

**One-Pot Reductive Amination of Carbonyl Compounds with Nitro Compounds
via Ir-Catalyzed Transfer Hydrogenation**

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Supporting Information

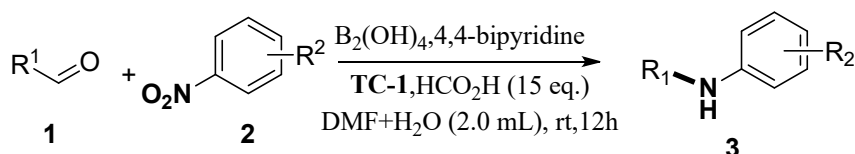
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A. General Information

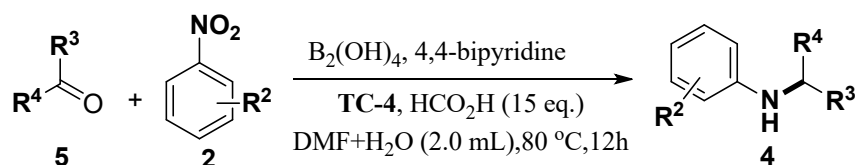
^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz for ^1H ; 100 MHz for ^{13}C), using CDCl_3 as solvent and TMS as an internal standard (CDCl_3 $\delta_{\text{H}} = 7.26$ ppm, downfield from TMS, $\delta_{\text{C}} = 77.16$ ppm). GC analyses were performed on a GC-7900 chromatograph with an FID and equipped with an AT.SE-30 capillary column (internal diameter: 0.32 mm, length: 30 mm). The materials used in the experiments were all purchased and without further purification. High-resolution mass spectra (HRMS) were recorded by a LCMS-IT-TOF mass spectrometer. Melting points were determined on a melting point instrument.

B. General Procedure for preparation of 3 [1]



To a 25 mL dried Schlenk tube were added nitrobenzene (1.0 mmol), $\text{B}_2(\text{OH})_4$ (3.0 mmol), and 4,4-bipyridine (0.05 mmol) and stirred in the DMF (1.0 mL) at room temperature for 5 minutes, then the aldehydes (0.5 mmol, 1.0 equiv.), Ir catalyst (1 mol %), HCO_2H (15.0 equiv.) and water (1.0 mL) were added successively. The mixture was stirred at room temperature for 12 h. After the completion of reaction, the mixture was diluted with H_2O (15.0 mL), neutralized with NaHCO_3 , and extracted with EtOAc (10 mL x 3). The organic extract then was washed with brine (10 mL x 3) and dried over anhydrous MgSO_4 and concentrated in vacuum, which was purified by flash column chromatography on silica gel to afford the desired product 3.

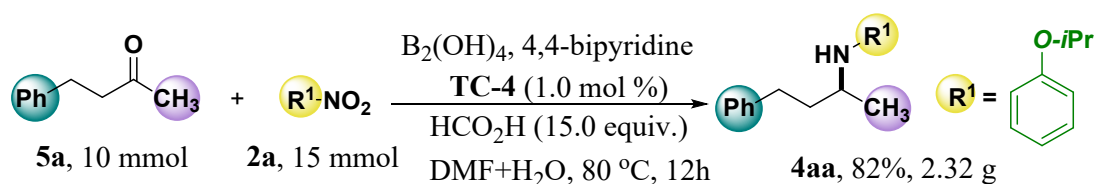
C. General Procedure for preparation of 4 [1]



To a 25.0 mL dried Schlenk tube were added nitrobenzene (0.75 mmol), $\text{B}_2(\text{OH})_4$ (2.25 mmol), and 4,4-bipyridine (0.0375 mmol) and stirred in the DMF (1.0 mL) at room temperature for 5.0 minutes, then the ketones (0.5 mmol, 1.0 equiv.), Ir catalyst (1.0 mol %), HCO_2H (15.0 equiv.) and water (1.0 mL) were added into the Schlenk

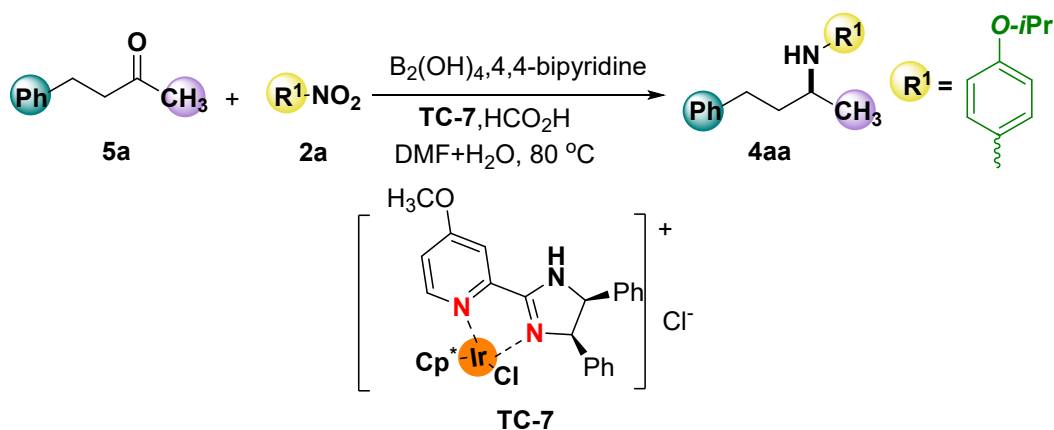
tube successively. The mixture was stirred at 80 °C for 12 h. After the completion of reaction, the mixture was diluted with H₂O (15.0 mL), neutralized with NaHCO₃, and extracted with EtOAc (10 mL x 3). The organic extract then was washed with brine (10 mL x 3) and dried over anhydrous MgSO₄ and concentrated in vacuum, which was purified by flash column chromatography on silica gel to afford the desired product **4**.

D. Large scale synthesis of **4aa**.^[1]



To a 100.0 mL dried Schlenk tube were added the mixture of **2a** (15 mmol, 1.5 equiv.), B₂(OH)₄ (45.0 mmol), 4,4-bipyridine (0.5 mmol), and DMF (25.0 mL) and stirred for 5.0 min, after which the **5a** (10.0 mmol, 1.0 equiv.), Ir catalyst (0.1 mol %), HCO₂H (15.0 equiv.) and water (25.0 mL) were added. The mixture was stirred at 80 °C for 12 h. After the completion of reaction, the mixture was diluted with H₂O (50.0 mL), neutralized with NaHCO₃, and extracted with EtOAc (20.0 mL x 3). The organic extract then was washed with brine (20.0 mL x 3) and dried over anhydrous MgSO₄ and concentrated in vacuum, which was purified by flash column chromatography (hexane/ethyl acetate = 30/1) on silica gel to afford the product of **4aa**.

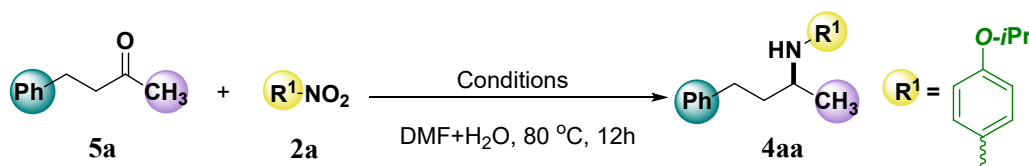
E. Asymmetric synthesis of **4aa**.^[1]



To a 25.0 mL dried Schlenk tube were added the mixture of **2a** (0.75 mmol, 1.5

equiv.), B₂(OH)₄ (2.25 mmol), 4,4-bipyridine (0.025 mmol) and DMF (1.0 mL) and stirred for 5.0 min, after which the **5a** (0.5 mmol, 1.0 equiv.), **TC-7** (1.0 mol %), HCO₂H (15.0 equiv.) and water (1.0 mL) were added. The mixture was stirred at 80 °C for 12 h. After the completion of reaction, the mixture was diluted with H₂O (15.0 mL), neutralized with NaHCO₃, and extracted with EtOAc (10.0 mL x 3). The organic extract then was washed with brine (10.0 mL x 3) and dried over anhydrous MgSO₄ and concentrated in vacuum. The residue was purified by chromatography on silica gel with (hexane/ethyl acetate = 30/1) as the eluent to afford the product of **4aa** in 83% yield. The enantiomeric excess was determined by HPLC using Daicel Chiralpak OD-H column, hexane/i-PrOH 85:15, flow rate 1.0 mL/min, UV detection at 220 nm, *t*_{minor} = 7.511 min, *t*_{major} = 7.881 min, 0% *ee*.

F. Control experiment



Entry	B ₂ (OH) ₄	4,4-Bipyridine	TC-4	HCO ₂ H	yield ^b
1	-	+	+	+	30
2	+	-	+	+	n.d
3	-	-	+	+	n.d
4	-	+	-	+	n.d
5	-	-	+	+	n.d
6 ^a	+	+	+	+	97
7	+	+	+	-	n.d

^[a] Reaction conditions: **5a** (0.5 mmol), **2a** (0.75 mmol), solvent (2.0 mL), catalyst (1.0% mol), hydrogen donor (15.0 equiv.), B₂(OH)₄(2.25 mmol), 4,4-bipyridine (0.0375 mmol) at 80 °C under air for 12h. ^[b] Determined by GC-MS.

G. Analysis Data for the Products

N-benzyl-4-isopropoxyaniline(**3aa**)

114.52 mg, 90% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): R_f = 0.26.

¹H NMR (400 MHz, CDCl₃) δ 7.36-7.29 (m, 4H), 7.27-7.23 (m, 1H), 6.76 (d, *J* = 8.3

Hz, 2H), 6.55 (d, $J = 8.3$ Hz, 2H), 4.36-4.24 (m, 1H), 4.24 (s, 2H), 1.27 (d, $J = 6.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 142.5, 139.6, 128.5, 127.5, 127.1, 117.8, 113.9, 71.0, 49.1, 22.1. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{16}\text{H}_{19}\text{NO}$, 242.1545; found, 242.1547.

4-isopropoxy-*N*-(2-methylbenzyl)aniline (3ba)

100.73 mg, 79% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.26$. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, $J = 6.4$ Hz, 1H), 7.18 (s, 3H), 6.78 (dd, $J = 8.9$, 2.3 Hz, 2H), 6.57 (dd, $J = 8.7$, 2.0 Hz, 2H), 4.39-4.32 (m, 1H), 4.20 (s, 2H), 2.35 (s, 3H), 1.28 (dd, $J = 6.0$, 2.3 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 142.8, 137.2, 136.3, 130.3, 128.2, 127.3, 126.0, 117.9, 113.7, 71.1, 47.1, 22.1, 18.9. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}$, 256.1701; found, 256.1690.

4-isopropoxy-*N*-(4-methylbenzyl)aniline (3ca)

87.98 mg, 69% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.26$. ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 7.9$ Hz, 2H), 6.78-6.76 (m, 2H), 6.58-6.56 (m, 2H), 4.38-4.32 (m, 1H), 4.22 (s, 2H), 2.34 (s, 3H), 1.28 (d, $J = 6.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 142.7, 136.8, 136.5, 129.2, 127.5, 117.9, 113.9, 71.1, 48.9, 22.2, 21.1. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}$, 256.1701; found, 256.1690.

4-isopropoxy-*N*-(2-methoxybenzyl)aniline (3da)

108.40 mg, 80% yield, brown solid, mp. 64.0-65.0 °C. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.26$. ^1H NMR (400 MHz, CDCl_3) δ 7.17 (d, $J = 7.4$ Hz, 1H), 7.10 (t, $J = 7.8$ Hz, 1H), 6.79-6.72 (m, 2H), 6.65-6.63 (m, 2H), 6.46 (dd, $J = 8.7$, 1.7 Hz, 2H), 4.24-4.18 (m, 1H), 4.14 (s, 2H), 3.68 (s, 3H), 1.15 (dd, $J = 6.1$, 1.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.2, 149.8, 142.7, 128.8, 128.0, 127.4, 120.3, 117.7, 114.1, 110.0, 70.8, 55.0, 44.2, 22.0. HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{17}\text{H}_{21}\text{NNaO}_2$, 294.1470; found, 294.1469.

4-isopropoxy-*N*-(3-methoxybenzyl)aniline (3ea)

111.11 mg, 82% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.26$. ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.22 (m, 1H), 6.95 (d, $J = 13.1$ Hz, 2H), 6.83-6.74 (m, 3H), 6.61-6.55 (m, 2H), 4.38-4.32 (m, 1H), 4.25 (s, 2H), 3.79 (d, $J = 1.7$ Hz, 3H),

1.28 (dd, $J = 6.1, 2.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.8, 150.1, 142.6, 141.4, 129.6, 119.8, 117.9, 114.0, 113.0, 112.6, 71.1, 55.2, 49.2, 22.2. HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{17}\text{H}_{21}\text{NNaO}_2$, 294.1470; found, 294.1469.

4-isopropoxy-*N*-(4-propoxybenzyl)aniline (3fa)

106.92 mg, 72% yield, yellow oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.26$. ^1H NMR (400 MHz, CDCl_3) δ 7.18 (d, $J = 8.0$ Hz, 2H), 6.78 (d, $J = 8.1$ Hz, 2H), 6.69 (d, $J = 8.5$ Hz, 2H), 6.50-6.48 (m, 2H), 4.29-4.23 (m, 1H), 4.09 (s, 2H), 3.81 (t, $J = 6.5$ Hz, 2H), 1.76-1.67 (m, 2H), 1.20 (d, $J = 6.1$ Hz, 6H), 0.94 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.3, 150.0, 142.7, 131.4, 128.8, 117.9, 114.5, 113.9, 71.1, 69.4, 48.6, 22.5, 22.1, 10.5. HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{17}\text{H}_{25}\text{NNaO}_2$, 322.1783; found, 322.1790.

4-isopropoxy-*N*-(4-isopropylbenzyl)aniline (3ga)

113.2 mg, 80% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.26$. ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, $J = 8.2$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 6.79 - 6.75 (m, 2H), 6.60-6.56 (m, 2H), 4.42-4.32 (m, 1H), 4.22 (s, 2H), 2.95-2.85 (m, 1H), 1.28 (d, $J = 6.1$ Hz, 6H), 1.24 (d, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 142.8, 136.9, 127.7, 126.6, 117.9, 113.9, 71.1, 48.9, 33.8, 24.0, 22.2. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{17}\text{H}_{25}\text{NO}$, 284.2014; found, 284.2030.

4-isopropoxy-*N*-(4-nitrobenzyl)aniline (3ha)

71.5 mg, 50% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.25$. ^1H NMR (400 MHz, CDCl_3) δ 8.21-8.13 (m, 2H), 7.53 (d, $J = 8.1$ Hz, 2H), 6.78-6.72 (m, 2H), 6.55-6.49 (m, 2H), 4.41 (s, 2H), 4.38-4.32 (m, 1H), 1.27 (d, $J = 6.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.5, 147.8, 147.0, 141.6, 127.7, 123.8, 117.8, 114.0, 71.0, 48.4, 22.1. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3$, 287.1396; found, 287.1381.

***N*-(2-fluorobenzyl)-4-isopropoxyaniline (3ia)**

108.78 mg, 84% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.25$. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.33 (m, 1H), 7.23-7.27 (m, 1H), 7.08-6.99 (m, 2H), 6.77-6.73 (m, 2H), 6.58 - 6.54 (m, 2H), 4.36-4.31 (m, 3H), 1.26 (d, $J = 6.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.0, 159.6, 150.2, 142.1, 129.4 (d, $J = 4.6$ Hz),

128.6 (d, $J = 8.1$ Hz), 126.5 (d, $J = 14.5$ Hz), 124.1 (d, $J = 3.5$ Hz), 117.8, 115.3, 115.1, 114.1, 70.9, 42.6 (d, $J = 4.1$ Hz), 22.1; ^{19}F NMR (377 MHz, CDCl_3) δ -119.1 (s, 1F). HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{17}\text{H}_{18}\text{FNO}$, 260.1451; found, 260.1455.

***N*-(2-aminobenzyl)-4-isopropoxyaniline (3ja)**

94.85 mg, 70% yield, brown solid, mp. 63.0-65.0 °C. TLC (hexane/ethyl acetate = 5/1, v/v): $R_f = 0.28$. ^1H NMR (400 MHz, CDCl_3) δ 7.15-7.11 (m, 2H), 6.81 (dd, $J = 8.7$, 1.8 Hz, 2H), 6.75-6.59 (m, 4H), 4.41-4.35 (m, 1H), 4.16 (s, 2H), 1.30 (dd, $J = 6.0$, 2.1 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.6, 146.0, 142.6, 130.0, 128.8, 123.1, 118.2, 117.8, 116.3, 115.8, 114.8, 71.0, 48.1, 22.1. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}$, 257.1654; found, 257.1652.

***N*-(2, 3-dimethylbenzyl)-4-isopropoxyaniline (3ka)**

111.64 mg, 83% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.29$. ^1H NMR (400 MHz, CDCl_3) δ 7.18 (d, $J = 7.1$ Hz, 1H), 7.12-7.05 (m, 2H), 6.79 (d, $J = 8.7$ Hz, 2H), 6.58 (d, $J = 8.7$ Hz, 2H), 4.39-4.33 (m, 1H), 4.21 (s, 2H), 2.31 (s, 3H), 2.26 (s, 3H), 1.29 (d, $J = 6.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 142.9, 137.1, 137.0, 135.1, 129.1, 126.6, 125.9, 125.5, 118.0, 115.1, 113.7, 71.2, 47.9, 22.2, 21.7, 20.4, 14.7. HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{18}\text{H}_{23}\text{NNaO}$, 292.1672; found, 292.1682.

***N*-(2, 5-dimethylbenzyl)-4-isopropoxyaniline (3la)**

100.88 mg, 75% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.27$. ^1H NMR (400 MHz, CDCl_3) δ 7.08 (s, 1H), 7.00 (d, $J = 7.6$ Hz, 1H), 6.93 (d, $J = 7.8$ Hz, 1H), 6.75-6.67 (m, 2H), 6.55-6.46 (m, 2H), 4.39-4.33 (m, 1H), 4.09 (s, 2H), 2.23 (d, $J = 8.6$ Hz, 6H), 1.21 (dd, $J = 6.1$, 1.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 143.0, 137.0, 135.6, 133.2, 130.3, 129.1, 128.0, 118.0, 113.8, 71.2, 47.3, 22.2, 21.0, 18.5. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{18}\text{H}_{23}\text{NO}$, 270.1858; found, 270.1873.

***N*-(2,4-dimethylbenzyl)-4-isopropoxyaniline (3ma)**

83.39 mg, 62% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.27$. ^1H NMR (400 MHz, CDCl_3) δ 7.11 (dd, $J = 7.2$, 2.8 Hz, 1H), 6.95-6.85 (m, 2H), 6.69 (dd, $J = 8.8$, 3.1 Hz, 2H), 6.48 (dd, $J = 8.8$, 3.1 Hz, 2H), 4.30-4.24 (m, 1H), 4.07 (d, $J =$

2.4 Hz, 2H), 2.23 (dd, $J = 6.8, 2.7$ Hz, 6H), 1.20 (dd, $J = 6.0, 3.3$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 142.9, 137.0, 136.2, 134.2, 131.2, 128.4, 126.7, 118.0, 113.7, 71.2, 47.0, 22.2, 21.0, 18.8. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{18}\text{H}_{23}\text{NO}$, 270.1858; found, 270.1839.

4-isopropoxy-*N*-(2,4,5-trimethylbenzyl)aniline (3na)

100.13 mg, 75% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.27$. ^1H NMR (400 MHz, CDCl_3) δ 6.81 (s, 2H), 6.74 (d, $J = 8.9$ Hz, 2H), 6.53 (d, $J = 8.9$ Hz, 2H), 4.32-4.26 (m, 1H), 4.06 (s, 2H), 2.27 (s, 6H), 2.20 (s, 3H), 1.22 (d, $J = 6.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.9, 143.3, 137.4, 137.1, 132.4, 129.0, 118.1, 113.5, 71.3, 43.1, 22.2, 20.9, 19.4. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{19}\text{H}_{25}\text{NO}$, 284.2014; found, 284.1995.

***N*-(4-fluoro-3-methylbenzyl)-4-isopropoxyaniline (3oa)**

101.01 mg, 74% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.26$. ^1H NMR (400 MHz, CDCl_3) δ 7.18-7.11 (m, 2H), 6.97-6.92 (m, 1H), 6.77 (dd, $J = 8.9, 2.1$ Hz, 2H), 6.56 (dd, $J = 8.9, 2.0$ Hz, 2H), 4.38-4.32 (m, 1H), 4.17 (s, 2H), 2.25 (s, 3H), 1.28 (dd, $J = 6.1, 2.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.4 (d, $J = 243.6$ Hz), 150.1, 142.5, 135.0 (d, $J = 3.5$ Hz), 130.6 (d, $J = 5.1$ Hz), 126.3 (d, $J = 8.0$ Hz), 124.8 (d, $J = 17.4$ Hz), 117.9, 114.9 (d, $J = 22.4$ Hz), 113.9, 71.0, 48.5, 22.1, 14.5 (d, $J = 3.5$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -112.8 (s, 1F). HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{17}\text{H}_{20}\text{FNO}$, 274.1607; found, 274.1590.

***N*-(2, 3-difluorobenzyl)-4-isopropoxyaniline (3pa)**

109.42 mg, 79% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.26$. ^1H NMR (400 MHz, CDCl_3) δ 7.11 (t, $J = 6.6$ Hz, 1H), 7.06-6.95 (m, 2H), 6.75 (d, $J = 8.6$ Hz, 2H), 6.55 (d, $J = 8.7$ Hz, 2H), 4.34 (s, 3H), 1.27 (d, $J = 6.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.7 (d, $J = 12.5$ Hz), 150.5, 150.0 (d, $J = 12.7$ Hz), 149.3 (d, $J = 12.4$ Hz), 147.5 (d, $J = 12.8$ Hz), 141.9, 129.3 (d, $J = 11.3$ Hz), 124.2, 124.1 (q, $J = 2.9$ Hz), 117.9, 115.9 (d, $J = 17.2$ Hz), 114.2, 71.1, 42.4 (t, $J = 3.6$ Hz), 22.2; ^{19}F NMR (377 MHz, CDCl_3) δ -138.8 (d, $J = 20.9$ Hz, 1F), -144.3 (d, $J = 20.8$ Hz, 1F). HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{16}\text{H}_{17}\text{F}_2\text{NO}$, 278.1356; found, 278.1358.

***N*-(2, 4-difluorobenzyl)-4-isopropoxyaniline (3qa)**

99.72 mg, 72% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): R_f = 0.25. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.30 (m, 1H), 6.85-6.74 (m, 4H), 6.61-6.54 (m, 2H), 4.39-4.33 (m, 1H), 4.30 (s, 2H), 1.28 (d, J = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.6 (dd, J = 135.6, 11.9 Hz), 160.2 (dd, J = 136.1, 11.8 Hz), 150.4, 141.9, 130.3 (dd, J = 9.6, 6.2 Hz), 122.4 (dd, J = 14.7, 3.7 Hz), 117.8, 114.2, 111.1 (dd, J = 21.0, 3.6 Hz), 103.8 (t, J = 25.4 Hz), 71.0, 42.3 (d, J = 3.4 Hz), 22.1; ^{19}F NMR (377 MHz, CDCl_3) δ -111.9 (d, J = 7.5 Hz, 1F), -115.0 (d, J = 7.0 Hz, 1F). HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{16}\text{H}_{17}\text{F}_2\text{NO}$, 278.1356; found, 278.1358.

***4*-isopropoxy-*N*-(2-phenylpropyl)aniline (3ra)**

82.05 mg, 61% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): R_f = 0.20. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, J = 7.5 Hz, 2H), 7.21 (d, J = 7.5 Hz, 3H), 6.76 - 6.74 (m, 2H), 6.51-6.49 (m, 2H), 4.37-4.31 (m, 1H), 3.28 (dd, J = 12.1, 6.1 Hz, 1H), 3.17 (dd, J = 12.0, 8.4 Hz, 1H), 3.18-2.99 (m, 1H), 1.31 (dd, J = 6.9, 1.9 Hz, 3H), 1.27 (d, J = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.9, 144.5, 142.5, 128.6, 127.2, 126.5, 117.9, 114.1, 71.1, 51.8, 39.2, 22.1, 19.7. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{18}\text{H}_{23}\text{NO}$, 270.1858; found, 270.1873.

***N*-(3, 5-di-*tert*-butylbenzyl)-4-isopropoxyaniline (3sa)**

135.91 mg, 77% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): R_f = 0.30. ^1H NMR (400 MHz, CDCl_3) δ 7.28 (s, 1H), 7.17-7.12 (m, 2H), 6.72 (d, J = 8.8 Hz, 2H), 6.55 (d, J = 8.8 Hz, 2H), 4.31-4.25 (m, 1H), 4.15 (s, 2H), 1.24 (s, 18H), 1.21 (d, J = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 150.0, 143.0, 138.5, 125.9, 122.2, 121.3, 118.1, 115.1, 114.0, 71.2, 50.1, 34.8, 31.4, 22.1. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{24}\text{H}_{35}\text{NO}$, 354.2797; found, 354.2801.

***4*-isopropoxy-*N*-(naphthalen-2-ylmethyl)aniline (3ta)**

77.12 mg, 53% yield, yellow solid, mp. 56.0 °C. TLC (hexane/ethyl acetate = 30/1, v/v): R_f = 0.23. ^1H NMR (400 MHz, CDCl_3) δ 7.83-7.79 (m, 4H), 7.50-7.44 (m, 3H), 6.77 (dd, J = 8.9, 2.1 Hz, 2H), 6.62 (dd, J = 8.9, 2.0 Hz, 2H), 4.43 (s, 2H), 4.38-4.32 (m, 1H), 1.28 (dd, J = 6.3, 2.1 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.2, 142.6, 137.2, 133.4, 132.7, 128.3, 127.7, 127.6, 126.1, 125.9, 125.8, 125.6, 117.9, 114.1,

71.1, 49.4, 22.2. HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{20}H_{21}NNaO$, 314.1521; found, 314.1526.

(Z)-4-isopropoxy-N-(4-methyl-1-phenylpent-1-en-1-yl)aniline (3ua)

81.89 mg, 53% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.19$. 1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 7.28-7.24 (m, 1H), 7.15 (d, $J = 7.5$ Hz, 2H), 6.76 (dd, $J = 8.9, 2.5$ Hz, 2H), 6.54 (dd, $J = 8.9, 2.5$ Hz, 2H), 5.70 (t, $J = 6.8$ Hz, 1H), 4.38-4.32 (m, 1H), 3.93 (s, 2H), 1.85 (t, $J = 6.0$ Hz, 2H), 1.62-1.53 (m, 1H), 1.28 (dd, $J = 6.0, 2.4$ Hz, 6H), 0.79 (dd, $J = 6.6, 2.3$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 142.5, 139.6, 138.2, 128.6, 128.4, 128.2, 126.8, 117.9, 114.4, 71.1, 52.2, 37.6, 28.8, 22.3, 22.2. HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{21}H_{27}NNaO$, 332.1990; found, 332.1978.

4-isopropoxy-N-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)aniline (3va)

78.38 mg, 55% yield, brown oil. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.18$. 1H NMR (400 MHz, $CDCl_3$) δ 6.77 (dd, $J = 8.9, 2.1$ Hz, 2H), 6.56 (dd, $J = 8.8, 2.1$ Hz, 2H), 5.69 (s, 1H), 4.71 (d, $J = 4.2$ Hz, 2H), 4.38-4.32 (m, 1H), 3.58 (s, 2H), 2.12 (t, $J = 13.9$ Hz, 4H), 1.99-1.83 (m, 3H), 1.74 (s, 3H), 1.29 (dd, $J = 6.1, 2.1$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 149.8, 143.0, 135.2, 127.7, 126.6, 122.3, 117.9, 113.9, 108.6, 71.1, 50.9, 41.1, 31.3, 30.5, 27.6, 27.2, 22.2, 20.8. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{27}NO$, 286.2171; found, 286.2168.

2-allyl-6-(((4-isopropoxyphenyl)amino)methyl)phenol (3wa)

69.80 mg, 47% yield, brown solid, mp. 55.0 °C. TLC (hexane/ethyl acetate = 30/1, v/v): $R_f = 0.30$. 1H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, $J = 7.5$ Hz, 1H), 6.98 (d, $J = 7.6$ Hz, 1H), 6.79 (d, $J = 8.6$ Hz, 5H), 6.09-5.94 (m, 1H), 5.13-5.01 (m, 2H), 4.44-4.38 (m, 1H), 4.33 (s, 2H), 3.40 (d, $J = 6.5$ Hz, 2H), 1.29 (d, $J = 6.0$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 152.5, 140.5, 136.9, 129.4, 127.3, 126.6, 122.5, 119.4, 117.7, 117.2, 115.4, 70.6, 50.1, 33.9, 22.0. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{23}NO_2$, 298.1807; found, 298.1809.

(E)-N-(3-(furan-3-yl)allyl)-4-isopropoxyaniline (3xa)

25.7 mg, 20% yield, brown oil. TLC (hexane/ethyl acetate = 20/1, v/v): $R_f = 0.36$. 1H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 6.78 (d, $J = 8.8$ Hz, 2H), 6.60 (d, $J = 8.8$ Hz,

2H), 6.43 (d, $J = 15.9$ Hz, 1H), 6.36-6.35 (m, 1H), 6.27 (dt, $J = 15.9, 5.6$ Hz, 1H), 6.19 (d, $J = 3.1$ Hz, 1H), 4.39-4.33 (m, 1H), 3.86 (d, $J = 5.4$ Hz, 2H), 1.29 (d, $J = 6.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.5, 150.2, 142.3, 141.8, 126.1, 119.6, 117.9, 114.2, 111.2, 107.5, 71.1, 46.7, 22.2. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{16}\text{H}_{19}\text{NO}_2$, 258.1494; found, 258.1469.

2-(benzylamino)benzoic acid (3ab)

48.81 mg, 43% yield, brown oil. TLC (hexane/ethyl acetate = 5/1, v/v): $R_f = 0.21$. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.0$ Hz, 1H), 7.28 (d, $J = 3.8$ Hz, 4H), 7.19 (s, 2H), 6.56 (t, $J = 8.4$ Hz, 2H) 4.42(s, 2H) ; ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 151.6, 138.7, 135.6, 132.6, 128.7, 127.2, 126.9, 115.1, 111.8, 108.8, 46.8. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{14}\text{H}_{13}\text{NO}_2$, 228.1025; found, 228.1020.

4-isopropoxy-*N*-(4-phenylbutan-2-yl)aniline (4aa)

133.01 mg, 94% yield, brown oil. TLC (petroleum ether/ethyl acetate = 10/1, v/v): $R_f = 0.26$. ^1H NMR (400 MHz, CDCl_3) δ 7.26 (m, $J = 8.9, 8.3$ Hz, 2H), 7.18 (d, $J = 7.4$ Hz, 3H), 6.75 (d, $J = 8.9$ Hz, 2H), 6.48 (d, $J = 9.0$ Hz, 2H), 4.38-4.32 (m, 1H), 3.43-3.35 (m, 1H), 2.72 (t, $J = 7.9$ Hz, 2H), 1.91-1.82 (m, 1H), 1.77-1.68 (m, 1H), 1.28 (d, $J = 6.0$ Hz, 6H), 1.19 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.8, 142.1, 142.0, 128.5, 128.4, 125.9, 118.1, 114.6, 71.2, 48.9, 38.9, 32.5, 22.3, 20.9. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{19}\text{H}_{25}\text{NO}$, 284.2014; found, 284.2030. The enantiomeric excess was determined by HPLC using Daicel Chiralpak OD-H column, hexane/*i*-PrOH 85:15, flow rate 1.0 mL/min, UV detection at 220 nm, $t_{\text{minor}} = 7.511$ min, $t_{\text{major}} = 7.881$ min, 0% *ee*.

***N*-cyclohexyl-4-isopropoxyaniline (4ba)**

103.69 mg, 89% yield, brown oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): $R_f = 0.28$. ^1H NMR (400 MHz, CDCl_3) δ 6.77-6.74 (m, 2H), 6.55-6.53 (m, 2H), 4.38-4.32 (m, 1H), 3.15 (tt, $J = 10.0, 3.6$ Hz, 1H), 3.08 (s, 1H), 2.06-2.02 (m, 2H), 1.75 (dt, $J = 13.2, 3.9$ Hz, 2H), 1.66-1.61 (m, 1H), 1.38-1.17 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.8, 141.8, 118.1, 114.6, 71.2, 52.7, 33.7, 26.0, 25.1, 22.3. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{15}\text{H}_{23}\text{NO}$, 234.1858; found, 234.1876.

***N*-cyclobutyl-4-isopropoxyaniline (4ca)**

80.98 mg, 79% yield, brown oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.23. ^1H NMR (400 MHz, CDCl_3) δ 6.76 (dd, J = 8.8, 1.6 Hz, 2H), 6.49 (dd, J = 8.8, 1.5 Hz, 2H), 4.38-4.32 (m, 1H), 3.87-3.81 (m, 1H), 2.39-2.38 (m, 2H), 1.80-1.77 (m, 4H), 1.28 (dd, J = 6.1, 1.5 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 141.7, 118.0, 114.3, 71.1, 49.8, 31.4, 22.3, 15.3. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{13}\text{H}_{19}\text{NO}$, 206.1545; found, 206.1552.

***N*-(1-cyclopropylethyl)-4-isopropoxyaniline (4da)**

82.13 mg, 75% yield, brown oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.25. ^1H NMR (400 MHz, CDCl_3) δ 6.55 (d, J = 6.8 Hz, 2H), 6.34 (d, J = 6.8 Hz, 2H), 4.17-4.11 (m, 1H), 2.67-2.61 (m, 1H), 1.07 (d, J = 6.1 Hz, 6H), 0.99 (d, J = 6.4 Hz, 3H), 0.72-0.65 (m, 1H), 0.26 (d, J = 8.4 Hz, 2H), 0.09 -0.00 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.9, 142.3, 117.9, 114.9, 71.1, 53.7, 22.3, 20.3, 18.0, 3.3, 2.6. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{14}\text{H}_{21}\text{NO}$, 220.1701; found, 220.1711.

***N*-(4-isopropoxyphenyl)-2, 3-dihydro-1*H*-inden-1-amine (4ea)**

92.12 mg, 69% yield, brown oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.43. ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, J = 7.2 Hz, 1H), 7.23-7.15 (m, 3H), 6.79 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 4.92 (t, J = 6.7 Hz, 1H), 4.39-4.33 (m, 1H), 3.02-2.95 (m, 1H), 2.89-2.81 (m, 1H), 2.58-2.49 (m, 1H), 1.87 (dt, J = 12.8, 7.1 Hz, 1H), 1.29 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 144.9, 143.7, 142.3, 127.9, 126.7, 124.9, 124.4, 118.2, 114.5, 71.2, 59.5, 34.0, 30.3, 22.3. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}$, 268.1701; found, 268.1671.

***N*-(4-isopropoxyphenyl)-5-methoxy-2, 3-dihydro-1*H*-inden-1-amine (4fa)**

102.47 mg, 69% yield, brown oil. TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.19. ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, J = 8.3 Hz, 1H), 6.82-6.76 (m, 3H), 6.74 (dd, J = 8.3, 2.4 Hz, 1H), 6.64 (d, J = 8.9 Hz, 2H), 4.88 (t, J = 6.3 Hz, 1H), 4.39-4.32 (m, 1H), 3.79 (s, 3H), 3.02-2.94 (m, 1H), 2.88-2.80 (m, 1H), 2.57-2.49 (m, 1H), 1.95-1.86 (m, 1H), 1.30 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.8, 149.9, 145.3, 142.2, 136.8, 124.9, 118.0, 114.3, 112.6, 109.8, 71.1, 58.7, 55.4, 34.0, 30.4, 22.2. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{19}\text{H}_{23}\text{NO}$, 298.1807; found, 298.1809.

***N*-(4-isopropoxyphenyl)-1, 2, 3, 4-tetrahydronaphthalen-1-amine (4ga)**

91.33 mg, 65% yield, brown oil. TLC (petroleum ether/ethyl acetate = 30/1, v/v): R_f = 0.21. ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, J = 6.5 Hz, 1H), 7.21-7.11 (m, 3H), 6.80 (d, J = 8.9 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 4.54 (t, J = 4.8 Hz, 1H), 4.40-4.34 (m, 1H), 2.87-2.71 (m, 2H), 1.96-1.74 (m, 4H), 1.30 (d, J = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.8, 141.9, 138.4, 137.5, 129.3, 129.0, 127.0, 126.0, 118.1, 114.1, 71.2, 51.8, 29.3, 28.6, 22.2, 19.3. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{19}\text{H}_{23}\text{NO}$, 282.1858; found, 282.1825.

4-isopropoxy-*N*-((1*S*)-2-methyl-5-(prop-1-en-2-yl)cyclohexyl)aniline (4ha)

101.18 mg, 71% yield, brown oil. TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.42. ^1H NMR (400 MHz, CDCl_3) δ 6.76 (dd, J = 9.0, 2.9 Hz, 2H), 6.56 (d, J = 9.1 Hz, 2H), 4.66 (d, J = 2.0 Hz, 2H), 4.37-4.31 (m, 1H), 3.55 (s, 1H), 2.11-1.57 (m, 11H), 1.28 (dd, J = 6.1, 2.7 Hz, 6H), 0.97 (dd, J = 6.8, 3.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 149.4, 142.6, 118.0, 114.1, 108.4, 71.1, 53.6, 38.4, 35.4, 35.2, 31.2, 29.1, 22.2, 21.0, 18.9. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{19}\text{H}_{29}\text{NO}$, 288.2373; found, 288.2363.

***N*-(4-isopropoxyphenyl)chroman-4-amine (4ia)**

96.22 mg, 68% yield, brown oil. TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.32. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (dd, J = 7.7, 1.7 Hz, 1H), 7.20-7.16 (m, 1H), 6.91-6.85 (m, 2H), 6.83-6.80 (m, 2H), 6.65-6.59 (m, 2H), 4.52 (t, J = 4.2 Hz, 1H), 4.41-4.35 (m, 1H), 4.25-4.18 (m, 2H), 2.12-2.08 (m, 2H), 1.30 (d, J = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 150.1, 140.9, 130.1, 129.0, 125.9, 123.4, 120.5, 118.1, 116.9, 115.1, 114.0, 71.1, 62.6, 47.4, 27.7, 22.2, 22.1. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_2$, 284.1651; found, 284.1616.

***N*-(1, 5-diphenylpentan-3-yl)-4-isopropoxyaniline (4ja)**

128.69 mg, 70% yield, brown oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.21. ^1H NMR (400 MHz, CDCl_3) δ 7.25 (t, J = 7.3 Hz, 4H), 7.19-7.15 (m, 2H), 7.11 (d, J = 8.1 Hz, 4H), 6.72 (d, J = 8.9 Hz, 2H), 6.38 (d, J = 8.9 Hz, 2H), 4.37-4.31 (m, 1H), 3.31-3.25 (m, 1H), 2.72-2.63 (m, 4H), 1.90-1.72 (m, 4H), 1.28 (dd, J = 6.1, 1.3 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 142.1, 142.0, 128.4, 128.3, 125.7,

117.9, 114.3, 71.0, 52.4, 36.7, 32.2, 22.2. HRMS (ESI, m/z): [M+H]⁺ Calcd. for C₂₆H₃₁NO, 374.2484; found, 374.2462.

4-isopropoxy-*N*-(nonan-2-yl)aniline (4ka)

114.96 mg, 70% yield, brown oil. TLC (petroleum ether/ethyl acetate = 15/1, v/v): R_f = 0.44. ¹H NMR (400 MHz, CDCl₃) δ 6.76 (dd, *J* = 8.8, 1.9 Hz, 2H), 6.52 (dd, *J* = 8.8, 1.9 Hz, 2H), 4.38-4.32 (m, 1H), 3.38-3.32 (m, 1H), 1.61-1.50 (m, 2H), 1.28 (dd, *J* = 6.1, 1.8 Hz, 16H), 1.14 (dd, *J* = 6.4, 1.7 Hz, 3H), 0.88 (t, *J* = 6.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.6, 142.1, 118.0, 114.4, 71.1, 49.3, 37.2, 31.8, 29.6, 29.3, 26.1, 22.6, 22.2, 20.8, 14.1. HRMS (ESI, m/z): [M+H]⁺ Calcd. for C₁₈H₃₁NO, 278.2484; found, 278.2484.

***N*-(1-(4-bromophenyl)ethyl)-4-isopropoxyaniline (4la)**

129.87 mg, 78% yield, brown oil. TLC (petroleum ether/ethyl acetate = 25/1, v/v): R_f = 0.25. ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.33 (m, 2H), 7.17-7.15 (m, 2H), 6.61-6.59 (m, 2H), 6.33-6.31 (m, 2H), 4.29-4.19 (m, 2H), 1.37 (d, *J* = 6.7 Hz, 3H), 1.17 (dd, *J* = 6.1, 1.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 150.0, 144.7, 141.4, 131.7, 127.7, 120.4, 117.7, 114.4, 71.0, 53.8, 25.1, 22.2. HRMS (ESI, m/z): [M+H]⁺ Calcd. for C₁₇H₂₀BrNO, 334.0807; found, 334.0794.

4-(1-((4-isopropoxyphenyl)amino)ethyl)benzotrile (4ma)

88.20 mg, 63% yield, brown oil. TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.20. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.48 (dd, *J* = 8.3, 1.5 Hz, 2H), 6.68 (dd, *J* = 8.9, 1.5 Hz, 2H), 6.37 (dd, *J* = 8.9, 1.5 Hz, 2H), 4.42 (q, *J* = 6.8 Hz, 1H), 4.34-4.28 (m, 1H), 1.48 (dd, *J* = 6.8, 1.4 Hz, 3H), 1.25 (dd, *J* = 6.2, 1.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 151.3, 150.1, 140.9, 132.5, 126.6, 119.0, 117.6, 114.3, 110.5, 70.9, 54.0, 24.9, 22.1, 22.1. HRMS (ESI, m/z): [M+H]⁺ Calcd. for C₁₈H₂₀N₂O, 281.1654; found, 228.1020.

