Supporting Information

Asymmetric cross- and self-aldol reactions of aldehydes in water with a polystyrene-supported triazolylproline organocatalyst

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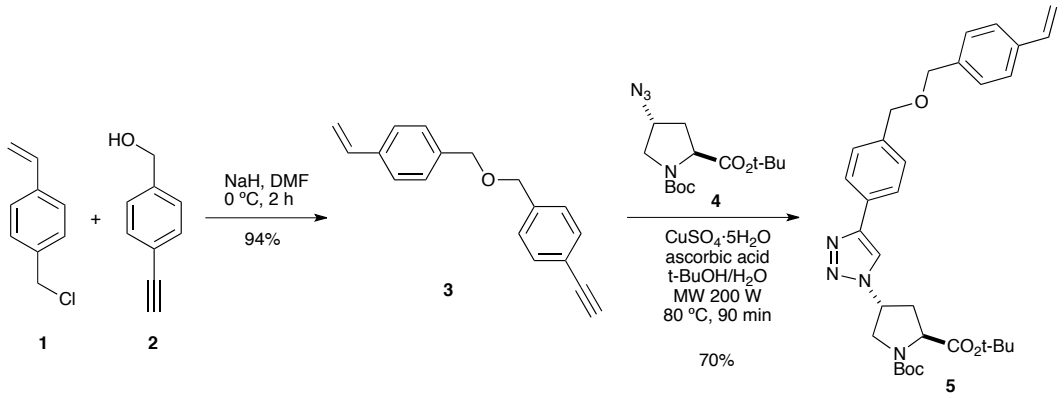
1. General remarks

All reactions were conducted under air. Synthesis grade solvents were used as received. Unless otherwise stated, all commercial reagents were used as received except the aldehydes that were distilled before using. The experiments under microwave irradiation were carried out in a CEM Discover microwave reactor. Flash chromatography was carried out using 60 mesh silica gel and dry-packed columns with a Teledyne Isco CombiFlash system with UV detector. Thin layer chromatography was carried out using Merck TLC Silicagel 60 F254 aluminum sheets. Components were visualized by UV light (λ = 254 nm) or by staining with phosphomolybdic acid (PMA) solution or anisaldehyde solution.

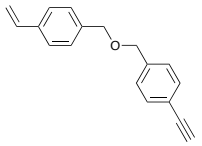
NMR spectra were recorded at 298 K on a Fourier 300 MHz Bruker, a Bruker Avance 400 Ultrashield or a Bruker Avance 500 Ultrashield apparatus. ^{1}H NMR spectroscopy chemical shifts are quoted in ppm relative to tetramethylsilane (TMS). $CDCl_3$ was used as internal standard for ^{13}C NMR spectra. Chemical shifts are given in δ and coupling constants in Hz. IR spectra were recorded on a BrukerTensor 27/Diamond ATR and are reported in wavenumbers (cm^{-1}). Elemental analyses were performed on a LECO CHNS 932 micro-analyzer at the Universidad Complutense de Madrid, Spain. FAB mass spectra were obtained on a Fisons V6-Quattro instrument, ESI mass spectra were obtained on a Waters LCT Premier Instrument and CI and EI spectra were obtained on a Waters GCT spectrometer. Specific optical rotation measurements were carried out on a Jasco P-1030 polarimeter.

High performance liquid chromatography (HPLC) was performed on Agilent Technologies chromatographs (Series 1100 and 1200), using Chiralpak IC, IB columns and guard columns as noted. Racemic standard products were prepared using DL-proline as catalyst in order to establish HPLC conditions.

2. Synthesis and characterization of the proline derivative 5



1-Ethynyl-4-(((4-vinylbenzyl)oxy)methyl)benzene (3)



A solution of (4-ethylphenyl)methanol **2** (0.935 g, 7.08 mmol) in DMF (12 mL) was added dropwise to a solution of sodium hydride (0.307 g, 7.67 mmol) in DMF (12 mL) under inert atmosphere at 0 ºC. After 30 min at this temperature, 4-vinylbenzyl chloride **1** (0.923 mL, 5.90 mmol) was added. The reaction mixture was stirred at 0 ºC for 2 h and after being warmed at room temperature it was quenched with water (70 mL). The organic phase was extracted with EtOAc and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. Flash chromatography using a gradient from cyclohexane to cyclohexane/EtOAc 90:10 and finishing with EtOAc provided compound **3** as a yellow solid (1.38 g, 5.56 mmol, 94%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.05 (s, 1H), 4.54 (s, 4H), 5.23 (d, J = 10.9 Hz, 1H), 5.74 (d, J = 17.6 Hz, 1H), 6.71 (dd, J = 17.6, 10.9 Hz, 1H), 7.30 (d, J = 8.0 Hz, 4H), 7.39 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 71.5, 71.9, 77.1, 83.5, 113.9, 121.3, 126.3 (×2), 127.5 (×2), 127.9 (×2), 132.2 (×2), 136.5, 137.1, 137.6, 139.1.

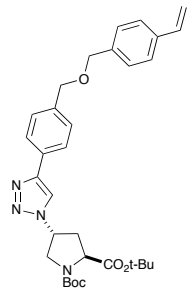
IR (ATR): ν 620, 820, 905, 1015, 1033, 1034, 1092, 1208, 1347, 1448, 1506, 1625, 2840, 3273 cm^{-1}.

Elemental analysis: calcd. for $C_{18}H_{16}O$ %C, 87.06; %H, 6.49; found: %C, 86.53, %H, 6.55.

HRMS (APCI): *m/z* $[M + H]^+$ calcd. for $C_{18}H_{17}O$ $[M + H]^+$: 249.1274; found: 249.1272.

mp: 41.8-42.6 ºC.

(2*S*,4*R*)-di-*tert*-Butyl 4-(4-(4-(((4-vinylbenzyl)oxy)methyl)phenyl)-1H-1,2,3-triazol-1-yl)pyrrolidine-1,2-dicarboxylate (5)



Alkyne **3** (0.26 g, 1.047 mmol), $CuSO_4 \cdot 5H_2O$ (5.23 mg, 0.021 mmol), ascorbic acid (0.041 g, 0.209 mmol) and (2*S*,4*R*)-di-*tert*-butyl 4-azidopyrrolidine-1,2-dicarboxylate **4**[1] (0.360 g, 1.152 mmol) were added to a microwave reaction flask, followed by *t*-BuOH (2 mL) and H_2O (2 mL). The reaction mixture was stirred in the MW (150 W, 80 ºC, 2 min ramp time, 90 min hold time). After cooling it down to room temperature, EtOAc (25 mL) and water (10 mL) were added to the reaction mixture, followed by extraction with EtOAc (3 × 25 mL), drying over $MgSO_4$ and solvent removal under reduced pressure. Purification by short flash column chromatography on silica gel (hexane/EtOAc 80:20) afforded the title product as a white solid (0.410 g, 0.731 mmol, 70%).

^{1}H NMR ($CDCl_3$, 300 MHz, rotamers): δ 1.46 (s, 9H), 1.50 (s, 9H), 2.51-2.56 (m, 1H), 2.79-2.98 (m, 1H), 3.81-3.98 (m, 1H), 4.06-4.12 (m, 1H), 4.41-4.50 (m, 1H), 4.56-4.57 (m, 4H), 5.22-5.34 (m, 2H), 5.75 (d, *J* = 17.6 Hz, 1H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 7.32-7.39 (m, 2H), 7.41-7.44 (m, 4H), 7.76 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz, rotamers*): δ 28.0 (×3), 28.3 (×3), 35.7*, 36.7, 51.7, 51.9*, 57.7, 58.4*, 58.6, 71.7, 71.9*, 80.9, 81.9*, 113.8, 118.2, 125.8 (×2), 126.3 (×2), 128.0 (×2), 128.3 (×2), 136.5, 137.1, 137.7, 138.5, 147.9, 153.6, 171.3.

IR (ATR): ν 770, 825, 906, 1036, 1076, 1147, 1221, 1365, 1391, 1453, 1696, 1738, 2885, 2932, 2977, 3060 cm^{-1}.

Elemental analysis: calcd. for $C_{32}H_{40}N_4O_5$ %C, 68.55; %H, 7.19; %N, 10.03; found: %C, 68.32; %H, 7.01; %N, 9.99.

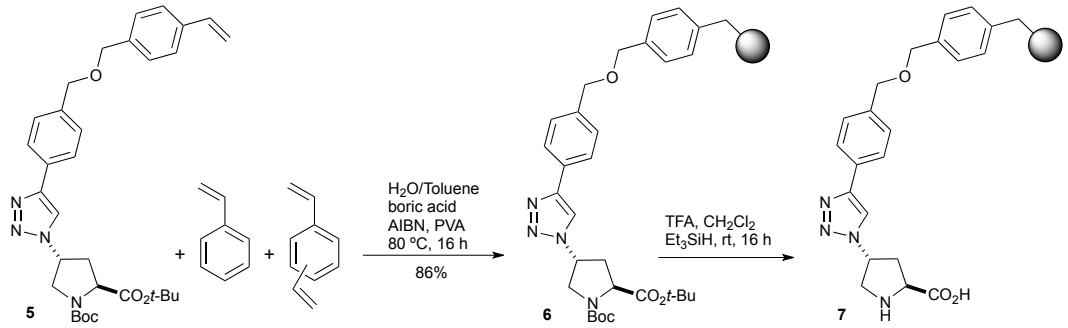
HRMS (TOF-ESI): *m/z* calcd. for $C_{18}H_{41}N_4O_5$ $[M + H]^+$: 561.3077; found: 561.3080.

mp: 102.4–105.6 ºC.

$[\alpha]_D^{25}$ = −4.5 (*c* 0.15, CH_2Cl_2).

[1] D. Font, S. Sayalero, A. Bastero, C. Jimeno, M. A. Pericàs, *Org. Lett.*, 2008, **10**, 337.

3. Preparation and characterization of resin 7



3.1. Copolymerization

Note: right before being used, deionized water and dry toluene were degassed. Divinylbenzene (DVB 80% w/w) was passed through a short pad of silica to remove radical inhibitors.

In a mechanically stirred reactor, polyvinyl alcohol (PVA, MW 104500, 0.052 g) was dissolved in water (30 mL) at 90 ºC under N_2. After cooling down, a solution of boric acid (0.232 g, 3.75 mmol) in water (16 mL) was added. In a separate flask, a solution was prepared containing DVB (0.350 mmol, 0.062 mL), monomer **5** (2.497 mmol, 1.4 g), toluene (2 mL), styrene (11 mmol, 1.262 mL) and AIBN (1% w/w, 0.1 mmol, 0.016 g). The volumetric ratio of organic phase to aqueous phase was chosen to be 1:20.

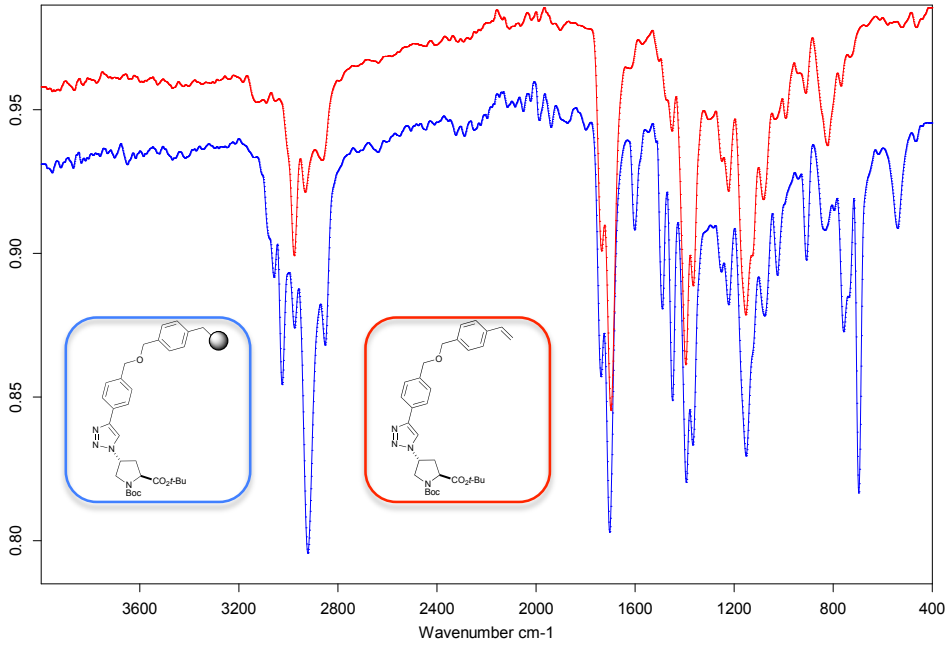
Then, the organic solution was added to the reactor with the aqueous solution under inert atmosphere. The temperature was set at 80 ºC and the reaction was allowed to proceed for 16 h at a stirring speed of 440 ppm. After the reaction was finished, the aqueous solution was decanted off. The polymer remaining in the suspension was then washed several times with water (50 ºC), methanol and acetone to remove any boric acid and PVA. Finally, the solid was dried overnight at 40 ºC in a vacuum oven (batch 1: 2.37 g, f = 0.9 mmol g^{-1}, 86% of monomer incorporation).

^{13}C NMR (gel phase, $CDCl_3$, 126 MHz): δ 28.2-28.5, 40.7, 51.9, 57.8, 71.9, 80.4-81.9, 113.9, 118.8, 125.5-129.2, 136.9-137.9, 145.6-147.9, 153.7, 171.5.

EA batch 1: found %C, 79.16; %H, 7.39; %N, 5.13; f = 0.9 mmol g^{-1}.

EA batch 2: found %C, 80.47; %H, 7.36; %N, 3.95; f = 0.7 mmol g^{-1}.

IR (ATR): ν 539, 697, 731, 797, 907, 1066, 1148, 1221, 1262, 1366, 1391, 1452, 1493, 1601, 1702, 1738, 2848, 2926, 2977, 3025, 3060 cm^{-1}.

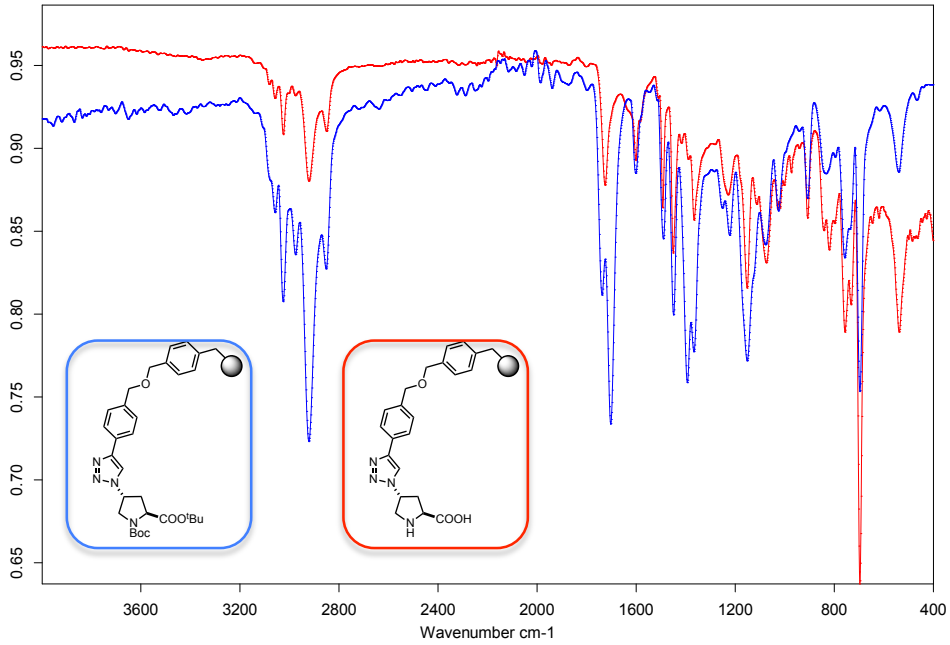


In red: IR spectrum of monomer **5**. In blue: IR spectrum of resin **6**

3.2. Deprotection

The polymer **6** (0.5 g) obtained in the previous step was swollen in a CH_2Cl_2/TFA 9:1 mixture (47.6 mL) and Et_3SiH (0.036 mmol, 5.68 µL) was added at room temperature. The resulting mixture was stirred overnight, the reaction progress being monitored by FTIR. When the IR signal of *t*-butyl and Boc groups had completely disappeared, the resin was filtered and washed with CH_2Cl_2 (100 mL), CH_2Cl_2/MeOH (1:1, 80 mL), MeOH (80 mL), H_2O/MeOH (1:1, 80 mL), buffer (pH = 5, 100 mL), buffer/MeOH (1:1, 100 mL), MeOH, (100 mL), CH_2Cl_2/MeOH (1:1, 50 mL) and CH_2Cl_2 (80 mL). Finally, the yellow resin was dried overnight at 40 ºC in a vacuum oven.

EA batch 1: found %C, 77.32; %H, 6.66; %N, 5.03; f = 0.9 mmol g^{-1}.
EA batch 2: found %C, 75.53; %H, 6.71; %N, 3.12; f = 0.6 mmol g^{-1}.
IR (ATR): ν 535, 697, 757, 820, 907, 969, 1018, 1074, 1113, 1152, 1229, 1361, 1390, 1418, 1451, 1492, 1601, 1725, 2849, 2921, 3024, 3058, 3081 cm^{-1}.



In red: IR spectrum of resin **7**. In blue: IR spectrum of resin **6**

3.3. Solvent uptake tests on resin 7

The solvent uptake of resin **7** was taken as a measurement of its ability to swell in the corresponding solvent. Solvent uptake data for each solvent were determined gravimetrically and expressed as g of solvent per g of dry resin.[2] Resin **7** (10 mg) was weighed into a tared 1 mL eppendorf tube and solvent (0.3 mL) was added. The eppendorf tubes were then closed and shaken overnight to allow equilibrium to be attained. After centrifugation (30 min at 4000 rpm) a syringe was used to remove excess solvent. The eppendorf tube containing the swollen resin was immediately weighed. From this value the weight of solvent absorbed per gram of resin was obtained.

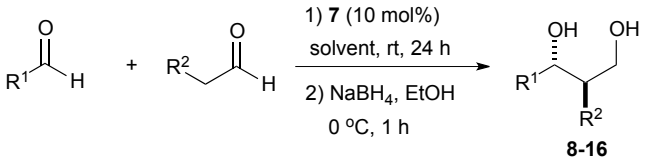
[2] (a) R. P. Washington, O. Steinbock, *J. Am. Chem. Soc.*, 2001, **123**, 7933. (b) P. Besenius, P. A. G. Cormack, J. Liu, S. Otto, J. K. M. Sanders, D. C. Sherrington, *Chem. Eur. J.*, 2008, **14**, 9006.

Table 1: Solvent uptake results.

Entry	Solvent	Solvent uptake [g g^{-1}][a]
1	H_2O	0.9
2	H_2O/THF (1:1)	3.1
3	H_2O/THF (4:96)	3.6
4	H_2O/DMF (1:1)	0.7
5	H_2O/DMF (4:96)	1.7
6	H_2O/DMSO (1:1)	0.7
7	H_2O/DMSO (4:96)	1.1

[a] Solvent uptake data for resin **7** as determined by gravimetry and expressed as g of adsorbed solvent per g of dry resin; solvent uptake = (swollen mass-dry mass)/dry mass.

4. General procedure for the asymmetric cross-aldol reaction of aldehydes catalyzed by 7

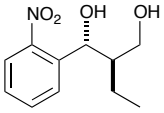


8-16

Resin **7** (10 mol%, f = 0.9 or 0.6 mmol g^{-1}) was placed in a vial and swollen in water (conditions A, see Table 2 in main text) or in a mixture of DMSO/water 94:6 (conditions B, see Table 2 in main text). Then, the aromatic aldehyde (1 equiv.) and butanal or propanal (3 equiv.) were added. The mixture was stirred at room temperature for 24 h. The solvent was removed by filtration and the resin was rinsed with EtOAc (1.5 mL). The solution containing the crude product was treated with a suspension of $NaBH_4$ (0.5 mmol) in EtOH (1 mL) at 0 ºC. One hour later, the reaction was diluted with water (1.5 mL) and extracted with EtOAc (3 × 1.5 mL). After drying with Na_2SO_4, solvents were removed *in vacuo*. The diastereomeric ratio of the diol was determined by ^{1}H NMR at this stage. After purification by flash chromatography on silica gel the diols were isolated as a mixture of diastereomers.

5. Characterization data for compounds 8-16

(1*R*,2*R*)-2-Ethyl-1-(2-nitrophenyl)propane-1,3-diol (8)



Conditions A: The title compound was prepared according to the general procedure using *o*-nitrobenzaldehyde (30 mg, 0.2 mmol), butanal (53 µL, 0.6 mmol) and **7** (35 mg, *f* = 0.6 mmol/g) in 64 µL of water. After purification by flash chromatography with CH_2Cl_2/EtOAc (10:1) as the eluent, it was isolated in 80% yield (36 mg, 0.159 mmol, yellow oil), *anti*/*syn* 93:7, 95% ee.

Conditions B: 80% yield, *anti*/*syn* 93:7, 96% ee.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.99 (t, *J* = 7.5 Hz, 3H), 1.51-1.59 (m, 2H), 1.79-1.82 (m, 1H), 2.40 (m, 1H), 3.69-3.71 (m, 2H), 3.79-3.82 (m, 1H), 5.44 (t, *J* = 5.4 Hz, 1H), 7.43-7.46 (m, 1H), 7.66-7.68 (m, 1H), 7.87-7.93 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 11.7, 21.5, 46.2, 63.4, 73.4, 124.6, 128.2, 128.8, 133.2, 138.9, 148.1.

IR (ATR): ν 786, 856, 1016, 1342, 1427, 1523, 2876, 2931, 2962, 3342 cm^{-1}.

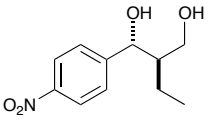
HRMS (ESI−): *m/z* calcd. for $C_{11}H_{14}NO_4$ $[M-H]^-$: 224.0928; found: 224.0935.

HPLC (Chiralpak IC, hexane/*i*-PrOH 95:5, 1 mL/min, 254 nm): t_R = 28.4 and 44.6 min (*anti*, 96% ee).

$[\alpha]_D^{25}$ = +74.9 (*c* 0.15, CH_2Cl_2); *anti/syn* 93:7, 95% ee.

Elemental Analysis: calcd. for $C_{11}H_{15}NO_4$ %C 58.66; %H 6.71; %N 6.22; found %C 58.56; %H 7.11; %N 5.71.

(1*R*,2*R*)-2-Ethyl-1-(4-nitrophenyl)propane-1,3-diol (9)



Conditions A: the title compound was prepared according to the general procedure using *p*-nitrobenzaldehyde (44 mg, 0.29 mmol), butanal (78 µL, 0.9 mmol) and **7** (52 mg, *f* = 0.6 mmol/g) in 94 µL of water. After purification by flash chromatography with CH_2Cl_2/EtOAc (10:1) as the eluent, it was isolated in 88% yield (58 mg, 0.257 mmol, yellow solid), *anti*/*syn* 87:13, 96% ee.

