Supporting Information

Diastereo- and Enantioselective *anti*-Alkoxyallylation Employing Allylic *gem*-Dicarboxylates as Allyl Donors *via* Iridium Catalyzed Transfer Hydrogenation

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General Methods

All reactions were run under an atmosphere of nitrogen. Tetrahydrofuran (THF) and toluene were obtained from Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Anhydrous solvents were transferred by an oven-dried syringe. Sealed tubes (13x100 mm^2) were purchased from Fischer Scientific and were dried in an oven overnight and cooled under a stream of nitrogen prior to use. Commercially available alcohols and aldehydes were purified by distillation or recrystallisation prior to use. Cesium carbonate was purchased from Alfa Aesar and was used directly without further purification. Isopropanol (Fisher) was purified by distillation prior to use. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F_{254}). Infrared spectra were recorded on a Perkin-Elmer 1600 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. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) spectra were recorded with a Varian Gemini (400 MHz) spectrometer for $CDCl_3$ solutions and chemical shifts are reported as parts per million (ppm) relative to residual $CHCl_3$ δ_H (7.26 ppm) and $CDCl_3$ δ_C (77.0 ppm), respectively, as internal standards. Coupling constants are reported in Hertz (Hz).

Preparation of *BIPHEP*-I

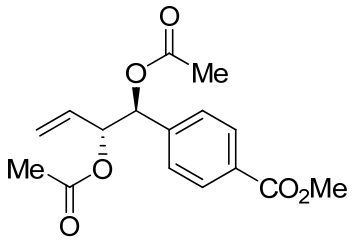
To a mixture of $[Ir(cod)Cl]_2$ (87.3 mg, 0.13 mmol, 100 mol%), BIPHEP (136 mg, 0.26 mmol, 200 mol%), Cs_2CO_3 (169 mg, 0.52 mmol, 400 mol%), 4-CN-3-NO_2BzOH (100 mg, 0.52 mmol, 400 mol%) and allyl acetate (65 mg, 0.65 mmol, 500 mol%) in a sealed tube under N_2 atmosphere was added THF (2.6 mL, 0.05 M). The reaction mixture was stirred for 30 min at ambient temperature and heated for 1.5 hr at 80 ^oC, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered and washed with THF (10 mL). The filtrate was concentrated *in vacuo* and hexanes (50 mL) was added. A yellow precipitate formed, which was collected by filtration and dried under vacuum (108 mg, 0.11 mmol, 88% yield).

Preparation of (*R*)-*SEGPHOS*-I

To a mixture of $[Ir(cod)Cl]_2$ (87.3 mg, 0.13 mmol, 100 mol%), (*R*)-SEGPHOS (159 mg, 0.26 mmol, 200 mol%), Cs_2CO_3 (169 mg, 0.52 mmol, 400 mol%), 4-CN-3-NO_2BzOH (100 mg, 0.52 mmol, 400 mol%) and allyl acetate (65 mg, 0.65 mmol, 500 mol%) in a sealed tube under N_2 atmosphere was added THF (2.6 mL, 0.05 M). The reaction mixture was stirred for 30 min at ambient temperature and heated for 1.5 hr at 80 ^oC, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered and washed with THF (10 mL). The filtrate was concentrated *in vacuo* and hexanes (50 mL) was added. A yellow precipitate formed, which was collected by filtration and dried under vacuum (101 mg, 0.098 mmol, 75% yield).

Detailed Procedure and Spectral Data for Diastereo- and Enantioselective *anti*-Alkoxyallylation

1-(4-(methoxycarbonyl)phenyl)but-3-ene-1,2-diyl diacetate



3c (a)

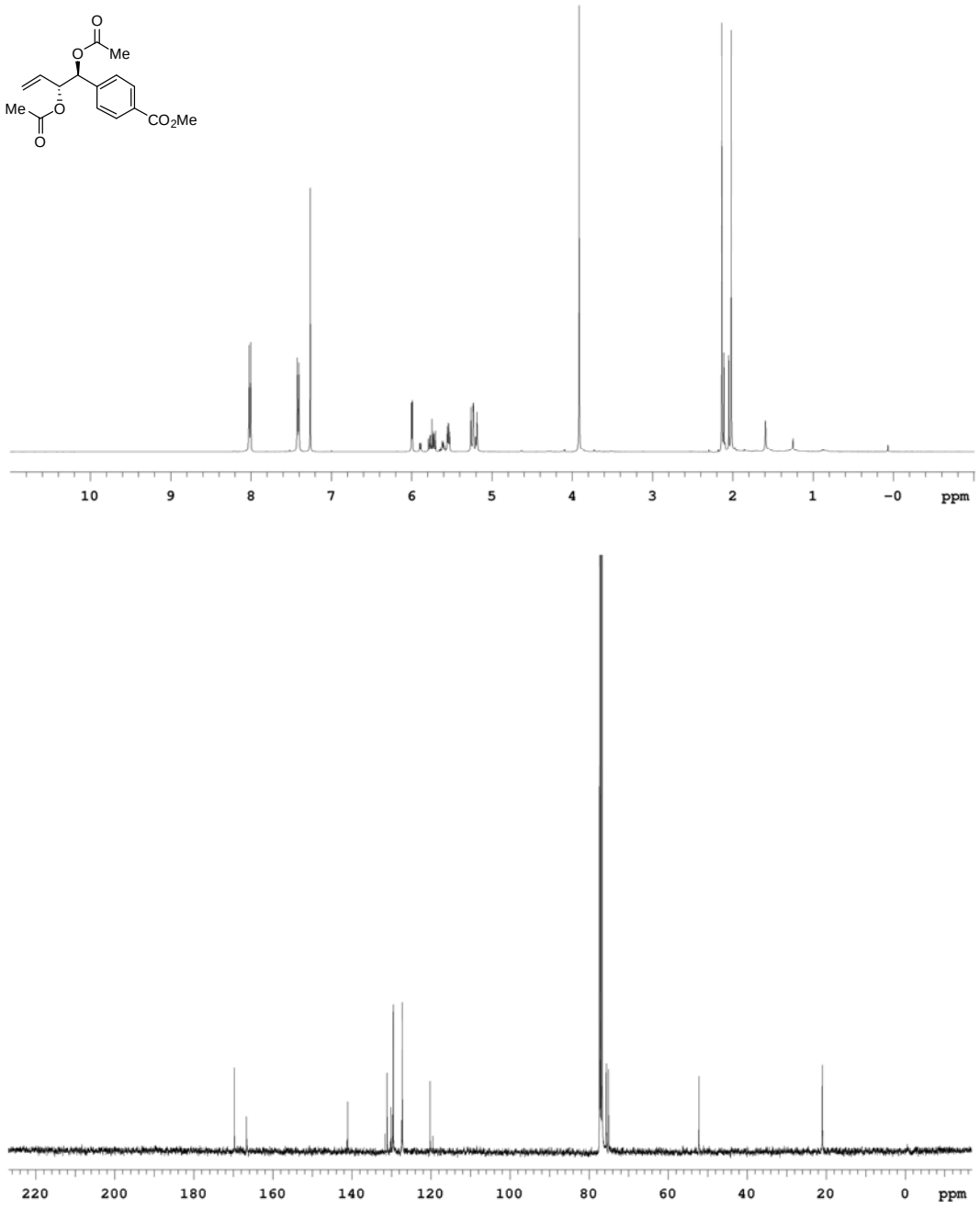
An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *BIPHEP*-**I** (9.5 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). Methyl 4-formylbenzoate **2c** (32.8 mg, 0.2 mmol, 100 mol%), acrolein *gem*-diacetate **1a**[1] (63 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. Acetyl chloride (71 μL, 1.0 mmol, 500 mol%), Et_3N (270 μL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:7) provided **3c (a)** (45 mg, 0.148 mmol) as a colorless oil in 74% yield (4:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 5.99 (d, *J* = 4.8 Hz, 1H), 5.79-5.70 (m, 1H), 5.55-5.53 (m, 1H), 5.26-5.18 (m, 2H), 3.91 (s, 3H), 2.14 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 166.7, 141.1, 131.1, 130.1, 129.7, 129.5, 127.2, 120.2, 75.6, 75.0, 52.2, 21.0, 20.9.

FTIR (neat): 1721, 1437, 1372, 1281, 1222, 1111, 1020, 988, 906, 816, 727 cm^{-1}.

[1] Saini, A.; Kumar, S.; Sandhu, J. S. *Synth. Commun*. **2008**, *38*, 106.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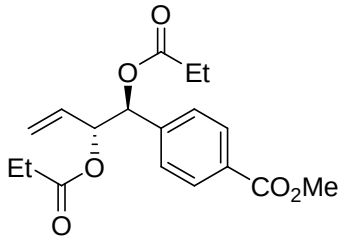
ppm

1-(4-(methoxycarbonyl)phenyl)but-3-ene-1,2-diyl dipropionate



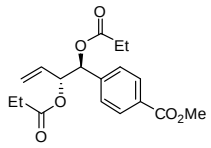
3c (b)

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *BIPHEP*-**I** (9.5 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). Methyl 4-formylbenzoate **2c** (32.8 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dipropionate **1b**[1] (74 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. Propionyl chloride (87 µL, 1.0 mmol, 500 mol%), Et_3N (270 µL, 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:9) provided **3c (b)** (43 mg, 0.13 mmol) as a colorless oil in 65% yield (5:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.01 (d, *J* = 5.2 Hz, 1H), 5.79-5.71 (m, 1H), 5.58-5.55 (m, 1H), 5.26-5.19 (m, 2H), 3.91 (s, 3H), 2.41 (qd, *J* = 7.6, 2.8 Hz, 2H), 2.28 (qd, *J* = 7.6, 2.0 Hz, 2H), 1.16 (t, *J* = 7.6 Hz, 3H), 1.08 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1 (two carbons are overlapped), 166.7, 141.3, 131.2, 130.0, 129.5, 127.2, 120.0, 75.4, 74.8, 52.2, 27.7, 27.6, 9.0, 8.9.

FTIR (neat): 1724, 1437, 1281, 1181, 1113, 1083, 1019, 905, 726 cm^{-1}.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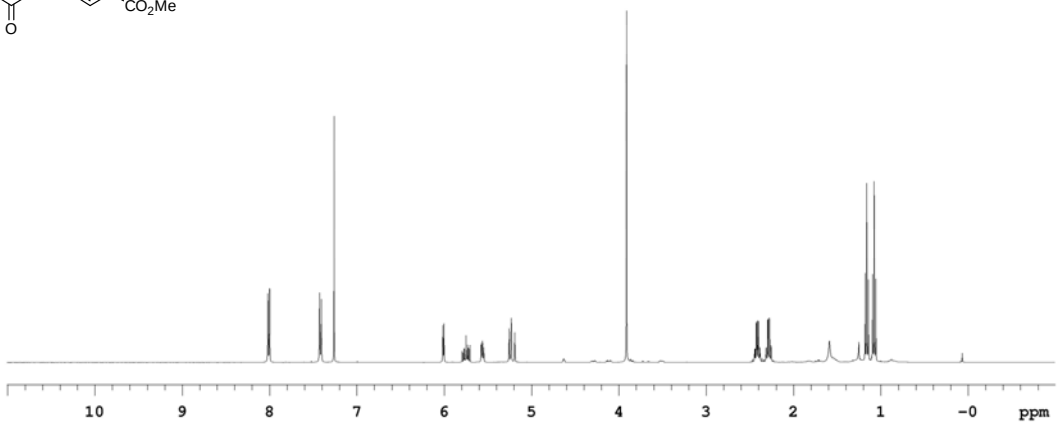
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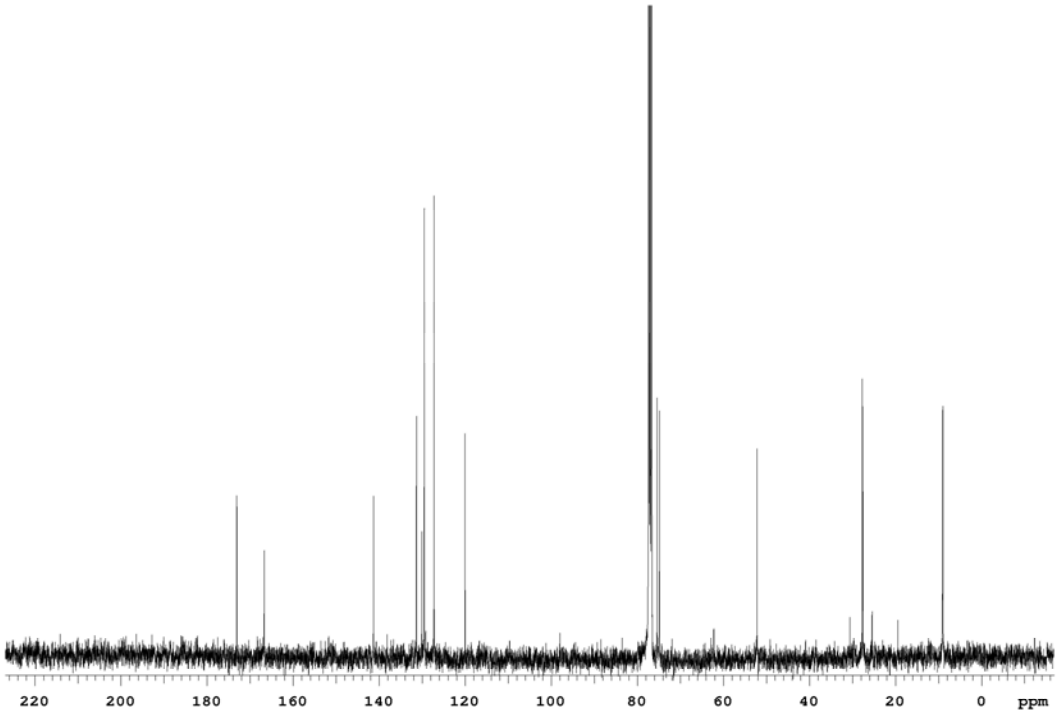
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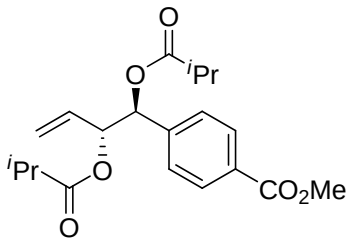
1-(4-(methoxycarbonyl)phenyl)but-3-ene-1,2-diyl bis(2-methylpropanoate)



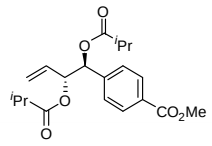
3c (c)

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *BIPHEP*-**I** (9.5 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). Methyl 4-formylbenzoate **2c** (32.8 mg, 0.2 mmol, 100 mol%), acrolein *gem*-diisobutyrate **1c**[1] (86 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. Isobutyryl chloride (105 μL, 1.0 mmol, 500 mol%), Et_3N (270 μL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:15) provided **3c (c)** (23 mg, 0.064 mmol) as a colorless oil in 32% yield (8:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 5.98 (d, J = 5.2 Hz, 1H), 5.79-5.70 (m, 1H), 5.56-5.53 (m, 1H), 5.25-5.19 (m, 2H), 3.90 (s, 3H), 2.65-2.45 (m, 2H), 1.20-1.16 (m, 6H), 1.10-1.15 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 175.4, 166.6, 141.4, 131.4, 130.0, 129.4, 127.2, 119.8, 75.2, 74.6, 52.1, 34.0 (two carbons overlap), 18.9, 18.8.

FTIR (neat): 1725, 1470, 1437, 1388, 1281, 1189, 1149, 1112, 1069, 1020, 989, 906, 854, 727 cm^{-1}.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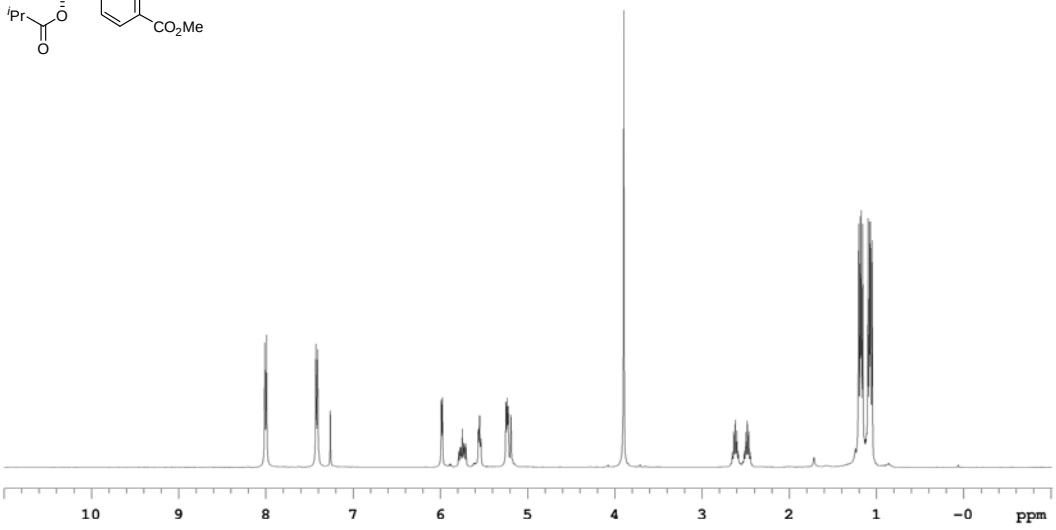
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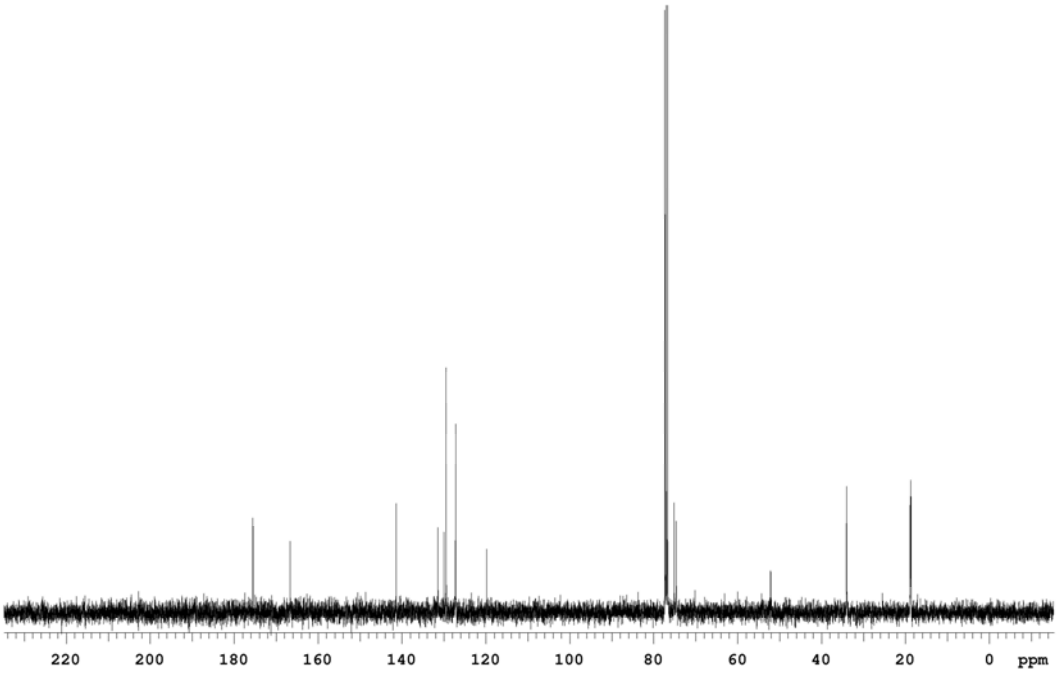
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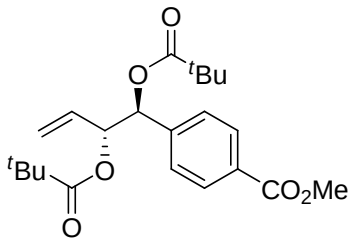


3c (d)

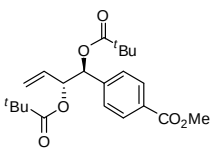
An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *BIPHEP*-**I** (9.5 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). Methyl 4-formylbenzoate **2c** (32.8 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dipivalate **1d**[2] (97 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. Pivaloyl chloride (123 µL, 1.0 mmol, 500 mol%), Et_3N (270 µL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:20) provided **3c (d)** (12 mg, 0.003 mmol) as a colorless oil in 15% yield (10:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 5.97 (d, J = 5.2 Hz, 1H), 5.79-5.71 (m, 1H), 5.55-5.52 (m, 1H), 5.26-5.19 (m, 2H), 3.91(s, 3H), 1.23 (s, 9H), 1.12 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 176.8, 166.7, 141.5, 131.4, 129.8, 129.5, 127.2, 119.6, 75.3, 74.8, 52.2, 38.9, 38.8, 27.1, 27.0.

