Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information for

Stereoselective titanium-mediated aldol reactions from a chiral isopropyl ketone

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1. Spectroscopic data of adducts **2**

(2*S*,5*S*)-1-Benxyloxy-5-hydroxy-2,4,4,6-tetramethyl-3-heptanone (2a). Colorless oil. $\mathbf{R_f}$ (hexane/EtOAc 7:3) = 0.50. **HPLC** (hexane/EtOAc 97:3) $\mathbf{t_R}$ = 23.6 min. $\mathbf{[\alpha]_D}$ = –3.6 (*c* 1.33, $CHCl_3$). **IR** (film) ν 3462, 3031, 2970, 2873, 1705, 1496, 1470, 1096. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.26 (5H, m, ArH), 4.50 (1H, d, *J* = 12.0 Hz, $PhCH_xH_y$), 4.42 (1H, d, *J* = 12.0 Hz, $PhCH_xH_y$), 3.70 (1H, dd, *J* = 9.5, 8.4 Hz, $BnOCH_xH_y$), 3.64 (1H, dd, *J* = 6.5, 3.3 Hz, CHOH), 3.45–3.39 (1H, m, $CHCH_3$), 3.36 (1H, d, *J* = 6.5 Hz, OH), 3.34 (1H, dd, *J* = 8.4, 4.5 Hz, $BnOCH_xH_y$), 1.92–1.81 (1H, m, $CH(CH_3)_2$), 1.18 (3H, s, $C(CH_3)_x(CH_3)_y$), 1.15 (3H, s, $C(CH_3)_x(CH_3)_y$), 1.00 (3H, d, *J* = 6.8 Hz, $CH(CH_3)_x(CH_3)_y$), 0.99 (3H, d, *J* = 6.8 Hz, $CHCH_3$), 0.88 (3H, d, *J* = 6.8 Hz, $CH(CH_3)_x(CH_3)_y$). ^{13}**C NMR** (100.6 MHz, $CDCl_3$) δ 218.7 (C), 137.3 (C), 128.4 (CH), 127.8 (CH), 127.7 (CH), 79.3 (CH), 73.6 (CH_2), 73.4 (CH_2), 53.8 (C), 40.5 (CH), 29.0 (CH), 23.2 (CH_3), 22.3 (CH_3), 18.3 (CH_3), 17.5 (CH_3), 15.6 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{18}H_{28}NaO_3$ $[M+Na]^+$: 315.1931, found: 315.1937.

(2*S*,5*S*)-1-Benxyloxy-5-hydroxy-2,4,4,7-tetramethyl-3-octanone (2b). Colorless oil. $\mathbf{R_f}$ (hexane/EtOAc 9:1) = 0.65. $\mathbf{[\alpha]_D}$ = –19.9 (*c* 1.20, $CHCl_3$). **IR** (film) ν 3465, 3031, 2955, 2869, 1707, 1468, 1367, 1078. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.25 (5H, m, ArH), 4.48 (1H, d, *J* = 11.9 Hz, $PhCH_xH_y$), 4.42 (1H, d, *J* = 11.9 Hz, $PhCH_xH_y$), 3.87 (1H, ddd, *J* = 10.6, 5.6, 1.6 Hz, CHOH), 3.74 (1H, dd, *J* = 10.1, 8.3 Hz, $BnOCH_xH_y$), 3.51–3.42 (1H, m, $CHCH_3$), 3.36 (1H, dd, *J* = 8.3, 4.1 Hz, $BnOCH_xH_y$), 3.22 (1H, dd, *J* = 5.6, 1.2 Hz, OH), 1.81–1.70 (1H, m, $CH(CH_3)_2$), 1.29 (1H, ddd, *J* = 14.1, 10.6, 3.8 Hz, $CH_xH_yCH(CH_3)_2$), 1.13–1.07 (1H, m, $CH_xH_yCH(CH_3)_2$), 1.12 (3H, s, $C(CH_3)_x(CH_3)_y$), 1.06 (3H, s, $C(CH_3)_x(CH_3)_y$), 0.98 (3H, d, *J* = 6.8 Hz, $CHCH_3$), 0.89 (3H, d, *J* = 6.5 Hz, $CH(CH_3)_x(CH_3)_y$), 0.88 (3H, d, *J* = 6.5 Hz, $CH(CH_3)_x(CH_3)_y$). ^{13}**C NMR** (100.6 MHz, $CDCl_3$) δ 218.4 (C), 137.0 (C), 128.5 (CH), 127.9 (CH), 127.8 (CH), 73.8 (CH_2), 73.5 (CH_2), 73.1 (CH), 53.7 (C), 40.2 (CH), 39.4 (CH_2), 24.7 (CH), 24.0 (CH_3), 21.4 (CH_3), 21.4 (CH_3), 17.0 (CH_3), 15.5 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{19}H_{30}NaO_3$ $[M+Na]^+$: 329.2087, found: 329.2081.

