Supporting Information

Synthesis of the C1–C14 Fragment of Sarcoglaucol-16-one via Z-Selective Ando-Type Horner-Wadsworth-Emmons Olefination

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Ligand 14 was synthesized from the known (1R,2R,3S,5R)-3-amino-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol 21 by alkylation with bis(bromoethyl)ether in the presence of NaH in DMSO in 46 % yield (Scheme S1).

Scheme S1

The synthesis of acetal-substituted phosphonate 22 started with phosphonate 10c (Scheme S2), which was deprotonated with NaH in DMSO, followed by reaction with 4-bromobut-1-ene to the product 17c in 83 % yield. Compound 17c was submitted to ozonolysis in MeOH and reductive workup with PPh3, which yielded the aldehyde 18c in 96 %. Treatment with ethyleneglycol and catalytic amounts of TsOH in benzene gave the desired phosphonate 22 in 96 %
Scheme S2

We surmised that steric and/or electronic constraints of the enal 7b in combination with those of the zinc reagent might be the reason for the loss of enantioselectivity for ethyl-2-(3-trimethylsilylpropenyl)zinc as compared to ethylisopropenylzinc. Therefore the benchmark substrate benzaldehyde 24 was treated with various organozinc species EtZnR in the presence of ligands 14, 15, 25 and the titanium complex 26 and the enantioselectivities of the corresponding secondary alcohols 27 were determined by capillary GC using a chiral stationary column (Scheme S3).
Table S1  Addition of various organozinc reagents to benzaldehyde 24 in the presence ligands 14, 15, 25, 26\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Entry</th>
<th>EtZnR, R =</th>
<th>Ligand</th>
<th>Temp. [°C]</th>
<th>Time [h]</th>
<th>Product</th>
<th>Yield [%]</th>
<th>%ee</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Et</td>
<td>14</td>
<td>r.t.</td>
<td>12</td>
<td>27a</td>
<td>80</td>
<td>85</td>
</tr>
<tr>
<td>(2)</td>
<td>Et</td>
<td>25</td>
<td>r.t.</td>
<td>18</td>
<td>27a</td>
<td>64</td>
<td>84</td>
</tr>
<tr>
<td>(3)</td>
<td>C(=CH\textsubscript{2})CH\textsubscript{3}</td>
<td>14</td>
<td>-20</td>
<td>16</td>
<td>27b</td>
<td>38</td>
<td>87</td>
</tr>
<tr>
<td>(4)</td>
<td>C(=CH\textsubscript{2})CH\textsubscript{3}</td>
<td>15</td>
<td>r.t.</td>
<td>16</td>
<td>27b</td>
<td>75</td>
<td>71</td>
</tr>
<tr>
<td>(5)</td>
<td>C(=CH\textsubscript{2})CH\textsubscript{3}</td>
<td>15</td>
<td>40</td>
<td>1</td>
<td>27b</td>
<td>41</td>
<td>60</td>
</tr>
<tr>
<td>(6)</td>
<td>C(=CH\textsubscript{2})CH\textsubscript{3}</td>
<td>25</td>
<td>r.t.</td>
<td>16</td>
<td>27b</td>
<td>52</td>
<td>75</td>
</tr>
<tr>
<td>(7)</td>
<td>C(=CH\textsubscript{2})CH\textsubscript{2}TMS</td>
<td>14</td>
<td>r.t.</td>
<td>14</td>
<td>27c</td>
<td>59</td>
<td>14</td>
</tr>
<tr>
<td>(8)</td>
<td>C(=CH\textsubscript{2})CH\textsubscript{2}TMS</td>
<td>25</td>
<td>0</td>
<td>16</td>
<td>27c</td>
<td>83</td>
<td>13</td>
</tr>
<tr>
<td>(9)</td>
<td>C(=CH\textsubscript{2})CH\textsubscript{2}tBu</td>
<td>25</td>
<td>r.t.</td>
<td>16</td>
<td>27d</td>
<td>74</td>
<td>4</td>
</tr>
<tr>
<td>(10)</td>
<td>C(=CH\textsubscript{2})CH\textsubscript{2}tBu</td>
<td>26</td>
<td>r.t.</td>
<td>3</td>
<td>27d</td>
<td>68</td>
<td>2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions according to Scheme S3. Yields refer to isolated yields.

