Ir-Catalyzed Reductive Amination and antifer Hydrogenation of Diketones: Access to *β*-and *γ*-Amino Alcohols

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Supporting Information

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A. General information

All the reactions were conducted in oven dried Schlenk tubes. All available reagents and anhydrous solvents were purchased from commercial sources and used without further purification. Flash chromatography was performed over Silica gel (100–200 mesh) bought from commercial sources. ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were collected on a Bruker DRX-400 spectrometer (400 MHz for ^1H; 101 MHz for ^{13}C, 376 MHz for ^{19}F) and referenced internally with TMS. And the syn/anti relationship was determined by ^1HNMR spectra. High-resolution mass spectra (HRMS) were recorded by an LCMS-IT-TOF mass spectrometer. Melting points were performed by using a melting point instrument without correcting. Chiral HPLC analyses were performed on an Aglient 1100 system using a Chiralcel OD-H column. Thin-layer chromatography (TLC) was conducted using commercially available 100-300 mesh silica gel plates with visualization at 254 nm.

B. General procedure for synthesis of products 3.

To a 25.0 mL dried Schlenk tube were added **1** (0.5 mmol, 1.0 equiv.), **2** (0.6 mmol, 1.1 equiv.), **TC-4** (0.005 mmol, 1.0 mol%), HCO_2H (12.5 mmol, 25.0 equiv.), and H_2O (2.0 mL) under air at 80 °C for 12 h. After completion, the reaction was quenched by saturated brines and then extracted with EtOAc (3 × 10.0 mL). The combined ethyl acetate layer was then dried over anhydrous $MgSO_4$ and concentrated in vacuum. After evaporating, the mixture was purified by flash column chromatography to obtain the desired products **3**.

C. General procedure for synthesis of products 5.

A dried 25.0 mL Schlenk tube was charged with **4** (0.5 mmol, 1.0 equiv.), **2** (0.6 mmol, 1.1 equiv.), **TC-4** (0.005 mmol, 1.0 mol%), HCO_2H (12.5 mmol, 25.0 equiv.), and H_2O (2.0 mL) under air at 80 °C for 12 h. After completion, the reaction was quenched by saturated brines and then extracted with EtOAc (3 × 10.0 mL). The combined ethyl acetate layer was then dried over anhydrous $MgSO_4$ and concentrated in vacuum. After evaporating, the mixture was purified by flash column chromatography to obtain the desired products **5**.

D. Large scale synthesis of 3aa.

To a 100.0 mL dried round bottom Schlenk was added **1a** (10.0 mmol, 1.0 equiv.), **2a** (11.0 mmol, 1.1 equiv.), **TC-4** (0.1 mmol, 1.0 mol%), HCO_2H (25.0 mmol, 25.0 equiv.), and H_2O (30.0 mL), then the reaction was stirred at 80 °C for 12 h. The organic layer was dried over anhydrous Na_2SO_4. The residue was purified by chromatography on silica gel with hexane to afford the product of **3aa**.

E. Analysis Data for the Products.

3-(phenylamino)butan-2-ol (3aa)[1]:

76.73 mg, 93% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 72:28; Yellow oil.

anti**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.14 (m, 2H), 6.75-6.71 (m, 1H), 6.69-6.61 (m, 2H), 3.98-3.92 (m, 1H), 3.49-3.43 (m, 1H), 2.91 (b, 2H), 1.25-1.17 (m, 3H), 1.14-1.11 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 129.2, 117.6, 113.6, 68.6, 53.5, 19.4, 14.0.

syn**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.14 (m, 2H), 6.75-6.71 (m, 1H), 6.69-6.61 (m, 2H), 3.65-3.58 (m, 1H), 3.34-3.28 (m, 1H), 2.91 (b, 2H), 1.25-1.17 (m, 3H), 1.14-1.11 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 129.2, 118.0, 114.1, 71.2, 55.8, 19.4, 17.1.

3-(p-tolylamino)butan-2-ol (3ba)[1]:

49.9 mg, 56% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 73:27. Pale yellow oil.

anti**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (dd, J = 8.1, 5.2 Hz, 2H), 6.55 (d, J = 8.0 Hz, 2H), 3.97-3.91 (m, 1H), 3.45-3.39 (m, 1H), 2.89 (s, 2H), 2.23 (s, 3H), 1.17 (d, J = 6.4 Hz, 3H), 1.10 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 129.7, 126.9, 114.0, 68.5, 53.9, 20.3, 19.3, 14.1.

syn**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.40. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.02-6.94 (m, 2H), 6.60 (d, J = 8.0 Hz, 2H), 3.61 - 3.55 (m, 1H), 3.28-3.22 (m, 1H), 2.89 (s, 2H), 2.24 (s, 3H), 1.23 (d, J = 6.1 Hz, 3H), 1.11 (d, J = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 129.7, 127.5, 114.5, 71.2, 56.5, 20.3, 19.3, 17.0.

3-((4-methoxyphenyl)amino)butan-2-ol (3ca)[1]:

52.5 mg, 57% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 66:34. Pale yellow oil.

anti**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.20. ^1H NMR (400 MHz, CDCl3) δ 6.79 - 6.76 (m, 2H), 6.64 - 6.60 (m, 2H), 3.98 - 3.92 (m, 1H), 3.74 (s, 3H), 3.42 - 3.35 (m, 1H), 2.63 (s, 2H), 1.18 (dd, J = 6.7, 2.1 Hz, 3H), 1.10 (dd, J = 6.8, 2.0 Hz, 2H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 141.3, 115.5, 114.8, 68.6, 55.7, 54.9, 18.8, 14.3.

syn**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.22. ^1H NMR (400 MHz, $CDCl_3$) δ 6.80-6.77 (m, 2H), 6.68 - 6.65 (m, 2H), 3.75 (s, 3H), 3.60-3.53 (m, 1H), 3.21-3.14 (m, 1H), 2.71 (b, 2H), 1.26 (d, J = 6.1 Hz, 1H), 1.12 (d, J = 6.5 Hz, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 141.5, 116.3, 114.8, 71.3, 58.0, 55.7, 19.4, 17.1.

3-((4-fluorophenyl)amino)butan-2-ol (3da)[1]:

75.0 mg, 82% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 65:35. Yellow oil.

anti**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.18. ^1H NMR (400 MHz, $CDCl_3$) δ 6.92-6.85 (m, 2H), 6.64-6.56 (m, 2H), 3.99-3.93 (m, 1H), 3.44-3.38 (m, 1H), 1.27-1.20 (m, 3H), 1.15-1.11 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (d, J = 235.4 Hz), 143.6, 115.7 (d, J = 22.3 Hz), 114.8 (d, J = 7.6 Hz), 68.7, 54.5, 19.0, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -127.4 (s, 1F).

syn**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.21. ^1H NMR (400 MHz, $CDCl_3$) δ 6.92-6.85 (m, 2H), 6.64-6.56 (m, 2H), 3.65-3.58 (m, 1H), 3.25-3.18 (m, 1H), 1.27-1.20 (m, 3H), 1.15-1.11 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (d, J = 235.4 Hz), 143.9, 115.7 (d, J = 22.3 Hz), 115.5 (d, J = 7.4 Hz), 71.3, 57.2, 19.5, 17.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -127.4 (s, 1F).

3-((4-chlorophenyl)amino)butan-2-ol (3ea)[1]:

73.8, 74% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 83:17. Yellow oil.

anti**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.08 (m, 2H), 6.55 (d, J = 8.8 Hz, 2H), 3.99-3.93 (m, 1H), 3.46-3.40 (m, 1H), 1.21 (d, J = 6.5 Hz, 3H), 1.13 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 129.1, 122.1, 114.7, 68.8, 53.7, 19.1, 13.9.

syn**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.08 (m, 2H), 6.59 (d, J = 8.8 Hz, 0H), 3.68- 3.62 (m, 1H), 3.31-3.24 (m, 1H), 1.21 (d, J = 6.5 Hz, 2H), 1.13 (d, J = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 129.1, 122.1, 115.2, 71.2, 56.0, 19.6, 17.2.

3-((4-bromophenyl)amino)butan-2-ol (3fa) [1]**:**

83.84 mg, 69% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 87:13. Pale yellow oil.

anti**:** TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 6.57-6.49 (m, 2H), 3.99-3.93 (m, 1H), 3.46-3.40 (m, 1H), 1.21 (d, J = 6.5 Hz, 3H), 1.13 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 132.0, 115.2, 109.1, 68.8, 53.6, 19.2, 13.9.

syn**:** TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 6.57-6.49 (m, 2H), 3.69-3.63 (m, 1H), 3.32-3.25 (m, 1H), 1.21 (d, J = 6.5 Hz, 3H), 1.13 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 132.0, 115.7, 109.1, 55.8, 19.6, 17.2.

3-((2-methoxyphenyl)amino)butan-2-ol (3ga)[1]**:**

97.5 mg, 73% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 80:20. Pale yellow oil.

anti**:** TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.06 (m, 1H), 6.32-6.24 (m, 2H), 6.19 (t, J = 2.1 Hz, 1H), 4.0-3.95 (m, 1H), 3.77 (s, 3H), 3.49-3.44 (m, 1H), 1.20 (d, J = 6.5 Hz, 3H), 1.13 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 148.7, 130.1, 106.8, 102.7, 99.7, 68.8, 55.1, 53.6, 19.1, 14.2.

syn**:** TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.06 (m, 1H), 6.32-6.24 (m, 2H), 6.19 (t, J = 2.1 Hz, 1H), 3.77 (s, 3H), 3.67-3.61 (m, 1H), 3.35-3.28 (m, 1H), 1.25 (d, J = 6.3 Hz, 3H), 1.13 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 149.2, 130.1, 107.3, 103.2, 100.2, 71.3, 55.9, 53.6, 19.6, 17.3.

3-((2-iodophenyl)amino)butan-2-ol (3ha)[1]:

94.0 mg, 65% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 85:15. Brown oil.

***anti*:** TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 1H), 7.21-7.16 (m, 1H), 6.61 (d, J = 8.3 Hz, 1H), 6.48-6.41 (m, 1H), 4.22 (b, 1H), 4.00-3.94 (m, 1H), 3.56-3.50 (m, 1H), 2.00 (s, 1H), 1.23 (dd, J = 6.5, 2.3 Hz, 3H), 1.18 (dd, J = 6.6, 2.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 139.2, 129.4, 118.9, 111.6, 86.5, 68.9, 54.1, 18.9, 14.4.

***syn*:** TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 1H), 7.21-7.16 (m, 1H), 6.67 (d, J = 9.8 Hz, 1H), 6.48-6.41 (m, 1H), 4.22 (b, 1H), 3.78 - 3.72 (m, 1H), 3.42 - 3.36 (m, 1H), 2.00 (s, 1H), 1.23 (dd, J = 6.5, 2.3 Hz, 3H), 1.18 (dd, J = 6.6, 2.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 139.2, 129.4, 119.2, 112.1, 87.0, 71.1, 56.0, 19.5, 17.3.

3-((2-fluoro-4-methylphenyl)amino)butan-2-ol (3ia):

98.5 mg, 69% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 85:15. Pale yellow oil.

***anti*:** TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75-6.70 (m, 2H), 6.56 (t, J = 8.8 Hz, 1H), 3.91 -3.85 (m, 1H), 3.40-3.34 (m, 1H), 2.16 (s, 3H), 1.13 (dd, J = 6.5, 1.6 Hz, 3H), 1.07 (dd, J = 6.6, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9 (d, J = 238.2 Hz), 133.1 (d, J = 11.7 Hz), 127.1 (d, J = 6.7 Hz), 124.7 (d, J = 3.0 Hz), 115.4 (d, J = 18.6 Hz), 113.5 (d, J = 3.5 Hz), 68.8, 54.0, 20.3 (d, J = 1.5 Hz), 18.8, 14.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -135.9 (s, 1F). HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{11}H_{16}FNO$, 198.1294; found, 198.1292.

***syn*:** TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75-6.70 (m, 2H), 6.62 (t, J = 8.7 Hz, 1H), 3.60 - 3.54 (m, 1H), 3.22-3.16 (m, 1H), 2.16 (s, 3H), 1.18 (dd, J = 6.5, 1.6 Hz), 1.07 (dd, J = 6.6, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9 (d, J = 238.2 Hz), 133.1 (d, J = 11.7 Hz), 127.1 (d, J

= 6.7 Hz), 124.7 (d, J = 3.0 Hz), 114.1 (d, J = 3.4 Hz), 71.2, 56.4, 20.3 (d, J = 1.5 Hz), 19.3, 17.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -131.5 (s, 1F). HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{11}H_{16}FNO$, 198.1294; found, 198.1292.

3-(naphthalen-2-ylamino)butan-2-ol (3ja)[1]:

44.1 mg, 41% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 85:15. Red oil.

anti**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.58 (m, 3H), 7.38-7.34 (m, 1H), 7.22-7.17 (m, 1H), 6.93-6.83 (m, 2H), 4.09-4.03 (m, 1H), 3.66-3.59 (m, 1H), 1.25 (dd, J = 6.5, 2.1 Hz, 3H), 1.19 (dd, J = 6.6, 2.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 135.0, 129.1, 127.6, 127.5, 126.3, 125.8, 122.1, 118.4, 105.4, 68.7, 53.5, 19.1, 14.0.

syn**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.58 (m, 3H), 7.36 (td, J = 7.4, 2.8 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 6.93-6.83 (m, 2H), 3.75 - 3.69 (m, 1H), 3.52-3.45 (m, 1H), 1.29 (dd, J = 6.3, 2.2 Hz, 3H), 1.19 (dd, J = 6.6, 2.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 135.0, 129.1, 127.6, 127.5, 126.3, 125.9, 122.3, 118.6, 106.2, 71.3, 55.7, 19.6, 17.1.

3-((4-cyclohexylphenyl)amino)butan-2-ol (3ka):

56.8 mg, 46% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 64:26. Red oil.

anti**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05-6.99 (m, 2H), 6.66-6.57 (m, 2H), 4.00-3.93 (m, 1H), 3.49-3.42 (m, 1H), 2.73 (b, 2H), 2.39 (s, 1H), 1.82 (s, 4H), 1.72 (d, J = 10.3 Hz, 1H), 1.43-1.33 (m, 5H), 1.24-1.18 (m, 3H), 1.14-1.18 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 137.7, 127.5, 115.2, 113.7, 68.6, 53.9, 43.5, 34.7, 26.9, 26.1, 18.7, 14.4. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{25}NO$, 248.2014; found, 248.2014.

syn**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05-6.99 (m, 2H), 6.66-6.57 (m, 2H), 3.62-3.55 (m, 1H), 3.31-3.23 (m, 1H), 2.73 (b, 2H), 2.39 (s, 1H), 1.82 (s, 4H), 1.72 (d, J = 10.3 Hz, 1H), 1.43-1.33 (m, 5H), 1.24-1.18 (m, 3H), 1.14-1.18 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 138.3, 127.5, 115.2, 114.4, 71.3, 56.6, 43.5, 34.7, 26.9, 26.1, 19.4, 17.2. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{16}H_{25}NO$, 248.2014; found, 248.2014.

3-((5,6,7,8-tetrahydronaphthalen-2-yl)amino)butan-2-ol (3la):

45.6 mg, 57% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 75:25. Red oil.

anti**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, J = 8.1 Hz, 1H), 6.49-6.43 (m, 1H), 6.37 (s, 1H), 3.99-3.93 (m, 1H), 3.48-3.42 (m, 1H), 2.67 (d, J = 10.3 Hz, 6H), 1.75 (s, 4H), 1.19 (dd, J = 6.6, 2.1 Hz, 3H), 1.13-1.11 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 137.8, 129.8, 126.7, 114.0, 112.0, 68.6, 54.0, 29.6, 28.4, 23.5, 23.3, 18.7, 14.4. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{21}NO$, 220.1701; found, 220.1711.

syn**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, J = 8.1 Hz, 1H), 6.49-6.43 (m, 1H), 6.37 (s, 1H), 3.60 - 3.54 (m, 1H), 3.29-3.22 (m, 1H), 2.67 (d, J = 10.3 Hz, 6H), 1.75 (s, 4H), 1.25 (dd, J = 6.1, 2.1 Hz, 1H), 1.13-1.11 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 137.9, 130.0, 127.2, 114.6, 112.6, 71.3, 56.7, 29.6, 28.4, 23.5, 23.2, 19.3, 17.2. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{21}NO$, 220.1701; found, 220.1711.

4-(phenylamino)hexan-3-ol (3ab):

57.9 mg, 60% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 75:25. Colorless oil.

anti**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, J = 7.9 Hz, 2H), 6.69 (t, J = 7.9 Hz, 1H), 6.64 (d, J = 4.4 Hz, 2H), 3.67-6.63 (m, 1H), 3.54 (b, 1H), 3.36-3.32 (m, 1H), 1.69 - 1.64 (m, 1H), 1.59-1.52 (m, 1H), 1.49 - 1.42 (m, 2H), 1.02 (t, J = 7.6 Hz, 3H), 0.97 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 129.3, 117.4, 113.4, 74.2, 59.3, 25.8, 22.7, 11.1, 10.7. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{12}H_{19}NO$, 194.1545; found, 194.1532.

syn**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, J = 7.9 Hz, 2H), 6.71 (d, J = 7.2 Hz, 1H), 6.67 (d, J = 7.2 Hz, 2H), 3.57-3.52 (m, 1H), 3.26-3.21 (m, 1H), 1.72 - 1.58 (m, 2H), 1.56-1.47 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 129.3, 117.6, 113.6, 74.4, 59.3, 26.9, 25.1, 10.6, 10.2. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{12}H_{19}NO$, 194.1545; found, 194.1532.

1-phenyl-2-(phenylamino)propan-1-ol (3ac)[1]:

72.6 mg, 64% yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of > 99:1. White solid, m.p. 119-121 °C. ***anti*:** TLC (petroleum ether/ethyl acetate = 10/1, v/v): $R_f = 0.24$. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 4.4 Hz, 4H), 7.32-7.26 (m, 1H), 7.24-7.18 (m, 2H), 6.77 - 6.69 (m, 3H), 4.98 (d, J = 3.0 Hz, 1H), 3.80-3.75 (m, 1H), 2.50 (b, 1H), 1.01 (dd, J = 6.6, 1.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 141.3, 129.4, 128.3, 127.4, 125.9, 118.0, 113.9, 74.2, 54.3, 13.9.

4-(phenylamino)pentan-2-ol (5aa)[2]:

67.1 mg, 75% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 60:40. Colorless oil.

***anti*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): $R_f = 0.35$. ^1H NMR (400 MHz, $CDCl_3$) δ 7.20-7.15 (m, 2H), 6.79-6.70 (m, 2H), 6.69 - 6.63 (m, 2H), 4.09-3.99 (m, 1H), 3.70-3.63 (m, 1H), 3.40 (b, 1H), 1.71-1.52 (m, 2H), 1.22-1.14 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 129.2, 118.7, 115.1, 67.9, 49.8, 45.5, 23.8, 21.3.

***syn*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): $R_f = 0.37$. ^1H NMR (400 MHz, $CDCl_3$) δ 7.20-7.15 (m, 2H), 6.79 - 6.70 (m, 2H), 6.69 - 6.63 (m, 2H), 4.09 - 3.99 (m, 1H), 3.79 - 3.71 (m, 1H), 3.40 (b, 1H), 1.71 - 1.52 (m, 2H), 1.22 - 1.14 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 129.2, 117.5, 113.6, 65.0, 46.1, 45.5, 23.8, 21.0.

4-(p-tolylamino)pentan-2-ol (5ba):

58.7 mg, 61% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 65:35. Pink oil.

***anti*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): $R_f = 0.26$. ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (t, J = 8.4 Hz, 2H), 6.66-6.58 (m, 2H), 4.11-4.02 (m, 1H), 3.69-3.60 (m, 1H), 3.23 (b, 2H), 2.26-2.24 (m, 3H), 1.73-1.49 (m, 2H), 1.23-1.13 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 129.7, 128.5, 115.8, 68.3, 51.0, 45.5, 23.8, 21.4, 20.4. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{12}H_{19}NO$, 194.1545; found, 194.1560.

***syn*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): $R_f = 0.28$. ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (t, J = 8.4 Hz, 2H), 6.66-6.58 (m, 2H), 4.11-4.02 (m, 1H), 3.76-3.70 (m, 1H), 3.23 (b, 2H), 2.26-2.24 (m, 3H), 1.73 - 1.49 (m, 2H), 1.23-1.13 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 129.7, 127.1, 114.2, 65.2, 46.7, 45.1, 23.7, 21.1, 20.3. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{12}H_{19}NO$, 194.1545; found, 194.1560.

4-((4-methoxyphenyl)amino)pentan-2-ol (5ca):

71.1 mg, 68% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 60:40. Brown oil.

***anti*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81-6.77 (m, 2H), 6.72-6.69 (m, 2H), 4.12 - 4.04 (m, 1H), 3.75 (s, 3H), 3.60-3.53 (m, 1H), 3.39 (s, 2H), 1.68-1.46 (m, 2H), 1.21 - 1.11 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 140.5, 117.6, 114.7, 68.5, 55.6, 52.3, 45.4, 23.8, 21.5. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{12}H_{19}NO_2$, 210.1494; found, 210.1508.

***syn*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81-6.77 (m, 2H), 6.67-6.64 (m, 2H), 4.12-4.04 (m, 1H), 3.75 (s, 3H), 3.70-3.65 (m, 1H), 3.39 (s, 2H), 1.68-1.46 (m, 2H), 1.21-1.11 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 141.3, 115.9, 114.8, 65.3, 55.7, 47.8, 44.7, 23.7, 21.1. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{12}H_{19}NO_2$, 210.1494; found, 210.1508.

4-((4-fluorophenyl)amino)pentan-2-ol (5da):

41.5 mg, 42% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 60:40. Yellow oil.

***anti*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92-6.85 (m, 2H), 6.66-6.63 (m, 2H), 4.11-4.00 (m, 1H), 3.61-3.55 (m, 1H), 3.31 (b, 1H), 1.60-1.51 (m, 2H), 1.23-1.12 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (d, J = 236.8 Hz), 143.0 (d, J = 2.1 Hz), 116.4 (d, J = 7.4 Hz), 115.7 (d, J = 22.4 Hz), 68.0, 51.0, 45.4, 23.8, 21.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -125.7 (s, 1F). HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{11}H_{16}FNO$, 198.1294; found, 198.1292.

***syn*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92-6.85 (m, 2H), 6.60-6.57 (m, 2H), 4.11-4.00 (m, 1H), 3.71-3.65 (m, 1H), 3.31 (b, 2H), 1.72-1.61 (m, 2H), 1.23-1.12 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.80 (d, J = 235.1 Hz), 143.7 (d, J = 2.0 Hz), 115.6 (d, J = 22.2 Hz), 114.8 (d, J = 7.3 Hz), 65.0, 47.1, 45.0, 23.8, 20.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -127.4 (s, 1F).HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{11}H_{16}FNO$, 198.1294; found, 198.1292.

