Supporting Information

Further Studies Towards the Stereocontrolled Synthesis of Silicon-Containing Peptide Mimics

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General Methods.

Unless otherwise noted all reactions were carried out under inert atmosphere. Solvents were dried according to standard procedures, reactions were monitored by thin-layer chromatography (TLC) analysis. All other chemicals were used as received from the appropriate suppliers. Flash chromatography was carried out on silica gel 60 (230-400 mesh). The $^1$H NMR spectra were recorded at 400 MHz and $^{13}$C NMR spectra were recorded at 100 MHz. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) and referenced using the residual CHCl$_3$ resonance ($\delta = 7.26$) for $^1$H NMR and the central CDCl$_3$ resonance ($\delta = 77.16$) for $^{13}$C NMR. $^1$H NMR spectra are reported as follows (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hex = hextet, br = broad; coupling constant(s) in Hz; integration). Optical rotations were measured at the sodium line at ambient temperature (22 ºC) in CHCl$_3$ solutions.

Additional experimental procedures.

2-(4-Methoxyphenyl)-1,3-dioxane (74).\textsuperscript{1} 4-Methoxybenzaldehyde dimethyl acetal (565 mg, 3.10 mmol) was dissolved in dry toluene (10 mL) in a dry round-bottomed flask. TsOH (31 mg, 0.18 mmol) and anhydrous MgSO$_4$ (1.0 g, 8.3 mmol) were added to the stirred solution, followed by addition of 1,3-propanediol (474 mg, 6.23 mmol). The reaction mixture was kept under argon flow and heated to 90 ºC to remove methanol. After 2.5 h the reaction was judged complete by TLC and all volatiles were removed \textit{in vacuo}. The resulting mixture was dissolved in EtOAc (30 mL) and washed with sat NaHCO$_3$ (4 × 30 mL). The organic phase was dried (MgSO$_4$), filtered and evaporated \textit{in vacuo}, giving
the crude compound 74 (602 mg, 95% purity, 2.944 mmol, 95%) which could not be separated from residual anisaldehyde (approx. 5% according to $^1$H NMR) by column chromatography. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.43–7.39 (m, 2H), 6.90–6.87 (m, 2H), 5.46 (s, 1H), 4.28–4.23 (m, 2H) 4.01–3.94 (m, 2H), 3.80 (s, 3H), 2.28–2.16 (m, 1H), 1.46–1.40 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 160.1, 131.5, 127.4 (2C) 113.7 (2C), 101.7, 67.5 (2C), 55.4, 25.9. HRMS C$_{11}$H$_{14}$O$_3$ [M+Na$^+$]: calculated: 217.0841, found: 217.0844.

3-(4-Methoxybenzyloxy)propan-1-ol (75). $^1$ Acetal 74 (597 mg, 3.07 mmol) was dissolved in Et$_2$O (15 mL) and then cooled to 0 °C under argon atmosphere. A 1.7 M solution of DIBAL in toluene (4.0 mL, 6.8 mmol) was added via syringe and stirring continued at 0 °C for 3.5 h. Then the reaction was quenched with an aqueous solution of Rochelles salt (0.5 M, 15 mL), resulting in a white jelly which was left to stir for additional 20 min. The aqueous solution was extracted with Et$_2$O (4 × 40 mL) and the combined organic phases were dried (MgSO$_4$), filtered and concentrated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 25% to 65% EtOAc in pentane as eluant), which gave 75 (584 mg, 2.98 mmol, 97%) as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.25 (d, $J$ = 8.4 Hz, 2H), 6.88 (d, $J$ = 8.0 Hz, 2H), 4.45 (s, 2H) 3.80 (s, 3H), 3.78 (t, $J$ = 5.6 Hz, 2H), 3.63 (t, $J$ = 5.6 Hz, 2H), 2.32 (br s, 1H), 1.85 (quin, $J$ = 5.6 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 159.4, 130.3, 129.4 (2C), 114.0 (2C), 73.1, 69.3, 62.1, 55.4, 32.2. HRMS C$_{11}$H$_{16}$O$_3$ [M+Na$^+$]; calculated: 219.0997, found: 219.1004.

3-(4-Methoxybenzyloxy)propanal (76). To a dry round-bottomed flask was added DMSO (1.7 mL, 24 mmol) and dry CH$_2$Cl$_2$ (25 mL), and the mixture was cooled to −60 °C under argon, followed by the dropwise addition of oxalylchloride (1.0 mL, 11.0 mmol). After 30 min alcohol 75 (974 mg, 4.96 mmol) in CH$_2$Cl$_2$ (5 mL) was added and the reaction was stirred for additional 1.5 h. NEt$_3$ (5 mL, 36.0 mmol) was then added and the reaction mixture was allowed to warm to rt. Then it was quenched with water
(50 mL), the phases were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 50 mL). The combined organic phases were washed with sat NaHCO$_3$ (3 × 50 mL), and brine (50 mL), dried (MgSO$_4$), filtered, and evaporated in vacuo giving 76 (1.02 g, 4.91 mmol, 99%), as a pungent yellow oil, which was used without further purification. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 9.78 (t, $J = 2.0$ Hz, 1H), 7.25 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.4$ Hz, 2H), 4.46 (s, 2H), 3.80 (s, 3H), 3.78 (t, $J = 6.0$ Hz, 2H), 2.67 (dt, $J = 6.0$, 2.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 201.3, 159.5, 130.1, 129.5 (2C), 114.0 (2C), 73.1, 63.7, 55.4, 44.0. HRMS C$_{11}$H$_{14}$O$_3$ [M+Na$^+$]; calculated: 217.0841, found: 217.0842.

(2,14,16) 

(R,E)-N-(2-(Benzyloxy)ethylidene)-2-methylpropane-2-sulfinamide (12).$^2$ General Procedure for Preparation of Sulfinimines. Method A. 2-Benzyloxyethanal$^3$ (400 mg, 2.66 mmol) was dissolved in dry CH$_2$Cl$_2$ (25 mL) and (R)-tert-butylsulfinamide (330 mg, 2.71 mmol), PPTS (5 mg, 0.02 mmol) and MgSO$_4$ were added. The reaction was heated at reflux for 18 h. Then the reaction mixture was filtered and the solids washed with CH$_2$Cl$_2$ (2 × 10 mL). The combined filtrates were evaporated in vacuo and the pure product was obtained by column chromatography (20% EtOAc in pentane as eluant) which gave 12 (667 mg, 79%) as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.13 (t, $J = 3.2$ Hz, 1H), 7.32–7.38 (m, 5H), 4.64 (s, 2H), 4.43 (dd, $J = 16.4$, 3.2 Hz, 1H), 4.38 (dd, $J = 16.4$, 3.2 Hz, 1H), 1.21 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 166.9, 137.4, 128.7 (2C), 128.2, 128.0 (2C), 73.5, 71.4, 57.1, 22.6 (3C). HRMS C$_{13}$H$_{19}$NO$_2$S [M+Na$^+$]; calculated: 276.1029, found: 276.1038.
(R,E)-N-(2-(4-(Benzyloxy)phenyl)ethylidene)-2-methylpropane-2-sulfinamide (14). It was prepared from 2-(4-(Benzyloxy)phenyl)ethanal\(^4\) (520 mg, 2.20 mmol 1.22 equiv) according to Method A. Increasing polarity from 15% to 20% EtOAc in pentane was used as eluant for column chromatography giving 14 (58%) as an oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ (ppm) 8.12 (t, \(J = 4.8\) Hz, 1H), 7.45–7.30 (m, 5H), 7.15 (d, \(J = 8.4\) Hz, 2H), 6.95 (d, \(J = 8.4\) Hz, 2H), 5.06 (s, 2H), 3.77 (ABX system, \(J = 5.0\) Hz, 1H), 3.74 (ABX system, \(J = 5.0\) Hz, 1H), 1.21 (s, 9H).

