# Supporting Information

# Chiral Anion Dependent Inversion of Diastereo- and Enantioselectivity in Carbonyl Crotylation *via* Ruthenium Catalyzed Butadiene Hydrohydroxyalkylation

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## Table of Contents

**General Information:** All reactions were run under an atmosphere of argon. Tetrahydrofuran (THF), dichloromethane and toluene were obtained from Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Anhydrous solvents were transferred by oven-dried syringe. Sealed tubes (13×100 mm$^2$) were purchased from Fisher Scientific (catalog number 14-959-35C) and were dried in an oven overnight and cooled under a stream of argon prior to use. $RuH_2(CO)(PPh_3)_3$ and (*R*)-$H_8$-Mes-Et BINOL phosphoric acid was prepared according to literature procedure.[1,2] All ligands were used as received from Strem Chemicals Inc. Alcohols were purified by distillation immediately prior to use. Preparative column chromatography employing silica gel was performed according to the method of Still.[3] Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Dynamic Adsorbents F254). Visualization was accomplished with UV light followed by dipping in a *p-anisaldehyde* solution and heating. Purification of reaction products was carried out by flash column chromatography using Silicycle silica gel (40-63 μm).

**Spectroscopy and Spectrometry:** Infrared spectra were recorded on a Thermo Nicolet 380 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+H, M or M-H) or a suitable fragment ion. $^1$H NMR spectra were recorded on a Varian Gemini (400 MHz) spectrometer at ambient temperature unless otherwise noted. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant(s) in Hz. $^{13}$C NMR spectra were recorded on a Varian Gemini (100 MHz) spectrometer and were routinely run with broadband decoupling. Chemical shifts are reported in ppm from tetramethylsilane, with the residual solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm).

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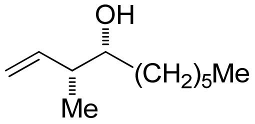
[1] Joseph, T.; Deshpande, S. S.; Halligudi, B. S.; Vinu, A.; Ernst, S.; Hartmann. M. *J. Mol. Catal. A* **2003,** *206,* 13.

[2] Zbieg, J. R.; Yamaguchi, E.; McInturff, E. L.; Krische, M. J. *Science* **2012**, *336*, 324.

[3] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978,** *43,* 2923.

## Procedures and Spectroscopic Data for Alcohols 2a-2j

### (3*R*,4*R*)-3-methyl-1-decen-4-ol (2a)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuH_2(CO)(PPh_3)_3$ (19.3 mg, 0.021 mmol, 7 mol%), (*S*)-SEGPHOS (12.8 mg, 0.021 mmol, 7 mol%), TADDOL-phosphoric acid (29.3 mg, 0.042 mmol, 14 mol%). The tube was sealed with a rubber septum and purged with argon. Alcohol **1a** (42 µL, 0.30 mmol, 100 mol%) and acetone (0.30 mL, 1.0 M concentration with respect to alcohol) were added and the solution was cooled to -78 °C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 3 days, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$; hexanes:ethyl acetate = 8:1) to furnish the title compound (42 mg, 0.25 mmol, *syn*:*anti* = 4.4:1, 95% ee) as a colorless oil in 82% yield.

**TLC ($SiO_2$)**: $R_f$ = 0.4 (hexanes:ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 5.77-5.72 (m, 1H), 5.06-4.99 (m, 2H), 3.44-3.39 (m, 1H), 2.25-2.15 (m, 1H), 1.57-1.16 (m, 10 H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.81 (t, *J* = 6.7 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 114.1, 115.2, 74.7, 43.4, 34.0, 31.8, 29.4, 26.1, 22.6, 14.1, 14.0.

**LRMS** (CI+) *m/z* 171 $[M+H]^+$.

**FTIR** (neat): 3392, 2957, 2927, 2856, 1458, 1119, 910, 733 $cm^{-1}$.

**GC** Cyclosil-B: Initial temperature: 50 °C (5 min hold); 130 °C, rate: 3 °C/min) $t_{minor}$ = 28.7 min, $t_{major}$ = 28.9 min.

**$[\alpha]_D^{25}$** = 37.5° (c = 1.0, $CHCl_3$).

*The spectroscopic properties of this compound were consistent with the data available in the literature.*[4]

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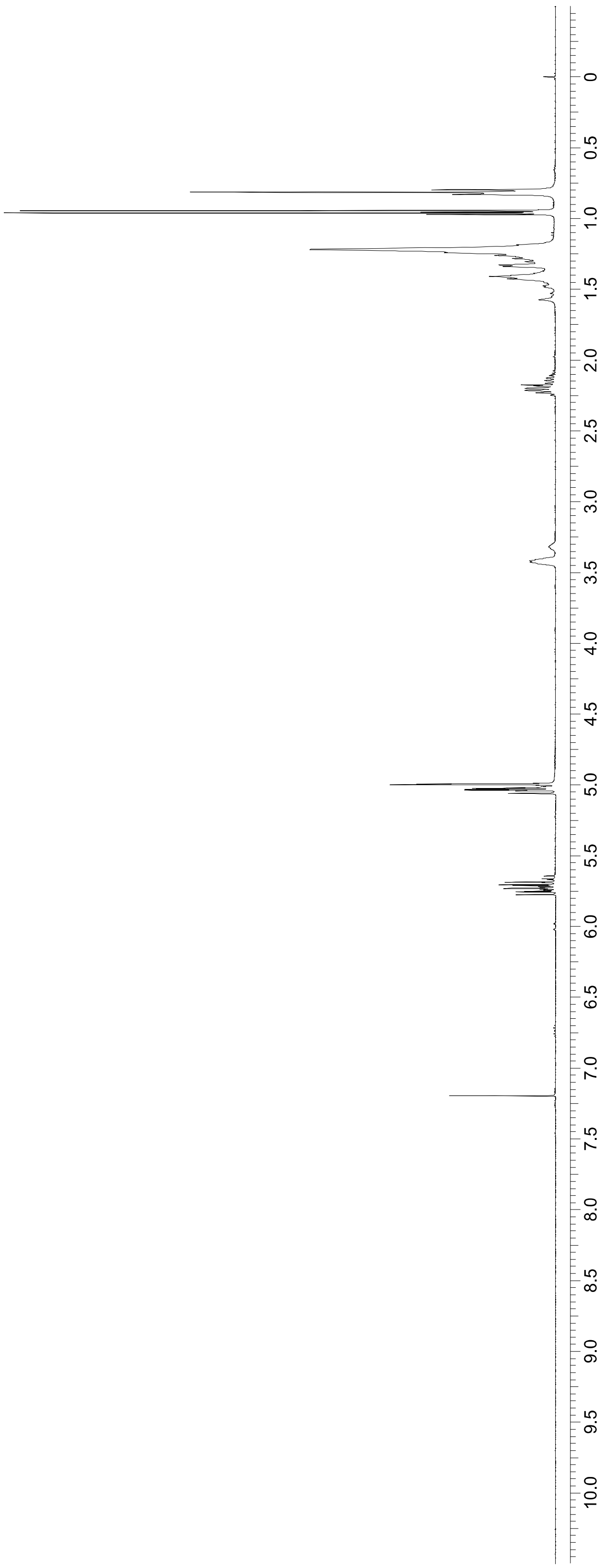
[4] Marshall, M. J.; Palovich, R. M. *J. Org. Chem.* **1998,** *63,* 4381.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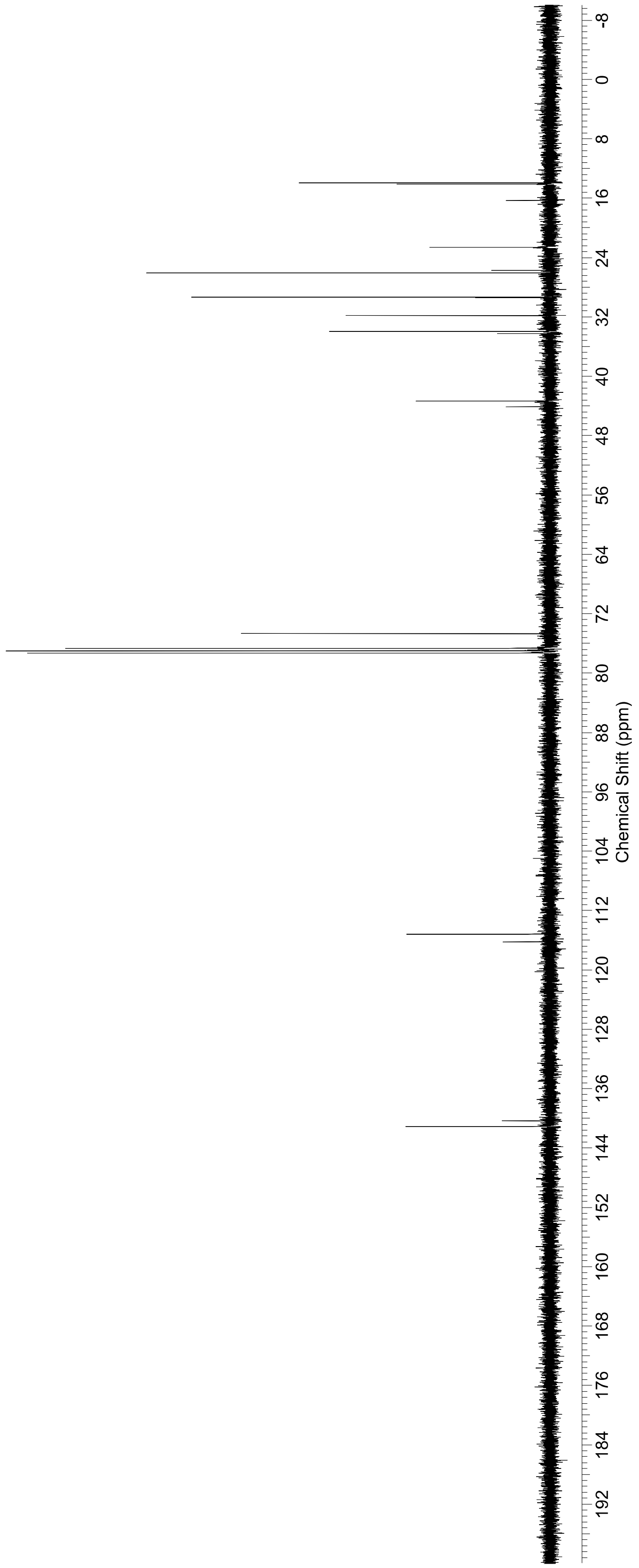
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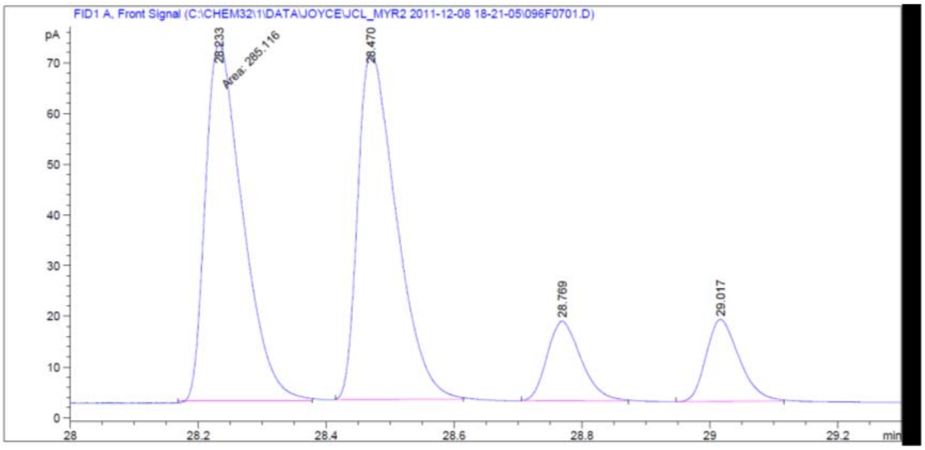
Chemical Shift (ppm)

**GC (*racemic*)**



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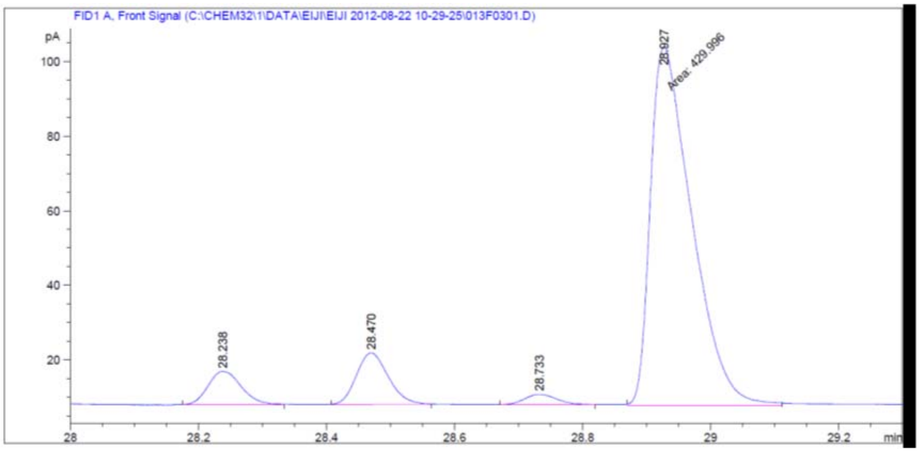

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   3  28.733 BB     0.0535    9.73064    2.78858  1.87133
   4  28.927 MM     0.0745  429.99585   96.17088 82.69380
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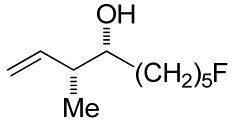
## (3*R*,4*R*)-9-Fluoro-3-methylnon-1-en-4-ol (2b)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuH_2(CO)(PPh_3)_3$ (19.3 mg, 0.021 mmol, 7 mol%), (*S*)-SEGPHOS (13.0 mg, 0.021 mmol, 7 mol%), TADDOL-phosphoric acid (29.3 mg, 0.042 mmol, 14 mol%). The tube was sealed with a rubber septum and purged with argon. Alcohol **1b** (37 µL, 0.30 mmol, 100 mol%) and acetone (0.30 mL, 1.0 M concentration with respect to alcohol) were added and the solution was cooled to –78 °C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 3 days, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$; hexanes : ethyl acetate = 10:1) to furnish the title compound (43.9 mg, 0.25 mmol, *syn*:*anti* = 4.8:1, 96% ee) as a colorless oil in 84 % yield.

**TLC ($SiO_2$)**: $R_f$ = 0.45 (hexanes:ethyl acetate = 10:1).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 5.83-5.74 (m, 1H), 5.14-5.06 (m, 2H), 4.50 (t, *J* = 6.2 Hz, 1H), 4.36 (t, *J* = 6.2 Hz, 1H), 3.49 (ddd, *J* = 8.6, 5.1, 3,3 Hz, 1H), 2.32-2.23 (m, 1H), 1.77-1.64 (m, 2H), 1.56-1.36 (m, 6H), 1.03 (d, *J* = 7.0 Hz, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 140.9, 115.4, 85.1 (d, *J* = 164.6 Hz), 74.5, 43.5, 33.8, 30.4 (*J* = 19.5 Hz), 25.7, 25.2 (*J* = 5.2 Hz), 14.0.

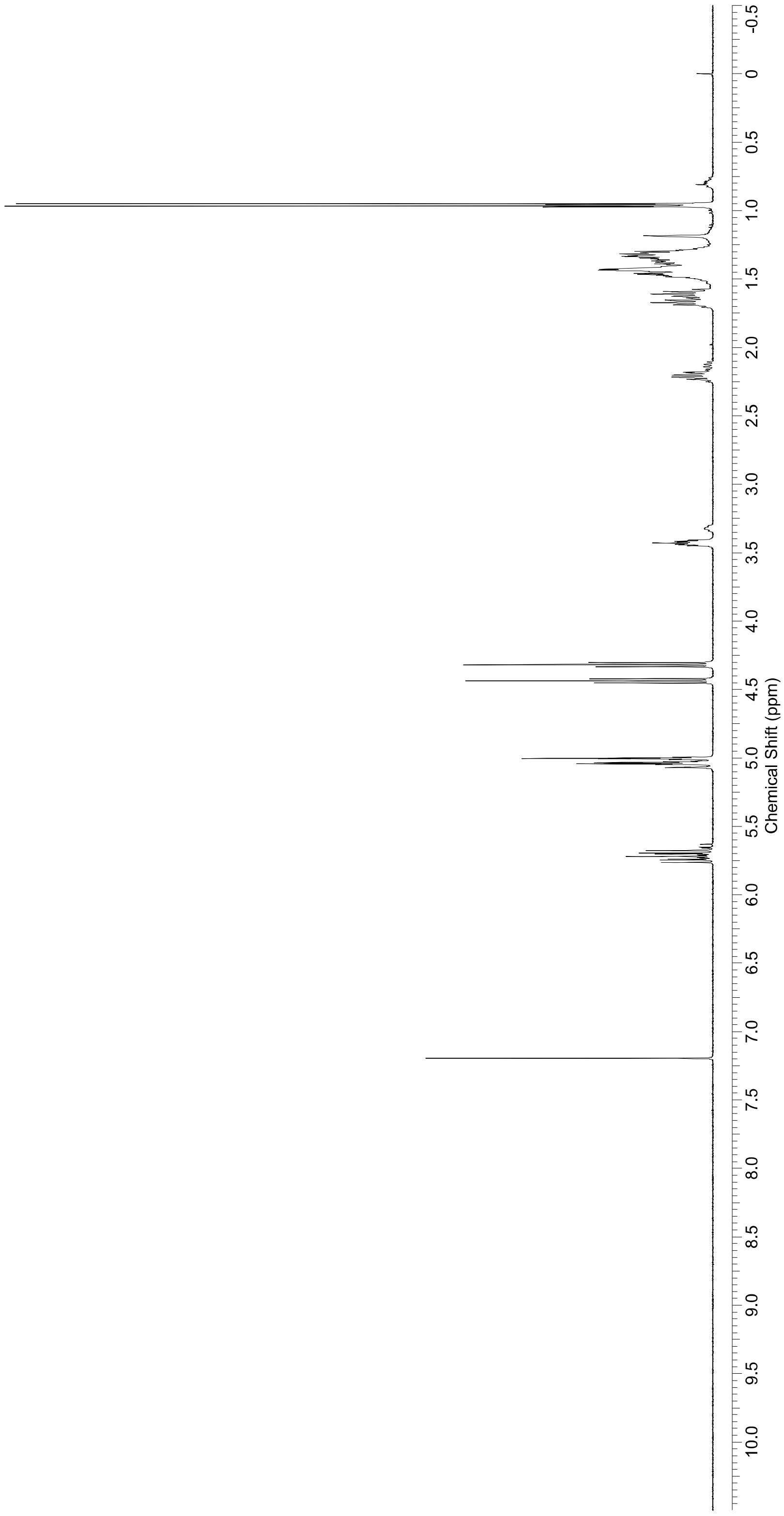
**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -218.0 to -218.4 (m).

**LRMS** (CI+) *m/z* 175 $[M+H]^+$

**FTIR** (neat): 3413, 2934, 2860, 1459, 1390, 1243, 997, 912 $cm^{-1}$.

**GC** Cyclosil-B: Initial temperature: 50 °C (5 min hold); 80°C (5 min hold), rate: 2 °C/min; 130 °C, rate: 1.5 °C/min) $t_{minor}$ = 48.3 min, $t_{major}$ = 48.5 min.

