

# Supplementary Information

## Electrochemical Dehydrogenative Cross-Coupling of Two Anilines: Facile Synthesis of Unsymmetrical Biaryls

Mu-Jia Luo, Yang Li,\* Xuan-Hui Ouyang, Jin-Heng Li,\* and De-Liang He\*

*State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, China, Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, China, and State Key Laboratory of Applied Organic Chemistry Lanzhou University, Lanzhou 730000, China*

E-mail: [liyang8825490@126.com](mailto:liyang8825490@126.com), [jhli@hnu.edu.cn](mailto:jhli@hnu.edu.cn), [delianghe@hnu.edu.cn](mailto:delianghe@hnu.edu.cn)

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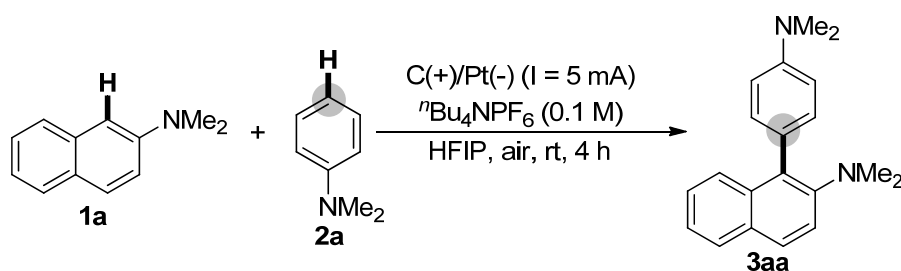
**(D) References**

## (A) Typical Experimental Procedure

### (a) General

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  solvent on a NMR spectrometer using TMS as internal standard. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected. The instrument for electrolysis is IKA ElectraSyn 2.0 and DC power source (PM3005B) (made in China). Cyclic voltammograms were obtained on a CHI 605E potentiostat.

### (b) General procedure for synthesis of compound **3aa**.

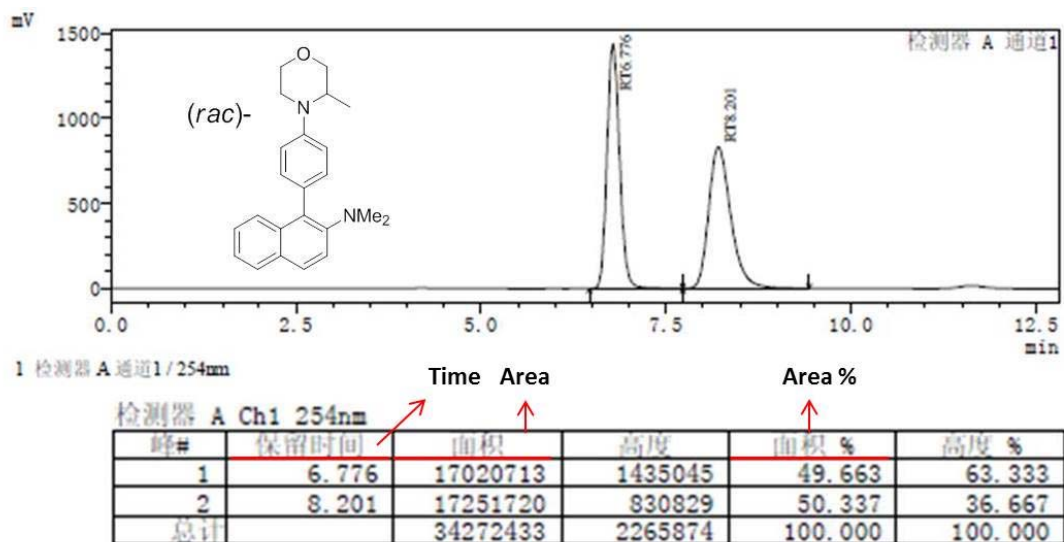
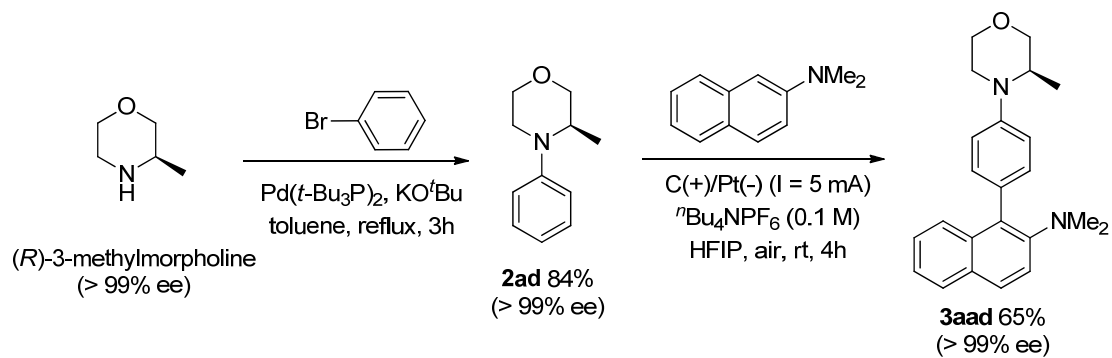


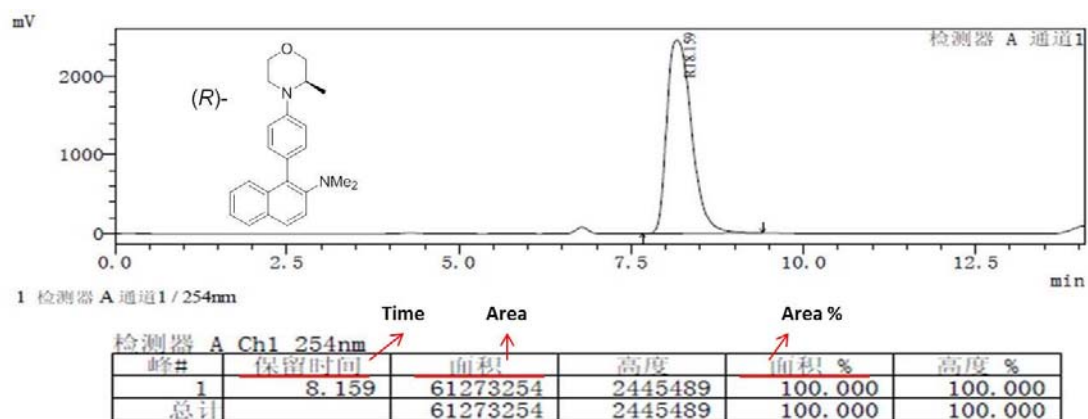
To an undivided three-necked bottle (10 mL) were added *N,N*-dimethylnaphthalen-2-amine **1a** (0.2 mmol), *N,N*-dimethylaniline **2a** (0.3 mmol) and HFIP (6 mL). The bottle was equipped with platinum electrodes ( $1.0 \times 1.0 \text{ cm}^2$ ) as cathode and graphite electrode as anode under air. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at room temperature for 4 h until complete consumption of **1a** as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the solution was extracted with EtOAc ( $3 \times 10 \text{ mL}$ ). The combined organic layer was dried with  $\text{Na}_2\text{SO}_4$ , filtered and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **3aa**.

### (c) Experimental device

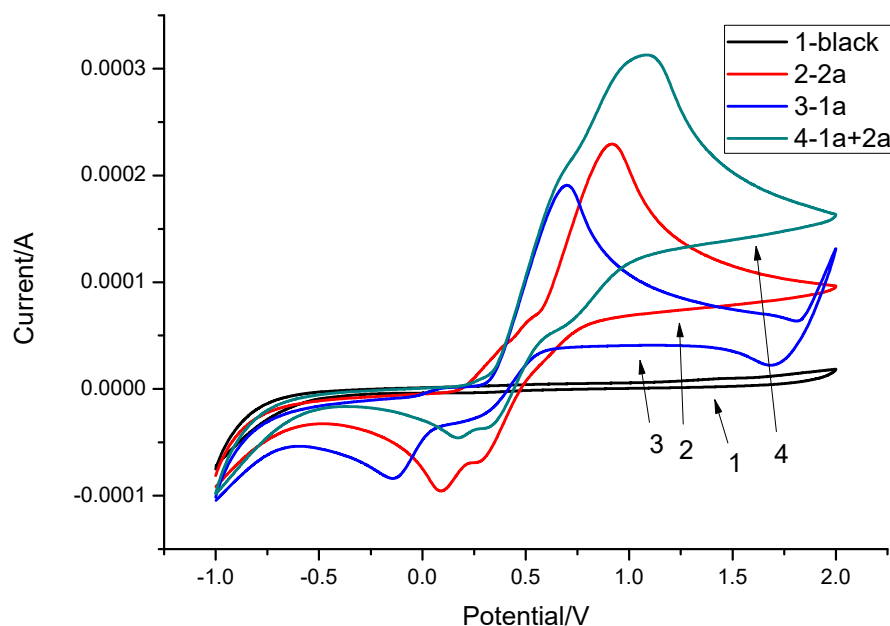


### (d) Synthesis of compound 3aad.



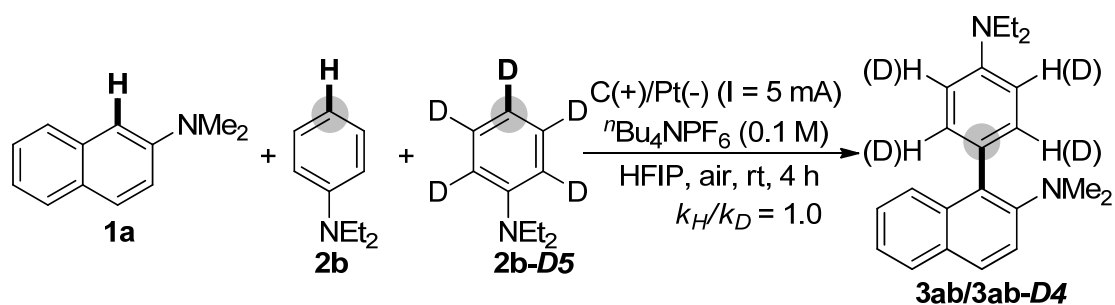


(e) Cyclic Voltammogram Curve

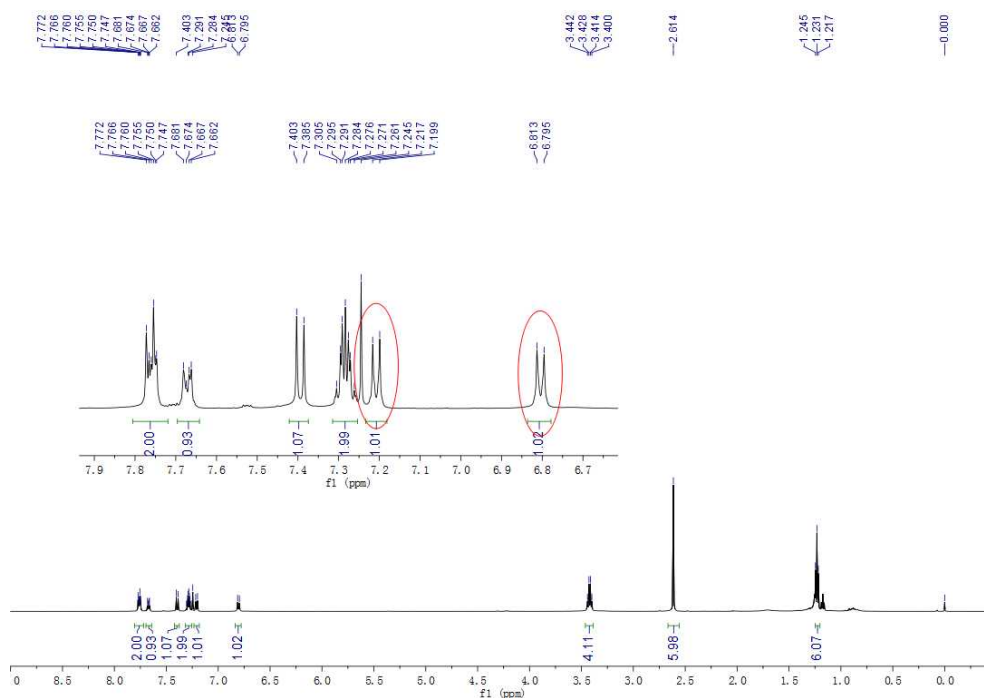


**Figure S1. Cyclic voltammogram curves.** using GC disk as working electrode, Pt slice, and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate: (1)  $n\text{Bu}_4\text{NPF}_6$  (0.1 M) and HFIP (6 mL); (2) **2a** (0.03 M),  $n\text{Bu}_4\text{NPF}_6$  (0.1 M) and HFIP (6 mL); (3) **1a** (0.05 M),  $n\text{Bu}_4\text{NPF}_6$  (0.1 M) and HFIP (6 mL); (4) **1a** (0.05 M), **2a** (0.03 M),  $n\text{Bu}_4\text{NPF}_6$  (0.1 M) and HFIP (6 mL).

**(f) KIE Experiment.**

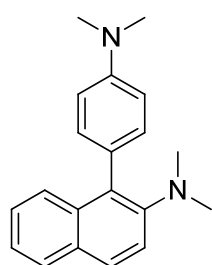


To an undivided three-necked bottle (10 mL) were added *N,N*-dimethylnaphthalen-2-amine **1a** (0.2 mmol), *N,N*-dimethylaniline **2b** (0.15 mmol), **2b-D5** (0.15 mmol) and HFIP (6 mL). The bottle was equipped with platinum electrodes ( $1.0 \times 1.0 \text{ cm}^2$ ) as cathode and graphite rod electrode as anode under air. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at room temperature for 4 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the solution was extracted with EtOAc ( $3 \times 10 \text{ mL}$ ). The combined organic layer was dried with  $\text{Na}_2\text{SO}_4$ , filtered and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **3ab/3ab-D4**.



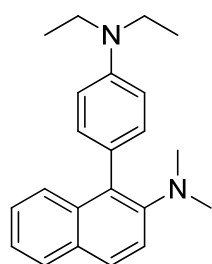
## (B) Analytical data

### 1-(4-(Dimethylamino)phenyl)-*N,N*-dimethylnaphthalen-2-amine (3aa):<sup>1</sup>



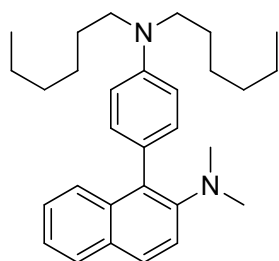
White solid, mp 129.8-131.4 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.78-7.75 (m, 2H), 7.63-7.61 (m, 1H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.30-7.23 (m, 4H), 6.88-6.85 (m, 2H), 3.02 (s, 6H), 2.60 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.2, 149.1, 134.2, 131.8, 130.4, 129.8, 127.8, 127.7, 126.9, 125.7 (2C), 123.5, 119.5, 112.4, 44.0, 40.7; LRMS (EI, 70 eV) *m/z* (%): 290 (M<sup>+</sup>, 100), 275 (18), 231 (15), 134 (22); The analytical data are in accordance with those reported in the literature.<sup>1</sup>

### 1-(4-(Diethylamino)phenyl)-*N,N*-dimethylnaphthalen-2-amine (3ab):



Light yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76-7.74 (m, 2H), 7.68-7.66 (m, 1H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.29-7.27 (m, 2H), 7.22-7.20 (m, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.41 (q, *J* = 7.0 Hz, 4H), 2.61 (s, 6H), 1.22 (t, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.2, 146.6, 134.3, 132.0, 130.5, 129.8, 127.7, 125.8, 125.7, 125.6, 123.4, 119.5, 111.8, 44.4, 44.0, 12.8; LRMS (EI, 70 eV) *m/z* (%): 318 (M<sup>+</sup>, 100), 303 (81), 274 (18), 151 (12); HRMS *m/z* (ESI) calcd for C<sub>22</sub>H<sub>27</sub>N<sub>2</sub> [M+H]<sup>+</sup> 319.2169, found 319.2186.

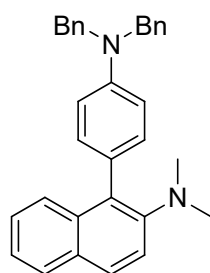
### 1-(4-(Dihexylamino)phenyl)-*N,N*-dimethylnaphthalen-2-amine (3ac):



Light yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76-7.74 (m, 2H), 7.69-7.67 (m, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.29-7.26 (m, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 3.33-3.29 (m, 4H), 2.61 (s, 6H), 1.67-1.64 (m, 4H), 1.35-1.32 (m, 12H), 0.91 (t, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.1, 147.0, 134.3, 131.9, 130.5, 129.8, 127.6, 127.6, 125.9, 125.6, 125.3, 123.4, 119.5, 111.5, 51.2, 44.0,

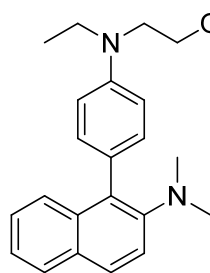
31.9, 27.4, 27.0, 22.8, 14.1; LRMS (EI, 70 eV)  $m/z$  (%): 430 ( $M^+$ , 90), 359 (100), 289 (70), 144 (30); HRMS  $m/z$  (ESI) calcd for  $C_{30}H_{43}N_2$   $[M+H]^+$  431.3421, found 431.3433.

**1-(4-(Dibenzylamino)phenyl)-*N,N*-dimethylnaphthalen-2-amine (3ad):**



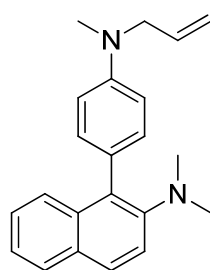
Light yellow solid, mp 151.6-152.8 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.76-7.74 (m, 2H), 7.66-7.64 (m, 1H), 7.39-7.26 (m, 13H), 7.17 (d,  $J$  = 8.5 Hz, 2H), 6.86 (d,  $J$  = 8.5 Hz, 2H), 4.71 (s, 4H), 2.59 (s, 6H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  149.1, 148.0, 138.9, 134.1, 131.9, 130.1, 129.7, 128.7, 127.8, 127.7, 127.1, 126.9 (2C), 125.7 (2C), 123.5, 119.5, 112.5, 54.26, 43.91; HRMS  $m/z$  (ESI) calcd for  $C_{32}H_{31}N_2$   $[M+H]^+$  443.2482, found 443.2476.

**2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethylamino)ethanol (3ae):**



Light yellow oil;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.78-7.75 (m, 2H), 7.64-7.62 (m, 1H), 7.40 (d,  $J$  = 9.0 Hz, 1H), 7.31-7.27 (m, 2H), 7.23 (d,  $J$  = 8.5 Hz, 2H), 6.89 (d,  $J$  = 8.5 Hz, 2H), 3.85 (t,  $J$  = 4.5 Hz, 2H), 3.53 (t,  $J$  = 5.5 Hz, 2H), 3.48 (q,  $J$  = 7.0 Hz, 2H), 2.61 (s, 6H), 1.92 (s, 1H), 1.23 (t,  $J$  = 6.5 Hz, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  149.1, 147.0, 134.2, 132.0, 130.3, 129.8, 127.9, 127.7, 127.2, 125.7, 125.6, 123.5, 119.5, 113.0, 60.3, 52.7, 45.9, 44.0, 12.1; HRMS  $m/z$  (ESI) calcd for  $C_{22}H_{27}N_2O$   $[M+H]^+$  335.2118, found 335.2141.

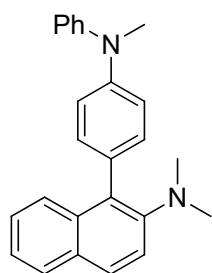
**1-(4-(Allyl(methyl)amino)phenyl)-*N,N*-dimethylnaphthalen-2-amine (3af):**



Light yellow solid, mp 141.5-142.3 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.77-7.74 (m, 2H), 7.65-7.63 (m, 1H), 7.38 (d,  $J$  = 9.0 Hz, 1H), 7.30-7.25 (m, 2H), 7.25-7.21 (m, 2H), 6.84 (d,  $J$  = 8.5 Hz, 2H), 5.96-5.88 (m, 1H), 5.25-5.18 (m, 2H), 3.98 (d,  $J$  = 5.0 Hz, 2H),

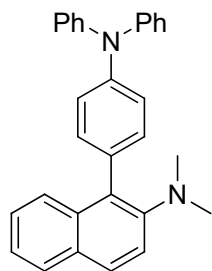
2.99 (s, 3H), 2.60 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 148.3, 134.3, 134.2, 131.9, 130.4, 129.8, 127.8, 127.7, 126.8, 125.7, 123.5, 119.5, 116.3, 112.3, 55.5, 44.0, 38.0; LRMS (EI, 70 eV)  $m/z$  (%): 316 ( $\text{M}^+$ , 100), 275 (21), 244 (22), 160 (11); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{22}\text{H}_{25}\text{N}_2$   $[\text{M}+\text{H}]^+$  317.2012, found 317.2031.

***N,N*-Dimethyl-1-(4-(methyl(phenyl)amino)phenyl)naphthalen-2-amine (3ag):**



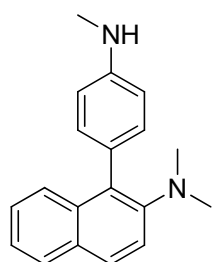
Light yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.76 (m, 2H), 7.64-7.62 (m, 1H), 7.41 (d,  $J$  = 9.0 Hz, 1H), 7.34-7.28 (m, 6H), 7.16-7.13 (m, 4H), 6.99 (t,  $J$  = 7.5 Hz, 1H), 3.41 (s, 3H), 2.63 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1 (2C), 147.4, 133.9, 132.0, 131.6, 129.9, 129.7, 129.3, 128.1, 127.8, 125.9, 125.4, 123.6, 121.4, 120.9, 119.8, 119.5, 44.0, 40.4; LRMS (EI, 70 eV)  $m/z$  (%): 352 ( $\text{M}^+$ , 100), 320 (10), 231 (20), 196 (13); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{25}\text{H}_{25}\text{N}_2$   $[\text{M}+\text{H}]^+$  353.2012, found 353.2036.

***1*-(4-(Diphenylamino)phenyl)-*N,N*-dimethylnaphthalen-2-amine (3ah):**



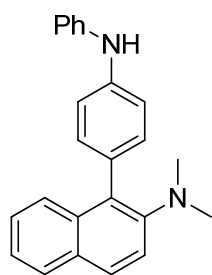
White solid, mp 163.8-165.1  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.77 (m, 2H), 7.67-7.65 (m, 1H), 7.40 (d,  $J$  = 8.5 Hz, 1H), 7.35-7.26 (m, 8H), 7.21-7.18 (m, 6H), 7.05-7.02 (m, 2H), 2.64 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 147.9, 146.2, 133.7, 133.3, 132.1, 129.4, 129.3, 128.2, 127.8, 125.9, 125.2, 124.7, 124.3, 123.7, 122.7, 119.5, 43.8; LRMS (EI, 70 eV)  $m/z$  (%): 414 ( $\text{M}^+$ , 100), 309 (19), 231 (17), 207 (10); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{20}\text{H}_{27}\text{N}_2$   $[\text{M}+\text{H}]^+$  415.2169, found 415.2183.

***N,N*-Dimethyl-1-(4-(methylamino)phenyl)naphthalen-2-amine (3ai):**



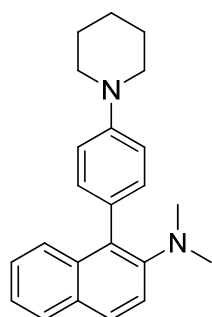
White solid, mp 138.6-139.8 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78-7.75 (m, 2H), 7.64-7.62 (m, 1H), 7.39 (d,  $J = 9.0$  Hz, 1H), 7.31-7.25 (m, 2H), 7.22-7.19 (m, 2H), 6.76- 6.73 (m, 2H), 3.76 (s, 1H), 2.91 (s, 3H), 2.61 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 148.0, 134.2, 131.9, 130.4, 129.8, 127.8, 127.7 (2C) 125.7, 125.6, 123.5, 119.5, 112.3, 44.0, 30.9; LRMS (EI, 70 eV)  $m/z$  (%): 276 ( $\text{M}^+$ , 100), 260 (20), 231 (20), 196 (13); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{19}\text{H}_{21}\text{N}_2$  [ $\text{M}+\text{H}$ ] $^+$  277.1699, found 277.1713.

***N,N*-Dimethyl-1-(4-(phenylamino)phenyl)naphthalen-2-amine (3aj):**



White solid, mp 144.4-145.0 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81-7.77 (m, 2H), 7.64-7.63 (m, 1H), 7.41 (d,  $J = 9.0$  Hz, 1H), 7.32-7.28 (m, 6H), 7.24-7.16 (m, 4H), 6.95 (t,  $J = 7.0$  Hz, 1H), 5.80 (s, 1H), 2.63 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 143.2, 141.6, 133.9, 132.1, 131.6, 130.0, 129.8, 129.41, 128.2, 127.8, 125.9, 125.4, 123.6, 121.0, 119.5, 117.9, 117.6, 44.0; LRMS (EI, 70 eV)  $m/z$  (%): 338 ( $\text{M}^+$ , 100), 306 (12), 231 (23), 182 (15); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{24}\text{H}_{23}\text{N}_2$  [ $\text{M}+\text{H}$ ] $^+$  339.1856, found 339.1848.

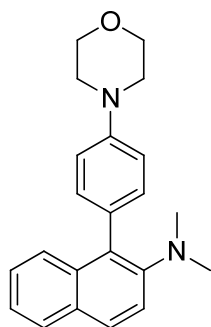
***N,N*-Dimethyl-1-(4-(piperidin-1-yl)phenyl)naphthalen-2-amine (3al):**



Light yellow solid, mp 145.3-146.8 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77-7.74 (m, 2H), 7.60 (d,  $J = 7.5$  Hz, 1H), 7.38 (d,  $J = 8.5$  Hz, 1H), 7.30-7.22 (m, 4H), 7.05 (d,  $J = 8.5$  Hz, 2H), 3.24 (t,  $J = 5.0$  Hz, 4H), 2.59 (s, 6H), 1.78-1.73 (m, 4H), 1.62-1.59 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 149.1, 134.1, 131.8, 130.1, 129.7,

129.5, 127.9, 127.7, 125.8, 125.6, 123.5, 119.5, 116.2, 50.6, 44.0, 26.1, 24.4; LRMS (EI, 70 eV)  $m/z$  (%): 330 ( $M^+$ , 100), 298 (11), 231 (11), 174 (11); HRMS  $m/z$  (ESI) calcd for  $C_{23}H_{27}N_2$   $[M+H]^+$  331.2169, found 331.2183.

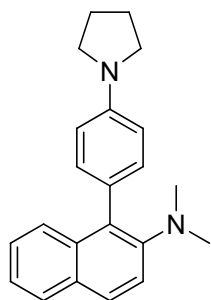
***N,N*-Dimethyl-1-(4-morpholinophenyl)naphthalen-2-amine (3am)<sup>1</sup>:**



Yellow solid, mp 156.2-157.3 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.80-7.76 (m, 2H), 7.57 (d,  $J$  = 8.0 Hz, 1H), 7.41 (d,  $J$  = 9.0 Hz, 1H), 7.32-7.26 (m, 4H), 7.04 (d,  $J$  = 9.0 Hz, 2H), 3.92 (t,  $J$  = 5.0 Hz, 4H), 3.27 (t,  $J$  = 5.0 Hz, 4H), 2.60 (s, 6H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  149.7, 149.1, 134.0, 131.9, 130.5, 129.9, 129.8, 128.1,

127.7, 125.8, 125.4, 123.6, 119.5, 115.3, 67.1, 49.3, 44.0; LRMS (EI, 70 eV)  $m/z$  (%): 332 ( $M^+$ , 100), 273 (40), 230 (22), 136 (27).

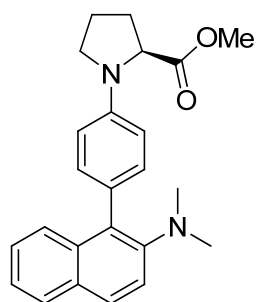
***N,N*-Dimethyl-1-(4-(pyrrolidin-1-yl)phenyl)naphthalen-2-amine(3an):**



Yellow solid, mp 150.4-151.3 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.77-7.55 (m, 2H), 7.64 (d,  $J$  = 8.0 Hz, 1H), 7.39 (d,  $J$  = 9.0 Hz, 1H), 7.31-7.22 (m, 4H), 6.70 (d,  $J$  = 8.5 Hz, 2H), 3.37 (t,  $J$  = 6.0 Hz, 4H), 2.61 (s, 6H), 2.05-2.03 (m, 4H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  149.1, 146.6, 134.3, 131.9, 130.6, 129.8, 127.7, 127.6, 125.8,

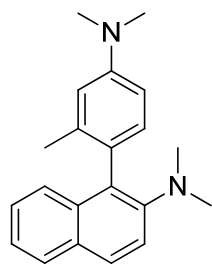
125.6, 123.4, 119.5, 111.4, 47.7, 44.0, 25.6; HRMS  $m/z$  (ESI) calcd for  $C_{22}H_{25}N_2$   $[M+H]^+$  317.2012, found 317.2031.

**(S)-Methyl-1-(4-(2-(dimethylamino)naphthalen-1-yl)phenyl)pyrrolidine-2-carboxylate (3ao):**



Light yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77-7.74 (m, 2H), 7.62-7.59 (m, 1H), 7.39 (d,  $J = 9.0$  Hz, 1H), 7.30-7.26 (m, 2H), 7.26-7.22 (m, 2H), 6.67 (d,  $J = 8.5$  Hz, 2H), 4.34-4.32 (m, 1H), 3.76 (s, 3H), 3.68-3.65 (m, 1H), 3.45 (q,  $J = 8.0$  Hz, 1H), 2.59 (s, 6H), 2.34-2.28 (m, 1H), 2.24-2.16 (m, 2H), 2.12-2.04 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  175.2, 149.1, 145.4, 134.2, 131.9, 130.4, 129.8, 127.8, 127.7, 127.0, 125.7, 123.5, 119.5, 111.9, 111.9, 61.0, 52.2, 48.5, 44.0, 31.1, 24.0; LRMS (EI, 70 eV)  $m/z$  (%): 374 ( $\text{M}^+$ , 41), 315 (100), 299 (18), 157 (12); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_2$  [ $\text{M}+\text{H}$ ] $^+$  375.2067, found 375.2088.

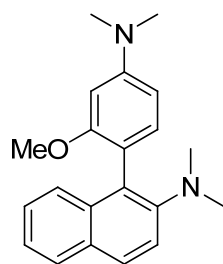
**1-(4-(Dimethylamino)-2-methylphenyl)-N,N-dimethylnaphthalen-2-amine (3ap):**



White solid, mp 146.8-147.7  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79-7.75 (m, 2H), 7.40-7.35 (m, 2H), 7.29 (d,  $J = 6.5$  Hz, 1H), 7.25-7.22 (m, 1H), 7.07 (d,  $J = 8.0$  Hz, 1H), 6.73-6.71 (m, 2H), 3.01 (s, 6H), 2.62 (s, 6H), 1.97 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.7, 149.2, 137.9, 134.2, 132.1, 129.8, 129.7, 127.9, 127.7, 127.0, 125.8, 125.6, 123.5, 119.5, 114.1, 110.3, 43.9, 40.8, 20.6; LRMS (EI, 70 eV)  $m/z$  (%): 304 ( $\text{M}^+$ , 100), 289 (27), 259 (18), 144 (13); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{21}\text{H}_{25}\text{N}_2$  [ $\text{M}+\text{H}$ ] $^+$  305.2012, found 305.2036.

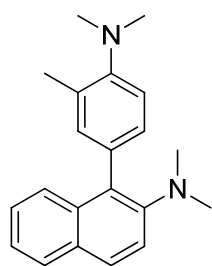
### 1-(4-(Dimethylamino)-2-methoxyphenyl)-*N,N*-dimethylnaphthalen-2-amine

(3aq):



Light yellow solid, mp 153.3-154.8 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77-7.73 (m, 2H), 7.39 (d,  $J = 8.5$  Hz, 2H), 7.28-7.23 (m, 2H), 7.01 (d,  $J = 8.0$  Hz, 1H), 6.47-6.43 (m, 2H), 3.70 (s, 3H), 3.04 (s, 6H), 2.63 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 151.3, 149.7, 134.4, 132.6, 129.6, 127.9, 127.7, 127.2, 125.8, 125.6, 123.3, 119.8, 116.4, 105.1, 96.3, 55.4, 43.9, 40.8; LRMS (EI, 70 eV)  $m/z$  (%): 320 ( $\text{M}^+$ , 100), 289 (25), 274 (46), 184 (27); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}$  [ $\text{M}+\text{H}$ ] $^+$  321.1961, found 321.1980.

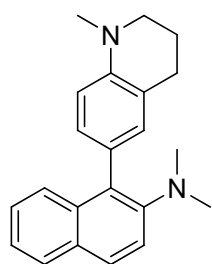
### 1-(4-(Dimethylamino)-3-methylphenyl)-*N,N*-dimethylnaphthalen-2-amine (3ar):



White solid, mp 147.4-148.8 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79-7.75 (m, 2H), 7.57-7.55 (m, 1H), 7.40 (d,  $J = 9.0$  Hz, 1H), 7.32-7.26 (m, 2H), 7.15-7.12 (m, 3H), 2.79 (s, 6H), 2.60 (s, 6H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  151.2, 148.9, 134.0, 133.8, 132.9, 131.5, 130.2, 129.7, 129.1, 128.0, 127.7, 125.8, 125.6, 123.5, 119.5, 118.0, 44.4, 44.1, 18.7; LRMS (EI, 70 eV)  $m/z$  (%): 304 ( $\text{M}^+$ , 100), 289 (20), 258 (18), 144 (15); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{21}\text{H}_{25}\text{N}_2$  [ $\text{M}+\text{H}$ ] $^+$  305.2012, found 305.2027.

### *N,N*-Dimethyl-1-(1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)naphthalen-2-amine

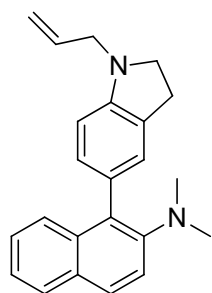
(3as):



Light yellow solid, mp 163.4-165.1 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78-7.71 (m, 2H), 7.66-7.64 (m, 1H), 7.37 (d,  $J = 9.0$  Hz, 1H), 7.31-7.24 (m, 2H), 7.06 (d,  $J = 8.5$  Hz, 1H), 6.95-6.94 (m, 1H), 6.70 (d,  $J = 8.5$  Hz, 1H), 3.32-3.25 (m, 2H), 2.95 (s, 3H), 2.81 (t,  $J = 6.5$  Hz, 2H), 2.61 (s, 6H), 2.06-2.01 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  148.9, 145.3,

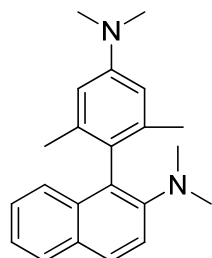
134.3, 131.4, 130.5, 129.7, 129.6, 127.6, 126.5, 125.7, 125.5, 123.3, 122.5, 119.5, 110.6, 51.4, 44.0, 39.1, 27.8, 22.6; HRMS  $m/z$  (ESI) calcd for  $C_{22}H_{25}N_2$   $[M+H]^+$  317.2012, found 317.2006.

**1-(1-Allylindolin-5-yl)-N,N-dimethylnaphthalen-2-amine (3at):**



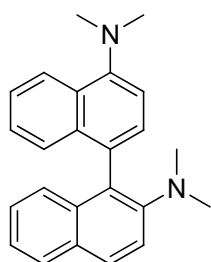
Light yellow oil;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.81-7.70 (m, 2H), 7.68-7.59 (m, 1H), 7.37 (d,  $J$  = 9.0 Hz, 1H), 7.34-7.22 (m, 2H), 7.12-7.00 (m, 2H), 6.63 (d,  $J$  = 8.0 Hz, 1H), 6.02-5.94 (m, 1H), 5.35-5.31 (m, 1H), 5.24-5.21 (m, 1H), 3.77 (t,  $J$  = 6.5 Hz, 2H), 3.42-3.37 (m, 2H), 3.04-3.00 (m, 2H), 2.60 (s, 6H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  150.9, 148.9, 134.5, 134.3, 130.6, 130.1, 129.9, 129.7, 128.2, 127.6, 127.6, 127.2, 125.6, 125.6, 123.3, 119.4, 117.3, 107.0, 53.4, 52.4, 43.9, 28.6; HRMS  $m/z$  (ESI) calcd for  $C_{23}H_{25}N_2$   $[M+H]^+$  329.2012, found 329.2028.

**1-(4-(Dimethylamino)-2,6-dimethylphenyl)-N,N-dimethylnaphthalen-2-amine (3au):**



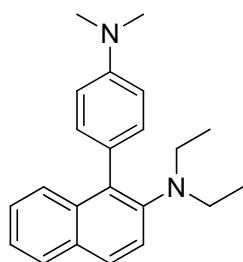
Light yellow solid, mp 123.6-124.2 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.79-7.76 (m, 2H), 7.38 (d,  $J$  = 9.0 Hz, 1H), 7.30-7.26 (m, 1H), 7.24-7.22 (m, 2H), 6.60 (s, 2H), 3.00 (s, 6H), 2.64 (s, 6H), 1.89 (s, 6H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  149.6, 148.9, 137.9, 133.7, 129.7, 128.4, 127.9, 127.7, 126.9, 125.9, 125.0, 123.4, 119.3, 112.1, 43.3, 40.8, 21.0; LRMS (EI, 70 eV)  $m/z$  (%): 318 ( $M^+$ , 100), 303 (25), 273 (19), 149 (19); HRMS  $m/z$  (ESI) calcd for  $C_{22}H_{27}N_2$   $[M+H]^+$  319.2169, found 319.2184.

***N*<sup>2</sup>,*N*<sup>2</sup>,*N*<sup>4'</sup>,*N*<sup>4'</sup>-Tetramethyl-[1,1'-binaphthalene]-2,4'-diamine (3av):**



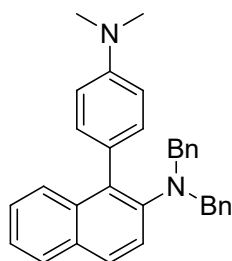
Yellow solid, mp 152.4-152.9 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.32 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.47-7.43 (m, 2H), 7.35-7.32 (m, 2H), 7.28-7.18 (m, 3H), 7.13 (d, *J* = 3.5 Hz, 2H), 2.98 (s, 6H), 2.50 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.3, 149.9, 134.7, 134.3, 131.6, 129.6, 129.0, 128.8, 128.6, 127.9, 127.7, 127.2, 126.0, 125.9, 125.6, 124.9, 124.4, 123.5, 119.8, 113.9, 45.5, 44.0; LRMS (EI, 70 eV) *m/z* (%): 340 (M<sup>+</sup>, 100), 295 (21), 281 (19), 170 (13); HRMS *m/z* (ESI) calcd for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub> [M+H]<sup>+</sup> 341.2012, found 341.2025.

