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Lewis Base-Catalyzed, Asymmetric Aldol Additions of Methyl Ketone Enolates

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SUPPORTING INFORMATION

General Experimental

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Unity 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C) spectrometer. Spectra are referenced to residual chloroform (δ 7.26 ppm, ^{1}H; δ 77.0 ppm, ^{13}C) or tetramethylsilane (δ 0 ppm, ^{1}H; ^{13}C) in $CDCl_3$ unless otherwise stated. Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Mass spectrometry was performed by the University of Illinois Mass Spectrometry Center. Electron impact (EI) spectra were performed on a Finnigan-MAT CH-5 spectrometer, chemical ionization (CI) spectra were obtained on a VG 70-VSE spectrometer using methane as the carrier gas, FAB spectra were performed on a VG ZAB-SE spectrometer with the "magic bullet" (3/1 dithiothreitol/dithioerythritol) as matrix. Data are reported in the form of *m*/z (intensity relative to base peak = 100). Infrared spectra (IR) were recorded on a Mattson Galaxy 5020 spectrophotometer. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Optical rotations were obtained on a Jasco DIP-360 digital polarimeter and are reported as follows: $[\alpha]_D^T$ temperature (T), concentration (*c* = g/100 mL) and solvent. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

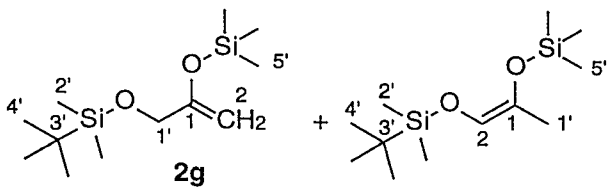
All reactions were performed in oven and/or flame dried glassware under an atmosphere of dry argon. Dichloromethane (CH_2Cl_2) was distilled from P_2O_5, THF was distilled from Na/benzophenone, toluene was distilled from Na, pentane was distilled from $LiAlH_4$, $SiCl_4$ was refluxed for 2-4 h then distilled immediatly before use. 4-Biphenylcarboxaldehdye was chromatographed and recrystallized prior to use. All other commercial reagents were purified by distillation prior to use. Diethyl ether (Et_2O) was of reagent grade and used as received; other solvents for chromatography and extraction were technical grade and distilled from the indicated drying agents: hexane, pentane, and dichloromethane ($CaCl_2$); ethyl acetate (K_2CO_3). *n*-

Butyllithium was titrated according to the method of Gilman.[1] Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Column chromatography was performed using EM Science 230-400 mesh silica gel by the method of Still.[2] Analytical high pressure liquid chromatography (HPLC) was performed on a Hewlett Packard 1090 Series II Liquid Chromatograph with a built-in photometric detector (λ = 254 nm). Chiral separations were performed using a DIACEL Chemical Industries Chiralpak AD or a Regis Naphthylleucine column. Retention times (t_R) and peak ratios were determined with a Hewlett Packard 3396 Series II integrator.

Melting points (mp) were determined in vacuum-sealed capillaries on a Thomas-Hoover apparatus and are corrected. Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr; boiling points (bp) correspond to uncorrected air-bath temperatures.

The following silyl enol ethers were prepared by kinetic trapping of the corresponding lithium enolate (as **2g** below) [(1-butylethenyl)oxy]-trimethylsilane[3] (**2b**), [(1-(2-methylpropyl)ethenyl)oxy]-trimethylsilane[4] (**2c**), [(1-(methylethyl)ethenyl)oxy]-trimethylsilane[5] (**2d**), [(1-phenylethenyl)oxy]-trimethylsilane[5] (**2f**). [(1-(1,1-Dimethylethyl)ethenyl)oxy]-trimethylsilane[5] (**2e**) was prepared by the method of Duboudin.[6] (1,1-Dimethylethyl)-dimethylsilyloxypropanone was prepared by the method of Floss.[7] Phosphoramide (*S*,*S*)-**1** was prepared as previously reported.[8]

Preparation of Trimethyl[(1-((1,1-dimethylethyl)-dimethylsilyloxymethyl)ethenyl)oxy]silane (2g) and Trimethyl[((1-methyl-2-(1,1-dimethylethyl)-dimethylsilyloxy)ethenyl)oxy]silane



2g

n-Butyllithium (27.8 mL of a 1.60 M (hexane) solution, 44.4 mmol, 1.1 equiv) was added over 3 min to a cold (–10 °C) solution of *i*-Pr_2NH (6.80 mL, 48.5 mmol, 1.2 equiv) in THF (200 mL). The solution was stirred at –10 °C for 5 min then cooled to –75 °C and TMSCl (6.2 mL, 48.5 mmol, 1.2 equiv) was added quickly. Then, (1,1-dimethylethyl)-dimethylsilyloxypropanone (7.61 g, 40.4 mmol) in THF (20 mL) was added dropwise over 30 min via cannula. Following this the now cloudy reaction mixture was warmed to 0 °C and poured into cold (0 °C) water. The layers were separated and the aqueous layer was extracted with pentane (3 × 50 mL). The organic

phases were combined, washed with water (50 mL), sat. aq. $CuSO_4$ (3 × 100 mL), water (50 mL) and brine (100 mL), dried (Na_2SO_4), filtered and concentrated to give a mixture (roughly 1/1 by ^1H NMR) of the two TMS enol ethers. Repeated column chromatography (SiO_2, hexane/benzene, 9/1) provided 2.89 g (27%) of **2g** as a clear, colorless oil, and 2.68 g (25%) of as a clear, colorless oil.

Data for **2g**:

^1H NMR: (500 MHz)

4.41 (d, J = 1.3, 1 H, HC(2)); 4.19 (d, J = 0.9, 1 H, HC(2)); 3.93 (t, J = 1.1, 2 H, $H_2C(1')$); 0.92 (s, 9 H, 3 × $H_3C(4')$); 0.21 (s, 9 H, 3 × $H_3C(5')$); 0.08 (s, 6 H, 2 × $H_3C(2')$)

^{13}C NMR: (126 MHz)

157.85 (C(1)); 89.03 (C(2)); 64.06 (C(1')); 25.87 (C(4')); 18.37 (C(3')); 0.08 (C(5')); –5.43 (C(2'))

MS: (EI, 70 eV)

260 (M^+ 3); 204 (19); 203 (100); 149 (11); 147 (34); 131 (22); 73 (19)

IR: (neat)

2957 (s); 2930 (s); 2896 (s); 2887 (s); 2858 (s); 1643 (s); 1472 (s); 1463 (m); 1389 (m); 1361 (m); 1299 (s); 1254 (s); 1126 (s); 1038 (s); 1007 (s); 911 (m); 896 (m); 845 (m); 777 (s); 698 (m); 666 (m)

TLC: R_f 0.18 (hexane/benzene, 9/1)

Analysis: $C_{12}H_{28}O_2Si_2$ (260.52)

Calculated:	C, 55.32;	H, 10.83%
Found:	C, 55.45;	H, 11.18%

Data for **Trimethyl[((1-methyl-2-(1,1-dimethylethyl)-dimethylsilyloxy)ethenyl)oxy]silane**:

^1H NMR: (500 MHz)

6.10 (t, J = 1.2, 1 H, HC(2)); 1.76 (s, 3 H, $H_3C(1')$); 0.92 (s, 9 H, 3 × $H_3C(4')$); 0.16 (s, 9 H, 3 × $H_3C(5')$); 0.10 (s, 6 H, 2 × $H_3C(2')$)

^{13}C NMR: (126 MHz)

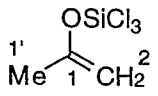
138.42 (C(1)); 126.94 (C(2)); 25.70 (C(4')); 18.20 (C(3')); 15.53 (C(1')); 0.22 (C(5')); –5.39 (C(2'))

IR: (neat)

2958 (s); 2931 (s); 2898 (m); 2859 (m); 1727 (m); 1472 (m); 1252 (s); 1229 (s); 1187 (s); 1170 (s); 1140 (m); 1106 (m); 1089 (m); 1062 (m); 1026 (m); 1006 (m); 845 (s); 780 (m); 757 (m); 505 (s)

TLC: R_f 0.06 (hexane/benzene, 9/1)

Preparation of Trichloro[(1-methylethenyl)oxy]silane (3a)



3a

Chloroacetone (6.37 mL, 80.0 mmol) was added dropwise over 15 min to a 0 °C solution of *n*-Bu_3N (19.06 mL, 80.0 mmol) and trichlorosilane (8.07 mL, 80.0 mmol) in pentane (40 mL). During the addition an oilly phase appeared, which eventaully solidified. After the addition the hetereogeneous mixture was warmed to rt and stirred for 18 h. The volatile materials were then vacuum transfered at 0.2 mmHg to a new flask. The pentane was removed at reduced pressure (200 mmHg) and the resulting oil was distilled twice through a 7.5 cm Vigreux column to give 9.65 g (63%) of the trichlorosilyl enolate (**3a**) as a clear, colorless liquid.

Data for **3a**:

bp: 63-64 °C (110 mmHg)

^{1}H NMR: (500 MHz)

4.55 (br d, J = 1.1, 1 H, HC(2)); 4.42 (br s, 1 H, HC(2)); 1.92 (s, 3 H, H_3C(1'))

^{13}C NMR: (126 MHz)

152.62 (C(1)); 96.94 (C(2)); 21.44 (C(1'))

MS: (CI, CH_4)

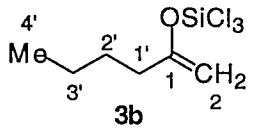
197 ($C_3H_6{}^{37}Cl_3OSi$, M+1, 15); 195 ($C_3H_6{}^{37}Cl_2{}^{35}ClOSi$, M+1, 14); 193 ($C_3H_6{}^{37}Cl{}^{35}Cl_2OSi$, M+1, 6); 191 ($C_3H_6{}^{35}Cl_3OSi$, M+1, 2); 117 (12); 99 (10); 59 (100)

HRMS: Calculated for $C_3H_6Cl_3OSi$: 190.9254; Found: 190.9250

IR: (neat)

3000 (w); 2930 (w); 1659 (s); 1376 (s); 1246 (s); 1077 (s); 998 (m); 856 (m); 714 (w); 599 (s)

Preparation of Trichloro[(1-butylethenyl)oxy]silane (3b)



3b

General Procedure I: Mercury-catalyzed formation of trichlorosilyl enolates.

Silicon tetrachloride (9.18 mL, 80.0 mmol, 2.0 equiv) was added quickly to a suspension of $Hg(OAc)_2$ (127.0 mg, 0.40 mmol, 0.01 equiv) in CH_2Cl_2 (40 mL). During the addition the mercury salt dissolved. [(1-Butylethenyl)oxy]-trimethylsilane (**2b**) (6.89 g, 40.0 mmol) was then added to the solution dropwise over 10 min and the solution was stirred at rt for an additional 50 min. During this time the reaction mixture became somewhat cloudy once again. Removal of an aliquot and ^1H NMR analysis indicated that the reaction was complete. The mixture was concentrated at at reduced pressure (100 mmHg) and the resulting oil was distilled twice through a 7.5 cm Vigreux column to give 7.76 g (83%) of the trichlorosilyl enolate **2b** as a clear, colorless oil.

