Supporting Information

A Formal Total Synthesis of (±)-Halichlorine and (±)-Pinnaic Acid

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(1*R,5*R**,7*R**)-1-Allyl-6-(benzyloxy)-7-(2-{[*tert*-butyl(dimethyl)silyl]oxy}-ethyl)-6-azaspiro[4.5]decan-1-ol (14).** To an ice-cooled solution of **10** (210 mg, 0.503 mmol) in THF (5 mL) was added dropwise a 1 M soluition of allylmagnesium bromide in THF (0.76 mL, 0.76 mmol), and the mixture was stirred for 30 min at 0 ℃. The reaction was quenched with saturated aqueous NH_4Cl (5 mL) and the mixture was extracted with Et_2O (3 x 20 mL). The combined extracts were washed with brine (5 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography (hexane/acetone, 50:1) to afford **14** (228 mg, 99%) as a colorless oil: IR (neat) 3466 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.060 (s, 6 H), 0.90 (s, 9 H), 1.10 (d, J = 13.1 Hz, 1 H), 1.29 (dd, J = 12.9, 2.4 Hz, 1 H), 1.44–2.23 (m, 13 H), 2.69 (dd, J = 14.1, 6.6 Hz, 1 H), 3.04–3.11 (m, 1 H), 3.68–3.73 (m, 1 H), 3.81–3.87 (m, 1 H), 3.96 (s, 1 H), 4.71 (A part of ABq, J = 10.6 Hz, 1 H), 4.95–5.03 (m, 2 H), 5.09 (B part of ABq, J = 10.6 Hz, 1 H), 5.98–6.12 (m, 1 H), 7.23–7.41 (m, 5 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ –5.31, –5.22, 18.30, 18.91, 19.92, 22.28, 24.05, 25.97 (3C), 33.00, 36.70, 36.93, 41.38, 58.28, 60.02, 73.61, 75.61, 82.95, 116.17, 127.70 (3C), 128.39 (2C), 136.31, 137.05; HRMS (ESI–TOF) calcd for $C_{27}H_{46}NO_3Si$ ($[M + H]^+$) 460.3247, found 460.3260.

[(1*R,5*R**,7*R**)-6-(Benzyloxy)-7-(2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl)-1-hydroxy-6-azaspiro[4.5]dec-1-yl]acetic Acid (15).** To an ice-cooled solution of **14**

(1.50 g, 3.26 mmol) in THF (33 mL) and H_2O (33 mL) was added dropwise a 4% aqueous solution of osmium tetroxide (2.07 g, 0.326 mmol), followed by sodium periodate (4.19 g, 19.6 mmol) by portions. After being stirred at room temperature for 2 h, the reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (80 mL) and extracted with Et_2O (3 x 200 mL). The combined extracts were washed with brine (30 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography (hexane/acetone, 20:1) to afford [(1*R**,5*R**,7*R**)-6-(benzyloxy)-7-(2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl)-1-hydroxy-6-azaspiro[4.5]dec-1-yl]acetaldehyde (1.24 g, 82%) as a colorless oil: IR (neat) 3450, 1722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ –0.005 (s, 6 H), 0.84 (s, 9 H), 1.00–1.10 (m, 1 H), 1.24–1.27 (m, 1 H), 1.51–2.08 (m, 12 H), 2.50 (dd, J = 15.0, 3.2 Hz, 1 H), 2.97–3.06 (m, 1 H), 2.99 (dd, J = 15.1, 2.8 Hz, 1 H), 3.59–3.68 (m, 1 H), 3.75–3.82 (m, 1 H), 4.23 (s, 1 H), 4.69 and 4.98 (ABq, J = 10.3 Hz, 2 H), 7.21–7.29 (m, 5 H), 9.94 (t, J = 3.0 Hz, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ –5.30, –5.22, 18.30, 19.33, 19.78, 22.18, 23.89, 25.96 (3C), 32.14, 36.97, 37.22, 51.13, 58.47, 59.89, 73.84, 75.99, 81.58, 127.70, 128.05 (2C), 128.54 (2C), 136.90, 204.07; HRMS (ESI–TOF) calcd for $C_{26}H_{44}NO_4Si$ ([M + H]$^+$) 462.3040, found 462.3061; Anal. Calcd for $C_{26}H_{43}NO_4Si$: C, 67.64; H, 9.39; N, 3.03. Found: C, 67.51; H, 9.41; N, 3.02.

