J. Braz. Chem. Soc., Vol. 24, No. 3, S1-S12, 2013.
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0103 - 5053 $6.00+0.00

Supplementary Information

Asymmetric Synthesis of Propranolol, Naftopidil and (*R*)-Monobutyrin using a Glycerol Desymmetrization Strategy

Mahendra N. Lokhande, Manojkumar U. Chopade, Dattatrya N. Bhangare and Milind D. Nikalje*

Department of Chemistry, University of Pune, Pune-411 007, India

Experimental

Solvents were purified and dried by standard procedures prior to use. Monitoring of the reactions was carried out using TLC, (thin layer chromatograph, silica gel 60 F254 (Merk)) and visualization with UV light (254 and 365 nm). Other techniques to identify the TLC were use of I_2 and solution of anisaldehyde in ethanol as developing reagents. IR spectra were recorded on Shimadzu FTIR 8400 instrument as a thin film or KBr pellets and the IR frequency expressed in terms of cm^{-1}. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on Bruker AC-200 NMR and Varian Mercury 300 MHz NMR spectrometers. Optical rotations were obtained on Jasco P-1020 digital Polarimeter. Elemental analysis was carried out with C, H, N-analyzer Thermoelectron Corporation Model EA-1112 series. GC-MS (gas chromatography-mass spectrometry) analyses were carried out using Shimadzu GCMS-QP5050A spectrometer and Phenomenex chiral HPLC analysis on Lux 5u Cellulose-1 (250 × 4.60 mm) column.

Synthesis of camphorsulfonamide[1,2]

Camphor-2-glycerol-spiro-ketal-10-sulfonylpyrrolidine (**5**)

Glycerol (3.22 g, 35 mmol) was suspended into a solution of camphor-10-sulfonamide (5 g, 17.5 mmol) with *p*-toluenesulfonic acid monohydrate (0.5 g) in 100 mL anhydrous toluene. The mixture was heated under reflux for 4 h with azeotropic removal of water. After completion of the reaction, the Dean-Stark apparatus was dismantled and the content of the round-bottomed flask was cooled. The whole solution was taken into separating funnel and diluted with ethyl acetate (150 mL). This organic layer was then washed with saturated $NaHCO_3$, water then extracted and dried over Na_2SO_4 and concentrated under reduced pressure to give crude. The compound was purified over silica gel 230-400 mesh under flash chromatographic separation with petroleum ether/ethyl acetate (70:30) to afford **2** as a white solid (3.65 g, 58%); mp 118-120 °C; $[\alpha]_D^{26}$ −18.6° (*c* 1, $CHCl_3$);[2] $[\alpha]_D^{25}$ −11.8° (*c* 1, $CHCl_3$); IR (KBr) ν_{max}/cm^{-1} 3497, 2891, 2934, 1448, 1332, 1145, 1047; ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (s, 3H, $7CH_3$), 0.98 (s, 3H, $7CH_3$), 1.31-1.38 (m, 1H, $6CH_2$), 1.48-1.52 (d, 1H, *J* 12.6 Hz, $3CH^2$), 1.63-1.82 (m, 2H, 4CH and $5CH_2$), 1.91-1.96 (m, 4H, $–NCH_2–CH_2$), 2.01-2.15 (m, 2H, $5CH_2$, $6CH_2$), 2.30-2.36 (m, 1H, $3CH_2$), 2.65-2.70 (d, 1H, *J* 14.4 Hz, $–CH_2SO_2$), 3.33-3.37 (m, 4H, NCH_2), 3.46-3.47-3.54 (m, 1H, $–CH_2–SO_2$), 3.69-3.73 (dd, 1H, *J* 1.7 and 9.4 Hz, –OCH–CH), 3.95-4.11 (m, 4H, $OCH_2–CH–CH_2–OH$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.06 (CH_3), 20.15 (CH_3), 24.74 ($N–CH_2–CH_2$), 25.55 ($6CH_2$), 26.70 ($5CH_2$), 43.80 (4CH), 44.10 (7C) ,47.49 ($3CH_2$), 50.11 (1C), 51.73 (CH_2SO_2), 58.30 (NCH_2), 60.75 (OCH_2), 64.41 (CH_2OH), 74.05 (CH), 115.25 (2C); anal. calcd. for $C_{17}H_{29}NO_5S$ (359.48): calcd. C, 56.80; H, 8.13; N, 3.90; S, 8.92%; found C, 56.75; H, 8.08; N, 3.96; S, 8.90%.

1-(((1*R*,2*R*,4*S*,4'*S*)-7,7-Dimethyl-4'-((naphthalen-1-loxy) methyl)spiro[bicyclo[2.2.1]heptane-2,2'-[1,3]dioxolane]-1-yl) methyl sulfonyl)pyrrolidine (**6**)

To a solution of alcohol **5** (2 g, 5.5 mmol), 1-naphthol (0.940 g, 8.25 mmol) and triphenylphosphine (1.731 g, 6.6 mmol) in 20 mL of anhydrous THF was added a solution of DIAD (1.28 mL, 6.6 mmol) in anhydrous THF (5 mL) under the N_2 atmosphere at room temperature. The resulting reaction monitored by TLC and stopped after 4 h looking at complete disappearance of alcohol **2**. The solvent from the reaction mixture was evaporated under reduced pressure. The residue thus obtained was purified over silica gel 230-400 mesh size by flash column chromatography technique. The product was eluted with mixture of petroleum ether:ethyl acetate (80:20) solvent system to afford **3** as a white solid (1.91 g, 71%); mp 95-97 °C; $[\alpha]_D^{25}$ −13.1° (*c* 1, CH_3OH); IR ($CHCl_3$) ν_{max}/cm^{-1} 2955, 2899, 1627, 1577, 1508, 1475, 1454, 1392, 1332, 1271, 1149, 1066, 1014, 979, 935, 908, 790, 775; ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (s, 3H, $7CH_3$), 1.06 (s, 3H,

*e-mail: mdnik@chem.unipune.ac.in

7CH_3), 1.25-1.37 (m, 2H, 5CH_2, 6CH_2), 1.52-1.58 (m, 2H, 4CH, 6CH_2), 1.72-1.80 (m, 4H, –NCH_2–CH_2), 2.00-2.11 (m, 2H, 3CH_2, 5CH_2), 2.22-2.34 (m, 1H, 3CH_2), 2.78-2.83 (d, 1H, *J* 14.4 Hz, CH_2SO_2), 3.21-3.37 (m, 5H, CH_2SO_2, SO_2NCH_2), 3.97-4.02 (m, 1H, OCH_2CH), 4.18-4.29 (m, 2H, OCH_2, CH_2OH), 4.40-4.50 (m, 2H, –CH_2–CH–CH_2), 6.89-6.91 (d, 1H, *J* 7.1 Hz, Ar-H), 7.33-7.50 (m, 4H, Ar-H), 7.77-7.80 (m, 1H, Ar-H), 8.19-8.22 (m, 1H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.33 (CH_3), 20.83 (CH_3), 25.43 (6CH_2), 25.66 (NCH_2CH), 26.78 (5CH_2), 44.47 (4CH_2), 44.64 (7C), 45.40 (3CH_2), 47.53 (1C), 49.99 (CH_2SO_2), 52.79 (N CH_2), 67.73 (OCH_2), 68.62 (CH_2O), 72.39 (OCH_2CHCH_2), 105.50 (Ar), 116.64 (2C), 120.53 (Ar), 121.83(Ar), 125.14(Ar), 125.56 (Ar), 125.94 (Ar), 126.30 (Ar), 127.46 (Ar), 134.43 (Ar), 154.31(Ar); anal. calcd. for $C_{27}H_{35}NO_5S$ (485.64) calcd. C, 66.78; H, 7.26; N, 2.88; S, 6.60 %; found C, 66.82; H, 7.24; N, 2.92; S, 6.68%.

