Diastereo- and Enantioselective Ruthenium Catalyzed Hydrohydroxyalkylation of 2-Silyl-Butadienes: Carbonyl *syn*-Crotylation from the Alcohol Oxidation Level

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Supporting Information

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General Information: All reactions were run under an atmosphere of argon. Tetrahydrofuran (THF) 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. $RuHCl(CO)(PPh_3)_3$ and diene **1** were prepared according to literature procedure.[1,2] All ligands were used as received from Strem Chemicals Inc. Alcohols were purified by distillation or recrystallization 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 F_{254}). 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). Microwave reactions were run in a CEM explorer 48 automated microwave synthesizer.

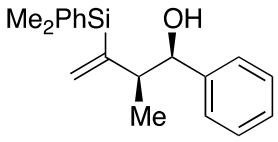
Spectroscopy and Spectrometry: Infrared spectra were recorded on a Thermo Nicolet 380 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+H, M or M-H) or a suitable fragment ion. ^1H NMR spectra were recorded on a Varian Gemini (400 MHz) spectrometer at ambient temperature unless

(1) Joseph, T. *et al.*, *J. Mol. Catal. A* **2003**, *206*, 13.
(2) Welker, M., *J. Org. Chem.*, **2009**, 74, 8290.
(3) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

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).

Experimental Procedures and Spectroscopic Data for Adduct 4a-4j

(1R,2R)-3-(dimethyl(phenyl)silyl)-2-methyl-1-phenylbut-3-en-1-ol (4a)



From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to alcohol), diene **1** (113 mg, 0.60 mmol, 200 mol%) and alcohol **2a** (32.4 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (72.0 mg, 0.24 mmol, *syn:anti* = 13:1) as a colorless oil in 81% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to aldehyde), diene **1** (113 mg, 0.60 mmol, 200 mol%), aldehyde **3a** (31.8 mg, 0.30 mmol, 100 mol%) and isopropanol (46 μL, 0.60 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (67.8 mg, 0.23 mmol, *syn:anti* = 12:1) as a colorless oil in 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.52 (m, 2H), 7.40–7.13 (m, 8H), 5.89 (dd, *J* = 2.2, 1.2 Hz, 1H), 5.64 (d, *J* = 2.2 Hz, 1H), 4.54 (dd, *J* = 4.1, 2.6 Hz, 1H), 2.66 (qdd, *J* = 6.9, 4.1, 1.2 Hz, 1H), 1.80 (d, *J* = 2.6 Hz, 1H), 0.86 (d, *J* = 6.9 Hz, 3H), 0.34 (s, 6H).

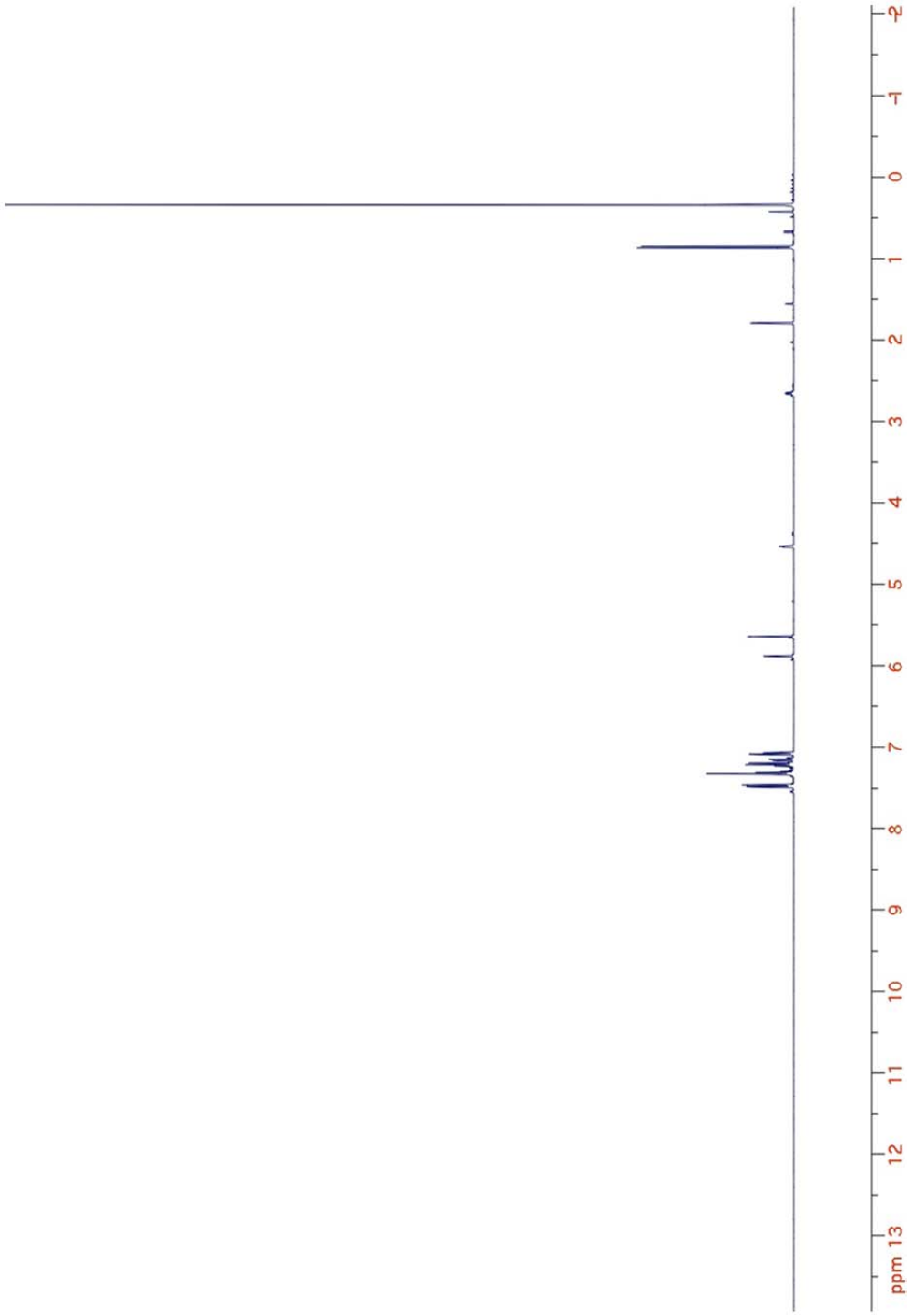
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 143.1, 137.9, 134.1, 129.3, 128.0 (2C), 127.5, 126.9, 126.1, 74.5, 44.9, 12.9, -2.6, -2.7.

HRMS (CI) Calcd. for $C_{19}H_{24}OSi$ (M+): 296.1596, Found: 296.1595.

$[\alpha]_D^{25}$ = -20 (c =1.0, CH_2Cl_2).

FTIR (neat): 2957, 1450, 1427, 1248, 1108, 908, 814, 730, 698 cm^{-1}.

HPLC (The alcohol was converted to the 4-nitrobenzoate ester for analysis; Chiralcel AD-H/AD-H column, hexanes:*i*-PrOH = 99:1, 1.0 mL/min, 254 nm), t_{major} = 23.1 min, t_{minor} = 19.1 min; ee = 87%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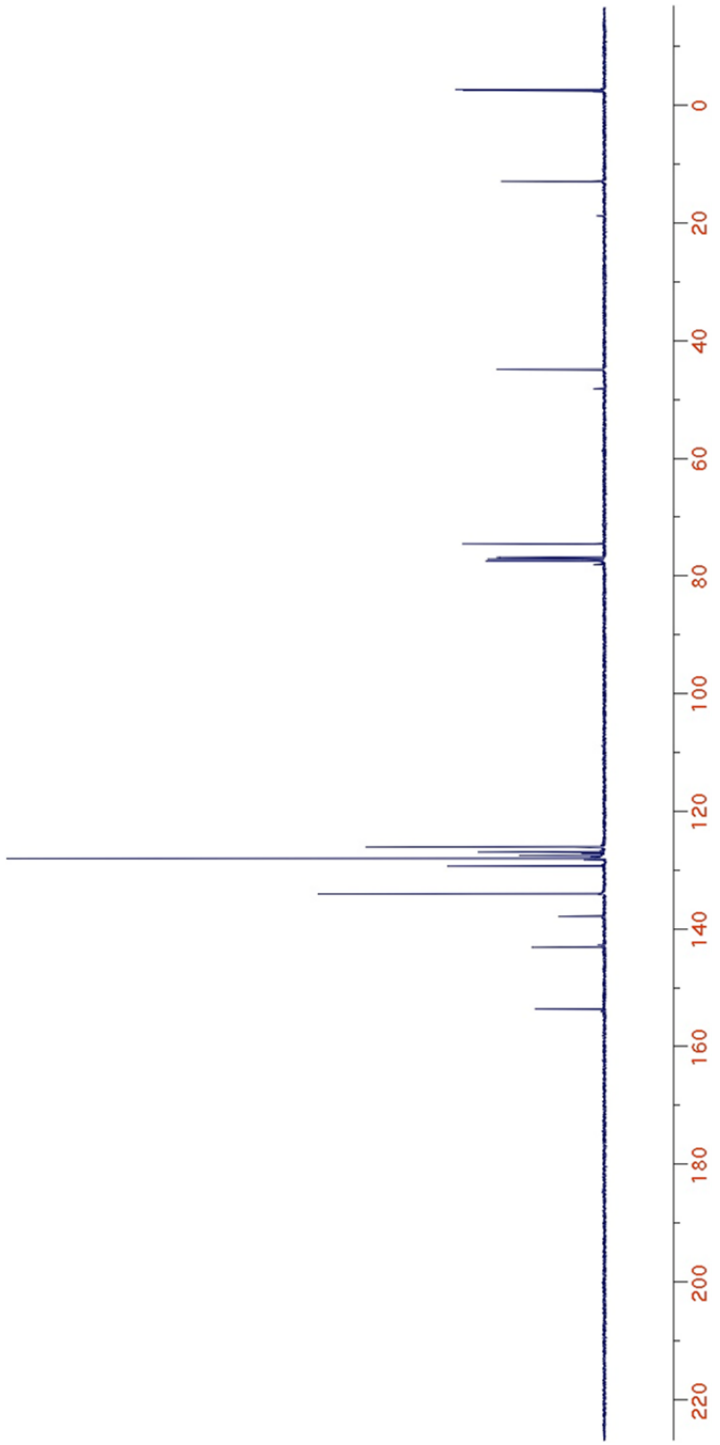
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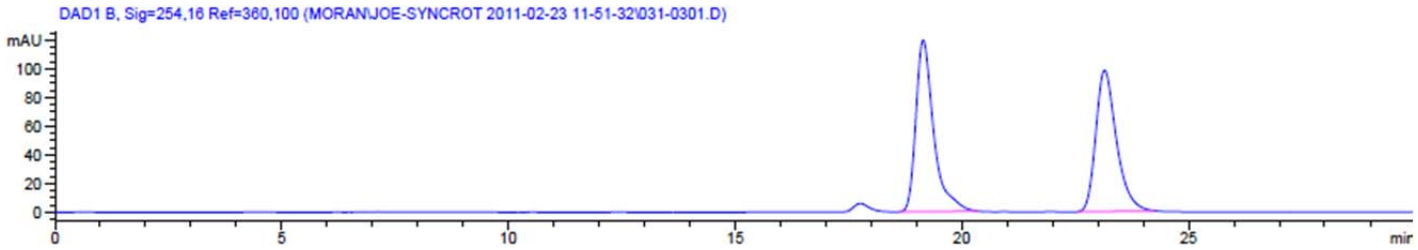

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

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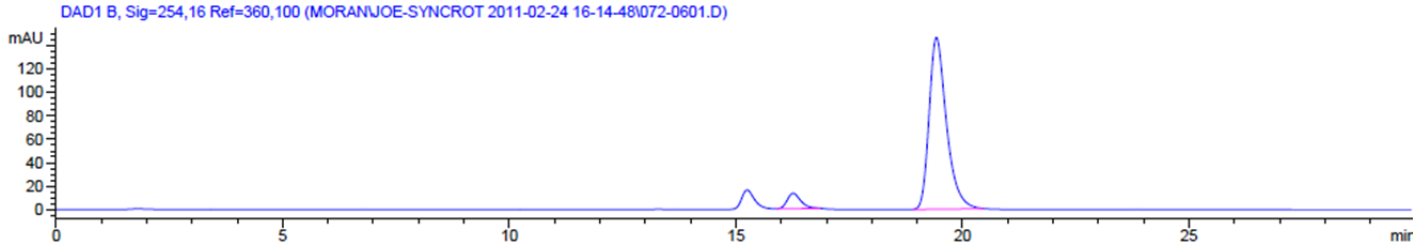
1	19.145	BB	0.4103	3283.78076	119.60905	51.1861
2	23.145	BB	0.4809	3131.59302	98.49988	48.8139
Totals :				6415.37378	218.10893	

(R)-DM-SEGPHOS (from alcohol oxidation level)



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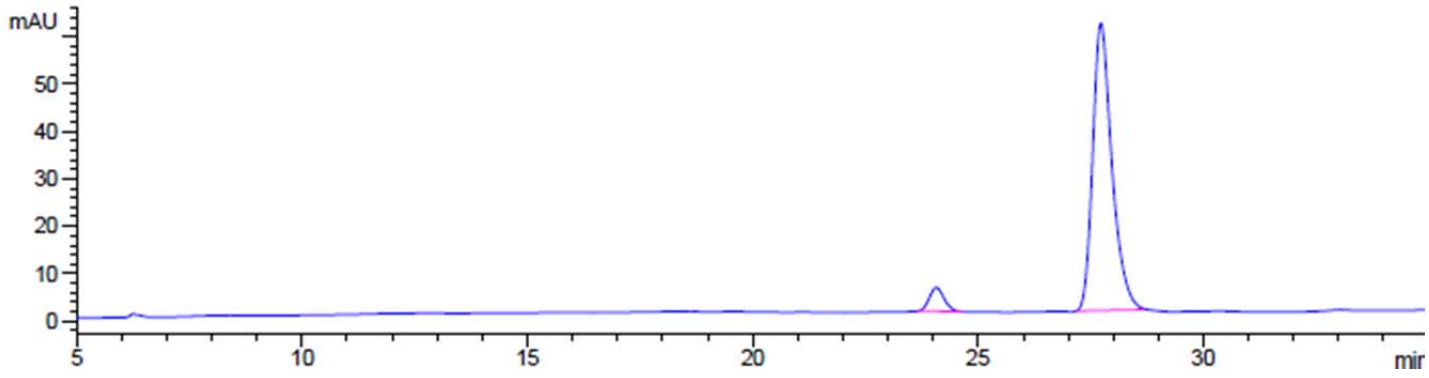
1	16.259	BB	0.3187	280.67160	13.27373	6.6723
2	19.421	BB	0.4018	3925.81860	146.88321	93.3277
Totals :				4206.49020	160.15694	

(R)-DM-SEGPHOS (from aldehyde oxidation level)



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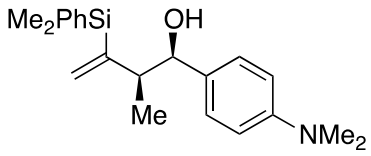
1	24.070	BB	0.3598	119.40488	5.08713	6.2115
2	27.722	BB	0.4447	1802.90039	60.67561	93.7885
Totals :				1922.30527	65.76274	

(1*R*,2*R*)-3-(dimethyl(phenyl)silyl)-1-(4-(dimethylamino)phenyl)-2-methylbut-3-en-1-ol (4b)



From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to alcohol), diene **1** (113 mg, 0.60 mmol, 200 mol%) and alcohol **2b** (45 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, 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; 0-10% EtOAc/hexanes) to furnish the title compound (88 mg, 0.26 mmol, *syn:anti* = ≥20:1) as a colorless oil in 87% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%), (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%) and aldehyde **3b** (45 mg, 0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to aldehyde), diene **1** (113 mg, 0.60 mmol, 200 mol%) and isopropanol (46 μL, 0.60 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, 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; 0-10% EtOAc/hexanes) to furnish the title compound (81 mg, 0.24 mmol, *syn:anti* = 19:1) as a colorless oil in 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 7.51-7.48 (m, 2H), 7.40-7.30 (m, 3H), 6.99 (d, J = 8.8 Hz, 2H), 6.39 (d, J = 8.8 Hz, 2H), 5.89 (dd, J = 2.2, 1.2 Hz, 1H), 5.63 (d, J = 2.2, 1H), 4.52 (dd, J = 4.8, 2.6 Hz, 1H), 2.90 (s, 6H), 2.70-2.62 (m, 1H), 1.69 (d, J = 2.6Hz, 1H), 0.93 (d, J = 6.8 Hz, 3H), 0.36 (s, 6H).

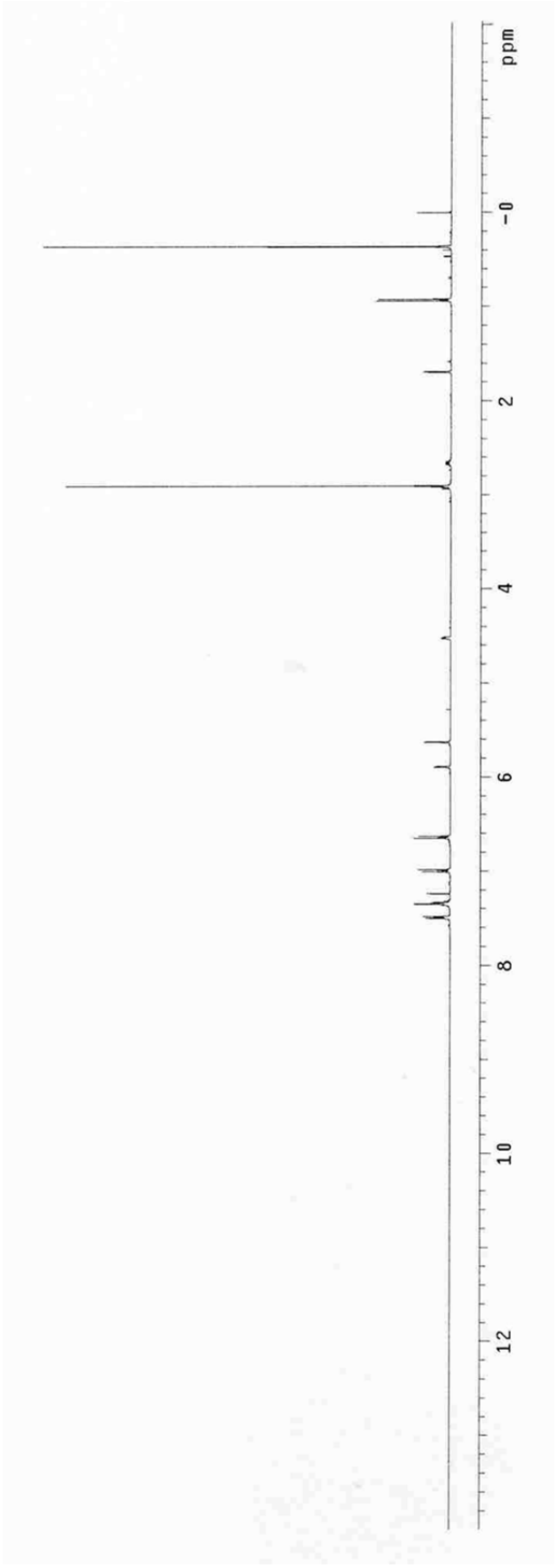
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 149.7, 138.0, 134.0, 131.2, 129.1, 127.8, 127.1, 126.8, 112.3, 74.5, 44.9, 40.7, 13.4, -2.6, -2.8.

FTIR (neat): 3439, 3046, 2956, 2882, 2798, 1614, 1521, 1345, 1247, 1109, 831, 815, 774, 733, 701 cm^{-1}.

HRMS (CI) Calcd. for $C_{21}H_{29}NOSi$ $[M+1]^+$: 340.2097, Found: 340.2088.

$[\alpha]_D^{25}$ = -20 (c =1.0, CH_2Cl_2).

HPLC: (Chiralcel AD-H/AD-H column, hexanes:*i*-PrOH = 99:1, 1 mL/min, 254 nm), t_{major} = 46.9 min, t_{minor} = 42.5 min; ee = 90%.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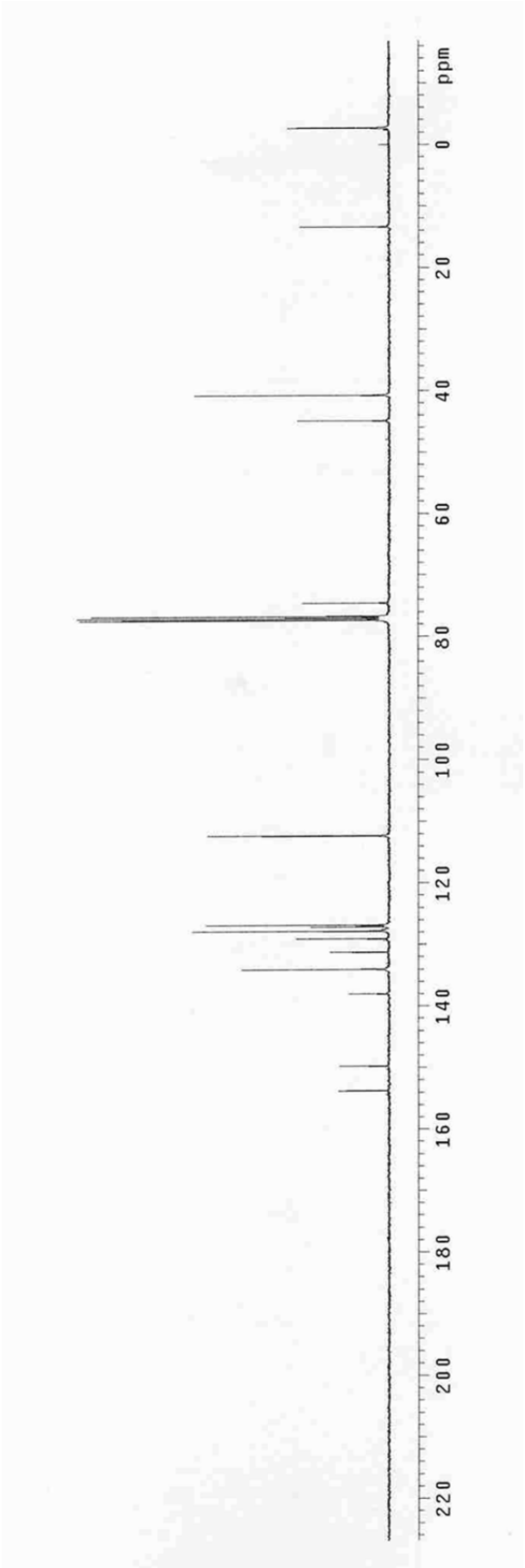
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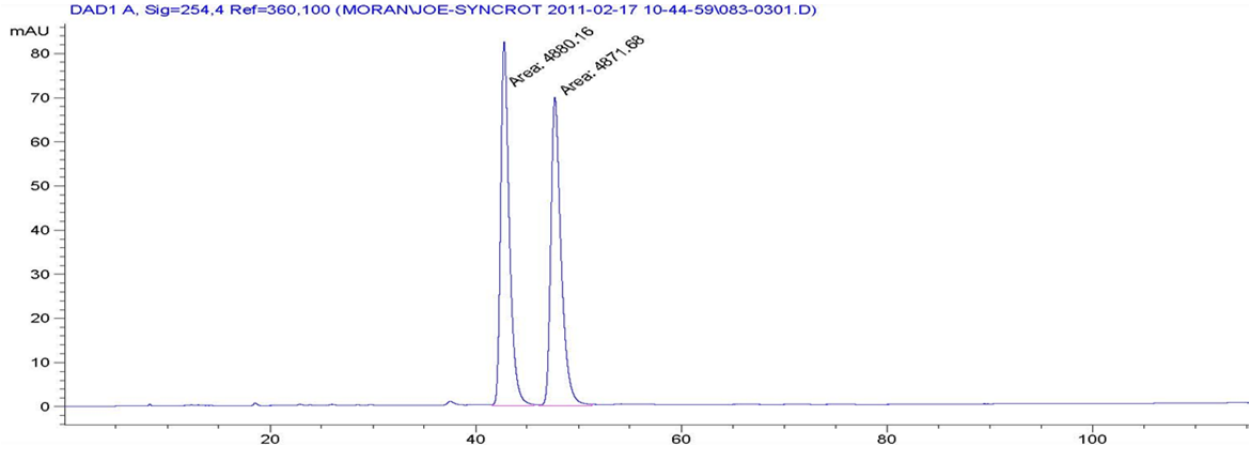
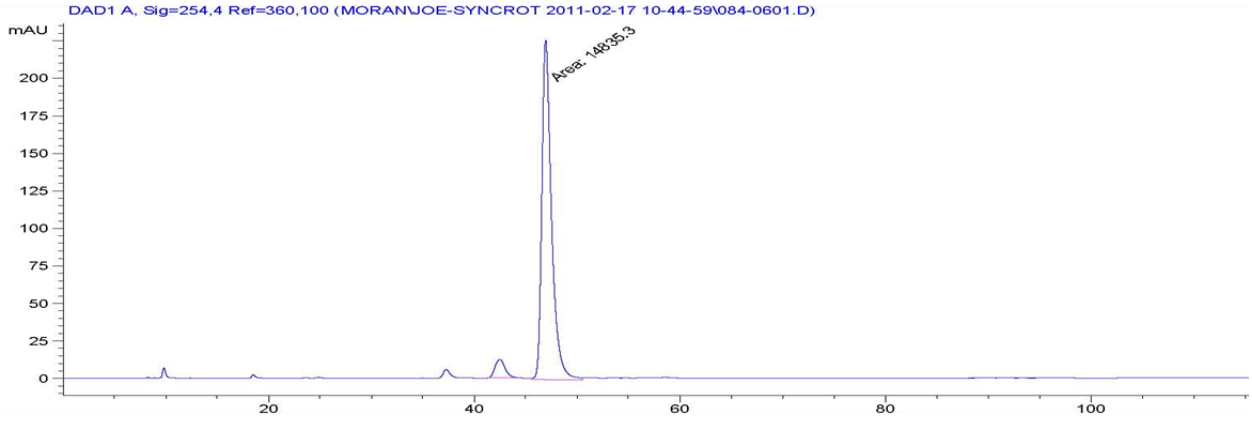