***N*-(1-(3, 5-dimethylphenyl)ethyl)-4-isopropoxyaniline (4na)**

111.79 mg, 79% yield, brown oil. TLC (petroleum ether/ethyl acetate = 15/1, v/v): R_f = 0.33. ¹H NMR (400 MHz, CDCl₃) δ 6.98 (s, 2H), 6.86 (s, 1H), 6.69 (d, *J* = 8.9 Hz, 2H), 6.46 (d, *J* = 8.9 Hz, 2H), 4.34-4.28 (m, 2H), 2.29 (s, 6H), 1.46 (d, *J* = 6.7 Hz, 3H), 1.25 (d, *J* = 6.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 149.7, 145.6, 142.0,

138.0, 128.5, 123.6, 117.7, 114.3, 71.0, 54.3, 25.1, 22.2, 22.2, 21.4. HRMS (ESI, m/z): [M+H]⁺ Calcd. for C₁₉H₂₅NO, 284.2014; found, 284.2030.

4-(3-((4-isopropoxyphenyl)amino)butyl)-N,N-dimethylaniline (4oa)

92.38 mg, 62% yield, brown oil. TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.32. ¹H NMR (400 MHz, CDCl₃) δ 7.05 (d, *J* = 6.8 Hz, 2H), 6.74 (d, *J* = 7.0 Hz, 2H), 6.68 (d, *J* = 6.8 Hz, 2H), 6.48 (d, *J* = 7.0 Hz, 2H), 4.36-4.31 (m, 1H), 3.40-3.34 (m, 1H), 2.89 (s, 6H), 2.65-2.58 (m, 2H), 1.86-1.77 (m, 1H), 1.72-1.62 (m, 1H), 1.27 (d, *J* = 4.1 Hz, 6H), 1.16 (d, *J* = 4.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.6, 148.9, 142.0, 130.1, 128.9, 117.9, 114.5, 112.9, 71.0, 48.7, 40.8, 39.0, 31.3, 22.1, 20.8. HRMS (ESI, m/z): [M+H]⁺ Calcd. for C₁₉H₂₆N₂NaO, 321.1943; found, 321.1958.

4-isopropoxy-N-(1-phenylbutyl)aniline (4pa)

106.13 mg, 75% yield, brown oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.44. ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.27 (m, 4H), 7.22-7.18 (m, 1H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.43 (d, *J* = 9.0 Hz, 2H), 4.32-4.20 (m, 2H), 1.80-1.65 (m, 2H), 1.45-1.31 (m, 2H), 1.23 (d, *J* = 6.1 Hz, 6H), 0.91 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.7, 144.5, 141.9, 128.4, 126.7, 126.4, 117.7, 114.2, 70.9, 58.7, 41.1, 22.1, 22.1, 19.5, 13.9. HRMS (ESI, m/z): [M+H]⁺ Calcd. for C₁₉H₂₅NO, 284.2014; found, 284.1995.

4-isopropoxy-N-(nonan-2-yl)aniline (4qa)

41.18 mg, 27% yield, brown oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.18. ¹H NMR (400 MHz, CDCl₃) δ 7.81-7.78 (m, 4H), 7.51-7.40 (m, 3H), 6.66 (d, *J* = 8.6 Hz, 2H), 6.52 (d, *J* = 8.5 Hz, 2H), 4.55 (q, *J* = 6.7 Hz, 1H), 4.29-4.24 (m, 1H), 1.55 (d, *J* = 6.7 Hz, 3H), 1.22 (d, *J* = 6.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 149.8, 143.1, 141.7, 133.5, 132.7, 128.4, 127.8, 127.6, 125.9, 125.4, 124.4, 124.2, 117.7, 114.4, 70.9, 54.4, 25.2, 22.1. HRMS (ESI, m/z): [M+H]⁺ Calcd. for C₁₉H₂₅NO, 306.1858; found, 306.1844.

N-(4-phenylbutan-2-yl)-2,3-dihydrobenzofuran-5-amine (4ac)

96.12 mg, 72% yield, brown oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.28. ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.25 (m, 2H), 7.21-7.16 (m, 3H), 6.61 (d, *J* = 8.4 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 6.32 (dd, *J* = 8.4, 2.5 Hz, 1H), 4.47 (t, *J* = 8.5

Hz, 2H), 3.39-3.33 (m, 1H), 3.10 (t, $J = 8.5$ Hz, 2H), 2.71 (t, $J = 8.3$ Hz, 2H), 1.90-1.81 (m, 1H), 1.76-1.67 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.4, 142.2, 141.9, 128.5, 128.4, 127.8, 125.9, 113.4, 111.2, 109.5, 70.9, 49.3, 38.9, 32.6, 30.5, 20.9. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}$, 268.1701; found, 268.1704.

4-ethyl-*N*-(4-phenylbutan-2-yl)aniline (4ad)

90.6 mg, 73% yield, red oil. TLC (petroleum ether/ethyl acetate = 50/1, v/v): $R_f = 0.34$. ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.24 (m, 2H), 7.18-7.15 (m, 3H), 6.99 - 6.96 (m, 2H), 6.48-6.45 (m, 2H), 3.47 - 3.49 (m, 1H), 3.05 (s, 1H), 2.69 (t, $J = 7.9$ Hz, 2H), 2.52 (q, $J = 7.6$ Hz, 2H), 1.88-1.79 (m, 1H), 1.76 - 1.67 (m, 1H), 1.20-1.16 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.4, 142.0, 132.6, 128.5, 128.3, 128.3, 125.7, 113.2, 48.0, 38.8, 32.4, 27.8, 20.8, 15.9. HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{18}\text{H}_{23}\text{N}$, 254.1909; found, 254.1889.

4-chloro-*N*-(4-phenylbutan-2-yl)aniline (4ae) ^[1]

124.5 mg, 92% yield, yellow oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): $R_f = 0.24$. ^1H NMR (400 MHz, CDCl_3) δ 7.26 (t, $J = 7.4$ Hz, 2H), 7.19-7.13 (m, 3H), 7.07-7.04 (m, 2H), 6.39-6.37 (m, 2H), 3.42 - 3.34 (m, 1H), 2.67 (t, $J = 8.0$ Hz, 3H), 1.86 - 1.67 (m, 2H), 1.16 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.9, 141.6, 128.9, 128.3, 125.8, 121.1, 114.0, 47.8, 38.4, 32.2, 20.5.

methyl 4-((4-phenylbutan-2-yl)amino)benzoate (4af) ^[1]

117.45mg, 83% yield, yellow oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): $R_f = 0.22$. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.8$ Hz, 2H), 7.27 (t, $J = 7.3$ Hz, 2H), 7.19 (d, $J = 8.6$ Hz, 1H), 7.15 (d, $J = 8.3$ Hz, 2H), 6.44 (d, $J = 8.8$ Hz, 2H), 4.02 (d, $J = 8.9$ Hz, 1H), 3.83 (s, 3H), 3.55 - 3.49 (m, 1H), 2.69 (t, $J = 7.8$ Hz, 2H), 1.91 - 1.73 (m, 2H), 1.21 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 151.2, 141.4, 131.5, 128.4, 128.3, 125.9, 117.6, 111.5, 51.4, 47.3, 38.4, 32.2, 20.5.

3-((4-phenylbutan-2-yl)amino)phenol (4ag)

108.5 mg, 90% yield, brown oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): $R_f = 0.17$. ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.16 (m, 5H), 7.01-6.94 (m, 1H), 6.15-6.10 (m, 2H), 5.94 (t, $J = 4.4$ Hz, 1H), 3.45-3.47 (m, 1H), 2.69 (t, $J = 7.8$ Hz, 2H), 1.91-1.80 (m, 1H), 1.77-1.68 (m, 1H), 1.18 (dd, $J = 6.4, 2.8$ Hz, 3H); ^{13}C NMR (100 MHz,

CDCl₃) δ 156.7, 149.0, 141.9, 130.2, 128.5, 128.4, 125.8, 106.3, 104.0, 100.0, 47.9, 38.6, 32.4, 20.7. HRMS (ESI, m/z): [M+H]⁺ Calcd. for C₁₆H₁₉NO, 242.1545; found, 242.1547.

7-((4-phenylbutan-2-yl)amino)-1, 2, 3, 4-tetrahydronaphthalen-1-ol (4ah)

89.5 mg, 80% yield, red oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.22. ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.24 (m, 2H), 7.18-7.15 (m, 3H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.59 - 6.57 (m, 1H), 6.40 (dd, *J* = 8.3, 2.8 Hz, 1H), 4.61 (t, *J* = 5.1 Hz, 1H), 3.49-3.41 (m, 1H), 2.67 (dt, *J* = 14.1, 6.8 Hz, 3H), 2.60-2.53 (m, 1H), 1.94-1.79 (m, 4H), 1.74-1.64 (m, 2H), 1.17 (dd, *J* = 6.3, 1.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.7 (d, *J* = 1.4 Hz), 141.9 (d, *J* = 1.6 Hz), 139.5, 129.6, 128.3, 128.2, 125.7, 125.3, 113.2, 112.5, 68.3 (d, *J* = 2.3 Hz), 47.9 (d, *J* = 2.5 Hz), 38.7 (d, *J* = 9.6 Hz), 32.3 (dd, *J* = 5.2, 2.7 Hz), 28.2, 20.7 (d, *J* = 4.2 Hz), 19.2 (d, *J* = 2.0 Hz). HRMS (ESI, m/z): [M+Na]⁺ Calcd. for C₂₀H₂₅NONa, 318.1834, found, 318.1823.

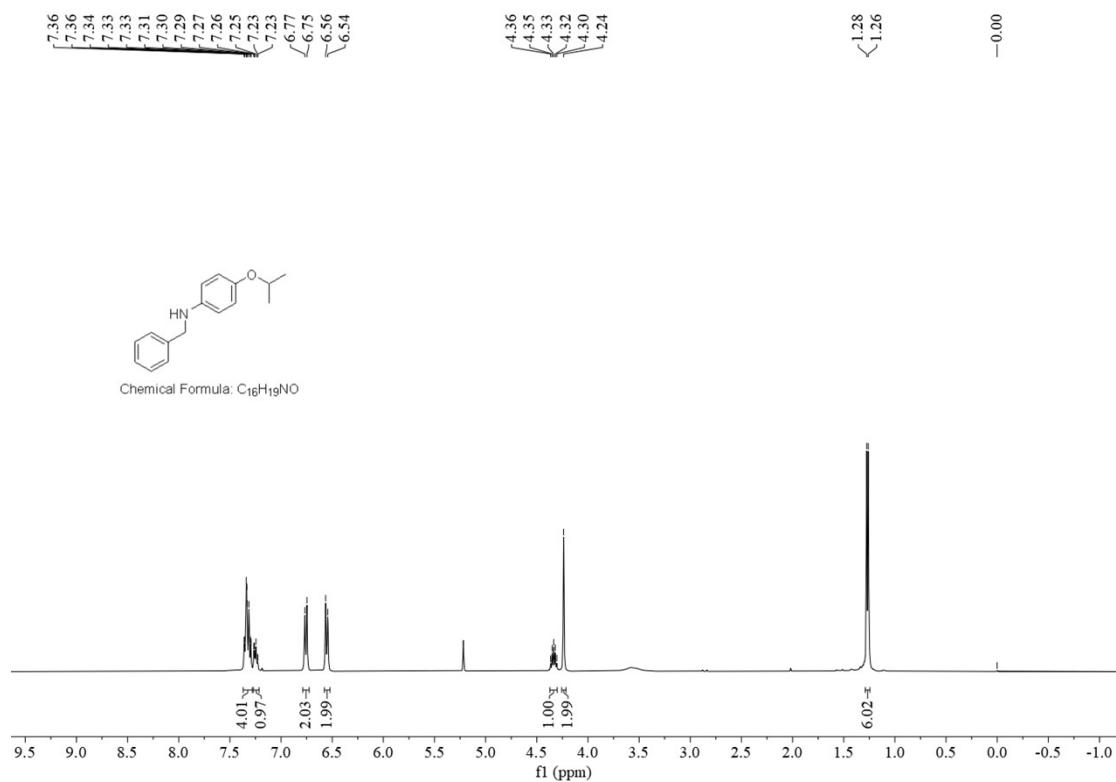
4-methyl-N-(4-phenylbutan-2-yl)aniline (4ai)^[1]

112.4 mg, 94% yield, red oil. TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.27. ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.23 (m, 2H), 7.15 (d, *J* = 6.0 Hz, 3H), 6.94 (d, *J* = 6.3 Hz, 2H), 6.44 (d, *J* = 6.1 Hz, 2H), 3.41 (qt, *J* = 6.4, 3.3 Hz, 1H), 3.09 (s, 1H), 2.68 (t, *J* = 6.8 Hz, 2H), 2.21 (s, 3H), 1.87-1.78 (m, 1H), 1.75-1.65 (m, 1H), 1.16 (dd, *J* = 6.3, 2.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 141.9, 129.6, 128.3, 128.2, 125.9, 125.7, 113.3, 48.0, 38.7, 32.4, 20.7, 20.3.

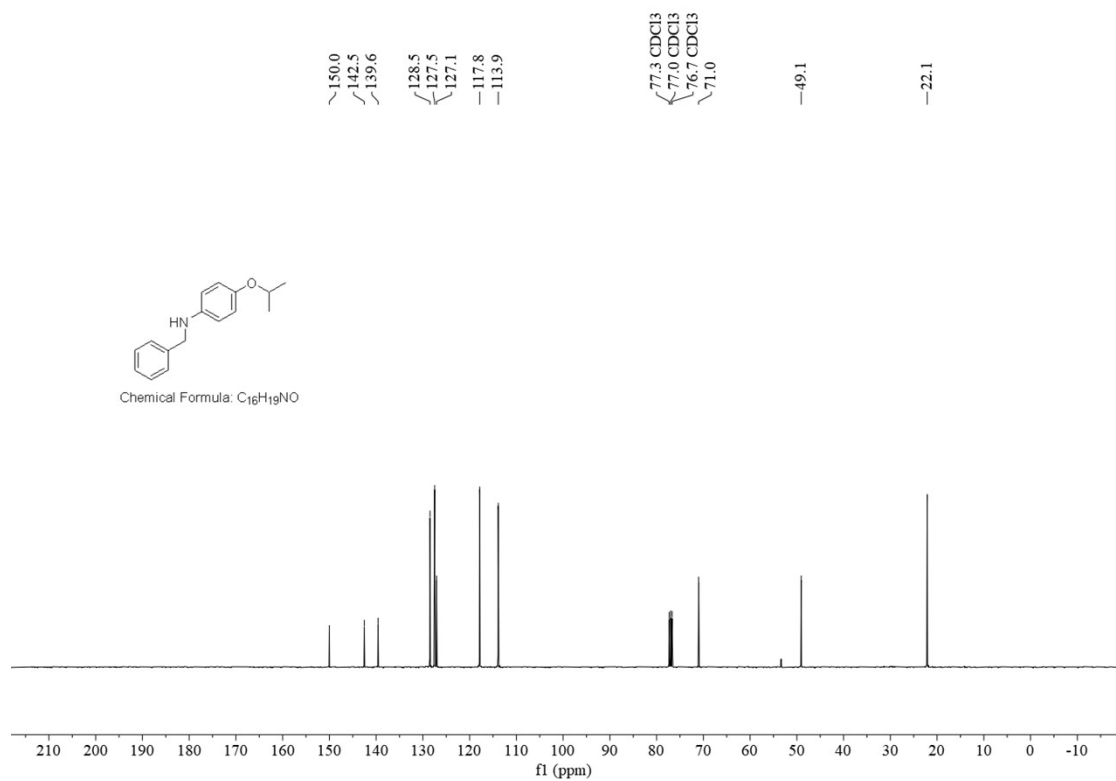
H. References

- [1] (a) Jang, M.; Lim, T.; Park, B. Y.; Han, M. S. *J. Org. Chem.* **2022**, *87*, 910.; (b) Ouyang, L.; Xia, Y.; Liao, J.; Luo, R. *Eur. J. Org. Chem.* **2020**, *2020*, 6387.; (c) Popov, K. K.; Campbell, J. L.; Kysilka, O.; Hosek, J.; Davies, C. D.; Pour, M.; Kocovsky, P. *J. Org. Chem.* **2021**, *87*, 920.; (d) Cosgrove, S. C.; Thompson, M. P.; Ahmed, S. T.; Parmeggiani, F.; Turner, N. J. *Angew. Chem. Int. Ed.* **2020**, *59*, 18156.

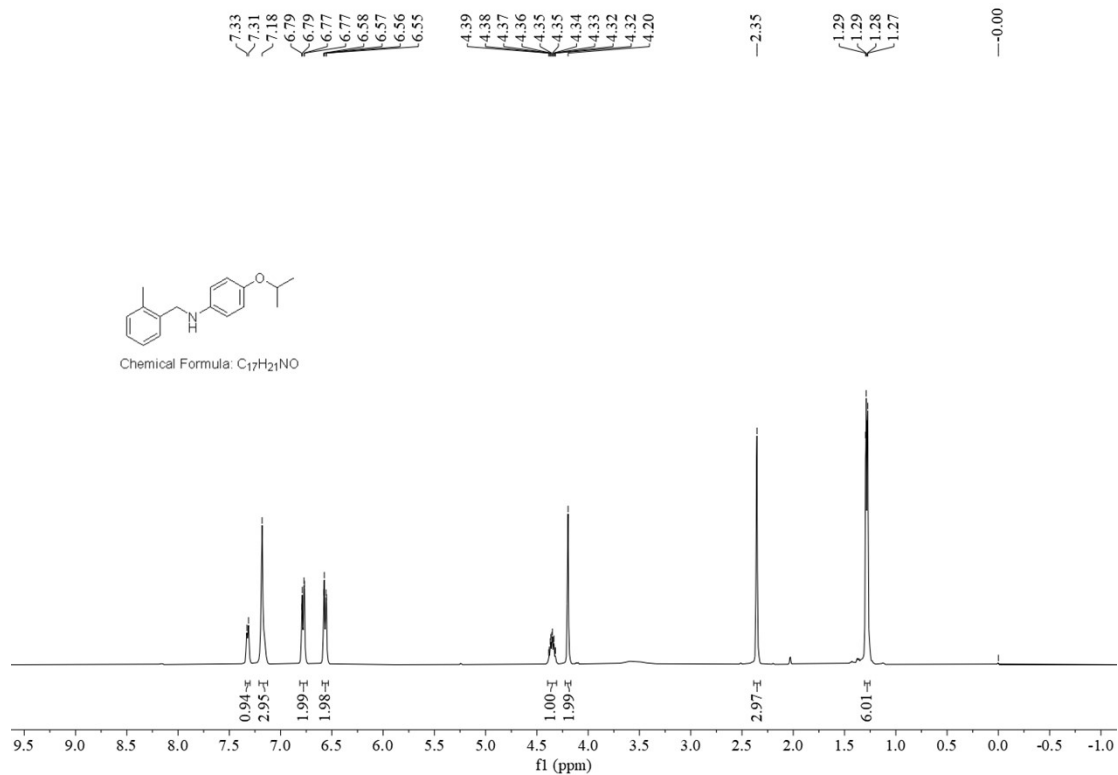
I. NMR Spectra of New Compounds



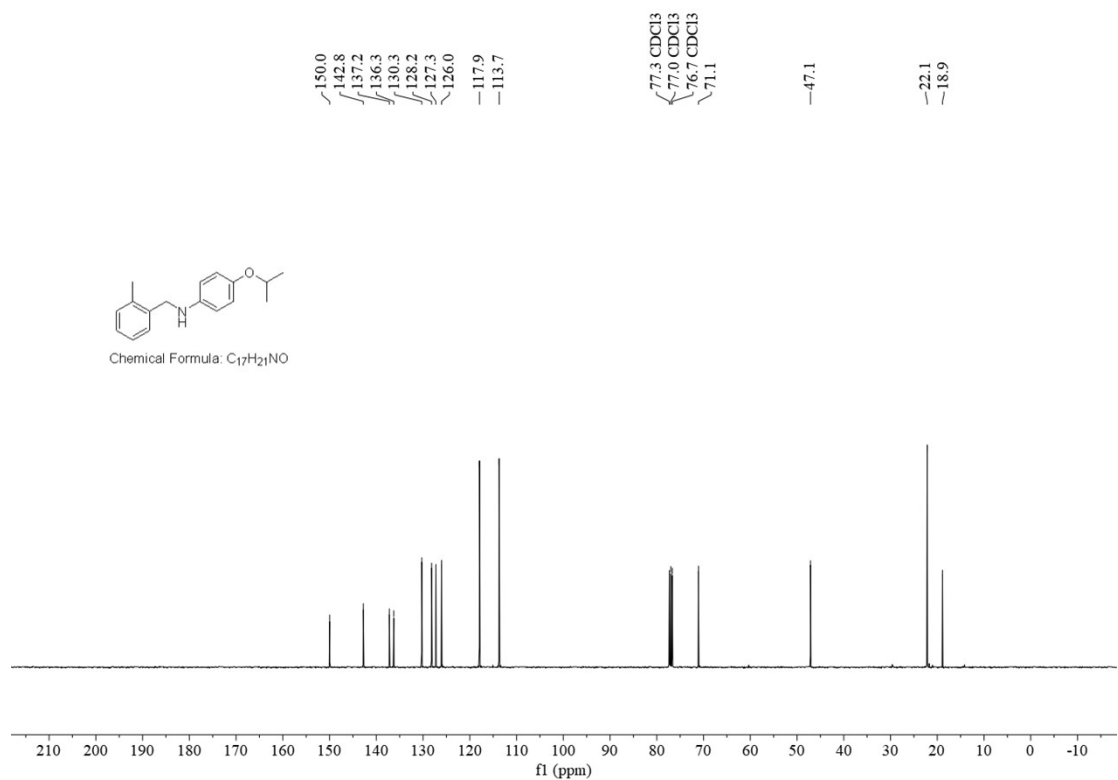
1H NMR Spectrum of **3aa** in $CDCl_3$ at 400 MHz



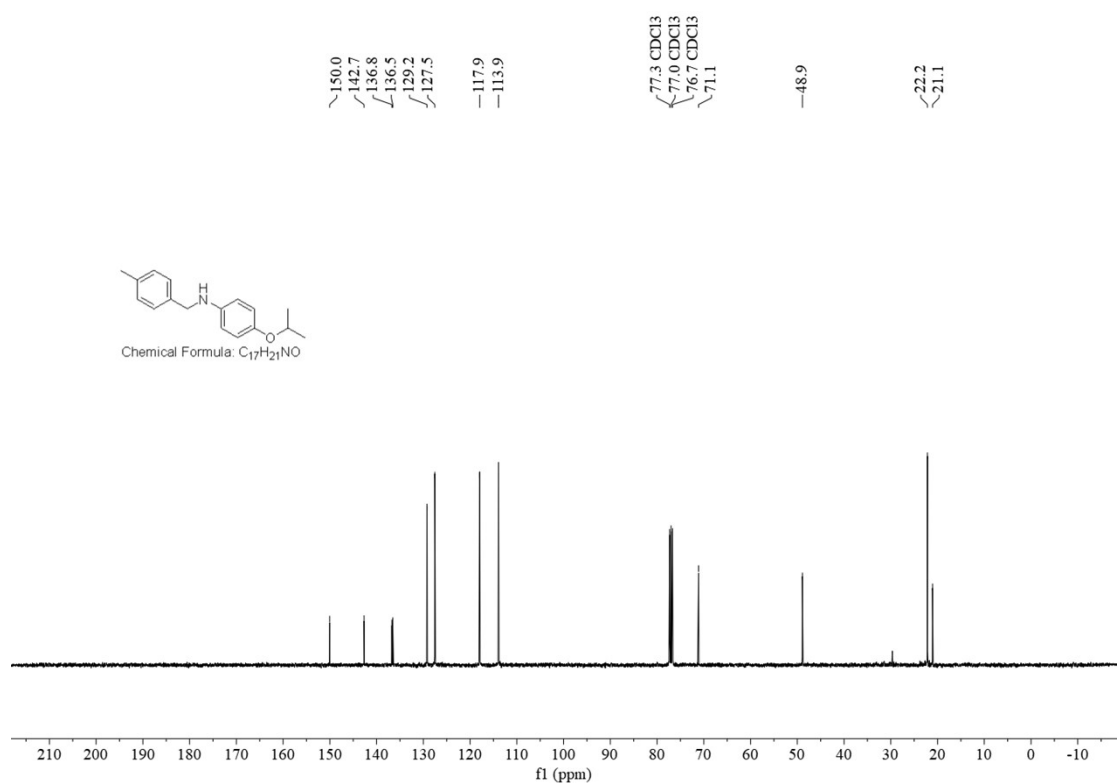
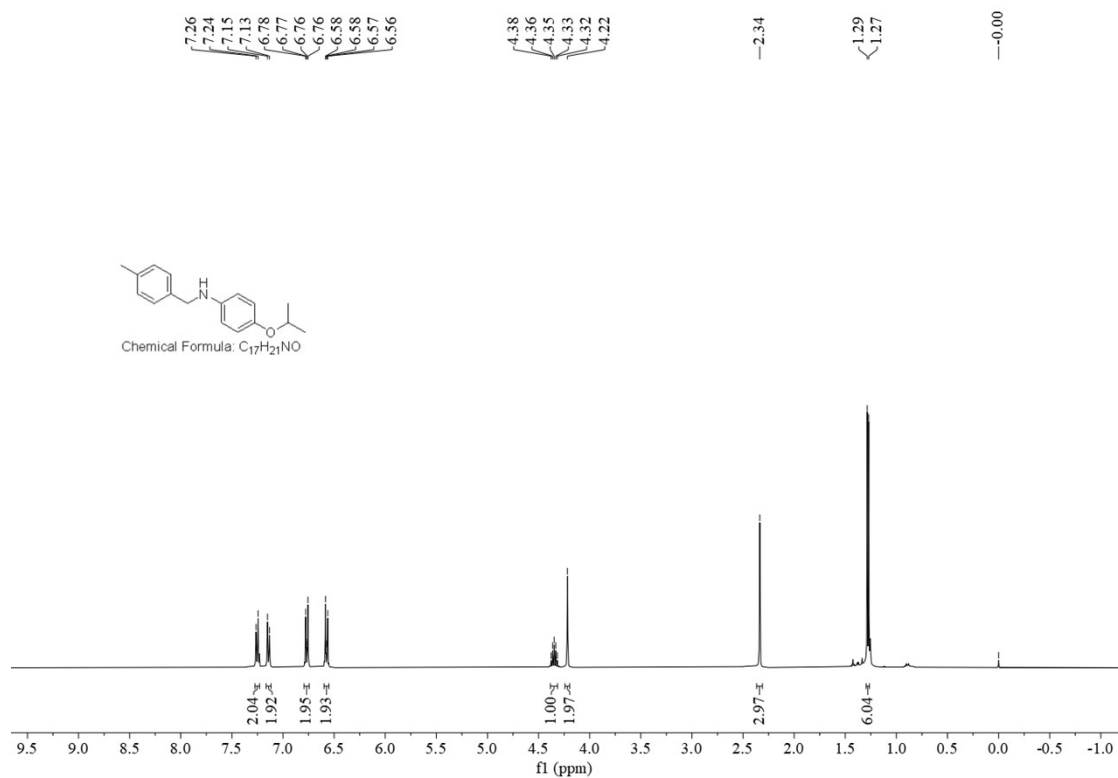
$^{13}C \{^1H\}$ NMR Spectrum of **3aa** in $CDCl_3$ at 100 MHz

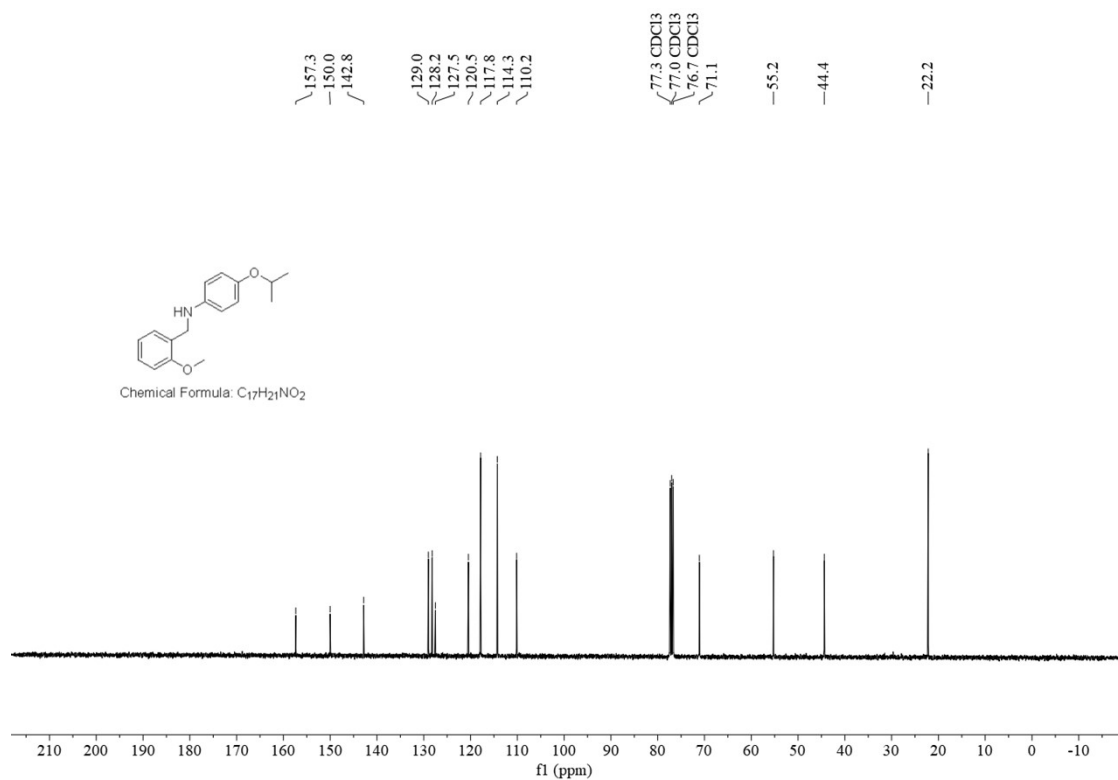
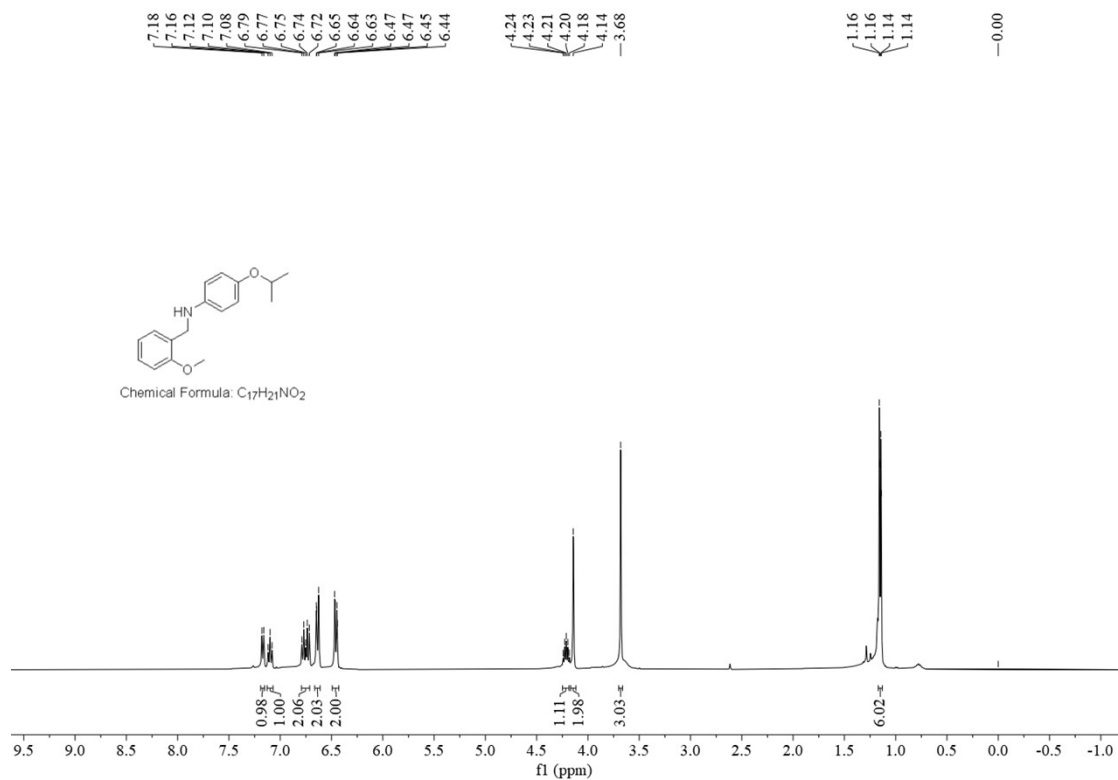


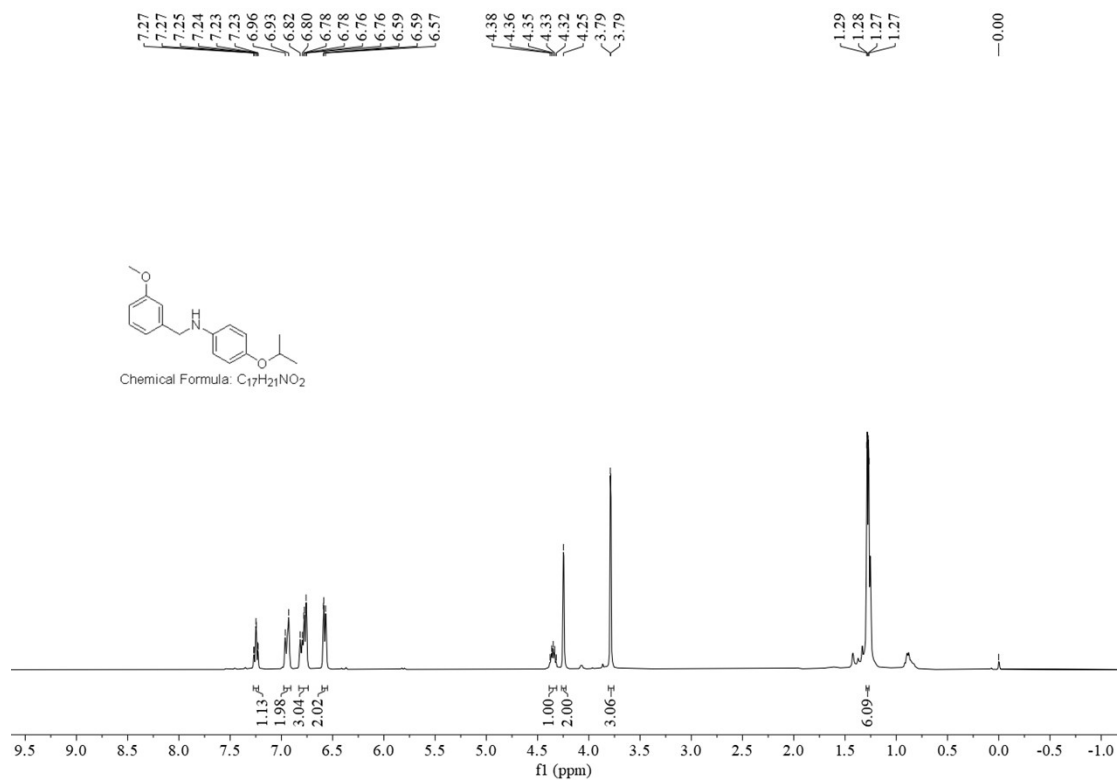
¹H NMR Spectrum of **3ba** in CDCl₃ at 400 MHz



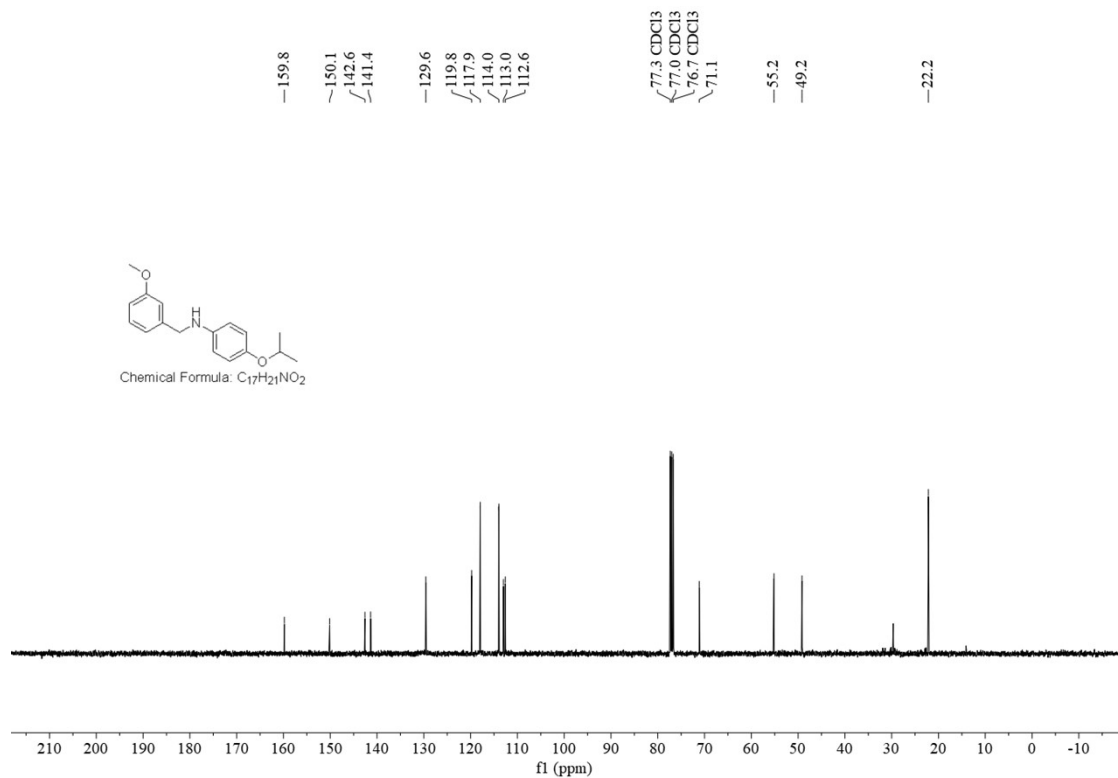
¹³C{¹H} NMR Spectrum of **3ba** in CDCl₃ at 100 MHz



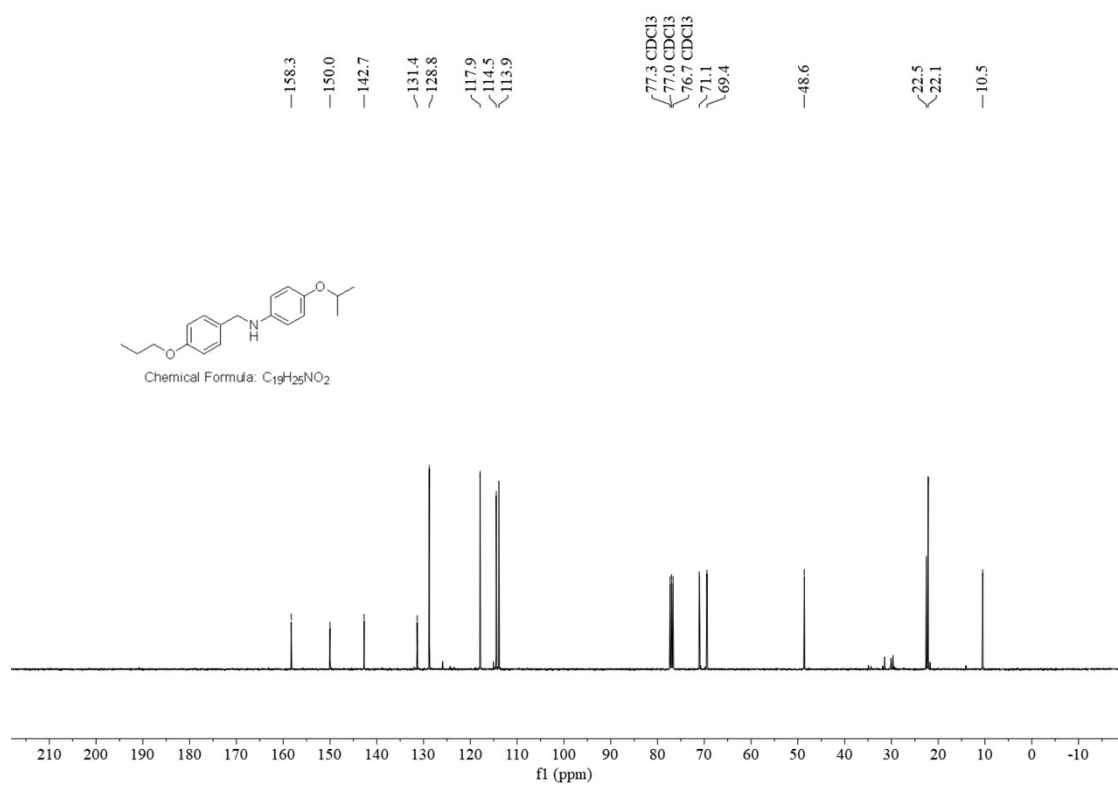
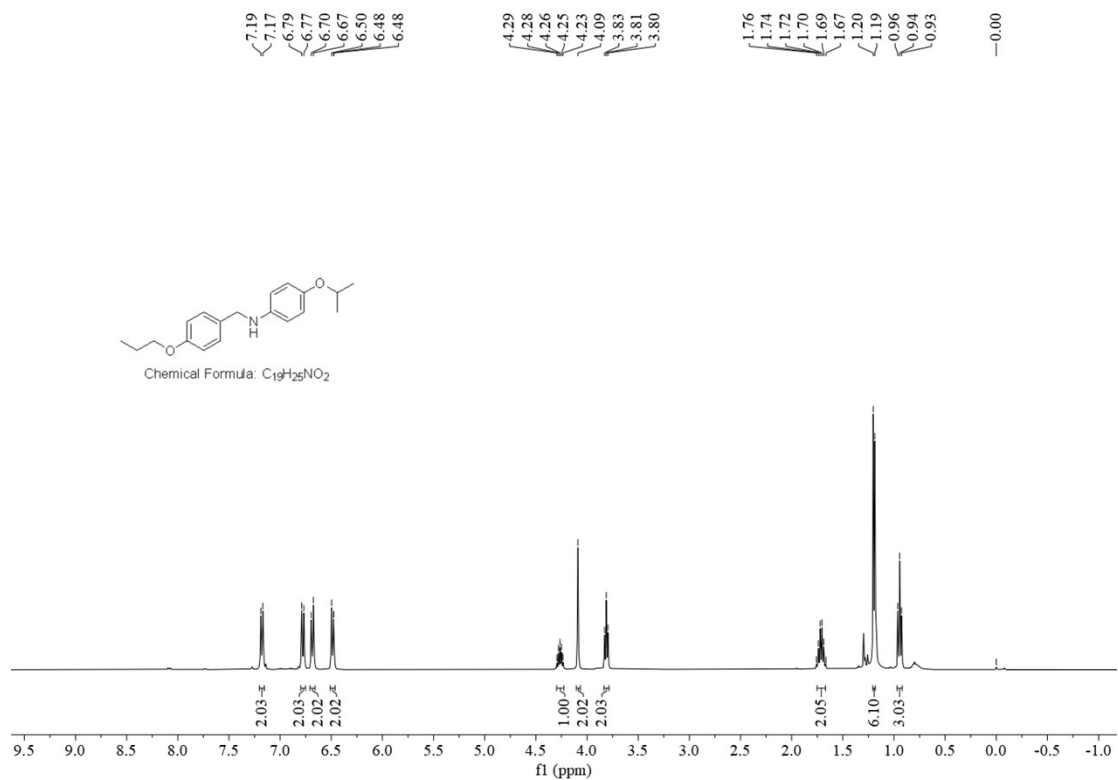