To a solution containing the above aldehyde (1.23 g, 2.66 mmol), 2-methyl-2-butene (27 mL), and sodium dihydrogenphosphate dihydrate (4.16 g, 26.6 mmol) in 2-methyl-2-propanol (53 mL)/water (27 mL) was added sodium chlorite (2.17 g, 24.0 mmol) by portions, and the mixture was stirred at room temperature. After 1 h, the reaction was quenched with saturated aqueous $Na_2S_2O_3$ (60 mL), acidified with 1 M aqueous HCl at 0 °C, and extracted with $CHCl_3$ (3 x 200 mL). The combined extracts were washed with brine (30 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography (hexane/acetone, 8:1) to afford **15** (1.21 g, 95%) as a white solid, which was recrystallized from hexane to give colorless plates: mp 119.5–121.0 °C; IR (KBr) 3466, 1707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.061 (s, 3 H), 0.066 (s, 3 H), 0.90 (s, 9 H), 1.05–1.31 (m, 3 H), 1.32–1.40 (m, 2 H), 1.59–1.93 (m, 6 H), 1.99–2.18 (m, 3 H), 2.38

(A part of ABq, J = 15.5 Hz, 1 H), 3.06–3.14 (m, 1 H), 3.09 (B part of ABq, J = 15.4 Hz, 1 H), 3.67–3.73 (m, 1 H), 3.80–3.87 (m, 1H), 4.80 and 4.92 (ABq, J = 10.2 Hz, 2 H), 7.29–7.37 (m, 5 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ –5.32, –5.22, 18.29, 18.94, 19.60, 21.78, 23.77, 25.95 (3C), 32.51, 36.37, 37.03, 41.42, 58.58, 59.77, 73.53, 76.30, 81.53, 127.96 (2C), 128.30, 128.69 (2C), 135.78, 171.16; Anal. Calcd for $C_{26}H_{43}NO_5Si$: C, 65.37; H, 9.07; N, 2.93. Found: C, 65.25; H, 9.02; N, 2.84.

[(1*S,5*R**,7*R**)-7-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl)-1-hydroxy-6-azaspiro[4.5]dec-1-yl]acetic Acid (16).** To a solution of **15** (1.21 g, 2.53 mmol) in EtOH (51 mL) was added 10% palladium on activated carbon (242 mg) and the resulting suspension was stirred under hydrogen at a balloon pressure for 2 h. The catalyst was removed by filtration, and the filtrate was concentrated in vacuo. The residue was purified by chromatography ($CHCl_3$/MeOH, 10:1) to afford **16** (913 mg, 97%) as a white solid, which was recrstallized from AcOEt–hexane to give colorless needles: mp 212.0–213.5 °C; IR (KBr) 3216, 1576 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.077 (s, 3 H), 0.085 (s, 3 H), 0.89 (s, 9 H), 1.43 (br d, J = 13.3 Hz, 1 H), 1.54–1.70 (m, 5 H), 1.75 (br d, J = 9.6 Hz, 1 H), 1.81–2.11 (m, 7 H), 2.66 and 2.83 (ABq, J = 16.8 Hz, 2 H), 2.94–2.99 (m, 1 H), 3.74 (td, J = 10.2, 3.3 Hz, 1 H), 3.86 (dt, J = 10.5, 4.3 Hz, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ –5.52, –5.29, 18.50, 18.75, 19.65, 26.04 (3C), 27.34, 29.42, 31.37, 35.91, 37.21, 44.44, 53.23, 61.82, 66.69, 80.17, 177.07; EIMS *m/z* (rel intensity) 371 (M^+, 84), 314 (M^+ – ^{t}Bu, 14), 268 (70), 255 (35), 213 (100); Anal. Calcd for $C_{19}H_{37}NO_4Si$: C, 61.41; H, 10.04; N, 3.77. Found: C, 61.15; H, 10.01; N, 3.78.

