Lewis Base Activation of Lewis Acids: Catalytic, Enantioselective Vinylogous Aldol Reactions

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SUPPORTING INFORMATION

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General Experimental

All reactions were performed in oven-dried (140 °C) or flame-dried glassware under an atmosphere of dry N₂ or Argon. All reaction temperatures correspond to internal temperatures measured by Teflon-coated thermocouples unless otherwise noted. Reaction solvents including dichloromethane (HPLC Grade), diethyl ether (BHT stabilized HPLC Grade) and tetrahydrofuran (HPLC Grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvent acetonitrile was used as

received. Solvents for chromatography and filtration were: diethyl ether, hexane (ACS grade), ethyl acetate (technical grade, distilled from K_2CO_3), pentane (ACS grade), dichloromethane (technical grade, distilled from CaCl_2), MeOH (ACS grade, distilled from K_2CO_3). Column chromatography was performed using SiliaFlash P60 (40-63 μ 60 Å pore size).

^1H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded at 400 MHz, ^1H ; 100 MHz, ^{13}C , 376 MHz, ^{19}F , and 500 MHz, ^1H ; 126 MHz, ^{13}C . Spectra were referenced to residual chloroform (7.26 ppm, ^1H , 77.00 ppm, ^{13}C) and ^{19}F spectra were referenced externally to C_6F_6 . Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants, J , are reported in Hertz. ^1H NMR and ^{13}C NMR assignments are corroborated by 2D experiments (COSY, HMBC, HMQC, and HETCOR). Spectra are available on request from denmark@scs.uiuc.edu. EI, CI, and FI mass spectra are reported in the form of (m/z). Infrared spectra (IR) are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Melting points (mp) were determined in sealed tubes and are corrected. Kugelrohr distillation temperatures reported are air bath temperatures (ABT). Rotary evaporations were performed at 30 °C and 14 mmHg. Analytical thin-layer chromatography was performed on silica gel 60 F₂₅₄ TLC plates. Visualization was accomplished with UV(254), and potassium permanganate (KMnO_4), staining solutions.

Optical rotation data was obtained on a digital polarimeter and are reported as follows: concentration (c = g/100 mL), and solvent. Analytical supercritical fluid chromatography (CSP-SFC) was performed with packed-column SFC with built-in photometric detector (220 nm) using Daicel Chiralpak OD, OJ, OB, AD and AS columns as well as a Regis Whelk-O1 column. Ozonolyses were performed with a 1 slpm flow rate. Fourier transform IR analysis was performed using a ReactIR 1000 purchased from ASI Applied Systems INC., 8223 Coverleaf Drive, Suite 120, Millersville, MD 21108. Reactions were monitored using 5/8" Dicomp probe fitted to an MCT detector. Acquisitions were recorded using software version 3.0.

Dienol ethers **32c**, **32d**, **33a**, **33c**, **43**, **81**, and **82** were too unstable to obtain full characterization and the assignments of these structures should be considered tentative. Similarly, minor products **17**, **39**, α -**50**, α -**51**, and **85** were not isolated in quantities sufficient for full characterization and the assignments of these structures should be considered tentative.

Literature Preparations

The preparation of 1-trimethylsilyloxy-1,3-cyclohexadiene (**10**) followed the procedure described by Fleming et. al.¹

The preparation of (*R,R*)-*N,N'*-bis[4,5-dihydro-3,5-dimethyl-4-(3H-dinaphtho[2,1-d:1',2'-f][1,3,2]-2-oxo-diazaphosphephepino)]-*N,N'*-dimethyl-1,5-pentanediamine ((*R,R*)-**3**), (*R,R*)-*N,N'*-bis[4,5-dihydro-3,5-dimethyl-4-(3H-dinaphtho[2,1-d:1',2'-f][1,3,2]-2-oxo-diazaphosphephepino)]-*N,N'*-dimethyl-1,4-butanediamine ((*R,R*)-**35**), and (*R,R*)-*N,N'*-bis[4,5-dihydro-3,5-dimethyl-4-(3H-dinaphtho[2,1-d:1',2'-f][1,3,2]-2-oxo-diazaphosphephepino)]-*N,N'*-dimethyl-1,6-hexanediamine ((*R,R*)-**36**), followed the procedure described by Denmark and Wynn.²

The preparation of (*R*)-1,3-dimethyl-2,3-dihydro-2-piperidinyl-dinaphtho-[2,1-c:1'2'-e]-1H-[1,3,2]diazaphosphepine 2-oxide ((*R*)-**37**), (4*R*,5*R*)-1,3-Dimethyl-4,5-diphenyl-1-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide ((*R,R*)-**38**) followed the procedure described by Denmark et. al.³

The preparation of 2-butenic acid dimethylamide, 2-butenic acid diethylamide, 1-[(2*E*)-1-oxo-2-butenyl]piperidine, 4-[(2*E*)-1-oxo-2-butenyl]morpholine, 4-[(2*E*)-1-oxo-2-methyl-2-butenyl]morpholine, and 4-[1-oxo-3-methyl-2-butenyl]morpholine, 4-[(2*E*)-1-oxo-2-pentenyl]morpholine followed the procedure described by Ongoka et. al.⁴

2-*tert*-Butyldimethylsilyloxyacetaldehyde,⁵ 2-benzyloxyacetaldehyde,⁶ 3-*tert*-butyldimethylsilyloxypropionaldehyde,⁷ 3-benzyloxypropionaldehyde,⁸ 3-allyloxypropionaldehyde,⁹ 3-benzoyloxypropionaldehyde,¹⁰ 3-pivoyloxypropionaldehyde,¹¹ 6-benzyloxyhexanal¹² were prepared by literature methods.

Experimental Procedures.

Preparations of Silyl Dienol Ethers

Representative Procedure 1. Enolization of α,β -Unsaturated Ketones to Form Silyl Dienol Ethers. Preparation of (Z)-1-(Phenylbuta-1,3-dienyloxy)trimethylsilane (**6**) (Scheme 3)

To a flame-dried 100-mL, 3-necked, round-bottomed flask fitted with a magnetic stir bar, thermocouple, gas inlet tube, and septum was added 2.85 g (20.0 mmol, 1.0 equiv) of 1-phenyl-2-buten-1-one, 3.46 mL (24.8 mmol, 1.24 equiv) of Et_3N and 3.15 mL (24.5 mmol, 1.24 equiv) of TMSCl . Then, a solution of 3.72 g (24.8 mmol, 1.24 equiv) of NaI in 25 mL of CH_3CN was added slowly dropwise over 5 min via cannula. The resulting solution was then placed in an oil bath at 80°C and stirred for 6 h. The mixture was cooled to rt and 50 mL of cold pentane was added. The organic layer was then separated and the aqueous layer was washed with pentane (3 x 50 mL). The combined organic extracts were washed with H_2O (2 x 50 mL), CuSO_4 (sat. aq.) (2 x 50 mL), and brine (50 mL), dried over Na_2SO_4 (10 g), filtered and the filtrate concentrated *in vacuo*. The resulting residue was purified by bulb-to-bulb distillation to yield 4.135 g (95%, *Z:E*, 60:40) of **6** as a clear, colorless oil.¹³

Data for **6**:

bp: 60°C (0.05 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

7.53 (dt, $J = 7.3, 1.7$, 2 H, (*Z*)-HC(6)), 7.42 (dt, $J = 7.1, 1.7$, 2 H, (*E*)-HC(6)), 7.37-7.31 (m, 6 H, (*Z*)-HC(7) and (*E*)-HC(7,8)), 7.28-7.25 (m, 1 H, (*Z*)-HC(8)), 6.74 (dt, $J = 17.1, 10.5$, 1 H, (*Z*)-HC(3)), 6.48 (dt, $J = 16.7, 10.8$, 1 H, (*E*)-HC(3)), 6.06 (d, $J = 10.7$, 1 H, (*Z*)-HC(2)), 5.78 (d, $J = 11.0$, 1 H, (*E*)-HC(2)), 5.22 (d, $J = 17.1$, 1 H, (*Z*)-HC(4)), 5.10 (d, $J = 16.8$, 1 H, (*E*)-HC(4)), 5.03 (d, $J = 10.3$, 1 H, (*Z*)-HC(4)), 4.85 (d, $J = 11.3$, 1 H, (*E*)-HC(4)), 0.19 (s, 9 H, (*E*)- $\text{H}_3\text{C}(9)$), 0.17 (s, 9 H, (*Z*)- $\text{H}_3\text{C}(9)$)

NOE ^1H NMR: (500 MHz, CDCl_3)

Irradiation at 6.06 ppm ((Z)-HC(2)) enhanced signal at 7.53 ppm ((Z)-HC(6)) and 5.22 ppm ((Z)-HC(4)). Irradiation at 6.48 ppm ((E)-HC(3)) enhanced signal at 7.42 ppm ((E)-HC(6)) and 4.85 ppm ((E)-HC(4))

^{13}C NMR: (126 MHz, CDCl_3)

152.9 ((E)-C(1)), 150.4 ((Z)-C(1)), 138.2 ((Z)-C(5)), 137.3 ((E)-C(5)), 133.6 ((E)-C(3)), 131.9 ((Z)-C(3)), 128.7 ((E)-C(6)), 128.3 ((E)-C(8)), 128.1 ((Z)-C(7)), 128.0 ((Z)-C(8)), 127.9 ((E)-C(7)), 125.5 ((Z)-C(6)), 114.5 ((Z)-C(4)), 113.4 ((E)-C(4)), 112.6 ((Z)-C(2)), 112.0 ((Z)-C(2)), 0.5 ((Z)-C(9)), 0.3 ((E)-C(9))

IR: (neat)

3086 (w), 3059 (w), 3037 (w), 3012 (w), 2961 (m), 2900 (w), 2360 (w), 2342 (w), 1950 (w), 1890 (w), 1783 (w), 1689 (m), 1670 (w), 1628 (s), 1590 (w), 1573 (w), 1492 (m), 1447 (m), 1416 (m), 1330 (s), 1308 (m), 1284 (m), 1253 (s), 1210 (s), 1174 (m), 1115 (s), 1067 (s), 1028 (m), 996 (m), 948 (m), 922 (m), 888 (s), 845 (s), 791 (m), 759 (s), 732 (m), 697 (s), 666 (m), 651 (w), 629 (w)

MS: (EI, 70 eV)

219 (12), 218 (M^+ , 51), 217 (35), 203 (30), 210 (13), 129 (68), 128 (27), 127 (11), 115 (14), 105 (23), 77 (25), 75 (43), 74 (12), 73 (100)

HRMS: Calcd for $\text{C}_{13}\text{H}_{18}\text{OSi}$: 218.1127, found: 218.1126

Preparation of (Z)-1-Phenylbuta-1,3-dienyloxy)trimethylsilane (6) (Scheme 3)

To a flame-dried 50-mL, 3-necked, round-bottomed flask fitted with a magnetic stir bar, thermocouple, gas inlet tube, and septum was added 1.10 g (5.5 mmol, 1.1 equiv) of potassium hexamethyldisilazide and 25 mL of THF. The solution was cooled to $-72\text{ }^{\circ}\text{C}$ and then 731 mg (5.0 mmol, 1.0 equiv) of 1-phenyl-2-buten-1-one was added slowly dropwise over 1 min via syringe. The resulting orange solution was stirred for 20 min at $-72\text{ }^{\circ}\text{C}$ prior to addition of a solution of 703 μL (5.5 mmol, 1.1 equiv) of TMSCl via syringe. The dry ice bath was then

removed and the solution was allowed to warm to 0 °C. The yellow solution was then concentrated *in vacuo*, and the resulting residue was taken up in 50 mL of pentane. The yellow precipitate which is formed was then filtered through a pad of Celite on a glass frit and the filtrate was concentrated *in vacuo*. The residue was purified by bulb-to-bulb distillation to afford 805 mg (74%, *Z:E*, 99:1) of **6** as a clear, colorless oil.¹³

Data for (Z)-6:

bp: 60 °C (0.05 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.53 (dt, *J* = 8.4, 1.6, 2 H, HC(6)), 7.34-7.30 (m, 2 H, HC(7)), 7.28-7.25 (m, 1 H, HC(8)), 6.73 (dt, *J* = 17.1, 10.5, 1 H, HC(3)), 6.05 (d, *J* = 10.7, 1 H, HC(2)), 5.24-5.20 (m, 1 H, HC(4)), 5.04-5.01 (m, 1 H, HC(4)), 0.17 (s, 9 H, H₃C(9))

¹³C NMR: (126 MHz, CDCl₃)

150.4 (C(1)), 138.3 (C(5)), 131.9 (C(3)), 128.1 (C(7)), 128.0 (C(8)), 125.5 (C(6)), 114.5 (C(4)), 112.0 (C(2)), 0.5 (C(9))

Preparation of ((Z)-2,2-Dimethylhexa-3,5-dien-3-yloxy)trimethylsilane (7) (Scheme 3)

Following Representative Procedure 1, 5.048 g (40.0 mmol, 1.0 equiv) of 2,2-dimethyl-4-hexen-3-one was combined with 6.91 mL (50.0 mmol, 1.25 equiv) of Et₃N, 6.91 mL (50.0 mmol, 1.25 equiv) of TMSCl, and 7.43 g (50.0 mmol, 1.20 equiv) of NaI to yield, after bulb-to-bulb distillation, 7.497 g (95%, *Z:E*, 89:11) of **7** as a clear, colorless oil.

Data for 7:

bp: 55 °C (8 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

6.81 (dt, *J* = 16.6, 10.9, 0.11 H, (*E*)-HC(5)) 6.50 (dt, *J* = 17.1, 10.5, 0.89 H, (*Z*)-HC(5)), 5.39 (d, *J* = 10.5, 0.89 H, (*Z*)-HC(4)), 5.34 (d, *J* = 11.5, 0.11 H (*E*)-HC(4)), 5.03 (dd, *J* = 17.1, 2.0, 0.89 H, (*Z*)-HC(6)), 4.89-4.84 (m, 1 H, (*Z*)-HC(6))

and (*E*)-HC(6)), 4.76 (dd, $J = 10.0, 2.0, 0.11$ H, (*E*)-HC(6)), 1.20 (s, 1 H, (*E*)-H₃C(1)), 1.08 (s, 8 H, (*Z*)-H₃C(1)), 0.25 (s, 8 H, (*Z*)-H₃C(7)), 0.21 (s, 1 H, (*E*)-H₃C(7))

NOE ¹H NMR: (500 MHz, CDCl₃)

Irradiation at 1.08 ppm ((*Z*)-HC(1)) enhanced signal at 5.39 ppm ((*Z*)-HC(4)) and 0.25 ppm ((*Z*)-HC(7)). Irradiation at 1.20 ppm ((*E*)-HC(1)) enhanced signal at 6.81 ppm ((*E*)-HC(5)) and 0.21 ppm (*E*)-HC(7))

Preparation of ((*Z*)-2,2-Dimethylhexa-3,5-dien-3-yloxy)trimethylsilane (7) (Scheme 3)

To a flame-dried 50-mL, 3-necked, round-bottomed flask fitted with a magnetic stir bar, thermocouple, gas inlet tube, and septum was added 1.10 g (5.5 mmol, 1.1 equiv) of potassium hexamethyldisilazide and 25 mL of THF. The solution was cooled to -72 °C and then 631 mg (5.0 mmol, 1.0 equiv) of 2,2-dimethyl-4-hexen-3-one was added slowly dropwise over 1 min via syringe. The resulting reddish-orange solution was stirred for 20 min at -72 °C prior to addition of a solution of 703 μ L (5.5 mmol, 1.1 equiv) of TMSCl via syringe. The dry ice bath was then removed and the solution was allowed to warm to rt. The clear solution was then concentrated *in vacuo*, and the resulting residue was taken up in 50 mL of pentane. The yellow precipitate that is formed was then filtered through a pad of Celite on a glass frit and the filtrate was concentrated *in vacuo*. The residue was purified by bulb-to-bulb distillation to afford 864 mg (87%, *Z:E*, >99:1) of 7 as a clear, colorless oil.

Data for (Z)-7:

bp: 55 °C (8 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

6.50 (dt, $J = 17.1, 10.5$, 1 H, HC(5)), 5.39 (d, $J = 10.5$, 1 H, HC(4)), 5.05-5.01 (m, 1 H, HC(6)), 4.87-4.84 (m, 1 H, HC(6)), 1.08 (s, 9 H, H₃C(1)), 0.25 (s, 9 H, H₃C(7))

¹³C NMR: (126 MHz, CDCl₃)
 161.2 (C(3)), 132.5 (C(5)), 112.2 (C(6)), 106.3 (C(4)), 36.5 (C(2)), 28.4 (C(1)),
 1.1 (C(7))

IR: (neat)
 3086 (w), 3066 (w), 2959 (s), 2906 (m), 2870 (w), 2362 (w), 1781 (w), 1716 (w),
 1641 (s), 1595 (w), 1481 (m), 1460 (w), 1417 (m), 1391 (w), 1358 (w), 1315 (s),
 1291 (m), 1254 (s), 1221 (m), 1190 (s), 1103 (s), 1029 (m), 994 (m), 963 (m), 930
 (s), 888 (s), 846 (s), 758 (m), 718 (w), 676 (m), 646 (w), 610 (w)

MS: (EI, 70 eV)
 198 (M⁺, 27), 183 (51), 141 (10), 75 (36), 73 (100), 57 (13)

HRMS: Calcd for C₁₁H₂₂OSi: 198.1440, found: 198.1439

Preparations of Bissilyl Dienol Ethers

Representative Procedure 2. Enolization of 1,3-Diketones to form Bissilyl Dienol Ethers.

Preparation of 2,4-Bis(trimethylsilyloxy)-1,3-pentadiene (**32a**) (Figure 3)

To a flame-dried, 250-mL, 3-necked, round-bottomed flask equipped with a magnetic stir bar, reflux condenser, septum and 125-mL addition funnel was added 2.57 mL (25.0 mmol, 1.0 equiv) of acetylacetone (**30**), 7.14 mL (51.25 mmol, 2.05 equiv) of Et₃N and 50 mL of Et₂O. The solution was cooled to 0 °C (bath temperature). The addition funnel was charged with 9.28 mL (51.25 mmol, 2.05 equiv) of TMSOTf and 10 mL of Et₂O and the solution was added slowly dropwise over 15 min. The resulting biphasic solution was stirred for 1 h at 0 °C prior to addition of 50 mL of cold H₂O. The organic layer was separated and aqueous layer washed with pentane (3 x 50 mL). The combined organic extracts were washed with NaHCO₃ (sat aq) (50 mL), H₂O (50 mL), brine (75 mL), dried of K₂CO₃ (10 g), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by bulb-to-bulb distillation to afford 5.765 g (94%, *Z:E*, 55:45) of **32a** as a clear, colorless oil.¹⁴

Data for **32a**:

bp: 55 °C (0.2 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

5.20 (s, 0.45 H, (*E*)-HC(3)), 4.75 (s, 0.45 H, (*E*)-HC(1)), 4.73 (s, 0.55 H, (*Z*)-HC(3)), 4.32 (d, *J* = 1.2, 0.45 H, (*E*)-HC(1)), 4.14 (s, 0.55 H, (*Z*)-HC(1)), 4.10 (s, 0.55 H, (*Z*)-HC(1)), 2.01 (s, 1.75 H, (*E*)-H₃C(5)), 1.85 (s, 1.25 H, (*Z*)-H₃C(5)), 0.24 (s, 4.95 H, (*Z*)-H₃C(6)), 0.22 (s, 4.05 H, (*E*)-H₃C(6)), 0.21 (s, 4.05 H, (*E*)-H₃C(7)), 0.20 (s, 4.95 H, (*Z*)-H₃C(7))

Preparation of 2,4-Bis(*tert*-butyldimethylsilyloxy)-1,3-pentadiene (32b**) (Figure 3)**

Following Representative Procedure 2, 2.05 mL (20 mmol) of acetylacetone (**30**) was combined with 6.13 mL (44 mmol, 2.2 equiv) of Et₃N, and 9.19 mL (40 mmol, 2.0 equiv) of TBSOTf to yield, after bulb-to-bulb distillation, 6.245 g (95%, *Z*:*E*, 55:45) of **32b** as a clear, colorless oil.

Data for **32b**:

bp: 90 °C (0.05 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

5.16 (s, 0.45 H, (*Z*)-HC(3)), 4.79 (s, 0.55 H, (*E*)-HC(1)), 4.68 (s, 0.45 H, (*E*)-HC(3)), 4.39 (d, *J* = 1.5, 0.55 H, (*E*)-HC(1)), 4.19 (s, 0.55 H, (*Z*)-HC(1)), 4.09 (s, 0.55 H, (*Z*)-HC(1)), 2.00 (d, *J* = 0.4, 1.75 H, (*Z*)-H₃C(5)), 1.87 (d, *J* = 0.4, 1.25 H, (*E*)-H₃C(5)), 0.95-0.92 (m, 18 H, (*E*)-H₃C(8), (*Z*)-H₃C(8), (*E*)-H₃C(11), (*Z*)-H₃C(11)), 0.19-0.13 (m, 12 H, (*E*)-H₃C(6), (*Z*)-H₃C(6), (*E*)-H₃C(9), (*Z*)-H₃C(9))

NOE ¹H NMR: (500 MHz, CDCl₃)

Irradiation at 4.79 ppm (HC(3)) enhanced signal at 2.01 ppm (HC(5))

¹³C NMR: (126 MHz, CDCl₃)154.8 ((*Z*)-C(2)), 152.7 ((*Z*)-C(4)), 152.3 ((*E*)-C(2)), 150.6 ((*E*)-C(4)), 108.6 ((*Z*)-

C(3)), 106.8 ((*E*)-C(3)), 94.2 ((*E*)-C(1)), 93.5 ((*Z*)-C(1)), 25.87, 25.86, 25.8, 25.6, 18.29, 18.26, 18.1, 18.0, -3.2, -4.37, -4.42, -4.5

IR: (neat)

3119 (w), 2958 (s), 2931 (s), 2887 (m), 2859 (s), 2805 (w), 2742 (w), 2712 (w), 2647 (w), 2263 (w), 1687 (w), 1654 (s), 1618 (m), 1473 (s), 1464 (m), 1437 (m), 1382 (s), 1362 (m), 1334 (s), 1254 (s), 1198 (s), 1173 (s), 1025 (s), 1004 (s), 938 (m), 877 (m), 838 (s), 811 (s), 780 (s), 747 (w), 697 (m), 671 (w)

MS: (EI, 70 eV)

328 (M^+ , 6), 313 (22), 271 (14), 216 (12), 215 (23), 173 (26), 158 (13), 157 (90), 149 (23), 147 (23), 133 (37), 75 (24), 73 (100), 59 (11), 57 (15)

HRMS: Calcd for $C_{17}H_{36}O_2Si_2$: 328.2254, found: 328.2250

Preparation of 2,4-Bis(triethylsilyloxy)-1,3-pentadiene (**32c**) (Figure 3)

Following Representative Procedure 2, 2.05 mL (20 mmol) of acetylacetone (**30**) was combined with 6.13 mL (44 mmol, 2.2 equiv) of Et_3N , and 9.05 mL (40 mmol, 2.0 equiv) of TESOTf to yield, after bulb-to-bulb distillation, 6.484 g (98%, *Z:E*, 55:45) of **32c** as a clear, colorless oil.

Data for **32c**:

bp: 150 °C (0.05 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

5.19 (s, 0.46 H, (*Z*)-HC(3)), 4.80 (s, 0.54 H, (*E*)-HC(1)), 4.71 (dd, $J = 1.7, 0.7$, 0.54 H, (*E*)-HC(3)), 4.36 (d, $J = 1.7, 0.54$ H, (*E*)-HC(1)), 4.15 (s, 0.46 H, (*Z*)-HC(1)), 4.05 (s, 0.46 H, (*Z*)-HC(1)), 2.03 (s, 1.35 H, (*Z*)- $\text{H}_3\text{C}(5)$), 1.88 (s, 1.65 H, (*E*)- $\text{H}_3\text{C}(5)$), 1.02-0.96 (m, 18 H, (*E*)- $\text{H}_3\text{C}(7)$, (*Z*)- $\text{H}_3\text{C}(7)$, (*E*)- $\text{H}_3\text{C}(9)$, (*Z*)- $\text{H}_3\text{C}(9)$), 0.77-0.66 (m, 12 H, (*E*)- $\text{H}_3\text{C}(6)$, (*Z*)- $\text{H}_3\text{C}(6)$, (*E*)- $\text{H}_3\text{C}(8)$, (*Z*)- $\text{H}_3\text{C}(8)$)

Preparation of 2,4-Bis(triisopropylsilyloxy)-1,3-pentadiene (32d) (Figure 3)

Following Representative Procedure 2, 0.257 mL (2.5 mmol) of acetylacetone (**30**) was combined with 0.767 mL (5.5 mmol, 2.2 equiv) of Et_3N , and 1.4 mL (5.5 mmol, 2.1 equiv) of TIPSOTf to yield, after bulb-to-bulb distillation, 0.910 g (88%, *Z:E*, 55:45) of **32d** as a clear, colorless oil.

Data for **32d**:

bp: 150 °C (0.05 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

5.19 (s, 0.55 H, (*Z*)-HC(3)), 4.82 (s, 0.45 H, (*E*)-HC(1)), 4.71 (dd, $J = 1.7, 0.9$, 0.45 H, (*E*)-HC(3)), 4.39 (d, $J = 1.7$, 0.45 H, (*E*)-HC(1)), 4.18 (s, 0.55 H, (*Z*)-HC(1)), 4.03 (s, 0.55 H, (*Z*)-HC(1)), 2.06 (d, $J = 0.6$, 1.75 H, (*Z*)- $\text{H}_3\text{C}(5)$), 1.92 (s, 1.25 H, (*E*)- $\text{H}_3\text{C}(5)$), 1.24-1.13 (m, 6 H, (*E*)- $\text{H}_3\text{C}(6)$, (*Z*)- $\text{H}_3\text{C}(6)$, (*E*)- $\text{H}_3\text{C}(8)$, (*Z*)- $\text{H}_3\text{C}(8)$), 1.11-1.05 (m, 36 H, (*E*)- $\text{H}_3\text{C}(7)$, (*Z*)- $\text{H}_3\text{C}(7)$, (*E*)- $\text{H}_3\text{C}(9)$, (*Z*)- $\text{H}_3\text{C}(9)$)

Preparation of (2*Z*/4*Z*)-3,5-Bis(trimethylsilyloxy)-2,5-heptadiene (33a) (Figure 3)

Following Representative Procedure 2, 2.71 mL (20 mmol) of 3,5-heptanedione (**31**) was combined with 6.13 mL (44 mmol, 2.2 equiv) of Et_3N , and 7.14 mL (40 mmol, 2.0 equiv) of TMSOTf to yield, after bulb-to-bulb distillation, 5.246 g (96%, 2*Z*,4*Z*:minor isomers, 90:10) of **33a** as a clear, colorless oil.

Data for **33a**:

bp: 90 °C (0.05 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

5.20 (q, $J = 7.0$, 1 H, HC(2)), 4.75 (d, $J = 0.5$, 1 H, HC(4)), 2.07 (q, $J = 7.5$, 2 H,

H₂C(6)), 1.60 (d, $J = 6.8$, 3 H, H₃C(1)), 1.06-1.01 (m, 3 H, H₃C(7)), 0.20 (s, 9 H, H₃C(8)), 0.17 (s, 9 H, H₃C(9))

Preparation of (2Z,4Z)-3,5-Bis(*tert*-butyldimethylsilyloxy)-2,4-heptadiene (**33b**) (Figure 3)

Following Representative Procedure 2, 2.71 mL (20 mmol) of 3,5-heptanedione (**31**) was combined with 6.13 mL (44 mmol, 2.2 equiv) of Et₃N, and 9.19 mL (40 mmol, 2.0 equiv) of TBSOTf to yield, after bulb-to-bulb distillation, 6.01 g (84%, 2Z,4Z:minor isomers, 90:10) of **33b** as a clear, colorless oil.

Data for (2Z,4Z)-**33b**:

bp: 150 °C (0.1 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

5.12 (q, $J = 6.9$, 1 H, HC(2)), 4.73 (s, 1 H, HC(4)), 2.09 (q, $J = 7.4$, 2 H, H₂C(6)), 1.61 (d, $J = 6.8$, 3 H, H₃C(1)), 1.08-1.02 (m, 3 H, H₃C(7)), 0.96 (s, 9 H, H₃C(10)), 0.94 (s, 9 H, H₃C(13)), 0.15 (s, 6 H, H₃C(8)), 0.11 (s, 6 H, H₃C(11))

NOE ¹H NMR: (500 MHz, CDCl₃)

Irradiation at 4.73 ppm (H₃C(4)) enhanced signals at 5.12 ppm (HC(2)) and 2.09 (H₂C(6)).

¹³C NMR: (126 MHz, CDCl₃)

153.5 (C(5)), 145.0 (C(3)), 106.1 (C(2)), 105.4 (C(4)), 30.2 (C(6)), 25.9 (C(10)), 25.8 (C(13)), 18.3 (C(9)), 18.2 (C(12)), 11.8 (C(7)), 10.8 (C(1)), -3.6 (C(8)), -3.9 (C(12))

IR: (neat)

2959 (s), 2931 (s), 2896 (s), 2859 (s), 2740 (w), 2711 (w), 2361 (w), 1655 (w), 1591 (w), 1473 (s), 1464 (s), 1406 (m), 1390 (m), 1362 (s), 1323 (m), 1301 (s), 1289 (s), 1255 (s), 1199 (s), 1168 (s), 1103 (m), 1076 (s), 1045 (s), 1004 (s), 938 (s), 904 (m), 880 (m), 839 (s), 811 (s), 778 (s), 704 (w), 697 (m), 623 (w)

MS: (EI, 70 eV)
 357 (13), 356 (M^+ , 35), 341 (12), 328 (16), 327 (54), 299 (27), 271 (35), 225 (16),
 185 (38), 149 (25), 147 (55), 133 (16), 95 (15), 75 (20), 59 (10), 57 (10)

HRMS: Calcd for $C_{19}H_{40}O_2Si_2$: 356.2567, found: 356.2567

Preparation of (2Z/4Z)-3,5-Bis(triethylsilyloxy)-2,4-heptadiene (33c) (Figure 3)

Following Representative Procedure 2, 2.71 mL (20 mmol) of 3,5-heptanedione (**31**) was combined with 6.13 mL (44 mmol, 2.2 equiv) of Et_3N , and 9.05 mL (40 mmol, 2.0 equiv) of TESOTf to yield, after bulb-to-bulb distillation, 6.955 g (97%, 2Z,4Z:minor isomers, 90:10) of **33c** as a clear, colorless oil.

Data for 33c:

bp: $90\text{ }^\circ\text{C}$ (0.05 mmHg, ABT)

1H NMR: (500 MHz, $CDCl_3$)
 5.21 (q, $J = 6.8$, 1 H, HC(2)), 4.69 (s, 1 H, HC(4)), 2.10 (q, $J = 7.3$, 2 H, $H_2C(6)$),
 1.62 (d, $J = 6.8$, 3 H, $H_3C(1)$), 1.04 (t, $J = 7.3$, 3 H, $H_3C(7)$), 1.01-0.91 (m, 18 H,
 $H_3C(9)$, $H_3C(11)$), 0.73-0.63 (m, 12 H, $H_2C(8)$), $H_2C(10)$)

Preparations of Conjugated *N,O*-Silyl Ketene Acetals From α,β -Unsaturated Amides.

Representative Procedure 2. Enolization of α,β -Unsaturated Amides to Form Conjugate *N,O*-Silyl Ketene Acetals. Preparation of (*Z*)-[1-(*tert*-Butyldimethylsilyloxy)-1,3-butadienyl]dimethylamine (**41**) (Figure 4)

To a flame-dried 200-mL, 3-necked, round-bottomed flask fitted with a magnetic stir bar, thermocouple, gas inlet tube, and septum, was added 1.13 g (10 mmol) of 2-butenic acid dimethylamide and 50 mL of THF. The solution was cooled to $-72\text{ }^{\circ}\text{C}$ and then a solution of 2.19 g (1.1 mmol, 1.1 equiv) of potassium hexamethyldisilazide in 20 mL THF was added slowly dropwise over 5 min via syringe. The resulting yellow solution was stirred for 30 min at $-72\text{ }^{\circ}\text{C}$ prior to addition of a solution of 1.66 g (11 mmol, 1.1 equiv) of TBSCl in 10 mL of THF via syringe. The dry ice bath was then removed and the solution was allowed to warm to $0\text{ }^{\circ}\text{C}$. The yellow solution was then concentrated *in vacuo*, and the resulting residue was taken up in 50 mL of pentane. The yellow precipitate which is formed was then filtered through a pad of Celite and the filtrate was concentrated *in vacuo*. The residue was purified by bulb-to-bulb distillation to afford 1.738 g (77%) of **41** as a clear, colorless oil.

Data for (*Z*)-**41**:

bp: $60\text{ }^{\circ}\text{C}$ (0.01 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

6.54 (dt, $J = 17.1, 10.5$, 1 H, HC(3)), 4.79 (dd, $J = 17.1, 2.2$, 1 H, HC(4)), 4.61 (d, $J = 10.7$, 1 H, HC(2)), 4.53 (dd, $J = 10.5, 2.3$, 1 H, HC(4)), 2.58 (s, 6 H, $\text{H}_3\text{C}(5)$), 1.00 (s, 9 H, $\text{H}_3\text{C}(8)$), 0.16 (s, 6 H, $\text{H}_3\text{C}(6)$)

NOE ^1H NMR: (500 MHz, CDCl_3)

Irradiation at 3.58 ppm ($\text{H}_3\text{C}(5)$) enhanced signal at 4.61 ppm (HC(2))

¹³C NMR: (126 MHz, CDCl₃)
 155.5 (C(1)), 133.4 (C(3)), 105.6 (C(4)), 89.2 (C(2)), 39.5 (C(5)), 25.7 (C(8)),
 18.3 (C(7)), -4.6 (C(6))

IR: (neat)
 3083 (m), 3060 (m), 3013 (m), 2955 (s), 2932 (s), 2886 (m), 2859 (s), 2793 (m),
 1631 (s), 1474 (s), 1461 (s), 1438 (m), 1419 (s), 1390 (m), 1346 (s), 1298 (m),
 1281 (m), 1254 (s), 1195 (s), 1145 (s), 1125 (s), 1102 (m), 1055 (m), 1023 (s),
 1005 (m), 996 (m), 944 (m), 881 (s), 839 (s), 825 (s), 810 (s), 782 (s), 739 (m),
 679 (m), 655 (m), 642 (m)

MS: (EI, 70 eV)
 228 (18), 227 (M⁺, 85), 212 (51), 171 (32), 170 (71), 157 (15), 156 (100), 147
 (12), 130 (14), 96 (19), 81 (13), 75 (13), 73 (52), 59 (12), 57 (19)

HRMS: Calcd for C₁₂H₂₅NOSi: 227.1705, found: 227.1694

Preparation of (Z)-[1-(*tert*-Butyldimethylsilanyloxy)-1,3-butadienyl]diethylamine (42**) (Figure 4)**

Following Representative Procedure 3, 1.41 g (10 mmol) of 2-butenamide diethylamide was combined with 2.19 g (1.1 mmol, 1.1 equiv) of potassium hexamethyldisilazide, and 1.66 g (11 mmol, 1.1 equiv) of TBSCl to yield, after bulb-to-bulb distillation, 2.27 g (89%) of **42** as a clear, colorless oil.

Data for (Z)-42:

bp: 90 °C (0.05 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)
 6.58 (dt, *J* = 17.1, 10.5, 1 H, HC(3)), 4.76 (dd, *J* = 17.2, 1.9, 1 H, HC(4)), 4.62 (d, *J* = 10.7, 1 H, HC(2)), 4.53 (dd, *J* = 10.3, 2.3, 1 H, HC(4)), 3.00 (q, *J* = 7.1, 4 H, H₂C(5)), 1.02 (t, *J* = 7.1, 6 H, H₃C(6)), 0.99 (s, 9 H, H₃C(9)), 0.15 (s, 6 H,

H₃C(7))NOE ¹H NMR: (500 MHz, CDCl₃)Irradiation at 3.00 ppm (H₂C(5)) enhanced signal at 4.62 ppm (HC(2)) and 1.02 ppm (H₃C(6))¹³C NMR: (126 MHz, CDCl₃)

153.1 (C(1)), 133.7 (C(3)), 104.8 (C(4)), 91.5 (C(2)), 42.0 (C(5)), 25.8 (C(9)), 18.3 (C(8)), 11.4 (C(6)), -4.5 (C(7))

IR: (neat)

3083 (m), 3057 (w), 3013 (m), 2961 (s), 2932 (s), 2896 (m), 2859 (s), 1631 (s), 1591 (m), 1473 (m), 1464 (m), 1449 (w), 1418 (s), 1390 (m), 1370 (s), 1343 (m), 1309 (m), 1282 (m), 1252 (s), 1238 (s), 1181 (m), 1126 (s), 1096 (w), 1071 (m), 1058 (m), 1036 (s), 1005 (m), 994 (m), 945 (m), 922 (m), 839 (s), 807 (s), 781 (s), 738 (w), 680 (m), 657 (w), 642 (w)

MS: (EI, 70 eV)256 (22), 255 (M⁺, 88), 254 (14), 241 (19), 240 (97), 226 (14), 199 (34), 198 (48), 185 (19), 184 (100), 171 (16), 170 (36), 156 (12), 144 (12), 124 (21), 100 (15), 95 (11), 75 (22), 73 (91), 68 (16), 67 (20), 59 (21), 57 (13)HRMS: Calcd for C₁₄H₂₉NOSi: 255.2018, found: 255.2016**Preparation of (Z)-1-[1-(*tert*-Butyldimethylsilanyloxy)-1,3-butadienyl]pyrrolidine (43) (Figure 4)**

Following Representative Procedure 3, 1.53 g (10 mmol) of 1-[(*2E*)-1-oxo-2-butenyl]pyrrolidine was combined with 2.19 g (1.1 mmol, 1.1 equiv) of potassium hexamethyldisilazide, and 1.66 g (11 mmol, 1.1 equiv) of TBSCl to yield, after bulb-to-bulb distillation, 1.012 g (40%) of **43** as a clear, colorless oil.

Data for (Z)-43:bp: 100 °C (0.05 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)
 6.52 (dt, *J* = 17.1, 10.5, 1 H, HC(3)), 4.68 (dd, *J* = 17.2, 2.2, 1 H, HC(4)), 4.48 (d, *J* = 10.5, 1 H, HC(2)), 4.39 (dd, *J* = 10.3, 2.2, 1 H, HC(4)), 3.11-3.08 (m, 4 H, H₂C(5)), 1.84-1.81 (m, 4 H, H₂C(6)), 1.00 (s, 9 H, H₃C(9)), 0.19 (s, 6 H, H₃C(7))

NOE ¹H NMR: (500 MHz, CDCl₃)

Irradiation at 3.11-3.08 ppm (H₂C(5)) enhanced signal at 4.48 ppm (HC(2)) and 1.84-1.81 ppm (H₂C(6))

¹³C NMR: (126 MHz, CDCl₃)
 153.0 (C(1)), 133.8 (C(3)), 102.3 (C(4)), 84.8 (C(2)), 47.6 (C(5)), 25.8 (C(9)), 25.0 (C(6)), 18.3 (C(8)), -4.1 (C(7))

IR: (neat)
 3374 (w) 3081 (w), 3058 (w), 2955 (s), 2931 (s), 2884 (s), 2858 (s), 1624 (s), 1472 (s), 1463 (m), 1421 (s), 1389 (m), 1362 (s), 1297 (m), 1254 (s), 1227 (m), 1191 (m), 1058 (s), 1005 (m), 940 (m), 914 (m), 882 (s), 839 (s), 810 (s), 781 (s), 738 (w), 672 (m), 646 (w)

Preparation of (Z)-1-[1-(*tert*-Butyldimethylsilanyloxy)-1,3-butadienyl]piperidine (44)
(Figure 4)

Following Representative Procedure 3, 1.531 g (10 mmol) of 1-[(2*E*)-1-oxo-2-butenyl]piperidine was combined with 2.19 g (1.1 mmol, 1.1 equiv) of potassium hexamethyldisilazide (1.1 mmol, 1.1 equiv), and 1.66 g (11 mmol, 1.1 equiv) of TBSCl to yield, after bulb-to-bulb distillation, 2.138 g (80%) of **44** as a clear, colorless oil.

Data for (Z)-44:bp: 100 °C (0.05 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)
6.57 (dt, $J = 17.1, 10.5$, 1 H, HC(3)), 4.83 (ddd, $J = 17.2, 2.2, 0.5$, 1 H, HC(4)),
4.66 (d, $J = 10.5$, 1 H, HC(2)), 4.58 (ddd, $J = 10.3, 2.2, 0.5$, 1 H, HC(4)), 2.85-
2.79 (m, 4 H, H₂C(5)), 1.59-1.48 (m, 6 H, H₂C(6), H₂C(7)), 0.99 (s, 9 H,
H₃C(10)), 0.16 (s, 6 H, H₃C(8))

NOE ¹H NMR: (500 MHz, CDCl₃)
Irradiation at 2.85 ppm (H₂C(5)) enhanced signal at 4.66 ppm (HC(2)) and 1.59-
1.48 ppm (H₂C(6,7))

¹³C NMR: (126 MHz, CDCl₃)
156.0 (C(1)), 133.3 (C(3)), 106.7 (C(4)), 91.0 (C(2)), 49.1 (C(5)), 25.8 (C(10)),
25.4 (C(6)), 24.4 (C(7)), 18.3 (C(9)), -4.5 (C(8))

IR: (neat)
3083 (w), 3057 (w), 2935 (s), 2858 (s), 2809 (m), 1634 (s), 1594 (m), 1471 (m),
1453 (m), 1444 (m), 1418 (s), 1381 (m), 1370 (s), 1344 (s), 1308 (m), 1274 (w),
1253 (s), 1214 (s), 1183 (w), 1156 (w), 1132 (s), 1057 (s), 1034 (m), 999 (s), 991
(s), 869 (s), 829 (s), 815 (m), 781 (s), 734 (w), 683 (w), 668 (w), 647 (w)

MS: (EI, 70 eV)
268 (26), 267 (M⁺, 90), 266 (19), 253 (22), 252 (97), 212 (10), 211 (40), 210 (40),
197 (19), 196 (100), 183 (16), 182 (11), 168 (10), 147 (26), 142 (11), 138 (10),
136 (22), 84 (17), 75 (31), 73 (86), 69 (12), 68 (10), 59 (26), 57 (72), 56 (13), 55
(16)

HRMS: Calcd for C₁₅H₂₉NOSi: 267.2018, found: 267.2016

Preparation of (Z)-1-[1-(*tert*-Butyldimethylsilanyloxy)-1,3-butadienyl]morpholine (45)
(Figure 4)

Following Representative Procedure 3, 1.55 g (10 mmol) of 4-[(2*E*)-1-oxo-2-butenyl]morpholine was combined with 2.19 g (1.1 mmol, 1.1 equiv) of potassium hexamethyldisilazide, and 1.66 g (11 mmol, 1.1 equiv) of TBSCl to yield, after bulb-to-bulb distillation, 2.11 g (78%) of **45** as a clear, colorless oil.

Data for (Z)-45:

bp: 100 °C (0.04 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

6.54 (dt, *J* = 17.1, 10.5, 1 H, HC(3)), 4.87 (dd, *J* = 17.1, 2.2, 1 H, HC(4)), 4.68 (d, *J* = 10.5, 1 H, HC(2)), 4.64 (dd, *J* = 10.3, 2.2, 1 H, HC(4)), 3.71-3.66 (m, 4 H, H₂C(6)), 2.90-2.88 (m, 4 H, H₂C(5)), 0.99 (s, 9 H, H₃C(9)), 0.17 (s, 6 H, H₃C(7))

NOE ¹H NMR: (500 MHz, CDCl₃)

Irradiation at 2.90-2.88 ppm (H₂C(5)) enhanced signal at 4.68 ppm (HC(2)) and 3.71-3.66 ppm (H₂C(6))

¹³C NMR: (126 MHz, CDCl₃)

154.8 (C(1)), 132.6 (C(3)), 108.0 (C(4)), 91.8 (C(2)), 66.5 (C(6)), 48.4 (C(5)), 25.8 (C(9)), 18.2 (C(8)), -4.5 (C(7))

IR: (neat)

3083 (w), 3060 (w), 2959 (m), 2931 (m), 2894 (m), 2857 (m), 2829 (m), 1636 (s), 1595 (m), 1473 (m), 1462 (m), 1454 (m), 1419 (m), 1390 (w), 1371 (m), 1362 (m), 1347 (s), 1312 (w), 1297 (w), 1283 (w), 1260 (m), 1218 (s), 1270 (s), 1183 (m), 1121 (s), 1063 (s), 1012 (m), 945 (m), 926 (w), 876 (s), 835 (s), 808 (m), 782 (s), 735 (w), 691 (w), 674 (m), 648 (w), 629 (w)

MS: (EI, 70 eV)

270 (28), 269 (M^+ , 100), 255 (10), 254 (47), 228 (37), 226 (13), 214 (15), 213 (22), 212 (29), 199 (10), 198 (46), 189 (11), 183 (27), 182 (13), 170 (12), 168 (13), 155 (10), 154 (11), 147 (25), 75 (53), 73 (56), 59 (14), 57 (28), 56 (11)

HRMS: Calcd for $C_{14}H_{27}NO_2Si$: 269.1811, found: 269.1805

Preparation of (*E*)-1-[1-(*tert*-Butyldimethylsilyloxy)-2-methyl-1,3-butadienyl]morpholine (72**) (Figure 5)**

Following Representative Procedure 3, 1.69 g (10 mmol) of 4-[(*2E*)-1-oxo-2-methyl-2-butenyl]morpholine was combined with 2.19 g (1.1 mmol, 1.1 equiv) of potassium hexamethyldisilazide, and 1.66 g (11 mmol, 1.1 equiv) of TBSCl to yield, after bulb-to-bulb distillation, 2.51 g (89%, *E*:*Z*, 72:28) of **72** as a clear, colorless oil.

