Supporting Information

Trading space for time under weakly activated catalysis: expeditious synthesis of *β*-NH_2 alcohols *via* a direct ammonolysis of epoxides with ammonia

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Table of Contents

1. General information

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were measured on a Bruker DRX 400 spectrometers at 400 MHz. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra was recorded on a Bruker DRX 400 spectrometers at 100 MHz. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV- 400 NMR spectrometers. The chemical shifts are given in ppm relative to tetramethylsilane [^{1}H: δ = ($SiMe_4$) = 0.00 ppm] as an internal standard or relative to the resonance of the solvent [^{1}H: δ = ($CDCl_3$) = 7.26, ^{13}C: δ = ($CDCl_3$) = 77.16 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as J values in Hz. High-resolution mass spectra (HRMS) were acquired using Agilent 1100HPLC/TOF with electrospray ionization (ESI) source. Optical rotations were reported as follows: $[\alpha]_D^{rt}$ (c: g/100 mL, in MeOH). Flash column chromatography was performed on silica gel (200–300 mesh) and TLC (silica GF254) were produced by Merch Chemicals Co. Ltd. (Shanghai). Reagents used in reactions were obtained commercially from Acros, Aldrich, Adamas-beta®, and were used without purification, unless otherwise indicated. All moisture-sensitive reactions were conducted in oven-dried glassware under a positive pressure of dry argon. Reagents and starting materials were accordingly transferred *via* syringe or cannula. Reaction temperatures refer to the external oil bath temperature.

2. Experimental section

2.1 General procedure for the preparation of epoxides

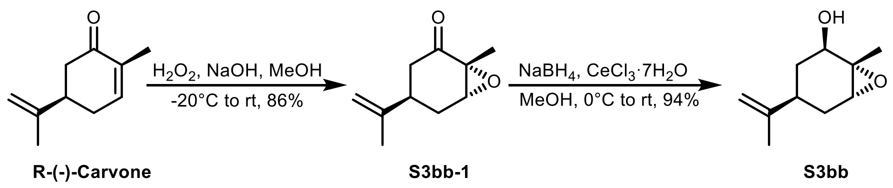
2.1.1 Epoxidation of alkenes using *m*-CPBA (Method A)

A dichloromethane (30 mL) solution of alkene (0.5 mmol) was cooled to 0 ºC，and to this solution was added *m*-CPBA (in CH_2Cl_2, 1.3 equiv) solution slowly through the addition funnel over 15 minutes at 0 ºC. The reaction mixture was allowed to warm to room temperature and stirred for an additional 2 h. After completion of the reaction (TLC monitoring), the reaction was quenched by addition of aq. 10% $Na_2S_2O_3$ (30 mL). And the resulting mixture was washed with aq. 5% $NaHCO_3$ (3 × 20 mL). And then aqueous phase was extracted with several portions of dichloromethane and the organic phases were combined and washed with brine, dried over unhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure to afford a crude solid, which was recrystallized from acetone and water (9 : 1) to afford with white crystals. All products were characterized on the basis of their spectroscopic data (NMR) and by comparison with those reported in the literature.[1-3]

2.1.2 Epoxidation of ketones by Corey-Chaykovsky reaction (Method B)

To an oven dried Schlenk flask was added trimethylsulfonium iodide (1.6 equiv) and dry DMSO/THF (30 mL, 2 : 1), and then NaH (60% dispersion in mineral oil, 1.5 equiv) was added to the above mixture at 0 °C under argon, the reaction was allowed to stir for 30 min at room temperature. Ketone (1.0 equiv) in THF was added to the reaction at 0 °C under argon. The reaction mixture is maintained at 0 °C for 1 h and allowed to stir at room temperature for overnight. Then the reaction was quenched with half-saturated brine (10 mL), the aqueous phase was extracted with THF. The combined organic extracts were washed with brine and dried over unhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure to afford the crude product, which was further purified by silica gel column chromatography (ethyl acetate : petroleum ether : triethylamine = 70 : 1 : 1) to afford the corresponding epoxides as a oil or white solid. The known products were identical to the literature.[4-13]

2.1.3 Preparation of S3bb



Following the literature procedure,[14] to a solution of (R)-(-)-Carvone (2.00 g, 13.3 mmol, 1.0 equiv) in methanol (30 mL) was added and 4M NaOH (1 mL, 4 mmol, 0.3 equiv) at −20 °C, followed by the dropwise addition of H_2O_2 (30 wt %, 17.47 mmol, 1.31 equiv) over 30 min. The solution was allowed to warm to 0 °C within 4 h. The reaction mixture was quenched by the addition of 1 mL 4M HCl and sat. aq $Na_2S_2O_3$.

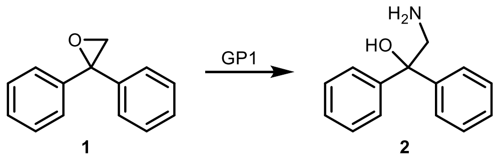
Et_2O and water were added and the phases were separated. The aqueous phase was extracted twice with Et_2O and the combined organic phases were dried with brine and $MgSO_4$. The solvent was removed under reduced pressure to afford **S3bb-1** as a colorless liquid (1.91 g, 86%). To a stirred solution of **S3bb-1** (500 mg, 3.01 mmol, 1.0 equiv) in methanol and dichloromethane (30 mL, methanol /dichloromethane = 2 : 1) was added $CeCl_3 \cdot 7H_2O$ (1.23 g, 3.31 mmol, 1.1 equiv), and followed by adding $NaBH_4$ (125.18 mg, 3.31 mmol, 1.1 equiv) in three portions carefully at 0 °C. After stirring for 45 min, the reaction was quenched by saturated NH_4Cl solution. The aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic phases were washed with brine, dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to afford the crude product, which was further purified by silica gel column chromatography (petroleum ether : ethyl acetate = 5 : 1) to afford the **S3bb** as a colorless oil (476 mg, 94%). The experimental data are in agreement with the literature reported[15].

2.2 General procedure for the preparation of *β*-NH_2 alcohols

2.2.1 Preparation of *β*-NH_2 alcohols from common epoxides (GP1)

A mixture of epoxide substrate (1.0 mmol), $NH_3 \cdot H_2O$ (25% in water, 2.26 mL, 15.0 mmol, 15.0 equiv), $HCOONH_4$ (126 mg, 2.0 mmol, 2.0 equiv) in methanol (4 mL) was put in a vial. The seal vial was then heated at 50 °C for 0.5 h and then cooled to room temperature. K_2CO_3 solid was added to the reaction mixture sequentially and the resulting mixture was loaded onto a deactivated silica gel column and separated by flash chromatography to afford the pure *β*-NH_2 alcohols.

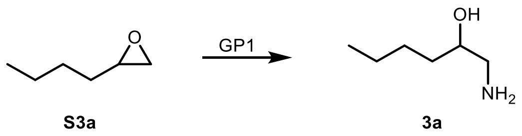
2-amino-1,1-diphenylethan-1-ol (2)



Prepared according to **GP1** from **1** (99 mg, 0.5 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **2** (99 mg, 92%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45

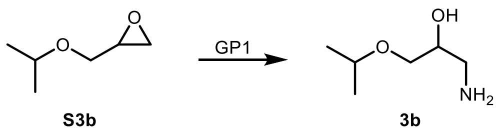
(dt, J = 8.4, 1.8 Hz, 4H), 7.35 – 7.29 (m, 4H), 7.25 – 7.20 (m, 2H), 3.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.54, 128.39, 127.08, 126.34, 51.13. HR-MS (EI) *m/z* calcd for $C_{14}H_{15}NO$ $[M+H]^+$: 214.1232; found: 214.1227.

1-aminohexan-2-ol (3a)



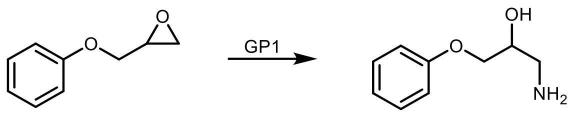
Prepared according to GP1 from **S3a** (101 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3a** (109 mg, 92%) as colorless dense oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 – 3.41 (m, 1H), 2.80 (d, J = 12.3 Hz, 1H), 2.50 (dd, J = 12.6, 8.4 Hz, 1H), 2.39 (d, J = 3.9 Hz, 3H), 1.52 – 1.18 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 72.04, 47.48, 34.64, 27.99, 22.89, 14.15. HR-MS (EI) *m/z* calcd for $C_6H_{15}NO$ $[M+H]^+$: 118.1232; found: 118.1226.

1-amino-3-isopropoxypropan-2-ol (3b)



Prepared according to GP1 from **S3b** (117 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3b** (126 mg, 94%) as colorless dense oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 – 3.64 (m, 1H), 3.56 (p, J = 6.1 Hz, 1H), 3.42 (dd, J = 9.5, 4.3 Hz, 1H), 3.34 (dd, J = 9.5, 6.6 Hz, 1H), 2.79 (dd, J = 12.9, 3.9 Hz, 1H), 2.68 (dd, J = 12.9, 7.3 Hz, 1H), 2.28 (s, 3H), 1.13 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 72.27, 71.37, 70.54, 44.61, 22.13. HR-MS (EI) *m/z* calcd for $C_6H_{15}NO_2$ $[M+H]^+$: 134.1181; found:134.1174.

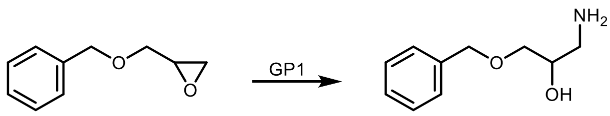
1-amino-3-phenoxypropan-2-ol (3c)



S3c 3c

Prepared according to GP1 from **S3c** (151 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3c** (159 mg, 95%) as colorless dense oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 6.89 (t, J = 7.3 Hz, 1H), 6.86 – 6.80 (m, 2H), 3.90 (d, J = 1.7 Hz, 3H), 2.94 – 2.86 (m, 1H), 2.84 – 2.72 (m, 1H), 2.16 (br, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.70, 129.64, 121.20, 114.62, 70.50, 70.09, 44.18. HR-MS (EI) m/z calcd for $C_9H_{13}NO_2$ [M+H] +: 168.1025; found:168.1020.

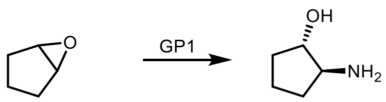
1-amino-3-(benzyloxy)propan-2-ol (3d)



S3d 3d

Prepared according to GP1 from **S3d** (165 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3d** (173 mg, 95%) as colorless dense oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (q, *J* = 9.1, 8.0 Hz, 5H), 4.46 (s, 2H), 3.76 – 3.67 (m, 1H), 3.39 (qd, *J* = 9.5, 5.0 Hz, 2H), 2.75 (dd, *J* = 12.8, 3.9 Hz, 1H), 2.65 (d, *J* = 16.3 Hz, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.07, 128.57, 127.91, 127.88, 73.56, 72.61, 70.78, 44.28. HR-MS (EI) *m/z* calcd for $C_{10}H_{15}NO_2$ $[M+H]^+$: 182.1181; found: 182.1181.

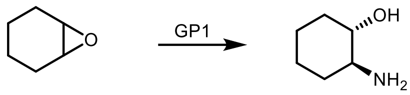
trans-2-aminocyclopentanol (3e)



S3e 3e

Prepared according to GP1 from **S3e** (85 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate = 5 : 1) to afford **3e** (85 mg, 83%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (q, *J* = 6.7 Hz, 1H), 3.00 (q, *J* = 7.5 Hz, 1H), 2.64 (br, 3H), 2.02 – 1.90 (m, 2H), 1.76 – 1.58 (m, 2H), 1.51 (ddt, *J* = 13.4, 9.7, 6.8 Hz, 1H), 1.29 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 79.87, 60.14, 32.38, 32.14, 19.86. HR-MS (EI) m/z calcd for $C_5H_{11}NO$ $[M+H]^+$: 102.0919; found: 102.0923.

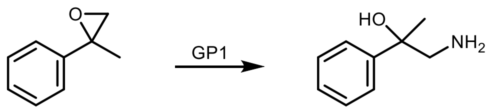
trans-2-aminocyclohexanol (3f)



S3f 3f

Prepared according to GP1 from **S3f** (98 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate = 5 : 1) to afford **3f** (105 mg, 91%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 – 3.04 (m, 1H), 2.40 (ddd, *J* = 11.2, 9.1, 4.1 Hz, 1H), 2.11 (br, 3H), 1.99 – 1.90 (m, 1H), 1.87 – 1.79 (m, 1H), 1.76 – 1.58 (m, 2H), 1.30 – 1.16 (m, 3H), 1.15 – 1.02 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 76.09, 57.25, 35.18, 33.76, 25.28, 24.84. HR-MS (EI) m/z calcd for $C_6H_{13}NO$ $[M+H]^+$: 116.1075; found: 116.1070.

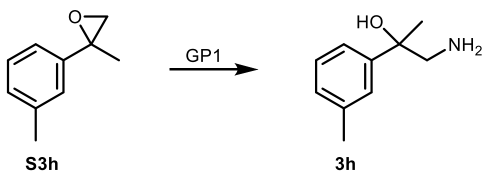
1-amino-2-phenylpropan-2-ol (3g)



S3g 3g

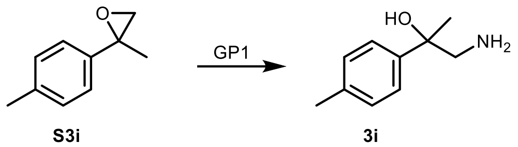
Prepared according to GP1 from **S3g** (135 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3g** (142 mg, 93%) as colorless dense oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.37 – 7.30 (m, 2H), 7.26–7.20 (m, 1H), 3.04 (d, *J* = 12.6 Hz, 1H), 2.78 (d, *J* = 12.6 Hz, 1H), 2.11 (br, 2H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.51, 128.33, 126.73, 125.19, 73.66, 52.93, 27.84. HR-MS (EI) *m/z* calcd for $C_9H_{13}NO$ $[M+H]^+$: 152.1075; found: 152.1065.

1-amino-2-(m-tolyl)propan-2-ol (3h)



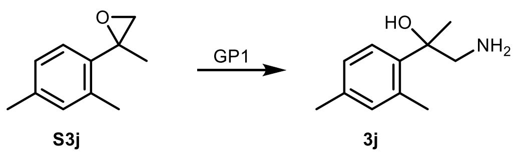
Prepared according to **GP1** from **S3h** (149 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3h** (150 mg, 90%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 3.0 Hz, 1H), 7.27 – 7.22 (t, *J* = 3.76 Hz2H), 7.08 (d, *J* = 6.2 Hz, 1H), 3.09 (d, *J* = 12.6 Hz, 1H), 2.81 (d, *J* = 12.5 Hz, 1H), 2.39 (s, 3H), 2.07 (br, 2H), 1.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.55, 137.94, 128.28, 127.51, 125.98, 122.25, 73.60, 52.91, 27.92, 21.75. HR-MS (EI) *m/z* calcd for $C_{10}H_{15}NO$ $[M+H]^+$: 166.1232; found: 166.1229.

1-amino-2-(p-tolyl)propan-2-ol (3i)



Prepared according to **GP1** from **S3i** (149 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3i** (145 mg, 87%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.19 – 7.11 (m, 2H), 3.05 (d, *J* = 12.5 Hz, 1H), 2.77 (d, *J* = 12.5 Hz, 1H), 2.34 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.61, 136.28, 129.05, 125.14, 73.55, 52.95, 27.90, 21.05. HR-MS (EI) *m/z* calcd for $C_{10}H_{15}NO$ $[M+H]^+$: 166.1232; found: 166.1221.

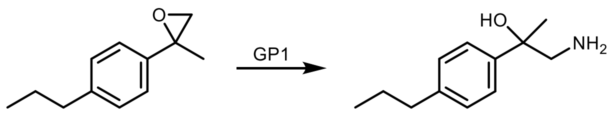
1-amino-2-(2,4-dimethylphenyl)propan-2-ol (3j)



Prepared according to **GP1** from **S3j** (163 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3j** (161 mg, 89%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$)

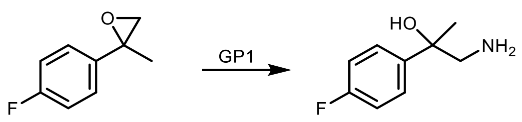
δ 7.34 (d, *J* = 8.5 Hz, 1H), 7.03 – 6.93 (m, 2H), 3.30 (d, *J* = 12.7 Hz, 1H), 2.79 (d, *J* = 12.7 Hz, 1H), 2.50 (s, 3H), 2.29 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.62, 136.53, 135.61, 133.64, 126.46, 126.37, 74.46, 51.02, 26.99, 22.35, 20.78. HR-MS (EI) *m/z* calcd for $C_{11}H_{17}NO$ [M+H]$^+$: 180.1388; found: 180.1386.

1-amino-2-(4-propylphenyl)propan-2-ol (3k)



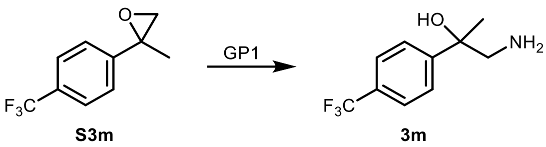
Prepared according to **GP1** from **S3k** (177 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3k** (179 mg, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 3.05 (d, *J* = 12.5 Hz, 1H), 2.78 (d, *J* = 12.5 Hz, 1H), 2.60 – 2.53 (m, 2H), 1.94 (br, 2H), 1.69 – 1.58 (m, 2H), 1.47 (s, 3H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.80, 141.14, 128.44, 125.10, 73.58, 52.96, 37.72, 27.89, 24.63, 14.02. HR-MS (EI) *m/z* calcd for $C_{12}H_{19}NO$ [M+H]$^+$: 194.1545; found: 194.1539.

1-amino-2-(4-fluorophenyl)propan-2-ol (3l)



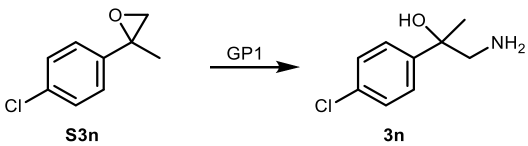
Prepared according to **GP1** from **S3l** (153 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3l** (152 mg, 89%) as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.30 (m, 2H), 7.12 – 6.84 (m, 2H), 3.03 (d, *J* = 12.5 Hz, 1H), 2.78 (d, *J* = 12.5 Hz, 1H), 1.94 (br, 3H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.83 (d, J^1 = 245.66 Hz), 142.40(d, J^4 = 3.07 Hz), 126.93(d, J^3 = 7.93 Hz), 115.06(d, J^2 = 21.10 Hz), 73.24, 52.85, 27.91. HR-MS (EI) *m/z* calcd for $C_9H_{12}FNO$ [M+H]$^+$: 170.0981; found: 170.0977.

1-amino-2-(4-(trifluoromethyl)phenyl)propan-2-ol (3m)



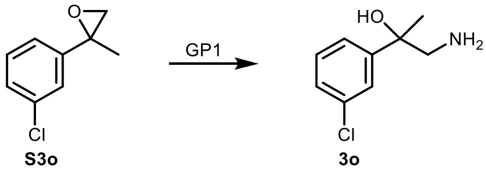
Prepared according to **GP1** from **S3m** (203 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3m** (178 mg, 81%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 3.09 (d, *J* = 12.5 Hz, 1H), 2.82 (d, *J* = 12.5 Hz, 1H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.92, 129.12 (d, *J* = 32.26 Hz), 125.72, 125.33 (d, *J* = 3.77 Hz), 123.04, 73.36, 52.62, 27.73. HR-MS (EI) *m/z* calcd for $C_{10}H_{13}F_3NO$ $[M+H]^+$: 220.0949; found: 220.0946.

1-amino-2-(4-chlorophenyl)propan-2-ol (3n)



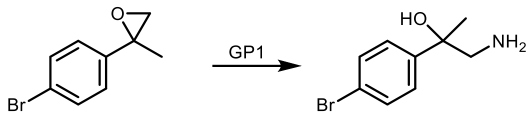
Prepared according to **GP1** from **S3n** (169 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3n** (175 mg, 94%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 3.03 (d, *J* = 12.5 Hz, 1H), 2.78 (d, *J* = 12.6 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.23, 132.59,128.45, 126.79, 73.25, 52.71, 27.77. HR-MS (EI) *m/z* calcd for $C_9H_{12}ClNO$ $[M+H]^+$: 186.0686; found: 186.0679.

1-amino-2-(3-chlorophenyl)propan-2-ol (3o)



Prepared according to **GP1** from **S3o** (169 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3o** (171 mg, 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.33 – 7.27 (m, 2H), 7.22 (dt, *J* = 7.4, 1.9 Hz, 1H), 3.07 (d, *J* = 12.6 Hz, 1H), 2.79 (d, J = 12.5 Hz, 1H), 1.96 (br, 2H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.98, 134.43, 129.67, 126.94, 125.74, 123.46, 73.29, 52.65, 27.75. HR-MS (EI) *m/z* calcd for $C_9H_{12}ClNO$ $[M+H]^+$: 186.0686; found: 186.0676.

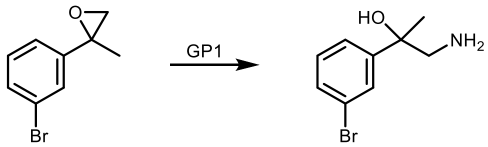
1-amino-2-(4-bromophenyl)propan-2-ol (3p)



S3p **3p**

Prepared according to **GP1** from **S3p** (214 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3p** (220 mg, 95%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 3.04 (d, J = 12.5 Hz, 1H), 2.78 (d, J = 12.5 Hz, 1H), 2.03 (br, 3H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.83, 131.43, 127.20, 120.76, 73.25, 52.63, 27.74. HR-MS (EI) *m/z* calcd for $C_9H_{12}BrNO$ $[M+H]^+$: 230.0181; found: 230.0178.

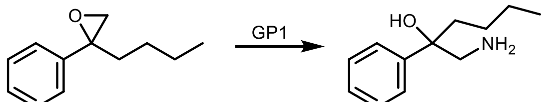
1-amino-2-(3-bromophenyl)propan-2-ol (3q)



S3q **3q**

Prepared according to **GP1** from **S3q** (214 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3q** (220 mg, 95%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, J = 1.9 Hz, 1H), 7.36 (tdd, J = 7.2, 1.9, 1.1 Hz, 2H), 7.20 (t, J = 7.8 Hz, 1H), 3.05 (d, J = 12.5 Hz, 1H), 2.78 (d, J = 12.5 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.28, 129.97, 129.89, 128.65, 123.94, 122.79, 73.23, 52.66, 27.77. HR-MS (EI) *m/z* calcd for $C_9H_{12}BrNO$ $[M+H]^+$: 230.0181; found: 230.0173.

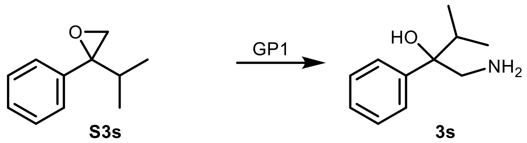
1-amino-2-phenylhexan-2-ol (3r)



S3r **3r**

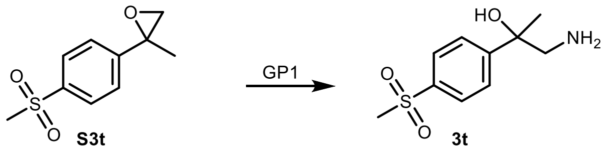
Prepared according to **GP1** from **S3r** (177 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3r** (175 mg, 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 3.10 (d, *J* = 12.3 Hz, 1H), 2.80 (d, *J* = 12.4 Hz, 1H), 1.79 – 1.65 (m, 2H), 1.40 – 1.14 (m, 3H), 1.07 – 0.92 (m, 1H), 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.28, 128.27, 126.55, 125.75, 75.95, 52.11, 40.44, 25.62, 23.27, 14.11. HR-MS (EI) *m/z* calcd for $C_{12}H_{19}NO$ $[M+H]^+$: 194.1545; found: 194.1537.

1-amino-3-methyl-2-phenylbutan-2-ol (3s)



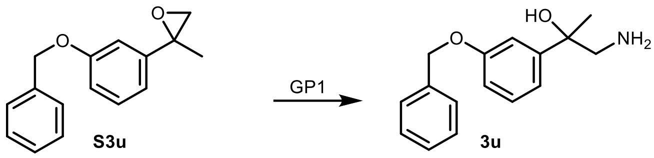
Prepared according to **GP1** from **S3s** (163 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3s** (155 mg, 86%) as dense oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.33 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.25 – 7.20 (m, 1H), 3.24 (d, *J* = 12.3 Hz, 1H), 2.90 (d, *J* = 12.3 Hz, 1H), 1.97 (dt, *J* = 13.7, 6.8 Hz, 1H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.64, 128.05, 126.53, 126.44, 78.00, 49.04, 36.46, 17.62, 17.02. HR-MS (EI) m/z calcd for $C_{11}H_{17}NO$ $[M+H]^+$: 180.1388; found: 180.1386.

1-amino-2-(4-(methylsulfonyl)phenyl)propan-2-ol (3t)



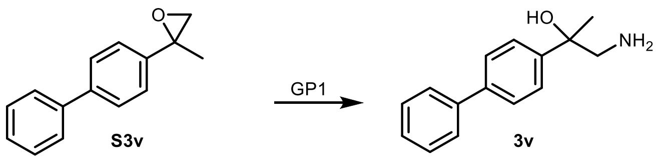
Prepared according to **GP1** from **S3t** (213 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3t** (221 mg, 96%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 3.08 (d, *J* = 12.6 Hz, 1H), 3.05 (s, 3H), 2.84 (d, *J* = 12.6 Hz, 1H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.46, 138.97, 127.48, 126.42, 73.39, 52.52, 44.64, 27.64. HR-MS (EI) *m/z* calcd for $C_{10}H_{16}NO_3S$ $[M+H]^+$: 230.0851; found: 230.0849.

1-amino-2-(3-(benzyloxy)phenyl)propan-2-ol (3u)



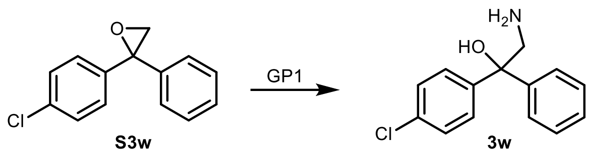
Prepared according to GP1 from **S3u** (241 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3u** (235 mg, 91%) as dense oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.8 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.15 – 7.11 (m, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.86 (dd, *J* = 8.2, 1.7 Hz, 1H), 5.08 (s, 2H), 3.08 (d, *J* = 12.5 Hz, 1H), 2.78 (d, *J* = 12.5 Hz, 1H), 1.90 (br, 3H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.02, 148.54, 137.20, 129.44, 128.71, 128.10, 127.73, 117.87, 112.88, 112.42, 73.55, 70.17, 52.79, 27.89. HR-MS (EI) m/z calcd for $C_{16}H_{19}NO_2$ $[M+H]^+$: 258.1494; found: 258.1491.

2-([1,1'-biphenyl]-4-yl)-1-aminopropan-2-ol (3v)



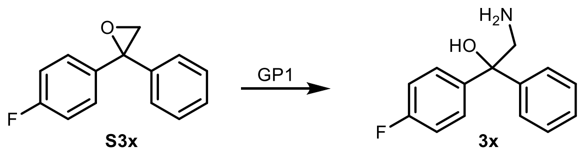
Prepared according to **GP1** from **S3v** (211 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3v** (208 mg, 91%) as a white solid. ^{1}H NMR (400 MHz, CD_3OD) δ 7.60 (d, *J* = 6.9 Hz, 4H), 7.53 (d, *J* = 9.5 Hz, 2H), 7.42 (dd, *J* = 7.7, 6.0 Hz, 2H), 7.34 – 7.25 (m, 1H), 2.91 – 2.79 (m, 2H), 1.53 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 146.77, 142.11, 140.91, 129.84, 128.27, 127.89, 127.82, 126.84, 75.36, 54.14, 27.52. HR-MS (EI) *m/z* calcd for $C_{15}H_{17}NO$ $[M+H]^+$: 228.1388; found: 228.1380.

2-amino-1-(4-chlorophenyl)-1-phenylethan-1-ol (3w)



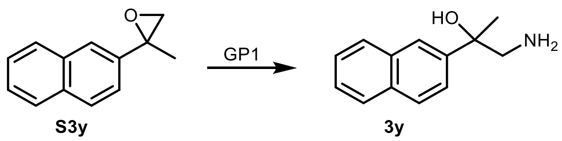
Prepared according to GP1 from **S3w** (231 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3w** (219 mg, 88%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 7.26 – 7.19 (m, 3H), 3.36 (d, J = 12.5 Hz, 1H), 3.29 (d, J = 12.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.04, 144.19, 132.93, 128.51, 128.48, 127.81, 127.30, 126.23, 50.95. HR-MS (EI) m/z calcd for $C_{14}H_{14}ClNO$ $[M+H]^+$: 248.0842; found: 248.0834.

2-amino-1-(4-fluorophenyl)-1-phenylethan-1-ol (3x)



Prepared according to GP1 from **S3x** (215 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3x** (188 mg, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.37 (m, 4H), 7.33 (t, J = 7.7 Hz, 2H), 7.25 (d, J = 6.7 Hz, 1H), 7.00 (t, J = 8.7 Hz, 2H), 3.43 – 3.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.90 (d, J^1 = 246.39 Hz), 145.29, 141.39 (d, J^4= 3.28 Hz), 128.47, 128.07 (J^3 = 8.07 Hz), 127.21, 126.27, 115.11 (J^2 = 21.26 Hz), 51.12. HR-MS (EI) m/z calcd for $C_{14}H_{14}FNO$ $[M+H]^+$: 232.1138; found: 232.1132.

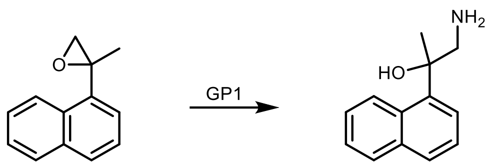
1-amino-2-(naphthalen-2-yl)propan-2-ol (3y)



Prepared according to **GP1** from **S3y** (185 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3y** (188 mg, 93%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 1H), 7.84 (t, J = 9.4 Hz, 3H), 7.53 – 7.43 (m, 3H), 3.21 (d, J = 12.5

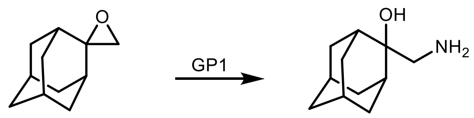
Hz, 1H), 2.87 (d, *J* = 12.5 Hz, 1H), 1.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.99, 133.36, 132.44, 128.24, 128.11, 127.60, 126.22, 125.84, 124.01, 123.72, 73.74, 52.71, 27.86. HR-MS (EI) *m/z* calcd for $C_{13}H_{15}NO$ $[M+H]^+$: 202.1232; found: 202.1224.

1-amino-2-(naphthalen-1-yl)propan-2-ol (3z)



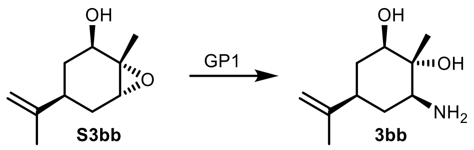
Prepared according to **GP1** from **S3z** (185 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **3z** (190 mg, 94%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.1 Hz, 1H), 7.87 (dd, *J* = 7.2, 2.5 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.66 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.53 – 7.37 (m, 3H), 3.63 (d, *J* = 12.6 Hz, 1H), 2.98 (d, *J* = 12.6 Hz, 1H), 1.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.47, 135.07, 131.06, 129.38, 128.63, 126.64, 125.41, 125.25, 125.11, 124.04, 74.66, 51.38, 27.89. HR-MS (EI) *m/z* calcd for $C_{13}H_{15}NO$ $[M+H]^+$: 202.1232; found: 202.1227.

2-(aminomethyl)adamantan-2-ol (3aa)



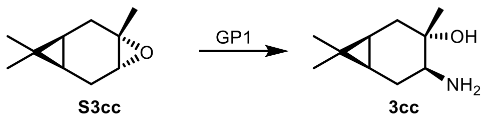
Prepared according to GP1 from **S3aa** (165 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 :10 : 1) to afford **3aa** (179 mg, 98%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.84 (s, 2H), 2.22 (d, *J* = 11.3 Hz, 2H), 2.06 (br, 3H), 1.85 – 1.73 (m, 4H), 1.69 (d, *J* = 11.0 Hz, 6H), 1.54 (d, *J* = 12.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 73.49, 47.39, 38.37, 35.67, 34.42, 33.22, 27.76, 27.43. HR-MS (EI) m/z calcd for $C_{11}H_{19}NO$ $[M+H]^+$: 182.1545; found: 182.1538.

(1R,4R,6S)-6-amino-1-methyl-4-(prop-1-en-2-yl)cyclohexane-1,2-diol (3bb)



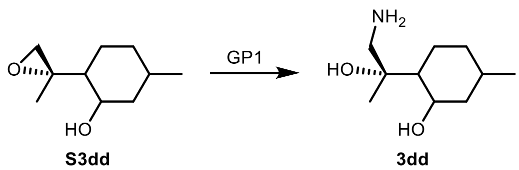
Prepared according to GP1 from **S3bb** (169 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol = 10 : 1) to afford **3bb** (149 mg, 80%) as a pale-yellow solid. $[\alpha]^{20}_{D}$ = −26.0 (*c* 1.0, methanol). ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.64 (d, *J* = 4.0 Hz, 2H), 3.54 (dd, *J* = 10.6, 5.2 Hz, 1H), 2.77 (s, 1H), 2.33 (ddt, *J* = 12.3, 7.6, 3.8 Hz, 1H), 1.74 (td, *J* = 12.8, 3.7 Hz, 1H), 1.66 (s, 3H), 1.50 – 1.35 (m, 2H), 1.27 (dq, *J* = 12.6, 2.6 Hz, 1H), 1.12 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.71, 108.29, 72.69, 69.90, 56.20, 36.85, 35.40, 33.35, 23.86, 20.80. HR-MS (EI) m/z calcd for $C_{10}H_{19}NO_2$ $[M+H]^+$: 186.1494; found: 186.1487.

(1S,3S,4S,6R)-4-amino-3,7,7-trimethylbicyclo[4.1.0]heptan-3-ol (3cc)



Prepared according to GP1 from **S3cc** (153 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol = 10 : 1) to afford **3cc** (141 mg, 83%) as a white solid. $[\alpha]^{20}_{D}$ = +35.5 (*c* 1.0, methanol). ^{1}H NMR (400 MHz, CD_3OD) δ 2.80 (dd, *J* = 10.6, 5.0 Hz, 1H), 1.98 – 1.83 (m, 2H), 1.26 (dd, *J* = 15.6, 7.2 Hz, 1H), 1.10 (s, 3H), 1.02 (s, 3H), 0.98 (s, 3H), 0.79 (m, 2H), 0.72 – 0.64 (m, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 73.89, 58.35, 34.76, 28.73, 26.80, 24.77, 23.12, 19.22, 19.10, 15.40. HR-MS (EI) m/z calcd for $C_{10}H_{19}NO$ $[M+H^+]$: 170.1545; found: 170.1537.

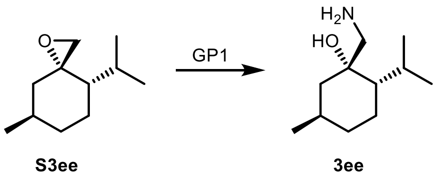
2-((S)-1-amino-2-hydroxypropan-2-yl)-5-methylcyclohexan-1-ol (3dd)



Prepared according to GP1 from **S3dd** (171 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol = 10 : 1) to afford **3dd** (160 mg, 85%) as a white solid. $[\alpha]^{20}_{D}$ = −7.2 (*c* 1.0, methanol). ^{1}H NMR (400 MHz,

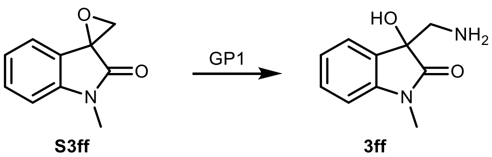
$CDCl_3$) δ 3.94 (s, 4H), 3.74 (td, *J* = 10.3, 4.2 Hz, 1H), 2.78 (d, *J* = 12.8 Hz, 1H), 2.57 (d, *J* = 12.8 Hz, 1H), 2.07 – 1.86 (m, 1H), 1.73 – 1.59 (m, 1H), 1.61 – 1.50 (m, 1H), 1.50 – 1.33 (m, 2H), 1.15 (s, 3H), 0.96 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 75.16, 71.91, 49.38, 49.02, 44.45, 34.50, 31.26, 26.39, 22.17, 20.50. HR-MS (EI) m/z calcd for $C_{10}H_{21}NO_2$ [M+H$^+$]: 188.1651; found: 188.1650.

(1S,2S,5R)-1-(aminomethyl)-2-isopropyl-5-methylcyclohexan-1-ol (3ee)



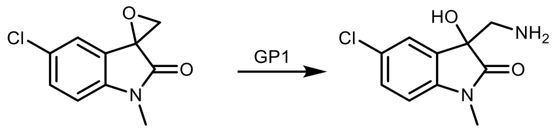
Prepared according to GP1 from **S3ee** (169 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 :10 : 1) to afford **3ee** (162 mg, 87%) as a white solid. $[\alpha]^{20}_D$ = −13.4 (*c* 1.0, methanol). ^1H NMR (400 MHz, $CDCl_3$) δ 2.84 (d, *J* = 12.7 Hz, 1H), 2.57 (d, *J* = 12.7 Hz, 1H), 2.02-1.95(m, 1H), 1.78-1.66 (m, 3H), 1.61-1.59 (m, 1H), 1.58-1.56 (m, 1H), 1.53 – 1.46 (m, 2H), 1.08 – 1.04 (m, 1H), 0.91 – 0.81 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 73.95, 49.99, 47.98, 45.83, 35.36, 28.05, 26.20, 23.86, 22.66, 20.97, 18.30. HR-MS (EI) m/z calcd for $C_{11}H_{23}NO$ $[M+H]^+$: 186.1858; found: 186.1848.

3-(aminomethyl)-3-hydroxy-1-methylindolin-2-one (3ff)



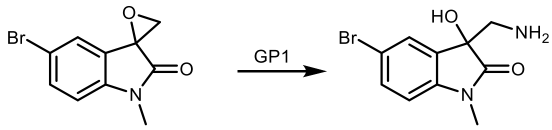
Prepared according to GP1 from **S3ff** (176 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 :10 : 1) to afford **3ff** (176 mg, 91%) as a dense oil. ^1H NMR (400 MHz, DMSO-d_6) δ 7.32 – 7.24 (m, 2H), 7.03 – 6.98 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 3.05 (s, 3H), 2.78 (q, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.33, 143.66, 130.74, 128.99, 123.67, 122.12, 108.26, 76.14, 48.72, 25.77. IR: 3366, 3056, 2935, 1715, 1613, 1493, 1470, 1374, 1348, 1302, 1241, 1158, 1091, 755 cm^{-1}. HR-MS (EI) m/z calcd for $C_{10}H_{12}N_2O_2$ $[M+H]^+$: 193.0977; found: 193.0974.

3-(aminomethyl)-5-chloro-3-hydroxy-1-methylindolin-2-one (3gg)



Prepared according to GP1 from **S3gg** (210 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 :10 : 1) to afford **3gg** (196 mg, 86%) as a dense oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 (s, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.00 (d, J = 8.2 Hz, 1H), 3.09 (s, 3H), 2.92 – 2.78 (q, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.99, 142.59, 132.88, 128.68, 126.28, 124.08, 109.75, 76.33, 48.35, 25.93. IR: 3361, 3064, 2937, 1722, 1611, 1490, 1467, 1362, 1268, 1104, 813, 735, 544 cm^{-1}. HR-MS (EI) m/z calcd for $C_{10}H_{11}ClN_2O_2$ $[M+H]^+$: 227.0587; found: 227.0585.

3-(aminomethyl)-5-bromo-3-hydroxy-1-methylindolin-2-one (3hh)



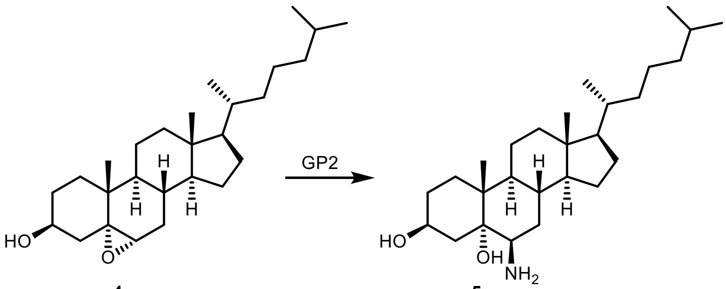
Prepared according to GP1 from **S3hh** (255 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 :10 : 1) to afford **3hh** (243 mg, 89%) as a dense oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51 (s, 1H), 7.49 (s, 1H), 6.96 (d, J = 8.2 Hz, 1H), 3.33 (br, 3H), 3.08 (s, 3H), 2.85 (q, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.03, 133.26, 131.55, 126.75, 110.31, 76.32, 48.34, 25.92. IR: 3343, 3202, 1721, 1666, 1609, 1488,1420, 1390, 1360, 1268, 1241, 1107, 813, 567, 534 cm^{-1}. HR-MS (EI) m/z calcd for $C_{10}H_{11}BrN_2O_2$ $[M+H]^+$: 271.0082; found: 271.0080.

2.2.2 Preparation of β-NH_2 alcohols from steroidal epoxides and tetra-substituted epoxides (GP2)

A mixture of steroidal epoxide substrate (1.0 mmol), $NH_3\cdot H_2O$ (25% in water, 2.26

mL, 15.0 mmol, 15.0 equiv), $HCOONH_4$ (126 mg, 2.0 mmol, 2.0 equiv) in n-butanol (4 mL) was put in a thick-walled pressure bottle. The sealed bottle was stirred for 8 h at 110 °C and then cooled to room temperature. K_2CO_3 solid was added to the reaction mixture sequentially and the resulting mixture was extracted with dichloromethane/methanol = 5 : 1. The combined organic phase was washed with brine and dried over unhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure to afford the crude product, which was further purified by flash chromatography to afford the pure steroidal β-NH_2 alchols.

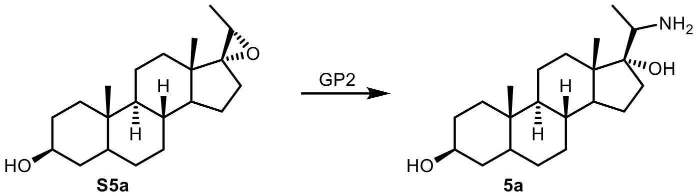
(3*S*,5*R*,6*R*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-6-amino-10,13-dimethyl-17-((*R*)-6-methylhep-tan-2-yl)hexadecahydro-5*H*-cyclopenta[a]phenanthrene-3,5-diol (5)



4 **5**

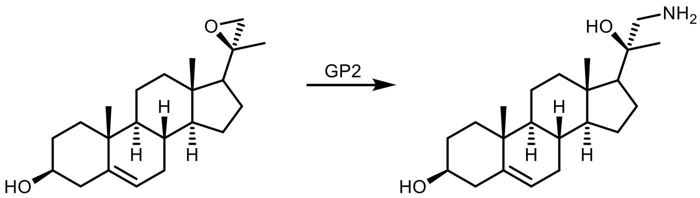
Prepared according to GP2 from **4** (101 mg, 0.25 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol : triethylamine = 100 :10 : 1) to afford **5** (97 mg, 93%) as a white solid. $[\alpha]^{20}_{D}$ = 5.0 (*c* 1.0, methanol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (dt, *J* = 11.2, 5.6 Hz, 1H), 2.75 (s, 1H), 2.28 (br, 4H), 2.00 (m, 2H), 1.90 – 1.68 (m, 3H), 1.67 – 1.45 (m, 6H), 1.33 (m, 9H), 1.20 – 0.95 (m, 11H), 0.87 (dd, *J* = 15.9, 6.4 Hz, 9H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 76.71, 67.75, 58.18, 56.43, 55.95, 45.98, 42.88, 41.40, 40.08, 39.64, 38.69, 36.31, 35.96, 34.92, 33.31, 30.97, 30.22, 28.36, 28.14, 24.38, 24.03, 22.95, 22.70, 21.33, 18.80, 18.18, 12.35. HR-MS (EI) m/z calcd for $C_{27}H_{49}NO_2$ $[M+H]^+$: 420.3842; found: 420.3836.

(3*S*,8*R*,9*S*,10*S*,13*S*,17*R*)-17-((*S*)-1-aminoethyl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthrene-3,17-diol (5a)



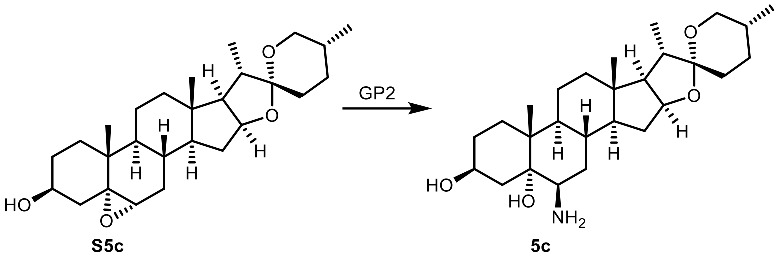
Prepared according to GP2 from **S5a** (319 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate: methanol: triethylamine = 100 :10 : 1) to afford **5a** (306 mg, 91%) as a white solid. $[\alpha]^{20}_{D}$ = −12.5 (*c* 1.0, methanol). ^{1}H NMR (400 MHz, CD_3OD) δ 3.54 (tt, *J* = 11.1, 4.6 Hz, 1H), 3.20 – 3.11 (m, 1H), 1.83 – 1.27 (m, 17H), 1.22 – 0.94 (m, 7H), 0.85 (d, *J* = 14.9 Hz, 6H), 0.74 - 0.63 (m, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 86.11, 71.84, 55.52, 52.37, 51.84, 48.51, 46.24, 38.89, 38.27, 37.04, 36.60, 36.29, 33.79, 33.40, 32.13, 29.95, 24.54, 22.14, 18.36, 15.42, 12.77. HR-MS (EI) m/z calcd for $C_{21}H_{37}NO_2$ [M+H$^+$]: 336.2903; found: 336.2898.

(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*)-17-(1-amino-2-hydroxypropan-2-yl)-10,13-dimethyl-2,3,4, 7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenan- thren-3-ol (5b)



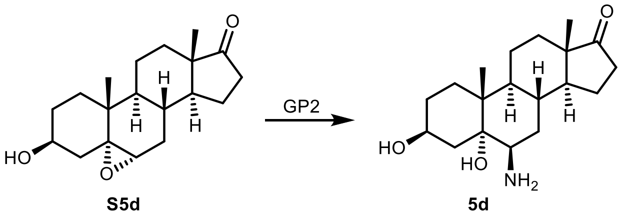
Prepared according to GP2 from **S5b** (331 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol : triethylamine = 100 :10 : 1) to afford **5b** (338 mg, 97%) as a white solid. $[\alpha]^{20}_{D}$ = −59.6 (*c* 1.0, methanol). ^{1}H NMR (600 MHz, Methanol-d_4) δ 5.26 (d, *J* = 4.9 Hz, 1H), 3.23 (m, 1H), 2.58 (s, 1H), 2.54 – 2.42 (m, 2H), 2.19 – 2.08 (m, 2H), 2.02 (m, 1H), 1.90 (m, 1H), 1.82 – 1.68 (m, 3H), 1.66 – 1.54 (m, 2H), 1.51 – 1.35 (m, 6H), 1.18 (s, 3H), 1.12 – 1.04 (m, 1H), 1.02 – 0.95 (m, 2H), 0.94 (s, 3H), 0.86 (td, *J* = 11.2, 5.5 Hz, 1H), 0.79 (s, 3H). ^{13}C NMR (151 MHz, Methanol-d_4) δ 142.26, 122.39, 75.35, 72.42, 58.46, 58.21, 52.42, 51.64, 43.80, 43.02, 41.31, 38.55, 37.68, 32.92, 32.73, 32.29, 24.91, 23.62, 23.31, 22.07, 19.86, 14.03. HR-MS (EI) m/z calcd for $C_{22}H_{37}NO_2$ [M+H$^+$]: 348.2903; found: 348.2903.

(2*R*,2a*R*,4*S*,5'*R*,6a*R*,6b*S*,8a*S*,8b*R*,9*S*,10*R*,11a*S*,12a*S*,12b*S*)-2-amino-5',6a,8a,9-tetramethylicosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-2a,4(2*H*)-diol (5c)



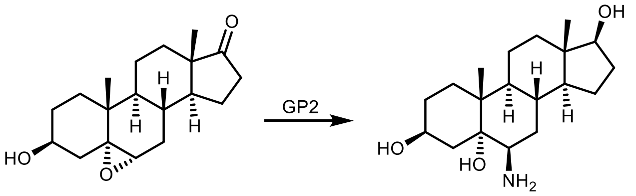
Prepared according to GP2 from **S5c** (431 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol : triethylamine = 100 :10 : 1) to afford **5c** (422 mg, 94%) as a white solid. $[\alpha]^{20}_D$ = −67.0 (*c* 1.0, methanol).^{1}H NMR (400 MHz, DMSO-d_6) δ 4.26 (q, *J* = 7.1 Hz, 1H), 3.82 (dt, *J* = 10.6, 5.4 Hz, 1H), 3.66 (s, 1H), 3.40 (d, *J* = 9.1 Hz, 1H), 3.18 (d, *J* = 14.6 Hz, 3H), 2.64 (s, 1H), 1.91 – 1.77 (m, 4H), 1.68 – 1.46 (m, 9H), 1.39 – 1.18 (m, 8H), 1.15-1.08 (m, 7H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.73 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d6) δ 108.36, 80.24, 74.76, 65.90, 65.82, 61.93, 57.01, 55.49, 48.59, 44.97, 41.12, 40.98, 40.22, 38.10, 34.65, 32.72, 31.48, 31.07, 30.90, 29.82, 29.32, 28.49, 20.58, 17.34, 17.08, 16.36, 14.63. HR-MS (EI) m/z calcd for $C_{27}H_{45}NO_4$ [M+H]$^+$: 448.3427; found: 448.3421.

(3*S*,5*R*,6*R*,8*R*,9*S*,10*R*,13*S*,14*S*)-6-amino-3,5-dihydroxy-10,13-dimethylhexadeca-hydro-17*H*-cyclopenta[a]phenanthren-17-one (5d)



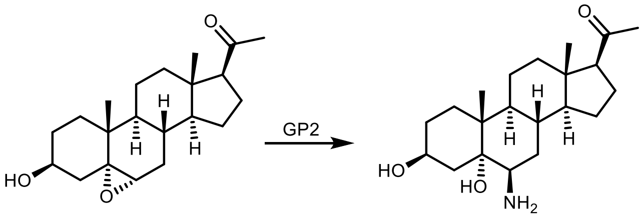
Prepared according to GP2 from **S5d** (305 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol = 10 : 1) to afford **5d** (310 mg, 96%) as a white solid. $[\alpha]^{20}_{D}$ = 53.1 (*c* 1.0, methanol). ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.24 (d, *J* = 5.4 Hz, 1H), 3.83 (m, 1H), 3.65 (s, 1H), 2.67 (s, 1H), 2.38 (dd, *J* = 19.0, 8.6 Hz, 1H), 2.00 (m, 1H), 1.90 – 1.78 (m, 3H), 1.72 (dd, *J* = 25.1, 4.2 Hz, 1H), 1.66 – 1.35 (m, 9H), 1.35 – 1.13 (m, 8H), 1.11 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 220.05, 75.00, 65.84, 57.06, 50.61, 47.25, 45.27, 41.04, 38.23, 35.39, 33.71, 32.76, 31.63, 31.11, 29.36, 21.51, 20.07, 17.40, 13.57. IR: 3390, 2937, 1716, 1680, 1517, 1471, 1449, 1370, 1236, 1154, 1056, 996, 845, 736 cm^{-1}. HR-MS (EI) m/z calcd for $C_{19}H_{31}NO_3$ [M+H$^+$]: 322.2382; found: 322.2375.

(3*S*,5*R*,6*R*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-6-amino-10,13-dimethylhexadecahydro-5*H*-cyclopenta[a]phenanthrene-3,5,17-triol (5e)



Prepared according to GP2 from **S5e** (304 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol : triethylamine = 100 :10 : 1) to afford **5e** (295 mg, 91%) as a white solid. $[\alpha]^{20}_{D}$ = −21.6 (*c* 1.0, methanol).^{1}H NMR (400 MHz, DMSO-d_6) δ 4.40 (br, 1H), 4.23 (br, 1H), 3.81 (dt, *J* = 11.3, 5.6 Hz, 1H), 3.61 (s, 1H), 3.41 (d, *J* = 8.8 Hz, 1H), 2.62 (s, 1H), 1.88 – 1.55 (m, 8H), 1.52 – 1.22 (m, 8H), 1.10 (d, *J* = 23.6 Hz, 6H), 0.90 (tt, *J* = 12.8, 7.0 Hz, 2H), 0.63 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6) δ 80.16, 74.93, 65.86, 57.07, 50.39, 45.23, 42.70, 41.07, 38.13, 36.91, 34.32, 32.78, 31.12, 29.92, 29.82, 23.21, 20.43, 17.41, 11.50. HR-MS (EI) m/z calcd for $C_{19}H_{33}NO_3$ [M+H]$^+$: 324.2539; found: 324.2531.