\(^1\)C NMR (100 MHz, CDCl\(_3\)) δ (ppm) 167.7, 158.0, 137.0, 130.3 (2C), 128.6 (2C), 128.0, 127.5 (2C), 127.1, 115.3 (2C), 70.1, 56.9, 41.8, 22.4 (3C). HRMS C\(_{19}\)H\(_{23}\)NO\(_2\)S [M+Na\(^+\)]; calculated: 352.1347, found: 352.1351.

(R,E)-N-((R)-2-(tert-Butyldiphenylsilyloxy)propylidene)-2-methylpropane-2-sulfinamide (16).\(^5\) It was prepared from (R)-2-(tert-butyldiphenylsilyloxy)propanal\(^6\) according to Method A. Increasing polarity from 5% to 10% EtOAc in pentane was used as eluant for column chromatography giving 16 (89%) as an oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ (ppm) 8.02 (d, \(J = 4.0\) Hz, 1H), 7.69–7.63 (m, 4H), 7.46–7.33 (m, 6H), 4.59 (qd, \(J = 6.8, 4.0\) Hz, 1H), 1.28 (d, \(J = 6.8\) Hz, 3H), 1.14 (s, 9H), 1.08 (s, 9H).

\(^1\)C NMR (100 MHz, CDCl\(_3\)) δ (ppm) 171.4, 136.0 (4C), 134.0 (2C) 130.0 (2C), 127.8 (4C), 71.5, 56.9, 27.0 (3C), 22.5 (3C), 21.7, 19.4. HRMS C\(_{23}\)H\(_{33}\)NO\(_2\)SSi [M+Na\(^+\)]; calculated: 438.1899, found: 438.1901.

(R,E)-N-(5-(tert-Butyldimethylsilyloxy)pentylidene)-2-methylpropane-2-sulfinamide (77). It was prepared from 5-(tert-butyldimethylsilyloxy)pentanal\(^7\) according to Method A. Increasing polarity from 5% to 20% EtOAc in pentane was used as eluant for column chromatography giving 77 (85%) as an oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ (ppm) 8.07 (t, \(J = 4.8\) Hz, 1H), 3.62 (t, \(J = 6.4\) Hz, 2H), 2.53 (td, \(J = 6.8\), \(J = 4.8\) Hz, 1H), 1.72 (s, 3H), 1.08 (s, 9H), 0.90 (s, 9H).
4.8 Hz, 2H), 1.73–1.64 (m, 2H), 1.62–1.53 (m, 2H), 1.18 (s, 9H), 0.88 (s, 9H), 0.03 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 169.7, 62.8, 36.0, 32.4, 28.3, 26.1 (3C), 24.9, 22.5 (3C), 22.1, 18.5, −5.2. HRMS C$_{15}$H$_{33}$NO$_2$SSi [M+Na$^+$]; calculated: 342.1899, found: 342.1896.

(R,E)-N-(3-(4-Methoxybenzyloxy)propylidene)-2-methylpropane-2-sulfinamide (78). It was prepared from aldehyde 76 according to Method A. Increasing polarity from 5% to 20% EtOAc in pentane was used as eluant for column chromatography giving 78 (77%) as a pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.09 (t, $J$ = 4.4 Hz, 1H), 7.23 (m, 2H), 6.87 (m, 2H), 4.44 (s, 2H), 3.79 (s, 3H), 3.74 (t, $J$ = 6.0 Hz, 2H), 2.79 (td, $J$ = 6.0, 4.4 Hz, 2H), 1.20 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 167.5, 159.4, 130.1, 129.4 (2C), 113.9 (2C), 73.0, 66.0, 56.8, 55.4, 36.7, 22.5 (3C). HRMS C$_{15}$H$_{23}$NO$_3$S [M+Na$^+$]; calculated: 320.1296, found: 320.1295.

(R,E)-2-Methyl-N-(3-methylbutylidene)propane-2-sulfinamide (46). It was prepared from isovaleraldehyde according to Method A. Increasing polarity from 5% to 10% EtOAc in pentane was used as eluant for column chromatography, giving 46 (95%) as an oil. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.05 (t, $J$ = 5.2 Hz, 1H), 2.40 (ddd, $J$ = 6.8, 5.6, 1.6 Hz, 2H), 2.05 (m, 1H), 1.19 (s, 9H), 0.98 (d, $J$ = 6.8 Hz, 3H), 0.98 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 169.4, 56.5, 45.0, 26.2, 22.6, 22.5, 22.4 (3C). HRMS C$_9$H$_{19}$NO$_3$S [M+Na$^+$]; calculated: 212.1085, found: 212.1087.

(R,E)-2-Methyl-N-(2-phenylethylidene)propane-2-sulfinamide (56). It was prepared from phenyl acetaldehyde according to Method A. CH$_2$Cl$_2$ was used as eluant for column chromatography giving 56 (87%) as an oil. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.13 (t, $J$ = 5.2 Hz, 1H), 7.35–7.22 (m, 5H), 3.85
(dd, J = 15.2, 5.2 Hz, 1H), 3.81 (dd, J = 15.2, 5.2 Hz, 1H), 1.19 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 167.6, 135.0, 129.4 (2C), 129.0 (2C), 127.3, 57.0, 42.8, 22.5 (3C). HRMS C$_{12}$H$_{17}$NOS [M+Na$^+$]; calculated: 246.0929, found: 246.0933.

(R,E)-N-(4-(4-Methoxybenzyl oxy)butylidene)-2-methylpropane-2-sulfinamide (79).$^{10}$ General Procedure for Preparation of Sulfinimines. Method B. (R)-tert-Butyisulfonamid e (672 mg, 5.54 mmol) and 4-(4-methoxybenzyl oxy)butanal$^{11}$ (5.09 mmol 0.92 equiv) were dissolved in CH$_2$Cl$_2$ (18 mL) and Cs$_2$CO$_3$ (2.17 g, 6.65 mmol, 1.2 equiv) was added. The mixture was heated to reflux for 18 h, then cooled and filtered through a pad of celite. The solids were washed with CH$_2$Cl$_2$, and then the combined filtrates were evaporated in vacuo. The pure product was obtained by column chromatography using 5% to 40% EtOAc in pentane as eluant, giving 79 (1.0 g, 3.21 mmol, 63%) as an oil. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.08 (t, J = 4.4 Hz, 1H), 7.23 (dt, J = 8.8, 2.0 Hz, 2H), 6.86 (dt, J = 8.8, 2.0 Hz, 2H), 4.41 (s, 2H), 3.78 (s, 3H), 3.49 (t, J = 6.0 Hz, 2H), 2.60 (td, J = 7.2, 4.4 Hz, 2H), 1.92 (pent, J = 6.8 Hz, 2H), 1.16 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 169.0, 159.1, 130.3, 129.2 (2C), 113.7 (2C), 72.6, 68.8, 56.4, 55.2, 32.9, 25.5, 22.2 (3C). HRMS C$_{16}$H$_{25}$NO$_3$S [M+Na$^+$]; calculated: 334.1453, found: 334.1407.