Data for **2b**:

bp: 68-70 °C (15 mmHg)

^1H NMR: (500 MHz)

4.56 (br d, J = 1.9, 1 H, HC(2)); 4.41 (br s, 1 H, HC(2)); 2.16 (t, J = 7.1, 2 H, $H_2C(1')$); 1.49 (m, 2 H, $H_2C(2')$); 1.35 (sext, J = 7.5, 2 H, $H_2C(3')$); 0.92 (t, J = 7.3, 3 H, $H_3C(4')$)

^{13}C NMR: (126 MHz)

156.43 (C(1)); 95.62 (C(2)); 34.77 (C(1')); 28.41 (C(2')); 21.94 (C(3')); 13.78 (C(4'))

MS: (CI, CH_4)

239 ($C_6H_{12}{}^{37}Cl_3OSi$, M+1, 4); 237 ($C_6H_{12}{}^{37}Cl_2{}^{35}ClOSi$, M+1, 4); 235 ($C_6H_{12}{}^{37}Cl^{35}Cl_2OSi$, M+1, 10); 233 ($C_6H_{12}{}^{35}Cl_3OSi$, M+1, 11); 208 (15); 180 (100); 179 (19); 178 (22); 165 (22); 136 (12); 135 (59); 101 (59); 85 (10); 83 (52); 81 (11); 69 (12); 57 (17); 55 (34)

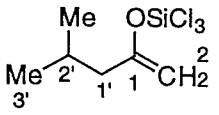
IR: (neat)

2960 (s); 2935 (s); 2875 (m); 2865 (m); 1655 (s); 1467 (m); 1330 (w); 1307 (w); 1288 (w); 1245 (s); 1195 (s); 1109 (s); 1067 (m); 1045 (s); 855 (m); 712 (w); 603 (s); 600 (s)

Analysis: $C_6H_{11}Cl_3OSi$ (233.60)

Calculated:	C, 30.85;	H, 4.75;	Cl, 45.53%
Found:	C, 30.93;	H, 5.04;	Cl, 45.54%

Preparation of Trichloro[(1-(2-methylpropyl)ethenyl)oxy]silane (3c)



3c

Following General Procedure I, $Hg(OAc)_2$ (127.0 mg, 0.4 mmol, 0.01 equiv), silicon tetrachloride (9.20 mL, 80.0 mmol, 2.0 equiv) and (1-(2-methylpropyl)ethenyloxy)-trimethylsilane (**2c**) (6.89 g, 40.0 mmol) were stirred in CH_2Cl_2 (40 mL) for 1 h. Concentration at reduced pressure (200 mmHg) provided a crude oil which was distilled twice through a 7.5 cm Vigreux column to give 6.91 g (74%) of the trichlorosilyl enolate **3c** as a clear, colorless oil.

Data for **3c**:

bp: 98-99 °C (90 mmHg)

^{1}H NMR: (500 MHz)

4.58 (br d, J = 2.1, 1 H, H(C(2)); 4.39 (br d, J = 1.1, 1 H, HC(2)); 2.01 (d, J = 7.1, 2 H, $H_2C(1')$); 1.88 (sept, J = 6.8, 1 H, HC(2')); 0.93 (d, J = 6.6, 6 H, 2 × $H_3C(3')$)

^{13}C NMR: (126 MHz)

155.36 (C(1)); 96.77 (C(2)); 44.49 (C(1')); 25.34 (C(2')); 22.09 (C(3'))

MS: (CI, CH_4)

239 ($C_6H_{12}{}^{37}Cl_3OSi$, M+1, 2); 237 ($C_6H_{12}{}^{37}Cl_2{}^{35}ClOSi$, M+1, 3); 235 ($C_6H_{12}{}^{37}Cl^{35}Cl_2OSi$, M+1, 6); 233 ($C_6H_{12}{}^{35}Cl_3OSi$, M+1, 12); 231 (23); 228 (17); 197 (11); 193 (25); 192 (24); 107 (12); 85 (38); 83 (100); 82 (74); 81 (24); 80 (16); 79 (26); 77 (28); 67 (40); 66 (12); 65 (12); 57 (15); 55 (64)

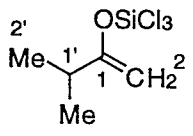
IR: (neat)

2960 (s); 2935 (m); 2910 (m); 2872 (m); 1655 (s); 1650 (s); 1465 (m); 1369 (m); 1293 (s); 1250 (s); 1217 (s); 1170 (w); 1121 (s); 1110 (s); 1048 (s); 850 (m); 716 (w); 600 (s)

Analysis: $C_6H_{11}Cl_3OSi$ (233.60)

Calculated:	C, 30.85;	H, 4.75;	Cl, 45.53%
Found:	C, 30.80;	H, 5.00;	Cl, 45.27%

Preparation of Trichloro[(1-(methylethyl)ethenyl)oxy]silane (3d)



3d

Following General Procedure I, $Hg(OAc)_2$ (74.0 mg, 0.23 mmol, 0.01 equiv), silicon tetrachloride (5.20 mL, 45.4 mmol, 2.0 equiv) and [(1-(methylethyl)ethenyl)oxy]trimethylsilane (**2d**) (3.60 g, 22.7 mmol) were stirred in CH_2Cl_2 (25 mL) for 1 h. Concentration at reduced pressure (120 mmHg) provided a crude oil which was distilled twice through a 7.5 cm Vigreux column to give 4.13 g (83%) of the trichlorosilyl enolate **3d** as a clear, colorless liquid.

Data for **3d**:

bp: 78-80 °C (75 mmHg)

^{1}H NMR: (500 MHz)

4.51 (d, J = 2.4, 1 H, HC(2)); 4.15 (dd, J = 2.4, 0.8, 1 H, HC(2)); 2.36 (sept d, J_{sept}= 6.8, J_d = 0.2, 1 H, HC(1')); 1.09 (d, J = 6.8, 6 H, 2 × H_3C(2'))

^{13}C NMR: (126 MHz)

161.63 (C(1)); 93.18 (C(2)); 33.60 (1')); 20.03 (C(2'))

MS: (CI, CH_4)

221 ($C_5H_{10}{}^{37}Cl^{35}Cl_2OSi$, M+1, 1); 219 ($C_5H_{10}{}^{35}ClOSi$, M+1, 1); 87 (98); 69 (18); 60 (100); 59 (13); 57 (22); 5 (12)

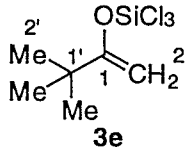
IR: (neat)

2972 (m); 2934 (m); 1647 (m); 1258 (m); 1211 (s); 1159 (m); 1119 (m); 1095 (s); 1045 (s); 851 (m); 826 (w); 601 (s)

Analysis: $C_5H_9Cl_3OSi$ (219.57)

Calculated:	C, 27.35;	H, 4.13;	Cl, 48.44%
Found:	C, 27.15;	H, 4.41;	Cl, 48.50%

Preparation of Trichloro[(1-(1,1-dimethylethyl)ethenyl)oxy]silane (3e)



3e

Following General Procedure I, $Hg(OAc)_2$ (127.0 mg, 0.4 mmol, 0.01 equiv), silicon tetrachloride (9.17 mL, 80.0 mmol, 2.0 equiv) and [(1-(1,1-dimethylethyl)ethenyl)oxy]-trimethylsilane (**2e**) (6.89 g, 40.0 mmol) were stirred in CH_2Cl_2 (40 mL) for 2 h. Concentration at reduced pressure (200 mmHg) provided a crude oil which was distilled twice through a 7.5 cm Vigreux column to give 7.60 g (81%) of the trichlorosilyl enolate **3e** as a clear, colorless liquid.

Data for **3e**:

bp: 90-91 °C (80 mmHg)

^{1}H NMR: (500 MHz)

4.47 (d, J = 2.8, 1 H, HC(2)); 4.46 (d, J = 2.7, 1 H, HC(2)); 1.11 (s, 9 H, 3 × H_3C(2'))

^{13}C NMR: (126 MHz)

164.23 (C(1)); 92.06 (C(2)); 36.23 (C(1')); 27.66 (C(2'))

MS: (CI, CH_4)

237 ($C_6H_{12}{}^{37}Cl_2{}^{35}ClOSi$, M+1, 1); 235 ($C_6H_{12}{}^{37}Cl{}^{35}Cl_2OSi$, M+1, 2); 233 ($C_6H_{12}{}^{35}Cl_3OSi$, M+1, 2); 101 (100); 87 (33); 83 (29); 71 (10); 69 (11); 61 (12); 59 (23); 57 (31); 55 (15)

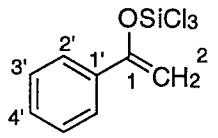
IR: (neat)

2973 (s); 2941 (m); 2913 (m); 2873 (m); 1643 (s); 1483 (m); 1363 (m); 1283 (m); 1222 (s); 1206 (m); 1170 (s); 1058 (s); 1022 (m); 853 (m); 801 (m); 691 (w); 646 (m); 601 (s)

Analysis: $C_6H_{11}Cl_3OSi$ (233.60)

Calculated:	C, 30.85;	H, 4.75;	Cl, 45.53%
Found:	C, 30.69;	H, 4.76;	Cl, 45.61%

Preparation of Trichloro[(1-phenylethenyl)oxy]silane (3f)



3f

Following General Procedure I, $Hg(OAc)_2$ (128.0 mg, 0.4 mmol, 0.01 equiv), silicon tetrachloride (9.20 mL, 80.0 mmol, 2.0 equiv) and [(1-phenylethenyl)oxy]-trimethylsilane (**2f**) (7.70 g, 40.0 mmol) were stirred in CH_2Cl_2 (40 mL) for 1 h. Concentration at reduced pressure (100 mmHg) provided a crude oil which was distilled twice through a 7.5 cm Vigreux column to give 6.98 g (69%) of the trichlorosilyl enolate **3f** as a clear, colorless oil. Note: unpon storage (>1d) this compound turns deep yellow. This does not seem to affect purity or reactivity.

Data for **3f**:

bp: 85-87 °C (3 mmHg)

^{1}H NMR: (500 MHz)

7.59-7.56 (m, 2 H, 2 × HC(2')); 7.40-7.35 (m, 3 H, 2 × H(C3') and HC(4')); 5.23 (d, J = 2.9, 1 H, HC(2)); 4.92 (d, J = 2.9, 1 H, HC(2))

^{13}C NMR: (126 MHz)

152.94 (C(1)); 134.31 (C(1')); 129.24 (C(3')), 128.46 (C(4')), 125.16(C(2')), 95.93 (C(2))

MS: (CI, CH_4)

255 ($C_8H_8{}^{37}Cl^{35}Cl_2OSi$, M+1, 1); 253 ($C_8H_8{}^{35}Cl_3OSi$, M+1, 2); 223 (38); 222 (95); 221 (92); 207 (14); 205 (14); 203 (10); 145 (25); 131 (10); 120 (23); 117 (19); 116 (13); 105 (100); 91 (22); 78 (12); 77 (70)

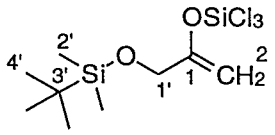
IR: (neat)

3080 (w); 3030 (w); 1631 (s); 1495 (m); 1445 (w); 1312 (m); 1296 (s); 1278 (s); 1114 (s); 1077 (s); 1042 (s); 854 (s); 828 (s); 770 (s); 734 (m); 707 (m); 684 (m); 600 (s)

Analysis: $C_8H_7Cl_3OSi$ (253.59)

Calculated:	C, 37.89;	H, 2.78;	Cl, 41.94%
Found:	C, 37.96;	H, 2.96;	Cl, 41.91%

Preparation of Trichloro[(1-((1,1-dimethylethyl)-dimethylsilyloxymethyl)ethenyl)oxy]silane (3g)



3g

Following General Procedure I, $Hg(OAc)_2$ (26.0 mg, 0.082 mmol, 0.01 equiv), silicon tetrachloride (2.8 mL, 16.4 mmol, 2.0 equiv) and trimethyl[((1,1-dimethylethyl)-dimethylsilyloxymethyl)ethenyl)oxy]silane (**2g**) (2.13 g, 8.2 mmol) were stirred in CH_2Cl_2 (8 mL) for 1 h. Concentration at reduced pressure (200 mmHg) provided a crude oil which was distilled twice through a 7.5 cm Vigreux column to give 1.70 g (65%) of the trichlorosilyl enolate **3g** as a clear, colorless oil.