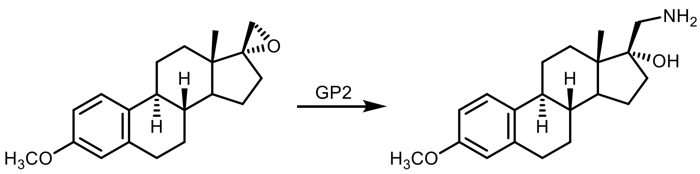
1-((3*S*,5*R*,6*R*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-6-amino-3,5-dihydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)ethan-1-one (5f)



S5f **5f**

Prepared according to GP2 from **S5f** (333 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol : triethylamine = 100 :10 : 1) to afford **5f** (326 mg, 93%) as a white solid. $[\alpha]^{20}_{D}$ = 27.9 (*c* 1.0, methanol). ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.24 (br, 1H), 3.82 (m, 1H), 3.65 (s, 1H), 2.64 (s, 1H), 2.57 (t, *J* = 8.9 Hz, 1H), 2.05 (s, 3H), 2.01 – 1.91 (m, 2H), 1.89 – 1.78 (m, 1H), 1.75 – 1.45 (m, 8H), 1.43 – 1.26 (m, 5H), 1.24 – 1.11 (m, 5H), 1.08 (s, 3H), 0.52 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 208.61, 74.88, 65.84, 62.80, 57.11, 55.82, 44.87, 43.71, 41.02, 38.49, 38.05, 34.74, 32.73, 31.18, 31.07, 29.73, 24.09, 22.23, 20.77, 17.35, 13.28. IR: 3370, 2939, 2870, 1700, 1564, 1441, 1408, 1358, 1251, 1173, 1073, 1008, 964, 735 cm^{-1}. HR-MS (EI) m/z calcd for $C_{21}H_{35}NO_3$ $[M+H]^+$: 350.2695; found: 350.2688.

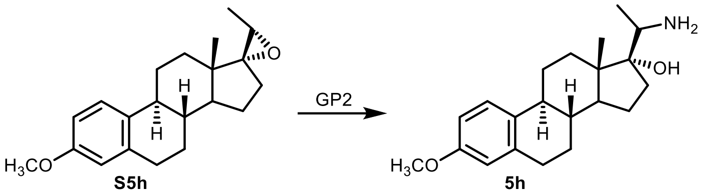
(8*R*,9*S*,13*S*,17*R*)-17-(aminomethyl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-ol (5g)



S5g **5g**

Prepared according to GP2 from **S5g** (299 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol : triethylamine = 100 :10 : 1) to afford **5g** (309 mg, 98%) as a white solid. $[\alpha]^{20}_{D}$ = 27.7 (*c* 1.0, methanol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 6.63 (s, 1H), 3.77 (s, 3H), 2.93 (d, *J* = 12.6 Hz, 1H), 2.89 – 2.82 (m, 2H), 2.71 (d, *J* = 12.6 Hz, 1H), 2.38 – 2.20 (m, 2H), 2.06 – 1.60 (m, 8H), 1.58 – 1.39 (m, 4H), 1.24 (m, 1H), 0.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.52, 138.24, 133.06, 126.42, 113.91, 111.55, 82.40, 55.34, 49.70, 46.66, 46.63, 43.70, 39.03, 35.67, 31.84, 30.05, 27.90, 26.42, 23.71, 15.39. HR-MS (EI) m/z calcd for $C_{20}H_{29}NO_2$ $[M+H]^+$: 316.2277; found: 316.2270.

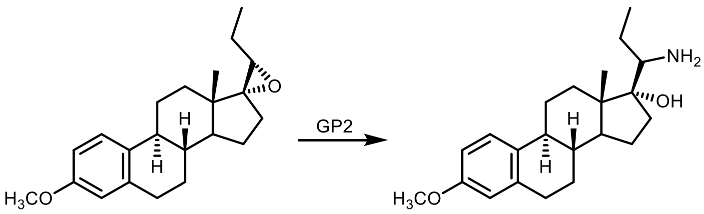
(8*R*,9*S*,13*S*,17*R*)-17-((*S*)-1-aminoethyl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-ol (5h)



S5h 5h

Prepared according to GP2 from **5h** (313 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol : triethylamine = 100 :10 : 1) to afford **5h** (321 mg, 97%) as a white solid. $[\alpha]^{20}_D$ = 45.7 (*c* 1.0, methanol).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 6.63 (s, 1H), 3.76 (s, 3H), 3.34 (q, *J* = 6.4 Hz, 1H), 2.85 (s, 2H), 2.37 – 2.16 (m, 2H), 2.02 – 1.33 (m, 11H), 1.17 (dd, *J* = 12.0, 6.1 Hz, 2H), 1.03 (d, *J* = 6.4 Hz, 3H), 0.79 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 157.52, 138.25, 133.02, 126.38, 113.90, 111.56, 83.89, 55.33, 49.95, 49.27, 47.56, 43.35, 39.14, 34.20, 33.36, 30.04, 27.78, 26.66, 23.42, 18.71, 15.60. HR-MS (EI) m/z calcd for $C_{21}H_{31}NO_2$ $[M+H]^+$: 330.2433; found: 330.2427.

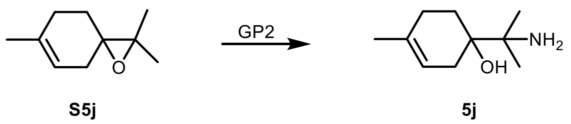
(8*R*,9*S*,13*S*,17*R*)-17-((*S*)-1-aminopropyl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-ol (5i)



S5i 5i

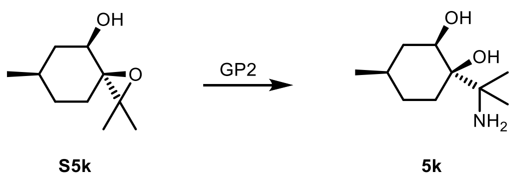
Prepared according to GP2 from **S5i** (327 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (ethyl acetate : methanol : triethylamine = 100 :10 : 1) to afford **5i** (318 mg, 92%) a as a white solid. $[\alpha]^{20}_D$ = 44.9 (*c* 1.0, methanol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.15 (d, *J* = 8.7 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 6.58 (s, 1H), 3.73 (s, 3H), 2.80 (d, *J* = 2.9 Hz, 3H), 2.37 – 2.21 (m, 1H), 2.21 – 2.01 (m, 1H), 2.03 – 1.84 (m, 3H), 1.84 – 1.67 (m, 3H), 1.65 – 1.12 (m, 7H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 158.87, 138.90, 133.77, 127.18, 114.65, 112.43, 86.83, 59.21, 55.54, 50.67, 44.87, 40.59, 36.18, 34.07, 30.85, 29.07, 27.76, 26.23, 24.28, 15.44, 11.82. HR-MS (EI) m/z calcd for $C_{21}H_{31}NO_2$ $[M+H]^+$: 344.2590; found: 344.2579.

1-(2-aminopropan-2-yl)-4-methylcyclohex-3-en-1-ol (5j)



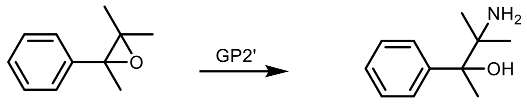
Prepared according to GP2 from **S5j** (153 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **5j** (155 mg, 91%) as colorless dense oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (d, *J* = 5.0 Hz, 1H), 2.21 (d, *J* = 16.8 Hz, 2H), 1.96 – 1.86 (m, 2H), 1.69 (s, 4H), 1.52 (td, *J* = 12.4, 5.7 Hz, 1H), 1.13 (d, *J* = 3.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.95, 118.59, 72.79, 55.19, 32.67, 27.69, 27.25, 26.36, 25.64, 23.44. HR-MS (EI) *m/z* calcd for $C_{10}H_{19}NO_2$ $[M+H]^+$: 170.1545; found: 170.1543.

(1R,2R,4R)-1-(2-aminopropan-2-yl)-4-methylcyclohexane-1,2-diol (5k)



Prepared according to GP2 from **S5k** (171 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **5k** (177 mg, 94%) as a dense oil. $[\alpha]^{20}_D = 3.7$ (c 1.0, methanol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.16 (s, 1H), 1.97 (td, *J* = 14.3, 3.9 Hz, 1H), 1.77 – 1.49 (m, 5H), 1.36 (d, *J* = 13.4 Hz, 1H), 1.31 (s, 3H), 1.23 (d, *J* = 5.3 Hz, 2H), 1.15 (s, 3H), 0.93 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 75.43, 74.01, 52.06, 39.97, 29.58, 25.75, 25.37, 25.22, 23.83, 22.25. HR-MS (EI) *m/z* calcd for $C_{10}H_{21}NO_2$ $[M+H]^+$: 188.1651; found: 188.1645.

3-amino-3-methyl-2-phenylbutan-2-ol (5l)



S5l 5l

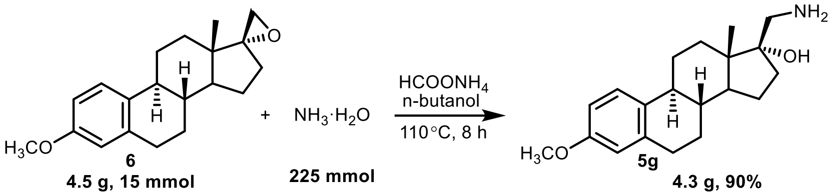
Except the reaction temperature is 180 ℃ and the reaction time is 72 h, other conditions are the same as that of GP2. Prepared from **S5l** (163 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **5l** (166 mg, 92%) as colorless dense oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.34 – 7.27 (m, 2H), 7.26 – 7.19 (m, 1H), 1.58 (s, 3H), 1.23 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.30, 127.47, 127.05, 126.60, 77.06, 55.60, 27.37, 26.46, 24.12. HR-MS (EI) *m/z* calcd for $C_{11}H_{17}NO$ $[M+H]^+$: 180.1388; found: 180.1384.

(1S,2S)-2-amino-1-(3-methoxy-3-methylbutyl)-2,6,6-trimethylcyclohexan-1-ol (5m)

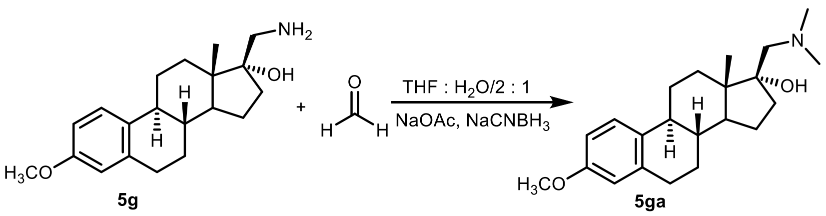
S5m 5m

Except the reaction temperature is 180 ℃ and the reaction time is 72 h, other conditions are the same as that of GP2. Prepared from **S5m**. Prepared from **S5m** (241 mg, 1.0 mmol, 1.0 equiv), purification by silica gel column chromatography (petroleum ether : ethyl acetate : triethylamine = 100 : 10 : 1) to afford **5m** (240 mg, 93%) as colorless dense oil. This reaction was completed at 180 °C for 72 h. $[\alpha]^{20}_{D}$ = −2.8 (c 1.0, methanol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 (s, 3H), 2.75 (br, 1H), 1.90 (dt, *J* = 16.1, 7.4 Hz, 2H), 1.74 – 1.54 (m, 5H), 1.39 (br, 1H), 1.21 (t, *J* = 11.2 Hz, 3H), 1.16 (s, 6H), 1.12 (s, 3H), 1.09 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 76.89, 75.29, 57.05, 49.18, 39.89, 38.18, 37.16, 36.73, 29.23, 28.32, 24.97, 24.87, 24.21, 23.82, 18.41. HR-MS (EI) *m/z* calcd for $C_{15}H_{31}NO_2$ $[M+H]^+$: 258.2433; found: 258.2431.

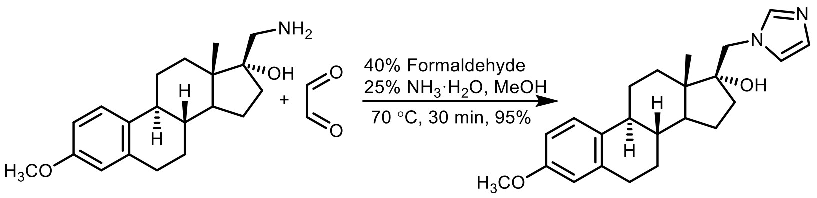
2.3 Gram-scale synthesis of 5g and practical transformations of 5g into 5ga – 5gd



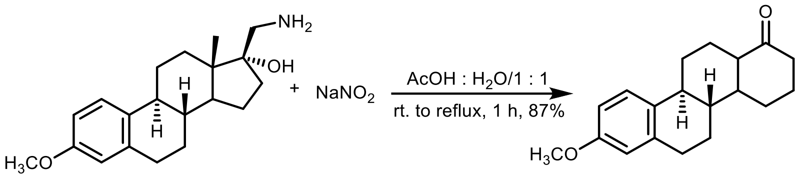
A mixture of steroidal epoxide **6** (4.5 g, 15 mmol), $NH_3{\cdot}H_2O$ (25% in water, 35 mL, 225.0 mmol, 15.0 equiv), $HCOONH_4$ (1.9 g, 30 mmol, 2.0 equiv) in n-butanol (60 mL) was put in a thick-walled pressure bottle. The sealed bottle was stirred for 8 h at 110 ℃ and then cooled to room temperature. After addition of K_2CO_3 (4.6g, 33mmol, 1.1 equiv) to the reaction mixture, most of the solvent was distilled off under reduced pressure and the resulting mixture was extracted with trichlormethane (3 × 20 mL). The combined organic phase was washed with brine and dried over unhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure to afford the crude product **5g** (4.3 g, 90%), which was found to be sufficiently pure and could be used directly in the subsequent transformations.



To a solution of **5g** (63.2 mg, 0.2 mmol, 1.0 equiv) and NaOAc (821.8 mg, 10.0 mmol, 50.0 equiv) in THF/H_2O (15 mL, 2 : 1) was cooled to 0 ℃ for 5 min followed by addition of formaldehyde (37% in water, 602.2 μL, 8.0 mmol, 40.0 equiv) and $NaCNBH_3$ (251.8 mg, 4.0 mmol, 20.0 equiv) before warmed to room temperature. The reaction mixture was stirred for another 2 h before treated with aq. satd. NH_4Cl (10 mL). Then the organic phase was separated and the aqueous phase was extracted with dichloromethane (3 × 10 mL), the organic extracts were combined and concentrated under vacuum to get a brown solid, which was purified by flash column chromatography (ethyl acetate to ethyl acetate : methanol = 5 : 1) to afford **5ga** (64.5 mg, 94%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.6 Hz, 1H), 6.71 (dd, J = 8.6, 2.8 Hz, 1H), 6.63 (d, J = 2.8 Hz, 1H), 3.78 (s, 3H), 2.85 (dd, J = 7.1, 3.2 Hz, 2H), 2.55 (d, *J* = 12.5 Hz, 1H), 2.34 (s, 6H), 2.32 – 2.25 (m, 1H), 2.21 (d, *J* = 12.5 Hz, 1H), 1.95 – 1.76 (m, 6H), 1.42 (m, 4H), 1.35 – 1.13 (m, 2H), 0.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.47, 138.31, 133.23, 126.47, 113.88, 111.50, 79.81, 64.13, 55.33, 51.76, 49.02, 47.22, 47.12, 43.70, 39.26, 38.92, 30.10, 30.07, 27.92, 26.28, 24.33, 14.18. HR-MS (EI) m/z calcd for $C_{22}H_{33}NO_2$ [M+H$^+$]: 344.2590; found: 344.2586.

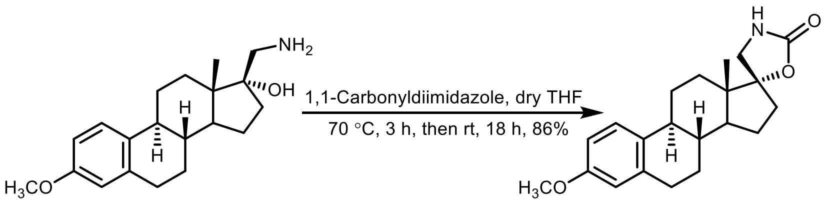


Following the literature procedure,[16] a solution of **5g** (63.2 mg, 0.2 mmol, 1.0 equiv) and formaldehyde (37% in water, 15.5 μL, 0.2 mmol, 1.0 equiv) in methanol (20 mL) was heated to 70 °C followed by addition of glyoxal (40% in water, 27.8 μL, 0.2 mmol, 1.0 equiv) and $NH_3 \cdot H_2O$ (25% in water, 30.2 μL, 0.2 mmol, 1.0 equiv). The mixture was refluxed for 30 min before cooled to room temperature. After removal of the solvent, the brown residue was poured into cool ethyl acetate, and 20 mL water was added. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with water, brine and dried over unhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 1 : 2) to afford **5gb** (70.0 mg, 95%) as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.19 (d, *J* = 8.6 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.71 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.63 (d, *J* = 2.8 Hz, 1H), 4.05 (s, 2H), 3.77 (s, 3H), 2.86 (d, *J* = 4.3 Hz, 2H), 2.36 – 2.17 (m, 2H), 2.11 – 1.94 (m, 2H), 1.93 – 1.73 (m, 3H), 1.58 – 1.23 (m, 7H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.62, 138.58, 138.06, 132.62, 128.75, 126.40, 120.62, 113.98, 111.59, 82.82, 55.34, 53.01, 49.34, 47.13, 43.66, 38.98, 36.31, 30.31, 29.94, 27.94, 26.17, 23.37, 15.46. HR-MS (EI) m/z calcd for $C_{23}H_{30}N_2O_2$ [M+H$^+$]: 367.2386; found: 367.2385.



5g **5gc**

Following the literature procedure,[17] a solution of **5g** (63.2 mg, 0.2 mmol, 1.0 equiv) in AcOH/H_2O (16 mL, 1 : 1) was added $NaNO_2$ (69.1 mg, 1.0 mmol, 5.0 equiv). An immediate evolution of N_2 was observed and the reaction mixture was refluxed for 1 h before cooled to room temperature. The reaction mixture was poured into water and extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with saturated $NaHCO_3$ (2 × 10 mL), 10% aqueous $NH_3 \cdot H_2O$ (10 mL), brine and dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 15 : 1) to afford **5gc** (49.4 mg, 87%) as a white solid. The experimental data are in agreement with the literature reported.[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.6 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.63 (d, *J* = 2.8 Hz, 1H), 3.78 (s, 3H), 2.86 (dd, *J* = 9.0, 4.3 Hz, 2H), 2.67 (td, *J* = 14.0, 6.8 Hz, 1H), 2.37 (dt, *J* = 13.3, 3.8 Hz, 1H), 2.29 – 2.20 (m, 2H), 2.16 – 2.05 (m, 2H), 2.00 – 1.85 (m, 2H), 1.78 – 1.56 (m, 2H), 1.56 – 1.37 (m, 4H), 1.36 – 1.22 (m, 1H), 1.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.57, 137.73, 111.73, 77.16, 55.30, 50.39, 48.51, 38.93, 37.30, 32.61, 30.21, 26.74, 26.03, 23.03, 16.99. IR: 3383, 3036, 2962, 2950, 2869, 2811, 1707, 1610, 1504, 1464, 1448, 1350, 1262, 1114, 1038, 970, 881, 830 cm^{-1}. HR-MS (EI) m/z calcd for $C_{22}H_{26}O_2$ [M+H$^+$]: 299.2011; found: 299.2001.

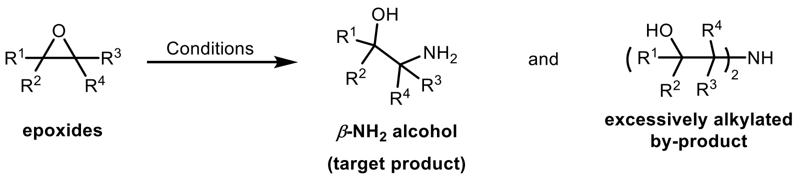


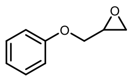
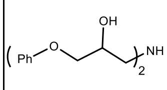
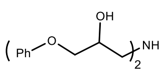
5g **5gd**

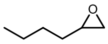
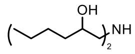
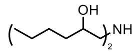
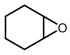
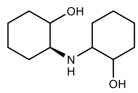
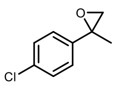
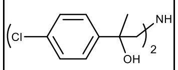
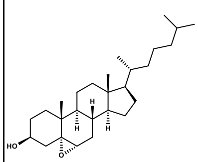
Following the literature procedure,[19] to a solution of **5g** (63.2 mg, 0.2 mmol, 1.0 equiv) in dry THF (5 mL) at room temperature under argon atmosphere was added 1,1-carbonyldiimidazole (32.5 mg, 0.2 mmol, 1.0 equiv). The reaction mixture was stirred at 70 ℃ for 3 h and at room temperature for 18 h before diluted with 10 mL ethyl acetate. The resulting solution was washed with 1N HCl (3 × 6 mL), 0.1 N K_2CO_3 (6 mL) and brine (6 mL). The organic phase was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 3 : 1) to afford **5gd** (58.7 mg, 86%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.7 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.64 (d, *J* = 2.8 Hz, 1H), 5.90 (s, 1H), 3.78 (s, 3H), 3.64 (d, *J* = 9.0 Hz, 1H), 3.38 (d, *J* = 8.9 Hz, 1H), 2.86 (t, *J* = 5.2 Hz, 2H), 2.44 – 2.34 (m, 1H), 2.31 – 2.17 (m, 2H), 2.05 – 1.95 (m, 1H), 1.94 – 1.87 (m, 3H), 1.81 (td, *J* = 13.0, 4.2 Hz, 1H), 1.62 – 1.54 (m, 1H), 1.50 – 1.39 (m, 3H), 1.35 (dd, *J* = 11.2, 5.9 Hz, 1H), 0.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.58, 157.60, 138.06, 132.46, 126.45, 113.94, 111.61, 94.06, 55.34, 49.42, 46.48, 45.45, 43.37, 39.17, 37.31, 29.89, 27.70, 25.88, 23.41, 14.41. IR: 3249, 2934, 2876, 1740, 1610, 1573, 1498, 1440, 1385, 1316, 1280, 1256, 1096, 1035, 984, 770, 735, 564 cm^{-1}. HR-MS (EI) m/z calcd for $C_{21}H_{27}NO_3$ [M+H$^+$]: 342.2069; found: 342.2059.

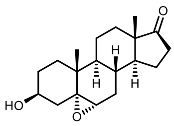
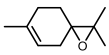
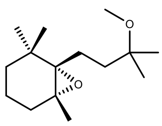
3. Comparison experiment (A couple of mono-, di-, tri- and tetra-substituted epoxides were selected as typical substrates for this comparison)

Table S1 Comparison experiments with those of "*Org. Lett*. 2017, **19**, 714" and "*Green Chemistry*, 2017, **19**, 2107"



Entry	Epoxides	Conditions	Reactivity	Yields	By-product	Comment
1		$NH_3·H_2O$ (15.0 eq.), EtOH, 60 °C, 16 h. (**Org. Lett. 2017, 19, 714**)	Completed within 0.5 h	87%	 8%	This reaction in 0.5 h, 2 h or 16 h gave the same result. Lower yield of target product with excessively alkylated by-product.
		NH_3 (15.0 eq.), MeOH, rt., 24 h. (**Green Chemistry, 2017, 19, 2107**)	Completed within 24 h	85%	 10%	Slow reaction, lower yield of target product with excessively alkylated by-product.
		$NH_3·H_2O$ (15.0 eq.), $HCOONH_4$ (2.0 eq.), MeOH, 50 °C, 0.5 h. (**This Work**)	Completed within 0.5 h	95%	None	Fast reaction, high yield of target product without excessively alkylated by-product.

2		$NH_3 \cdot H_2O$ (15.0 eq.), EtOH, 60 °C, 16 h. (**Org. Lett. 2017, 19, 714**)	Completed within 0.5 h	84%	 11%	This reaction in 0.5 h, 2 h or 16 h gave the same result. Lower yield of target product with excessively alkylated by-product.
		NH_3 (15.0 eq.), MeOH, rt., 24 h. (**Green Chemistry, 2017, 19, 2107**)	Completed within 24 h	82%	 10%	Slow reaction, lower yield of target product with excessively alkylated by-product.
		$NH_3 \cdot H_2O$ (15.0 eq.), $HCOONH_4$ (2.0 eq.), MeOH, 50 °C, 0.5 h. (**This Work**)	Completed within 0.5 h	92%	None	Fast reaction, high yield of target product without excessively alkylated by-product.
3		$NH_3 \cdot H_2O$ (15.0 eq.), EtOH, 60 °C, 16 h. (**Org. Lett. 2017, 19, 714**)	Completed within 2 h	78%	 9%	This reaction in 2 h or 16 h gave the same result. Lower yield of target product with excessively alkylated by-product.
		NH_3 (15.0 eq.), MeOH, rt., 24 h. (**Green Chemistry, 2017, 19, 2107**)	Very sluggish	trace	—	Di-substituted epoxide showed lower reactivity than that of mono-substituted epoxide at room temperature. However, 71% yield of target product accompanied with 8% yield of excessively alkylated by-product could be obtained when the reaction temperature was raised to 50℃ for 0.5 h.
		$NH_3 \cdot H_2O$ (15.0 eq.), $HCOONH_4$ (2.0 eq.), MeOH, 50 °C, 0.5 h. (**This Work**)	Completed within 0.5 h	91%	None	Fast reaction, high yield of target product without excessively alkylated by-product.
4		$NH_3 \cdot H_2O$ (15.0 eq.), EtOH, 60 °C, 16 h. (**Org. Lett. 2017, 19, 714**)	Completed within 2 h	82%	 7%	This reaction in 2 h or 16 h gave the same result. Lower yield of target product with excessively alkylated by-product.
		NH_3 (15.0 eq.), MeOH, rt., 24 h. (**Green Chemistry, 2017, 19, 2107**)	Very sluggish	trace	—	Di-substituted epoxide showed lower reactivity than that of mono-substituted epoxide at room temperature. However, 78% yield of target product accompanied with 9% yield of excessively alkylated by-product could be obtained when the reaction temperature was raised to 50℃ for 0.5 h.
		$NH_3 \cdot H_2O$ (15.0 eq.), $HCOONH_4$ (2.0 eq.), MeOH, 50 °C, 0.5 h. (**This Work**)	Completed within 0.5 h	94%	None	Fast reaction, high yield of target product without excessively alkylated by-product.
5		$NH_3 \cdot H_2O$ (15.0 eq.), EtOH, 60 °C, 16 h. (**Org. Lett. 2017, 19, 714**)	No reaction	0	—	54% yield of target product could be obtained when reaction temperature was raised to 110 °C in 8 h. The unreacted starting material was remained.
		NH_3 (15.0 eq.), MeOH, rt., 24 h. (**Green Chemistry, 2017, 19, 2107**)	No reaction	0	—	61% yield of target product could be obtained when reaction temperature was raised to 110 °C in 8 h. The unreacted starting material was remained.

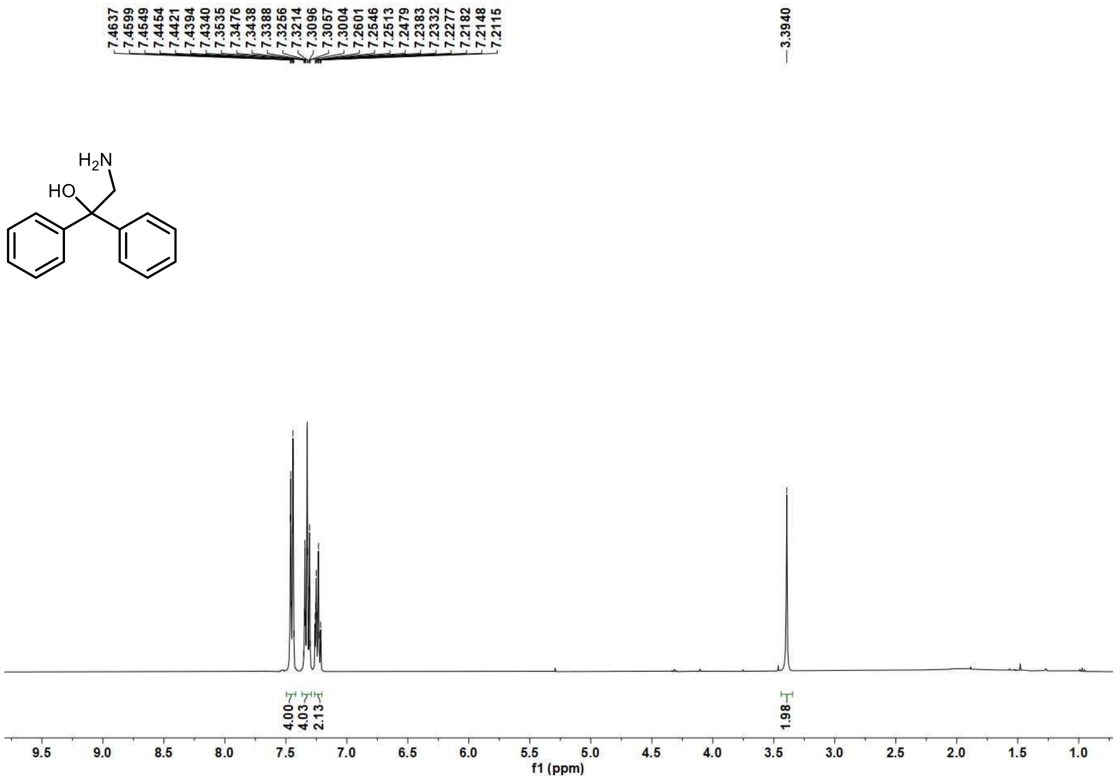
		$NH_3 \cdot H_2O$ (15.0 eq.), $HCOONH_4$ (2.0 eq.), n-butanol, 110 °C, 8 h. (**This Work**)	Completed within 8 h	92%	None	Progress smoothly, high yield of target product without excessively alkylated by-product.
6		$NH_3 \cdot H_2O$ (15.0 eq.), EtOH, 60 °C, 16 h. (**Org. Lett. 2017, 19, 714**)	No reaction	0	—	57% yield of target product could be obtained when reaction temperature was raised to 110 °C for 8 h. The unreacted starting material was remained.
		NH_3 (15.0 eq.), MeOH, rt., 24 h. (**Green Chemistry, 2017, 19, 2107**)	No reaction	0	—	68% yield of target product could be obtained when reaction temperature was raised to 110 °C for 8 h. The unreacted starting material was remained.
		$NH_3 \cdot H_2O$ (15.0 eq.), $HCOONH_4$ (2.0 eq.), n-butanol, 110 °C, 8 h. (**This Work**)	Completed within 8 h	96%	None	Progress smoothly, high yield of target product without excessively alkylated by-product.
7		$NH_3 \cdot H_2O$ (15.0 eq.), EtOH, 60 °C, 16 h. (**Org. Lett. 2017, 19, 714**)	No reaction	0	—	35% yield of target product could be obtained when reaction temperature was raised to 110 °C in 8 h. The unreacted starting material was remained.
		NH_3 (15.0 eq.), MeOH, rt., 24 h. (**Green Chemistry, 2017, 19, 2107**)	No reaction	0	—	41% yield of target product could be obtained when reaction temperature was raised to 110 °C in 8 h. The unreacted starting material was remained.
		$NH_3 \cdot H_2O$ (15.0 eq.), $HCOONH_4$ (2.0 eq.), n-butanol, 110 °C, 8 h. (**This Work**)	Completed within 8 h	91%	None	Progress smoothly, high yield of target product without excessively alkylated by-product.
8		$NH_3 \cdot H_2O$ (15.0 eq.), EtOH, 60 °C, 16 h. (**Org. Lett. 2017, 19, 714**)	No reaction	0	—	The reaction was sluggish even at a higher reaction temperature of 180 ℃ for 72 h, only trace amount of target product was detected.
		NH_3 (15.0 eq.), MeOH, rt., 24 h. (**Green Chemistry, 2017, 19, 2107**)	No reaction	0	—	The reaction was sluggish even at a higher reaction temperature of 180 ℃ for 72 h , only trace amount of target product was detected.
		$NH_3 \cdot H_2O$ (15.0 eq.), $HCOONH_4$ (2.0 eq.), n-butanol, 180 ℃, 72 h. (**This Work**)	Completed within 72 h	93%	None	The adverse effects of steric hindrance could be overcome by raising the reaction temperature under our standard conditions. Stoichiometric amount of HCO_2NH_4 as an additive plays a dual role in global activation of substrate and completely suppressing side-reaction of the excessive alkylation.

4. Supplementary References

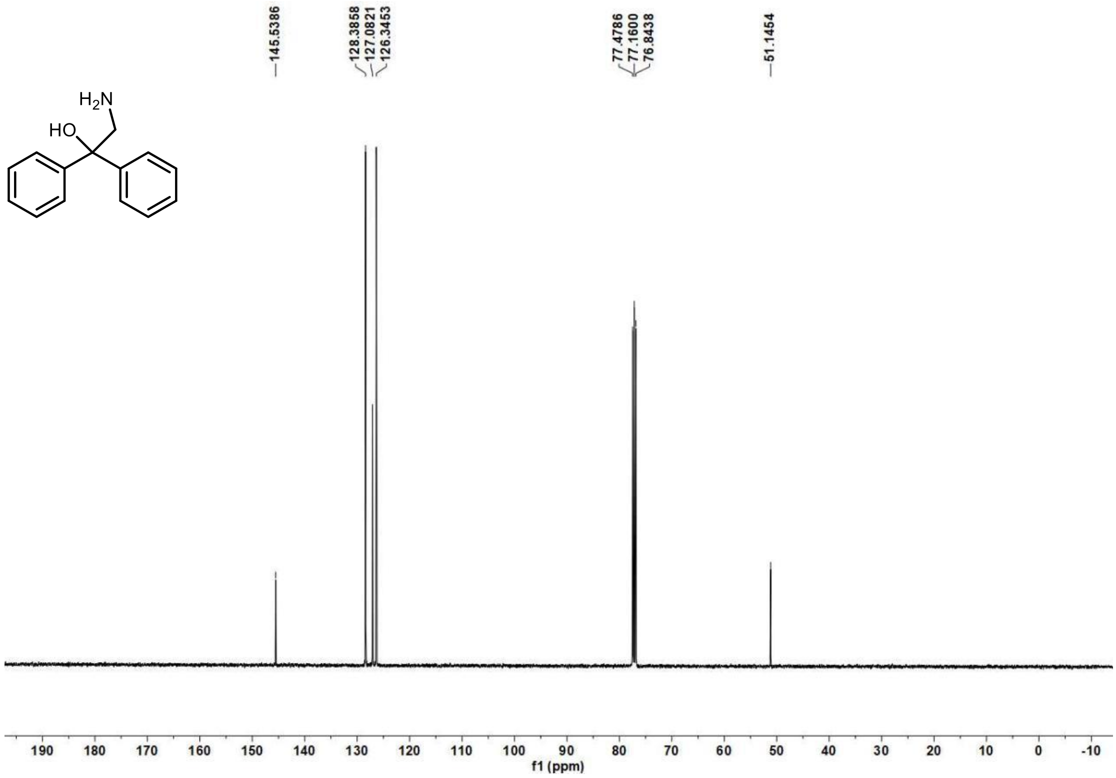
1. P. de Medina, M. R. Paillasse, B. Payre, S. Silvente-Poirot and M. Poirot, *J Med Chem*, 2009, **52**, 7765-7777.
2. J. R. Hanson, A. C. Hunter and S. Roquier, *Collection of Czechoslovak Chemical Communications*, 1998, **63**, 1646-1654.
3. E. Ma, H. Kim and E. Kim, *Steroids*, 2005, **70**, 245-250.
4. P. S. M. Amado, L. M. T. Frija, J. A. S. Coelho, P. M. O'Neill and M. L. S. Cristiano, *J Org Chem*, 2021, **86**, 10608-10620.
5. N. Brugat, J. Duran, A. Polo, J. Real, Á. Álvarez-Larena and J. F. Piniella, *Tetrahedron: Asymmetry*, 2002, **13**, 569-577.
6. A. Cabré, J. Cabezas-Giménez, G. Sciortino, G. Ujaque, X. Verdaguer, A. Lledós and A. Riera, *Advanced Synthesis & Catalysis*, 2019, **361**, 3624-3631.
7. C. Cimarelli, D. Fratoni and G. Palmieri, *Tetrahedron: Asymmetry*, 2011, **22**, 603-608.
8. J. Deregnaucourt, A. Archelas, F. Barbirato, J.-M. Paris and R. Furstoss, *Advanced Synthesis & Catalysis*, 2007, **349**, 1405-1417.
9. C. Molinaro, A. A. Guilbault and B. Kosjek, *Org Lett*, 2010, **12**, 3772-3775.
10. A. K. Pandey and P. Banerjee, *Asian Journal of Organic Chemistry*, 2016, **5**, 360-366.
11. F. Santamarta, M. Vilas, E. Tojo and Y. Fall, *RSC Advances*, 2016, **6**, 31177-31180.
12. H. Schirok, *Synthesis*, 2008, **2008**, 1404-1414.
13. D. J. Vyas, E. Larionov, C. Besnard, L. Guenee and C. Mazet, *J Am Chem Soc*, 2013, **135**, 6177-6183.
14. J. P. Feng, Z. F. Shi, Y. Li, J. T. Zhang, X. L. Qi, J. Chen and X. P. Cao, *J Org Chem*, 2008, **73**, 6873-6876.
15. S. Kirsch; T. Bach, *Synthesis,* 2003, 1827.
16. H. Zhang, J. Liu, J. Chen, J. Zhao, Y. Zhao and L. Li, *Synthesis*, 2003, **17**, 2661-2666.
17. E. W. Della and P. E. Pigou, *Journal of the American Chemical Society*, 1984, **106**, 1085-1092.
18. H. Z. Kaplan, V. L. Rendina and J. S. Kingsbury, *Molecules*, 2017, **22**.
19. H. S. Wilkinson, P. T. Grover, C. P. Vandenbossche, R. P. Bakale, N. N. Bhongle, S. A. Wald and C. H. Senanayake, *Org Lett*, 2001, **3**, 553-556.

5. [1]H and [13]C NMR spectra of *β*-NH_2 alcohols and derivatives

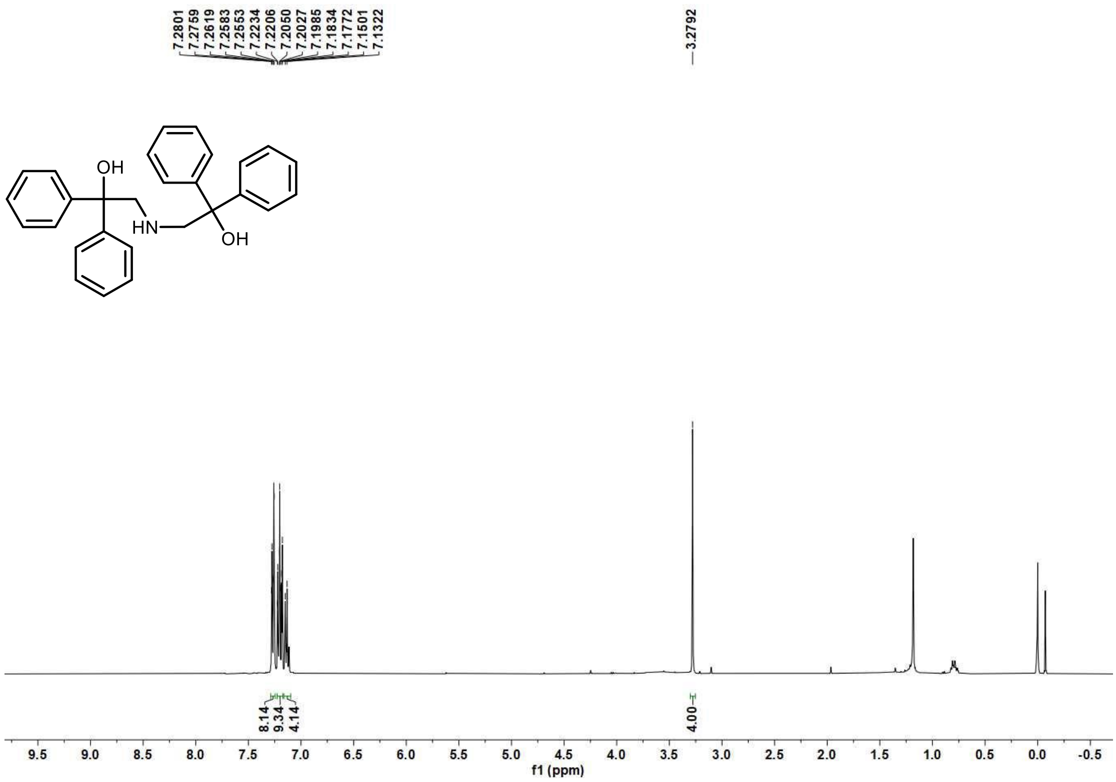
[1]H NMR (400 MHz, $CDCl_3$) of 2-amino-1,1-diphenylethan-1-ol (**2**)



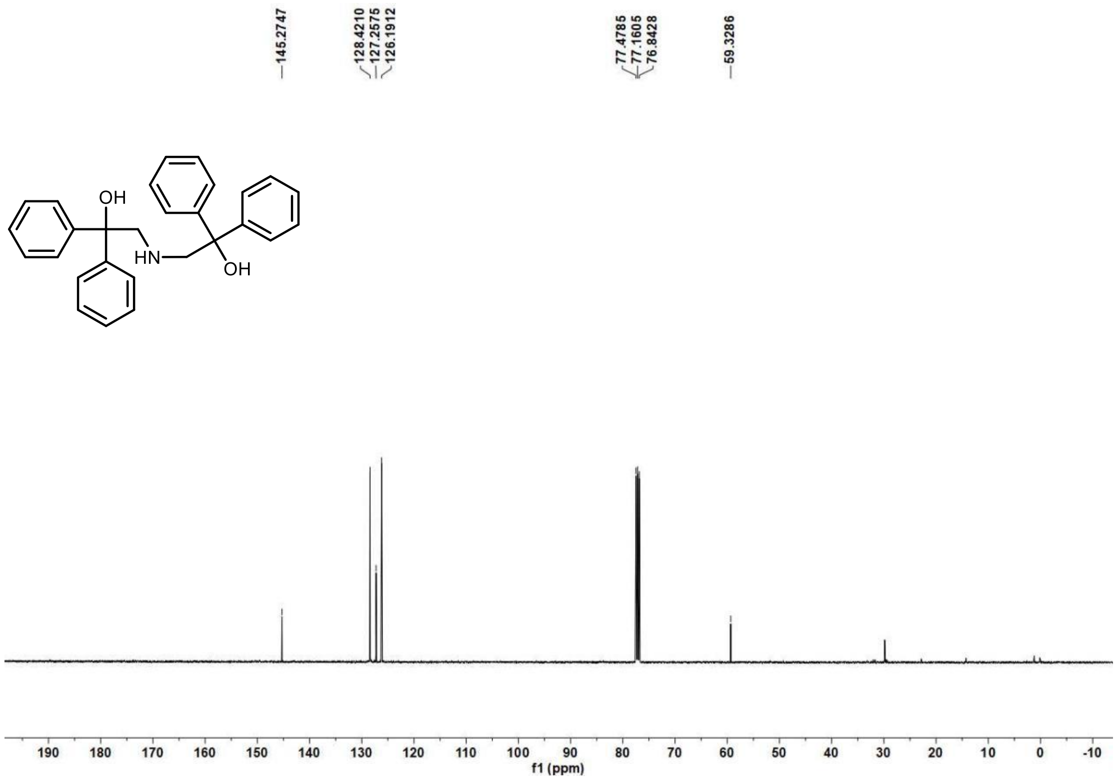
[13]C NMR (101 MHz, $CDCl_3$) of 2-amino-1,1-diphenylethan-1-ol (**2**)



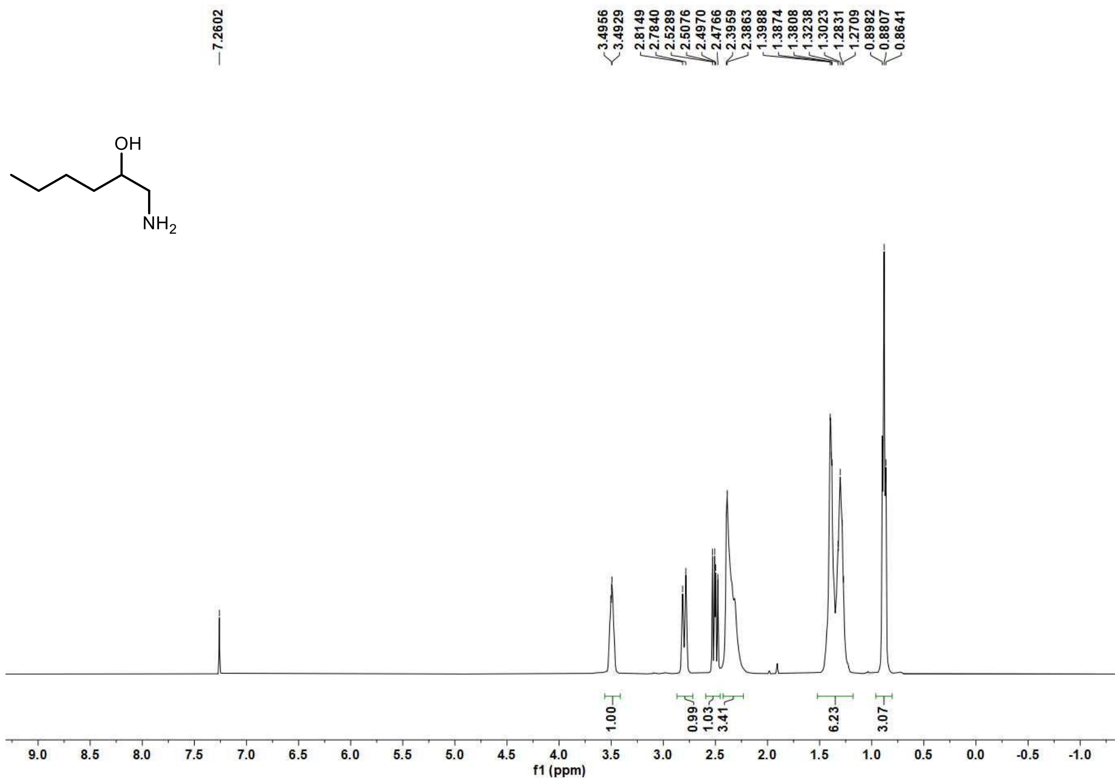
^{1}H NMR (400 MHz, $CDCl_3$) of **2′**



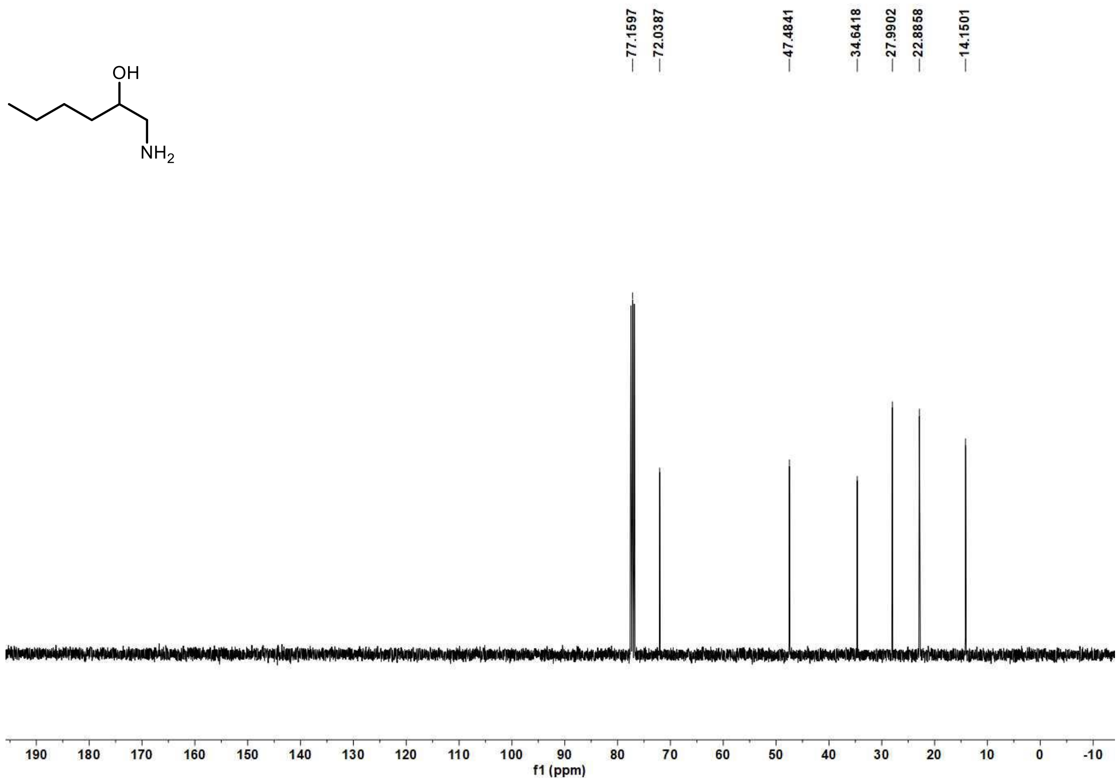
^{13}C NMR (101 MHz, $CDCl_3$) of **2′**



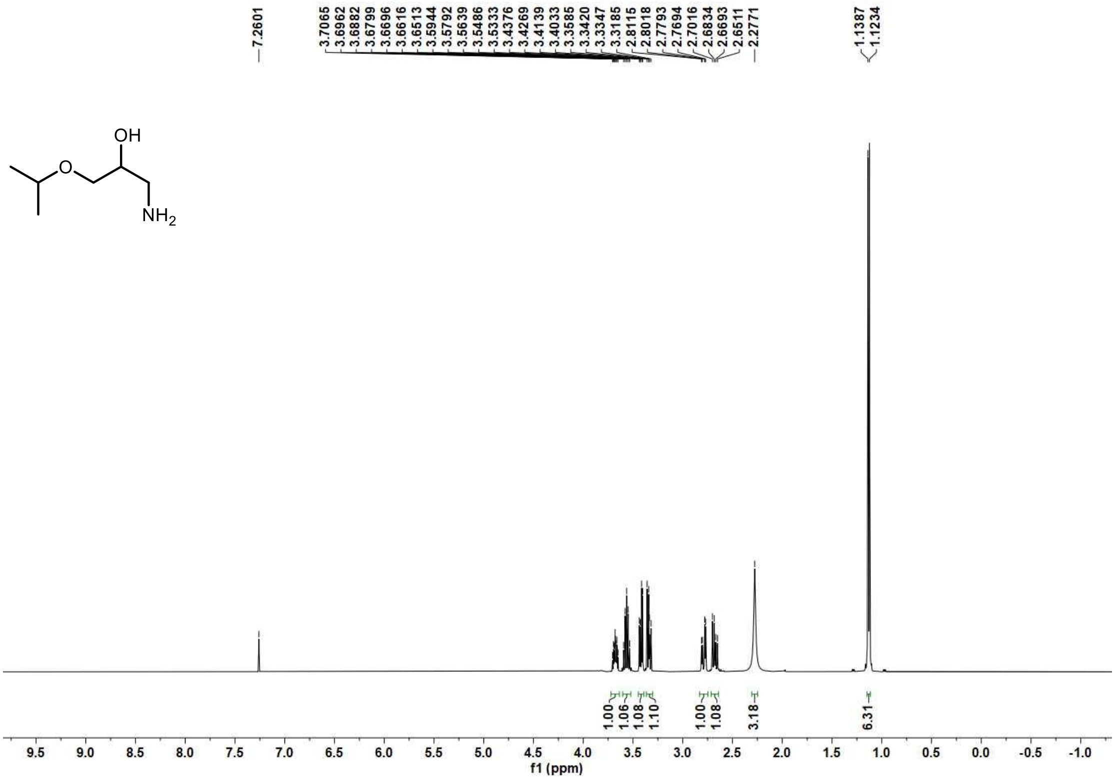
^{1}H NMR (400 MHz, $CDCl_3$) of 1-aminohexan-2-ol (**3a**)



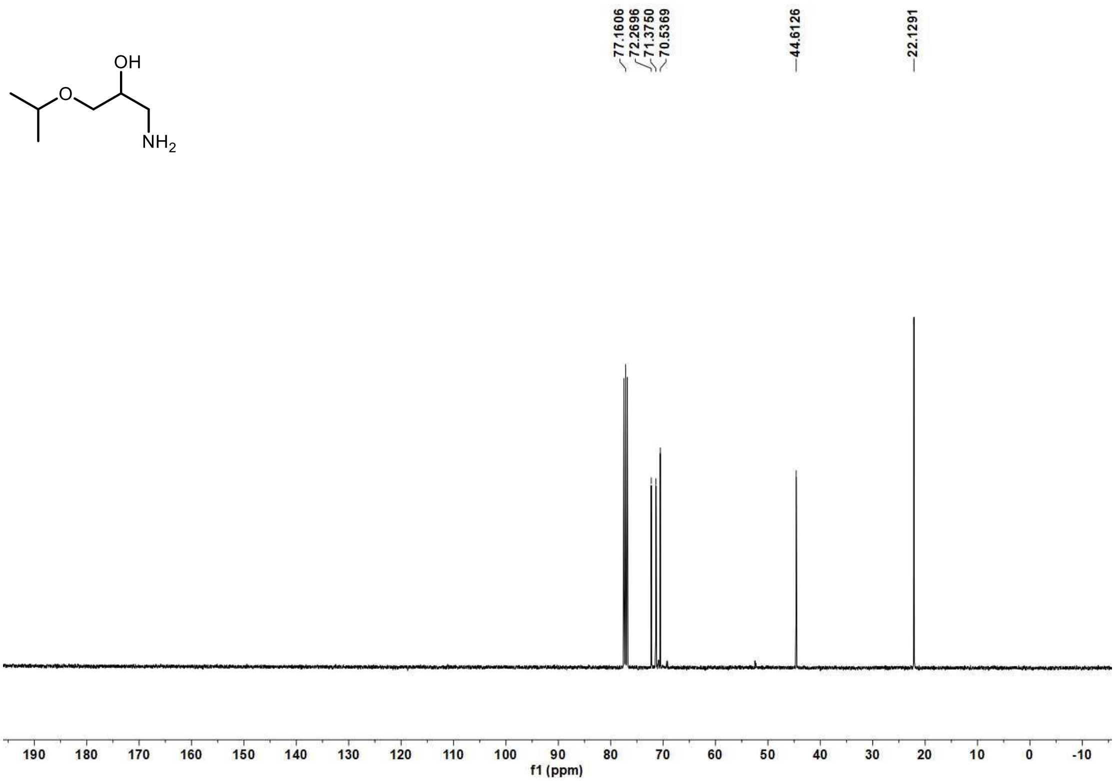
^{13}C NMR (101 MHz, $CDCl_3$) of 1-aminohexan-2-ol (**3a**)