4-((4-chlorophenyl)amino)pentan-2-ol (5ea):

35.1 mg, 33% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 80:20. Yellow oil.

anti**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.25. ^1H NMR (400 MHz, $CDCl_3$) δ 7.15-7.10 (m, 2H), 6.64-6.61 (m, 2H), 4.10 -3.99 (m, 1H), 3.68-3.60 (m, 1H), 3.26 (b, 2H), 1.63-1.59 (m, 2H), 1.21 (dd, J = 1.6, 0.7 Hz, 3H), 1.17 (dd, J = 1.6, 0.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 129.2, 123.3, 116.0, 67.9, 49.8, 45.6, 24.1, 21.3. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{11}H_{16}ClNO$, 214.0999; found, 214.1010.

syn**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.27. ^1H NMR (400 MHz, $CDCl_3$) δ 7.15-7.10 (m, 2H), 6.58-6.55 (m, 2H), 4.10-3.99 (m, 1H), 3.75-3.69 (m, 1H), 3.26 (b, 2H), 1.63-1.59 (m, 2H), 1.21 (dd, J = 1.6, 0.7 Hz, 3H), 1.17 (dd, J = 1.6, 0.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 129.2, 123.3, 114.7, 65.2, 49.8, 45.6, 24.1, 20.9. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{11}H_{16}ClNO$, 214.0999; found, 214.1010.

4-((4-(tert-butyl)phenyl)amino)pentan-2-ol (5fa):

37.6 mg, 32% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 66:34. Yellow oil.

anti**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.25. ^1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 2H), 6.70-6.60 (m, 2H), 4.12- 4.02 (m, 1H), 3.71-3.62 (m, 1H), 3.33 (s, 1H), 1.74-1.52 (m, 2H), 1.28 (s, 9H), 1.23- 1.14 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 142.0, 126.0, 115.3, 68.3, 50.7, 45.6, 33.9, 31.5, 23.8, 21.6. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{25}NO$, 236.2014; found, 236.2015.

syn**:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.27. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 2H), 6.71-6.65 (m, 2H), 4.12-4.02 (m, 1H), 3.78-3.72 (m, 1H), 3.33 (s, 1H), 1.74-1.52 (m, 2H), 1.28 (s, 9H), 1.23-1.14 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.6, 126.0, 113.6, 65.2, 46.6, 45.1, 33.9, 31.5, 23.8, 21.2. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{25}NO$, 236.2014; found, 236.2015.

4-((3-benzylphenyl)amino)pentan-2-ol (5ma):

26.9 mg, 20% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 60:40. Yellow oil.

***anti*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.19-7.17 (m, 3H), 7.02-6.99 (m, 2H), 6.65 (dd, J = 8.6, 2.2 Hz, 2H), 4.10-4.00 (m, 1H), 3.88 (s, 2H), 3.68-3.60 (m, 1H), 3.07 (b, 2H), 1.72-1.49 (m, 2H), 1.23-1.13 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 141.9, 141.7, 131.7, 129.7, 128.3, 128.3, 125.8, 115.6, 114.0, 68.2, 50.5, 45.5, 41.0, 23.8, 21.5. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{18}H_{23}NO$, 270.1858; found, 270.1873.

***syn*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.19-7.17 (m, 3H), 7.02-6.99 (m, 2H), 6.59 (dd, J = 8.6, 2.2 Hz, 2H), 4.10-4.00 (m, 1H), 3.87 (s, 2H), 3.77-3.70 (m, 1H), 3.07 (b, 2H), 1.72-1.49 (m, 2H), 1.23-1.13 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 141.9, 141.7, 130.4, 129.7, 128.7, 128.3, 125.7, 115.6, 114.0, 65.2, 46.5, 45.1, 40/9, 23.8, 21.1. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{18}H_{23}NO$, 270.1858; found, 270.1873.

4-((2,3-dihydro-1H-inden-5-yl)amino)pentan-2-ol (5na):

68.0 mg, 62% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 64:36. Yellow oil.

***anti*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (t, J = 8.0 Hz, 1H), 6.64 (s, 1H), 6.53 (d, J = 10.4 Hz, 1H), 4.12-4.03 (m, 1H), 3.69-3.60 (m, 1H), 3.33 (s, 2H), 2.85-2.78 (m, 4H), 2.08-1.99 (m, 2H), 1.73-1.48 (m, 2H), 1.23-1.13 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 145.4, 135.1, 124.7 (d, J = 1.7 Hz), 114.1, 112.0, 68.3, 51.3, 45.5, 33.0, 31.9, 25.6, 23.7, 21.5. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{21}NO$, 220.1701; found, 220.1711.

***syn*:** TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (t, J = 8.0 Hz, 1H), 6.58 (s, 1H), 6.47 (d, J = 10.5 Hz, 1H), 4.12-4.03 (m, 1H), 3.77-3.71 (m, 1H), 3.33 (s, 2H), 2.85-2.78 (m, 4H), 2.08-1.99 (m, 2H), 1.73-1.48 (m, 2H), 1.23-1.13 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 145.4, 133.7, 124.7 (d, J = 1.7 Hz), 112.5, 110.3, 65.2, 46.9, 45.0, 33.0, 31.8, 25.6, 23.7, 21.1. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{21}NO$, 220.1701; found, 220.1711.

1-phenyl-3-(phenylamino)butan-1-ol (5ab)[2]:

78.5 mg, 65% total yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of 50:50. Yellow oil.

***anti*:** TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 4H), 7.29 -7.25 (m, 1H), 7.23-7.14 (m, 2H), 6.80-6.69 (m, 2H), 6.61 (d, J = 7.9 Hz, 1H), 4.97-4.91 (m, 1H), 3.77-3.64 (m, 1H), 3.32 (b, 2H), 2.02-1.79 (m, 2H), 1.17 (dd, J = 6.3, 2.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 144.5, 129.3, 128.4, 127.4, 125.7, 118.7, 115.1, 74.1, 49.5, 46.1, 21.3.

***syn*:** TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 4H), 7.29 -7.25 (m, 1H), 7.23-7.14 (m, 2H), 6.80-6.69 (m, 2H), 6.61 (d, J = 7.9 Hz, 1H), 4.97-4.91 (m, 1H), 3.77-3.64 (m, 1H), 3.32 (b, 2H), 2.02-1.79 (m, 2H), 1.17 (dd, J = 6.3, 2.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 144.7, 129.2, 128.4, 127.3, 125.6, 118.0, 114.2, 71.8, 46.5, 45.4, 21.1.

5-(phenylamino)heptan-3-ol (5ac):

56.9 mg, 55% yield, mixture of the ***anti*** and ***syn*** isomers in the ratio of > 99:1. Colorless oil. TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.35. ***anti*:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 7.0 Hz, 2H), 6.78 (t, J = 7.3 Hz, 1H), 6.72 (d, J = 7.6 Hz, 1H), 3.81-3.76 (m, 1H), 3.56 - 3.49 (m, 1H), 1.75 - 1.70 (m, 1H), 1.63 - 1.46 (m, 5H), 0.95 (t, J = 7.4 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 129.3, 118.9, 115.3, 73.5, 55.8, 40.1, 30.7, 27.8, 9.7 (d, J = 1.6 Hz). HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{13}H_{21}NO$, 208.1701; found, 208.1689.

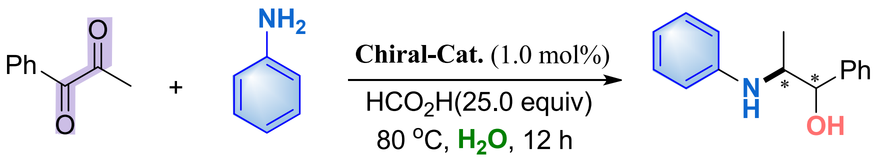
F. References

[1] a) Kenzo Arai; Simone Lucarini; Matthew M. Salter; Kentaro Ohta; Yasuhiro Yamashita; Shuj Kobayashi. *J. Am. Chem. Soc,* **2007**, 129, 8103; b) Kureshy, R. I.; Prathap, K. J.; Roy, T.; Maity, N. C.; Khan, N.-u. H.; Abdi, S. H. R.; Bajaj, H. C. *Adv. Synth. Catal.,* **2010**, *352*, 3053; c) Kokubo, M.; Naito, T.; Kobayashi, S. *Tetrahedron,* **2010**, *66*, 1111; d) Pan, S.; Jiang, M.; Hu, J.; Xu, R.; Zeng, X.; Zhong, G. *Green Chem.* **2020**, *22*, 336.

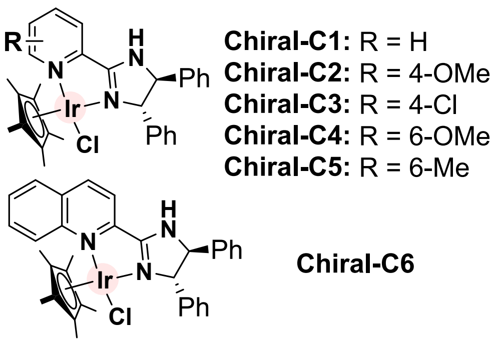
[2] Bartoli, G.; Cimarelli, C.; Palmieri, G. *J. Chem. Soc.*, **1994**, *5*, 537.

G. Enantioselectivities as Determined by Chiral HPLC

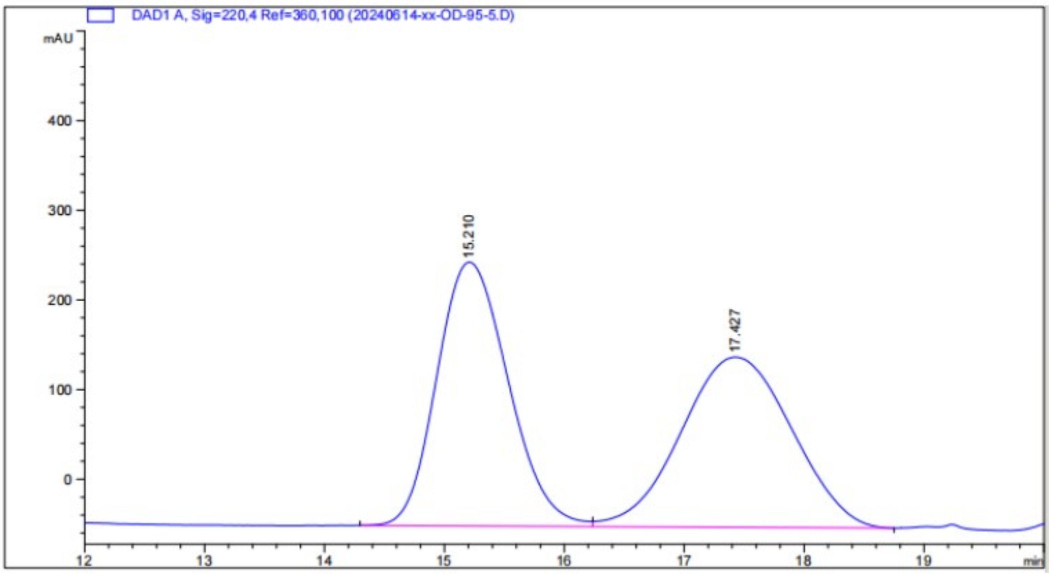
Scheme S1 Asymmetric reduction amination of **3aa**.



1a **2a** **3aa**

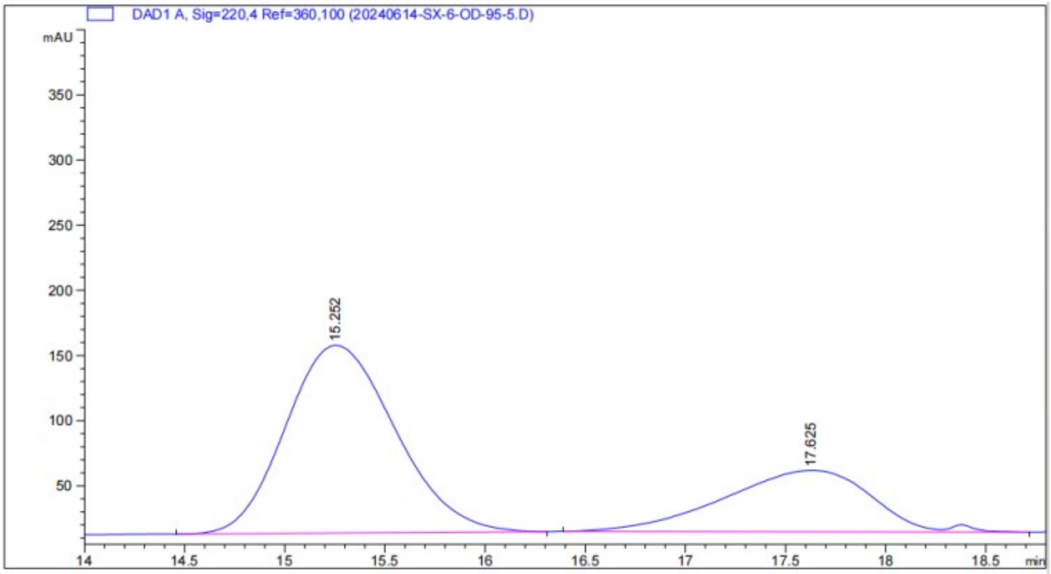


Cat.	Yield of 3ca (%)	*ee* of 3ca (%)
Chiral-C1	44	23
Chiral-C2	42	15
Chiral-C3	35	29
Chiral-C4	46	37
Chiral-C5	42	29
Chiral-C6	19	39



Peak #	RetTime [min]	Type	Width [min]	Area [mAu*s]	Height [mAu]	Area %
1	15.210	BV	0.6464	1.21616e4	294.12781	49.9656
2	17.427	VB	0.9605	1.21784e4	189.81523	50.0344

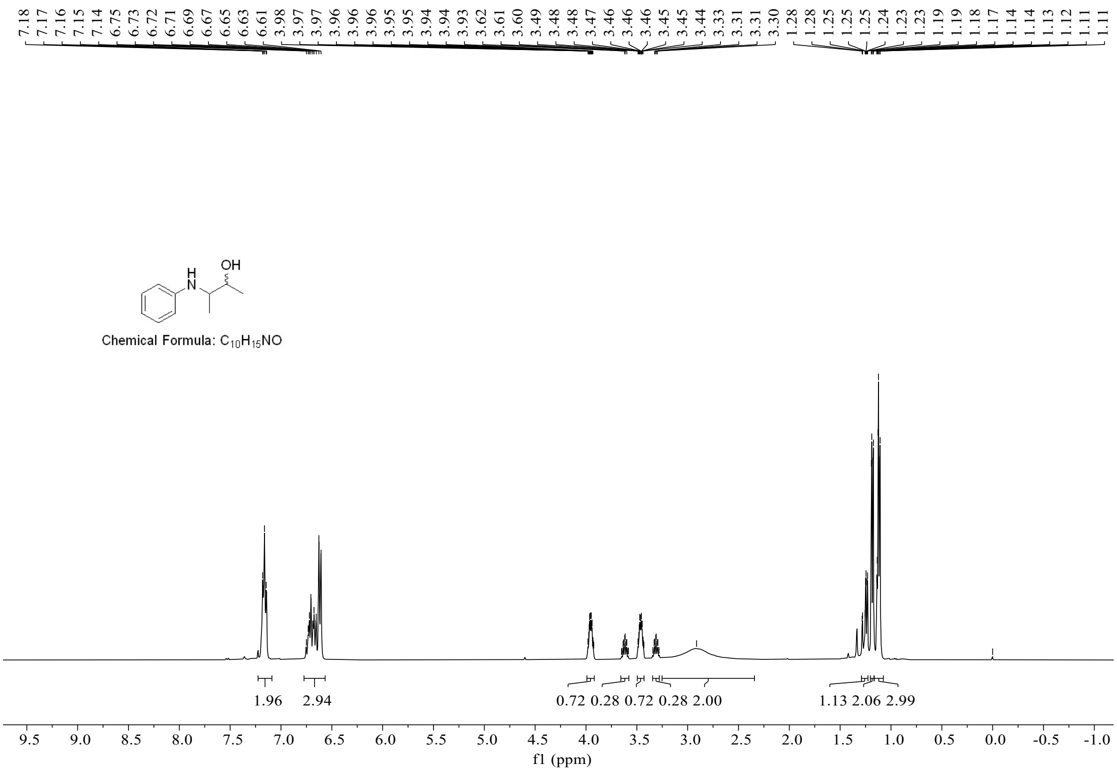
HPLC traces of *racemic*-**3ca**.



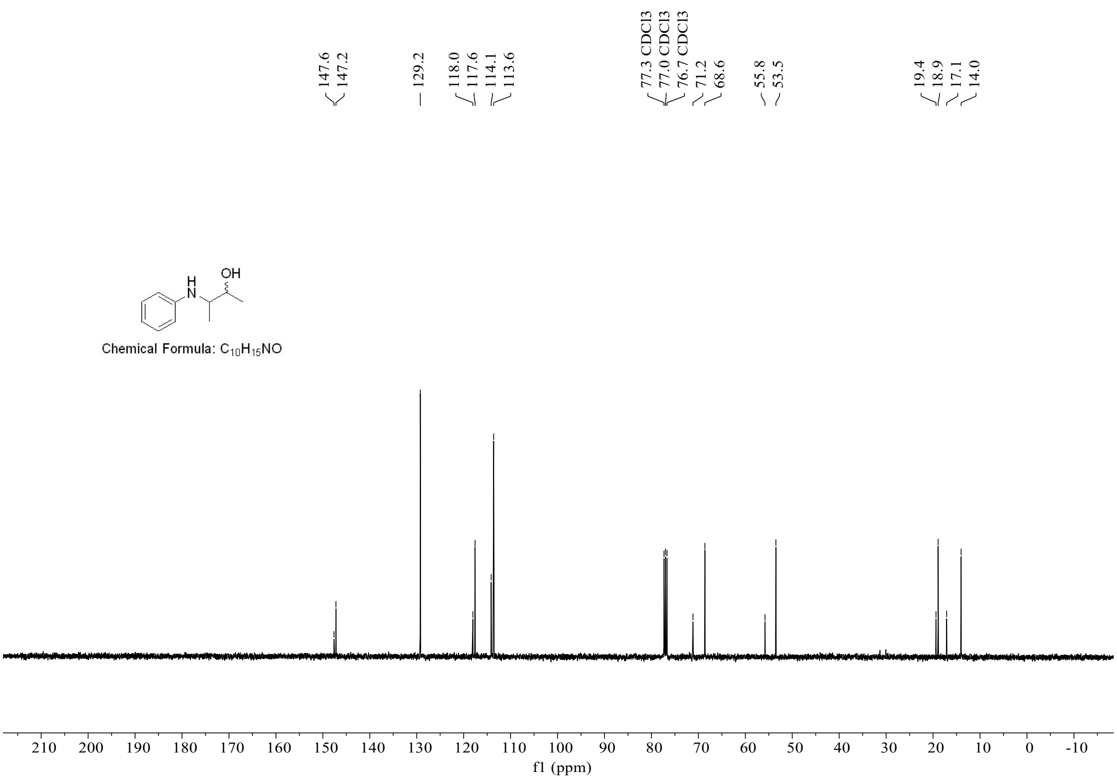
Peak #	RetTime [min]	Type	Width [min]	Area [mAu*s]	Height [mAu]	Area %
1	15.252	BB	0.5797	5480.72070	144.10695	69.3511
2	17.625	BV R	0.6040	2422.13452	47.09615	30.6489

HPLC traces of *chiral*-**3ca** (**Chiral-C6**, 39%*ee*).

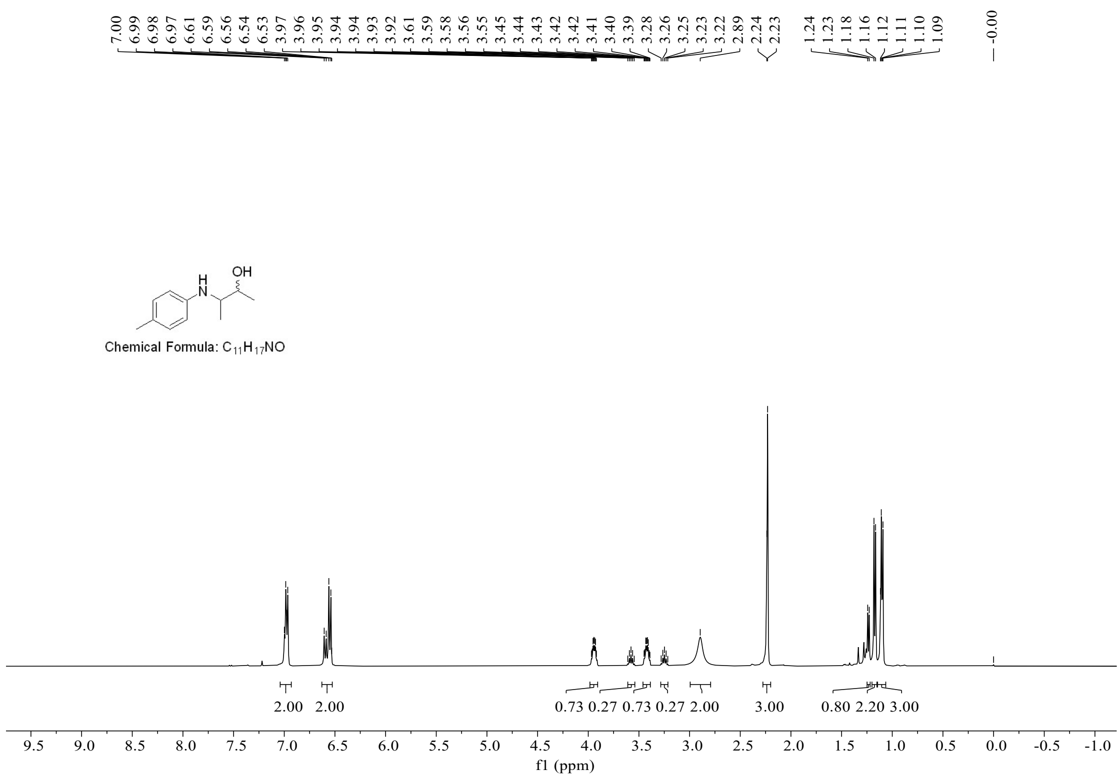
H. NMR Spectra



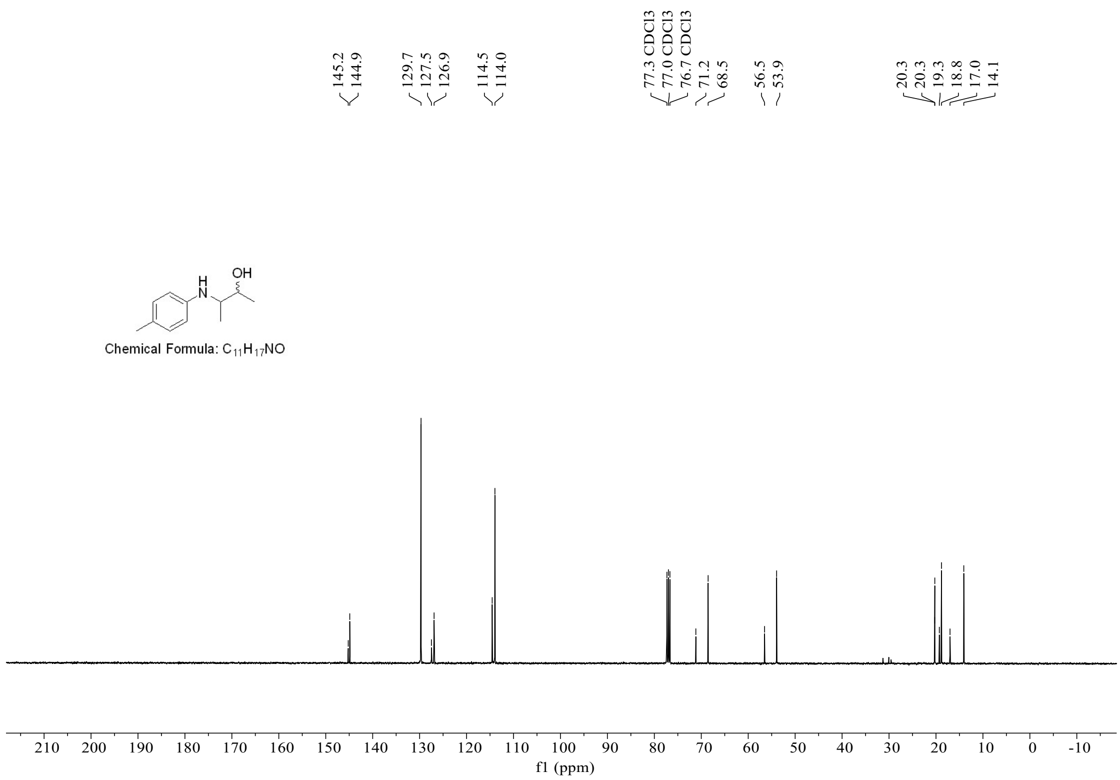
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aa**