\textsuperscript{b} Enantioselectivities were determined by capillary GC using a chiral stationary phase Bondex \( \alpha \) un \( \beta \). The configuration of the major enantiomers 27a-d were assigned to (S) in agreement with the literature.\textsuperscript{30–32}

The results in Table S1 clearly reveal that all tested ligands catalyzed the addition with moderate to good yields regardless of the type of organozinc reagent. However, the enantioselectivity seemed to be dramatically dependent on the organozinc reagent. Whereas diethylzinc and ethyl-2-isopropenylzinc\textsuperscript{33} produced the corresponding alcohols 27a, b with ee-values of 60-80 % (entries 1–6), the use of ethyl-2-(trimethylsilyl-isopropenyl)zinc resulted in a significant decrease of the enantioselectivity to 13–14 %ee (entries 7, 8). By using (4,4-di-methyl-2-isopentenyl)ethylzinc almost racemic alcohol 27d was obtained irrespective of the ligand (entries 9, 10). One might argue that the steric bulkiness of the organozinc reagent causes the decreased stereoselectivities. However, the reaction of 24 with ethyl-2-(TMS-isopropenyl)zinc yielded 83 % of the desired alcohol 27c albeit with 13 %ee together with traces of 1-phenylpropanol 27a with 15 %ee, the latter originating from traces of diethylzinc.
from the preparation of the mixed zinc species. This indicated that the lithium salts, which
could not be removed from organozinc reagents employed in entries 7–10 compromised the
stereocontrol of the ligand 25 (or 14, 26 respectively), even for the benchmark reagent
diethylzinc. This outcome is in good agreement with results by Seebach.34


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    2003, 59, 4085-4102.


(33) C. Petrier, J. D. S. Barbosa, C. Dupuy, J. L. Luche, J. Org. Chem. 1985, 50,
    5765-5769.


The following compounds were prepared according to literature procedures: (1R,2R,3S,5R)-3-
amino-2,6,6-trimethyl-bicyclo[3.1.1]heptan-2-ol,21 disulfide ligand 2528 and TADDOL com-
plex 26.29

(1R,2R,3S,5R)-2,6,6-Trimethyl-3-morpholinobicyclo[3.1.1]heptan-2-ol (14)

To a solution of (1R,2R,3S,5R)-3-amino-2,6,6-trimethyl-bicyclo[3.1.1]heptan-2-ol (200 mg,
1.18 mmol) in DMSO (2 mL) and NEt3 (1 mL) was added a solution of bis(bromoethyl)-
ethylether (356 mg, 1.53 mmol) in DMSO (2 mL) and the mixture was stirred for 48 h at r.t.
Then the mixture was hydrolyzed with H₂O (10 mL) and 1N NaOH (10 mL), extracted with Et₂O (3 × 20 mL) and concentrated in vacuo. The residue was dissolved in Et₂O (20 mL), extracted with 1N HCl (20 mL). The HCl layer was neutralized with 1N NaOH and extracted with Et₂O (3 × 20 mL). The combined organic layers were dried over Na₂SO₄, evaporated and the crude product was recrystallized from n-hexane to yield 14 as a colorless solid; yield: 130 mg (46 %); mp. 174°C.

FT-IR (ATR): \( \tilde{\nu} = 3499 \) (w), 3427 (m), 2980 (m), 2955 (m), 2915 (m), 2902 (m), 2865 (m), 2849 (m), 2812 (w), 2753 (w), 2559 (w), 2367 (w), 2184 (w), 1968 (w), 1476 (w), 1446 (m), 1364 (m), 1355 (m), 1332 (w), 1286 (w), 1276 (m), 1137 (s), 1111 (vs), 1076 (m), 1038 (w), 1003 (s), 950 (m), 899 (m), 879 (s), 842 (m), 729 (w), 598 (w).

