Supporting Information

Diastereoselective Aldol Additions to α -amino- β -silyloxy Aldehydes. Divergent Synthesis of Aminodiols.

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Content:

S2-S11: General procedure for the aldol reaction and spectral data characterization for compounds **1-6** and **8, 9**.

S12-S33: ^1H and ^{13}C NMR spectra for compounds **1-6** and **8, 9**.

General Methods.

^1H and ^{13}C NMR spectra were recorded in CDCl_3 or $d_6\text{-DMSO}$, using the residual peak of CHCl_3 (^1H NMR δ 7.26, ^{13}C NMR δ 77.0) or DMSO (^1H NMR δ 2.50, ^{13}C NMR δ 39.5) as internal standard. Chemical shifts are reported in the δ -scale with multiplicity (b=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), integration and coupling constants (Hz). Only the strongest/structurally most important peaks (ν , cm^{-1}), in the IR spectra, are listed. Analytical thin layer chromatography plates were visualized with UV light and phosphomolybdic acid/cerium sulfate staining reagent. Air- and moisture sensitive reactions were carried out in flame-dried, septum-capped flasks under an atmospheric pressure of nitrogen. All liquid reagents were transferred via oven-dried syringes. THF was distilled from sodium-benzophenone ketyl before use; CH_2Cl_2 and $\text{BF}_3\cdot\text{OEt}_2$ were distilled from CaH_2 .

General procedure for the aldol reaction

To a stirred solution of the aldehyde **1c** (130 mg, 236 μmol) in freshly distilled CH_2Cl_2 (5 mL) cooled to $-60\text{ }^\circ\text{C}$ was added the $\text{BF}_3\cdot\text{OEt}_2$ (90 μL , 710 μmol) with a syringe. After 5 min **7** (102 μL , 472 μmol) was added and the mixture stirred at $-60\text{ }^\circ\text{C}$ for 18h. The reaction was quenched with saturated NaHCO_3 (5 mL) and extracted with CH_2Cl_2 (3x10 mL). The combined organic phases were dried (MgSO_4), filtered and evaporated to give a colorless oil. The diastereomeric ratio was determined by ^1H NMR on the crude reaction mixture. Flash chromatography of the residue (pentane:EtOAc 20:1) yielded **3b** (141 mg, 92%) as a colorless oil.

***N*-[(1*S**,2*S**)-2-(*tert*-Butyl-dimethyl-silanyloxy)-1-formyl-4-phenyl-butyl]-4-methyl-benzenesulfonamide (1a)**

¹H NMR (400 MHz, CDCl₃) δ 9.59 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.33-7.19 (m, 7H), 5.47 (d, *J* = 5.4 Hz, 1H), 4.08 (m, 1H), 3.82 (dd, *J* = 5.4, 3.7 Hz, 1H), 2.81 (m, 1H), 2.42 (s, 3H), 2.67 (m, 1H), 2.05 (m, 2H), 0.87 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 144.0, 141.0, 136.1, 129.9, 128.6, 128.3, 127.2, 126.2, 74.7, 65.1, 36.5, 31.7, 25.7, 21.5, 17.9, -4.6, -4.7; IR (neat) 2950, 1730, 1160 cm⁻¹.

***N*-[(1*S**,2*S**)-2-(*tert*-Butyl-dimethyl-silanyloxy)-2-cyclohexyl-1-formyl-ethyl]-4-methyl-benzenesulfonamide (1b)**

¹H NMR (CDCl₃, 400MHz) δ 9.56 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.54 (d, *J* = 4.8 Hz, 1H), 3.91 (dd, *J* = 4.8, 2.1 Hz, 1H), 3.82 (dd, *J* = 7.1, 2.0 Hz, 1H), 2.41 (s, 3H), 1.89-0.80 (m, 20H) 0.02 (s, 3H), 0.01 (s, 3H); ¹³C NMR (CDCl₃, 100MHz) 197.1, 144.1, 136.3, 130.0, 127.4, 80.4, 64.4, 42.6, 30.0, 29.5, 26.3, 26.2, 26.0, 21.7, 18.3, -3.9, -4.4; IR (neat) 3250, 2939, 1730, 1160 cm⁻¹.

