Aerobic oxidative synthesis of *o*-phenylenediamines from cyclohexanones

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Supporting Information

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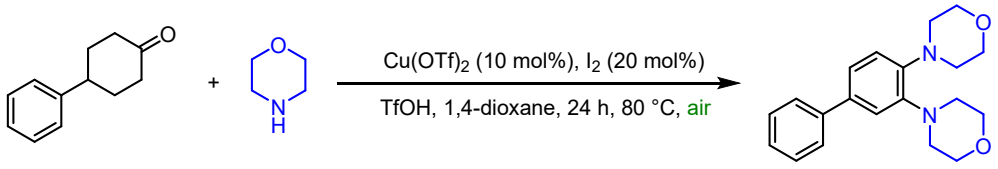
1. General remarks

All commercially available compounds were purchased from Sigma-Aldrich, J&K Chemicals, Bide Pharmatech, Shanghai Macklin Biochemical Technology Co., Ltd., etc. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Products were purified by flash chromatography on silica gel. ^{1}H-NMR spectra were recorded on Bruker AVANCE III-400 spectrometers. Chemical shifts (in ppm) were referenced with TMS in $CDCl_3$ (0 ppm). ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). High resolution mass spectra were obtained with a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer.

2. Condition Optimization

Table S1. Optimization details for effect of Bronsted acid on the transformation of oxidative aromatization [a]

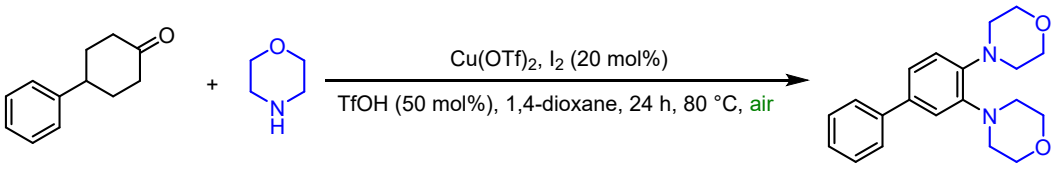


1a **2a**, 3.0 equiv. **3a**

Entry	Equiv. of TfOH	Yield (%)
1	0.2 mL	0
2	3	0
3	1	56
4	0.5	67
5	0.2	59

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 equiv.), **2a** (0.9 mmol, 3.0 equiv.), $Cu(OTf)_2$ (10 mol%), I_2 (20 mol%), TfOH, 1,4-dioxane (1.5 ml), under air, 80 °C, 24h. The yield was determined by ^1H NMR using 1,1,2,2-tetrachloroethane as the internal standard.

Table S2. Optimization details for effect of Lewis acid on the transformation of oxidative aromatization [a]



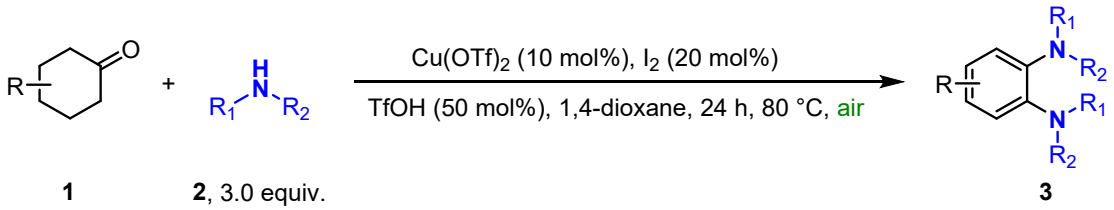
1a **2a**, 3.0 equiv. **3a**

Entry	Equiv. of $Cu(OTf)_2$	Yield (%)
1	0.5	67
2	0.2	68
3	0.1	67
4	0.05	52
5	0	37

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 equiv.), **2a** (0.9 mmol, 3.0 equiv.), $Cu(OTf)_2$, I_2 (20 mol%), TfOH (50 mol%), 1,4-dioxane (1.5 ml), under air, 80 °C, 24h. The yield was determined by ^1H NMR using 1,1,2,2-tetrachloroethane as the internal standard.

3. Experimental Procedure and Characterization Data of Products

3.1 Experimental Procedure

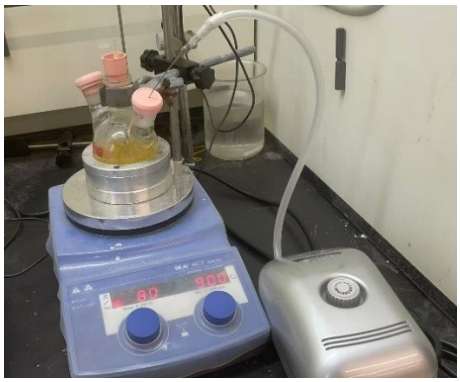


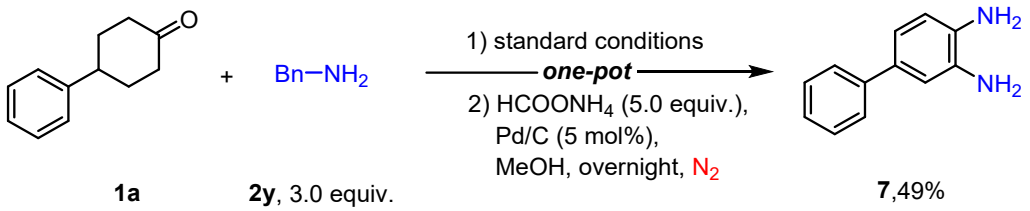
1 **2**, 3.0 equiv. **3**

General procedure A: Cyclohexanone **1** (0.5 mmol, 1 equiv.), copper(II) trifluoromethanesulfonate (18.1 mg, 0.05 mmol, 10 mol%), iodine (25.4 mg, 0.1 mmol, 20 mol%), trifluoromethanesulfonic acid (37.5 mg, 22 µl, 0.25 mmol, 50 mol%) were dissolved in 2.5 mL of 1,4-dioxane in a Schlenk tube equipped with a magnetic stir bar. After the solvent was heated to 80 ºC, amine **2** (1.5 mmol, 3.0 equiv.) was added respectively with syringe. The mixture was stirred at 80 ºC under air for 24 hours. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by chromatography on silica gel to afford the *o*-phenylenediamine.

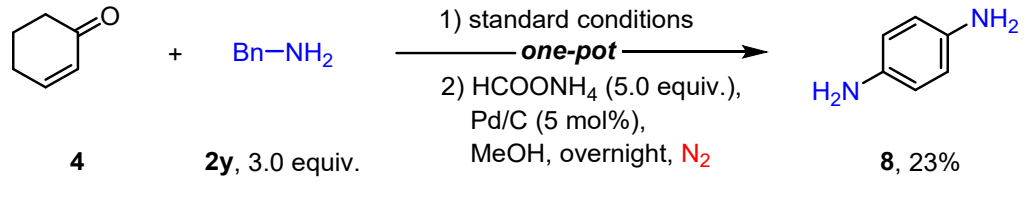
Procedure B: 4-phenylcyclohexanone **1a** (1.74 g, 10 mmol, 1 equiv.), copper(II) trifluoromethanesulfonate (180.9 mg, 1.0 mmol, 10 mol%), iodine (507.6 mg, 2.0 mmol, 20 mol%), trifluoromethanesulfonic acid (750.5 mg, 442 µL, 5.0 mmol, 50 mol%) were dissolved in 50 mL of 1,4-dioxane in a three-neck flask equipped with a magnetic stir bar and a gas pump. After the solvent was heated to 80 ºC, morpholine **2a** (2.61 g, 2.62 mL, 1.5 mmol, 3.0 equiv.) was added respectively with syringe. The mixture was stirred at 80 ºC with continuously air bubbling for 24 hours. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by chromatography on silica gel to afford the 4,4'-([1,1'-biphenyl]-3,4-diyl)dimorpholine (**3a**).

Figure S1. Apparatus for large-scale preparation experiments.





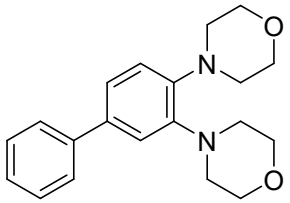
Procedure C: 4-Phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1 equiv.), iodine (25.4 mg, 0.1 mmol, 20 mol%), trifluoromethanesulfonic acid (37.5 mg, 22 µl, 0.25 mmol, 50 mol%) were dissolved in 2.5 mL of 1,4-dioxane in a Schlenk tube. After the solvent was heated to 80 ºC, benzylamine **2y** (164 µl, 1.5 mmol, 3.0 equiv.) was added respectively with syringe. The mixture was stirred at 80 ºC under air for 12 hours. After cooling to room temperature, the solution was directly concentrated under vacuum to evaporate all the solvent. Ammonium formate (157.6 mg, 2.5 mmol, 5.0 equiv.) and 10% Pd/C (26.6 mg, 0.025 mmol, 5 mol%) were added to the same Schlenk tube, then the tube was evacuated and backfilled with N_2 for 3 times. Methanol (2.5 mL) was added with syringe under N_2. The mixture was stirred at reflux temperature under N_2 overnight. After completion of the reaction, the catalyst was removed by filtration through a celite pad, which was then washed with 5 ml of methanol. The combined organic filtrate was concentrated under vacuum and purified by column chromatography on silica gel to afford the [1,1'-biphenyl]-3,4-diamine.[1]



Procedure D: Cyclohex-2-en-1-one **4** (48.1 mg, 0.5 mmol, 1 equiv.), iodine (25.4 mg, 0.1 mmol, 20 mol%), trifluoromethanesulfonic acid (37.5 mg, 22 µl, 0.25 mmol, 50 mol%) were dissolved in 2.5 mL of 1,4-dioxane in a Schlenk tube. After the solvent was heated to 80 ºC, benzylamine **2y** (164 µl, 1.5 mmol, 3.0 equiv.) was added respectively with syringe. The mixture was stirred at 80 ºC under air for 12 hours. After cooling to room temperature, the solution was directly concentrated under vacuum to evaporate all the solvent. Ammonium formate (157.6 mg, 2.5 mmol, 5.0 equiv.)

and 10% Pd/C (26.6 mg, 0.025 mmol, 5 mol%) were added to the same Schlenk tube, then the tube was evacuated and backfilled with N_2 for 3 times. Methanol (2.5 mL) was added with syringe under N_2. The mixture was stirred at reflux temperature under N_2 overnight. After completion of the reaction, the catalyst was removed by filtration through a celite pad, which was then washed with 5 ml of methanol. The combined organic filtrate was concentrated under vacuum and purified by column chromatography on silica gel to afford the *p*-phenylenediamine.

3.2 Characterization Data of Products



3a

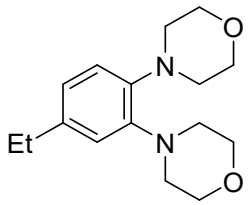
4,4'-([1,1'-biphenyl]-3,4-diyl)dimorpholine (3a): Following the general procedure A, the reaction was performed with 4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3a** as a white solid (108.1 mg, 67%).

Following the procedure B, the reaction was performed with 4-phenylcyclohexanone **1a** (1.74 g, 10.0 mmol, 1.0 equiv.), $Cu(OTf)_2$ (180.9 mg , 1.0 mmol, 10 mol%), I_2 (507.6 mg, 2.0 mmol, 20 mol%), TfOH (750.5 mg, 442 μL, 5.0 mmol, 50 mol%), and morpholine **2a** (2.61 g, 2.62 mL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (50 mL) at 80 °C with continuously air bubbling for 24 hours. The mixture was purified by column chromatography to obtain **3a** as a white solid (2.07 g, 64%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 3.89 (t, *J* = 4.6 Hz, 8H), 3.27 (d, *J* = 4.6 Hz, 8H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 144.61, 143.73, 141.12, 136.17, 128.71, 126.87, 121.75, 118.74, 117.45, 67.55, 50.08, 50.05.

HRMS (ESI) m/z calcd. for $C_{20}H_{25}N_2O_2^+$ $(M+H)^+$: 325.1911, found: 325.1910



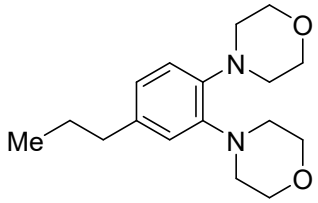
3b

4,4'-(4-ethyl-1,2-phenylene)dimorpholine (3b): Following the general procedure A, the reaction was performed with 4-ethylcyclohexanone **1b** (63.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3b** as a white solid (90.1 mg, 65%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 6.85 (br-s, 2H), 6.75 (s, 1H), 3.83 (s, 8H), 3.20 (s, 4H), 3.15 (s, 4H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 144.51, 142.35, 139.29, 122.25, 118.46, 118.24, 67.74, 50.36, 50.24, 28.52, 15.76.

HRMS (ESI) m/z calcd. for $C_{16}H_{25}N_2O_2^+$ $(M+H)^+$: 277.1911, found: 277.1909



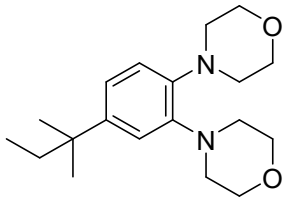
3c

4,4'-(4-propyl-1,2-phenylene)dimorpholine (3c): Following the general procedure A, the reaction was performed with 4-propylcyclohexanone **1c** (70.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3c** as a white solid (88.6 mg, 61%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 6.83 (br-s, 2H), 6.73 (s, 1H), 3.83 (d, *J* = 4.2 Hz, 8H), 3.26 – 3.11 (m, 8H), 2.52 (t, *J* = 7.9 Hz, 2H), 1.75 – 1.47 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 144.40, 142.33, 137.80, 122.91, 118.76, 118.33, 67.74, 50.36, 50.25, 37.82, 24.82, 14.14.

HRMS (ESI) m/z calcd. for $C_{17}H_{27}N_2O_2^+$ $(M+H)^+$: 291.2067, found: 291.2060



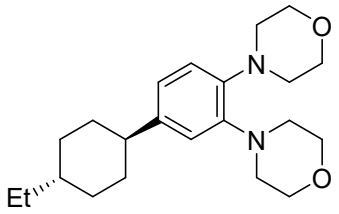
3d

4,4'-(4-(tert-pentyl)-1,2-phenylene)dimorpholine (3d): Following the general procedure A, the reaction was performed with 4-tert-pentylcyclohexanone **1d** (77.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3d** as a white solid (111.8 mg, 70%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 6.96 – 6.94 (m, 1H), 6.88 – 6.84 (m, 2H), 3.84 (s, 8H), 3.19 (s, 8H), 1.61 (q, *J* = 7.6 Hz, 2H), 1.26 (s, 6H), 0.70 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 144.43, 143.88, 141.86, 120.57, 117.74, 116.28, 67.73, 50.24, 37.71, 37.01, 28.55, 9.33.

HRMS (ESI) m/z calcd. for $C_{19}H_{31}N_2O_2^+$ $(M+H)^+$:319.2380, found: 319.2377



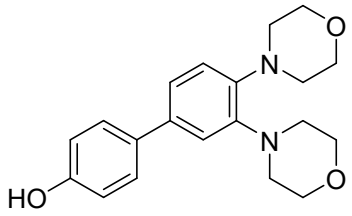
3e

4,4'-(4-((1r,4r)-4-ethylcyclohexyl)-1,2-phenylene)dimorpholine (3e): Following the general procedure A, the reaction was performed with 4-((1r,4r)-4-ethylcyclohexyl)-cyclohexanone **1e** (104.3 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3e** as a white solid (118.3 mg, 66%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 6.85 (br-s, 2H), 6.76 (s, 1H), 3.84 – 3.80 (m, 8H), 3121 – 3.11(m, 8H), 2.45 – 2.31 (m, 1H), 1.93 – 1.83 (m, 4H), 1.48 – 1.37 (m, 2H), 1.30 – 1.16 (m, 3H), 1.08 – 0.98 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 144.36, 142.97, 142.37, 121.03, 118.31, 117.31, 67.74, 50.32, 50.25, 44.33, 39.23, 34.56, 33.35, 30.13, 11.69.

HRMS (ESI) m/z calcd. for $C_{22}H_{35}N_2O_2^+$ $(M+H)^+$: 359.2693, found: 359.2695



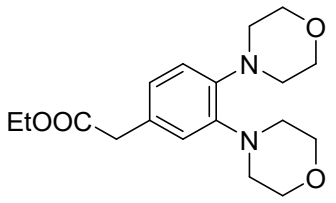
3f

3',4'-dimorpholino-[1,1'-biphenyl]-4-ol (3f): Following the general procedure A, the reaction was performed with 4-(4-hydroxyphenyl)cyclohexan-1-one **1f** (95.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3f** as a white solid (86.8 mg, 51%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.10 (s, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.95 – 5.20 (br-s, 1H), 3.89 (br-s, 8H), 3.26 (br-s, 8H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 155.02, 144.60, 143.24, 135.90, 133.76, 128.08, 121.32, 118.77, 117.07, 115.63, 67.58, 50.11.

HRMS (ESI) m/z calcd. for $C_{20}H_{25}N_2O_3^+$ $(M+H)^+$: 340.1860, found: 340.1864



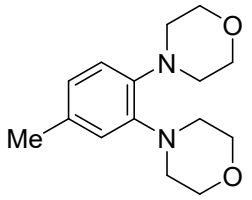
3g

Ethyl 2-(3,4-dimorpholinophenyl)acetate (3g): Following the general procedure A, the reaction was performed with ethyl 2-(4-oxocyclohexyl)acetate **1g** (92.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3g** as a white solid (103.5 mg, 62%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 6.91 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.83 (s, 1H), 4.15 (q, *J* = 7.6 Hz, 2H), 3.82 (s, 8H), 3.54 (s, 2H), 3.17 (s, 8H), 1.26 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 171.98, 144.50, 143.44, 128.94, 123.89, 119.53, 118.58, 67.63, 60.91, 50.13, 50.08, 40.99, 14.34.

HRMS (ESI) m/z calcd. for $C_{18}H_{27}N_2O_4^+$ $(M+H)^+$: 335.1965, found: 335.1960



3h

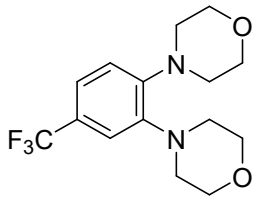
4,4'-(4-methyl-1,2-phenylene)dimorpholine (3h): Following the general procedure A, the reaction was performed with 4-methylcyclohexanone **1h** (56.0 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3h** as a white solid (78.8 mg, 60%).

Following the general procedure A, the reaction was performed with 3-methylcyclohexanone **1h'** (56.0 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3h** as a white solid (68.1 mg, 52%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 6.82 (br-s, 2H), 6.73 (s, 1H), 3.83 (br-s, 8H), 3.21 – 3.11 (m, 8H), 2.29 (s, 3H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) 144.50, 142.21, 132.89, 123.62, 119.41, 118.47, 67.75, 67.72, 50.39, 50.25, 21.07.

HRMS (ESI) m/z calcd. for $C_{15}H_{23}N_2O_2^+$ $(M+H)^+$: 263.1754, found: 263.1756



3i

4,4'-(4-(trifluoromethyl)-1,2-phenylene)dimorpholine (3i): Following the general procedure A, the reaction was performed with 4-trifluoromethylcyclohexanone **1i** (83.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3i** as a white solid (111.1 mg, 70%).

Following the general procedure A, the reaction was performed with 3-trifluoromethylcyclohexanone **1i'** (83.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and

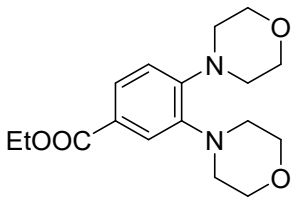
morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3i** as a white solid (93.3 mg, 59%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.28 (d, *J* = 8.0 Hz, 1H), 7.14 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 3.87 (t, *J* = 3.6 Hz, 8H), 3.26 (t, *J* = 3.6 Hz, 4H), 3.22 (t, *J* = 3.6 Hz, 4H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 147.25, 144.39, 125.02 (q, *J* = 32.1 Hz), 124.61 (q, *J* = 269.9 Hz), 120.37 (q, *J* = 4.0 Hz), 115.48 (q, *J* = 3.7 Hz), 67.44, 67.42, 49.81, 49.67.

^{19}F NMR (**400 MHz**, Chloroform-*d*) δ -61.79

HRMS (ESI) m/z calcd. for $C_{15}H_{20}F_3N_2O_2^+$ $(M+H)^+$: 317.1471, found: 317.1471



3j

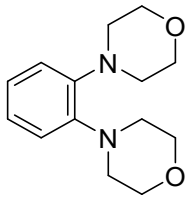
Ethyl 3,4-dimorpholinobenzoate (3j): Following the general procedure A, the reaction was performed with ethyl 4-oxocyclohexane-1-carboxylate **1j** (85.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3j** as a white solid (100.3 mg, 63%).

Following the general procedure A, the reaction was performed with ethyl 3-oxocyclohexane-1-carboxylate **1j'** (85.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3j** as a white solid (83.3 mg, 52%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.70 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.35 (q, *J* = 6.8 Hz, 2H), 3.84 (t, *J* = 4.4 Hz, 8H), 3.28 (t, *J* = 4.4 Hz, 4H), 3.18 (t, *J* = 4.4 Hz, 4H), 1.37 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 166.79, 148.49, 143.75, 125.41, 124.78, 119.95, 117.80, 67.51, 67.41, 60.83, 49.95, 49.57, 14.56.

HRMS (ESI) m/z calcd. for $C_{17}H_{25}N_2O_4^+$ $(M+H)^+$: 321.1809, found: 321.1810



3k

1,2-dimorpholinobenzene (3k): Following the general procedure A, the reaction was performed with cyclohexanone **1ka** (49.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3k** as a white solid (74.0 mg, 60%).

Following the general procedure A, the reaction was performed with 4-hydroxycyclohexan-1-one **1kb** (57.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3k** as a white solid (69.5 mg, 56%).

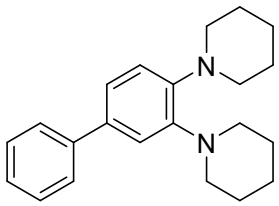
Following the general procedure A, the reaction was performed with 4-methoxycyclohexan-1-one **1kc** (64.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3k** as a white solid (99.5 mg, 80%).

Following the general procedure A, the reaction was performed with *N*-(4-oxocyclohexyl)acetamide **1kd** (77.6 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3k** as a white solid (51.1 mg, 41%).

Following the general procedure A, the reaction was performed with 2-(4-oxocyclohexyl)isoindoline-1,3-dione **1ke** (121.6 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3k** as a white solid (87.0 mg, 70%).

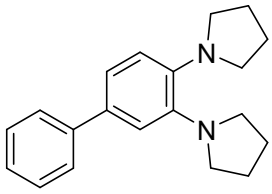
Following the general procedure A, the reaction was performed with 4-(cyclohex-1-en-1-yl)morpholine **9** (83.7 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (43.6 mg, 44 μL, 0.5 mmol, 1.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3k** as a white solid (68.5 mg, 55%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.03 – 7.00 (m, 2H), 6.99 – 6.91 (m, 2H), 3.84 (t, *J* = 4.8 Hz, 8H), 3.82 (t, *J* = 4.8 Hz, 8H).
^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 144.62, 123.36, 118.56, 67.70, 50.16.
HRMS (ESI) m/z calcd. for $C_{14}H_{21}N_2O_2^+$ $(M+H)^+$: 249.1598, found: 249.1600



3m

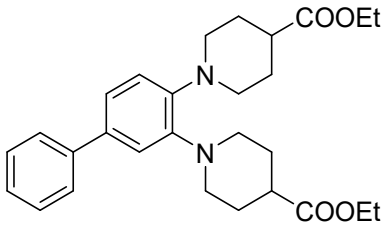
1,1'-([1,1'-biphenyl]-3,4-diyl)dipiperidine (3m): Following the general procedure A, the reaction was performed with 4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and piperidine **2m** (127.7 mg, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3m** as a white solid (94.5 mg, 59%).
^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.19 – 7.10 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 3.12 (br-s, 8H), 1.78 – 1.68 (m, 8H), 1.62 – 1.55 (m, 4H).
^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 146.40, 145.65, 141.65, 134.99, 128.56, 126.84, 126.43, 120.78, 118.83, 117.67, 50.99, 50.92, 26.88, 26.85, 24.69.
HRMS (ESI) m/z calcd. for $C_{22}H_{29}N_2^+$ $(M+H)^+$: 321.2325, found: 321.2323



3n

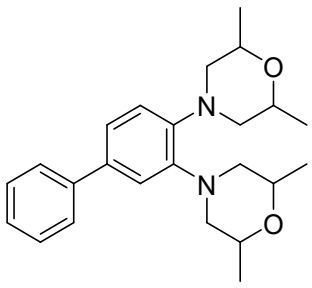
1,1'-([1,1'-biphenyl]-3,4-diyl)dipyrrolidine (3n): Following the general procedure A, the reaction was performed with 4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and pyrrolidine **2n** (106.8 mg, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 12 hours. The mixture was purified by column chromatography to obtain **3n** as a white solid (66.0 mg, 45%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.58 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.15 – 7.09 (m, 2H), 6.96 (d, *J* = 7.2 Hz, 1H), 3.18 – 3.10 (m, 8H), 1.95 – 1.89 (m, 8H).
^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 142.28, 141.99, 141.85, 133.36, 128.67, 126.88, 126.31, 119.41, 116.79, 115.71, 49.21, 24.49, 24.38.
HRMS (ESI) m/z calcd. for $C_{20}H_{25}N_2^+$ $(M+H)^+$: 293.2012, found: 293.2012



3o

diethyl 1,1'-([1,1'-biphenyl]-3,4-diyl)bis(piperidine-4-carboxylate) (3o): Following the general procedure A, the reaction was performed with 4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and ethyl piperidine-4-carboxylate **2o** (235.8 mg, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3o** as a white solid (141.2 mg, 61%).
^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.14 (s, *J* = 2.8 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 4H), 3.75 (d, *J* = 11.6 Hz, 4H), 2.65 (q, *J* = 10.8 Hz, 4H), 2.43 (t, *J* = 11.6 Hz, 2H), 2.07 (d, *J* = 12.8 Hz, 4H), 1.89 (q, *J* = 11.6 Hz, 4H), 1.30 (t, *J* = 7.2 Hz, 6H).
^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 175.38, 145.69, 144.86, 141.41, 135.69, 126.93, 126.75, 121.38, 119.12, 117.89, 60.49, 49.67, 49.63, 41.42, 29.26, 29.24, 14.36.
HRMS (ESI) m/z calcd. for $C_{28}H_{37}N_2O_4^+$ $(M+H)^+$: 465.2748, found: 465.2745



3p

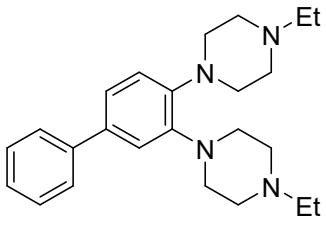
4,4'-([1,1'-biphenyl]-3,4-diyl)bis(2,6-dimethylmorpholine) (3p): Following the general

procedure A, the reaction was performed with 4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and 2,6-dimethylmorpholine **2p** (173.0 mg, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3p** as a white solid (114.1 mg, 60%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.57 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.35 – 7.30 (m, 1H), 7.22 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 3.85 – 3.75 (m, 4H), 3.71 – 3.67 (m, 2H), 3.67 – 3.62 (m, 2H), 2.38 (m, 4H), 1.27 (d, *J* = 6.3 Hz, 12H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 144.22, 143.37, 141.30, 135.97, 128.79, 126.95, 126.89, 121.59, 118.83, 117.50, 72.57, 72.54, 55.45, 55.43, 19.24.