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.730	MM	0.9860	4880.16162	82.49023	50.0435
2	47.667	MM	1.1612	4871.68457	69.92348	49.9565
Totals :				9751.84619	152.41371	

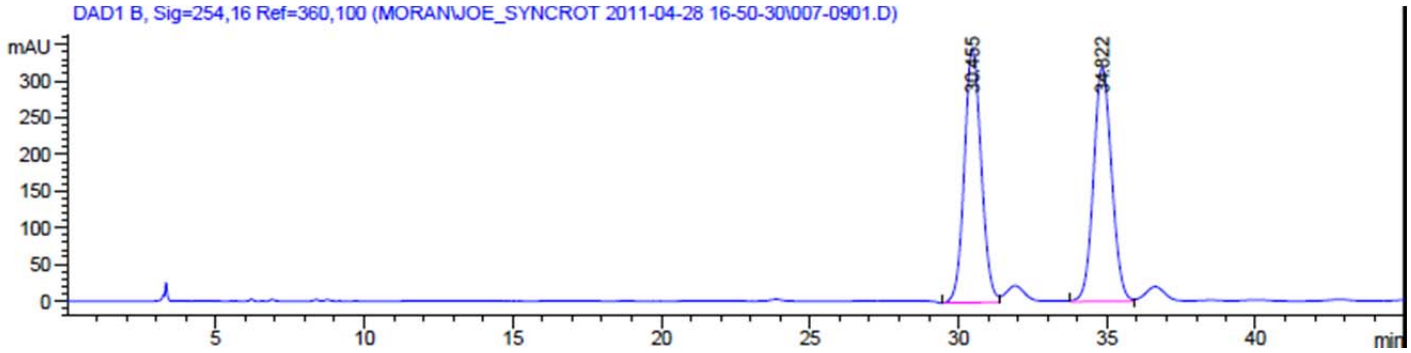
***(R)*-DM-Segphos (from alcohol oxidation level):**



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.451	BB	0.9936	824.62164	12.21539	5.2658
2	46.913	MM	1.0930	1.48353e4	226.21429	94.7342
Totals :				1.56599e4	238.42968	

Racemate



Signal 2: DAD1 B, Sig=254,16 Ref=360,100

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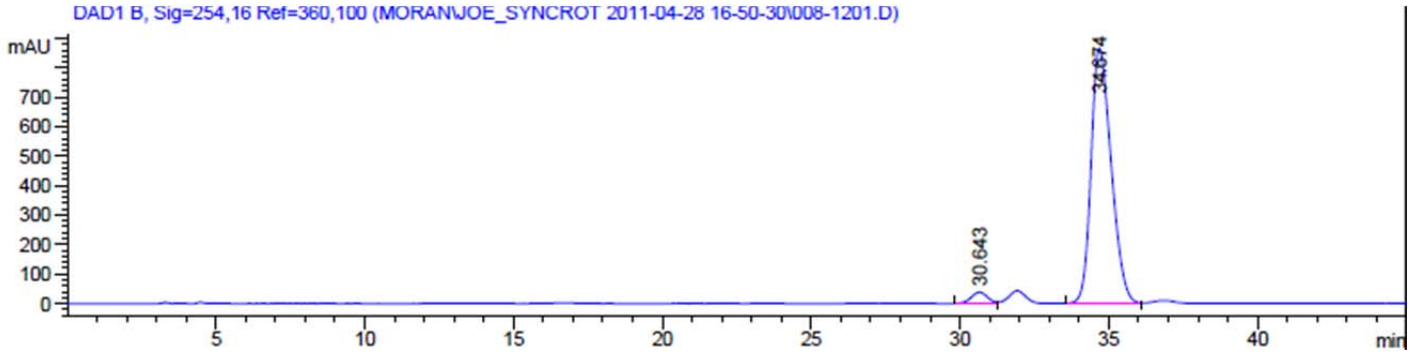
1	30.455	BV	0.6088	1.37060e4	347.04153	50.2119
2	34.822	BV	0.6581	1.35903e4	319.57437	49.7881
Totals :				2.72964e4	666.61591	

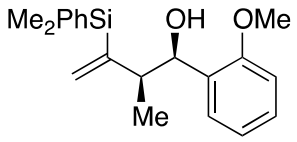
***(R)*-DM-Segphos (from aldehyde oxidation level):**



Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.643	BV	0.5874	1509.72009	38.84896	3.5734
2	34.674	BB	0.7265	4.07393e4	866.54004	96.4266
Totals :				4.22490e4	905.38900	

(1*R*,2*R*)-3-(dimethyl(phenyl)silyl)-1-(2-methoxyphenyl)-2-methylbut-3-en-1-ol (4c)



From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R)*-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to alcohol), diene **1** (113 mg, 0.60 mmol, 200 mol%) and alcohol **2c** (41 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 0-5% EtOAc/hexanes) to furnish the title compound (82 mg, 0.25 mmol, *syn:anti* = ≥20:1) as a colorless oil in 84% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R)*-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to aldehyde), diene **1** (113 mg, 0.60 mmol, 200 mol%), aldehyde **3c** (41 mg, 0.30 mmol, 100 mol%) and isopropanol (46 μL, 0.60 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 0-5% EtOAc/hexanes) to furnish the title compound (70 mg, 0.21 mmol, *syn:anti* = ≥20:1) as a colorless oil in 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.51 (m, 2H), 7.37-7.32 (m, 4H), 7.22-7.20 (m, 1H), 6.94 (t, *J* = 7.2 Hz, 1 H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.96 (dd, *J* = 2.4, 1.2, 1H), 5.66 (d, *J* = 2.4, 1H), 4.91 (t, *J* = 4.4, 1H), 3.78 (s, 3H), 3.01-2.94 (m, 1H), 2.19 (d, *J* = 4.4Hz, 1H), 0.94 (d, *J* = 7.2 Hz, 3H), 0.43 (s, 3H), 0.40 (s, 3H).

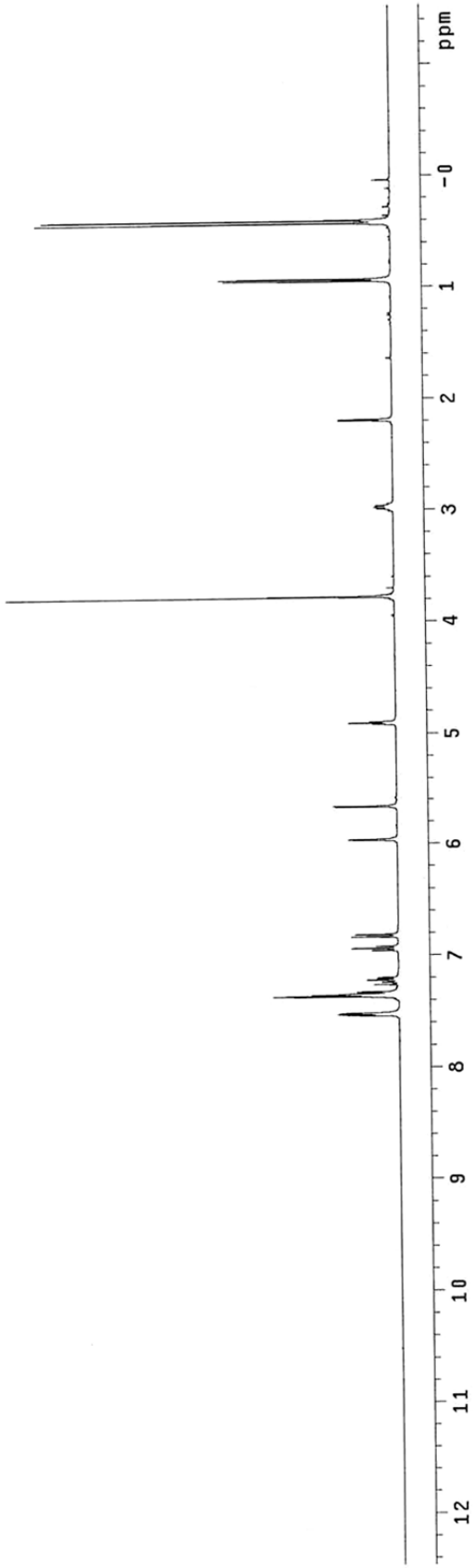
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 154.1, 138.6, 134.1, 131.1, 129.3, 128.2, 128.0, 127.9, 127.6, 120.5, 110.3, 71.3, 55.1, 42.0, 13.9, -2.5, -2.7.

HRMS (CI) Calcd. for $C_{26}H_{26}O_2Si$ $[M+1]^+$: 327.1780, Found: 327.1773.

$[\alpha]_D^{25}$ = -30 (c =1.0, CH_2Cl_2).

FTIR (neat): 3565, 3050, 2958, 2835, 1600, 1489, 1463, 1438, 1427, 1286, 1237, 1160, 1108, 1049, 1027, 978, 934, 752, 731, 700 cm^{-1}.

HPLC (Chiralcel AD-H/AD-H column, hexanes:*i*-PrOH = 99:1, 1 mL/min, 230 nm), t_{major} = 33.2 min, t_{minor} = 26.4 min; ee = 90%.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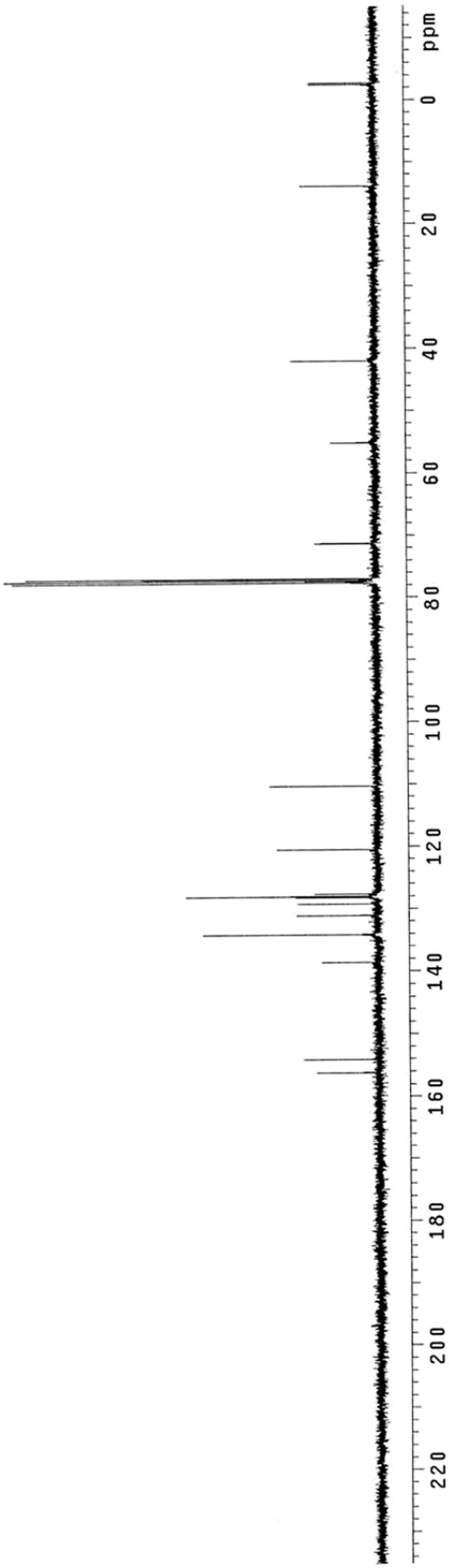
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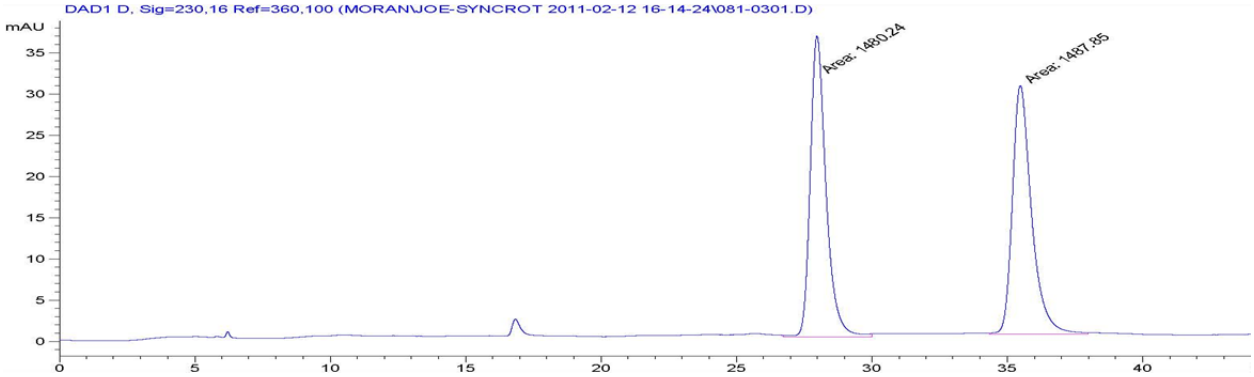

Signal 1: DAD1 D, Sig=230,16 Ref=360,100

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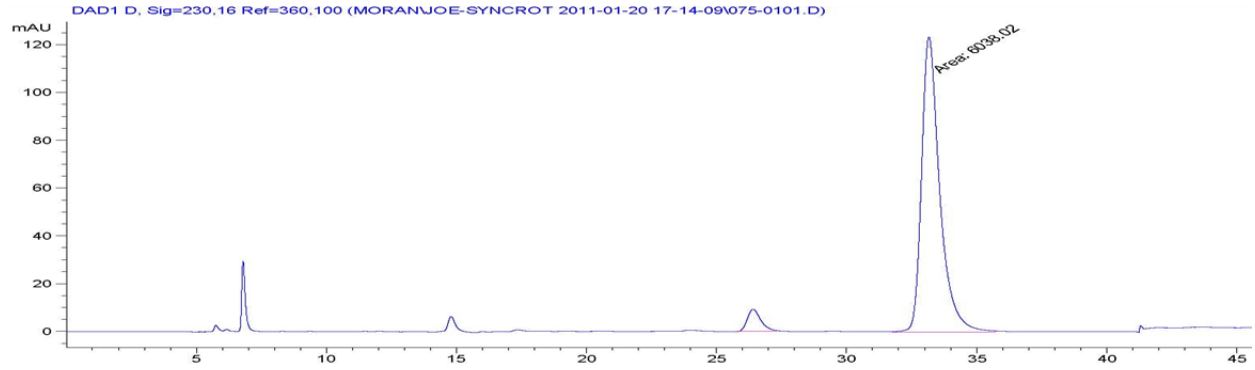
2	35.472	MM	0.8219	1487.85242	30.16965	50.1283
Totals :				2968.08838	66.64502	

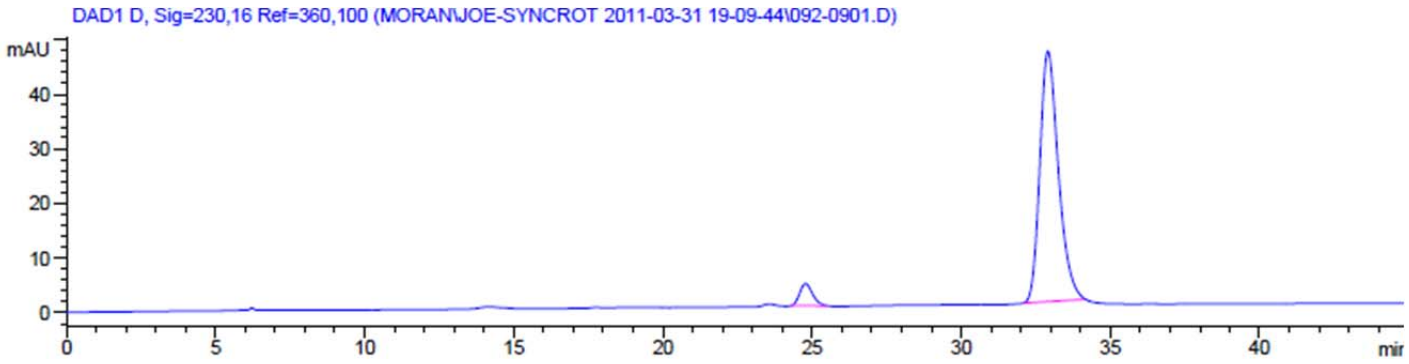
(R)-DM-Segphos (from alcohol oxidation level):



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.387	BB	0.5349	329.78067	9.22776	5.1789
2	33.148	MM	0.8137	6038.01514	123.66703	94.8211
Totals :				6367.79581	132.89479	

(R)-DM-Segphos (from aldehyde oxidation level):



Signal 4: DAD1 D, Sig=230,16 Ref=360,100

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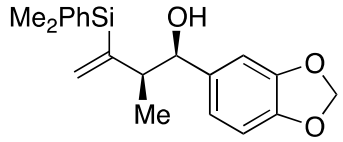
1	24.773	BB	0.4526	123.21796	4.07750	5.8366
2	32.898	BB	0.6550	1987.91248	45.92183	94.1634
Totals :				2111.13043	49.99933	

(1*R*,2*R*)-1-(benzo[*d*][1,3]dioxol-5-yl)-3-(dimethyl(phenyl)silyl)-2-methylbut-3-en-1-ol (4d)



From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)- SEGPHOS (9.2 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to alcohol), diene **1** (113 mg, 0.60 mmol, 200 mol%) and alcohol **2d** (46 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 0-10% EtOAc/hexanes) to furnish the title compound (87 mg, 0.26 mmol, *syn:anti* = ≥20:1) as a colorless oil in 85% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)- SEGPHOS (9.2 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to aldehyde), diene **1** (113 mg, 0.60 mmol, 200 mol%), aldehyde **3d** (45 mg, 0.30 mmol, 100 mol%) and isopropanol (46 μL, 0.60 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 0-10% EtOAc/hexanes) to furnish the title compound (93 mg, 0.27 mmol, *syn:anti* = ≥20:1) as a colorless oil in 91% yield.

Microwave:
To a 10 ml microwave vial equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (43 mg, 0.045 mmol, 5 mol%) and (*R*)- SEGPHOS (32 mg, 0.045 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.45 mL, 2.0 M concentration with respect to alcohol), diene **1** (339 mg, 1.80 mmol, 200 mol%) and alcohol **2d** (138 mg, 0.90 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a microwave cap. The mixture was heated at 95 °C for 4 hrs, 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; 0-10% EtOAc/hexanes) to furnish the title compound (269 mg, 0.79 mmol, *syn:anti* = ≥20:1) as a colorless oil in 88% yield and 93% ee..

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 2H), 7.40-7.35 (m, 3H), 6.70 (d, *J* = 8.0 Hz, 1 H), 6.62 (d, *J* = 1.3 Hz, 1H), 6.57 (ddd, *J* = 8.0, 1.3, 0.8 Hz, 1H), 5.92 – 5.91 (m, 3H), 5.68 (d, *J* = 2.4, 1H), 4.49 (dd, *J* = 4.4, 2.4 Hz, 1H), 2.67 - 2.61 (m, 1H), 1.81 (d, *J* = 2.4Hz, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.40 (s, 6H).

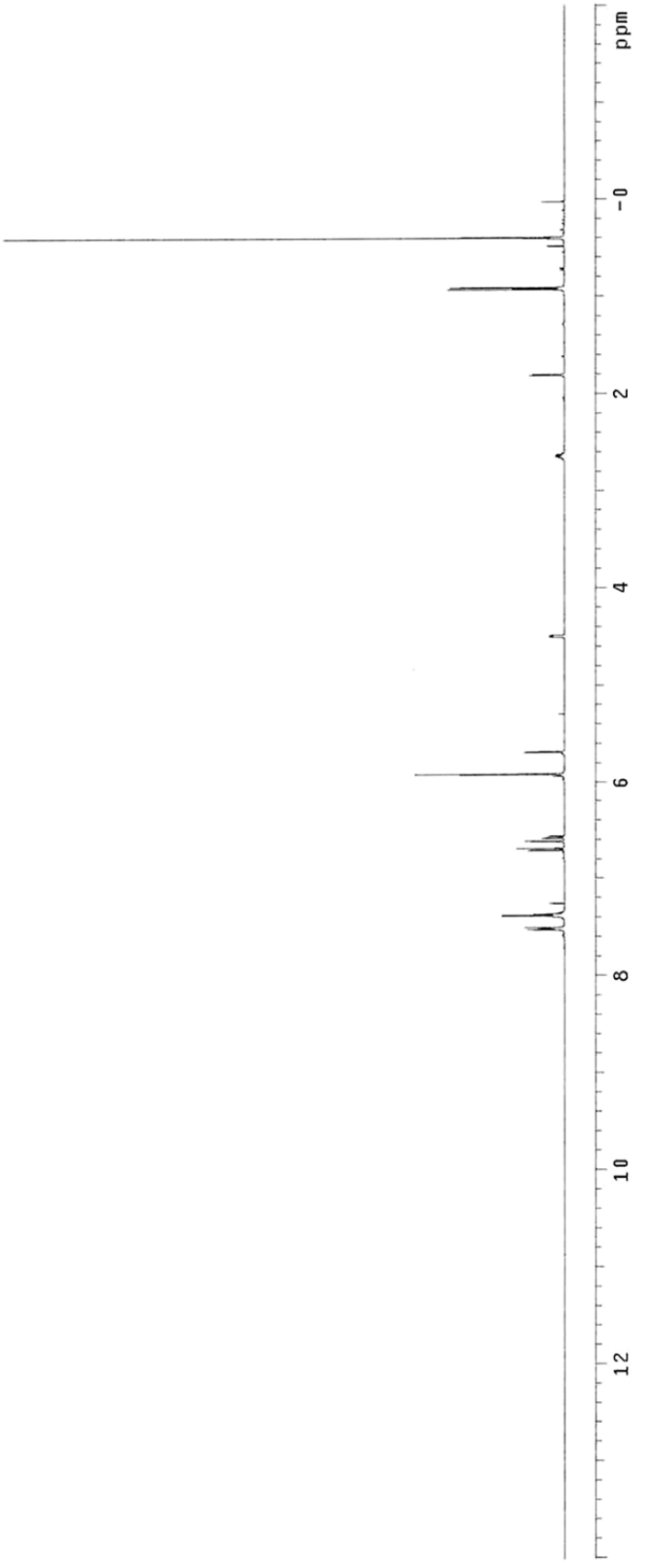
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 147.2, 146.2, 137.7, 137.1, 133.9, 129.2, 127.9, 127.3, 119.1, 107.7, 106.7, 100.7, 74.3, 44.9, 13.0, -2.7, -2.8.

FTIR (neat): 3449, 3048, 2957, 2891, 1502, 1487, 1440, 1421, 1245, 1109, 1039, 984, 932, 814, 774, 732, 700 cm^{-1}.

HRMS (CI) Calcd. for $C_{20}H_{24}O_3Si$ $[M-1]^+$: 339.1416, Found: 339.1417.

$[\alpha]_D^{25}$ = -26 (c =1.0, CH_2Cl_2).

