Supporting Information
for DOI: 10.1055/s-0036-1588360
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Formal Syntheses of 5, 8-Disubstituted Indolizidine Alkaloids (-)-205A, (-)-207A and (-)-235B

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General Experimental:

Reaction progress was monitored by thin-layer chromatography (TLC) carried out on silica plates (silica gel 60 F254, Merck) using UV-light and anisaldehyde for visualization. Evaporation of solvents was conducted under reduced pressure using rotary evaporator. Column chromatography was executed on silica gel (60–120 mesh) using hexanes and ethyl acetate as eluent. Optical rotations were measured on digital polarimeter using a 1 mL cell with a 1 dm path length. FTIR spectra were recorded as KBr thin films or neat. $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ solvent on a 300 MHz NMR spectrometer at ambient temperature. Chemical shifts $\delta$ and coupling constant $J$ are given in ppm (parts per million) and Hz (hertz) respectively. For low (MS) and High (HRMS) resolution, m/z ratios are reported as values in atomic mass units.
Experimental Procedures

\((2R, 3R)\)-6-(benzyl)oxy)-1-(tert-butyldiphenylsilyloxy)-2-methylhexan-3-ol (11):

![Structure](image)

To a stirred solution of aldol adduct 6 (1.0 g, 2.43 mmol) in THF:MeOH (20 mL) was added Lithium borohydride (1.13 g, 52.7 mmol) at 0 °C. The reaction mixture was stirred for the same temperature for 1 h. After completion of the reaction, the mixture was diluted by the addition of saturated aqueous HCl (20 mL) and the aqueous phase was extracted with EtOAc (2 x 20 mL). The combined organic layer was washed with brine (20 mL), dried over Na₂SO₄ and evaporated the organic solvent under reduced pressure to get the diol, which was used for the next step without further purification.

To a stirred solution of the diol (1.0 g, 4.20 mmol) in CH₂Cl₂ (10 mL), was added imidazole (571 mg, 8.4 mmol) followed by tert-butyldiphenylsilyl chloride (1.09 g, 3.78 mmol) at 0 °C. The reaction mixture was allowed to room temperature and stirred for 5 h. After completion of the reaction, the mixture was diluted by the addition of sat. aq. NaHCO₃ (20 mL) and the aq. phase was extracted with ether (2 x 20 mL). The combined organic layer was washed with brine (20 mL), dried over Na₂SO₄ and evaporated the organic solvent under reduced pressure. The crude residue was purified by column chromatography (hexanes: EtOAc = 95:5) to give 11 (1.56 g, 78%) as a colorless oil. R₉ = 0.50 (5% EtOAc in Hexanes); Optical Rotation: \([\alpha]_D^{27} = -2.7\) (c = 1.20, CHCl₃); IR (KBr): \(\nu_{max}\) 3416, 3076, 2931, 2858, 1604, 1466, 1363, 1254, 1035, 913, 667 cm⁻¹; \(^1\)H NMR (300 MHz, CDCl₃): \(\delta\) 7.17-7.63 (m, 4H), 7.48-7.25 (m, 11H), 4.51 (s, 2H), 3.89-3.81 (m, 1H), 3.77-3.63 (m, 2H), 3.56-3.46 (m, 2H), 1.88-1.62 (m, 3H), 1.59-1.48 (m, 2H), 1.05 (s, 9H), 0.92 (d, \(J = 6.7\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl₃): \(\delta\) 138.3, 135.5, 135.4, 133.0, 132.9, 129.6, 128.2, 127.6, 127.5, 127.4, 73.6, 72.7, 70.3, 68.3, 39.3, 31.0, 26.7, 26.5, 19.0, 10.5; MS (ESI): \(m/z\) 477 (M + H)+; HRMS (ESI) \(m/z\) calcd for C₃₀H₄₁O₃Si (M+H)+ 477.2819, found 477.2822.
(2R, 3R)-6-(Benzyloxy)-1-(tert-butyldiphenylsilyloxy)-2-methylhexan-3-yl 4-methylbenzenesulfonate (12):

\[ \text{TBDPSO} \quad \text{O}^{\text{Ts}} \quad \text{O}^{\text{Bn}} \]