***N*-Benzyl-*N*-[(1*S**,2*S**)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-formyl-4-phenyl-butyl]-4-methyl-benzenesulfonamide (1c)**

¹H NMR (400 MHz, CDCl₃) δ 9.78 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.42-7.18 (m, 12H), 4.92 (d, *J* = 15.6 Hz, 1H), 4.59 (d, *J* = 8.8 Hz, 1H) 4.36 (d, *J* = 15.6 Hz, 1H), 4.12 (m, 1H), 2.83 (dt, *J* = 12.7, 5.2 Hz, 1H), 2.55 (m, 4H), 2.05 (m, 1H), 1.87 (m, 1H), 0.93 (s, 9H), 0.02 (s, 3H), -0.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.8, 143.8, 141.9, 136.8, 136.7,

129.7, 128.7, 128.5, 128.4, 128.0, 127.6, 125.8, 70.7, 68.0, 67.2, 50.6, 35.6, 29.1, 25.8, 25.6, 21.6, 18.0, -4.0, -5.0; IR (neat) 2950, 1740 cm^{-1} .

***N*-Benzyl-*N*-[(1*S**,2*S**)-2-(*tert*-butyl-dimethyl-silanyloxy)-2-cyclohexyl-1-formyl-ethyl]-4-methyl-benzenesulfonamide (1d)**

^1H NMR (CDCl_3 , 400MHz) 9.58 (s, 1H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.31 (m, 7H), 4.88 (d, $J = 16.5$ Hz, 1H), 4.61 (d, $J = 7.6$ Hz, 1H), 4.26 (d, $J = 16.5$ Hz, 1H) 3.79 (dd, $J = 7.6, 1.3$ Hz, 1H), 2.43 (s, 3H), 1.85-0.79 (m, 20H), -0.12 (s, 3H), -0.21 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz) δ 200.2, 143.6, 137.7, 136.9, 129.6, 128.5, 128.1, 127.7, 127.5, 75.9, 66.9, 50.6, 40.7, 29.5, 26.5, 26.4, 26.2, 25.9, 25.4, 21.6, 18.2, -3.8, -4.7; IR (neat) 2930, 1730, 1160 cm^{-1} .

***N*-[(1*R**,2*S**)-2-(*tert*-Butyl-dimethyl-silanyloxy)-1-formyl-4-phenyl-butyl]-4-methyl-benzenesulfonamide (2a)**

^1H NMR (400 MHz, CDCl_3) δ 9.57 (s, 1H), 7.76 (d, $J = 8.3$ Hz, 2H), 7.31-7.07 (m, 7H), 5.49 (d, $J = 7.3$ Hz, 1H), 4.20 (m, 1H), 3.85 (dd, $J = 7.3, 3.0$ Hz, 1H), 2.54 (m, 1H), 2.41 (m, 4H), 1.91 (m, 1H), 1.57 (m, 1H), 0.86 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.7, 144.0, 140.9, 136.7, 129.8, 128.5, 128.2, 127.1, 126.1, 71.8, 64.7, 35.2, 31.8, 25.7, 21.5, 17.9, -4.5, -4.8; IR (neat) 3290, 2950, 1730, 1160 cm^{-1} .

***N*-[(1*R**,2*S**)-2-(*tert*-Butyl-dimethyl-silanyloxy)-2-cyclohexyl-1-formyl-ethyl]-4-methyl-benzenesulfonamide (2b)**

^1H NMR (CDCl_3 , 400MHz) δ 9.56 (s, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 5.54 (d, J = 4.8 Hz, 1H), 3.91 (dd, J = 4.8, 2.1 Hz, 1H), 3.82 (dd, J = 7.1, 2.0 Hz, 1H), 2.41 (s, 3H), 1.89-0.80 (m, 20H) 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz) 197.1, 144.1, 136.3, 130.0, 127.4, 80.4, 64.4, 42.6, 30.0, 29.5, 26.3, 26.2, 26.0, 21.7, 18.3, -3.9, -4.4; IR (neat) 2930, 1730, 1160 cm^{-1} .