Conditions B: 82% yield, *anti*/*syn* 90:10, 96% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.96 (t, *J* = 7.5 Hz, 3H), 1.44-1.48 (m, 2H), 1.74-1.77 (m, 1H), 2.18 (t, *J* = 4.8 Hz, 1H), 3.60 (d, *J* = 4.8 Hz, 1H), 3.75-3.77 (m, 1H), 3.80 (ddd, *J* = 2.9, 4.9, 10.9 Hz, 1H), 4.91 (t, *J* = 5.7 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 8.24 (d, *J* = 8.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz, *anti*): δ 11.7, 21.1, 47.9, 63.6, 77.4, 123.6 (×2), 127.2 (×2), 147.3, 151.3.

IR (ATR): ν 701, 846, 1011, 1346, 1518, 1601, 2931, 3295 cm^{-1}.

HRMS (ESI−): *m/z* calcd. for $C_{11}H_{14}NO_4$ $[M-H]^-$: 224.0928; found: 224.0922.

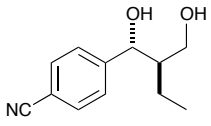
HPLC (Chiralpak IC, hexane/THF 92:8, 1 mL/min, 254 nm): t_R = 43.9 and 47.4 min (*anti*, 96% ee); (Chiralpak IC, hexane/*i*-PrOH 97:3, 1 mL/min, 254 nm): t_R = 50.3 and 53.5 min (*syn*, 15% ee).

mp: 59.6-61.7 ºC

$[\alpha]_D^{25}$ = +50.3 (*c* 0.06, CH_2Cl_2); *anti/syn* 87:13, 96% ee.

Elemental Analysis: calcd. for $C_{11}H_{15}NO_4$: %C 58.66; %H 6.71; %N 6.22; found %C 58.53; %H 6.63; %N 6.19.

4-((1*R*,2*R*)-1-Hydroxy-2-(hydroxymethyl)butyl)benzonitrile (10)



Conditions A: the title compound was prepared according to the general procedure using 4-cyanobenzaldehyde (38 mg, 0.29 mmol), butanal (78 μL, 0.9 mmol) and **7** (52 mg, *f* = 0.6 mmol/g) in 94 μL of water. After purification by flash chromatography with CH_2Cl_2/EtOAc (10:1) as the eluent, it was isolated in 85% yield (50 mg, 0.244 mmol, yellow oil), *anti*/*syn* 92:8, 93% ee.

Conditions B: 98% yield, *anti*/*syn* 90:10, 95% ee.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.93 (t, *J* = 7.8 Hz, 3H), 1.39-1.44 (m, 2H), 1.68-1.73 (m, 1H), 2.19 (br s, 1H), 3.46 (br s, 1H), 3.69-3.72 (m, 1H), 3.79-3.81 (m, 1H), 4.83-4.84 (m, 1H), 7.48-7.49 (m, 2H), 7.64-7.67 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 11.7, 21.1, 47.8, 63.6, 77.6, 111.1, 118.8, 127.1 (×2), 132.2 (×2), 149.2.

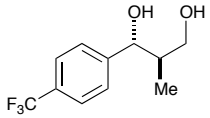
IR (ATR): ν 832, 1016, 1038, 1074, 1408, 1608, 2228, 2877, 2931, 2692, 3364 (br) cm^{-1}.

HRMS (ESI+): *m/z* calcd. for $C_{12}H_{15}NaO_2$ $[M+Na]^+$: 228.0995; found: 228.0985.

HPLC (Chiralpak IC, hexane/IPA 93:7, 1 mL/min, 220 nm): t_R = 20.8 and 22.9 min (*syn,* 13%) and 29.6 and 31.8 min (*anti*, 93% ee).

$[\alpha]_D^{25}$ = +27.0 (*c* 0.13, CH_2Cl_2); *anti/syn* 92:8, 93% ee.

(1*R*,2*R*)-2-Methyl-1-(4-(trifluoromethyl)phenyl)propane-1,3-diol (11)[3]



Conditions A: the title compound was prepared according to the general procedure using 4-(trifluoromethyl)benzaldehyde (50 μL, 0.37 mmol), propanal (80 μL, 1.1 mmol) and **7** (41 mg, *f* = 0.9 mmol/g) in 119 μL of water. After purification by flash chromatography with CH_2Cl_2/EtOAc (10:1) as the eluent, it was isolated in 85% yield (73 mg, 0.312 mmol, colourless oil), *anti*/*syn* 93:7, 81% ee.

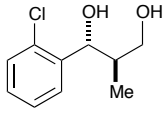
Conditions B: 84% yield, *anti*/*syn* 82:18, 97% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.76 (dd, *J*= 7.0, 1.9 Hz, 3H), 2.05 (br s, 1H), 2.48-2.56 (m, 1H), 3.29-3.37 (m, 1H), 3.69-3.74 (m, 1H), 3.78-3.83 (m, 1H), 4.64-4.66 (m, 1H), 7.46-7.48 (m, 2H), 7.61-7.63 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 13.7, 41.5, 67.6, 79.9, 123.8 (q, $^1J_{CF}$ = 221 Hz), 125.3 (q, $^3J_{CF}$ = 4 Hz, 2 × CH), 126.9 (×2), 129.9 (q, $^2J_{CF}$ = 33 Hz), 147.3.

HPLC (Chiralpak IC, hexane/*i*-PrOH/CH_2Cl_2 82:1:17, 1 mL/min, 254 nm): t_R = 38.8 and 41.2 min (*anti*, 97% ee).

(1*R*,2*R*)-1-(2-Chlorophenyl)-2-ethylpropane-1,3-diol (12)[3,4]



Conditions A: the title compound was prepared according to the general procedure using 2-chlorobenzaldehyde (22 μL, 0.2 mmol), propanal (43 μL, 0.6 mmol) and **7** (36 mg, *f* = 0.6 mmol/g) in 65 μL of water. After purification by flash chromatography with CH_2Cl_2/EtOAc (10:1) as the eluent, it was isolated in 99% yield (40 mg, 0.199 mmol, colourless oil), *anti*/*syn* 89:11, 95% ee.

Conditions B: 60% yield, *anti*/*syn* 94:6, 99% ee.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.88 (d, *J* = 7.1 Hz, 3H), 2.08-2.13 (m, 1H), 2.85 (br s, 1H), 3.36 (br s, 1H), 3.68-3.78 (m, 2H), 5.12-5.13 (m, 1H), 7.20-7.23 (m, 1H), 7.29-7.34 (m, 2H), 7.56-7.58 (m, 1H).

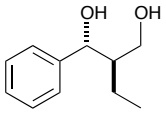
^{13}C NMR ($CDCl_3$, 126 MHz): δ 13.7, 40.7, 67.2, 76.1, 127.2, 128.1, 128.6, 129.4, 132.4, 140.9.

HPLC (Chiralpak IB, hexane/*i*-PrOH 98:2, 0.5 mL/min, 220 nm): t_R = 54.7 and 56.2 min (*anti*, 99% ee).

[3] Y. Hayashi, S. Aratake, T. Itoh, T. Okano, T. Sumiya, M. Shoji, *Chem. Commun*., 2007, 957.

[4] (a) Y. Hayashi, S. Aratake, T. Okano, J. Takahashi, T. Sumiya, M. Shoji, *Angew. Chem*., 2006, **118**, 5653. (b) Y. Hayashi, S. Aratake, T. Itoh, T. Okano, T. Sumiya, M. Shoji, *Angew. Chem. Int. Ed.*, 2006, **45**, 5527.

(1*R*,2*R*)-2-Ethyl-1-phenylpropane-1,3-diol (13)[5]



Conditions A: the title compound was prepared according to the general procedure using benzaldehyde (21 μL, 0.2 mmol), butanal (56 μL, 0.6 mmol) and **7** (36 mg, *f* = 0.6 mmol/g) in 65 μL of water. After purification by flash chromatography with CH_2Cl_2/EtOAc (10:1) as the eluent, it was isolated in 92% yield (33 mg, 0.183 mmol, colourless oil), *anti*/*syn* 91:9, 89% ee.

Conditions B: 32% yield, *anti*/*syn* 97:3, 90% ee.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.90 (t, *J* = 7.5 Hz, 3H), 1.28-1.36 (m, 2H), 1.78 (m, 1H), 2.71 (br s, 1H), 2.83 (br s, 1H), 3.71-3.76 (m, 1H), 3.86-3.89 (m, 1H), 4.73-4.75 (m, 1H), 7.28 (m, 1H), 7.37 (m, 4H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 11.7, 21.1, 48.2, 64.3, 79.0, 126.5 (×2), 127.7, 128.5 (×2), 143.6.

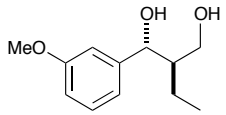
IR (ATR): ν 700, 1016, 1453, 2876, 2929, 2961, 3326 cm^{-1}.

HRMS (ESI+): *m/z* calcd. for $C_{11}H_{16}NaO_2$ $[M+Na]^+$: 203.1043, found: 203.1045.

$[\alpha]_D^{25}$ = +20.8 (*c* 0.13, CH_2Cl_2); *anti/syn* 91:9, 89% ee.

HPLC (Chiralpak IC, hexane/IPA 90:10, 0.3 mL/min, 215 nm): t_R = 32.2 and 36.0 min (*anti,* 90% ee); 26.7 and 30.7 min (*syn,* 53% ee).

(1*R*,2*R*)-2-Ethyl-1-(3-methoxyphenyl)propane-1,3-diol (14)



Conditions A: the title compound was prepared according to the general procedure using 3-methoxybenzaldehyde (25 μL, 0.2 mmol), butanal (56 μL, 0.6 mmol) and **7** (36 mg, *f*= 0.6 mmol/g) in 65 μL of water. After purification by flash chromatography with CH_2Cl_2/EtOAc (10:1) as the eluent, it was isolated in 59% yield (25 mg, 0.119 mmol, colourless oil), *anti*/*syn* 97:3, 81% ee.

Conditions B: 43% yield, *anti*/*syn* 97:3, 95% ee.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.91 (t, 3H *J* = 7.5 Hz), 1.31-1.37 (m, 2H), 1.76-1.79 (m, 1H), 2.73 (br s, 1H), 2.91 (br s, 1H), 3.72-3.73 (m, 1H), 3.85 (s, 3H), 3.86-3.89 (m, 1H), 4.71-4.72 (m, 1H), 6.84-6.86 (m, 1H), 6.95-6.96 (m, 2H), 7.28-7.32 (m, 1H).

^{13}C NMR ($CDCl_3$, 126 MHz): 11.6, 21.1, 48.0, 55.2, 64.2, 78.9, 112.0, 112.9, 118.8, 129.4, 145.3, 159.7 ppm.

[5] For the characterization of the *syn* isomer, see: (a) A. F. Houri, M. T. Didiuk, Z. Xu, N. R. Horan, A. H. Hoveyda, *J. Am. Chem. Soc*. 1993, **115**, 6614. (b) L. Lin, K. Yamamoto, S. Matsunaga, M. Kanai, *Angew. Chem. Int. Ed*. 2012, **51**, 10275; for a mixture of *syn/anti* isomers, see: (c) D. B. Millward, A. P. Cole, R. M. Waymouth, *Organometallics*, 2000, **19**, 1870.

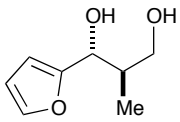
IR (ATR): ν 701, 787, 1039, 1156, 1256, 1320, 1456, 1601, 1714, 2933, 2960, 3380 cm^{-1}.

HRMS (ESI+): *m/z* calcd. for $C_{12}H_{18}NaO_3$ $[M+Na]^+$: 233.1148, found: 233.1145.

$[\alpha]_D^{25}$ = +22.6 (*c* 0.11, CH_2Cl_2); *anti/syn* 97:3, 81% ee.

HPLC (Chiralpak IB, hexane/*i*-PrOH 90:10, 1 mL/min, 220 nm): t_R = 10.4 and 12.4 min (*anti*, 95% ee).

(1*R*,2*R*)-1-(Furan-2-yl)-2-methylpropane-1,3-diol (15)[6]



Conditions A: the title compound was prepared according to the general procedure using furfural (24 μL, 0.3 mmol), propanal (63 μL, 0.9 mmol) and **7** (52 mg, *f* = 0.6 mmol/g) in 94 μL of water, but the reaction time was extended to 48 h. After purification by flash chromatography with CH_2Cl_2/MeOH (99:1) as the eluent, it was isolated in 52% yield (24 mg, 0.154 mmol, yellow oil), *anti*/*syn* 83:17, 82% ee.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.80 (d, *J* = 6.9 Hz, 3H), 2.23-2.29 (m, 1H), 2.53 (br s, 1H), 2.91 (d, *J* = 4.0 Hz, 1H), 3.69-3.82 (m, 2H), 4.62 (dd, *J* = 8.4, 3.7 Hz, 1H), 6.28 (d, *J* = 3.0 Hz, 1H), 6.35 (dd, *J* = 3.2, 1.8 Hz, 1H), 7.38-7.39 (m, 1H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 13.5, 39.6, 67.4, 73.3, 107.0, 110.1, 142.1, 155.6.

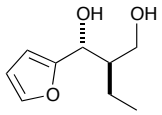
IR (ATR): ν 735, 1008, 1149, 1336, 1424, 2879, 2932, 2964, 3361 cm^{-1}.

HRMS (ESI+): *m/z* calcd. for $C_8H_{12}NaO_3$ $[M+Na]^+$: 179.0679; found: 179.0682.

$[\alpha]_D^{25}$ = −2.2 (*c* 0.1, CH_2Cl_2); *anti/syn* 83:17, 82% ee.

HPLC (Chiralpak IC, hexane/*i*-PrOH 90:10, 1 mL/min, 215 nm): t_R = 14.9 and 17.5 min (*syn,* 52% ee); 15.8 and 27.4 min (*anti*, 82% ee).

(1*R*,2*R*)-2-Ethyl-1-(furan-2-yl)propane-1,3-diol (16)[7]



Conditions A: the title compound was prepared according to the general procedure furfural (24 μL, 0.29 mmol), butanal (78 μL, 0.9 mmol) and **7** (52 mg, *f* = 0.6 mmol/g) in 94 μL of water, but the reaction time was extended to 48 h. After purification by flash chromatography with CH_2Cl_2/MeOH (99:1) as the eluent, it was isolated in 70% yield (35 mg, 0.21 mmol, yellow oil), *anti*/*syn* 80:20, 77% ee.

Conditions B: 30% yield, *anti*/*syn* 70:30, 78% ee.

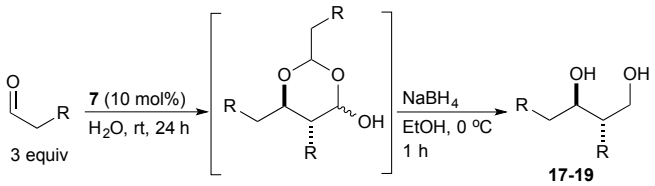
Neat conditions: 69% yield, *anti*/*syn* 70:30, 82% ee.

[6] M. Christlieb, J. E. Davies, J. Eames, R. Hooley, S. Warren. *J. Chem. Soc. Perkin Trans. 1*, 2001, 2983.

[7] L. Lin, K. Yamamoto, S. Matsunaga, M. Kanai, *Chem. Asian J.* 2013, **8**, 2974.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.91 (t, *J* = 7.5 Hz, 3H), 1.30-1.37 (m, 2H), 1.92-2.03 (m, 1H), 2.5 (m, 1H), 2.99 (d, *J* = 4.7 Hz, 1H), 3.72-3.75 (m, 1H), 3.87-3.90 (m, 1H), 4.75 (dd, *J* = 7.3, 4.4 Hz, 1H), 6.28-6.29 (m, 1H), 6.34-6.36 (m, 1H) 7.38 (m, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz): δ 11.6, 20.9, 45.9, 64.1, 72.1, 106.8, 110.2, 141.9, 155.9.
IR (ATR): ν 733, 1009, 1036, 1149, 1462, 2875, 2932, 2960, 3326 cm^{-1}.
HRMS (ESI+): *m/z* calcd. for $C_9H_{14}NaO_3$ $[M+Na]^+$: 193.0835, found: 193.0836.
$[\alpha]_D^{25}$ = −8.5 (*c* 0.1, CH_2Cl_2); *anti/syn* 80:20, 77% ee.
HPLC (Chiralpak IC, hexane/*i*-PrOH 90:10, 1 mL/min, 230 nm): t_R = 11.4 and 14.5 min (*syn,* 65% ee) and 13.0 and 16.8 min (*anti*, 82% ee).

6. General procedure for the asymmetric self-aldol reaction of aldehydes in water catalyzed by 7.



General Procedure 1:

Resin **7** (10 mol%, *f* = 0.9 mmol g^{-1}) was placed in a vial and swollen in water (0.4 mL). Then the aldehyde (1 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. After that, the resin was separated by filtration and rinsed with EtOAc (1.5 mL). The solution containing the crude product was treated with a cooled suspension of $NaBH_4$ (2 mmol) in EtOH (1 mL) at 0 ºC. After 1 hour, the reaction was diluted with water (1.5 mL) and extracted with EtOAc (3 × 1.5 mL). After drying with Na_2SO_4, solvents were removed *in vacuo*. The diastereomeric ratio of diols was determined by ^{1}H NMR analysis of the crude mixture. After purification by flash chromatography on silica gel, the diols were isolated as a mixture of diastereomers.

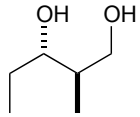
General Procedure 2:

Resin **7** (10 mol%, *f* = 0.9 mmol g^{-1}) was placed in a vial and swollen in water. After removing all excess of water with a syringe, 2-methyltetrahydrofuran (0.11 mL) was added, followed by aldehyde (1 mmol) and the reaction mixture was stirred at room temperature for 24 h. After that, the resin was separated by filtration and rinsed with EtOAc (1.5 mL). The solution containing the crude product was treated with a cooled suspension of $NaBH_4$ (2 mmol) in EtOH (1 mL) at 0 ºC. After 1 hour, the reaction was diluted with water (1.5 mL), extracted with EtOAc (3 × 1.5 mL), dried with

Na_2SO_4 and the solvents were removed *in vacuo*. The diastereomeric ratio of diols was determined by achiral HPLC of the crude mixture. After purification by flash chromatography on silica gel, the diols were isolated as a mixture of diastereomers.

7. Characterization data for compounds 17-19

(2*R*,3*S*)-2-Methylpentane-1,3-diol (17)[8]



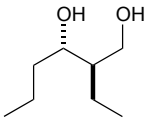
The title compound was prepared according to the General Procedure 1 using propanal (71 µL, 1 mmol) and **7** (177 mg, f = 0.6 mmol/g) in 0.3 mL of water. After purification by flash chromatography with cyclohexane/EtOAc (80:20) as the eluent, compound **17** was isolated in 30% yield (13 mg, 0.110 mmol, colourless oil), *anti*/*syn* 70:30, 91% ee.

The enantiomeric excess was determined after derivatization of the diol as its monobenzoyl ester and HPLC analysis (Chiralpak IC, hexane/*i*-PrOH/EtOH 98:1.5:0.5, 1 mL/min, 230 nm): t_R = 36.4 and 54.7 min (*syn*); 47.0 and 60.8 min (*anti*, 91% ee).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.91 (d, J = 7.0 Hz, 3H), 0.99 (t, J = 7.4 Hz, 3H) 1.44-1.54 (m, 1H), 1.61-1.76 (m, 2H), 2.12 (br s, 1H, OH), 2.54 (br s, 1H, OH), 3.52 (dt, J = 7.7, 3.5 Hz, 1H), 3.65 (dd, J = 10.8, 7.2 Hz, 1H), 3.73-3.80 (m, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 9.4, 13.9, 28.0, 39.4, 67.8, 78.7.

(2*R*,3*S*)-2-Ethylhexane-1,3-diol (18)[8a]



The title compound was prepared according to the General Procedure 1 using butanal (98 µL, 1 mmol) and **7** (123 mg, f = 0.9 mmol/g) in 0.36 mL of water. After purification by flash chromatography with cyclohexane/EtOAc (80:20) as the eluent, compound **18** was isolated in 82% yield (40 mg, 0.274 mmol, colourless oil), *anti*/*syn* 60:40, 87% ee.

The enantiomeric excess was determined after derivatization of the diol as its monobenzoyl ester and HPLC analysis (Chiralpak IC, hexane/*i*-PrOH/EtOH 98:1.5:0.5, 1 mL/min, 230 nm): t_R = 26.1 and 31.7 min (*syn*); 35.9 and 39.7 min (*anti*, 87% ee).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.98 (t, J = 7.2 Hz, 6H), 1.35-1.62 (m, 7H), 2.38 (br s, 1H, OH), 2.64 (br s, 1H, OH), 3.70-3.97 (m, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz, only the *trans* isomer is described): δ 11.8, 14.0, 18.9, 21.5, 37.9, 45.9, 63.7, 75.4.

IR (ATR): ν 633, 974, 1011, 1334, 1415, 1460, 2874, 2932, 2958, 3362 cm^{-1}.

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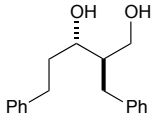
[8] (a) G. Bartoli, M. C. Bellucci, M. Bosco, R. Dalpozzo, E. Marcantoni, L. Sambri, *Chem. Eur. J.* 2000, **6**, 2590. (b) S. Aratake, T. Itoh, T. Okano, T. Usui, M. Shoji, Y. Hayashi. *Chem. Commun.* 2007, 2524.

HRMS (ESI+): *m/z* calcd. for $C_8H_{18}NaO_2$ $[M+Na]^+$:169.1199, found: 169.1198.
$[\alpha]_D^{25}$ = −27.6 (*c* 0.1, CH_2Cl_2); *anti/syn* 60:40, 87% ee.

(2*R*,3*S*)-2-Benzyl-5-phenylpentane-1,3-diol (19)[9]



The title compound was prepared according to the General Procedure 1 using 3-phenylpropanal (60 μL, 0.4 mmol) and **7** (48 mg, *f* = 0.9 mmol/g) in 0.14 mL of water. After purification by flash chromatography with cyclohexane/EtOAc (80:20) as the eluent, compound **19** was isolated in 61% yield (22 mg, 0.081 mmol, colourless oil), *anti*/*syn* 79:21, 96% ee.

The enantiomeric excess was determined by HPLC (Chiralpak IB, hexane/*i*-PrOH/CH_2Cl_2 82:2:16, 1 mL/min, 254 nm): t_R = 18.4 and 25.2 min (*syn*); 21.5 and 24.9 min (*anti*, 96% ee).
The diasteriomeric excess was determined by achiral HPLC (SunFire Prep Silica hexane/*i*-PrOH 95:5, 1 mL/min, 254 nm): t_R = 6.7 min (*anti*) and 7.6 min (*syn*).

General Procedure 2: 70% yield, *anti*/*syn,* 56:44, 73% ee.

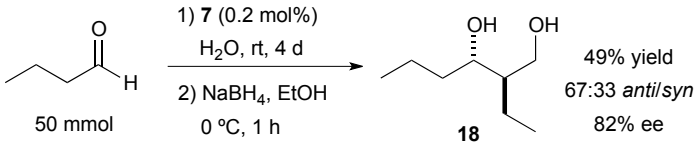
^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.79-1.88 (m, 1H), 1.89-1.99 (m, 2H), 2.0-2.65 (br s, 2H, OH), 2.64-2.69 (m, 2H), 2.74-2.92 (m, 2H), 3.60-3.75 (m, 2H), 3.94 (m, 1H), 7.13-7.30 (m, 10H).
^{13}C NMR ($CDCl_3$, 101 MHz, only the *trans* isomer is described): δ 32.4, 35.1, 37.7, 46.1, 62.9, 74.4, 125.9, 126.1, 128.3 (×2), 128.4 (×2), 128.4 (×2), 129.1 (×2), 140.2, 141.9.
$[\alpha]_D^{25}$ = −11.1 (*c* 0.1, CH_2Cl_2); *anti/syn* 79:21, 96% ee; **lit**.[10b] $[\alpha]_D^{24}$ = −4.7 (*c* 1.0, CH_2Cl_2); *anti/syn* 93:7, 92% ee.