Tosyl chloride (1.79 g, 9.45 mmol) was added to an ice cooled solution of 11 (1.50 g, 3.15 mmol) in dry pyridine (10 mL). The resulting solution was stirred at room temperature for 8 h. It was then diluted with ice-water and extracted with diethyl ether (2 x 25 ml). The combined organic layer was washed with water, dil. HCl, water, aq. NaHCO₃ solution and brine, dried over Na₂SO₄ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography (hexanes: EtOAc = 90:10) to give 12 (1.42 g, 72%) as a colorless oil. R₆f = 0.50 (20% EtOAc in hexanes); Optical Rotation: [\(\alpha\)]D²⁷ = -4.6 (c = 1.20, CHCl₃); IR (KBr): \(\nu_{\text{max}}\) 3393, 3074, 2978, 2933, 2857, 1726, 1641, 1457, 1369, 1261, 1099, 986, 667 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl₃): \(\delta\) 7.73 (d, \(J = 8.3 \text{ Hz}\), 2H), 7.62-7.56 (m, 4H), 7.52-7.27 (m, 12H), 7.19 (d, \(J = 7.5 \text{ Hz}\), 1H), 4.88-4.81 (m, 1H), 4.45 (s, 2H), 3.45-3.36 (m, 3H), 2.36 (s, 3H), 1.92-1.83 (m, 1H), 1.82-1.72 (m, 2H), 1.61-1.52 (m, 3H), 1.03 (s, 9H), 0.84 (d, \(J = 6.7 \text{ Hz}\), 3H); \(^1^3\)C NMR (75 MHz, CDCl₃): \(\delta\) 144.1, 138.3, 135.5, 134.7, 134.5, 133.5, 133.4, 129.6, 129.5, 129.4, 128.3, 127.5, 84.4, 72.7, 69.5, 64.9, 38.8, 29.6, 28.7, 26.7, 25.4, 21.5, 11.2; MS (ESI): \(m/z\) 653 (M + Na); HRMS (ESI) \(m/z\) calcd for C₃₇H₄₆O₅SSiNa (M+Na)\(^+\) 653.9042, found 653.9043.

((2S, 3S)-3-Azido-6-(benzyloxy)-2-methylhexyloxy) tert-butyl diphenylsilane (13):

\[ \text{TBDPSO} \quad \text{N}_3 \quad \text{O}^{\text{Bn}} \]
Sodium azide (670 mg, 10.3 mmol) was added to a solution of 12 (1.30 g, 2.06 mmol) in dry DMF (10 mL). The mixture was heated under reflux for 1 h. It was then diluted with ice-water and extracted with diethyl ether (2 x 25 ml). The combined organic layer was washed with water, and brine, dried over Na₂SO₄ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography (silica gel, hexanes:EtOAc = 90 : 10) to give 13 (875 mg, 85%) as a colorless oil. Rf = 0.50 (80% EtOAc in Hexanes); Optical Rotation: [α]D²⁷ = -6.9 (c = 1.40, CHCl₃); IR (KBr): νmax 3487, 3074, 2926, 2859, 2128, 1780, 1694, 1481, 1386, 1211, 1104, 757 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.65 (d, J = 6.0 Hz, 2H), 7.45-7.27 (m, 13H), 4.50 (s, 2H), 3.69-3.55 (m, 2H), 3.48 (t, J = 6.0 Hz, 3H), 1.94-1.76 (m, 2H), 1.75-1.41 (m, 3H), 1.05 (s, 9H), 0.94 (d, J = 6.7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 138.4, 135.5, 133.4, 129.6, 128.3, 127.6, 127.5, 72.8, 69.7, 65.5, 64.7, 39.6, 27.5, 26.8, 26.6, 19.2, 13.4; MS (ESI): m/z 502 (M + H)⁺; HRMS (EI) m/e calcd for C₃₀H₄₀N₃O₂Si (M+H)⁺ 502.2884, found 502.2881.

(2S, 3S)-3-azido-6-(benzyloxy)-2-methylhexan-1-ol (6):

A solution of 13 (800 mg, 2.91 mmol) in THF (15 mL) was cooled to 0 °C and TBAF (2.39 mL, 1.0 M so solution in THF) was added dropwise. The resulting brown solution was stirred at room temperature for 2 h. The reaction was quenched with sat. aq. NH₄Cl (20 mL) and extracted with EtOAc (2 x 25 mL). The combined organic layer was washed with brine (15 mL), dried over Na₂SO₄ and evaporated to dryness under reduced pressure. The residue was purified by column chromatography (hexanes: EtOAc = 80:20) to give 6 (344 mg, 82%) as a colorless oil. Rf = 0.50 (30% EtOAc in hexanes); Optical Rotation: [α]D²⁷ = -9.7 (c = +4.20, CHCl₃); IR (KBr): νmax 3453, 3078, 2930, 2857, 2132, 1782, 1639, 1458, 1354, 1289, 1098, 913, 774 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.41-7.28 (m, 5H), 4.51 (s, 2H), 3.63 (t, J = 4.3 Hz, 2H), 3.56-3.45 (m, 2H),
3.43-3.34 (m, 1H), 1.92-1.51 (m, 6H), 1.00 (d, J = 6.9 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 138.1, 134.6, 129.3, 127.5, 72.7, 69.5, 65.2, 64.5, 39.2, 27.8, 26.3, 13.8; MS (ESI): m/z 286 (M + Na)$^+$; HRMS (EI) m/e calcd for C$_{14}$H$_{21}$N$_3$NaO$_2$ (M+Na)$^+$ 286.1526, found 286.1527.