\(^1\)H NMR (300 MHz, CDCl₃): \( \delta = 0.98 \) (s, 3H, 9-H), 1.26 (s, 3-H, 8-H), 1.27 (s, 3H, 8'-H), 1.27-1.29 (m, 1H, 3a-H), 1.91-2.03 (m, 4H, 7-H, 6-H, 4-H, 3b-H), 2.11-2.21 (m, 1H, 7-H), 2.77-2.85 (m, 4H, 10-H, 10'-H), 2.85-2.92 (m, 1H, 2-H), 3.68-3.82 (m, 4H, 11-H, 11'-H), 4.03 (s, 1H, -OH).

\(^{13}\)C NMR (125 MHz, CDCl₃): \( \delta = 24.1 \) (C-9), 26.5 (C-2), 27.9 (C-8), 28.0 (C-8’), 31.5 (C-3), 37.9 (C-7, C-5), 40.5 (C-4), 52.9 (C-6), 64.4 (C-10), 67.7 (C-11), 74.2 (C-1).

GC/MS (EI): \( m/z \) (%) = 221 (10), 196 (3), 178 (2), 168 (5), 152 (3), 139 (13), 124 (6), 119 (7), 113 (100), 98 (34), 91 (11), 83 (24), 67 (6), 55 (26).

MS (ESI): \( m/z \) = 240.2 [M + H]⁺, 222.2, 167.1, 135.1, 119.1, 107.1, 100.1, 91.1, 86.1.


Anal. Calcd. for C₁₄H₂₅NO₂: C, 70.25; H, 10.53; N, 5.85. Found: C, 70.28; H, 10.51; N, 5.80.

**Ethyl 2-(diethoxyphosphoryl)hex-5-enoate (17c)**

NaH (216 mg, 8.98 mmol, 60 % in mineral oil) was added to a solution of phosphonate 10c (3.00 g, 8.98 mmol) in DMSO (11 mL) and the mixture was stirred for 20 min at r.t. Then was
dropwise added 1-bromo-3-butene (1.05 mL, 10.3 mmol) and stirring was continued for 1 h. The mixture was warmed to 45°C and stirred for 16 h. After cooling to r.t. the mixture was hydrolyzed with sat. NH₄Cl (50 mL), the layers were separated, the aqueous layer was extracted with EtOAc (3 × 50 mL), the combined organic layers were dried over Na₂SO₄ and evaporated. The crude product was purified by flash chromatography on SiO₂ (hexanes/EtOAc 2 : 1) to yield 17c as a yellow oil and starting material 10c (505 mg, 1.53 mmol); yield: 2.08 g (83 %); Rf = 0.35 (hexanes/EtOAc 2 : 1).

FT-IR (ATR): \( \nu = 3478 \) (w), 2982 (m), 2936 (m), 2910 (m), 2203 (w), 1967 (w), 1731 (s), 1642 (m), 1445 (m), 1392 (m), 1368 (m), 1332 (m), 1244 (s), 1158 (s), 1113 (m), 1097 (m), 1017 (vs), 961 (s), 913 (s), 864 (m), 848 (m), 790 (m), 760 (m), 717 (w), 641 (w), 548 (m), 538 (m), 522 (w) cm⁻¹.

\(^1\)H NMR (500 MHz, CDCl₃): \( \delta = 1.29 \) (t, \( J = 7.0 \) Hz, 3H, COCH₂CH₃), 1.33 (td, \( J = 7.0 \) Hz, \( J = 0.5 \) Hz, 3H, POCH₂CH₃), 1.34 (td, \( J = 7.0 \) Hz, \( J = 0.5 \) Hz, 3H, POCH₂CH₃’), 1.88–1.98 (m, 1H, 3-H), 2.01-2.21 (m, 3H, 3-H, 4-H), 2.97 (ddd, \( J = 22.8 \) Hz, \( J = 10.8 \) Hz, \( J = 3.5 \) Hz, 1H, 2-H), 4.15 (qd, \( J = 7.0 \) Hz, \( J = 2.5 \) Hz, 4H, POCH₂CH₃), 4.22 (qd, \( J = 7.0 \) Hz, \( J = 1.6 \) Hz, 2H, COCH₂CH₃), 4.99-5.03 (m, 1H, 6-H), 5.05 (dd, \( J = 3.3 \) Hz, \( J = 1.5 \) Hz, 1H, 6-H’), 5.7-5.79 (m, 1H, 5-H).