**1-(4-(Dimethylamino)phenyl)-*N,N*-diethylnaphthalen-2-amine (3ba):<sup>1</sup>**



Light yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.77 (t, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 9.0 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 7.24-7.21 (m, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.02 (s, 6H), 2.93 (q, *J* = 7.0 Hz, 4H), 0.86 (t, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.2, 146.5, 134.4, 131.8, 130.4, 127.6, 127.3, 127.0, 126.1, 125.5, 123.9, 122.1, 112.2, 47.5, 40.8, 12.9; LRMS (EI, 70 eV) *m/z* (%): 318 (M<sup>+</sup>, 85), 303 (42), 274 (100), 159 (11); The analytical data are in accordance with those reported in the literature.<sup>1</sup>

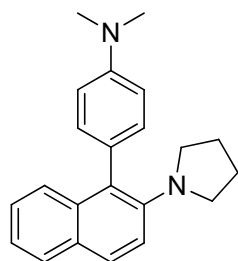
***N,N*-Dibenzyl-1-(4-(dimethylamino)phenyl)naphthalen-2-amine (3ca):<sup>1</sup>**



Light yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.32-7.25 (m, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.19-7.12 (m, 6H), 7.04 (d, *J* = 7.0 Hz, 4H), 6.89 (d, *J* = 8.5 Hz, 2H), 3.99 (s, 4H), 3.02 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.7, 146.9, 138.9, 134.5, 134.0, 131.8, 130.7, 129.2, 128.1, 127.7, 127.6, 126.9, 126.3, 125.7, 124.2,

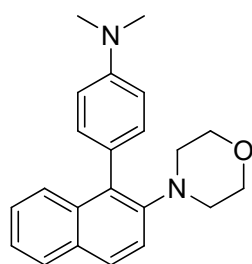
122.4, 112.8, 57.0, 41.0; The analytical data are in accordance with those reported in the literature.<sup>1</sup>

***N,N*-Dimethyl-4-(2-(pyrrolidin-1-yl)naphthalen-1-yl)aniline (3da):<sup>1</sup>**



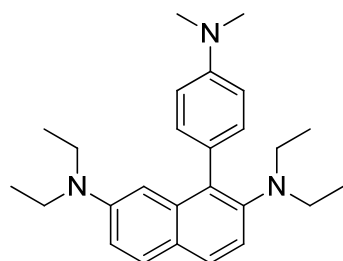
Light yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.22-7.20 (m, 3H), 7.18-7.15 (m, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 3.02-3.00 (m, 10H), 1.75-1.72 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.2, 145.6, 135.2, 132.6, 128.3, 127.6 (2C), 127.3, 125.7, 124.8, 122.1, 121.6, 117.1, 112.1, 51.0, 40.7, 25.7; The analytical data are in accordance with those reported in the literature.<sup>1</sup>

***N,N*-Dimethyl-4-(2-morpholinonaphthalen-1-yl)aniline (3ea):<sup>1</sup>**



White solid, mp 167.4-168.7 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.79-7.76 (m, 2H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.34-7.28 (m, 5H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.53 (t, *J* = 4.5 Hz, 4H), 3.01 (s, 6H), 2.87 (t, *J* = 4.5 Hz, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.4, 147.6, 133.8, 131.9, 131.8, 130.5, 128.1, 127.8, 125.9 (3C), 124.1, 119.4, 112.3, 67.4, 51.8, 40.7; LRMS (EI, 70 eV) *m/z* (%): 332 (M<sup>+</sup>, 100), 273 (39), 230 (22), 136 (26); The analytical data are in accordance with those reported in the literature.<sup>1</sup>

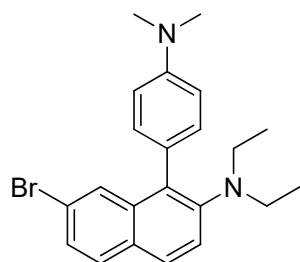
**1-(4-(Dimethylamino)phenyl)-*N*<sup>2</sup>,*N*<sup>2</sup>,*N*<sup>7</sup>,*N*<sup>7</sup>-tetraethylnaphthalene-2,7-diamine (3ga):**



Light yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.63 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.24-7.21 (m, 2H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.98-6.96 (m, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.64 (s, 1H), 3.26 (q, *J* = 7.0 Hz, 4H), 3.00 (s, 6H), 2.89 (q, *J* = 7.0 Hz, 4H), 1.06 (t, *J* = 7.0 Hz, 6H), 0.85 (t, *J* = 7.0 Hz, 6H);

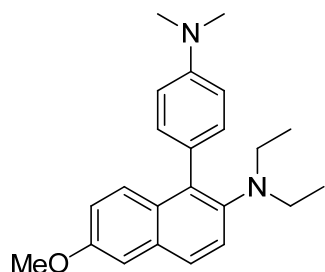
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 146.6, 145.4, 135.9, 132.6, 131.9, 128.6, 128.1, 126.8, 123.6, 117.8, 114.2, 112.5, 105.0, 47.7, 44.8, 41.0, 12.9, 12.6; LRMS (EI, 70 eV)  $m/z$  (%): 389 ( $\text{M}^+$ , 100), 374 (48), 345 (70), 165 (25); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{26}\text{H}_{36}\text{N}_3$   $[\text{M}+\text{H}]^+$  390.2904, found 390.2917.

**7-Bromo-1-(4-(dimethylamino)phenyl)-*N,N*-diethylnaphthalen-2-amine (3ha):**



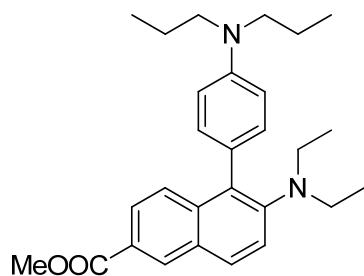
White solid, mp 134.3-135.6 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (s, 1H), 7.69 (d,  $J$  = 9.0 Hz, 1H), 7.61 (d,  $J$  = 8.5 Hz, 1H), 7.43-7.33 (m, 2H), 7.18 (d,  $J$  = 8.0 Hz, 2H), 6.85 (d,  $J$  = 8.0 Hz, 2H), 3.02 (s, 6H), 2.91 (q,  $J$  = 7.0 Hz, 4H), 0.85 (t,  $J$  = 7.0 Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.3, 147.7, 135.7, 132.9, 131.7, 129.3, 128.6, 128.0, 127.2, 127.1, 126.1, 122.4, 120.1, 112.4, 47.1, 40.7, 12.8; LRMS (EI, 70 eV)  $m/z$  (%): 396 ( $\text{M}^+$ , 100), 381 (50), 352 (99), 273 (56); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{22}\text{H}_{26}\text{BrN}_2$   $[\text{M}+\text{H}]^+$  397.1274, found 397.1260.

**1-(4-(Dimethylamino)phenyl)-*N,N*-diethyl-6-methoxynaphthalen-2-amine (3ia):**



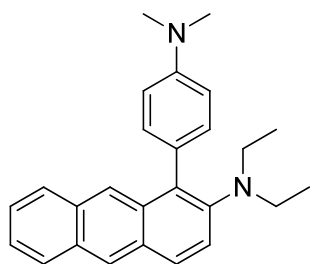
Light yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J$  = 9.0 Hz, 1H), 7.52 (d,  $J$  = 9.0 Hz, 1H), 7.38 (d,  $J$  = 9.0 Hz, 1H), 7.21-7.18 (m, 2H), 7.10 (d,  $J$  = 3.0 Hz, 1H), 6.97-6.95 (m, 1H), 6.83 (t,  $J$  = 5.5 Hz, 2H), 3.88 (s, 3H), 3.00 (s, 6H), 2.89 (q,  $J$  = 7.0 Hz, 4H), 0.85 (t,  $J$  = 7.0 Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 149.2, 144.6, 135.4, 131.8, 131.6, 129.8, 128.0, 127.1, 126.2, 122.9, 118.0, 112.1, 105.7, 55.4, 47.9, 40.8, 12.9; LRMS (EI, 70 eV)  $m/z$  (%): 348 ( $\text{M}^+$ , 89), 333 (32), 304(100), 152 (18); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{23}\text{H}_{29}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  349.2274, found 349.2293.

**Methyl 6-(diethylamino)-5-(4-(diethylamino)phenyl)-2-naphthoate (3ja):**



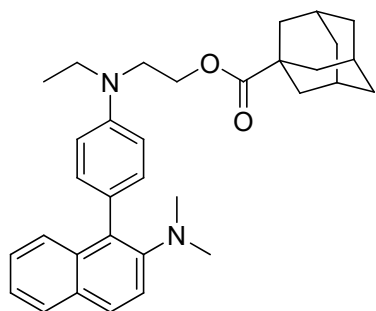
Light yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51 (s, 1H), 7.82 (d,  $J = 8.5$  Hz, 2H), 7.69 (d,  $J = 9.0$  Hz, 1H), 7.42 (d,  $J = 8.5$  Hz, 1H), 7.15 (d,  $J = 8.0$  Hz, 2H), 6.75 (d,  $J = 8.5$  Hz, 2H), 3.94 (s, 3H), 3.30 (t,  $J = 7.5$  Hz, 4H), 2.97 (q,  $J = 6.5$  Hz, 4H), 1.69 (q,  $J = 7.5$  Hz, 4H), 0.97 (t,  $J = 7.0$  Hz, 6H), 0.88 (t,  $J = 7.0$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.6, 149.2, 147.1, 136.8, 132.7, 131.8, 130.9, 128.8, 128.5, 126.1, 124.9, 124.8, 124.7, 122.4, 111.6, 53.0, 52.0, 46.7, 20.6, 12.8, 11.6; LRMS (EI, 70 eV)  $m/z$  (%): 432 ( $\text{M}^+$ , 76), 403 (100), 388(27), 194 (13); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{28}\text{H}_{37}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  433.2850, found 433.2838.

**1-(4-(Dimethylamino)phenyl)-*N,N*-diethylantracen-2-amine (3ka):**



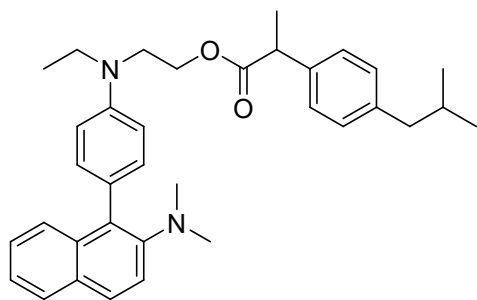
Yellow solid, mp 159.3-160.1  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 (s, 1H), 8.14 (s, 1H), 7.92 (d,  $J = 9.0$  Hz, 2H), 7.78 (d,  $J = 8.0$  Hz, 1H), 7.45 (d,  $J = 9.0$  Hz, 1H), 7.36-7.22 (m, 4H), 6.90 (d,  $J = 8.5$  Hz, 2H), 3.05 (s, 6H), 2.96 (q,  $J = 7.0$  Hz, 4H), 0.89 (t,  $J = 7.0$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.2, 145.5, 133.2, 132.8, 132.0, 131.7, 130.5, 129.6, 128.6, 127.8, 127.7, 127.2, 125.8, 124.9, 124.6, 124.3, 122.8, 47.4, 40.8, 13.1; HRMS  $m/z$  (ESI) calcd for  $\text{C}_{26}\text{H}_{29}\text{N}_2$   $[\text{M}+\text{H}]^+$  369.2325, found 369.2354.

**(3r,5r,7r)-2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethylamino)ethyl  
adamantane-1-carboxylate (3aw):**



Light yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77-7.75 (m, 2H), 7.65-7.63 (m, 1H), 7.39 (d,  $J = 8.5$  Hz, 1H), 7.31-7.25 (m, 2H), 7.22 (d,  $J = 8.5$  Hz, 2H), 6.85 (d,  $J = 9.0$  Hz, 2H), 4.28 (t,  $J = 6.5$  Hz, 2H), 3.62 (t,  $J = 6.0$  Hz, 2H), 3.48 (q,  $J = 7.0$  Hz, 2H), 2.60 (s, 6H), 2.01 (s, 3H), 1.91-1.90 (m, 6H), 1.74-1.67 (m, 6H), 1.24 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  177.9, 149.1, 146.4, 134.2, 132.0, 130.3, 129.8, 127.7 (2C), 126.3, 125.7 (2C), 123.5, 119.5, 111.7, 62.0, 48.7, 45.1, 44.0, 40.8, 38.9, 36.5, 28.0, 12.4; HRMS  $m/z$  (ESI) calcd for  $\text{C}_{33}\text{H}_{41}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  497.3163, found 497.3182.

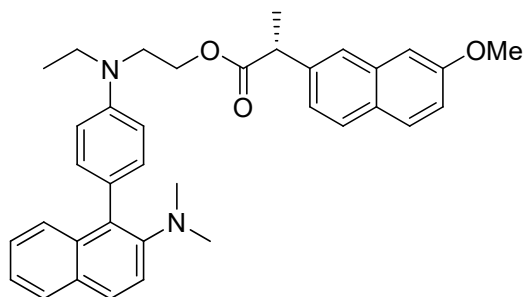
**2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethylamino)ethyl-2-(4-isobutylphenyl)propanoate (3ax):**



Light yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78-7.75 (m, 2H), 7.63 (d,  $J = 7.0$  Hz, 1H), 7.40 (d,  $J = 9.0$  Hz, 1H), 7.31-7.24 (m, 2H), 7.22-7.20 (m, 4H), 7.10 (d,  $J = 8.0$  Hz, 2H), 6.79 (d,  $J = 8.0$  Hz, 2H), 4.31-4.28 (m, 2H), 3.71 (q,  $J = 7.5$  Hz, 1H), 3.56 (t,  $J = 6.5$  Hz, 2H), 3.35 (q,  $J = 7.0$  Hz, 2H), 2.60 (s, 6H), 2.44 (d,  $J = 7.0$  Hz, 2H), 1.89-1.80 (m, 1H), 1.50 (d,  $J = 7.0$  Hz, 3H), 1.16 (t,  $J = 7.0$  Hz, 3H), 0.89 (d,  $J = 6.5$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  174.8, 149.1, 146.2, 140.6, 137.6, 134.1, 131.9, 130.3, 129.7, 129.4, 127.7, 127.6, 127.2, 126.3, 125.6, 123.4, 119.4, 111.6, 62.4, 48.6, 45.2, 45.1, 45.0, 43.9, 30.2, 22.4, 18.5, 12.3; HRMS  $m/z$  (ESI) calcd for  $\text{C}_{35}\text{H}_{43}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  523.3319, found 523.3331.

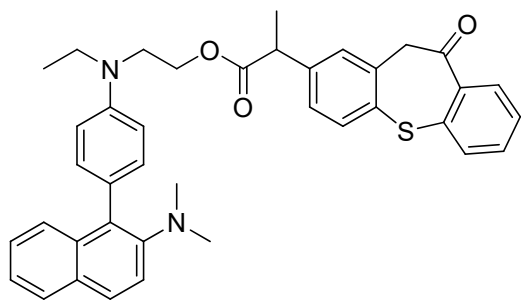
**(R)-2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethyl)amino)ethyl**

**2-(7-methoxynaphthalen-2-yl)propanoate (3ay):**



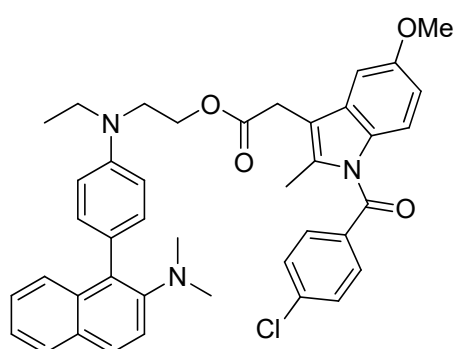
Light yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77-7.74 (m, 2H), 7.71-7.67 (m, 3H), 7.63 (d,  $J = 8.5$  Hz, 1H), 7.41-7.38 (m, 2H), 7.30-7.25 (m, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 7.13-7.10 (m, 2H), 6.78 (d,  $J = 8.0$  Hz, 2H), 4.33-4.27 (m, 2H), 3.88-3.84 (m, 4H), 3.54 (t,  $J = 6.0$  Hz, 2H), 3.33-3.28 (m, 2H), 2.59 (s, 6H), 1.58 (d,  $J = 7.2$  Hz, 3H), 1.11 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  174.7, 157.6, 149.1, 146.2, 135.5, 134.1, 133.7, 131.9, 130.3, 129.7, 129.2, 128.9, 127.7, 127.6, 127.2, 126.3, 126.2, 126.0, 125.6, 123.4, 119.4, 119.0, 111.7, 105.5, 62.4, 55.3, 48.6, 45.5, 45.0, 43.9, 18.4, 12.3; HRMS  $m/z$  (ESI) calcd for  $\text{C}_{36}\text{H}_{39}\text{N}_2\text{O}_3$   $[\text{M}+\text{H}]^+$  547.2955, found 547.2973.

**2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethyl)amino)ethyl-2-(10-oxo-1,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoate (3az):**



Light yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (d,  $J = 7.5$  Hz, 1H), 7.77-7.75 (m, 2H), 7.63-7.57 (m, 3H), 7.41-7.38 (m, 3H), 7.31-7.26 (m, 3H), 7.20 (d,  $J = 8.5$  Hz, 2H), 7.15-7.13 (m, 1H), 6.77 (d,  $J = 8.5$  Hz, 2H), 4.39-4.23 (m, 4H), 3.72 (q,  $J = 7.0$  Hz, 1H), 3.55 (t,  $J = 6.5$  Hz, 2H), 3.34-3.30 (m, 2H), 2.59 (s, 6H), 1.49 (d,  $J = 7.0$  Hz, 3H), 1.12 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  191.3, 173.9, 149.0, 146.1, 142.5, 140.1, 137.9, 136.1, 134.1, 133.3, 132.5, 131.9, 131.5, 131.5, 130.8, 130.3, 129.7, 128.6, 127.7, 127.6, 126.8, 126.4, 125.6, 123.4, 119.4, 111.7, 62.5, 51.0, 48.5, 45.2, 45.1, 43.9, 18.4, 12.3; HRMS  $m/z$  (ESI) calcd for  $\text{C}_{39}\text{H}_{39}\text{N}_2\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$  615.2676, found 615.2664.

**2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethylamino)ethyl-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (3aaa):**

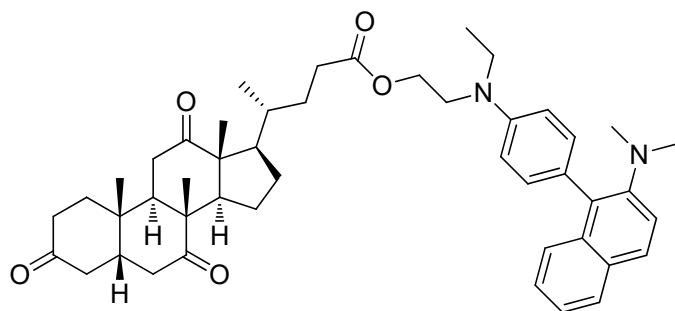


Light yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$

7.77-7.74 (m, 2H), 7.65-7.61 (m, 3H), 7.44 (d,  $J$  = 8.0 Hz, 2H), 7.39 (d,  $J$  = 8.5 Hz, 1H), 7.30-7.25 (m, 2H), 7.23-7.21 (m, 3H), 6.97 (s, 1H), 6.86 (d,  $J$  = 9.0 Hz, 1H), 6.81 (d,  $J$  = 8.5 Hz,

2H), 6.67 (d,  $J$  = 7.5 Hz, 1H), 4.34 (t,  $J$  = 6.0 Hz, 2H), 3.81 (s, 3H), 3.69 (s, 2H), 3.61 (t,  $J$  = 6.0 Hz, 2H), 3.38 (q,  $J$  = 7.0 Hz, 2H), 2.59 (s, 6H), 2.39 (s, 3H), 1.18 (t,  $J$  = 6.5 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 168.2, 156.0, 149.0, 146.1, 139.2, 135.9, 134.1, 133.8, 132.0, 131.1, 130.8, 130.6, 130.2, 129.7, 129.1, 127.7, 127.6, 126.5, 125.6, 125.5, 123.4, 119.4, 114.9, 112.4, 111.7, 111.6, 101.3, 62.6, 55.7, 48.7, 45.2, 43.9, 30.3, 13.3, 12.3; HRMS  $m/z$  (ESI) calcd for  $\text{C}_{41}\text{H}_{41}\text{ClN}_3\text{O}_4$   $[\text{M}+\text{H}]^+$  674.2780, found 673.2796.

**(R)-2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethylamino)ethyl 4-((5*S*,8*R*,9*R*,10*S*,13*R*,14*R*,17*R*)-8,10,13-trimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (3aab):**



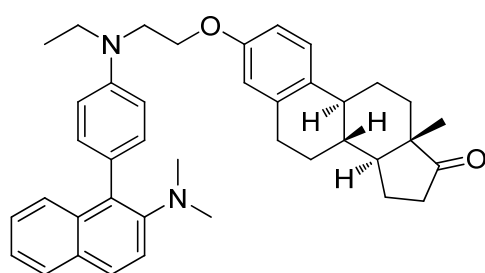
Light yellow oil;  $^1\text{H}$  NMR

(500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78-7.75 (m, 2H), 7.65-7.63 (m, 1H), 7.40 (d,  $J$  = 9.0 Hz, 1H), 7.30-7.27 (m, 2H), 7.22 (d,  $J$  =

9.0 Hz, 2H), 6.83 (d,  $J$  = 8.5 Hz, 2H), 4.30 (t,  $J$  = 6.5 Hz, 2H), 3.62 (t,  $J$  = 6.5 Hz, 2H), 3.48 (q,  $J$  = 7.0 Hz, 2H), 2.91-2.80 (m, 3H), 2.61 (s, 6H), 2.46-2.40 (m, 1H), 2.36-2.30 (m, 7H), 2.14-2.09 (m, 2H), 2.07-2.00 (m, 3H), 1.96-1.93 (m, 1H),

1.90-1.81 (m, 2H), 1.63-1.56 (m, 1H), 1.44-1.29 (m, 6H), 1.25-1.21 (m, 3H), 1.05 (s, 3H), 0.86 (d,  $J = 6.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  211.9, 209.0, 208.7, 174.1, 149.0, 146.2, 134.1, 131.9, 130.2, 129.7, 127.7, 127.6, 126.3, 125.6 (2C), 123.4, 119.4, 111.6, 61.8, 56.8, 51.7, 48.9, 48.8, 46.8, 45.6, 45.5, 45.3, 44.9, 43.9, 42.7, 38.6, 36.42, 35.9, 35.4, 35.2, 31.4, 30.4, 27.6, 25.1, 21.8, 18.6, 12.4, 11.8; HRMS  $m/z$  (ESI) calcd for  $\text{C}_{47}\text{H}_{61}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  733.4575, found 733.4589.

**(8R,9S,13S,14S)-3-(2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethyl)amino)ethoxy)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[*a*]phenanthren-17(14H)-one (3aac):**



Light yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

$\delta$  7.77-7.74 (m, 2H), 7.65 (d,  $J = 8.0$  Hz, 1H),

7.39 (d,  $J = 8.5$  Hz, 1H), 7.30-7.25 (m, 2H),

7.23-7.20 (m, 3H), 6.83 (d,  $J = 8.5$  Hz, 2H),

6.75 (d,  $J = 8.0$  Hz, 1H), 6.68 (s, 1H), 4.17 (t,  $J = 6.0$  Hz, 2H), 3.78 (t,  $J = 6.0$  Hz, 2H),

3.56-3.52 (m, 2H), 2.88 (d,  $J = 4.0$  Hz, 2H), 2.61 (s, 6H), 2.52-2.48 (m, 1H),

2.39-2.37 (m, 1H), 2.25 (d,  $J = 9.5$  Hz, 1H), 2.16-2.10 (m, 1H), 2.06-1.94 (m, 3H),

1.64-1.47 (m, 6H), 1.27 (t,  $J = 7.0$  Hz, 3H), 0.89 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

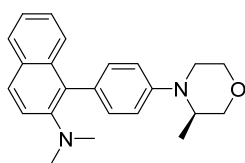
$\delta$  220.9, 156.8, 149.0, 146.2, 137.8, 134.1, 132.2, 131.9, 130.2, 129.7, 127.7, 127.6,

126.3, 126.1, 125.6, 125.6, 123.4, 119.4, 114.4, 112.1, 111.5, 65.5, 50.3, 49.7, 48.0,

45.7, 43.9, 38.3, 35.8, 31.5, 29.6, 26.5, 25.9, 21.5, 13.8, 12.5; HRMS  $m/z$  (ESI) calcd

for  $\text{C}_{40}\text{H}_{47}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  587.3632, found 587.3642.

**(R)-N,N-Dimethyl-1-(4-(3-methylmorpholino)phenyl)naphthalen-2-amine(3aad):**

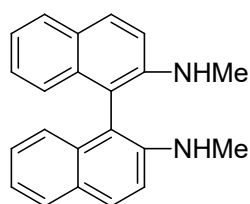


White solid, mp 135.1-135.9 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$

7.80-7.76 (m, 2H), 7.60 (d,  $J = 7.5$  Hz, 1H), 7.40 (d,  $J = 9.0$  Hz,

1H), 7.32-7.27 (m, 4H), 7.02 (d,  $J = 8.5$  Hz, 2H), 4.05-4.02 (m, 1H), 3.93-3.91 (m, 1H), 3.89-3.84 (m, 1H), 3.80-3.75 (m, 2H), 3.27-3.19 (m, 2H), 2.60 (s, 6H), 1.18 (d,  $J = 6.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 148.4, 134.0, 132.0, 130.0, 129.8, 129.7, 128.0, 127.7, 125.8, 125.4, 123.5, 119.4, 116.1, 72.1, 67.3, 51.0, 43.9, 43.8, 11.6; LRMS (EI, 70 eV)  $m/z$  (%): 346 ( $\text{M}^+$ , 100), 331 (45), 288 (26), 202 (13); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  347.2118, found 347.2141.

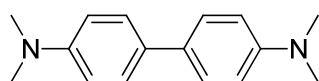
**$N^2,N^{2'}$ -Dimethyl-[1,1'-binaphthalene]-2,2'-diamine (4):<sup>2</sup>**



White solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 8.5$  Hz, 2H), 7.81-7.79 (m, 2H), 7.26 (d,  $J = 3.5$  Hz, 2H), 7.21-7.13 (m, 4H), 6.96 (dd,  $J = 8.0, 1.0$  Hz, 2H), 3.68 (s, 2H), 2.82 (s, 6H);

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  145.6, 133.7, 129.6, 128.1, 127.6, 126.7, 123.6, 121.7, 113.4, 111.7, 31.1; LRMS (EI, 70 eV)  $m/z$  (%): 312 ( $\text{M}^+$ , 100), 280 (27), 267 (22), 170 (71); The analytical data are in accordance with those reported in the literature.<sup>2</sup>

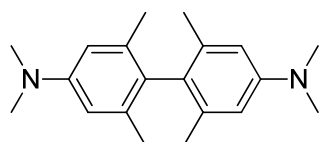
**$N^4,N^4,N^{4'},N^{4'}$ -Tetramethyl-[1,1'-biphenyl]-4,4'-diamine (5):<sup>3</sup>**



White solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 9.0$  Hz, 4H), 6.80 (d,  $J = 9.0$  Hz, 4H), 2.96 (s, 12H);  $^{13}\text{C}$  NMR

(125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.2, 129.8, 126.9, 113.0, 40.8; LRMS (EI, 70 eV)  $m/z$  (%): 240 ( $\text{M}^+$ , 100), 225 (34), 152 (9), 119 (26); The analytical data are in accordance with those reported in the literature.<sup>3</sup>

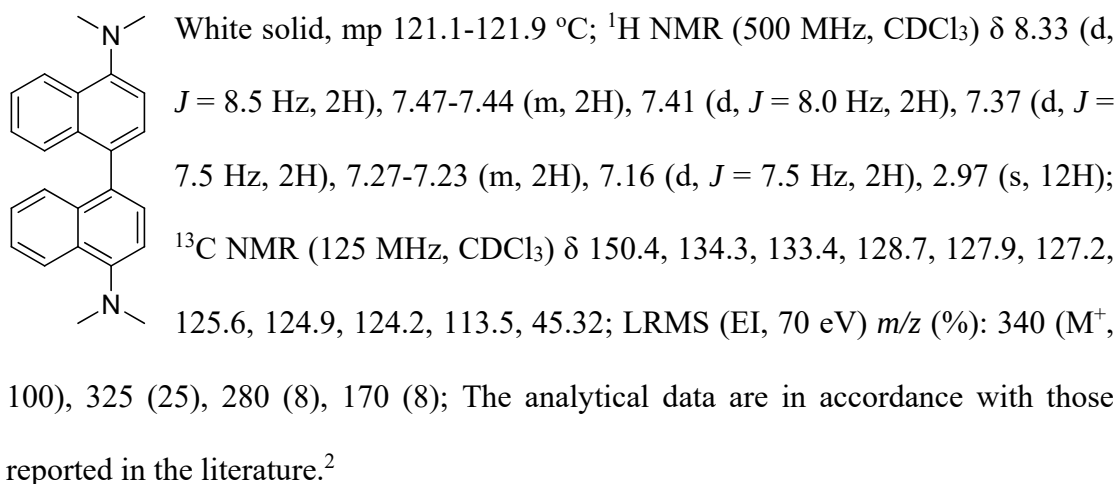
**$N^4,N^4,N^{4'},N^{4'},2,2',6,6'$ -Octamethyl-[1,1'-biphenyl]-4,4'-diamine (6):<sup>4</sup>**



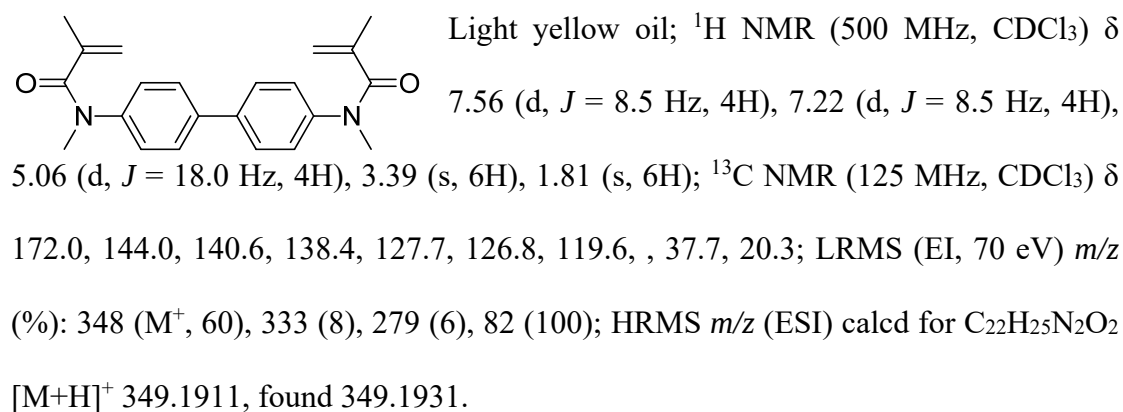
White solid, mp 103.1-104.3 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.52 (s, 4H), 2.95 (s, 12H), 1.88 (s, 12H);  $^{13}\text{C}$

NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 137.0, 129.2, 111.7, 40.7, 20.6; LRMS (EI, 70 eV)  $m/z$  (%): 296 ( $\text{M}^+$ , 100), 281 (9), 266 (10), 147 (28); The analytical data are in accordance with those reported in the literature.<sup>4</sup>

***N*<sup>4</sup>,*N*<sup>4</sup>,*N*<sup>4'</sup>,*N*<sup>4'</sup>-Tetramethyl-[1,1'-binaphthalene]-4,4'-diamine (7):**<sup>2</sup>

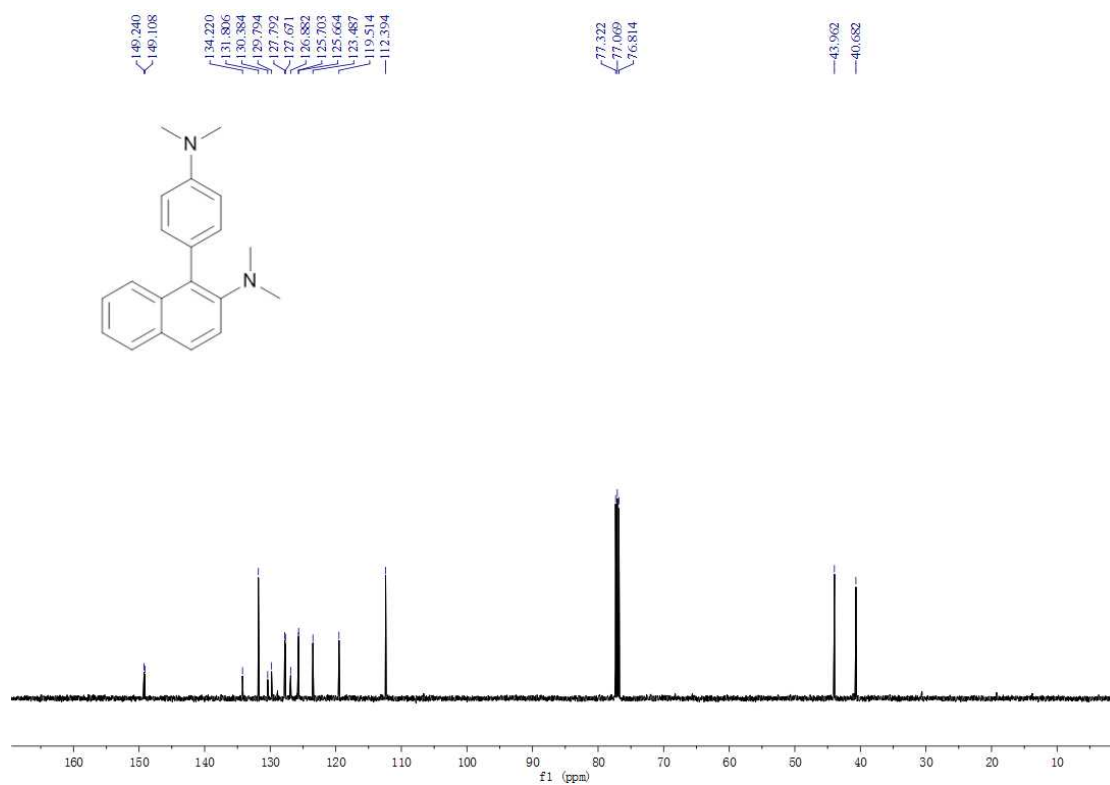
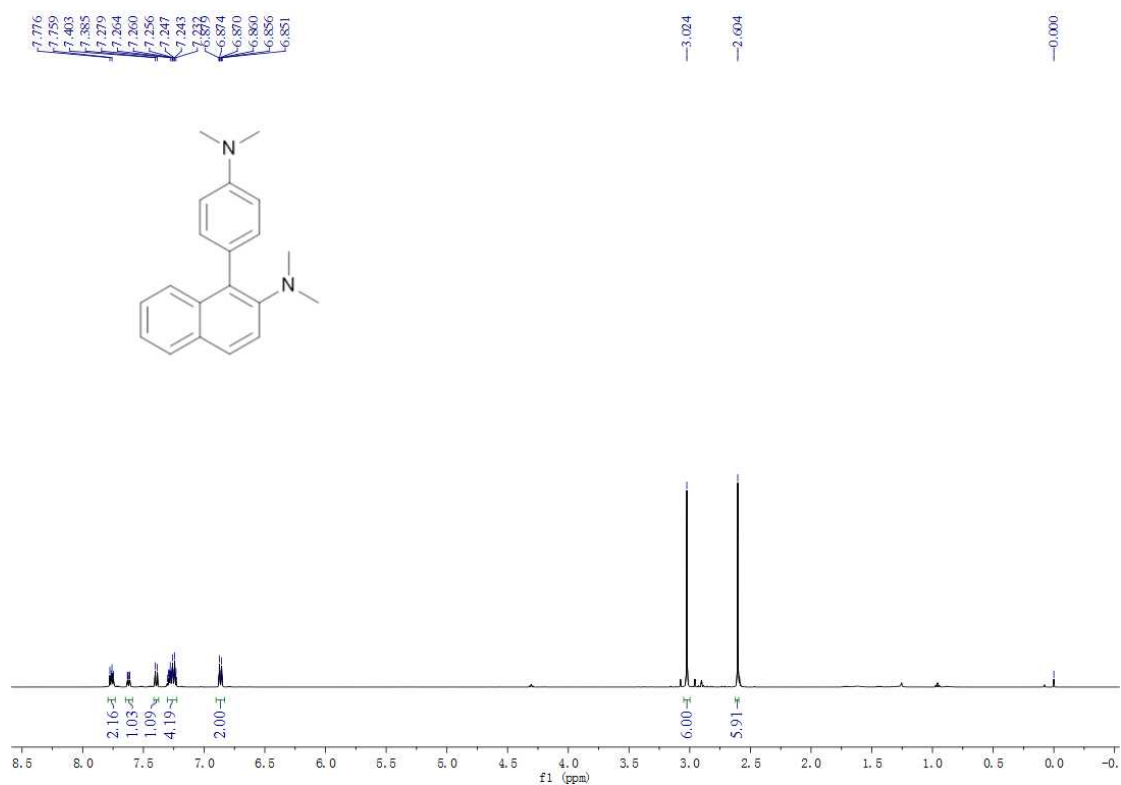