(2*S*,5*S*)-1-Benxyloxy-5-hydroxy-2,4,4-trimethyl-3-octanone (2c). Colorless oil. $\mathbf{R_f}$ (hexane/EtOAc 7:3) = 0.55. $\mathbf{[\alpha]_D}$ = –11.4 (*c* 1.08, $CHCl_3$). **IR** (film) ν 3465, 3031, 2959, 2871, 1706, 1455, 1366, 1099. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.25 (5H, m, ArH), 4.48 (1H, d, *J* = 11.9 Hz, $PhCH_xH_y$), 4.42 (1H, d, *J* = 11.9 Hz, $PhCH_xH_y$), 3.81–3.76 (1H, m, CHOH), 3.74 (1H, dd, *J* = 10.1, 8.3 Hz, $BnOCH_xH_y$), 3.50–3.41 (1H, m, $CHCH_3$), 3.36 (1H, dd, *J* = 8.3, 4.1 Hz, $BnOCH_xH_y$), 3.25 (1H, dd, *J* = 5.6, 1.0 Hz, OH), 1.60–1.47 (1H, m, $CH_xH_yCH_3$), 1.42–1.19 (3H, m, $CH_2CH_xH_yCH_3$), 1.13 (3H, s, $C(CH_3)_x(CH_3)_y$), 1.06 (3H, s, $C(CH_3)_x(CH_3)_y$), 0.97 (3H, d, *J* = 6.8 Hz, $CHCH_3$), 0.90 (3H, t, *J* = 7.1 Hz, CH_2CH_3). ^{13}**C NMR** (100.6 MHz, $CDCl_3$) δ 218.4 (C), 137.1 (C), 128.4 (CH), 127.9 (CH), 127.8 (CH), 75.1 (CH), 73.8 (CH_2), 73.5 (CH_2), 53.7 (C), 40.2 (CH), 32.5 (CH_2), 21.5 (CH_3), 20.0 (CH_2), 17.1 (CH_3), 15.5 (CH_3), 14.0 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{18}H_{28}NaO_3$ $[M+Na]^+$: 315.1931, found: 315.1928.

(2*S*,5*S*,6*E*)-1-Benxyloxy-5-hydroxy-2,4,4-trimethyl-6-octen-3-one (2d). Colorless oil. $\mathbf{R_f}$ (hexane/EtOAc 8:2) = 0.40. **HPLC** (hexane/EtOAc 9:1) $\mathbf{t_R}$ = 9.5 min. $\mathbf{[\alpha]_D}$ = –16.3 (*c* 0.95, $CHCl_3$). **IR** (film) ν 3454, 3030, 2937, 2875, 1704, 1454, 1364, 1091. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.25 (5H, m, ArH), 5.70 (1H, dqd, *J* = 15.2, 6.4, 0.9 Hz, $CH=CHCH_3$), 5.44 (1H, ddq, *J* = 15.2, 7.5, 1.5 Hz, $CH=CHCH_3$), 4.49 (1H, d, *J* = 12.1 Hz, $PhCH_xH_y$), 4.42 (1H, d, *J* = 12.1 Hz, $PhCH_xH_y$), 4.31–4.27 (1H, m, CHOH), 3.70 (1H, dd, *J* = 9.8, 8.3 Hz, $BnOCH_xH_y$), 3.49–3.40 (1H, m, $BnOCH_2CH$), 3.42 (1H, d, *J* = 4.9 Hz, OH), 3.35 (1H, dd, *J* = 8.3, 4.5 Hz, $BnOCH_xH_y$), 1.71 (3H, dd, *J* = 6.4, 1.5 Hz, $CH=CHCH_3$),

1.09 (3H, s, C(C<u>H</u>$_3$)$_x$(CH$_3$)$_y$), 1.08 (3H, s, C(CH$_3$)$_x$(C<u>H</u>$_3$)$_y$), 0.98 (3H, d, J = 6.8 Hz, BnOCH$_2$CHC<u>H</u>$_3$). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 218.4 (C), 137.1 (C), 129.1 (CH), 128.6 (CH), 128.4 (CH), 127.8 (CH), 127.7 (CH), 76.8 (CH), 73.5 (CH_2), 73.4 (CH_2), 53.4 (C), 40.2 (CH), 21.7 (CH_3), 17.8 (CH_3), 17.2 (CH_3), 15.3 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{18}H_{25}O_2$ [M-OH]$^+$: 273.1849, found: 273.1852.