FTIR (neat): 1725, 1479, 1437, 1397, 1279, 1140, 1020, 988, 907, 729 cm^{-1}.

[2] Lombardo, M.; Licciulli, S.; Pasi, F.; Angelici, G.; Trombini, C. *Adv. Synth. Catal*. **2005**, *347*, 2015.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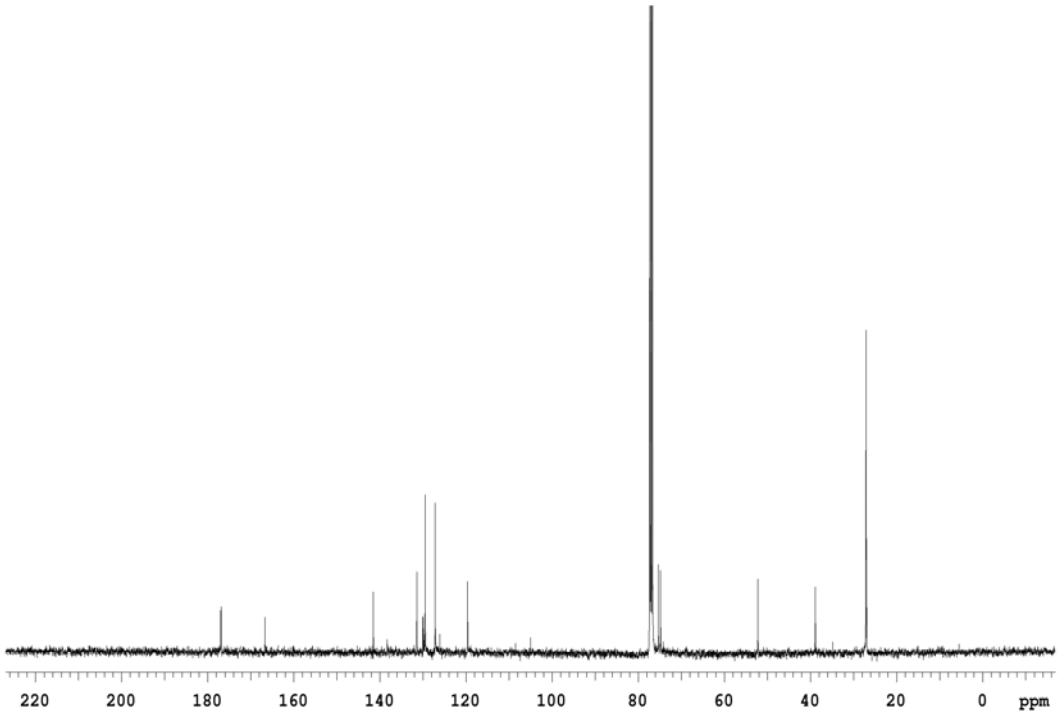
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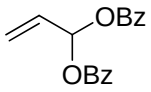
Acrolein *gem*-dibenzoate



1e

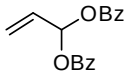
In accordance with a modified literature procedure[2], 3 drops of H_2SO_4 were added to a solution of benzoic anhydride (22.6 g, 100 mmol, 100 mol%) in CH_2Cl_2 (1.0 M, 100 mL). A solution of freshly distilled acrolein (10 mL, 150 mmol, 150 mol%) in CH_2Cl_2 (10 mL) was added drop by drop, at a rate slow enough to maintain the solution at ambient temperature. The reaction mixture was stirred at ambient temperature for 72 hr and filtered through a short pad of K_2CO_3. The solvent was removed *in vacuo* and the residue was disolved in hexane. Filtration, evaporation *in vacuo* and purification of the residue by column chromatography (SiO_2; hexanes: TEA, 150:1) provided **1e** (14 g, 50 mmol) as a colorless oil in 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.07 (m, 4H), 7.70-7.68 (m, 1H), 7.61-7.56 (m, 2H), 7.48-7.43 (m, 4H), 6.18 (dq, *J* = 17.2, 5.2 Hz, 1H), 5.76 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.43 (dt, *J* = 10.8, 1.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 133.5, 131.4, 130.0, 129.1, 128.4, 120.7, 90.0.

FTIR (neat): 1736, 1601, 1452, 1316, 1274, 1243, 1178, 1115, 1079, 1059, 1023, 949, 906, 801, 729, 707, 686 cm^{-1}.

HRMS (CI) Calcd. for $C_{17}H_{14}O_4$ $[M]^+$: 282.0892, Found: 282.0888.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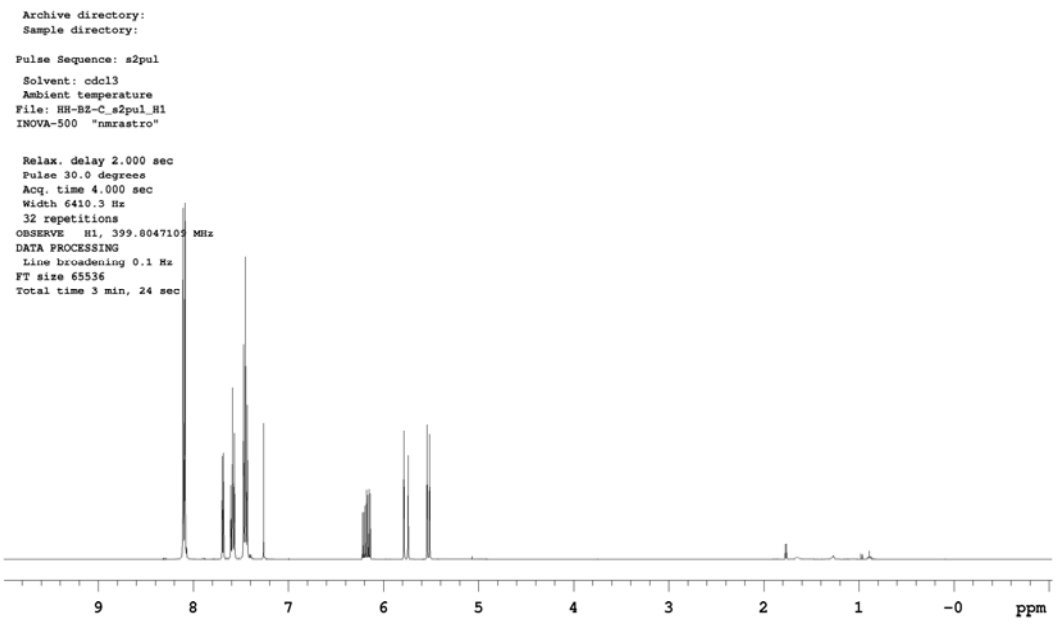
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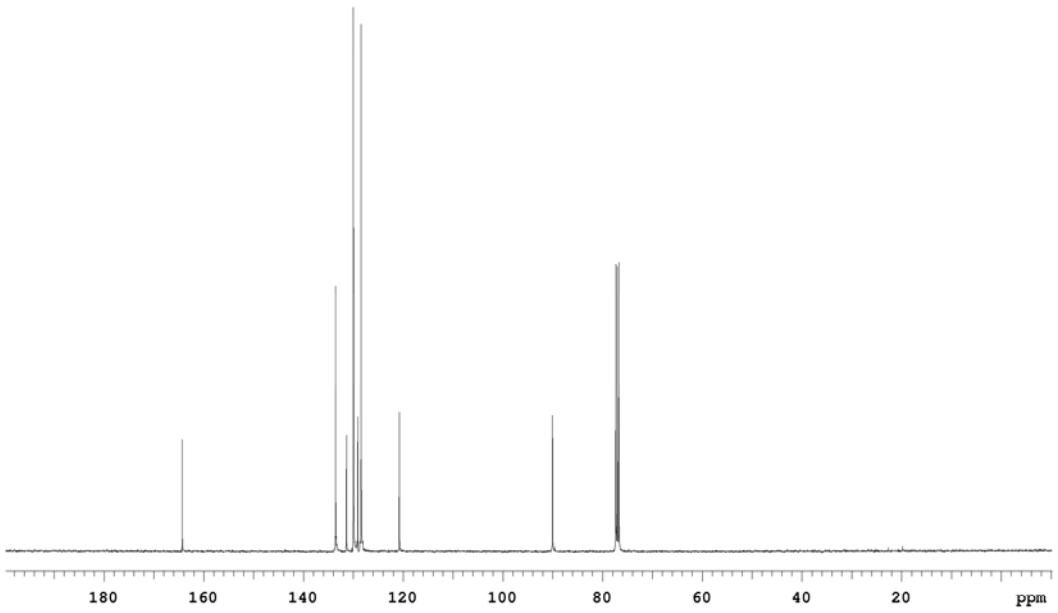
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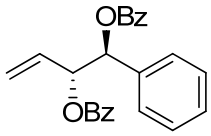
(1*S*, 2*R*)-1-phenylbut-3-ene-1, 2-diyl dibenzoate



3a

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). Benzaldehyde **2a** (21 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 72 hr, at which point the reaction mixture was cooled to ambient temperature. Benzoyl chloride (116 μL, 1.0 mmol, 500 mol%), Et_3N (270 μL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:10) provided **3a** (47 mg, 0.126 mmol) as a colorless oil in 63% yield (18:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.08 (m, 2H), 8.00-7.98 (m, 2H), 7.60-7.26 (m, 11H), 6.34 (d, J = 4.4 Hz, 1H), 6.02-5.93 (m, 2H), 5.42-5.31 (m, 2H).

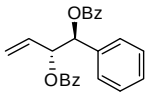
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 136.1, 133.2, 133.1, 131.5, 129.9, 129.8, 129.7, 129.6, 128.5, 128.4, 128.3, 128.2, 127.2, 119.9, 76.4, 76.3.

HPLC: (Chiralcel OJ-H + OJ-H columns, hexanes:*i*-PrOH = 93:7, 0.5 mL/min, 230 nm), t_{major} = 47.5 min, t_{minor} = 51.7 min; ee = 99%.

$[\alpha]_D^{25}$= -7.30 (c =1.31, CH_2Cl_2).

FTIR (neat): 1711, 1601, 1451, 1314, 1264, 1176, 1106, 1068, 1026, 989, 964, 932, 858, 763, 736, 704, 685 cm^{-1}.

HRMS (CI) Calcd. for $C_{24}H_{21}O_4$ $[M+H]^+$: 373.1440, Found: 373.1444.


OBz
OBz

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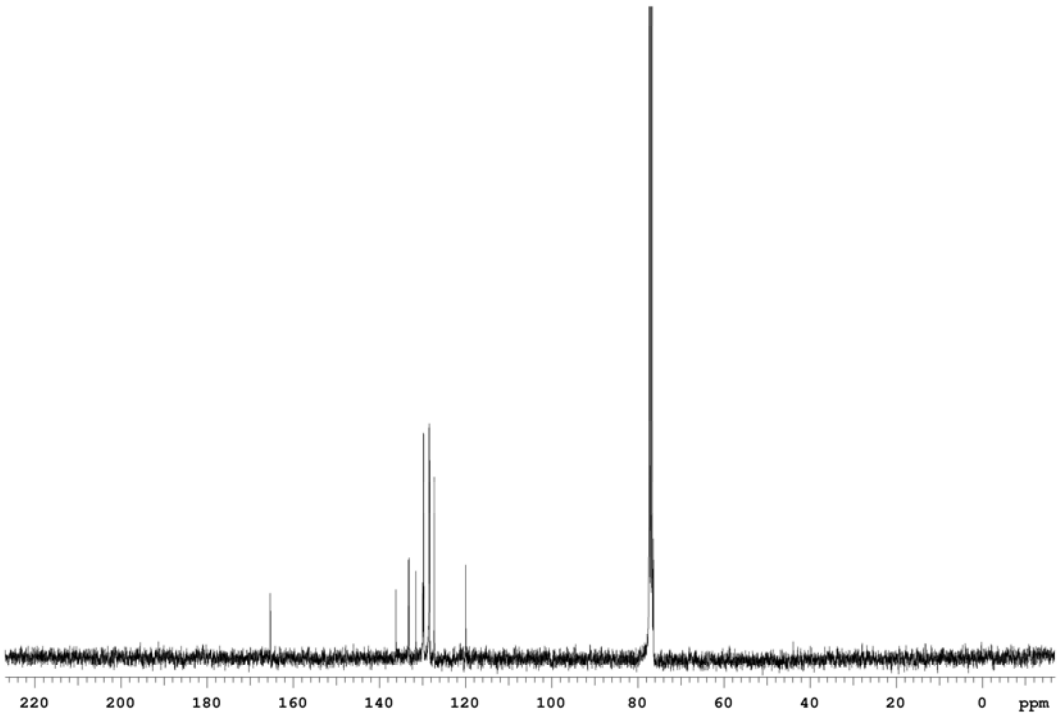
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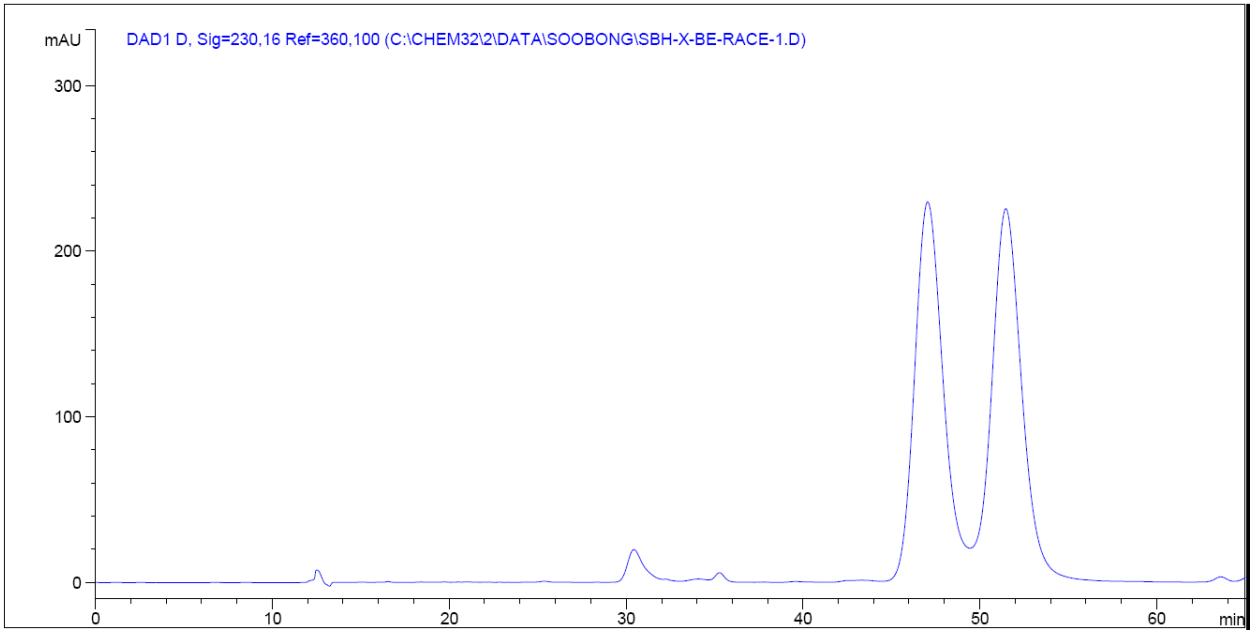
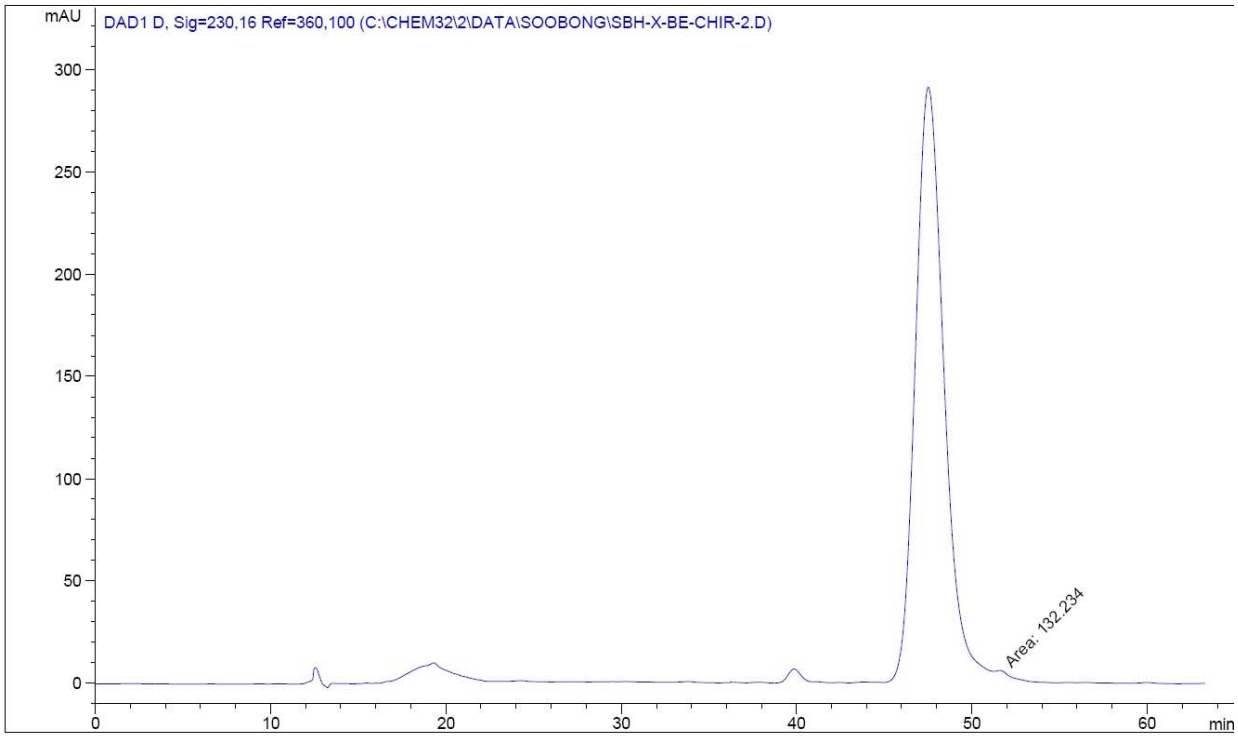
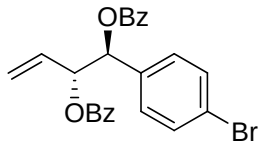


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.034	BV	1.7081	2.53740e4	228.04851	49.7539
2	51.457	VB	1.7504	2.56250e4	222.37338	50.2461



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.507	BB	1.7091	3.18705e4	288.43912	99.5868
2	51.673	MM	0.7651	132.23447	2.88064	0.4132

(1*S*, 2*R*)-1-(4-bromophenyl)but-3-ene-1, 2-diyl dibenzoate



3b

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). 4-Bromobenzaldehyde **2b** (37 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. Benzoyl chloride (116 μL, 1.0 mmol, 500 mol%), Et_3N (270 μL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:10) provided **3b** (63 mg, 0.14 mmol) as a colorless oil in 70% yield (16:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.05 (m, 2H), 8.00-7.97 (m, 2H), 7.61-7.55 (m, 2H), 7.51-7.42 (m, 6H), 7.39-7.26 (m, 2H), 6.26 (d, J = 4.0 Hz, 1H), 6.00-5.90 (m, 2H), 5.42-5.33 (m, 2H).

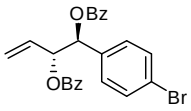
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 165.1, 135.2, 133.4, 133.3, 131.5, 131.3, 129.8, 129.7, 129.6, 129.0, 128.5, 128.4, 122.5, 120.3, 76.0, 75.8.