(*R*)-3-(Naphthalene-1-yloxy) propane-1,2-diol (**7**)

In a 100 mL round bottom flask was added naphthyl ether **6** (1 g, 2 mmol) and a solution of hydrochloric acid in methanolic (5 mL of 3 mol L^{-1} HCl in 20 mL of MeOH). The content of the flask stirred at 70 °C for 10 h and the reaction monitored by TLC. After completion of the reaction, the methanol was removed under reduced pressure. The crude residue was dissolved in water and extracted with ethyl acetate (20 mL × 3). The combined organic layer dried over sodium sulfate, filtered and evaporated under reduced pressure to yield crude product. It was then purified by flash chromatographic separation (silica gel, 100-200 mesh) using petroleum ether:ethyl acetate (70:30) solvent system for elution to give white colored solid (431 mg, 96% yield); mp 102-104 °C; $[\alpha]_D^{25}$ +6.2° (*c* 1.05, EtOH),[3] $[\alpha]_D^{25}$ +6.69° (*c* 1.05, EtOH); IR (KBr) ν_{max}/cm^{-1} 3313, 3290, 3227, 2953, 2933, 2874, 1726, 1579, 1508, 1442, 1392, 1348, 1273, 1240, 1226, 1211; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34 (brs, 2H, –OH), 3.84-3.97 (m, 2H, –CH_2OH), 4.21-4.28 (m, 3H, CH, CH_2), 6.83-6.85 (d, 1H, *J* 7.53 Hz, Ar-H), 7.34-7.53 (m, 5H, Ar-H), 7.79-7.82 (m, 1H, Ar-H), 8.20-8.22 (m, 1H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.29 (CH_2OH), 68.62 (CH), 69.97 (CH_2), 104.32, 119.72, 121.50, 124.54, 124.97, 125.36, 125.80, 126.83, 133.83, 153.86; chiral HPLC analysis: Lux 5u Cellulose-1 (250 × 4.60 mm) column; eluent isopropanol:hexane 25:75; flow rate: 1 mL min^{-1}, detector: 254 nm t_R 9.37 min (minor 2%), t_R 11.26 min (major 98%); GC-MS 218, 184, 169, 144, 127, 115, 89, 72, 58, 43, 41.

(*S*)-2-((Methylsulfonyl)oxy)-3-(naphthalen-1-yloxy)propyl 4-nitrobenzoate (**9**)

(*i*) To a solution of diol **7** (0.5 g, 2.2 mmol) in dry dichloromethane (5 mL) was added pyridine (0.46 mL, 5.7 mmol) followed by solution of 4-nitrobenzoyl chloride (4.24 g, 2.2 mmol) in dichloromethane (5 mL) at 0 °C and stirred the reaction mixture 4 h. Reaction monitored by TLC and it was stopped after complete disappearance of starting material on TLC. The solid thus formed in the reaction mixture was filtered and the dichloromethane was concentrated under reduced pressure. The residue was purified by column chromatography on 100-200 mesh silica and eluted with ethyl acetate. Subsequent evaporation of ethyl acetate under vacuum afforded (*S*)-2-hydroxy-3-(naphthalene-1-yloxy)propyl-4-nitrobenzoate as yellow colored gum (0.714 g, 85%).

(*ii*) To a solution of (*S*)-2-hydroxy-3-(naphthalene-1-yloxy)propyl-4-nitrobenzoate (0.5 g, 1.36 mmol) and methanesulfonyl chloride (0.12 mL, 1.63 mmol) in dry ethyl acetate was added Et_3N (0.47 mL, 3.4 mmol) at 0 °C. The reaction was stirred for 10 min and quenched with addition of additional 50 mL ethyl acetate and transferred whole mixture to a separating funnel. This layer was washed with dil. HCl (20 ml) followed by water (25 mL × 2) and the organic layer dried over $MgSO_4$ and concentrate on rotary evaporator under reduced pressure. The residue thus obtained was purified by column chromatography over 100-200 mesh silica with petroleum ether:ethyl acetate (70:30) was used as a solvent system to afford compound **9** as a gummy liquid; 0.557 g, over all yield of two steps 78%; $[\alpha]_D^{28}$ –8.0° (*c* 1, $CHCl_3$); IR (KBr) ν_{max}/cm^{-1} 2958, 2926, 1728, 1633, 1462, 1301, 1263, 1215, 1174, 1103, 1016, 939, 869, 759; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.03 (s, CH_3), 4.30-4.39 (m, 2H, OCH_2), 4.60-4.72 (m, 2H, $COOCH_2$), 5.38-5.50 (m, 1H, CH), 6.74-6.87 (d, 1H, *J* 7.6 Hz, Ar-H), 7.19-7.45 (m, 5H, Ar-H), 7.60-7.70 (m, 1H, Ar-H), 8.16-8.23 (m, 4H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.85 (CH_3), 66.74 (CH_2), 68.54 (CH_2), 68.81 (CH), 104.87 (Ar), 121.06 (Ar), 121.45 (Ar), 123.44 (Ar), 125.22 (Ar), 125.39 (Ar), 125.63 (Ar), 126.52 (Ar), 127.55 (Ar), 129.63 (Ar), 129.80 (ArH), 130.77 (Ar), 134.40 (Ar), 134.88 (Ar), 150.46 (Ar), 153.73 (Ar), 164.78 (C=O).

(*S*)-2-((Naphthalene-1-yloxy) methyl)oxirane (**8b**)

To a solution of (*S*)-2-(methylsulfonyloxy)-3-(napthalen-1-yloxy)propyl 4-nitrobenzoate (**9**) (0.5 g, 1.12 mmol) in 1,4-dioxane (5 mL) was added aqueous solution of NaOH (0.053 g, 1.34 mmol, in 10 mL H_2O). Whole content of the flask was stirred for 18 h at 70 °C. Reaction was monitored by TLC and was looked at complete disappearance of starting material on the TLC. Reaction was then stopped and the 1,4-dioxane solvent was evaporated under reduced pressure over rotary evaporator. The residue thus obtained was purified by column chromatography on 100-200 mesh silica with petroleum ether:ethyl acetate (80:20) was used

as solvent system for the elution of the product. It afforded epoxide **8b** as colorless liquid (0.190 g, 85%), $[\alpha]_D^{25}$ –32.5° (*c* 1.5, MeOH),[4] $[\alpha]^{25}_D$ –33.9° (*c* 1.55, MeOH)); IR (KBr) ν_{max}/cm^{-1} 3053, 2999, 2926, 1676, 1579, 1508, 1464, 1396, 1271, 1240, 1101, 1020, 916, 862, 792, 771; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.67-2.70 (dd, 1H, *J* 5.0, 2.7 Hz, CH_2O), 2.78-2.81 (t, 1H, *J* 5, 4.1 Hz, CH–O), 3.30-3.35 (m, 1H, CH), 3.90-3.96 (dd, 1H, *J* 5.3, 7.0 Hz, OCH_2), 4.20-4.24 (dd, 1H, *J* 7.6, 2.9 Hz, OCH_2,), 6.65-6.67 (d, 1H, *J* 7.6 Hz, Ar-H), 7.25-7.30 (t, 1H, *J* 7.7, 8.2 Hz, Ar-H), 7.40-7.45 (m, 3H, Ar-H), 7.72-7.75 (dd, 1H, *J* 6.2, 3.5 Hz, Ar-H), 8.26-8.29 (dd, 1H, *J* 6.2, 3.4 Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.34 (CH_2O), 49.96 (CH), 68.66 (OCH_2), 104.77 (Ar), 120.58 (Ar), 121.84 (Ar), 125.11 (Ar), 125.36 (Ar), 125.57 (Ar), 126.31 (Ar), 127.26 (Ar), 134.31 (Ar), 153.99 (Ar).