**$[\alpha]_D^{25}$** = 66.6° (c = 1.0, $CHCl_3$).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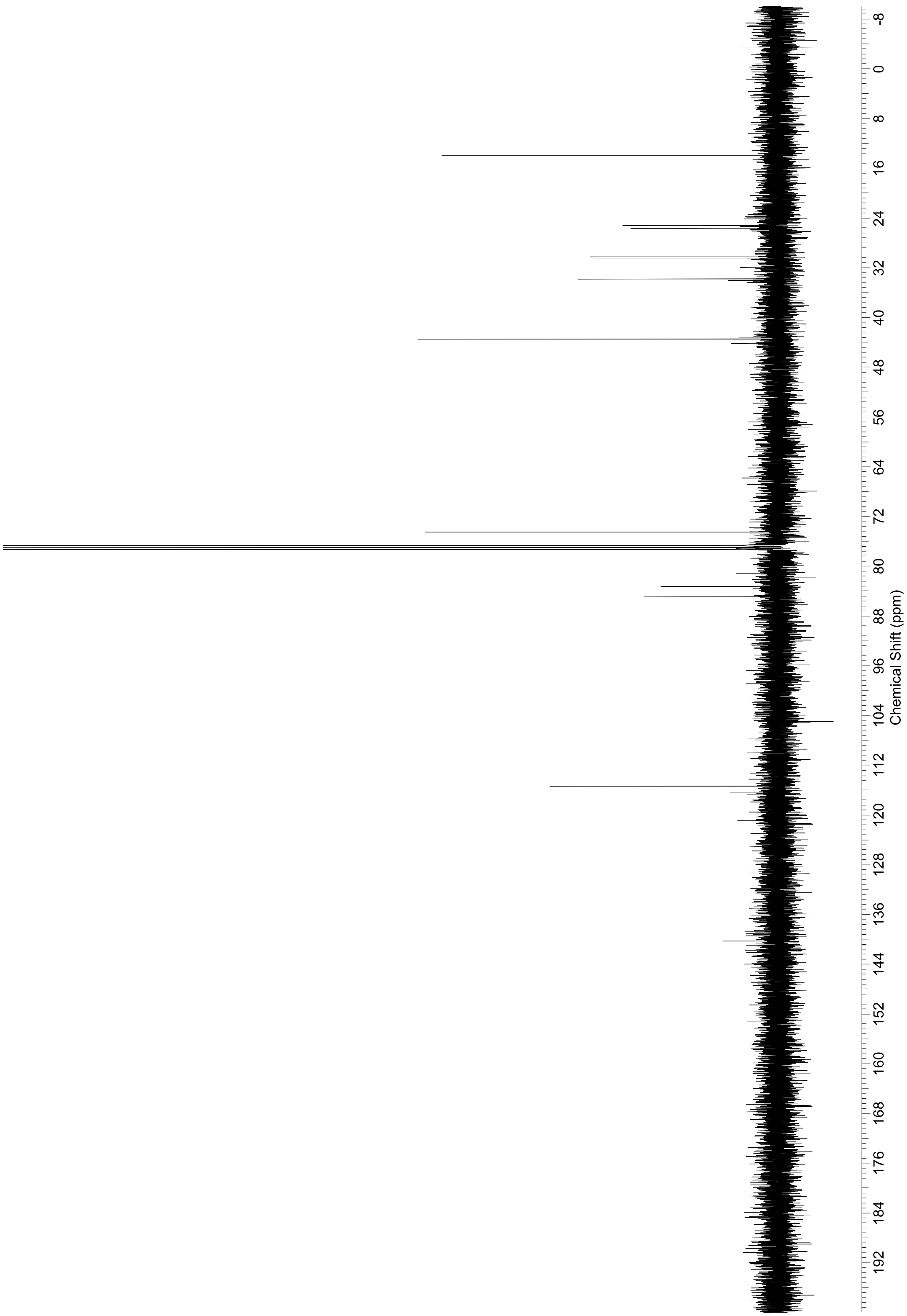

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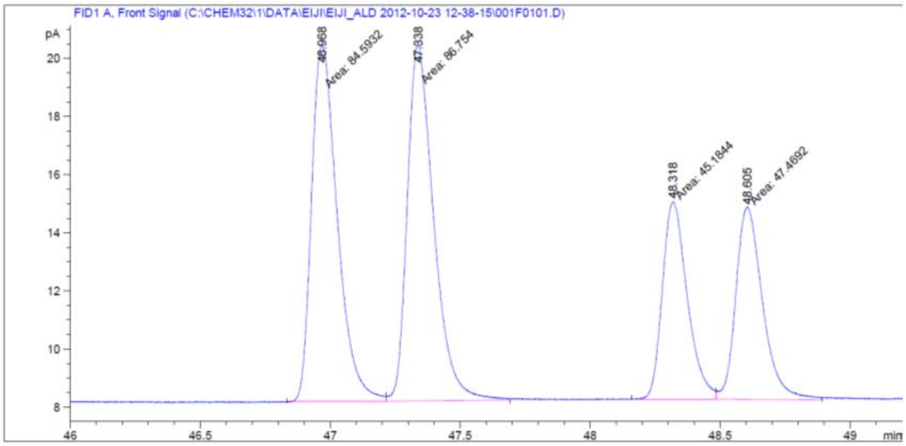
Chemical Shift (ppm)

## GC (*racemic)*



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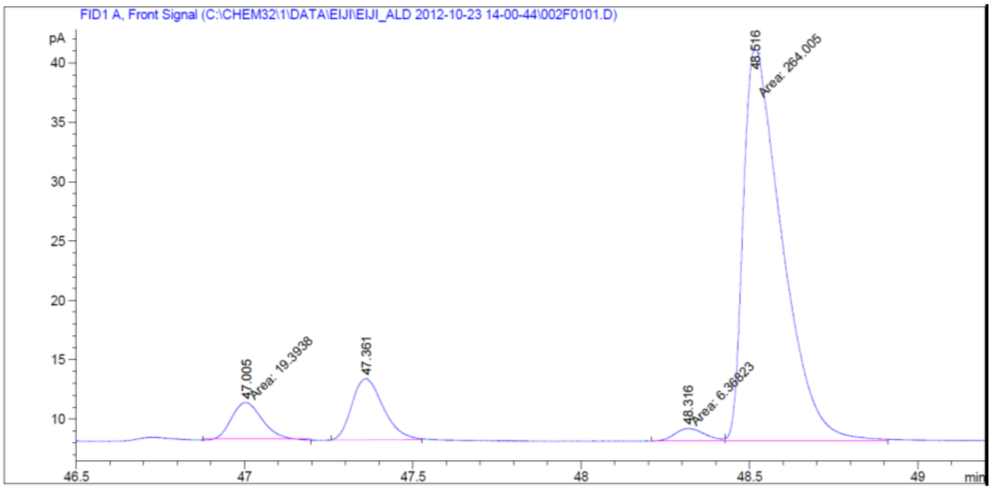
## GC (*chiral*)



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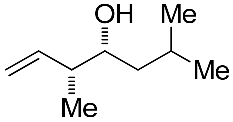
## (3*R*,4*R*)-3,6-dimethylhept-1-en-4-ol (2c)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuH_2(CO)(PPh_3)_3$ (13.8 mg, 0.015 mmol, 5 mol%), (*S*)-SEGPHOS (9.2 mg, 0.015 mmol, 5 mol%), TADDOL-phosphoric acid (20.9 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Alcohol **1c** (33 µL, 0.30 mmol, 100 mol%) and acetone (0.30 mL, 1.0 M concentration with respect to alcohol) were added and the solution was cooled to -78 °C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 3 days, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$; hexanes:ethyl acetate = 8:1) to furnish the title compound (26.9 mg, 0.19 mmol, *syn*:*anti* = 4.6:1, 94% ee) as a colorless oil in 64% yield.

**TLC ($SiO_2$)**: $R_f$ = 0.4 (hexanes:ethyl acetate = 8:1).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 5.73 (ddd, *J* = 17.6, 10.0, 7.4 Hz, 1H), 5.07-4.99 (m, 2H), 3.62-3.57 (m, 1H), 2.28-2.23 (m, 1H), 1.83-1.77 (m, 1H), 1.45 (brs, 1H), 1.38-1.22 (m, 2H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H)..

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 141.0, 115.3, 72.5, 43.8, 43.1, 24.7, 23.7, 21.7, 14.0.

**LRMS** (CI+) *m/z* 143 $[M+H]^+$

**FTIR** (neat): 3623, 2955, 2924, 1718, 1464, 1367, 966, 910, 694 $cm^{-1}$.

**GC** Cyclosil-B: Initial temperature: 50 °C (5 min hold); 130 °C, rate: 3 °C/min) $t_{minor}$ = 19.1 min, $t_{major}$ = 19.5 min.

**$[\alpha]_D^{25}$** = 56.2° (c = 1.50, $CH_2Cl_2$). $[\alpha]_D^{25}$ = 45.2° (c =1.45, $CH_2Cl_2$) was reported for 96% ee of the (3*R,*4*R*) compound.[5]

*The spectroscopic properties of this compound were consistent with the data available in the literature.*[5]

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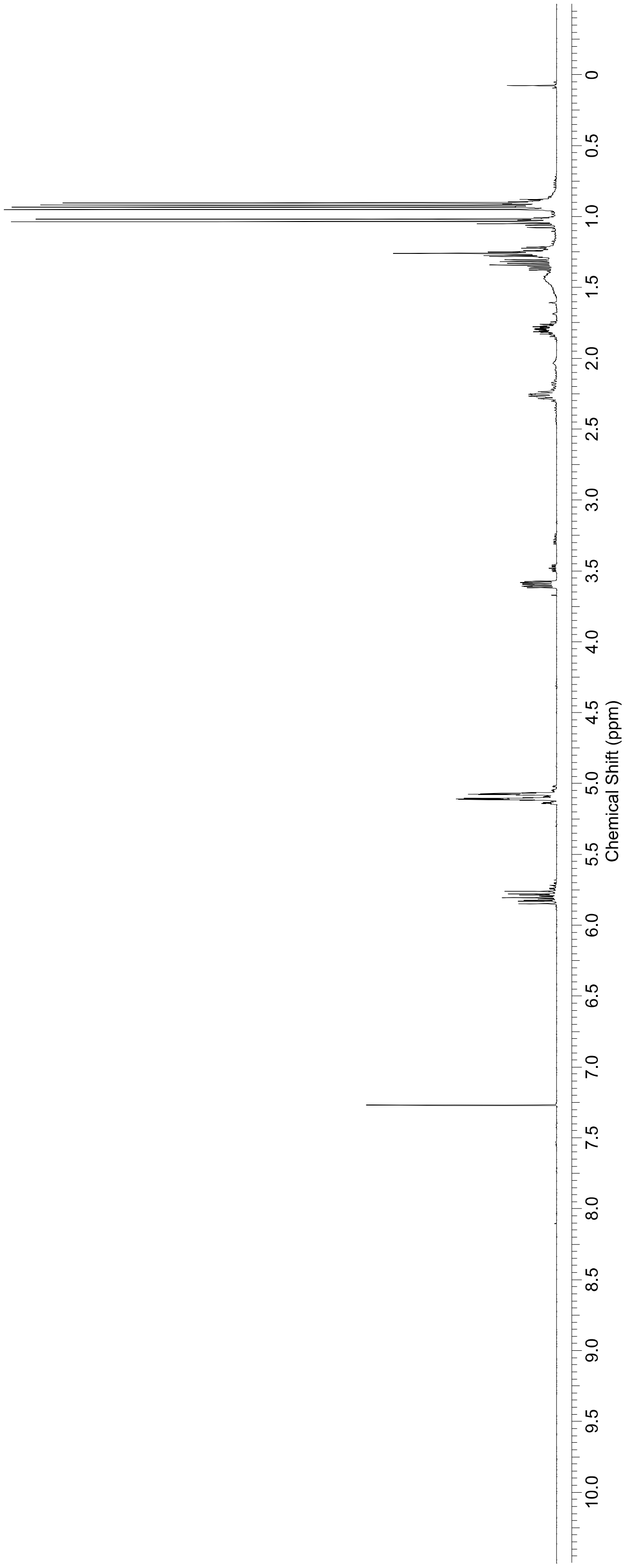
[5] Hackman, B. M.; Lombardi, P. J.; Leighton, J. L. *Org. Lett.* **2004**, *6, 4375.*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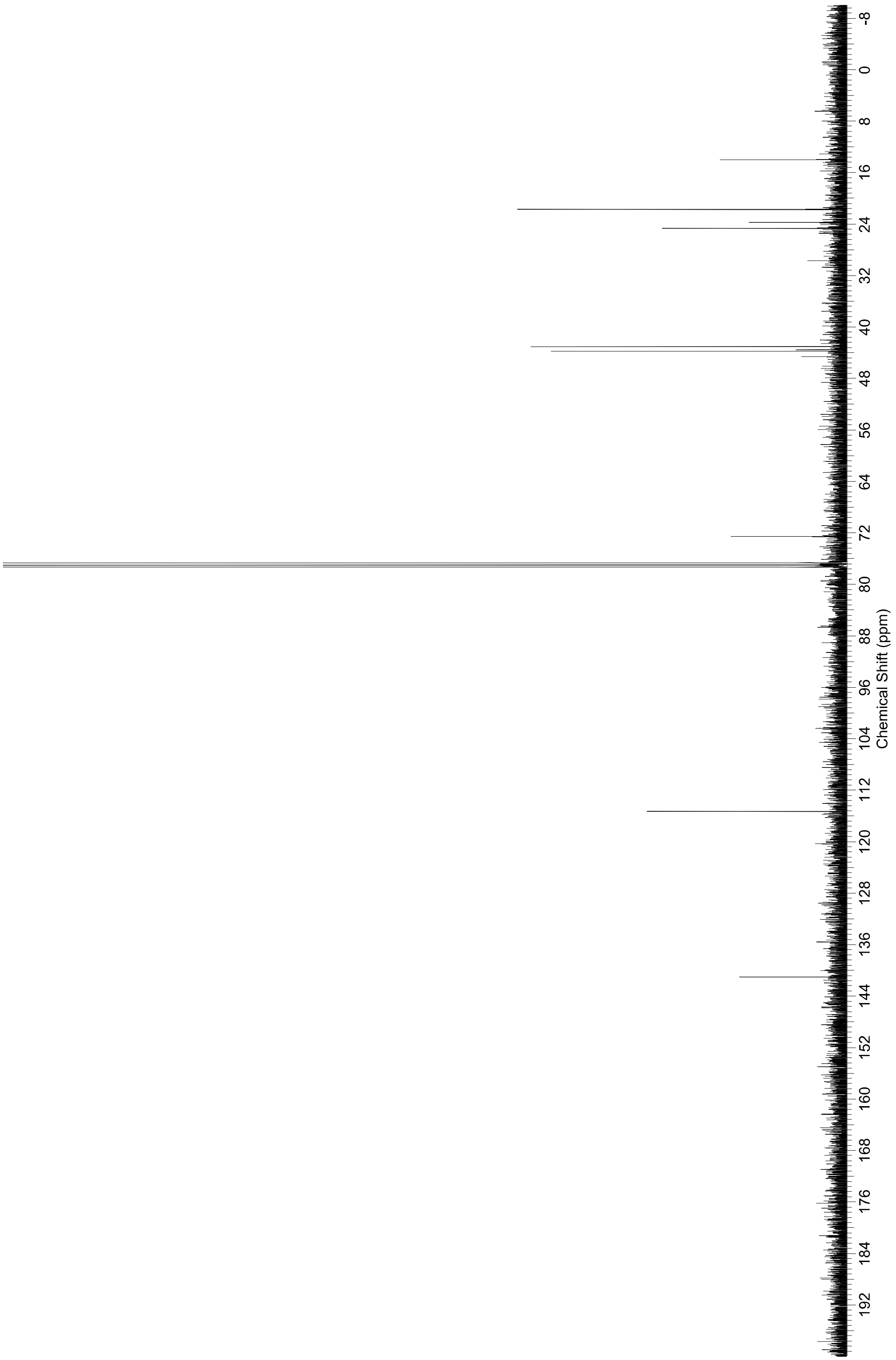
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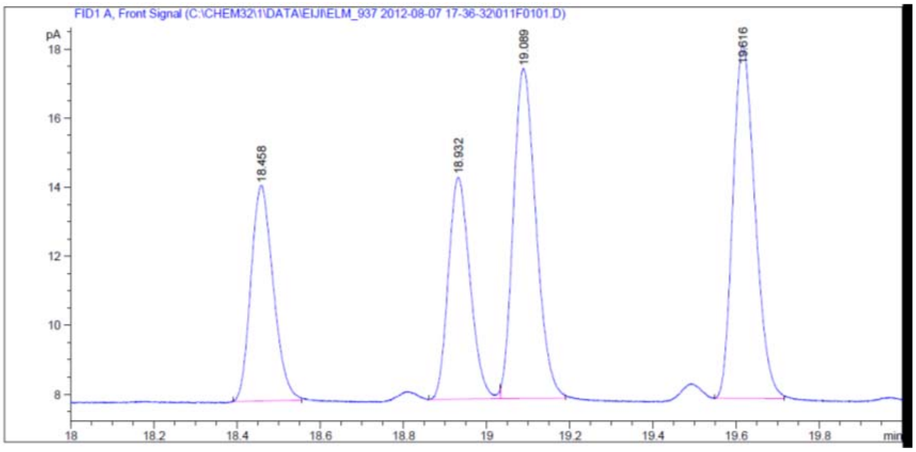
Chemical Shift (ppm)

**GC (*racemic*)**



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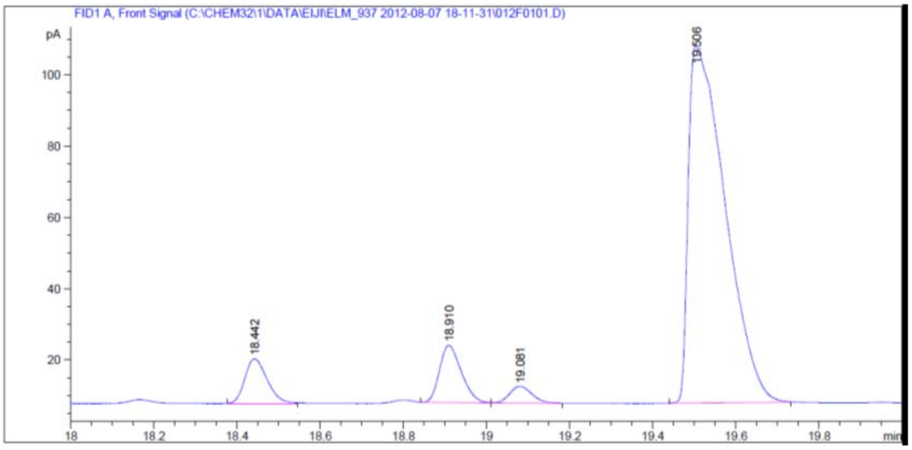
**GC (*chiral*)**



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   4  19.506 BB    0.0829  615.76196  100.21123 83.48616
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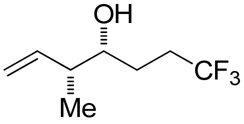
### (3*R*,4*R*)-7,7,7-Trifluoro-3-methylhept-1en-4-ol (2d)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuH_2(CO)(PPh_3)_3$ (19.3 mg, 0.021 mmol, 7 mol%), (*S*)-SEGPHOS (13.0 mg, 0.021 mmol, 7 mol%), TADDOL-phosphoric acid (29.3 mg, 0.042 mmol, 14 mol%). The tube was sealed with a rubber septum and purged with argon. Alcohol **1d** (32 µL, 0.30 mmol, 100 mol%) and acetone (0.30 mL, 1.0 M concentration with respect to alcohol) were added and the solution was cooled to -78 °C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 3 days, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$; hexanes:ethyl acetate = 10:1) to furnish the title compound (39 mg, 0.21 mmol, *syn*:*anti* = 4.3:1, 96% ee) as a colorless oil in 72% yield.

**TLC ($SiO_2$)**: $R_f$ = 0.4 (hexanes:ethyl acetate = 10:1).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 5.80-5.68 (m, 1H), 5.20-5.11 (m, 2H), 3.54-3.49 (m, 1H), 2.43-2.26 (m, 2H), 2.22-2.06 (m, 1H), 1.82-1.73 (m, 1H), 1.64-1.53 (m, 2H), 1.06 (d, *J* = 6.9 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 139.8, 127.4 (q, *J* = 276.0 Hz), 116.3, 73.4, 43.9, 30.7 (q, *J* = 29.2 Hz), 26.3 (q, *J* = 3.0 Hz), 14.5.

