Supporting Information

Cascade Reactions with Grubbs' Catalyst and AD-mix-α/β Using PDMS Thimbles

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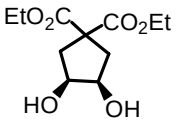
Materials. Grubbs' second-generation catalyst was purchased from Aldrich and maintained in a glove box under nitrogen. Substrates and reagents were purchased from Acros/Fisher (4-methoxystyrene, styrene, 4-methylstyrene, 1-chlorobutane, *N*-methylimidazole, hexafluorophosphoric acid, methane sulfonamide, europium tris[3-(heptafluoropropylhydroxy-methylene)-(+)-camphorate] ($Eu(hfc)_3$), diallyl sulfide, butyl acrylate, ethyl acrylate, diallylamine, and sodium sulfite) or from Aldrich (diethyl diallylmalonate, 1,6-heptadien-4-ol, AD-mix-α, AD-mix-β, (R,R)- and (S,S)-1,2-diphenylethane-1,2-diol) and used as supplied. Organic solvents (except the ionic liquid) were purchased from Acros or Aldrich at the highest purity and used as supplied. The ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM), was prepared according to literature procedures.[1,2] All solvents used for metathesis reactions were degassed and maintained under nitrogen. All solvent ratios are by volume (v/v) unless otherwise stated. Polydimethylsiloxane (PDMS) preparation kit (Sylgard 184) was purchased from Essex Brownell and used as supplied. PDMS thimbles were prepared according to literature.[1] All olefin metathesis reactions were performed under a nitrogen atmosphere using either Schlenk flasks or a glove box.

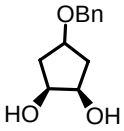
Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 instrument using $CDCl_3$ as solvent and TMS as an internal standard unless otherwise stated. For all compounds not reported in literature, a mass spectrum was run to obtain the molecular weight. Enantiomeric excesses (ee) were determined by running a ^{1}H NMR spectrum of the pure products in presence of 0.65 molar equivalents $Eu(hfc)_3$. Leaching of ruthenium and osmium across the thimble walls was determined by ICP-MS on a Varian Ultra mass 700 ICP-MS (EPA 200.8 heavy metal analysis protocol).

(3*S*,4*R*)-diethyl 3,4-dihydroxycyclopentane-1,1-dicarboxylate. We provide the experimental procedure that was followed for the cascade reactions for this substrate. Any deviations from this method are given for all subsequent substrates.

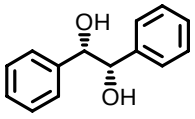


In a glove box, Grubbs' second-generation catalyst (43 mg, 0.05 mmoles) was placed in a PDMS thimble contained in a Schlenk flask. The flask was sealed, removed from the glove box and placed under N_2. Solvent mixture (1 mL of 1/1 CH_2Cl_2/BMIM) was added to the interior of the thimble followed by diethyl diallylmalonate (300 μL, 1.25 mmoles). The reaction mixture was allowed to stir at ambient conditions for 2 h. To the exterior of the thimble was added AD-mix-α (3.6 g, 0.0063 mmoles of osmium catalyst) and methane sulfonamide (0.238 g, 2.5 mmoles) in 10 mL of solvent (1/2/3 BMIM/H_2O/acetone), and the reaction was allowed to stir vigorously for a further 36 h. To the reaction mixture on the exterior was added Na_2SO_3 (3.2 g, 25 mmoles). The product was extracted from the solvent on the interior and exterior with 3 x 50 mL Et_2O, solvent was removed *in vacuo*, and the product was purified using a silica gel column eluting with 25% EtOAc in hexanes to give the target diol in 75 % yield. ^{1}H NMR ($CDCl_3$): δ 4.03-4.17 (m, 6H, overlapping signals), 3.47 (br S, 2H), 2.34 (m, 4H), 1.15-1.21 (m, 6H, overlapping triplets). ^{13}C NMR ($CDCl_3$): δ 172.40, 172.12, 72.89, 61.75, 61.62, 56.34, 38.45, 30.89, 13.80, 13.77. Calcd for $C_{11}H_{18}O_6$ 246.1103; Found, 247.1176 (M+1).

This reaction was repeated using 1/1 *t*-BuOH/$H_2O$for the dihydroxylation step to give the target diol in 68% yield. The characterization was identical.



(1S,2R)-4-phenythylcyclopentane-1,2-diol. Reaction of 4-benzyloxy hepta-1,6-diene (0.51 g, 2.5 mmoles) with Grubbs' second-generation catalyst (85 mg, 0.1 mmoles) for 4 h, followed by reaction of the subsequent product with site-isolated AD-mix-α (7.2 g, 0.012 mmoles of osmium catalyst) for 19 h gave title compound in 82 % yield and 63% diastereoselectivity. NMR data agreed with those reported in literature.[3] ^{1}H NMR ($CDCl_3$): δ 7.40 (m, 5H), 4.52 (s, 0.8H), 4.47 (s, 1.2H), 4.23 (m, 1H), 4.18 (m, 1H), 3.38 (br s, 1.7 H), 3.04 (s, 0.4H), 2.01- 2.06 (m 4H). ^{13}C NMR ($CDCl_3$): δ 138.41, 137.84, 128.60, 128.53, 127.95, 127.93, 127.81, 127.73, 77.89, 77.64, 73.26, 72.65, 71.10, 71.02, 38.52, 38.43.



(1S,2S)-Diphenylethane-1,2-diol. Reaction of styrene (0.13 g, 1.25 mmoles) with Grubbs' second-generation catalyst (42.5 mg, 0.05 mmoles) for 6 h, followed by reaction of the subsequent product with site-isolated AD-mix-α (1.75 g, 0.003 mmoles of osmium) for 13 h, gave the title compound in 72% yield and 85% ee. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[4,5] ^{1}H NMR ($CDCl_3$): δ 7.23-7.25 (m, 3H), 7.12-7.15 (m, 2H), 4.72 (s, 1H), 2.87 (s, 1H) ^{13}C NMR ($CDCl_3$): δ 128.11, 127.92, 126.90, 79.10.

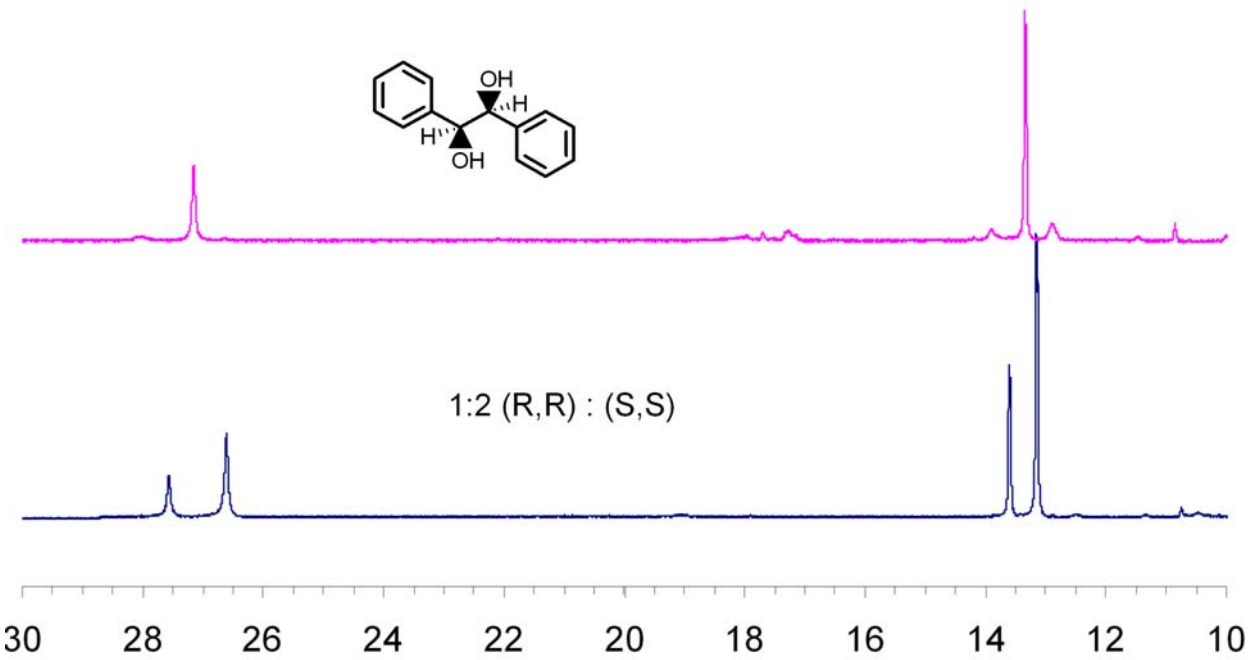


Figure 1. NMR spectra of the product from our cascade reaction (top) and the 1:2 mixture of pure (R,R) : (S,S)-isomers showing the resolution of the enantiomeric benzylic protons at 27.11 and 28.02 ppm. The ratio of these two peaks was used to determine the ee.

To determine the enantiomeric excess, the product diol (8.8 mg, 0.041 mmoles) and $Eu(hfc)_3$ (31.9 mg, 0.027 mmoles) were dissolved in $CDCl_3$ in a glove box and mixed well. The mixture was then analyzed by ^1H NMR spectroscopy and the ratio of the peaks at 28.02 and 27.11 ppm was used to determine the enantiomeric excess. To confirm the peak assignment, commercially available (R,R)- and (S,S)-diphenylethane-1,2-diol were used. A stock solution made of a mixture of the (R,R) isomer (21 mg, 0.098 mmoles) and the (S,S) isomer (39.5 mg, 0.184 mmoles) was prepared using 3 ml of $CDCl_3$ in the glove box. To 1 ml of the stock was added $Eu(hfc)_3$ (67 mg, 0.056 mmoles) and the mixture was analyzed by ^1H NMR spectroscopy. Our ^1H NMR spectra are given above (Figure 1). The data showed that we obtained the (S,S) enantiomer in our cascade reaction using AD-mix-α as previously reported.[5,6] This result agreed with literature precedence. The chiral diols below were assigned by inference from this experiment and literature.[5]

Similarly, the reaction was repeated using AD-mix-β for the dihydroxylation step to give the antipode in 72 % yield and >98% ee.