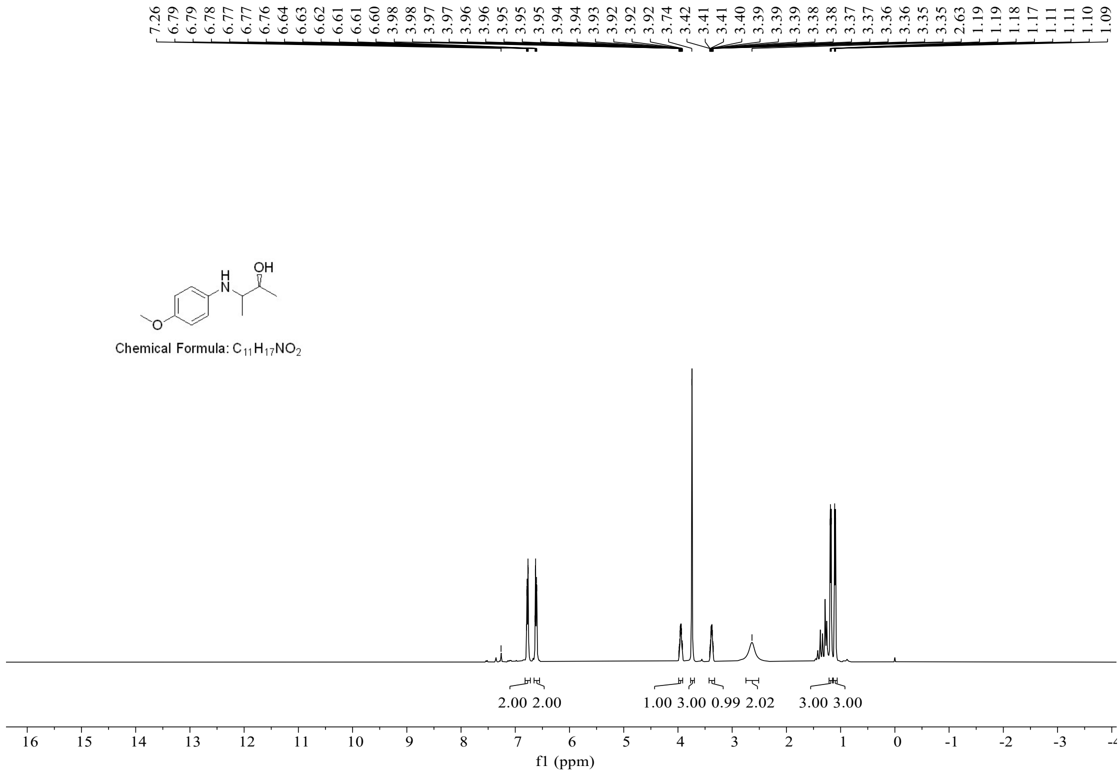
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3aa**



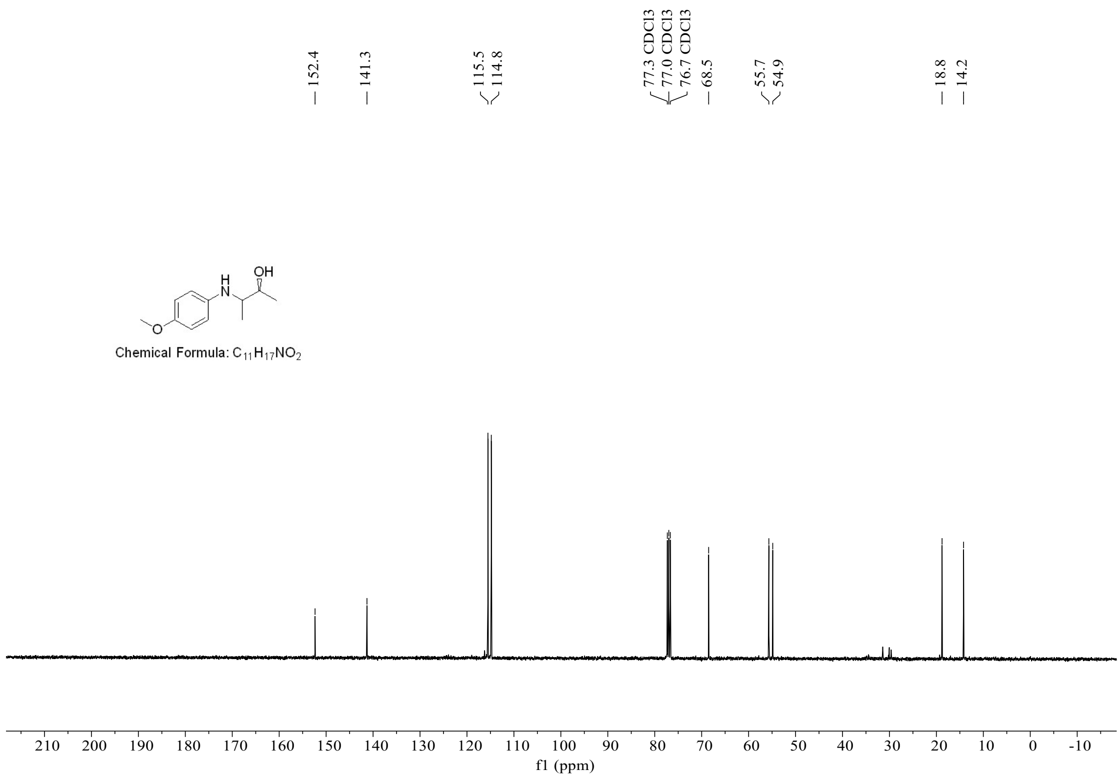
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ba**



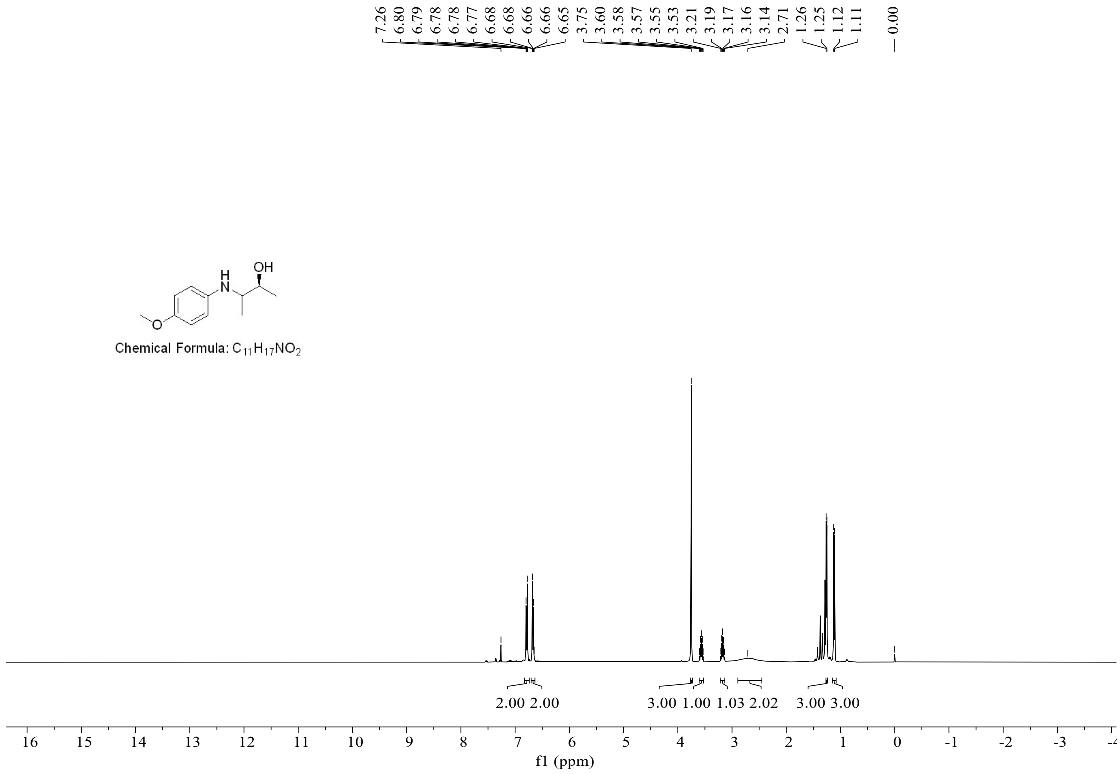
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ba**



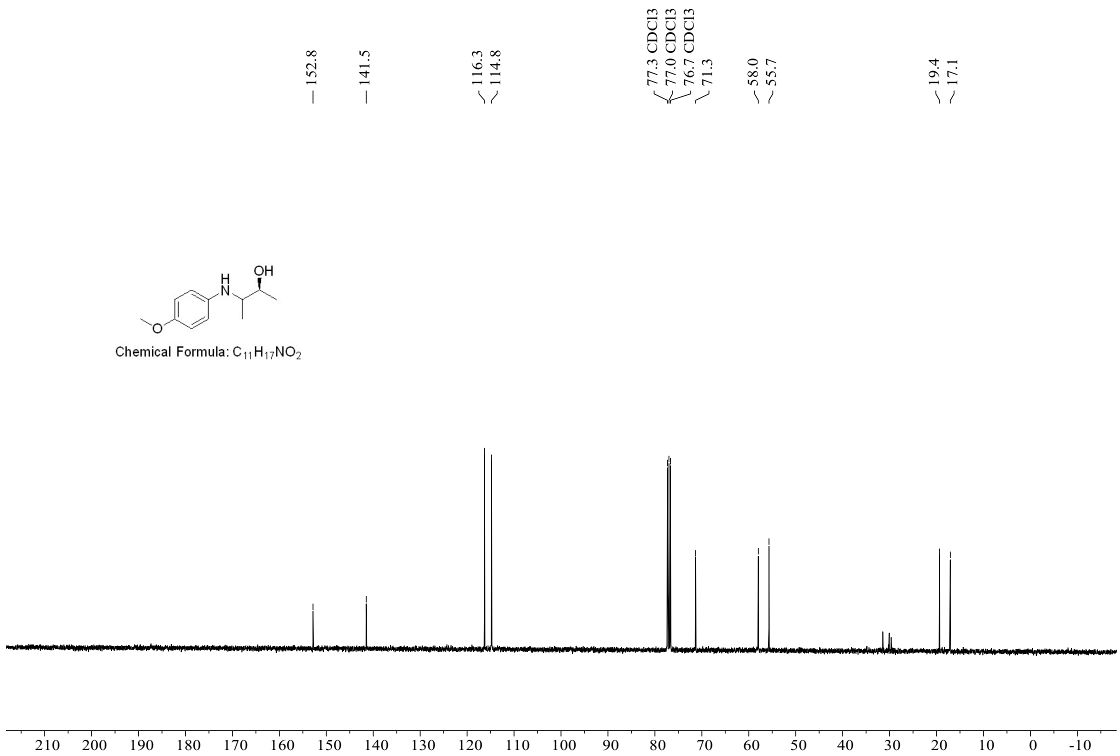
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ca** (*anti*)



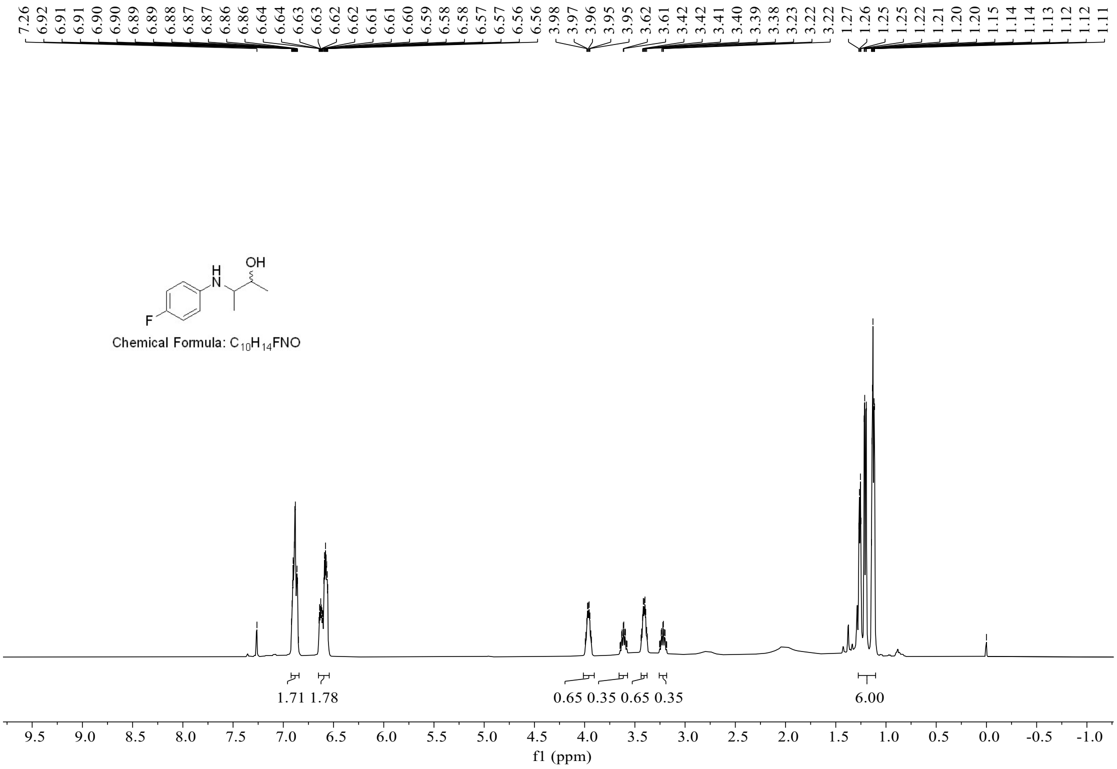
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ca** (*anti*)



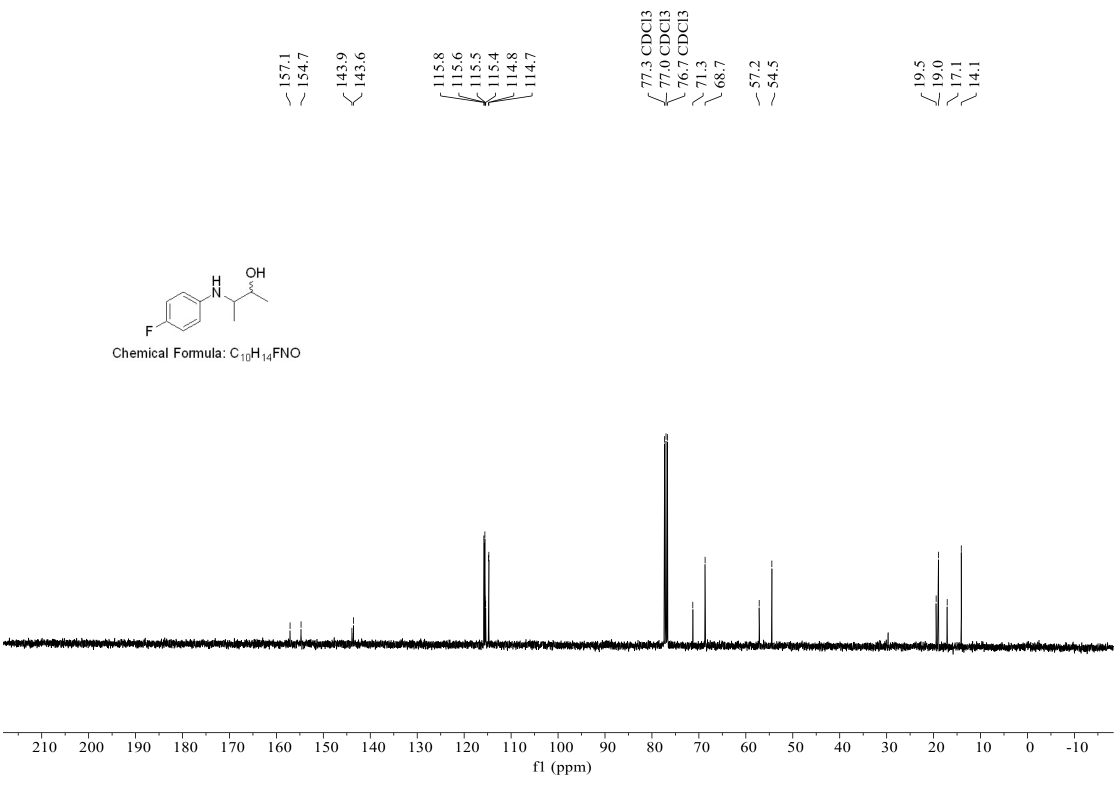
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ca** (*syn*)



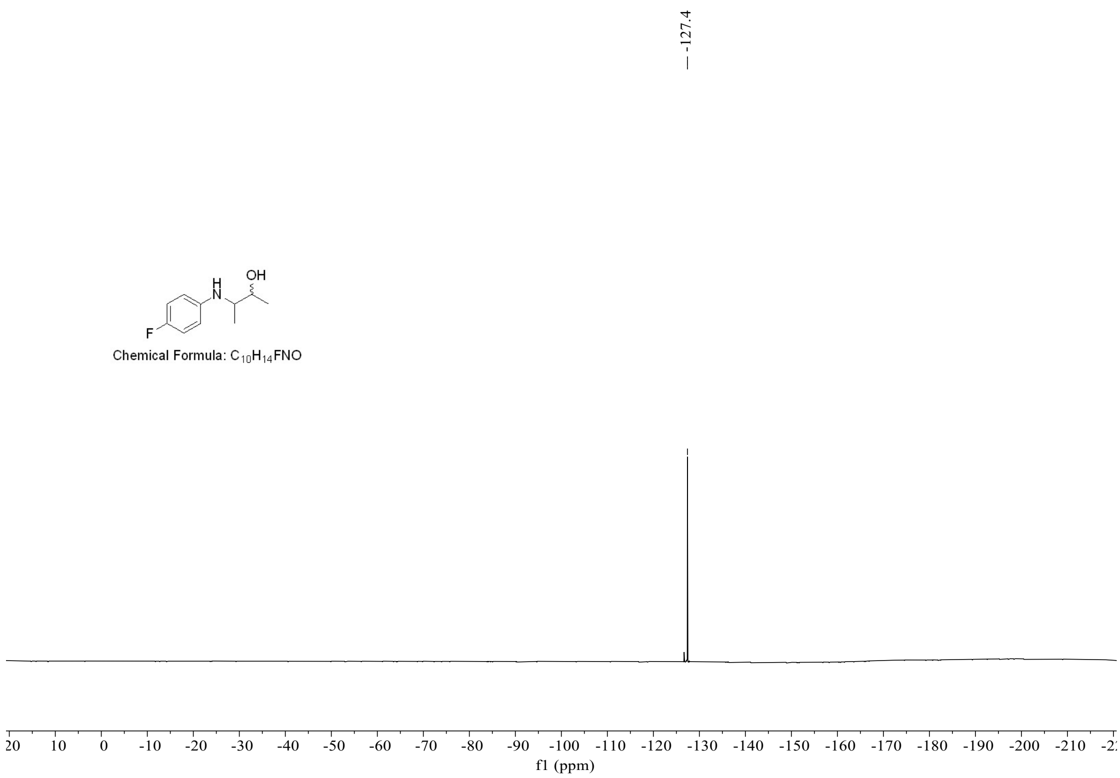
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ca** (*syn*)



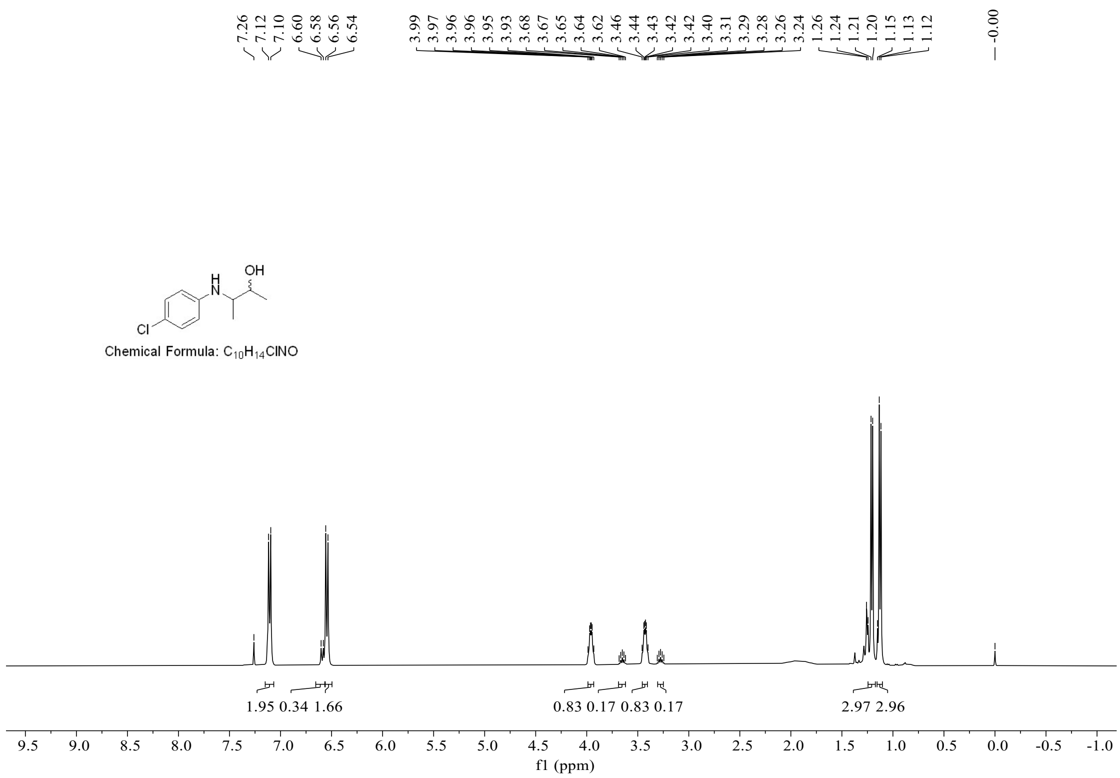
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3da**