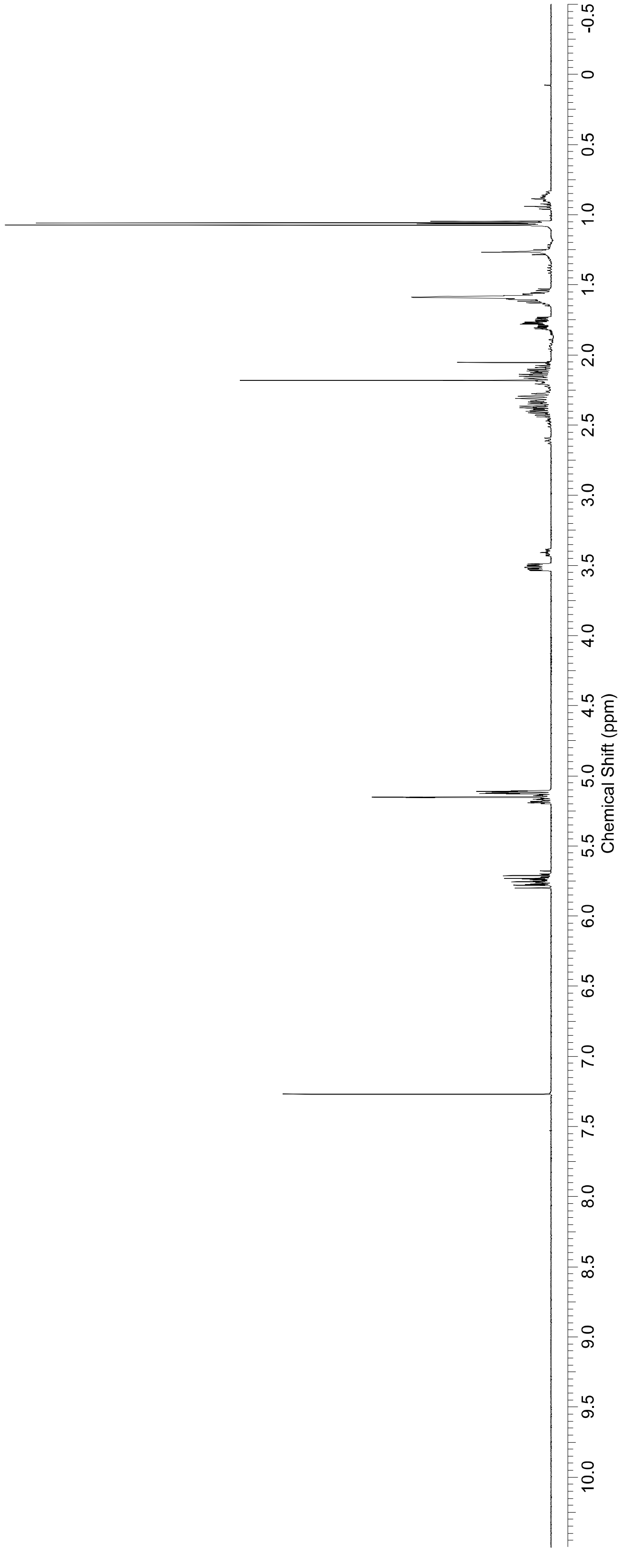
**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -66.37 (*J* = 10.9 Hz).

**LRMS** (CI+) *m/z* 183 $[M+H]^+$

**FTIR** (neat): 3373, 2964, 2358, 1455, 1383, 1225, 1138, 1032, 1005, 918, 800 cm$^{-1}$.

**GC** (Cyclosil-B: Initial temperature: 50 °C (5 min hold); 130 °C, rate: 3 °C/min), $t_{minor}$ = 18.1 min, $t_{major}$ = 18.9 min.

**$[\alpha]_D^{25}$** = 20.1° (c = 1.0, $CHCl_3$).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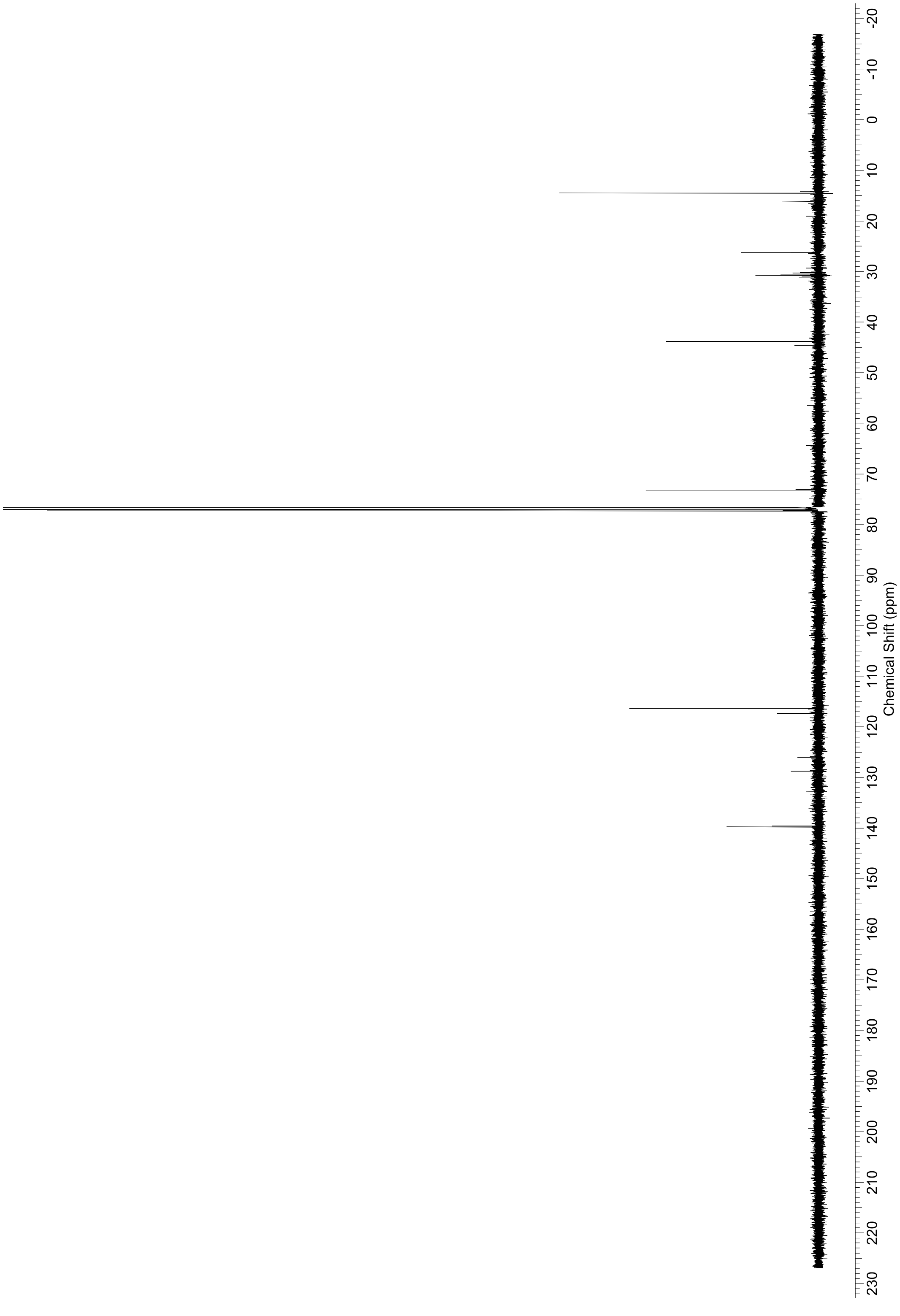
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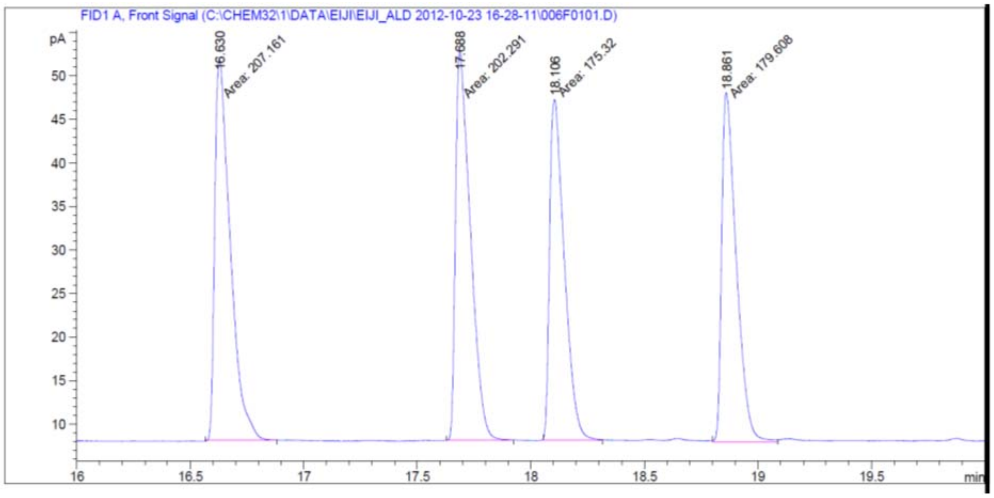
Chemical Shift (ppm)

**GC (*racemic*)**



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   3  18.106 MM    0.0747  175.31981   39.09904 22.93621
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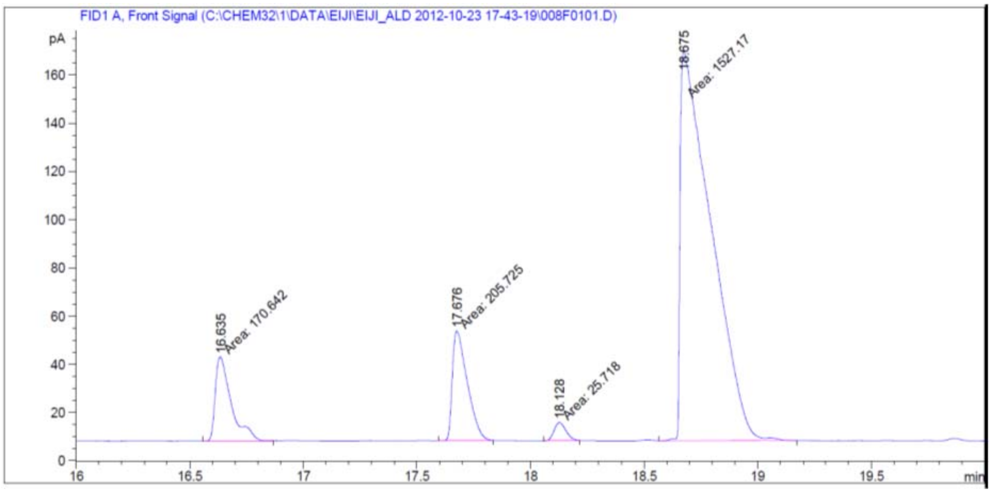
**GC (*chiral*)**



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Peak RetTime Type  Width     Area      Height     Area
 #    [min]        [min]    [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  16.635 MM    0.0813  170.64178   34.98223  8.84494
   2  17.676 MM    0.0757  205.72536   45.31288 10.66344
   3  18.128 MM    0.0581   25.71798    7.37326  1.33305
   4  18.675 MM    0.1568 1527.17419  162.28458 79.15858
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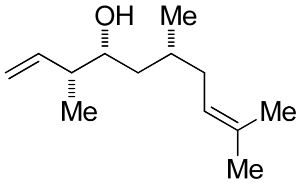
## (3*R*,4*R*,6*R*)-3,6,10-trimethylundeca-1,9-dien-4-ol (2e)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuH_2(CO)(PPh_3)_3$ (13.8 mg, 0.015 mmol, 5 mol%), (*S*)-SEGPHOS (9.3 mg, 0.015 mmol, 5 mol%), TADDOL-phosphoric acid (20.9 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Alcohol **1e** (41 µL, 0.30 mmol, 100 mol%) and acetone (0.30 mL, 1.0 M concentration with respect to alcohol) were added and the solution was cooled to -78 °C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 3 days, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$; hexanes:ethyl acetate = 8:1) to furnish the title compound (52.3 mg, 0.27 mmol, *syn*:*anti* = 4.6:1, 95% ee) as a colorless oil in 89% yield.

**TLC ($SiO_2$)**: $R_f$ = 0.45 (hexanes:ethyl acetate = 8:1).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 5.81 (ddd, *J* = 17.6, 9.8, 7.2 Hz, 1H), 5.13-5.06 (m, 3H), 3.65-3.59 (m, 1H), 2.30-2.21 (m, 1H), 2.07-1.88 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.59 (brs, 1H), 1.49-1.38 (m, 2H), 1.35-1.05 (m, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 141.13, 131.24, 124.8, 115.3, 72.5, 43.4, 41.4, 36.3, 29.4, 25.7, 25.3, 20.5, 17.6, 13.6.

**LRMS** (CI+) *m/z* 211 $[M+H]^+$

**FTIR** (neat): 3358, 2963, 2924, 1639, 1455, 1376, 1091, 996, 910, 734 $cm^{-1}$.

**GC** (GC Cyclosil-B: Initial temperature: 50 °C (5 min hold); 100 °C (5 min hold), rate: 1 °C/ min; 150 °C, rate 0.5 °C/min): $t_{minor}$ = 89.4 min, $t_{major}$ = 89.8 min.

**$[\alpha]_D^{25}$** = -38.33° (c = 1.0, $CHCl_3$)

*The spectroscopic properties of this compound were consistent with the data available in the literature.*[6]

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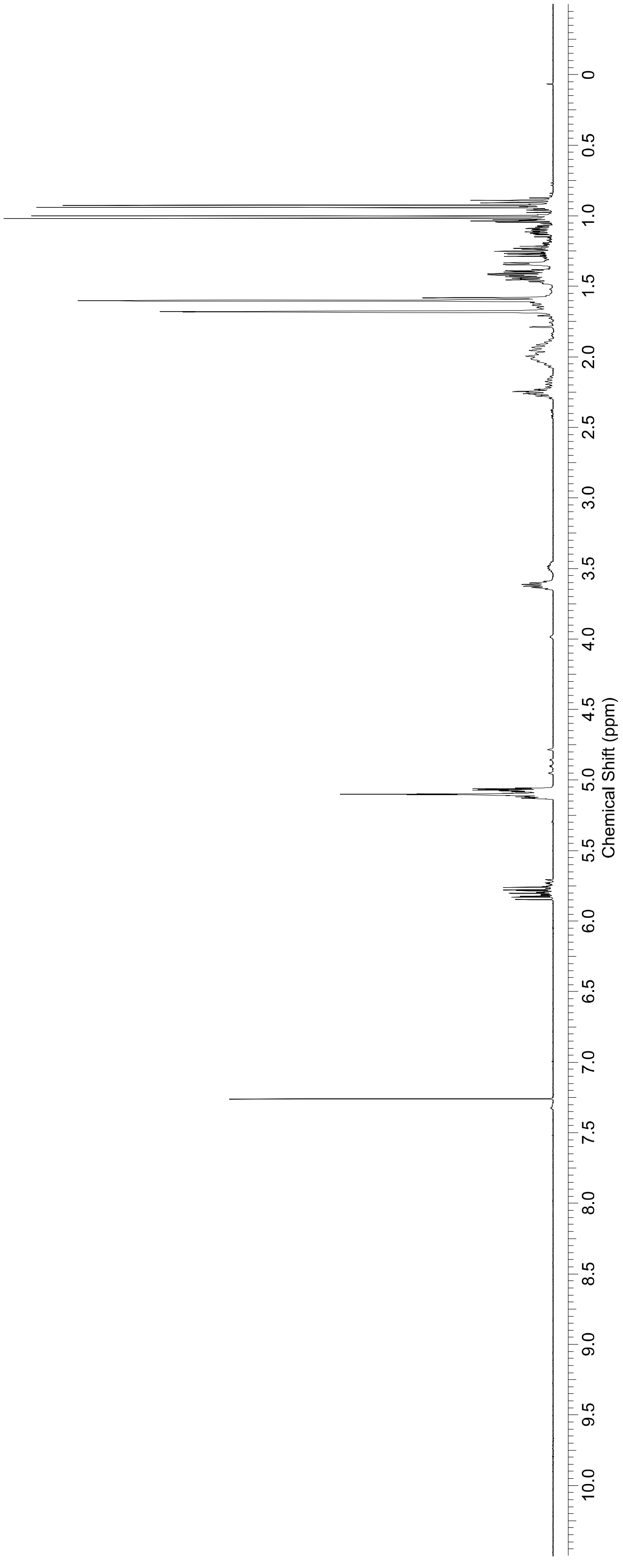
[6] Millan, A., Campana, A.G., Bazdi, B., Miguel, D., Alvarez de Cienfuegos, L., Cuerva, J.M., Echavarren, A.M. *Chem. Eur. J.* **2011**, *17*, 3985.



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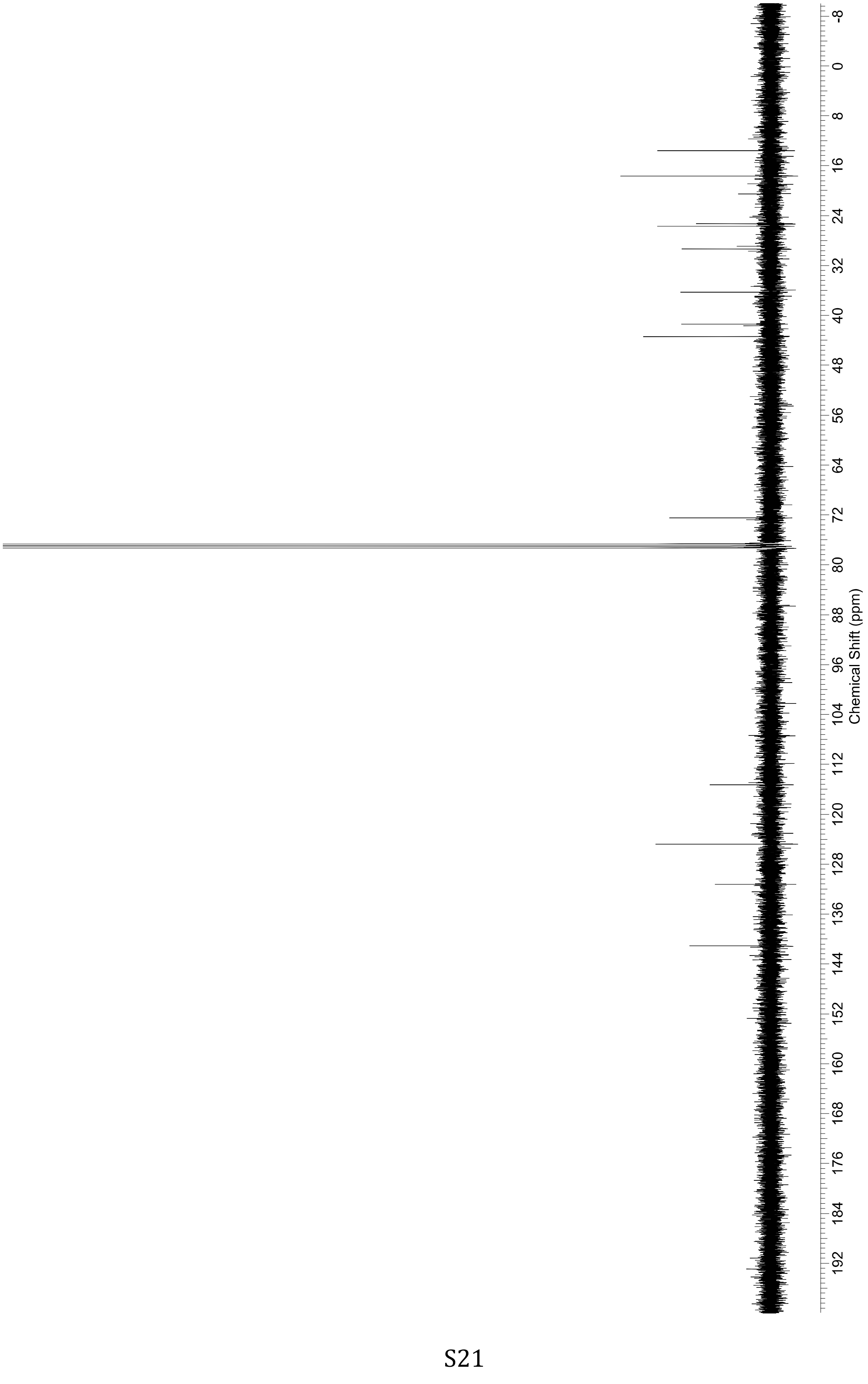
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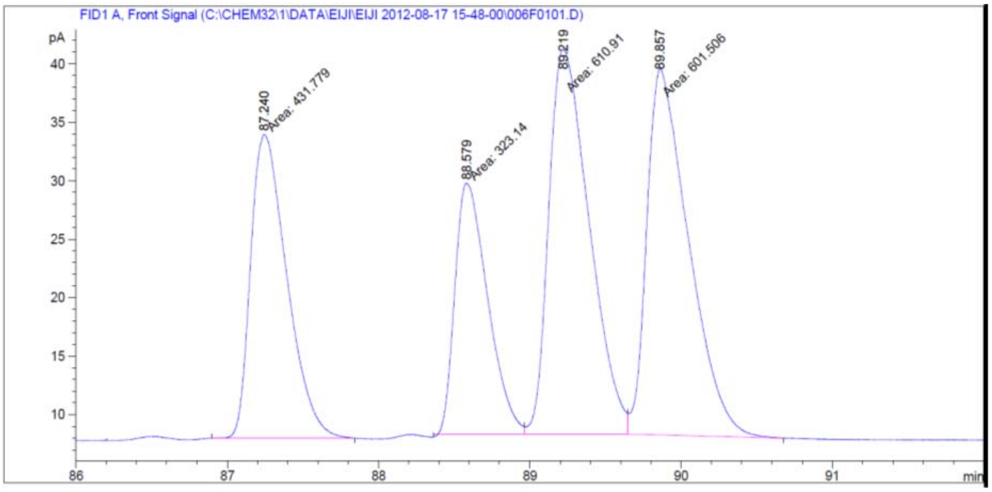
Chemical Shift (ppm)

