SUPPORTING INFORMATION

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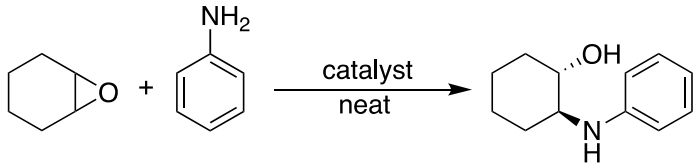
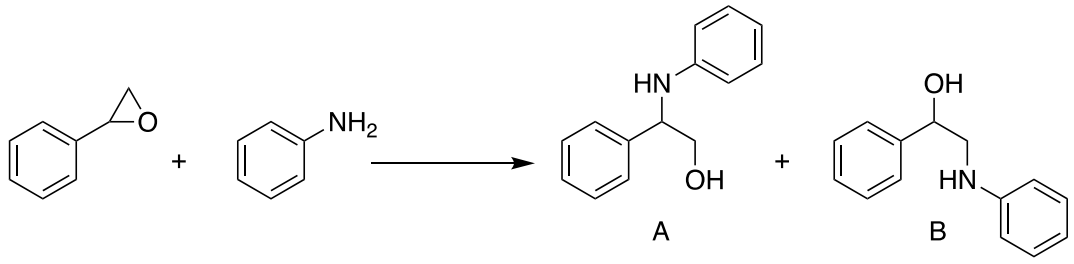
TABLE OF CONTENTS

Table S1 pKa and catalytic performance of selected organic acids.



Entry	Catalyst (eq.)	Temp/℃	Time/h	Yield[b](%)	pKa
1	TfOH (1.0)	r.t	1	68	-14.0
3	TsOH (1.0)	r.t	1	82	-0.43
4	CF_3COOH (1.0)	r.t	1	90	-0.30
5	HCOOH (1.0)	r.t	1	75	3.75
6	CH_3COOH (1.0)	r.t	1	99	4.74
7	C_2H_5COOH (1.0)	r.t	1	85	4.86
8	*n*-C_3H_7COOH (1.0)	r.t	1	76	4.83

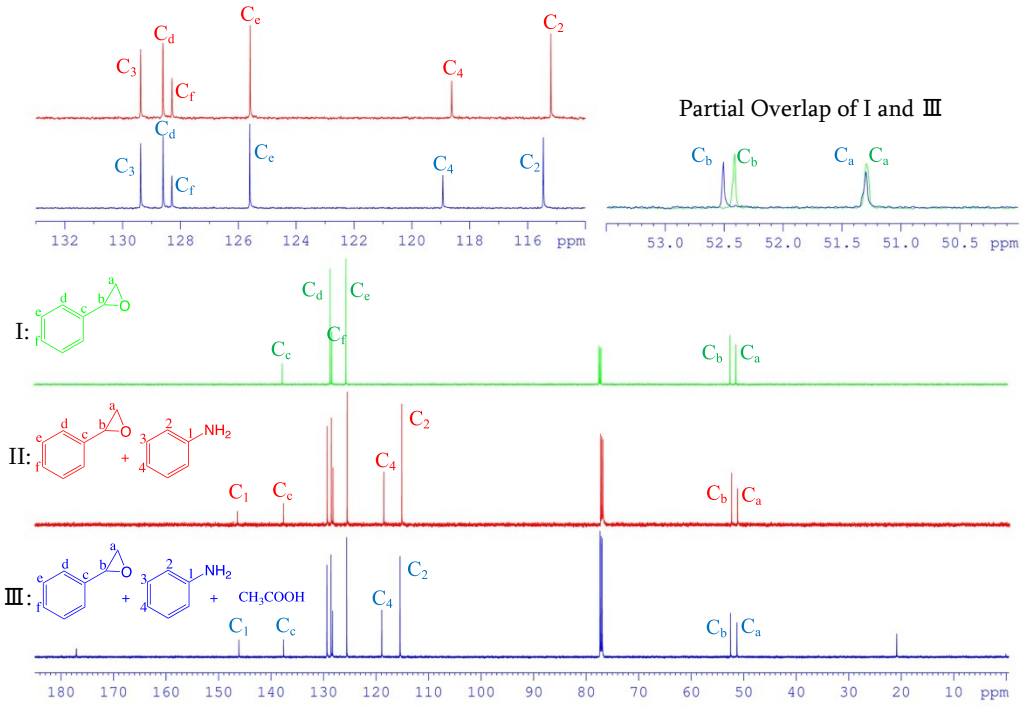
Table S2 Comparison of the catalytic activity and regioselectivity of acetic acid as a catalyst with that of other related reported systems



Catalyst	Reaction Condition	Yield (%)	Ratio (A:B)	TOF (h^{-1})	Ref.
H_2O	Styrene oxide(5.0 mmol), aniline(6.0 mmol),Water(2 ml), r.t, 14h	97	96:4	----	1

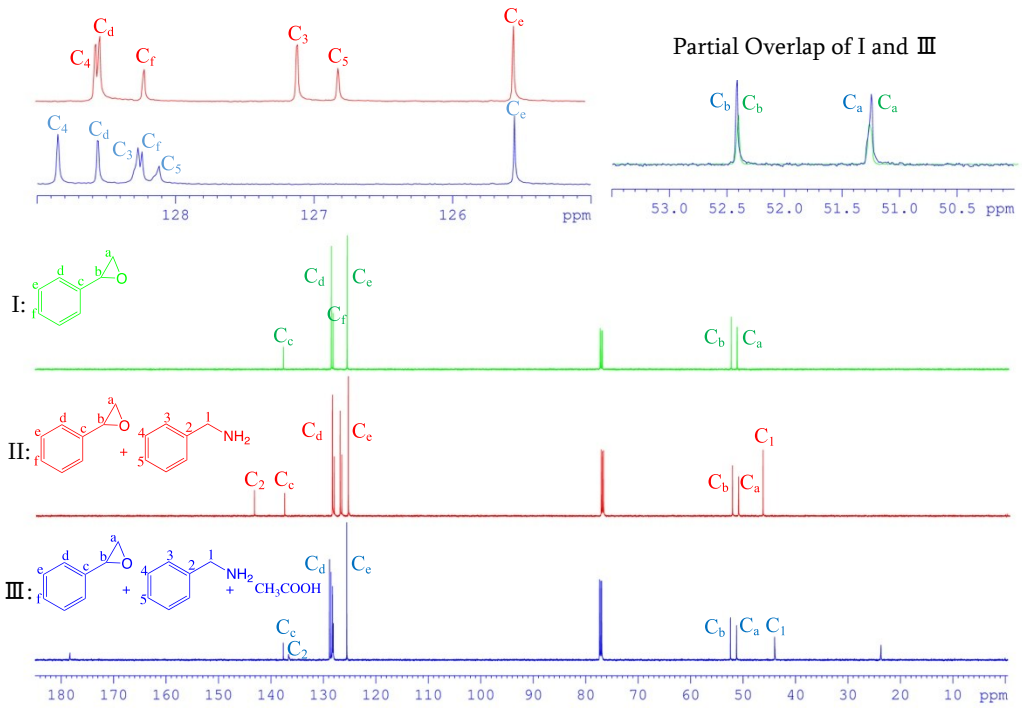
2,2,2-trifluoroethanol	Styrene oxide(1.0 mmol), aniline(1.0 mmol), 2,2,2-trifluoroethanol(2 ml), r.t, 6h	92	100:0	----	2
Silica gel(60-120 mesh)	Styrene oxide(2.5 mmol), aniline(2.5 mmol), silica gel(25mg, 10% w/w), solvent-free, r.t, 3h	93	95:5	----	3
Boric acid / glycerol	Styrene oxide(2.5 mmol), aniline(3.0 mmol), boric acid(30%mol), glycerol(1-2 drops), water(5 ml), 35℃, 15-18h	94	86:14	----	4
Acetic acid	Styrene oxide(3.0 mmol), aniline(3.15 mmol), acetic acid(3.0 mmol), solvent-free, r.t, 1h	96	100:0	0.96	Present study
$MnCl_2 \cdot 4H_2O$	Styrene oxide(20mmol), aniline(20mmol), 50mg $MnCl_2 \cdot 4H_2O$, solvent-free, 308K, 6h	46	85:15	6	5
$ZnCl_2$	Styrene oxide(20mmol), aniline(20mmol), 50mg $ZnCl_2$, solvent-free, 308K, 6h	73	96:4	7	5
Anhydrous $AlCl_3$	Styrene oxide(20mmol), aniline(20mmol), 50mg Anhydrous $AlCl_3$, solvent-free, 308K, 6h	77	99:1	7	5
Fe@SBSAL	Styrene oxide(1.0 mmol), aniline(1.0 mmol), Fe@SBSAL(20 mg, 0.4 mo% of Fe), solvent-free, r.t, 1h	97	100:0	242	6

Figure S1 13C-NMR spectral changes induced by addition of $PhNH_2$ and CH_3COOH to Styrene oxide



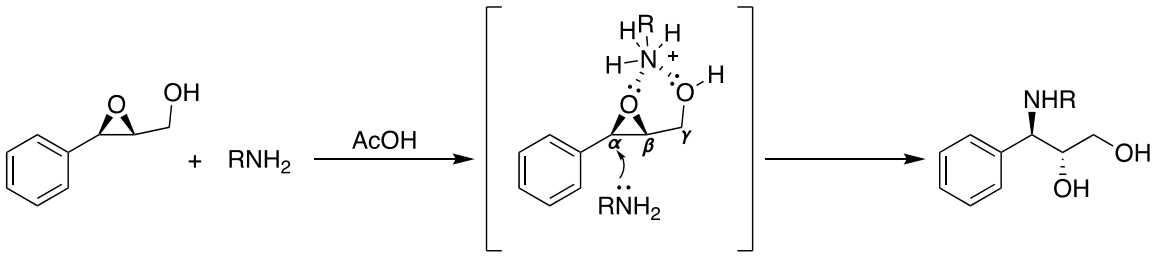
It was observed from the above 13C-NMR spectra that the peak of benzylic carbon of styrene oxide (C_b) significantly shifted downfield by 0.1 ppm while the peak of terminal carbon (C_a) kept almost the same position after addition of $PhNH_2$ and CH_3COOH. It can be infered from the above information that a differential polarization of the benzylic carbon and the terminal carbon of the epoxide took place, and positive charge buildup occurred on the benzylic carbon.

Figure S2 13C-NMR spectral changes induced by addition of $BnNH_2$ and CH_3COOH to Styrene oxide



It was observed from the above 13C-NMR spectra that the peaks of $BnNH_2$ shifted significantly downfield or upfield while the peaks of benzylic carbon (C_b) and terminal carbon (C_a) of styrene oxide kept almost the same position after addition of $BnNH_2$ and CH_3COOH. It can be infered from the above information that the nitrogen-onium ion formed by acetic acid and $BnNH_2$ was less acidic and exerted a weak activation of the epoxide.

Figure S3 Plausible mechanism for the benzylic attack of aliphatic or aromatic amines on trans-2,3-epoxycinnamyl alcohol



The neighboring hydroxy group (γ-OH) is conducive to the formation of a five-membered ring transition state, thereby strengthening the polarization of the benzylic carbon by electronic effects; this transition state also greatly increases the steric hindrance at the β-position. The synergistic steric effects and electronic factors favor nucleophilic attack at the benzylic position by aliphatic amines or aromatic amines.

General Methods and Materials

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker Avance 300 or Bruker DRX 400 spectrometer at 300 or 400 MHz. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) was recorded on a Bruker Avance 300 or Bruker DRX 400 spectrometer at 75 or 100 MHz. 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 were taken on AB QSTAR Pulsar mass spectrometer. Melting points were obtained on a XT-4 melting-point apparatus and were uncorrected.

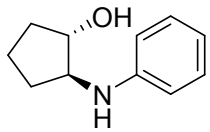
The 2,3-epoxy-3-phenyl-1-propanol and 5α,6α-epoxy steroid precursors were prepared by *m*-CPBA-mediated epoxidation. Unless otherwise stated, all reagents were commercially available and used as received without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI and Alfa-Aesar. TLC was performed with Merck TLC Silica gel 60 F_{254} plates with detection under UV light (254 nm) and/or stained with I_2, phosphomolybdic acid (5.0 g /100 mL EtOH). Silica gel (200-300 mesh, Qingdao) was used for flash chromatography.

General procedure (A) and characterization for the acetic acid-catalyzed regioselective ring-opening of epoxides by amines.

General procedure (A)

A screw-capped vial equipped with a stir bar was charged with epoxide (3.00 mmol), amine (3.15 mmol, 1.05 eq.) and acetic acid (3.00 mmol, 1.00 eq.) under solvent-free condition. The reaction mixture Swas stirred at room temperature for 1h. After the reaction was done, K_2CO_3 was added to the reaction mixture sequentially. The crude material was loaded onto a deactivated silica gel column and separated by flash chromatography to afford the pure β-amino alcohol. All compounds were characterized on the basis of their spectroscopic data (NMR) and by comparison with those reported in the literature.[7-16]

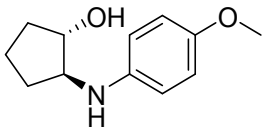
***trans*-2-(phenylamino)cyclopentanol (6a)**



The reaction was performed following the general procedure (A) with cyclopentene oxide (252 mg, 3.00 mmol), aniline (293 mg, 3.15 mmol) and acetic acid (180 mg, 3.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (

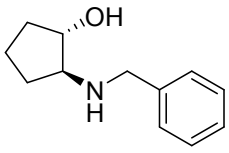
EtOAc : PE = 1 : 5) as yellow solid (510 mg, 96%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.31 – 7.25 (m, 2H), 6.85 – 6.80 (m, 1H), 6.79 – 6.70 (m, 2H), 4.10 – 4.04 (m, 1H), 3.67 – 3.62 (m, 1H), 3.45 (s, 2H), 2.37 – 2.26 (m, 1H), 2.05 – 1.97 (m, 1H), 1.90 – 1.65 (m, 3H), 1.50 – 1.39 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 147.7, 129.2, 117.5, 113.4, 77.9, 61.9, 32.56, 30.9, 20.9. The spectroscopic data (NMR) of this compound match the literature data.[7]

***trans*-2-((4-methoxyphenyl)amino) cyclopentanol (6b)**



The reaction was performed following the General Procedure (A) with cyclopentene oxide (252 mg, 3.00 mmol), 4-methoxy-aniline (388 mg, 3.15 mmol), and acetic acid (180 mg, 3.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 5) as brown oil (609 mg, 98%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 6.78 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 4.06 – 4.01 (m, 1H), 3.75 (s, 3H), 3.56 – 3.50 (m, 1H), 2.30 – 2.21 (m, 1H), 2.02 – 1.93 (m, 1H), 1.83 – 1.59 (m, 3H), 1.41 – 1.34 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 152.4, 142.0, 115.0, 114.9, 78.3, 63.1, 55.9, 32.9, 31.3, 21.1. The spectroscopic data (NMR) of this compound match the literature data.[7]

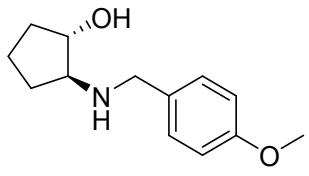
***trans*-2-(benzylamino)cyclopentanol (6c)**



The reaction was performed following the General Procedure with (A) cyclopentene oxide (252 mg, 3.00 mmol), benzylamine (338 mg, 3.15 mmol) and acetic acid (180 mg, 3.00

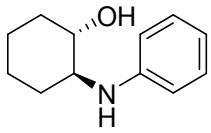
mmol). The title compound was separated by flash chromatography on deactivated silica gel (DCM : MeOH = 5 : 1) as yellow oil (562 mg, 98%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.28 – 7.22 (m, 5H), 3.83 – 3.63 (m, 3H), 3.18 (s, 2H), 2.86 – 2.79 (m, 1H), 2.00 – 1.81 (m, 2H), 1.66 – 1.58 (m, 2H), 1.53 – 1.44 (m, 1H), 1.32 – 1.25 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 139.8, 128.2, 128.1, 126.8, 77.3, 65.8, 52.4, 32.4, 29.7, 20.1. The spectroscopic data (NMR) of this compound match the literature data.[8]

***trans*-2-((4-methoxybenzyl)amino)cyclopentanol (6d)**



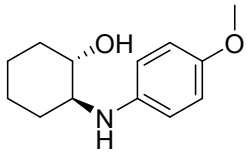
The reaction was performed following the General Procedure (A) with cyclopentene oxide (252 mg, 3.00 mmol), 4-methoxy-benzylamine (432 mg, 3.15 mmol), and acetic acid (180 mg, 3.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (DCM : MeOH = 30 : 1) as yellow solid (657 mg, 99%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.27 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.93 (q, *J* = 6.6 Hz, 1H), 3.81 (d, *J* = 13.2 Hz, 1H), 3.79 (s, 3H), 3.70 (d, *J* = 13.2 Hz, 1H), 3.50 (s, 2H), 2.94 – 2.87 (m, 1H), 2.04 – 1.91 (m, 2H), 1.71 – 1.63 (m, 2H), 1.55 – 1.39 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 159.1, 130.5, 130.0, 114.1, 77.6, 66.3, 55.4, 51.8, 32.5, 29.6, 20.5. The spectroscopic data (NMR) of this compound match the literature data.[9]

***trans*-2-(phenylamino)cyclohexanol (6e)**



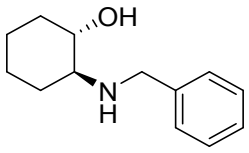
The reaction was performed following the General Procedure (A) with cyclohexane-1,2-epoxide (300 mg, 3.05 mmol), aniline (298 mg, 3.20 mmol) and acetic acid (183 mg, 3.05 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 3) as pale yellow solid (571 mg, 99%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 7.21 – 7.17 (m, 2H), 6.80 – 6.71 (m, 3H), 3.38 – 3.33 (m, 1H), 3.18 – 3.11 (m, 1H), 2.91 (s, 2H), 2.14 – 2.10 (m, 2H), 1.80 – 1.71 (m, 2H), 1.42 – 1.28 (m, 3H), 1.10 – 1.01 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 147.9, 129.5, 118.5, 114.5, 74.6, 60.3, 33.3, 31.7, 25.1, 24.4. The spectroscopic data (NMR) of this compound match the literature data.[7]

***trans*-2-((4-methoxyphenyl)amino)cyclohexanol (6f)**



The reaction was performed following the General Procedure (A) with cyclohexane-1,2-epoxide (300 mg, 3.05 mmol), 4-methoxy-aniline (394 mg, 3.20 mmol) and acetic acid (183 mg, 3.05 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 3) as yellow oil (661 mg, 98%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 6.78 (d, *J* = 9.0 Hz, 2H), 6.68 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H), 3.36 – 3.28 (m, 1H), 3.03 – 2.95 (m, 3H), 2.13 – 2.05 (m, 2H), 1.78 – 1.68 (m, 2H), 1.40 – 1.24 (m, 3H), 1.07 – 0.94 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 153.0, 141.7, 116.5, 115.0, 74.5, 61.8, 55.8, 33.2, 31.6, 25.2, 24.4. The spectroscopic data (NMR) of this compound match the literature data.[7]

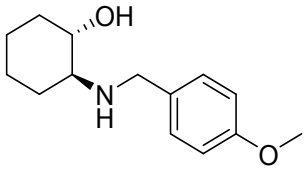
***trans*-2-(benzylamino)cyclohexanol (6g)**



The reaction was performed following the General Procedure (A) with cyclohexane-1,2-epoxide (300 mg, 3.05 mmol), benzylamine (343 mg, 3.20 mmol) and acetic acid (183

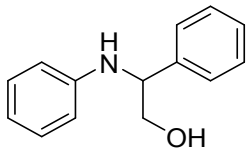
mg, 3.05 mmol). The title compound was separated by flash chromatography on deactivated silica gel (DCM : MeOH = 10 : 1) as pale yellow solid (613 mg, 98%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.34 – 7.25 (m, 5H), 3.96 (d, *J* = 12.6 Hz, 1H), 3.69 (d, *J* = 12.6 Hz, 1H), 3.24 – 3.16 (m, 1H), 2.33 – 2.25 (m, 1H), 2.21 – 2.14 (m, 1H), 2.05 – 2.01 (m, 1H), 1.76 – 1.70 (m, 2H), 1.28 – 1.23 (m, 3H), 1.05 – 0.92 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.6, 128.6, 128.2, 127.2, 74.1, 63.2, 50.9, 33.4, 30.7, 25.3, 24.4. The spectroscopic data (NMR) of this compound match the literature data.[8]

***trans*-2-((4-methoxybenzyl)amino)cyclohexanol (6h)**



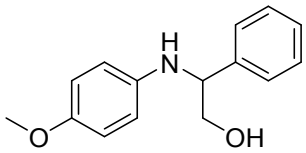
The reaction was performed following the General Procedure (A) with cyclohexane-1,2-epoxide (300 mg, 3.05 mmol), 4-methoxy-benzylamine (438 mg, 3.20 mmol) and acetic acid (183 mg, 3.05 mmol). The title compound was separated by flash chromatography on deactivated silica gel (DCM : MeOH = 10 : 1) as pale yellow solid (710 mg, 99 %). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.25 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.89 (d, *J* = 12.6 Hz, 1H), 3.80 (s, 3H), 3.62 (d, *J* = 12.6 Hz, 1H), 3.22 – 3.14 (m, 1H), 2.31 – 2.23 (m, 1H), 2.20 – 2.13 (m, 1H), 2.05 – 2.00 (m, 1H), 1.74 – 1.70 (m, 2H), 1.28 – 1.22 (m, 3H), 1.04 – 0.95 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 158.7, 132.7, 129.4, 113.9, 74.1, 63.0, 55.4, 50.2, 33.4, 30.6, 25.3, 24.4. The spectroscopic data (NMR) of this compound match the literature data.[10]