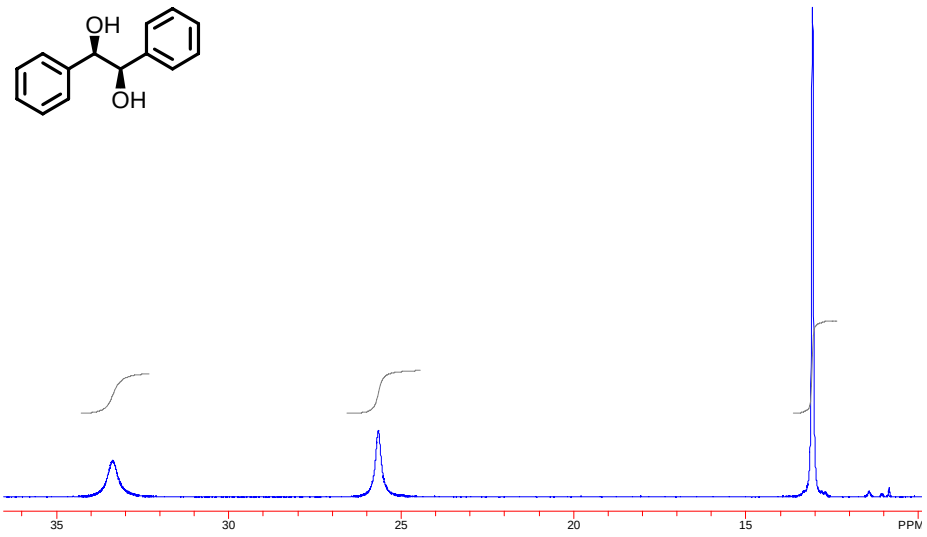
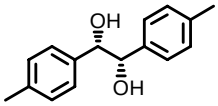


Figure 2. NMR spectrum showing how we determined the ee for (1*R*,2*R*)-diphenylethane-1,2-diol.

(1S,2S)-di-*p*-tolylethane-1,2-diol. Reaction of 4-methyl styrene (0.15g, 1.25 mmoles) with Grubbs' second generation catalyst (42.5 mg, 0.05 mmoles) for 8 h, followed by reaction of the subsequent product with site-isolated AD-mix-α (1.75 g, 0.003 mmoles of osmium) for 12 h gave the title compound in 86% yield and 84% ee. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[4,7] ^{1}H NMR ($CDCl_3$): δ 7.05 (m, 4H), 4.69 (s, 1H), 2.30 (s, 3H) $CDCl_3$): δ 137.51, 136.96, 128.83, 126.82, 78.80, 21.14



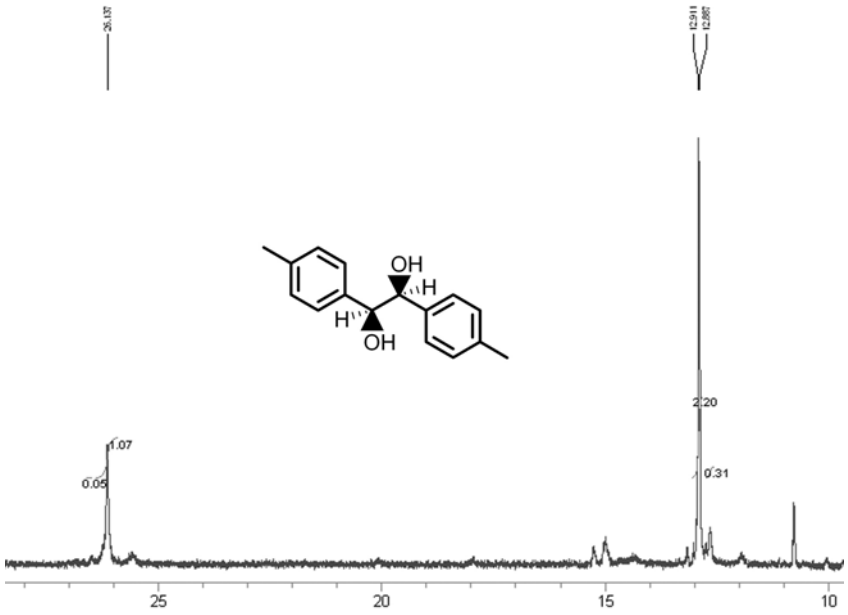


Figure 3. NMR spectrum showing how we determined the ee for the (1*S*,2*S*)-di-p-tolylethane-1,2-diol.

Similarly, the reaction was repeated using AD-mix-β for the dihydroxylation step to give the antipode in 95 % yield and >98% ee.

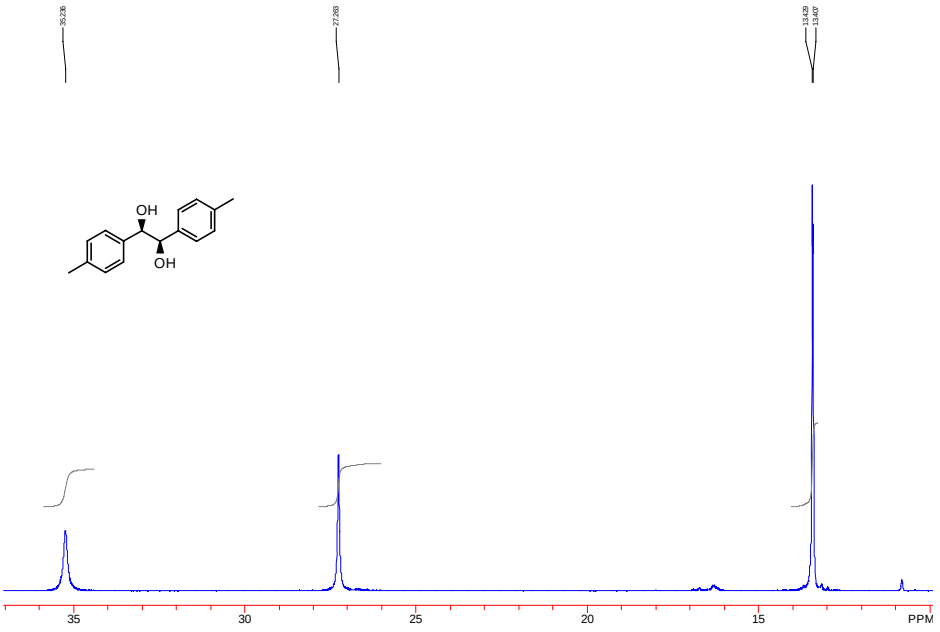


Figure 4. NMR spectrum showing how we determined the ee for the (1*S*,2*S*)-di-*p*-tolylethane-1,2-diol.

(1*S*,2*S*)-1,2-bis(4-methoxyphenyl) ethane-1,2-diol. Reaction of 4-methoxy styrene (0.34 g, 2.5 mmoles) with Grubbs' second generation catalyst (85 mg, 0.1 mmoles) for 6 h, followed by reaction of the subsequent product with site-isolated AD-mix-α (7.2 g, 0.012 mmoles of osmium) for 12 h gave the title compound in 61% yield and 94% ee. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[7-9] ^{1}H NMR ($CDCl_3$): δ 7.05 (d, 2H), 6.76 (d, 2H), 4.63 (s, 1H), 3.77 (s, 3H), 2.78 (br s, 1H) ^{13}C NMR ($CDCl_3$): δ 159.15, 132.04, 128.14, 113.46, 78.76, 55.17

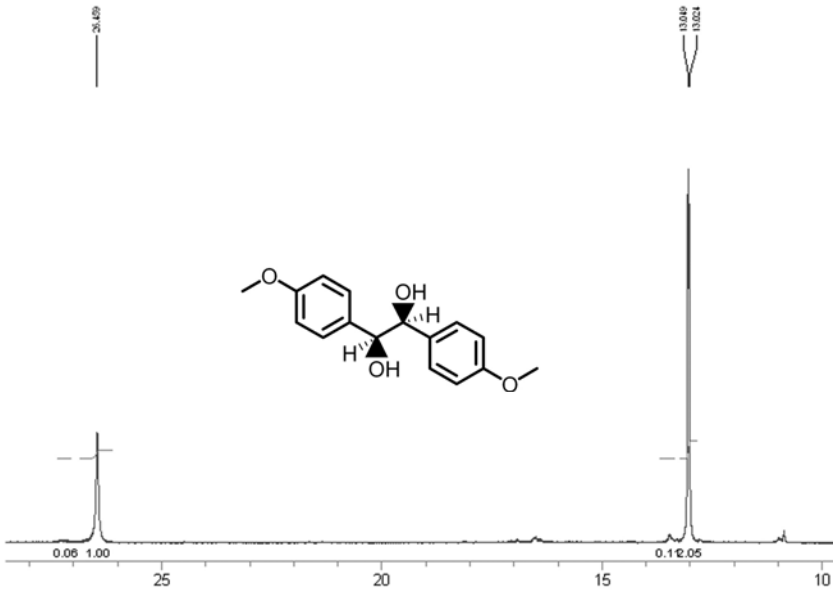


Figure 5. NMR spectrum showing how we determined the ee for the (1*S*,2*S*)-1,2-bis(4-methoxyphenyl) ethane-1,2-diol.