HPLC: (Chiralcel AD-H/AD-H column, hexanes:*i*-PrOH = 99:1, 1 mL/min, 230 nm), t_{major} = 75.5 min, t_{minor} = 79.5 min;
GC: (The alcohol was treated with TBAF to give the crotylation product for analysis Cyclosil-B: Initial temperature: 50 °C (1 min hold), final temperature: 225 °C; rate: 1.5 C/min) t_{major} = 78.578 min, t_{minor} = 79.136 min ee = 93%.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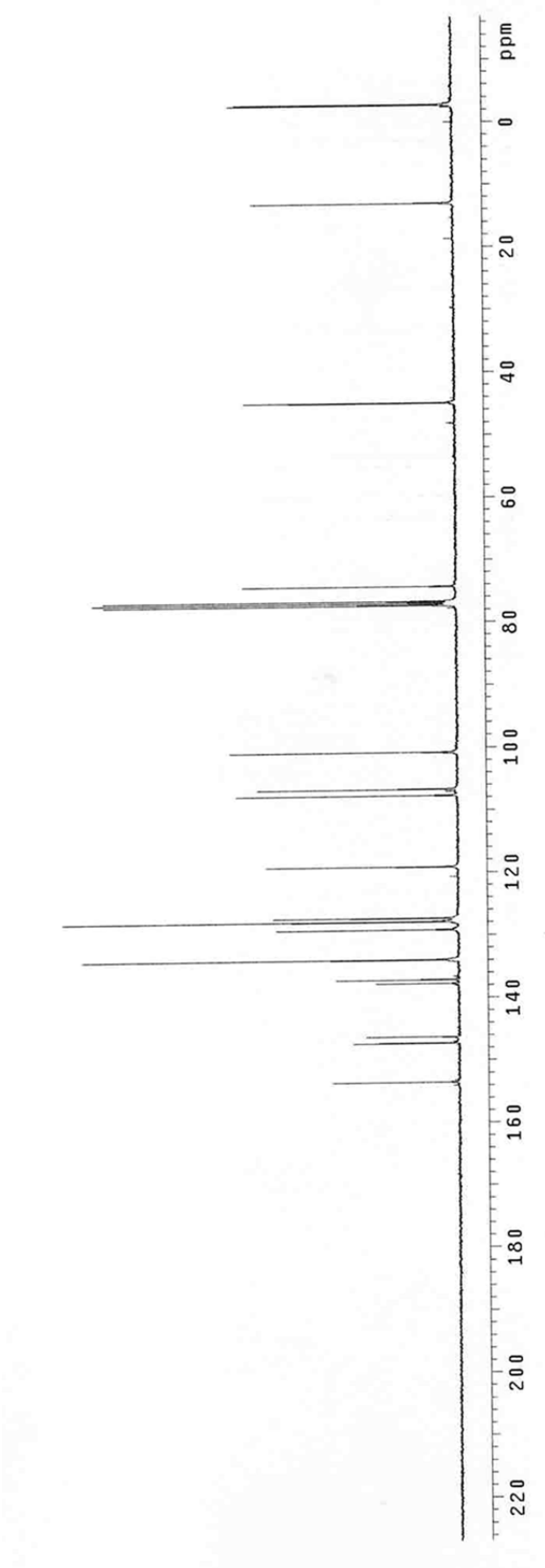
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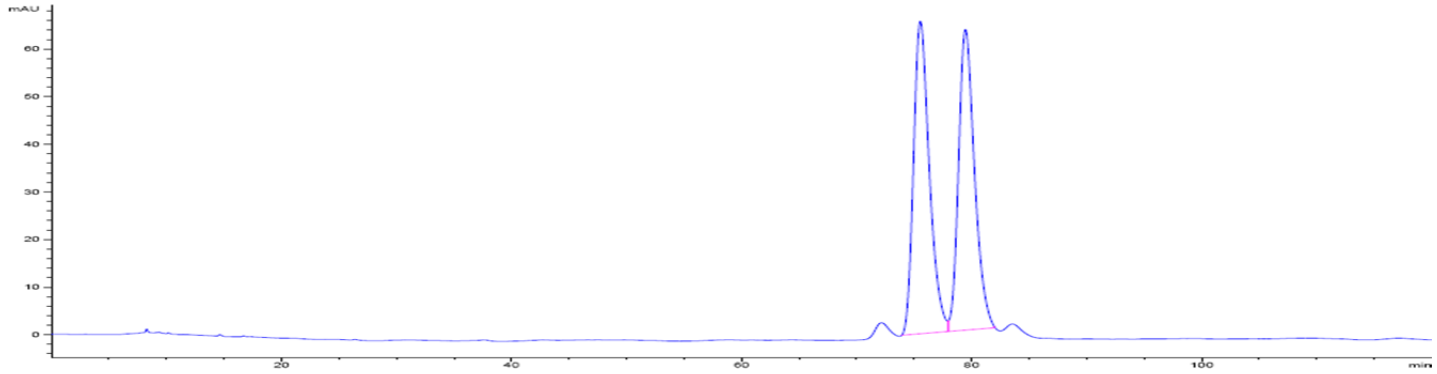
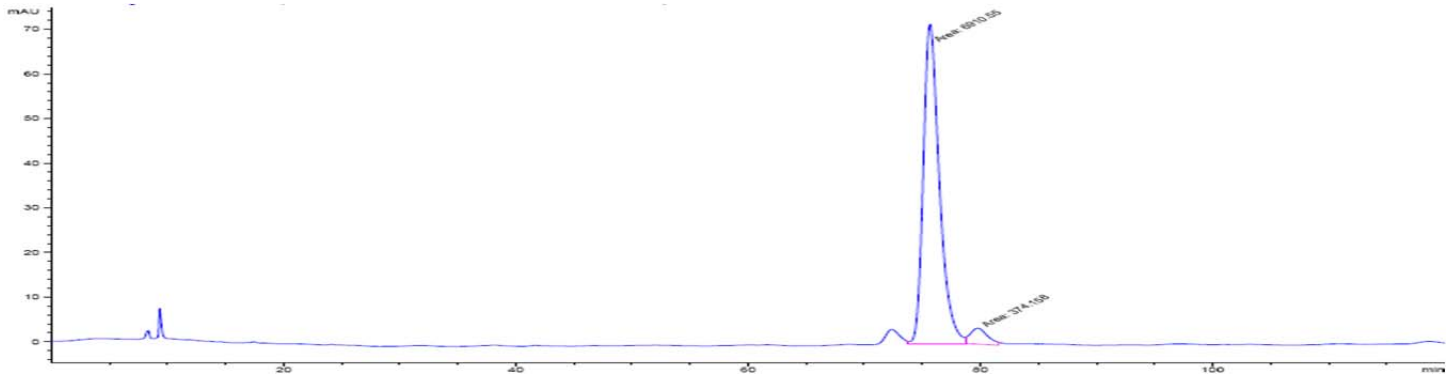
Racemic (HPLC):



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

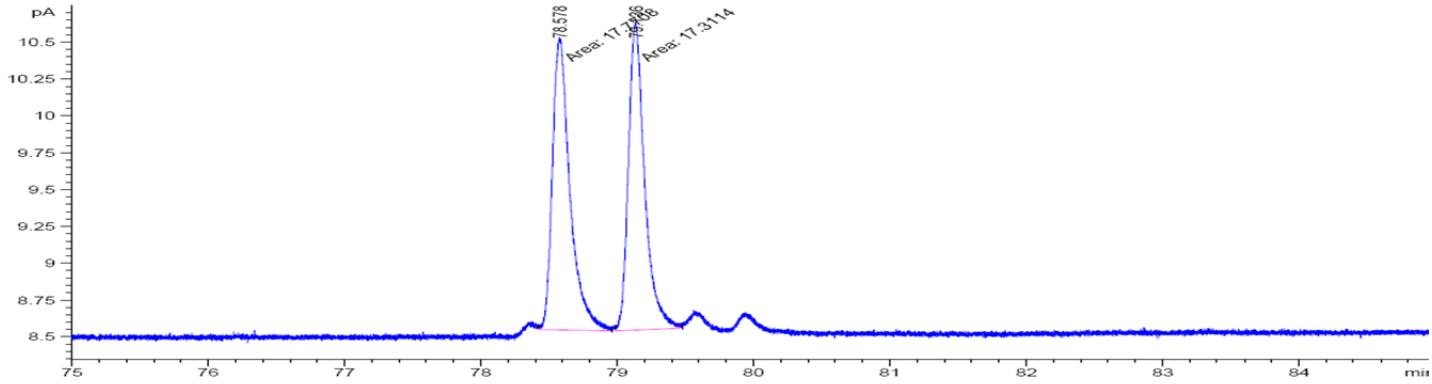
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	75.526	BB	1.4397	6291.15918	65.66846	50.8017
2	79.449	BB	1.4290	6092.60205	63.18338	49.1983
Totals :				1.23838e4	128.85184	

***(R)*-Segphos (from alcohol oxidation level):**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	75.665	MM	1.6095	6910.55127	71.56133	94.8638
2	79.785	MM	1.7348	374.15778	3.59471	5.1362
Totals :				7284.70905	75.15605	

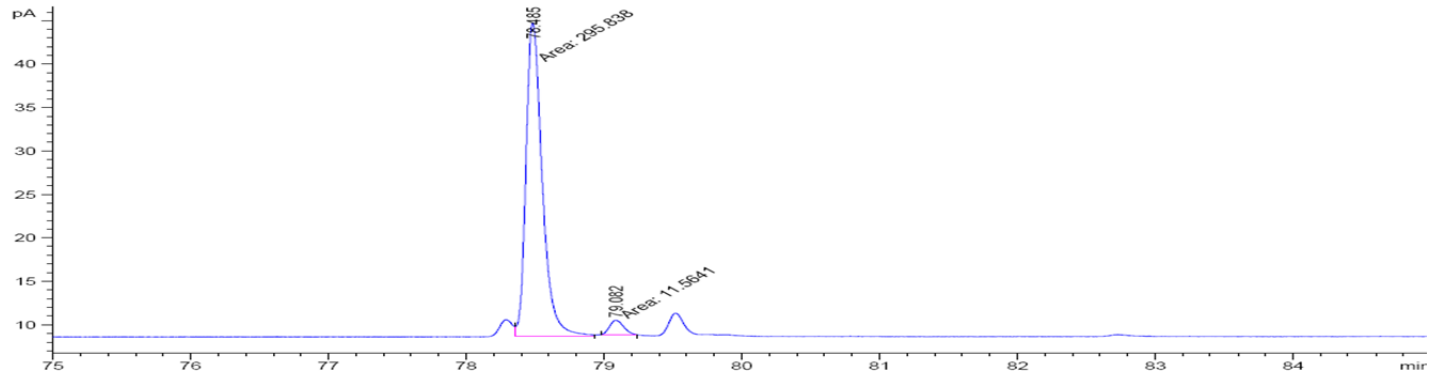
Racemic (GC):



Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	78.578	MM	0.1498	17.77085	1.97775	50.65485
2	79.136	MM	0.1384	17.31138	2.08490	49.34515
Totals :				35.08222	4.06266	

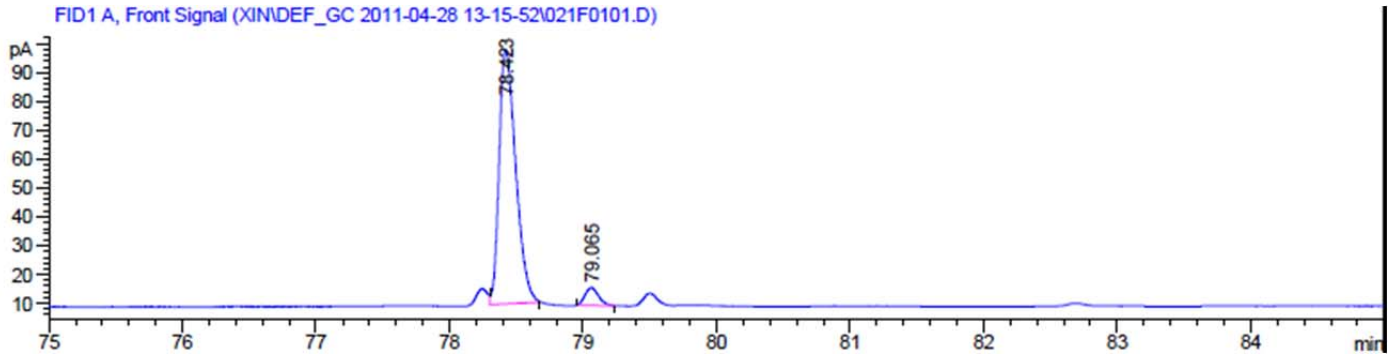
***(R)*-DM-Segphos (Microwave from alcohol oxidation level):**



Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	78.485	MM	0.1367	295.83792	36.06434	96.23810
2	79.082	MM	0.1164	11.56415	1.65544	3.76190
Totals :				307.40207	37.71977	

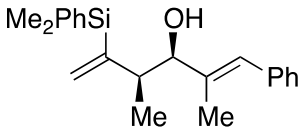
***(R)*-Segphos (from aldehyde oxidation level):**



Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	78.423	VB	0.1255	760.12622	88.06185	94.51224
2	79.065	BB	0.1021	44.13599	6.21072	5.48776
Totals :				804.26221	94.27257	

(3*R*,4*R*,*E*)-5-(dimethyl(phenyl)silyl)-2,4-dimethyl-1-phenylhexa-1,5-dien-3-ol (4e)



From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-SEGPHOS (9.2 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to alcohol), diene **1** (141 mg, 0.75 mmol, 250 mol%) and alcohol **2e** (44.5 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (70.7 mg, 0.21 mmol, *syn:anti* = 11:1) as a colorless oil in 70% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-SEGPHOS (9.2 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to aldehyde), diene **1** (141 mg, 0.75 mmol, 250 mol%), aldehyde **3e** (43.9 mg, 0.30 mmol, 100 mol%) and isopropanol (46 μL, 0.60 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (75.9 mg, 0.23 mmol, *syn:anti* = 11:1) as a colorless oil in 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H), 7.33-7.12 (m, 8H), 6.46 (dd, *J* = 1.6, 1.1 Hz, 1H), 5.88 (dd, *J* = 2.2, 1.3 Hz, 1H), 5.65 (dd, *J* = 2.2, 0.3 Hz, 1H), 3.94 (ddd, *J* = 4.0, 2.6, 1.6 Hz, 1H), 2.69 (qdd, *J* = 7.0, 4.0, 1.1 Hz, 1H), 1.64 (d, *J* = 2.6 Hz, 1H), 1.56 (d, *J* = 1.1 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.40 (s, 6H).

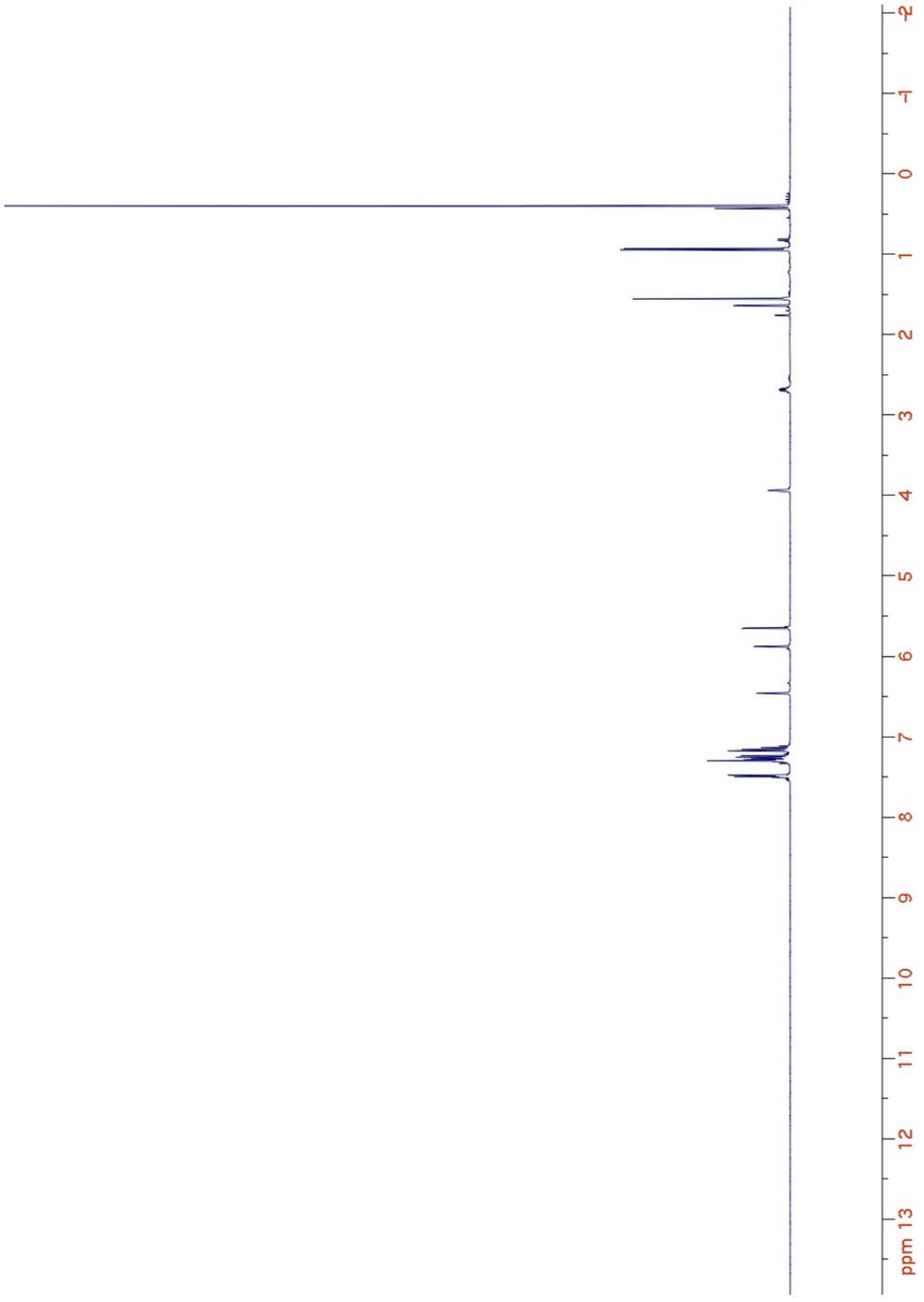
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 138.1, 137.99, 137.96, 134.1, 129.3, 129.1, 128.1, 128.0, 127.6, 126.2, 125.1, 76.4, 41.1, 15.1, 12.8, -2.1, -2.4.

HRMS (CI) Calcd. for $C_{22}H_{28}OSi$ (M+): 336.1909, Found: 336.1904.

$[\alpha]_D^{25}$ = +39 (c =1.0, CH_2Cl_2).

FTIR (neat): 2959, 1738, 1446, 1427, 1372, 1248, 1109, 997, 910, 832, 815, 774, 731, 698 cm^{-1}.

HPLC (Chiralcel AD-H/AD-H column, hexanes:*i*-PrOH = 99:1, 1.0 mL/min, 254 nm), t_{major} = 31.6 min, t_{minor} = 26.8 min; ee = 90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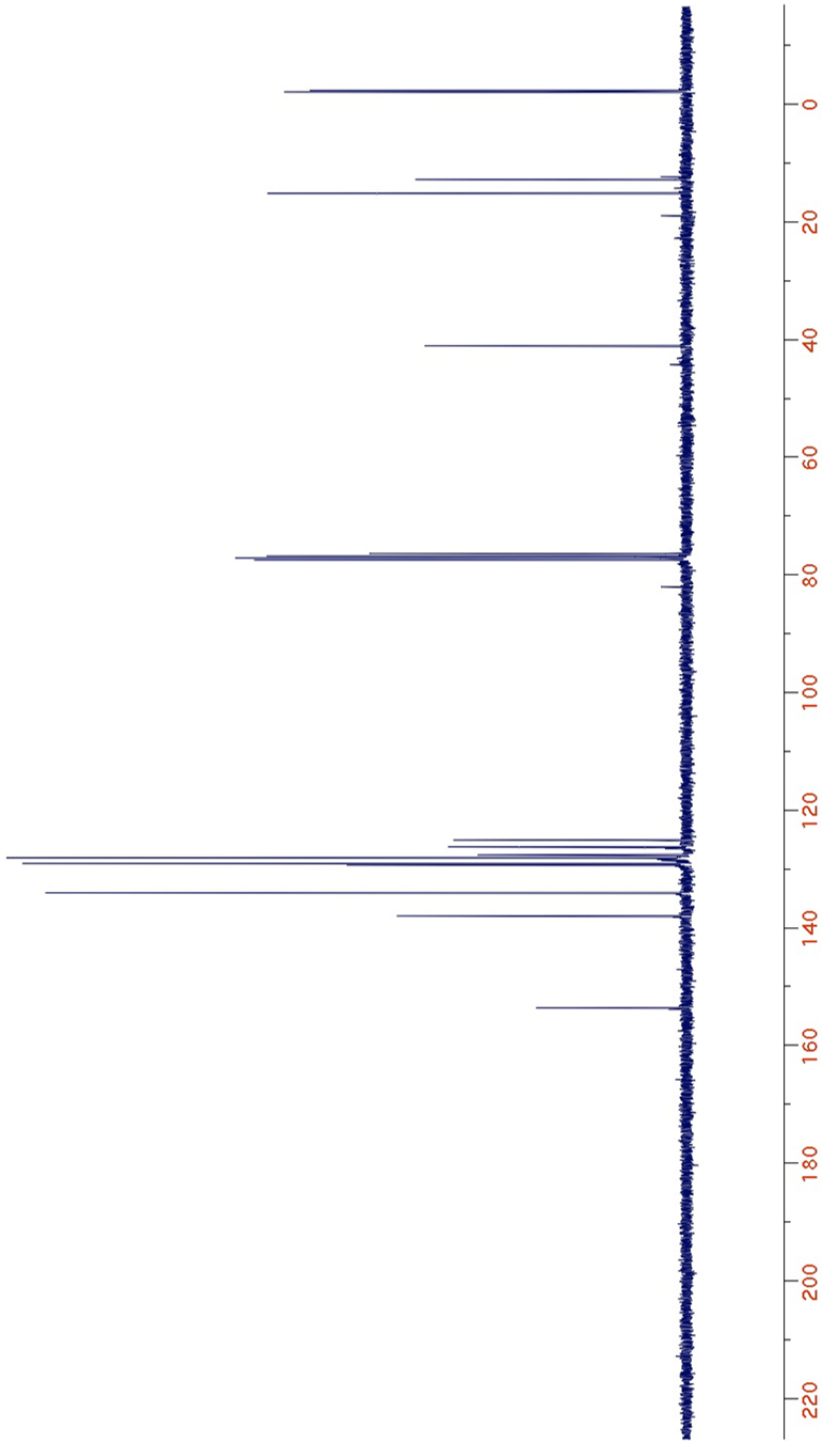
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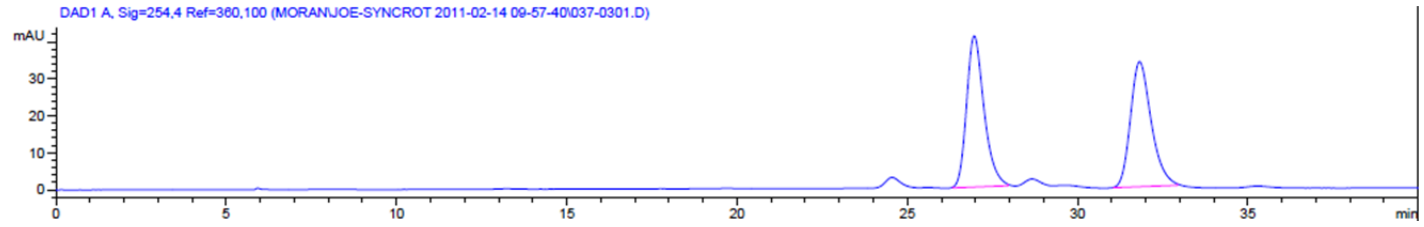
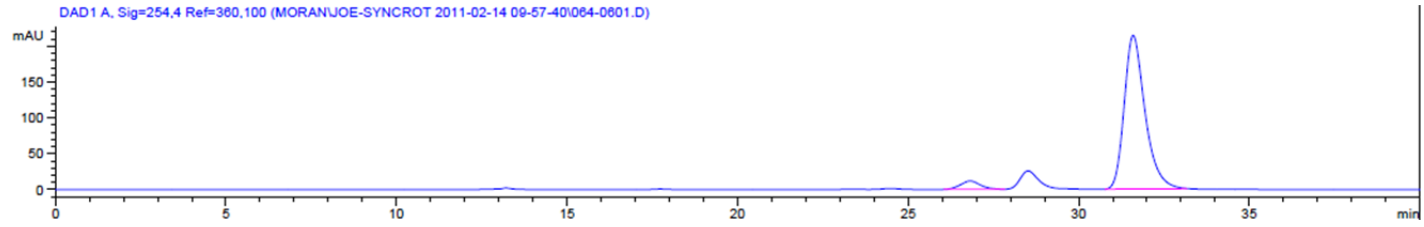
Racemate:



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.964	BB	0.5381	1459.54590	40.92148	50.3969
2	31.820	BB	0.6429	1436.55566	33.86212	49.6031
Totals :				2896.10156	74.78360	

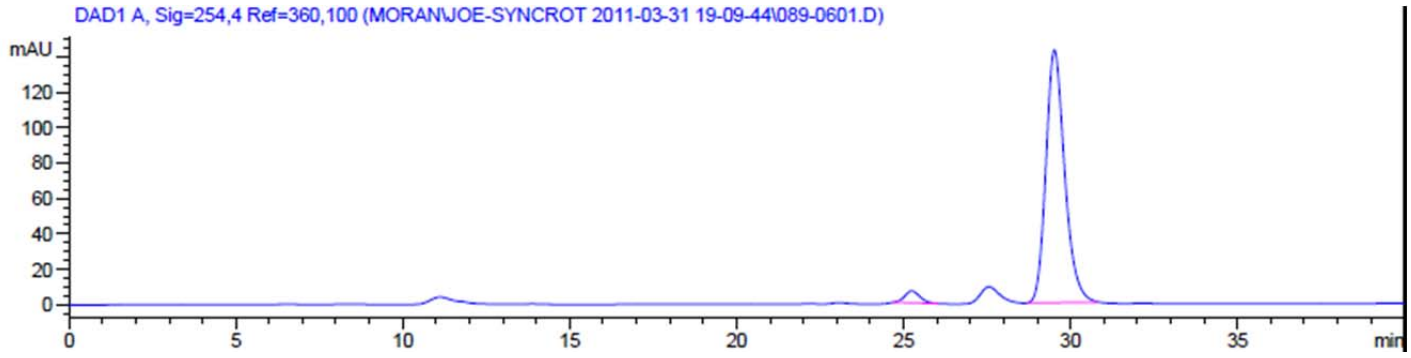
(R)-SEGPHOS (from alcohol oxidation level):



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.815	BB	0.5965	467.62494	11.59643	4.8742
2	31.593	BB	0.6401	9126.27930	214.61650	95.1258
Totals :				9593.90424	226.21293	

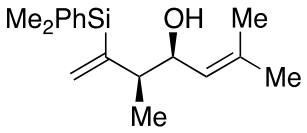
(R)-SEGPHOS (from aldehyde oxidation level):



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.236	BB	0.4840	220.40227	6.83803	3.7834
2	29.506	BB	0.5933	5605.09668	142.98344	96.2166
Totals :				5825.49895	149.82148	

(3*R*,4*S*)-2-(dimethyl(phenyl)silyl)-3,6-dimethylhepta-1,5-dien-4-ol (4f)



From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.15 mL, 2.0 M concentration with respect to alcohol), diene **1** (141 mg, 0.75 mmol, 250 mol%) and alcohol **2f** (25.8 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (55.2 mg, 0.20 mmol, *syn:anti* = ≥20:1) as a colorless oil in 67% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.15 mL, 2.0 M concentration with respect to aldehyde), diene **1** (141 mg, 0.75 mmol, 250 mol%), aldehyde **3f** (25.2 mg, 0.30 mmol, 100 mol%) and isopropanol (46 μL, 0.60 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (46.0 mg, 0.17 mmol, *syn:anti* = ≥20:1) as a colorless oil in 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.50 (m, 2H), 7.37-7.34 (m, 3H), 5.83 (dd, *J* = 2.3, 1.0 Hz, 1H), 5.61 (d, *J* = 2.3 Hz, 1H), 5.05 (dqq, *J* = 8.7, 1.4, 1.2 Hz, 1H), 4.18 (dd, *J* = 8.7, 5.5 Hz, 1H), 2.43 (qdd, *J* = 6.9, 5.5, 1.0 Hz, 1H), 1.65 (d, *J* = 1.4 Hz, 3H), 1.51 (d, *J* = 1.2 Hz, 3H), 1.38 (s, 1H), 1.06 (d, *J* = 6.9 Hz, 3H), 0.404 (s, 3H), 0.402 (s, 3H).