**GC *(racemic)***



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   2  88.579 MM     0.2510  323.14011   21.45309 16.42527
   3  89.219 MM     0.3093  610.90973   32.91447 31.05265
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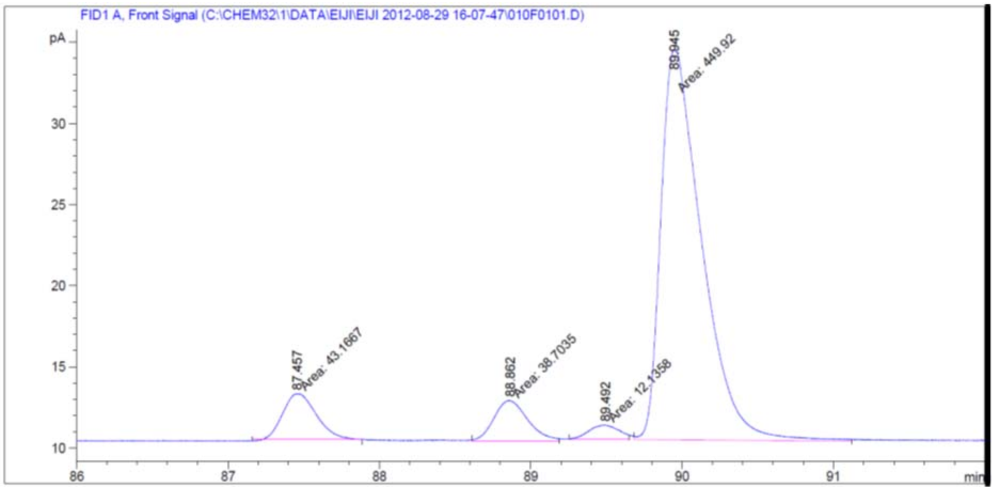
**GC (*chiral*)**



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Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [pA*s]       [pA]          %
----|-------|----|-------|----------|----------|--------|
   1  87.457 MM     0.2560   43.16674    2.81008  7.93615
   2  88.862 MM     0.2582   38.70352    2.49848  7.11559
   3  89.492 MM     0.2313   12.13580 8.74436e-1  2.23115
   4  89.945 MM     0.3118  449.91974   24.05206 82.71712
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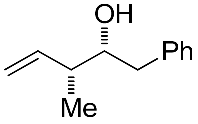
## (2*R*,3*R*)-3-methyl-1-phenylpent-4-en-2-ol (2f)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuH_2(CO)(PPh_3)_3$ (13.8 mg, 0.015 mmol, 5 mol%), (*S*)-SEGPHOS (9.3 mg, 0.015 mmol, 5 mol%), TADDOL-phosphoric acid (20.9 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Alcohol **1f** (36 µL, 0.30 mmol, 100 mol%) and acetone (0.30 mL, 1.0 M concentration with respect to alcohol) were added and the solution was cooled to – 78 °C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 3 days, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$; hexanes:ethyl acetate = 8:1) to furnish the title compound (45.0 mg, 0.26 mmol, *syn*:*anti* = 3.8:1, 91% ee) as a colorless oil in 85% yield.

**TLC ($SiO_2$)**: $R_f$ = 0.5 (hexanes:ethyl acetate = 8:1).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.33-7.30 (m, 2H), 7.25-7.21 (m, 3H), 5.92-5.82 (m, 1H), 5.17-5.09 (m, 2H), 3.74-3.67 (m, 1H), 2.91-2.85 (m, 1H), 2.66-2.58 (m, 1H), 2.34-2.27 (m, 1H), 1.56 (brs, 1H), 1.12 (d, *J* = 6.9 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 140.9, 129.3, 128.6, 128.5, 126.4, 115.4, 75.7, 43.1, 40.8, 14.5.

**LRMS** (CI+) *m/z* 177 $[M+H]^+$

**FTIR** (neat): 3432, 3063, 2964, 1637, 1497, 1453, 1030, 998, 912, 699 $cm^{-1}$.

**HPLC** (Chiralcel OD-H/OD-H/OD-H column, hexanes:*i*-PrOH = 98.5:1.5, 0.4 mL/min, 210 nm). $t_{minor}$ = 135.3 min, $t_{major}$ = 81.3 min.

**$[\alpha]_D^{25}$** = 58.3° (c = 1.0, $CHCl_3$).

*The spectroscopic properties of this compound were consistent with the data available in the literature.*[7]

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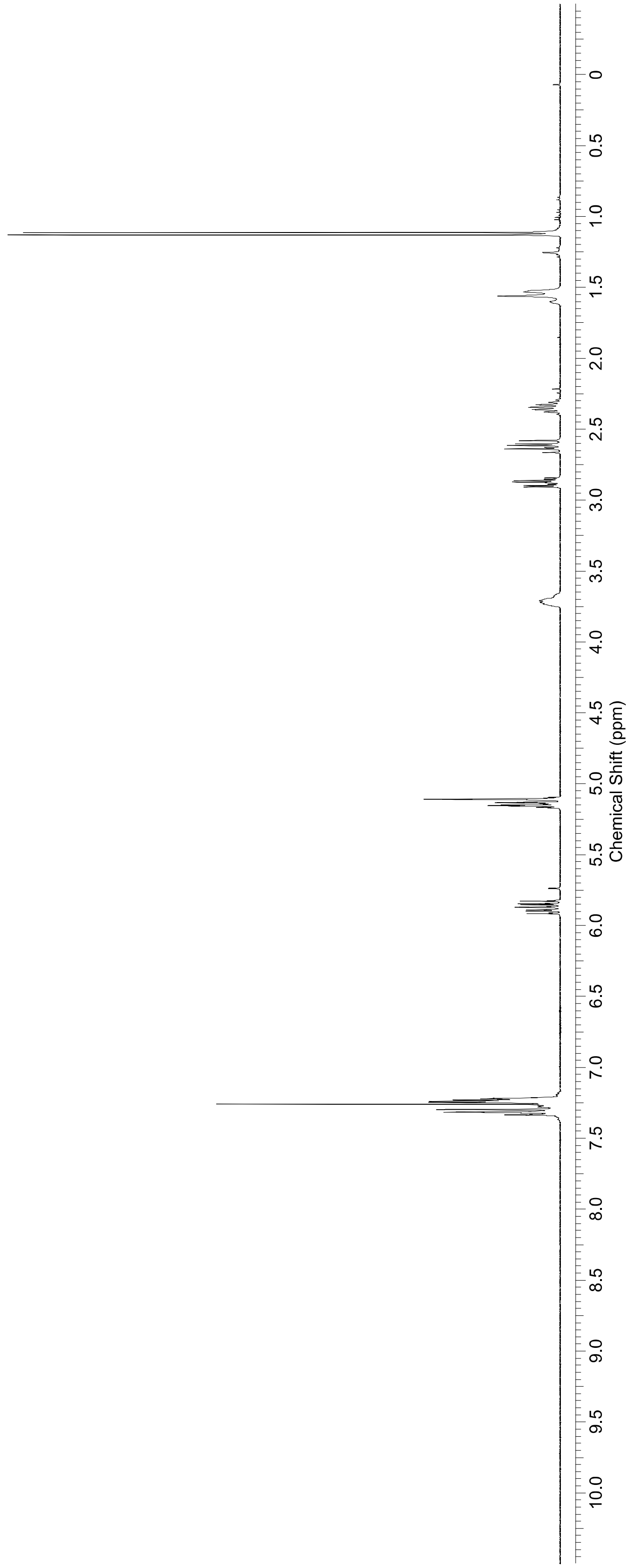
[7] Canterbury, D.P., Mcalizio, G.C. *J. Am. Chem. Soc.* **2010**, *132*, 7602.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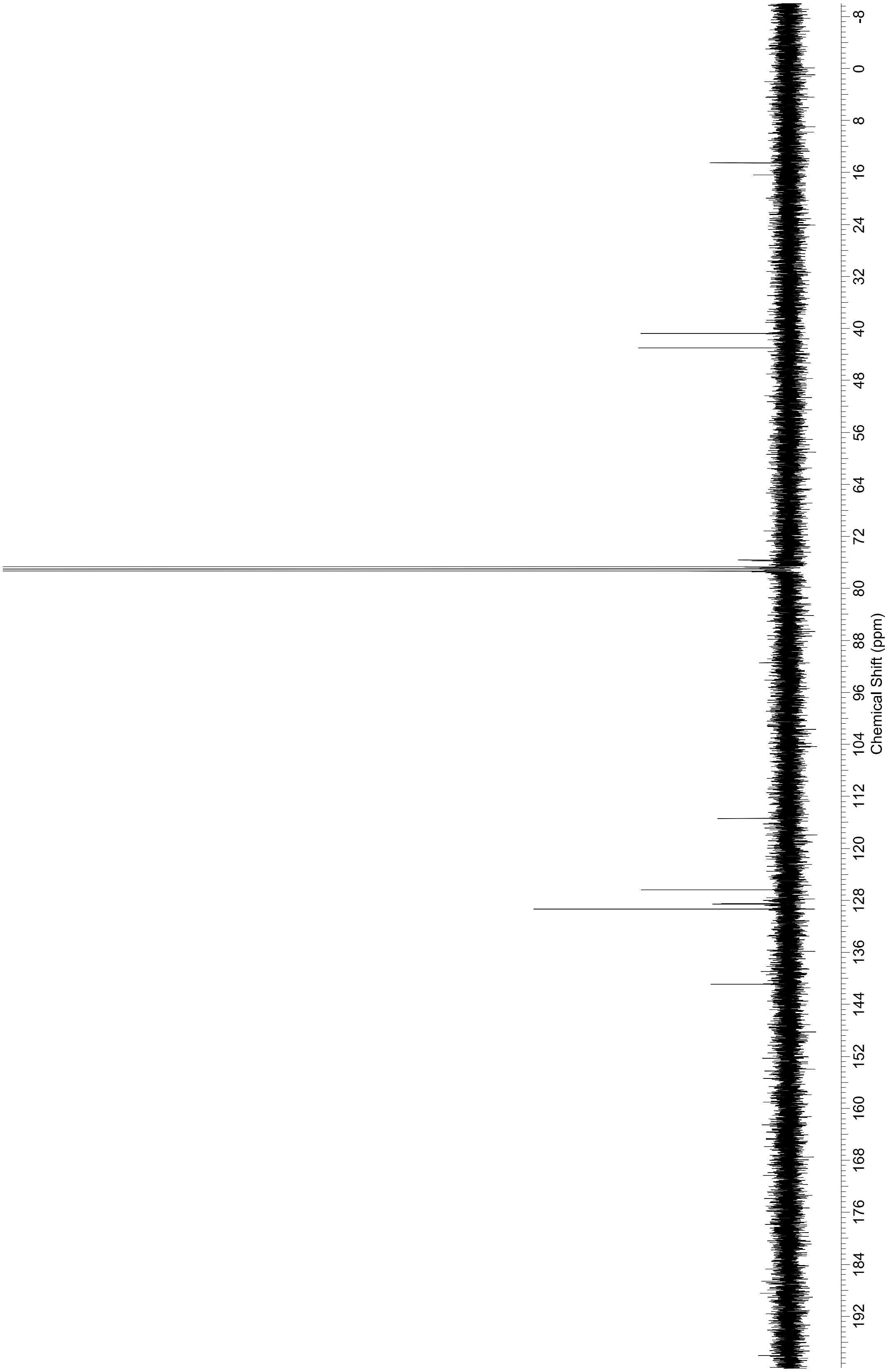
Chemical Shift (ppm)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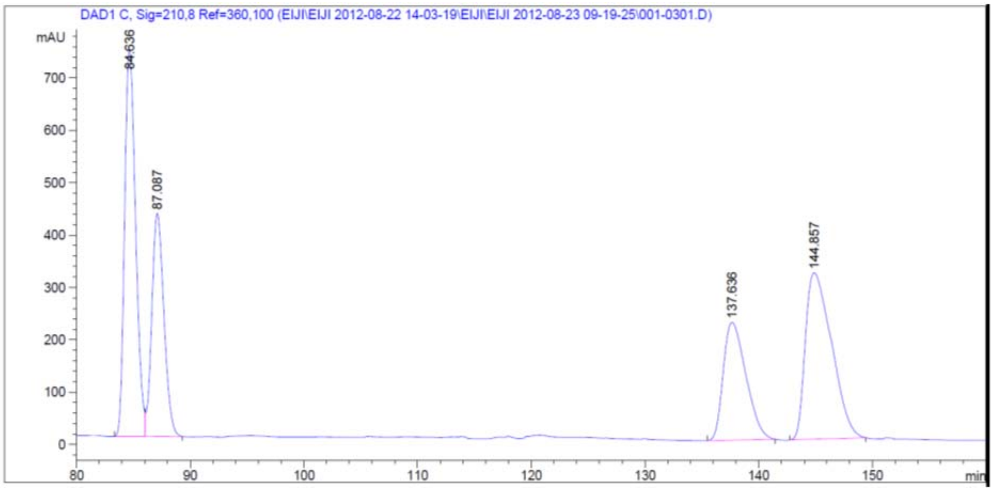
Chemical Shift (ppm)

## HPLC (*racemic)*



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
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   1  84.636 BV    1.0331 4.99310e4  740.07764  30.4366
   2  87.087 VB    1.1297 3.15808e4  426.56256  19.2508
   3 137.636 BB    1.9088 3.13079e4  225.36082  19.0844
   4 144.857 BB    2.1288 5.12296e4  318.45074  31.2282
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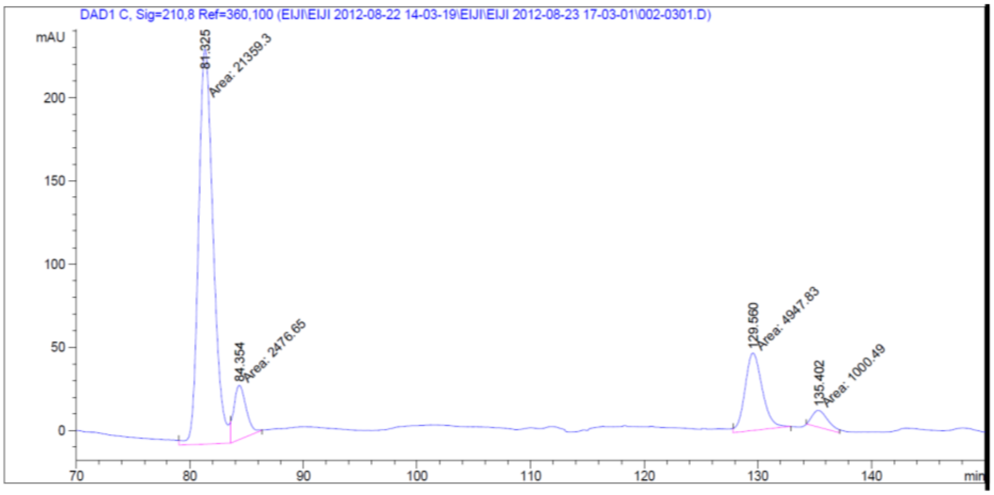
## HPLC (*chiral*)



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
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   1  81.325 MM    1.4988 2.13593e4  237.52106  71.7133
   2  84.354 MM    1.2600 2476.65283  32.76032   8.3153
   3 129.560 MM    1.7695 4947.82715  46.60183  16.6122
   4 135.402 MM    1.6332 1000.48926  10.20993   3.3591
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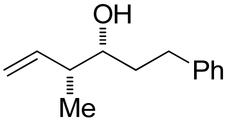
## (3*R*,4*R*)-4-methyl-1-phenylhex-5-en-3-ol (2g)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuH_2(CO)(PPh_3)_3$ (13.8 mg, 0.015 mmol, 5 mol%), (*S*)-SEGPHOS (9.3 mg, 0.015 mmol, 5 mol%), TADDOL-phosphoric acid (20.9 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Alcohol **1g** (41 µL, 0.30 mmol, 100 mol%) and acetone (0.30 mL, 1.0 M concentration with respect to alcohol) were added and the solution was cooled to -78 °C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 3 days, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$; hexanes:ethyl acetate = 8:1) to furnish the title compound (44.3 mg, 0.23 mmol, *syn*:*anti* = 5.5:1, 95% ee) as a colorless oil in 78% yield.

**TLC ($SiO_2$)**: $R_f$ = 0.4 (hexanes:ethyl acetate = 8:1).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H), 7.22-7.17 (m, 3H), 5.77 (ddd, *J* = 17.4, 9.8, 7.4 Hz, 1H), 5.12-5.07 (m, 2H), 3.53 (ddd, *J* = 9.2, 5.1, 3.1 Hz, 1H), 2.86 (ddd, *J* = 13.7, 10.0, 5.1 Hz, 1H), 2.65 (ddd, *J* = 13.7, 9.8, 6.8 Hz, 1H), 2.34-2.27 (m, 1H), 1.82 (dddd, *J* = 13.9, 10.0, 6.8, 3.1 Hz, 1H), 1.69 (ddd, *J* = 13.9, 9.8, 5.1, Hz, 1H), 1.69 (d, *J* = 6.9 Hz, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 142.3, 140.7, 128.5, 128.4, 125.8, 115.6, 74.0, 43.6, 35.8, 32.5, 14.2.