Similarly, the reaction was repeated using AD-mix-β for the dihydroxylation step to give the antipode in 87 % yield and >98% ee.

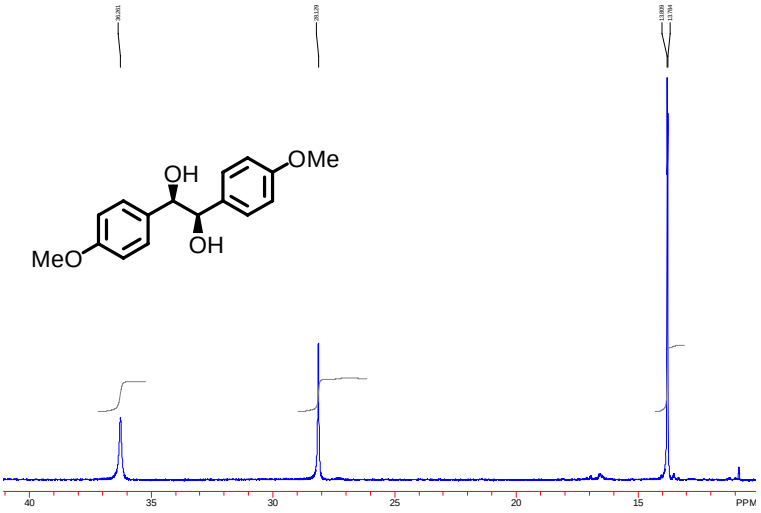


Figure 6. NMR showing how we determined the ee for the (1S,2S)-1,2-bis(4-methoxyphenyl) ethane-1,2-diol.

(2*S*,3*R*)-Ethyl 2,3-dihydroxy-3-phenylpropanoate. Reaction of ethyl acrylate (0.5 g, 5 mmoles) and styrene (0.26 g, 2.5 mmoles) with Grubbs' second generation catalyst (85 mg, 0.1 mmoles) was allowed to proceed for 9 h followed by pumping off the excess acrylate and reaction of the subsequent product with site-isolated AD-mix-β (7.2 g, 0.012 mmoles of osmium catalyst) for 12 h gave title compound in 82% yield and >98% ee. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[5,10,11] ^{1}H NMR ($CDCl_3$): δ 7.26-7.42 (m, 5H), 5.00 (d, J= 3 Hz, 1H), 4.36 (d, J= 3, 1H), 4.26 (q, J= 7.1Hz, 2H), 3.16 (br S, 1H), 2.84 (br S, 1H), 1.27 (t, J= 7.1 Hz, 3H) ^{13}C NMR ($CDCl_3$): δ 172.70, 139.92, 128.42, 128.04, 126.24, 74.63, 62.20, 14.06.

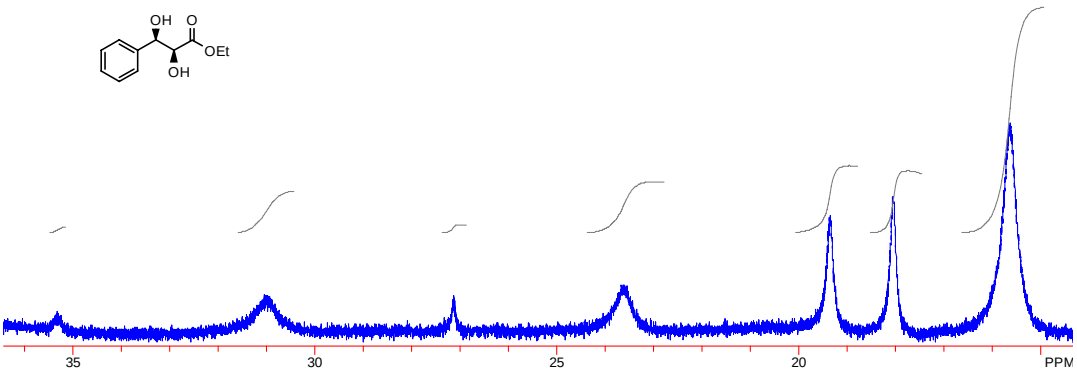


Figure 7. NMR spectrum showing how we determined the ee for the (2S,3R)-Ethyl 2,3-dihydroxy-3-phenylpropanoate.

(2*S*,3*R*)-Butyl 2,3-dihydroxy-3-phenylpropanoate. Reaction of butyl acrylate (0.64 g, 5 mmoles) and styrene (0.26 g, 2.5 mmoles) with Grubbs' second generation catalyst (43 mg, 0.05 mmoles) was allowed to proceed for 8 h followed by pumping off the excess acrylate and reaction of the subsequent product with site-isolated AD-mix-α (3.6 g, 0.0063 mmoles of osmium catalyst) for 20 h gave title compound in 78% yield and >98% ee. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature. ^{1}H NMR ($CDCl_3$): δ 7.31-7.43 (m, 5H), 5.01 (dd, J= 7.2, 3 Hz, 1H), 4.38 (dd, J= 5.7, 3, 1H), 4.22 (t, J= 7.2 Hz, 2H), 3.11 (d, J= 6 Hz, 1H), 2.71 (d, J= 7.2 Hz,1H), 1.61 (m, 2H), 1.33 (m, 2H), 0.93 (t, J= 7.2 Hz, 3H) ^{13}C NMR ($CDCl_3$): δ 172.74, 139.90, 128.27, 127.87, 126.25, 74.81, 74.60, 30.33, 18.85, 13.53

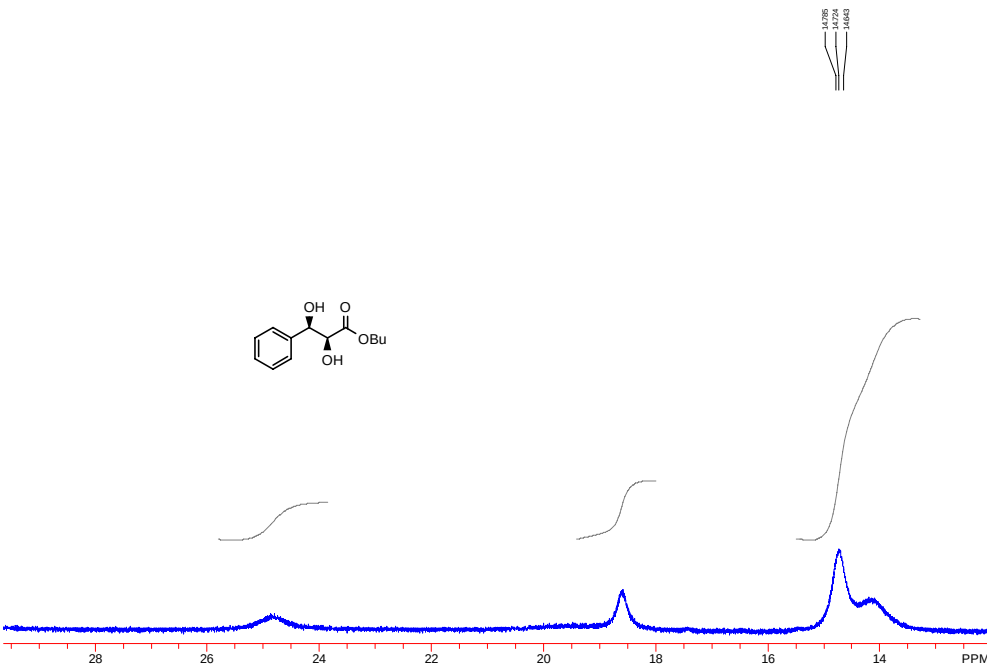
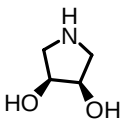


Figure 8. NMR spectrum showing how we determined the ee for the (2S,3R)-Butyl 2,3-dihydroxy-3-phenylpropanoate.

1,1-Dioxido-(3R,4S)-tetrahydrothiophene-3,4-diol. In a glove box, Grubbs' second generation catalyst (85 mg, 0.01 mmoles) was placed in a PDMS thimble contained in a Schlenk flask. The flask was sealed, removed from the glove box and placed under N_2. Solvent mixture (1 mL of 1/1 CH_2Cl_2/BMIM) was added to the interior of the thimble followed by diallyl sulfide (322 μL, 2.5 mmoles). The reaction mixture was allowed to stir at 35 °C for 6 h after which the walls of the glass flask were rinsed with 1 mL CH_2Cl_2 and the washes put into the thimble. To the exterior of the thimble was placed a mixture of $K_2Os(OH)_6$ (2 mg, 0.005 mmoles) and citric acid (0.72 g, 3.76 mmoles) in 15 mL 1/1 *t*-BuOH/H_2O. To the exterior was also added 1/1 (w/w) aqueous *N*-methylmorpholine *N*-oxide (NMO) (1.3 mL, 4.5 mmoles NMO) and the reaction was allowed to stir vigorously for a further 15 h. Solvent was distilled off and the resulting residue was purified using a silica gel column eluting with 25% hexanes in EtOAc to give the title

compound in 79 % yield. ^{1}H NMR (d_6-DMSO): δ 4.7-4.9 (br, s, 2H), 4.51 (m, 2H), 3.20 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 70.93, 57.70. Calcd for $C_4H_8O_4S$ 152.0143; Found, 153.0222 (M+1)

(3S, 4R)–Pyrrolidine-3,4-diol. The reaction of diallylamine (0.48 g, 5 mmoles) with



Grubbs' second generation catalyst (170 mg, 0.02 mmoles) in presence of *p*-toluenesulfonic acid (0.95 g, 5 mmoles) was allowed to proceed for 6 h. Subsequent addition of 0.5 mL saturated NaOH in 1/1 MeOH/H_2O gave the intermediate 2,5-dihydro-1*H*-pyrrole. The intermediate was reacted with site-isolated of $K_2Os(OH)_6$ (2 mg, 0.005 mmoles) as described above for 24 h. The crude product was distilled under reduced vacuum, the distillate was pumped dry, residue dissolved in MeOH then filtered over celite to give a light yellow solution. The yellow filtrate was concentrated *in vacuo* and passed through a short alumina column eluting with 1:1 MeOH: CH_2Cl_2 to give the title compound as a white solid in 80 % yield. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[12,13] ^{1}H NMR (d_6-Acetone): δ 3.52 (ddd, J= 1.8, 11.5, 11.7 2H), 3.05-3.08 (br, m, 2H), 2.82 (ddd, J= 3.6, 11.4, 11.7, 2H), 2.371 (dm, J= 10.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 65.40, 61.68.

