Dichloroketene-Chiral Olefin Based Approach to Pyrrolizidines: Highly Stereocontrolled Synthesis of (+)-Amphorogynine A

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SUPPORTING INFORMATION[1]

2-[(*S*)-1-(Pent-4-en-1-ynyloxy)-ethyl]-1,3,5-triisopropylbenzene (3a). IR (film) 3005, 2960, 2930, 2869, 2269, 1608, 1460, 1230 cm^{-1}. ^1H NMR (300 MHz) δ 1.15-1.35 (m, 18 H), 1.72 (d, *J* = 6.9 Hz, 3 H), 2.75-2.95 (m, 3 H), 3.15-3.45 (m, 2 H), 4.85-5.05 (m, 2 H), 5.65-5.80 (m, 2 H), 7.00 (s, 2 H). ^{13}C NMR (75.5 MHz) δ 21.6 (CH_3), 23.9 (CH), 23.9 (CH_3), 24.5 (CH_3), 29.3 (CH), 34.1 (CH_2), 83.0 (CH), 91.7 (C), 114.8 (CH_2), 119.3 (CH), 120.4 (CH), 122.0 (C), 130.9 (C), 134.1 (CH), 148.5 (C).

2-((*S*)-1-((*Z*)-Penta-1,4-dienyloxy)-ethyl)-1,3,5-triisopropylbenzene (3b). IR (film) 2961, 2935, 2867, 1667, 1612, 1464, 1384 cm^{-1}. ^1H NMR (300 M Hz) δ 1.20-1.35 (m, 18 H), 1.63 (d, *J* = 6.9 Hz, 3 H), 2.80-3.00 (m, 2 H), 3.30-3.70 (m, 2 H), 4.31 (m: dddd, *J* = 7.3, 7.3, 6.3, 1.1 Hz, 1 H), 4.95 (br d, *J* = 10.0 Hz, 1 H), 5.05 (br d, J = 17.2 Hz, 1 H), 5.37 (q, *J* = 6.9 Hz, 1 H), 5.85 (m: ddddd, *J* = 17.2, 10.0, 6.2, 6.2, 1.1 Hz, 1 H), 6.03 (m: dddd, *J* = 6.3, 1.4, 1.4, 1.4 Hz, 1 H), 7.03 (s, 2 H). ^{13}C NMR (75.5 MHz) δ 22.5 (CH_3), 23.9 (CH_3), 24.5 (CH_3), 28.5 (CH_2), 29.1 (CH), 34.0 (CH), 75.4 (CH), 103.3 (CH), 113.9 (CH_2), 121.9 (CH), 133.0 (C), 137.7 (CH), 144.5 (CH), 147.7 (C).

[1] Complex multiplets (m) have been analyzed, when possible, by using the method of Hoye and coworkers: Hoye, T. R.; Hanson, P. R.; Vyvyan, J. R. *J. Org. Chem.* **1994**, *59*, 4096-4103. Hoye, T. R.; Zhao, H. *Ibid*. **2002**, *67*, 4014-4016.

(3*S*,4*R*)-4-Allyl-2,2-dichloro-3-[(*S*)-1-(2,4,6-triisopropylphenyl)-ethoxy]-cyclobutanone (4). IR (film) 2965, 2931, 2871, 1806, 1608, 1458, 1382 cm^{-1}. ^1H NMR (300 MHz) δ 1.10-1.40 (m, 18 H), 1.66 (d, *J* = 6.9 Hz, 3 H), 2.45-2.65 (m, 2 H), 2.87 (hept, *J* = 6.9 Hz, 1 H), 3.29 (hept, *J* = 6.9 Hz, 1 H), 3.52 (m: ddd, *J* = 9.4, 9.4, 6.3 Hz, 1 H), 3.83 (hept, *J* = 6.9 Hz, 1 H), 4.33 (d, *J* = 9.4 Hz, 1 H), 5.02-5.18 (m, 2 H), 5.45 (q, *J* = 6.9 Hz, 1 H), 5.86 (m: dddd, *J* = 17.0, 10.1, 6.9, 6.9 Hz, 1 H), 7.00 (d, *J* = 2.0 Hz, 1 H), 7.07 (d, *J* = 2.0 Hz, 1 H). ^{13}C NMR (75.5 MHz) δ 22.5 (CH_3), 23.9 (CH_3), 24.9 (CH_3), 25.4 (CH_3), 28.2 (CH), 29.2 (CH), 29.7 (CH_2), 34.0 (CH), 58.5 (CH), 73.4 (CH), 77.2 (CH), 88.3 (C), 117,1 (CH_2), 120.8 (CH), 123.4 (CH), 134.5 (CH), 147.1 (C), 148.3 (C), 148.9 (C), 195.8 (C). MS (DCI, NH_3+isobutane) *m/z* 444, 429, 427, 425 (MH^+), 232, 231 (100%), 230.