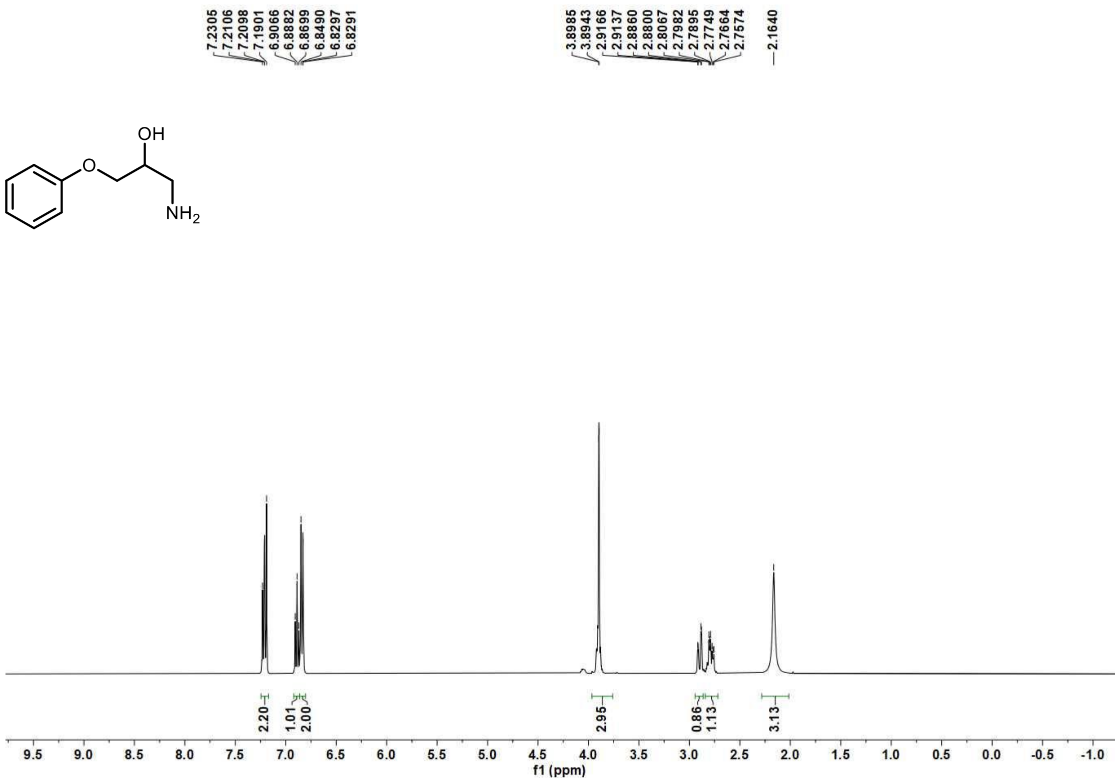
^{1}H NMR (400 MHz, $CDCl_3$) of 1-amino-3-isopropoxypropan-2-ol (**3b**)



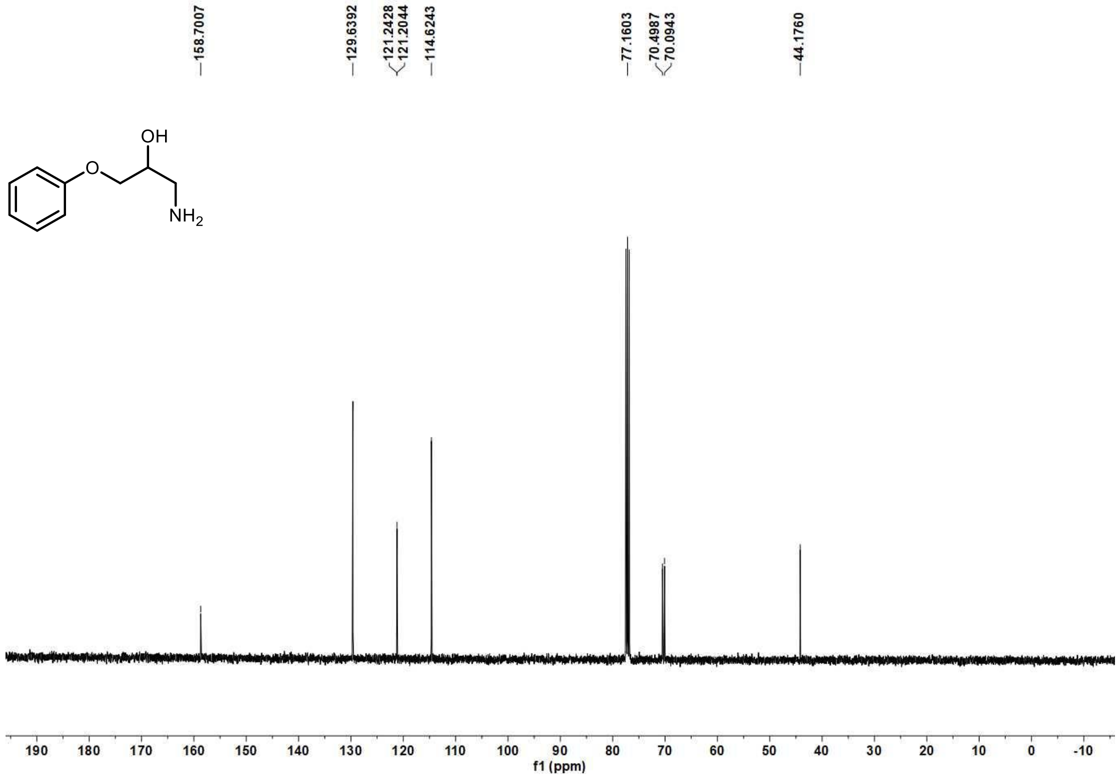
^{13}C NMR (101 MHz, $CDCl_3$) of 1-amino-3-isopropoxypropan-2-ol (**3b**)



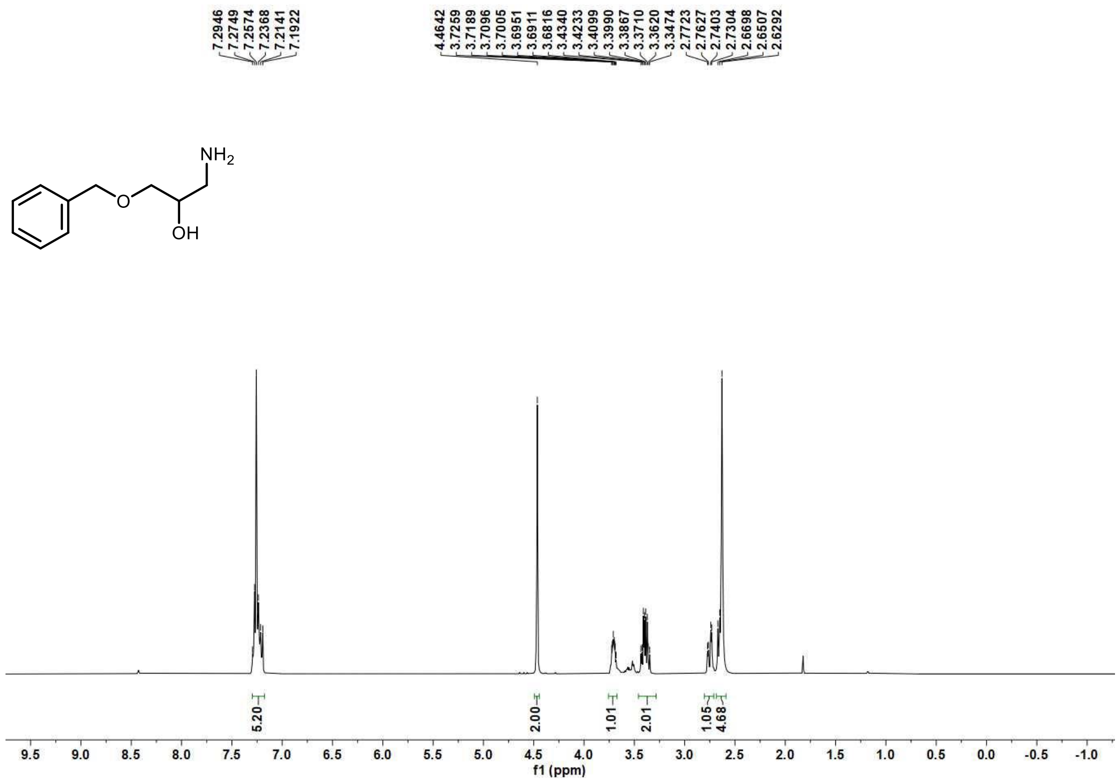
^{1}H NMR (400 MHz, $CDCl_3$) of 1-amino-3-phenoxypropan-2-ol (**3c**)



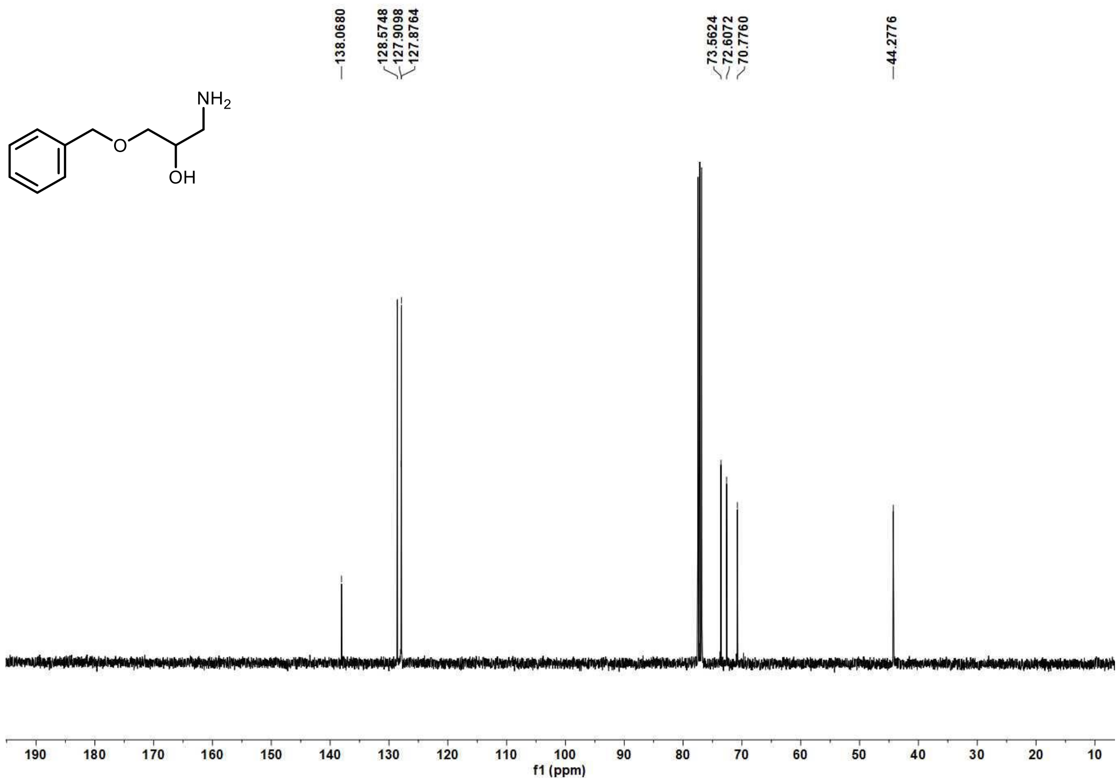
^{13}C NMR (101 MHz, $CDCl_3$) of 1-amino-3-phenoxypropan-2-ol (**3c**)



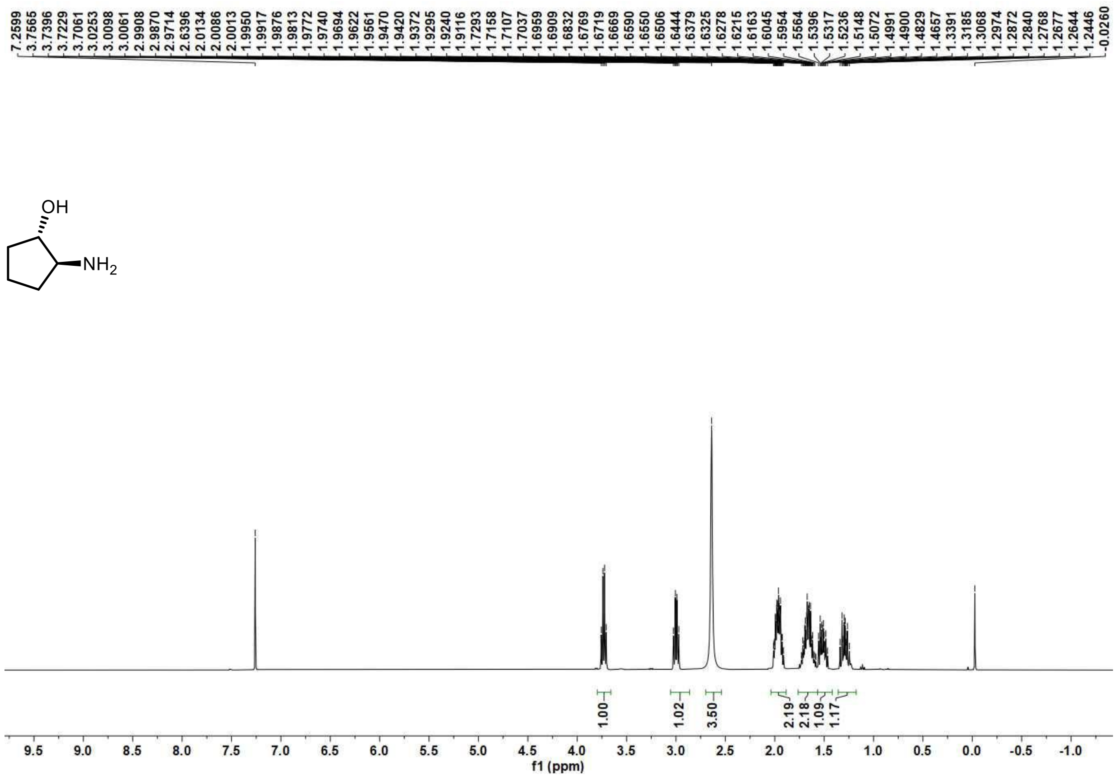
^{1}H NMR (400 MHz, $CDCl_3$) of 1-amino-3-(benzyloxy)propan-2-ol (**3d**)



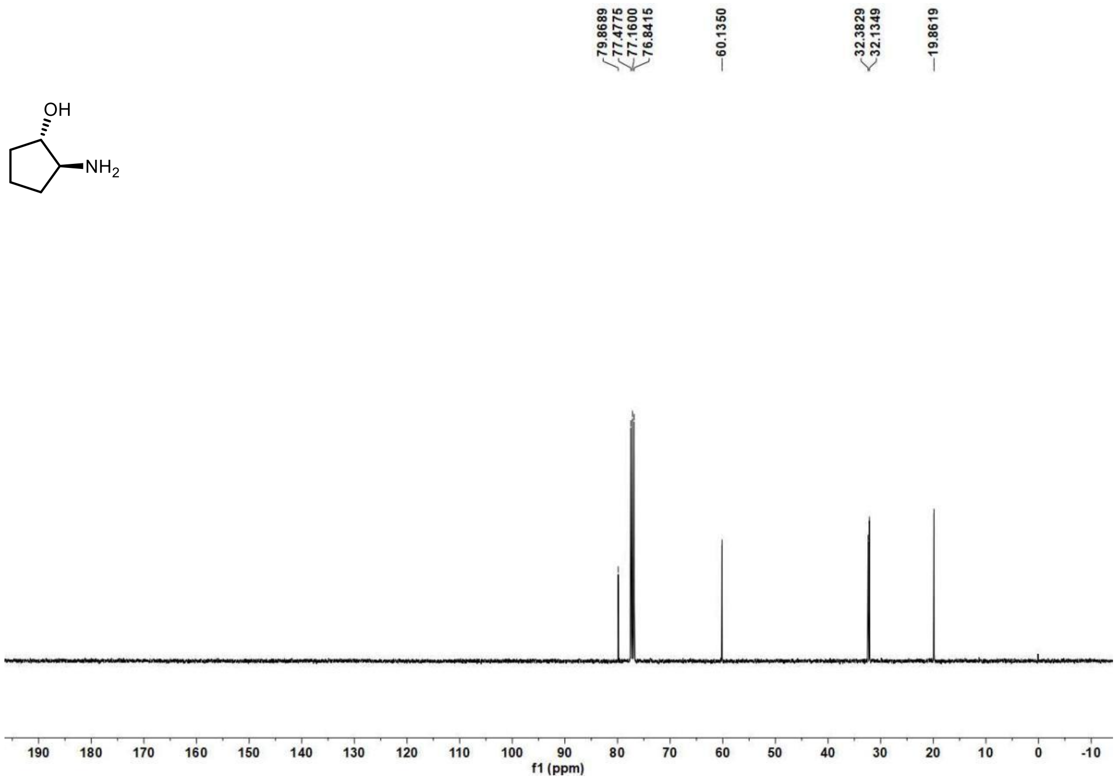
^{13}C NMR (101 MHz, $CDCl_3$) of 1-amino-3-(benzyloxy)propan-2-ol (**3d**)



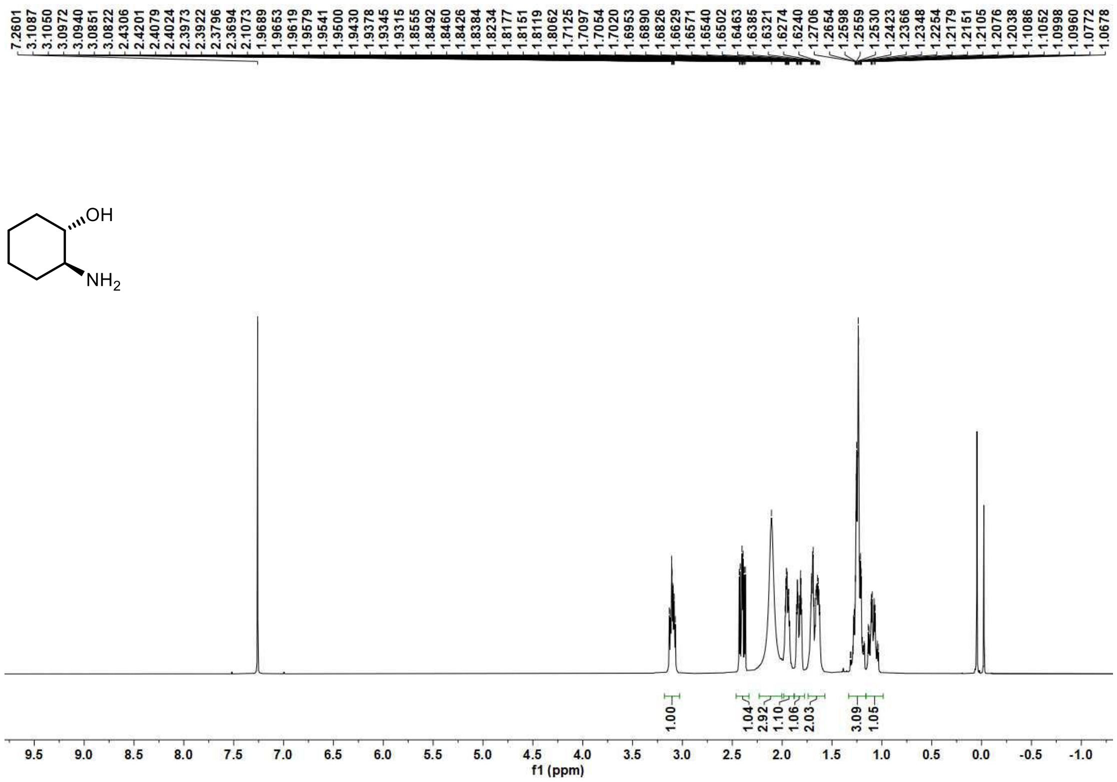
^{1}H NMR (400 MHz, $CDCl_3$) of trans-2-aminocyclopentanol (**3e**)



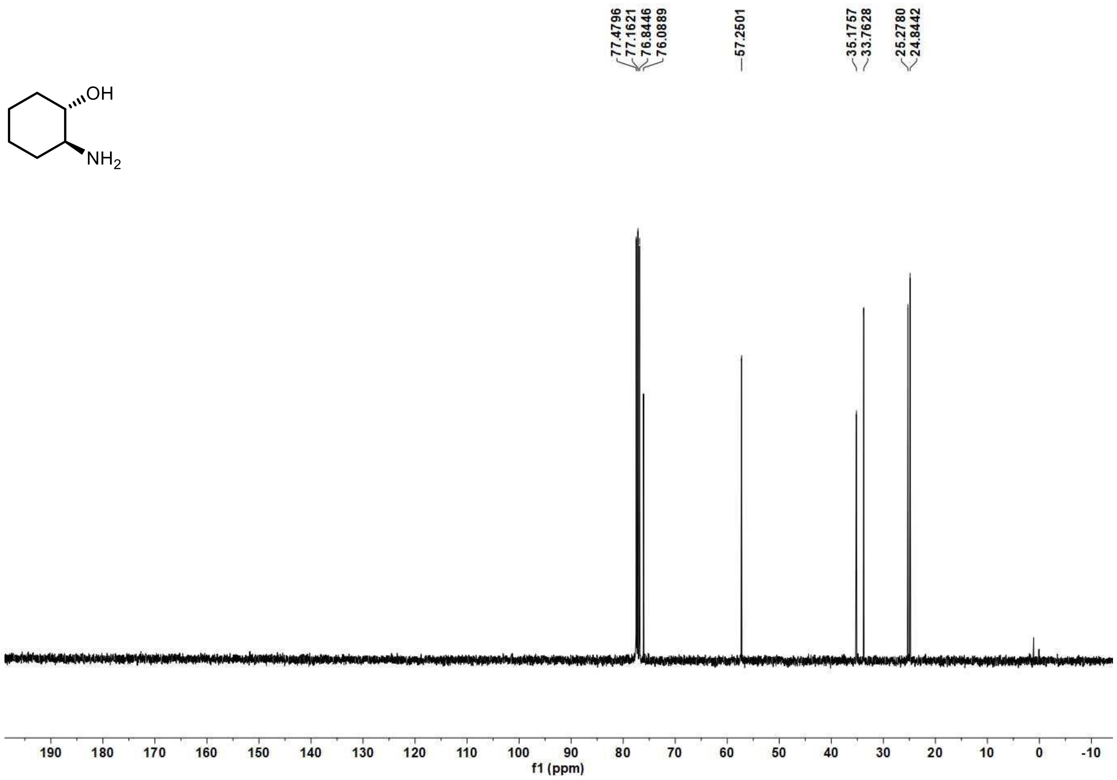
^{13}C NMR (101 MHz, $CDCl_3$) of trans-2-aminocyclopentanol (**3e**)



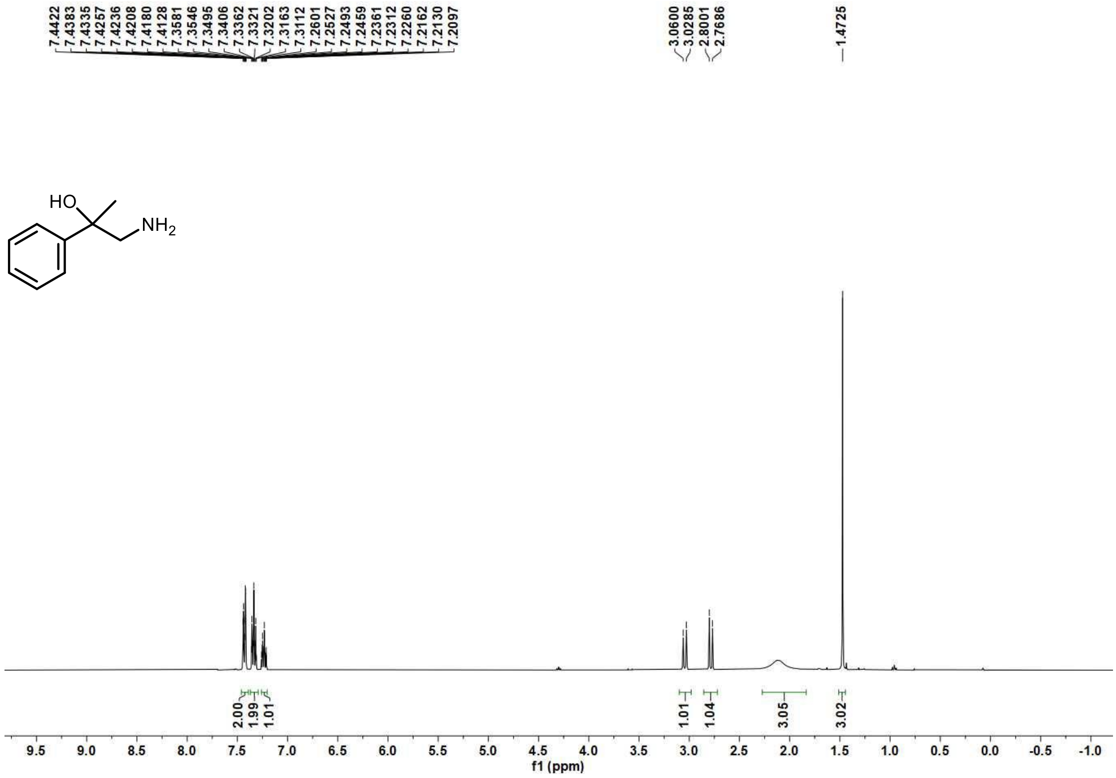
^{1}H NMR (400 MHz, $CDCl_3$) of trans-2-aminocyclohexanol (**3f**)



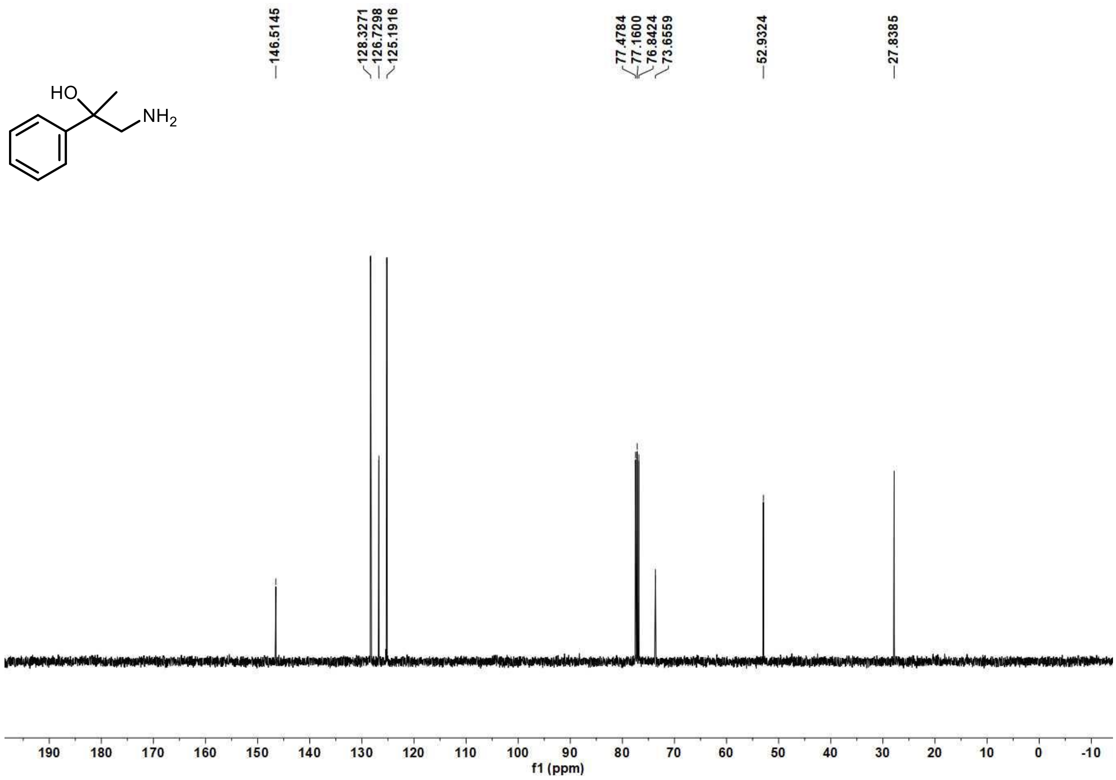
^{13}C NMR (101 MHz, $CDCl_3$) of trans-2-aminocyclohexanol (**3f**)



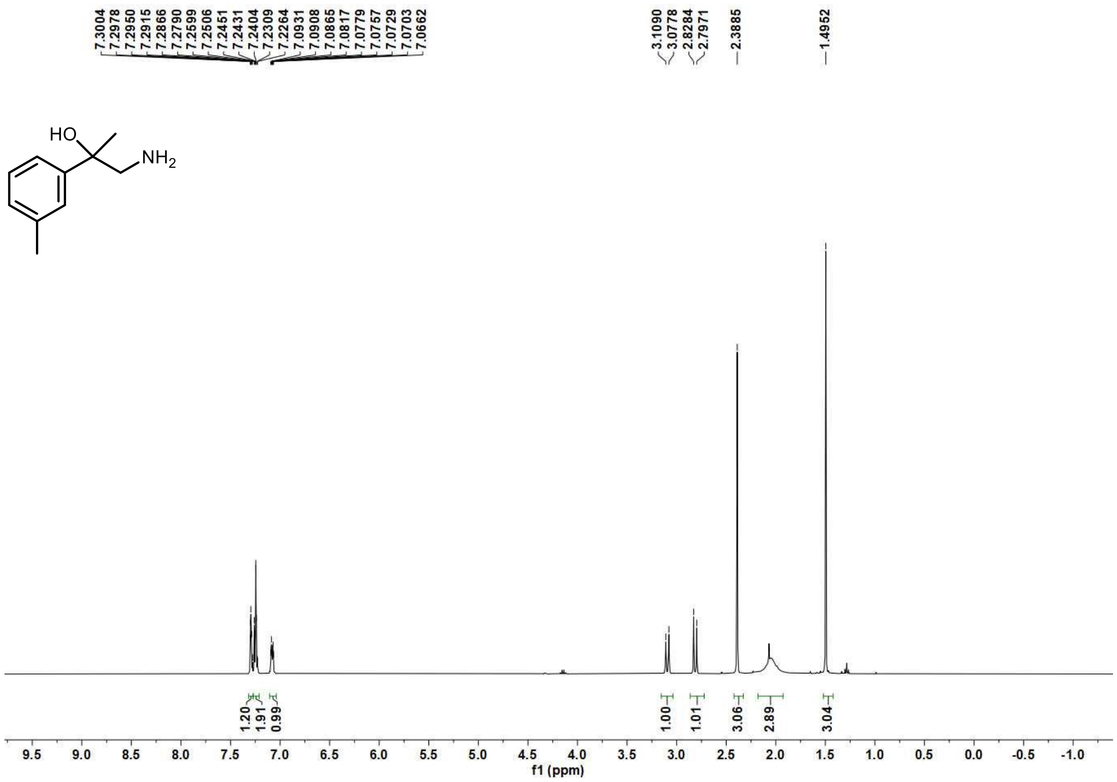
[1]H NMR (400 MHz, $CDCl_3$) of 1-amino-2-phenylpropan-2-ol (**3g**)



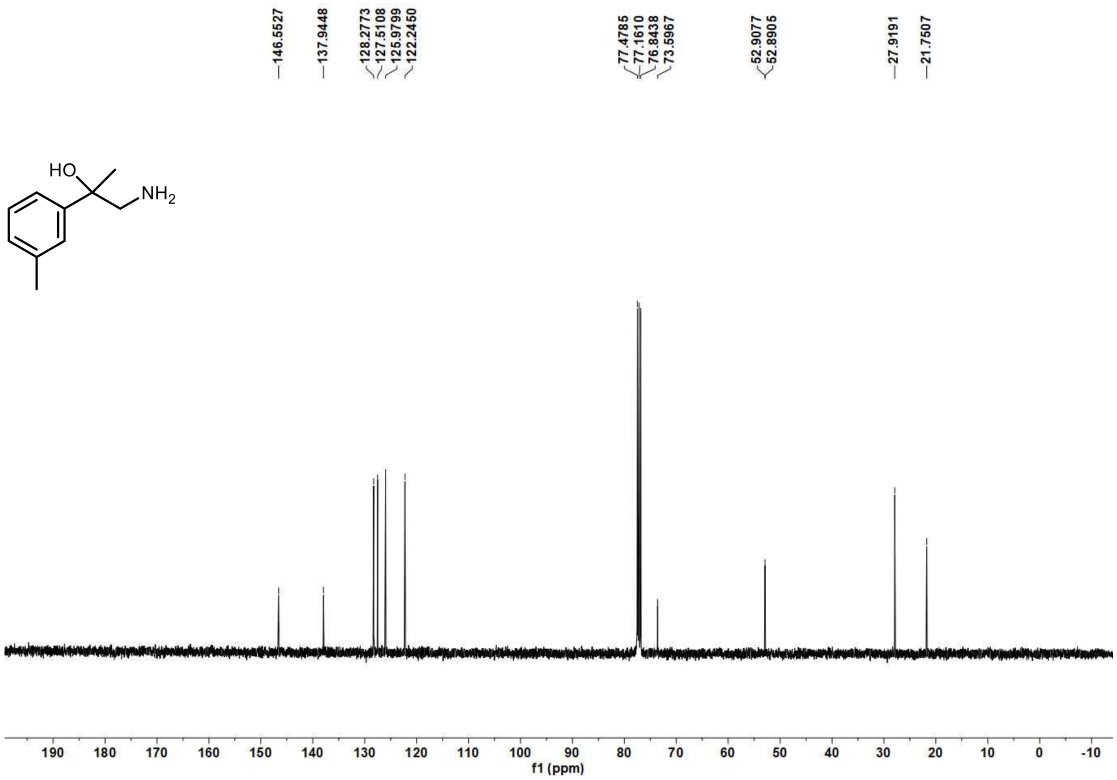
[13]C NMR (101 MHz, $CDCl_3$) of 1-amino-2-phenylpropan-2-ol (**3g**)



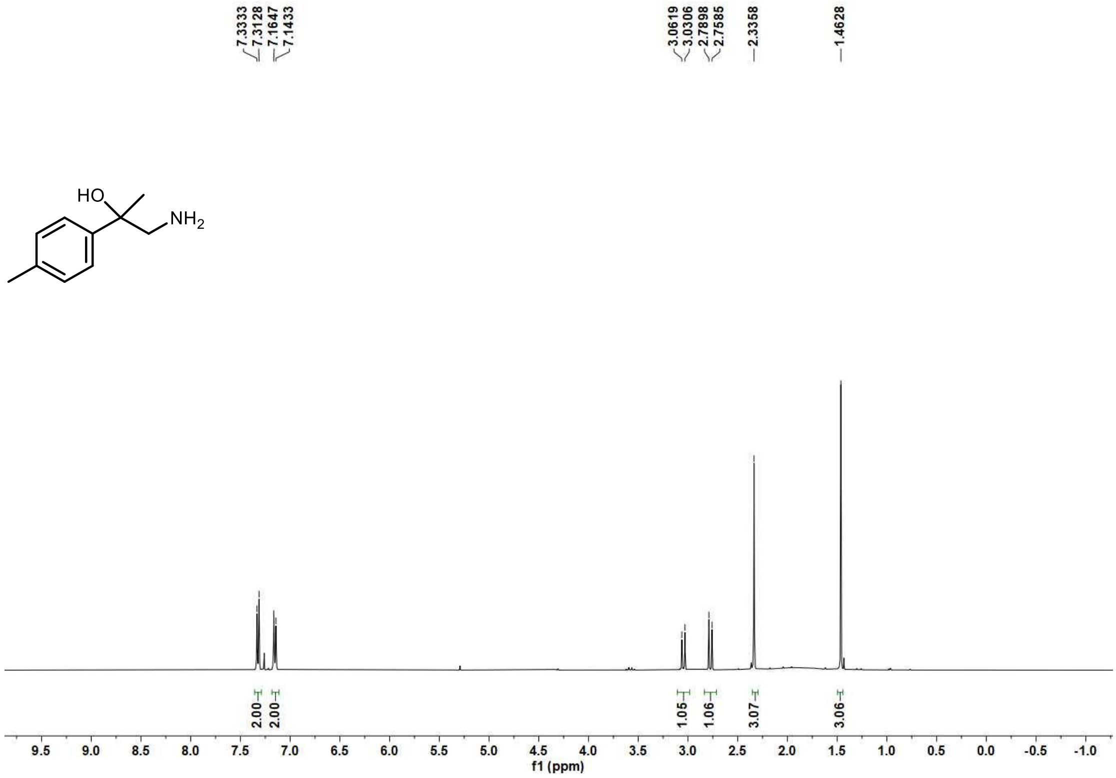
^{1}H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(m-tolyl)propan-2-ol (**3h**)



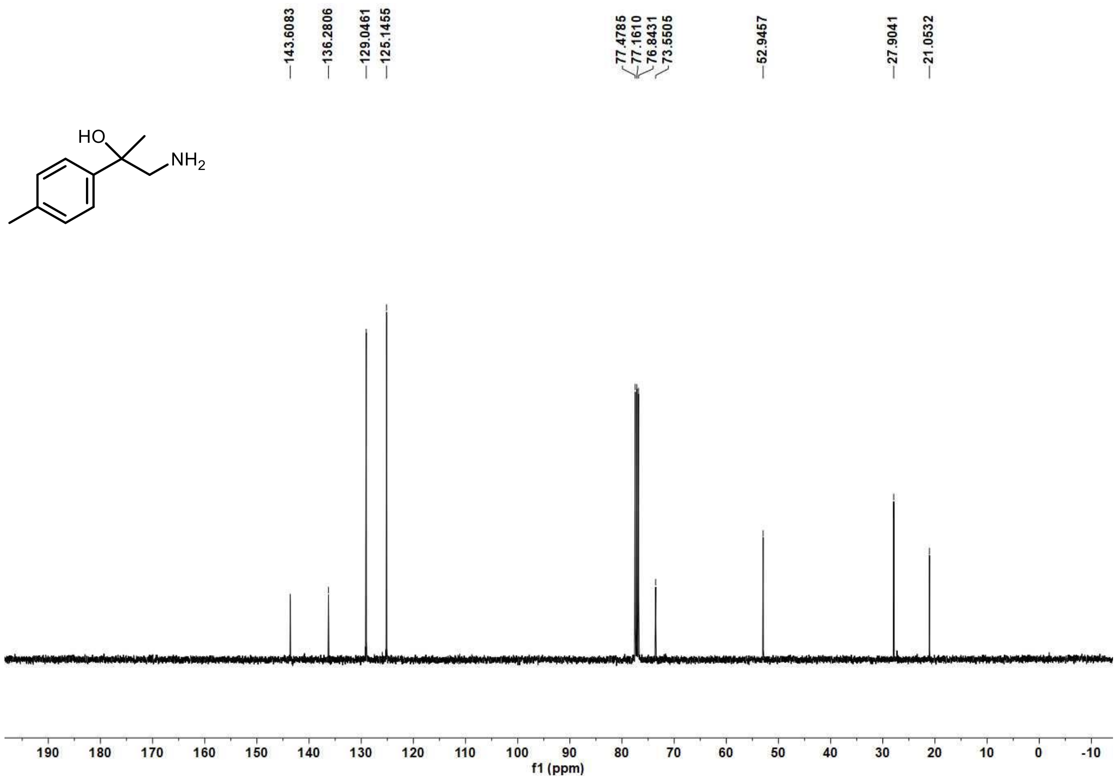
^{13}C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(m-tolyl)propan-2-ol (**3h**)



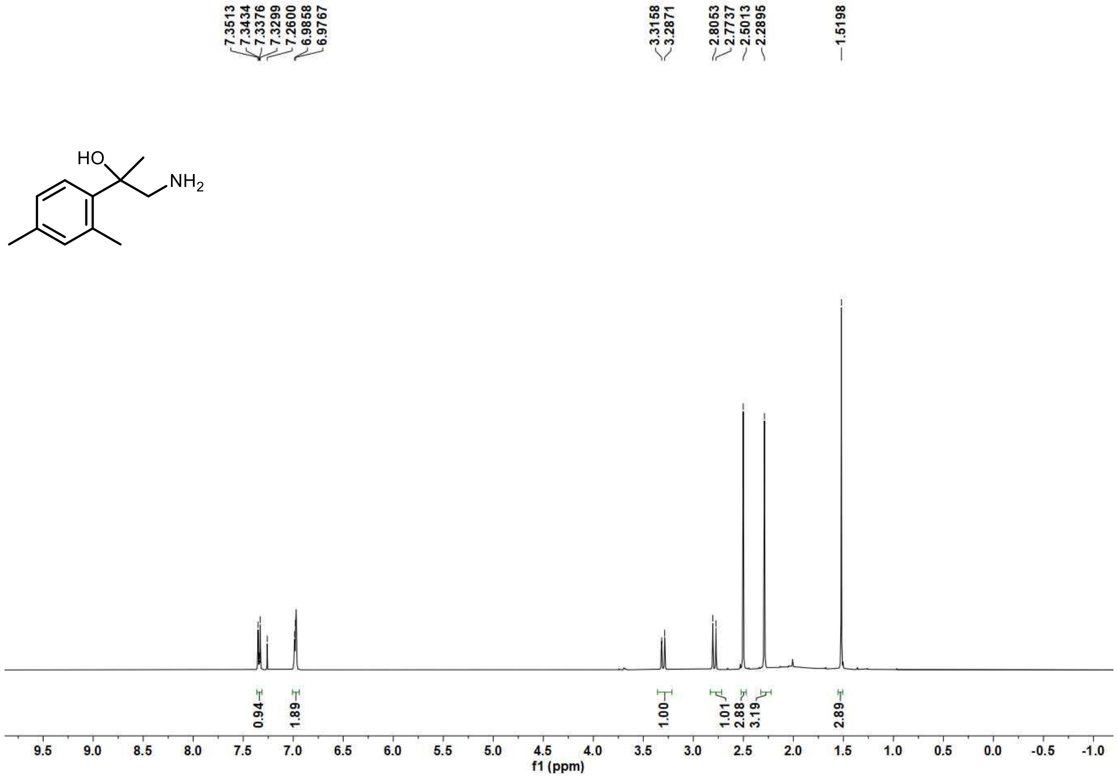
^{1}H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(p-tolyl)propan-2-ol (**3i**)



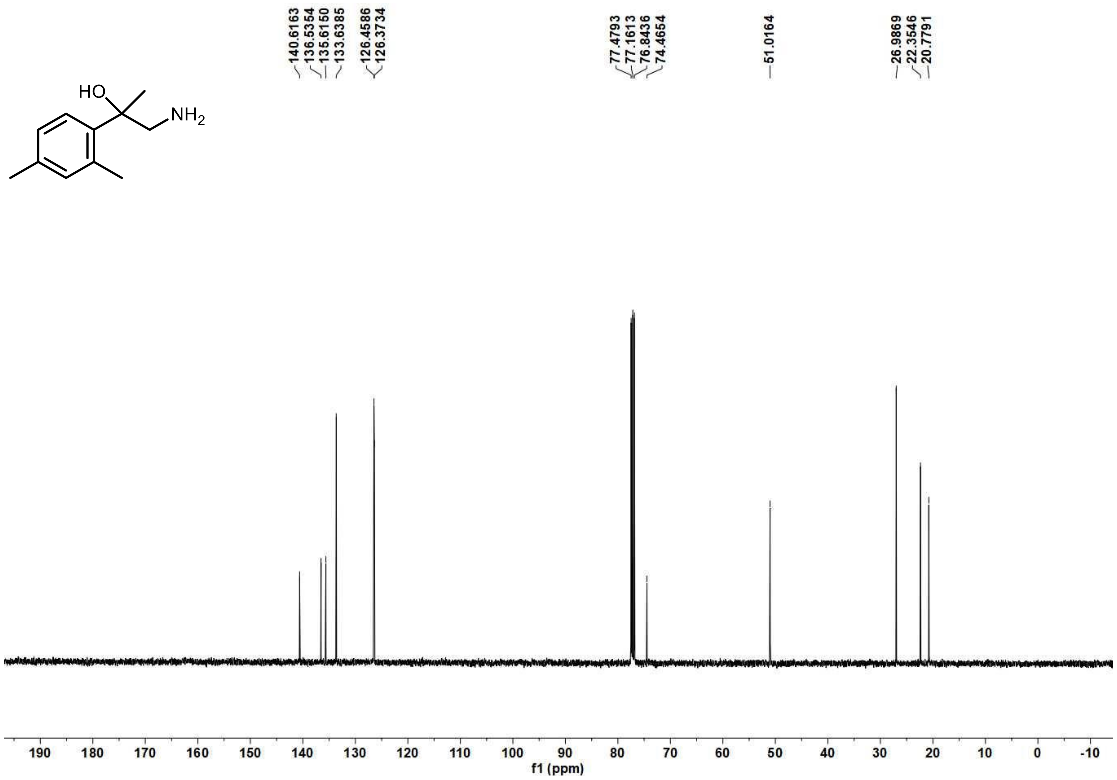
^{13}C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(p-tolyl)propan-2-ol (**3i**)



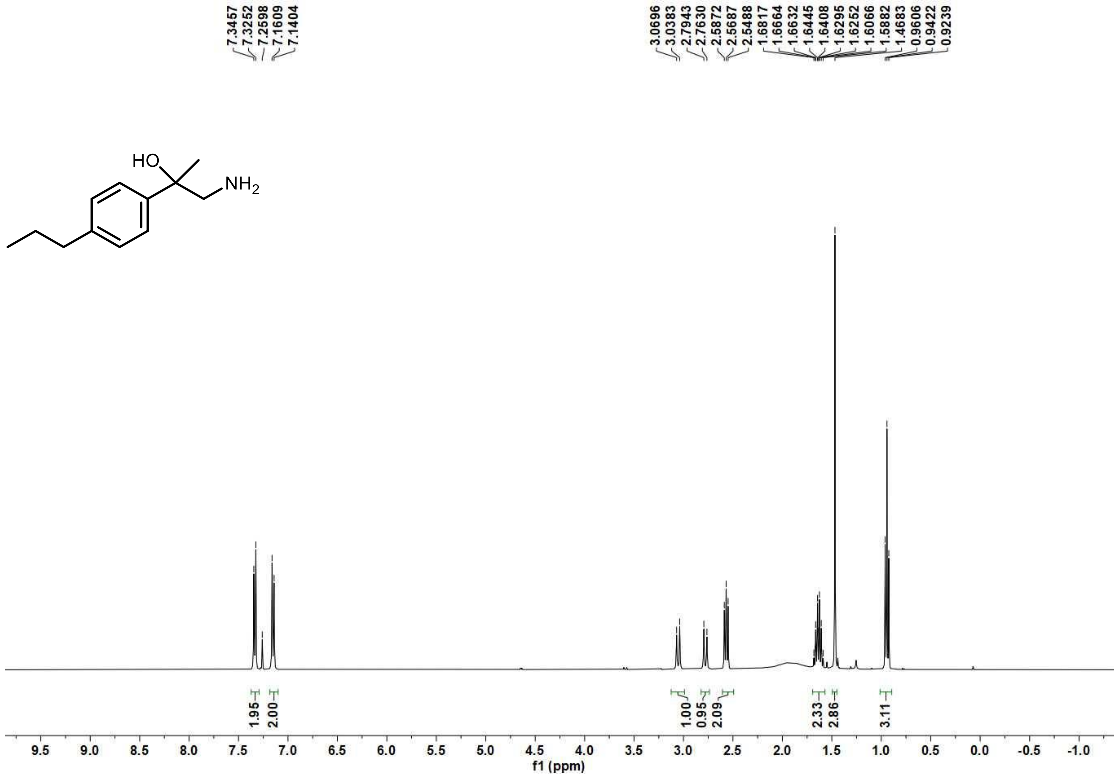
^{1}H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(2,4-dimethylphenyl)propan-2-ol (**3j**)



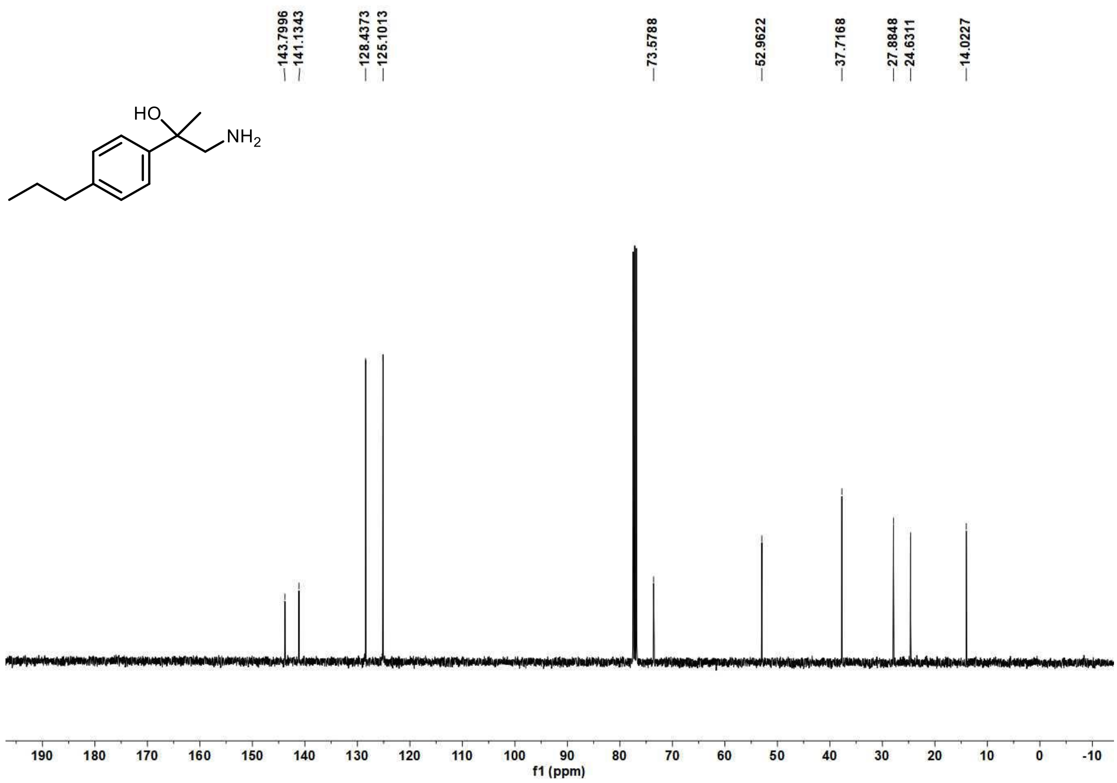
^{13}C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(2,4-dimethylphenyl)propan-2-ol (**3j**)



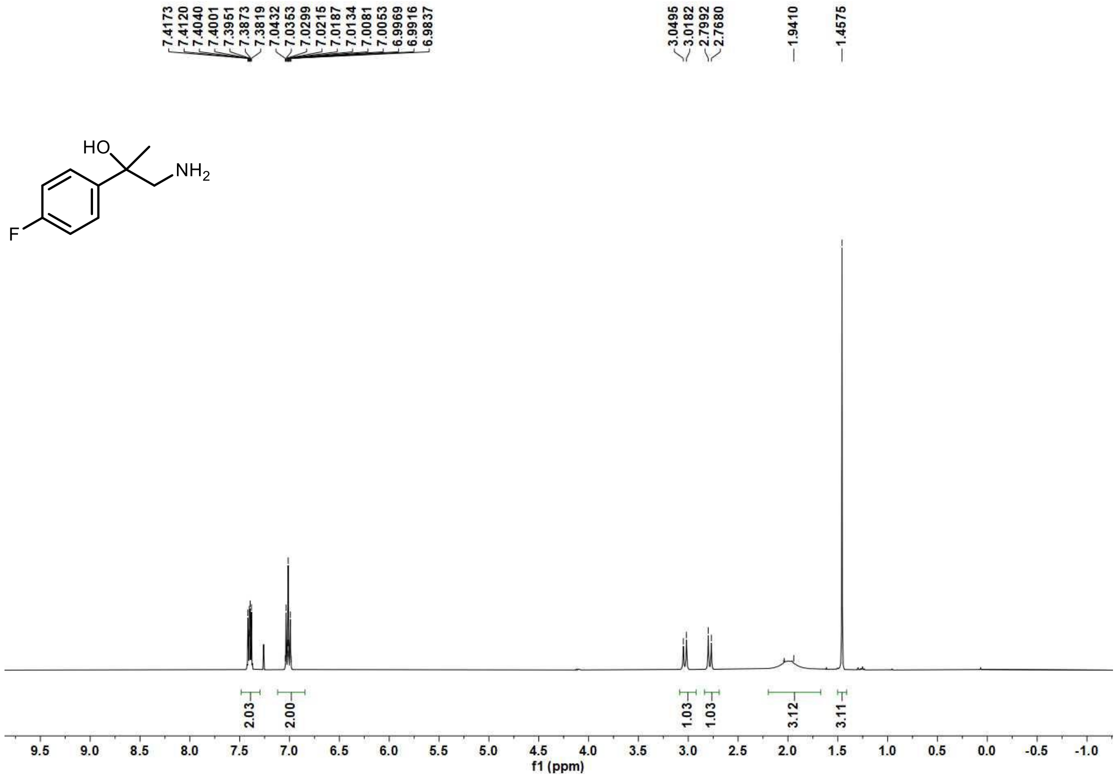
^{1}H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(4-propylphenyl)propan-2-ol (**3k**)



