**INVESTIGATION OF THE RH-CATALYZED ASYMMETRIC REDUCTIVE
ALDOL REACTION. EXPANDED SCOPE BASED ON REACTION ANALYSIS.**

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Supplementary Material

General. Infrared spectra were recorded on a Nicolet Magna 560 spectrometer, $\nu_{\max}$ in cm^{-1} . Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on Varian Gemini (300 MHz) and Bruker (400 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : 7.24 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and assignment. ^{13}C NMR were recorded on a Varian Gemini 300 (75 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (CDCl_3 : 77.0 ppm). Microanalyses were performed by Robertson Microlit.

Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on Sigma silica gel 60 (SiO_2 , 230-400 mesh). Thin layer chromatography was performed on EM Science 0.25 mm silica gel 60 plates. Visualization was achieved with phosphomolybdic acid in ethanol followed by heating. Analytical gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 6890 Series chromatograph equipped with a split mode capillary injection system, the indicated chiral GLC column, a flame ionization detector and using helium as the carrier gas.

All reactions were conducted in oven or flame dried glassware under an inert atmosphere of dry nitrogen. Dichloroethane was sequentially washed with concentrated H_2SO_4 , water, aqueous Na_2CO_3 , and water, then dried with MgSO_4 and fractionally distilled from CaH_2 . Chloro(1,5-cyclooctadiene)rhodium (I) dimer and (*R*)-BINAP were purchased from Strem Chemical Company. All other reagents were purchased from either Lancaster or Aldrich Chemical Companies. $[(\text{cod})\text{RhBINAP}]\text{BF}_4$ was synthesized according to the procedure by: Miyshita, A.; Takaya, H.; Souchi, T.; Noyori, R. *Tetrahedron* **1984**, 40, 1245-1253.

Procedure for catalytic reductive aldol reaction with (*R*)-binap/[(cod)RhCl]₂ (Scheme 1):

A 10 mL flame-dried round bottom flask was charged with 17.1 mg [(cod)RhCl]₂ (0.035 mmol) and 56 mg (*R*)-BINAP (0.090 mmol) in 1.7 mL of 1,2-dichloroethane. The catalyst solution was stirred for 30 minute and 171 mg of Et₂MeSiH (1.66 mmol) added to the reaction vessel. The resulting solution was stirred at room temperature for 15 minutes. Next, 1.7 mL of 1,2-dichloroethane was added followed by 246 mg phenyl acrylate (1.66 mmol) and 81 mg of propionaldehyde (1.38 mol). The vessel was then sealed and allowed to stir for 24 hours. Solvent was then evaporated from the reaction and 10% HF/ CH₃CN was added and the reaction stirred for 45min at room temperature. Water and chloroform was then added and the water layer was extracted with chloroform (3 x 25 mL). The combined organic layers were washed with a saturated aqueous sodium chloride solution (1 x 10 mL), dried over Na₂SO₄, and filtered. The solvent was removed by rotary evaporation to yield crude product which was used for calculation of diastereomer ratios by NMR. The crude material which was purified *via* flash chromatography (8:1 then 5:1 hexanes:ethyl acetate) to yield **1** and **2**.

(2*R*,3*R*)-3-propionyloxy-2-methyl-pentanoic acid phenyl ester.

IR (neat) 3000 (br, w), 1756 (s), 1593 (m), 1193 (s) cm⁻¹; ¹H NMR: δ 7.02-7.45 (5H, m, aromatic), 5.31 (1H, m, J= 7.0 Hz, CHCHOC(O)Et), 2.99 (1H, m, J= 7.0 Hz, CH₃CH), 2.42 (2H, q, J= 8 Hz CO₂CH₂CH₃), 1.71 (2H, m, CH₂CH₃), 1.31 (3H, d, J= 7.0 Hz CHCH₃), 1.15 (3H, t, J= 7.0 Hz, CH₂CH₃) 0.997 (3H, t, J= 8.0 Hz, RO₂CCH₂CH₃); ¹³C NMR: δ

174.0, 150.5, 129.8, 126.3, 121.8, 75.7, 75.2, 43.6, 28.5, 25.4, 12.9, 9.7. High Resolution Mass spec for C₁₅H₂₁O₄: calc. 265.1440 [M+H]⁺, found 265.1447.

(2*R*,3*R*)-3-hydroxy-2-methylpentanoic acid phenyl ester.

IR (neat) 3450 (br, s), 2980 (s), 1790 (s), 1593 (m), 1500 (m), 1200 (s) cm⁻¹; ¹H NMR: δ 7.02-7.37 (5H, m, aromatic), 3.98 (1H, dt, J=7.5 Hz, EtCHOH), 2.811 (1H, dq, J=7.19 Hz, CH₃CH), 2.41 (EtCHOH), 1.6 (2H, m, CH₃CH₂CHOH), 1.34 (3H, d, J=7.0 Hz, CHCH₃), 1.04 (3H, q, J=7.0 Hz,

OHCHCH₂CH₃). ¹³C NMR: δ 174.0, 150.5, 129.8, 126.3, 121.8, 75.7, 45.6, 29.5, 10.0. High Resolution Mass spec for C₁₂H₁₇O₃ [M+H]⁺: calc. 209.1178, found 209.112.

The enantiomeric excess for **1** and **2** from this experiment was determined by GLC analysis (*Supelco*, β -dex, 105°C, 15psi) after conversion to 2-methyl-1,3 pentane diol by DIBAL reduction.