Data for **3g**:

bp: 74-75 °C (3 mmHg)

^{1}H NMR: (500 MHz)

4.76 (br s, 1 H, HC(2)); 4.71 (br s, 1 H, HC(2)); 4.06 (br t, J = 1.1, 2 H, $H_2C(1')$); 0.92 (s, 9 H, 3 × $H_3C(4')$); 0.09 (s, 6 H, 2 × $H_3C(2')$)

^{13}C NMR: (126 MHz)

154.54 (C(1)); 95.29 (C(2)); 62.82 (C(1')); 25.81 (C(4')); 18.33 (C(3')); –5.46 (C(2'))

MS: (CI, CH_4)

327 ($C_9H_{20}{}^{37}Cl_3O_2Si_2$, M+1, 4); 325 ($C_9H_{20}{}^{37}Cl_2{}^{35}ClO_2Si_2$, M+1, 12); 323 ($C_9H_{20}{}^{37}Cl^{35}Cl_2O_2Si_2$, M+1, 23); 321 ($C_9H_{20}{}^{35}Cl_3O_2Si_2$, M+1, 18); 307 (24); 306 (17); 305 (77); 304 (25); 303 (97); 287 (16); 269 (18); 267 (14); 265 (22); 263 (18); 250 (10); 249 (13); 245 (10); 231 (31); 229 (31); 211 (10); 209 (22); 207 (18); 191 (22); 189 (11); 174 (17); 173 (100); 171 (72); 153 (77); 131 (56); 115 (65); 93 (11); 75 (51); 73 (74); 57 (24)

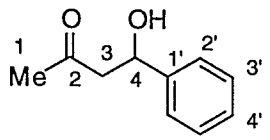
IR: (neat)

2956 (s); 2931 (s); 2895 (m); 2886 (m); 2859 (s); 1663 (s); 1472 (m); 1463 (m); 1279 (s); 1253 (s); 1231 (s); 1133 (s); 1070 (s); 1045 (s); 840 (s); 815 (m); 800 (m); 778 (s); 604 (s)

Analysis: $C_9H_{19}Cl_3O_2Si_2$ (321.78)

Calculated:	C, 33.59;	H, 5.95;	Cl, 33.05%
Found:	C, 33.89;	H, 6.27;	Cl, 33.16%

Preparation of 4-Hydroxy-4-phenyl-2-butanone (4a)



(±)-**4a**

General Procedure II: Unpromoted aldol additions of trichlorosilyl enolates.

Benzaldehyde (203 μL, 2.0 mmol) was added dropwise over 2 min to a solution of enolate **3a** (421.0 mg, 2.2 mmol, 1.1 equiv) in CH_2Cl_2 (4.0 mL) at rt. The mixture was stirred at rt for 4 h then was poured into cold (0 °C) sat. aq. $NaHCO_3$ solution and was stirred for 15 min. The two-phase mixture was filtered through Celite, then the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated. The resulting crude residue was purified by column chromatography (SiO_2, pentane/Et_2O, 1/1) to give an oil which was crystallized from hexane at –20 °C to afford 302.3 mg (92%) of (±)-**4a** as a flakey white solid.

Data for (±)-**4a**:

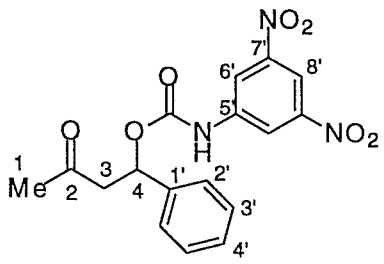
mp: 36-37 °C (hexane)

Analysis: $C_{10}H_{12}O_2$ (164.20)

Calculated:	C, 73.15;	H, 7.37%
Found:	C, 73.07;	H, 7.44%

Full characterization for (–)-**4a** can be found below.

Preparation of 4-[(3,5-Dinitrophenyl)-carbamoyloxy]-4-phenyl-2-butanone (17)



(±)-**17**

A solution of hydroxy ketone (±)-**4a** (132.0 mg, 0.80 mmol) and 3,5-dinitrobenzoylazide (229 mg, 0.97 mmol, 1.2 equiv) was heated to reflux in toluene (20 mL) for 1.5 h. The reaction mixture was cooled, concentrated and the residue was purified by column chromatography (SiO_2,

hexane/EtOAc, 2/1) to give a light yellow solid which was recrystallized from EtOAc/hexane to afford 235.0 mg (78%) of the 3,5-DNP carbamate (±)-**17** as light yellow crystals.

Data for (±)-**17**:

mp: 142 °C (dec) (EtOAc/hexane)

^{1}H NMR: (500 MHz)

8.67 (br t, J = 2.0, 1 H, HC(8')); 8.60 (br d, J = 1.5, 2 H, 2 × HC(6')); 7.48 (br s, 1 H, NH); 7.41-7.31 (m, 5 H, HAr); 6.26 (dd, J = 9.1, 4.0, 1 H, HC(4)); 3.23 (dd, J = 17.4, 9.2, 1 H, HC(3)); 2.95 (dd, J = 17.4, 4.2, 1 H, HC(3)); 2.23 (s, 3 H, H_3C(1))

^{13}C NMR: (126 MHz)

204.91 (C(2)); 151.79 (C=O); 148.78 (C(7')); 140.42 (C(1')); 138.63 (C(5')); 128.91 (C(3')); 128.40 (C(4')); 126.35 (C(2')); 117.92 (C(6')); 112.80 (C(8')); 73.67 (C(4)); 49.51 (C(3)); 30.41 (C(1))

MS: (FAB)

374 (M+1, 8); 309 (22); 307 (10); 195 (15); 155 (59); 154 (17); 153 (22); 152 (21); 147 (50); 137 (12); 135 (41); 121 (16); 119 (100)

IR: ($CHCl_3$)

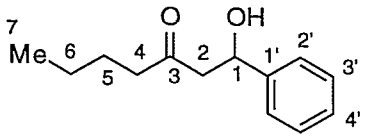
3430 (w); 3027 (w); 3022 (w); 1745 (m); 1722 (m); 1604 (w); 1549 (s); 1527 (m); 1423 (w); 1346 (m); 1242 (m); 1226 (w); 1203 (m); 896 (w); 787 (w); 772 (m); 767 (s); 758 (m); 725 (m)

TLC: R_f 0.096 (hexane/EtOAc, 3/1)

Analysis: $C_{17}H_{15}N_3O_7$ (373.32)

Calculated:	C, 54.69;	H, 4.05;	N, 11.26%
Found:	C, 54.51;	H, 4.10;	N, 11.19%

Preparation of 1-Hydroxy-1-phenyl-3-heptanone (4b)



(±)-**4b**

Following General Procedure II, enolate **3b** (514.0 mg, 2.2 mmol, 1.1 equiv), and benzaldehyde (203 μL, 2.0 mmol) were stirred in CH_2Cl_2 (4 mL) for 4 h. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 4/1) and the resulting oil was distilled (bulb-to-bulb) to give 391.5 mg (95%) of (±)-**4b** as a clear, thick oil.

Data for (±)-**4b**:

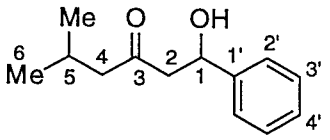
bp: 85 °C abt (5×10^{-5} mmHg)

Analysis: $C_{13}H_{18}O_2$ (206.28)

Calculated:	C, 75.69;	H, 8.79%
Found:	C, 75.61;	H, 8.68%

Full characterization for (–)-**4b** can be found below.

Preparation of 1-Hydroxy-5-methyl-1-phenyl-3-hexanone (4c)



(±)-**4c**

Following General Procedure II, enolate **3c** (514.0 mg, 2.2 mmol, 1.1 equiv), and benzaldehyde (203 μL, 2.0 mmol) were stirred in CH_2Cl_2 (4 mL) for 4 h. The crude product was purified by chromatography (SiO_2, pentane/Et_2O, 4/1) and the resulting oil was distilled (bulb-to-bulb) to give 392.4 mg (95%) of (±)-**4c** as a clear, colorless oil.

Data for (±)-**4c**:

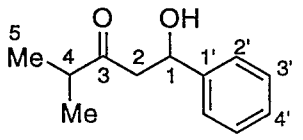
bp: 130 °C abt (0.3 mmHg)

Analysis: $C_{13}H_{18}O_2$ (206.28)

Calculated:	C, 75.69;	H, 8.79%
Found:	C, 75.55;	H, 8.98%

Full characterization for (–)-**4c** can be found below.

Preparation of 1-Hydroxy-4-methyl-1-phenyl-3-pentanone (4d)



(±)-**4d**

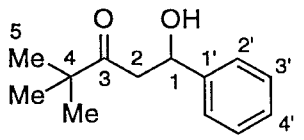
Following General Procedure II, enolate **3d** (483.0 mg, 2.2 mmol, 1.1 equiv), and benzaldehyde (203 μL, 2.0 mmol) were stirred in CH_2Cl_2 (4 mL) for 5 h. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 4/1) and the resulting oil was distilled (bulb-to-bulb) to give 359.0 mg (93%) of (±)-**4d** as a clear, colorless oil.

Data for (±)-**4d**:
bp: 100 °C abt (0.2 mmHg)
Analysis: $C_{12}H_{16}O_2$ (192.26)

Calculated:	C, 74.97;	H, 8.39%
Found:	C, 75.15;	H, 8.51%

Full characterization for (–)-**4d** can be found below.

Preparation of 1-Hydroxy-4,4-dimethyl-1-phenyl-3-pentanone (4e)



(±)-**4e**

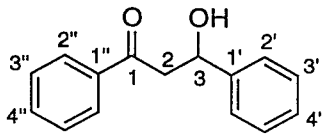
Following General Procedure II, enolate **3e** (494.0 mg, 2.1 mmol, 1.05 equiv), and benzaldehyde (203 μL, 2.0 mmol) were stirred in CH_2Cl_2 (4 mL) for 10 h. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 10/1) and the resulting oil was distilled (bulb-to-bulb) to give 395 mg (96%) of (±)-**4e** as a clear, thick oil.

Data for (±)-**4e**:
bp: 155 °C abt (0.3 mmHg)
Analysis: $C_{13}H_{18}O_2$ (206.29)

Calculated:	C, 75.69;	H, 8.80%
Found:	C, 75.39;	H, 8.96%

Full characterization for (–)-**4e** can be found below.

Preparation of 3-Hydroxy-1,3-diphenyl-1-propanone (4f)



(±)-**4f**

Following General Procedure II, enolate **3f** (560.0 mg, 2.2 mmol, 1.1 equiv), and benzaldehyde (203 μL, 2.0 mmol) were stirred in CH_2Cl_2 (4 mL) for 4 h. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 4/1) and the resulting oil was crystallized from Et_2O/pentane at –20 °C to give 410.3 mg (91%) of (±)-**4f** as a white crystals.

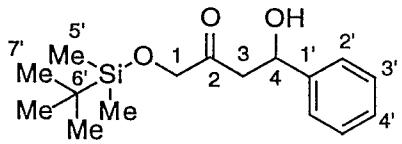
Data for (±)-**4f**:
mp: 53-54 °C (Et_2O/pentane)

Analysis: $C_{15}H_{14}O_2$ (226.27)

Calculated:	C, 79.62;	H, 6.23%
Found:	C, 79.60;	H, 6.22%

Full characterization for (–)-**4f** can be found below.

Preparation of 4-Hydroxy-1-((1,1-dimethylethyl)-dimethylsilyloxy)-4-phenyl-2-butanone (4g)



(±)-**4g**

Following General Procedure II, enolate **3g** (708.0 mg, 2.2 mmol, 1.1 equiv), and benzaldehyde (203 μL, 2.0 mmol) were stirred in CH_2Cl_2 (4 mL) for 6 h. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 4/1) to give 547.7 mg (93%) of (±)-**4g** as a clear, colorless oil.

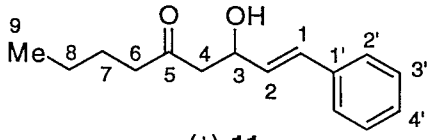
Data for (±)-**4g**:

Analysis: $C_{16}H_{20}O_2Si$ (294.47)

Calculated:	C, 65.20;	H, 8.90%
Found:	C, 65.00;	H, 9.15%

Full characterization for (–)-**4g** can be found below.

Preparation of 3-Hydroxy-1-phenyl-1-nonen-5-one (11)



(±)-**11**

Following General Procedure II, enolate **3b** (513.0 mg, 2.2 mmol, 1.1 equiv), and cinnamaldehyde (**5**) (252 μL, 2.0 mmol) were stirred in CH_2Cl_2 (4 mL) for 7 h. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 6/1) and the resulting oil was crystallized from hexane at –20 °C to give 422.8 mg (91%) of (±)-**11** as a white solid.

Data for (±)-**11**:

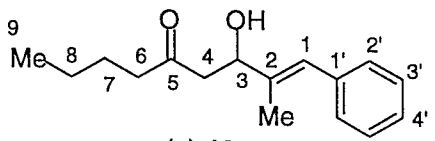
mp: 29-30 °C (hexane)

Analysis: $C_{15}H_{20}O_2$ (232.32)

Calculated:	C, 77.55;	H, 8.68%
Found:	C, 77.62;	H, 8.95%

Full characterization for (–)-**11** can be found below.