(4*R*,5*R*)-5-Allyl-3,3-dichloro-4-[(*S*)-1-(2,4,6-triisopropylphenyl)-ethoxy]-pyrrolidin-2-one (5a). Mp 112-116 °C (pentane). IR (film) 3248, 2964, 2924, 2864, 1735, 1610, 1462 cm^{-1}. ^1H NMR (300 MHz) δ 1.12-1.40 (m, 18 H, CH_3), 1.72 (d, *J* = 6.8 Hz, 3 H), 2.15-2.40 (m, 1 H), 2.55-2.65 (m, 1 H), 2.84 (hept, *J* = 6.9 Hz, 1 H), 3.34 (hept, *J* = 6.8 Hz, 1 H), 3.55-3.64 (m, 1 H), 3.89 (hept, *J* = 6.8 Hz, 1 H), 4.44 (d, *J* = 7.0 Hz, 1 H), 5.08-5.18 (m, 2 H), 5.60- 5.80 (m, 2 H), 6.96 (d, *J* = 1.8 Hz, 1 H), 7.04 (d, *J* = 1.8 Hz, 1 H). ^{13}C NMR (75.5 MHz) δ 23.0 (CH_3), 23.9 (CH_3), 25.0 (CH_3), 25.5 (CH_3), 28.3 (CH), 28.9 (CH), 33.9 (CH), 34.4 (CH_2), 55.0 (CH), 73.6 (CH), 81.8 (CH), 82.5 (C), 119.0 (CH_2), 120.9 (CH), 123.4 (CH), 133.5 (CH), 146.5 (C), 148.1 (C), 148.8 (C), 167.5 (C). MS (DCI, NH_3+isobutane) *m/z* 461, 459, 457, 444, 442, 440 (MH^+, 100%), 406, 231, 230. Anal. Calcd for $C_{24}H_{35}Cl_2NO_2$: C, 65.45; H, 8.01; N, 3.18; Cl, 16.10. Found: C, 65.43; H, 8.12; N, 3.15; Cl, 16.18.

(4*R*,5*R*)-5-Allyl-4-[(*S*)-1-(2,4,6-triisopropylphenyl)-ethoxy]-pyrrolidin-2-one (5b). Mp 102-104 °C (pentane). IR (film) 3213, 2955, 2927, 2867, 1703, 1107, 1080 cm^{-1}. ^1H NMR (300 MHz) δ 1.10-1.30 (m, 18 H, CH_3), 1.52 (d, *J* = 6.8 Hz, 3 H), 2.10-2.30 (m, 1 H), 2.45-2.55 (m, 3 H), 2.83 (hept, *J* = 6.9 Hz, 1 H), 3.13 (hept, *J* = 6.8 Hz, 1 H), 3.62 (m: ddd, *J* = 10.2, 7.0, 2.8 Hz, 1 H), 3.85 (hept, *J* =6.8 Hz, 1 H), 4.14 (m: ddd, *J* = 7.0, 7.0, 7.0 Hz, 1 H), 5.00-5.15 (m, 3 H), 5.74 (m: dddd, *J* = 17.8, 9.7, 8.2, 6.1 Hz,

1 H), 6.1 (s, 1 H), 6.93 (s, 1 H), 7.03 (s, 1 H). ^{13}C NMR (75.5 MHz) δ 23.0 (CH_3), 23.8 (CH_3), 24.8 (CH_3), 27.9 (CH), 29.0 (CH), 33.8 (CH), 34.6 (CH_2), 36.5 (CH_2), 57.2 (CH), 71.1 (CH), 72.2 (CH), 118.0 (CH_2), 120.4 (CH), 123.1 (CH), 131.9 (C), 134.5 (CH), 145.7 (C), 147.5 (C), 148.6 (C), 175.1 (C). MS (DCI, NH_3+isobutane) *m/z* 372 (MH^+, 100%), 371, 231. Anal. Calcd for $C_{24}H_{37}NO_2$: C, 77.58; H, 10.04; N, 3.77. Found: C, 77.61; H, 10.10; N, 3.62.