HPLC: (Chiralcel AD-H + OD-H columns, hexanes:*i*-PrOH = 96:4, 0.5 mL/min, 230 nm), t_{major} = 38.4 min, t_{minor} = 46.1 min; ee = 90%.

$[\alpha]_D^{25}$= -7.5 (c =1.73, CH_2Cl_2).

FTIR (neat): 1721, 1602, 1489, 1451, 1315, 1264, 1177, 1107, 1096, 1070, 1026, 1012, 987, 938, 895, 830, 734, 709 cm^{-1}.

HRMS (CI) Calcd. for $C_{24}H_{20}O_4Br$ $[M+H]^+$: 451.0545, Found: 451.0555.


OBz
OBz
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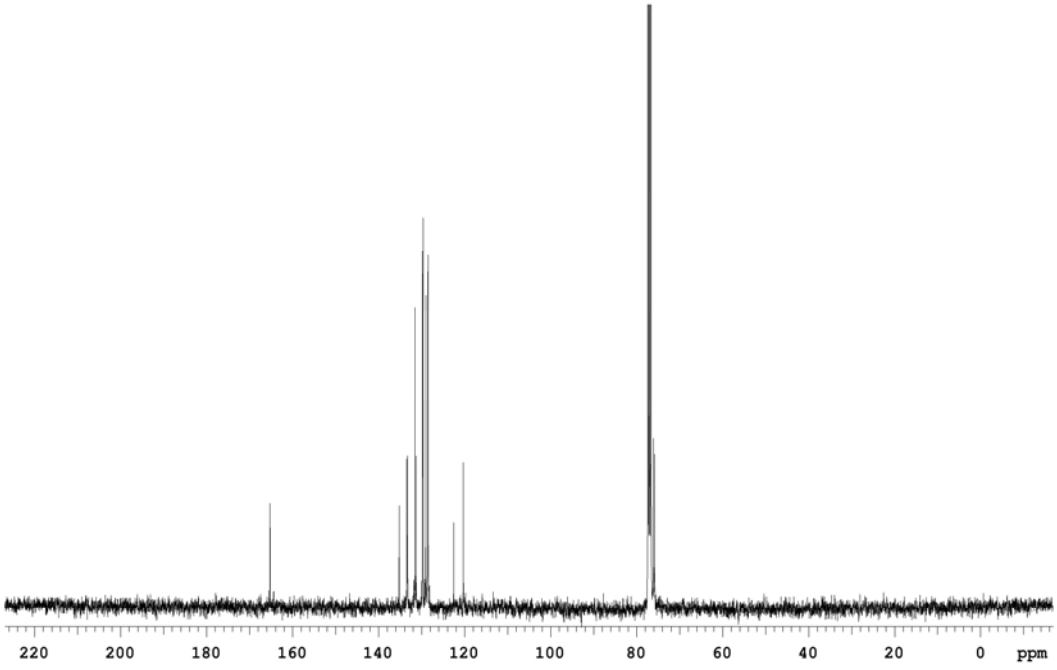
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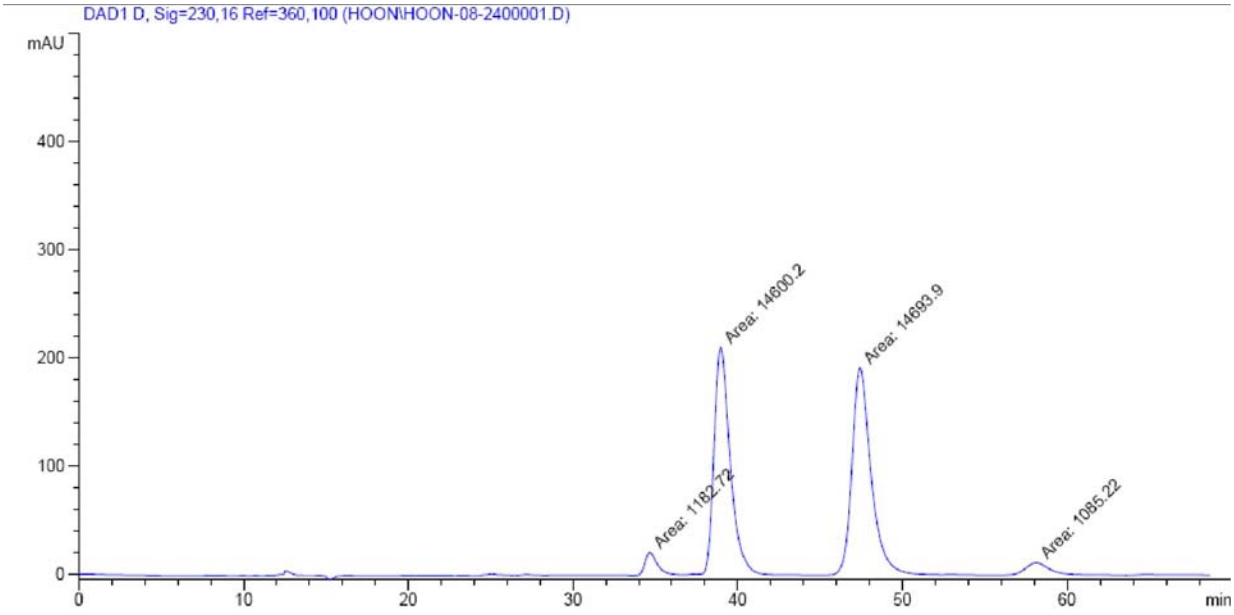
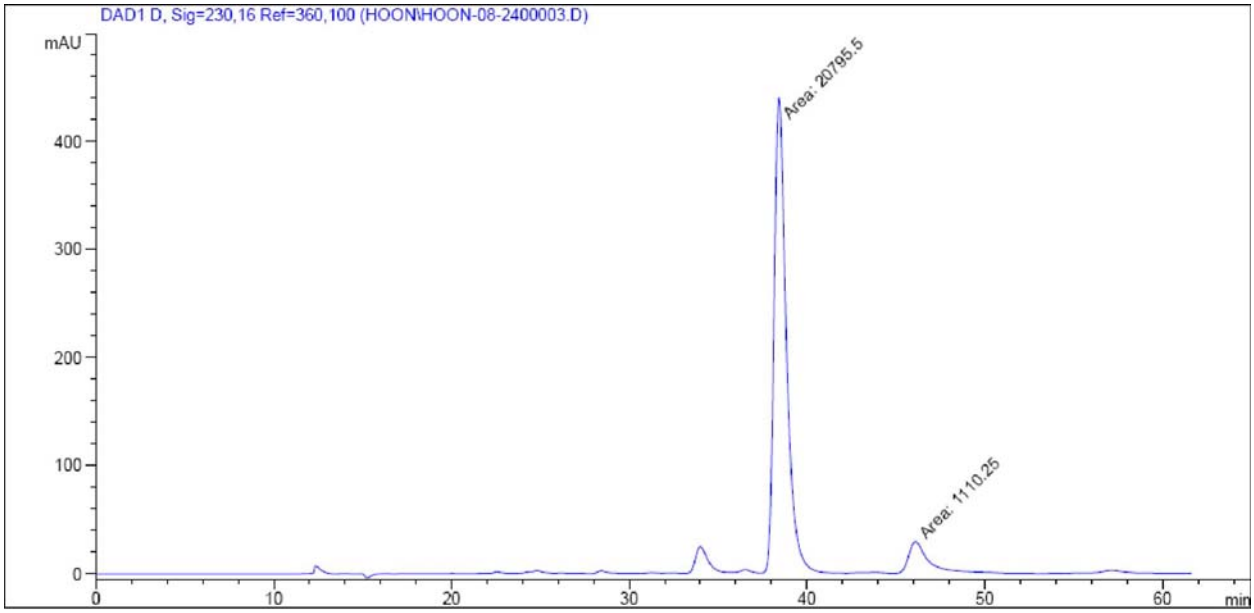
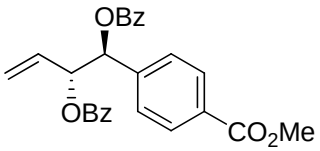


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.650	MM	0.9142	1182.72314	21.56188	3.7473
2	38.954	MM	1.1528	1.46002e4	211.08905	46.2586
3	47.415	MM	1.2924	1.46939e4	189.49086	46.5557
4	58.124	MM	1.6137	1085.22400	11.20851	3.4384



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.422	MM	0.7918	2.07955e4	437.72488	94.9317
2	46.100	MM	0.8224	1110.25488	22.49984	5.0683

(1*S*, 2*R*)-1-(4-(methoxycarbonyl)phenyl)but-3-ene-1, 2-diyl dibenzoate



3c

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). Methyl 4-formylbenzoate **2c** (33 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. Benzoyl chloride (116 µL, 1.0 mmol, 500 mol%), Et_3N (270 µL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:10) provided **3c** (65 mg, 0.152 mmol) as a colorless oil in 76% yield (14:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.03 (m, 4H), 8.00-7.97 (m, 2H), 7.62-7.54 (m, 4H), 7.49-7.37 (m, 4H), 6.37 (d, J = 4.0 Hz, 1H), 6.00-5.92 (m, 2H), 5.41-5.32 (m, 2H), 3.91 (s, 3H).

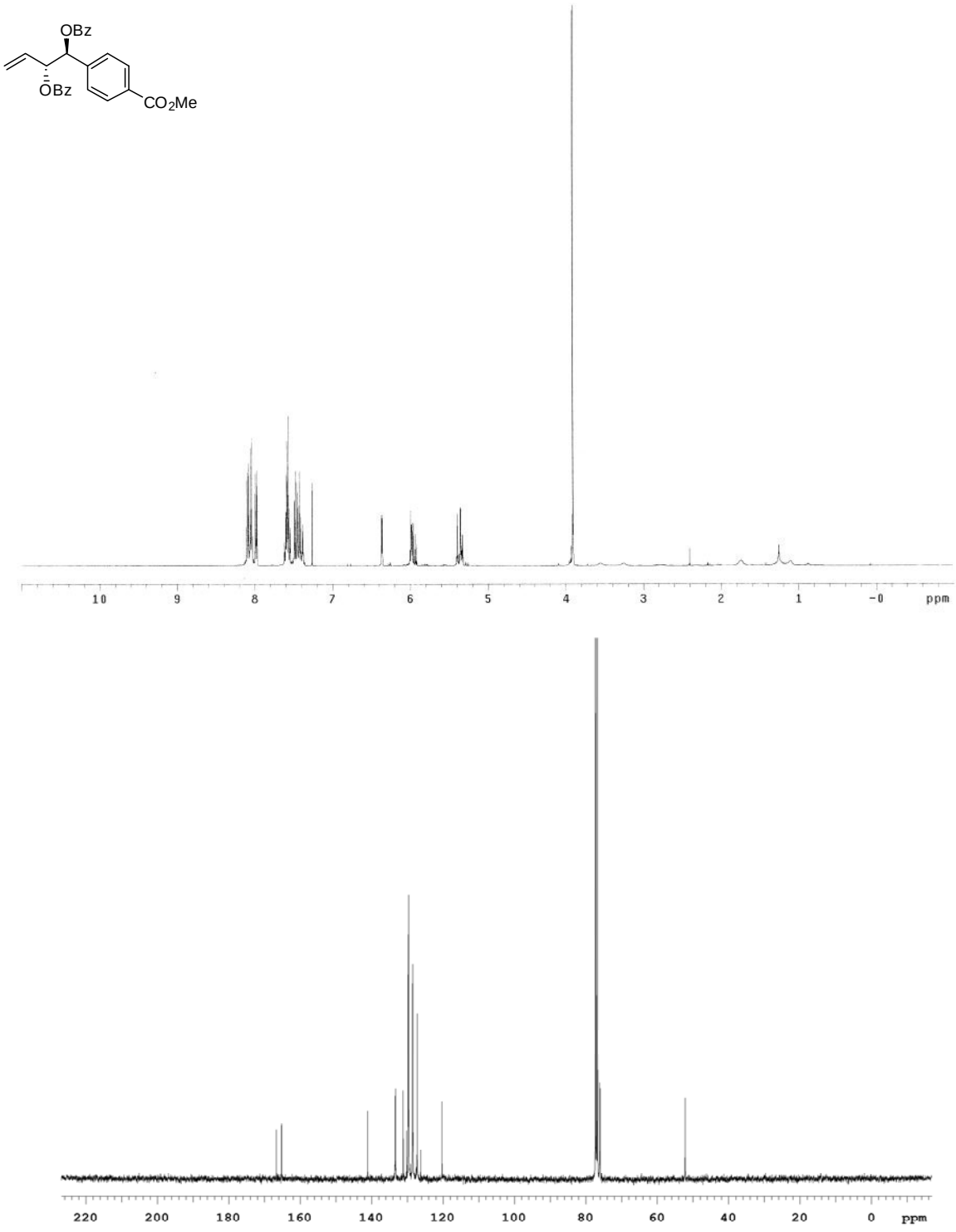
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 165.2, 165.1, 141.1, 133.4, 133.3, 131.1, 130.2, 129.8, 129.7, 129.6, 128.5, 128.4, 128.3, 127.2, 126.2, 120.3, 76.1, 76.0, 52.2.

HPLC: (Chiralcel OJ-H + OD-H columns, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 230 nm), t_{major} = 47.7 min, t_{minor} = 52.9 min; ee = 99%.

$[\alpha]_D^{25}$= +4.05 (c =1.42, CH_2Cl_2).

FTIR (neat): 1719, 1601, 1451, 1436, 1314, 1263, 1178, 1106, 1069, 1026, 987, 937, 855, 803, 772, 733, 708 cm^{-1}.

HRMS (CI) Calcd. for $C_{26}H_{23}O_6$ $[M+H]^+$: 413.1495, Found: 431.1497.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OBz
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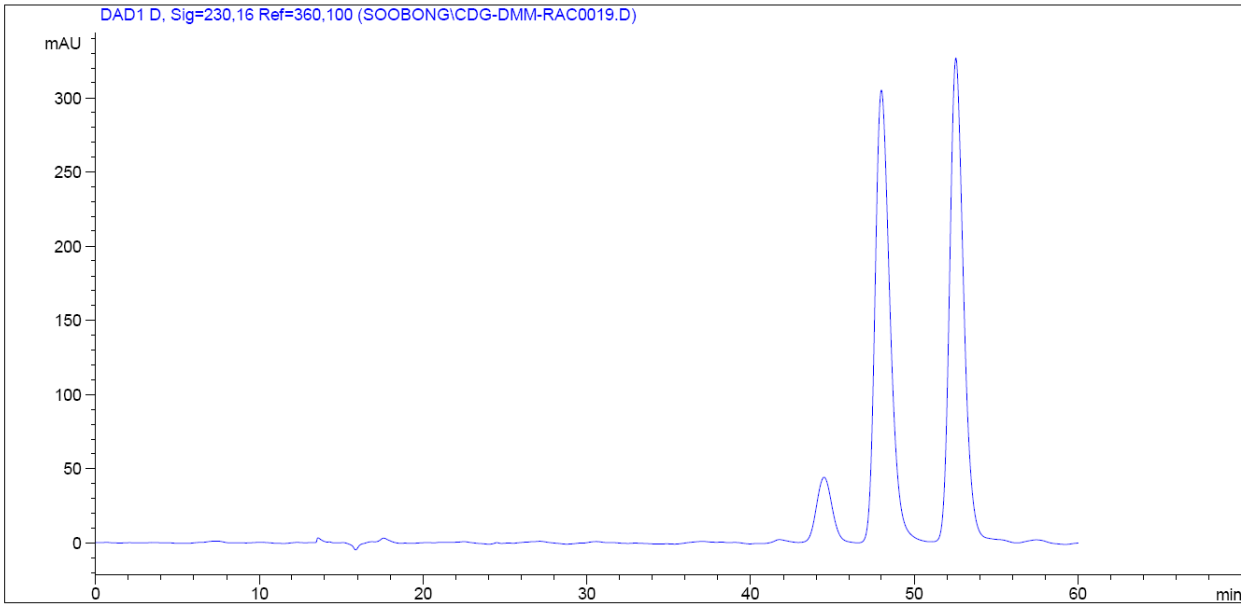
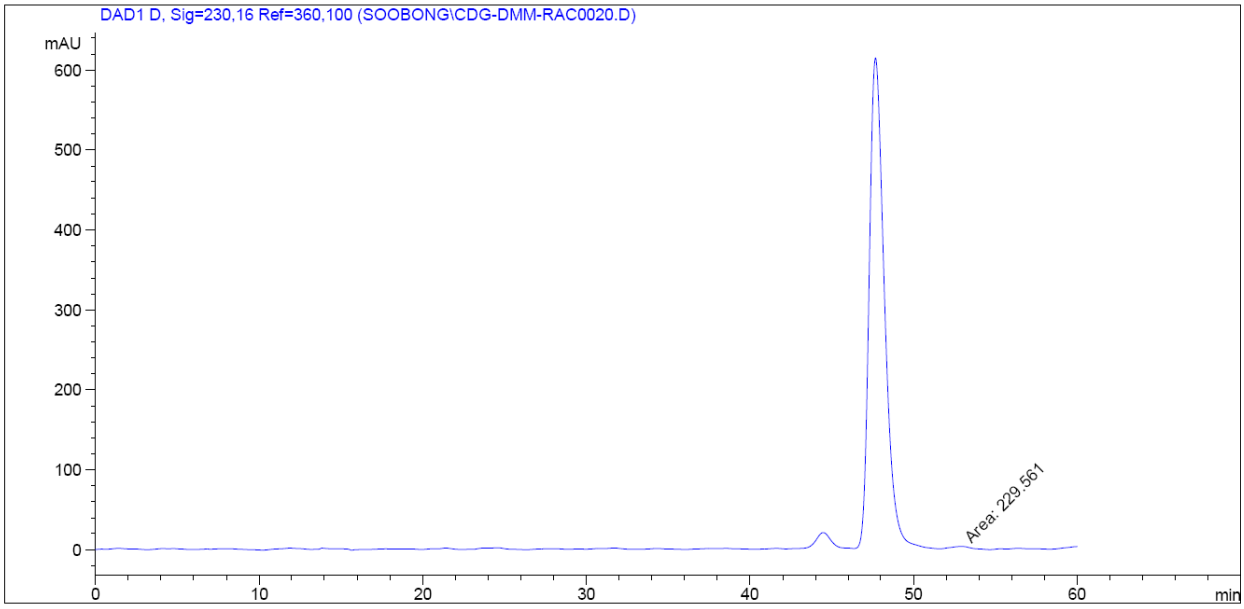
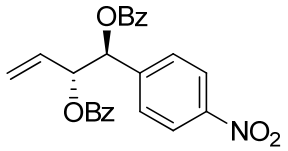


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.477	BB	1.0228	2862.70825	43.78297	7.0007
2	47.975	BB	0.9641	1.90887e4	304.19873	46.6808
3	52.524	BB	0.8964	1.89405e4	324.77338	46.3185



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.658	BB	0.9798	3.95134e4	613.18939	99.4224
2	52.899	MM	0.8887	229.56148	4.30505	0.5776

(1*S*, 2*R*)-1-(4-nitrophenyl)but-3-ene-1, 2-diyl dibenzoate



3d

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). 4-Nitrobenzaldehyde **2d** (30 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. Benzoyl chloride (116 μL, 1.0 mmol, 500 mol%), Et_3N (270 μL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:10) provided **3d** (64 mg, 0.154 mmol) as a colorless oil in 77% yield (11:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.22 (m, 2H), 8.09-8.06 (m, 2H), 7.99-7.96 (m, 2H), 7.68-7.66 (m, 2H), 7.62-7.56 (m, 2H), 7.50-7.42 (m, 4H), 6.36 (d, *J* = 4.4 Hz, 1H), 6.02-5.92 (m, 2H), 5.41-5.36 (m, 2H).