8. Recycling experiments of resin 7

After performing the general procedure for the self-aldol reaction of butanal, the resin **7** was separated by filtration, rinsed with EtOAc (2 × 1 mL), dried *in vacuo* at 40 ºC for 2 h and reused in the next run.

[9] (a) S.-T. Tong, M. A. Brimble, D. Barker, *Tetrahedron* 2009, **65**, 4801. (b) A. Seifert, U. Scheffler, M. Markert, R. Mahrwald. *Org. Lett.* 2010, **12**, 1660.

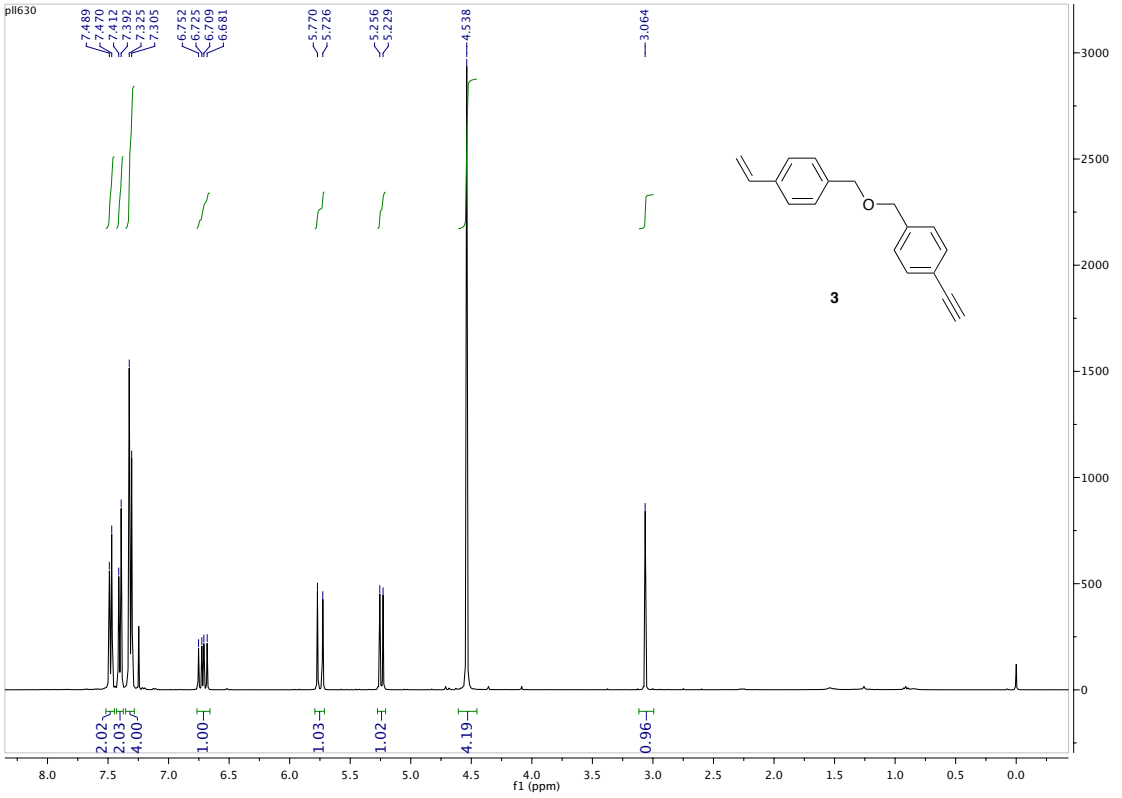
9. Scale-up of the self-aldol reaction of butanal

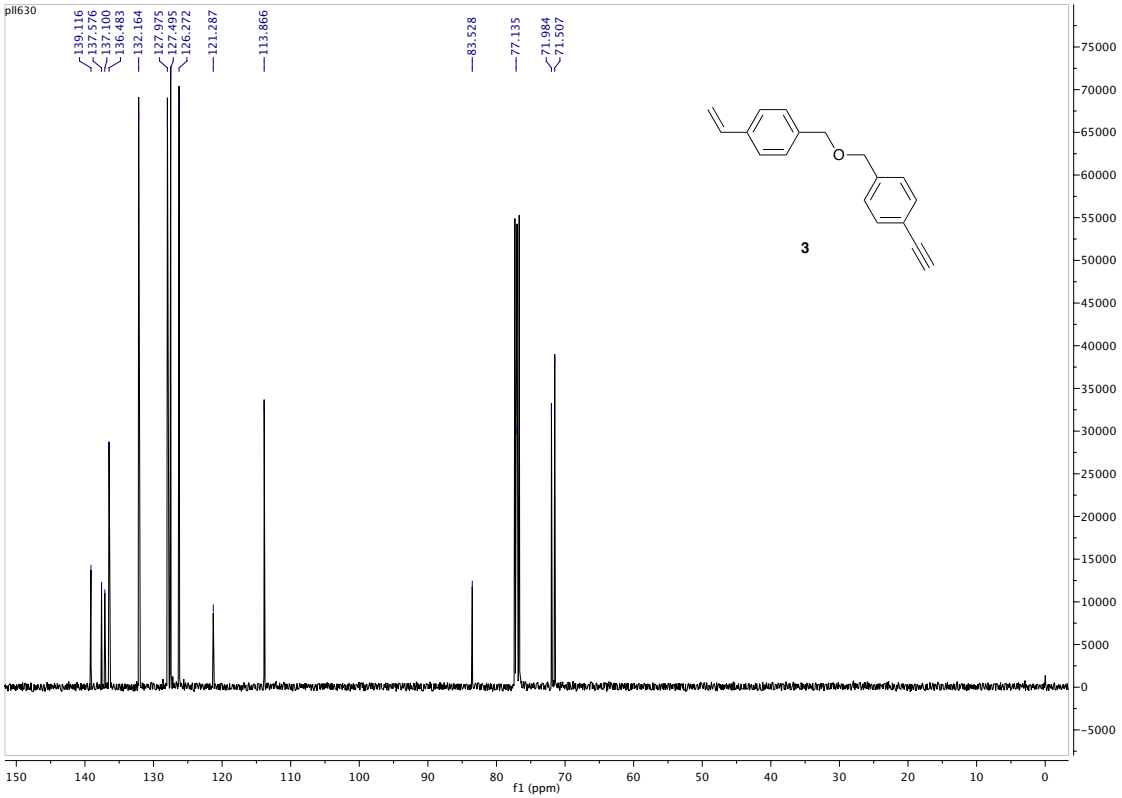


Resin **7** (173 mg, 0.2 mol%, f = 0.6 mmol g^{-1}) was placed in a vial and swollen in water (0.3 mL). Then, butanal (4.5 mL, 50 mmol) was added and the reaction mixture was stirred at room temperature for 4 days. After that, the resin was separated by filtration and rinsed with EtOAc (2 × 5 mL). The solution containing the crude product was treated with a cooled suspension of $NaBH_4$ (40 mmol) in EtOH (10 mL) at 0 ºC. One hour later, the reaction was diluted with water (20 mL) and extracted with EtOAc (5 × 10 mL). After drying with Na_2SO_4, solvents were removed *in vacuo*. The diastereomeric ratio of diols was determined by ^{1}H NMR analysis of the crude mixture. After purification by flash chromatography on silica gel, compound **18** was isolated as a mixture of diastereomers in 49% yield (1.17 g, 8 mmol).

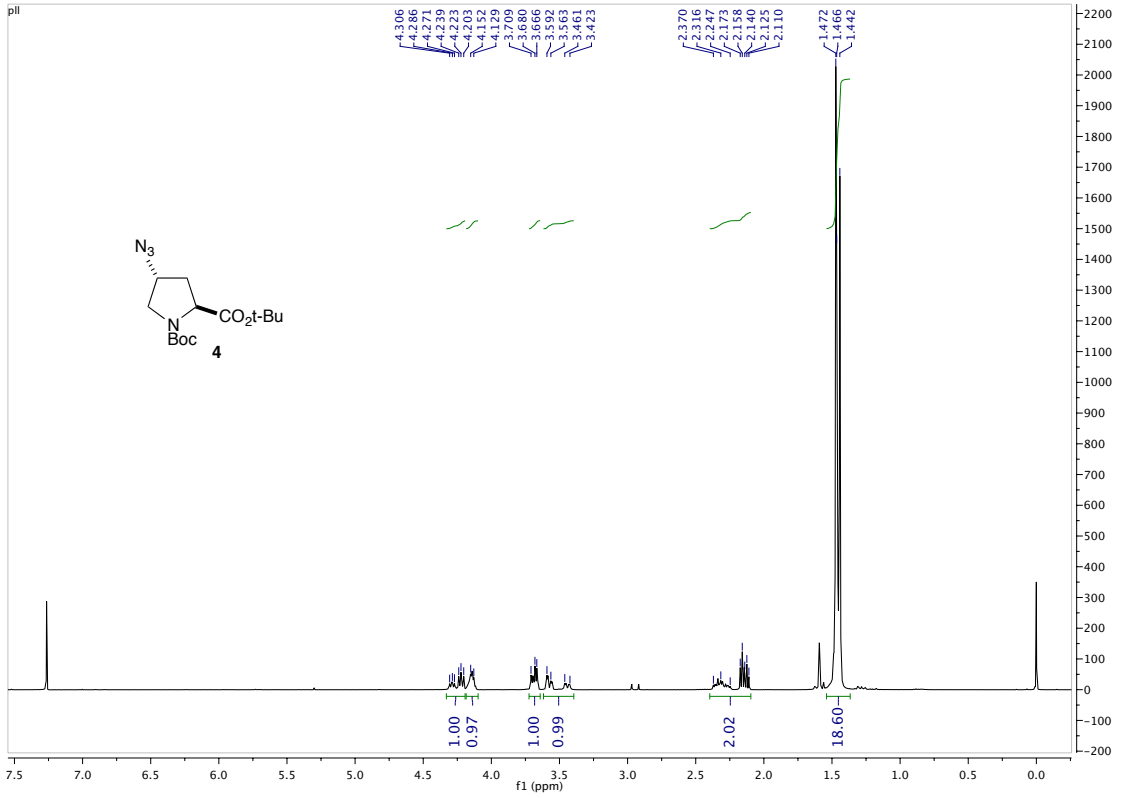
10. NMR spectra and HPLC chromatograms for compounds 3-5, 8-19

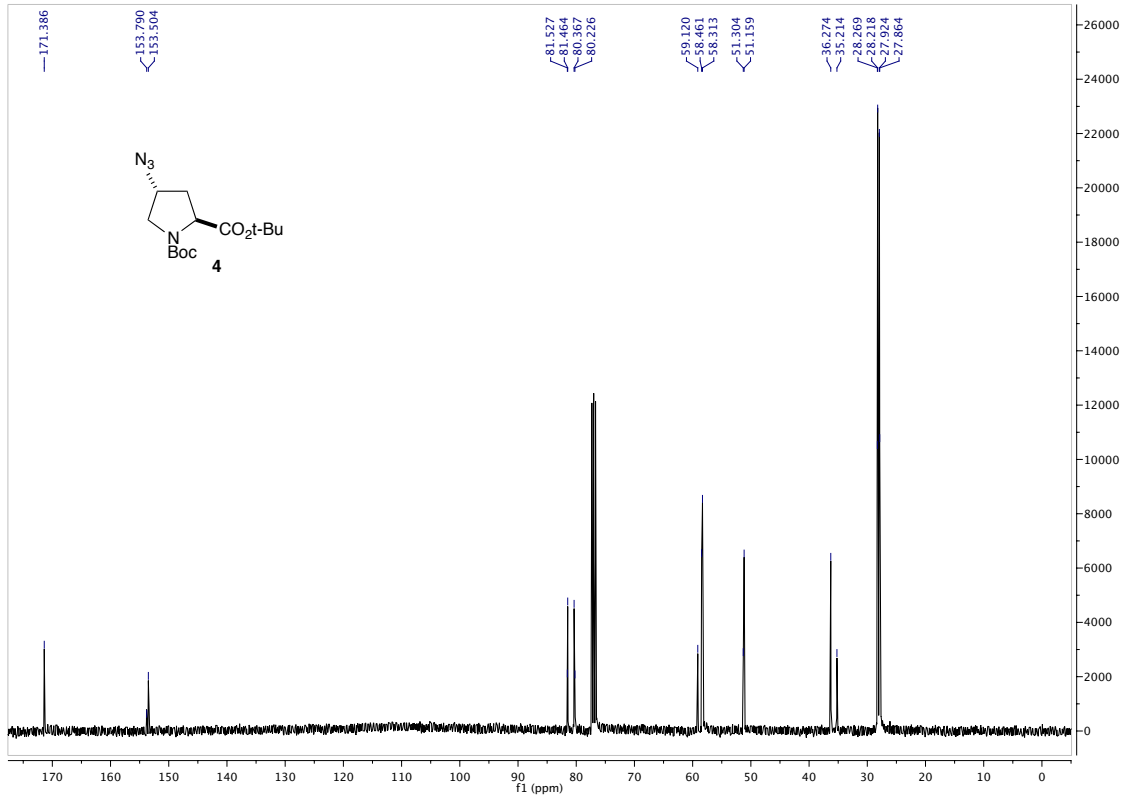
1-Ethynyl-4-(((4-vinylbenzyl)oxy)methyl)benzene (3)



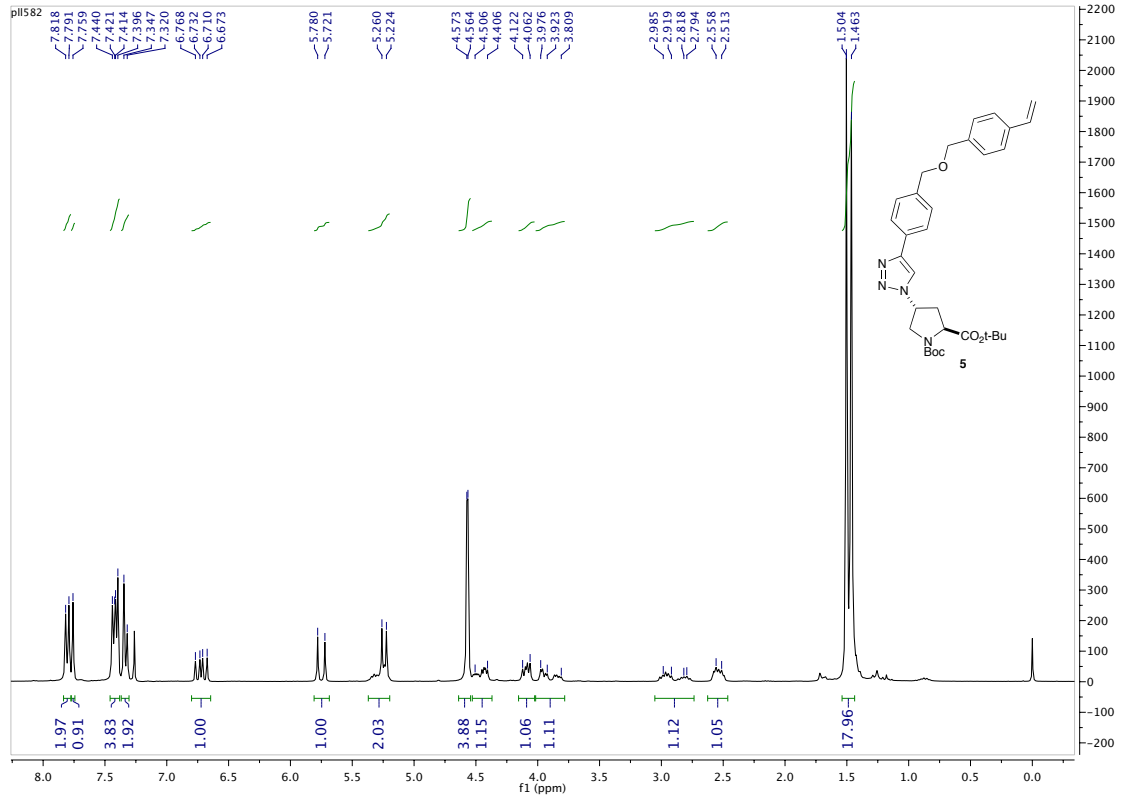


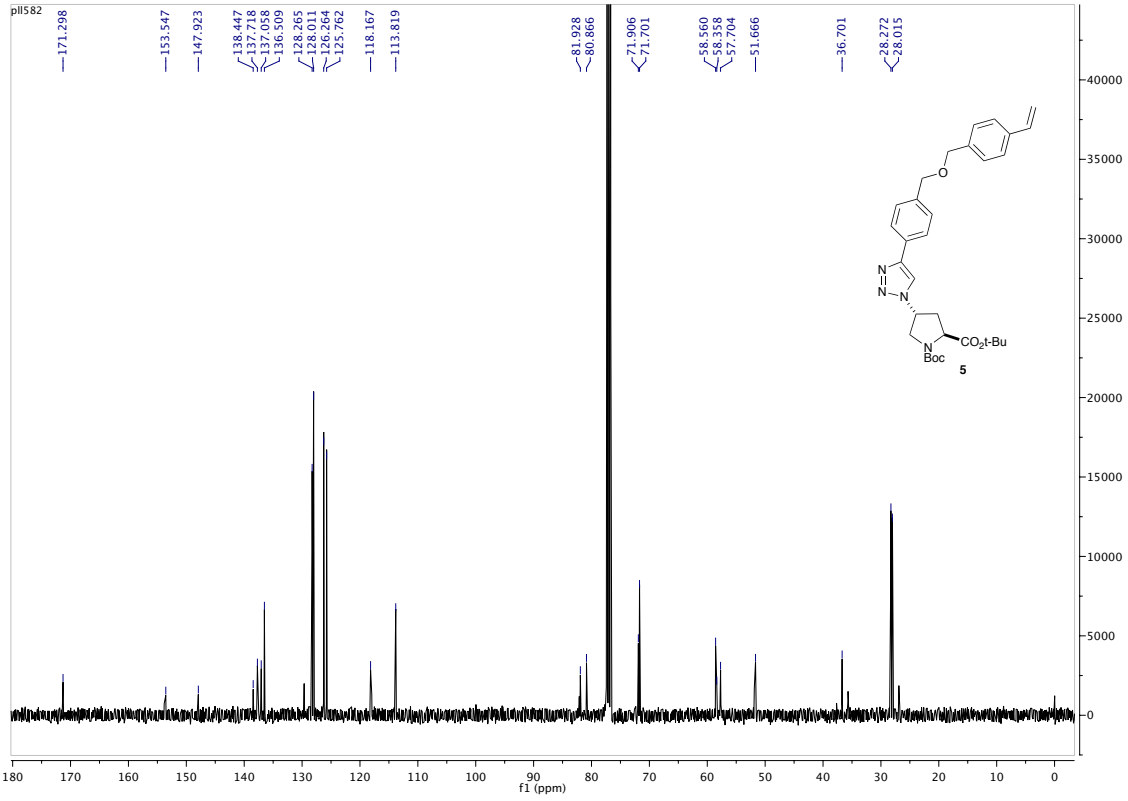
(2*S*,4*R*)-di-*tert*-Butyl 4-azidopyrrolidine-1,2-dicarboxylate (4)



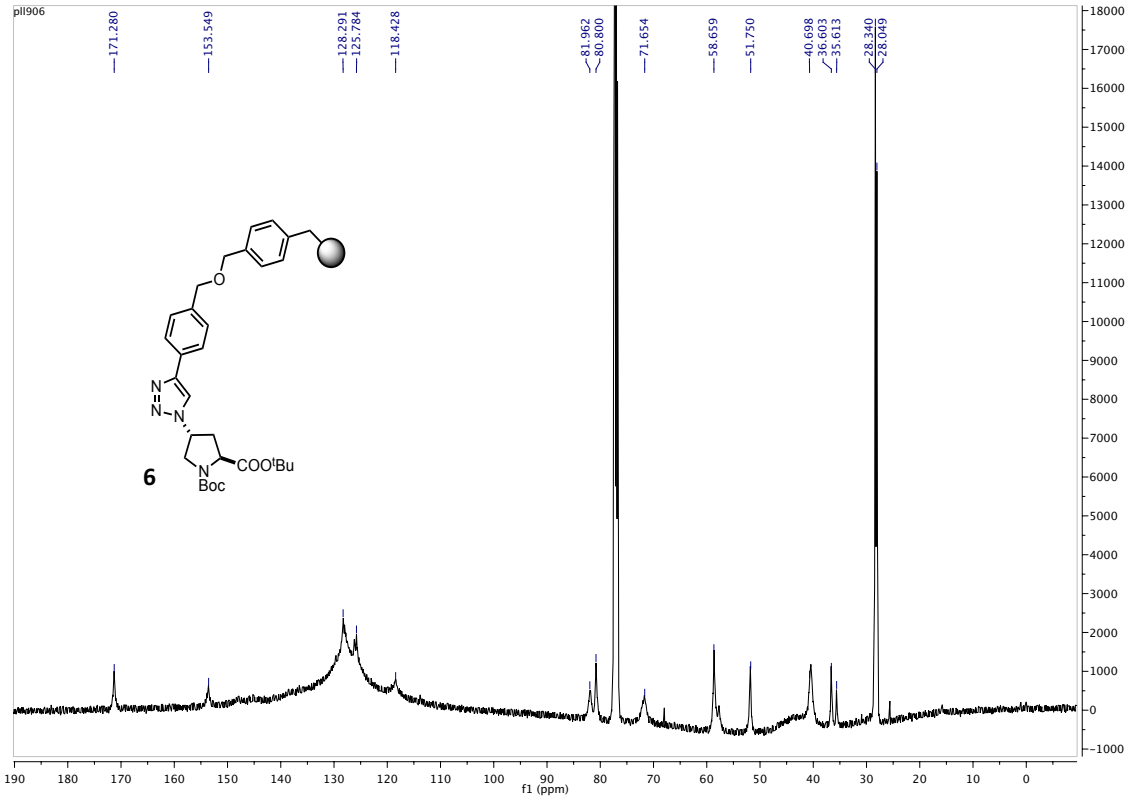


(2*S*,4*R*)-di-*tert*-Butyl 4-(4-(4-(((4-vinylbenzyl)oxy)methyl)phenyl)-1H-1,2,3-triazol-1-yl)pyrrolidine-1,2-dicarboxylate (5)