(4*R*,5*R*)-5-(2,3-Dihydroxypropyl)-4-[(*S*)-1-(2,4,6-triisopropylphenyl)-ethoxy]-pyrrolidin-2-one (6a). Mp 145-147 °C. ^{1}H NMR (300 MHz) δ 1.10-1.30 (m, 18 H, CH_3), 1.51 (d, *J* = 6.8 Hz, 3 H), 1.52-1.80 (m, 2 H), 2.45 (d, *J* = 6.8 Hz, 2 H), 2.82 (hept, *J* = 6.9 Hz, 1 H), 3.04-3.18 (m, 2 H), 3.35-3.45 (m, 1 H), 3.50-3.60 (m, 1 H), 3.68-3.90 (m, 4 H), 4.07 (m: ddd, *J* = 6.8, 6.8, 6.8 Hz, 1 H), 5.05 (q, *J* = 6.8 Hz, 1 H), 6.87 (s br, 1 H), 6.93 (s, 1 H), 7.01 (s, 1 H). ^{13}C NMR (75.5 MHz) δ 23.10 (CH_3), 23.14 (CH_3), 25.0 (CH_3), 28.0 (CH), 29.2 (CH), 30.9 (CH), 32.5 (CH_2), 33.9 (CH_2), 36.6 (CH_2), 57.9 (CH), 67.0 (CH_2), 70.9 (CH), 72.2 (CH), 72.6 (CH), 120.7 (CH), 123.2 (CH), 131.8 (C), 146.0 (C), 147.8 (C), 148.7 (C), 175.3 (C). OH-Epimer: Mp 161-162 °C. IR (film) 3292, 3052, 2960, 2929, 2874, 1675, 1607, 1467, 1423, 1265, 1166, 1064, 740 cm^{-1}. ^{1}H NMR (300 MHz) δ 1.10-1.30 (m, 18 H), 1.50 (d, *J* = 6.8 Hz, 3 H), 1.60-1.70 (m, 2 H), 2.46 (d, *J* = 6.8 Hz, 2 H), 2.83 (hept, *J* = 6.9 Hz, 1 H), 3.04-3.18 (m, 1 H), 3.34-3.48 (m, 1 H), 3.50-3.60 (m, 1 H), 3.70-3.94 (m, 4 H), 4.00-4.08 (m, 1 H), 4.11 (m: ddd, *J* = 6.8, 6.8, 6.8 Hz, 1 H), 5.03 (q, *J* = 6.8 Hz, 1 H), 6.93 (s, 1 H), 7.01 (s, 1 H), 7.41 (s, 1 H). ^{13}C NMR (75.5 MHz) δ 23.1 (CH_3), 23.9 (CH_3), 23.9 (CH_3), 25.0 (CH_3), 28.0 (CH), 29.1 (CH), 32.4 (CH_2), 34.0 (CH), 36.6 (CH_2), 57.6 (CH), 67.0 (CH_2), 69.0 (CH), 71.1 (CH), 72.5 (CH), 120.6 (CH), 123.2 (CH), 131.9 (C), 145.9 (C), 147.7 (C), 148.8 (C), 176.0 (C). MS (DCI, NH_3+isobutane) *m/z* 406 (MH^+, 100%), 231, 175. Anal. Calcd for $C_{24}H_{39}NO_4$: C, 71.07; H, 9.69; N, 3.45. Found: C, 71.02; H, 9.78; N, 3.42.