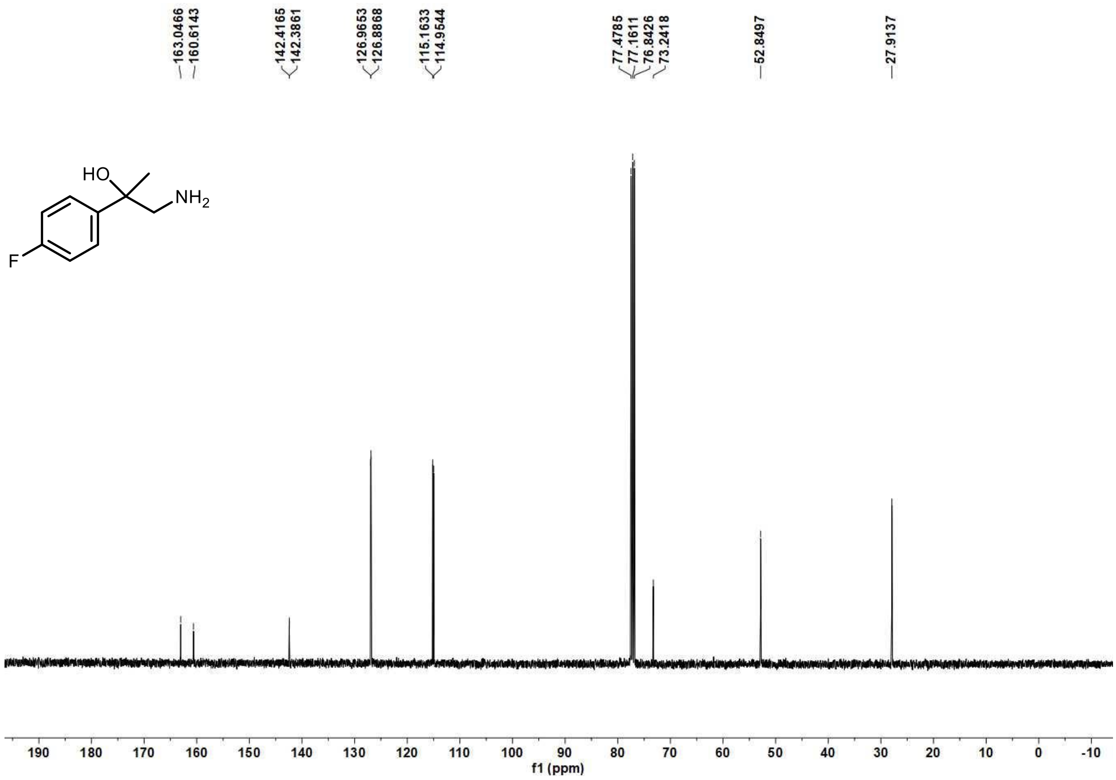
^{13}C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(4-propylphenyl)propan-2-ol (**3k**)



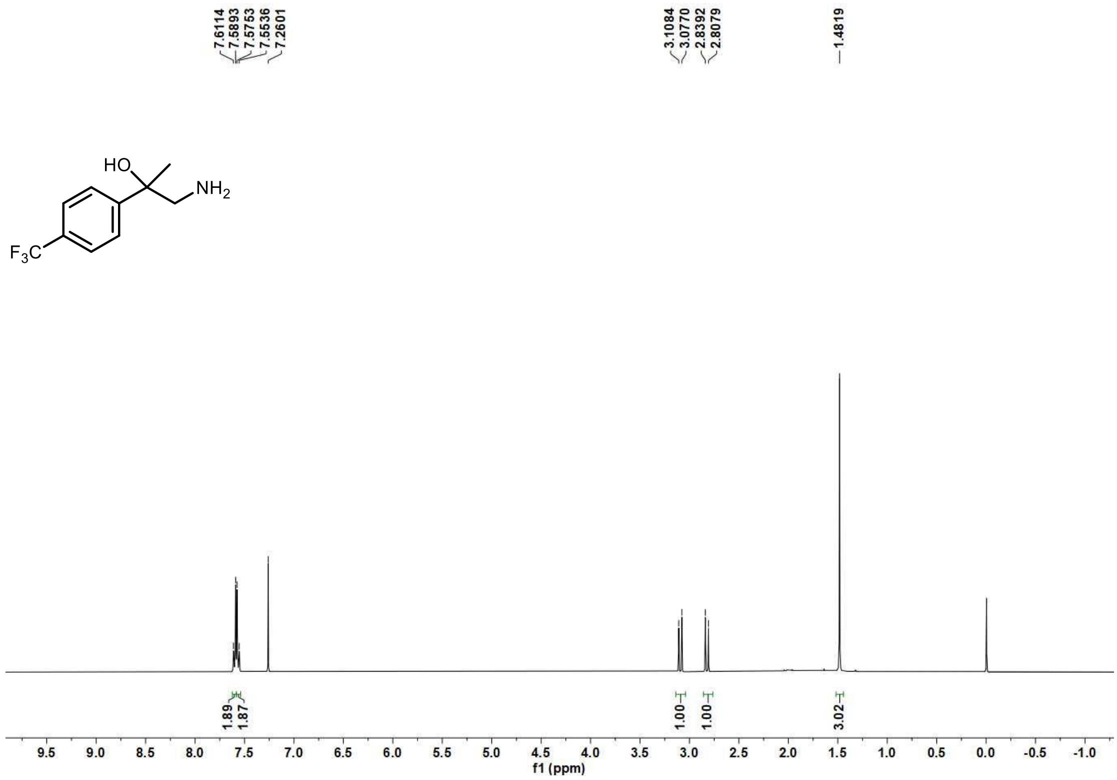
^{1}H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(4-fluorophenyl)propan-2-ol (**3l**)



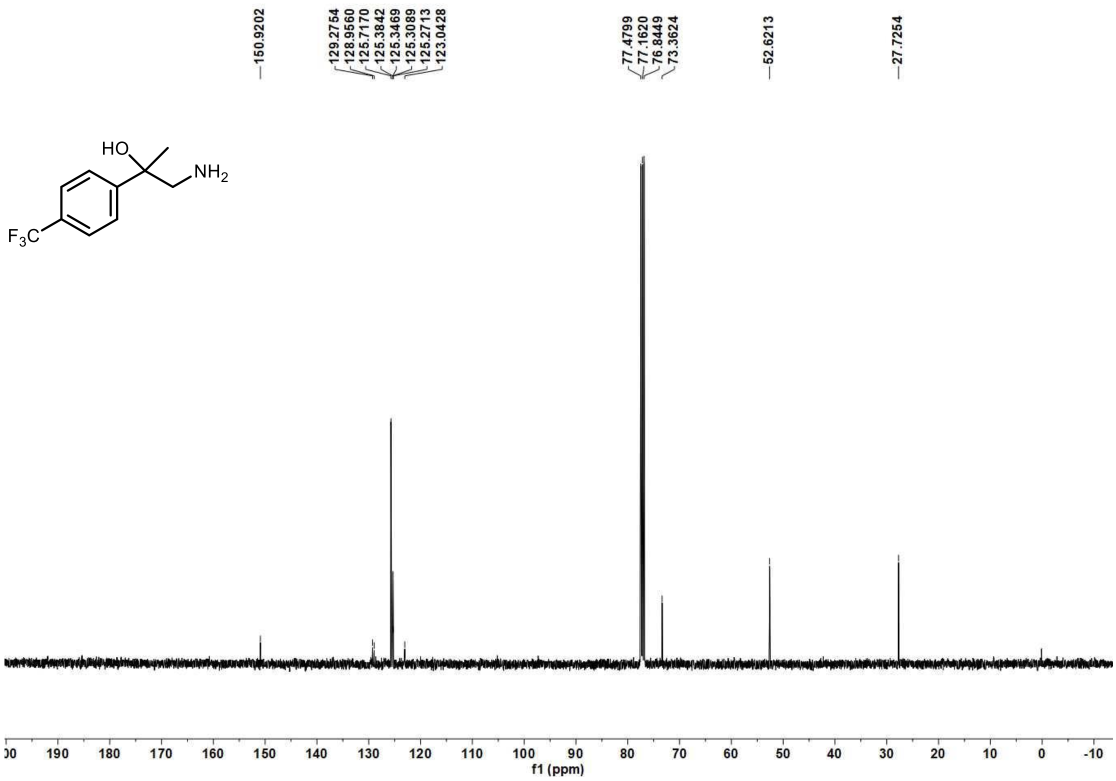
^{13}C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(4-fluorophenyl)propan-2-ol (**3l**)



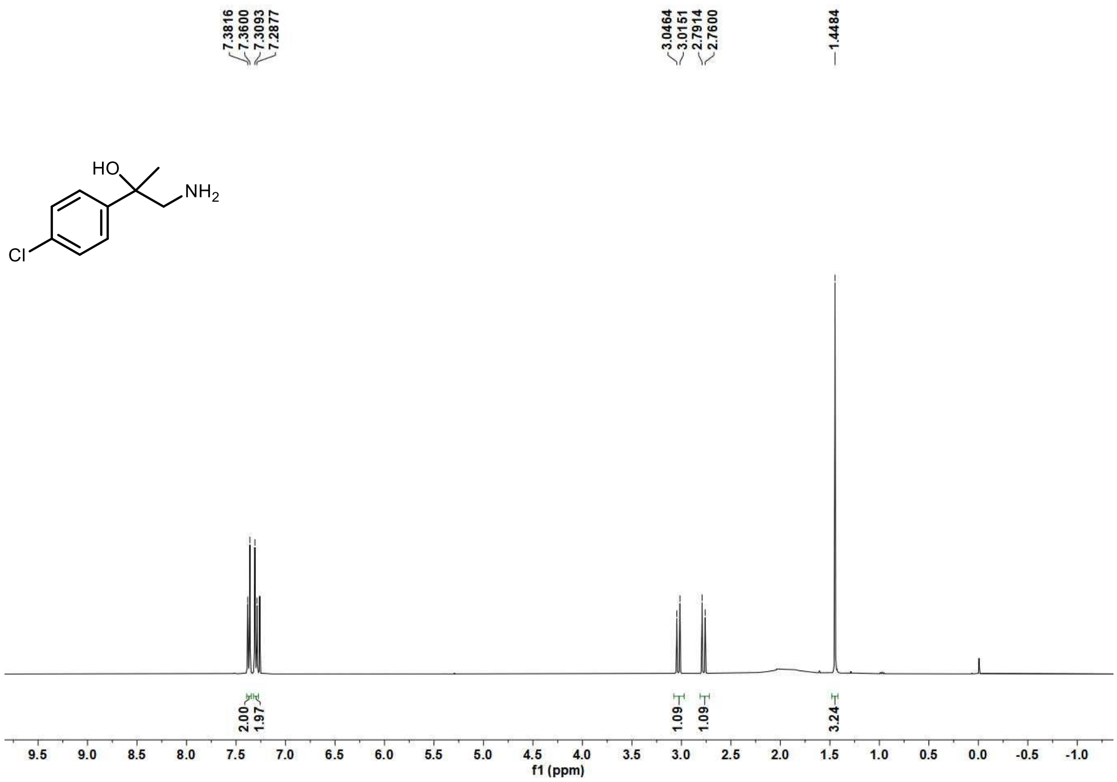
[1]H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(4-(trifluoromethyl)phenyl)propan-2-ol (**3m**)



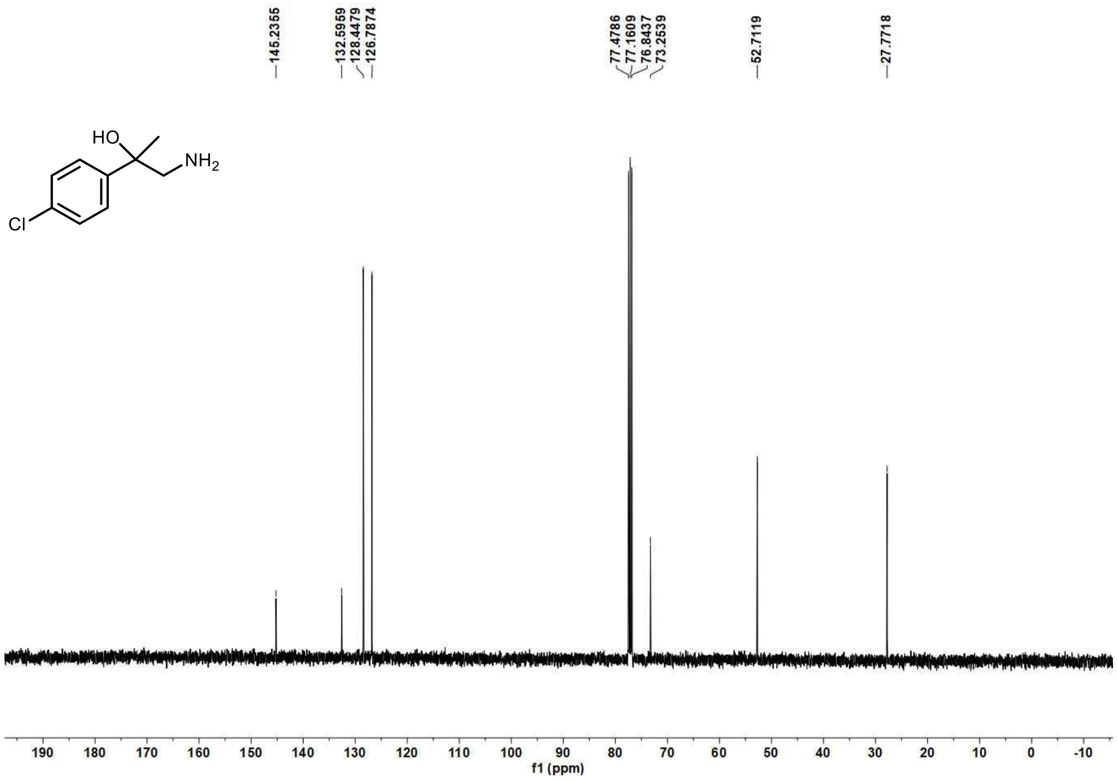
[13]C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(4-(trifluoromethyl)phenyl)propan-2-ol (**3m**)



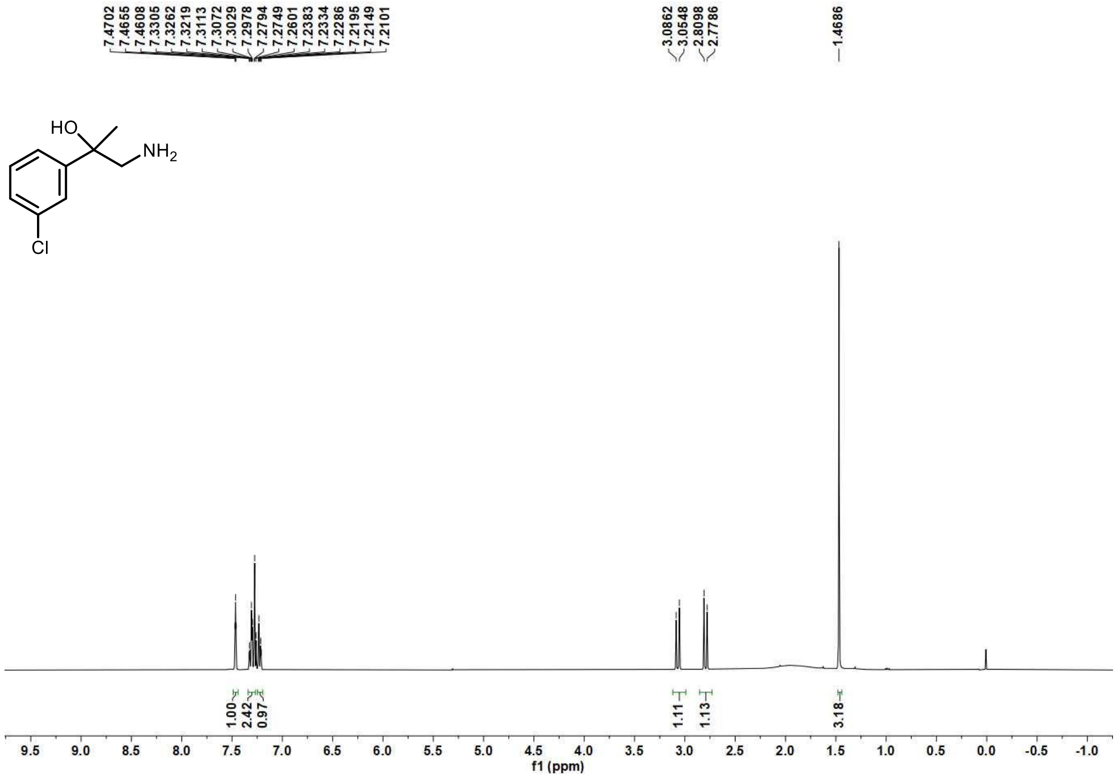
[1]H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(4-chlorophenyl)propan-2-ol (**3n**)



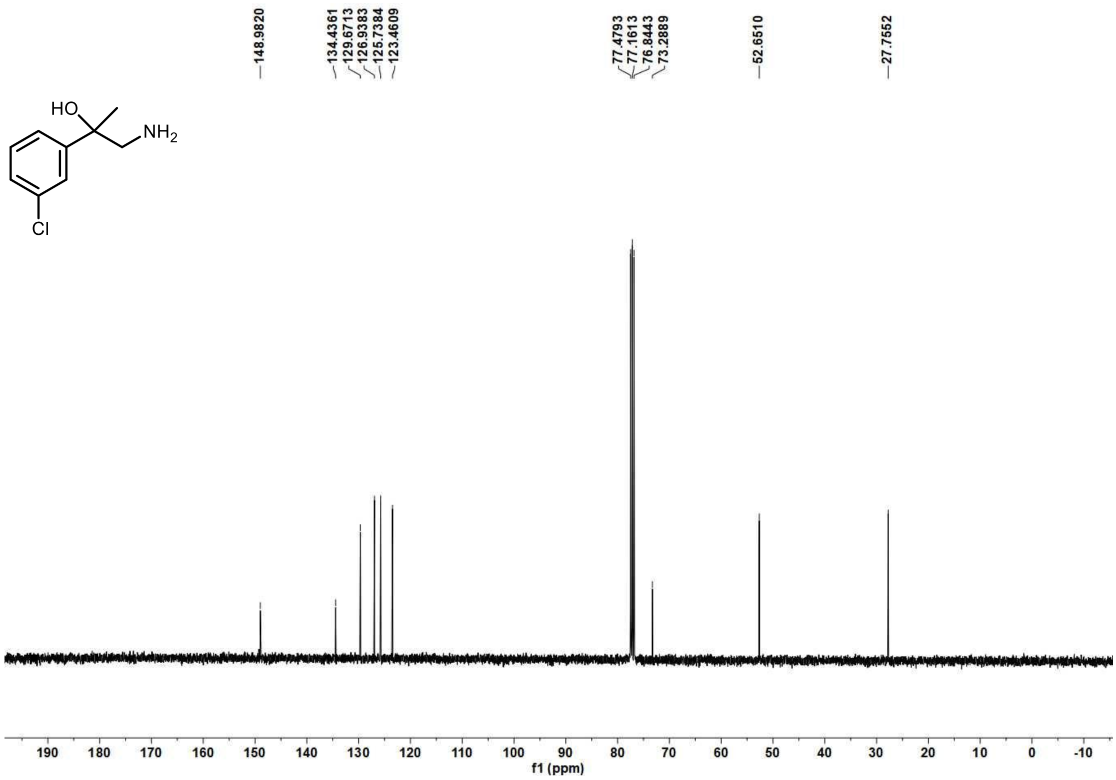
[13]C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(4-chlorophenyl)propan-2-ol (**3n**)



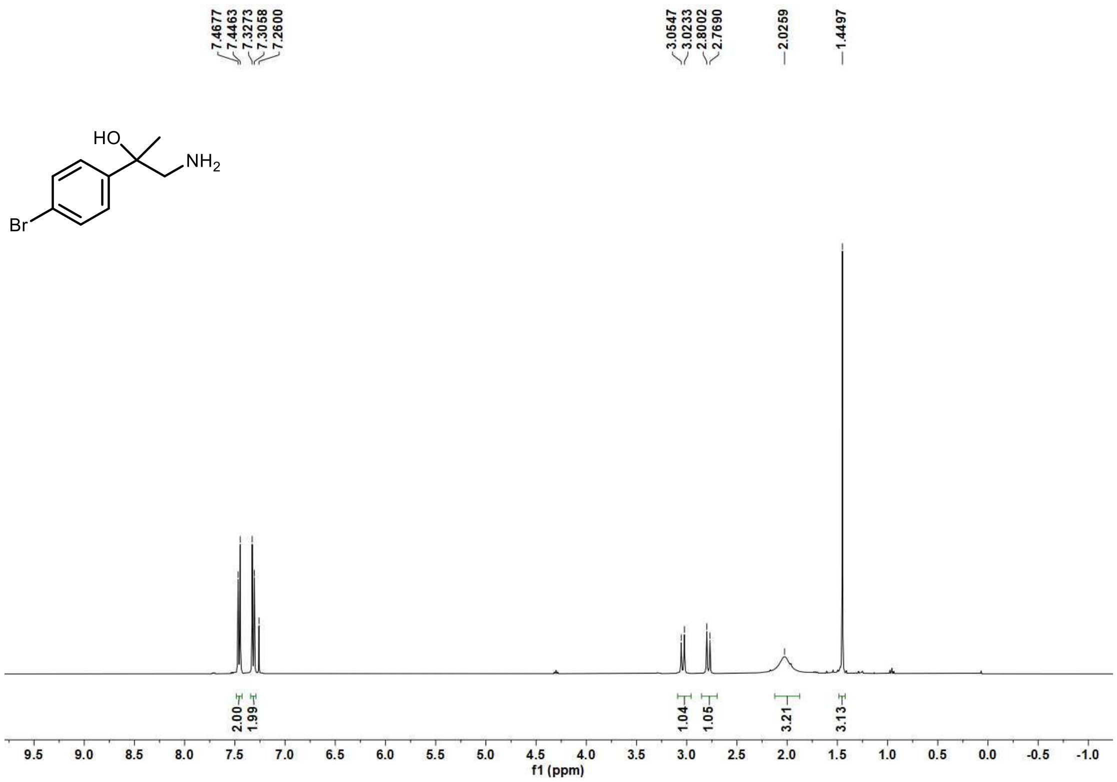
[1]H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(3-chlorophenyl)propan-2-ol (**3o**)



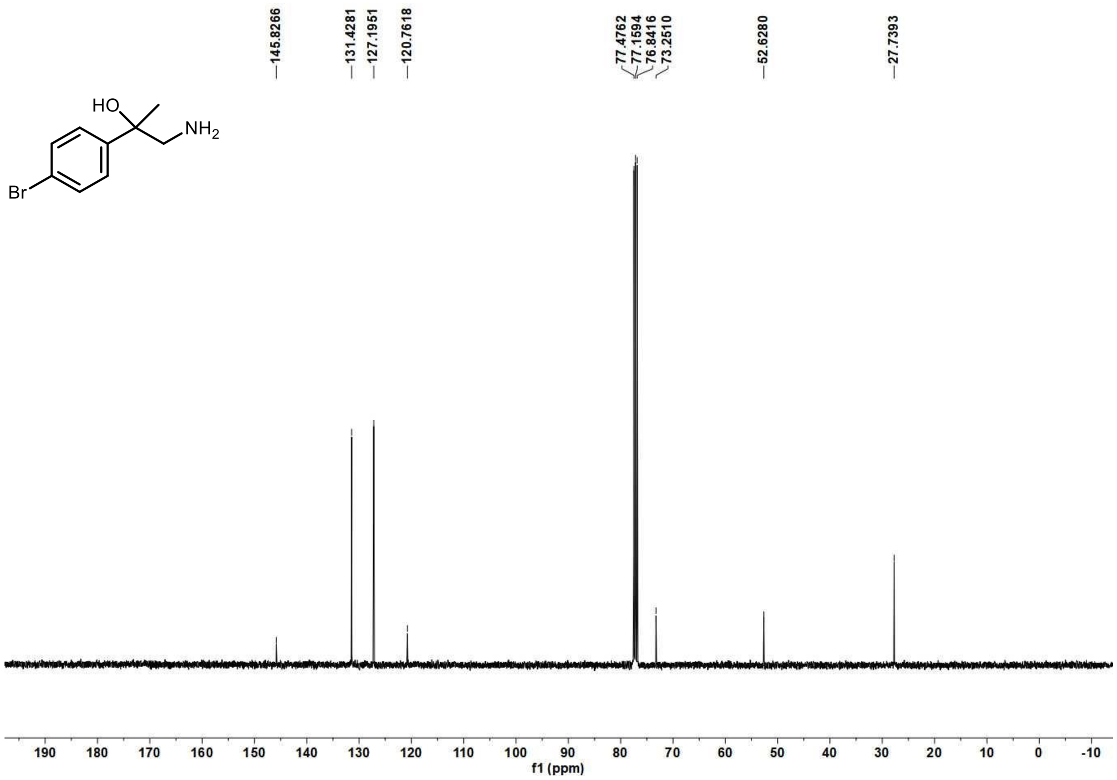
[13]C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(3-chlorophenyl)propan-2-ol (**3o**)



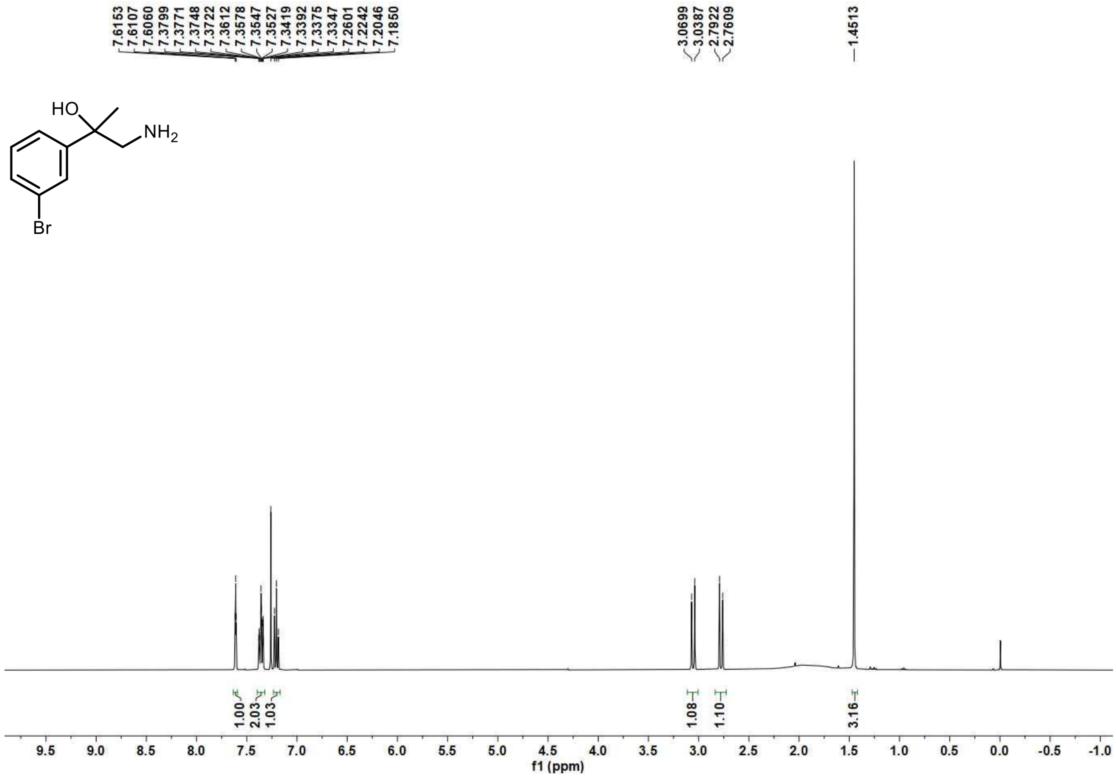
^{1}H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(4-bromophenyl)propan-2-ol (**3p**)



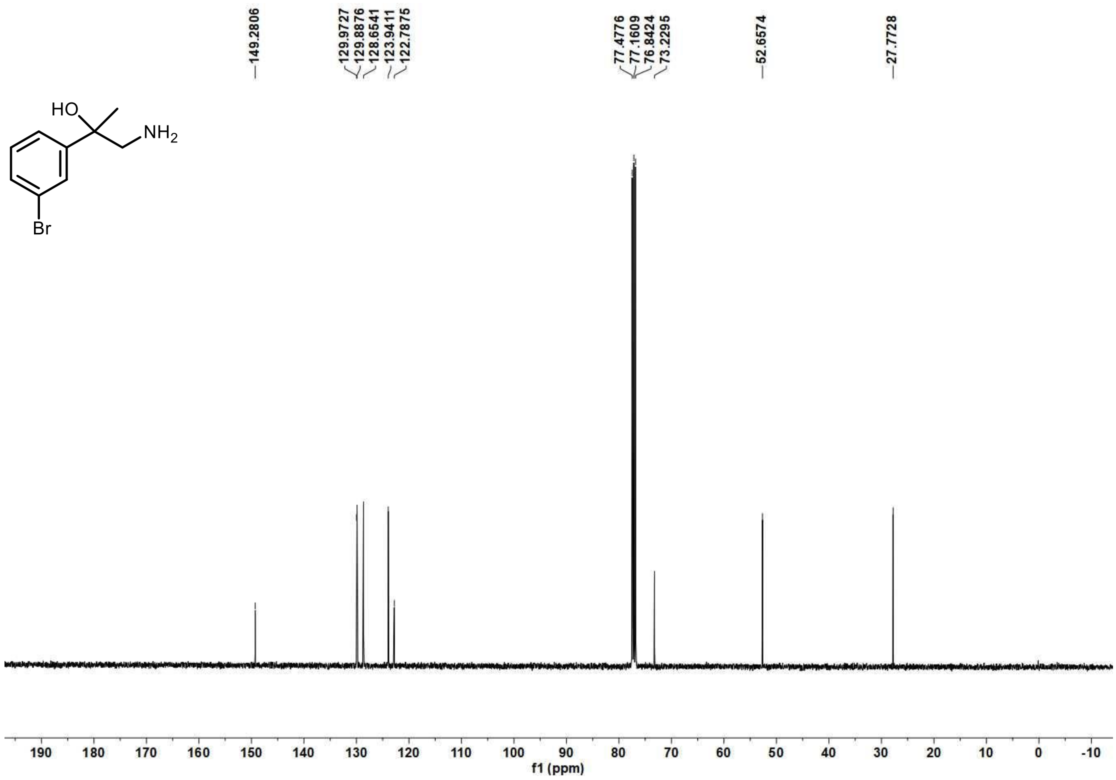
^{13}C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(4-bromophenyl)propan-2-ol (**3p**)



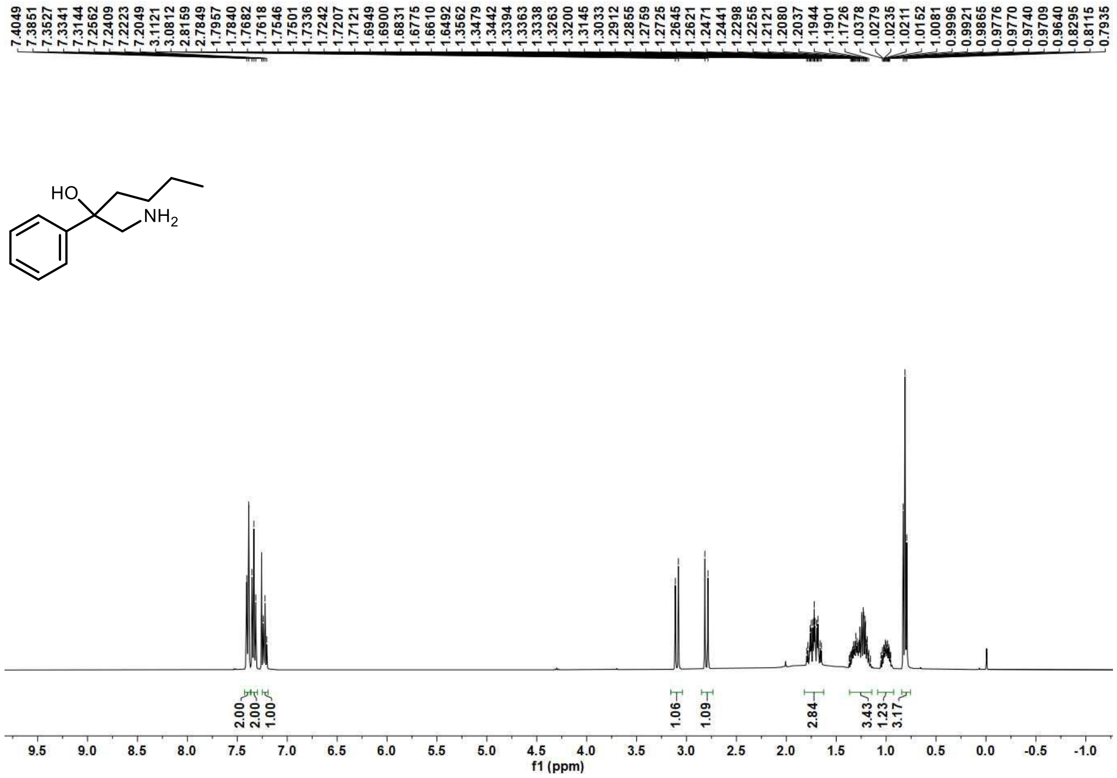
[1]H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(3-bromophenyl)propan-2-ol (**3q**)



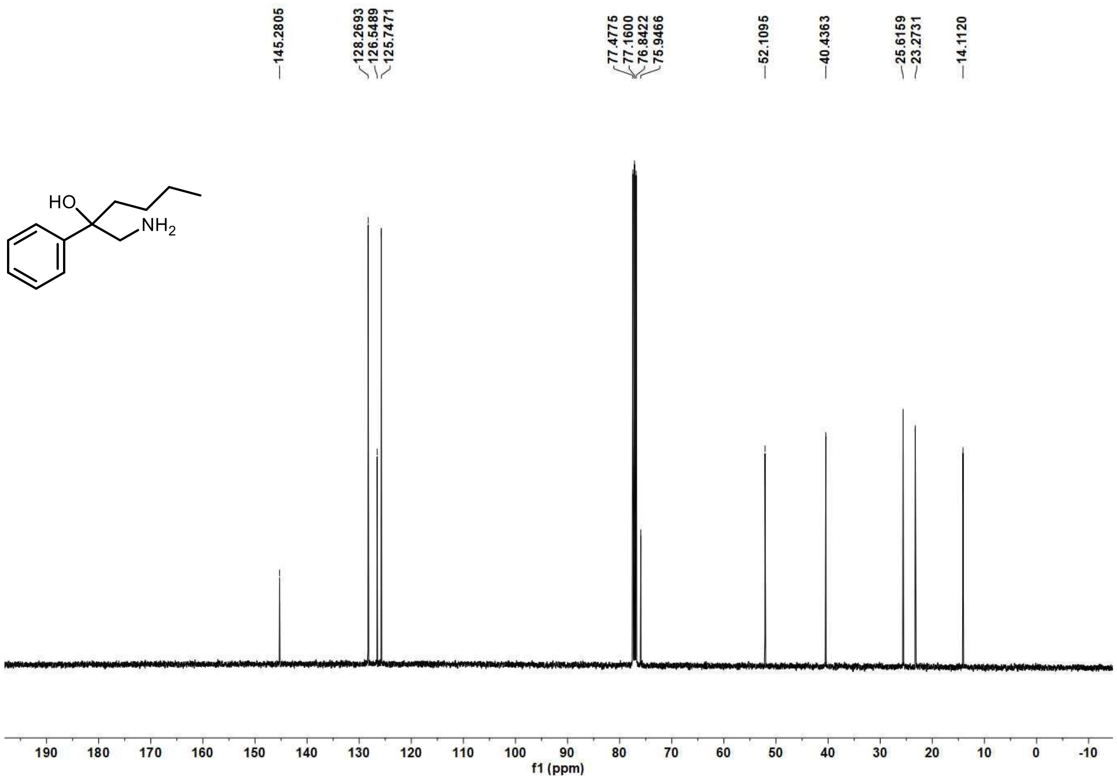
[13]C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(3-bromophenyl)propan-2-ol (**3q**)



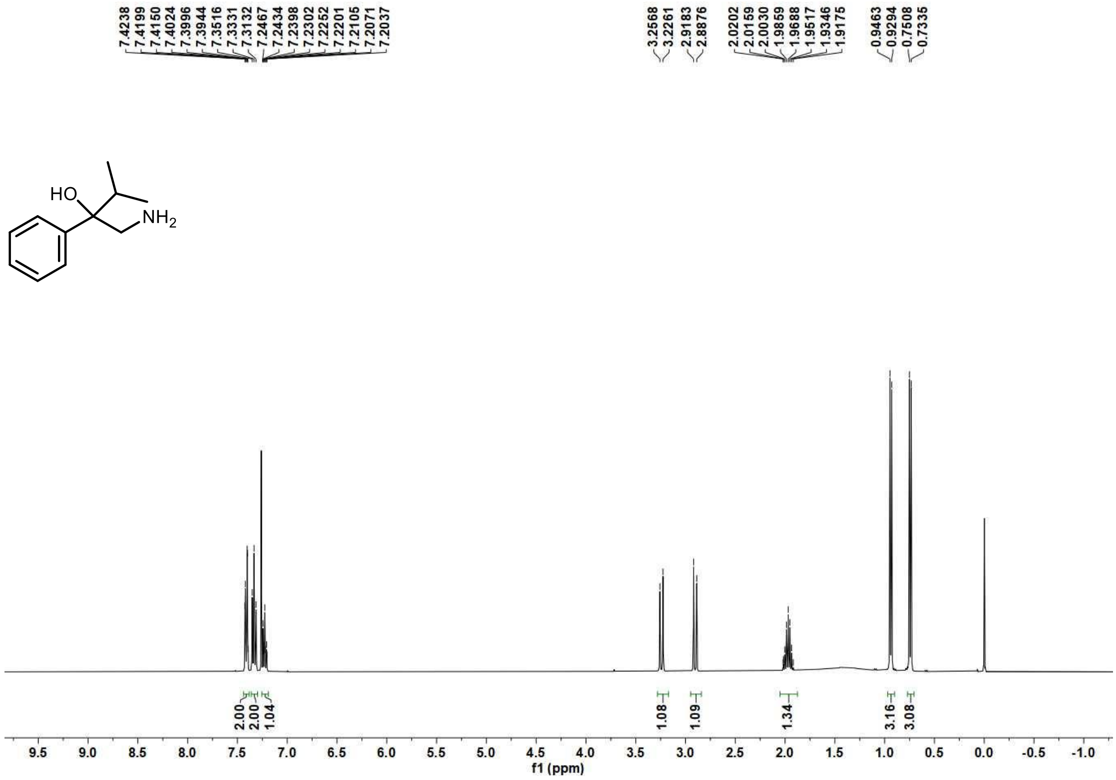
[1]H NMR (400 MHz, $CDCl_3$) of 1-amino-2-phenylhexan-2-ol (**3r**)



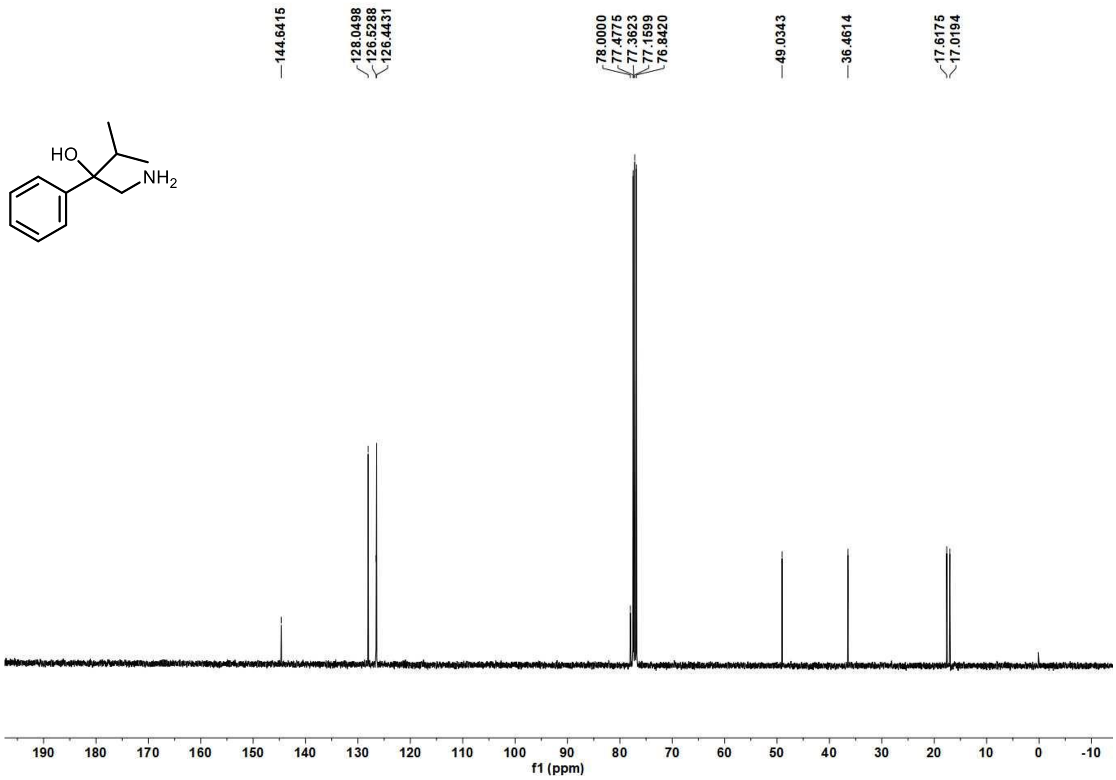
[13]C NMR (101 MHz, $CDCl_3$) of 1-amino-2-phenylhexan-2-ol (**3r**)



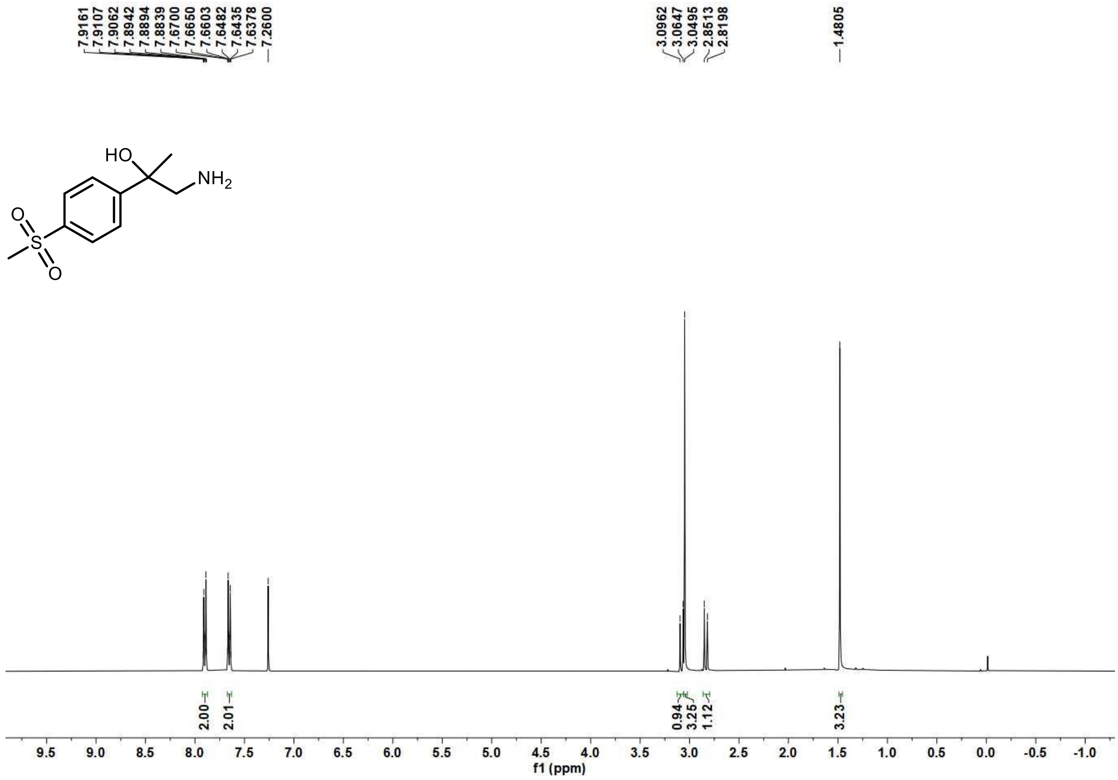
^{1}H NMR (400 MHz, $CDCl_3$) of (1-amino-3-methyl-2-phenylbutan-2-ol (**3s**)



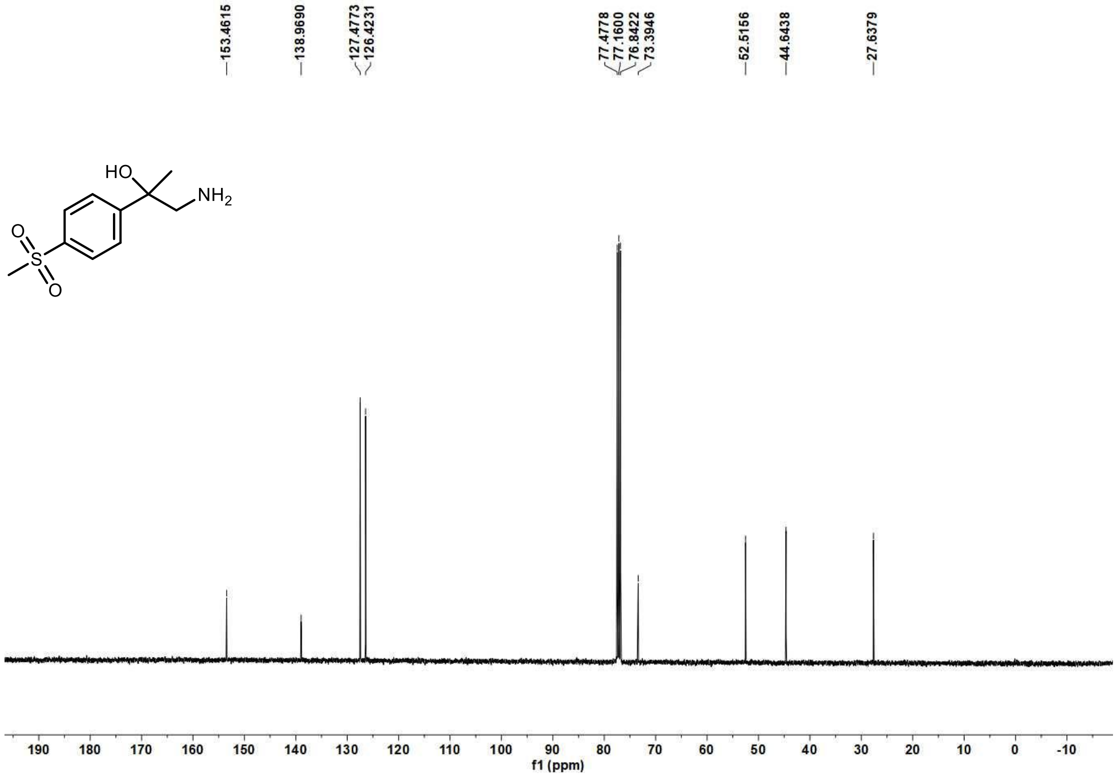
^{13}C NMR (101 MHz, $CDCl_3$) of (1-amino-3-methyl-2-phenylbutan-2-ol (**3s**)



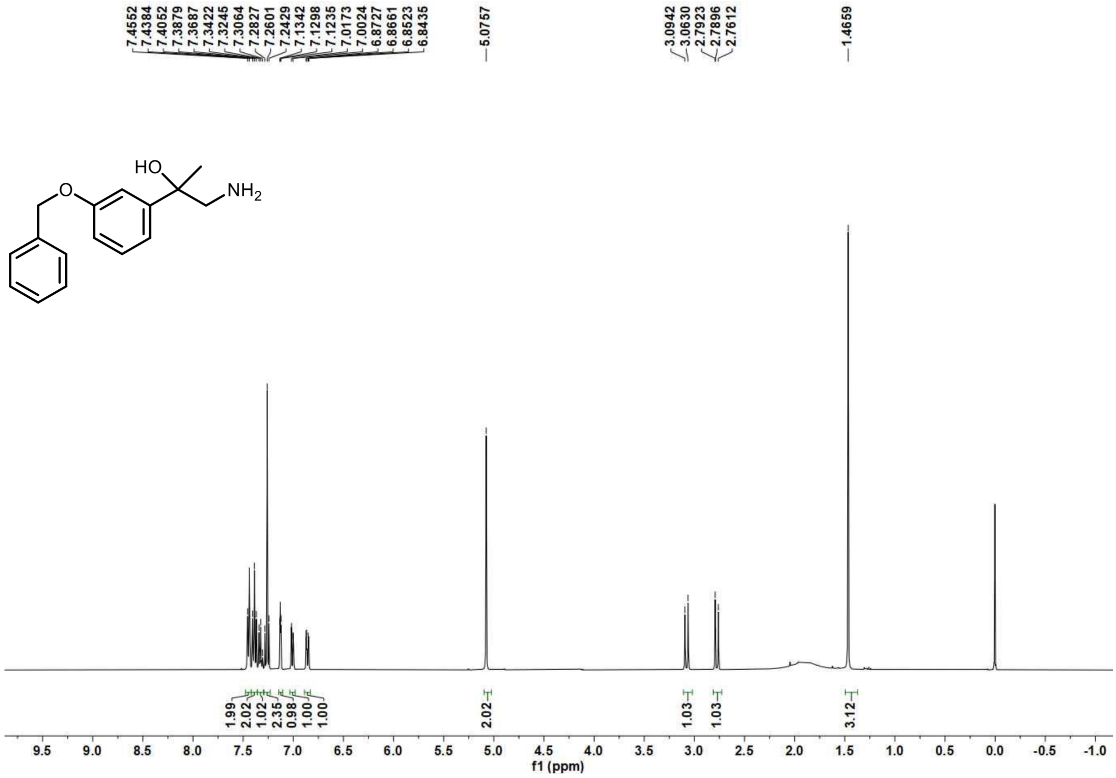
[1]H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(4-(methylsulfonyl)phenyl)propan-2-ol (**3t**)



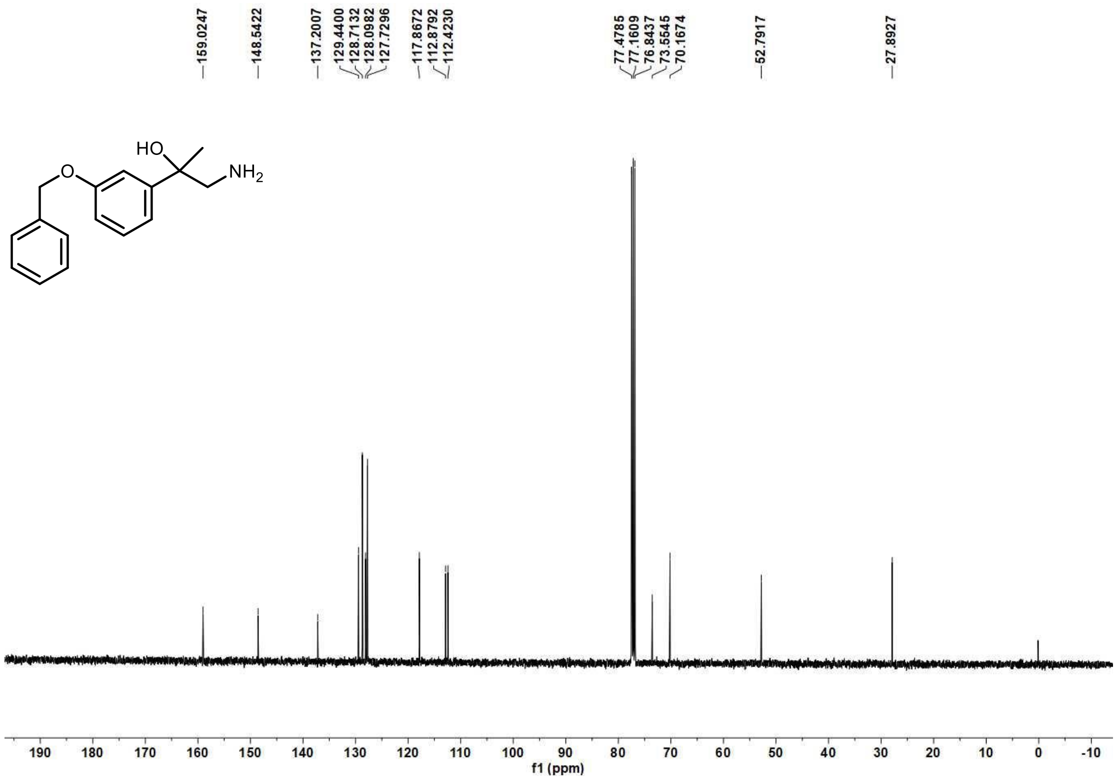
[13]C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(4-(methylsulfonyl)phenyl)propan-2-ol (**3t**)



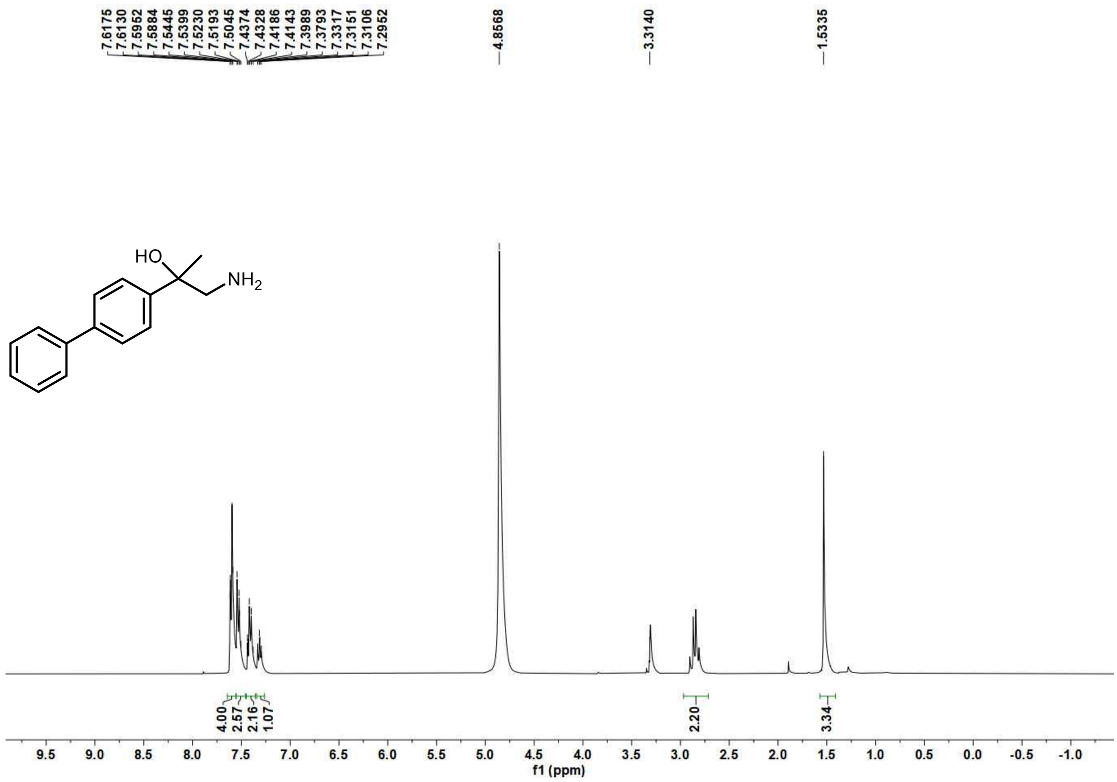
[1]H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(3-(benzyloxy)phenyl)propan-2-ol (**3u**)