HRMS (ESI) m/z calcd. for $C_{24}H_{33}N_2O_2^+$ $(M+H)^+$: 381.2537, found: 381.2532



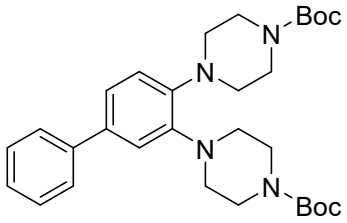
3q

1,1'-([1,1'-biphenyl]-3,4-diyl)dipiperidine (3q): Following the general procedure A, the reaction was performed with 4-Phenylcyclohexanone **1a** (52.3 mg, 0.3 mmol, 1.0 equiv.), I_2 (17.2 mg, 0.06 mmol, 20 mol%), $Cu(OTf)_2$ (10.8 mg , 0.03 mmol, 10 mol%), TfOH (22.5 mg, 13 μL, 0.15 mmol, 50 mol%), and amantadine **2v** (136.2 mg, 0.9 mmol, 3.0 equiv.) in 1,4-dioxane (1.5 mL)
4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and 2,6-dimethylmorpholine **2q** (171.3 mg, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3q** as a white solid (77.6 mg, 41%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H),7.16 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 3.63 – 3.05 (m, 8H), 2.73 – 2.55 (m, 8H), 2.51 (q, *J* = 7.3 Hz, 4H), 1.18 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 144.71, 143.89, 141.38, 135.62, 128.65, 126.87, 126.66, 121.30, 118.69, 117.36, 53.68, 52.57, 49.25, 12.16.

HRMS (ESI) m/z calcd. for $C_{24}H_{35}N_4^+$ $(M+H)^+$: 379.2856, found: 379.2864



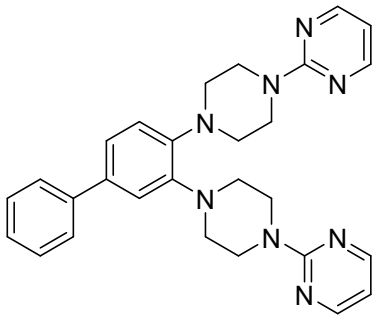
3r

di-tert-butyl 4,4'-([1,1'-biphenyl]-3,4-diyl)bis(piperazine-1-carboxylate) (3r): Following the general procedure A, the reaction was performed with 4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and tert-Butyl 1-piperazinecarboxylate **2r** (279.3 mg, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3r** as a white solid (73.1 mg, 28%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.27 (m, 1H), 7.26 – 7.18 (m, 1H), 7.13 (s, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 3.62 – 3.54 (m, 8H), 3.20 – 3.11 (m, 8H), 1.50 (s, 18H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 154.98, 154.95, 145.08, 144.18, 141.08, 136.40, 128.79, 126.97, 126.90, 122.00, 119.25, 117.96, 79.87, 77.48, 77.16, 76.84, 67.45, 67.39, 49.84, 49.80, 28.54.

HRMS (ESI) m/z calcd. for $C_{30}H_{43}N_4O_4^+$ $(M+H)^+$: 523.3279, found: 523.3281



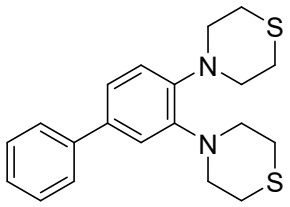
3s

2,2'-([1,1'-biphenyl]-3,4-diylbis(piperazine-4,1-diyl))dipyrimidine (3s): Following the general procedure A, the reaction was performed with 4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and 2-(piperidin-4-yl)pyrimidine **2s** (328.4 mg, 2.0 mmol, 4.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3s** as a white solid (95.7 mg, 40%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 8.39 – 8.35 (m, *J* = 4.7 Hz, 4H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.21 (s, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.54 (t, *J* = 4.8 Hz, 2H), 4.02 (t, *J* = 5.3 Hz, 8H), 3.45 – 3.20 (m, 8H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 161.97, 161.95, 157.76, 145.15, 144.28, 141.15, 136.22, 128.71, 126.87, 126.84, 121.84, 119.13, 117.84, 110.13, 77.37, 77.05, 76.73, 49.77, 49.75, 44.57, 44.53.

HRMS (ESI) m/z calcd. for $C_{28}H_{31}N_8^+$ $(M+H)^+$: 479.2666, found: 479.2662



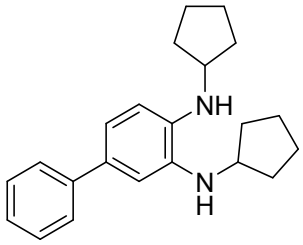
3t

4,4'-([1,1'-biphenyl]-3,4-diyl)bis(thiomorpholine) (3t): Following the general procedure A, the reaction was performed with 4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and thiomorpholine **2t** (154.7 mg, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3t** as a white solid (73.1 mg, 41%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.54 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.23 (m, 2H), 7.19 – 7.13 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 3.36 (br-s, 8H), 2.83 (s, 8H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 147.11, 146.19, 141.11, 136.76, 128.85, 127.05, 126.98, 122.36, 120.40, 119.13, 53.13, 53.08, 29.00, 28.97.

HRMS (ESI) m/z calcd. for $C_{20}H_{25}N_8S_2^+$ $(M+H)^+$: 357.1454, found: 357.1453



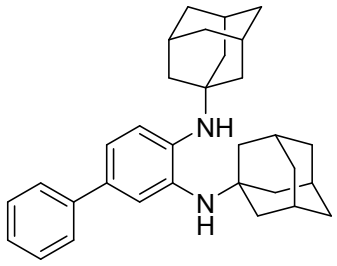
3u

***N*^{3},*N*^{4}-dicyclopentyl-[1,1'-biphenyl]-3,4-diamine (3u):** Following the general procedure A, the reaction was performed with 4-Phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%),and cyclopentylamine **2u** (127.7 mg, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3u** as a white solid (71.7 mg, 45%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.61 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.98 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.87 (dt, *J* = 14.4, 6.4 Hz, 2H), 3.27 (br-s, 2H), 2.18 – 2.04 (m, 4H), 1.87 – 1.75 (m, 4H), 1.73 – 1.65 (m, 4H), 1.65 – 1.54 (m, 4H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 142.31, 137.25, 136.83, 131.80, 128.57, 126.74, 126.05, 117.61, 112.52, 111.62, 54.87, 33.82, 24.46, 24.43.

HRMS (ESI) m/z calcd. for $C_{22}H_{29}N_2^+$ $(M+H)^+$: 321.2325, found: 321.2328



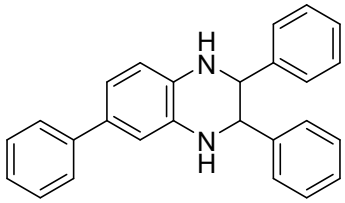
3v

***N*^{3},*N*^{4}-di((3S,5S,7S)-adamantan-1-yl)-[1,1'-biphenyl]-3,4-diamine (3v):** Following the general procedure A, the reaction was performed with 4-Phenylcyclohexanone **1a** (52.3 mg, 0.3 mmol, 1.0 equiv.), I_2 (17.2 mg, 0.06 mmol, 20 mol%), TfOH (22.5 mg, 13 μL, 0.15 mmol, 50 mol%), and amantadine **2v** (136.2 mg, 0.9 mmol, 3.0 equiv.) in chlorobenzene (1.5 mL) under air at 120 °C for 24 hours. The mixture was purified by column chromatography to obtain **3v** as a white solid (69.1 mg, 51%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.19 (s, 1H), 7.10 – 7.03 (m, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 3.72 (br-s, 2H), 2.12 (br-s, 6H), 1.96 – 1.87 (m, 12H), 1.73 – 1.60 (m, 12H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 141.83, 139.22, 136.69, 132.09, 128.69, 126.57, 126.20, 122.17, 120.21, 120.11, 53.07, 52.50, 43.64, 43.41, 36.71, 36.68, 29.90.

HRMS (ESI) m/z calcd. for $C_{32}H_{41}N_2^+$ $(M+H)^+$: 453.3264, found: 453.3265



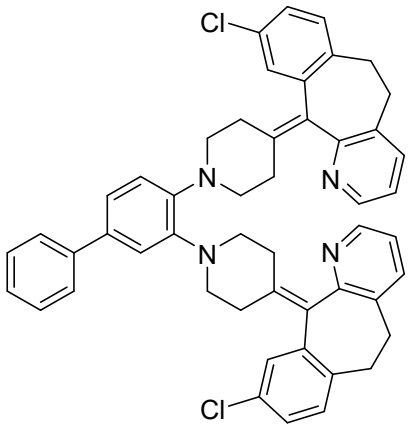
3w

2,3,6-triphenyl-1,2,3,4-tetrahydroquinoxaline (3w): Following the general procedure A, the reaction was performed with 4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and 1,2-diphenylethane-1,2-diamine **2w** (318.5 mg, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3w** as a white solid (136.1 mg, 75%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.59 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.21 (m, 7H), 7.16 – 7.07 (m, 4H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.92 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.32 (s, 2H), 4.20 (s, 2H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 141.65, 139.97, 133.79, 133.25, 131.81, 128.62, 128.24, 127.98, 127.92, 126.53, 126.16, 117.60, 114.09, 112.50, 62.21, 62.09.

HRMS (ESI) m/z calcd. for $C_{26}H_{23}N_2^+$ $(M+H)^+$: 363.1856, found: 363.1855



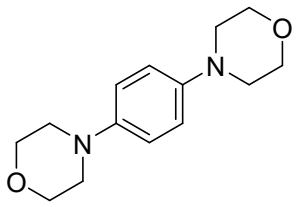
3x

11,11'-([1,1'-biphenyl]-3,4-diylbis(piperidin-1-yl-4-ylidene))bis(9-chloro-6,11-dihydro-5H-benzo[5,6]cyclohepta[1,2-b]pyridine) (3x): Following the general procedure A, the reaction was performed with 4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and 2-(piperidin-4-yl)pyrimidine desloratadine **2x** (466.2 mg, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **3x** as a white solid (150.5 mg, 39%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 8.52 – 8.47 (s, 2H), 7.58 – 7.51 (m, 2H), 7.51 – 7.44 (m, 2H), 7.43 – 7.37 (m, 2H), 7.32 – 7.18 (m, 8H), 7.17 – 7.10 (m, 3H), 6.95 (t, *J* = 7.6 Hz, 1H), 3.71 (m, 4H), 3.46 (m, 4H), 2.96 – 2.48 (m, 16H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 157.56, 146.83, 146.77, 145.58, 145.55, 144.76, 141.29, 139.75, 139.70, 138.83, 138.79, 138.75, 138.06, 137.99, 137.45, 135.57, 133.51, 133.46, 133.11, 133.07, 132.79, 132.77, 131.04, 130.89, 128.99, 128.68, 126.81, 126.69, 126.18, 126.13, 122.23, 122.18, 121.32, 119.22, 118.05, 51.89, 51.77, 51.52, 51.47, 51.40, 51.34, 51.14, 51.02, 32.07, 31.90, 31.86, 31.64, 31.61.

HRMS (ESI) m/z calcd. for $C_{26}H_{23}N_2^+$ $(M+H)^+$: 771.3016, found: 771.3018



6

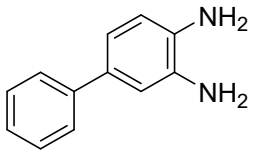
1,4-dimorpholinobenzene (6): Following the general procedure A, the reaction was performed with cyclohex-2-en-1-one **4** (48.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 μL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **6** as a white solid (88.0 mg, 71%).

Following the general procedure A, the reaction was performed with 1,4-cyclohexanedione **5** (56.1 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 µL, 0.25 mmol, 50 mol%), and morpholine **2a** (130.7mg, 131 µL, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **6** as a white solid (100.6 mg, 81%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 6.92 (s, 4H), 3.98 – 3.83 (m, 8H), 3.16 – 3.01 (m, 8H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 145.49, 117.37, 67.02, 50.46.

HRMS (ESI) m/z calcd. for $C_{14}H_{21}N_2O_2^+$ $(M+H)^+$: 249.1598, found: 249.1596



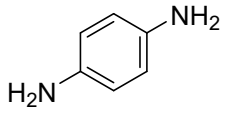
7

[1,1'-biphenyl]-3,4-diamine (7): Following the procedure C, the reaction was performed with 4-phenylcyclohexanone **1a** (87.1 mg, 0.5 mmol, 1.0 equiv.), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 µL, 0.25 mmol, 50 mol%), and benzylamine **2y** (164 µl, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours, then ammonium formate (157.6 mg, 2.5 mmol, 5.0 equiv.) and 10% Pd-C (26.6 mg, 0.025 mmol, 5 mol%) and 2.5 mL of MeOH under N_2 at reflux temperature for overnight. The mixture was purified by column chromatography to obtain **7** as a brown solid (45.6 mg, 49%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.55 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.45 – 7.37 (m, 2H), 7.33 – 7.26 (m, 1H), 7.02 – 6.98 (m, 2H), 6.83 – 6.77 (m, 1H), 3.47 (br-s, 4H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 141.35, 134.92, 134.32, 133.54, 128.60, 126.60, 126.37, 119.11, 116.96, 115.50.

HRMS (ESI) m/z calcd. for $C_{12}H_{23}N_2^+$ $(M+H)^+$: 185.1079, found: 185.1083



8

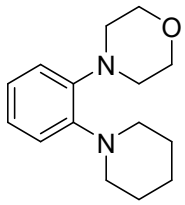
Benzene-1,4-diamine (7): Following the procedure D, the reaction was performed with cyclohex-2-en-1-one **4** (48.1 mg, 0.5 mmol, 1.0 equiv.), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 µL, 0.25 mmol, 50 mol%), and benzylamine **2y** (164 µl, 1.5 mmol, 3.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours, then ammonium formate (157.6 mg, 2.5 mmol, 5.0 equiv.) and 10% Pd-C (26.6 mg, 0.025 mmol, 5 mol%) and 2.5 mL of MeOH under N_2 at reflux temperature for overnight. The mixture was purified by column chromatography to obtain **8** as a brown solid

(12.1 mg, 22%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 6.59 (s, 4H), 3.35 (br-s, 4H).

^{13}C NMR (**100 MHz**, Chloroform-*d*) δ 138.60, 116.74, 77.37, 77.05, 76.73.

HRMS (ESI) m/z calcd. for $C_6H_9N_2^+$ $(M+H)^+$: 109.0766, found: 109.0761



10

4-(2-(piperidin-1-yl)phenyl)morpholine (10): Following the general procedure A, the reaction was performed with 4-(cyclohex-1-en-1-yl)morpholine **9** (83.7 mg, 0.5 mmol, 1.0 equiv.), $Cu(OTf)_2$ (18.1 mg , 0.05 mmol, 10 mol%), I_2 (25.4 mg, 0.1 mmol, 20 mol%), TfOH (37.5 mg, 22 μL, 0.25 mmol, 50 mol%), and piperidine **2m** (42.6 mg, 0.5 mmol, 1.0 equiv.) in 1,4-dioxane (2.5 mL) under air at 80 °C for 24 hours. The mixture was purified by column chromatography to obtain **10** as a white solid (49.0 mg, 40%).

^{1}H NMR (**400 MHz**, Chloroform-*d*) δ 7.08 – 6.84 (m, 4H), 3.89 (t, *J* = 4.6 Hz, 4H), 3.22 (t, *J* = 4.8 Hz, 4H), 3.09 (t, *J* = 5.3 Hz, 4H), 1.74 – 1.67 (m, 4H), 1.63 – 1.56 (m, 2H).

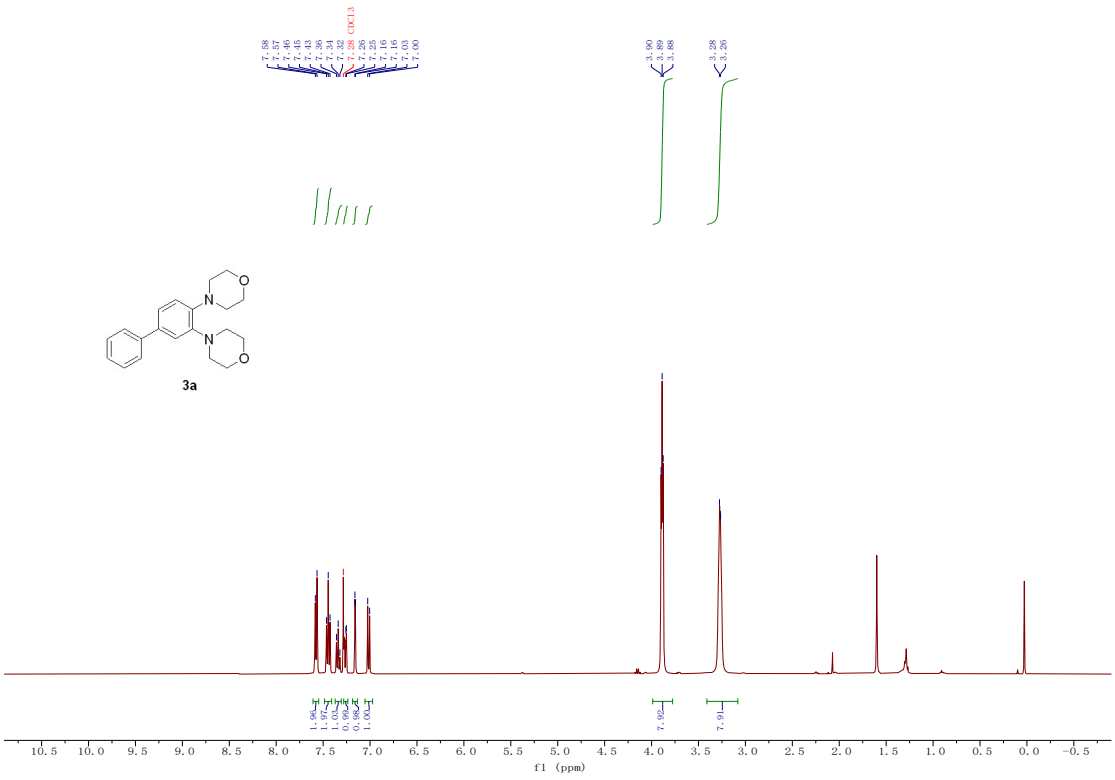
^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.14, 144.66, 122.86, 122.55, 118.97, 117.97, 67.74, 51.06, 49.86, 26.77, 24.56.

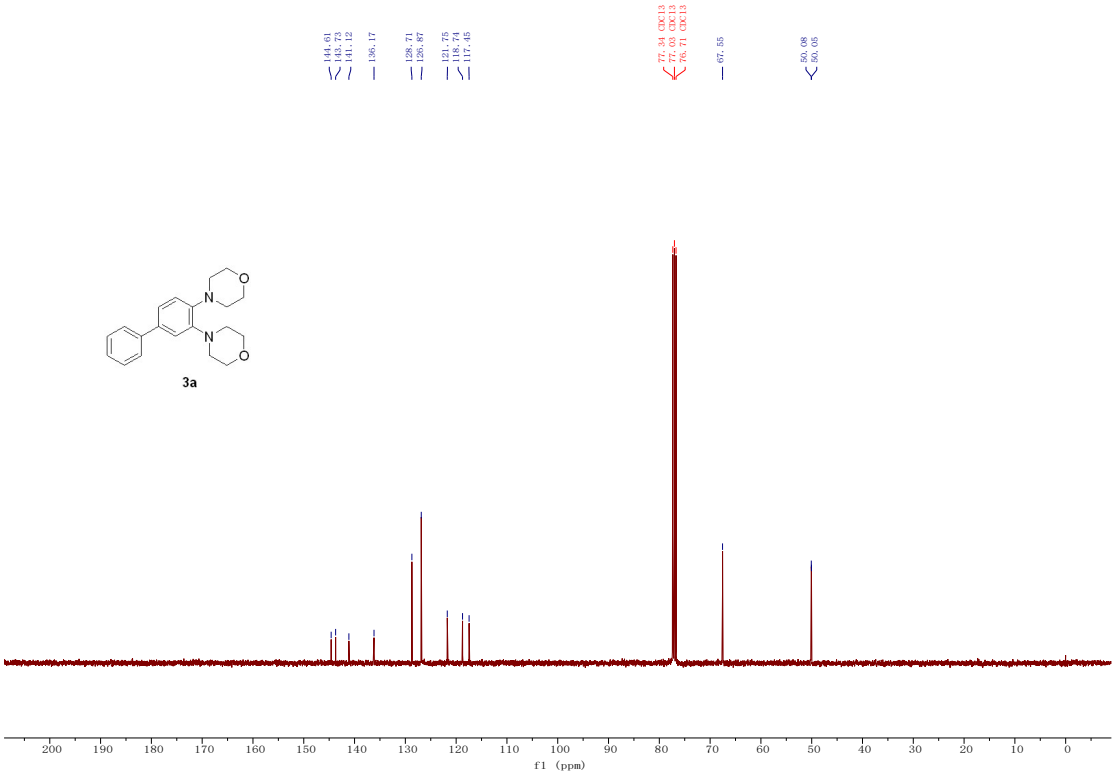
HRMS (ESI) m/z calcd. for $C_6H_9N_2^+$ $(M+H)^+$: 247.1810, found: 247.18

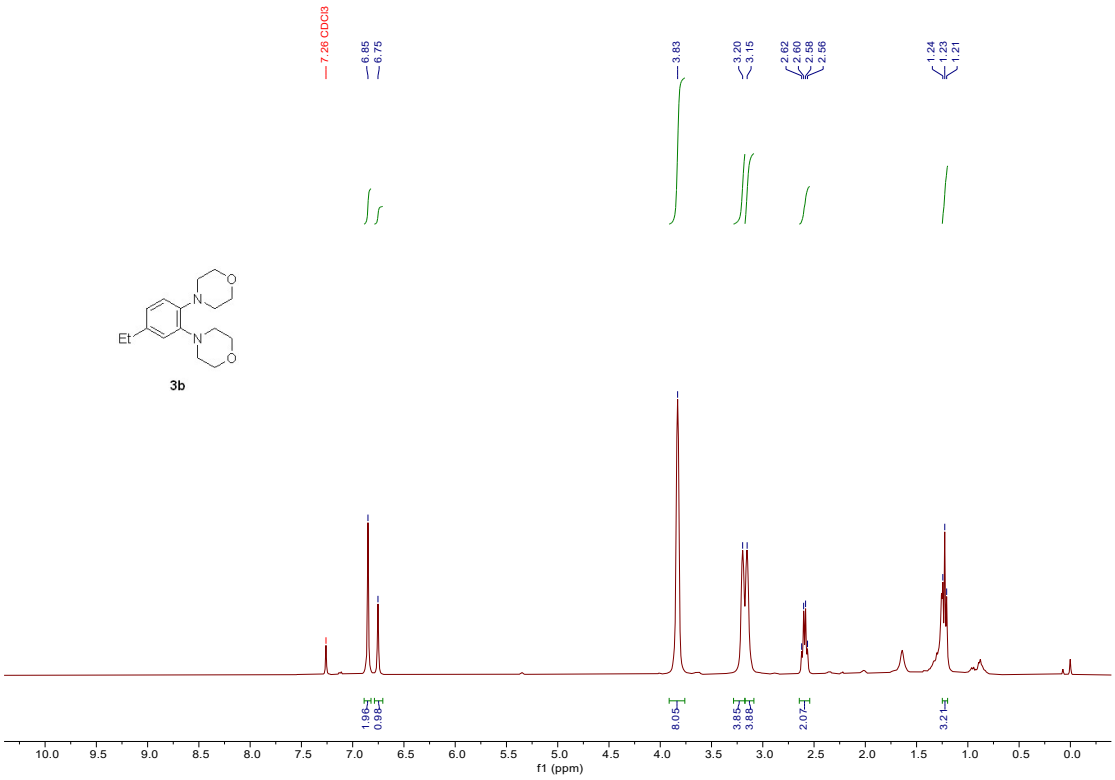
4. References

(1)(a) Ram, S.; Spicer, L. D. *Synthetic Communications*, 1987, **17**, 415-418. (b) Anwer, M. K.; Spatola, A. F. *Tetrahedron Letters*, 1981, **22**, 4369-4372.