(2*S*,5*S*)-1-Benxyloxy-5-hydroxy-2,4,4,6-tetramethyl-6-hepten-3-one (2e). Colorless oil. **R_f** (hexane/EtOAc 7:3) = 0.60. **HPLC** (hexane/EtOAc 97:3) **t_R** = 23.1 min. **[α]$_D$** = –11.3 (*c* 1.10, $CHCl_3$). **IR** (film) ν 3447, 2974, 2936, 2874, 1706, 1455, 1371, 1075, 1026. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.26 (5H, m, Ar<u>H</u>), 5.02–5.00 (1H, m, C=C<u>H</u>$_x$H$_y$), 4.91–4.90 (1H, m, C=CH$_x$<u>H</u>$_y$), 4.52 (1H, d, J = 12.3 Hz, PhC<u>H</u>$_x$H$_y$), 4.47 (1H, d, J = 4.7 Hz, C<u>H</u>OH), 4.43 (1H, d, J = 12.3 Hz, PhCH$_x$<u>H</u>$_y$), 3.69 (1H, dd, J = 9.7, 8.4 Hz, BnOC<u>H</u>$_x$H$_y$), 3.58 (1H, d, J = 4.7 Hz, O<u>H</u>), 3.50–3.41 (1H, m, C<u>H</u>CH$_3$), 3.34 (1H, dd, J = 8.4, 4.5 Hz, BnOCH$_x$<u>H</u>$_y$), 1.79 (3H, s, C=CC<u>H</u>$_3$), 1.13 (3H, s, C(C<u>H</u>$_3$)$_x$(CH$_3$)$_y$), 1.12 (3H, s, C(CH$_3$)$_x$(C<u>H</u>$_3$)$_y$), 0.99 (3H, d, J = 6.8 Hz, CHC<u>H</u>$_3$). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 218.3 (C), 143.9 (C), 137.2 (C), 128.4 (CH), 127.9 (CH), 127.8 (CH), 114.5 (CH_2), 78.5 (CH), 73.4 (CH_2), 73.3 (CH_2), 53.7 (C), 40.3 (CH), 22.4 (CH_3), 20.2 (CH_3), 17.6 (CH_3), 15.4 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{18}H_{26}NaO_3$ [M+Na]$^+$: 313.1774, found: 313.1773.

(1*S*,4*S*)-5-Benxyloxy-1-hydroxy-2,2,4-trimethyl-1-phenyl-3-pentanone (2f). White solid. **P_f** = 70–72 ºC. **R_f** (hexane/EtOAc 7:3) = 0.65. **[α]$_D$** = +15.0 (*c* 1.00, $CHCl_3$). **IR** (KBr) ν 3508, 2976, 2866, 1695, 1494, 1454, 1077, 1055. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.26 (10H, m, Ar<u>H</u>), 5.11 (1H, d, J = 4.2 Hz, C<u>H</u>OH), 4.55 (1H, d, J = 12.3 Hz, PhC<u>H</u>$_x$H$_y$), 4.45 (1H, d, J = 12.3 Hz, PhCH$_x$<u>H</u>$_y$), 3.83 (1H, d, J = 4.2 Hz, O<u>H</u>), 3.73 (1H, dd, J = 10.0, 8.3 Hz, BnOC<u>H</u>$_x$H$_y$), 3.60–3.51 (1H, m, C<u>H</u>CH$_3$), 3.39 (1H, dd, J = 8.3, 4.4 Hz, BnOCH$_x$<u>H</u>$_y$), 1.03 (3H, s, C(C<u>H</u>$_3$)$_x$(CH$_3$)$_y$), 1.02 (3H, d, J = 6.6 Hz, CHC<u>H</u>$_3$), 1.02 (3H, s, C(CH$_3$)$_x$(C<u>H</u>$_3$)$_y$). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 218.3 (C), 139.5 (C), 137.1 (C), 128.5 (CH), 127.9 (CH), 127.8 (CH), 127.6 (CH), 127.4 (CH), 76.9 (CH), 73.5 (CH_2), 73.4 (CH_2), 54.3 (C), 40.2 (CH), 22.2 (CH_3), 16.3 (CH_3), 15.4 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{21}H_{26}NaO_3$ [M+Na]$^+$: 349.1774, found: 349.1773.

(2*S*,5*S*)-1-Benxyloxy-6-*tert*-butyldiphenylsilyloxy-5-hydroxy-2,4,4-trimethyl-3-hexanone (2h). Yellowish oil. **R_f** (hexane/EtOAc 9:1) = 0.20. **HPLC** (hexane/EtOAc 97:3) **t_R** = 9.4 min. **[α]$_D$** = –8.1 (*c* 1.30, $CHCl_3$). **IR** (film) ν 3453, 3070, 2932, 2858, 1708, 1472, 1428, 1112. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.66 (4H, m, Ar<u>H</u>), 7.44–7.24 (11H, m, Ar<u>H</u>), 4.45 (1H, d, J = 12.0 Hz, PhC<u>H</u>$_x$H$_y$), 4.38 (1H, d, J = 12.0 Hz, PhCH$_x$<u>H</u>$_y$), 4.02 (1H, dt, J = 7.6, 3.7 Hz, C<u>H</u>OH), 3.73 (1H, dd, J = 10.6, 3.5 Hz, SiOC<u>H</u>$_x$H$_y$), 3.67–3.63 (1H, m, BnOC<u>H</u>$_x$H$_y$), 3.61 (1H, dd, J = 10.5, 7.7 Hz, SiOCH$_x$<u>H</u>$_y$), 3.40–3.31 (2H, m, BnOCH$_x$<u>H</u>$_y$C<u>H</u>), 3.26 (1H, d, J = 4.0 Hz, O<u>H</u>), 1.06 (3H, s, C(C<u>H</u>$_3$)$_x$(CH$_3$)$_y$), 1.06 (9H, s, SiC(C<u>H</u>$_3$)$_3$), 1.02 (3H, s, C(CH$_3$)$_x$(C<u>H</u>$_3$)$_y$), 0.97 (3H, d, J = 6.6 Hz, CHC<u>H</u>$_3$). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 217.3 (C), 137.5 (C), 135.6 (CH), 133.4 (C), 133.2 (C), 129.7 (CH), 129.7 (CH), 128.4 (CH), 127.7 (CH), 127.6 (CH), 75.6 (CH), 73.5 (CH_2), 73.3 (CH_2), 64.7 (CH_2), 51.8 (C), 40.4 (CH), 26.8 (CH_3), 20.8 (CH_3), 19.2 (C), 18.0 (CH_3), 15.4 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{32}H_{46}NO_4Si$ [M+NH$_4$]$^+$: 536.3191, found: 536.3191.