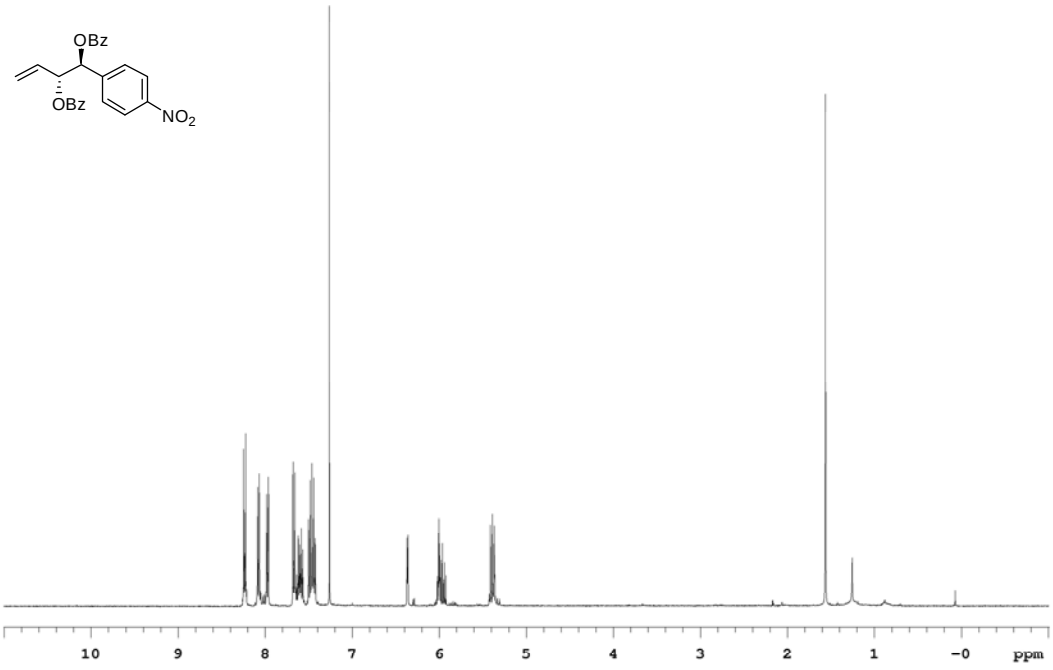
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 147.9, 143.3, 133.7, 133.5, 130.9, 129.8, 129.6, 129.4, 129.2, 128.7, 128.6, 128.2, 123.6, 120.7, 75.8, 75.6.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 230 nm), t_{minor} = 35.7 min, t_{major} = 44.1 min; ee = 99%.

$[\alpha]_D^{25}$= -25.3 (c =0.75, CH_2Cl_2).

FTIR (neat): 1721, 1602, 1522, 1451, 1347, 1315, 1262, 1177, 1095, 1069, 1026, 987, 937, 855, 709 cm^{-1}.

HRMS (CI) Calcd. for $C_{24}H_{20}O_6N$ $[M+H]^+$: 418.1291, Found: 418.1289.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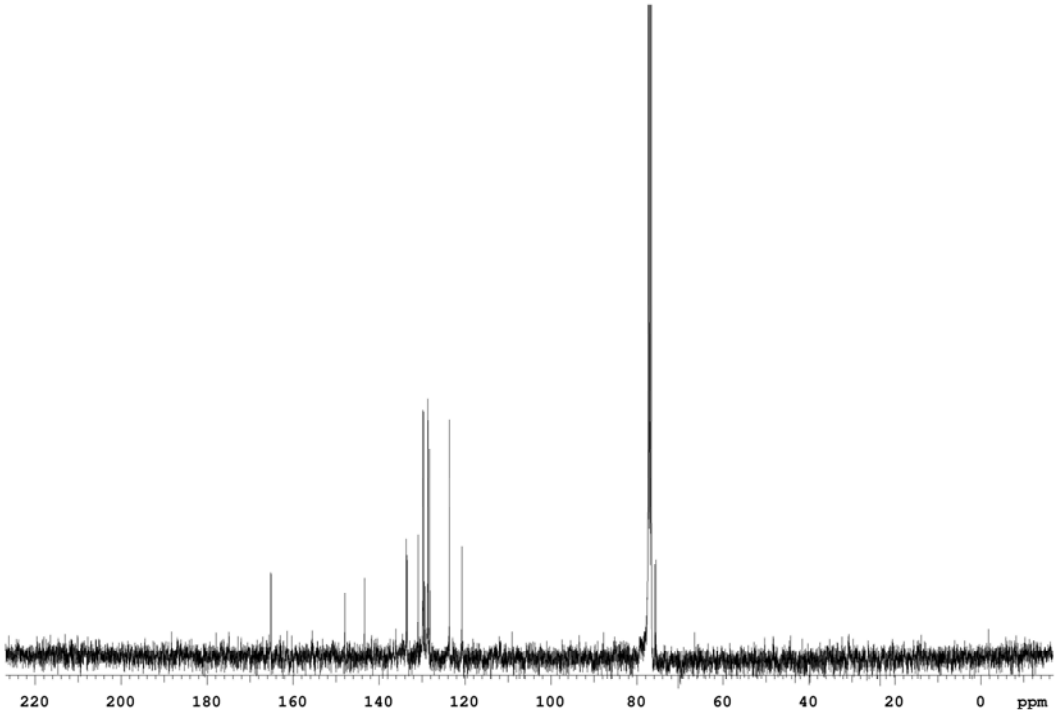
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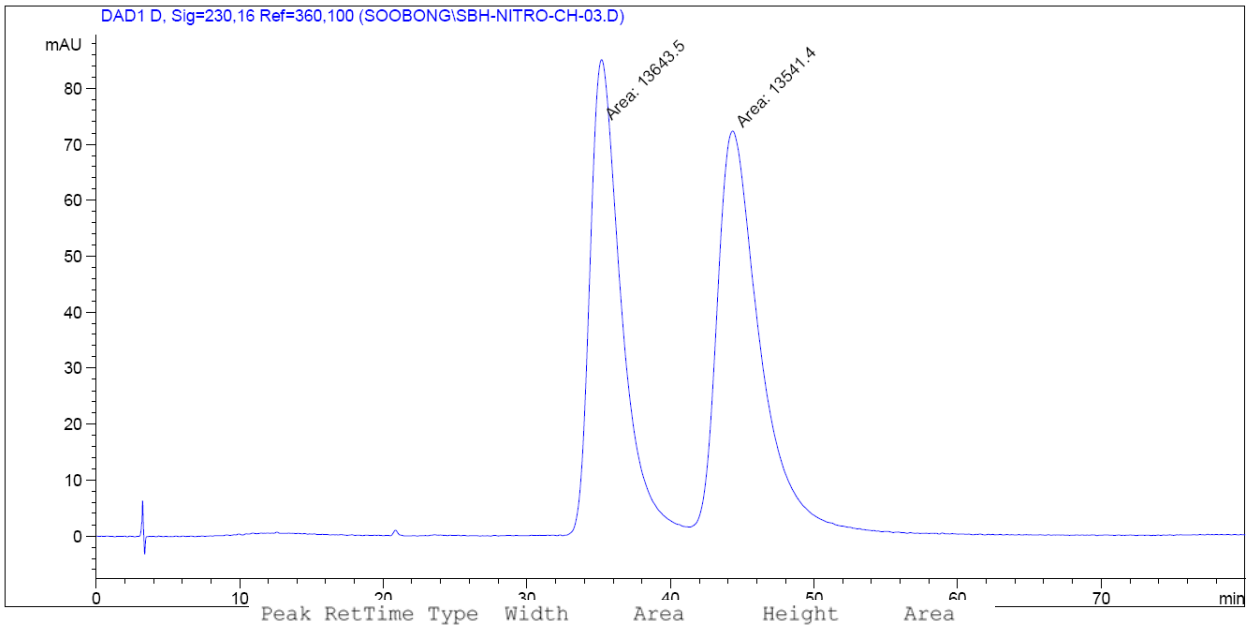
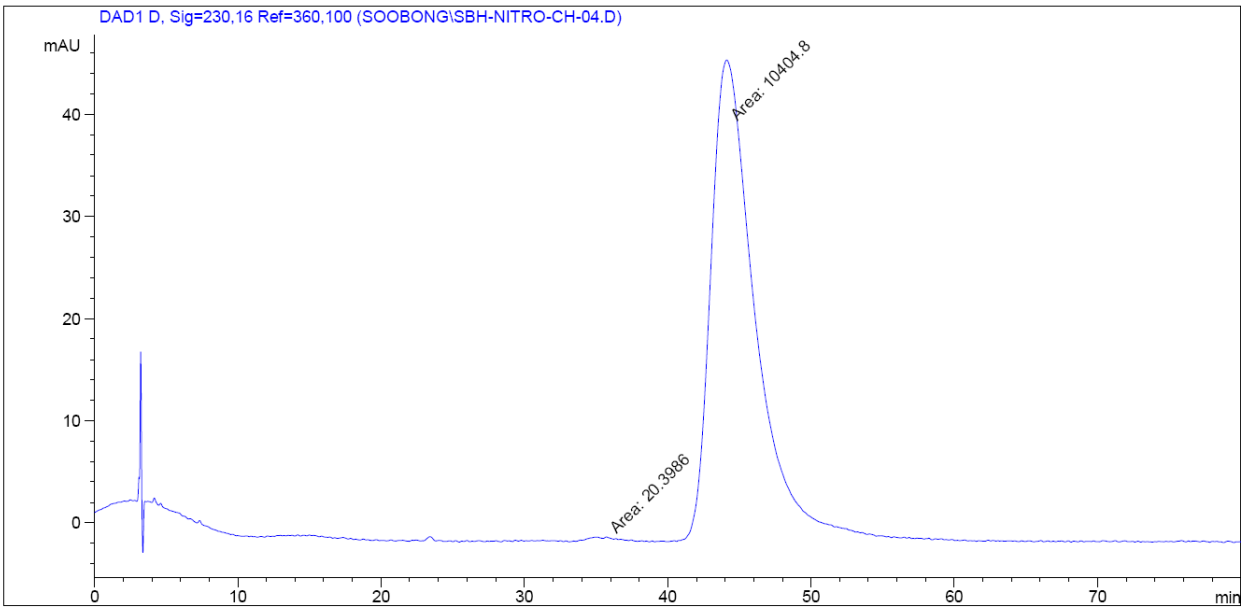
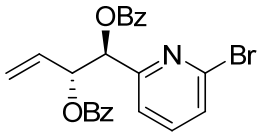


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.186	MM	2.6607	1.36435e4	85.46252	50.1878
2	44.315	MM	3.0993	1.35414e4	72.81871	49.8122



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.716	MM	1.4756	20.39858	2.30392e-1	0.1957
2	44.110	MM	3.6663	1.04048e4	47.29942	99.8043

(1*S*, 2*R*)-1-(6-bromopyridin-2-yl)but-3-ene-1, 2-diyl dibenzoate



3e

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). 6-Bromopyridine-2-carboxaldehyde **2e** (37 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. Benzoyl chloride (116 µL, 1.0 mmol, 500 mol%), Et_3N (270 µL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:7) provided **3e** (64 mg, 0.142 mmol) as a colorless oil in 71% yield (10:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.10 (m, 2H), 7.99-7.97 (m, 2H), 7.63-7.60 (m, 1H), 7.57-7.47 (m, 4H), 7.43-7.38 (m, 4H), 6.41 (d, J = 4.8 Hz, 1H), 6.19-6.16 (m, 1H), 6.06-5.98 (m, 1H), 5.42-5.32 (m, 2H).

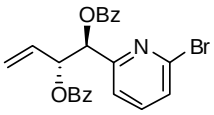
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 165.1, 157.4, 141.5, 138.8, 133.5, 133.1, 131.2, 129.9, 129.8, 129.7, 129.4, 128.6, 128.4, 127.7, 120.3, 120.1, 76.3, 75.6.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 230 nm), t_{major} = 20.4 min, t_{minor} = 33.5 min; ee = 99%.

$[\alpha]_D^{25}$= +1.96 (c =1.53, CH_2Cl_2).

FTIR (neat): 1721, 1601, 1582, 1558, 1451, 1436, 1409, 1315, 1263, 1177, 1157, 1105, 1094, 1069, 1026, 986, 937, 795, 735, 708, 687, 670 cm^{-1}.

HRMS (CI) Calcd. for $C_{23}H_{19}NO_4Br$ $[M+H]^+$: 452.0497, Found: 452.0501.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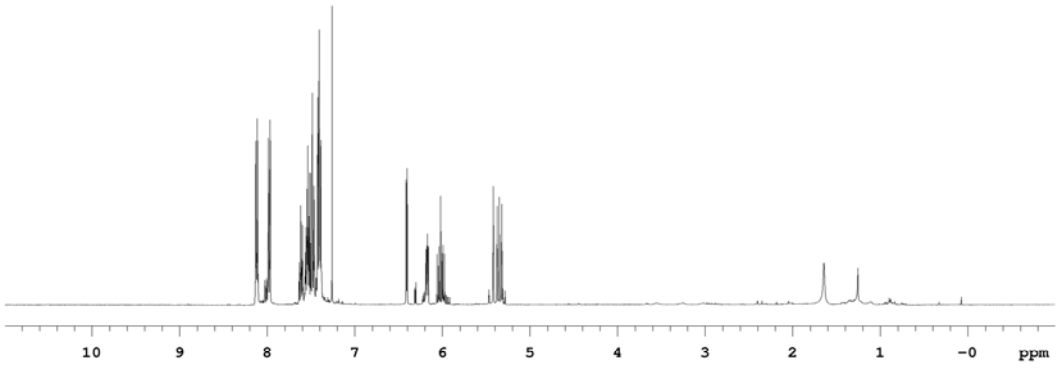
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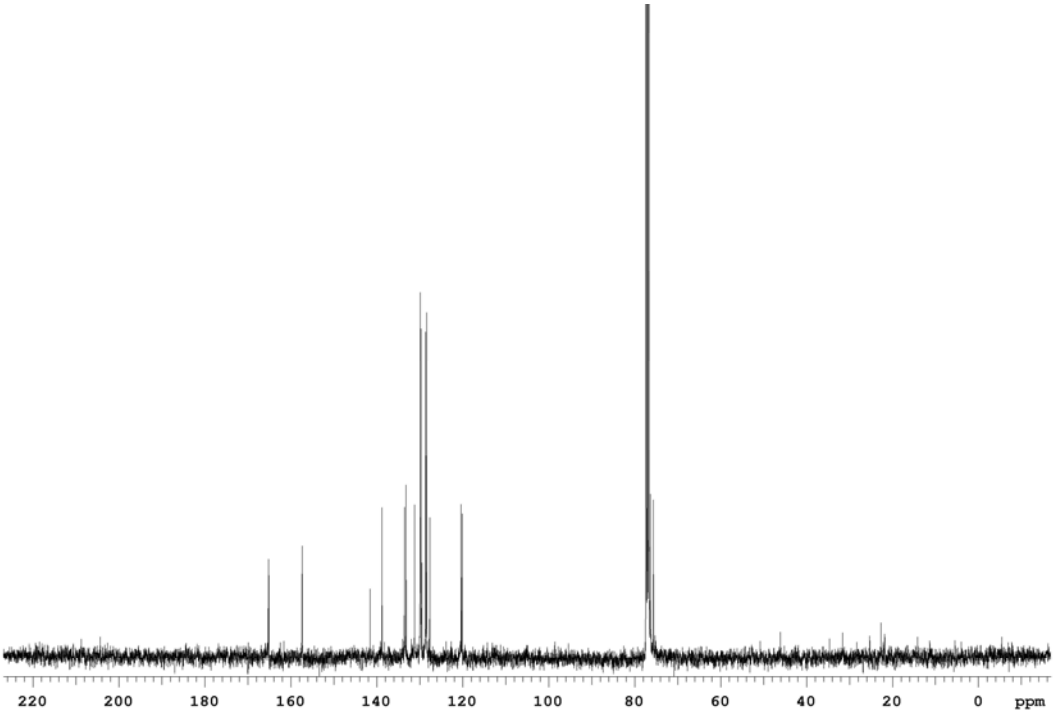
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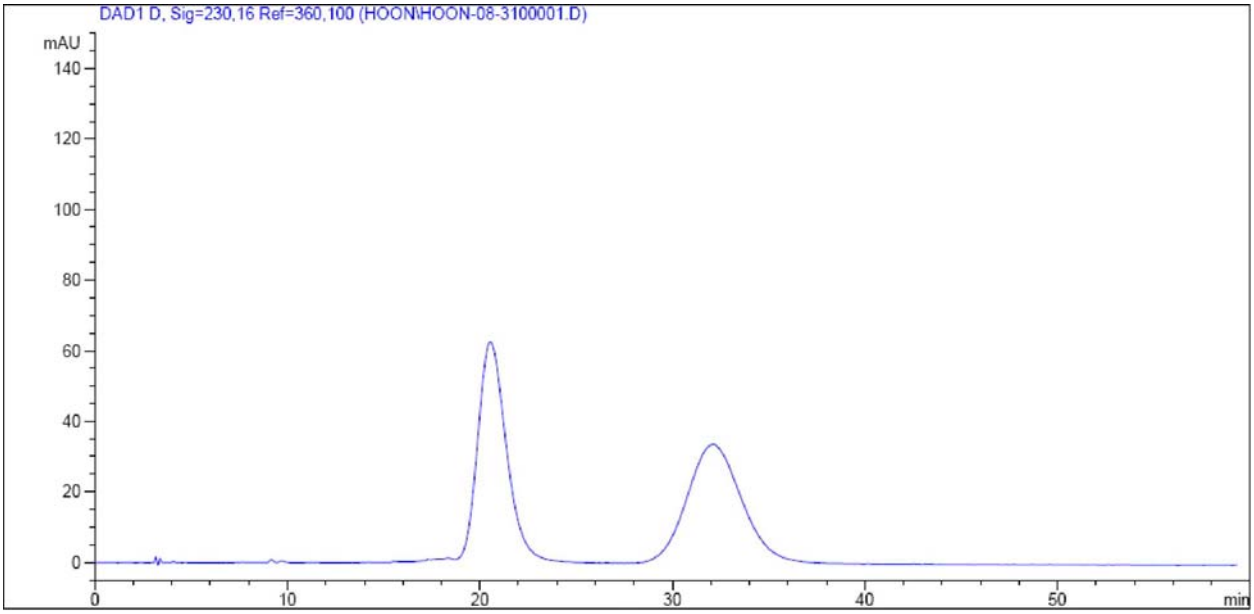

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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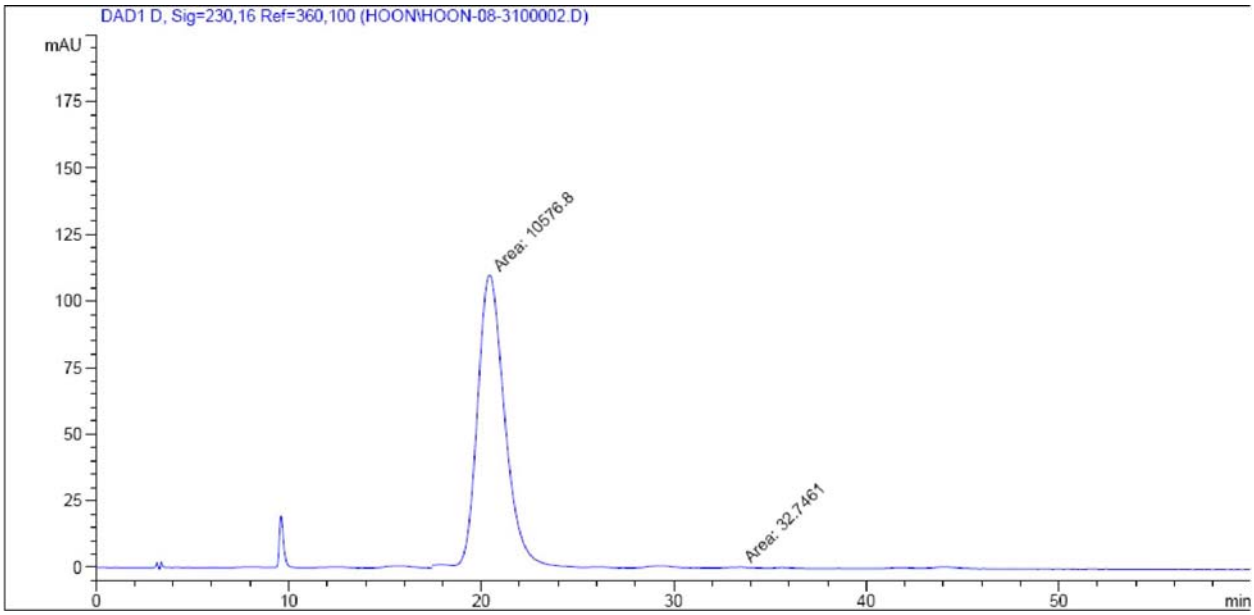
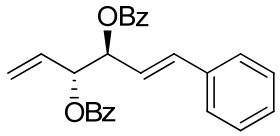
2	32.106	BB	2.9883	6655.58203	33.75521	50.2987



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.424	MM	1.6123	1.05768e4	109.33726	99.6914
2	33.460	MM	0.7790	32.74608	7.00597e-1	0.3086

(3*S*, 4*R*, *E*)-1-phenylhexa-1,5-diene-3, 4-diyl dibenzoate



3f

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). Cinnamaldehyde **2f** (26 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 72 hr, at which point the reaction mixture was cooled to ambient temperature. Benzoyl chloride (116 μL, 1.0 mmol, 500 mol%), Et_3N (270 μL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:20) provided **3f** (65 mg, 0.164 mmol) as a colorless oil in 82% yield (16:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.04 (m, 4H), 7.59-7.55 (m, 2H), 7.47-7.40 (m, 6H), 7.35-7.26 (m, 3H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.34 (dd, *J* = 17.2, 7.6 Hz, 1H), 6.11-6.03 (m, 1H), 6.00-5.97 (m, 1H), 5.90-5.87 (m, 1H), 5.52 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.41 (dt, *J* = 10.4, 1.2 Hz, 1H).