2-phenyl-2-(phenylamino)ethanol (6i)



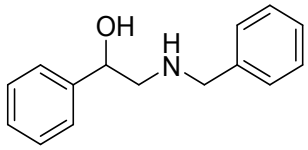
The reaction was performed following the General Procedure (A) with styrene oxide (360 mg, 3.00 mmol), aniline (293 mg, 3.15 mmol) and acetic acid (180 mg, 3.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 3) as pale yellow oil (614 mg, 96%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 7.42 – 7.36 (m, 4H), 7.33 – 7.28 (m, 1H), 7.16 – 7.12 (m, 2H), 6.75 – 6.71 (m, 1H), 6.61 (dd, *J* = 8.8, 1.2 Hz, 2H), 4.54 (dd, *J* = 6.8, 4.0 Hz, 1H), 3.97 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.78 (dd, *J* = 11.2, 6.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 147.2, 140.2, 129.3, 129.0, 127.7, 126.9, 118.1, 114.0, 67.4, 60.0. The spectroscopic data (NMR) of this compound match the literature data.[7]

2-phenyl-2-((4-methoxyphenyl)amino)ethanol (6j)



The reaction was performed following the General Procedure (A) with styrene oxide (360 mg, 3.00 mmol), 4-methoxy-aniline (388 mg, 3.15 mmol) and acetic acid (180 mg, 3.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 3) as yellow oil (438 mg, 96%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.23 – 7.14 (m, 5H), 6.59 (d, *J* = 9.0 Hz, 2H), 6.42 (d, *J* = 9.0 Hz, 2H), 4.29 (dd, *J* = 7.8, 4.2 Hz, 1H), 3.76 (dd, *J* = 11.1, 4.2 Hz, 1H), 3.58 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 152.4, 141.4, 140.4, 128.8, 128.7, 127.6, 126.8, 115.4, 115.2, 115.0, 114.8, 67.4, 60.9, 55.8. The spectroscopic data (NMR) of this compound match the literature data.[11]

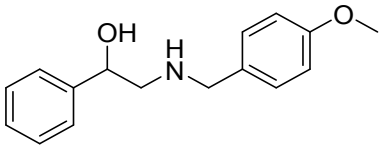
1-phenyl-2-(benzylamino)ethanol (6k)



The reaction was performed following the General Procedure (A) with styrene oxide (360 mg, 3.00 mmol), benzylamine (337 mg, 3.15 mmol) and acetic acid (180 mg, 3.00

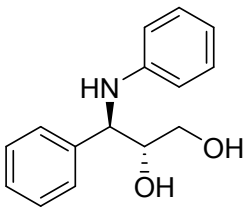
mmol). The title compound was separated by flash chromatography on deactivated silica gel (DCM : MeOH = 10 : 1) as pale yellow solid (668 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 7.35 – 7.25 (m, 10H), 4.73 (dd, *J* = 9.2, 3.6 Hz, 1H), 3.82 (dd, *J* = 19.6, 13.2 Hz, 2H), 2.92 (dd, *J* = 12.0, 3.2 Hz, 1H), 2.75 (dd, *J* = 12.0, 8.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 142.6, 140.0, 128.6, 128.5, 128.2, 127.6, 127.3, 125.9, 72.0, 56.7, 53.7. The spectroscopic data (NMR) of this compound match the literature data.[8]

1-phenyl-2-((4-methoxybenzyl)amino)ethanol (6l)



The reaction was performed following the General Procedure (A) with styrene oxide (360 mg, 3.00 mmol), 4-methoxy-benzylamine (432 mg, 3.15 mmol) and acetic acid (180 mg, 3.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (DCM : MeOH = 10 : 1) as yellow solid (756 mg, 98%). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.31 – 7.29 (m, 4H), 7.20 (d, *J* = 8.8 Hz, 3H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.28 (d, *J* = 4.0 Hz, 1H), 4.65 – 4.61 (m, 1H), 3.72 (s, 3H), 3.64 (d, *J* = 3.2 Hz, 2H), 2.57 (d, *J* = 6.0 Hz, 2H), 1.99 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 158.5, 145.1, 133.2, 129.6, 128.4, 127.2, 126.3, 114.0, 72.0, 57.4, 55.4, 52.6. The spectroscopic data (NMR) of this compound match the literature data.[12]

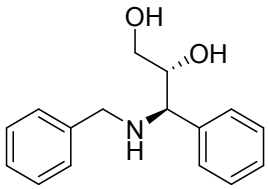
(2R,3R)-3-phenyl-3-(phenylamino)propanediol (6m)



The reaction was performed following the General Procedure (A) with 2,3-epoxy-3-phenyl-1-propanol (300 mg, 2.00 mmol), aniline (195 mg, 2.10 mmol) and acetic acid (120 mg, 2.00 mmol). The title compound was separated by flash chromatography on

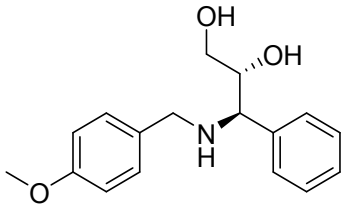
deactivated silica gel (EtOAc : PE = 1 : 1) as yellow oil (457 mg, 94%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.38 – 7.29 (m, 5H), 7.17 – 7.11 (m, 2H), 6.75 – 6.70 (m, 1H), 6.62 – 6.59 (m, 2H), 4.61 (d, *J* = 4.8 Hz, 1H), 4.04 – 4.00 (m, 1H), 3.66 (dd, *J* = 11.7, 3.6 Hz, 1H), 3.53 (dd, *J* = 11.7, 6.0 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 146.9, 139.2, 129.3, 128.9, 127.8, 127.4, 118.1, 114.1, 74.2, 63.7, 60.7. The spectroscopic data (NMR) of this compound match the literature data.[13]

(2R,3R)-3-phenyl-3-(benzylamino)propanediol (6n)



The reaction was performed following the General Procedure (A) with 2,3-epoxy-3-phenyl-1-propanol (300 mg, 2.00 mmol), benzylamine (225 mg, 2.10 mmol) and acetic acid (120 mg, 2.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as pale yellow oil (494 mg, 96%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.31 – 7.13 (m, 10H), 3.76 – 3.70 (m, 2H), 3.63 (d, *J* = 12.9 Hz, 1H), 3.43 (d, *J* = 6.0 Hz, 2H) 3.42 (d, *J* = 12.9 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 139.6, 139.4, 128.9, 128.6, 128.4, 127.9, 127.3, 73.7, 65.8, 64.6, 51.4. The spectroscopic data (NMR) of this compound match the literature data.[14]

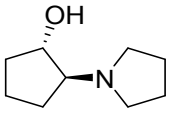
(2R,3R)-3-phenyl-3-(4-methoxybenzylamino)propanediol (6o)



The reaction was performed following the General Procedure (A) with 2,3-epoxy-3-phenyl-1-propanol (300 mg, 2.00 mmol), 4-methoxy-benzylamine (288 mg, 2.10 mmol) and acetic acid (120 mg, 2.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as pale yellow oil (557

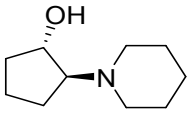
mg, 97%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 7.43 – 7.32 (m, 5H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 3.87 – 3.83 (m, 2H), 3.81 (s, 3H), 3.69 (d, *J* = 12.8 Hz, 1H), 3.56 (dd, *J* = 4.4, 2.0 Hz, 2H), 3.49 (d, *J* = 12.8 Hz, 1H), 2.99 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 158.9, 139.4, 131.6, 129.6, 128.9, 127.9, 127.8, 114.0, 73.5, 65.8, 64.7, 55.4, 50.8. The spectroscopic data (NMR) of this compound match the literature data.[15]

***trans*-2-(pyrrolidin-1-yl)cyclopentanol (6p)**



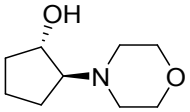
The reaction was performed following the general procedure (A) with cyclopentene oxide (252 mg, 3.00 mmol), pyrrolidine (224 mg, 3.15 mmol) and acetic acid (180 mg, 3.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as yellow oil (447 mg, 96%). The spectroscopic data (NMR) of this compound match the literature data.[7]

***trans*-2-(piperidin-1-yl)cyclopentanol (6q)**



The reaction was performed following the general procedure (A) with cyclopentene oxide (252 mg, 3.00 mmol), piperidine (268 mg, 3.15 mmol) and acetic acid (180 mg, 3.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as colorless oil (492 mg, 97%). The spectroscopic data (NMR) of this compound match the literature data.[7]

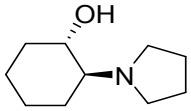
***trans*-2-(morpholin-4-yl)cyclopentanol (6r)**



The reaction was performed following the general procedure (A) with cyclopentene oxide (252 mg, 3.00 mmol), morpholine (274 mg, 3.15 mmol) and acetic acid (180 mg, 3.00 mmol). The title compound was separated by flash chromatography on deactivated silica

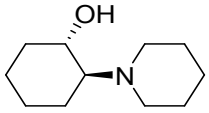
gel (EtOAc : PE = 1 : 1) as brown oil (503 mg, 98%). The spectroscopic data (NMR) of this compound match the literature data.[7]

***trans*-2-(pyrrolidin-1-yl)cyclohexanol (6s)**



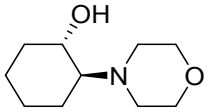
The reaction was performed following the General Procedure (A) with cyclohexane-1,2-epoxide (300 mg, 3.05 mmol), pyrrolidine (227 mg, 3.20 mmol) and acetic acid (183 mg, 3.05 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as yellow oil (495 mg, 96%). The spectroscopic data (NMR) of this compound match the literature data.[7]

***trans*-2-(piperidin-1-yl)cyclohexanol (6t)**



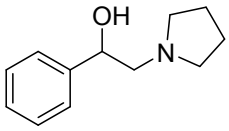
The reaction was performed following the General Procedure (A) with cyclohexane-1,2-epoxide (300 mg, 3.05 mmol), piperidine (272 mg, 3.20 mmol) and acetic acid (183 mg, 3.05 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as colorless oil (536 mg, 96%). The spectroscopic data (NMR) of this compound match the literature data.[7]

trans-2-(morpholin-4-yl)cyclohexanol (6u)



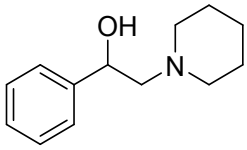
The reaction was performed following the General Procedure (A) with cyclohexane-1,2-epoxide (300 mg, 3.05 mmol), morpholine (279 mg, 3.20 mmol) and acetic acid (183 mg, 3.05 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as yellow oil (548 mg, 97%). The spectroscopic data (NMR) of this compound match the literature data.[7]

1-phenyl-2-(pyrrolidin-1-yl)ethanol (6v)



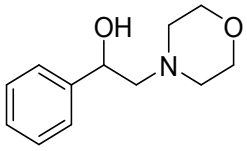
The reaction was performed following the General Procedure (A) with styrene oxide (360 mg, 3.00 mmol), pyrrolidine (427 mg, 6.00 mmol) and acetic acid (180 mg, 3.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (DCM : MeOH = 10 : 1) as yellow oil (533 mg, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 7.42 – 7.28 (m, 5H), 4.72 (dd, *J* = 11.2, 3.6 Hz, 1H), 2.83 – 2.77 (m, 3H), 2.57 – 2.48 (m, 3H), 1.85 – 1.81 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 142.6, 128.4, 127.5, 126.0, 70.8, 64.2, 54.0, 23.8. The spectroscopic data (NMR) of this compound match the literature data.[16]

1-phenyl-2-(piperidin-1-yl)ethanol (6w)



The reaction was performed following the General Procedure (A) with styrene oxide (360 mg, 3.00 mmol), piperidine (511 mg, 6.00 mmol) and acetic acid (180 mg, 3.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (DCM : MeOH = 10 : 1) as colorless oil (585 mg, 95%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.45 – 7.31 (m, 5H), 4.77 (dd, *J* = 10.2, 3.9 Hz, 1H), 4.24 (s, 1H), 2.79 – 2.71 (m, 2H), 2.57 – 2.39 (m, 4H), 1.71 – 1.50 (m, 6H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 142.6, 128.5, 128.2, 126.1, 125.8, 68.6, 67.0, 54.5, 26.2, 24.3. The spectroscopic data (NMR) of this compound match the literature data.[16]

1-phenyl-2-(morpholin-4-yl)ethanol (6x)



The reaction was performed following the General Procedure (A) with styrene oxide (360 mg, 3.00 mmol), morpholine (523 mg, 6.00 mmol) and acetic acid (180 mg, 3.00

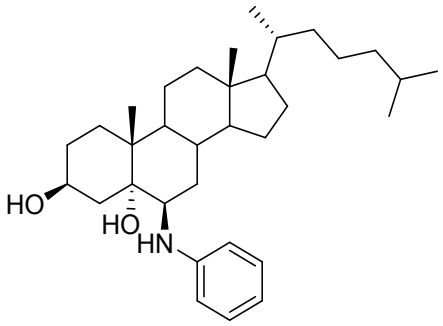
mmol). The title compound was separated by flash chromatography on deactivated silica gel (DCM : MeOH = 10 : 1) as yellow oil (597 mg, 96%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.30 – 7.18 (m, 5H), 4.66 (dd, *J* = 9.6, 4.2 Hz, 1H), 3.67 – 3.63 (m, 4H), 2.67 – 2.60 (m, 2H), 2.43 – 2.34 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 142.0, 128.3, 127.6, 126.0, 68.6, 67.0, 66.8, 53.5. The spectroscopic data (NMR) of this compound match the literature data.[16]

General procedure (B) and characterization for the acetic acid-catalyzed regioselective ring-opening of steroidal epoxides by amines.

General procedure (B)

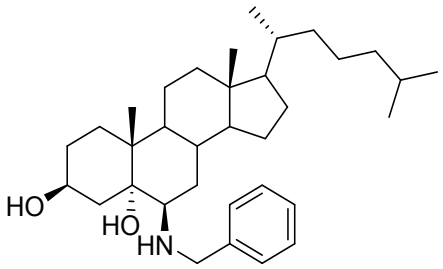
All 5α,6α-epoxy steroid precursors were prepared by *m*-CPBA-mediated epoxidation.[17] A screw-capped vial equipped with a stir bar was charged with epoxide (0.50 mmol), amine (4.00 mmol, 8.00 eq.) and acetic acid (2.00 mmol, 4.00 eq.) under solvent-free condition.The reaction mixture was stirred at 150℃ for 1h. After the reaction was done, K_2CO_3 was added to the reaction mixture sequentially. The crude material was loaded onto a deactivated silica gel column and separated by flash chromatography to afford the pure 6β-amino steroid.

6β-phenylaminocholestan-3β,5α-diol (10a)



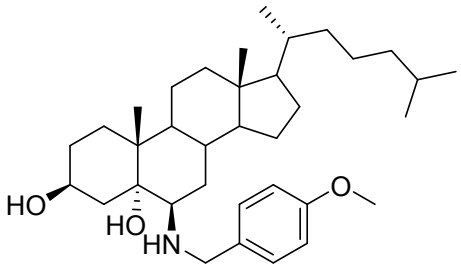
The reaction was performed following the General Procedure (B) with 5α,6α-epoxycholestan-3β-ol (201 mg, 0.50 mmol), aniline (373 mg, 4.00 mmol) and acetic acid (120 mg, 2.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as yellow oil (231 mg, 93%). The spectroscopic data (NMR) of this compound match the literature data.[18]

6β-benzylaminocholestan-3β,5α-diol (10b)



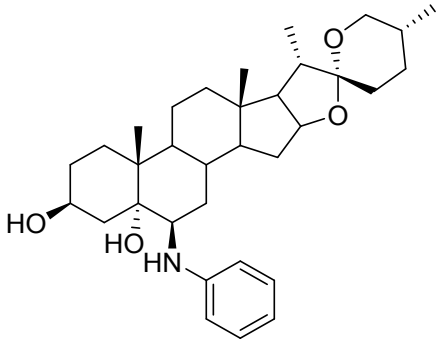
The reaction was performed following the General Procedure (B) with 5α,6α-epoxycholestan-3β-ol (201 mg, 0.50 mmol), benzylamine (429 mg, 4.00 mmol) and acetic acid (120 mg, 2.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as yellow oil (239 mg, 94%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.35 – 7.23 (m, 5H), 4.14 – 4.03 (m,1H), 3.85 (d, *J* = 13.4 Hz, 1H), 3.65 (d, *J* = 13.4 Hz, 1H), 2.45 (d, *J* = 3.7 Hz, 1H), 2.15 (t, *J* = 12.3 Hz, 1H), 1.98 (d, *J* = 12.2 Hz, 1H), 1.86 – 1.76 (m, 3H), 1.60 – 1.43 (m, 10H), 1.43 – 1.30 (m, 8H), 1.21 – 1.09 (m, 10H), 0.91 (dd, *J* = 10.8, 6.2 Hz, 11H), 0.66 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 141.3, 128.4, 128.2, 127.0, 68.1, 64.5, 56.4, 56.0, 53.6, 46.5, 42.9, 41.7, 40.1, 39.7, 38.8, 36.3, 36.0, 33.1, 31.1, 30.6, 28.4, 28.2, 24.3, 24.0, 23.0, 22.7, 21.3, 18.8, 17.8, 12.4. HRMS calc'd for $C_{34}H_{56}NO_2^+$ 510.4306, found 510.4304 $[M+H]^+$.

6β-(4-methoxybenzyl)aminocholestan-3β,5α-diol (10c)



The reaction was performed following the General Procedure (B) with 5α,6α-epoxycholestan-3β-ol (200 mg, 0.50 mmol), 4-methoxy-benzylamine(549 mg, 4.00 mmol) and acetic acid (120 mg, 2.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as yellow oil (264 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 7.25 (d, *J* = 5.3 Hz, 2H), 6.84 (d, *J* = 6.5 Hz, 2H), 4.07 – 4.03 (m, 1H), 3.78 (s, 1H), 3.80 (d, *J* = 8.9 Hz, 1H), 3.59 (d, *J* = 9.8 Hz, 1H), 2.44 – 2.42 (m, 1H), 2.17 (dd, *J* = 9.7, 8.3 Hz, 1H), 2.05 – 1.94 (m, 2H), 1.86 – 1.76 (m, 3H), 1.57 – 1.44 (m, 10H), 1.36 – 1.31 (m, 7H), 1.27 – 1.21 (m, 4H), 1.16 (s, 3H), 1.13 – 1.05 (m, 7H), 1.01 – 0.93 (m, 3H), 0.89 (d, *J* = 4.8 Hz, 3H), 0.86 (d, *J* = 1.4 Hz, 3H), 0.85 (d, *J* = 1.4 Hz, 3H), 0.65 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 158.7, 129.4, 113.8, 77.3, 68.0, 64.1, 56.4, 55.9, 55.4, 46.3, 42.9, 39.6, 38.7, 36.3, 35.9, 33.0, 31.0, 30.6, 28.3, 28.1, 24.3, 24.0, 23.0, 22.7, 21.3, 18.8, 17.7, 12.3. HRMS calc'd for $C_{35}H_{58}NO_3^+$ 540.4411, found 540.4412 $[M+H]^+$.

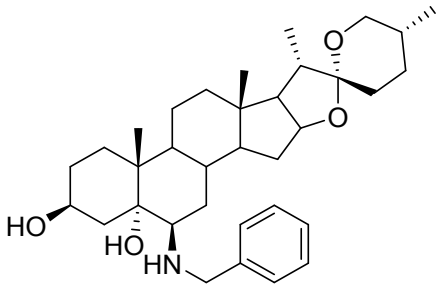
(25R)-6β-phenylaminospirostan-3β,5α-diol (10d)



The reaction was performed following the General Procedure (B) with 5α,6α-epoxyspirostan-22α-O-3β-ol (223 mg, 0.50 mmol), aniline(373 mg, 4.00 mmol) and acetic acid (120 mg, 2.00 mmol). The title compound was separated by flash

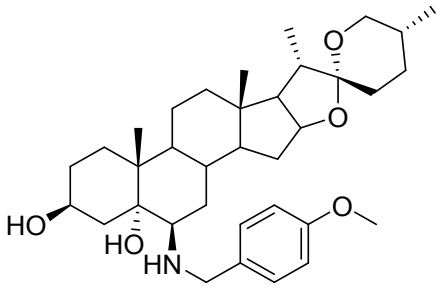
chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as pale yellow oil (236 mg, 90%). The spectroscopic data (NMR) of this compound match the literature data[18].