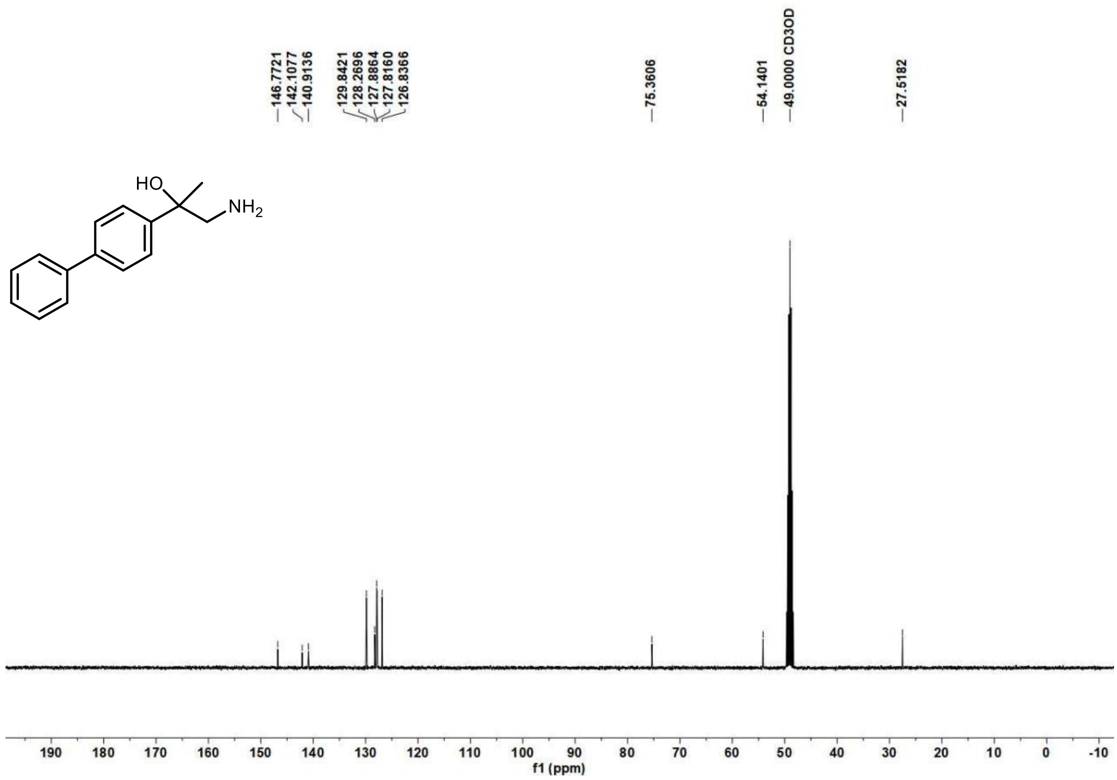
[13]C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(3-(benzyloxy)phenyl)propan-2-ol (**3u**)



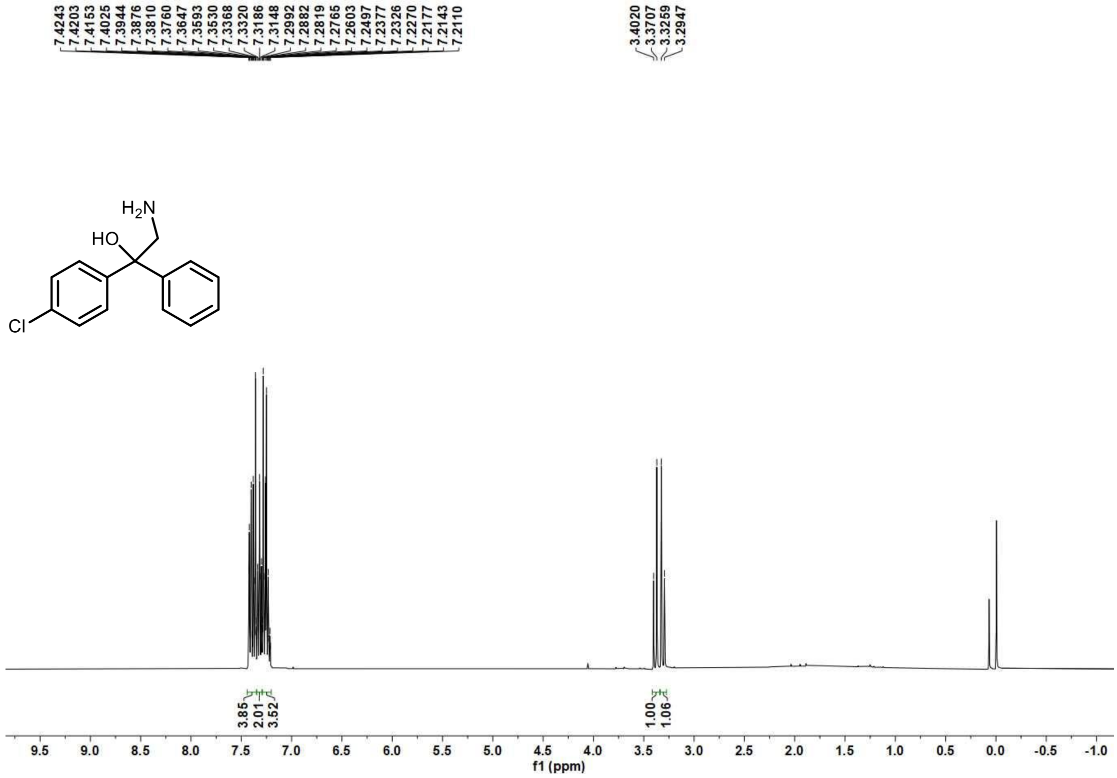
^{1}H NMR (400 MHz, CD_3OD) of 2-([1,1'-biphenyl]-4-yl)-1-aminopropan-2-ol (**3v**)



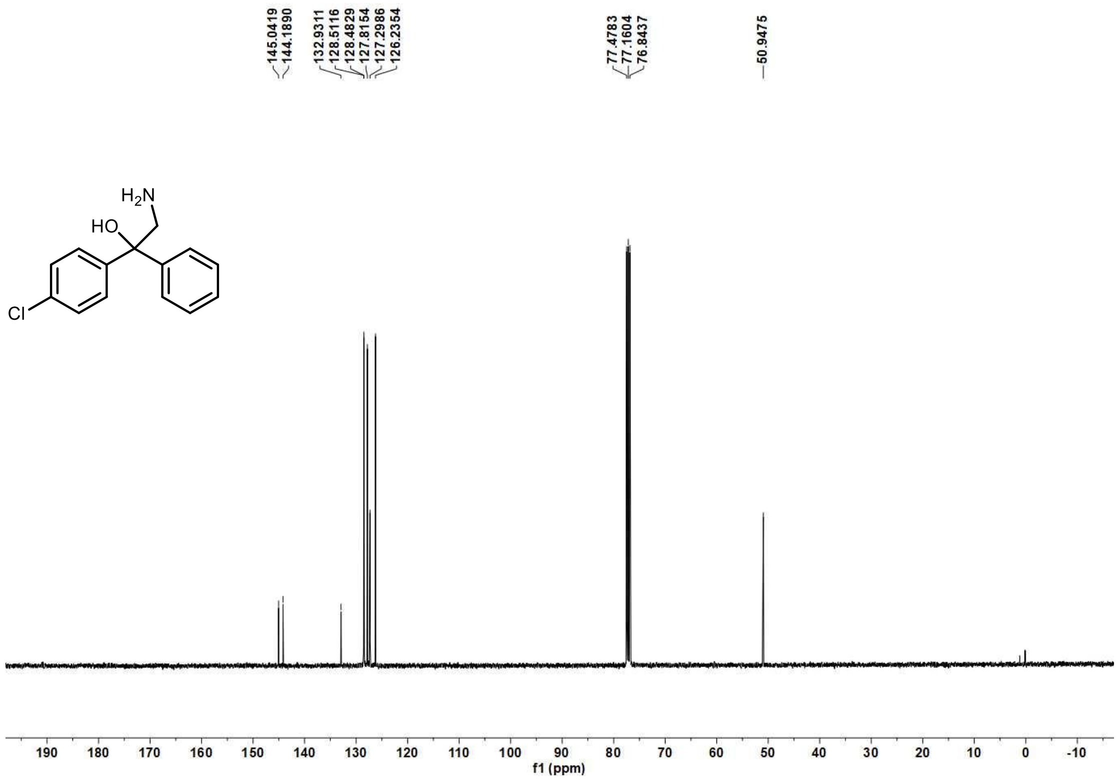
^{13}C NMR (101 MHz, CD_3OD) of 2-([1,1'-biphenyl]-4-yl)-1-aminopropan-2-ol (**3v**)



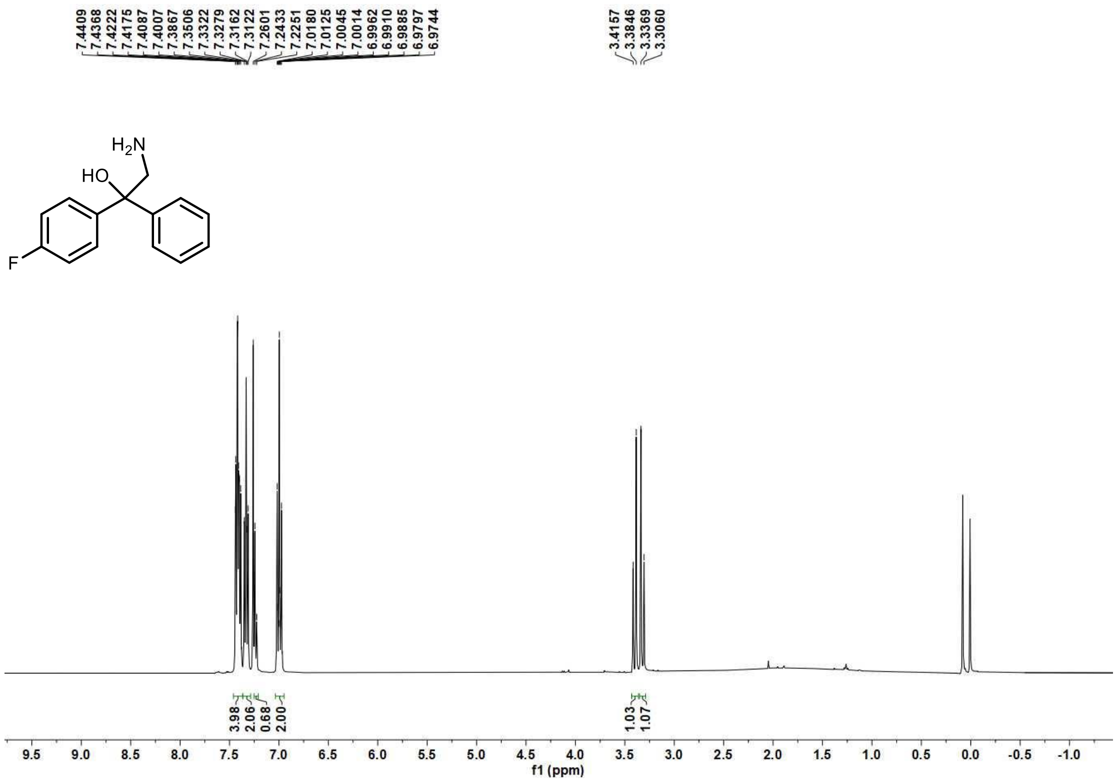
^{1}H NMR (400 MHz, $CDCl_3$) of 2-amino-1-(4-chlorophenyl)-1-phenylethan-1-ol (**3w**)



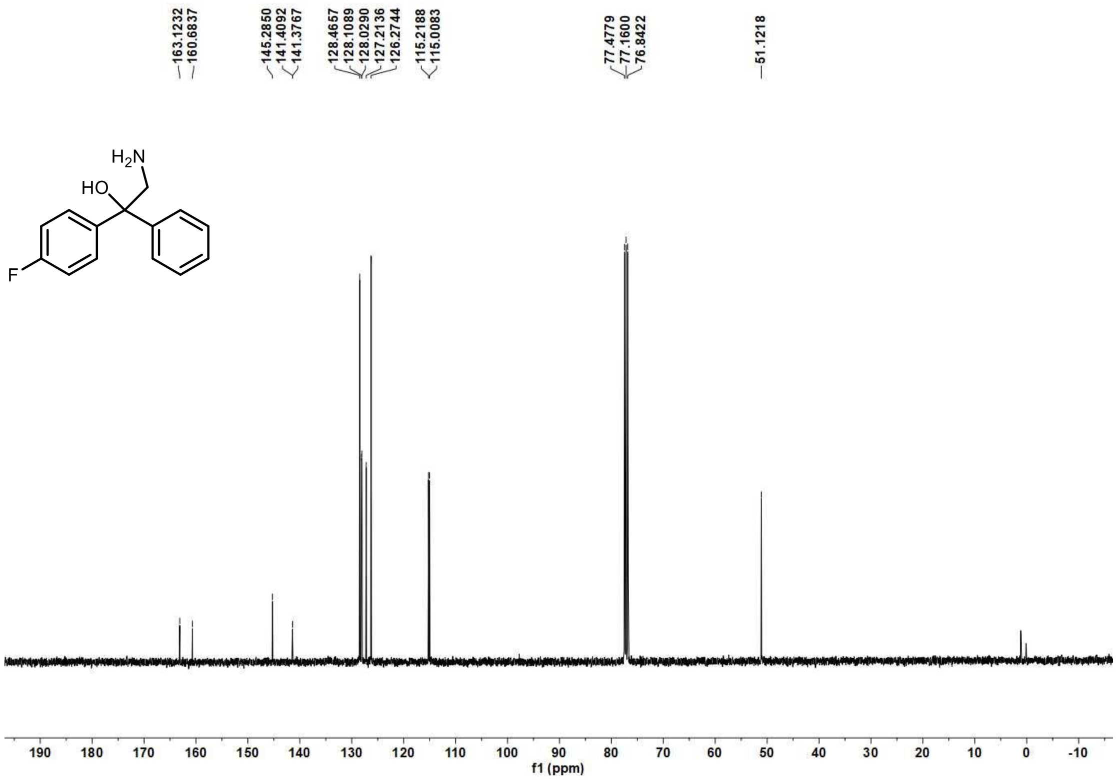
^{13}C NMR (101 MHz, $CDCl_3$) of 2-amino-1-(4-chlorophenyl)-1-phenylethan-1-ol (**3w**)



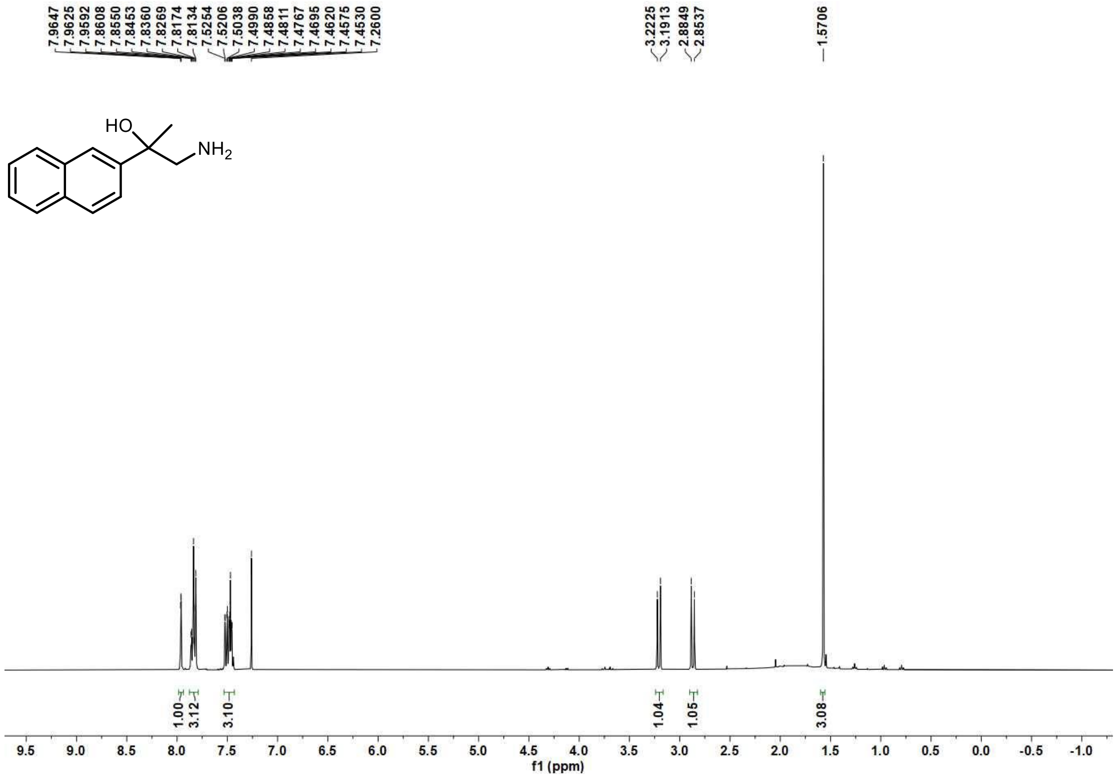
[1]H NMR (400 MHz, $CDCl_3$) of 2-amino-1-(4-fluorophenyl)-1-phenylethan-1-ol (**3x**)



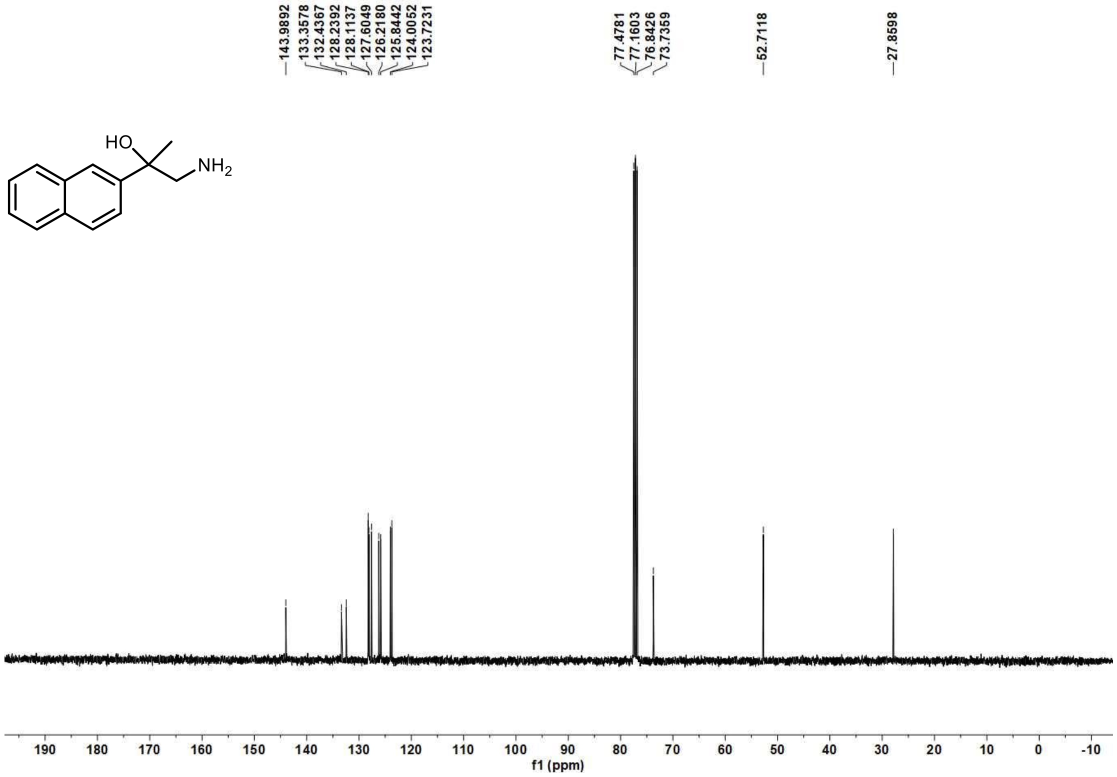
[13]C NMR (101 MHz, $CDCl_3$) of 2-amino-1-(4-fluorophenyl)-1-phenylethan-1-ol(**3x**)



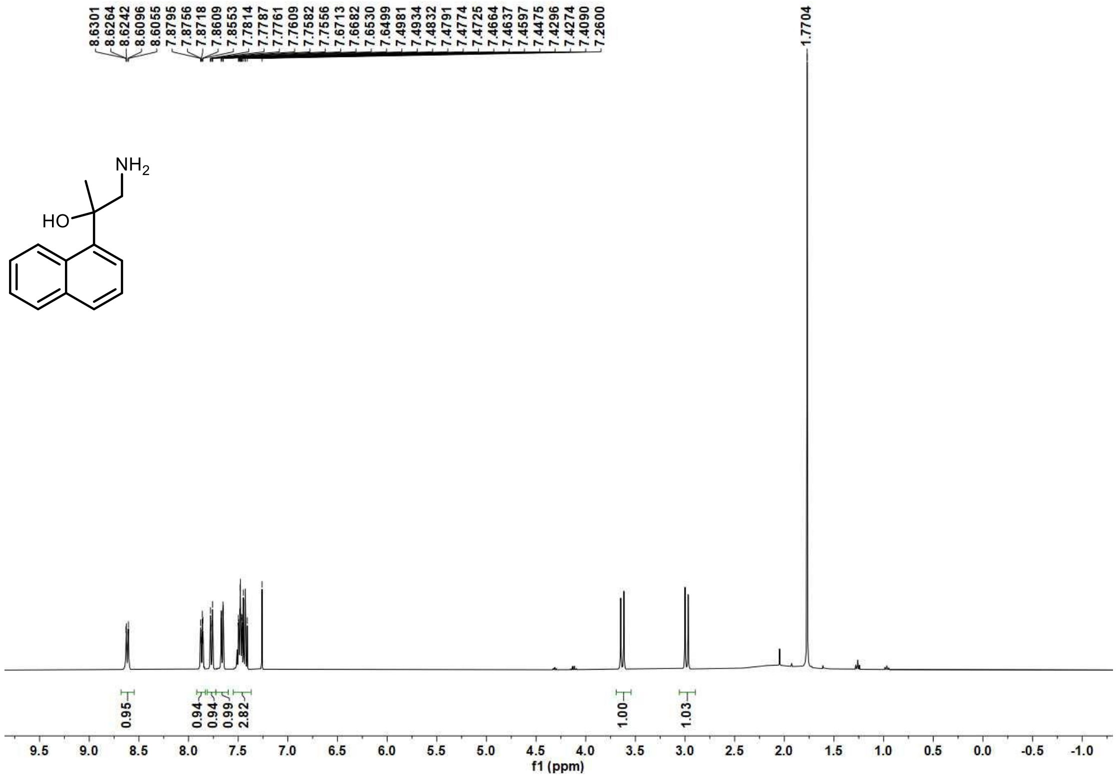
[1]H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(naphthalen-2-yl)propan-2-ol (**3y**)



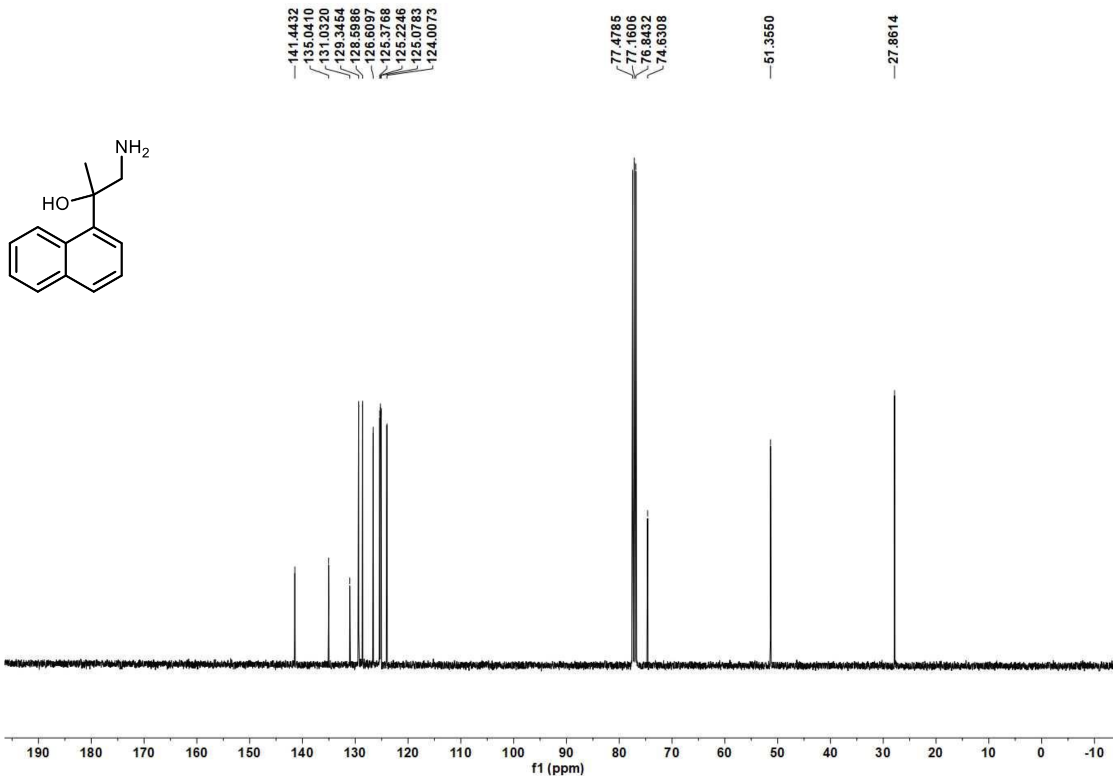
[13]C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(naphthalen-2-yl)propan-2-ol (**3y**)



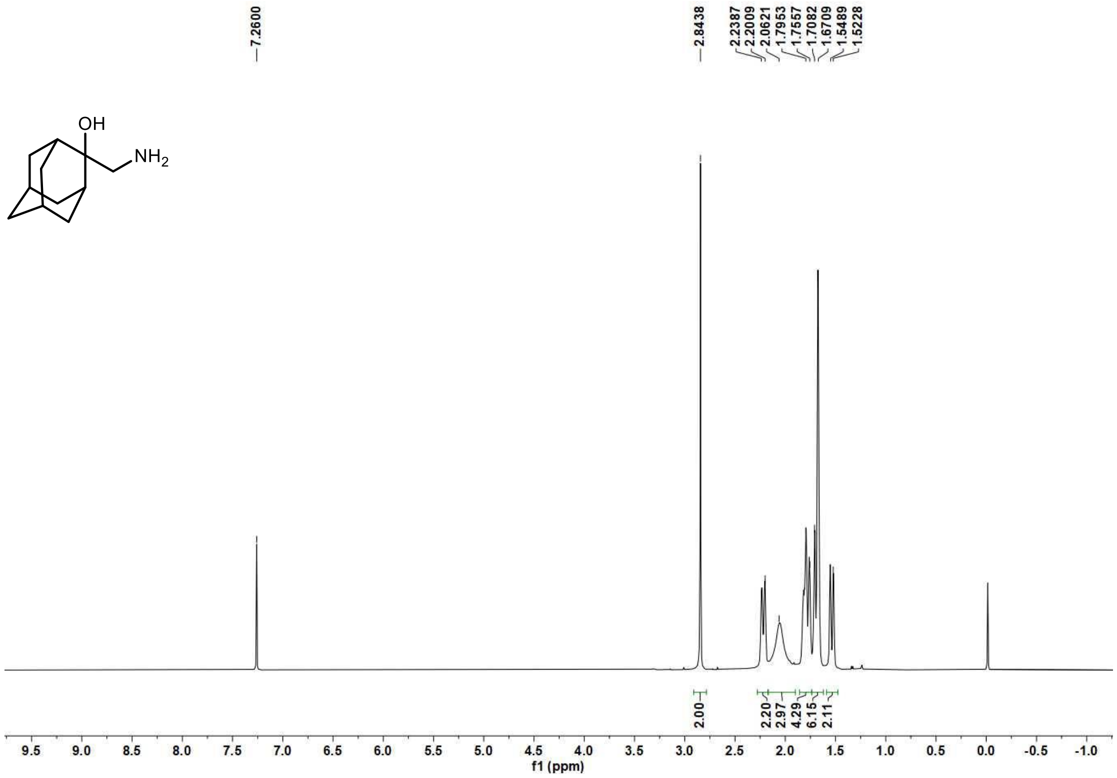
[1]H NMR (400 MHz, $CDCl_3$) of 1-amino-2-(naphthalen-1-yl)propan-2-ol (**3z**)



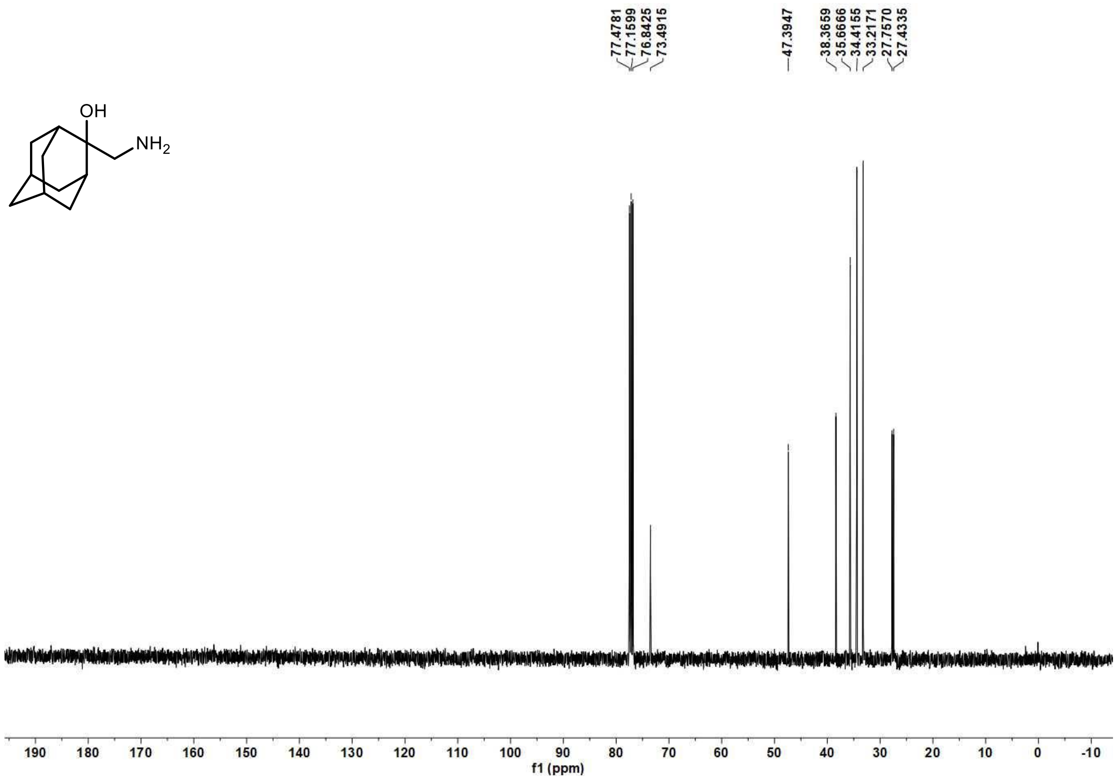
[13]C NMR (101 MHz, $CDCl_3$) of 1-amino-2-(naphthalen-1-yl)propan-2-ol (**3z**)



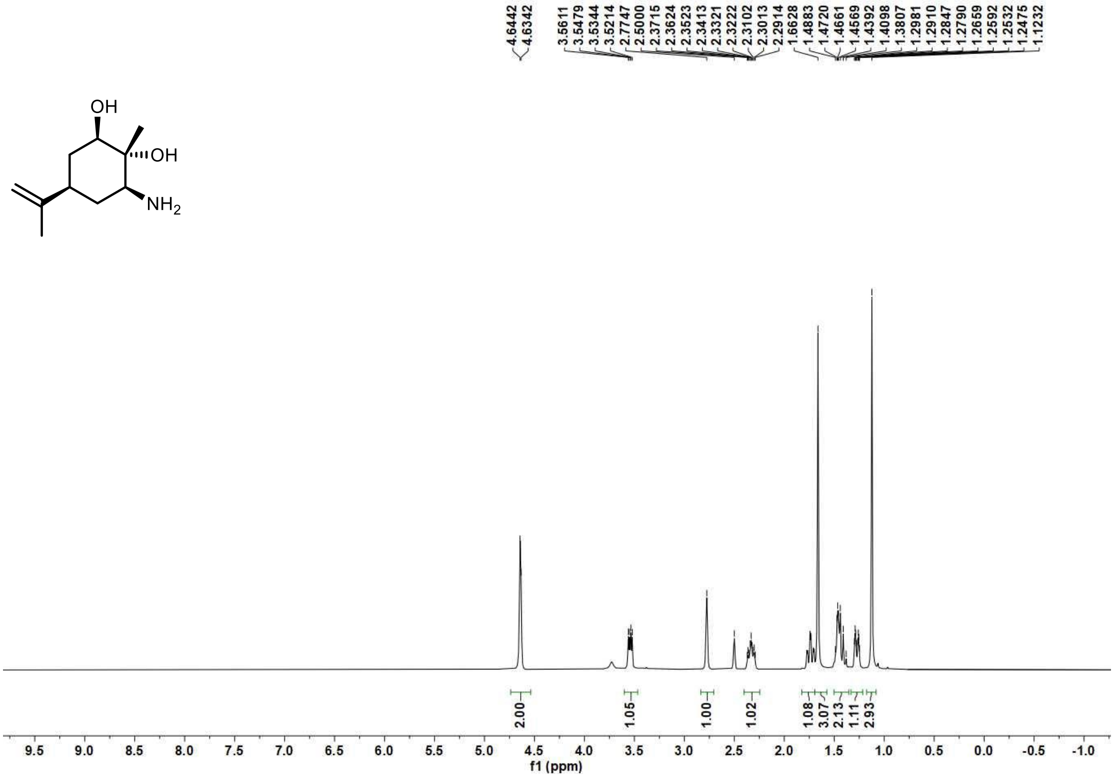
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(aminomethyl)adamantan-2-ol (**3aa**)



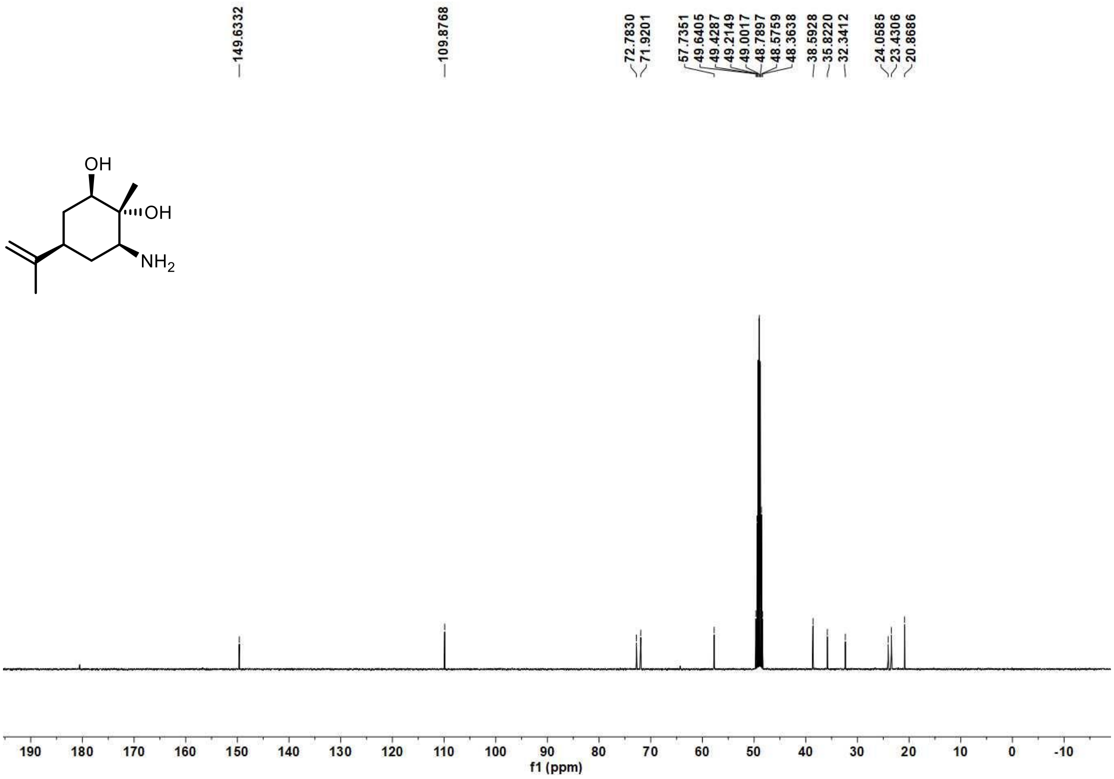
^{13}C NMR (101 MHz, $CDCl_3$) of 2-(aminomethyl)adamantan-2-ol (**3aa**)



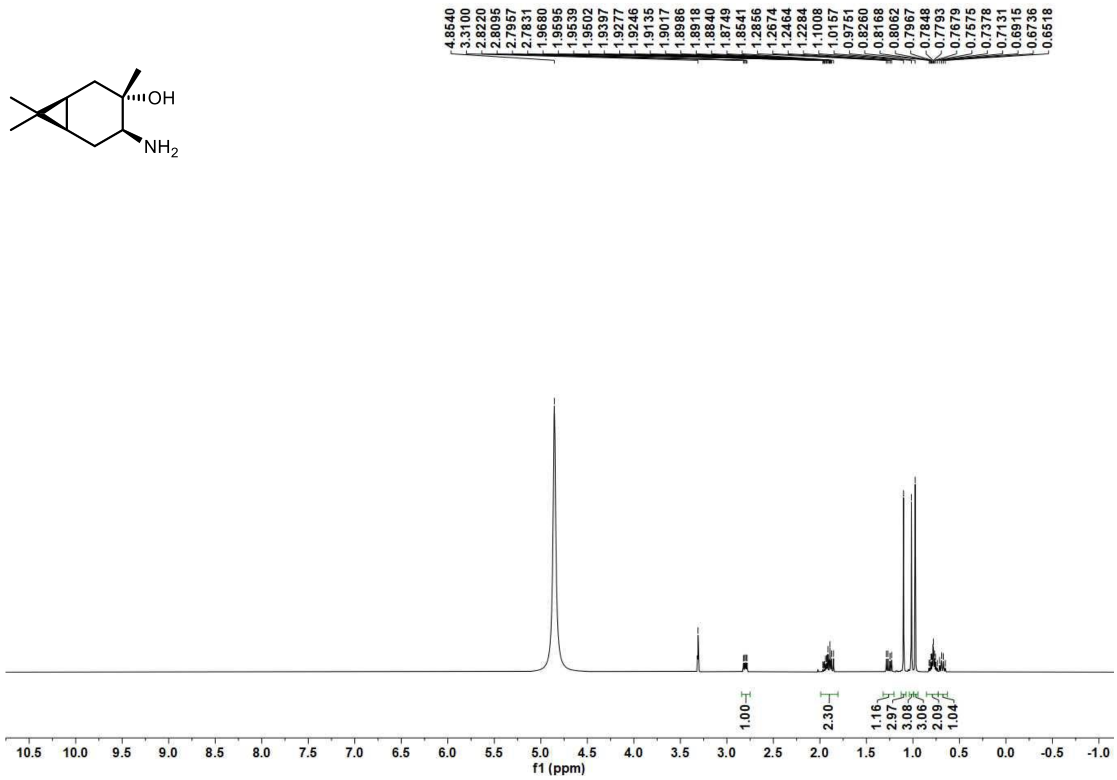
[1]H NMR (400 MHz, DMSO-d_6) of (1R,4R,6S)-6-amino-1-methyl-4-(prop-1-en-2-yl) cyclohexane-1,2-diol (**3bb**)



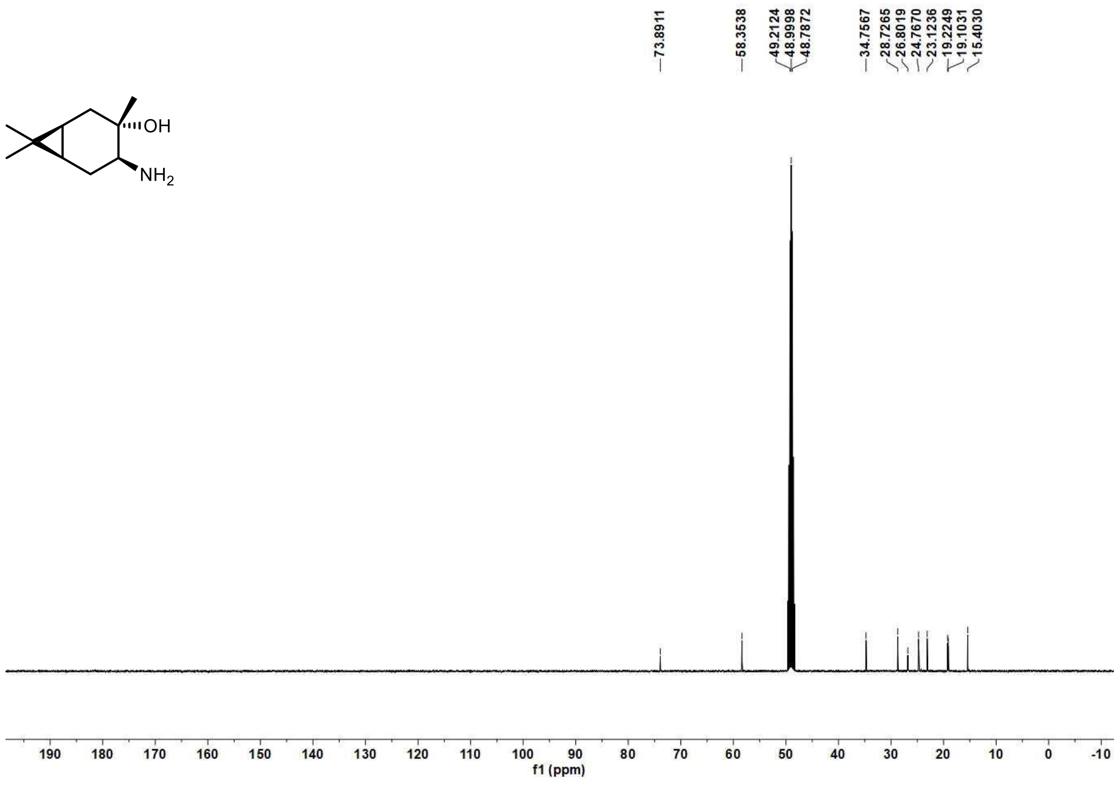
[13]C NMR (101 MHz, DMSO-d_6) of (1R,4R,6S)-6-amino-1-methyl-4-(prop-1-en-2-yl) cyclohexane-1,2-diol (**3bb**)



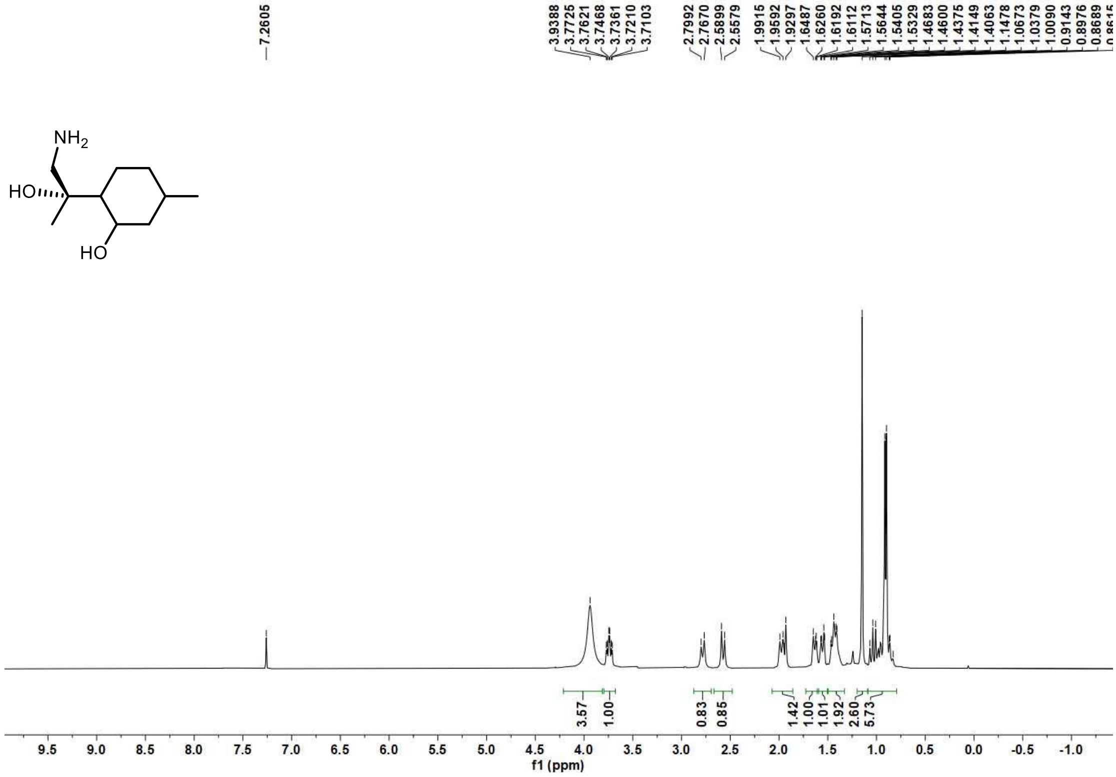
^{1}H NMR (400 MHz, CD_3OD) of (1S,3S,4S,6R)-4-amino-3,7,7-trimethylbicyclo[4.1.0] heptan-3-ol (**3cc**)



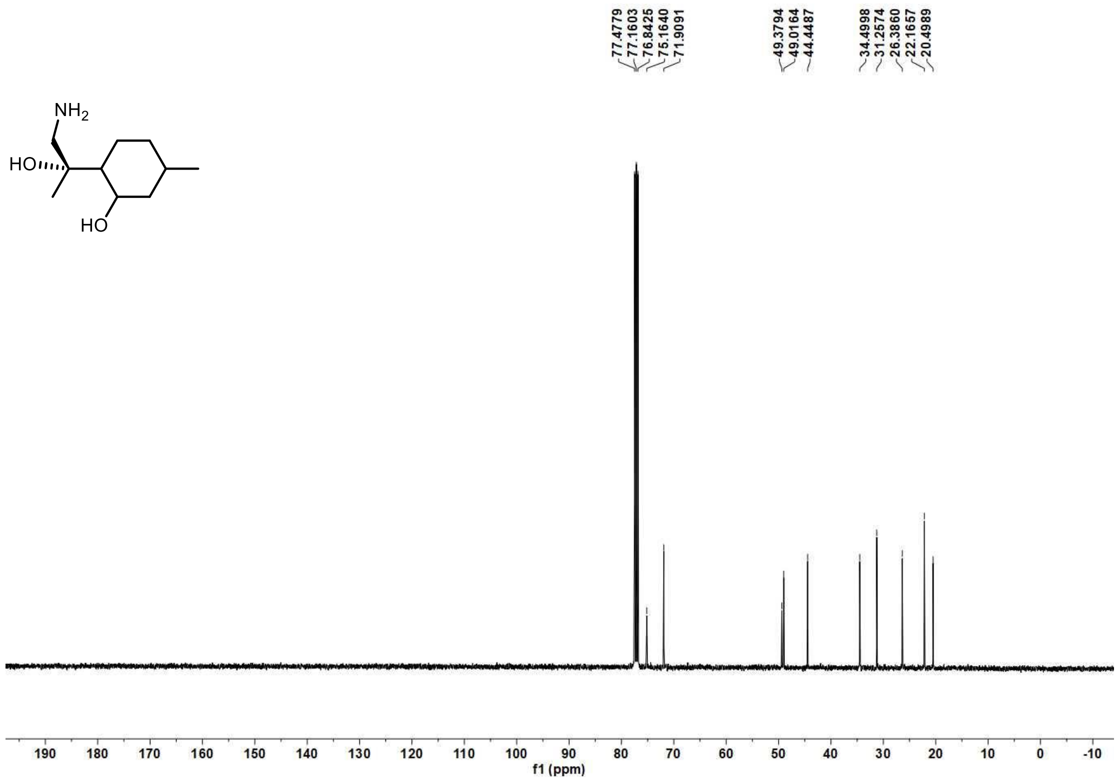
^{13}C NMR (101 MHz, CD_3OD) of (1S,3S,4S,6R)-4-amino-3,7,7-trimethylbicyclo[4.1.0] heptan-3-ol (**3cc**)



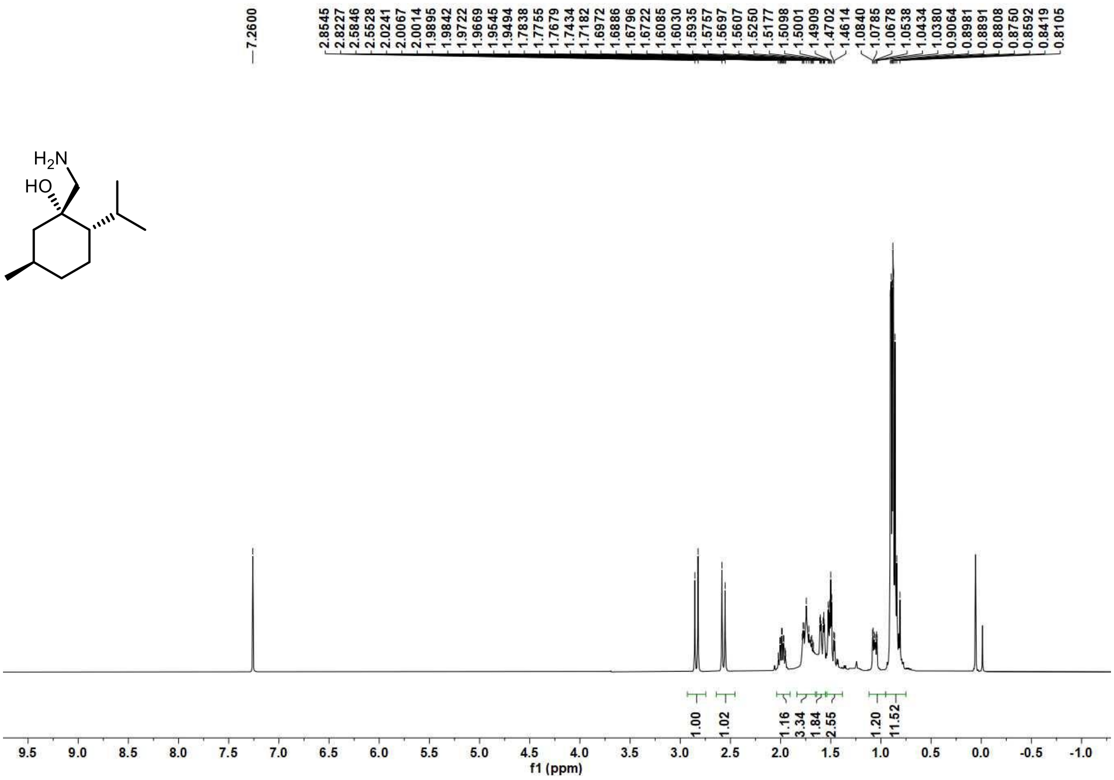
^{1}H NMR (400 MHz, $CDCl_3$) of 2-((S)-1-amino-2-hydroxypropan-2-yl)-5-methylcyclohexan-1-ol (**3dd**)



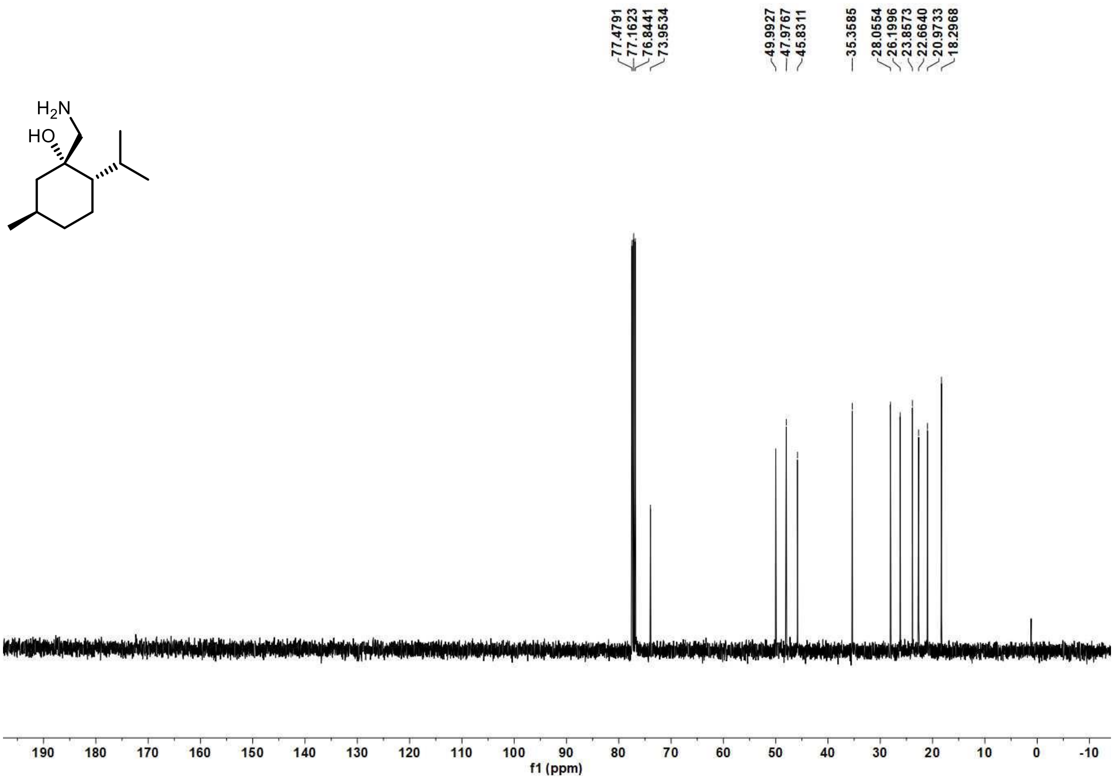
^{13}C NMR (101 MHz, $CDCl_3$) of 2-((S)-1-amino-2-hydroxypropan-2-yl)-5-methylcyclohexan-1-ol (**3dd**)