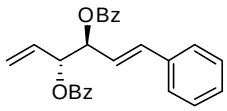
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 135.9, 135.3, 133.2, 131.8, 130.0, 129.9, 129.7, 128.6, 128.4, 128.3, 126.8, 122.6, 120.0, 75.8, 75.5.

HPLC: (Chiralcel OD-H + OD-H columns, hexanes:*i*-PrOH = 95:5, 0.3 mL/min, 254 nm), t_{minor} = 39.4 min, t_{major} = 40.7 min; ee = 94%.

$[\alpha]_D^{25}$= +14.26 (c =2.23, CH_2Cl_2).

FTIR (neat): 1720, 1602, 1451, 1315, 1264, 1177, 1108, 1069, 1026, 967, 734, 708 cm^{-1}.

HRMS (CI) Calcd. for $C_{26}H_{23}O_4$ $[M+H]^+$: 399.1596, Found: 399.1593.


OBz
OBz

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10
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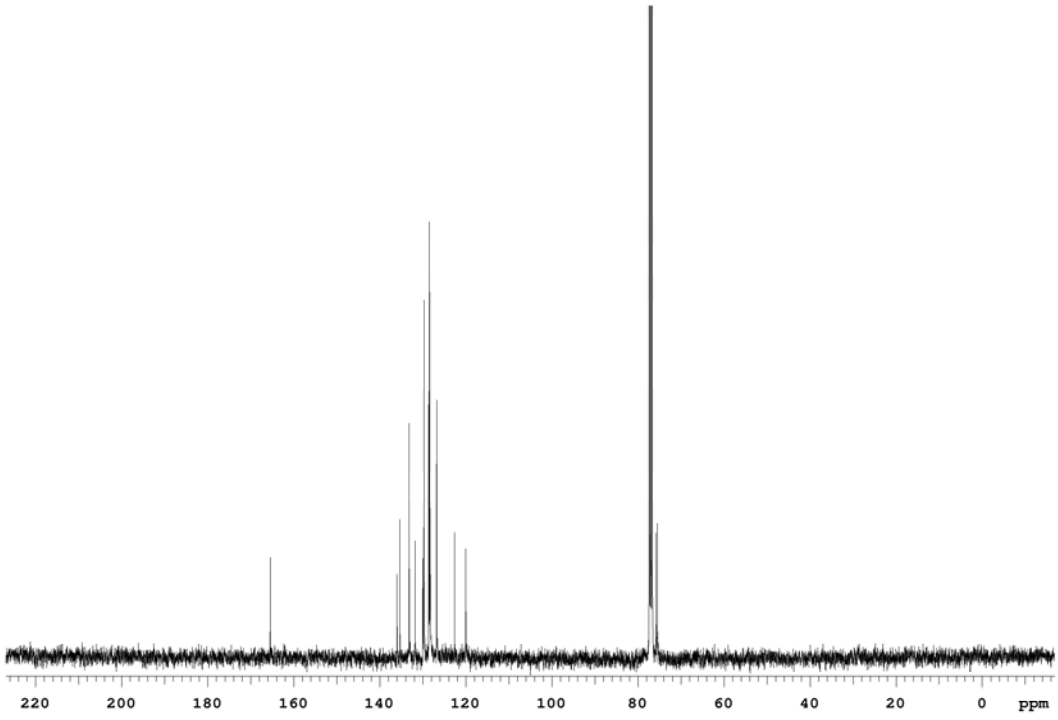
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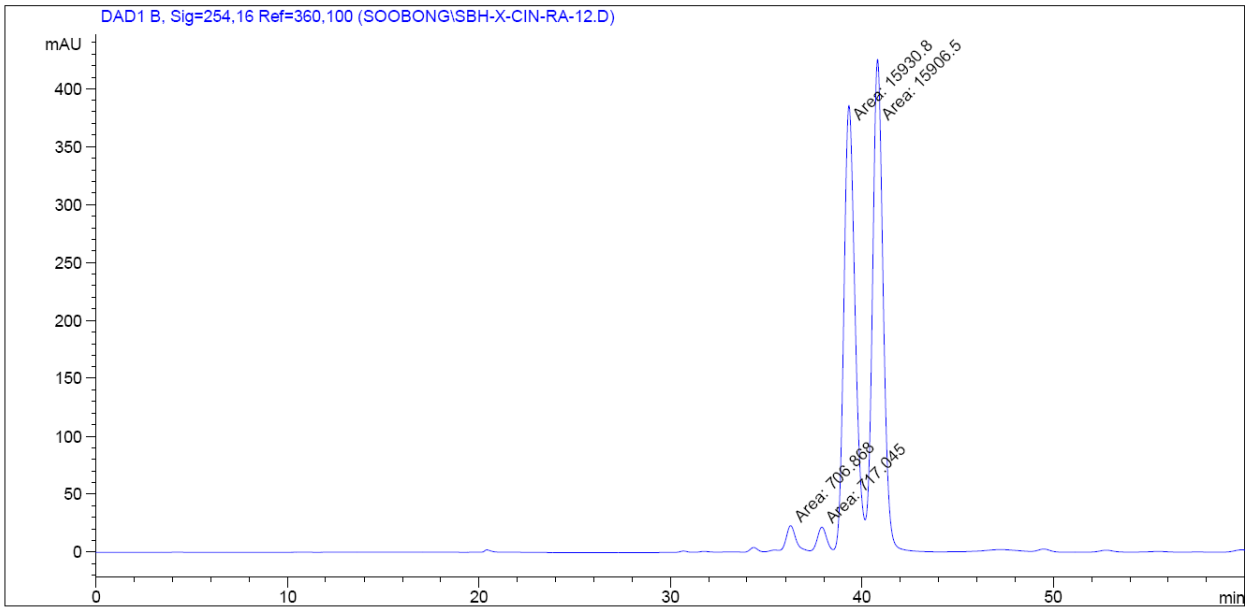
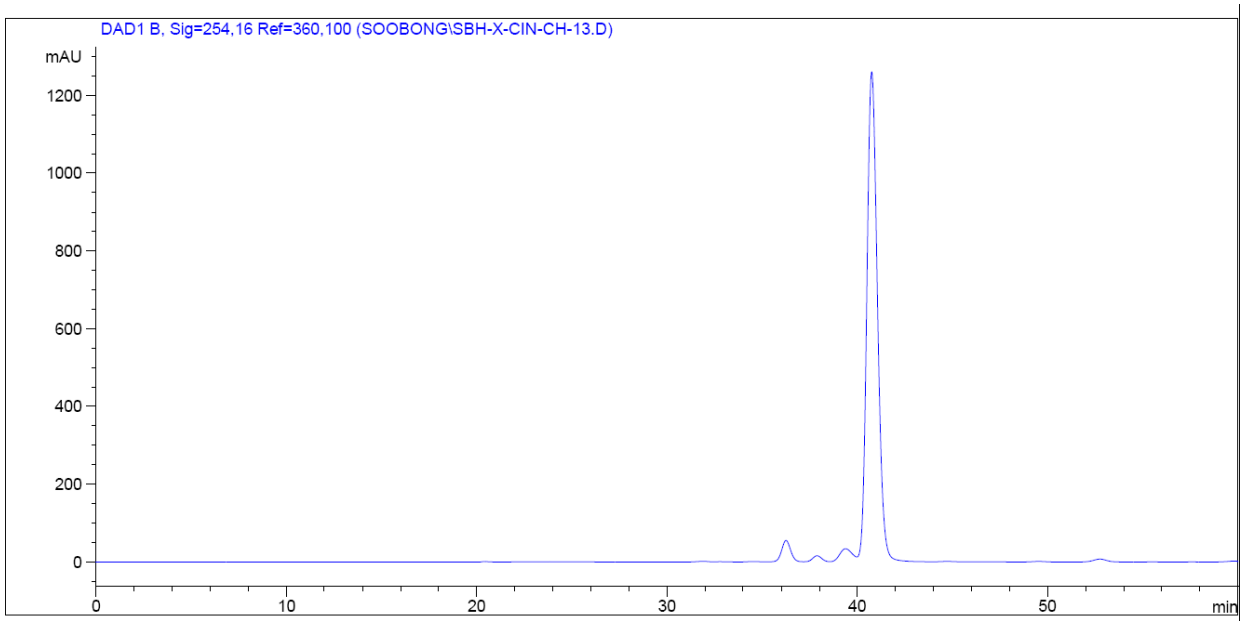
ppm

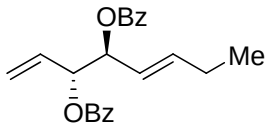


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.266	MM	0.5374	706.86798	21.92301	2.1252
2	37.899	MM	0.5642	717.04517	21.18078	2.1558
3	39.313	MM	0.6888	1.59308e4	385.44916	47.8961
4	40.806	MM	0.6238	1.59065e4	424.95596	47.8229



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.372	VV	0.7025	1492.40503	33.07291	2.9853
2	40.747	VB	0.6012	4.85001e4	1259.55396	97.0147

(3*R*, 4*S*, *E*)-octa-1,5-diene-3,4-diyl dibenzoate



3g

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). (*E*)-Pent-3-enal **2g** (17 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. Benzoyl chloride (116 μL, 1.0 mmol, 500 mol%), Et_3N (270 μL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:20) provided **3g** (50 mg, 0.142 mmol) as a colorless oil in 71% yield (13:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.02 (m, 4H), 7.58-7.54 (m, 2H), 7.45-7.41 (m, 4H), 6.05-5.96 (m, 2H), 5.78-5.74 (m, 2H), 5.63-5.57 (m, 1H), 5.47 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.37 (dt, *J* = 10.4, 1.2 Hz, 1H), 2.13-2.06 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

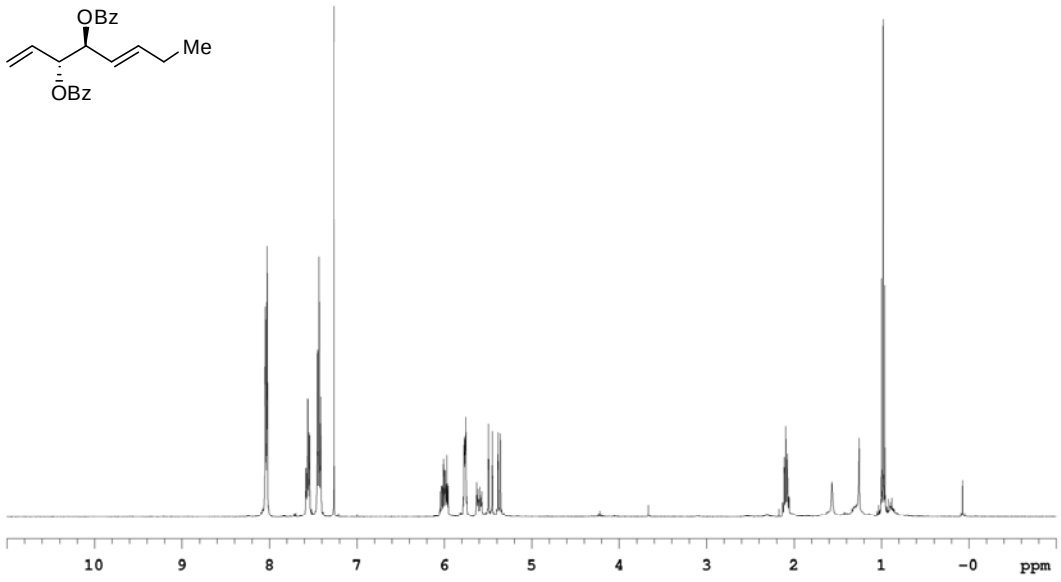
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 139.1, 133.1, 133.0, 131.9, 130.2, 130.1, 129.7, 128.4, 122.4, 119.7, 75.8, 75.6, 25.4, 13.1.

HPLC: (Chiralcel AD-H + AD-H columns, hexanes:*i*-PrOH = 98:2, 0.5 mL/min, 230 nm), t_{major} = 35.3 min, t_{minor} = 37.6 min; ee = 98%.

$[\alpha]_D^{25}$= +9.0 (c =2.00, CH_2Cl_2).

FTIR (neat): 1720, 1452, 1315, 1264, 1212, 1175, 1109, 1070, 1039, 1026, 970, 734, 705 cm^{-1}.

HRMS (CI) Calcd. for $C_{22}H_{23}O_4$ $[M+H]^+$: 351.1596, Found: 351.1599.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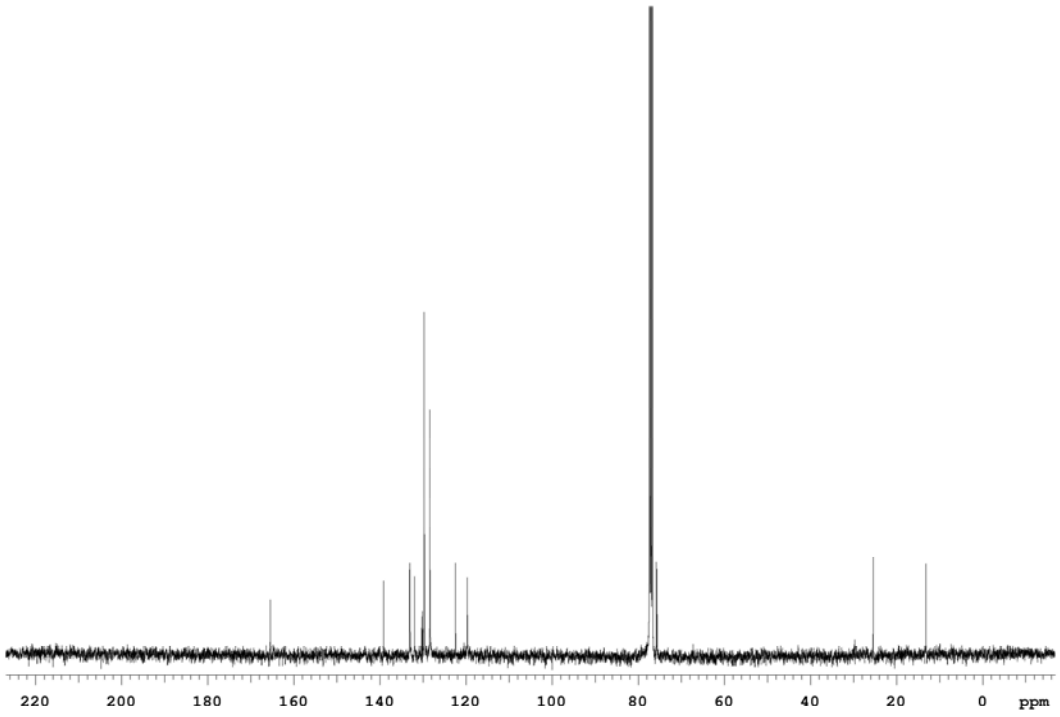
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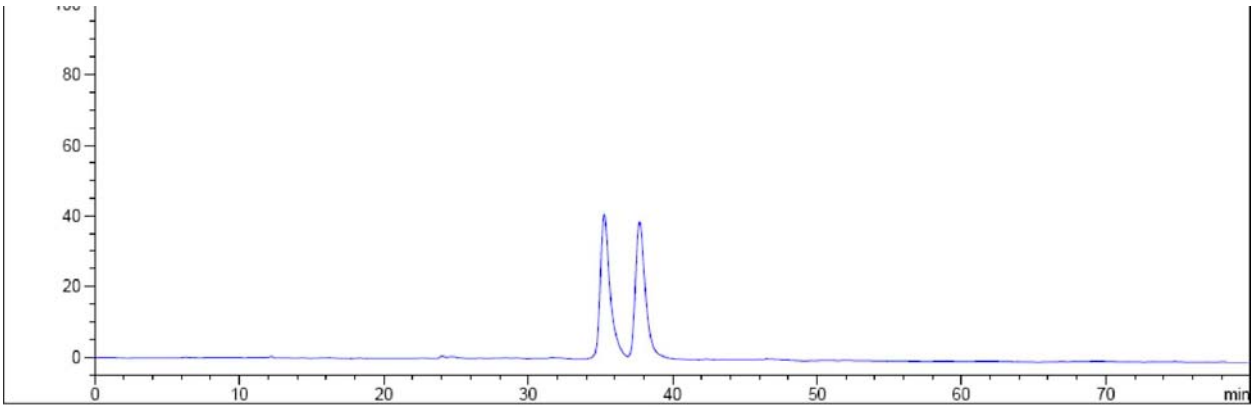

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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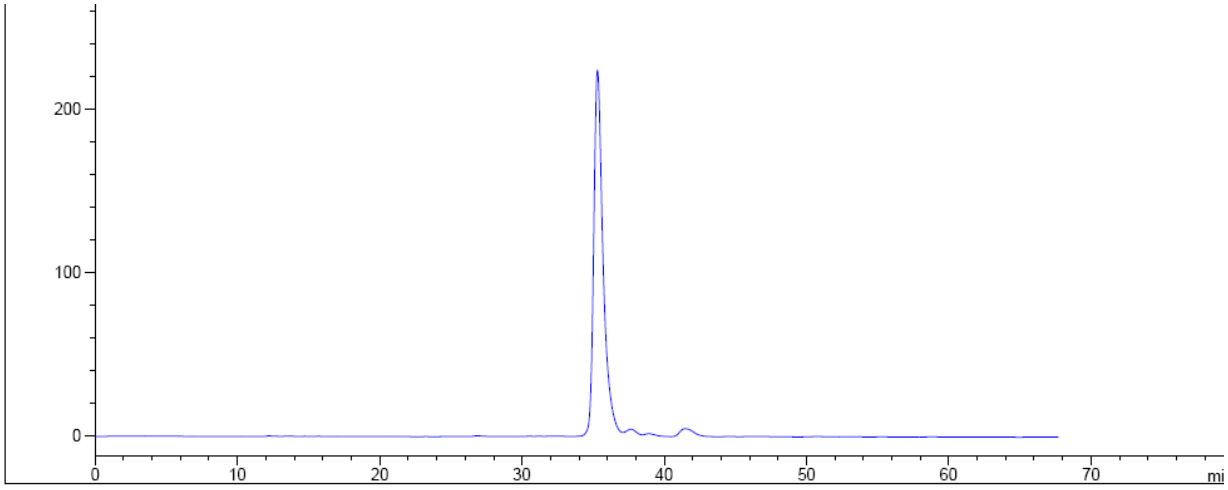
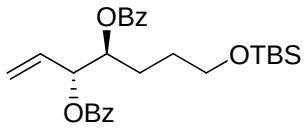
2	37.692	VV	0.7500	1950.56238	39.10119	49.4745



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.294	BB	0.6723	1.00818e4	222.64949	99.2252
2	37.648	BB	0.4330	78.72734	2.33729	0.7748

(3*R*, 4*S*)-7-(tert-butyldimethylsilyloxy)hept-1-ene-3,4-diyl dibenzoate



3h

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). 4-(*tert*-butyldimethylsilyloxy)butanal **2h** (40 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. Benzoyl chloride (116 μL, 1.0 mmol, 500 mol%), Et_3N (270 μL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:20) provided **3h** (66 mg, 0.14 mmol) as a colorless oil in 70% yield (12:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-8.00 (m, 4H), 7.58-7.53 (m, 2H), 7.45-7.39 (m, 4H), 6.05-5.97 (m, 1H), 5.75-5.72 (m, 1H), 5.50-5.45 (m, 2H), 5.37 (dt, *J* = 10.4, 1.2 Hz, 1H), 3.69-3.59 (m, 2H), 1.93-1.86 (m, 2H), 1.66-1.56 (m, 2H), 0.87 (s, 9H), 0.02 (s, 6H).