(2*S*,5*S*)-1-Benxyloxy-7-*tert*-butyldimethylsilyloxy-5-hydroxy-2,4,4-trimethyl-3-heptanone (2i). Yellowish oil. **R_f** (hexane/EtOAc 7:3) = 0.70. **HPLC** (hexane/EtOAc 97:3) **t_R** = 7.5 min. **[α]$_D$** = –20.4 (*c* 1.00, $CHCl_3$). **IR** (film) ν 3469, 2954, 2928, 2856, 1708, 1469, 1251, 1082. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.23 (5H, m, Ar<u>H</u>), 4.48 (1H, d, J = 11.9 Hz, PhC<u>H</u>$_x$H$_y$), 4.43 (1H, d, J = 11.9 Hz, PhCH$_x$<u>H</u>$_y$), 4.05

(1H, ddd, *J* = 10.5, 4.2, 1.7 Hz, CHOH), 3.75–3.69 (3H, m, BnOCH$_x$H$_y$ i SiOCH$_2$), 3.51 (1H, dd, *J* = 4.2, 1.1 Hz, OH), 3.50–3.39 (1H, m, BnOCH$_2$CH), 3.36 (1H, dd, *J* = 8.3, 4.6 Hz, BnOCH$_x$H$_y$), 1.68–1.57 (1H, m, SiOCH$_2$CH$_x$H$_y$), 1.52–1.40 (1H, m, SiOCH$_2$CH$_x$H$_y$), 1.12 (3H, s, C(CH$_3$)$_x$(CH$_3$)$_y$), 1.09 (3H, s, C(CH$_3$)$_x$(CH$_3$)$_y$), 1.00 (3H, d, *J* = 6.8 Hz, CHCH$_3$), 0.91 (9H, s, OSiC(CH$_3$)$_3$), 0.06 (3H, s, OSi(CH$_3$)$_x$(CH$_3$)$_y$), 0.06 (3H, s, OSi(CH$_3$)$_x$(CH$_3$)$_y$). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 218.1 (C), 137.3 (C), 128.4 (CH), 127.8 (CH), 127.8 (CH), 73.7 (CH_2), 73.5 (CH_2), 72.7 (CH), 61.1 (CH_2), 53.3 (C), 40.3 (CH), 33.4 (CH_2), 25.9 (CH_3), 21.0 (CH_3), 18.3 (C), 17.4 (CH_3), 15.5 (CH_3), –5.4 (CH_3), –5.4 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{23}H_{41}O_4Si$ $[M+H]^+$: 409.2769, found: 409.2766.

(2*S*,5*S*,6*S*)-1-Benxyloxy-6-*tert*-butyldiphenylsilyloxy-*5*-hydroxy-2,4,4-trimethyl-3-heptanone (2j). Colorless oil. **R_f** (hexane/EtOAc 9:1) = 0.30. **HPLC** (hexane/EtOAc 97:3) **t_R** = 18.7 min. **$[\alpha]_D$** = –15.4 (*c* 0.95, $CHCl_3$). **IR** (film) ν 3443, 3070, 2970, 2932, 2858, 1709, 1472, 1428, 1362, 1110. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75–7.69 (5H, m, ArH), 7.43–7.23 (10H, m, ArH), 4.48 (1H, d, *J* = 12.1 Hz, PhCH$_x$H$_y$), 4.40 (1H, d, *J* = 12.1 Hz, PhCH$_x$H$_y$), 3.99–3.93 (2H, m, SiOCHCHOH), 3.63 (1H, dd, *J* = 9.4, 8.3 Hz, BnOCH$_x$H$_y$), 3.33 (1H, d, *J* = 4.7 Hz, OH), 3.29 (1H, dd, *J* = 8.3, 4.7 Hz, BnOCH$_x$H$_y$), 3.26–3.19 (1H, m, BnOCH$_2$CH), 1.10 (3H, d, *J* = 6.1 Hz, SiOCHCH$_3$), 1.06 (9H, s, SiC(CH$_3$)$_3$), 1.01 (3H, s, C(CH$_3$)$_x$(CH$_3$)$_y$), 0.91 (3H, d, *J* = 6.7 Hz, BnOCH$_2$CHCH$_3$), 0.90 (3H, s, C(CH$_3$)$_x$(CH$_3$)$_y$). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 217.3 (C), 137.3 (C), 135.9 (C), 135.8 (C), 134.4 (CH), 133.9 (CH), 129.7 (CH), 129.6 (CH), 128.4 (CH), 127.8 (CH), 127.7 (CH), 127.7 (CH), 127.5 (CH), 78.3 (CH), 73.4 (CH_2), 73.4 (CH_2), 70.2 (CH), 52.5 (C), 40.2 (CH), 27.0 (CH_3), 21.5 (CH_3), 19.2 (C), 19.1 (CH_3), 17.8 (CH_3), 15.6 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{33}H_{48}NO_4Si$ $[M+NH_4]^+$: 550.3347, found: 550.3338.