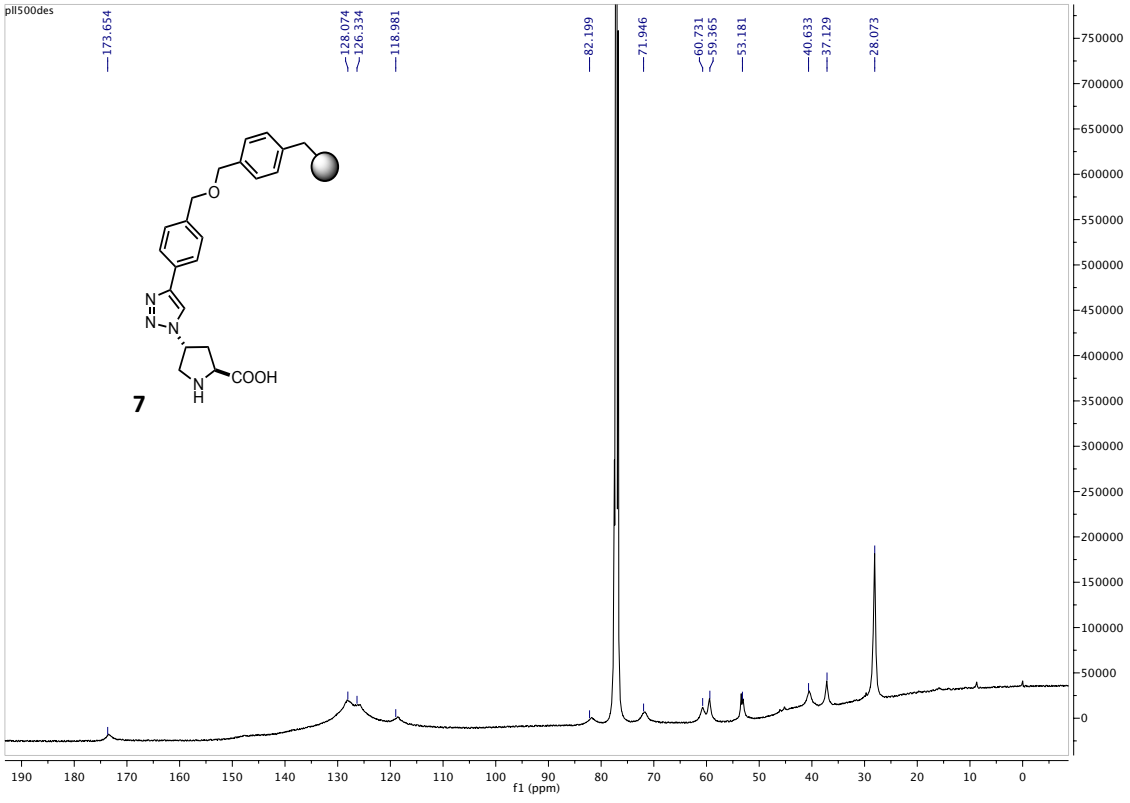




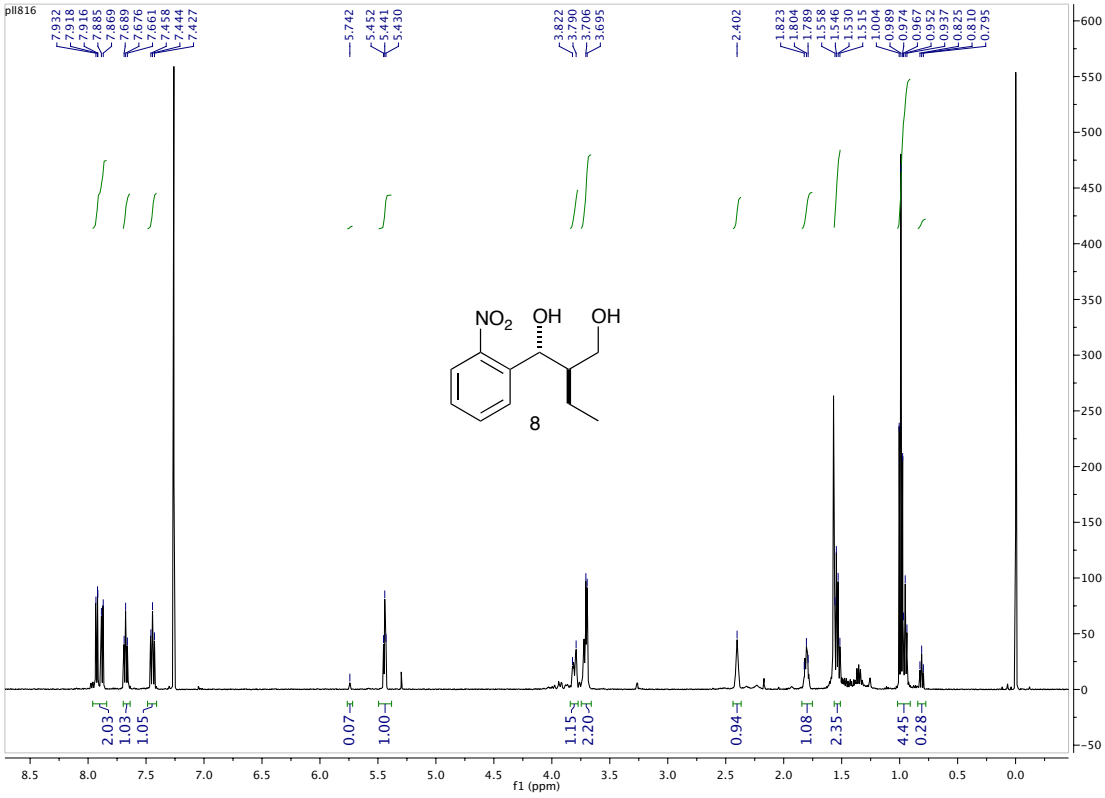
Resin 6

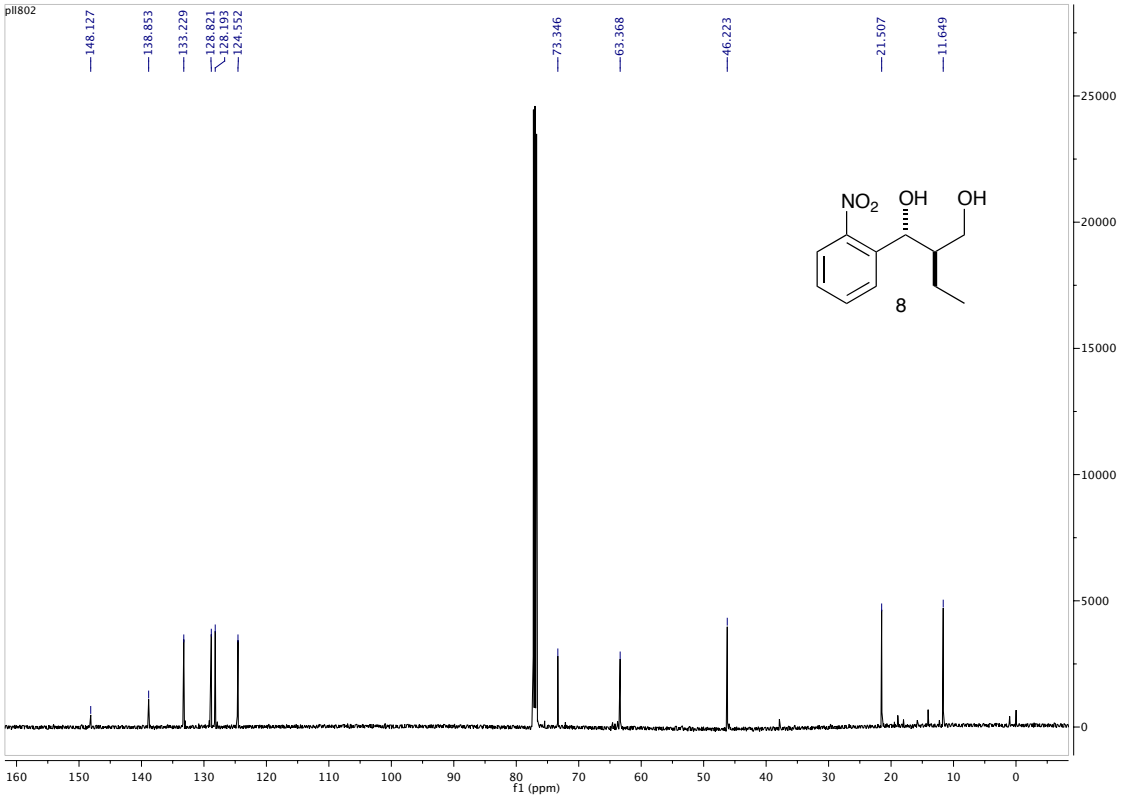


Resin 7

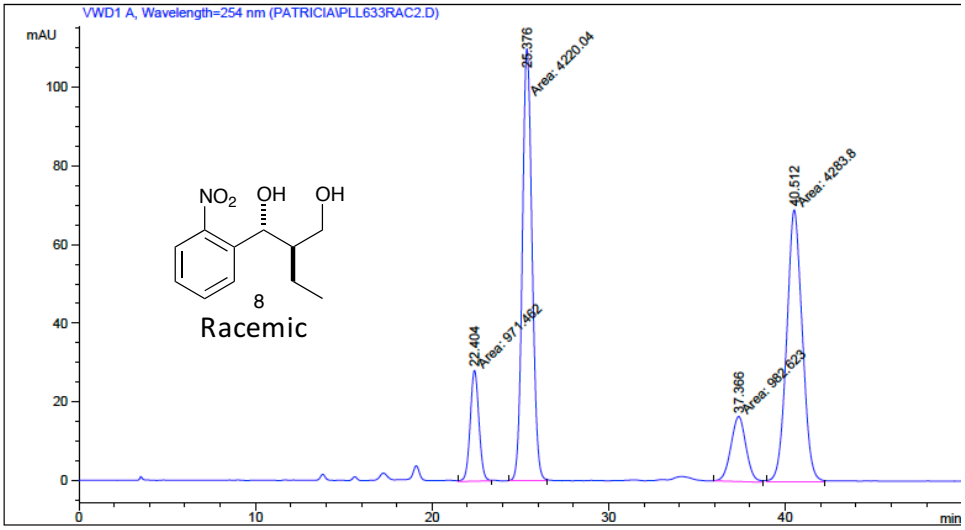


(1*R*,2*R*)-2-Ethyl-1-(2-nitrophenyl)propane-1,3-diol (8)

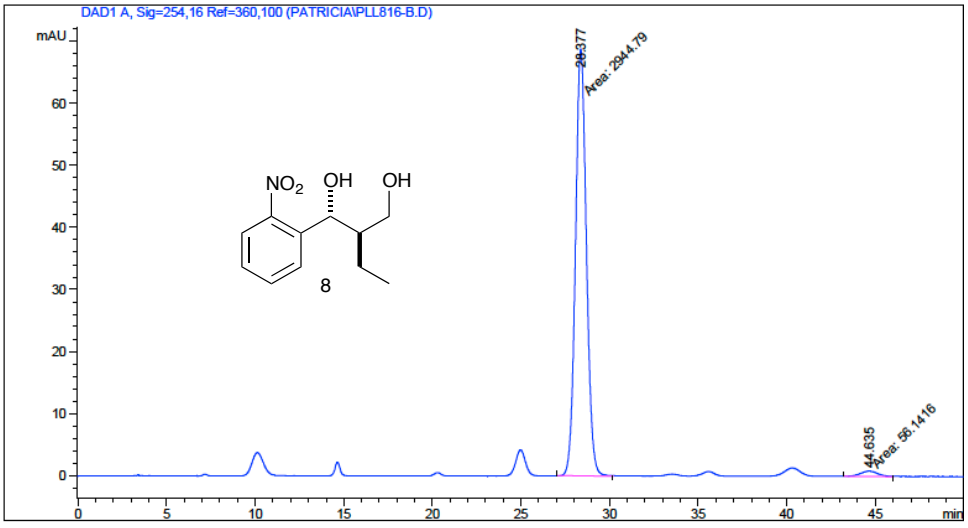




Diol 8. IC, Hex/IPA (95:5), 254 nm, 1 mL/min

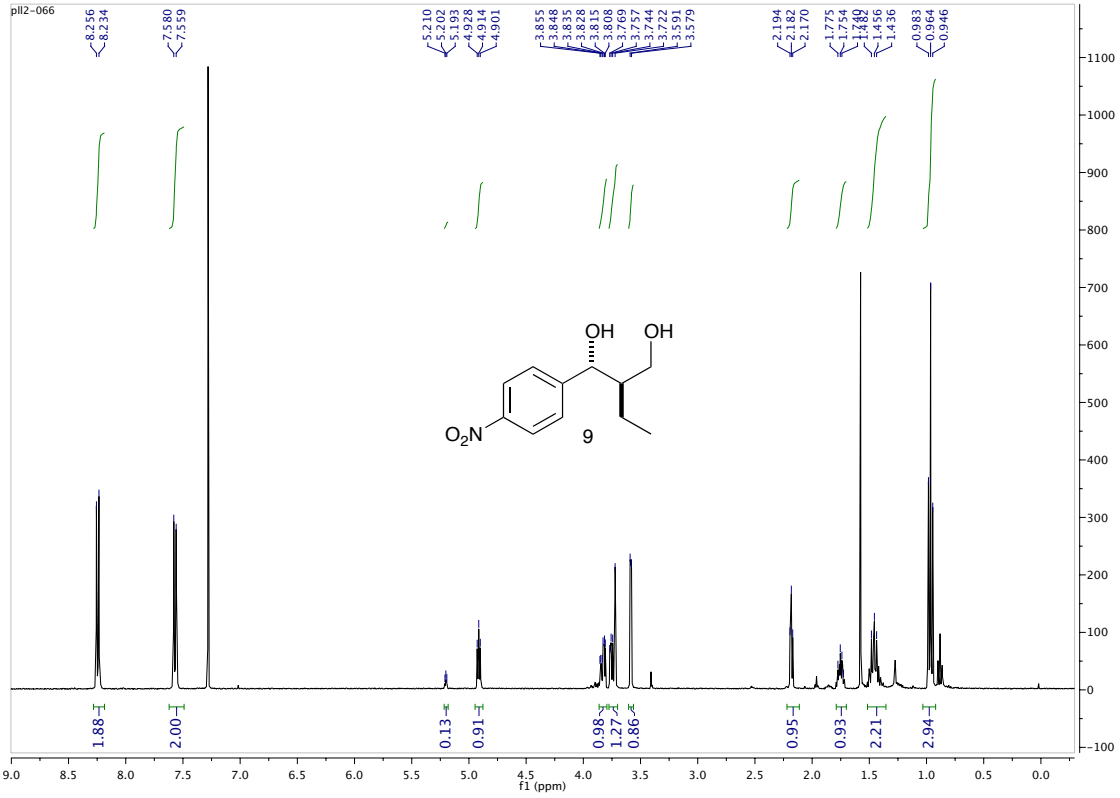


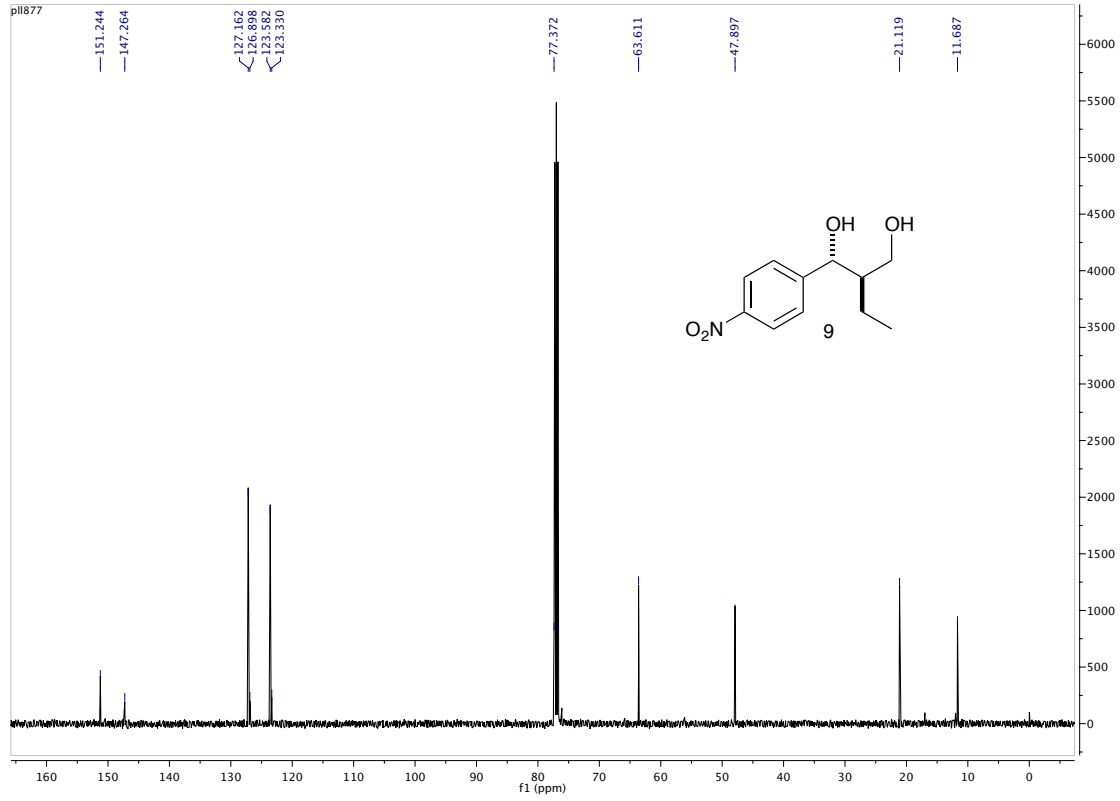
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.404	MM	0.5741	971.46234	28.20341	9.2892
2	25.376	MM	0.6400	4220.03955	109.90191	40.3526
3	37.366	MM	0.9896	982.62329	16.54923	9.3960
4	40.512	MM	1.0305	4283.79883	69.28139	40.9622
Totals :				1.04579e4	223.93594	



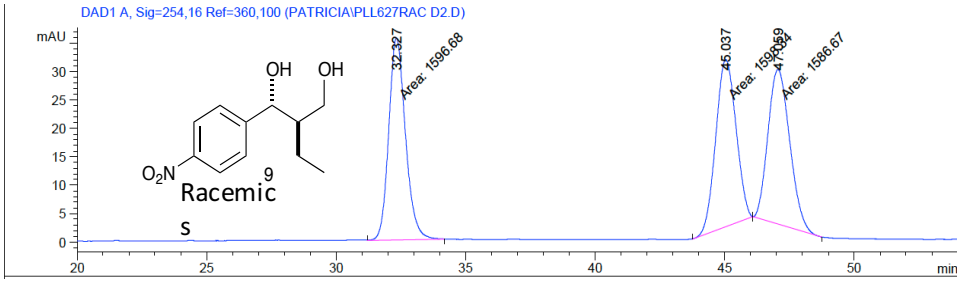
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.377	MM	0.7149	2944.79395	68.65749	98.1292
2	44.635	MM	1.1085	56.14158	8.44089e-1	1.8708

(1*R*,2*R*)-2-Ethyl-1-(4-nitrophenyl)propane-1,3-diol (9)



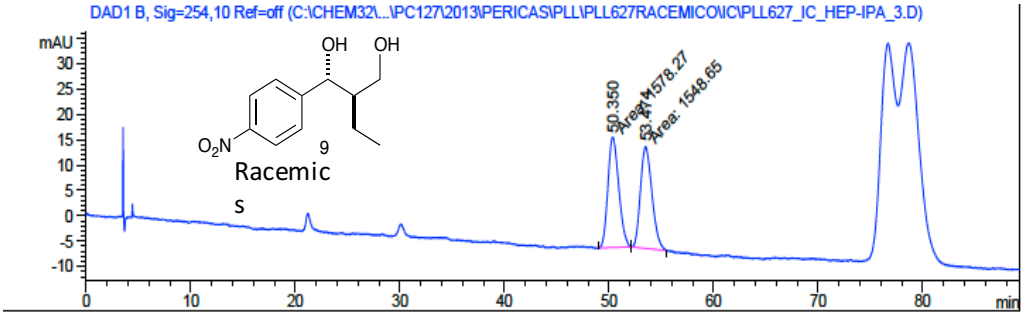


(9) IC, Hex:THF (92:8) 254 nm 1 mL/min (*anti*)

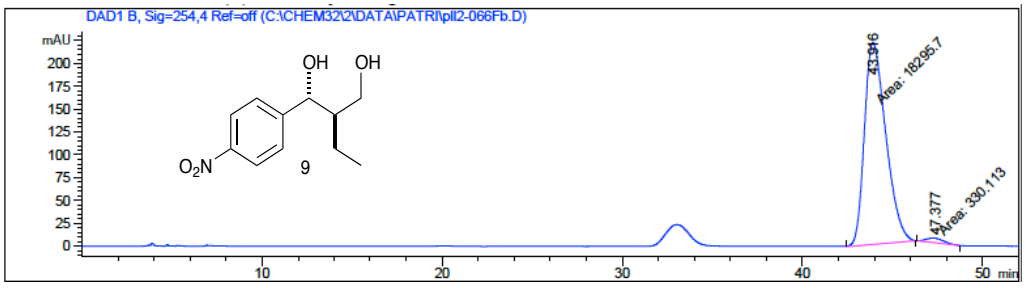


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.327	MM	0.7486	1596.68054	35.54654	33.3916
2	45.037	MM	0.9054	1598.33887	29.42275	33.4263
3	47.059	MM	0.9729	1586.66760	27.18021	33.1822

IC, Hex:IPA (97:3) 254 nm 1 mL/min (*syn*)