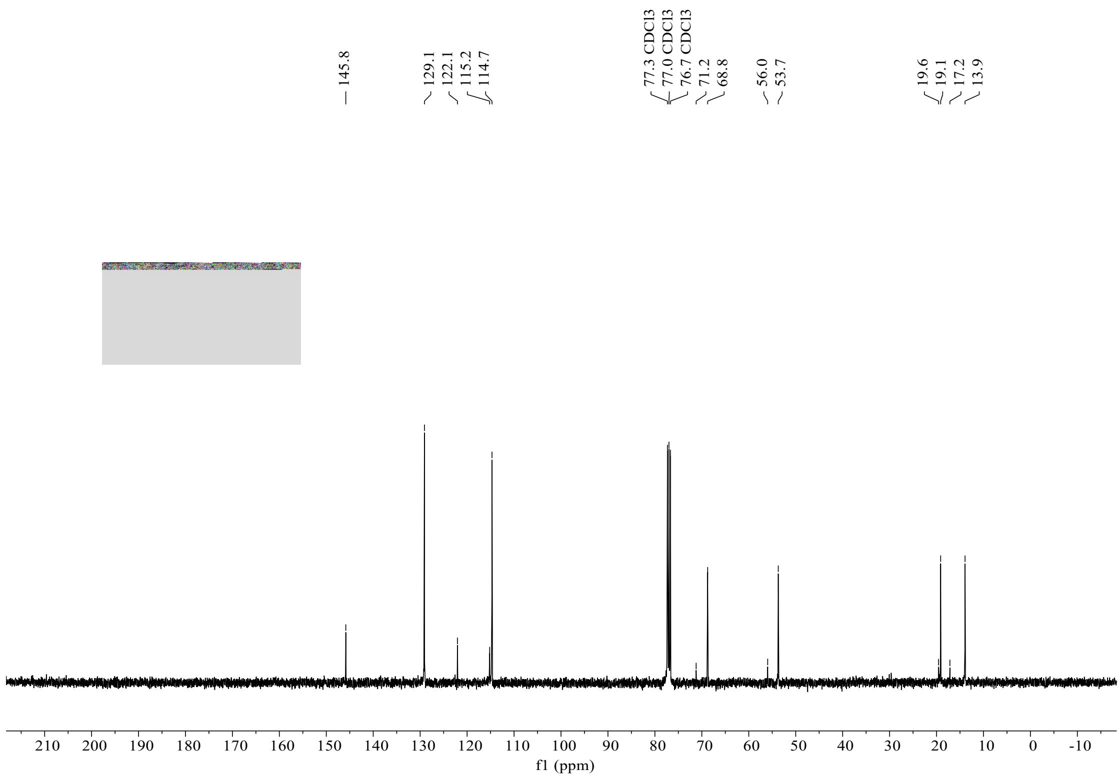
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3da**



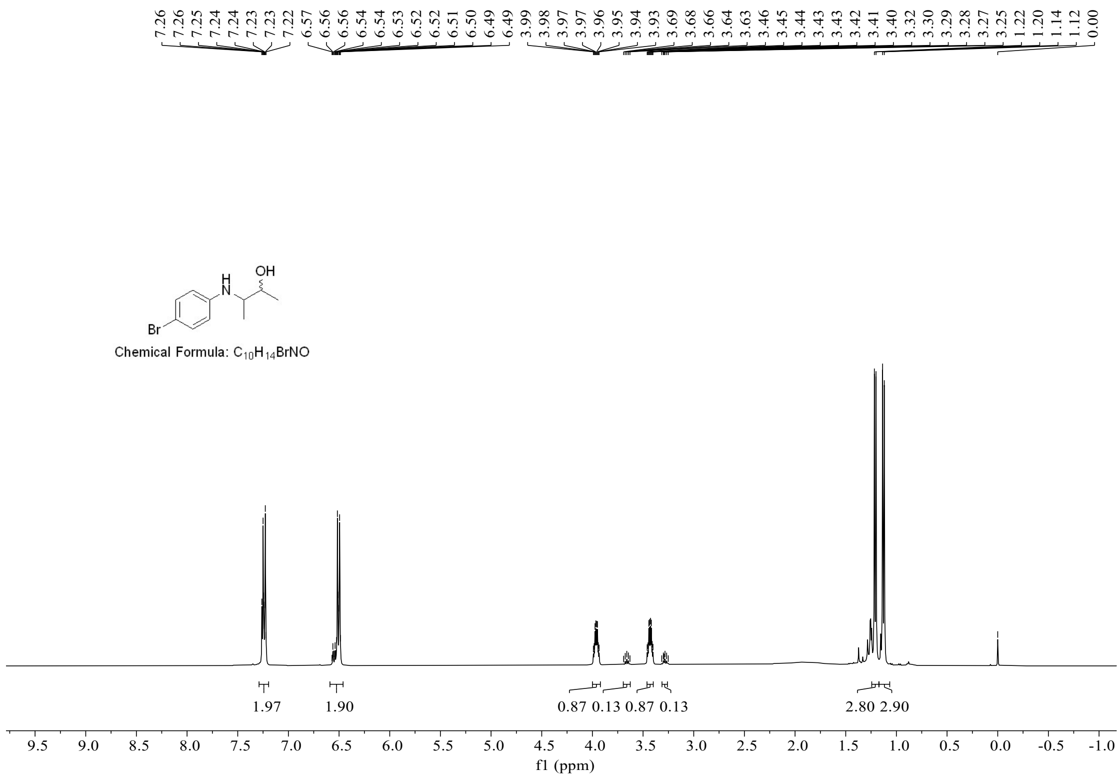
[19]F NMR (377 MHz, $CDCl_3$) spectrum of **3da**



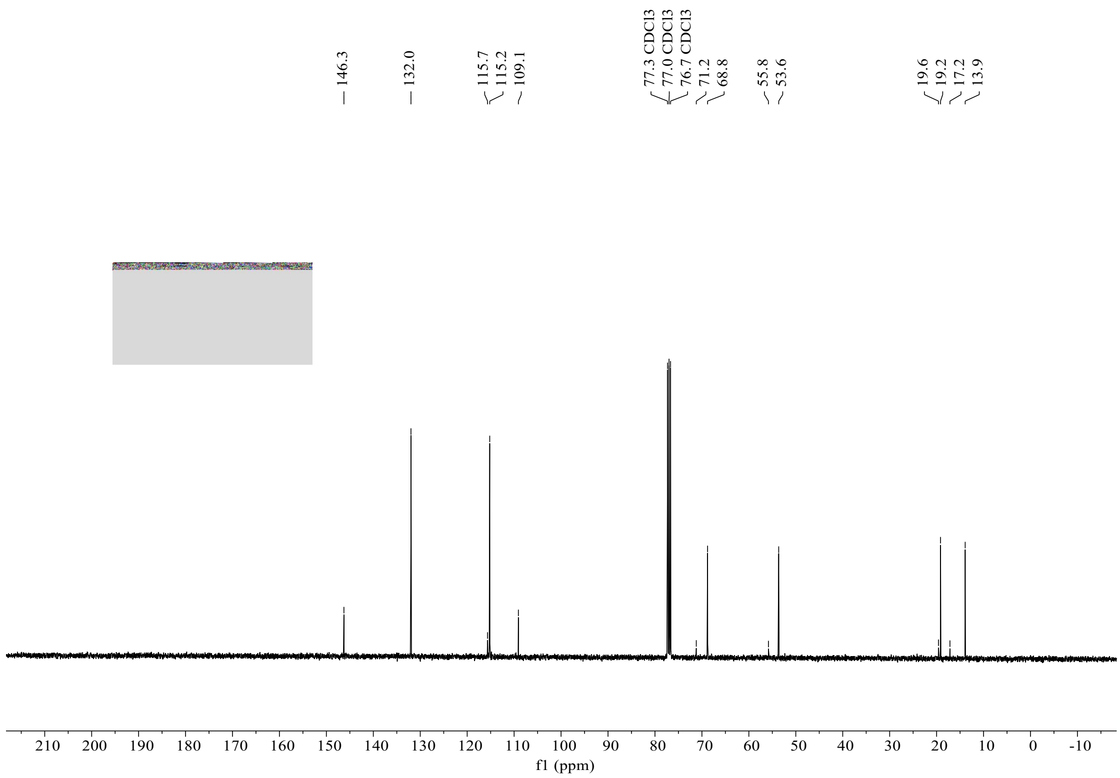
[1]H NMR (400 MHz, $CDCl_3$) spectrum of **3ea**



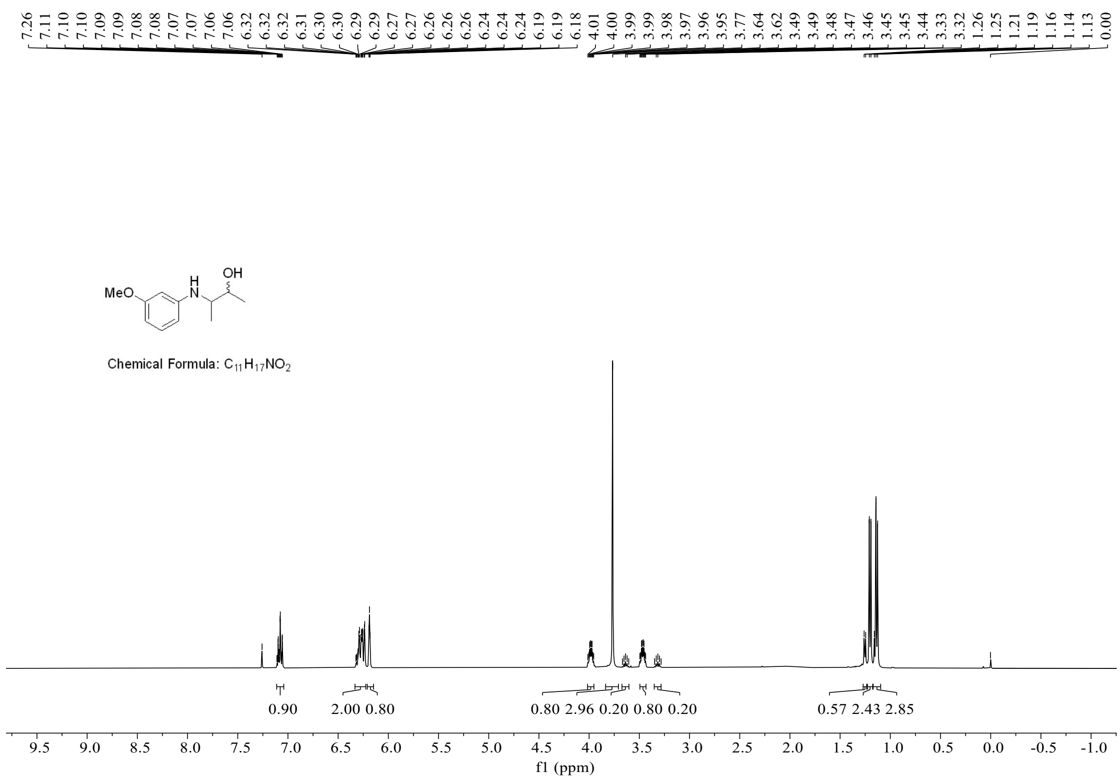
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ea**



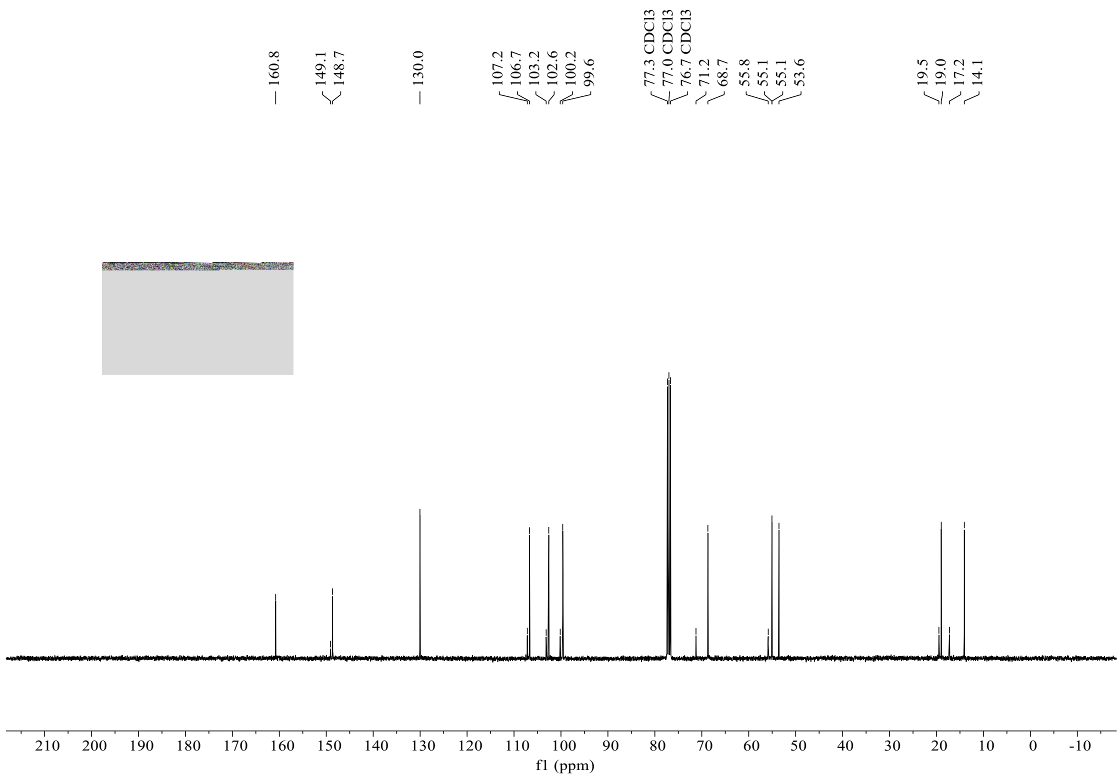
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3fa**



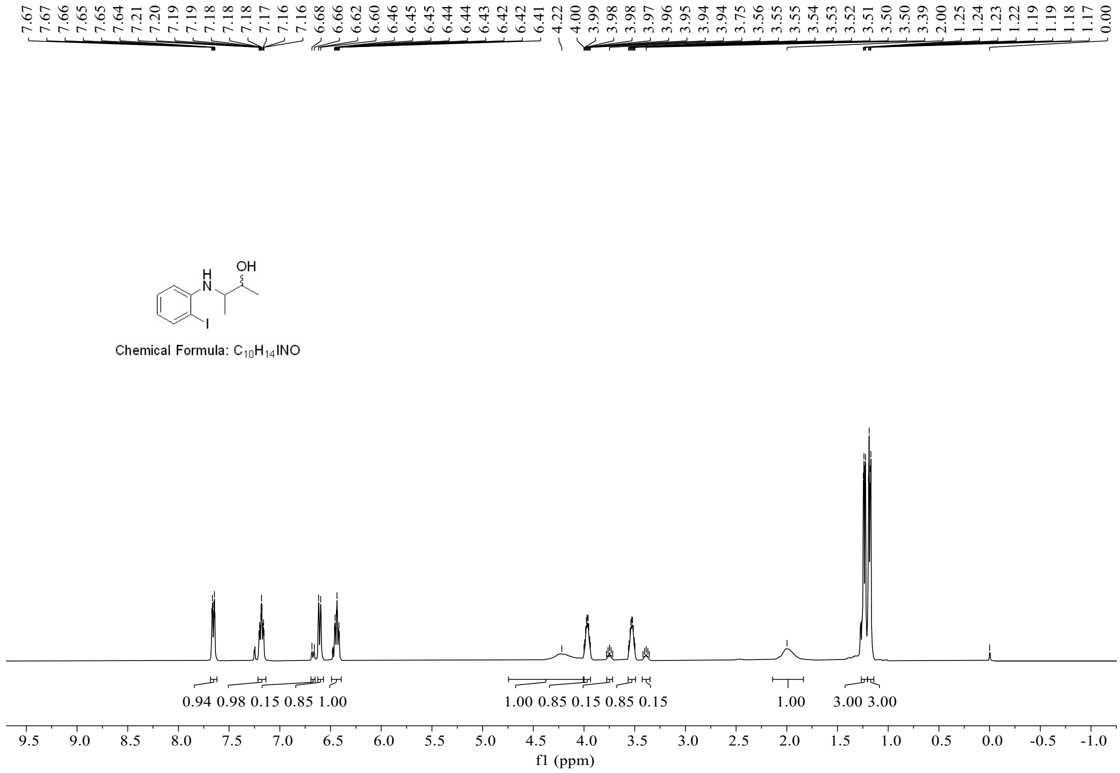
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3fa**



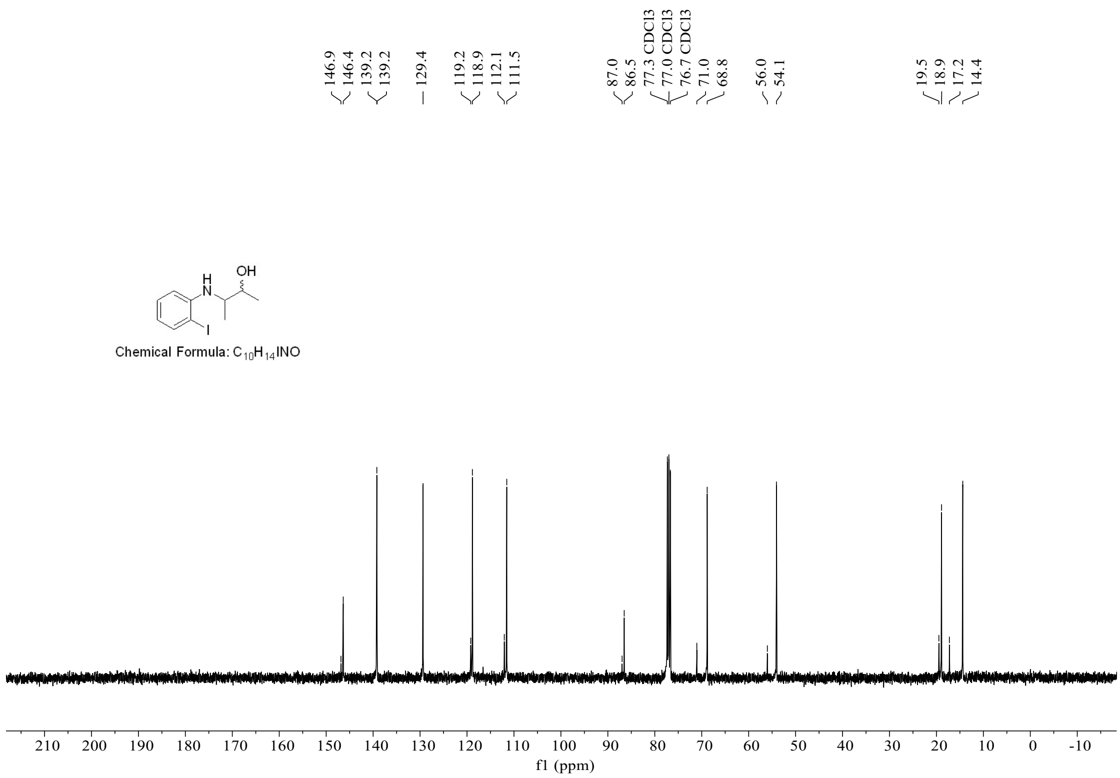
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ga**



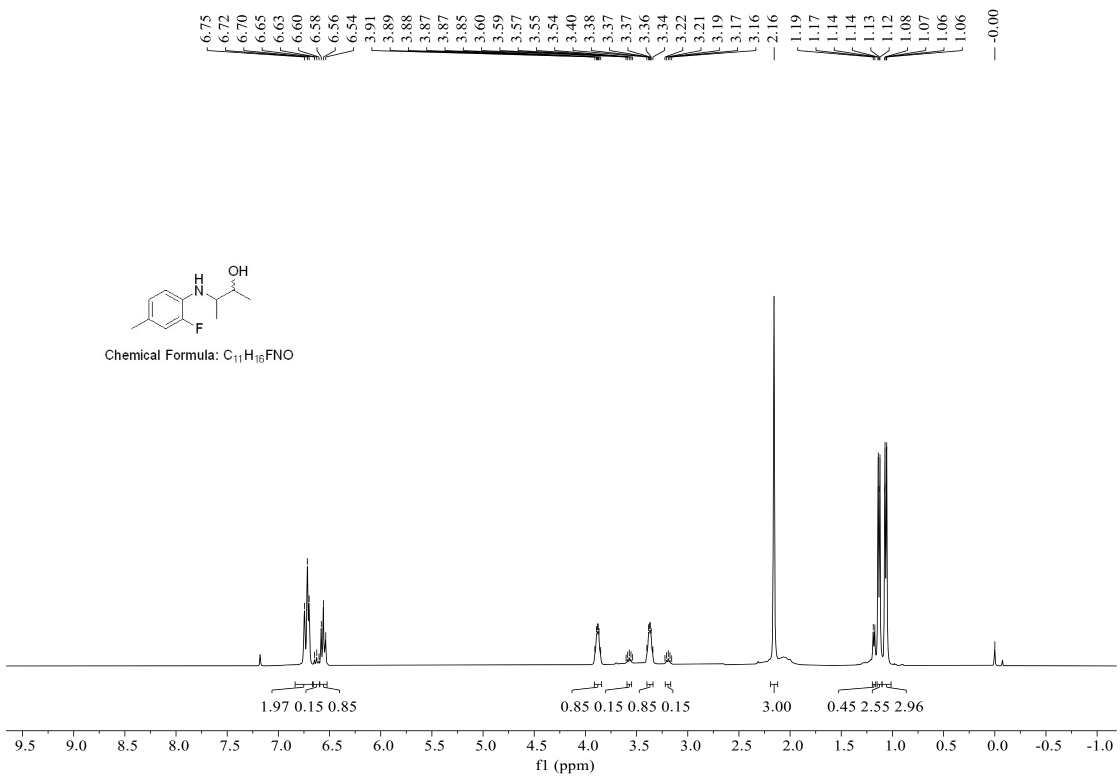
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ga**



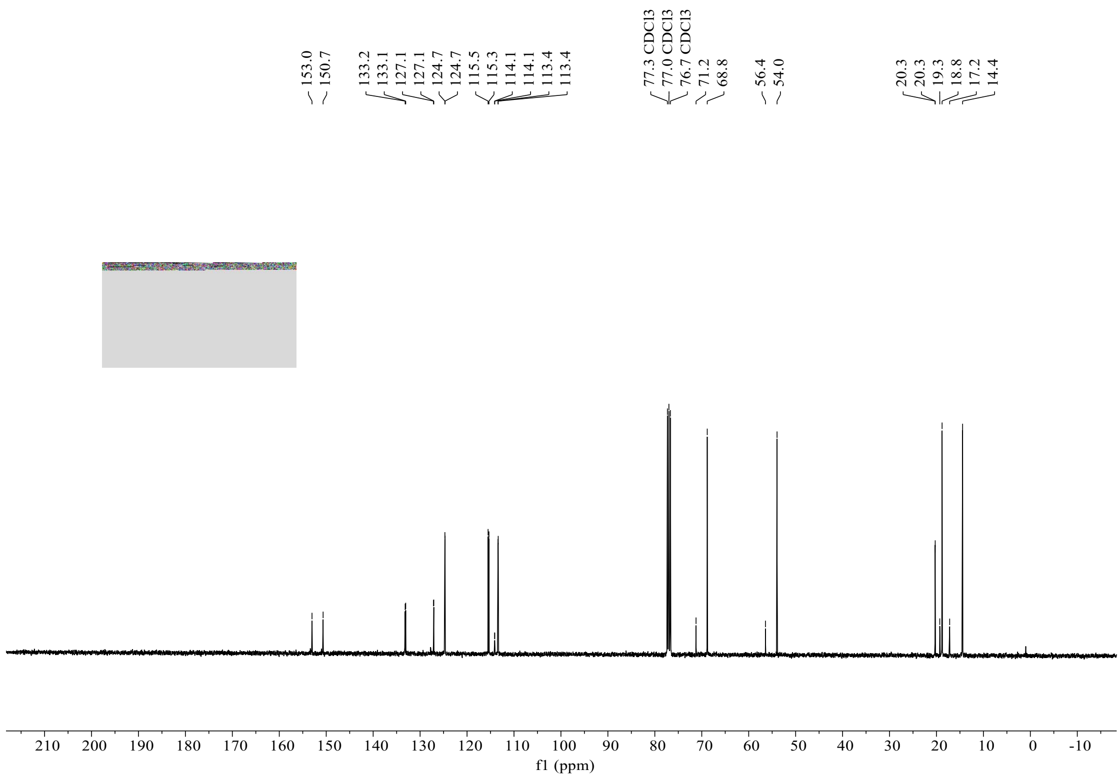
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ha**