(4*R*,5*R*)-5-(2-Hydroxy-3-(toluene-4-sulfonyloxy)-propyl)-4-[(*S*)-1-(2,4,6-triisopropyl-phenyl)-ethoxy]-pyrrolidin-2-one (6b). IR (film, mixture of diastereomers) 3416, 3053, 2965, 2929, 2870, 1693, 1608, 1362, 1265 cm^{-1}. ^{1}H NMR (300 MHz, mixture of diastereomers) δ 1.08-1.28 (m, 18 H),

1.50 (d, *J* = 6.8 Hz, 3 H), 1.52-1.90 (m, 2 H), 2.40 (s, 3 H), 2.42-2.50 (m, 2 H), 2.83 (hept, *J* = 2.3 Hz , 1 H), 3.13 (hept, *J* = 6.6 Hz, 1 H), 3.68-4.02 (m, 5 H), 4.02-4.17 (m, 1 H), 4.40 (s, 1 H), 4.96-5.14 (m, 1 H), 6.94 (s, 1 H), 7.02 (s, 1 H), 7.30 (d, *J* = 8.3 Hz, 2 H), 7.43 (s, 1 H), 7.76 (d, *J* = 8.3 Hz, 2 H). ^{13}C NMR (75.5 MHz, mixture of diastereomers) δ 22.9 (CH_3), 22.9 (CH_3), 23.7 (CH_3), 24.8 (CH_3), 27.8 (CH), 28.9 (CH), 32.0 (CH_2), 32.3 (CH_2), 33.8 (CH), 36.3 (CH_2), 53.8 (CH), 57.3 (CH), 65.5 (CH), 68.7 (CH), 70.7 (CH), 70.9 (CH), 72.2 (CH), 72.5 (CH), 73.5 (CH_2), 73.9 (CH_2), 120.4 (CH), 120.5 (CH), 123.0 (CH), 127.8 (CH), 129.7 (CH), 131.6 (C), 131.8 (C), 132.4 (C), 132.5 (C), 144.7 (C), 144.7 (C), 145.7 (C), 145.8 (C), 147.4 (C), 147.6 (C), 148.5 (C), 148.5 (C), 175.0 (C), 175.5 (C). MS (DCI, NH_3+isobutane) *m/z* 560 (MH^+), 388, 231 (100%). Anal. Calcd for $C_{31}H_{45}NO_6S$ + 0.5H_2O: C, 65.46; H, 8.15; N, 2.46; S, 5.64. Found: C, 65.65; H, 8.15; N, 2.46; S, 6.01.

(1*R*,7a*R*)-[1-(2,4,6-Triisopropylphenyl)-ethoxy]-hexahydropyrrolizin-6-ol (7). Mp 95-97 °C (pentane). $[\alpha]^{26}_D$ – 62.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz) δ 1.08-1.33 (m, 18 H), 1.54 (d, *J* = 6.7 Hz, 3 H), 1.65-1.78 (m, 1 H), 1.86-1.98 (m, 1 H), 2.11-2.26 (m, 2 H), 2.75-2.88 (m, 2 H), 2.91-3.06 (m, 2 H), 3.13-3.30 (m, 2 H), 3.53-3.63 (m, 1 H), 3.71-3.80 (m, 1 H), 3.84 (hept, *J* = 6.8 Hz, 1 H), 4.15-4.25 (m, 1 H), 4.74 (br s), 5.31 (q, *J* = 6.7 Hz, 1 H), 6.93 (s, 1 H), 7.02 (s, 1 H). ^{13}C NMR (75.5 MHz) δ 23.0 (CH_3), 23.8 (CH_3), 23.8 (CH_3), 24.1 (CH_3), 24.9 (CH_3), 25.1 (CH_3), 25.5 (CH_3), 27.8 (CH), 29.0 (CH), 31.2 (CH_2), 33.7 (CH_2), 33.9 (CH), 53.4 (CH_2), 62.8 (CH_2), 68.0 (CH), 69.2 (CH), 73.3 (CH), 75.7 (CH), 120.8 (CH), 123.2 (CH), 130.7 (C), 146.4 (C), 147.8 (C), 148.7 (C). MS (DCI, NH_3+isobutane) *m/z* 408, 375, 374 (MH^+, 100%), 231, 144. Anal. Calcd for $C_{24}H_{39}NO_2$ + 0.67 H_2O: C, 74.76; H, 10.54; N, 3.63. Found: C, 74.75; H, 10.34; N, 3.67. **7·HCl.** Mp 183-189 °C (pentane; decomposition). $[\alpha]^{26}_D$ –65.4 (*c* 1.3, $CHCl_3$). IR (film) 3322, 2958, 2931, 2868, 2575, 1459, 1264 cm^{-1}. ^{1}H NMR (300 MHz) δ 1.06-1.30 (m, 18 H), 1.59 (d, *J* = 6.8 Hz, 3 H), 2.02-2.20 (m, 1 H), 2.24 (m: ddd, *J* = 15.2, 10.2, 4.9 Hz, 1 H), 2.32-2.48 (m, 2 H), 2.83 (hept, *J* = 6.9 Hz , 1 H), 3.05-3.18 (m, 2 H), 3.22-3.38 (m, 1 H), 3.54 (m: dd, *J* = 12.5, 3.6 Hz, 1 H), 3.65 (hept, *J* = 6.8 Hz, 1 H), 3.89 (m: dd, *J* = 10.5, 7.4 Hz, 1 H), 4.04 (m: dd, *J* = 4.5, 4.5