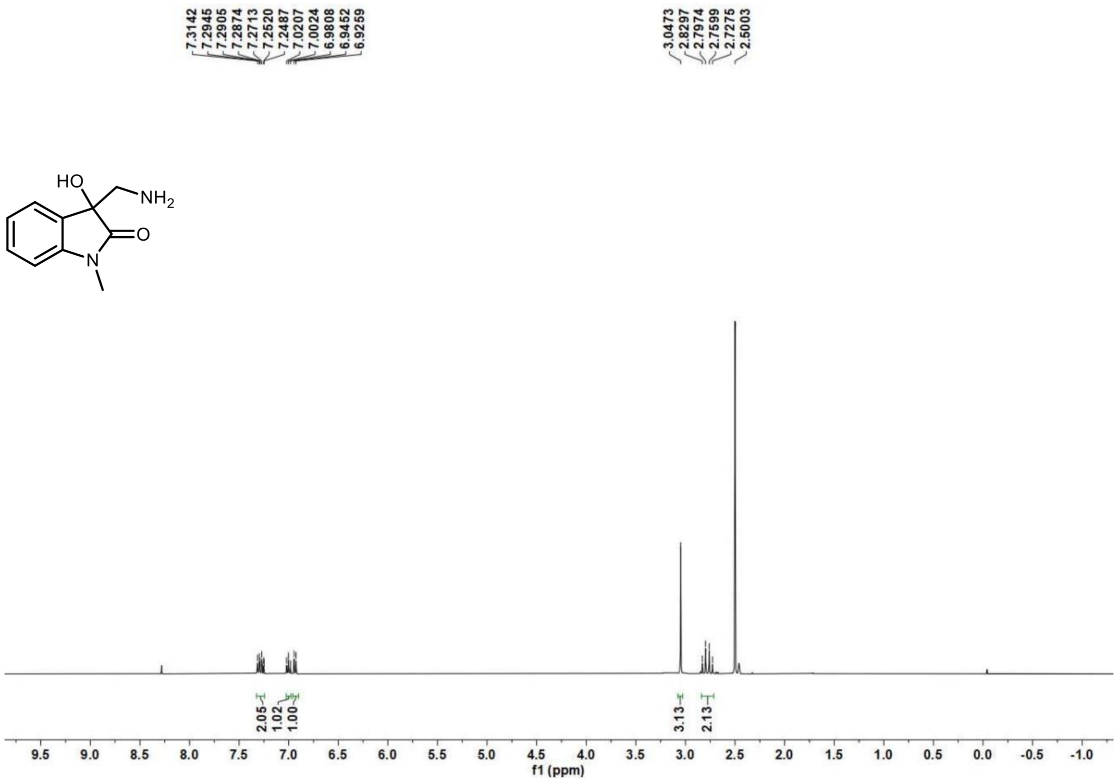
^{1}H NMR (400 MHz, $CDCl_3$) of (1S,2S,5R)-1-(aminomethyl)-2-isopropyl-5-methylcyclohexan-1-ol (**3ee**)



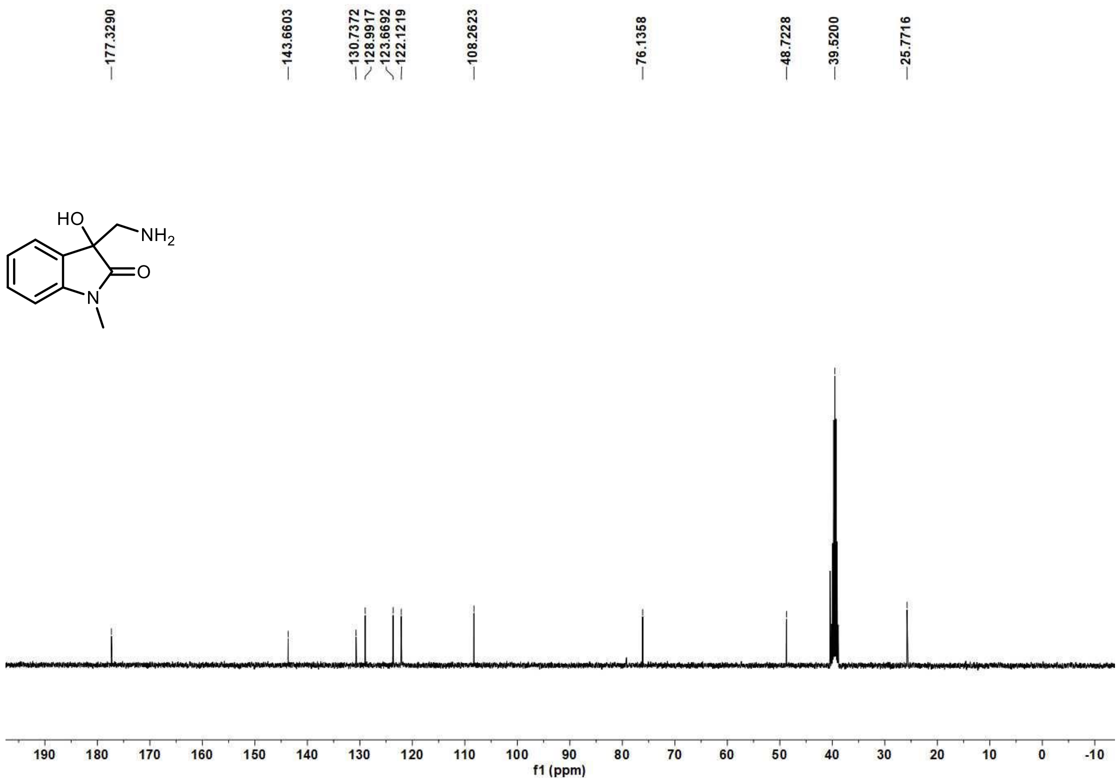
^{13}C NMR (101 MHz, $CDCl_3$) of (1S,2S,5R)-1-(aminomethyl)-2-isopropyl-5-methylcyclohexan-1-ol (**3ee**)



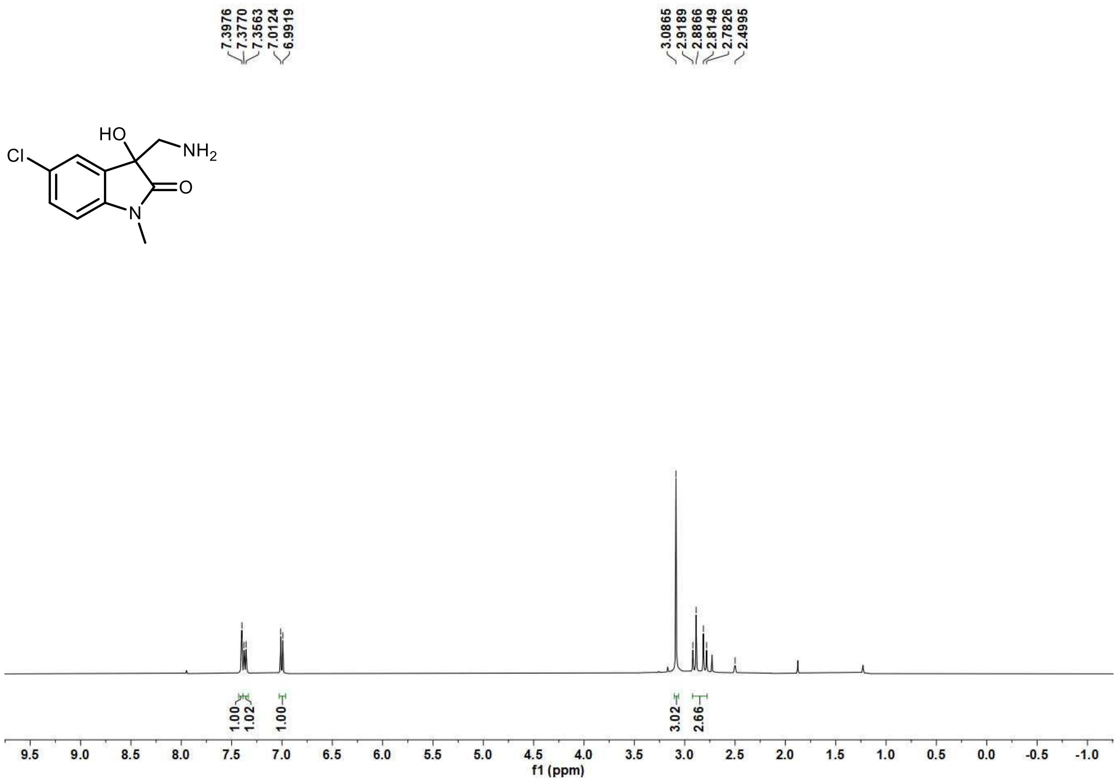
^{1}H NMR (400 MHz, DMSO-d_6) of 3-(aminomethyl)-3-hydroxy-1-methylindolin-2-one (**3ff**)



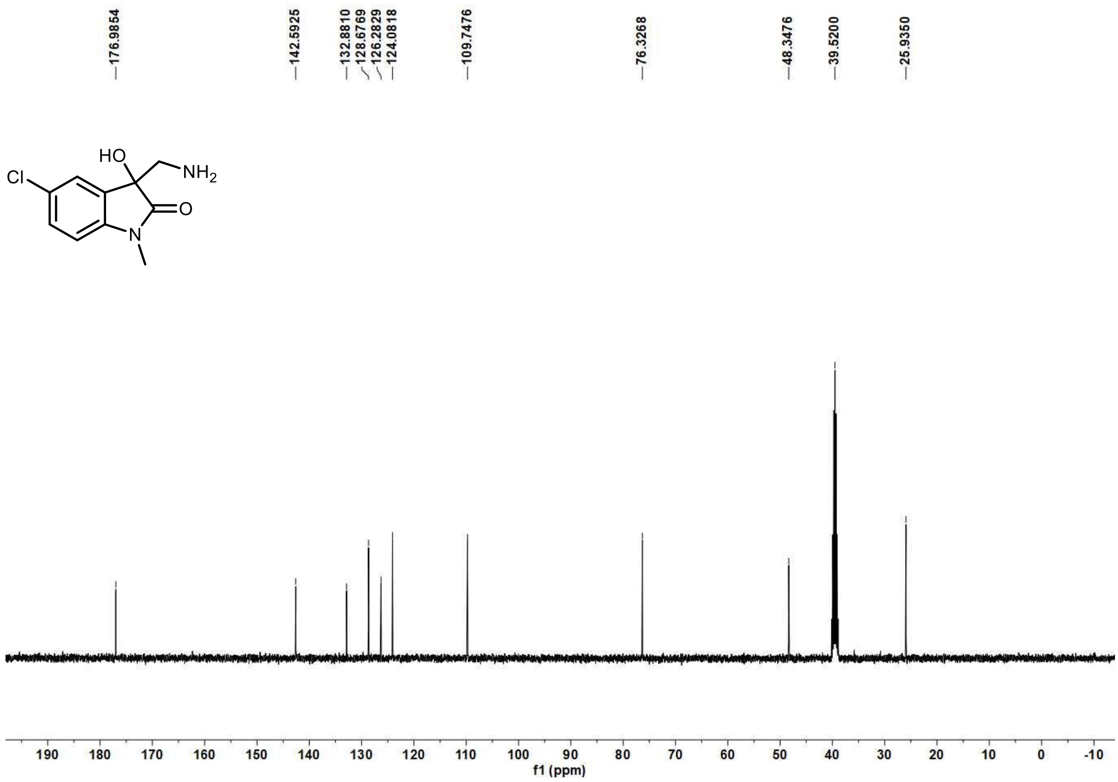
^{13}C NMR (101 MHz, DMSO-d_6) of 3-(aminomethyl)-3-hydroxy-1-methylindolin-2-one (**3ff**)



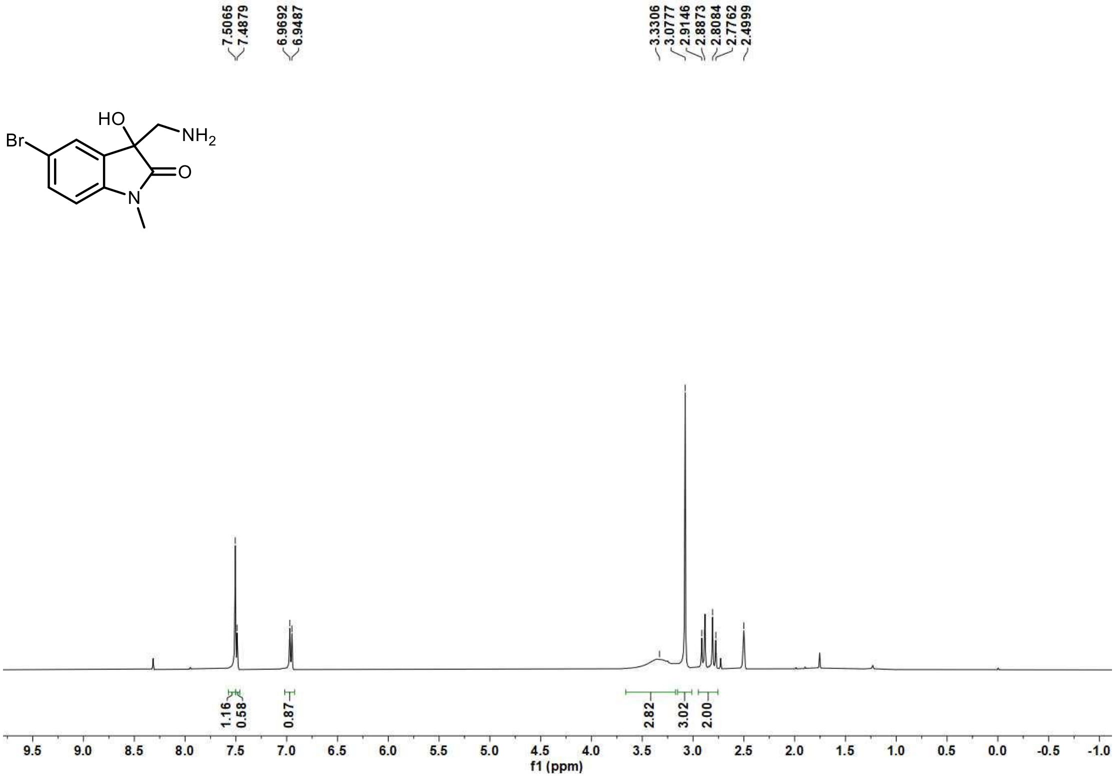
^{1}H NMR (400 MHz, DMSO-d_6) of 3-(aminomethyl)-5-chloro-3-hydroxy-1-methylindolin-2-one (**3gg**)



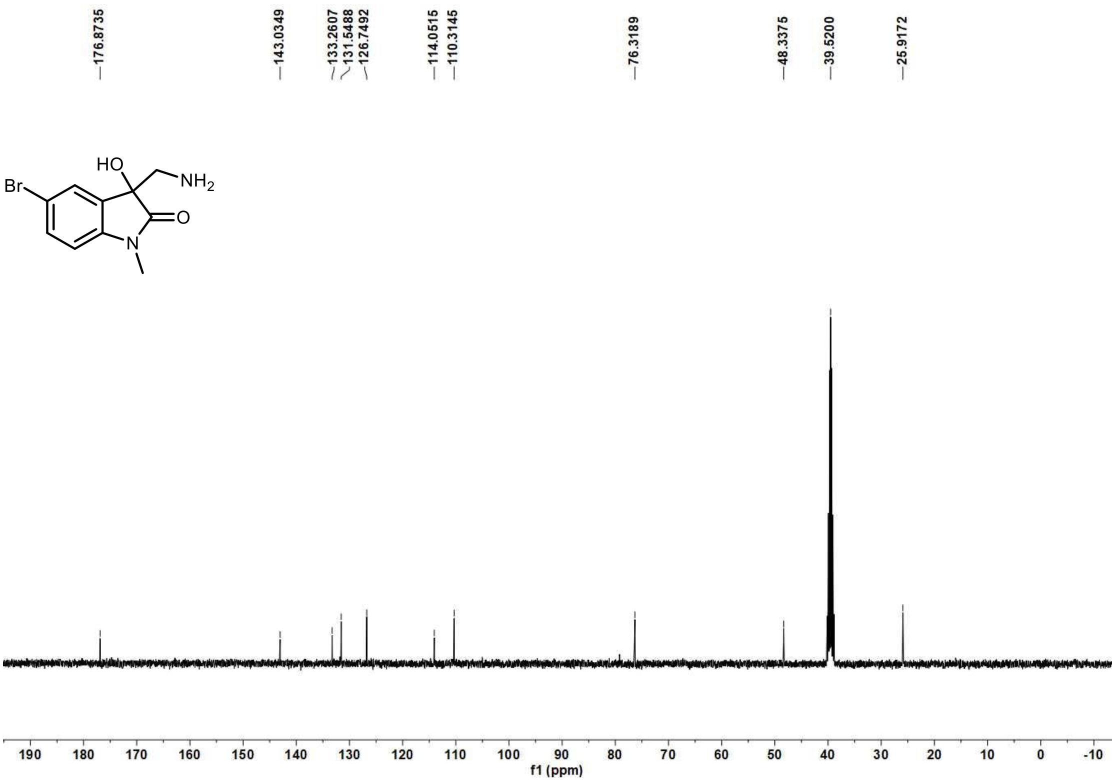
^{13}C NMR (101 MHz, DMSO-d_6) of 3-(aminomethyl)-5-chloro-3-hydroxy-1-methylindolin-2-one (**3gg**)



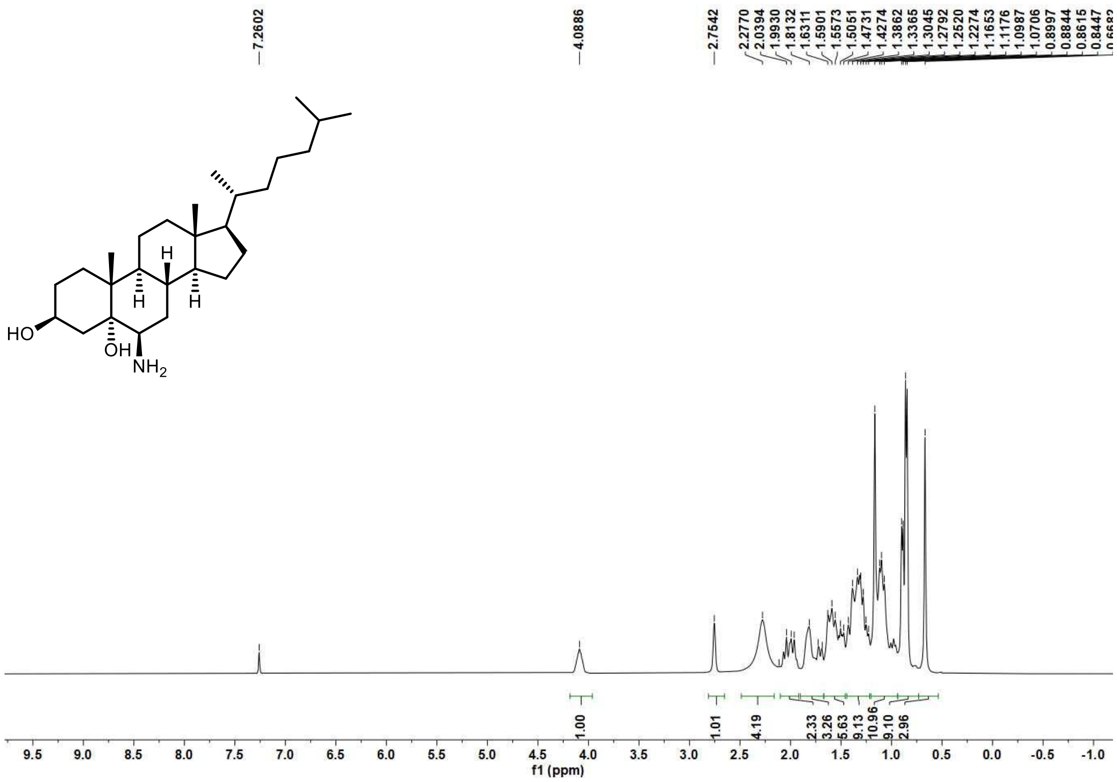
^{1}H NMR (400 MHz, DMSO-d_6) of 3-(aminomethyl)-5-bromo-3-hydroxy-1-methylindolin-2-one (**3hh**)



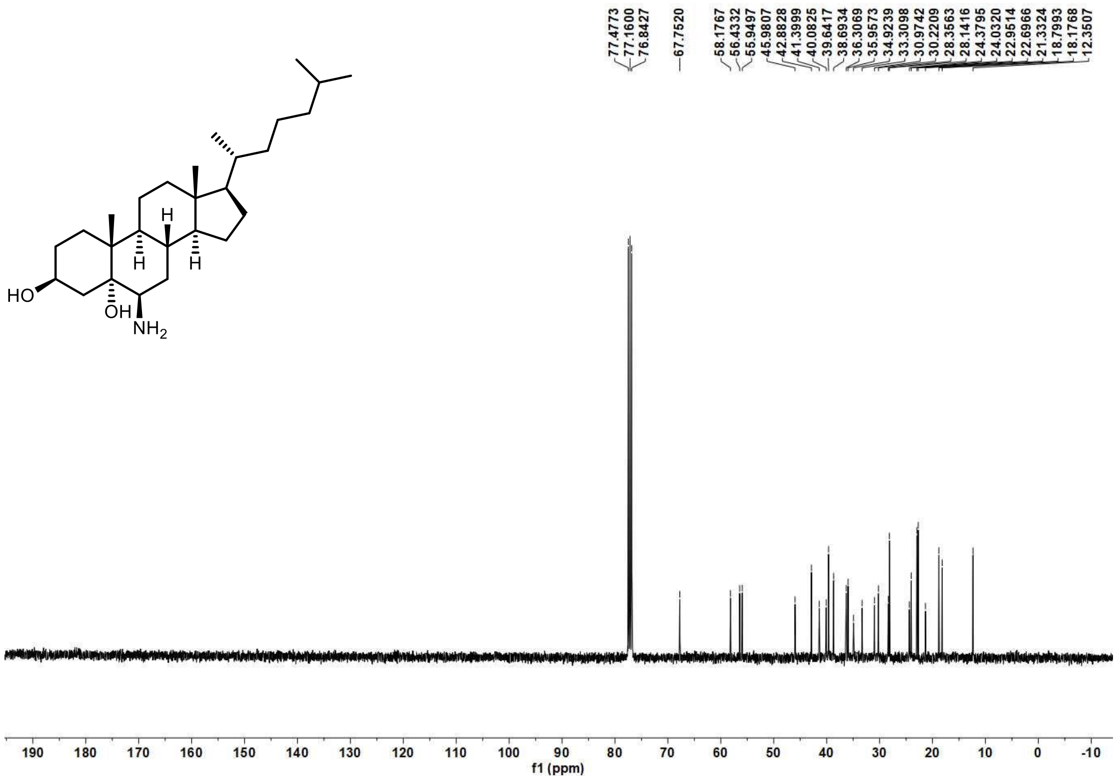
^{13}C NMR (101 MHz, DMSO-d_6) of 3-(aminomethyl)-5-bromo-3-hydroxy-1-methylindolin-2-one (**3hh**)



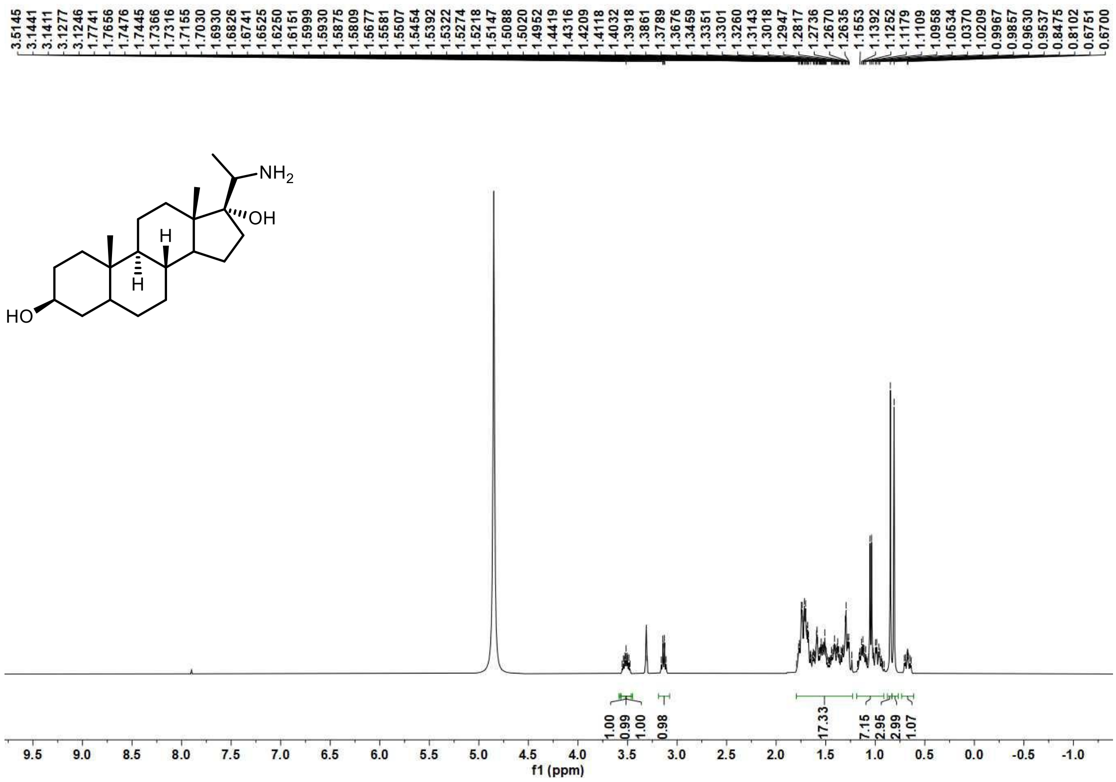
[1]H NMR (400 MHz, $CDCl_3$) of **5**



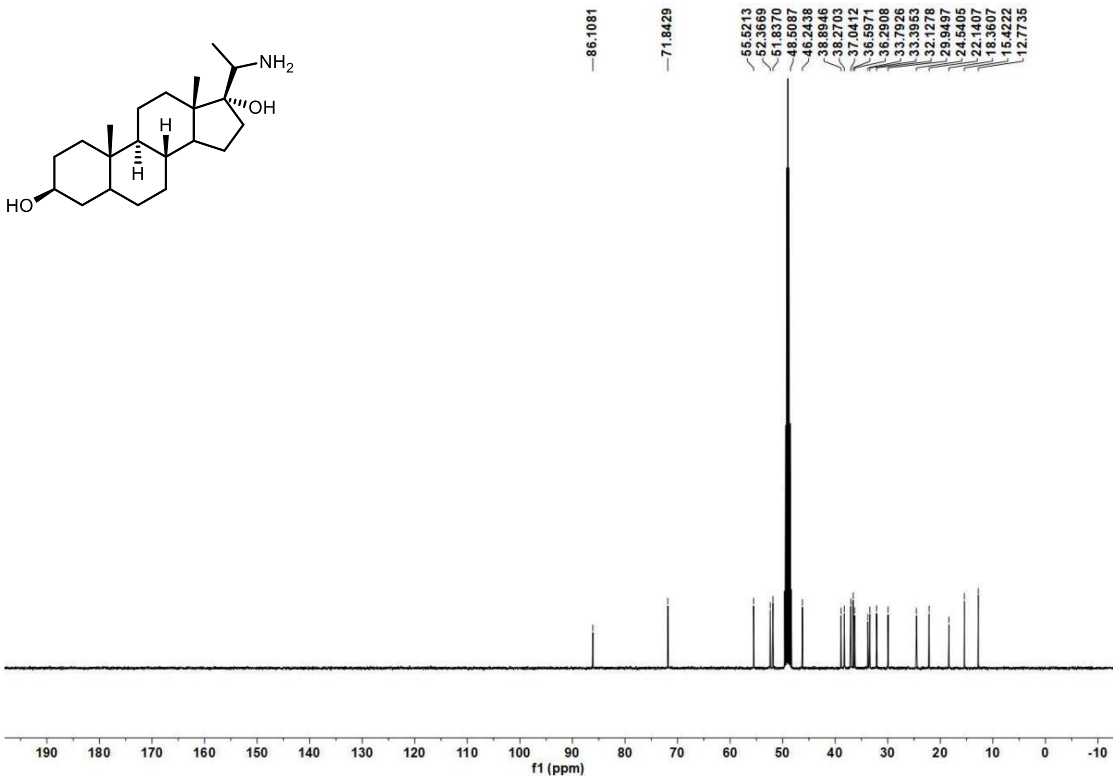
[13]C NMR (101 MHz, $CDCl_3$) of **5**



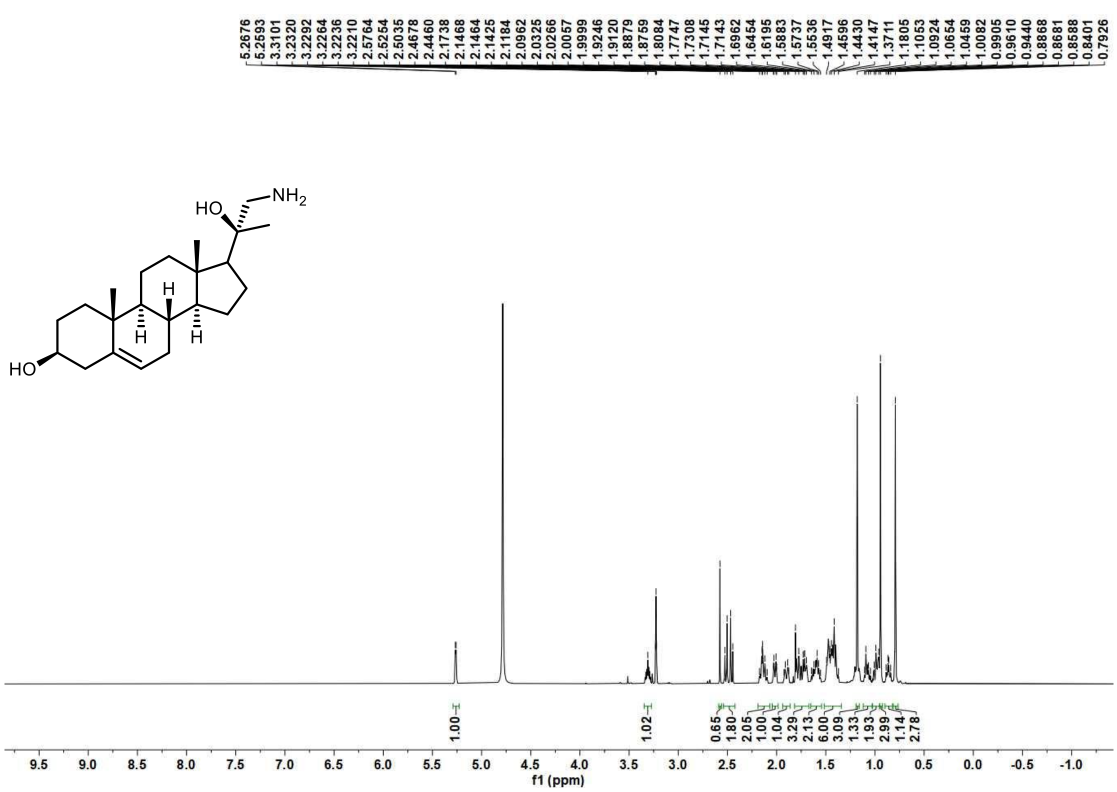
^{1}H NMR (400 MHz, CD_3OD) of **5a**



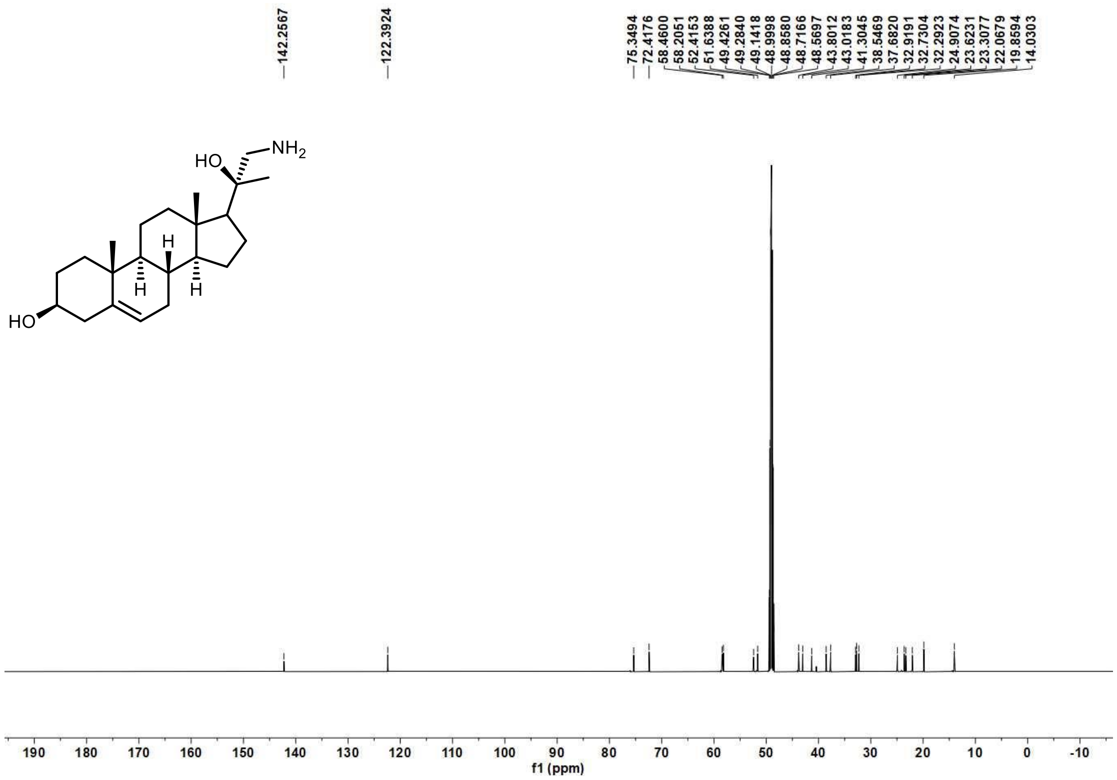
^{13}C NMR (101 MHz, CD_3OD) of **5a**



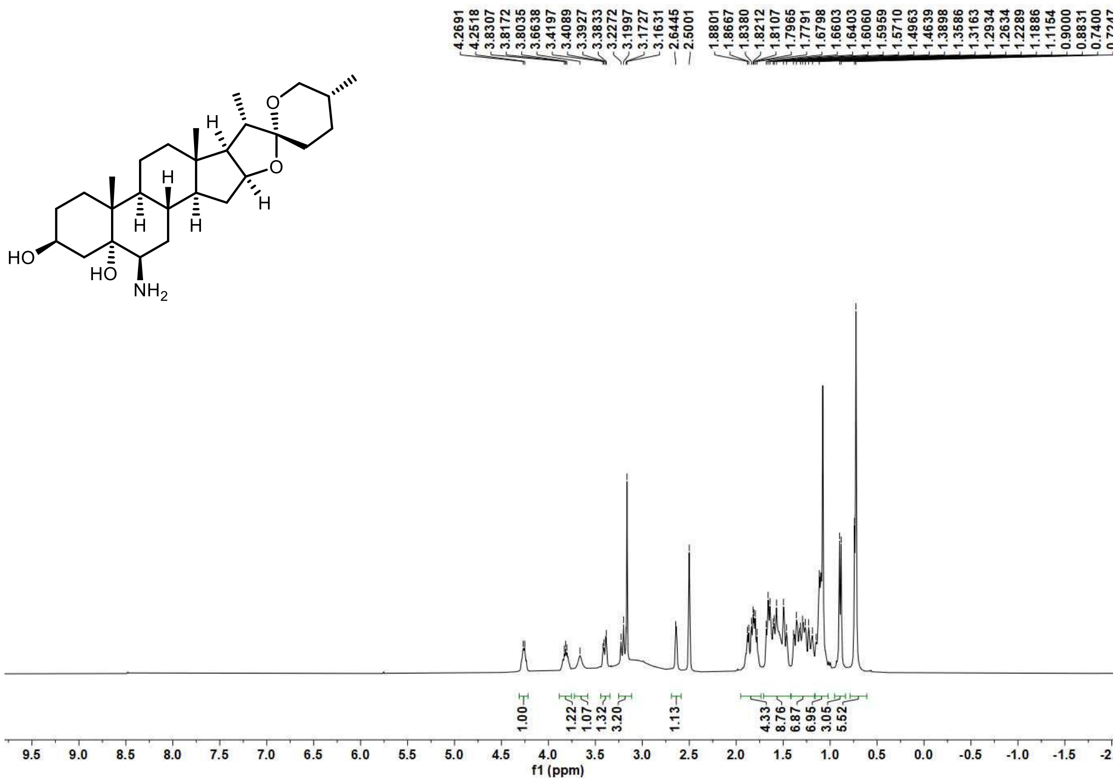
^{1}H NMR (400 MHz, CD_3OD) of **5b**



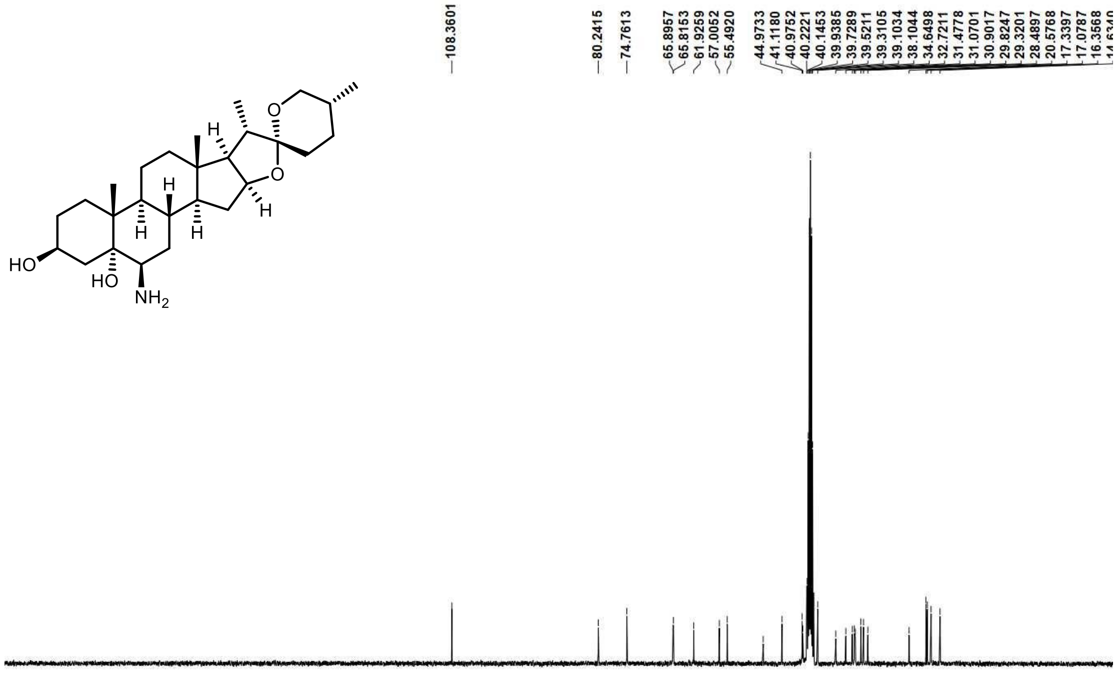
^{13}C NMR (101 MHz, CD_3OD) of **5b**



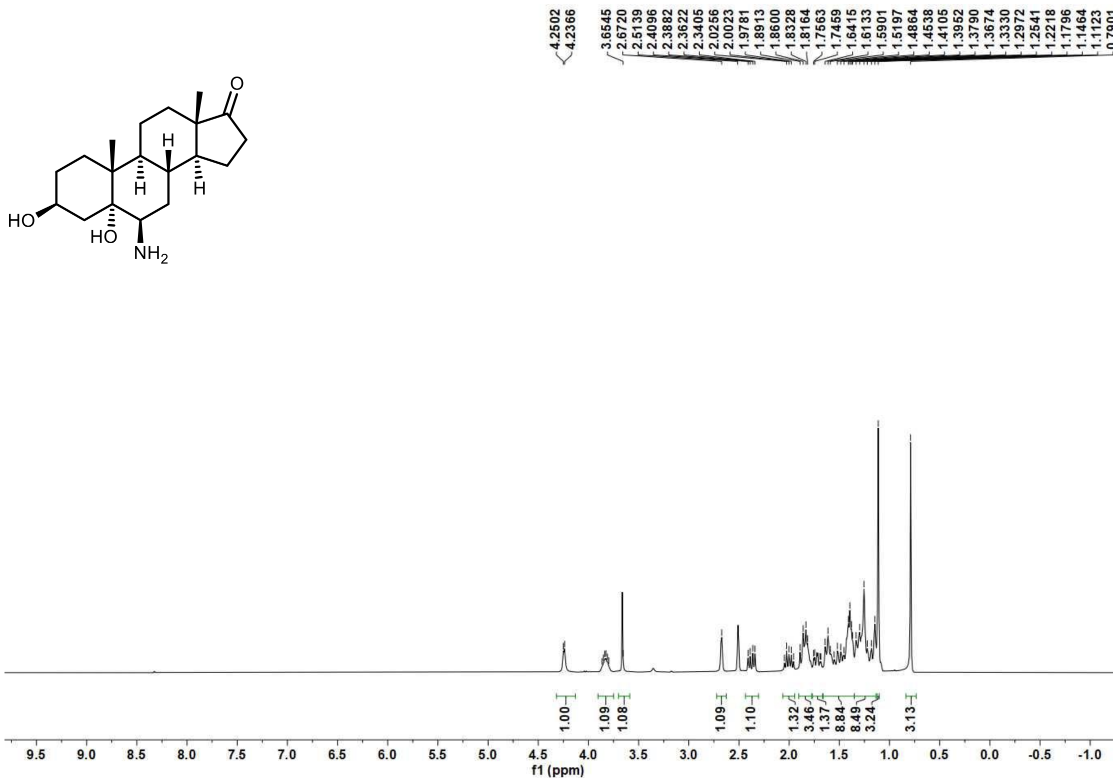
[1]H NMR (400 MHz, $CDCl_3$) of **5c**



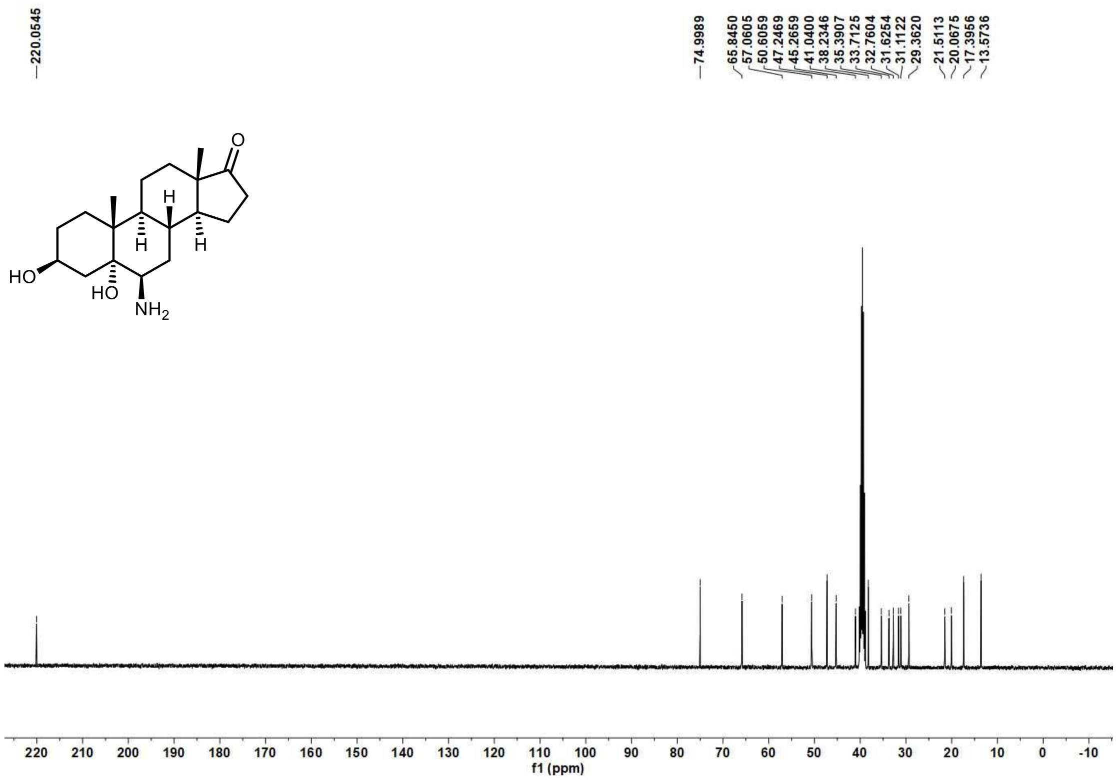
[13]C NMR (101 MHz, $CDCl_3$) of **5c**



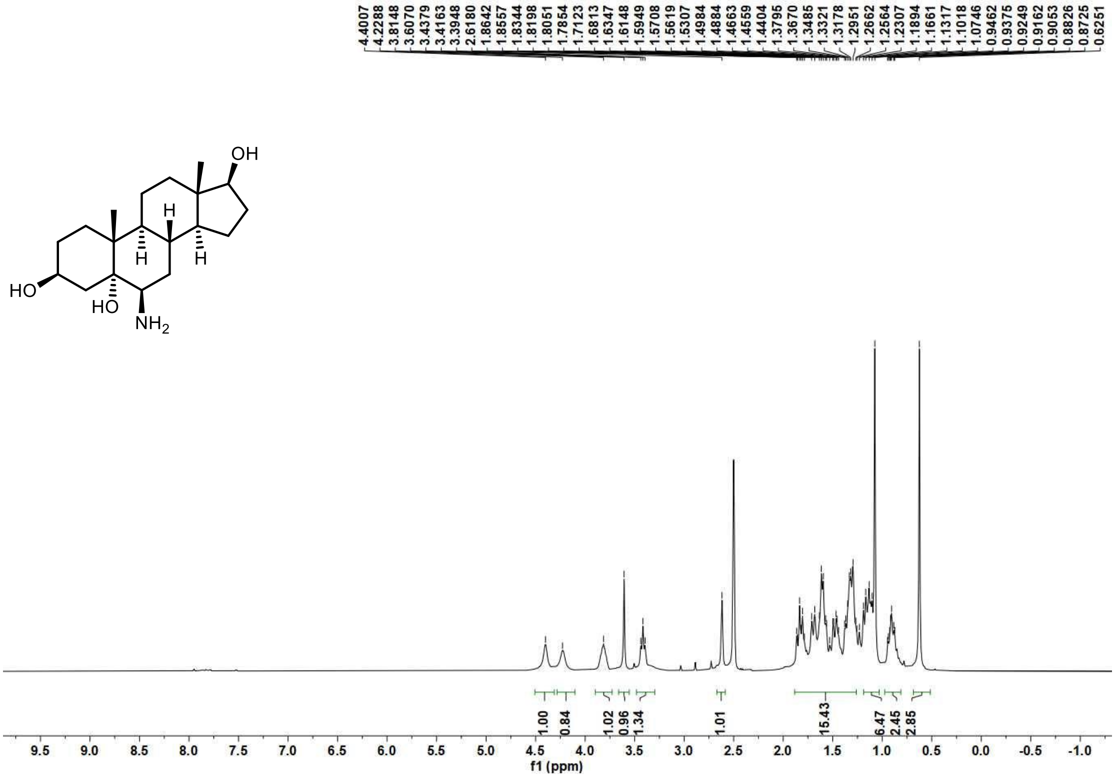
^{1}H NMR (400 MHz, DMSO-d_6) of **5d**



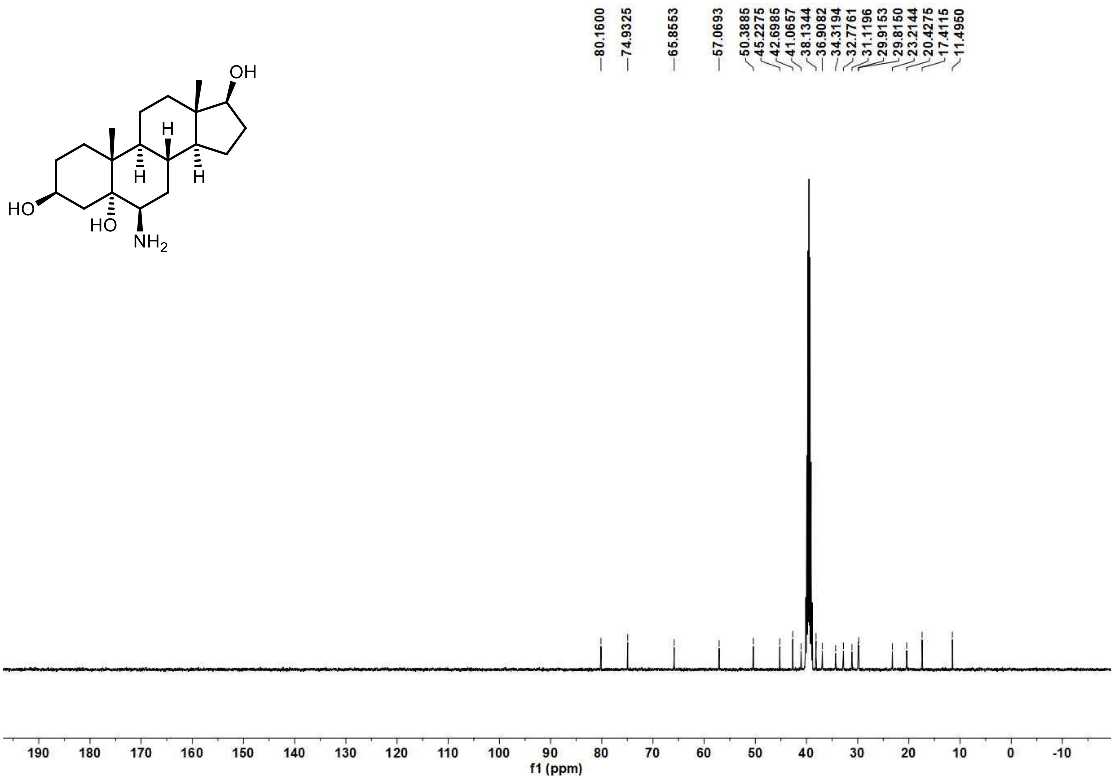
^{13}C NMR (101 MHz, DMSO-d_6) of **5d**