**(8R, 9S, E)-9-azido-12-(benzyl)oxy)-1-(tert-butyldimethylsilyloxy)-8-methyldodec-6-en-5-one (5):**

To a solution of keto phosphonate 7 (569 mg, 1.68 mmol) in THF (50 mL) was added Ba(OH)$_2$.8H$_2$O (639 mg, 3.36 mmol) under N$_2$ and stirred for 45 min at r.t. The reaction mixture was cooled to 0 °C, added aldehyde (220 mg, 0.84 mmol) corresponding to compound 6 in 20 mL of THF/H$_2$O (40:1) slowly and mixture was allowed to warm to r.t. and stirring continued for 1 h. The reaction mixture was diluted with CH$_2$Cl$_2$ (50 mL), organic layer was washed with sat. aq. NaHCO$_3$ (50 mL), brine (50 mL), dried overNa$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexanes/EtOAc 95:5) afforded enone 5 (299 mg, 75%) as a colorless oil. R$_f$ = 0.50 (5% EtOAc in hexanes); Optical Rotation: [α]$_D^{27}$ = -15.1 (c = 1.10, CHCl$_3$); IR (KBr): $\nu_{\text{max}}$ 3329, 3075, 2930, 2856, 2175, 1830, 1648, 1574, 1494, 1343, 1252, 1164, 1026, 913, 693 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$): δ 7.41-7.27 (m, 5H), 6.71 (dd, J = 16.0, 8.3 Hz, 1H), 6.11 (dd, 16.0, 8.3 Hz, 1H), 4.50 (s, 2H), 3.62 (t, J = 6.4 Hz, 2H), 3.53-3.45 (m, 2H), 3.37-3.28 (m, 1H), 2.62-2.43 (m, 3H), 1.80-1.45 (m, 8H), 1.14 (d, J = 6.7 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 200.2, 146.4, 138.2, 131.1, 128.3, 127.5, 125.4, 72.8, 69.4, 66.9, 62.8, 41.3, 39.7, 32.2, 30.2, 29.2, 26.4, 25.8, 20.5, 16.8, -5.3; MS (ESI): m/z 474 (M + H)$^+$; HRMS (EI) m/e calcd for C$_{26}$H$_{46}$N$_3$O$_3$Si (M+H)$^+$ 474.3146, found 474.3143.
(5R, 8R, 8aS)-5-(4-(tert-butyldimethylsilyloxy) butyl)-8-methyloctahydroindolizine (15):

![Chemical Structure]

To a solution of 14 (100 mg, 0.29 mmol) in dichloromethane (10 mL) at -20 °C were added Et$_3$N (117 mg, 0.16 mL, 1.16 mmol) and MsCl (0.03 mL, 0.43 mmol) in dichloromethane (10 mL) successively. The reaction mixture was continued to stir at 0 °C for 3 h and quenched by adding water (20 mL), the layers were separated and aq. layer was extracted with dichloromethane (2x30 mL). The dichloromethane extracts were washed with 1 M HCl (20 mL), water (20 mL), sat. aq. NaHCO$_3$ (20 mL), brine (20 mL), dried over Na$_2$SO$_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexanes/EtOAc 3:7) to obtain compound 15 (68.2 mg, 72%). R$_f$ = 0.50 (75% EtOAc in hexanes); Optical Rotation: [α]$_D^{27}$ = -25.3 (c = +4.20, CHCl$_3$); IR (KBr): $\nu_{\text{max}}$ 3246, 2928, 2856, 1709, 1588, 1457, 1294, 1110, 1007, 837, 779 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 3.58 (dt, $J = 6.7$, 1.5 Hz, 2H), 3.25 (dt, $J = 9.1$, 3.0 Hz, 1H), 1.99-1.17 (m, 18H), 0.87 (s, 9H), 0.84 (d, $J = 6.7$ Hz, 3H), 0.02 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 72.8, 70.3, 62.9, 57.9, 39.3, 35.9, 34.2, 34.1, 33.3, 32.7, 29.9, 25.9, 22.4, 18.4, 18.2, -5.4; MS (ESI): m/z 326 (M + H)$^+$; HRMS (EI) m/e calcd for C$_{19}$H$_{30}$NOSi (M+H)$^+$ 326.2874, found 326.2876.
$^1$H NMR Spectrum of compound 11 (300 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of compound 11 (75 MHz, CDCl$_3$)
$^1$H NMR Spectrum of compound 12 (300 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of compound 12 (75 MHz, CDCl$_3$)
\[ ^1H \text{NMR Spectrum of compound 13 (300 MHz, CDCl}_3 \]
13C NMR Spectrum of compound 13 (75 MHz, CDCl3)
$^1$H NMR Spectrum of compound 6 (300 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of compound 6 (75 MHz, CDCl$_3$)
$^1$H NMR Spectrum of compound 5 (300 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of compound 5 (75 MHz, CDCl$_3$)
$^1$H NMR Spectrum of compound 15 (300 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of compound 15 (75 MHz, CDCl$_3$)
$^1$H NMR Spectrum of compound 15 (300 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of compound **15** (75 MHz, CDCl$_3$)
$^1$H NMR Spectrum of compound 4 (300 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of compound 4 (75 MHz, CDCl$_3$)