Procedure for catalytic reductive aldol acylation reaction with [(*R*)-binapRh(cod)]BF₄ (Scheme 2):

Representative: A 10 mL flame-dried round bottom flask was charged with 64 mg of [(cod)RhBinap]BF₄ (0.069 mmol) and 500 μ L of 1,2-dichloroethane. The catalyst solution was stirred for one minute to dissolve the rhodium species, and 105 μ L of dimethylphenylsilane (0.69 mmol) were added to the reaction vessel. The resulting solution was stirred at room temperature for 30 minutes. Next, 1.7 mL of 1,2-dichloroethane was added followed by 192 μ L phenyl acrylate (1.38 mmol) and 200 μ L of propionaldehyde (2.76 mmol). The vessel was then sealed and allowed to stir for 24 hours. Solvent was evaporated from the reaction and 10% HF/ CH₃CN was added and the reaction stirred for 45 min at room temperature. Water and chloroform were then added and the water layer was extracted with chloroform (3 x 25 mL). The combined organic layers were washed with a saturated aqueous sodium chloride solution (1 x 10 mL), dried over Na₂SO₄, and filtered. The solvent was removed by rotary evaporation to yield crude product which was purified *via* flash chromatography (8:1 then 5:1 hexanes:ethyl acetate) to yield 40 mg (0.27 mmol, 40 % yield) of **2** and 25.9 mg (0.12 mmol, 18% yield) of **1**. The enantiomeric excess of each compound was determined by GLC analysis (*Supelco*, β -dex, 105°C, 15psi) after conversion to 2-methyl-1,3 pentanediol by DIBAL reduction.

Procedure for preparation of [(*R*-binap)RhH]₂ (4) (Scheme 3):

12.5 mg of [(cod)Rh(*R*)-BINAP]BF₄ (0.013 mmol) was weighed into an NMR tube equipped with a teflon screw cap. The tube was charged with 500 μL of deuterated 1,2-dichloroethane and allowed to stand for 1 minute. 56 μL (0.365 mmol) of phenyldimethylsilane was then added and the reaction periodically shaken for 45 minutes. ¹H NMR analysis of the mixture revealed an overlapping triplet of quintets at -8.18 ppm (*J*=16.8 Hz) which resolves to a binomial triplet (*J*= 17 Hz) in the {³¹P}¹H NMR. ³¹P NMR revealed a doublet at 38.5 ppm (*J*=147.1 Hz) corresponding to **4** in addition to a doublet at 25.8 ppm (*J*=145.6 Hz) for unreacted **3**. ¹⁹F NMR analysis of the catalyst mixture revealed signals corresponding to PhMe₂SiF at -161.4 ppm (septet, *J*=7.5 Hz, ²⁹Si satellites exhibit ¹*J*_{SiF} = 278 Hz) and the precatalyst **3** at -153.0 ppm (singlet, shoulder at -152.9 due to ¹⁰B isotope). BF₃ was not detected in the mixture.

¹H NMR:

31P NMR after partial
conversion of 3 to 4.

F2 - Acquisition Parameters
Date_ 20030327
Time 18.20
INSTRUM spect
PROBHD 5mm QNP 1H/13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 62
DS 2
SWH 51282.051 Hz
FIDRES 0.782502 Hz
AQ 0.6390358 sec
RG 14596.5
DW 9.750 usec
DE 6.00 usec
TE 293.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 31P
P1 5.70 usec
PL1 0.00 dB
SFO1 161.9786325 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.00 dB
PL13 14.50 dB
SFO2 400.1316005 MHz

F2 - Processing parameters

F2 - Acquisition Parameters
Date_ 20030327
Time 18.28
INSTRUM spect
PROBHD 5mm QNP 1H/13C
PULPROG zgflgn
TD 131072
SOLVENT C6D6
NS 64
DS 4
SWH 90090.094 Hz
FIDRES 0.687333 Hz
AQ 0.7275051 sec
RG 2580.3
DW 5.550 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 19F
P1 18.00 usec
PL1 0.00 dB
SFO1 376.4608844 MHz

F2 - Processing parameters
SI 65536
SF 376.4985340 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 p

(2R,3R)-3-benzoyloxy-2-methyl-3-phenylpropionic acid phenyl ester. IR (neat) 3400 (br, w), 2900 (br, m), 1760 (s), 1720 (s), 1500 (m), 1250 (s) cm^{-1} ; ^1H NMR: δ 6.8-8.1 (15H, m, aromatic), 6.44 (1H, d, $J=7.0$ Hz, $\text{CHO}(\text{O})\text{Ar}$), 3.44 (1H, m, CH_3CH), 1.48 (3H, d, $J=7.0$ Hz, CHCH_3); ^{13}C NMR: δ 172.0, 165.8, 150.8, 138.6, 133.7, 130.2, 129.8, 129.0, 128.9, 128.8, 127.8, 127.2, 126.3, 121.8, 76.6, 46.7, 13.2. HRMS Calc'd for $\text{C}_{23}\text{H}_{20}\text{O}_4$: Calc. 361.1440, Found 361.1442 $[\text{M}+\text{H}]^+$.

(2R,3R)-3-hydroxy-2-methyl-3-phenylpropionic acid phenyl ester. This compound was identical to that reported in: Taylor, S.J.; Duffey, M.O.; Morken, J.P. *J. Am. Chem. Soc.* **2000**, 122, 4528.

The enantiomeric excess of each compound was determined by GLC analysis (*Supelco*, β -dex, 160°C , 15psi) after conversion to the derived 1,3-diol by DIBAL reduction.