Hz, 1 H), 4.34-4.46 (m, 1 H), 4.48-4.56 (m, 2 H), 5.31 (q, *J* = 6.8 Hz, 1 H), 6.96 (s, 1 H), 7.03 (s, 1 H), 12.5-13.0 (br s, 1 H). ^{13}C NMR (75.5 MHz) δ 22.7 (CH_3), 23.7 (CH_3), 23.8 (CH_3), 24.0 (CH_3), 24.8 (CH_3), 25.2 (CH_3), 25.5 (CH_3), 28.2 (CH), 29.3 (CH), 31.2 (CH_2), 32.2 (CH_2), 34.0 (CH), 53.3 (CH_2), 60.2 (CH_2), 68.7 (CH), 71.0 (CH), 71.9 (CH), 74.0 (CH), 121.3 (CH), 123.5 (CH), 129.0 (C), 146.5 (C), 148.4 (C), 148.8 (C). MS (DCI, NH_3+isobutane) *m/z* 374 (MH^+, 100%), 231, 141. Anal. Calcd for $C_{24}H_{40}ClNO_2$: C, 70.30; H, 9.83; N, 3.42. Found: C, 69.93; H, 9.84; N, 3.44.

(1*R*,7a*R*,6*S*)-6-(*t*-Butyldiphenylsilanoxy)-1-(2,4,6-triisopropyl-phenyl)-ethoxy]-hexahydro-pyrrolizine. $[\alpha]^{26}_D$ –27.9 (*c* 1.3, $CHCl_3$). IR (film) 3070, 2959, 2927, 2863, 1607, 1470, 1382, 1360, 1112, 1076 cm^{-1}. ^{1}H NMR (300 MHz) δ 1.03 (s, 9 H), 1.10-1.30 (m, 18 H), 1.55 (d, *J* = 6.8 Hz, 3 H), 1.62-1.81 (m, 2 H), 2.10-2.25 (m, 2 H), 2.52 (m: dd, *J* = 8.4, 8.4 Hz, 1 H), 2.73 (m: ddd, *J* = 9.7, 9.7, 6.0 Hz, 1 H), 2.83 (hept, *J* = 6.9 Hz, 1 H), 2.94-3.08 (m, 2 H), 3.15-3.29 (m, 2 H), 3.72 (m: ddd, *J* = 4.8, 4.8, 3.0 Hz, 1 H), 3.98 (hept, *J* = 7.2 Hz, 1 H), 4.41 (m: dddd, *J* = 8.4, 8.4, 6.6, 6.6 Hz, 1 H), 5.12 (q, *J* = 6.8 Hz, 1 H), 6.93 (s, 1 H), 7.02 (s, 1 H), 7.30-7.42 (m, 6 H), 7.60-7.68 (m, 4 H). ^{13}C NMR (75.5 MHz) δ 19.1 (C), 23.6 (CH_3), 23.9 (CH_3), 24.4 (CH_3), 24.8 (CH_3), 25.2 (CH_3), 25.2 (CH_3), 26.9 (CH_3), 28.0 (CH), 29.1 (CH), 32.0 (CH_2), 33.1 (CH_2), 33.9 (CH), 52.1 (CH_2), 62.1 (CH_2), 65.9 (CH), 70.4 (CH), 75.3 (CH), 76.2 (CH), 120.4 (CH), 123.1 (CH), 127.5 (CH), 127.6 (CH), 129.5 (CH), 129.6 (CH), 133.1 (C), 134.1 (C), 134.2 (C), 135.6 (CH), 135.7 (CH), 147.2 (C). MS (DCI, NH_3+isobutane) *m/z* 612 (MH^+, 100%), 611, 379, 231, 105. HRMS calcd for $C_{40}H_{58}NO_2Si$: 612.4236. Found: 612.4178 (MH^+).