5. NMR Spectral Data



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2.56
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3b
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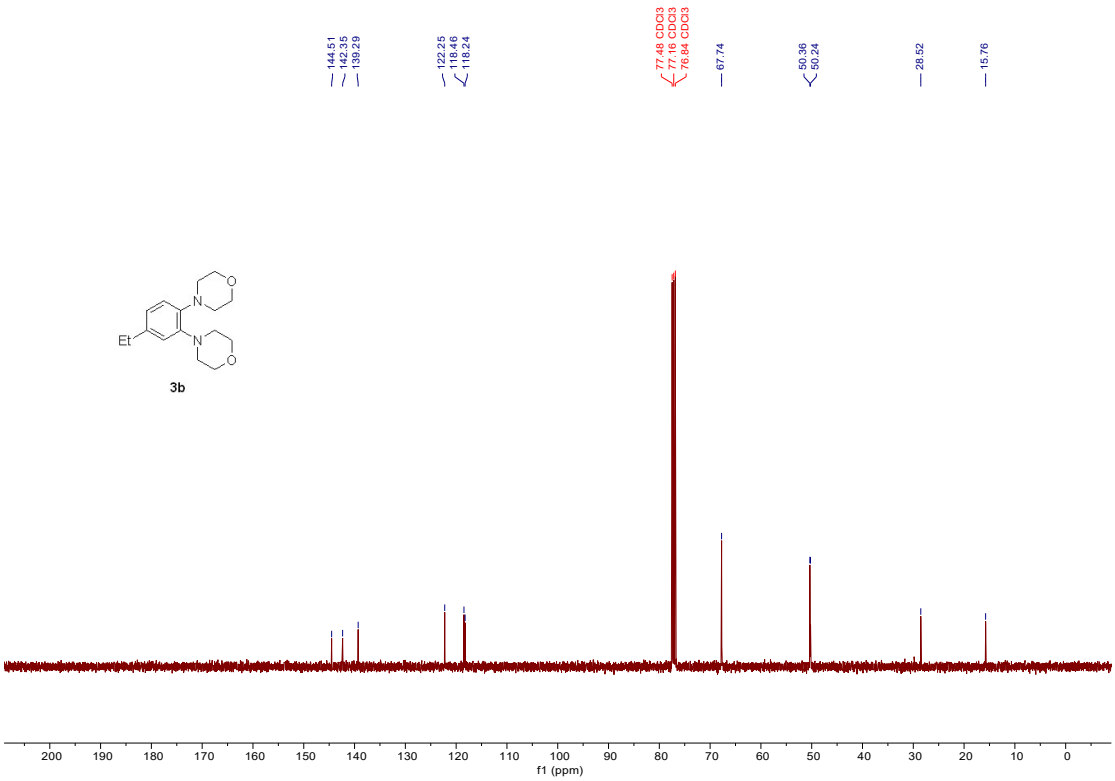
3.21
f1 (ppm)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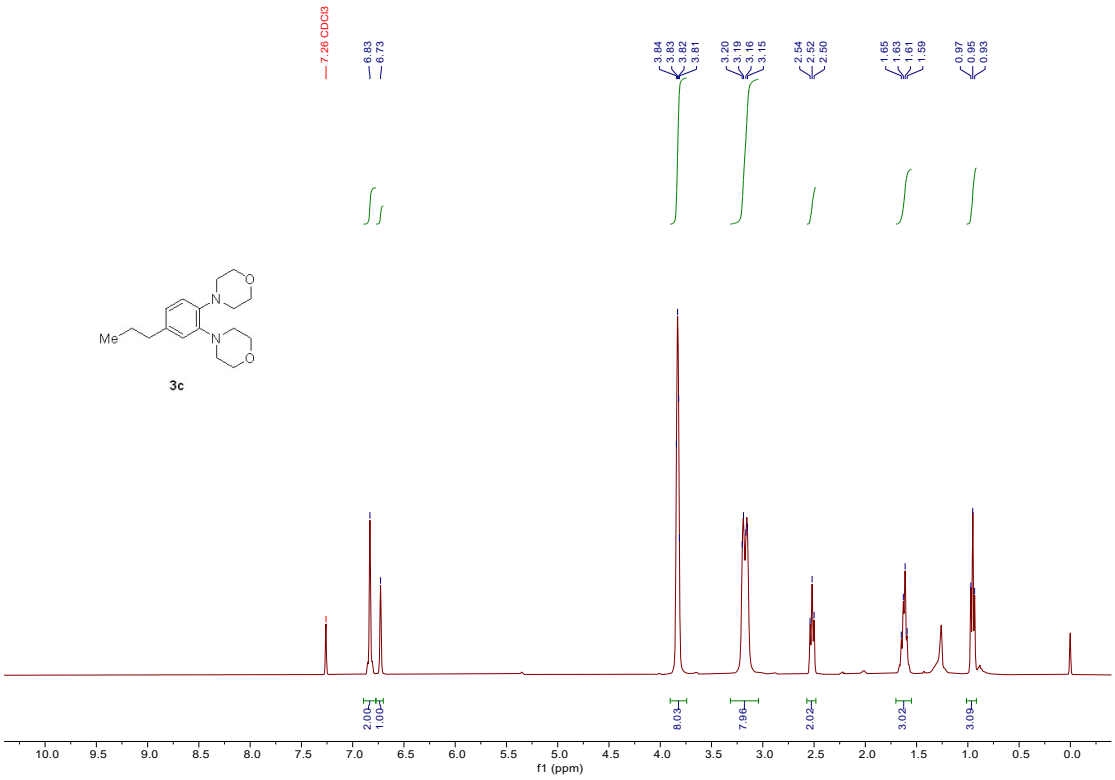
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1.63
1.61
1.59
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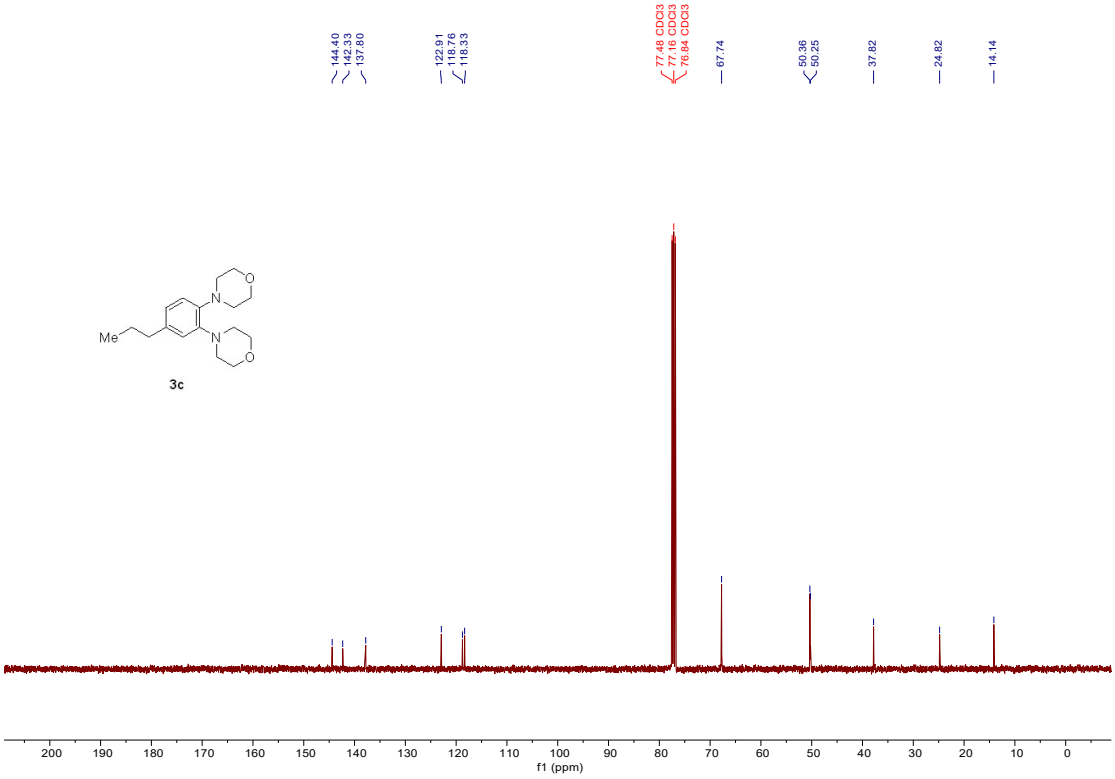
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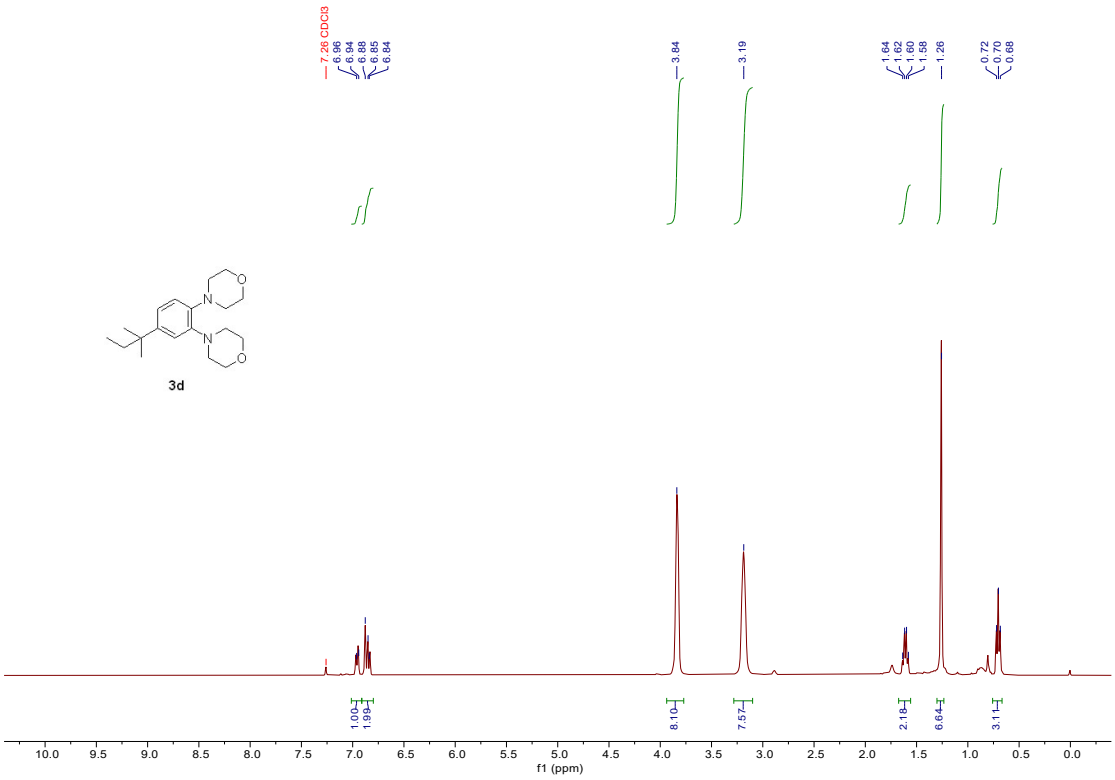
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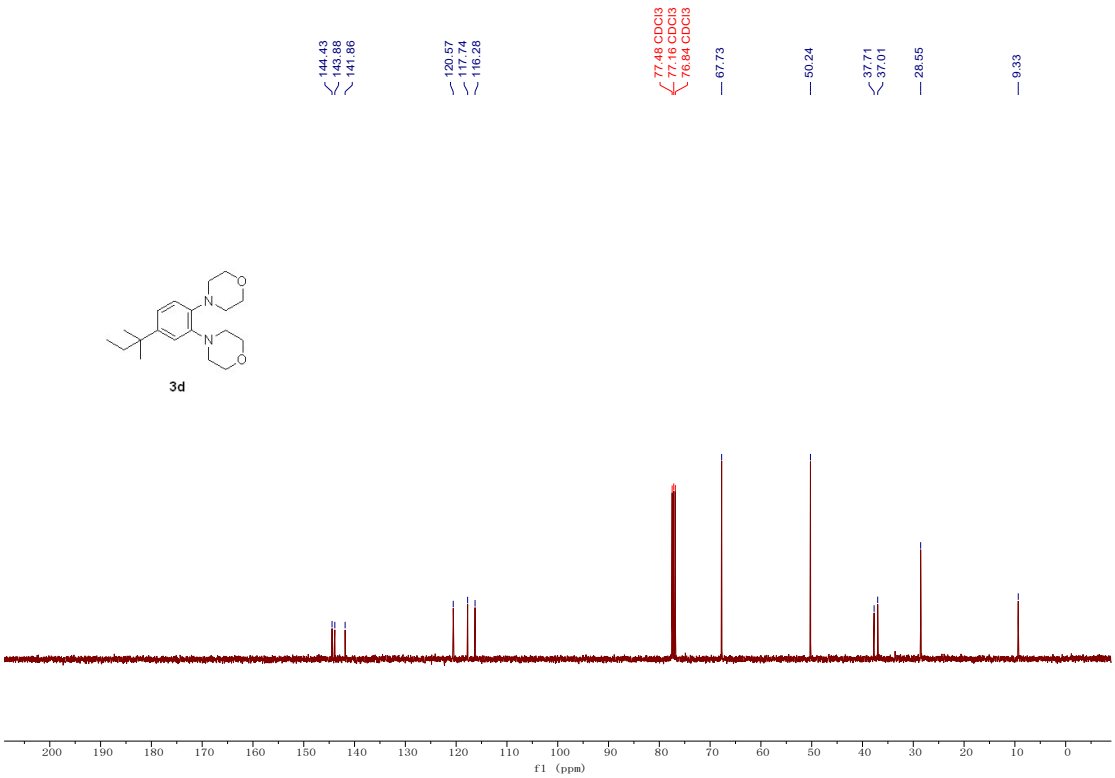
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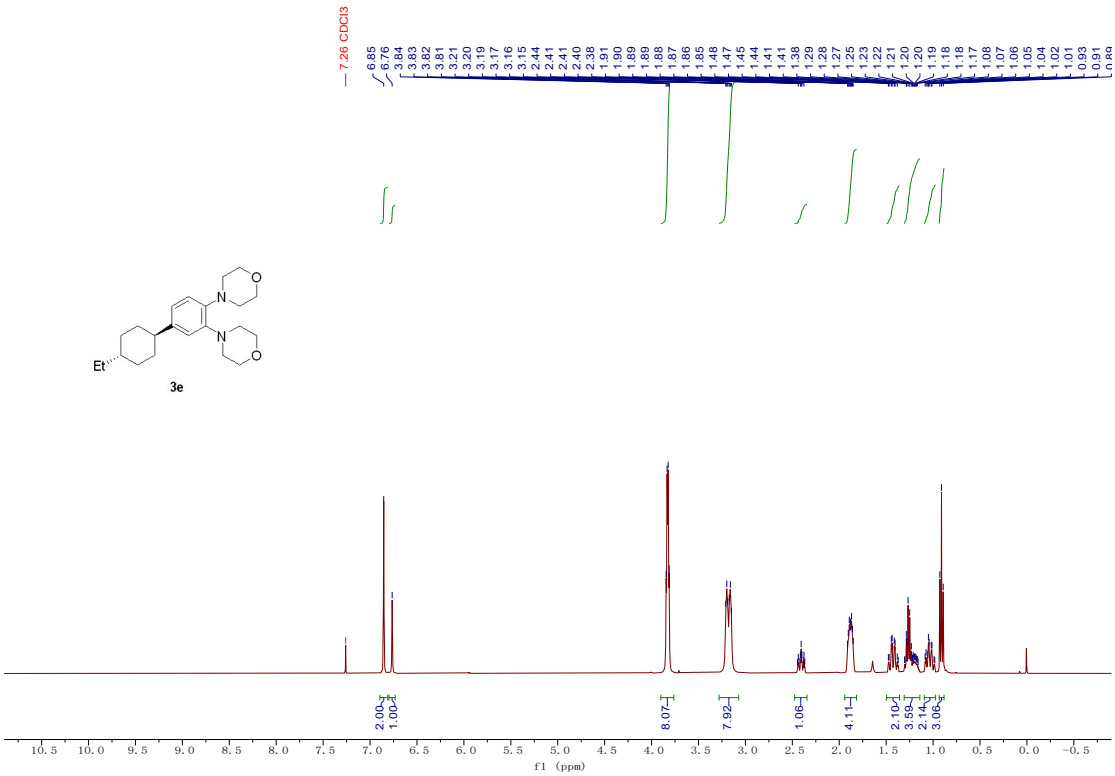
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1.41
1.38
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1.21
1.20
1.20
1.19
1.18
1.18
1.17
1.08
1.07
1.06
1.05
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1.02
1.01
0.93
0.91
Et
3e
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3.06
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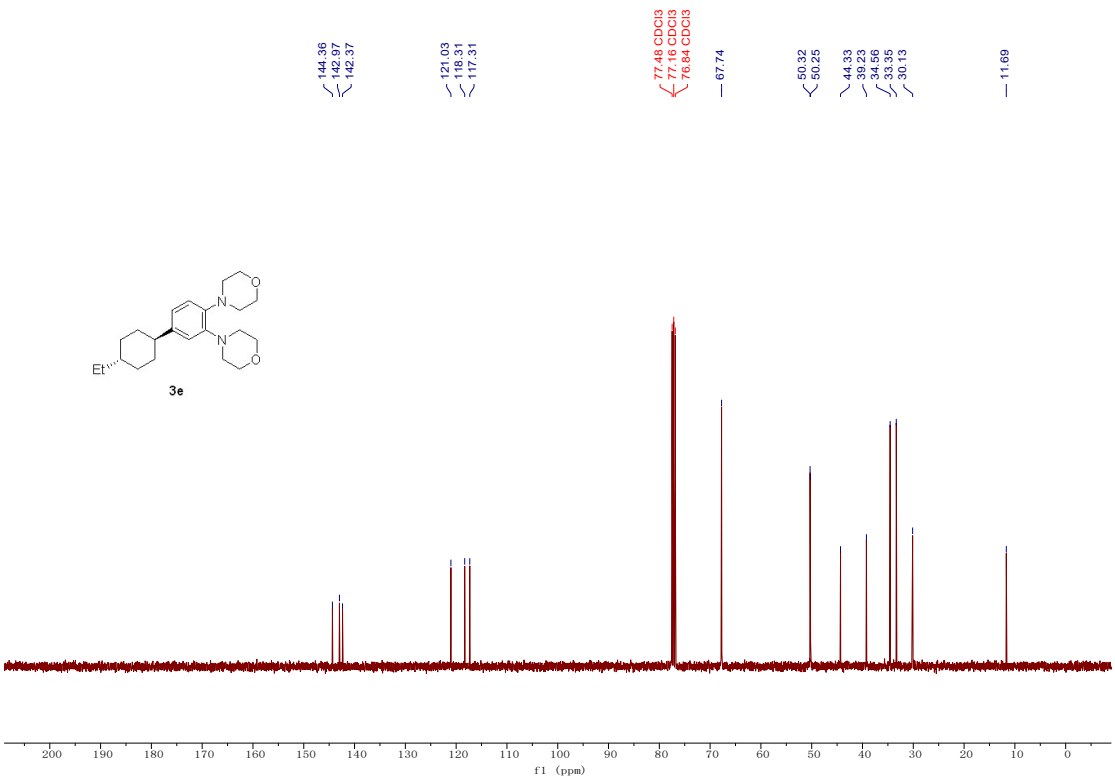
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Et
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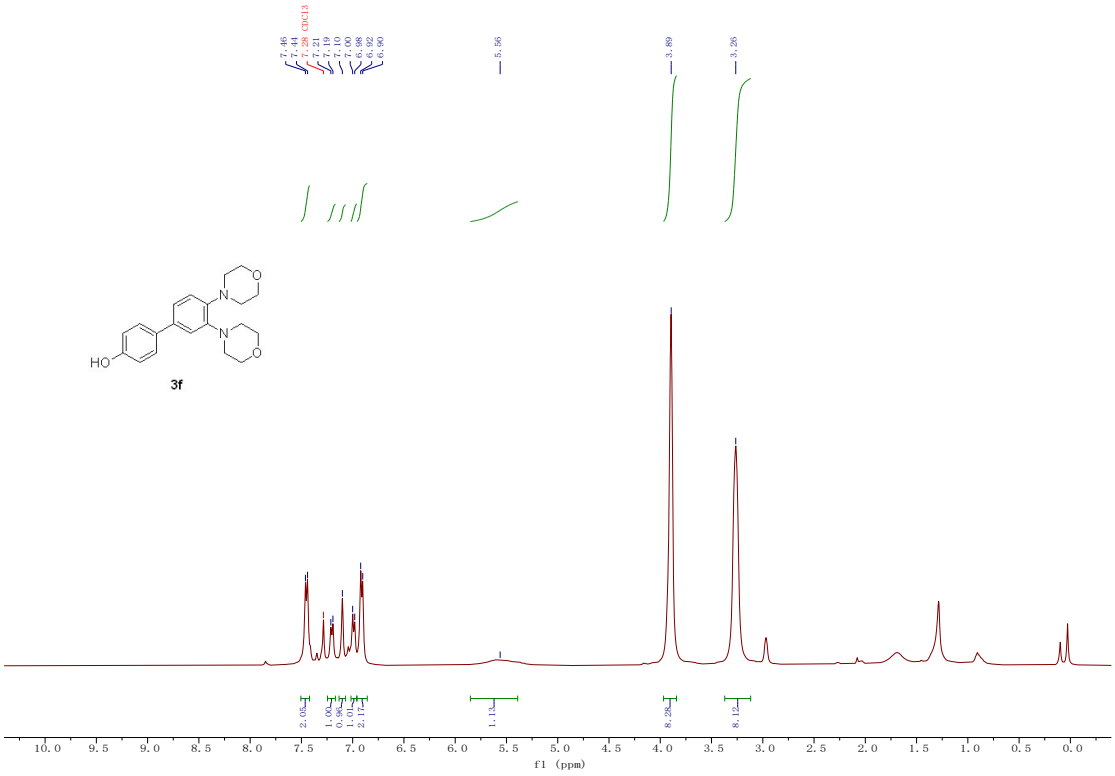
f1 (ppm)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3.26
HO
3f
2.05
1.00
0.98
1.04
2.17
1.13
8.28
8.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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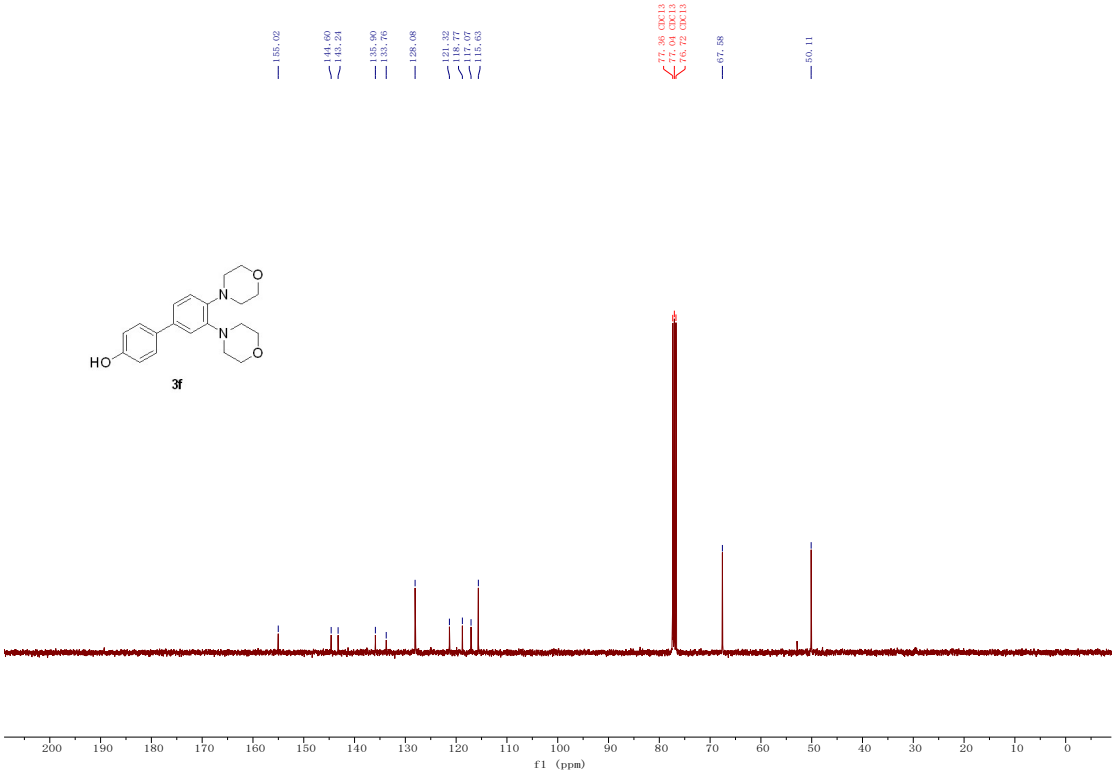
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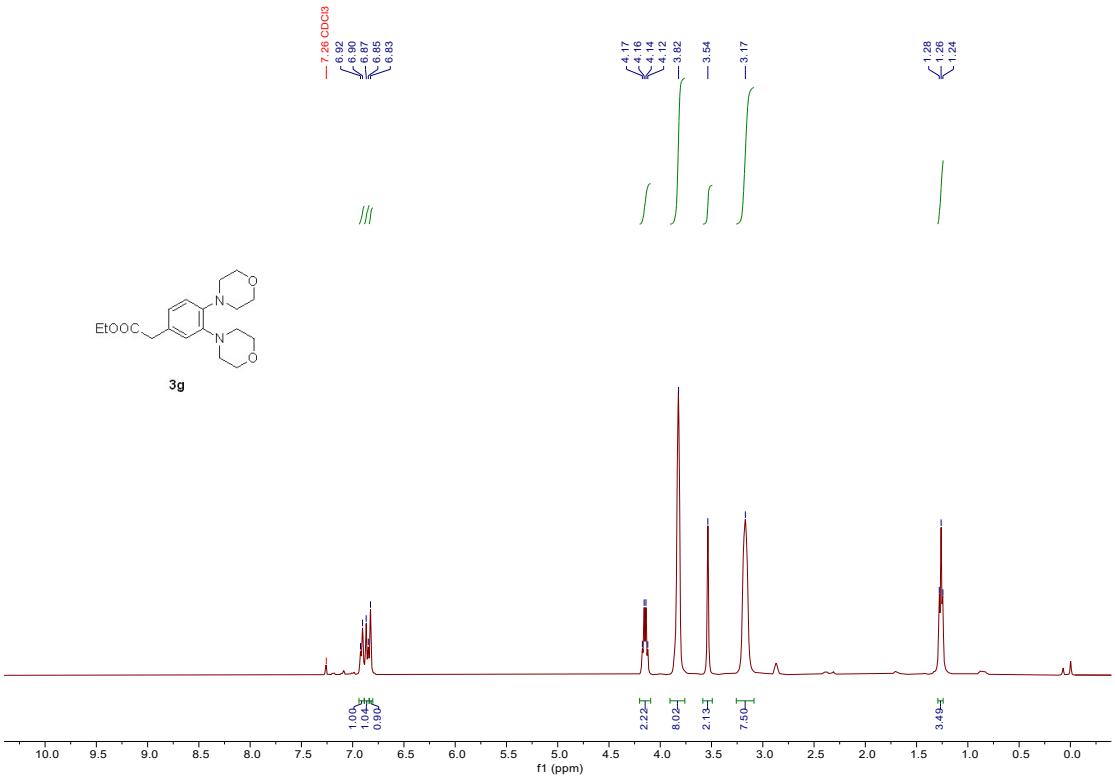
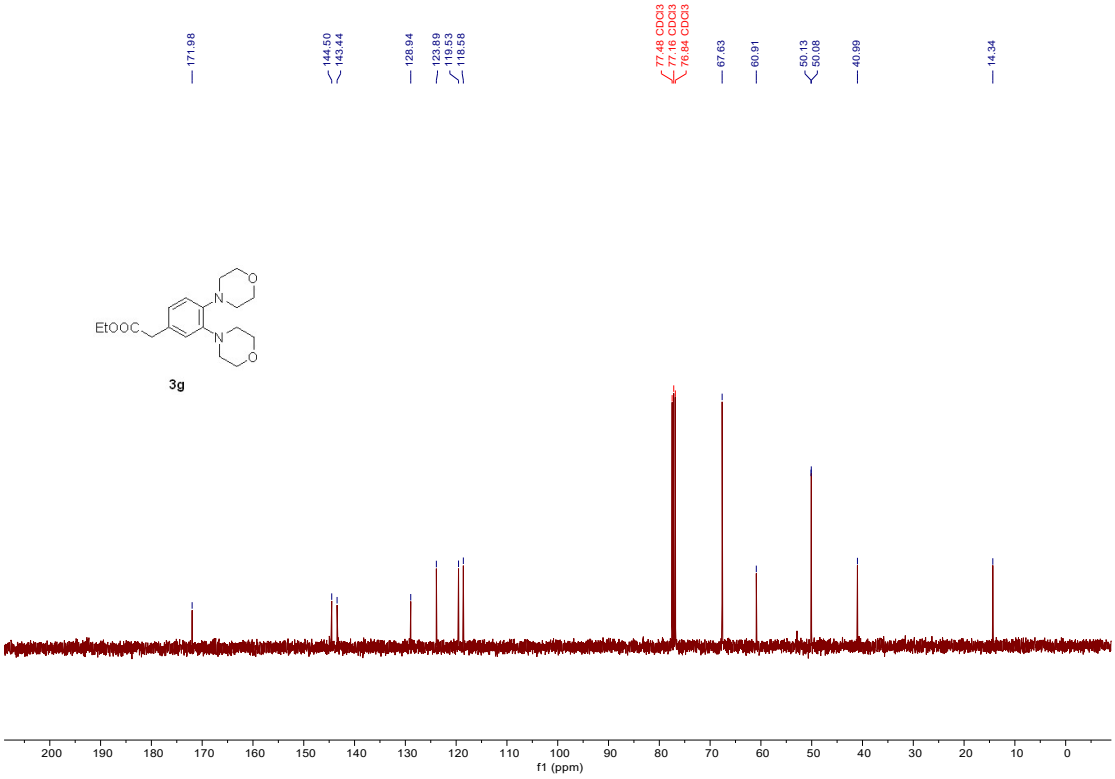
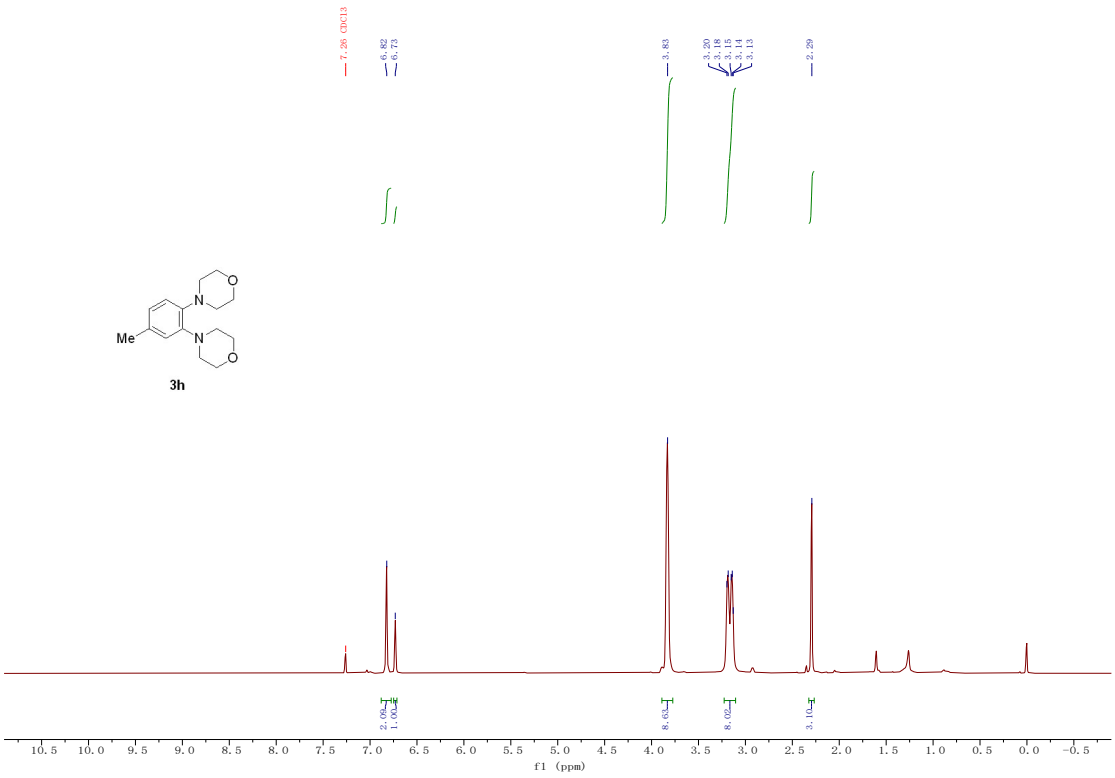
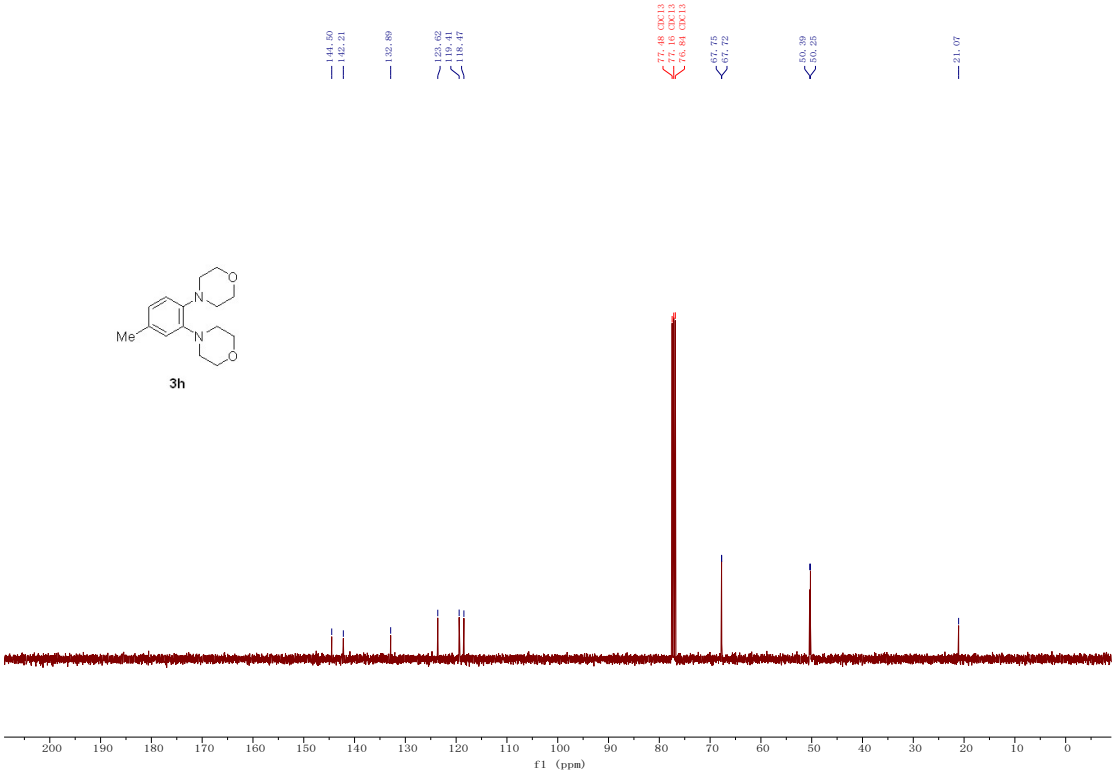
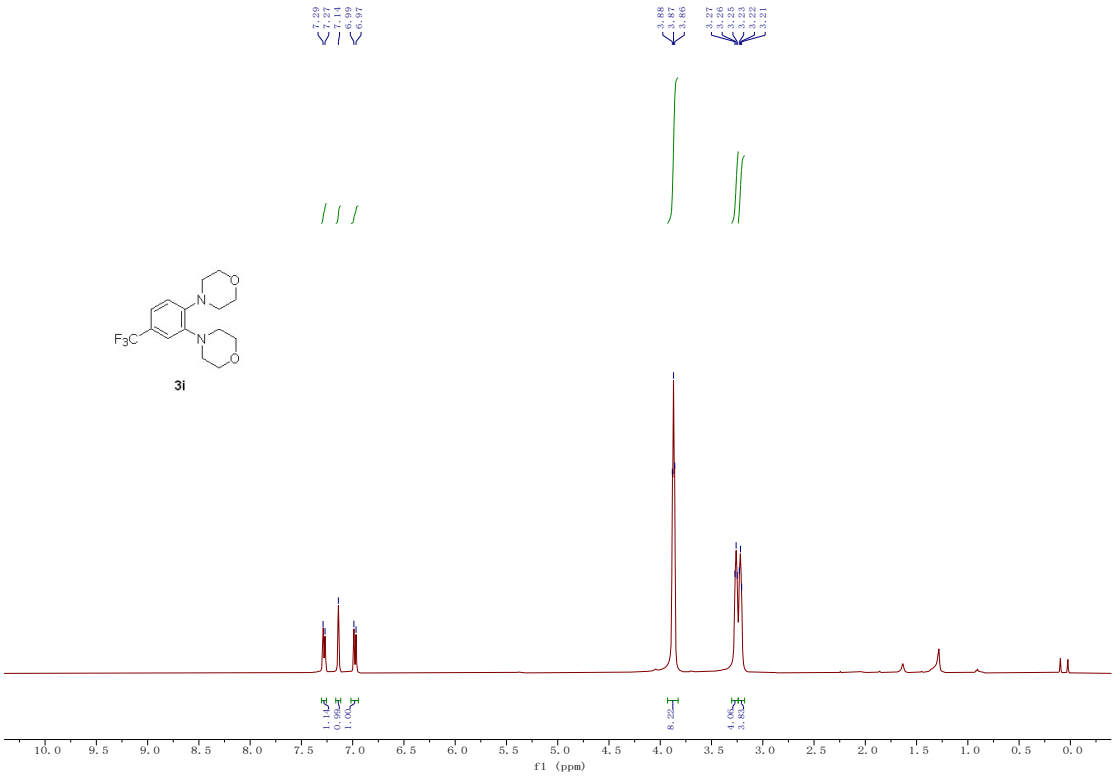
HO
3f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