(*R*)-2-((Naphthalene-1-yloxy) methyl)oxirane (**8a**)

An stirred mixture of diol 7 (0.50 g, 1.87 mmol), triphenylphosphine (0.52 g, 1.96 mmol) and diethyl azodicarboxylate (0.34 g, 1.96 mmol) in dry chloroform (16 mL) was refluxed for 4 h; after evaporation of the solvent at reduced pressure, the crude residue was purified by column chromatography on 230-400 silica gel, eluting with hexane/ethyl acetate mixtures, to give 0.36 g (79% yield) of the title compound as colorless liquid; $[\alpha]_D^{25}$ +28° (*c* 1.5, MeOH).

(*S*)-1-(Isopropylamino)-(naphthalene-1-yloxy)propane-2-ol (**1b**)

To a solution of epoxide **8b** (0.1 g, 2.5 mmol) in dichloromethane (10 mL) was added slowly the isopropyl amine (0.295 g, 25 mmol). The whole reaction mixture was stirred under nitrogen atmosphere at room temperature. Reaction was monitored by TLC and the reaction stopped after 30 h. The excess isopropyl amine and the dichloromethane were removed under reduced pressure to dryness. The residue thus obtained was dissolved in water and extracted with EtOAc (25 mL × 2). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated on rotary evaporator under reduced pressure. Purification was carried out by flash column chromatography (230-400 mesh silica) using EtOAc:petroleum ether (75:25) as a solvent system to give (-)-propranolol **1b** as white solid (0.056 mg, 71%); mp 87-89 °C; $[\alpha]_D^{25}$ –9.5° (*c* 0.55, EtOH),[3] $[\alpha]_D^{25}$ –9.9° (*c* 0.5, EtOH); IR (KBr) ν_{max}/cm^{-1} 3269, 2966, 2922, 2864, 1627, 1587, 1510, 1462, 1398, 1338, 1269, 1180, 1101, 999, 920, 879, 786, 763; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15-1.26 (d, 6H, *J* 6.2 Hz, CH_3), 2.87-2.98 (m, 2H, CH_2), 3.03-3.08 (dd, 1H, *J* 8.8, 3.5 Hz, NH–CH–), 3.17 (bs, 2H, OH, NH), 4.10-4.19 (m, 2H, OCH_2), 4.22-4.29 (m, 1H, CH), 6.80-6.82 (d, 1H, *J* 7.4 Hz), 7.33-7.38 (t, 1H, *J* 8.2, 7.7 Hz), 7.40-7.51 (m, 3H), 7.78-7.81 (dd, 1H, *J* 5.8, 3.5 Hz), 8.23-8.26 (dd, 1H, *J* 6.7, 3.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.90 (CH_3), 49.07 (CH), 49.63 (CH_2), 68.45 (OCH_2), 70.79 (CH), 104.96 (Ar), 120.64 (Ar), 121.89 (Ar), 125.29 (Ar), 125.87 (Ar), 126.46 (Ar), 127.56 (Ar), 134.54 (Ar), 154.39 (Ar); LC-MS *m/z* 260.17 (M^+ + 1), 282.20 (M^+ + Na); For compound **1a**: $[\alpha]_D^{25}$ +6.02° (*c* 1.6, EtOH),[5] +5.1° (*c* 1.6, EtOH).

(*S*)-1-(4-(2-Methoxyphenyl)piperazin-1-yl)-3-(naphthalene-1-yloxy)propan-2-ol (**2b**)

To a solution of epoxide **8b** (0.1 g, 0.5 mmol) in anhydrous 2-propanol (10 mL) was added 1-(2-methoxyphenyl) piperazine (0.096 g, 0.5 mmol) and the reaction mixture was refluxed for 32 h. After completion of reaction, the solvent was removed under reduced pressure and purification was carried out by flash column chromatography (230-400 mesh silica). The EtOAc:petroleum ether (60:40) was used as solvent system for elution, it afforded the (*S*)-(+)-naftopidil **2b** as a yellow solid (0.156 g, 80%); mp 126-127°C; $[\alpha]_D^{25}$ +4.3° (*c* 1.55, MeOH);[3] $[\alpha]_D^{25}$ +4.5° (*c* 1.5, MeOH); IR ($CHCl_3$) ν_{max}/cm^{-1} 3403, 3031, 2977, 2907, 1261, 1225; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.58-2.70 (m, 4H, N-CH_2), 2.80-2.85 (m, 2H, CH_2N), 3.03-3.51 (m, 4H, NCH_2), 3.51 (bs, 1H, OH), 3.75 (s, 3H, OCH_3), 4.02-4.10 (m, 2H, OCH_2), 4.19-4.23 (m, 1H, CH), 6.72-6.85 (m, 2H, Ar-H), 6.83-6.85 (d, 2H, *J* 3.9 Hz, Ar-H), 6.87-6.95 (1H, m, Ar-H), 7.14-7.29 (1H, m, Ar-H), 7.33-7.42 (3H, m, Ar-H), 7.69-7.72 (m, 1H, Ar-H), 8.19-8.22 (m, 1H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 50.44 (NCH_2), 53.43 (NCH_2), 55.17 (OCH_3), 60.85 (CH_2N), 65.47 (CH), 70.36 (OCH_2), 104.73 (Ar), 111.03 (Ar), 118.05 (Ar), 120.39 (Ar), 120.83 (Ar), 121.78 (Ar), 122.91 (Ar), 125.07 (Ar), 125.41 (Ar), 125.67 (Ar), 126.26 (Ar), 127.32 (Ar), 134.31 (Ar), 140.87 (Ar), 152.04 (Ar), 154.21 (Ar); LC-MS *m/z* 393.36 (M^+ + 1), 415.36 (M^+ + Na); For compound **2a**: $[\alpha]_D^{25}$ –10.6° (*c* 1, MeOH,);[6] $[\alpha]_D^{25}$ –11.7° (*c* 1, MeOH).

(*R*)-2,3-Dihydroxypropyl butyrate (**3**)

To a stirred solution of ketal ester **10** (0.200 g, 0.46 mmol) dissolved in water (0.4 mL) and acetonitrile (5 mL) was added solid CAN (cerium ammonium nitrate; 0.012 g, 0.023 mmol, 5 mol%). The resulting solution was stirred 1 h at room temperature. After that, NH_4OH (20 mL) was added and resulting yellow-orange suspension was filtered through celite, washed with CH_3OH and solvent evaporated to dryness under reduced pressure. Reaction mixture was purified by using petroleum ether: ethyl acetate (60:40) on column chromatography to get (*R*)-monobutyrin

as clear liquid (49 mg, 65 %); $[\alpha]_D^{25}$ +5° (*c* 1, $CHCl_3$);[7] +5.13° (*c* 1.13, $CHCl_3$); IR (KBr) ν_{max}/cm^{-1} 3412, 2950, 1746, 1420, 1356, 1130; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89-0.94 (t, 3H, *J* 7.4 Hz, CH_3), 1.57-1.69 (m, 2H, CH_2), 2.28-2.33 (t, 2H, *J* 7.4 Hz, CH_2), 2.48 (s, br, 2H, OH), 3.53-3.59 (dd, 1H, *J* 5.9, 11.4Hz, CH–OH), 3.64-3.69 (dd, 1H, *J* 3.8, 11.4Hz, CH–OH), 3.86-3.93 (q, 1H, *J* 4.7, 9.4 Hz, CH), 4.08-4.20 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.56 (CH_3), 18.35 (CH_2), 35.96 (CH_2), 63.32 (CH_2), 65.09 (CH_2), 70.24 (CH), 174.17 (CO).