(25R)-6β-benzylaminospirostan-3β,5α-diol (10e)



The reaction was performed following the General Procedure (B) with 5α,6α-epoxyspirostan-22α-O-3β-ol (223 mg, 0.50 mmol), benzylamine(429 mg, 4.00 mmol) and acetic acid (120 mg, 2.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as white solid (247 mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 7.26 – 7.15 (m, 5H), 4.35 – 4.30 (m, 1H), 4.02 – 3.97 (m, 1H), 3.79 (d, *J* = 10.0 Hz, 1H), 3.59 (d, *J* = 10.0 Hz, 1H), 3.43 – 3.38 (m, 1H), 3.31 (t, *J* = 8.2 Hz, 1H), 2.39 (d, *J* = 3.0 Hz, 1H), 2.12 – 2.06 (m, 1H), 1.94 – 1.89 (m, 1H), 1.80 – 1.68 (m, 5H), 1.60 – 1.51 (m, 5H), 1.49 – 1.38 (m, 5H), 1.36 – 1.28 (m, 3H), 1.25 – 1.19 (m, 3H), 1.17 – 1.13 (m, 6H), 1.01 (d, *J* = 5.3 Hz, 1H), 0.90 (d, *J* = 5.2 Hz, 3H), 0.73 – 0.70 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 128.5, 128.3, 127.1, 109.4, 80.9, 77.2, 67.9, 67.0, 64.2, 62.3, 55.8, 53.5, 46.3, 41.8, 41.6, 40.9, 40.1, 38.9, 33.0, 31.8, 31.5, 31.0, 30.4, 30.2, 28.9, 21.1, 17.7, 17.3, 16.7, 14.6. HRMS calc'd for $C_{34}H_{52}NO_4^+$ 538.3891, found 538.3892 $[M+H]^+$.

(25R)-6β-(4-methoxybenzyl)aminospirostan-3β,5α-diol (10f)



The reaction was performed following the General Procedure (B) with 5α,6α-epoxyspirostan-22α-O-3β-ol (223 mg, 0.05 mmol), 4-methoxy-benzylamine(549 mg, 4.00 mmol) and acetic acid (120 mg, 2.00 mmol). The title compound was separated by flash chromatography on deactivated silica gel (EtOAc : PE = 1 : 1) as yellow oil (275 mg, 97%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 7.19 (d, *J* = 4.0 Hz, 2H), 6.78 (d, *J* = 6.1 Hz, 2H), 4.34 – 4.28 (m, 1H), 4.03 – 3.95 (m, 1H), 3.77 – 3.72 (m, 4H), 3.55 (d, *J* = 8.1 Hz, 1H), 3.40 (dd, *J* = 8.3, 3.2 Hz, 1H), 3.30 (t, *J* = 8.2 Hz, 1H), 2.40 (s, 1H), 2.12 – 1.99 (m, 2H), 1.90 – 1.87 (m, 1H), 1.81 – 1.71 (m, 3H), 1.56 – 1.47 (m, 6H), 1.44 – 1.38 (m, 5H), 1.32 – 1.28 (m, 2H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.19 – 1.07 (m, 2H), 1.22 – 1.07 (m, 7H), 0.92 – 0.88 (m, 4H), 0.72 (d, *J* = 5.4 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 141.3, 128.4, 128.2, 127.0, 68.1, 64.5, 56.4, 56.0, 53.6, 46.5, 42.9, 41.7, 40.1, 39.7, 38.8, 36.3, 36.0, 33.1, 31.2, 30.6, 28.4, 28.2, 24.3, 24.0, 23.0, 22.7, 21.3, 18.8, 17.8, 12.4. HRMS calc'd for $C_{35}H_{54}NO_5^+$ 568.3997, found 568.3994 $[M+H]^+$.

Supplementary References

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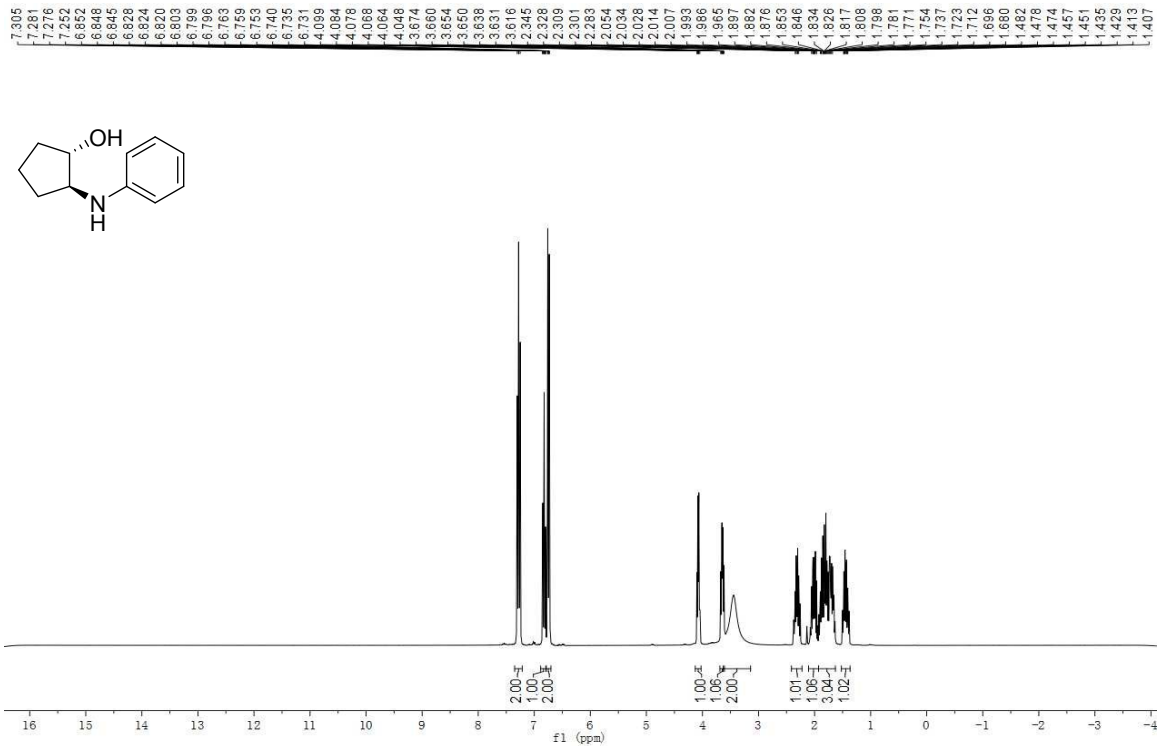
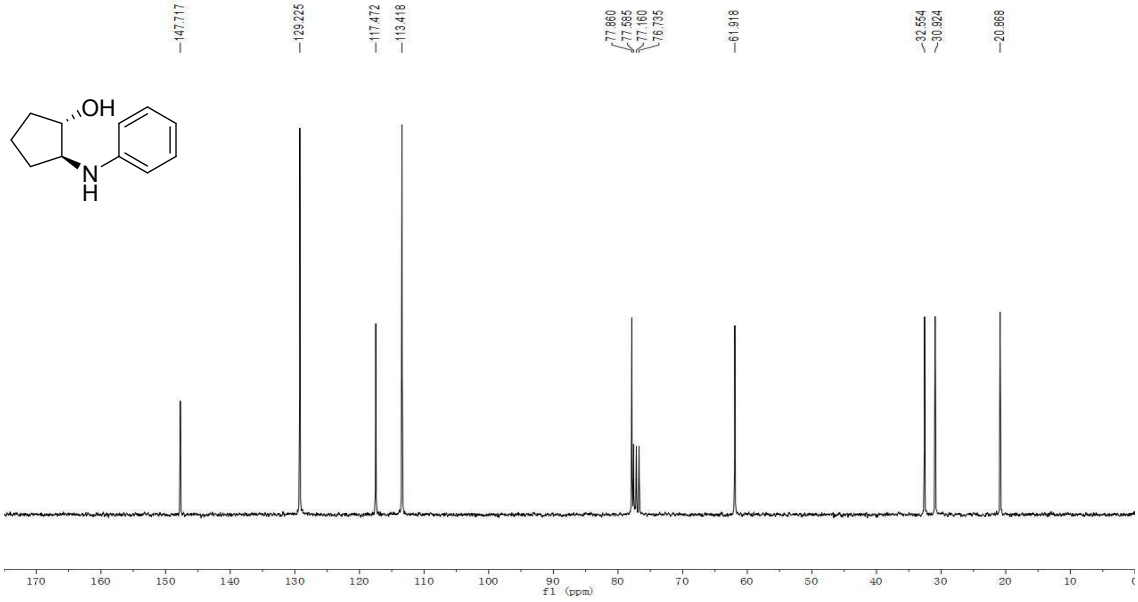
NMR spectra of β-aminoalchols

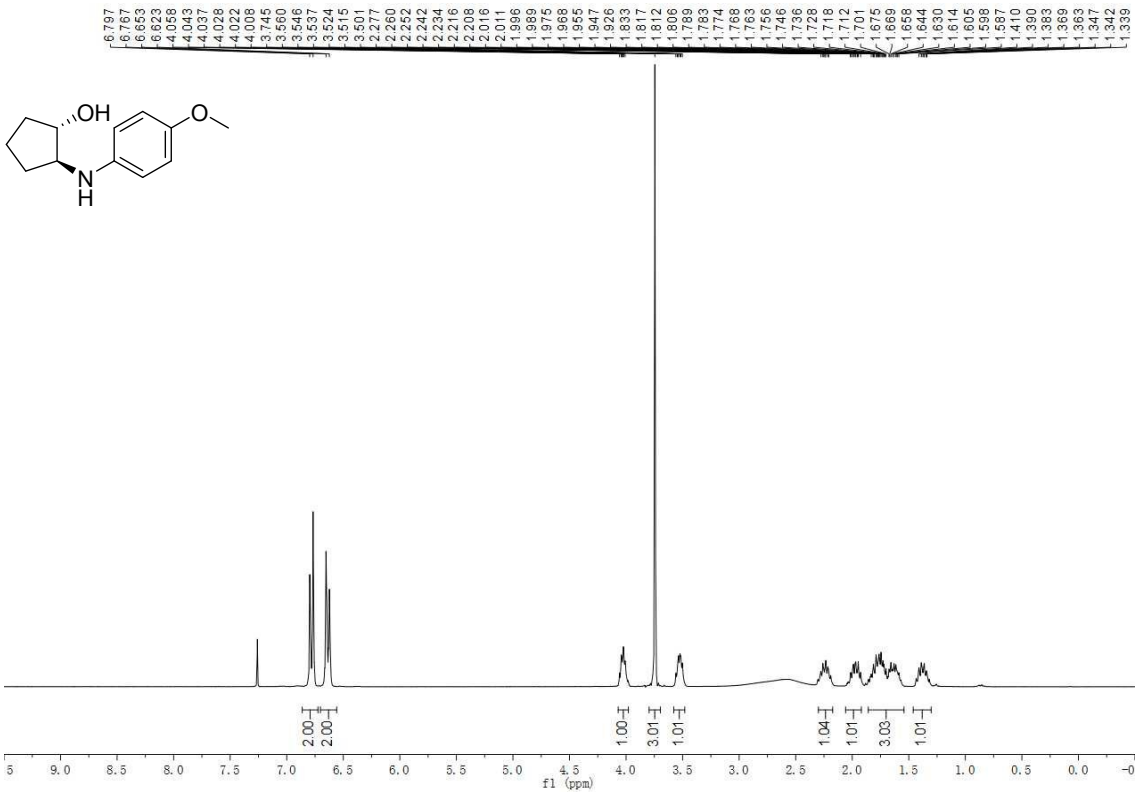
^{1}H NMR (300 MHz, Chloroform-*d*) of trans-2-(phenylamino)cyclopentanol (6a)



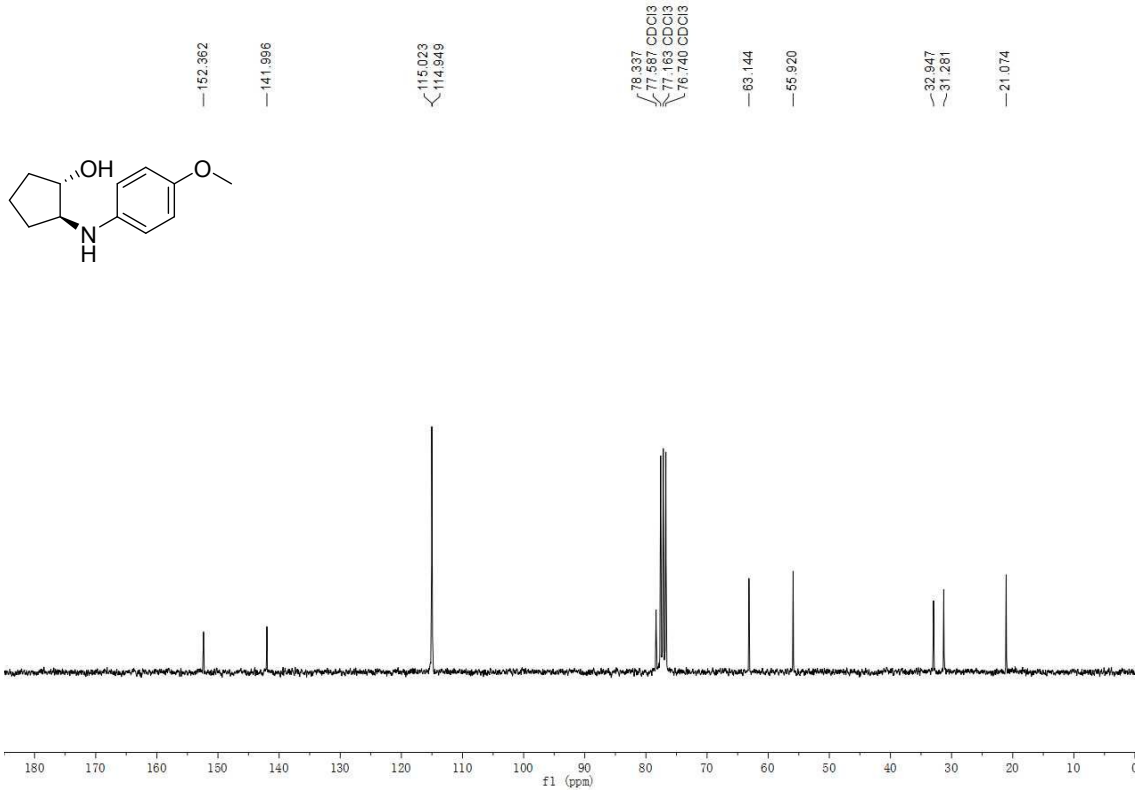
^{13}C NMR (75 MHz, Chloroform-*d*) of trans-2-(phenylamino)cyclopentanol (6a)



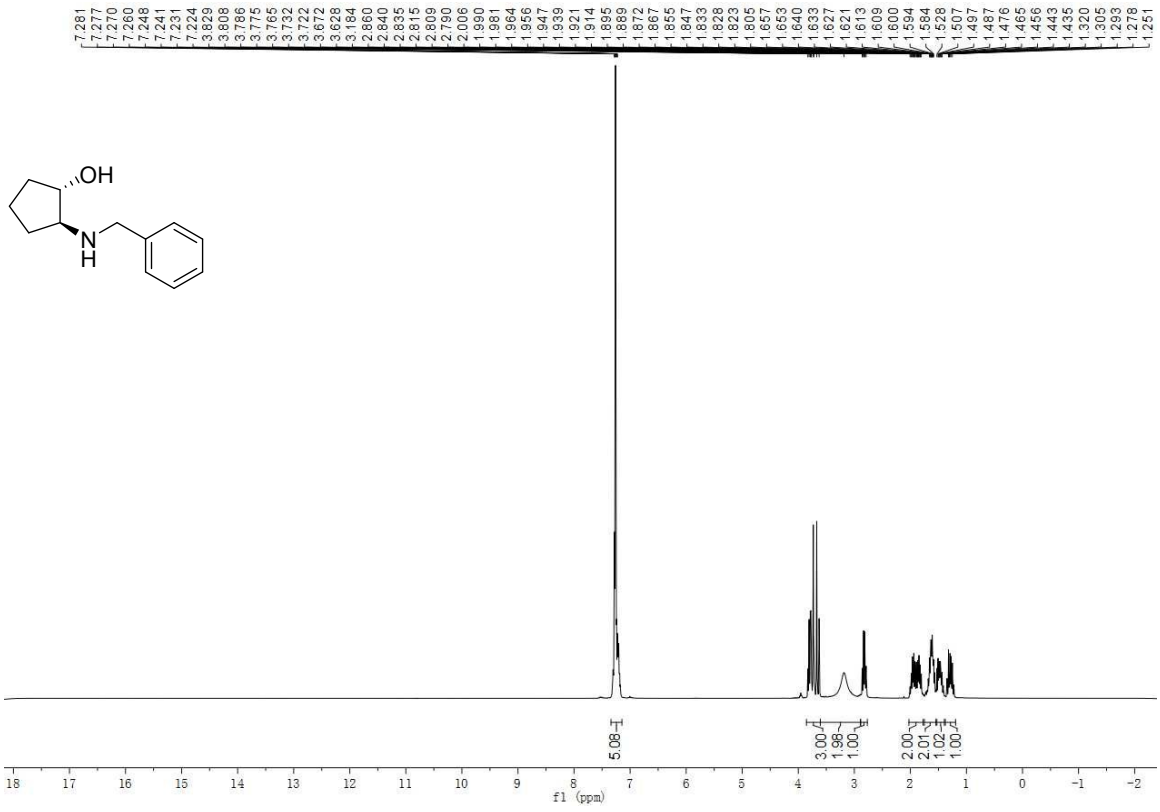
^{1}H NMR (300 MHz, Chloroform-*d*) of trans-2-((4-methoxyphenyl)amino)cyclopentanol (6b)



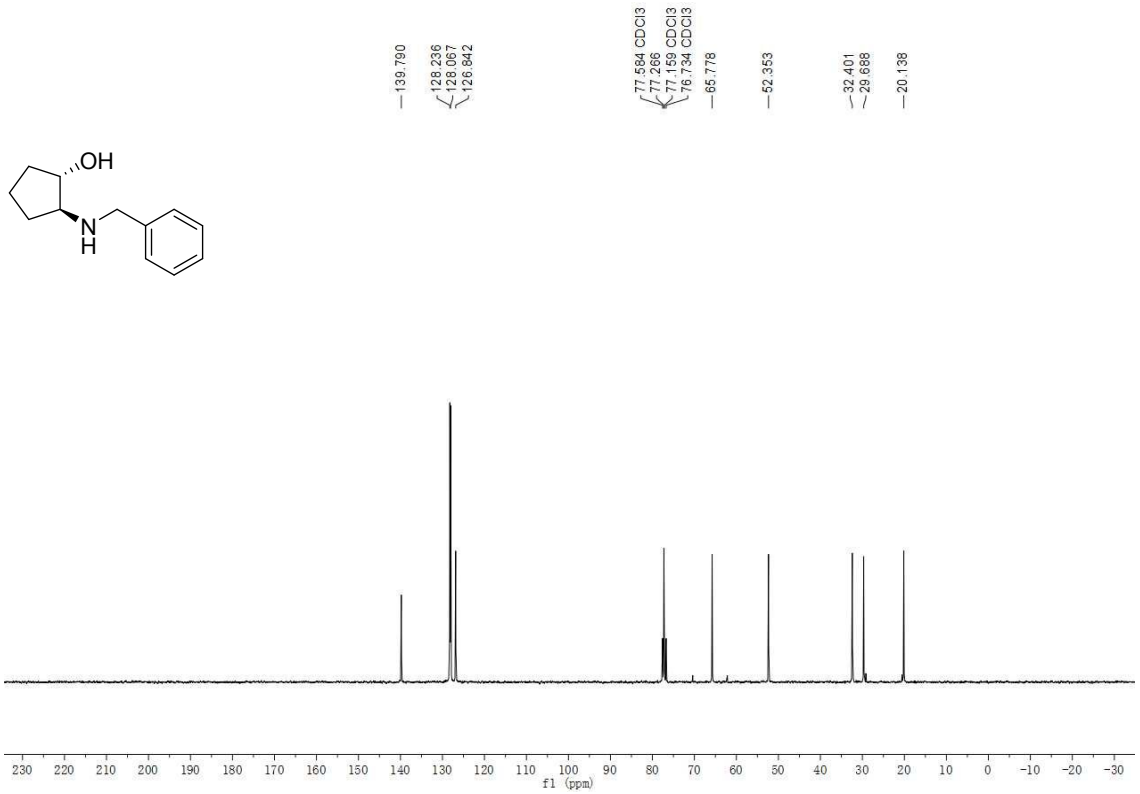
^{13}C NMR (75 MHz, Chloroform-*d*) of trans-2-((4-methoxyphenyl)amino)cyclopentanol (6b)