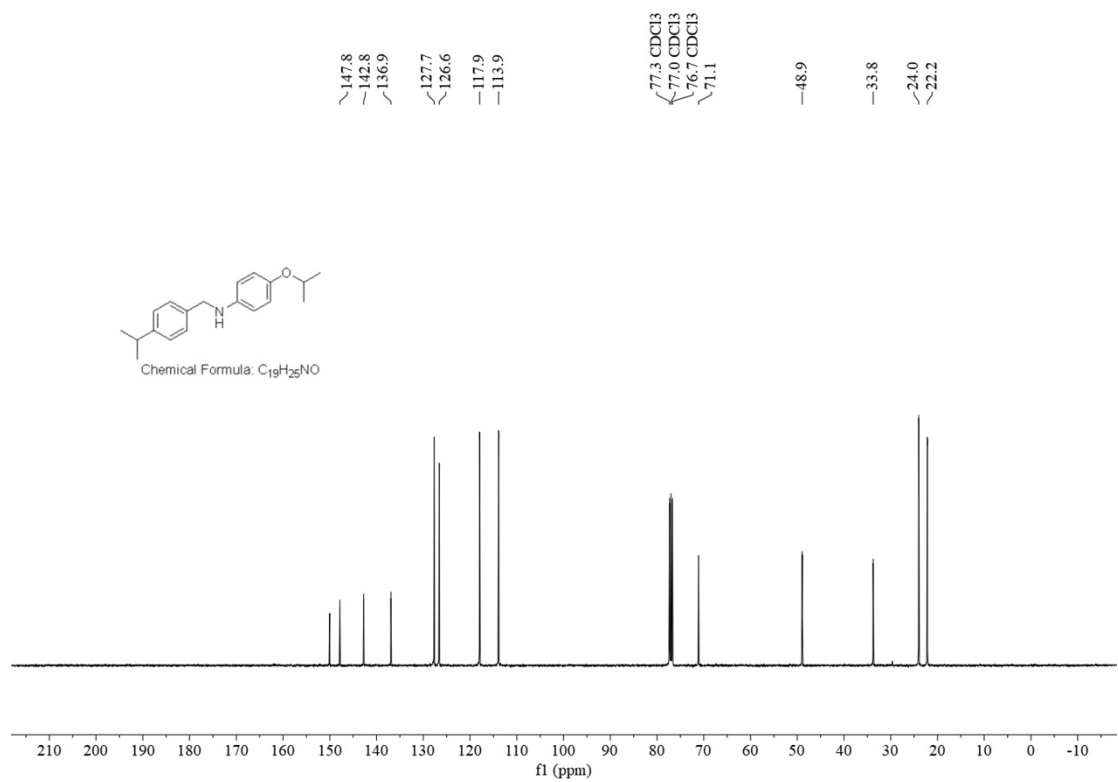
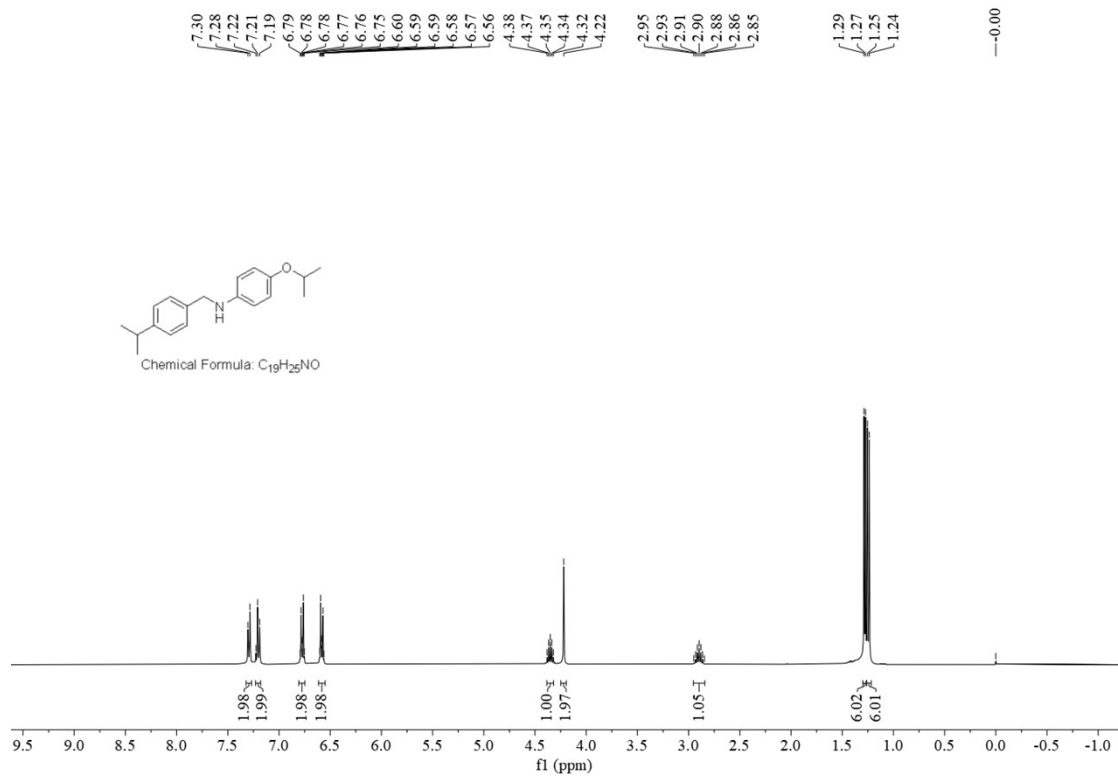


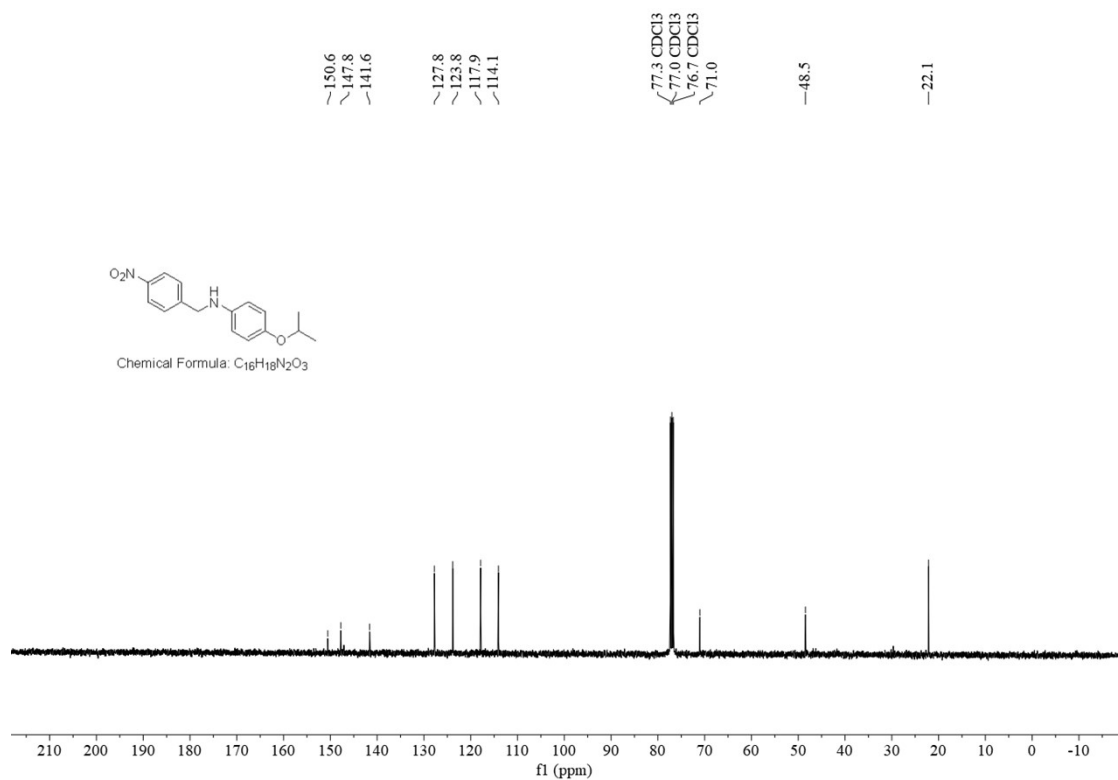
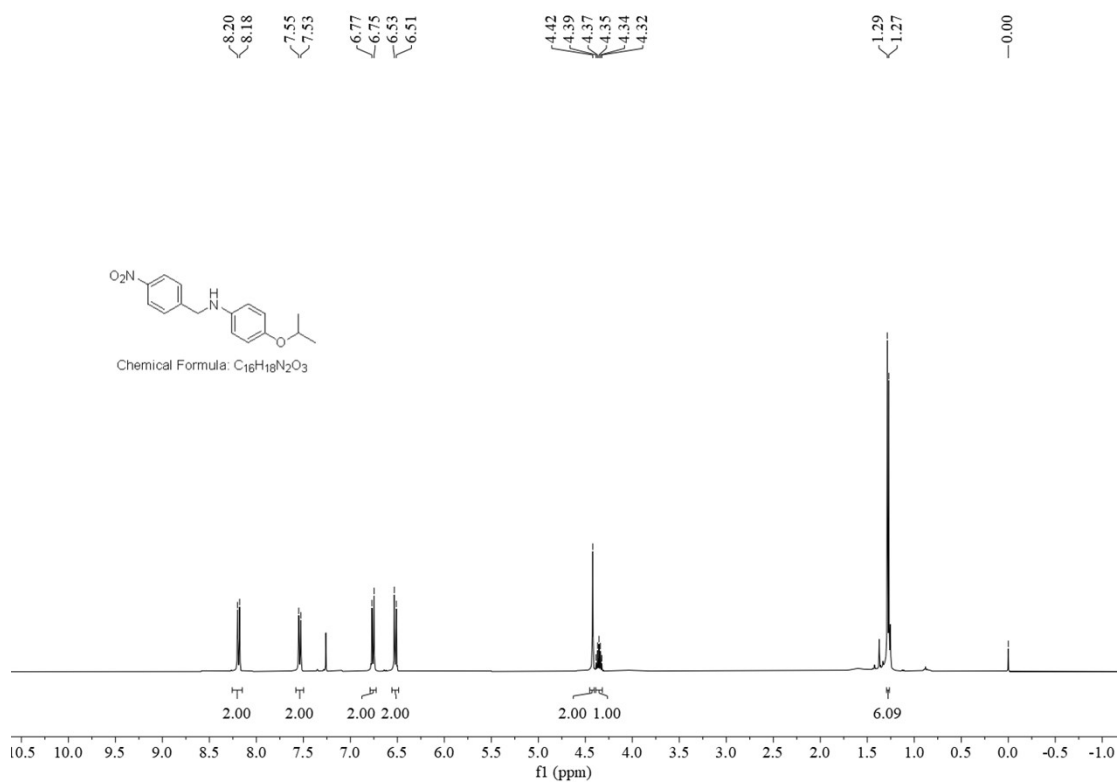
1H NMR Spectrum of **3ea** in $CDCl_3$ at 400 MHz

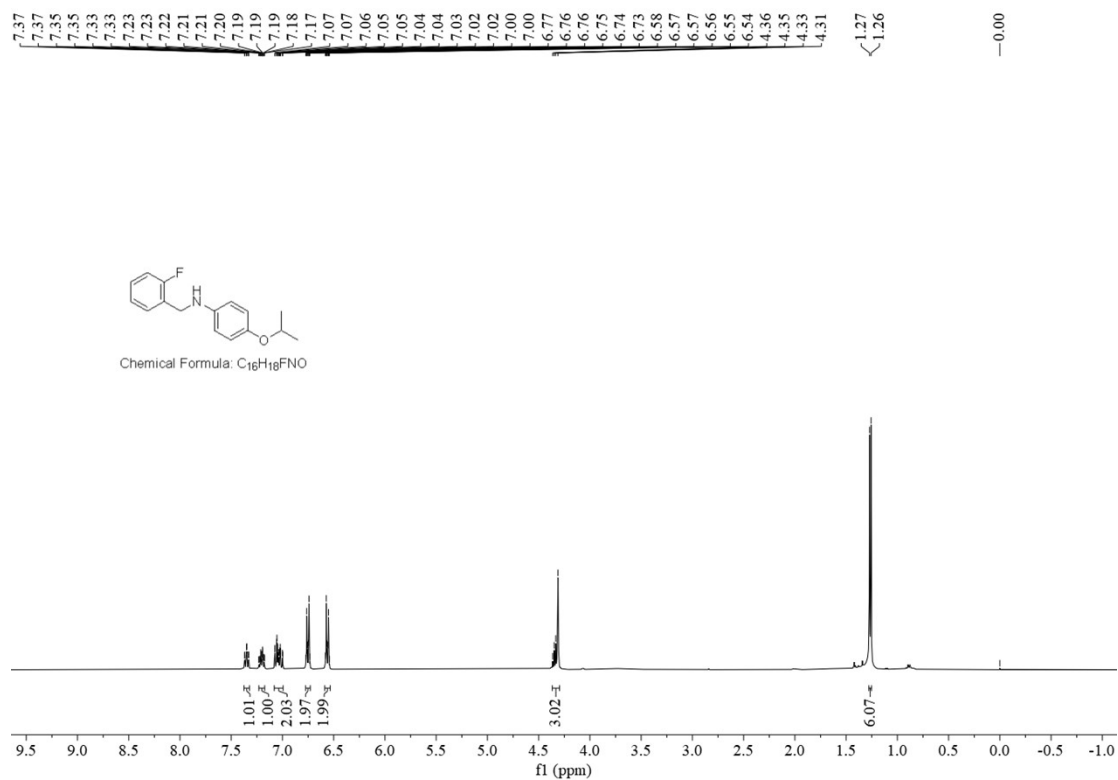


$^{13}C\{^1H\}$ NMR Spectrum of **3ea** in $CDCl_3$ at 100 MHz

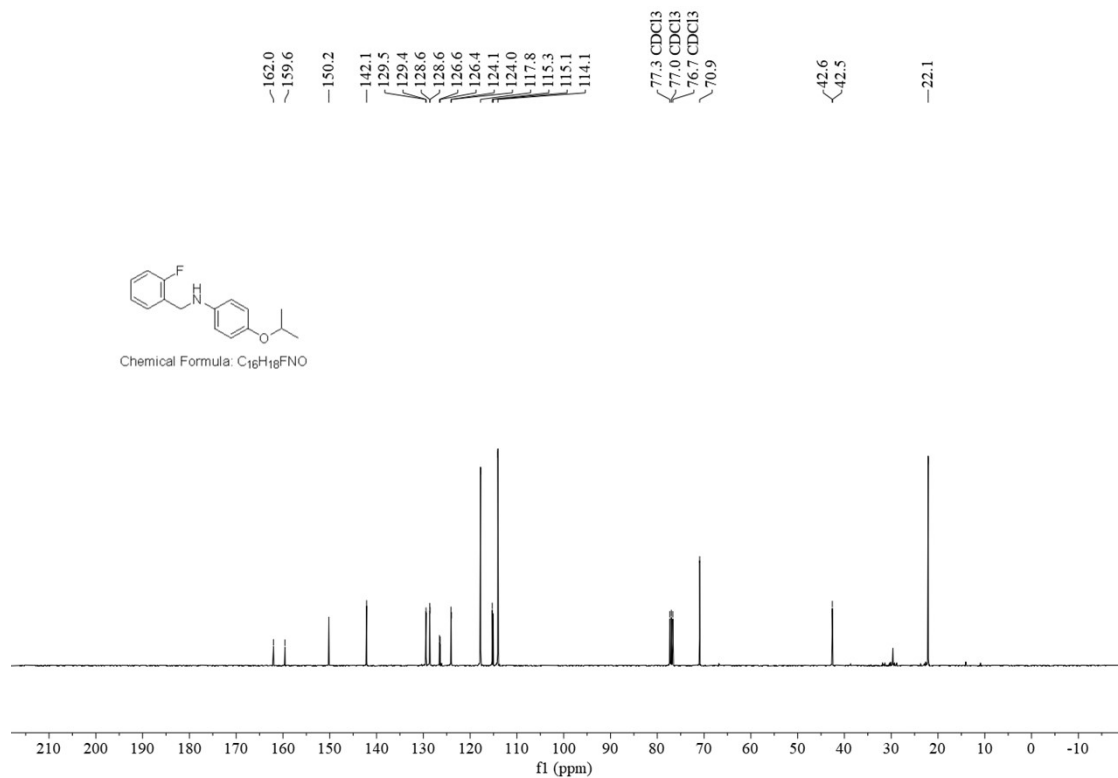




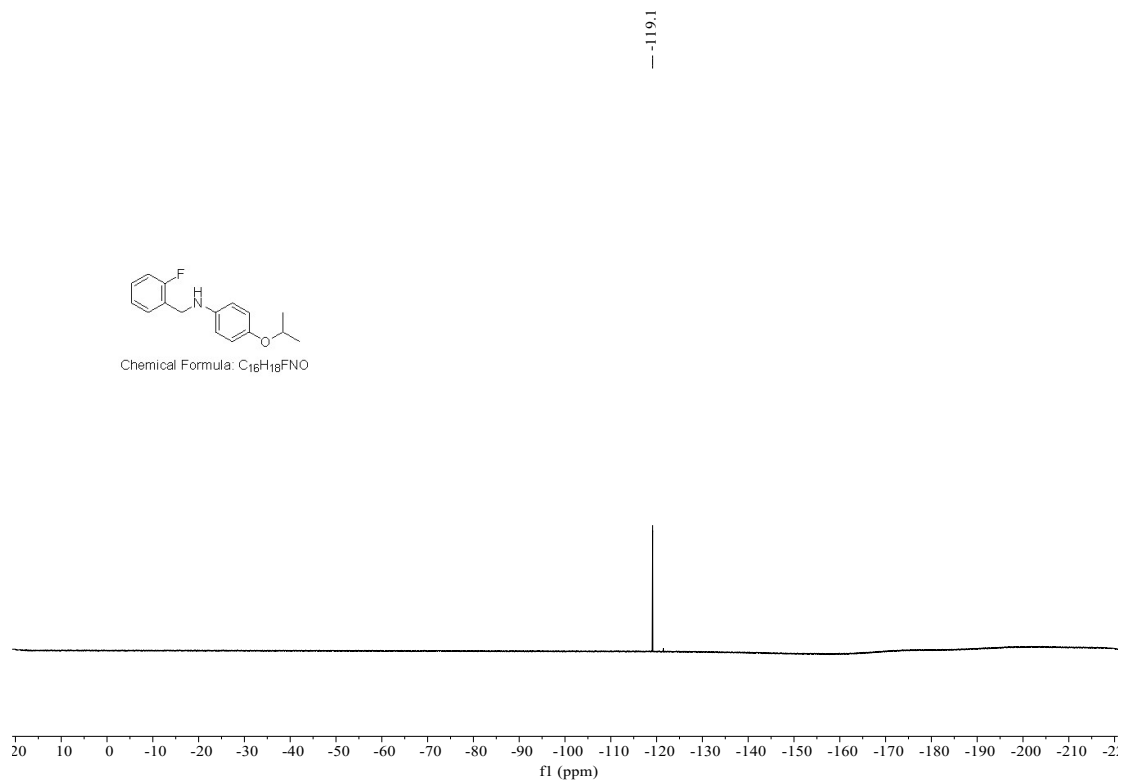




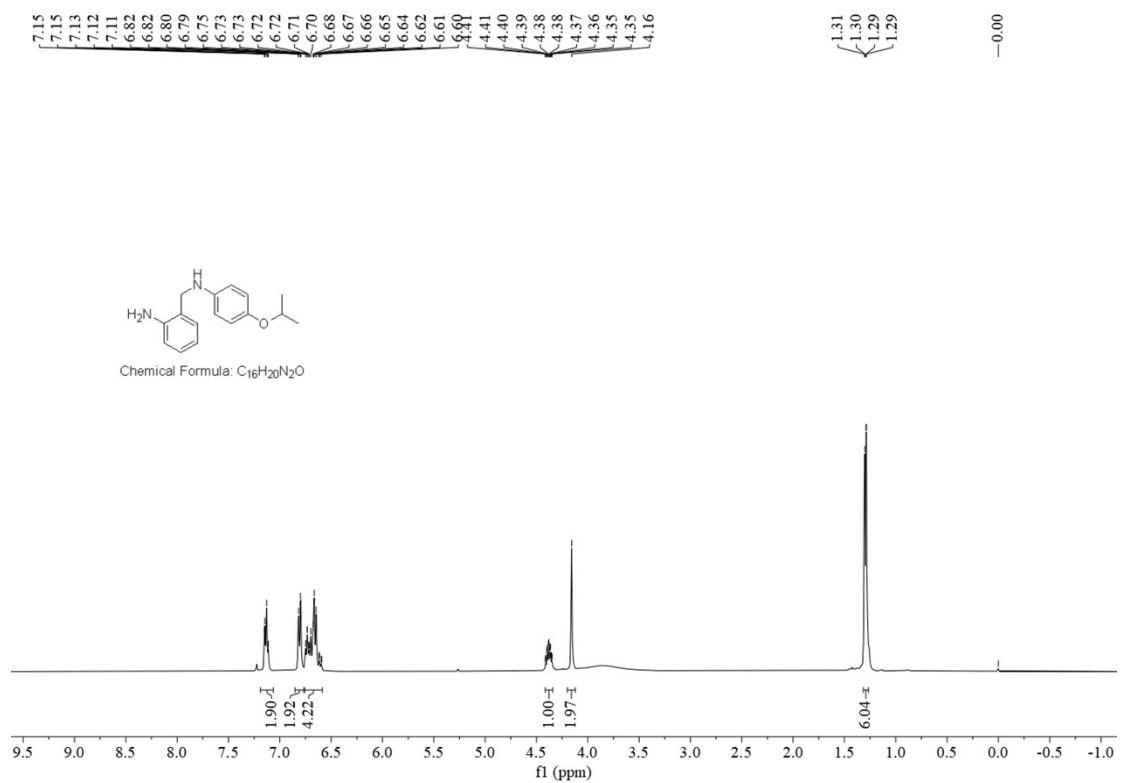
1H NMR Spectrum of **3ia** in $CDCl_3$ at 400 MHz



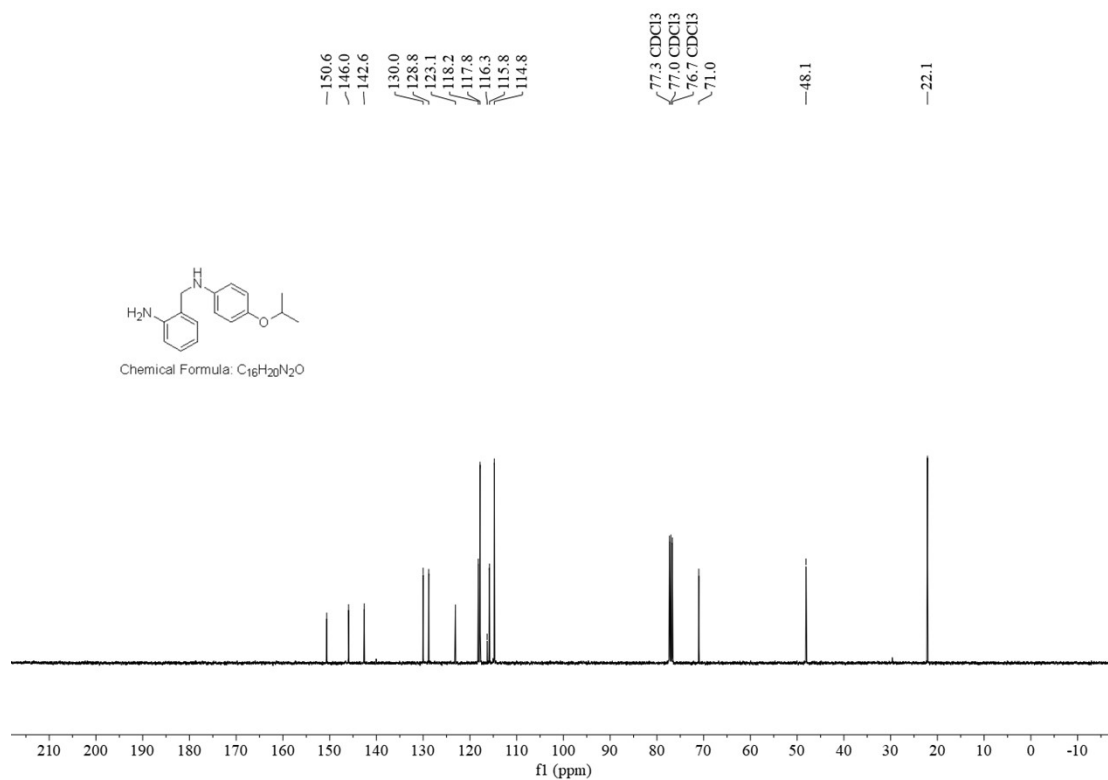
$^{13}C\{^1H\}$ NMR Spectrum of **3ia** in $CDCl_3$ at 100 MHz



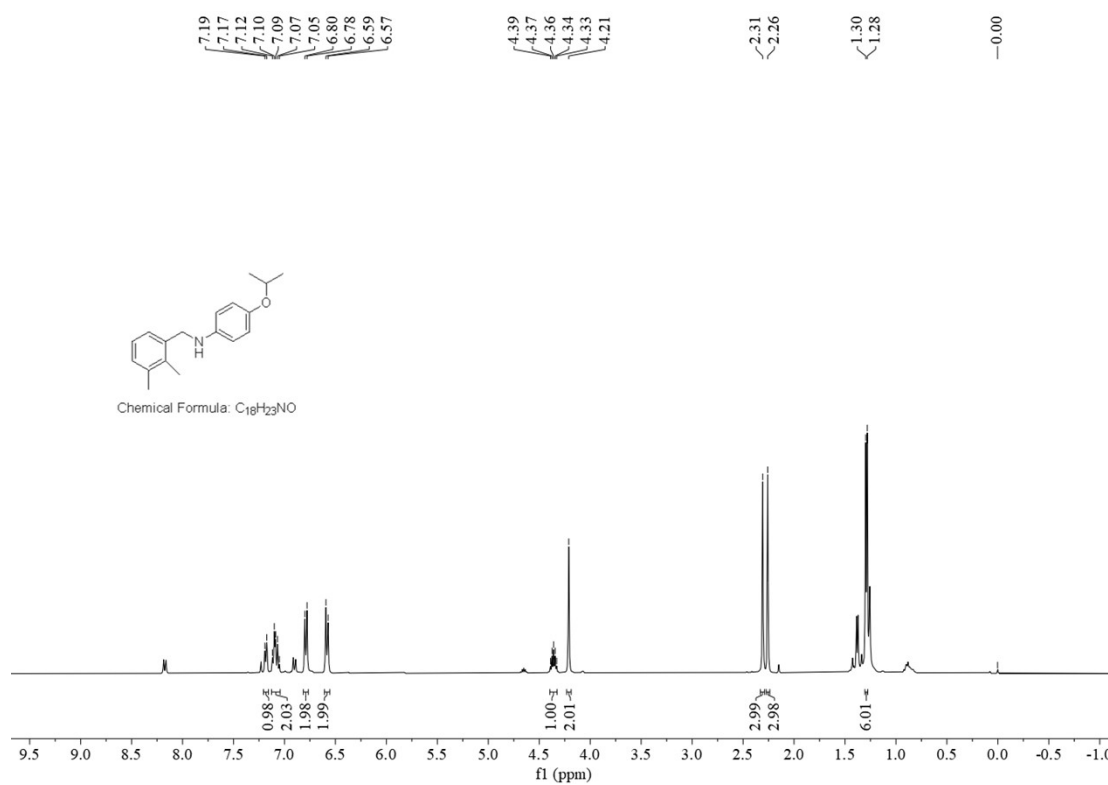
¹⁹F NMR Spectrum of **3ia** in CDCl₃ at 377 MHz



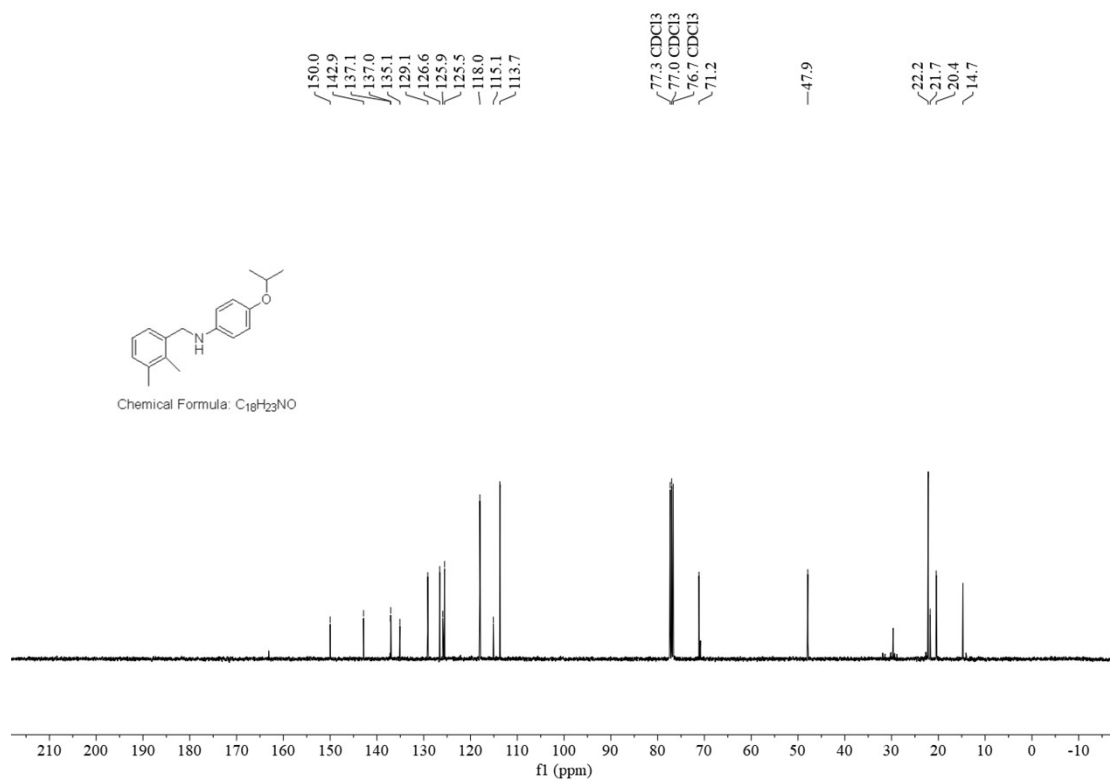
¹H NMR Spectrum of **3ja** in CDCl₃ at 400 MHz



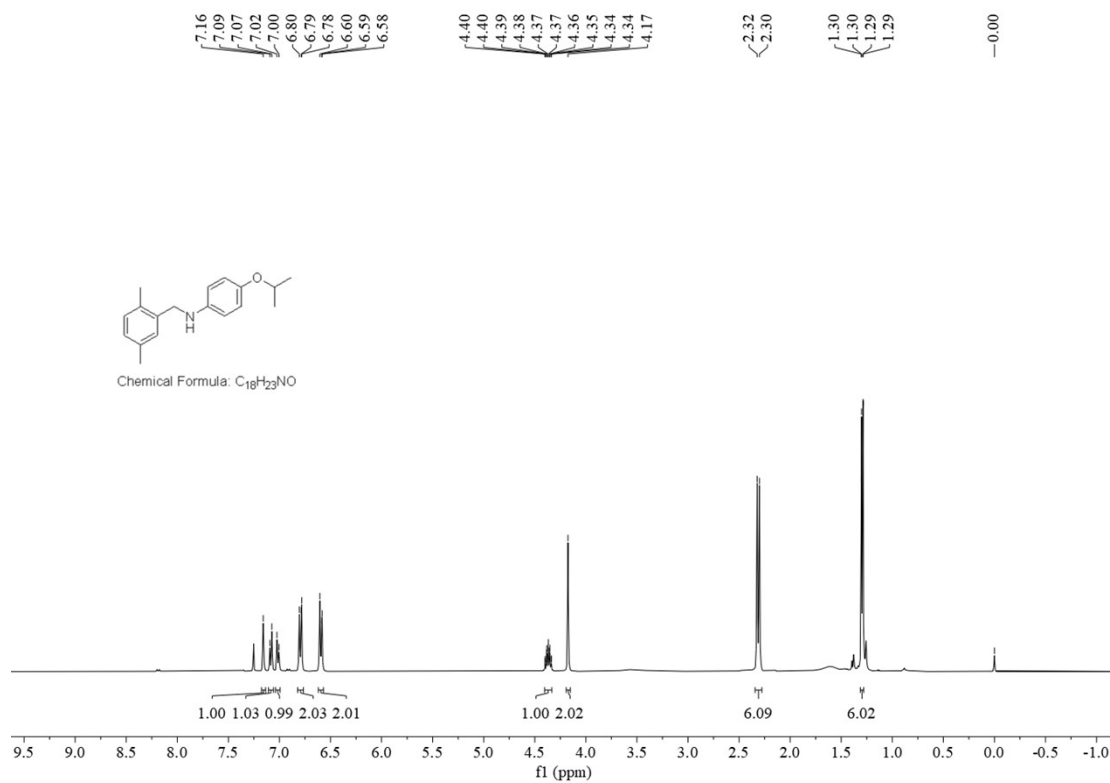
$^{13}C\{^1H\}$ NMR Spectrum of **3ja** in $CDCl_3$ at 100 MHz



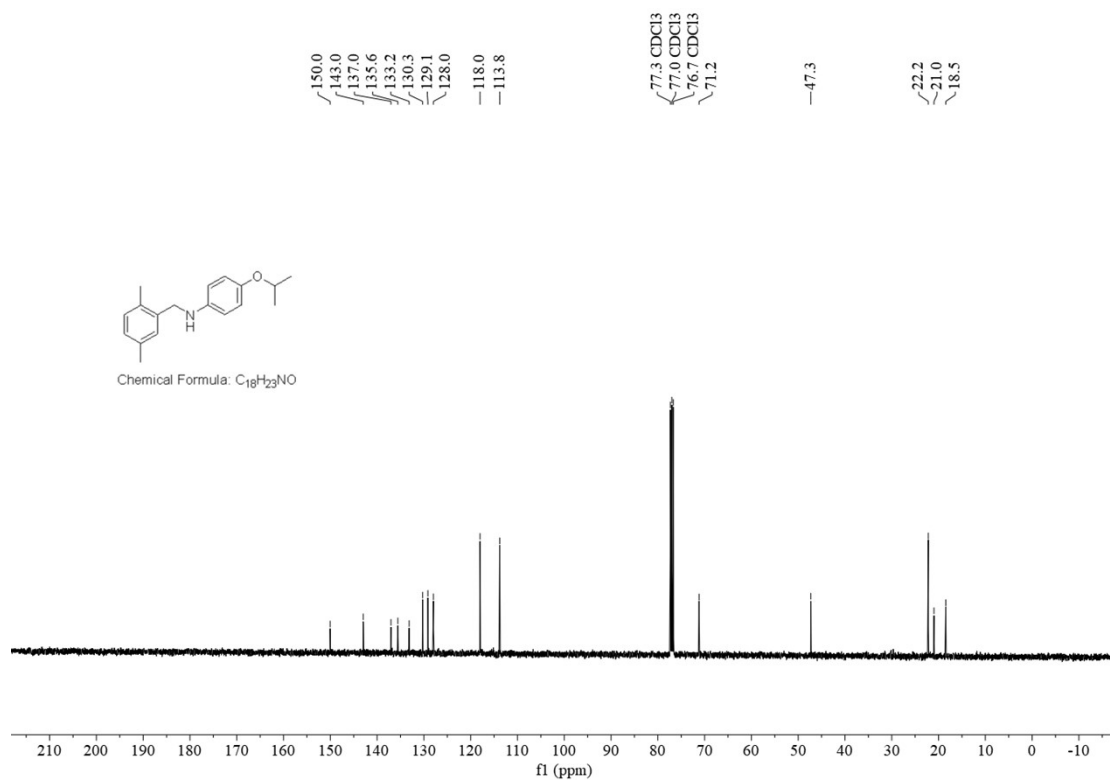
1H NMR Spectrum of **3ka** in $CDCl_3$ at 400 MHz



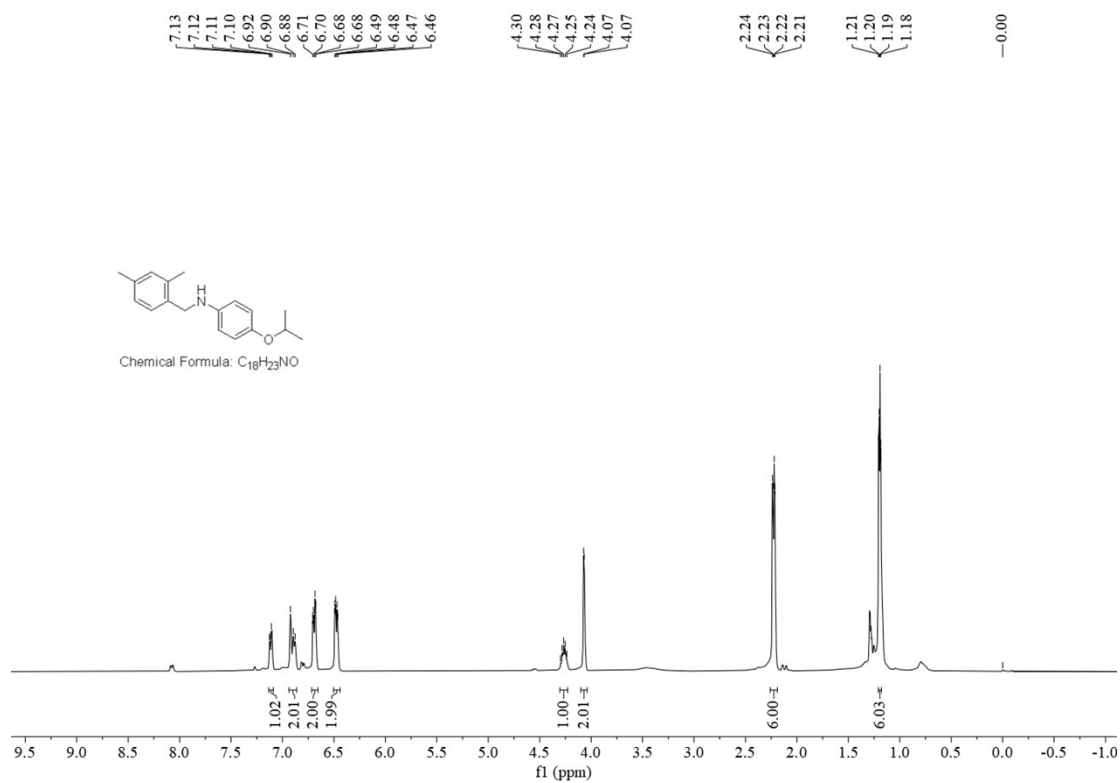
¹³C{¹H} NMR Spectrum of **3ka** in CDCl₃ at 100 MHz



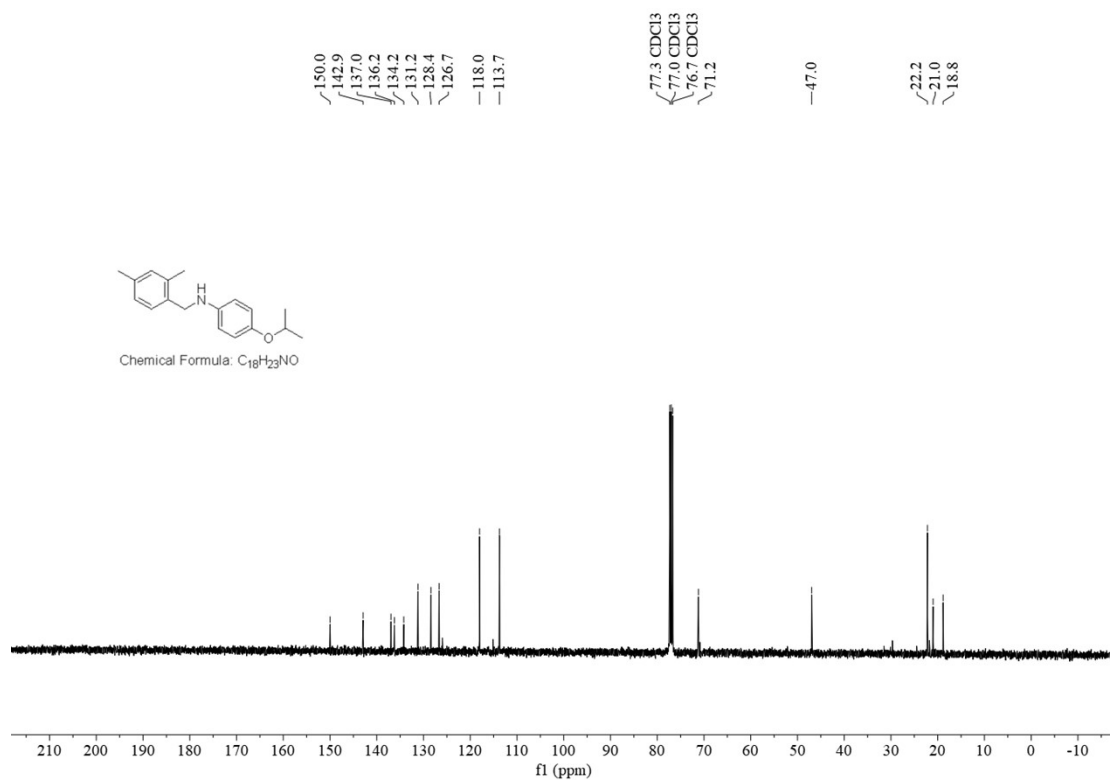
¹H NMR Spectrum of **3la** in CDCl₃ at 400 MHz