Representative procedure for catalytic reductive aldol reaction of α,β -unsaturated aldehydes (Table 1): A 10 mL flame-dried round bottom flask was charged with 16.5 mg of [(cod)Rh(*R*)-binap]BF₄ (0.018 mmol), and 500 μ L of dichloroethane. The resulting solution was stirred at room temperature for approximately one minute or until the rhodium complex was fully dissolved. After the complex was fully dissolved, 62 μ L of diethylmethylsilane (0.428 mmol) was added to the mixture and the reaction vessel stirred for 30 minutes. Next, 250 μ L of dichloroethane followed by 50 μ L of phenyl acrylate (0.357 mmol) and 172 μ L 2-methyl-2-butenal (1.78 mmol) was added to the solution. The vessel was then sealed and allowed to stir for 24 hours, after which time 0.5 equivalents of diethylmethylsilane (0.1785 mmol) was added and the reaction was stirred an additional 24 h. Solvent was then evaporated from the reaction and 1 mL each of THF, MeOH, and 4N HCl were added. This mixture was stirred at room temperature for an additional 45 minutes. Ethyl acetate was then used to extract the product (3 x 25 mL). The combined organic layers were washed with a saturated aqueous sodium bicarbonate solution (2 x 20 mL), dried over Na₂SO₄, and filtered. The solvent was removed by rotary evaporation to yield crude product which was purified *via* flash chromatography (16:1, 14:1 then 13:1 hexanes:ethyl acetate) to yield 71 mg (0.303 mmol, 85% yield) of a 2.5:1 ratio of (2*R*,3*R*)-3-hydroxy-2,4-dimethyl-hex-4-ene-onic acid phenyl ester (74% ee).

(2*R*,3*R*)-3-hydroxy-2,4-dimethyl-hex-4-ene-onic acid methyl ester. IR (KBr)

3550 (br, m) 2990 (m), 1780 (s) 1490 (m), 1200 (s) cm⁻¹; ¹H NMR: δ 7.5-6.98 (5H, m, aromatic), 5.61 (1H, br q, *J*=6.8 Hz, vinyl CH), 4.36 (1H, d, *J*=5.9 Hz, CHOH), 2.90 (1H, m, CH₃CH), 2.06 (1H, br d, *J*=3.2 Hz, OH), 1.68 (3H, s, vinyl CH₃), 1.65 (3H, s, vinyl CH₃), 1.32 (3H, d, *J*=7.0 Hz, CHCH₃); ¹³C NMR: δ 174.2, 151.0, 135.5, 129.8, 126.3, 122.4, 121.9, 78.2, 43.9, 30.1, 14.8, 13.5, 12.4. HRMS Calc'd for C₁₄H₁₉O₃ [M+H]⁺: 235.1334, Found: 235.1323.

Proof of Stereochemistry. Determination of stereochemical ratios was accomplished through chiral SFC analysis in comparison authentic adducts prepared by asymmetric aldol methodology (Crimmins, M.T.; Chaudhary, K. *Org. Lett.* **2000**, *2*, 775) and in comparison to non-selective aldol adducts.

Chiral SFC Analysis of Racemic and Catalytic Reaction Products.

(2R,3R)-3-hydroxy-2,5-dimethyl-hex-4-ene-oic acid phenyl ester. IR (KBr) 3450 (br, s) 2980 (m), 1780 (s) 1490 (m), 1200 (s) cm^{-1} ; ^1H NMR: δ 7.5-7.01 (5H, m, aromatic), 5.35 (br d, $J=8.0$ Hz, vinylic CH) 4.71 (1H, m, CHOH), 2.75 (1H, dq, $J=6.7, 6.8$ Hz, CH_3CH), 2.26 (1H, d, $J=4.6$ Hz, OH), 1.78 (3H, s, vinyl CH_3), 1.74 (3H, s, vinyl CH_3), 0.88 (3H, d, $J=7.2$ Hz, CHCH_3); ^{13}C NMR: δ 174.0, 151.0, 137.6, 129.8, 126.3, 124.8, 121.9, 70.1, 46.3, 26.3, 18.8, 12.8. HRMS Calc'd for $\text{C}_{14}\text{H}_{19}\text{O}_3$ $[\text{M}+\text{H}]^+$: 235.1334, Found: 235.1342.

Proof of Stereochemistry. Determination of stereochemical ratios was accomplished through chiral SFC analysis in comparison to non-selective aldol adducts prepared according to the method described above. Absolute configuration of the syn diastereomer was established by comparison to the authentic 2S,3S isomer prepared by the use of a chiral auxiliary as described above.

SFC (Chiracel OD, Supelco) analysis of reductive aldol reaction product and racemic mixture of diastereomers:

Reaction product

Racemic

Authentic

(2R,3R)-3-cyclohexene-3-hydroxyl-2-methylpropionic acid phenyl ester. IR (neat) 3480 (br, s), 2950 (m), 1800 (m), 1800 (m), 1770 (m) cm^{-1} ; ^1H NMR: δ 7.50 - 7.01 (5H, m, aromatic), 5.80 (1H, s, $\text{CH}=\text{CHOH}$), 4.35 (1H, br t, $J=4.5$ Hz, CHOH), 2.89 (1H, m, CHCH_3), 2.0-2.1 (4H, m, allylic hydrogens), 1.5-1.7 (4H, d, $J=7.8$ Hz, aliphatic), 1.3 (3H, d, $J=7.0$ Hz, CH_3); ^{13}C NMR: δ 174.3, 151.1, 137.4, 129.8, 126.2, 124.7, 121.8, 77.0, 43.7, 25.3, 24.8, 22.9 (2 C), 12.2; HRMS Calc'd for $\text{C}_{16}\text{H}_{24}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$: 278.1756. Found: 278.1767.