\(^13\)C NMR (125 MHz, CDCl₃): \( \delta = 14.2 \) (COCH₂CH₃), 16.4 (d, \( J = 4.5 \) Hz, POCH₂CH₃), 16.4 (d, \( J = 4.5 \) Hz, POCH₂CH₃’), 26.1 (d, \( J = 4.6 \) Hz, C-4), 32.3 (d, \( J = 15.3 \) Hz, C-3), 44.9 (d, \( J = 129.9 \) Hz, C-2), 61.3 (COCH₂CH₃), 62.6 (d, \( J = 6.8 \) Hz, POCH₂CH₃), 62.7 (d, \( J = 6.8 \) Hz, POCH₂CH₃’), 116.2 (C-6), 136.7 (C-5), 169.2 (d, \( J = 5.0 \) Hz, C-1).

\(^31\)P NMR (202 MHz, CDCl₃): \( \delta = 22.4-23.2 \) (m).

GC/MS (EI): m/z (%): 224 (100), 209 (18), 205 (21), 197 (62), 180 (23), 177 (52), 169 (31), 152 (58), 149 (40), 133 (12), 125 (42), 122 (30), 109 (75), 95 (17), 91 (28), 83 (51), 81 (60), 73 (12), 67 (50), 65 (25), 55 ([C₄H₈], 76).
**MS (APCI):** m/z = 279.13, 251.1, 233.09, 205.06, 177.03.

**HRMS (ESI):** calcd for C$_{12}$H$_{23}$O$_5$P$^+$ [M + H]$^+$: 279.1356, found: 279.1347.

**Ethyl 2-(diethoxyphosphoryl)-5-oxopentanoate (18c)**

A solution of phosphonate 17c (4.90 g, 17.6 mmol) in CH$_2$Cl$_2$ (70 mL) and MeOH (30 mL) was cooled to -78°C. Then ozone was bubbled through until the blue color of the solution remained. After 5 min of bubbling argon through the solution PPh$_3$ (11.6 g, 44.1 mmol) was added and the reaction mixture was warmed to r.t over 12 h. Evaporation of the solvent and distillation of the residue (10$^{-2}$ mbar, 73°C) yielded 18c as a yellow oil; yield: 2.38 g (48%).

**FT-IR (ATR):** ν = 3446 (w), 2983 (m), 2936 (w), 2909 (w), 2728 (w), 1745 (s), 1723 (s)
1445 (m), 1392 (m), 1369 (m), 1326 (m), 1247 (s), 1156 (s), 1096 (m), 1016 (vs), 961 (s), 850 (m), 791 (m), 760 (m), 722 (m), 697 (m), 645 (m), 542 (s) cm$^{-1}$.

**$^1$H NMR (500 MHz, CDCl$_3$):** δ = 1.29 (t, $J = 7.2$ Hz, 3H, COCH$_2$C$_3$H$_3$), 1.34 (td, $J = 7.1$ Hz, $J = 0.7$ Hz, 3H, POCH$_2$CH$_3$), 1.35 (td, $J = 7.1$ Hz, $J = 0.7$ Hz, 3H, POCH$_2$CH$_3$'), 2.17-2.29 (m, 2H, 3-H), 2.49-2.67 (m, 2H, 4-H), 3.00 (ddd, $J = 23.2$ Hz, $J = 8.3$ Hz, $J = 6.7$ Hz, 1H, 2-H), 4.1-4.27 (m, 6H, COCH$_2$CH$_3$, POCH$_2$CH$_3$, POCH$_2$CH$_3$'), 9.76 (t, $J = 1.1$ Hz, 1H, 5-H).

**$^{13}$C NMR (125 MHz, CDCl$_3$):** δ = 14.1 (COCH$_2$CH$_3$), 16.3 (d, $J = 3.3$ Hz, POCH$_2$CH$_3$), 16.4 (d, $J = 3.3$ Hz, POCH$_2$CH$_3$'), 19.6 (d, $J = 4.6$ Hz, C-4), 41.9 (d, $J = 12.8$ Hz, C-3), 44.5 (d, $J = 131.6$ Hz, C-2), 61.6 (COCH$_2$CH$_3$), 62.8 (d, $J = 6.5$ Hz, POCH$_2$CH$_3$), 62.9 (d, $J = 6.6$ Hz, POCH$_2$CH$_3$'), 168.8 (d, $J = 5.0$ Hz, C-1), 200.7 (C-5).