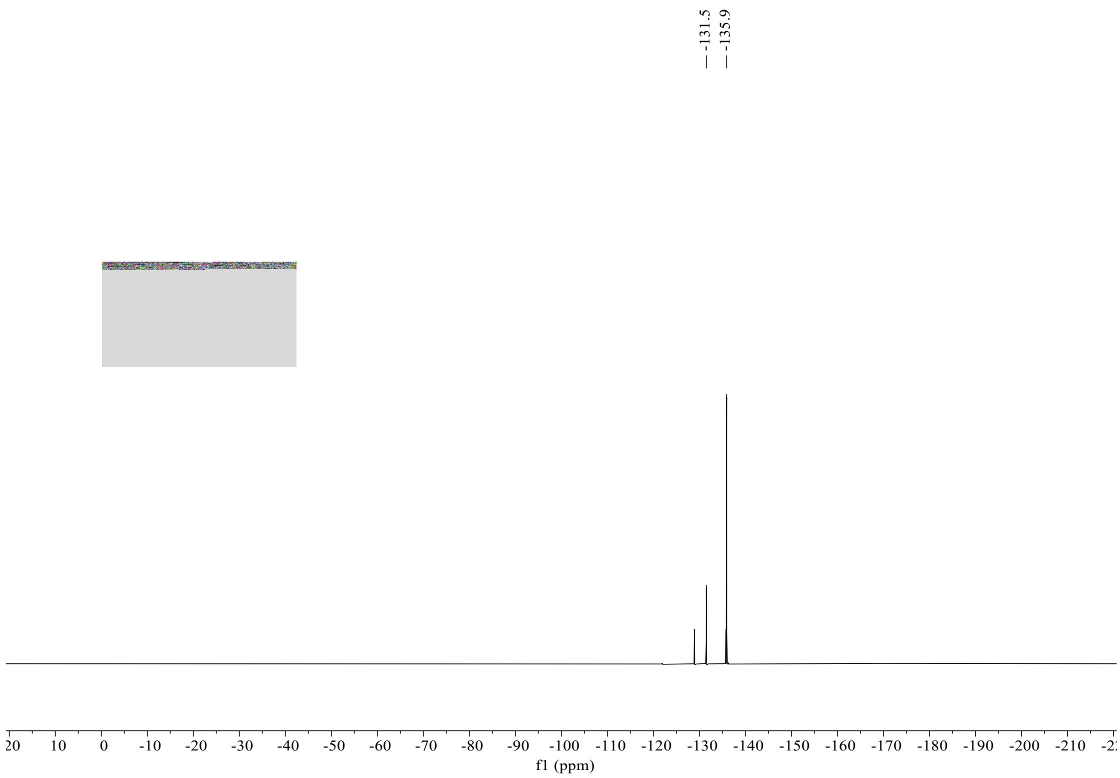
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ha**



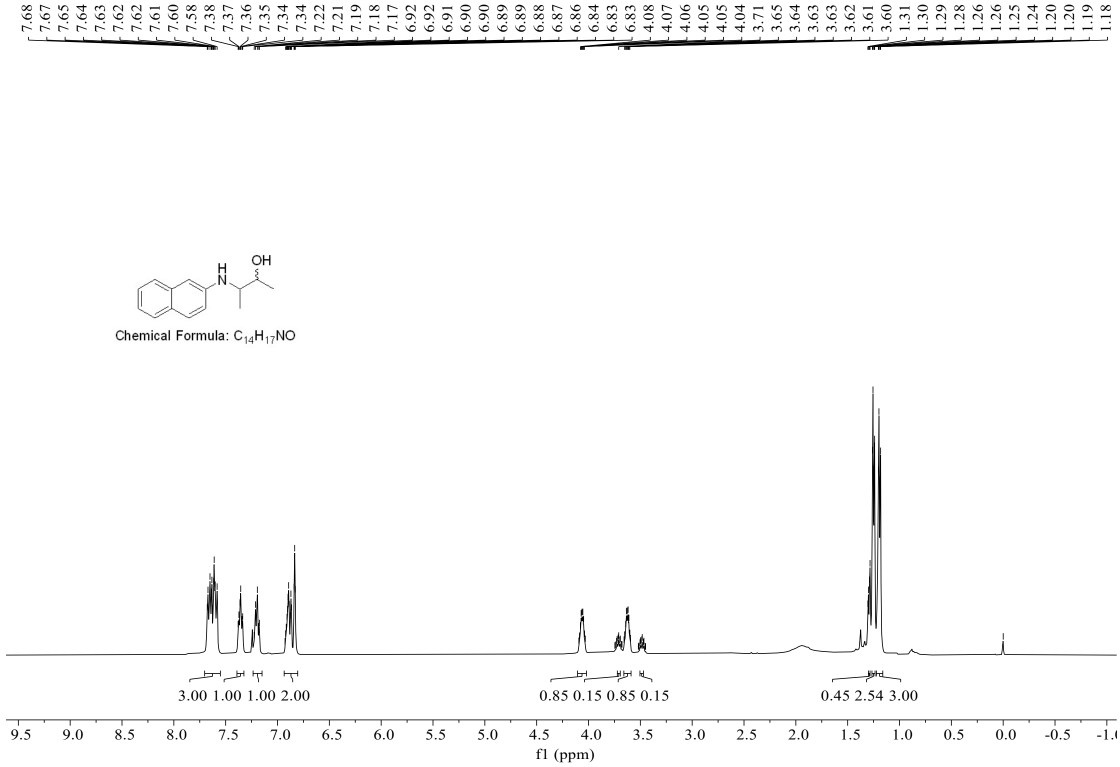
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ia**



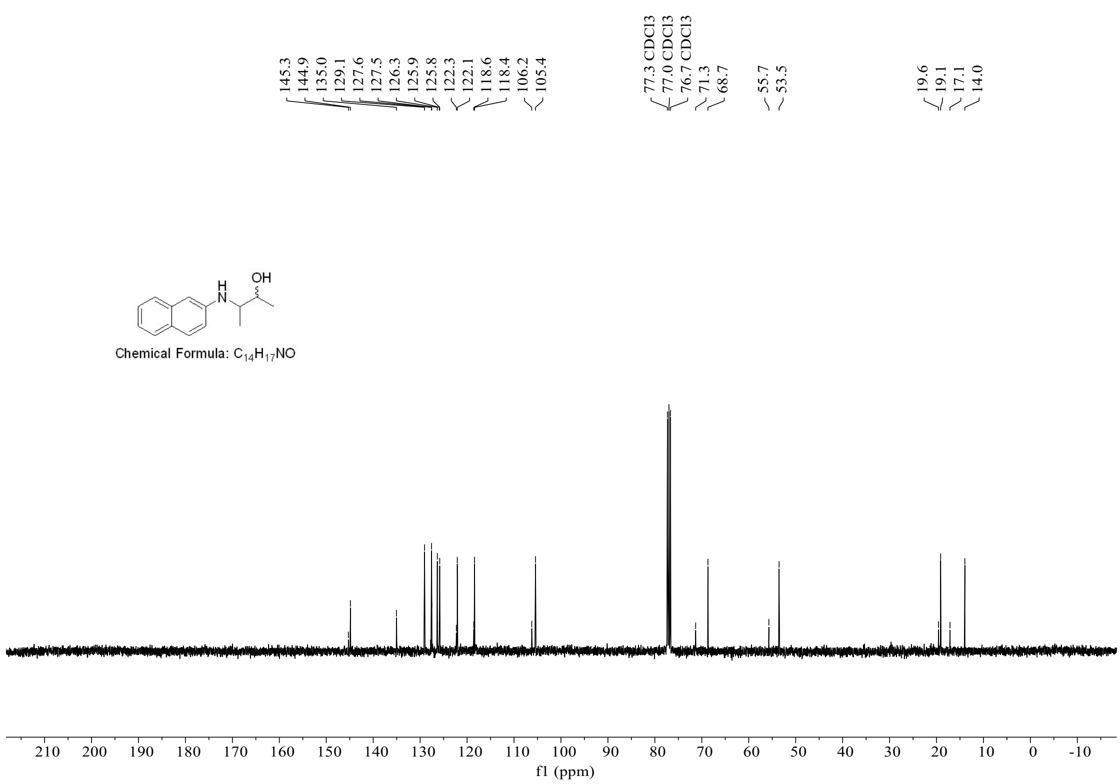
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ia**



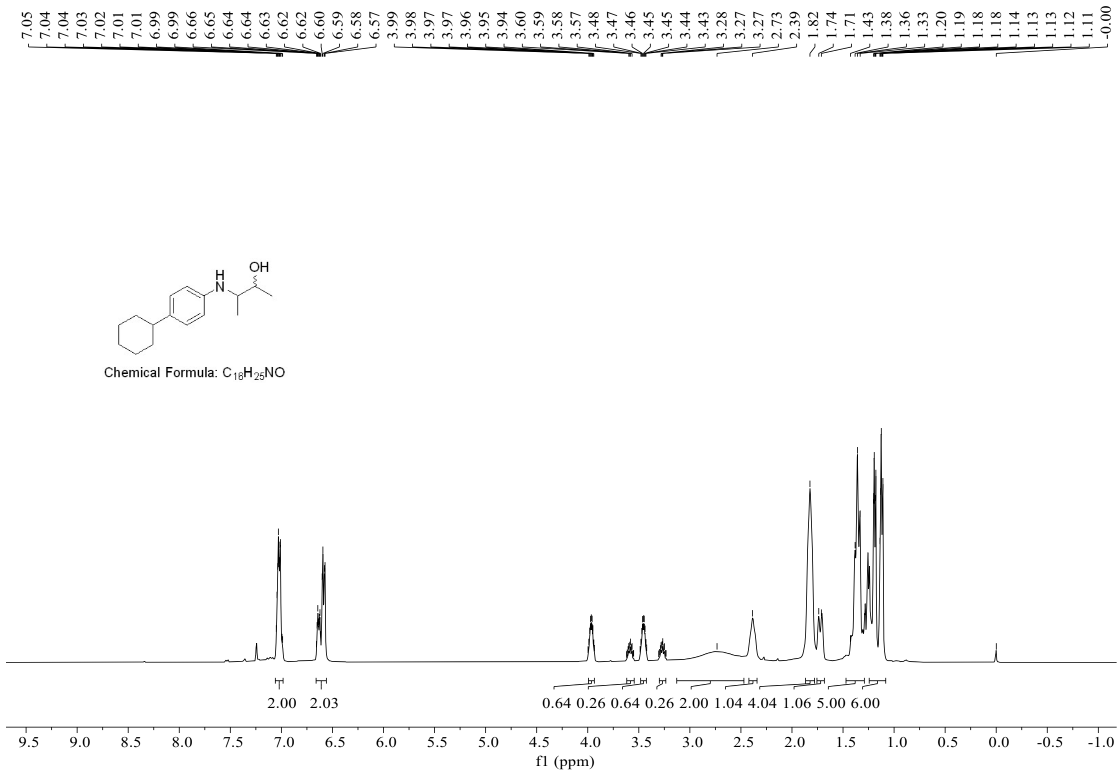
^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **3ia**



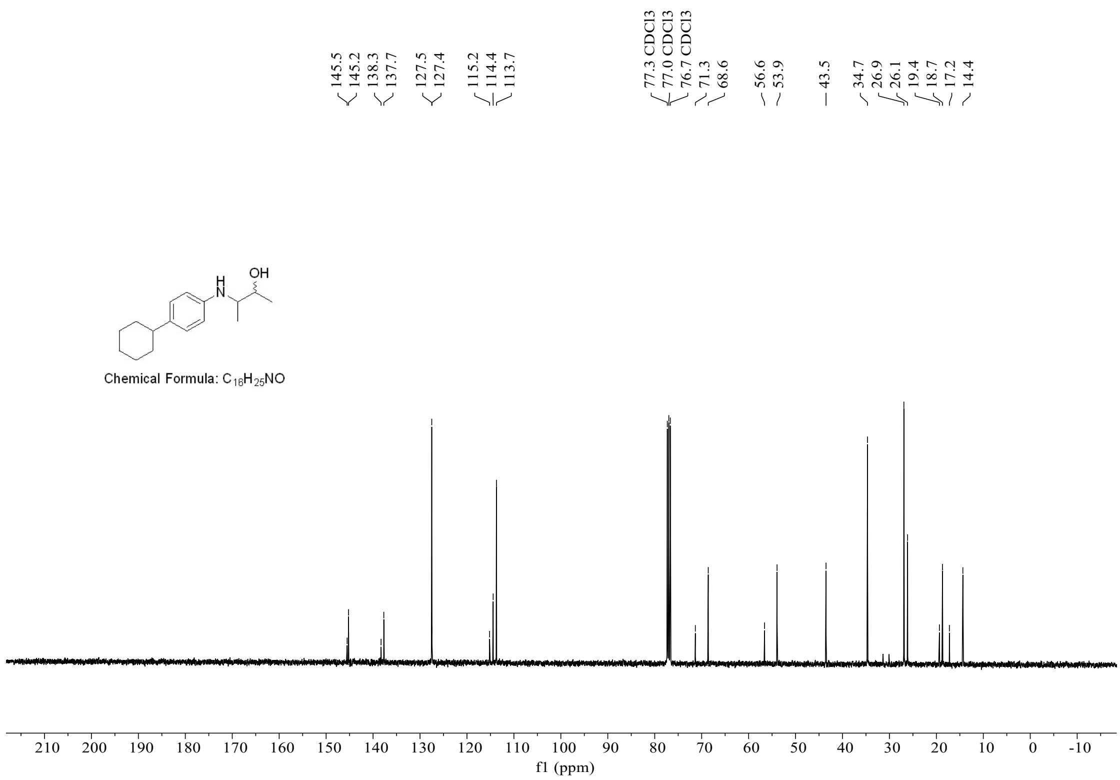
^1H NMR (400 MHz, $CDCl_3$) spectrum of **3ja**



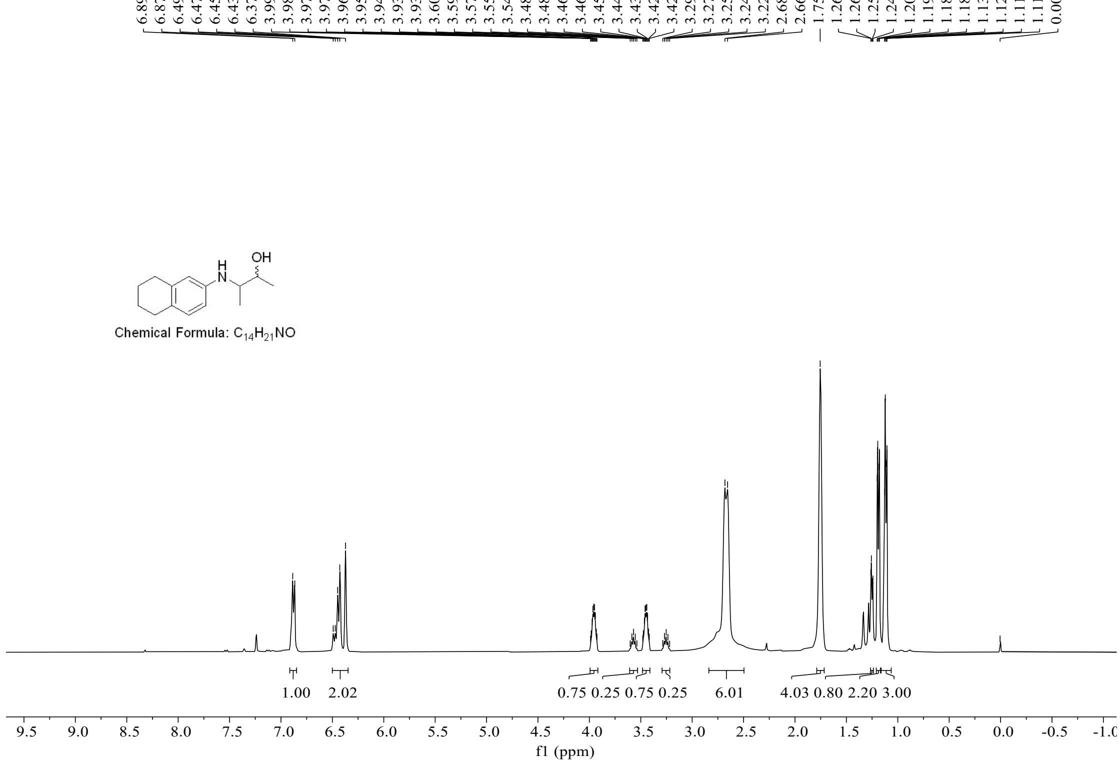
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ja**



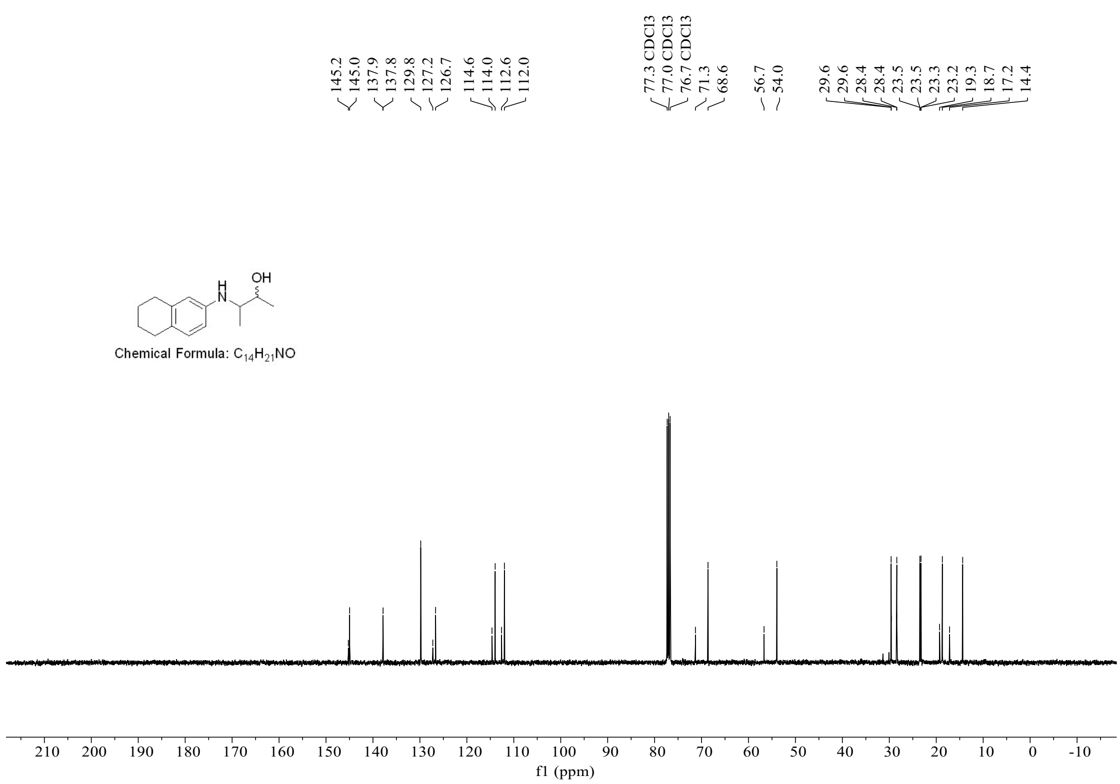
^1H NMR (400 MHz, $CDCl_3$) spectrum of **3ka**



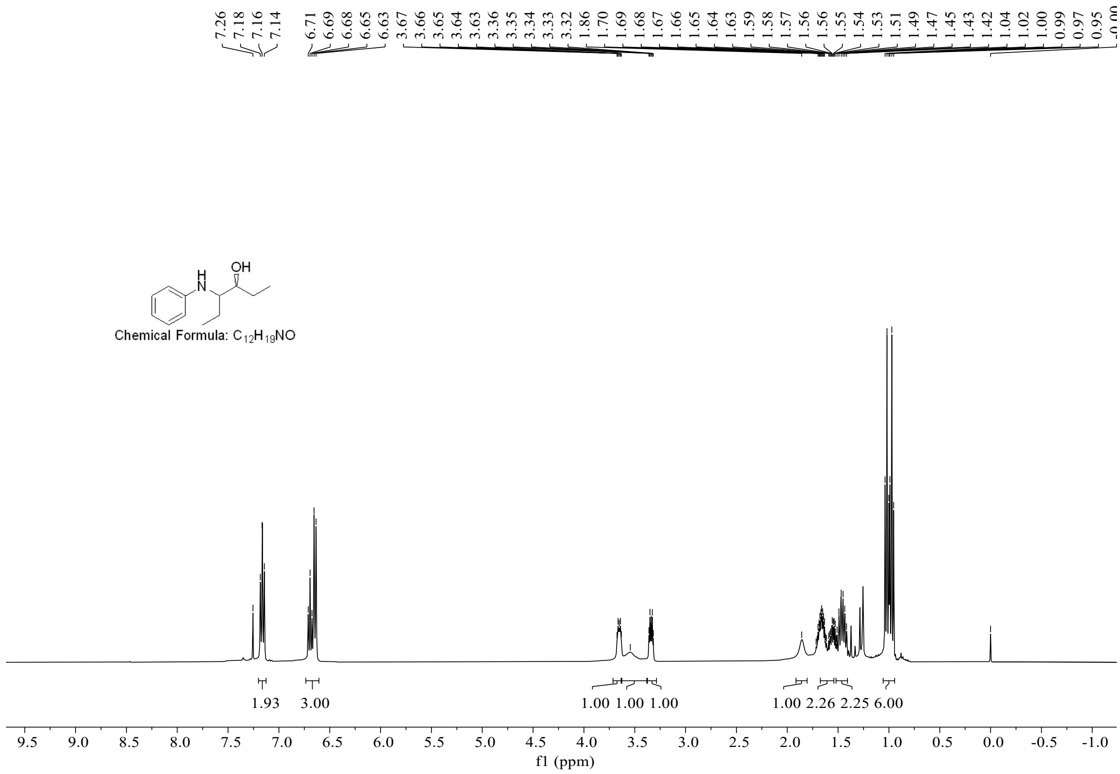
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ka**