Recycling of Grubbs' catalysts followed by dihydroxylation. In a glove box, Grubbs' second generation catalyst (85 mg, 0.01 mmoles) was placed in a PDMS thimble contained in a Schlenk flask (A). The flask was sealed, removed from the glove box and placed under N_2. Solvent mixture (1 mL of 1/1 CH_2Cl_2/BMIM) was added to the interior of the thimble followed by diethyl diallylmalonate (300 μL, 1.25 mmoles). The reaction mixture was allowed to stir at ambient conditions for 1 h. For each cycle an aliquot was removed and a ^{1}H NMR spectrum was obtained to check the conversion of the metathesis reaction. Degassed 1/2/3 BMIM/H_2O/acetone (15 mL) was added to the exterior of the thimble and the metathesis product was allowed to flux to the exterior for 1 h. Solvent on the exterior of the thimble was removed and placed in a clean flask (B) containing AD-mix-α (3.6 g, 0.0063 mmoles of osmium catalyst) and methane sulfonamide (0.238

g, 2.5 mmoles) and the reaction was allowed to stir vigorously for 12 h. Na_2SO_3 (3.2 g, 25 mmoles) was then added and the product was extracted with 3 x 50 mL Et_2O and purified using a silica gel column eluting with 25% EtOAc in hexanes to give the target diol.

To the thimble in flask (A) was added 0.5 mL CH_2Cl_2 and diethyl diallylmalonate and the procedure above repeated for a total of 7 cycles. Solvent removed from the exterior of the thimble was placed in a new flask for each cycle.

Table 1. Isolated yields of the cis-diol in recycling experiments.

Cycle number	Isolated yield (%)
1	59
2	78
3	88
4	83
5	91
6	86
7	72

Control reactions to investigate if Grubbs' catalyst interferes with dihydroxylation and vice-versa. a) Does Grubbs' catalyst poison the AD-mixes? In a glove box, Grubbs' second-generation catalyst (21 mg, 0.025 mmoles) in 1 ml CH_2Cl_2 was placed in a Schlenk flask. The flask was sealed, removed from the glove box and placed under N_2. Diethyl diallylmalonate (150 μL, 0.62 mmoles) was added to the flask under nitrogen and allowed to stir for 3.5 h. To the reaction mixture was then added degassed 1/2/3 BMIM/H_2O/acetone (5 mL), AD-mix-α (1.8 g, 0.0025 mmoles of osmium catalyst) and methane sulfonamide (0.06 g, 0.62 mmoles) and the reaction was allowed to stir vigorously for a further 16 h. The reaction mixture was then extracted with 3 x 15 mL Et_2O, dried over $MgSO_4$, solvent removed *in vacuo*, and residue analyzed by ^1H NMR spectroscopy. Similarly, the above reaction was repeated using 5.3 mg and 0.53 mg of Grubbs' catalyst.

b) Is the Grubbs' catalyst poisoning the $K_2Os(OH)_6$? In a glove box, Grubbs' second-generation catalyst (5.3 mg, 0.0062 mmoles) in 1 ml CH_2Cl_2 was placed in a Schlenk flask. The flask was sealed, removed from the glove box and placed under N_2. Diethyl diallylmalonate (150 μL, 0.62 mmoles) was added to the flask under nitrogen and allowed to stir for 3.5 h. To the reaction mixture was added degassed 1/2/3 BMIM/H_2O/acetone (5 mL), $K_2Os(OH)_6$ (0.228 g, 0.62 mmoles), $(DHQ)_2PHAL$ (0.483g, 0.62 mmoles), K_2CO_3 (0.308 g, 2.23 mmoles), and methane sulfonamide (0.06 g, 0.62 mmoles). The reaction was allowed to stir vigorously for a further 16 h. The reaction mixture was then extracted with 3 x 15 mL Et_2O, dried over $MgSO_4$, and solvent removed *in vacuo* and residue analyzed by ^1H NMR spectroscopy.

ICP-MS analysis to investigate if Grubbs' catalyst was leaching to the exterior and the Sharpless catalyst to the interior. The amount of ruthenium and/or osmium leaching into or out of the thimbles was studied for the three solvent systems we used for our reactions. The metathesis reaction was run to 100% conversion before adding the reagents for dihydroxylation. The dihydroxylation step was run for 10 and 25 h to see if the catalysts leached on prolonged reaction times.

1/2/3 BMIM/H_2O/acetone. In a glove box, Grubbs' second generation catalyst (43 mg, 0.05 mmoles) was placed in a PDMS thimble contained in a Schlenk flask. The flask was sealed, removed from the glove box and placed under N_2. Solvent mixture (1 mL of 1/1 CH_2Cl_2/BMIM) was added to the interior of the thimble followed by diethyl diallylmalonate (300 μL, 1.25 mmoles). The reaction mixture was allowed to stir at ambient conditions for 1 h. To the exterior of the thimble was added AD-mix-α (3.6 g, 0.0126 mmoles of osmium catalyst) and methane sulfonamide (0.119 g, 1.25 mmoles) in 15 mL of solvent (1/2/3 BMIM/H_2O/acetone), and the reaction was allowed to stir vigorously for a further 10 h. All solvent from the exterior of the thimble was

removed and amount of osmium and ruthenium quantified by ICP-MS. Similarly, all contents of the thimble were removed and amount of ruthenium and osmium present quantified by ICP-MS.

The above experiment was repeated but the dihydroxylation step was allowed to run for 25 h. amount of ruthenium and osmium in the interior and exterior of the thimbles were similarly quantified.

Using 1/1 *t*-BuOH/H_2O under basic conditions (AD-mix-α). In a glove box, Grubbs' second generation catalyst (43 mg, 0.05 mmoles) was placed in a PDMS thimble contained in a Schlenk flask. The flask was sealed, removed from the glove box, and placed under N_2. Solvent mixture (1 mL of 1/1 CH_2Cl_2/BMIM) was added to the interior of the thimble followed by diethyl diallylmalonate (300 μL, 1.25 mmoles). The reaction mixture was allowed to stir at ambient conditions for 1 h. To the exterior of the thimble was added AD-mix-α (3.6 g, 0.0126 mmoles of osmium catalyst) and methane sulfonamide (0.119 g, 1.25 mmoles) in 15 mL of solvent (1/1 *t*-BuOH/H_2O), and the reaction was allowed to stir vigorously for a further 10 h. All solvent from the exterior of the thimble was removed and amount of osmium and ruthenium quantified by ICP-MS. Similarly, all contents of the thimble were removed and amount of ruthenium and osmium present quantified by ICP-MS.

The above experiment was repeated but the dihydroxylation step was allowed to run for 25 h. The amounts of ruthenium and osmium in the interior and exterior of the thimbles were similarly quantified.

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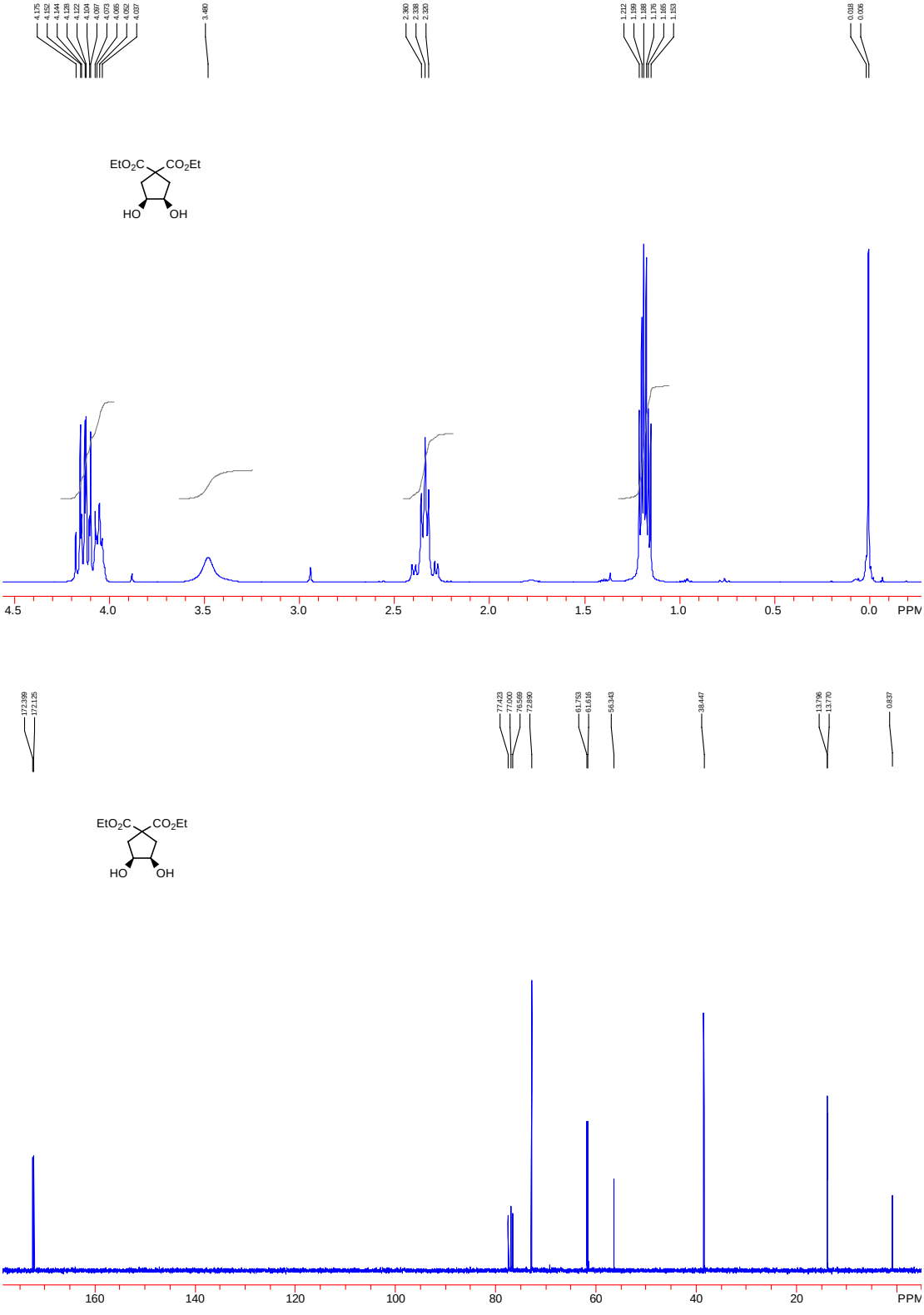
(3S,4R)-diethyl 3,4-dihydroxycyclopentane-1,1-dicarboxylate