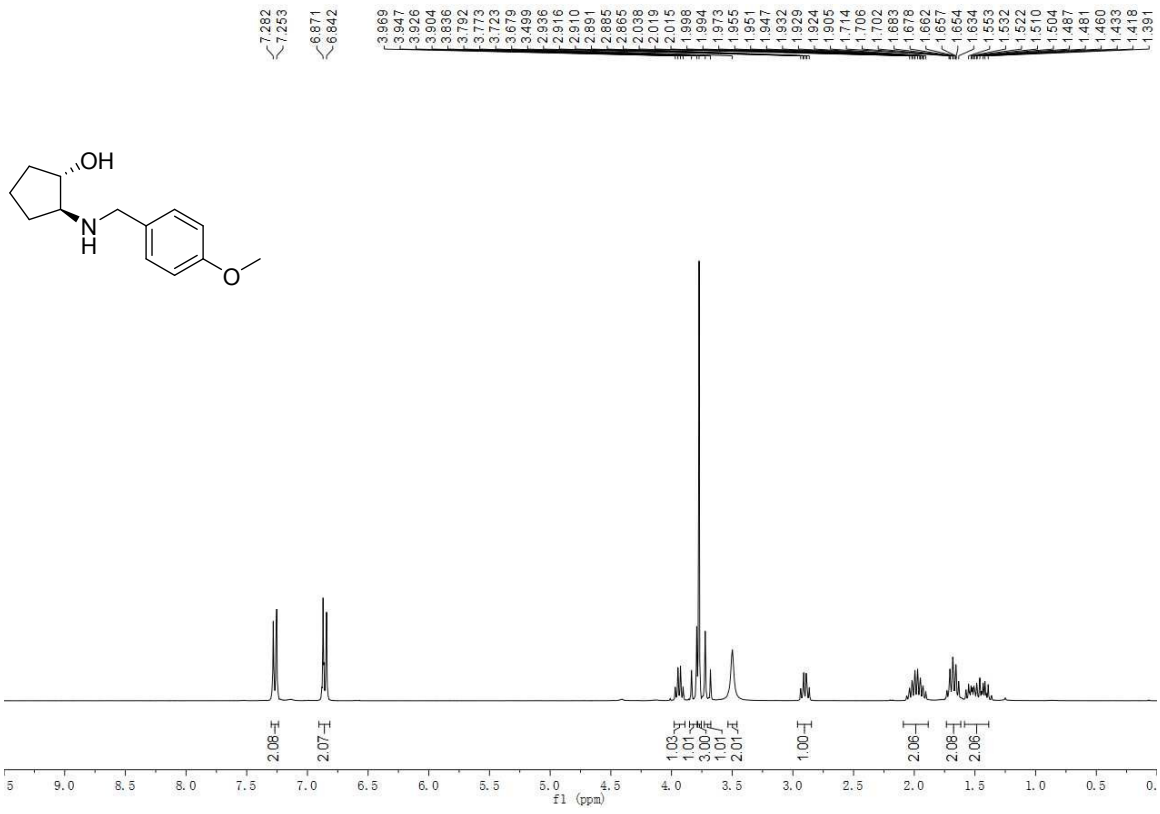
^{1}H NMR (300 MHz, Chloroform-*d*) of trans-2-(benzylamino)cyclopentanol (6c)



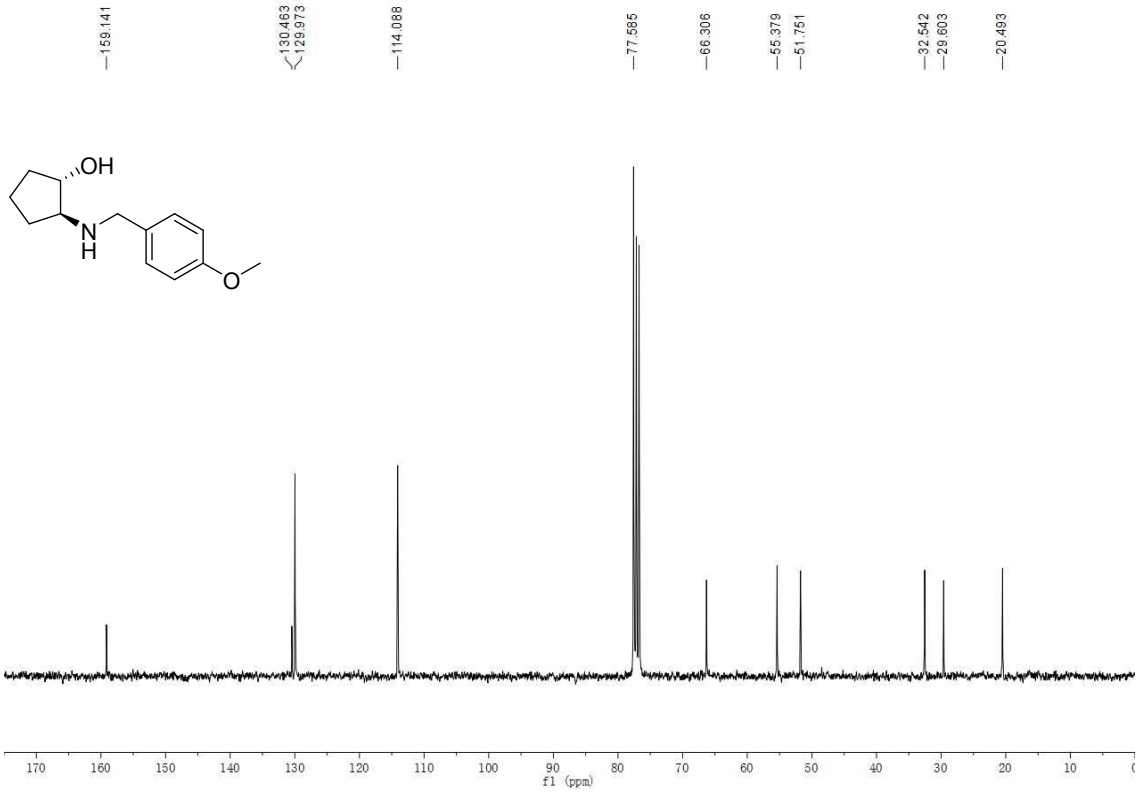
^{13}C NMR (75 MHz, Chloroform-*d*) of trans-2-(benzylamino)cyclopentanol (6c)



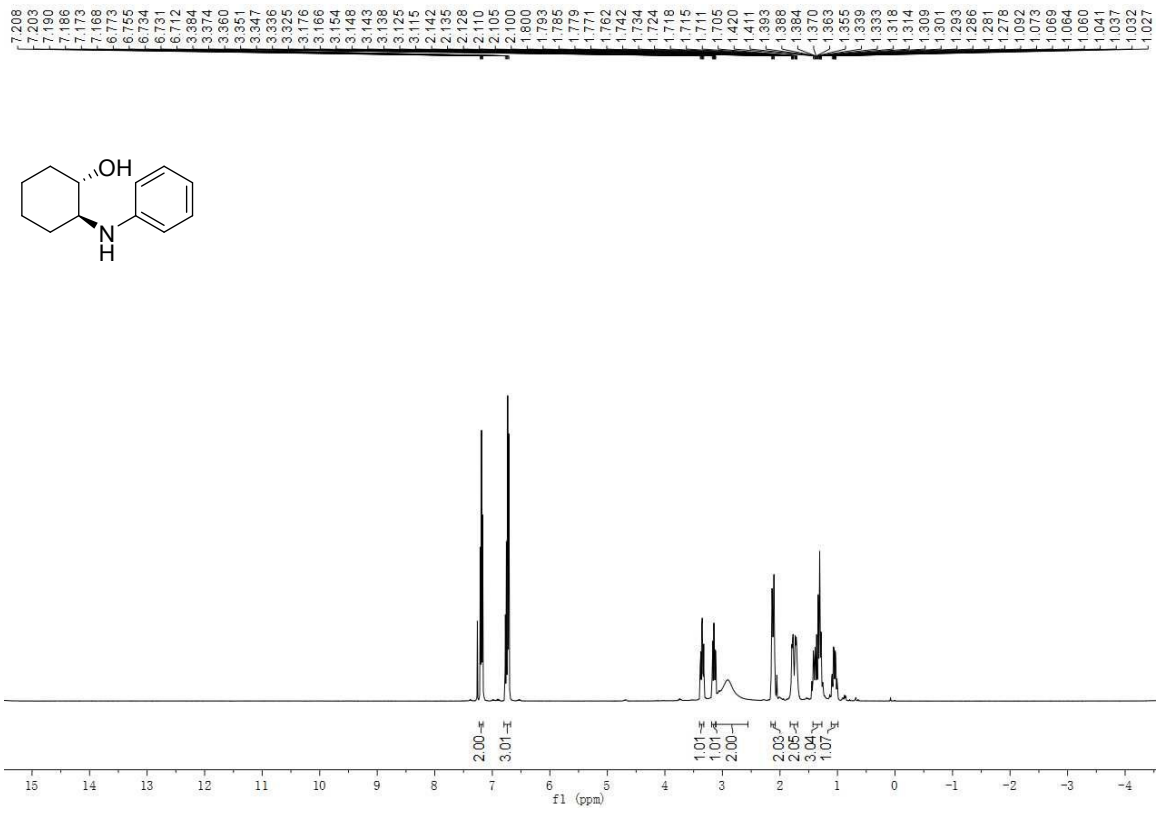
^{1}H NMR (300 MHz, Chloroform-*d*) of trans-2-((4-methoxybenzyl)amino)cyclopentanol (6d)



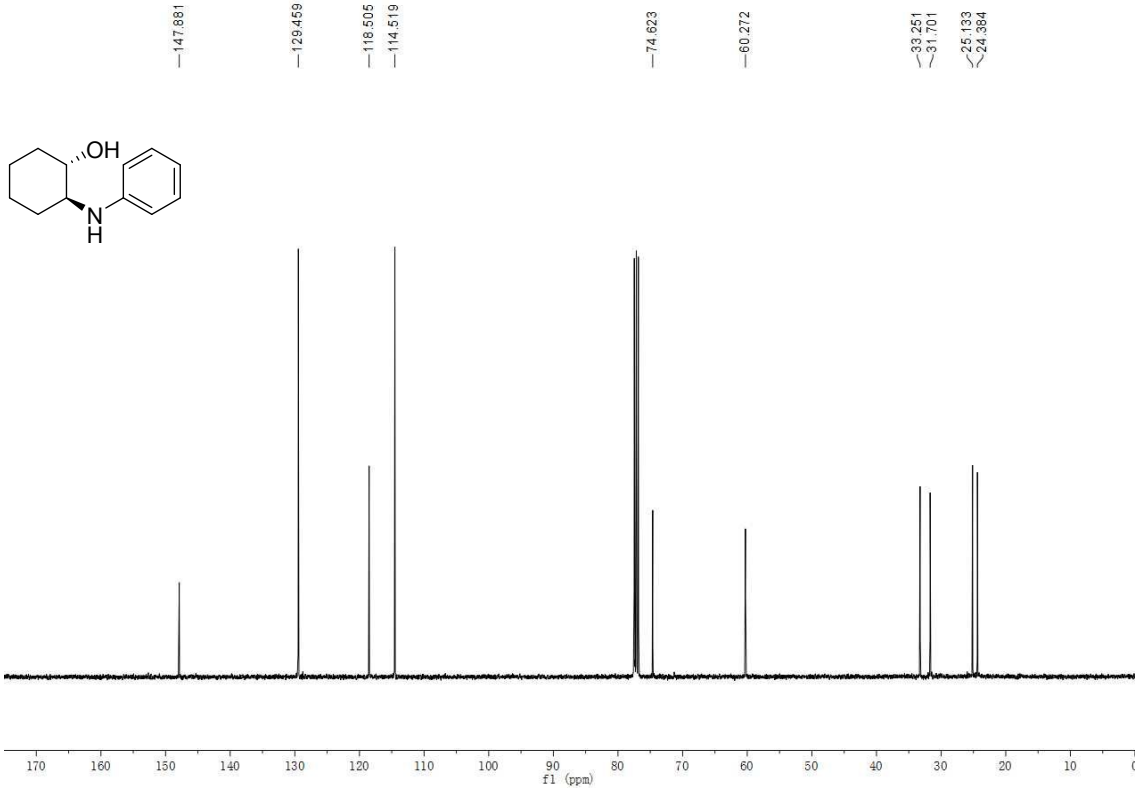
^{13}C NMR (75 MHz, Chloroform-*d*) of trans-2-((4-methoxybenzyl)amino)cyclopentanol (6d)



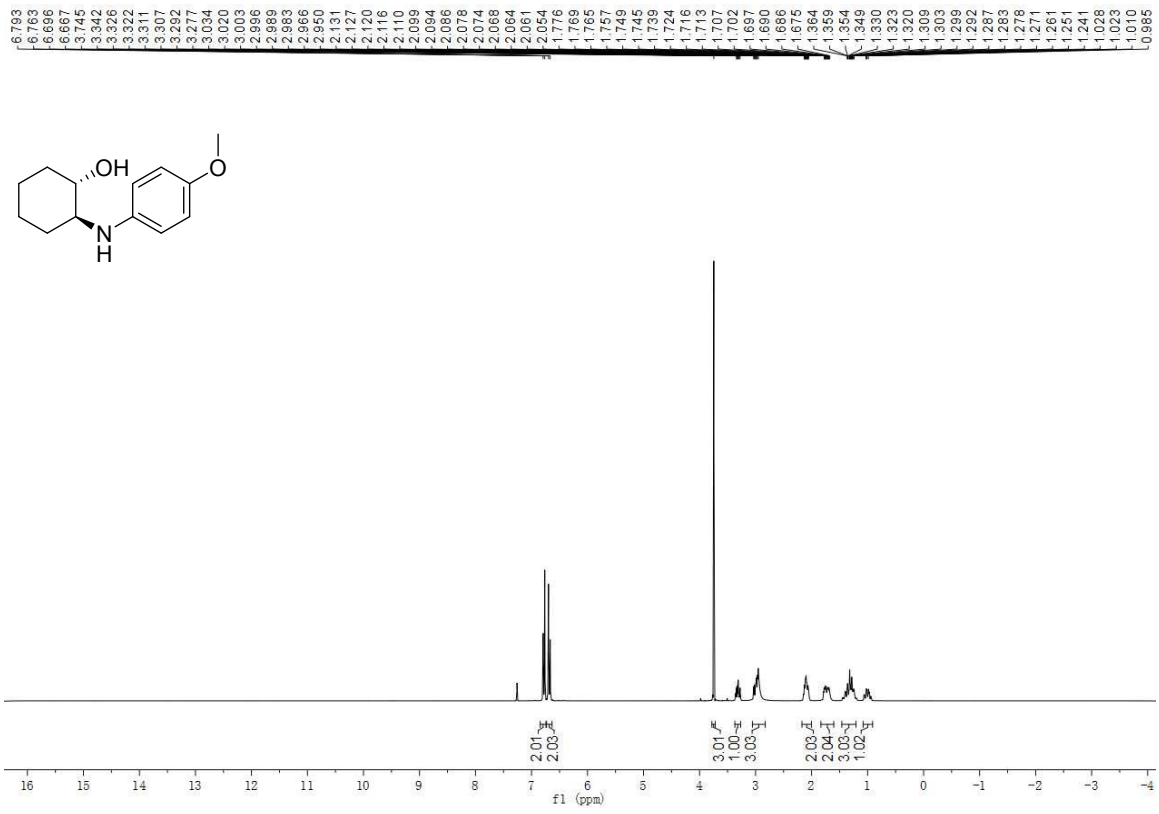
^{1}H NMR (400 MHz, Chloroform-*d*) of trans-2-(phenylamino)cyclohexanol (6e)



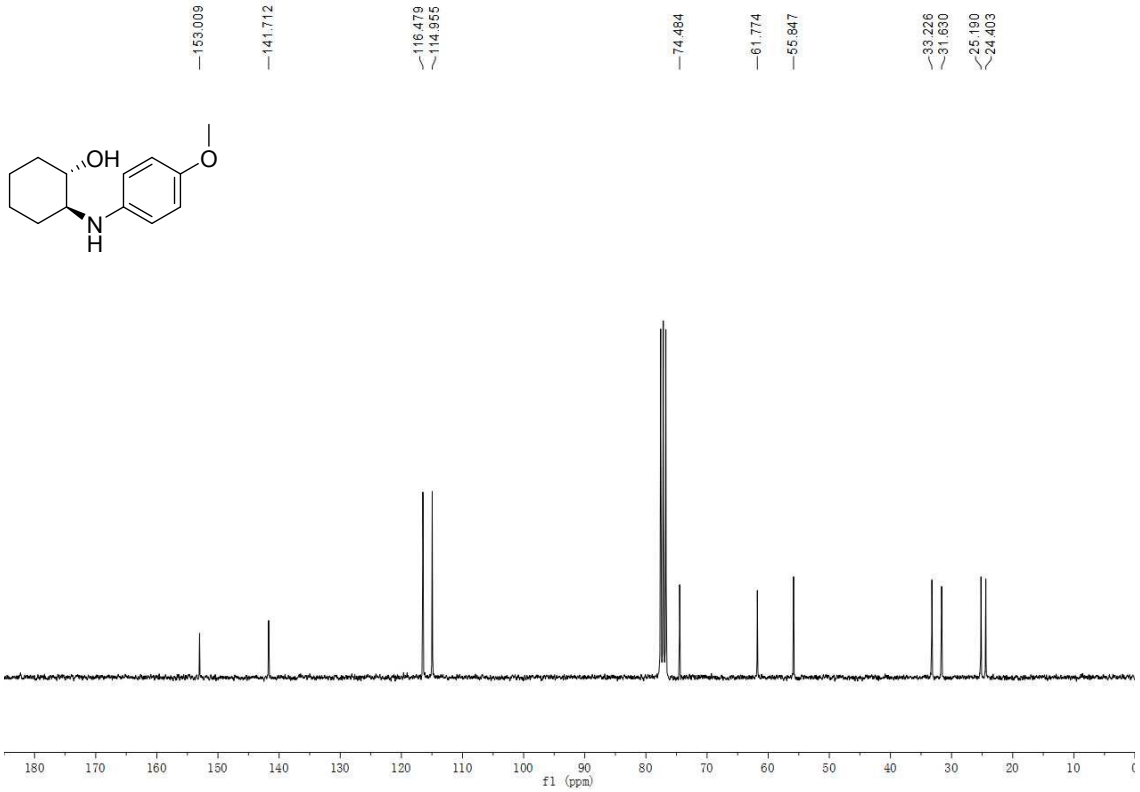
^{13}C NMR (100 MHz, Chloroform-*d*) of trans-2-(phenylamino)cyclohexanol (6e)



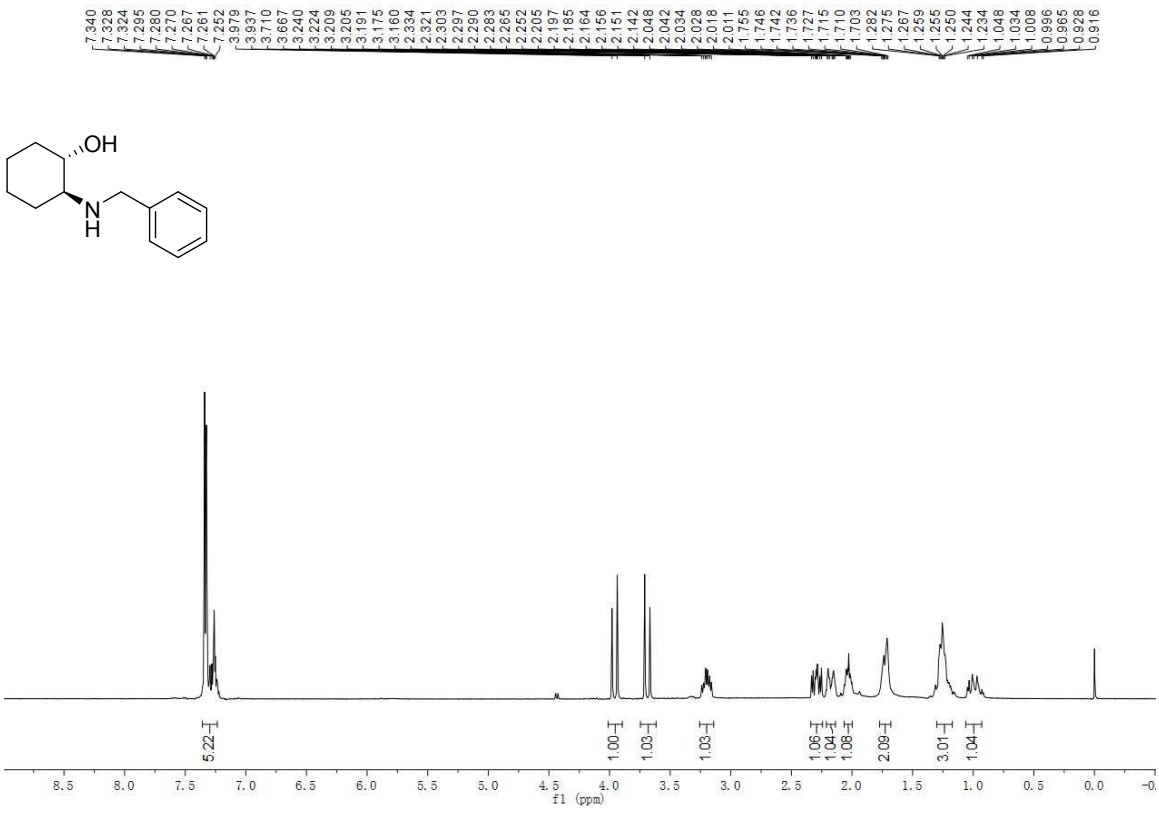
^{1}H NMR (300 MHz, Chloroform-*d*) of trans-2-((4-methoxyphenyl)amino)cyclohexanol (6f)