***N,N'*-([1,1'-Biphenyl]-4,4'-diyl)bis(*N*,2-dimethylacrylamide) (8):**

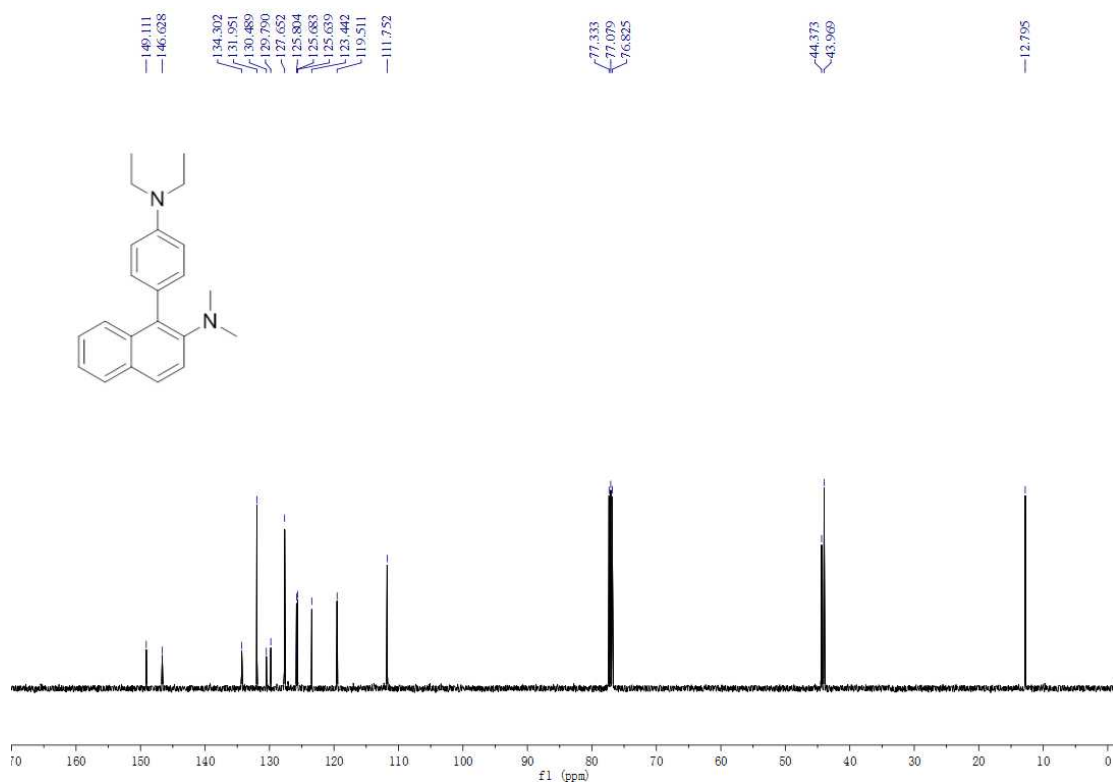
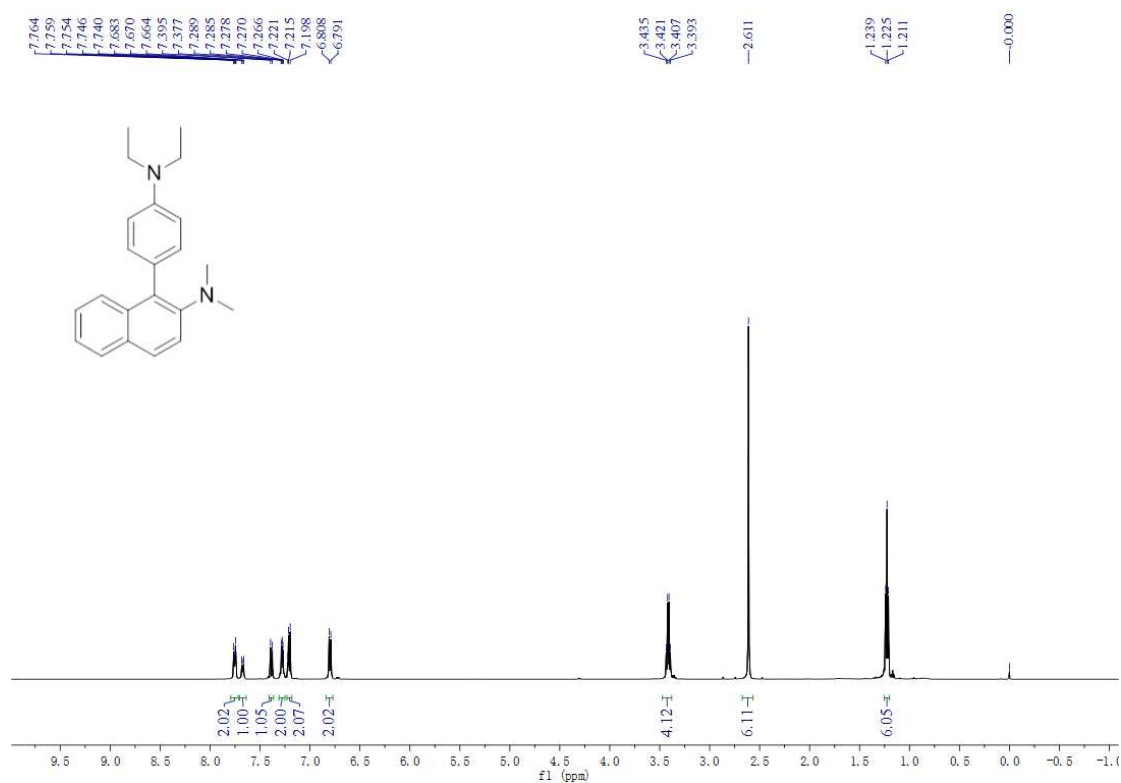


## (C) Spectra

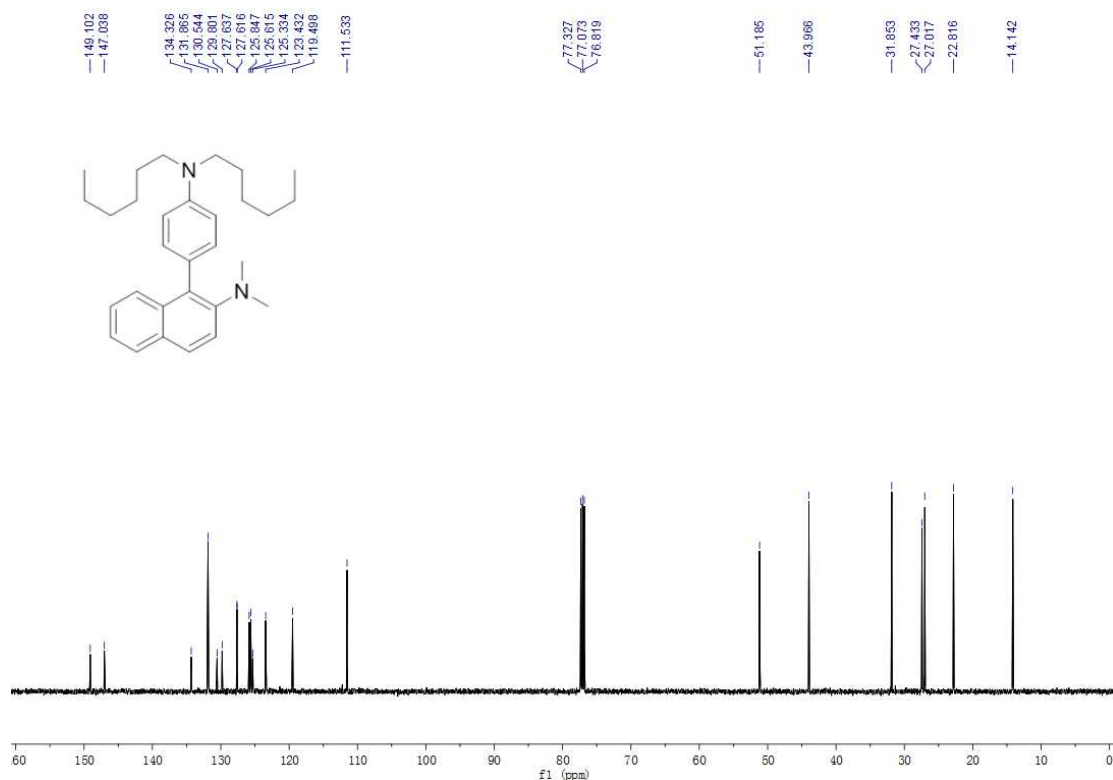
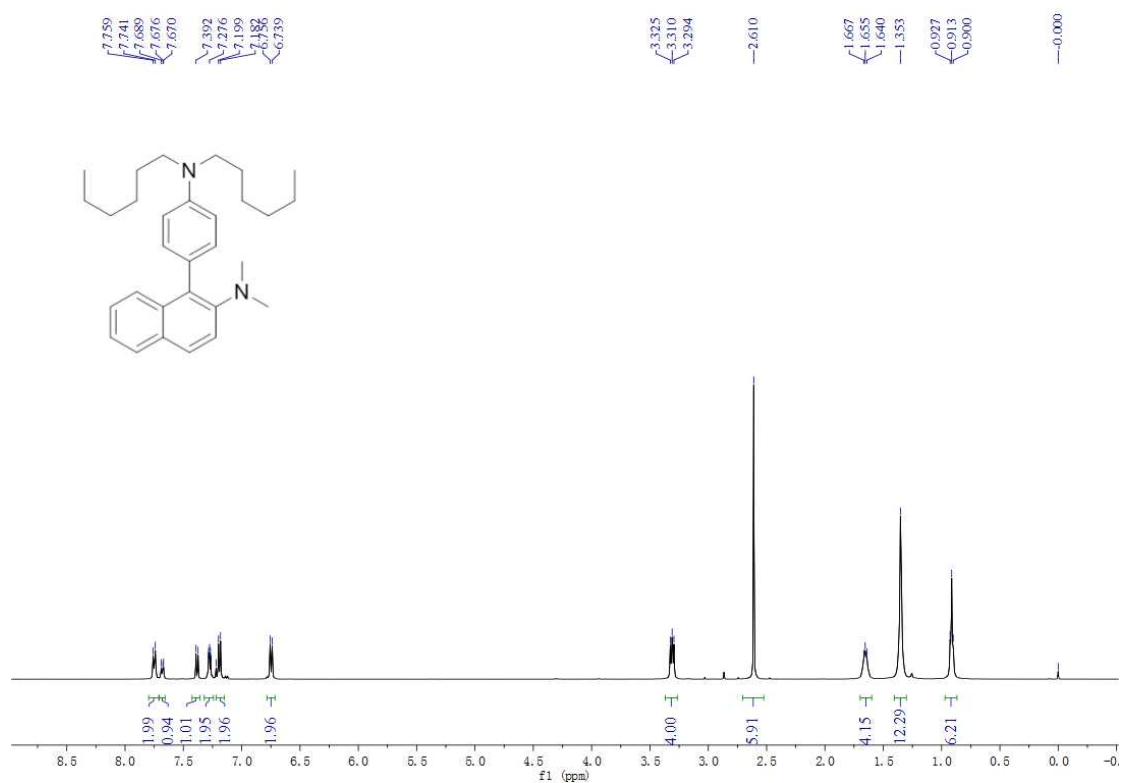
### 1-(4-(Dimethylamino)phenyl)-*N,N*-dimethylnaphthalen-2-amine (3aa):



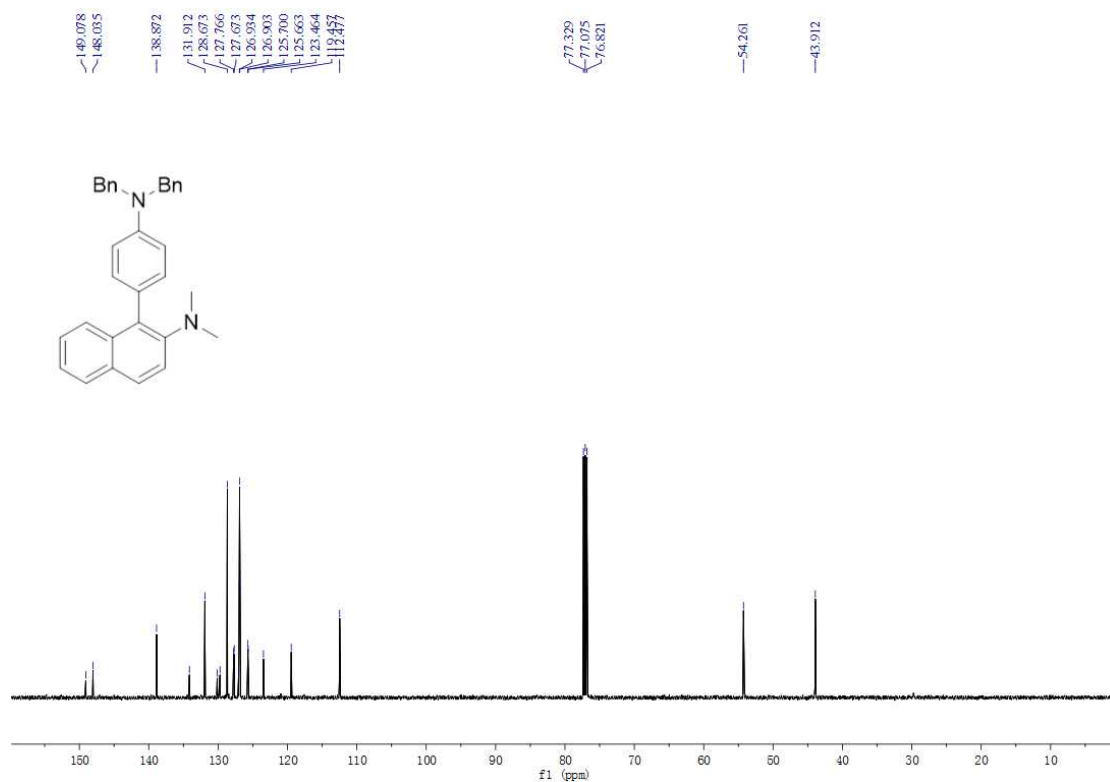
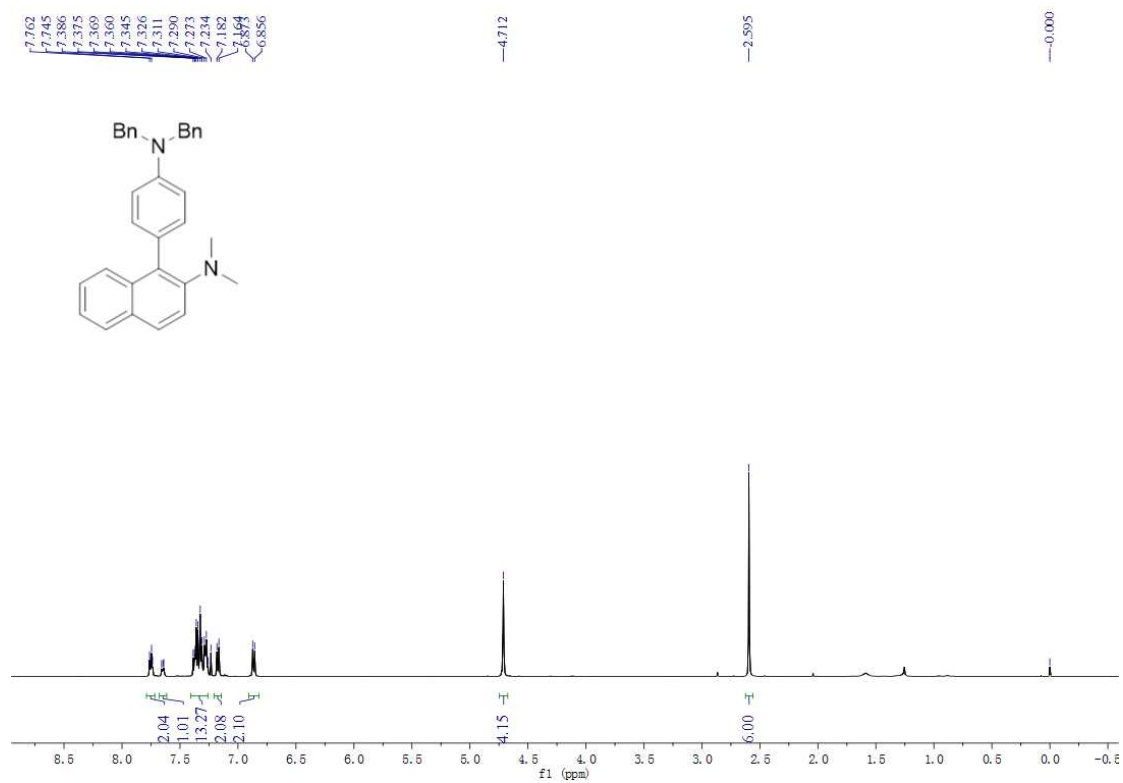
# 1-(4-(Diethylamino)phenyl)-*N,N*-dimethylnaphthalen-2-amine (3ab):



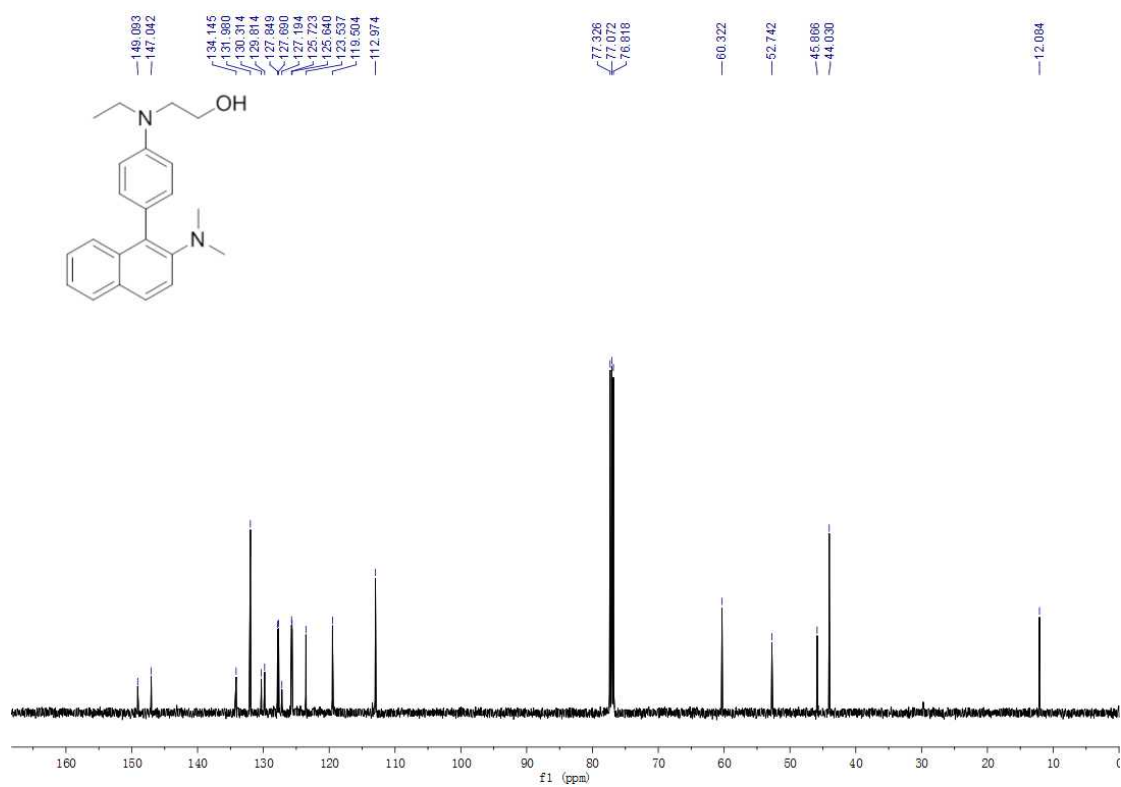
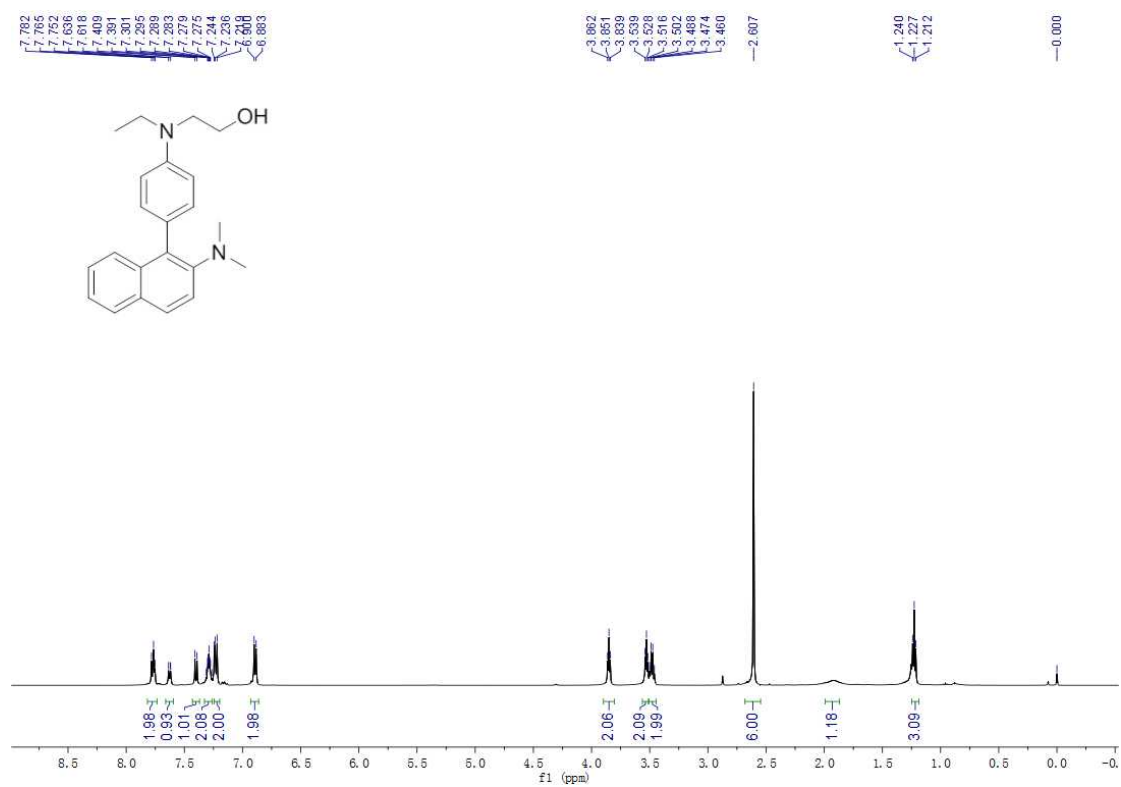
# 1-(4-(Dihexylamino)phenyl)-*N,N*-dimethylnaphthalen-2-amine (3ac):



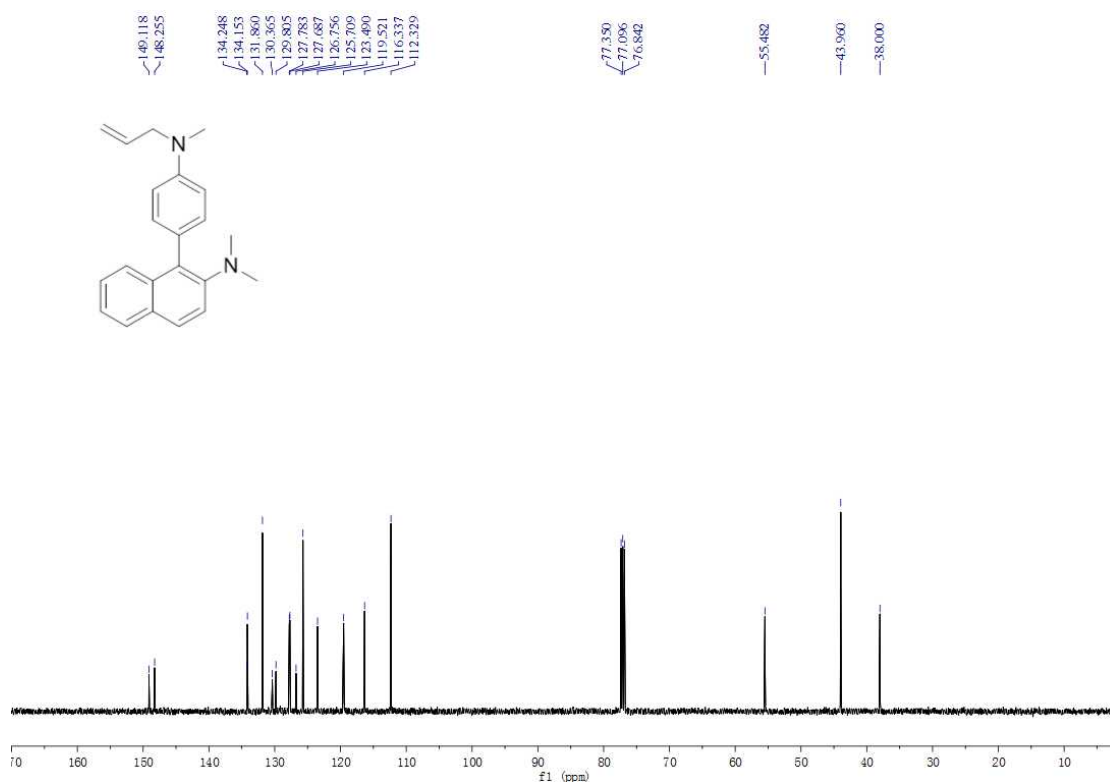
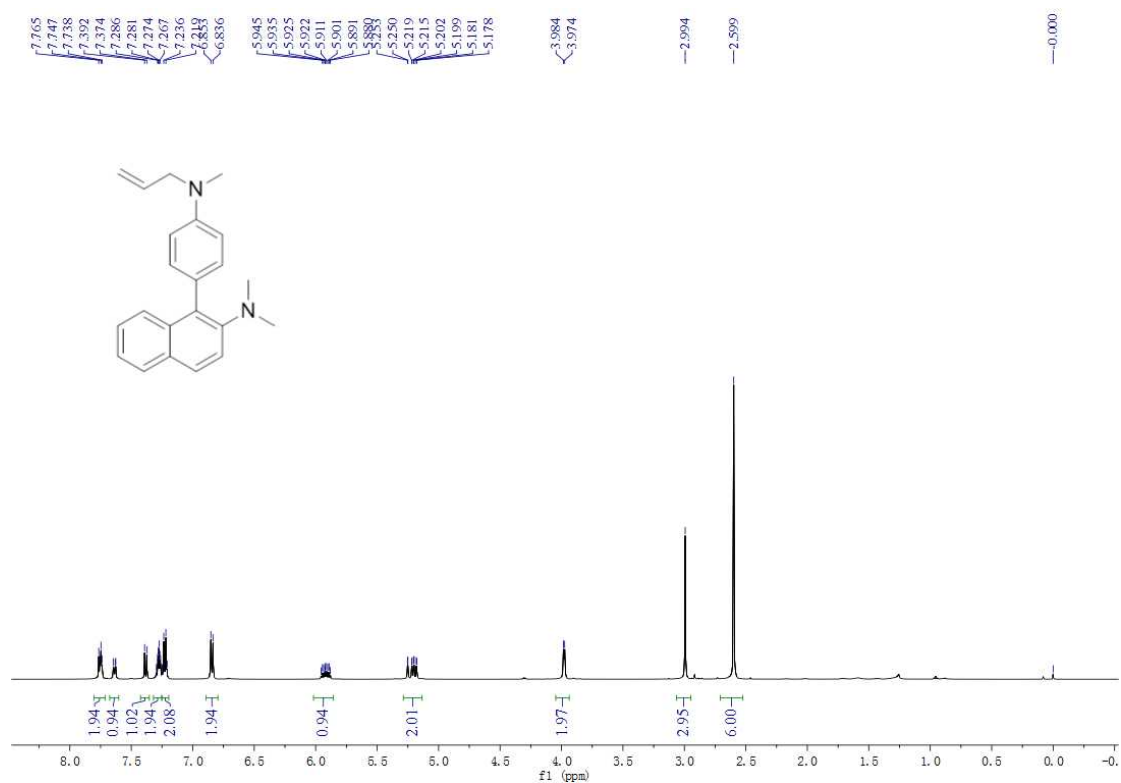
# 1-(4-(Dibenzylamino)phenyl)-*N,N*-dimethylnaphthalen-2-amine (3ad):



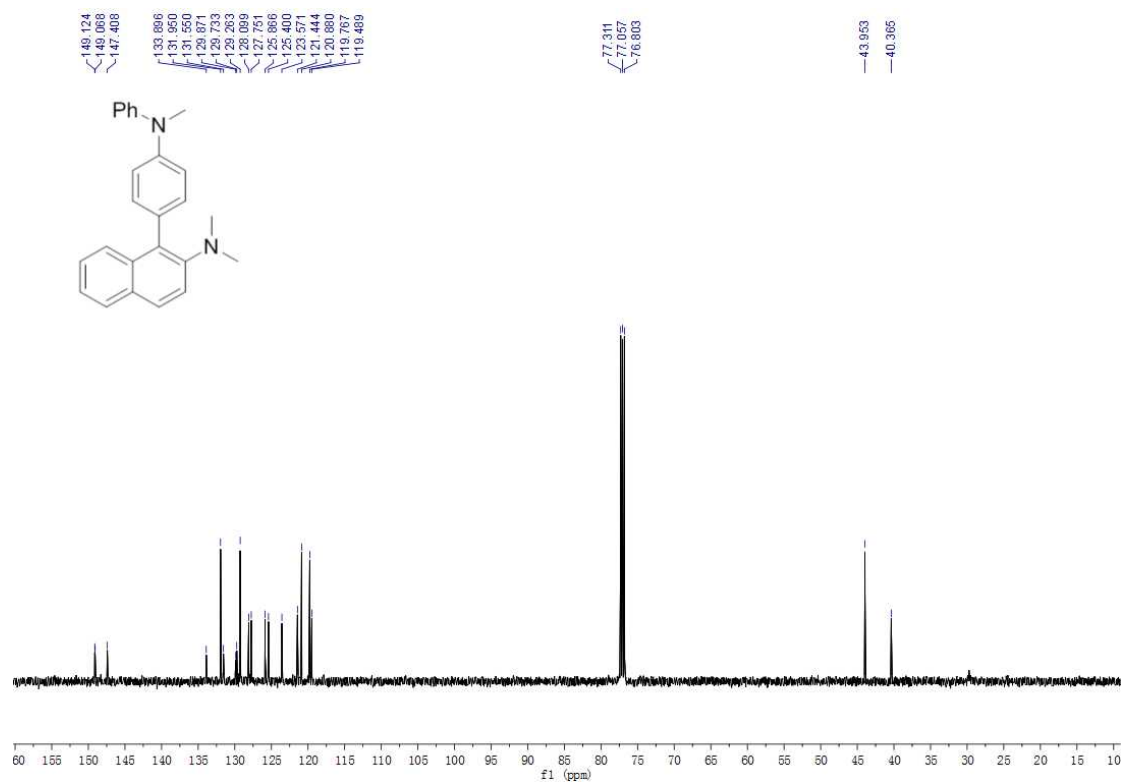
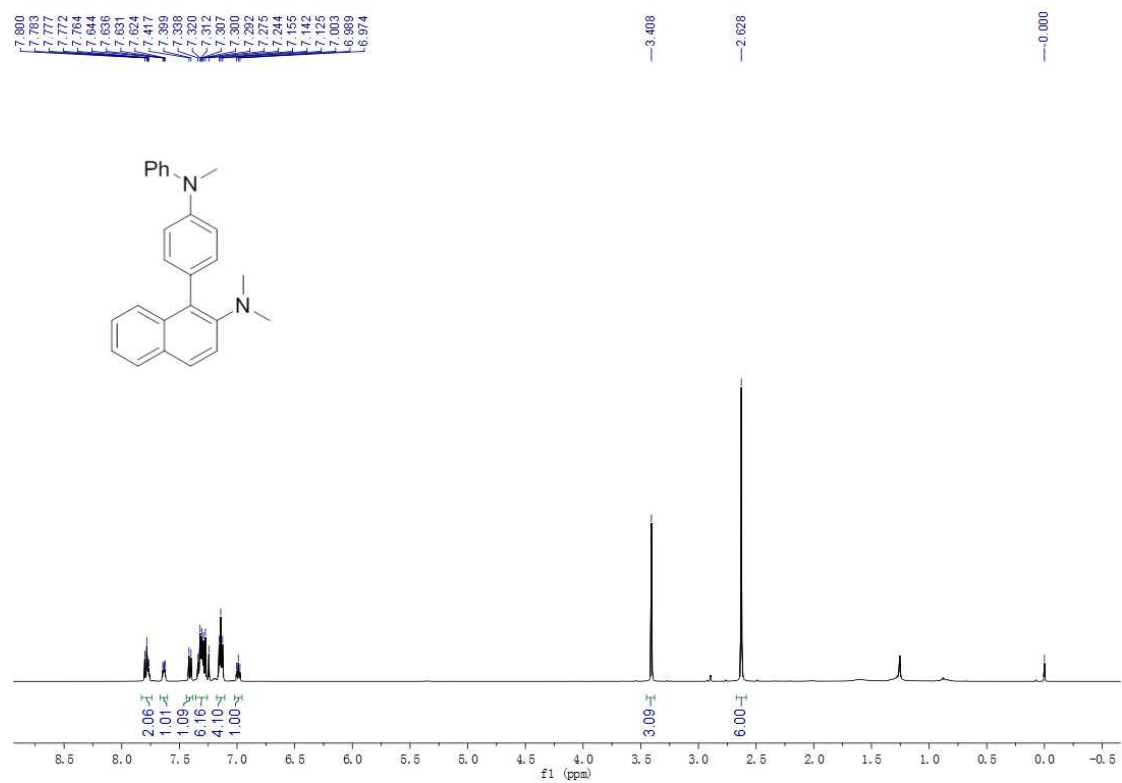
**2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethyl)amino)ethanol (3ae):**



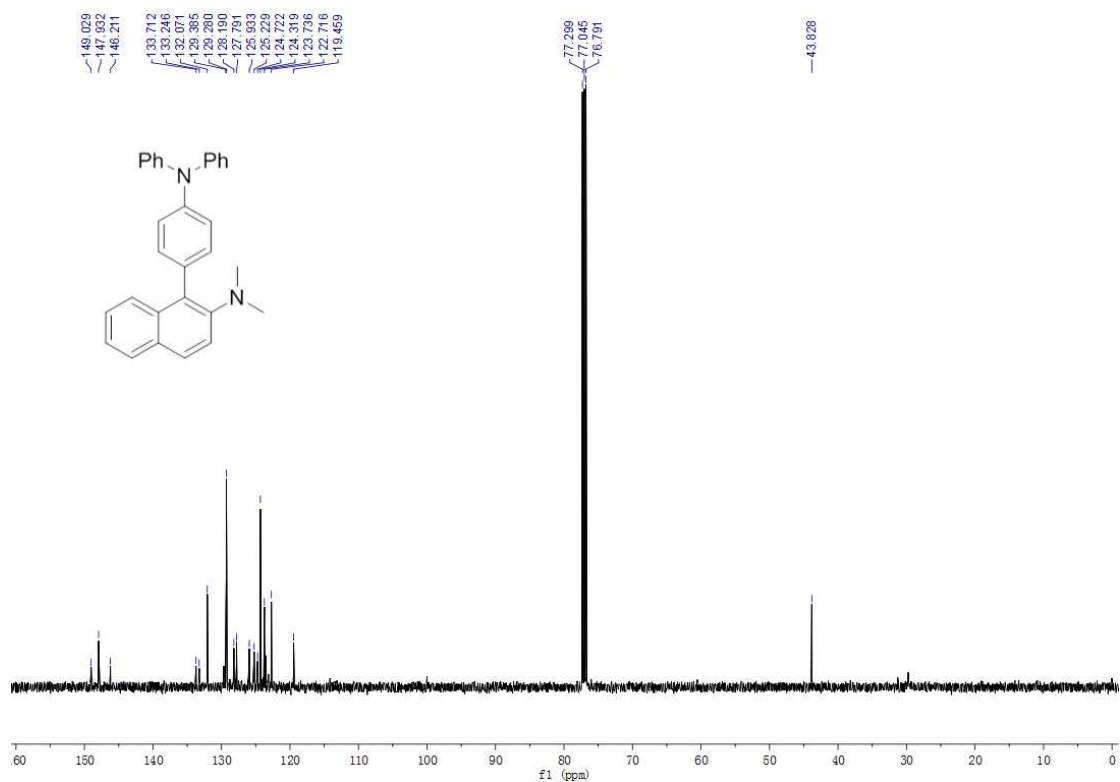
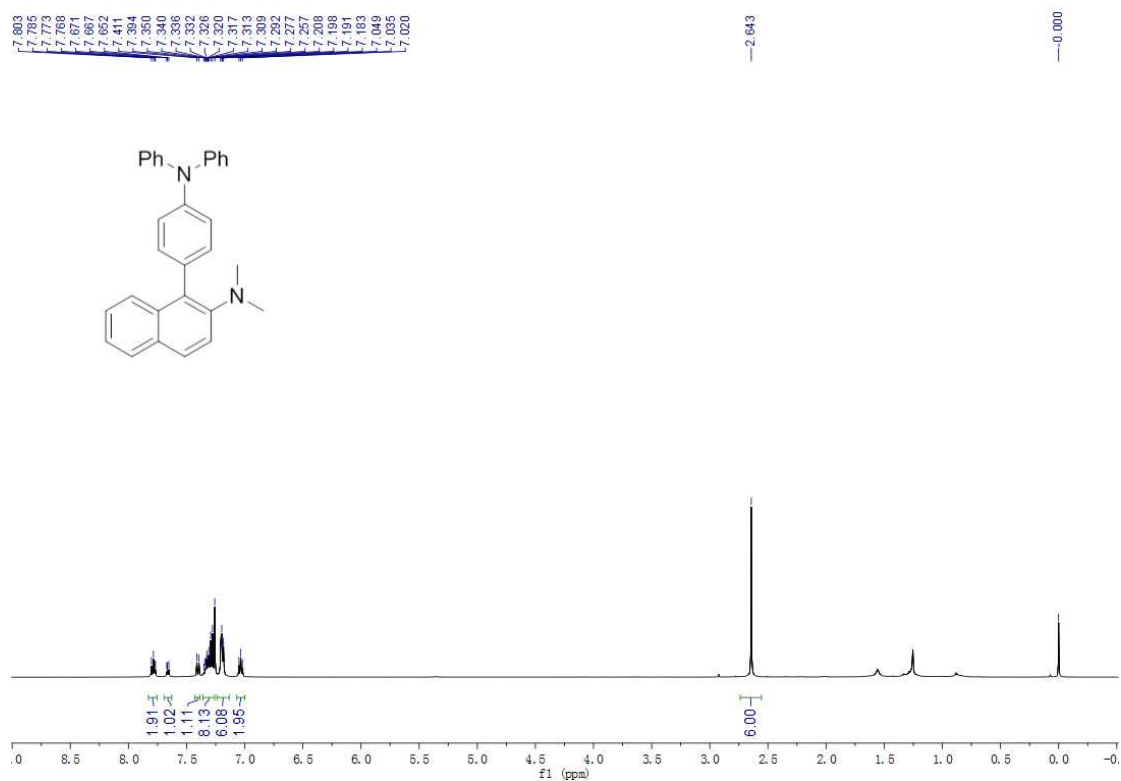
# 1-(4-(Allyl(methyl)amino)phenyl)-*N,N*-dimethylnaphthalen-2-amine (3af):