Data for (*E*)-**72**:

bp: 130 °C (0.05 mmHg, ABT)

1H NMR: (500 MHz, $CDCl_3$)

6.80 (dd, $J = 17.5, 10.9$, 1 H, HC(3)), 4.89 (dd, $J = 17.5, 1.6$, 1 H, HC(4)), 4.81 (dd, $J = 11.0, 1.7$, 1 H, HC(4)), 3.72-3.70 (m, 4 H, $H_2C(6)$), 2.94-2.92 (m, 4 H, $H_2C(5)$), 1.68 (s, 3 H, $H_3C(7)$), 0.99 (s, 9 H, $H_3C(10)$), 0.20 (s, 6 H, $H_3C(8)$)

NOE 1H NMR: (500 MHz, $CDCl_3$)

Irradiation at 1.68 ppm ($H_3C(7)$) enhanced signal at 4.88 ppm (HC(4)), 0.99 ppm ($H_3C(10)$) and 0.20 ppm ($H_3C(8)$)

^{13}C NMR: (126 MHz, $CDCl_3$)

151.7 (C(1)), 136.0 (C(3)), 108.0 (C(4)), 104.9 (C(2)), 67.2 (C(6)), 49.7 (C(5)), 26.0 (C(10)), 18.5 (C(9)), 12.2 (C(7)), -3.2 (C(8))

IR: (neat)

3088 (w), 3015 (w), 2957 (s), 2931 (s), 2892 (s), 2857 (s), 1628 (s), 1473 (m),

1462 (s), 1420 (m), 1389 (m), 1362 (s), 1343 (m), 1328 (m), 1299 (m), 1281 (s), 1260 (m), 1195 (s), 1171 (s), 1070 (s), 1052 (m), 1029 (m), 1006 (s), 971 (s), 939 (w), 923 (m), 874 (s), 838 (s), 780 (s), 691 (m), 668 (m), 621 (w)

MS: (EI, 70 eV)

283 (M^+ , 26), 268 (32), 242 (37), 212 (28), 188 (13), 185 (27), 168 (13), 154 (15), 149 (13), 147 (29), 143 (12), 133 (12), 114 (15), 86 (14), 83 (19), 82 (12), 75 (83), 74 (11), 73 (100), 70 (21), 59 (25), 58 (13), 57 (84), 56 (37), 55 (35), 54 (18), 53 (21)

HRMS: Calcd for $C_{15}H_{29}NO_2Si$: 283.1968, found: 283.1962

Preparation of (Z)-1-[1-(*tert*-Butyldimethylsilanyloxy)-3-methyl-1,3-butadienyl]morpholine (73) (Figure 5)

Following Representative Procedure 3, 1.69 g (10 mmol) of 4-[(2*E*)-1-oxo-3-methyl-2-butenyl]morpholine was combined with 2.19 g (1.1 mmol, 1.1 equiv) of potassium hexamethyldisilazide, and 1.66 g (11 mmol, 1.1 equiv) of TBSCl to yield, after bulb-to-bulb distillation, 2.32 g (82%, *Z*:*E*, 95:5) of **73** as a clear, colorless oil.

Data for (Z)-73:

bp: 130 °C (0.05 mmHg, ABT)

1H NMR: (500 MHz, $CDCl_3$)

4.96 (dd, $J = 2.7, 0.7$, 1 H, HC(4)), 4.72 (dd, $J = 2.8, 1.5$, 1 H, HC(4)), 4.34 (s, 1 H, HC(2)), 3.72-3.70 (m, 4 H, $H_2C(6)$), 2.85-2.83 (m, 4 H, $H_2C(5)$), 1.87 (s, 3 H, $H_3C(7)$), 0.95 (s, 9 H, $H_3C(10)$), 0.18 (s, 6 H, $H_3C(8)$)

NOE 1H NMR: (500 MHz, $CDCl_3$)

Irradiation at 4.34 ppm (HC(2)) enhanced signal at 2.84-2.82 ppm ($H_2C(5)$) and 4.96 ppm (HC(4))

¹³C NMR: (126 MHz, CDCl₃)
 154.5 (C(1)), 139.6 (C(3)), 110.7 (C(4)), 92.4 (C(2)), 66.5 (C(6)), 49.5 (C(5)),
 26.1 (C(10)), 24.4 (C(7)), 18.2 (C(9)), -3.8 (C(8))

IR: (neat)
 3078 (w), 2960 (s), 2931 (s), 2894 (s), 2857 (s), 2826 (s), 1640 (s), 1472 (m),
 1462 (m), 1454 (s), 1409 (m), 1390 (m), 1371 (s), 1362 (s), 1299 (m), 1260 (s),
 1212 (m), 1197 (s), 1171 (m), 1121 (s), 1077 (s), 1015 (m), 970 (s), 938 (w), 927
 (w), 902 (m), 881 (s), 841 (s), 826 (s), 810 (s), 781 (s), 741 (w), 722 (w), 688 (w),
 668 (w), 630 (w)

MS: (EI, 70 eV)
 283 (M⁺, 14), 268 (37), 226 (20), 212 (44), 168 (13), 127 (10), 83 (26), 82 (13),
 75 (34), 73 (100), 59 (34), 57 (64), 56 (19), 55 (24), 54 (12), 53 (18)

HRMS: Calcd for C₁₅H₂₉NO₂Si: 283.1968, found: 283.1964

Preparation of (Z)-1-[1-(Trimethylsilyloxy)-3-methyl-1,3-butadienyl]morpholine (81)
 (Table 14, entry 2)

Following Representative Procedure 3, 0.846 g (5 mmol) of 4-[(2E)-1-oxo-3-methyl-2-butenyl]morpholine was combined with 1.10 g (5.5 mmol, 1.1 equiv) of potassium hexamethyldisilazide, and 0.696 mL (5.5 mmol, 1.1 equiv) of TMSCl to yield, after bulb-to-bulb distillation, 1.03 g (85%, *Z:E*, 95:5) of **81** as a clear, colorless oil.

Data for (Z)-81:

bp: 100 °C (0.05 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)
 4.96 (dd, *J* = 2.7, 0.7, 1 H, HC(4)), 4.72 (dd, *J* = 2.8, 1.5, 1 H, HC(4)), 4.34 (s, 1
 H, HC(2)), 3.72-3.70 (m, 4 H, H₂C(6)), 2.85-2.83 (m, 4 H, H₂C(5)), 1.87 (s, 3 H,
 H₃C(7)), 0.21 (s, 9 H, H₃C(8))

Preparation of (Z)-1-[1-(Triisopropylsilyloxy)-3-methyl-1,3-butadienyl]morpholine (82**)**
(Table 14, entry 3)

Following Representative Procedure 3, 0.846 g (5 mmol) of 4-[(2*E*)-1-oxo-3-methyl-2-butenyl]morpholine was combined with 1.10 g (5.5 mmol, 1.1 equiv) of potassium hexamethyldisilazide, and 1.18 g (5.5 mmol, 1.1 equiv) of TIPSCl to yield, after bulb-to-bulb distillation, 1.597 g (98%, *Z:E*, 95:5) of **82** as a clear, colorless oil.

Data for (Z)-**82**:

bp: 140 °C (0.05 mmHg, ABT)
¹H NMR: (500 MHz, CDCl₃)
 4.96 (dd, *J* = 2.7, 0.7, 1 H, HC(4)), 4.72 (dd, *J* = 2.8, 1.5, 1 H, HC(4)), 4.34 (s, 1 H, HC(2)), 3.72-3.70 (m, 4 H, H₂C(6)), 2.85-2.83 (m, 4 H, H₂C(5)), 1.87 (s, 3 H, H₃C(7)), 1.21-0.81 (m, 21 H, H₃C(9), HC(8))

Preparation of (1Z,3Z)-1-[1-(*tert*-Butyldimethylsilyloxy)-1,3-pentadienyl]morpholine (74**)**
(Figure 5)

Following Representative Procedure 3, 1.69 g (10 mmol) of 4-[(2*E*)-1-oxo-2-pentenyl]morpholine was combined with 2.19 g (1.1 mmol, 1.1 equiv) of potassium hexamethyldisilazide, and 1.66 g (11 mmol, 1.1 equiv) of TBSCl to yield, after bulb-to-bulb distillation, 2.526 g (89%, 1*Z*,3*Z*:minor isomers, 90:10) of **74** as a clear, colorless oil.

Data for (1Z,3Z)-**74**:

bp: 150 °C (0.05 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)
6.21-6.16 (m, 1 H, HC(3)), 5.17-5.10 (m, 1 H, HC(4)), 4.75 (d, $J = 11.0$, 1 H, HC(2)), 3.72-3.70 (m, 4 H, H₂C(6)), 2.91-2.89 (m, 4 H, H₂C(5)), 1.68 (dd, $J = 7.1$, 1.7, 3 H, H₃C(7)), 0.98 (s, 9 H, H₃C(10)), 0.16 (s, 6 H, H₃C(8))

NOE ¹H NMR: (500 MHz, CDCl₃)
Irradiation at 4.75 ppm (HC(2)) enhanced signal at 2.90-2.89 ppm (HC(5)), and 1.69 ppm (H₃C(7))

¹³C NMR: (126 MHz, CDCl₃)
154.5 (C(1)), 124.9 (C(3)), 117.9 (C(4)), 86.1 (C(2)), 66.5 (C(6)), 48.6 (C(5)), 25.8 (C(10)), 18.2 (C(9)), 13.2 (C(7)), -4.5 (C(8))

IR: (neat)
3033 (w), 2959 (s), 2931 (s), 2894 (s), 2857 (s), 2827 (m), 1645 (s), 1604 (s), 1560 (w), 1473 (s), 1454 (s), 1415 (m), 1390 (m), 1373 (s), 1362 (s), 1342 (s), 1310 (m), 1297 (m), 1253 (s), 1214 (s), 1203 (s), 1195 (s), 1178 (m), 1122 (s), 1076 (s), 1036 (m), 987 (s), 929 (m), 874 (s), 838 (s), 809 (s), 782 (s), 714 (s), 689 (m), 667 (m), 644 (w)

MS: (EI, 70 eV)
284 (26), 283 (M⁺, 100), 282 (11), 268 (18), 255 (10), 254 (44), 242 (17), 226 (32), 212 (28), 198 (22), 168 (10), 147 (11), 75 (24), 73 (77), 59 (16)

HRMS: Calcd for C₁₅H₂₉NO₂Si: 283.1968, found: 283.1966

Vinylogous Aldol Additions of Silyl Dienol Ethers

Representative Procedure 4. Addition of Acyclic α,β -Unsaturated Ketone-Derived Silyl Dienol Ethers to Aldehydes. Preparation of (+)-(5*R*,2*E*)-5-Hydroxy-1,5-diphenyl-2-penten-1-one (**11**) (Table 1, entry 1)

Diisopropylethylamine (35 μ L, 0.2 mmol, 0.2 equiv) was added via syringe to a flame-dried, 5-mL, Schlenk flask under Ar containing a solution of 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3** CH_2Cl_2 (2 mL). To this solution was added 102 μ L (1.0 mmol, 1.0 equiv) of benzaldehyde in one portion and the reaction mixture was cooled to $-50\text{ }^\circ\text{C}$ over 15 min. To the resulting solution was added 172 μ L (1.1 mmol, 1.1 equiv) of SiCl_4 in one portion. Then, 284 μ L (1.2 mmol, 1.2 equiv) of **6** was added dropwise over 1 min via syringe. The resulting mixture was stirred at $-50\text{ }^\circ\text{C}$ for 24 h whereupon 3.0 mL of chilled CH_2Cl_2 was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO_3 / sat. aq. KF (25 mL) at $0\text{ }^\circ\text{C}$. This biphasic mixture was stirred vigorously for 1 h before being filtered through Celite on a glass frit. The phases were then separated and the aqueous layer was washed with CH_2Cl_2 (3 x 40 mL). The combined organic extracts were dried over Na_2SO_4 (5 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (SiO_2 (25 g), 3 cm diam., hexanes/EtOAc, 4/1 to yield 201 mg (80%) of (+)-**11** as a thick, colorless oil.

Data for (+)-**11**:

^1H NMR: (500 MHz, CDCl_3)

7.88 (d, $J = 7.1$, 2 H, HC(11)), (dt, $J = 7.5$, 1.5, 1 H, HC(13)), 7.43 (t, $J = 7.6$ 2 H, HC(12)), 7.39-7.35 (m, 4 H, HC(7,8)), 7.32-7.28 (m, 1 H, HC(9)), 7.06-7.00 (m, 1 H, HC(3)), 6.91 (dt, $J = 15.4$, 1.3, 1 H, HC(2)), 4.90 (dd, $J = 7.7$, 5.1, 1 H, HC(5)), 2.83-2.71 (m, 2 H, HC(4)), 2.31 (br s, 1 H, OH)

¹³C NMR: (125 MHz, CDCl₃)
 190.7 (C(1)), 145.0 (C(3)), 143.5 (C(6)), 137.6 (C(10)), 132.8 (C(13)), 128.6 (C(11)), 128.6 (C(8)), 128.6 (C(2) or C(12)), 128.5 (C(2) or C(12)), 127.9 (C(9)), 125.8 (C(7)), 73.2 (C(5)), 42.5 (C(4))

IR: (neat)
 4057 (w), 3430 (m), 3061 (w), 3030 (w), 2894 (w), 2360 (w), 2340 (w), 1964 (w), 1901 (w), 1817 (w), 1668 (m), 1652 (m), 1621 (m), 1598 (m), 1578 (w), 1494 (w), 1448 (m), 1418 (w), 1344 (m), 1285 (m), 1226 (m), 1180 (w), 1020 (m), 987 (m), 915 (w), 894 (w), 834 (w), 764 (m), 698 (m), 667 (m)

MS: (CI, CH₄)
 253 (M⁺+H, 17), 236 (10), 235 (51), 175 (18), 148 (11), 147 (100), 146 (43), 145 (11), 107 (71), 105 (79), 79 (13)

Opt. Rot.: [α]_D²⁴ +14.40° (c = 1.00, EtOH)

TLC: *R_f* 0.30 (hexanes/EtOAc, 3/2) [UV (254 nm)]

SFC: (*R*)-**11**, *t_R* 3.04 min (99.0%); (*S*)-**11**, *t_R* 4.06 min (1.0%) (Chiralpak AD, 175 psi, 40 °C, 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₇H₁₆O₂ (252.31)
 Calcd: C, 80.93; H, 6.39%
 Found: C, 80.63; H, 6.33%

Preparation of (+)-(7*R*,4*E*)-7-Hydroxy-2,2-dimethyl-7-phenyl-4-hepten-3-one (12**) (Table 1, entry 2)**

Following Representative Procedure 4, 102 μ L (1.0 mmol) of benzaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 35 μ L (0.2 mmol, 0.2 equiv) of diisopropylethylamine, 172 μ L (1.5 mmol, 1.5 equiv) of SiCl₄ and 290 μ L (1.2 mmol, 1.2 equiv) of **7** to yield, after column chromatography (SiO₂ (20 g), 2 cm diam., hexanes/EtOAc 3/1) to yield 218 mg (94%) of (+)-**12** as a white solid. The ratio of γ/α -addition

products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-12:

mp: 49-50 °C (benzene)

^1H NMR: (500 MHz, CDCl_3)
7.38-7.34 (m, 4 H, HC(9,10)), 7.30-7.27 (m, 1 H, HC(11)), 6.94-6.88 (m, 1 H, HC(5)), 6.53 (dt, $J = 15.3, 1.4$, 1 H, HC(4)), 4.84 (dd, $J = 7.6, 5.4$, 1 H, HC(7)), 2.72-2.61 (m, 2 H, $\text{H}_2\text{C}(6)$), 2.02 (br s, 1 H, OH), 1.11 (s, 9 H, $\text{H}_3\text{C}(1)$)

^{13}C NMR: (125 MHz, CDCl_3)
204.2 (C(3)), 143.5 (C(8)), 142.6 (C(5)), 128.6 (C(10)), 127.8 (C(11)), 127.0 (C(4)), 125.8 (C(9)), 73.1 (C(7)), 42.8 (C(2)), 42.2 (C(6)), 26.0 (C(1))

IR: (CHCl_3)
4059 (w), 3436 (m), 3087 (w), 3063 (w), 3016 (m), 2970 (s), 2934 (m), 2906 (m), 2871 (m), 2444 (w), 1951 (w), 1879 (w), 1809 (w), 1686 (s), 1624 (s), 1494 (m), 1478 (s), 1455 (m), 1396 (m), 1367 (m), 1334 (m), 1295 (m), 1218 (m), 1178 (w), 1102 (m), 1082 (m), 1066 (m), 1047 (m), 1028 (m), 992 (m), 940 (w), 866 (w), 844 (w), 756 (s), 700 (s), 667 (m), 630 (w)

MS: (CI, CH_4)
233 (M^+H , 4), 215 (26), 155 (10), 129 (13), 127 (59), 126 (25), 109 (15), 107 (91), 105 (13), 85 (37), 79 (20), 69 (21), 63 (16), 57 (100), 55 (12)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +6.12^\circ$ ($c = 0.95$, EtOH)

TLC: R_f 0.34 (hexanes/EtOAc, 3/2) [UV (254 nm)]

SFC: (*R*)-12, t_R 5.63 min (99.4%); (*S*)-12, t_R 6.41 min (0.6%) (Chiralpak AD, 150 psi, 40 °C, 3.5% MeOH in CO_2 , 3.5 mL/min, 220 nm)

Analysis: $\text{C}_{15}\text{H}_{20}\text{O}_2$ (232.32)

Calcd: C, 77.55; H, 8.68%

Found: C, 77.58; H, 8.72%

Preparation of (+)-(7*R*,4*E*)-7-Hydroxy-2,2-dimethyl-7-naphthalen-1-yl-4-hepten-3-one (13)
(Table 1, entry 3)

Following Representative Procedure 4, 136 μL (1.0 mmol) of 1-naphthaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 35 μL (0.2 mmol, 0.2 equiv) of diisopropylethylamine, 172 μL (1.5 mmol, 1.5 equiv) of SiCl_4 and 290 μL (1.2 mmol, 1.2 equiv) of **7** to yield, after column chromatography (SiO_2 (20 g), 2 cm diam., pentane/ Et_2O 2/1) to yield 239 mg (85%) of (+)-**13** as a thick, clear oil. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-13**:**

^1H NMR: (500 MHz, CDCl_3)

8.07 (d, $J = 8.3$, 1 H, HC(9')), 7.89 (d, $J = 8.8$, 1 H, HC(6')), 7.80 (d, $J = 8.1$, 1 H, HC(4')), 7.67 (d, $J = 7.1$, 1 H, HC(2')), 7.56-7.47 (m, 3 H, HC(3', 7', 8')), 7.08-7.02 (m, 1 H, HC(5')), 6.57 (dd, $J = 15.3$, 1.4, 1 H, HC(4)), 5.64 (dd, $J = 8.0$, 4.4, 1 H, HC(7)), 2.92-2.75 (m, 2 H, $\text{H}_2\text{C}(6)$), 2.11 (br s, 1 H, OH), 1.11 (s, 9 H, $\text{H}_3\text{C}(1)$)

^{13}C NMR: (125 MHz, CDCl_3)

204.3 (C(3)), 143.1 (C(5)), 139.1 (C(1')), 133.7 (C(5')), 130.0 (C(10')), 129.0 (C(6')), 128.1 (C(4')), 126.8 (C(4)), 126.1 (C(8')), 125.5 (C(7')), 125.4 (C(3')), 122.9 (C(2')), 122.8 (C(9')), 69.7 (C(7)), 42.8 (C(2)), 41.2 (C(6)), 26.0 (C(1))

IR: (neat)

3437 (s), 3052 (m), 2968 (s), 2932 (s), 2906 (m), 2870 (m), 2719 (w), 2416 (w), 2249 (w), 1945 (w), 1814 (w), 1687 (s), 1621 (s), 1599 (m), 1512 (m), 1477 (s), 1464 (m), 1423 (m), 1395 (s), 1366 (s), 1326 (s), 1295 (m), 1266 (m), 1222 (m), 1163 (m), 1143 (w), 1104 (s), 1080 (s), 1051 (s), 1005 (s), 987 (s), 968 (s), 939 (m), 910 (s), 864 (m), 801 (s), 779 (s), 733 (s), 647 (m), 631 (m)

MS: (EI, 70 eV)

282 (M^+ , 3), 158 (13), 157 (100), 130 (10), 129 (86), 128 (49), 127 (33), 126 (59),

69 (23), 57 (27)

Opt. Rot.: $[\alpha]_D^{24} +57.11^\circ$ ($c = 1.10$, EtOH)TLC: R_f 0.49 (hexanes/EtOAc, 3/2) [UV (254 nm)]SFC: (*S*)-**13**, t_R 3.59 min (1.1%); (*R*)-**13**, t_R 4.81 min (98.9%) (Chiralpak OD, 125 psi, 40 °C, 17.5% MeOH in CO₂, 3.0 mL/min, 220 nm)Analysis: C₁₉H₂₂O₂ (282.38)

Calcd: C, 80.82; H, 7.85%

Found: C, 80.70; H, 7.83%

Preparation of (+)-(7*R*,4*E*)-7-Hydroxy-2,2-dimethyl-7-(2-furanyl)-4-hepten-3-one (14)
(Table 1, entry 4)

Following Representative Procedure 4, 84 μ L (1.0 mmol) of 2-furfuraldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 35 μ L (0.2 mmol, 0.2 equiv) of diisopropylethylamine, 172 μ L (1.5 mmol, 1.5 equiv) of SiCl₄ and 290 μ L (1.2 mmol, 1.2 equiv) of **7** to yield, after column chromatography (SiO₂ (20 g), 2 cm diam., pentane/Et₂O 2/1) to yield 199 mg (90%) of (+)-**14** as a waxy solid. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-**14**:¹H NMR: (500 MHz, CDCl₃)

7.38 (dd, $J = 1.7, 0.9$, 1 H, HC(11)), 6.89 (dt, $J = 15.4, 7.5$, 1 H, HC(5)), 6.58 (dt, $J = 15.3, 1.3$, 1 H, HC(4)), 6.33 (dd, $J = 3.2, 1.7$, 1 H HC(10)), 6.26 (d, $J = 3.2$, 1 H, HC(9)), 4.85 (t, $J = 6.6$, 1 H, HC(7)), 2.80-2.76 (m, 2 H, H₂C(6)), 2.02 (br s, 1 H, OH), 1.13 (s, 9 H, H₃C(1))

¹³C NMR: (125 MHz, CDCl₃)

204.1 (C(3)), 155.4 (C(8)), 142.2 (C(11)), 141.7 (C(5)), 127.1 (C(4)), 110.2 (C(10)), 106.5 (C(9)), 66.5 (C(7)), 42.8 (C(2)), 38.5 (C(6)), 26.0 (C(1))

IR: (neat)

3428 (s), 3122 (m), 3055 (w), 2969 (s), 2935 (s), 2908 (m), 2872 (m), 2301 (w), 1760 (m), 1688 (s), 1624 (s), 1569 (w), 1505 (m), 1478 (s), 1465 (s), 1396 (s), 1367 (s), 1329 (s), 1295 (m), 1223 (m), 1148 (s), 1069 (s), 1009 (s), 884 (m), 865 (m), 813 (m), 792 (m), 742 (s)

MS: (CI, CH₄)

223 (M⁺+H, 3), 206 (16), 205 (100), 127 (44), 126 (30), 109 (11), 97 (92), 85 (16), 69 (16), 57 (47)

Opt. Rot.: [α]_D²⁴ +3.80° (c = 1.00, EtOH)

TLC: *R_f* 0.34 (hexanes/EtOAc, 3/2) [UV (254 nm)]

SFC: (*R*)-**14**, *t_R* 5.73 min (95.8%); (*S*)-**14**, *t_R* 6.63 min (4.2%) (Chiralpak AD, 150 psi, 40 °C, 2.5% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₃H₁₈O₃ (222.28)

Calcd: C, 70.24; H, 8.16%

Found: C, 69.89; H, 8.20%

Preparation of (–)-(7*R*,4*E*)-7-Hydroxy-2,2-dimethyl-7-(2-thienyl)-4-hepten-3-one (15)
(Table 1, entry 5)

Following Representative Procedure 4, 94 μ L (1.0 mmol) of 2-thiophenecarboxaldehyde was combined with 84 mg (0.1 mmol, 0.1 equiv) of bisphosphoramidate (*R,R*)-**3**, 35 μ L (0.2 mmol, 0.2 equiv) of diisopropylethylamine, 172 μ L (1.5 mmol, 1.5 equiv) of SiCl₄ and 290 μ L (1.2 mmol, 1.2 equiv) of **7** to yield, after column chromatography (SiO₂ (20 g), 2 cm diam., hexanes/EtOAc 4/1) a solid which was recrystallized from hexanes (3 mL) at -20 °C to yield 119 mg (50%) of (–)-**15** as white needles. The ratio of γ / α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-**15**:

mp: 49-51 °C (hexanes)

¹H NMR: (500 MHz, CDCl₃)
7.27-7.25 (m, 1 H, HC(11)), 6.99-6.93 (m, 2 H, HC(9,10)), 6.89 (dt, *J* = 15.4, 7.4, 1 H, HC(5)), 6.58 (dt, *J* = 15.1, 1.5, 1 H, HC(4)), 5.09 (dd, *J* = 7.0, 6.1, 1 H, HC(7)), 2.82-2.71 (m, 2 H, H₂C(6)), 2.12 (br s, 1 H, OH), 1.13 (s, 9 H, H₃C(1))

¹³C NMR: (125 MHz, CDCl₃)
204.3 (C(3)), 147.4 (C(8)), 141.9 (C(5)), 127.2 (C(4)), 126.7 (C(10)), 124.8 (C(11)), 124.0 (C(9)), 67.0 (C(7)), 42.8 (C(2)), 42.2 (C(6)), 26.0 (C(1))

IR: (CHCl₃)
3436 (w), 3109 (w), 3017 (m), 2971 (m), 2934 (w), 2906 (w), 2871 (w), 2401 (w), 2361 (w), 2341 (w), 1686 (s), 1624 (s), 1534 (m), 1478 (m), 1464 (w), 1440 (w), 1396 (m), 1367 (m), 1321 (w), 1295 (w), 1216 (s), 1151 (w), 1100 (m), 1066 (m), 1038 (m), 1007 (m), 988 (m), 934 (w), 896 (w), 853 (w), 833 (w), 758 (s), 702 (s), 668 (m)

MS: (FI)
239 (15), 238 (M⁺, 100)

Opt. Rot.: [α]_D²⁴ -5.26° (c = 1.00, EtOH)

TLC: *R_f* 0.33 (hexanes/EtOAc, 3/2) [UV (254 nm)]

SFC: (*R*)-**15**, *t_R* 5.63 min (93.8%); (*S*)-**15**, *t_R* 6.33 min (6.2%) (Chiralpak AD, 150 psi, 40 °C, 5.0% MeOH in CO₂, 2.75 mL/min, 220 nm)

Analysis: C₁₃H₁₈O₂S (238.35)
Calcd: C, 65.51; H, 7.61%
Found: C, 65.30; H, 7.66%

Preparation of (–)-(7*R*,2*E*)-7-Hydroxy-2,2-dimethyl-9-phenyl-4,8-nonadien-3-one (16)
(Table 1, entry 6)

Following Representative Procedure 4, 126 μL (1.0 mmol) of cinnamaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 35 μL (0.2 mmol, 0.2 equiv) of diisopropylethylamine, 172 μL (1.5 mmol, 1.5 equiv) of SiCl_4 and 290 μL (1.2 mmol, 1.2 equiv) of **7** to yield, after column chromatography (SiO_2 (20 g), 2 cm diam., pentane/ Et_2O 2/1) to yield 211 mg (82%) of (–)-**16** as a white solid. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-16**:**

mp: 47–48 $^\circ\text{C}$ (benzene)

^1H NMR: (500 MHz, CDCl_3)

7.37 (d, $J = 7.1$, 2 H, HC(11)), 7.32 (t, $J = 7.5$, 2 H, HC(12)), 7.27–7.24 (m, 1 H, HC(13)), 6.96 (dt, $J = 15.1$, 7.6, 1 H, HC(5)), 6.64–6.60 (m, 2 H, HC(4,9)), 6.23 (dd, $J = 15.9$, 6.6, 1 H, HC(8)), 4.84 (dd, $J = 7.6$, 5.4, 1 H, HC(7)), 2.56 (t, $J = 7.1$ 2 H, $\text{H}_2\text{C}(6)$), 1.82 (br s, 1 H, OH), 1.15 (s, 9 H, $\text{H}_3\text{C}(1)$)

^{13}C NMR: (125 MHz, CDCl_3)

204.1 (C(3)), 142.4 (C(5)), 136.3 (C(10)), 131.0 (C(8)), 130.9 (C(9)), 128.6 (C(12)), 127.9 (C(13)), 127.1 (C(4)), 126.5 (C(11)), 71.5 (C(7)), 42.8 (C(2)), 40.5 (C(6)), 26.1 (C(1))

IR: (CHCl_3)

3440 (w), 3082 (w), 3058 (m), 3016 (m), 2969 (s), 2932 (m), 2905 (w), 2870 (w), 2401 (w), 2361 (w), 2340 (w), 1948 (w), 1877 (w), 1685 (s), 1623 (s), 1578 (w), 1493 (w), 1477 (m), 1463 (w), 1449 (m), 1395 (m), 1366 (m), 1330 (m), 1294 (w), 1216 (s), 1091 (m), 1060 (m), 1030 (m), 1002 (m), 968 (s), 890 (w), 849 (w), 753 (s), 694 (s), 667 (m), 620 (w)

MS: (FI, 70 eV)
259 (21), 258 (M^+ , 100)

Opt. Rot.: $[\alpha]_D^{24} -27.42^\circ$ ($c = 0.90$, EtOH)

TLC: R_f 0.39 (hexanes/EtOAc, 3/2) [UV (254 nm)]

SFC: (*R*)-**16**, t_R 2.93 min (99.7%); (*S*)-**16**, t_R 3.62 min (0.3%) (Chiralpak OD, 125 psi, 40 °C, 15.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₇H₂₂O₂ (258.36)

Calcd:	C, 79.03;	H, 8.58%
Found:	C, 79.00;	H, 8.71%

Preparation of (7*R*,4*E*)-7-Hydroxy-2,2-dimethyl-9-phenyl-4,8-nonadien-3-one (17**) (Table 1, entry 6)**

Following Representative Procedure 4, 70 μ L (0.5 mmol) of 2-methylcinnamaldehyde was combined with 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μ L (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μ L (0.75 mmol, 1.5 equiv) of SiCl₄ and 145 μ L (0.6 mmol, 1.2 equiv) of **7** to yield, after column chromatography (SiO₂ (14 g), 2 cm diam., pentane/Et₂O 1/1) to yield 33 mg (24 %) of **17** as a clear, colorless oil. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for **17:**

¹H NMR: (500 MHz, CDCl₃)
7.35-7.32 (m, 2 H, HC(11)), 7.26-7.21 (m, 3 H, HC(12,13)), 6.95 (dt, $J = 15.1$, 7.3, 1 H, HC(5)), 6.62 (dt, $J = 15.4$, 1.5, 1 H, HC(4)), 6.54 (s, 1 H, HC(9)), 4.34 (t, $J = 6.6$, 1 H, HC(7)), 2.57 (t, $J = 7.1$, 2 H, H₂C(6)), 1.89 (d, $J = 1.2$, 3 H, HC(14)), 1.72 (br s, 1 H, OH), 1.15 (s, 9 H, H₃C(1))

TLC: R_f 0.41 (hexanes/EtOAc, 3/2) [UV (254 nm)]

SFC: (*R*)-**17**, t_R 3.31 min (64.7%); (*S*)-**17**, t_R 3.66 min (35.3%) (Chiralpak OD, 125 psi, 40 °C, 11.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (–)-(7*R*,4*E*)-7-Hydroxy-2,2-dimethyl-9-phenyl-4-nonen-8-yn-3-one (18)
(Table 1, entry 8)

Following Representative Procedure 4, 122 μ L (1.0 mmol) of 3-phenyl-2-propynal was combined with 84 mg (0.1 mmol, 0.1 equiv) of bisphosphoramidate (*R,R*)-**3**, 35 μ L (0.2 mmol, 0.2 equiv) of diisopropylethylamine, 172 μ L (1.5 mmol, 1.5 equiv) of SiCl₄ and 290 μ L (1.2 mmol, 1.2 equiv) of **7** at -68 °C to yield, after column chromatography (SiO₂ (20 g), 2 cm diam., hexanes/EtOAc 6/1) to yield 102 mg (40%) of (–)-**18** as a clear oil. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-**18**:

¹H NMR: (500 MHz, CDCl₃)

7.43–7.41 (m, 2 H, HC(11)), 7.35–7.29 (m, 3 H, HC(12,13)), 7.02 (dt, J = 15.4, 7.5, 1 H, HC(5)), 6.69 (dt, J = 15.4, 1.2, 1 H, HC(4)), 4.75 (t, J = 6.1, 1 H, HC(7)), 2.73 (dt, J = 6.1, 1.2, 2 H, H₂C(6)), 1.65 (br s, 1 H, OH), 1.16 (s, 9 H, H₃C(1))

¹³C NMR: (125 MHz, CDCl₃)

204.1 (C(3)), 141.1 (C(5)), 131.7 (C(11)), 128.6 (C(13)), 128.3 (C(12)), 127.5 (C(4)), 122.2 (C(10)), 88.8 (C(8)), 85.8 (C(9)), 61.6 (C(7)), 42.9 (C(2)), 40.7 (C(6)), 26.1 (C(1))

IR: (CHCl₃)

3405 (s), 3079 (m), 3057 (m), 3033 (m), 3021 (m), 2966 (s), 2932 (s), 2906 (s), 2870 (s), 2718 (w), 2336 (w), 2232 (w), 2205 (w), 1959 (w), 1884 (w), 1681 (s), 1621 (s), 1599 (s), 1573 (m), 1489 (s), 1477 (s), 1464 (s), 1443 (s), 1395 (s), 1366 (s), 1325 (s), 1292 (s), 1221 (m), 1199 (m), 1176 (m), 1102 (s), 1070 (s), 1035 (s),

1005 (s), 953 (s), 919 (m), 885 (m), 864 (m), 845 (m), 819 (m), 789 (m), 757 (s), 692 (s), 669 (m)

MS: (CI, CH₄)

257 (M⁺+H, 4), 239 (31), 183 (15), 155 (21), 131 (53), 127 (36), 126 (10), 105 (39), 103 (22), 85 (27), 57 (100)

Opt. Rot.: [α]_D²⁴ -15.96° (c = 0.99, EtOH)

TLC: *R_f* 0.39 (hexanes/EtOAc, 3/2) [UV (254 nm)]

SFC: (*R*)-**18**, *t_R* 1.90 min (83.9%); (*S*)-**18**, *t_R* 3.60 min (16.1%) (Chiralpak OD, 125 psi, 40 °C, 17.5% MeOH in CO₂, 3.00 mL/min, 220 nm)

Analysis: C₁₇H₂₀O₂ (256.34)

Calcd: C, 79.65; H, 7.86%

Found: C, 79.68; H, 7.72%

Representative Procedure 5. Addition of Cyclic Ketone-Derived Silyl Dienol Ether **10 to Aldehydes. Preparation of (+)-(4*R*,7*R*)-4-(7-Hydroxy(phenyl)methyl)-2-cyclohexen-1-one. (**20**) (Table 2, entry 1)**

Diisopropylethylamine (18 μ L, 0.1 mmol, 0.1 equiv) was added via syringe to a flame-dried, 5-mL, Schlenk flask under N₂ containing a solution of 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3** in CH₂Cl₂ (2 mL). To this solution was added 102 μ L (1.0 mmol) of benzaldehyde in one portion. To the resulting solution was added 172 μ L (1.5 mmol, 1.5 equiv) of SiCl₄ in one portion and the reaction mixture was cooled to -72 °C over 15 min. Then, 224 μ L (1.2 mmol, 1.2 equiv) of **10** was added dropwise over 1 min. The resulting mixture was stirred at -72 °C for 2 h whereupon 3.0 mL of chilled CH₂Cl₂ was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO₃/ sat. aq. KF (25 mL) at 0 °C. This biphasic mixture was stirred vigorously for 1 h before being filtered through Celite on a glass frit. The phases were then separated and the aqueous layer was washed with CH₂Cl₂ (3 x 40 mL). The combined organic extracts were dried over Na₂SO₄, filtered and the filtrate

was concentrated *in vacuo*. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (SiO_2 (25 g), 3 cm diam., pentane/ Et_2O , 1/1 to yield 182 mg (90%) of (+)-**20** as a thick, colorless oil, solidified upon standing. The diastereomeric ratio was determined to be *anti/syn*, 97.5/2.5 by SFC analysis. The spectroscopic data for **20** matched those in the literature.¹⁵

Data for (+)-(*anti*)-**20**:

^1H NMR: (500 MHz, CDCl_3)
7.43-7.32 (m, 5H, HC(9,10,11)), 7.25 (dt, $J = 10.3, 1.7$, 1 H, HC(3)), 6.09 (dd, $J = 10.3, 2.4$, 1 H, HC(2)), 4.59 (dd, $J = 7.8, 3.2$, 1 H, HC(7)), 2.78-2.73 (m, 1 H, HC(4)), 2.49-2.21 (m, 1 H, HC(6)), 2.35-2.28 (m, 1 H, HC(6)), 2.03 (br s, 1H, OH), 1.75-1.68 (m, 2 H, $\text{H}_2\text{C}(5)$)

^{13}C NMR: (125 MHz, CDCl_3)
200.0 (C(1)), 151.6 (C(3)), 142.2 (C(8)), 129.8 (C(2)), 128.6 (C(10)), 128.1 (C(11)), 126.2 (C(9)), 76.5 (C(7)), 43.6 (C(4)), 36.7 (C(6)), 25.8 (C(5))

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +114.38^\circ$ ($c = 1.00$, EtOH)

TLC: R_f 0.10 (pentane/ Et_2O , 1/1) [UV (254 nm)]

SFC: (4*S*,7*S*)-**20** t_r 6.52 min (2.5%); (4*R*,7*R*)-**20** t_r 9.65 min (97.5%) (Chiralpak OJ, 150 psi, 40 $^\circ\text{C}$, 6.0% MeOH in CO_2 , 2.75 mL/min, 220 nm)

Preparation of (+)-(4*R*,7*R*)-4-(7-Hydroxy-(1-naphthalenyl)methyl)-2-cyclohexen-1-one (21)
(Table 2, entry 2)

Following Representative Procedure 5, 136 μL (1.0 mmol) of 1-naphthaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 35 μL (0.2 mmol, 0.2 equiv) of diisopropylethylamine, 172 μL (1.5 mmol, 1.5 equiv) of SiCl_4 and 224 μL (1.2 mmol, 1.2 equiv) of **10** for 10 h to yield, after column chromatography (SiO_2 (20 g), 2 cm diam.,

Pentane/Et₂O 2/1) to yield 202 mg (80%) of (+)-**21** as a white foam. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture. The diastereomeric ratio was determined to be *anti/syn*, 89.0/11.0 by SFC analysis.

Data for (+)-(*anti*)-**21**:

¹H NMR: (500 MHz, CDCl₃)

8.13 (d, *J* = 8.3, 1 H, HC(9')), 7.89 (d, *J* = 8.8, 1 H, HC(6')), 7.85 (d, *J* = 8.3, 1 H, HC(4')), 7.69 (d, *J* = 7.1, 1 H, HC(2')), 7.57-7.51 (m, 3H, HC(3',7',8')), 7.25 (dd, *J* = 10.3, 1.5, 1 H, HC(3)), 6.11 (dd, *J* = 10.4, 2.6, 1 H, HC(2)), 5.40 (d, *J* = 6.6, 1 H, HC(7)), 3.08-3.03 (m, 1 H, HC(4)), 2.51 (td, *J* = 16.7, 4.3, 1 H, HC(6)), 2.30 (ddd, *J* = 16.8, 11.5, 5.2, 1 H, HC(6)), 2.13 (br s, 1 H, OH), 1.99-1.91 (m, 1 H, HC(5)), 1.86-1.82 (m, 1 H, HC(5))

¹³C NMR: (125 MHz, CDCl₃)

200.0 (C(1)), 151.4 (C(3)), 137.8 (C(1')), 133.8 (C(5')), 130.4 (C(10')), 129.8 (C(2)), 129.1 (C(6')), 128.5 (C(4')), 126.2 (C(8')), 125.7 (C(7')), 125.3 (C(4')), 124.0 (C(2')), 122.9 (C(9')), 73.4 (C(7)), 42.8 (C(4)), 36.9 (C(6)), 26.5 (C(5))

IR: (neat)

3417 (s), 3058 (m), 3011 (m), 2954 (m), 1666 (s), 1597 (m), 1509 (m), 1393 (m), 1352 (m), 1332 (m), 1256 (m), 1216 (m), 1140 (m), 1092 (m), 1048 (m), 1015 (m), 861 (m), 848 (m), 805 (m), 784 (s), 756 (s), 666 (m), 632 (m)

MS: (ESI)

253 (M⁺+H, 12), 236 (21), 235 (100), 157 (54)

Opt. Rot.: [α]_D²⁴ +89.08° (c = 0.90, EtOH)

TLC: *R_f* 0.20 (hexanes/EtOAc, 3/2) [UV (254 nm)]

SFC: (4*S*,7*S*)-**21** t_r 2.50 min (5.0%); (4*R*,7*R*)-**21** t_r 5.08 min (95.0%); (Chiralpak OJ, 125 psi, 40 °C, 20.0% MeOH in CO₂, 4.0 mL/min, 220 nm)

HRMS: Calcd for C₁₇H₁₇O₂: 253.1229, found: 253.1224

Preparation of (–)-(4*R*,7*R*)-4-(7-Hydroxy-(9-phenyl-8-propenyl))-2-cyclohexen-1-one (22)
(Table 2, entry 3)

Following Representative Procedure 5, 126 μL (1.0 mmol) of cinnamaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 35 μL (0.2 mmol, 0.2 equiv) of diisopropylethylamine, 172 μL (1.5 mmol, 1.5 equiv) of SiCl_4 and 224 μL (1.2 mmol, 1.2 equiv) of **10** for 2 h to yield, after column chromatography (SiO_2 (20 g), 2 cm diam., hexanes/EtOAc 2/1) to yield 173 mg (76%) of (–)-**22** as a thick, clear oil. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The diastereomeric ratio was determined to be *anti/syn*, 98.0/2.0 by SFC analysis.

Data for (–)-(anti)-**22**:

^1H NMR: (500 MHz, CDCl_3)

7.41 (d, $J = 7.8$, 2 H, HC(11)), 7.34 (t, $J = 7.3$, 2 H, HC(12)), 7.30–7.27 (m, $J = 7.3$, 1.2, 1 H, HC(13)), 7.16 (ddd, $J = 10.3$, 2.3, 1.6, 1 H, HC(3)), 6.67 (d, $J = 15.9$, 1 H, HC(9)), 6.26 (dd, $J = 15.9$, 6.8, 1 H, HC(8)), 6.10 (ddd, $J = 10.3$, 2.4, 0.7, 1 H, HC(2)), 4.23 (t, $J = 6.8$, 1 H, HC(7)), 2.69–2.63 (m, 1 H, HC(4)), 2.55 (dt, $J = 16.8$, 4.2, 1 H, HC(6)), 2.39 (ddd, $J = 16.8$, 13.2, 5.0, 1 H, HC(6)), 2.14–2.08 (m, 1 H, HC(5)), 1.90–1.82 (m, 1 H, HC(5)), 1.71 (br s, 1 H, OH)

^{13}C NMR: (125 MHz, CDCl_3)

199.9 (C(1)), 151.1 (C(3)), 136.0 (C(10)), 132.3 (C(9)), 130.2 (C(2)), 129.6 (C(8)), 128.7 (C(12)), 128.1 (C(13)), 126.5 (C(11)), 75.0 (C(7)), 42.3 (C(4)), 36.9 (C(6)), 25.5 (C(5))

IR: (neat)

3417 (s), 3082 (m), 3058 (m), 3028 (m), 2953 (m), 2872 (m), 2247 (w), 1954 (w), 1883 (w), 1812 (w), 1682 (s), 1651 (s), 1600 (m), 1578 (m), 1494 (s), 1450 (s), 1415 (s), 1391 (s), 1351 (s), 1331 (s), 1255 (s), 1217 (s), 1178 (s), 1140 (m), 1110 (s), 1071 (s), 1037 (s), 969 (s), 913 (m), 879 (m), 843 (m), 752 (s), 695 (s)

MS: (FI)
228 (M^+ , 40), 211 (15), 210 (100)

Opt. Rot.: $[\alpha]_D^{24} -52.73^\circ$ ($c = 1.43$, EtOH)

TLC: R_f 0.16 (hexanes/EtOAc, 3/2) [UV (254 nm)]

SFC: (4*R*,7*R*)-**22** t_r 4.91 min (84.5%); (4*S*,7*S*)-**22** t_r 6.47 min (15.5%) (Chiralpak OD, 125 psi, 40 °C, 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₅H₁₆O₂ (228.29)
Calcd: C, 78.92; H, 7.06%
Found: C, 79.03; H, 7.06%

Preparation of (+)-(4*R*,7*R*)-4-(7-Hydroxy-(2-furanyl)methyl)-2-cyclohexen-1-one. (23)
(Table 2, entry 4)

Following Representative Procedure 5, 84 μ L (1.0 mmol) of 2-furfuraldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 35 μ L (0.2 mmol, 0.2 equiv) of diisopropylethylamine, 172 μ L (1.5 mmol, 1.5 equiv) of SiCl₄ and 224 μ L (1.2 mmol, 1.2 equiv) of **10** to yield, after column chromatography (SiO₂ (20 g), 2 cm diam., hexanes/EtOAc 3/2) to yield 180 mg (94%) of (+)-**23** as clear oil. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture. The diastereomeric ratio was determined to be *anti/syn*, 81.5/18.5 by SFC analysis.