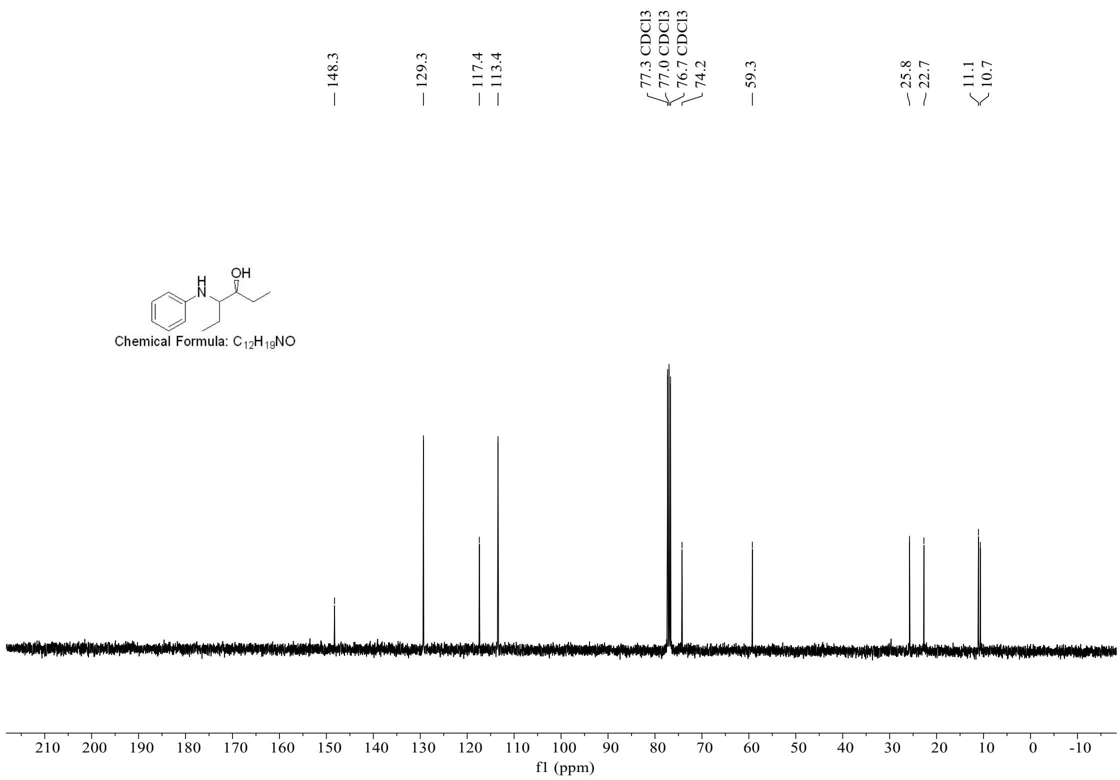
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3la**



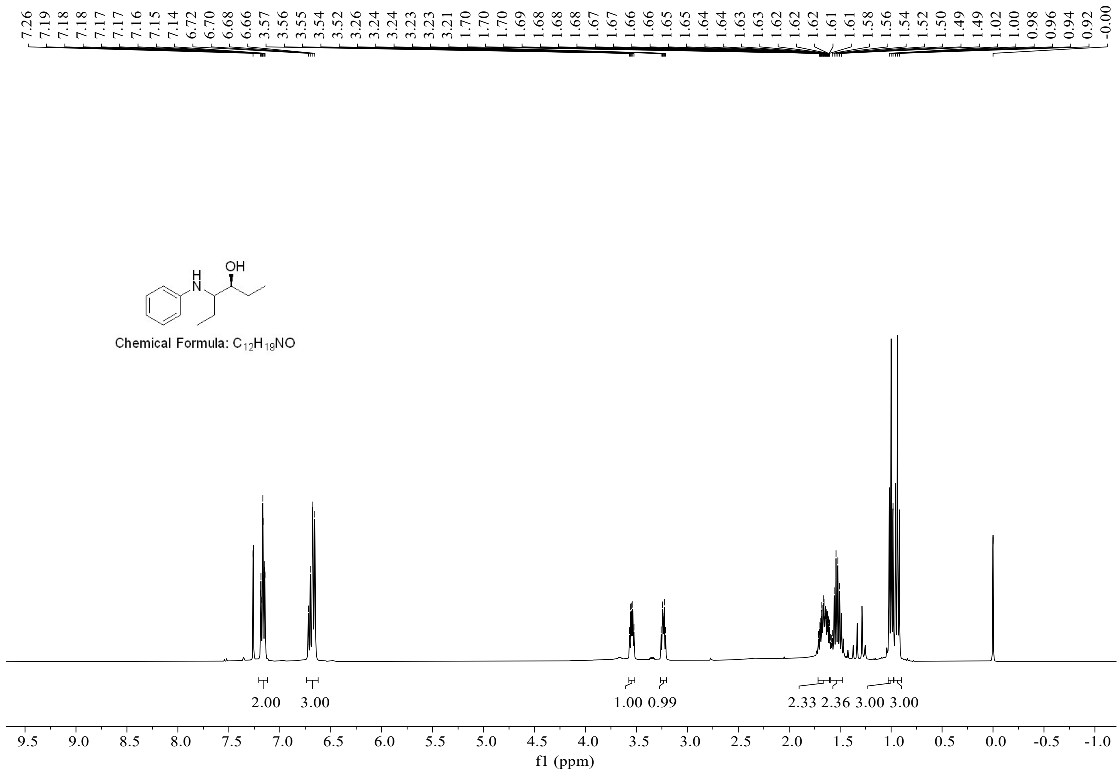
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3la**



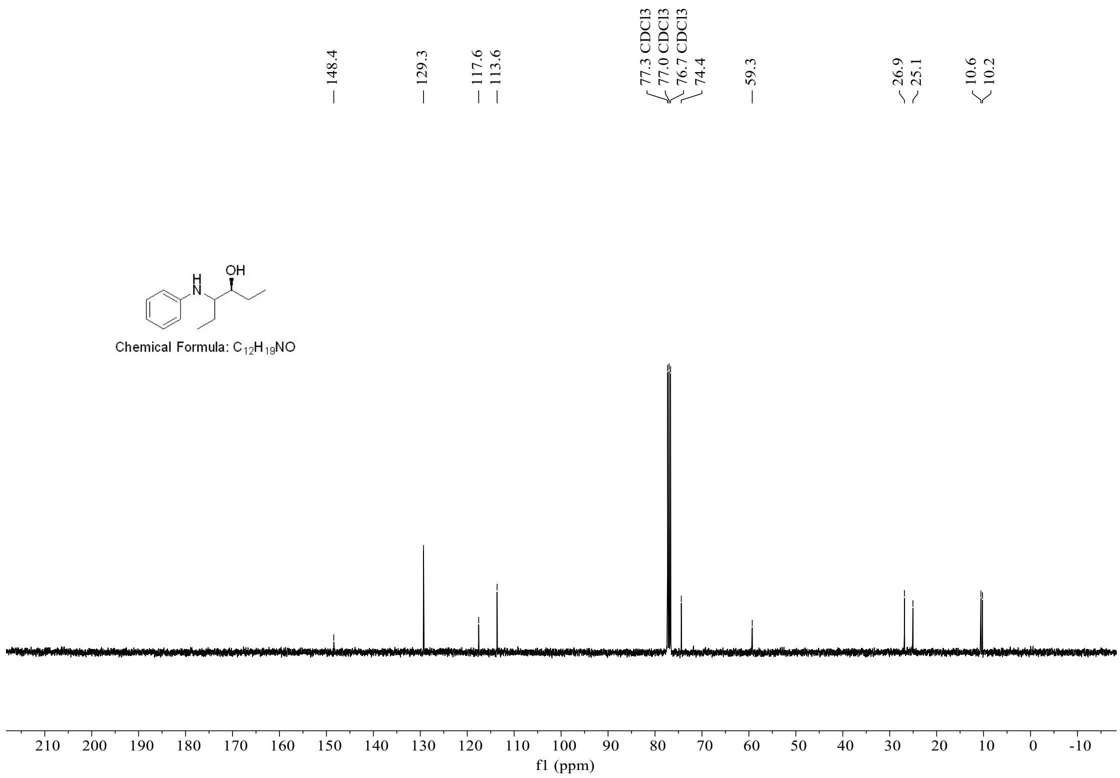
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ab** (*anti*)



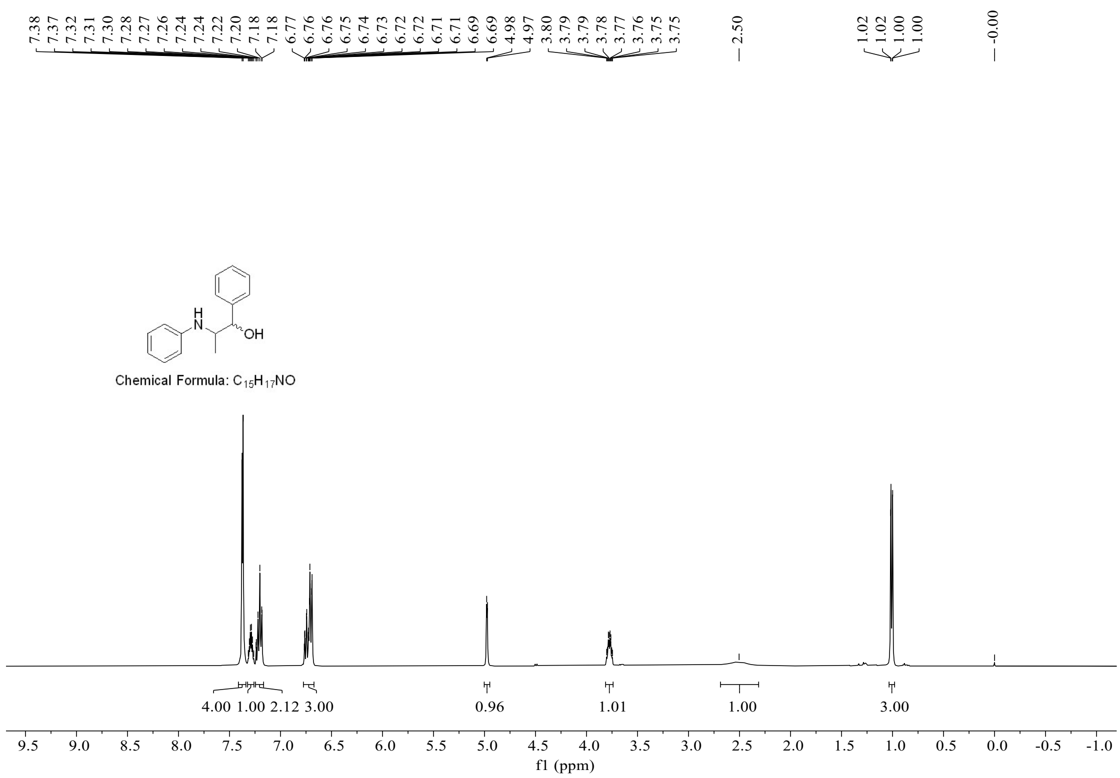
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ab** (*anti*)



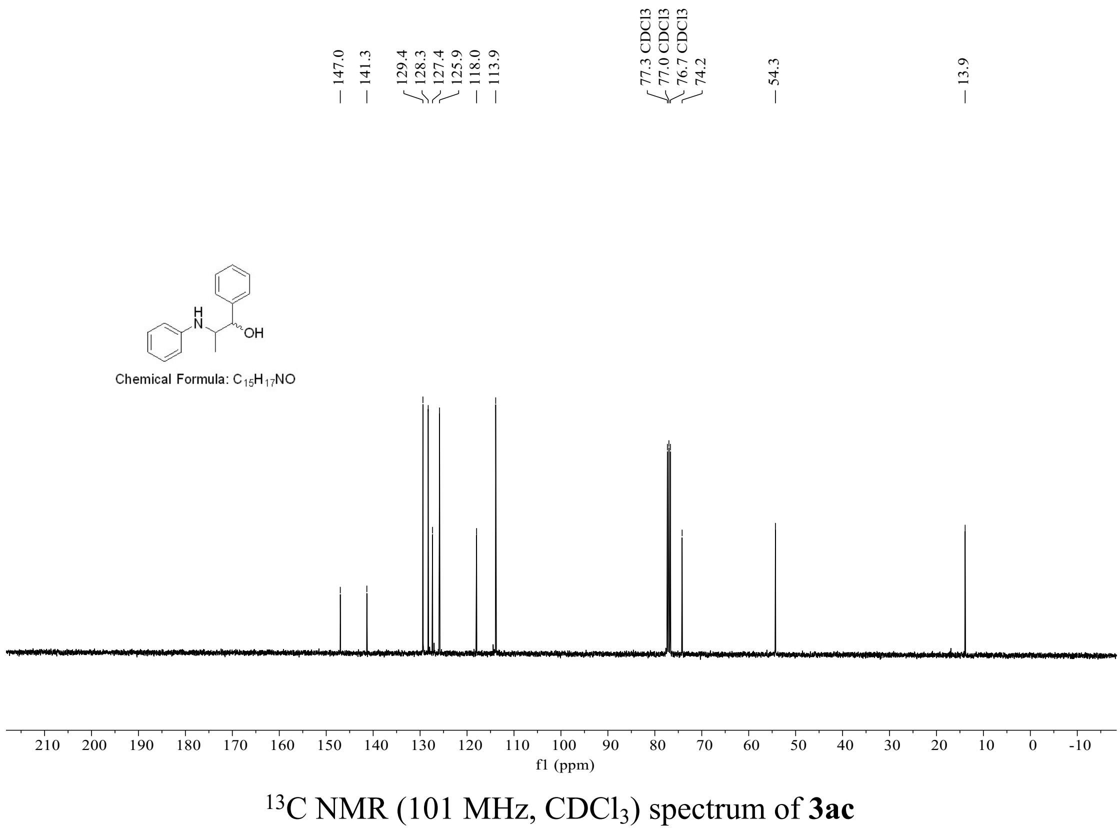
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ab** (*syn*)



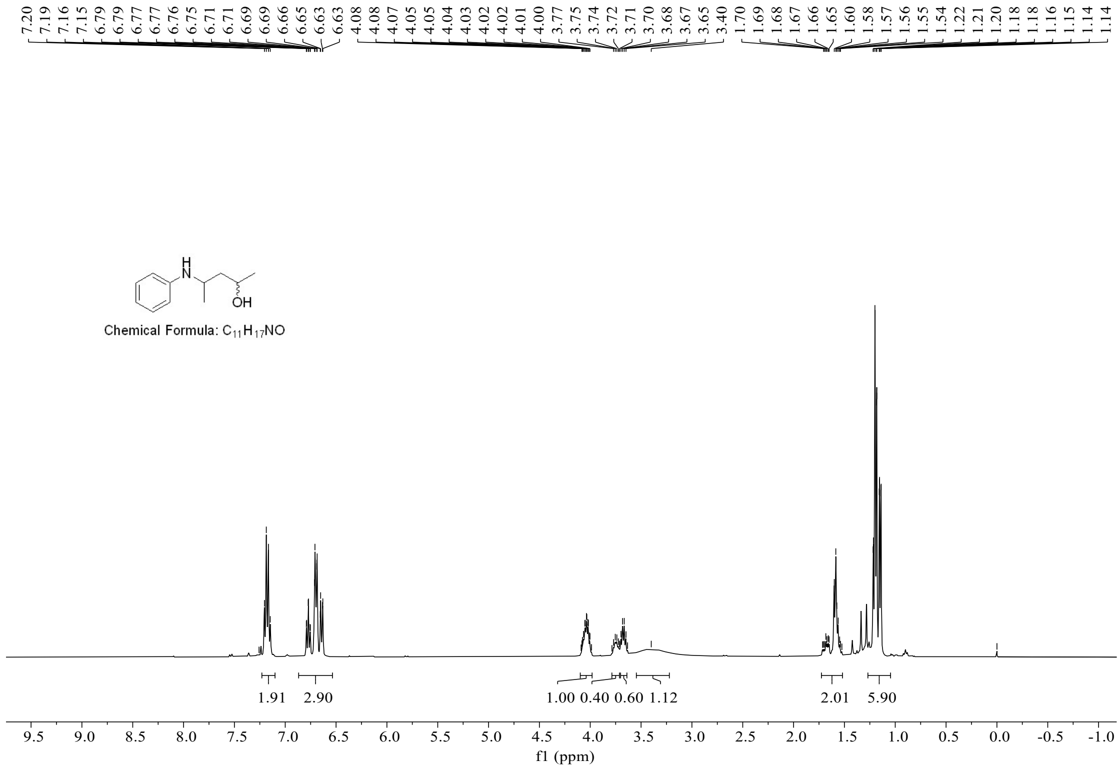
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ab** (*syn*)



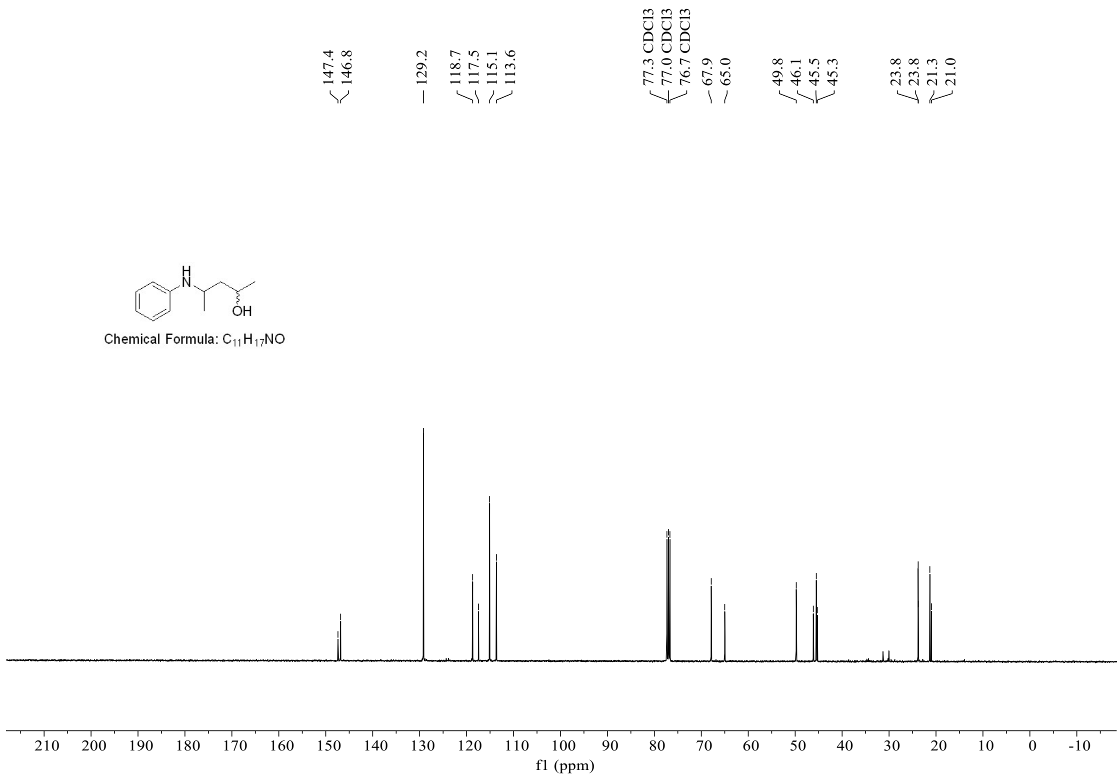
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ac**



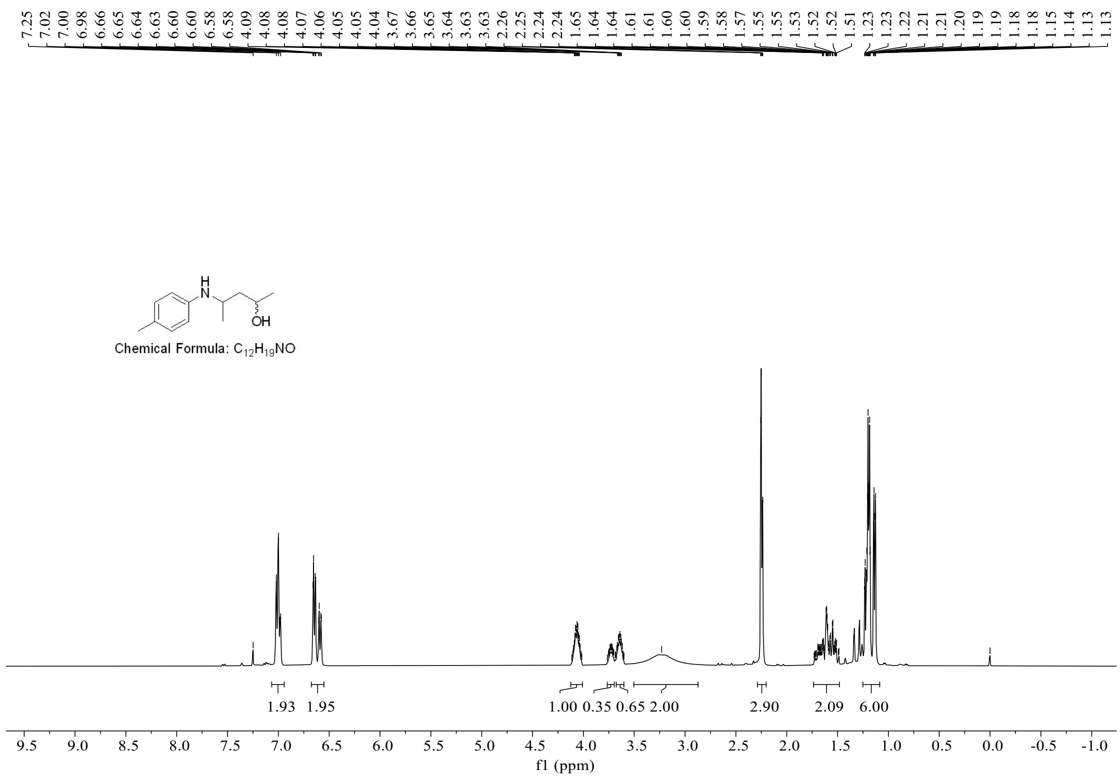
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ac**



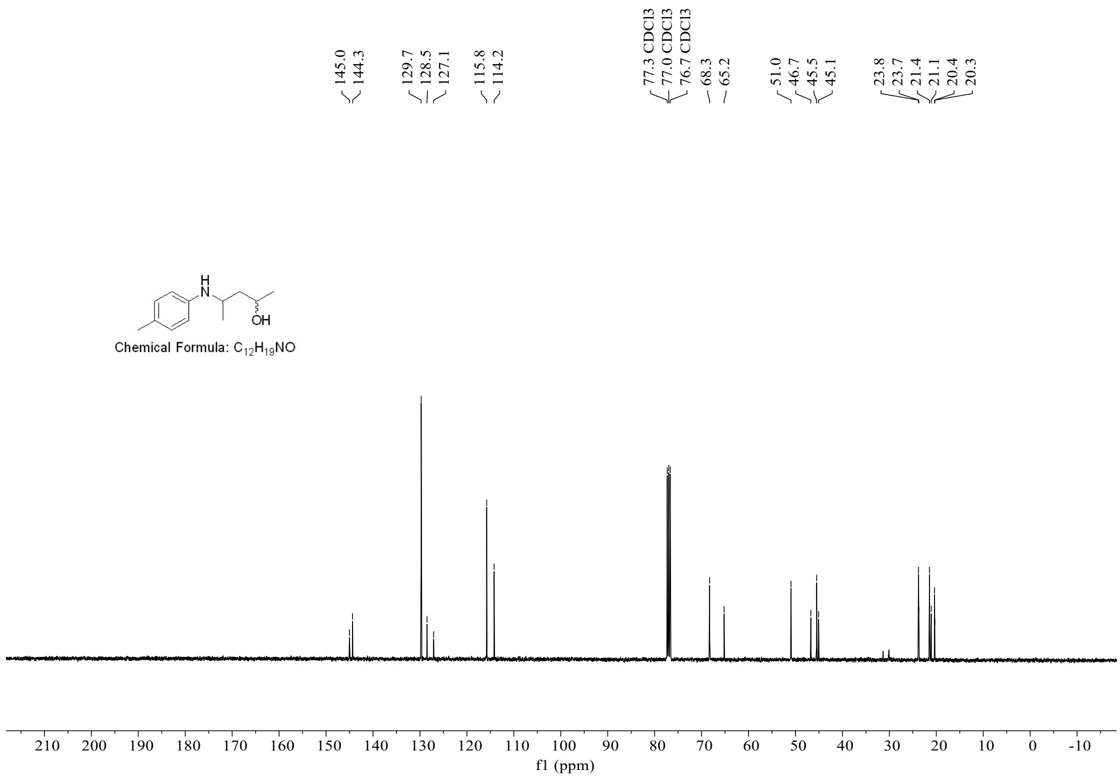
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5aa**