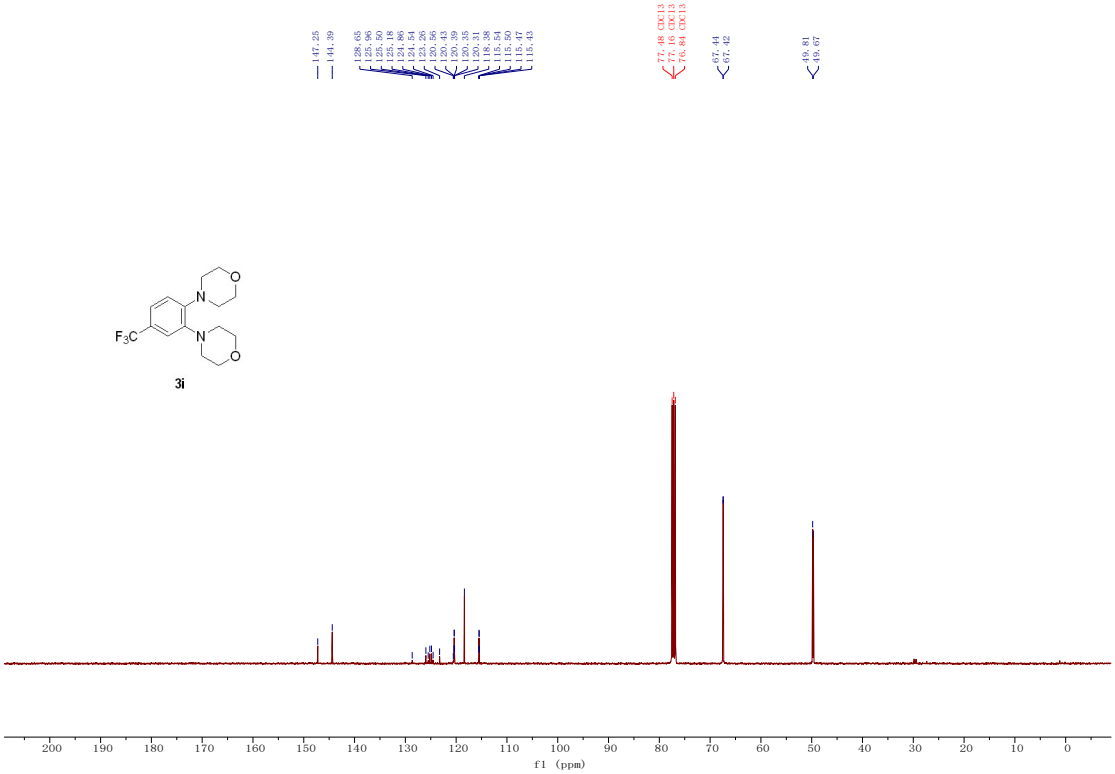

7.26 CDCl3
6.92
6.90
6.87
6.85
6.83
4.17
4.16
4.14
4.12
3.82
3.54
3.17
1.28
1.26
1.24
EtOOC
3g
1.00
1.04
0.90
2.22
8.02
2.13
7.50
3.49
f1 (ppm)

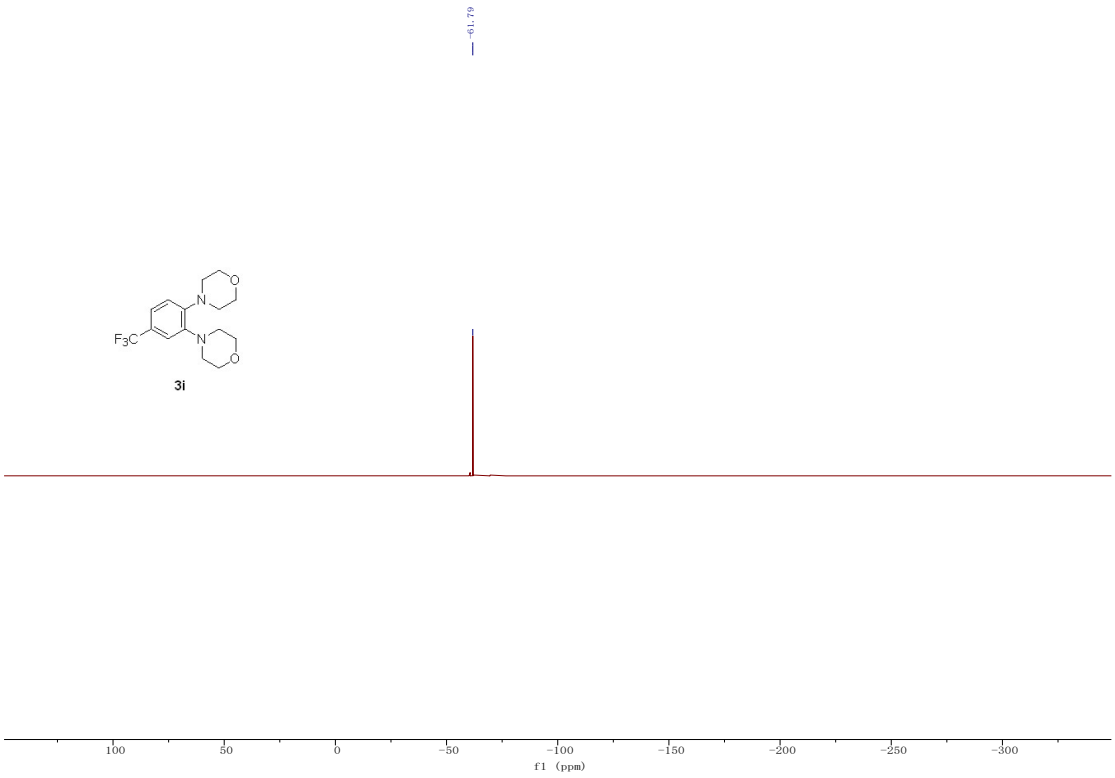

171.98
144.50
143.44
128.94
123.89
119.53
118.58
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.63
60.91
50.13
50.08
40.99
14.34
EtOOC
3g
f1 (ppm)

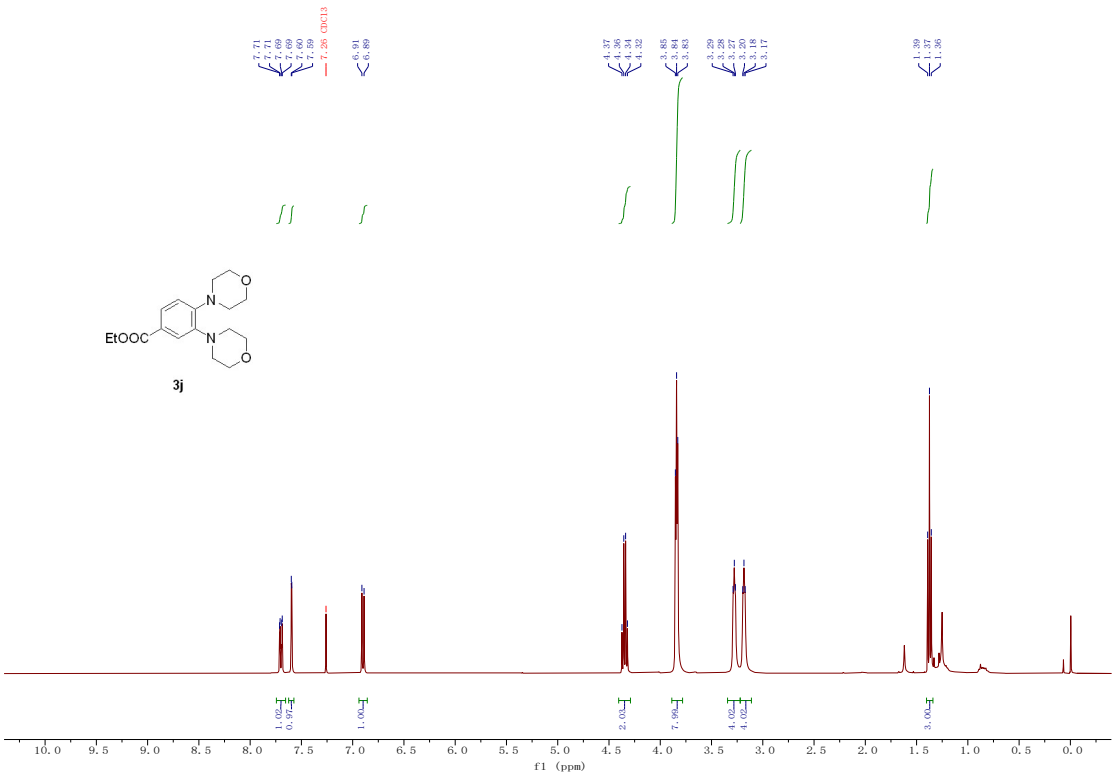

7.26 CDCl3
6.82
6.73
3.83
3.20
3.18
3.15
3.14
3.13
2.29
Me
3h
2.09
1.00
8.64
8.02
3.10
f1 (ppm)

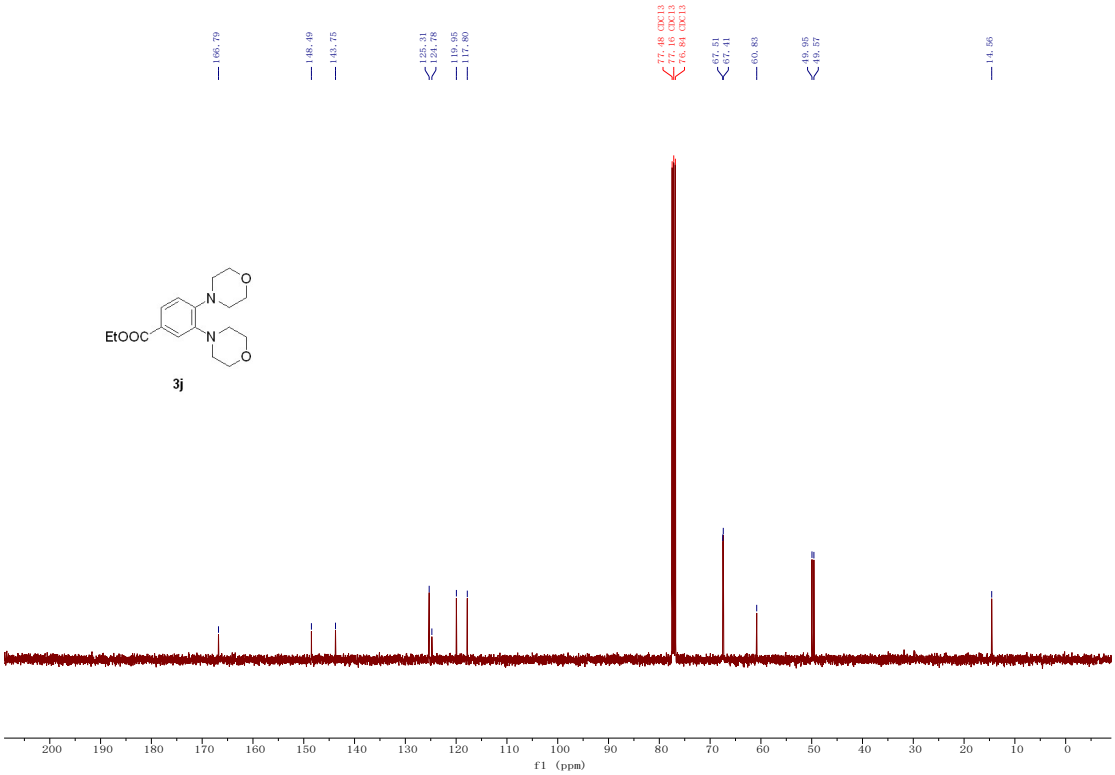

144.50
142.21
132.89
123.62
119.41
118.47
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.75
67.72
50.39
50.25
21.07
Me
3h
f1 (ppm)