(R,E)-N-Butylidene-2-methylpropane-2-sulfinamide (80).$^{12}$ It was prepared from butyraldehyde according to Method B. 10% EtOAc in pentane was used as eluant for column chromatography, giving 80 (63%) as an oil. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.06 (t, J = 4.8 Hz, 1H), 2.49 (td, J = 7.2, 4.8 Hz, 2H), 1.65 (sext, J = 7.2 Hz, 2H), 1.19 (s, 9H), 0.99 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 169.8, 56.6, 38.2, 22.5 (3C), 19.1, 13.9. HRMS C$_8$H$_{17}$NOS [M+Na$^+$]; calculated: 198.0929, found: 198.0925.
(R)-N-((R)-2-(4-(Benzyloxy)phenyl)-1-(methylidiphenylsilyl)ethyl)-2-methylpropane-2-sulfinamide (15). General Procedure for the Addition of (Diphenylmethylsilyl)lithium to Sulfinimines. Lithium (36 mg, 6.0 mmol, 12.0 equiv) was suspended in THF (5 mL) under argon atmosphere, and then diphenylmethylchlorosilane (0.31 ml, 1.50 mmol, 3.0 equiv) was added, before the mixture was stirred at rt for 4 h. In a separate flask sulfinimine 14 (164.5 mg, 0.50 mmol, 1 equiv) was dissolved in THF (5 mL) and the solution cooled to −78 °C under argon atmosphere. To this cooled solution, the solution of lithium diphenylmethylsilane was added dropwise over 5 min via syringe. The solution was stirred at −78 °C for 18h, then water (2 mL) was added and the mixture allowed to warm to rt. The mixture was poured into water (50 mL) and extracted with EtOAc (3 × 20 mL), then the combined organic portions were dried (MgSO₄), filtered and evaporated in vacuo. The pure product was obtained by column chromatography using 15% to 30% EtOAc in pentane as eluant, giving 15 (120 mg, 0.23 mmol, 45%) as an oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.57–7.31 (m, 15H), 7.10 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.03 (s, 2H), 3.75 (dt, J = 9.2, 6.4 Hz, 1H), 3.17 (d, J = 9.2 Hz, 1H), 3.14 (ABX system, J = 6.4 Hz, 1H), 3.06 (ABX system, J = 6.4 Hz, 1H), 1.02 (s, 9H), 0.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 157.5, 137.2, 135.0 (4C), 134.8, 134.7, 131.0 (2C), 130.8 (2C), 129.6 (2C), 128.6 (2C), 128.0 (4C), 127.5 (2C), 114.8 (2C), 70.0, 56.4, 47.5, 38.5, 22.5 (3C), −5.1. HRMS C₃₂H₃₇NO₂SSi [M+Na⁺]; calculated: 550.2212, found: 550.2222.
(R)-N-((1R,2R)-2-(tert-Butyldiphenylsilyloxy)-1-(methyldiphenylsilyl)propyl)-2-methylpropane-2-sulfinamide (17). It was prepared from sulfinimine 16 according to the previous general procedure. An 8:8:1 mixture of pentane:CH₂Cl₂:diethylether was used as eluant for column chromatography, giving 17 (48%) as an oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.71–7.56 (m, 6H), 7.47–7.30 (m, 14H), 4.48 (qd, J = 6.4, 2.8 Hz, 1H), 3.45 (m, 1H), 3.36 (m, 1H), 1.16 (d, J = 6.4 Hz, 3H), 1.07 (s, 9H), 0.99 (s, 9H), 0.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 136.1 (2C), 136.0 (2C), 135.8, 135.5 (2C), 135.3, 134.9 (2C), 134.2, 133.7, 129.8, 129.7 (2C), 129.5, 128.0 (4C), 127.8 (2C), 127.6 (2C), 71.5, 56.4, 52.8, 27.3 (3C), 22.7 (3C), 21.9, 19.3, −3.4. HRMS C₃₆H₄₇NO₂SSi [M+Na⁺]; calculated: 636.2746, found: 636.2767.

(R)-N-(1R)-4-(4-Methoxybenzoyloxy)-1-(methyldiphenylsilyl)butyl)-2-methylpropane-2-sulfinamide (23). It was prepared from sulfinimine 79 according to the previous general procedure. Increasing polarity from 10% to 60% EtOAc in pentane was used as eluant for column chromatography giving 23 (97%) as an oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.53–7.60 (m, 4H), 7.32–7.43 (m, 6H), 7.20 (dt, J = 8.4, 2.8 Hz, 2H), 6.86 (dt, J = 8.4, 2.8 Hz, 2H), 4.38 (s, 2H), 3.79 (s, 3H), 3.36–3.50 (m, 2H), 2.87 (d, J = 10 Hz, 1H), 1.87–2.04 (m, 2H), 1.59–1.80 (m, 2H), 1.01 (s, 9H), 0.63 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 158.9, 134.9 (2C), 134.8 (2C), 134.5, 134.4, 130.7, 129.6, 129.5, 129.0 (2C), 127.93 (2C), 127.91 (2C), 113.6 (2C), 72.2, 69.4, 56.1, 55.1, 46.5, 29.9, 27.4, 22.5 (3C), −5.2. HRMS C₂₉H₃₉NO₃SSi [M+Na⁺]; calculated: 532.2318, found: 532.2310.

(R)-N-((R)-3-(4-Methoxybenzoyloxy)-1-(methyldiphenylsilyl)propyl)-2-methylpropane-2-sulfinamide (31). It was prepared from sulfinimine 78 according to the previous general procedure. Increasing polarity from 25% to 60% EtOAc in pentane was used as eluant for column chromatography giving 31 (87%) as a colourless wax. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.57–7.55 (m, 4H), 7.40–7.33 (m, 6H),
**General Procedure for the Addition of (Diphenylalkylsilyl)lithium to Sulfinimines.** Diphenyl[3-(tetrahydro-2H-pyran-2-yloxy)propyl]silane<sup>10</sup> (70 mg, 0.21 mmol) was dissolved in dry THF (2 mL) and then freshly cut lithium pieces (15 mg, 2.1 mmol) were added. The mixture was stirred under argon atmosphere for 4 h, by which time the mixture had turned a rich dark brown colour. In a separate flask, the imine 80 (19 mg, 0.11 mmol) was dissolved in dry THF (2 mL) and the solution was cooled to −78 °C. To this cooled solution was added the silyl lithium reagent (2 mL) dropwise via syringe over 3-5 min. The mixture was stirred at −78 °C for 18 h, and then quenched via the addition of water. It was poured into water (30 mL) and extracted with EtOAc (3 × 20 mL). The combined organic portions were dried (MgSO<sub>4</sub>), filtered and evaporated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 20% to 30% EtOAc in pentane as eluant) which gave 39 (42 mg, 0.084 mmol, 76%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.57–7.53 (m, 4H), 7.44–7.34 (m, 6H), 4.51 (t, J = 2.8 Hz, 1H), 3.84–3.79 (m, 1H), 3.70–3.64 (m, 1H), 3.48–3.38 (m, 2H), 3.56–3.31 (m, 1H), 2.68 (br d, J = 10.0 Hz, 1H), 1.82–1.37 (m, 12H), 1.19–1.14 (m,
2H), 1.04 (s, 9H), 0.88 (t, \( J = 7.2 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm) 135.7 (2C), 135.6 (2C), 133.3, 133.1, 129.94, 129.88, 128.2 (2C), 128.1 (2C), 98.9, 70.1, 62.5, 56.6, 46.0, 36.0, 30.9, 25.6, 23.9, 22.8 (3C), 21.0, 19.8, 14.2, 8.4. HRMS \( C_{28}H_{43}NO_3SSi [M+Na]^+ \); calculated: 524.2631, found: 524.2624.