(1*R*,7a*R*,6*S*)-6-(*t*-Butyldiphenylsilanoxy)-hexahydropyrrolizin-1-ol (8a). Mp 113-115 °C (pentane). $[\alpha]^{26}_D$ +22.9 (*c* 1.1, $CHCl_3$). IR (film) 3432-3350, 3070, 2962, 2931, 2857, 1589, 1473, 1430, 1116 cm^{-1}. ^{1}H NMR (300 MHz) δ 1.06 (s, 9 H, CH_3), 1.78-2.15 (m, 2 H), 2.23 (m: dddd, *J* = 14.3, 1.9, 1.9, 1.9 Hz, 1 H), 2.64 (m: ddd, *J* = 12.8, 1.9, 1.9 Hz, 1 H), 2.73 (m: dd, *J* =12.8, 3.5 Hz, 1 H), 2.96-3.07 (m, 1 H), 3.20 (m: ddd, *J* = 7.6, 7.6, 7.6 Hz, 1 H), 3.65-3.73 (m, 1 H), 3.88-3.95 (m, 1 H), 4.08-4.16 (m, 1 H), 4.30-4.37 (m, 1 H), 7.33-7.48 (m, 6 H), 7.60-7.70 (m, 4 H). ^{13}C NMR (75.5 MHz) δ 18.9 (C), 26.8

(CH_3), 33.8 (CH_2), 37.1 (CH_2), 53.7 (CH_2), 61.5 (CH_2), 68.9 (CH), 72.5 (CH), 76.2 (CH), 127.8 (CH), 127.9 (CH), 130.0 (CH), 130.1 (CH), 132.5 (C), 132.8 (C), 135.8 (CH). MS (DCI, NH_3+isobutane) *m/z* 383, 382 (MH^+, 100%). HRMS calcd for $C_{23}H_{32}NO_2Si$: 382.2202. Found: 382.2226 (MH^+). Anal. Calcd for $C_{23}H_{31}NO_2Si + 2H_2O$: C, 66.15; H, 8.45; N, 3.35. Found: C, 66.33; H, 8.14; N, 3.17.

(7a*R*,6*S*)-6-(*t*-Butyldiphenylsilanoxy)-hexahydropyrrolizin-1-one (8b). IR (film) 2934, 2891, 2864, 1749, 1470, 1427, 1113, 1033 cm^{-1}. ^1H NMR (300 MHz) δ 1.00 (s, 9 H), 1.93-2.10 (m, 2 H), 2.28-2.41 (m, 1 H), 2.66-2.82 (m, 2 H), 3.17 (dd, *J* = 12.2, 4.1 Hz, 1 H), 3.26-3.36 (m, 2 H), 3.42-3.53 (m, 1 H), 4.23-4.29 (m, 1 H), 7.30-7.45 (m, 6 H), 7.55-7.68 (m, 4 H). ^{13}C NMR (75.5 MHz) δ 18.9 (C), 26.8 (CH_3), 26.8 (CH_3), 35.5 (CH_2), 39.0 (CH_2), 50.5 (CH_2), 64.2 (CH_2), 67.5 (CH), 73.7 (CH), 127.7 (CH), 129.8 (CH), 129.9 (CH), 133.0 (CH), 133.3 (C) 135.6 (C), 135.8 (C), 218.6 (C). MS (DCI, NH_3+isobutane) *m/z* 380 (MH^+), 274, 196, 140, 102 (100%).