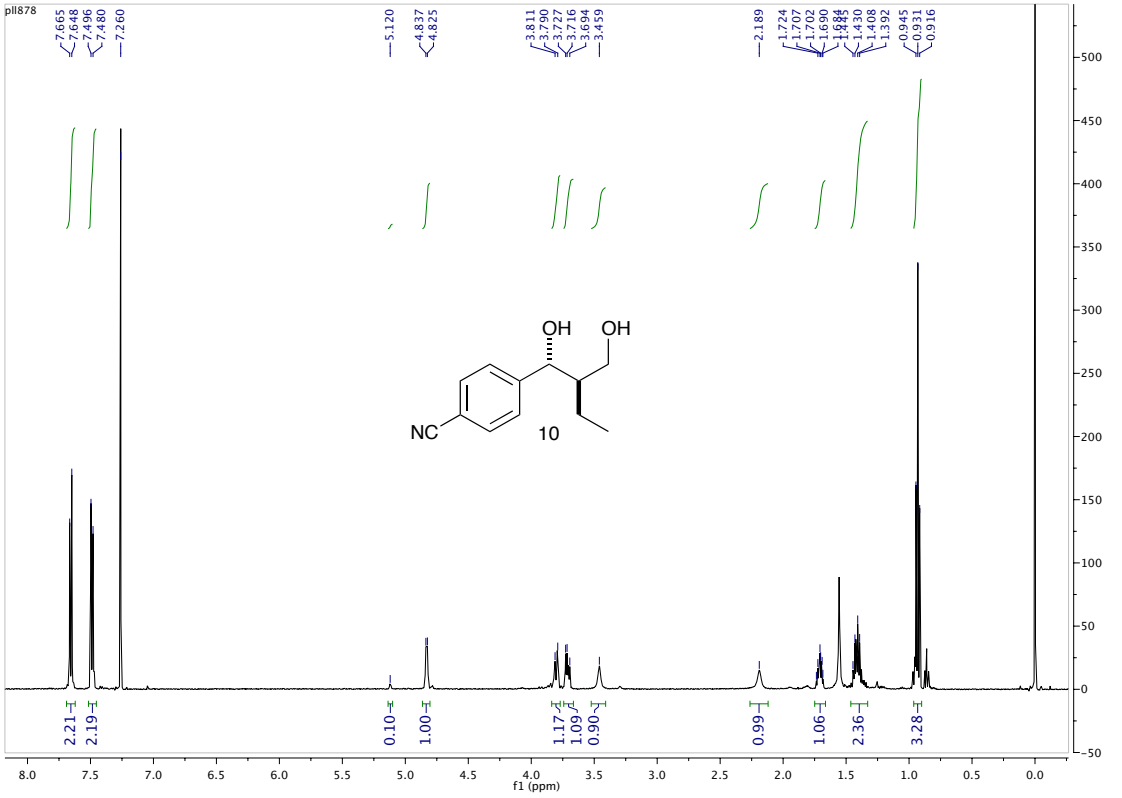


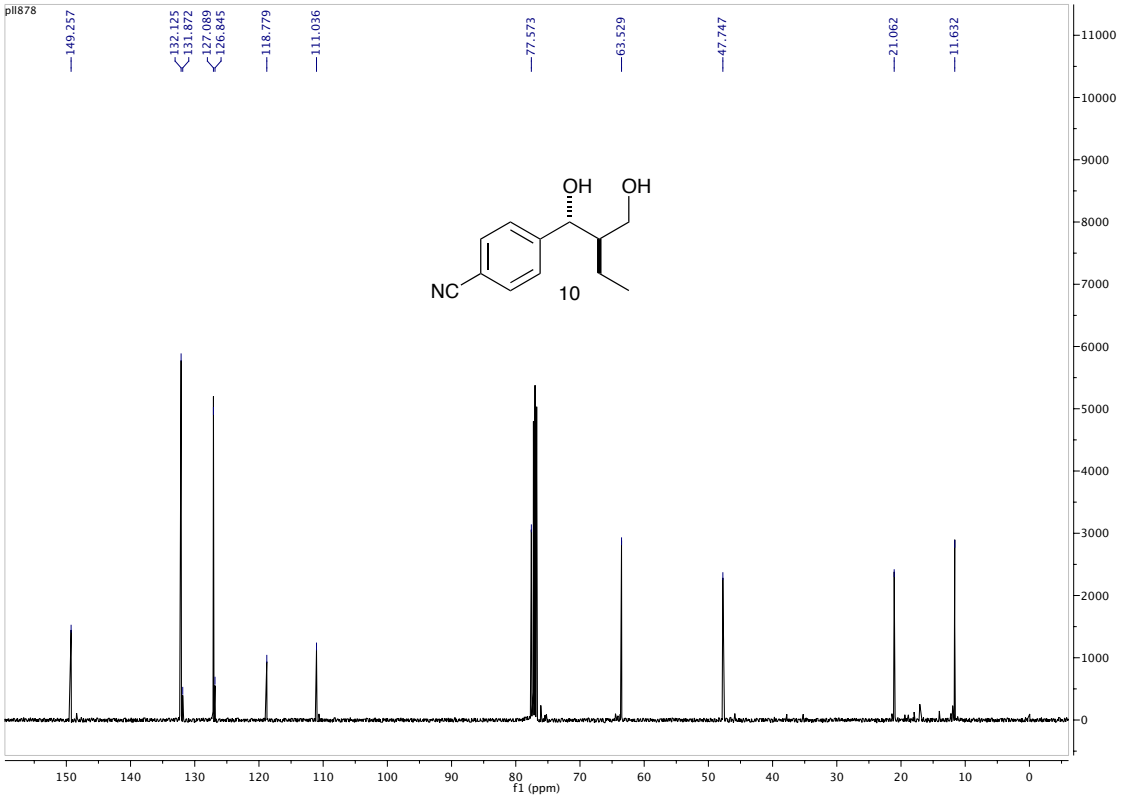
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.350	MM	1.2061	1578.26733	21.80905	50.4736
2	53.474	MM	1.2824	1548.65173	20.12679	49.5264
Totals :				3126.91907	41.93585	



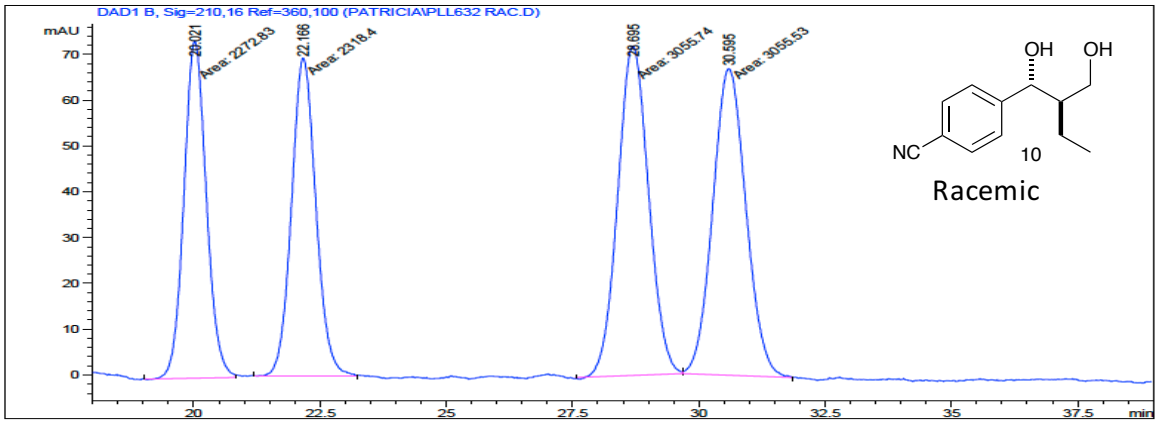
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.916	MM	1.3774	1.82957e4	221.37424	98.2277
2	47.377	MM	1.0804	330.11334	5.09263	1.7723
Totals :				1.86258e4	226.46687	

4-((1*R*,2*R*)-1-Hydroxy-2-(hydroxymethyl)butyl)benzonitrile (10)

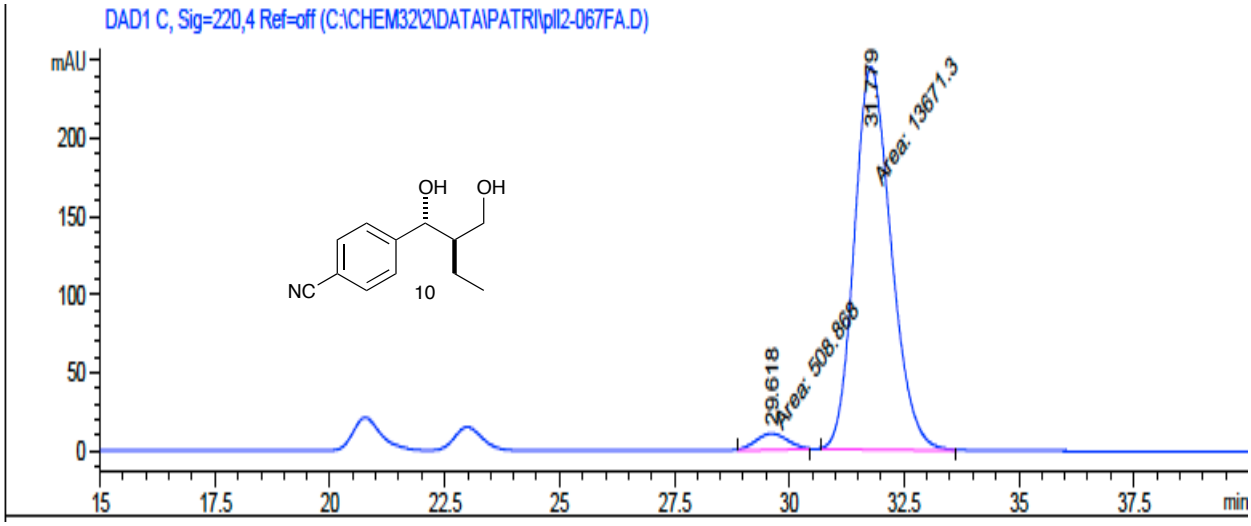




Diol 10. IC, Hex/IPA (93:7), 220 nm, 1 mL/min

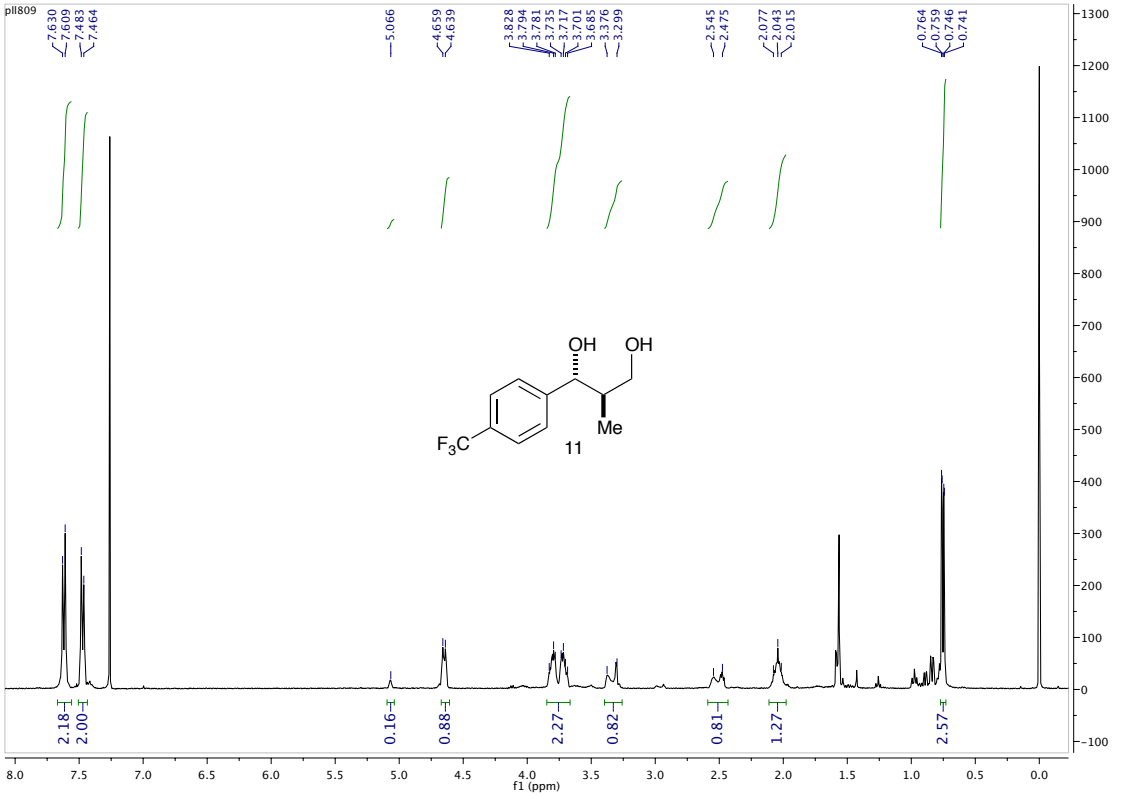


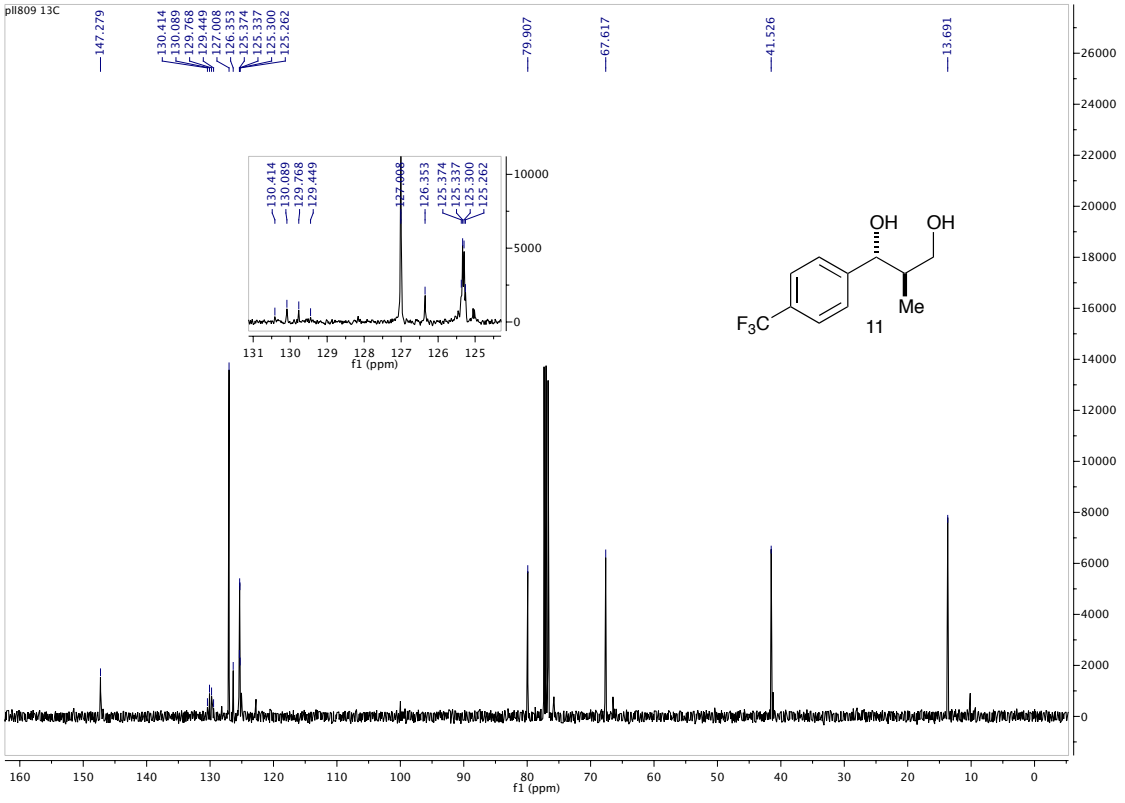
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.021	MM	0.5149	2272.83154	73.57178	21.2364
2	22.166	MM	0.5575	2318.40356	69.30641	21.6623
3	28.695	MM	0.7079	3055.73584	71.94269	28.5516
4	30.595	MM	0.7609	3055.53369	66.92465	28.5497



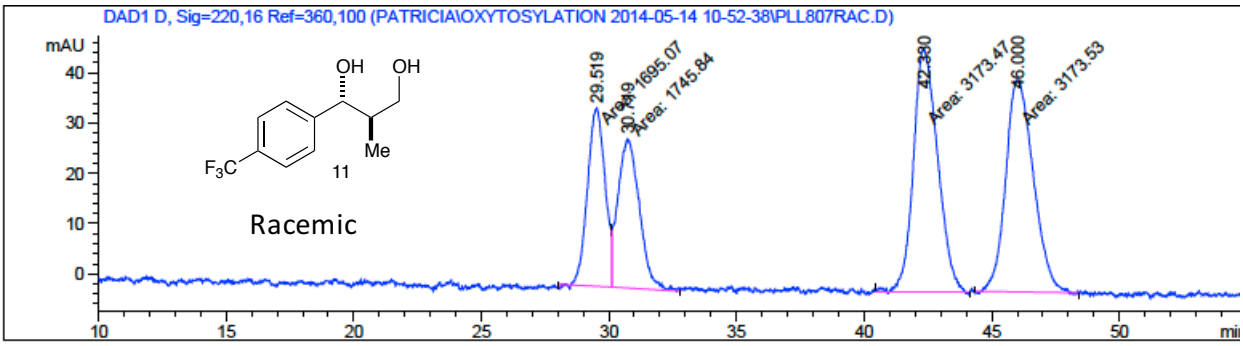
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.618	MM	0.8123	508.86823	10.44109	3.5886
2	31.779	MM	0.9299	1.36713e4	245.04491	96.4114
Totals :				1.41802e4	255.48600	

(1*R*,2*R*)-2-Methyl-1-(4-(trifluoromethyl)phenyl)propane-1,3-diol (11)

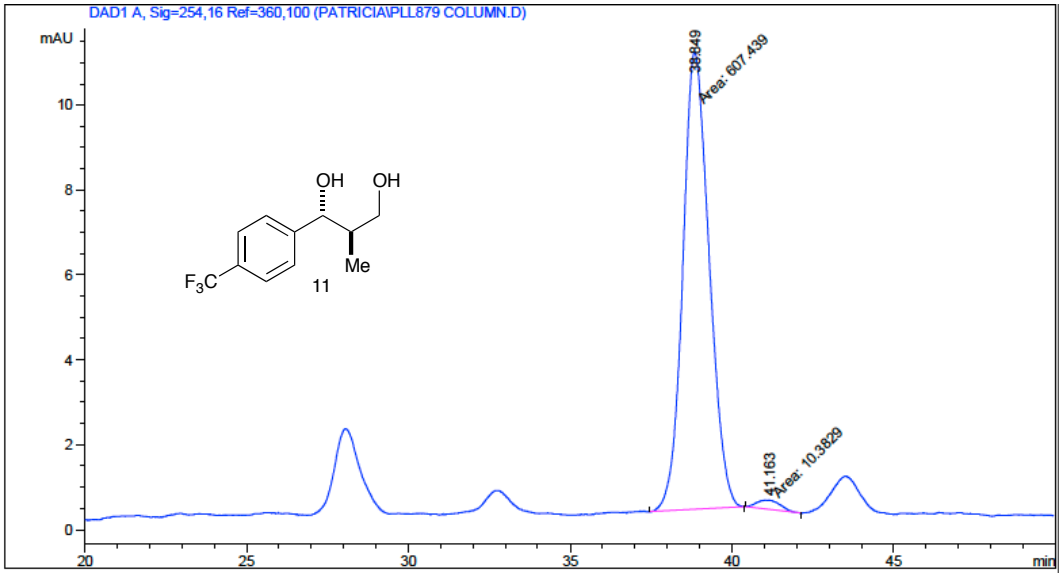




Diol 11. IC, Hex/IPA/CH_2Cl_2 (82:1:17), 254nm, 1 mL/min

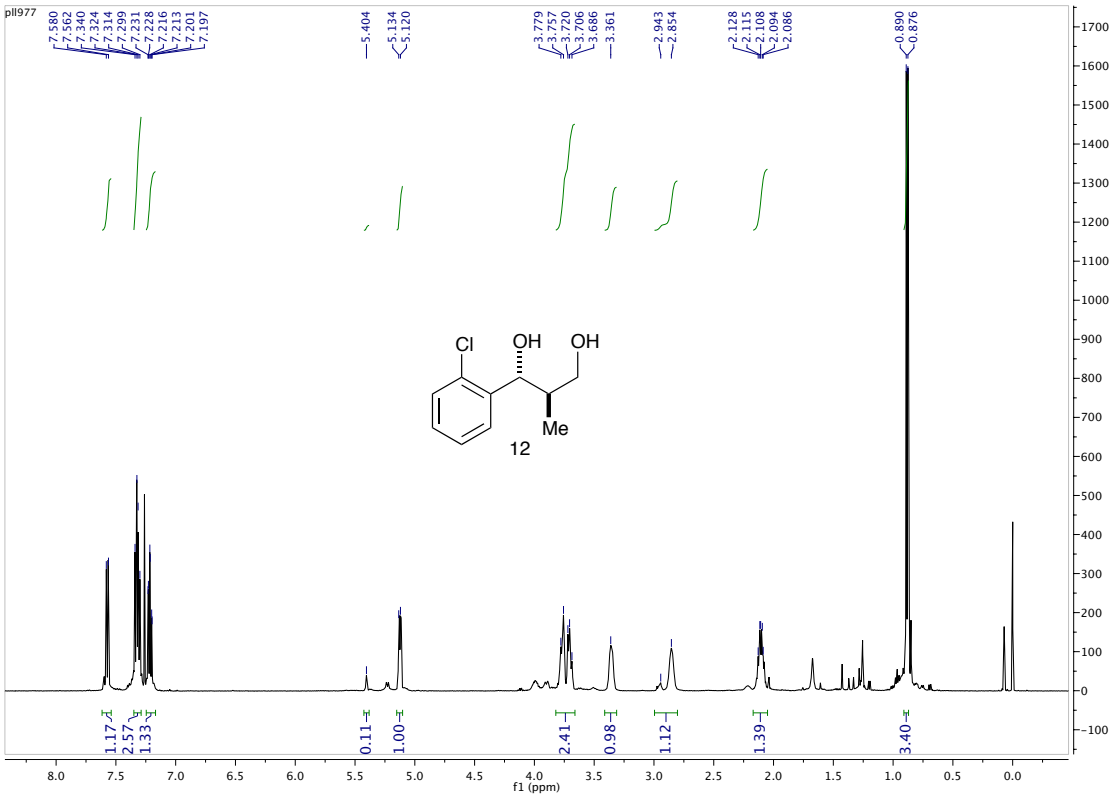


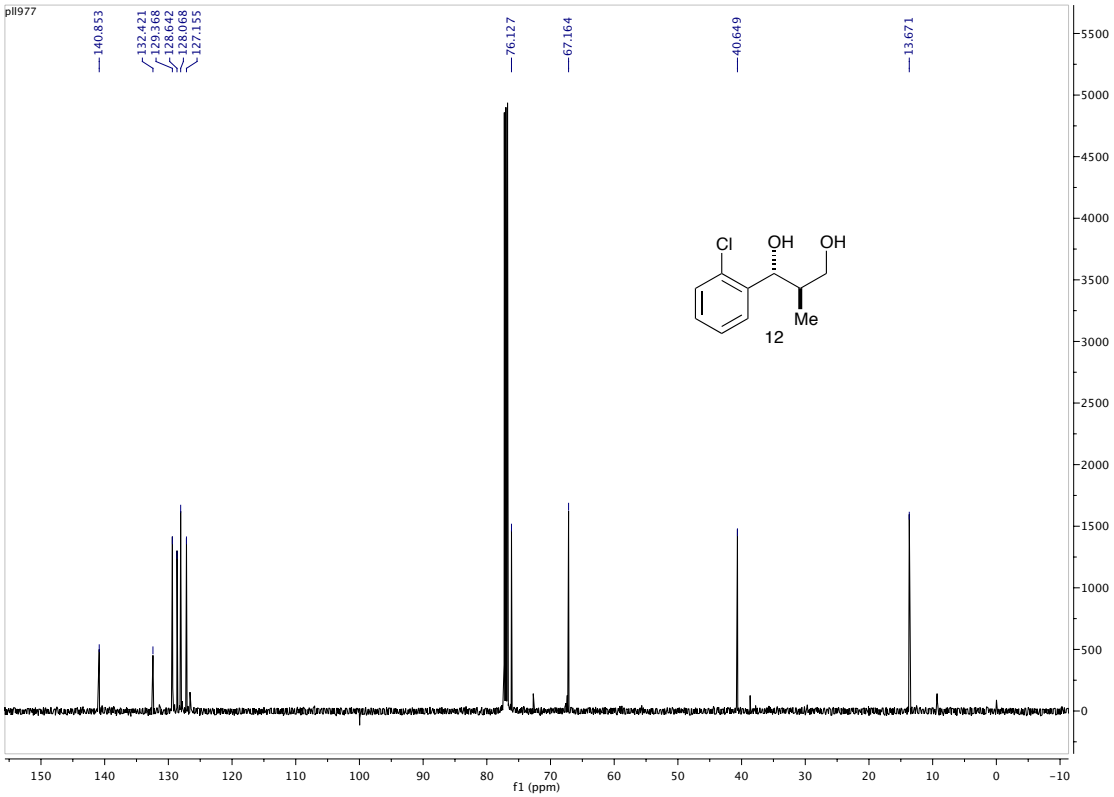
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.519	MF	0.7963	1695.07336	35.47699	17.3180
2	30.719	FM	0.9799	1745.84241	29.69554	17.8367
3	42.330	MM	1.0950	3173.46826	48.30040	32.4223
4	46.000	MM	1.2553	3173.52588	42.13657	32.4229
Totals :				9787.90991	155.60950	