***N*-Benzyl-*N*-[(1*R**,2*S**)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-formyl-4-phenyl-butyl]-4-methyl-benzenesulfonamide (2c)**

^1H NMR (400 MHz, CDCl_3) δ 9.43 (s, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 6.8 Hz, 2H), 7.31-7.14 (m, 10H), 4.84 (m, 2H), 4.61 (d, J = 3.3 Hz, 1H), 4.58 (d, J = 16.1 Hz, 1H), 2.70 (m, 1H), 2.57 (m, 1H), 2.39 (s, 3H), 2.14 (m, 1H), 1.77 (m, 1H), 0.74 (s, 9H), 0.05 (s, 3H), -0.05 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.1, 143.8, 141.0, 137.7, 136.4, 129.6, 128.4, 128.3, 128.0, 127.5, 127.2, 126.0, 72.4, 69.6, 51.9, 35.7, 31.6, 25.8, 25.7, 21.5, 17.9, -4.0, -5.0; IR (neat) 2930, 1740, 1160 cm^{-1} .

***N*-Benzyl-*N*-[(1*R**,2*S**)-2-(*tert*-butyl-dimethyl-silanyloxy)-2-cyclohexyl-1-formyl-ethyl]-4-methyl-benzenesulfonamide (2d)**

^1H NMR (CDCl_3 , 400MHz) δ 9.56 (s, 1H), 7.54 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 7.3 Hz, 2H), 7.25 (m, 5H), 4.87 (d, J = 16.3 Hz, 1H), 4.55 (m, 2H), 4.13 (dd, J = 5.9, 3.7 Hz, 1H), 2.40 (s, 3H), 1.60-0.77 (m, 11H), 0.78 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz) δ 199.9, 143.7, 138.3, 136.6, 129.7, 128.4, 128.2, 127.7, 127.3, 77.7, 69.8, 51.9, 40.3, 30.5, 28.6, 26.3, 26.23, 26.21, 21.7, 18.5, 1.2, -3.7, -4.3; IR (neat) 2930, 1730, 1340 cm^{-1} .

***N*-{(1*R**,2*S**)-1-[(*S**)-1-(*tert*-Butyl-dimethyl-silanyloxy)-3-phenyl-propyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (3a)**

¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.31-7.14 (m, 7H), 5.14 (d, *J* = 9.0 Hz, 1H), 4.55 (t, *J* = 6.3 Hz, 1H), 3.89 (m, 1H), 3.42 (s, 1H), 3.40 (dd, *J* = 9.1 Hz, 3.0 Hz, 1H), 2.65 (m, 2H), 2.50 (dd, *J* = 18.2, 6.3 Hz, 1H), 2.39 (s, 3H), 1.98 (dd, *J* = 18.2, 6.3 Hz, 1H), 1.92 (m, 2H), 1.02 (s, 9H), 0.89 (s, 9H), 0.02 (s, 3H), -0.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 214.5, 143.3, 141.3, 138.6, 129.8, 128.5, 128.4, 126.9, 126.0, 65.5, 56.8, 44.0, 39.8, 36.1, 31.2, 26.2, 25.8, 21.4, 17.9, -4.7, -4.8; IR (neat) 3340, 2960, 1700 cm⁻¹; HRMS (FAB+) calcd for C₃₀H₄₈NO₅SSi (M+H): 562.3022, found: 562.3009.