**LRMS** (CI+) *m/z* 191 $[M+H]^+$

**FTIR** (neat): 3414, 2928, 2869, 1737, 1454, 1373, 1216, 1032, 938, 699 $cm^{-1}$.

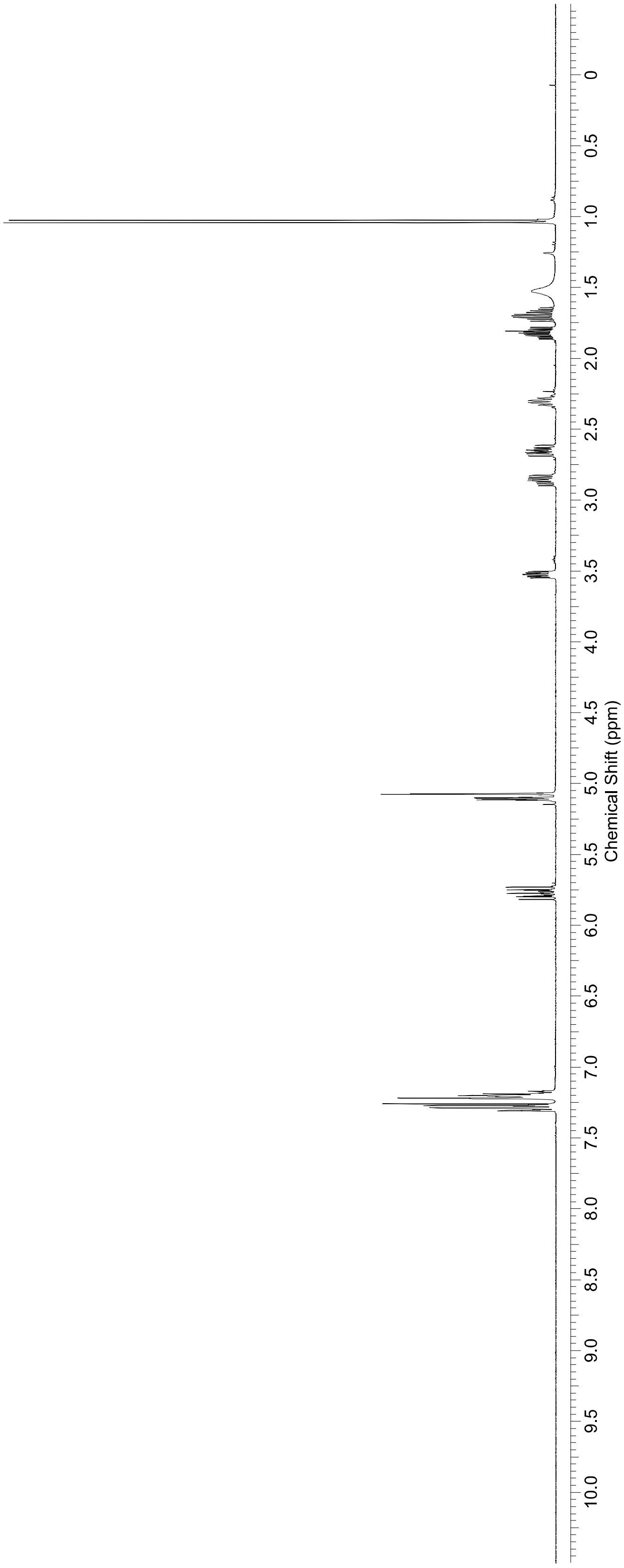
**HPLC** (Chiralcel OD-H column, hexanes:*i*-PrOH = 97:3, 0.7 mL/min, 210 nm), $t_{minor}$ = 15.5 min, $t_{major}$ = 27.6 min.

**$[\alpha]_D^{25}$** = 33.0° (c = 1.0, $CHCl_3$ ) reported for 96% ee of the (3*S*,4*S*) compound $[\alpha]_D^{25}$ = -32.5° (c = 0.8, $CHCl_3$).[8]

*The spectroscopic properties of this compound were consistent with the data available in the literature.*[8]

---

[8] Lachance, H.; Lu, Xiaosong.; Gravel, M.; Hall, G. D. *J. Am. Chem. Soc.* **2003**, *125*, 10160.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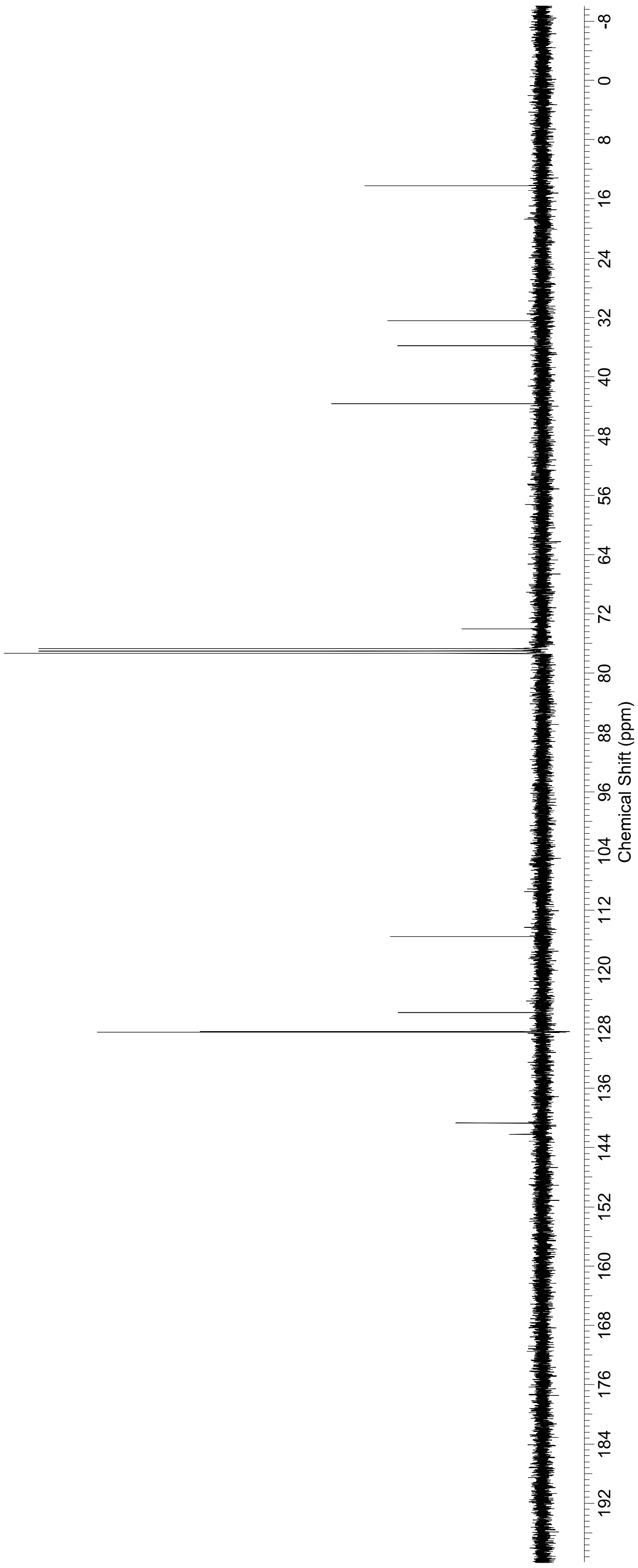
Chemical Shift (ppm)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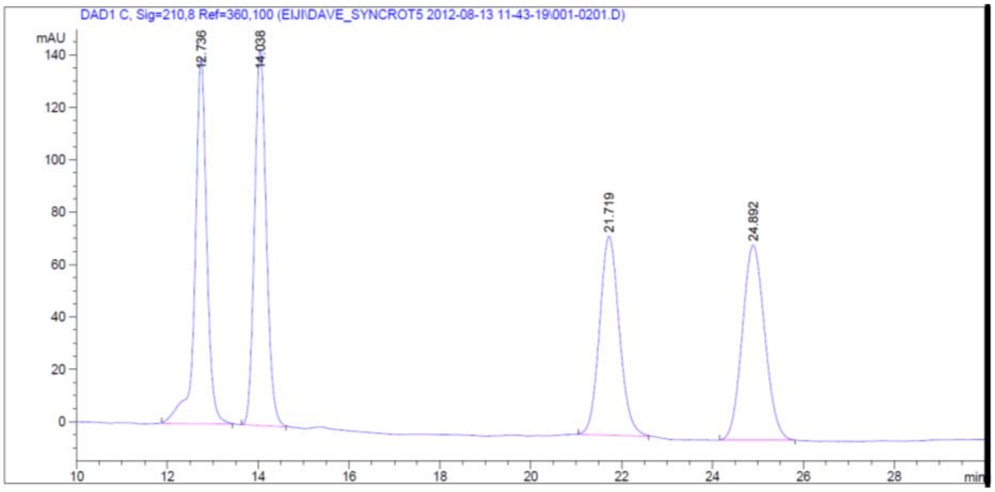
Chemical Shift (ppm)

**HPLC (*racemic*)**



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  1  12.736 BB    0.2711 2524.78613  139.55258  25.2787
  2  14.038 BB    0.2783 2585.83911  143.46355  25.8900
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
  3  21.719 BB    0.4677 2304.21509   76.01109  23.0703
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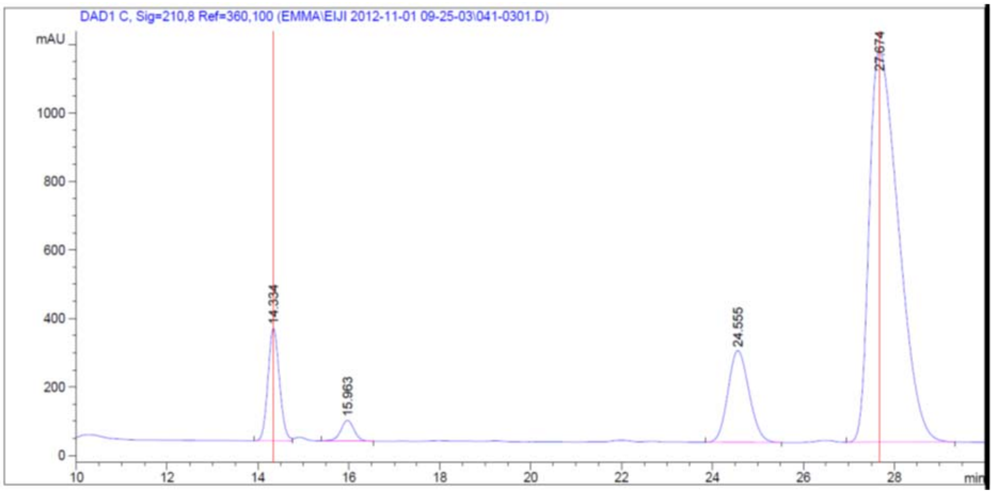
**HPLC (*chiral*)**



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Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
  1  14.334 BV    0.2731 5775.56641  328.56348   8.6294
  2  15.963 BB    0.3206 1251.60791   60.69165   1.8701
  3  24.555 BB    0.5039 8682.60645  268.08081  12.9729
  4  27.674 VB    0.7027 5.12189e4  1143.29968  76.5276
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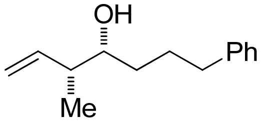
## (3*R*,4*R*)-4-methyl-1-phenylhex-5-en-3-ol (2h)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuH_2(CO)(PPh_3)_3$ (13.8 mg, 0.015 mmol, 5 mol%), (S)-SEGPHOS (9.3 mg, 0.015 mmol, 5 mol%), TADDOL-phosphoric acid (20.9 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Alcohol **1h** (46 µL, 0.30 mmol, 100 mol%) and acetone (0.30 mL, 1.0 M concentration with respect to alcohol) were added and the solution was cooled to -78 °C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 3 days, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$; hexanes:ethyl acetate = 8:1) to furnish the title compound (36 mg, 0.19 mmol, *syn*:*anti* = 4.5:1, 95% ee) as a colorless oil in 62% yield.

**TLC ($SiO_2$)**: $R_f$ = 0.6 (hexanes:ethyl acetate = 8:1).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 2H), 7.22-7.17 (m, 3H), 5.80 (ddd, *J* = 17.6, 10.0, 7.4 Hz, 1H), 5.12-5.07 (m, 2H), 3.56-3.51 (m, 1H), 2.71-2.59 (m, 2H), 2.33-2.22 (m, 1H), 1.90-1.70 (m, 1H), 1.72-1.62 (m, 1H), 1.62-1.42 (m, 2H), 1.02 (d, *J* = 6.9 Hz, 3H).

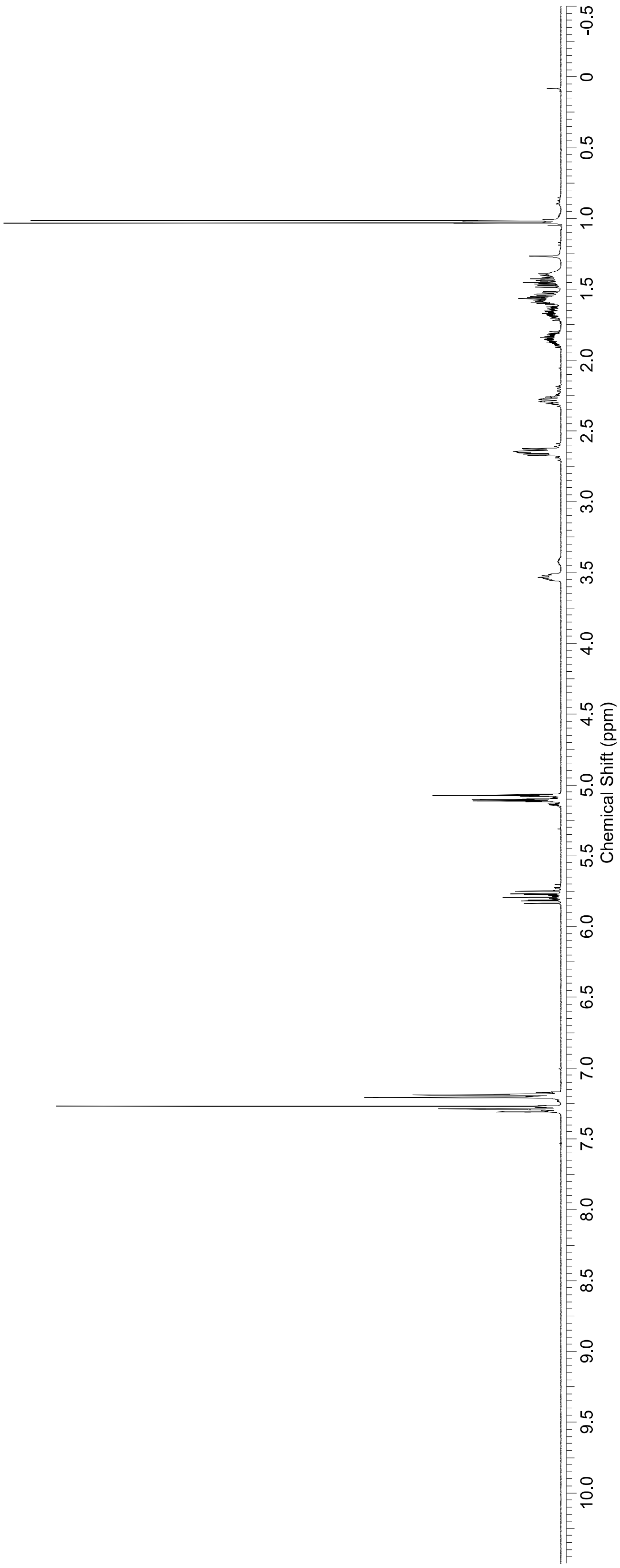
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 142.4, 140.9, 128.4, 128.3, 125.7, 115.4, 74.5, 43.4, 35.9, 33.6, 27.9, 13.9.

**LRMS** (CI+) *m/z* 205 $[M+H]^+$

**FTIR** (neat): 3410, 2935, 1712, 1638, 1453, 1374, 1248, 907, 729, 698 $cm^{-1}$.

**HPLC** (Chiralcel OD-H column, hexanes:*i*-PrOH = 97:3, 0.7 mL/min, 254 nm), $t_{major}$ = 15.7 min, $t_{minor}$ = 19.5 min.

**$[\alpha]_D^{25}$** = 28.5° (c = 0.8, $CHCl_3$).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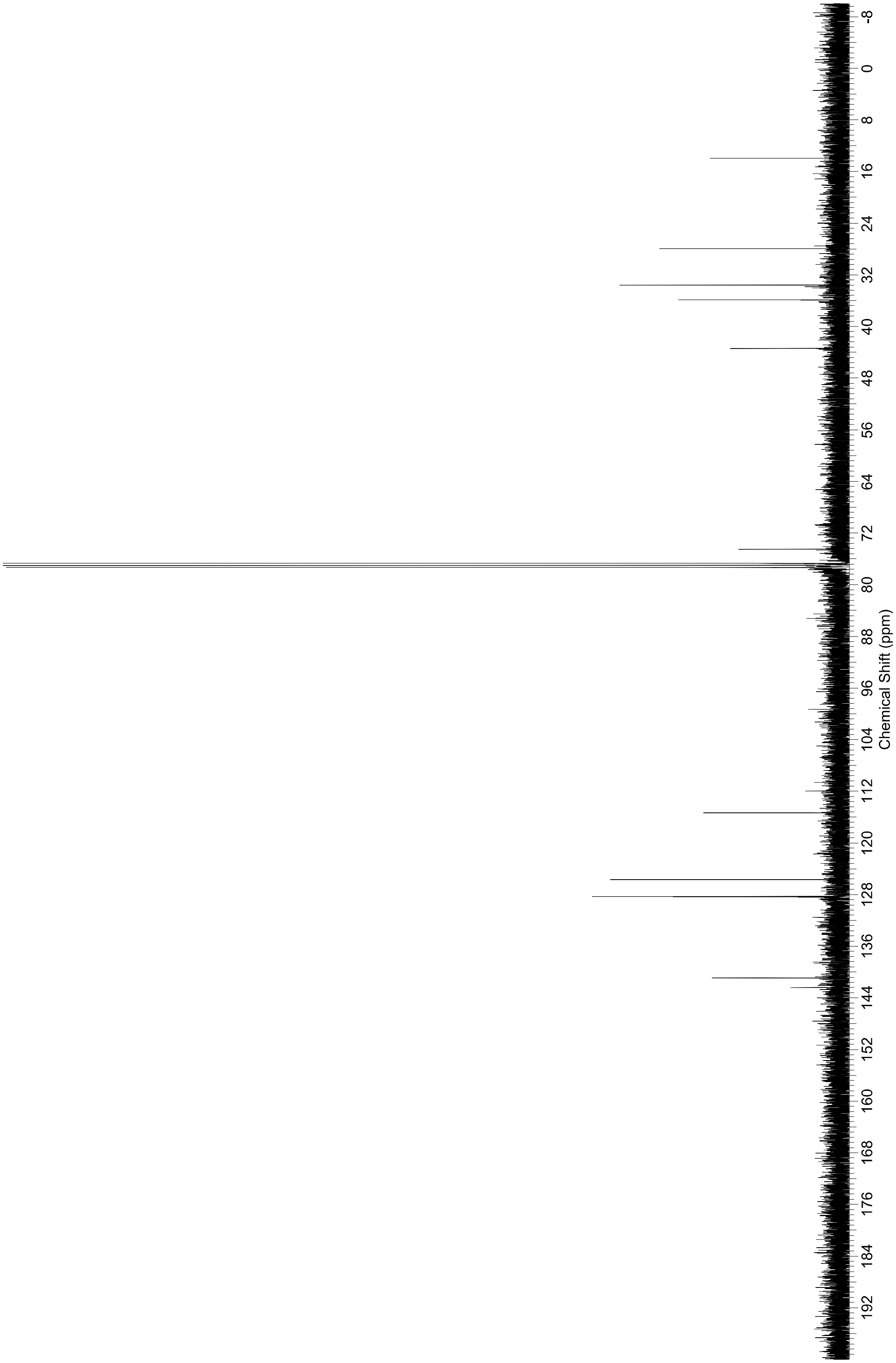
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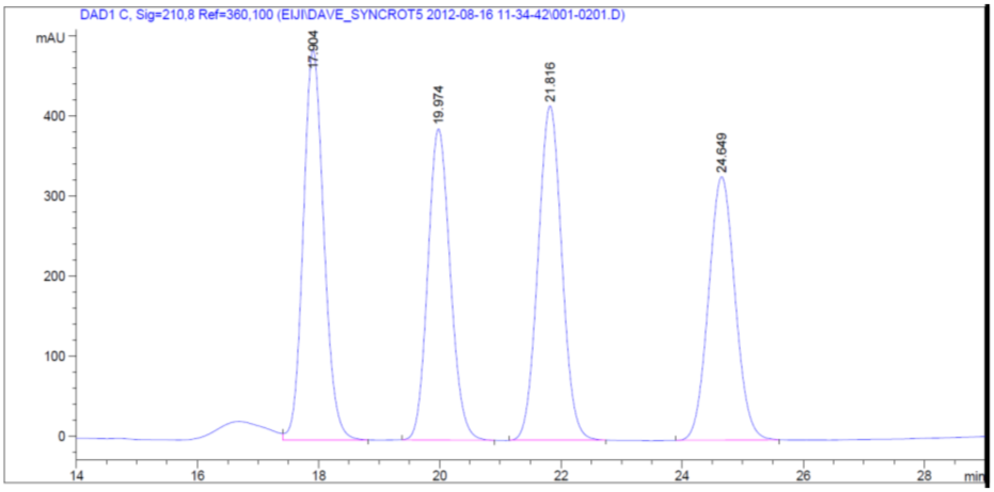
Chemical Shift (ppm)