(7a*R*,6*S*)-Trifluoromethanesulfonic Acid 6-(*t*-Butyldiphenylsilanoxy)-5,6,7,7a-tetrahydro-3*H*-pyrrolizin-1-yl Ester. $[\alpha]^{26}_D$ –13.4 (*c* 1.1, $CHCl_3$). IR (film) 3071, 3049, 2959, 2931, 2859, 1670, 1471, 1428, 1214, 1139 cm^{-1}. ^1H NMR (300 MHz) δ 1.01 (s, 9 H, CH_3), 1.83-1.90 (m, 2 H), 2.74 (A part of ABX system, *J* = 11.4, 2.7 Hz, 1 H), 2.98 (B part of ABX system, *J* = 11.4, 4.1 Hz, 1 H), 3.69 (m: ddd, *J* = 15.0, 5.2, 2.4 Hz, 1 H), 4.01 (m: ddd, *J* = 15.0, 3.2, 1.8 Hz, 1 H), 4.06-4.16 (m, 1 H), 4.34 (m: dddd, *J* = 4.0, 4.0, 4.0, 4.0 Hz, 1 H), 5.67-5.68 (m, 1 H), 7.32-7.45 (m, 6 H), 7.56-7.68 (m, 4 H). ^{13}C NMR (75.5 MHz) δ 18.9 (C), 26.7 (CH_3), 37.0 (CH_2), 59.7 (CH_2), 64.3 (CH_2), 66.5 (CH), 74.0 (CH), 112.2 (CH), 127.7 (CH), 129.8 (CH), 129.8 (CH), 133.4 (CH), 133.5 (C), 135.6 (CH), 135.7 (CH), 135.7 (CH), 148.1 (C). MS (DCI, NH_3+isobutane) *m/z* 512 (MH^+, 100%). HRMS calcd for $C_{24}H_{29}F_3NO_4SSi$: 512.1538. Found: 512.1544 (MH^+).

(7a*R*,6*S*)-6-(*t*-Butyldiphenylsilanoxy)-5,6,7,7a-tetrahydro-3*H*-pyrrolizine-1-carboxylic Acid Methyl Ester (9a). $[\alpha]^{26}_D$ –1.1 (*c* 1. 0, $CHCl_3$). IR (film) 3416, 3070, 2952, 2856, 1721, 1437, 1264, 1114 cm^{-1}. ^1H NMR (300 MHz) δ 0.99 (s, 9 H, CH_3), 1.80-1.90 (m, 1 H), 2.10 (m: ddd, *J* = 13.0, 7.5, 4.5

Hz, 1 H), 2.68 (m: ddd, *J* = 10.7, 4.6, 1.2 Hz, 1 H), 3.01 (m: dd, *J* = 10.7, 4.4 Hz, 1 H), 3.74 (s, 3 H), 3.80 (m: ddd, *J* = 18.0, 5.4, 2.0 Hz, 1 H), 4.03 (m: ddd, *J* = 18.0, 3.6, 2.0 Hz, 1 H), 4.24-4.35 (m, 2 H), 6.72 (m: ddd, *J* = 2.0, 2.0, 2.0 Hz, 1 H), 7.28-7.70 (m, 10 H). ^{13}C NMR (75.5 MHz) δ 19.0 (C), 26.7 (CH_3), 39.2 (CH_2), 51.4 (CH_3), 63.5 (CH_2), 63.8 (CH_2), 69.2 (CH), 74.0 (CH), 127.6 (CH), 128.4 (CH), 128.5 (CH), 129.6 (CH), 132.0 (CH), 132.1 (CH), 133.7 (C), 133.8 (C), 135.6 (CH), 135.7 (CH), 136.8 (C), 139.0 (CH), 164.2 (C). MS (DCI, NH_3+isobutane) *m/z* 422 (MH^+), 279. HRMS calcd for $C_{25}H_{32}NO_3Si$: 422.2151. Found: 422.2166 (MH^+).