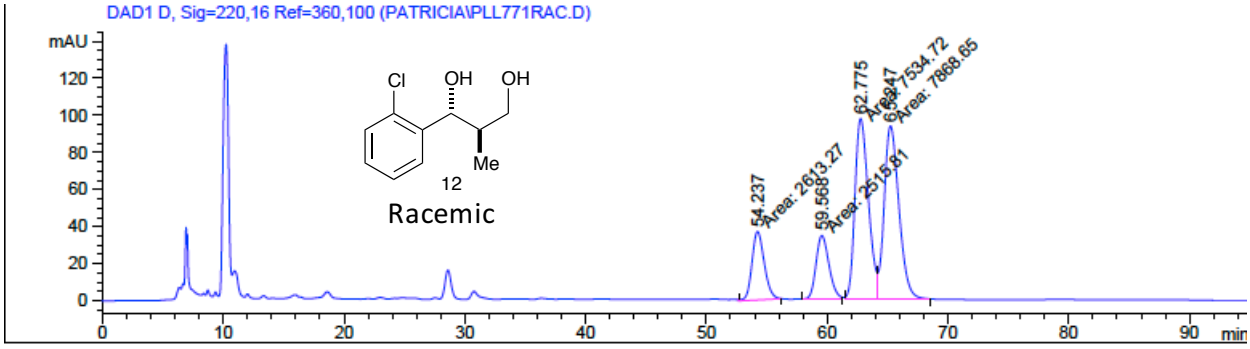
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.849	MM	0.9421	607.43872	10.74634	98.3194
2	41.163	MM	0.8043	10.38288	2.15152e-1	1.6806

(1*R*,2*R*)-1-(2-Chlorophenyl)-2-methylpropane-1,3-diol (12)

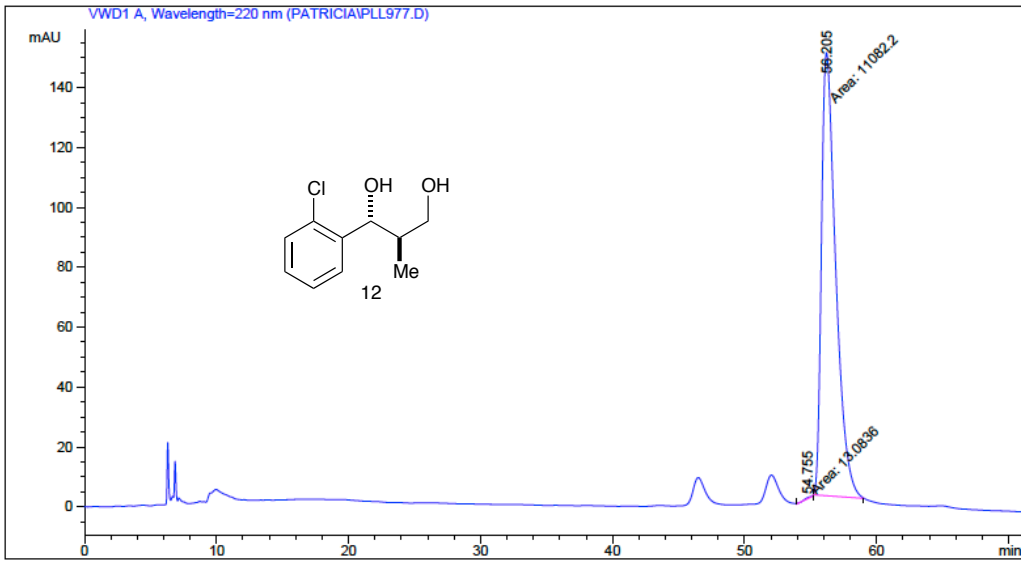




Diol 12. IB, Hex/IPA (98:2), 220 nm, 0.5 mL/min

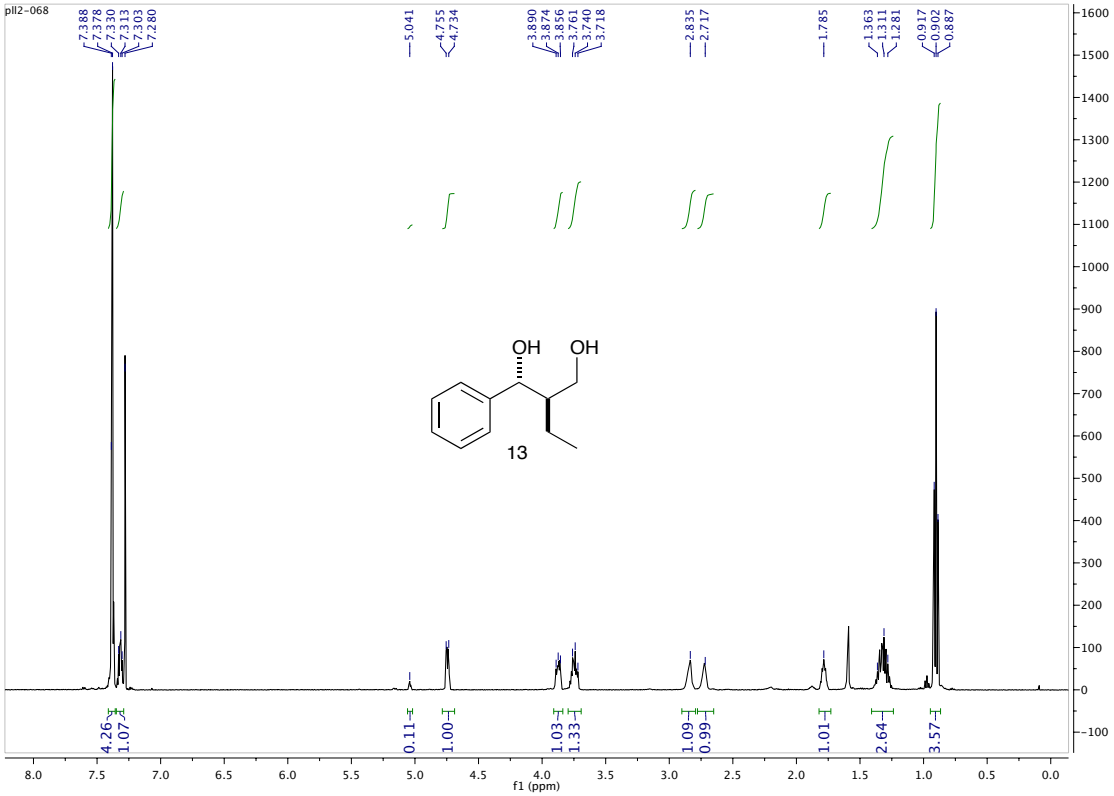


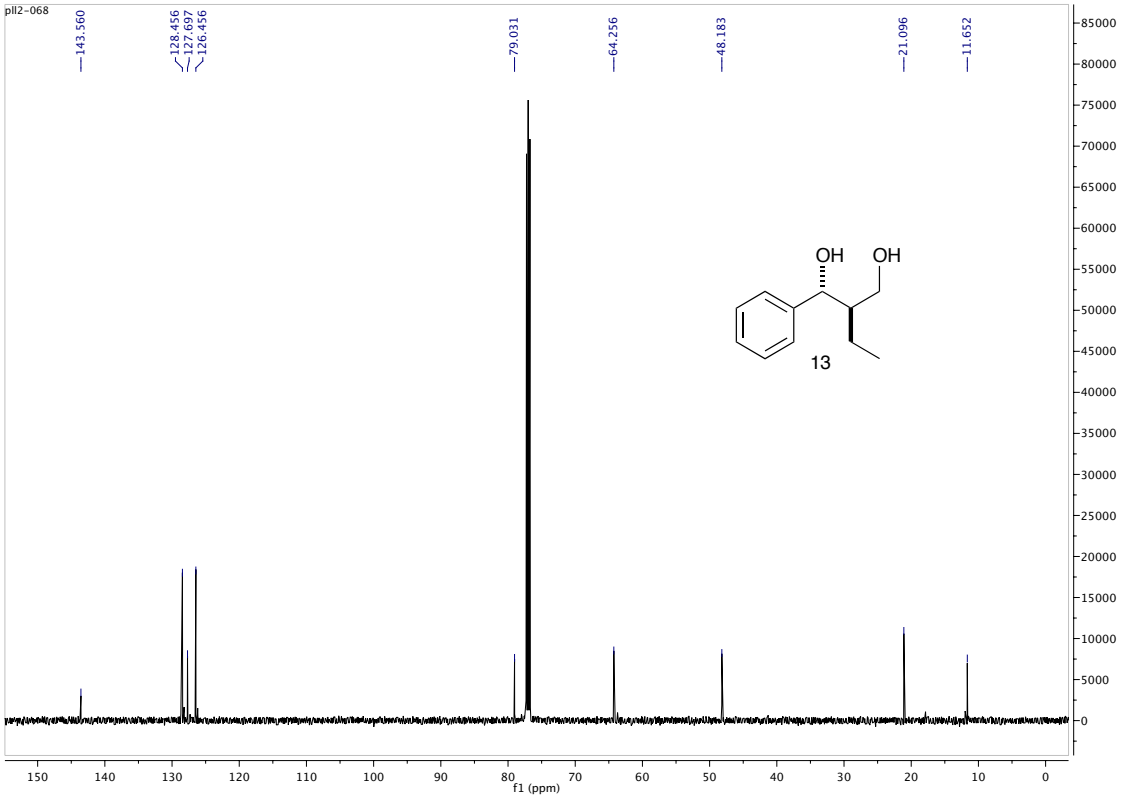
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	54.237	MM	1.1817	2613.26807	36.85831	12.7275
2	59.568	MM	1.2319	2515.80981	34.03756	12.2528
3	62.775	MF	1.2931	7534.72168	97.11120	36.6967
4	65.247	FM	1.4089	7868.64795	93.08503	38.3230
Totals :				2.05324e4	261.09210	



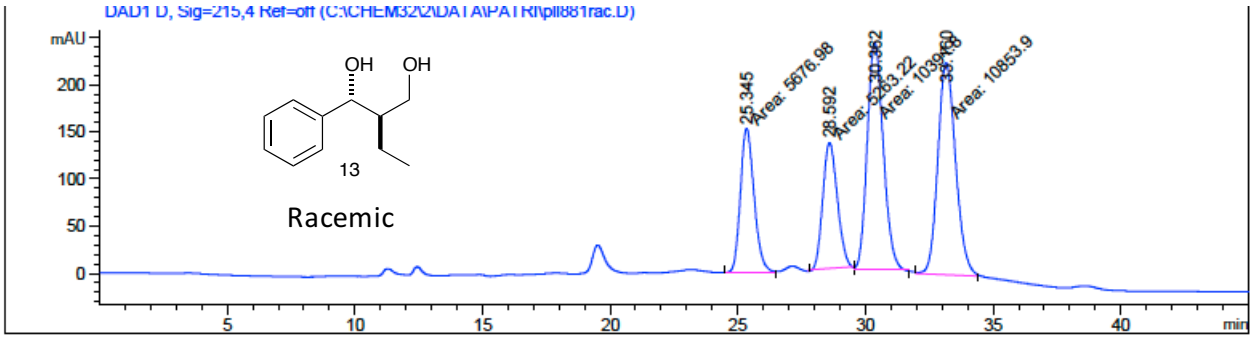
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	54.755	MM	0.6097	13.08359	3.57633e-1	0.1179
2	56.205	MM	1.2489	1.10822e4	147.89011	99.8821

(1*R*,2*R*)-2-Ethyl-1-phenylpropane-1,3-diol (13)

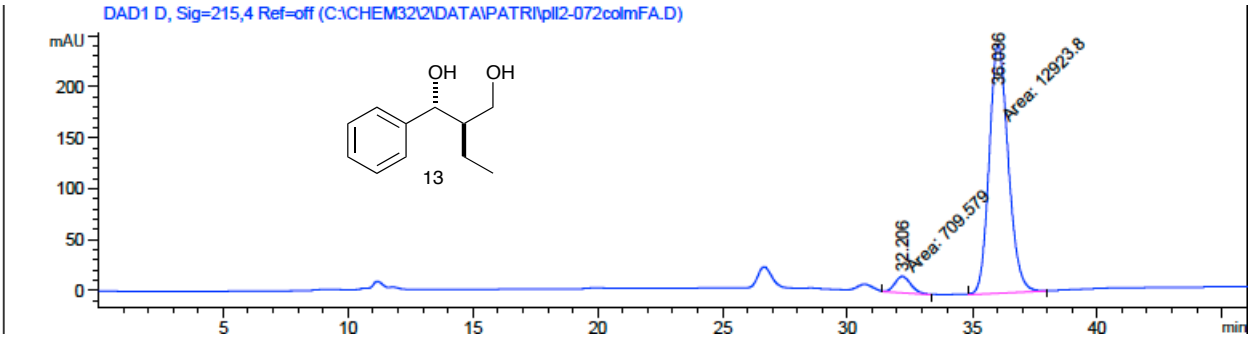




Diol 13. IC, Hex/IPA (90:10), 215 nm, 0.3 mL/min

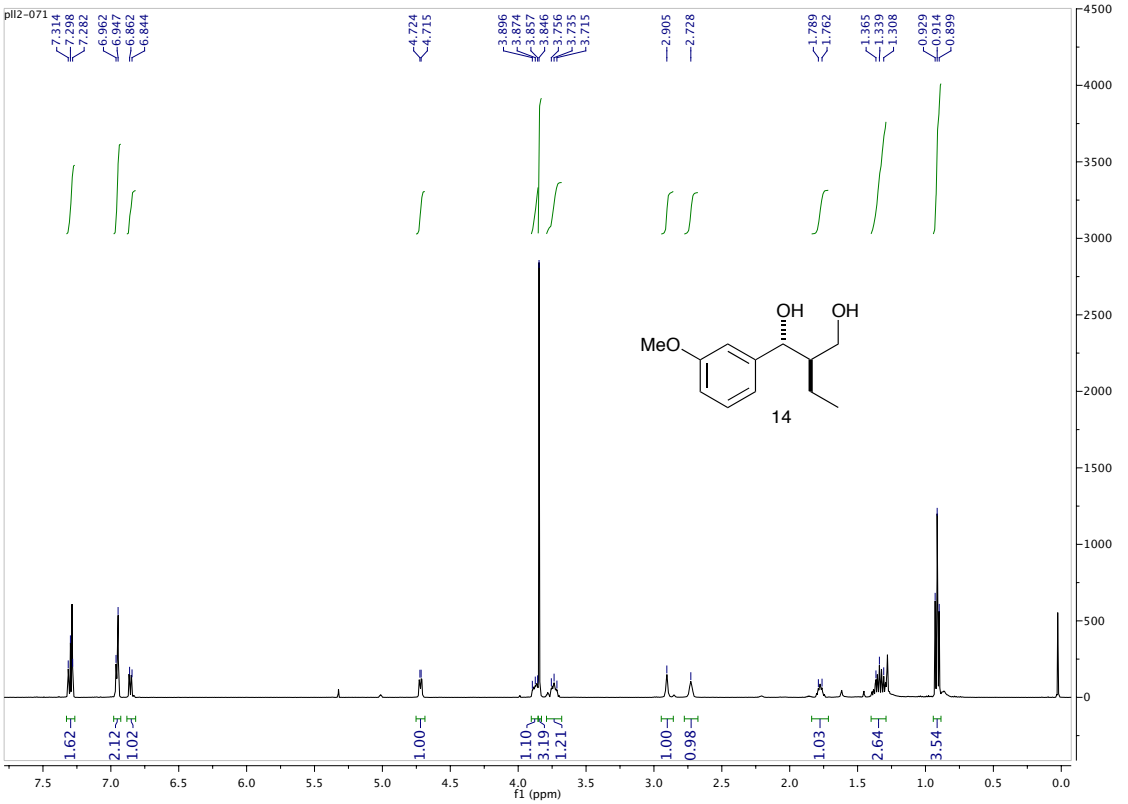


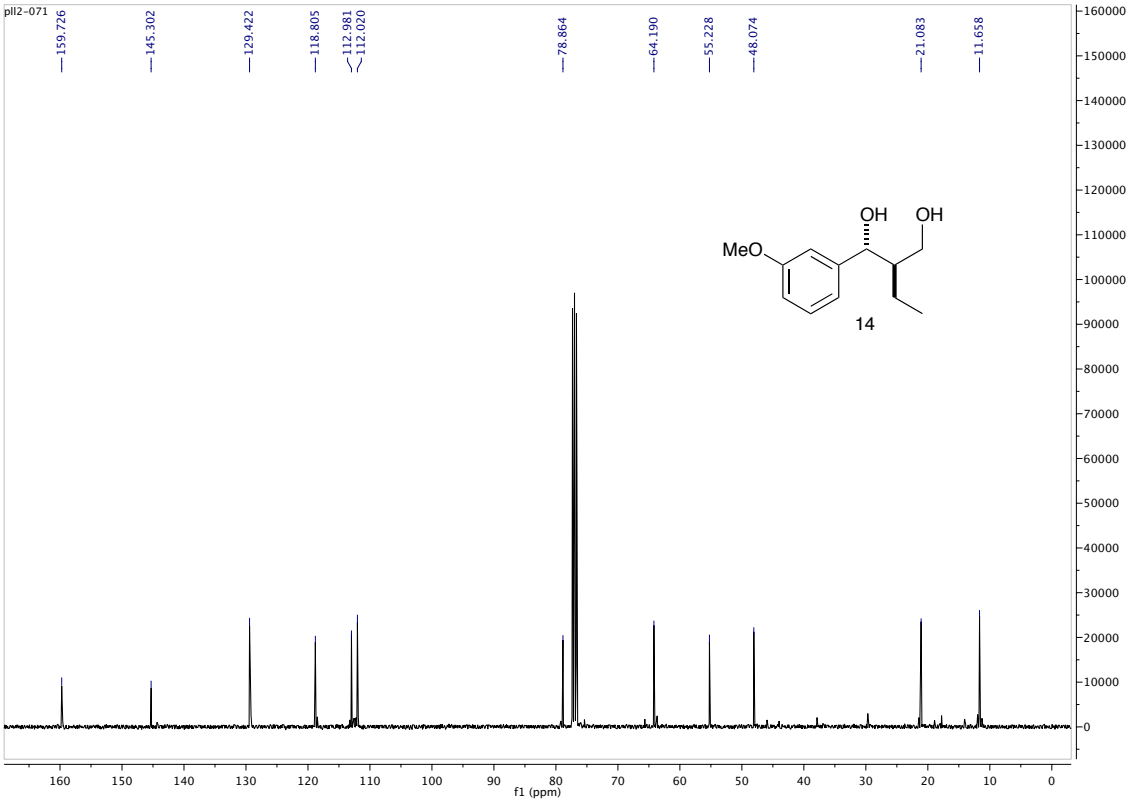
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.345	MM	0.6211	5676.97754	152.33017	17.6381
2	28.592	MM	0.6587	5263.21533	133.17528	16.3525
3	30.362	MM	0.7228	1.03918e4	239.61218	32.2869
4	33.160	MM	0.8059	1.08539e4	224.46213	33.7225
Totals :				3.21859e4	749.57976	



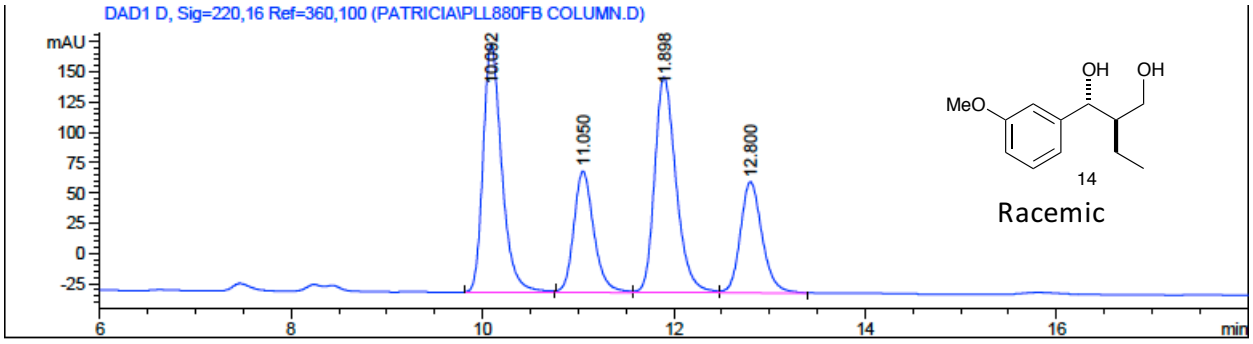
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.206	MM	0.7426	709.57922	15.92507	5.2047
2	36.036	MM	0.8830	1.29238e4	243.92601	94.7953

(1*R*,2*R*)-2-Ethyl-1-(3-methoxyphenyl)propane-1,3-diol (14)



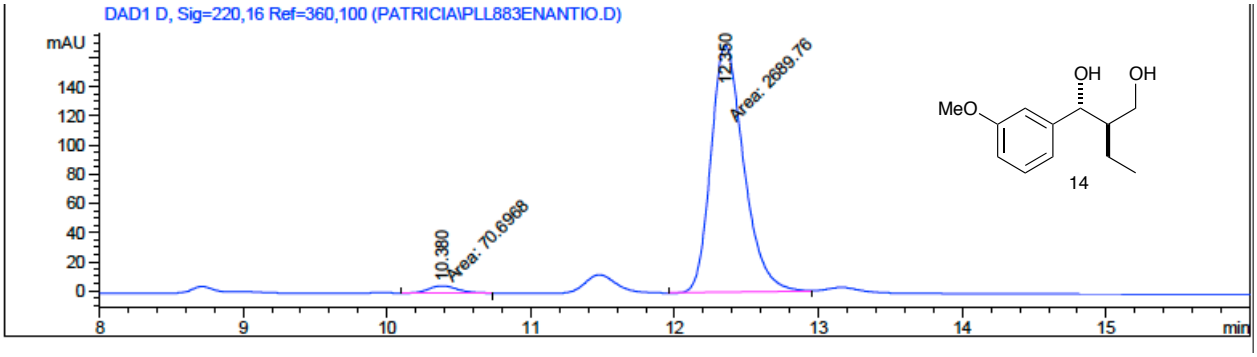


Diol 14. IB, Hex/IPA (90:10), 220 nm, 1 mL/min



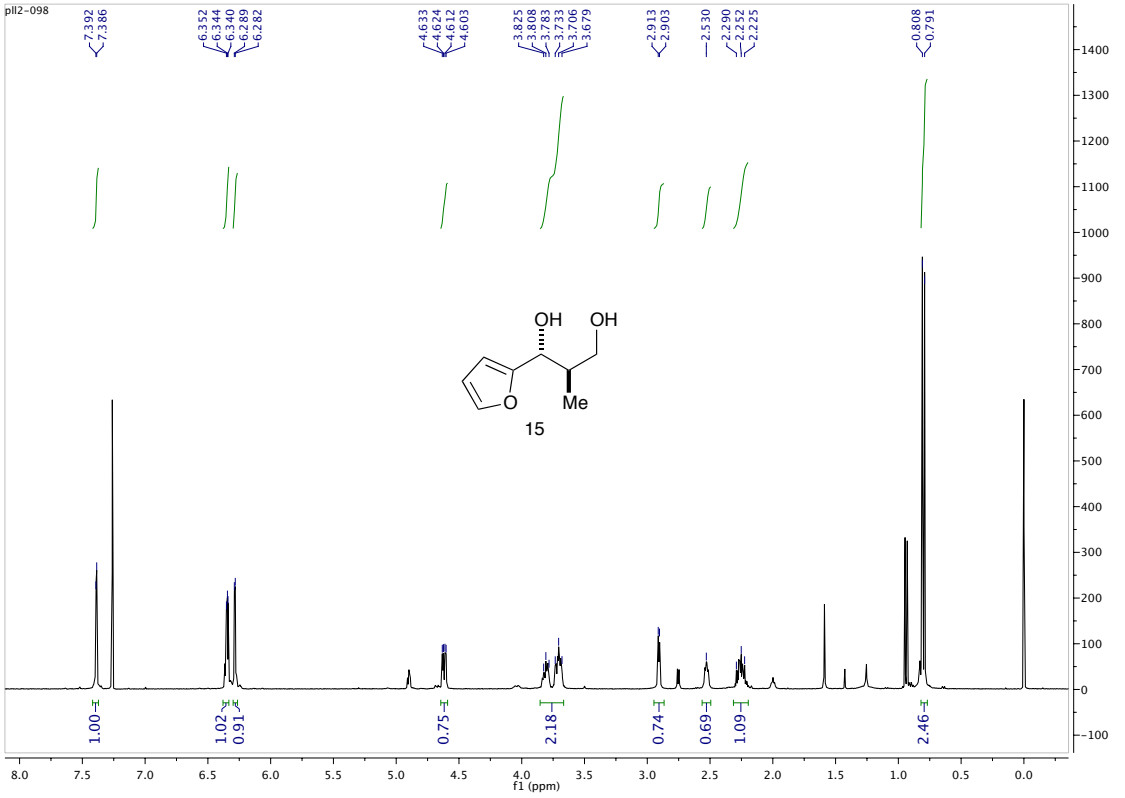
Signal 2: DAD1 D, Sig=220,16 Ref=360,100