\((R)-N-((1R)-(1-(Diphenyl(3-(tetrahydro-2H-pyran-2-yloxy)propyl)silyl)-3-methylbutyl)-2-methyl-propane-2-sulfinamide (48).\) It was prepared from sulfinimine 46 according to the previous general procedure. The pure product was obtained by column chromatography using 5% to 30% EtOAc in pentane as eluant which gave \( 48 \) (99%) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 7.60–7.50 (m, 4H), 7.44–7.32 (m, 6H), 4.55–4.46 (m 1H), 3.81 (ddd, \( J = 10.8, 7.6, 3.2 \) Hz, 1H), 3.66 (ddt, \( J = 8.8, 7.2, 2.0 \) Hz, 1H), 5.53–3.40 (m, 2H), 3.32 (ddt, \( J = 9.6, 6.8, 2.8 \) Hz, 1H), 2.56 (d, \( J = 9.6 \) Hz, 1H), 2.13–2.02 (m, 1H), 1.85–1.36 (m, 10H), 1.20–1.10 (m, 2H), 1.02 (s, 9H), 0.94 (d, \( J = 6.4 \) Hz, 3H), 0.87 (d, \( J = 6.8 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) (ppm) 135.7 (2C), 135.6 (2C), 133.1, 132.8, 129.91, 128.89, 128.2 (2C), 128.1 (2C), 109.9, 98.9, 70.0, 62.5, 56.6, 43.6, 42.9, 30.8, 25.6, 25.0, 23.9, 22.8 (3C), 21.3, 19.8, 8.3. HRMS \( C_{29}H_{45}NO_3SSi [M+Na]^+ \); calculated: 538.2782, found: 538.2801.

\(S(R)-N-((1R)-1-(Diphenyl[3-(tetrahydro-2H-pyran-2-yloxy)propyl]silyl)-2-phenylethyl)-2-methyl-ropane-2-sulfinamide (58).\) It was prepared from sulfinimine 56 according to the previous general procedure. The pure product was obtained by column chromatography using 10% to 50% EtOAc in pentane as eluant which gave \( 58 \) (47%) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 7.48–7.53 (m, 4H), 7.33–7.42 (m, 5H), 7.15–7.23 (m, 5H), 4.46 (dt, \( J = 5.2, 3.2 \) Hz, 1H), 3.76–3.81 (m, 2H), 3.54 (ddt, \( J = 8.0, 6.8, 1.2 \) Hz, 1H), 3.43–3.45 (m, 1H), 3.90 (d, \( J = 9.6, 6.8, 4.8 \) Hz, 1H), 3.08–3.11 (m, 2H), 3.02 (d, \( J = 8.4 \) Hz, 1H), 1.75–1.83 (m, 1H), 1.62–1.69 (m, 1H),
1.40–1.55 (m, 6H), 0.96–1.06 (m, 2H), 1.00 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 138.9, 135.6 (4C), 132.9 (2C), 129.8, 129.7, 129.7 (2C), 128.4 (2C), 128.1 (2C), 128.0 (2C), 126.6, 98.7, 69.9, 62.3, 56.6, 46.8, 39.8, 30.8, 25.5, 23.9, 22.6 (3C), 19.7, 8.7. HRMS C$_{32}$H$_{43}$NO$_3$SSi [M+Na$^+$]; calculated: 572.2631, found: 572.2629.

$(R)$-N-((($R$)-4-Hydroxy-1-(methyldiphenylsilyl)butyl)-2-methylpropane-2-sulfinamide (24). $p$-Methoxybencyl ether 23 (635 mg, 1.23 mmol) was dissolved in CH$_2$Cl$_2$ (45 mL), and then water (6 mL) and DDQ (362 mg, 1.55 mmol) were added. The mixture was stirred vigorously at rt for 3 h, then poured into water (50 mL) and extracted with CH$_2$Cl$_2$ (3 × 40 mL). The combined organic portions were dried (MgSO$_4$), filtered and evaporated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 1% to 5% MeOH in CH$_2$Cl$_2$ as eluant) which gave 24 (461 mg, 1.18 mmol, 96%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.59–7.52 (m, 4H), 7.43–7.33 (m, 6H), 3.63 (dt, J = 5.4, 5.4 Hz, 1H), 3.52 (ddd, J = 11.6, 7.2, 4.4 Hz, 1H), 3.42 (ddd, J = 10.0, 8.0, 4.4 Hz, 1H), 3.07 (d, J = 10.0 Hz, 1H), 2.84 (br s, 1H), 2.05–1.94 (m, 1H), 1.85–1.73 (m, 1H), 1.73–1.61 (m, 2H), 1.02 (s, 9H), 0.62 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 135.1 (2C), 134.9 (2C), 134.6, 134.4, 129.8, 129.7, 128.1 (2C), 128.0 (2C), 62.2, 56.4, 47.2, 30.4, 29.7, 22.7 (3C), −5.2. HRMS C$_{32}$H$_{31}$NO$_3$SSi [M+Na$^+$]; calculated: 412.1737, found: 412.1744.

$(R)$-tert-Butyl 4-hydroxy-1-(methyldiphenylsilyl)butylcarbamate (25). Sulfinamide 24 (461 mg, 1.18 mmol) was dissolved in anhydrous HCl in MeOH (20 mL, 0.5 M) and the mixture was stirred at rt for 3 h. All volatiles were removed in vacuo giving the crude amino alcohol. The residue was dissolved in dry
CH₂Cl₂ (15 mL) and then Boc₂O (250 mg, 1.19 mmol) and NEt₃ (250 mg, 2.50 mmol) were added. The mixture was stirred at rt for 18 h, then poured into water (50 mL) and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic portions were dried (MgSO₄), filtered and evaporated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 10% to 50% EtOAc in pentane as eluant) which gave 25 (434 mg, 1.13 mmol, 95%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.57 (dd, J = 7.6, 1.6 Hz, 2H), 7.53 (dd, J = 7.6, 1.6 Hz, 2H), 7.43–7.33 (m, 6H), 4.32 (d, J = 10.0 Hz, 1H), 3.85 (td, J = 10.8, 2.8 Hz, 1H), 3.70–3.56 (m, 2H), 1.93 (br s, 1H), 1.76–1.49 (m, 3H), 1.48–1.36 (m, 1H), 1.39 (s, 9H), 0.60 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 156.7, 135.1 (2C), 135.0 (2C), 134.5, 134.3, 129.82, 129.76, 128.1 (4C), 79.4, 62.7, 38.6, 29.9, 28.8, 28.5 (3C), −5.7.

HRMS C₂₂H₃₁NO₃Si [M+Na⁺]; calculated: 408.1965, found: 408.1979.

(R)-4-(tert-Butoxycarbonylamino)-4-(methyldiphenylsilyl)butyl methanesulfonate (26). The alcohol 25 (57 mg, 0.15 mmol) was dissolved in CH₂Cl₂ (5 mL) and then NEt₃ (30 mg, 0.30 mmol) and MsCl (19 mg, 0.23 mmol) were added. The mixture was stirred at rt for 30 min, then poured into water (50 mL) and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic portions were dried (MgSO₄), filtered and evaporated in vacuo, giving the crude mesylate 26 that was used without further purification. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.59–7.50 (m, 4H), 7.44–7.32 (m, 6H), 4.30–4.20 (m, 2H), 3.84–3.74 (m, 1H), 3.65 (br s, 1H), 2.92 (s, 3H), 1.94–1.80 (m, 1H), 1.80–1.67 (m, 2H), 1.47–1.34 (m, 1H), 1.38 (s, 9H), 0.60 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 156.5, 135.0 (2C), 134.9 (2C), 134.1, 134.0, 129.95, 129.89, 128.2 (4C), 79.4, 69.9, 37.9, 37.2, 28.4 (3C), 27.8, 26.6, −5.7.