Data for (+)-(anti)-23**:**

¹H NMR: (500 MHz, CDCl₃)
7.41 (t, $J = 1.5$, 1 H, HC(11)), 7.35 (t, $J = 2.0$, 1 H, HC(3)), 6.38 (dd, $J = 3.2$, 2.0, 1 H, HC(10)), 6.33 (d, $J = 3.2$, 1 H, HC(9)), 6.10 (dd, $J = 10.3$, 2.4, 1 H, HC(2)), 4.64 (dd, $J = 7.5$, 5.0, 1 H, HC(7)), 2.98-2.94 (m, 1H, HC(4)), 2.51 (dt, $J = 16.8$, 4.4, 1 H, HC(6)), 2.38 (ddd, $J = 16.8$, 12.9, 5.1, HC(6)), 2.03 (d, $J = 5.1$, 1 H, OH), 1.90-1.74 (m, 2H, HC(5))

¹³C NMR: (125 MHz, CDCl₃)
199.9 (C(1)), 154.4 (C(8)), 151.1 (C(3)), 142.4 (C(11)), 130.2 (C(2)), 110.3 (C(10)), 107.5 (C(9)), 70.1 (C(7)), 41.5 (C(4)), 36.7 (C(6)), 25.4 (C(5))

IR: (neat)
3405 (s), 3147 (m), 3120 (m), 3039 (w), 2953 (m), 2875 (m), 2361 (w), 2343 (w), 2079 (w), 1667 (s), 1505 (s), 1453 (m), 1416 (s), 1391 (s), 1353 (s), 1326 (s), 1258 (s), 1219 (s), 1177 (s), 1148 (s), 1068 (s), 1042 (s), 1011 (s), 971 (s), 939 (m), 918 (s), 884 (s), 853 (s), 816 (s), 745 (s), 683 (m)

MS: (CI, CH₄)
193 (M⁺+H, 3), 175 (25), 97 (100), 96 (14)

Opt. Rot.: [α]_D²⁴ +58.18° (c = 1.05, EtOH)

TLC: *R*_f 0.19 (hexanes/EtOAc, 3/2) [UV (254 nm)]

SFC: (4*S*,7*S*)-**23** t_r 5.77 min (18.5%); (4*R*,7*R*)-**23** t_r 7.14 min (81.5%) (Chiralpak OJ, 125 psi, 40 °C, 5.0% MeOH in CO₂, 2.5 mL/min, 220 nm)

Analysis: C₁₁H₁₂O₃ (192.21)
Calcd: C, 68.74; H, 6.29%
Found: C, 68.59; H, 6.34%

Vinylogous Aldol Additions of Bissilyl Dienol Ethers

Preparation of (–)-(2*R*)-2,3-Dihydro-6-methyl-2-phenylpyran-4-one (34) (Table 3, entry 1)

Diisopropylamine (18 μ L, 0.1 mmol, 0.2 equiv) was added via syringe to a flame-dried, 20-mL, 2-necked, round bottomed flask fitted with a magnetic stir bar, gas inlet tube, and septum under N₂ containing a solution of 5 mg (0.005 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3** in CH₂Cl₂ (2 mL). To this solution was added 51 μ L (0.5 mmol) of benzaldehyde in one portion. The resulting solution was cooled to -78 $^{\circ}$ C (bath temperature) over 15 min and to the reaction mixture was added 86 μ L (0.75 mmol, 1.5 equiv) of SiCl₄ in one portion. Then, 147 mg (0.6

mmol, 1.2 equiv) of **32a** was added dropwise over 5 min. The resulting mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 2 h whereupon 3.0 mL of chilled CH_2Cl_2 was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO_3 / sat. aq. KF (25 mL) at $0\text{ }^{\circ}\text{C}$. This biphasic mixture was stirred vigorously for 3 h after which the aqueous layer was washed with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4 (5 g) filtered through Celite on a glass frit, and the filtrate was concentrated *in vacuo*. The residue was dissolved in 10 mL of CH_2Cl_2 and cooled in an ice water bath for 15 min and to the reaction mixture 10 drops of TFA was added. The resulting mixture was stirred at rt for 16 h whereupon 10 ml of sat. aq. NaHCO_3 added. This biphasic mixture was stirred for 10 min after which the aqueous layer was washed with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over Na_2SO_4 (5 g), filtered through Celite on a glass frit, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by column chromatography (12 g SiO_2 , 2 cm diam., pentane/ Et_2O , 1/1) to yield 83 mg (95%) of **34** as a clear oil. The spectroscopic data for **34** matched those in the literature.¹⁶

Data for **34**:

¹H NMR: (500 MHz, CDCl_3)

7.44-7.37 (m, 5 H, HC(8,9,10)), 5.44 (s, 1 H, CH(5)), 5.39 (dd, $J = 14.3$, 3.2 HC(2)); 2.82 (dd, $J = 16.8$, 14.4, 1 H, HC(3)); 2.60 (dd, $J = 16.8$, 3.4, HC(3)); 2.08 (s, 3 H, $\text{H}_3\text{C}(11)$)

TLC: R_f 0.29 (hexanes/ EtOAc , 4/1) [UV (254 nm)]

SFC: (*S*)-**34** t_r 2.24 min (37.9%); (*R*)-**34** t_r 2.47 min (62.1%); (Chiralpak OD, 150 psi, $40\text{ }^{\circ}\text{C}$, 11.0% MeOH in CO_2 , 3.0 mL/min, 220 nm)

Preparation of (2*R*)-2,3-Dihydro-6-methyl-2-phenylpyran-4-one (**34**) (Table 3, entry 2)

Diisopropylamine (18 μL , 0.1 mmol, 0.2 equiv) was added via syringe to a flame-dried, 20-mL, 2-neck, round bottomed flask fitted with a magnetic stir bar, gas inlet tube, and septum under N_2 containing a solution of 5 mg (0.05 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3** in

CH₂Cl₂ (2 mL). To this solution was added 51 μ L (0.5 mmol) of benzaldehyde in one portion. The resulting solution was cooled to -78 °C (bath temperature) over 15 min and to the reaction mixture was added 86 μ L (0.75 mmol, 1.5 equiv) of SiCl₄ in one portion. Then, 197 mg (0.6 mmol, 1.2 equiv) of **32b** was added dropwise over 5 min. The resulting mixture was stirred at -78 °C for 2 h whereupon 3.0 mL of chilled CH₂Cl₂ was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO₃/ sat. aq. KF (25 mL) at 0 °C. This biphasic mixture was stirred vigorously for 3 h after which the aqueous layer was washed with CH₂Cl₂ (3 x 30 mL). The combined organic extracts were dried over Na₂SO₄ (5 g) filtered through Celite on a glass frit, and the filtrate was concentrated *in vacuo*. The residue was dissolved in 10 mL of CH₂Cl₂ and cooled in an ice water bath for 15 min and to the reaction mixture 10 drops of TFA was added. The resulting mixture was stirred at rt for 16 h whereupon 10 ml of sat. aq. NaHCO₃ added. This biphasic mixture was stirred for 10 min after which the aqueous layer was washed with CH₂Cl₂ (3 x 20 mL). The combined organic extracts were dried over Na₂SO₄ (5 g), filtered through Celite on a glass frit, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by column chromatography (13 g SiO₂, 2 cm diam., pentane/Et₂O, 1/1) to yield 82 mg (94%) of **34** as a clear oil. The spectroscopic data for **34** matched those in the literature.¹⁶

Data for **34**:

¹H NMR: (500 MHz, CDCl₃)

7.44-7.36 (m, 5 H, HC(8,9,10)), 5.43 (s, 1 H, CH(5)), 5.38 (dd, J = 14.2, 3.2 HC(2)), 2.81 (dd, J = 16.7, 14.4, 1 H, HC(3)), 2.61 (dd, J = 16.8, 3.3, HC(3)), 2.09 (s, 3 H, H₃C(11))

TLC: R_f 0.29 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (*S*)-**34** t_r 2.23 min (25.2%); (*R*)-**34** t_r 2.46 min (74.8%); (Chiralpak OD, 150 psi, 40 °C, 11.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Representative Procedure 6. Addition of Bissilyl Dienol Ethers to Conjugated Aldehydes.**Preparation of (–)-(2*R*)-2,3-Dihydro-6-methyl-phenylpyran-4-one (**34**) (Table 3, entry 3)**

Diisopropylamine (18 μL , 0.1 mmol, 0.1 equiv) was added via syringe to a flame-dried, 20-mL, 2-necked, rounded bottom flask fitted with a magnetic stir bar, thermocouple, gas inlet tube, and septum under N_2 containing a solution of 9 mg (0.01 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3** in CH_2Cl_2 (2 mL). To this solution was added 102 μL (1.0 mmol) of benzaldehyde in one portion. The resulting solution was cooled to $-90\text{ }^\circ\text{C}$ over 15 min and to the reaction mixture was added 172 μL (1.5 mmol, 1.5 equiv) of SiCl_4 in one portion. Then, 394 mg (1.2 mmol, 1.2 equiv) of **32b** was added dropwise over 5 min. The resulting mixture was stirred at $-90\text{ }^\circ\text{C}$ for 2 h whereupon 3.0 mL of chilled CH_2Cl_2 was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO_3 / sat. aq. KF (25 mL) at $0\text{ }^\circ\text{C}$. This biphasic mixture was stirred vigorously for 3 h after which the aqueous layer was washed with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4 (5 g) filtered through Celite on a glass frit, and the filtrate was concentrated *in vacuo*. The residue was dissolved in 10 mL of CH_2Cl_2 and cooled in an ice water bath for 15 min and to the reaction mixture 10 drops of TFA was added. The resulting mixture was stirred at rt for 16 h whereupon 10 mL of sat. aq. NaHCO_3 added. This biphasic mixture was stirred for 10 min after which the aqueous layer was washed with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over Na_2SO_4 (5 g), filtered through Celite on a glass frit, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by column chromatography (30 g SiO_2 , 2 cm column diam., hexanes/EtOAc, 2/1). The product-containing fractions were combined and the solvent was removed *in vacuo* to yield 165 mg (88%) of (–)-**34** as a clear oil. The spectroscopic data for **34** matched those in the literature.¹⁶

Data for (–)-34**:**

¹H NMR: (500 MHz, CDCl_3)

7.44-7.36 (m, 5 H, HC(8,9,10)), 5.43 (s, 1 H, CH(5)), 5.38 (dd, $J = 14.2, 3.2$ HC(2)), 2.81 (dd, $J = 16.7, 14.4$, 1 H, HC(3)), 2.610 (dd, $J = 16.8, 3.3$, HC(3)),

2.09 (s, 3 H, H₃C(11))

¹³C NMR: (125 MHz, CDCl₃)
 192.1 (C(5)), 174.1 (C(6)), 138.1 (C(7)), 128.7 (C(8,9)), 126.1 (C(8)), 105.1 (C(5)), 80.7 (C(2)), 42.3 (C(3)), 21.0 (C(11))

Opt. Rot.: [α]_D²⁴ -48.00° (c = 1.15, CH₂Cl₂)

TLC: R_f 0.28 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (*S*)-**34** t_r 1.86 min (19.9%); (*R*)-**34** t_r 2.02 min (80.1%); (Chiralpak OD, 150 psi, 40 °C, 15.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (2*R*)-2,3-Dihydro-6-methyl-2-phenylpyran-4-one (**34**) (Table 3, entry 4)

Following Representative Procedure 6, 51 μL (0.5 mmol) of benzaldehyde was combined with 5 mg (0.005 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μL (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μL (0.75 mmol, 1.5 equiv) of SiCl₄ and 197 μL (0.6 mmol, 1.2 equiv) of **32c** to yield, after column chromatography (SiO₂ (12 g), 2 cm diam., pentane/Et₂O 1/1) to yield 67 mg (77%) of **34** as a white solid. The spectroscopic data for **34** matched those in the literature.¹⁶

Data for 34:

¹H NMR: (500 MHz, CHCl₃)
 7.44-7.34 (m, 5 H, HC(8,9,10)), 5.44 (s, 1 H, CH(5)), 5.38 (dd, *J* = 14.2, 3.3 HC(2)), 2.83 (dd, *J* = 16.7, 14.2, 1 H, HC(3)), 2.60 (dd, *J* = 16.8, 3.2, HC(3)), 2.10 (s, 3 H, H₃C(11))

TLC: R_f 0.28 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (*S*)-**34** t_r 4.67 min (38.8%); (*R*)-**34** t_r 5.31 min (61.2%); (Chiralpak OD, 125 psi, 40 °C, 3.5% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (2*R*)-2,3-dihydro-6-methyl-2-phenylpyran-4-one (218) (Table 3, entry 5)

Following Representative Procedure 6, 51 μL (0.5 mmol) of benzaldehyde was combined with 5 mg (0.005 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μL (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μL (0.75 mmol, 1.5 equiv) of SiCl_4 and 248 mg (0.6 mmol, 1.2 equiv) of **32d** to yield, after column chromatography (SiO_2 (12 g), 2 cm diam., pentane/ Et_2O 1/1) to yield 72 mg (83%) of **34** as a white solid. The spectroscopic data for **34** matched those in the literature.¹⁶

Data for **34:**

¹H NMR: (500 MHz, CDCl_3)

7.44-7.34 (m, 5 H, HC(8,9,10)), 5.44 (s, 1 H, CH(5)), 5.38 (dd, $J = 14.2$, 3.3 HC(2)), 2.83 (dd, $J = 16.7$, 14.2, 1 H, HC(3)), 2.60 (dd, $J = 16.8$, 3.2, HC(3)), 2.10 (s, 3 H, $\text{H}_3\text{C}(11)$)

TLC: R_f 0.28 (hexanes/ EtOAc , 4/1) [UV (254 nm)]

SFC: (*S*)-**34** t_r 4.67 min (38.8%); (*R*)-**34** t_r 5.31 min (61.2%); (Chiralpak OD, 125 psi, 40°C , 3.5% MeOH in CO_2 , 3.0 mL/min, 220 nm)

Preparation of (2*R*)-2,3-Dihydro-6-methyl-2-phenylpyran-4-one (34) (Table 3, entry 6)

Following Representative Procedure 6, 51 μL (0.5 mmol) of benzaldehyde was combined with 4 mg (0.005 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**35**, 18 μL (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μL (0.75 mmol, 1.5 equiv) of SiCl_4 and 197 mg (0.6 mmol, 1.2 equiv) of **32b** to yield, after column chromatography (SiO_2 (12 g), 2 cm diam., pentane/ Et_2O 1/1) to yield 66 mg (76%) of **34** as a white solid. The spectroscopic data for **34** matched those in the literature.¹⁶

Data for **34**:¹H NMR: (500 MHz, CDCl₃)7.44-7.34 (m, 5 H, HC(8,9,10)), 5.44 (s, 1 H, CH(5)), 5.38 (dd, *J* = 14.2, 3.3 HC(2)), 2.83 (dd, *J* = 16.7, 14.2, 1 H, HC(3)), 2.60 (dd, *J* = 16.8, 3.2, HC(3)), 2.10 (s, 3 H, H₃C(11))TLC: *R_f* 0.28 (hexanes/EtOAc, 4/1) [UV (254 nm)]SFC: (*S*)-**34** *t_r* 4.67 min (12.5%); (*R*)-**34** *t_r* 5.31 min (87.5%); (Chiralpak OD, 125 psi, 40 °C, 3.5% MeOH in CO₂, 3.0 mL/min, 220 nm)**Preparation of (2*R*)-2,3-Dihydro-6-methyl-2-phenylpyran-4-one (**34**) (Table 3, entry 7)**

Following Representative Procedure 6, 51 μL (0.5 mmol) of benzaldehyde was combined with 5 mg (0.005 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**36**, 18 μL (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μL (0.75 mmol, 1.5 equiv) of SiCl₄ and 197 mg (0.6 mmol, 1.2 equiv) of **32b** to yield, after column chromatography (SiO₂ (12 g), 2 cm diam., pentane/Et₂O 1/1) to yield 70 mg (80%) of **34** as a white solid. The spectroscopic data for **34** matched those in the literature.¹⁶

Data for **34**:¹H NMR: (500 MHz, CHCl₃)7.45-7.34 (m, 5 H, HC(8,9,10)), 5.42 (s, 1 H, CH(5)), 5.38 (dd, *J* = 14.2, 3.3 HC(2)), 2.83 (dd, *J* = 16.7, 14.2, 1 H, HC(3)), 2.62 (dd, *J* = 16.9, 3.2, HC(3)), 2.07 (s, 3 H, H₃C(11))TLC: *R_f* 0.28 (hexanes/EtOAc, 4/1) [UV (254 nm)]SFC: (*S*)-**34** *t_r* 4.51 min (15.0%); (*R*)-**34** *t_r* 5.13 min (85.0%); (Chiralpak OD, 125 psi, 40 °C, 3.5% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (2*R*)-2,3-Dihydro-6-methyl-2-phenylpyran-4-one (34) (Table 3, entry 8)

Following Representative Procedure 6, 51 μL (0.5 mmol) of benzaldehyde was combined with 5 mg (0.005 mmol, 0.01 equiv) of bisphosphoramidate (*R*)-**37**, 18 μL (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μL (0.75 mmol, 1.5 equiv) of SiCl_4 and 197 mg (0.6 mmol, 1.2 equiv) of **32b** to yield, after column chromatography (SiO_2 (12 g), 2 cm diam., pentane/ Et_2O 1/1) to yield 50 mg (57%) of **34** as a white solid. The spectroscopic data for **34** matched those in the literature.¹⁶

Data for 34:

¹H NMR: (500 MHz, CDCl_3)

7.44-7.34 (m, 5 H, HC(8,9,10)), 5.44 (s, 1 H, CH(5)), 5.38 (dd, $J = 14.2, 3.3$ HC(2)), 2.83 (dd, $J = 16.7, 14.2$, 1 H, HC(3)), 2.60 (dd, $J = 16.8, 3.2$, HC(3)), 2.10 (s, 3 H, $\text{H}_3\text{C}(11)$)

TLC: R_f 0.29 (hexanes/ EtOAc , 4/1) [UV (254 nm)]

SFC: (*S*)-**34** t_r 4.67 min (17.2%); (*R*)-**34** t_r 5.31 min (82.8%); (Chiralpak OD, 125 psi, 40 $^\circ\text{C}$, 3.5% MeOH in CO_2 , 3.0 mL/min, 220 nm)

Preparation of (2*R,R*)-2,3-Dihydro-6-methyl-2-phenylpyran-4-one (34) (Table 3, entry 9)

Following Representative Procedure 6, 51 μL (0.5 mmol) of benzaldehyde was combined with 3 mg (0.005 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**38**, 18 μL (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μL (0.75 mmol, 1.5 equiv) of SiCl_4 and 197 mg (0.6 mmol, 1.2 equiv) of **32b** to yield, after column chromatography (SiO_2 (12 g), 2 cm diam., pentane/ Et_2O 1/1) to yield 85 mg (98%) of **34** as a white solid. The spectroscopic data for **34** matched those in the literature.¹⁶

Data for 34:

¹H NMR: (500 MHz, CDCl₃)
 7.44-7.34 (m, 5 H, HC(8,9,10)), 5.44 (s, 1 H, CH(5)), 5.38 (dd, *J* = 14.2, 3.3 HC(2)), 2.83 (dd, *J* = 16.7, 14.2, 1 H, HC(3)), 2.60 (dd, *J* = 16.8, 3.2, HC(3)), 2.10 (s, 3 H, H₃C(11))

TLC: *R_f* 0.29 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (*S*)-**34** *t_r* 4.67 min (38.8%); (*R*)-**34** *t_r* 5.31 min (61.2%); (Chiralpak OD, 125 psi, 40 °C, 3.5% MeOH in CO₂, 3.0 mL/min, 220 nm)

Representative Procedure 7. Vinylogous Aldol Additions of Bissilyl Dienol Ethers 32a-c to Hydrocinnamaldehyde. Preparation of (2*S*)-2,3-Dihydro-6-methyl-2-phenylethylpyran-4-one (39) (Table 4, entry 1)

Diisopropylamine (18 μ L, 0.1 mmol, 0.1 equiv) was added via syringe to a flame-dried, 20-mL, 2-necked, rounded bottom flask fitted with a magnetic stir bar, gas inlet tube and septum under N₂ containing a solution of 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3** in CH₂Cl₂ (2 mL). To this solution was added 66 μ L (0.5 mmol) of hydrocinnamaldehyde in one portion. The resulting solution was cooled to –78 °C (bath temperature) over 15 min and to the reaction mixture was added 86 μ L (0.75 mmol, 1.5 equiv) of SiCl₄ in one portion. Then, 197 mg (0.6 mmol, 1.2 equiv) of **32b** was added dropwise over 5 min. The resulting mixture was stirred at –78 °C for 24 h whereupon 3.0 mL of chilled CH₂Cl₂ was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO₃/ sat. aq. KF (25 mL) at 0 °C. This biphasic mixture was stirred vigorously for 3 h after which the aqueous layer was washed with CH₂Cl₂ (3 x 30 mL). The combined organic extracts were dried over Na₂SO₄ (5 g) filtered through Celite on a glass frit, and the filtrate was concentrated *in vacuo*. The residue was dissolved in 10 mL of CH₂Cl₂ and cooled in an ice water bath for 15 min and to the reaction mixture 10 drops of TFA was added. The resulting mixture was stirred at rt for 16 h whereupon 10 ml of sat. aq. NaHCO₃ added. This biphasic mixture was stirred for 10 min after which the

aqueous layer was washed with CH₂Cl₂ (3 x 20 mL). The combined organic extracts were dried over Na₂SO₄ (5 g), filtered through Celite on a glass frit, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by column chromatography (12 g SiO₂, 2 cm column diam., pentane/Et₂O, 1/1). The product-containing fractions were combined and the solvent was removed *in vacuo* to yield 23 mg (21%) of **39** as a clear, colorless oil.

Data for **39**:

¹H NMR: (500 MHz, CHCl₃)
 7.32-7.29 (m, 2 H, HC(11)), 7.23-7.19 (m, 3 H, HC(10,12)), 5.32 (s, 1 H, CH(5)),
 4.38-4.32 (m, 1 H, HC(2)), 2.86-2.73 (m, 2 H, H₂C(8)), 2.48-2.35 (m, 2 H, HC(3)),
 2.22-2.12 (m, 1 H, HC(7)), 2.02 (s, 3 H, H₃C(13)), 1.99-1.92 (m, 2 H, HC(7))

TLC: *R_f* 0.28 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (*R*)-**39** *t_r* 2.67 min (30.0%); (*S*)-**39** *t_r* 3.43 min (70.0%); (Chiralpak OD, 125 psi, 40 °C, 15.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (2*S*)-2,3-Dihydro-6-methyl-2-phenylethylpyran-4-one (39**) (Table 4, entry 2)**

Following Representative Procedure 7, 66 µL (0.5 mmol) of hydrocinnamaldehyde was combined with 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**35**, 18 µL (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 µL (0.75 mmol, 1.5 equiv) of SiCl₄ and 197 mg (0.6 mmol, 1.2 equiv) of **32b** to yield, after column chromatography (SiO₂ (13 g), 2 cm diam., pentane/Et₂O 1/1) to yield 23 mg (21%) of **39** as a clear, colorless oil.

Data for **39**:

¹H NMR: (500 MHz, CHCl₃)
 7.32-7.28 (m, 2 H, HC(11)), 7.23-7.19 (m, 3 H, HC(10,12)), 5.32 (s, 1 H, CH(5)),
 4.38-4.32 (m, 1 H, HC(2)), 2.86-2.72 (m, 2 H, H₂C(8)), 2.48-2.35 (m, 2 H, HC(3)),
 2.22-2.13 (m, 1 H, HC(7)), 2.01 (s, 3 H, H₃C(13)), 1.98-1.91 (m, 2 H, HC(7))

TLC: *R_f* 0.28 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (*R*)-**39** *t_r* 2.66 min (37.0%); (*S*)-**39** *t_r* 3.41 min (63.0%); (Chiralpak OD, 125 psi,

40 °C, 15.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (2*S*)-2,3-Dihydro-6-methyl-2-phenylethylpyran-4-one (39**) (Table 4, entry 3)**

Following Representative Procedure 7, 66 μ L (0.5 mmol) of hydrocinnamaldehyde was combined with 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**36**, 18 μ L (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μ L (0.75 mmol, 1.5 equiv) of SiCl₄ and 197 mg (0.6 mmol, 1.2 equiv) of **32b** to yield, after column chromatography (SiO₂ (13 g), 2 cm diam., pentane/Et₂O 1/1) to yield 14 mg (13%) of **39** as a clear, colorless oil.

Data for **39**:

¹H NMR: (500 MHz, CHCl₃)

7.32-7.28 (m, 2 H, HC(11)), 7.23-7.19 (m, 3 H, HC(10,12)), 5.32 (s, 1 H, CH(5)), 4.38-4.32 (m, 1 H, HC(2)), 2.86-2.72 (m, 2 H, H₂C(8)), 2.48-2.35 (m, 2 H, HC(3)), 2.22-2.13 (m, 1 H, HC(7)), 2.01 (s, 3 H, H₃C(13)), 1.98-1.91 (m, 2 H, HC(7))

TLC: *R_f* 0.28 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (*R*)-**39** *t_r* 2.63 min (46.1%); (*S*)-**39** *t_r* 3.38 min (53.9%); (Chiralpak OD, 125 psi, 40 °C, 15.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (2*S*)-2,3-Dihydro-6-methyl-2-phenylethylpyran-4-one (39**) (Table 4, entry 4)**

Following Representative Procedure 7, 66 μ L (0.5 mmol) of hydrocinnamaldehyde was combined with 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μ L (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μ L (0.75 mmol, 1.5 equiv) of SiCl₄ and 147 mg (0.6 mmol, 1.2 equiv) of **32a** to yield, after column chromatography (SiO₂ (13 g), 2 cm diam.,

pentane/Et₂O 1/1) to yield 33 mg (31%) of **39** as a clear, colorless oil.

Data for **39**:

¹H NMR: (500 MHz, CHCl₃)
 7.33-7.28 (m, 2 H, HC(11)), 7.22-7.19 (m, 3 H, HC(10,12)), 5.32 (s, 1 H, CH(5)),
 4.38-4.32 (m, 1 H, HC(2)), 2.86-2.72 (m, 2 H, H₂C(8)), 2.49-2.35 (m, 2 H, HC(3)),
 2.21-2.13 (m, 1 H, HC(7)), 2.01 (s, 3 H, H₃C(13)), 1.98-1.91 (m, 2 H, HC(7))

TLC: *R_f* 0.28 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (*R*)-**39** *t_r* 2.67 min (46.8%); (*S*)-**39** *t_r* 3.40 min (53.2%); (Chiralpak OD, 125 psi, 40 °C, 15.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (2*S*)-2,3-Dihydro-6-methyl-2-phenylethylpyran-4-one (39**) (Table 4, entry 5)**

Following Representative Procedure 7, 66 μ L (0.5 mmol) of hydrocinnamaldehyde was combined with 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μ L (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μ L (0.75 mmol, 1.5 equiv) of SiCl₄ and 197 mg (0.6 mmol, 1.2 equiv) of **32c** to yield, after column chromatography (SiO₂ (13 g), 2 cm diam., pentane/Et₂O 1/1) to yield 20 mg (19%) of **39** as a clear, colorless oil.

Data for **39**:

¹H NMR: (500 MHz, CHCl₃)
 7.32-7.28 (m, 2 H, HC(11)), 7.23-7.19 (m, 3 H, HC(10,12)), 5.32 (s, 1 H, CH(5)),
 4.38-4.32 (m, 1 H, HC(2)), 2.86-2.72 (m, 2 H, H₂C(8)), 2.48-2.35 (m, 2 H, HC(3)),
 2.22-2.13 (m, 1 H, HC(7)), 2.01 (s, 3 H, H₃C(13)), 1.98-1.91 (m, 2 H, HC(7))

TLC: *R_f* 0.28 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (*R*)-**39** *t_r* 2.65 min (41.1%); (*S*)-**39** *t_r* 3.40 min (58.9%); (Chiralpak OD, 125 psi, 40 °C, 15.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (2S)-2,3-Dihydro-6-methyl-2-phenylethylpyran-4-one (39) (Table 4, entry 6)

Following Representative Procedure 7, 66 μL (0.5 mmol) of hydrocinnamaldehyde was combined with 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μL (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μL (0.75 mmol, 1.5 equiv) of SiCl_4 and 248 mg (0.6 mmol, 1.2 equiv) of **32d** to yield, after column chromatography (SiO_2 (13 g), 2 cm diam., pentane/ Et_2O 1/1) to yield 10 mg (9%) of **39** as a clear, colorless oil.

Data for **39**:

$^1\text{H NMR}$: (500 MHz, CHCl_3)

7.32-7.28 (m, 2 H, HC(11)), 7.23-7.19 (m, 3 H, HC(10,12)), 5.32 (s, 1 H, CH(5)), 4.38-4.31 (m, 1 H, HC(2)), 2.86-2.72 (m, 2 H, $\text{H}_2\text{C}(8)$), 2.48-2.36 (m, 2 H, HC(3)), 2.22-2.12 (m, 1 H, HC(7)), 2.00 (s, 3 H, $\text{H}_3\text{C}(13)$), 1.98-1.92 (m, 2 H, HC(7))

TLC: R_f 0.28 (hexanes/ EtOAc , 4/1) [UV (254 nm)]

SFC: (*R*)-**39** t_r 2.63 min (32.5%); (*S*)-**39** t_r 3.35 min (67.5%); (Chiralpak OD, 125 psi, 40 $^\circ\text{C}$, 15.0% MeOH in CO_2 , 3.0 mL/min, 220 nm)

Preparation of (–)-(2*R*,3*S*)-6-Ethyl-2,3-dihydro-3-methyl-2-phenylpyran-4-one (40) (Table 5, entry 1)

Diisopropylamine (35 μL , 0.2 mmol, 0.2 equiv) was added via syringe to a flame-dried, 20-mL, schlenk flask under N_2 containing a solution of 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3** in CH_2Cl_2 (2 mL). To this solution was added 102 μL (1.0 mmol) of benzaldehyde in one portion. The resulting solution was cooled to $-72\text{ }^\circ\text{C}$ over 15 min and to the reaction mixture was added 172 μL (1.5 mmol, 1.5 equiv) of SiCl_4 in one portion. Then, 394 mg

(1.2 mmol, 1.2 equiv) of **33b** was added dropwise over 5 min. The resulting mixture was stirred at $-72\text{ }^{\circ}\text{C}$ for 2 h whereupon 3.0 mL of chilled CH_2Cl_2 was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO_3 / sat. aq. KF (25 mL) at $0\text{ }^{\circ}\text{C}$. This biphasic mixture was stirred vigorously for 3 h after which the aqueous layer was washed with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4 (5 g) filtered through Celite on a glass frit, and the filtrate was concentrated *in vacuo*. The residue was dissolved in 10 mL of CH_2Cl_2 and cooled in an ice water bath for 15 min and to the reaction mixture 10 drops of TFA was added. The resulting mixture was stirred at rt for 16 h whereupon 10 ml of sat. aq. NaHCO_3 added. This biphasic mixture was stirred for 10 min after which the aqueous layer was washed with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over Na_2SO_4 (5 g), filtered through Celite on a glass frit, and the filtrate was concentrated *in vacuo*. The *anti/syn* ratio was determined to be 96.0/4.0 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The resulting residue was purified by column chromatography (30 g SiO_2 , 2 cm column diam., hexanes/EtOAc, 2/1). The product-containing fractions were combined and the solvent was removed *in vacuo* to yield 190 mg (88%) of (–)-*anti*-**40** as a clear oil and 8 mg (4%) of *syn*-**40** as a clear oil (overall yield 92%).

Data for (–)-*anti*-**40**:

^1H NMR: (500 MHz, CHCl_3)

7.46-7.39 (m, 5 H, HC(8,9,10)), 5.45 (s, 1 H, HC(5)), 4.93 (d, $J = 13.2$, 1 H, HC(2)), 2.73 (dt, $J = 13.6$, 6.8, 1 H, HC(3)), 2.32 (q, $J = 7.6$, 2 H, HC(11)), 1.16 (t, $J = 7.3$, 3 H, HC(12)), 0.93 (d, $J = 7.1$, 3 H, HC(13))

^{13}C NMR: (125 MHz, CDCl_3)

192.8 (C(4)), 177.9 (C(6)), 137.7 (C(7)), 128.9 (C(10)), 128.6 (C(9)), 127.3 (C(8)), 102.5 (C(5)), 86.7 (C(2)), 44.1 (C(3)), 27.7 (C(11)), 10.5 (C(12)), 10.3 (C(13))

IR: (neat)

3065 (w), 3035 (w), 2974 (m), 2937 (w), 2879 (w), 2361 (w), 1958 (w), 1889 (w), 1671 (s), 1641 (s), 1499 (w), 1456 (s), 1424 (w), 1395 (s), 1365 (s), 1335 (m), 1279 (m), 1234 (m), 1212 (m), 1157 (m), 1091 (m), 1077 (m), 1065 (m), 1011 (s), 971 (m), 947 (m), 916 (w), 900 (w), 856 (m), 821 (m), 794 (w), 760 (s), 700 (s), 656 (w), 616 (w)

MS: (EI, 70 eV)
 216 (M^+ , 6), 159 (11), 119 (10), 118 (100), 117 (38), 91 (12)

Opt. Rot.: $[\alpha]_D^{24} -51.36^\circ$ ($c = 1.15$, EtOH)

TLC: R_f 0.25 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (2*R*,3*S*)-**40** t_r 3.89 min (83.0%); (2*S*,3*R*)-**40** t_r 4.27 min (17.0%) (Chiralpak OJ, 125 psi, 40 °C, 1.5% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₄H₁₆O₂ (216.28)

Calcd:	C, 77.75;	H, 7.46 %
Found:	C, 77.66;	H, 7.49%

Data for *syn*-40**:**

¹H NMR: (500 MHz, CHCl₃)
 7.43-7.32 (m, 5 H, HC(8,9,10)), 5.48 (d, $J = 3.2$, 1 H, HC(2)), 5.38 (s, 1 H, HC(5)), 2.52 (dq, $J = 3.2, 0.8$, 1 H, HC(3)), 2.40 (q, $J = 7.6$, 2 H, HC(11)), 1.21 (t, $J = 7.6$, 3 H, HC(12)), 0.90 (d, $J = 7.3$, 3 H, HC(13))

MS: (EI, 70 eV)
 216 (M^+ , 4), 159 (22), 119 (10), 118 (100), 117 (45), 91 (12)

TLC: R_f 0.17 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: *syn*-**40** t_r 2.75 min (48.7%); *syn*-**40** t_r 3.26 min (51.3%) (Chiralpak OD, 125 psi, 40 °C, 5.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₄H₁₇O₂: 217.1229, found: 217.1230

Preparation of (2*R*,3*S*)-6-Ethyl-2,3-dihydro-3-methyl-2-phenylpyran-4-one (40**) (Table 5, entry 2)**

Following Representative Procedure 6, 51 μ L (0.5 mmol) of benzaldehyde was combined with 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μ L (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μ L (0.75 mmol, 1.5 equiv) of SiCl₄ and 214 mg (0.6 mmol, 1.2

equiv) of **33b** to yield, after column chromatography (13 g SiO₂, 2 cm diam., pentane/Et₂O, 2/1) 77 mg (66%) of *anti*-**40** as a clear, colorless oil and 3 mg (3%) of *syn*-**40** as a clear, colorless oil (overall yield 69%). The *anti*/*syn* ratio was determined to be 95.0/5.0 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for *anti*-**40**:

¹H NMR: (500 MHz, CHCl₃)

7.46-7.38 (m, 5 H, HC(8,9,10)), 5.45 (s, 1 H, HC(5)), 4.93 (d, *J* = 13.2, 1 H, HC(2)), 2.73 (dt, *J* = 13.5, 6.9, 1 H, HC(3)), 2.32 (q, *J* = 7.5, 2 H, HC(11)), 1.15 (t, *J* = 7.2, 3 H, HC(12)), 0.93 (d, *J* = 7.1, 3 H, HC(13))

TLC: *R_f* 0.25 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (2*R*,3*S*)-**40** *t_r* 3.76 min (84.5%); (2*S*,3*R*)-**40** *t_r* 4.13 min (15.5%) (Chiralpak OJ, 125 psi, 40 °C, 1.5% MeOH in CO₂, 3.0 mL/min, 220 nm)

Data for *syn*-**40**:

¹H NMR: (500 MHz, CHCl₃)

7.42-7.32 (m, 5 H, HC(8,9,10)), 5.49 (d, *J* = 3.2, 1 H, HC(2)), 5.40 (s, 1 H, HC(5)), 2.52 (dq, *J* = 3.1, 0.9, 1 H, HC(3)), 2.40 (q, *J* = 7.6, 2 H, HC(11)), 1.21 (t, *J* = 7.5, 3 H, HC(12)), 0.90 (d, *J* = 7.3, 3 H, HC(13))

TLC: *R_f* 0.17 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: *syn*-**40** *t_r* 2.68 min (46.9%); *syn*-**40** *t_r* 3.20 min (53.1%) (Chiralpak OD, 125 psi, 40 °C, 5.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (2*R*,3*S*)-6-Ethyl-2,3-dihydro-3-methyl-2-phenylpyran-4-one (40**) (Table 5, entry 3)**

Following Representative Procedure 6, 51 μ L (0.5 mmol) of benzaldehyde was combined with 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μ L (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μ L (0.75 mmol, 1.5 equiv) of SiCl₄ and 164 mg (0.6 mmol, 1.2

equiv) of **33a** to yield, after column chromatography (13 g SiO₂, 2 cm diam., pentane/Et₂O, 2/1) 101 mg (93%) of *anti*-**40** as a clear oil and 3 mg (3%) of *syn*-**40** as a clear oil (overall yield 96%). The *anti*/*syn* ratio was determined to be 95.0/5.0 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for *anti*-**40**:

¹H NMR: (500 MHz, CHCl₃)

7.45-7.39 (m, 5 H, HC(8,9,10)), 5.45 (s, 1 H, HC(5)), 4.93 (d, *J* = 13.1, 1 H, HC(2)), 2.73 (dt, *J* = 13.6, 6.8, 1 H, HC(3)), 2.33 (q, *J* = 7.5, 2 H, HC(11)), 1.16 (t, *J* = 7.2, 3 H, HC(12)), 0.93 (d, *J* = 7.1, 3 H, HC(13))

TLC: *R_f* 0.25 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (2*R*,3*S*)-**40** *t_r* 3.84 min (69.6%); (2*S*,3*R*)-**40** *t_r* 4.21 min (30.4%) (Chiralpak OJ, 125 psi, 40 °C, 1.5% MeOH in CO₂, 3.0 mL/min, 220 nm)

Data for *syn*-**40**:

¹H NMR: (500 MHz, CHCl₃)

7.44-7.32 (m, 5 H, HC(8,9,10)), 5.48 (d, *J* = 3.2, 1 H, HC(2)), 5.39 (s, 1 H, HC(5)), 2.54 (dq, *J* = 3.2, 0.8, 1 H, HC(3)), 2.41 (q, *J* = 7.6, 2 H, HC(11)), 1.20 (t, *J* = 7.6, 3 H, HC(12)), 0.90 (d, *J* = 7.3, 3 H, HC(13))

TLC: *R_f* 0.17 (hexanes/EtOAc, 4/1) [UV (254 nm)]

Preparation of (2*R*,3*S*)-6-Ethyl-2,3-dihydro-3-methyl-2-phenylpyran-4-one (40**) (Table 5, entry 4)**

Following Representative Procedure 6, 51 μ L (0.5 mmol) of benzaldehyde was combined with 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μ L (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 86 μ L (0.75 mmol, 1.5 equiv) of SiCl₄ and 214 mg (0.6 mmol, 1.2 equiv) of **33c** to yield, after column chromatography (13 g SiO₂, 2 cm diam., pentane/Et₂O, 2/1) 88 mg (81%) of *anti*-**40** as a clear, colorless oil and 3 mg (3%) of *syn*-**40** as a clear, colorless oil

(overall yield 91%). The *anti/syn* ratio was determined to be 95.0/5.0 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for *anti*-40:

^1H NMR: (500 MHz, CHCl_3)

7.46-7.38 (m, 5 H, HC(8,9,10)), 5.43 (s, 1 H, HC(5)), 4.95 (d, $J = 13.2$, 1 H, HC(2)), 2.74 (dt, $J = 13.6$, 6.8, 1 H, HC(3)), 2.31 (q, $J = 7.6$, 2 H, HC(11)), 1.16 (t, $J = 7.3$, 3 H, HC(12)), 0.92 (d, $J = 7.1$, 3 H, HC(13))

TLC: R_f 0.25 (hexanes/EtOAc, 4/1) [UV (254 nm)]

SFC: (2*R*,3*S*)-40 t_r 3.85 min (72.6%); (2*S*,3*R*)-40 t_r 4.27 min (27.4%) (Chiralpak OJ, 125 psi, 40 °C, 1.5% MeOH in CO_2 , 3.0 mL/min, 220 nm)

Data for *syn*-40:

^1H NMR: (500 MHz, CHCl_3)

7.43-7.32 (m, 5 H, HC(8,9,10)), 5.48 (d, $J = 3.2$, 1 H, HC(2)), 5.38 (s, 1 H, HC(5)), 2.52 (dq, $J = 3.2$, 0.8, 1 H, HC(3)), 2.40 (q, $J = 7.6$, 2 H, HC(11)), 1.21 (t, $J = 7.6$, 3 H, HC(12)), 0.90 (d, $J = 7.3$, 3 H, HC(13))

TLC: R_f 0.17 (hexanes/EtOAc, 4/1) [UV (254 nm)]

Vinylogous Aldol Additions of Conjugated N,O-Silyl Ketene Acetals

Preparation of (+)-(2*E*,5*S*)-5-Hydroxy-5-phenyl-2-pentenoic Acid Dimethylamide (46) (Table 6, entry 1)

Diisopropylethylamine (9 μL , 0.05 mmol, 0.2 equiv) was added via syringe to a flame-dried, 5-mL, Schlenk flask under Ar containing a solution of 11 mg (0.0125 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-3 in CH_2Cl_2 (1.25 mL). To this solution was added 25 μL (0.25 mmol) of benzaldehyde in one portion. The reaction mixture was cooled to $-78\text{ }^\circ\text{C}$ (bath temperature) in a dry ice/isopropanol bath over 15 min and then 32 μL (0.275 mmol, 1.1 equiv)

of SiCl₄ was added in one portion. Then 68 mg (0.3 mmol, 1.2 equiv) of **41** was added dropwise over 2 min via syringe to the reaction mixture. The resulting mixture was stirred at –78 °C for 2 h in a dry ice/isopropanol bath whereupon 3.0 mL of chilled CH₂Cl₂ was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO₃/ sat. aq. KF (25 mL) at 0 °C. This biphasic mixture was stirred vigorously for 2 h after which the organic layer was removed and aqueous layer was washed with CH₂Cl₂ (3 x 30 mL). The combined organic extracts were dried over Na₂SO₄ (3 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ/α-addition products was determined to be 95/5 by ¹H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (SiO₂ (15 g), 2 cm diam., EtOAc to yield 45 mg (82%) of (+)-**46** as a white solid.

Data for (+)-γ-**46**:

mp: 86-87 °C

¹H NMR: (500 MHz, CDCl₃)

7.37-7.26 (m, 5 H, HC(7,8,9)), 6.84 (dt, *J* = 15.1, 7.6, 1 H, HC(3)), 6.31 (d, *J* = 15.1, 1 H, HC(2)), 4.83 (dd, *J* = 7.3, 5.6, 1 H, HC(5)), 3.01-2.98 (m, 6 H, H₃C(10)), 2.67-2.64 (m, 2 H, H₂C(4)), 2.05 (br s, 1 H, OH)

¹³C NMR: (126 MHz, CDCl₃)

166.6 (C(1)), 143.7 (C(6)), 141.6 (C(3)), 128.4 (C(8)), 127.6 (C(9)), 125.8 (C(7)), 123.2 (C(2)), 73.0 (C(5)), 42.4 (C(4)), 37.3 (C(10)), 35.7 (C(10))

IR: (CHCl₃)

3367 (w), 3061 (w), 3029 (w), 2935 (w), 1658 (m), 1602 (m), 1493 (w), 1453 (w), 1398 (w), 1260 (w), 1148 (w), 1057 (w), 980 (w), 912 (w), 835 (w), 755 (w), 730 (w), 700 (m), 626 (w)

MS: (CI, CH₄)

220 (M⁺+H, 25), 203 (17), 202 (100), 113 (17), 107 (11), 72 (11)

Opt. Rot.: [α]_D²⁴ +8.98 (c = 0.86, EtOH)

TLC: *R_f* 0.11 (EtOAc) [UV(254 nm)]

SFC: (*R*)-**46**, *t_R* 2.76 min (76.9 %); (*S*)-**46**, *t_R* 3.26 min (23.1 %) (Chiralpak AD, 125 psi, 40 °C, 15.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₃H₁₈NO₂: 220.1338, found: 220.1337

Preparation of (2*E*,5*S*)-5-Hydroxy-5-phenyl-2-pentenoic Acid Diethylamide (47**) (Table 6, entry 2)**

Diisopropylethylamine (9 μL , 0.05 mmol, 0.2 equiv) was added via syringe to a flame-dried, 5-mL, Schlenk flask under Ar containing a solution of 11 mg (0.0125 mmol, 0.05 equiv) of bisphosphoramidate (R,R) -**3** in CH_2Cl_2 (1.25 mL). To this solution was added 25 μL (0.25 mmol) of benzaldehyde in one portion. The reaction mixture was cooled to -78°C (bath temperature) in a dry ice/isopropanol bath over 15 min and then 32 μL (0.275 mmol, 1.1 equiv) of SiCl_4 was added in one portion. Then 77 mg (0.3 mmol, 1.2 equiv) of **42** was added dropwise over 2 min via syringe to the reaction mixture. The resulting mixture was stirred at -78°C for 2 h in a dry ice/isopropanol bath whereupon 3.0 mL of chilled CH_2Cl_2 was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO_3 / sat. aq. KF (25 mL) at 0°C . This biphasic mixture was stirred vigorously for 2 h after which the organic layer was removed and aqueous layer was washed with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4 (3 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ/α -addition products was determined to be 98/2 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (15 g SiO_2 , 2 cm diam., 3/1 hexanes/EtOAc) to yield 61 mg (98%) of **47** as a clear, colorless oil.