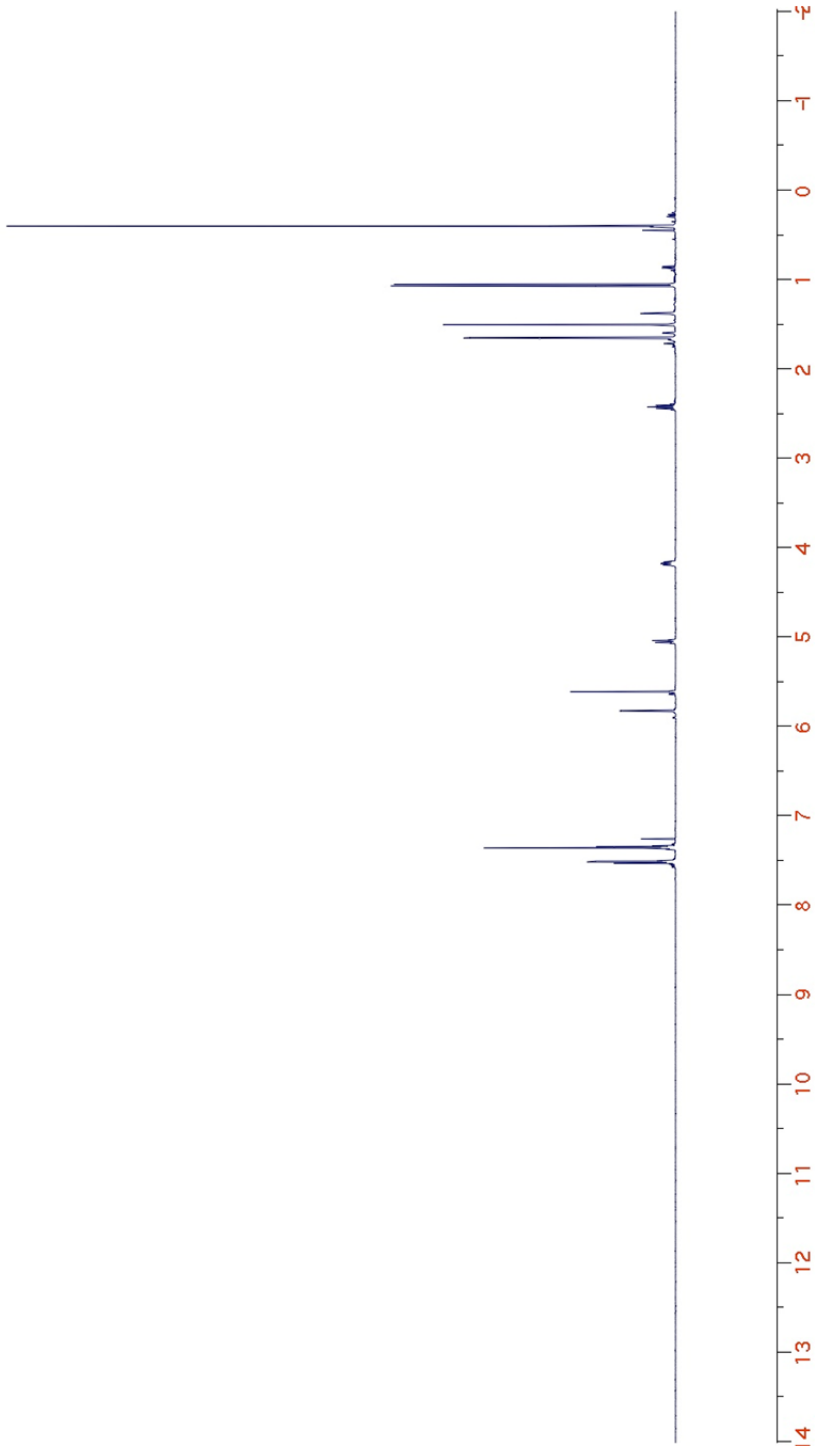
^{13}C NMR (100 MHz, $CDCl_3$):
δ153.6, 138.2, 134.7, 134.1, 129.2, 128.0, 127.2, 126.8, 70.5, 43.6, 26.0, 18.5, 15.2, –2.6, –2.4.

HRMS (CI) Calcd. for $C_{17}H_{26}OSi$ (M+): 274.1753, Found: 274.1752.

$[\alpha]_D^{25}$ = -12 (c =1.0, CH_2Cl_2).

FTIR (neat): 2960, 1427, 1375, 1247, 1108, 997, 926, 831, 816, 731, 699 cm^{-1}.

HPLC (Chiralcel AD-H/AD-H column, hexanes:*i*-PrOH = 99:1, 1.0 mL/min, 210 nm), t_{major} = 17.7 min, t_{minor} = 19.1 min; ee = 90%.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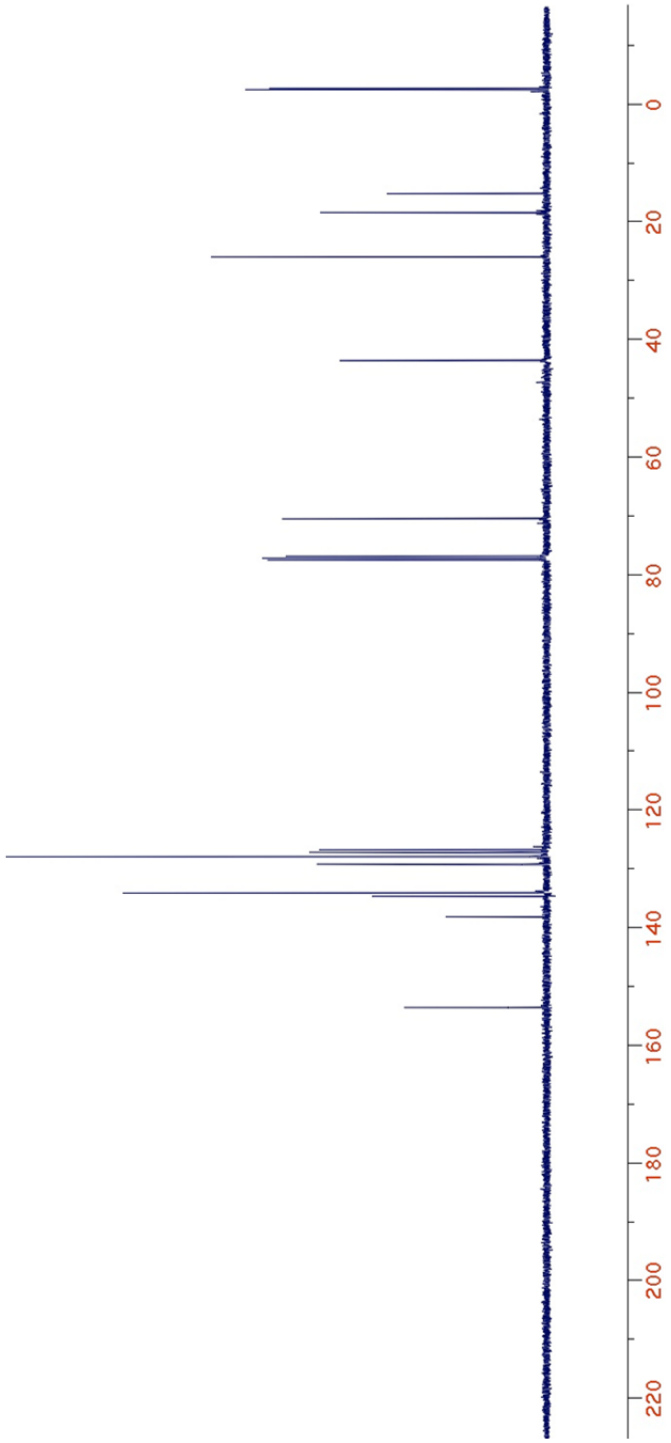
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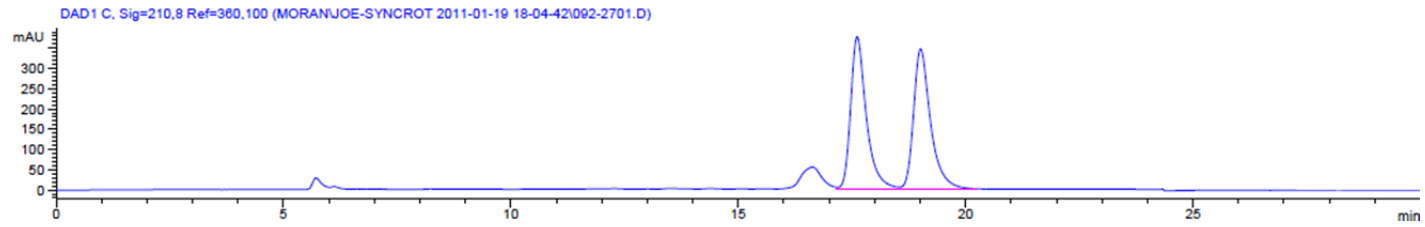
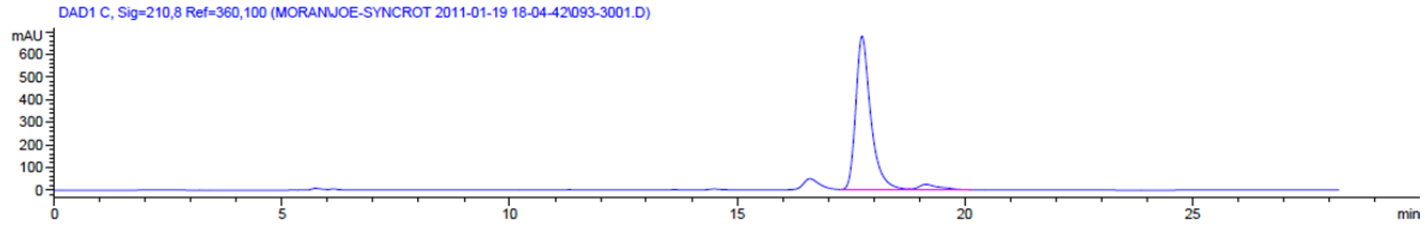
Racemate:



Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.610	VV	0.3572	8997.88184	375.93353	49.9955
2	19.005	VB	0.3874	8999.51074	346.06354	50.0045
Totals :				1.79974e4	721.99707	

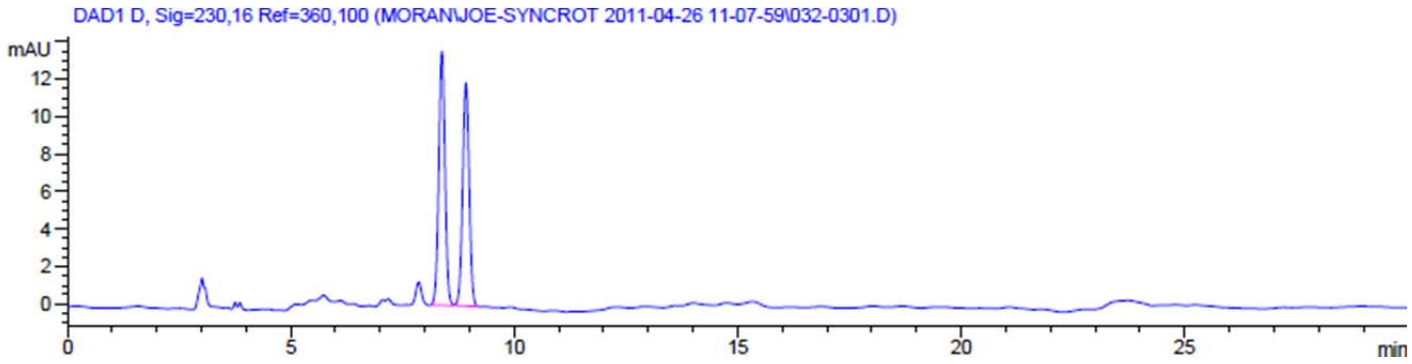
(R)-DM-SEGPHOS (from alcohol oxidation level):



Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.739	VV	0.3411	1.57060e4	680.85144	95.1293
2	19.146	VB	0.4569	804.15765	24.63239	4.8707
Totals :				1.65102e4	705.48383	

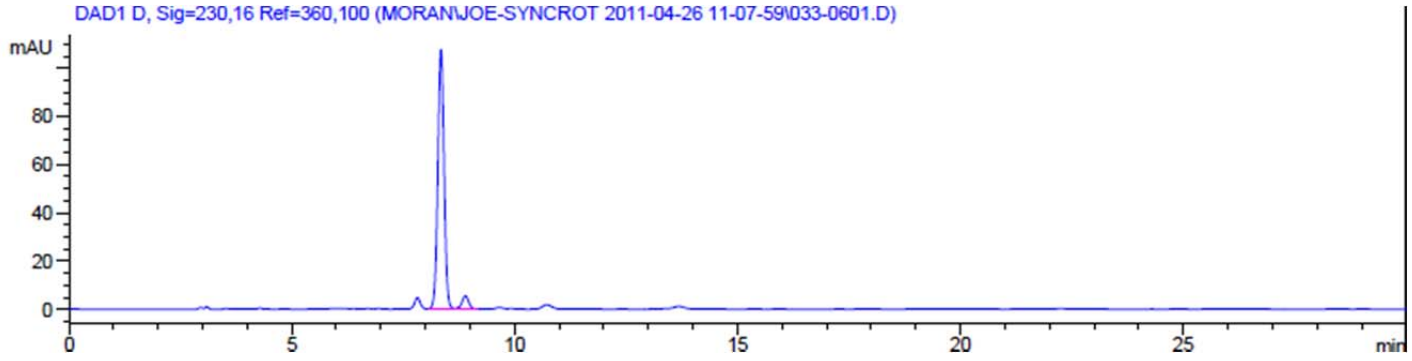
Racemate



Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.375	BB	0.1512	131.79037	13.58567	52.1620
2	8.912	BB	0.1583	120.86557	11.92097	47.8380
Totals :				252.65594	25.50664	

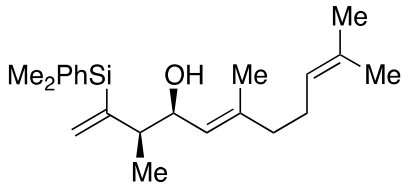
(R)-DM-SEGPHOS (from aldehyde oxidation level):



Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.339	BB	0.1516	1049.18921	107.78114	94.9326
2	8.887	BB	0.1571	56.00493	5.48624	5.0674
Totals :				1105.19414	113.26737	

(3*R*,4*S*,*E*)-2-(dimethyl(phenyl)silyl)-3,6,10-trimethylundeca-1,5,9-trien-4-ol (4g)



From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to alcohol), diene **1** (141 mg, 0.75 mmol, 250 mol%) and alcohol **2g** (46.3 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (71.8 mg, 0.21 mmol, *syn:anti* = ≥20:1) as a colorless oil in 70% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to aldehyde), diene **1** (141 mg, 0.75 mmol, 250 mol%), aldehyde **3g** (45.3 mg, 0.30 mmol, 100 mol%) and isopropanol (46 μL, 0.60 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (72.9 mg, 0.21 mmol, *syn:anti* = ≥20:1) as a colorless oil in 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 2H), 7.36-7.33 (m, 3H), 5.83 (dd, *J* = 2.3, 1.1 Hz, 1H), 5.62 (d, *J* = 2.3 Hz, 1H), 5.11-5.04 (m, 2H), 4.20 (dd, *J* = 8.5, 5.2 Hz, 1H), 2.44 (qdd, *J* = 6.9, 5.2, 1.1 Hz, 1H), 2.08-2.03 (m, 2H), 1.97-1.93 (m, 2H), 1.68 (d, *J* = 1.1 Hz, 3H), 1.59 (d, *J* = 0.7 Hz, 3H), 1.49 (d, *J* = 1.3 Hz, 3H), 1.34 (s, 1H), 1.05 (d, *J* = 6.9 Hz, 3H), 0.409 (s, 3H), 0.407 (s, 3H).

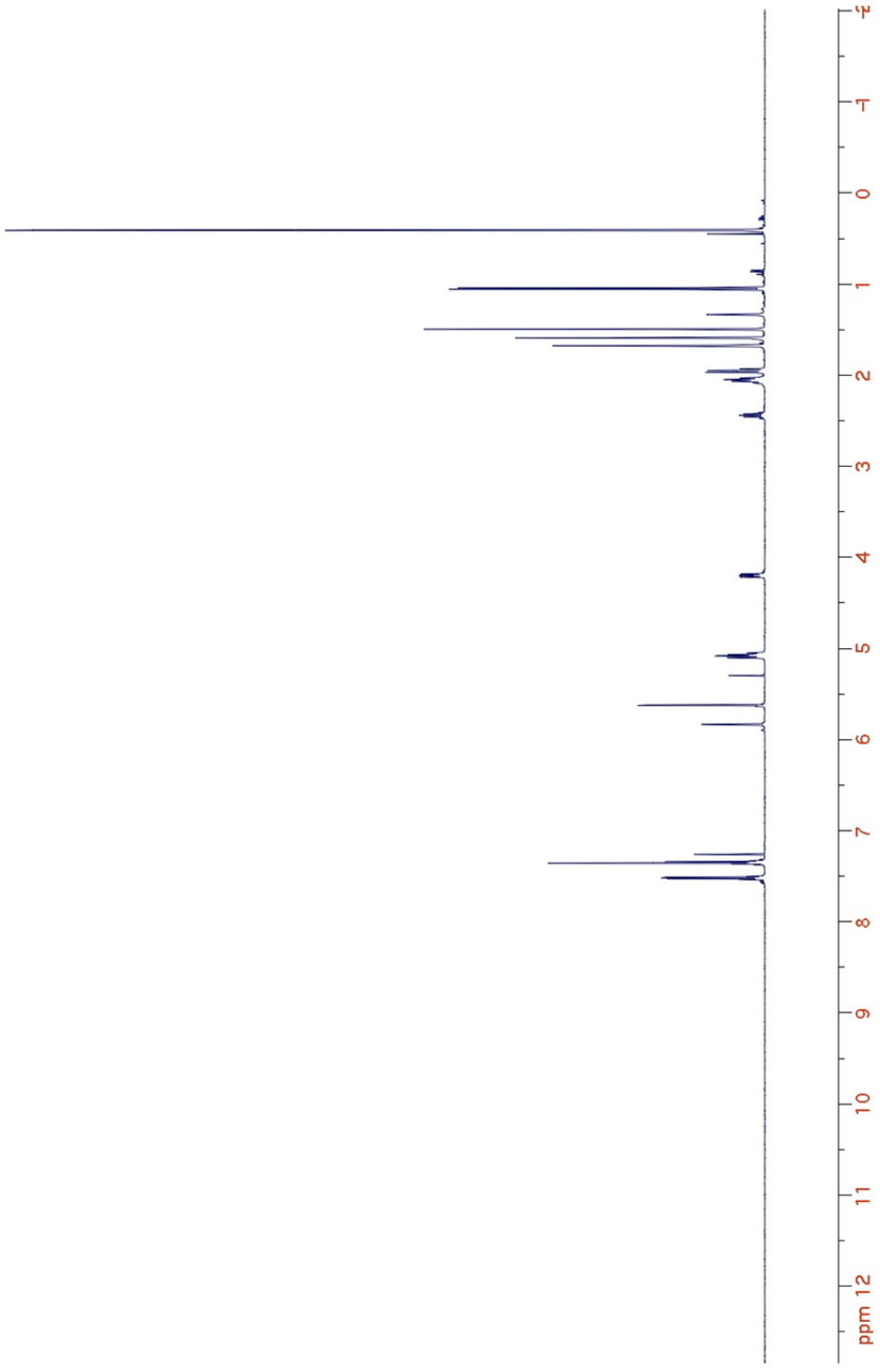
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 138.1, 138.0, 134.1, 131.7, 129.2, 127.9, 127.3, 126.5, 124.2, 70.2, 43.7, 39.8, 26.5, 25.8, 17.8, 16.8, 14.8, -2.4, -2.7.

HRMS (CI) Calcd. for $C_{22}H_{34}Osi$ (M+): 342.2379, Found: 342.2375.

$[\alpha]_D^{25}$ = -4 (c =1.0, CH_2Cl_2).

FTIR (neat): 2963, 1427, 1247, 1109, 969, 926, 831, 816, 773, 731, 700 cm^{-1}.