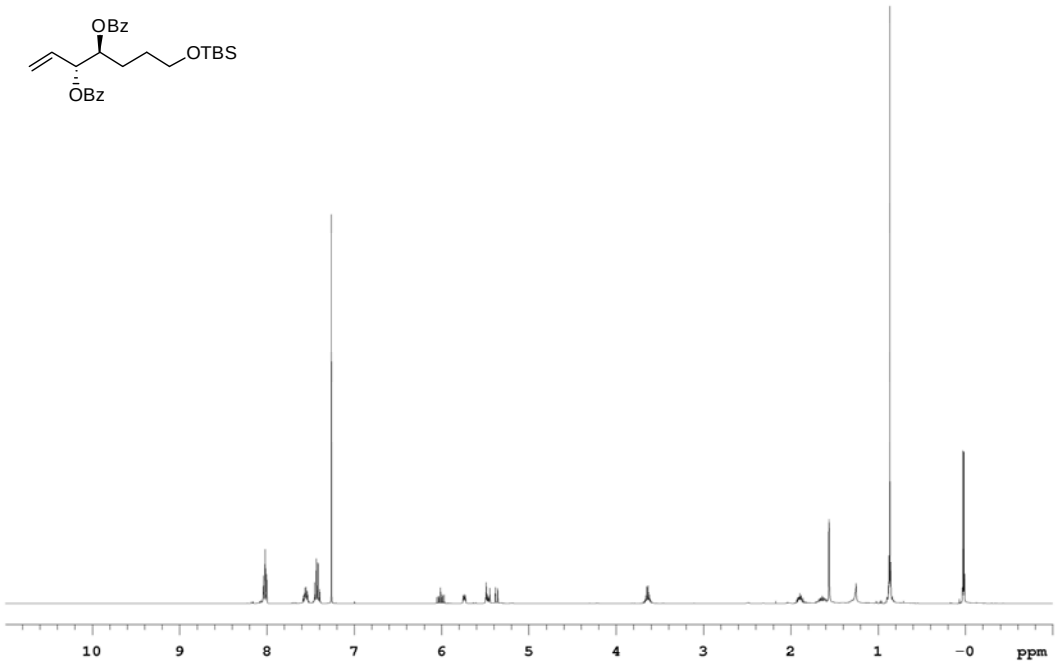
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 165.4, 133.0, 132.0, 130.1, 129.7, 128.4, 119.7, 75.9, 74.3, 62.4, 28.6, 26.3, 25.9, 18.3, -5.3.

HPLC: (Chiralcel AD-H + AD-H columns, hexanes:*i*-PrOH = 99.5:0.5, 0.3 mL/min, 230 nm), t_{major} = 43.9 min, t_{minor} = 51.9 min; ee = 94%.

$[\alpha]_D^{25}$= +6.93 (c =2.02, CH_2Cl_2).

FTIR (neat): 1717, 1451, 1315, 1273, 1247, 1177, 1097, 1059, 1024, 949, 834, 776, 737, 708, 687 cm^{-1}.

HRMS (CI) Calcd. for $C_{27}H_{37}O_5Si$ $[M+H]^+$: 469.2410, Found: 469.2419.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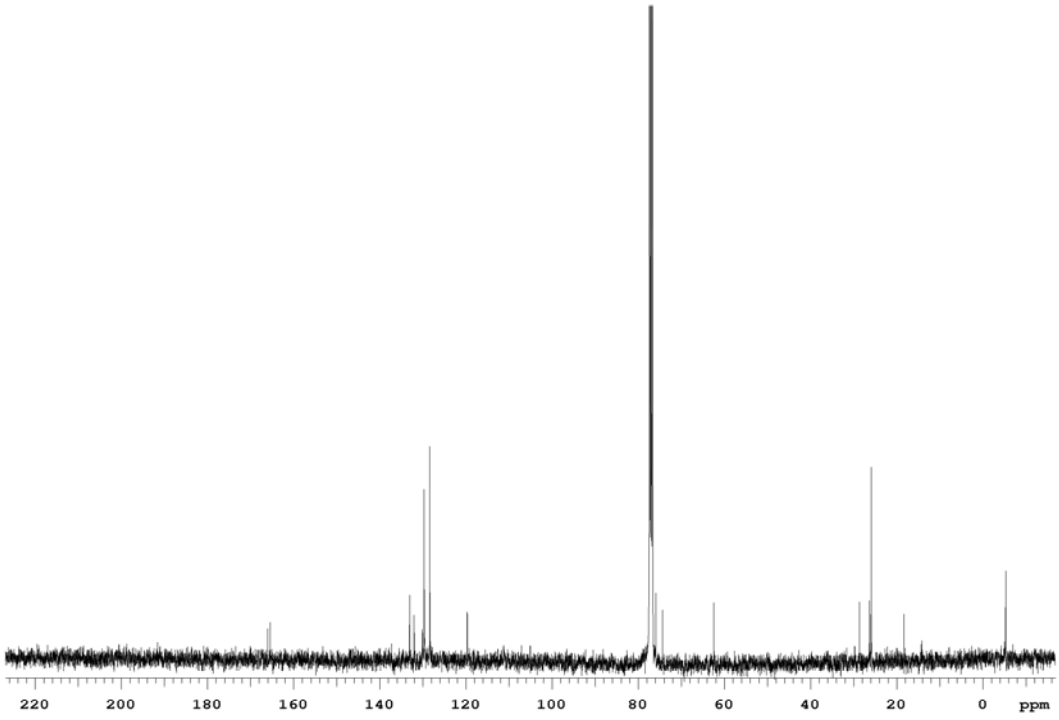
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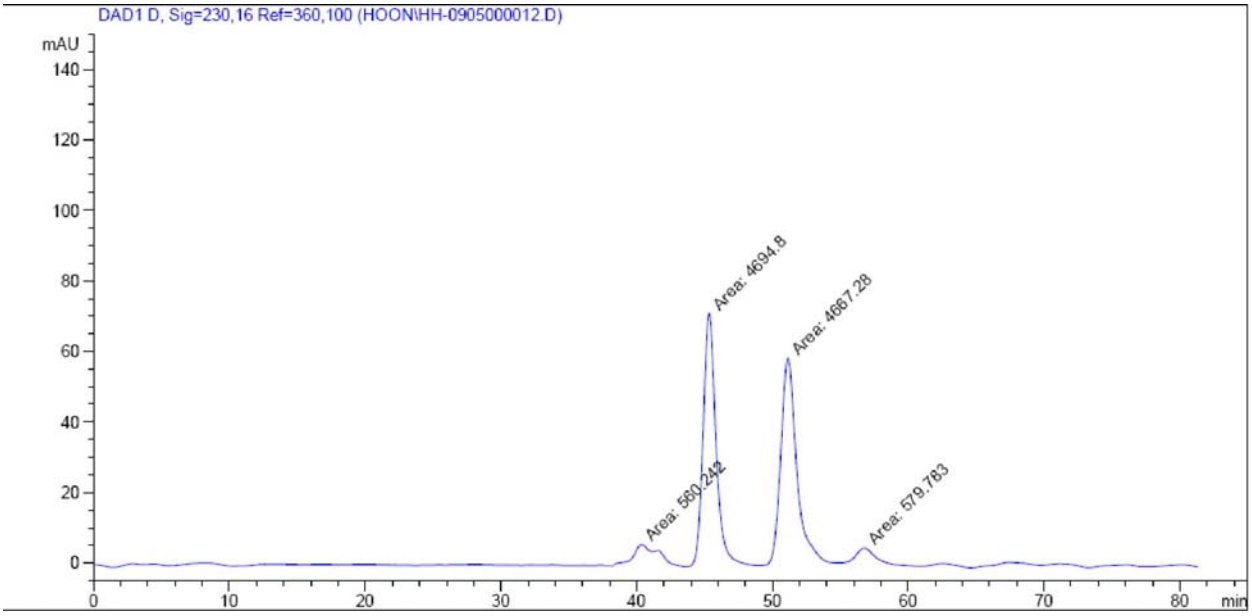
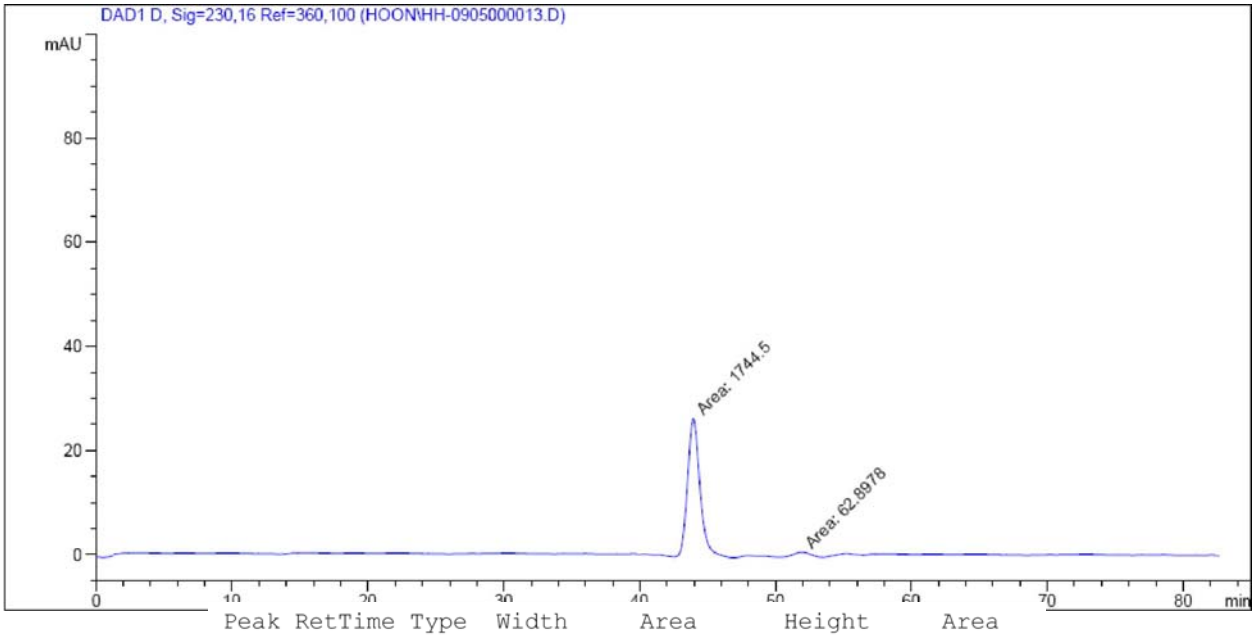
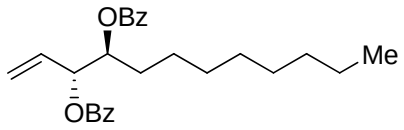


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.341	MM	1.7646	560.24200	5.29159	5.3346
2	45.319	MM	1.0921	4694.80225	71.64735	44.7034
3	51.122	MM	1.3344	4667.28418	58.29272	44.4414
4	56.784	MM	1.9118	579.78314	5.05436	5.5206



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.938	MM	1.0875	1744.50208	26.73516	96.5200
2	51.910	MM	1.2049	62.89781	8.70048e-1	3.4800

(3*R*, 4*S*)-dodec-1-ene-3, 4-diyl dibenzoate



3i

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). Nonanal **2i** (28 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. Benzoyl chloride (116 µL, 1.0 mmol, 500 mol%), Et_3N (270 µL , 2.0 mmol, 1000 mol%), DMAP (1.2 mg , 0.01 mmol, 5 mol%) and CH_2Cl_2 (0.6 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 20 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:20) provided **3i** (58 mg, 0.142 mmol) as a colorless oil in 71% yield (13:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.00 (m, 4H), 7.59-7.53 (m, 2H), 7.47-7.40 (m, 4H), 6.07-5.98 (m, 1H), 5.73-5.70 (m, 1H), 5.49-5.45 (m, 2H), 5.37 (dt, *J* = 10.4, 1.2 Hz, 1H), 1.84-1.74 (m, 2H), 1.45-1.24 (m, 12H), 0.86 (t, *J* = 7.2 Hz, 3H)

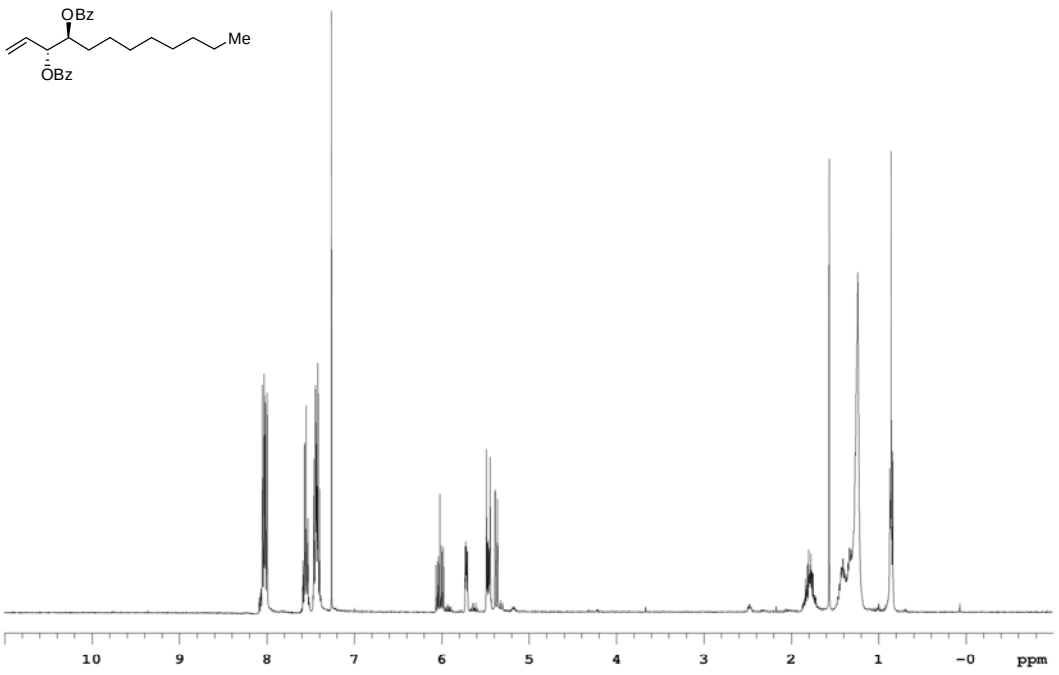
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 165.4, 133.0, 132.9, 132.0, 130.2, 130.1, 130.0, 128.4, 119.7, 75.9, 74.5, 31.8, 30.0, 29.4, 29.3, 29.2, 25.4, 22.6, 14.1.

HPLC: (Chiralcel AD-H + OD-H columns, hexanes:*i*-PrOH = 99:1, 0.3 mL/min, 230 nm), t_{major} = 39.3 min, t_{minor} = 42.4 min; ee = 97%.

$[\alpha]_D^{25}$= +8.47 (c =1.77, CH_2Cl_2).

FTIR (neat): 1721, 1602, 1452, 1315, 1264, 1177, 1108, 1080, 1060, 1024, 949, 802, 736, 708, 687 cm^{-1}.

HRMS (CI) Calcd. for $C_{26}H_{33}O_4$ $[M+H]^+$: 409.2379, Found: 409.2379.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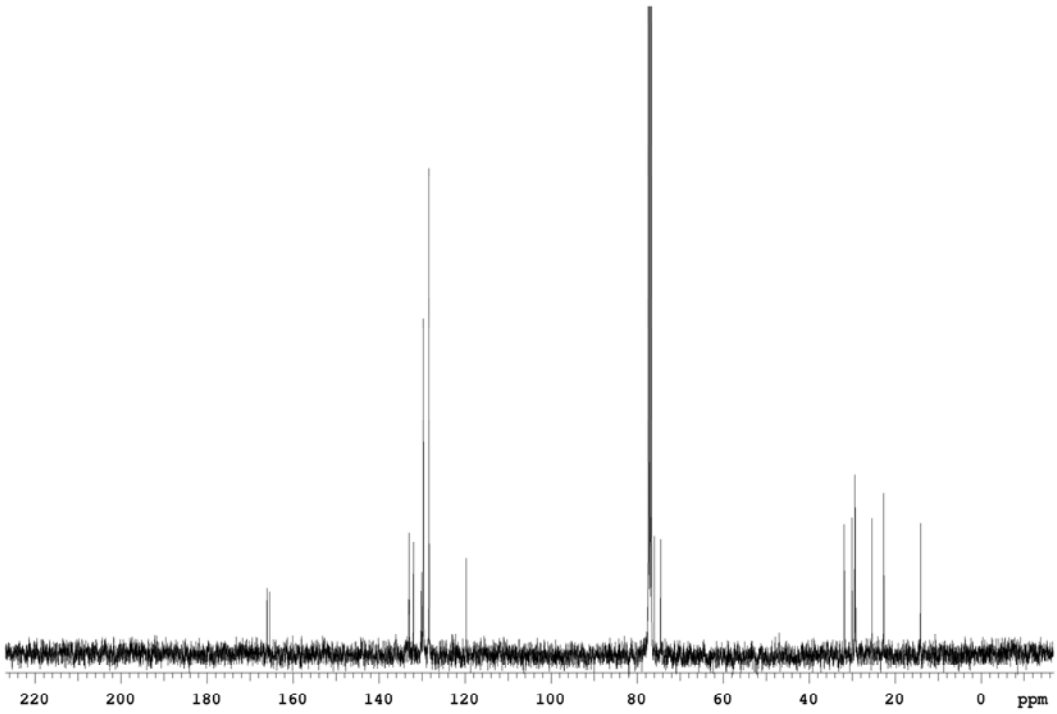
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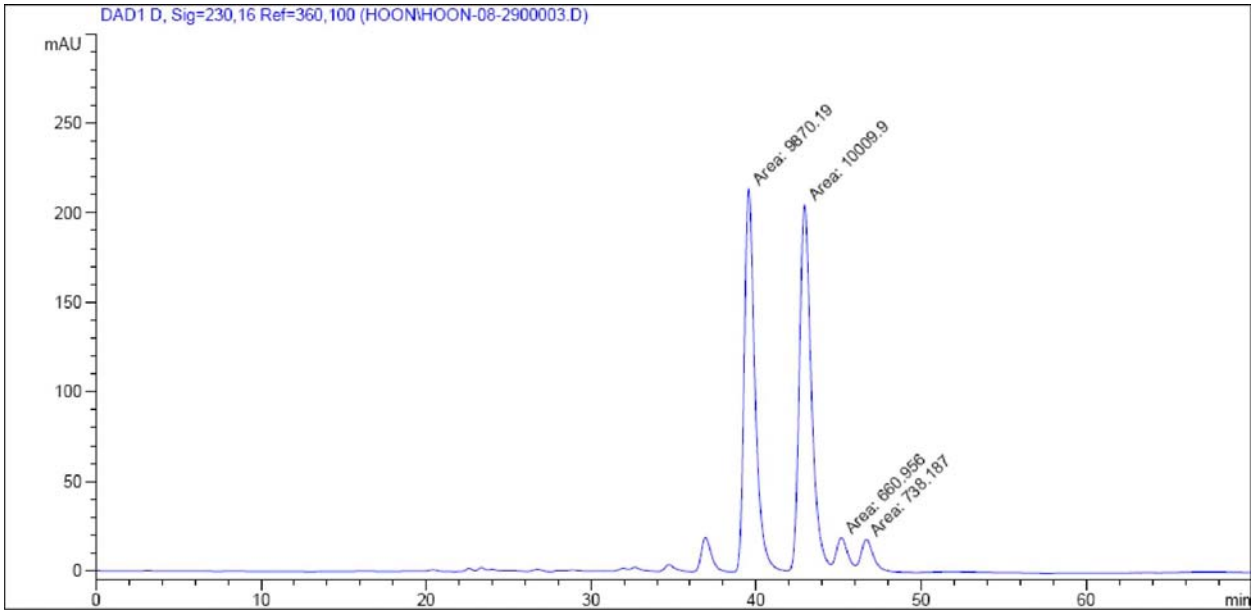
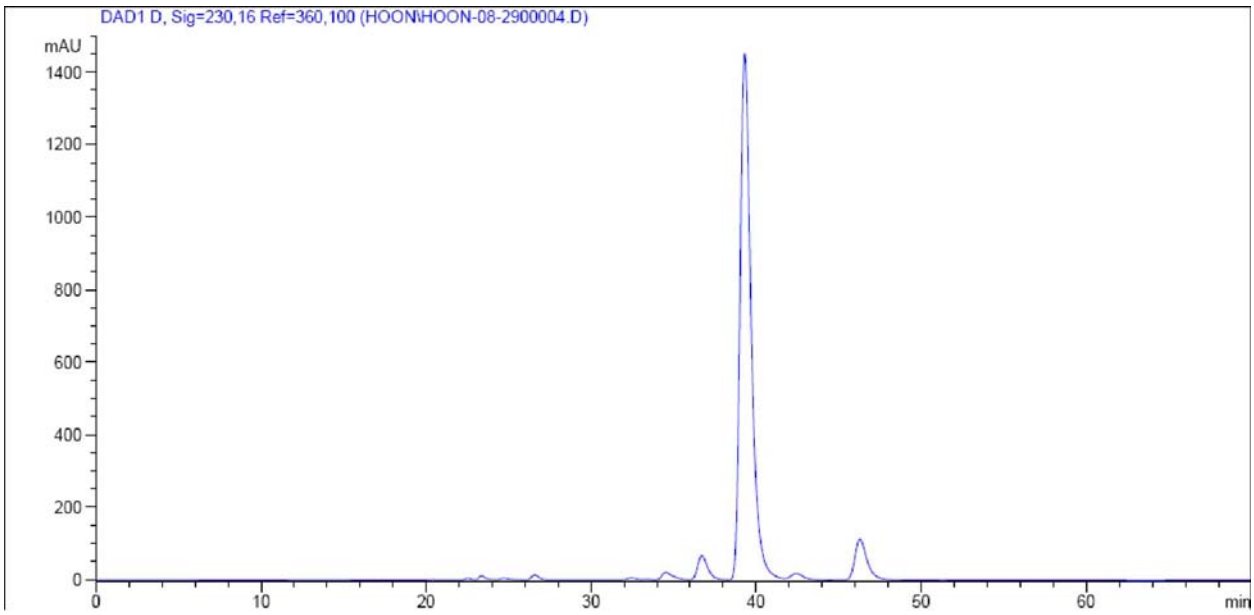
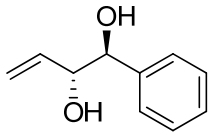