Data for γ -**47**:

^1H NMR: (500 MHz, CDCl_3)

7.38-7.26 (m, 5 H, HC(7,8,9)), 6.88 (dt, $J = 15.1, 7.4$, 1 H, HC(3)), 6.26 (d, $J = 14.9$, 1 H, HC(2)), 4.84 (dd, $J = 7.0, 5.6$, 1 H, HC(5)), 3.48-3.27 (m, 4 H, $\text{H}_2\text{C}(10)$), 2.70-2.63 (m, 2 H, $\text{H}_2\text{C}(4)$), 2.03 (br s, 1 H, OH), 1.15-1.11 (m, 6 H, $\text{H}_3\text{C}(11)$)

^{13}C NMR: (126 MHz, CDCl_3)

166.1 (C(1)), 143.9 (C(3)), 142.0 (C(6)), 128.7 (C(8)), 127.8 (C(9)), 126.1 (C(7)), 123.7 (C(2)), 73.2 (C(5)), 42.8 (C(4)), 42.5 (C(10)), 41.1 (C(10)), 15.0 (C(11)),

13.3 (C(11))

IR: (neat)

3377 (m), 3062 (m), 3030 (m), 2978 (m), 2935 (m), 1954 (w), 1714 (m), 1694 (m), 1682 (m), 1660 (m), 1652 (m), 1645 (m), 1634 (m), 1621 (m), 1600 (m), 1547 (m), 1557 (m), 1538 (m), 1514 (w), 1486 (m), 1463 (m), 1455 (m), 1435 (m), 1382 (m), 1361 (m), 1265 (m), 1218 (m), 1175 (m), 1145 (m), 1073 (m), 1053 (m), 1027 (m), 974 (m), 915 (m), 843 (m), 757 (m), 701 (m), 651 (m), 620 (m)

MS: (CI, CH₄)

248 (M⁺+H, 52), 231 (17), 230 (100), 141 (20), 123 (29), 107 (10), 100 (11)

TLC: *R_f* 0.25 (EtOAc) [UV(254 nm)]

SFC: (*R*)-**47**, *t_R* 3.19 min (66.2 %); (*S*)-**47**, *t_R* 3.53 min (33.8 %) (Chiralpak AD, 125 psi, 40 °C, 11.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₅H₂₂NO₂: 248.1651, found: 248.1653

Preparation of 1-[(5*S*,2*E*)-1-Oxo-5-phenyl-5-hydroxy-2-pentenyl]pyrrolidine (48**) (Table 6, entry 3)**

Diisopropylethylamine (18 μ L, 0.1 mmol, 0.2 equiv) was added via syringe to a flame-dried, 5-mL, Schlenk flask under Ar containing a solution of 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3** in CH₂Cl₂ (2.5 mL). To this solution was added 51 μ L (0.5 mmol) of benzaldehyde in one portion. The reaction mixture was cooled to -78 °C (bath temperature) in a dry ice/isopropanol bath over 15 min and then 64 μ L (0.55 mmol, 1.1 equiv) of SiCl₄ was added in one portion. Then 152 mg (0.6 mmol, 1.2 equiv) of **43** was added dropwise over 2 min via syringe to the reaction mixture. The resulting mixture was stirred at -78 °C for 2 h in a dry ice/isopropanol bath whereupon 3.0 mL of chilled CH₂Cl₂ was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO₃/ sat. aq. KF (25 mL) at 0 °C. This biphasic mixture was stirred vigorously for 2 h after which the organic layer was

removed and aqueous layer was washed with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4 (3 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ/α -addition products was determined to be 80/20 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (15 g SiO_2 , 2 cm diam., 19/1 EtOAc/MeOH) to yield 68 mg (56%) of **48** as a white solid.

Data for **48**:

mp: 98-99 °C

^1H NMR: (500 MHz, CDCl_3)

7.38-7.33 (m, 4 H, HC(7,8)), 7.29-7.26 (m, 1 H, HC(9)), 6.90 (dt, $J = 15.1, 7.6$, 1 H, HC(3)), 6.18 (d, $J = 15.1$, 1 H, HC(2)), 4.83 (dd, $J = 7.0, 5.9$, 1 H, HC(5)), 3.51-3.42 (m, 4 H, $\text{H}_2\text{C}(10)$), 2.66-2.63 (m, 2 H, $\text{H}_2\text{C}(4)$), 1.96-1.82 (m, 6 H, $\text{H}_2\text{C}(11)$)

^{13}C NMR: (126 MHz, CDCl_3)

164.7 (C(1)), 143.9 (C(6)), 141.5 (C(3)), 128.3 (C(8)), 127.4 (C(9)), 125.8 (C(7)), 124.3 (C(2)), 72.8 (C(5)), 46.5 (C(10)), 45.8 (C(10)), 42.4 (C(4)), 26.0 (C(11)), 24.2 (C(11))

IR: (CHCl_3)

3367 (m), 3086 (w), 3062 (w), 3030 (w), 2975 (m), 2953 (m), 2877 (m), 2238 (w), 1660 (s), 1601 (s), 1493 (m), 1446 (s), 1341 (m), 1306 (m), 1254 (m), 1228 (m), 1193 (m), 1173 (m), 1115 (w), 1042 (m), 974 (m), 911 (s), 862 (m), 843 (w), 814 (w), 731 (s), 701 (s), 645 (s)

MS: (CI, CH_4)

246 ($\text{M}^+\text{+H}$, 33), 229 (11), 228 (58), 141 (10), 140 (100), 139 (17), 107 (35), 98 (24), 79 (11), 57 (14), 55 (13)

TLC: R_f 0.15 (EtOAc) [UV(254 nm)]

SFC: (*R*)-**48**, t_R 2.93 min (56.5 %); (*S*)-**48**, t_R 3.97 min (43.5 %) (Chiralpak AD, 125 psi, 40 °C, 20.0% MeOH in CO_2 , 3.0 mL/min, 220 nm)

HRMS: Calcd for $\text{C}_{15}\text{H}_{20}\text{NO}_2$: 246.1494, found: 246.1497

Preparation of (+)-1-[(5*S*,2*E*)-1-Oxo-5-phenyl-5-hydroxy-2-pentenyl]piperidine (49**) (Table 6, entry 4)**

Diisopropylethylamine (18 μL , 0.1 mmol, 0.2 equiv) was added via syringe to a flame-dried, 5-mL, Schlenk flask under Ar containing a solution of 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (R,R) -**3** in CH_2Cl_2 (2.5 mL). To this solution was added 51 μL (0.5 mmol) of benzaldehyde in one portion. The reaction mixture was cooled to $-78\text{ }^\circ\text{C}$ (bath temperature) in a dry ice/isopropanol bath over 15 min and then 64 μL (0.55 mmol, 1.1 equiv) of SiCl_4 was added in one portion. Then 160 mg (0.6 mmol, 1.2 equiv) of **44** was added dropwise over 2 min via syringe to the reaction mixture. The resulting mixture was stirred at $-78\text{ }^\circ\text{C}$ for 2 h in a dry ice/isopropanol bath whereupon 3.0 mL of chilled CH_2Cl_2 was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO_3 / sat. aq. KF (25 mL) at $0\text{ }^\circ\text{C}$. This biphasic mixture was stirred vigorously for 2 h after which the organic layer was removed and aqueous layer was washed with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4 (3 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ/α -addition products was determined to be 95/5 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (15 g SiO_2 , 2 cm diam., EtOAc) to yield 126 mg (98%) of (+)- γ -**49** as a white solid.

Data for (+)-**49**:

mp: 89-90 $^\circ\text{C}$

^1H NMR: (500 MHz, CDCl_3)

7.38-7.33 (m, 4 H, HC(7,8)), 7.29-7.27 (m, 1 H, HC(9)), 6.90 (dt, $J = 15.1, 7.4$, 1 H, HC(3)), 6.18 (dt, $J = 15.1, 1.2$, 1 H, HC(2)), 4.83 (dd, $J = 7.3, 5.6$, 1 H, HC(5)), 3.57-3.40 (m, 4 H, $\text{H}_2\text{C}(10)$), 2.69-2.61 (m, 2 H, $\text{H}_2\text{C}(4)$), 1.98 (br s, 1 H, OH), 1.66-1.62 (m, 2 H, $\text{H}_2\text{C}(12)$), 1.54 (br s, 4 H, $\text{H}_2\text{C}(11)$)

^{13}C NMR: (126 MHz, CDCl_3)

165.4 (C(1)), 143.9 (C(6)), 141.2 (C(3)), 128.2 (C(8)), 127.3 (C(9)), 125.8 (C(7)), 123.4 (C(2)), 72.8 (C(5)), 46.8 (C(10)), 42.9 (C(10)), 42.5 (C(4)), 26.4 (C(11)),

25.4 (C(11)), 24.4 (C(12))

IR: (CHCl₃)

3370 (m), 3085 (w), 3062 (w), 3029 (w), 3006 (w), 2939 (s), 2857 (m), 2239 (w), 1656 (s), 1598 (s), 1493 (m), 1444 (s), 1366 (m), 1353 (m), 1254 (s), 1225 (m), 1176 (w), 1140 (m), 1125 (w), 1090 (w), 1053 (m), 1024 (m), 973 (m), 912 (m), 883 (m), 808 (w), 731 (s), 701 (s), 668 (m), 645 (m)

MS: (CI, CH₄)261 (10), 260 (M⁺+H, 55), 244 (11), 243 (18), 242 (100), 154 (61), 153 (22), 138 (11), 112 (24), 107 (48), 79 (14), 59 (15), 57 (17), 55 (14)Opt. Rot.: [α]_D²⁴ +8.55 (c = 0.83, EtOH)TLC: *R_f* 0.27 (EtOAc) [UV(254 nm)]SFC: (*R*)-**49**, *t_R* 3.57 min (87.0%); (*S*)-**49**, *t_R* 4.17 min (13.0%) (Chiralpak AD, 125 psi, 40 °C, 15.0% MeOH in CO₂, 3.0 mL/min, 220 nm)HRMS: Calcd for C₁₆H₂₂NO₂: 260.1651, found: 260.1655**Preparation of 1-[(5*S*,2*E*)-1-Oxo-5-phenyl-5-hydroxy-2-pentenyl]morpholine (**50**) (Table 6, entry 5)**

Diisopropylethylamine (18 μ L, 0.1 mmol, 0.2 equiv) was added via syringe to a flame-dried, 5-mL, Schlenk flask under Ar containing a solution of 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3** in CH₂Cl₂ (2.5 mL). To this solution was added 51 μ L (0.5 mmol) of benzaldehyde in one portion. The reaction mixture was cooled to -78 °C (bath temperature) in a dry ice/isopropanol bath over 15 min and then 64 μ L (0.55 mmol, 1.1 equiv) of SiCl₄ was added in one portion. Then 162 mg (0.6 mmol, 1.2 equiv) of **45** was added dropwise over 2 min via syringe to the reaction mixture. The resulting mixture was stirred at -78 °C for 2 h in a dry ice/isopropanol bath whereupon 3.0 mL of chilled CH₂Cl₂ was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO₃/ sat. aq. KF (25 mL) at 0 °C. This biphasic mixture was stirred vigorously for 2 h after which the organic layer was

removed and aqueous layer was washed with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4 (3 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (15 g SiO_2 , 2 cm diam., EtOAc) to yield 90 mg (69%) of **50** as a white solid.

Data for 50:

^1H NMR: (500 MHz, CDCl_3)

7.38-7.33 (m, 4 H, HC(7,8)), 7.29-7.27 (m, 1 H, HC(9)), 6.90 (dt, $J = 15.1, 7.4$, 1 H, HC(3)), 6.18 (dt, $J = 15.1, 1.2$, 1 H, HC(2)), 4.83 (dd, $J = 7.3, 5.6$, 1 H, HC(5)), 3.57-3.40 (m, 4 H, $\text{H}_2\text{C}(10)$), 2.69-2.61 (m, 2 H, $\text{H}_2\text{C}(4)$), 1.98 (br s, 1 H, OH), 1.66-1.62 (m, 2 H, $\text{H}_2\text{C}(12)$), 1.54 (br s, 4 H, $\text{H}_2\text{C}(11)$)

TLC: R_f 0.17 (EtOAc) [UV(254 nm)]

SFC: (*R*)-**50**, t_R 3.38 min (95.0%); (*S*)-**50**, t_R 4.05 min (5.0%) (Chiralpak OB, 125 psi, 40 °C, 10.0% MeOH in CO_2 , 3.0 mL/min, 220 nm)

Preparation of 4-[(5*R*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2,6-heptadienyl]morpholine (51**) (Table 7, entry 1)**

Diisopropylethylamine (18 μL , 0.1 mmol, 0.2 equiv) was added via syringe to a flame-dried, 20-mL, Schlenk flask under Ar containing a solution of 21 mg (0.025 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3** in CH_2Cl_2 (2.5 mL). To this solution was added 63 μL (0.5 mmol, 1.0 equiv) of cinnamaldehyde in one portion and the reaction mixture was cooled to -78°C over 15 min. To the resulting solution was added 63 μL (0.55 mmol, 1.1 equiv) of SiCl_4 in one portion. Then, 162 mg (0.6 mmol, 1.2 equiv) of **45** was added dropwise over 2 min via syringe.

The resulting mixture was stirred at $-72\text{ }^{\circ}\text{C}$ for 2 h whereupon 3.0 mL of chilled CH_2Cl_2 was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO_3 /sat. aq. KF (25 mL) at $0\text{ }^{\circ}\text{C}$. This biphasic mixture was stirred vigorously for 3 h after which the organic layer was removed and the aqueous layer was washed with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4 (5 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ -1,2-**51**/ α -1,2-**51**/ γ -1,4-**51**/ α -1,4-**51** was determined to be 97/0/1/2 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (SiO_2 (12 g), 2 cm diam., EtOAc (100 mL) to EtOAc/MeOH, 19/1 (100 mL)) to yield 131 mg (91%) of γ -1,2-**51** as a white solid.

Data for γ -1,2-**51**:

^1H NMR: (500 MHz, CDCl_3)

7.37 (dd, $J = 8.2, 1.1$, 2 H, HC(9)), 7.32 (dt, $J = 7.6, 1.7$, 2 H, HC(10)) 7.25 (tt, $J = 7.3, 1.3$, 1 H, HC(11)), 6.91 (dt, $J = 15.1, 7.3$, 1 H, HC(3)), 6.61 (d, $J = 15.9$, 1 H, HC(7)), 6.32 (dt, $J = 15.1, 1.4$, 1 H, HC(2)), 6.24 (dd, $J = 15.9, 6.3$, 1 H, HC(6)), 4.47 (dq, $J = 6.6, 1.2$, 1 H, HC(5)), 3.65 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.58-2.54 (m, 2 H, $\text{H}_2\text{C}(4)$), 2.08 (br s, 1 H, OH)

TLC: R_f 0.14 (EtOAc) [UV(254 nm)]

SFC: (*R*)- γ -1,2-**51**, t_R 2.38 min (92.6%); (*S*)- γ -1,2-**51**, t_R 4.14 min (7.4%) (Chiralpak OB, 125 psi, $40\text{ }^{\circ}\text{C}$, 20.0% MeOH in CO_2 , 3.0 mL/min, 220 nm)

Preparation of 4-[(5*R*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2,6-heptadienyl]morpholine (51**)**
(Table 7, entry 2)

Diisopropylethylamine (18 μL , 0.1 mmol, 0.2 equiv) was added via syringe to a flame-

dried, 20-mL, Schlenk flask under Ar containing a solution of 8 mg (0.01 mmol, 0.02 equiv) of bisphosphoramidate (*R,R*)-**3** in CH₂Cl₂ (2.5 mL). To this solution was added 63 μ L (0.5 mmol, 1.0 equiv) of cinnamaldehyde in one portion and the reaction mixture was cooled to -78°C (bath temperature) over 15 min. To the resulting solution was added 63 μ L (0.55 mmol, 1.1 equiv) of SiCl₄ in one portion. Then, 162 mg (0.6 mmol, 1.2 equiv) of **45** was added dropwise over 2 min via syringe. The resulting mixture was stirred at -72°C for 2 h whereupon 3.0 mL of chilled CH₂Cl₂ was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO₃/ sat. aq. KF (25 mL) at 0°C . This biphasic mixture was stirred vigorously for 3 h after which the organic layer was removed and the aqueous layer was washed with CH₂Cl₂ (3 x 30 mL). The combined organic extracts were dried over Na₂SO₄ (5 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ -1,2-**51**/ α -1,2-**51**/ γ -1,4-**51**/ α -1,4-**51** was determined to be 97/0/1/2 by ¹H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (SiO₂ (12 g), 2 cm diam., EtOAc (100 mL) to EtOAc/MeOH, 19/1 (100 mL)) to yield 140 mg (97%) of γ -1,2-**51** as a white solid.

Data for γ -1,2-**51**:

¹H NMR: (500 MHz, CDCl₃)

7.38 (dd, $J = 8.2, 1.2$, 2 H, HC(9)), 7.32 (dt, $J = 7.6, 1.8$, 2 H, HC(10)), 7.26 (tt, $J = 7.3, 1.2$, 1 H, HC(11)), 6.91 (dt, $J = 15.1, 7.3$, 1 H, HC(3)), 6.61 (d, $J = 15.9$, 1 H, HC(7)), 6.33 (dt, $J = 15.1, 1.4$, 1 H, HC(2)), 6.24 (dd, $J = 15.9, 6.3$, 1 H, HC(6)), 4.46 (dq, $J = 6.6, 1.2$, 1 H, HC(5)), 3.62 (m, 8 H, H₂C(12,13)), 2.59-2.54 (m, 2 H, H₂C(4)), 2.08 (br s, 1 H, OH)

TLC: R_f 0.14 (EtOAc) [UV(254 nm)]

SFC: (*R*)- γ -1,2-**51**, t_R 2.40 min (94.7%); (*S*)- γ -1,2-**51**, t_R 4.16 min (5.3%) (Chiralpak OB, 125 psi, 40°C , 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of 4-[(5*R*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2,6-heptadienyl]morpholine (51**)**
(Table 7, entry 3)

Diisopropylethylamine (9 μL , 0.05 mmol, 0.2 equiv) was added via syringe to a flame-dried, 20-mL, Schlenk flask under Ar containing a solution of 4 mg (0.005 mmol, 0.02 equiv) of bisphosphoramidate (*R,R*)-**3** in CH_2Cl_2 (2.5 mL). To this solution was added 32 μL (0.25 mmol, 1.0 equiv) of cinnamaldehyde in one portion and the reaction mixture was cooled to -78°C (bath temperature) over 15 min. To the resulting solution was added 32 μL (0.275 mmol, 1.1 equiv) of SiCl_4 in one portion. Then, 81 mg (0.3 mmol, 1.2 equiv) of **45** was added dropwise over 2 min via syringe. The resulting mixture was stirred at -78°C for 2 h whereupon 3.0 mL of chilled CH_2Cl_2 was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO_3 / sat. aq. KF (25 mL) at 0°C . This biphasic mixture was stirred vigorously for 2 h after which the organic layer was removed and the aqueous layer was washed with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4 (5 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ -1,2-**51**/ α -1,2-**51**/ γ -1,4-**51**/ α -1,4-**51** was determined to be 97/0/1/2 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (SiO_2 (12 g), 2 cm diam., EtOAc (100 mL) to EtOAc/MeOH, 19/1 (100 mL)) to yield 70 mg (97%) of γ -1,2-**51** as a white solid.

Data for γ -1,2-**51**:

^1H NMR: (500 MHz, CDCl_3)

7.38 (d, $J = 8.4$, 2 H, HC(9)), 7.32 (dt, $J = 7.7$, 1.7, 2 H, HC(10)) 7.25 (tt, $J = 7.5$, 1.3, 1 H, HC(11)), 6.92 (dt, $J = 15.1$, 7.3, 1 H, HC(3)), 6.61 (d, $J = 15.9$, 1 H, HC(7)), 6.32 (dt, $J = 15.1$, 1.5, 1 H, HC(2)), 6.24 (dd, $J = 15.9$, 6.3, 1 H, HC(6)), 4.48 (dq, $J = 6.6$, 1.2, 1 H, HC(5)), 3.65 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.58-2.54 (m, 2 H,

H₂C(4)), 2.09 (br s, 1 H, OH)

TLC: *R_f* 0.14 (EtOAc) [UV(254 nm)]

SFC: (*R*)- γ -1,2-**51**, *t_R* 2.40 min (95.6%); (*S*)- γ -1,2-**51**, *t_R* 4.15 min (4.4%) (Chiralpak OB, 125 psi, 40 °C, 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of 4-[(5*R*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2,6-heptadienyl]morpholine (51**) (Table 7, entry 4)**

Diisopropylethylamine (9 μ L, 0.05 mmol, 0.2 equiv) was added via syringe to a flame-dried, 20-mL, Schlenk flask under Ar containing a solution of 4 mg (0.005 mmol, 0.02 equiv) of bisphosphoramidate (*R,R*)-**3** in CH₂Cl₂ (1.25 mL). To this solution was added 32 μ L (0.25 mmol, 1.0 equiv) of cinnamaldehyde in one portion and the reaction mixture was cooled to -78 °C (bath temperature) over 15 min. To the resulting solution was added 32 μ L (0.275 mmol, 1.1 equiv) of SiCl₄ in one portion. Then, a solution of 81 mg (0.3 mmol, 1.2 equiv) of **45** in 1.25 mL of CH₂Cl₂ was added dropwise over 5 min via syringe. The resulting mixture was stirred at -72 °C for 2 h whereupon 3.0 mL of chilled CH₂Cl₂ was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO₃/ sat. aq. KF (25 mL) at 0 °C. This biphasic mixture was stirred vigorously for 2 h after which the organic layer was removed and the aqueous layer was washed with CH₂Cl₂ (3 x 30 mL). The combined organic extracts were dried over Na₂SO₄ (5 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ -1,2-**51**/ α -1,2-**51**/ γ -1,4-**51**/ α -1,4-**51** was determined to be 100/0/0/0 by ¹H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (SiO₂ (12 g), 2 cm diam., EtOAc (100 mL) to EtOAc/MeOH, 19/1 (100 mL)) to yield 70 mg (97%) of γ -1,2-**51** as a white solid.

Data for γ -1,2-**51**: ^1H NMR: (500 MHz, CDCl_3)

7.36 (dd, $J = 8.0, 1.1$, 2 H, HC(9)), 7.32 (dt, $J = 7.5, 1.6$, 2 H, HC(10)) 7.25 (tt, $J = 7.3, 1.4$, 1 H, HC(11)), 6.91 (dt, $J = 15.1, 7.3$, 1 H, HC(3)), 6.61 (d, $J = 15.9$, 1 H, HC(7)), 6.32 (dt, $J = 15.1, 1.5$, 1 H, HC(2)), 6.24 (dd, $J = 15.9, 6.3$, 1 H, HC(6)), 4.49 (dq, $J = 6.7, 1.2$, 1 H, HC(5)), 3.67 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.57-2.54 (m, 2 H, $\text{H}_2\text{C}(4)$), 2.08 (br s, 1 H, OH)

TLC: R_f 0.14 (EtOAc) [UV(254 nm)]SFC: (*R*)- γ -1,2-**51**, t_R 2.39 min (96.0%); (*S*)- γ -1,2-**51**, t_R 4.14 min (4.0%) (Chiralpak OB, 125 psi, 40 °C, 20.0% MeOH in CO_2 , 3.0 mL/min, 220 nm)

Preparation of 4-[(5*R*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2,6-heptadienyl]morpholine (51**)**
(Table 7, entry 5)

Diisopropylethylamine (9 μL , 0.05 mmol, 0.2 equiv) was added via syringe to a flame-dried, 20-mL, Schlenk flask under Ar containing a solution of 4 mg (0.005 mmol, 0.02 equiv) of bisphosphoramidate (*R,R*)-**21** in CH_2Cl_2 (2.5 mL). To this solution was added 32 μL (0.25 mmol, 1.0 equiv) of cinnamaldehyde in one portion and the reaction mixture was cooled to -78°C (bath temperature) over 15 min. To the resulting solution was added 32 μL (0.275 mmol, 1.1 equiv) of SiCl_4 in one portion. Then, a solution of 81 mg (0.3 mmol, 1.2 equiv) of **45** in 2.5 mL of CH_2Cl_2 was added dropwise over 5 min via syringe. The resulting mixture was stirred at -72°C for 2 h whereupon 3.0 mL of chilled CH_2Cl_2 was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO_3 / sat. aq. KF (25 mL) at 0°C . This biphasic mixture was stirred vigorously for 2.5 h after which the organic layer was removed and the

aqueous layer was washed with CH₂Cl₂ (3 x 30 mL). The combined organic extracts were dried over Na₂SO₄ (5 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ -1,2-**51**/ α -1,2-**51**/ γ -1,4-**51**/ α -1,4-**51** was determined to be 100/0/0/0 by ¹H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (SiO₂ (12 g), 2 cm diam., EtOAc (100 mL) to EtOAc/MeOH, 19/1 (100 mL)) to yield 68 mg (94%) of γ -1,2-**51** as a white solid.

Data for γ -1,2-**51**:

¹H NMR: (500 MHz, CDCl₃)

7.36 (dd, *J* = 8.2, 1.1, 2 H, HC(9)), 7.32 (dt, *J* = 7.6, 1.7, 2 H, HC(10)) 7.25 (tt, *J* = 7.3, 1.3, 1 H, HC(11)), 6.91 (dt, *J* = 15.1, 7.3, 1 H, HC(3)), 6.61 (d, *J* = 15.9, 1 H, HC(7)), 6.32 (dt, *J* = 15.4, 1.4, 1 H, HC(2)), 6.24 (dd, *J* = 15.7, 6.3, 1 H, HC(6)), 4.48 (dq, *J* = 6.6, 1.2, 1 H, HC(5)), 3.66 (m, 8 H, H₂C(12,13)), 2.59-2.53 (m, 2 H, H₂C(4)), 2.12 (br s, 1 H, OH)

TLC: *R_f* 0.14 (EtOAc) [UV(254 nm)]

SFC: (*R*)- γ -1,2-**51**, *t_R* 2.46 min (98.1%); (*S*)- γ -1,2-**51**, *t_R* 4.22 min (1.9%) (Chiralpak OB, 125 psi, 40 °C, 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Representative Procedure 8. Vinylogous Aldol Additions of Conjugated *N,O*-Silyl Ketene Acetals to Conjugated Aldehydes. Preparation of (+)-4-[(5*R*,2*E*)-1-Oxo-5-phenyl-5-hydroxy-2-pentenyl]morpholine (50**) (Table 8, entry 1)**

Diisopropylethylamine (18 μ L, 0.1 mmol, 0.1 equiv) was added via syringe to a flame-dried, 20-mL, Schlenk flask under Ar containing a solution of 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3** in CH₂Cl₂ (5 mL). To this solution was added 102 μ L (1.0 mmol) of benzaldehyde in one portion. To the resulting solution was added 126 μ L (1.1 mmol, 1.1 equiv) of SiCl₄ in one portion and the reaction mixture was cooled to -72 °C over 15 min. Then, a solution of 324 mg (1.2 mmol, 1.2 equiv) of **45** in 5 mL of CH₂Cl₂ was added dropwise over 5

min via syringe. The resulting mixture was stirred at $-72\text{ }^{\circ}\text{C}$ for 1 h whereupon 3.0 mL of chilled CH_2Cl_2 was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO_3 / sat. aq. KF (25 mL) at $0\text{ }^{\circ}\text{C}$. This biphasic mixture was stirred vigorously for 3 h after which the organic layer was removed and aqueous layer was washed with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4 (5 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (SiO_2 (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)) to yield a solid which was recrystallized by precipitation from hot EtOAc (5 mL) with minimal amounts of hexanes to yield 247 mg (95%) of (+)-**50** as white needles.

Data for (+)-**50**:

mp: 108-109 $^{\circ}\text{C}$ (EtOAc/hexanes)

^1H NMR: (500 MHz, CDCl_3)

7.38-7.27 (m, 5 H, HC(7,8,9)), 6.87 (dt, $J = 15.1, 7.1$, 1 H, HC(3)), 6.24 (dt, $J = 15.1, 1.4$, 1 H, HC(2)), 4.85 (dd, $J = 7.5, 5.5$, 1 H, HC(5)), 3.66-3.56 (m, 8 H, $\text{H}_2\text{C}(10,11)$), 2.72-2.63 (m, 2 H, $\text{H}_2\text{C}(4)$), 2.15 (br s, 1 H, OH)

^{13}C NMR: (126 MHz, CDCl_3)

165.5 (C(1)), 143.9 (C(6)), 142.5 (C(3)), 128.2 (C(8)), 127.4 (C(9)), 125.7 (C(7)), 122.3 (C(2)), 72.7 (C(5)), 66.5 (C(11)), 45.9 (C(10)), 42.4 (C(4)), 42.0 (C(10))

IR: (CHCl_3)

3674 (w), 3647 (w), 3600 (m), 3392 (s), 3058 (m), 3063 (s), 3010 (s), 2972 (s), 2924 (s), 2902 (s), 2861 (s), 2762 (m), 2714 (m), 2686 (m), 2581 (w), 2459 (m), 2402 (m), 2360 (m), 2334 (w), 2233 (w), 2016 (w), 1952 (w), 1881 (w), 1812 (w), 1759 (w), 1732 (w), 1657 (s), 1607 (s), 1493 (s), 1437 (s), 1389 (s), 1362 (s), 1302 (s), 1227 (s), 1217 (s), 1115 (s), 1068 (s), 1042 (s), 1008 (s), 977 (s), 917 (s), 893 (m), 855 (s), 756 (s), 701 (s), 667 (s), 628 (s)

MS: (CI , CH_4)

262 ($\text{M}^+\text{+H}$, 29), 245 (20), 244 (100), 156 (14), 155 (31), 114 (11), 107 (27)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +10.42$ (c = 0.90, EtOH)

TLC: R_f 0.17 (EtOAc) [UV(254 nm)]

SFC: (*R*)-**50**, t_R 3.39 min (97.1 %); (*S*)-**50**, t_R 4.11 min (2.9 %) (Chiralpak OB, 125 psi, 40 °C, 10.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₅H₁₉NO₃ (261.32)

Calcd: C, 68.94; H, 7.33; N, 5.36%

Found: C, 68.92; H, 7.33; N, 5.36%

Preparation of (+)-4-[(5*R*,2*E*)-1-Oxo-5-(4-methoxyphenyl)-5-hydroxy-2-pentenyl]morpholine (52**) (Table 8, entry 2)**

Following Representative Procedure 8, 121 μ L (1.0 mmol) of *p*-anisaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μ L (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μ L (1.1 mmol, 1.1 equiv) of SiCl₄ and 324 mg (1.2 mmol, 1.2 equiv) of **45** to yield, after column chromatography (SiO₂ (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)) a solid which was recrystallized by precipitation from hot EtOAc (5 mL) with minimal amounts of hexanes to yield 277 mg (95%) of (+)-**52** as white crystals. The ratio of γ / α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-52**:**

mp: 95-96 °C (EtOAc/hexanes)

¹H NMR: (500 MHz, CDCl₃)

7.29-7.27 (m, 2 H, HC(7)), 6.90-6.83 (m, 3 H, HC(3,8)), 6.24 (dt, J = 15.1, 1.4, 1 H, HC(2)), 4.80 (dd, J = 7.6, 5.4, 1 H, HC(5)), 3.80 (s, 3 H, H₃C(10)), 3.67-3.57 (m, 8 H, H₂C(11,12)), 2.71-2.59 (m, 2 H, H₂C(4)), 1.96 (br s, 1 H, OH)

¹³C NMR: (126 MHz, CDCl₃)

165.5 (C(1)), 158.8 (C(9)), 142.5 (C(3)), 136.0 (C(6)), 126.9 (C(7)), 122.1 (C(2)), 113.5 (C(8)), 72.3 (C(5)), 66.5 (C(12)), 55.1 (C(10)), 45.9 (C(11)), 42.2 (C(4)), 41.9 (C(11))

IR: (CHCl₃)

3388 (m), 3014 (m), 2971 (w), 2926 (w), 2903 (w), 2862 (w), 2839 (w), 2458 (w), 2401 (w), 2058 (w), 1887 (w), 1765 (w), 1657 (m), 1611 (s), 1514 (s), 1462 (m), 1440 (s), 1389 (m), 1362 (w), 1303 (m), 1266 (m), 1248 (s), 1217 (s), 1175 (m), 1115 (m), 1069 (w), 1037 (m), 1007 (w), 977 (w), 931 (w), 887 (w), 834 (m), 810 (w), 757 (s), 667 (m)

MS: (ESI)

292 (M⁺+H, 45), 275 (20), 274 (100), 169 (12)

Opt. Rot.: [α]_D²⁴ +9.95 (c = 0.90, EtOH)

TLC: *R_f* 0.15 (EtOAc) [UV(254 nm)]

SFC: (*R*)-**52**, *t_R* 4.11 min (99.0%); (*S*)-**52**, *t_R* 4.95 min (1.0%) (Chiralpak OB, 125 psi, 40 °C, 12.5% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₆H₂₁NO₄ (291.34)

Calcd: C, 65.96; H, 7.27; N, 4.81%

Found: C, 65.87; H, 7.28; N, 4.78%

Preparation of (+)-4-[(5*R*,2*E*)-1-Oxo-5-(4-trifluoromethylphenyl)-5-hydroxy-2-pentenyl]morpholine (53**) (Table 8, entry 3)**

Following Representative Procedure 8, 137 μ L (1.0 mmol) of *p*-trifluoromethylbenzaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μ L (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μ L (1.1 mmol, 1.1 equiv) of SiCl₄ and 324 mg (1.2 mmol, 1.2 equiv) of **45** to yield, after column chromatography (SiO₂ (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)) a solid which was recrystallized by precipitation from hot EtOAc (5 mL) with minimal amounts of hexanes to yield 306 mg (93%) of (+)-**53** as white crystals. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-53:

<u>mp:</u>	122-123 °C (EtOAc/hexanes)
<u>¹H NMR:</u>	(500 MHz, CDCl ₃) 7.62 (d, <i>J</i> = 8.1, 2 H, HC(7)), 7.49 (d, <i>J</i> = 8.3, 2 H, HC(8)), 6.89 (dt, <i>J</i> = 14.9, 7.6, 1 H, HC(3)), 6.25 (dt, <i>J</i> = 15.1, 1.4, 1 H, HC(2)), 4.94 (t, <i>J</i> = 6.3, 1 H, HC(5)), 3.67-3.58 (m, 8 H, H ₂ C(11,12)), 2.66 (t, <i>J</i> = 6.6, 2 H, H ₂ C(4)), 2.18 (br s, 1 H, OH)
<u>¹³C NMR:</u>	(126 MHz, CDCl ₃) 165.5 (C(1)), 148.0 (C(6)), 142.1 (C(3)), 129.4 (q, <i>J</i> _{CF} = 32, C(9)), 126.1 (C(7)), 125.2 (q, <i>J</i> _{CF} = 4, C(8)), 124.0 (q, <i>J</i> _{CF} = 272, C(10)), 122.6 (C(2)), 72.7 (C(5)), 66.5 (C(12)), 45.9 (C(11)), 42.4 (C(4)), 42.0 (C(11))
<u>¹⁹F NMR:</u>	(237 MHz, CDCl ₃ w/C ₆ F ₆) -62.716
<u>IR:</u>	(CHCl ₃) 3678 (w), 3603 (w), 3380 (w), 3018 (m), 2975 (w), 2926 (w), 2903 (w), 2863 (w), 2763 (w), 2717 (w), 2401 (w), 2349 (w), 1925 (w), 1807 (w), 1658 (m), 1607 (m), 1518 (w), 1462 (m), 1439 (m), 1389 (w), 1362 (w), 1326 (s), 1303 (w), 1268 (m), 1216 (s), 1167 (m), 1115 (s), 1068 (s), 1042 (w), 1017 (m), 977 (w), 930 (w), 887 (w), 846 (m), 767 (s), 668 (m)
<u>MS:</u>	(EI, 70 eV) 329 (M ⁺ , 2), 225 (13), 175 (64), 155 (100), 140 (46), 127 (36), 86 (25), 69 (29), 56 (21)
<u>Opt. Rot.:</u>	[α] _D ²⁴ +10.94 (c = 1.00, EtOH)
<u>TLC:</u>	<i>R</i> _f 0.22 (EtOAc) [UV(254 nm)]
<u>SFC:</u>	(<i>R</i>)-53, <i>t</i> _R 10.42 min (95.4%); (<i>S</i>)-53, <i>t</i> _R 11.62 min (4.6%) (Chiralpak OB, 200 psi, 40 °C, 2.0% MeOH in CO ₂ , 2.0 mL/min, 220 nm)
<u>Analysis:</u>	C ₁₆ H ₁₈ F ₃ NO ₃ (329.31) Calcd: C, 58.35; H, 5.51; N, 4.25% Found: C, 58.35; H, 5.60; N, 4.48%

Preparation of (+)-4-[(5*R*,2*E*)-1-Oxo-5-furanyl-5-hydroxy-2-pentenyl]morpholine (54)
(Table 8, entry 4)

Following Representative Procedure 8, 83 μL (1.0 mmol) of 2-furfuraldehyde, was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μL (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μL (1.1 mmol, 1.1 equiv) of SiCl_4 , and 324 mg (1.2 mmol, 1.2 equiv) of **45** to yield, after column chromatography (SiO_2 (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)) an oil which was crystallized from Et_2O (4 mL) to yield 236 mg (94%) of (+)-**54** as white crystals. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-**54**:

mp: 50-52 $^\circ\text{C}$ (Et_2O)

^1H NMR: (500 MHz, CDCl_3)

7.38 (dd, $J = 1.7, 0.7$, 1 H, HC(9)), 6.86 (dt, $J = 15.1, 7.3$, 1 H, HC(3)), 6.34 (dd, $J = 3.2, 2.0$, 1 H, HC(8)), 6.31 (d, $J = 15.1$, 1 H, HC(2)), 6.27 (d, $J = 3.2$, 1 H, HC(7)), 4.86 (t, $J = 6.6$, 1 H, HC(5)), 3.68-3.60 (m, 8 H, $\text{H}_2\text{C}(10,11)$), 2.80-2.76 (m, 2 H, $\text{H}_2\text{C}(4)$), 1.87 (br s, 1 H, OH)

^{13}C NMR: (126 MHz, CDCl_3)

165.5 (C(1)), 155.9 (C(6)), 141.8 (C(3)), 141.7 (C(9)), 122.4 (C(2)), 110.0 (C(8)), 106.0 (C(7)), 66.5 (C(11)), 66.2 (C(5)), 45.9 (C(10)), 42.0 (C(10)), 38.7 (C(4))

IR: (neat)

3379 (s), 3146 (m), 3117 (m), 3059 (w), 2966 (m), 2903 (s), 2859 (s), 2761 (w), 2715 (w), 2361 (w), 2243 (w), 1961 (w), 1660 (s), 1614 (s), 1505 (m), 1435 (s), 1387 (m), 1362 (m), 1301 (s), 1267 (s), 1237 (s), 1195 (m), 1180 (m), 1146 (s), 1115 (s), 1068 (s), 1041 (s), 1011 (s), 978 (s), 918 (s), 884 (m), 854 (s), 812 (m), 734 (s), 700 (m), 646 (m)

MS: (CI, CH₄)

252 (M⁺+H, 6), 235 (17), 234 (100), 155 (23), 97 (21)

Opt. Rot.: [α]_D²⁴ +8.52 (c = 0.90, EtOH)

TLC: *R*_f 0.11 (EtOAc) [UV(254 nm)]

SFC: (*R*)-**54**, *t*_R 7.16 min (93.8%); (*S*)-**54**, *t*_R 8.21 min (6.2%) (Chiralpak AD, 150 psi, 40 °C, 8.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₃H₁₇NO₄ (251.28)

Calcd: C, 62.14; H, 6.82; N, 5.57%

Found: C, 62.07; H, 6.82; N, 5.54%

Preparation of (–)-4-[(5*R*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2,6-heptadienyl]morpholine (51**) (Table 8, entry 5)**

Following Representative Procedure 8, 126 μ L (1.0 mmol) of cinnamaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μ L (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μ L (1.1 mmol, 1.1 equiv) of SiCl₄ and 324 mg (1.2 mmol, 1.2 equiv) of **45** to yield, after column chromatography (SiO₂ (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)) a solid which was recrystallized by precipitation from hot EtOAc (5 mL) with minimal amounts of hexanes to yield 270 mg (94%) of (–)-**51** as white crystals. The ratio of γ / α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-**51**:

mp: 87–88 °C (EtOAc/hexanes)

¹H NMR: (500 MHz, CDCl₃)

7.37 (dd, *J* = 8.2, 1.1, 2 H, HC(9)), 7.32 (dt, *J* = 7.6, 1.7, 2 H, HC(10)) 7.25 (tt, *J* = 7.3, 1.3, 1 H, HC(11)), 6.91 (dt, *J* = 15.1, 7.3, 1 H, HC(3)), 6.61 (d, *J* = 15.9, 1 H, HC(7)), 6.32 (dt, *J* = 15.1, 1.4, 1 H, HC(2)), 6.24 (dd, *J* = 15.9, 6.3, 1 H,

HC(6)), 4.47 (dq, $J = 6.6, 1.2$, 1 H, HC(5)), 3.65-3.45 (m, 8 H, H₂C(12,13)), 2.58-2.54 (m, 2 H, H₂C(4)), 2.08 (br s, 1 H, OH)

¹³C NMR: (126 MHz, CDCl₃)

165.5 (C(1)), 142.4 (C(3)), 136.4 (C(8)), 131.4 (C(6)), 130.1 (C(7)), 128.4 (C(10)), 127.5 (C(11)), 126.2 (C(9)), 122.4 (C(2)), 71.0 (C(5)), 66.5 (C(13)), 66.4 (C(13)), 45.9 (C(12)), 42.0 (C(12)), 40.5 (C(4))

IR: (CHCl₃)

3676 (w), 3601 (w), 3383 (w), 3083 (w), 3061 (w), 3014 (m), 2925 (w), 2902 (w), 2862 (w), 2762 (w), 2716 (w), 2686 (w), 2453 (w), 2401 (w), 2231 (w), 1951 (w), 1879 (w), 1805 (w), 1658 (m), 1607 (s), 1494 (w), 1460 (m), 1438 (s), 1389 (w), 1362 (w), 1302 (m), 1268 (m), 1236 (m), 1216 (s), 1115 (s), 1068 (m), 1039 (m), 968 (m), 926 (w), 854 (w), 752 (s), 694 (m), 668 (m), 628 (w)

MS: (CI, CH₄)

288 (M⁺+H, 10), 272 (16), 271 (22), 270 (100), 183 (10), 156 (23), 155 (35), 133 (36), 114 (20), 88 (15), 63 (43), 62 (11), 61 (16)

Opt. Rot.: $[\alpha]_D^{24} -17.23$ (c = 1.20, EtOH)

TLC: R_f 0.14 (EtOAc) [UV(254 nm)]

SFC: (*R*)-**51**, t_R 2.41 min (98.2%); (*S*)-**51**, t_R 4.16 min (1.8%) (Chiralpak OB, 125 psi, 40 °C, 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₇H₂₁NO₃ (287.35)

Calcd: C, 71.06; H, 7.37; N, 4.87%

Found: C, 70.95; H, 7.42; N, 4.85%

Preparation of (+)-4-[(5*R*,2*E*)-1-Oxo-7-phenyl-6-methyl-5-hydroxy-2,6-heptadienyl]morpholine (55**) (Table 8, entry 6)**

Following Representative Procedure 8, 140 μ L (1.0 mmol) of α -methylcinnamaldehyde

was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μ L (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μ L (1.1 mmol, 1.1 equiv) of SiCl_4 and 324 mg (1.2 mmol, 1.2 equiv) of **45** to yield, after column chromatography (SiO_2 (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)) an oil which was crystallized from Et_2O (4 mL) to yield 273 mg (91%) of (+)-**55** as white crystals. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-**55**:

mp: 79-80 $^\circ\text{C}$ (Et_2O)

^1H NMR: (500 MHz, CDCl_3)

7.37 (dt, $J = 7.6, 1.3$, 2 H, HC(10)), 7.27 (dt, $J = 7.6, 1.7$, 2 H, HC(9)) 7.25 (dt, $J = 7.5, 1.2$, 1 H, HC(11)), 6.91 (dt, $J = 15.0, 7.3$, 1 H, HC(3)), 6.54 (s, 1 H, HC(7)), 6.32 (dt, $J = 15.1, 1.3$, 1 H, HC(2)), 4.34 (t, $J = 6.6$, 1 H, HC(5)), 3.66-3.61 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.59-2.55 (m, 2 H, $\text{H}_2\text{C}(4)$), 2.01 (br s, 1 H, OH), 1.90 (d, $J = 1.2$, 3 H, $\text{H}_3\text{C}(14)$)

^{13}C NMR: (126 MHz, CDCl_3)

165.5 (C(1)), 142.8 (C(3)), 139.3 (C(6)), 137.2 (C(8)), 128.8 (C(9)), 128.0 (C(10)), 126.4 (C(11)), 125.7 (C(7)), 122.4 (C(2)), 76.1 (C(5)), 66.48 (C(13)), 66.54 (C(13)), 46.0 (C(12)), 45.1 (C(12)), 38.6 (C(4)), 13.5 (C(14))

IR: (neat)

3392 (m), 3055 (m), 3023 (w), 2966 (m), 2918 (m), 2858 (m), 2714 (w), 2361 (w), 2243 (w), 1957 (w), 1812 (w), 1659 (s), 1606 (s), 1491 (m), 1436 (s), 1362 (m), 1301 (m), 1267 (s), 1236 (s), 1190 (m), 1116 (s), 1069 (m), 1042 (s), 1019 (m), 977 (m), 920 (m), 855 (m), 810 (w), 733 (s), 701 (s), 646 (m), 619 (w)

MS: (EI, 70 eV)

301 (M^+ , 2), 155 (66), 147 (40), 140 (30), 129 (24), 115 (10), 91 (18), 87 (11), 69 (14), 62 (100), 61 (26)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +0.82$ ($c = 1.07$, EtOH)

TLC: R_f 0.14 (EtOAc) [UV(254 nm)]

SFC: (*R*)-**55**, t_R 8.67 min (75.5 %); (*S*)-**55**, t_R 10.02 min (24.5 %) (Chiralpak OB, 150 psi, 40 $^\circ\text{C}$, 5.0% MeOH in CO_2 , 3.5 mL/min, 220 nm)

Analysis: $\text{C}_{18}\text{H}_{23}\text{NO}_3$ (301.38)

Calcd:	C, 71.73;	H, 7.69;	N, 4.65%
Found:	C, 71.68;	H, 7.73;	N, 4.66%

Preparation of 4-[(2*E*)-1-Oxo-5-phenyl-5-hydroxy-2-pentenyl]morpholine (50**) (Scheme 6)**

Following Representative Procedure 8, 51 μL (0.5 mmol) of benzaldehyde was combined with 18 μL (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 63 μL (0.55 mmol, 1.1 equiv) of SiCl_4 and 162 mg (0.6 mmol, 1.2 equiv) of **45** to yield, after column chromatography (SiO_2 (12 g), 2 cm diam., EtOAc (150 mL) to EtOAc/MeOH, 19/1 (100 mL)) to yield 48 mg (37%) of α -**50** as a clear, colorless oil and 77 mg (59%) of γ -**50** as a white solid.