Proof of Stereochemistry. Determination of stereochemical ratios was accomplished through chiral SFC analysis in comparison to non-selective aldol adducts prepared according to the method described above. (2R,3R)-3-cyclohex-3-ene-3-hydroxyl-2-methylpropionic acid phenyl ester was converted to (2R,3R)-3-cyclohexyl-3-hydroxyl-2-methylpropionic acid phenyl ester *via* hydrogenation with H_2 and PtO_2 in ethanol. The resulting compound was analyzed by SFC. Absolute configuration was established by comparison to the known 2R,3R cyclohexyl reductive aldol adduct previously prepared in an asymmetric fashion (Taylor, S.J.; Duffey, M.O.; Morken, J.P. *J. Am. Chem. Soc.* **2000**, 122, 4528).

SFC (Chiracel OD, Supelco) analysis of reductive aldol reaction product and racemic mixture of stereoisomer:

(2R,3R)-3-hydroxy-2-methyl-hex-4-ene-onic acid phenyl ester. IR (KBr) 3500 (br, s), 3000 (m), 1780 (s), 1500 (m), 1200 (s) cm^{-1} ; ^1H NMR: δ 7.5-7.03 (5H, m, aromatic), 5.58 (1H, br dq, $J = 15.3, 6.4$ Hz), 5.60 (1H, ddq, $J = 15.3, 6.9, 1.5$ Hz), 4.44 (1H, q, $J=5.1$ Hz, CHOH), 2.88 (1H, m, CH_3CHCO), 2.32 (1H, d, $J=4.5$ Hz, OH), 1.75 (3H, d, $J=6.4$ Hz, $\text{CH}=\text{CHCH}_3$), 1.37 (3H, d, $J=7.2$ Hz, CHCH_3); ^{13}C NMR: δ 174.1, 150.9, 130.8, 129.9, 129.3, 126.4, 121.9, 74.0, 45.9, 18.2, 12.3. HRMS Calc'd for $\text{C}_{13}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$: 221.1178, Found: 221.1177.

Proof of Stereochemistry. Stereochemical ratios were determined in comparison to racemic material and in comparison to authentic materials prepared by asymmetric aldol methodology.

Supercritical fluid chromatography (Chiralcel AS, Supelco) analysis of reductive aldol product:

(Z)-Phenyl Crotonate: To a flame-dried 100 mL flask under N₂ were added 18-crown-6 (3.77 g, 14.26 mmol) and 40 mL of dry THF. Phenylbis(trifluoroethoxy)phosphonoacetate (1.63 g, 4.28 mmol) was dissolved in 17 mL dry THF and transferred to reaction flask via syringe. The flask was then cooled to -78 °C, and potassium hexamethyldisilazide (8.58 mL, 0.5 M in toluene, 4.28 mmol) added dropwise via syringe. Acetaldehyde (0.16 mL, 2.85 mmol) was added and the reaction was stirred for 45 min at -78 °C. The reaction was then quenched by addition of saturated NH₄Cl. Extraction of the aqueous layer was done with three portions of diethyl ether. The organic layer was dried over Na₂SO₄, filtered, and concentrated. Purification by flash column chromatography in 20:1 hexane:ethyl acetate (*R_f* = 0.74, 4:1 hexanes:ethyl acetate), provided 0.19 grams (31%) of pure product. ¹H NMR: δ 7.37 (2 H, t, *J* = 7.8 Hz, ArH), 7.2 (1 H, t, *J* = 7.7 Hz, ArH), 7.1 (2 H, d, *J* = 7.3 Hz, ArH), 6.52 (1 H, dq, *J* = 7 Hz, *J* = 11 Hz, CHCH₃), 6.02 (1 H, dq, *J* = 10 Hz, *J* = 2 Hz, C(O)CH), 2.20 (3 H, dd, *J* = 4.0 Hz, *J* = 1.6 Hz, CH₃); ¹³C NMR: δ 164.7, 150.7, 146.7, 129.3, 125.5, 122.1, 121.6, 15.5.

3-Methyl-but-2-enoic Acid Phenyl Ester: To a flame-dried 250 mL flask under N₂ were added phenol (7.94 g, 84 mmol) and dry CH₂Cl₂ (84 mL), and the mixture was cooled to 0 °C. Triethylamine (23.5 mL, 168 mmol) was added and the reaction mixture was stirred at 0 °C for 45 minutes. After addition of 3,3-dimethyl-acryloyl chloride (84 mmol), a bright yellow mixture formed which was stirred at 0 °C for 1 h, then warmed to ambient temperature and stirred overnight. The reaction was quenched with 1 M HCl, and the organic and aqueous layers were separated. The organic layer was washed with saturated NaHCO₃ and brine, then dried over MgSO₄, filtered, and concentrated. Purification via column chromatography in 8:1 hexanes:ethyl acetate (*R_f* = 0.73, 4:1 hexanes:ethyl acetate) provided 5.98 g (80%) of the desired ester. ¹H NMR: δ 7.35 (2 H, t, *J* = 8.2 Hz, ArH), 7.2 (1 H, t, *J* = 7.4 Hz, ArH), 7.08 (2 H, d, *J* = 7.5 Hz, ArH), 5.90 (1 H, s, C(O)CH), 2.21 (3 H, s, CCH₃), 1.97 (3 H, s, CCH₃); ¹³C NMR: δ 164.8, 159.7, 150.7, 129.3, 125.4, 121.8, 115.3, 27.6, 20.4.