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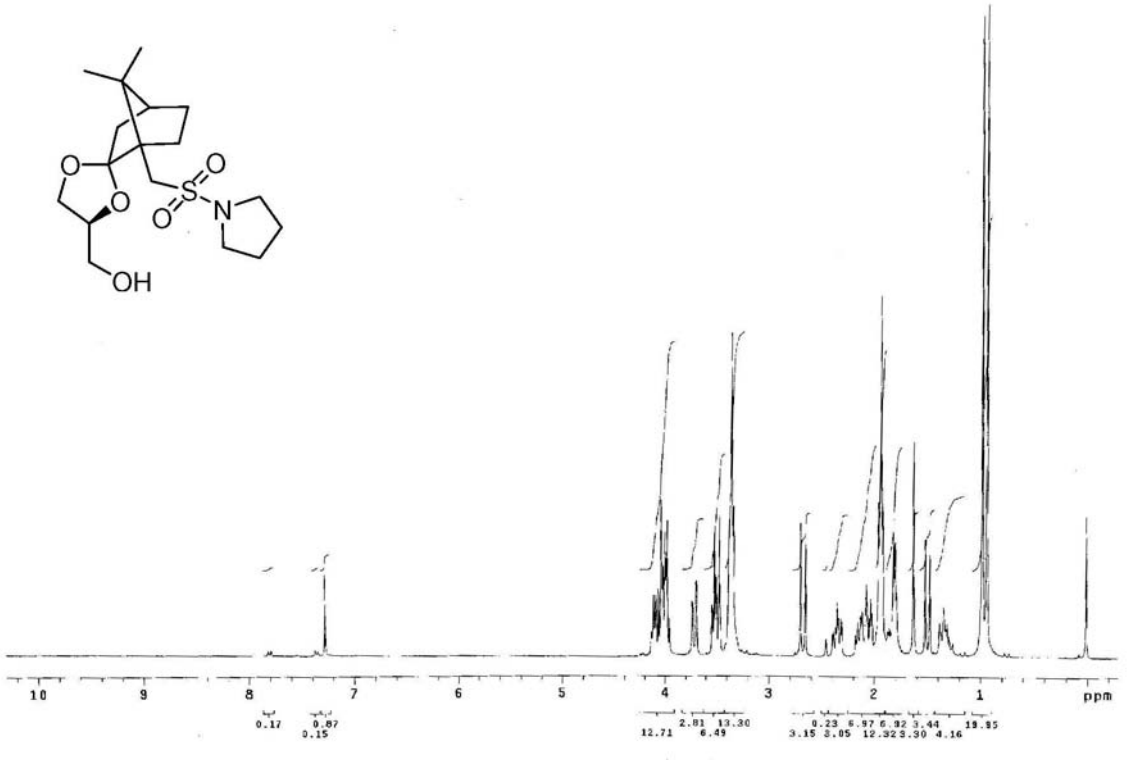

Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (1*R*)-camphor-2-glycerol-spiro-ketal-10-sulfonylpyrro-lidine.

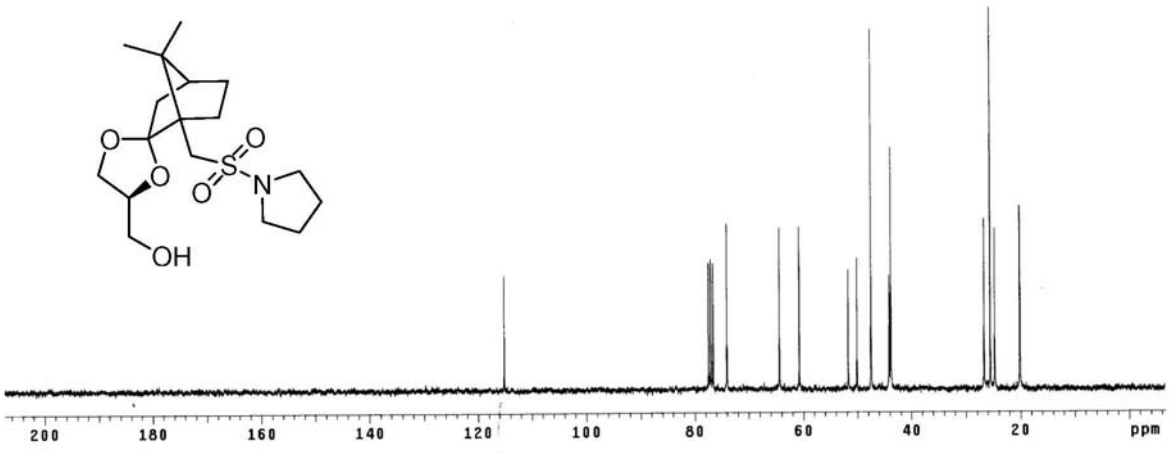

Figure S2. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of (1*R*)-camphor-2-glycerol-spiro-ketal-10-sulfonylpyrro-lidine.

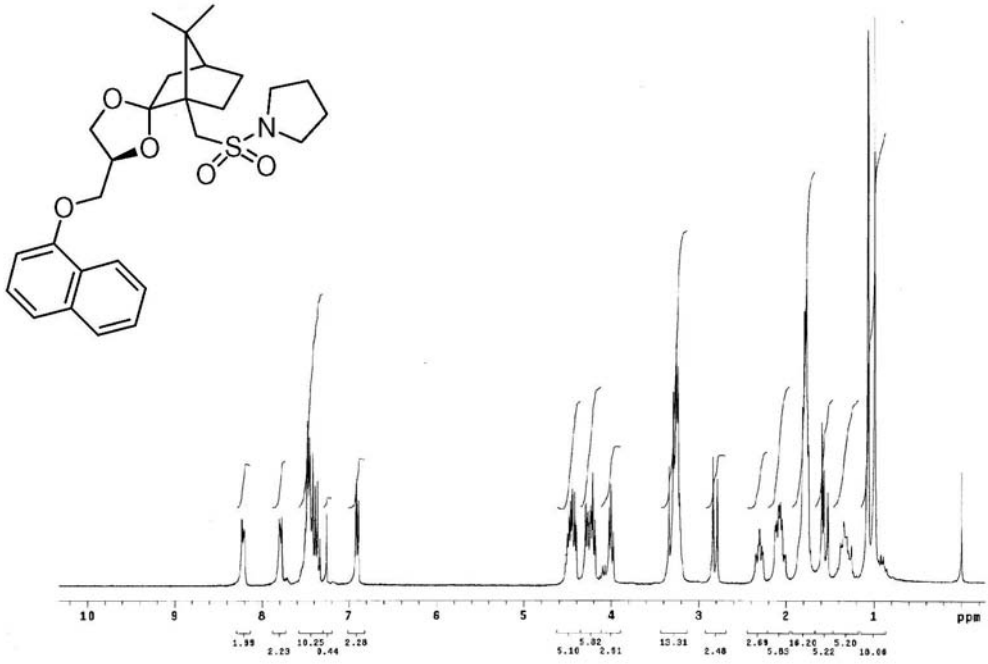

Figure S3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 1-(((1*R*,2*R*,4*S*,4'*S*)-7,7-dimethyl-4'-((naphthalen-1-loxy)methyl)spiro[bicyclo[2.2.1]heptane-2,2'-[1,3] dioxolane]-1-yl)methylsulfonyl)pyrrolidine.

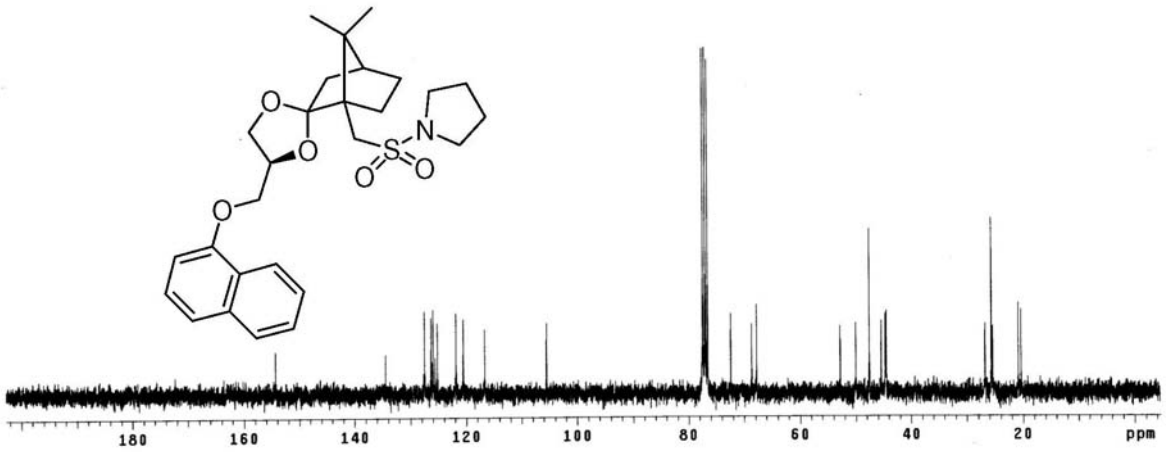

Figure S4. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of 1-(((1*R*,2*R*,4*S*,4'*S*)-7,7-dimethyl-4'-((naphthalen-1-loxy)methyl)spiro[bicyclo[2.2.1]heptane-2,2'-[1,3]dioxolane]-1-yl)methylsulfonyl)pyrrolidine.