HRMS C₂₃H₃₃NO₅SSi [M+Na⁺]; calculated: 486.1741, found: 486.1754.

(R)-tert-Butyl 4-azido-1-(methyldiphenylsilyl)butyl carbamate (28). Mesylate 26 (68 mg, 0.15 mmol) was dissolved in DMF (3 mL) and then NaN₃ (165 mg, 2.54 mmol) was added. The mixture was stirred at rt for 18 h, then poured into water (50 mL) and extracted with EtOAc (3 × 50 mL). The organic
portion was dried ($\text{MgSO}_4$), filtered and evaporated *in vacuo*. The pure product was obtained by column chromatography (increasing polarity from 5% to 10% EtOAc in pentane as eluant) which gave 28 (47 mg, 0.114 mmol, 77%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.60–7.52 (m, 4H), 7.44–7.34 (m, 6H), 4.24 (d, $J = 10.4$ Hz, 1H), 3.81 (td, $J = 11.2$, 2.0 Hz, 1H), 3.35–3.20 (m, 2H), 1.76–1.56 (m, 3H), 1.50–1.35 (m, 1H), 1.40 (s, 9H), 0.61 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 156.4, 135.1 (2C), 135.0 (2C), 134.4, 134.1, 129.92, 129.86, 128.2 (4C), 79.3, 51.1, 38.3, 29.2, 28.5 (3C), 26.5, −5.6. HRMS $\text{C}_{22}\text{H}_{30}\text{N}_4\text{O}_2\text{Si} [\text{M}+\text{Na}^+]$; calculated: 433.2030, found: 433.2034.

(R)-N-((R)-3-Hydroxy-1-(methylidiphenylsilyl)propyl)-2-methylpropane-2-sulfinamide (32). A solution of DDQ (996 mg, 4.29 mmol) in CH$_2$Cl$_2$ (10 mL) and water (1 mL, 55.0 mmol) was cooled to 0 °C. Compound 31 (532 mg, 1.07 mmol) was dissolved in CH$_2$Cl$_2$ (1 mL) and added to the stirred solution. After 1 h the reaction mixture was allowed to warm up to rt and the stirring continued for 3 h. Them the reaction was quenched with water (10 mL) and extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined organic portions were washed with sat NaHCO$_3$, dried ($\text{MgSO}_4$), filtered and evaporated *in vacuo*. The pure product was obtained by column chromatography (increasing polarity from 0:2:1 to 4:96:0 MeOH:EtOAc:pentane as eluant), which gave 32 (385 mg, 1.03 mmol, 96%) as a redish wax. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.57–7.54 (m, 4H), 7.43–7.34 (m, 6H), 4.03 (t, $J = 6.6$ Hz, 1H), 3.79 (q, $J = 6.0$ Hz, 2H), 3.63 (ddd, $J = 11.6$, 8.8, 3.2 Hz, 1H), 3.07 (d, $J = 9.2$ Hz, 1H), 2.02–1.94 (m, 1H), 1.67–1.59 (m, 1H), 1.03 (s, 9H), 0.61 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 135.2 (2C), 135.1
(R)-tert-Butyl 3-hydroxy-1-(methyldiphenylsilyl)propylcarbamate (33). Sulfinamide 32 (51 mg, 0.14 mmol) was dissolved in anhydrous 0.5 M HCl in MeOH (4 mL) and the mixture was stirred at rt for 5 h. All volatiles were removed in vacuo to give the crude amine as its hydrochloride. This was dissolved in THF (2 mL) and then NEt₃ (0.1 mL, 73 mg, 0.721 mmol) and Boc₂O (104 mg, 0.48 mmol) were added. The mixture was stirred at rt for 22 h, and then 2 M NaOH (10 mL) was added. The mixture was stirred vigorously for a further 1 h. The two phases were separated and the aqueous portion was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic portions were dried (MgSO₄), filtered and evaporated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 5% to 35% EtOAc in pentane as eluant) which gave 33 (21 mg, 0.06 mmol, 40%) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.57–7.51 (m, 4H), 7.44–7.37 (m, 6H), 4.31 (d, J = 10.4 Hz, 1H), 3.98 (ddd, J = 13.2, 10.0, 2.8 Hz, 1H), 3.85 (dd, J = 10.0, 4.4 Hz, 1H), 3.62–3.51 (m, 2H), 1.85 (dddd, J = 13.6, 11.2, 5.6, 2.8 Hz, 1H), 1.44–1.35 (m, 1H), 1.41 (s, 9H), 0.61 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 158.5, 135.1 (4C), 134.0, 133.8, 130.1, 130.0, 128.34 (2C), 128.31 (2C), 80.3, 58.2, 34.4, 34.0, 28.4 (3C), −5.3. HRMS C₂₁H₂₉NO₃Si [M+Na⁺]; calculated: 394.1814, found: 394.1819.

(R)-tert-Butyl 1-[(3-hydroxypropyl)diphenylsilyl]butylcarbamate (40). Sulfinamide 39 (424 mg, 0.85 mmol) was dissolved in methanol containing anhyd HCl (50 mL, 0.4 M). The mixture was stirred at rt for 18 h, and all volatiles were removed in vacuo which gave the crude amine as its corresponding
HCl salt. Toluene (2 mL) was added and evaporated repeatedly until dryness. The residue was dissolved in CH$_2$Cl$_2$ (60 mL), and triethyl amine (0.18 mL, 1.3 mmol, 1.5 equiv) and di-tert-butyl dicarbonate (0.55 g, 2.5 mmol, 3 equiv) was added and the reaction stirred at rt for 18 h. Aqueous NaOH (50 mL, 1 M) was added and the mixture stirred for 10 min and then extracted with CH$_2$Cl$_2$ (3 × 50 mL). The combined organic extracts were washed with brine (50 mL), dried (MgSO$_4$), and concentrated in vacuo. The pure product was obtained by column chromatography (25% ethyl acetate in pentane as eluant) which gave 40 (229 mg, 0.55 mmol, 65%) as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.58–7.55 (m, 2H), 7.52–7.50 (m, 2H), 7.45–7.35 (m, 6H), 4.14 (br d, J = 10.8 Hz, 1H), 3.90 (td, J = 10.8, 2.8 Hz, 1H), 3.63–3.51 (m, 2H), 1.64–1.52 (m, 5H), 1.49–1.44 (m, 2H), 1.41 (s, 9H), 1.36–1.06 (m, 2H), 0.87 (t, J = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 156.5, 135.7 (2C), 135.5 (2C), 133.5, 133.1, 129.9, 129.8, 128.2 (2C), 128.1 (2C), 79.2, 65.4, 37.8, 34.4, 28.5 (3C), 26.9, 20.4, 13.9, 7.5. HRMS (ES) C$_{24}$H$_{35}$NO$_3$Si [M+Na$^+$]; calcd: 436.2284, found: 436.2277.