Phenyl 2-nonenoate. LiBr (0.45 g, 5.16 mmol) was weighed into a dry 25 mL flask under N₂. Then a solution of phenyl diethylphosphonoacetate (1.17 g, 4.3 mmol) in dry THF (4.3 mL) was added via syringe. The mixture was stirred for 5 min, then triethylamine was added (0.66 mL, 4.73 mmol). After stirring for 10 min heptaldehyde (0.6 mL, 4.3 mmol) was added dropwise and the reaction allowed to stir overnight at ambient temperature. The reaction was quenched by addition of 1 M HCl and the mixture extracted with three portions of diethyl ether. The organic layer was dried over Na₂SO₄, filtered, and concentrated. Purification by column chromatography in 10:1 hexanes:ethyl acetate (*R_f* = 0.41), provided 0.49 g (50%) of the desired ester. ¹H NMR: δ 7.36 (2H, t, *J* = 8 Hz, ArH), 7.23 (1 H, t, *J* = 7.4 Hz, ArH), 7.16 (1 H, dt, *J* = 15.6 Hz, *J* = 8.6 Hz, CHCHCH₂), 7.10 (2 H, d, *J* = 7.5 Hz, ArH), 6.00 (1 H, dt, *J* = 15.6 Hz, *J* = 1.5 Hz, C(O)CH), 2.26 (2 H, dq, *J* = 7.1 Hz, *J* = 1.5 Hz, CHCH₂CH₂), 1.50 (2 H, m, CHCH₂CH₂), 1.30 (6 H, m, CH₂CH₂CH₂CH₃), 0.88 (3 H, t, *J* = 6.8 Hz, CH₃); ¹³C NMR: δ 165.5, 152.4, 151.2, 129.8, 126.1, 122.1, 120.9, 32.8, 32.0, 29.3, 28.3, 23.0, 14.5.

6-(tert-Butyl-dimethyl-silanoxy)-hex-2-enoic Acid Phenyl Ester. To a flame-dried 10 mL flask were added (triphenyl-λ⁵-phosphanylidene)-acetic acid phenyl ester (1.38 g, 3.5 mmol), 4-(tert-butyl-dimethyl-silanoxy)-butyraldehyde (0.47 g, 2.33 mmol), and dry CH₂Cl₂ (5.8 mL). The flask was fit with a reflux condenser and heated at reflux for 16 h, at which point it was cooled to RT, and the solvent was removed. The crude reaction mixture was directly purified by silica gel chromatography with 5:1

hexanes:ethyl acetate as eluent (R_f = 0.61), yielding 0.55 g of the ester (74%). ^1H NMR: δ 7.36 (2 H, t, J = 8.0 Hz, ArH), 7.23 – 7.15 (3 H, m, 2 ArH, C(O)CHCH), 7.10 (2 H, m, ArH), 6.02 (1 H, d, J = 15.6 Hz, C(O)CH), 3.65 (2 H, t, J = 6.4 Hz, CH₂OSi), 2.35 (2 H, q, J = 6.7 Hz, CHCHCH₂), 1.71 (2 H, quin, J = 6.8 Hz, CH₂CH₂O), 0.89 (9 H, s, (CH₃)₃CSi), 0.05 (6 H, s, (CH₃)₂Si); ^{13}C NMR: δ 165.3, 151.8, 151.1, 129.7, 126.0, 122.1, 121.1, 63.0, 62.5, 31.4, 29.3, 26.4, 18.7, -4.9.

6-Phenyl-hex-2-enoic Acid Phenyl Ester. LiBr (0.57 g, 6.55 mmol) was weighed into a dry 25 mL flask under N₂. A solution of phenyl diethylphosphonoacetate (1.48 g, 5.46 mmol) in dry THF (5.5 mL) was added via syringe. After stirring for 5 min triethylamine (0.84 mL, 6.0 mmol) was added. After stirring for another 10 min, 4-phenylbutyraldehyde was added dropwise and the reaction allowed to stir at room temperature for 16 h. The reaction was quenched by addition of 1 M HCl, then the mixture was extracted with three portions of diethyl ether. The organic layer was dried over MgSO₄, filtered, and concentrated. Purification by flash column chromatography in 10:1 hexanes:ethyl acetate (R_f = 0.38), provided 0.31 g (22%) of the ester. ^1H NMR: δ 7.37 (2 H, t, J = 8.0 Hz, ArH), 7.28 (2 H, m, ArH), 7.23 – 7.08 (7 H, m, 6 ArH, C(O)CHCH), 6.02 (1 H, dt, J = 7.2 Hz, J = 1.6 Hz, C(O)CH), 2.67 (2 H, t, J = 7.7 Hz, ArCH₂), 2.30 (2 H, q, J = 6.8, CHCHCH₂), 1.84 (2 H, quin, J = 7.6 Hz, CHCH₂CH₂); ^{13}C NMR: δ 165.4, 151.6, 141.9, 129.7, 128.9, 128.8, 128.7, 126.4, 126.0, 122.0, 121.3, 35.6, 32.2, 29.9.

Octa-2,7-dienoic Acid Phenyl Ester. Charged a flame-dried 50 mL flask with (triphenyl- λ^5 -phosphanylidene)-acetic acid phenyl ester (4.4 g, 13.7 mmol), hex-5-enal (0.90 g, 9.17 mmol), and dry CH₂Cl₂ (23 mL). The flask was fitted with reflux condenser and heated at reflux for 16 h. After cooling to room temperature the solvent was removed and directly purified by silica gel chromatography using 5:1 hexanes:ethyl acetate (R_f = 0.74), resulting in isolation of 1.08 g (54%) of the desired product. ^1H NMR: δ 7.52 (2 H, t, J = 8.0 Hz, ArH), 7.39 – 7.23 (4 H, m, 3 ArH, C(O)CHCH), 6.19 (1 H, dt, J = 15.6 Hz, J = 1.6 Hz, C(O)CH), 5.98 (1 H, ddt, J = 17.0 Hz, J = 10.2 Hz, J = 6.6 Hz, C₃H₆CHCH₂), 5.16 (2 H, m, C₃H₆CHCH₂), 2.45 (2 H, q, J = 7.6 Hz, CHCHCH₂), 2.27 (2 H, q, J = 7.1 Hz, C₂H₄CH₂CHCH₂), 1.77 (2 H, quin, J = 7.6 Hz, CHCHCH₂CH₂); ^{13}C NMR: δ 151.2, 150.8, 137.8, 129.3, 125.6, 121.6, 121.5, 120.8, 115.2, 33.0, 31.6, 27.0.