***N*-{(1*R**,2*S**)-1-[(*S**)-(*tert*-Butyl-dimethyl-silanyloxy)-cyclohexyl-methyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (3b)**

¹H NMR (CDCl₃, 400MHz) δ 7.75 (d, *J* = 8.2, 2H), 7.31 (d, *J* = 8.2, 2H), 5.13 (d, *J* = 8.9 Hz, 1H), 4.51 (t, *J* = 3.5 Hz, 1H), 3.60 (dd, *J* = 7.4, 2.6 Hz, 1H), 3.48 (s, 1H), 3.41 (dd, *J* = 8.9, 2.3 Hz, 1H), 2.53 (dd, *J* = 18.0, 6.3 Hz, 1H), 2.42 (s, 3H), 2.19 (dd, *J* = 18.0, 6.1 Hz, 1H), 1.76-0.89 (m, 29H), 0.16 (s, 3H), 0.04 (s, 3H); ¹³C NMR (CDCl₃, 100MHz) δ 214.4, 143.4, 138.4, 129.8, 127.0, 82.4, 66.3, 64.8, 56.0, 44.0, 41.4, 40.1, 29.4, 29.3, 26.9, 26.3, 26.2, 26.1, 26.0, 25.8, 21.4, 18.3, -3.5, -4.5; IR (neat) 3400, 2930, 1700 cm⁻¹; HRMS (FAB+) calcd for C₂₈H₅₀NO₅SSi (M+H): 540.3179, found: 540.3179.

***N*-{(1*R**,2*R**)-1-[(*S**)-1-(*tert*-Butyl-dimethyl-silanyloxy)-3-phenyl-propyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (4a)**

¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.28-7.11 (m, 7H), 4.84 (d, *J* = 8.3 Hz, 1H), 4.22 (m, 1H), 3.64 (m, 1H), 3.47 (m, 1H), 3.23 (d, *J* = 4.9 Hz, 1H), 2.79 (dd, *J* = 17.9, 2.6 Hz, 1H), 2.69 (dd, *J* = 17.9, 8.9 Hz, 1H), 2.60 (m, 1H), 2.45 (m, 4H), 1.90 (m, 1H), 1.72 (m, 1H), 1.09 (s, 9H), 0.86 (s, 9H), 0.01 (s, 3H), -0.01 (s, 3H); IR (neat) 3400, 2930, 1700 cm⁻¹; HRMS (FAB+) calcd for C₃₀H₄₈NO₅SSi (M+H): 562.3022, found: 562.3028.

***N*-Benzyl-*N*-{(1*R**,2*R**)-1-[(*S**)-1-(*tert*-butyl-dimethyl-silanyloxy)-3-phenyl-propyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (4c)**

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 6.8 Hz, 2H), 7.37-7.18 (m, 10H), 4.81 (d, *J* = 15.2 Hz, 1H), 4.40 (d, *J* = 15.2 Hz, 1H), 4.24 (m, 1H), 4.07 (m, 1H), 3.91 (m, 1H), 3.64 (d, *J* = 2.3 Hz, 1H), 2.88 (dt, *J* = 13.0, 4.6 Hz, 1H), 2.69 (m, 1H), 2.61 (dt, *J* = 13.0, 4.6 Hz, 1H), 2.45 (s, 3H), 2.21 (d, 18 Hz, 1H), 2.0 (m, 1H), 1.63 (m, 1H), 1.03 (s, 9H), 0.92 (s, 9H), 0.02 (s, 3H), -0.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 215.6, 143.5, 142.6, 138.0, 137.7, 129.8, 129.0, 128.6, 128.5, 128.3, 127.7, 127.3, 125.6, 72.4, 68.9, 44.0, 41.6, 35.8, 28.8, 26.0, 21.4, 18.1, -4.3, -4.4; IR (neat) 2960, 1690, 1160 cm⁻¹; HRMS (FAB+) calcd for C₃₇H₅₄NO₅SSi (M+H): 652.3492, found: 652.3484.