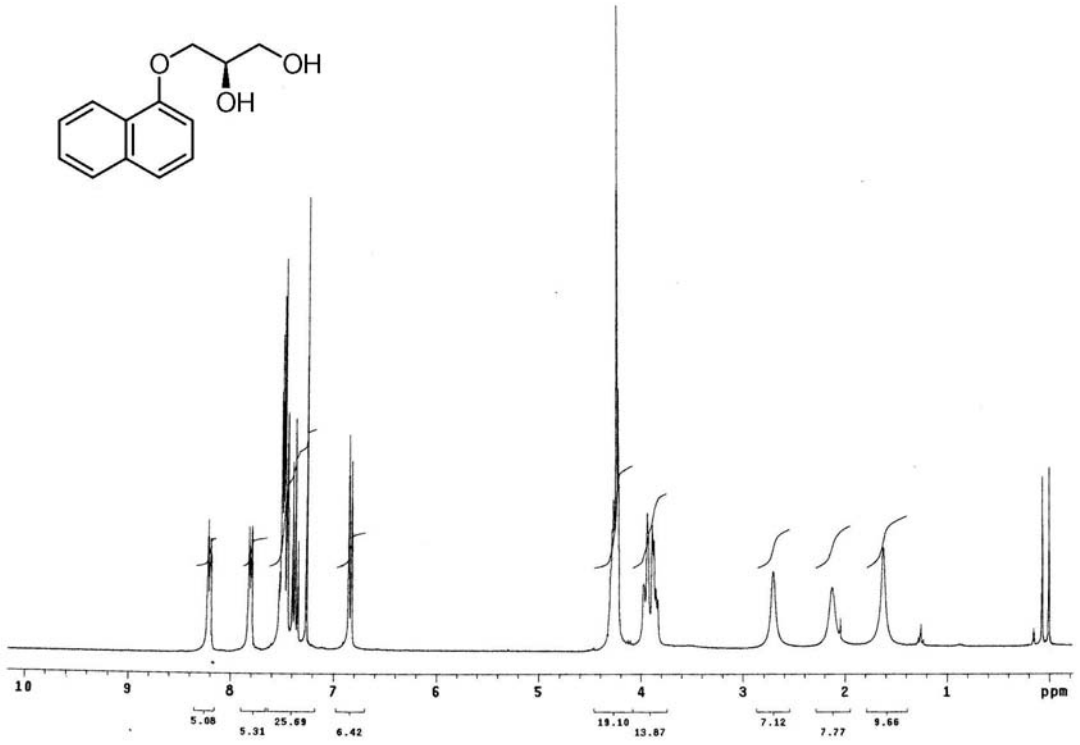

Figure S5. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (*R*)-3-(naphthalene-1-yloxy) propane-1,2-diol.

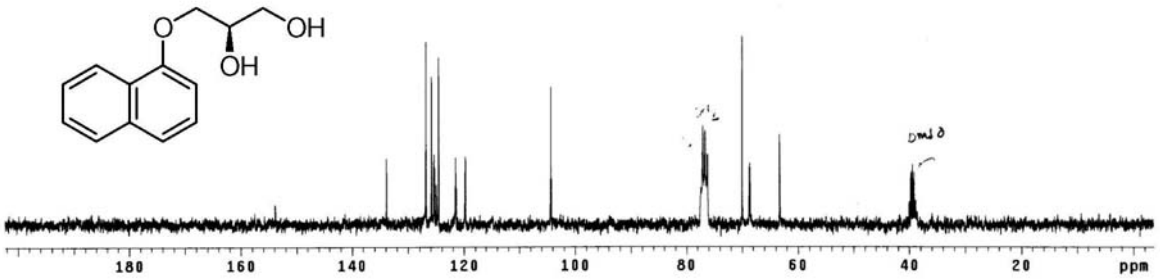

Figure S6. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of (*R*)-3-(naphthalene-1-yloxy) propane-1,2-diol.

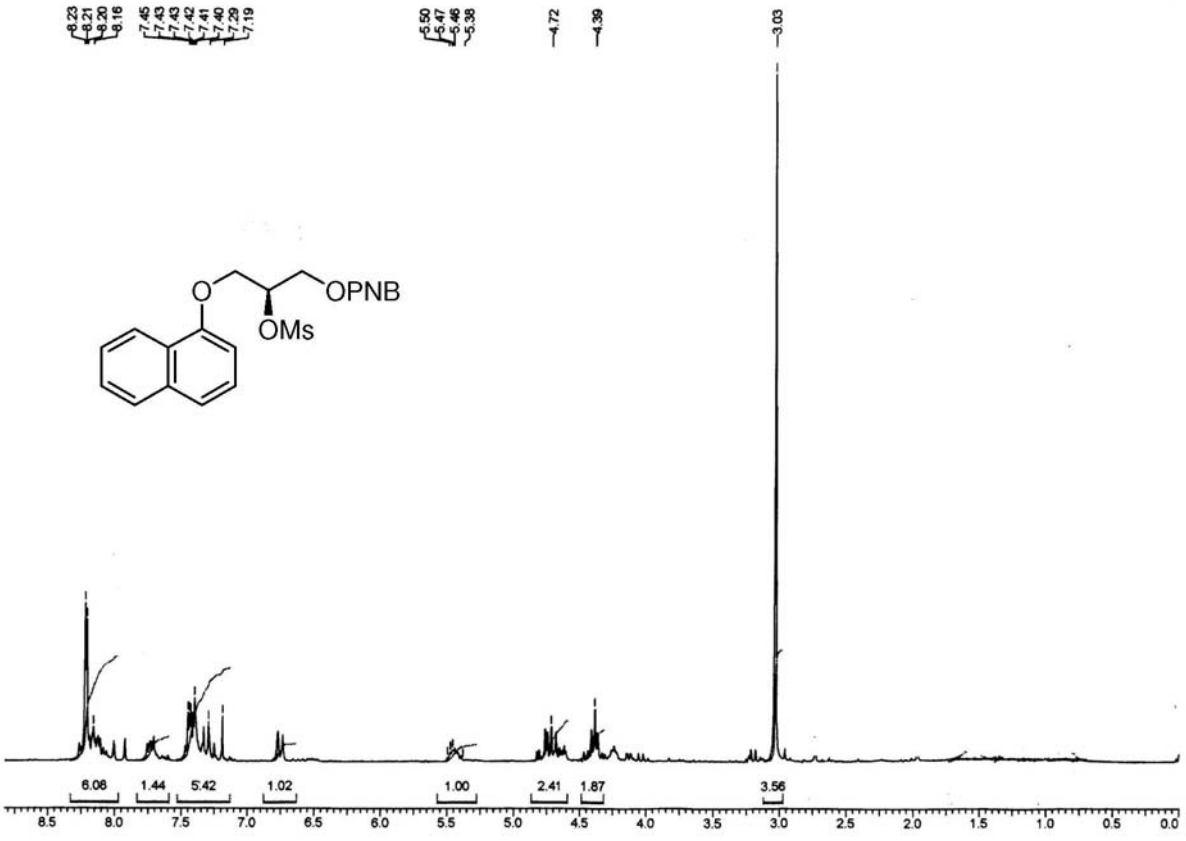

Figure S7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (*S*)-3-(4-nitrobenzoyloxy)-1-(naphthalen-5-yloxy)propan-2-yl metanesulfonate.