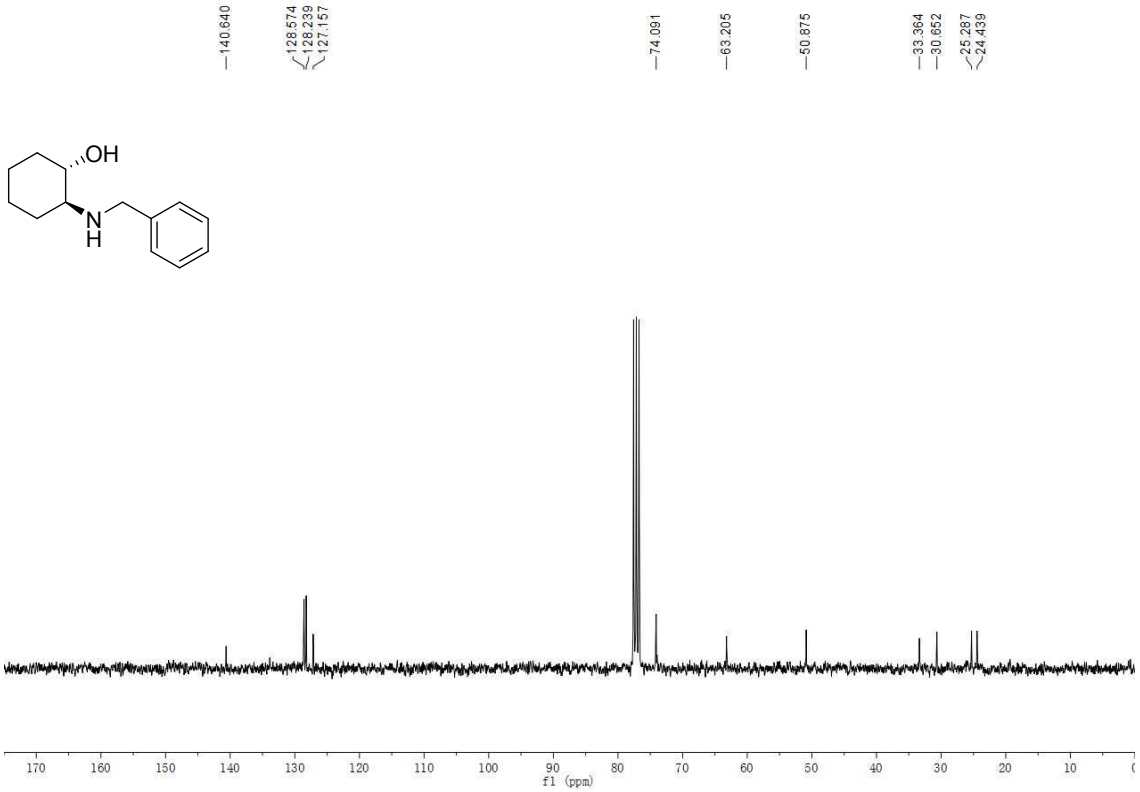
^{13}C NMR (75 MHz, Chloroform-*d*) of trans-2-((4-methoxyphenyl)amino)cyclohexanol (6f)



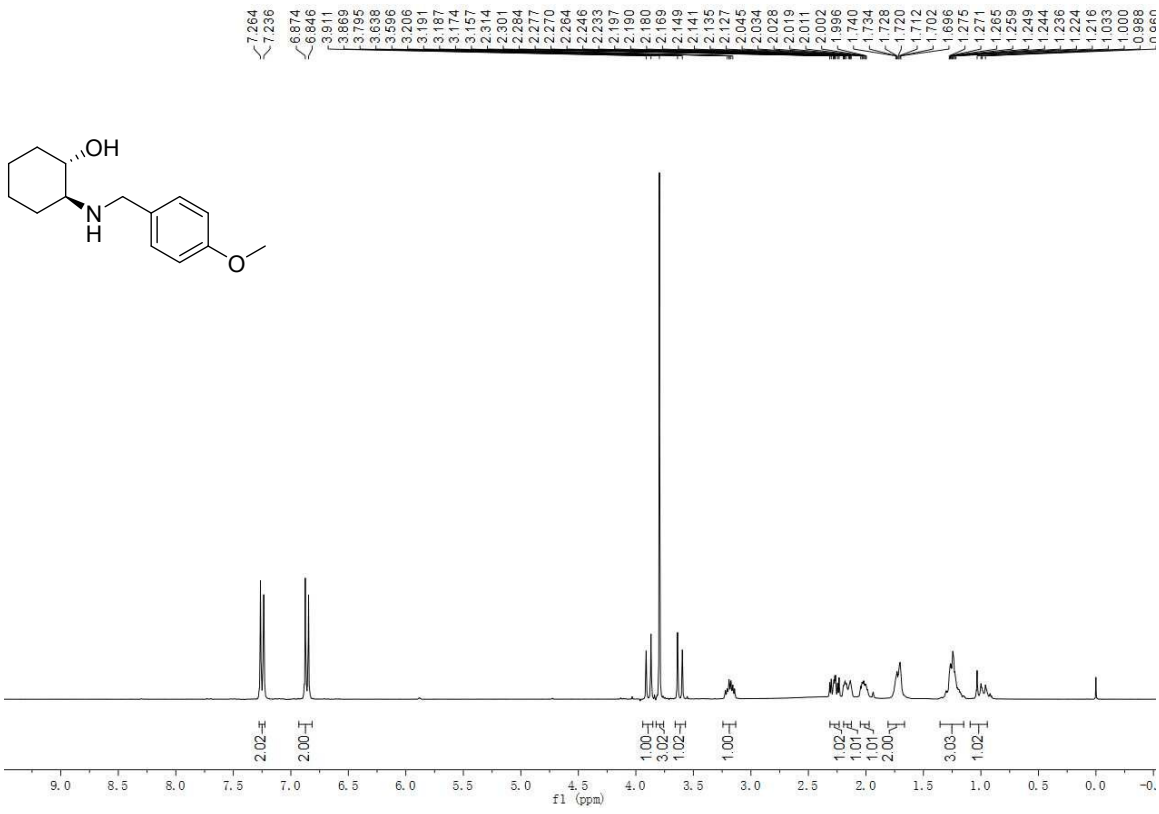
^{1}H NMR (300 MHz, Chloroform-*d*) of trans-2-(benzylamino)cyclohexanol (6g)



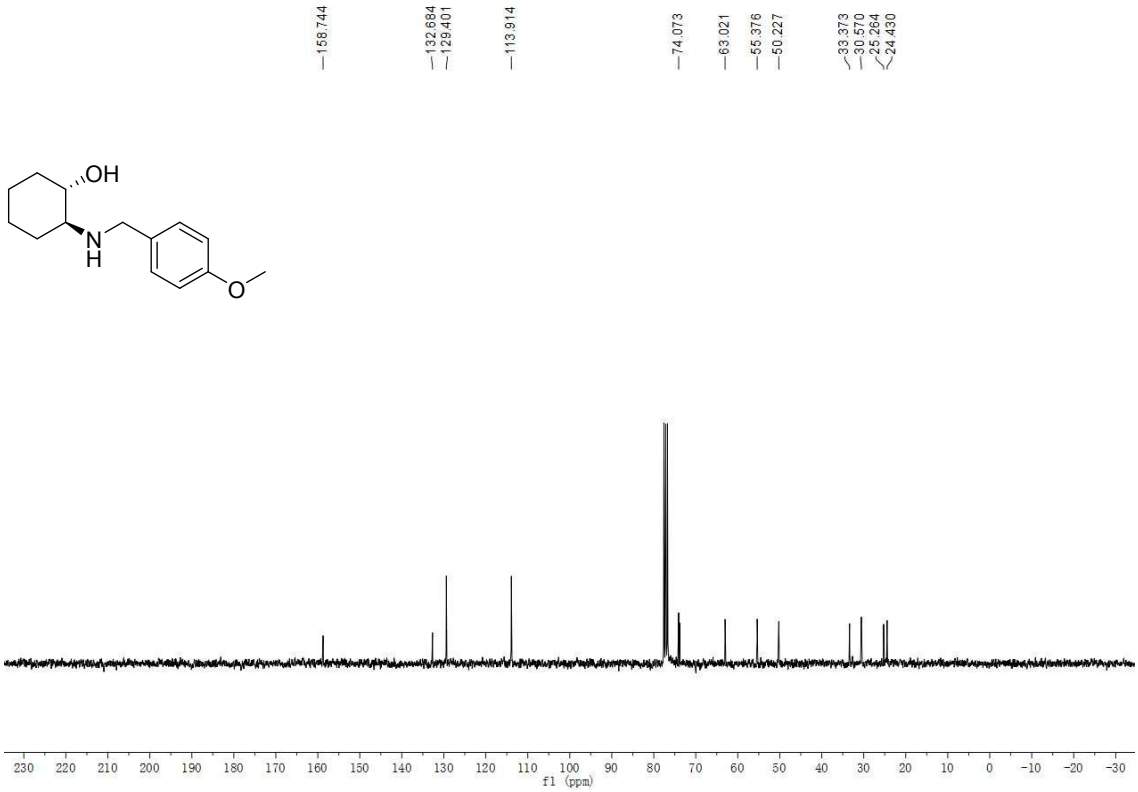
^{13}C NMR (75 MHz, Chloroform-*d*) of trans-2-(benzylamino)cyclohexanol (6g)



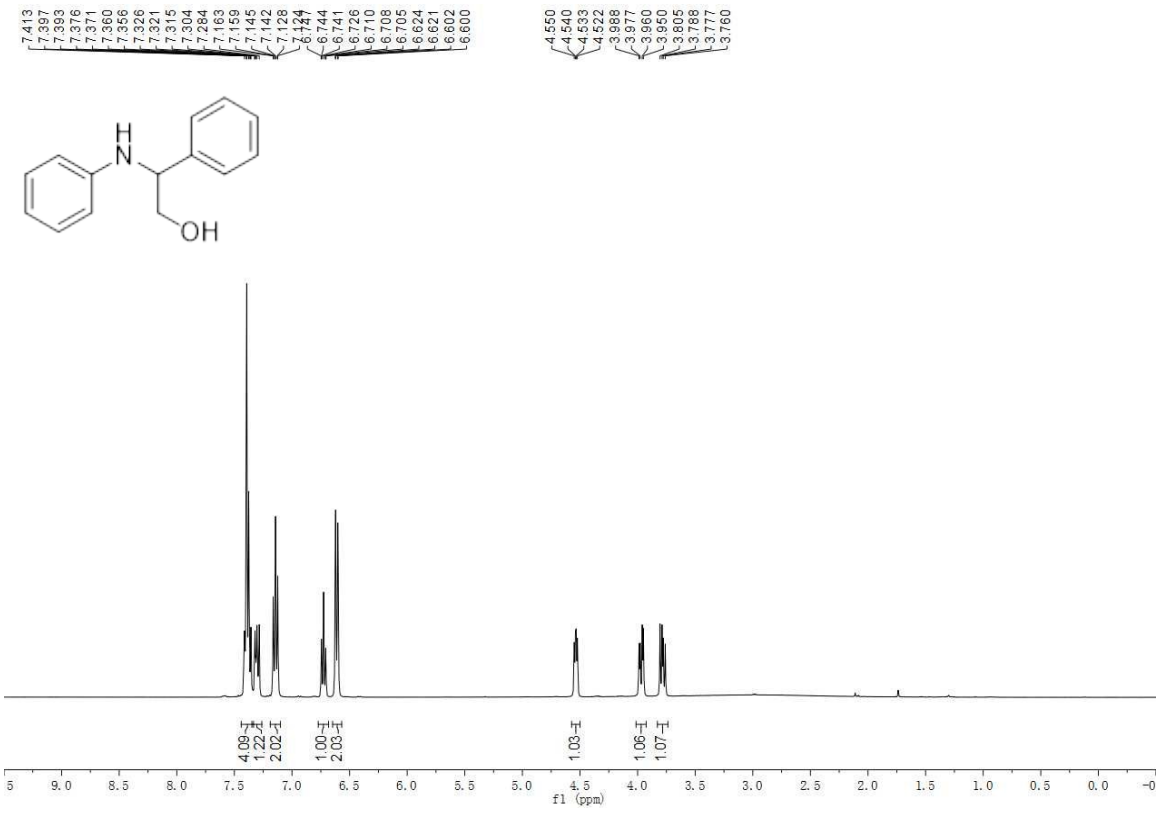
^{1}H NMR (300 MHz, Chloroform-*d*) of trans-2-((4-methoxybenzyl)amino)cyclohexanol (6h)



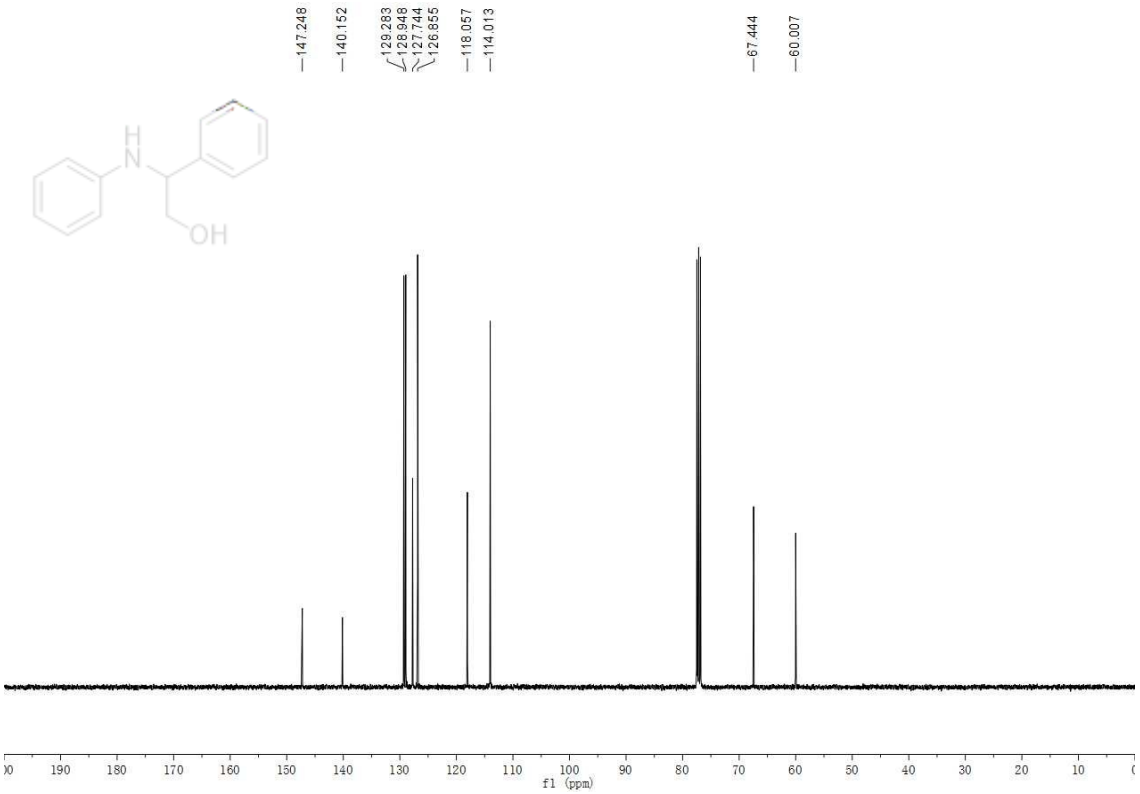
^{13}C NMR (75 MHz, Chloroform-*d*) of trans-2-((4-methoxybenzyl)amino)cyclohexanol (6h)



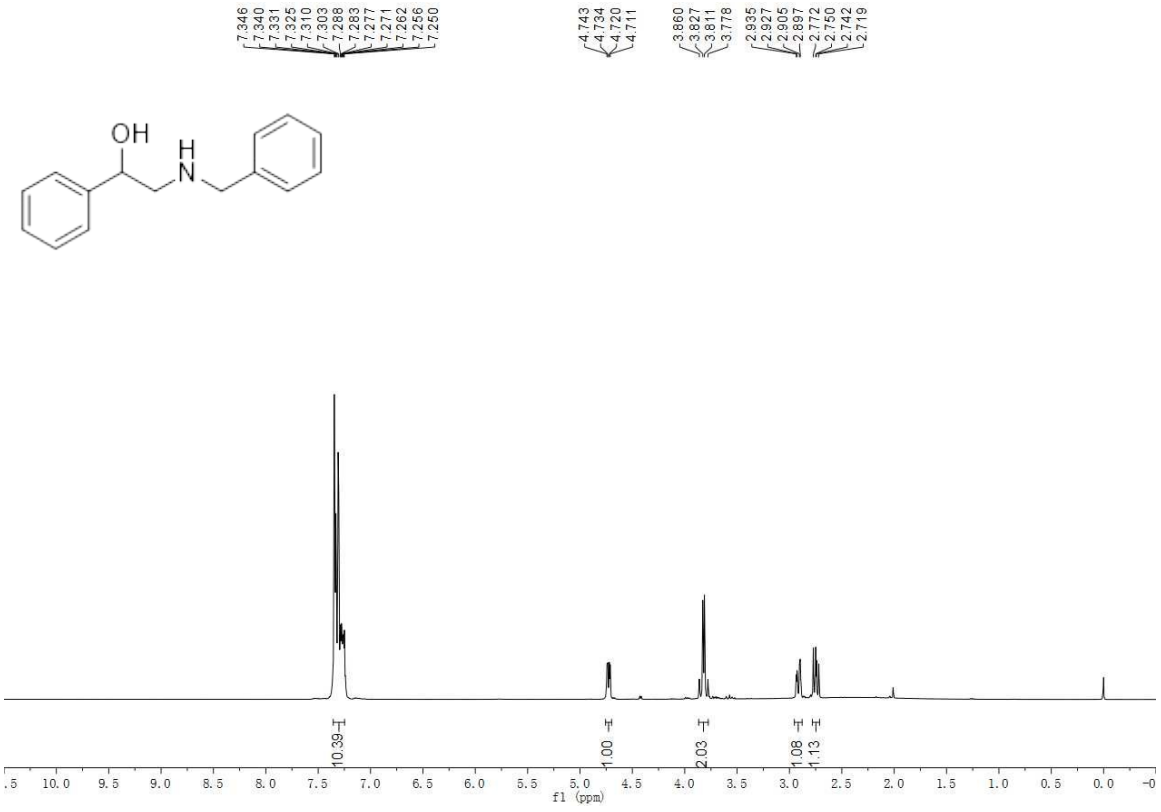
^{1}H NMR (400 MHz, Chloroform-*d*) of 2-phenyl-2-(phenylamino)ethanol (6i)



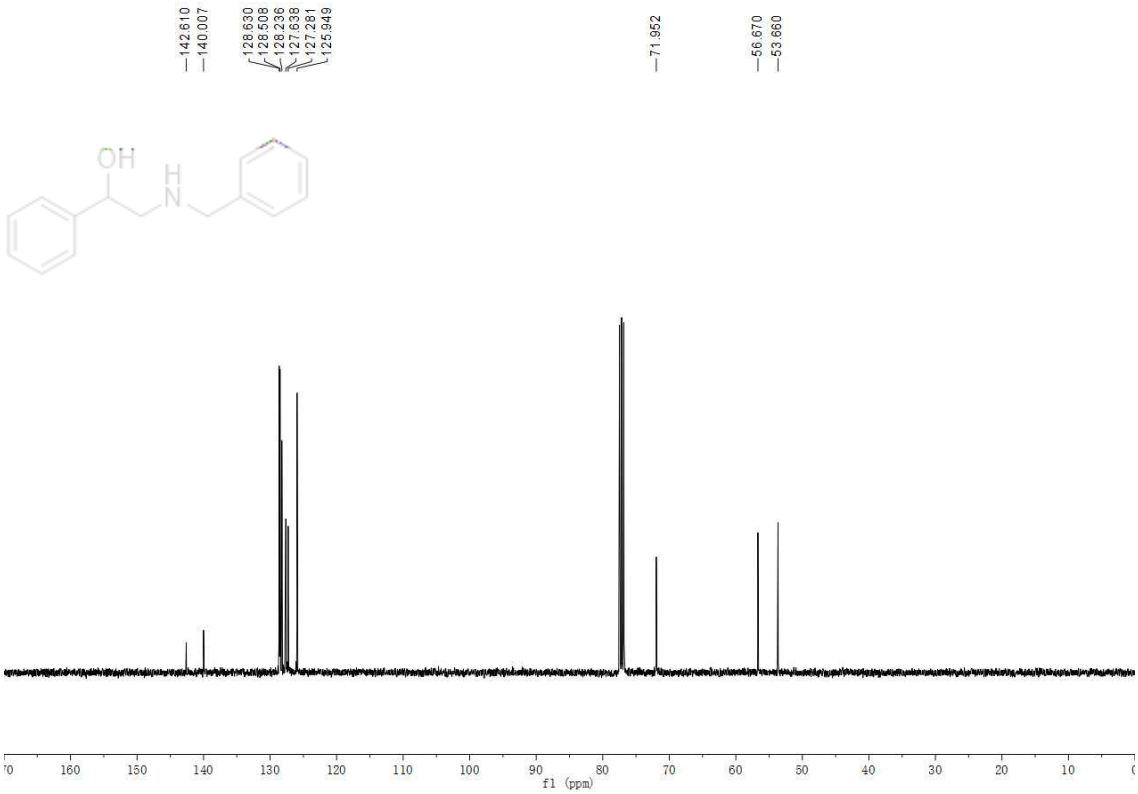
^{13}C NMR (100 MHz, Chloroform-*d*) of 2-phenyl-2-(phenylamino)ethanol (6i)