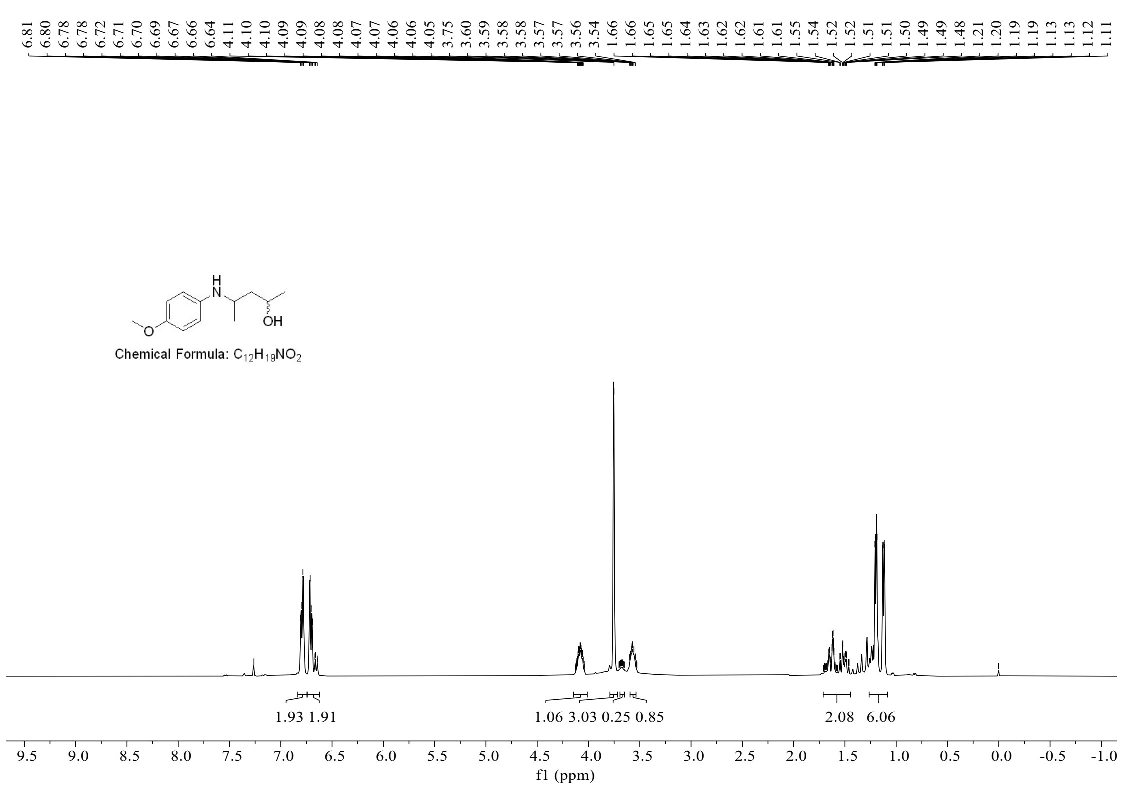
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5aa**



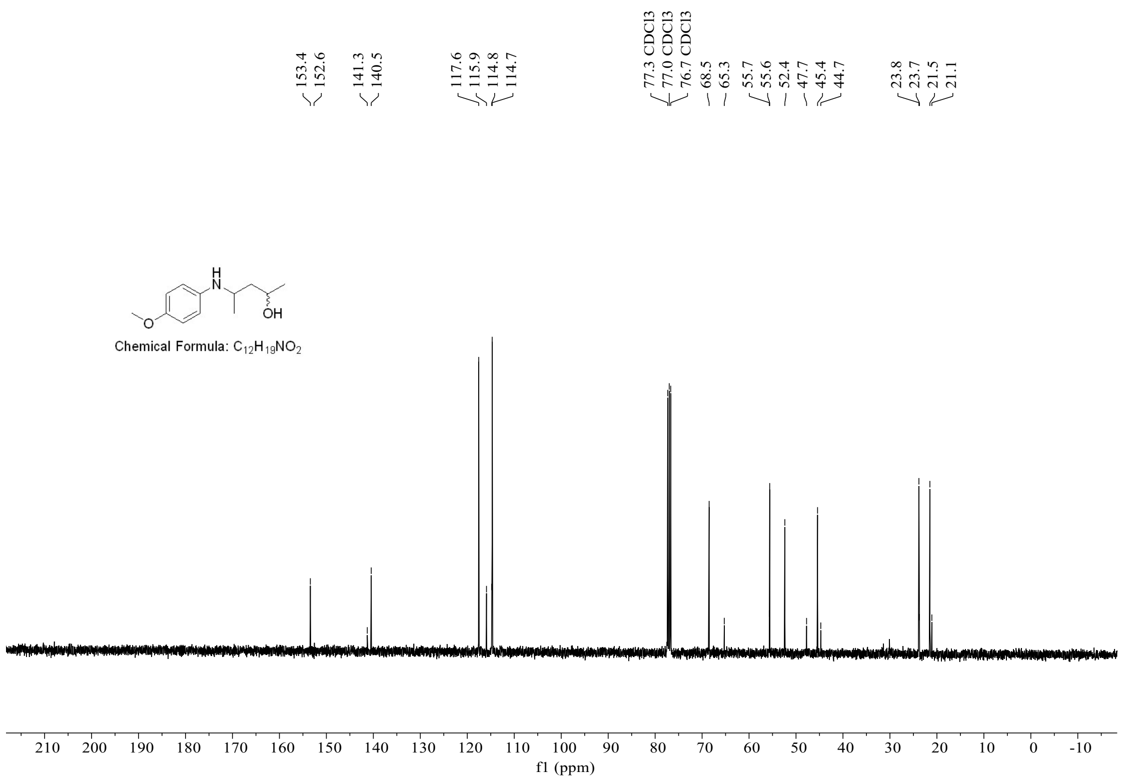
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5ba**



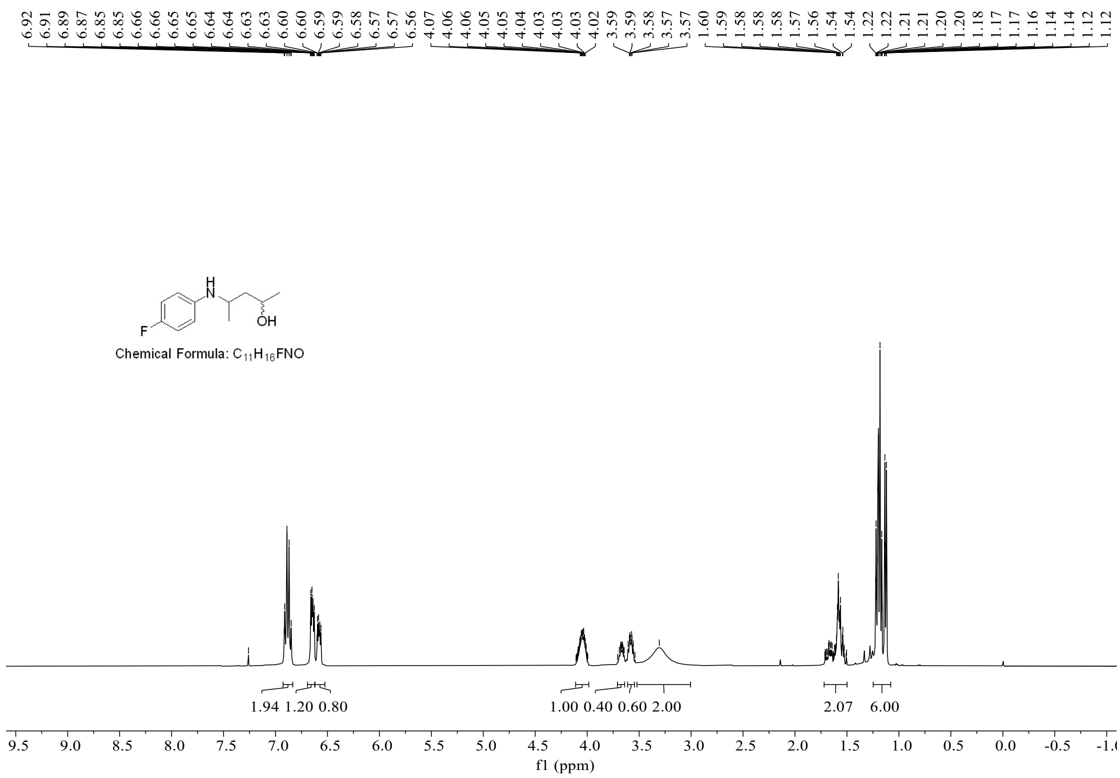
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5ba**



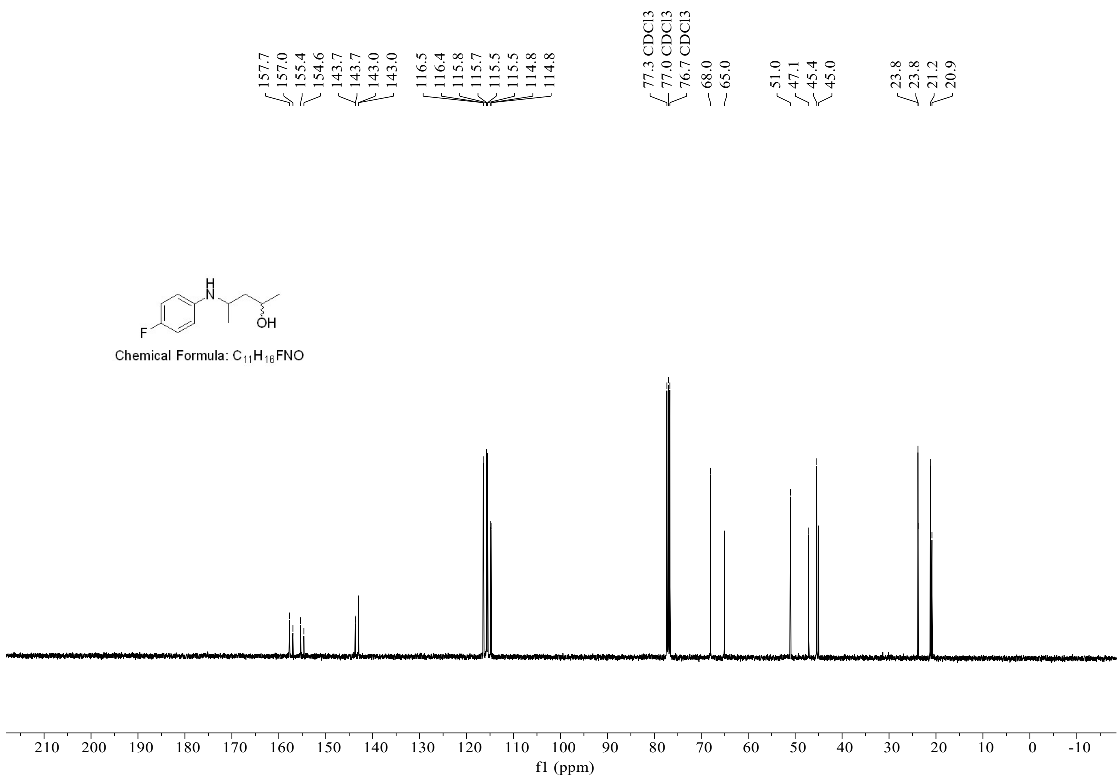
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5ca**



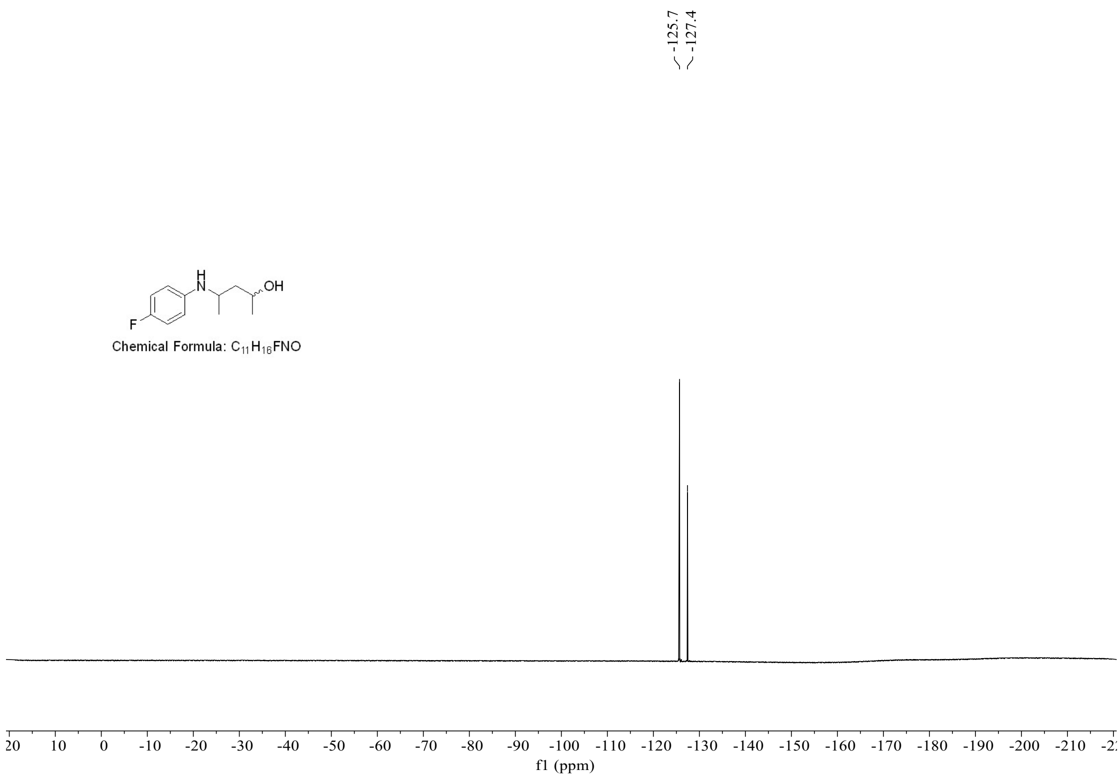
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5ca**



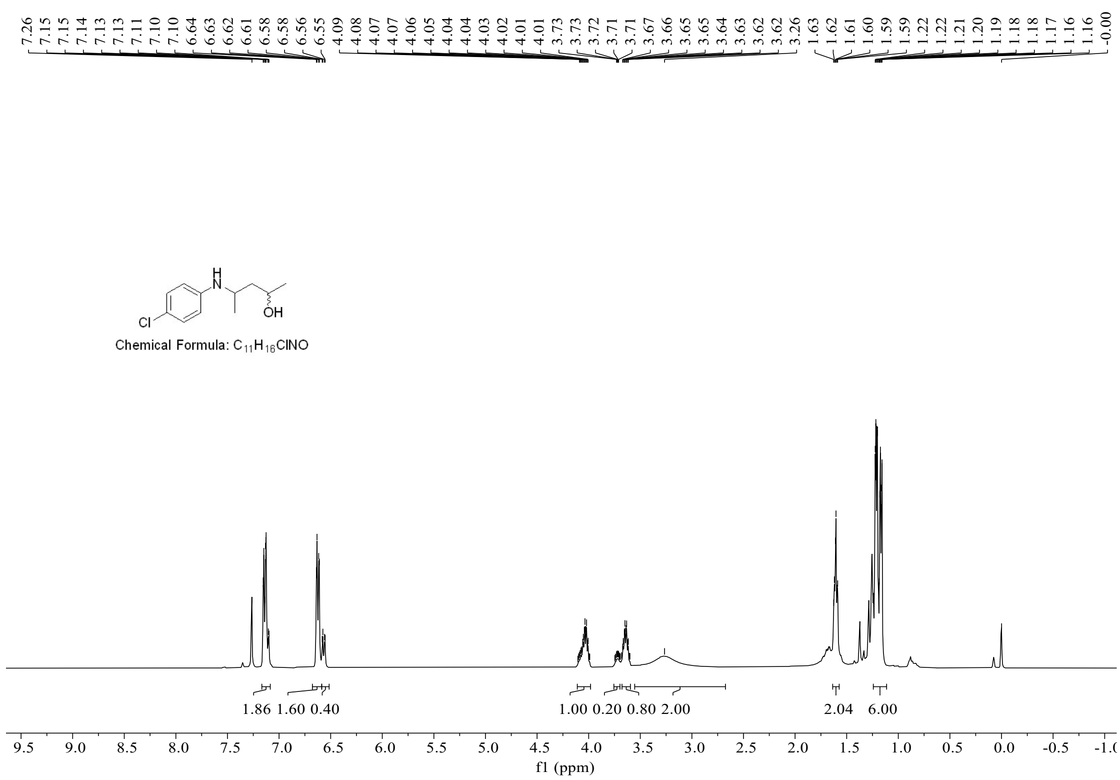
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5da**



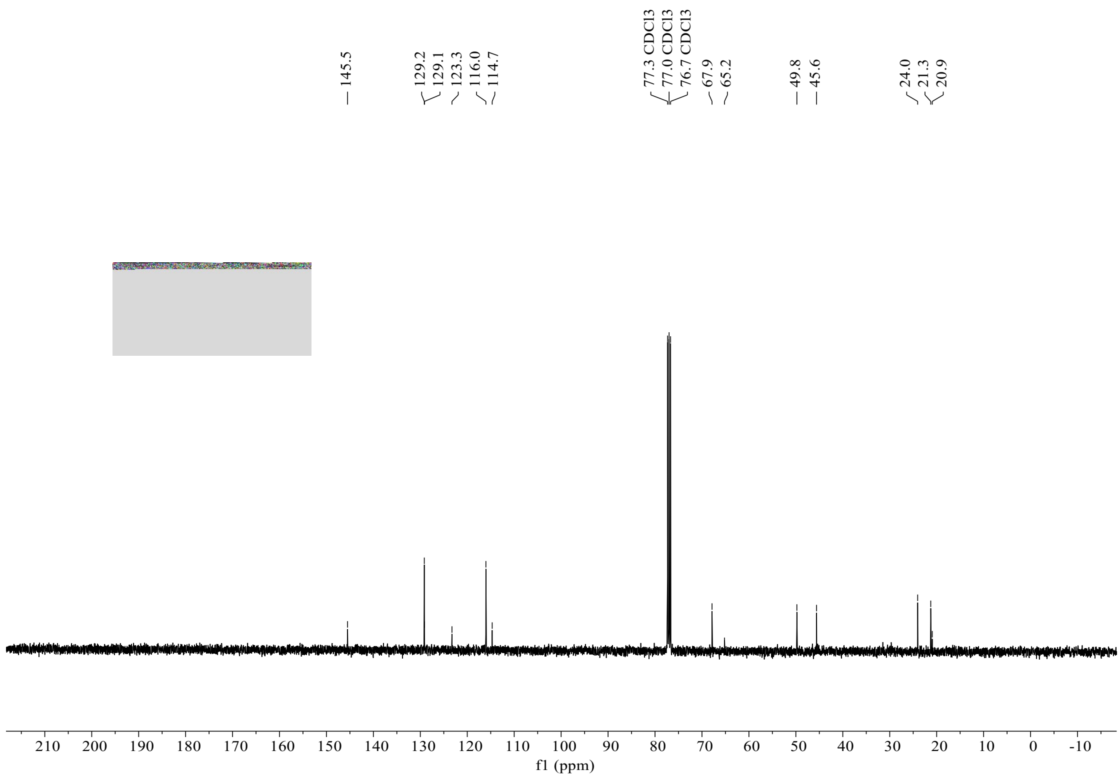
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5da**



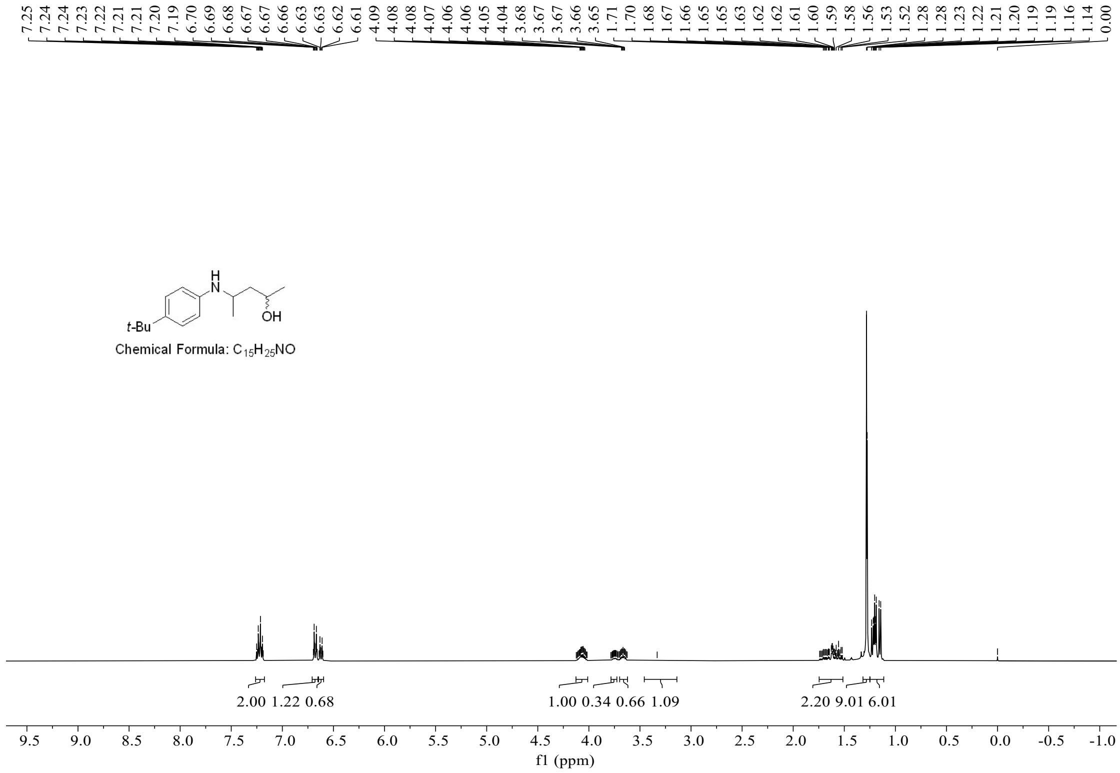
^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **5da**