Preparation of 3-Hydroxy-2-methyl-1-phenyl-1-nonen-5-one (12)



(±)-**12**

Following General Procedure II, enolate **3b** (513.0 mg, 2.2 mmol, 1.1 equiv), and α-methylcinnamaldehyde (**6**) (280 μL, 2.0 mmol) were stirred in CH_2Cl_2 (4 mL) for 13 h. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 6/1) and the resulting oil was crystallized from hexane at –20 °C to give 453.3 mg (92%) of (±)-**12** as a white crystals.

Data for (±)-**12**:

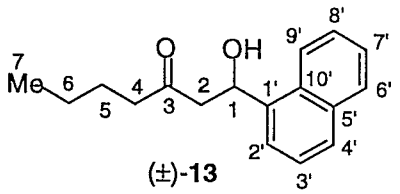
mp: 39-40 °C (hexane)

Analysis: $C_{16}H_{22}O_2$ (246.35)

Calculated:	C, 78.01;	H, 9.00%
Found:	C, 78.09;	H, 9.09%

Full characterization for (–)-**12** can be found below.

Preparation of 1-Hydroxy-1-(1-naphthyl)-3-heptanone (13)



(±)-**13**

Following General Procedure II, enolate **3b** (514.0 mg, 2.2 mmol, 1.1 equiv), and 1-naphthaldehyde (**7**) (271 μL, 2.0 mmol) were stirred in CH_2Cl_2 (4 mL) for 4 h. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 6/1) and the resulting oil was crystallized from hexane at –20 °C to give 469.3 mg (92%) of (±)-**13** as white crystals.

Data for (±)-**13**:

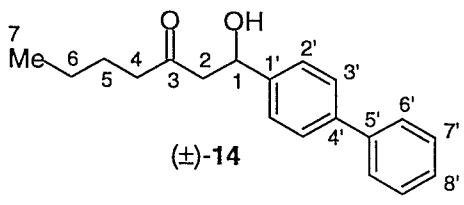
mp: 65-66 °C (hexane)

Analysis: $C_{17}H_{20}O_2$ (256.34)

Calculated:	C, 79.65;	H, 7.86%
Found:	C, 79.63;	H, 7.90%

Full characterization for (–)-**13** can be found below.

Preparation of 1-(4-Biphenyl)-1-hydroxy-3-heptanone (14)



(±)-**14**

A solution of 4-phenylbenzaldehyde (**8**) (376.4 mg, 2.0 mmol) in CH_2Cl_2 (2 mL) was added dropwise via cannula to a solution of enolate **3b** (514.0 mg, 2.2 mmol, 1.1 equiv), in

CH_2Cl_2 (2 mL) and the resulting solution was stirred at rt for 4 h. Standard workup provided a solid which was purified by chromatography (SiO_2, hexane/EtOAc, 4/1) and the resulting solid was recrystallized from hexane at to give 513.5 mg (91%) of (±)-**14** as white plates.

Data for (±)-**14**:

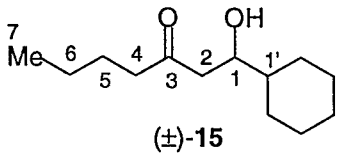
mp: 85-86 °C (hexane)

Analysis: $C_{19}H_{22}O_2$ (282.38)

Calculated:	C, 80.82;	H, 7.85%
Found:	C, 80.66;	H, 7.93%

Full characterization for (–)-**14** can be found below.

Preparation of 1-Cyclohexyl-1-hydroxy-3-heptanone (15)



(±)-**15**

Following General Procedure II, enolate **3b** (514.0 mg, 2.2 mmol, 1.1 equiv), and cyclohexanecarboxaldehyde (**9**) (242 mg, 2.0 mmol) were stirred in CH_2Cl_2 (4 mL) for 9 h. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 6/1) and the resulting solid was recrystallized from hexane at to give 394.9 mg (93%) of (±)-**15** as white crystals.

Data for (±)-**15**:

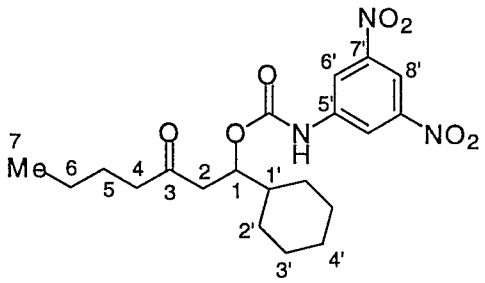
mp: 47-48 °C (hexane)

Analysis: $C_{13}H_{24}O_2$ (212.33)

Calculated:	C, 73.54;	H, 11.39%
Found:	C, 73.51;	H, 11.55%

Full characterization for (–)-**15** can be found below.

Preparation of 1-Cyclohexyl-1-(3,5-dinitrophenylcarbamoyloxy)-3-heptanone (18)



(±)-**18**

A solution of hydroxy ketone (±)-**15** (101.7 mg (0.48 mmol) and 3,5-dinitrobenzoylazide (137.0 mg, 0.57 mmol, 1.2 equiv) was heated to reflux in toluene (20 mL) for 1.5 h. The mixture was cooled to rt, concentrated and the residue puriified by column chromatography (SiO_2, hexane/EtOAc, 4/1) to give a solid which was recrystallized from EtOAc/hexane to afford 170.0 mg (84%) of the 3,5-DNP carbamate (±)-**18** as a floculent white solid.

Data for (±)-**18**:

mp: 154-155 °C

^{1}H NMR: (500 MHz)

8.70 (t, J = 2.0, 1 H, HC(8')); 8.65 (d, J = 1.6, 2 H, 2 × HC(6')); 7.10 (s, 1 H, NH); 5.23 (dt, J_d = 7.6, J_t = 5.1, 1 H, HC(1)); 2.74 (ABX, J_{AB} = 14.8, J_{AX} = 4.8, 1 H, HC(3)); 2.71 (ABX, J_{AB} = 14.8, J_{BX} = 1.0, 1 H, HC(2)); 2.50-2.40 (m, 2 H, $H_2C(4)$); 1.80-1.60 (m, 5 H); 1.55 (quint, J = 7.3, 2H, $H_2C(5)$); 1.31 (sext, J = 7.3, 2 H, $H_2C(6)$); 1.30-1.00 (m, 6 H); 0.89 (t, J = 7.3, 3 H, $H_3C(7)$)

^{13}C NMR: (126 MHz)

209.30 (C(3)); 152.61 (C=O); 148.75 (C(7')); 140.89 (C(5')); 117.92 (C(6')); 112.41 (C(8')); 75.92 (C(1)); 44.12 (C(2)); 42.87 (C(4)); 41.52 (C(5)); 28.57; 28.11; 26.11; 25.48; 25.82; 25.62; 22.18 (C(6)); 13.76 (C(7))

MS: (FAB)

422 (M+1, 7); 196 (15); 195 (100); 155 (10); 135 (20); 119 (32); 113 (11)

IR: ($CHCl_3$)

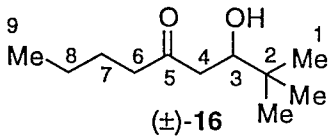
3425 (w); 3112 (w); 3033 (w); 2959 (w); 2933 (m); 2857 (w); 1741 (m); 1720 (m); 1716 (m); 1534 (s); 1526 (m); 1346 (s); 1334 (m); 1242 (w); 1115 (w); 1050 (w); 970 (w); 813 (w)

TLC: R_f 0.40 (hexane/EtOAc, 3/1)

Analysis: $C_{20}H_{27}N_2O_7$ (421.45)

Calculated:	C, 57.00;	H, 6.46;	N, 9.97%
Found:	C, 56.93;	H, 6.50;	N, 10.03%

Preparation of 3-Hydroxy-2,2-dimethyl-5-nonanone (16)



(±)-**16**

Trimethylacetaldehyde (**10**) (217 μL, 2.0 mmol) was added dropwise to a solution of enolate **3b** (514.0 mg, 2.2 mmol, 1.1 equiv) and HMPA (35 μL, 0.20 mmol, 0.1 equiv) in CH_2Cl_2 (4 mL) at rt. The mixture was allowed to stir at rt for 1 h, then was poured into cold (0 °C) sat. aq. $NaHCO_3$ solution. The resulting slurry was stirred for 15 min, then was filtered through Celite. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL). The organic phases were combined, dried (Na_2SO_4), filtered and concentrated. The resulting crude residue was purified by column chromatography (SiO_2, pentane/Et_2O, 4/1) to afford an oil which was crystallized from hexane at –20 °C to give 320.1 mg (86%) of (±)-**16** as a white solid.

Data for (±)-**16**:

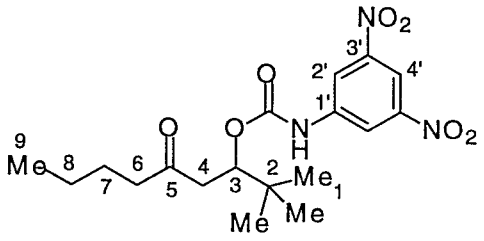
mp: 39-40.5 °C (hexane)

Analysis: $C_{11}H_{22}O_2$ (186.29)

Calculated:	C, 70.92;	H, 11.90%
Found:	C, 71.17;	H, 12.16%

Full characterization for (–)-**16** can be found below.

Preparation of 2,2-Dimethyl-3-((3,5-dinitrophenyl)carbamoyloxy)-5-nonanone (19)



(±)-**19**

A solution of hydroxyketone (±)-**16** (57.0 mg 0.31 mmol) and 3,5-dinitrobenzoylazide (87.0 mg, 0.37 mmol, 1.2 equiv) was heated to reflux in toluene (10 mL) for 2h. The reaction mixture was cooled to rt, concentrated and the residue purified by chromoatography (SiO_2, hexane/EtOAc, 4/1) to give a solid which was recrystallized from EtOAc/hexane to give 101.3 mg (84%) of the 3,5-DNP carbamate (±)-**19** as floculent needles.

Data for (±)-**19**:

mp: 145 °C (dec) (EtOAc/hexane)

^{1}H NMR: (500 MHz)

8.65 (s, 2 H, 2 × HC(2')); 7.52 (s, 1 H, HC(4')); 5.19 (dd, J = 10.0, 2.3, 1 H, HC(3)); 2.75 (dd, J = 15.9, 2.4, 1 H, HC(4)); 2.63 (dd, J = 15.9, 10.1, 1 H, H(C4)); 2.57 (dt, J_d = 17.0, J_t = 7.5, 1 H, HC(6)); 2.46 (dt, J_d = 17.0, J_t = 7.3, 1 H, HC(6)); 1.56 (quint, J = 7.2, 2 H, $H_2C(7)$); 1.31 (sext, J = 7.4, 2 H, $H_2C(8)$); 0.89 (t, J = 7.5, 3 H, $H_3C(9)$)

^{13}C NMR: (126 MHz)

209.13 (C(5)); 152.58 (OC(=O)N); 148.81 (C(3')); 140.81 (C(1')); 117.89 (C(2')); 112.50 (C(4')); 78.70 (C(3)); 43.18 (C(4)); 42.71 (C(6)); 34.76 (C(2)); 25.71 (C(1)); 25.66 (C(7)); 22.19 (C(8)); 13.78 (C(9))

MS: (FAB)

396 (M+1, 13); 279 (10); 170 (11); 169 (100); 119 (12)

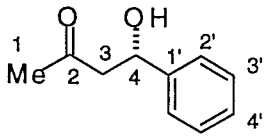
IR: ($CHCl_3$)

3425 (w); 3306 (w); 3118 (w); 3030 (w); 2966 (m); 2937 (w); 1738 (m); 1712 (m); 1653 (w); 1632 (w); 1548 (s); 1526 (m); 1478 (w); 1423 (m); 1368 (m); 1346 (s); 1334 (m); 1275 (w); 1243 (m); 1212 (w); 1203 (m); 1079 (m); 966 (m); 814 (m); 724 (w)

Analysis: $C_{18}H_{25}N_3O_7$ (395.4114)

Calculated:	C, 54.68;	H, 6.37;	N, 10.63%
Found:	C, 54.58;	H, 6.35;	N, 10.38%

Preparation of (-)-(*S*)-4-Hydroxy-4-phenyl-2-butanone (-)-(4a)



(–)-**4a**

General Procedure III: Aldol additions of trichlorosilyl enolates catalyzed by (*S*,*S*)-1.