(2*S*,5*S*,6*R*)-1-Benxyloxy-6-*tert*-butyldiphenylsilyloxy-*5*-hydroxy-2,4,4-trimethyl-3-heptanone (2k). Colorless oil. **R_f** (hexane/EtOAc 9:1) = 0.30. **HPLC** (hexane/EtOAc 97:3) **t_R** = 16.5 min. **$[\alpha]_D$** = +12.6 (*c* 1.45, $CHCl_3$). **IR** (film) ν 3513, 3070, 2968, 2933, 2858, 1701, 1472, 1428, 1362, 1111. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75–7.64 (5H, m, ArH), 7.45–7.24 (10H, m, ArH), 4.47 (1H, d, *J* = 12.1 Hz, PhCH$_x$H$_y$), 4.40 (1H, d, *J* = 12.1 Hz, PhCH$_x$H$_y$), 3.93 (1H, qd, *J* = 6.3, 3.0 Hz, SiOCH), 3.70 (1H, dd, *J* = 6.8, 3.0 Hz, CHOH), 3.61–3.55 (1H, m, BnOCH$_x$H$_y$), 3.37–3.28 (2H, m, BnOCH$_x$H$_y$CH), 3.26 (1H, d, *J* = 6.8 Hz, OH), 1.20 (3H, s, C(CH$_3$)$_x$(CH$_3$)$_y$), 1.06 (3H, s, C(CH$_3$)$_x$(CH$_3$)$_y$), 6.06–6.03 (6H, m, BnOCH$_2$CHCH$_3$ + SiOCHCH$_3$), 1.03 (9H, s, SiC(CH$_3$)$_3$). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 217.9 (C), 135.9 (CH), 135.8 (CH), 129.9 (CH), 129.7 (CH), 128.3 (CH), 127.8 (CH), 127.5 (CH), 127.4 (CH), 77.9 (CH), 73.2 (CH_2), 73.2 (CH_2), 69.7 (CH), 52.4 (C), 40.9 (CH), 27.1 (CH_3), 23.1 (CH_3), 21.5 (CH_3), 20.1 (CH_3), 19.3 (C), 15.5 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{33}H_{48}NO_4Si$ $[M+NH_4]^+$: 550.3347, found: 550.3343.

(2*S*,5*S*,6*R*)-1-Benxyloxy-7-*tert*-butyldiphenylsilyloxy-*5*-hydroxy-2,4,4,6-tetramethyl-3-heptanone (2l). Colorless oil. **R_f** (hexane/EtOAc 9:1) = 0.30. **HPLC** (hexane/EtOAc 97:3) **t_R** = 22.0 min. **$[\alpha]_D$** = –13.4 (*c* 1.05, $CHCl_3$). **IR** (film) ν 3460, 3070, 2932, 2858, 1708, 1471, 1428, 1112. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.67 (5H, m, ArH), 7.43–7.23 (10H, m, ArH), 4.50 (1H, d, *J* = 12.2 Hz, PhCH$_x$H$_y$), 4.43 (1H, d, *J* = 12.2 Hz, PhCH$_x$H$_y$), 4.25 (1H, dd, *J* = 5.3, 0.9 Hz, CHOH), 3.69 (1H, dd, *J* = 9.7, 8.4 Hz, BnOCH$_x$H$_y$), 3.59 (1H, dd, *J* = 9.7, 8.1 Hz, SiOCH$_x$H$_y$), 3.51 (1H, dd, *J* = 9.7, 5.5 Hz, SiOCH$_x$H$_y$), 3.46–3.40 (1H, m, BnOCH$_2$CH), 3.36 (1H, d, *J* = 5.3 Hz, OH), 3.33 (1H, dd, *J* = 8.4, 4.4 Hz, BnOCH$_x$H$_y$), 1.96–1.87 (1H, m, SiOCH$_2$CH), 1.14 (3H, s, C(CH$_3$)$_x$(CH$_3$)$_y$), 1.13 (3H, s, C(CH$_3$)$_x$(CH$_3$)$_y$), 1.08 (9H, s, SiC(CH$_3$)$_3$), 0.98 (3H, d, *J* = 6.8 Hz, BnOCH$_2$CHCH$_3$), 0.84 (3H, d, *J* = 6.9 Hz, SiOCH$_2$CHCH$_3$). **^{13}C**

NMR (100.6 MHz, $CDCl_3$) δ 218.4 (C), 137.2 (C), 135.6 (C), 135.6 (C), 133.8 (CH), 133.8 (CH), 129.6 (CH), 128.4 (CH), 127.8 (CH), 127.7 (CH), 73.6 (CH_2), 73.4 (CH_2), 73.1 (CH), 68.4 (CH_2), 54.0 (C), 40.2 (CH), 35.8 (CH), 26.9 (CH_3), 21.9 (CH_3), 19.3 (C), 18.3 (CH_3), 15.6 (CH_3), 11.0 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{34}H_{47}O_4Si$ $[M+H]^+$: 547.3238, found: 547.3235.