Data for α -**50**:

$^1\text{H NMR}$: (500 MHz, CDCl_3)
 7.36-7.23 (m, 5 H, HC(7,8,9)), 5.91-5.78 (m, 1 H, HC(3)), 5.22 (d, $J = 10.5$, 1 H, HC(4)), 5.04 (d, $J = 17.3$, 1.2, 1 H, HC(4)), 4.94-4.91 (m, 1 H, HC(5)) 3.72-3.25 (m, 9 H, HC(2), $\text{H}_2\text{C}(10,11)$)

MS: (CI , CH_4)
 262 ($\text{M}^+\text{+H}$, 28), 244 (30), 184 (12), 157 (11), 156 (100), 155 (29), 114 (96), 107 (90), 106 (11), 105 (12), 88 (29), 79 (25), 69 (13)

TLC: R_f 0.32 (EtOAc) [UV(254 nm)]

Data for γ -**50**:

$^1\text{H NMR}$: (500 MHz, CDCl_3)
 7.35-7.25 (m, 5 H, HC(7,8,9)), 6.84 (dt, $J = 15.0$, 6.9, 1 H, HC(3)), 6.22 (dt, $J = 15.0$, 1.4, 1 H, HC(2)), 4.83 (dd, $J = 7.4$, 5.6, 1 H, HC(5)), 3.62-3.43 (m, 8 H, $\text{H}_2\text{C}(10,11)$), 2.69-2.59 (m, 3 H, $\text{H}_2\text{C}(4)$, OH)

TLC: R_f 0.17 (EtOAc) [UV(254 nm)]

Preparation of 4-[(2*E*)-1-Oxo-7-phenyl-5-hydroxy-2,6-heptadienyl]morpholine (51)
(Scheme 6) [JRH-VIII-39]

Following Representative Procedure 8, 63 μL (0.5 mmol) of cinnamaldehyde was combined with 18 μL (0.1 mmol, 0.2 equiv) of diisopropylethylamine, 63 μL (0.55 mmol, 1.1 equiv) of SiCl_4 and 162 mg (0.6 mmol, 1.2 equiv) of **45** to yield, after column chromatography (SiO_2 (12 g), 2 cm diam., EtOAc (150 mL) to EtOAc/MeOH, 19/1 (100 mL)) to yield 4 mg (3%) of $\alpha\text{-51}$ as a clear, colorless oil and 106 mg (74%) of $\gamma\text{-51}$ as a white solid.

Data for $\alpha\text{-51}$:

$^1\text{H NMR}$: (500 MHz, CDCl_3)
 7.41 (d, $J = 8.0$, 2 H), 7.32 (t, $J = 7.5$, 2 H), 7.27 (t, $J = 7.3$, 1 H), 6.61 (d, $J = 15.8$, 1 H), 6.24 (dd, $J = 15.7$, 6.1, 1 H), 5.93-5.87 (m, 1 H), 5.31-5.19 (m, 2 H), 4.57 (t, $J = 6.7$, 1 H), 3.89-3.47 (m, 9 H), 3.78 (t, $J = 6.8$, 1 H)

MS: (CI, CH_4)
 288 ($\text{M}^+\text{+H}$, 12), 270 (17), 156 (68), 155 (12), 134 (10), 133 (100), 132 (10), 114 (53), 107 (18), 88 (32)

TLC: R_f 0.28 (EtOAc) [UV(254 nm)]

Data for $\gamma\text{-51}$:

$^1\text{H NMR}$: (500 MHz, CDCl_3)
 7.36 (d, $J = 8.0$, 2 H, HC(9)), 7.31 (t, $J = 7.6$, 2 H, HC(10)), 7.26 (t, $J = 7.5$, 1 H, HC(11)), 6.90 (dt, $J = 15.0$, 7.3, 1 H, HC(3)), 6.61 (d, $J = 15.9$, 1 H, HC(7)), 6.32

(dt, $J = 15.0, 1.5$, 1 H, HC(2)), 6.24 (dd, $J = 15.9, 6.3$, 1 H, HC(6)), 4.46 (q, $J = 5.9$, 1 H, HC(5)), 3.66-3.52 (m, 8 H, H₂C(12,13)), 2.55 (t, $J = 6.3$, 2 H, H₂C(4)), 2.23 (br s, 1 H, OH)

TLC: R_f 0.14 (EtOAc) [UV(254 nm)]

Representative Procedure 9. Addition of Conjugate *N,O*-Ketene Acetals to Aliphatic Aldehydes. Preparation of (–)-(2*E*,5*S*)- 5-Hydroxy-7-phenyl-2-heptenoic Acid Dimethylamide (56**) (Table 9, entry 1)**

Diisopropylethylamine (18 μ L, 0.1 mmol, 0.1 equiv) was added via syringe to a flame-dried, 20-mL, Schlenk flask under Ar containing a solution of 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3** and 20 mg (0.05 mmol, 0.05 equiv) of tetrabutylammonium triflate in CH₂Cl₂ (5 mL). To this solution was added 132 μ L (1.0 mmol, 1.0 equiv) of hydrocinnamaldehyde in one portion and the reaction mixture was cooled to -72 °C over 15 min. To the resulting solution was added 126 μ L (1.1 mmol, 1.1 equiv) of SiCl₄ in one portion. Then, a solution of 273 mg (1.2 mmol, 1.2 equiv) of **41** in 5 mL of CH₂Cl₂ was added dropwise over 5 min via syringe. The resulting mixture was stirred at -72 °C for 16 h whereupon 3.0 mL of chilled CH₂Cl₂ was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO₃/ sat. aq. KF (25 mL) at 0 °C. This biphasic mixture was stirred vigorously for 3 h after which the organic layer was removed and the aqueous layer was washed with CH₂Cl₂ (3 x 50 mL). The combined organic extracts were dried over Na₂SO₄ (5 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ/α -addition products was determined to be 92/8 by ¹H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (SiO₂ (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)) to yield 171 mg (69%) of (–)-**56** as a colorless oil.¹⁷ The ratio of γ/α -addition products was determined to be 92/8 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (-)-56:

<u>bp:</u>	140 °C (6.5 x 10 ⁻⁵ mmHg, ABT)
<u>¹H NMR:</u>	(500 MHz, CDCl ₃) 7.28 (dt, <i>J</i> = 7.6, 2.0, 2 H, HC(10)), 7.21-7.17 (m, 3 H, HC(9,11)), 6.88 (dt, <i>J</i> = 15.0, 7.8, 1 H, HC(3)), 6.34 (dt, <i>J</i> = 15.0, 1.3, 1 H, HC(2)), 3.81-3.76 (m, 1 H, HC(5)), 3.04 (br s, 6 H, H ₃ C(12)), 2.82 (dt, <i>J</i> = 13.9, 7.6, 1 H, HC(7)), 2.69 (dt, <i>J</i> = 13.8, 8.1, 1 H, HC(7)), 2.47-2.33 (m, 2 H, H ₂ C(4)), 2.00 (br s, 1 H, OH), 1.84-1.79 (m, 2 H, H ₂ C(6))
<u>¹³C NMR:</u>	(100 MHz, CDCl ₃) 166.6 (C(1)), 142.4 (C(3)), 142.0 (C(8)), 128.3 (C(9)), 128.2 (C(10)), 125.6 (C(11)), 122.6 (C(12)), 69.5 (C(2)), 40.7 (C(4)), 38.6 (C(6)), 37.2 (C(12)), 35.6 (C(12)), 31.9 (C(7))
<u>IR:</u>	(neat) 3391 (m), 3085 (w), 3061 (w), 3026 (m), 2931 (m), 2863 (m), 2361 (w), 1951 (w), 1875 (w), 1810 (w), 1660 (s), 1605 (s), 1495 (s), 1455 (m), 1398 (s), 1261 (m), 1225 (w), 1152 (m), 1086 (m), 1053 (m), 1032 (m), 978 (m), 929 (w), 876 (w), 824 (w), 750 (m), 701 (s), 639 (m)
<u>MS:</u>	(CI, CH ₄) 249 (16), 248 (M ⁺ +H, 100), 230 (44), 113 (22), 98 (12), 91 (20), 72 (13), 59 (11)
<u>Opt. Rot.:</u>	[α] _D ²⁴ -6.48 (c = 1.02, EtOH)
<u>TLC:</u>	<i>R</i> _f 0.11 (EtOAc) [UV (254 nm)]
<u>SFC:</u>	(<i>S</i>)- 56 , <i>t</i> _R 5.89 min (90.9%); (<i>R</i>)- 56 , <i>t</i> _R 6.37 min (9.1%) (Chiralpak AD, 125 psi, 40 °C, 10.0% MeOH in CO ₂ , 2.5 mL/min, 220 nm)
<u>HRMS:</u>	Calcd for C ₁₅ H ₂₂ NO ₂ : 248.1651, found: 248.1649

Preparation of (–)-(2*E*,5*S*)-5-Hydroxy-7-phenyl-2-heptenoic Acid Diethylamide (57) (Table 9, entry 2)

Following Representative Procedure 9, 132 μL (1.0 mmol) of hydrocinnamaldehyde, was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 20 mg (0.05 mmol, 0.05 equiv) of tetrabutylammonium triflate, 18 μL (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μL (1.1 mmol, 1.1 equiv) of SiCl_4 and 307 mg (1.2 mmol, 1.2 equiv) of **42** to yield after column chromatography (30 g SiO_2 , 3 cm diam., EtOAc), 215 mg (78%) of (–)-**57** as a colorless oil.¹⁷ The ratio of γ/α -addition products was determined to be 95/5 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-**57**:

bp: 150 $^\circ\text{C}$ (6.5×10^{-5} mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

7.28 (dt, $J = 7.5, 1.8$, 2 H, HC(10)), 7.21–7.17 (m, 3 H, HC(9,11)), 6.93 (dt, $J = 15.1, 7.1$, 1 H, HC(3)), 6.28 (dt, $J = 15.1, 1.2$, 1 H, HC(2)), 3.79 (dp, $J = 5.9, 1.0$, 1 H, HC(5)), 3.43–3.38 (m, 4 H, $\text{H}_2\text{C}(12)$), 2.83 (dt, $J = 13.7, 7.7$, 1 H, HC(7)), 2.69 (dt, $J = 13.8, 8.2$, 1 H, HC(7)), 2.47–2.33 (m, 3 H, $\text{H}_2\text{C}(4)$, OH), 1.84–1.80 (m, 2 H, $\text{H}_2\text{C}(6)$), 1.25–1.18 (m, 6 H, $\text{H}_3\text{C}(13)$)

^{13}C NMR: (126 MHz, CDCl_3)

165.7 (C(1)), 142.3 (C(3)), 142.0 (C(8)), 128.4 (C(9)), 128.2 (C(10)), 125.6 (C(11)), 123.0 (C(12)), 69.6 (C(2)), 42.0 (C(12)), 40.72 (C(4)), 40.65 (C(12)), 38.6 (C(6)), 31.9 (C(7)), 14.7 (C(13)), 13.0 (C(13))

IR: (neat)

3391 (m), 3085 (w), 3061 (w), 3026 (w), 2976 (m), 2933 (m), 1951 (w), 1875 (w), 1810 (w), 1659 (m), 1602 (m), 1484 (m), 1454 (m), 1434 (m), 1380 (m), 1362 (m), 1326 (w), 1271 (m), 1219 (w), 1144 (m), 1081 (m), 1052 (w), 1032

(w), 976 (w), 934 (w), 842 (w), 814 (w), 777 (w), 748 (w), 701 (m), 622 (w)

MS: (CI, CH₄)

277 (20), 276 (M⁺+H, 100), 258 (26), 141 (13), 126 (14), 91 (18), 59 (11)

Opt. Rot.: [α]_D²⁴ -8.36 (c = 0.94, EtOH)

TLC: *R_f* 0.28 (EtOAc) [UV (254 nm)]

SFC: (*S*)-**57**, *t_R* 10.18 min (84.5%); (*R*)-**57**, *t_R* 11.10 min (15.2%) (Chiralpak AD, 150 psi, 40 °C, 3.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₇H₂₆NO₂: 276.1964, found: 276.1972

Preparation of (-)-1-[(5*S*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2-heptenyl]piperidine (59**) (Table 9, entry 4)**

Following Representative Procedure 9, 132 μ L (1.0 mmol) of hydrocinnamaldehyde, was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 20 mg (0.05 mmol, 0.05 equiv) of tetrabutylammonium triflate, 18 μ L (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μ L (1.1 mmol, 1.1 equiv) of SiCl₄ and 321 mg (1.2 mmol, 1.2 equiv) of **44** to yield after silica gel column chromatography (SiO₂ (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1(150 mL)), 201 mg (70%) of (-)-**59** as a colorless oil.¹⁷ The ratio of γ/α -addition products was determined to be 93/7 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (-)-**59**:

bp: 170 °C (4.5 x 10⁻⁵ mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.28 (dt, *J* = 7.4, 1.8, 2 H, HC(10)), 7.20-7.17 (m, 3 H, HC(9,11)), 6.82 (dt, *J* = 15.0, 7.5, 1 H, HC(3)), 6.34 (dt, *J* = 14.9, 1.2, 1 H, HC(2)), 3.80-3.75 (m, 1 H, HC(5)), 3.59-2.88 (m, 4 H, H₂C(12)), 2.82 (dt, *J* = 13.9, 7.8, 1 H, HC(7)), 2.68

(m, $J = 13.9, 8.2$, 1 H, HC(7)), 2.45-2.32 (m, 2 H, H₂C(4)), 2.02 (br s, 1 H, OH), 1.83-1.77 (m, 2 H, H₂C(6)), 1.68-1.63 (m, 2 H, H₂C(14)), 1.58-1.55 (m, 4 H, H₂C(13))

¹³C NMR: (126 MHz, CDCl₃)

165.3 (C(1)), 142.1 (C(8)), 141.9 (C(3)), 128.4 (C(9)), 128.2 (C(10)), 125.6 (C(11)), 123.0 (C(12)), 69.5 (C(2)), 46.8 (C(12)), 43.0 (C(12)), 40.8 (C(4)), 38.6 (C(6)), 31.9 (C(7)), 26.4 (C(13)), 25.4 (C(13)), 24.4 (C(14))

IR: (neat)

3391 (s), 3084 (m), 3061 (m), 3025 (m), 3003 (m), 2935 (s), 2856 (s), 2668 (w), 2362 (w), 2341 (w), 1947 (w), 1871 (w), 1808 (w), 1652 (s), 1600 (s), 1495 (s), 1454 (s), 1367 (m), 1352 (s), 1253 (s), 1224 (s), 1162 (m), 1140 (s), 1125 (m), 1085 (s), 1052 (s), 1017 (s), 975 (s), 954 (m), 928 (m), 853 (m), 829 (m), 807 (m), 749 (s), 701 (s), 668 (m), 634 (m)

MS: (CI, CH₄)

289 (17), 288 (M⁺+H, 100), 276 (10), 270 (24), 153 (13), 138 (15), 91 (17), 63 (11)

Opt. Rot.: $[\alpha]_D^{24} -10.49$ (c = 1.18, EtOH)

TLC: R_f 0.21 (EtOAc) [UV (254 nm)]

SFC: (*S*)-**59**, t_R 5.11 min (96.0%); (*R*)-**59**, t_R 5.67 min (4.0%) (Chiralpak AD, 125 psi, 40 °C, 12.5% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₈H₂₆NO₂: 288.1964, found: 288.1966

Preparation of (–)-4-[(5*S*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2-heptenyl]morpholine (60**)**
(Table 9, entry 5 and Table 10, entry 1)

Following Representative Procedure 9, 132 μ L (1.0 mmol) of hydrocinnamaldehyde, was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 20 mg (0.05 mmol,

0.05 equiv) of tetrabutylammonium triflate, 18 μL (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μL (1.1 mmol, 1.1 equiv) of SiCl_4 and 324 mg (1.2 mmol, 1.2 equiv) of **45** to yield after column chromatography (SiO_2 (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)), 230 mg (80%) of (–)-**60** as a colorless oil.¹⁷ The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-**60**:

bp: 170 $^\circ\text{C}$ (6.5×10^{-5} mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

7.27 (t, $J = 7.4$, 2 H, HC(10)), 7.21-7.18 (m, 3 H, HC(9,11)), 6.90 (dt, $J = 15.0$, 7.8, 1 H, HC(3)), 6.29 (dt, $J = 15.0$, 1.3, 1 H, HC(2)), 3.81-3.77 (m, 1 H, HC(5)), 3.68-3.64 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.82 (dt, $J = 13.9$, 7.4, 1 H, HC(7)), 2.69 (dt, $J = 13.9$, 8.1, 1 H, HC(7)), 2.47-2.33 (m, 2 H, $\text{H}_2\text{C}(4)$), 2.19 (br s, 1 H, OH), 1.84-1.79 (m, 2 H, $\text{H}_2\text{C}(6)$)

^{13}C NMR: (126 MHz, CDCl_3)

165.5 (C(1)), 143.3 (C(3)), 141.9 (C(8)), 128.3 (C(9)), 128.3 (C(10)), 125.7 (C(11)), 121.9 (C(2)), 69.5 (C(5)), 66.6 (C(13)), 66.5 (C(13)), 45.9 (C(12)), 42.1 (C(12)), 40.7 (C(4)), 38.6 (C(6)), 31.8 (C(7))

IR: (neat)

3401 (s), 3084 (m), 3060 (m), 3026 (m), 3001 (m), 2921 (s), 2857 (s), 2761 (w), 2714 (w), 1958 (w), 1878 (w), 1813 (w), 1660 (s), 1652 (s), 1663 (s), 1614 (s), 1495 (s), 1463 (s), 1455 (s), 1434 (s), 1362 (s), 1301 (s), 1267 (s), 1192 (s), 1117 (s), 1069 (s), 1043 (s), 977 (s), 930 (m), 854 (s), 810 (m), 750 (s), 701 (s)

MS: (CI, CH_4)

291 (20), 290 ($\text{M}^+ + \text{H}$, 100), 289 (10), 272 (32), 155 (21), 91 (21), 63 (11)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} -9.86$ ($c = 1.10$, EtOH)

TLC: R_f 0.11 (EtOAc) [UV (254 nm)]

SFC: (S)-**60**, t_R 4.31 min (99.0%); (R)-**60**, t_R 5.08 min (1.0%) (Chiralpak OB, 125 psi, 40 $^\circ\text{C}$, 8.0% MeOH in CO_2 , 3.0 mL/min, 220 nm)

HRMS: Calcd for $\text{C}_{17}\text{H}_{24}\text{NO}_3$: 290.1756, found: 290.1750

Preparation of (–)-4-[(5*S*,2*E*)-1-Oxo-7-methyl-5-hydroxy-2-octenyl]morpholine (61**) (Table 10, entry 2)**

Following Representative Procedure 9, 107 μL (1.0 mmol) of isovaleraldehyde, was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 20 mg (0.05 mmol, 0.05 equiv) of tetrabutylammonium triflate, 18 μL (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μL (1.1 mmol, 1.1 equiv) of SiCl_4 and 324 mg (1.2 mmol, 1.2 equiv) of **45** to yield after column chromatography (SiO_2 (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)), 203 mg (84%) of (–)-**61** as a colorless oil.¹⁷ The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-**61**:

bp: 140 $^\circ\text{C}$ (6.5×10^{-5} mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

6.94 (dt, $J = 15.0, 7.4$, 1 H, HC(3)), 6.30 (dt, $J = 15.1, 1.3$, 1 H, HC(2)), 3.88–3.83 (m, 1 H, HC(5)), 3.71–3.63 (m, 8 H, $\text{H}_2\text{C}(9,10)$), 2.44–2.29 (m, 2 H, $\text{H}_2\text{C}(4)$), 2.04 (br s, 1 H, OH), 1.79 (d, hept., $J = 6.6, 2.2$, 1 H, HC(7)), 1.48–1.43 (m, 1 H, HC(6)), 1.42–1.24 (m, 1 H, HC(6)), 0.93 (d, $J = 6.8$, 3 H, $\text{H}_3\text{C}(8)$), 0.91 (d, $J = 6.8$, 3 H, $\text{H}_3\text{C}(8)$)

^{13}C NMR: (126 MHz, CDCl_3)

165.5 (C(1)), 143.4 (C(3)), 121.8 (C(2)), 68.2 (C(5)), 66.7 (C(10)), 66.6 (C(10)), 46.1 (C(6)), 46.0 (C(9)), 42.1 (C(9)), 41.1 (C(4)), 24.4 (C(7)), 23.3 (C(8)), 21.8 (C(8))

IR: (neat)

3402 (s), 3059 (m), 2955 (s), 2922 (s), 2867 (s), 2761 (w), 2718 (w), 2349 (w), 2229 (w), 2107 (w), 1962 (w), 1660 (s), 1614 (s), 1434 (s), 1385 (s), 1366 (s),

1301 (s), 1267 (s), 1237 (s), 1189 (s), 1139 (s), 1116 (s), 1069 (s), 1037 (s), 979 (s), 920 (m), 855 (s), 814 (m), 702 (m)

MS: (CI, CH₄)

243 (15), 242 (M⁺+H, 100), 244 (38), 155 (42), 140 (11), 69 (19),

Opt. Rot.: $[\alpha]_D^{24}$ -4.80 (c = 1.21, EtOH)

TLC: *R_f* 0.12 (EtOAc) [UV(254 nm)]

SFC: (*S*)-**61**, *t_R* 2.23 min (99.8 %); (*R*)-**61**, *t_R* 2.54 min (0.2 %) (Chiralpak AD, 125 psi, 40 °C, 12.5 % MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₃H₂₄NO₃: 242.1756, found: 242.1753

Preparation of (+)-4-[(5*R*,2*E*)-1-Oxo-5-cyclohexyl-5-hydroxy-2-pentenyl]morpholine (62**) (Table 10, entry 3)**

Following Representative Procedure 9, 121 μL (1.0 mmol) of cyclohexanecarboxaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 20 mg (0.05 mmol, 0.05 equiv) of tetrabutylammonium triflate, 18 μL (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μL (1.1 mmol, 1.1 equiv) of SiCl₄ and 324 mg (1.2 mmol, 1.2 equiv) of **45** to yield after column chromatography (SiO₂ (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL), a solid which was recrystallized by precipitation from hot EtOAc (4 mL) with minimal amounts of hexanes to yield 168 mg (63%) of (+)-**62** as white crystals. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-62**:**

mp: 85-86 °C (EtOAc/hexanes)

¹H NMR: (500 MHz, CDCl₃)

6.91 (dt, *J* = 15.0, 7.4, 1 H, HC(3)), 6.30 (dt, *J* = 15.1, 1.2, 1 H, HC(2)), 3.68-3.49 (m, 9 H, HC(5), H₂C(12,13)), 2.46-2.28 (m, 2 H, H₂C(4)), 1.90 (br s, 1 H,

OH), 1.85-1.82 (m, 1 H), 1.78-1.73 (m, 2 H), 1.68-1.65 (m, 2 H), 1.41-1.33 (m, 1 H, HC(6)), 1.28-0.97 (m, 5 H)

¹³C NMR: (126 MHz, CDCl₃)
165.7 (C(1)), 144.4 (C(3)), 121.9 (C(2)), 74.7 (C(5)), 66.93 (C(12)), 66.85 (C(12)), 46.2 (C(13)), 43.4 (C(6)), 42.3 (C(13)), 37.6 (C(4)), 29.3, 28.1, 26.6, 26.3, 26.2

IR: (CHCl₃)
3431 (w), 3017 (m), 2971 (w), 2928 (m), 2856 (m), 2672 (w), 2438 (w), 2400 (w), 2349 (w), 2233 (w), 1962 (w), 1657 (m), 1608 (m), 1461 (m), 1438 (m), 1362 (w), 1300 (m), 1259 (m), 1236 (m), 1216 (s), 1173 (m), 1115 (m), 1087 (w), 1069 (w), 1036 (m), 976 (m), 950 (w), 926 (w), 893 (w), 854 (w), 758 (s), 668 (m), 640 (w)

MS: (CI, CH₄)
269 (18), 268 (M⁺+H, 100), 266 (25), 251 (14), 250 (75), 234 (10), 156 (29), 155 (52), 140 (13), 114 (10), 95 (30), 88 (21), 86 (10), 69 (20), 63 (28), 57 (16), 55 (18)

Opt. Rot.: [α]_D²⁴ +10.84 (c = 0.90, EtOH)

TLC: *R_f* 0.11 (EtOAc) [UV(254 nm)]

SFC: (*R*)-**62**, *t_R* 1.88 min (99.4 %); (*S*)-**62**, *t_R* 2.15 min (0.6 %) (Chiralpak OJ, 125 psi, 40 °C, 9.0 % MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₅H₂₅NO₃ (267.36)

Calcd: C, 67.38; H, 9.42; N, 5.24%

Found: C, 67.25; H, 9.63; N, 5.40%

Preparation of (+)-4-[(5*S*,2*E*)-1-Oxo-5-hydroxy-2-decenyl]morpholine (63**) (Table 10, entry 4)**

Following Representative Procedure 9, 120 μL (1.0 mmol) of hexanal, was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 20 mg (0.05 mmol, 0.05 equiv) of tetrabutylammonium triflate, 18 μL (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μL (1.1 mmol, 1.1 equiv) of SiCl_4 (1.2 mmol, 1.2 equiv) and 324 mg of **45** to yield after column chromatography (SiO_2 (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)), 201 mg (79%) of (+)-**63** as a colorless oil.¹⁷ The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-**63**:

bp: 125 $^\circ\text{C}$ (5.0×10^{-5} mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

6.92 (dt, $J = 15.1, 7.4$, 1 H, HC(3)), 6.30 (dt, $J = 15.1, 1.3$, 1 H, HC(2)), 3.78-3.74 (m, 1 H, HC(5)), 3.70-3.62 (m, 8 H, $\text{H}_2\text{C}(11,12)$), 2.45-2.29 (m, 2 H, $\text{H}_2\text{C}(4)$), 1.93-1.85 (m, 1 H, OH), 1.51-1.42 (m, 4 H, $\text{H}_2\text{C}(6,7)$), 1.36-1.25 (m, 4 H, $\text{H}_2\text{C}(8,9)$), 0.89 (t, $J = 7.0$, 3 H, $\text{H}_3\text{C}(10)$)

^{13}C NMR: (126 MHz, CDCl_3)

165.5 (C(1)), 143.5 (C(3)), 121.7 (C(2)), 70.2 (C(5)), 66.6 (C(11)), 45.9 (C(12)), 42.1 (C(12)), 40.5 (C(4)), 36.9 (C(6)), 31.6 (C(8)), 25.1 (C(7)), 22.4 (C(9)), 13.9 (C(10))

IR: (neat)

3412 (s), 2956 (s), 2929 (s), 2857 (s), 2760 (w), 2718 (w), 2360 (w), 1658 (s), 1607 (s), 1435 (s), 1378 (m), 1361 (m), 1301 (s), 1267 (s), 1236 (s), 1194 (m), 1116 (s), 1070 (s), 1035 (s), 977 (s), 929 (w), 854 (m), 812 (w), 762 (w), 699 (w), 668 (w)

MS: (CI, CH_4)

257 (16), 256 ($\text{M}^+\text{+H}$, 100), 254 (15), 238 (41), 156 (21), 155 (42), 140 (13), 88,

(11), 83 (10), 69 (21)

Opt. Rot.: $[\alpha]_D^{24} +2.26$ ($c = 1.20$, EtOH)TLC: R_f 0.13 (EtOAc) [UV(254 nm)]SFC: (*S*)-**63**, t_R 2.92 min (94.3%); (*R*)-**63**, t_R 3.33 min (5.7%) (Chiralpak OB, 125 psi, 40 °C, 3.5 % MeOH in CO₂, 3.0 mL/min, 220 nm)HRMS: Calcd for C₁₄H₂₆NO₃: 256.1913, found: 256.1905**Preparation of (–)-4-[(5*S*,2*E*)-1-Oxo-7-benzyloxy-5-hydroxy-2-heptenyl]morpholine (**67**) (Table 11, entry 4)**

Following Representative Procedure 9, 164 mg (1.0 mmol) of 3-benzyloxypropanal, was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 20 mg (0.05 mmol, 0.05 equiv) of tetrabutylammonium triflate, 18 μ L (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μ L (1.1 mmol, 1.1 equiv) of SiCl₄ and 324 mg (1.2 mmol, 1.2 equiv) of **45** to yield after column chromatography (SiO₂ (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)), 155 mg (49%) of (–)-**67** as a colorless oil.¹⁷ The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-**67**:¹H NMR: (500 MHz, CDCl₃)

7.37–7.26 (m, 5 H, HC(10,11,12)), 6.89 (dt, $J = 14.9$, 7.3, 1 H, HC(3)), 6.29 (dd, $J = 15.1$, 1.2, 1 H, HC(2)), 4.52 (s, 2 H, H₂C(8)), 4.01–3.96 (m, 1 H, HC(5)), 3.75–3.55 (m, 10 H, H₂C(7,12,13)), 3.03 (br s, 1 H, OH), 2.45–2.35 (m, 2 H, H₂C(4)), 1.81–1.76 (m, 2 H, H₂C(6))

¹³C NMR: (126 MHz, CDCl₃)

165.3 (C(1)), 142.9 (C(3)), 137.8 (C(9)), 128.3 (C(11)), 127.6 (C(12)), 127.5 (C(10)), 121.7 (C(2)), 73.1 (C(8)), 69.5 (C(5)), 68.4 (C(14)), 66.6 (C(7)), 45.9 (C(13)), 42.1 (C(13)), 40.4 (C(4)), 36.0 (C(6))

IR: (neat)

3413 (s), 3087 (w), 3062 (w), 3030 (m), 2919 (s), 2858 (s), 2715 (w), 2239 (w), 1960 (w), 1878 (w), 1815 (w), 1659 (s), 1614 (s), 1496 (m), 1434 (s), 1363 (s), 1301 (s), 1267 (s), 1238 (s), 1115 (s), 1029 (s), 978 (s), 918 (m), 853 (m), 809 (m), 739 (s), 700 (s), 639 (m)

MS: (CI, CH₄)

321 (21) 320 (M⁺+H, 100), 213 (10), 91 (26), 86 (43), 85 (19), 84 (69), 83 (28)

Opt. Rot.: [α]_D²⁴ -2.15 (c = 1.01, EtOH)

TLC: *R_f* 0.11 (EtOAc) [UV (254 nm)]

SFC: (*S*)-**67**, *t_R* 3.29 min (83.7%); (*R*)-**67** *t_R* 3.73 min (16.3%) (Chiralpak OB, 125 psi, 40 °C, 10.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₈H₂₆NO₄: 320.1862, found: 320.1856

Preparation of (–)-4-[(5*S*,2*E*)-1-Oxo-7-(2-propenyl)-5-hydroxy-2-heptenyl]morpholine (68**) (Table 11, entry 5)**

Following Representative Procedure 9, 31 μ L (0.25 mmol) of 3-allyloxypropanal, was combined with 11 mg (0.0125 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 5 mg (0.0125 mmol, 0.05 equiv) of tetrabutylammonium triflate, 32 μ L (0.275 mmol, 1.1 equiv) of SiCl₄ and 81 mg (0.3 mmol, 1.2 equiv) of **45** to yield after column chromatography (SiO₂ (14 g), 2 cm diam., EtOAc (150 mL) to EtOAc/MeOH, 19/1 (100 mL)), 20 mg (30%) of (–)-**68** as a colorless oil. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-68****

¹H NMR: (500 MHz, CDCl₃)

6.92 (dt, *J* = 15.1, 7.2, 1 H, HC(3)), 6.31 (dt, *J* = 15.0, 1.4, 1 H, HC(2)), 5.93-5.85

(m, 1 H, HC(9)), 5.27 (dq, $J = 17.2, 1.6$, 1 H, HC(10)), 5.19 (dq, $J = 10.3, 1.5$, 1 H, HC(10)), 4.01-3.96 (m, 3 H, HC(5), H₂C(8)), 3.71-3.60 (m, 10 H, H₂C(7,11,12)), 2.52-2.38 (m, 3 H, OH, H₂C(4)), 1.79-1.75 (m, 2 H, H₂C(6))

¹³C NMR: (126 MHz, CDCl₃)
165.4 (C(1)), 142.9 (C(3)), 134.2 (C(9)), 122.0 (C(2)), 117.2 (C(10)), 72.1 (C(8)), 70.3 (C(5)), 68.9 (C(7)), 66.8 (C(12)), 46.1 (C(11)), 42.2 (C(11)), 40.5 (C(4)), 36.0 (C(6))

MS: (CI, CH₄)
298 (16), 271 (17), 270 (M⁺+H, 100), 252 (11), 155 (10)

Opt. Rot.: $[\alpha]_D^{24} -0.76$ ($c = 0.66$, EtOH)

TLC: R_f 0.07 (EtOAc) [UV (254 nm)]

SFC: (*S*)-**68**, t_R 6.51 min (83.5%); (*R*)-**68**, t_R 6.87 min (16.5%) (Chiralpak AD, 175 psi, 40 °C, 8.0% MeOH in CO₂, 2.0 mL/min, 220 nm)

HRMS: Calcd for C₁₄H₂₄NO₄: 270.1705, found: 270.1703

Preparation of (–)-4-[(5*S*,2*E*)-1-Oxo-7-benzoate-5-hydroxy-2-heptenyl]morpholine (69**)**
(Table 11, entry 6)

Following Representative Procedure 9, 45 mg (0.25 mmol) of 3-benzoyloxypropanal, was combined with 11 mg (0.0125 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 5 mg (0.0125 mmol, 0.05 equiv) of tetrabutylammonium triflate, 32 μ L (0.275 mmol, 1.1 equiv) of SiCl₄ and 81 mg (0.3 mmol, 1.2 equiv) of **45** to yield after column chromatography (SiO₂ (14 g), 2 cm diam., EtOAc (150 mL) to EtOAc/MeOH, 19/1 (100 mL)), 34 mg (41%) of (–)-**69** as a colorless oil. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (-)-69:¹H NMR: (500 MHz, CDCl₃)

8.04 (dt, $J = 8.3, 1.6$, 2 H, HC(10)), 7.57 (tt, $J = 7.4, 1.4$, 1 H, HC(12)), 7.45 (dt, $J = 8.1, 1.6$, 2 H, HC(11)), 6.91 (dt, $J = 15.1, 7.6$, 1 H, HC(3)), 6.29 (dt, $J = 15.0, 1.4$, 1 H, HC(2)), 4.65-4.60 (m, 1 H, HC(7)), 4.43-4.39 (m, 1 H, HC(7)), 3.95-3.90 (m, 1 H, HC(5)), 3.67-3.54 (m, 8 H, H₂C(12,13)), 2.49 (m, 3 H, OH, H₂C(4)), 2.03-2.00 (m, 1 H, HC(6)), 1.86-1.82 (m, 1 H, HC(6))

¹³C NMR: (126 MHz, CDCl₃)

166.9 (C(8)), 165.4 (C(1)), 142.7 (C(3)), 133.1 (C(12)), 130.0 (C(9)), 129.6 (C(10)), 128.4 (C(11)), 122.3 (C(2)), 67.2 (C(5)), 66.7 (C(14)), 61.8 (C(7)), 46.1 (C(13)), 42.3 (C(13)), 40.5 (C(4)), 36.2 (C(6))

MS: (CI, CH₄)

334 (M⁺+H, 50), 123 (100), 122 (10), 105 (29), 79 (16)

Opt. Rot.: [α]_D²⁴ -3.81 ($c = 0.75$, EtOH)TLC: R_f 0.11 (EtOAc) [UV (254 nm)]

SFC: (*S*)-**69**, t_R 3.53 min (70.0%); (*R*)-**69**, t_R 4.00 min (30.0%) (Chiralpak OB, 125 psi, 40 °C, 9.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₈H₂₄NO₅: 334.1654, found: 334.1656

Preparation of (+)-4-[(5*S*,2*E*)-1-Oxo-10-benzyloxy-5-hydroxy-2-decenyl]morpholine (71**)**
(Table 11, entry 8)

Following Representative Procedure 9, 206 mg (1.0 mmol) of 6-benzyloxypropanal, was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 20 mg (0.05 mmol, 0.05 equiv) of tetrabutylammonium triflate, 18 μ L (0.1 mmol, 0.1 equiv) of

diisopropylethylamine, 126 μ L (1.1 mmol, 1.1 equiv) of SiCl_4 and 324 mg (1.2 mmol, 1.2 equiv) of **45** to yield after column chromatography (SiO_2 (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (200 mL)), 308 mg (85%) of (+)-**71** as a colorless oil.¹⁷ The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-**71**:

^1H NMR: (500 MHz, CDCl_3)

7.36-7.32 (m, 4 H, HC(13,14)), 7.29-7.26 (m, 1 H, HC(15)), 6.93 (dt, $J = 15.1$, 7.1, 1 H, HC(3)), 6.31 (d, $J = 15.1$, 1 H, HC(2)), 4.50 (s, 2 H, $\text{H}_2\text{C}(11)$), 3.78-3.64 (m, 9 H, HC(5), $\text{H}_2\text{C}(16,17)$), 3.47 (t, $J = 6.5$, 2 H, $\text{H}_2\text{C}(10)$), 2.45-2.30 (m, 2 H, $\text{H}_2\text{C}(4)$), 2.17 (br s, 1 H, OH), 1.63 (p, $J = 6.8$, 2 H, $\text{H}_2\text{C}(9)$), 1.52-1.35 (m, 6 H, $\text{H}_2\text{C}(6,7,8)$)

^{13}C NMR: (126 MHz, CDCl_3)

165.4 (C(1)), 143.4 (C(3)), 138.4 (C(12)), 128.1 (C(14)), 127.4 (C(13)), 127.2 (C(15)), 121.6 (C(2)), 72.6 (C(11)), 70.1 (C(10)), 70.0 (C(5)), 66.5 (C(17)), 45.9 (C(16)), 42.0 (C(16)), 40.4 (C(4)), 36.8 (C(6)), 29.5 (C(9)), 26.0 (C(8)), 25.3 (C(7))

IR: (neat)

3415 (m), 3087 (w), 3062 (w), 3030 (w), 2932 (s), 2857 (s), 2361 (w), 2341 (w), 1959 (w), 1812 (w), 1657 (s), 1606 (s), 1496 (m), 1454 (s), 1435 (s), 1362 (m), 1267 (s), 1237 (s), 1163 (m), 1116 (s), 1070 (s), 1031 (s), 978 (s), 917 (w), 854 (m), 817 (w), 739 (s), 699 (s), 640 (m)

MS: (CI, CH_4)

362 ($\text{M}^+\text{+H}$, 40), 156 (14), 107 (12), 91 (19), 63 (100), 62 (24)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +0.35$ ($c = 1.15$, EtOH)

TLC: R_f 0.12 (EtOAc) [UV (254 nm)]

SFC: (*S*)-**71**, t_R 2.36 min (92.5%); (*R*)-**71**, t_R 3.41 min (7.5%) (Chiralpak OB, 150 psi, 40 $^\circ\text{C}$, 20.0% MeOH in CO_2 , 3.0 mL/min, 220 nm)

HRMS: Calcd for $\text{C}_{21}\text{H}_{32}\text{NO}_4$: 362.2331, found: 362.2326

Preparation of 4-[(5*S*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2-methyl-2-heptenyl]morpholine (75**)**
(Table 12, entry 1)

Following Representative Procedure 9, 33 μL (0.25 mmol) of hydrocinnamaldehyde, was combined with 11 mg (0.0125 mmol, 0.05 equiv) of bisphosphoramidate (R,R) -**3**, 5 mg (0.0125 mmol, 0.05 equiv) of tetrabutylammonium triflate, 4 μL (0.025 mmol, 0.1 equiv) of diisopropylethylamine, 32 μL (0.275 mmol, 1.1 equiv) of SiCl_4 and 85 mg (0.3 mmol, 1.2 equiv) of **72** to yield after column chromatography (SiO_2 (10 g), 2 cm diam., EtOAc (100 mL) to EtOAc/MeOH, 19/1 (100 mL)), 24 mg (32%) of **75** as a colorless oil. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for **75:**

^1H NMR: (500 MHz, CDCl_3)

7.29 (t, $J = 7.5$, 2 H, HC(10)), 7.23–7.19 (m, 3 H, HC(9,11)), 5.61 (dt, $J = 7.3$, 1.5, 1 H, HC(3)), 3.76–3.56 (m, 9 H, HC(5), $\text{H}_2\text{C}(12,13)$), 2.81 (dt, $J = 13.9$, 7.6, 1 H, HC(7)), 2.68 (dt, $J = 13.9$, 8.1, 1 H, HC(7)), 2.31 (t, $J = 6.6$, 2 H, $\text{H}_2\text{C}(4)$), 1.85 (s, 3 H, $\text{H}_3\text{C}(14)$), 1.82–1.78 (m, 2 H, $\text{H}_2\text{C}(6)$)

TLC: R_f 0.10 (EtOAc) [UV (254 nm)]

SFC: (R) -**75**, t_R 9.27 min (1.0%); (S) -**75**, t_R 9.97 min (99.0%) (Chiralpak OJ, 200 psi, 40 $^\circ\text{C}$, 4.0% MeOH in CO_2 , 2.25 mL/min, 220 nm)

Preparation of (–)-4-[(5*S*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2-methyl-2-heptenyl]morpholine (75) (Table 12, entry 2)

Diisopropylethylamine (18 μL , 0.1 mmol, 0.1 equiv) was added via syringe to a flame-dried, 20-mL, Schlenk flask under Ar containing a solution of 84 mg (0.1 mmol, 0.1 equiv) of bisphosphoramidate (R,R) -**3** and 20 mg (0.05 mmol, 0.05 equiv) of tetrabutylammonium triflate in CH_2Cl_2 (1.25 mL). To this solution was added 132 μL (1.0 mmol, 1.0 equiv) of hydrocinnamaldehyde in one portion and the reaction mixture was cooled to $-50\text{ }^\circ\text{C}$ over 15 min. To the resulting solution was added 126 μL (1.1 mmol, 1.1 equiv) of SiCl_4 in one portion. Then, a solution of 340 mg (1.2 mmol, 1.2 equiv) of **72** in 1.25 mL of CH_2Cl_2 was added dropwise over 5 min via syringe. The resulting mixture was stirred at $-50\text{ }^\circ\text{C}$ for 16 h whereupon 3.0 mL of chilled CH_2Cl_2 was added before the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. NaHCO_3 / sat. aq. KF (25 mL) at $0\text{ }^\circ\text{C}$. This biphasic mixture was stirred vigorously for 3 h after which the organic layer was removed and the aqueous layer was washed with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4 (5 g), filtered and the filtrate was concentrated *in vacuo*. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The residue was purified by column chromatography (SiO_2 (25 g), 3 cm diam., EtOAc (150 mL) to EtOAc/MeOH, 19/1 (200 mL)) to yield 199 mg (66%) of (–)-**75** as a colorless oil.¹⁷

Data for (–)-**75**:

bp: $160\text{ }^\circ\text{C}$ (5.0×10^{-5} mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

7.29 (t, $J = 7.6$, 2 H, HC(10)), 7.21–7.18 (m, 3 H, HC(9,11)), 5.60 (dt, $J = 7.3$, 1.5, 1 H, HC(3)), 3.74–3.56 (m, 9 H, HC(5), $\text{H}_2\text{C}(12,13)$), 2.81 (dt, $J = 13.9$, 7.6, 1 H, HC(7)), 2.69 (dt, $J = 13.9$, 8.1, 1 H, HC(7)), 2.30 (t, $J = 6.7$, 2 H, $\text{H}_2\text{C}(4)$), 1.90 (br s, 1 H, OH), 1.85 (s, 3 H, $\text{H}_3\text{C}(14)$), 1.82–1.78 (m, 2 H, $\text{H}_2\text{C}(6)$)

NOE ^1H NMR: (500 MHz, CDCl_3)

Irradiation at 5.61 ppm (HC(3)) enhanced signal at 3.72-3.67 ppm (HC(5)), 3.62-3.54 (H₂C(12,13)) and 2.28 ppm (H₂C(4))

^{13}C NMR: (126 MHz, CDCl_3)

172.2 (C(1)), 141.9 (C(8)), 132.4 (C(2)), 128.0 (C(9), C(10)), 127.7 (C(3)), 125.5 (C(11)), 69.8 (C(5)), 66.5 (C(13)), 47.1 (C(12)), 41.9 (C(12)), 38.5 (C(6)), 35.4 (C(4)), 31.7 (C(7)), 14.3 (C(14))

IR: (neat)