(4*R,7a*S**,10a*R**)-4-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl)-7a-hydroxyoctahydrocyclopenta[*i*]indolizin-6(7*H*)-one (17).** To an ice-cooled solution of **16** (913 mg, 2.46 mmol) and triethylamine (273 mg, 2.70 mmol) in toluene (49 mL) was added dropwise isobutyl chloroformate (369 mg, 2.70 mmol), and the mixture was stirred at room temperature for 1 h. The resulting insoluble material was removed by filtration and the filtrate was

concentrated in vacuo. The residue was redissolved in AcOEt (300 mL) and successively washed with saturated aqueous $NaHCO_3$ (20 mL), water (20 mL), and brine (20 mL). The solution was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by chromatography (hexane/acetone, 20:1) to afford **17** (782 mg, 90%) as a white solid, which was recrstallized from AcOEt–hexane to give colorless needles: mp 92.5–93.5 °C; IR (KBr) 3432, 1682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.026 (s, 3 H), 0.030 (s, 3 H), 0.87 (s, 9 H), 1.22 (tdd, *J* = 12.6, 4.4, 2.3 Hz, 1 H), 1.38 (dt, *J* = 12.6, 3.4 Hz, 1 H), 1.46–1.62 (m, 1 H), 1.67–1.96 (m, 6 H), 2.15–2.28 (m, 1 H), 2.17 (d, *J* = 1.8 Hz, 1 H), 2.39 (A part of ABq, *J* = 16.6 Hz, 1 H), 2.57–2.65 (m, 1 H), 2.61 (B part of ABq, *J* = 16.6 Hz, 1 H), 3.21 (dddd, *J* = 11.5, 8.6, 6.3, 2.7 Hz, 1 H), 3.64–3.76 (m, 2 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ –5.35, –5.29, 18.24, 22.21, 24.37, 25.60, 25.94 (3C), 27.54, 29.32, 31.39, 35.48, 42.27, 54.17, 60.05, 76.39, 83.76, 179.66; EIMS *m/z* (rel intensity) 296 (M^+ – ^{t}Bu, 100), 194 (6), 96 (9), 75 (20), 57 (30); Anal. Calcd for $C_{19}H_{35}NO_3Si$: C, 64.54; H, 9.98; N, 3.96. Found: C, 64.42; H, 9.87; N, 3.73.

(4*R,10a*S**)-4-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl)-1,2,3,4,9,10-hexahydrocyclopenta[*i*]indolizin-6(8*H*)-one (18) and (4*R**,10a*R**)-4-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl)-1,2,3,4,9,10-hexahydrocyclopenta[*i*]indolizin-6(7*H*)-one (19).** To a cooled (–40 °C) solution of **17** (782 mg, 2.21 mmol) and triethylamine (668 mg, 6.60 mmol) in CH_2Cl_2 (44 mL) was added dropwise thionyl chloride (396 mg, 3.33 mmol). After being stirred for 30 min, the reaction was quenched with saturated aqueous $NaHCO_3$ (40 mL) and the mixture was extracted with Et_2O (3 x 100 mL). The combined extracts were washed with brine (30 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography (hexane/acetone, 50:1). The first fractions afforded **19** (230 mg, 31%) as a white solid, which was recrystallized from AcOEt–hexane to give colorless needles: mp 64.5–65.5 °C; IR (KBr) 1689, 1670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.003 (s, 3H), 0.011 (s, 3 H), 0.86 (s, 9 H), 1.07 (tdd, *J* = 13.0, 4.0, 1.6 Hz, 1 H), 1.20–1.35 (m, 2 H), 1.57 (tt, *J* = 13.1, 3.6 Hz, 1 H), 1.62–1.70 (br m, 1 H), 1.77–1.85 (m, 2 H), 1.91 (br dt, *J* = 13.0,

3.2 Hz, 1 H), 1.95–2.00 (m, 1 H), 2.03–2.17 (m, 2 H), 2.41–2.58 (m, 2 H), 2.93 (ddt, J = 14.0, 9.4, 4.7 Hz, 1 H), 3.36 (dddd, J = 11.7, 8.8, 5.8, 2.8 Hz, 1 H), 2.99–3.82 (m, 2 H), 5.56 (s, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ –5.33, –5.29, 18.27, 21.94, 22.35, 25.14, 25.96 (3C), 29.64, 32.44, 34.01, 35.23, 53.84, 60.95, 73.14, 117.93, 172.05, 173.11; EIMS *m/z* (rel intensity) 335 (M^+, 1), 320 (M^+ – Me, 2), 278 (M^+ – ^{t}Bu, 100); Anal. Calcd for $C_{19}H_{33}NO_2Si$: C, 68.01; H, 9.91; N, 4.17. Found: C, 67.88; H, 9.80; N, 4.16.