Representative Procedure for Catalytic, Enantioselective Reductive Aldol Reaction of Crotonate Derivatives (Table 2). In an inert atmosphere glovebox, an oven-dried 250 mL flask equipped with a stir bar was charged with 0.37 g (0.76 mmol) of chloro(1,5-cyclooctadiene)rhodium (I) dimer, 1.21 g (1.98 mmol) of (*S*)-BINAP, and 30 mL dry dichloroethane under an argon atmosphere. After stirring for one hour, diethylmethylsilane (21.7 mL, 5.00 mmol) was added and the reaction mixture was stirred for 30 min. Propionaldehyde (2.2 mL, 31 mmol), phenyl crotonate (5.5 mL, 36 mmol), and 30 mL of dry dichloroethane were then added, and the reaction was stirred at ambient temperature for 48 h. After 48 h, the solvent was removed by rotary evaporation, and the crude mixture was stirred with a 1:1:1 THF:MeOH:4 N HCl mixture (39 mL) for 1 h. Water (30 mL) was then added and the layers separated. The aqueous layer was extracted with ethyl acetate three times, and then the combined organic layers were washed twice with saturated NaHCO₃, dried over Na₂SO₄, filtered, and concentrated. The product was purified by flash column chromatography in 4:1 hexanes:ethyl acetate (R_f = 0.12, 7:1 hexanes:ethyl acetate), providing 5.13 g (76%) of 2-ethyl-3-hydroxy-pentanoic acid phenyl ester in a 4.3:1 *syn:anti* ratio of diastereomers (88% *ee* for the *syn* diastereomer).

2-Ethyl-3-hydroxy-pentanoic acid phenyl ester. IR (neat): 3446 (br, s), 1756 (s), 1646 (s), 1594 (s), 1495 (s), 1383 (s), 1349 (s) cm^{-1} ; ^1H NMR: δ 7.53 (2 H, t, $J = 7.8$ Hz, ArH), 7.38 (1 H, t, $J = 7.4$ Hz, ArH), 7.22 (2 H, d, $J = 7.0$ Hz, ArH), 4.13 (1 H, m, CHOH), 2.79 (1 H, m, C(O)CH), 2.33 (1 H, d, $J = 5.0$ Hz, OH), 2.06 – 1.9 (2 H, m, C(O)CHCH₂), 1.8 – 1.7 (2 H, m, CHCHCH₂), 1.23 (3 H, t, $J = 7.5$ Hz, C(O)CHCH₂CH₃), 1.18 (3 H, t, $J = 7.4$ Hz, CHCHCH₂CH₃); ^{13}C NMR: δ 173.7, 150.4, 129.4, 125.9, 121.5, 73.5, 52.7, 27.5, 20.6, 12.1, 10.2. HRMS (FAB) Calc'd for C₁₃H₁₈O₃ (M + Na)⁺: 245.1148. Found (M + Na)⁺: 245.1152.

^1H NMR of the *anti* diastereomer: δ 7.53 (2 H, t, $J = 7.8$ Hz, ArH), 7.38 (1 H, t, $J = 7.4$ Hz, ArH), 7.22 (2 H, d, $J = 7.0$ Hz, ArH), 3.90 (1 H, m, CHOH), 2.79 (1 H, m, C(O)CH), 2.46 (1 H, d, $J = 8.0$ Hz, OH), 2.06 – 1.9 (2 H, m, C(O)CHCH₂), 1.8 – 1.7 (2 H, m, CHCHCH₂), 1.23 (3 H, t, $J = 7.5$ Hz, C(O)CHCH₂CH₃), 1.18 (3 H, t, $J = 7.4$ Hz, CHCHCH₂CH₃).

Proof of Stereochemistry: Stereochemical ratios were determined in comparison to racemic materials prepared via the reductive aldol reaction using *racemic*-BINAP as ligand. Absolute stereochemistry established in comparison to authentic 2(*S*), 3(*R*) isomer prepared via a Crimmins aldol reaction using the thiazolidinethione butyrate to provide the appropriate Evans-*syn* aldol product (Chaudhary, K and Crimmins, M. T. *Org. Lett.* **2000**, 2, 775).

Chiral capillary electrophoresis (5% γ -cyclodextrin, -15 kV, 20°C) analysis of reductive aldol product.

Reductive Aldol Product

Racemic Aldol Product

Racemic + Reductive Aldol Product
Coinjection

2-(1-Hydroxy-propyl)-nonanoic acid phenyl ester: IR (neat): 3577 (br, d), 1756 (s), 1652 (s), 989 (s), 567 (m) cm^{-1} ; ^1H NMR: δ 7.39 (2 H, t, $J = 7.6$ Hz, ArH), 7.22 (1 H, t, $J = 8.0$ Hz, ArH), 7.05 (2 H, d, $J = 7.6$ Hz, ArH), 3.85 (1 H, m, CHOH), 2.67 (1 H, m, C(O)CH), 2.19 (1 H, br s, OH), 1.90 – 1.20 (14 H, m, methylene protons), 1.02 (3 H, t, $J = 7.4$ Hz, CHCH_2CH_3), 0.86 (3 H, t, $J = 6.9$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR: δ 174.4, 150.8, 126.5, 121.8, 74.1, 73.9, 51.1, 50.9, 32.2, 29.9, 29.5, 28.2, 27.8, 23.0, 14.5, 10.7. HRMS (FAB) Calc'd for $\text{C}_{18}\text{H}_{28}\text{O}_3$ ($\text{M} + \text{Na}$) $^+$: 315.1931. Found ($\text{M} + \text{Na}$) $^+$: 315.1919.