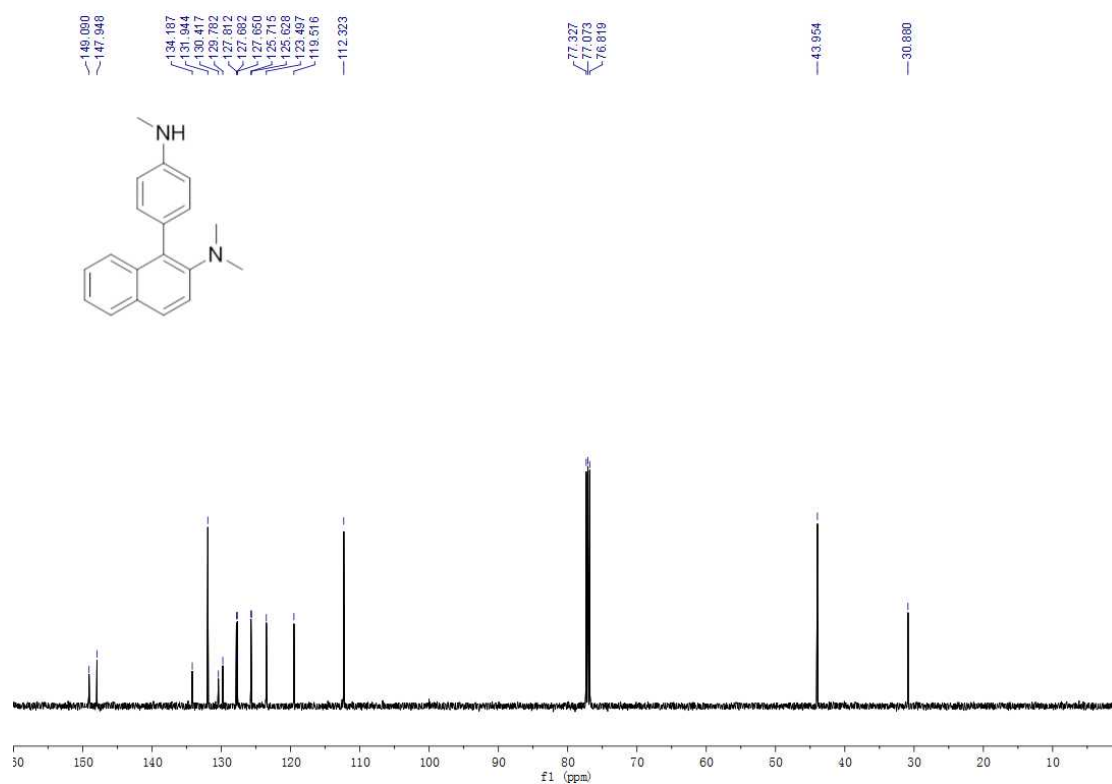
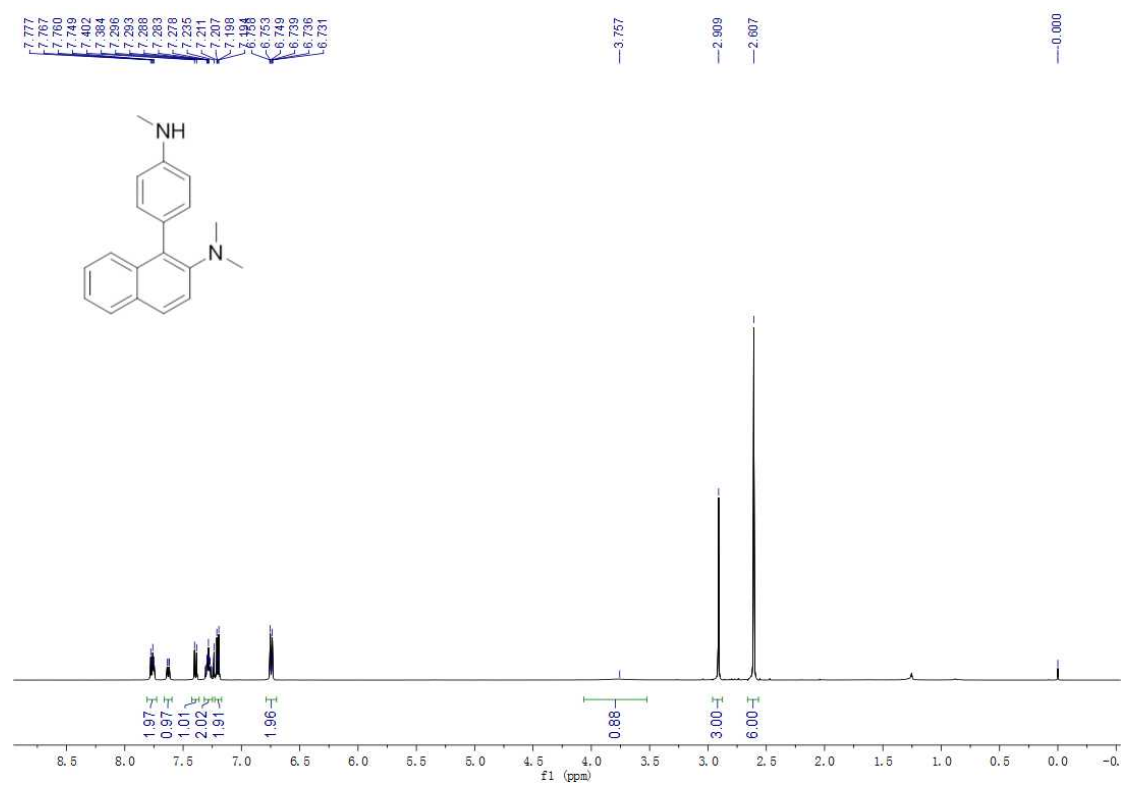
***N,N*-Dimethyl-1-(4-(methyl(phenyl)amino)phenyl)naphthalen-2-amine (3ag):**



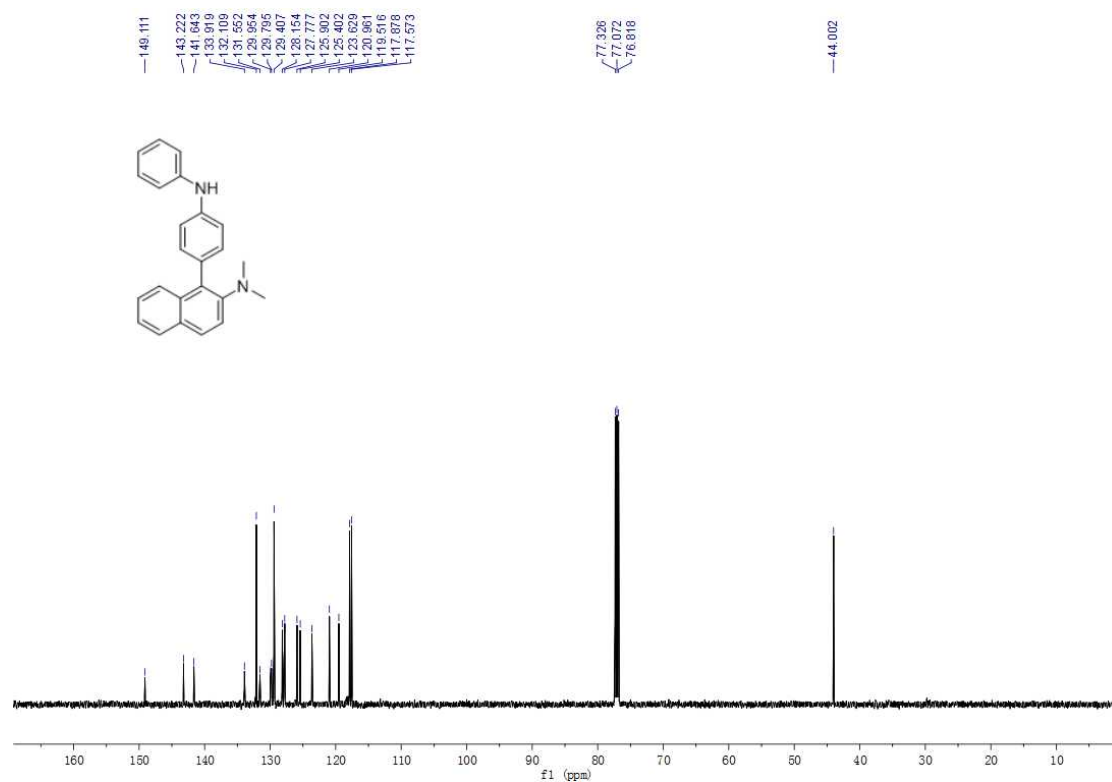
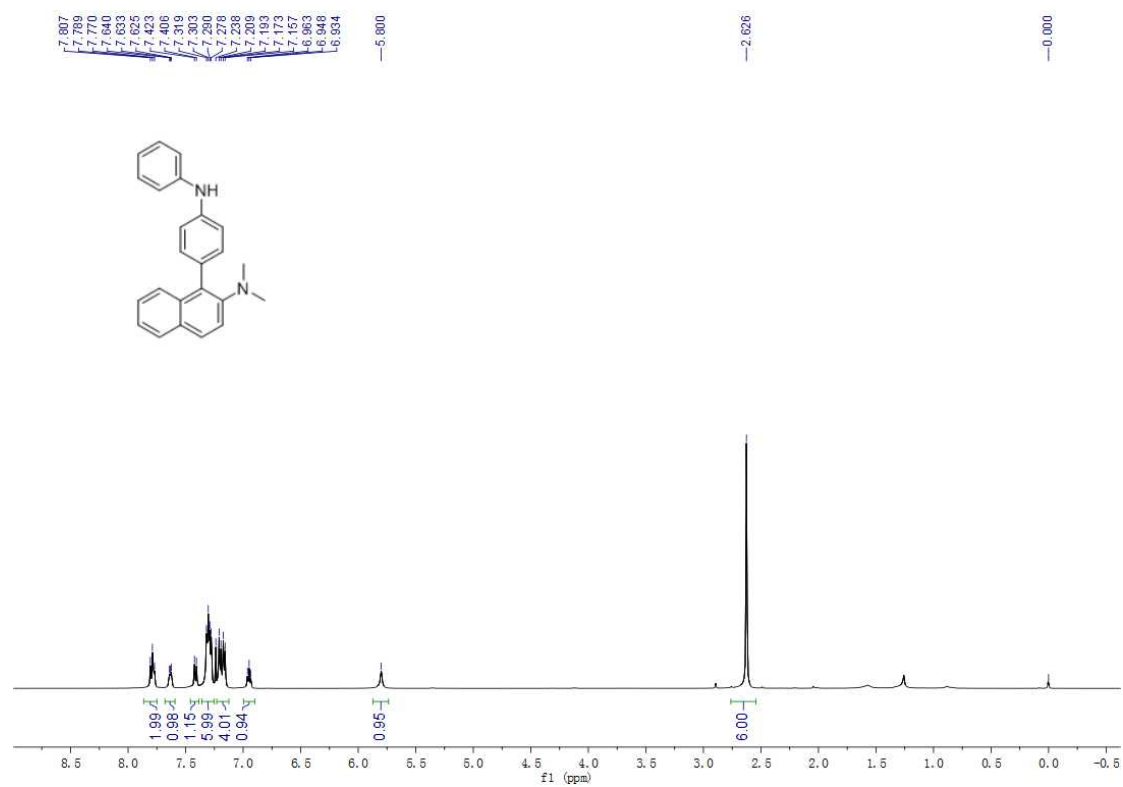
# 1-(4-(Diphenylamino)phenyl)naphthalen-2-amine (3ah)



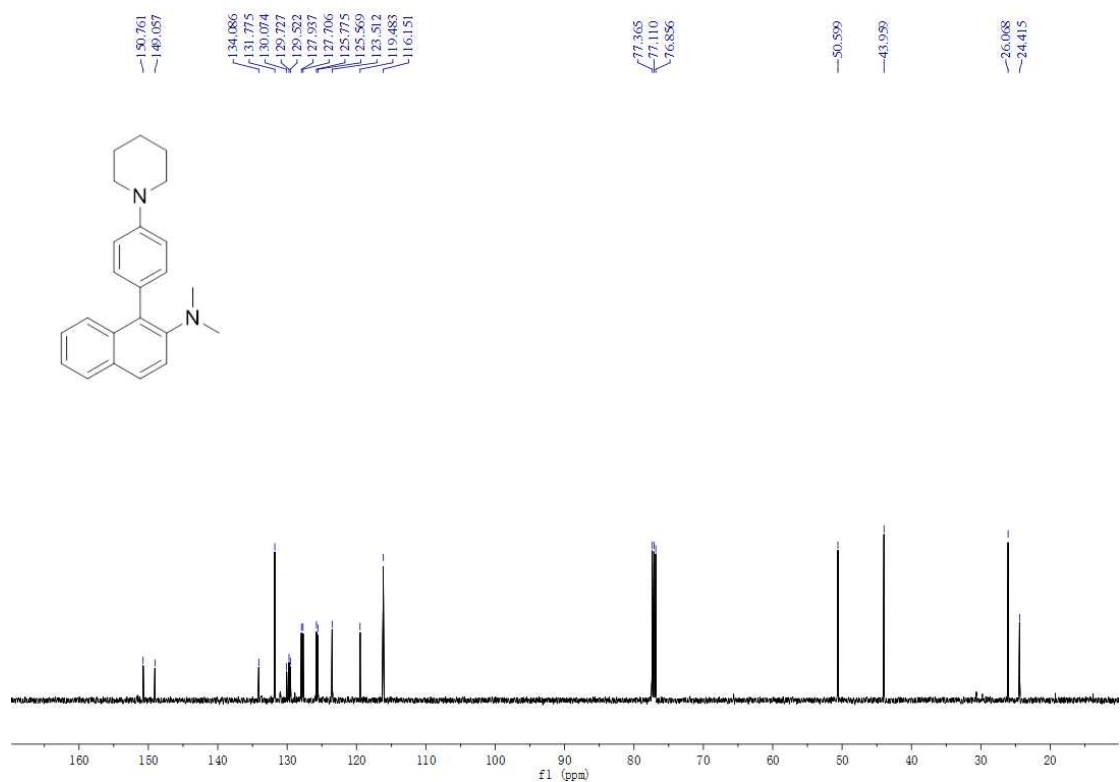
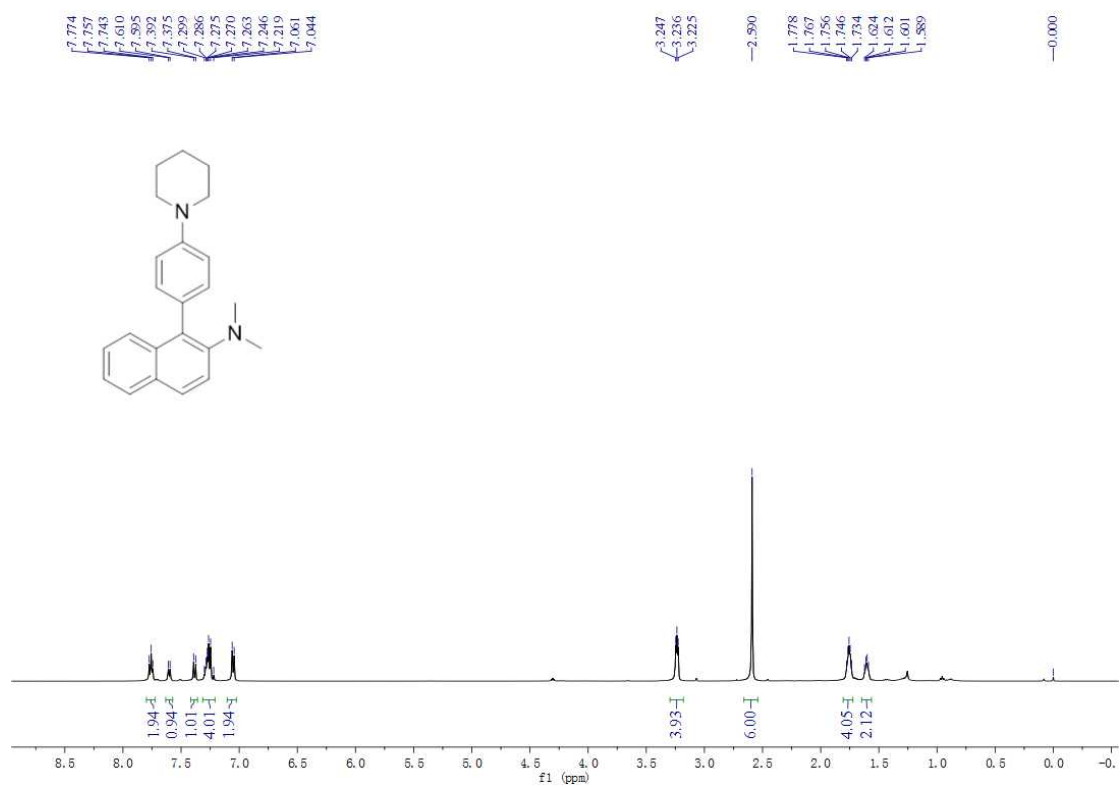
***N,N*-Dimethyl-1-(4-(methyl(phenyl)amino)phenyl)naphthalen-2-amine (3ai):**



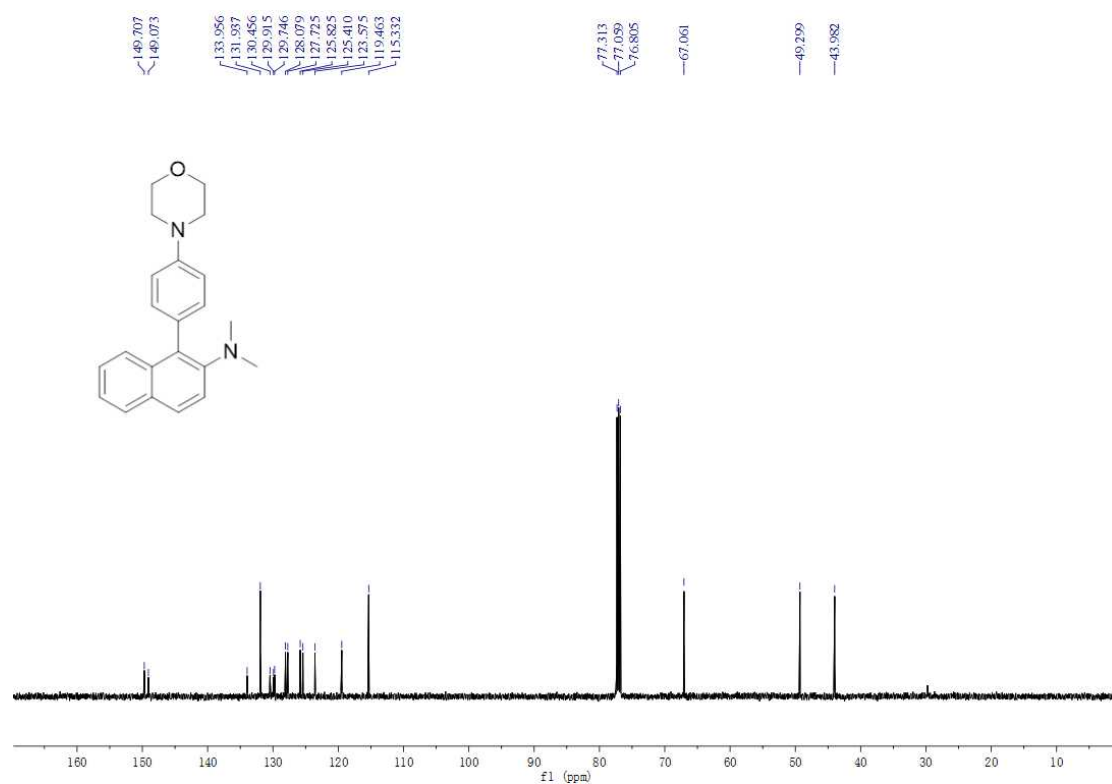
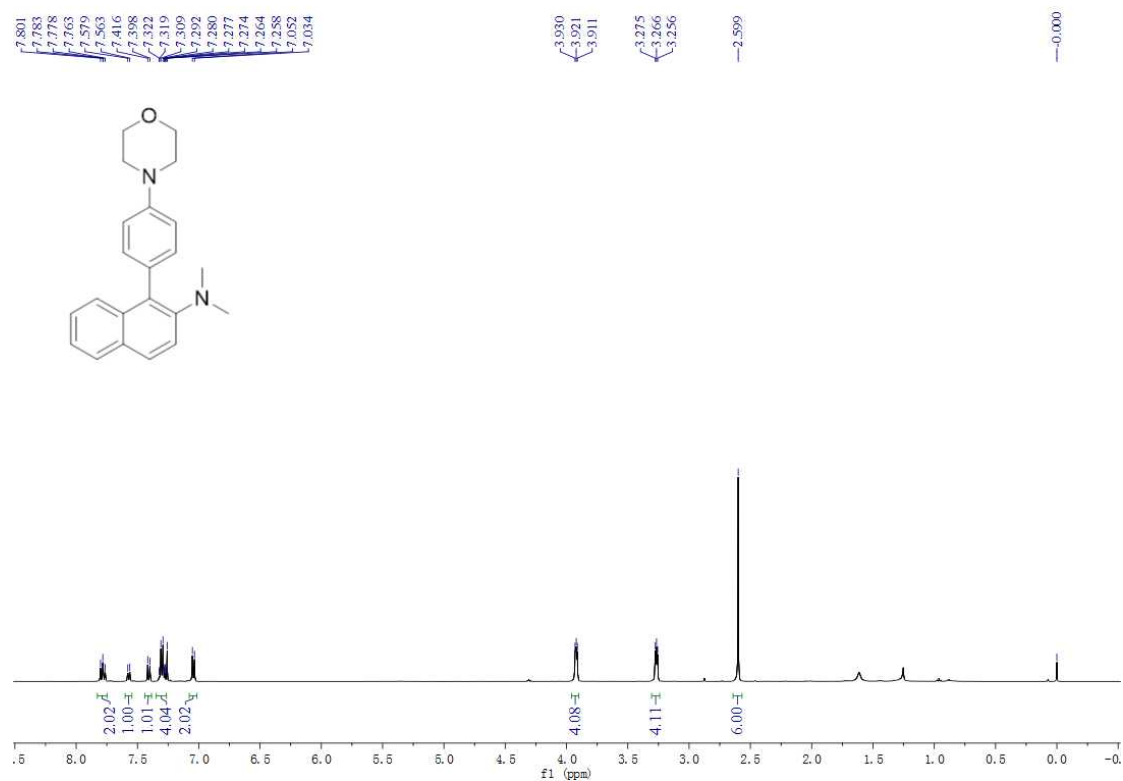
***N,N*-Dimethyl-1-(4-(phenylamino)phenyl)naphthalen-2-amine (3aj):**



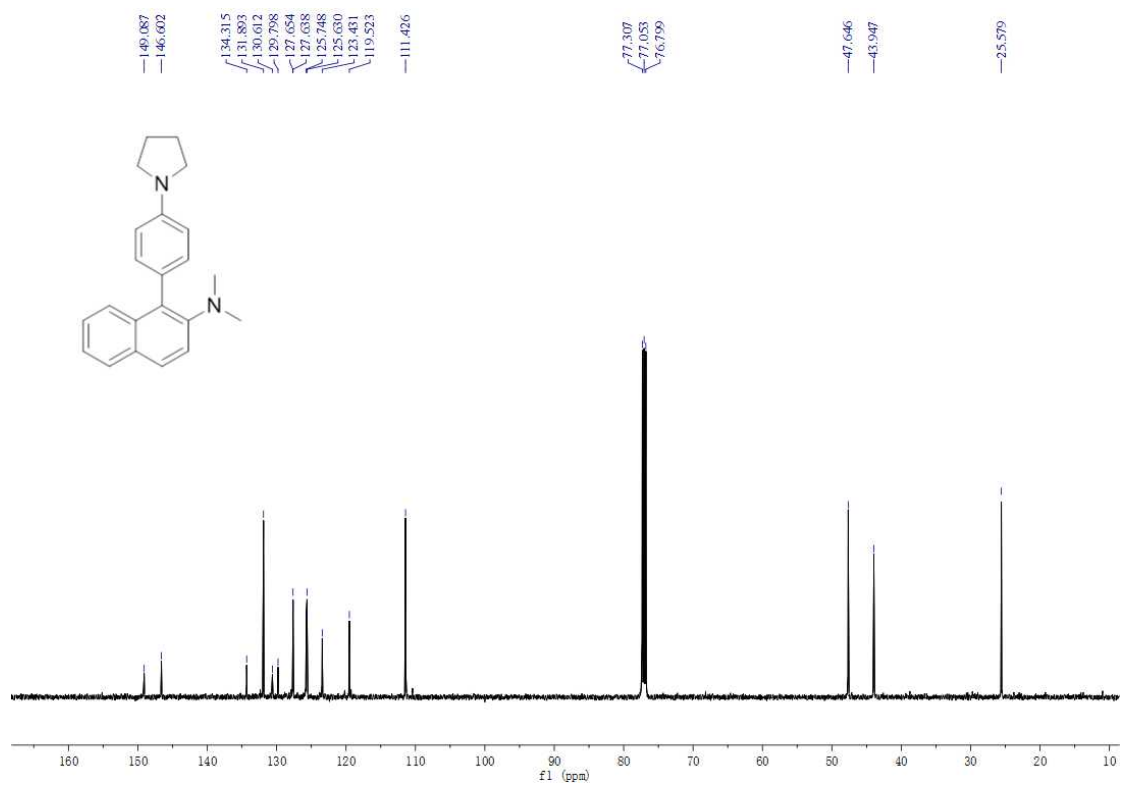
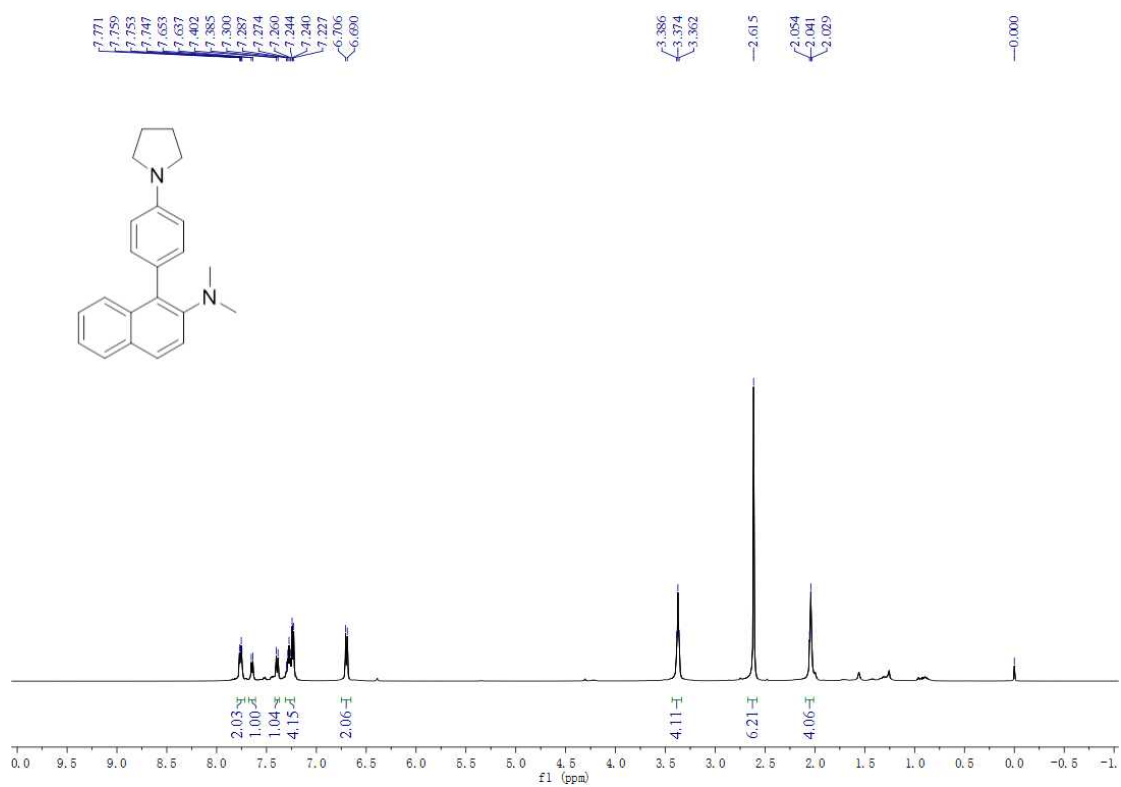
***N,N*-Dimethyl-1-(4-(piperidin-1-yl)phenyl)naphthalen-2-amine (3aI):**



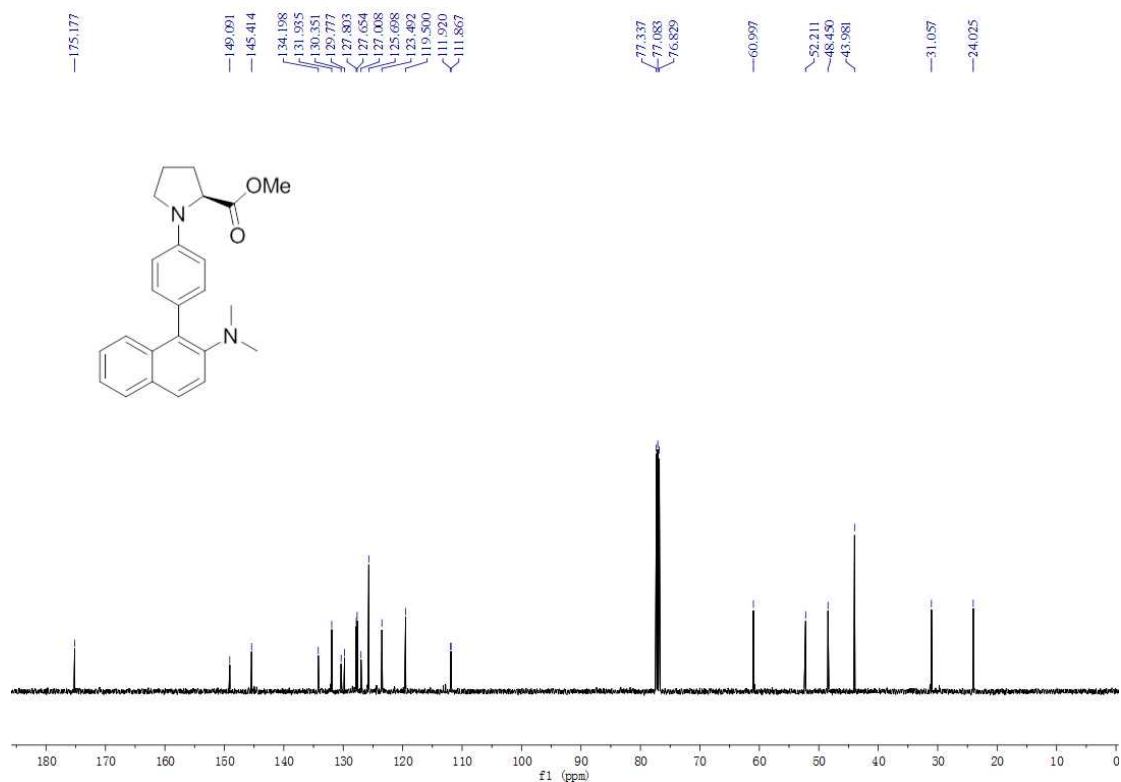
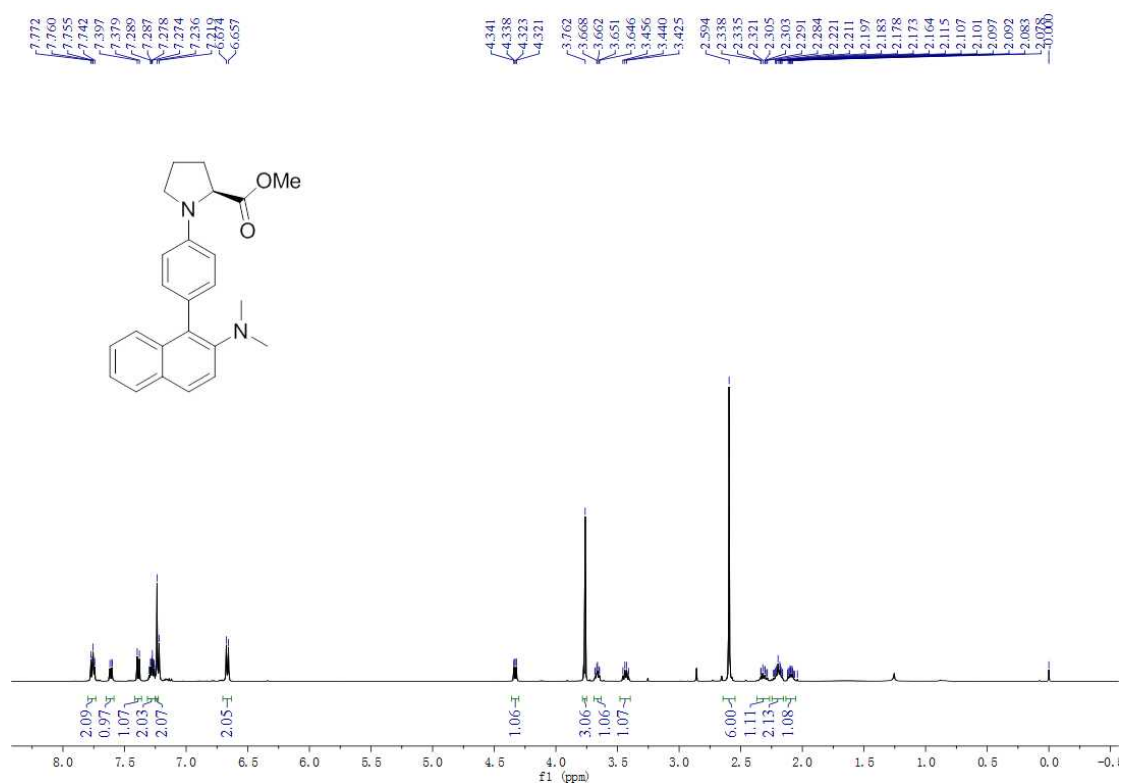
# ***N,N*-Dimethyl-1-(4-morpholinophenyl)naphthalen-2-amine (3am):**



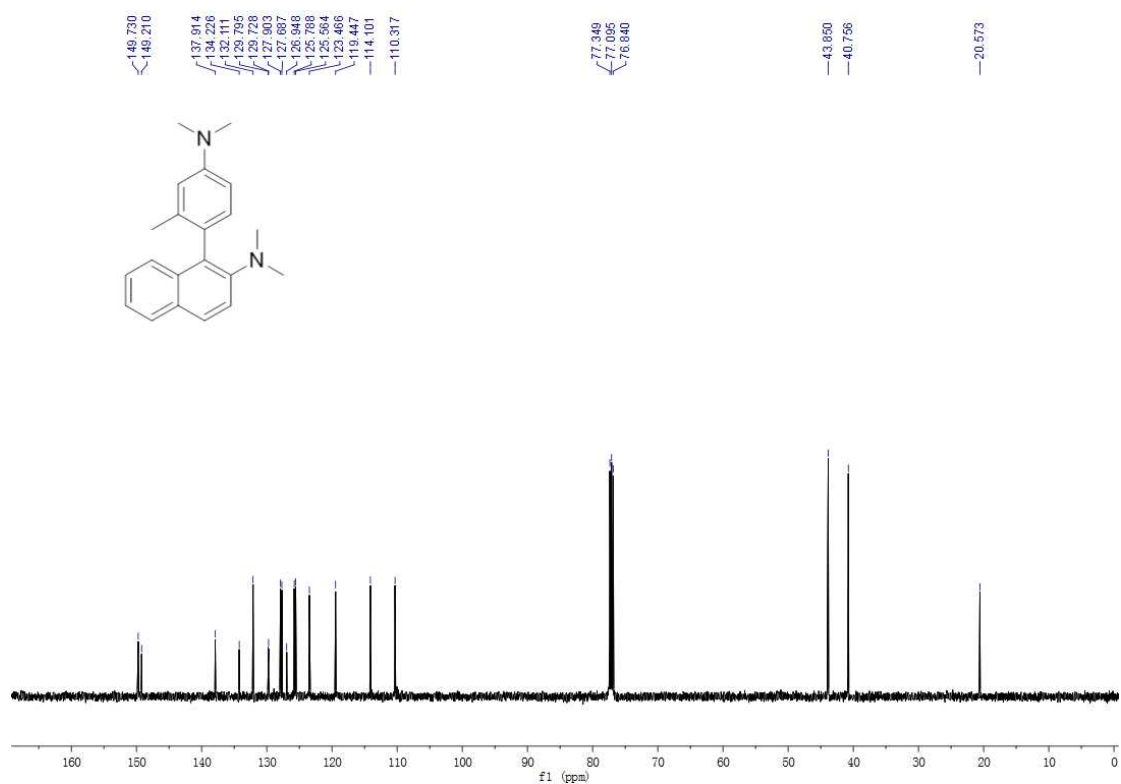
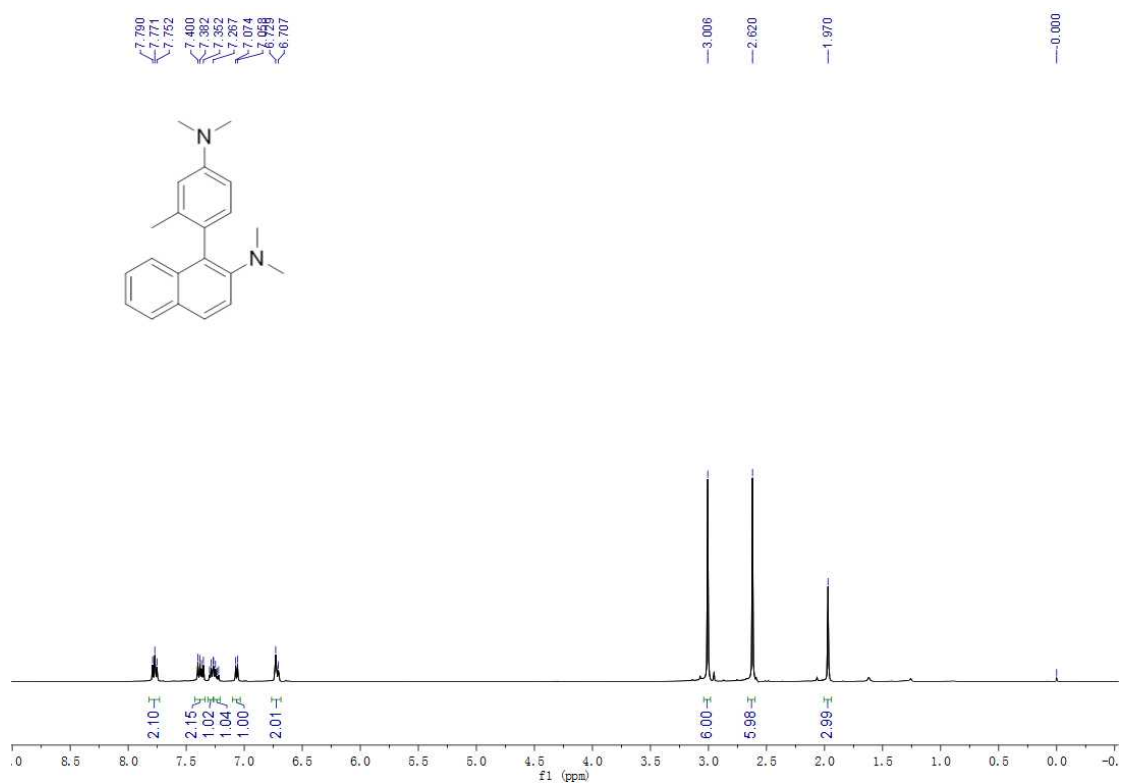
***N,N*-Dimethyl-1-(4-(pyrrolidin-1-yl)phenyl)naphthalen-2-amine(3an):**