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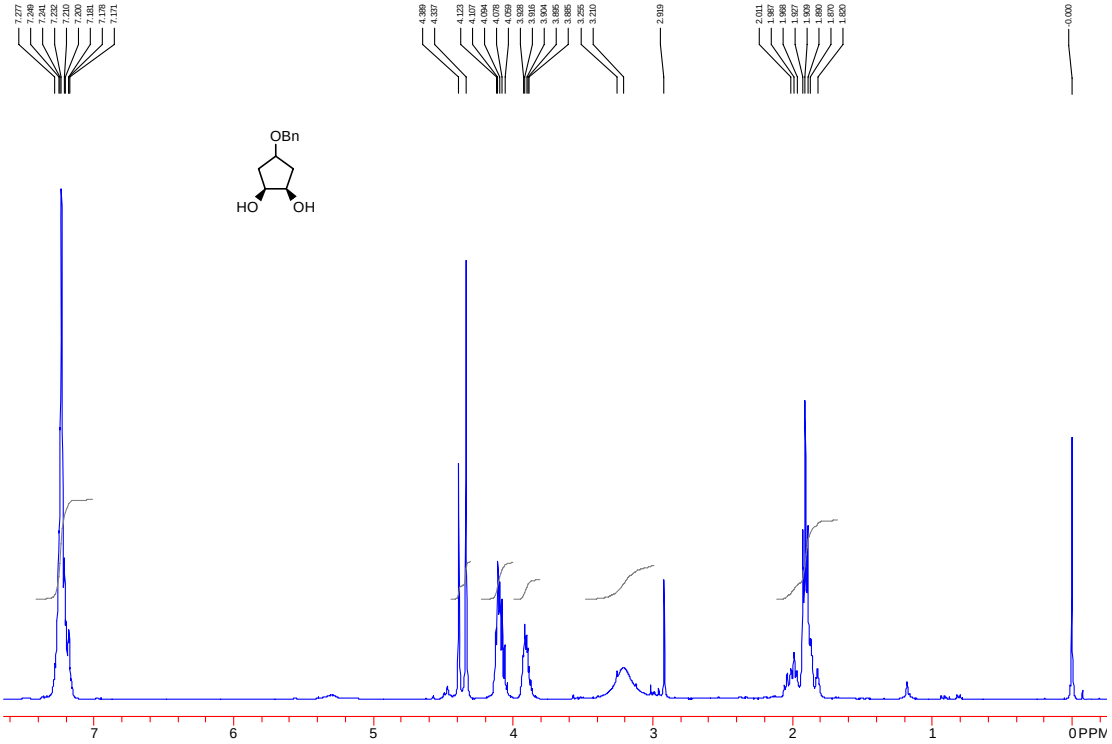

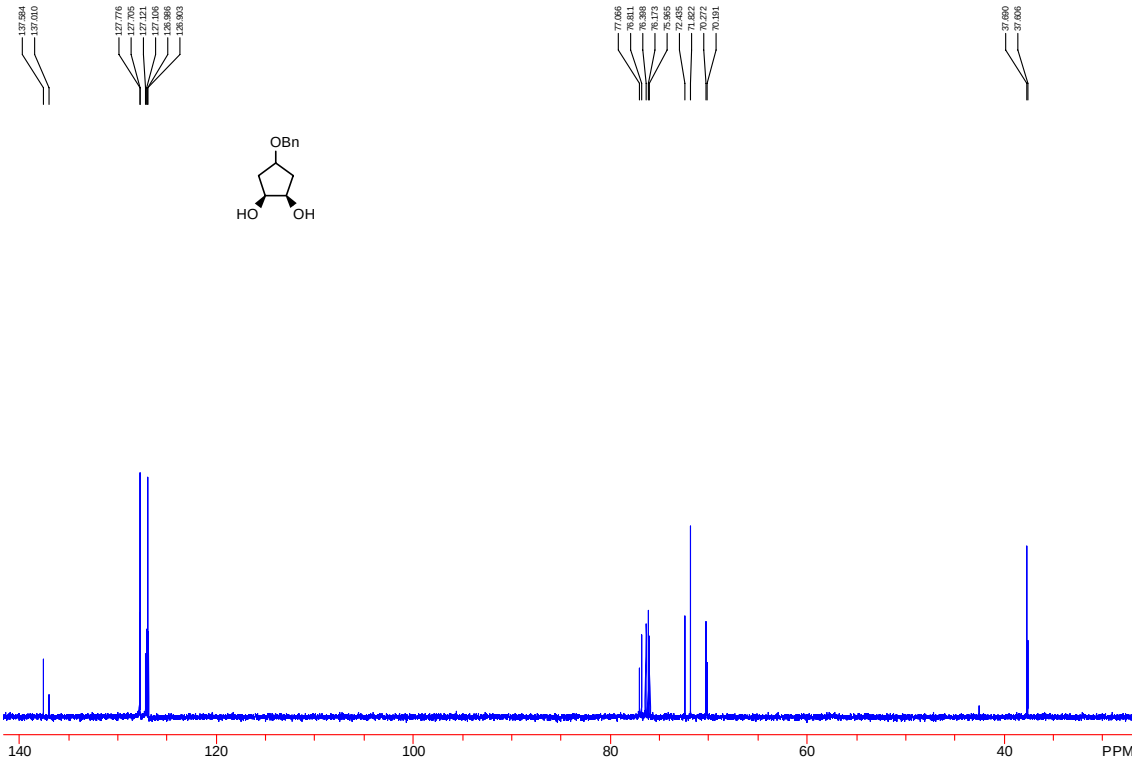

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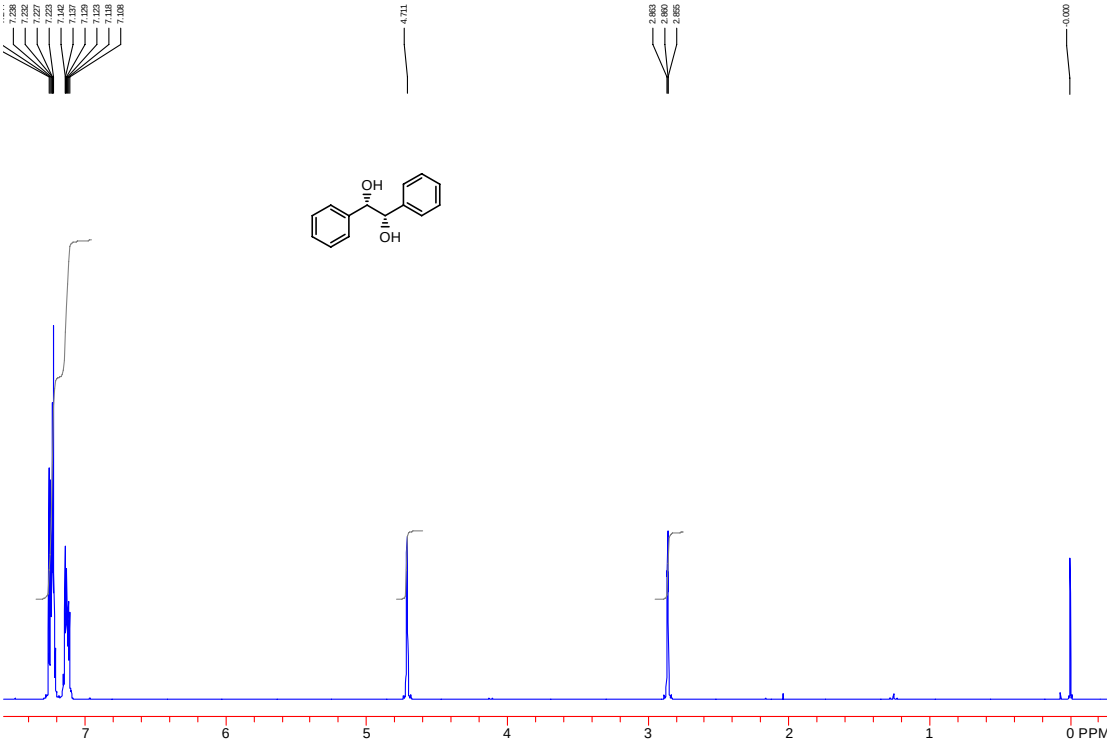