***N*-Benzyl-*N*-{(1*R**,2*R**)-1-[(*S**)-(*tert*-butyl-dimethyl-silanyloxy)-cyclohexyl-methyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (4d)**

¹H NMR (d8-PhMe, 90 °C, 500MHz) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.13-6.82 (m, 5H), 4.68 (d, *J* = 15.4 Hz, 1H), 4.50 (m, 1H), 4.34 (d, *J* = 15.4 Hz, 1H), 4.04-3.90 (m, 2H), 3.47 (s, 3H), 2.71 (dd, *J* = 17.0, 9.6 Hz, 1H), 2.27 (d, *J* = 17.0 Hz, 1H), 1.99-0.94 (m, 29H), 0.17 (s, 3H), -0.02 (s, 3H); ¹³C NMR (d6-DMSO, 125MHz) δ 213.8, 134.8,

137.9, 130.4, 129.1, 128.6, 127.8, 127.6, 75.6, 67.9, 62.7, 43.8, 43.2, 30.1, 27.0, 26.3, 24.5, 21.4, 19.1, -1.7, -4.5; IR (neat) 3450, 2970, 1690, 1340, 1160 cm^{-1} ; HRMS (FAB+) calcd for $\text{C}_{35}\text{H}_{56}\text{NO}_5\text{SSi}$ (M+H): 630.3648, found: 630.3643.

***N*-{(1*S**,2*R**)-1-[(*S**)-1-(*tert*-Butyl-dimethyl-silanyloxy)-3-phenyl-propyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (5a)**

^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, 8.2 Hz, 2H), 7.37-7.05 (m, 7H), 5.31 (d, J = 7.9 Hz, 1H), 4.21 (m, 1H), 3.89 (m, 1H), 3.32 (s, 1H), 3.14 (m, 1H), 2.55 (m, 1H), 2.31 (m, 5H), 2.18 (dd, J = 16.1, 9.6 Hz, 1H), 1.72 (m, 1H), 1.58 (m, 1H), 0.96 (s, 9H), 0.82 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 217.1, 143.4, 141.8, 138.8, 129.7, 128.3, 127.1, 125.8, 73.6, 65.5, 59.1, 44.2, 40.7, 34.3, 32.6, 26.0, 25.8, 21.4, 17.9, -2.8; IR(neat) 3400, 2960, 1700 cm^{-1} ; HRMS (FAB+) calcd for $\text{C}_{30}\text{H}_{48}\text{NO}_5\text{SSi}$ (M+H): 562.3022, found: 562.3018.

***N*-{(1*S**,2*R**)-1-[(*S**)-(*tert*-Butyl-dimethyl-silanyloxy)-cyclohexyl-methyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (5b)**

^1H NMR (CDCl_3 , 400MHz) δ 7.77 (d, J = 8.1, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.33 (d, J = 6.9 Hz, 1H), 4.12 (m, 1H), 3.55 (m, 1H), 3.26 (d, J = 3.1 Hz, 1H), 3.17 (m, 1H), 2.53 (dd, J = 17.8, 2.7 Hz, 1H), 2.41 (s, 3H), 2.30 (dd, J = 17.8 Hz, 9.7 Hz, 1H), 1.67-0.73 (m, 29H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (CDCl_3 , 100MHz) δ 217.4, 143.4, 138.1, 129.6, 127.3, 75.9, 66.7, 58.2, 44.3, 41.5, 40.6, 29.6, 28.6, 26.29, 26.26, 26.20, 26.1, 26.0, 21.4, 18.2, -4.2, -4.3; IR (neat) 3400, 2930, 1700 cm^{-1} ; HRMS (FAB+) calcd for $\text{C}_{28}\text{H}_{50}\text{NO}_5\text{SSi}$ (M+H): 540.3179, found: 540.3195.

***N*-Benzyl-*N*-{(1*S**,2*S**)-1-[(*S**)-1-(*tert*-butyl-dimethyl-silanyloxy)-3-phenyl-propyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (5c)**

¹H NMR (CDCl₃, 400MHz) δ 7.49-7.02 (m, 14H), 4.72 (d, *J* = 16.0 Hz, 1H), 4.62 (d, *J* = 16.0 Hz, 1H), 4.30 (m, 1H), 4.11 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.94 (dt, *J* = 6.1, 2.5 Hz, 1H), 2.97 (d, *J* = 4.5 Hz, 1H), 2.82 (dd, *J* = 18.0, 2.0 Hz, 1H), 2.57 (m, 3H), 2.34 (s, 3H), 1.96 (m, 1H), 1.62 (m, 1H), 1.11 (s, 9H), 0.82 (s, 9H), 0.08 (s, 3H), 0.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 216.3, 142.6, 141.5, 138.3, 137.8, 128.8, 128.7, 128.5, 128.3, 128.0, 127.9, 127.0, 125.9, 74.1, 65.3, 64.2, 49.7, 44.3, 41.2, 35.7, 32.3, 26.2, 25.9, 21.4, 18.0, -4.4, -4.5; IR (neat) 2960, 1700, 1160 cm⁻¹; HRMS (FAB+) calcd for C₃₇H₅₄NO₅SSi (M+H): 652.3492, found: 652.3503.