Trichlorosilyl enolate **3a** (421.3 mg, 2.2 mmol, 1.1 equiv) was added quickly to a cold (–74 °C) solution of (*S*,*S*)-**1** (37.3 mg, 0.1 mmol, 0.05 equiv) in CH_2Cl_2 (2 mL). A soltuion of benzaldehyde (203 μL, 2.0 mmol) in CH_2Cl_2 (2 mL) was cooled to –78 °C and was added quickly, via a short cannula to the first solution. During the addition the temperature rose to –67 °C. The reaction mixture was stirred at –75 °C for 2 h, then was quickly poured into cold (0 °C) sat. aq. $NaHCO_3$ solution and the slurry was stirred for 15 min. The two-phase mixture was filtered through Celite, the phases separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The organic phases were combined, dried Na_2SO_4, filtered and concentrated. The resulting residue was purified by column chromatography (SiO_2, pentane/Et_2O, 1/1) to give 321.6 mg (98%) of (–)-**4a**[9] as a clear, colorless oil.

Data for (–)-**4a**:

^{1}H NMR: (500 MHz)

7.36-7.27 (m, 5H, HAr); 5.15 (dd, J = 9.1, 3.3, 1H, HC(4)); 3.30 (s, 1H, OH); 2.88 (ABX, J_{AB} = 17.5, J_{AX} = 9.5, 1H, HC(3)); 2.81 (ABX, J_{AB} = 17.5, J_{BX} = 2.7, 1H, HC(4)); 2.19 (s, 3H, H_3C(1))

^{13}C NMR: (126 MHz)

209.09 (C(2)); 142.71 (C(1')); 128.53 (C(3')); 127.66 (C(4')); 125.59 (C(2')); 69.81 (C(4)); 51.92 (C(3)); 30.71 (C(1))

MS: (CI, CH_4)

164 (M^+, 19); 147 (30); 146 (18); 107 (100); 106 (21); 105 (15); 79 (26); 59 (27)

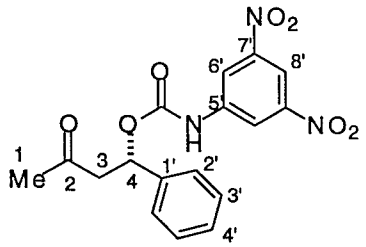
IR: (neat)

3466 (m); 3424 (m); 2910 (w); 1710 (s); 1417 (m); 1361 (m); 1062 (m); 756 (m); 701 (s)

TLC: R_f 0.16 (hexane/EtOAc, 3/1)
Optical Rotation: $[\alpha]_D^{24}$ –51.4 ° (c = 1.47, $CHCl_3$)
Analysis: $C_{10}H_{22}O_2$ (164.20)

Calculated:	C, 73.15;	H, 7.37%
Found:	C, 72.97;	H, 7.43%

Preparation of (-)-(*S*)-4-(3,5-Dinitrophenylcarbamoyloxy)-4-phenyl-2-butanone (-)-(17)

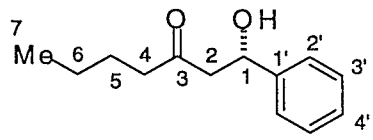


(–)-**17**

Hydroxyketone (–)-**4a** (20.1 mg, 0.12 mmol) and 3,5-dinitrobenzoylazide (37.7 mg, 0.16 mmol, 1.3 equiv) were heated to reflux in toluene (10 mL) for 2h. The solution was then cooled, concentrated, and the residue purified by column chromatography (SiO_2, hexane/EtOAc, 3/1) to give 37.7 mg (84%) of the 3,5-DNP carbamate (–)-**17** as a slightly yellow solid.

Data for (–)-**17**:
Optical Rotation: $[\alpha]_D^{24}$ –30.0 ° (c = 0.90, $CHCl_3$)
HPLC: t_R 14.42 min (*R*-**17**) (6.4%); t_R 23.25 min (*S*-**17**) (93.6%) (Naphthylleucine, hexane/*i*-PrOH, 90/10; 1.0 mL min^{-1})
Full characterization for (±)-**17** can be found above.

Preparation of (-)-(*S*)-1-Hydroxy-1-phenyl-3-heptanone (-)-(4b)



(–)-**4b**

Following General Procedure III: enolate **3b** (514.0 mg, 2.2 mmol, 1.1 equiv), benzaldehyde (203 µL, 2.0 mmol) and (*S*,*S*)-**1** (37.1 mg, 0.1 mmol, 0.05 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 2 hours. The crude product was purified by chromatography (SiO_2, pentane/Et_2O, 4/1) to give 402.0 mg (98%) of (–)-**4b**[10] as a clear, colorless oil.

Data for (–)-**4b**:

^{1}H NMR: (500 MHz)

7.36-7.25 (m, 5 H, HAr); 5.15 (dd, J = 9.0, 3.3, 1 H, HC(1)); 3.43 (br s, 1 H, OH); 2.84 (ABX, J_{AB} = 17.4, J_{AX} = 9.6, 1 H, HC(2)); 2.78 (ABX, J_{AB} = 17.4, J_{BX} = 2.8, 1 H, HC(2)); 2.42 (t, J = 7.3, 2 H, $H_2C(4)$); 1.56 (quint, J = 7.5, 2 H, $H_2C(5)$); 1.30 (sext, J = 7.4, 2 H, $H_2C(6)$); 0.90 (t, J = 7.3, 3 H, $H_3C(7)$)

^{13}C NMR: (126 MHz)

211.71 (C(3)); 142.83 (C(1')); 128.49 (C(3')); 127.59 (C(4')); 125.59 (C(2')); 69.89 (C(1)); 50.95 (C(2)); 43.37 (C(4)); 25.56 (C(5)); 22.18 (C(6)); 13.75 (C(7))

MS: (CI, CH_4)

206 (M^+, 7); 189 (12); 149 (11); 107 (46); 101 (30); 85 (100); 79 (11)

IR: (neat)

3440 (m); 3032 (m); 2958 (s); 2933 (s); 2873 (s); 1709 (s); 1495 (m); 1466 (m); 1454 (s); 1406 (s); 1371 (m); 1333 (m); 1291 (m); 1260 (w); 1127 (m); 1068 (m); 1030 (m); 1008 (m); 757 (m); 701 (s)

TLC: R_f 0.30 (hexane/EtOAc, 3/1)

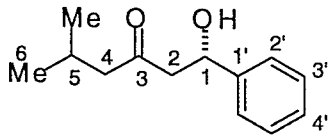
Optical Rotation: $[\alpha]_D^{24}$ –55.3 ° (c = 1.20, $CHCl_3$)

HPLC: t_R (*R*)-**4b** 18.42 min (7.7%); t_R (*S*)-**4b** 21.90 min (92.3%) (Chiralpak AD, hexane/EtOH, 96/4; 1.0 mL min^{-1})

Analysis: $C_{13}H_{18}O_2$ (206.28)

Calculated:	C, 75.69;	H, 8.79%
Found:	C, 75.65;	H, 8.94%

Preparation of (-)-(*S*)-1-Hydroxy-5-methyl-1-phenyl-3-hexanone (-)-(4c)



(–)-**4c**

Following General Procedure III: enolate **3c** (514 mg, 2.2 mmol, 1.1 equiv), benzaldehyde (203 µL, 2.0 mmol) and (*S*,*S*)-**1** (36.9 mg, 0.1 mmol, 0.05 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 2 hours. The crude product was purified by chromatography (SiO_2, pentane/Et_2O, 4/1) to give 395.0 mg (95%) of (–)-**4c**[11] as a clear, colorless oil.

Data for (–)-**4c**:

^{1}H NMR: (500 MHz)

7.36-7.26 (m, 5 H, HAr); 5.15 (dd, J = 9.2, 3.3, 1 H, HC(1)); 3.35 (br s, 1 H, OH); 2.82 (ABX, J_{AB} = 17.5, J_{AX} = 9.4, 1 H, HC(2)); 2.76 (ABX, J_{AB} 17.5, J_{BX} = 2.8, 1 H, HC(2)); 2.30 (d, J = 6.8, 2 H, H_2C(4)); 2.14 (nonet, J = 6.8, 1 H, HC(5)); 0.91 (d, J = 6.5, 6 H, 2 × H_3C(6))

^{13}C NMR: (126 MHz)

211.32 (C(3)); 142.84 (C(1')); 128.47 (C(3')); 127.58 (C(4')); 125.60 (C(2')); 69.84 (C(1)); 52.58 (C(2)); 51.45 (C(4)); 24.44 (C(5)); 22.46 (C(6))

MS: (CI, CH_4)

206 (M^+, 6); 107 (30); 101 (17); 85 (100); 57 (12)

IR: (neat)

3435 (s); 2957 (s); 2931 (s); 2899 (m); 2872 (s); 1708 (s); 1698 (s); 1467 (m); 1453 (s); 1403 (s); 1386 (s); 1367 (s); 1333 (m); 1295 (m); 1068 (m); 1044 (s); 755 (s); 701 (s)

TLC: R_f 0.38 (hexane/EtOAc, 3/1)

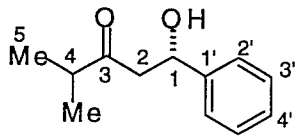
Optical Rotation: $[\alpha]_D^{24}$ –50.5 ° (c = 1.78, $CHCl_3$)

HPLC: t_R 17.69 (*R*)-**4c** min (9.3%);t_R (*S*)-**4c** 21.13 min (90.7%) (Chiralpak AD, hexane/EtOH, 96/4; 1.0 mL min^{-1})

Analysis: $C_{13}H_{18}O_2$ (206.28)

Calculated:	C, 75.69;	H, 8.79%
Found:	C, 75.47;	H, 8.93%

Preparation of (-)-(*S*)-1-Hydroxy-4-methyl-1-phenyl-3-pentanone (-)-(4d)



(–)-**4d**

Following General Procedure III: enolate **3d** (483.0 mg, 2.2 mmol, 1.1 equiv), benzaldehyde (203 µL, 2.0 mmol) and (*S*,*S*)-**1** (36.9 mg, 0.1 mmol, 0.05 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 2 hours. The crude product was purified by chromatography (SiO_2, pentane/Et_2O, 4/1) to give 375.0 mg (97%) of (–)-**4d** as a clear, colorless oil.

Data for (–)-**4d**:

^{1}H NMR: (500 MHz)

7.38-7.24 (m, 5 H, HAr); 5.15 (dd, J = 8.4, 5.7, 1 H, HC(1)); 3.45 (br s, 1 H, OH); 2.88 (ABX, J_{AB} = 15.0, J_{AX} = 9.2, 1 H, HC(2)); 2.84 (ABX, J_{AB} = 15.0, J_{BX} = 6.6, 1 H, HC(2)); 2.59 (sept, J = 7.0, 1 H, HC(4)); 1.10 (d, J = 7.0, 6 H, 2 × H_3C(5))

^{13}C NMR: (126 MHz)

215.26 (C(3)); 142.92 (C(1')); 128.47 (C(3')); 127.57 (C(4')); 125.59 (C(2')); 69.94 (C(1)); 48.70 (C(2)); 41.49 (C(4)); 17.82 (C(5))

MS: (CI, CH_4)

192 (M^+, 10); 149 (30); 107 (50); 87 (20); 79 (10); 71 (100)

IR: (neat)

3430 (s); 2971 (m); 1708 (s); 1651 (m); 1646 (m); 1466 (m); 1454 (m); 1067 (m); 1038 (m); 757 (s); 701 (s)

TLC: R_f 0.35 (hexane/EtOAc, 3/1)

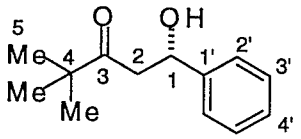
Optical Rotation: $[\alpha]_D^{24}$ –56.6 ° (c = 3.64, $CHCl_3$)

HPLC: t_R (*R*)-**4d** 16.28 min (9.0%); t_R (*S*)-**4d** 23.00 min (91.0%) (Chiralpak AD, hexane/EtOH, 96/4; 1.0 mL min^{-1})

Analysis: $C_8H_{16}O_2$ (192.26)

Calculated:	C, 74.97;	H, 8.39%
Found:	C, 74.69;	H, 8.50%

Preparation of (-)-(*S*)-1-Hydroxy-4,4-dimethyl-1-phenyl-3-pentanone (-)-(4e)



(–)-**4e**

Following General Procedure III: enolate **3e** (514.0 mg, 2.2 mmol, 1.1 equiv), benzaldehyde (203 μL, 2.0 mmol) and (*S*,*S*)-**1** (37.3 mg, 0.1 mmol, 0.05 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 2 hours. The crude product was purified by chromatography (SiO_2, pentane/Et_2O, 4/1) and the resluting oil was distilled (bulb-to-bulb) to give 391.1 mg (95%) of (–)-**4e**[12] as a clear, colorless oil.