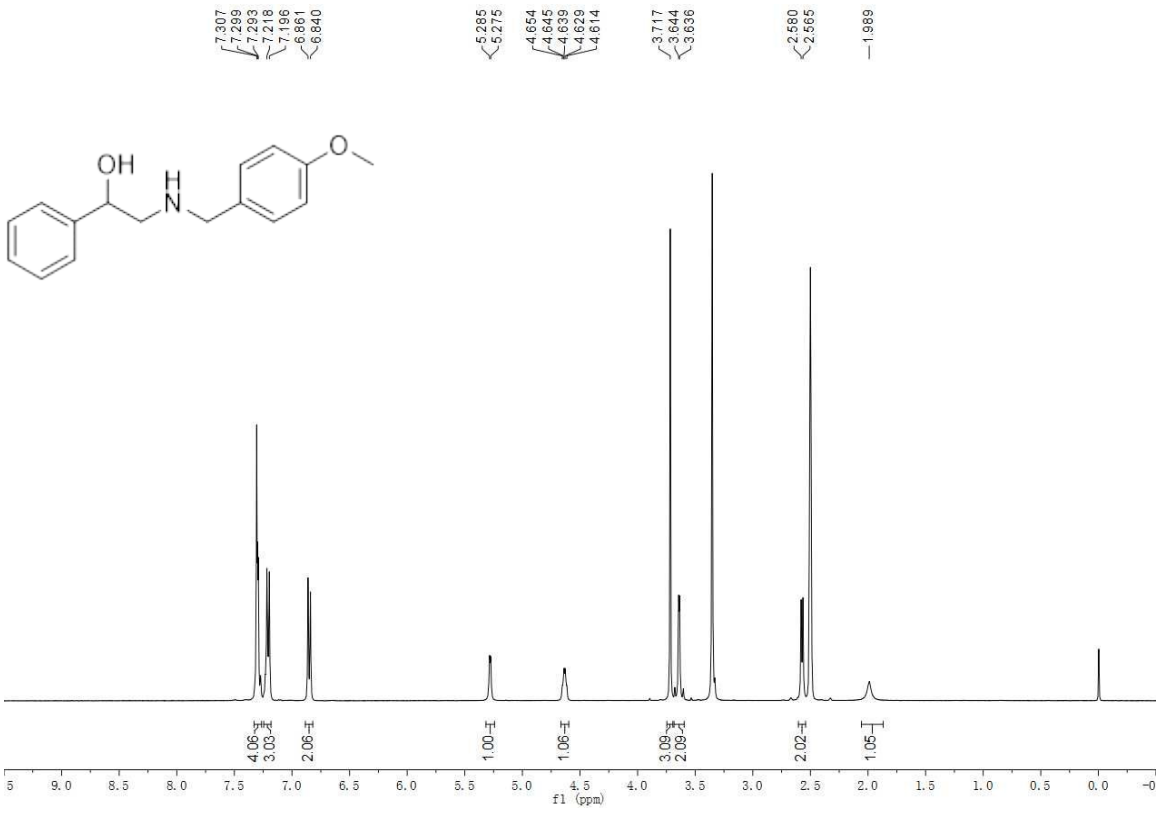
^{1}H NMR (400 MHz, Chloroform-*d*) of 1-phenyl-2-(benzylamino)ethanol (6k)



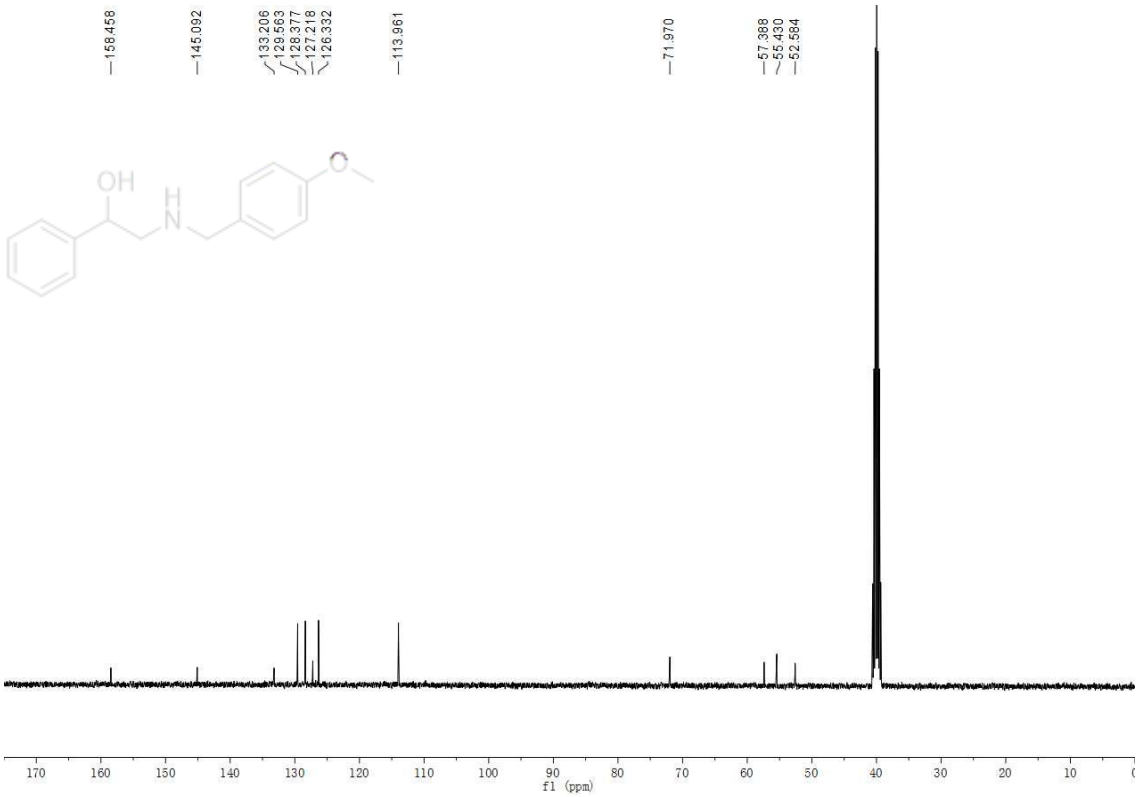
^{13}C NMR (100 MHz, Chloroform-*d*) of 1-phenyl-2-(benzylamino)ethanol (6k)



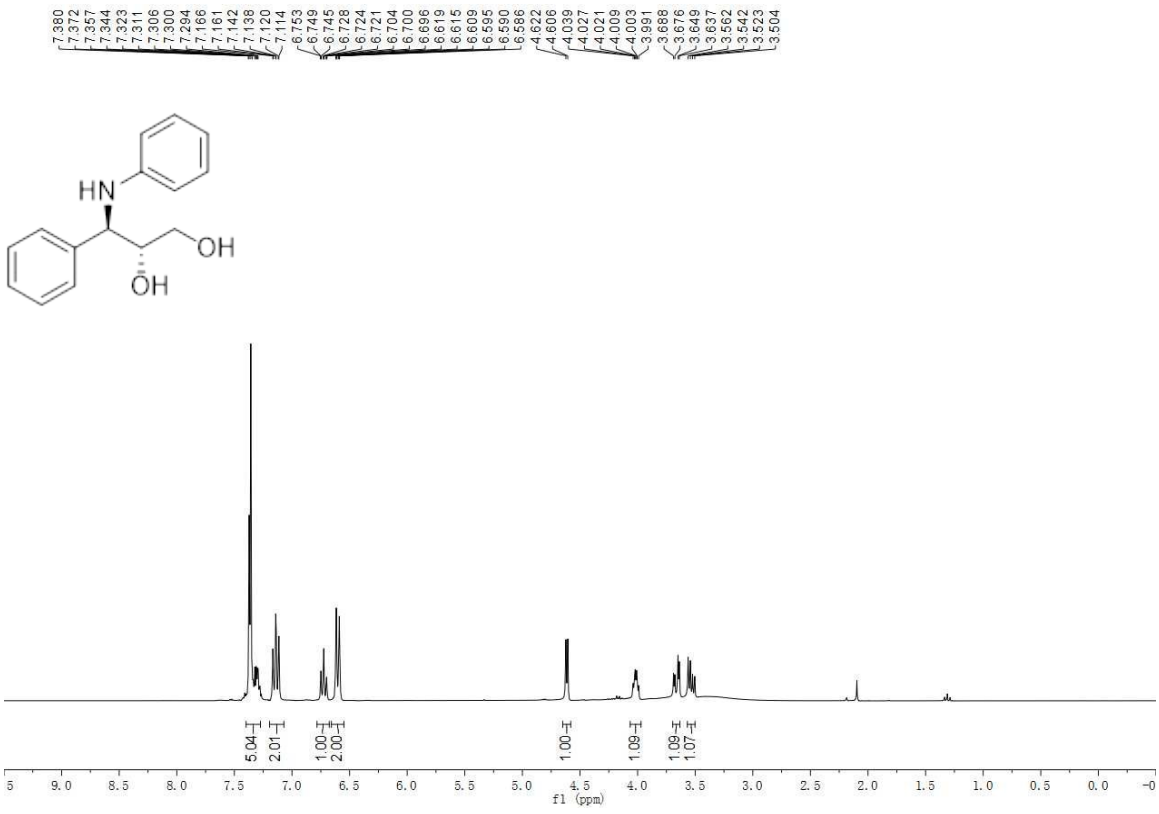
^{1}H NMR (400 MHz, DMSO-d_6) of 1-phenyl-2-((4-methoxybenzyl)amino)ethanol (6l)



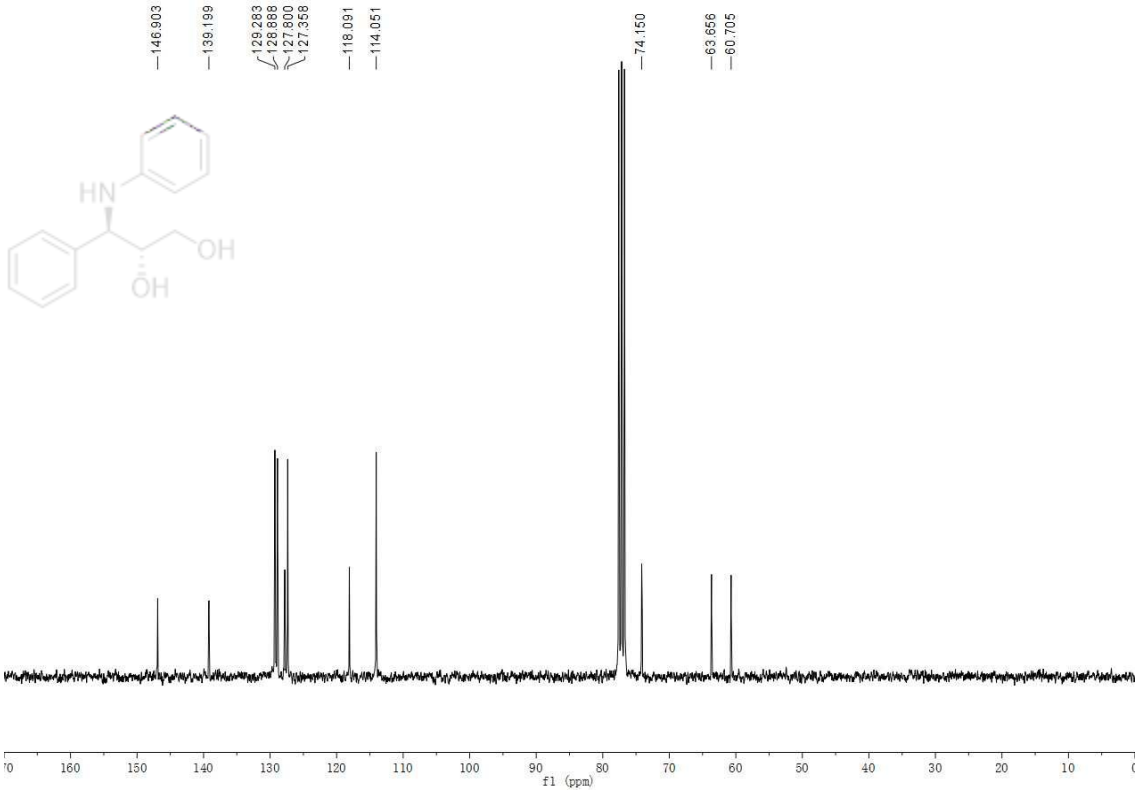
^{13}C NMR (100 MHz, DMSO-d_6) of 1-phenyl-2-((4-methoxybenzyl)amino)ethanol (6l)



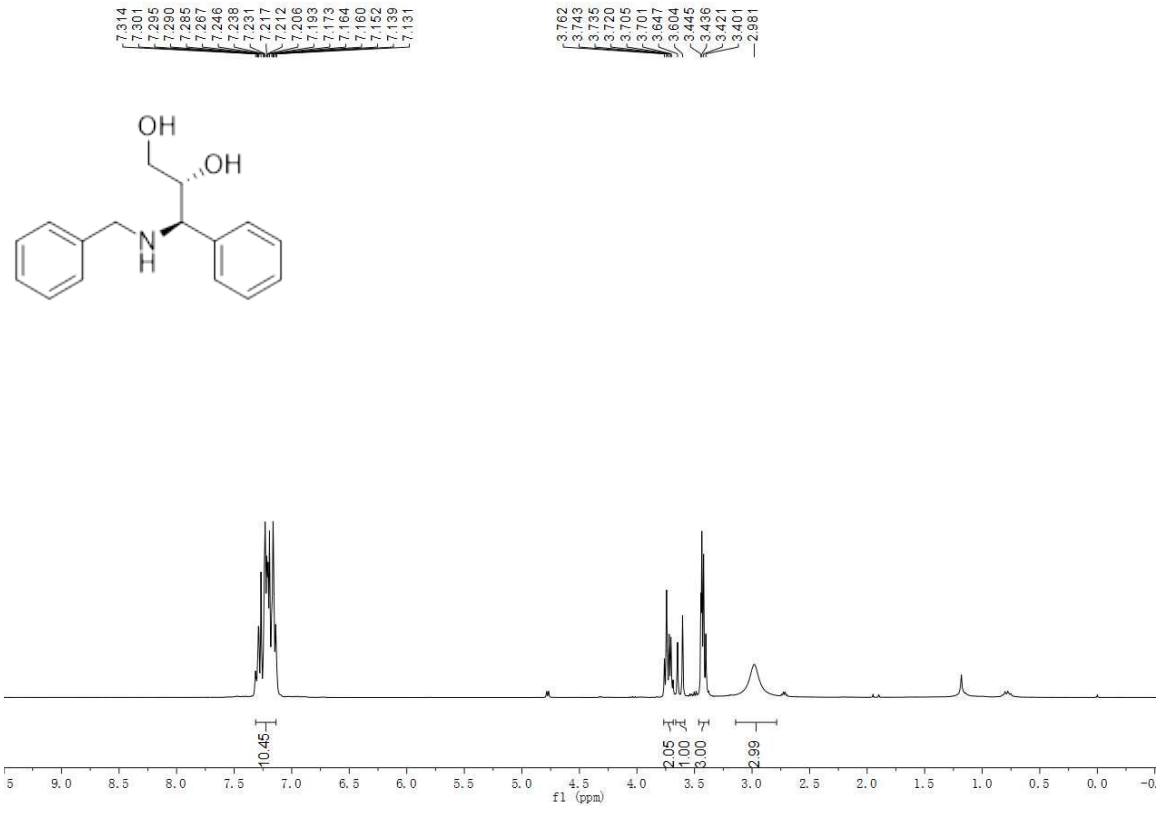
^{1}H NMR (300 MHz, Chloroform-*d*) of (2R,3R)-3-phenyl-3-(phenylamino)propanediol (6m)



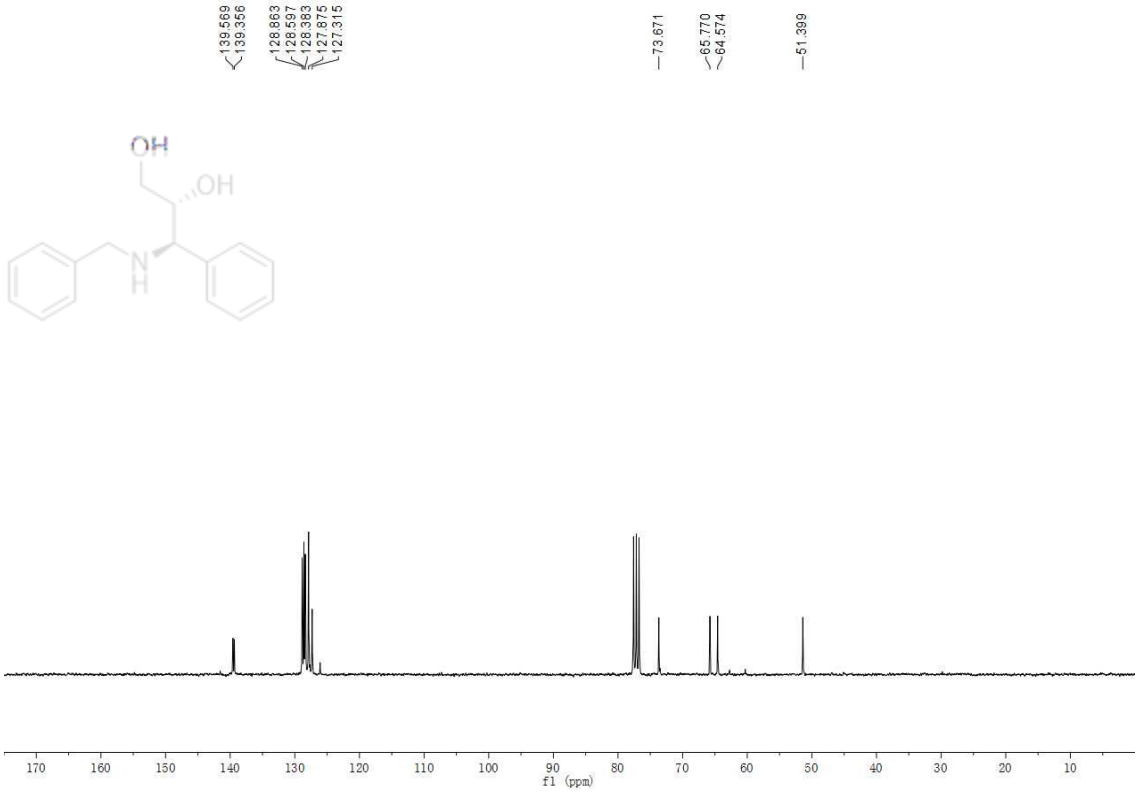
^{13}C NMR (75 MHz, Chloroform-*d*) of (2R,3R)-3-phenyl-3-(phenylamino)propanediol (6m)



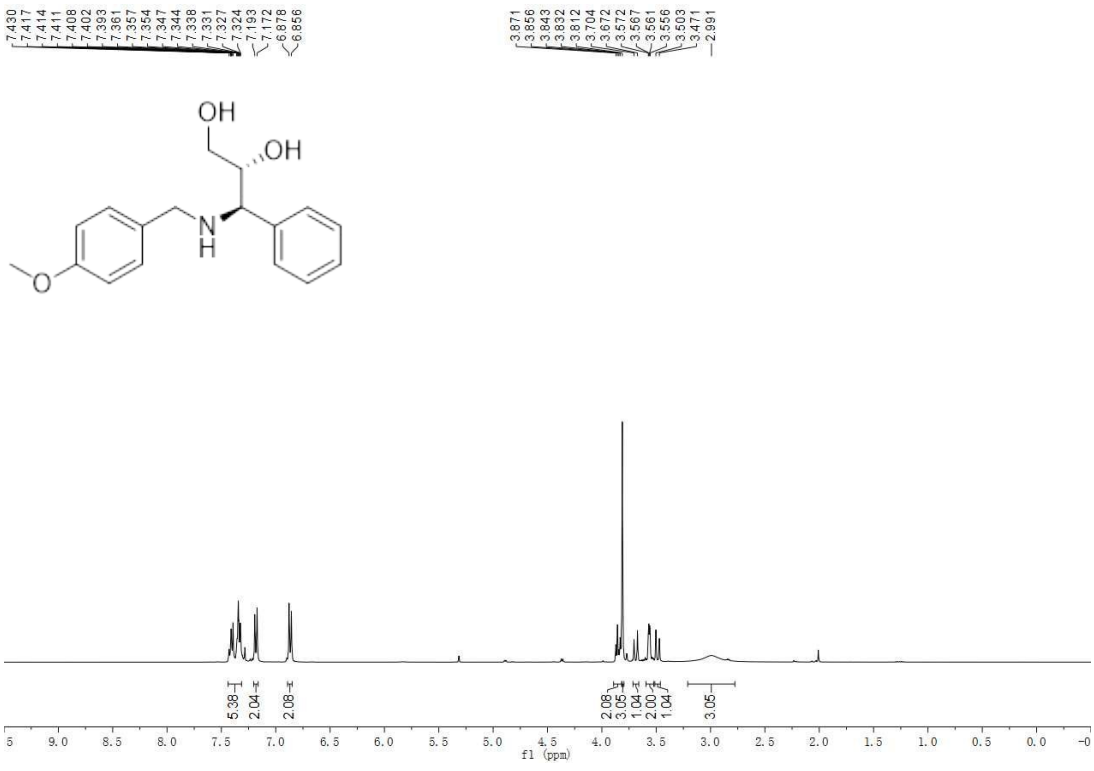
^{1}H NMR (300 MHz, Chloroform-*d*) of (2R,3R)-3-phenyl-3-(benzylamino)propanediol (6n)