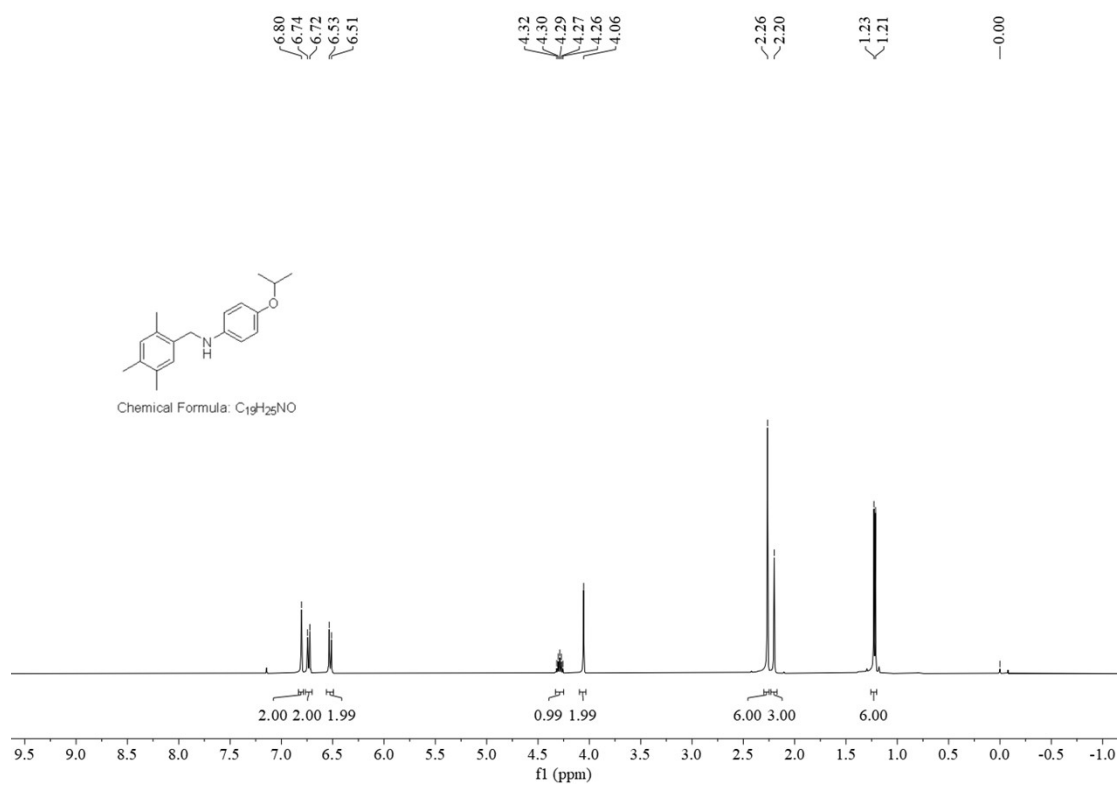
¹³C{¹H} NMR Spectrum of **3la** in CDCl₃ at 100 MHz



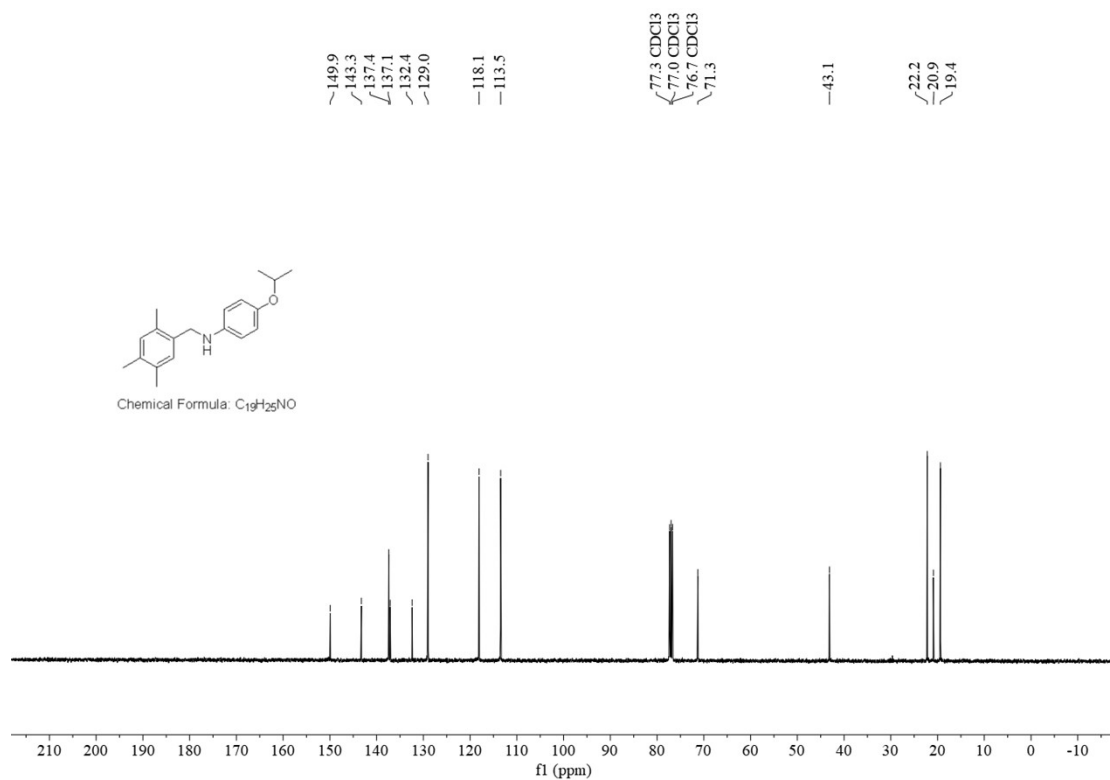
¹H NMR Spectrum of **3ma** in CDCl₃ at 400 MHz



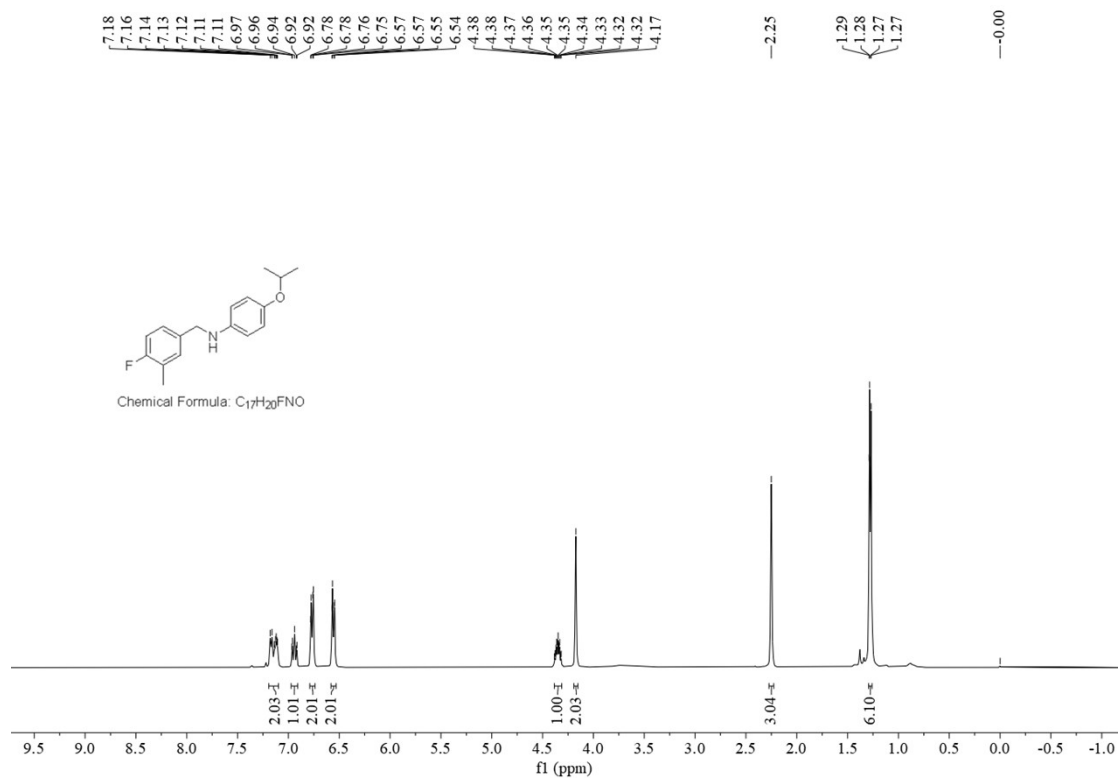
$^{13}C\{^1H\}$ NMR Spectrum of **3ma** in $CDCl_3$ at 100 MHz



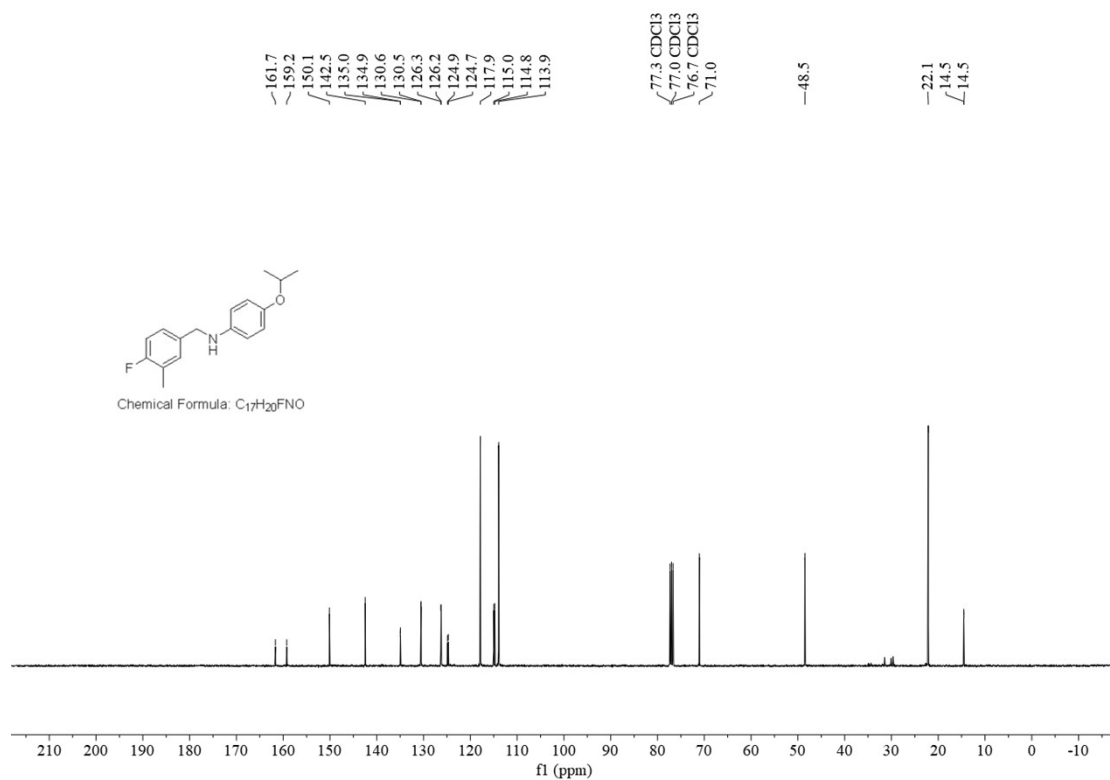
1H NMR Spectrum of **3na** in $CDCl_3$ at 400 MHz



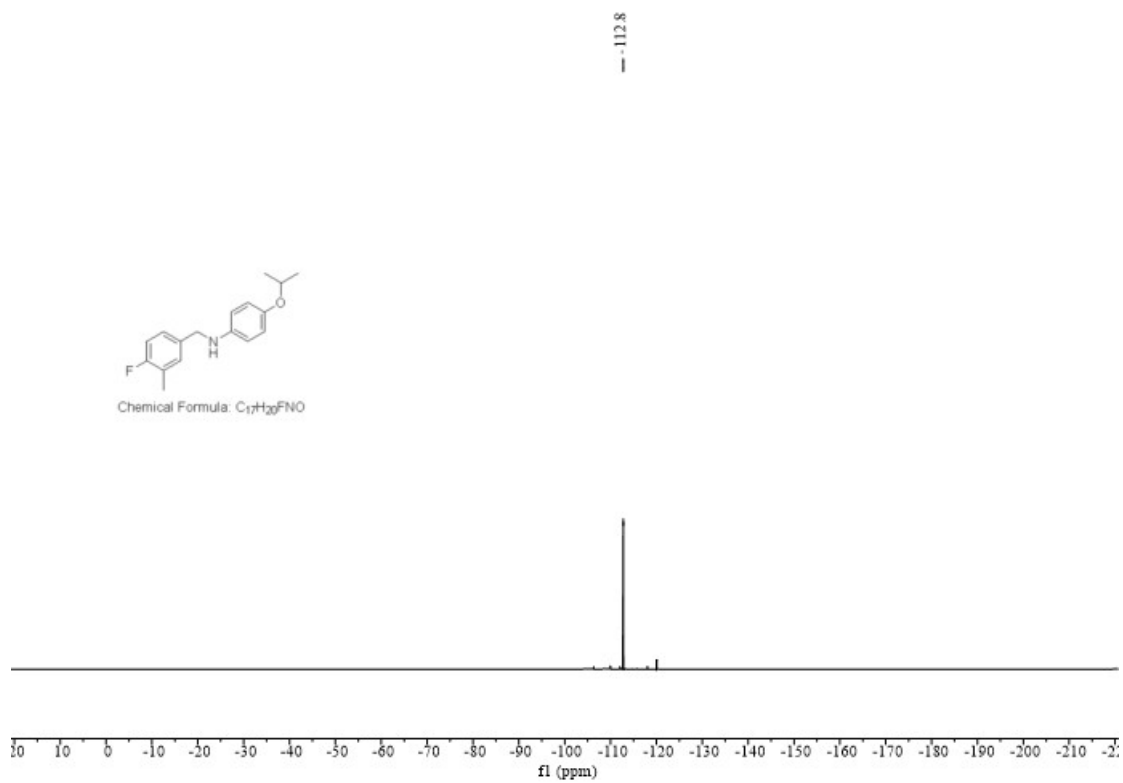
$^{13}C\{^1H\}$ NMR Spectrum of **3na** in $CDCl_3$ at 100 MHz



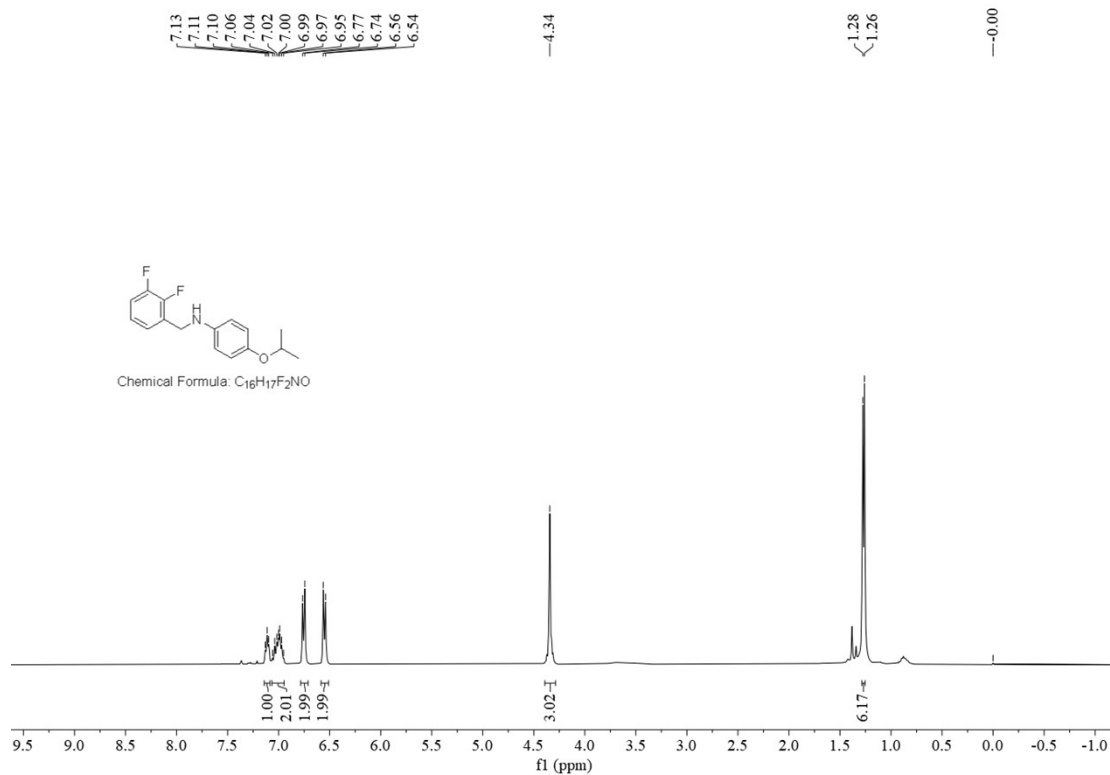
1H NMR Spectrum of **3oa** in $CDCl_3$ at 400 MHz



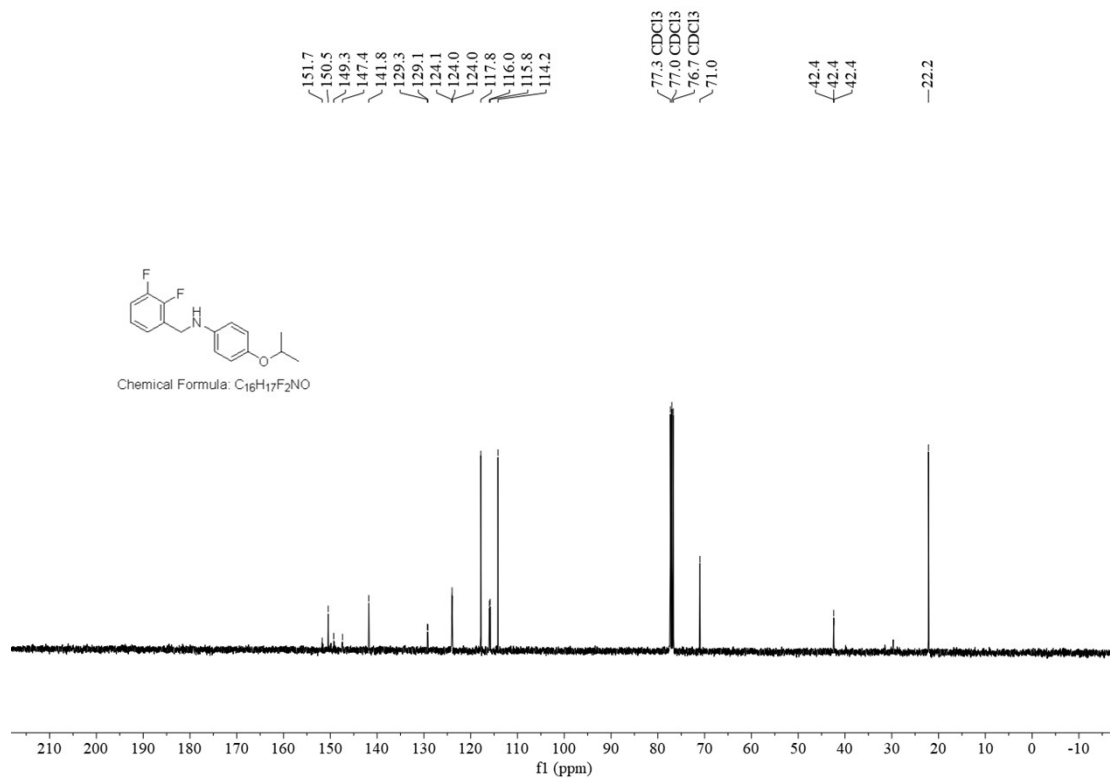
¹³C{¹H} NMR Spectrum of **30a** in CDCl₃ at 100 MHz



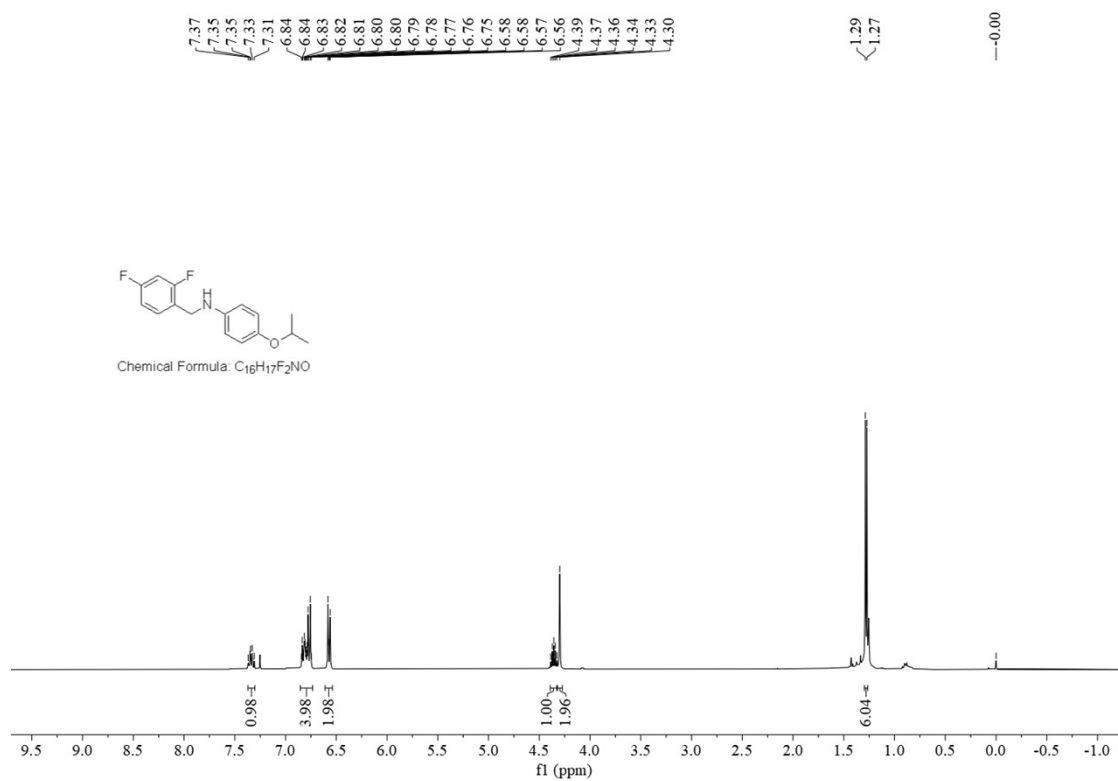
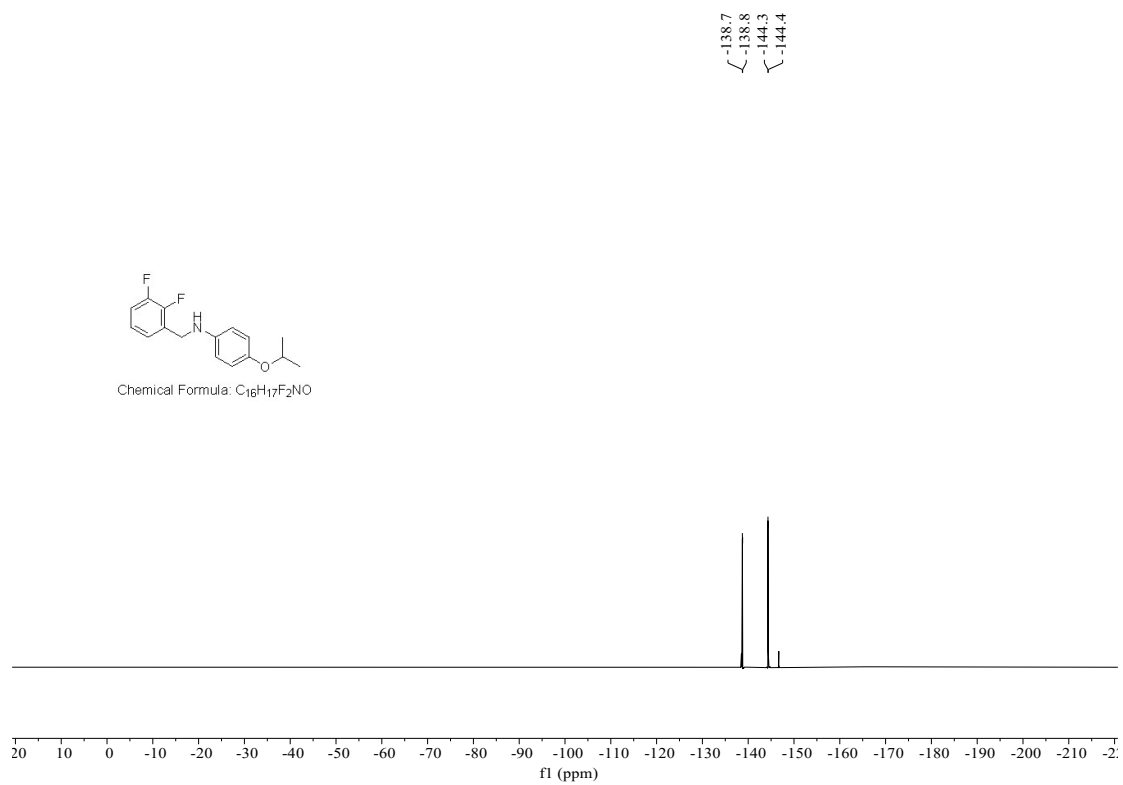
¹⁹F NMR Spectrum of **30a** in CDCl₃ at 377 MHz

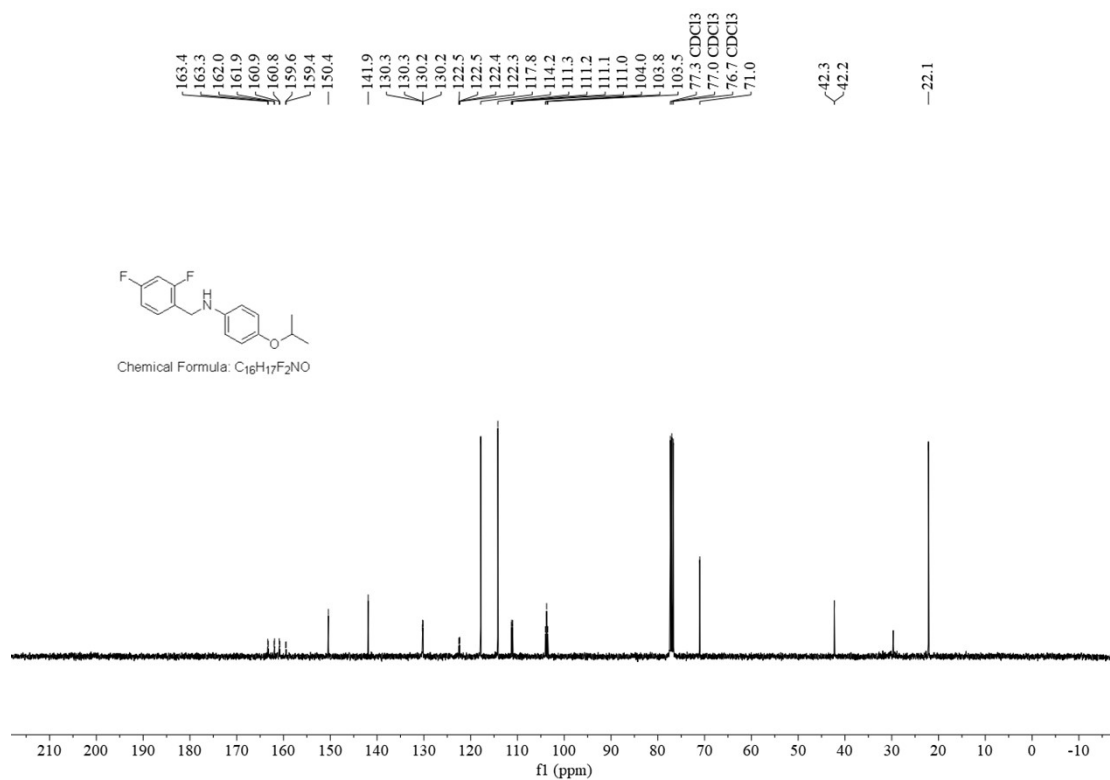


^1H NMR Spectrum of **3pa** in CDCl_3 at 400 MHz

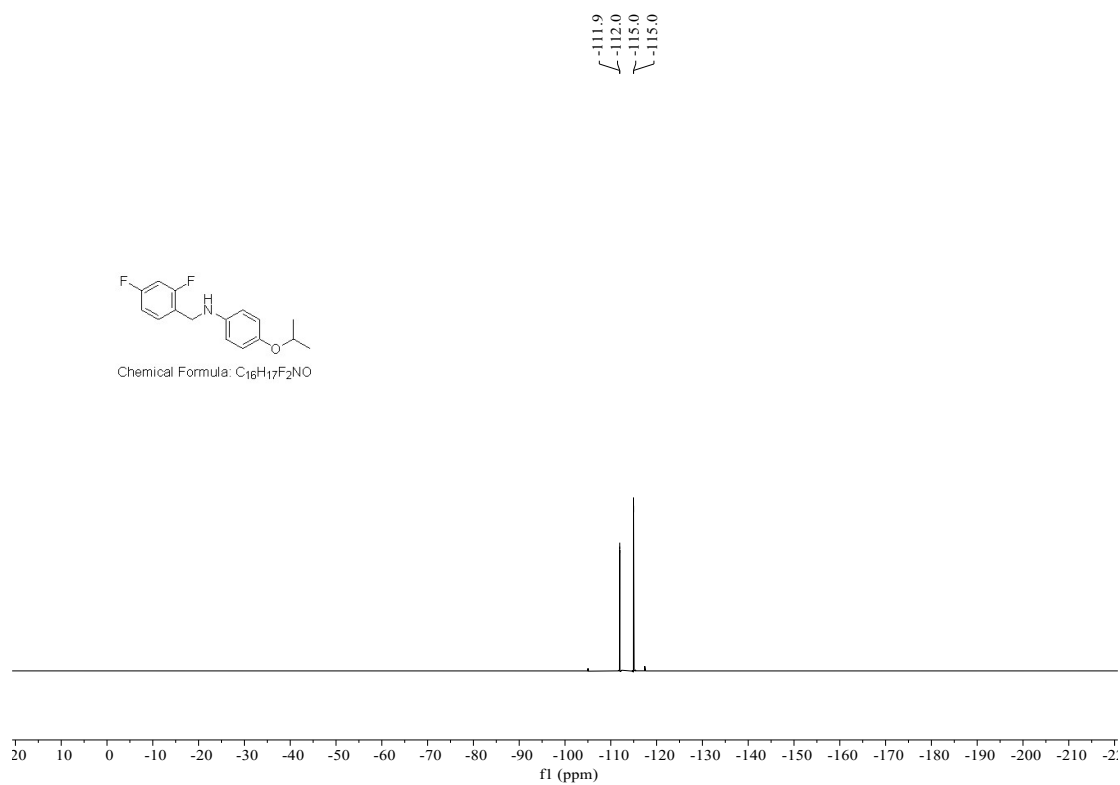


$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **3pa** in CDCl_3 at 100 MHz

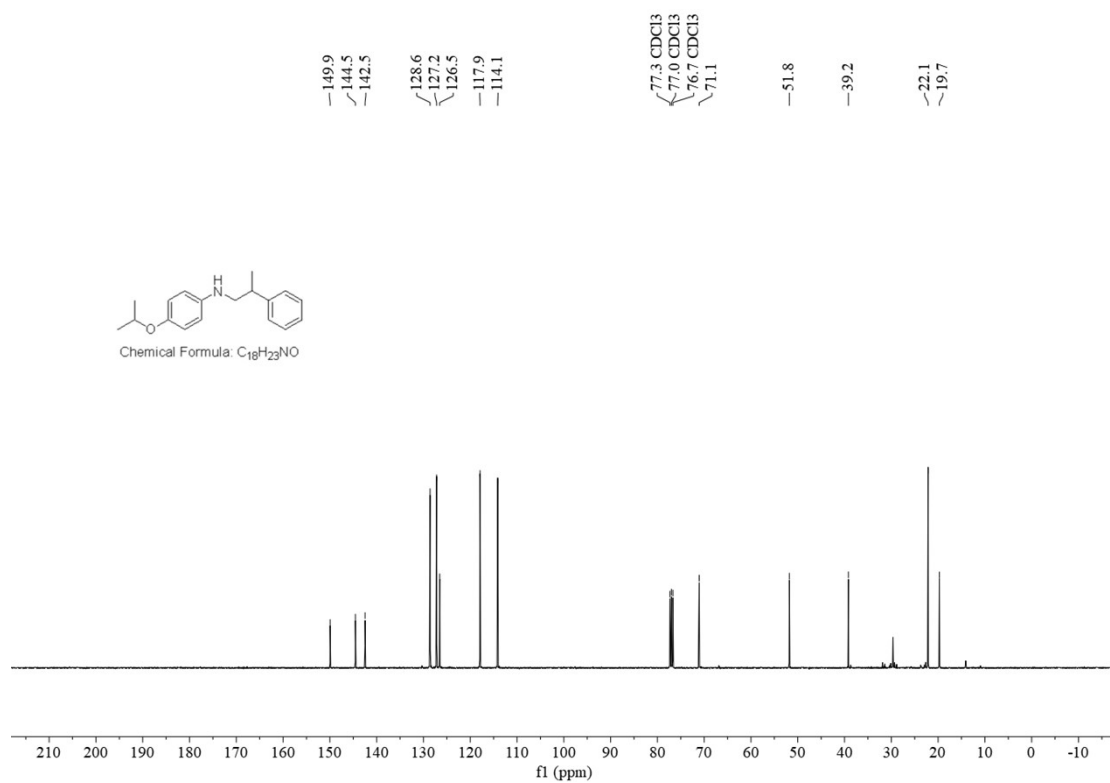
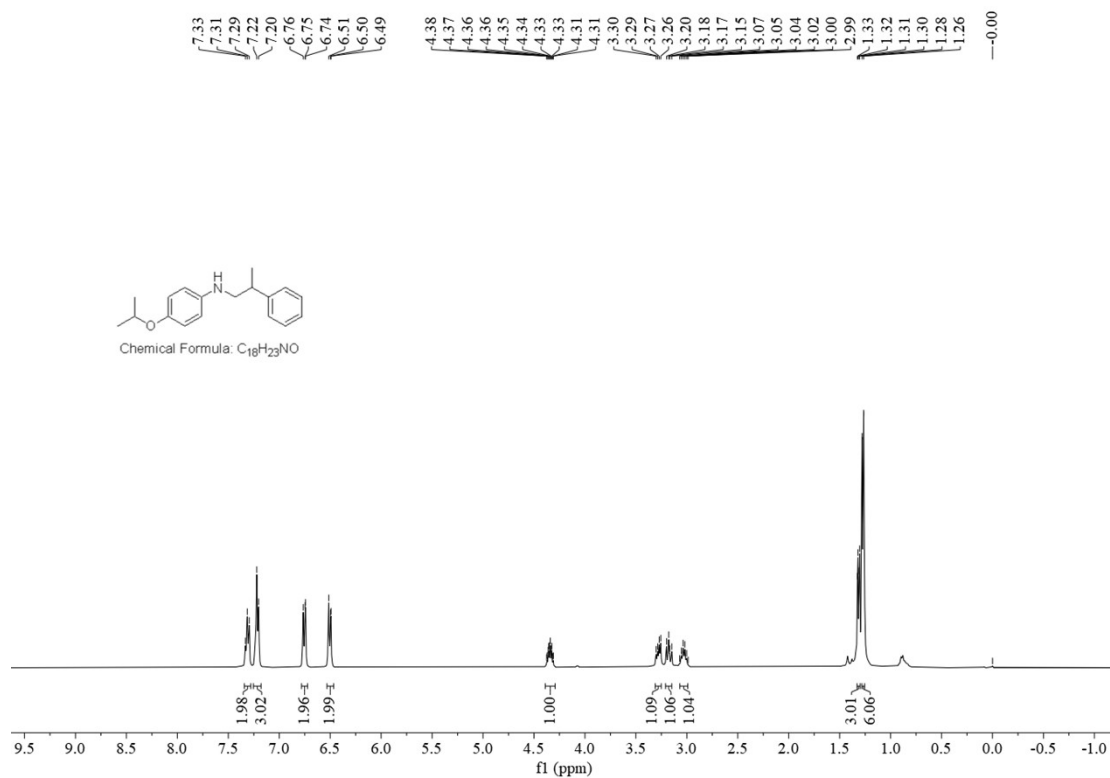


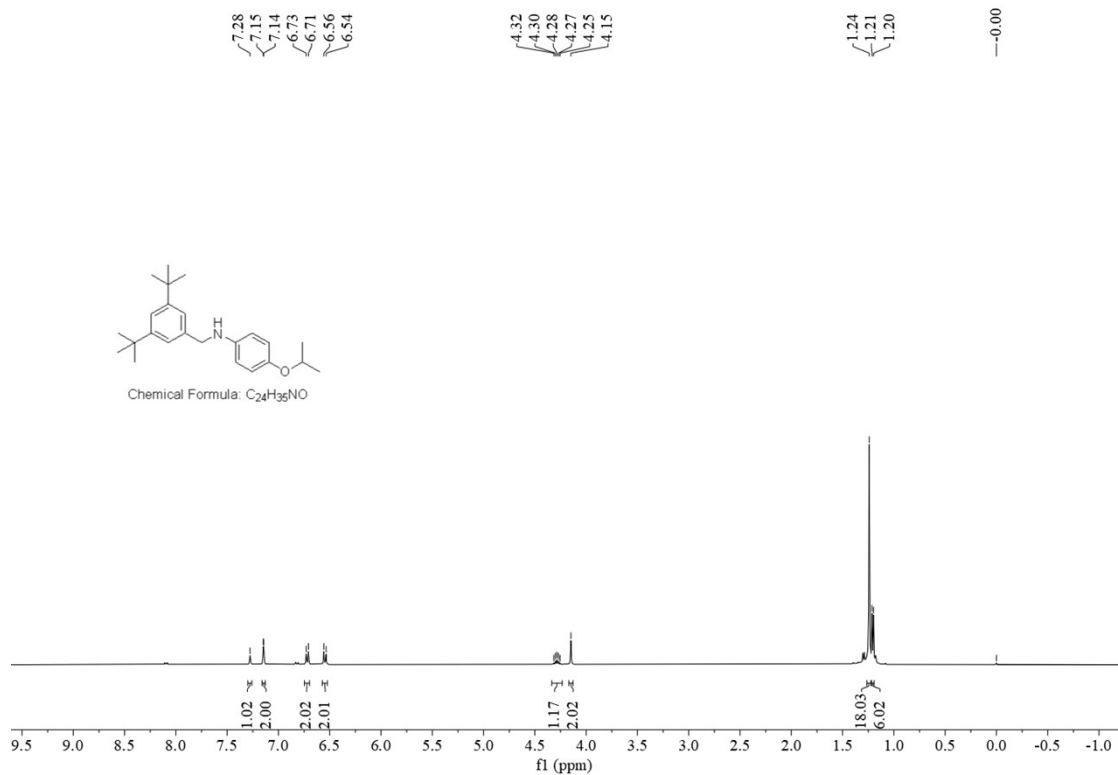


$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **3qa** in CDCl_3 at 100 MHz