**$^{31}$P NMR (202 MHz, CDCl$_3$):** δ = 21.4-22.2 (m).

**GC/MS (EI):** m/z (%) = 269 (3), 252 (4), 238 (14), 235 (16), 224 (100), 213 (6), 206 (22), 197 (46), 188 (10), 179 (20), 169 (24), 161 (51), 152 (38), 141 (10), 135 (18), 123 (48), 109 (22), 99 (34), 97 (28), 70 (18), 65 (22), 55 (80).

**HRMS (ESI):** calcd for C$_{11}$H$_{21}$O$_6$P$^+$ [M + H]$^+$: 281.1149, found: 281.1140.
Ethyl 2-(diethoxyphosphoryl)-4-(1,3-dioxan-2-yl)butanoate (22)

To a solution of aldehyde 18c (110 mg, 0.36 mmol) in toluene (4 mL) were added 1,3-propandiol (40 μl, 0.53 mmol) and p-TsOH • H2O (8 mg, 0.04 mmol) and the mixture was refluxed in a Dean-Stark trap for 4 d. After cooling to r.t. the mixture was filtered via basic Al2O3 and evaporated to yield 22 as a colorless oil; yield: 117 mg (96%).

FT-IR (ATR): ν = 2979 (m), 2933 (m), 2852 (m), 2189 (w), 1965 (w), 1730 (s), (1446 (m), 1391 (m), 1330 (m), 1241 (s), 1143 (s), 1134 (s), 1093 (s), 1046 (s), 1016 (vs), 681 (s), 893 (m), 849 (m), 792 (m), 721 (w), 643 (w), 579 (m), 556 (m) cm⁻¹.

1H NMR (500 MHz, CDCl3): δ = 1.28 (t, J = 7.2 Hz, 3H, CO₂CH₂C₃H₃), 1.3-1.35 (m, 2H, 2'-H), 1.32 (td, J = 7.0 Hz, J = 0.6 Hz, 3H, POCH₂CH₃), 1.33 (td, J = 7.0 Hz, J = 0.6 Hz, 3H, POCH₂CH₃), 1.57-1.7 (m, 2H, 3-H), 1.94-2.12 (m, 2H, 4-H), 2.98 (ddd, J = 22.8 Hz, J = 10.9 Hz, J = 4.1 Hz, 1H, 2-H), 3.72 (ddd, J = 11.6 Hz, J = 4.5 Hz, J = 2.5 Hz, 1H, 1''a-Ha²), 3.75 (ddd, J = 11.2 Hz, J = 4.6 Hz, J = 2.6 Hz, 1H, 1''b-Ha²), 4.05-4.10 (m, 2H, 1''a-Hb, 1''b-Hb), 4.12-4.17 (m, 4-H, POCH₃, POCH₃), 4.17-4.24 (m, 2H, CO₂CH₂), 4.52 (t, J = 5.1 Hz, 1H, 5-H).

13C NMR (125 MHz, CDCl₃): δ = 14.2 (CO₂CH₂CH₃), 16.4 (d, J = 2.4 Hz, POCH₂CH₃), 16.4 (d, J = 2.4 Hz, POCH₂CH₃), 21.72 (d, J = 4.5 Hz, C-3), 25.73 (C-2'), 33.5 (d, J = 14.7 Hz, C-4), 45.5 (d, J = 130.3 Hz, C-2), 61.4 (CO₂CH₂), 62.68 (d, J = 6.6 Hz, POCH₂), 62.74 (d, J = 6.6 Hz, POCH₂'), 66.82 (C-1''b), 66.84 (C-1''b), 101.5 (d, J = 1.4 Hz, C-5), 169.1 (d, J = 4.8 Hz, C-1).

31P NMR (202 MHz, CDCl₃): δ = 22.4-22.8 (m).