***N*-Benzyl-*N*-{(1*S**,2*S**)-1-[(*S**)-(*tert*-butyl-dimethyl-silanyloxy)-cyclohexyl-methyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (5d)**

¹H NMR (CDCl₃, 400MHz) δ 7.51-7.12 (m, 9H), 4.72 (d, *J* = 16.2 Hz, 1H), 4.56 (d, 16.2 Hz, 1H), 4.34 (m, 1H), 3.98 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.75 (t, *J* = 3.5 Hz, 1H), 3.10 (d, *J* = 17.3 Hz, 1H), 2.90 (d, *J* = 4.6 Hz, 1H), 2.51 (dd, 17.3, 9.0 Hz, 1H), 2.37 (s, 3H), 1.57-0.79 (m, 29H), 0.16 (s, 3H), 0.13 (s, 3H); ¹³C NMR (CDCl₃, 100MHz) δ 216.7, 142.6, 138.7, 137.7, 128.9, 128.7, 128.1, 127.9, 127.1, 79.7, 77.3, 65.2, 49.8, 44.3, 42.1, 39.7, 31.8, 28.6, 26.3, 26.2, 26.09, 26.05, 21.4, 18.5, -3.3, -4.7; IR (neat) 3490, 1700, 1340, 1100 cm⁻¹; HRMS (FAB+) calcd for C₃₅H₅₆NO₅SSi (M+H): 630.3648, found: 630.3651.

***N*-{(1*S**,2*S**)-1-[(*S**)-(*tert*-Butyl-dimethyl-silanyloxy)-cyclohexyl-methyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (6b)**

¹H NMR (CDCl₃, 400MHz) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.26 (d, *J* = 7.6 Hz, 1H), 3.76 (m, 2H), 3.53 (d, *J* = 4.2 Hz, 1H), 3.28 (m, 1H), 3.02 (d, *J* = 18.6 Hz, 1H), 2.70 (dd, *J* = 18.6, 8.9 Hz, 1H), 2.43 (s, 3H), 1.57-0.69 (m, 29H), 0.11 (s, 3H), 0.07 (s, 3H); IR (neat) 3500, 2950, 1700 cm⁻¹; HRMS (FAB+) calcd for C₂₈H₅₀NO₅SSi (M+H): 540.3179, found: 540.3177.

***N*-Benzyl-*N*-{(1*S**,2*R**)-1-[(*S**)-1-(*tert*-butyl-dimethyl-silanyloxy)-3-phenyl-propyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (6c)**

¹H NMR (CDCl₃, 400MHz) δ 7.43 (m, 2H), 7.32-7.18 (m, 8H), 7.07 (d, *J* = 7.0 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 4.79 (d, *J* = 14.5 Hz, 1H), 4.61 (d, *J* = 14.5 Hz, 1H), 4.43 (dt, *J* = 6.3, 2.3 Hz, 1H), 4.27 (m, 1H), 3.97 (dd, *J* = 10.2, 2.3 Hz, 1H), 3.59 (d, *J* = 3.2 Hz, 1H), 2.87 (d, *J* = 18.5 Hz, 1H), 2.73-2.51 (m, 3H), 2.24 (s, 3H), 2.22 (m, 2H), 1.10 (s, 9H), 0.87 (s, 9H), 0.14 (s, 3H), 0.05 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 218.6, 142.8, 141.6, 138.3, 137.3, 129.8, 129.0, 128.4, 128.3, 128.0, 127.5, 127.3, 125.8, 72.4, 65.1, 63.5, 49.9, 44.3, 40.9, 36.7, 32.7, 26.4, 26.2, 21.4, 18.3, -4.2, -5.2; IR (neat) 2960, 1690, 1160 cm⁻¹; HRMS (FAB+) calcd for C₃₇H₅₃NO₅SSiNa (M+Na): 674.3311, found: 674.3324.