^1H NMR of the *anti* diastereomer: δ 7.39 (2 H, t, $J = 7.6$ Hz, ArH), 7.22 (1 H, t, $J = 8.0$ Hz, ArH), 7.05 (2 H, d, $J = 7.6$ Hz, ArH), 3.70 (1 H, m, CHOH), 2.67 (1 H, m, C(O)CH), 2.29 (1 H, d, $J = 8.0$ Hz, OH), 1.90 – 1.20 (14 H, m, methylene protons), 1.02 (3 H, t, $J = 7.4$ Hz, CHCH_2CH_3), 0.86 (3 H, t, $J = 6.9$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$).

Chiral GLC (β -dex, Supelco) analysis of diols prepared by DIBAL reduction of reductive aldol products:

6-(*tert*-Butyl-dimethylsilanoxy)-2-(1-hydroxy-propyl)-hexanoic acid phenyl ester. IR (neat): 3566 (br, d), 1756 (s), 1646 (s), 559 (m) cm^{-1} ; ^1H NMR: δ 7.52 (2 H, t, $J = 8.3$ Hz, ArH), 7.38 (1 H, t, $J = 7.5$ Hz, ArH), 7.21 (2 H, d, $J = 7.5$ Hz, ArH), 4.01 (1 H, q, $J = 6.8$ Hz, CHOH), 3.78 (2 H, t, $J = 6.2$ Hz, CH_2OSi), 2.84 (1 H, m, C(O)CH), 2.39 (1 H, br s, OH), 2.10 – 1.85 (2 H, m, C(O)CHCH $_2$), 1.8 – 1.6 (6 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{OSi}$, C(O)CHCHCH $_2$), 1.18 (3 H, t, $J = 7.4$ Hz, CH_2CH_3), 1.04 (9 H, s, $(\text{CH}_3)_3\text{CSi}$), 0.18 (6 H, s, $(\text{CH}_3)_2\text{Si}$); ^{13}C NMR: δ 173.8, 150.4, 129.4, 125.9, 121.5, 73.6, 62.8, 51.0, 32.7, 27.4, 27.1, 25.9, 24.1, 18.3, 10.2, 5.3. HRMS (FAB) Calc'd for $\text{C}_{21}\text{H}_{36}\text{SiO}_4$ ($\text{M} + \text{Na}$) $^+$: 403.2275. Found ($\text{M} + \text{Na}$) $^+$: 403.2268.

^1H NMR of the *anti* diastereomer: δ 7.52 (2 H, t, $J = 8.3$ Hz, ArH), 7.38 (1 H, t, $J = 7.5$ Hz, ArH), 7.21 (2 H, d, $J = 7.5$ Hz, ArH), 3.88 (1 H, q, $J = 6.8$ Hz, CHOH), 3.78 (2 H, t, $J = 6.2$ Hz, CH_2OSi), 2.84 (1 H, m, C(O)CH), 2.39 (1 H, br s, OH), 2.10 – 1.85 (2 H, m, C(O)CHCH $_2$), 1.8 – 1.6 (6 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{OSi}$, C(O)CHCHCH $_2$), 1.18 (3 H, t, $J = 7.4$ Hz, CH_2CH_3), 1.04 (9 H, s, $(\text{CH}_3)_3\text{CSi}$), 0.18 (6 H, s, $(\text{CH}_3)_2\text{Si}$).

Chiral capillary electrophoresis (5% β -cyclodextrin, -15 kV, 10°C) analysis of the diol resulting from deprotection of the silyl ether:

2-(1-Hydroxy-propyl)-6-phenyl-hexanoic acid phenyl ester: IR (neat): 3566 (br, d), 1756 (s), 1646 (s), 1594 (s), 1495 (s), 989 (br, s), 559 (m) cm^{-1} ; ^1H NMR: δ 7.52 (2 H, t, $J = 8.9$ Hz, ArH), 7.42 (3 H, m, ArH), 7.33 (3 H, m, ArH), 7.13 (2 H, m, ArH), 4.02 (1 H, m, CHOH), 2.83 (1 H, m, C(O)CH), 2.80 (2 H, t, $J = 7.6$ Hz, CH_2Ar), 2.35 (1 H, br s, OH), 2.10 – 1.55 (8 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ar}$, CHCH_2CH_3), 1.18 (3 H, t, $J = 7.4$ Hz, CH_3); ^{13}C NMR: δ 174.3, 150.7, 142.7, 129.8, 128.8, 128.7, 126.4, 126.1, 121.9, 74.0, 51.3, 36.0, 31.7, 27.9, 27.7, 27.5, 10.6. HRMS (FAB) Calc'd for $\text{C}_{21}\text{H}_{26}\text{O}_3$ ($\text{M} + \text{Na}$) $^+$: 349.1774. Found ($\text{M} + \text{Na}$) $^+$: 349.1778.

^1H NMR of the *anti* diastereomer: δ 7.52 (2 H, t, $J = 8.9$ Hz, ArH), 7.42 (3 H, m, ArH), 7.33 (3 H, m, ArH), 7.13 (2 H, m, ArH), 3.87 (1 H, m, CHOH), 2.83 (1 H, m, C(O)CH), 2.80 (2 H, t, $J = 7.6$ Hz, CH_2Ar), 2.45 (1 H, d, $J = 8.0$ Hz, OH), 2.10 – 1.55 (8 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ar}$, CHCH_2CH_3), 1.18 (3 H, t, $J = 7.4$ Hz, CH_3).