**(S)-Methyl-1-(4-(2-(dimethylamino)naphthalen-1-yl)phenyl)pyrrolidine-2-carboxylate (3ao):**

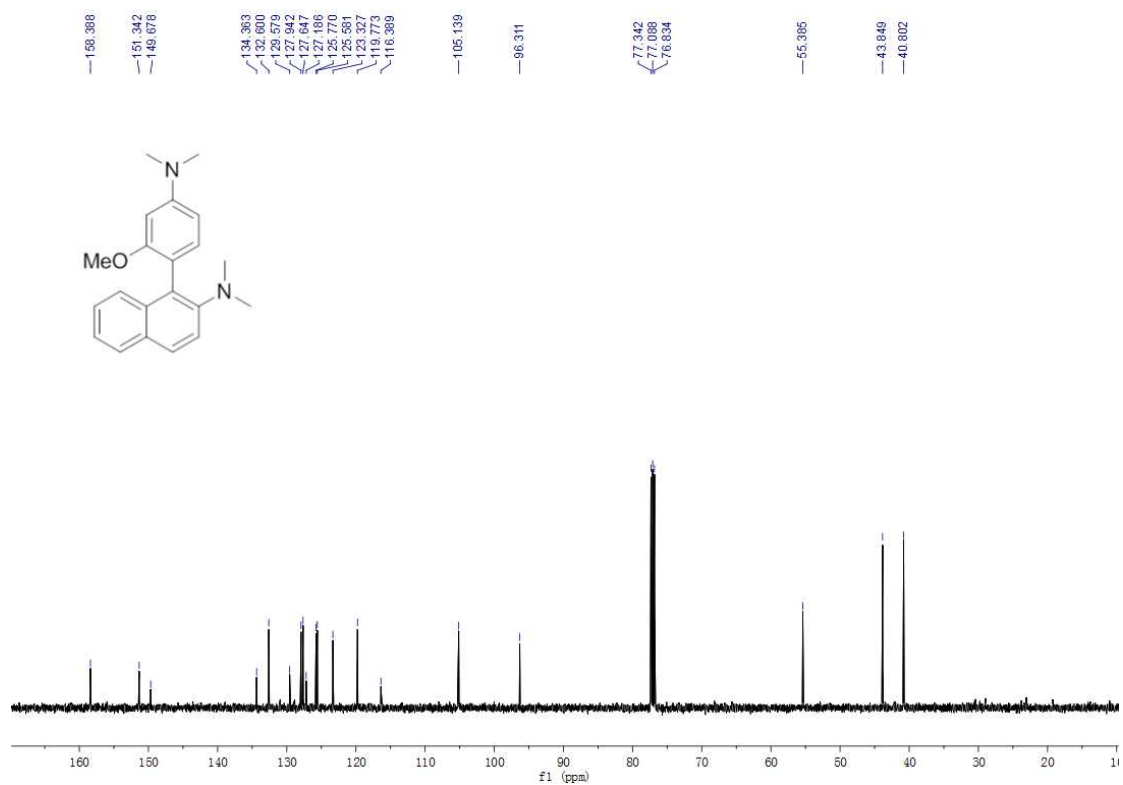
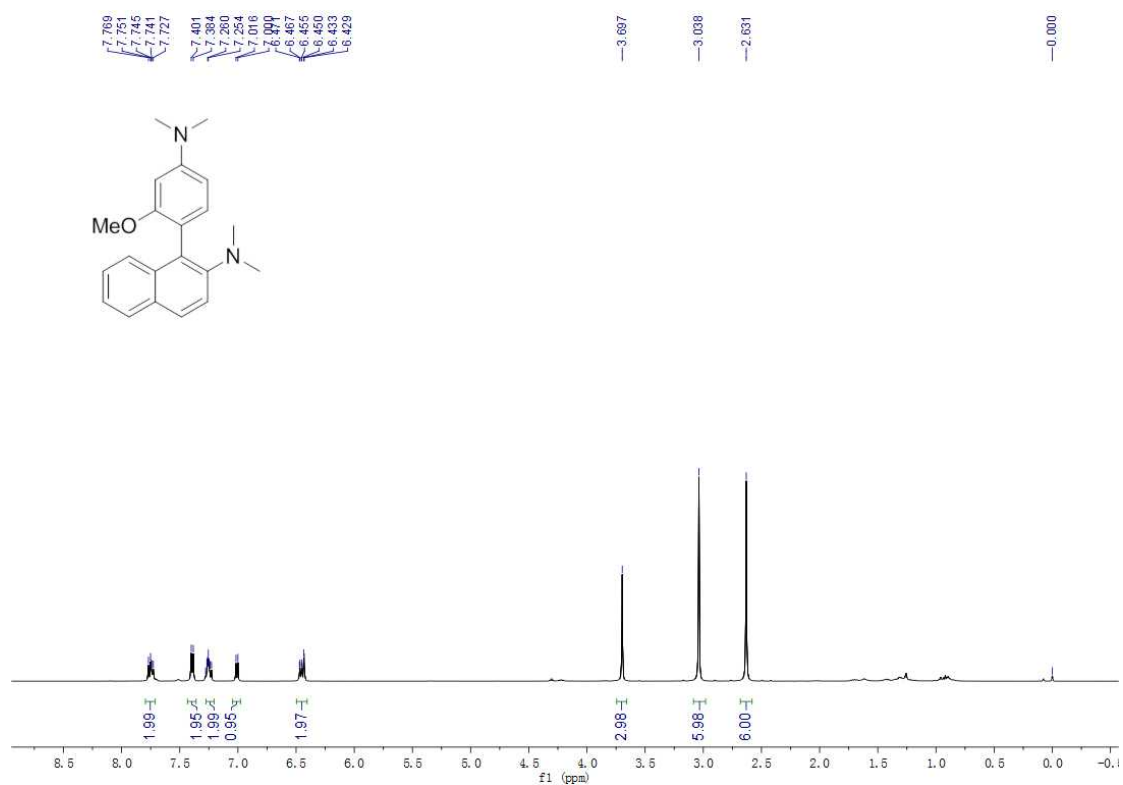


# 1-(4-(Dimethylamino)-2-methylphenyl)-*N,N*-dimethylnaphthalen-2-amine (3ap):

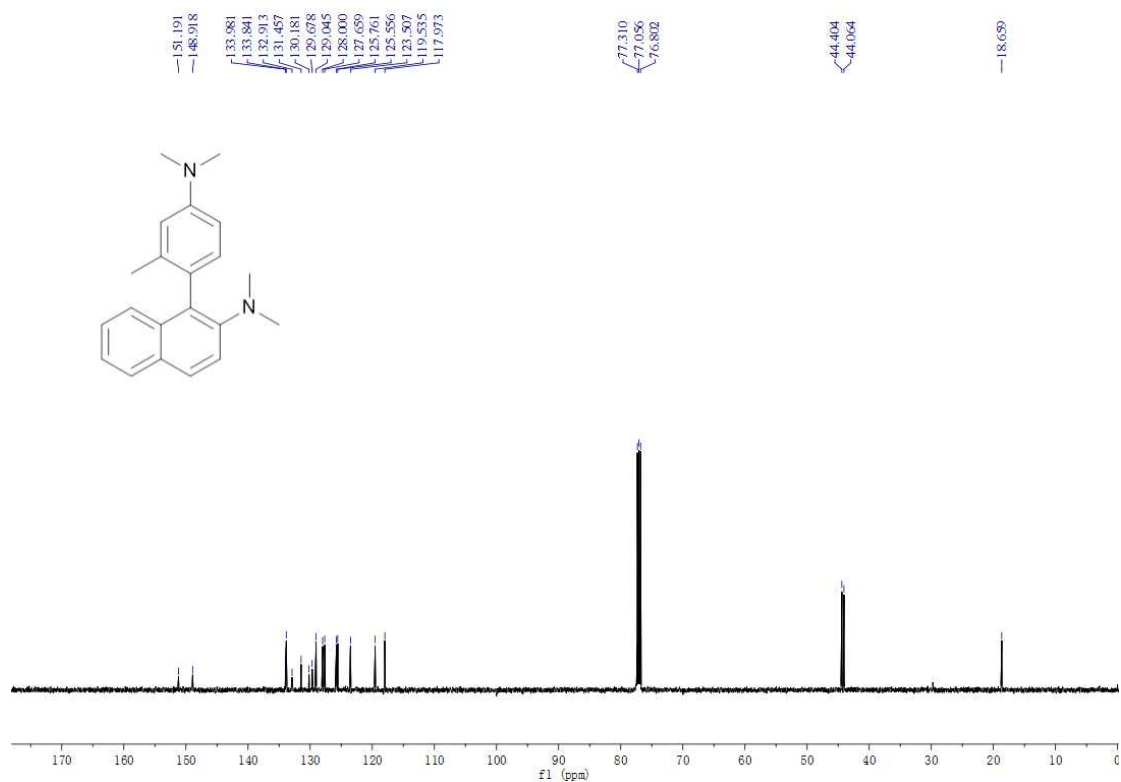
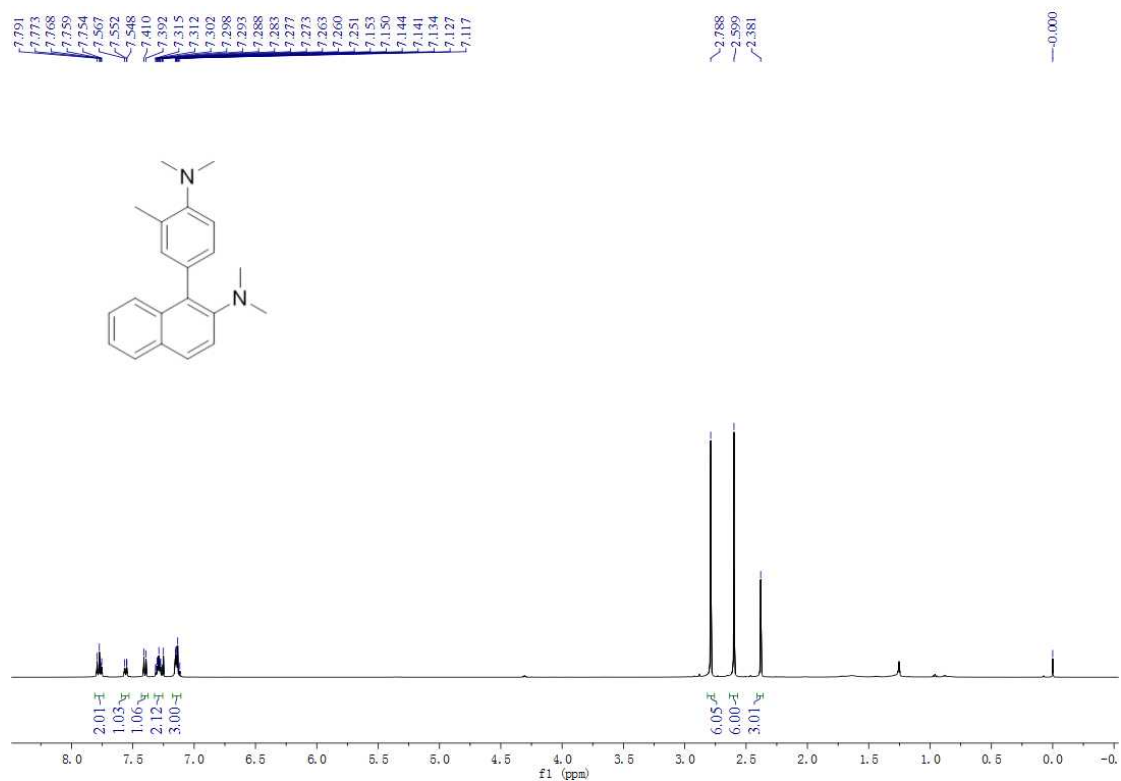


# 1-(4-(Dimethylamino)-2-methoxyphenyl)-N,N-dimethylnaphthalen-2-amine

(3aq):

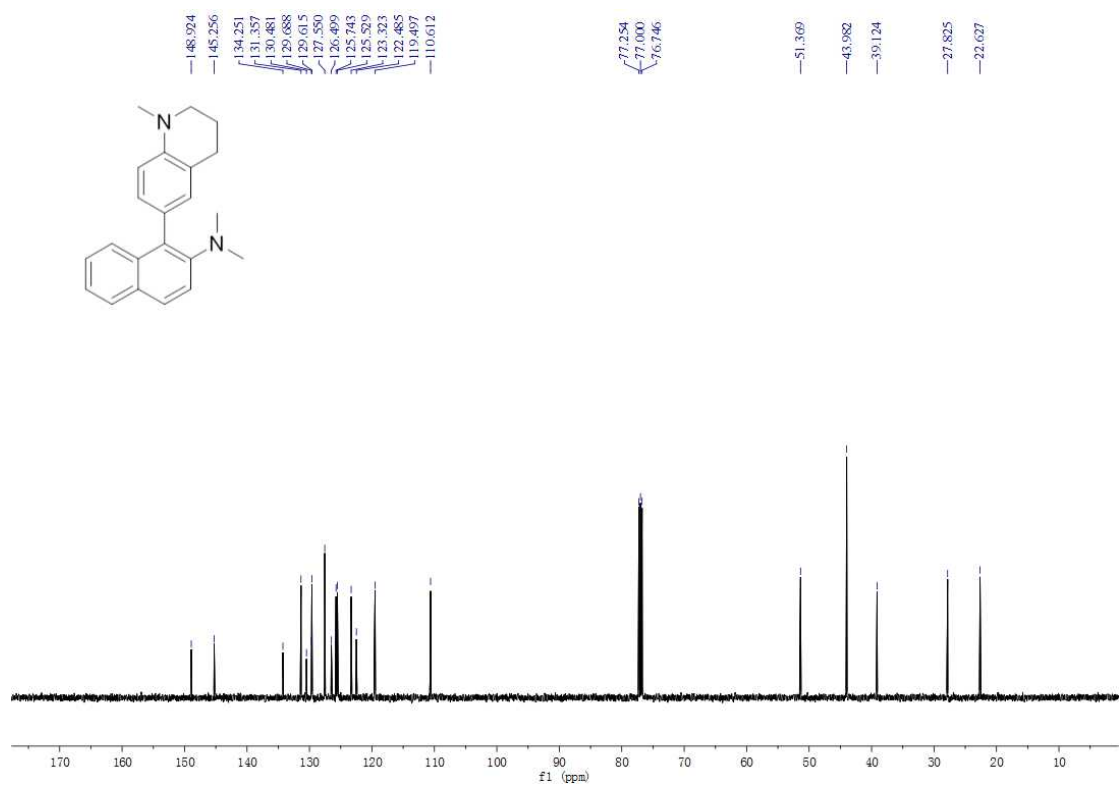
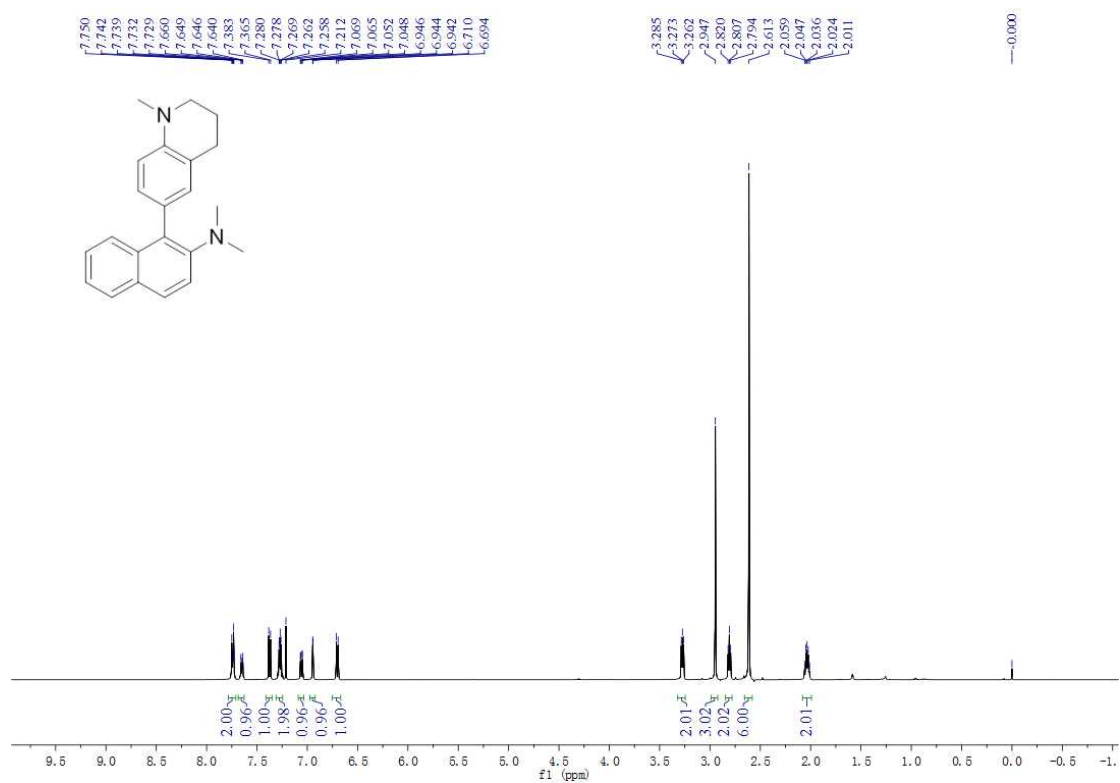


# 1-(4-(Dimethylamino)-3-methylphenyl)-*N,N*-dimethylnaphthalen-2-amine (3ar):

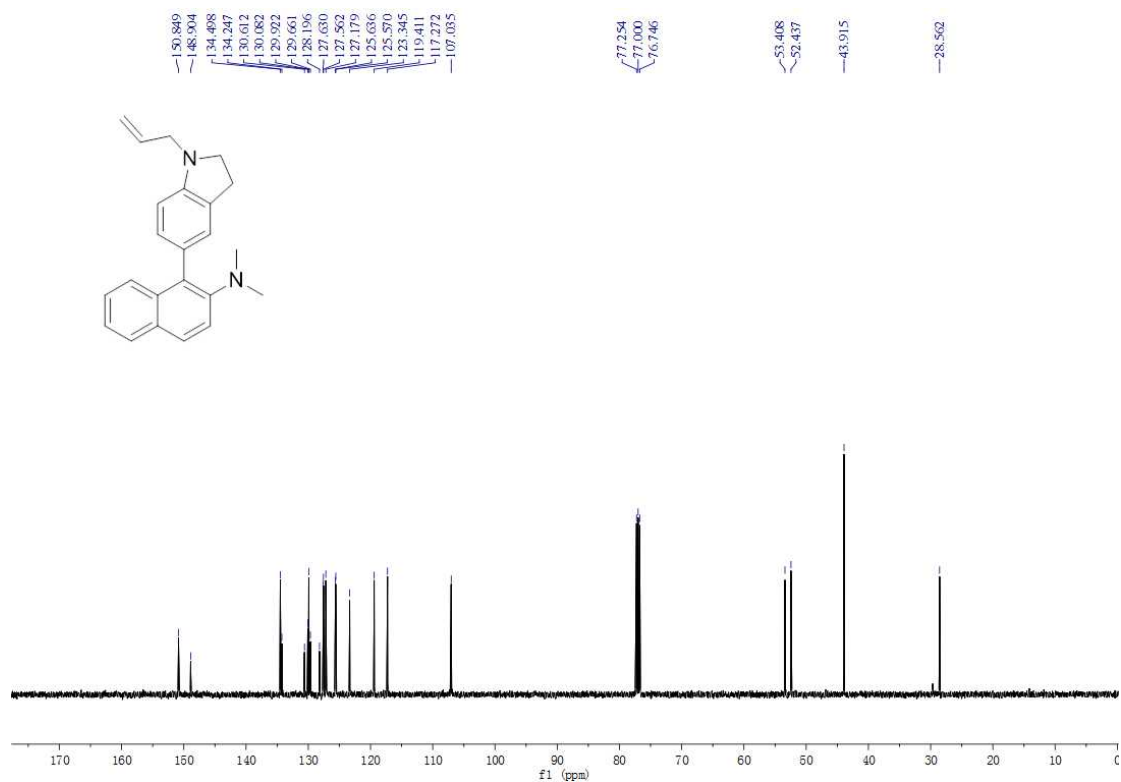
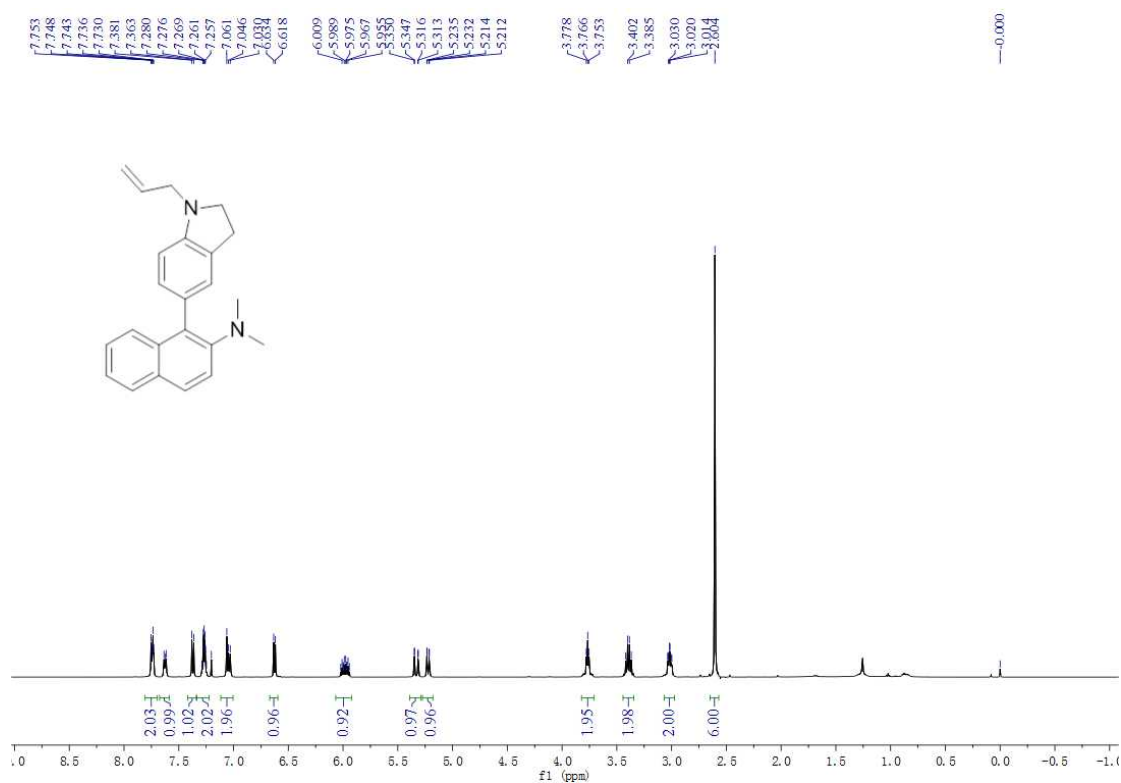


***N,N*-Dimethyl-1-(1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)naphthalen-2-amine**

**(3as):**

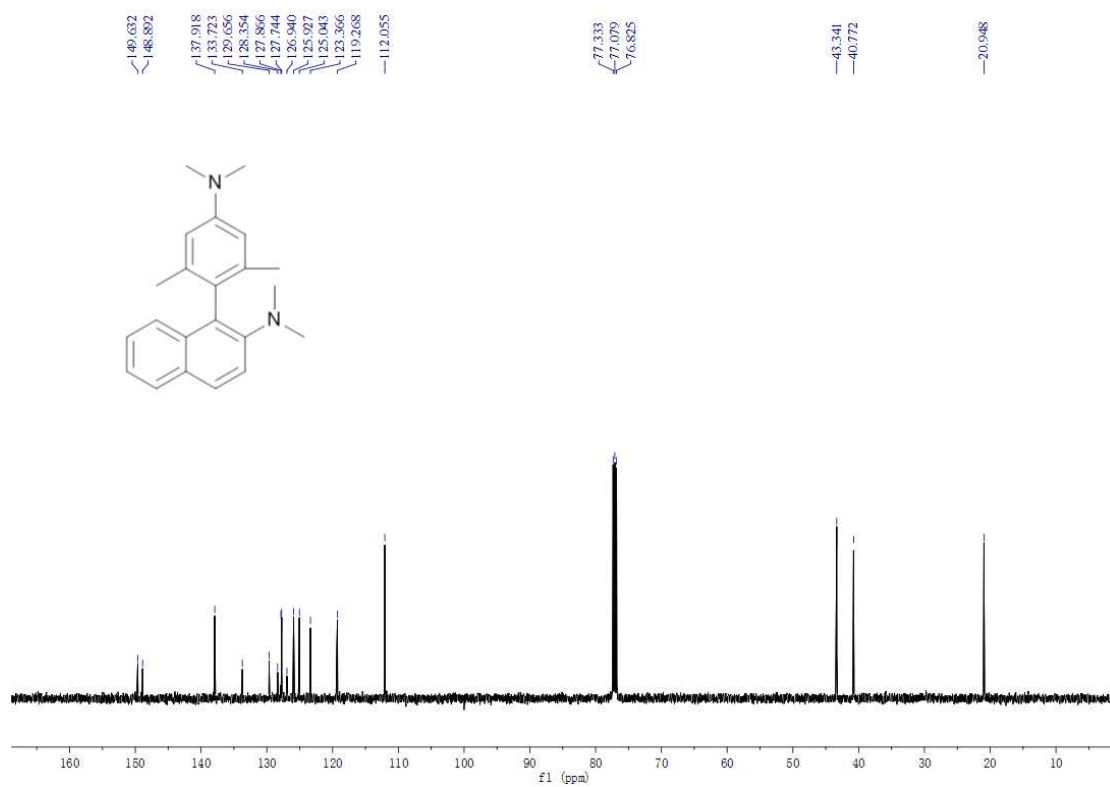
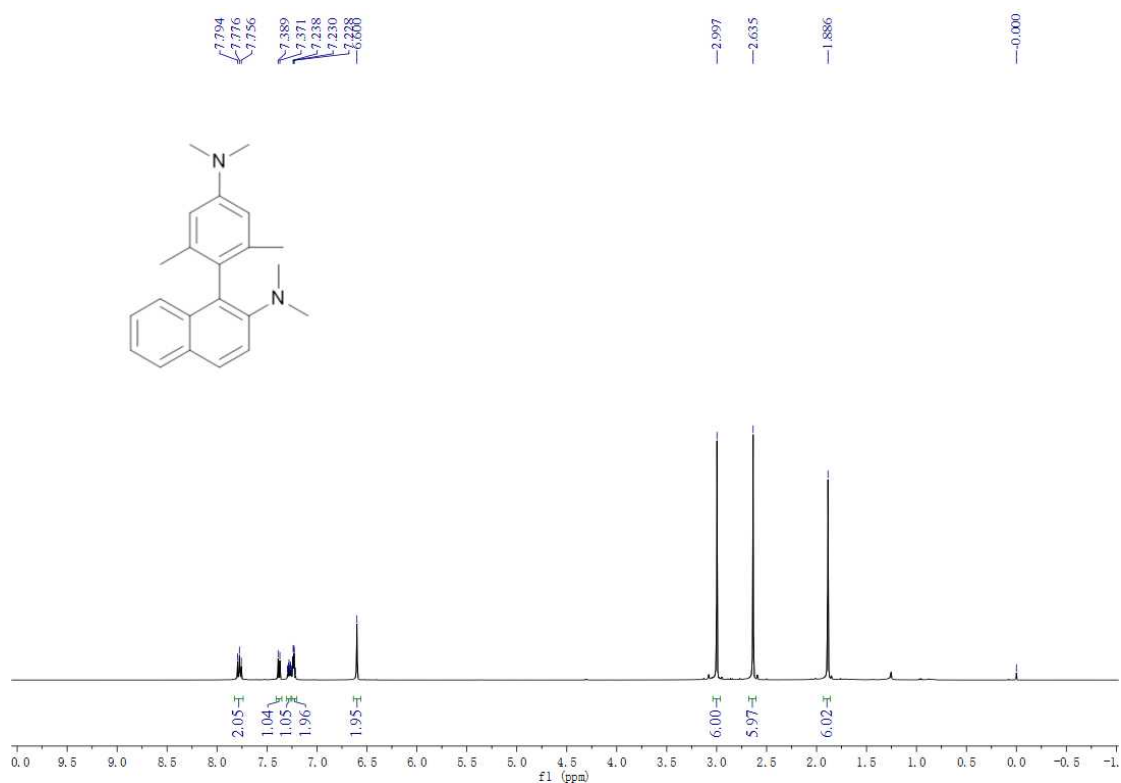


# 1-(1-Allylindolin-5-yl)-N,N-dimethylnaphthalen-2-amine (3at):

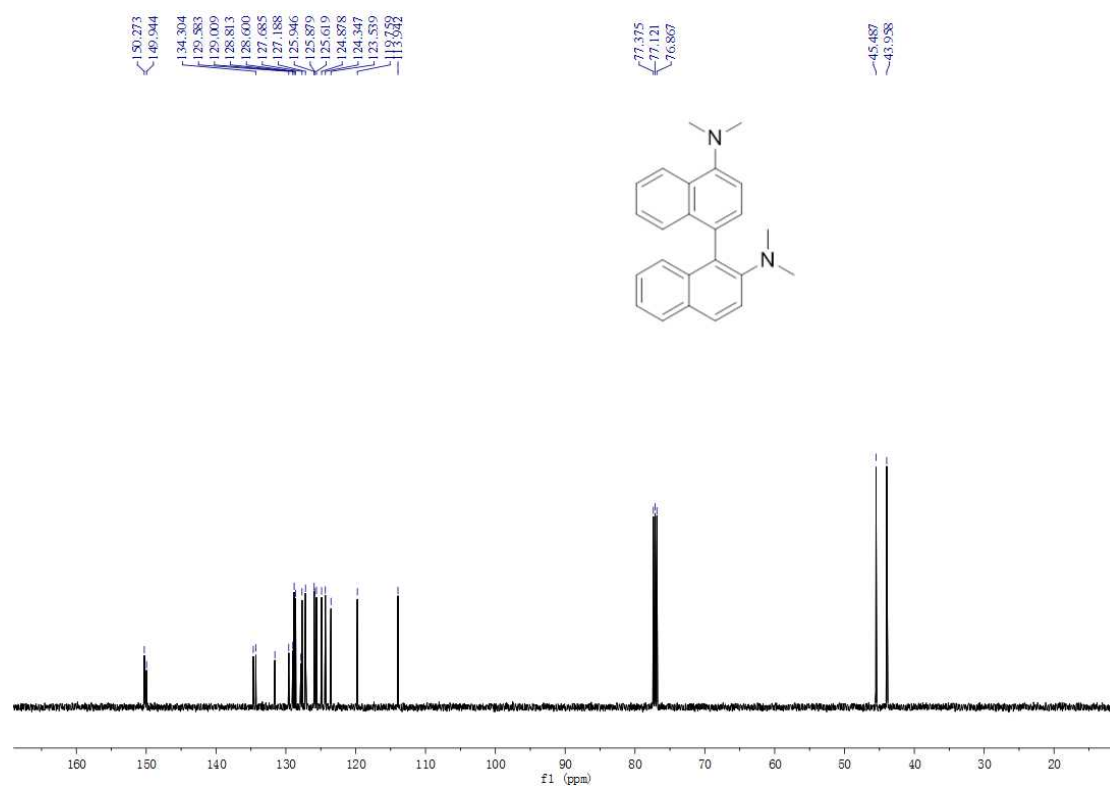
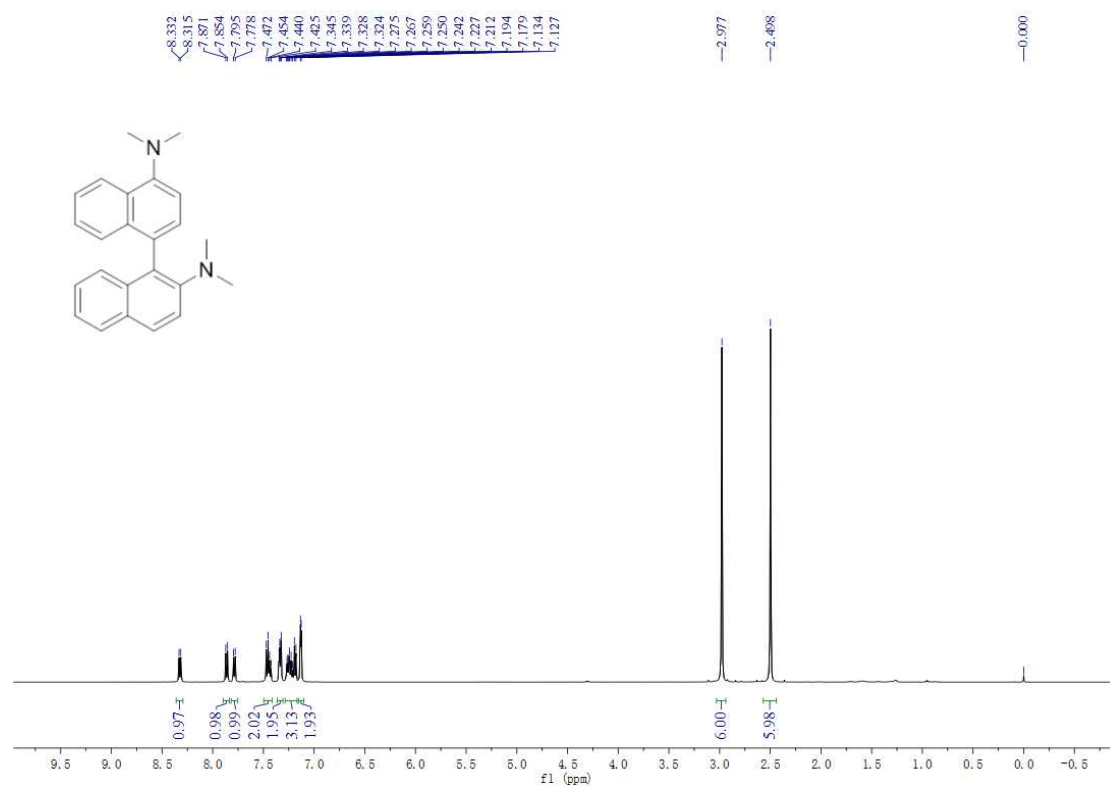


# 1-(4-(Dimethylamino)-2,6-dimethylphenyl)-*N,N*-dimethylnaphthalen-2-amine

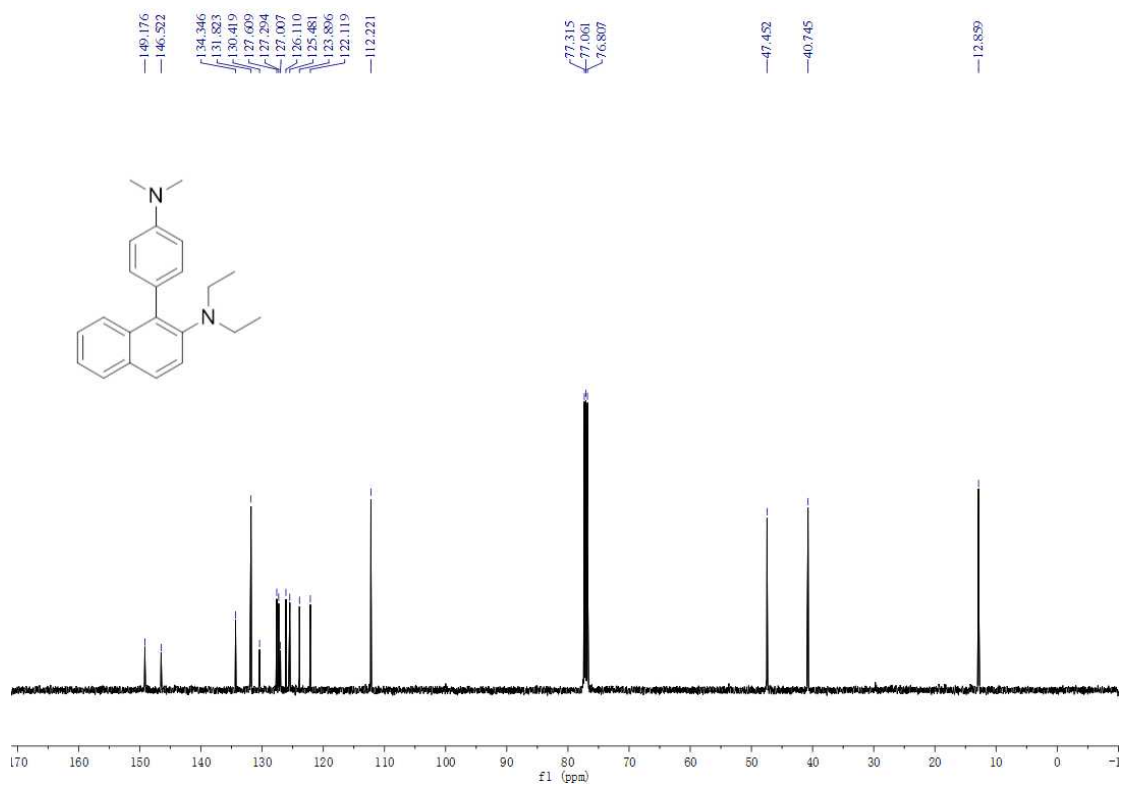
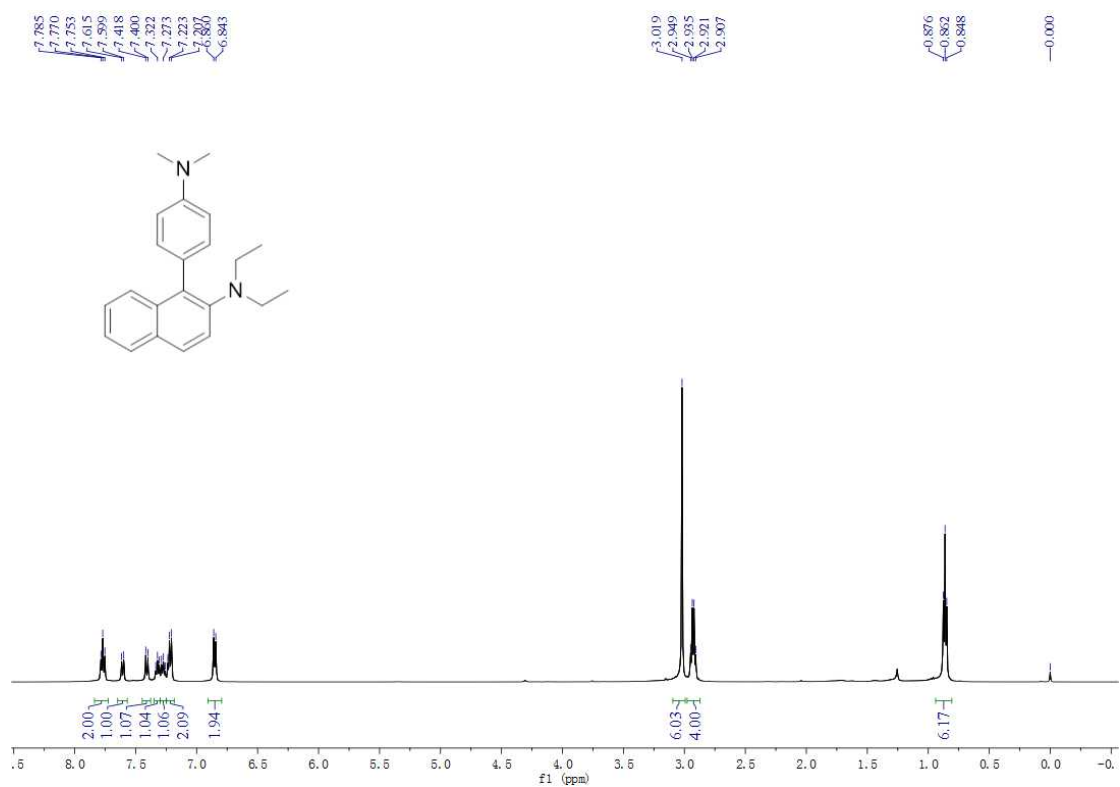
(3au):