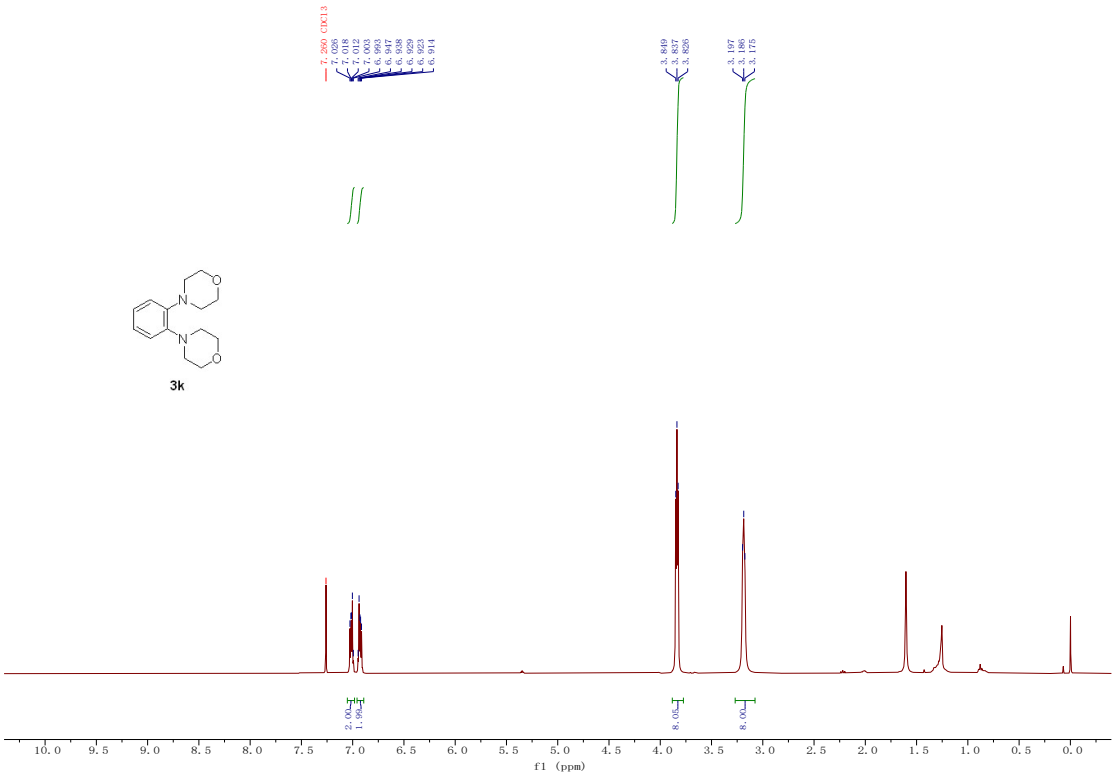

7.29
7.27
7.14
6.99
6.97
3.88
3.87
3.86
3.27
3.26
3.25
3.23
3.22
3.21
F3C
N
O
3i
1.12
0.94
1.00
8.22
4.06
3.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

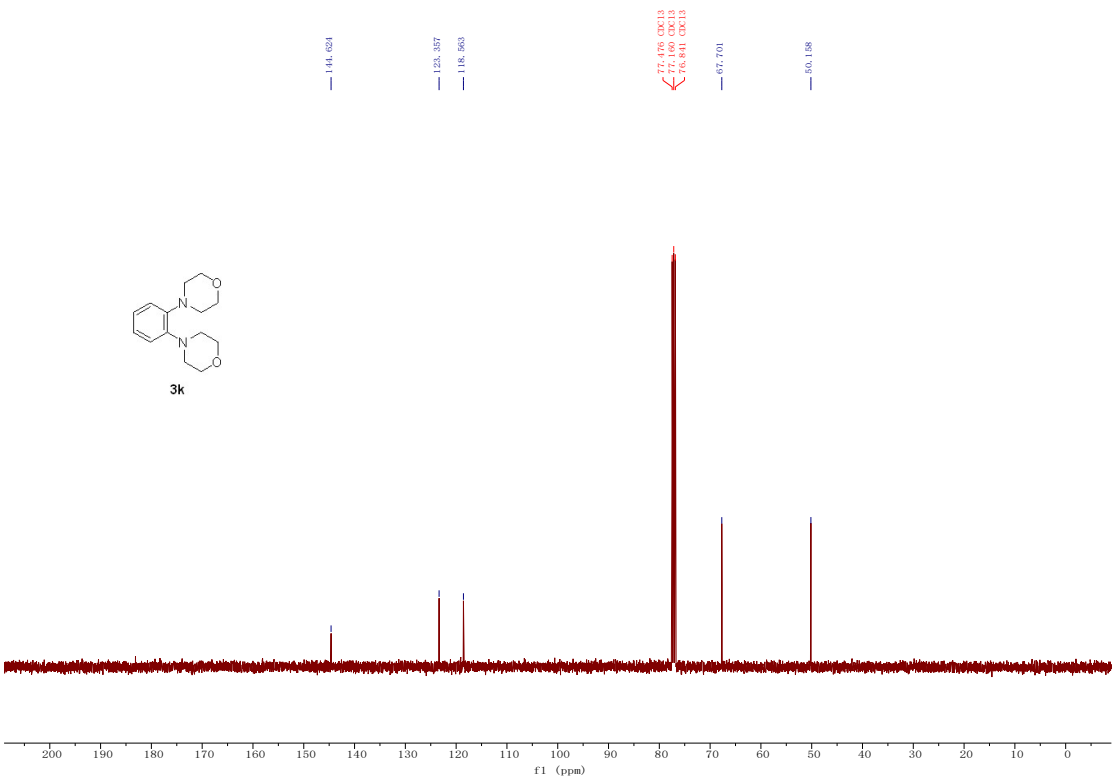

147.25
144.39
128.65
125.96
125.38
125.18
124.86
124.54
123.26
120.56
120.43
120.39
120.35
120.31
118.38
115.54
115.50
115.47
115.43
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.44
67.42
49.81
49.67
F3C
N
O
3i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

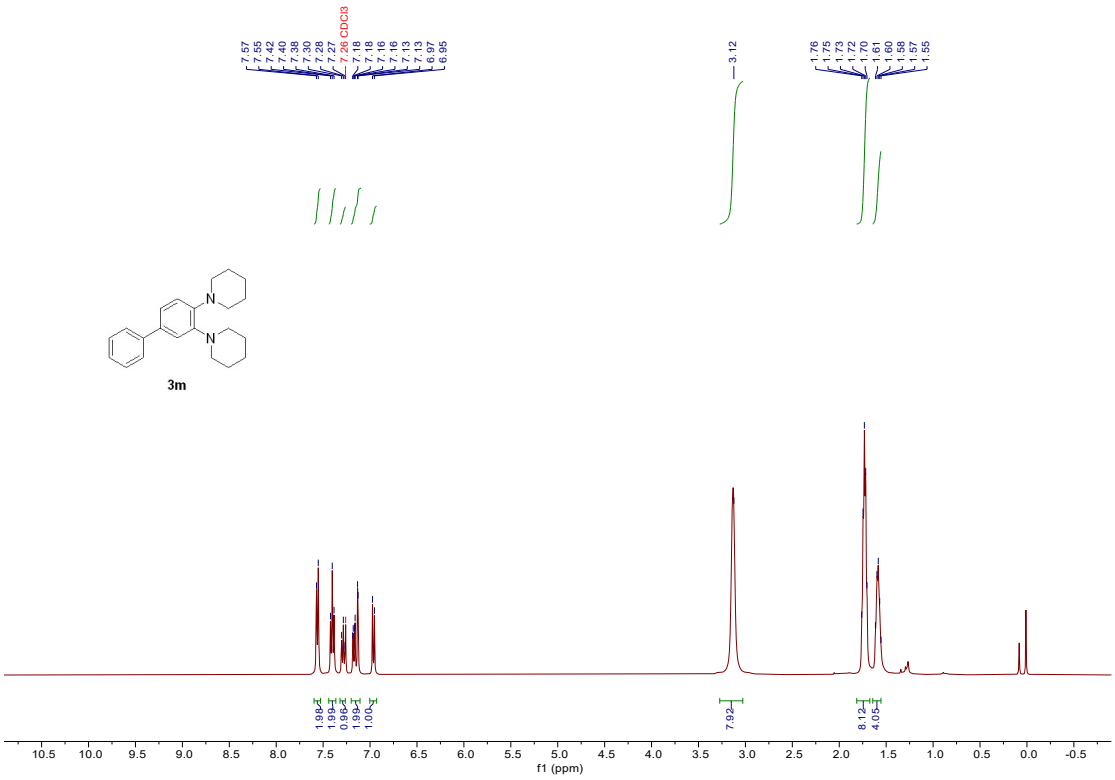

-61.79
F3C
N
O
3i
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

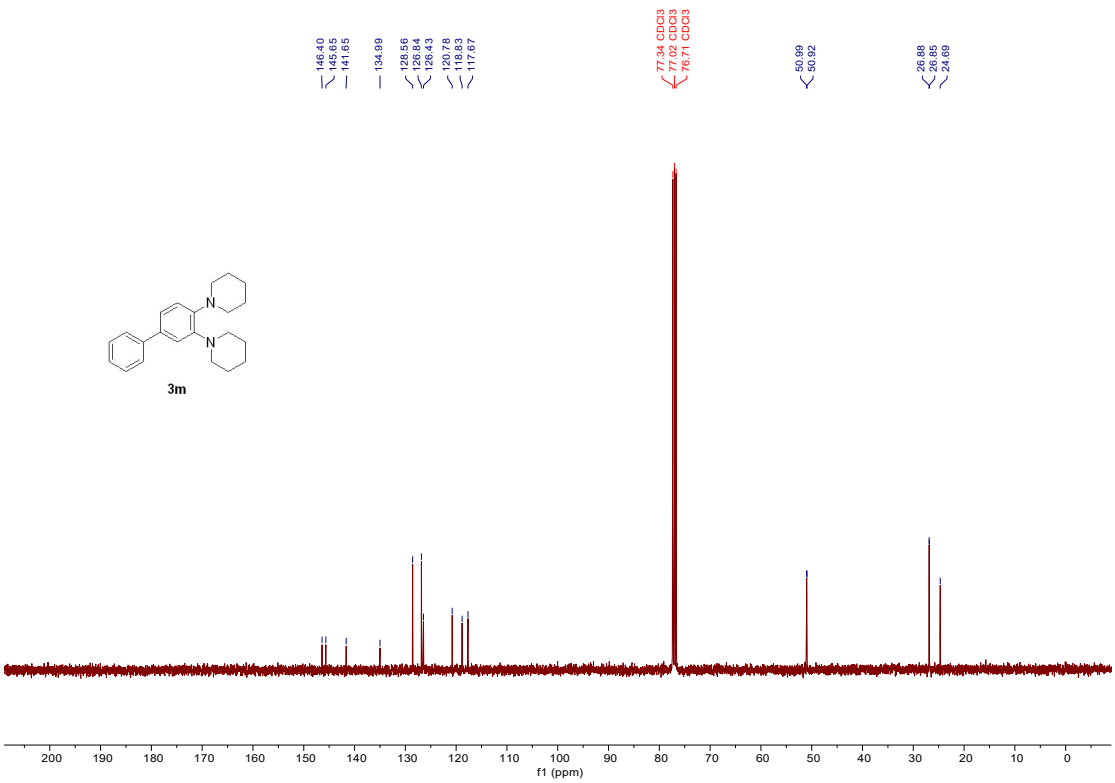

7.71
7.71
7.69
7.69
7.60
7.59
7.26 CDCl3
6.91
6.89
4.37
4.36
4.34
4.32
3.85
3.84
3.83
3.29
3.28
3.27
3.20
3.18
3.17
1.39
1.37
1.36
EtOOC
N
O
3j
1.02
0.97
1.00
2.04
7.98
4.02
4.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.79
148.49
143.75
125.31
124.78
119.95
117.80
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.51
67.41
60.83
49.95
49.57
14.56
EtOOC
N
O
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.290 CDCl3
7.029
7.018
7.012
7.003
6.965
6.947
6.938
6.929
6.655
6.914
3.849
3.837
3.826
3.197
3.186
3.175
3k
2.00
1.94
8.04
8.00
f1 (ppm)


144.624
123.357
118.563
77.476 CDCl3
77.160 CDCl3
76.841 CDCl3
67.701
50.158
3k
f1 (ppm)


7.57
7.55
7.42
7.40
7.38
7.30
7.28
7.27
7.26 CDCl3
7.18
7.16
7.15
7.13
6.97
6.95
3.12
1.76
1.75
1.73
1.72
1.70
1.61
1.60
1.58
1.57
1.55
3m
1.98
1.99
0.96
1.98
1.00
7.92
8.12
4.05
f1 (ppm)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145.65
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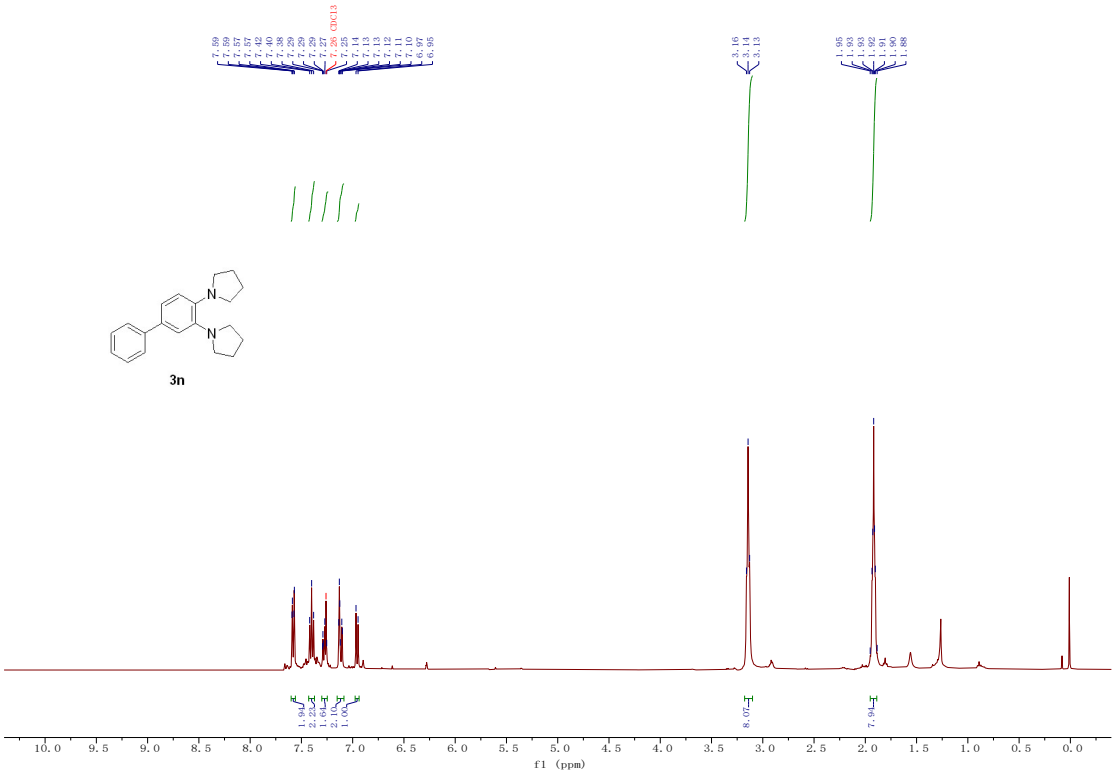
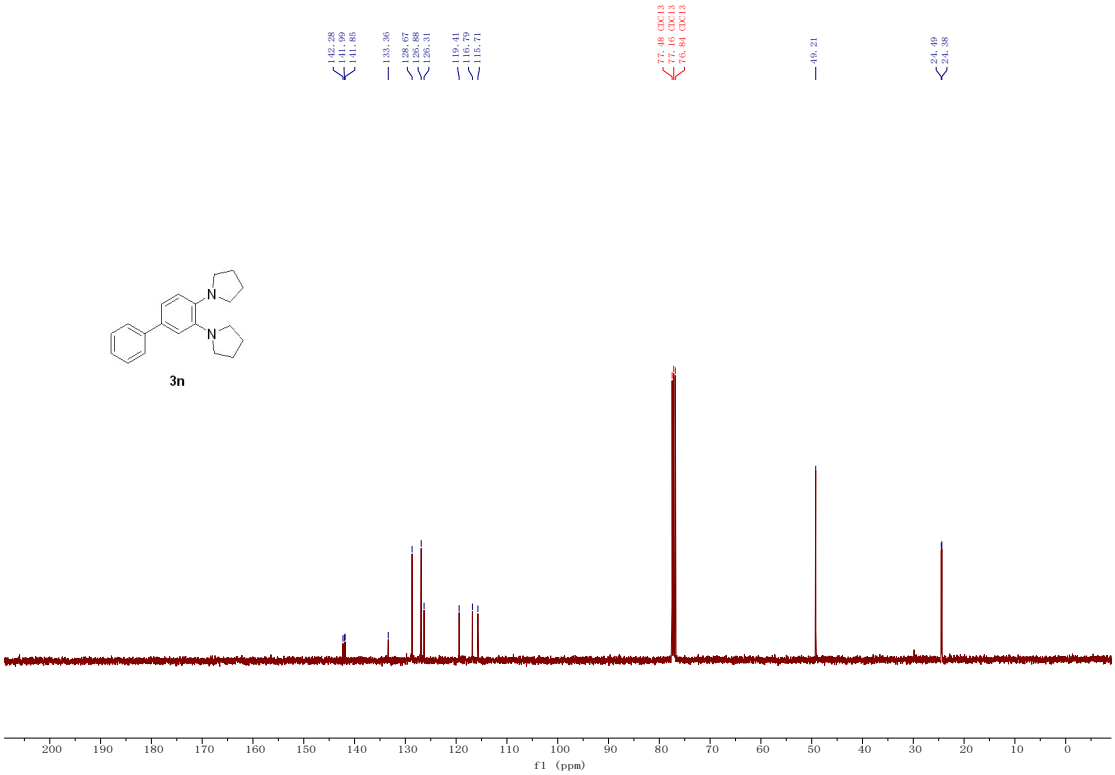
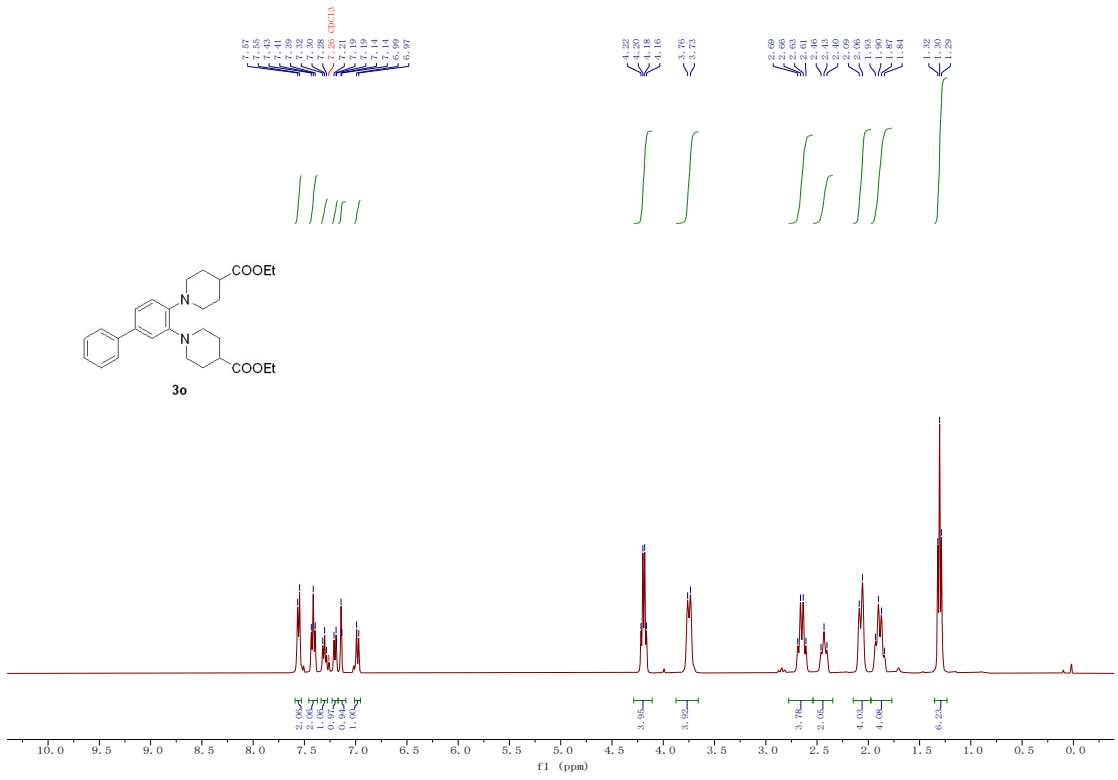
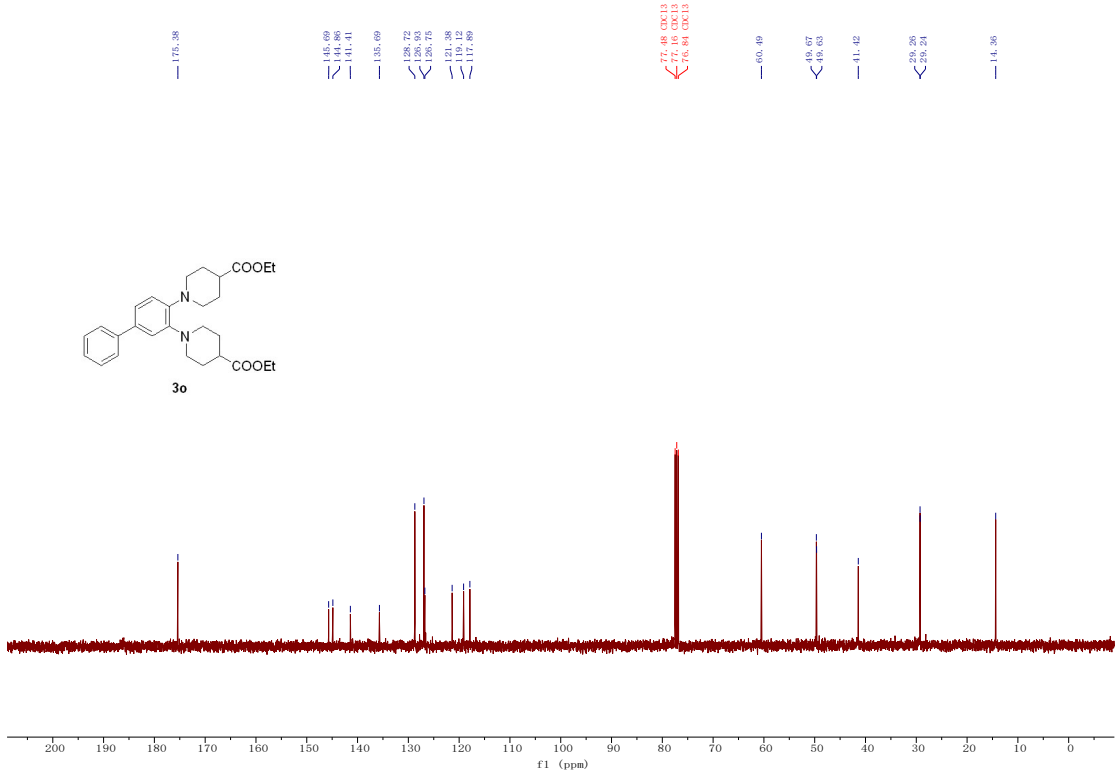
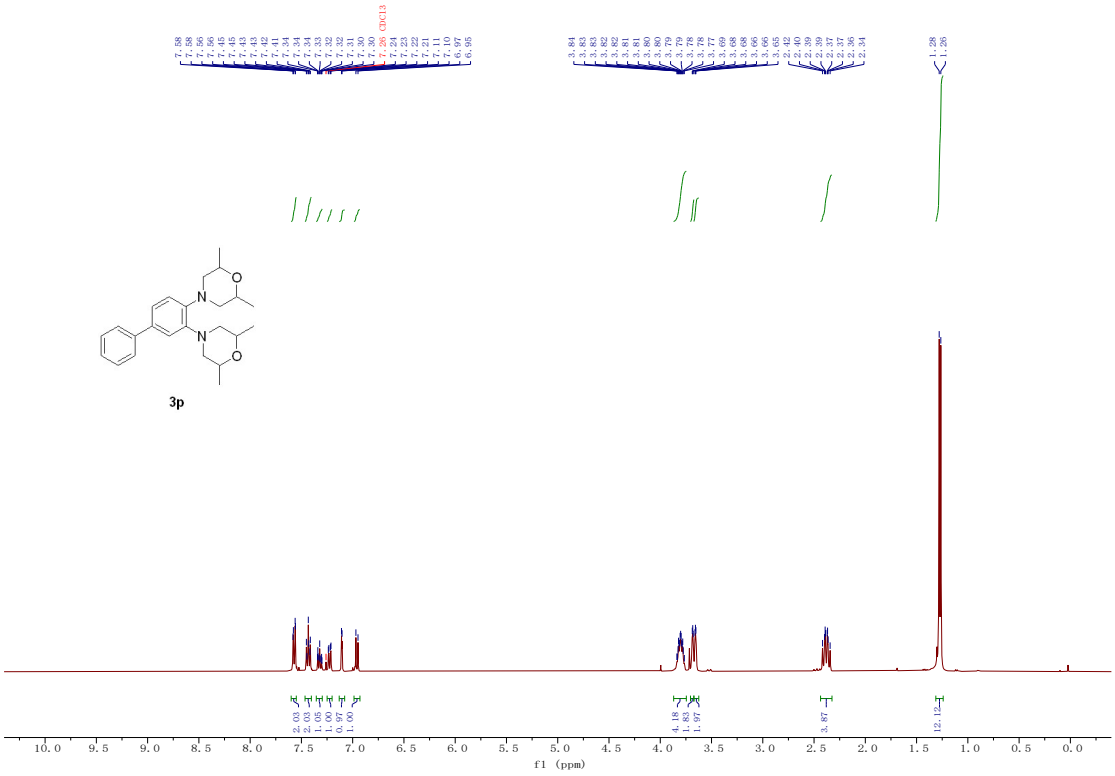
128.56
126.84
126.43
120.78
118.83
117.67
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
50.99
50.92
26.88
26.85
24.69
3m
f1 (ppm)