HPLC (The alcohol was converted to the 4-nitrobenzoate for analysis; Chiralcel AD-H/AD-H column, hexanes:*i*-PrOH = 99:1, 1.0 mL/min, 254 nm), t_{major} = 10.1 min, t_{minor} = 11.8 min; ee = 92%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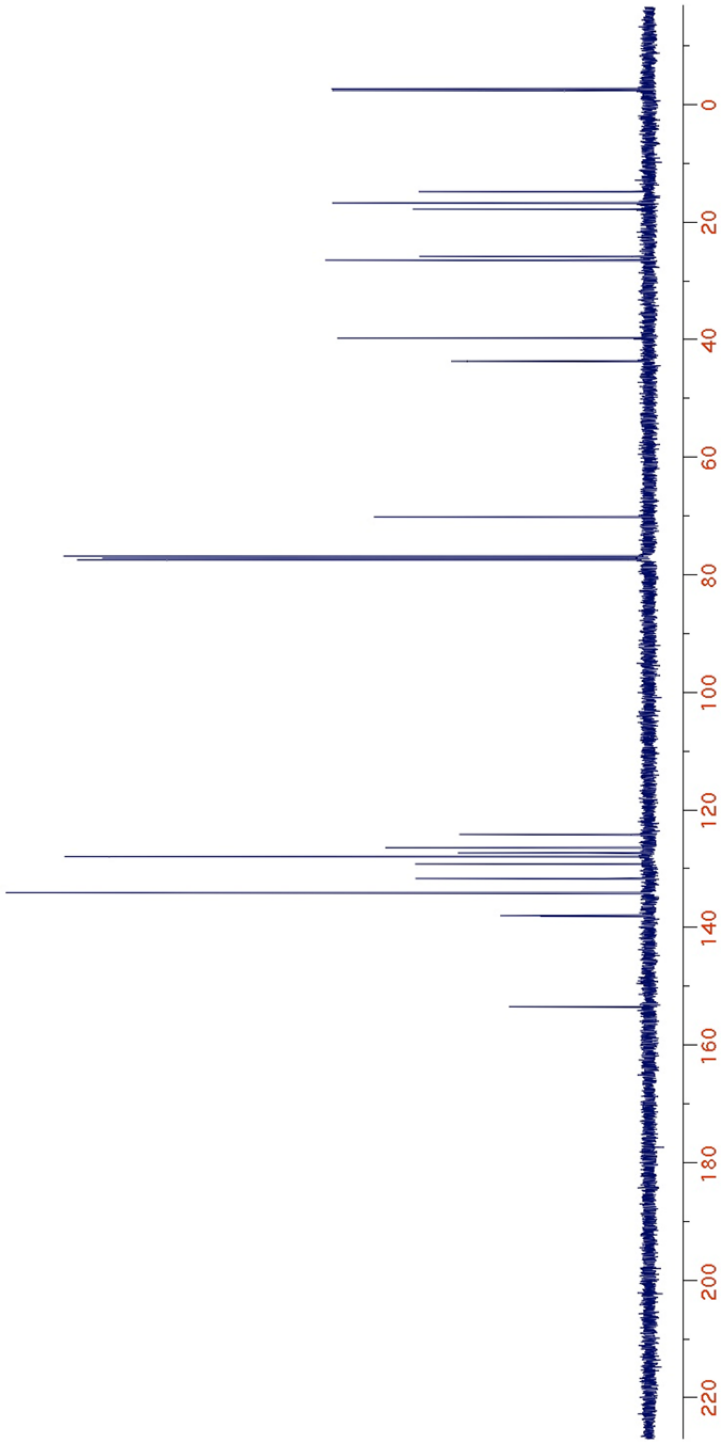
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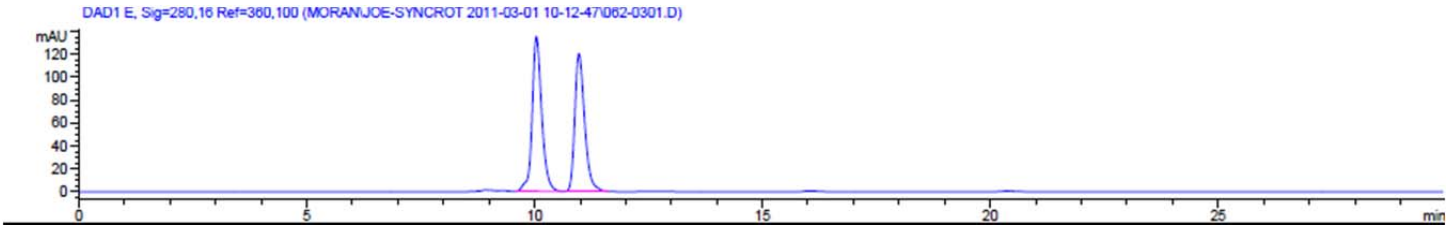
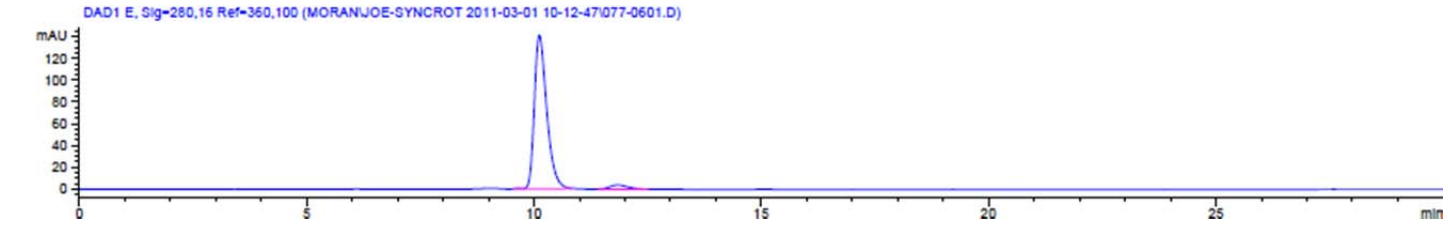
Racemate:



Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.039	BB	0.2187	1978.67078	135.19614	52.2246
2	10.973	BB	0.2273	1810.09985	120.48206	47.7754
Totals :				3788.77063	255.67819	

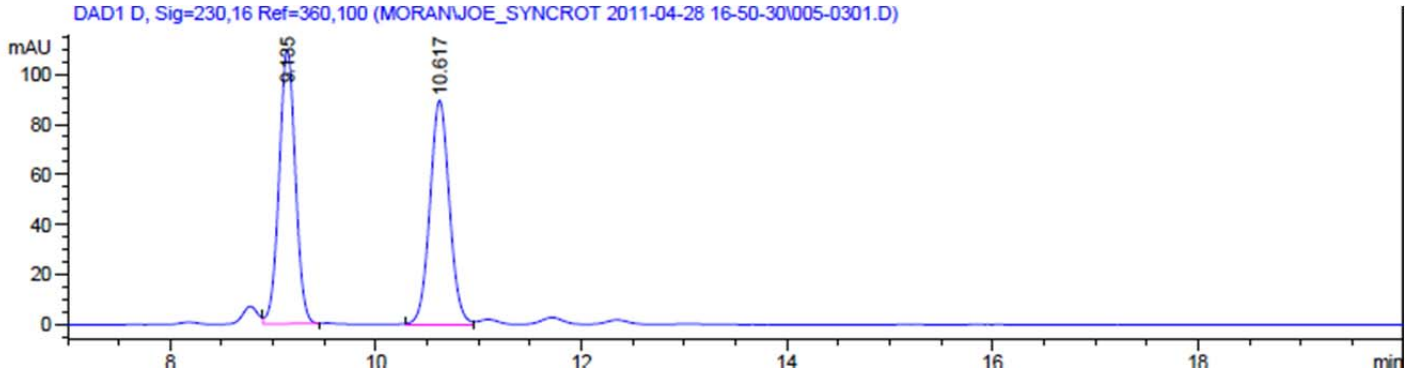
(R)-DM-SEGPHOS (from alcohol oxidation level):



Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.117	BB	0.2869	2673.25366	141.15735	96.1476
2	11.840	BB	0.4148	107.11011	3.84681	3.8524
Totals :				2780.36377	145.00416	

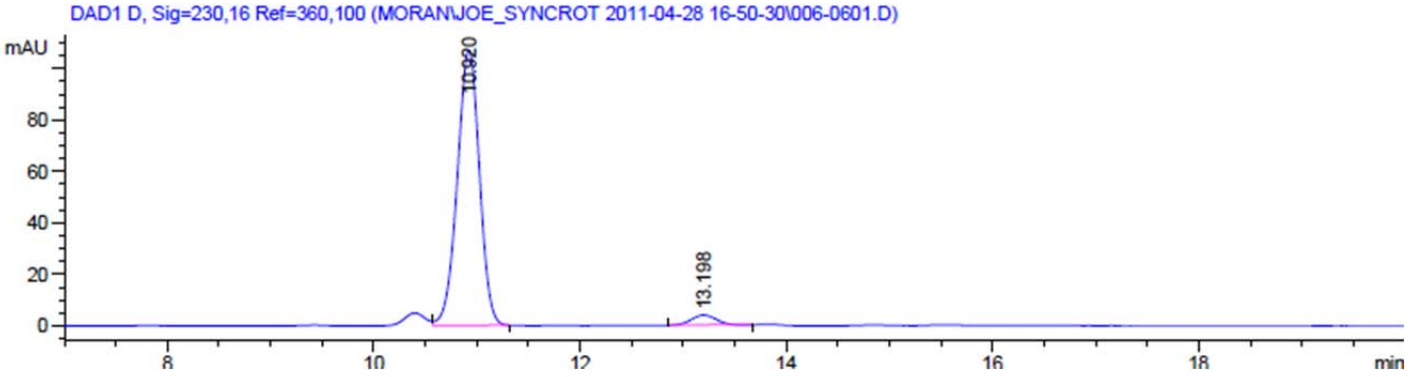
Racemate



Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.135	VB	0.1683	1206.18140	109.68349	50.6125
2	10.617	BV	0.2035	1176.98633	89.46140	49.3875
Totals :				2383.16772	199.14490	

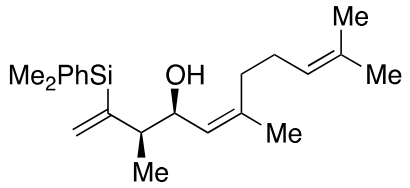
(R)-DM-SEGPHOS (from aldehyde oxidation level):



Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.920	VB	0.2321	1598.96094	107.14587	96.0828
2	13.198	BB	0.2653	65.18731	3.89334	3.9172
Totals :				1664.14825	111.03922	

(3*R*,4*S*,*Z*)-2-(dimethyl(phenyl)silyl)-3,6,10-trimethylundeca-1,5,9-trien-4-ol (4h)



From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.15 mL, 2.0 M concentration with respect to alcohol), diene **1** (141 mg, 0.75 mmol, 250 mol%) and alcohol **2h** (46.3 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (65.7 mg, 0.192 mmol, *syn:anti* = ≥20:1) as a colorless oil in 64% yield.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to aldehyde), diene **1** (113 mg, 0.6 mmol, 200 mol%), aldehyde **3h** (45.7 mg, 0.30 mmol, 100 mol%) and isopropanol (46 μL, 0.60 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (67.4 mg, 0.20 mmol, *syn:anti* = ≥20:1) as a colorless oil in 66% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.48 (m, 2H), 7.36-7.32 (m, 3H), 5.83 (dd, *J* = 2.3, 1.0 Hz, 1H), 5.60 (d, *J* = 2.3 Hz, 1H), 5.07-5.01 (m, 2H), 4.18 (ddd, *J* = 8.8, 5.7, 2.8 Hz, 1H), 2.41 (qdd, *J* = 6.9, 5.7, 1.0 Hz, 1H), 2.07-1.86 (m, 4H), 1.68 (s, 3H), 1.64 (d, *J* = 1.4 Hz, 3H), 1.59 (s, 3H), 1.31 (d, *J* = 2.8 Hz, 1H), 1.05 (d, *J* = 6.9 Hz, 3H), 0.390 (s, 3H), 0.388 (s, 3H).

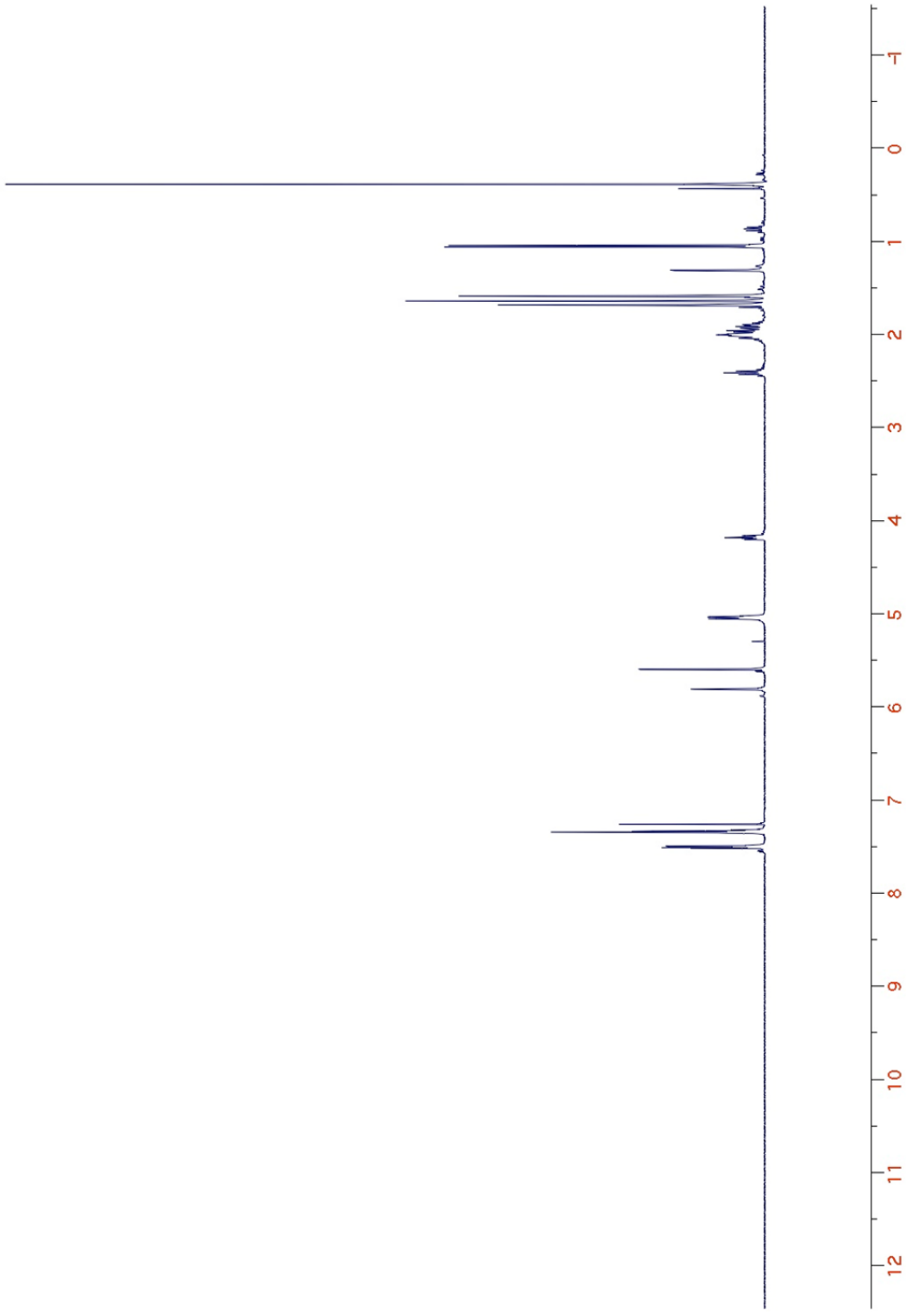
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 138.4, 138.2, 134.1, 132.2, 129.2, 127.9, 127.6, 127.3, 124.2, 70.0, 43.7, 32.4, 26.5, 25.8, 23.4, 17.9, 15.4, -2.5, -2.7.

HRMS (CI) Calcd. for $C_{22}H_{34}OSi$ (M+): 342.2379, Found: 342.2376.

$[\alpha]_D^{25}$ = -2 (c =1.0, CH_2Cl_2).

FTIR (neat): 2962, 1448, 1427, 1375, 1247, 1109, 996, 927, 831, 815, 773, 731, 700 cm^{-1}.

GC The compound was converted to the conventional crotylation product for analysis; (Cyclosil-B: Initial temperature: 80 °C (1 min hold), final temperature: 220 °C; rate: 2.5 C/min) t_{major} = 25.0 min, t_{minor} = 24.8 min ee = 86%.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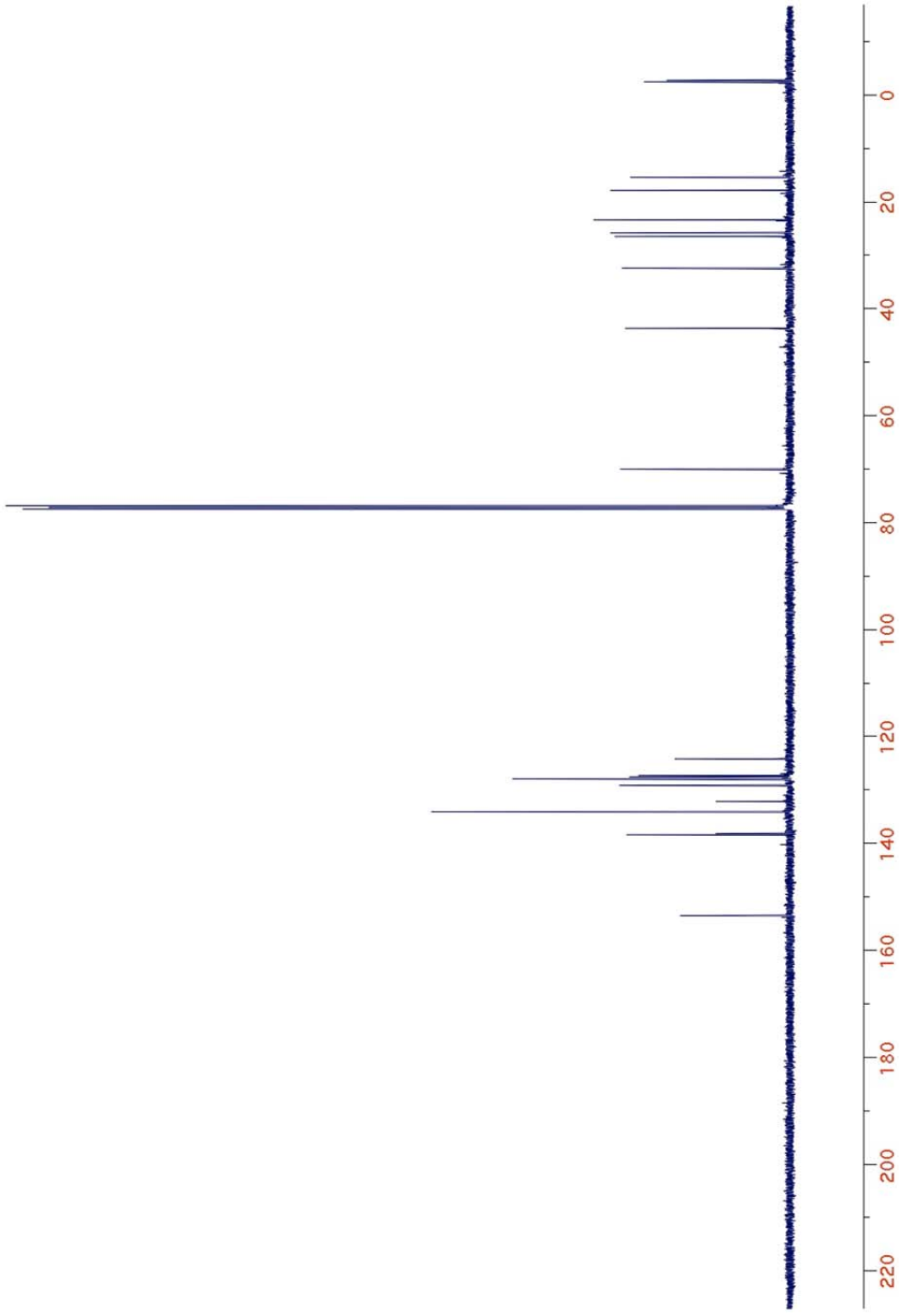
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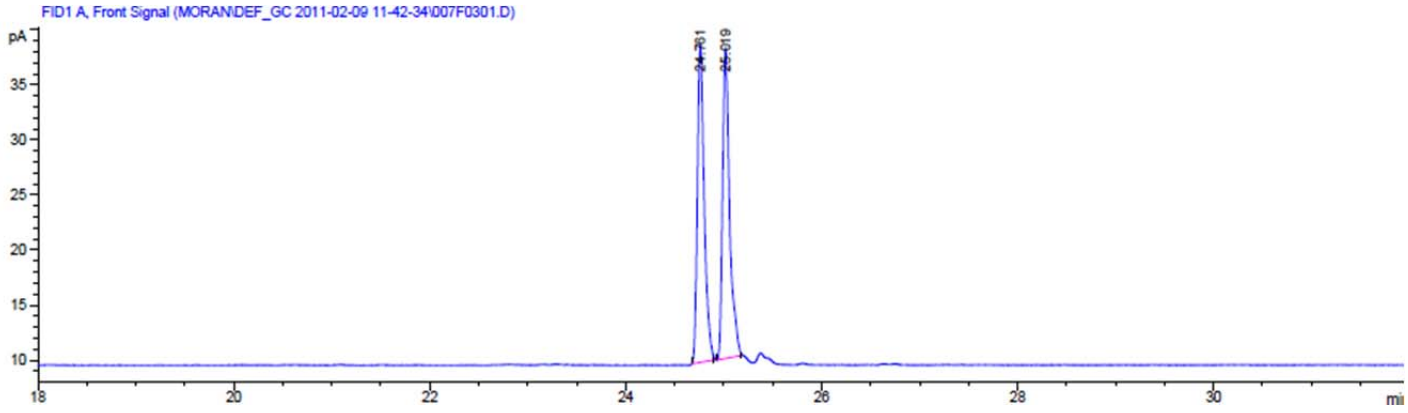
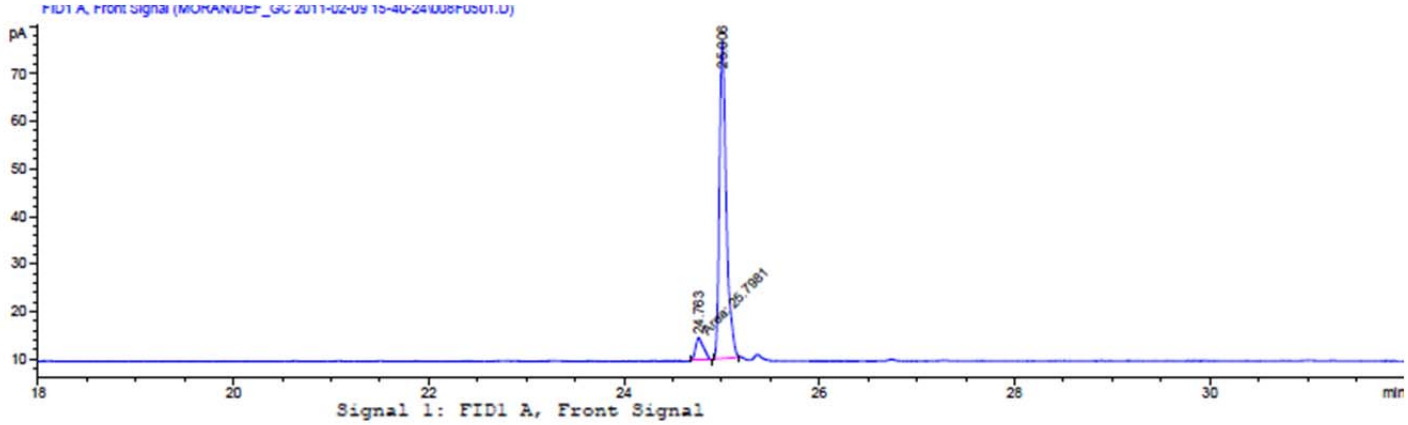
Racemate



Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	24.761	BB	0.0723	139.23294	28.85896	49.84236
2	25.019	BB	0.0732	140.11368	28.19425	50.15764
Totals :				279.34662	57.05321	

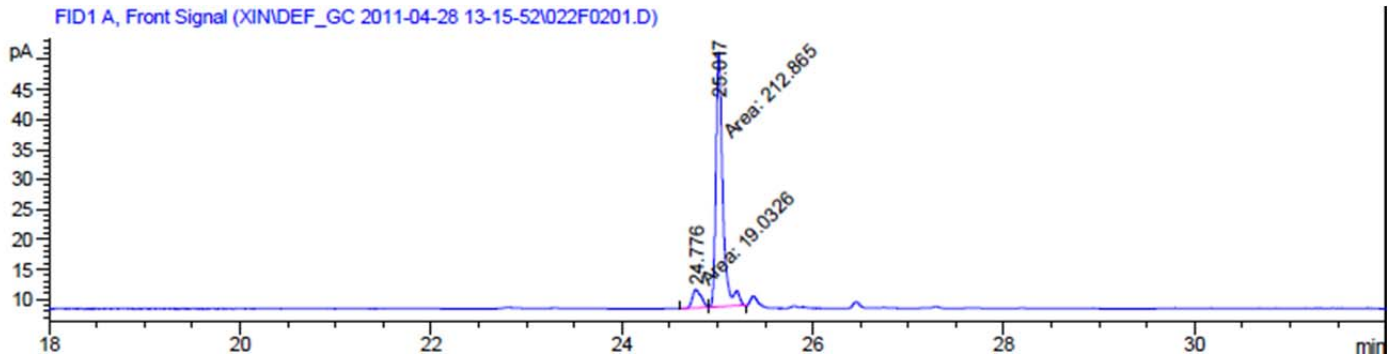
(R)-DM-SEGPHOS (from alcohol oxidation level)



Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	24.763	MM	0.0927	25.79811	4.63718	7.31921
2	25.006	BB	0.0739	326.67331	66.80246	92.68079
Totals :				352.47142	71.43964	

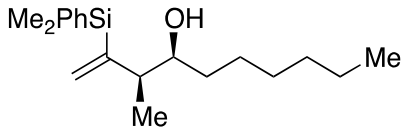
(R)-DM-SEGPHOS (from aldehyde oxidation level)



Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	24.776	MF	0.1042	19.03261	3.04311	8.20734
2	25.017	FM	0.0835	212.86478	42.46641	91.79266
Totals :				231.89738	45.50951	

(3*R*,4*S*)-2-(dimethyl(phenyl)silyl)-3-methyldec-1-en-4-ol (4i)



From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (20.0 mg, 0.021 mmol, 7 mol%) and (*R*)-DM-SEGPHOS (15.2 mg, 0.021 mmol, 7 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.15 mL, 2.0 M concentration with respect to alcohol), diene **1** (141 mg, 0.75 mmol, 250 mol%) and alcohol **2i** (34.9 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (59.1 mg, 0.20 mmol, *syn:anti* = ≥20:1) as a colorless oil in 65% yield and 88% ee.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (20.0 mg, 0.021 mmol, 7 mol%) and (*R*)-DM-SEGPHOS (15.2 mg, 0.021 mmol, 7 mol%). The tube was sealed with a rubber septum and purged with nitrogen. THF (0.15 mL, 2.0 M concentration with respect to aldehyde), diene **1** (141 mg, 0.75 mmol, 250 mol%), isopropyl alcohol (0.046 mL, 0.6 mmol, 200 mol%) and aldehyde **3i** (34.2 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 72 hrs, 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; 3% EtOAc/hexanes) to furnish the title compound (49 mg, 0.16 mmol, *syn:anti* = ≥20:1) as a colorless oil in 53% yield and 84% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.50 (m, 2H), 7.38-7.34 (m, 3H), 5.81 (dd, *J* = 2.4, 1.1 Hz, 1H), 5.62 (d, *J* = 2.4 Hz, 1H), 3.40-3.35 (m, 1H), 2.41 (qdd, *J* = 6.9, 4.4, 1.0 Hz, 1H), 1.40 (d, *J* = 3.2 Hz, 1H), 1.35-1.12 (m, 10H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.41 (s, 3H), 0.40 (s, 3H).