3402 (s), 3084 (w), 3061 (w), 3026 (m), 2921 (s), 2857 (s), 2759 (w), 2683 (w), 1952 (w), 1877 (w), 1810 (w), 1614 (s), 1495 (m), 1455 (s), 1434 (s), 1380 (m), 1363 (m), 1300 (s), 1278 (s), 1258 (s), 1210 (m), 1157 (m), 1115 (s), 1068 (s), 1031 (s), 973 (m), 934 (m), 904 (m), 840 (m), 749 (m), 701 (s), 639 (m), 606 (m)

MS: (CI, CH₄)

305 (23), 304 (M⁺+H, 100), 286 (28), 169 (23), 91 (11), 86 (21), 84 (30)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} -6.08$ (c = 1.30, EtOH)

TLC: R_f 0.10 (EtOAc) [UV (254 nm)]

SFC: (*R*)-**75**, t_R 5.90 min (3.0%); (*S*)-**75**, t_R 6.26 min (97.0%) (Chiralpak AD, 150 psi, 40 °C, 8.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₈H₂₆NO₃: 304.1913, found: 304.1908

Preparation of (+)-4-[(5*R*,2*E*)-1-Oxo-5-phenyl-5-hydroxy-2-methyl-2-pentenyl]morpholine (76**) (Table 12, entry 3)**

Following Representative Procedure 8, 102 μL (1.0 mmol) of benzaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μL (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μL (1.1 mmol, 1.1 equiv) of SiCl_4 and 340 mg (1.2 mmol, 1.2 equiv) of **72** to yield, after column chromatography (SiO_2 (30 g), 3 cm diam., EtOAc

(200 mL) to EtOAc/MeOH, 19/1 (150 mL)) 270 mg (98%) of (+)-**76** as a clear oil.¹⁷ The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-**76**:

¹H NMR: (500 MHz, CDCl₃)

7.35-7.26 (m, 5 H, HC(7,8,9)), 5.53 (dt, $J = 7.3, 1.5$, 1 H, HC(3)), 4.81 (t, $J = 6.6$, 1 H, HC(5)), 3.56 (br s, 8 H, H₂C(10,11)), 2.67-2.54 (m, 2 H, H₂C(4)), 2.26 (br s, 1 H, OH), 1.77 (s, 3 H, H₃C(14))

¹³C NMR: (126 MHz, CDCl₃)

172.2 (C(1)), 144.0 (C(6)), 132.3 (C(2)), 128.2 (C(8)), 127.3 (C(3)), 127.2 (C(9)), 125.7 (C(7)), 72.8 (C(5)), 66.6 (C(11)), 47.0 (C(10)), 41.7 (C(10)), 37.0 (C(4)), 14.3 (C(12))

IR: (neat)

3390 (s), 3061 (m), 3029 (m), 2966 (s), 2856 (s), 1955 (w), 1891 (w), 1814 (w), 1660 (s), 1633 (s), 1455 (s), 1362 (s), 1301 (s), 1278 (s), 1153 (m), 1114 (s), 1033 (s), 978 (m), 907 (m), 838 (m), 757 (s), 702 (s)

MS: (CI, CH₄)

276 (M⁺+H, 34), 259 (19), 258 (100), 169 (19), 86 (11), 84 (17)

Opt. Rot.: [α]_D²⁴ +11.00 (c = 1.22, EtOH)

TLC: R_f 0.20 (EtOAc) [UV (254 nm)]

SFC: (*S*)-**76**, t_R 4.12 min (1.5%); (*S*)-**76**, t_R 4.61 min (98.5%) (Chiralpak OB, 200 psi, 40 °C, 7.0% MeOH in CO₂, 2.5 mL/min, 220 nm)

HRMS: Calcd for C₁₆H₂₂NO₃: 276.1600, found: 276.1601

Preparation of 4-[(2*E*)-1-Oxo-5-phenyl-5-hydroxy-2-methyl-2-pentenyl]morpholine (76**) (Table 12, entry 4)**

Following Representative Procedure 8, 25 μL (0.25 mmol) of benzaldehyde was combined with 4 μL (0.025 mmol, 0.1 equiv) of diisopropylethylamine, 32 μL (0.275 mmol, 1.1 equiv) of SiCl_4 and 85 mg (0.3 mmol, 1.2 equiv) of **72** to yield, after column chromatography (SiO_2 (10 g), 2 cm diam., EtOAc (100 mL) to EtOAc/MeOH, 19/1 (100 mL)) 24 mg (35%) of **76** as a clear oil. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for **76**:

^1H NMR: (500 MHz, CDCl_3)

7.37-7.26 (m, 5 H, HC(7,8,9)), 5.52 (dt, $J = 7.3, 1.5$, 1 H, HC(3)), 4.81 (t, $J = 6.5$, 1 H, HC(5)), 3.56-3.31 (m, 8 H, $\text{H}_2\text{C}(10,11)$), 2.67-2.54 (m, 2 H, $\text{H}_2\text{C}(4)$), 2.25 (br s, 1 H, OH), 1.77 (s, 3 H, $\text{H}_3\text{C}(14)$)

TLC: R_f 0.20 (EtOAc) [UV (254 nm)]

Preparation of (-)-4-[(5*R*,2*E*,6*E*)-1-Oxo-7-phenyl-5-hydroxy-2-methyl-2,6-heptadienyl]morpholine (77**) (Table 12, entry 5)**

Following Representative Procedure 8, 126 μL (1.0 mmol) of cinnamaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μL (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μL (1.1 mmol, 1.1 equiv) of SiCl_4 and 340 mg (1.2 mmol, 1.2 equiv) of **72** to yield, after column chromatography (SiO_2 (30 g), 3 cm diam., EtOAc

(200 mL) to EtOAc/MeOH, 19/1 (150 mL)) 274 mg (91%) of (–)-**77** as a clear oil.¹⁷ The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-**77**:

¹H NMR: (500 MHz, CDCl₃)

7.36 (dd, $J = 7.1, 1.5$, 2 H, HC(9)), 7.32 (dt, $J = 7.0, 1.8$, 2 H, HC(10)), 7.27-7.24 (m, 1 H, HC(11)), 6.58 (d, $J = 15.9$, 1 H, HC(7)), 6.23 (dd, $J = 15.9, 6.8$, 1 H, HC(6)), 5.62 (dt, $J = 7.3, 1.5$, 1 H, HC(3)), 4.43 (dq, $J = 6.1, 1.0$, 1 H, HC(5)), 3.53 (br s, 8 H, H₂C(12,13)), 2.54-2.44 (m, 2 H, H₂C(4)), 2.05 (br s, 1 H, OH), 1.87 (s, 3 H, H₃C(14))

¹³C NMR: (126 MHz, CDCl₃)

172.2 (C(1)), 136.2 (C(8)), 132.2 (C(2)), 131.6 (C(6)), 129.8 (C(7)), 128.3 (C(10)), 127.4 (C(11)), 127.1 (C(3)), 126.0 (C(9)), 71.3 (C(5)), 66.4 (C(13)), 47.2 (C(12)), 41.7 (C(12)), 35.3 (C(4)), 14.4 (C(14))

IR: (neat)

3390 (m), 3026 (w), 2965 (w), 2918 (m), 2921 (s), 2856 (m), 1732 (w), 1660 (m), 1614 (m), 1494 (m), 1463 (m), 1434 (m), 1361 (m), 1300 (m), 1279 (m), 1257 (w), 1114 (m), 1068 (m), 1033 (m), 970 (m), 907 (m), 840 (m), 752 (m), 696 (m)

MS: (CI, CH₄)

302 (M⁺+H, 6), 285 (22), 284 (100), 198 (13), 197 (28), 170 (13), 169 (70), 154 (17), 133 (40), 114 (28)

Opt. Rot.: [α]_D²⁴ –14.62 (c = 0.85, EtOH)

TLC: R_f 0.18 (EtOAc) [UV (254 nm)]

SFC: (*R*)-**77**, t_R 1.66 min (99.2%); (*S*)-**77**, t_R 2.10 min (0.8%) (Chiralpak OB, 125 psi, 40 °C, 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₈H₂₄NO₃: 302.1756, found: 302.1757

Preparation of 4-[(2*E*,6*E*)-1-Oxo-7-phenyl-5-hydroxy-2-methyl-2,6-heptadienyl]morpholine (77) (Table 12, entry 6)

Following Representative Procedure 8, 32 μL (0.25 mmol) of cinnamaldehyde was combined with 4 μL (0.025 mmol, 0.1 equiv) of diisopropylethylamine, 32 μL (0.275 mmol, 1.1 equiv) of SiCl_4 and 85 mg (0.3 mmol, 1.2 equiv) of **72** to yield, after column chromatography (SiO_2 (10 g), 2 cm diam., EtOAc (100 mL) to EtOAc/MeOH, 19/1 (100 mL)) 42 mg (56%) of **77** as a clear oil. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for **77**:

^1H NMR: (500 MHz, CDCl_3)

7.38-7.24 (m, 5 H, HC(9,10,11)), 6.58 (d, $J = 15.8$, 1 H, HC(7)), 6.22 (dd, $J = 15.9$, 6.7, 1 H, HC(6)), 5.61 (dt, $J = 7.4$, 1.5, 1 H, HC(3)), 4.42 (dq, $J = 6.0$, 1.0, 1 H, HC(5)), 3.53 (br s, 8 H, $\text{H}_2\text{C}(12,13)$), 2.53-2.43 (m, 2 H, $\text{H}_2\text{C}(4)$), 1.98 (d, $J = 3.7$, 1 H, OH), 1.87 (s, 3 H, $\text{H}_3\text{C}(14)$)

TLC: R_f 0.18 (EtOAc) [UV (254 nm)]

Preparation of (-)-4-[(5*S*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-3-methyl-2-heptenyl]morpholine (78) (Table 13, entry 1)

Following Representative Procedure 9, 132 μL (1.0 mmol) of hydrocinnamaldehyde, was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 20 mg (0.05 mmol, 0.05 equiv) of tetrabutylammonium triflate, 18 μL (0.1 mmol, 0.1 equiv) of

diisopropylethylamine, 126 μ L (1.1 mmol, 1.1 equiv) of SiCl_4 and 340 mg (1.2 mmol, 1.2 equiv) of **73** to yield after column chromatography (SiO_2 (30 g), 3 cm diam., EtOAc (150 mL) to EtOAc/MeOH, 19/1 (200 mL)) 205 mg (68%) of (–)-(2*E*)-**78** as a colorless oil.¹⁷ The (2*E*)-**78**/(2*Z*)-**78** ratio was determined to be 88/12 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-(2*E*)-**78**:

bp: 140 °C (5.0×10^{-5} mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

7.29 (t, $J = 7.4$, 2 H, HC(10)), 7.21–7.18 (m, 3 H, HC(9,11)), 5.84 (s, 1 H, HC(2)), 3.86–3.81 (m, 1 H, HC(5)), 3.68–3.59 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.83 (dt, $J = 13.7$, 7.7, 1 H, HC(7)), 2.71 (dt, $J = 13.9$, 8.1, 1 H, HC(7)), 2.29 (ABX, $J_{\text{AB}} = 13.5$, $J_{\text{AX}} = 3.5$, 1 H, $\text{H}_a\text{C}(4)$), 2.22 (ABX, $J_{\text{AB}} = 13.5$, $J_{\text{BX}} = 9.2$, 1 H, $\text{H}_b\text{C}(4)$), 1.92 (s, 3 H, $\text{H}_3\text{C}(14)$), 1.82–1.78 (m, 2 H, $\text{H}_2\text{C}(6)$)

NOE ^1H NMR: (500 MHz, CDCl_3)

Irradiation at 5.80 ppm (HC(2)) enhanced signal at 3.82–3.80 ppm (HC(5)), 3.63–3.47 ($\text{H}_2\text{C}(12,13)$) and 2.27–2.18 ppm ($\text{H}_2\text{C}(4)$)

^{13}C NMR: (126 MHz, CDCl_3)

167.2 (C(1)), 146.3 (C(3)), 141.9 (C(8)), 128.3 (C(9), C(10)), 125.8 (C(11)), 119.7 (C(2)), 68.3 (C(5)), 66.8 (C(13)), 47.7 (C(4)), 46.5 (C(12)), 41.6 (C(12)), 39.0 (C(6)), 32.0 (C(7)), 18.9 (C(14))

IR: (neat)

3402 (m), 3084 (w), 3061 (w), 3026 (m), 2919 (m), 2857 (m), 1958 (w), 1605 (m), 1495 (w), 1435 (m), 1381 (m), 1362 (w), 1329 (w), 1300 (w), 1272 (m), 1242 (m), 1180 (m), 1115 (m), 1038 (m), 975 (w), 931 (w), 852 (w), 750 (m), 701 (m)

MS: (CI, CH_4)

305 (23), 304 ($\text{M}^+\text{+H}$, 100), 286 (26), 169 (15), 91 (15), 83 (12)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} -0.84$ ($c = 1.75$, EtOH)

TLC: R_f 0.09 (EtOAc) [UV (254 nm)]

SFC: (*S*)-**78**, t_R 1.51 min (97.1%); (*R*)-**78**, t_R 1.85 min (2.9%) (Chiralpak OB, 125 psi,

40 °C, 15.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₈H₂₆NO₃: 304.1913, found: 304.1905

Preparation of (+)-4-[(5*R*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-3-methyl-2-heptenyl]morpholine (79**) (Table 13, entry 2)**

Following Representative Procedure 8, 102 μ L (1.0 mmol) of benzaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μ L (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μ L (1.1 mmol, 1.1 equiv) of SiCl₄ and 340 mg (1.2 mmol, 1.2 equiv) of **73** to yield after column chromatography (SiO₂ (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)) 30 mg (10%) of (*2Z*)-**79** as clear oil and (*2E*)-**79** as an oil which was crystallized from Et₂O (3 mL) to yield 245 mg (89%) of white crystals. The (*2E*)-**79**/(*2Z*)-**79** ratio was determined to be 88/12 by ¹H NMR (500 MHz) analysis of the crude reaction mixture. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-(*2E*)-79**:**

mp: 81-82 °C (Et₂O)

¹H NMR: (500 MHz, CDCl₃)

7.35-7.32 (m, 4 H, HC(7,8)), 7.29-7.25 (m, 1 H, HC(9)), 5.69 (s, 1 H, HC(2)), 3.86 (dd, *J* = 8.1, 5.6, 1 H, HC(5)), 3.55-3.17 (m, 8 H, H₂C(10,11)), 2.63-2.46 (m, 3 H, OH, H₂C(4)), 1.91 (s, 3 H, H₃C(12))

¹³C NMR: (126 MHz, CDCl₃)

167.1 (C(1)), 144.8 (C(3)), 144.0 (C(6)), 128.2 (C(8)), 127.3 (C(9)), 125.8 (C(7)), 120.4 (C(2)), 71.7 (C(5)), 66.6 (C(11)), 66.5 (C(11)), 49.2 (C(4)), 46.1 (C(10)), 41.3 (C(10)), 18.5 (C(12))

IR: (CHCl₃)

3392 (m), 3086 (w), 3063 (w), 3030 (w), 2969 (w), 2918 (m), 2858 (m), 2759 (w), 2683 (w), 2244 (w), 1955 (w), 1881 (w), 1814 (w), 1651 (m), 1614 (s), 1494

(w), 1440 (m), 1382 (m), 1362 (w), 1330 (w), 1301 (m), 1273 (m), 1244 (m), 1202 (w), 1181 (m), 1115 (s), 1085 (w), 1067 (w), 1029 (m), 974 (m), 912 (m), 852 (w), 835 (w), 821 (w), 733 (s), 702 (m), 646 (m)

MS: (CI, CH₄)

304 (15), 276 (M⁺+H, 31), 270 (11), 259 (19), 258 (100), 170 (10), 169 (22), 153 (12), 151 (10), 114 (31), 107 (20), 83 (16), 59 (11)

Opt. Rot.: $[\alpha]_D^{24} +28.41$ (c = 1.07, EtOH)

TLC: *R_f* 0.16 (EtOAc) [UV (254 nm)]

SFC: (5*R*,2*E*)-**79**, *t_R* 1.70 min (98.4%); (5*S*,2*E*)-**79**, *t_R* 1.98 min (1.6%) (Chiralpak OB, 125 psi, 40 °C, 14.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₆H₂₁NO₃ (275.34)

Calcd: C, 69.79; H, 7.69; N, 5.09%

Found: C, 69.65; H, 7.69; N, 5.16%

Data for (2*Z*)-**79**:

¹H NMR: (500 MHz, CDCl₃)

7.44 (d, *J* = 7.3, 2 H, HC(7)), 7.34 (t, *J* = 7.3, 2 H, HC(8)), 7.24 (t, *J* = 7.3, 1 H, HC(9)), 6.10 (d, *J* = 1.0, 1 H, HC(2)), 5.81 (br s, 1H, OH), 4.87 (dd, *J* = 10.5, 2.9, 1 H, HC(5)), 3.71-3.47 (m, 8 H, H₂C(12,13)), 3.00 (dd, *J* = 12.9, 10.6, 1 H, HC(4)), 2.33 (dd, *J* = 12.8, 2.9, 1 H, HC(4)), 1.99 (d, *J* = 1.2, 3 H, H₃C(14))

MS: (CI, CH₄)

276 (M⁺+H, 17), 259 (18), 258 (100), 189 (18), 171 (12), 170 (33), 169 (14), 114 (21), 107 (10), 88 (14), 58 (43)

TLC: *R_f* 0.34 (EtOAc) [UV (254 nm)]

SFC: (2*Z*)-**79**, *t_R* 3.47 min (42.8%); (2*Z*)-**79**, *t_R* 3.98 min (57.2%) (Chiralpak AD, 125 psi, 40 °C, 15.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₆H₂₂NO₃: 276.1600, found: 276.1598

Preparation of 4-[(2*E*)-1-Oxo-7-phenyl-5-hydroxy-3-methyl-2-heptenyl]morpholine (79**)**
(Table 13, entry 3)

Following Representative Procedure 8, 25 μL (0.25 mmol) of benzaldehyde was combined with 4 μL (0.025 mmol, 0.1 equiv) of diisopropylethylamine, 32 μL (0.275 mmol, 1.1 equiv) of SiCl_4 and 85 mg (0.3 mmol, 1.2 equiv) of **73** to yield after column chromatography (SiO_2 (10 g), 2 cm diam., EtOAc)) 35 mg (51%) of (2*Z*)-**79** as clear, colorless oil and 34 mg (49%) of (2*E*)-**79** as clear, colorless oil. The (2*E*)-**79**/(2*Z*)-**79** ratio was determined to be 48/52 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (2*E*)-**79**:

^1H NMR: (500 MHz, CDCl_3)
 7.35-7.31 (m, 4 H, HC(7,8)), 7.29-7.25 (m, 1 H, HC(9)), 5.68 (s, 1 H, HC(2)),
 3.87 (dd, $J = 8.2, 5.6$, 1 H, HC(5)), 3.55-3.17 (m, 8 H, $\text{H}_2\text{C}(10,11)$), 2.63-2.44 (m,
 3 H, OH, $\text{H}_2\text{C}(4)$), 1.91 (s, 3 H, $\text{H}_3\text{C}(12)$)

TLC: R_f 0.16 (EtOAc) [UV (254 nm)]

Data for (2*Z*)-**79**:

^1H NMR: (500 MHz, CDCl_3)
 7.46 (d, $J = 7.3$, 2 H, HC(7)), 7.34 (t, $J = 7.2$, 2 H, HC(8)), 7.25 (t, $J = 7.3$, 1 H,
 HC(9)), 6.10 (d, $J = 1.0$, 1 H, HC(2)), 5.81 (br s, 1H, OH), 4.87 (dd, $J = 10.5, 2.9$,
 1 H, HC(5)), 3.71-3.47 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 3.01 (dd, $J = 12.9, 10.6$, 1 H,
 HC(4)), 2.33 (dd, $J = 12.8, 2.9$, 1 H, HC(4)), 1.99 (d, $J = 1.2$, 3 H, $\text{H}_3\text{C}(14)$)

TLC: R_f 0.30 (EtOAc) [UV (254 nm)]

Preparation of (–)-4-[(5*R*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-3-methyl-2,6-heptadienyl]morpholine (80**) (Table 13, entry 4)**

Following Representative Procedure 8, 126 μL (1.0 mmol) of cinnamaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 18 μL (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μL (1.1 mmol, 1.1 equiv) of SiCl_4 and 340 mg (1.2 mmol, 1.2 equiv) of **73** to yield after column chromatography (SiO_2 (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)) to yield 24 mg (8%) of (2*Z*)-**80** as a clear oil and (–)-(2*E*)-**80** as a solid which was recrystallized by precipitation from hot EtOAc (5 mL) with minimal amounts of hexanes to yield 271 mg (90%) of white needles. The (2*E*)-**80**/(2*Z*)-**80** ratio was determined to be 88/12 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (–)-(2*E*)-**80**:

mp: 69–70 $^\circ\text{C}$ (Et_2O)

^1H NMR: (500 MHz, CDCl_3)

7.36 (d, $J = 7.1$, 2 H, HC(9)), 7.31 (t, $J = 7.6$, 2 H, HC(10)), 7.25 (t, $J = 7.3$, 1 H, HC(11)), 6.58 (d, $J = 15.9$, 1 H, HC(7)), 6.22 (dd, $J = 15.9$, 6.6, 1 H, HC(6)), 5.83 (s, 1 H, HC(2)), 4.52–4.48 (m, 1 H, HC(5)), 3.59–3.44 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.46–2.38 (m, 3 H, OH, $\text{H}_2\text{C}(4)$), 1.93 (s, 3 H, $\text{H}_3\text{C}(14)$)

^{13}C NMR: (126 MHz, CDCl_3)

167.2 (C(1)), 144.7 (C(3)), 136.3 (C(8)), 131.7 (C(6)), 130.0 (C(7)), 128.5 (C(10)), 127.6 (C(11)), 126.2 (C(9)), 120.3 (C(2)), 70.2 (C(5)), 66.5 (C(13)), 47.4 (C(4)), 46.4 (C(12)), 41.4 (C(12)), 18.8 (C(14))

IR: (CHCl_3)

3352 (s), 3081 (m), 3057 (m), 3027 (m), 2968 (m), 2952 (m), 2898 (m), 2857 (s), 2710 (w), 2243 (m), 1952 (w), 1822 (w), 1651 (s), 1601 (s), 1494 (m), 1460 (s),

1440 (s), 1380 (s), 1362 (s), 1318 (m), 1301 (m), 1271 (s), 1242 (s), 1176 (m), 1154 (m), 1113 (s), 1069 (s), 1033 (s), 1006 (m), 971 (s), 919 (s), 872 (m), 851 (m), 750 (s), 732 (s), 696 (s), 662 (m), 646 (m)

MS: (CI, CH₄)

330 (12), 302 (M⁺+H, 7), 285 (20), 284 (100), 170 (18), 169 (22), 133 (36), 114 (20), 83 (11)

Opt. Rot.: [α]_D²⁴ -6.05 (c = 1.09, EtOH)

TLC: *R_f* 0.18 (EtOAc) [UV (254 nm)]

SFC: (5*R*,2*E*)-**80**, *t_R* 1.74 min (98.6%); (5*S*,2*E*)-**80**, *t_R* 2.85 min (1.4%) (Chiralpak OB, 125 psi, 40 °C, 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₈H₂₃NO₃ (301.38)

Calcd: C, 71.73; H, 7.69; N, 4.65%

Found: C, 71.64; H, 7.73; N, 4.73%

Data for (2*Z*)-**80**:

¹H NMR: (500 MHz, CDCl₃)

7.39 (d, *J* = 7.3, 2 H, HC(9)), 7.29 (t, *J* = 7.7, 2 H, HC(10)), 7.21 (dt, *J* = 7.3, 0.6, 1 H, HC(11)), 6.71 (dd, *J* = 15.9, 0.7, 1 H, HC(7)), 6.30 (dd, *J* = 15.9, 5.6, 1 H, HC(6)), 6.07 (d, *J* = 1.2, 1 H, HC(2)), 4.48-4.44 (m, 1 H, HC(5)), 3.79-3.35 (m, 9 H, OH, H₂C(12,13)), 2.86 (dd, *J* = 12.7, 10.0, 1 H, HC(4)), 2.32 (dd, *J* = 12.9, 3.4, 1 H, HC(4)), 1.99 (s, 3 H, H₃C(14))

MS: (CI, CH₄)

302 (M⁺+H, 5), 285 (20), 284 (100), 215 (10), 170 (51), 169 (15), 133 (26), 114 (22), 88 (16), 58 (24)

TLC: *R_f* 0.31 (EtOAc) [UV (254 nm)]

SFC: (2*E*)-**80**, *t_R* 3.21 min (53.2%); (2*E*)-**80**, *t_R* 3.98 min (46.8%) (Chiralpak OD, 125 psi, 40 °C, 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

HRMS: Calcd for C₁₈H₂₃NO₃: 301.1678, found: 301.1679

Preparation of 4-[(2*E*,6*E*)-1-Oxo-7-phenyl-5-hydroxy-3-methyl-2,6-heptdienyl]morpholine (80**) (Table 13, entry 5)**

Following Representative Procedure 8, 32 μL (0.25 mmol) of cinnamaldehyde was combined with 4 μL (0.025 mmol, 0.1 equiv) of diisopropylethylamine, 32 μL (0.3 mmol, 1.1 equiv) of SiCl_4 and 85 mg (0.3 mmol, 1.2 equiv) of **73** to yield after column chromatography (SiO_2 (10 g), 2 cm diam., EtOAc (100 mL) to EtOAc/MeOH, 19/1 (100 mL)) 52 mg (69%) of (2*Z*)-**80** as a clear, colorless oil and 19 mg (25%) of (2*E*)-**80** as a clear, colorless oil. The (2*E*)-**80**/(2*Z*)-**80** ratio was determined to be 32/68 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (2*E*)-**80**:

^1H NMR: (500 MHz, CDCl_3)

7.36 (d, $J = 7.1$, 2 H, HC(9)), 7.31 (t, $J = 7.6$, 2 H, HC(10)), 7.25 (t, $J = 7.3$, 1 H, HC(11)), 6.58 (d, $J = 15.9$, 1 H, HC(7)), 6.22 (dd, $J = 15.9$, 6.6, 1 H, HC(6)), 5.83 (s, 1 H, HC(2)), 4.52-4.48 (m, 1 H, HC(5)), 3.59-3.44 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.46-2.38 (m, 3 H, OH, $\text{H}_2\text{C}(4)$), 1.93 (s, 3 H, $\text{H}_3\text{C}(14)$)

TLC: R_f 0.18 (EtOAc) [UV (254 nm)]

Data for (2*Z*)-**80**:

^1H NMR: (500 MHz, CDCl_3)

7.38 (d, $J = 7.2$, 2 H, HC(9)), 7.28 (t, $J = 7.5$, 2 H, HC(10)), 7.22 (t, $J = 7.4$, 1 H, HC(11)), 6.71 (dd, $J = 15.8$, 0.7, 1 H, HC(7)), 6.30 (dd, $J = 15.9$, 5.7, 1 H, HC(6)), 6.05 (d, $J = 1.1$, 1 H, HC(2)), 4.48-4.45 (m, 1 H, HC(5)), 3.79-3.50 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.86 (dd, $J = 12.7$, 10.1, 1 H, HC(4)), 2.34 (dd, $J = 12.9$, 3.5, 1 H, HC(4)), 1.99 (s, 3 H, $\text{H}_3\text{C}(14)$)

TLC: R_f 0.31 (EtOAc) [UV (254 nm)]

Preparation of 4-[(5*R*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-3-methyl-2,6-heptdienyl]morpholine (80**) (Table 14, entry 2)**

Following Representative Procedure 8, 32 μL (0.25 mmol) of cinnamaldehyde was combined with 11 mg (0.0125 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 4 μL (0.025 mmol, 0.1 equiv) of diisopropylethylamine, 32 μL (0.3 mmol, 1.1 equiv) of SiCl_4 and 72 mg (1.2 mmol, 1.2 equiv) of **81** to yield after column chromatography (SiO_2 (10 g), 2 cm diam., EtOAc (100 mL) to EtOAc/MeOH, 19/1 (100 mL)) 6 mg (8%) of (*2Z*)-**80** as a clear, colorless oil and 50 mg (67%) of (*2E*)-**80** as a clear, colorless oil. The (*2E*)-**80**/(*2Z*)-**80** ratio was determined to be 82/18 by ^1H NMR (500 MHz) analysis of the crude reaction mixture. The ratio of γ/α -addition products was determined to be >99/1 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (*2E*)-**80**:

^1H NMR: (500 MHz, CDCl_3)

7.35 (d, $J = 7.2$, 2 H, HC(9)), 7.32 (t, $J = 7.4$, 2 H, HC(10)), 7.24 (t, $J = 7.3$, 1 H, HC(11)), 6.58 (d, $J = 15.8$, 1 H, HC(7)), 6.22 (dd, $J = 15.7$, 6.6, 1 H, HC(6)), 5.84 (s, 1 H, HC(2)), 4.54-4.50 (m, 1 H, HC(5)), 3.66-3.41 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.47-2.39 (m, 2 H, $\text{H}_2\text{C}(4)$), 1.93 (s, 3 H, $\text{H}_3\text{C}(14)$), 1.91 (d, $J = 3.4$, 1 H, OH)

TLC: R_f 0.18 (EtOAc) [UV (254 nm)]

SFC: (*5R,2E*)-**80**, t_R 1.72 min (97.4%); (*5S,2E*)-**80**, t_R 2.83 min (2.6%) (Chiralpak OB, 125 psi, 40 $^\circ\text{C}$, 20.0% MeOH in CO_2 , 3.0 mL/min, 220 nm)

Data for (*2Z*)-**80**:

^1H NMR: (500 MHz, CDCl_3)

7.39 (d, $J = 7.3$, 2 H, HC(9)), 7.29 (t, $J = 7.7$, 2 H, HC(10)), 7.21 (dt, $J = 7.3$, 0.6, 1 H, HC(11)), 6.71 (dd, $J = 15.9$, 0.7, 1 H, HC(7)), 6.30 (dd, $J = 15.9$, 5.6, 1 H, HC(6)), 6.07 (d, $J = 1.2$, 1 H, HC(2)), 4.48-4.44 (m, 1 H, HC(5)), 3.79-3.35 (m, 9 H, OH, $\text{H}_2\text{C}(12,13)$), 2.86 (dd, $J = 12.7$, 10.0, 1 H, HC(4)), 2.32 (dd, $J = 12.9$, 3.4,

1 H, HC(4)), 1.99 (s, 3 H, H₃C(14))

TLC: *R_f* 0.31 (EtOAc) [UV (254 nm)]

SFC: (2*Z*)-**80**, *t_R* 3.24 min (88.1%); (2*Z*)-**80**, *t_R* 4.00 min (11.9%) (Chiralpak OD, 125 psi, 40 °C, 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of 4-[(5*R*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-3-methyl-2,6-heptdienyl]morpholine (80**) (Table 14, entry 3)**

Following Representative Procedure 8, 32 μ L (0.25 mmol) of cinnamaldehyde was combined with 11 mg (0.0125 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 4 μ L (0.025 mmol, 0.1 equiv) of diisopropylethylamine, 32 μ L (0.3 mmol, 1.1 equiv) of SiCl₄ and 72 mg (1.2 mmol, 1.2 equiv) of **82** to yield after column chromatography (SiO₂ (10 g), 2 cm diam., EtOAc (100 mL) to EtOAc/MeOH, 19/1 (100 mL)) to yield 5 mg (7%) of (2*Z*)-**80** as a clear, colorless oil and 56 mg (75%) of (2*E*)-**80** as a clear, colorless oil. The (2*E*)-**80**/(2*Z*)-**80** ratio was determined to be 87/13 by ¹H NMR (500 MHz) analysis of the crude reaction mixture. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (2*E*)-80**:**

¹H NMR: (500 MHz, CDCl₃)

7.36 (d, *J* = 7.1, 2 H, HC(9)), 7.31 (t, *J* = 7.6, 2 H, HC(10)), 7.24 (t, *J* = 7.3, 1 H, HC(11)), 6.38 (d, *J* = 15.7, 1 H, HC(7)), 6.22 (dd, *J* = 15.8, 6.6, 1 H, HC(6)), 5.84 (s, 1 H, HC(2)), 4.52-4.48 (m, 1 H, HC(5)), 3.60-3.44 (m, 8 H, H₂C(12,13)), 2.46-2.38 (m, 2 H, H₂C(4)), 1.93 (s, 3 H, H₃C(14))

TLC: *R_f* 0.18 (EtOAc) [UV (254 nm)]

SFC: (5*S*,2*E*)-**80**, *t_R* 1.72 min (99.5%); (5*S*,2*E*)-**80**, *t_R* 2.82 min (0.5%) (Chiralpak OB, 125 psi, 40 °C, 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Data for (2Z)-80:¹H NMR: (500 MHz, CDCl₃)

7.40 (d, $J = 7.3$, 2 H, HC(9)), 7.29 (t, $J = 7.7$, 2 H, HC(10)), 7.21 (t, $J = 7.4$, 1 H, HC(11)), 6.72 (dd, $J = 15.8$, 0.7, 1 H, HC(7)), 6.30 (dd, $J = 15.9$, 5.6, 1 H, HC(6)), 6.07 (d, $J = 1.2$, 1 H, HC(2)), 4.48-4.44 (m, 1 H, HC(5)), 3.79-3.35 (m, 9 H, OH, H₂C(12,13)), 2.86 (dd, $J = 12.7$, 10.0, 1 H, HC(4)), 2.32 (dd, $J = 12.9$, 3.4, 1 H, HC(4)), 1.99 (s, 3 H, H₃C(14))

TLC: R_f 0.31 (EtOAc) [UV (254 nm)]SFC: (2Z)-80, t_R 3.11 min (86.6%); (2Z)-80, t_R 4.21 min (13.4%) (Chiralpak OD, 125 psi, 40 °C, 20.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (+)-4-[(4R,5R,2E)-1-Oxo-5-phenyl-5-hydroxy-4-methyl-2-pentenyl]morpholine (84) (Table 15, entry 2)

Following Representative Procedure 8, 102 μL (1.0 mmol) of benzaldehyde was combined with 42 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-3, 18 μL (0.1 mmol, 0.1 equiv) of diisopropylethylamine, 126 μL (1.1 mmol, 1.1 equiv) of SiCl₄ and 340 mg (1.2 mmol, 1.2 equiv) of **74** to yield, after column chromatography (SiO₂ (30 g), 3 cm diam., EtOAc (200 mL) to EtOAc/MeOH, 19/1 (150 mL)) an oil which was crystallized from Et₂O (3 mL) to yield 270 mg (98%) of (+)-**84** as white crystals. The ratio of γ/α -addition products was determined to be >99/1 by ¹H NMR (500 MHz) analysis of the crude reaction mixture.

Data for (+)-84:mp: 84-86 °C (Et₂O)¹H NMR: (500 MHz, CDCl₃)

7.36-7.26 (m, 5 H, HC(7,8,9)), 6.89 (dd, $J = 15.1$, 8.5, 1 H, HC(3)), 6.23 (d, $J = 15.1$, 1 H, HC(2)), 4.52 (d, $J = 7.6$, 1 H, HC(5)), 3.66-3.47 (m, 8 H, H₂C(10,11)), 2.68-2.64 (m, 2 H, HC(4)), 2.42 (br s, 1 H, OH), 0.94 (d, $J = 6.8$, 3 H, H₃C(12))

¹³C NMR: (126 MHz, CDCl₃)

165.6 (C(1)), 148.5 (C(3)), 142.6 (C(6)), 128.1 (C(8)), 127.4 (C(9)), 126.6 (C(7)), 120.4 (C(2)), 77.5 (C(5)), 66.5 (C(11)), 45.9 (C(10)), 44.9 (C(4)), 42.0 (C(10)), 16.3 (C(12))

IR: (CHCl₃)

3401 (w), 3086 (w), 3063 (w), 3030 (m), 2968 (w), 2926 (w), 2901 (w), 2861 (w), 2760 (w), 2717 (w), 2244 (w), 1955 (w), 1813 (w), 1656 (s), 1606 (s), 1493 (w), 1455 (m), 1438 (s), 1362 (w), 1301 (w), 1271 (m), 1241 (m), 1194 (w), 1116 (s), 1069 (w), 1044 (m), 1001 (w), 975 (m), 911 (s), 851 (w), 826 (w), 792 (w), 762 (m), 732 (s), 703 (s), 647 (m)

MS: (CI, CH₄)

305 (11), 276 (M⁺+H, 25), 259 (18), 258 (100), 170 (43), 169 (26), 114 (19), 107 (46), 88 (12), 79 (11), 59 (11)

Opt. Rot.: [α]_D²⁴ +50.30 (c = 1.09, EtOH)

TLC: *R_f* 0.15 (EtOAc) [UV (254 nm)]

SFC: syn-**84**, 4.63 min (3.4%); (4*R*,5*R*)-**84**, *t_R* 5.27 min (85.2%); (4*S*,5*S*)-**84**, *t_R* 6.51 min (11.4%) (Chiralpak OJ, 125 psi, 40 °C, 7.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₆H₂₁NO₃ (275.34)

Calcd: C, 69.79; H, 7.69; N, 5.09%

Found: C, 69.64; H, 7.67; N, 5.15%

Preparation of 4-[(2*E*)-1-Oxo-5-phenyl-5-hydroxy-4-methyl-2-pentenyl]morpholine (84**) (Table 15, entry 3)**

Following Representative Procedure 8, 25 μ L (0.25 mmol) of benzaldehyde was combined with 4 μ L (0.025 mmol, 0.1 equiv) of diisopropylethylamine, 32 μ L (0.275 mmol, 1.1

equiv) of SiCl_4 and 85 mg (0.3 mmol, 1.2 equiv) of **74** to yield, after column chromatography (SiO_2 (10 g), 3 cm diam., EtOAc/hexanes, 1/1 (100 mL) to EtOAc (200 mL)) to yield 60 mg (87%, *anti/syn* 66/37) of **84** as clear, colorless oil. The ratio of γ/α -addition products was determined to be 95/5 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for **84**:

^1H NMR: (500 MHz, CDCl_3)

7.36-7.24 (m, 5 H, HC(7,8,9)), 6.87 (dd, $J = 15.3, 8.6$, 1 H, HC(3)), 6.24 (d, $J = 15.0$, 1 H, HC(2)), 4.51 (d, $J = 7.7$, 1 H, HC(5)), 3.66-3.48 (m, 8 H, $\text{H}_2\text{C}(10,11)$), 2.68-2.64 (m, 2 H, HC(4)), 2.42 (br s, 1 H, OH), 0.94 (d, $J = 6.8$, 3 H, $\text{H}_3\text{C}(12)$)

TLC: R_f 0.15 (EtOAc) [UV (254 nm)]

Preparation of 4-[(4*R*,5*R*,2*E*,6*E*)-1-Oxo-7-phenyl-5-hydroxy-4-methyl-2,6-heptadienyl]morpholine (85**) (Scheme 7)**

Following Representative Procedure 8, 25 μL (0.25 mmol) of benzaldehyde was combined with 11 mg (0.0125 mmol, 0.05 equiv) of bisphosphoramidate (R,R) -**3**, 4 μL (0.025 mmol, 0.1 equiv) of diisopropylethylamine, 32 μL (0.275 mmol, 1.1 equiv) of SiCl_4 and 85 mg (0.3 mmol, 1.2 equiv) of **74** to yield after column chromatography (SiO_2 (10 g), 3 cm diam., EtOAc/hexanes, 1/1 (100 mL) to EtOAc (200 mL)) 41 mg (55%) of α -1,4-**85** and 30 mg (40%) of a 69/31 mixture of γ -1,2-**85**/ γ -1,4-**85** as clear, colorless oil. The diastereomeric ratio of γ -1,2-**85** was determined to be *anti/syn*, 82/18 by SFC analysis. The ratio of γ -1,2-**85**/ α -1,2-**85**/ γ -1,4-**85**/ α -1,4-**85** was determined to be 31/0/14/55 by ^1H NMR (500 MHz) analysis.

Data for α -1,4-**85**: ^1H NMR: (500 MHz, CDCl_3)9.59 (d, $J = 1.5$, 1 H) 7.31-7.21 (m, 5 H), 5.76-5.69 (m, 1 H), 5.61-5.56 (m, 1 H), 3.85-3.76 (m, 2 H), 3.59-3.50 (m, 1 H), 3.45-3.41 (m, 1 H), 3.30-3.15 (m, 4 H), 2.93-2.84 (m, 2 H), 2.72-2.67 (m, 1 H), 1.65 (dd, $J = 6.8$, 1.7, 3 H)MS: (CI, CH_4)303 (20), 302 (M^+H , 100), 284 (16), 170 (34), 169 (16), 168 (11), 161 (10), 133 (23), 114 (18), 88 (13)TLC: R_f 0.30 (EtOAc) [UV (254 nm)]Data for γ -1,2-**85**: ^1H NMR: (500 MHz, CDCl_3)7.38 (dd, $J = 7.3$, 1.2, 2 H, HC(9)), 7.32 (dt, $J = 7.8$, 1.7, 2 H, HC(10)), 7.25 (t, $J = 7.3$, 1 H, HC(11)), 6.89 (dd, $J = 15.1$, 8.3, 1 H, HC(3)), 6.60 (dd, $J = 15.9$, 5.4, 1 H, HC(7)), 6.29 (dd, $J = 15.2$, 1.0, 1 H, HC(2)), 6.20 (dd, $J = 15.9$, 6.8, 1 H, HC(6)), 4.20-4.17 (m, 1 H, HC(5)), 3.67-3.53 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.59-2.52 (m, 1 H, HC(4)), 2.15 (d, $J = 3.4$, 1 H, OH), 1.12 (d, $J = 6.8$, 3 H, $\text{H}_3\text{C}(12)$)TLC: R_f 0.13 (EtOAc) [UV (254 nm)]SFC: (4*R*,5*R*)-**85**, t_R 2.49 min (65.2%); (4*S*,5*S*)-**85**, t_R 3.17 min (34.8%) (Chiralpak AD, 125 psi, 40 °C, 25.0% MeOH in CO_2 , 3.0 mL/min, 220 nm)**Preparation of 4-[(2*E*)-1-Oxo-7-phenyl-5-hydroxy-4-methyl-2,6-heptadienyl]morpholine (**85**) (Scheme 7)** Following Representative Procedure 8, 25 μL (0.25 mmol) of benzaldehyde was

combined with 4 μL (0.025 mmol, 0.1 equiv) of diisopropylethylamine, 32 μL (0.275 mmol, 1.1 equiv) of SiCl_4 and 85 mg (0.3 mmol, 1.2 equiv) of **74** to yield after column chromatography (SiO_2 (10 g), 3 cm diam., EtOAc/hexanes, 1/1 (100 mL) to EtOAc (200 mL)) 71 mg (95%) of a 98/2 mixture of γ -1,2-**85**/ γ -1,4-**85** as clear, colorless oil. The ratio of γ -1,2-**85**/ α -1,2-**85**/ γ -1,4-**85**/ α -1,4-**85** was determined to be 87/0/2/11 by ^1H NMR (500 MHz) analysis of the crude reaction mixture.

Data for γ -1,2-**85**:

^1H NMR: (500 MHz, CDCl_3)

7.38 (dd, $J = 7.3, 1.2$, 2 H, HC(9)), 7.32 (dt, $J = 7.8, 1.7$, 2 H, HC(10)), 7.25 (t, $J = 7.3$, 1 H, HC(11)), 6.89 (dd, $J = 15.1, 8.3$, 1 H, HC(3)), 6.60 (dd, $J = 15.9, 5.4$, 1 H, HC(7)), 6.29 (dd, $J = 15.2, 1.0$, 1 H, HC(2)), 6.20 (dd, $J = 15.9, 6.8$, 1 H, HC(6)), 4.20-4.17 (m, 1 H, HC(5)), 3.67-3.53 (m, 8 H, $\text{H}_2\text{C}(12,13)$), 2.59-2.52 (m, 1 H, HC(4)), 2.15 (d, $J = 3.4$, 1 H, OH), 1.12 (d, $J = 6.8$, 3 H, $\text{H}_3\text{C}(12)$)

TLC: R_f 0.13 (EtOAc) [UV (254 nm)]

Preparation of Silyl Ether **86**

Preparation of (+)-4-[(5*S*,2*E*)-1-Oxo-7-phenyl-5-(*tert*-butyldimethylsilyloxy)-2-heptenyl]morpholine (**86**) (Scheme 8)

To a stirred solution of 302 mg (1.04 mmol) of (*S*)-**60** in 1.21 mL of DMF in a 25 mL 1-neck, round bottom flask was added 170 mg (2.5 mmol, 2.4 equiv) of imidazole, and 181 mg (1.2 mmol, 1.15 equiv) of TBSCl at room temperature under argon. After the addition was complete, the solution was allowed to stir at room temperature for 18 h. The reaction mixture was then poured into a stirring sat. aq. NaHCO_3 solution (25 mL). The organic layer was removed from the biphasic mixture and the aqueous layer was washed with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4 (5 g), filtered and the filtrate was

concentrated *in vacuo*. The residue was purified by column chromatography (SiO₂ (30 g), 3 cm diam., EtOAc/ hexanes, 1/1) to yield 392 mg (93%) of (+)-**86** as a colorless oil.¹⁷

Data for (+)-**86**:

bp: 180 °C (2.5 x 10⁻⁵ mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.26 (t, *J* = 7.7, 2 H, HC(10)), 7.17-7.15 (m, 3 H, HC(9,11)), 6.91 (dt, *J* = 15.1, 7.6, 1 H, HC(3)), 6.23 (d, *J* = 14.9, 1 H, HC(2)), 3.86 (p, *J* = 5.7, 1 H, HC(5)), 3.64-3.51 (m, 8 H, H₂C(12,13)), 2.71 (dt, *J* = 13.7, 8.3, 1 H, HC(7)), 2.59 (dt, *J* = 13.7, 8.8, 1 H, HC(7)), 2.42-2.40 (m, 2 H, H₂C(4)), 1.79-1.75 (m, 2 H, H₂C(6)), 0.92 (s, 9 H, H₃C(16)), 0.07 (s, 3 H, H₃C(14)), 0.07 (s, 3 H, H₃C(14))

¹³C NMR: (126 MHz, CDCl₃)

165.0 (C(1)), 142.9 (C(3)), 141.9 (C(8)), 128.11 (C(9)), 128.05 (C(10)), 125.5 (C(11)), 121.4 (C(2)), 70.6 (C(5)), 66.5 (C(13)), 45.8 (C(12)), 41.9 (C(12)), 40.3 (C(4)), 38.7 (C(6)), 31.5 (C(7)), 25.6 (C(16)), 17.7 (C(15)), -4.6 (C(14)), -4.8 (C(14))

IR: (neat)

3085 (w), 3062 (w), 3027 (w), 3955 (m), 2929 (s), 2897 (m), 2857 (s), 2709 (w), 1958 (w), 1804 (w), 1661 (s), 1622 (s), 1496 (w), 1472 (m), 1455 (m), 1434 (s), 1388 (w), 1361 (m), 1301 (w), 1256 (m), 1236 (m), 1192 (m), 1155 (w), 1117 (s), 1090 (m), 1070 (m), 1044 (m), 1005 (m), 981 (m), 940 (w), 921 (w), 881 (w), 837 (s), 812 (m), 776 (s), 749 (m), 700 (m), 664 (w)

MS: (CI, CH₄)

405 (30), 404 (M⁺+H, 100), 388 (27), 347 (22), 246 (84), 300 (10), 272 (42), 249 (25), 212 (13), 91 (11), 73 (11)

Opt. Rot.: [α]_D²⁴ +3.42 (c = 1.21, EtOH)

TLC: *R_f* 0.49 (EtOAc) [UV (254 nm)]

HRMS: Calcd for C₂₃H₃₈NO₃Si: 404.2621, found: 404.2622

Preparation of Methyl Ketone 87

Preparation of (+)-(6*S*,3*E*)-6-(*tert*-Butyldimethylsilyloxy)-8-phenyl-3-octen-2-one (87) (Scheme 8)

A 25 mL, 2-necked, round-bottomed flask fitted with a magnetic stir bar, gas inlet tube and septum containing a stirring solution of 130 mg (0.32 mmol) of (*S*)-**86** in 3.20 mL of THF under Ar was cooled to 0 °C (bath temperature) in an ice water bath and then 0.21 mL of a solution of MeMgBr in Et₂O (3.0 M, 0.64 mmol, 2.0 equiv) was added slowly over 2 min via syringe. After the addition was complete, the ice water bath removed and the solution was allowed to stir at room temperature for 3 h. The reaction mixture was then poured into a stirring sat. aq. NH₄Cl solution (30 mL). The layers separated and the aqueous layer was washed with CH₂Cl₂ (3 x 30 mL). The combined organic extracts were dried over Na₂SO₄ (5 g), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (SiO₂ (15 g), 2 cm diam., hexanes/EtOAc, 10/1) to yield, after Kugelrohr distillation, 89 mg (84%) of (+)-**87** as a colorless oil.