Data for (–)-**4e**:

bp: 105 °C abt (0.1 mmHg)

^{1}H NMR: (500 MHz)

7.38-7.26 (m, 5 H, HAr); 5.13 (t, J = 6.1, 1 H, HC(1)); 3.58 (br s, 1 H, OH); 2.88 (d, J = 6.2, 2 H, $H_2C(2)$); 1.13 (s, 9 H, 3 × $H_3C(5)$)

^{13}C NMR: (126 MHz)

216.91 (C(3)); 143.03 (C(1')); 128.47 (C(3')); 127.56 (C(4')); 125.64 (C(2')); 70.06 (C(1)); 45.43 (C(2)); 44.36 (C(4)); 26.10 (C(5))

MS: (EI, 70 eV)

207 (M+1, 1); 206 (8); 149 (29); 131 (8); 107 (100); 105 (11); 104 (11); 85 (10); 79 (28); 77 (24); 57 (48)

IR: (neat)

3447 (m); 2970 (m); 2934 (w); 1702 (s); 1478 (m); 1454 (m); 1367 (m); 1086 (m); 1072 (m); 1056 (m); 701 (s)

TLC: R_f 0.41 (hexane/EtOAc, 3/1)

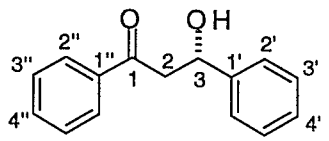
Optical Rotation: $[\alpha]_D^{24}$ –33.9 ° (c = 2.27, $CHCl_3$)

HPLC: t_R (*R*)-**4e** 11.68 min (24.0%); t_R (*S*)-**4e** 15.26 min (76.0%) (Chiralpak AD, hexane/EtOH, 96/4; 1.0 mL min^{-1})

Analysis: $C_{13}H_{18}O_2$ (206.29)

Calculated:	C, 75.69;	H, 8.79%
Found:	C, 75.59;	H, 8.77%

Preparation of (-)-(*S*)-3-Hydroxy-1,3-diphenyl-1-propanone (-)-(4f)



(–)-**4f**

Following General Procedure III: enolate **3f** (507.0 mg, 2.2 mmol, 1.1 equiv), benzaldehyde (203 μL, 2.0 mmol) and (*S*,*S*)-**1** (37.0 mg, 0.1 mmol, 0.05 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 2 hours. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 4/1) to give 421.3 mg (93%) of (–)-**4f**[13] as a clear, colorless oil.

Data for (–)-**4f**:

^{1}H NMR: (500 MHz)

7.96 (d, J = 7.3, 2 H, 2 × HC(2'')); 7.59 (t, J = 7.5, 1 H, HC(4'')); 7.49-7.43 (m, 4 H, 2 × HC(3'') + 2 × HC(2')); 7.39 (t, J = 7.3, 2 H, 2 × HC(3')); 7.31 (t, J = 7.5, 1 H, HC(4')); 5.35 (dd, J = 6.8, 5.5, 1 H, HC(1)); 3.61 (br s, 1 H, OH); 3.38 (m, 2 H, H_2C(2))

^{13}C NMR: (126 MHz)

200.17 (C(3)); 142.92 (C(1')); 136.52 (C(1'')); 133.63 (C(4')); 128.68 (C(2')); 128.54 (C(3')); 128.13 (C(2'')); 127.65 (C(4')); 125.73 (C(3''); 69.97 (C(1)); 47.34 (C(2))

MS: (CI, CH_4)

226 (M^+, 8); 209 (15); 208 (11); 121 (63); 120 (13); 107 (53); 106 (16); 105 (100); 79 (10)

IR: ($CHCl_3$)

3524 (m); 3064 (m); 3030 (m); 3013 (m); 1677 (s); 1600 (m); 1580 (m); 1545 (w); 1495 (w); 1407 (m); 1356 (m); 1331 (m); 1303 (m); 1228 (m); 1203 (m); 1160 (w); 1081 (w); 1001 (w); 771 (w); 700 (s)

TLC: R_f 0.27 (hexane/EtOAc, 3/1)

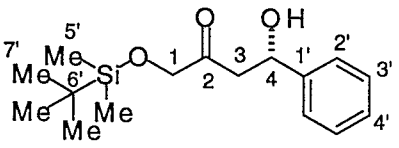
Optical Rotation: $[\alpha]_D^{24}$ –37.2 ° (c = 1.28, $CHCl_3$)

HPLC: t_R (*R*)-**4f** 33.72 min (25.5%); t_R (*S*)-**4f** 37.0 min (74.48%) (Chiralpak AD, hexane/EtOH, 94/6; 1.0 mL min^{-1})

Analysis: $C_{15}H_{14}O_2$ (226.27)

Calculated:	C, 79.62;	H, 6.23%
Found:	C, 79.46;	H, 6.11%

Preparation of (-)-(*S*)-4-Hydroxy-1-((1,1-dimethylethyl)-dimethylsilyloxy)-4-phenyl-2-butanone (-)-(4g)



(–)-**4g**

Following General Procedure III: enolate **3g** (708.0 mg, 2.2 mmol, 1.1 equiv), benzaldehyde (203 μL, 2.0 mmol) and (*S*,*S*)-**1** (37.1 mg, 0.1 mmol, 0.05 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 2 hours. The crude product was puridied by chromatography (SiO_2, hexane/EtOAc, 4/1) to give 554.0 mg (94%) of (–)-**4g** as a clear, colorless oil.

Data for (–)-**4g**:

^{1}H NMR: (500 MHz)

7.37-7.26 (m, 5 H, HAr); 5.18 (dd, J = 9.0, 3.5, 1 H, HC(4)); 4.19 (d, J = 1.0, 2 H, $H_2C(1)$); 3.24 (br s, 1 H, OH); 2.95 (ABX, J_{AB} = 17.3, J_{AX} = 9.5, 1 H, HC(3)); 2.89 (ABX, J_{AB} = 17.3, J_{BX} = 3.0, 1 H, HC(3)); 0.91 (s, 9 H, 3 × $H_3C(7')$); 0.08 (s, 6 H, 2 × $H_3C(5')$)

^{13}C NMR: (126 MHz)

211.04 (C(2)); 142.85 (C(1')); 128.56 (C(3')); 127.70 (C(4')); 125.62 (C(2')); 69.78 (C(4)); 69.99 (C(1)); 47.01 (C(3)); 25.73 (C(7')); 18.26 (C(6')); –5.55 (C(5'))

MS: (CI, CH_4)

294 (M^+, 1); 278 (17); 277 (64); 261 (28); 219 (10); 217 (18); 174 (12); 173 (75); 146 (12); 145 (77); 133 (17); 132 (13); 131 (100); 117 (12); 115 (13); 107 (66); 105 (18); 89 (72); 79 (72); 79 (17); 75 (13); 73 (15); 59 (52)

IR: (neat)

3448 (s); 2953 (s); 2929 (s); 2894 (s); 2886 (s); 1722 (s); 1472 (s); 1463 (m); 1454 (m); 1407 (m); 1389 (m); 1361 (m); 1255 (s); 1189 (m); 1157 (s); 1104 (s); 1029 (m); 838 (s); 816 (m); 779 (s); 755 (m); 700 (s)

TLC: R_f 0.41 (hexane/EtOAc, 3/1)

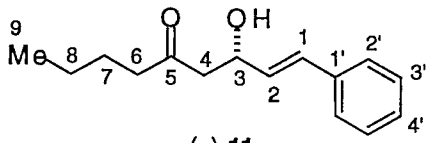
Optical Rotation: $[\alpha]_D^{24}$ –37.2 ° (c = 1.18, $CHCl_3$)

HPLC: t_R (*R*)-**4g** 7.59 min (7.0%); t_R (*S*)-**4g** 10.54 min (93.0%) (Chiralpak AD, hexane/EtOH, 96/4; 1.0 mL min^{-1})

Analysis: $C_{16}H_{20}O_3Si$ (294.47)

Calculated:	C, 65.26;	H, 8.90%
Found:	C, 65.22;	H, 9.05%

Preparation of (-)-(*S*)-3-Hydroxy-1-phenyl-1-nonen-5-one (-)-(11)



(–)-**11**

Following General Procedure III: enolate **3b** (513.0 mg, 2.2 mmol, 1.1 equiv), cinnamaldehyde (**5**) (252 µL, 2.0 mmol) and (*S*,*S*)-**1** (36.7 mg, 0.1 mmol, 0.05 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 2 hours. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 6/1) to give 437.3 mg (94%) of (–)-**11** as a clear, colorless oil.

Data for (–)-**11**:

^{1}H NMR: (500 MHz)

7.36 (d, J = 7.1, 2 H, 2 × HC(2')); 7.31 (t, J = 7.3, 2 H, 2 × HC(3')); 7.25 (d, J = 5.5, 1 H, HC(4')); 6.63 (d, J = 15.9, 1 H, HC(1)); 6.20 (dd, J = 15.9, 6.0, 1 H, HC(2)); 4.75 (q, J = 5.8, 1 H, HC(3)); 3.22 (br s, 1 H, OH); 2.74-2.71 (m, 2 H, H_2C(4)); 2.45 (t, J = 7.4, 2 H, H_2C(6)); 1.58 (quint, J = 7.4, 2 H, H_2C(7)); 1.32 (sext, J = 7.5, 2 H, H_2C(8)); 0.91 (t, J = 7.3, 3 H, H_3C(9))

^{13}C NMR: (126 MHz)

211.54 (C(5)); 136.51 (C(1')); 130.38 (C(1)); 130.19 (C(2)); 128.53 (C(3')); 127.68 (C(4')); 126.44 (C(2')); 68.48 (C(3)); 48.90 (C(4)); 43.42 (C(6)); 25.59 (C(7)); 22.19 (C(8)); 13.75 (C(9))

MS: (CI, CH_4)

232 (M^+, 10); 215 (11); 133 (56); 104 (10); 85 (100); 57 (15)

IR: (neat)

3450 (s); 3026 (s); 2968 (s); 2941 (s); 2873 (s); 1710 (s); 1495 (m); 1450 (s); 1380 (s); 1114 (s); 1070 (s); 968 (s); 750 (s); 695 (s)

TLC: R_f 0.32 (hexane/EtOAc, 3/1)

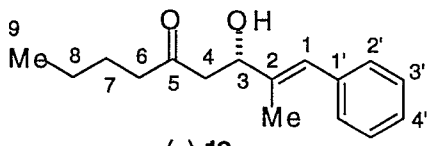
Optical Rotation: $[\alpha]_D^{24}$ –19.1 ° (c = 1.30, $CHCl_3$)

HPLC: t_R (*R*)-**11** 17.19 min (8.0%); t_R (*S*)-**11** 22.77 min (92.0%) (Chiralpak AD, hexane/EtOH, 92/8; 1.0 mL min^{-1})

Analysis: $C_{15}H_{20}O_2$ (232.32)

Calculated:	C, 77.55;	H, 8.68%
Found:	C, 77.69;	H, 8.95%

Preparation of (-)-(*S*)-3-Hydroxy-2-methyl-1-phenyl-1-nonen-5-one (-)-(12)



(–)-**12**

Following General Procedure III: enolate **3b** (513.0 mg, 2.2 mmol, 1.1 equiv), α-methyl-cinnamaldehyde (**6**) (280 μL, 2.0 mmol) and (*S*,*S*)-**1** (36.8 mg, 0.1 mmol, 0.05 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 2 hours. The crude product was purified by chromatographed (SiO_2, hexane/EtOAc, 6/1) to give 468.0 mg (95%) of (–)-**12** as a clear, colorless oil.

