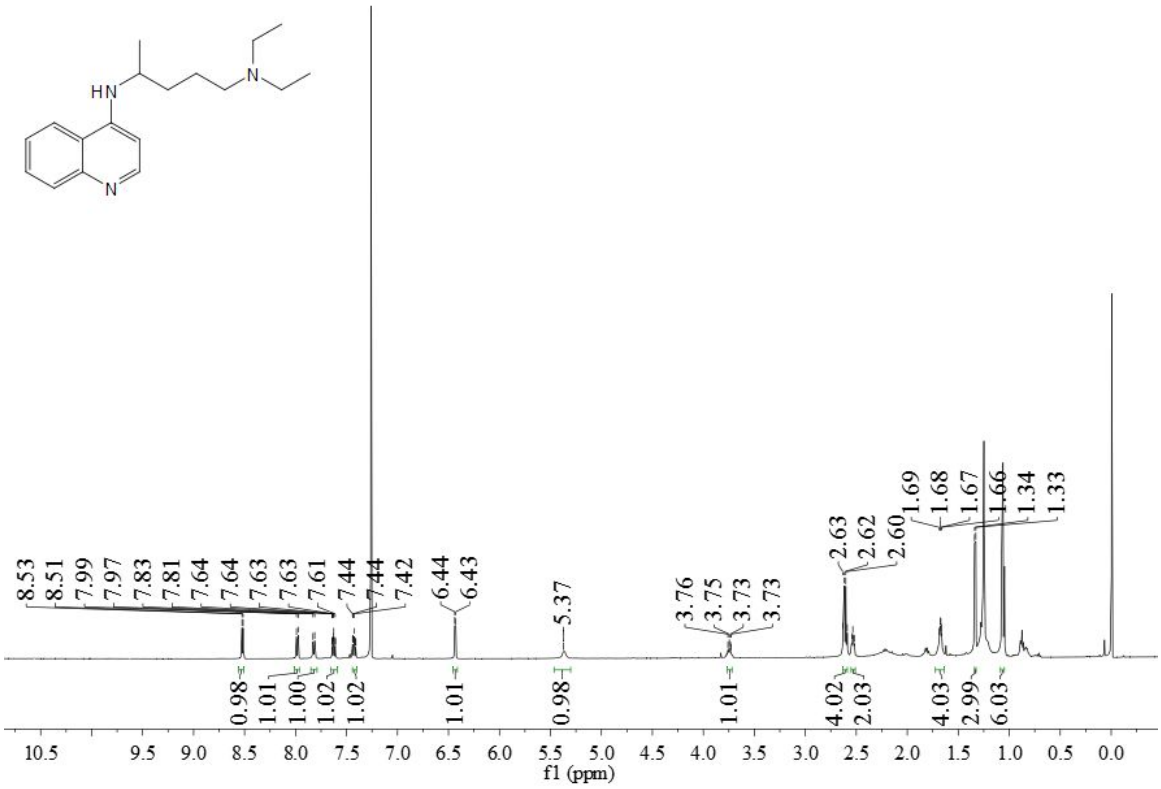


^{13}C NMR spectra of 4tm (126 MHz, $CDCl_3$)





^{1}H NMR spectra of 4tm' (500MHz, $CDCl_3$)



^{13}C NMR spectra of 4tm' (126 MHz, $CDCl_3$)