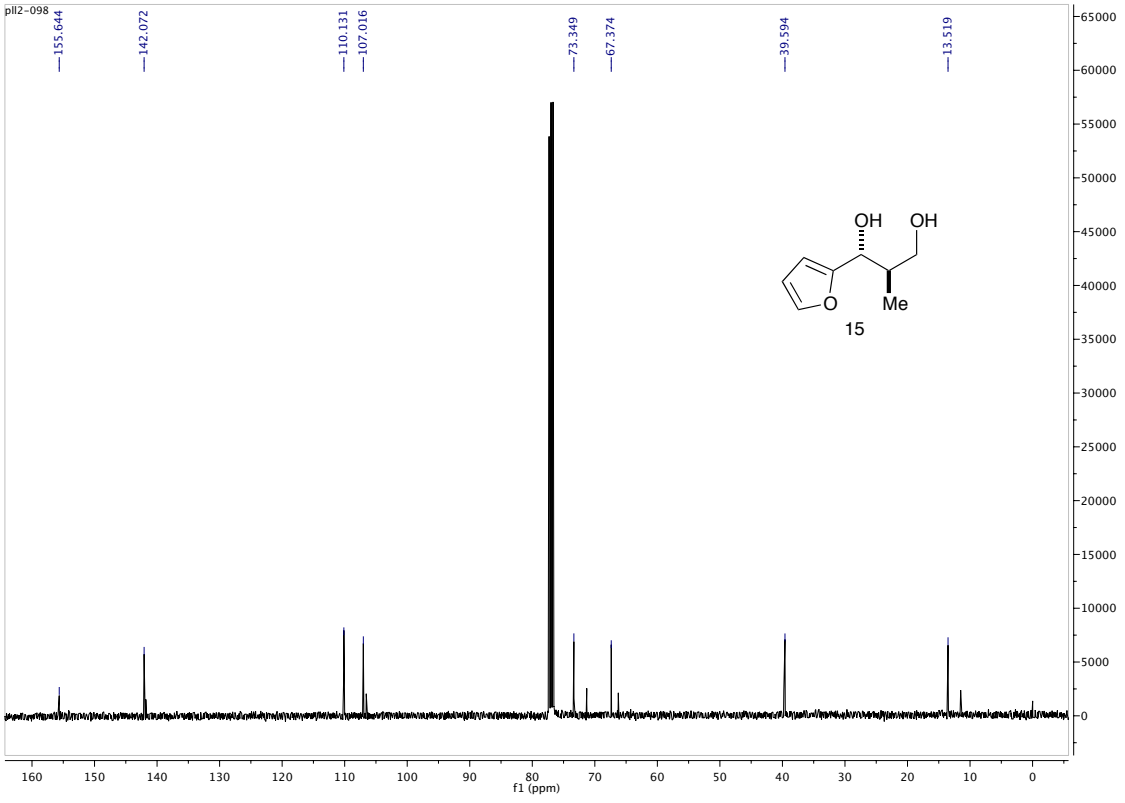
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.092	BB	0.2083	2769.79907	204.17961	32.7805
2	11.050	BV	0.2221	1458.24011	99.98925	17.2582
3	11.898	VV	0.2397	2768.81030	177.75703	32.7688
4	12.800	VB	0.2426	1452.69519	91.80216	17.1926
Totals :				8449.54468	573.72806	



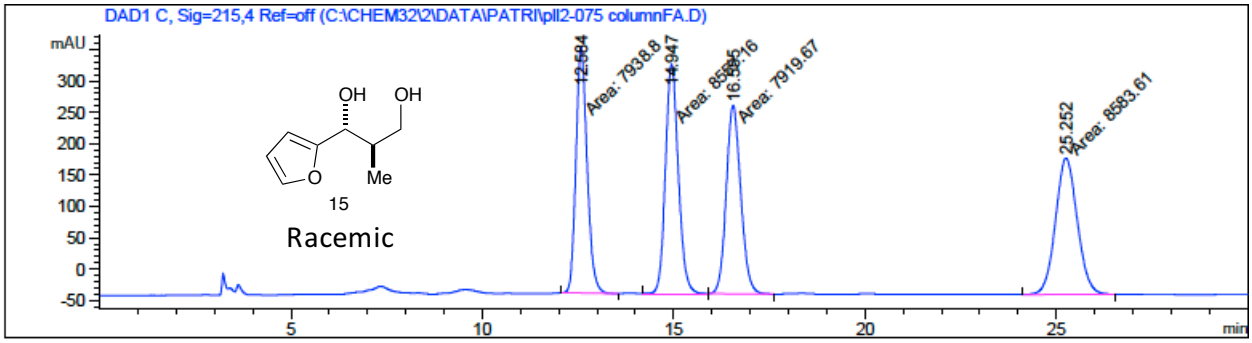
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.380	MM	0.2304	70.69678	5.11426	2.5610
2	12.350	MM	0.2639	2689.76489	169.88129	97.4390

(1*R*,2*R*)-1-(Furan-2-yl)-2-methylpropane-1,3-diol (15)

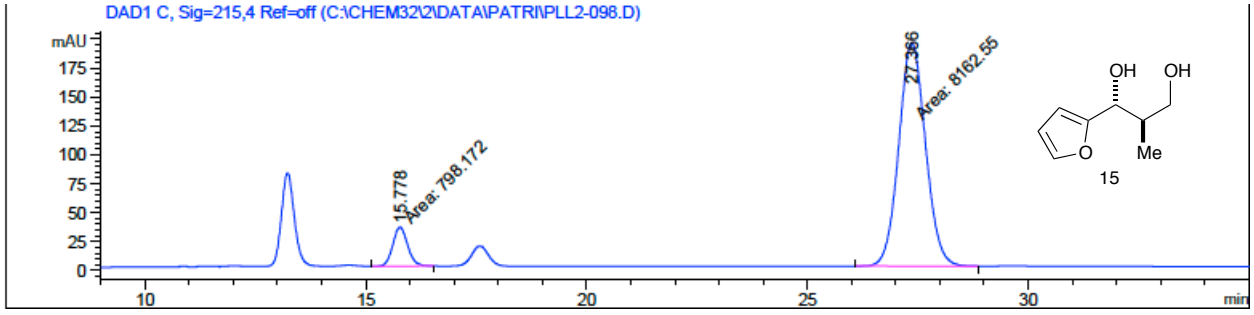




Diol 15. IC, Hex/IPA (90:10), 215 nm, 1 mL/min

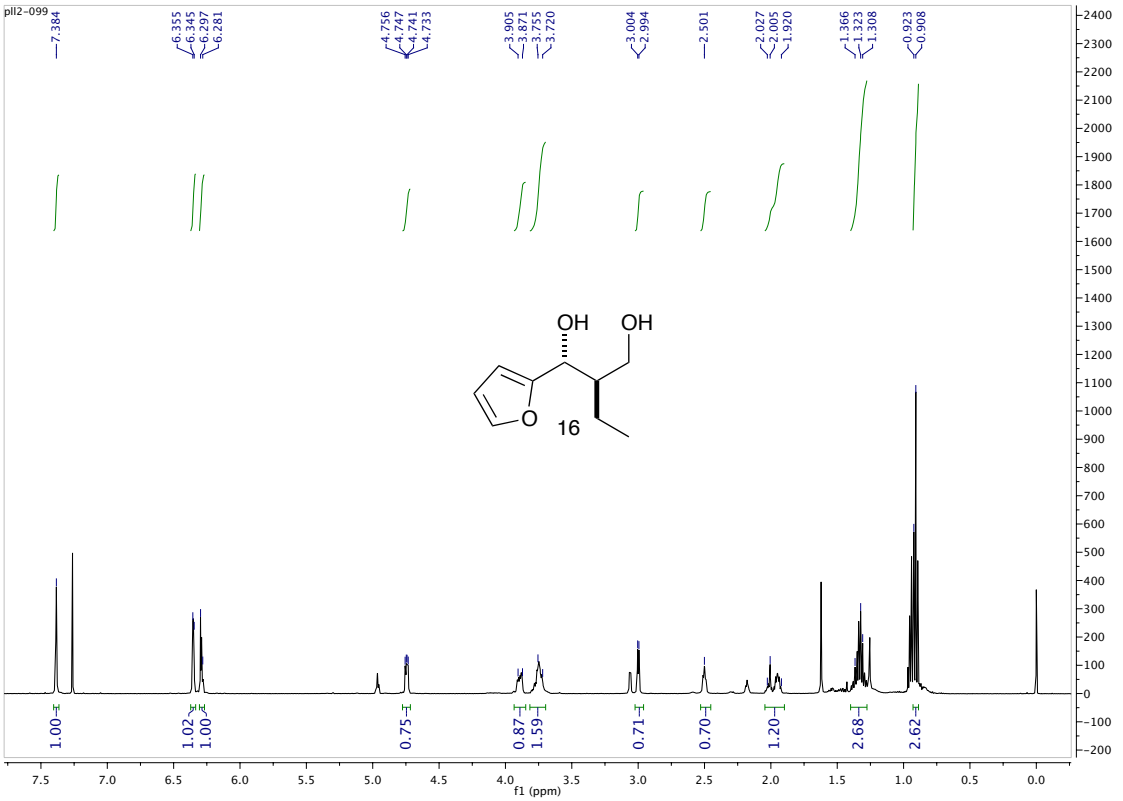


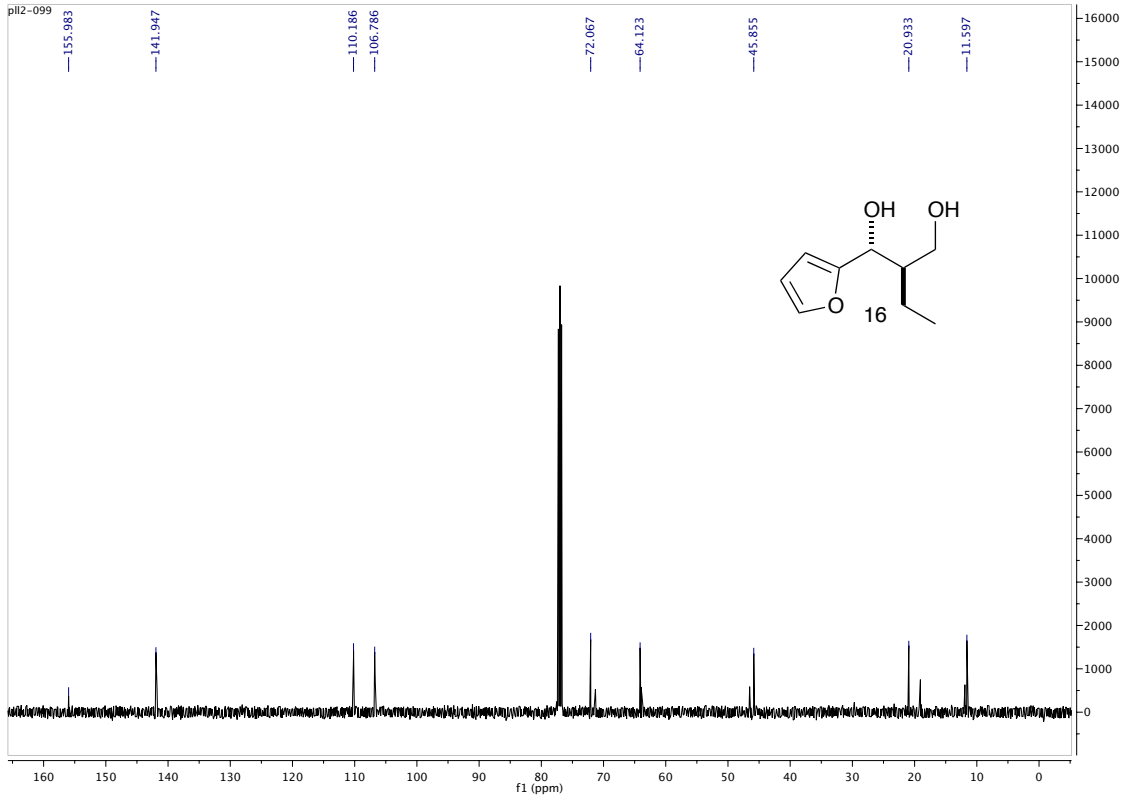
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.584	MM	0.3367	7938.79980	392.92911	24.0575
2	14.947	MM	0.3903	8557.16406	365.43088	25.9314
3	16.555	MM	0.4401	7919.67041	299.92285	23.9995
4	25.252	MM	0.6596	8583.61328	216.87856	26.0115
Totals :				3.29992e4	1275.16139	



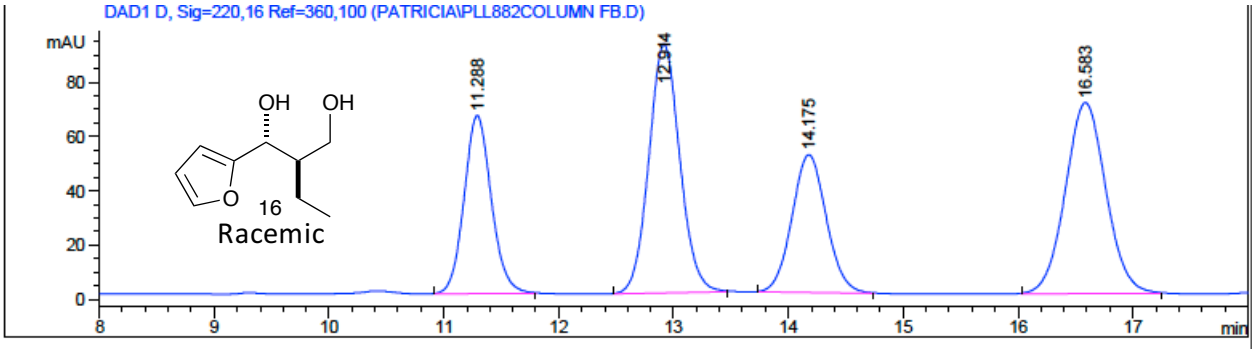
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.778	MM	0.3931	798.17206	33.84436	8.9075
2	27.366	MM	0.7035	8162.54688	193.37753	91.0925
Totals :				8960.71893	227.22190	

(1*R*,2*R*)-2-Ethyl-1-(furan-2-yl)propane-1,3-diol (16)

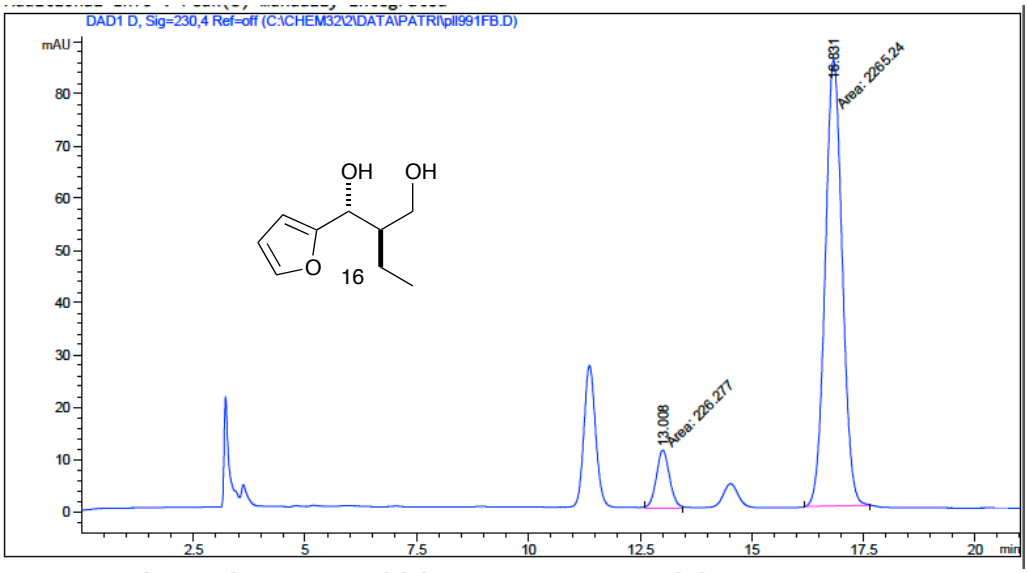




Diol 16. IC, Hex/IPA (90:10), 230 nm, 1 mL/min

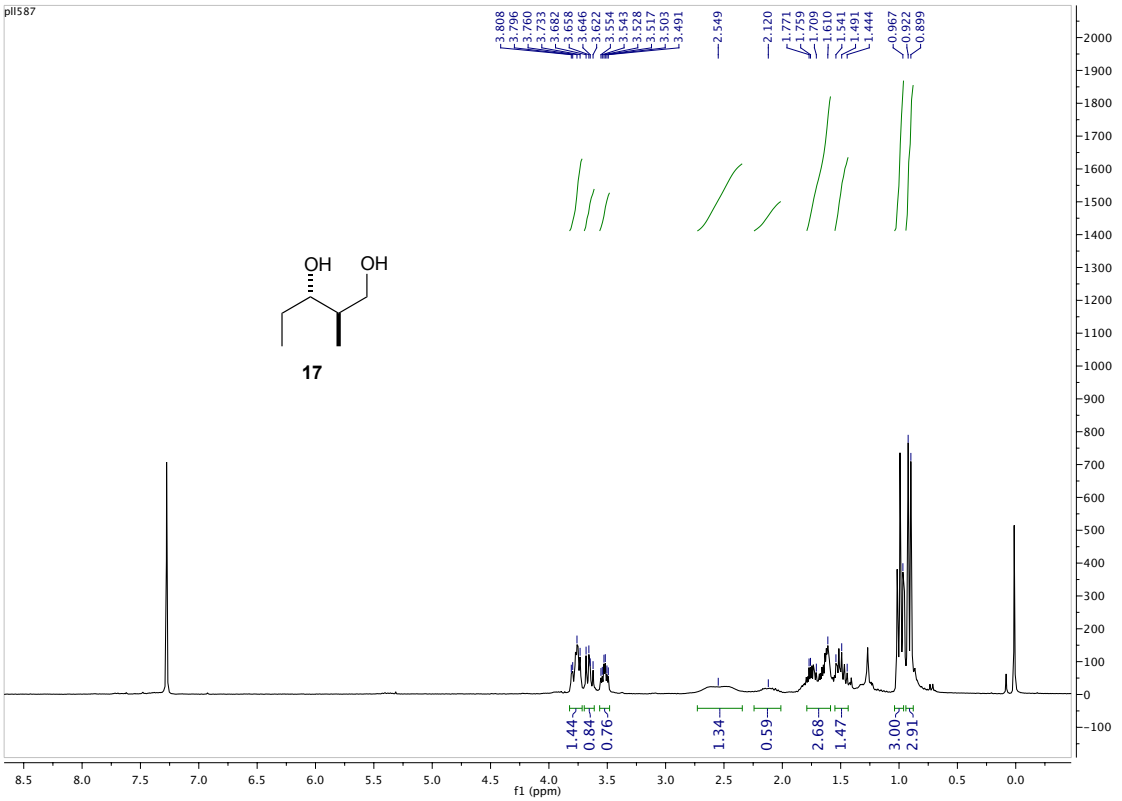


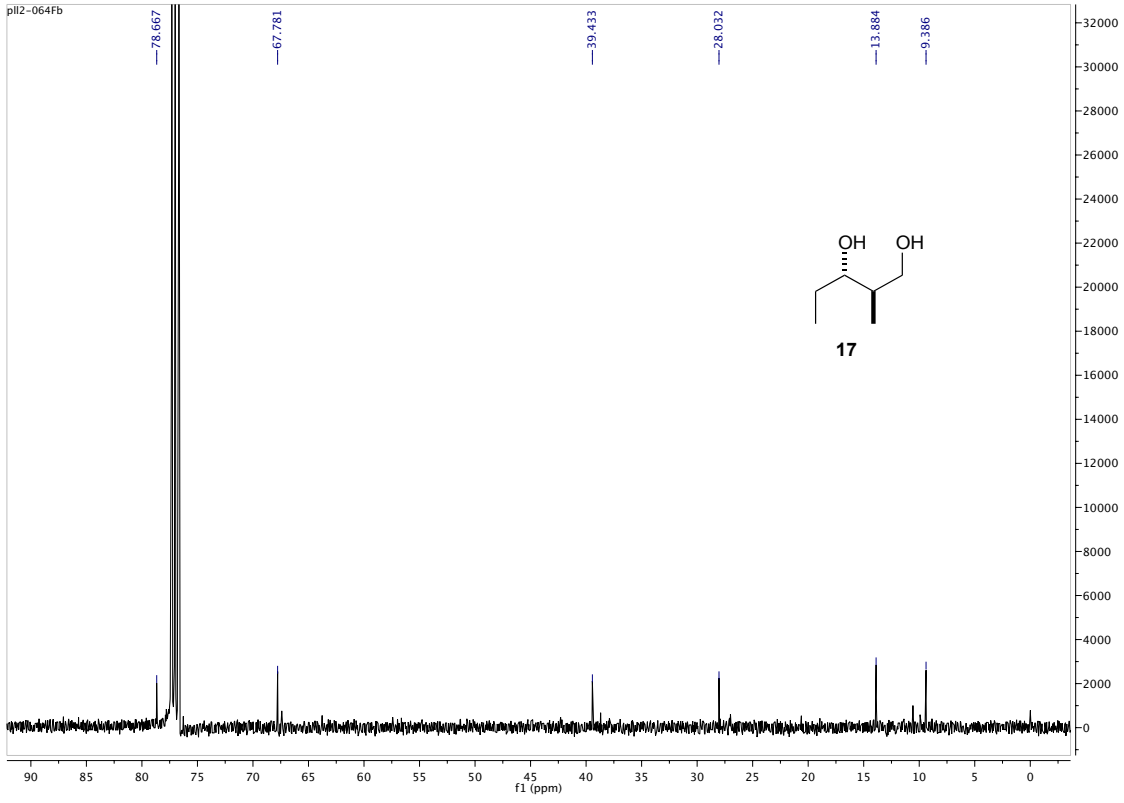
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.288	BB	0.2527	1083.39233	65.57537	19.3855
2	12.914	BB	0.2886	1716.34619	91.59896	30.7112
3	14.175	BB	0.3210	1057.45825	50.76537	18.9215
4	16.583	BB	0.3811	1731.47278	70.36579	30.9818
Totals :				5588.66956	278.30549	