***N*-Benzyl-*N*-{(1*S**,2*R**)-1-[(*S**)-(*tert*-butyl-dimethyl-silanyloxy)-cyclohexyl-methyl]-2-hydroxy-5,5-dimethyl-4-oxo-hexyl}-4-methyl-benzenesulfonamide (6d)**

¹H NMR (CDCl₃, 400MHz) δ 7.31-7.01 (m, 9H), 4.82 (d, *J* = 14.5 Hz, 1H), 4.48 (d, *J* = 14.5 Hz, 1H), 4.33 (m, 1H), 4.13 (m, 2H), 3.36 (s, 1H), 2.91 (m, 1H), 2.69 (m, 1H), 2.33 (s, 3H), 1.99-0.80 (m, 29H), 0.21 (s, 3H), 0.13 (s, 3H); ¹³C NMR (CDCl₃, 125MHz) δ 218.6, 142.6, 138.5, 136.8, 129.7, 128.9, 127.9, 127.5, 127.3, 109.0, 64.9, 62.1, 50.3, 44.4, 41.2, 39.8, 31.1,

29.7, 29.4, 26.9, 26.4, 26.3, 26.0, 21.3, 18.7, -3.5, -4.5; IR (neat) 3500, 1690, 1160 cm^{-1} ; HRMS (FAB+) calcd for $\text{C}_{35}\text{H}_{56}\text{NO}_5\text{SSi}$ (M+H): 630.3648, found: 630.3648.

***N*-Benzyl-*N*-((*S*^{*})-1-formyl-2-methyl-propyl)-4-methyl-benzenesulfonamide (8)**

^1H NMR (400 MHz, CDCl_3) δ 9.30 (s, 1H), 7.71 (d, J = 8.2 Hz, 2H), 7.27 (m, 7H), 4.45 (d, J = 15.3 Hz, 1H), 4.35 (d, J = 15.3 Hz, 1H), 3.76 (d, J = 10.3 Hz, 1H), 2.42 (s, 3H), 0.95 (d, J = 6.5 Hz, 1H), 0.71 (d, J = 6.5 Hz, 1H); ^{13}C NMR (CDCl_3 , 100MHz) δ 198.3, 143.7, 137.5, 136.1, 129.7, 129.0, 128.6, 128.2, 127.4, 71.3, 50.3, 27.0, 21.5, 20.2, 20.1; IR (neat) 2920, 1730, 1160 cm^{-1} ;

***N*-Benzyl-*N*-((1*S**,2*R*^{*})-2-hydroxy-1-isopropyl-5,5-dimethyl-4-oxo-hexyl)-4-methyl-benzenesulfonamide (9)**

^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 7.0 Hz, 2H), 7.35-7.21 (m, 5H), 4.61 (d, 15.4 Hz, 1H), 4.36 (d, 15.4 Hz, 1H), 4.01 (m, 1H), 3.43 (m, 1H), 3.26 (d, J = 2.2 Hz, 1H), 2.53 (m, 2H), 2.42 (s, 3H), 1.91 (m, 1H), 1.04 (s, 9H), 0.74 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 217.5, 143.2, 138.2, 137.6, 129.6, 129.1, 128.4, 127.7, 127.3, 69.2, 44.2, 41.7, 29.3, 26.3, 22.3, 21.5, 20.2; IR (neat) 3400, 2970, 1690, 1160 cm^{-1} ; HRMS (FAB+) calcd for $\text{C}_{25}\text{H}_{36}\text{NO}_4\text{S}$ (M+H): 446.2365, found: 446.2359.

1c

2a

2d

3a

3b

4a

4c

5a

5c

5d

6b

6c