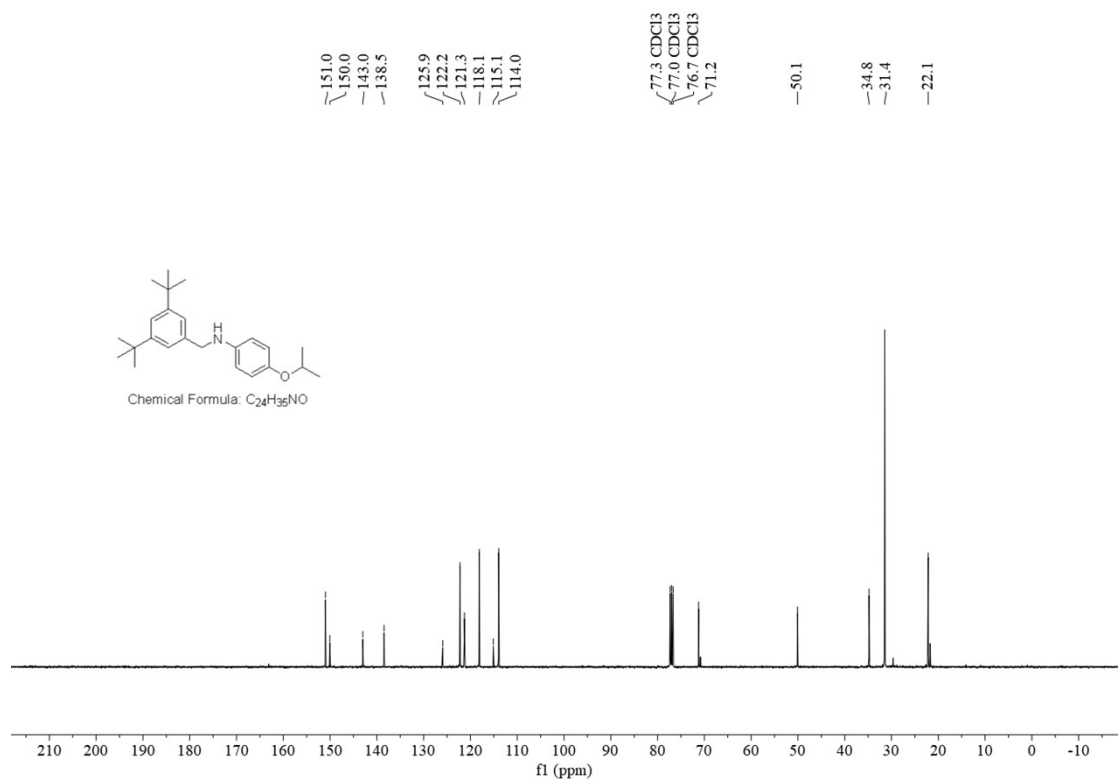


^{19}F NMR Spectrum of **3qa** in CDCl_3 at 377 MHz

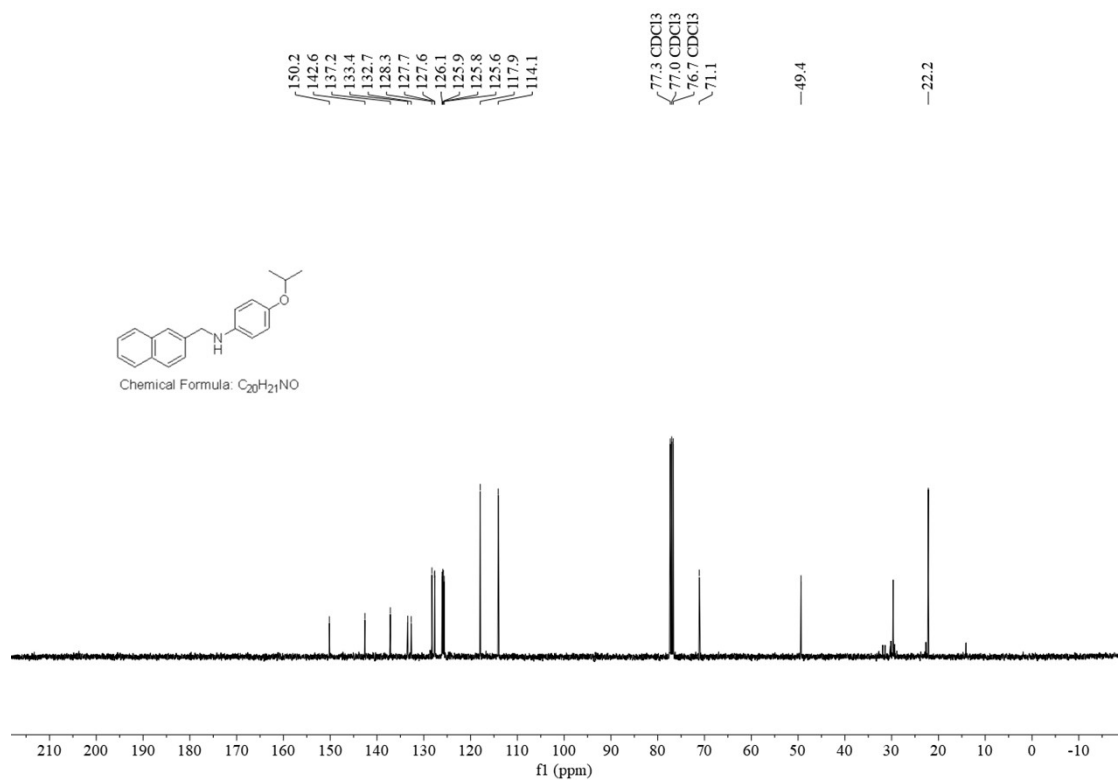
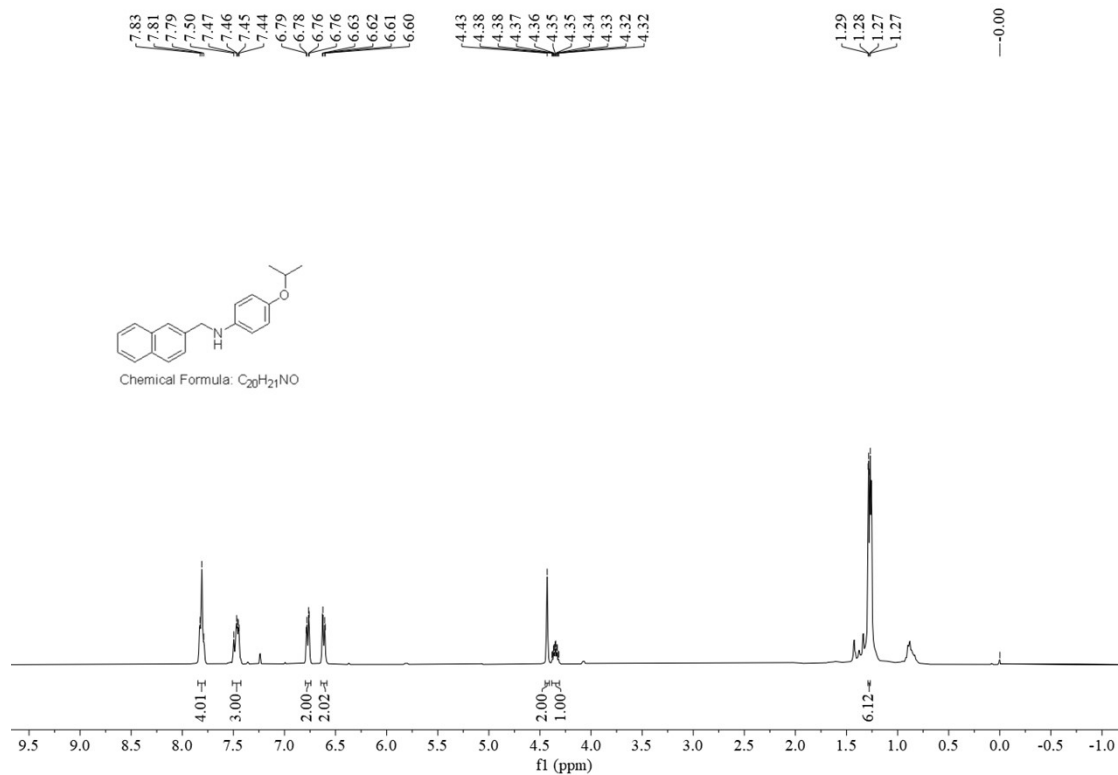


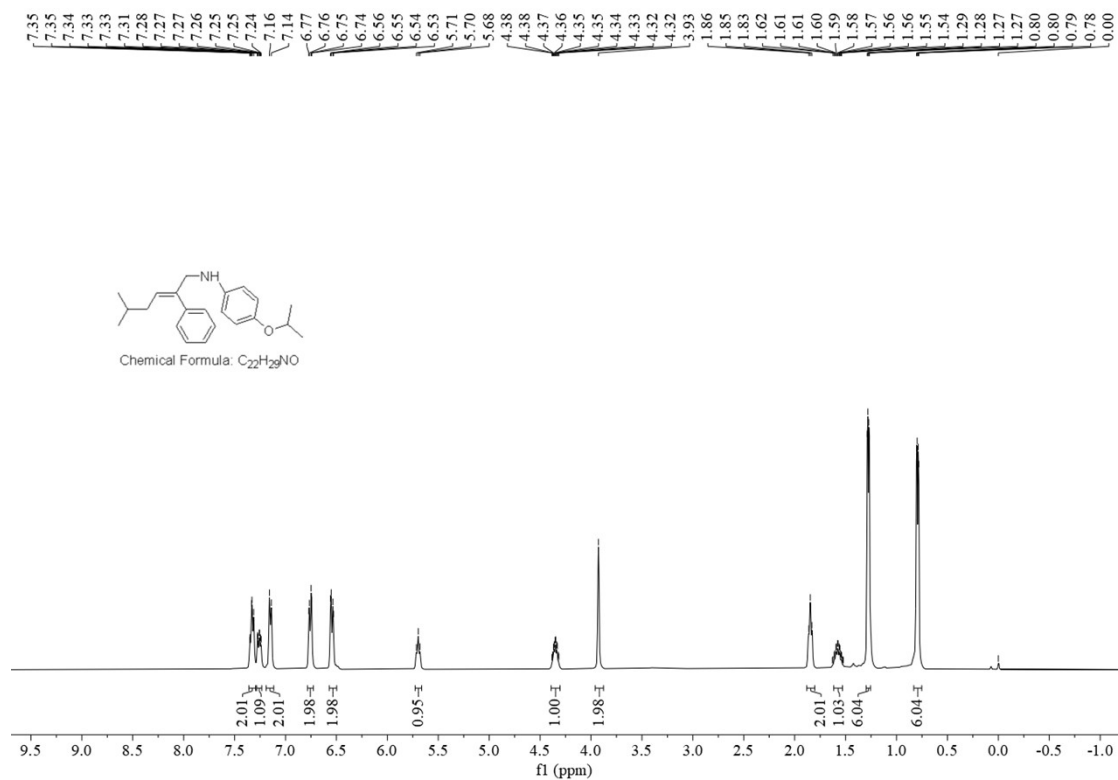


1H NMR Spectrum of **3sa** in $CDCl_3$ at 400 MHz

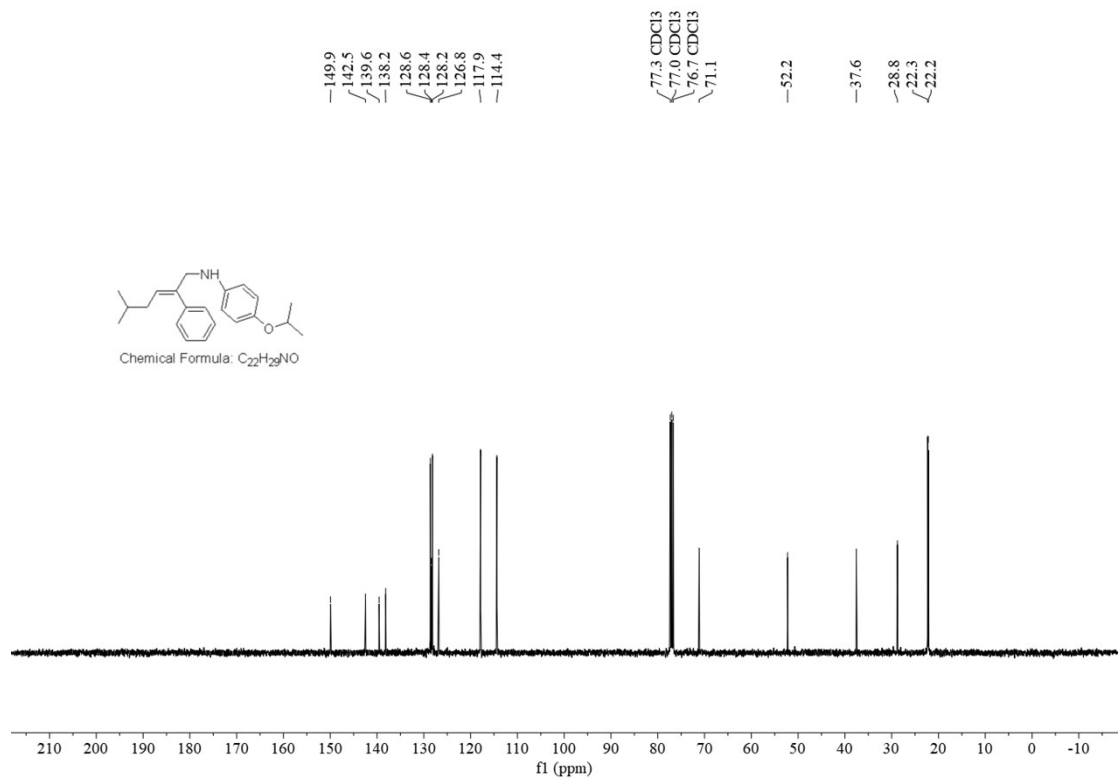


$^{13}C\{^1H\}$ NMR Spectrum of **3sa** in $CDCl_3$ at 100 MHz

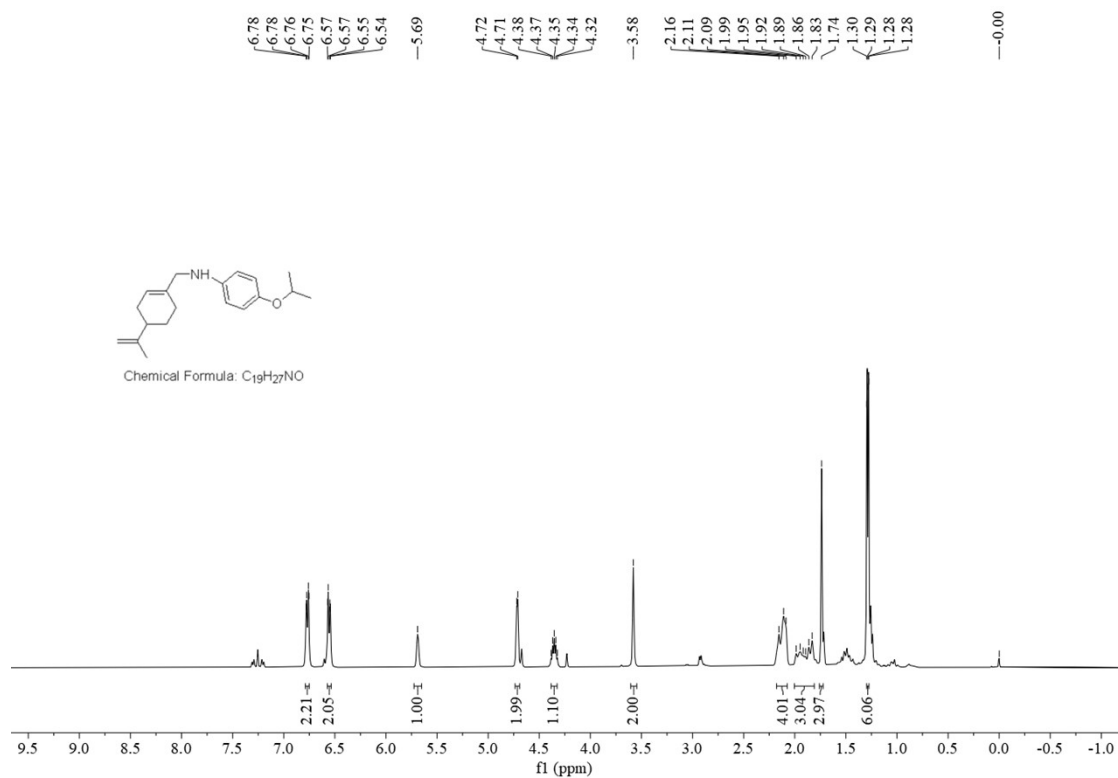




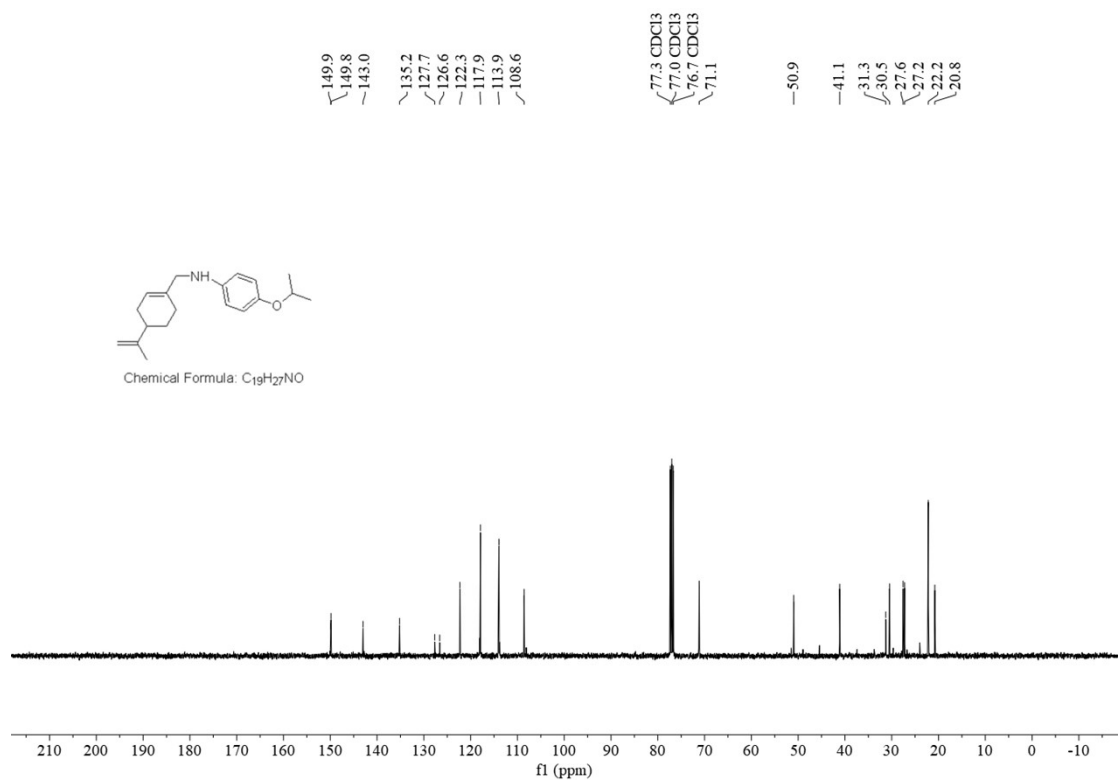
¹H NMR Spectrum of **3ua** in CDCl₃ at 400 MHz



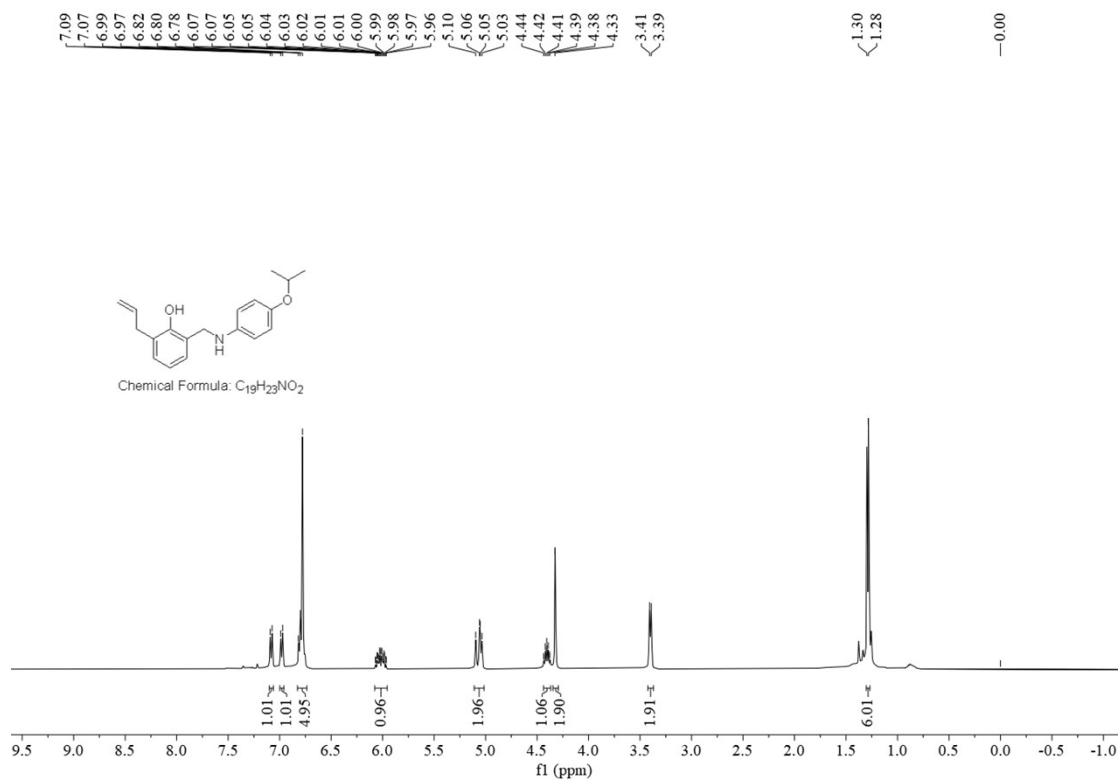
¹³C{¹H} NMR Spectrum of **3ua** in CDCl₃ at 100 MHz



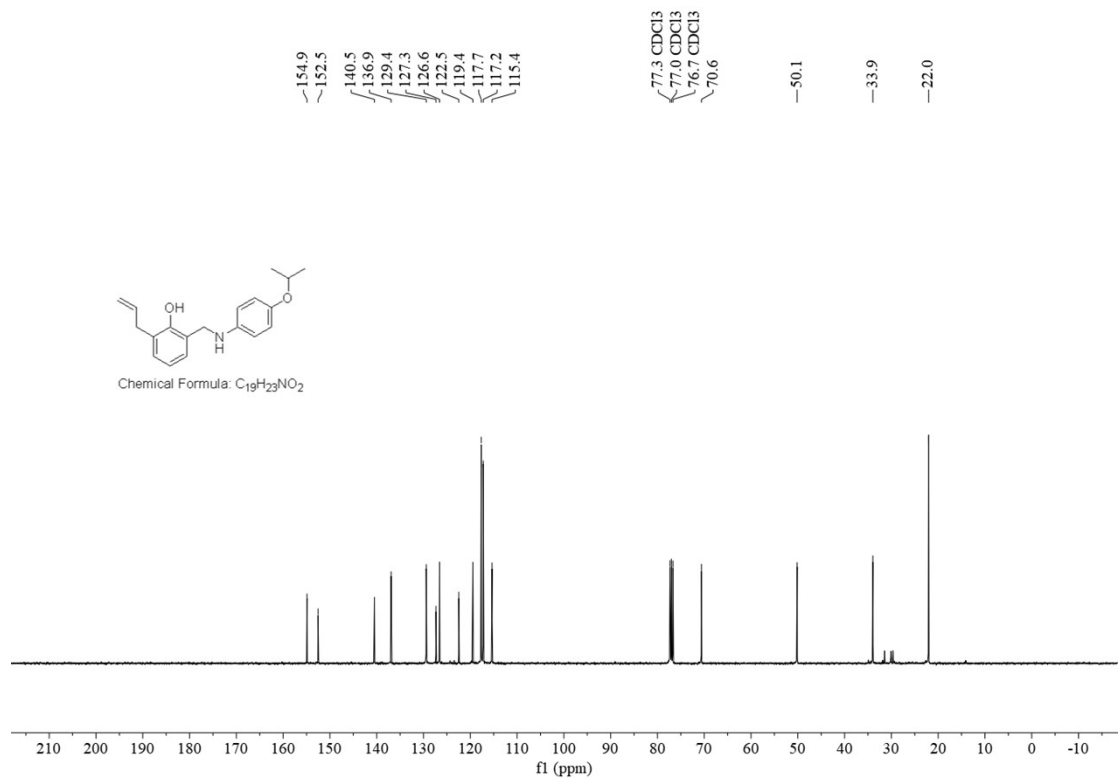
¹H NMR Spectrum of **3va** in CDCl₃ at 400 MHz



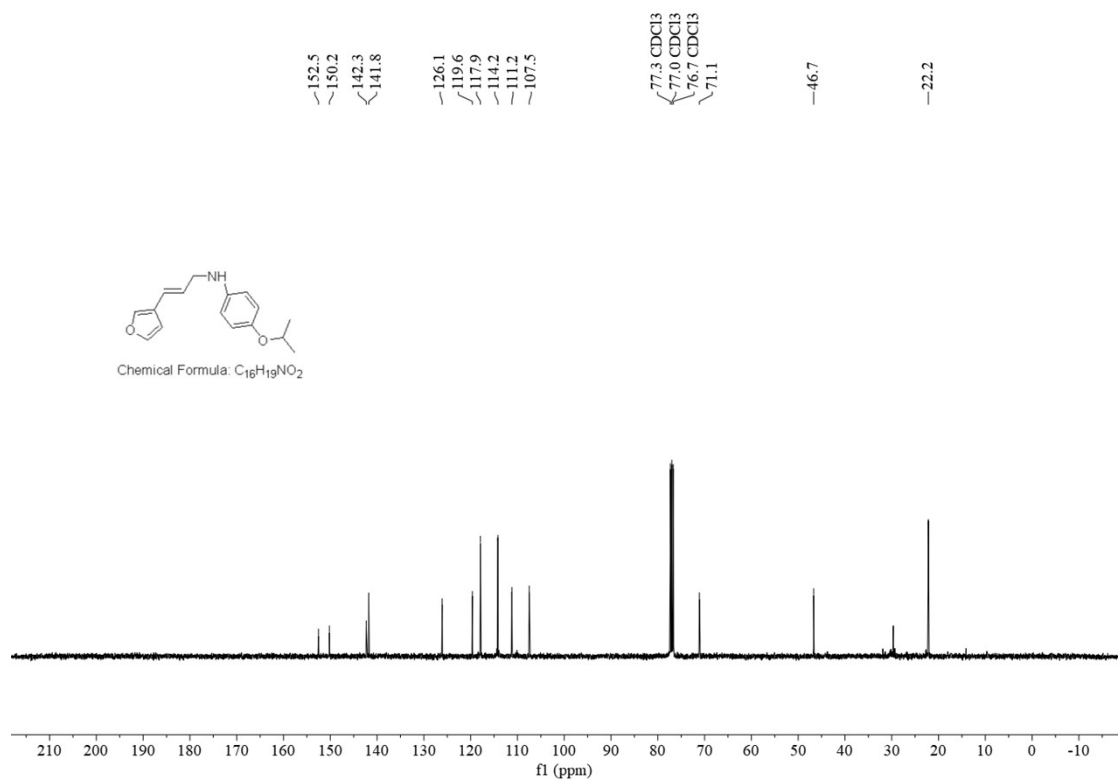
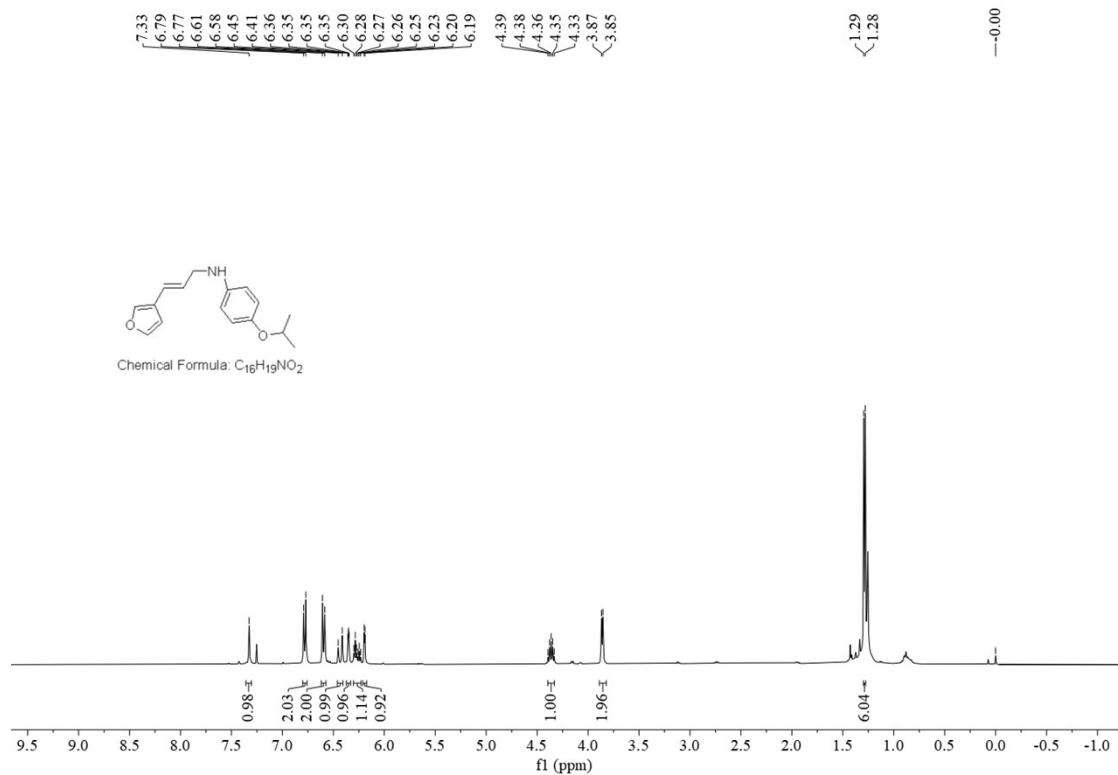
¹³C {¹H} NMR Spectrum of **3va** in CDCl₃ at 100 MHz

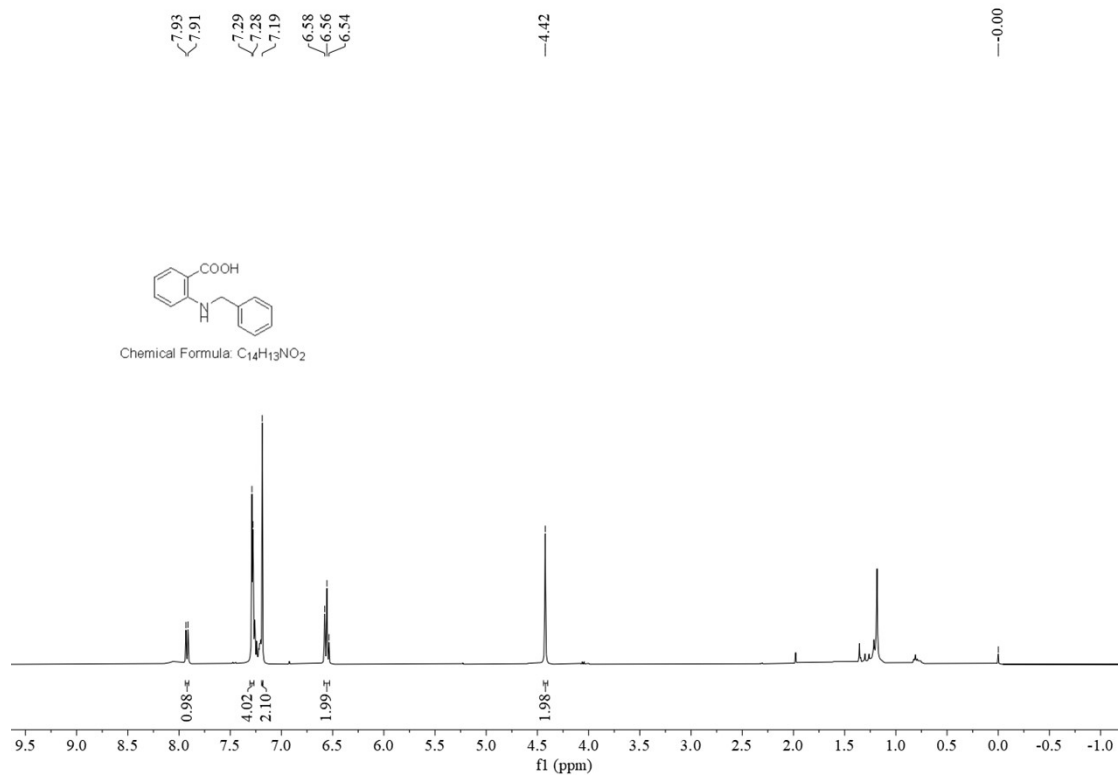


1H NMR Spectrum of **3wa** in $CDCl_3$ at 400 MHz

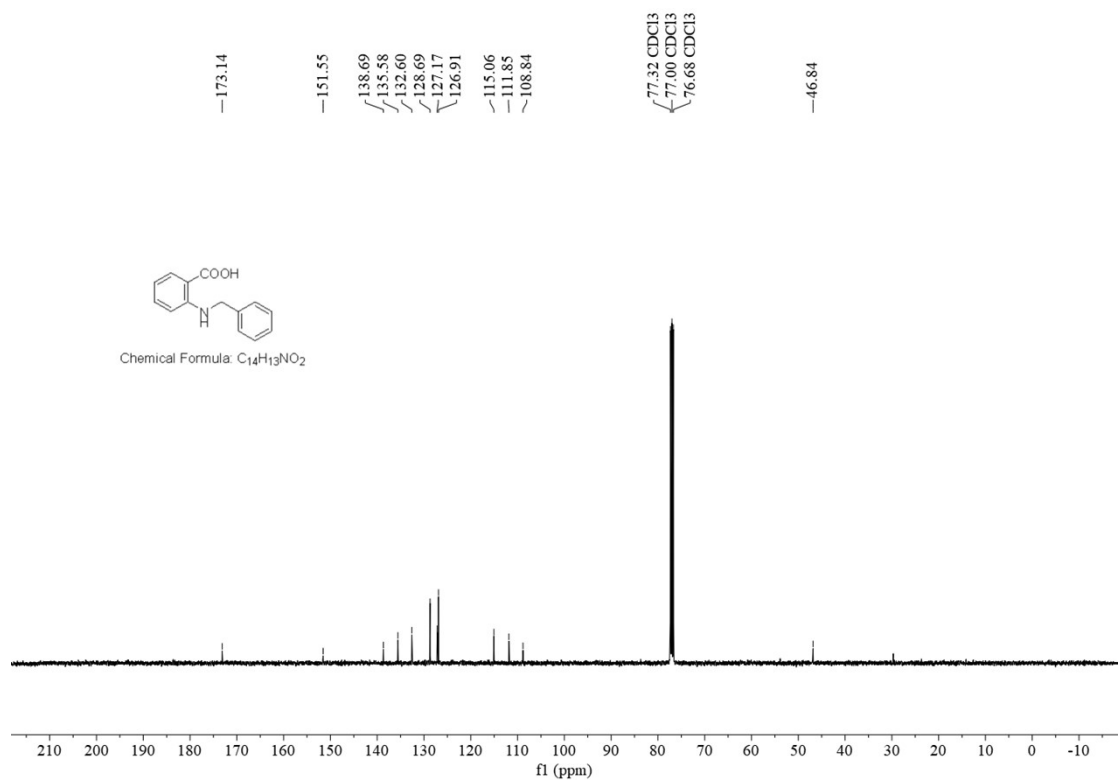


$^{13}C\{^1H\}$ NMR Spectrum of **3wa** in $CDCl_3$ at 100 MHz

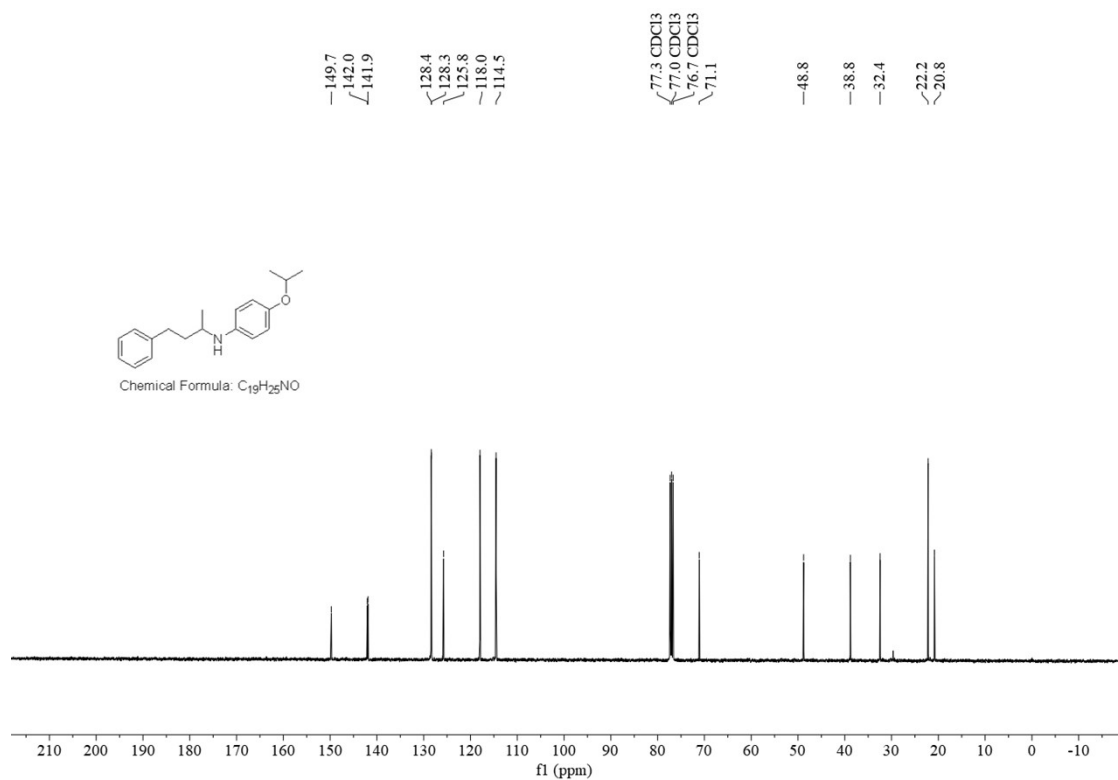
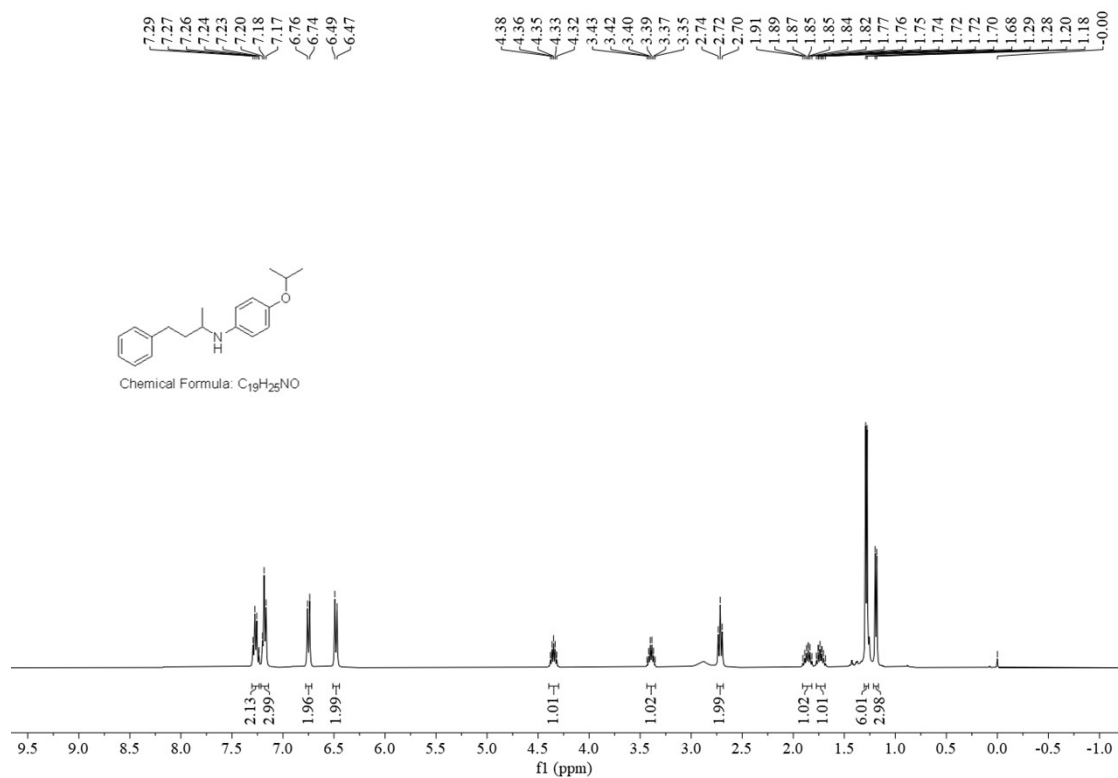