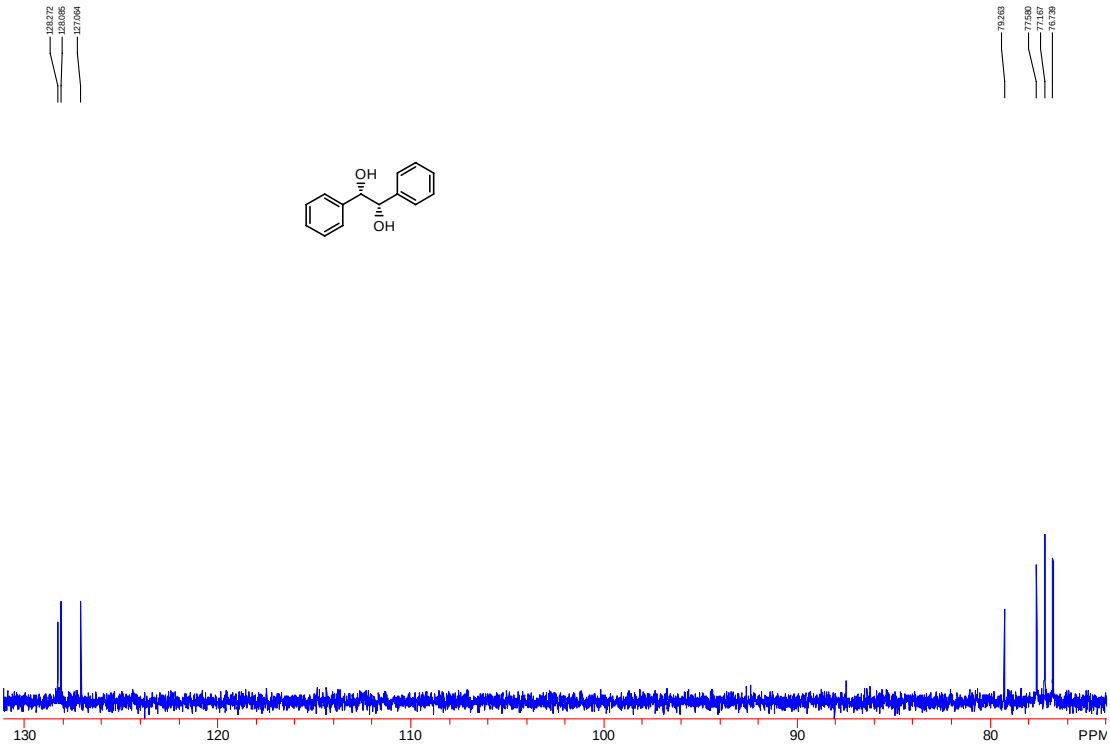

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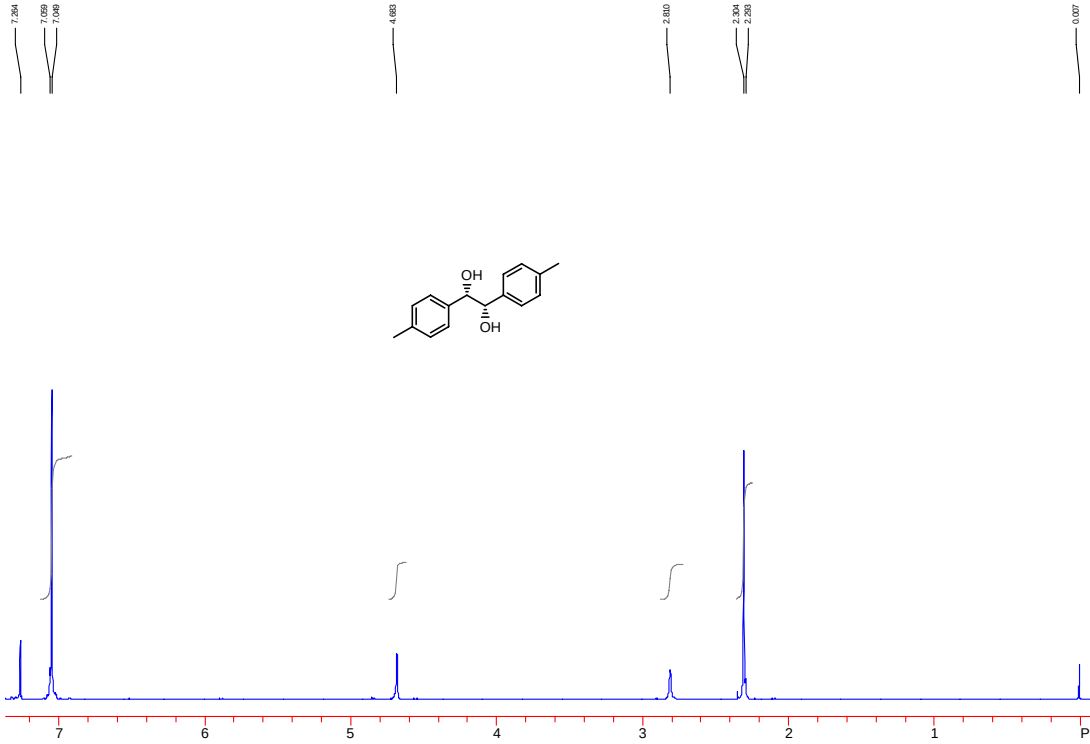
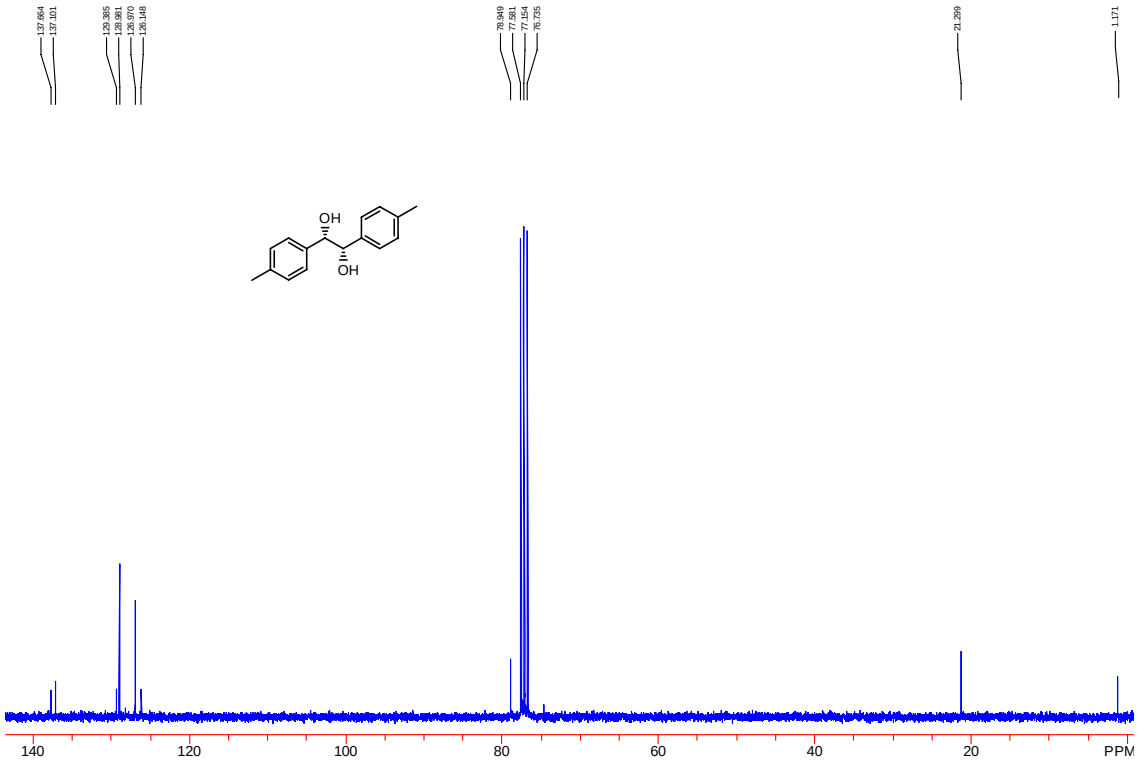
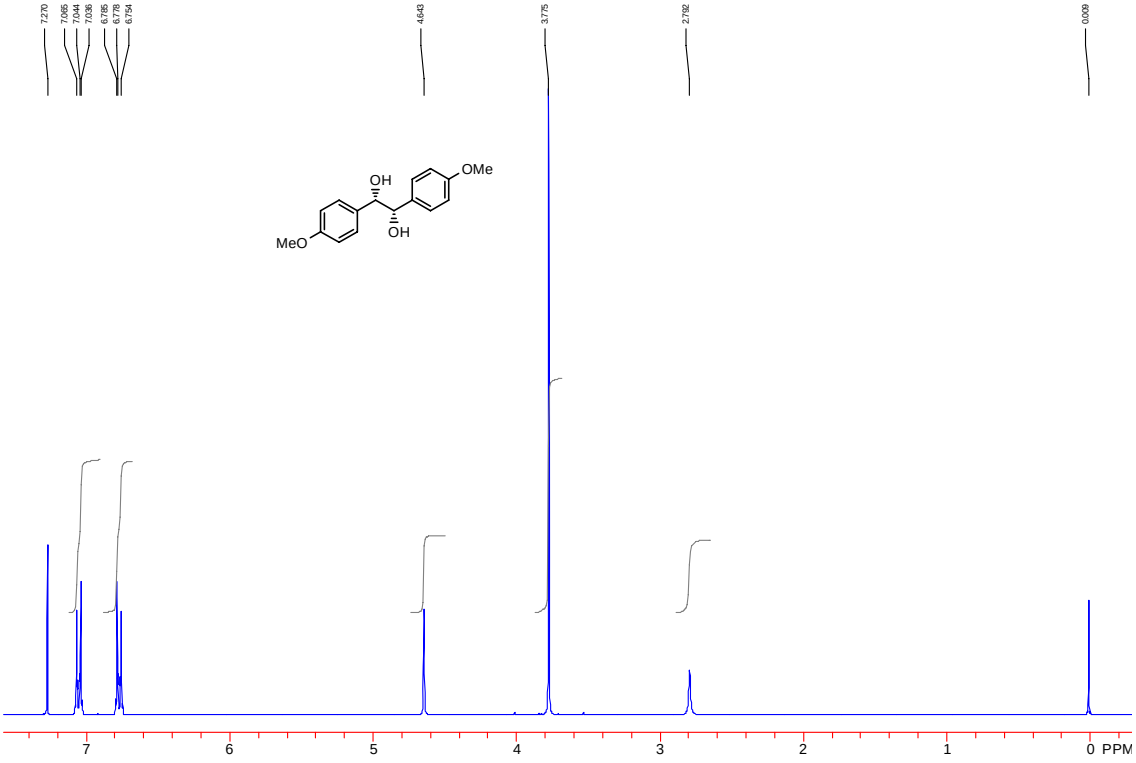
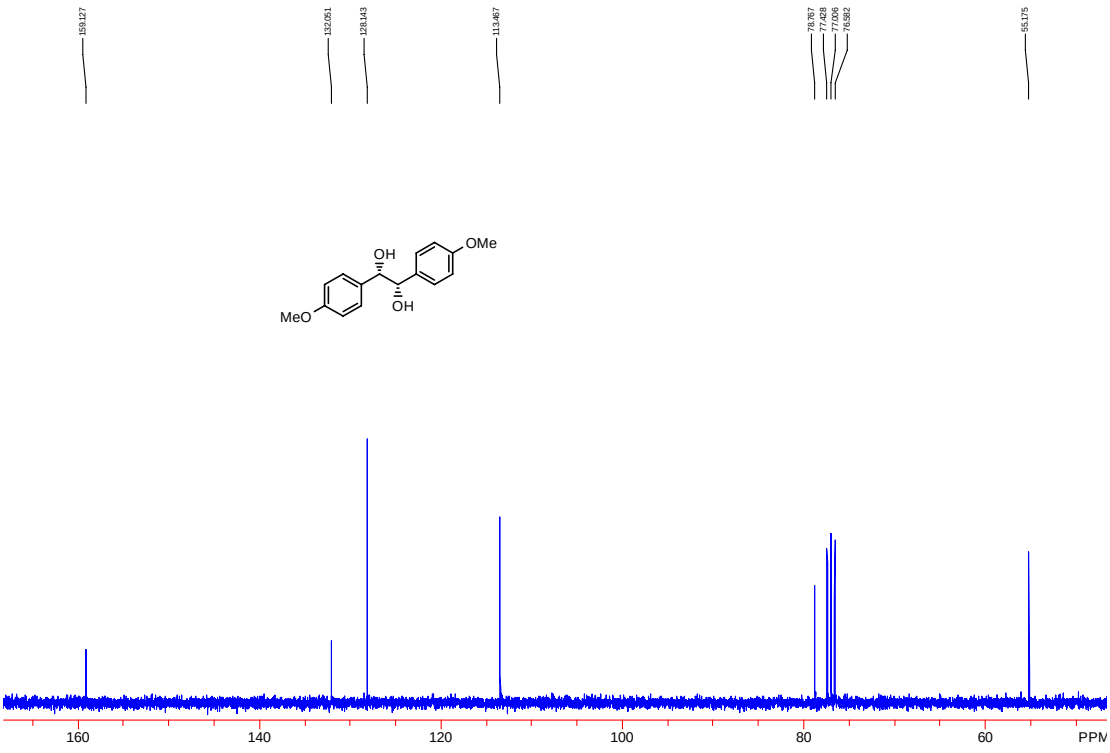