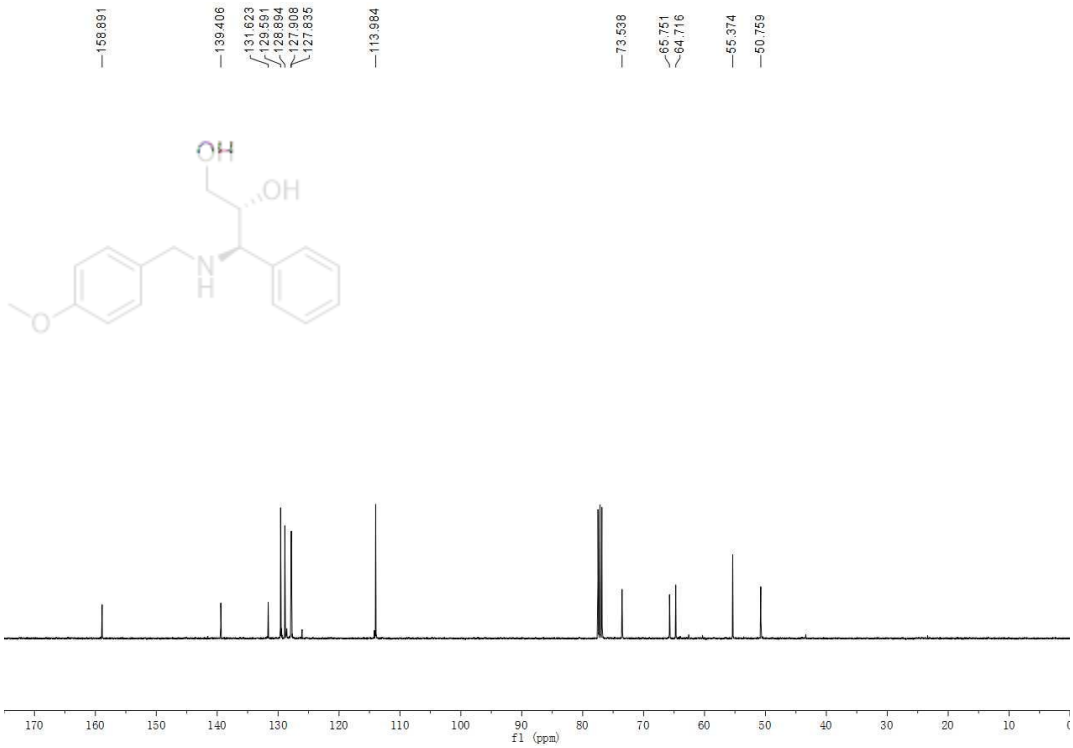
^{13}C NMR (75 MHz, Chloroform-*d*) of (2R,3R)-3-phenyl-3-(benzylamino)propanediol (6n)



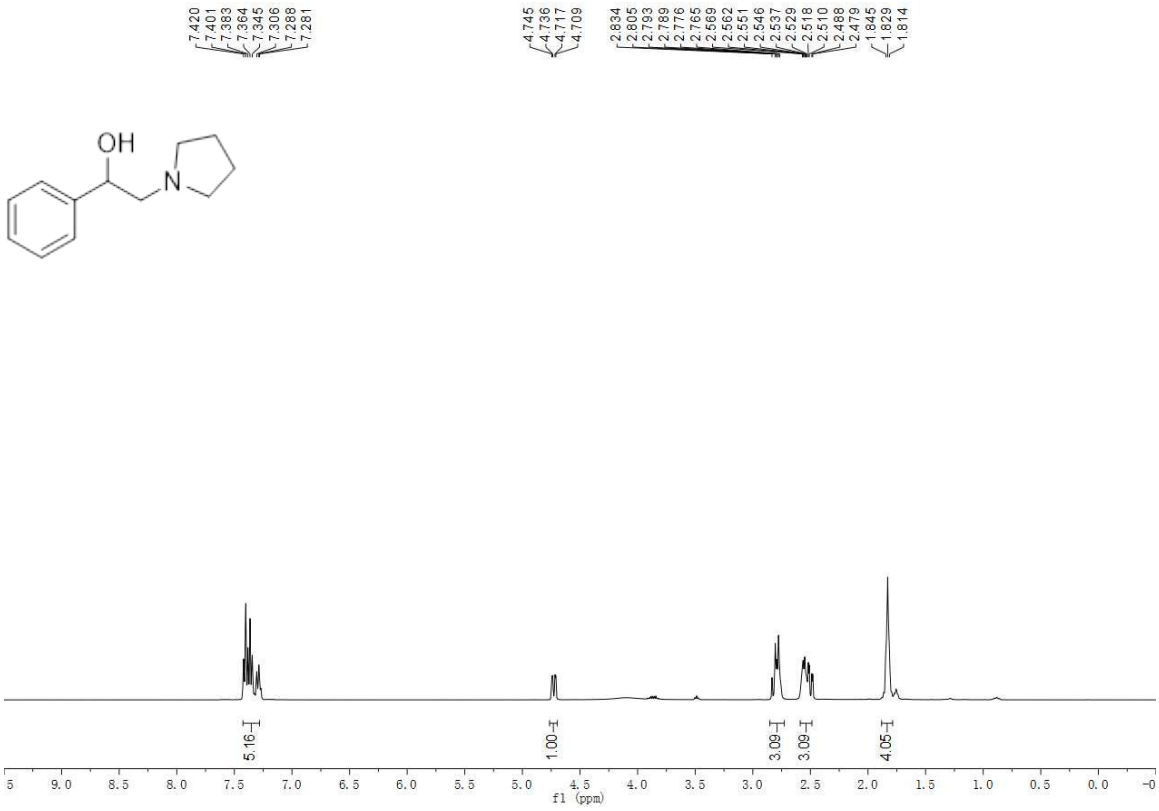
^{1}H NMR (400 MHz, Chloroform-*d*) of (2R,3R)-3-phenyl-3-(4-methoxybenzylamino)propanediol (6o)



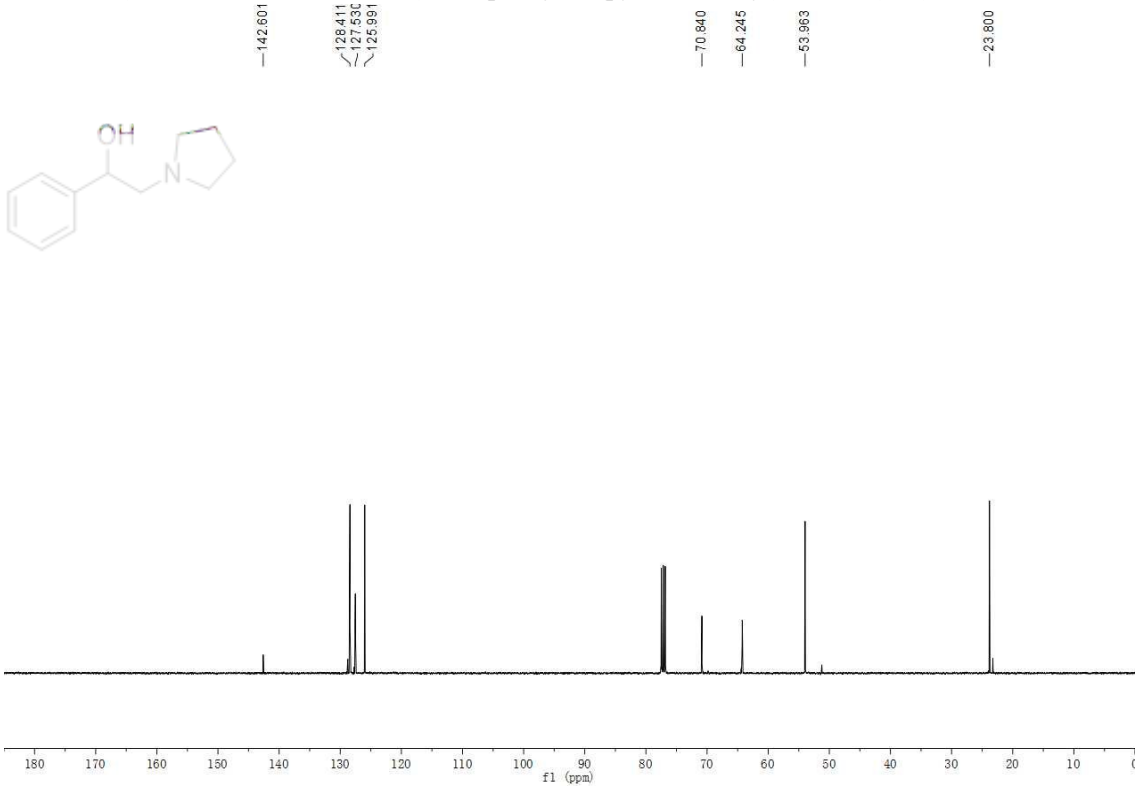
^{13}C NMR (100 MHz, Chloroform-*d*) of (2R,3R)-3-phenyl-3-(4-methoxybenzylamino)propanediol (6o)



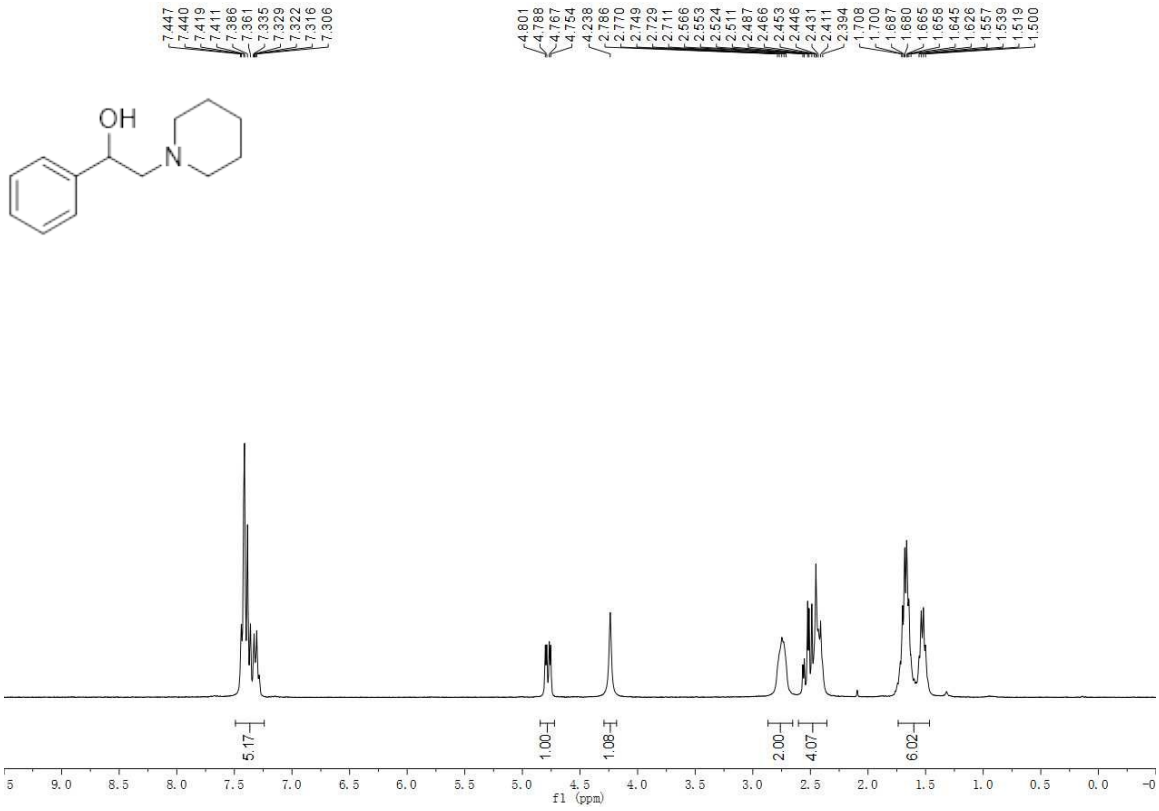
^{1}H NMR (400 MHz, Chloroform-*d*) of 1-phenyl-2-(pyrrolidin-1-yl)ethanol (6v)



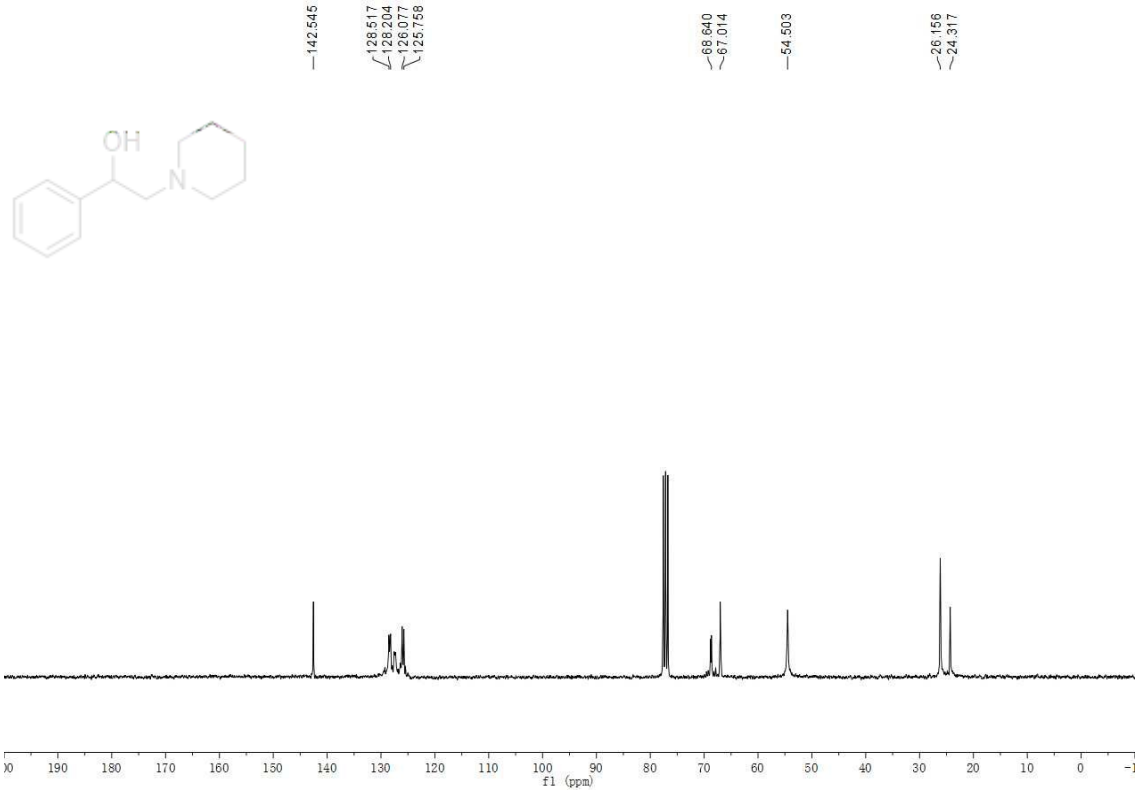
^{13}C NMR (100 MHz, Chloroform-*d*) of 1-phenyl-2-(pyrrolidin-1-yl)ethanol (6v)



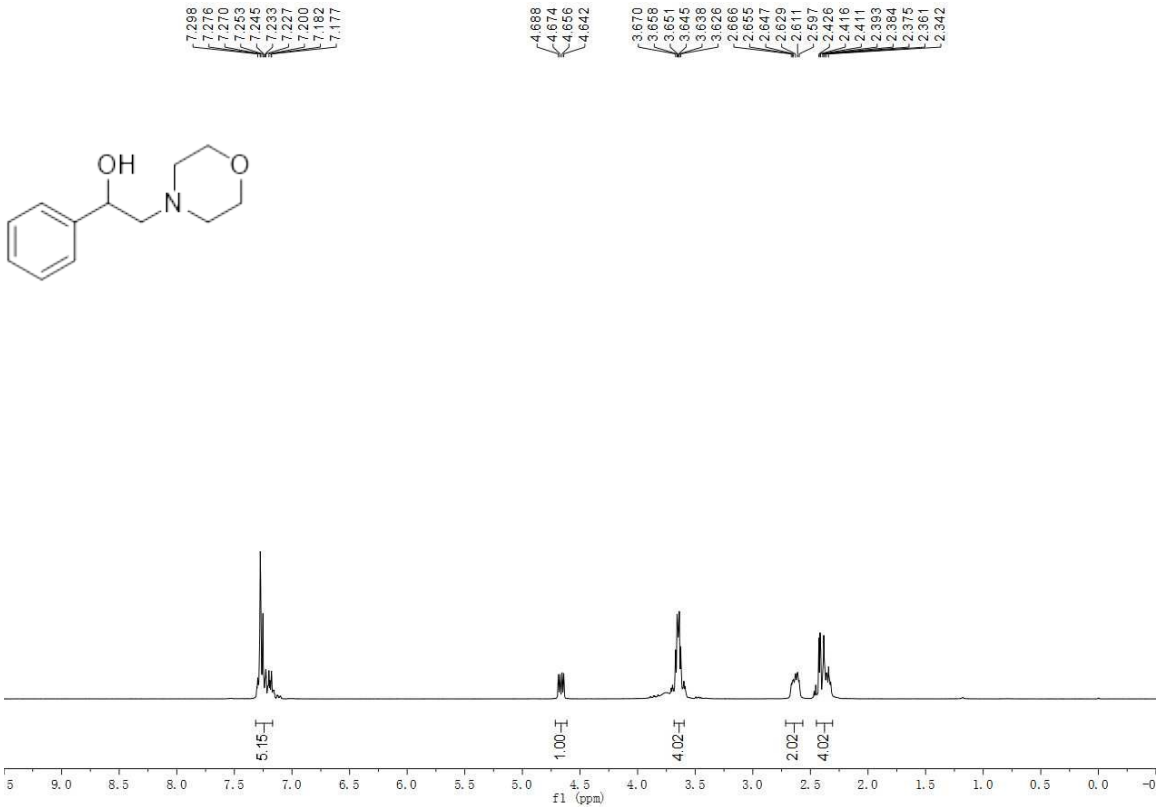
^{1}H NMR (300 MHz, Chloroform-*d*) of 1-phenyl-2-(piperidin-1-yl)ethanol (6w)



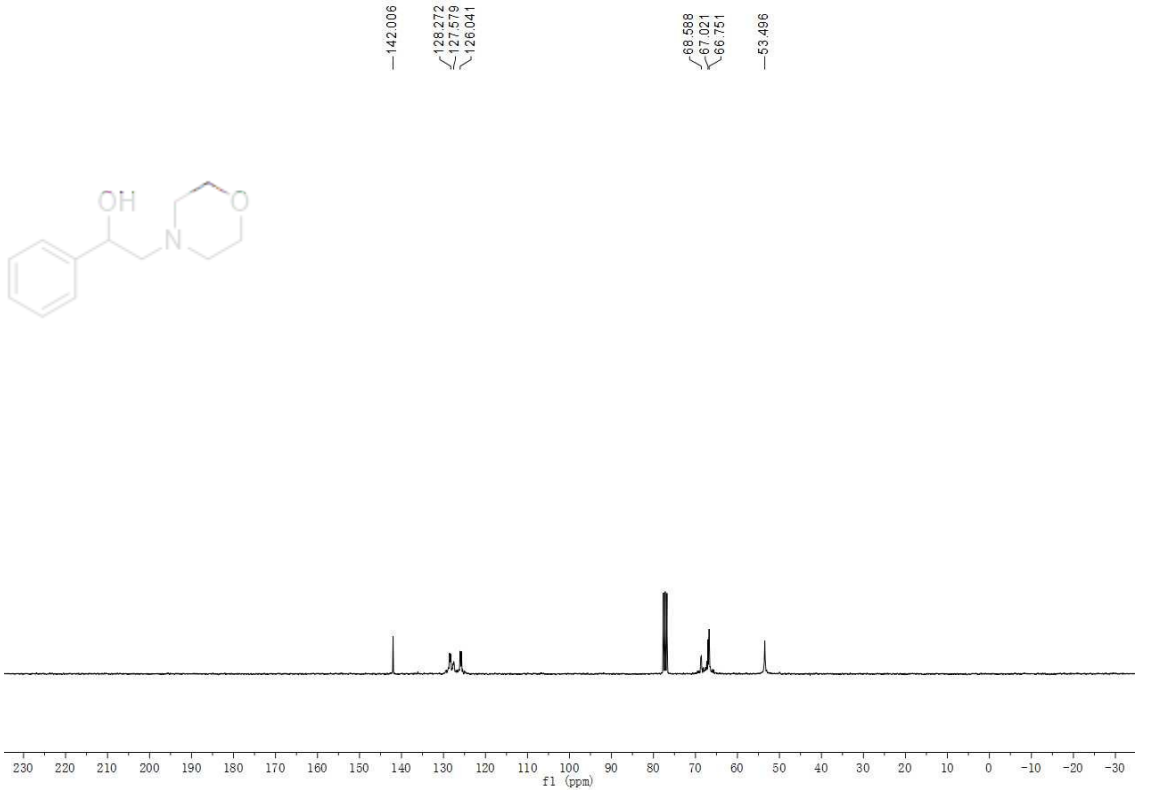
^{13}C NMR (75 MHz, Chloroform-*d*) of 1-phenyl-2-(piperidin-1-yl)ethanol (6w)