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.538	MM	0.7659	9870.18652	214.78496	46.3842
2	42.922	MM	0.8208	1.00099e4	203.26117	47.0406
3	45.147	MM	0.6987	660.95630	15.76637	3.1061
4	46.666	MM	0.7657	738.18695	16.06814	3.4691



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.300	VV	0.7131	6.78376e4	1451.94287	98.4050
2	42.425	VV	0.8677	1099.52930	18.76268	1.5950

(1*S*,2*R*)-1-phenylbut-3-ene-1, 2-diol[3]



4a

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). Benzaldehyde **2a** (21 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. K_2CO_3 (55 mg, 0.4 mmol, 200 mol%) and MeOH (2.0 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 18 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with ethyl acetate. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:10) provided **4a** (25 mg, 0.154 mmol) as a colorless oil in 77% yield (17:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.30 (m, 5H), 5.89-5.74 (m, 1H), 5.38-5.22 (m, 2H), 4.77 (d, J = 4.4 Hz, 1H), 4.35-4.31 (m, 1H), 2.46 (br, 1H), 2.08 (br, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 135.8, 128.3, 127.9, 126.6, 117.9, 76.5 (two carbons overlap).

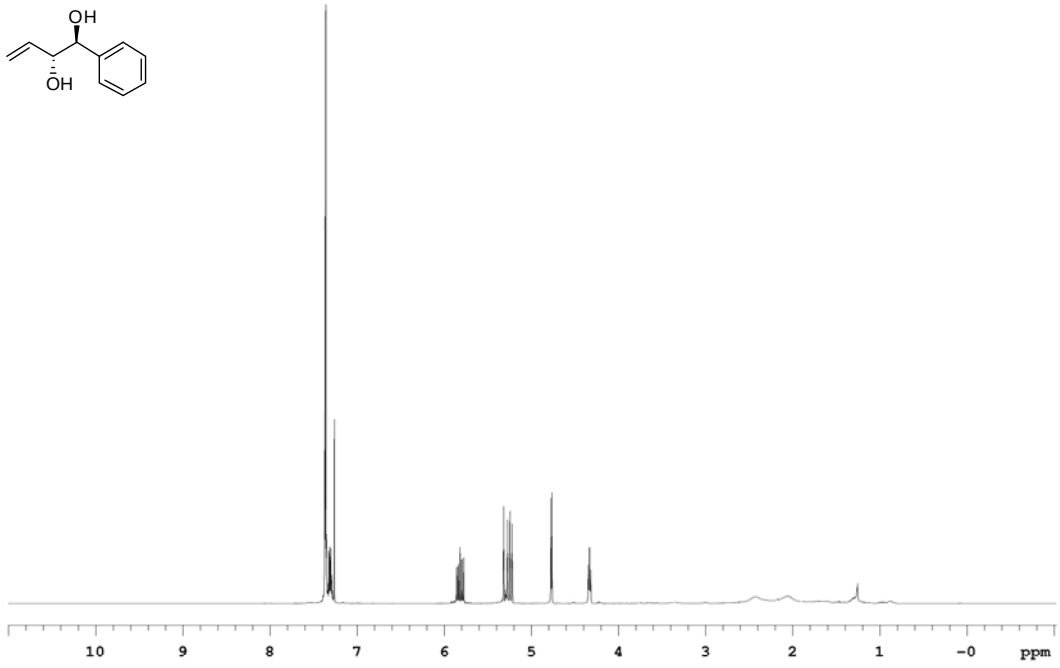
GC: (Cyclosil-B: initial temperature: 100 ^oC (5 min hold), final temperature: 220 ^oC (2 min hold), rate: 2 ^oC/min): t_{major} = 37.2 min, t_{minor} = 37.5 min; ee = 99%.

$[\alpha]_D^{25}$= +71.0 (c =0.91, $CHCl_3$). To corroborate the assignement of absolute stereochemistry, the optical rotation was correlated with a known compound.[3]

FTIR (neat): 3388, 2920, 1494, 1452, 1427, 1197, 1122, 1091, 1063, 1028, 995, 927, 863, 830, 763, 724, 700 cm^{-1}.

HRMS (CI) Calcd. for $C_{10}H_{11}O_2$ $[M-H]^+$: 163.0759, Found: 163.0757.

[3] Lombard, M.; Licciulli, S.; Trombini, C. *Tetrahedron: Asymmetry* **1988**, *9*, 293.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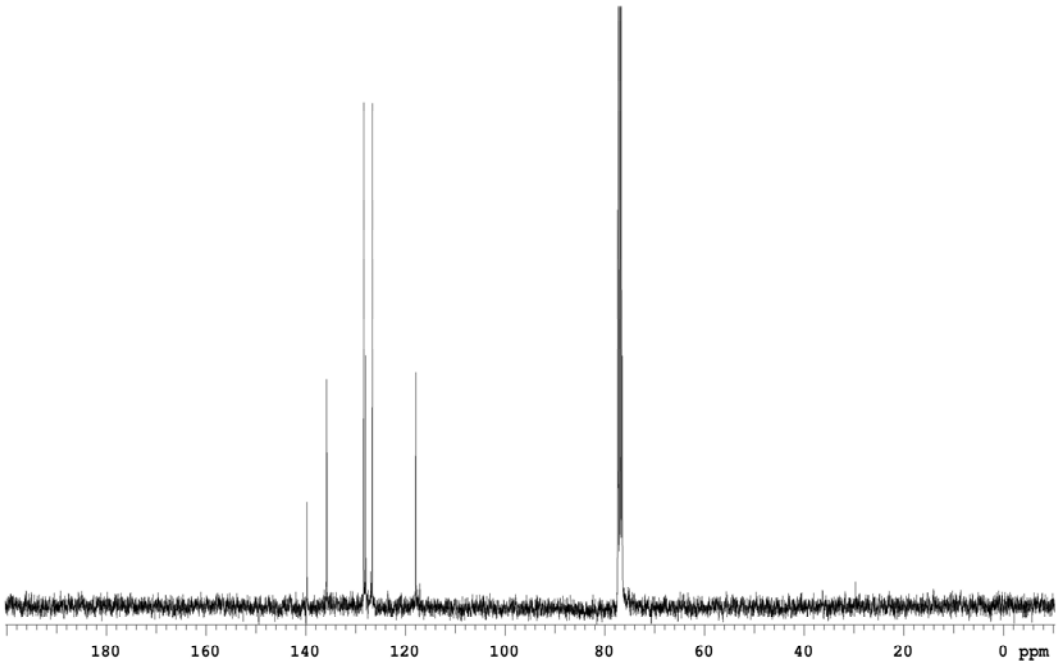
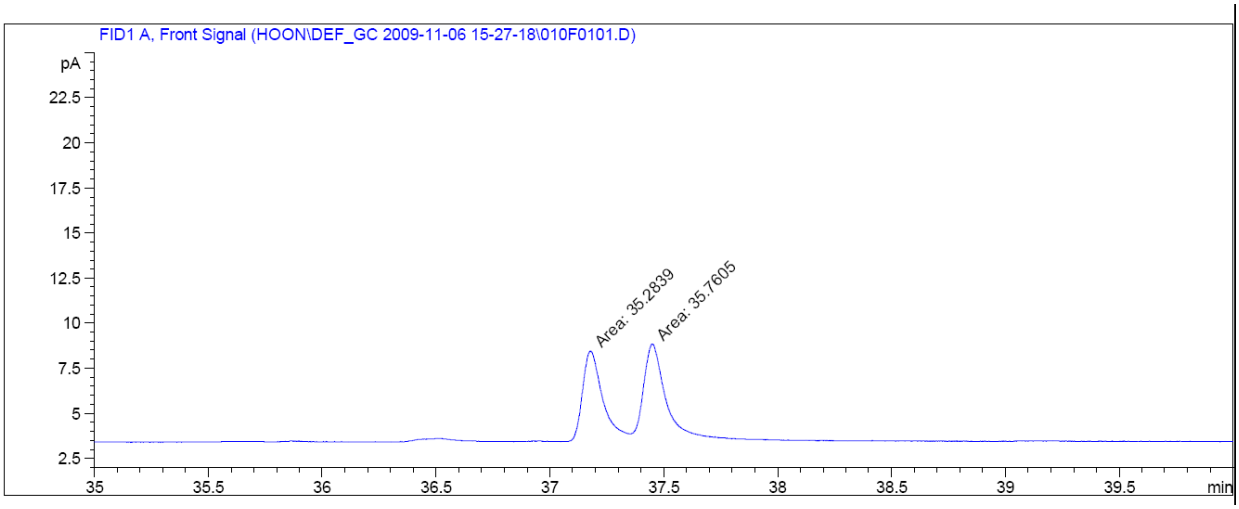
9
8
7
6
5
4
3
2
1
-0
ppm


180
160
140
120
100
80
60
40
20
0 ppm



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
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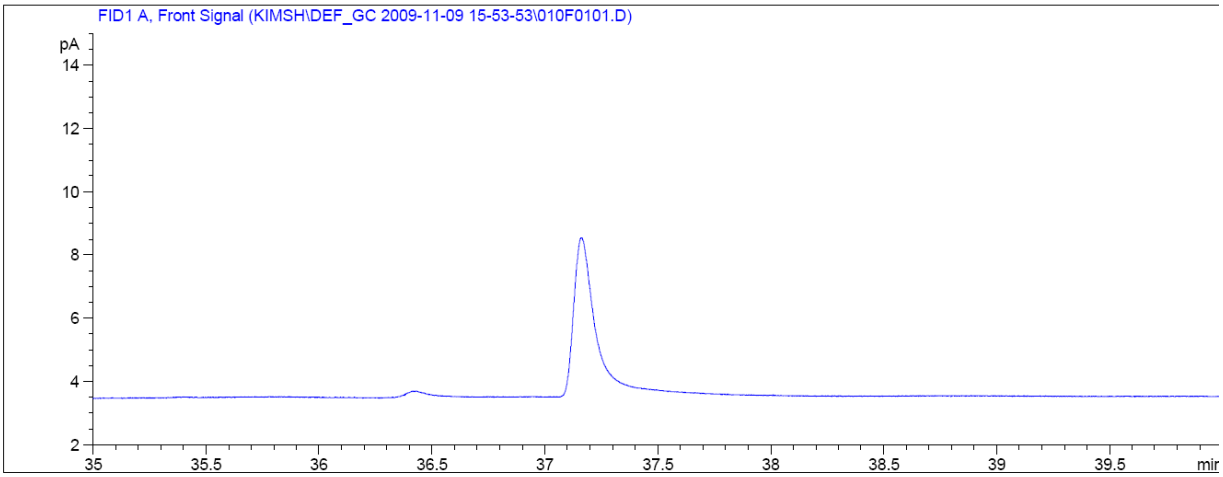
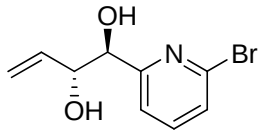


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	37.164	MM	0.1189	36.23504	5.08130	1.000e2

(1*S*, 2*R*)-1-(6-bromopyridin-2-yl)but-3-ene-1, 2-diol



4e

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). 6-Bromopyridine-2-carboxaldehyde **2e** (37 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. K_2CO_3 (55 mg, 0.4 mmol, 200 mol%) and MeOH (2.0 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 18 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with ethyl acetate. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:10) provided **4e** (30 mg, 0.124 mmol) as a colorless oil in 62% yield (7:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.55 (m, 1H), 7.44-7.41 (m, 1H), 7.36-7.33 (m, 1H), 5.84-5.76 (m, 1H), 5.29 (dt, *J* = 17.6, 1.6 Hz, 1H), 5.22 (dt, *J* = 10.8, 1.6 Hz, 1H), 4.74 (d, *J* = 4.8 Hz, 1H), 4.45-4.23 (m, 1H), 3.57 (br, 1H), 2.87 (br, 1H).

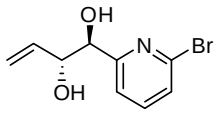
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 140.9, 139.0, 135.7, 127.2, 120.6, 117.9, 76.1, 74.8.

GC: (Cyclosil-B: initial temperature: 120 ^oC (10 min hold), final temperature: 180 ^oC (5min hold), rate: 1.5 ^oC/min): t_{minor} = 47.7 min, t_{major} = 48.2 min; ee = 96%.

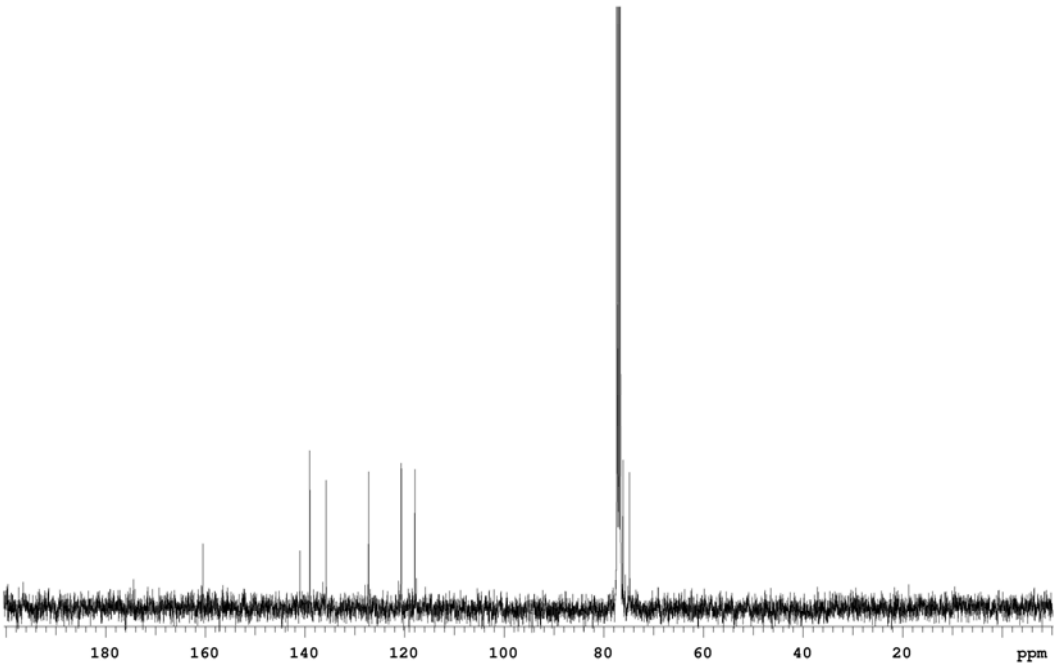
$[\alpha]_D^{25}$= +20.8 (c =0.90, CH_2Cl_2).

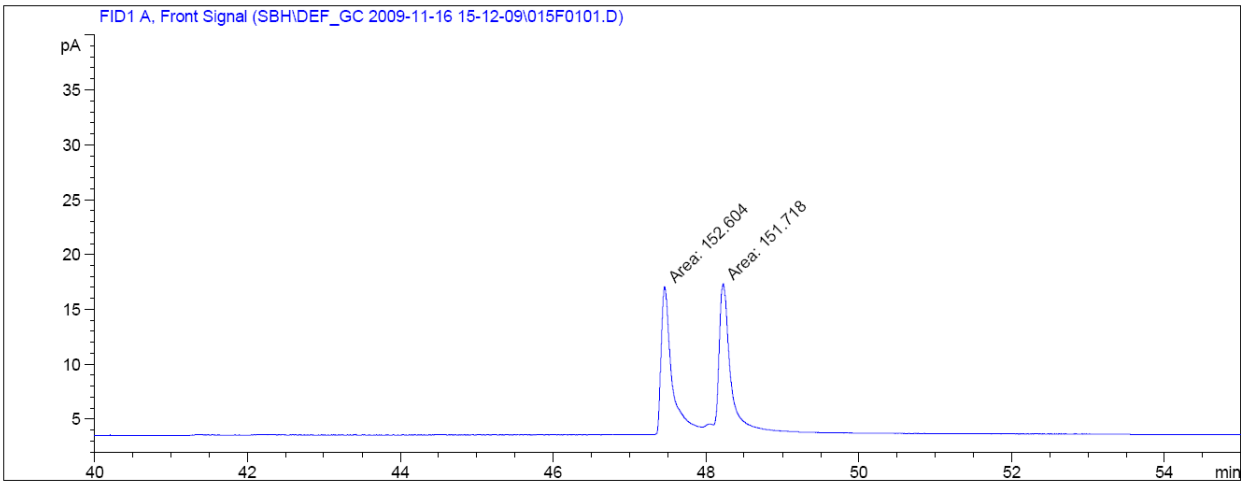
FTIR (neat): 2304, 1557, 1440, 1265, 896, 733, 704 cm^{-1}.

HRMS (CI) Calcd. for $C_9H_{11}NO_2Br$ $[M+H]^+$: 243.9973, Found: 243.9975.