Data for (+)-**87**:

bp: 100 °C (5.5 x 10⁻⁵ mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)
 7.28 (t, *J* = 7.4, 2 H, HC(11)), 7.20-7.16 (m, 3 H, HC(10,12)), 6.82 (dt, *J* = 16.0, 7.4, 1 H, HC(4)), 6.09 (d, *J* = 16.1, 1 H, HC(3)), 3.87 (p, *J* = 5.6, 1 H, HC(6)), 2.73-2.58 (m, 2 H, H₂C(8)), 2.47-2.39 (m, 2 H, H₂C(5)), 2.25 (s, 3 H, H₃C(1)), 1.77 (dq, *J* = 5.9, 2.0, 2 H, H₂C(7)), 0.91 (s, 9 H, H₃C(15)), 0.07 (s, 3 H, H₃C(13)), 0.05 (s, 3 H, H₃C(13))

¹³C NMR: (126 MHz, CDCl₃)
 198.2 (C(2)), 144.7 (C(4)), 141.9 (C(9)), 133.3 (C(3)), 128.3 (C(10)), 128.2 (C(11)), 125.8 (C(12)), 70.7 (C(6)), 40.1 (C(5)), 39.0 (C(7)), 31.5 (C(8)), 26.6

(C(1)), 25.7 (C(15)), 17.9 (C(14)), -4.58 (C(13)), -4.62 (C(13))

IR: (neat)

3086 (w), 3063 (w), 3028 (m), 3003 (w), 2953 (s), 2930 (s), 2895 (m), 2857 (s), 2803 (w), 1943 (w), 1871 (w), 1803 (w), 1699 (s), 1678 (s), 1630 (m), 1604 (w), 1585 (w), 1496 (m), 1472 (m), 1462 (m), 1455 (m), 1430 (m), 1388 (m), 1361 (s), 1320 (w), 1254 (s), 1180 (m), 1155 (w), 1091 (s), 1063 (s), 1031 (m), 1004 (m), 984 (s), 939 (m), 920 (w), 880 (w), 836 (s), 810 (m), 775 (s), 748 (m), 700 (s), 666 (w), 618 (w), 604 (w)

MS: (ESI)

333 ($M^+ + H$, 48), 250 (32), 249 (100), 193 (12)

Opt. Rot.: $[\alpha]_D^{24} +10.30$ ($c = 0.95$, EtOH)

TLC: R_f 0.45 (hexanes/EtOAc, 10/1) [UV (254 nm)]

Analysis: $C_{20}H_{32}O_2Si$ (332.55)

Calcd: C, 72.23; H, 9.70%

Found: C, 72.06; H, 10.02%

Preparation of (+)-(6*S*,3*E*)-6-(*tert*-Butyldimethylsilanyloxy)-8-phenyl-3-octen-2-one (87)
(Scheme 8)

A 5-mL, Schlenk flask containing a stirring solution of 36 mg (0.09 mmol) of (*S*)-**86** in 1.0 mL of THF under Ar was cooled to -78 °C (bath temperature) and then 0.066 mL of a solution of MeMgBr in hexanes (1.5 M, 0.099 mmol, 1.1 equiv) was added slowly over 2 min via syringe. After the addition was complete, the solution was allowed to stir at -78 °C for 30 min. The reaction mixture was then poured into a stirring sat. aq. NH_4Cl solution (30 mL). The layers separated and the aqueous layer was washed with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over Na_2SO_4 (5 g), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2 (10 g), 2 cm diam., hexanes/EtOAc,

10/1) to yield 28 mg (93%) of (+)-**87** as a clear, colorless oil.

Data for (+)-**87**:

¹H NMR: (500 MHz, CDCl₃)

7.27 (t, $J = 7.3$, 2 H, HC(11)), 7.20-7.17 (m, 3 H, HC(10,12)), 6.87 (dt, $J = 16.0$, 7.6, 1 H, HC(4)), 6.10 (d, $J = 16.2$, 1 H, HC(3)), 3.88 (p, $J = 5.5$, 1 H, HC(6)), 2.74-2.58 (m, 2 H, H₂C(8)), 2.46-2.38 (m, 2 H, H₂C(5)), 2.26 (s, 3 H, H₃C(1)), 1.78 (dq, $J = 5.9$, 2.2, 2 H, H₂C(7)), 0.92 (s, 9 H, H₃C(15)), 0.07 (s, 3 H, H₃C(13)), 0.05 (s, 3 H, H₃C(13))

TLC: R_f 0.45 (hexanes/EtOAc, 10/1) [UV (254 nm)]

Determination of the Absolute Configuration of the Vinylogous Aldol Adducts.

Representative Procedure 10. Ozonolysis of an α,β -Unsaturated Ketones or Amides.

Preparation of (+)-(3*R*)-1-Phenylpropane-1,3-diol ((3*R*)-25**) from (+)-(*R*)-5-hydroxy-1,5-diphenyl-pent-2-en-1-on ((5*R*,2*E*)-**11**) (Figure 2)**

A 25-mL, 1-necked, round-bottomed flask containing a solution of 70 mg of **11** (0.28 mmol) in 5 mL of CH₂Cl₂ was cooled to $-78\text{ }^{\circ}\text{C}$ (bath temperature) and a solution of ozone in oxygen was passed through it using a gas dispersion tube for 20 min. The solution was sparged with N₂ (to remove residual ozone) and then 0.56 mL of a solution of LiAlH₄ in THF (2.0 M, 1.12 mmol, 4 equiv) was added slowly at $-78\text{ }^{\circ}\text{C}$. The flask was then fitted with a reflux condenser and was heated at $65\text{ }^{\circ}\text{C}$ for 1.5 h. The mixture was cooled to room temperature and 5 mL of sat. aq. sodium potassium tartrate solution was added and the mixture was stirred to break up the resulting precipitate. The organic layer was separated and the aqueous layer was washed CH₂Cl₂ (3 x 10 mL). The combined organic extracts were washed with brine (25 mL), then were dried over Na₂SO₄, filtered and was concentrated *in vacuo*. The residue was purified by column chromatography (SiO₂ (15 g), 2 cm diam., EtOAc/hexanes, 2/1) to yield 30 mg (71%) of (3*R*)-**25** as a clear, colorless oil. The spectroscopic data for **25** matched those in the literature.¹⁸

Data for (+)-(3R)-**25**:¹H NMR: (500 MHz, CDCl₃)7.39-7.27 (m, 5 H, HC(5,6,7)), 4.98 (dd, *J* = 8.9, 3.7, 1 H, HC(3)), 3.88 (t, *J* = 5.5, 2 H, H₂C(1)), 2.20 (br s, 2 H, OH); 2.08-1.92 (m, 2 H, H₂C(2))TLC: *R_f* 0.28 (EtOAc/hexanes, 2/1) [p-anisaldehyde]Opt. Rot.: [α]_D²⁴ +61.80° (*c* = 0.97, CHCl₃), lit. [α]_D²⁴ -63.0 (*c* = 0.958, CHCl₃) for (3*S*)-**25**¹⁸**Preparation of (+)-(3R)-1-Phenylpropane-1,3-diol ((3R)-**25**) from (+)-(R)-7-Hydroxy-2,2-dimethyl-7-phenyl-4-hepten-3-one ((7*R*,4*E*)-**12**) (Figure 2)**

Following Representative Procedure 10, a solution of 75 mg (0.32 mmol) of **12** in 5 mL of CH₂Cl₂ at -78 °C (bath temperature) in was treated with a solution of ozone in oxygen followed by reduction with 0.64 mL of a solution of LiAlH₄ in THF (2.0 M, 1.28 mmol, 4.0 equiv) to yield, after column chromatography (SiO₂ (20 g), 2 cm diam., EtOAc/hexanes, 2/1) 37 mg (76%) of (3*R*)-**25** as a colorless oil. The spectroscopic data for **25** matched those in the literature.¹⁸

Data for (+)-(3R)-**25**:¹H NMR: (500 MHz, CDCl₃)7.41-7.26 (m, 5 H, HC(5,6,7)), 4.99 (dd, *J* = 8.9, 3.7, 1 H, HC(3)), 3.88 (t, *J* = 5.6, 2 H, H₂C(1)), 2.17 (br s, 1 H), 2.08-1.92 (m, 2 H, H₂C(2))TLC: *R_f* 0.28 (EtOAc/hexanes, 2/1) [p-anisaldehyde]Opt. Rot.: [α]_D²⁴ +66.39° (*c* = 1.0, CHCl₃), lit. [α]_D²⁴ -63.0 (*c* = 0.958, CHCl₃) for (3*S*)-**25**¹⁸

Preparation of (+)-(4*R*,7*R*)-4-(Hydroxy(phenyl)methyl)-2-cyclohexen-1-one ((4*R*,7*R*)-20**) from (6*R*,7*R*)-6-(Hydroxy(phenyl)methyl)-3-methoxy-2-cyclohexenone ((6*R*,7*R*)-**26**). (Figure 2)**

A 25-mL, 1-necked, round-bottomed flask fitted with a magnetic stir bar and septum containing a solution of 70 mg of **26**¹⁹ (99 mg, 0.43 mmol) in 5 mL of Et₂O was cooled to 0 °C (bath temperature). A solution of LiAlH₄ in THF (2.0 M, 1.12 mmol, 4 equiv) was then added via syringe. The flask was then fitted with a reflux condenser and was heated at 45 °C for 1.0 h. The mixture was cooled to room temperature and 1 mL of H₂O was added followed by 5 mL of 1 N HCl and the resulting biphasic mixture was stirred for 30 min. The layers were then separated and the aqueous layer was extracted twice with 25 mL of Et₂O. The combined organic extracts were washed with a sat. aq. NaHCO₃ solution (25 mL), then were dried over NaSO₄, filtered and was concentrated *in vacuo*. The residue was purified by column chromatography ((SiO₂ (15 g), 2 cm diam., pentane/Et₂O, 1/1) to give 75 mg (86%, *anti/syn* 93.5/6.5) of **20** as thick oil, which solidified upon standing. The spectroscopic data for **20** matched those in the literature.¹⁵

Data for (+)-(4*R*,7*R*)-**20**:

¹H NMR: (500 MHz, CDCl₃)

7.43-7.32 (m, 5H, HC(9,10,11)); 7.25 (dt, *J* = 10.3, 1.7, 1 H, HC(3)); 6.09 (dd, *J* = 10.3, 2.4, 1 H, HC(2)); 4.59 (dd, *J* = 7.8, 3.2, 1 H, HC(7)); 2.78-2.73 (m, 1 H, HC(4)); 2.49-2.21 (m, 1 H, HC(6)); 2.35-2.28 (m, 1 H, HC(6)); 2.03 (br s, 1H, OH); 1.75-1.68 (m, 2 H, H₂C(5))

¹³C NMR: (125 MHz, CDCl₃)

199.5 (C(1)), 151.1 (C(3)), 142.1 (C(8)), 130.1 (C(2)), 128.7 (C(10)), 128.3 (C(11)), 126.3 (C(9)), 76.7 (C(7)), 43.7 (C(4)), 36.9 (C(6)), 26.0 (C(5))

Opt. Rot.: [α]_D²⁴ +54.49° (*c* = 1.15, EtOH)

TLC: *R_f* 0.10 (pentane/Et₂O, 1/1) [UV (254 nm)]

Preparation of (+)-(5*R*)-4-(Hydroxy(phenyl)methyl)cyclohexan-1-one ((5*R*)-27a) from (+)-(4*R*,7*R*)-4-(Hydroxy(phenyl)methyl)-2-cyclohexen-1-one ((4*R*,7*R*)-20) (Figure 2)

A 25 mL, 1-necked, round-bottomed flask containing a suspension of 112 mg of **20** (0.55 mmol) and 8.0 mg of 10% Pd-C in 10 mL of EtOAc was stirred for 3 h at 23 °C under 1 atm of H₂. After briefly evacuating the flask and venting with N₂, the suspension was then filtered through Celite on a glass frit and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (SiO₂ (13 g), 2 cm diam., hexanes/EtOAc, 2/1) to yield 90 mg (88%) of (5*R*)-**27a** as a white solid.

Data for (+)-(5*R*)-27a:

¹H NMR: (500 MHz, CHCl₃)

7.39-7.29 (m, 5 H, HC(7,8,9)), 4.50 (d, *J* = 7.3, 1 H, HC(5)), 2.46-2.23 (m, 5 H, H₂C(2), HC(4)), 2.12-2.05 (m, 1 H, HC(3)), 1.95 (br s, 1 H, OH), 1.75-1.70 (m, 1 H, HC(3)), 1.61-1.52 (m, 1 H, HC(3)), 1.48-1.42 (m, 1 H, HC(3))

¹³C NMR: (125 MHz, CDCl₃)

212.4 (C(1)), 143.1 (C(6)), 128.3 (C(7)), 127.7 (C(9)), 126.3 (C(8)), 77.5 (C(5)), 42.9 (C(4)), 40.3 (C(2)); 40.2 (C(2)), 28.7 (C(3)), 28.4 (C(3))

IR: (CHCl₃)

3459 (s), 3085 (m), 3062 (s), 3028 (s), 2933 (m), 2875 (s), 1964 (m), 1892 (m), 1828 (m), 1760 (s), 1733 (s), 1682 (s), 1602 (m), 1494 (s), 1462 (s), 1453 (s), 1428 (s), 1416 (s), 1367 (s), 1336 (s), 1323 (s), 1301 (s), 1288 (s), 1244 (s), 1211 (s), 1161 (s), 1112 (s), 1091 (s), 1061 (s), 1027 (s), 1006 (s), 977 (s), 955 (s), 937 (s), 917 (s), 858 (m), 834 (m), 816 (m), 767 (s), 716 (s), 700 (s), 659 (s), 630 (m)

MS: (EI, 70 eV)

204 (M⁺, 4), 108 (10), 107 (100), 98 (67), 83 (14), 79 (50), 88 (27)

Opt. Rot.: [α]_D²⁴ +22.31 (c = 0.73, EtOH)

TLC: *R*_f 0.13 (hexanes/EtOAc, 2/1) [UV (254 nm)]

HRMS: Calcd for C₁₃H₁₆O₂: 204.1150, found: 204.1154

Preparation of (+)-(5*R*)-cyclohexyl(phenyl)methanol ((1*R*)-27**) from (+)-(5*R*)-4-(Hydroxy(phenyl)methyl)cyclohexan-1-one ((5*R*)-**27a**) (Figure 2)**

A 25 mL, 1-necked, round-bottomed flask fitted with a magnetic stir bar and septum containing a solution of 101 mg of **27a** (0.49 mmol), and 350 mg of KOH (6.2 mmol, 1.7 equiv) in 2 mL of ethylene glycol was added 71 μ L of N₂H₄-H₂O (1.47 mmol, 3.0 equiv). The flask was then fitted with a reflux condenser and was heated at 110 °C for 13 h while rapidly stirring. The reaction was then warmed to 180 °C and stirred for 3 h while rapidly stirring. The mixture was cooled to room temperature and poured into 50 mL of H₂O. The solution was then extracted 3 x 30 mL of CH₂Cl₂. The combined organic layers were washed with H₂O, dried over Na₂SO₄ (5 g), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (SiO₂ (14 g), 2 cm diam., pentane/Et₂O, 4/1) to yield 58 mg (62%) of (1*R*)-**27** as a white solid. The spectroscopic data for **27** matched those in the literature.²⁰

Data for (+)-(1*R*)-27**:**

¹H NMR: (500 MHz, CHCl₃)

7.36-7.26 (m, 5 H, HC(7,8,9)), 4.38 (d, *J* = 7.3, 1 H, HC(1)), 2.00-1.98 (m, 1 H)
1.79-1.75 (m, 2 H), 1.69-1.59 (m, 3 H), 1.40-1.37 (m, 1 H), 1.28-0.89 (m, 5 H)

¹³C NMR: (125 MHz, CDCl₃)

143.6 (C(6)), 128.2 (C(7)), 127.4 (C(9)), 126.6 (C(8)), 79.4 (C(1)), 43.7, 29.2,
28.8, 26.3, 26.0, 26.0

Opt. Rot.: [α]_D²⁴ +25.98 (*c* = 0.99, benzene) lit. [α]_D²⁴ -28.27 (*c* = 3.29, CHCl₃) for (1*S*)-**27**²⁰

TLC: *R*_f 0.44 (hexanes/EtOAc, 2/1) [UV(254 nm)]

Preparation of (-)-(3*S*)-5-Phenylpentane-1,3-diol ((3*S*)-88**) from (-)-4-[(5*S*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2-heptenyl]morpholine ((5*S*,2*E*)-**60**) (Figure 6)**

Following Representative Procedure 10, a solution of 62 mg (0.22 mmol) of **60** in 5 mL of CH₂Cl₂ at -78 °C (bath temperature) in was treated with a solution of ozone in oxygen followed by reduction with 0.42 mL of a solution of LiAlH₄ in THF (2.0 M, 0.84 mmol, 4.0 equiv) to yield, after column chromatography (SiO₂ (5 g), 2 cm diam., EtOAc/hexanes, 2/1) 34 mg (85%) of (3*S*)-**88** as a colorless oil. The spectroscopic data for **88** matched those in the literature.¹⁸

Data for (-)-(3*S*)-**88**:

¹H NMR: (500 MHz, CDCl₃)

7.31-7.18 (m, 5 H, HC(7,8,9)), 3.93-3.88 (m, 2 H, H₂C(1)), 3.86-3.82 (m, 1 H, HC(3)), 2.82-2.66 (m, 2 H, H₂C(5)), 2.21 (br s, 2 H, OH), 1.89-1.69 (m, 4 H, H₂C(2,4))

Opt. Rot.: [α]_D²⁴ -11.69 (c = 1.07, EtOH), lit. [α]_D²⁴ -7.21 (c = 1.52, EtOH) for (3*S*)-**88**¹⁸

TLC: *R_f* 0.22 (EtOAc/hexanes, 2/1) [p-anisaldehyde]

Preparation of (-)-4-[(5*R*)-1-Oxo-5-hydroxy-7-phenylheptyl]morpholine ((5*R*)-89**) from (-)-4-[(5*R*,2*E*)-1-Oxo-7-phenyl-5-hydroxy-2,6-heptadienyl]morpholine ((5*R*,2*E*)-**60**) (Figure 6)**

A 50 mL, 1-necked, round-bottomed flask containing a suspension of 58 mg of **60** (0.2 mmol) and 7.0 mg of 10% Pd-C in 5 mL of EtOAc was stirred for 3 h at 23 °C under 1 atm of H₂. After briefly evacuating the flask and venting with N₂, the suspension was then filtered through Celite on a glass frit and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (SiO₂ (7 g), 2 cm diam., EtOAc) to yield 55 mg (95%) of (5*R*)-**89** as

a colorless oil.

Data for (-)-(5R)-89:

¹H NMR: (500 MHz, CDCl₃)

7.29-7.21 (m, 2 H, HC(10)), 7.19-7.17 (m, 3 H, HC(9,11)), 3.67-3.45 (m, 9 H, HC(5), H₂C(12,13)), 2.83-2.77 (m, 1 H, HC(7)), 2.71-2.65 (m, 1 H, HC(7)), 2.40-2.29 (m, 2 H, H₂C(2)), 1.88-1.73 (m, 5 H, OH, H₂C(6), H₂C(3)), 1.58-1.46 (m, 2 H, H₃C(4))

Opt. Rot.: [α]_D²⁴ -7.53 (c = 1.01, EtOH)

TLC: *R_f* 0.11 (EtOAc) [UV (254 nm)]

Preparation of (-)-4-[(5R)-1-Oxo-5-hydroxy-7-phenylheptyl]morpholine ((5R)-89) from (-)-4-[(5R,2E,6E)-1-Oxo-7-phenyl-5-hydroxy-2,6-heptadienyl]morpholine ((5R,2E,6E)-51) (Figure 6)

A 50 mL, 1-neck round-bottom flask containing a suspension of 172 mg of **60** (0.6 mmol) and 7.0 mg of 5% Pd-C in 15 mL of EtOAc was stirred for 3 h at 23 °C under 1 atm of H₂. After briefly evacuating the flask and venting with N₂, the suspension was then filtered through Celite on a glass frit and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (SiO₂ (12 g), 2 cm diam., EtOAc) to yield 161 mg (92%) of (5R)-**89** as a colorless oil.

Data for (-)-(5R)-89:

bp: 130°C (4.0 x 10⁻⁵ mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.29-7.21 (m, 2 H, HC(10)), 7.19-7.17 (m, 3 H, HC(9,11)), 3.67-3.47 (m, 9 H, HC(5), H₂C(12,13)), 2.83-2.77 (m, 1 H, HC(7)), 2.71-2.65 (m, 1 H, HC(7)), 2.40-2.30 (m, 2 H, H₂C(2)), 1.81-1.74 (m, 4 H, H₂C(6), H₂C(3)), 1.58-1.46 (m, 2 H, H₃C(4))

¹³C NMR: (126 MHz, CDCl₃)
 171.7 (C(1)), 142.2 (C(8)), 128.3 (C(9)), 128.2 (C(10)), 125.5 (C(11)), 70.0 (C(5)), 66.7 (C(13)), 66.4 (C(13)), 45.7 (C(12)), 41.7 (C(12)), 39.0 (C(6)), 36.9 (C(4)), 32.5 (C(2)), 31.9 (C(7)), 20.6 (C(3))

IR: (neat)
 3418 (s), 3084 (w), 3060 (w), 3025 (m), 2921 (s), 2858 (s), 2760 (w), 2714 (w), 2683 (w), 2362 (w), 1956 (w), 1877 (w), 1810 (w), 1633 (s), 1495 (m), 1455 (s), 1435 (s), 1362 (m), 1330 (m), 1301 (m), 1272 (s), 1238 (s), 1196 (m), 1177 (m), 1116 (s), 1069 (s), 1032 (s), 974 (m), 915 (m), 848 (m), 818 (w), 750 (m), 701 (s)

MS: (CI, CH₄)
 292 (M⁺+H, 34), 275 (20), 274 (100), 186 (12), 88 (10)

Opt. Rot.: [α]_D²⁴ -7.32 (c = 1.03, EtOH)

TLC: R_f 0.11 (EtOAc) [UV (254 nm)]

HRMS: Calcd for C₁₇H₂₅NO₃: 292.1913, found: 292.1914

Preparation of (+)-(3*R*)-1-Phenylpropane-1,3-diol ((3*R*)-25**) from (+)-4-[(5*R*,2*E*)-1-Oxo-5-phenyl-5-hydroxy-2-pentenyl]morpholine ((5*R*,2*E*)-**50**) (Figure 6)**

Following Representative Procedure 10, a solution of 65 mg (0.25 mmol) of (**50**) in 5 mL of CH₂Cl₂ at -78 °C (bath temperature) in was treated with a solution of ozone in oxygen followed by reduction with 0.50 mL of a solution of LiAlH₄ in THF (2.0 M, 1.0 mmol, 4.0 equiv) to yield, after column chromatography (SiO₂ (10 g), 2 cm diam., EtOAc/hexanes, 1/1) 36 mg (95%) of (3*R*)-**25** as a clear, colorless oil. The spectroscopic data for **25** matched those in the literature.¹⁸

Data for (+)-(3*R*)-25**:**

¹H NMR: (500 MHz, CDCl₃)
 7.39-7.26 (m, 5 H, HC(5,6,7)), 4.98 (dd, *J* = 9.0, 3.6, 1 H, HC(3)), 3.88 (t, *J* = 5.5, 2 H, H₂C(1)), 2.28 (br s, 2 H, OH), 2.08-1.93 (m, 2 H, H₂C(2))

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +56.30$ ($c = 1.00$, CHCl_3), lit. $[\alpha]_{\text{D}}^{24} -63.0$ ($c = 0.958$, CHCl_3) for (3*S*)-**25**¹⁸

TLC: R_f 0.28 (EtOAc/hexanes, 2/1) [p-anisaldehyde]

Preparation of (+)-(3*R*)-1-Phenylpropane-1,3-diol ((3*R*)-25**) from (+)-4-[(5*R*,2*E*)-1-Oxo-5-phenyl-5-hydroxy-2-methyl-2-pentenyl]morpholine ((5*R*,2*E*)-**76**) (Figure 6)**

Following Representative Procedure 10, a solution of 41 mg (0.15 mmol) of **76** in 5 mL of CH_2Cl_2 at -78°C (bath temperature) in was treated with a solution of ozone in oxygen followed by reduction with 0.3 mL of a solution of LiAlH_4 in THF (2.0 M, 0.60 mmol, 4.0 equiv) to yield, after column chromatography (SiO_2 (10 g), 2 cm diam., EtOAc/hexanes, 2/1) 18 mg (78%) of (3*R*)-**25** as a colorless oil. The spectroscopic data for **25** matched those in the literature.¹⁸

Data for (+)-(3*R*)-**25**:

^1H NMR: (500 MHz, CDCl_3)

7.40-7.26 (m, 5 H, HC(5,6,7)), 4.99 (dd, $J = 9.0, 3.7$, 1 H, HC(3)), 3.89 (t, $J = 5.5$, 2 H, $\text{H}_2\text{C}(1)$), 2.08-1.93 (m, 4 H, OH, $\text{H}_2\text{C}(2)$)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +66.22$ ($c = 0.59$, CHCl_3), lit. $[\alpha]_{\text{D}}^{24} -63.0$ ($c = 0.958$, CHCl_3) for (3*S*)-**25**¹⁸

TLC: R_f 0.28 (EtOAc/hexanes, 2/1) [p-anisaldehyde]

Preparation of (+)-(4*R*)-4-(Acetyloxy)-4-phenyl-2-butanone ((4*R*)-90**) from (+)-4-[(5*R*,2*E*)-1-Oxo-5-phenyl-5-hydroxy-3-methyl-2-pentenyl]morpholine ((5*R*,2*E*)-**79**) (Figure 6)**

To a 25-mL, 1-necked, round-bottomed flask fitted with a magnetic stir bar containing a solution of 55 mg of **79** (0.2 mmol) in 0.44 mL of acetic anhydride (4.6 mmol, 23 equiv) was

slowly added 0.44 mL of pyridine (5.4 mmol, 27 equiv). The solution was allowed to stir at room temperature for 2 h before the addition of 10 mL of Et₂O. The cloudy solution was then washed with 0.1 M aq. HCl (20 mL) followed by washing with brine (20 mL). The organic layer was then separated and dried over Na₂SO₄ (5 g), filtered through Celite on a glass frit and the filtrate was concentrated *in vacuo*. The resulting residue was then dissolved in a mixture of 2 mL CH₂Cl₂, 2 mL CH₃CN, and 2 mL H₂O. To this solution was added 1 mg of RuCl₃·H₂O (0.0046 mmol, 0.023 equiv) and 180 mg of NaIO₄ (0.84 mmol, 4.2 equiv). The biphasic mixture was stirred at room temperature for 2 h prior to the addition of 10 mL of 0.1 M HCl. The solution was then extracted with CH₂Cl₂ (2 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na₂SO₄ (5 g), filtered through Celite on a glass frit and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (SiO₂ (10 g), 2 cm diam., hexanes/EtOAc, 4/1) to yield 11 mg (27%) of (4*R*)-**90** as a colorless oil. The spectroscopic data for **90** matched those in the literature.²¹

Data for (+)-(4*R*)-**90**:

¹H NMR: (500 MHz, CDCl₃)

7.36-7.26 (m, 5 H, HC(6,7,8)), 6.19 (dd, *J* = 8.8, 4.9, 1 H, HC(4)), 3.12 (dd, *J* = 16.6, 8.8, 1 H, HC(3)), 2.82 (dd, *J* = 16.6, 8.8, 1 H, HC(3)), 2.15 (s, 3 H, H₃C(1)), 2.04 (s, 3 H, H₃C(10))

Opt. Rot.: [α]_D²⁴ +56.19 (c = 0.57, CHCl₃), lit. [α]_D²⁴ +64.6 (c = 0.71, CHCl₃) for (4*R*)-**90**²¹

TLC: *R*_f 0.36 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

Preparation of (+)-(2*R*,3*R*)-2-Methyl-1-phenylpropane-1,3-diol ((2*R*,3*R*)-91**) from (+)-4-[(4*R*,5*R*,2*E*)-1-Oxo-5-phenyl-5-hydroxy-4-methyl-2-pentenyl]morpholine ((4*R*,5*R*,2*E*)-**84**) (Figure 6)**

Following Representative Procedure 10, a solution of 45 mg (0.16 mmol) of **84** in 5 mL of CH₂Cl₂ at –78 °C (bath temperature) in was treated with a solution of ozone in oxygen

followed by reduction with 0.32 mL of a solution of LiAlH₄ in THF (2.0 M, 0.64 mmol, 4.0 equiv) to yield, after column chromatography (SiO₂ (10 g), 2 cm diam., EtOAc/hexanes, 2/1) 21 mg (78%) of (2*R*,3*R*)-**91** as a colorless oil. The spectroscopic data for **91** matched those in the literature.¹⁸

Data for (+)-(2*R*,3*R*)-**91**:

¹H NMR: (500 MHz, CDCl₃)

7.40-7.26 (m, 5 H, HC(5,6,7)), 4.99 (dd, *J* = 9.0, 3.7, 1 H, HC(3)), 3.89 (t, *J* = 5.5, 2 H, H₂C(1)), 2.08-1.93 (m, 4 H, OH, H₂C(2))

Opt. Rot.: [α]_D²⁴ +34.74 (*c* = 1.8, CHCl₃), lit. [α]_D²⁴ -46.8 (*c* = 0.35, CHCl₃) for (2*S*,3*S*)-**91**¹⁸

TLC: *R_f* 0.46 (EtOAc/hexanes, 2/1) [*p*-anisaldehyde]

Calculated Structure of the Aldehyde-Silyl Cation Complex (Figure 7)

Model created using the PC version of GAMESS(US) QC package at the PM3 level. The structure was visualized using Chem3D with some hydrogens omitted for clarity.

RESULTS FROM SUCCESSFUL RHF GEOMETRY SEARCH COORDS, ORBS, GRADIENT, AND APPROX. HESSIAN COORDINATES OF SYMMETRY UNIQUE ATOMS (ANGS)				
Atom	Charge	X	Y	Z
C	6	7.08576704	-4.5424505	1.57103129
C	6	6.08218144	-4.0270331	2.34543123
C	6	7.58284018	-3.8025013	0.4749762
N	7	3.09338375	2.87554011	-0.9171932
C	6	4.38728795	3.56600712	-0.7167774
C	6	7.08350719	-2.5599204	0.19138778
C	6	1.92993776	3.7958594	-0.9008909
C	6	-7.2085942	-3.4755011	-2.1077765
C	6	6.05483553	-1.9853507	0.98920839

C	6	-6.1601344	-2.956205	-2.8182928
C	6	5.5376727	-2.7467525	2.05815336
C	6	-7.6321253	-2.8499385	-0.9136188
C	6	4.44903291	-2.2436369	2.81991553
C	6	3.89064544	-1.0383337	2.51255091
N	7	-2.3332423	2.99282974	1.34782975
C	6	4.42341075	-0.2434609	1.45625281
N	7	3.8325934	1.05664464	1.17831691
P	15	2.98423692	1.19529317	-0.369194
C	6	3.14900452	1.69617355	2.32357157
C	6	5.51289579	-0.6842203	0.71804805
C	6	6.0835264	0.11188875	-0.3844739
C	6	5.31651495	0.46432015	-1.4871189
C	6	5.92328216	1.05520637	-2.6348737
C	6	7.24848938	1.37708094	-2.6267067
C	6	8.02977845	1.16572693	-1.4572445
C	6	7.45173738	0.53917565	-0.332999
N	7	3.8915398	0.19019543	-1.4901711
C	6	3.28534912	-0.1521728	-2.7909756
C	6	8.24509409	0.37740293	0.83604997
C	6	9.54559151	0.80514202	0.8640058
C	6	10.1256877	1.41077288	-0.2729728
C	6	9.38480434	1.58773717	-1.4106807
O	8	1.43829019	0.8459831	-0.2343668
C	6	-3.5073538	3.89364582	1.34410533
C	6	-7.0111372	-1.7152737	-0.4653716
C	6	-1.0291729	3.70053866	1.37850526
C	6	-5.9293722	-1.1395062	-1.1886361
C	6	-5.4942699	-1.7855505	-2.3648527

C	6	-4.3731716	-1.2772519	-3.0754057
C	6	-3.7023782	-0.1830386	-2.614299
C	6	-4.1386783	0.48869015	-1.4353189
N	7	-3.4203128	1.66442233	-0.9709396
P	15	-2.5163114	1.43970645	0.53509634
C	6	-2.7179272	2.43939767	-2.0178926
C	6	-5.2582695	0.04797492	-0.7436125
C	6	-5.7350767	0.73251409	0.47215967
C	6	-4.9267832	0.84520687	1.59538953
C	6	-5.4548627	1.35797418	2.81693834
C	6	-6.7348392	1.82568815	2.87587216
C	6	-7.5448992	1.84770351	1.70775565
C	6	-7.047356	1.31001446	0.50198775
N	7	-3.5426296	0.4026807	1.53451516
C	6	-2.9660842	-0.1082445	2.7946377
C	6	-7.8610444	1.38839779	-0.6617041
C	6	-9.1062855	1.95555341	-0.608108
C	6	-9.6088062	2.46920802	0.60844805
C	6	-8.8452813	2.41718157	1.7437368
O	8	-1.1077169	0.78398494	0.27987444
C	6	1.77335343	4.61231188	0.38236941
C	6	0.4974222	5.43758389	0.35940293
C	6	-0.7624381	4.60701199	0.17756687
Si	14	0.16093784	-0.2901569	-0.1590629
Cl	17	1.65015594	-1.9801939	-0.6569166
C	6	-3.8744603	-4.7385572	-0.7390823
C	6	-2.9764927	-3.6869722	-0.5995046
C	6	-3.6753199	-5.9271124	-0.0442317
C	6	-2.5728252	-6.0682579	0.79672271

C	6	-1.6722593	-5.0234167	0.94444001
C	6	-1.8708786	-3.8212407	0.24794536
C	6	-0.882289	-2.7613019	0.43127183
O	8	-1.0141064	-1.6489997	-0.1172918
Cl	17	-0.332367	0.01412551	-2.3465979
H	1	7.50778321	-5.5297699	1.78662992
H	1	5.67937416	-4.5947499	3.19217981
H	1	8.37324461	-4.2365027	-0.1469472
H	1	4.55258745	3.8781661	0.32622329
H	1	4.42363112	4.46553184	-1.3481828
H	1	5.20963442	2.90316721	-1.0243493
H	1	7.47459334	-1.9909497	-0.6616107
H	1	2.05317413	4.47800962	-1.7683671
H	1	1.00095639	3.21225118	-1.096765
H	1	-7.7291413	-4.3743424	-2.4559593
H	1	-5.8208021	-3.4311596	-3.7467341
H	1	-8.4670763	-3.283	-0.3517147
H	1	4.04781548	-2.850567	3.64008225
H	1	2.99322169	-0.683301	3.05202645
H	1	2.63456527	2.61100289	1.9815884
H	1	3.9060297	1.97989419	3.06657863
H	1	2.41246464	1.02687348	2.81255911
H	1	5.30397866	1.22505132	-3.5307543
H	1	7.72453902	1.81397805	-3.5126961
H	1	3.61540486	-1.1661222	-3.0568319
H	1	3.596459	0.53593268	-3.5967975
H	1	2.18561167	-0.1655842	-2.7018778
H	1	7.79608535	-0.1030063	1.71501439
H	1	10.1504283	0.67928963	1.76873653

H	1	11.1708397	1.73620315	-0.2316536
H	1	9.82356374	2.05842189	-2.2983242
H	1	-3.6856804	4.37236442	0.36839182
H	1	-3.3592422	4.68909769	2.08851946
H	1	-4.4041629	3.32386687	1.6300928
H	1	-7.3478444	-1.2304918	0.46016825
H	1	-1.0136067	4.29529785	2.31608622
H	1	-0.2358062	2.93070665	1.48008196
H	1	-4.0460068	-1.7865202	-3.9902654
H	1	-2.7934601	0.17692827	-3.1335076
H	1	-2.0340438	3.16841843	-1.546832
H	1	-3.4673021	2.98761173	-2.6036034
H	1	-2.1303043	1.80000029	-2.7073704
H	1	-4.817367	1.3545742	3.71605523
H	1	-7.1496912	2.20384779	3.81816037
H	1	-3.3865838	-1.1061538	2.97951041
H	1	-3.2098129	0.52479694	3.66693259
H	1	-1.8701298	-0.199569	2.70408964
H	1	-7.4736197	0.9826044	-1.6051449
H	1	-9.7264919	2.01544693	-1.5093816
H	1	-10.611732	2.90968257	0.63021091
H	1	-9.2228027	2.81612361	2.69270944
H	1	2.63885458	5.2936438	0.51565653
H	1	1.78665575	3.94558337	1.2763146
H	1	0.5566113	6.18181015	-0.4606421
H	1	0.42716934	6.02861665	1.29479141
H	1	-0.6775895	3.99348215	-0.7551649
H	1	-1.6181704	5.29299007	0.01034665
H	1	-4.7455983	-4.618108	-1.4001566

H	1	-3.1433686	-2.7556586	-1.1618859
H	1	-4.3849028	-6.7545854	-0.159032
H	1	-2.4153423	-7.0071483	1.33998442
H	1	-0.801655	-5.1390102	1.60289515
H	1	0.00262044	-2.9457676	1.07499146
Cl	17	0.50006703	-0.603103	2.12263458

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exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 27 2006	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~ dpwr		18
data/ui500nb/Orpha~ dof			0
ns/heemstra/JRHXIV~ dm			nnn
	26D.fid	dmm	c
		dmm	200
ACQUISITION			
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
ffb	not used	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
ppw	7.7	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used		PROCESSING
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
rsp	-250.1	werr	
wp	5500.7	wexp	
ws	25	wbs	
esc	0	wnt	
wc	250		
hzmm	22.00		
is	1089.92		
rf1	5133.3		
rfp	3630.5		
th	7		
ins	1.000		
ai			
ph

JRHXIV23D

exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 27 2006	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~	dof		0
ns/heemstra/JRHXIV~	dm	nnn	c
23D.fid	dmm		200
ACQUISITION			
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	not used	dn2	1
bs	16	dpwr2	0
tpwr	55	dof2	n
pw	7.7	dm2	c
dl	0	dmm2	200
tof	0	dmf2	1.0
nt	8	dseq2	n
ct	8	dres2	
alock	n	homo2	
gain	not used	PROCESSING	0.30
FLAGS			
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	16	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	33.57		
rfl	5133.1		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

(Z)-7

ppm

1

2

3

4

5

6

7

8

9

10

9.55

1.00

0.89

0.94 1.02

9.10

JRHVII06C1

exp1 s2pul

SAMPLE DEC. & VT
 date May 29 2004 dfrq 499.699
 solvent CDCl3 dn H1
 file /export/home/~ dpwr 20
 data/Orphans/heems~ dof 0
 tra/JRHVII06C2.fid dm nm
 ACQUISITION dmm c
 sfrq 499.699 dmf 200
 tn H1 dseq
 at 4.665 dres 1.0
 np 65536 homo n
 sw 7024.9
 PROCESSING
 fb 4000 wfile
 bs 4 proc ft
 tpwr 63 fn not used
 pw 5.8 math f
 dl 0
 tof 2.0 werr
 nt 1 wexp
 ct 1 wbs
 alock n wnt
 gain not used
 FLAGS
 il n
 in n
 dp y
 hs nn
 DISPLAY
 sp -249.9
 wp 5496.5
 vs 43
 sc 0
 wc 250
 hzmm 21.99
 is 1097.67
 rfl 4643.7
 rfp 3627.8
 th 7
 ins 1.000
 ai ph

ppm

1

2

3

4

5

6

7

8

9

10

1.95 2.06 1.05 1.00 0.79
 1.00 2.06 0.79

JRHV113C

expl s2pul

SAMPLE DEC. & VT
 date Mar 4 2004 dfrq 500.075
 solvent CDCl3 dn H1
 file /export/home/~ dpwr 18
 data/u400/Orphans/~ dof 0
 heemstra/JRHV113C.~ dm nnn
 fid dnm c

ACQUISITION
 sfrq 500.075 dseq 200
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2
 sw 8000.0 dfrq2 0
 fb 4000 dn2
 bs 16 dpwr2 1
 tpwr 55 dof2 0
 pw 7.6 dm2 n
 d1 0 dnm2 c
 tof 0 dmf2 200
 nt 8 dseq2
 ct 8 dres2 1.0
 alock n homo2 n

PROCESSING
 gain not used
 flags lb 0.30
 il n wtfile
 in n proc ft
 dp y fn not used
 hs nn math f

DISPLAY
 sp -250.1 werr
 wp 5500.7 wexp
 vs 11 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 714.78
 rfl 5133.8
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

12

JRHVI93C

exp1 s2pul

SAMPLE DEC. & VT
 date May 20 2004 dfrq 500.075
 solvent CDCl3 dn H1
 file /export/home/~ dpwr 18
 data/orphans/heems~ dof 0
 tra/JRHVI93C.fid dm nnn
 ACQUISITION dmm c
 sfrq 500.075 dmf 200
 tn H1 dseq
 at 4.096 dres 1.0
 np 65536 homo n
 sw 8000.0 PROCESSING
 fb 4000 lb 0.30
 bs 16 wtfile
 tpwr 55 proc ft
 pw 7.6 fn not used
 dl 0 math f
 tof 0
 nt 8 werr
 ct 8 wexp
 alock n wbs
 gain not used wnt

FLAGS

il n
 in n
 dp y
 hs nn

DISPLAY

sp -250.2
 wp 5500.7
 vs 12
 sc 0
 wc 250
 hzmm 22.00
 is 646.92
 rfl 5133.2
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

13

JRHVI71C

exp1 s2pul

SAMPLE DEC. & VT
 date Apr 19 2004 dfir 500.075
 solvent CDCl3 dn H1
 file /export/home/~dpwr 18
 data/u400/Orphans/~dof 0
 heemstra/JRHVI71C.~dm nnn c
 fid dnm 200
 ACQUISITION
 sfrq 500.075 dseq dmf
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2
 sw 8000.0 dfir2 0
 fb 4000 dnm2 1
 bs 16 dpwr2 0
 tpwr 55 dof2 n
 pw 7.6 dnm2 c
 dl 0 dnm2 200
 tof 0 dmf2 1.0
 nt 16 dseq2 n
 ct 16 dres2
 alock n homo2
 gain not used PROCESSING
 FLAGS lb 0.30
 il n wtfile
 in n proc ft
 dp y fn not used
 hs nn math f
 DISPLAY
 sp -250.1 werr
 wp 5500.7 wexp
 vs 11 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 613.27
 rfl 5133.5
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

14

JRHVI83C

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 29 2004	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~dpwr		18
data/u400/Orphans/~dof			0
heemstra/JRHVI83C.~dm		nnn	c
		fid	dm
		dmf	200
ACQUISITION			
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
dl	0	dm2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	25	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	653.65		
rfl	5134.0		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