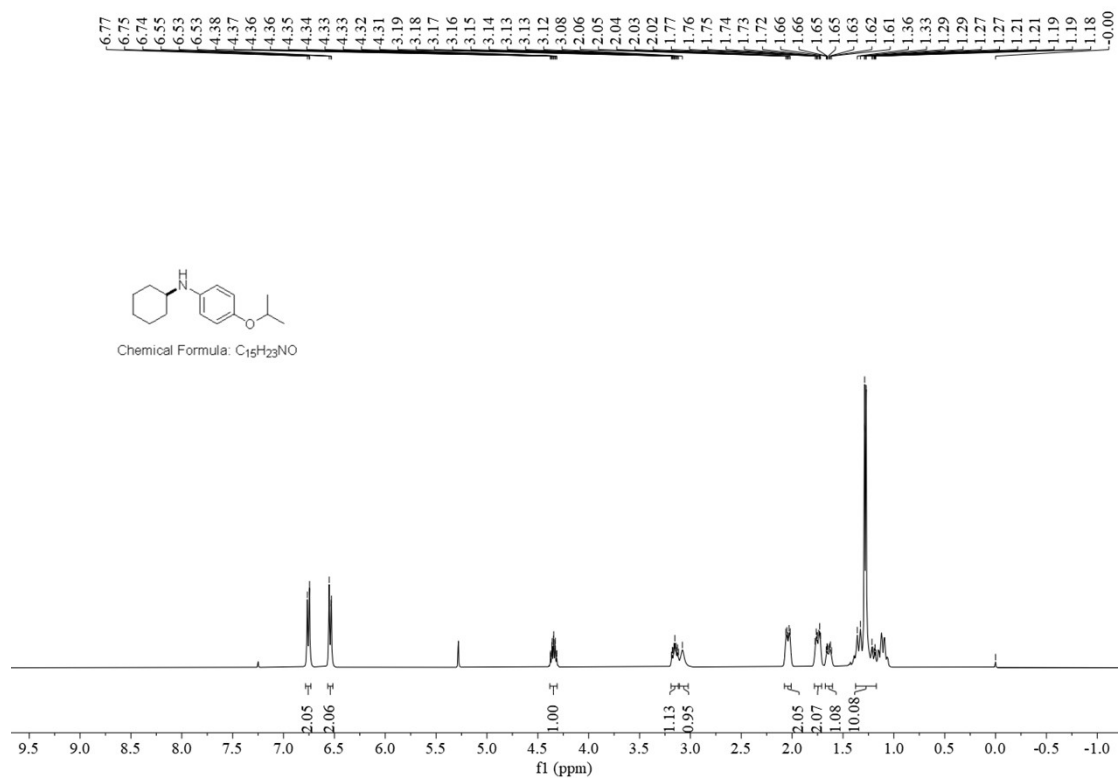


¹H NMR Spectrum of **3ab** in CDCl₃ at 400 MHz

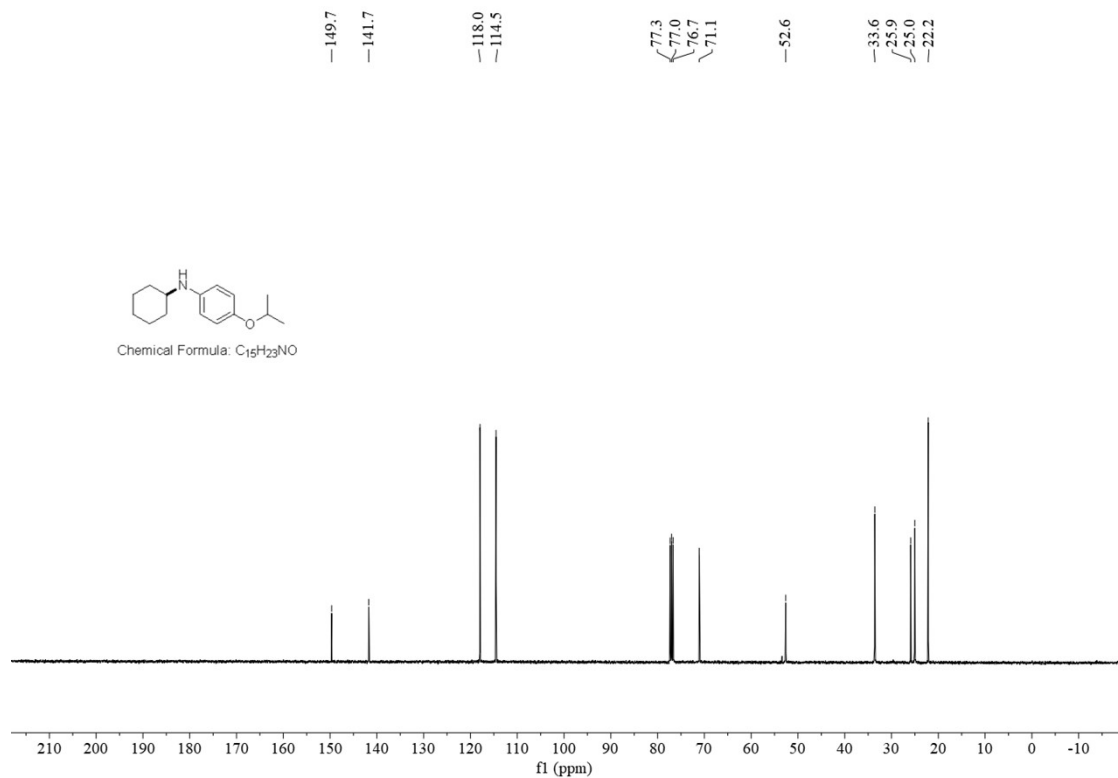


¹³C{¹H} NMR Spectrum of **3ab** in CDCl₃ at 100 MHz

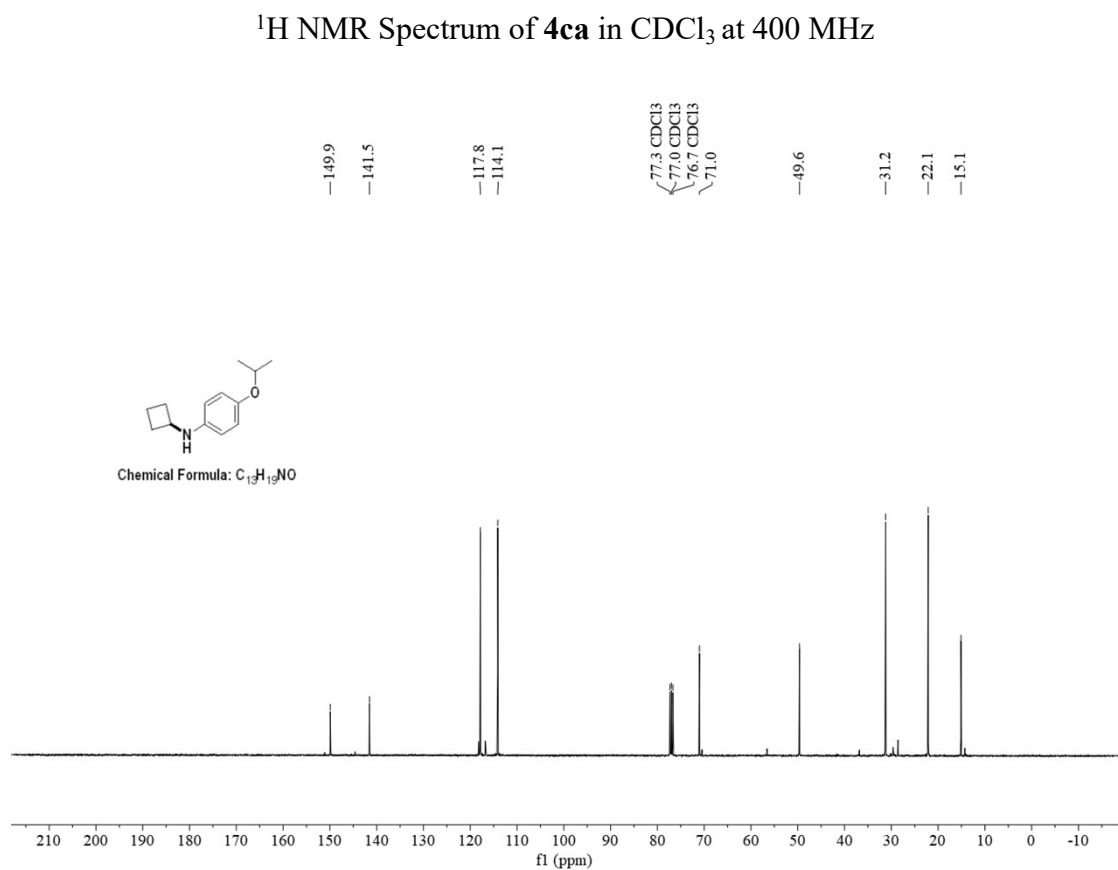
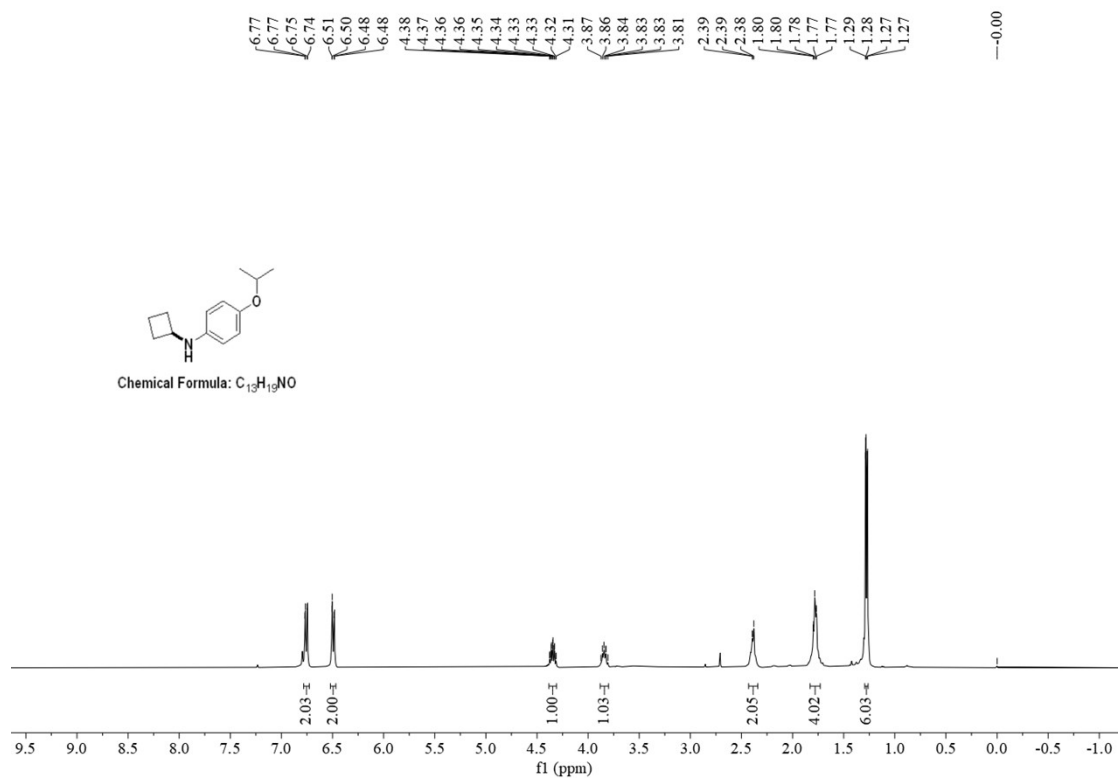




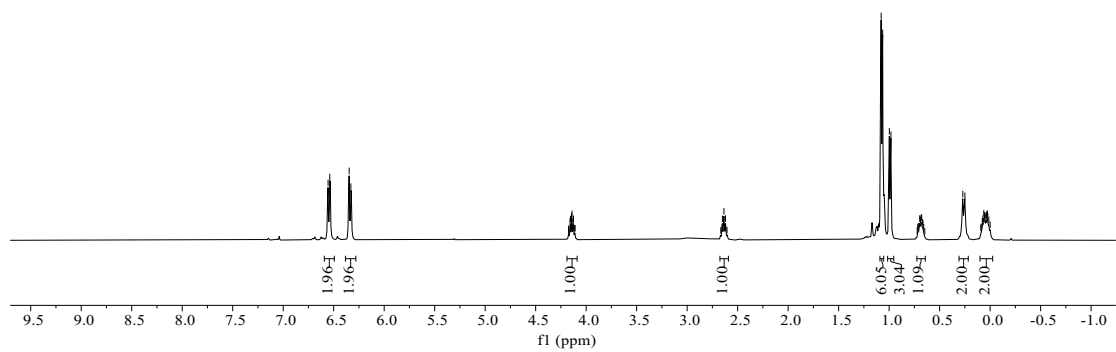
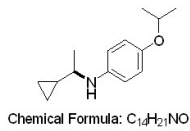
¹H NMR Spectrum of **4ba** in CDCl₃ at 400 MHz



¹³C {¹H} NMR Spectrum of **4ba** in CDCl₃ at 100 MHz

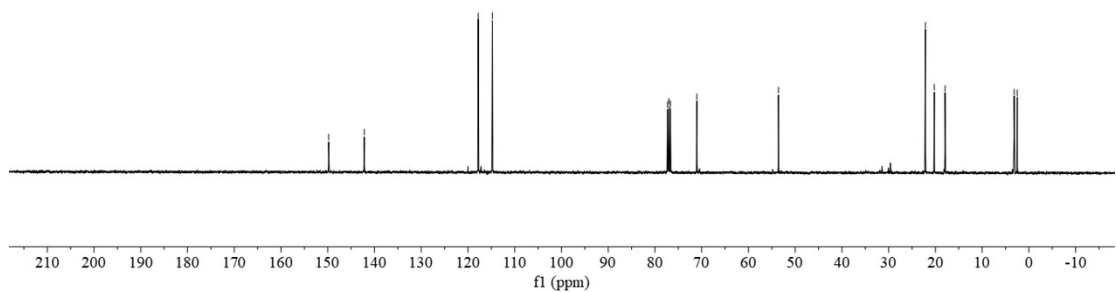
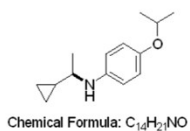


6.56
6.54
6.35
6.33
4.17
4.17
4.16
4.16
4.14
4.14
4.13
4.12
4.11
4.11
2.67
2.65
2.64
2.62
2.61
1.08
1.06
1.00
0.98
0.72
0.72
0.71
0.70
0.69
0.68
0.68
0.67
0.66
0.66
0.65
0.27
0.25
0.09
0.09
0.08
0.07
0.06
0.06
0.04
0.04
0.03
0.03
0.02
0.01
-0.00

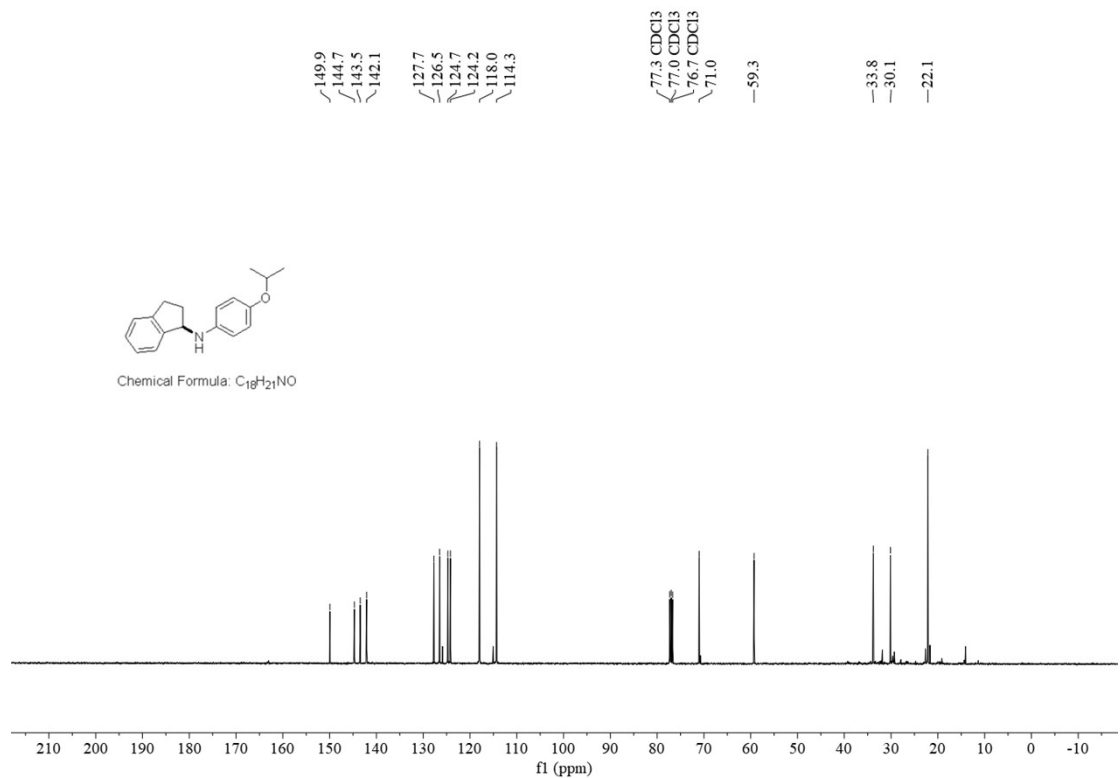
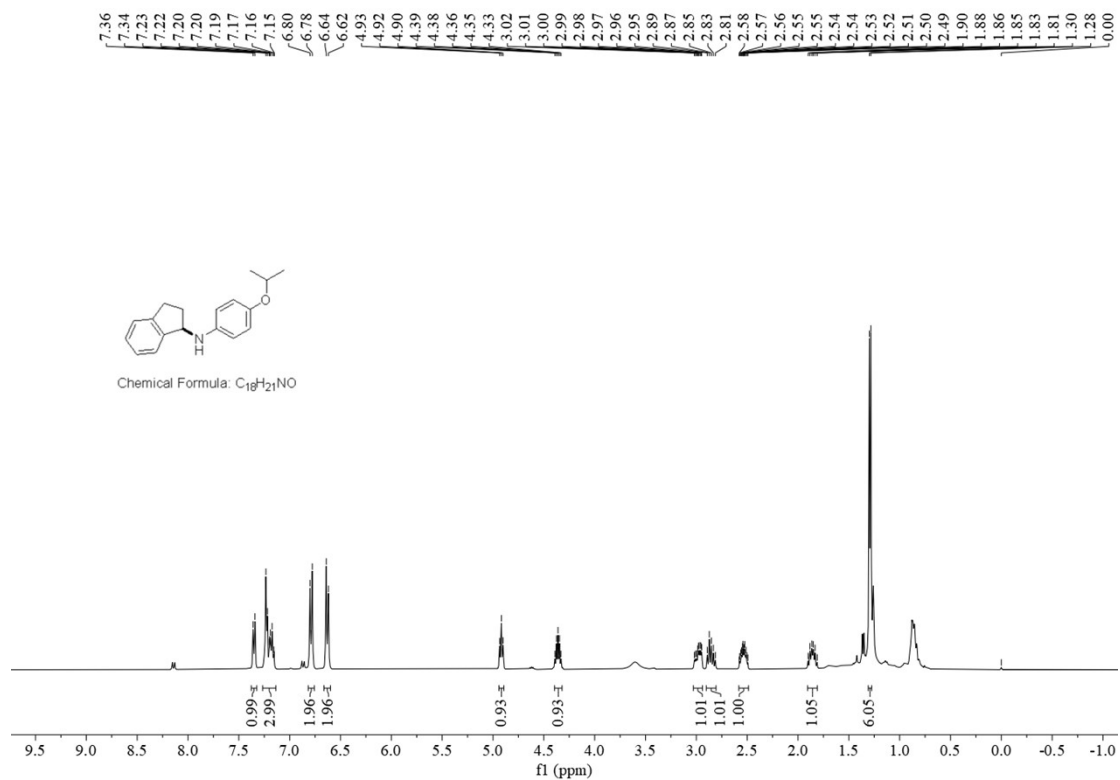


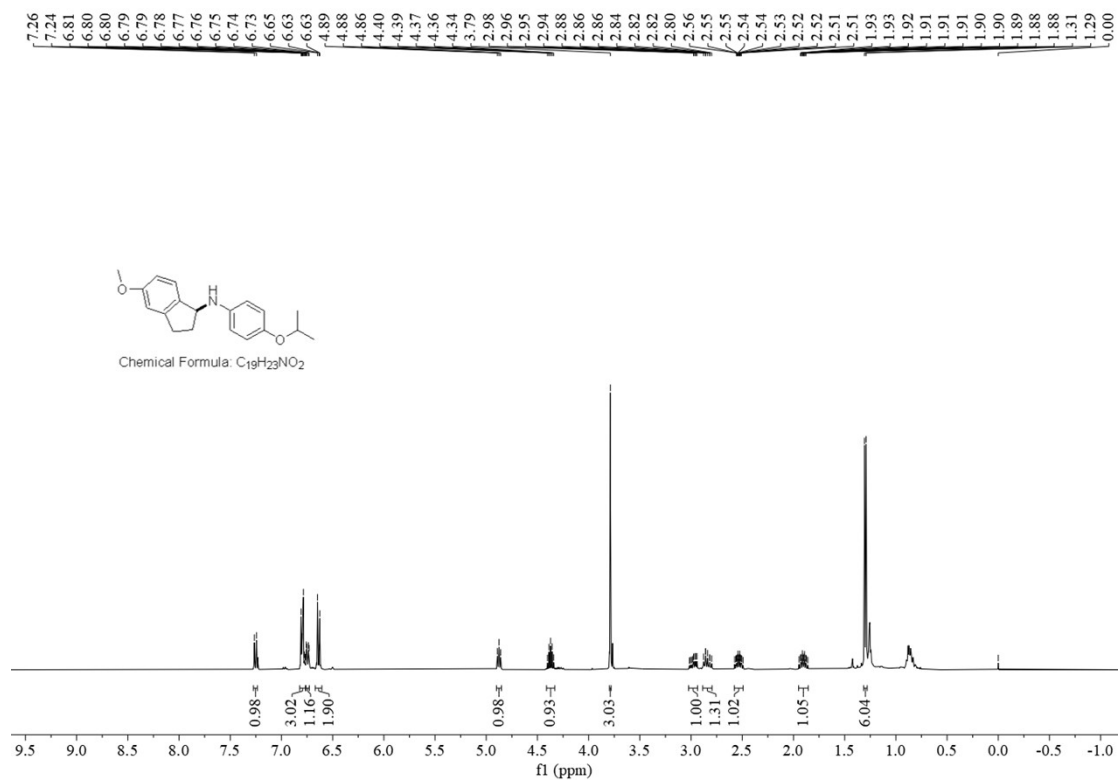
¹H NMR Spectrum of **4da** in CDCl₃ at 400 MHz

149.8
142.2
117.8
114.8
77.3 CDCl₃
77.0 CDCl₃
76.7 CDCl₃
71.0
53.6
22.1
20.2
17.9
3.1
2.5

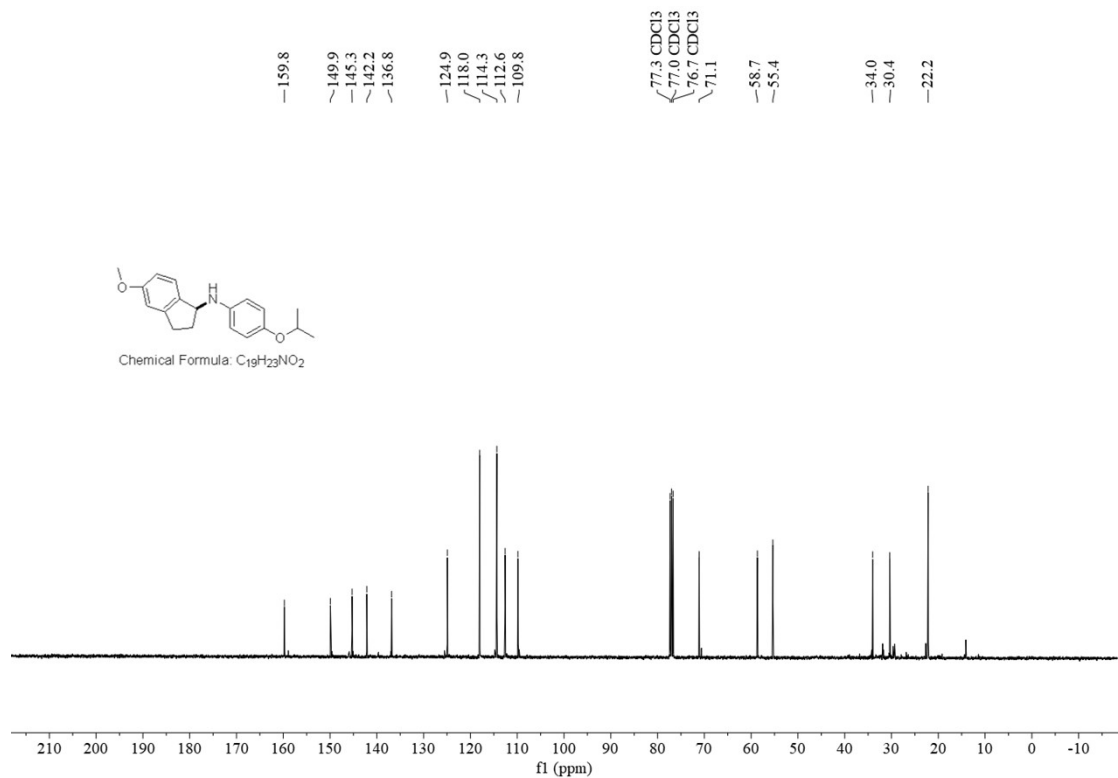


¹³C {¹H} NMR Spectrum of **4da** in CDCl₃ at 100 MHz

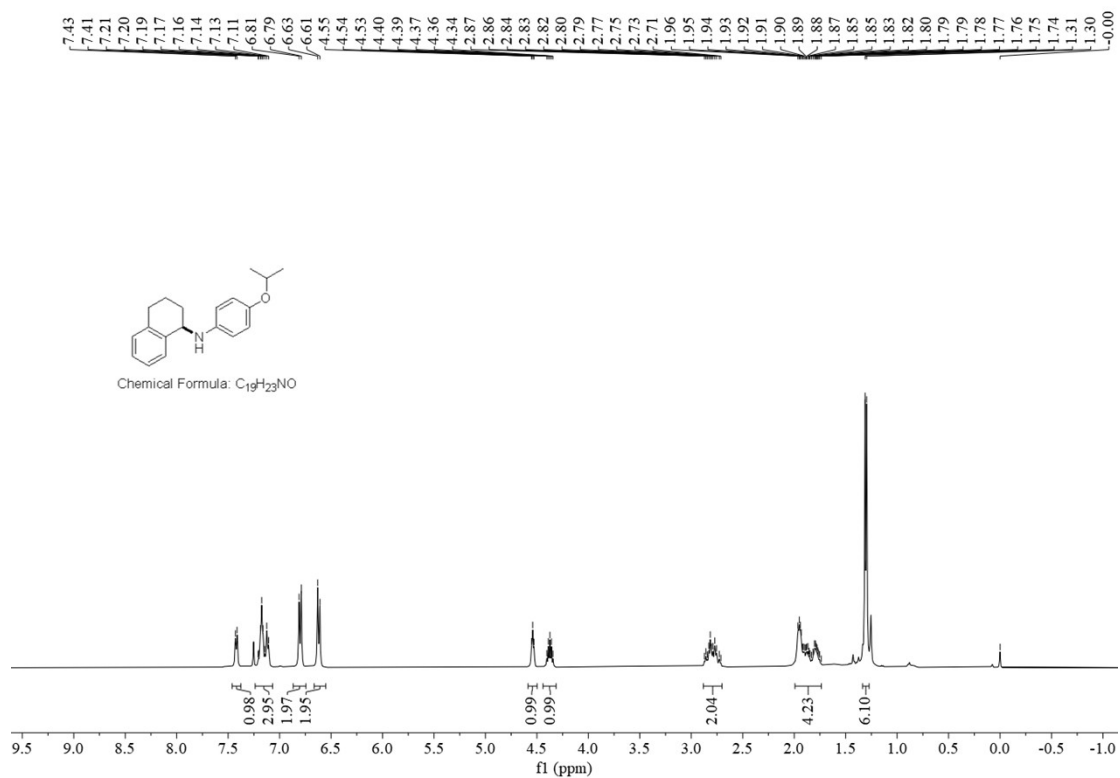




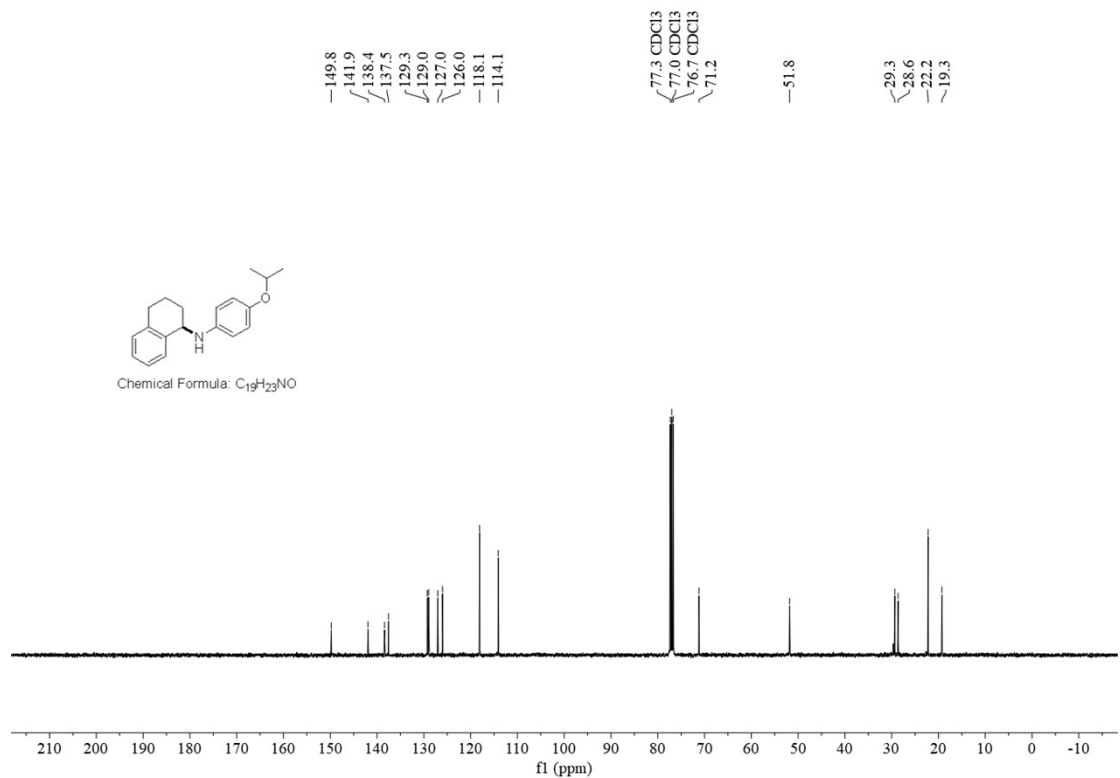
¹H NMR Spectrum of **4fa** in CDCl₃ at 400 MHz



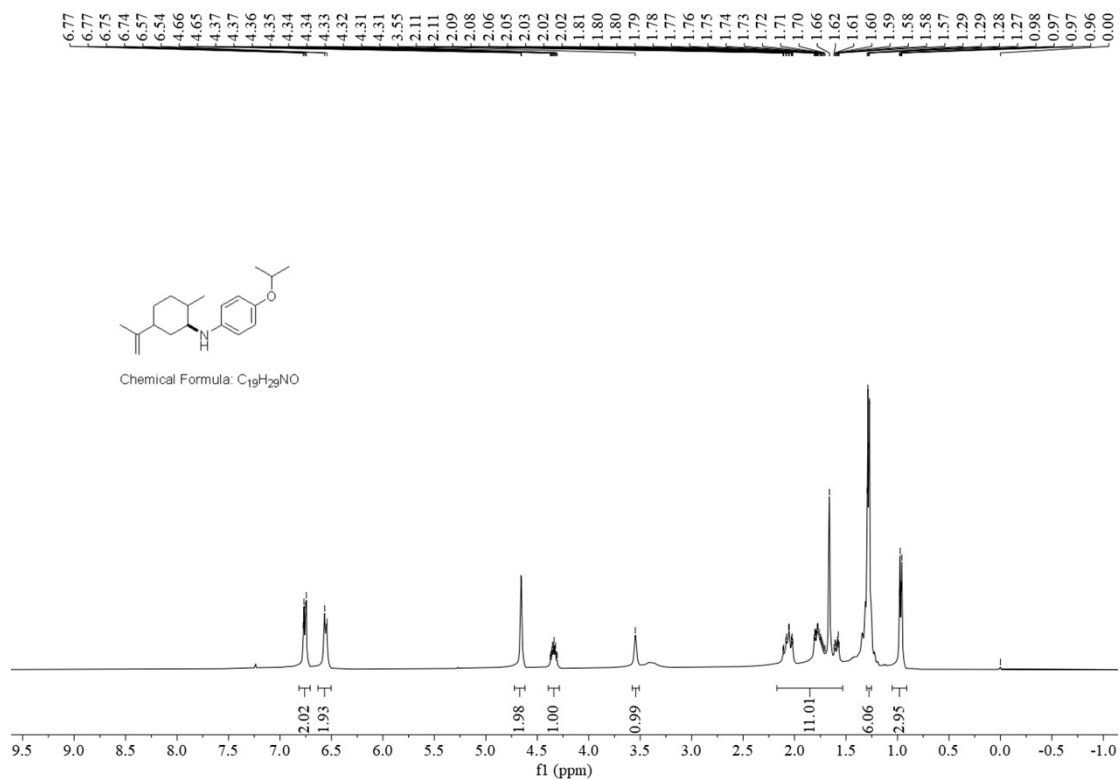
¹³C{¹H} NMR Spectrum of **4fa** in CDCl₃ at 100 MHz



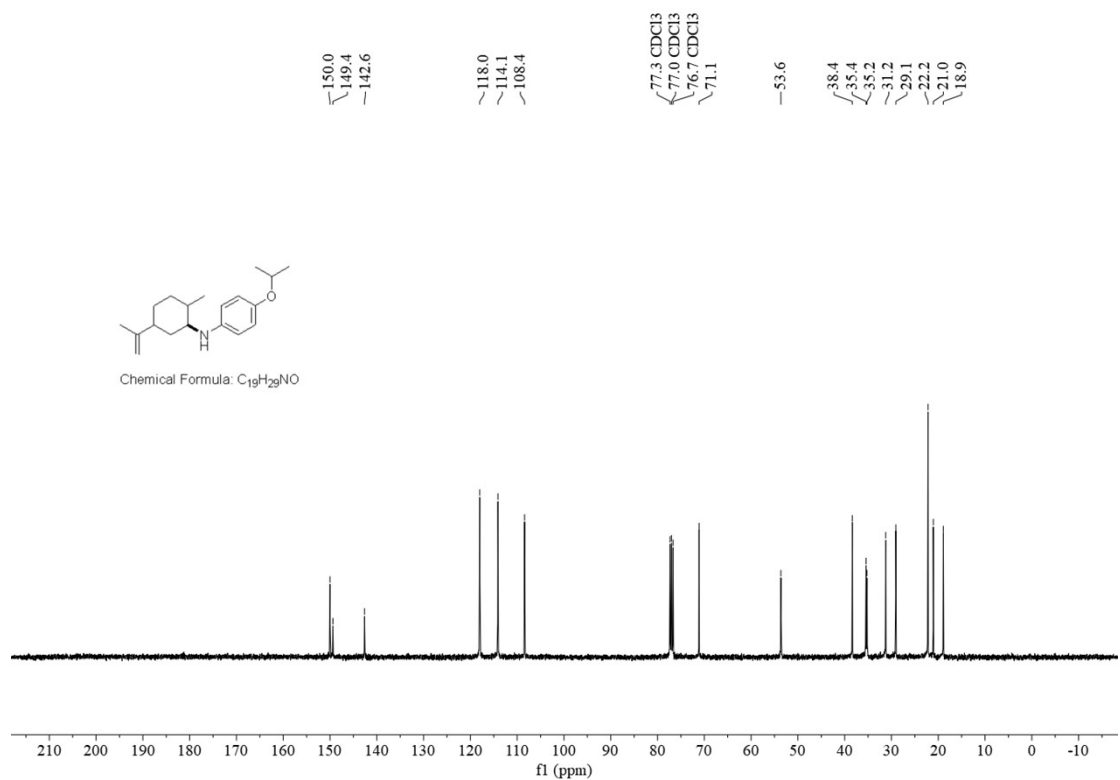
1H NMR Spectrum of **4ga** in $CDCl_3$ at 400 MHz



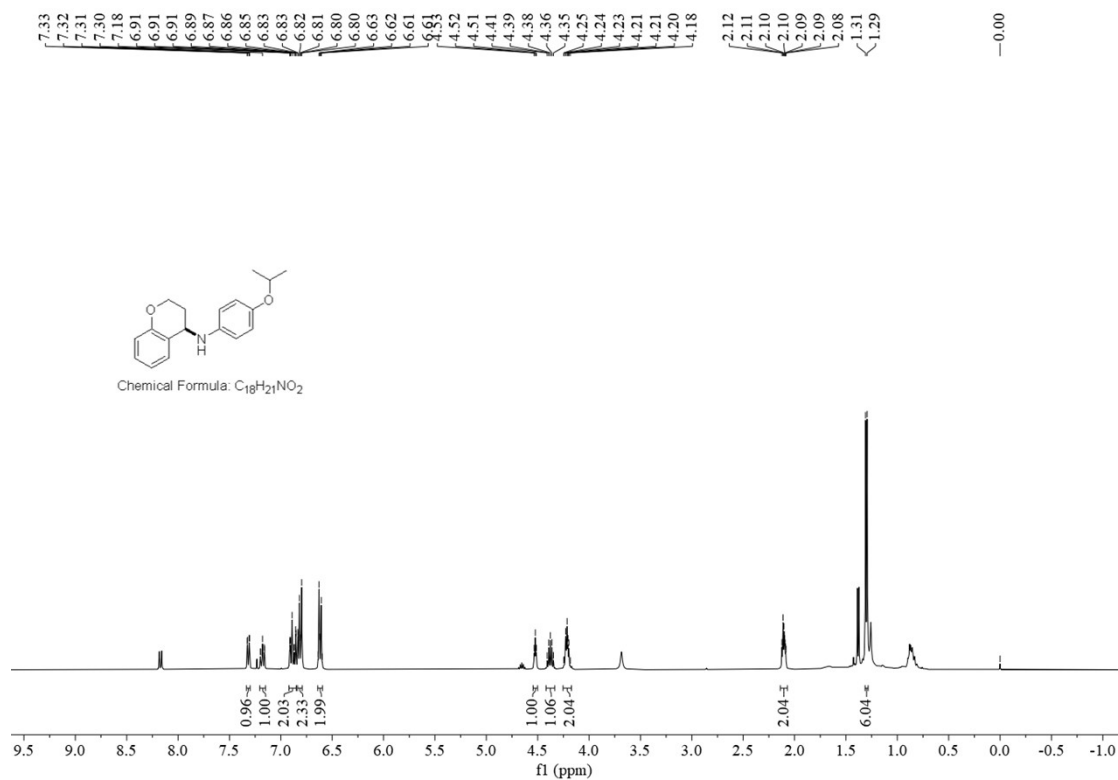
$^{13}C\{^1H\}$ NMR Spectrum of **4ga** in $CDCl_3$ at 100 MHz



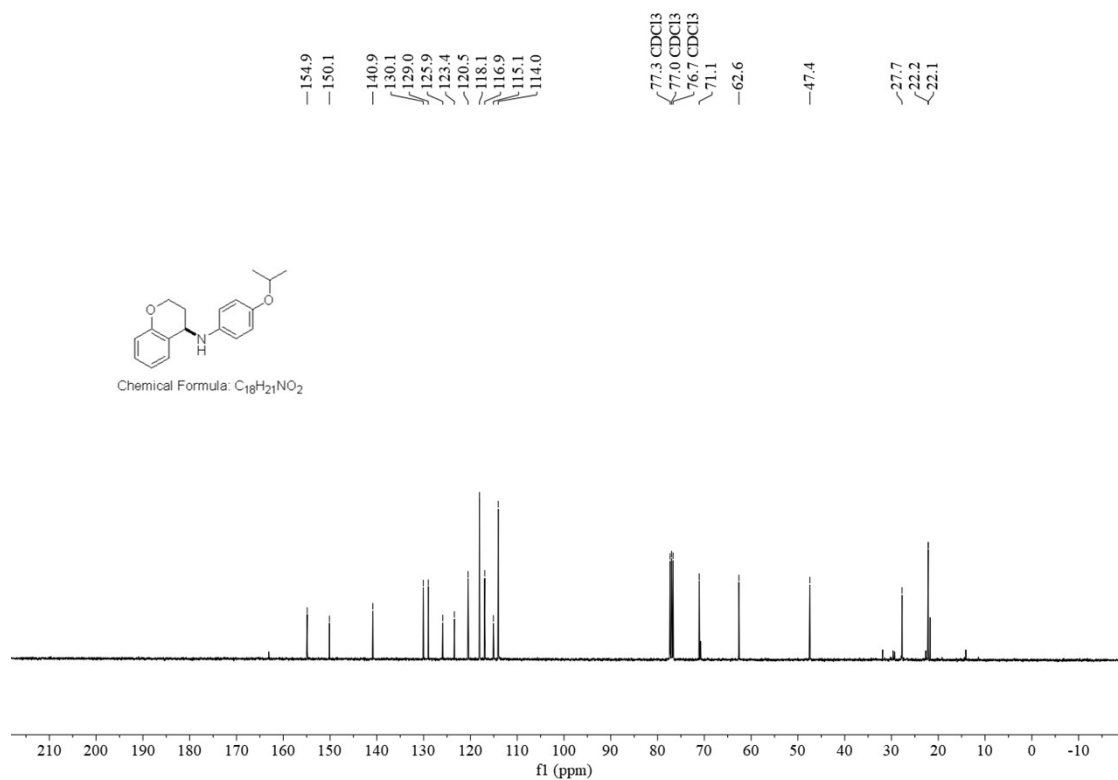
¹H NMR Spectrum of **4ha** in CDCl₃ at 400 MHz



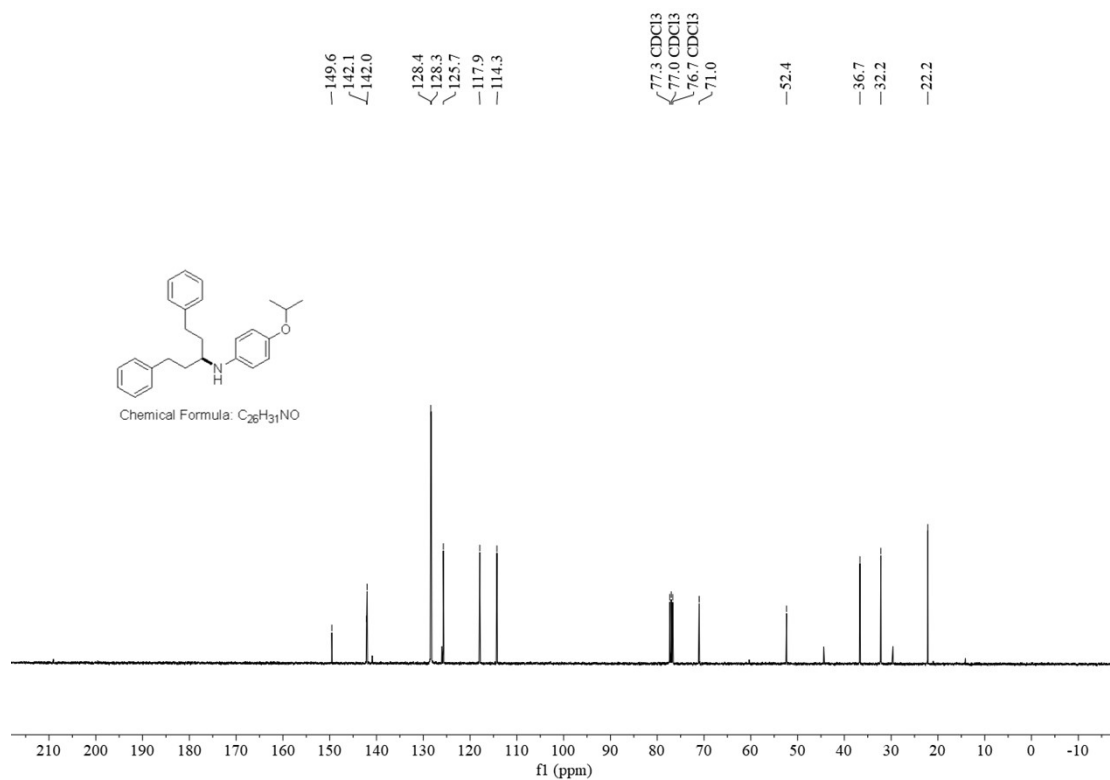
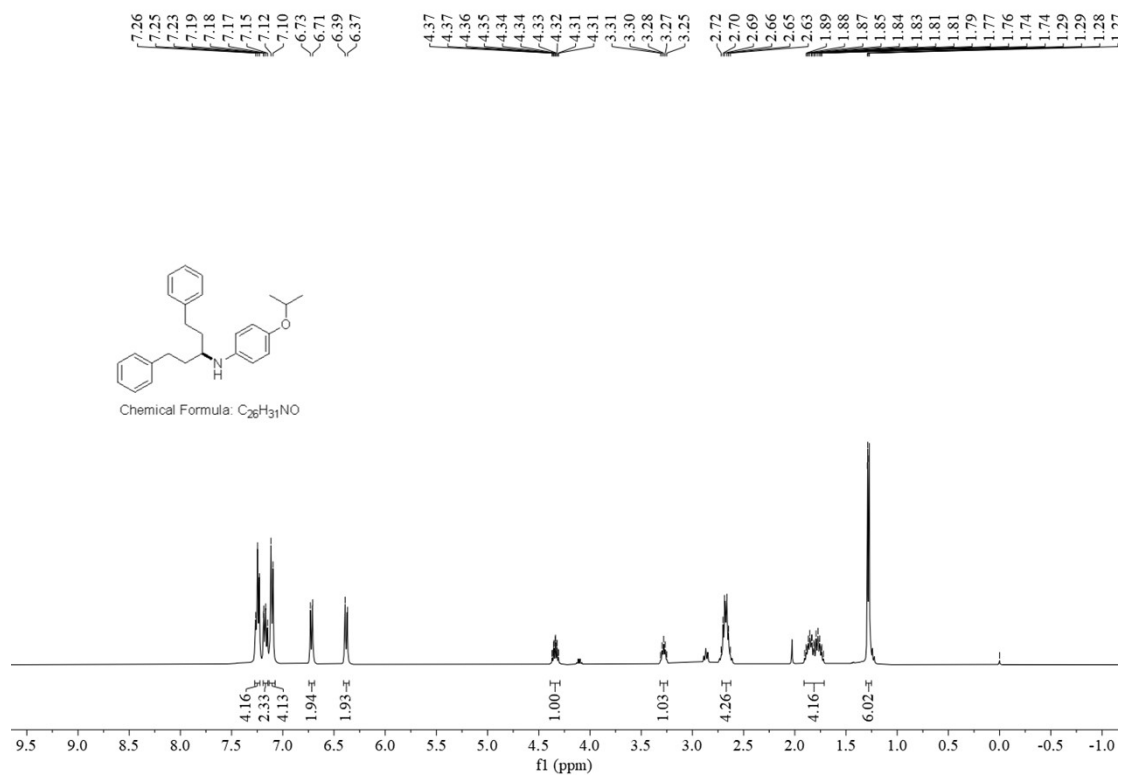
¹³C {¹H} NMR Spectrum of **4ha** in CDCl₃ at 100 MHz