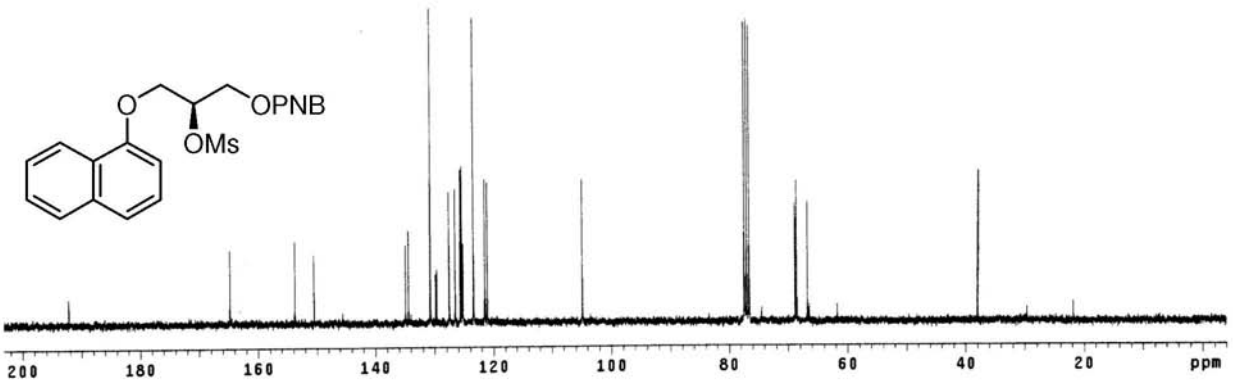

Figure S8. ^{13}C NMR spectrum (75 MHz, $CDCl_3$)of (*S*)-3-(4-nitrobenzoyloxy)-1-(naphthalen-5-yloxy)propan-2-yl metanesulfonate.

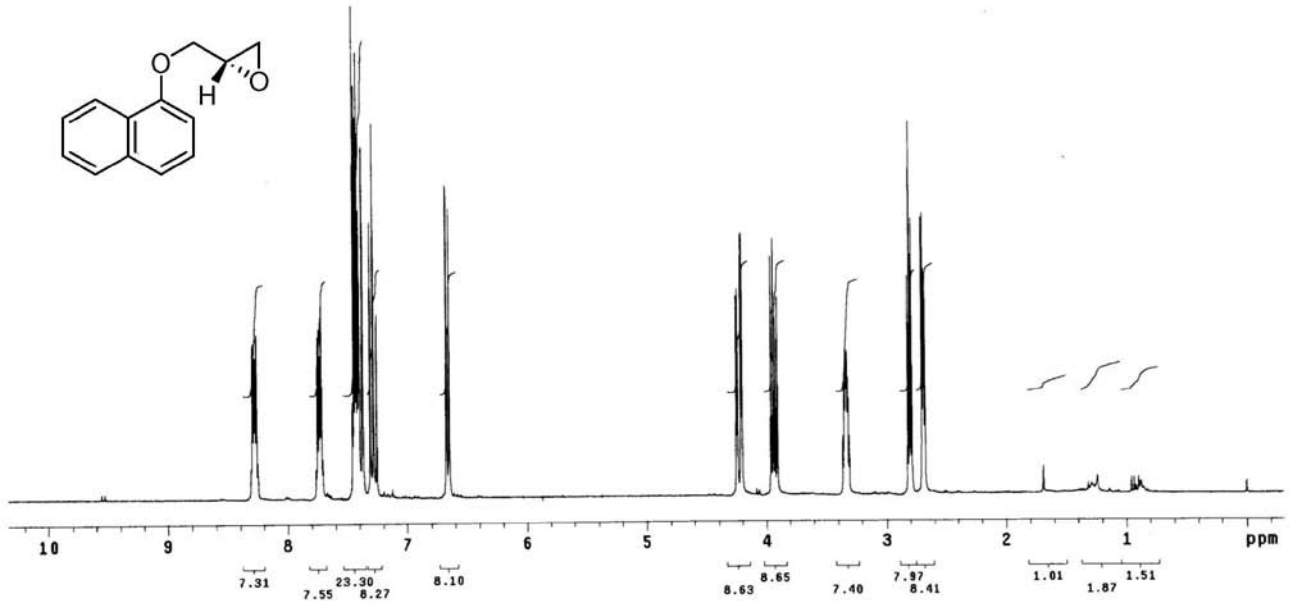

Figure S9. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (*S*)-2-((naphthalene-1-yloxy)methyl)oxirane.

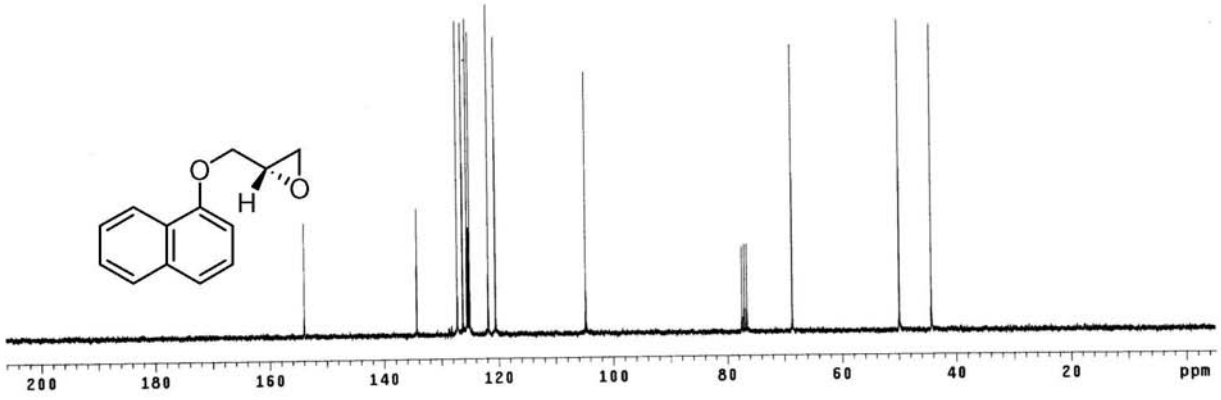

Figure S10. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of (*S*)-2-((naphthalene-1-yloxy)methyl)oxirane.

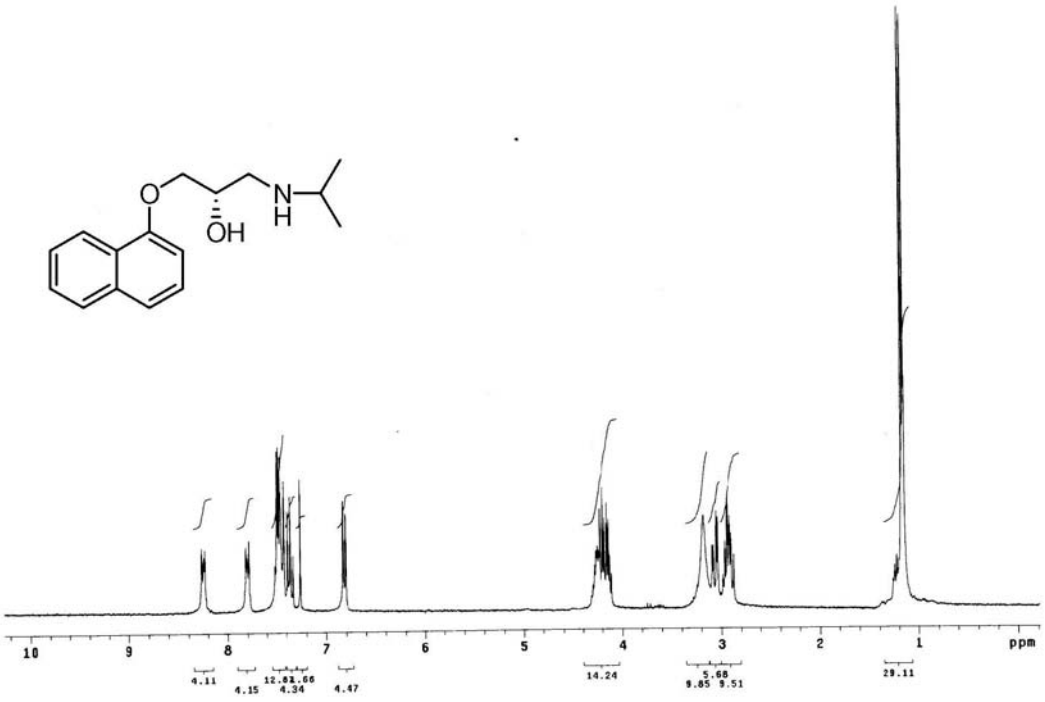

Figure S11. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (*S*)-1-(isopropylamino)-(naphthalene-1-yloxy) propane-2-ol.