(1S,2S)-1,2-bis(4-methoxyphenyl) ethane-1,2-diol





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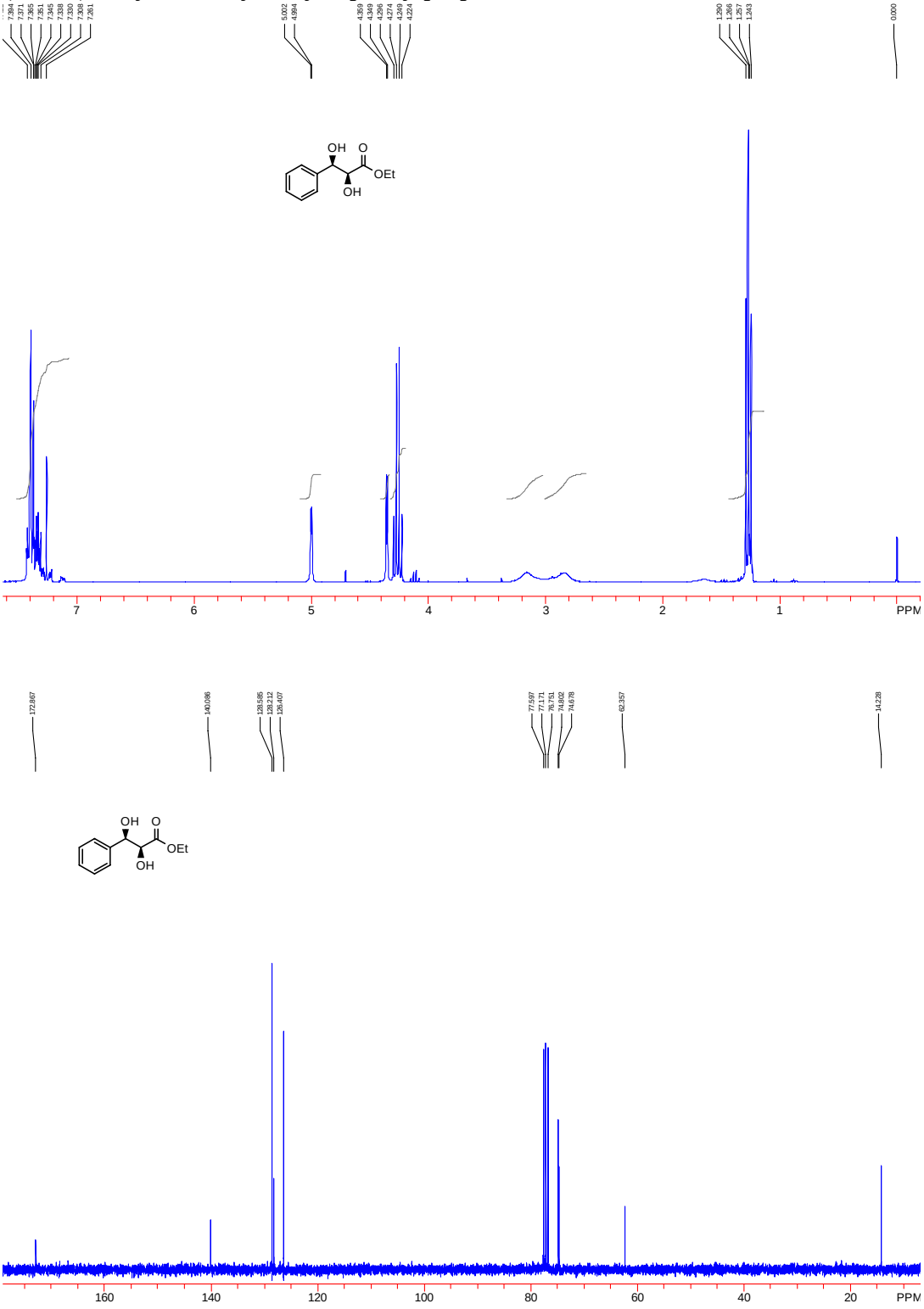
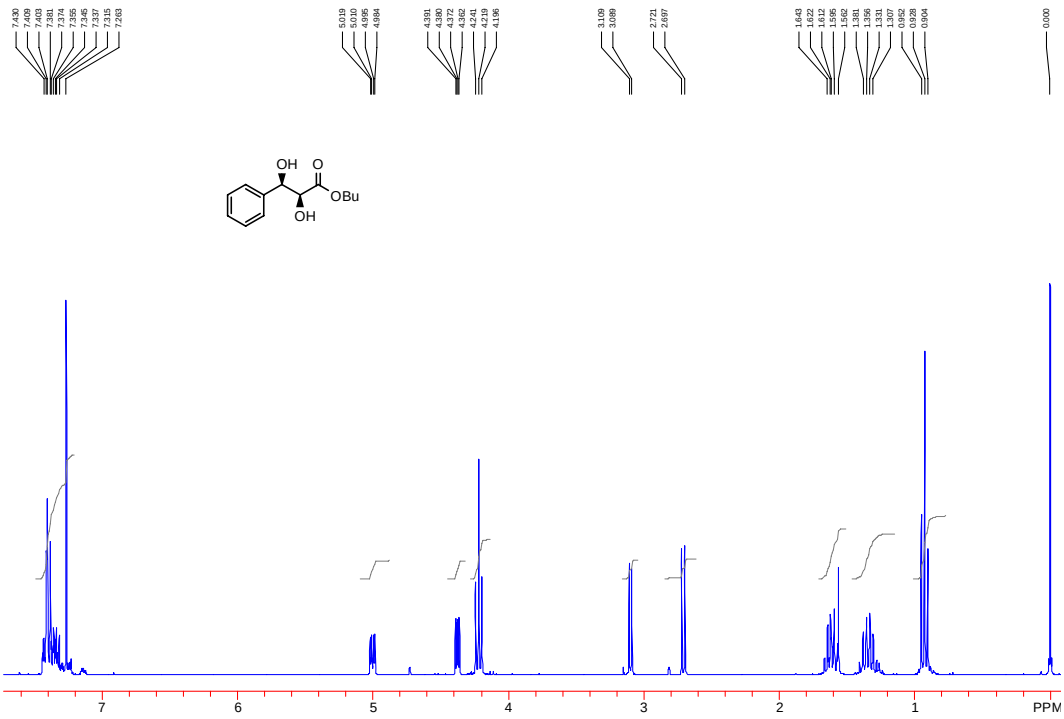