GC/MS (EI): m/z (%) = 338 (M⁺, 13), 293 (18), 287 (14), 269 (12), 249 (17), 224 (23), 208 (27), 179 (31), 164 (12), 160 (11), 149 (18), 135 (15), 116 (18), 105 (6), 91 (4), 87 (100), 71 (12), 64 (22), 59 (10).
MS (APCI): m/z = 339.16, 293.11, 283.13, 265.12, 249.09, 237.09, 225.09, 209.06, 179.04, 149.02.

HRMS (ESI): calcd for C_{14}H_{27}O_7P\textsuperscript{+} [M + H]\textsuperscript{+}: 339.1567; found: 339.1575.

(\textit{S})-1-Phenylpropan-1-ol (27a)

To a solution of diethylzinc (0.33 mL, 3.21 mmol) in toluene (10 mL) was dropwise added chiral ligand (0.06 mmol) and stirred for 5 min at r.t. Then was added dropwise benzaldehyde 24 (190 \muL, 1.89 mmol) and the mixture was stirred for 18 h at r.t. The mixture was cooled to 0\degree C, hydrolyzed with 1N HCl (5 mL), extracted with EtOAc (3 \times 20 mL), dried over Na_2SO_4 and evaporated. Purification of the crude product by flash chromatography on SiO_2 (hexanes/EtOAc 9 : 1) yielded 27a as a colorless oil; yield: 165 mg (64 %); 84%ee (via GC on Bondex \textsuperscript{D}un \textsuperscript{E}).

\textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}): \delta = 0.94 (t, J = 7.4 Hz, 3H, 3-H), 1.78 (m, 2H, 2-H), 1.99 (s, 1H, -O\textsubscript{H}), 4.58 (m, 1H, 1-H), 7.33 (m, 5H, Ph).

\textsuperscript{13}C NMR (63 MHz, CDCl\textsubscript{3}): \delta = 10.2 (C-3), 31.9 (C-2), 76.0 (C-1), 126.0 (C-5, C-5\textsuperscript{\textprime}), 127.5 (C-7), 128.4 (C-6, C 6\textsuperscript{\textprime}), 144.6 (C-4).

The spectroscopic data are in agreement with ref.\textsuperscript{30}

(\textit{S})-2-Methyl-1-phenylprop-2-en-1-ol (27b)

To a solution of diisopropylzinc (0.26 mL, 0.26 mmol, 1M in toluene) in toluene (10 mL) was dropwise added diethylzinc (27 \muL, 0.26 mmol) and the mixture was stirred for 10 min at r.t. Then was added chiral ligand (0.03 mmol) and stirred for 10 min at r.t. Then was added dropwise benzaldehyde 24 (33 \muL, 0.33 mmol) and the mixture was stirred for 16 h at r.t. The mixture was cooled to 0\degree C, hydrolyzed with 1N HCl (5 mL), extracted with EtOAc (3 \times 20 mL), dried over Na_2SO_4 and evaporated. Purification of the crude product by flash
chromatography on SiO$_2$ (hexanes/EtOAc 10 : 1) yielded 27b as a colorless oil; yield: 25 mg (52 %); 75%ee (via GC on Bondex α un β).

$^1$H NMR (250 MHz, CDCl$_3$): δ = 1.61 (s, 3H, 4-H), 1.98 (s, 1H, -OH), 4.94-4.97 (m, 1H, 3$^a$-H), 5.11-5.14 (m, 1H, 1-H), 5.19-5.22 (m, 1H, 3$^b$-H), 7.21-7.38 (m, 5H, Ph).

$^{13}$C NMR (63 MHz,CDCl$_3$): δ = 18.3 (C-4), 77.9 (C-1), 111.2 (C-3), 126.5 (C-7, C-7’), 127.7 (C-8), 128.4 (C-6, C-6’), 141.9 (C-5), 146.8 (C-2).