(2*S*,5*S*,6*S*)-1-Benxyloxy-7-*tert*-butyldiphenylsilyloxy-*5*-hydroxy-2,4,4,6-tetramethyl-3-heptanone (2m). Colorless oil. $\mathbf{R_f}$ (hexane/EtOAc 9:1) = 0.30. **HPLC** (hexane/EtOAc 97:3) $\mathbf{t_R}$ = 22.2 min. $\mathbf{[\alpha]_D}$ = +7.0 (*c* 1.00, $CHCl_3$). **IR** (film) ν 3460, 3070, 2962, 2932, 2858, 1708, 1471, 1428, 1112 . **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.65 (5H, m, ArH), 7.44–7.21 (10H, m, ArH), 4.45 (1H, d, *J* = 12.0 Hz, $PhCH_xH_y$), 4.39 (1H, d, *J* = 12.0 Hz, $PhCH_xH_y$), 3.90 (1H, t, *J* = 5.1 Hz, $BnOCH_xH_y$), 3.81 (1H, d, *J* = 4.9 Hz, $BnOCH_xH_y$), 3.72–3.67 (2H, sistema ABX segon ordre, CHOH), 3.66 (1H, t, *J* = 8.2 Hz, $SiOCH_xH_y$), 3.41–3.36 (1H, m, $BnOCH_2CH$), 3.33 (1H, dd, *J* = 15.8, 7.7 Hz, $SiOCH_xH_y$), 1.89–1.80 (1H, m, $SiOCH_2CH$), 1.14 (3H, s, $C(CH_3)_x(CH_3)_y$), 1.11 (3H, s, $C(CH_3)_x(CH_3)_y$), 1.05 (9H, s, $SiC(CH_3)_3$), 1.04 (3H, d, *J* = 7.0 Hz, $SiOCH_2CHCH_3$), 1.00 (3H, d, *J* = 6.6 Hz, $BnOCH_2CHCH_3$). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 218.0 (C), 137.6 (CH), 135.6 (CH), 135.6 (CH), 133.4 (CH), 129.7 (CH), 129.6 (CH), 128.4 (CH), 127.7 (CH), 78.6 (CH), 73.5 (CH_2), 73.3 (CH_2), 67.4 (CH_2), 53.7 (C), 40.6 (CH), 37.0 (CH), 26.9 (CH_3), 21.0 (CH_3), 19.2 (C), 18.7 (CH_3), 17.4 (CH_3), 15.8 (CH_3). **HRMS** (+ESI) *m/z* calcd for $C_{34}H_{47}O_4Si$ $[M+H]^+$: 547.3238, found: 547.3233.

2. Spectroscopic data of complex **I** and **II**

I. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60–7.34 (5H, m, ArH), 5.45 (2H, s, $PhCH_2$), 4.23 (1H, dd, *J* = 13.0, 2.0 Hz, $BnOCH_xH_y$), 4.14 (1H, dd, *J* = 13.0, 5.8 Hz, $BnOCH_xH_y$), 3.32–3.08 (2H, m, $CHCH_3$ i $CH(CH_3)_2$), 1.47 (3H, d, *J* = 7.6 Hz, $CHCH_3$), 1.34 (3H, d, *J* = 7.1 Hz, $CH(CH_3)_x(CH_3)_y$), 1.28 (3H, d, *J* = 6.4 Hz, $CH(CH_3)_x(CH_3)_y$).

II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.24 (5H, m, ArH), 5.77 (1H, d, *J* = 14.0 Hz, $PhCH_xH_y$), 4.84 (1H, d, *J* = 14.2 Hz, $PhCH_xH_y$), 4.34 (1H, d, *J* = 11.7 Hz, $BnOCH_xH_y$), 3.56 (1H, d, *J* = 10.6 Hz, $BnOCH_xH_y$), 3.00–2.85 (1H, m, $CHCH_3$), 1.83 (3H, s, $C(CH_3)_x(CH_3)_y$), 1.59 (3H, s, $C(CH_3)_x(CH_3)_y$), 1.34 (3H, d, *J* = 5.8 Hz, $CHCH_3$). **^{13}C NMR** (125.0 MHz, $CDCl_3$) δ 82.0 (CH_2), 76.5 (CH_2), 31.9 (CH), 18.3 (CH_3), 17.3 (CH_3), 17.2 (CH_3).

3. X-ray crystal structure of adduct **2f**

Table 1. Crystal data and structure refinement for uroc10a.