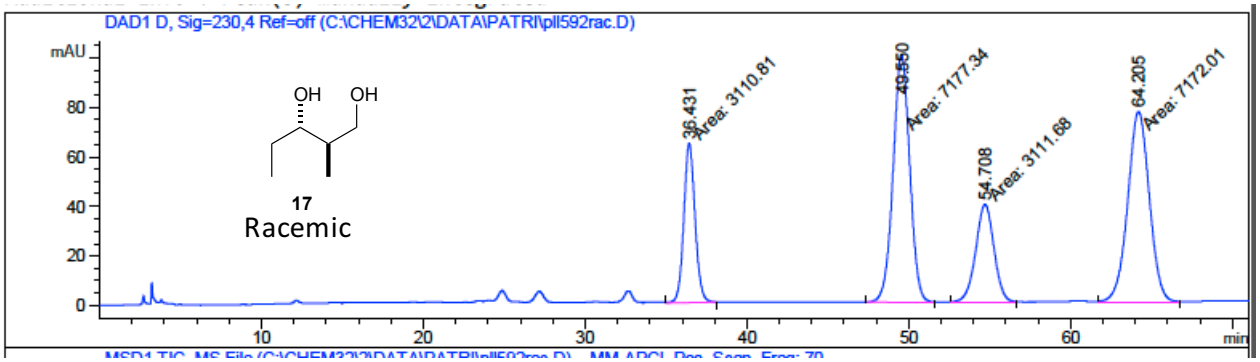
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.008	MM	0.3411	226.27684	11.05670	9.0819
2	16.831	MM	0.4420	2265.24438	85.41044	90.9181

(2*R*,3*S*)-2-Methylpentane-1,3-diol (17)

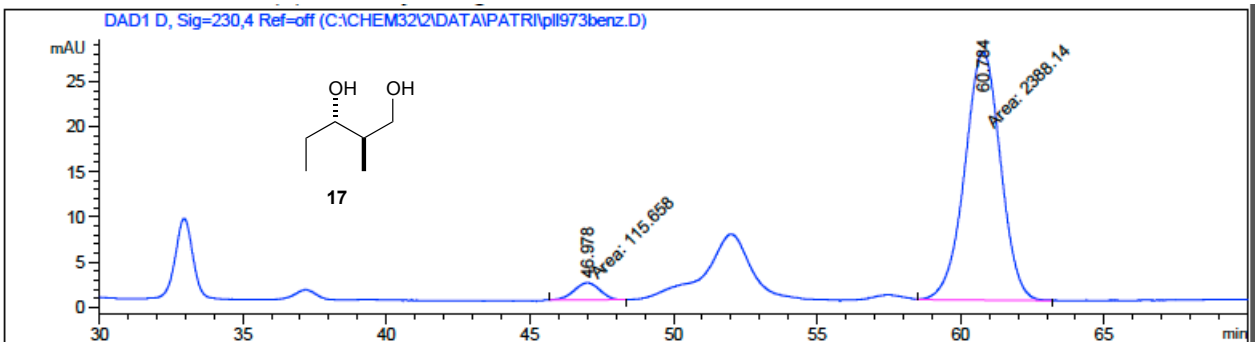




Diol 17. IC, Hex/IPA/EtOH (98:1.5:0.5), 230 nm, 1 mL/min

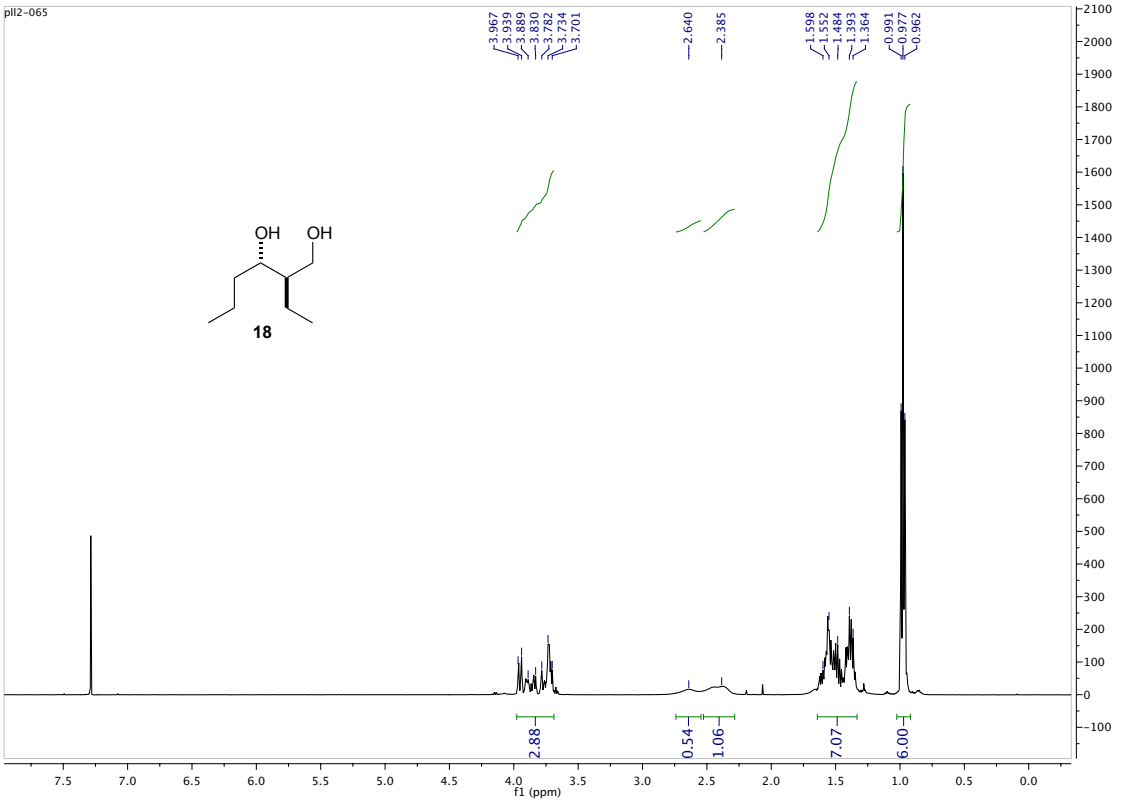


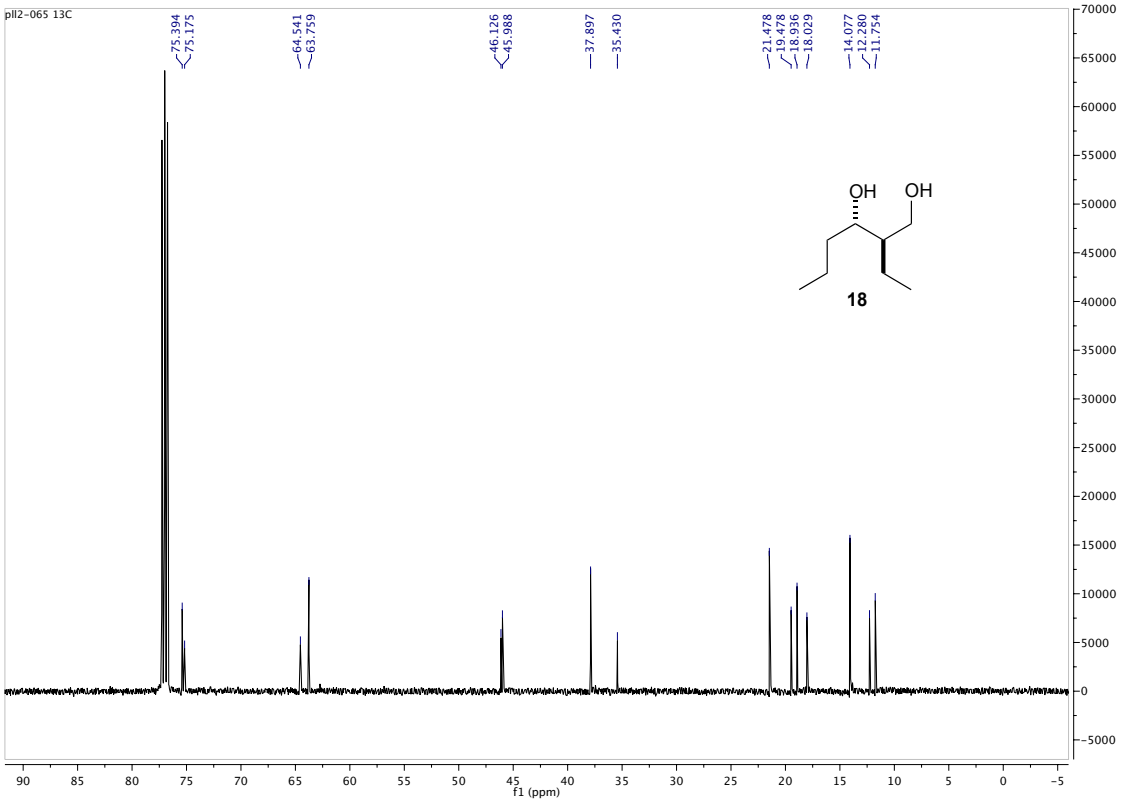
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.431	MM	0.8043	3110.81445	64.46426	15.1217
2	49.550	MM	1.1946	7177.34229	100.13543	34.8892
3	54.708	MM	1.3130	3111.67700	39.49830	15.1259
4	64.205	MM	1.5532	7172.01123	76.96103	34.8632



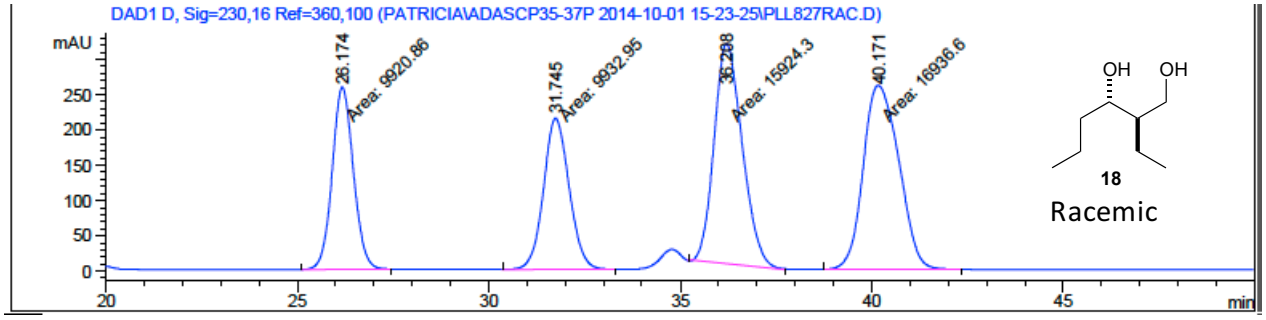
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.978	MM	1.0319	115.65791	1.86805	4.6193
2	60.784	MM	1.4459	2388.13770	27.52857	95.3807

(2*R*,3*S*)-2-Ethylhexane-1,3-diol (18)

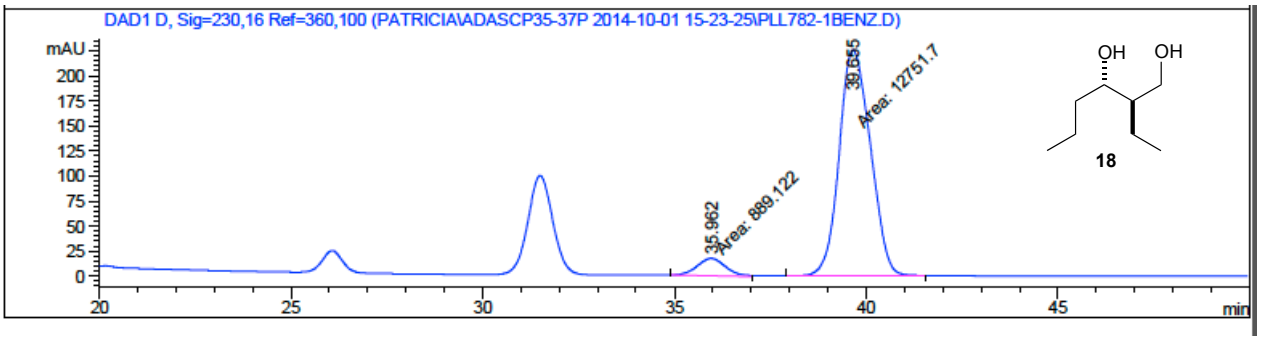




Diol 18. IC, Hex/IPA/EtOH (98:1.5:0.5), 230 nm, 1 mL/min

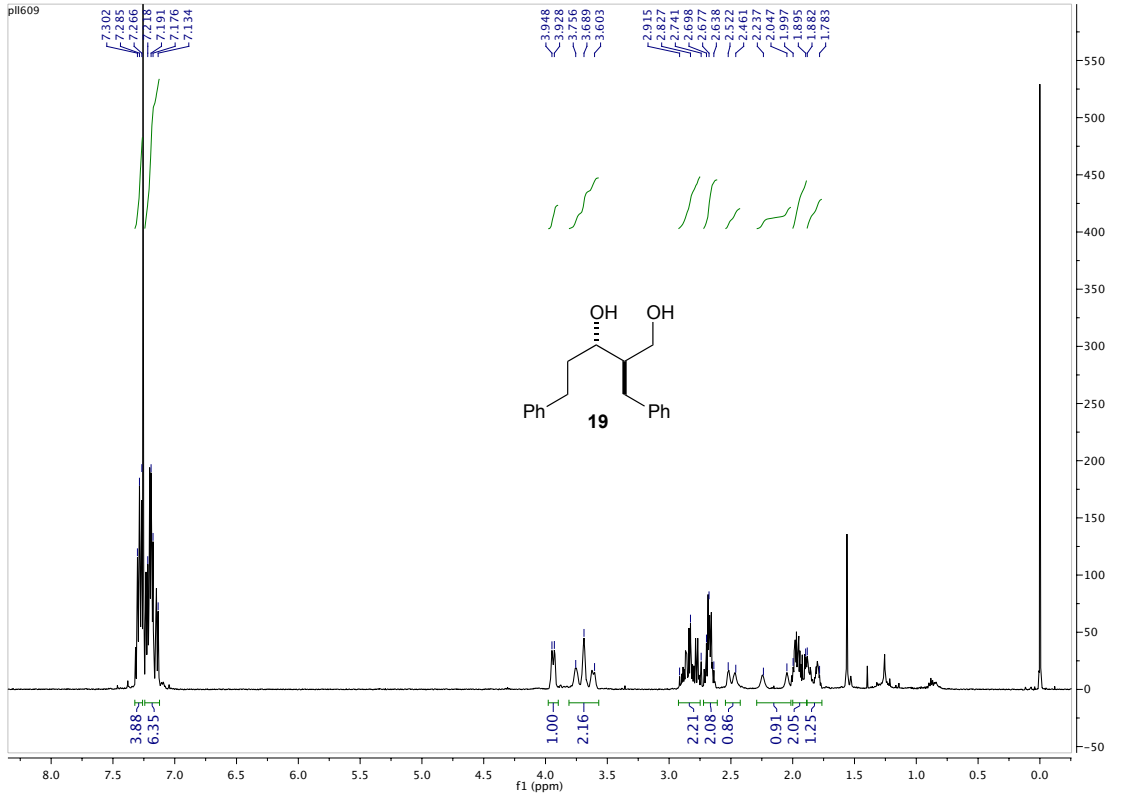


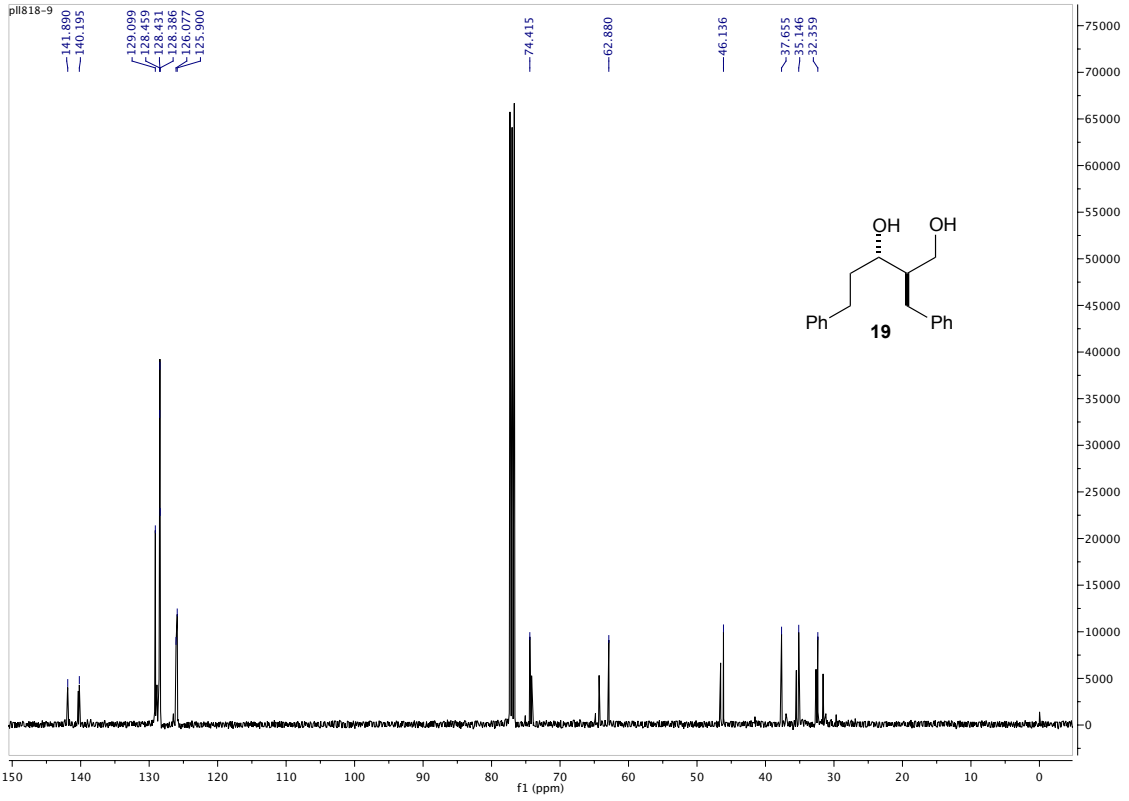
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.174	MM	0.6402	9920.86426	258.27808	18.8199
2	31.745	MM	0.7739	9932.95313	213.92650	18.8429
3	36.208	MM	0.8524	1.59243e4	311.37750	30.2085
4	40.171	MM	1.0822	1.69366e4	260.82797	32.1287
Totals :				5.27147e4	1044.41005	



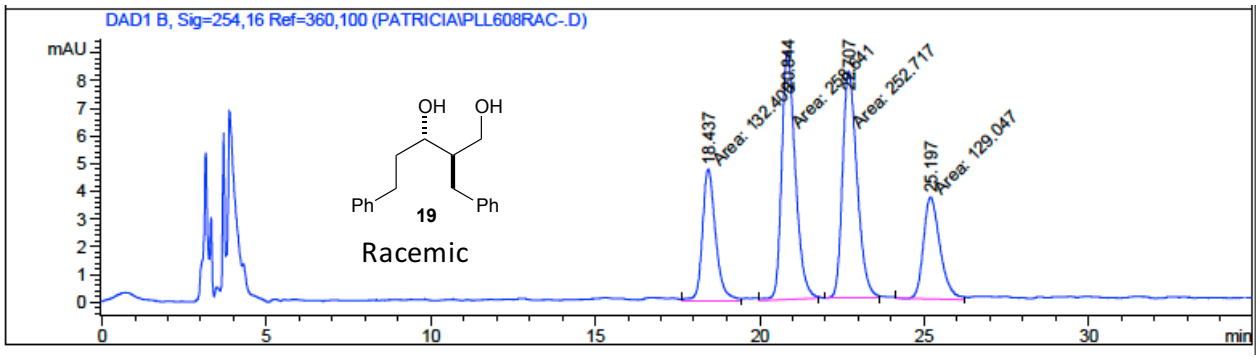
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.962	MM	0.8569	889.12207	17.29246	6.5181
2	39.655	MM	0.9424	1.27517e4	225.50647	93.4819
Totals :				1.36408e4	242.79893	

(2*R*,3*S*)-2-Benzyl-5-phenylpentane-1,3-diol (19)

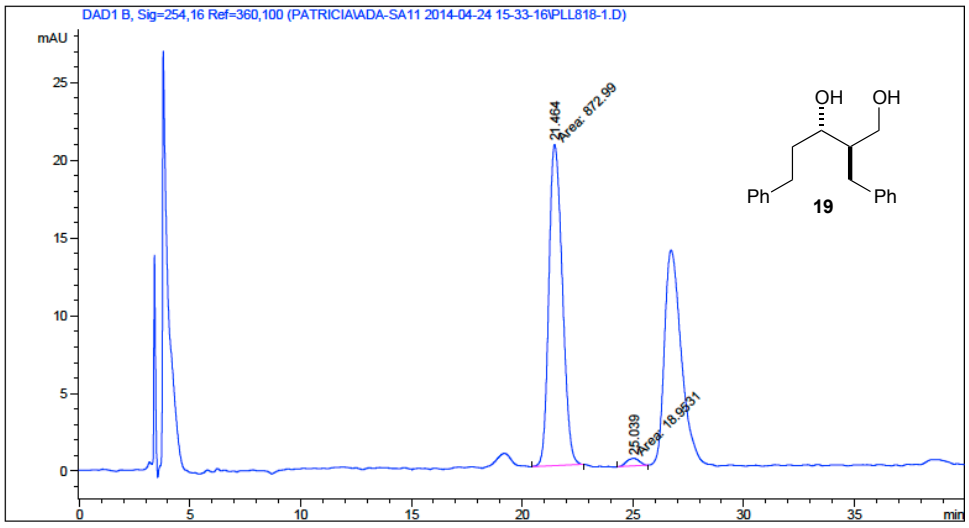




Diol 19. IB, Hex/IPA/CH_2Cl_2 (82:2:16), 254 nm, 1 mL/min



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.437	MM	0.4647	132.40588	4.74905	17.1330
2	20.844	MM	0.4805	258.64117	8.97157	33.4676
3	22.707	MM	0.5134	252.71664	8.20430	32.7010
4	25.197	MM	0.5860	129.04659	3.67045	16.6984
Totals :				772.81029	25.59537	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.464	MM	0.7041	872.98999	20.66331	97.8751
2	25.039	MM	0.6540	18.95309	4.83039e-1	2.1249
Totals :				891.94308	21.14634	