**HPLC (*racemic*)**



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   2  19.974 BB     0.4009 1.00295e4  388.81464  23.2783
   3  21.816 BB     0.4279 1.14574e4  417.88657  26.5924
   4  24.649 BB     0.4742 1.00498e4  329.15356  23.3255
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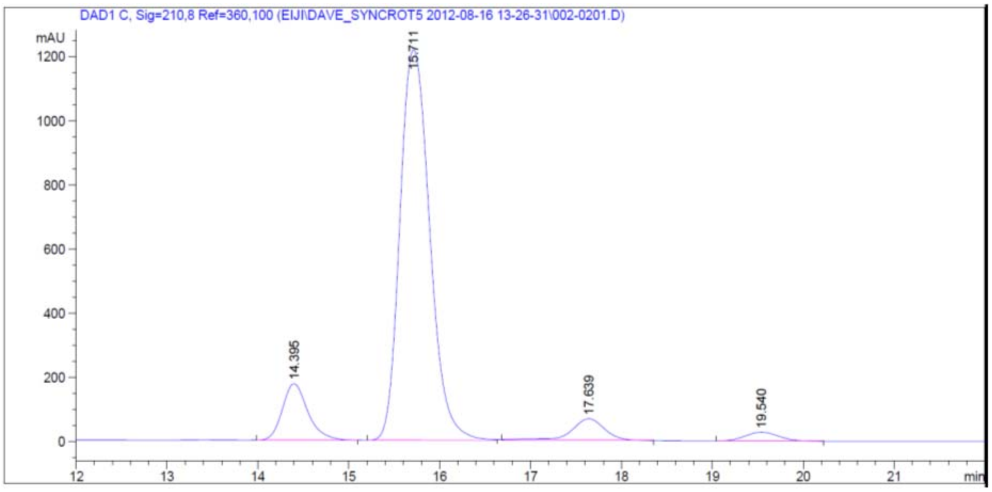
**HPLC (*chiral*)**



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   2  15.711 BB     0.3603 2.77890e4 1217.29614  82.3107
   3  17.639 BB     0.3953 1806.00403   68.11464   5.3494
   4  19.540 BB     0.3905  717.86218   27.86927   2.1263
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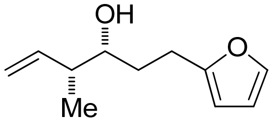
### (3*R*,4*R*)-1-(furan-2-yl)-4-methylhex-5-en-3-ol (2i)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuH_2(CO)(PPh_3)_3$ (19.3 mg, 0.021 mmol, 7 mol%), (*S*)-SEGPHOS (13.0 mg, 0.021 mmol, 7 mol%), TADDOL-phosphoric acid (29.3 mg, 0.042 mmol, 14 mol%). The tube was sealed with a rubber septum and purged with argon. Alcohol **1i** (36 µL, 0.30 mmol, 100 mol%) and acetone (0.30 mL, 1.0 M concentration with respect to alcohol) were added and the solution was cooled to -78 °C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 3 days, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$; hexanes:ethyl acetate = 10:1) to furnish the title compound (37.3 mg, 0.21 mmol, *syn*:*anti* = 4.0:1, 95% ee) as a colorless oil in 69% yield.

**TLC ($SiO_2$)**: $R_f$ = 0.35 (hexanes:ethyl acetate = 10:1).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 2.1 Hz, 1H), 6.29 (dd, *J* = 3.1, 2.2 HZ, 1H), 6.02 (d, *J* = 3.1 Hz, 1H), 5.83-5.71 (m, 1H), 5.16-5.08 (m, 2H), 3.52 (dd, *J* = 9.6, 5.1, 3.3 Hz, 1H), 2.90-2.82 (m, 1H), 2.77-2.67 (m, 1H), 2.35-2.25 (m, 1H), 1.95-1.84 (m, 1H), 1.73-1.63 (m, 1H), 1.56 (brs, 1H), 1.05 (d, *J* = 6.9 Hz, 3H).

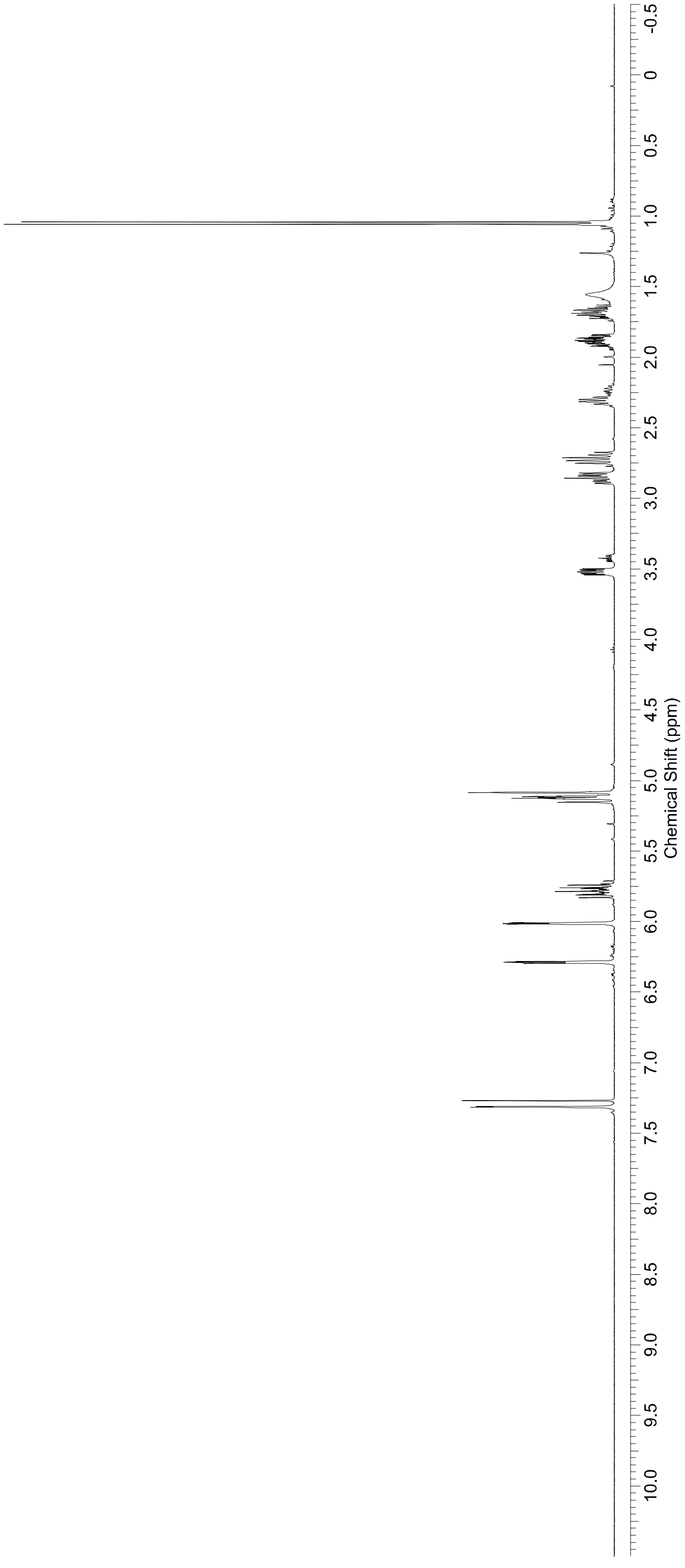
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 155.9, 140.9, 146.6, 115.6, 110.1, 104.9, 73.9, 43.7, 32.4, 24.7, 14.3.

**LRMS** (CI+) *m/z* 181 $[M+H]^+$

**FTIR** (neat): 3370, 2961, 1639, 1507, 1452, 1145, 1043, 914, 726 $cm^{-1}$.

**HPLC** (Chiralpak AS-H/AS-H column, hexanes:*i*-PrOH = 99:1, 0.5 mL/min, 254 nm). $t_{minor}$ = 29.5 min, $t_{major}$ = 31.4 min.

**$[\alpha]_D^{25}$** = 49.3° (c = 1.0, $CHCl_3$).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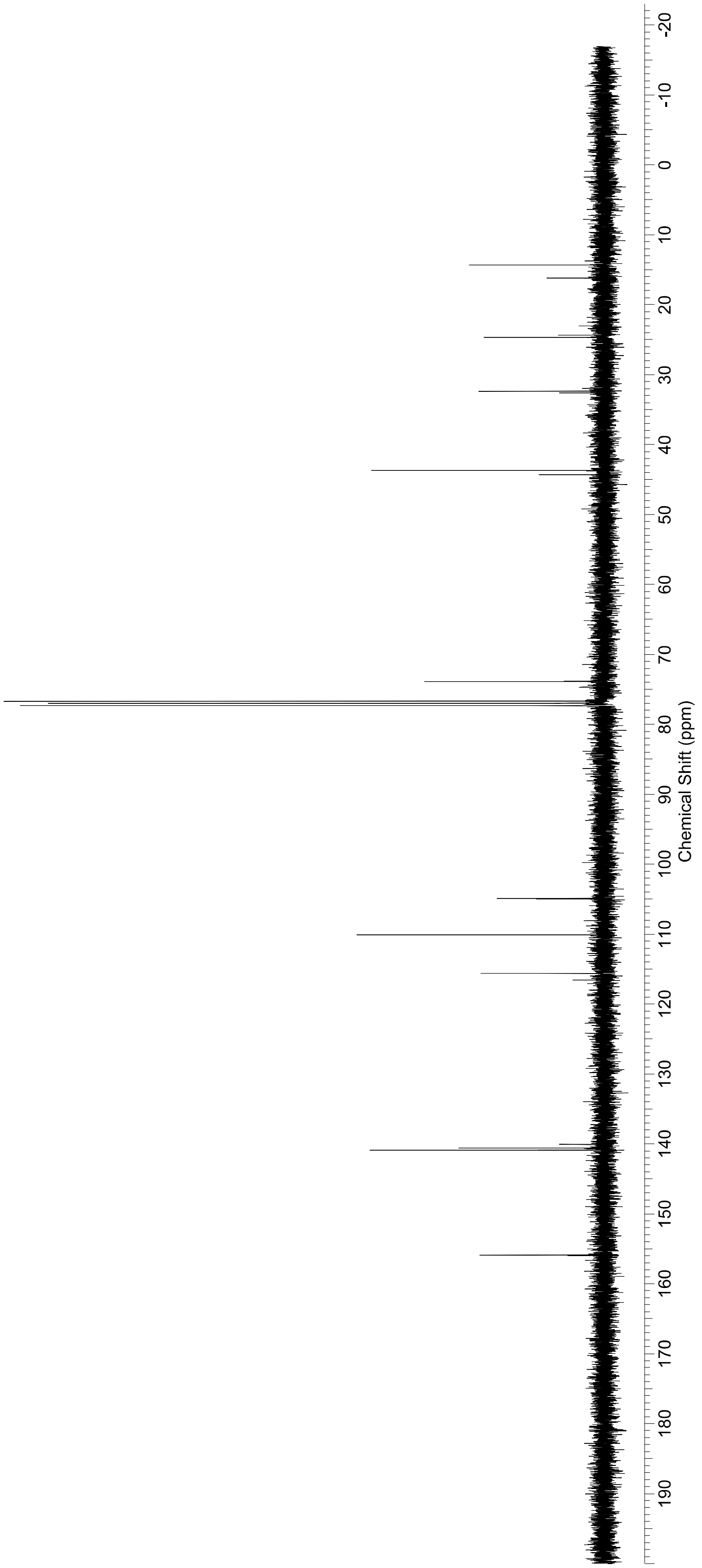
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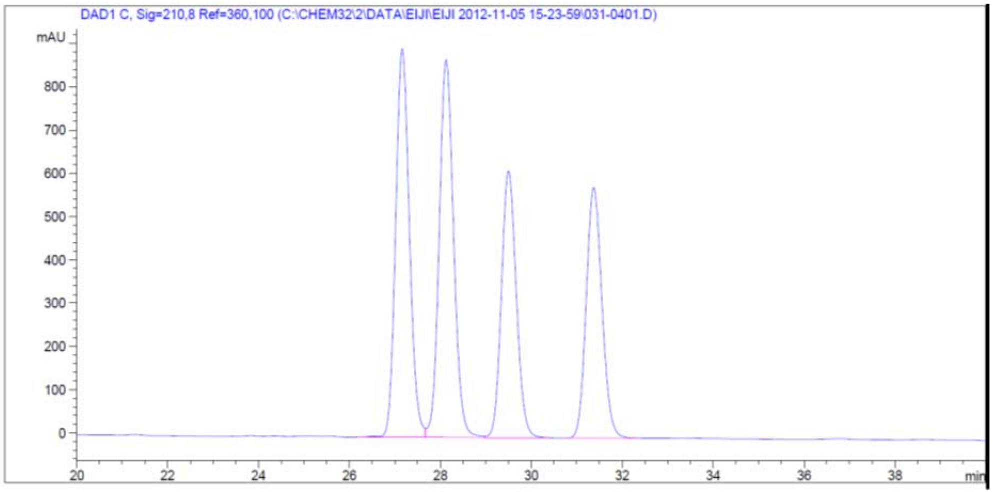
**HPLC (*racemic*)**



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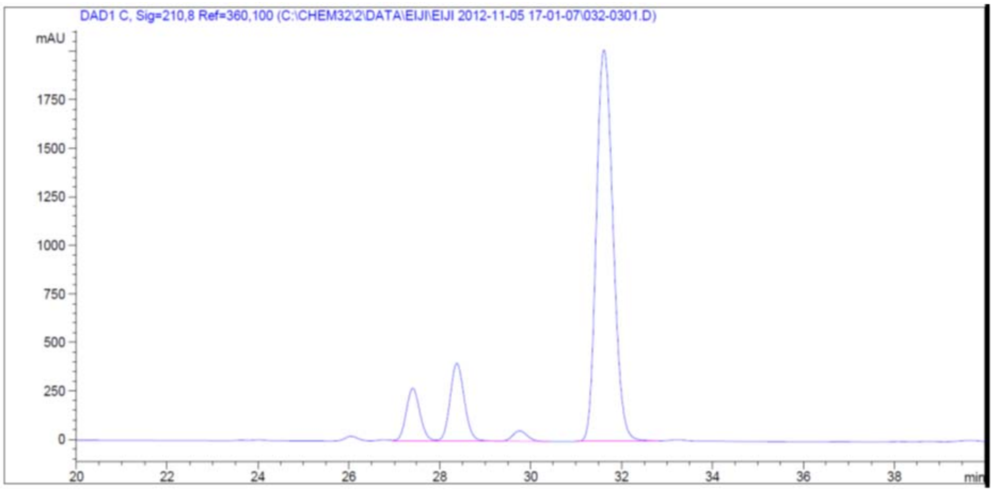
**HPLC (*chiral*)**



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Peak RetTime Type  Width     Area      Height     Area
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   2  28.371 VB     0.3397 8798.17676  401.36823  13.0562
   3  29.753 BB     0.3517 1231.96143   54.50950   1.8282
   4  31.609 BB     0.4027 5.16164e4 2015.88220  76.5970
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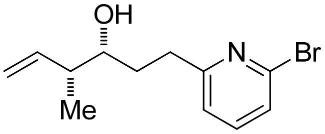
### (3*R*,4*R*)-1-(6-bromopyridin-2-yl)-4-methylhex-5-en-3-ol (2j)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuH_2(CO)(PPh_3)_3$ (19.3 mg, 0.021 mmol, 7 mol%), (*S*)-SEGPHOS (13.0 mg, 0.021 mmol, 7 mol%), TADDOL-phosphoric acid (29.3 mg, 0.042 mmol, 14 mol%). The tube was sealed with a rubber septum and purged with argon. Alcohol **1j** (64.5 mg, 0.30 mmol, 100 mol%) and acetone (0.30 mL, 1.0 M concentration with respect to alcohol) were added and the solution was cooled to –78 °C. Butadiene (0.10 mL, 1.20 mmol, 400 mol%) was quickly added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 3 days, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography ($SiO_2$; hexanes:ethyl acetate = 4:1) to furnish the title compound (52 mg, 0.19 mmol, *syn*:*anti* = 3.8:1, 96% ee) as a colorless oil in 63% yield.

**TLC ($SiO_2$)**: $R_f$ = 0.3 (hexanes:ethyl acetate = 4:1).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 7.8, 7,4 Hz, 1H), 7.32 (*J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 5.82-5.74 (m, 1H), 5.12-5.05 (m, 2H), 3.51 (ddd, *J* = 9.8, 5.4, 2.9 Hz, 1H, 3.01-2.96 (m, 1H), 2.89-2.76 (m, 1H), 2.33-2.28 (m, 1H), 1.98-1.93 (m, 1H), 1.79-1.68 (m, 1H), 1.05 (d, *J* = 6.9 Hz, 1H).

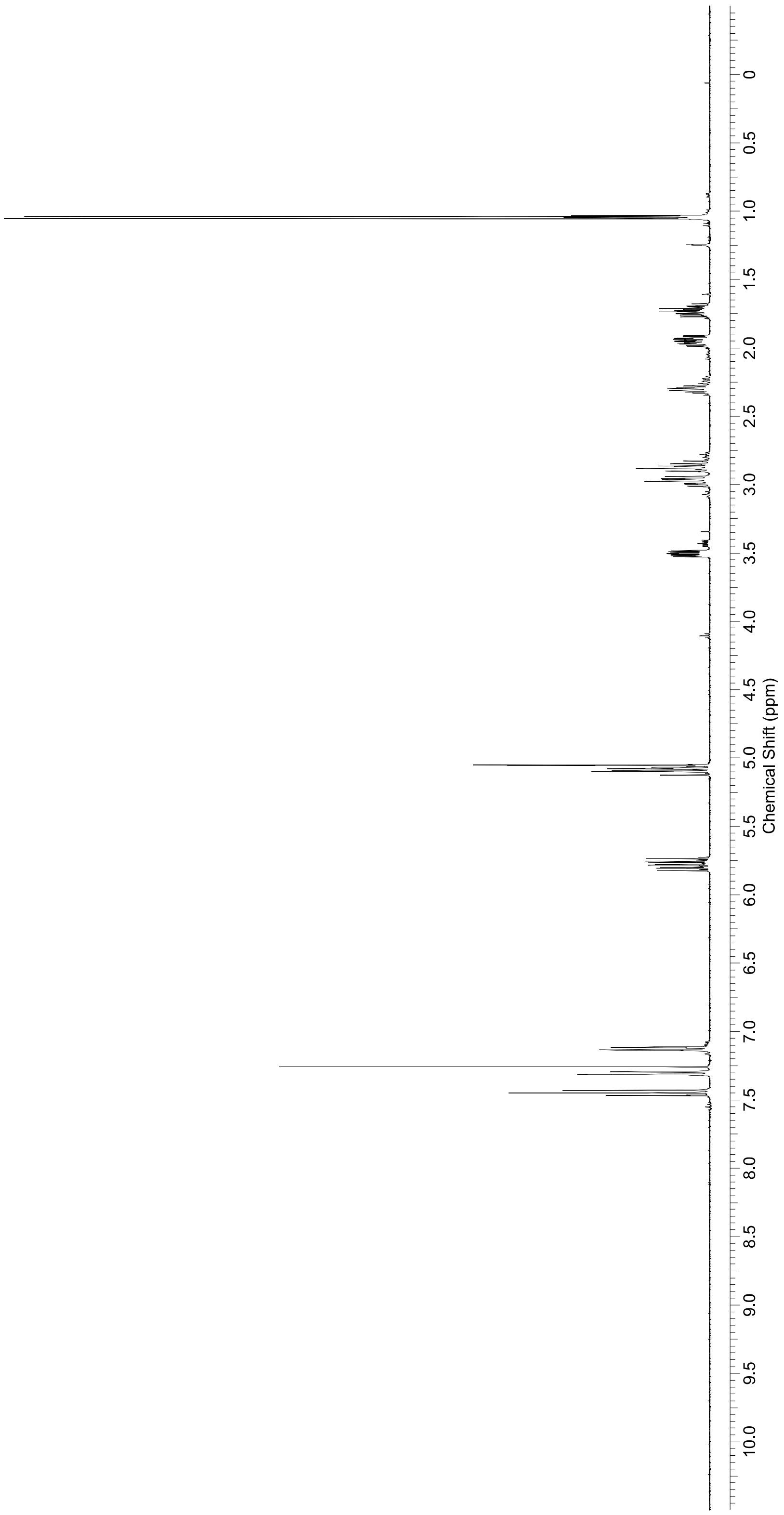
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 163.6, 141.4, 140.8, 138.8, 125.4, 121.8, 115.4, 74.2, 43.9, 34.6, 33.5, 14.7.