Data for (–)-**12**:

^{1}H NMR: (500 MHz)

7.33 (t, J = 7.4, 2 H, 2 × HC(2')); 7.26 (d, J = 7.1, 2 H, 2 × HC(3')); 7.21 (t, J = 7.3, 1 H, HC(4')); 6.57 (s, 1 H, HC(1)); 4.63 (dd, J = 7.7, 4.3, 1 H, HC(3)); 3.14 (br s, 1 H, OH); 2.77-2.67 (m, 2 H, H_2C(4)); 2.48 (t, J = 7.5, 2 H, H_2C(6)); 1.88 (d, J = 1.3, 3 H, H_3CC(2)); 1.59 (pent, J = 7.4, 2 H, H_2C(7)); 1.33 (sext, J = 7.5, 2 H, H_2C(8)); 0.92 (t, J = 7.3, 3 H, H_3C(9))

^{13}C NMR: (126 MHz)

211.91 (C(5)); 138.36 (C(2)); 137.39 (C(1')); 128.95 (C(3')); 128.09 (C(2')); 126.50 (C(4')); 125.66 (C(1)); 73.08 (C(3)); 47.66 (C(4)); 43.52 (C(6)); 25.63 (C(7)); 22.24 (C(8)); 13.97 (H_3CC(2)); 13.79 (C(9))

MS: (CI, CH_4)

246 (M^+, 17); 147 (55); 146 (19); 118 (14); 85 (100); 57 (17)

IR: (neat)

3450 (s); 2958 (s); 2932 (s); 2872 (s); 1709 (s); 1492 (m); 1465 (m); 1406 (m); 1380 (m); 1328 (m); 1127 (m); 1097 (m); 1075 (m); 1011 (s); 750 (s); 700 (s)

TLC: R_f 0.40 (hexane/EtOAc, 3/1)

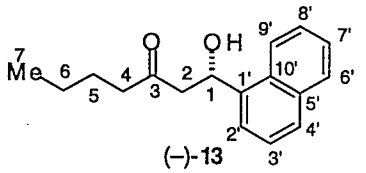
Optical Rotation: $[\alpha]_D^{24}$ –13.4 ° (c = 1.38, $CHCl_3$)

HPLC: t_R (*R*)-**12** 11.38 min (4.4%); t_R (*S*)-**12** 18.38 min (95.6%) (Chiralpak AD, hexane/EtOH, 92/8; 1.0 mL min^{-1})

Analysis: $C_{16}H_{22}O_2$ (246.35)

Calculated:	C, 87.01;	H, 9.00%
Found:	C, 78.10;	H, 8.94%

Preparation of (-)-(*S*)-1-Hydroxy-1-(1-naphthyl)-3-heptanone (-)-(13)



(–)-13

Following General Procedure III: enolate **3b** (514.0 mg, 2.2 mmol, 1.1 equiv), 1-naphthaldehyde (**7**) (271 μL, 2.0 mmol) and (*S*,*S*)-**1** (37.0 mg, 0.1 mmol, 0.05 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 2 hours. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 6/1) to give 472.0 mg (92%) of (–)-**13** as a clear, colorless thick oil.

Data for (–)-**13**:

^{1}H NMR: (500 MHz)

8.00 (d, J = 8.2, 1 H, HC(2')); 7.88 (d, J = 7.7, 1 H, HC(6')); 7.79 (d, J = 8.2, 1 H, HC(4')); 7.70 (d, J = 7.1, 1 H, HC(9')); 7.55-7.45 (m, 3 H, HC(3'), HC(7'), HC(8')); 5.96 (dd, J = 8.2, 3.5, 1 H, HC(1)); 3.00-2.91 (m, 2 H, H_2C(2)); 2.45 (t, J = 7.4, 2 H, H_2C(4)); 1.59 (quint, J = 7.5, 2 H, H_2C(5)); 1.32 (sext, J = 7.5, 2 H, H_2C(6)); 0.91 (t, J = 7.3, 3 H, H_3C(7))

^{13}C NMR: (126 MHz)

211.84 (C(3)); 138.36 (C(1')); 133.75 (C(5')); 129.86 (C(10')); 129.01 (C(6')); 128.03 (C(4')); 126.18 (C(6')); 125.55 (C(7')); 125.53 (C(3')); 122.96 (C(9')); 122.73 (C(2')); 66.76 (C(1)); 50.30 (C(2)); 43.41 (C(4)); 25.64 (C(5)); 22.22 (C(6)); 13.78 (C(7))

MS: (CI, CH_4)

256 (M^+, 29); 158 (10); 157 (100); 156 (71); 155 (15); 129 (40); 128 (28); 101 (17); 85 (82); 58 (20); 57 (11)

IR: (neat)

3450 (s); 2956 (s); 2930 (s); 2872 (s); 1710 (s); 1510 (m); 1465 (m); 1405 (m); 1394 (m); 1377 (s); 1306 (m); 1267 (m); 1163 (m); 1101 (m); 1050 (m); 1017 (m); 800 (s); 780 (s); 617 (s)

TLC: R_f 0.41 (hexane/EtOAc, 3/1)

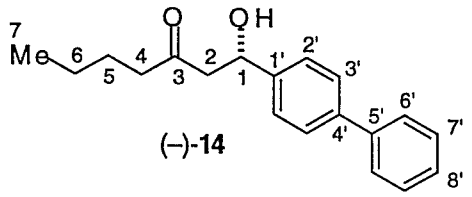
Optical Rotation: $[\alpha]_D^{24}$ –76.2 ° (c = 1.15, $CHCl_3$)

HPLC: t_R (*R*)-**13** 12.62 min (7.1%); t_R (*S*)-**13** 14.24 min (92.9%) (Chiralpak AD, hexane/EtOH, 92/8; 1.0 mL min^{-1})

Analysis: $C_{17}H_{20}O_2$ (256.34)

Calculated:	C, 79.56;	H, 7.86%
Found:	C, 79.77;	H, 7.74%

Preparation of (-)-(*S*)-1-Hydroxy-1-(4-biphenyl)-3-heptanone (-)-(14)



(–)-14

Following General Procedure III: enolate **3b** (514.0 mg, 2.2 mmol, 1.1 equiv), 4-biphenylcarboxaldehyde (**8**) (376 mg, 2.0 mmol) and (*S*,*S*)-**1** (37.0 mg, 0.1 mmol, 0.05 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 2 hours. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 4/1) to give 538.3 mg (95%) of (–)-**14** as a floculent white solid.

Data for (–)-**14**:

^{1}H NMR: (500 MHz)

7.60-7.55 (m, 4 H); 7.46-7.38 (m, 4 H); 7.35 (tt, J = 7.3, 1.5, 1 H, HC(8')); 5.21 (dd, J = 8.8, 3.5, 1 H, HC(1)); 3.40 (br s, 1 H, OH); 2.89 (ABX, J_{AB} = 17.4, J_{AX} = 9.6, 1 H, HC(2)); 2.84 (ABX, J_{AB} = 17.4, J_{BX} = 2.8, 1 H, HC(2)); 2.46 (t, J = 7.5, 2 H, H_2C(4)); 1.58 (quint, J = 7.3, 2 H, H_2C(5)); 1.32 (sext, J = 7.5, 2 H, H_2C(6)); 0.91 (t, J = 7.3, 3 H, H_3C(7))

^{13}C NMR: (126 MHz)

211.74 (C(3)); 141.86 (C(5')); 140.79 (C(1')); 128.77; 127.31 127.88; 127.08; 126.08; 69.70 (C(1)); 50.90 (C(2)); 43.42 (C(4)); 25.62 (C(5)); 22.22 (C(6)); 13.79 (C(7))

MS: (CI, CH_4)

282 (M^+, 6); 265 (17); 184 (14); 183 (100); 182 (32); 181 (13); 155 (20); 101 (34); 85 (36); 83 (12); 58 (11); 57 (13); 55 (12)

IR: ($CHCl_3$)

3600 (w); 3028 (m); 3013 (s); 2961 (s); 2934 (m); 2902 (w); 1703 (s); 1487 (m); 1406 (m); 1383 (m); 1227 (m); 1215 (w); 1076 (m); 1041 (w); 1008 (m); 839 (w); 786 (m); 772 (s); 748 (s); 727 (m); 699 (s)

TLC: R_f 0.32 (hexane/EtOAc, 3/1)

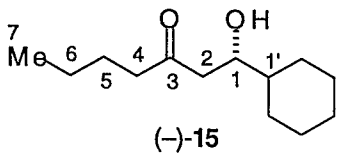
Optical Rotation: $[\alpha]_D^{24}$ –41.6 ° (c = 0.86, $CHCl_3$)

HPLC: t_R (*S*)-**14** 20.62 min (92.7%); t_R (*R*)-**14** 24.14 min (7.3%) (Chiralpak AD, hexane/EtOH, 92/8; 1.0 mL min^{-1})

Analysis: $C_{19}H_{22}O_2$ (282.38)

Calculated:	C, 80.82;	H, 7.85%
Found:	C, 80.87;	H, 7.88%

Preparation of (-)-(*S*)-1-Cyclohexyl-1-hydroxy-3-heptanone (-)-(15)



(–)-**15**

Following General Procedure III: enolate **3b** (513.0 mg, 2.2 mmol, 1.1 equiv), cyclohexanecarboxaldehyde (**9**) (242 µL, 2.0 mmol) and (*S*,*S*)-**1** (74.0 mg, 0.2 mmol, 0.1 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 6 hours. The crude product was purified by chromatography (SiO_2, hexane/EtOAc, 6/1) to give 335.3 mg (79%) of (–)-**15** as a floculent white solid.

Data for (–)-**15**:

mp: 64-65 °C

^{1}H NMR: (500 MHz)

3.78 (ddd, J = 9.2, 5.9, 2.4, 1 H, HC(1)); 2.90 (br s, 1 H, OH); 2.58 (ABX, J_{AB} = 17.3, J_{BX} = 9.8, 1 H, HC(2)); 2.49 (ABX, J_{AB} = 17.3, J_{BX} = 2.1, 1 H, HC(2)); 2.42 (t, J = 7.3, 2 H, H_2C(4)); 1.82 (m, 1 H); 1.76-1.70 (m, 2 H); 1.66-1.60 (m, 2 H); 1.54 (quint, J = 7.5, 2 H, H_2C(5)); 1.29 (sext, J = 7.5, 2 H, H_2C(6)); 1.36-1.30 (m, 1 H); 1.25-1.11 (m, 3 H); 1.08-0.94 (m, 2 H); 0.89 (t, J = 7.3, 3 H, H_3C(7))

^{13}C NMR: (126 MHz)

212.97 (C(3)); 71.67 (C(1)); 46.03 (C(2)); 43.43 (C(4)); 42.93 (C(1')); 28.79; 28.22; 26.40; 26.14; 26.03; 25.67 (C(5)); 22.22 (C(6)); 13.77 (C(7))

MS: (CI, CH_4)

212 (M^+, 1); 194 (11); 137 (15); 113 (11); 112 (27); 111 (10); 95 (92); 94 (24); 86 (36); 85 (99); 83 (34); 81 (27); 71 (14); 69 (11); 68 (15); 67 (33); 59 (13); 58 (69); 57 (100); 55 (85)

IR: ($CHCl_3$)

3534 (w); 3136 (w); 3009 (w); 2960 (m); 2930 (s); 1702 (m); 1451 (m); 1350 (w); 1290 (w); 1218 (m); 1214 (m); 1106 (w); 1006 (w); 893 (w); 779 (m); 762 (m); 728 (m); 701 (w)

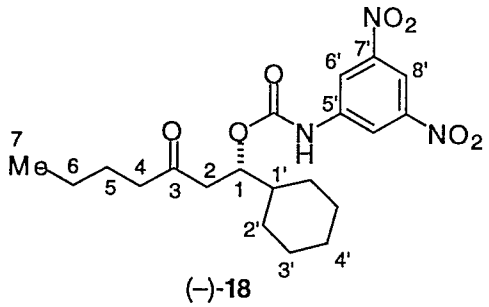
TLC: R_f 0.49 (hexane/EtOAc, 3/1)

Optical Rotation: $[\alpha]_D^{24}$ –48.0 ° (c = 0.61, $CHCl_3$)

Analysis: $C_{13}H_{24}O_2$ (212.33)

Calculated:	C, 73.54;	H, 11.39%
Found:	C, 73.64;	H, 11.60%

Preparation of (-)-(*S*)-1-Cyclohexyl-1-((3,5-dinitrophenyl)carbamoyloxy)-3-heptanone (-)-(18)



(–)-**18**

A solution of hydroxy ketone (–)-**15** (50.0 mg, 0.24 mmol) and 3,5-dinitrobenzoylazide (67.0 mg, 0.28 mmol, 1.2 equiv) was heated to reflux in toluene (15 mL) for 2h. The reaction mixture was cooled, concentrated and the resulting was solid purified by column chromatography (SiO_2, hexane/EtOAc, 4/1) to give 78.6 mg (79%) of the 3,5-DNP carbamate (–)-**18** as a white solid.