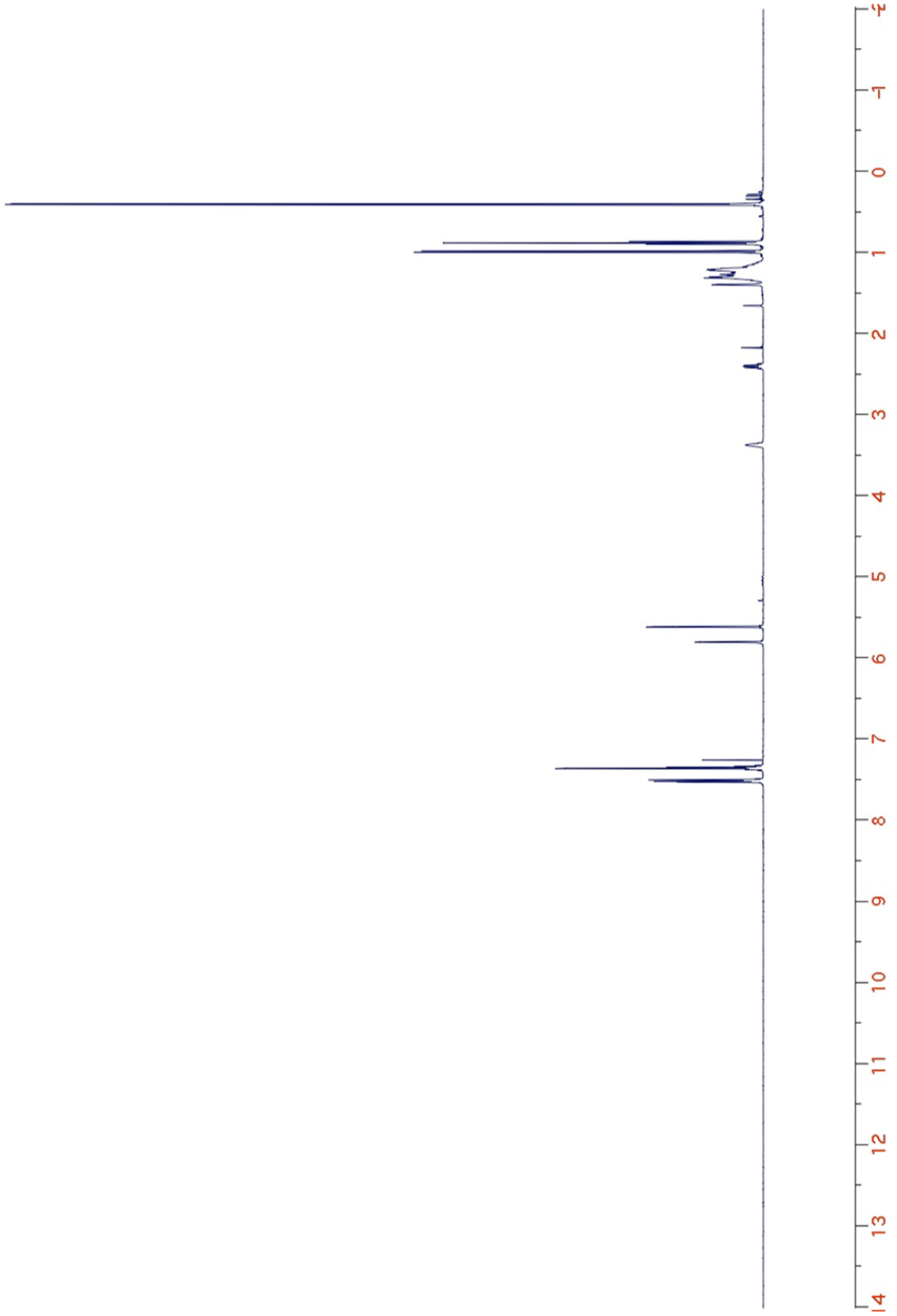
^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 138.1, 134.0, 129.2, 128.0, 126.8, 72.7, 43.1, 34.7, 31.9, 29.4, 26.3, 22.8, 14.2, 13.4, -2.44, -2.58.

HRMS (CI) Calcd. for $C_{19}H_{32}OSi$ (M+-H): 303.2144, Found: 303.2145.

$[\alpha]_D^{25}$ = -14 (c =1.0, CH_2Cl_2).

FTIR (neat): 2955, 2926, 1427, 1248, 1109, 928, 908,831, 815, 773, 731, 699 cm^{-1}.

HPLC (Chiralcel AD-H/AD-H column, hexanes:*i*-PrOH = 99.5:0.5, 0.4 mL/min, 210 nm), t_{major} = 41.2 min, t_{minor} = 44.3 min.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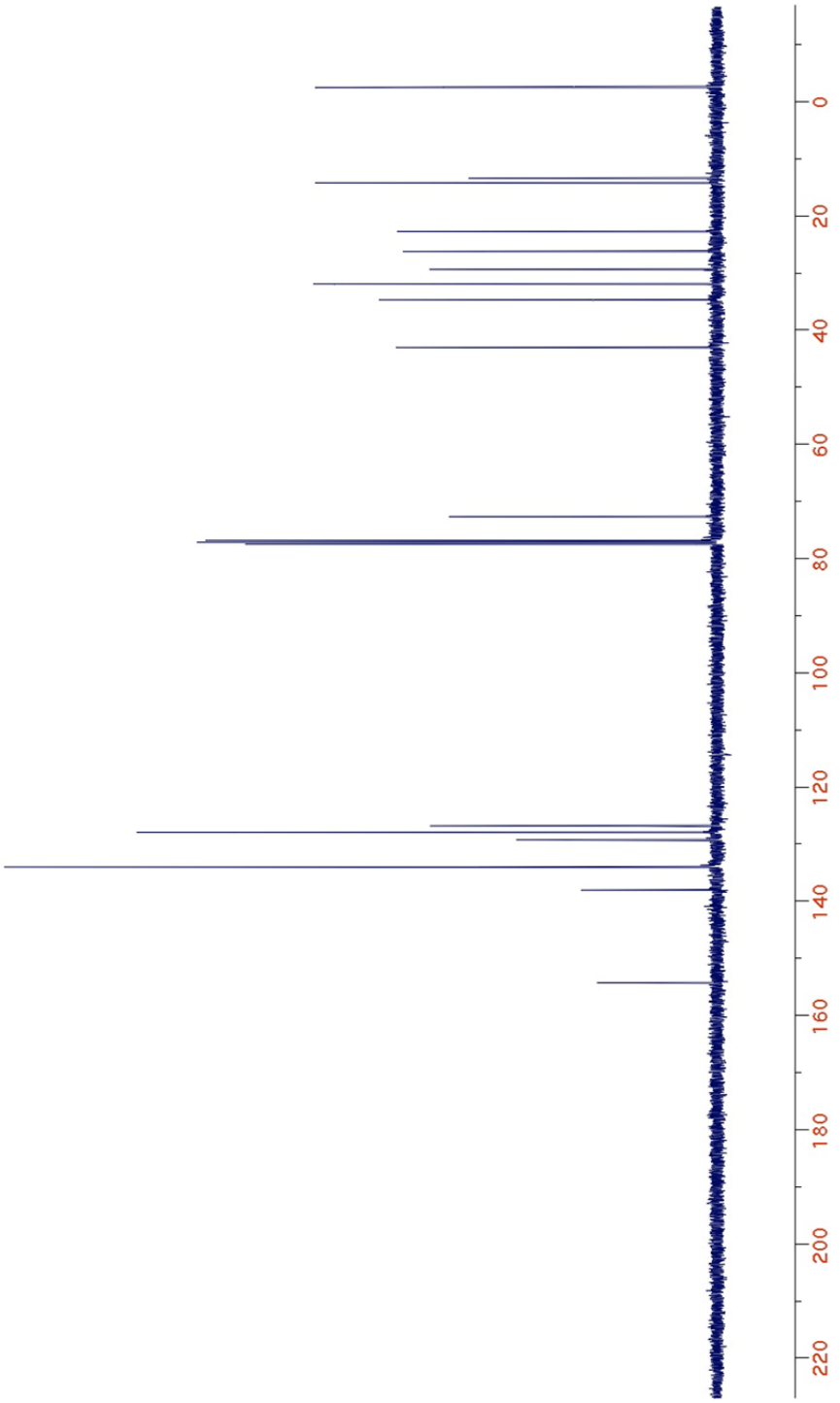
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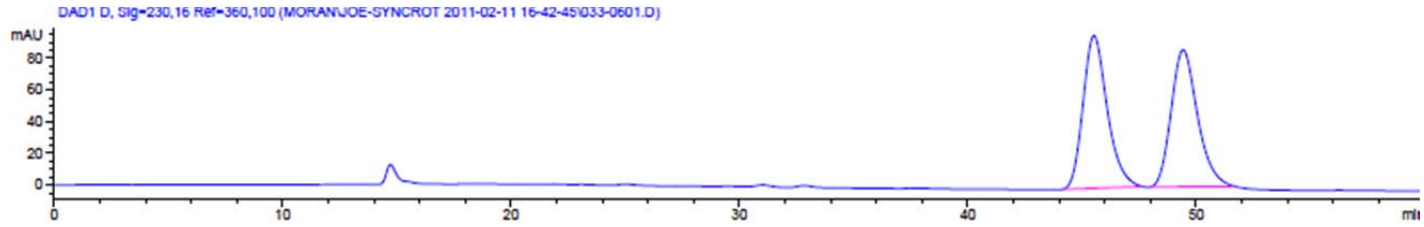
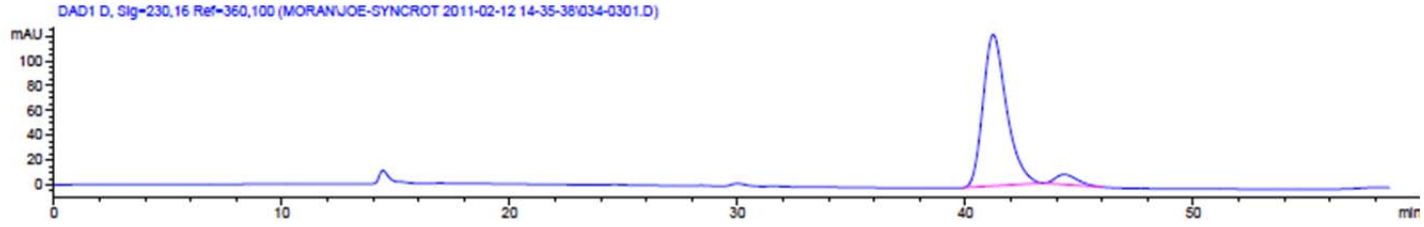
Racemate



Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.523	BB	1.1157	2.61189e4	351.97995	50.0715
2	49.426	BB	1.2408	2.60443e4	316.91095	49.9285
Totals :				5.21631e4	668.89090	

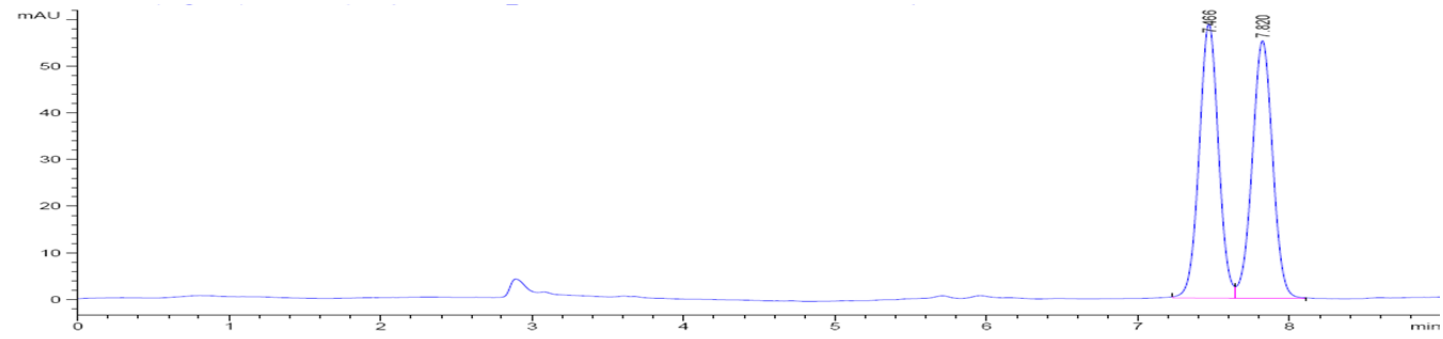
(R)-DM-SEGPHOS (from alcohol oxidation level)



Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.223	BB	1.0877	8788.80957	122.10503	94.1352
2	44.341	BB	0.9771	547.56091	8.13638	5.8648
Totals :				9336.37048	130.24141	

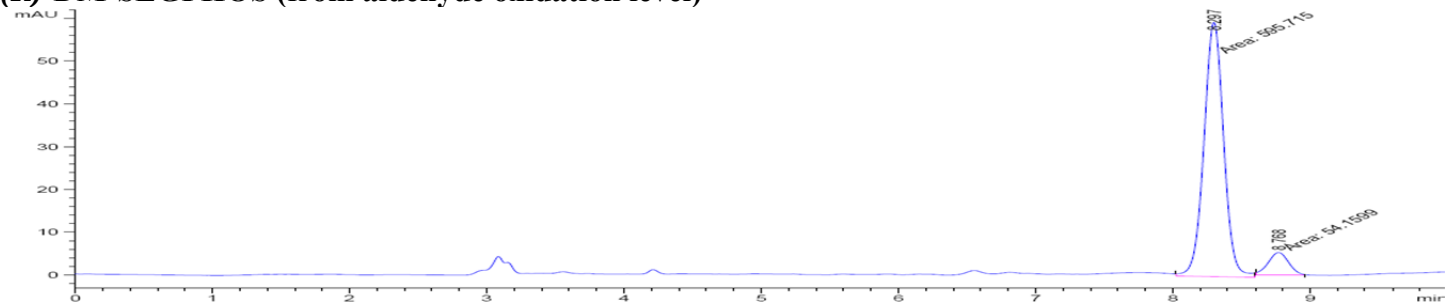
Racemate:



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.466	BV	0.1374	521.84729	58.85293	50.2049
2	7.820	VB	0.1452	517.58765	55.27609	49.7951

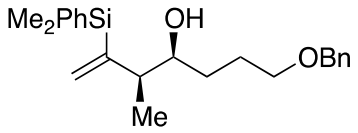
***(R)*-DM-SEGPHOS (from aldehyde oxidation level)**



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.297	MM	0.1667	595.71478	59.57350	91.6661
2	8.768	MM	0.1713	54.15990	5.27011	8.3339

(3*R*,4*S*)-7-(benzyloxy)-2-(dimethyl(phenyl)silyl)-3-methylhept-1-en-4-ol (4j)



From Alcohol Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to alcohol), diene **1** (113 mg, 0.60 mmol, 200 mol%) and alcohol **2j** (54 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 48 hrs, 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; 0-15% EtOAc/hexanes) to furnish the title compound (70 mg, 0.20 mmol, *syn:anti* = ≥20:1) as a colorless oil in 66% yield and 86% ee.

From Aldehyde Oxidation Level: To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (20.0 mg, 0.021 mmol, 7 mol%) and (*R*)-DM-SEGPHOS (15.2 mg, 0.021 mmol, 7 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to aldehyde), diene **1** (141 mg, 0.75 mmol, 250 mol%), isopropyl alcohol (0.046 mL, 0.6 mmol, 200 mol%) and aldehyde **3j** (49 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95 °C (oil bath temperature) for 72 hrs, 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; 0-15% EtOAc/hexanes) to furnish the title compound (54 mg, 0.15 mmol, *syn:anti* = ≥20:1) as a colorless oil in 50% yield and 84% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.48 (m, 2H), 7.35-7.24 (m, 8H), 5.78 (dd, *J* = 2.2, 1.2 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.47 (s, 2H), 3.39 (t, *J* = 6.0, 2H), 3.44 – 3.37 (m, 1H), 2.42 – 2.34 (m, 1H), 1.92 (d, *J* = 3.2 Hz, 1H), 1.72 – 1.42 (m, 3H), 1.40 – 1.25 (m, 1H), 1.00 (d, *J* = 7.2 Hz, 3H), 0.39 (s, 3H), 0.38 (s, 3H).

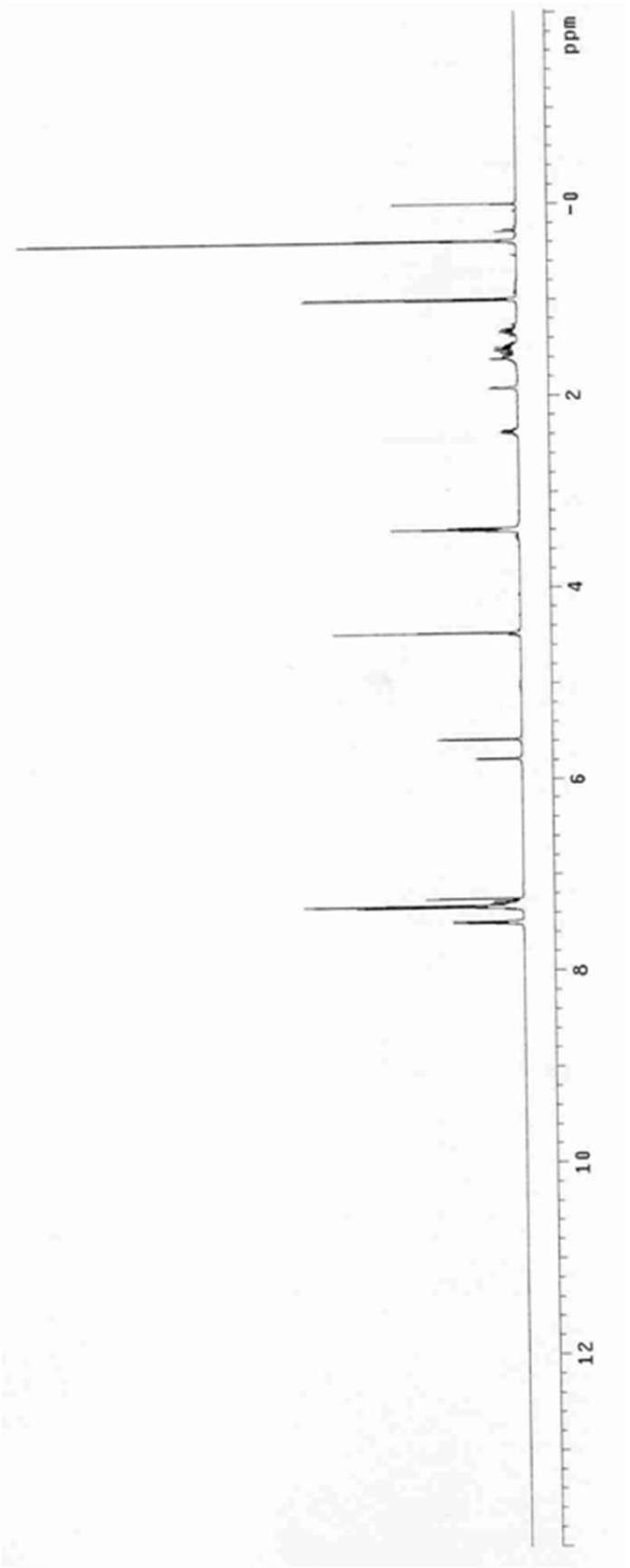
^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 138.4, 138.0, 133.9, 129.1, 128.3, 127.8, 127.6, 127.5, 126.8, 72.9, 72.8, 70.3, 43.5, 31.8, 26.6, 14.2, -2.6, -2.7.

FTIR (neat): 3427, 3066, 2955, 2867, 1495, 1453, 1427, 1407, 1362, 1248, 1203, 1108, 1027, 966, 929, 832, 816, 774, 733, 699cm^{-1}.

HRMS (CI) Calcd. for $C_{23}H_{32}O_2Si$ $[M\text{-}OH]^+$: 351.2144, Found: 351.2139.

$[\alpha]_D^{25}$ = -12 (c =1.0, CH_2Cl_2).

HPLC: (Chiralcel AD-H/AD-H column, hexanes:*i*-PrOH = 99:1, 1 mL/min, 230 nm), t_{major} = 32.6 min, t_{minor} = 35.9 min;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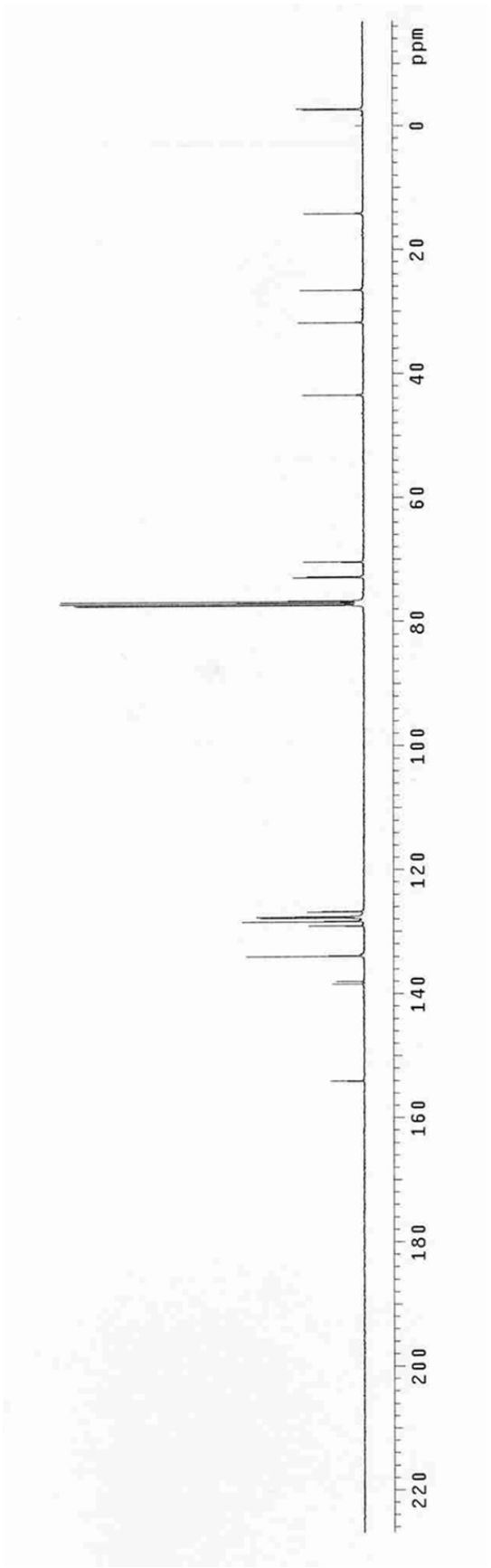
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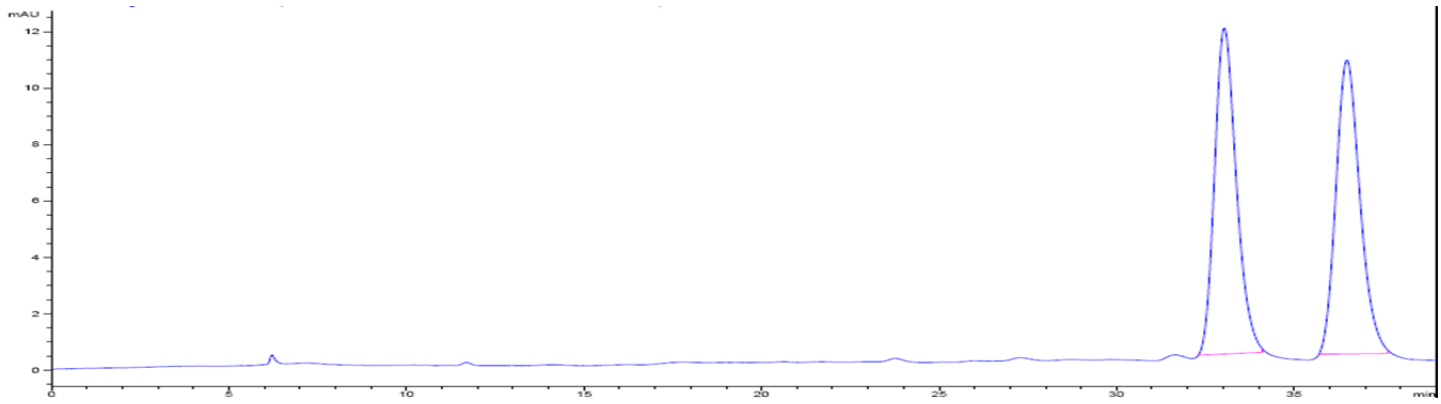
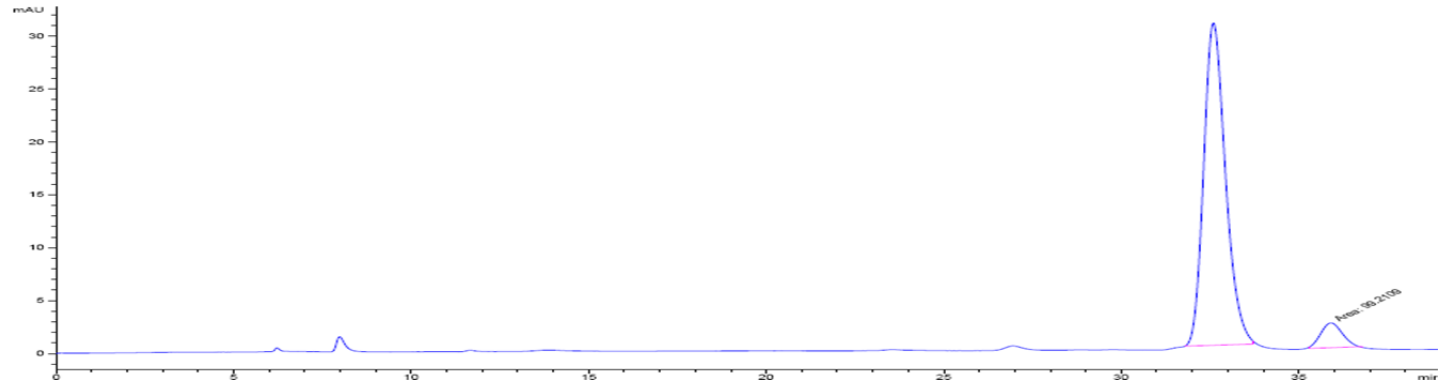
Racemic:



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.032	BB	0.6446	492.28772	11.56510	50.1202
2	36.487	BB	0.7103	489.92709	10.42418	49.8798
Totals :				982.21481	21.98927	