**LRMS** (CI+) *m/z* 270 $[M]^+$

**FTIR** (neat): 3376, 2961, 1582, 1552, 1436, 1405, 1121, 985, 909, 789, 730 $cm^{-1}$.

**HPLC** (Chiralcel OD-H column, hexanes:*i*-PrOH = 99:1, 0.4 mL/min, 254 nm). $t_{minor}$ = 49.0 min, $t_{major}$ = 62.4 min.

**$[\alpha]_D^{25}$** = -95.6° (c = 1.0, $CHCl_3$ ).



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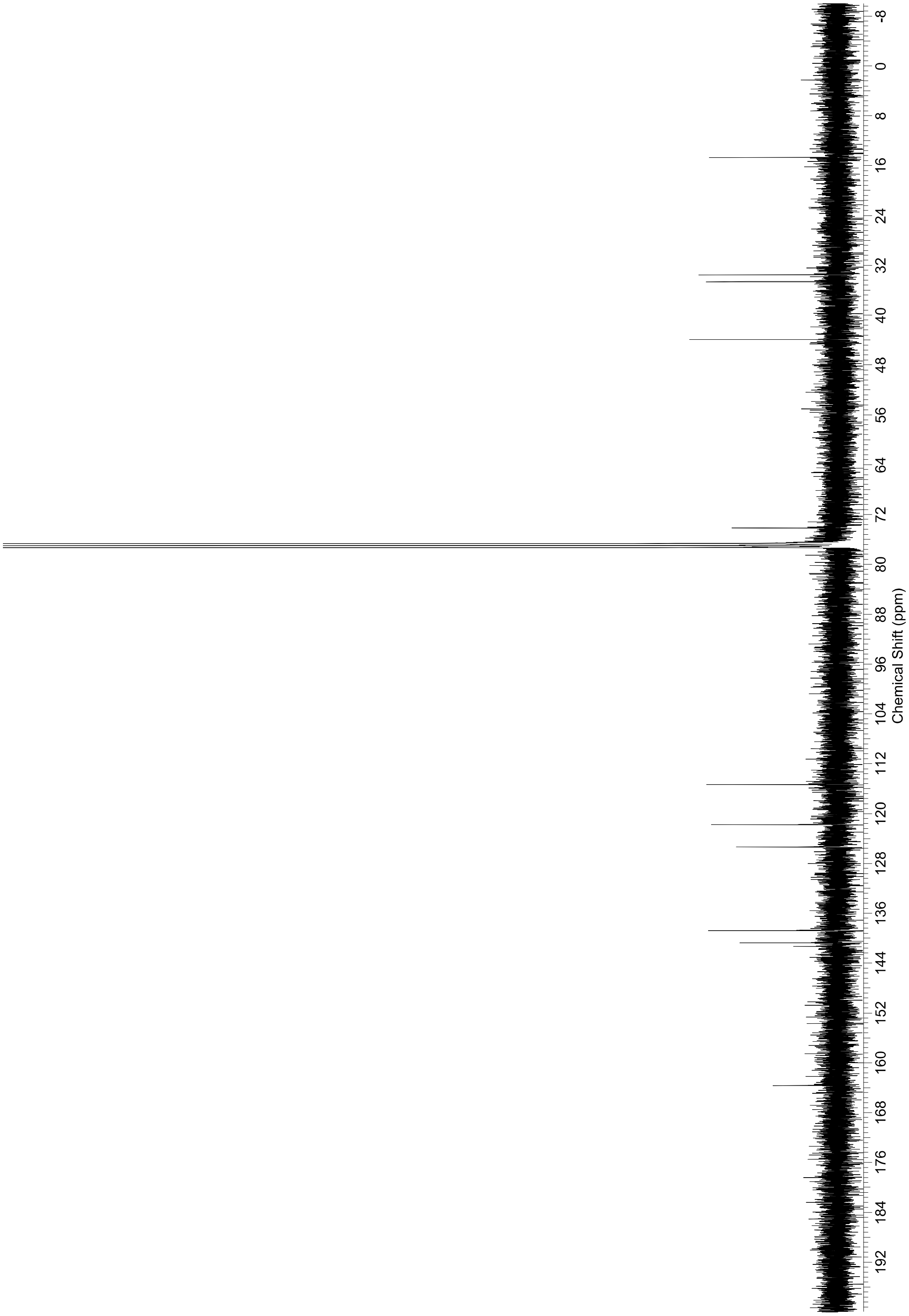
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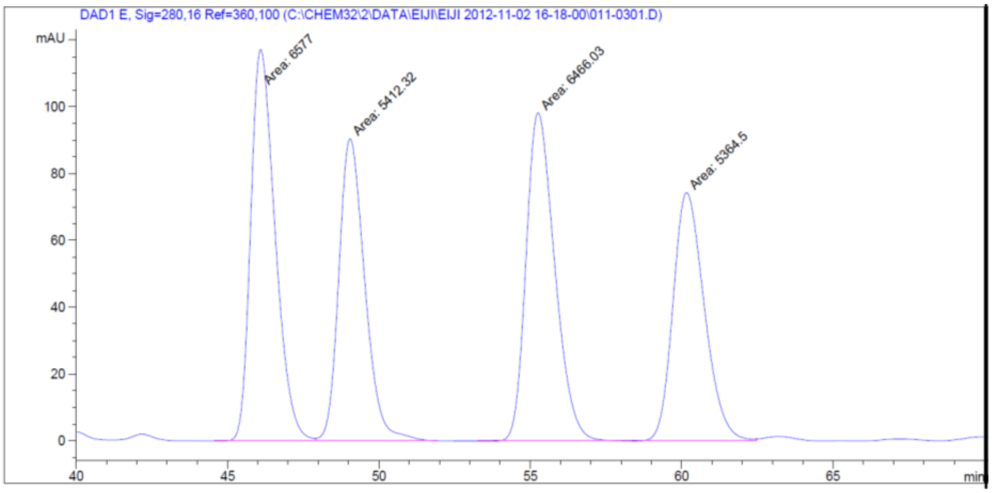
Chemical Shift (ppm)

## HPLC (*racemic*)



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  3  55.250 MM    1.0966 6466.02979   98.27155  27.1456
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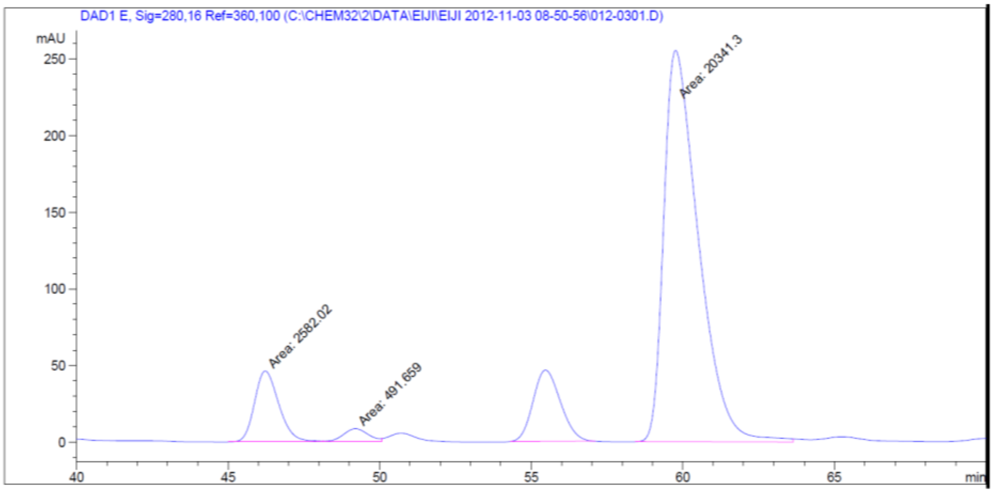
## HPLC (*chiral*)