Supercritical fluid chromatography (AD-H, 150 psi, 50°C, flow = 3 mL/min, 3% MeOH) analysis of the reductive aldol product:

2-(1-Hydroxy-propyl)-oct-7-enoic acid phenyl ester:

Product obtained as a 1:1.8 mixture of reductive aldol product and olefin isomerized reductive aldol product. IR (neat): 3566 (br, d),

1756 (s), 1717 (s), 1652 (s), 1461 (s), 989 (s), 542 (m) cm^{-1} ; ^1H NMR: δ 7.53 (2 H, t, $J = 7.9$ Hz, ArH), 7.38 (1 H, t, $J = 7.5$ Hz, ArH), 7.21 (2 H, d, $J = 8.5$ Hz, ArH), 5.95 (1 H, m, CH_2CHCH_2), 5.12 (2 H, m, $\text{CH}_2\text{CH}_2\text{CHCH}_2$), 4.01 (1 H, m, CHOH), 2.84 (1 H, m, C(O)CH), 2.34 (1 H, br s, OH), 2.23 (2 H, m, $\text{CH}_2\text{CH}_2\text{CHCH}_2$), 2.10 – 1.80 (2 H, m, C(O)CHCH_2), 1.80 – 1.55 (6 H, $\text{C(O)CHCH}_2\text{CH}_2\text{CH}_2$, CHCH_2CH_3), 1.18 (3 H, t, $J = 7.4$ Hz, CH_2CH_3); ^{13}C NMR: δ 173.8, 150.4, 129.4, 125.9, 121.5, 114.5, 73.6, 51.0, 33.4, 32.4, 28.7, 27.6, 26.7, 17.8, 10.2. HRMS (FAB) Calc'd for $\text{C}_{17}\text{H}_{24}\text{O}_3$ ($\text{M} + \text{Na}$) $^+$: 299.1618. Found ($\text{M} + \text{Na}$) $^+$: 299.1630.

^1H NMR of the *anti* diastereomer: δ 7.53 (2 H, t, $J = 7.9$ Hz, ArH), 7.38 (1 H, t, $J = 7.5$ Hz, ArH), 7.21 (2 H, d, $J = 8.5$ Hz, ArH), 5.95 (1 H, m, CH_2CHCH_2), 5.12 (2 H, m, $\text{CH}_2\text{CH}_2\text{CHCH}_2$), 3.87 (1 H, m, CHOH), 2.84 (1 H, m, C(O)CH), 2.45 (1 H, d, $J = 8.0$ Hz, OH), 2.23 (2 H, m, $\text{CH}_2\text{CH}_2\text{CHCH}_2$), 2.10 – 1.80 (2 H, m, C(O)CHCH_2), 1.80 – 1.55 (6 H, $\text{C(O)CHCH}_2\text{CH}_2\text{CH}_2$, CHCH_2CH_3), 1.18 (3 H, t, $J = 7.4$ Hz, CH_2CH_3).

^1H NMR of the internal olefin product: δ 7.53 (2 H, t, $J = 7.9$ Hz, ArH), 7.38 (1 H, t, $J = 7.5$ Hz, ArH), 7.21 (2 H, d, $J = 8.5$ Hz, ArH), 5.62 (2 H, m, $\text{CH}_2\text{CHCHCH}_3$), 4.01 (1 H, m, CHOH), 2.84 (1 H, m, C(O)CH), 2.34 (1 H, br s, OH), 2.23 (2 H, m, $\text{CH}_2\text{CHCHCH}_3$), 2.10 – 1.80 (2 H, m, C(O)CHCH_2), 1.80 – 1.55 (7 H, $\text{C(O)CHCH}_2\text{CH}_2$, CHCH_2CH_3 , CHCHCH_3), 1.18 (3 H, t, $J = 7.4$ Hz, CH_2CH_3).

Current Data Parameters
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 PROCNO 1

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 Time 8:17
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 WDW no
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 LB 0.00 Hz
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Current Data Parameters
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EXTNO 1
PROCNO 1

F2 - Acquisition Parameters
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Time 22.01

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TD 65536
SOLVENT CDCl3
NS 4800

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AQ 0.399445 Hz
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D11 1.00000000 sec
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F2 - Processing parameters
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Current Data Parameters
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EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

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Time 18.02
Spect 1H/13C
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SOLVENT CDCl3
NS 192
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5560319 sec
RG 2896.3
DW 78.000 usec
DE 6.00 usec
TE 293.0 K
D1 1.00000000 sec

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F2 - Processing parameters
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SF 400.1300172 MHz
WDW no
SSB 0
LB 0.00 Hz
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3.708
2.711
2.699
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2.651
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Current Data Parameters
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 EXPRNO 1
 PROCNO 1

F2 - Acquisition Parameters
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 Time 21.02
 Instrument spect
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 INVERT no
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 NS 64
 DS 2
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 143.7
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

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 MDW no
 SSB no
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Current Data Parameters
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 EXPRNO 1
 PROCNO 1

F2 - Acquisition Parameters

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 NS 16
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 AQC 2.7329011 sec
 RG 143.7
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====

NUC1 1H
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 PL1 -3.00 dB
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 F2 - Processing parameters
 SI 32768
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 WDW no
 SSB 0
 LB 0
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Current Data Parameters
NAME NF-II-115P13C
EXRNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20031209
Time 22.12

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TD 65536
SOLVENT CDCl3
NS 3287

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TE 300.0 K
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d11 0.03000000 sec
d12 0.0002000 sec

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PL1 0.00 dB
SFO1 100.6237964 MHz

===== CHANNEL f2 =====
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F2 - Processing Parameters
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