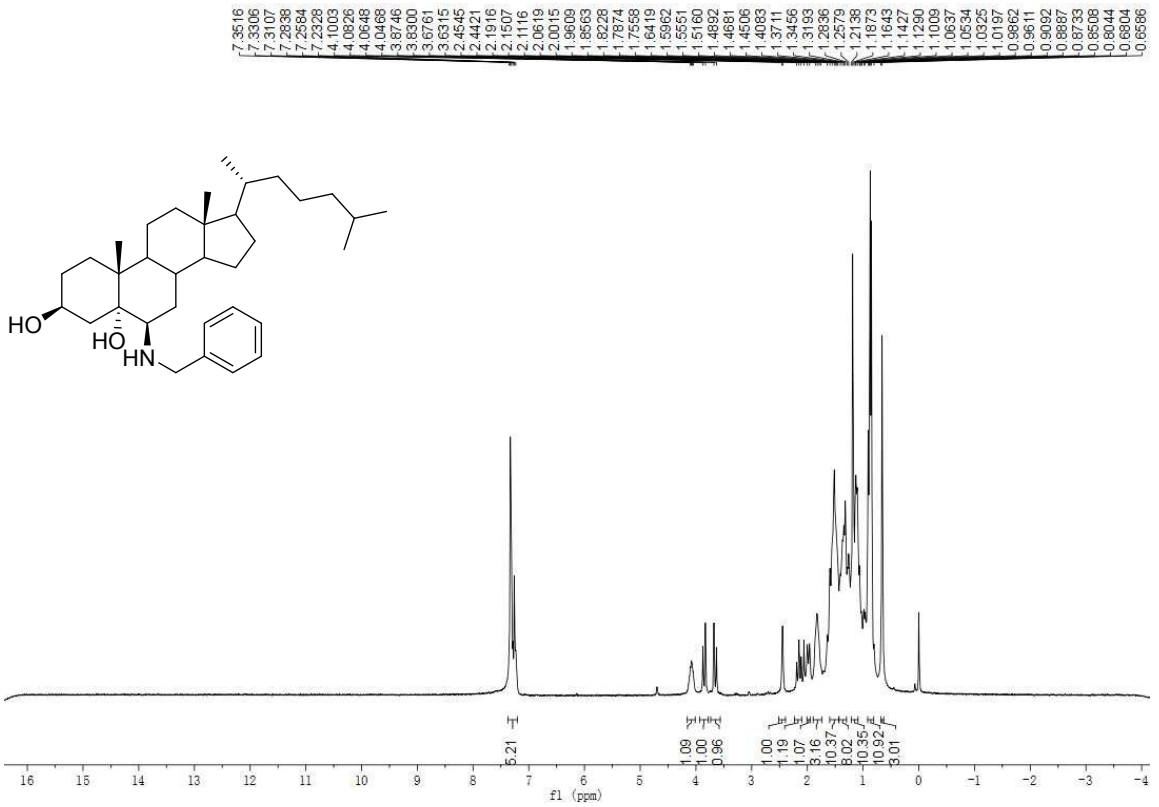
^{1}H NMR (300 MHz, Chloroform-*d*) of 1-phenyl-2-(morpholin-4-yl)ethanol (6x)



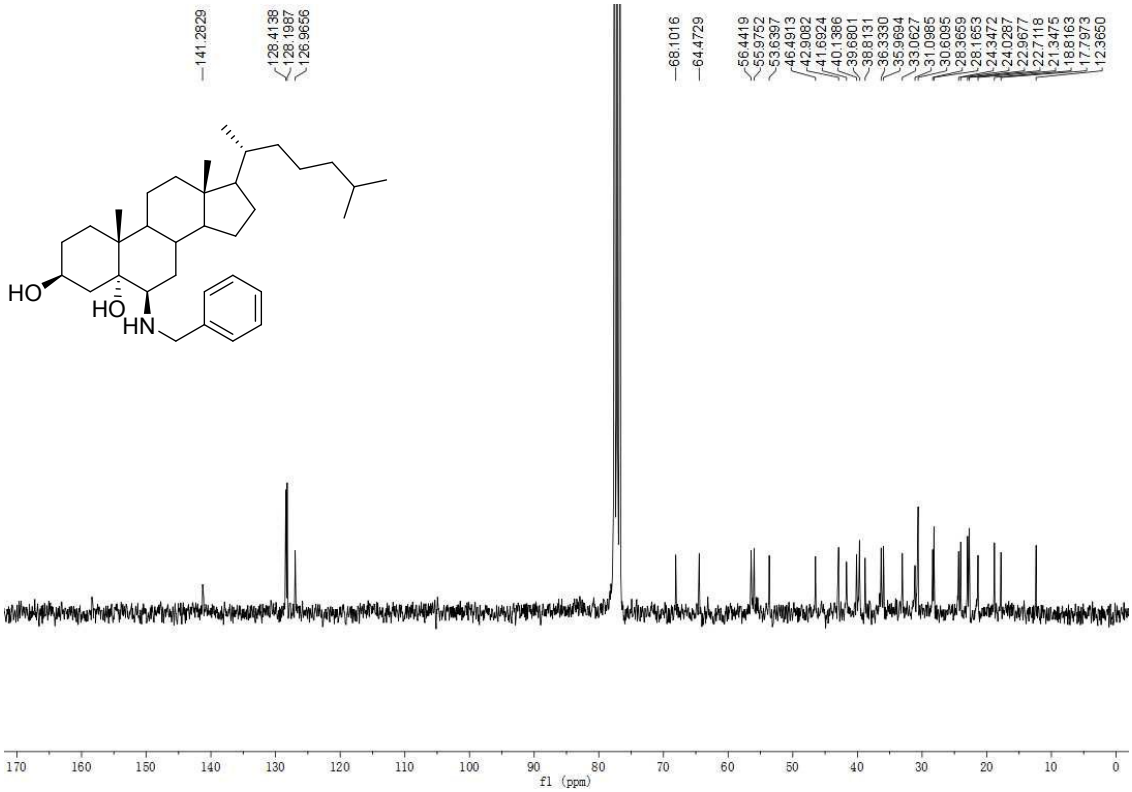
^{13}C NMR (75 MHz, Chloroform-*d*) of 1-phenyl-2-(morpholin-4-yl)ethanol (6x)



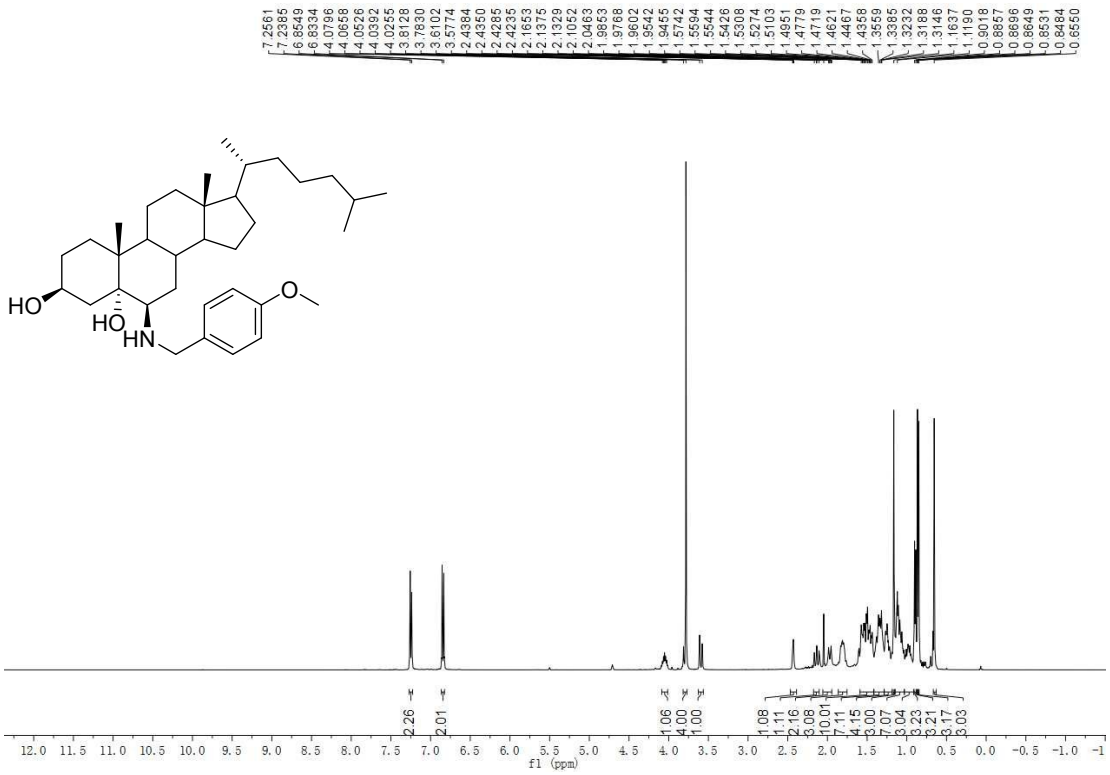
^{1}H NMR (300 MHz, Chloroform-*d*) of 6β-benzylaminocholestan-3β,5α-diol (10b)



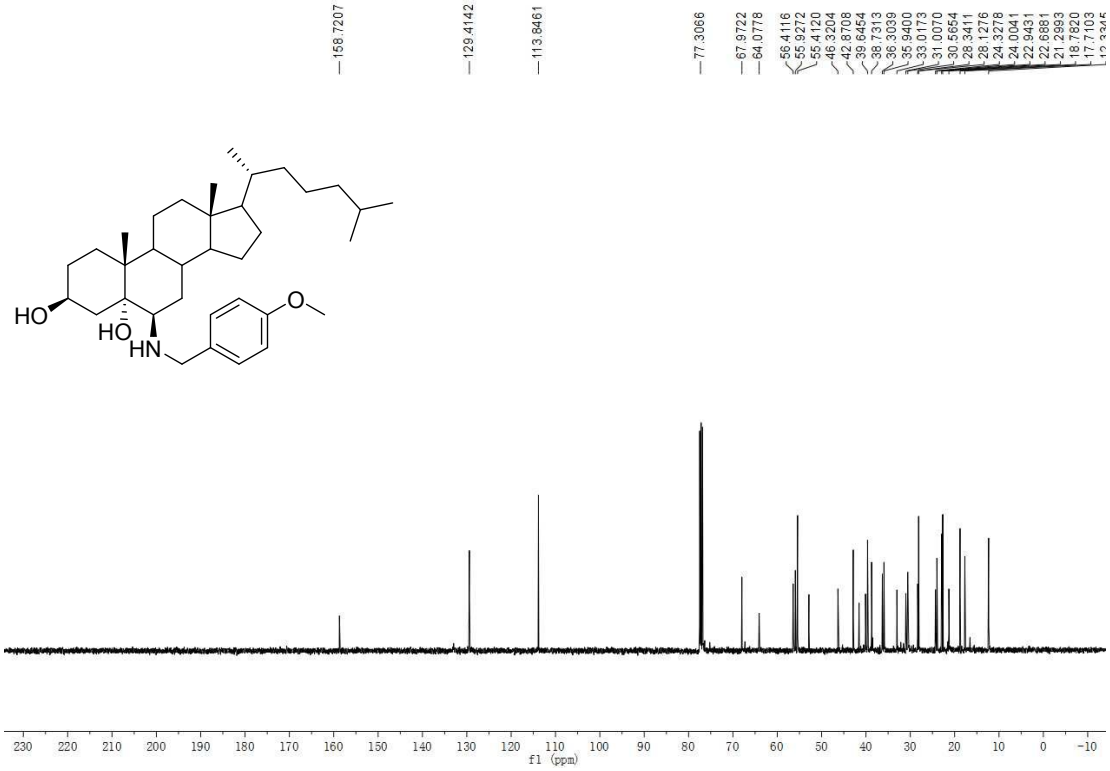
^{13}C NMR (75 MHz, Chloroform-*d*) of 6β-benzylaminocholestan-3β,5α-diol (10b)



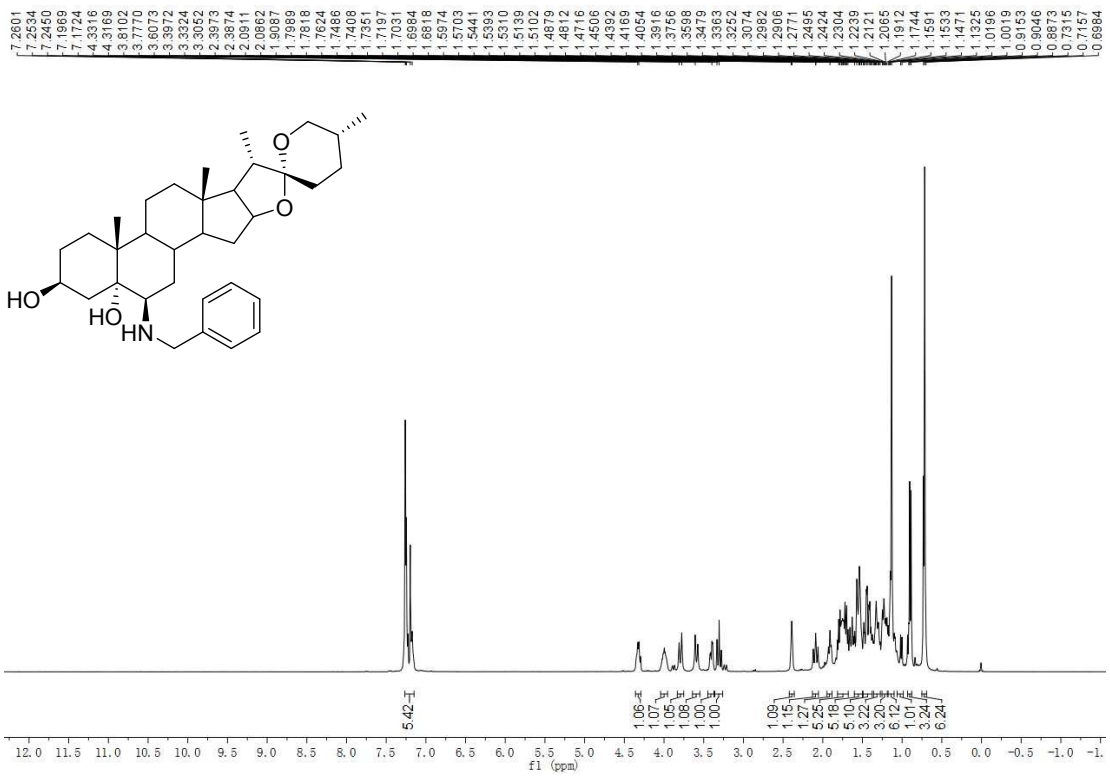
^{1}H NMR (400 MHz, Chloroform-*d*) of 6β-(4-methoxybenzyl)aminocholestan-3β,5α-diol (10c)



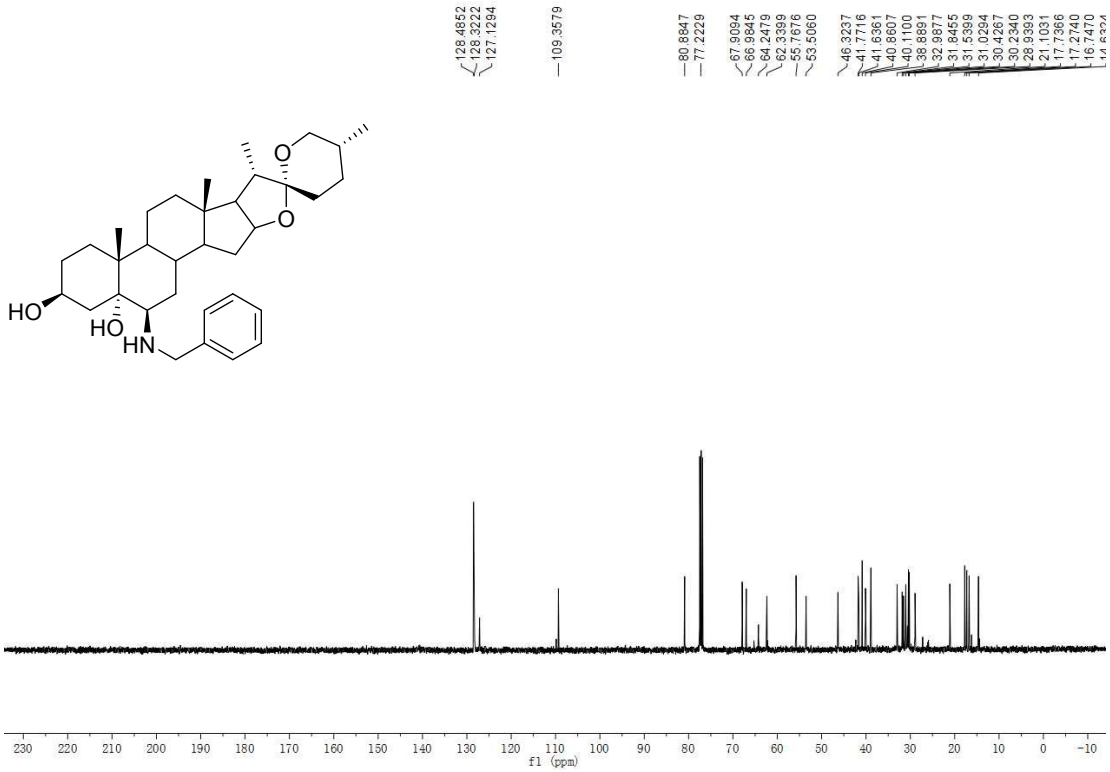
^{13}C NMR (100 MHz, Chloroform-*d*) of 6β-(4-methoxybenzyl)aminocholestan-3β,5α-diol (10c)



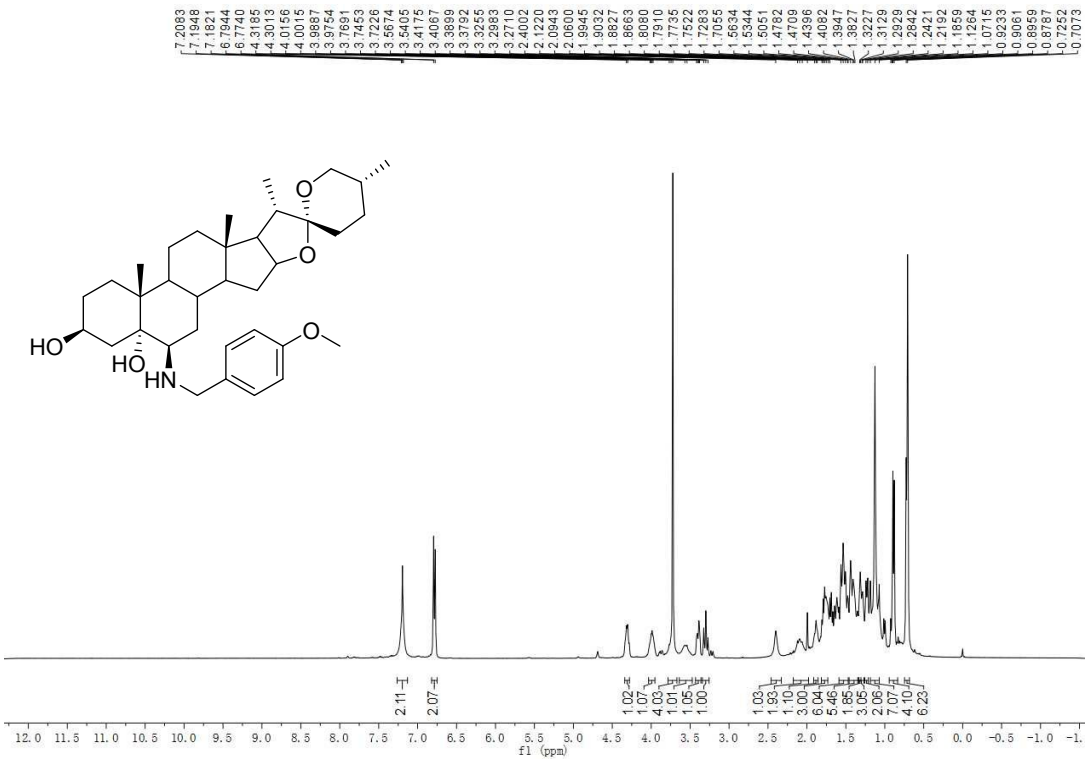
^{1}H NMR (400 MHz, Chloroform-*d*) of (25R)-6β-benzylaminospirostan-3β,5α-diol (10e)



^{13}C NMR (100 MHz, Chloroform-*d*) of (25R)-6β-benzylaminospirostan-3β,5α-diol (10e)



^{1}H NMR (400 MHz, Chloroform-*d*) of (25R)-6β-(4-methoxybenzyl)aminospirostan-3β,5α-diol (10f)



^{13}C NMR (100 MHz, Chloroform-*d*) of (25R)-6β-(4-methoxybenzyl)aminospirostan-3β,5α-diol (10f)