15

JRHVI99C

exp1 s2pul

SAMPLE		DEC. & VT	
date	May 21 2004	dfrq	499.699
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	20	
data/Orphans/heems~dof		0	
tra/JRHVI99C.fid	dm	nnn	
ACQUISITION		dm	c
sfrq	499.699	dmf	200
tn	H1	dseq	
at	4.665	dres	1.0
np	65536	homo	n
sw	7024.9	PROCESSING	
fb	4000	wtfile	
bs	4	proc	ft
tpwr	63	fn	not used
pw	5.8	math	f
d1	0		
tof	2.0	werr	
nt	16	wexp	
ct	16	wbs	
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-249.9		
wp	5496.5		
vs	7		
sc	0		
wc	250		
hzmm	21.99		
is	658.99		
rfl	4643.7		
rfp	3627.8		
th	7		
ins	1.000		
ai	ph

16

JRHVI22C

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 21 2007	dfrq	499.432
solvent	CDC13	dn	H1
file	exp	dpwr	25
ACQUISITION		dof	0
sfrq	499.432	dm	nnn
tn	H1	dmu	c
at	4.096	dmf	200
np	65536	dseq	
sw	8000.0	dres	1.0
fb	4000	homo	n
bs	4	DEC2	
tpwr	62	dfrq2	0
pw	5.0	dn2	
d1	0	dpwr2	1
tof	0	dof2	0
nt	16	dm2	n
ct	16	dmu2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	PROCESSING	
dp	y	lb	0.30
hs	nm	wfile	
DISPLAY		proc	ft
sp	-249.9	fn	not used
wp	5493.7	math	f
vs	162		
sc	0	werr	
wc	250	wexp	
hzmm	21.97	wbs	
is	942.50	wnt	
rfl	5135.5		
rfp	3625.9		
th	7		
ins	1.000		
nm	ph

17

JRHVII18C

expl s2pul

SAMPLE DEC. & VT
 date Jun 23 2004 dfrq 500.075
 solvent CDCl3 dn H1
 file /export/home/~ dpwr 18
 data/orphans/heems~ dof 0
 tra/JRHVII18C.fid dm nnn
 ACQUISITION
 sfrq 500.075 dmf 200
 tn H1 dseq
 at 4.096 dres 1.0
 np 65536 homo n
 sw 8000.0 PROCESSING
 fb 4000 lb 0.30
 bs 16 wfile
 tpwr 55 proc ft
 pw 7.6 fn not used
 dl 0 math f
 tof 0
 nt 8 werr
 ct 8 wexp
 alock n wbs
 gain not used wnt
 FLAGS
 il n
 in n
 dp y
 hs nn
 DISPLAY
 sp -250.2
 wp 5500.7
 vs 17
 sc 0
 wc 250
 hzmm 22.00
 is 761.55
 rfl 5133.5
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

JRHVII41CX

exp1 s2pul

SAMPLE DEC. & VT
 date Jul 1 2004 dfrq 500.075
 solvent CDCl3 dn H1
 file /export/home/~dpwr 18
 data/ui500nb/Orpha~ dof 0
 ns/heemstra/JRHVII~ dm nnn
 41CX.fid dmm c
 ACQUISITION dmf 200
 sfrq 500.075 dseq
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2
 sw 8000.0 dfrq2 0
 fb 4000 dn2
 bs 16 dpwr2 1
 tpwr 55 dof2 0
 pw 7.6 dm2 n
 dl 0 dmm2 c
 tof 0 dmf2 200
 nt 8 dseq2
 ct 8 dres2 1.0
 alock n homc2 n
 gain not used PROCESSING
 FLAGS lb 0.30
 il n wtfile
 in n proc ft
 dp y fn not used
 hs nn math f
 DISPLAY
 sp -250.0 werr
 wp 5500.7 wexp
 vs 27 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 1259.15
 rf1 1499.5
 rfp 0
 th 7
 ins 1.000
 ai ph

21

S147

ppm

1

2

3

4

5

6

7

8

9

10

1.68 1.05

1.04 1.11

0.97

1.00

0.83

0.940.992.98

1.00.99 0.89

JRHVII33C

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jun 17 2004	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~dpwr		18
data/u400/Orphans/~dof			0
heemstra/JRHVII33C-dm		nnn	nnn
	.fid	dm	c
ACQUISITION		dmf	200
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		
sw	8000.0	dfrq2	0
fb	4000	dn2	1
bs	16	dpwr2	0
tpwr	55	dof2	n
pw	7.6	dm2	c
d1	0	dm2	200
tof	0	dseq2	1.0
nt	8	dres2	n
ct	8	homo2	
alock	not used		
gain	0.30		
PROCESSING			
il	n	wfile	ft
in	n	proc	not used
dp	y	fn	f
hs	nn	math	
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	64	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	2529.80		
rfl	5133.3		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

22

JRHVII30C

exp1 s2pul

SAMPLE

DEC. & VT

date Jun 15 2004 dfrq 500.075
 solvent CDCl3 dn H1
 file /export/home/~dpwr 18
 data/u500/Orphans/~ dof 0
 heemstra/JRHVII30C~ dm nnn
 .fid dmm c
 200

ACQUISITION

sfrq 500.075 dseq dmf
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536
 sw 8000.0 dfrq2 DEC2 0
 fb 4000 dn2
 bs 16 dpwr2 1
 tpwr 55 dof2 0
 pw 7.6 dm2 n
 dl 0 dmm2 c
 tof 0 dmf2 200
 nt 8 dseq2
 ct 8 dres2 1.0
 alock n homo2 n
 gain not used PROCESSING

FLAGS

il lb wtfile 0.30
 in n proc ft
 dp y fn not used
 hs nn math f

DISPLAY

sp -250.1 werr
 wp 5500.7 wexp
 vs 27 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 2067.99
 rfl 5133.3
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

23

JRHVII43C

exp1 s2pul

SAMPLE DEC. & VT
 date Dec 18 2006 dfreq 500.075
 solvent CDCl3 dn H1
 file /export/home/~dpwr 18
 data/ui500nb/Orpha~ dof 0
 ns/heemstra/JRHVII~ dm nnn
 43C.fid dmm c
 ACQUISITION dmf 200
 sfreq 500.075 dseq
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2
 sw 8000.0 dfreq2 0
 fb not used dn2
 bs 16 dpwr2 1
 tpwr 55 dof2 0
 pw 7.7 dm2 n
 dc 0 dmm2 c
 tbf 0 dm2 200
 nt 8 dseq2
 ct 8 dres2 1.0
 allock h homo2 n
 gain not used PROCESSING
 lb 0.30
 FLAGS n wfile
 in n pdoc ft
 ep y fa not used
 bs nn math f
 DISPLAY
 sp -250.1 weir
 wp 5500.7 wexp
 vs 158 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 2814.92
 rfl 5133.3
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

27a

JRHV81D

expl stdlh

SAMPLE		DEC. & VT	
date	Feb 11 2004	dn	H1
solvent	CDC13	dof	0
file	/export/home/~dm	nnn	nnn
data	/ui500nb/orpha~dmn	c	c
ns	/heemstra/JRHV81~dmf	200	200
D.fid	dpwr	20	20
ACQUISITION			
sfrq	399.951	lb	0.30
tn	H1	wtfile	
at	4.096	proc	ft
np	65536	fn	not used
sw	8000.0	math	f
fb	4400		
bs	16	werr	
tpwr	63	wexp	
pw	9.6	wbs	
d1	0	wnt	
tof	-425.7		DISPLAY
nt	16	sp	-200.1
ct	16	wp	4399.4
alock	n	vs	162
gain	not used	sc	0
FLAGS			
il	n	hzmm	250
in	n	is	17.60
dp	y	rfl	621.13
hs	nn	rfp	4903.3
	th	ins	2903.6
	nm	ph	20
			1.000

32a

10

9

8

7

6

5

4

3

2

1

ppm

48.05

JRHVI10D

exp1 s2pul

SAMPLE		DEC. & VT	
date	Feb 28 2004	dfrq	499.699
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	20	
data	/ui500nb/Orpha~dof	0	
ns	/heemstra/JRHVI1~dm	nmn	
	OD.fid	dm	c
ACQUISITION		dmf	200
sfrq	499.699	dseq	
tn	H1	dres	1.0
at	4.000	homo	n
np	56198		
sw	7024.9	dfrq2	0
fb	4000	dn2	
bs	4	dpwr2	1
tpwr	63	dof2	0
pw	5.2	dm2	n
dl	0	dmm2	c
tof	2.0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	wtfile		
il	n	proc	ft
in	n	fn	not used
dp	y	math	f
hs	nn		
DISPLAY		werr	
sp	-250.0	wexp	
wp	5496.6	wbs	
vs	162	wnt	
sc	0		
wc	250		
hzmm	21.99		
is	595.76		
rfl	4643.6		
rfp	3627.8		
th	7		
ins	1.000		
nm	ph

32b

JRHVI48D

exp1 s2pul

SAMPLE		DEC. & VT	
date	Dec 14 2006	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	18	
data/ui500nb/Orpha~dof	0		
ns/heemstra/JRHVI4~dm	nnn		
8D.fid	dm	c	
8D.fid	dm	200	
ACQUISITION			
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536	DEC2	
sw	8000.0	dfrq2	0
fb	not used	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.7	dm2	n
dl	0	dm2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	136	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	1236.18		
rfl	5133.3		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

32c

ppm

1

2

3

4

5

6

7

8

9

10

51.12

0.648.90

1.18 1.41

1.61 1.621.45

34.48

0.64.83

JRHVI65D

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 13 2004	dfrq	499.699
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		20
data/ui500nb/Orpha~	dof		0
ns/heemstra/JRHVI6~	dm		nmn
5D.fid	dmm		c
ACQUISITION	dmf		200
sfrq	499.699	dseq	
tn	H1	dres	1.0
at	4.000	homo	n
np	56198		DEC2
sw	7024.9	dfrq2	0
fb	4000	dn2	
bs	4	dpwr2	1
tpwr	63	dof2	0
pw	5.2	dm2	n
d1	0	dmm2	c
tof	2.0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	wfile		
il	n	proc	ft
in	n	fn	not used
dp	y	math	f
hs	nm		
DISPLAY		werr	
sp	-250.0	wexp	
wp	5496.6	wbs	
vs	162	wnt	
sc	0		
wc	250		
hzmm	21.99		
is	545.48		
rfl	4643.3		
rfp	3627.8		
th	7		
ins	1.000		
nm	ph

32d

JRHVI33D

exp1 s2pul

SAMPLE		DEC. & VT	
date	Dec 14 2006	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~dof			0
ns/heemstra/JRHVI3~dm			nnn
3D.fid	dmf		c
ACQUISITION			200
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		
sw	8000.0	dfrq2	0
fb	not used	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.7	dm2	n
dl	0	dmf2	c
tof	0		200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used		
PROCESSING			
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	31	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	1343.48		
rfl	5133.3		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

33a

JRHVI49D

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 3 2004	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	18	
data/ui500nb/Orpha~dof		0	
ns/heemstra/JRHVI4~dm		nmn	
9D.fid	dm	c	
ACQUISITION		200	
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536	DEC2	
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	61	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	613.53		
rfl	5133.3		
rfp	3630.5		
th	7		
ins	1.000		
ai		ph

33c

ppm

1

2

3

4

5

6

7

8

9

10

15.17
27.79
0.47
2.34
3.39

1.00
1.16

JRHVI81C

exp1 s2pul

SAMPLE DEC. & VT
 date Apr 29 2004 dfrq 500.075
 solvent CDCl3 dn H1
 file /export/home/~dpwr 18
 data/ui500nb/Orpha~ dof 0
 ns/heemstra/JRHVI8~ dm nnn
 1C.fid dmm c
 ACQUISITION
 sfreq 500.075 dseq 200
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2
 sw 8000.0 dfrq2 0
 fb 4000 dn2 1
 bs 16 dpwr2 0
 tpwr 55 dof2 n
 pw 7.6 dm2 c
 d1 0 dmm2 200
 tof 0 dmf2 1.0
 nt 8 dseq2 n
 ct 8 dres2 n
 alock n homo2 0.30
 gain not used PROCESSING
 FLAGS lb wtfile
 il n n proc ft
 in n y fn not used
 dp y nn math f
 hs
 DISPLAY
 sp -250.0 werr
 wp 5500.7 wexp
 vs 128 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 924.82
 rfl 1499.5
 rfp 0
 th 7
 ins 1.000
 ai ph

39

JRHIV21CF2

exp1 s2pul

SYN-40

SAMPLE		DEC. & VT	
date	Oct 25 2006	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~dpwr		18
data	/ui500nb/Orpha~	dof	0
ns	/heemstra/JRHIV~	dm	nnn
	21CF2.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.075	dseq	
ta	H1	dres	1.0
at	4.096	homo	n
np	65536	DEC2	
sp	8000.0	dfrq2	0
fb	not used	dn2	
ps	16	dpwr2	1
tpwr	55	dof2	0
pw	7.7	dn2	n
d1	0	dmm2	c
tof	0	dmmf2	200
at	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	an	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	147	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	3172.66		
rfl	5133.5		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

JRHXIV21cf1a

exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 24 2006	dfrq	499.432
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		25
data/orphans/heems~dof			0
tra/JRHXIV21cf1a.f~dm		nm	
	id	dm	c
	id	dm	200
ACQUISITION			
sfrq	499.432	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536	PROCESSING	
sw	8000.0	lb	0.30
fb	4000	wtfile	
bs	4	proc	ft
tpwr	62	fn	not used
pw	5.0	math	f
dl	0		
tof	0	werr	
nt	8	wexp	
ct	8	wbs	
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-249.7		
wp	5493.6		
vs	162		
sc	0		
wc	250		
hzmm	21.97		
is	779.58		
rfl	5134.7		
rfp	3625.9		
th	7		
ins	1.000		
nm		ph

anti-40

JRHIIV79D

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jul 25 2005	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~	dof		0
ns/heemstra/JRHIIV7~	dm	nnn	
	9D.fid	dmm	c
	dmf		200
ACQUISITION			
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	15	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	784.34		
rfl	5132.8		
rffp	3630.5		
th	7		
ins	1.000		
ai	ph

41

JRHIV81D

exp1 s2pul

SAMPLE DEC. & VT
 date Jul 27 2005 dfrq 500.075
 solvent CDC13 dn H1
 file /export/home/~dpwr 18
 data/ui500nb/Orpha~ dof 0
 ns/heemstra/JRHIV8~ dm nnn
 ID.fid dnm c
 ACQUISITION
 sfrq 500.075 dseq 200
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2
 sw 8000.0 dfrq2 0
 fb 4000 dnm 1
 bs 16 dpwr2 0
 tpwr 55 dof2 n
 pw 7.6 dnm2 c
 dl 0 dnm2 200
 tof 0 dnm2 200
 nt 16 dseq2
 ct 16 dres2 1.0
 alock n homo2 n
 gain not used
 PROCESSING
 FLAGS lb 0.30
 il n wtfile
 in n proc ft
 dp y fn not used
 hs nn math f
 DISPLAY
 sp -250.1 weyr
 wp 5500.7 wexp
 vs 28 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 1102.40
 rfl 5132.8
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

42

JRHIX83D

exp1 s2pul

SAMPLE		DEC. & VT	
date	Aug 1 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	18	
data/ui500nb/Orpha~dof		0	
ns/heemstra/JRHIX8~dm		nmn	
3D.fid	dmn	c	
ACQUISITION		200	
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
dl	0	dmn2	c
tof	0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	22	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	1190.04		
rfl	5132.6		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

43

JRHIX86D

exp1 s2pul

SAMPLE		DEC. & VT	
date	Aug 4 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~	dof		0
ns/heemstra/JRHIX8~	dm	nmn	
6D.fid	dmm	c	
ACQUISITION	dmf	200	
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536	DEC2	
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	20	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	1239.94		
rfl	5132.8		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

44

STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jul 23 2005	dfrq	499.699
solvent	CDC13	dn	H1
file	/export/home/~dpwr		20
data/ui500nb/Orpha~dof			0
ns/heemstra/JRHIX7~dm		nnn	c
8D1H.fid	dmm		200
ACQUISITION			
sfrq	499.698	dseq	
tn	H1	dres	1.0
at	4.665	homo	n
np	41376		DEC2
sw	4435.1	dfrq2	0
fb	2400	dn2	
bs	4	dpwr2	1
tpwr	63	dof2	0
pw	5.8	dm2	n
dl	0	dmm2	c
tof	-752.7	dmf2	200
nt	4	dseq2	
ct	4	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS		wfile	
il	n	proc	ft
in	n	fn	not used
dp	y	math	f
hs	nn		
DISPLAY		werr	
sp	-475.8	wexp	
wp	4434.9	wbs	
vs	24	wnt	
sc	0		
wc	250		
hzmm	17.74		
is	1094.95		
rfl	4103.7		
rfp	3627.8		
th	7		
ins	1.000		
ai	ph

45

JRHVII89CF3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 27 2004	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~dof			0
ns/heemstra/JRHVII~dm			nnn
89CF3.fid	dm		c
ACQUISITION		dmf	200
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
d1	0	dm2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	59	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	33.57		
rfl	5133.3		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

46

JRHVII97CF2

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 13 2004	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~dof			0
ns/heemstra/JRHVII~dm		nnn	
97CF2.fid	dm	c	
ACQUISITION	dmf	200	
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	114	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	973.55		
rfl	5133.1		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

JRHVII11CF3

exp1 s2pul

SAMPLE DEC. & VT
 date Nov 23 2004 dfrq 500.075
 solvent CDCl3 dn H1
 file /export/home/~dpwr 18
 data/ui500nb/Orpha~ dof 0
 ns/heemstra/JRHVII~ dm nnn
 I11CF3.fid dmm c
 ACQUISITION dmf 200
 sfrq 500.075 dseq
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2
 sw 8000.0 dfrq2 0
 fb 4000 dn2
 bs 16 dpwr2 1
 tpwr 55 dof2 0
 pw 7.6 dm2 n
 dl 0 dmm2 c
 tof 0 dmf2 200
 nt 8 dseq2
 ct 8 dres2 1.0
 alock n homo2 n
 gain not used PROCESSING
 FLAGS lb 0.30
 il n wfile
 in n proc ft
 dp y fn not used
 hs nn math f
 DISPLAY
 sp -250.1 werr
 wp 5500.7 wexp
 vs 121 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 1302.56
 rfl 5132.8
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

48

JRHVII118CF3

expl s2pul

SAMPLE

DEC. & VT

date Dec 3 2004 dfrq 500.075
 solvent CDCl3 dn H1
 file /export/home/~dpwr 18
 data/ui500nb/Orpha~ dof 0
 ns/heemstra/JRHVII~ dm nnn
 I18CF3.fid dmm c

ACQUISITION

sfrq 500.075 dseq
 tn H1 dres 1.0
 at 4.096 homo n

DEC2

np 65536
 sw 8000.0 dfrq2 0
 fb 4000 dn2

bs 16 dpwr2 1
 tpwr 55 dof2 0
 pw 7.6 dm2 n

dl 0 dmm2 c
 tof 0 dm2 200
 nt 8 dseq2

ct 8 dres2 1.0
 alock n homo2 n

gain not used
 FLAGS lb 0.30

PROCESSING

il n wtfile
 in n proc ft

dp y fn not used
 hs nn math f

DISPLAY

sp -250.1 werr
 wp 5500.7 wexp
 vs 67 wbs

sc 0 wnt
 wc 250

hzmm 22.00
 is 1257.86

rfl 5132.8
 rfp 3630.5

th 7
 ins 1.000

ai ph

49

JRHIV56CX

expl s2pul

SAMPLE		DEC. & VT	
date	Jul 20 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	18	
data/Orphans/heems~	dof	0	
tra/JRHIV56CX.fid	dm	nmn	
ACQUISITION	dmm	c	
sfrq	500.075	dmf	200
tn	H1	dseq	
at	4.096	dres	1.0
np	65536	homo	n
sw	8000.0	PROCESSING	
fb	4000	lb	0.30
bs	16	wtfile	
tpwr	55	proc	ft
pw	7.6	fn	not used
dl	0	math	f
tof	0		
nt	16	werr	
ct	16	wexp	
alock	n	wbs	
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	5500.7		
vs	67		
sc	0		
wc	250		
hzmm	22.00		
is	786.34		
rfl	5132.7		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

50

JRHVII37CF1

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jan 22 2005	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~ dpwr		18
data	/u500/Orphans/~ dof		0
heemstra	JRHVII37~ dm	nnn	c
CF1.fid	dmn		200
ACQUISITION			
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
d1	0	dmn2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	mn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	111	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	874.86		
rfl	5132.6		
rfp	3630.5		
th	7		
ins	3.000		
ai	ph

α -50

STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Aug 18 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	18	
data/orphans/heems~	dof	0	
tra/JRHIX69CX.fid	dm	nnn	
ACQUISITION		dm	c
sfrq	500.075	dmf	200
tn	H1	dseq	
at	4.096	dres	1.0
np	65536	homo	n
sw	8000.0	PROCESSING	
fb	4000	lb	0.30
bs	16	wtfile	
tpwr	55	proc	ft
pw	7.6	fn	not used
dl	0	math	f
tof	0		
nt	4	werr	
ct	4	wexp	
alock	n	wbs	
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.0		
wp	5500.7		
vs	198		
sc	0		
wc	250		
hzmm	22.00		
is	658.30		
rfl	5098.6		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

51

10 9 8 7 6 5 4 3 2 1 ppm

1.87 0.95 1.99
1.8189 0.98

1.00
9.17
2.07

JRHVII39CF2

exp1 s2pul

SAMPLE DEC. & VT
 date Jan 24 2005 dfrq 500.075
 solvent CDC13 dn H1
 file /export/home/~ dpwr 18
 data/u500/Orphans/~ dof 0
 heemstra/JRHVII39~ dm nnn
 CF2.fid dnm c
 ACQUISITION
 sfrq 500.075 dseq 200
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2
 sw 8000.0 dfrq2 0
 fb 4000 dn2
 bs 16 dpwr2 1
 tpwr 55 dof2 0
 pw 7.6 dm2 n
 d1 0 dnm2 c
 tof 0 dmf2 200
 nt 8 dseq2
 ct 8 dres2 1.0
 alock n homo2 n
 gain not used PROCESSING
 FLAGS lb 0.30
 il n wtfile
 in n proc ft
 dp y fn not used
 hs mn math f
 DISPLAY
 sp -250.1 weerr
 wp 5500.7 wexp
 vs 67 wbs
 sc 0 wnt
 wc 250
 hzmm 13.75
 is 33.57
 rfl 5132.3
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

51

JRHIV58CX

expl s2pul

SAMPLE		DEC. & VT	
date	Jul 20 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data	/Orphans/heems~dof		0
tra	/JRHIV58CX.fid	dm	nmn
ACQUISITION		dmm	c
sfrq	500.075	dmf	200
tn	H1	dseq	
at	4.096	dres	1.0
np	65536	homo	n
sw	8000.0	PROCESSING	
fb	4000	lb	0.30
bs	16	wtfile	
tpwr	55	proc	ft
pw	7.6	fn	not used
d1	0	math	f
tof	0		
nt	8	werr	
ct	8	wexp	
alock	n	wbs	
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	5500.7		
vs	30		
sc	0		
wc	250		
hzmm	22.00		
is	853.43		
rfl	5132.7		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

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JRHIV59CX

expl s2pul

SAMPLE DEC. & VT
date Jul 20 2005 dfrq 500.075
solvent CDCl3 dn H1
file /export/home/~dpwr 18
data/orphans/heems~ dof 0
tra/JRHIV59CX.fid dm nnn
ACQUISITION dmm c
sfrq 500.075 dmf 200
tn H1 dseq
at 4.096 dres 1.0
np 65536 homo n
sw 8000.0 PROCESSING
fb 4000 lb 0.30
bs 16 wfile
tpwr 55 proc ft
pw 7.6 fn not used
dl 0 math f
tof 0
nt 8 werr
ct 8 wexp
alock n wbs
gain not used wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 5500.7
vs 23
sc 0
wc 250
hzmm 22.00
is 971.41
rfl 5132.7
rfp 3630.5
th 7
ins 1.000
ai ph

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STANDARD PROTON PARAMETERS

expl s2pul

SAMPLE DEC. & VT
 date Sep 2 2005 dfreq 500.075
 solvent CDCl3 dn H1
 file /export/home/~ dpwr 18
 data/u500/Orphans/~ dof 0
 heemstra/JRHIX67CX~ dm nm
 .fid dmm c
 ACQUISITION
 sfrq 500.075 dmf 200
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2 0
 sw 8000.0 dfreq2
 fb 4000 dn2
 bs 16 dpwr2 1
 tpwr 55 dof2 0
 pw 7.6 dm2 n
 dl 0 dmm2 c
 tof 0 dmf2 200
 nt 1 dseq2
 ct 1 dres2 1.0
 alock n homo2 n
 gain not used PROCESSING
 FLAGS lb 0.30
 il n wfile
 in n proc ft
 dp y fn not used
 hs nm math f
 DISPLAY
 sp -250.1 werr
 wp 5500.7 wexp
 vs 112 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 686.38
 rfl 5132.8
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

54

JRHIV68CX

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jul 15 2005	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~dpwr	18	
data	u500/Orphans/~dof	0	
heemstra	JRHIV68CX~dm	nnn	c
	.fid	dmf	200
ACQUISITION			
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	4000	dm2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
d1	0	dm2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	46	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	726.45		
rfl	5132.8		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

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JRHX80CD

exp1 s2pul

SAMPLE

date Sep 16 2005 dfrq 500.075

solvent CDCl3 dn H1

file /export/home/~dpwr 18

data/ui500nb/Orpha~ dof 0

ns/heemstra/JRHX8~ dm nnn

OCDA.fid dmm c

ACQUISITION dmf 200

sfrq 500.075 dseq

tn H1 dres 1.0

at 4.096 homo n

np 65536 DEC2

sw 8000.0 dfrq2 0

fb 4000 dn2

bs 16 dpwr2 1

tpwr 55 dof2 0

pw 7.6 dm2 n

dl 0 dmm2 c

tof 0 dmf2 200

nt 16 dseq2

ct 16 dres2 1.0

alock n homo2 n

gain not used

PROCESSING

FLAGS lb 0.30

il n wtfile

in n proc ft

dp y fn not used

hs nn math f

DISPLAY

sp -250.1 werr

wp 5500.7 wexp

vs 55 wbs

sc 0 wnt

wc 250

hzmm 22.00

is 1232.05

rfl 5132.8

rfp 3630.5

th 7

ins 1.000

ai ph

56

JRHX87CD

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 19 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	18	
data	/ui500nb/Orpha~	dof	0
ns	/heemstra/JRHX8~	dm	nnn
	7CD.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
d1	0	dmm2	c
tof	0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	160	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	1569.36		
rfl	5132.8		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

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JRH06CD

exp1 s2pul

SAMPLE

DEC. & VT

date Sep 22 2005 dfreq 500.075
 solvent CDCl3 dn H1
 file /export/home/~dpwr 18
 data/ui500nb/Orpha~ dof 0
 ns/heemstra/JRH06~ dm nnn
 CDe.fid dmm c

ACQUISITION

sfrq 500.075 dseq
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2
 sw 8000.0 dfrq2 0
 fb 4000 dn2
 bs 16 dpwr2 1
 tpwr 55 dof2 0
 pw 7.6 dm2 n
 dl 0 dmm2 c
 tof 0 dm2 200
 nt 16 dseq2
 ct 16 dres2 1.0
 alock n homo2 n

PROCESSING

gain not used
 flags lb 0.30

DISPLAY

il n wtfile
 in n proc ft
 dp y fn not used
 hs nn math f

sp -250.1 werr
 wp 5500.7 wexp
 vs 45 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 713.37
 rfl 5132.8
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

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STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 16 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	18	
data/ui500nb/Orpha~	dof	0	
ns/heemstra/JRHIX6~	dm	nnn	
5CDB.fid	dmm	c	
ACQUISITION	dmm	200	
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536	DEC2	
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
d1	0	dmm2	c
tof	0	dmf2	200
nt	4	dseq2	
ct	4	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb	0.30	
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	weir	
wp	5500.7	wexp	
vs	113	wbs	
sc	0	wnt	
wc	250		
hzmnm	22.00		
is	1058.59		
rfl	5132.6		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

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STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 24 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data/u500/Orphans/~dof			0
heemstra/JRHIX70CX~dm		nnn	
	.fid	dm	c
ACQUISITION		dmf	200
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	33482		DEC2
sw	4087.1	dfrq2	0
fb	2000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
d1	0	dmm2	c
tof	-412.1	dmf2	200
nt	1	dseq2	
ct	1	dres2	1.0
alock	n	homo2	n
gain	14	PROCESSING	
il	lb	lb	0.30
in	n	wtfile	
dp	n	proc	ft
hs	y	fn	not used
	nn	math	f
DISPLAY			
sp	42.4	werr	
wp	4086.9	wexp	
vs	492	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	980.19		
rfl	3588.3		
rfl	3630.5		
th	7		
ins	1.000		
ai	ph

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JRHK09CD

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 21 2005	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~dpwr		18
data	/ui500nb/Orpha~	dof	0
ns	/heemstra/JRHK09-	dm	nnn
	CD.fid	dmm	c
	500.075	dmf	200
ACQUISITION			
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
d1	0	dmm2	c
tof	0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	101	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	994.39		
rfl	5132.8		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

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JRHXIV16C

exp1 s2pul

SAMPLE DEC. & VT
 date Oct 16 2006 dfreq 500.075
 solvent CDCl3 dn H1
 file /export/home/~dpwr 18
 data/ui500nb/Orpha~ dof 0
 ns/heemstra/JRHXIV~ dm nnn
 16C.fid dmm c
 ACQUISITION
 sfreq 500.075 dseq 200
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2
 sw 8000.0 dfreq2 0
 fb not used dn2 1
 bs 16 dpwr2 0
 tpwr 55 dof2 n
 pw 7.7 dm2 c
 dl 0 dmm2 200
 tof 0 dmf2 1.0
 nt 16 dseq2 n
 ct 16 dres2 n
 alock n homo2
 gain not used PROCESSING
 FLAGS lb 0.30
 il n wfile ft
 in n proc not used
 dp y fn f
 hs nn math
 DISPLAY
 sp -250.1 werr
 wp 5500.7 wexp
 vs 183 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 1305.15
 rfl 5132.3
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

JRH94C

expl s2pul

SAMPLE		DEC. & VT	
date	Oct 26 2006	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~	dof		0
ns/heemstra/JRH94~	dm	nmn	
	C.fid	c	
	dmm	200	
ACQUISITION			
sfrq	500.075	dseq	200
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	not used	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.7	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used		PROCESSING
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	297	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	2668.97		
rfl	5133.3		
rfp	3630.5		
th	7		
ins	1.000		
ai		ph

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JRHXI44C

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 7 2006	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	18	
data/ui500nb/Orpha~dof		0	
ns/heemstra/JRHXI4~dm		nnn	
4C.fid	dm	c	
ACQUISITION			
sfrq	500.075	dseq	200
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.7	dm2	n
dl	0	dm2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	87	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	803.73		
rf1	5132.8		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

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JRHXIV27C

exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 30 2006	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~	dof		0
ns/heemstra/JRHXIV~	dm	nnn	
27C.fid	dmm	c	
ACQUISITION		dmf	200
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		
sw	8000.0	dfrq2	0
fb	not used	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.7	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	218	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	3313.71		
rfl	5132.8		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

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JRHX65D

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 30 2005	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~dof			0
ns/heemstra/JRHX65~dm			nmn
			c
			200
ACQUISITION			
sfrq	500.075	dseq	dmf
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.7	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used		PROCESSING
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	34	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	1941.04		
rfl	5132.6		
rfp	3630.5		
th	7		
ins	4.000		
ai		ph

exp1 s2pul

SAMPLE			DEC. & VT	
date	Dec 1 2005	dfrq	499.438	
solvent	CDCl3	dn	H1	
file	/export/home/~dpwr		25	
data/ui500nb/Orpha~	dof		0	
ns/heenstra/JRHX68~	dmf		nmn	
	D.fid	dmm	c	
	200			
ACQUISITION				
sfrq	499.438	dseq		
tn	H1	dres	1.0	
at	4.096	homo	n	
np	65536		DEC2	
sw	8000.0	dfrq2	undefined	
fb	4400	dn2	undefined	
bs	4	dpwr2	undefined	
tpwr	63	dof2	undefined	
pw	5.0	dm2	undefined	
d1	0	dmm2	undefined	
tof	0	dmf2	undefined	
nt	8	dseq2	undefined	
ct	8	dres2	undefined	
alock	n	homo2	undefined	
gain	not used		PROCESSING	
FLAGS	lb		0.30	
il	n	wtfile		
in	n	proc	ft	
dp	y	fn	not used	
hs	nn	math	f	
DISPLAY				
ssp	-249.8	werr		
wp	5493.7	wexp		
vs	162	wbs		
sc	0	wnt		
wc	250			
hzmm	21.98			
is	2230.38			
rfl	5133.3			
rpf	3625.9			
th	7			
ins	1.000			
nm				
ph

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JRHX77D

expl s2pul

SAMPLE		DEC. & VT	
date	Jan 7 2006	dfrq	499.438
solvent	CDC13	dn	H1
file	/export/home/~dpwr		25
data/ui500nb/Orpha~dof			0
ns/heemstra/JRHX77~dm		nm	nm
	D.fid dmm	c	
	200		
ACQUISITION			
sfrq	499.438	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	undefined
fb	4400	dn2	undefined
bs	4	dpwr2	undefined
tpwr	63	dof2	undefined
pw	5.0	dm2	undefined
dl	0	dmm2	undefined
tof	0	dmf2	undefined
nt	16	dseq2	undefined
ct	16	dres2	undefined
alock	n	homo2	undefined
gain	not used		PROCESSING
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-249.8	werr	
wp	5493.7	wexp	
vs	162	wbs	
sc	0	wnt	
wc	250		
hzmm	21.98		
is	2194.16		
rfl	5133.1		
rfp	3625.9		
th	7		
ins	1.000		
nm	ph

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JRHX76CD

exp1 s2pul

SAMPLE		DEC. & VT	
date	Dec 19 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~dof			0
ns/heemstra/JRHX76~dm		nnn	c
			200
ACQUISITION			
sfrq	500.075	dseq	dmc
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	4000	dn2	1
bs	16	dpwr2	0
tpwr	55	dof2	n
pw	7.7	dm2	c
dl	0	dmm2	200
tof	0	dmf2	1.0
nt	16	dseq2	n
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	0.30
il	lb	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	32	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	780.88		
rfl	5132.8		
rfp	3630.5		
th	7		
ins	1.000		
ai			
ph

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JRHXII180C

exp1 s2pul

SAMPLE

DEC. & VT

date Aug 21 2006 dfrq 499.438

solvent CDCl3 dn H1

file /export/home/~dpwr 25

data/ui500nb/Orpha- dof 0

ns/heemstra/JRHXII- dm nm

I80C.fid dnm c

ACQUISITION dmf 200

sfrq 499.438 dseq

tn H1 dres 1.0

at 4.096 homo n

np 65536 DEC2

sw 8000.0 dfrq2 undefined

fb 4400 dn2 undefined

bs 4 dpwr2 undefined

tpwr 62 dof2 undefined

pw 5.0 dm2 undefined

dl 0 dnm2 undefined

tof 0 dmf2 undefined

nt 8 dseq2 undefined

ct 8 dres2 undefined

alock n homo2 undefined

gain not used PROCESSING

FLAGS lb 0.30

il n wfile

in n proc ft

dp y fn not used

hs nn math f

DISPLAY

sp -249.8 werr

wp 5493.7 wexp

vs 77 wbs

sc 0 wnt

wc 250

hzmm 21.98

is 1797.21

rfl 5135.0

rfp 3625.9

th 7

ins 1.000

nm ph

76

JRHXIII181C

exp1 s2pul

SAMPLE		DEC. & VT	
date	Aug 21 2006	dfrq	499.438
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		25
data/ui500nb/Orpha~dof			0
ns/heemstra/JRHXII~dm			nmn
	I81C.fid	dm	c
	200		
ACQUISITION			
sfrq	499.438	dseq	dmf
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	undefined
fb	4400	dn2	undefined
bs	4	dpwr2	undefined
tpwr	62	dof2	undefined
pw	5.0	dm2	undefined
d1	0	dm2	undefined
tof	0	dm2	undefined
nt	8	dseq2	undefined
ct	8	dres2	undefined
alock	n	homo2	undefined
gain	not used		PROCESSING
il	lb		0.30
in	n	wtfile	
dp	n	proc	ft
hs	y	fn	not used
	nn	math	f
DISPLAY			
sp	-249.8	werr	
wp	5493.7	wexp	
vs	120	wbs	
sc	0	wnt	
wc	250		
hzmm	21.98		
is	1892.96		
rfl	5135.0		
rfp	3625.9		
th	7		
ins	1.000		
nm	ph

77

78

JRHX75CD
exp1 s2pul

SAMPLE		DEC. & VT	
date	Dec 20 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~dof			0
ns/heemstra/JRHX75~dm			nnn
	CDf2.fid	dm	c
ACQUISITION		dmf	200
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	4000	dn2	1
bs	16	dpwr2	0
tpwr	55	dof2	0
pw	7.7	dm2	n
dl	0	dm2	c
tof	0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	56	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	919.09		
rfl	5132.8		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph		

ppm

1

2

3

4

5

6

7

8

9

10

3.58 2.51
1.00
8.79 1.15
1.31 1.17 2.22 2.12
2.95

JRHXIV10CX

exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 12 2006	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~dpwr		18
data/u500/Orphans/~dof			0
heemstra/JRHXIV10C~dm			nnn
	X.fid	dm	c
ACQUISITION		dmf	200
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	not used	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.7	dm2	n
d1	0	dmm2	c
tof	0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used		PROCESSING
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	146	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	1340.40		
rfl	5132.3		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

79

ppm

1

2

3

4

5

6

7

8

9

10

2.94

3.25

8.50

1.00

1.01

3.56

0.93

JRXIV10Cf1

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 27 2006	dfrq	499.438
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		25
data/ui500nb/Orpha~dof			0
ns/heemstra/JRXIV~dm			nnn
10Cf1.fid	dmf		c
200			
ACQUISITION			
sfrq	499.438	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	undefined
fb	4400	dn2	undefined
bs	4	dpwr2	undefined
tpwr	62	dof2	undefined
pw	5.0	dm2	undefined
dl	0	dm2	undefined
tof	0	dm2	undefined
nt	8	dseq2	undefined
ct	8	dres2	undefined
alock	n	homo2	undefined
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-249.8	werr	
wp	5493.7	wexp	
vs	162	wbs	
sc	0	wnt	
wc	250		
hzmm	21.98		
is	2019.76		
rfl	5133.3		
rfp	3625.9		
th	7		
ins	1.000		
nm	ph

80

JRHXIV11CX

exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 12 2006	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	18	
data/u500/Orphans/~dof		0	
heemstra/JRHXIV11C~dm		nnn	c
x.fid	dmf	200	
ACQUISITION			
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536	DEC2	
sw	8000.0	dfrq2	0
fb	not used	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.7	dm2	n
d1	0	dmm2	c
tof	0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	60	wbs	
sc	0	wnt	
wc	250		
hzmum	22.00		
is	1034.85		
rfl	5132.6		
rfd	3630.5		
th	7		
ins	1.000		
ai	ph

JRXIV11Cf1

exp1 s2pul

SAMPLE		DEC. & VT	
date	Oct 18 2006	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data/ui500nb/Orpha~	dof		0
ns/heemstra/JRXIV~	dm		nnn
	11Cf1.fid	dmn	c
	dmf		200
ACQUISITION			
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	not used	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.7	dm2	n
dl	0	dmn2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used		
PROCESSING			
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	156	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	1389.34		
rfl	5132.3		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

JRHX43D

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 5 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data/ui500mb/Orpha~dof			0
ns/heemstra/JRHX43~dm		nnn	c
ACQUISITION		D.fid dnm	
sfrq	500.075	dseq	200
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	4000	dn2	1
bs	16	dpwr2	0
tpwr	55	dof2	n
pw	7.6	dm2	c
d1	0	dm2	200
tof	0	dmf2	1.0
nt	8	dseq2	n
ct	8	dres2	0.30
alock	n	homo2	
gain	not used	PROCESSING	
FLAGS	lb	0.30	
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	17	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	985.28		
rfl	5132.6		
rfd	3630.5		
th	7		
ins	1.000		
ai	ph

81

82

JRHX46D

exp1 std1h

SAMPLE		DEC. & VT	
date	Nov 8 2005 dn	H1	
solvent	CDCl3	dof	0
file	/export/home/~dm	nmn	
data	/ui500nb/Orpha~dmm	c	
ns	/heemstra/JRHX46~dmf	200	
	D.fid dpwr	20	
ACQUISITION		PROCESSING	
sfrq	399.951 lb		0.30
tn	H1 wfile		
at	4.096 proc	ft	
np	65536 fn	not used	
sw	8000.0 math	f	
fb	4400		
bs	16 werf		
tpwr	63 wexp		
pw	6.2 wbs		
dl	0 wnt		
tof	-425.7	DISPLAY	
nt	16 sp	-200.1	
ct	16 wp	4399.4	
alock	n vs	162	
gain	not used sc	0	
FLAGS	wc	250	
il	n hzmm	17.60	
in	n is	845.24	
dp	y rfl	4903.3	
hs	nn rfp	2903.6	
	th	20	
	ins	1.000	
	nm		
	ph

JRHXIV13CX

exp1 s2pul

SAMPLE DEC. & VT
 date Oct 12 2006 dfrq 500.075
 solvent CDCl3 dn H1
 file /export/home/~ dpwr 18
 data/u500/Orphans/~ dof 0
 heemstra/JRHXIV13C~ dm nnn
 X.fid dnm c
 ACQUISITION dmf 200
 sfrq 500.075 dseq
 tn H1 dres 1.0
 at 4.096 homo n
 np 65536 DEC2
 sw 8000.0 dfrq2 0
 fb not used dn2 1
 bs 16 dpwr2 0
 tpwr 55 dof2 0
 pw 7.7 dm2 n
 dl 0 dnm2 c
 tof 0 dmf2 200
 nt 16 dseq2
 ct 16 dres2 1.0
 alock n homo2 n
 gain not used PROCESSING
 FLAGS lb 0.30
 il n wfile
 in n proc ft
 dp y fn not used
 hs nn math f
 DISPLAY
 sp -250.1 werr
 wp 5500.7 wexp
 vs 104 wbs
 sc 0 wnt
 wc 250
 hzmm 22.00
 is 1357.78
 rfl 5132.6
 rfp 3630.5
 th 7
 ins 1.000
 ai ph

84

JRH80Cf3

expl s2pul

SAMPLE		DEC. & VT	
date	Jan 12 2006	dfrq	499.438
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		25
data/ui500nb/Orpha~	dof		0
ns/heemstra/JRH80~	dm	nnn	nnn
	cf3.fid	dmm	c
ACQUISITION		dmf	200
sfrq	499.438	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	undefined
fb	4400	dn2	undefined
bs	4	dpwr2	undefined
tpwr	63	dof2	undefined
pw	5.0	dm2	undefined
dl	0	dmm2	undefined
tof	0	dmm2	undefined
nt	8	dseq2	undefined
ct	8	dres2	undefined
alock	n	homo2	undefined
gain	not used		PROCESSING
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-249.8	werr	
wp	5493.7	wexp	
vs	216	wbs	
sc	0	wnt	
wc	250		
hzmm	13.73		
is	33.57		
rfl	5133.3		
rfl	3625.9		
th	7		
ins	100.000		
nm	ph

γ -1,4-85 γ -1,2-85

JRH80Cf1

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jan 12 2006	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	18	
data/ui500nb/Orpha~	dof	0	
ns/heemstra/JRH80~	dm	nnn	
Cf1.fid	dmm	c	
ACQUISITION			
sfrq	500.075	dseq	200
tn	H1	dres	1.0
at	4.096	homo	n
np	65536	DEC2	
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.7	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	154	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	1325.78		
rfl	5132.6		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

α -1,4-85

JRXH08CD

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 23 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr		18
data	/ui500nb/Orpha~dof		0
ns	/heemstra/JRXH08~dm		nmn
	CD.fid	dm	c
ACQUISITION		dmf	200
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		DEC2
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
dl	0	dmm2	c
tof	0	dmf2	200
nt	16	dseq2	
ct	16	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	24	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	1289.47		
rfl	5132.8		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

86

JRHX13C

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 29 2005	dfrq	500.075
solvent	CDC13	dn	H1
file	/export/home/~dpwr		18
data/u500/Orphans/~dof			0
heemstra/JRHX13C.f~dm		nnn	c
		id	dm
		dmf	200
ACQUISITION			
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536		
sw	8000.0	dfrq2	0
fb	4000	dn2	
bs	16	dpwr2	1
tpwr	55	dof2	0
pw	7.6	dm2	n
d1	0	dm2	c
tof	0	dmf2	200
nt	8	dseq2	
ct	8	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS	lb		0.30
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-250.1	werr	
wp	5500.7	wexp	
vs	26	wbs	
sc	0	wnt	
wc	250		
hzmm	22.00		
is	1284.25		
rfl	5132.6		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

87

JRHXL5CD

expl s2pul

SAMPLE		DEC. & VT	
date	Oct 18 2005	dfrq	500.075
solvent	CDCl3	dn	H1
file	/export/home/~dpwr	18	
data/ui500nb/Orpha~	dof	0	
ns/heemstra/JRHXL5~	dm	nnn	
CD.fid	dmm	c	
ACQUISITION		200	
sfrq	500.075	dseq	
tn	H1	dres	1.0
at	4.096	homo	n
np	65536	temp	25.0
sw	8000.0	DEC2	
fb	4000	dfrq2	0
bs	16	dn2	
tpwr	55	dpwr2	1
pw	7.6	dof2	0
dl	0	dm2	n
tof	0	dmm2	c
nt	16	dmf2	200
ct	16	dseq2	
alock	n	dres2	1.0
gain	not used	homo2	n
PROCESSING			
il	n	lb	0.30
in	n	wfile	
dp	y	proc	ft
hs	nn	fn	not used
DISPLAY		math	f
sp	-250.1		
wp	5500.7	werr	
vs	48	wexp	
sc	0	wbs	
wc	250	wnt	
hzmm	22.00		
is	677.24		
rfl	5132.6		
rfp	3630.5		
th	7		
ins	1.000		
ai	ph

89