Identification code	uroc10a
Empirical formula	$C_{21}H_{26}O_3$
Formula weight	326.42
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 8.284(7) Å α= 108.28(2) °. b = 9.776(2) Å β= 99.72(4) °. c = 12.577(3) Å γ= 104.90(3) °.
Volume	899.4(8) $Å^3$
Z, Calculated density	2, 1.205 Mg/m^3
Absorption coefficient	0.079 mm^{-1}
F(000)	352
Crystal size	0.2 x 0.1 x 0.1 mm
Theta range for data collection	2.33 to 29.97 °.
Limiting indices	-11<=h<=11, -13<=k<=13, 0<=l<=17
Reflections collected / unique	5243 / 5243 [R(int) = 0.0307]
Completeness to theta = 29.97	100.0 %
Absorption correction	Empirical
Max. and min. transmission	0.99 and 0.98
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5243 / 16 / 217
Goodness-of-fit on F^2	0.882
Final R indices [I>2σ(I)]	R1 = 0.0359, wR2 = 0.0781
R indices (all data)	R1 = 0.1223, wR2 = 0.1001
Largest diff. peak and hole	0.169 and -0.243 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for uroc10a.
U(eq) is defined as one third of the trace of the orthogonalized
U_{ij} tensor.

	x	y	z	U(eq)
O(1)	9818(1)	6558(1)	3179(1)	48(1)
O(2)	6079(1)	5339(1)	1155(1)	46(1)
O(3)	2676(1)	3191(1)	486(1)	53(1)
C(1)	13869(2)	7988(2)	4557(1)	52(1)
C(2)	15563(2)	8017(2)	4572(2)	63(1)
C(3)	16225(2)	8234(2)	3688(2)	68(1)
C(4)	15242(2)	8465(2)	2809(2)	71(1)
C(5)	13558(2)	8449(2)	2799(1)	58(1)
C(6)	12857(2)	8198(2)	3665(1)	45(1)
C(7)	10994(2)	8094(2)	3630(1)	52(1)
C(8)	9670(2)	5779(2)	1993(1)	44(1)
C(9)	8240(2)	4245(1)	1534(1)	40(1)
C(10)	6468(2)	4430(1)	1532(1)	35(1)
C(11)	5211(1)	3462(1)	1983(1)	37(1)
C(12)	3425(2)	3714(2)	1710(1)	39(1)
C(13)	2085(2)	2916(1)	2200(1)	38(1)
C(14)	968(2)	1438(2)	1558(1)	48(1)
C(15)	-267(2)	726(2)	2002(1)	55(1)
C(16)	-403(2)	1469(2)	3085(1)	54(1)
C(17)	690(2)	2936(2)	3730(1)	53(1)
C(18)	1917(2)	3653(2)	3284(1)	45(1)
C(19)	8195(2)	3341(2)	291(1)	56(1)
C(20)	5006(2)	1769(2)	1426(1)	55(1)
C(21)	6004(2)	4045(2)	3298(1)	50(1)

Table 3. Bond lengths [Å] and angles [°] for uroc10a.

O(1)-C(8)	1.4135(16)
O(1)-C(7)	1.4325(17)
O(2)-C(10)	1.2158(14)
O(3)-C(12)	1.4268(16)
O(3)-H(3O)	0.8200
C(1)-C(6)	1.385(2)
C(1)-C(2)	1.392(2)
C(1)-H(1)	0.9300
C(2)-C(3)	1.370(2)
C(2)-H(2)	0.9300
C(3)-C(4)	1.373(2)
C(3)-H(3)	0.9300
C(4)-C(5)	1.389(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.3759(19)
C(5)-H(5)	0.9300
C(6)-C(7)	1.512(2)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.5160(19)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(19)	1.5241(18)
C(9)-C(10)	1.524(2)
C(9)-H(9)	0.9800
C(10)-C(11)	1.5264(18)
C(11)-C(21)	1.5293(19)
C(11)-C(20)	1.5321(18)
C(11)-C(12)	1.561(2)
C(12)-C(13)	1.5195(18)
C(12)-H(12)	0.9800
C(13)-C(18)	1.3777(18)
C(13)-C(14)	1.3870(19)
C(14)-C(15)	1.383(2)
C(14)-H(14)	0.9300
C(15)-C(16)	1.367(2)
C(15)-H(15)	0.9300
C(16)-C(17)	1.374(2)
C(16)-H(16)	0.9300
C(17)-C(18)	1.383(2)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(8)-O(1)-C(7)	112.55(11)
C(12)-O(3)-H(3O)	109.5
C(6)-C(1)-C(2)	120.68(15)