The spectroscopic data are in agreement with ref.31

1-Phenyl-2-trimethylsilylmethylprop-2-en-1-ol (27c)

To a solution of 2-bromo-3-trimethylsilyl-prop-1-ene (154 mg, 0.80 mmol) in Et$_2$O (10 mL) was dropwise added at -78°C t-BuLi (1.09 mL, 1.63 mmol, 1.5 M in pentane) and the mixture was warmed to -30°C. Then a solution of ZnCl$_2$ (55 mg, 0.40 mmol) in Et$_2$O (2 mL) was dropwise added at -78°C and the mixture was warmed to r.t. Then were added diethylzinc (41 μL, 0.41 mmol), stirred for 10 min, Et$_2$O was removed in vacuo, followed by sequential addition of toluene (10 mL) and ligand (0.03 mmol) and the resulting mixture was stirred for 10 min. Then was added a solution of benzaldehyde 26 (0.05 mL, 0.50 mmol) in toluene (1 mL), the mixture was stirrred for 16 h at 0°C, hydrolyzed with 1N HCl (5 mL), extracted with EtOAc (3 × 20 mL), dried over Na$_2$SO$_4$ and the solvent was evaporated. Purification of the crude product by flash chromatography on SiO$_2$ (hexanes/EtOAc 9 : 1) yielded 27c as colorless oil; yield: 25 mg (52 %); 13%ee (via GC on Bondex α un β).

$^1$H NMR (250 MHz, CDCl$_3$): δ = -0.14 (s, 9H, TMS), 1.12 (dd, J = 14.2 Hz, J = 0.6 Hz, 1H, 4$^a$-H), 1.38 (dd, J = 14.2 Hz, J = 0.9 Hz, 1H, 4$^b$-H), 1.83 (s, 1H, -OH), 4.63-4.68 (m, 1H, 3$^a$-H), 4.83-4.89 (m, 1H, 1-H), 4.98-5.01 (m, 1H, 3$^b$-H), 7.09-7.25 (m, 5H, Ph).

$^{13}$C NMR (63 MHz,CDCl$_3$): δ = -1.2 (TMS), 22.7 (C-4), 77.9 (C-1), 107.9 (C-3), 127.1 (C-7, C-7’), 127.8 (C-8), 128.4 (C-6, C-6’), 142.1 (C-5), 148.6 (C-3).
The spectroscopic data are in agreement with ref.32

4,4-Dimethyl-2-methylen-1-phenylpentan-1-ol (27d)

To a solution of 2-bromo-4,4-dimethyl-pent-1-ene (94 mg, 0.53 mmol) in Et₂O (10 mL) was dropwise added at -78°C t-BuLi (0.72 mL, 1.07 mmol, 1.5 M in pentane) and the mixture was warmed to -30°C. Then a solution of ZnCl₂ (35 mg, 0.26 mmol) in Et₂O (2 mL) was dropwise added at -78°C and the mixture was warmed to r.t. and Et₂O was removed in vacuo. Then were sequentially added toluene (10 mL), diethylzinc (41 μl, 0.41 mmol), stirred for 10 min, ligand (0.03 mmol) was added and the resulting mixture was stirred for 10 min. Then was added a solution of benzaldehyde 26 (0.05 mL, 0.50 mmol) in toluene (1 mL), the mixture was stirred for 16 h at r.t., hydrolyzed with 1N HCl (5 mL), extracted with EtOAc (3 × 20 mL), dried over Na₂SO₄ and the solvent was evaporated. Purification of the crude product by flash chromatography on SiO₂ (hexanes/EtOAc 10 : 1) yielded 27d as colorless oil; yield: 76 mg (47 %); 4%ee (via GC on Bondex α un β).

¹H NMR (250 MHz, CDCl₃): δ = 0.87 (s, 9H, C(CH₃)₃), 1.60 (d, J = 13.9 Hz, 1H, 3a-H), 1.84 (s, 1H, -OH), 1.89 (d, J = 13.9 Hz, 1H, 3b-H), 4.93-4.96 (m, 1H, 4a-H), 5.05-5.08 (m, 1H, 1-H), 5.32-5.36 (m, 1H, 4b-H), 7.19 (m, 5H, Ph).

¹³C NMR (63 MHz,CDCl₃): δ = 28.9 (C(CH₃)₃), 30.6 (C(CH₃)₃), 45.2 (C-3), 76.52 (C-1), 111.7 (C-2), 126.4 (C-6, C-6’), 126.9 (C-8), 127.5 (C-7, C-7’), 141.3 (C-5), 147.57 (C-2).