(2S,3R)-Butyl 2,3-dihydroxy-3-phenylpropanoate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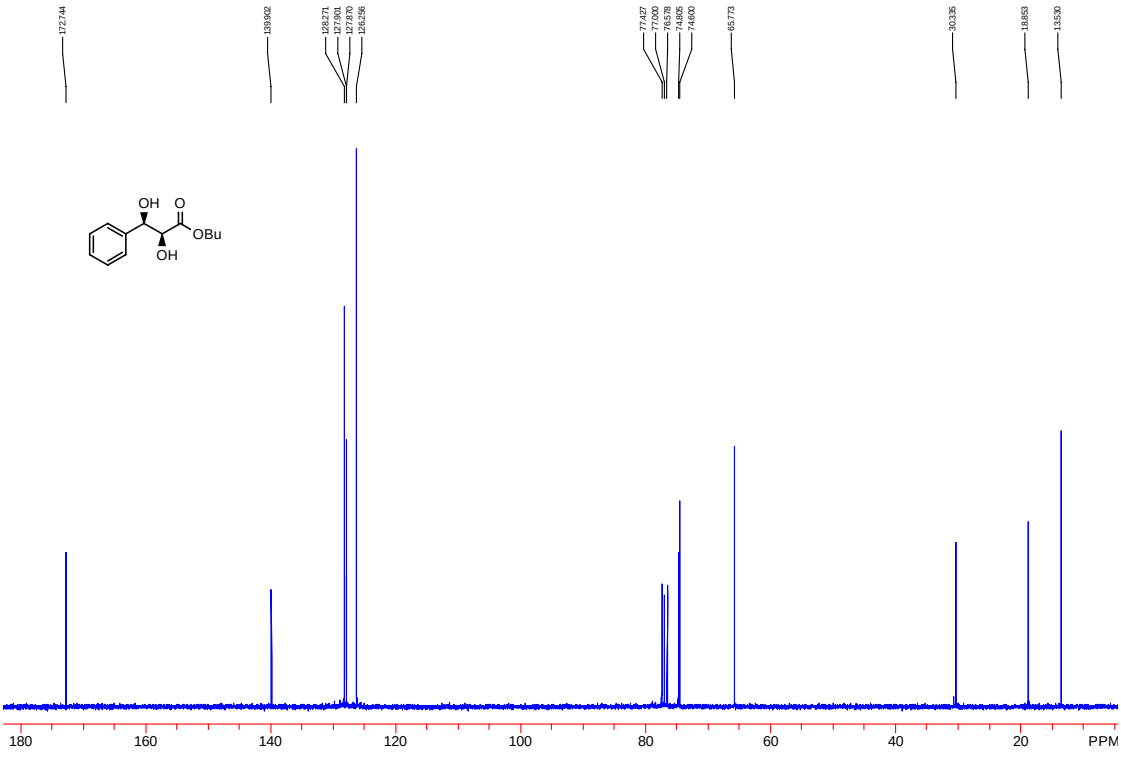
OBu
OH
7
6
5
4
3
2
1
PPM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13.530
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OBu
OH
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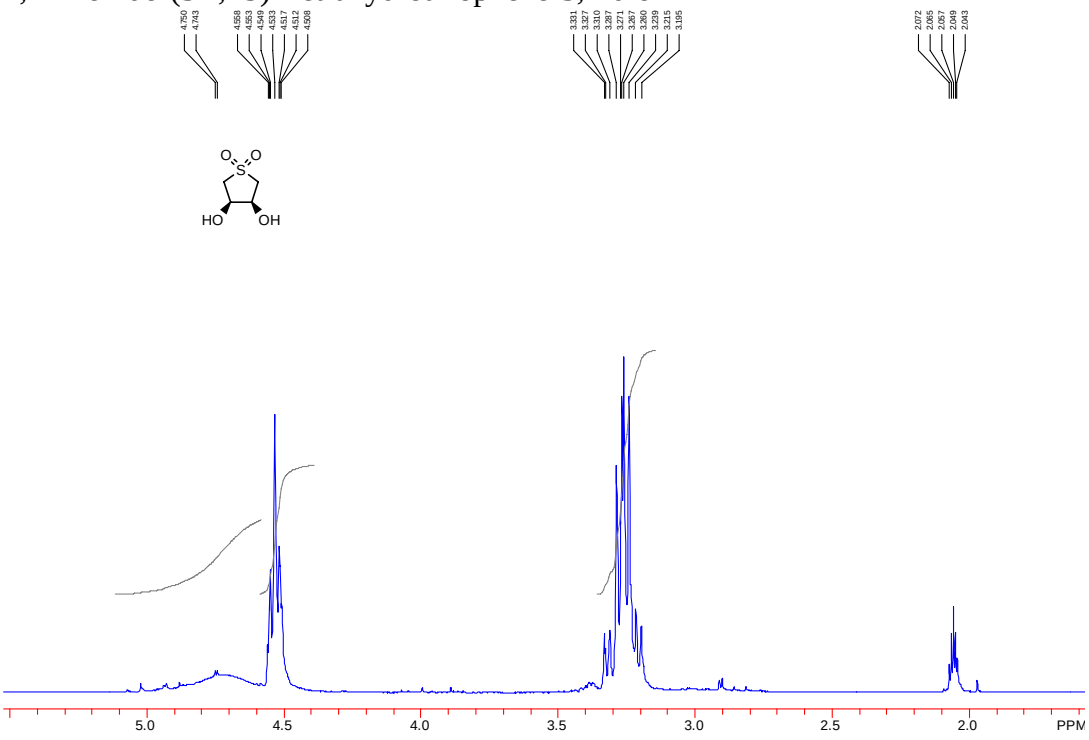
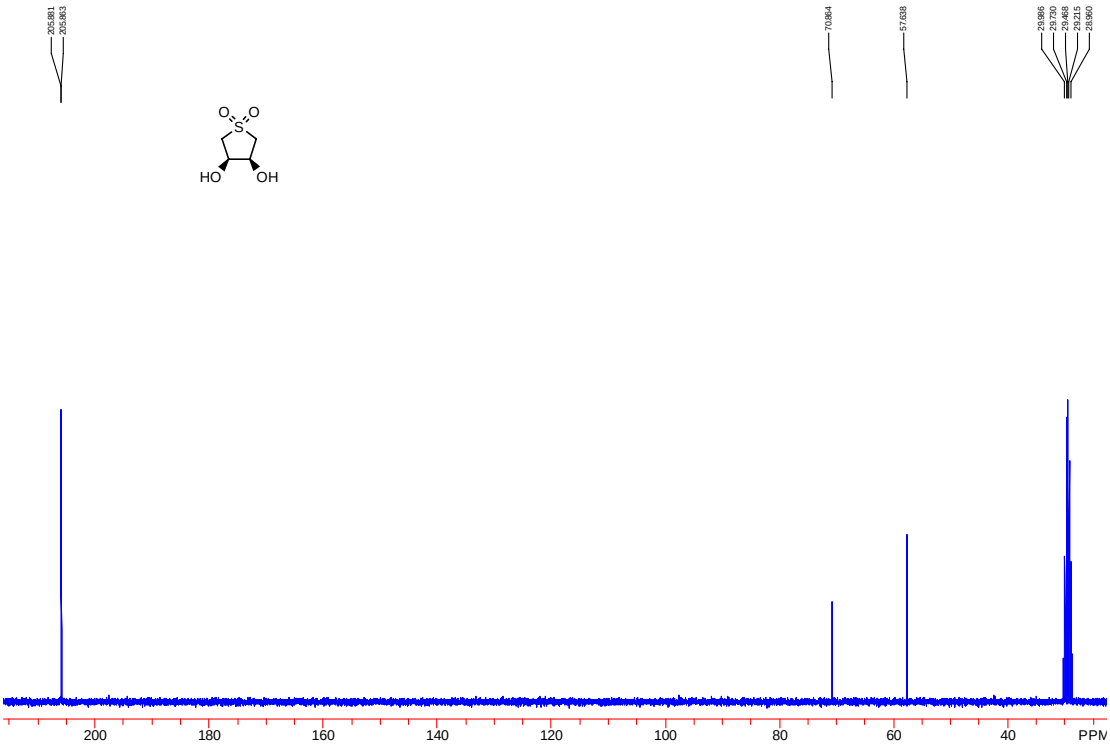
100
80
60
40
20
PPM

1,1-Dioxido-(3R,4S)-Tetrahydrothiophene-3,4-diol





(3S, 4R)–Pyrrolidine-3,4-diol