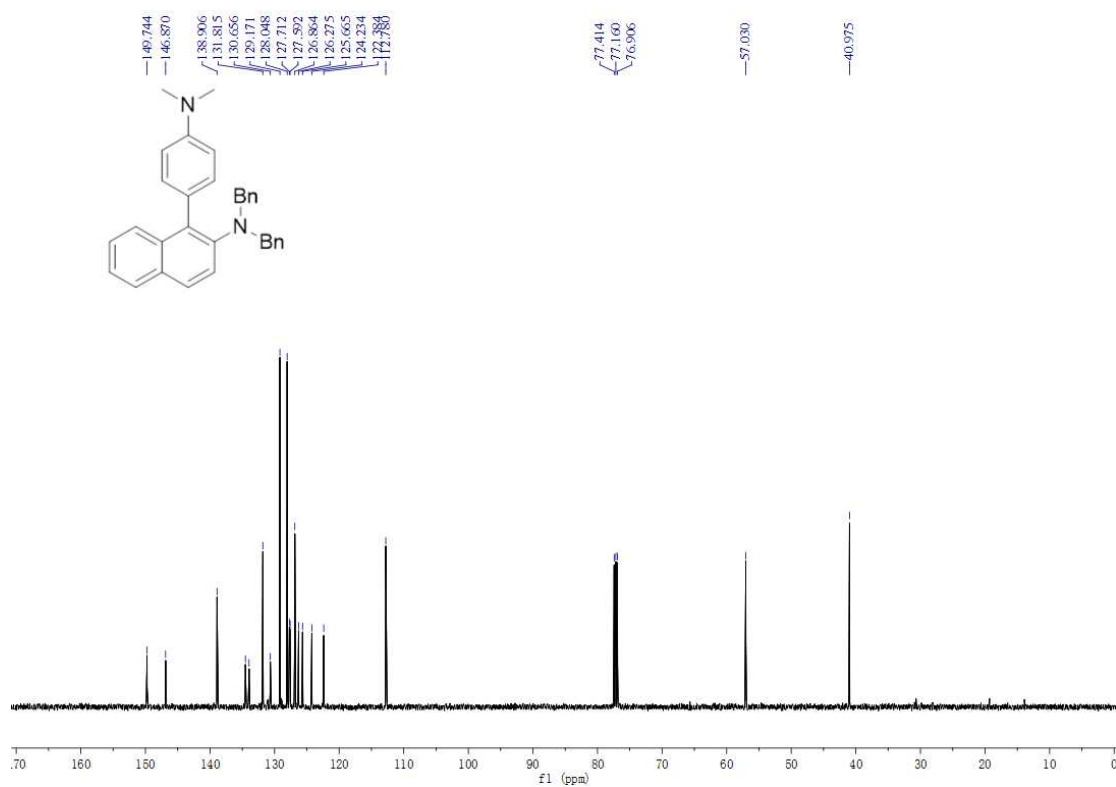
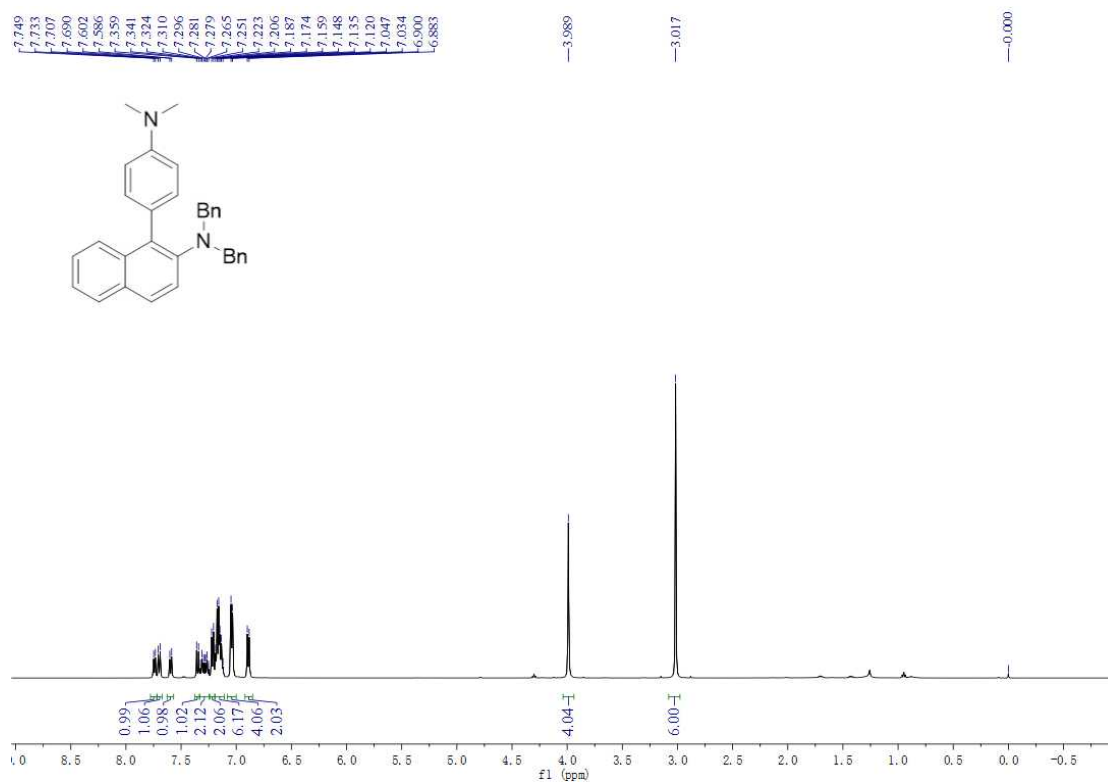
***N*<sup>2</sup>,*N*<sup>2</sup>,*N*<sup>4</sup>',*N*<sup>4</sup>'-Tetramethyl-[1,1'-binaphthalene]-2,4'-diamine (3av):**



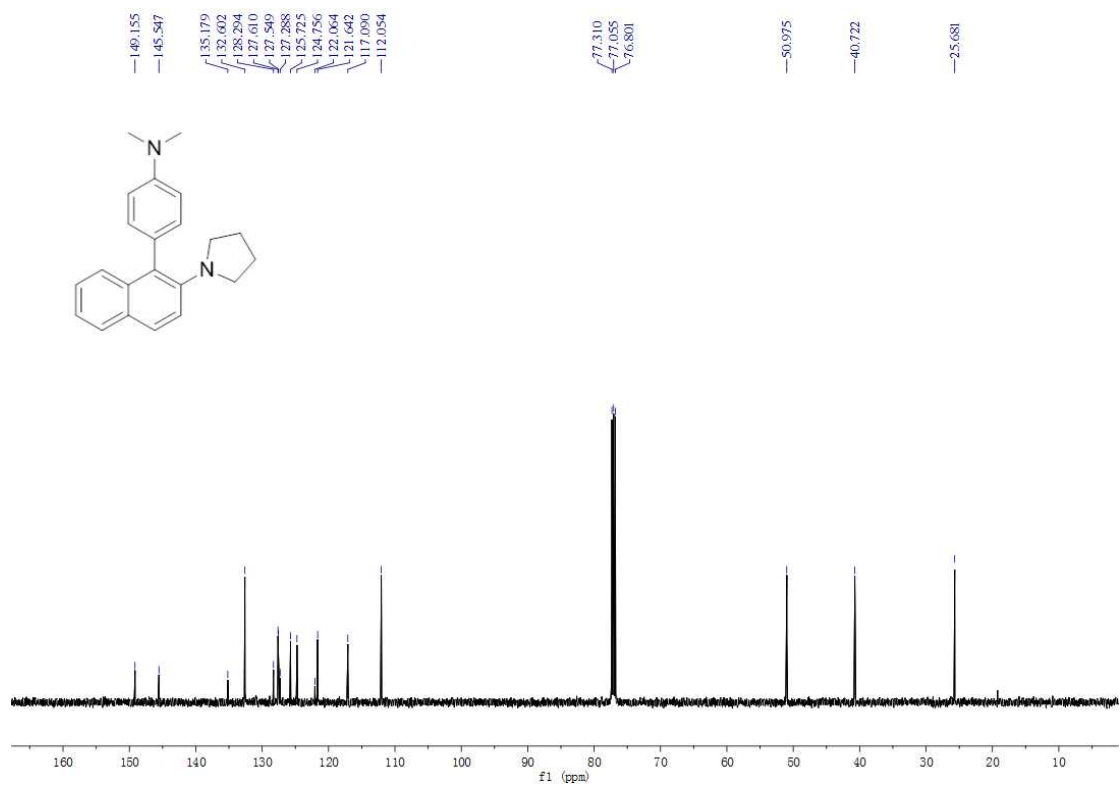
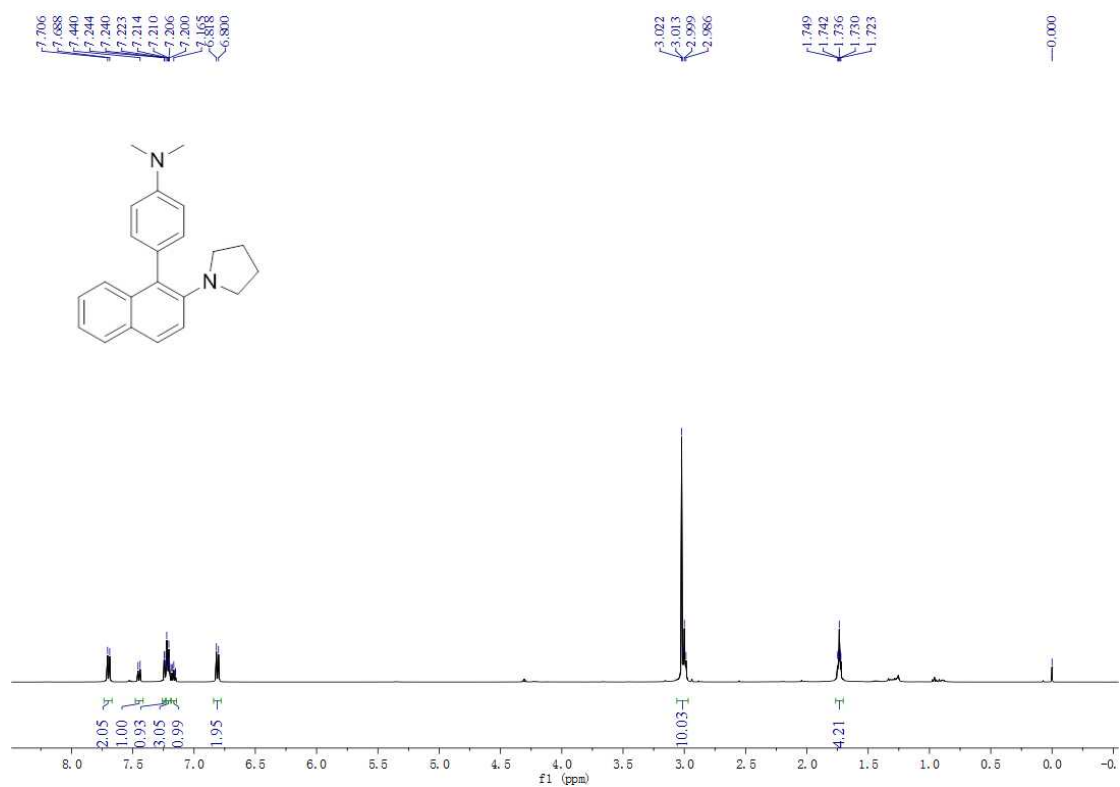
# 1-(4-(Dimethylamino)phenyl)-*N,N*-diethynaphthalen-2-amine (3ba):



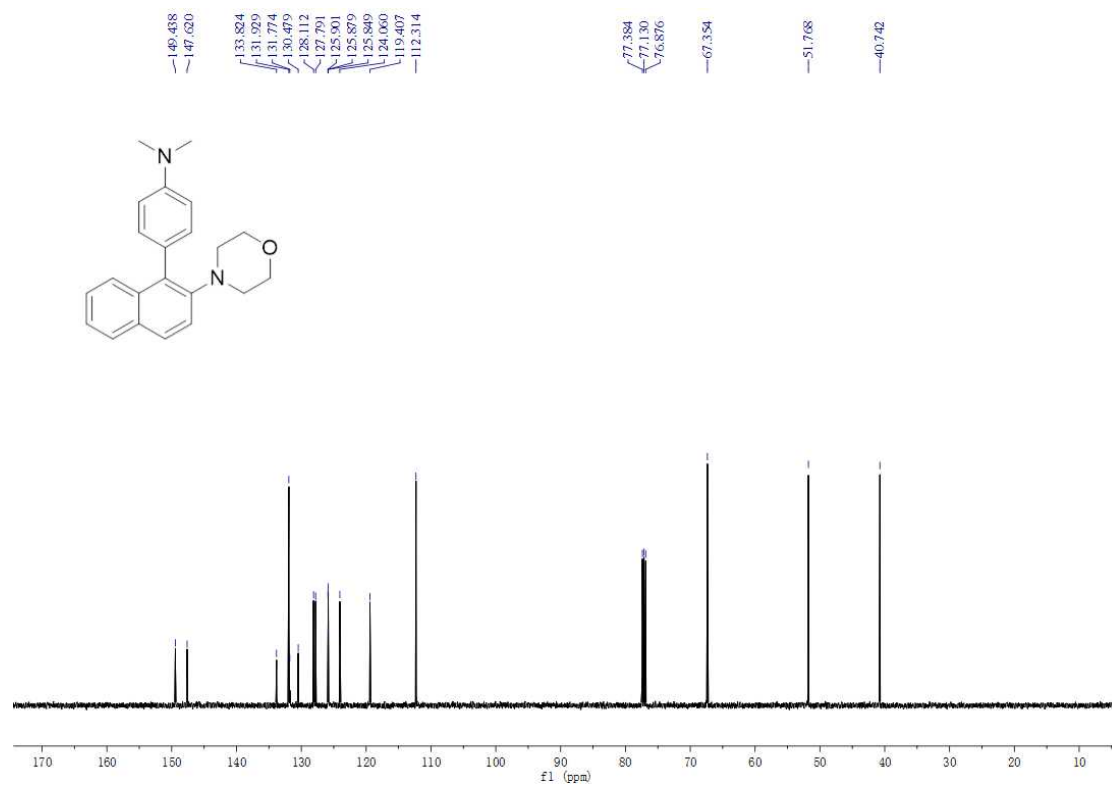
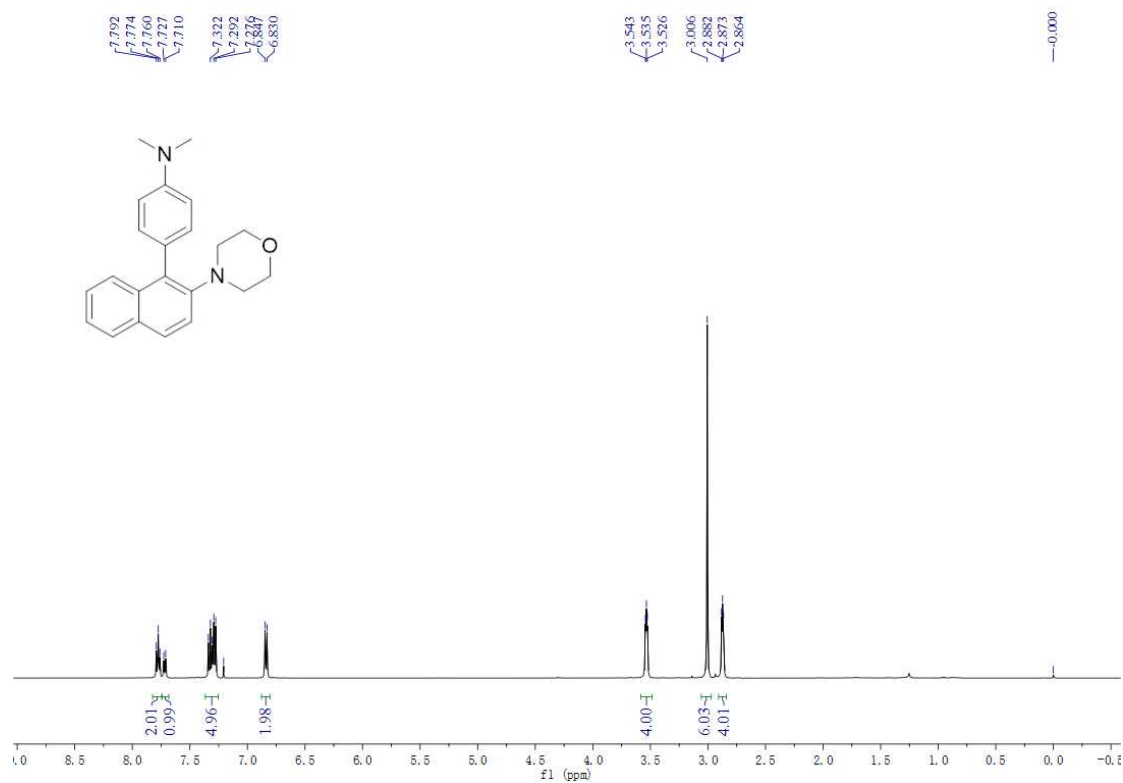
***N,N*-Dibenzyl-1-(4-(dimethylamino)phenyl)naphthalen-2-amine (3ca):**



***N,N*-Dimethyl-4-(2-(pyrrolidin-1-yl)naphthalen-1-yl)aniline (3da):**

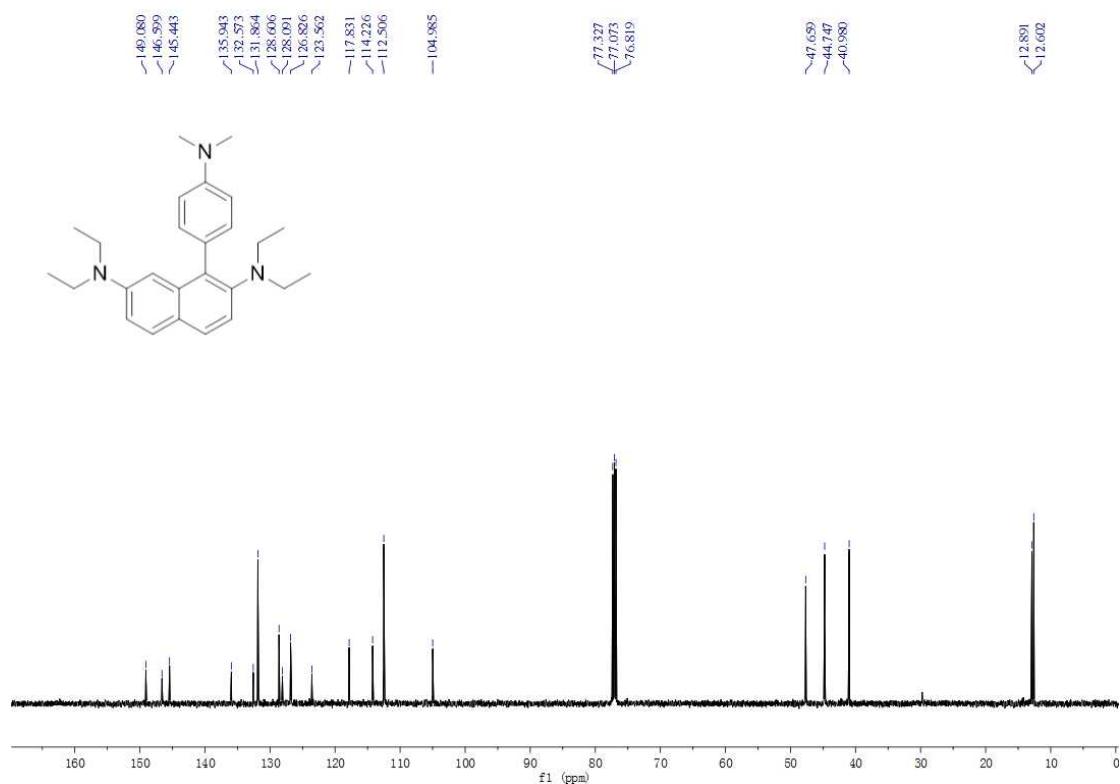
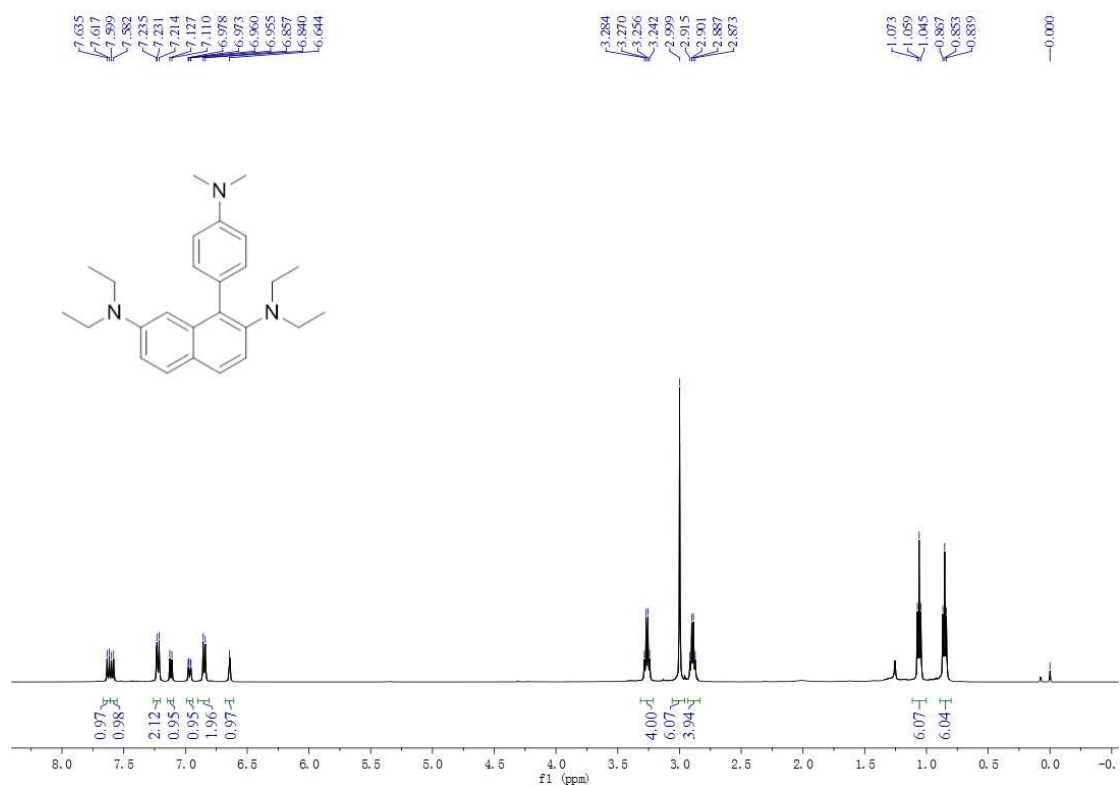


***N,N*-Dimethyl-4-(2-morpholinonaphthalen-1-yl)aniline (3ea):**

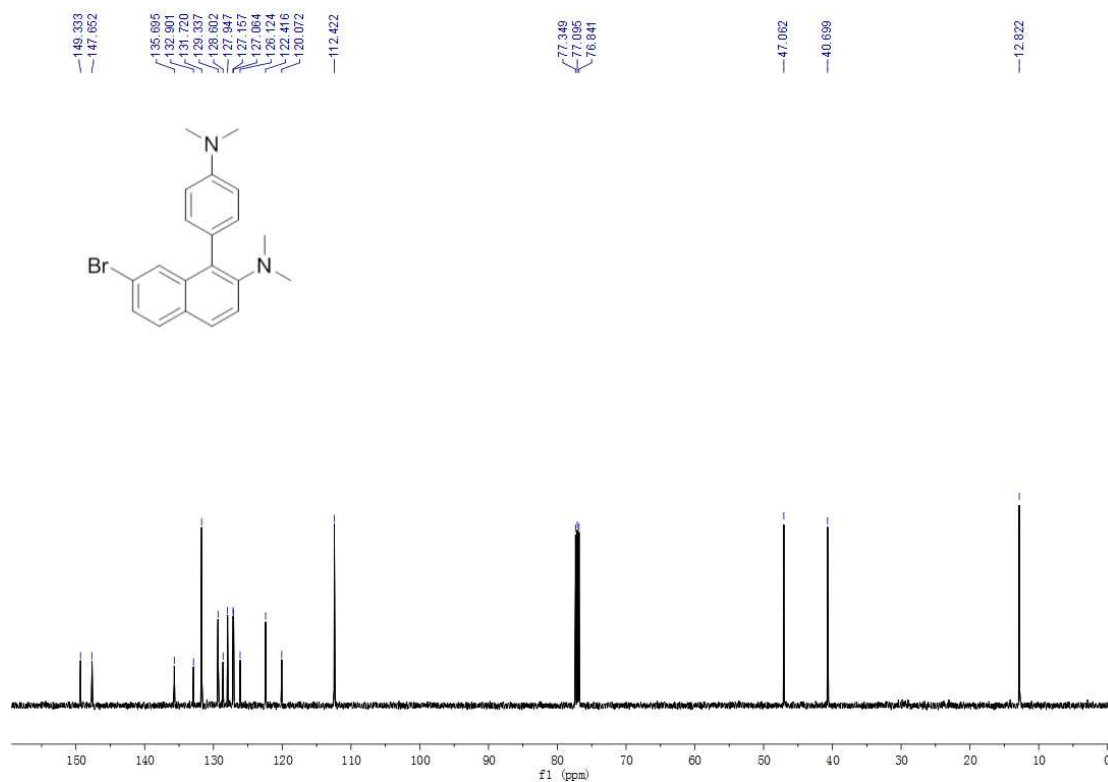
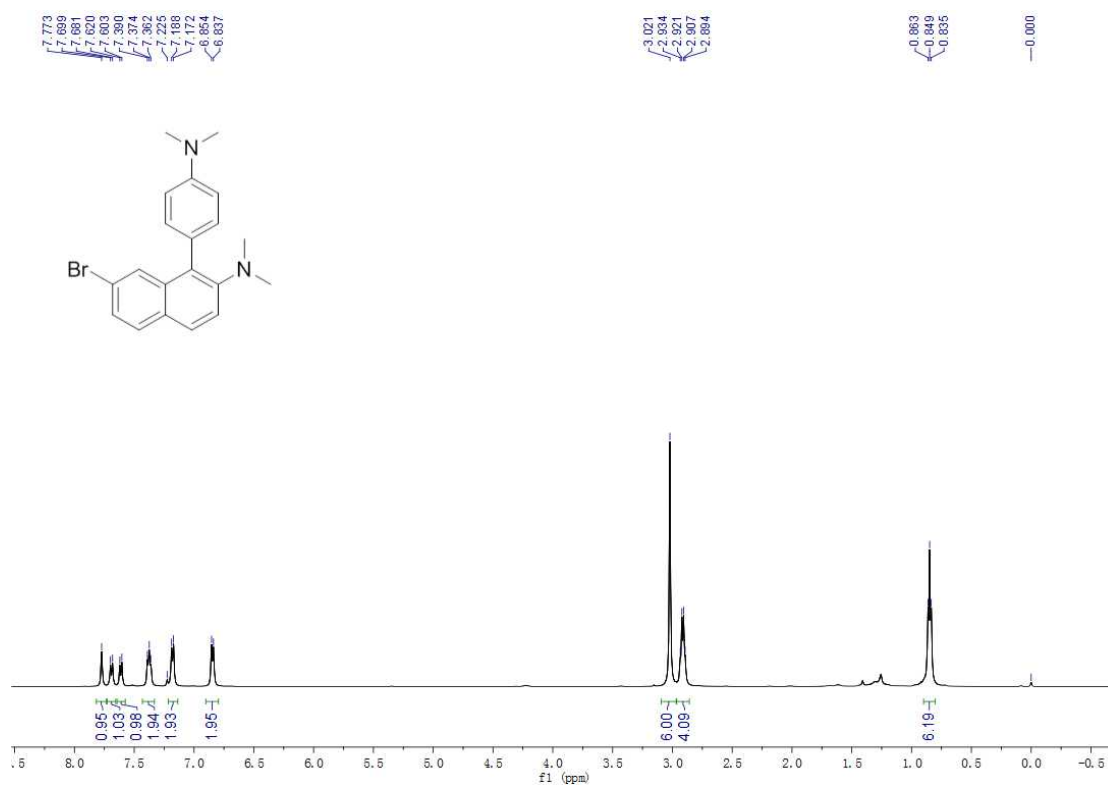


# 1-(4-(Dimethylamino)phenyl)-*N*<sup>2</sup>,*N*<sup>2</sup>,*N*<sup>7</sup>,*N*<sup>7</sup>-tetraethylnaphthalene-2,7-diamine

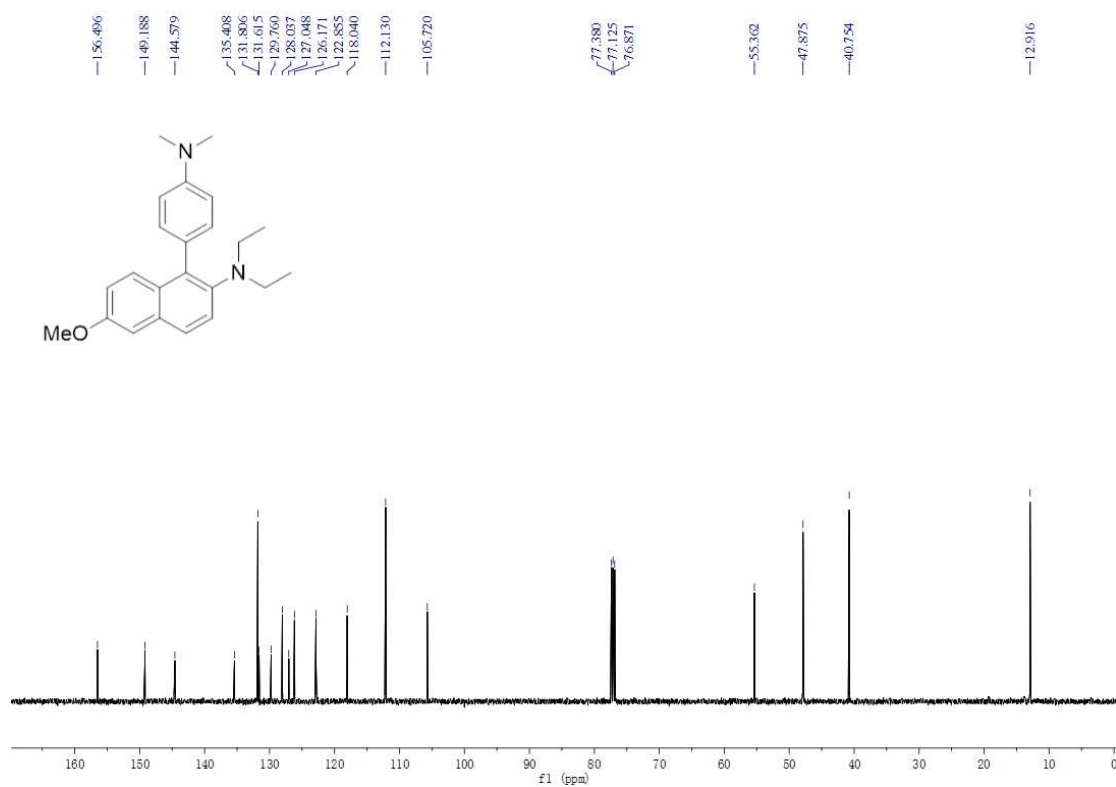
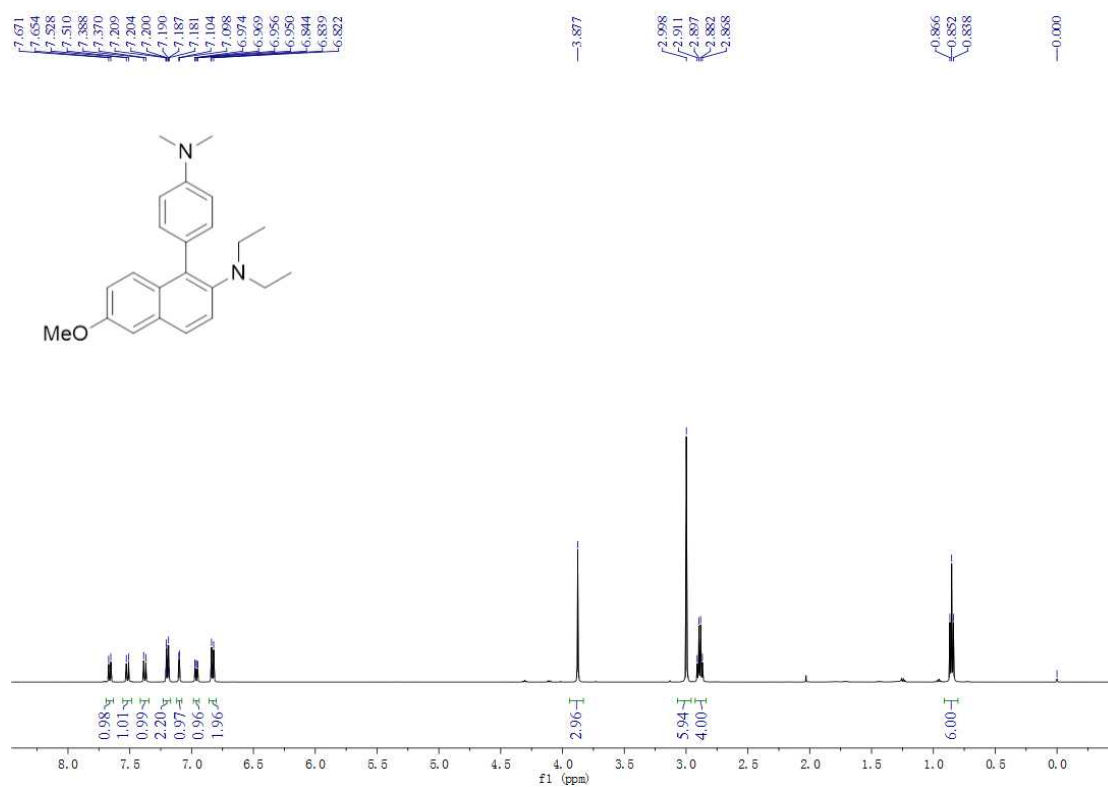
(3ga):



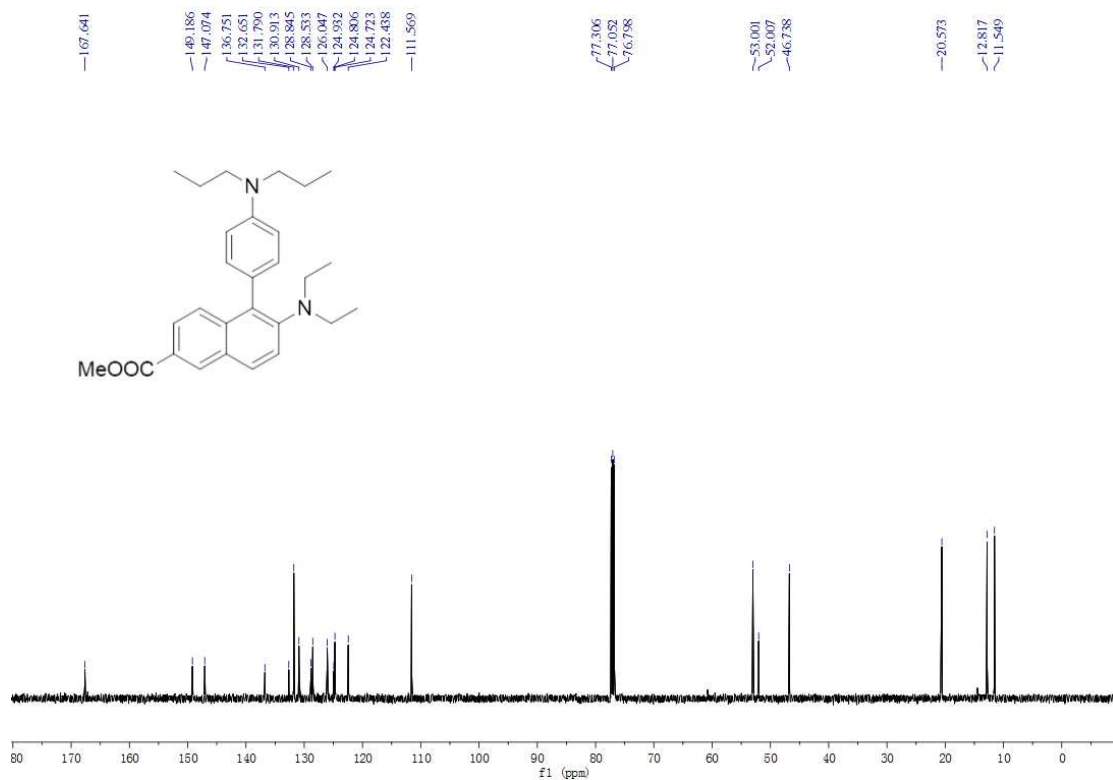
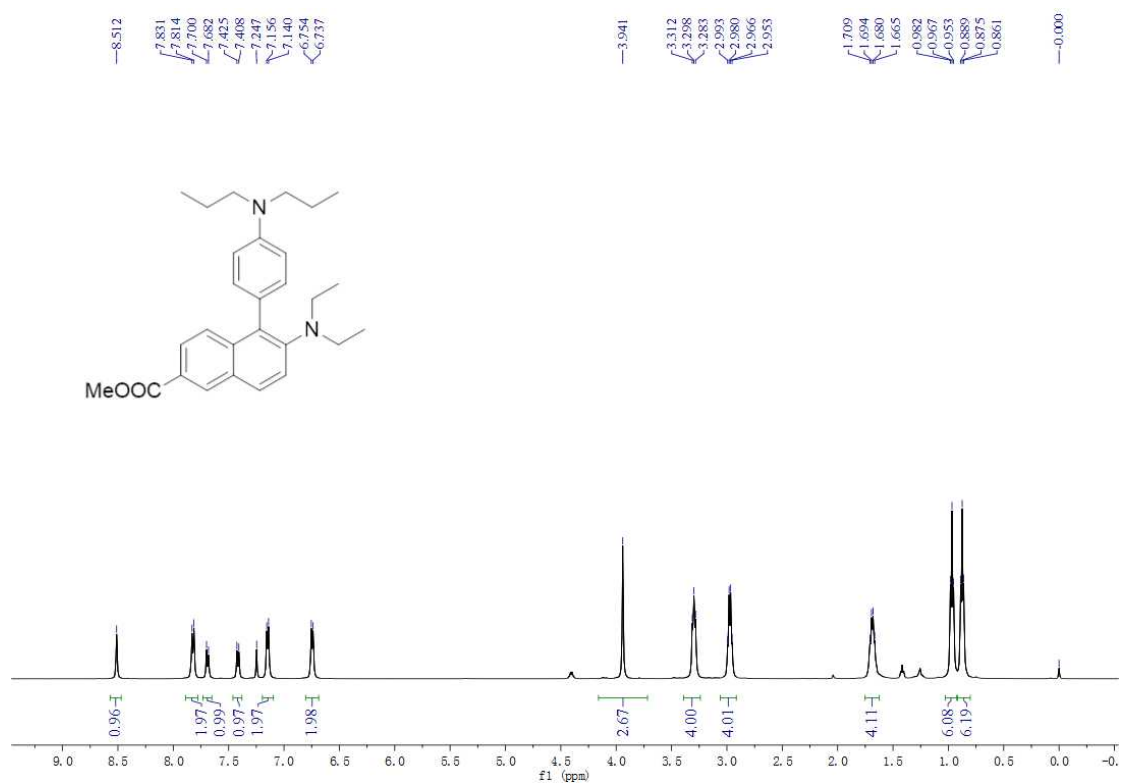
**7-Bromo-1-(4-(dimethylamino)phenyl)-N,N-diethylnaphthalen-2-amine (3ha):**