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  3  55.461 BB    0.9808 2953.74561   46.64143  11.2017
  4  59.753 MM    1.3280 2.03413e4   255.28479  77.1418
```

## Synthesis of TADDOL-derived phosphoric acid

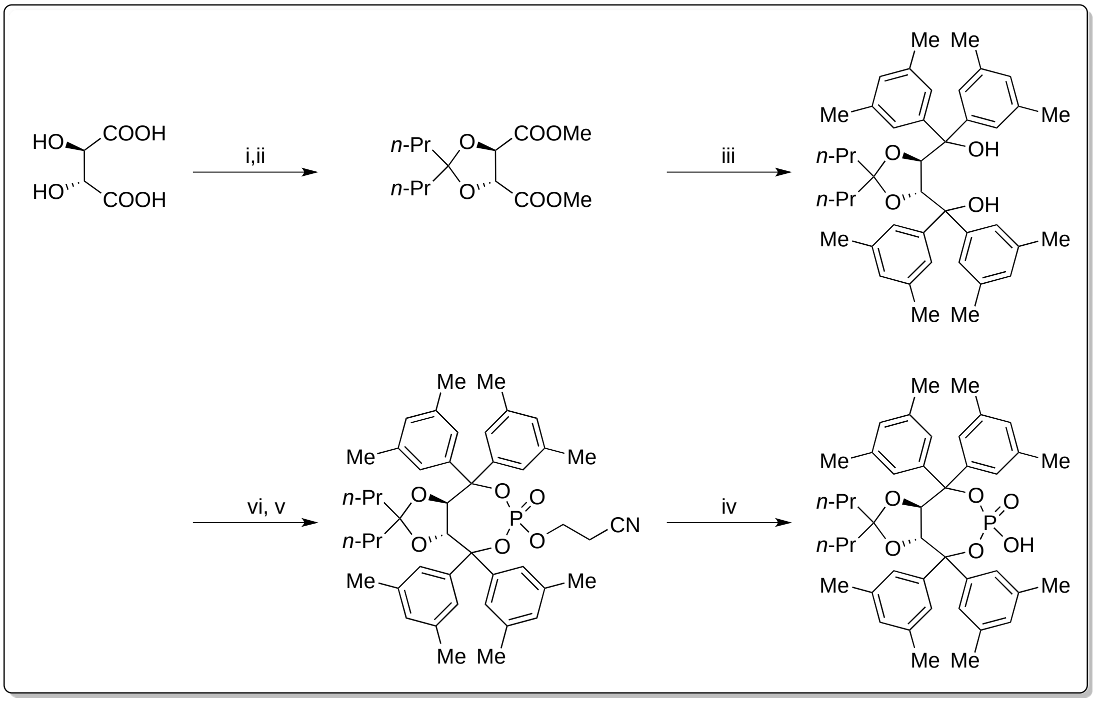
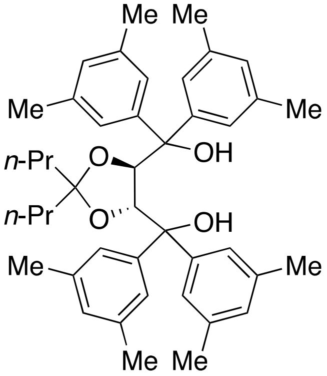


**Figure S1: Synthetic Approach to TADDOL-derived Phosphoric Acids**
(i) $SOCl_2$, MeOH, rt, 18h.[9] (ii) 4-heptanone (100 mol%), $HC(OMe)_3$ (130 mol%), PTSA (10 mol%), reflux, 8h.[10] (iii) 3,5-dimethylphenylmagnesium bromide (800 mol%), THF, reflux, 18h. (vi) $PCl_3$ (105 mol%), $Et_3N$ (340 mol%), THF, 0 °C 1h then 3-hydroxypropionitrile (110 mol%), rt, 18h. (v) $H_2O_2$ (620 mol%), DCM, rt, 30 min. (iv) DBU (105 mol%), THF, rt, 30 min.

---

[9] Lu, X.; Byun, H.-S.; Bittman, R. *J. Org. Chem.* **2004**, *69*, 5433.
[10] Jozak, T.; Sun, Y.; Thiel, R. W. *New J. Chem*. **2011**, *35*, 2114.

**((4R,5R)-2,2-dipropyl-1,3-dioxolane-4,5-diyl)bis{di(3,5-dimethylphenyl)-3-ylmethanol}**



(R,R)-2,2-Dipropyl-[1,3]dioxolane-4,5-dicarboxlic acid dimethylester (1.37 g, 5 mmol) in THF (10 mL) was added dropwise to a solution of 3,5-dimethylphenylmagnesium bromide (40 mmol, prepared from 5.5 mL of 5-bromo-*m*-xylene and 1.10 g of Mg) in THF (40 mL). The reaction mixture was stirred for 18h and then treated with saturated aqueous $NH_4Cl$ solution. The organic layer was extracted with $Et_2O$ (3x50 mL) and the combined organic extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo.* The residue was purified by column chromatography ($SiO_2$; hexanes:$Et_2O$ = 10:1) to provide the title compound (2.07 g, 1.3 mmol) as a white form in 65% yield.

**TLC ($SiO_2$)**: $R_f$ = 0.13 (hexanes:$Et_2O$ = 10:1)

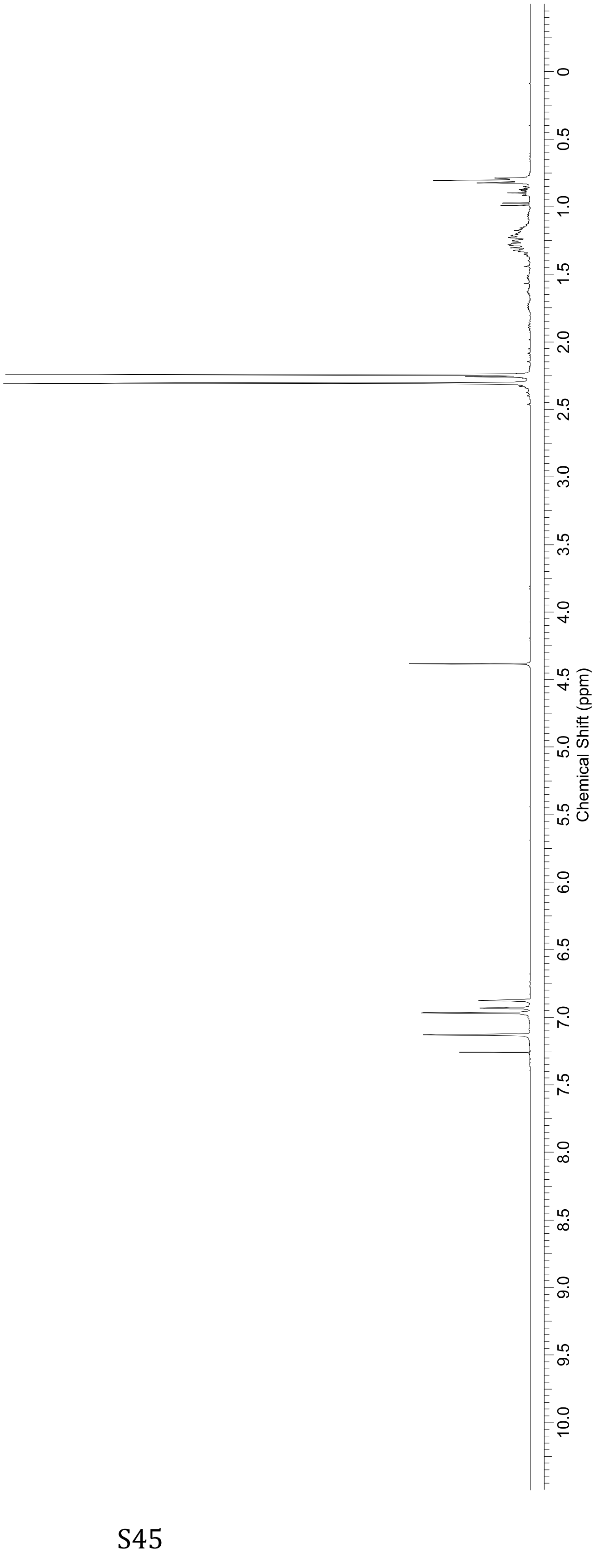
**m.p.**: 106-108 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.13 (s, 4H), 6.97 (s, 4H), 6.93 (s, 2H), 6.87 (s, 2H), 4.38 (s, 2H), 4.05 (brs, 2H), 2.31 (s, 12H), 2.24 (s, 12H), 1.35-1.16 (m, 8 H), 0.81 (t, *J* = 7.04 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 146.2, 142.6, 137.3, 136.3, 129.1, 126.6, 126.3, 125.4, 111.2, 80.5, 78.0, 39.9, 21.6, 17.2, 14.4.

**HRMS** (ESI) Calcd. for $C_{43}H_{54}NaO_4$ $[M+Na]^+$: 657.3914, Found: 657.3910.

**FTIR** (neat): 3293, 2958, 2916, 2359, 1601, 1454, 1314, 1167, 1060, 850, 736 $cm^{-1}$.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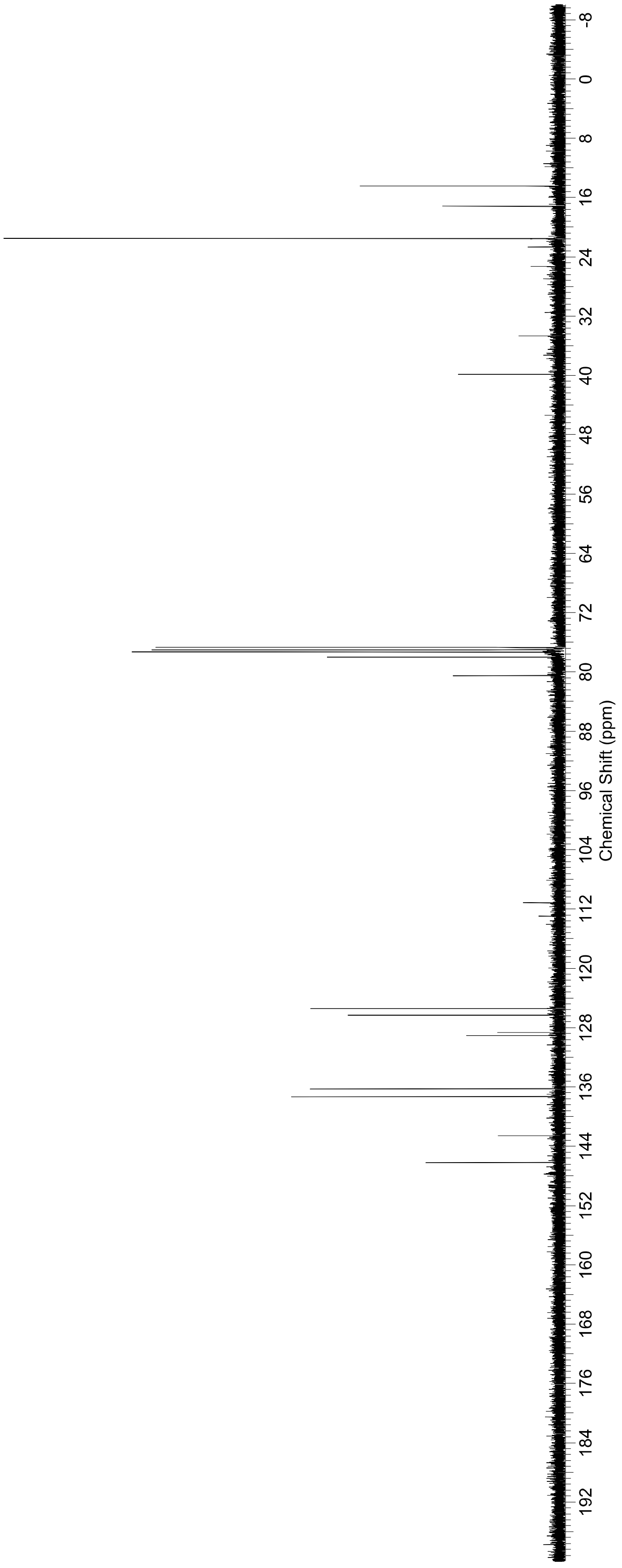
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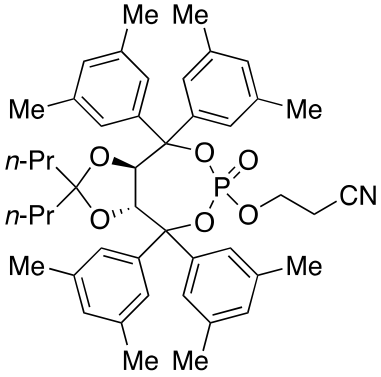
Chemical Shift (ppm)

### 3-{[(3a*R*,8a*R*)-2,2-dipropyl-4,4,8,8-tetrakis(3,5-dimethylphenyl)-6-oxidotetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl]oxy}propanenitrile



To a stirred solution of (*R,R*)-(*n*-Pr,*n*-Pr)-TADDOL-(xylyl) (1.26 g, 2.0 mmol) and triethylamine (0.94 mL, 6.8 mmol, 340 mol%) in dry THF (10 mL) at 0 °C was added dropwise $PCl_3$ (184 µL, 2.1 mmol, 105 mol%). The resulting mixture was stirred at 0 °C for 1h. The 3-hydroxypropionitrile (150 µL, 2.2 mmol, 110 mol%) in dry THF (10 mL) was then added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 18h. The reaction mixture was diluted with $Et_2O$ and the triethylammonium chloride salts were filtered through a celite pad. The solvent was removed in vacuo. To the crude phosphine in $CH_2Cl_2$ (20 mL) was added 30% aqueous $H_2O_2$ (1.40 mL, 12.4 mmol, 6.2 equiv). The biphasic mixture was stirred vigorously for 30 min and then quenched by the addition of 50 mL of saturated aqueous $NaHCO_3$ solution. The mixture was extracted with $CH_2Cl_2$ and the combined organic extracts were washed with saturated aqueous NaCl, dried ($MgSO_4$), filtered and concentrated. Purification by flash chromatography (hexane:$Et_2O$ = 80:20 to 0:100) afforded 1.16 g (77% for two steps) of title compound as a white solid.

**TLC ($SiO_2$)**: $R_f$ = 0.35 (hexanes:$Et_2O$ = 1:1)

**m.p.**: 120-122 ºC.

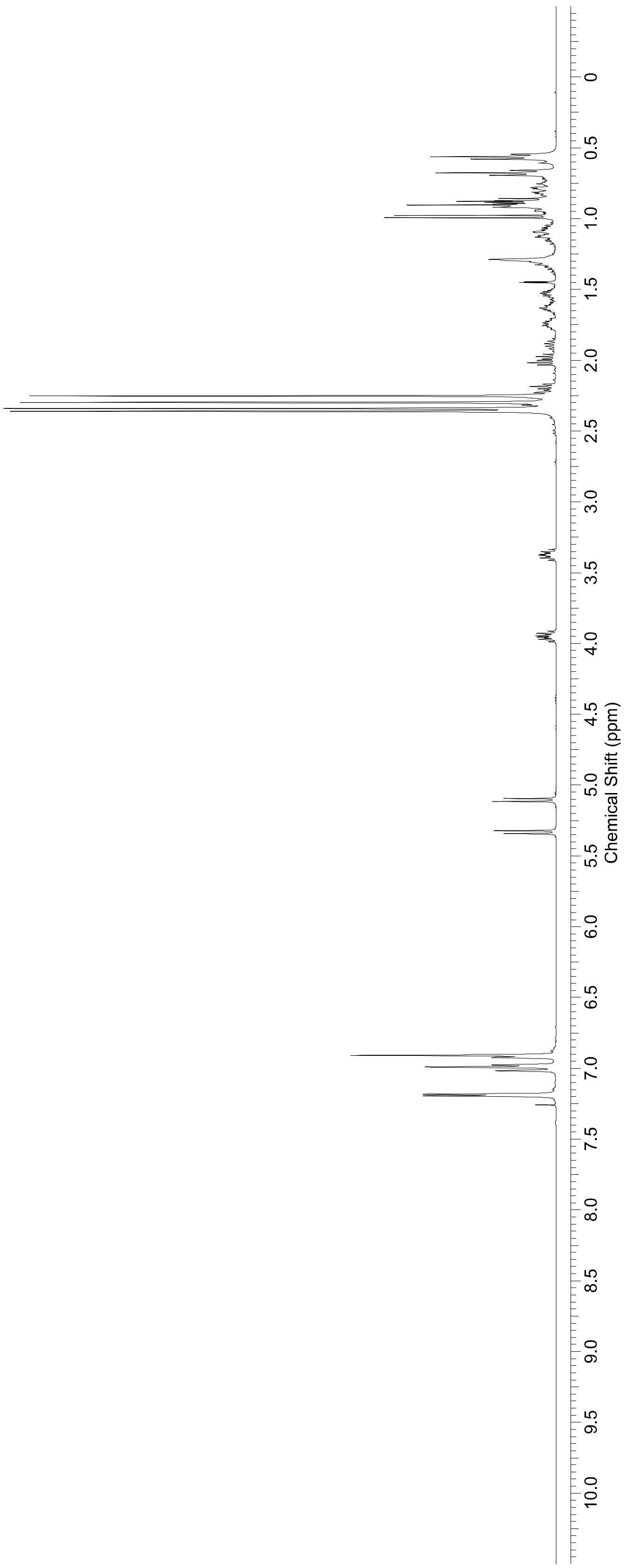
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.20n (s, 2H), 7.18 (s, 2H), 7.02 (s, 1H), 6.99 (s, 2H), 6.96 (s, 1H), 6.92 (s, 1H), 6.91 (s, 1H0, 6.91 (s, 2H), 5.32 (d, *J* = 8.4 Hz, 1H), 5.11 (d, *J* = 8.4 Hz, 1H), 3.99-3.91 (m, 1H), 3.41-3.34 (m, 1H), 2.36 (s, 6H), 2.34 (s, 6H), 2.30 (s, 6H), 2.25 (s, 6H), 2.23-2.17 (m, 1H), 2.03-1.97 (m, 1H), 1.31-0.86 (m, 8H), 0.68 (t, *J* = Hz, 3H), 0.56 (t, *J* = Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 143.9, 143.4 (d, $J_{P\text{-}C}$ = 3.0 Hz), 140.1 (d, $J_{P\text{-}C}$ = 7.5 Hz), 139.5 (d, $J_{P\text{-}C}$ = 6.0 Hz), 137.9, 137.4, 136.7, 136.4, 130.0, 129.9, 129.4, 129.3, 126.8, 126.2, 125.2, 124.7, 116.3, 116.1, 89.5 (d, $J_{P\text{-}C}$ = 7.5 Hz), 88.5 (d, $J_{P\text{-}C}$ = 8.3 Hz), 79.5, 61.7 (d, $J_{P\text{-}C}$ = 4.5 Hz), 39.6, 39.2, 21.6, 21.5, 21.5, 21.4, 18.9 (d, $J_{P\text{-}C}$ = 8.9 Hz), 16.6, 16.7, 14.2, 14.1.

**$^{31}$P NMR** (162 MHz, $CDCl_3$): δ -13.1.

**HRMS** (ESI) Calcd. for $C_{46}H_{56}NNaO_6P$ $[M+Na]^+$: 772.3738, Found: 772.3738.

**FTIR** (neat): 2953, 2240, 1603, 1456, 1285, 1032, 994, 854, 741 $cm^{-1}$.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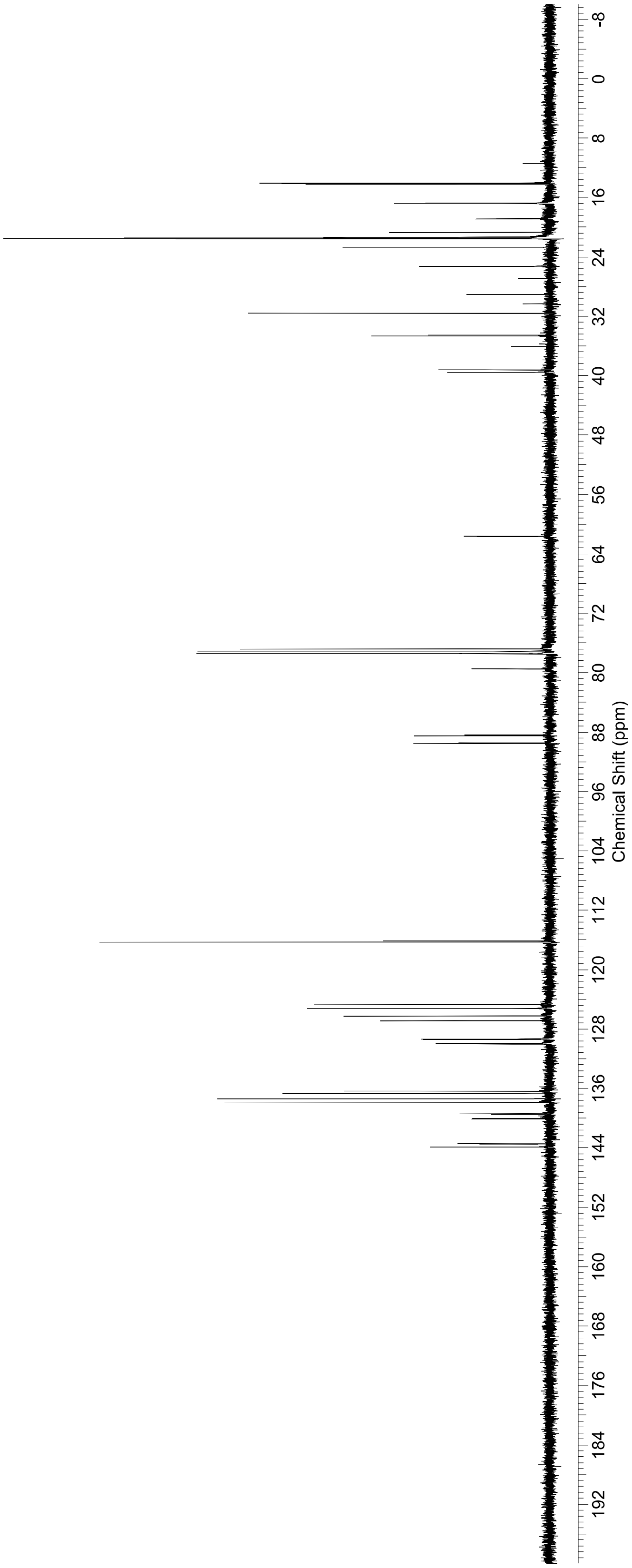
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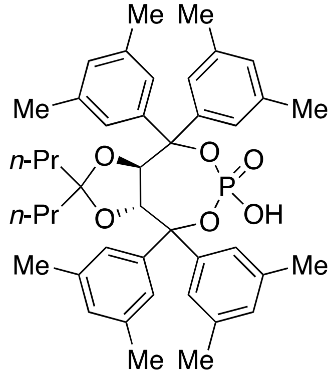
Chemical Shift (ppm)

## (3a*R*,8a*R*)-2,2-dipropyl-4,4,8,8-tetrakis(3,5-dimethylphenyl)tetrahydro[1,3]-dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-ol 6-oxide



To a stirred solution of ester (2.92 g, 3.9 mmol) in dry $CH_2Cl_2$ (40 mL) was added, dropwise at room temperature, DBU (0.61 mL, 4.1 mmol, 1.05 equiv). The solution was stirred 30 min at room temperature and when the reaction was complete by TLC, AcOH (0.3 mL) was added, followed by $H_2O$ (40 mL). The organic layer was then washed two times by a 0.3M HCl solution, saturated aqueous NaCl, and dried ($MgSO_4$), filtered and concentrated. The residue was purified by column chromatography ($SiO_2$; 0-10% IPA:$CH_2Cl_2$,) and concentrated *in vacuo*. The residue was diluted with $CH_2Cl_2$ then washed with a solution of hydrochloric acid (10 mL, 0.3M aq. sol.) and concentrated *in vacuo* to provide the title compound (2.55 g, 3.7 mmol) as a white solid in 94% yield.

**TLC ($SiO_2$)**: $R_f$ = 0.43 ($CH_2Cl_2$:IPA = 100:5)

**m.p.**: 160-162 °C.

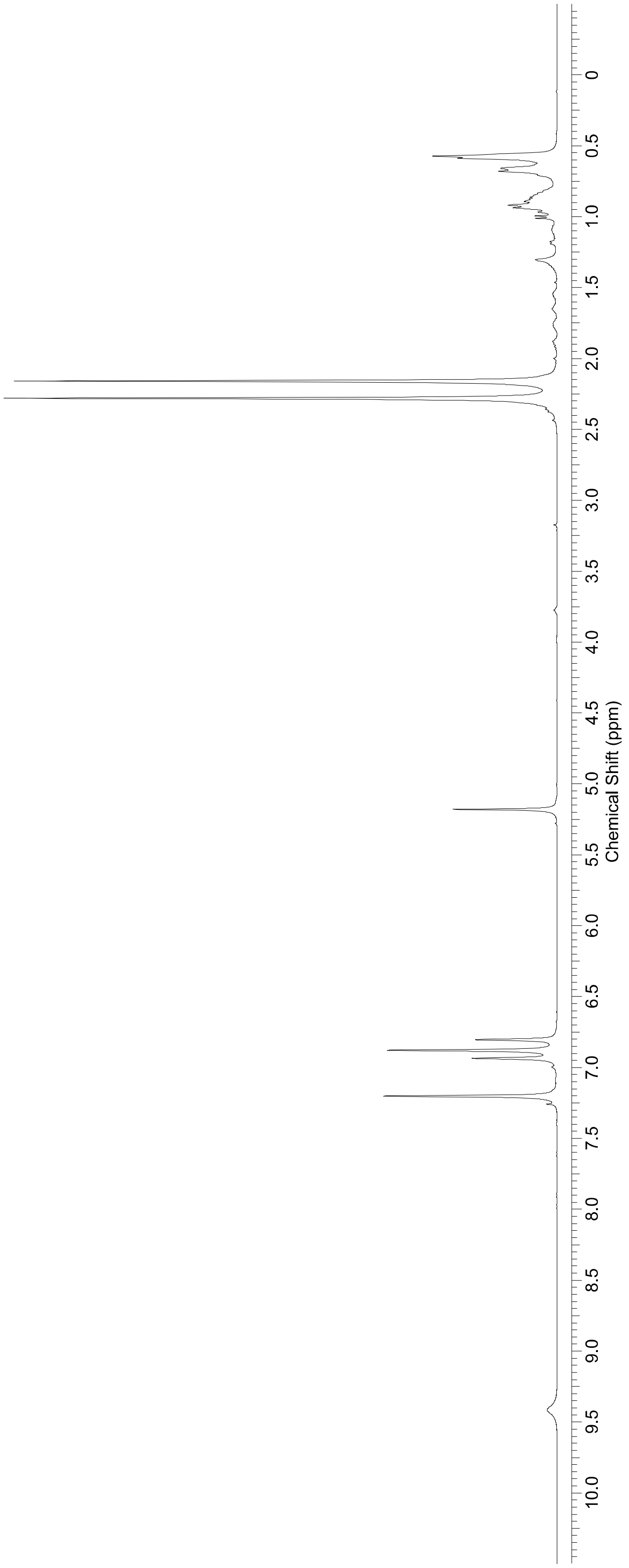
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 9.41 (brs, 1H), 7.20 (s, 4H), 6.94 (s, 2H), 6.88 (s, 4H), 6.80 (s, 2H), 5.18 (s, 2H), 2.28 (s, 12H), 2.16 (s, 12H), 1.01-0.82 (m, 4H), 0.66-0.56 (m, 10 H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 143.0, 140.1 (d, $J_{P-C}$ = 12.0 Hz), 137.3, 136.2, 129.8, 129.0, 126.3, 125.0, 116.6, 88.4, 79.2, 39.7, 21.5, 21.3, 16.6, 14.2.

**$^{31}$P NMR** (162 MHz, $CDCl_3$): $\delta$ -7.67.

**HRMS** (ESI) Calcd. for $C_{43}H_{52}O_6P$ $[M]^+$: 695.35065, Found: 695.35070.

**FTIR** (neat): 2958, 2918, 1603, 1455, 1264, 1235, 1013, 737 $cm^{-1}$.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5.5
6.0
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7.0
7.5
8.0
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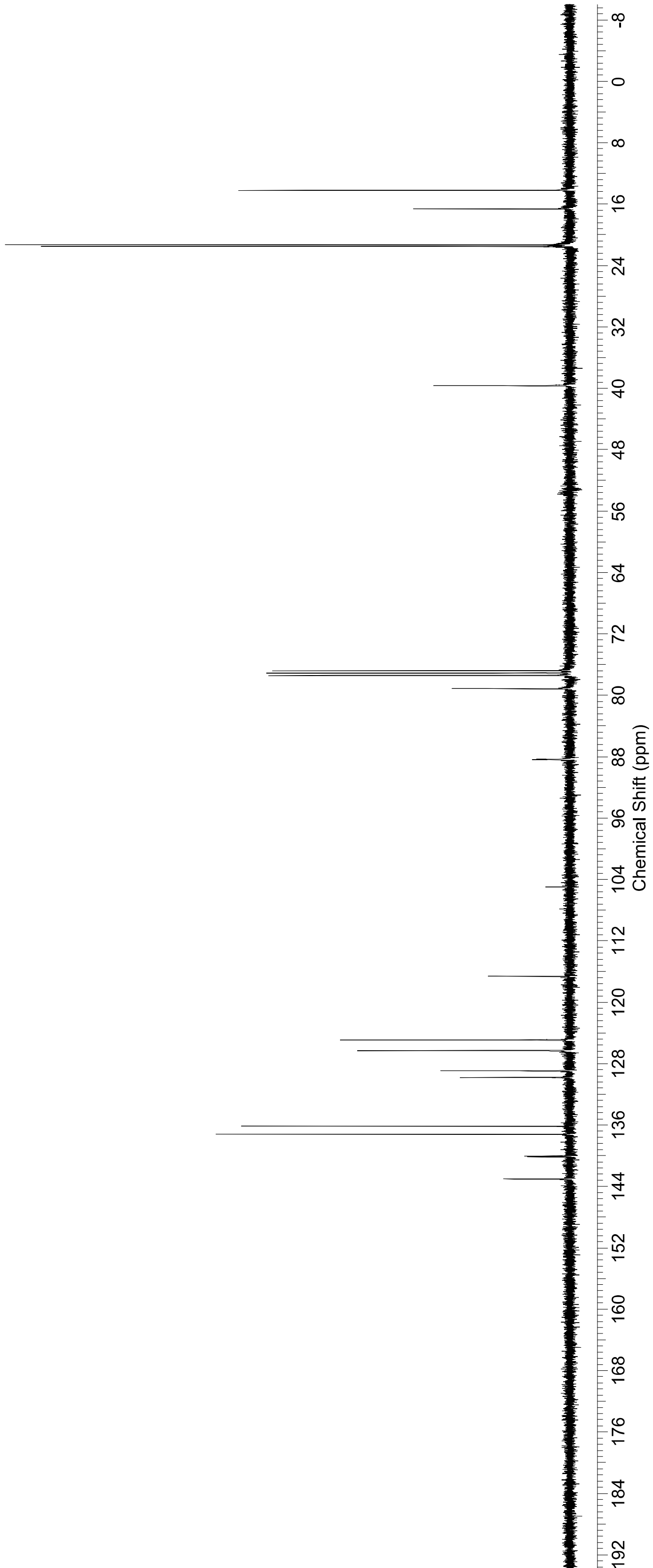
9.0
9.5
10.0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8
16
24
32
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48
56
64
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80
88
96
104
112
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128
136
144
152
160
168
176
184
192
Chemical Shift (ppm)