(R)-tert-Butyl 2,2-dimethyl-4,10-dioxo-7,7-diphenyl-6-propyl-3-oxa-5,11-diaza-7-silatridecan-13-oate (42). Alcohol 40 (45 mg, 0.11 mmol) was dissolved in a mixture of MeCN, ethyl acetate and H$_2$O (1 mL, 2:2:3), and NaIO$_4$ (95 mg, 0.44 mmol, 4.1 equiv) and RuCl$_3$ (1 mg) were added. The reaction was stirred at rt for 2 h, and then H$_2$O (5 mL) was added. The mixture was extracted with ethyl acetate (2 × 10 mL) and the combined organic extracts were dried (MgSO$_4$), filtered and concentrated in vacuo to give the crude carboxylic acid. The residue was dissolved in CH$_2$Cl$_2$ (3 mL) and NMM (60 µL, 0.54 mmol, 5 equiv), tert-butyl glycinate hydrochloride (18 mg, 0.11 mmol, 1 equiv), HOBt (33 mg, 0.22 mmol, 2 equiv), and EDC-HCl (41 mg, 0.22 mmol, 2 equiv) were added and the reaction stirred at rt for 20 h. H$_2$O (15 mL) was added and the mixture extracted with CH$_2$Cl$_2$ (2 × 10 mL). The combined organic extracts were dried (MgSO$_4$), filtered and concentrated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 10% to 25% ethyl acetate in pentane as eluant)
which gave 42 (37 mg, 0.069 mmol, 63%) as a colourless oil. 1H NMR (400 MHz, CDCl3) δ (ppm)
7.57–7.54 (m, 2H), 7.51–7.49 (m, 2H), 7.46–7.35 (m 6H), 5.98 (br s, 1H), 4.22 (br d, J = 10.4 Hz, 1H),
3.93–3.90 (m, 1H), 3.87–3.84 (m, 2H), 2.34–2.26 (m, 1H), 2.19–2.11 (m, 1H), 1.61–1.47 (m, 2H), 1.46
(s, 9H), 1.40 (s, 9H), 1.36–1.19 (m, 4H), 0.86 (t, J = 6.8 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ (ppm)
174.0, 169.2, 156.5, 135.6 (2C), 135.5 (2C), 132.8, 132.5, 130.0 (2C), 128.3 (2C), 128.2 (2C), 82.3,
79.2, 42.2, 37.6, 34.2, 30.4, 28.5 (3C), 28.2 (3C), 20.4, 13.9, 7.4. HRMS (ES) C30H44N2O5Si [M+Na+];
calcd: 563.2917, found: 563.2916.

(R)-tert-Butyl 6-oxo-3,3-diphenyl-2-propyl-1,3-azasilinane-1-carboxylate (43). Alcohol 40 (45 mg,
0.11 mmol) was dissolved in acetone and cooled to 0 ° C. Aqueous H2Cr2O7 (0.32 mL, 0.5 M, 0.16
mmol) was added and the reaction stirred at 0 °C for 2 h. Excess oxidant was quenched by addition of 2-
propanol and the mixture filtered through celite. Solvents were removed in vacuo and the residue
dissolved in CH2Cl2 (20 mL) and washed successively with H2O (10 mL) and brine (10 mL), dried
(MgSO4), filtered and concentrated in vacuo. The crude product was reacted with NMM (60 µL, 0.54
mmol), tert-butyl glycinate hydrochloride (18 mg, 0.11 mmol), HOBT (33 mg, 0.22 mmol), and
EDC·HCl (41 mg, 0.22 mmol) and the reaction stirred at rt for 20 h. The pure product was obtained by
column chromatography (increasing polarity from 10% to 25% ethyl acetate in pentane) which gave
amide 42 (34 mg, 0.062 mmol, 58%) and 43 (7.3 mg, 0.017 mmol, 17%). 1H NMR (400 MHz, CDCl3)
δ (ppm) 7.56–7.52 (m, 4H), 7.48–7.34 (m, 6H), 4.49 (dd, J = 10.0, 5.6 Hz, 1H), 2.98 (ddd, J = 15.6, 6.0,
3.6 Hz, 1H), 2.84 (ddd, J = 15.6, 14.4, 5.6 Hz, 1H), 1.69 (ddd, J = 15.6, 5.6, 3.6 Hz, 1H), 1.57–1.51 (m,
1H), 1.48 (s, 9H), 1.45–1.32 (m, 3H), 1.26–1.15 (m, 1H), 0.76 (t, J = 6.0 Hz, 3H). 13C NMR (100 MHz,
CDCl3) δ (ppm) 174.9, 154.1, 135.3 (2C), 134.7 (2C), 134.0, 132.5, 130.5, 130.2, 128.4 (2C), 128.3
(2C), 82.8, 44.1, 35.6, 34.5, 28.1 (3C), 20.9, 14.0, 5.6. HRMS (ES) C24H31NO3Si [M+Na+]; calcd:
(R)-tert-Butyl 1-[(3-oxo-propyl)-di-phenyl-silyl]-butyl-carbamate (44). Alcohol 40 (43 mg, 0.10 mmol) was dissolved in CH$_2$Cl$_2$ (0.5 mL) and TEMPO (approx. 1 mg, 3 µmol), H$_2$O (0.3 mL), sat aqueous NaHCO$_3$ (0.9 mL), potassium bromide (approx. 1 mg, 0.01 mmol), and TBAB (approx. 2 mg, 0.5 µmol) were added. The mixture was cooled to 0 °C and aqueous NaOCl (0.16 mL, 15 vol%, 0.31 mmol) was added dropwise. The reaction was stirred at rt for 1.5 h and after addition of a few drops of methanol it was stirred for 5 min. The solution was acidified by dropwise addition of concd HCl and extracted with CH$_2$Cl$_2$ (3 × 20 mL), and the combined organic extracts were dried over anhyd MgSO$_4$ and concentrated in vacuo. The title compound was obtained with a minor impurity of the starting material. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 9.70 (s, 1H), 7.58–7.38 (m, 10H), 4.15 (br d, $J = 11.2$ Hz, 1H), 3.93 (td, $J = 11.2$, 2.8 Hz, 1H), 2.51 (d$_{ABdd}$, $J_{AB} = 17.2$ Hz, $J = 11.6$, 4.8 Hz, 1H), 2.39 (d$_{ABdd}$, $J_{AB} = 17.2$ Hz, $J = 11.2$, 5.2 Hz, 1H), 1.50–1.45 (m, 3H), 1.41 (s, 9H), 1.39–1.12 (m, 3H), 0.88 (t, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 202.2, 135.5 (2C), 135.3 (2C), 135.1, 134.5, 130.0, 129.7, 128.2, 128.0, 79.1, 38.0, 37.4, 34.2, 28.4 (3C), 20.2, 13.7, 3.2.