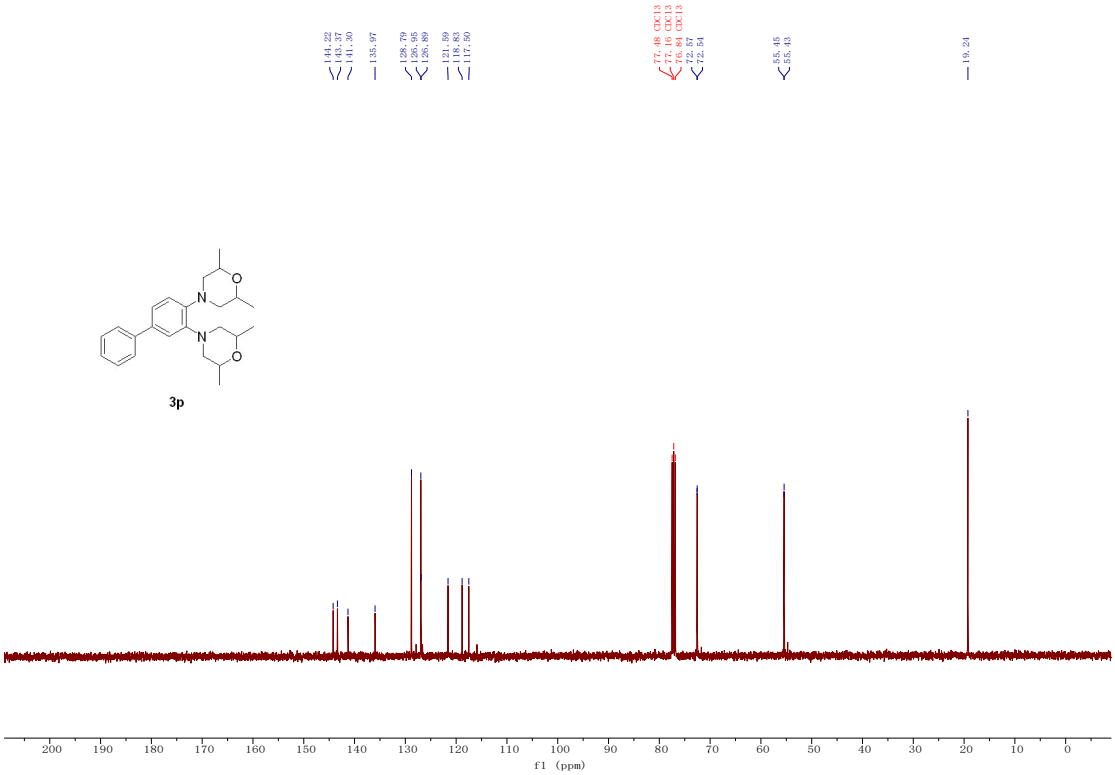

7.59
7.59
7.57
7.57
7.42
7.40
7.38
7.29
7.29
7.27
7.26 CDCl3
7.25
7.14
7.13
7.13
7.12
7.11
7.10
6.97
6.95
3.16
3.14
3.13
1.95
1.93
1.93
1.92
1.91
1.90
1.88
N
N
3n
1.94
2.22
1.64
2.10
1.00
8.07
7.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.28
141.99
141.85
133.36
128.67
126.88
126.31
119.41
116.79
115.71
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
49.21
24.49
24.38
N
N
3n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


COOEt
COOEt
3o
f1 (ppm)


COOEt
COOEt
3o
f1 (ppm)


7.58
7.56
7.45
7.43
7.42
7.41
7.34
7.33
7.32
7.30
7.26 CDCl3
7.24
7.23
7.22
7.21
7.11
7.10
6.97
6.95
3.84
3.83
3.82
3.81
3.80
3.79
3.78
3.77
3.69
3.68
3.66
3.65
2.42
2.40
2.39
2.37
2.36
2.34
1.28
1.26
O
N
N
O
3p
2.03
2.03
1.05
1.00
0.97
1.00
4.18
1.83
1.97
3.87
12.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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143.37
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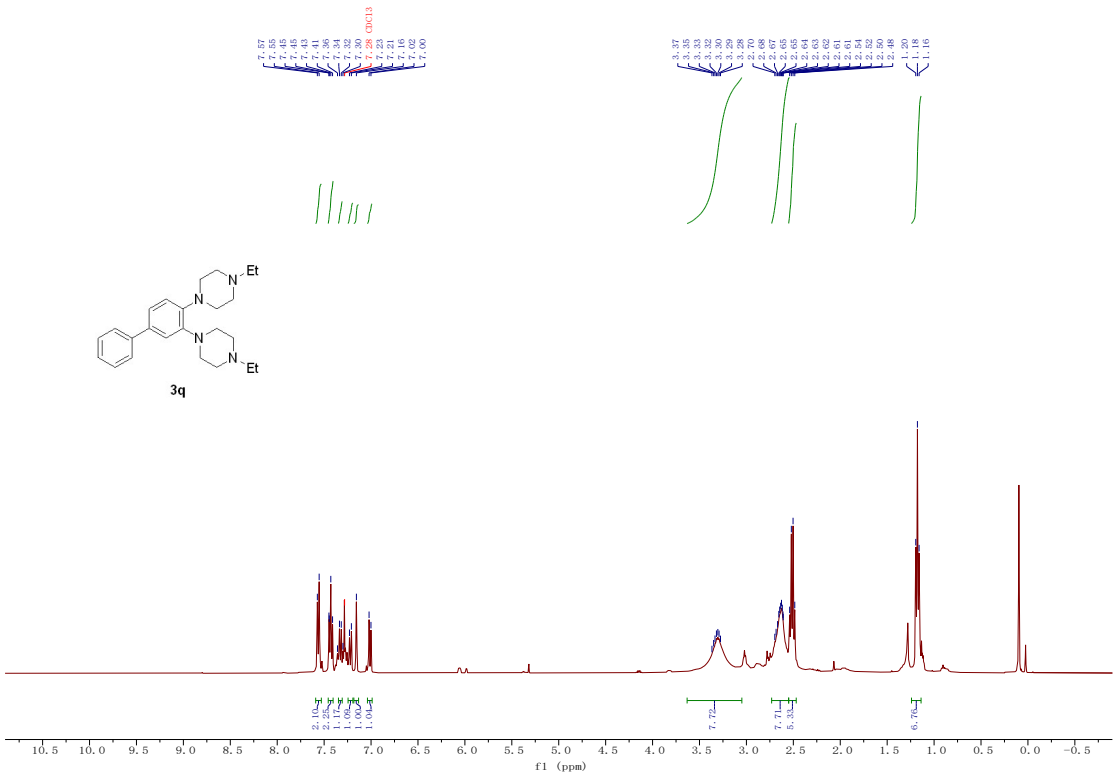
126.95
126.89
121.59
118.83
117.50
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
72.87
72.54
55.45
55.43
19.24
O
N
N
O
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.45
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7.41
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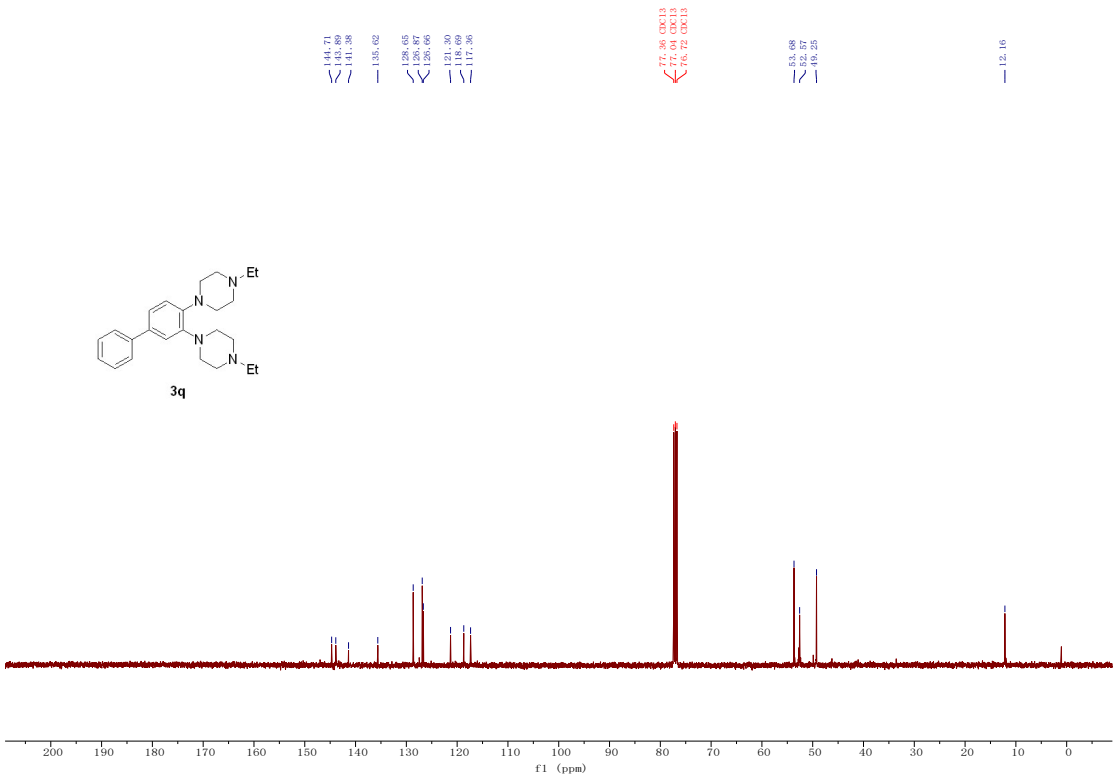
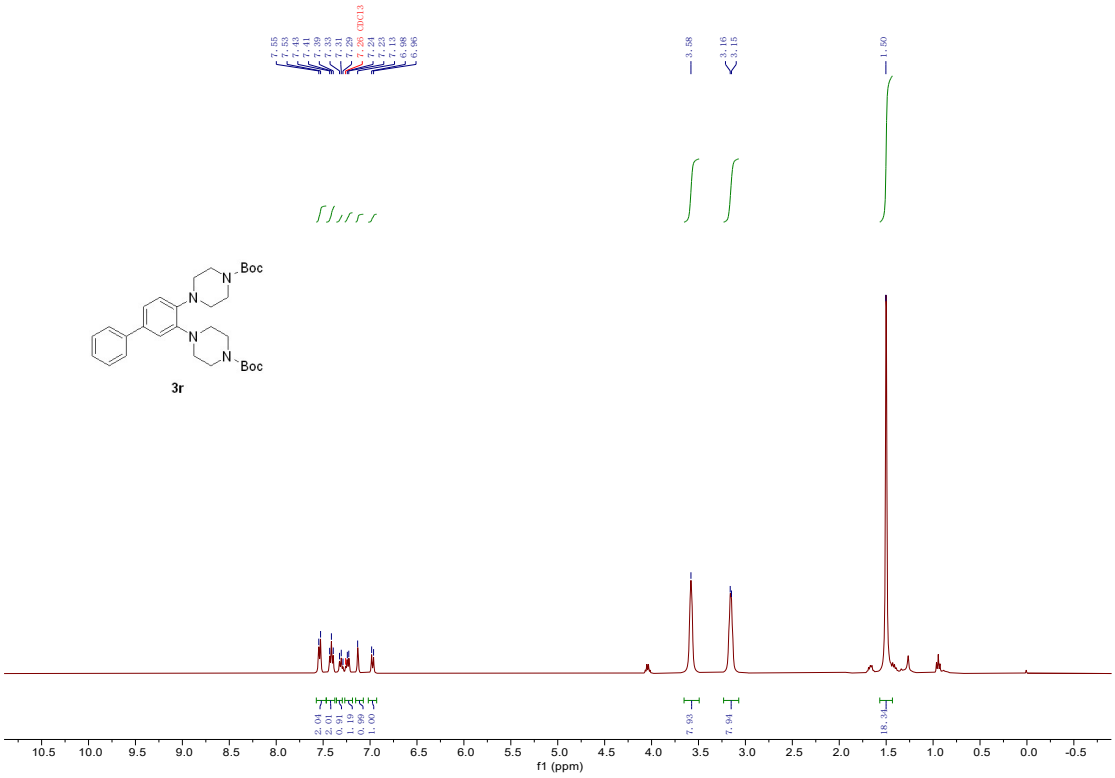
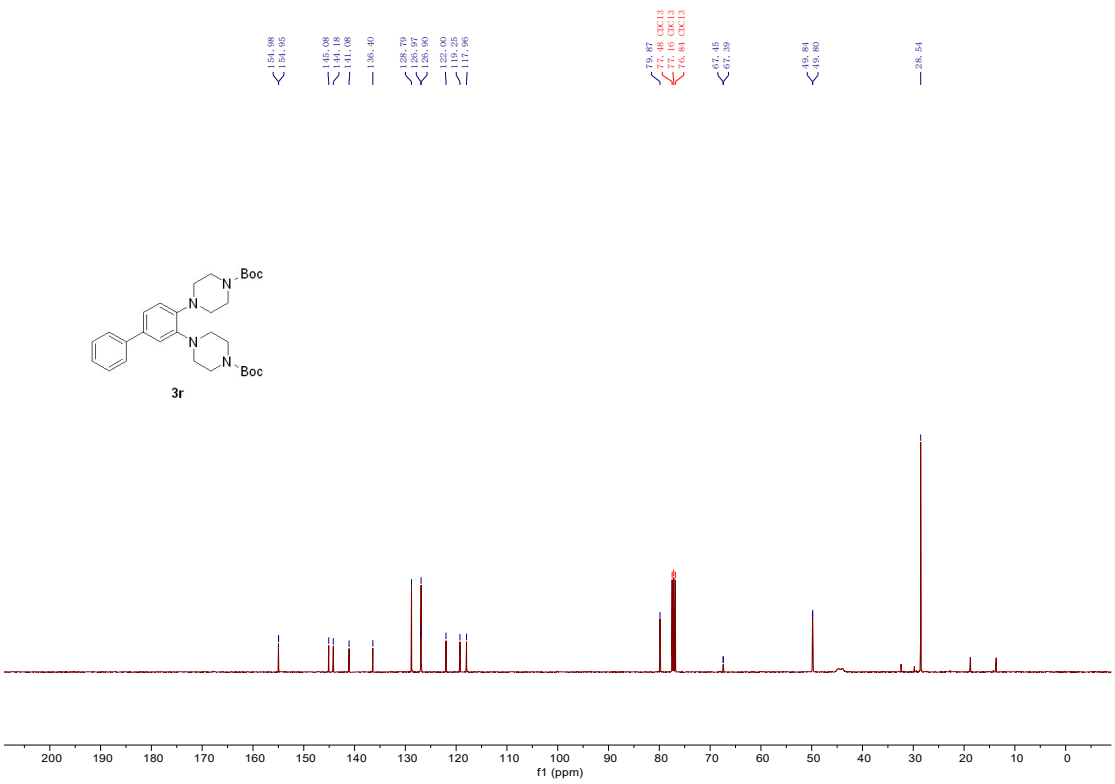
7.34
7.32
7.30
CDCl3
7.23
7.21
7.16
7.02
7.00
3.37
3.35
3.33
3.32
3.30
3.29
3.28
2.70
2.68
2.67
2.65
2.65
2.64
2.63
2.62
2.61
2.61
2.54
2.52
2.50
2.48
1.20
1.18
1.16
Et
N
N
N
N
Et
3q
2.10
2.25
1.14
1.00
1.00
1.04
7.72
7.71
5.33
6.76
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