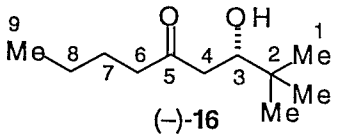
Data for (–)-**18**:

Optical Rotation: $[\alpha]_D^{24}$ –0.81 ° (*c* = 1.23, $CHCl_3$)

HPLC: t_R (*S*)-**18** 9.60 min (94.5%); t_R (*R*)-**18** 20.22 min (5.5%) (Naphthylleucine, hexane/*i*-PrOH, 90/10; 1.0 mL min^{-1})

Full characterization for (±)-**18** can be found above.

Preparation of (-)-(*S*)-3-Hydroxy-2,2-dimethyl-5-nonanone (-)-(16)



(–)-**16**

Following General Procedure III: enolate **3b** (514.0 mg, 2.2 mmol, 1.1 equiv), trimethylacetaldehyde (**10**) (217 µL, 2.0 mmol) and (*S*,*S*)-**1** (73.5 mg, 0.2 mmol, 0.1 equiv) were stirred in CH_2Cl_2 (4 mL) at –75 °C for 6 hours. The crude product was purified by chromatography (SiO_2, pentane/Et_2O, 4/1) to give 301.5 mg (81%) of (–)-**16** as a clear, colorless oil.

Data for (–)-**16**:

^{1}H NMR: (500 MHz)

3.71 (ddd, J = 7.1, 3.3, 1.8, 1 H, HC(3)); 2.96 (d, J = 3.3, 1 H, OH); 2.60 (dd, J = 17.0, 1.8, 1 H, HC(4)); 2.44 (dd, J = 17.0, 7.1, 1 H, HC(4)); 2.43 (t, J = 3.1, 2 H, $H_2C(6)$); 1.56 (quint, J = 7.5, 2 H, $H_2C(7)$); 1.31 (sext, J = 7.5, 2 H, $H_2C(8)$); 0.90 (t, J = 8.0, 3 H, $H_3C(9)$); 0.90 (s, 9 H, 3 × $H_3C(1)$)

^{13}C NMR: (126 MHz)

213.13 (C(5)); 74.88 (C(3)); 43.95 (C(4)); 43.49 (C(6)); 34.11 (C(2)); 25.67 (C(7)); 25.60 (C(1)); 22.24 (C(8)); 13.81 (C(9))

MS: (CI, CH_4)

187 (M+1, 12); 170 (11); 169 (66); 129 (27); 101 (19); 87 (13); 85 (100); 57 (45)

IR: ($CHCl_3$)

3500 (w); 3003 (w); 2962 (s); 2936 (m); 2909 (m); 2873 (m); 1703 (s); 1479 (m); 1467 (m); 1407 (m); 1390 (m); 1381 (m); 1365 (m); 1298 (w); 1128 (w); 1006 (m); 763 (w); 745 (m)

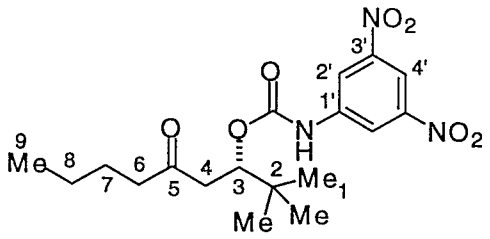
TLC: R_f 0.64 (hexane/EtOAc, 3/1)

Optical Rotation: $[\alpha]_D^{24}$ –55.1 ° (c = 1.01, $CHCl_3$)

Analysis: $C_{11}H_{22}O_2$ (186.29)

Calculated:	C, 70.92;	H, 11.90%
Found:	C, 70.89;	H, 12.08%

Preparation of (+)-(*S*)-2,2-Dimethyl-3-((3,5-dinitrophenyl)carbamoyloxy)-5-nonanone (+)-(19)



(+)-**19**

A solutio of hydroxy ketone (–)-**16** (43.3 mg, 0.23 mmol) and 3,5-dinitrobenzoylazide (66.1 mg, 0.28 mmol, 1.2 equiv) was heated to reflux in toluene (15 mL) for 2.5 h. The reaction mixture was cooled, concentrated and the resulting solid was purified by column chromatography (SiO_2, hexane/EtOAc, 4/1) to give 73.1 mg (80%) of the 3,5-DNP carbamate (+)-**19** as a white solid.

Data for (+)-**19**:

Optical Rotation: $[\alpha]_D^{24}$ +20.37 ° (c = 0.638, $CHCl_3$)

HPLC: t_R (*S*)-**19** 8.03 min (96.0%); t_R (*R*)-**19** 24.02 min (4.0%) (Naphthylleucine, hexane/*i*-PrOH, 90/10; 1.0 mL min^{-1})

Full characterization for (±)-**19** can be found above.

Preparation of (–)-12 from TMS enol ether 2b.

[(1-Butylethenyl)oxy]-trimethylsilane (**2b**) (431.0 mg, 2.5 mmol, 1.25 quiv) was added dropwise over 10 min to a stirred suspension of $SiCl_4$ (573 µL, 5.0 mmol, 2.5 equiv) and $Hg(OAc)_2$ (8.0 mg, 2.5 µmol, 0.013 equiv) in CH_2Cl_2 (2.5 mL) at rt. After complete addition the reaction mixture was stirred at rt for 50 min, then the volatiles were removed under reduced pressure (50 mmHg) to give a cloudy residue. CH_2Cl_2 (1.0 mL) was added and the was mixture cooled to –78 °C. A solution of (*S*,*S*)-**1** (37.0 mg, 0.1 mmol, 0.05 equiv) in CH_2Cl_2 (1.0 mL) was then added quickly via cannula. α-Methylciannamaldehyde (**6**) (280 µL, 2.0 mmol) was cooled to –78 °C in CH_2Cl_2 (2.0 mL) and this solution was also added quickly, via cannula, to the first solution and the reaction mixture was stirred at –78 °C for 3 h. The reaction mixture was then rapidly poured into cold (0 °C) sat. aq. $NaHCO_3$ solution and was stirred for 15 min. The hetereogeneous mixture was filtered through Celite, the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL). The organic phases were combined, dried (Na_2SO_4), filtered and concentrated to give a crude oil. Purification by column chromatography (SiO_2, hexane/EtOAc, 6/1) to afford 438.0 mg (89%) of (–)-**12** as a clear, colorless oil.

Data for (–)-**12**:

HPLC: t_R (*R*)-**12** 11.37 min (4.1%); t_R (*S*)-**12** 19.12 min (95.9%) (Chiralpak AD, hexane/EtOH, 92/8; 1.0 mL min^{-1})

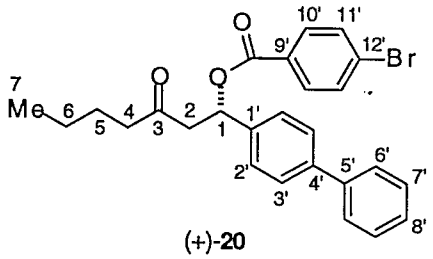
Full characterization for (–)-**12** can be found above.

Recovery experiment with 4-biphenylcarboxaldehyde (8)

4-Biphenylcarboxaldehyde (**8**) (376.6 mg, 2.0 mmol) was cooled to –75 °C in CH_2Cl_2 (2.0 mL). A solution of enolate **3b** (514 mg, 2.2 mmol, 1.1 equiv) in CH_2Cl_2 (2.0 mL) was cooled –76 °C and this solution was added quickly, via cannula, to the first solution. During the addition the temperature rose to –72 °C. The reaction mixture was stirred at –75 °C for 2 h then quickly poured into cold (0 °C) sat. aq. $NaHCO_3$ solution and was stirred for 15 min. The resulting mixture was passed through Celite and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL), the organic phases were combined, dried

(Na_2SO_4), filtered and concentrated to give a crude solid. Purification by column chromatography (SiO_2, 4/1, hexane/EtOAc) provided 23.1 mg (4%) of aldol adduct (±)-**14** and 358.0 mg (95%) of unchanged aldehyde **8**.

Preparation of (+)-(*S*)-1-(4-biphenyl)-1-(4-bromobenzoyloxy)-3-heptanone (+)-(20)



(+)-**20**

A solution of 4-bromobenzoyl chloride (171 mg, 0.78 mmol, 1.1 equiv) and Et_3N (200 μL, 1.42 mmol, 2.0 equiv) in CH_2Cl_2 (3 mL) was added dropwise over 10 min to a solution of hydroxyketone (−)-**14** (84.5% ee, HPLC) (200.0 mg, 0.71 mmol) and 4,4-dimethylaminopyridine (95.0 mg, .78 mmol, 1.1 equiv) in CH_2Cl_2 (4 mL) at 0 °C. After the final addition the solution was stirred at 0 °C for 1 min, then poured into water. The phases were seperated and the aqueous phase extraced with CH_2Cl_2 (3 × 20 mL). The organic phases were combined, dried (Na_2SO_4), filtered, and concentrated to give a white solid which was purified by column chromatography (SiO_2, hexane/EtOAc, 9/1) to give 290.1 mg (88%) of the bromobenzoate (+)-**20** as a white solid. Chiral HPLC analysis established the enantiomeric excess to be 84%. Repeated recrystallization from EtOAc/hexane provided 183.0 mg of the bromobenzoate judged to >99% ee by HPLC. An analytical sample was obtained by recrystallization from EtOH. Single crystals for X-ray analysis were obtained by slow cooling of a MeOH solution.

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

mp: 101-103 °C (EtOH)

^{1}H NMR: (500 MHz)

7.89 (d, J = 8.4, 2 H, 2 × HC(10')); 7.59-7.54 (m, 6 H); 7.50 (d, J = 8.2, 2H, 2 × HC(11')); 7.43 (t, J = 7.5, 2 H, 2 × HC(6')); 7.35 (t, J = 7.7, 1 H, HC(8')); 6.47 (dd, J = 8.4, 5.3, 1 H, HC(1)); 3.28 (dd, J = 16.7, 9.4, 1 H, HC(2)); 2.98 (dd, J = 16.5, 5.1, 1 H, HC(2)); 2.50-2.38 (m, 2 H, H_2C(4)); 1.54 (quint, J = 7.1, 2 H, H—2 C(5)); 1.27 (sext, J = 7.5, 2 H, H_2C(6)); 0.87 (t, J = 7.3, 3 H, H_3C(7))

^{13}C NMR: (126 MHz)

206.80 (C(3)); 164.72 (OC=O); 141.32 (C(5')); 140.53 (C(4')); 138.52 (C(1'))' 131.71; 131.16; 128.96 (C(9')); 128.77; 128.20 (C(12')); 127.45; 127.09; 126.91; 72.50 (C(1)); 48.89 (C(4)); 25.56 (C(5)); 22.16 (C(6)); 13.78 (C(7))

MS: (EI, 70 eV)

464 (M^+, 2); 282 (10); 281 (45); 264 (10); 222 (35); 208 (11); 207 (61); 202 (14); 200 (14); 185 (36); 183 (38); 182 (15); 181 (100); 180 (23); 179 (24); 178 (35); 165 (15); 157 (13); 155 (14); 152 (15); 85 (36); 76 (19); 75 (16); 57 (58); 50 (18)

IR: ($CHCl_3$)

3029 (m); 3024 (m); 3015 (m); 2962 (w); 1721 (s); 1648 (m); 1591 (m); 1576 (w); 1543 (m); 1417 (w); 1398 (m); 1268 (s); 1228 (m); 1213 (m); 1205 (m); 1113 (m); 1069 (m); 1012 (m); 926 (w); 791 (m); 749 (m); 723 (m)

TLC: R_f 0.62 (hexane/EtOAc, 3/1)

Optical Rotation: $[\alpha]_D^{24}$ +24.05 ° (c = 1.364, $CHCl_3$)

HPLC: (*R*)-**20**, t_R 22.9 min (0%); (*S*)-**20**, t_R 37.8 min (100%) (Chiralpak AD, hexane/EtOH, 80/20; 1.0 mL min^{-1})

Analysis: $C_{20}H_{25}BrO_3$ (465.39)

Calculated:	C, 67.12;	H, 5.41;	Br, 17.17%
Found:	C, 67.16;	H, 5.45;	Br, 17.15%

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