C(6)-C(1)-H(1)	119.7
C(2)-C(1)-H(1)	119.7
C(3)-C(2)-C(1)	119.65(16)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(2)-C(3)-C(4)	120.18(16)
C(2)-C(3)-H(3)	119.9
C(4)-C(3)-H(3)	119.9
C(3)-C(4)-C(5)	120.11(17)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	120.50(16)
C(6)-C(5)-H(5)	119.8
C(4)-C(5)-H(5)	119.8
C(5)-C(6)-C(1)	118.85(14)
C(5)-C(6)-C(7)	120.99(13)
C(1)-C(6)-C(7)	120.13(13)
O(1)-C(7)-C(6)	113.55(12)
O(1)-C(7)-H(7A)	108.9
C(6)-C(7)-H(7A)	108.9
O(1)-C(7)-H(7B)	108.9
C(6)-C(7)-H(7B)	108.9
H(7A)-C(7)-H(7B)	107.7
O(1)-C(8)-C(9)	109.59(11)
O(1)-C(8)-H(8A)	109.8
C(9)-C(8)-H(8A)	109.8
O(1)-C(8)-H(8B)	109.8
C(9)-C(8)-H(8B)	109.8
H(8A)-C(8)-H(8B)	108.2
C(8)-C(9)-C(19)	109.63(12)
C(8)-C(9)-C(10)	111.51(11)
C(19)-C(9)-C(10)	108.38(11)
C(8)-C(9)-H(9)	109.1
C(19)-C(9)-H(9)	109.1
C(10)-C(9)-H(9)	109.1
O(2)-C(10)-C(9)	118.86(11)
O(2)-C(10)-C(11)	121.37(11)
C(9)-C(10)-C(11)	119.76(11)
C(10)-C(11)-C(21)	106.00(11)
C(10)-C(11)-C(20)	111.05(10)
C(21)-C(11)-C(20)	109.99(11)
C(10)-C(11)-C(12)	108.42(10)
C(21)-C(11)-C(12)	110.59(11)
C(20)-C(11)-C(12)	110.68(11)
O(3)-C(12)-C(13)	106.95(11)
O(3)-C(12)-C(11)	111.31(11)
C(13)-C(12)-C(11)	114.09(11)
O(3)-C(12)-H(12)	108.1
C(13)-C(12)-H(12)	108.1
C(11)-C(12)-H(12)	108.1
C(18)-C(13)-C(14)	118.06(13)
C(18)-C(13)-C(12)	120.90(12)
C(14)-C(13)-C(12)	121.03(12)
C(15)-C(14)-C(13)	120.75(14)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-H(14)	119.6
C(16)-C(15)-C(14)	120.40(14)
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8

C(15)-C(16)-C(17)	119.59(14)
C(15)-C(16)-H(16)	120.2
C(17)-C(16)-H(16)	120.2
C(16)-C(17)-C(18)	120.06(14)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(13)-C(18)-C(17)	121.14(13)
C(13)-C(18)-H(18)	119.4
C(17)-C(18)-H(18)	119.4
C(9)-C(19)-H(19A)	109.5
C(9)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(9)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(11)-C(20)-H(20A)	109.5
C(11)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(11)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(11)-C(21)-H(21A)	109.5
C(11)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(11)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for uroc10a.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	40(1)	54(1)	49(1)	20(1)	13(1)	12(1)
O(2)	39(1)	53(1)	55(1)	29(1)	14(1)	16(1)
O(3)	38(1)	68(1)	53(1)	31(1)	10(1)	10(1)
C(1)	50(1)	49(1)	57(1)	22(1)	13(1)	15(1)
C(2)	50(1)	60(1)	77(1)	27(1)	11(1)	18(1)
C(3)	47(1)	62(1)	90(1)	21(1)	21(1)	16(1)
C(4)	57(1)	73(1)	77(1)	24(1)	25(1)	12(1)
C(5)	52(1)	60(1)	56(1)	22(1)	14(1)	11(1)
C(6)	39(1)	41(1)	50(1)	14(1)	10(1)	10(1)
C(7)	44(1)	52(1)	59(1)	20(1)	14(1)	16(1)
C(8)	33(1)	53(1)	48(1)	21(1)	12(1)	12(1)
C(9)	30(1)	47(1)	46(1)	22(1)	10(1)	14(1)
C(10)	29(1)	40(1)	36(1)	15(1)	8(1)	10(1)
C(11)	30(1)	42(1)	43(1)	21(1)	11(1)	12(1)
C(12)	32(1)	39(1)	48(1)	19(1)	11(1)	11(1)
C(13)	27(1)	44(1)	46(1)	22(1)	9(1)	12(1)
C(14)	41(1)	49(1)	51(1)	18(1)	11(1)	9(1)
C(15)	44(1)	54(1)	62(1)	23(1)	11(1)	8(1)
C(16)	43(1)	61(1)	61(1)	31(1)	16(1)	13(1)
C(17)	44(1)	63(1)	57(1)	26(1)	17(1)	19(1)
C(18)	37(1)	47(1)	51(1)	17(1)	11(1)	13(1)
C(19)	51(1)	63(1)	55(1)	22(1)	18(1)	20(1)
C(20)	48(1)	49(1)	72(1)	25(1)	19(1)	18(1)
C(21)	41(1)	65(1)	49(1)	28(1)	11(1)	17(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for uroc10a.

	x	y	z	U(eq)
H(3O)	3364	3609	194	79
H(1)	13414	7827	5151	62
H(2)	16240	7890	5180	76
H(3)	17344	8225	3684	82
H(4)	15705	8632	2218	85
H(5)	12899	8608	2202	69
H(7A)	10935	8608	4412	63
H(7B)	10625	8627	3154	63
H(8A)	10762	5630	1908	53
H(8B)	9406	6382	1548	53
H(9)	8475	3675	2025	48
H(12)	3622	4813	2045	47
H(14)	1049	921	820	58
H(15)	-1009	-264	1561	66
H(16)	-1229	985	3383	64
H(17)	605	3446	4468	63
H(18)	2640	4651	3723	54
H(19A)	7297	2366	6	83
H(19B)	9295	3194	279	83
H(19C)	7965	3893	-194	83
H(20A)	4207	1185	1720	83
H(20B)	6113	1634	1611	83
H(20C)	4570	1426	597	83
H(21A)	5259	3472	3628	75
H(21B)	6126	5106	3640	75
H(21C)	7123	3924	3450	75