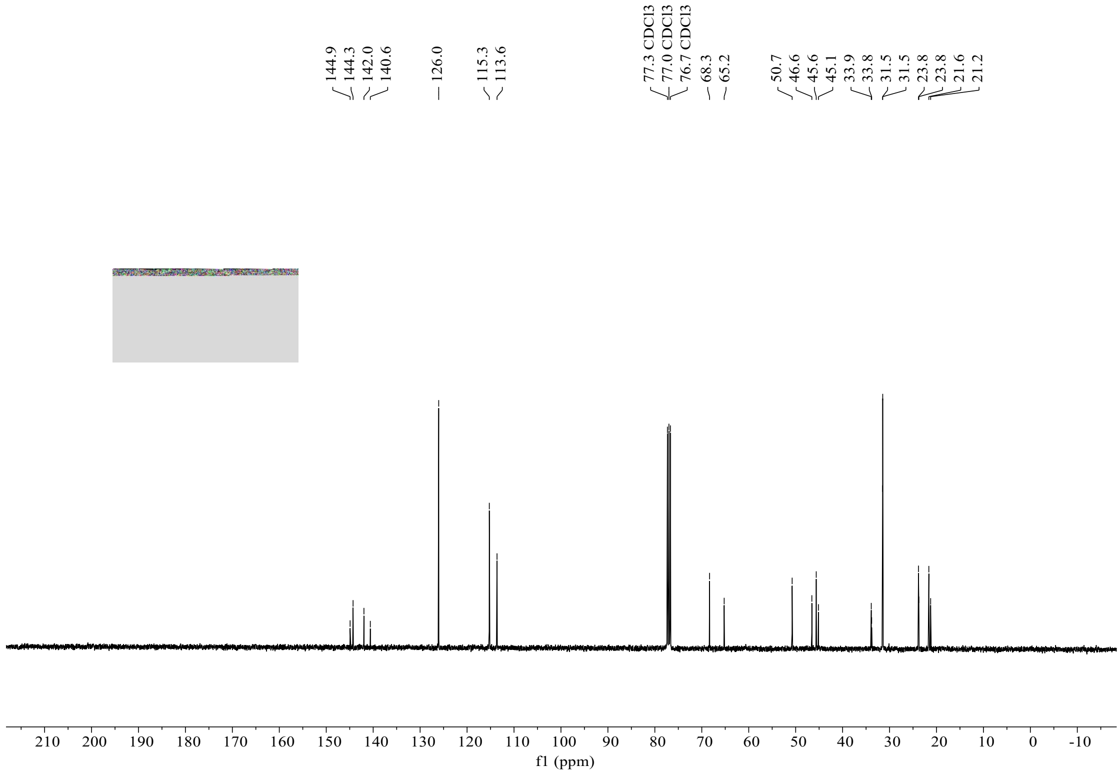
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5ea**



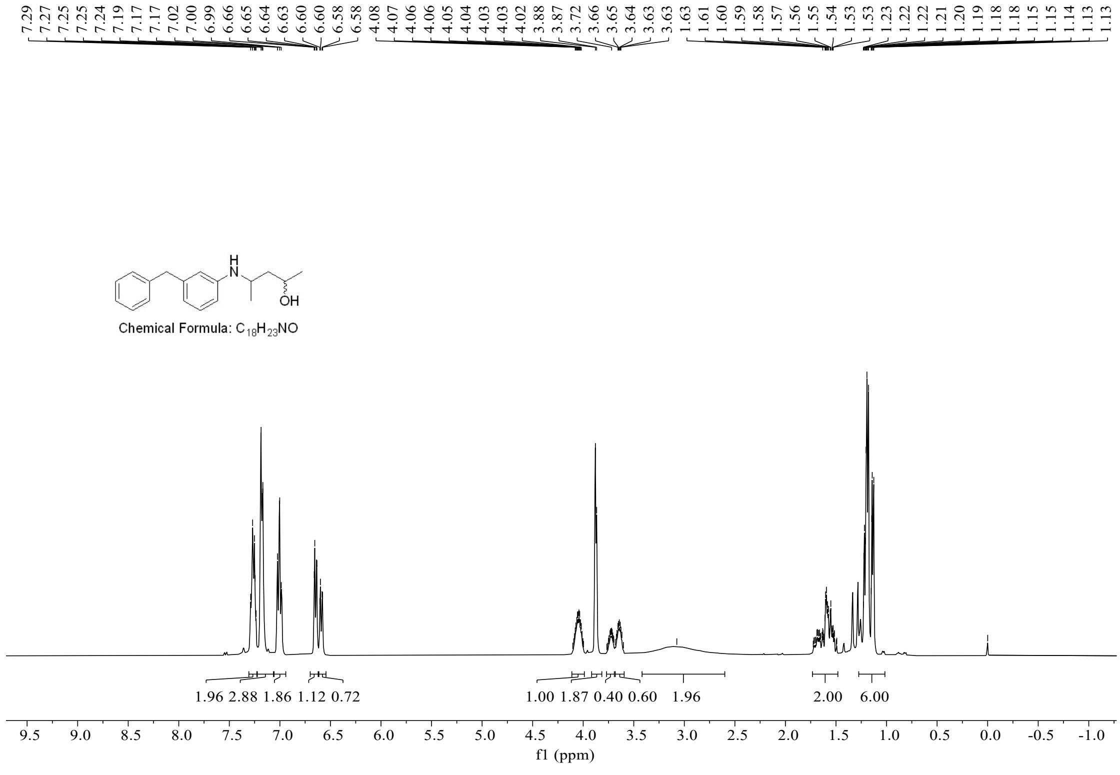
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5ea**



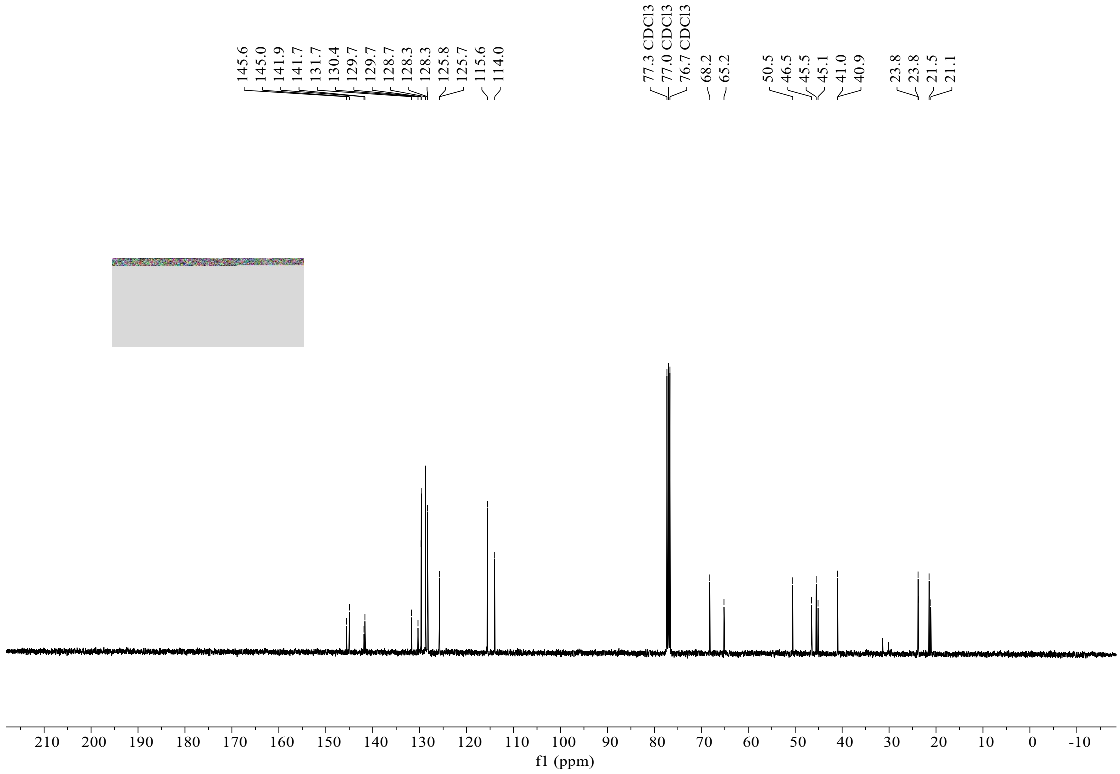
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5fa**



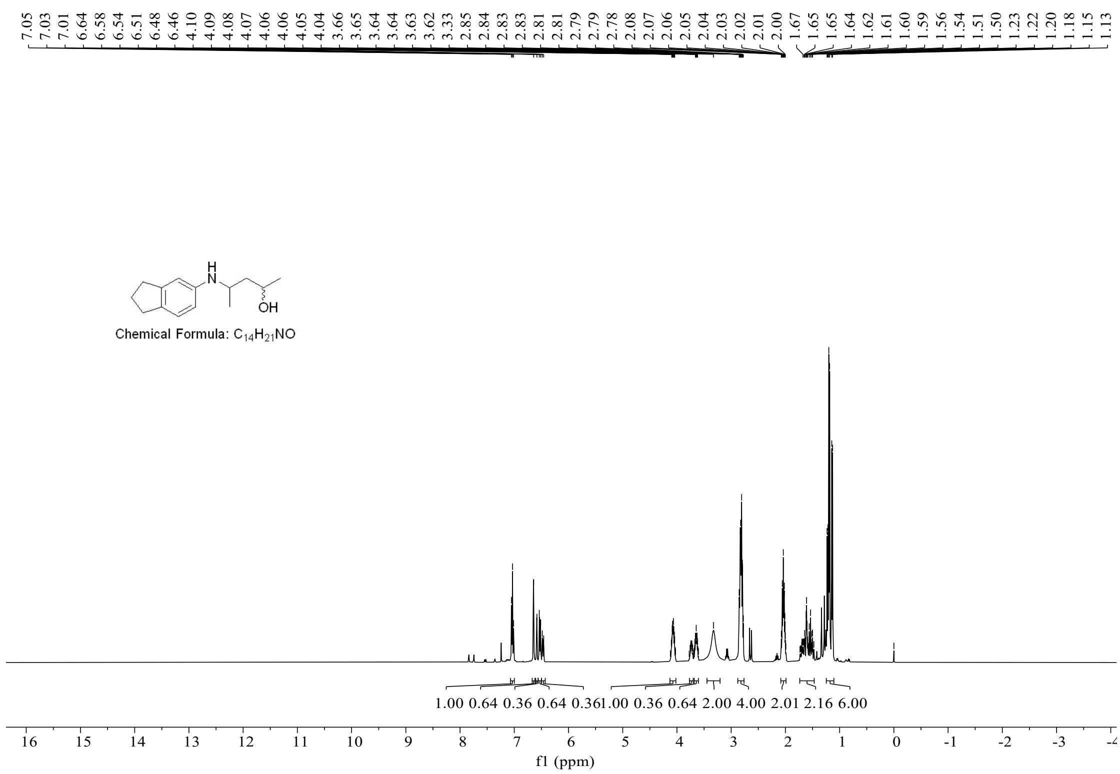
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5fa**



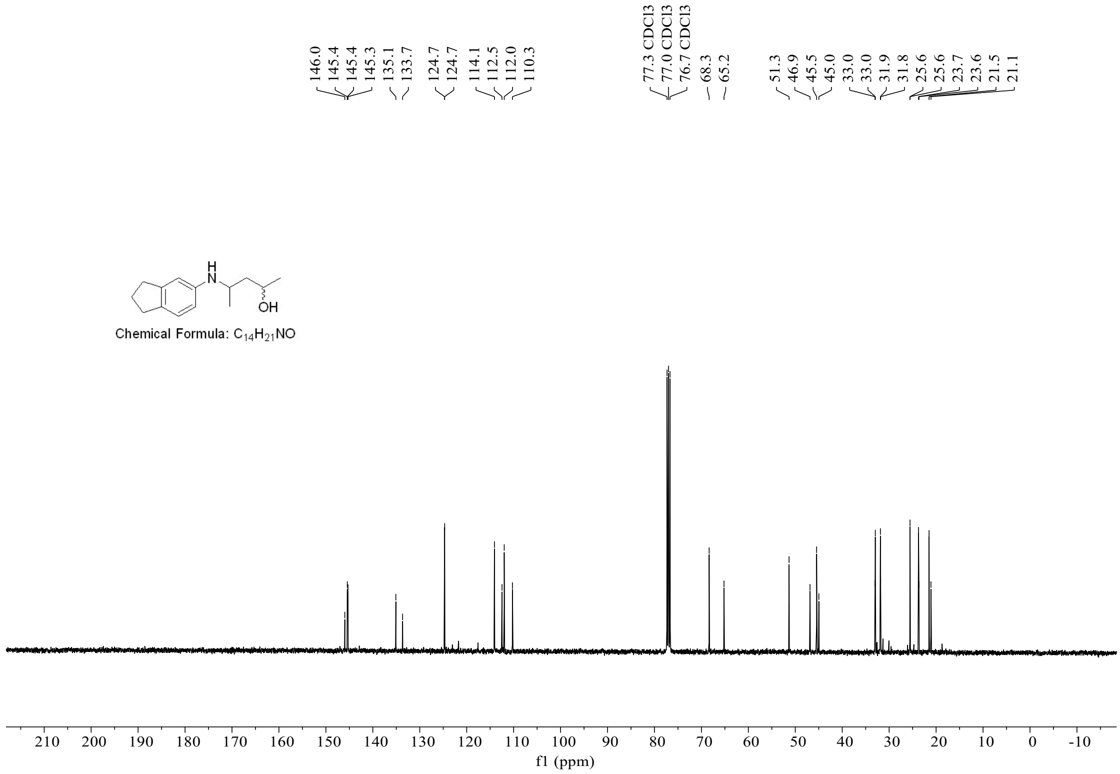
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5ma**



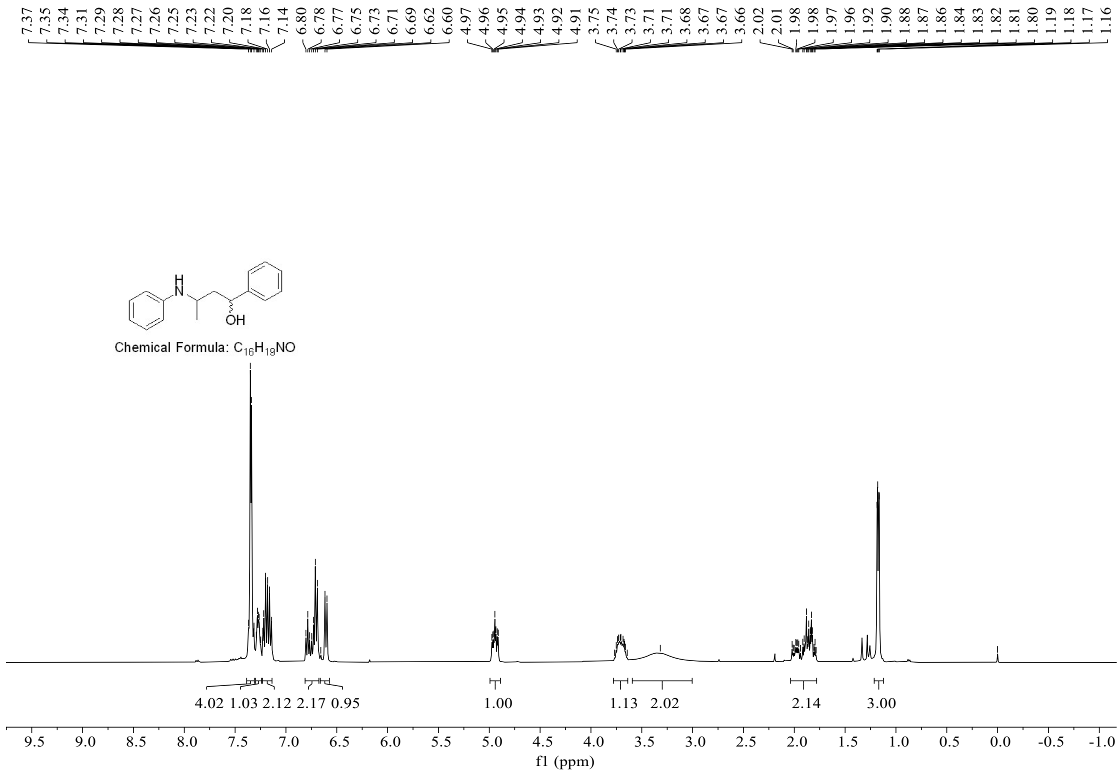
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5ma**



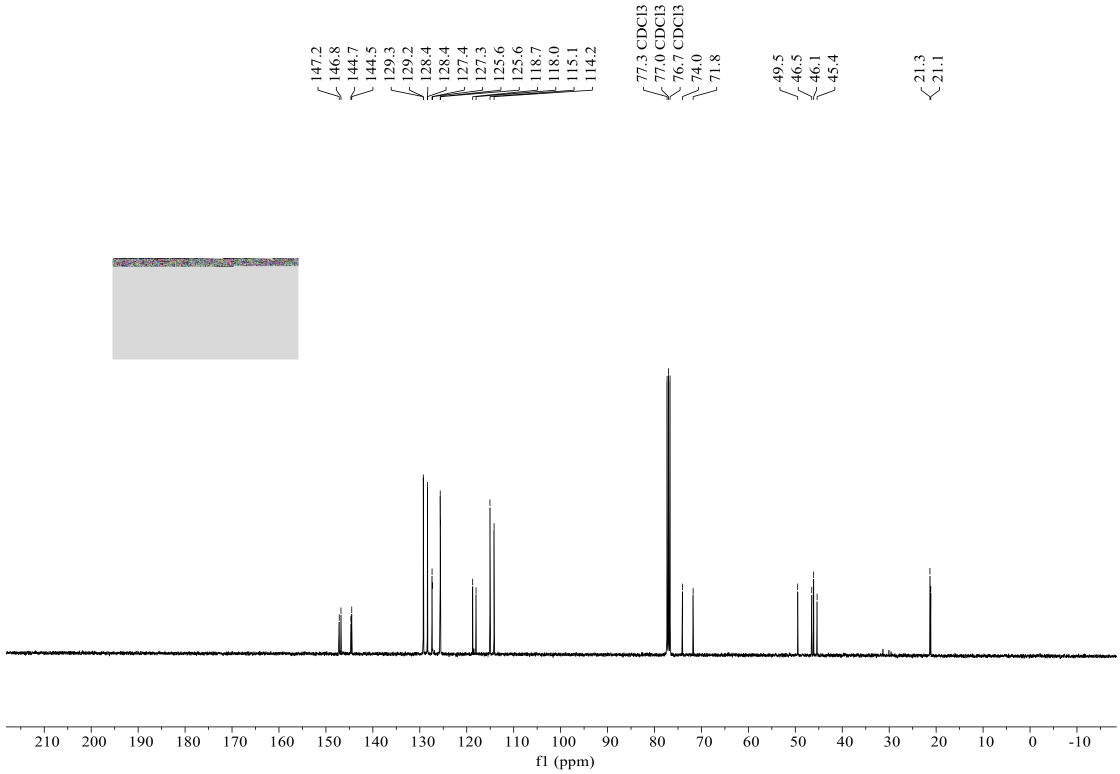
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5na**



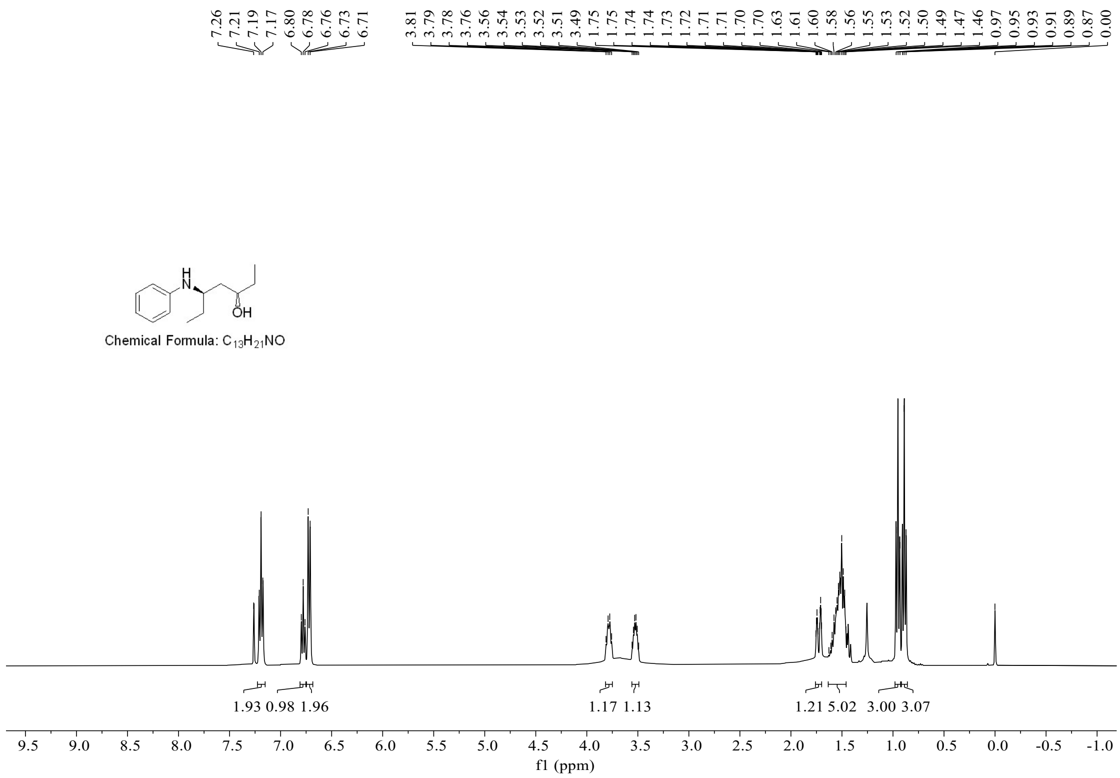
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5na**



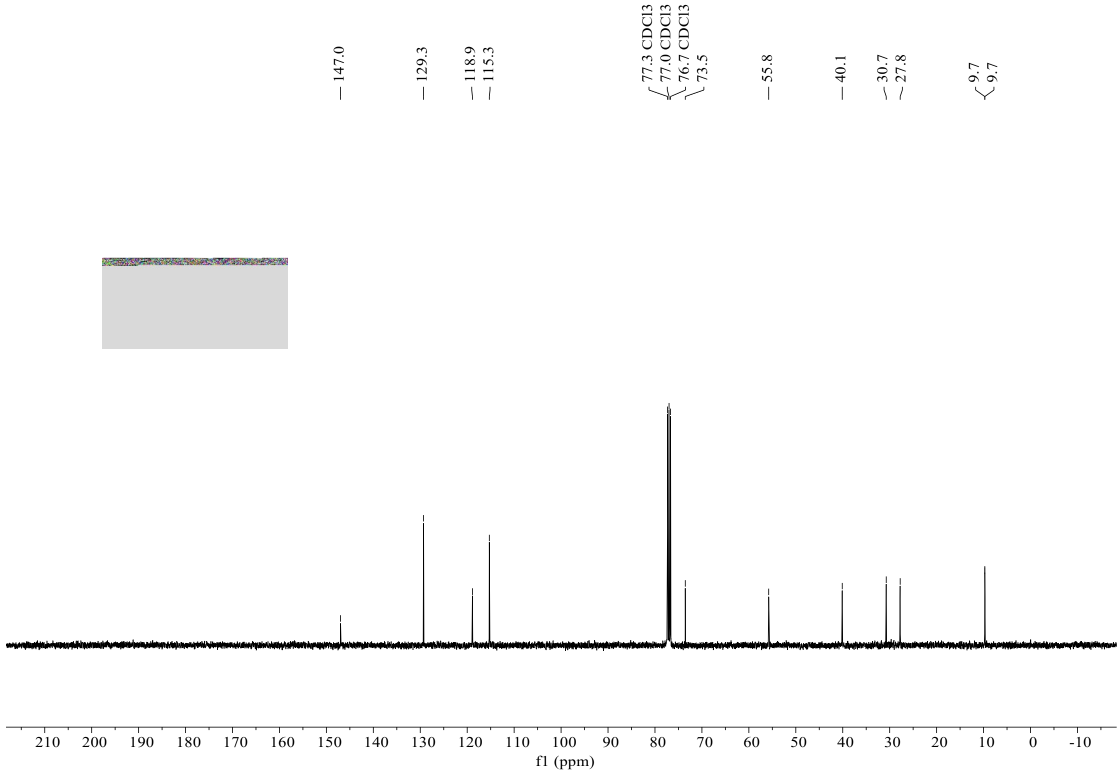
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5ab**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5ab**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5ac** (*anti*)



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5ac** (*anti*)