(1*R*,7a*R*,6*S*)-6-(*t*-Butyldiphenylsilanoxy)-hexahydropyrrolizine-1-carboxylic Acid Methyl Ester (9b). $[\alpha]^{26}_D$ +9.2 (*c* 1.0, $CHCl_3$). IR (film) 3440, 3070, 3052, 2931, 2857, 1734, 1437, 1197, 1118 cm^{-1}. ^{1}H NMR (300 MHz) δ 1.02 (s, 9 H, CH_3), 1.46 (m: ddd, *J* = 17.8, 9.9, 8.0 Hz, 1 H), 1.80-1.94 (m, 2 H), 2.20-2.46 (m, 1 H), 2.58 (m: dd, *J* = 9.7, 7.2 Hz, 1 H), 2.90-3.12 (m, 4 H) 3.55-3.65 (m, 1 H), 3.66 (s, 3 H), 4.27-4.38 (m, 1 H), 7.30-7.70 (m, 10 H). ^{13}C NMR (75.5 MHz) δ 19.0 (C), 26.3 (CH), 26.8 (CH_3), 37.5 (CH_2), 47.5 (C), 51.6 (CH_3), 53.9 (CH_2), 61.9 (CH_2), 63.8 (CH), 73.7 (CH), 127.6 (CH), 127.7 (CH), 128.4 (CH), 128.6 (CH), 129.6 (CH), 129.7 (CH), 129.7 (CH), 131.9 (CH), 131.9 (CH), 132.0 (CH), 132.2 (CH), 133.7 (C), 133.8 (C), 135.7 (CH), 135.7 (CH), 173.5 (C). HRMS calcd for $C_{25}H_{34}NO_3Si$: 424.2308. Found: 424.2311 (MH^+)

(1*R*,7a*R*,6*S*)-6-Hydroxyhexahydropyrrolizine-1-carboxylic Acid Methyl Ester. $[\alpha]^{26}_D$ +40.2 (*c* 0.9, $CHCl_3$). IR (film) 3290, 3117, 2924, 2884, 1725, 1439, 1374, 1205 cm^{-1}. ^{1}H NMR (300 MHz) δ 1.45-1.56 (m, 1 H), 1.92-2.05 (m, 1 H), 2.15-2.39 (m, 2 H), 2.66 (m: dd, *J* = 10.4, 6.3 Hz, 1 H), 2.97-3.20 (m, 3 H), 3.34 (m: dd, *J* = 10.4, 5.6 Hz, 1 H), 3.71 (s, 3 H), 3.87 (m: ddd, *J* = 8.1, 8.1, 8.1 Hz, 1 H), 4.38-4.48 (m, 1 H). ^{13}C NMR (75.5 MHz) δ 27.3 (CH_2), 37.4 (CH_2), 47.4 (CH), 51.9 (CH_3), 54.1 (CH_2), 62.2 (CH_2), 64.9 (CH), 72.4 (C), 174.2 (C). MS (DCI, NH_3+isobutane) *m/z* 186 (MH^+). HRMS calcd for $C_9H_{16}NO_3$: 186.1130. Found: 186.1114 (MH^+).

(1*R*,7a*R*,6*S*)-6-{3-[4-(*t*-Butyldimethylsilanyloxy)-3-methoxyphenyl)-propionyloxy]}-hexahydropyrrolizine-1-carboxylic Acid Methyl Ester. $[\alpha]^{26}_{D}$ +30.5 (*c* 0.9, $CHCl_3$). IR (film) 2954, 2929, 2857, 1734, 1514, 1283 cm^{-1}. ^1H NMR (300 MHz) δ 0.10 (s, 6 H), 0.96 (s, 9 H), 1.50 (m: ddd, *J* = 14.1, 8.4, 6.0 Hz, 1 H), 1.85-1.97 (m, 1 H), 2.18-2.32 (m, 2 H), 2.55 (t, *J* = 7.4 Hz 2 H), 2.73 (m: dd, *J* = 11.9, 4.6 Hz, 1 H), 2.77-2.88 (m, 3 H), 2.97-3.07 (m, 1 H), 3.15-3.30 (m, 2 H), 3.67 (s, 3 H), 3.75 (s, 3 H), 3.70-3.85 (m, 1 H), 5.12-5.21 (m, 1 H). 6.55-6.75 (m, 3 H). ^{13}C NMR (75.5 MHz) δ -4.7 (CH_3), 18.4 (C), 25.7 (CH_3), 26.4 (CH_2), 30.6 (CH_2), 34.4 (CH_2), 36.2 (CH_2), 47.2 (CH), 51.7 (CH_3), 53.9 (CH_2), 55.5 (CH_3), 59.4 (CH_2), 64.6 (CH), 75.4 (CH), 112.4 (CH), 120.3 (CH), 120.8 (CH), 133.8 (C), 143.5 (C), 150.8 (C), 172.6 (C), 173.4 (C). MS (DCI, NH_3+isobutane) *m/z* 478 (MH^+). HRMS calcd for $C_{25}H_{40}NO_6Si$: 478.2625. Found: 478.2638 (MH^+).