The second fractions afforded **18** (453 mg, 61%) as a white solid, which was recrystallized from AcOEt–hexane to give colorless needles: mp 69.5–70.5 °C; IR (KBr) 1665 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.013 (s, 3 H), 0.020 (s, 3 H), 0.87 (s, 9 H), 1.29 (tdd, J = 13.1, 4.3, 1.7 Hz, 1 H), 1.45 (qd, J = 9.4, 3.8 Hz, 1 H), 1.55 (dt, J = 13.2, 3.1 Hz, 1 H), 1.60–1.75 (m, 4 H), 1.82 (ddd, J = 13.5, 13.4, 6.5 Hz, 1 H), 1.85–1.93 (m, 1 H), 2.17 (dd, J = 11.8, 5.9 Hz, 1 H), 2.34–2.44 (m, 1 H), 2.45–2.55 (m, 1 H), 2.75 (ddt, J = 14.0, 9.4, 4.7 Hz, 1 H), 2.87 (d, J = 19.3 Hz, 1 H), 2.96 (dquint, J = 19.6, 2.3 Hz, 1 H), 3.27 (dddd, J = 11.8, 8.9, 6.1, 2.6 Hz, 1 H), 3.69–3.73 (m, 2 H), 5.51 (s, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ –5.38, –5.26, 18.28, 23.08, 25.97 (3C), 30.20, 30.92, 32.23, 33.85, 35.11, 35.51, 53.32, 60.50, 76.63, 121.75, 142.37, 173.88; EIMS *m/z* (rel intensity) 335 (M^+, 2), 320 (M^+ – Me, 2), 278 (M^+ – ^{t}Bu, 100); Anal. Calcd for $C_{19}H_{33}NO_2Si$: C, 68.01; H, 9.91; N, 4.17. Found: C, 67.92; H, 9.88; N, 4.15.

(4*R,7a*R**,10a*S**)-4-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl)octahydrocyclopenta[*i*]indolizin-6(7*H*)-one (13).** To a solution of **18** (453 mg, 1.35 mmol) and **19** (230 mg, 0.685 mmol) in MeOH (10 mL) was added 10% palladium on activated carbon (140 mg), and the resulting suspension was stirred under hydrogen at a balloon pressure for 1 h. The catalyst was removed by filtration, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (hexane/acetone, 20:1) to afford **13** (680 mg, 99%) as a colorless oil: IR (neat) 1686 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.016 (s, 3 H), 0.023 (s, 3 H), 0.87 (s, 9 H),

1.30–1.43 (m, 2 H), 1.45–1.64 (m, 6 H), 1.65–1.74 (m, 1 H,), 1.75–1.80 (m, 2 H), 1.82–1.97 (m, 2 H), 2.01–2.09 (m, 1 H), 2.11 (dd, J = 17.7, 2.4 Hz, 1 H), 2.57 (dd, J = 17.5, 9.6 Hz, 1 H), 2.85 (ddt, J = 14.0, 9.3, 4.7 Hz, 1 H), 3.33–3.39 (m, 1 H), 3.70 and 3.71 (ABq, J = 4.8 Hz, 2 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ –5.33 (2C), 18.25, 23.13, 25.38, 25.96 (3C), 31.67, 33.86, 35.07 (2C), 36.75, 38.18, 42.13, 52.28, 60.94, 73.76, 173.72; EIMS *m/z* (rel intensity) 337 (M^+, 2), 280 (M^+ – ^{t}Bu, 100), 136 (9); Anal. Calcd for $C_{19}H_{35}NO_2Si$: C, 67.60; H, 10.45; N, 4.15. Found: C, 67.47; H, 10.37; N, 4.26.