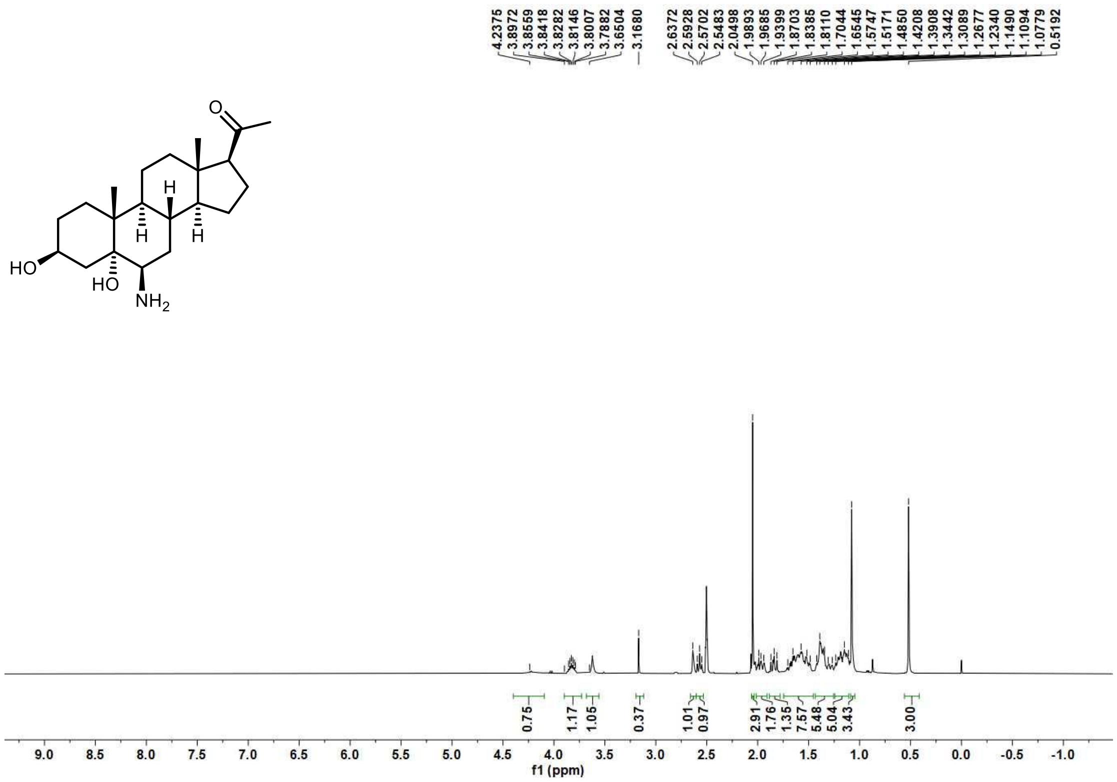
^{1}H NMR (400 MHz, DMSO-d_6) of **5e**



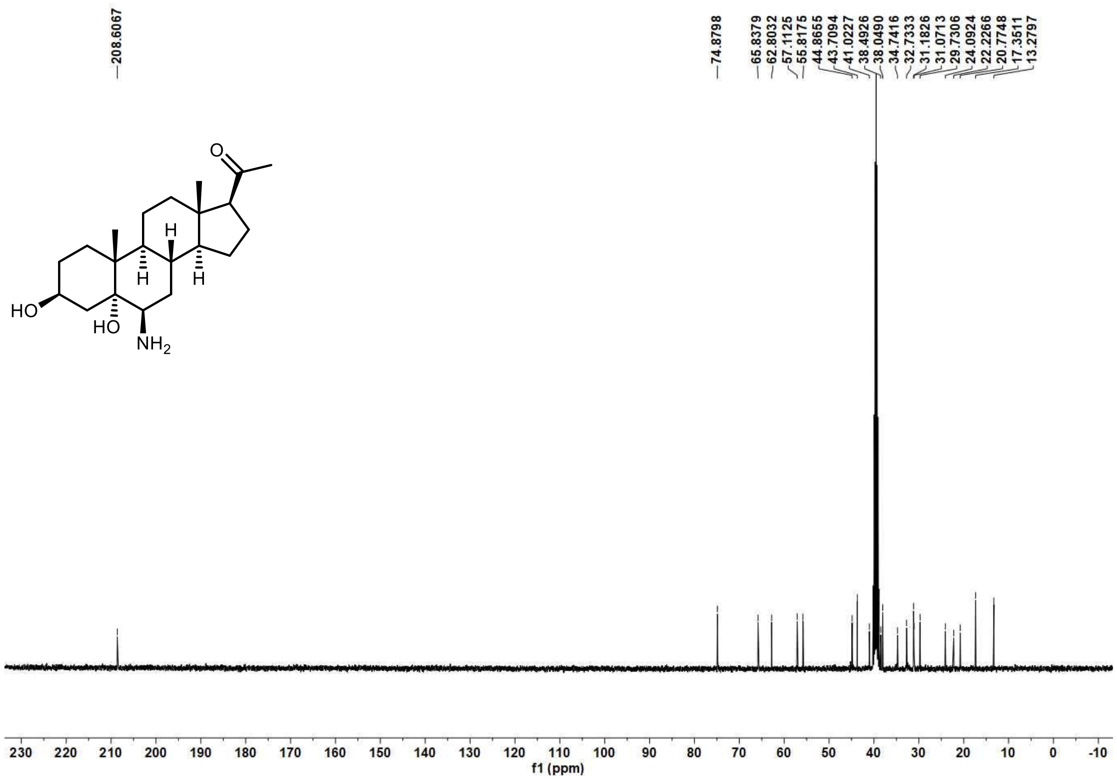
^{13}C NMR (101 MHz, DMSO-d_6) of **5e**



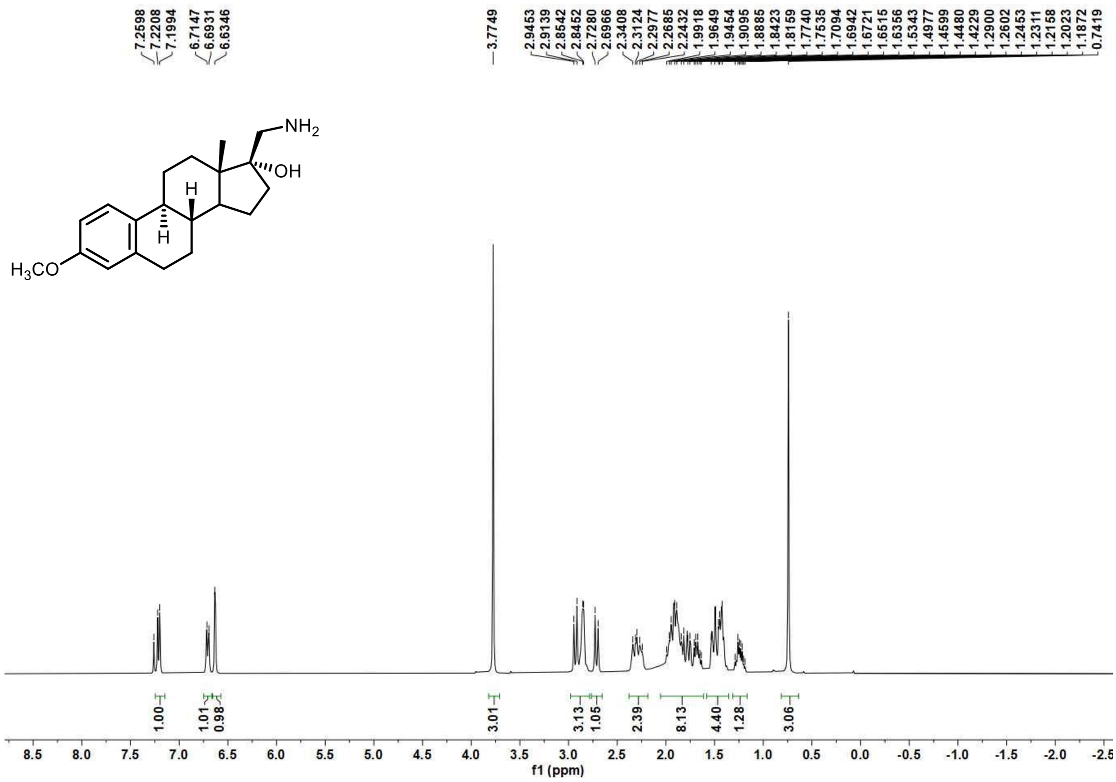
^{1}H NMR (400 MHz, DMSO-d_6) of **5f**



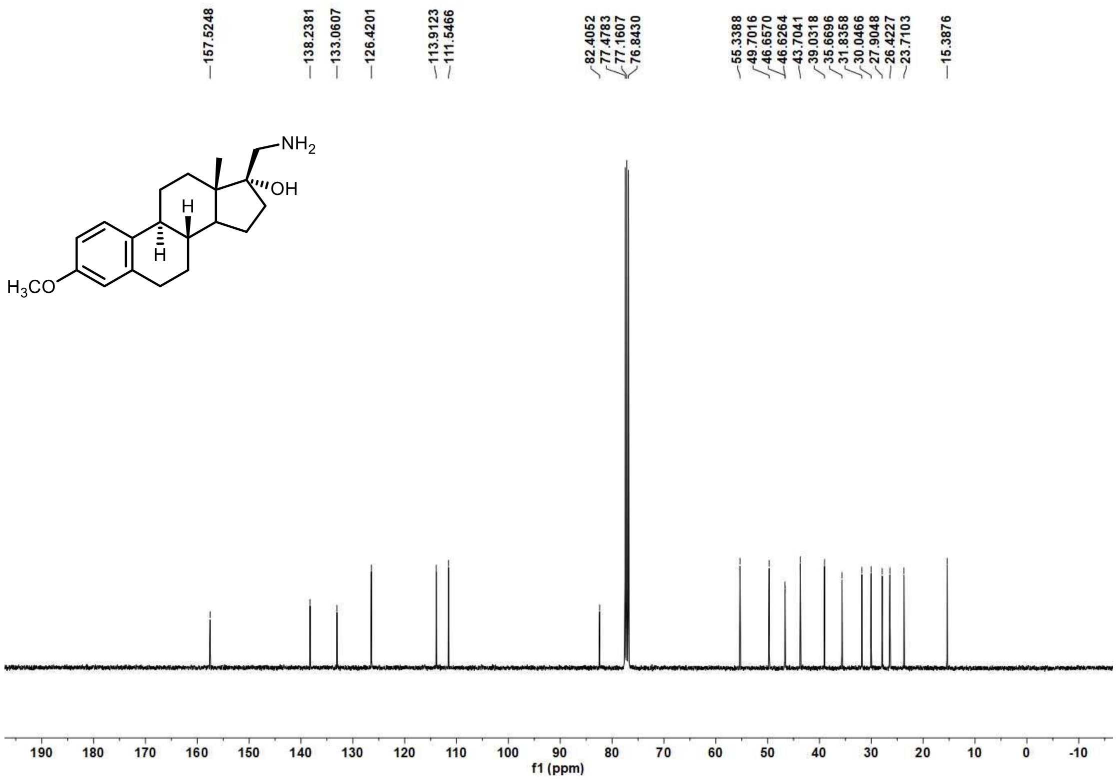
^{13}C NMR (101 MHz, DMSO-d_6) of **5f**



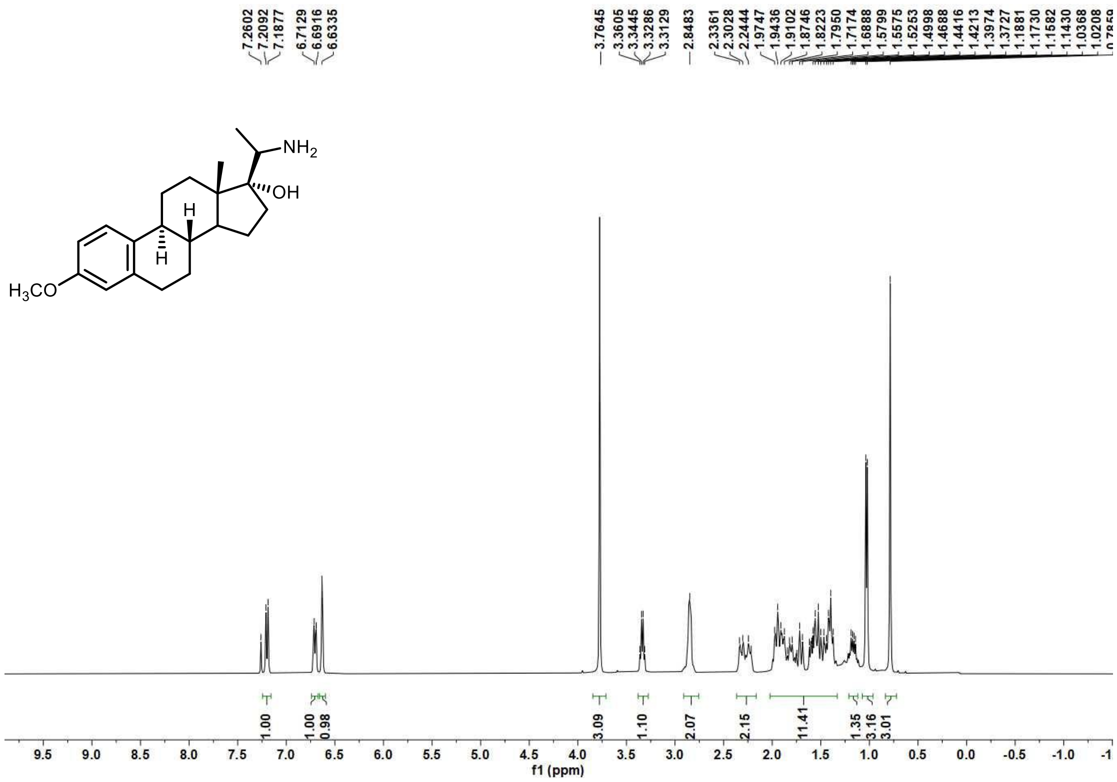
^{1}H NMR (400 MHz, $CDCl_3$) of **5g**



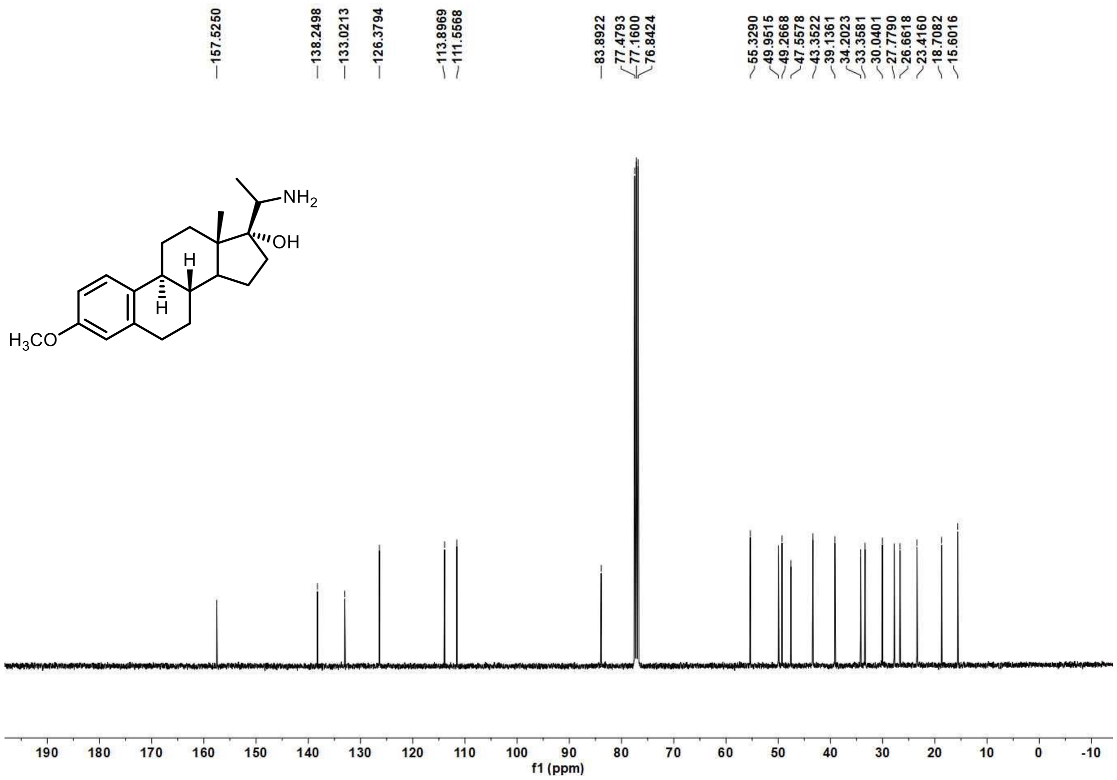
^{13}C NMR (101 MHz, $CDCl_3$) of **5g**



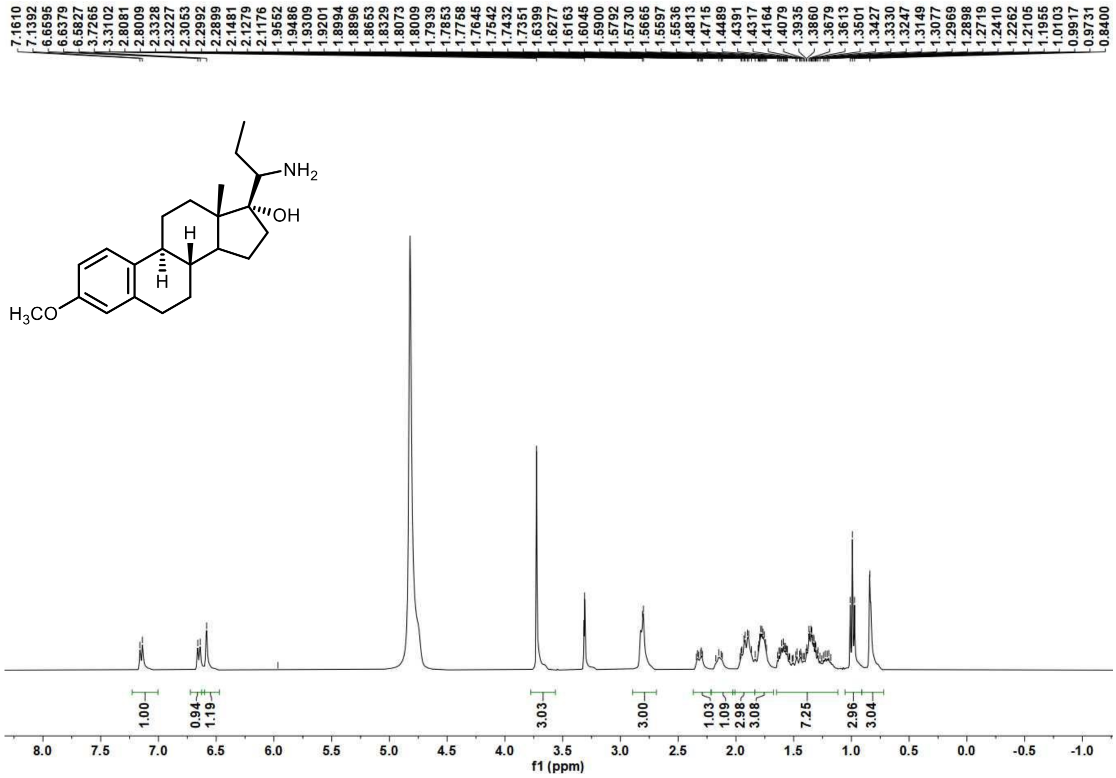
^{1}H NMR (400 MHz, $CDCl_3$) of **5h**



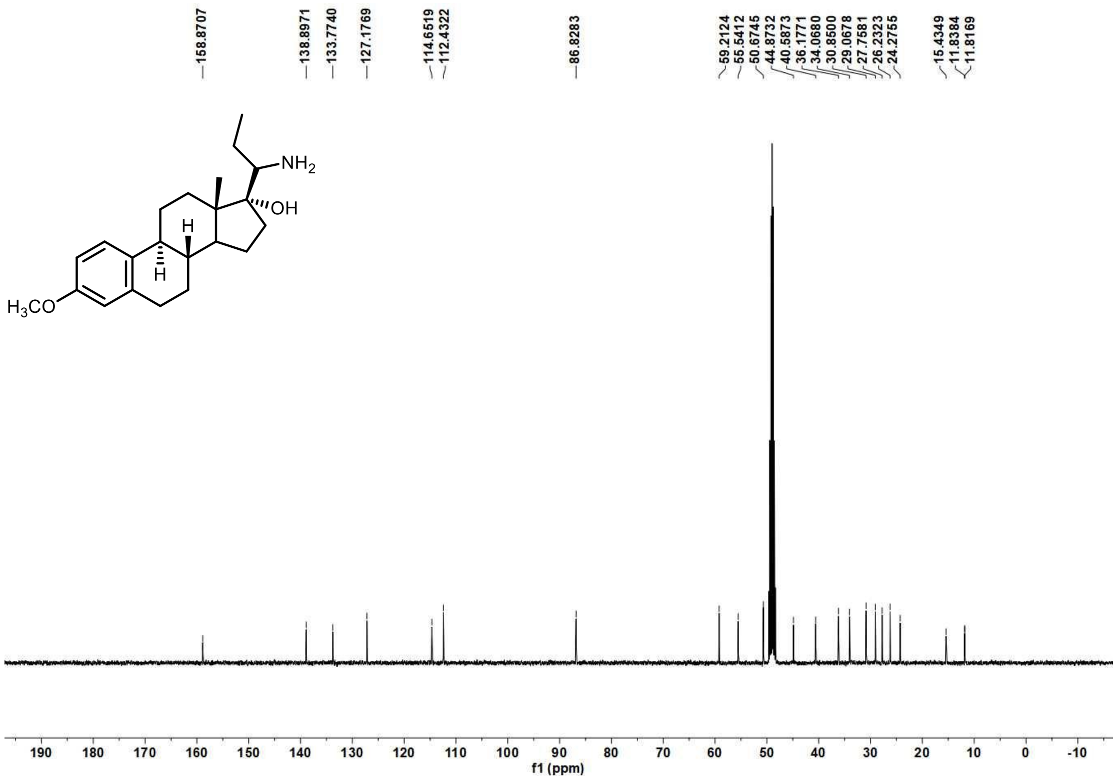
^{13}C NMR (101 MHz, $CDCl_3$) of **5h**



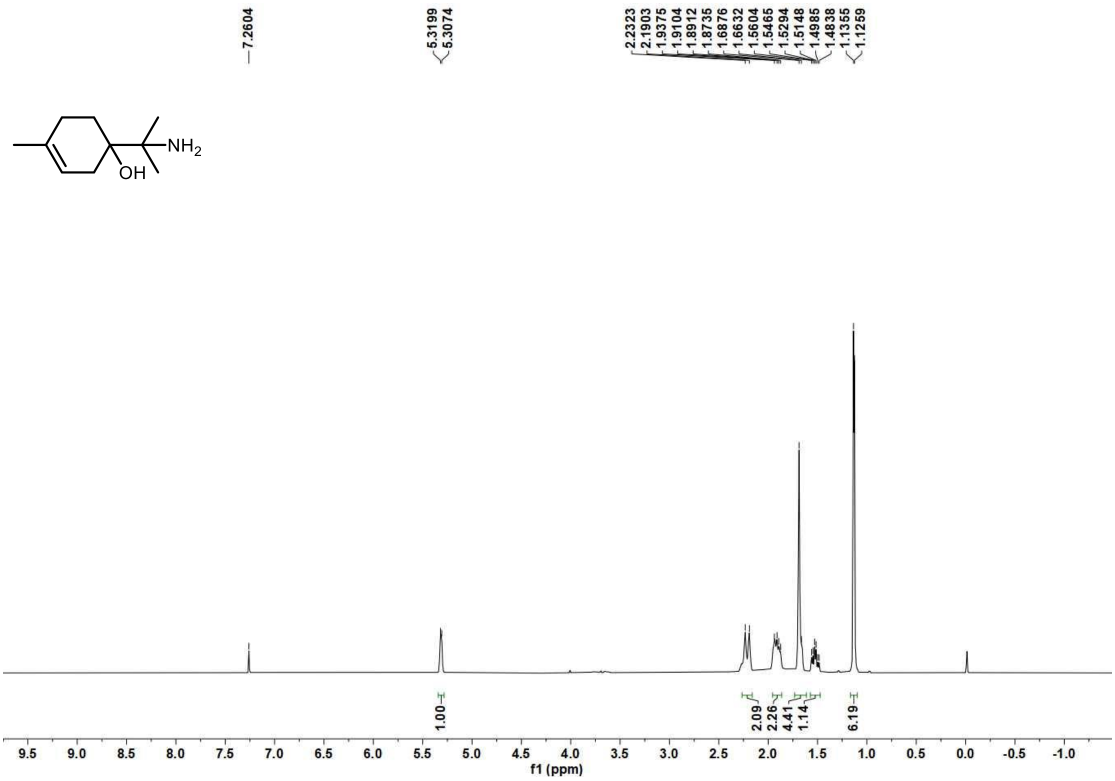
^{1}H NMR (400 MHz, CD_3OD) of **5i**



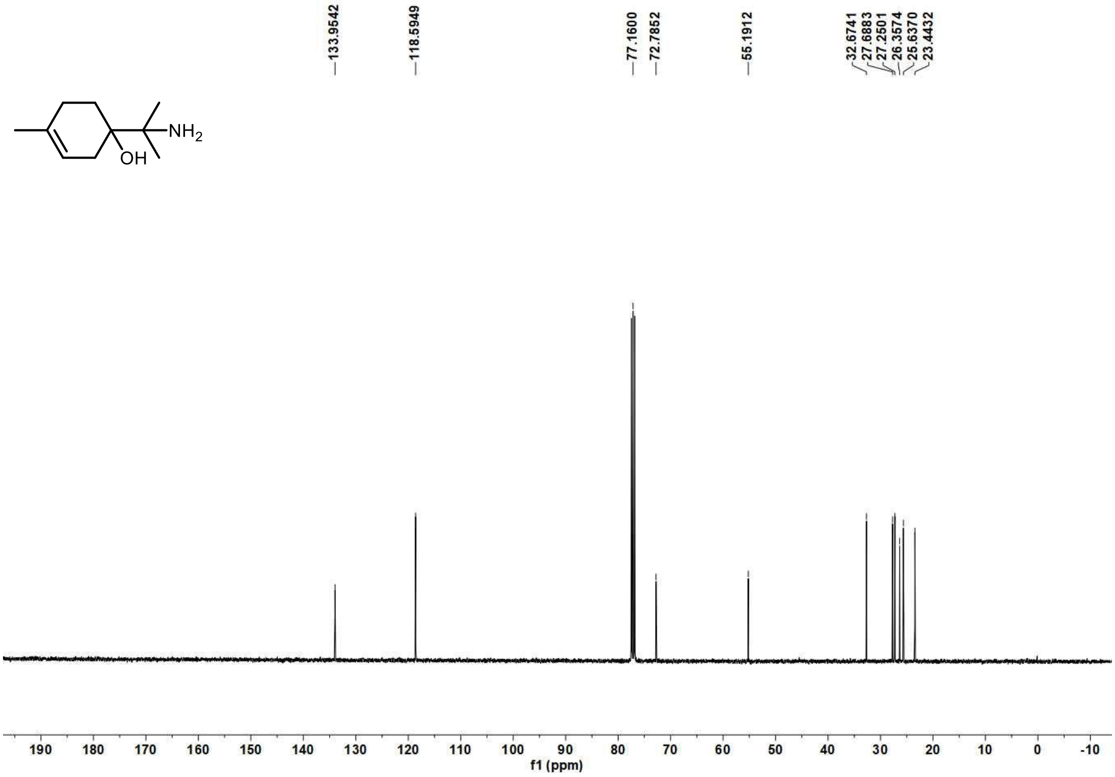
^{1}C NMR (101 MHz, CD_3OD) of **5i**



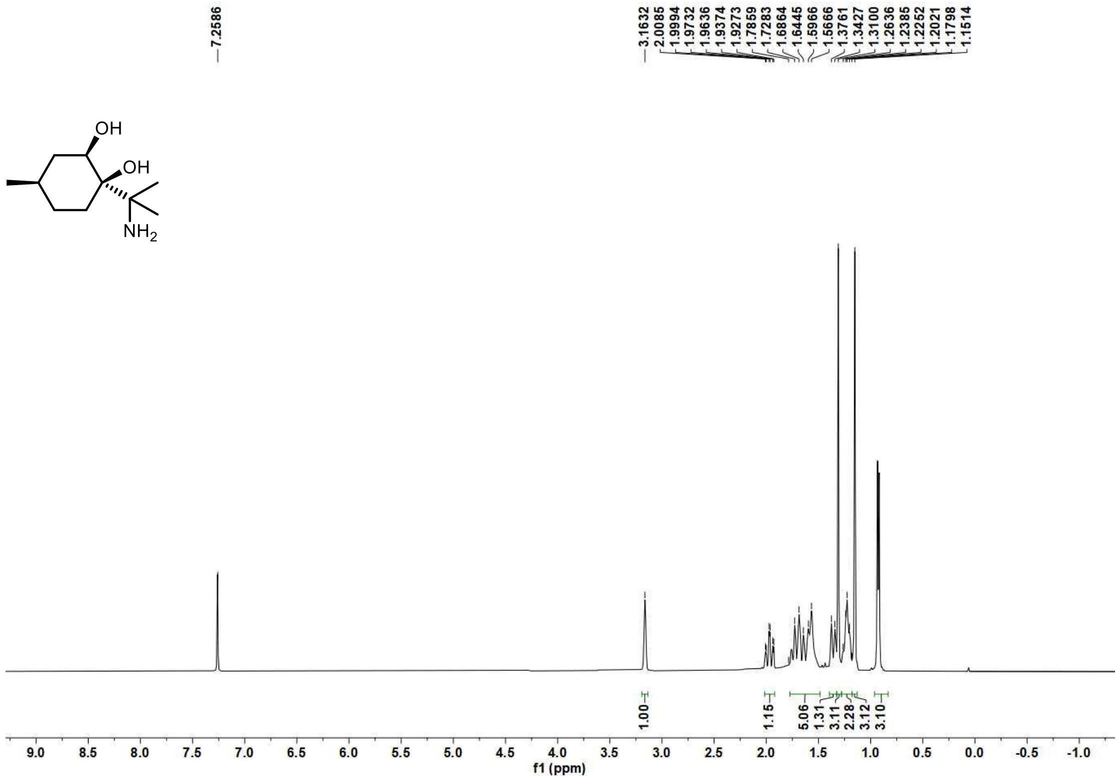
[1]H NMR (400 MHz, $CDCl_3$) of **5j**



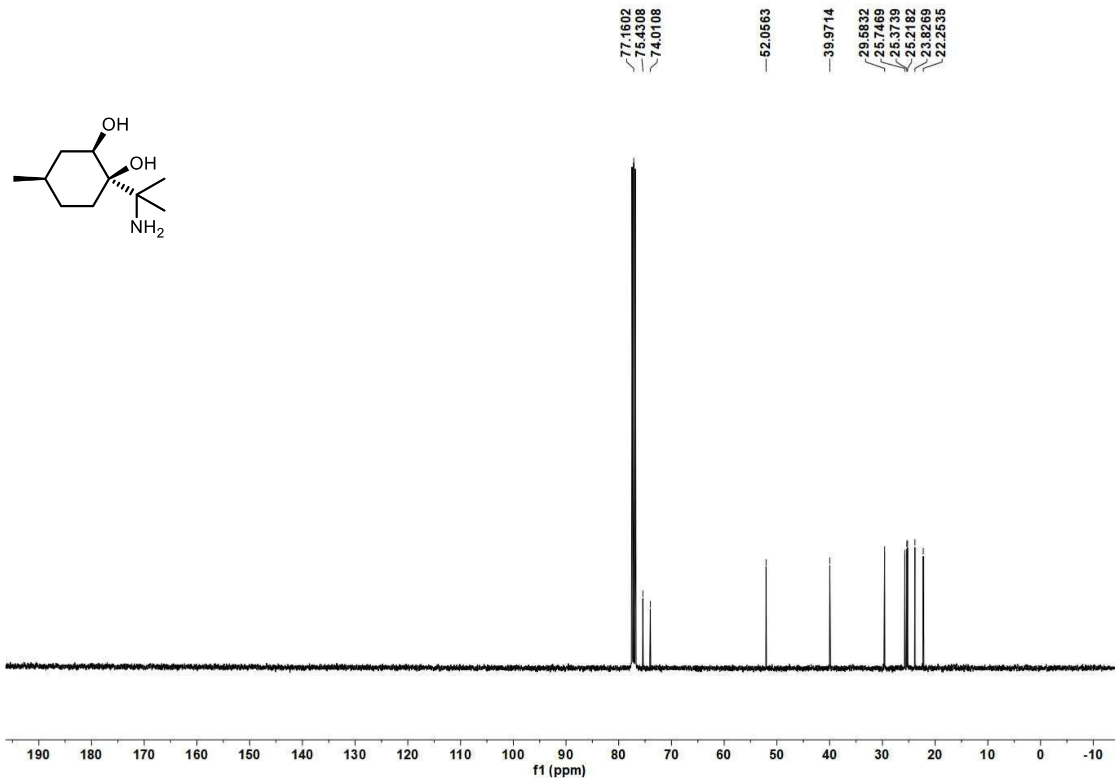
[13]C NMR (101 MHz, $CDCl_3$) of **5j**



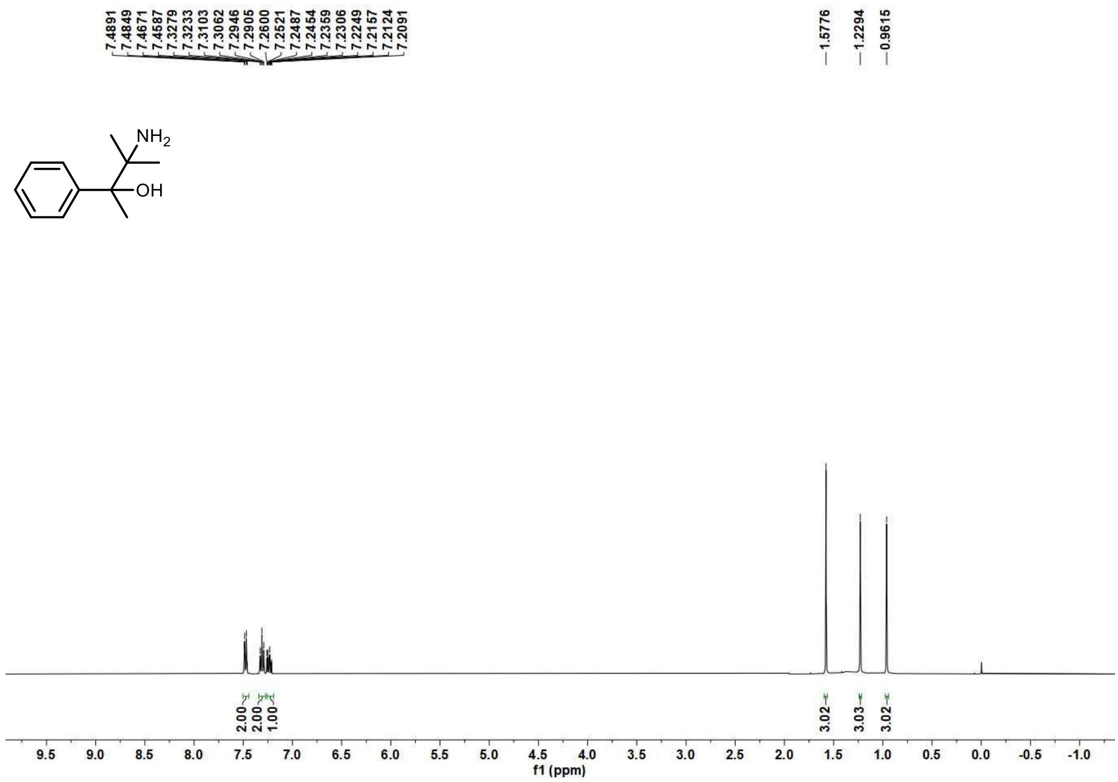
^{1}H NMR (400 MHz, $CDCl_3$) of **5k**



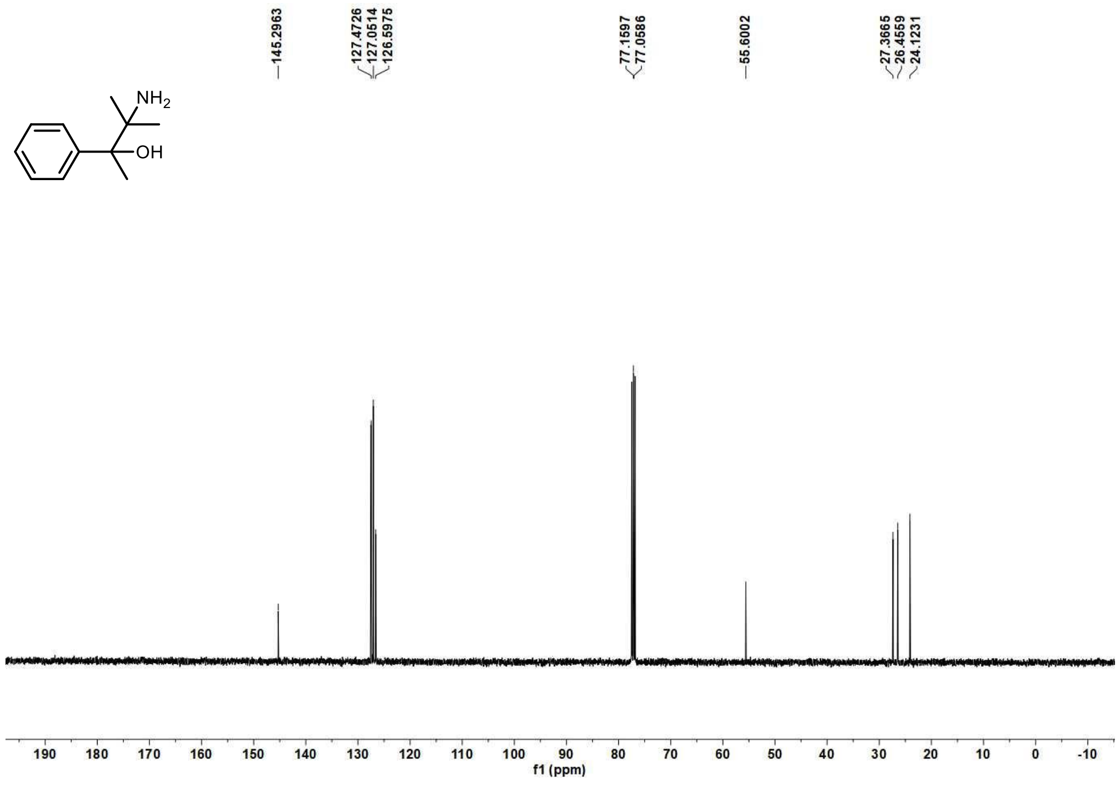
^{13}C NMR (101 MHz, $CDCl_3$) of **5k**



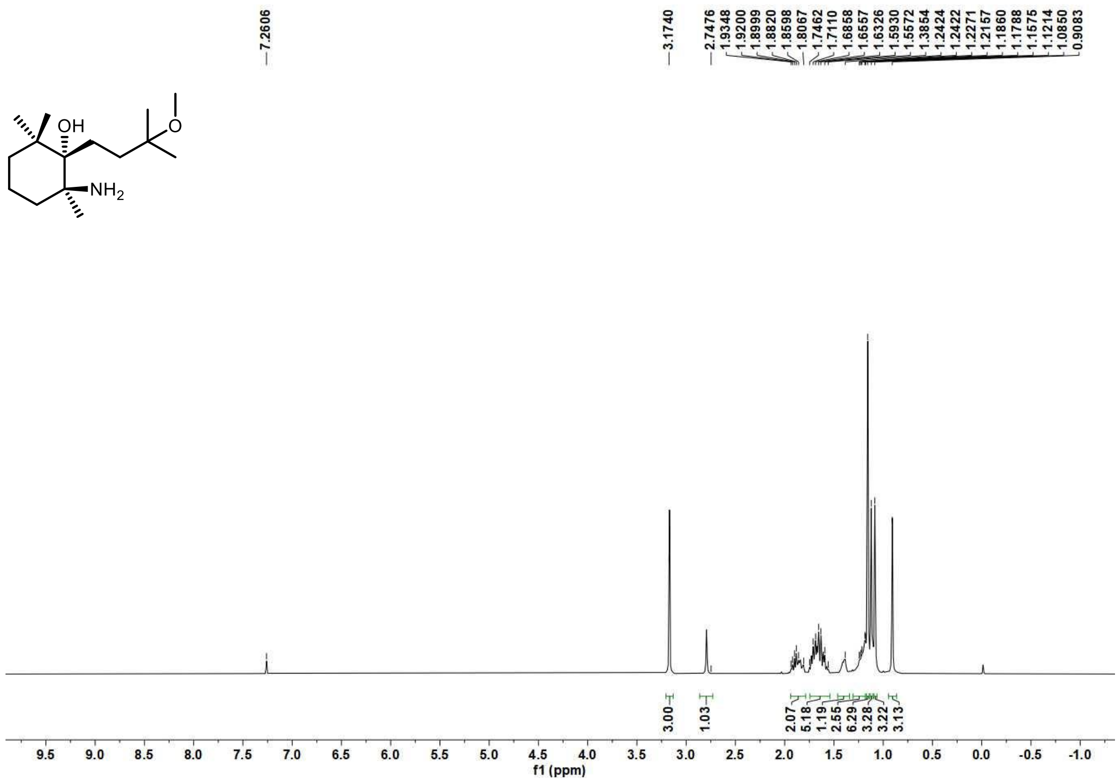
[1]H NMR (400 MHz, $CDCl_3$) of **5l**



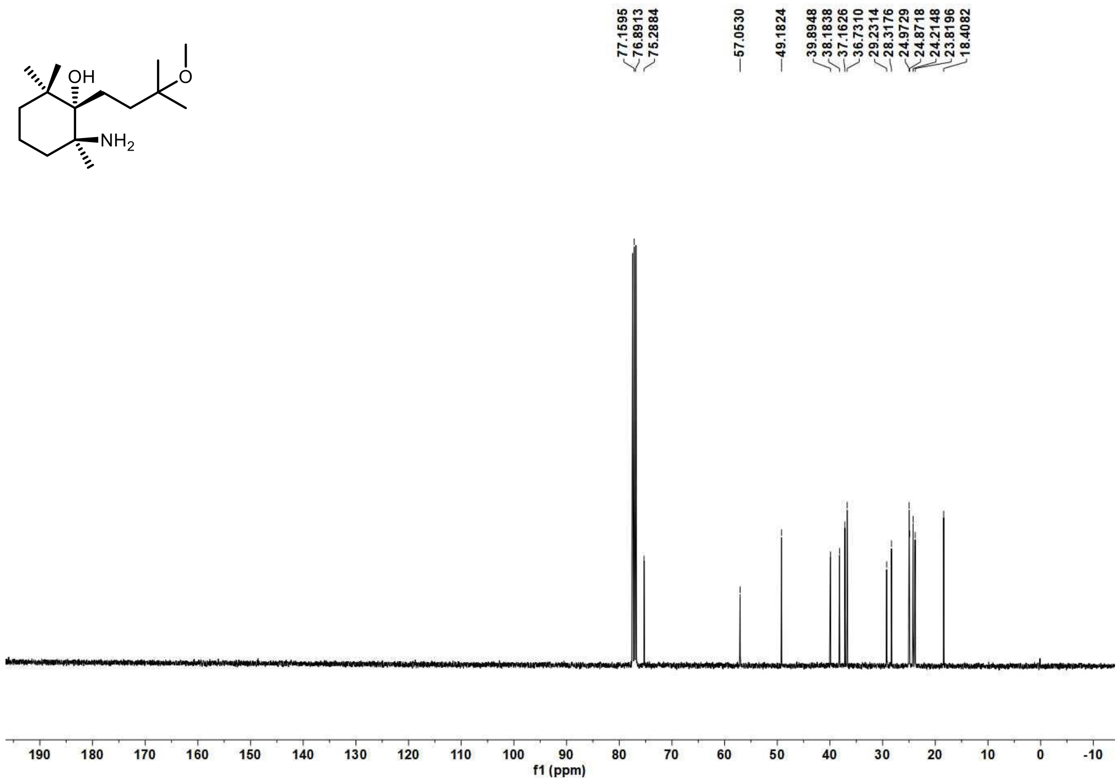
[13]C NMR (101 MHz, $CDCl_3$) of **5l**



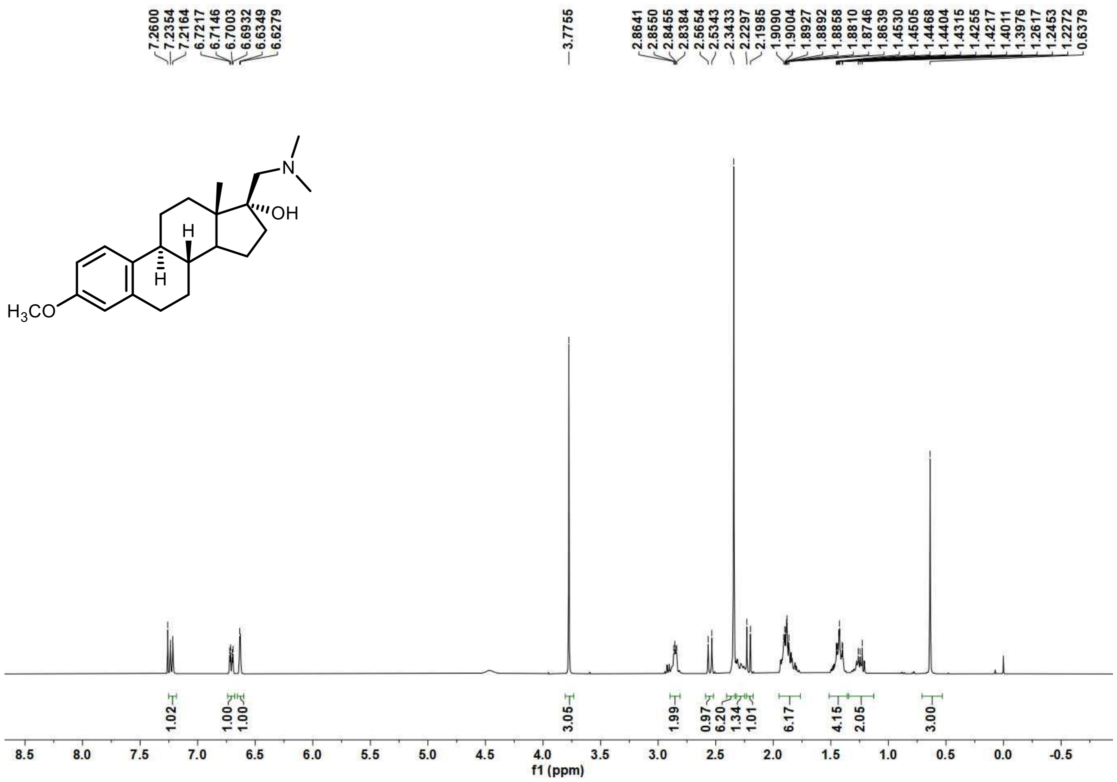
[1]H NMR (400 MHz, $CDCl_3$) of **5m**



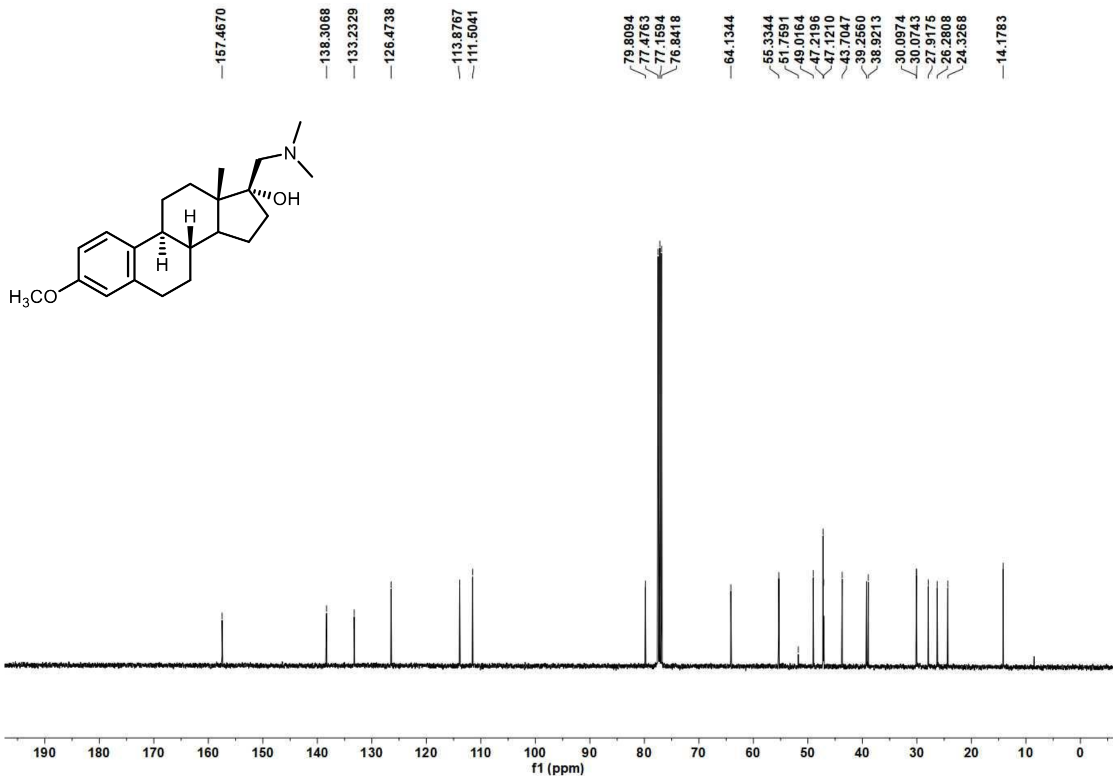
[13]C NMR (101 MHz, $CDCl_3$) of **5m**



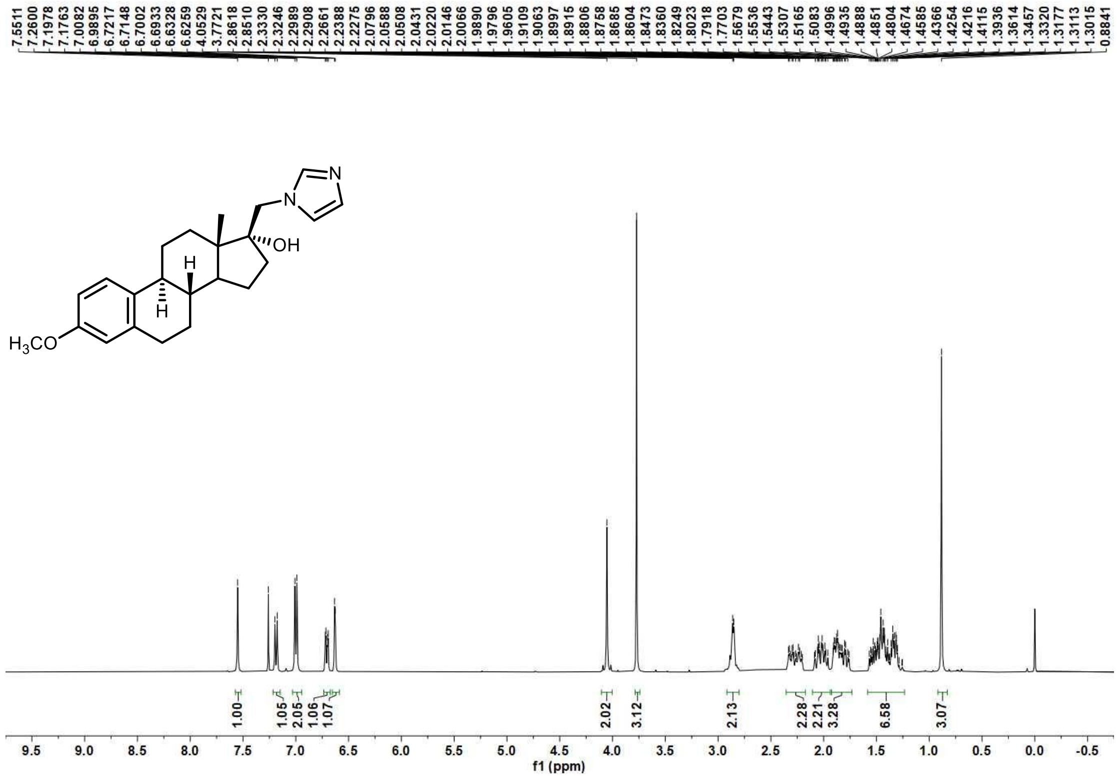
^{1}H NMR (400 MHz, $CDCl_3$) of **5ga**



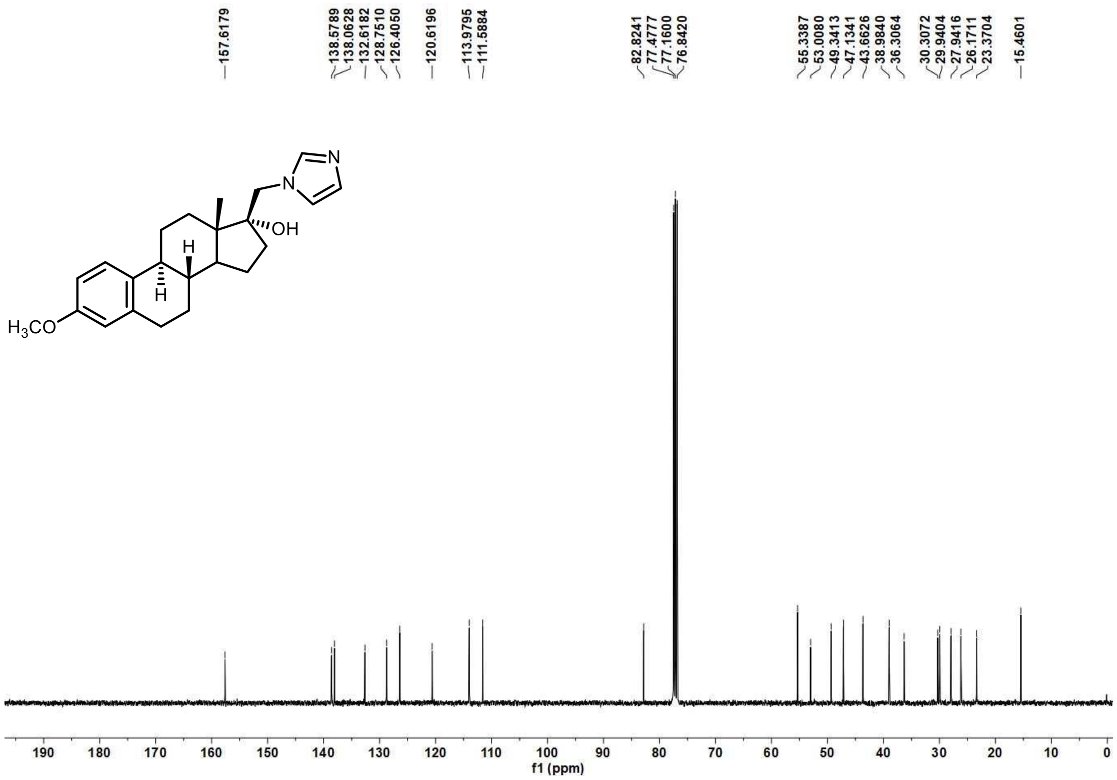
^{13}C NMR (101 MHz, $CDCl_3$) of **5ga**