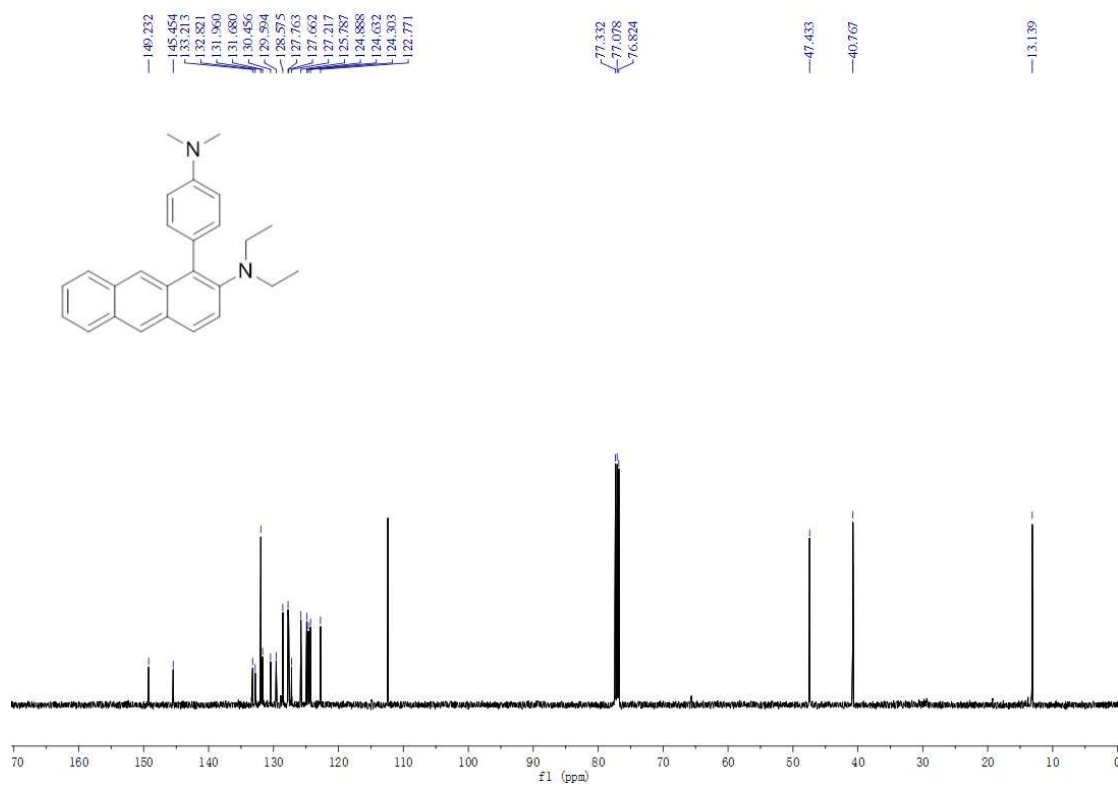
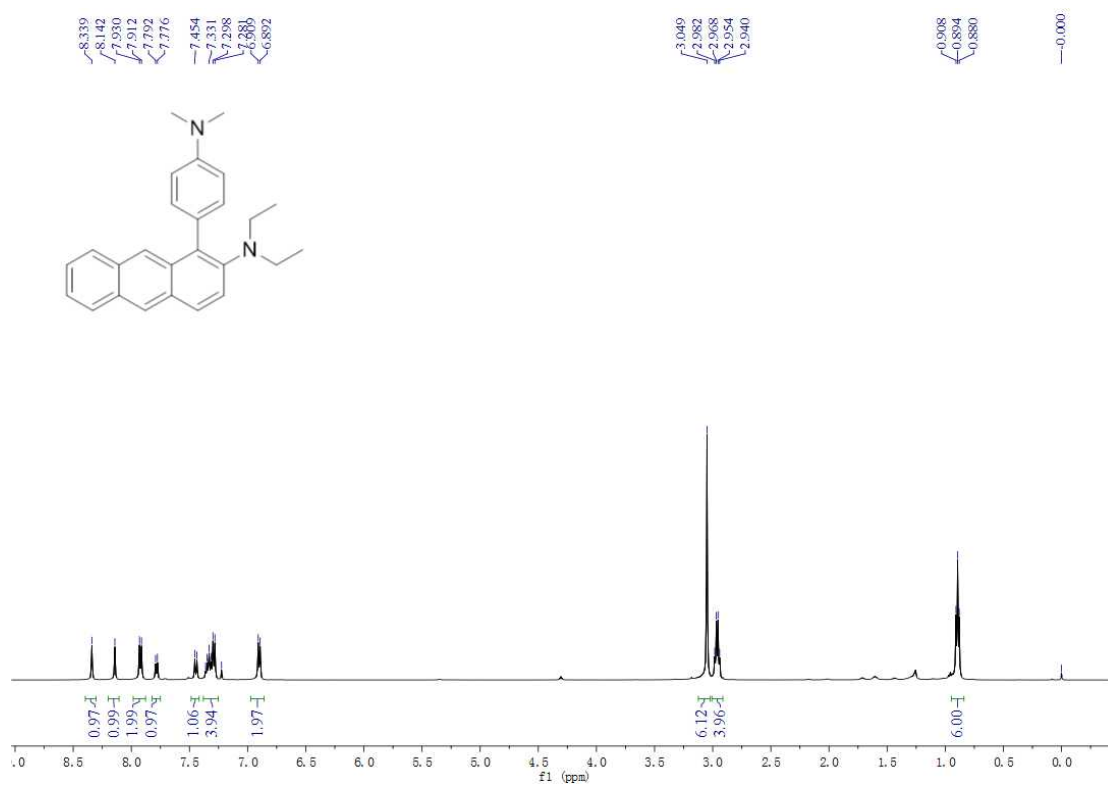
# 1-(4-(Dimethylamino)phenyl)-*N,N*-diethyl-6-methoxynaphthalen-2-amine (3ia):



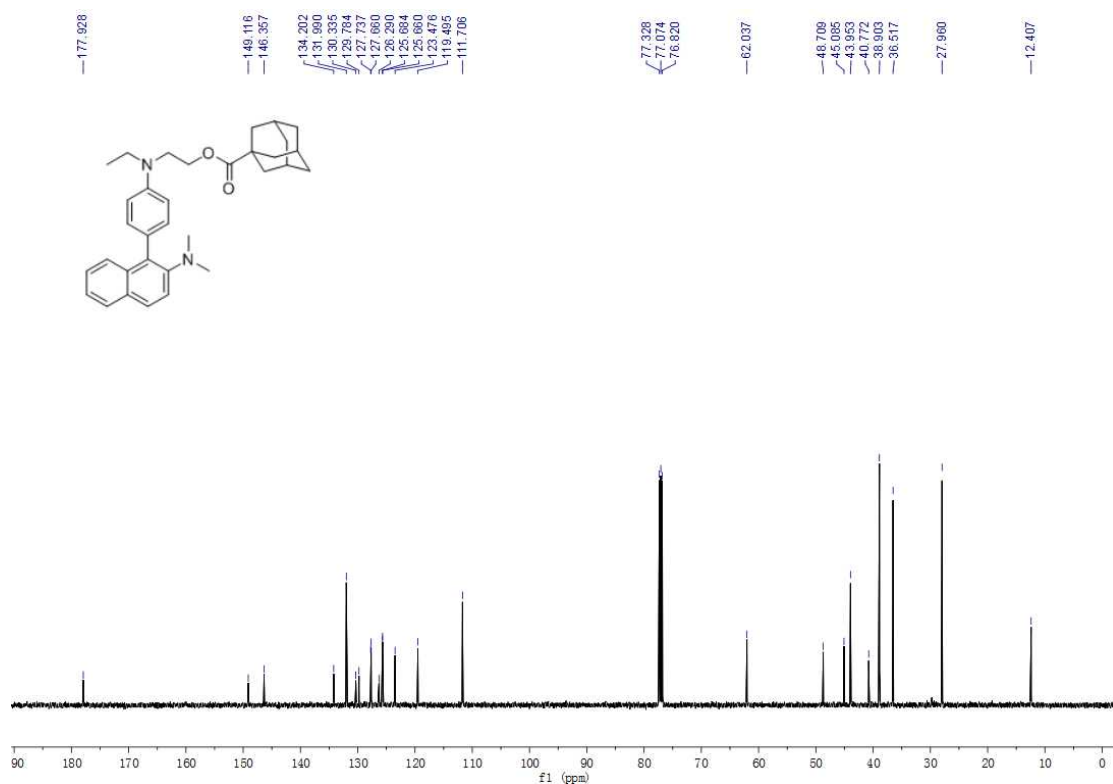
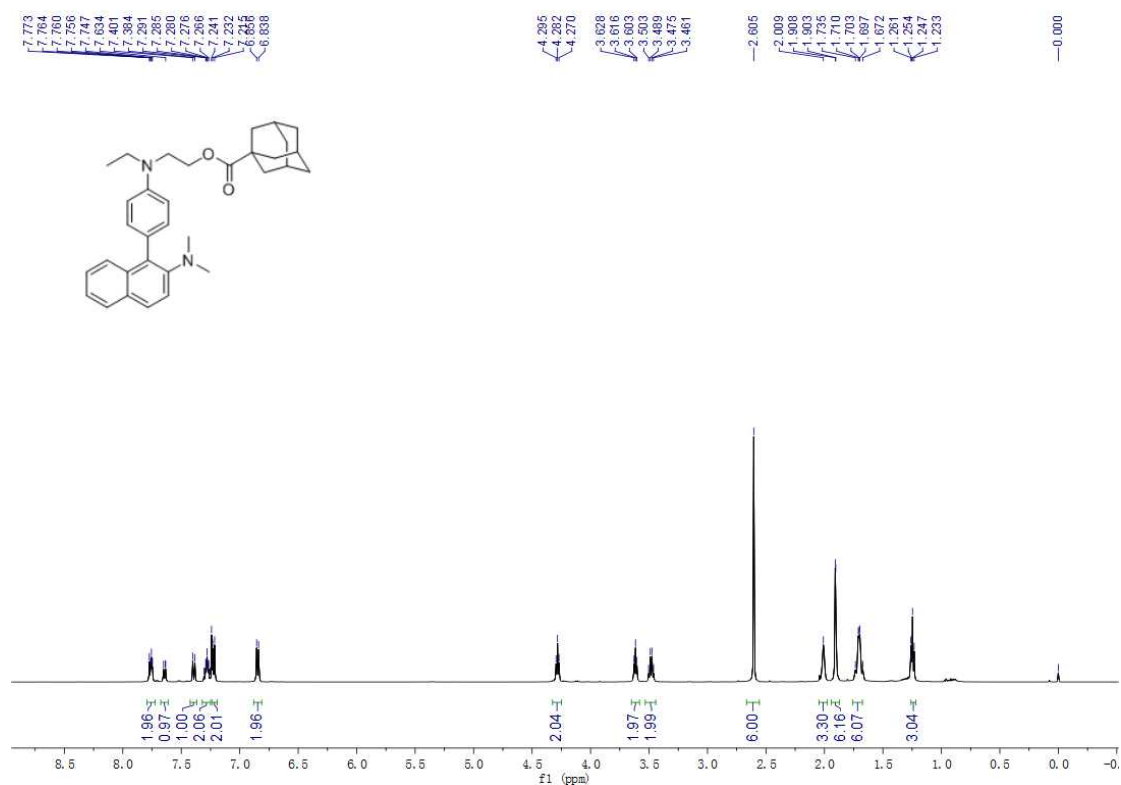
# **Methyl 6-(diethylamino)-5-(4-(diethylamino)phenyl)-2-naphthoate (3ja):**



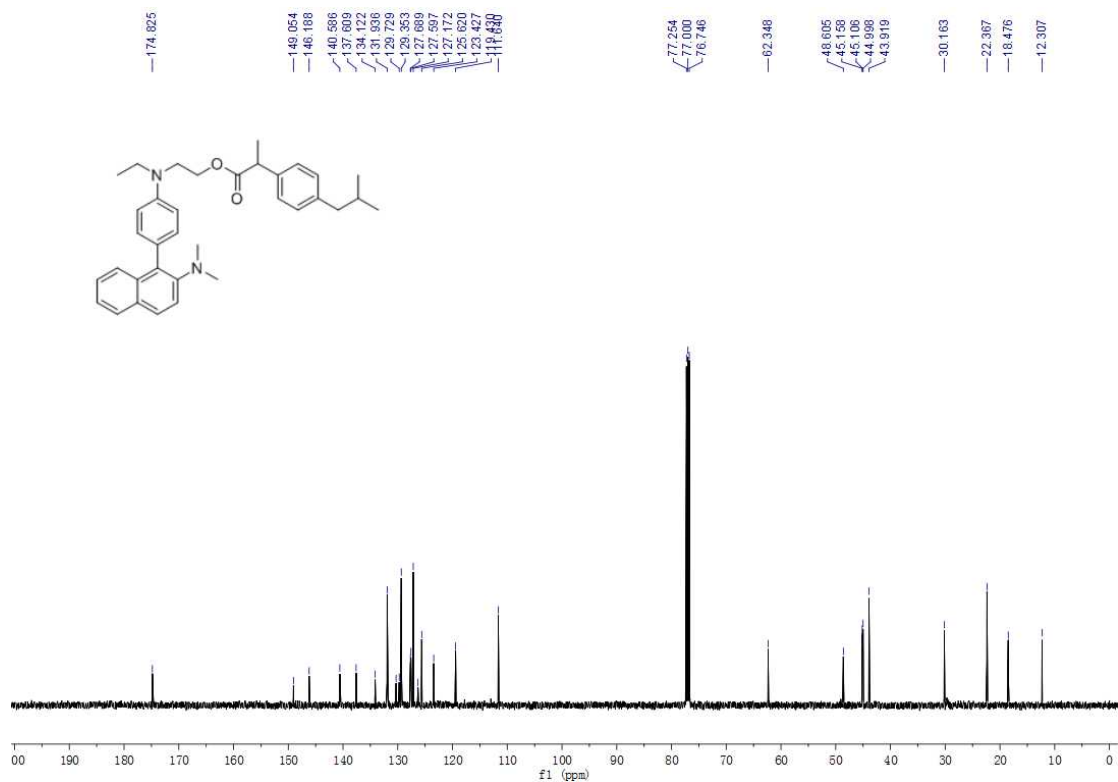
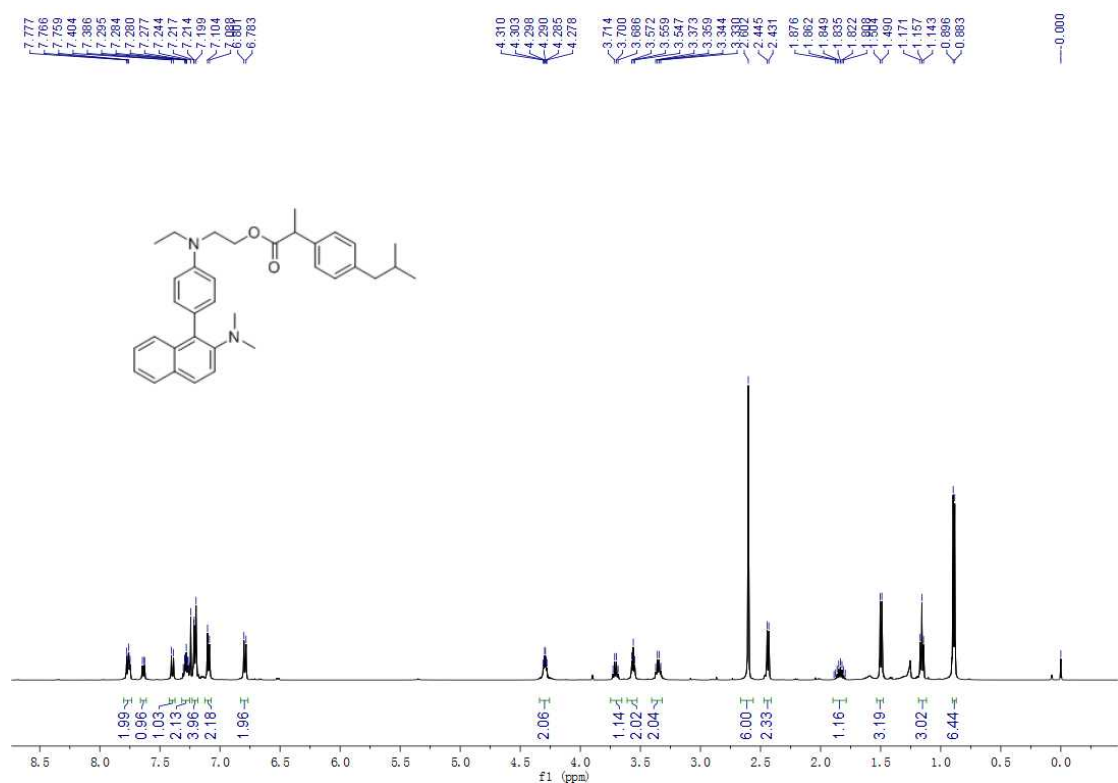
# 1-(4-(Dimethylamino)phenyl)-*N,N*-diethylantracen-2-amine (3ka):



**(3r,5r,7r)-2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethyl)amino)ethyl  
adamantane-1-carboxylate (3aw):**

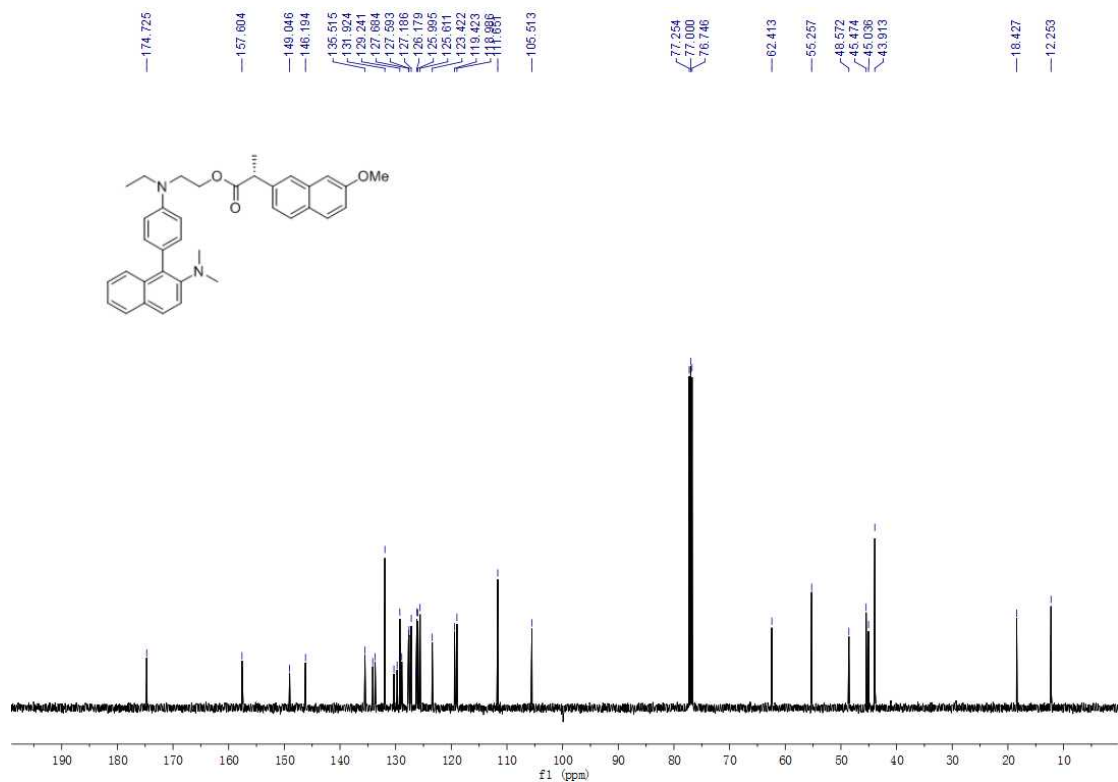
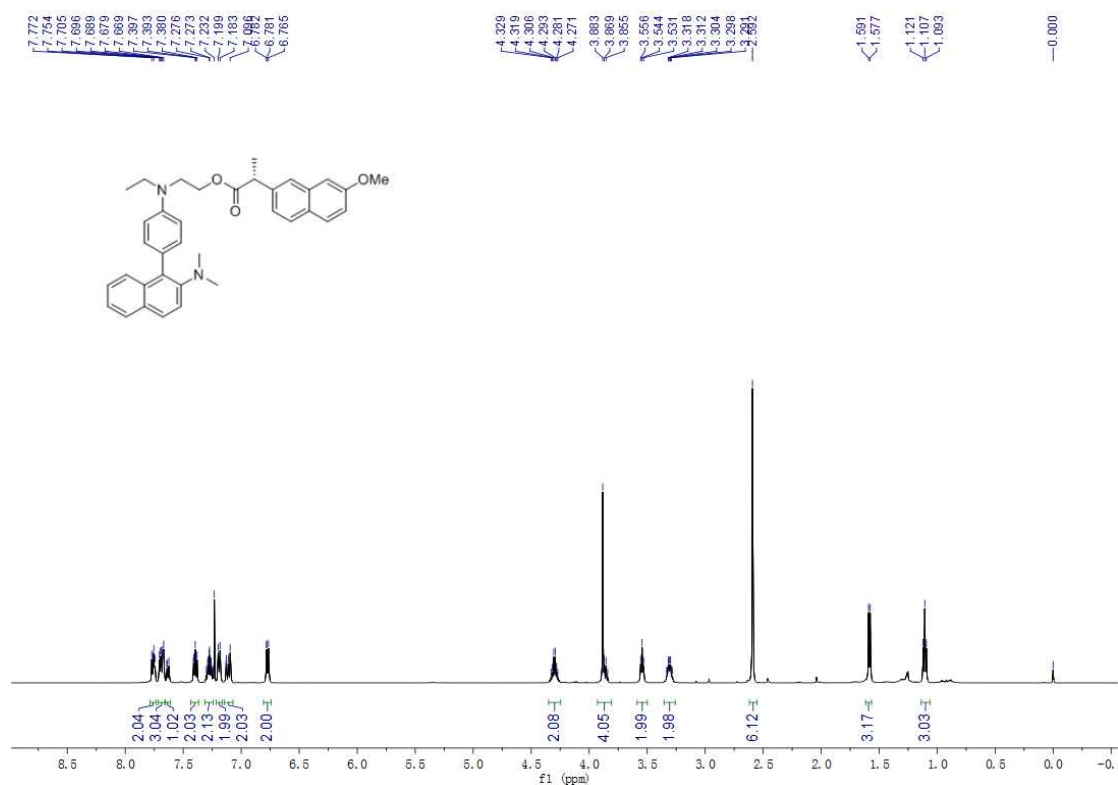


**2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethyl)amino)ethyl-2-(4-isobutylphenyl)propanoate (3ax):**

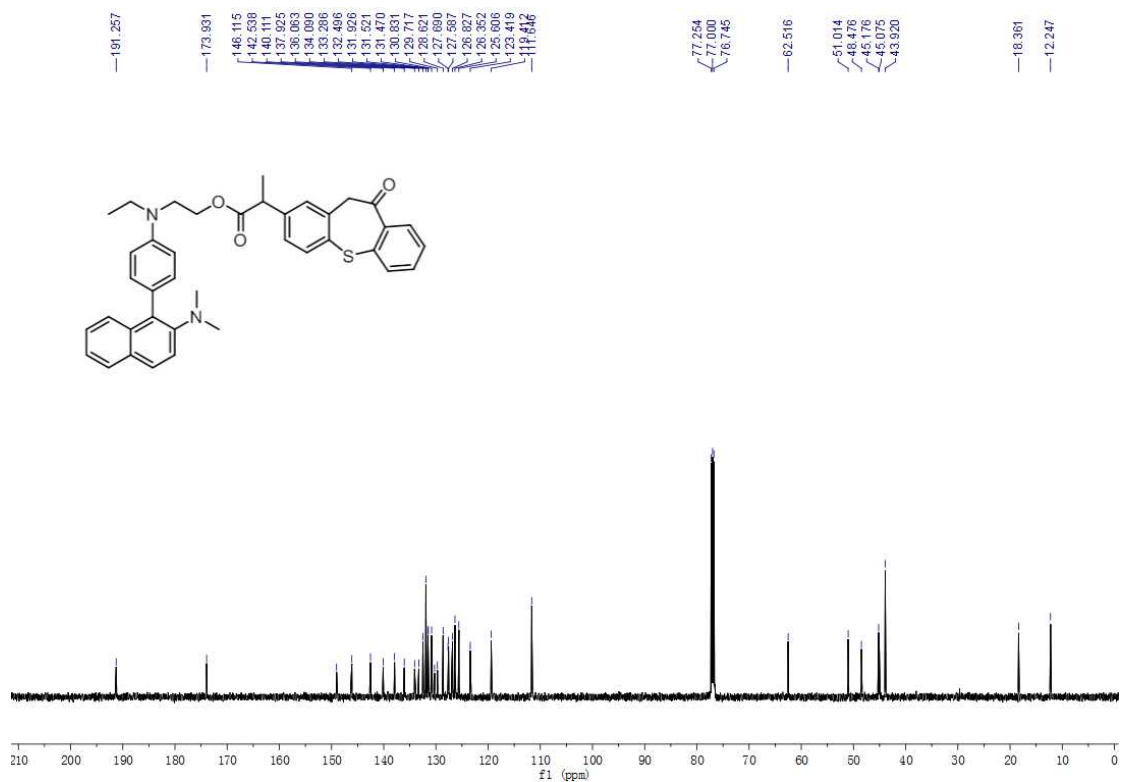
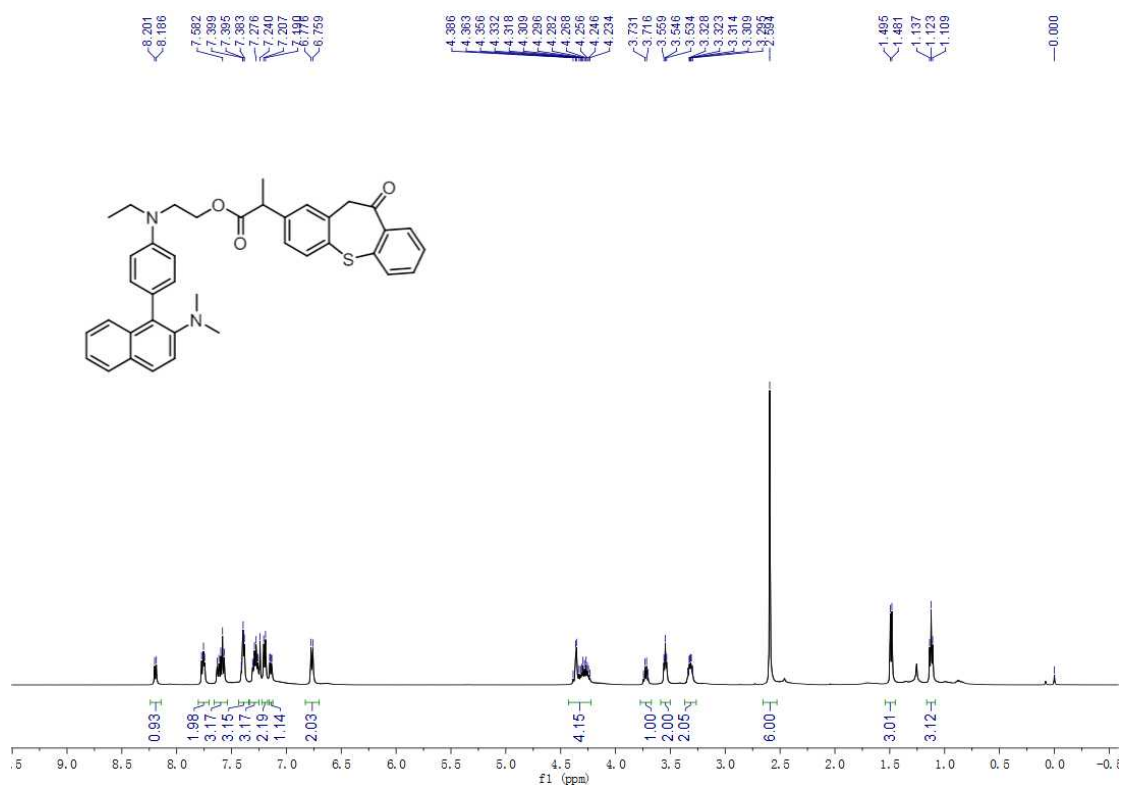


**(R)-2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethyl)amino)ethyl**

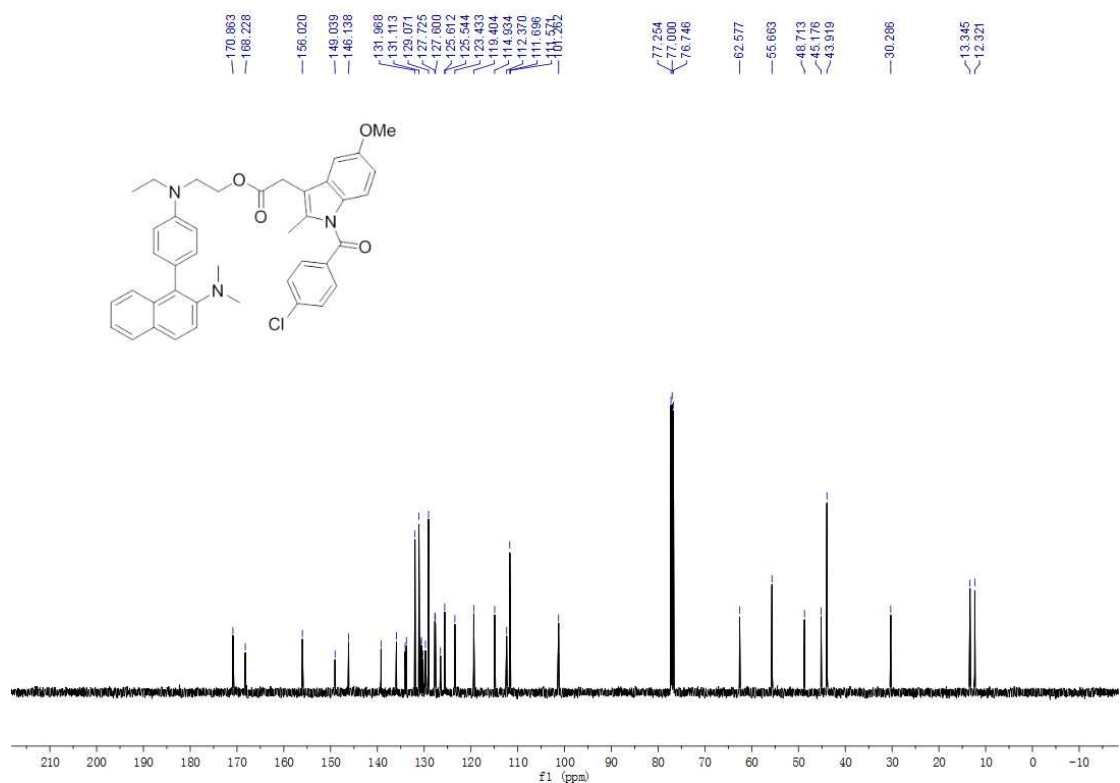
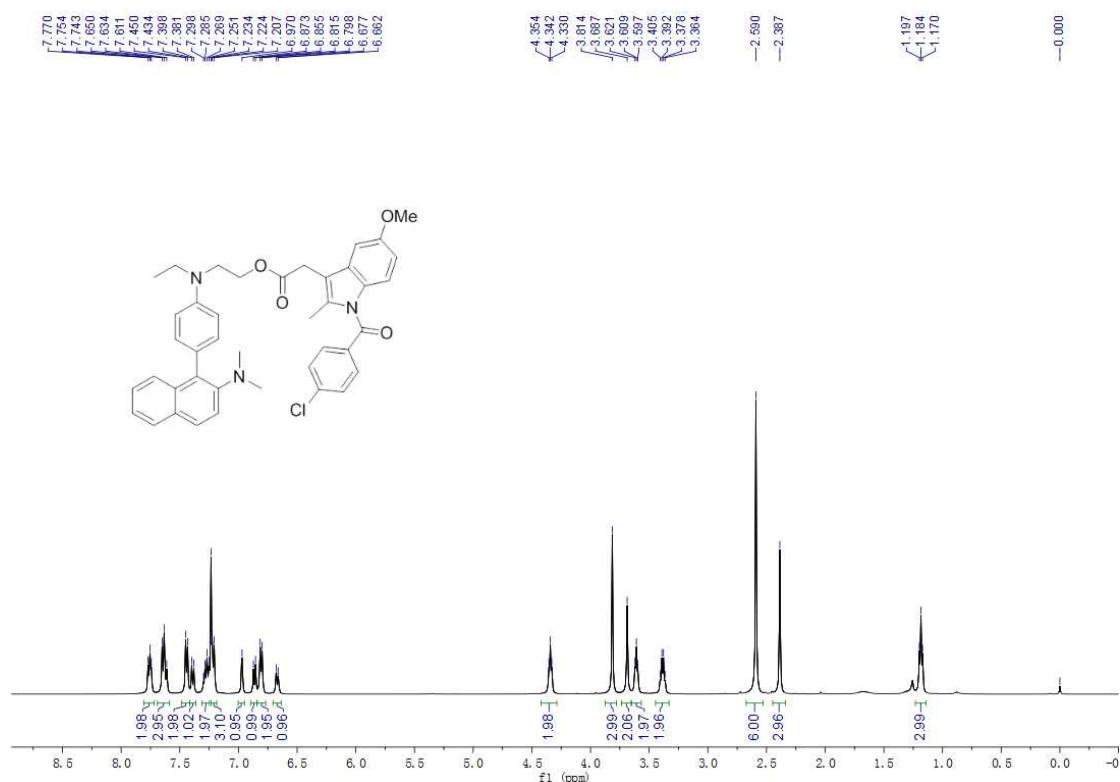
**2-(7-methoxynaphthalen-2-yl)propanoate (3ay):**



**0,11-dihydrodibenzo[*b,f*]thiepin-2-yl)propanoate (3az):**



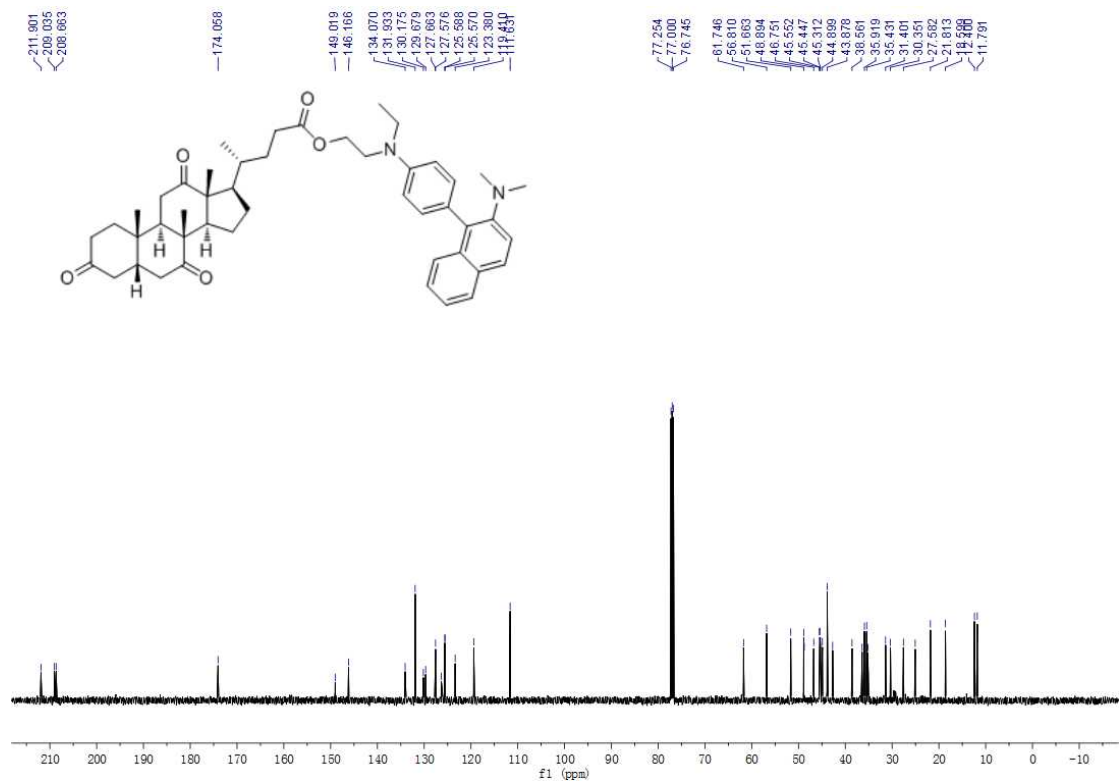
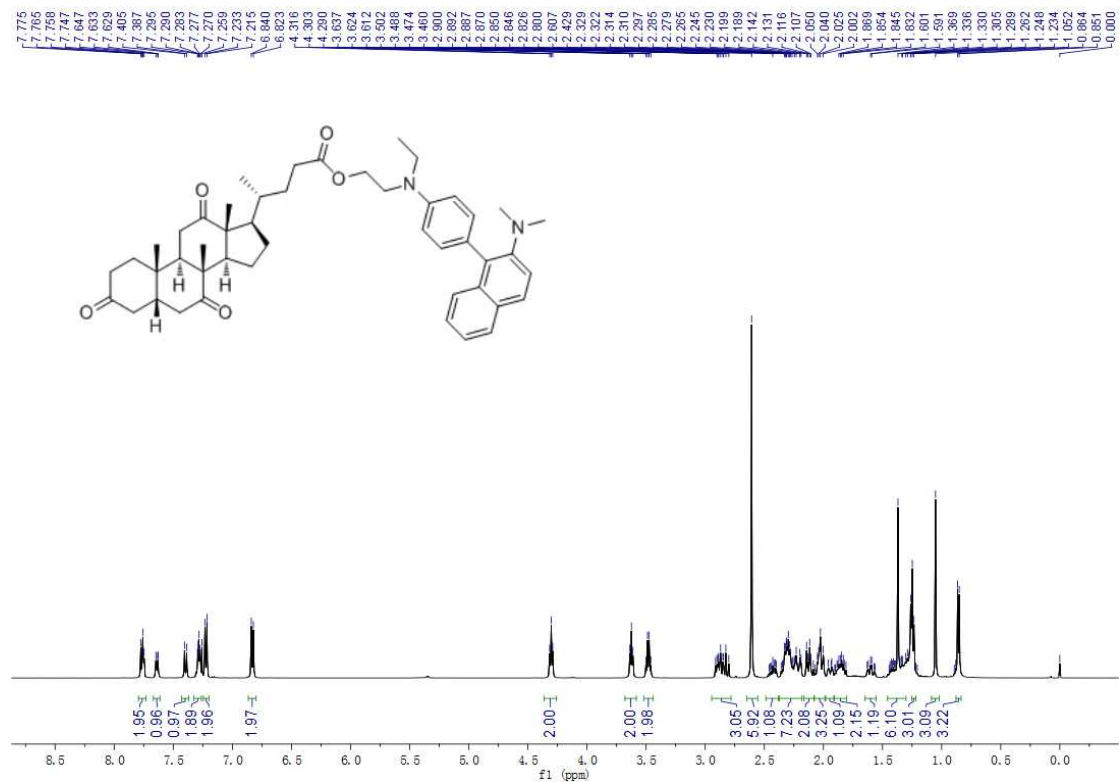
**2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethyl)amino)ethyl-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (3aaa):**