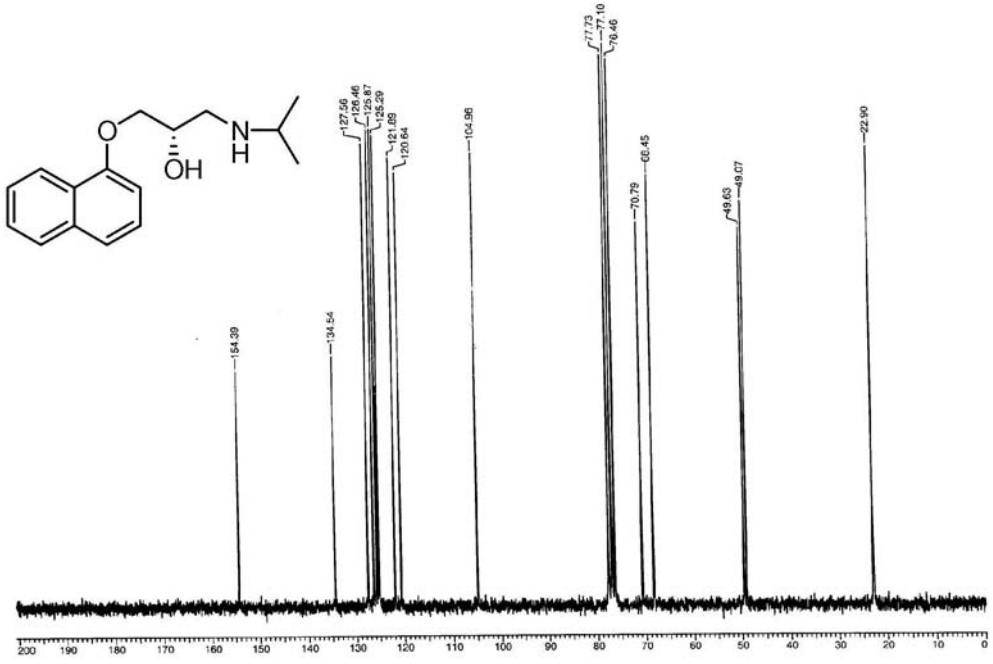

Figure S12. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of (*S*)-1-(isopropylamino)-(naphthalene-1-yloxy) propane-2-ol.

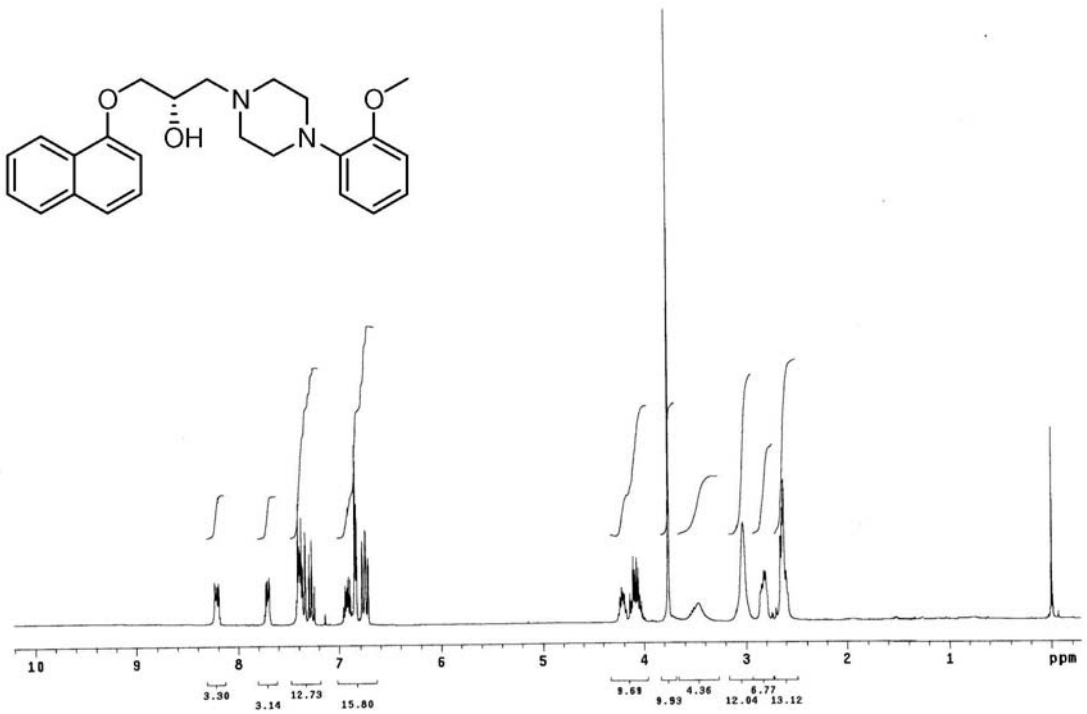

Figure S13. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (*S*)-1-(4-(2-methoxyphenyl)piperazin-1-yl)-3-(naphthalene-1-yloxy)propan-2-ol.

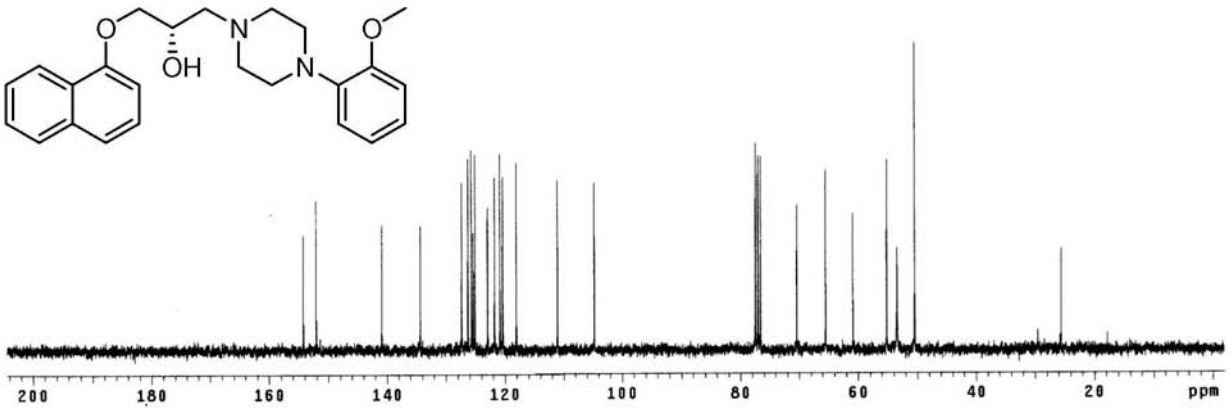

Figure S14. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of (*S*)-1-(4-(2-methoxyphenyl)piperazin-1-yl)-3-(naphthalene-1-yloxy)propan-2-ol.