144.71
143.88
141.38
135.62
128.65
126.87
126.66
121.30
118.69
117.36
77.36
CDCl3
77.04
CDCl3
76.72
CDCl3
53.68
52.57
49.25
12.16
Et
N
N
N
N
Et
3q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.55
7.53
7.43
7.41
7.39
7.33
7.31
7.29
7.26 CDCl3
7.24
7.23
7.13
6.98
6.96
3.58
3.16
3.15
1.50
Boc
Boc
3r
2.04
2.01
0.91
1.93
0.99
1.00
7.93
7.94
18.34
f1 (ppm)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154.95
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141.08
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126.97
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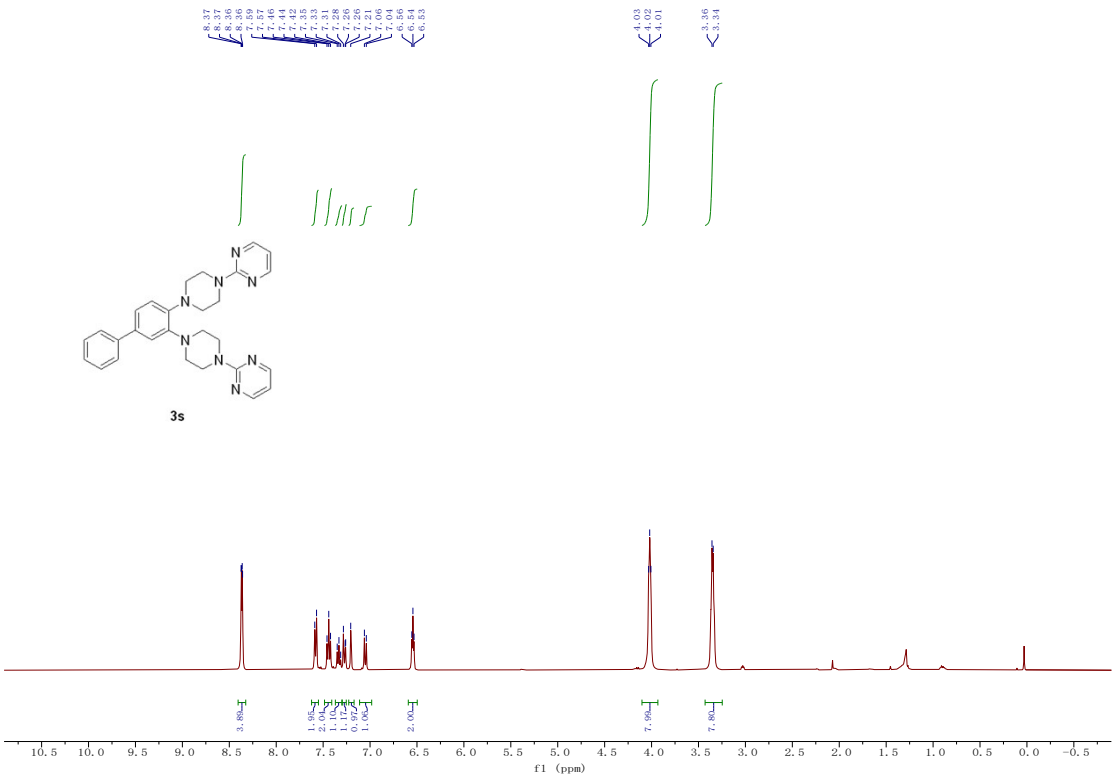
122.00
119.25
117.96
79.87
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.45
67.39
49.84
49.80
28.54
Boc
Boc
3r
f1 (ppm)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8.36
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7.57
7.46
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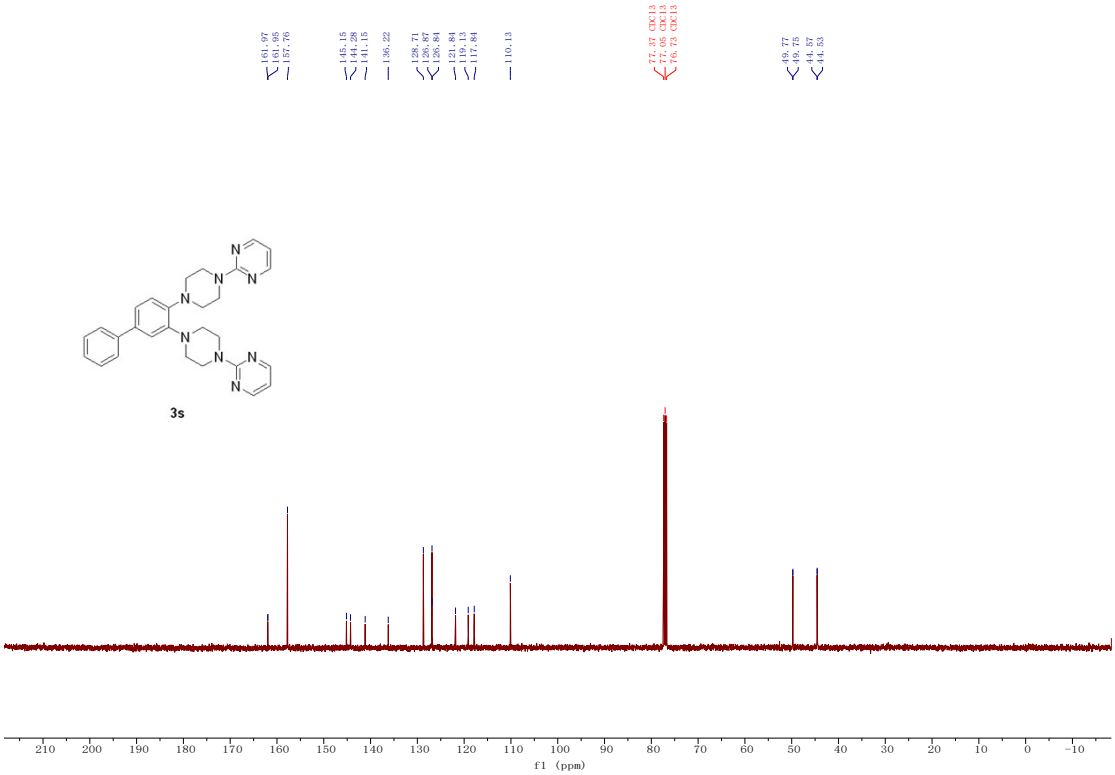
7.35
7.33
7.31
7.28
7.26
7.21
7.06
7.04
6.56
6.54
6.53
4.03
4.02
4.01
3.36
3.34
3s
3.80
1.95
2.04
1.10
1.17
0.97
1.04
2.00
7.99
7.80
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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161.95
157.76
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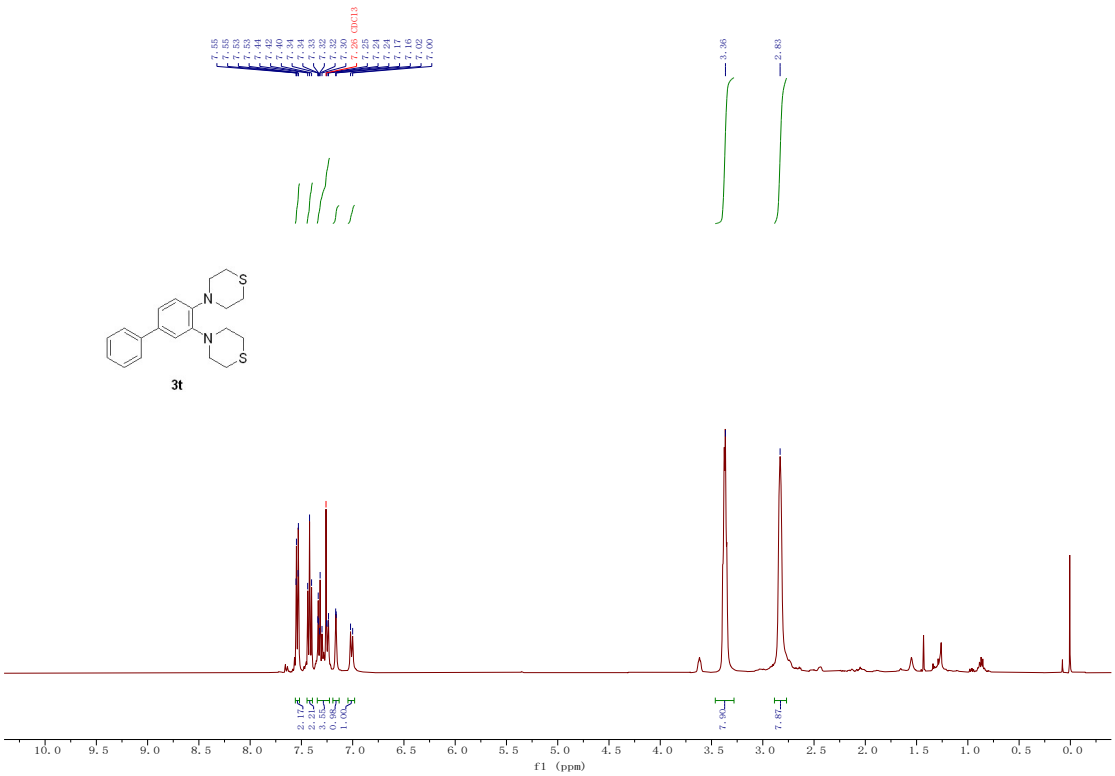
144.28
141.15
136.22
128.71
126.87
126.84
121.84
119.13
117.84
110.13
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
49.77
49.75
44.57
44.53
3s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.55
7.55
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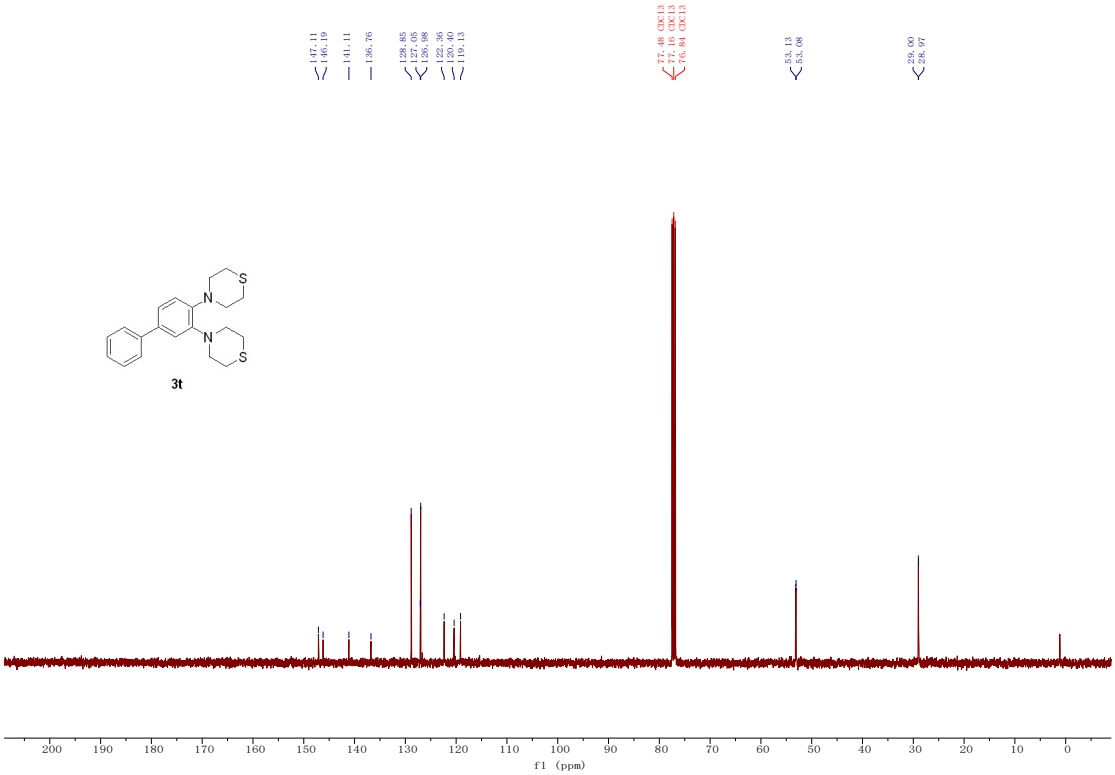
7.44
7.42
7.40
7.34
7.33
7.32
7.30
7.26 CDCl3
7.24
7.24
7.17
7.16
7.02
7.00
3.36
2.83
3t
2.17
2.21
2.04
0.98
1.00
7.90
7.87
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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126.98
122.36
120.40
119.13
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
53.13
53.08
29.00
28.97
3t
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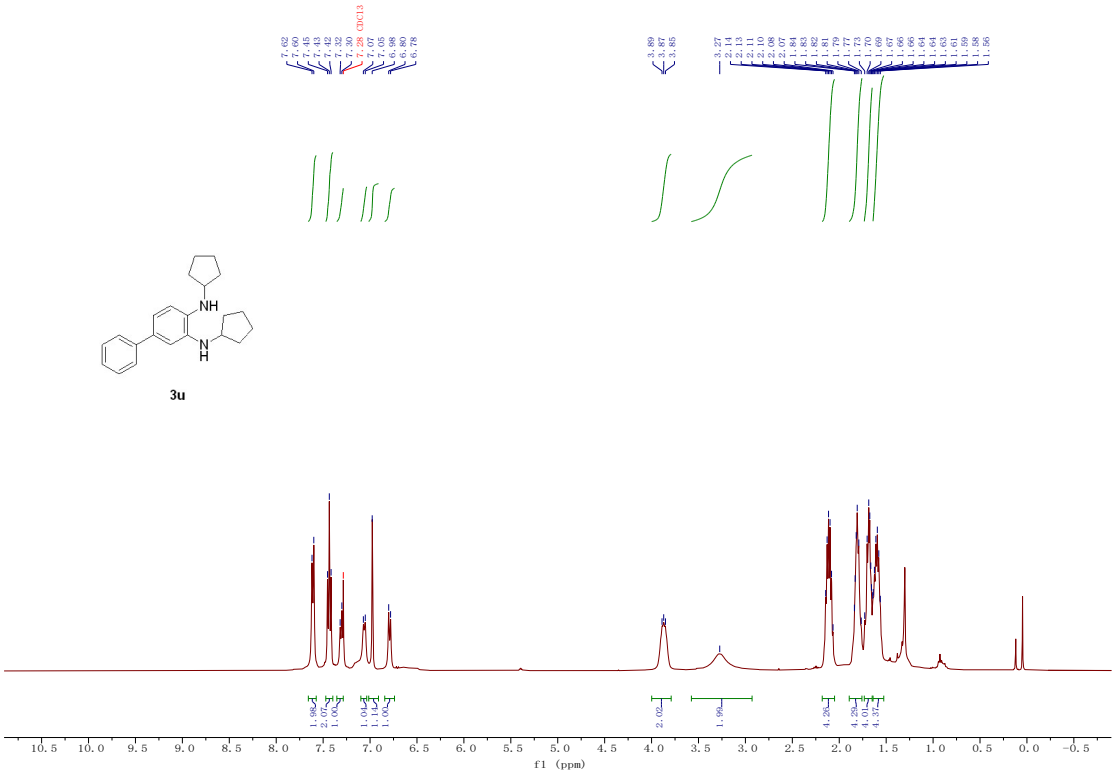
f1 (ppm)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1.67
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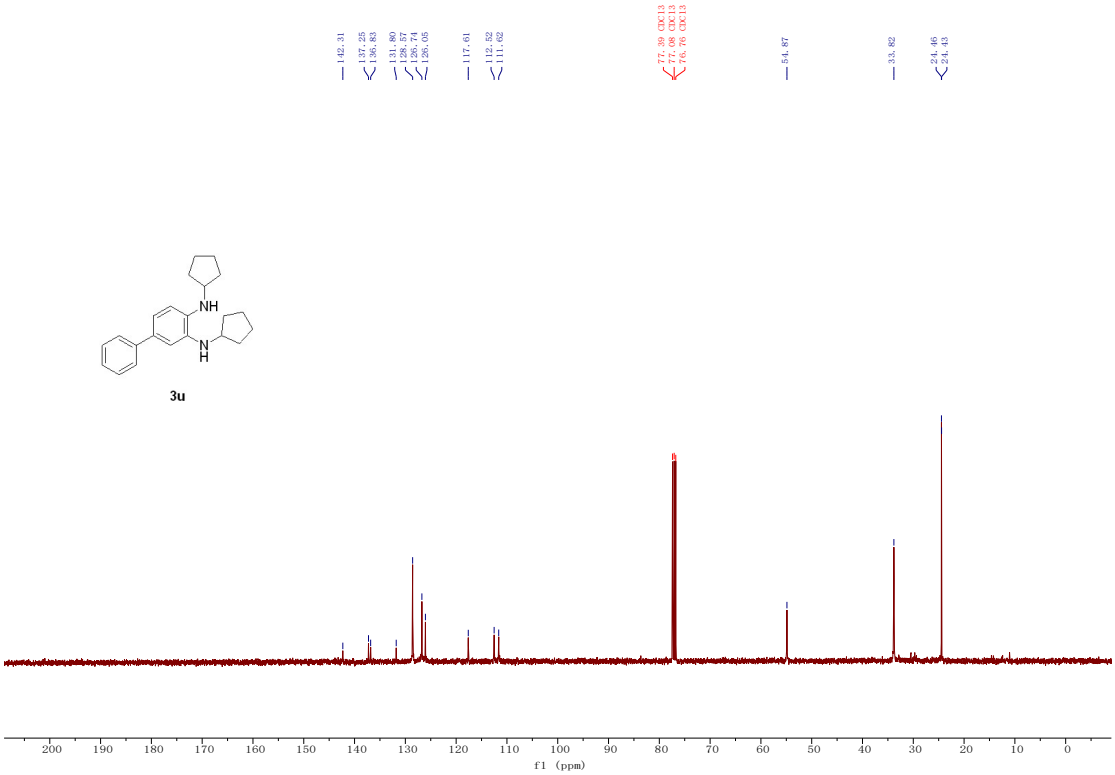
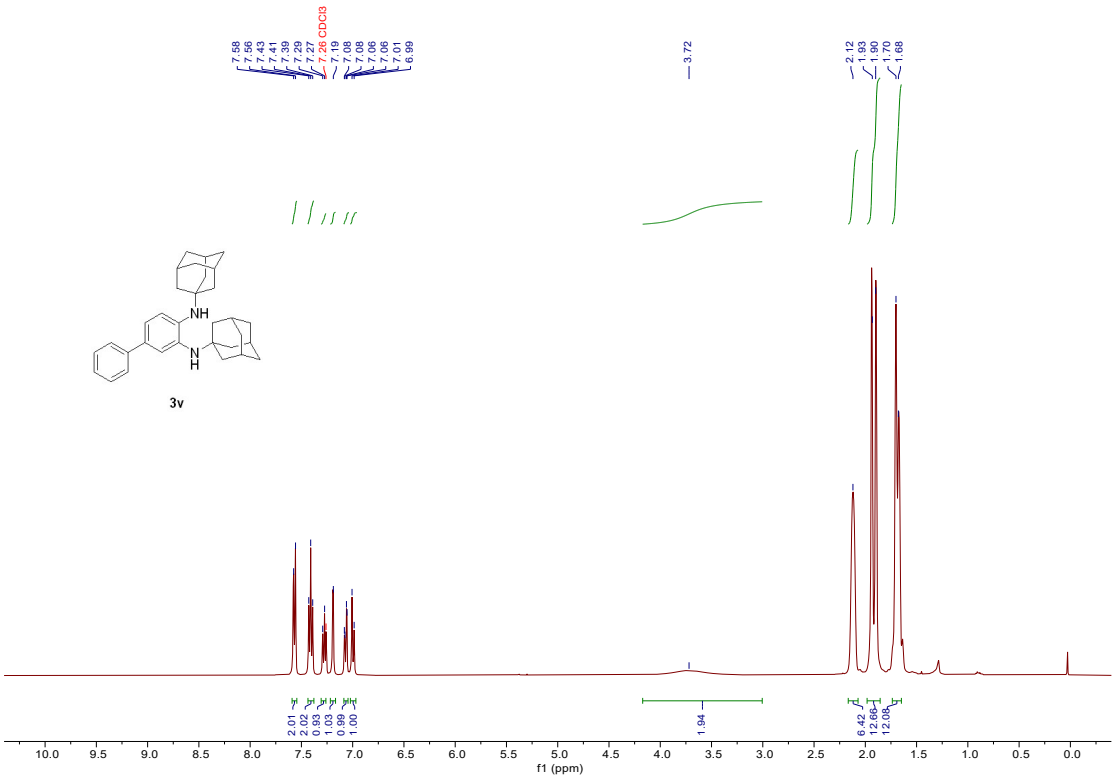
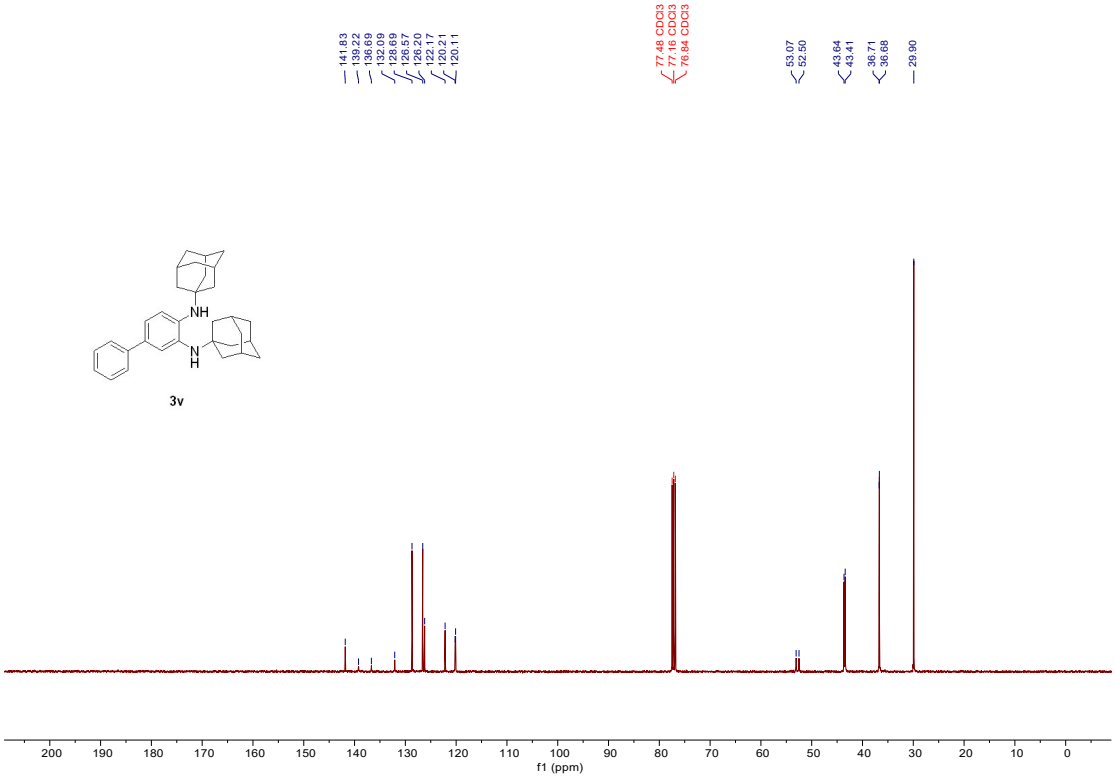
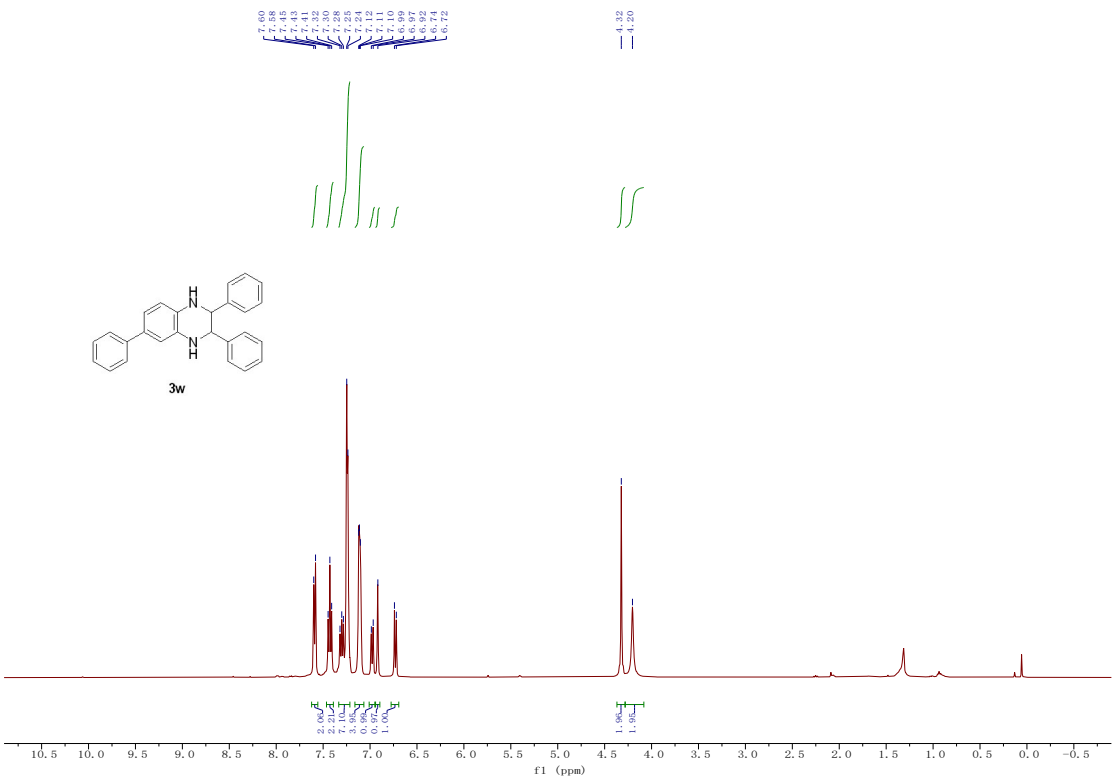
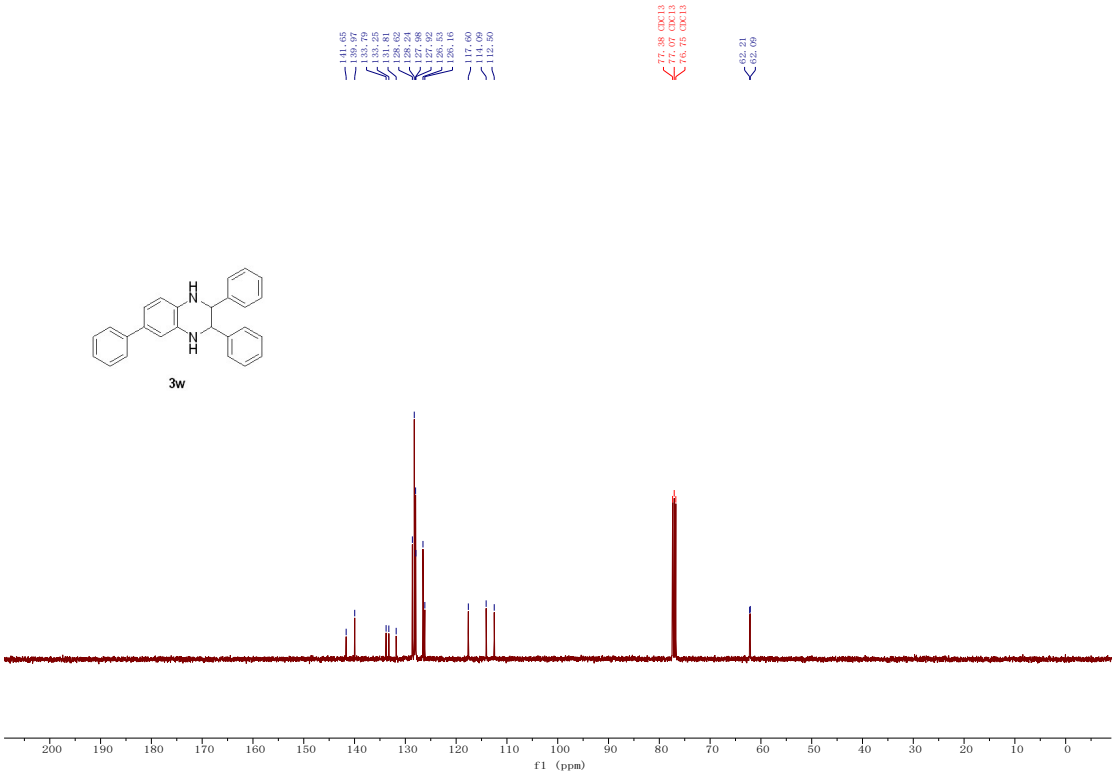
1.65
1.64
1.63
1.61
1.59
1.58
1.56
NH
N
H
3u
1.98
2.07
1.00
1.04
1.14
1.00
2.02
1.99
4.28
4.29
4.01
4.37
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

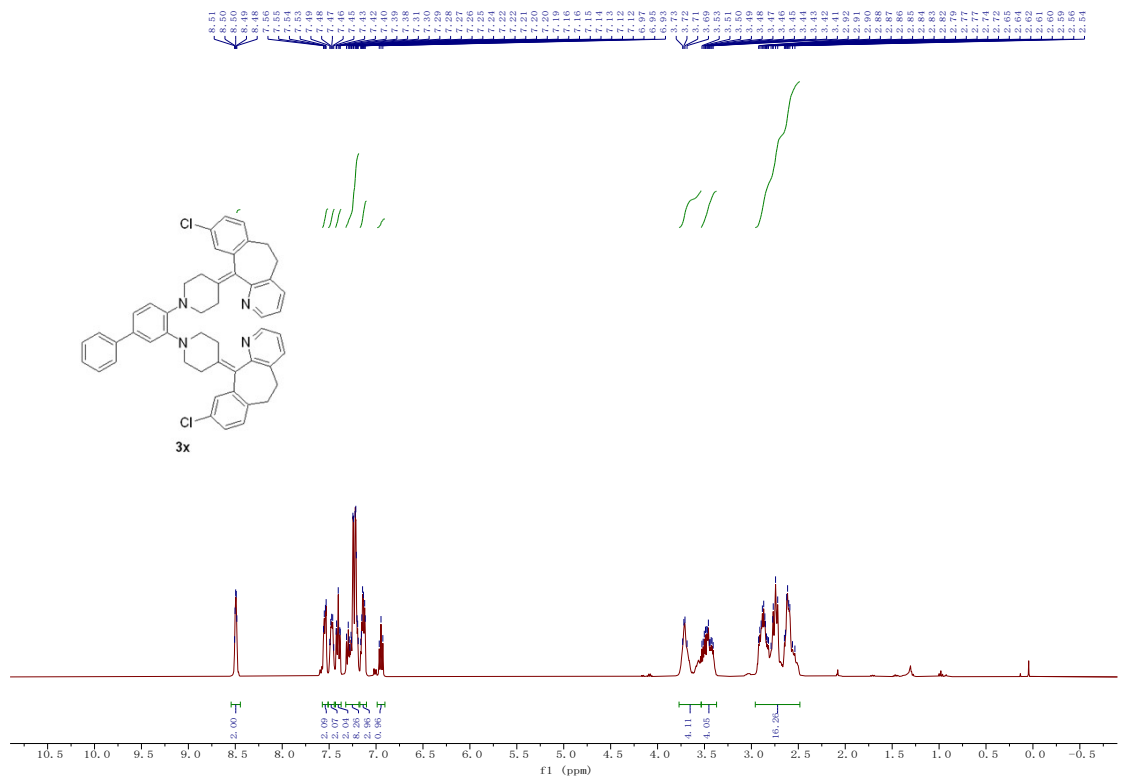

142.31
137.25
136.83
131.80
128.57
126.74
126.05
117.61
112.52
111.62
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
54.87
33.82
24.46
24.43
NH
N
H
3u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