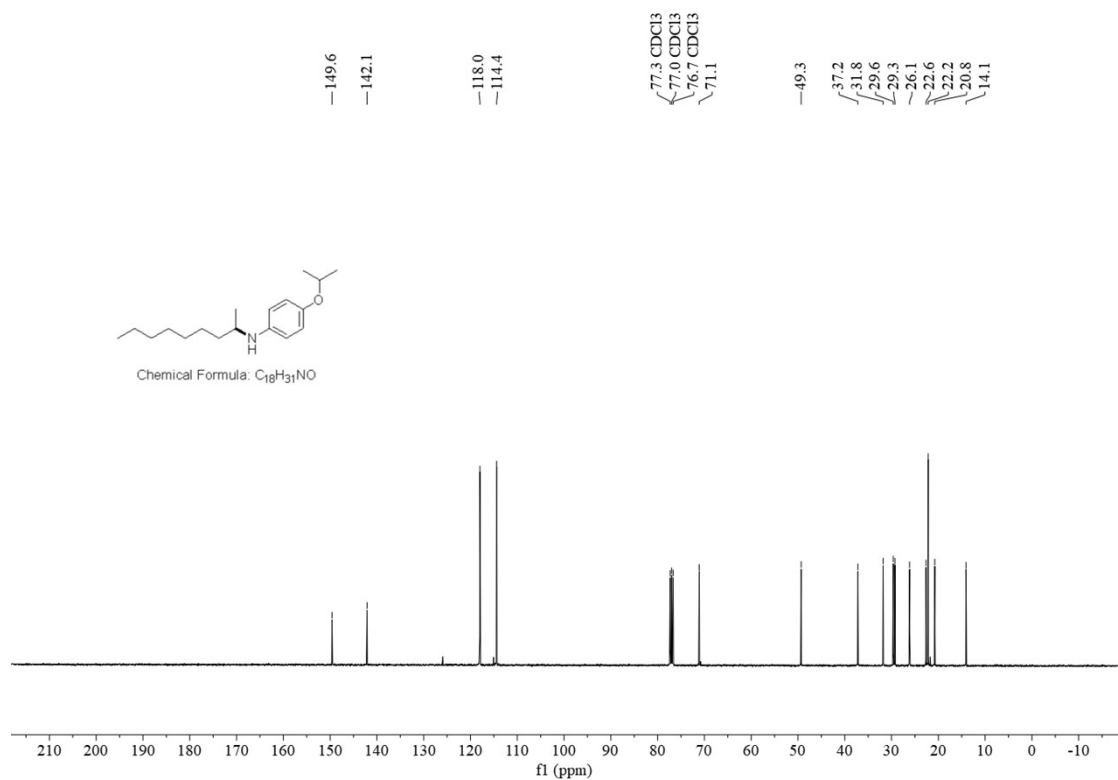
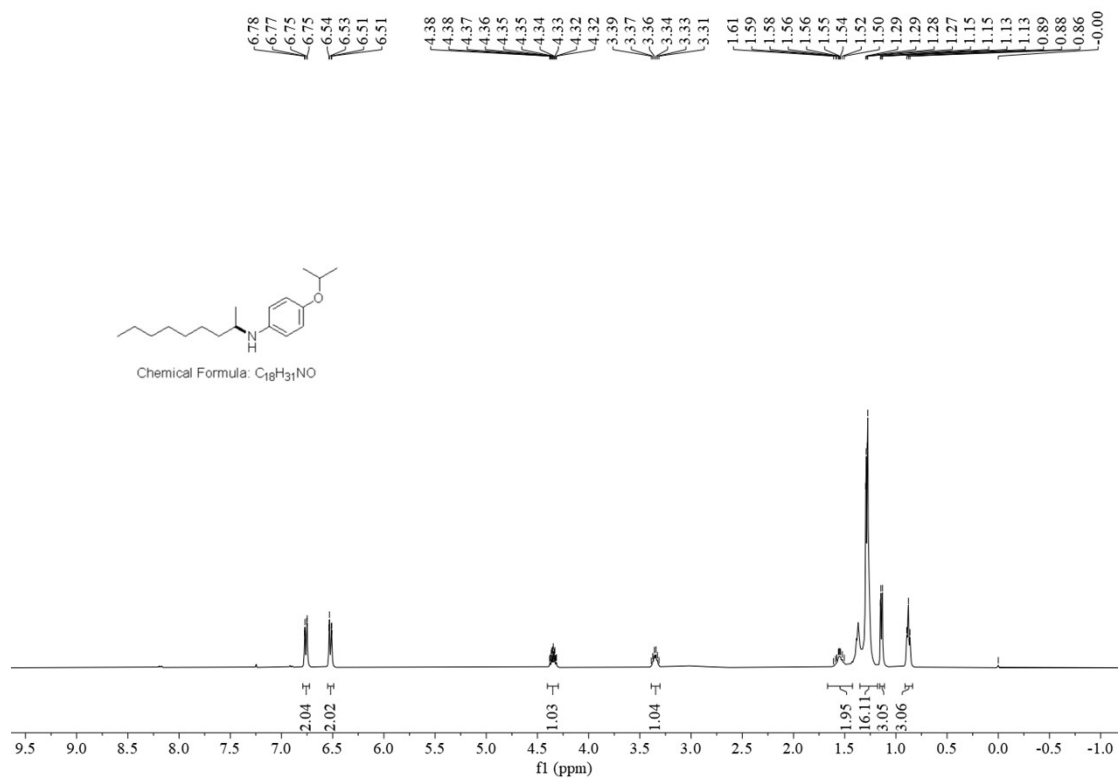


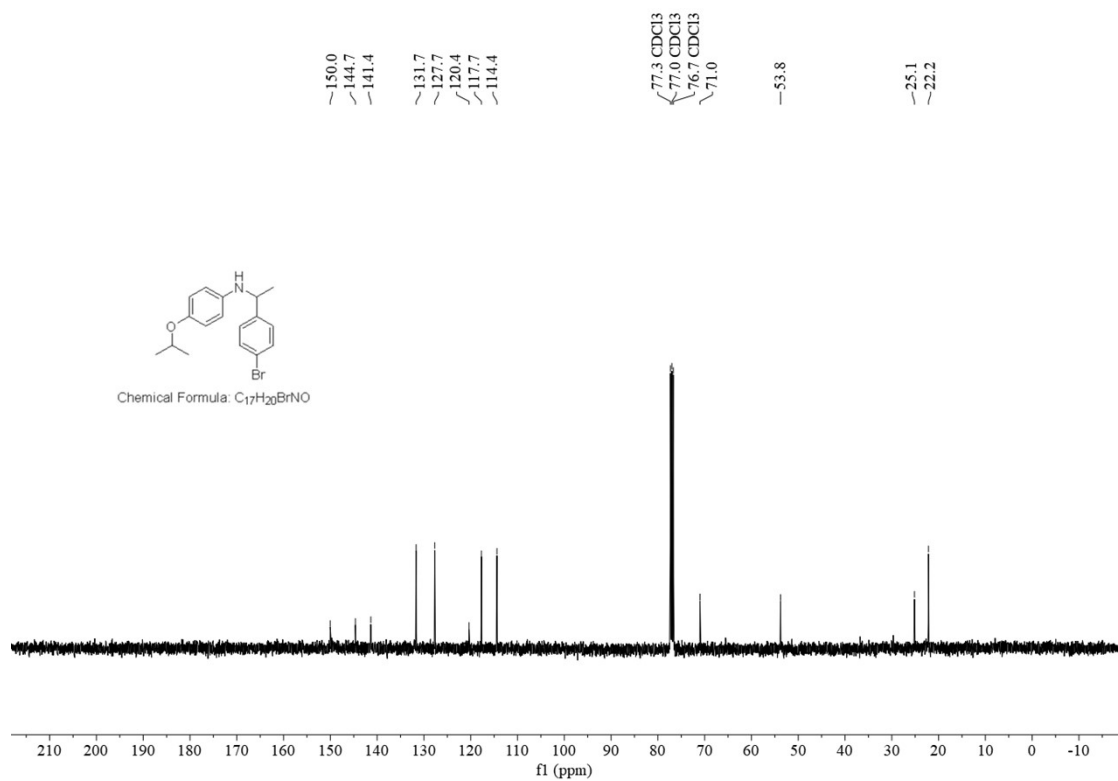
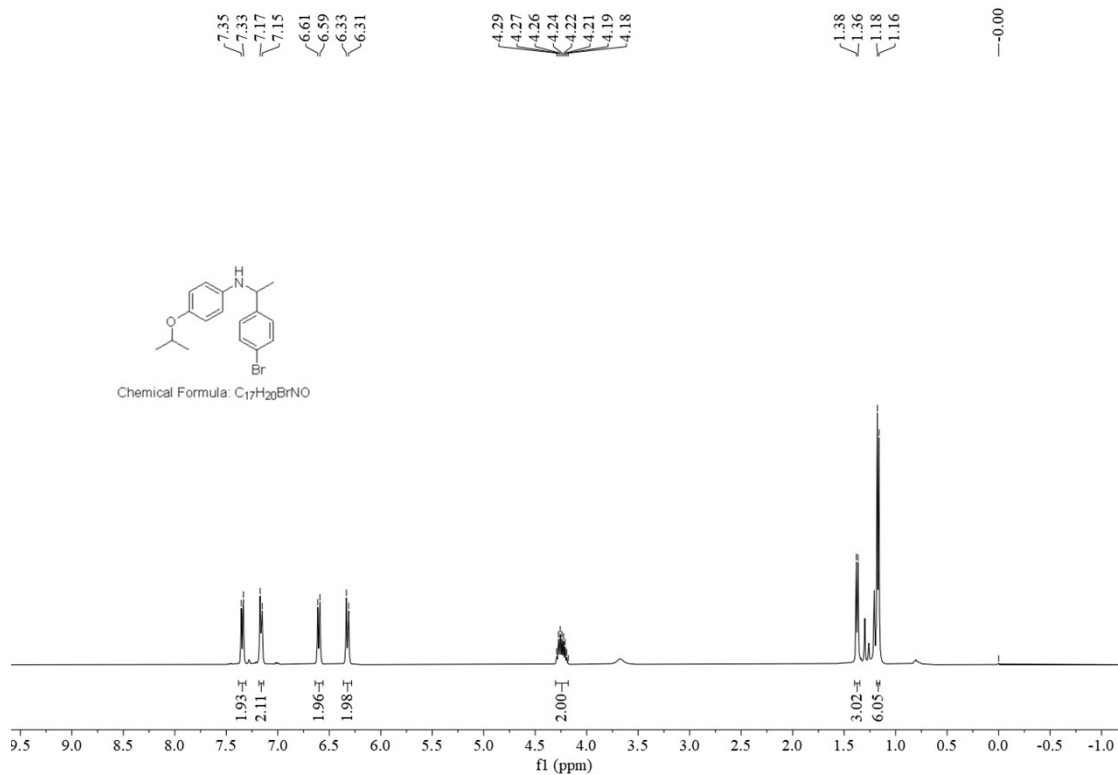
1H NMR Spectrum of **4ia** in $CDCl_3$ at 400 MHz

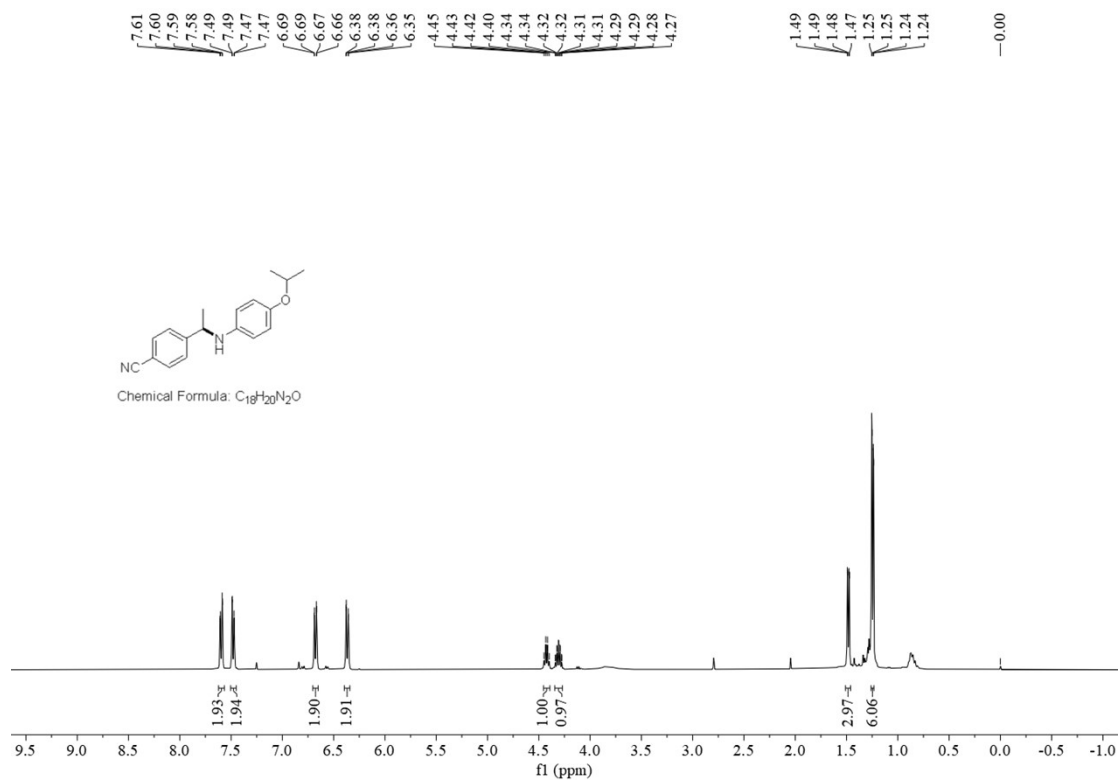


$^{13}C\{^1H\}$ NMR Spectrum of **4ia** in $CDCl_3$ at 100 MHz

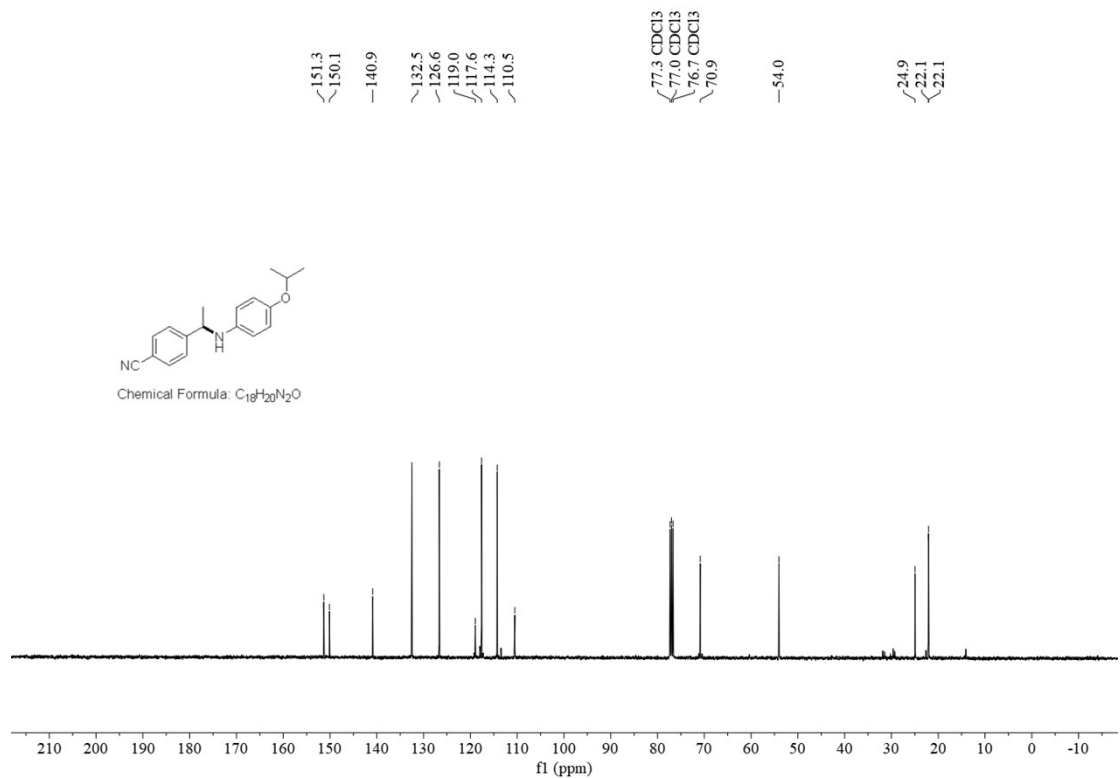




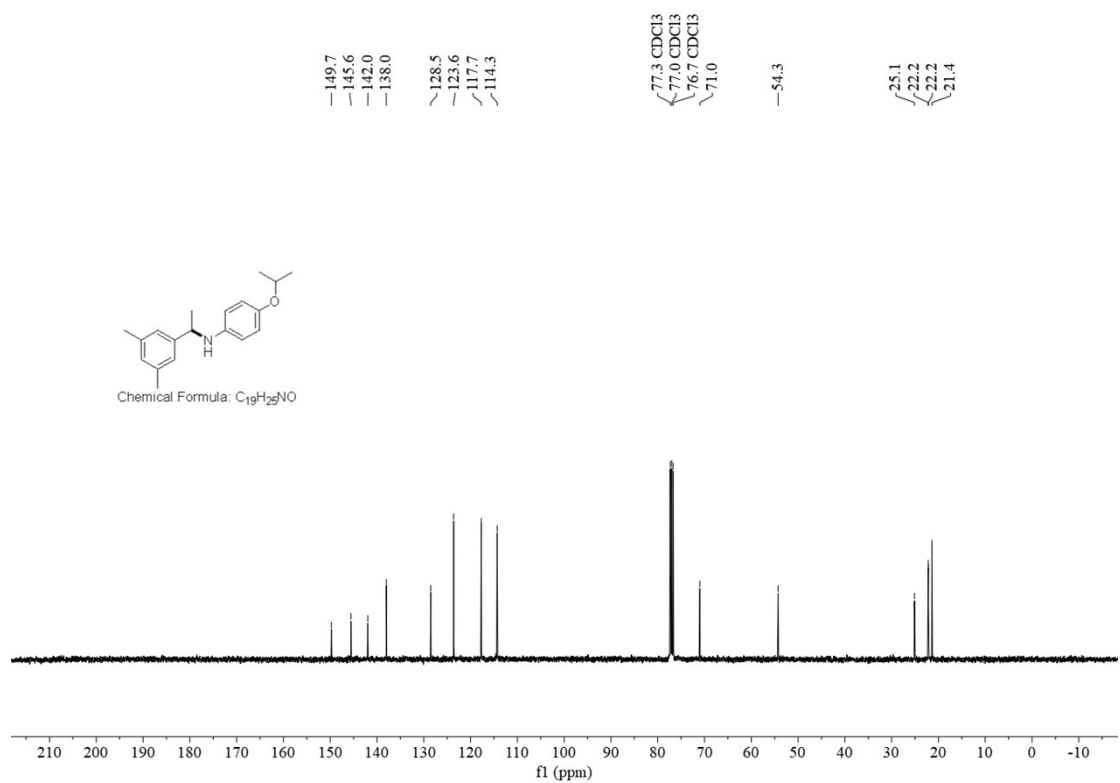
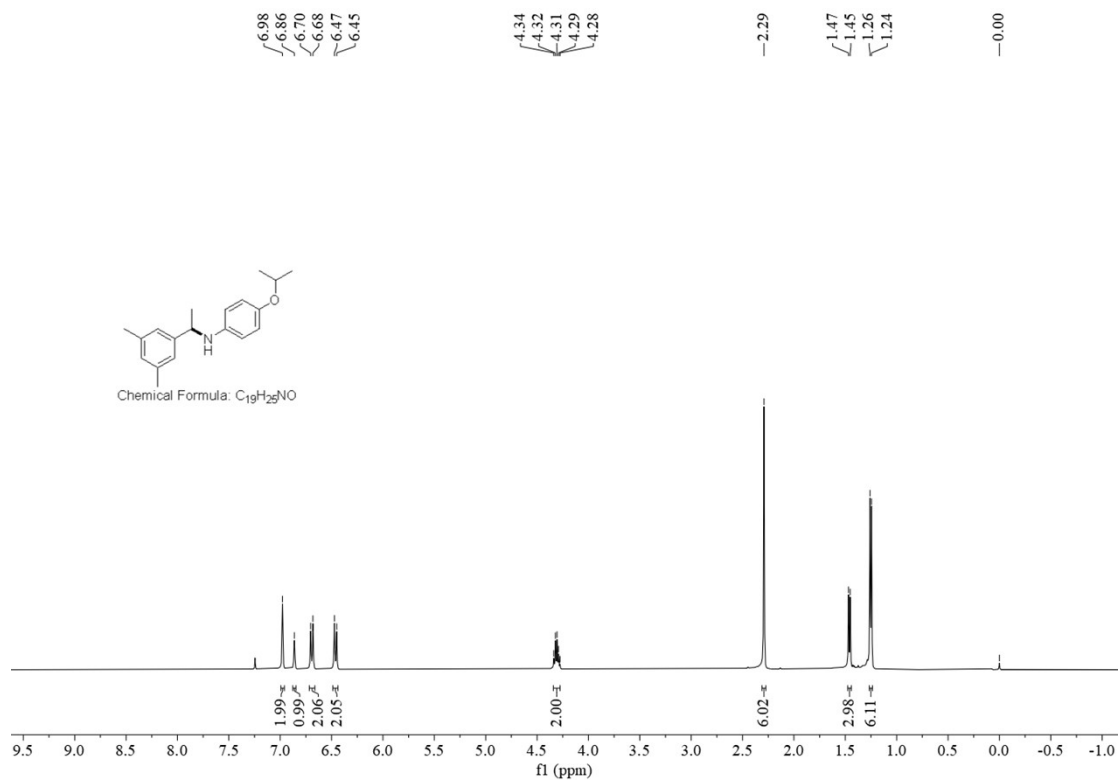


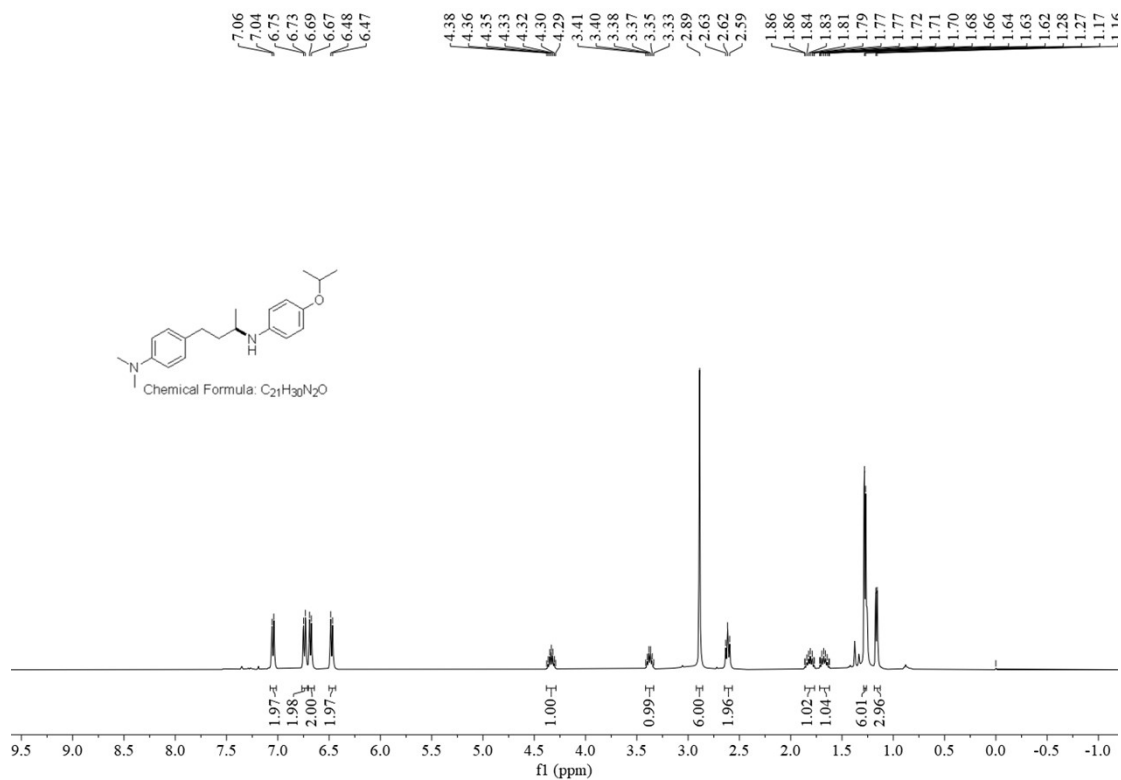


¹H NMR Spectrum of **4ma** in CDCl₃ at 400 MHz

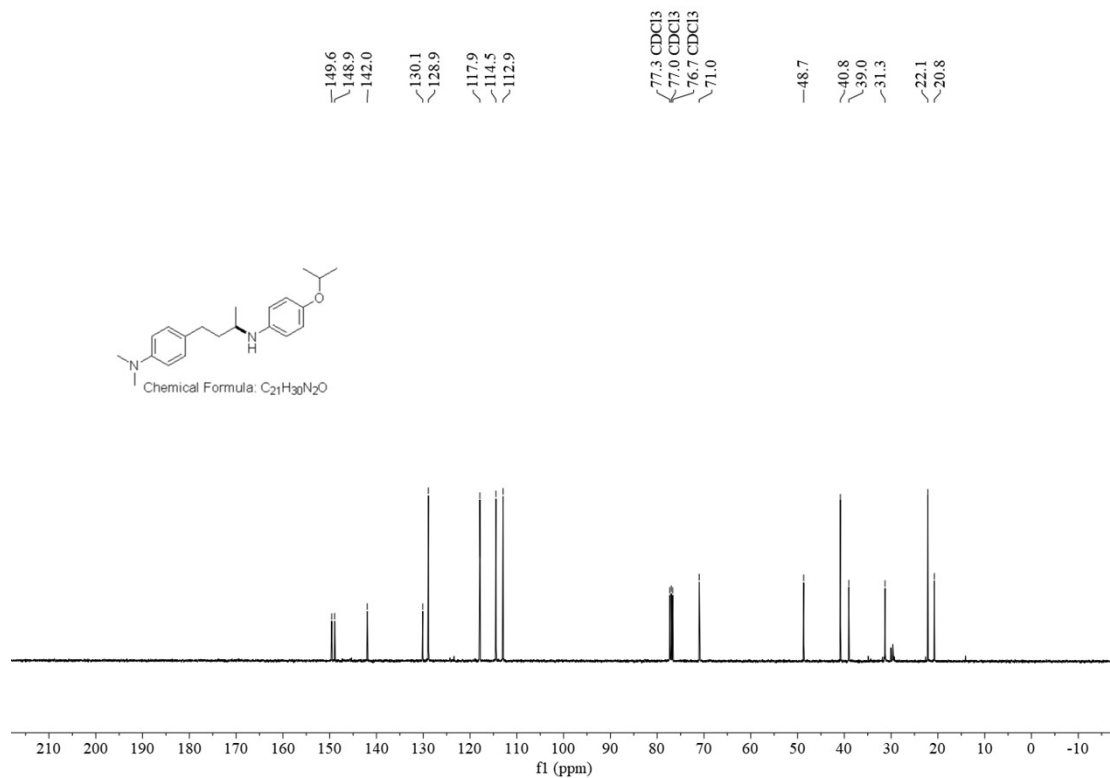


¹³C{¹H} NMR Spectrum of **4ma** in CDCl₃ at 100 MHz

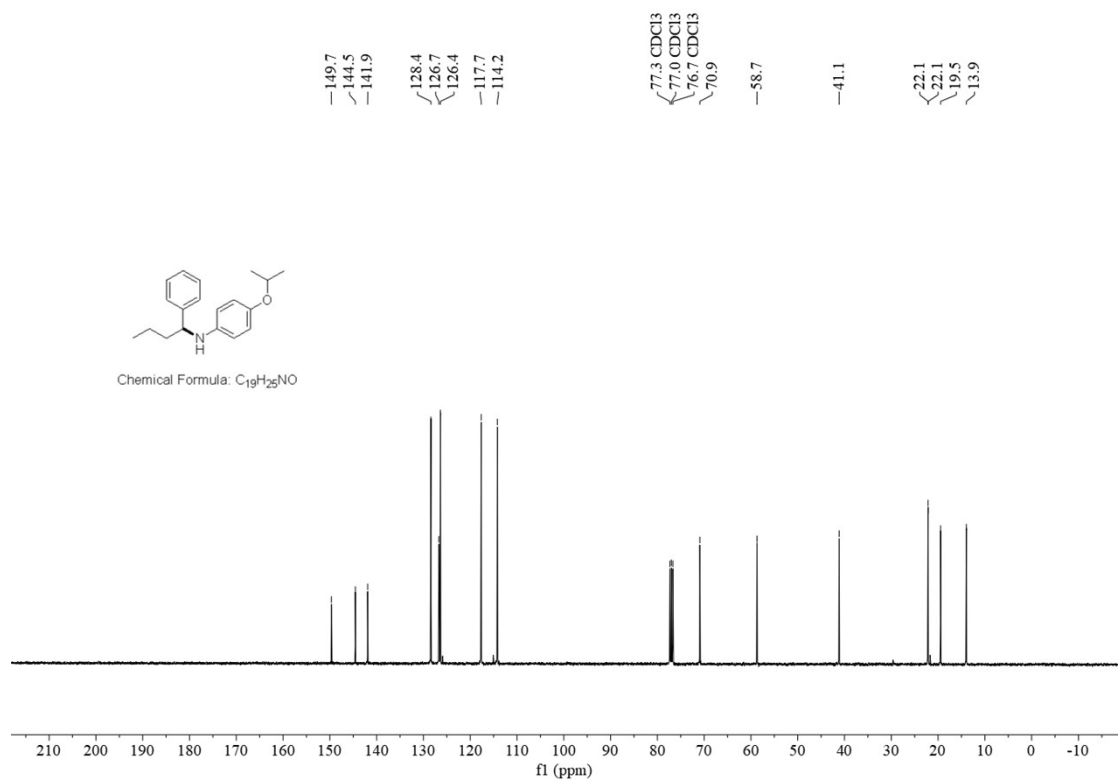
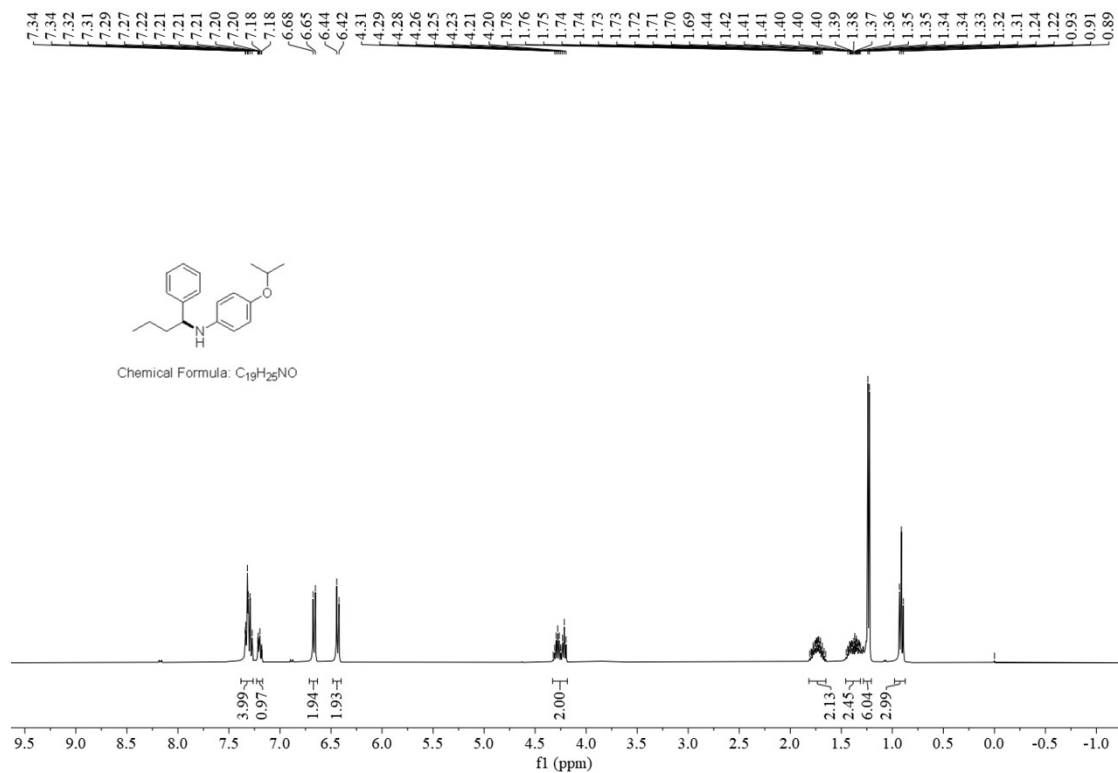


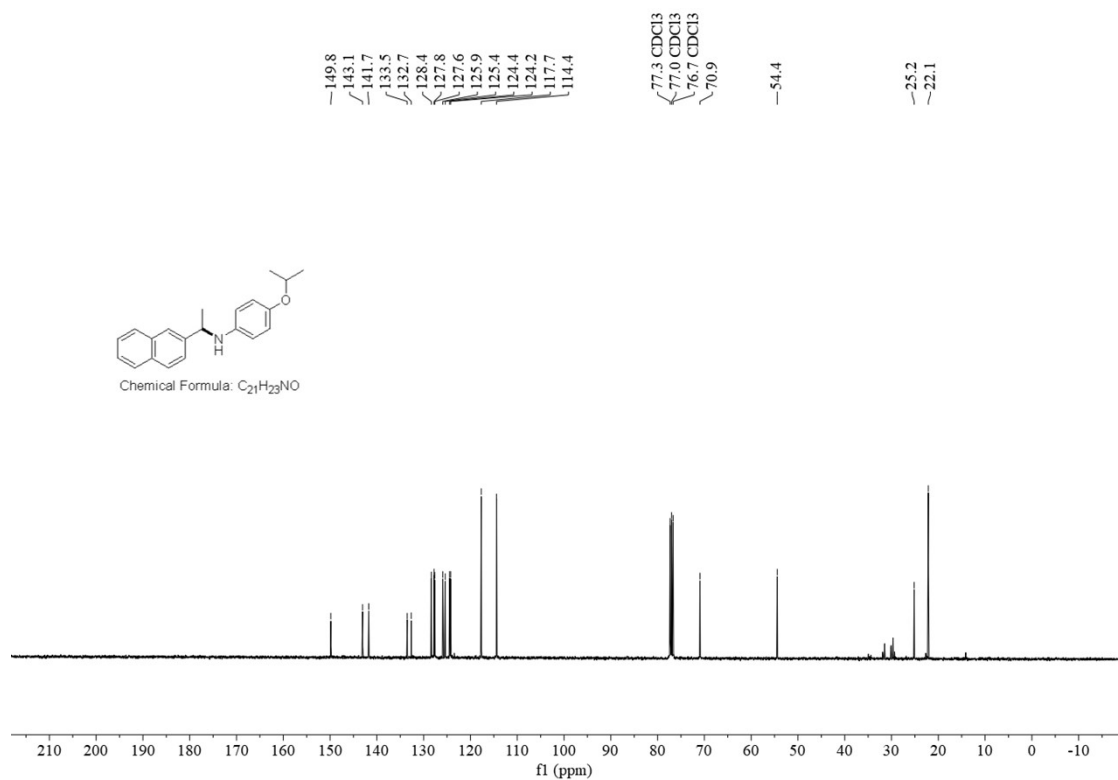
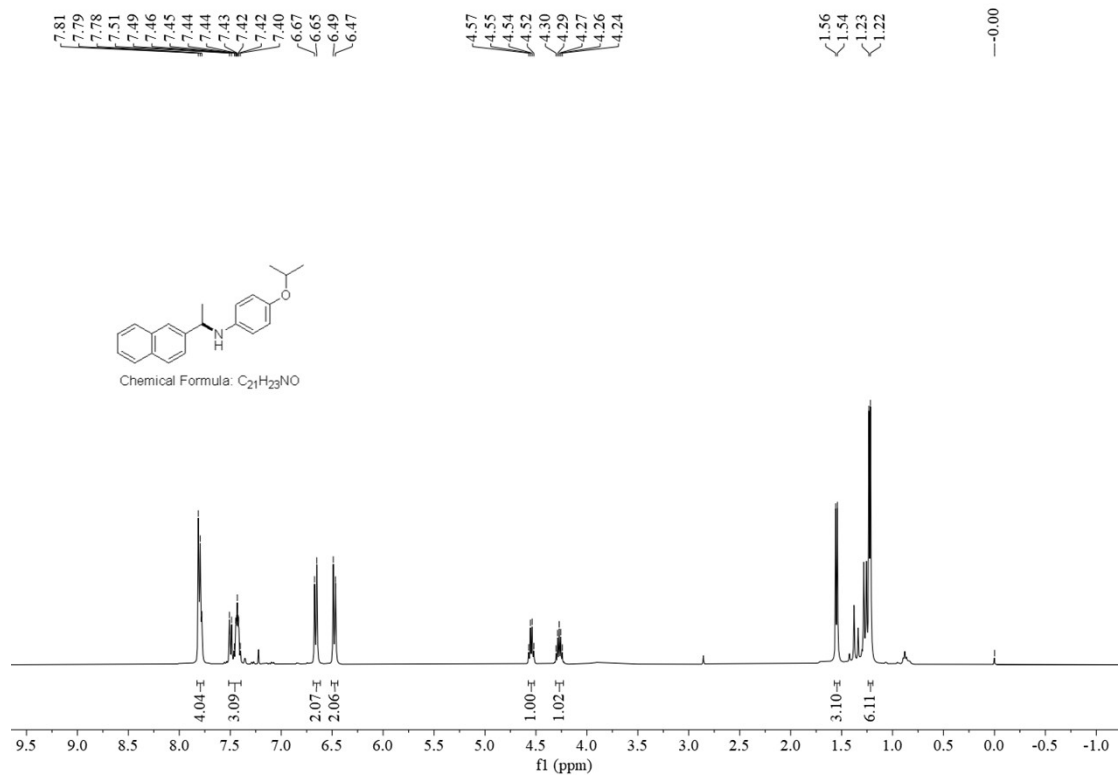