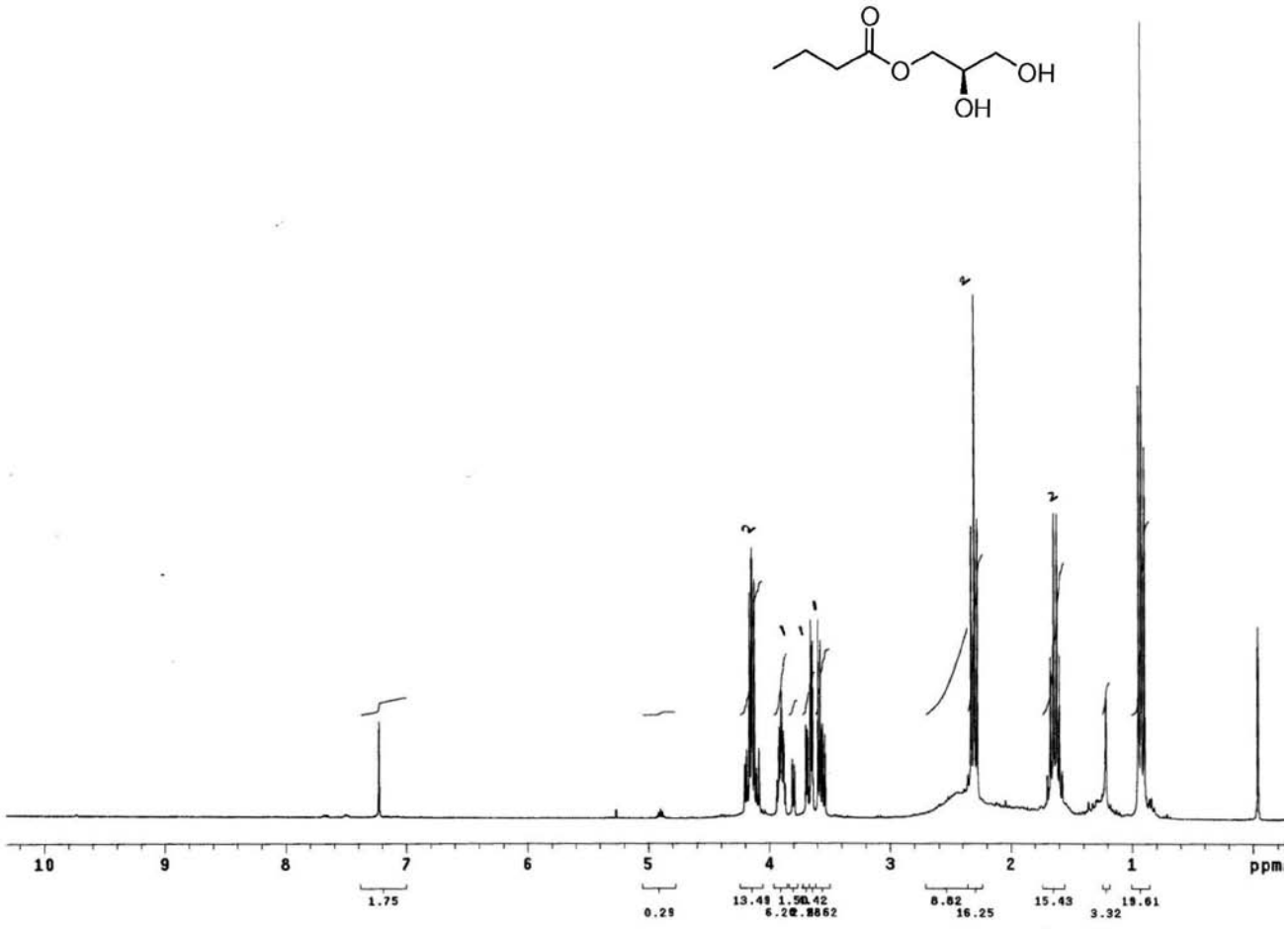

Figure S15. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (*R*)-2,3-dihydroxypropyl butyrate (**3**).

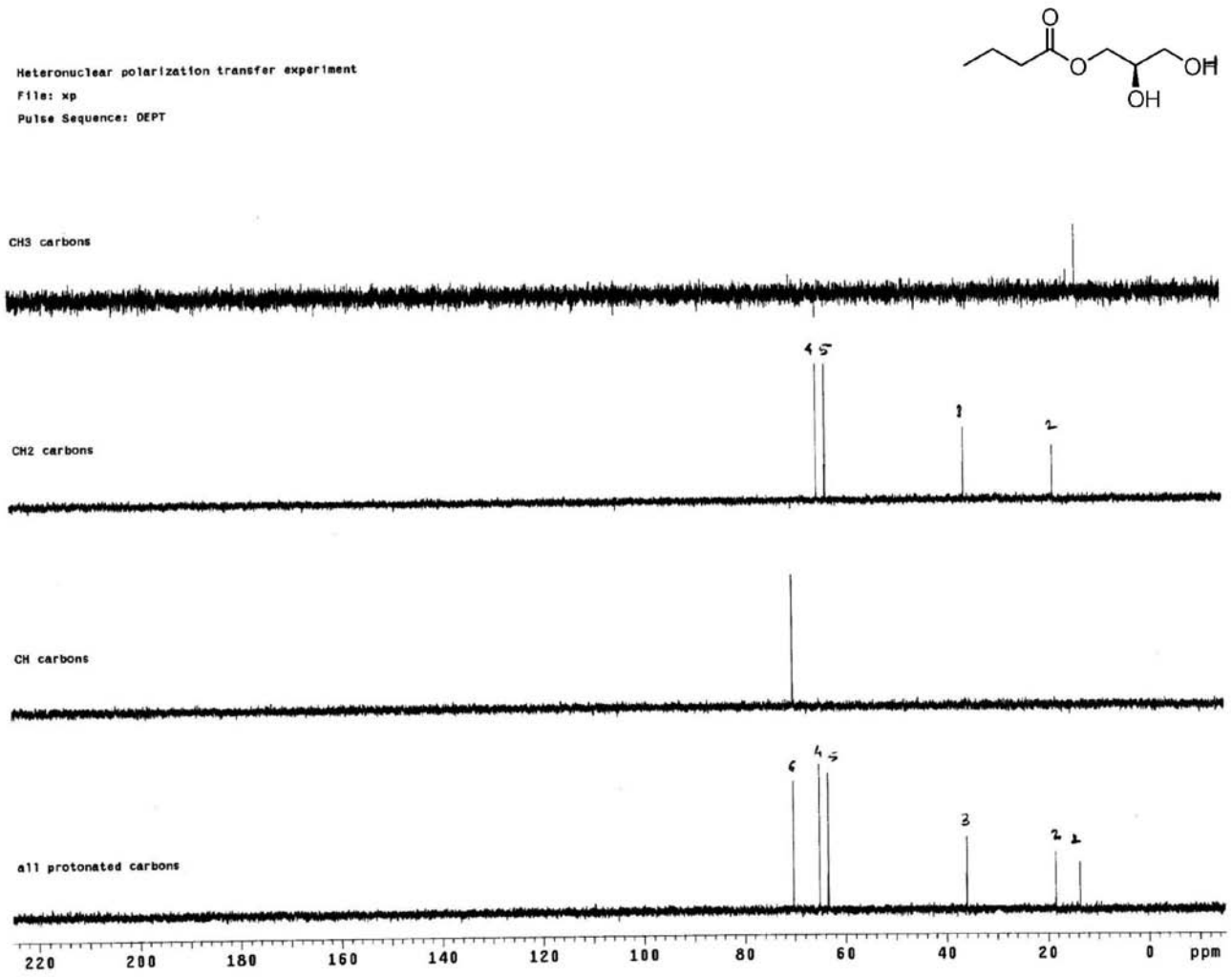

Figure S16. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of (*R*)-2,3-dihydroxypropyl butyrate (**3**).