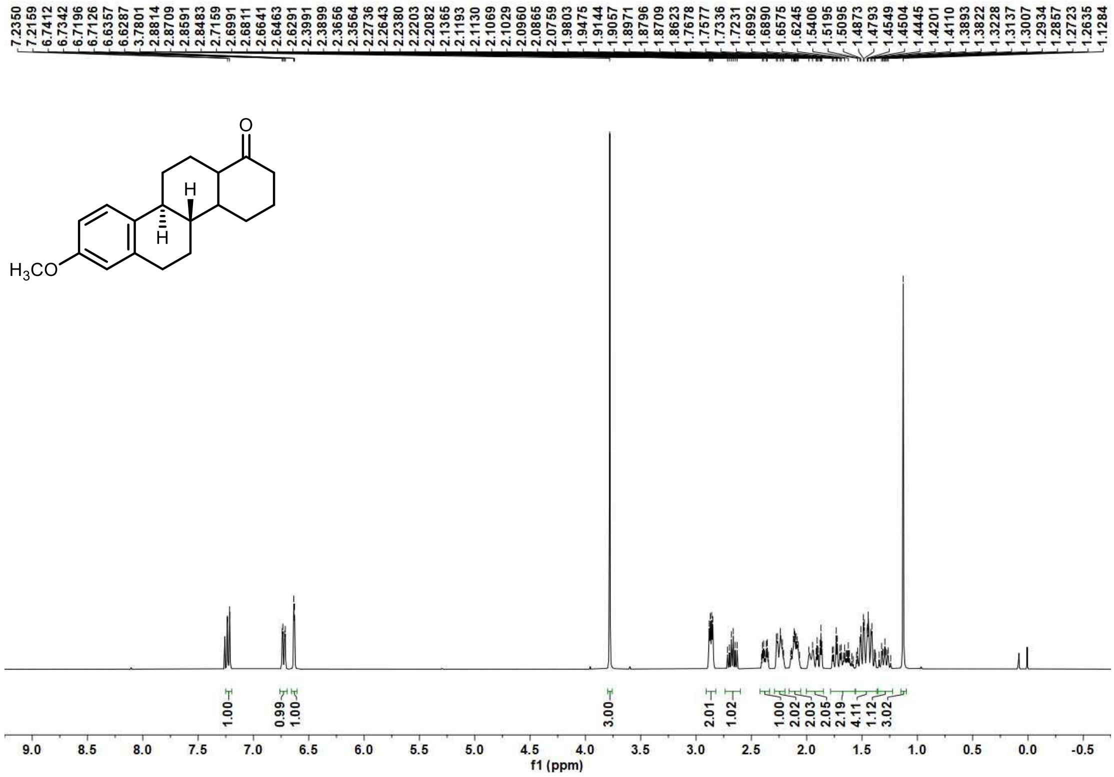
^{1}H NMR (400 MHz, $CDCl_3$) of **5gb**



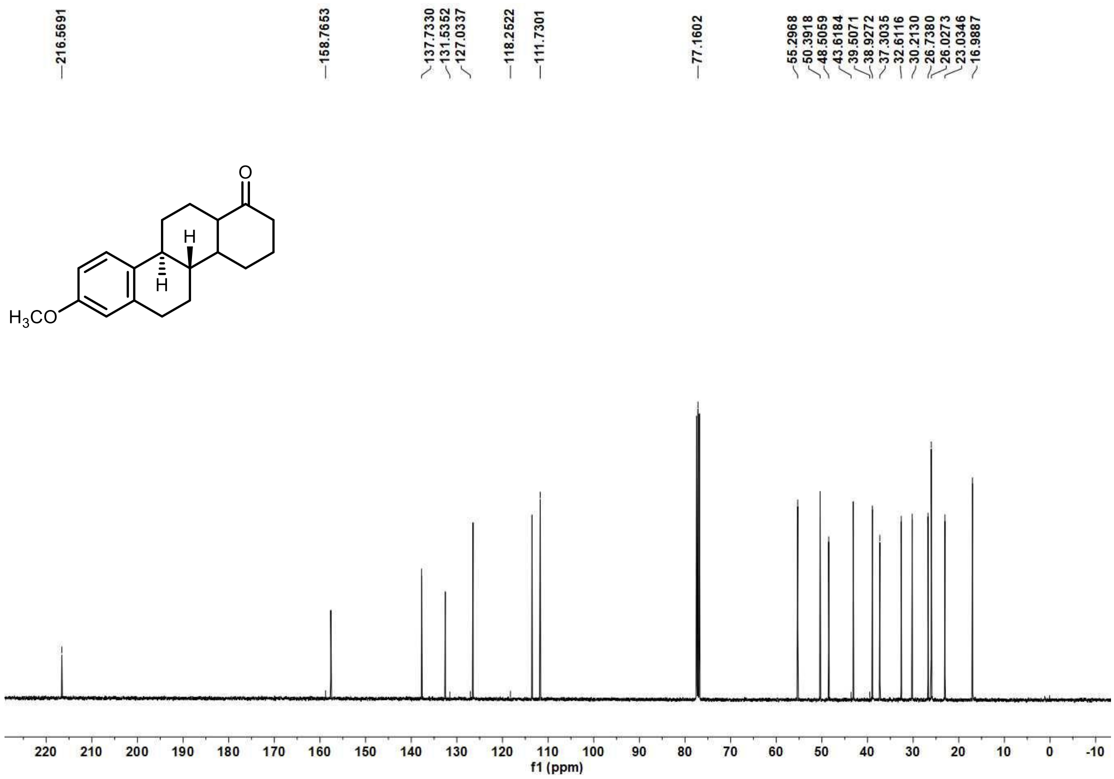
^{13}C NMR (101 MHz, $CDCl_3$) of **5gb**



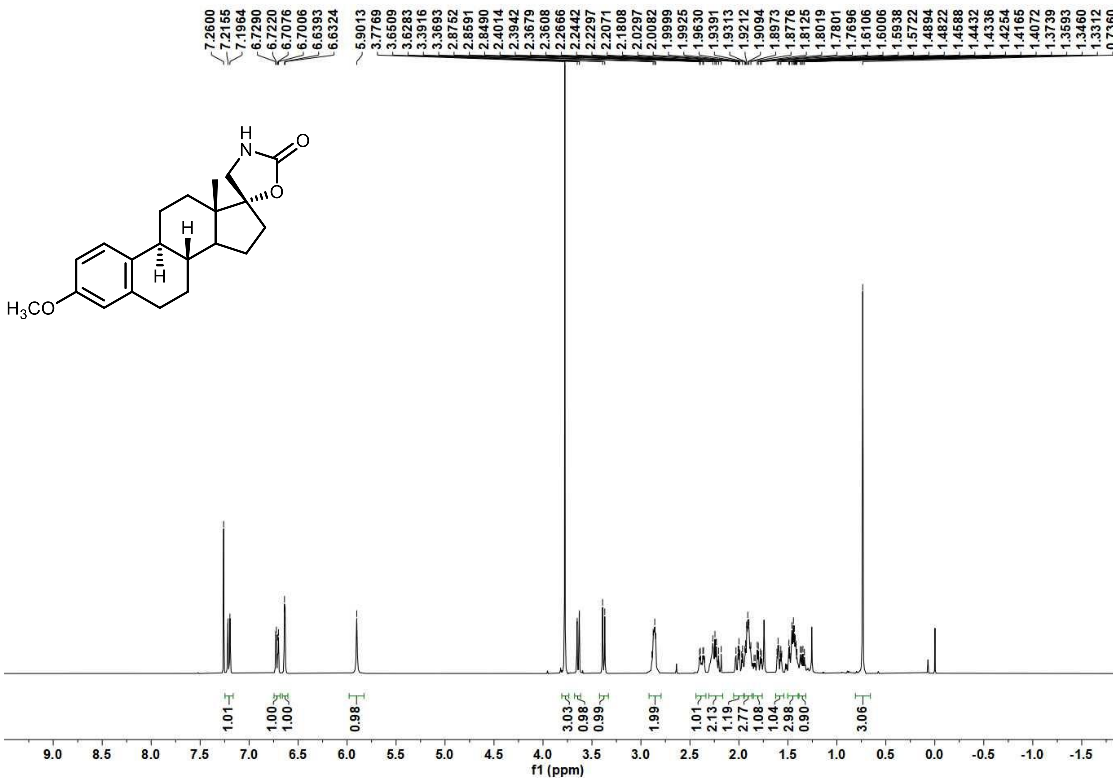
^{1}H NMR (400 MHz, $CDCl_3$) of **5gc**



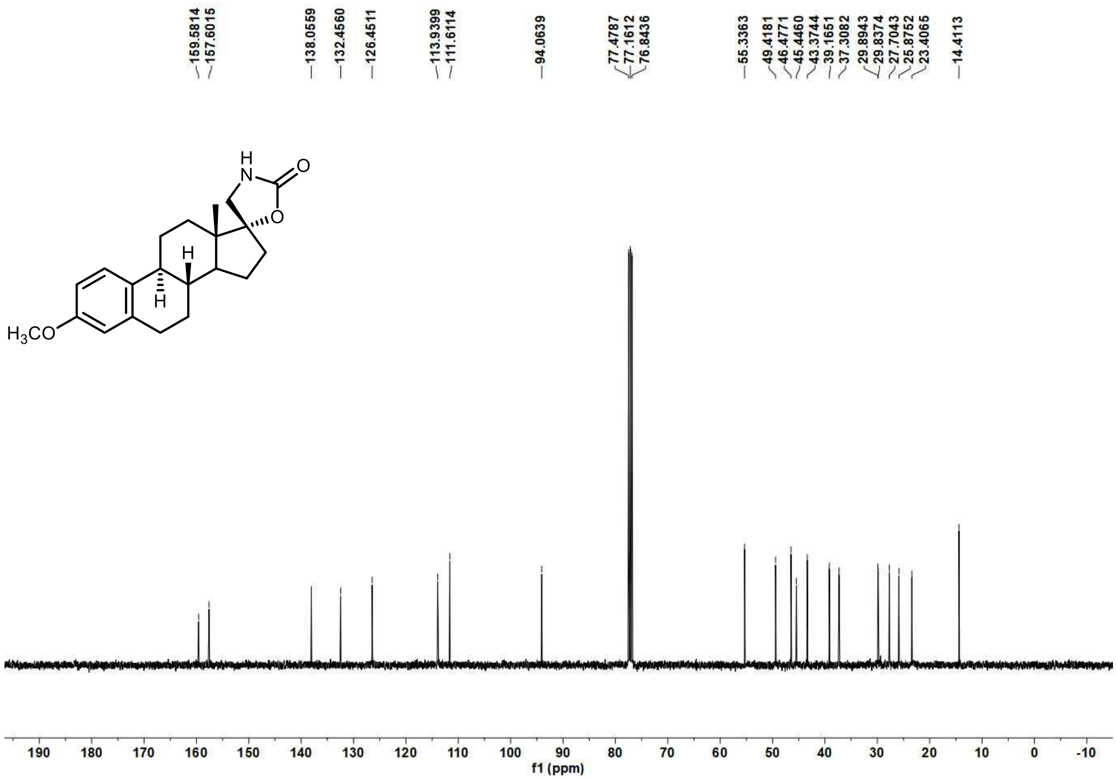
^{13}C NMR (101 MHz, $CDCl_3$) of **5gc**



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



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



6. Computional study

Computational details:

All quantum mechanical calculations have been performed with Gaussian 16[1]. Geometry optimizations and frequency analyses were performed at the M062X-D3/def2-SVP-SMD-(methanol) level of theory as well as the thermal corrections to free energy (G_{corr}) at the temperature of 308 K. Single-point energies were calculated at the M062X-D3/def2-TZVPP level of theory using the optimized structure in gas phase. The Gibbs free energies of solvation (ΔG_{solv}) were calculated at the M052X/6-31G(d) level of theory using SMD model of solvation. CYLview20 was utilized to generate 3D structures[2]. Imaginary frequencies were inspected to determine the stationary points (no imaginary frequencies) or transition states (only one imaginary frequency). All transition states were confirmed by IRC calculations using the same theory level with geometry optimization. The thermal-corrected, solvated Gibbs free energies were calculated as $G = SP + G_{corr} + \Delta G_{solv}$.

Table S2 Energies of intermediates and transition states

Structure	SP (Hartree)	G_{corr} (Hartree)	ΔG_{solv} (Hartree)	Imaginary frequency
1	-615.874326272	0.180010000	-0.013740629	none
2	-672.464085127	0.219823000	-0.021577731	none
2'	-1288.385219540	0.426709000	-0.037818556	none
A	-672.809293212	0.227453000	-0.105781926	none
B	-729.405455771	0.266122000	-0.110298518	none
B'	-672.832743395	0.235119000	-0.111400519	none
C	-1345.347990820	0.475944000	-0.103384196	none
C'	-1288.774685400	0.442591000	-0.104914576	none
D1	-729.405315716	0.265431000	-0.111240853	none
D2	-729.417360472	0.264520000	-0.098558911	none
D3a	-672.832740997	0.235117000	-0.111402723	none
D3b	-672.824491591	0.236017000	-0.111402723	-72.10
D3c	-672.839355965	0.233930000	-0.109103505	none
D3d	-672.828963346	0.233288000	-0.110061266	none

NH_3	-56.551545832	0.015409000	0.013186072	none
NH_4^+	-56.887825220	0.028494000	-0.127870207	none
TSA-B	-729.348242351	0.259983000	-0.099144216	-660.66
TSA-C	-1345.274447570	0.469215000	-0.109686246	-644.03
TSD1-D2	-729.412946949	0.262052000	-0.101460387	-624.74

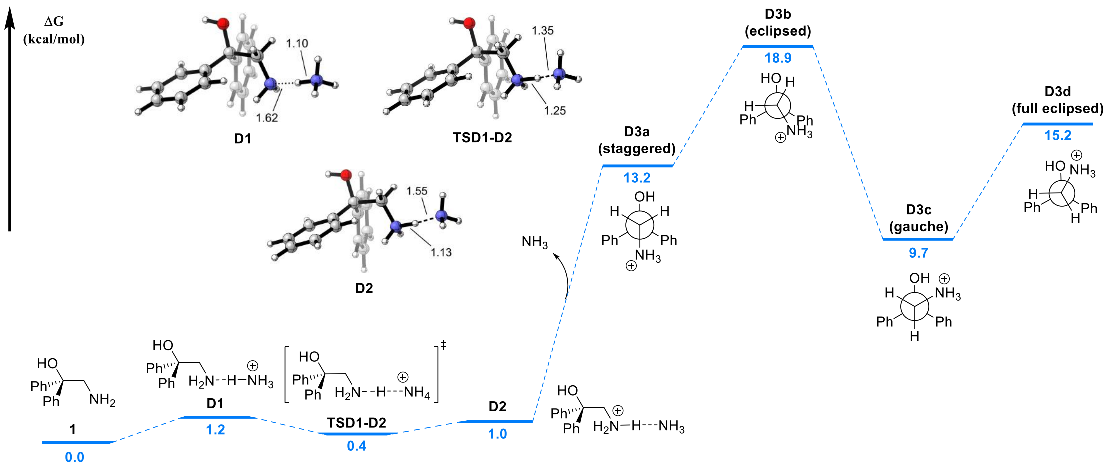


Figure S1 The energy profile for the protonation of **2** and the conformational changes of **D3** (protonated **1**)

When adding 2 equiv of HCO_2NH_4 in the reaction, **2** is prone to form complex **D1** with ammonium ion with only 1.2 kcal/mol rise in energy (Figure S1). The transition state of proton transfer reaction (**D1** to **D2)** has been located but the $\Delta G^{\neq}$ is negative, which seems unusual but suggesting a very low energy barrier for this process. **D2** is more stable than protonated **2** (**D3a**) because the energy raised in 13.2 kcal/mol from **D1** to **D3a**. These results showed that **2** is preferred to remain bonded with ammonium ion through N-H interaction once upon adding ammonium formate, thus preventing **2** to perform a nucleophilic attack on **1**.

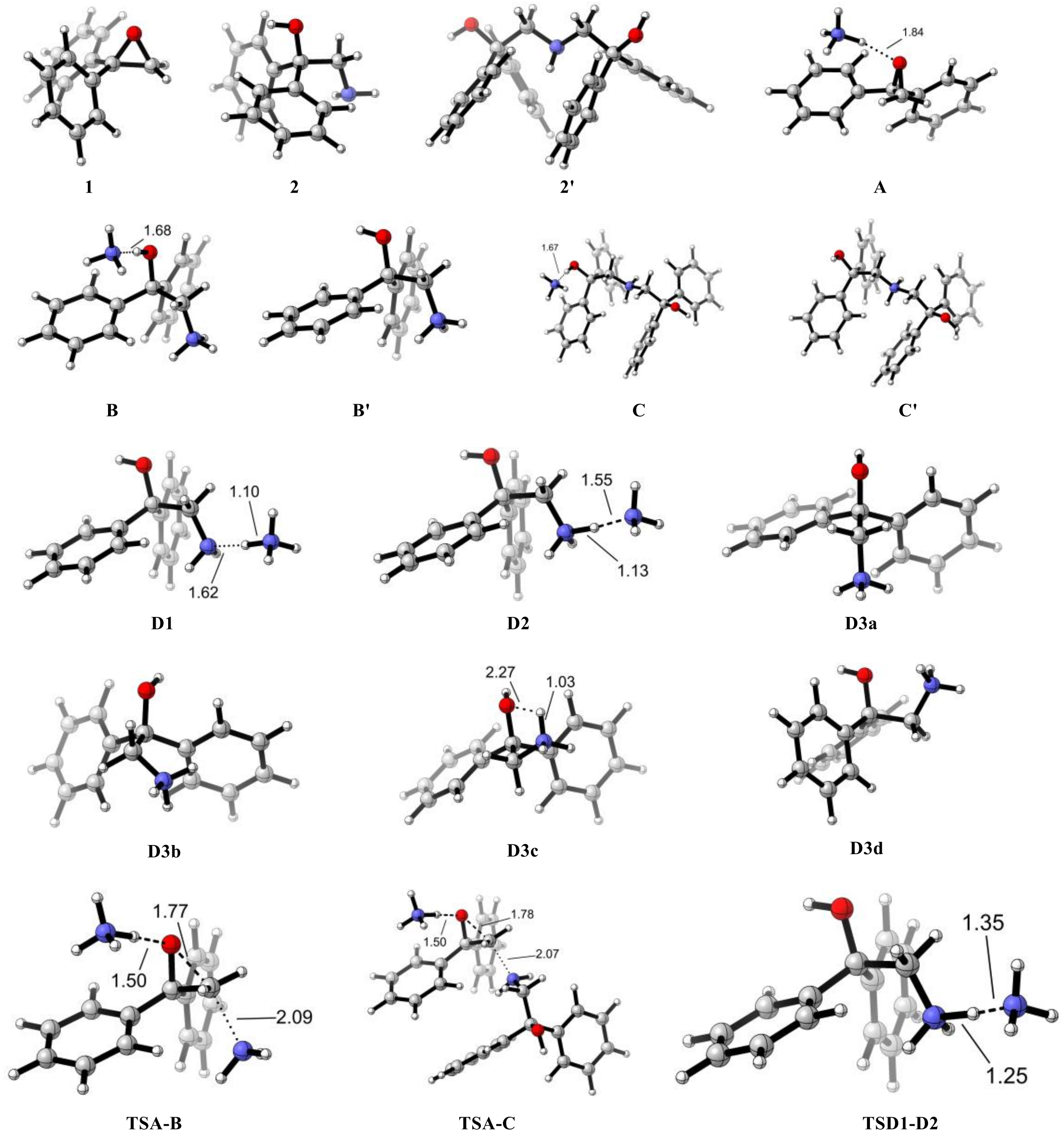


Figure S2 The optimized structure of intermediates, reactants and products

The cartesian coordinates of all optimized structures

1

C	0.03771300	1.01204000	0.14487200
C	0.09590600	2.30918700	0.84593500
O	0.11749400	2.23670500	-0.56844100
H	1.03939200	2.61156800	1.31263100
H	-0.81952200	2.72452700	1.28023100
C	-1.28077900	0.30272800	0.02526000
C	-2.03706800	-0.00842300	1.15754000
C	-1.74217400	-0.07171800	-1.24127300
C	-3.24749800	-0.69176200	1.02571700
H	-1.67526200	0.28575100	2.14582400
C	-2.95440800	-0.74677900	-1.37292200

H	-1.14779400	0.17404500	-2.12485200
C	-3.70723200	-1.05998000	-0.23870000
H	-3.83447100	-0.93325200	1.91379200
H	-3.31378700	-1.03138900	-2.36362100
H	-4.65552000	-1.59069800	-0.34235800
C	1.27853500	0.16288000	0.07097700
C	1.26039400	-1.17563200	0.47814800
C	2.47561700	0.72060100	-0.39428200
C	2.42607200	-1.94121700	0.43124200
H	0.33150100	-1.62529300	0.83471700
C	3.63738900	-0.04779600	-0.44438300
H	2.48824300	1.76039900	-0.72583700
C	3.61699900	-1.38077000	-0.03019600
H	2.39973400	-2.98378600	0.75355700
H	4.56376700	0.39655000	-0.81338000
H	4.52697000	-1.98221600	-0.07078500

2

C	-0.00187800	0.84865300	0.60756600
C	-0.09241000	2.25877900	0.00088900
O	-0.00960300	1.09378200	2.00689300
H	-0.94258200	2.74779000	0.51196000
H	0.81373200	2.80623100	0.30089500
C	1.28751600	0.10161900	0.24744300
C	1.45342700	-1.20299000	0.73598600
C	2.32832600	0.67547200	-0.48807000
C	2.63027900	-1.91196600	0.50774000
H	0.64528500	-1.67497000	1.30282800
C	3.50745800	-0.03655500	-0.72467200
H	2.21897100	1.67713600	-0.90229600
C	3.66439300	-1.32860700	-0.22751300
H	2.73886700	-2.92483700	0.90029700
H	4.30775500	0.42683500	-1.30502300
H	4.58671800	-1.88194800	-0.41409000
C	-1.23681200	0.04515900	0.19144800
C	-1.27555000	-0.64138500	-1.02974900
C	-2.37476000	0.04067900	1.00499800
C	-2.42753400	-1.32081500	-1.42461300
H	-0.39553900	-0.64493900	-1.67632300
C	-3.52609800	-0.64474300	0.61232300
H	-2.35507900	0.57536000	1.95566000
C	-3.55654200	-1.32712000	-0.60312800
H	-2.44109600	-1.85306100	-2.37774200
H	-4.40346200	-0.64420400	1.26222600

H	-4.45574100	-1.86475800	-0.90984900
H	0.04909400	0.24763200	2.47350900
N	-0.19331600	2.25126000	-1.44618100
H	-1.13012000	1.95821500	-1.72440400
H	-0.08564600	3.20336600	-1.79340900

2’

C	-2.35610800	0.71381300	1.06636800
C	-1.19276300	0.24391100	1.96698300
O	-3.28492300	1.40313100	1.88837700
H	-0.94170400	1.10943200	2.61548100
H	-1.55823100	-0.56085300	2.62898400
C	-3.07905600	-0.42661800	0.34612400
C	-2.60365800	-1.74027500	0.30578500
C	-4.28874800	-0.12476900	-0.29551800
C	-3.32126500	-2.73093800	-0.37146700
H	-1.65707900	-1.99080100	0.78452300
C	-5.00453200	-1.11135300	-0.96843300
H	-4.66926100	0.89865000	-0.26037900
C	-4.51973600	-2.42135100	-1.01051600
H	-2.93394700	-3.75146000	-0.39758500
H	-5.94420300	-0.85864500	-1.46358800
H	-5.07695300	-3.19657200	-1.53997300
C	-1.80498700	1.73779100	0.07198500
C	-1.35256200	1.35330900	-1.19670600
C	-1.64647000	3.07062000	0.47120300
C	-0.74344400	2.27998800	-2.04476300
H	-1.47012500	0.31834000	-1.52588900
C	-1.04902700	3.99902400	-0.38211600
H	-1.99622900	3.38156800	1.45654200
C	-0.59149300	3.60633000	-1.64080500
H	-0.39122300	1.96124100	-3.02775700
H	-0.93726600	5.03583200	-0.05844900
H	-0.11773200	4.33196000	-2.30476500
H	-3.63151900	0.77514100	2.53938500
N	-0.05853100	-0.22841100	1.20847800
H	0.17256000	0.45983200	0.49443300
C	1.11630800	-0.50983900	1.99943200
H	1.34383200	0.28376800	2.74015200
H	0.97647500	-1.44423100	2.56773600
C	2.36009300	-0.69798500	1.11665100
O	3.39005400	-0.99788900	2.04396300
H	4.21953400	-1.11690000	1.55847900
C	2.11446100	-1.87385100	0.16598300

C	1.43193100	-1.70252200	-1.04645600
C	2.50186700	-3.16236900	0.54409100
C	1.13744400	-2.79785300	-1.85616100
H	1.12776800	-0.70213700	-1.36303800
C	2.21313200	-4.26045100	-0.27019700
H	3.03113000	-3.30673500	1.48707500
C	1.52798400	-4.08254200	-1.47053400
H	0.60243700	-2.64652200	-2.79580500
H	2.52578500	-5.25956300	0.03977600
H	1.29997700	-4.93989900	-2.10664600
C	2.73764900	0.58118700	0.35232500
C	2.21809300	1.84011100	0.67946300
C	3.69663100	0.50171200	-0.66777100
C	2.63445700	2.98409800	-0.00667900
H	1.47737800	1.95187300	1.47428400
C	4.11836700	1.64183500	-1.34844300
H	4.11652800	-0.47072300	-0.93791200
C	3.58213000	2.88930000	-1.02371200
H	2.21108600	3.95434300	0.26058200
H	4.86544100	1.55473100	-2.13962100
H	3.90401600	3.78339500	-1.56079100

A

C	0.17318100	0.70045300	0.41970200
C	0.04116600	1.88134500	1.29317200
O	-0.04547200	2.01007200	-0.12104800
H	0.94711600	2.30700100	1.73507300
H	-0.89493300	2.05988400	1.83154600
C	-0.99620100	-0.22528500	0.23368000
C	-1.89353700	-0.49905800	1.26825600
C	-1.21024900	-0.78333400	-1.03421500
C	-3.00430200	-1.31391600	1.03498000
H	-1.72505500	-0.07906000	2.26198600
C	-2.32310400	-1.58804700	-1.26776700
H	-0.50394600	-0.57436500	-1.84196900
C	-3.22339400	-1.85277700	-0.23175300
H	-3.70011000	-1.52620500	1.84856500
H	-2.48893200	-2.01254400	-2.25956000
H	-4.09432300	-2.48500800	-0.41399000
C	1.54332000	0.14203400	0.15349900
C	1.82452900	-1.19928000	0.43572600
C	2.55598800	0.96695200	-0.34809100
C	3.10669000	-1.70642700	0.22552700
H	1.03855700	-1.85112300	0.82316100

C	3.83524600	0.45518800	-0.56226000
H	2.33500300	2.01091800	-0.57710800
C	4.11465900	-0.88146000	-0.27469500
H	3.31691600	-2.75349000	0.45107200
H	4.61755700	1.10498700	-0.95895800
H	5.11652000	-1.28059200	-0.44305700
H	-1.78023300	2.23722800	-0.68450000
N	-2.80620900	2.22127900	-0.87027700
H	-3.31491100	2.25999700	0.02114800
H	-3.07525800	3.02457800	-1.45007400
H	-3.05069400	1.34993100	-1.35758000

B

C	0.07037200	0.79813400	-0.08516100
C	0.10486100	1.82538400	1.06555300
O	-0.12431300	1.55135800	-1.25431800
H	0.83792100	2.59563600	0.80099600
H	-0.87559100	2.29959700	1.19407500
C	-1.06304500	-0.22876800	0.03914900
C	-2.07539000	-0.16329500	0.99904200
C	-1.14047900	-1.21770300	-0.95283100
C	-3.13376300	-1.07833400	0.98127900
H	-2.08401200	0.60838000	1.77159800
C	-2.19639100	-2.12283000	-0.97794500
H	-0.36391200	-1.26565800	-1.72015300
C	-3.19884500	-2.05746200	-0.00529400
H	-3.91360300	-1.01213000	1.74210100
H	-2.24120600	-2.88264700	-1.76047500
H	-4.02786300	-2.76725200	-0.02184000
C	1.43699700	0.11264100	-0.16857900
C	1.73223700	-1.01727800	0.60479200
C	2.43378800	0.65446000	-0.98698300
C	3.00306200	-1.59237700	0.56343500
H	0.96018300	-1.46530600	1.23611900
C	3.70144000	0.07394400	-1.03361700
H	2.20840100	1.53015000	-1.59596000
C	3.99068300	-1.04924900	-0.25816200
H	3.21690400	-2.47476300	1.16929000
H	4.46759900	0.50240100	-1.68265500
H	4.98266900	-1.50292600	-0.29695100
H	-1.09737500	1.82906400	-1.28884800
N	-2.74097600	2.15425200	-1.30336000
H	-3.24281900	1.27199500	-1.42779400
H	-3.10308900	2.56093900	-0.43853000

H	-3.05139800	2.76938600	-2.05788200
N	0.51877200	1.26979000	2.38071100
H	0.48156900	1.99431800	3.11040600
H	-0.08208200	0.49456400	2.69508600
H	1.48447600	0.91149100	2.35643200

B'

C	0.00769500	0.82434100	0.59512800
C	-0.07319500	2.22146800	-0.04023700
O	0.01164900	1.13917100	1.97353600
H	-0.97795800	2.71644600	0.33055800
H	0.79787500	2.82447200	0.23746600
C	1.29537200	0.06530500	0.24930100
C	2.43518900	0.69887700	-0.25799900
C	1.36822900	-1.30271000	0.55116600
C	3.61155800	-0.02224500	-0.47905100
H	2.43977400	1.76673300	-0.48605100
C	2.54373800	-2.01924400	0.34323400
H	0.49213800	-1.81499600	0.95577100
C	3.66986000	-1.38101500	-0.18036700
H	4.48662800	0.48938500	-0.88347000
H	2.57929400	-3.08247600	0.58724300
H	4.58987200	-1.94248100	-0.35221000
C	-1.25123700	0.03653300	0.21000800
C	-1.32212400	-0.69183500	-0.98517900
C	-2.38023200	0.10038100	1.03337500
C	-2.50124900	-1.34373200	-1.34778000
H	-0.44745600	-0.76694200	-1.63682700
C	-3.55548400	-0.56001300	0.67426900
H	-2.33334800	0.66747500	1.96379700
C	-3.62017800	-1.28231100	-0.51709700
H	-2.53986200	-1.90936800	-2.28038600
H	-4.42565300	-0.50855300	1.33131600
H	-4.53984100	-1.79926500	-0.79691400
N	-0.15980600	2.18735800	-1.51881100
H	-1.00742000	1.69760200	-1.84227700
H	-0.19489100	3.14152000	-1.90334000
H	0.64827700	1.71678400	-1.95298200
H	0.09036900	0.31600100	2.47905300

C

C	-2.17539300	1.04982100	0.78195600
C	-1.02897100	0.74423600	1.76747800
O	-3.21964000	1.59123600	1.54379900

H	-0.79855000	1.64964300	2.34109600
H	-1.31872700	-0.05669700	2.45919500
C	-2.66874500	-0.20705500	0.04939600
C	-2.21093200	-1.50148400	0.31592100
C	-3.69992300	-0.03722400	-0.88522200
C	-2.76213700	-2.60181300	-0.35060200
H	-1.43447900	-1.69631200	1.06075800
C	-4.25307500	-1.13028700	-1.54360500
H	-4.07406300	0.96941700	-1.08767500
C	-3.78114400	-2.42033200	-1.28062100
H	-2.39211400	-3.60450300	-0.12812700
H	-5.05715500	-0.97882000	-2.26608700
H	-4.21292000	-3.27908500	-1.79741300
C	-1.68186600	2.11048100	-0.20760600
C	-1.00701100	1.75617900	-1.38290600
C	-1.83470600	3.46541100	0.10503900
C	-0.48467800	2.73936800	-2.22485000
H	-0.89303900	0.70335900	-1.65670800
C	-1.32205700	4.44756000	-0.74307300
H	-2.36301600	3.74820700	1.01598500
C	-0.64260700	4.08806600	-1.90742500
H	0.03906000	2.44626000	-3.13661000
H	-1.45421700	5.50125500	-0.49029900
H	-0.24033800	4.85788900	-2.56867500
H	-3.66400800	0.82902700	2.04178700
N	-4.36726800	-0.52883600	2.72113900
H	-4.80950100	-1.06987700	1.97410900
H	-3.70543300	-1.16486300	3.17088900
H	-5.09686200	-0.34271600	3.41177200
N	0.21672500	0.31894300	1.06609800
H	-0.03704400	-0.27226900	0.25737600
H	0.67430100	1.14523600	0.65094900
C	1.17458100	-0.43885400	1.90649300
H	1.52763300	0.21548300	2.71233800
H	0.62163100	-1.27898600	2.34706500
C	2.34145500	-1.02391100	1.09038900
O	2.97873400	-1.84480500	2.04813900
H	3.76558400	-2.23944600	1.64335600
C	1.74394700	-1.86087900	-0.05114600
C	1.45198700	-1.29723900	-1.30118900
C	1.37596400	-3.18825600	0.19677200
C	0.79296200	-2.04455200	-2.27933600
H	1.73748900	-0.26434700	-1.51780300
C	0.73185300	-3.93844900	-0.78720500

H	1.60038700	-3.63358700	1.16716600
C	0.43333400	-3.36768800	-2.02543400
H	0.56785900	-1.58835200	-3.24514700
H	0.45700900	-4.97487100	-0.58211200
H	-0.07843500	-3.95333900	-2.79125100
C	3.33169600	0.02732400	0.57875500
C	3.32505300	1.35867000	1.00519300
C	4.34020500	-0.39149500	-0.30224500
C	4.29254500	2.25717400	0.54567200
H	2.57627000	1.72921500	1.70865600
C	5.31190700	0.49897100	-0.74967100
H	4.36136900	-1.42924300	-0.64504400
C	5.28670900	1.83116200	-0.33075400
H	4.26489300	3.29423600	0.88373700
H	6.08943900	0.15304400	-1.43306000
H	6.04231500	2.53339800	-0.68743500

C’

C	-2.30600000	0.95605900	1.10727200
C	-1.08059600	0.65877600	1.99362700
O	-3.27690000	1.54536300	1.94515800
H	-0.83030300	1.55897700	2.56752500
H	-1.28729400	-0.16613300	2.68710700
C	-2.88897900	-0.29599900	0.44605400
C	-2.36953200	-1.58396700	0.60678200
C	-4.03320800	-0.12262700	-0.34675000
C	-2.97029000	-2.67545400	-0.03096900
H	-1.49966900	-1.78191200	1.23896800
C	-4.63427300	-1.20770600	-0.97497700
H	-4.45078200	0.87984000	-0.46730600
C	-4.09865700	-2.49054400	-0.82351000
H	-2.55018900	-3.67363700	0.10529200
H	-5.52418500	-1.05472700	-1.58812500
H	-4.56636400	-3.34269000	-1.31968000
C	-1.90375900	2.00154600	0.06418200
C	-1.40458300	1.62152300	-1.18809300
C	-1.95018600	3.36026700	0.39583500
C	-0.95013800	2.58425800	-2.09028800
H	-1.37258300	0.56461800	-1.46748500
C	-1.50717100	4.32150400	-0.51249900
H	-2.33895300	3.66524500	1.36807400
C	-1.00258500	3.93689500	-1.75530900
H	-0.56213400	2.27233700	-3.06160800
H	-1.55535900	5.37870000	-0.24517600

H	-0.65321900	4.69076900	-2.46298400
H	-3.58722200	0.87535800	2.57305300
N	0.11653800	0.29130500	1.18703500
H	-0.16719500	-0.33867900	0.41781300
H	0.47614000	1.13523200	0.71365600
C	1.19664900	-0.37220700	1.95698600
H	1.58970800	0.34026600	2.69175100
H	0.74360200	-1.21768100	2.49038500
C	2.30623600	-0.93129300	1.04768200
O	3.10444000	-1.64074400	1.97292700
H	3.85885300	-2.02877400	1.50438800
C	1.64394400	-1.88073800	0.03763600
C	1.18431200	-1.42823100	-1.20701300
C	1.38646000	-3.20346900	0.41595400
C	0.47210000	-2.28158600	-2.05228300
H	1.37900100	-0.40034200	-1.52448100
C	0.68543700	-4.05808700	-0.43472700
H	1.74076100	-3.56200900	1.38356200
C	0.22275800	-3.59886900	-1.66899100
H	0.11737300	-1.91239700	-3.01631500
H	0.49711600	-5.08890100	-0.12881500
H	-0.33135000	-4.26701600	-2.33072500
C	3.14858700	0.14910300	0.36105200
C	3.09879100	1.49914900	0.72093300
C	4.06609000	-0.25001300	-0.62226800
C	3.93210900	2.43288200	0.09825500
H	2.42220600	1.85799200	1.49923700
C	4.90635000	0.67627500	-1.23291800
H	4.12161400	-1.30175100	-0.91498200
C	4.83663000	2.02559800	-0.87827400
H	3.87142000	3.48327700	0.38801600
H	5.61545500	0.34454400	-1.99334400
H	5.48849100	2.75512500	-1.36199100

D1

C	0.00601100	0.15948200	0.86594500
C	-0.10881100	1.68644800	0.68194000
O	0.02074000	0.01447900	2.27711300
H	-1.01126100	1.99886900	1.22724600
H	0.74637800	2.15829100	1.18780300
C	1.30388900	-0.42918000	0.29790100
C	1.41942100	-1.82309200	0.18620600
C	2.41514700	0.35781700	-0.02425500
C	2.60750300	-2.41328200	-0.23791100

H	0.56441700	-2.45674000	0.43553300
C	3.60480200	-0.23154700	-0.46018100
H	2.37763900	1.44518200	0.06225700
C	3.70547800	-1.61656000	-0.56861200
H	2.67517900	-3.50006600	-0.31471200
H	4.45736000	0.40161200	-0.71273800
H	4.63557800	-2.07565700	-0.90848400
C	-1.23090200	-0.50443500	0.25611900
C	-1.30155800	-0.78185100	-1.11620800
C	-2.34433400	-0.77757600	1.05718000
C	-2.46101200	-1.32090300	-1.67297300
H	-0.43865300	-0.58517300	-1.75705900
C	-3.50248300	-1.32406900	0.50112300
H	-2.30027600	-0.56279600	2.12567100
C	-3.56539200	-1.59616600	-0.86490900
H	-2.49840800	-1.53277500	-2.74322400
H	-4.36007100	-1.53808100	1.14196900
H	-4.47052300	-2.02415600	-1.29971100
H	0.13530700	-0.92250900	2.49366100
N	-0.19824900	2.18043200	-0.68403900
H	0.58129900	1.84389500	-1.25345500
H	-1.05042300	1.84262700	-1.13578000
H	-0.19723300	3.80301500	-0.61633800
N	-0.19157200	4.89567600	-0.48953800
H	0.64111900	5.30182300	-0.92840100
H	-1.02453900	5.30846800	-0.92165900
H	-0.18661000	5.13506000	0.50737200

D2

C	0.00926700	0.16446700	0.87021400
C	-0.12188800	1.68729200	0.70948900
O	0.02242900	0.01928300	2.27857300
H	-1.02868200	2.00199200	1.24159500
H	0.73515500	2.18737000	1.17767900
C	1.31447600	-0.40516600	0.29907500
C	1.44136000	-1.79743900	0.17998200
C	2.41899900	0.39445100	-0.01390400
C	2.63582500	-2.37349600	-0.24442100
H	0.59200700	-2.44027700	0.42432400
C	3.61461600	-0.18164500	-0.45141800
H	2.37702100	1.48101800	0.08292600
C	3.72725500	-1.56471300	-0.56794800
H	2.71382500	-3.45907600	-0.32687100
H	4.46200200	0.46090200	-0.69699600

H	4.66224600	-2.01348100	-0.90798100
C	-1.22553200	-0.50603800	0.25579100
C	-1.28693300	-0.80864000	-1.11136900
C	-2.34384500	-0.76173400	1.05596000
C	-2.44440900	-1.35565400	-1.66513300
H	-0.42011800	-0.62772500	-1.75225100
C	-3.49869600	-1.31669600	0.50281300
H	-2.30514200	-0.52791600	2.12059000
C	-3.55324200	-1.61413100	-0.85852900
H	-2.47520100	-1.58740600	-2.73132300
H	-4.36052900	-1.51764600	1.14199200
H	-4.45635100	-2.04886800	-1.29067400
H	0.15361800	-0.91596500	2.49437100
N	-0.23282900	2.15725600	-0.67973700
H	0.55458200	1.84657000	-1.26127500
H	-1.09112400	1.81712100	-1.12890700
H	-0.25009400	3.28223900	-0.67697900
N	-0.25314800	4.82789900	-0.52609800
H	0.56450300	5.26553300	-0.95609200
H	-1.07276100	5.25910100	-0.95885600
H	-0.25605300	5.12101000	0.45338000

D3a

C	0.00772800	0.82430600	0.59506600
C	-0.07322600	2.22145900	-0.04024900
O	0.01174700	1.13912200	1.97348200
H	-0.97794200	2.71640300	0.33070400
H	0.79787000	2.82445600	0.23738400
C	1.29540200	0.06526800	0.24921500
C	1.36821000	-1.30279600	0.55086500
C	2.43529800	0.69891700	-0.25781400
C	2.54374400	-2.01930500	0.34296800
H	0.49206700	-1.81514600	0.95527100
C	3.61168900	-0.02217600	-0.47883400
H	2.43991700	1.76681400	-0.48567800
C	3.66994000	-1.38099900	-0.18037500
H	2.57925700	-3.08257700	0.58680300
H	4.48681800	0.48951700	-0.88304600
H	4.58996900	-1.94244300	-0.35219200
C	-1.25122700	0.03651400	0.21000700
C	-1.32220700	-0.69179600	-0.98520900
C	-2.38015700	0.10031200	1.03346800
C	-2.50135500	-1.34368500	-1.34774700
H	-0.44759000	-0.76686300	-1.63693100

C	-3.55543300	-0.56007200	0.67442400
H	-2.33320100	0.66735900	1.96391500
C	-3.62021800	-1.28231300	-0.51697100
H	-2.54003900	-1.90927700	-2.28037600
H	-4.42554900	-0.50864900	1.33154400
H	-4.53990000	-1.79926200	-0.79673800
H	0.09049000	0.31594300	2.47898200
N	-0.16005000	2.18749300	-1.51882000
H	0.64800900	1.71705400	-1.95318800
H	-1.00768200	1.69773900	-1.84223900
H	-0.19526100	3.14170600	-1.90321500

D3b

C	0.01522300	0.93063300	0.37628600
C	-0.12685900	2.12978100	-0.61031800
O	-0.07222400	1.52752400	1.65463600
H	-0.27020000	3.03522800	-0.01162500
H	0.76258800	2.25885800	-1.23291800
C	1.37585900	0.25289500	0.17951400
C	2.14603800	-0.11770400	1.28476300
C	1.85987900	-0.02959700	-1.10491600
C	3.36990800	-0.76701200	1.11149800
H	1.80494300	0.11089700	2.29507000
C	3.07977400	-0.68089700	-1.27882400
H	1.27926200	0.25408000	-1.98713200
C	3.83963600	-1.05319000	-0.16889600
H	3.95976100	-1.04491500	1.98691800
H	3.43924900	-0.89389100	-2.28715200
H	4.79724200	-1.55924700	-0.30359000
C	-1.14622600	-0.07175800	0.21669300
C	-1.05181800	-1.25406000	-0.52522100
C	-2.36989800	0.24372200	0.82853300
C	-2.15655100	-2.09913500	-0.65351900
H	-0.11410100	-1.53854800	-1.00217000
C	-3.47123600	-0.59987800	0.69735400
H	-2.45713900	1.16000700	1.41562400
C	-3.36797400	-1.77638700	-0.04569600
H	-2.06116400	-3.02057000	-1.23062800
H	-4.41316700	-0.33682200	1.18208800
H	-4.22805300	-2.44063500	-0.14670000
H	-0.17653700	0.83256300	2.32199400
N	-1.28415100	2.03723900	-1.53580200
H	-2.18427700	1.99322300	-1.03837200
H	-1.31425900	2.86091700	-2.15244200

H	-1.23182400	1.20351200	-2.13894900

D3c

C	0.00849800	0.89360900	0.28459300
C	-0.12454600	2.06582500	-0.69087400
O	-0.07994600	1.50915300	1.55602000
H	0.68201200	2.78840700	-0.52194100
H	-0.12158700	1.73664300	-1.73537700
C	1.35593900	0.18506800	0.12327400
C	1.62067300	-0.90781600	0.96074000
C	2.32920600	0.58248800	-0.79672100
C	2.83763500	-1.57910600	0.89196700
H	0.85970300	-1.24190000	1.67210400
C	3.54804800	-0.09806300	-0.87273600
H	2.15974400	1.42221400	-1.47196800
C	3.80730900	-1.17498400	-0.02921300
H	3.02828500	-2.42565600	1.55396800
H	4.29712700	0.22248100	-1.59896000
H	4.76046800	-1.70319700	-0.09004300
C	-1.14400800	-0.09432900	0.06037800
C	-1.16014900	-0.89194200	-1.09181100
C	-2.20124200	-0.18638700	0.96877000
C	-2.21380600	-1.77120100	-1.32606400
H	-0.33485000	-0.83010300	-1.80613200
C	-3.25570000	-1.07416100	0.73492700
H	-2.20506100	0.43463300	1.86585000
C	-3.26482200	-1.86691000	-0.40982700
H	-2.21301700	-2.38949900	-2.22554200
H	-4.07255700	-1.14204800	1.45575800
H	-4.08787300	-2.56045500	-0.59109300
H	-0.01440800	0.84117000	2.25499000
N	-1.40036600	2.77465300	-0.42764900
H	-1.47280200	3.00529200	0.57467500
H	-1.46098000	3.65155000	-0.96119700
H	-2.22027200	2.20213000	-0.67411100

D3d

C	-0.04763400	0.82529200	0.13378000
C	-0.11459400	1.90240800	-0.99989000
O	-0.15832900	1.54841600	1.34655300
H	0.80364500	1.91214700	-1.59460700
H	-0.96259300	1.73737200	-1.67222700
C	1.29234900	0.09238200	0.04916900
C	2.14217200	0.01559900	1.15257500

C	1.67515800	-0.52478400	-1.15010300
C	3.35520800	-0.67395400	1.06371700
H	1.86269900	0.50156000	2.08801200
C	2.88247000	-1.21212600	-1.23858100
H	1.01664400	-0.47922800	-2.02224100
C	3.72778000	-1.28983500	-0.12825800
H	4.01051500	-0.72498100	1.93529300
H	3.16525900	-1.69133800	-2.17767800
H	4.67442600	-1.82882900	-0.19664200
C	-1.24125700	-0.13921300	0.03693600
C	-1.10500400	-1.52917000	0.08080900
C	-2.53185700	0.41086300	0.00389500
C	-2.23478600	-2.35257400	0.06786900
H	-0.11659100	-1.98720500	0.12603800
C	-3.65674200	-0.40839300	-0.00733500
H	-2.66659500	1.49563100	-0.00760700
C	-3.51053100	-1.79760900	0.02042000
H	-2.10880300	-3.43633300	0.09773100
H	-4.65206200	0.03860800	-0.03694800
H	-4.39112700	-2.44242900	0.00855100
H	-0.39552300	0.93770100	2.05998700
N	-0.26591500	3.26462700	-0.43290000
H	0.51131900	3.49509500	0.19998100
H	-0.29111500	3.96948300	-1.18043900
H	-1.12845200	3.34971700	0.12064600

NH_3

N	0.00000000	0.00000000	0.12532200
H	0.00000000	0.93243500	-0.29241900
H	-0.80751300	-0.46621800	-0.29241900
H	0.80751300	-0.46621800	-0.29241900

NH_4^+

H	0.99716600	0.03719900	-0.24502500
N	0.00010200	0.00003800	-0.00010700
H	-0.28141000	-0.97772100	0.14329000
H	-0.16044800	0.53230900	0.86364500
H	-0.55602200	0.40794500	-0.76116400

TSA-B

C	0.10388800	0.72103000	-0.14384400
C	0.07068800	2.04074500	0.48177900
O	-0.14908900	1.60092600	-1.21732100
H	0.95761000	2.66244700	0.39482100

H	-0.88838100	2.50024600	0.71121800
C	-1.04331800	-0.23803400	0.10960300
C	-2.04003100	0.01146100	1.05654200
C	-1.16039000	-1.35674400	-0.72642800
C	-3.13895400	-0.84524400	1.16633400
H	-1.97174200	0.87855900	1.71575000
C	-2.25958100	-2.20584800	-0.62321100
H	-0.38506500	-1.55454200	-1.47116800
C	-3.25339500	-1.95088200	0.32588800
H	-3.90900900	-0.64255200	1.91290100
H	-2.34230100	-3.07076300	-1.28400900
H	-4.11407400	-2.61687800	0.41010200
C	1.46125900	0.05167800	-0.18503400
C	1.83948200	-0.82724200	0.83753000
C	2.35945800	0.33434300	-1.21560000
C	3.10476300	-1.41167600	0.82935600
H	1.13634400	-1.05920300	1.64201900
C	3.62297200	-0.26082400	-1.22849800
H	2.05966700	1.02105600	-2.00831400
C	3.99932600	-1.13144000	-0.20653700
H	3.39248300	-2.09369900	1.63172000
H	4.31630000	-0.04133700	-2.04281200
H	4.98776400	-1.59453000	-0.21634400
H	-1.59001600	1.59409500	-1.62207200
N	-2.66193300	1.56556700	-1.88579000
H	-2.81448600	1.95033700	-2.82325800
H	-2.99882000	0.59656200	-1.86616000
H	-3.20787400	2.11280400	-1.21262900
N	0.49270800	1.81134000	2.51127400
H	0.29027900	2.66512700	3.03454800
H	-0.02520100	1.05053300	2.95507500
H	1.48680300	1.60804200	2.63149800

TSA-C

C	-2.36897900	0.76263500	0.76770000
C	-1.41749700	0.84201800	1.87581900
O	-3.19070300	0.94214900	1.89939400
H	-1.17513900	1.83031000	2.25795400
H	-1.24555700	-0.03324100	2.50167100
C	-2.58425800	-0.57401400	0.08167800
C	-1.79331700	-1.69743200	0.34047000
C	-3.69405300	-0.70335100	-0.76491600
C	-2.11279600	-2.93287000	-0.23141500
H	-0.92590300	-1.63140200	1.00073400

C	-4.01201100	-1.93351500	-1.33499500
H	-4.31750100	0.17067800	-0.97016800
C	-3.22056100	-3.05401600	-1.06767300
H	-1.49026200	-3.80296100	-0.01557700
H	-4.88109000	-2.02040300	-1.98975400
H	-3.46903700	-4.01939400	-1.51227700
C	-2.34579300	1.93867600	-0.18742300
C	-1.62319000	1.86275900	-1.38471500
C	-3.00418400	3.12491300	0.14287800
C	-1.55288900	2.96536100	-2.23481800
H	-1.12065200	0.93064000	-1.65999500
C	-2.94286300	4.22473000	-0.71506400
H	-3.56721500	3.17616000	1.07580300
C	-2.21530800	4.14920100	-1.90250600
H	-0.98500500	2.89749900	-3.16461500
H	-3.46746000	5.14564200	-0.45287200
H	-2.16671200	5.01017400	-2.57176800
H	-3.82586700	-0.34328100	2.33277500
N	-4.26716500	-1.31328700	2.61978100
H	-4.65330400	-1.77777200	1.79048000
H	-3.55014500	-1.92197800	3.02689900
H	-5.01736600	-1.18338200	3.30592900
N	0.47222200	0.67012400	1.04237100
H	0.26236100	0.24275500	0.13759700
H	0.83784200	1.60470300	0.85051900
C	1.40534100	-0.14455500	1.79840000
H	1.77008500	0.42415600	2.66458400
H	0.87494100	-1.02440300	2.19773900
C	2.61113200	-0.70320800	1.01101200
O	3.26437000	-1.51419800	1.97279400
H	4.05924400	-1.89435100	1.57068200
C	2.07281700	-1.54851900	-0.14790000
C	1.69593700	-0.96150400	-1.36452500
C	1.86833900	-2.92136000	0.02820900
C	1.11822800	-1.72915900	-2.37674200
H	1.86187600	0.10617800	-1.52997600
C	1.30798400	-3.69254800	-0.99165200
H	2.15733900	-3.38911700	0.97030500
C	0.92573700	-3.09906400	-2.19469900
H	0.82753400	-1.25319800	-3.31529100
H	1.16461200	-4.76440300	-0.84054100
H	0.48051100	-3.70146600	-2.98869200
C	3.58692700	0.37394400	0.52511900
C	3.58969100	1.67678200	1.03405600

C	4.58020700	0.01584700	-0.39882000
C	4.54928700	2.60306400	0.61757300
H	2.84877300	1.99403500	1.76948600
C	5.54423000	0.93430900	-0.80742300
H	4.59786700	-0.99821900	-0.80649300
C	5.52785400	2.23641600	-0.30351000
H	4.52859100	3.61690600	1.02148100
H	6.30895700	0.63342100	-1.52586500
H	6.27687700	2.96099900	-0.62802700

TSD1-D2

C	0.00920400	0.16612200	0.87277500
C	-0.12299100	1.69022300	0.71132500
O	0.02416900	0.01359600	2.28133300
H	-1.02974600	1.99741500	1.24955800
H	0.73098400	2.18209700	1.19589400
C	1.31418200	-0.40172400	0.29945700
C	1.44247100	-1.79327800	0.17356100
C	2.41850200	0.39970500	-0.01008800
C	2.63724600	-2.36693700	-0.25369200
H	0.59346300	-2.43786400	0.41467200
C	3.61457000	-0.17356600	-0.44997100
H	2.37414300	1.48571100	0.09082800
C	3.72826100	-1.55611000	-0.57322500
H	2.71572400	-3.45209800	-0.34155400
H	4.46162000	0.47055000	-0.69281100
H	4.66349700	-2.00265400	-0.91557300
C	-1.22409200	-0.50415500	0.25735900
C	-1.28798500	-0.79396600	-1.11253600
C	-2.33975800	-0.77204200	1.05720200
C	-2.44439800	-1.34047900	-1.66880800
H	-0.42334000	-0.60243800	-1.75304500
C	-3.49407300	-1.32607000	0.50153500
H	-2.29981100	-0.54798500	2.12391000
C	-3.55072400	-1.61085900	-0.86232400
H	-2.47691900	-1.56222100	-2.73712200
H	-4.35367900	-1.53617800	1.14085000
H	-4.45317800	-2.04493100	-1.29655900
H	0.15105600	-0.92329000	2.49224900
N	-0.22792300	2.17640800	-0.66671500
H	0.56064600	1.86721900	-1.24447800
H	-1.07998600	1.83219800	-1.12067800
H	-0.25158400	3.42447500	-0.64539700
N	-0.26694600	4.76781500	-0.52988900

H	0.55279500	5.19485500	-0.96841600
H	-1.09437700	5.17510700	-0.97271000
H	-0.27305800	5.06053600	0.45051500

Reference:

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16*, revision C.01; Gaussian, Inc., Wallingford CT, 2019.

[2] Legault, C. Y., *CYLview20*; Université de Sherbrooke, 2020 (http://www.cylview.org)