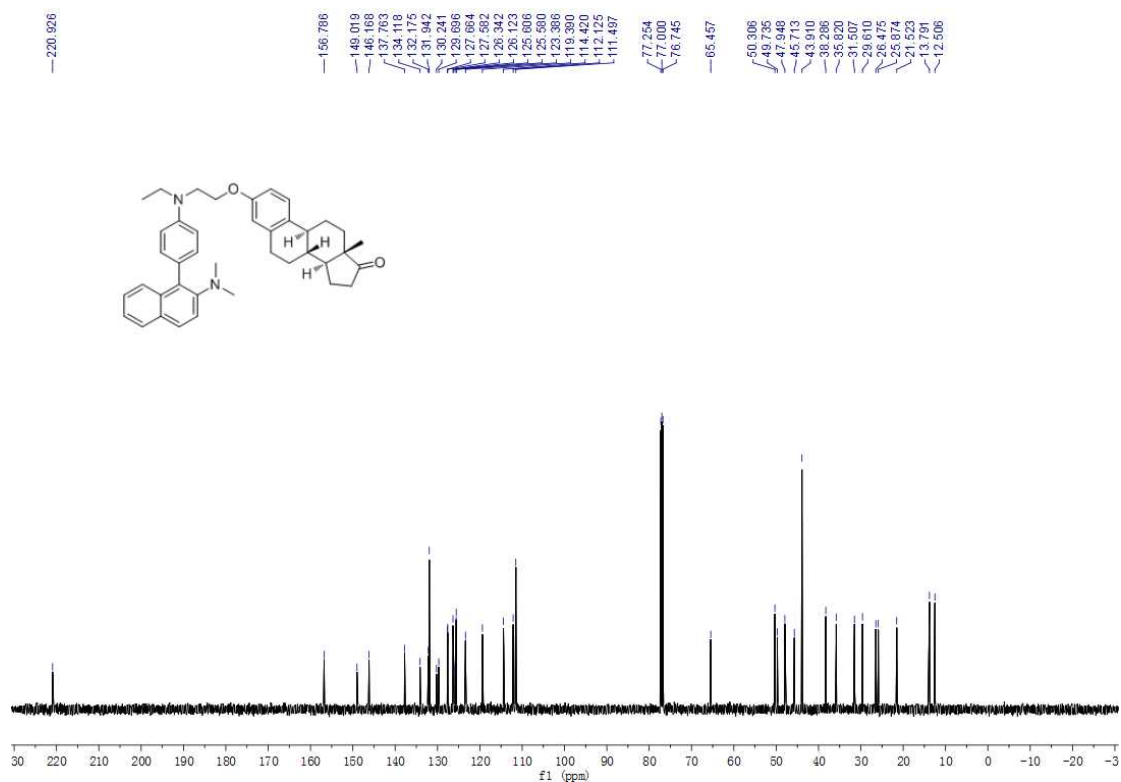
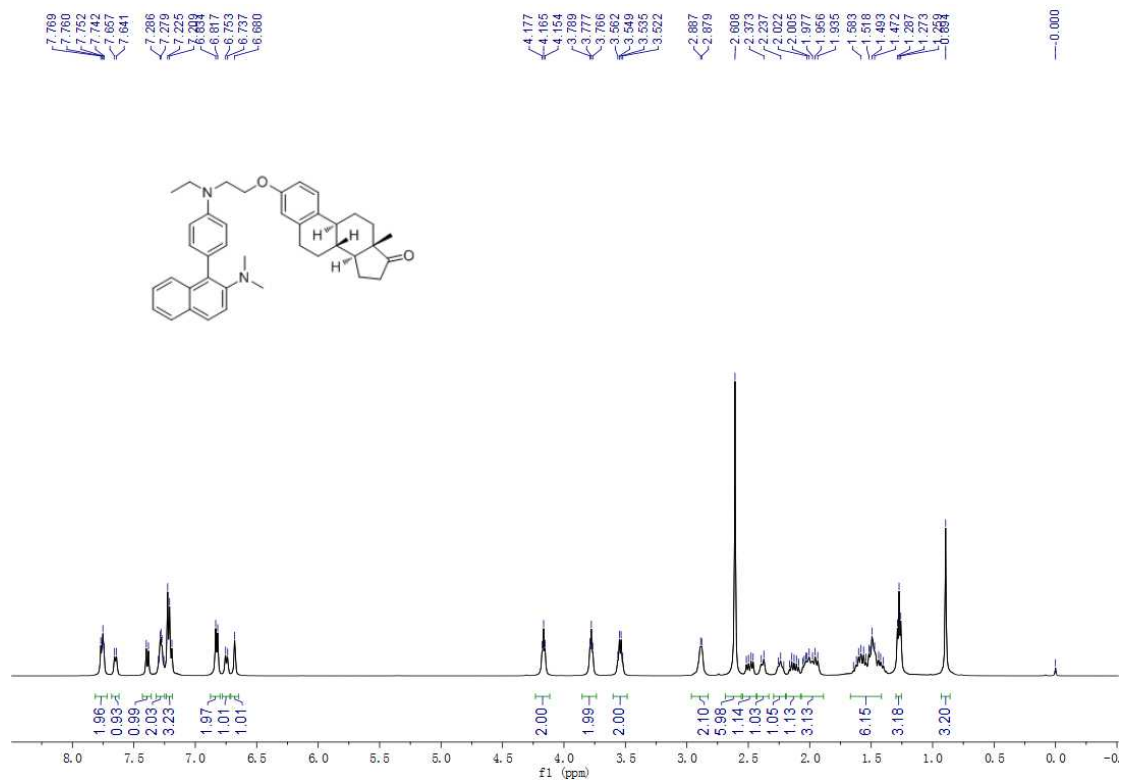
**(R)-2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethyl)amino)ethyl**

**4-((5S,8R,9R,10S,13R,14R,17R)-8,10,13-trimethyl-3,7,12-trioxohexadecahydro-1**

**H-cyclopenta[a]phenanthren-17-yl)pentanoate (3aab):**

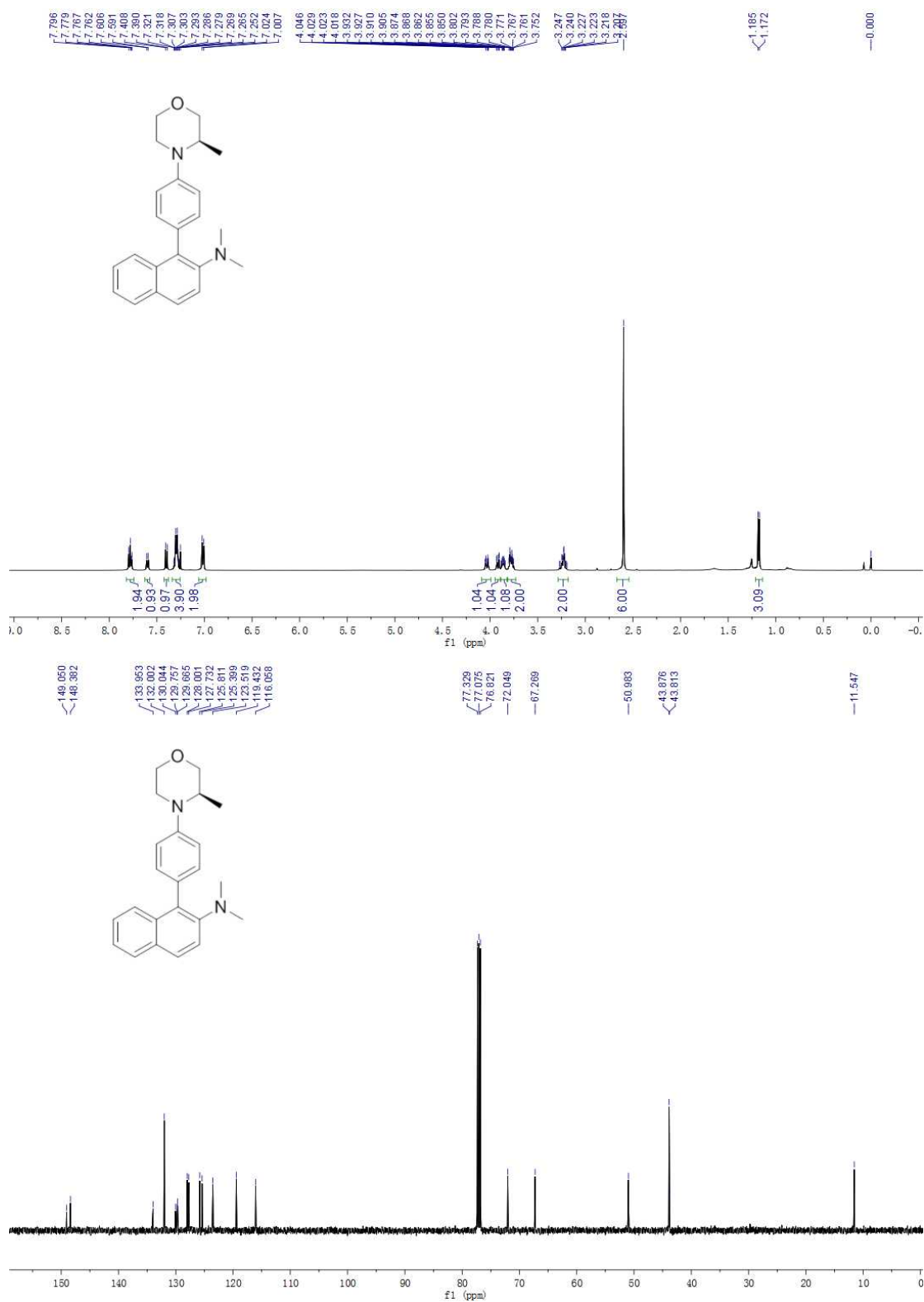


**(8R,9S,13S,14S)-3-(2-((4-(2-(Dimethylamino)naphthalen-1-yl)phenyl)(ethyl)amino)ethoxy)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (3aac):**

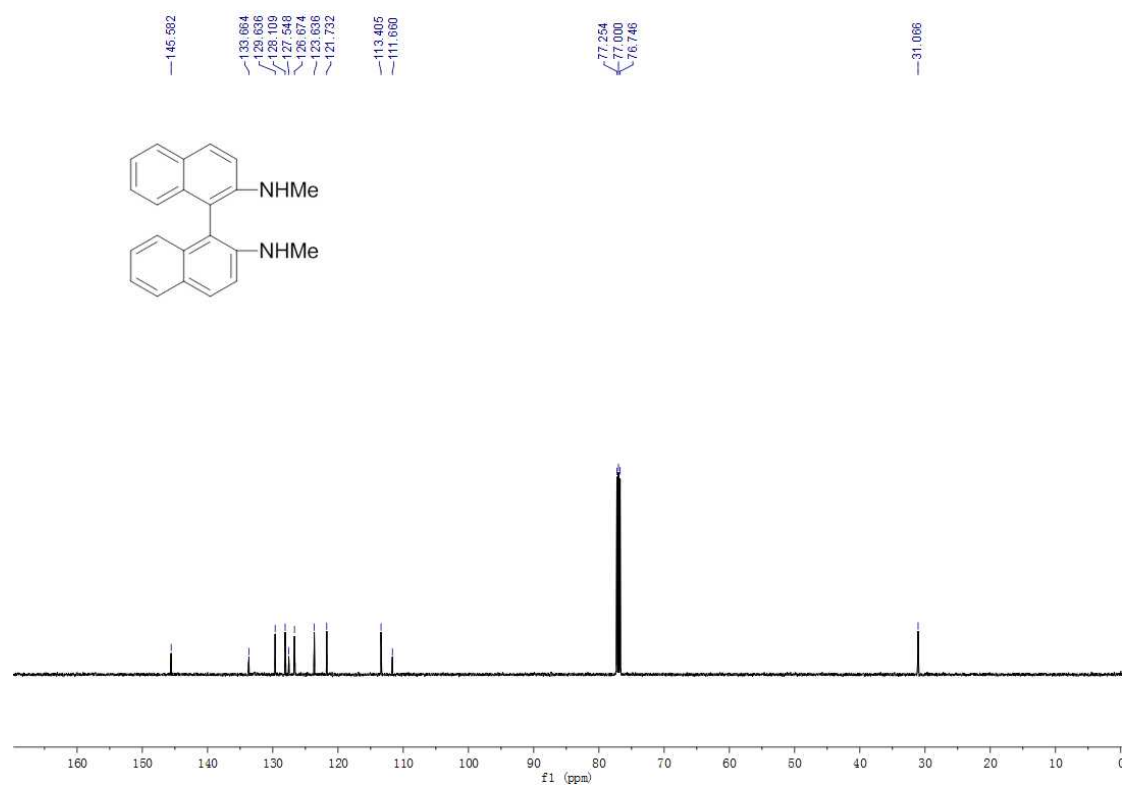
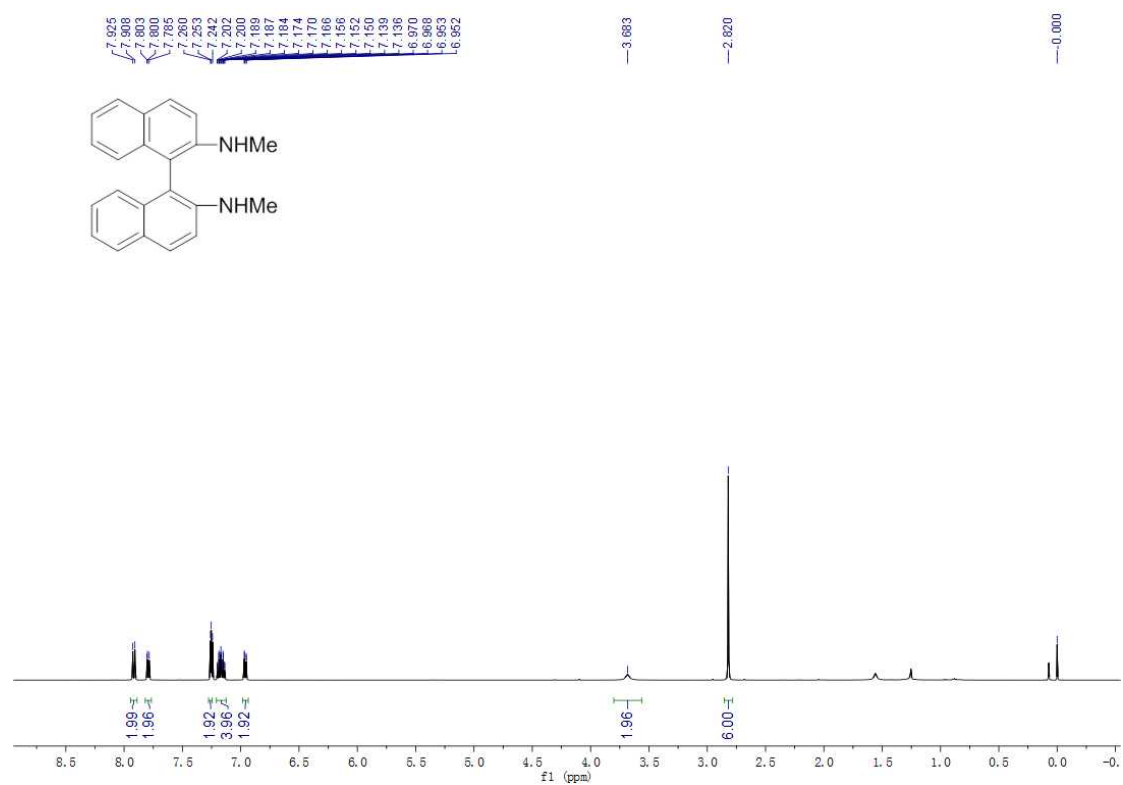


**(R)-N,N-Dimethyl-1-(4-(3-methylmorpholino)phenyl)naphthalen-2-amine**

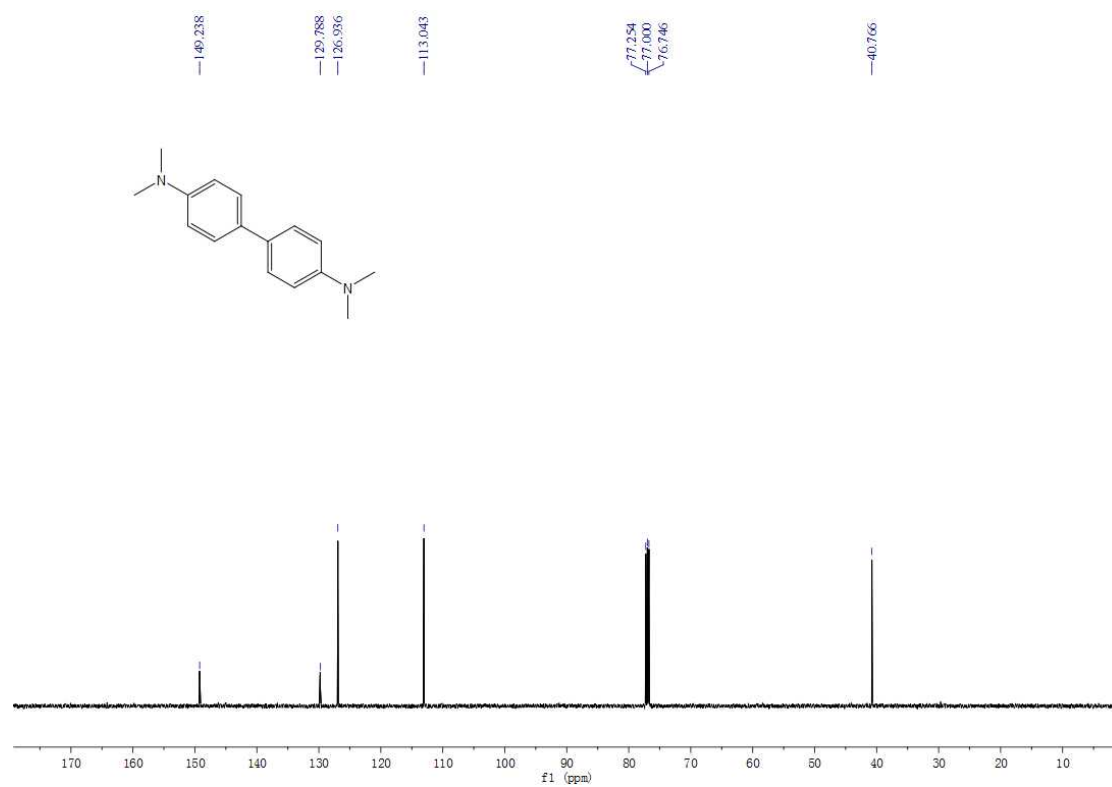
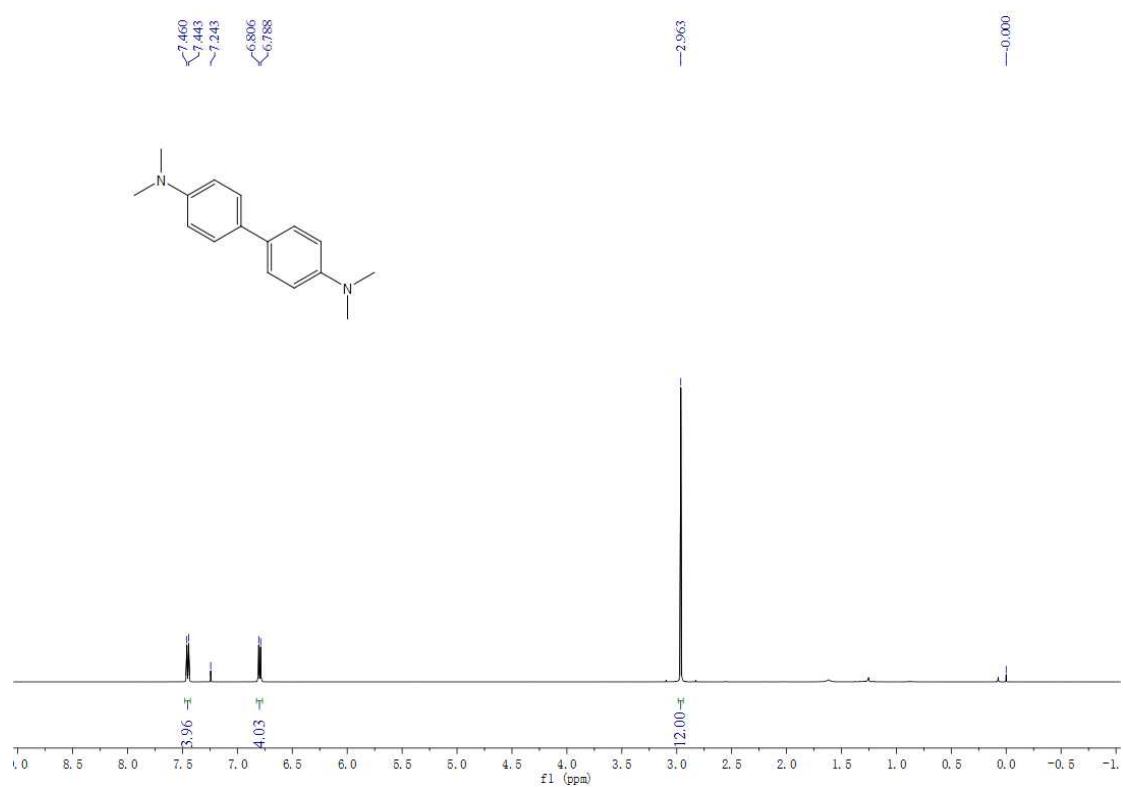
**(3aad):**



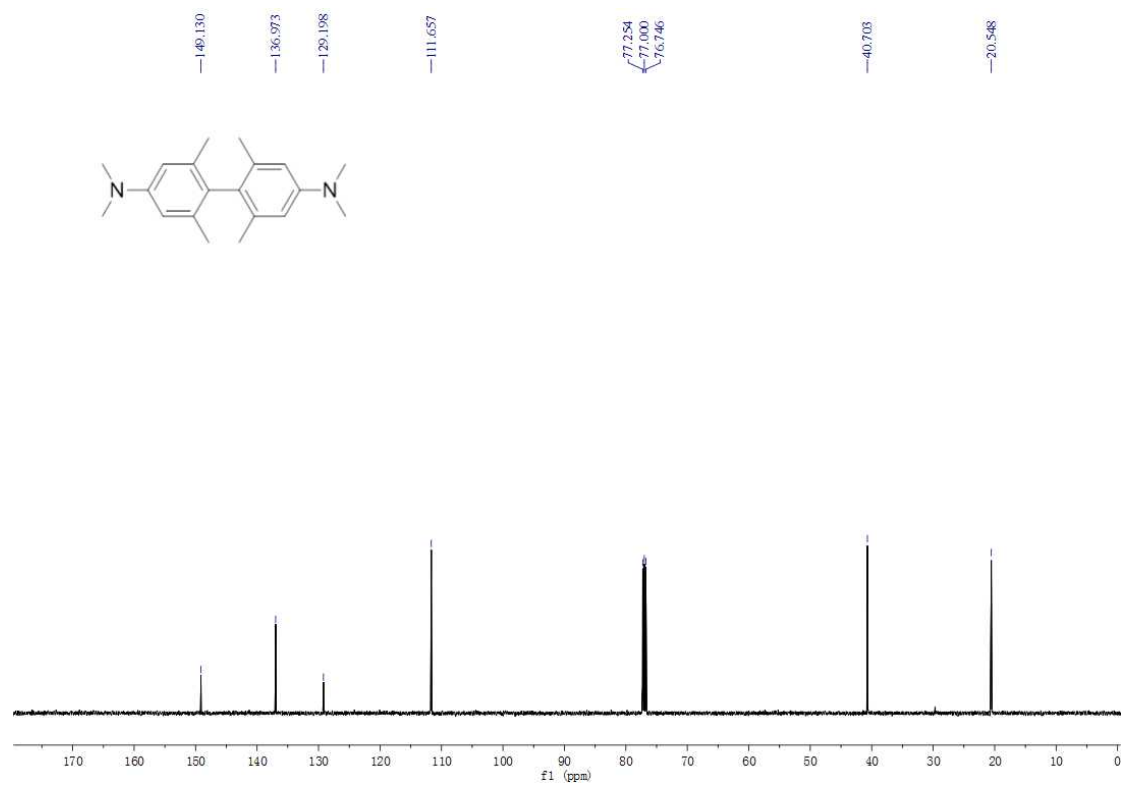
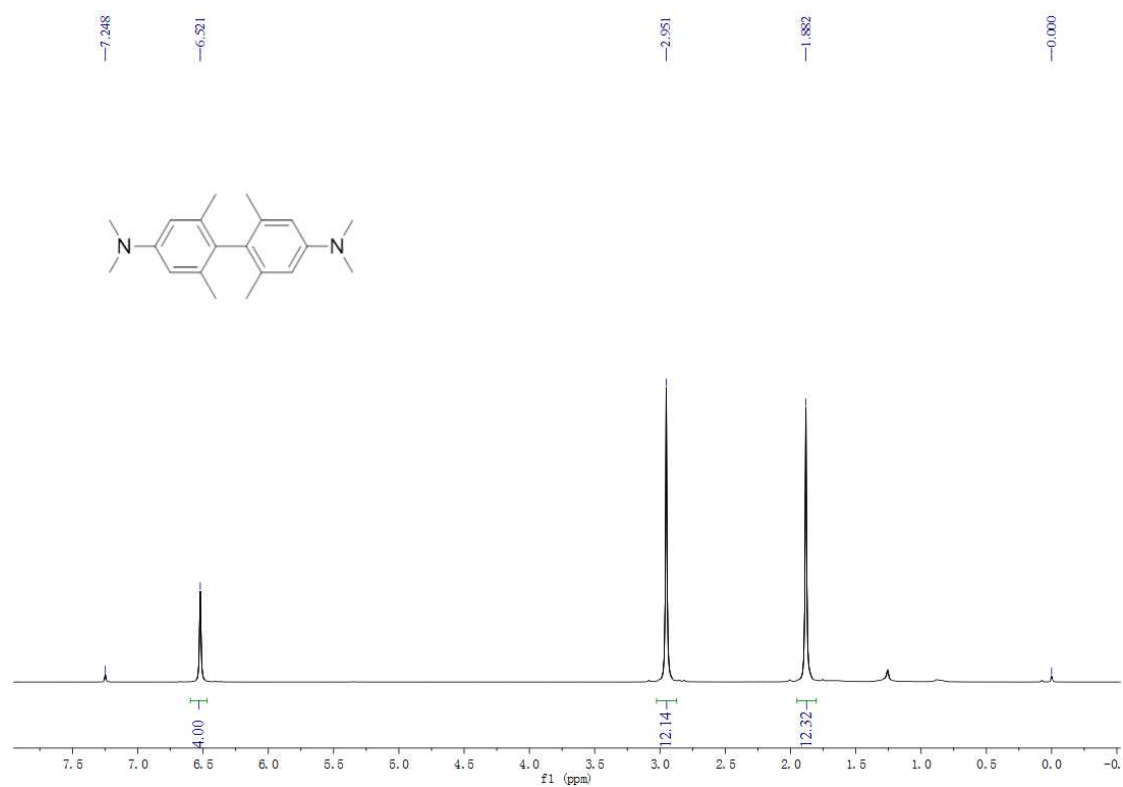
**$N,N'$ -Dimethyl-[1,1'-binaphthalene]-2,2'-diamine (4):**



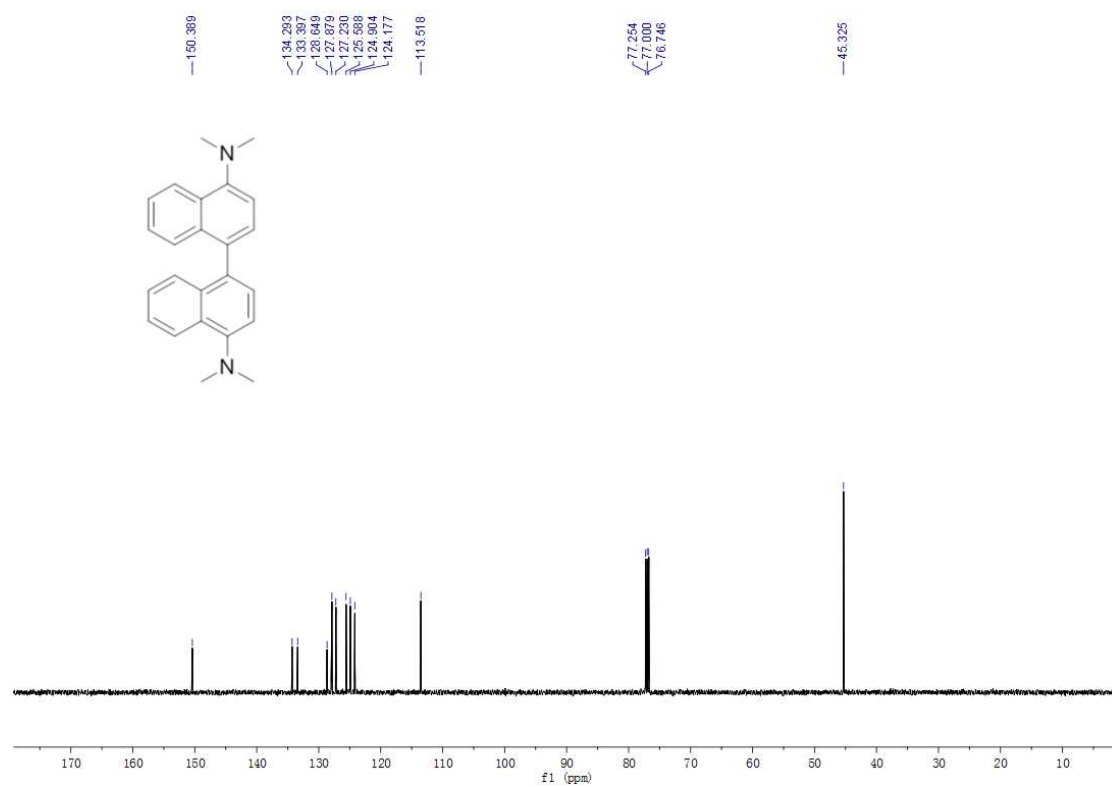
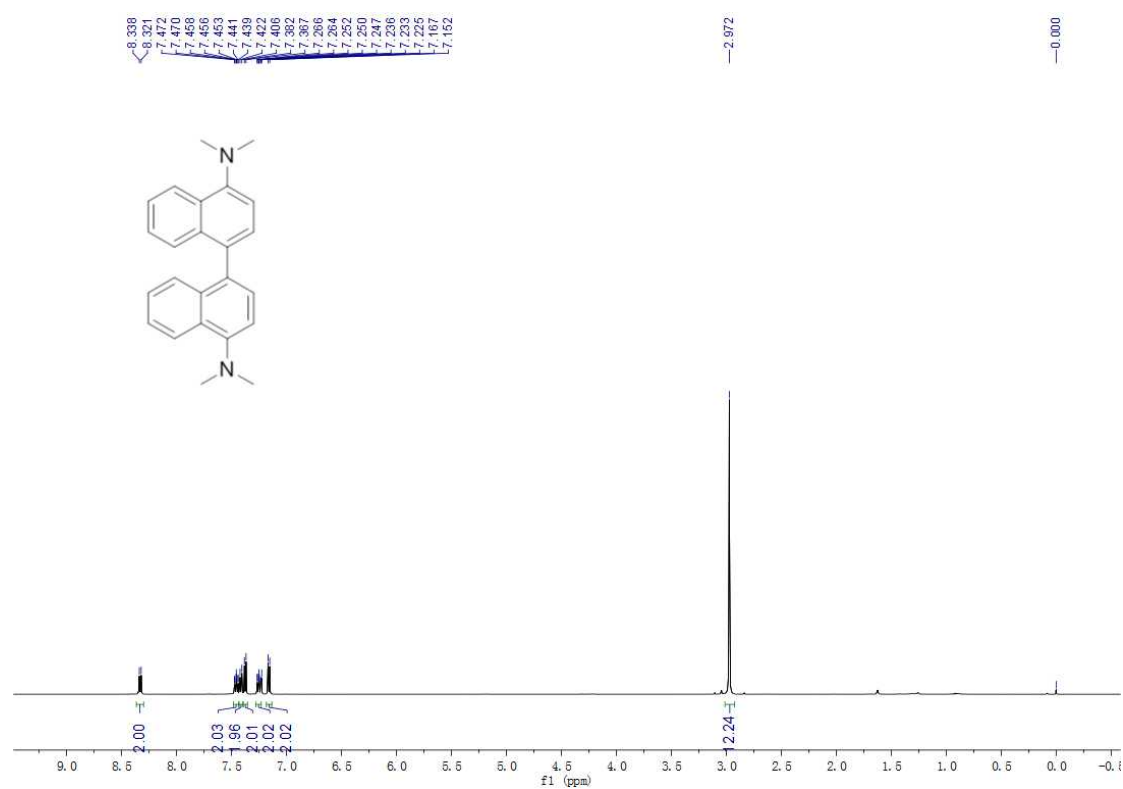
***N*<sup>4</sup>,*N*<sup>4</sup>,*N*<sup>4</sup>',*N*<sup>4</sup>'-Tetramethyl-[1,1'-biphenyl]-4,4'-diamine (5):**



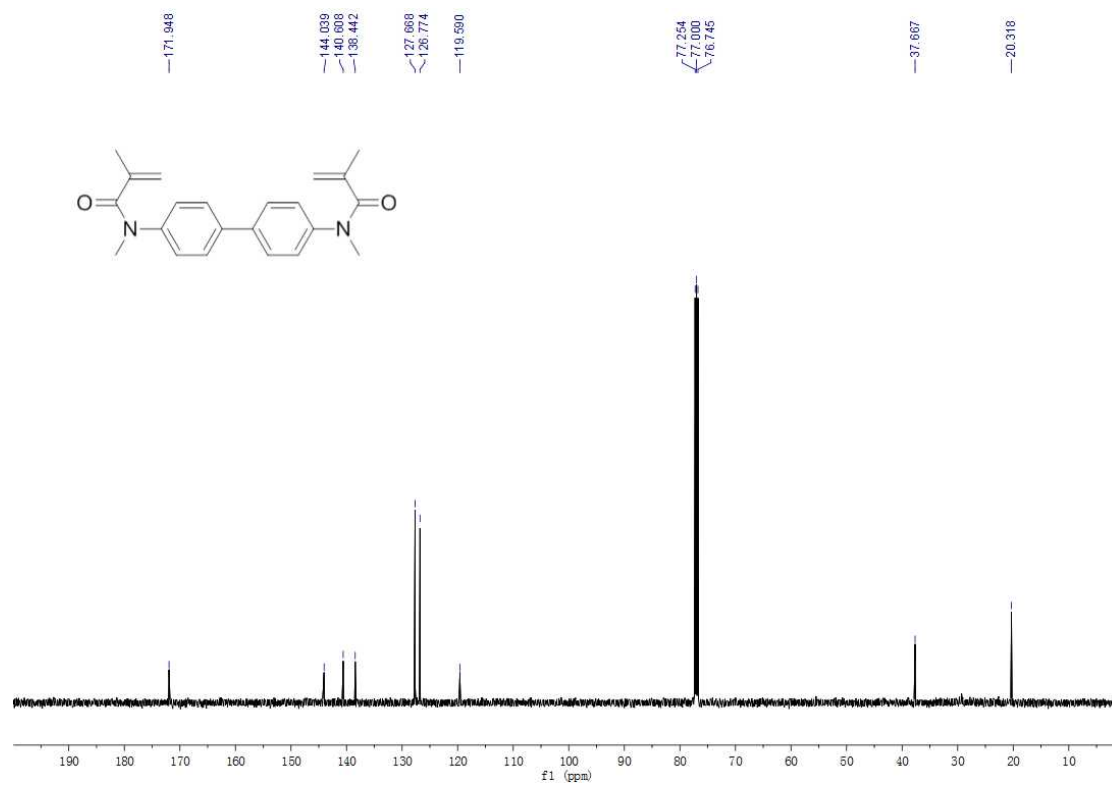
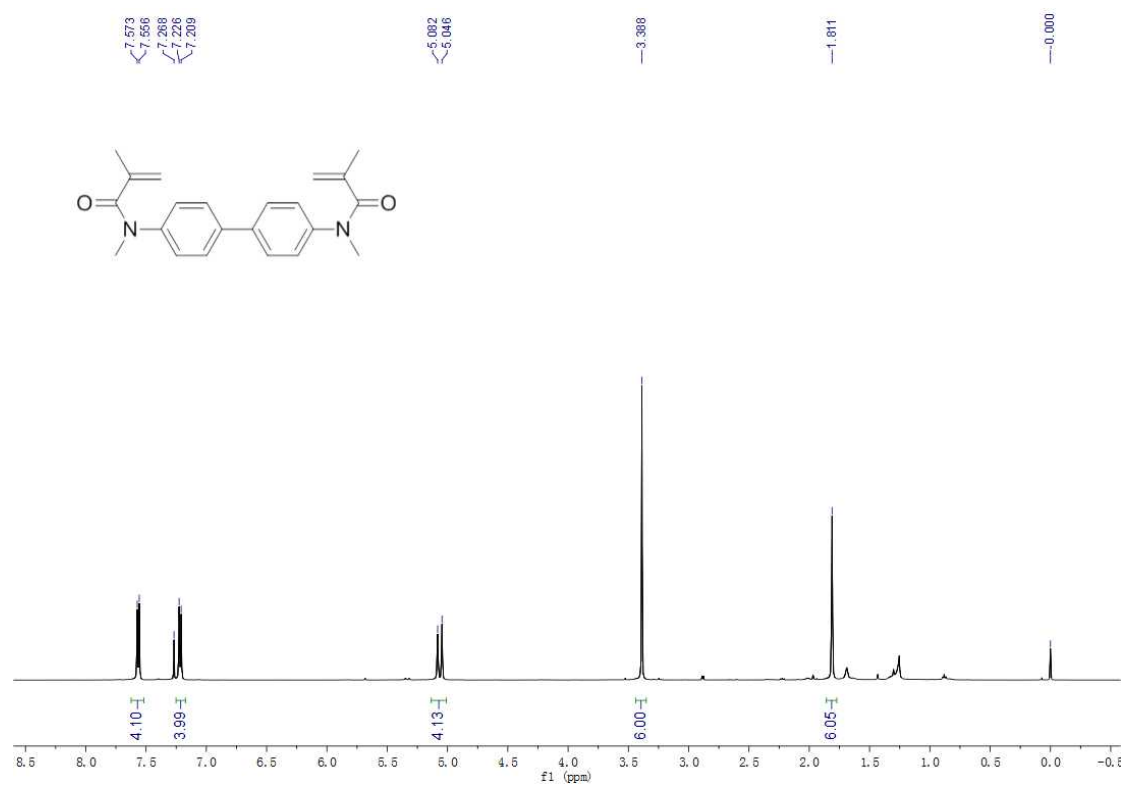
***N*<sup>4</sup>,*N*<sup>4</sup>,*N*<sup>4</sup>',*N*<sup>4</sup>',2,2',6,6'-octamethyl-[1,1'-biphenyl]-4,4'-diamine (6):**



***N*<sup>4</sup>,*N*<sup>4</sup>,*N*<sup>4'</sup>,*N*<sup>4'</sup>-Tetramethyl-[1,1'-binaphthalene]-4,4'-diamine (7):**



***N,N'*-([1,1'-Biphenyl]-4,4'-diyl)bis(*N*,2-dimethylacrylamide) (8):**



## (D) References

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