OH
N
Br
OH

10
9
8
7
6
5
4
3
2
1
−0
ppm


180
160
140
120
100
80
60
40
20
ppm



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
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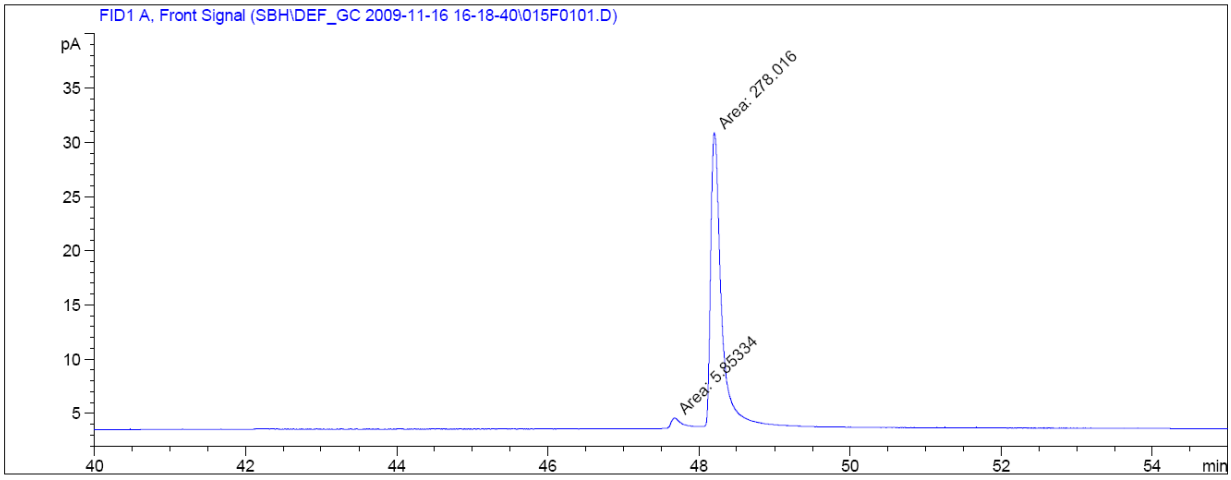
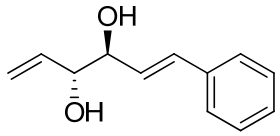
2	48.223	MM	0.1805	151.71806	14.00641	49.85450



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	47.676	MM	0.1165	5.85334	8.37402e-1	2.06199
2	48.202	MM	0.1702	278.01581	27.21951	97.93801

(3*S*, 4*R*, *E*)-1-phenylhexa-1,5-diene-3, 4-diol



4f

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). Cinnamaldehyde **2f** (26 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. K_2CO_3 (55 mg, 0.4 mmol, 200 mol%) and MeOH (2.0 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 18 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with ethyl acetate. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:10) provided **4f** (26 mg, 0.136 mmol) as a colorless oil in 68% yield (18:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.16 (m, 5H), 6.60 (dd, *J* = 16.0, 0.8 Hz, 1H), 6.17 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.90-5.82 (m, 1H), 5.31 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.22 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.32-4.20 (m, 2H), 2.19 (br, 2H).

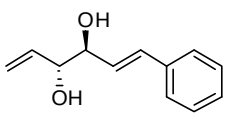
^{13}C NMR (100 MHz, $CDCl_3$): δ 136.3, 136.0, 132.8, 128.6, 127.9, 126.9, 126.6, 117.7, 75.7, 75.3.

GC: (Cyclosil-B: initial temperature: 100 ^oC (5 min hold), final temperature: 200 ^oC (5 min hold), rate: 2.5 ^oC/min): t_{major} = 41.0 min, t_{minor} = 41.3 min; ee = 97%.

$[\alpha]_D^{25}$= +15.4 (c =0.80, CH_2Cl_2).

FTIR (neat): 3388, 1699, 1494, 1450, 1265, 1026, 993, 969, 931, 734, 702 cm^{-1}.

HRMS (CI) Calcd. for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1072, Found: 191.1074.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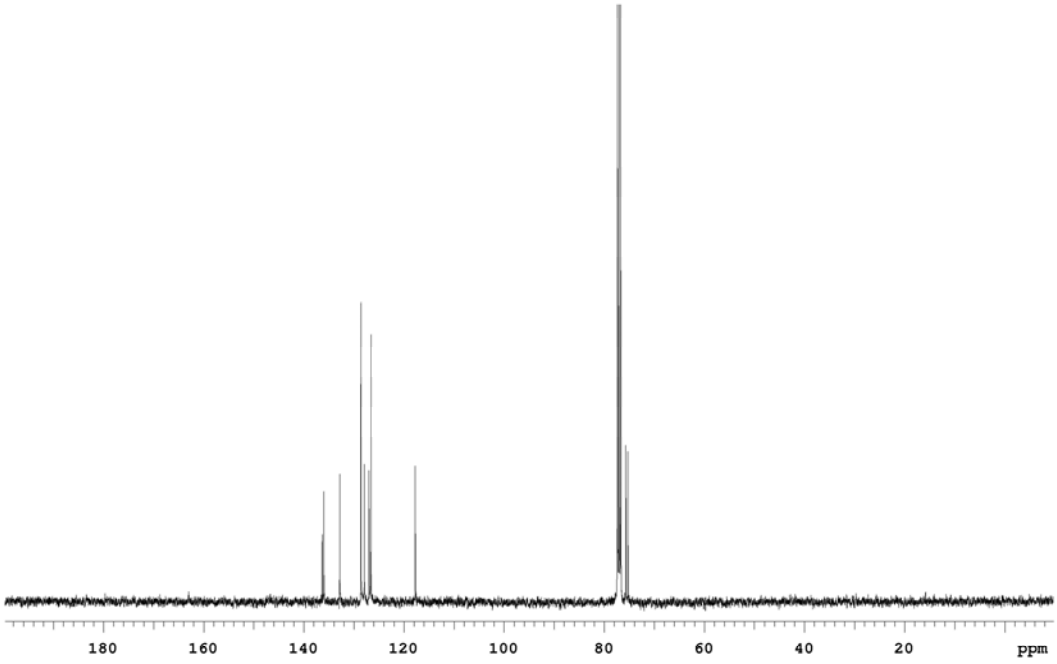
-0
ppm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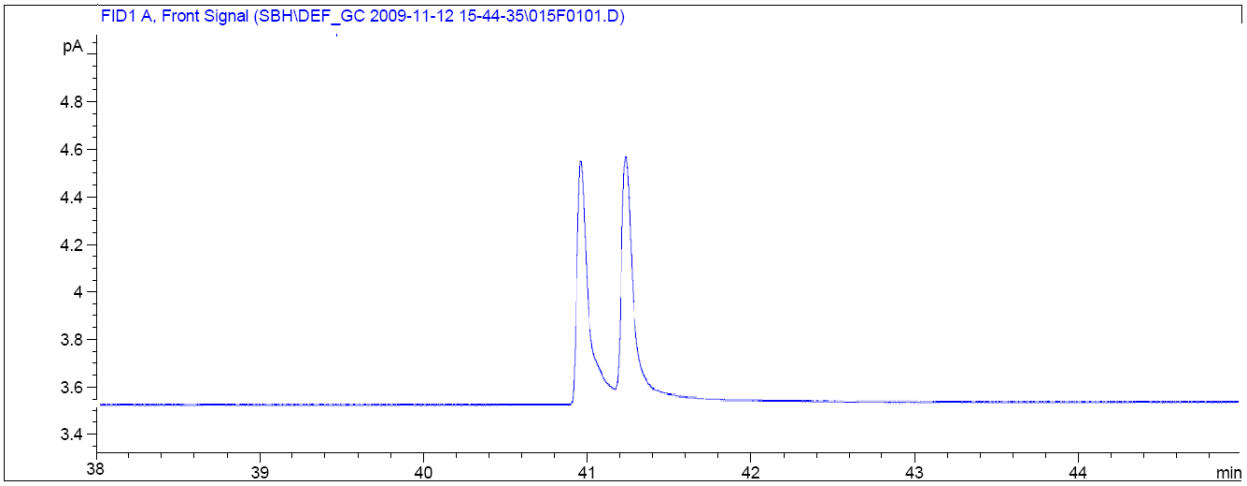
ppm



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
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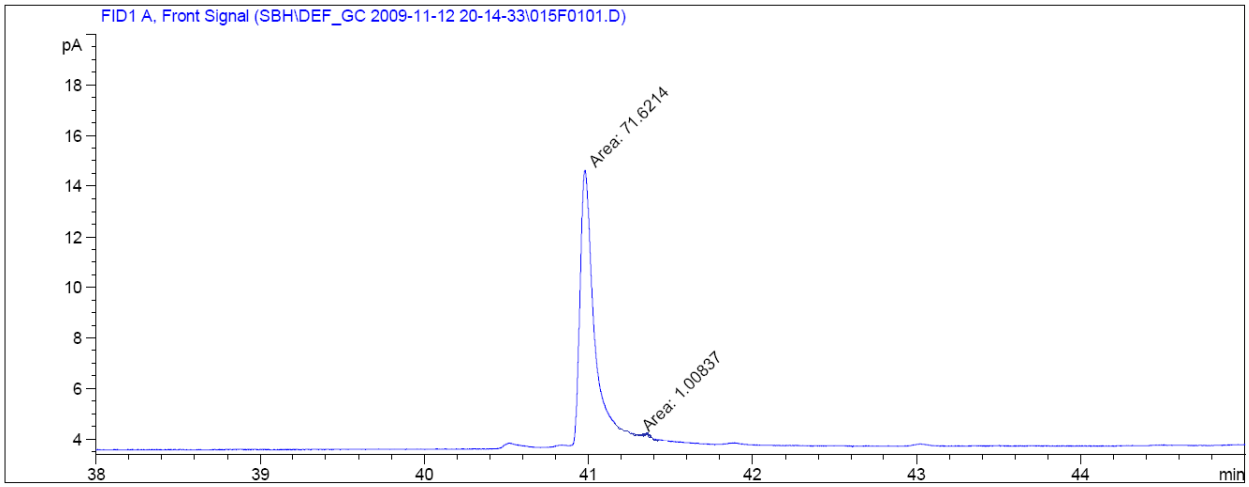
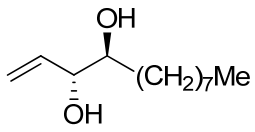
2	41.249	MM	0.1169	3.59936	5.13012e-1	49.63924



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	40.978	MM	0.1085	71.62141	11.00668	98.61163
2	41.304	MM	0.0279	1.00837	6.02053e-1	1.38837

(3*R*, 4*S*)-dodec-1-ene-3,4-diol



4i

An oven-dried sealed tube under one atmosphere of nitrogen gas was charged with *(R)-SEGPHOS*-**I** (10.3 mg, 0.01 mmol, 5 mol%) and THF (1.0 M, 0.2 mL). Nonanal **2i** (28 mg, 0.2 mmol, 100 mol%), acrolein *gem*-dibenzoate **1e** (113 mg, 0.4 mmol, 200 mol%), anhydrous K_3PO_4 (43 mg, 0.2 mmol, 100 mol%) and isopropanol (24 mg, 0.4 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 60 ^oC for 48 hr, at which point the reaction mixture was cooled to ambient temperature. K_2CO_3 (55 mg, 0.4 mmol, 200 mol%) and MeOH (2.0 mL) were added. The reaction mixture was allowed to stir at ambient temperature for 18 hr, at which point the reaction mixture was quenched with aqueous NH_4Cl (3 mL) and extracted with ethyl acetate. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification of the residue by column chromatography (SiO_2; ethyl acetate:hexanes, 1:10) provided **4i** (28 mg, 0.14 mmol) as a colorless oil in 70% yield (14:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.97-5.89 (m, 1H), 5.37-5.27 (m, 2H), 4.12-4.09 (m, 1H), 3.72-3.68 (m, 1H),1.50-1.24 (m, 14H), 0.88 (t, J = 7.2 Hz, 3H).

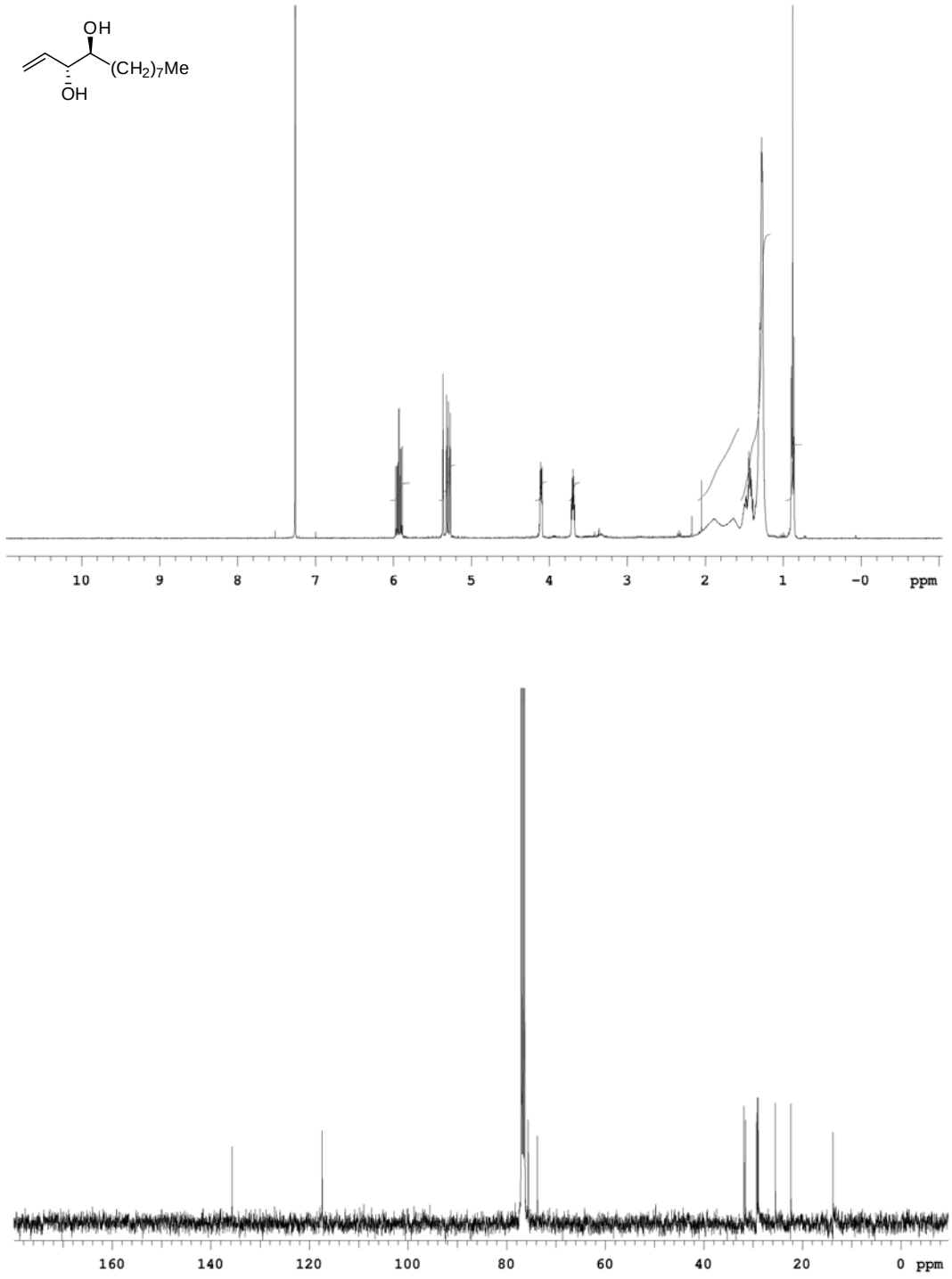
^{13}C NMR (100 MHz, $CDCl_3$): δ 135.7, 117.4, 75.6, 73.7, 31.8, 31.5, 29.3, 29.2, 28.9, 25.5, 22.3, 13.8.

GC: (Cyclosil-B: initial temperature: 150 ^oC (5 min hold), final temperature: 200 ^oC (5 min hold), rate: 2.0 ^oC/min): t_{major} = 12.5 min, t_{minor} = 12.8 min; ee = 99%.

$[\alpha]_D^{25}$= +7.9 (c =0.65, CH_2Cl_2).

FTIR (neat): 3298, 2953, 2917, 2851, 1705, 1467, 1378, 1317, 1264, 1118, 1072, 1028, 1006, 926, 737, 711cm^{-1}.

HRMS (CI) Calcd. for $C_{10}H_{11}O_2$ $[M-H]^+$: 199.1698, Found: 199.1695.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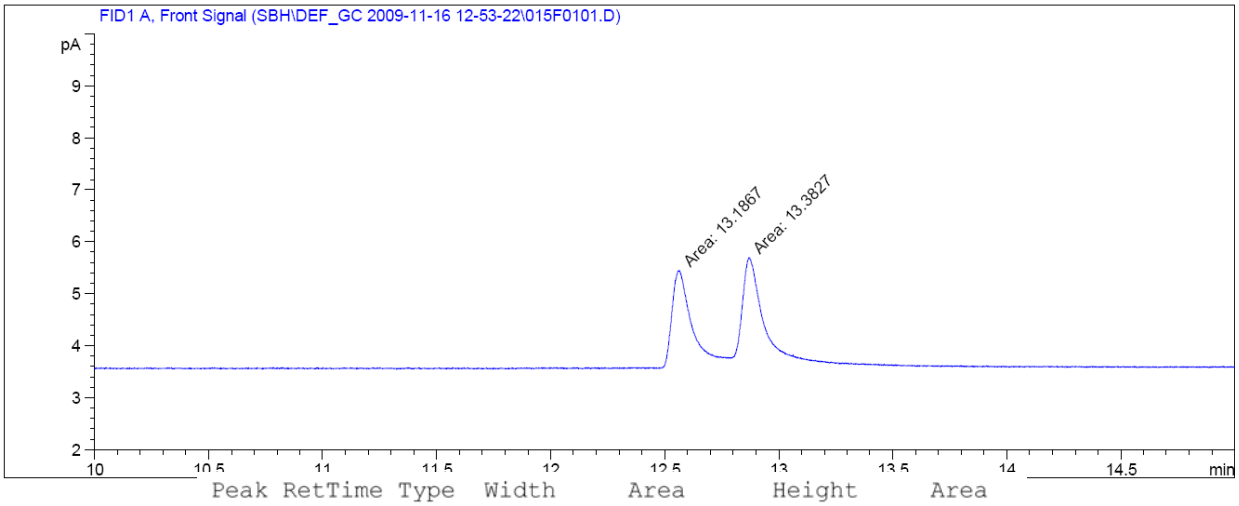

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
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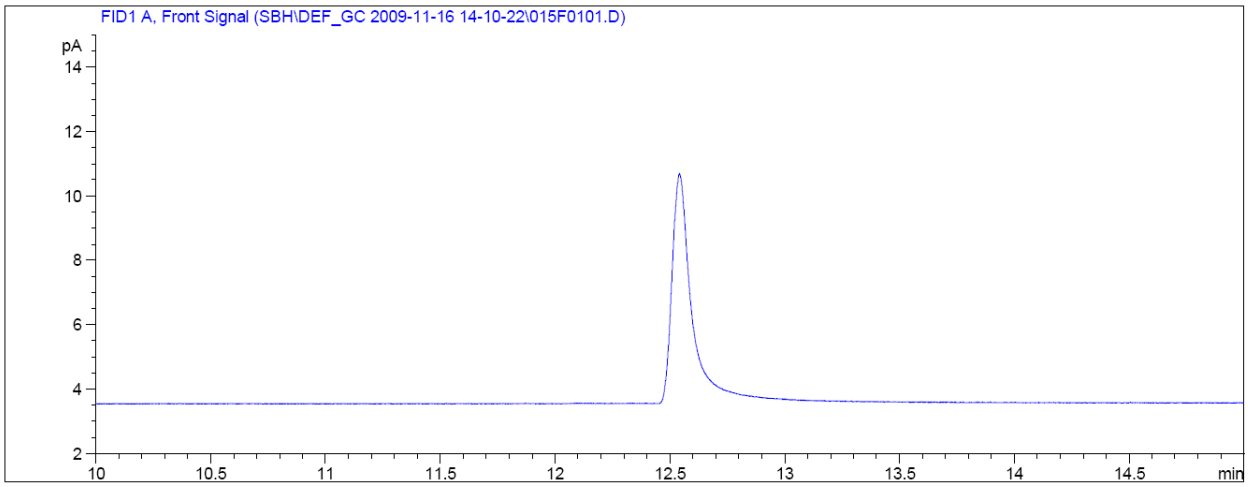
2	12.870	MM	0.1061	13.38273	2.10142	50.36897



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
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