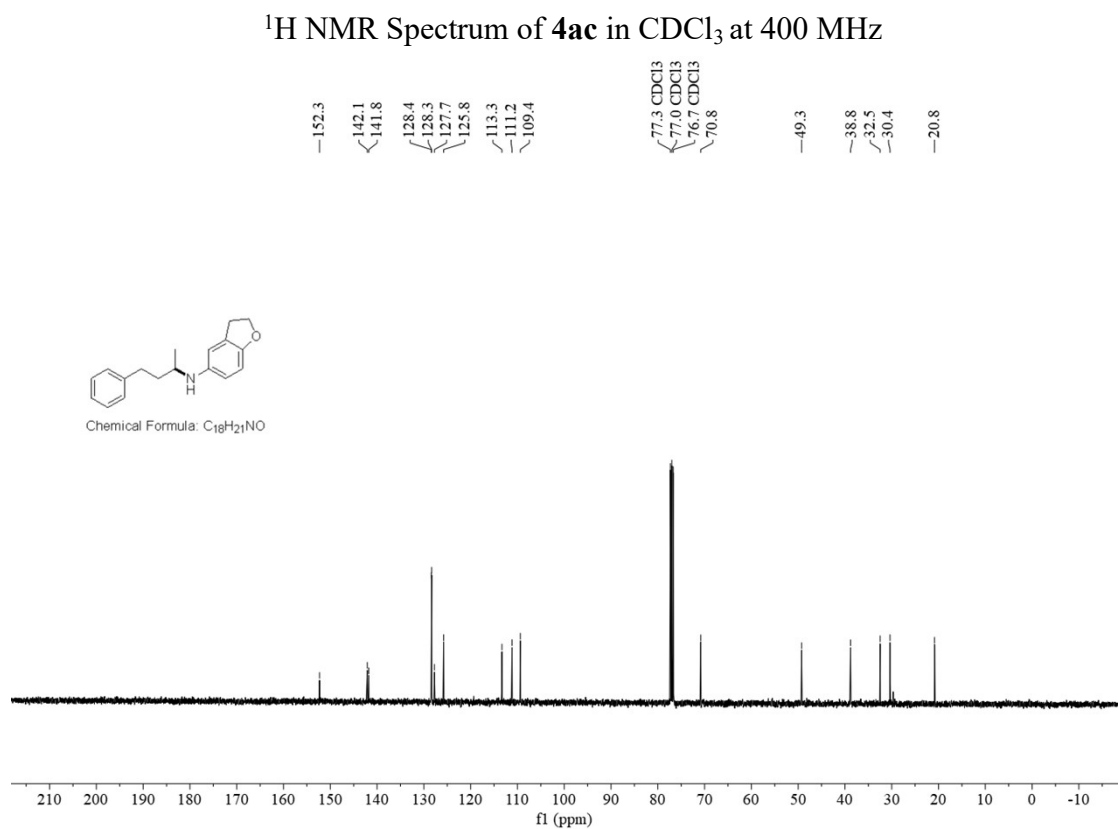
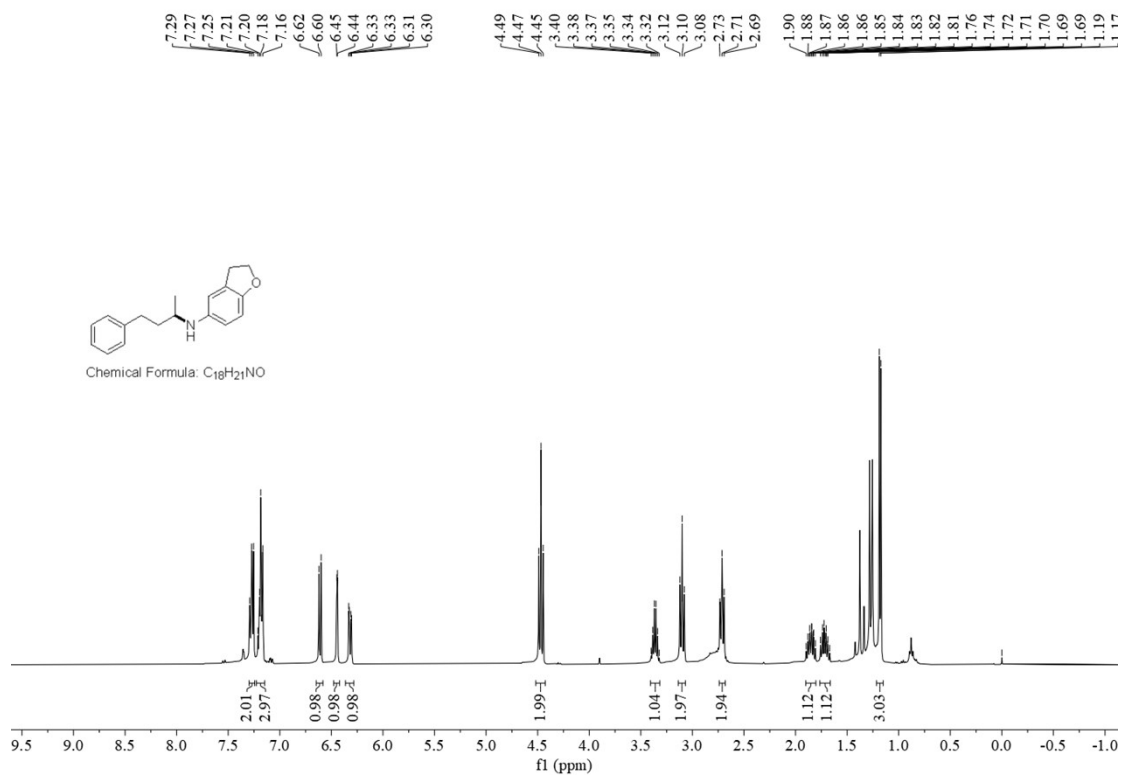
1H NMR Spectrum of **40a** in $CDCl_3$ at 400 MHz

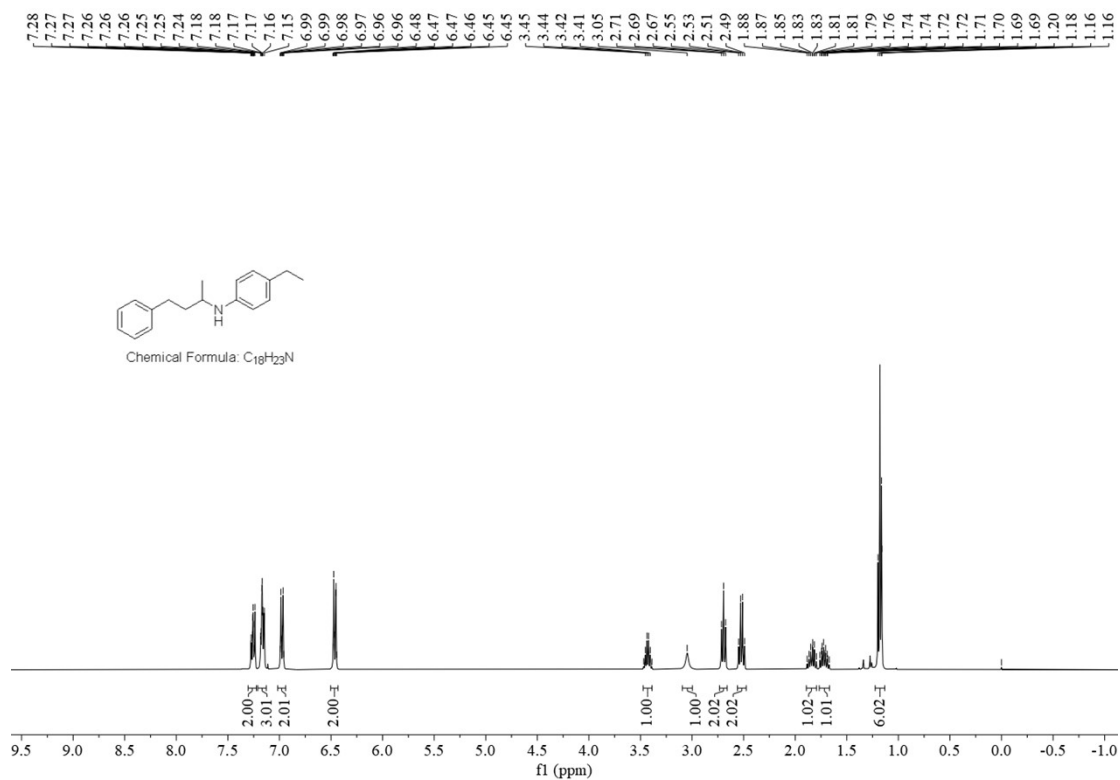


$^{13}C\{^1H\}$ NMR Spectrum of **40a** in $CDCl_3$ at 100 MHz

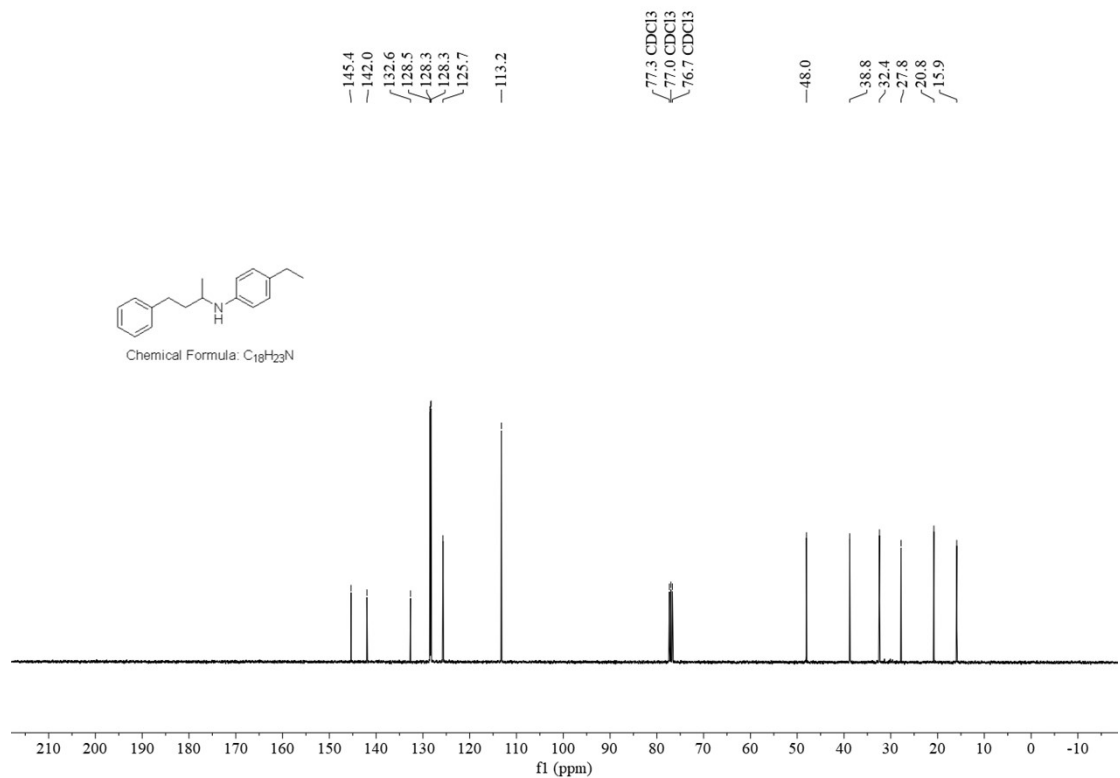




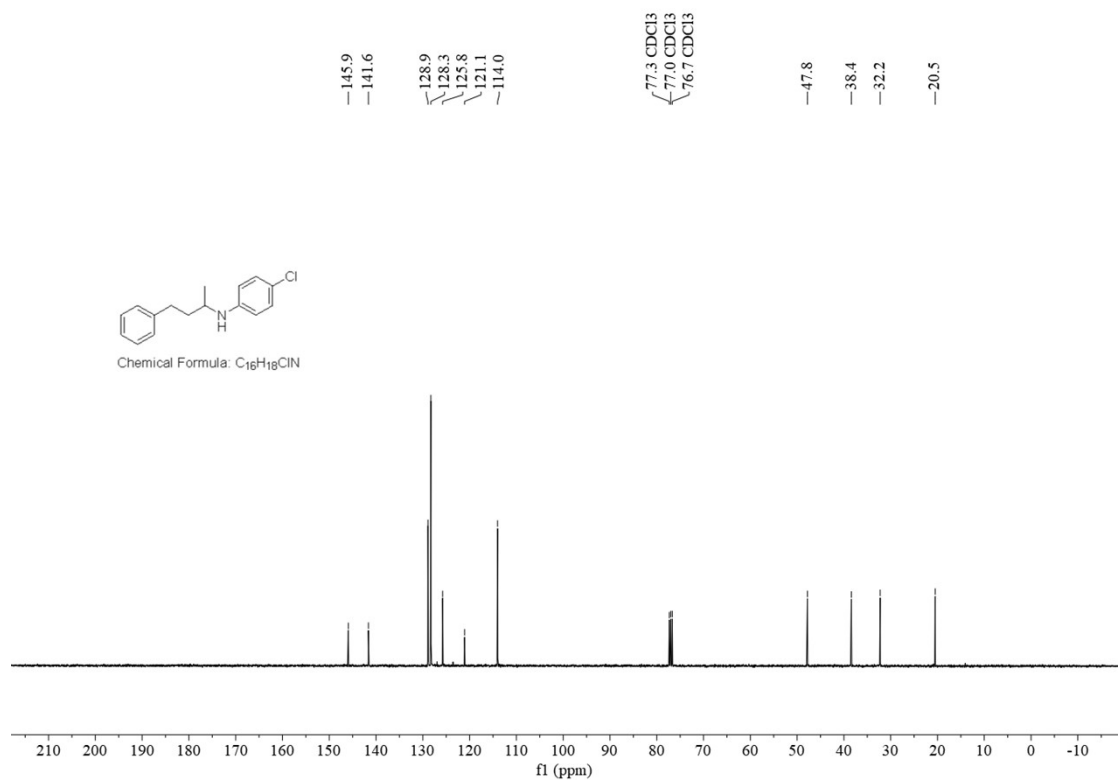
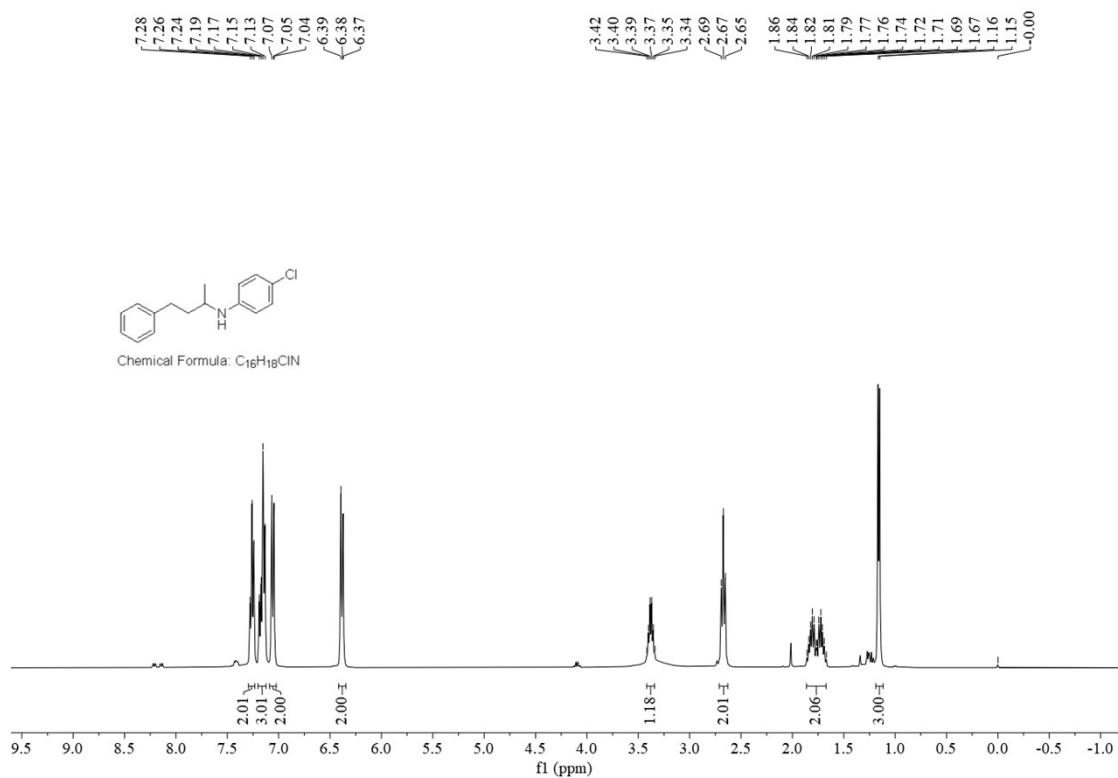


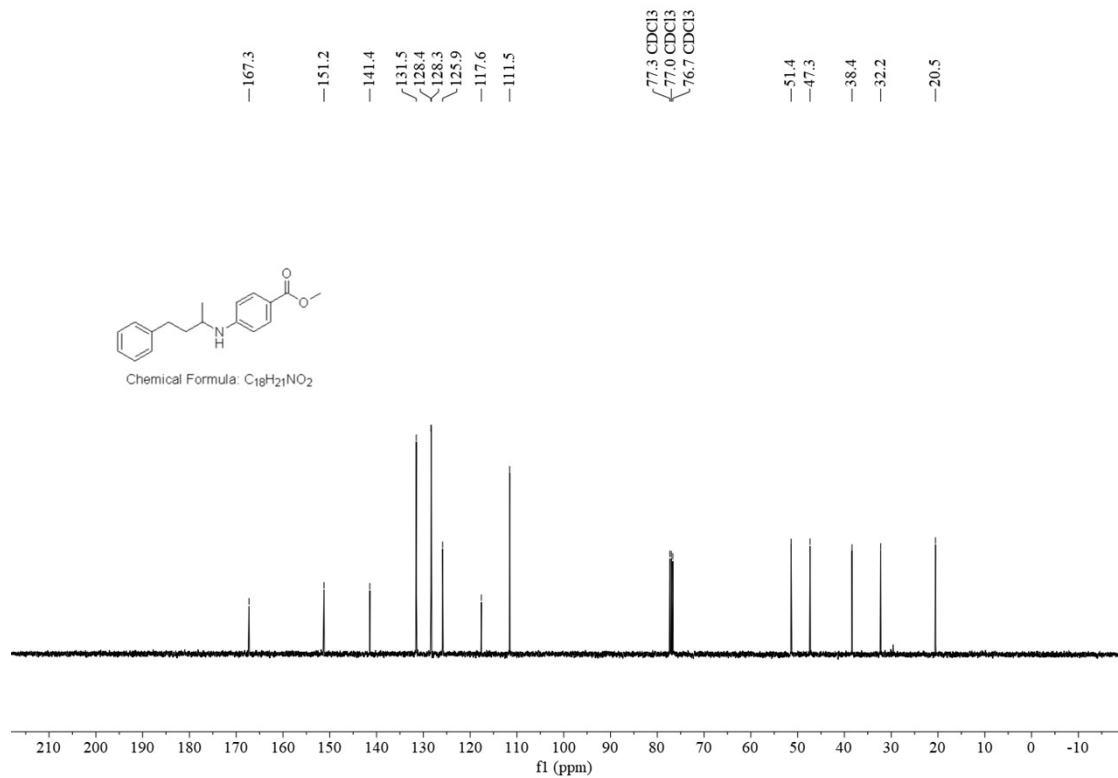
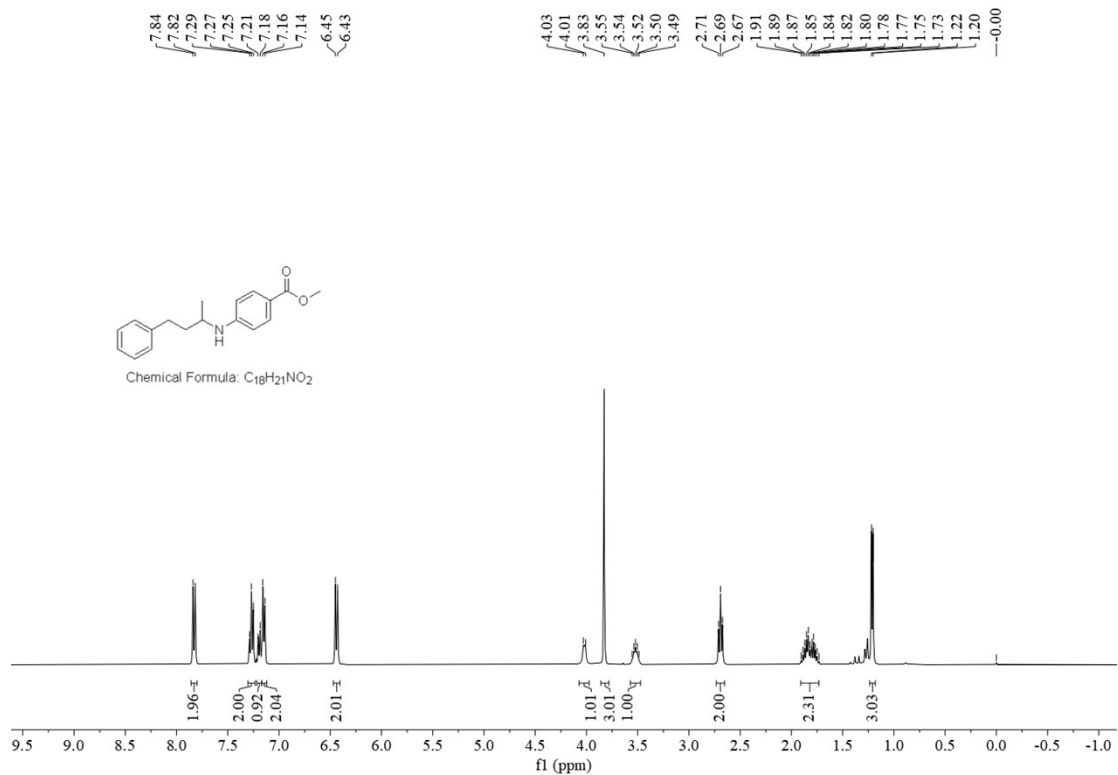


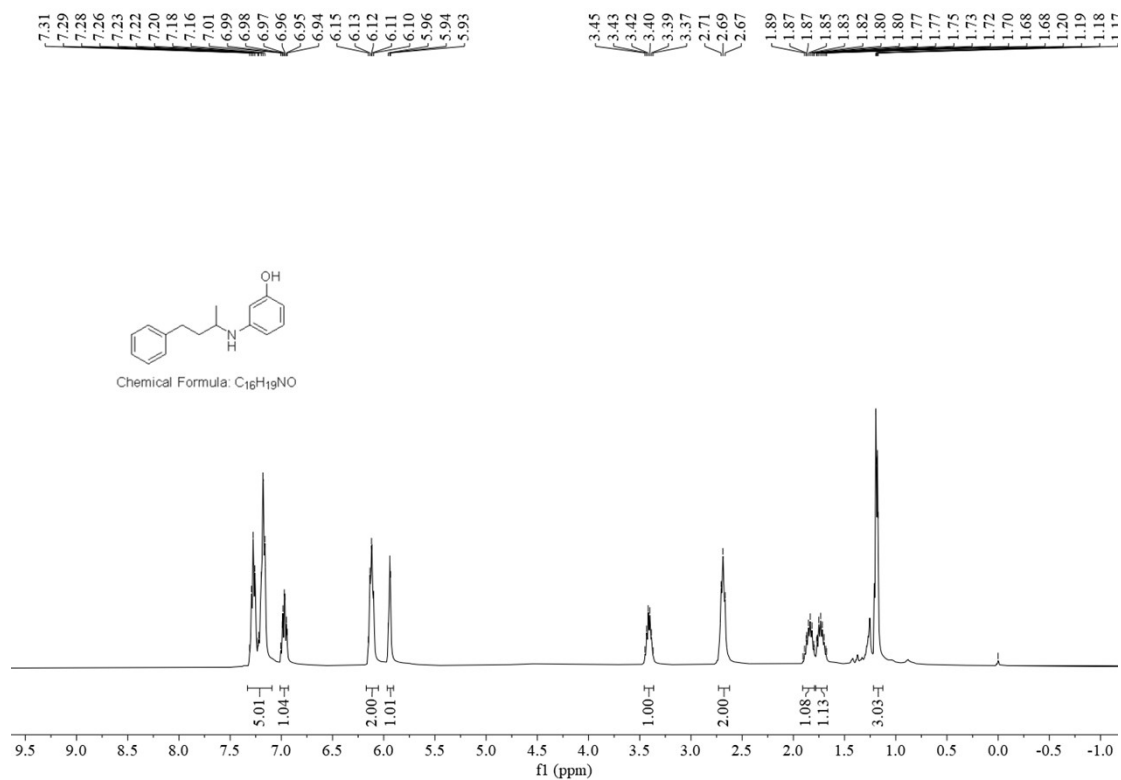
¹H NMR Spectrum of **4ad** in CDCl₃ at 400 MHz



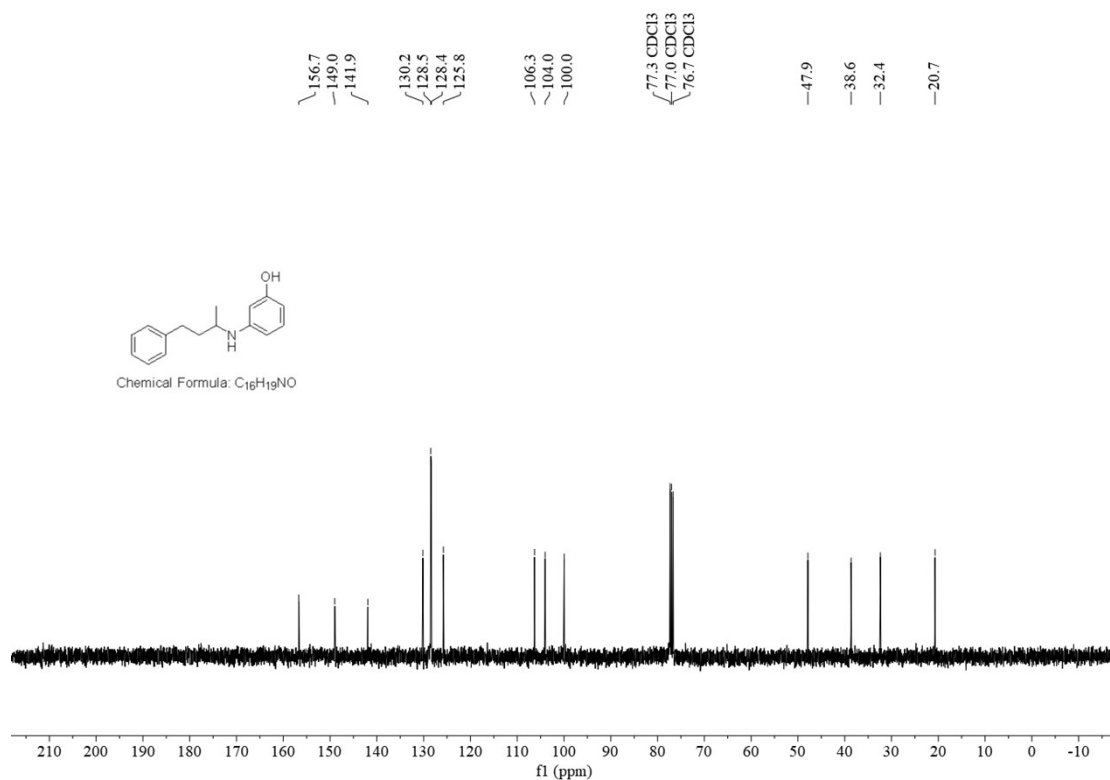
¹³C{¹H} NMR Spectrum of **4ad** in CDCl₃ at 100 MHz



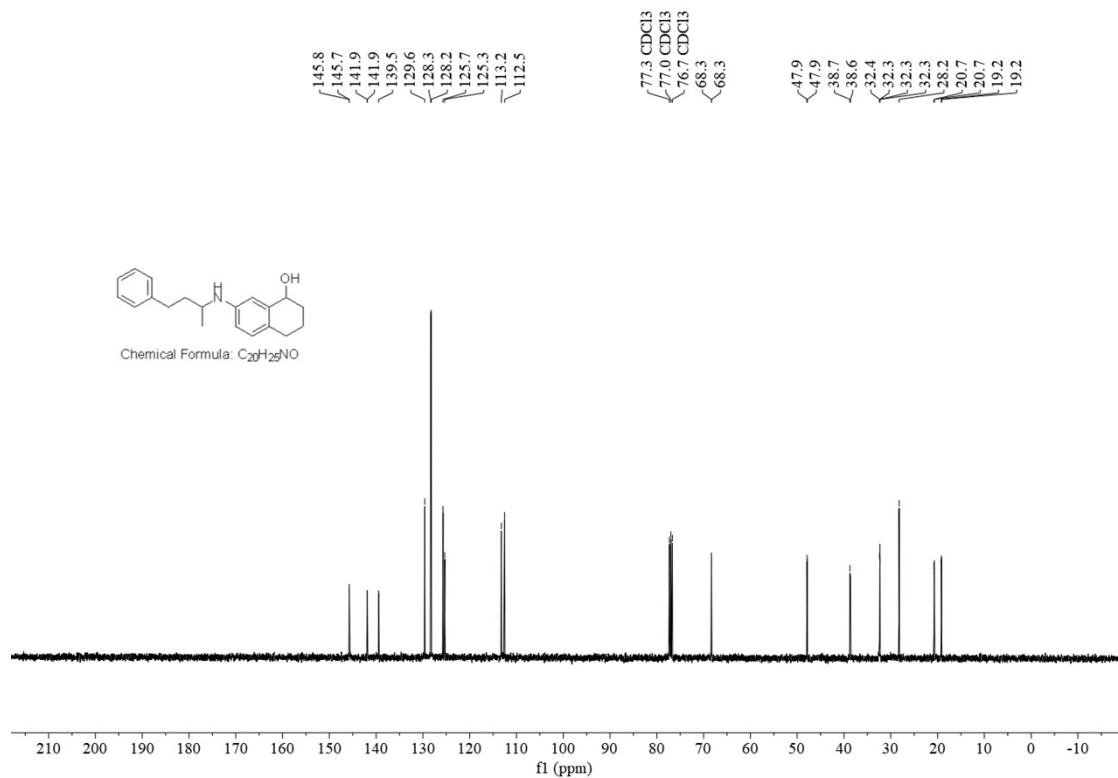
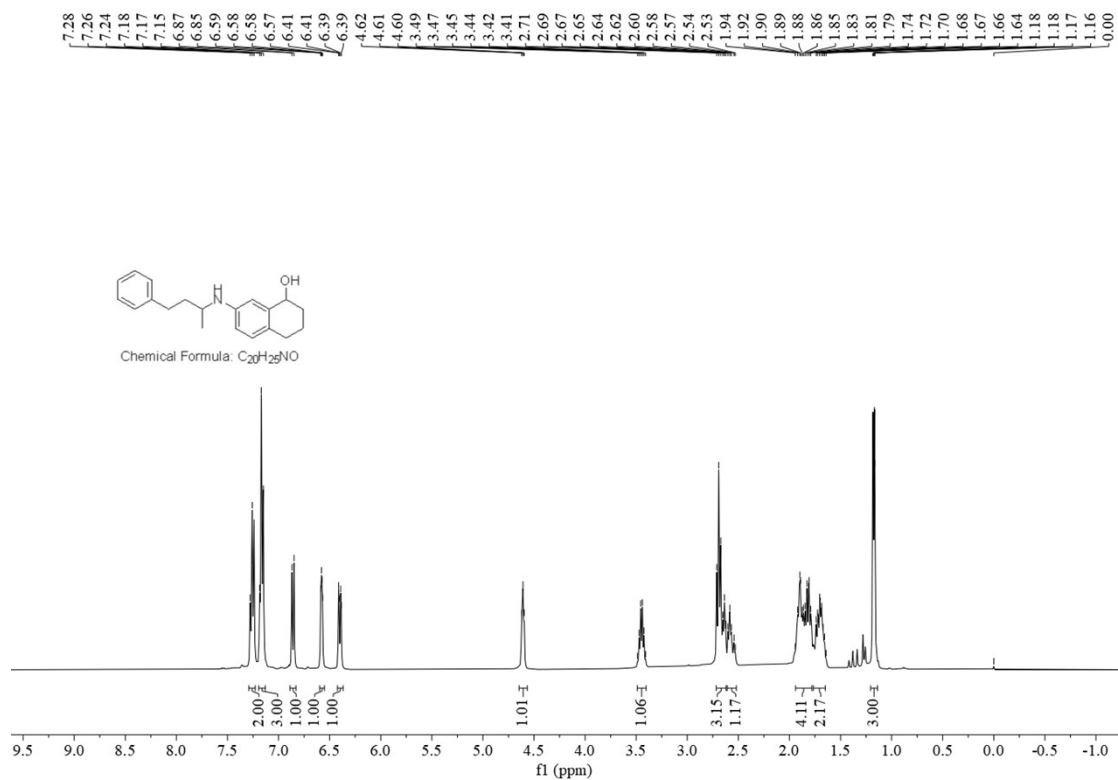


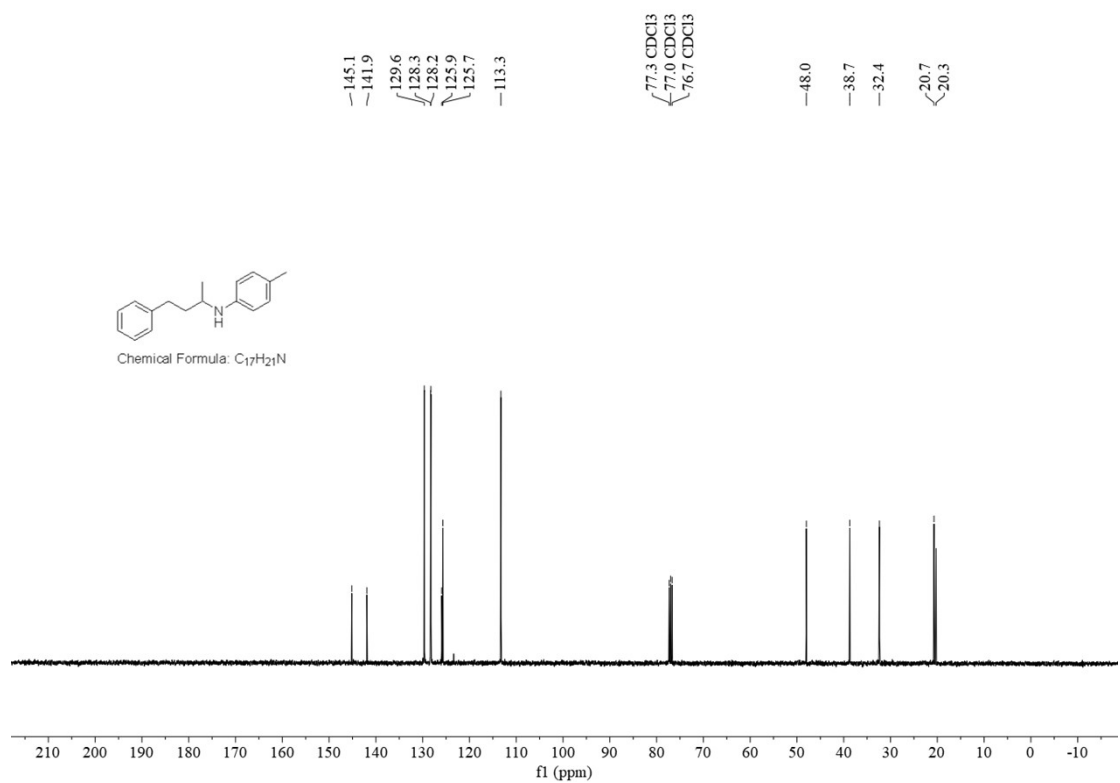
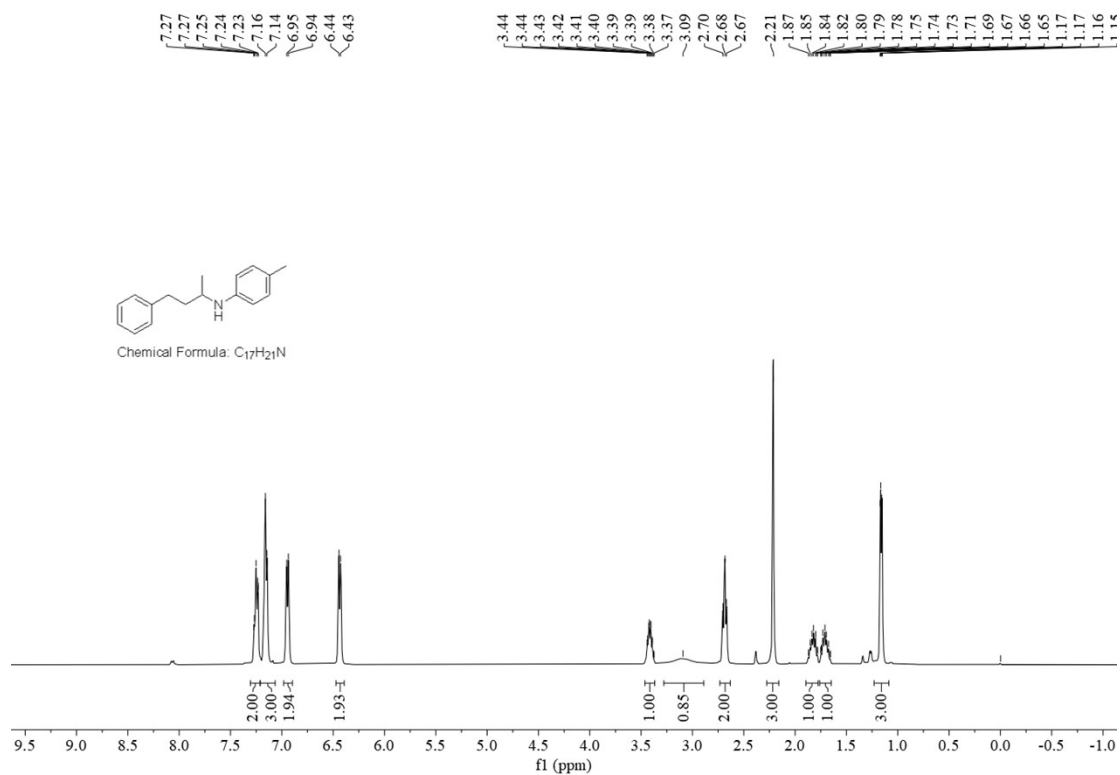


¹H NMR Spectrum of **4ag** in CDCl₃ at 400 MHz



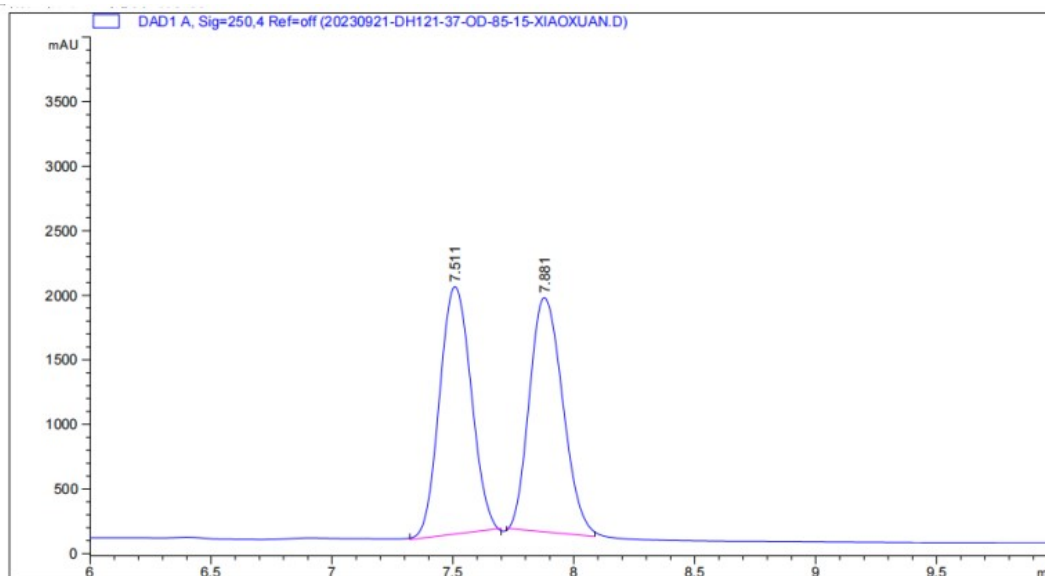
¹³C{¹H} NMR Spectrum of **4ag** in CDCl₃ at 100 MHz





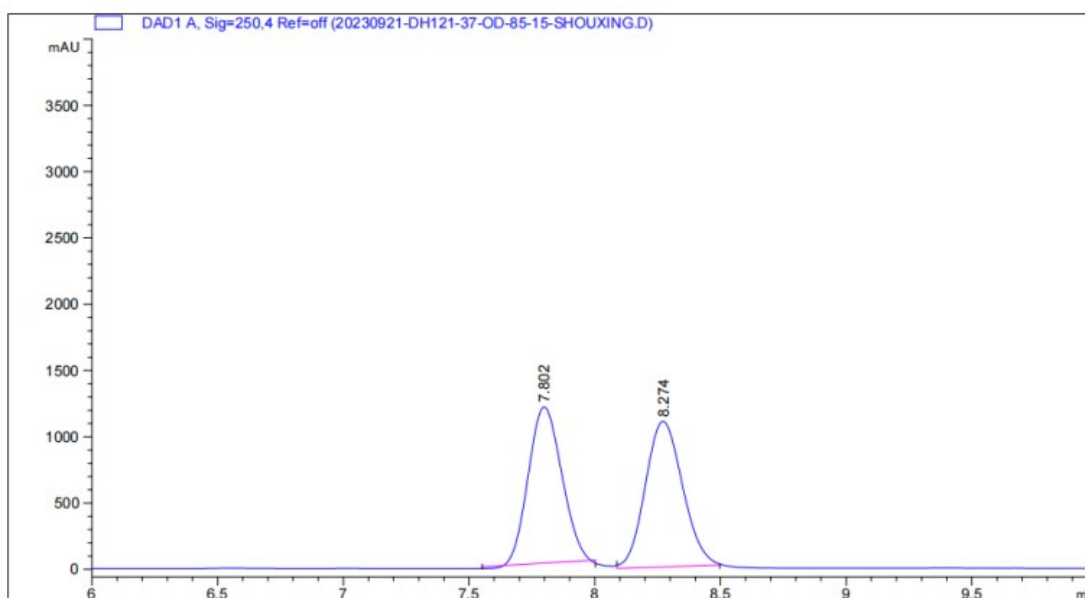
J. HPLC spectra

Racemic product of 4-isopropoxy-*N*-(4-phenylbutan-2-yl)aniline (4aa)



Peak #	RetTime [min]	Type	Width [min]	Area [mAu*s]	Height [mAu]	Area %
1	7.511	MM R	0.1509	1.73659e4	1918.45862	49.9851
2	7.881	MM R	0.1595	1.73762e4	1816.04834	50.0149

Chiral product of 4-isopropoxy-*N*-(4-phenylbutan-2-yl)aniline (4aa)



Peak #	RetTime [min]	Type	Width [min]	Area [mAu*s]	Height [mAu]	Area %
1	7.802	MM R	0.1538	1.08774e4	1178.90771	49.0168
2	8.274	MM R	0.1715	1.13137e4	1099.60254	50.9832