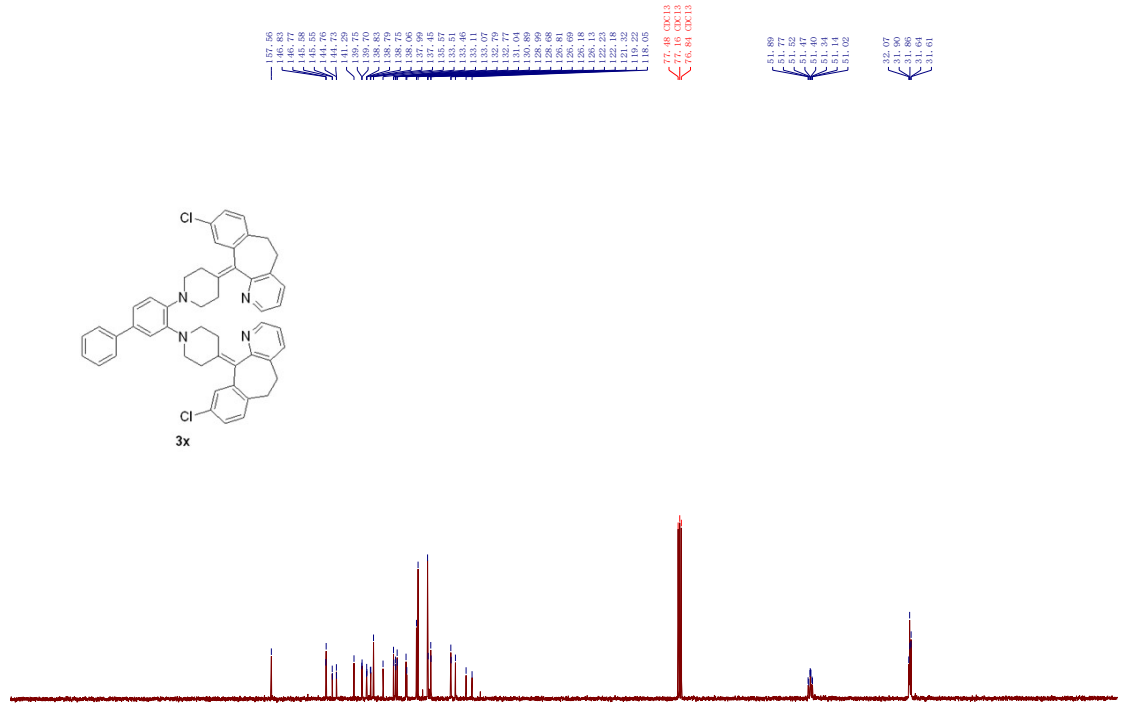

7.58
7.56
7.43
7.41
7.39
7.29
7.27
7.26 CDCl3
7.19
7.08
7.08
7.06
7.06
7.06
7.01
6.99
3.72
2.12
1.93
1.90
1.70
1.68
NH
N
H
3v
2.01
2.02
0.93
1.03
0.99
1.00
1.94
6.42
12.66
12.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

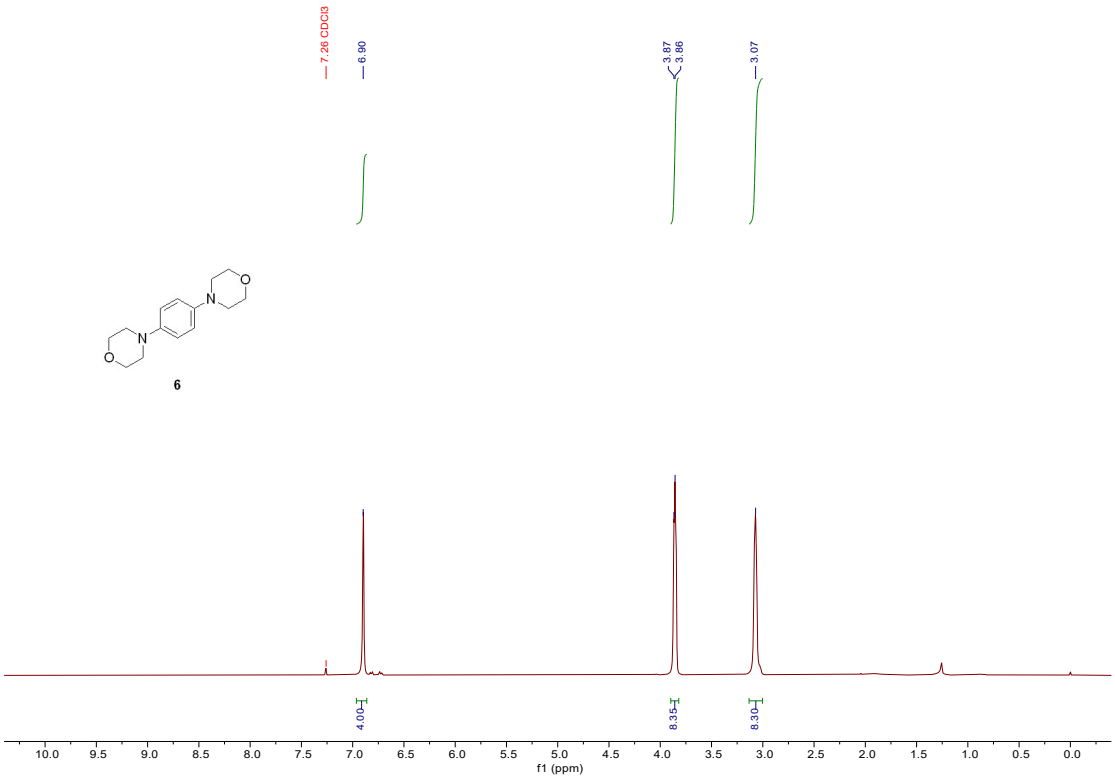

141.83
139.22
136.69
132.09
128.69
126.57
126.20
122.17
120.21
120.11
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
53.07
52.50
43.64
43.41
36.71
36.68
29.90
NH
N
H
3v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

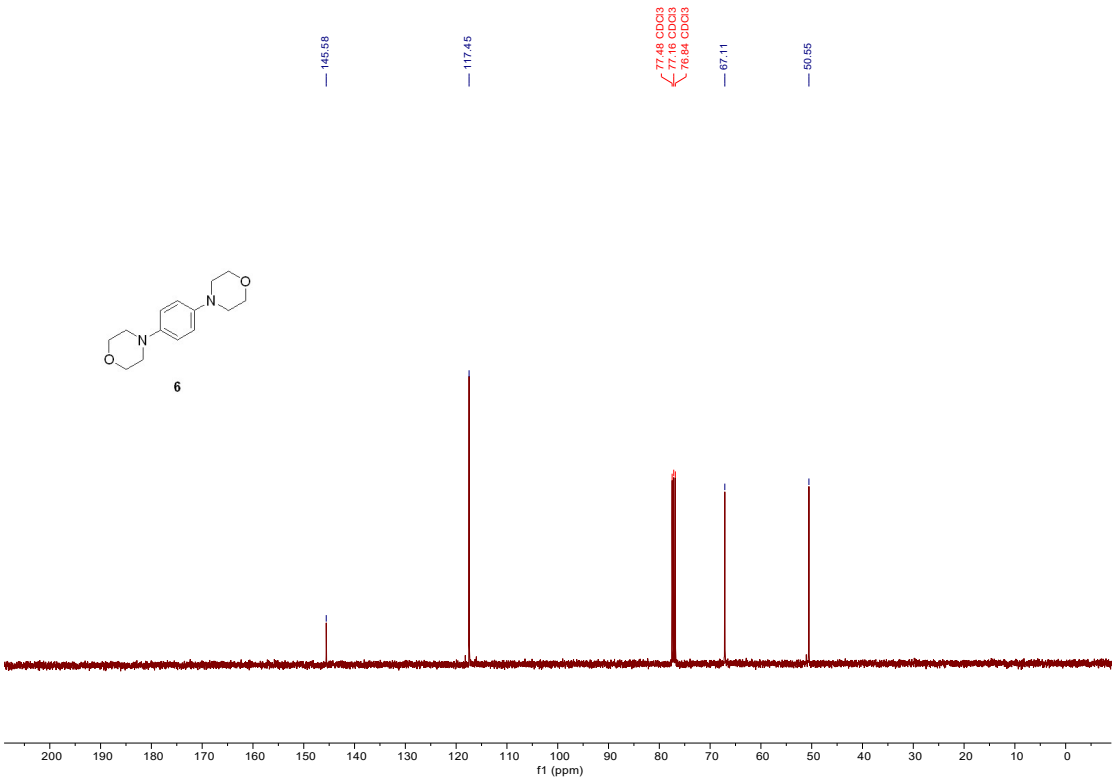

7.60
7.58
7.45
7.43
7.41
7.32
7.30
7.28
7.25
7.24
7.12
7.11
7.10
6.99
6.97
6.92
6.74
6.72
4.32
4.30
3w
2.00
2.21
7.10
3.96
3.93
0.97
1.00
1.96
1.96
f1 (ppm)

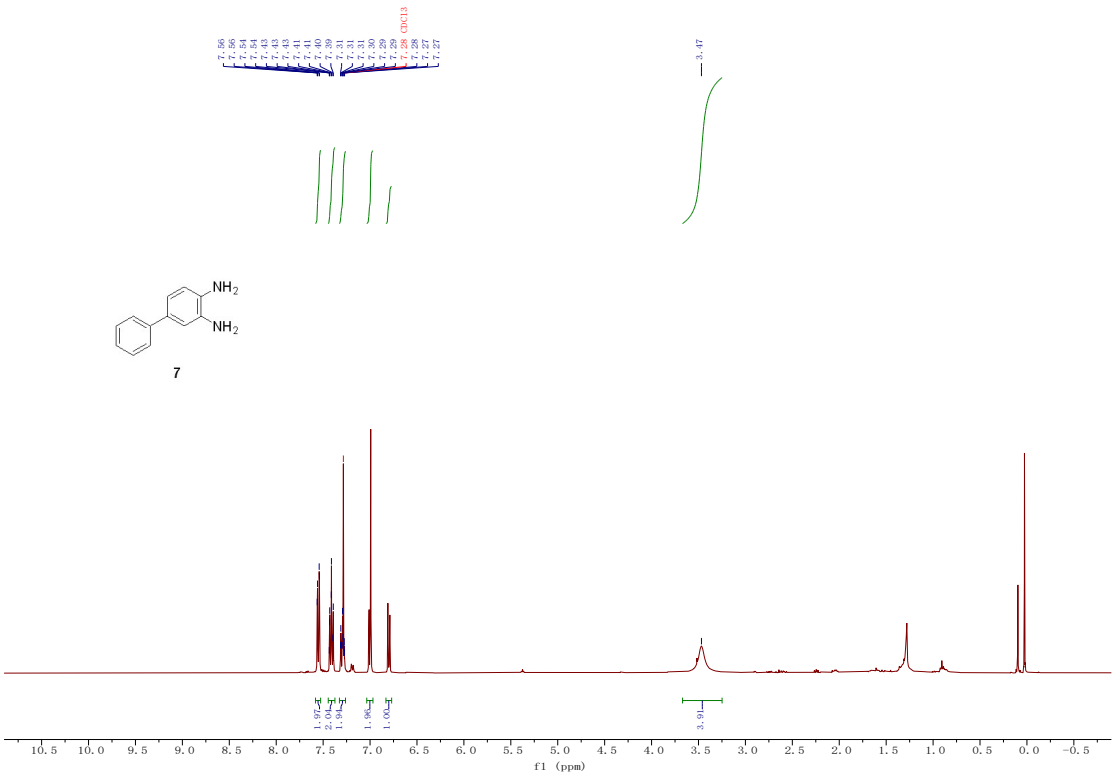

141.65
139.97
131.79
133.25
131.81
128.62
128.21
127.98
127.92
126.53
126.16
117.60
114.69
112.80
77.38 CDCl3
77.07 CDCl3
76.75 CDCl3
62.21
62.09
3w
f1 (ppm)

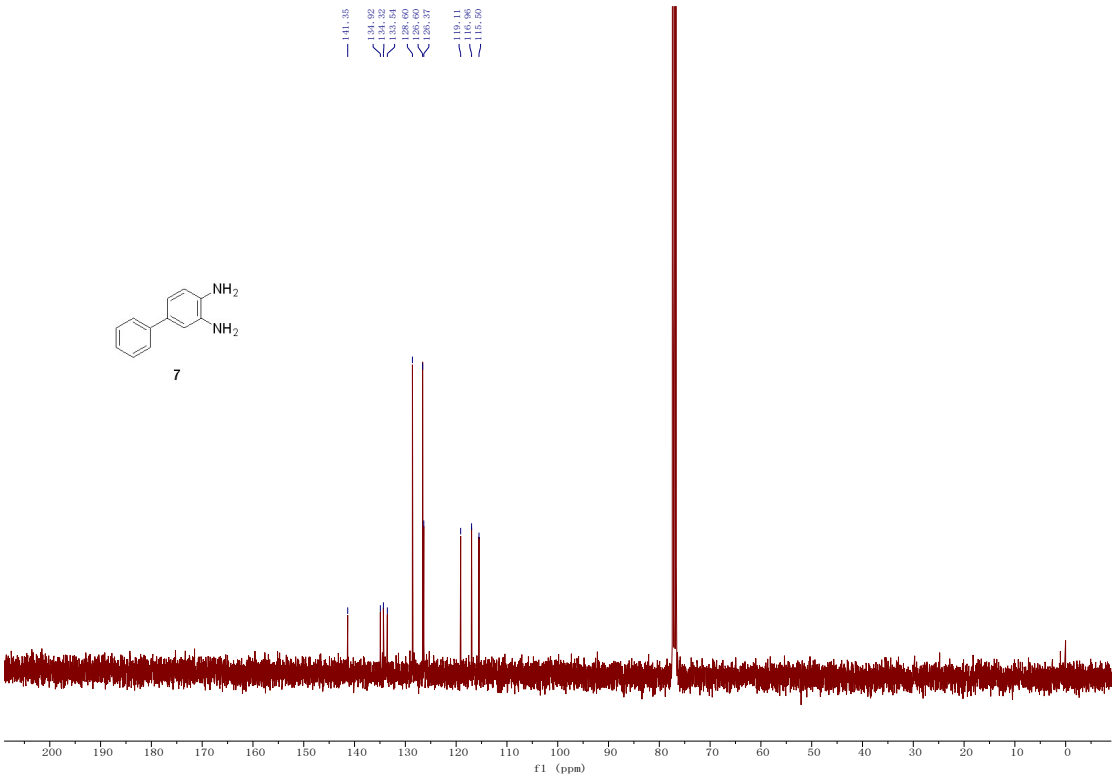

Cl
N
N
N
N
Cl
3x
f1 (ppm)

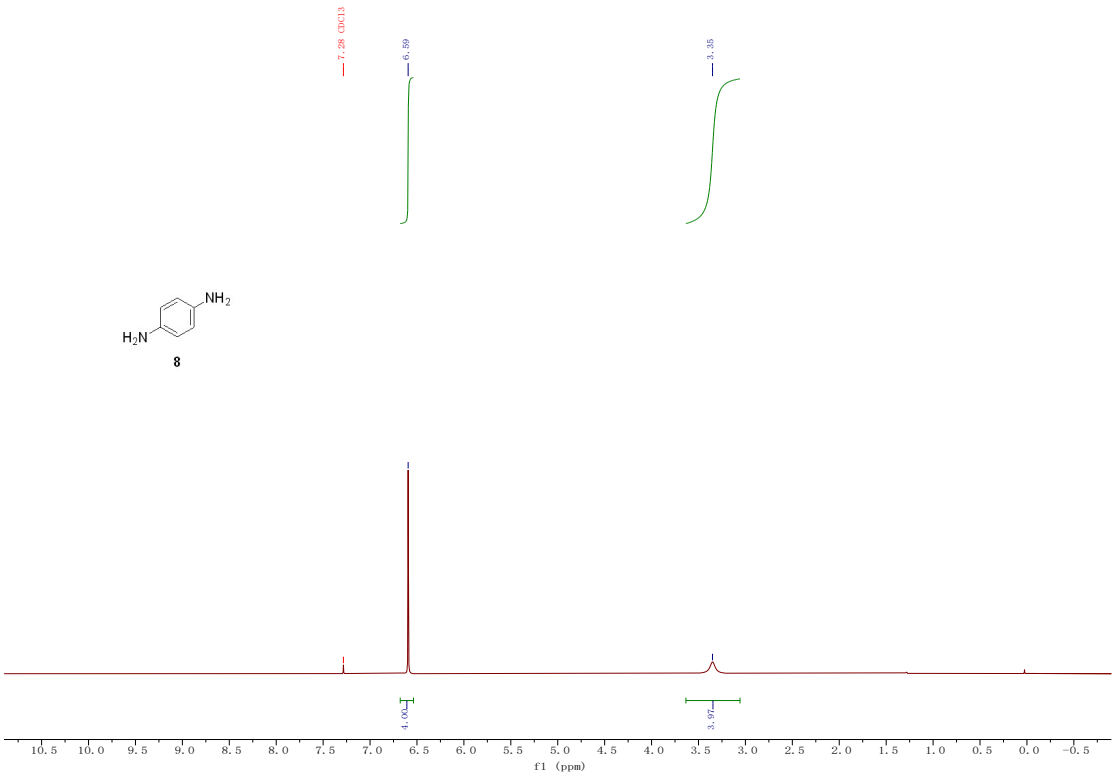

Cl
N
N
N
N
Cl
3x

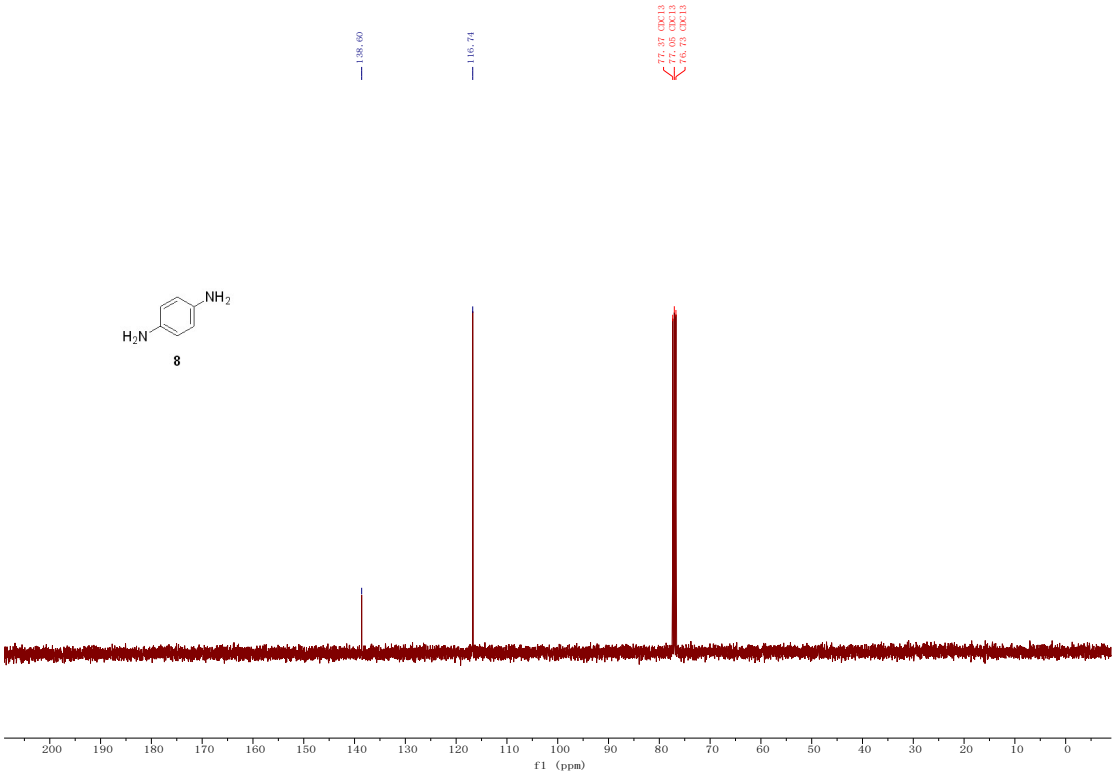

7.26 CDCl3
6.90
3.87
3.86
3.07
6
4.00
8.35
8.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

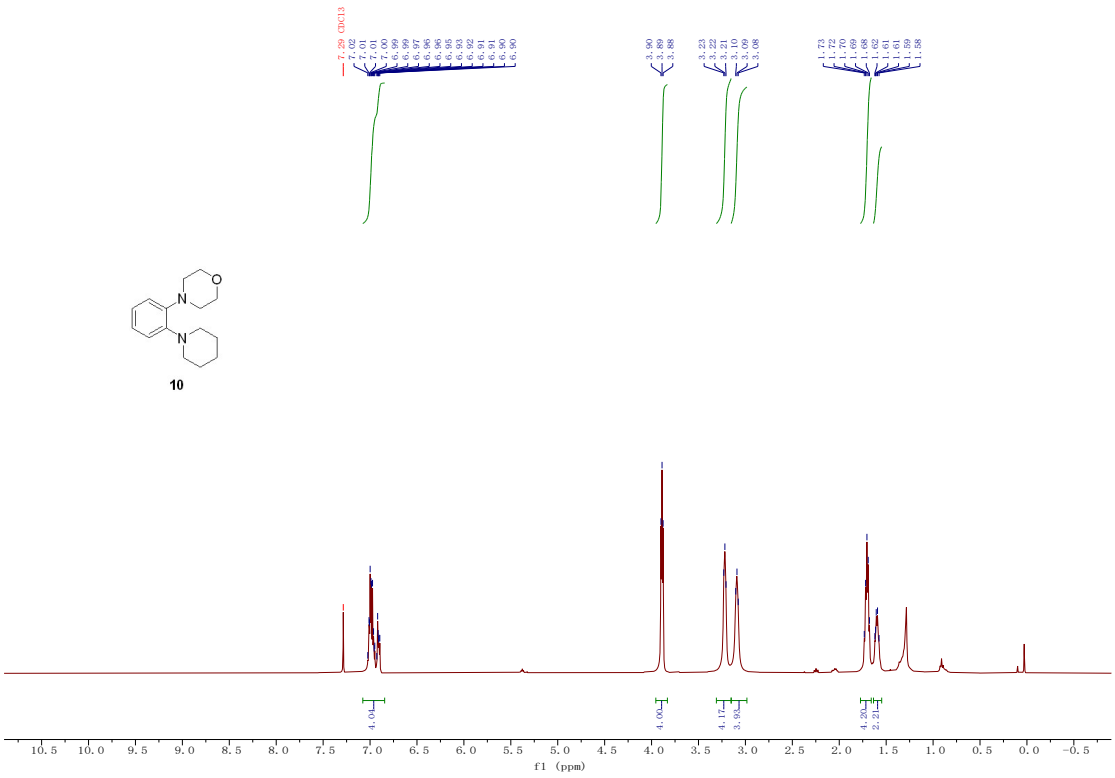

145.58
117.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.11
50.55
6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.56
7.56
7.54
7.54
7.43
7.43
7.41
7.41
7.40
7.39
7.31
7.31
7.30
7.29
7.28
7.28
CDCl3
7.27
7.27
3.47
NH2
NH2
7
1.97
2.04
1.94
1.96
1.00
3.91
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

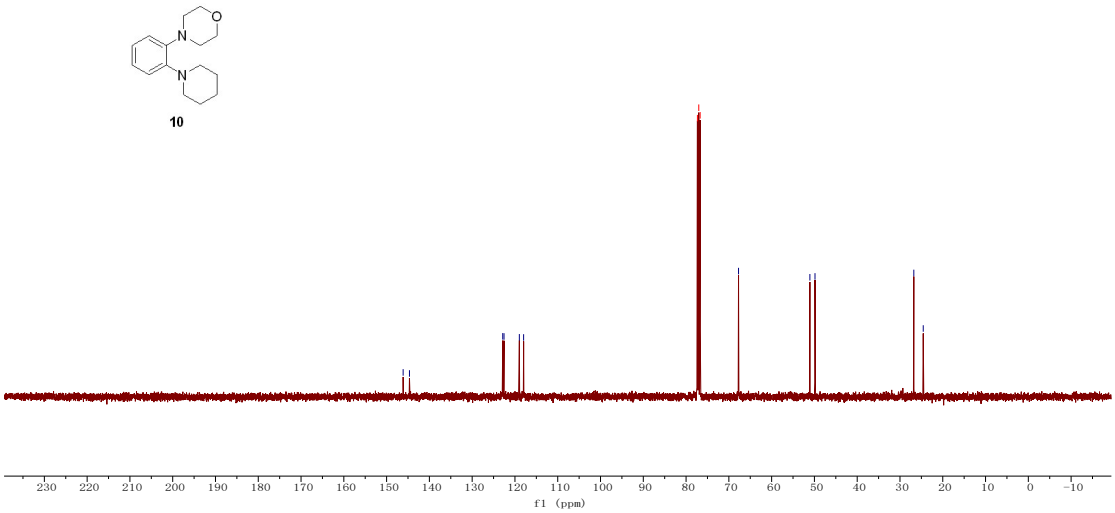

141.35
134.92
134.32
133.34
128.60
126.60
126.37
119.11
116.96
115.30
NH2
NH2
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.28 CDCl3
6.59
3.35
NH2
H2N
8
4.00
3.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


138.60
116.74
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
NH2
H2N
8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.29 CDCl3
7.02
7.01
7.01
7.00
6.99
6.99
6.97
6.96
6.96
6.95
6.93
6.92
6.91
6.91
6.90
6.90
3.90
3.89
3.88
3.23
3.22
3.21
3.10
3.09
3.08
1.73
1.72
1.70
1.69
1.68
1.62
1.61
1.61
1.59
1.58
4.04
4.00
4.17
3.93
4.20
2.21
f1 (ppm)

10


146.14
144.66
122.86
122.55
118.97
117.97
77.35 CDCl3
77.03 CDCl3
76.72 CDCl3
67.74
61.06
49.86
26.77
24.56
f1 (ppm)

10