(R)-tert-Butyl 1-((3-hydroxypropyl)di-phenylsilyl)-2-phenylethylcarbamate (59). Sulfinamide 58 (110 mg, 0.20 mmol) was dissolved in anhydrous 0.5 M HCl in MeOH (5 mL) and the mixture was stirred at rt for 18 h. All volatiles were removed in vacuo to give the crude amine as its hydrochloride
salt. This was dissolved in CH₂Cl₂ (4 mL) and then NEt₃ (137 µL, 0.98 mmol) and Boc₂O (86 mg, 0.40 mmol) were added. The mixture was stirred at rt for 18 h, and the 2 M NaOH (5 mL) was added. The mixture was stirred vigorously for a further 2 h. The two phases were separated and the aqueous portion was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic portions were dried (MgSO₄), filtered and evaporated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 10% to 40% EtOAc in pentane as eluant), which gave 59 (68 mg, 0.15 mmol, 74%) as a colorless gum. ¹H NMR (400 MHz, CDCl₃) δ (ppm) major rotamer 7.62−7.57 (m, 4H), 7.39 (m, 7H), 7.25−7.22 (m, 2H), 7.17−7.15 (m, 3H), 4.25−4.20 (m, 1H), 3.59−3.48 (m, 2H), 3.01−2.97 (m, 1H), 2.53 (dd, J = 14.0, 10.0 Hz, 1H), 1.85 (br s, 1H), 1.64−1.51 (m, 2H), 1.28 (s, 9H), 1.20−1.05 (m, 2H). Minor rotamer inter alia 5.73 (d, J = 10.4 Hz, 1H), 4.20 (d, J = 7.2 Hz, 1H), 1.10 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 156.0, 139.5, 135.7 (2C), 135.5 (2C), 133.3, 132.9, 130.0 (2C), 129.1 (2C), 128.3 (4C), 128.2 (2C), 126.2, 79.3, 65.3, 39.5, 38.3, 28.4 (3C), 26.9, 7.6. HRMS C₂₆H₃₅NO₃Si [M+Na⁺]; calculated: 484.2278, found: 484.2278.

(R)-3-((1-tert-Butoxycarbonylamino)-2-phenylethyl)diphenylsilyl)propanoic acid (60). Alcohol 59 (61 mg, 0.13 mmol) was dissolved in a mixture of H₂O, MeCN and CCl₄ (3.5 mL, 3:2:2). NaIO₄ (113 mg, 0.53 mmol) and RuCl₃ (2 mg, 0.01 mmol) were added and the reaction was stirred under air at rt for 2 h. The reaction mixture was diluted with H₂O (5 mL) and extracted with EtOAc (2 × 10 mL), and then the combined organic portions were dried (MgSO₄), filtered and concentrated in vacuo. The obtained crude mixture of title compound 60 was used in the following step without further purification or characterization.

tert-Butyl (S,8S,11S,17R)-5-isobutyl-8-isopropyl-11-methyl-4,7,10,13-tetraoxo-16,16,18-triphenyl-3,6,9,12-tetraaza-16-silaoctadecan-17-ylcarbamate (62). Trifluoroacetic acid (4 mL) was added to a solution of N-Boc-L-alanyl-L-isoleucyl-L-leucinamide 61 (88 mg, 0.20 mmol) in CH₂Cl₂ (4 mL).
The mixture was stirred at rt for 1 h and then the solvents were evaporated in vacuo. The residue was redissolved in CH$_2$Cl$_2$ (4 mL) and the solvent was evaporated in vacuo, giving the crude trifluoroacetate ammonium salt as a colorless gum. The crude material was redissolved in CH$_2$Cl$_2$ (3 mL) and N-methyl morpholine (73 µL, 0.66 mmol), carboxylic acid 60 (0.13 mmol), HOBt (41 mg, 0.26 mmol) and EDC (51 mg, 0.26 mmol) were added. The mixture was stirred at rt for 3 days and then poured into water (10 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 10 mL) and the combined organic portions were dried (MgSO$_4$), filtered and evaporated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 40% to 80% EtOAc in CH$_2$Cl$_2$ as eluant), which gave 62 (63 mg, 0.078 mmol, 59%) as a colorless solid. $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ (ppm) major rotamer 7.58–7.65 (m, 4H), 7.37–7.47 (m, 6H), 7.10–7.22 (m, 5H), 6.23 (d, $J = 10.4$ Hz, 1H), 4.35 (dd, $J = 9.6$, 5.2 Hz, 1H), 4.26 (q, $J = 6.8$ Hz, 1H), 4.15 (d, $J = 7.2$ Hz, 1H), 4.01–4.08 (m, 1H), 3.19 (q, $J = 7.2$ Hz, 2H), 2.87 (dd, $J = 14.4$, 3.6 Hz, 1H), 2.59 (dd, $J = 14.0$, 12.2 Hz, 1H), 2.27–2.31 (m, 2H), 1.81–1.88 (m, 1H), 1.46–1.66 (m, 6H), 1.29 (d, $J = 7.2$ Hz, 3H), 1.25 (s, 9H), 1.14–1.23 (m, 1H), 1.11 (t, $J = 6.8$ Hz, 3H), 0.88–0.93 (m, 12H). Minor rotamer inter alia 5.73 (d, $J = 10.4$ Hz, 1H), 4.20 (d, $J = 7.2$ Hz, 1H), 1.10 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 173.8, 173.1, 171.9, 171.5, 155.8, 139.4, 135.54 (2C), 135.48 (2C), 132.8, 132.7, 130.0 (2C), 129.1 (2C), 128.3 (4C), 128.2 (2C), 126.2, 79.0, 57.9, 51.7, 48.7, 41.4, 39.6, 38.2, 34.3, 29.9, 28.4 (3C), 28.0, 25.4, 25.1, 22.9, 22.5, 20.1, 15.4, 14.7, 11.7, 7.1. HRMS C$_{43}$H$_{65}$N$_5$O$_6$Si [M+Na$^+$]; calculated: 822.4596, found: 822.4604.

Additional references:


Substrate: DMSO
Temp: 26.0 °C / 299.1 K
File: KN00N
Mercury-400N "macro410"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Avg. time 1.994 sec
Width 6410.3 Hz
5 repetitions

Observ. SL: 400.4998269 MHz
DATA PROCESSING
FT nine 685384
Total time 5 min. 23 sec.
15

15
Pulse Sequence: zgul
Solvent: CDCl3
Temp. 26.0 C / 299.1 K
File: NM1.23_colum_16
Mercury-400BR "nmc460"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 0.450.3 Hz
F repetitions
S/N 50, 600.6694269 MHz
DATA PROCESSING
FT size 32768
Total time 0 min. 25 sec
Pulse Sequence: zgpi1
Solvent: CDCl3
Temp: 26.0 C / 299.1 K
File: R11.24_column2_f20-22_1H

Experiment:

Sample delay 1.000 sec
Pulse width 45.0 degrees
Avg. time 1.994 sec
No. of scans 1
6 repetitions

Data Processing:

PT size 32768
Total time 6 min, 29 sec

S27
Pulse Sequence: nqpoq
Solvent: CDCl3
Temp. 25.0 °C / 299.1 K
File: hbl572x6_9
Mesoc400

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.594 sec
Width 6410.3 Hz
8 repetitions

RETRIEVE XL: 400.16900249 MHz
DATA PROCESSING
FT size 32768
Total time 0 min. 25 sec
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 29.8 C / 299.1 K
Probe: krl7426_32
Mercury-400 BR "ncroc66"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.894 sec
Width 6412.3 Hz
0 repetitions

SOURCE 12. 600. 450024 MHz
DATA PROCESSING
FT size 32768
Total time 0 min. 25 sec

S29
Pulse Sequence: zgut
Solvent: CDCl3
Temp. 26.0 C / 299.1 K
File: hbl574a12_17
Mercury-400SG "zgut400"

Delay: delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 6410.0 Hz
8 repetitions

GAINFAC: 64, 640.4692169 MHz
DATA PROCESSING
FT size 32768
Total time 8 min, 25 sec
Pulse Sequence: xypul

Solvent: CDCl3
Temp: 298.1 K
Pulse: 45.6 degrees
Acq. time: 1.994 sec
Agq. time: 1.994 sec
9 repetitions

Wavenumber: 600.665 and 200 MHz

Total time: 19.6 min, 29 sec
S32

Hb1576a4.9

Archive directory: /export/home/auke/remage/data
Sample directory:

Pulse Sequence: m2pm
Solvent: CDCl3
Temp: 26.0 C / 299.1 K
Pila: hbl576a4.9
Memory-6088B "nrec400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.394 sec
Width 6413.3 Hz
# repetitions

Obserr 21.400.46.002069 MHz

Data processing
ET size 32768
Total time 0 min, 25 sec
S33

archive directory: /export/home/auto/emreysy/data
Sample directory:

Pulse sequence: aliph
Solvent: CDCl3
Temp. 29.0 C / 293.1 K
File: khl577a_3.4
Mercury-400B 'nema400'

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.294 sec
Width 6410.3 Hz
6 repetitions
OBSERVE SI: 410.4009269 MHz
DATA PROCESSING
FT size 32768
Total time 6 min, 23 sec
Pulse Sequence: z2pol
Solvent: CDCl3
Temp. 29.8 °C / 298.1 K
File: kbl361b11.16
Mercury-400B "macro600"

Delay: delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 6410.3 Hz
8 repetitions

RESONANCE H1, 400.4698269 MHz
DATA PROCESSING
FT size 32768
Total time 6 min, 25 sec

ppm

ppm
Sample directory:

Pulse Sequence: sincol
Solvent: CDCl3
Temp. 26.0 °C / 299.1 K
File: mb1500h13_15

Relax. delay 1.005 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 6410.3 Hz
8 repetitions

Chemical shift 1H, 400.696269 MHz

DATA PROCESSING
FT size 32768
Total time 9 min, 25 sec
Nbo513a_crude

Archive directory: /export/home/auto/nucreys/data
Sample directory:

Pulse sequence: zgul

Solvent: CDCl3
Temp. 29.0 C / 299.1 K
File: nbo513a_crude
Mercury-400BS "nse400"

Relax delay 1.090 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 6413.3 Hz
8 repetitions

OBSESSION 82.660.459.263 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec
Pulse sequence: al2pol
Solvent: CDCl3
Temp. 26.0 C / 299.1 K
Date: 5/31/1991 (15)
Hercules-400B "maco400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Avg. time 1.994 sec
Width 6410.3 Hz
8 repetitions

SPECTRO: H1, 400.0000 Hz 269 MHz
DATA PROCESSING
PT min 32760
Total time 0 min, 25 sec

---

S39
S40

Archive directory: /export/home/auto/vemsys/data
Sample directory:

Pulse Sequence: a2p1
Solvent: CDCl3
Temp. 26.6°C / 299.1 K
File: Prii_1-12_crude
Mercury-400 MHz "mae400"

Relax. delay 1.000 sec
Pulse 45.6 degrees
Avg. time 1.994 sec
Width 0.416.3 Hz
8 repetitions

OSLO: ETEX 600.6491265 MHz
DATA PROCESSING
FT size 32768
Total time 3 min. 25 sec
Pulse Sequence: zgul
Solvent: CDC13
Temp.: 25.0 C / 298.1 K
File: Frkla.1-13_cel_17-41
M.orient-400H "nemoc400"

Relax delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.794 sec
Width 4400.3 Hz
8 repetitions

S.orient H: 400.6099269 MHz

DATA PROCESSING
FT size 32768
Total time 6 min, 23 sec
Pulse Sequence: zpsal
Solvent: CDCl3
Temp: 24.0 °C / 299.1 K
File: Friis_1-21_col_24-33
Mercury-400SB "naco400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 6.106 ° Hz
8 repetitions
OBSERVE 1H, 400.439281 MHz
DATA PROCESSING
FT size 32768
Total time 0 min. 25 sec
Frills_1-8_cool_22-24

S44

**SPECIAL**

**SAMPLE**

- **date**: Feb 23 2009
- **temp**: 26.0
- **solvent**: CDCl3
- **spin**: not used
- **file**: /export/home/-spin
- **auto**: 187/Frills/Frills-lat
- **s_t**: 187-0-24_fi-pw90
- **d**: alfa

**ACQUISITION**

- **flags**: aw, 6410.3, il, n, st, 1.994, np, 25560, dp, y, fn, not used, m, bw, 16, PROCESSING, df, 1.00, fn, not used, nt, b, DISPLAY, ot, 8, sp, -80.5
- **transmitter**: wp, 4066.7
- **tn**: E1, sfl, 0.002, 3
- **s Perp**: 400.472, wfp, 0
- **tpwr**: 56, lp, 8.5
- **pw**: 5.50, S, PLOT
- **decoupler**: wc, 2700
- **de**: 013, wc, 0
- **dof**: 9, ve, 53
- **dof**: nam, th, 45
- **dov**: 4, xi, odo, ph
- **doup**: 46
- **def**: 17180

**Diagram**

- Chart showing chemical shifts and peaks for compounds labeled as 33.
Friss.1-20_coi.30-35_vaccine

Archive directory: /export/home/auto/vmsr3ys/data
Sample directory:

Pulse Sequence: zgpr1

Solvent: CDCl3
Temp: 25.0 C / 298.1 K
File: Friss.1-20_coi.30-35_vaccine

Resonance: 600 MHz

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.994 sec
Width 0410.3 Hz
6 repetitions

OBSERVE 1H, 600.669290 MHz
DATA PROCESSING
FT size 30720
Total time 0 min. 25 sec
exp1 $2pul$

**SPECIAL**

data: DMSO-6 D2O  Tpcp  35.0

column:  C60  Wave  not used
file: export/home/mon/2004/mon/data

**SPECIAL**

- Name 44
- $N,N$-Boc-SiPh$_2$Ph

![NMR Spectrogram](image)

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**NMR99**

**Sample directory:**

Sample name: 44

**Pulse sequence:** $2pul$

**Solvent:** CDCl$_3$

- Temperature: 24.1°C / 299.1 K
- Mercury: 400.88 MHz

**Relax delay:** 1.000 sec

**Pulse width:** 45.6 degrees

**Acq. time:** 1.558 sec

**Data size:** 85526

**Total time:** 1 hr, 22 min, 16 sec

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**SPECIAL**

- Name 44
- $N,N$-Boc-SiPh$_2$Ph

![NMR Spectrogram](image)
Pulse Sequence: zg2pul
Solvent: CDCl3
Temp: 296.0 °C / 299.1 K
File: k61557a20_34
Memory: 400MHz "nuclear"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 6415.3 Hz
8 repetitions

Observe 31.6004698269 MHz
DATA PROCESSING
FT size 32768
Total time 0 min. 25 sec
Pulse Sequence: z2pol
Solvent: CDCl₃
Temp. 298.15 K
File: khl559a16.21
Mercury-400BB "micro600"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 6410.3 Hz
8 repetitions

RESOLVE H1, 400.4698269 MHz
DATA PROCESSING
FT size 32768
Total time 6 min, 25 sec
Sample directory:

Pulse Sequence: zpul

Solvent: CDCl3
Temp. 26.0 C / 299.1 K
File: kb1661a7_22_2nd
Mercury-400B "nset400"

Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4410.3 Hz
8 repetitions

PROCESSING
FT algo 3DFT
Total time 5 min, 25 sec
Pulse Sequence: alqal
Solvent: CDCl3
Temp. 29.0 °C / 299.1 K
File: 82156358_53
NMR-4000B "narc400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.996 sec
Width 1.010 Hz
8 repetitions

OBSERV 1H, 400.164926 MHz
DATA PROCESSING
FT size 32768
Total time 6 min, 25 sec