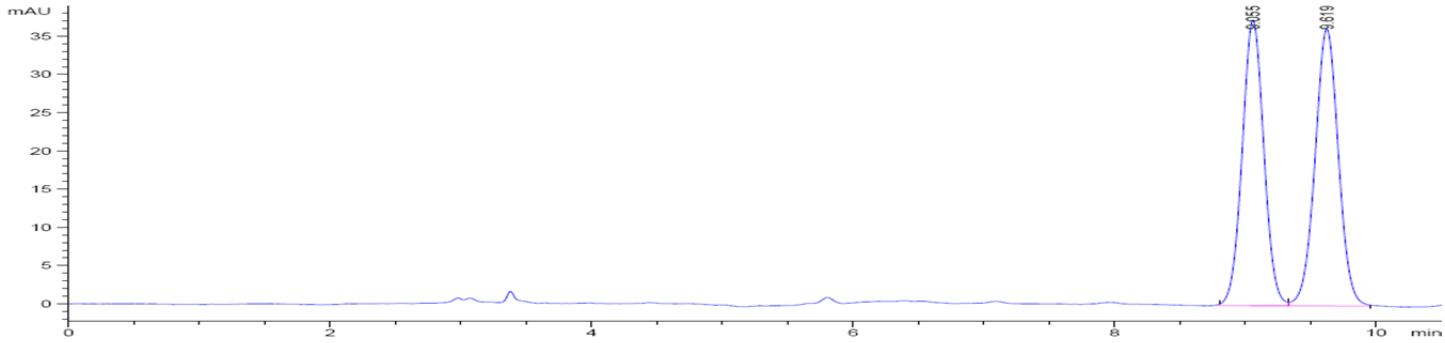
***(R)*-DM-Segphos (from alcohol oxidation level):**



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

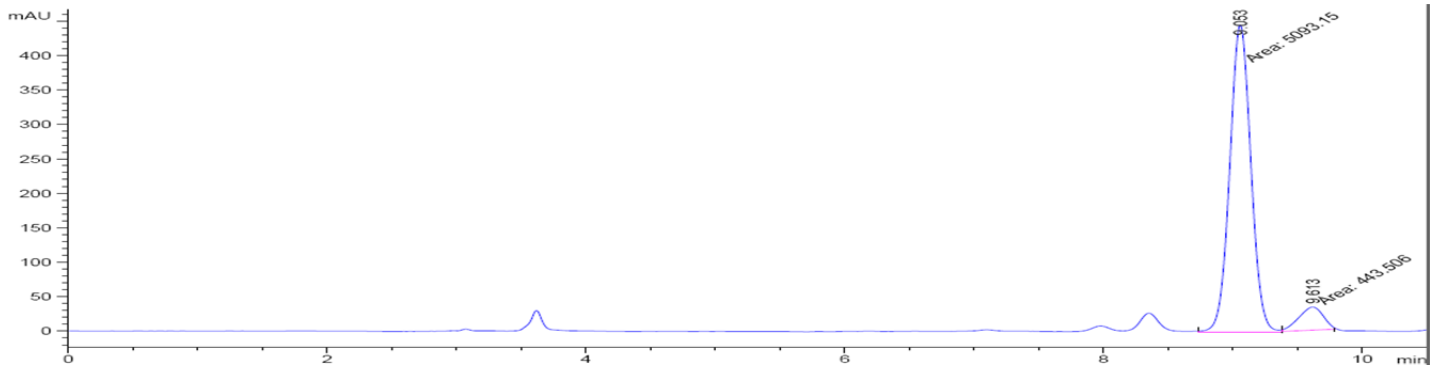
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.591	BB	0.6532	1302.37231	30.43635	92.9215
2	35.900	MM	0.7039	99.21086	2.34906	7.0785
Totals :				1401.58318	32.78541	

Racemic:



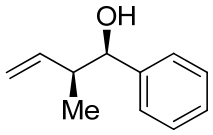
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.055	BV	0.1782	430.01682	37.38885	48.7918
2	9.619	VB	0.1911	451.31348	36.27737	51.2082

***(R)*-DM-Segphos (from aldehyde oxidation level):**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.053	MM	0.1898	5093.15234	447.21216	91.9896
2	9.613	MM	0.2187	443.50574	33.79377	8.0104
Totals :				5536.65808	481.00593	

(1R,2S)-2-methyl-1-phenylbut-3-en-1-ol (7a)



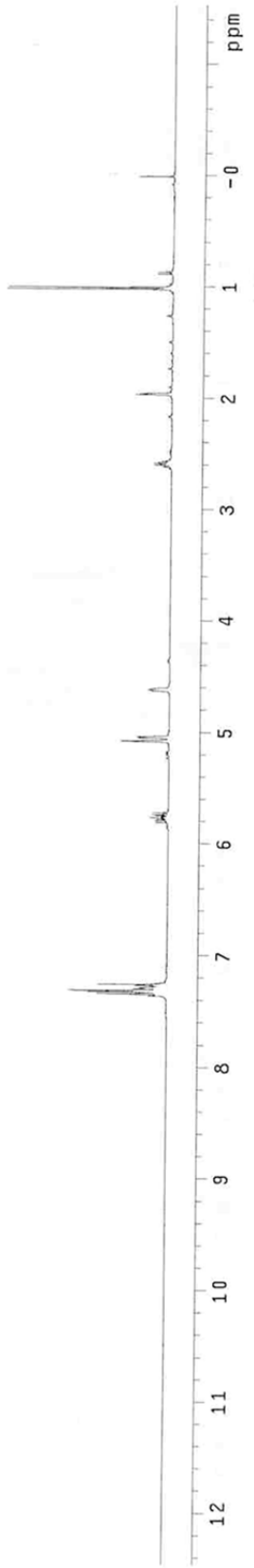
To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%) and (*R*)-DM-SEGPHOS (10.8 mg, 0.015 mmol, 5 mol%). The tube was sealed with a rubber septum and purged with nitrogen. Toluene (0.15 mL, 2.0 M concentration with respect to alcohol **2a**), diene **1** (113 mg, 0.60 mmol, 200 mol%) and alcohol **2a** (32.4 mg, 0.30 mmol, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 95°C (oil bath temperature) for 48 hrs, at which point the reaction mixture was allowed to cool to ambient temperature. A solution of TBAF (0.9 mL, 0.9 mmol, 300 mol%, 1.0 M in THF) was added to the reaction mixture under atmosphere of nitrogen. The reaction mixture was diluted with DMSO (1.0 mL, 0.3 M concentration with respect to alcohol **2a**), capped and heated to 80 ^{o}C for 2 hr. The reaction mixture was diluted with EtOAc (25 mL) and washed with H_2O (4x10 mL). The organic layer was then dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by flash column chromatography (SiO_2; 0-20% EtOAc/hexane) furnished the title compound (40 mg, 0.25 mmol, *syn:anti* = 13:1) as a colorless oil in 83% yield. *Spectral data is consistent with the reported literature data*[4].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.27 (m, 5H), 5.78 (ddd, *J* = 17.0, 10.0, 6.9 Hz, 1H), 5.08 (m, 2H), 4.65 (d, *J* = 5.3, 1H), 2.65-2.58 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H).

$[\alpha]_D^{25}$ = +24 (c =1.15, $CHCl_3$) (Lit$[\alpha]_D^{24}$ = -23.55 (c = 1.15, $CHCl_3$) for 94% ee of the (1*S*,2*R*)-**4a**)

GC: (Cyclosil-B: Initial temperature: 50 °C (5 min hold), final temperature: 220 °C; rate: 5 C/min) t_{major} = 21.426 min, t_{minor} = 21.536 min ee = 87%.

[4] Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **2001**, *123*, 9488.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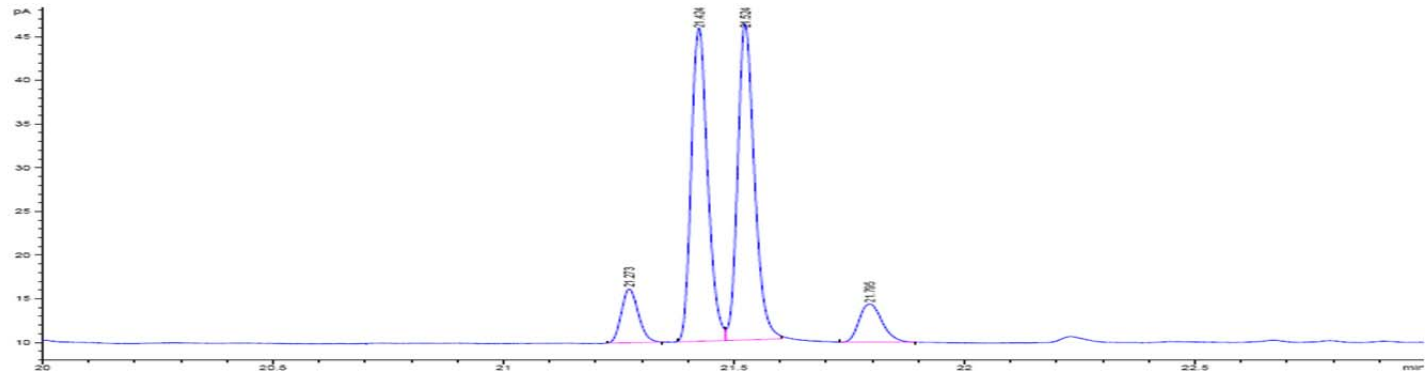
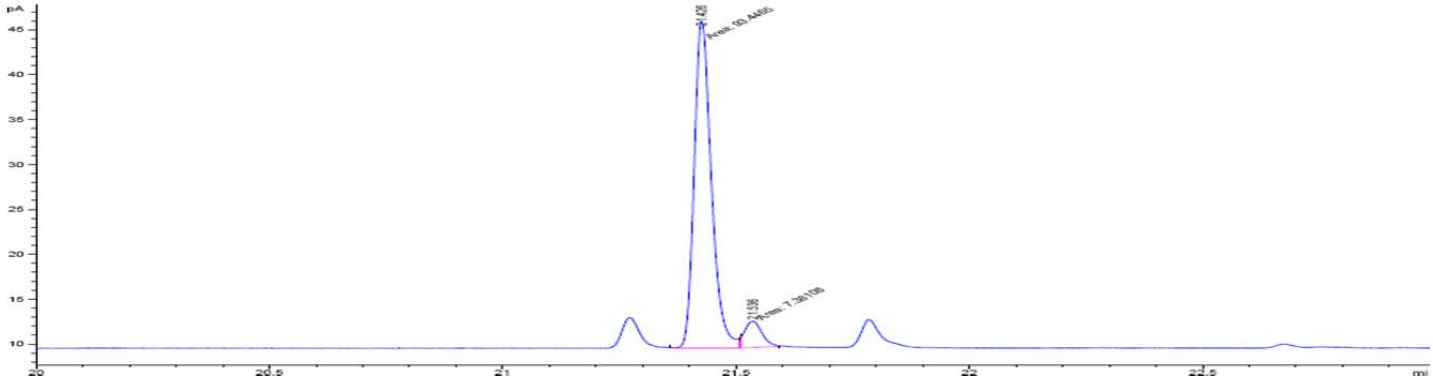


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	21.273	BB	0.0404	15.75859	6.13524	7.46287
2	21.424	BV	0.0377	88.71522	35.82502	42.01329
3	21.524	VB	0.0384	91.52621	36.13225	43.34545
4	21.795	BB	0.0550	15.15786	4.36031	7.17838
Totals :				211.15987	82.45283	

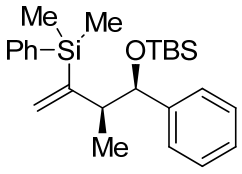
(*R*)-DM-Segphos:



Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	21.426	MM	0.0427	93.44648	36.45899	92.67950
2	21.536	MM	0.0418	7.38108	2.94164	7.32050
Totals :				100.82756	39.40063	

tert-butyl((-3-(dimethyl(phenyl)silyl)-2-methyl-1-phenylbut-3-en-1-yl)oxy)dimethylsilane



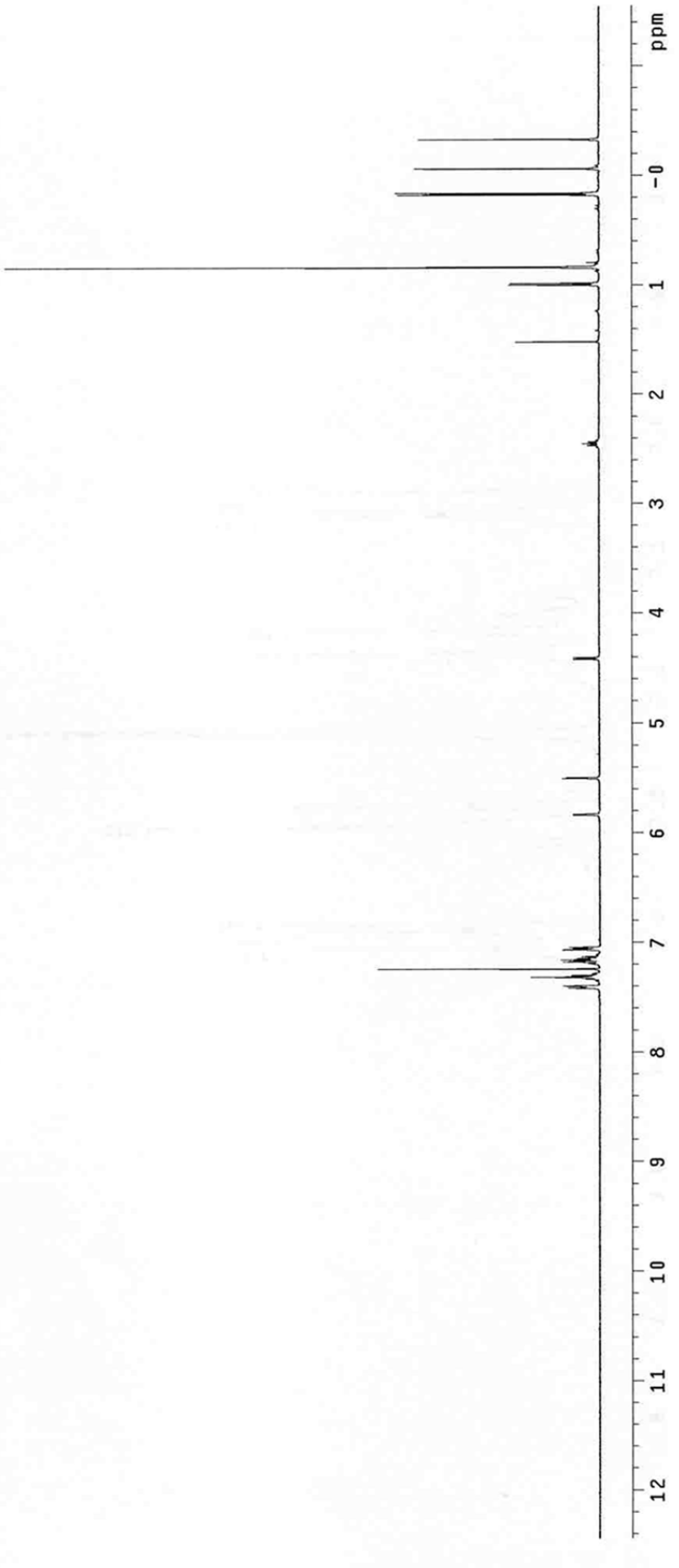
A flame dried 25 mL round bottom flask equipped with a magnetic stir bar was charged with alcohol **4a** (112 mg, 0.38 mmol, 100 mol%) and purged with nitrogen. DMF was added (1.3 mL, 0.3 M with respect to alcohol **4a**). To this solution imidazole (39 mg, 0.57mmol, 150 mol%) and TBSCl (68mg, 0.46 mmol, 120 mol%) were added sequentially. Upon complete consumption of starting material, as determined by TLC analysis, ammonium chloride (5 mL, sat. aq. sol.) was added. The organic layer was extracted with Et_2O (3x50 mL) and the combined organic extracts dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by flash column chromatography (SiO_2; hexanes) furnished the title compound (126 mg, 0.31 mmol) as a colorless oil in 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H), 7.36-7.28 (m, 3H), 7.20-7.10 (m, 3H), 7.07 – 7.05 (m, 2H), 5.84 (d, *J* = 2.4, 1H), 5.50 (d, *J* = 2.4, 1H), 4.41 (d, *J* = 4.0, 1H), 2.50 - 2.40 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.84 (s, 9H), 0.18 (s, 3H), .16 (s, 3H), -0.06 (s, 3H), -0.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 145.2, 138.4, 134.4, 129.2, 128.0, 127.7, 127.3, 126.9, 77.9, 45.9, 26.2, 18.5, 16.6, -2.8, -3.0, -4.2, -4.5.

FTIR (neat): 2956, 2928, 2856, 1471, 1462, 1427, 1244, 1110, 1080, 1067, 1016, 929, 871, 831, 814, 774, 751, 733, 699 cm^{-1}.

HRMS (CI) Calcd. for $C_{25}H_{38}OSi_2$ $[M-1]^+$: 409.2383, Found: 409.2387.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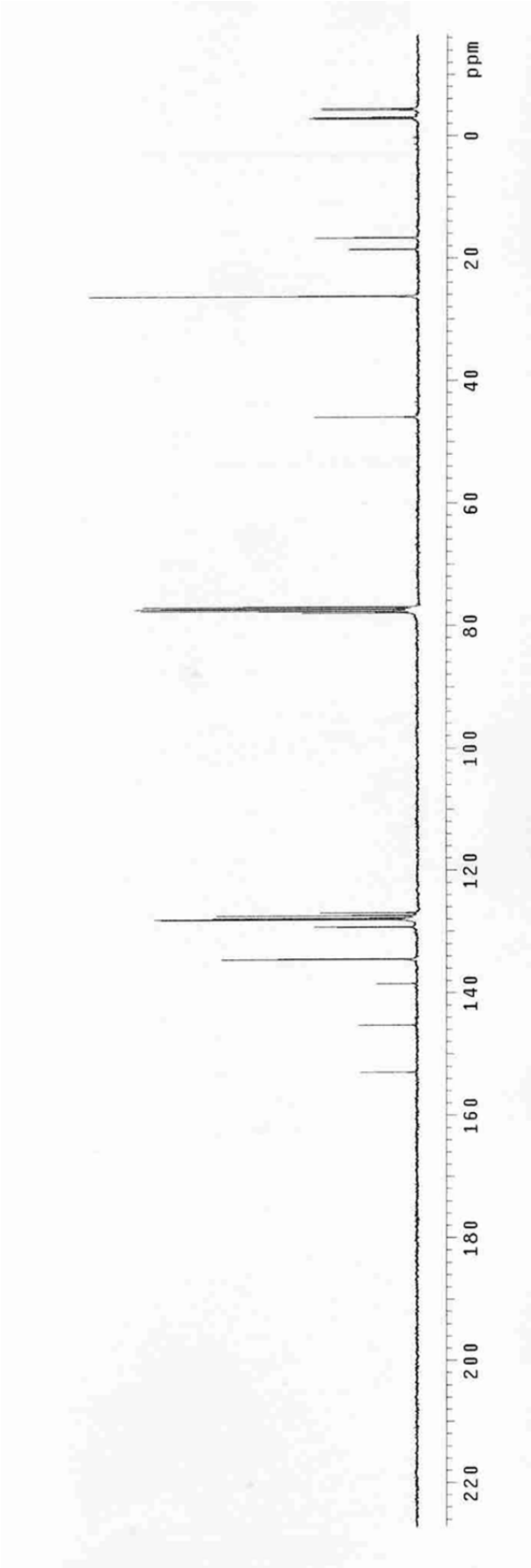
ppm
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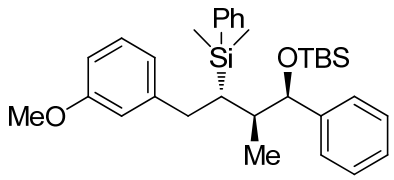
tert-butyl(3-(dimethyl(phenyl)silyl)-4-(3-methoxyphenyl)-2-methyl-1-phenylbutoxy)dimethylsilane (5a)



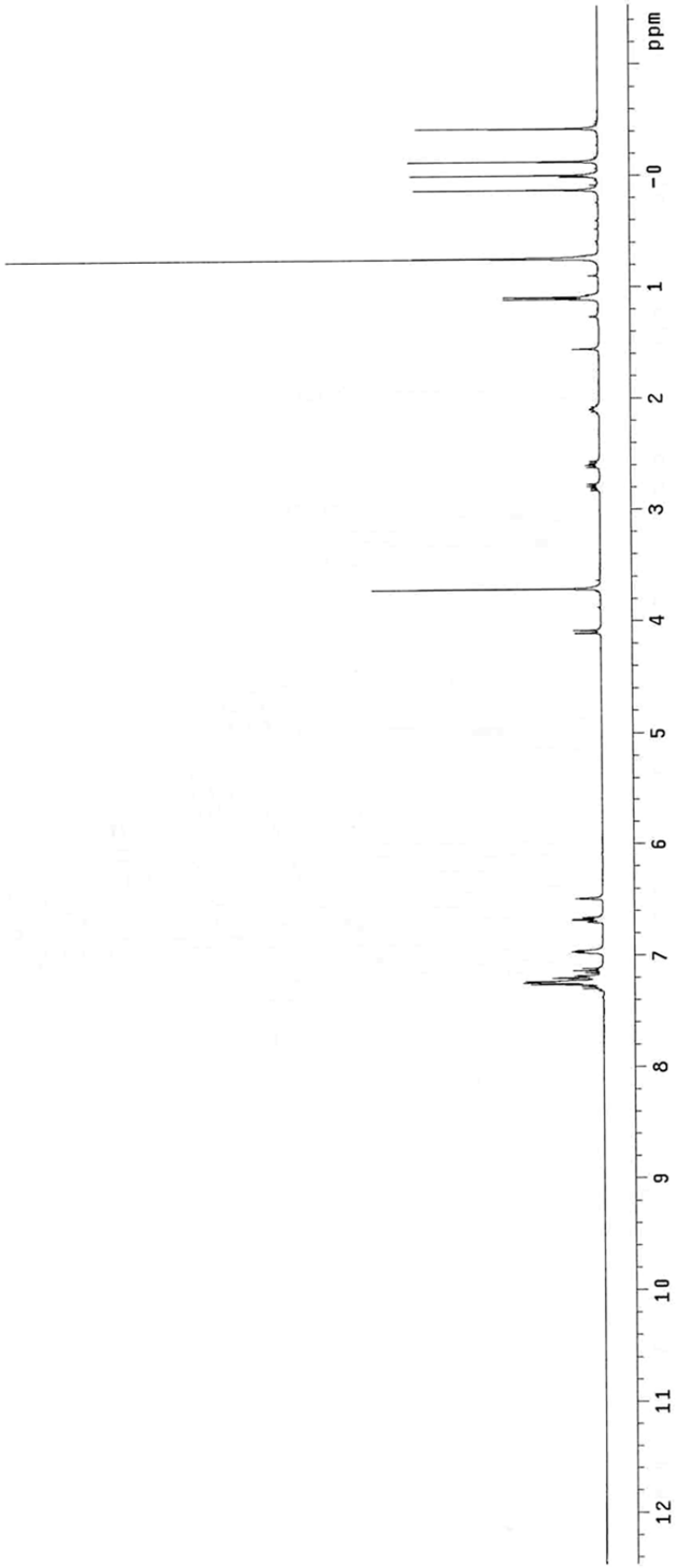
A flame dried 25 mL conical flask equipped with a magnetic stir bar was charged with TBS protected alcohol **4a** (214 mg, 0.52 mmol, 100 mol%) and purged with nitrogen. 9-BBN was added (3.1 mL, 1.56 mmol, 300 mol%, 0.5 M in THF) and the mixture was heated at 55 ^{o}C for 11hr. This solution was then added to a flame dried sealed tube that contained 3-Bromoanisole (0.144 mL, 1.30 mmol, 250 mol%), $Pd^{(0)}(PPh_3)_4$ (61 mg, 0.052 mmol, 10 mol%), NaOH (0.86 mL, 1.72 mmol, 330 mol%, 2.0 M aq. sol.), and THF (2.1 mL, 0.25 M with respect to TBS protected alcohol **4a**) under a atmosphere of nitrogen. The reaction mixture was vigorously degassed with nitrogen, capped, heated to 70 ^{o}C and let stir for 22 hr. The reaction was cooled to room temperature, filtered through a plug of celite with DCM and concentrated *in vacuo*. Purification of the residue by flash column chromatography (SiO_2; 15% Tol/Hex) furnished the title compound (201 mg, 0.389 mmol) as a colorless oil in 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.10 (m, 9H), 6.98-6.96 (m, 2H), 6.70-6.66 (m, 2H), 6.49 (s, 1H), 4.09 (d, *J* = 9.6, 1H), 3.71 (s, 3H), 2.80 (dd, *J* = 14.0, 8.0, 1H), 2.59 (dd, *J* = 14.0, 7.6, 1H), 2.15-2.05 (m, 1H), 1.12-1.08 (m, 1H), 1.10 (d, *J* = 4.2 Hz, 3H), 0.75 (s, 9H), 0.13 (s, 3H), -0.01 (s, 3H), -0.13 (s, 3H), -0.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 145.1, 144.8, 139.1, 134.0, 129.3, 128.8, 128.1, 128.0, 127.4, 122.0, 114.8, 111.9, 79.4, 55.3, 41.3, 31.5, 28.2, 26.1, 18.4, 14.7, -3.0, -3.1, -4.4, -4.7.

FTIR (neat): 2954, 2855, 1600, 1583, 1489, 1454, 1427, 1256, 1151, 1110, 1074, 1048, 872, 833, 811, 772, 754, 733, 699 cm^{-1}.

HRMS (CI) Calcd. for $C_{32}H_{46}O_2Si_2$ $[M-1]^+$: 517.2958, Found: 517.2959.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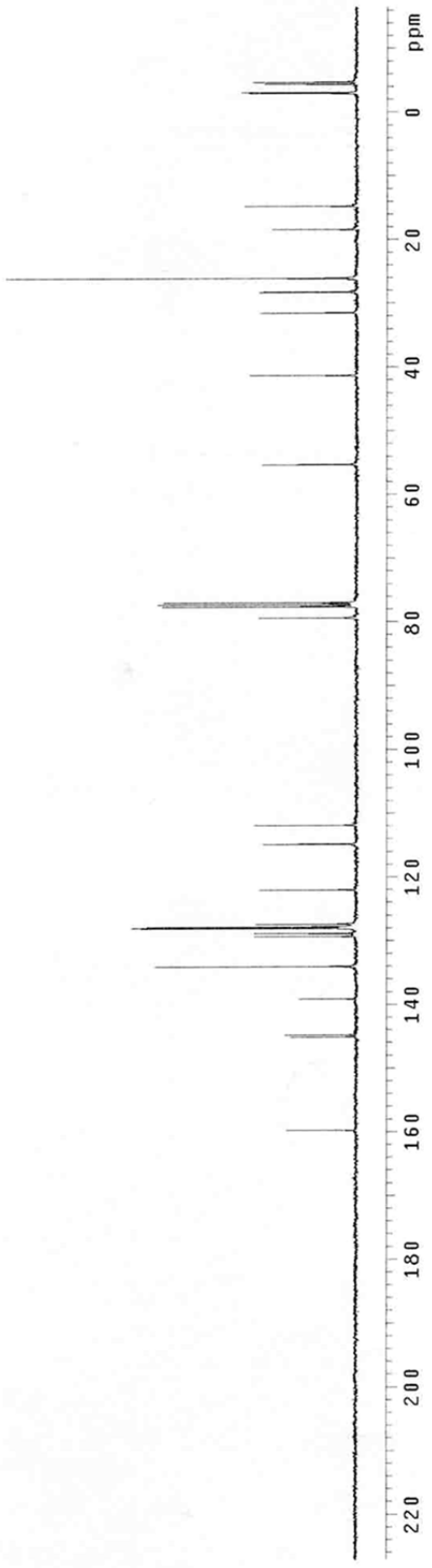
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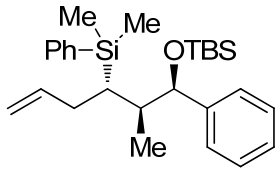
tert-butyl((3-(dimethyl(phenyl)silyl)-2-methyl-1-phenylhex-5-en-1-yl)oxy)dimethylsilane (5b)



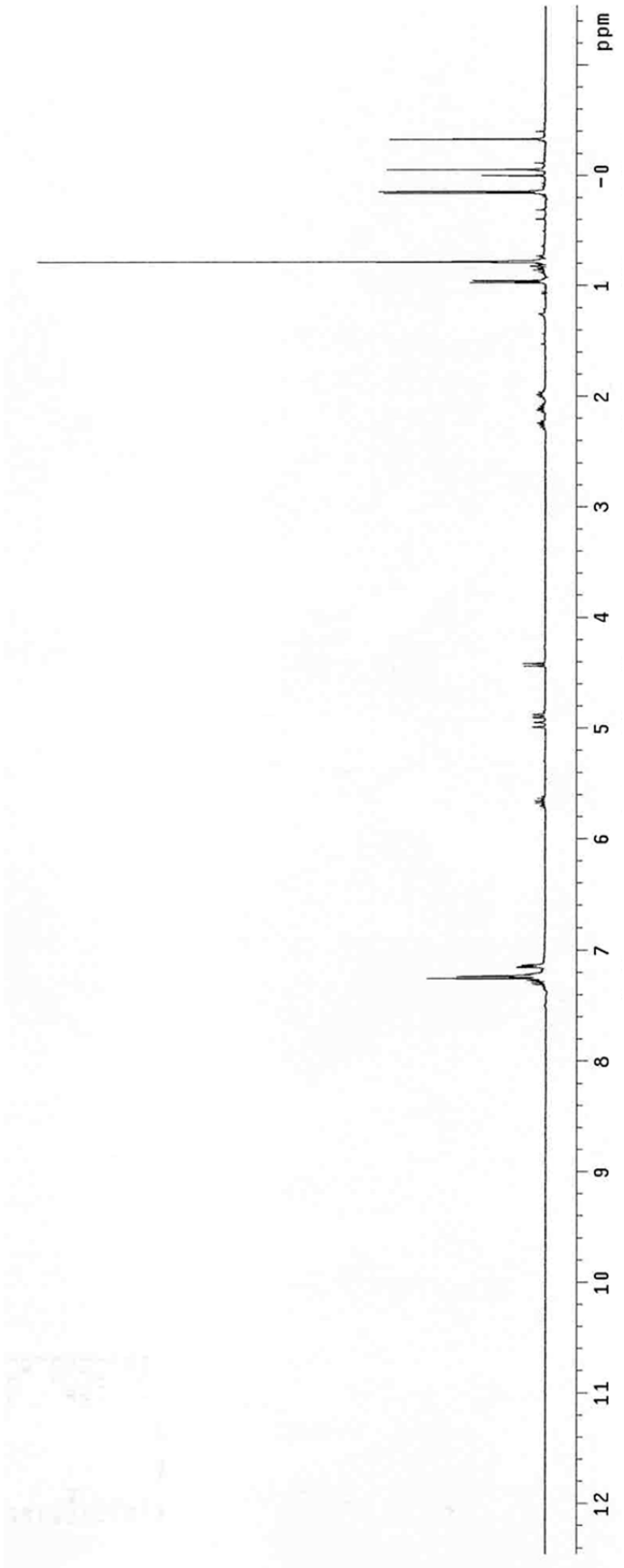
A flame dried 25 mL conical flask equipped with a magnetic stir bar was charged with TBS protected alcohol **4a** (45 mg, 0.11 mmol, 100 mol%) and purged with nitrogen. 9-BBN was added (0.66 mL, 0.33 mmol, 300 mol%, 0.5 M in THF) and the mixture was heated at 55 ^{o}C for 5 hr. This solution was then added to a flame dried sealed tube that contained $Pd^{(0)}(PPh_3)_4$ (13 mg, 0.011 mmol, 10 mol%), NaOH (0.18 mL, 0.36 mmol, 330 mol%, 2.0 M aq. sol.), and THF (0.22 mL, 0.5 M with respect to TBS protected alcohol **4a**) under a atmosphere of nitrogen. The reaction mixture was vigorously degassed with nitrogen and vinyl bromide (0.28 mL, 0.28 mmol, 250 mol%, 1.0 M in THF) was added. The sealed tube was capped, heated to 70 ^{o}C and let stir for 22 hr. The reaction was cooled to room temperature, filtered through a plug celite with DCM and concentrated *in vacuo*. Purification of the residue by flash column chromatography (SiO_2; hexane) furnished the title compound (27 mg, 0.062 mmol) as a colorless oil in 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.12 (m, 8H), 7.10-7.04 (m, 2H), 5.65-5.55 (m, 1H), 4.90 (dd, *J* = 16.8, 1.6, 1H), 4.82 (dd, *J* = 11.6, 1.6, 1H), 4.35 (dd, *J* = 9.2, 1.6, 1H), 2.22-2.15 (m,1H), 2.07-1.99 (m, 1H), 1.96-1.87 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.80-.70 (m, 1H), 0.71 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H), -0.12 (s, 3H), -0.41 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 144.9, 141.2, 139.2, 134.1, 128.9, 128.1, 127.8, 127.3, 114.8, 79.6, 41.4, 30.5, 26.1, 25.8, 18.4, 14.0, -2.6, -2.9, -4.4, -4.7.

FTIR (neat): 2955, 2928, 2856, 1490, 1471, 1453, 1427, 1360, 1249, 1078, 1056, 1027, 1004, 908, 835, 812, 700 cm^{-1}.

HRMS (CI) Calcd. for $C_{27}H_{42}OSi_2$ $[M-1]^+$: 437.2696, Found: 437.2698.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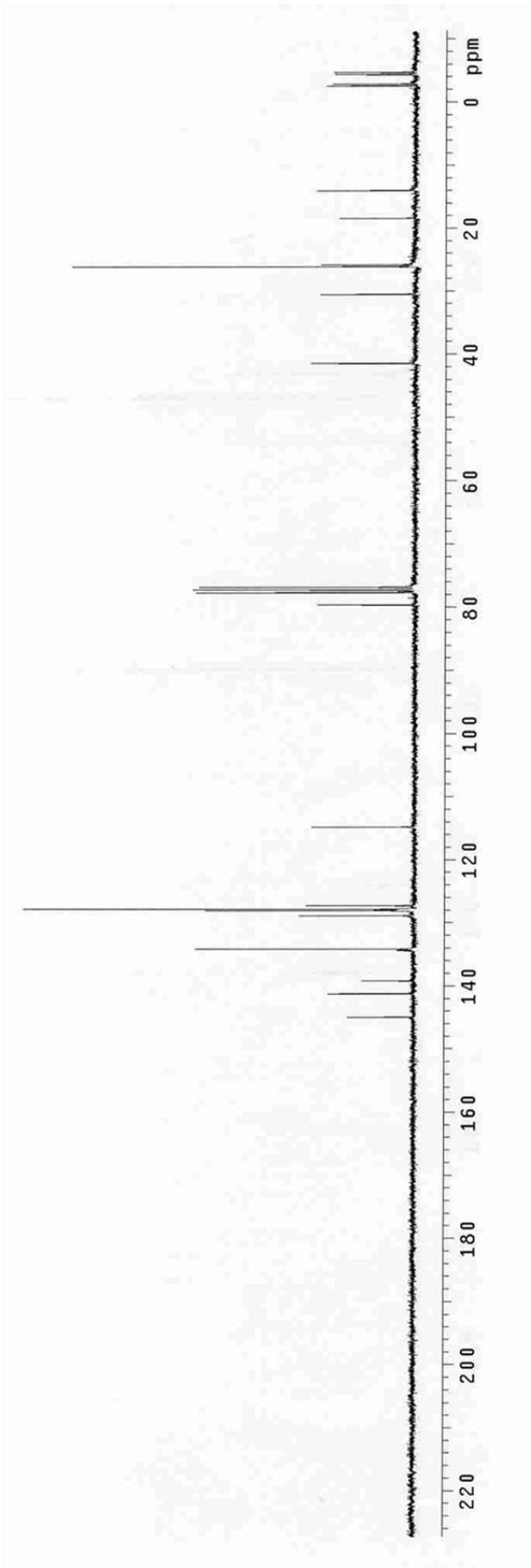
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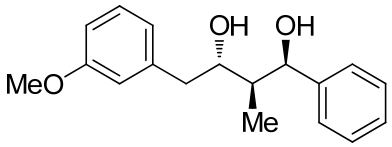
4-(3-methoxyphenyl)-2-methyl-1-phenylbutane-1,3-diol (6a)



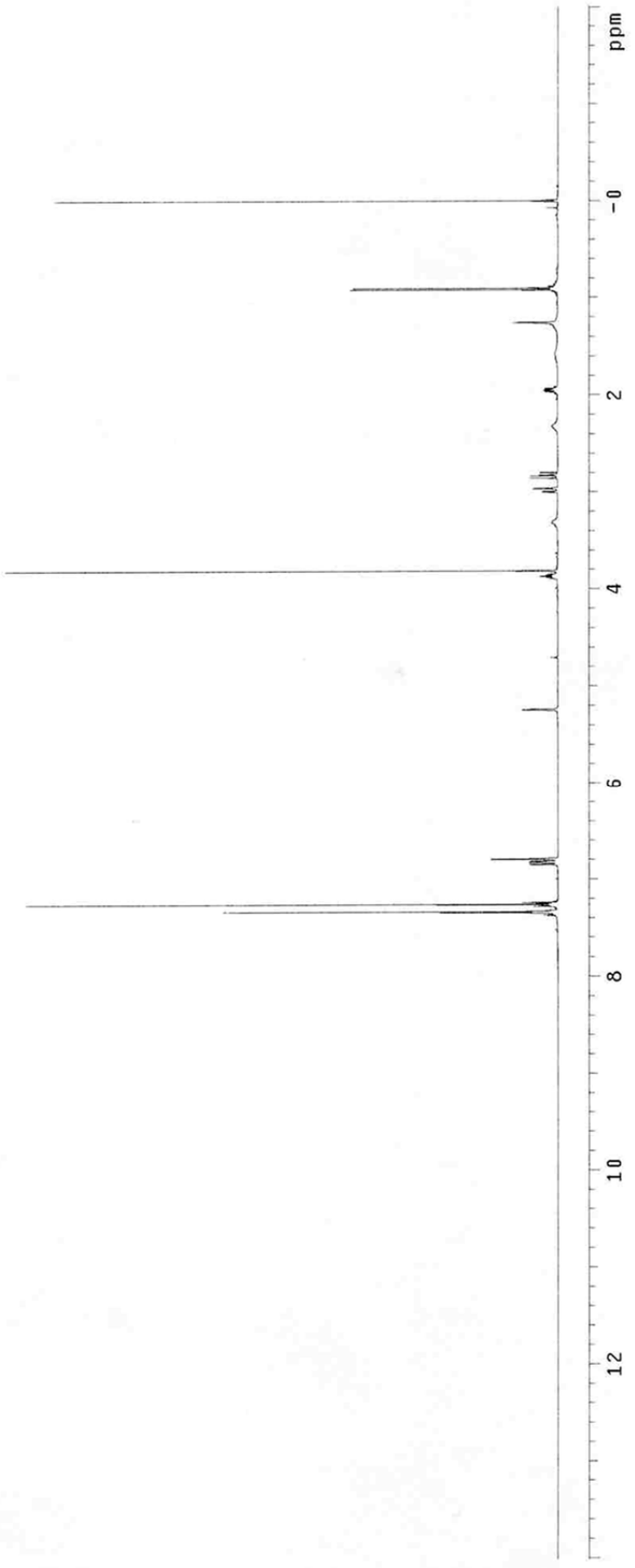
A flame dried 25 mL round bottom flask equipped with a magnetic stir bar was charged with KH (85 mg, 0.636 mmol, 600 mol%, 30% in mineral oil) and purged with nitrogen. NMP was added (1.3 mL, 0.1 M with respect to compound **5a**) and cooled to 0 ^{o}C. To this solution *t*-butyl hydroperoxide (0.212 mL, 0.636 mmol, 600 mol%, 3.0 M in Tol) was added and stirred for 10 min. Compound **5a** (55 mg, 0.106 mmol, 100 mol%) was added to the reaction as a solution in NMP (0.2 mL), warmed to room temperature and stirred for 15 min. TBAF (0.318 mL, 0.318 mmol, 300 mol%, 1.0 M in THF) was added and the reaction was heated to 70 ^{o}C for 2 hr. Upon complete consumption of starting material, as determined by TLC analysis, $Na_2S_2O_5$ (1.5 mL, sat. aq. sol.) was added. The organic layer was extracted with Et_2O (4 x 50 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification of the residue by flash column chromatography (SiO_2; 5-30% EA/Hex) provided the title compound (26 mg, 0.091 mmol) as a colorless oil in 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.32 (m, 4H), 7.28-7.24 (m, 2H), 6.85-6.78 (m, 3H), 5.25 (d, *J* = 2.4, 1H), 3.89-3.85 (m, 1H), 3.81 (s, 3H), 3.40-3.20 (bs, 1H), 2.97 (dd, *J* = 17.2, 13.4, 1H), 2.82 (dd, *J* = 22.8, 13.4, 1H), 2.40-2.20 (bs, 1H), 1.99-1.91 (m, 1H), 0.91 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 142.9, 139.8, 129.8, 128.1, 126.9, 122.0, 121.4, 121.7, 115.0, 112.1, 76.1, 74.2, 55.2, 43.8, 42.1, 11.2.

FTIR (neat): 3361, 2923, 1601, 1584, 1489, 1452, 1436, 1259, 1153, 1090, 1066, 1043, 977, 777, 748, 734, 700 cm^{-1}.

HRMS (CI) Calcd. for $C_{18}H_{22}O_3$ $[M-1]^+$: 286.1569, Found: 286.1568.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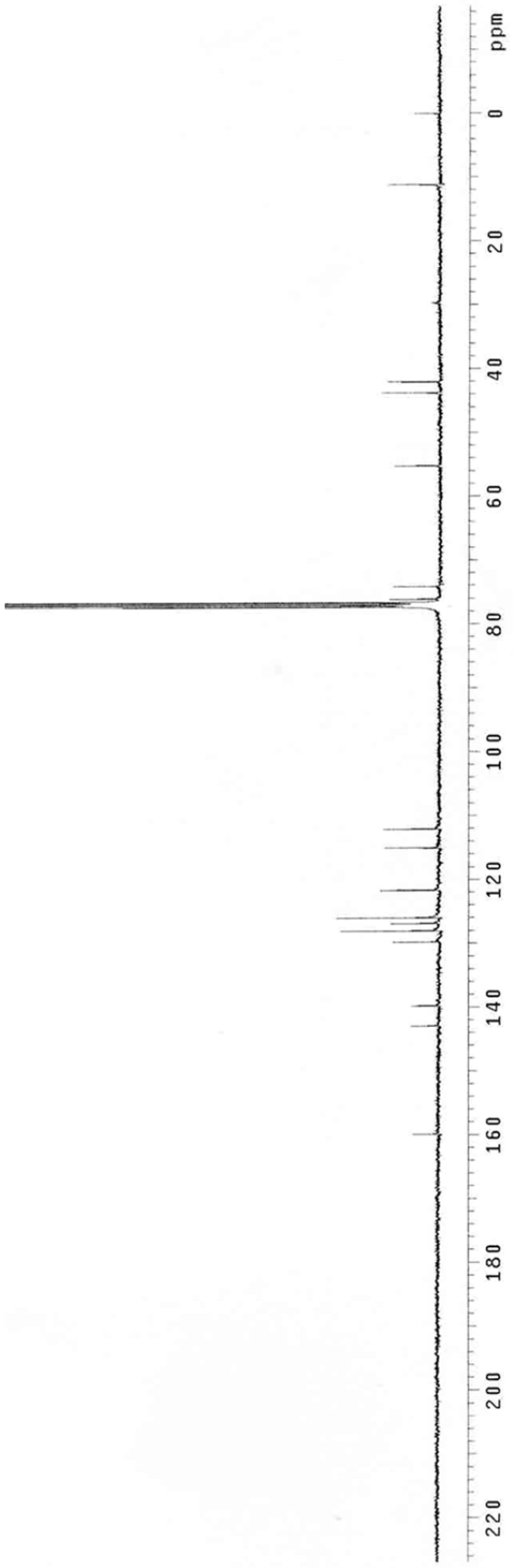
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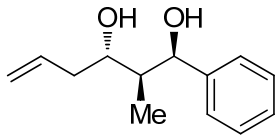
2-methyl-1-phenylhex-5-ene-1,3-diol (6b)



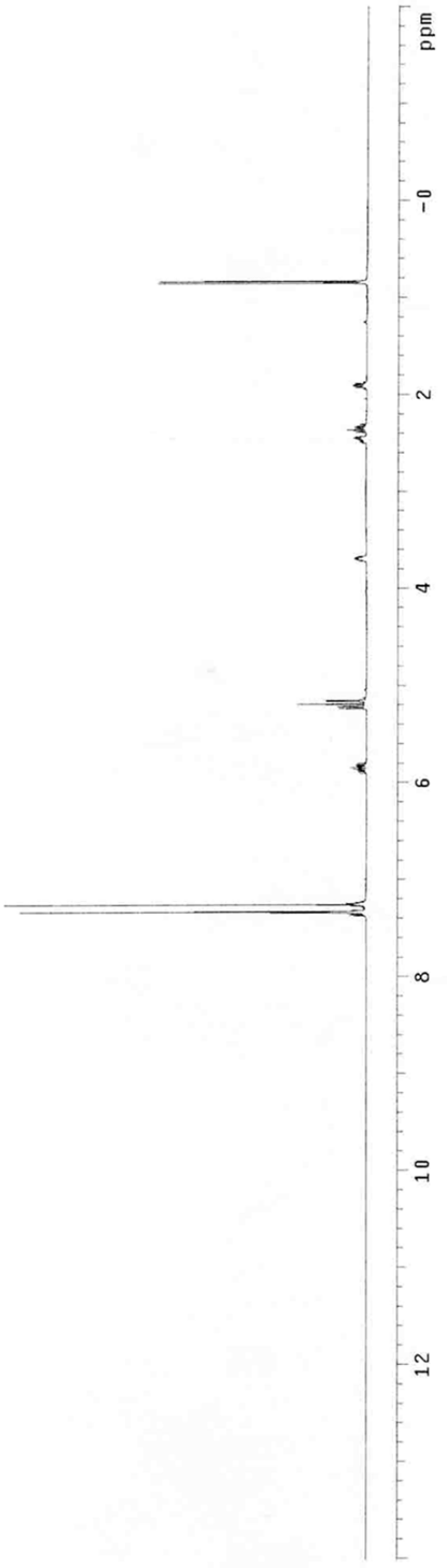
A flame dried 25 mL round bottom flask equipped with a magnetic stir bar was charged with KH (46 mg, 0.342 mmol, 600 mol%, 30% in mineral oil) and purged with nitrogen. NMP was added (0.6 mL, 0.1 M with respect to compound **5b**) and cooled to 0 ^{o}C. To this solution *t*-butyl hydroperoxide (0.155 mL, 0.343 mmol, 600 mol%, 3 M in Tol) was added and stirred for 10 min. Compound **5b** (25 mg, 0.057 mmol, 100 mol%) was added to the reaction as a solution in NMP (0.1 mL), warmed to room temperature and stirred for 15 min. TBAF (0.171 mL, 0.171 mmol, 300 mol%, 1.0 M in THF) was added and the reaction was heated to 70 ^{o}C for 2 hr. Upon complete consumption of starting material, as determined by TLC analysis, $Na_2S_2O_5$ (1.5 mL, sat. aq. sol.) was added. The organic layer was extracted with EtOAc (4 x 50 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification of the residue by flash column chromatography (SiO_2; 5-20% EA/Hex) provided the title compound (9 mg, 0.044 mmol) as a colorless oil in 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.30 (m, 4H), 7.28-7.22 (m, 1H), 5.82-5.80 (m, 1H), 5.24 -5.21 (m, 1H), 5.19 (t, *J* = 1.0 Hz, 1H), 5.16 (d, *J* = 2.8 Hz, 1H), 3.72-3.67 (m, 1H), 2.49-2.43 (m, 1H), 2.38-2.31 (m, 1H), 1.96-1.86 (m, 1H), 0.84 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 134.6, 128.0, 126.9, 126.0, 118.8, 74.4, 73.7, 43.5, 40.0, 11.1.

FTIR (neat): 3347, 2976, 2906, 1697, 1493, 1451, 1316, 1261, 1092, 1065, 1025, 975, 915, 700 cm^{-1}.

HRMS (CI) Calcd. for $C_{13}H_{18}O_2$ $[M-1]^+$: 205.1229, Found: 205.1231.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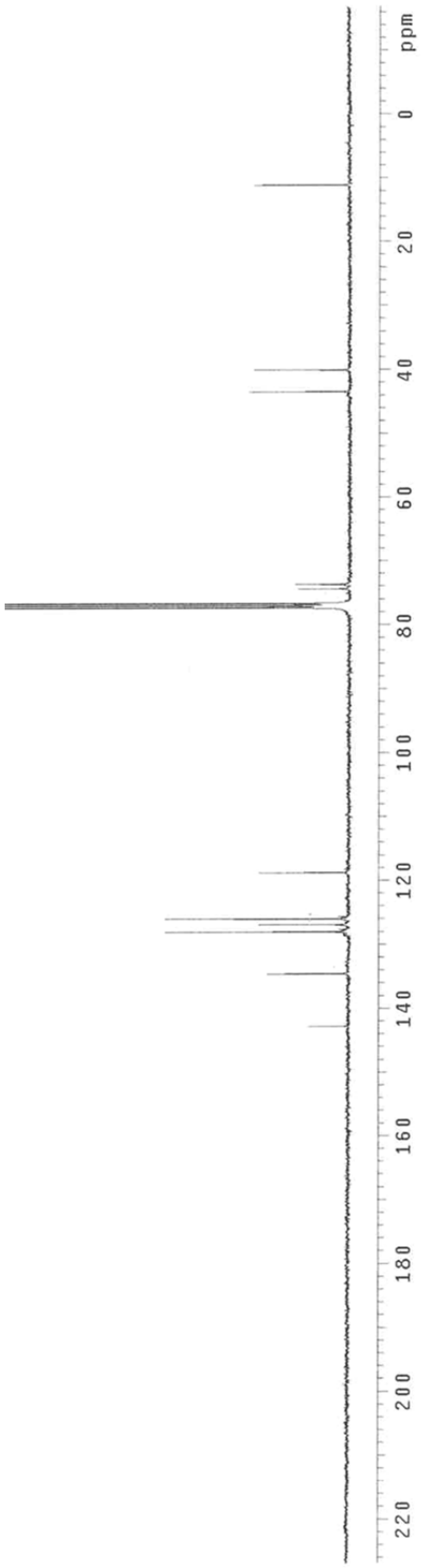
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