(4*R,7a*R**,10a*S**)-4-(2-Hydroxyethyl)octahydrocyclopenta[*i*]indolizin-6(7*H*)-one (20).** A solution of **13** (680 mg, 2.01 mmol) in THF (20 mL) containing 1 M aqueous HCl (6.0 mL, 6.04 mmol) was stirred at room temperature for 30 min. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$ (30 mL) and extracted with Et_2O (3 x 150 mL). The combined extracts were washed with brine (30 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography ($CHCl_3$/MeOH, 50:1) to afford **20** (445 mg, 99%) as a colorless oil: IR (neat) 3396, 1659 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30–1.39 (m, 1 H), 1.38–1.57 (m, 2 H), 1.56–1.64 (m, 5 H), 1.63–1.72 (m, 1 H), 1.74–1.94 (m, 4 H), 2.02–2.11 (m, 2 H), 2.60 (dd, J = 18.0, 10.3 Hz, 1 H), 2.79–2.88 (m, 1 H), 3.13 (br s, 1 H), 3.24–3.30 (br m, 1 H), 3.65–3.75 (m, 2 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.49, 25.16, 32.04, 33.62, 34.90, 35.37, 36.46, 38.40, 41.99, 53.56, 60.76, 73.99, 174.13; EIMS *m/z* (rel intensity) 223 (M^+, 100), 205 (92), 178 (38), 150 (29), 121 (39); Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 69.71; H, 9.48; N, 6.21.

(4*R,7*R**,7a*R**,10a*S**)- and (4*R**,7*S**,7a*R**,10a*S**)-4-(2-Hydroxyethyl)-7-methyloctahydrocyclopenta[*i*]indolizin-6(7*H*)-one (21 and 22).** To an ice-cooled solution of diisopropylamine (504 mg, 4.98 mmol) in THF (15 mL) was added dropwise a 1.58 M solution of butyllithium in THF (2.77 mL, 4.38 mmol). After being stirred at 0 ℃ for 30 min, the mixture was cooled to –78 ℃. A solution of **20** (445 mg, 1.99 mmol) in THF (5 mL) was added

and the mixture was stirred at –78 °C for 1 h. To this was added dropwise iodomethane (1.41 g, 9.93 mmol) and the mixture was stirred at –78 °C for 30 min. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and the mixture was extracted with Et_2O (3 x 150 mL). The combined extracts were washed successively with saturated aqueous $Na_2S_2O_3$ (20 mL), water (20 mL), and brine (20 mL. After being dried over $MgSO_4$, the solvent was removed in vacuo. The residue was chromatographed (hexane/acetone, 2:1). The first fractions afforded 7*S**-product **22** (23.1 mg, 5%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (d, *J* = 7.4 Hz, 3 H), 1.33–1.57 (m, 4 H), 1.58–1.83 (m, 9 H), 2.12 (q, *J* = 8.6 Hz, 1 H), 2.62 (dq, *J* = 9.1, 7.4 Hz, 1 H), 2.83–2.98 (m, 2 H), 3.26 (tdd, *J* = 11.1, 4.2, 2.3 Hz, 1 H), 3.67–3.78 (m, 2 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 11.31, 22.91, 25.29, 27.26, 32.43, 35.05, 35.10, 35.67, 38.75, 47.61, 53.63, 61.14, 71.64, 176.41.

The second fractions yielded 7*R**-product **21** (346 mg, 73%) as a colorless oil: IR (neat) 3417, 1650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, *J* = 7.4 Hz, 3 H), 1.39–1.52 (m, 3 H), 1.55–1.71 (m, 6 H), 1.72–1.85 (m, 3 H), 1.87–1.95 (m, 2 H), 2.15 (dq, *J* = 6.9, 6.7 Hz, 1 H), 2.75 (dddd, *J* = 15.3, 9.3, 5.8, 5.2 Hz, 1 H), 3.17 (br s, 1 H), 3.34–3.40 (m, 1 H), 3.67–3.77 (m, 2 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 18.48, 21.75, 25.16, 31.71, 32.54, 35.16, 35.60, 38.13, 44.73, 51.72, 53.30, 60.80, 71.96, 177.02; HRMS (ESI–TOF) calcd for $C_{14}H_{24}NO_2$ ([M + H]$^+$) 238.1807, found 238.1806.

(4*R,7*R**,7a*R**,10a*S**)-4-[2-(Benzyloxy)ethyl]-7-methyloctahydrocyclopenta[*i*]-indolizin-6(7*H*)-one (23).** To an ice-cooled solution of **21** (369 mg, 1.55 mmol) in THF (31 mL) was added sodium hydride (60% dispersion in mineral oil, 248 mg, 6.20 mmol) followed by tetrabutylammonium iodide (57.4 mg, 0.155 mmol) and benzyl bromide (532 mg, 3.12 mmol), and the mixture was stirred at room temperature. After 12 h, the reaction was quenched with water (30 mL) and the mixture was extracted with Et_2O (3 x 100 mL). The combined extracts were washed with brine (20 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was

purified by chromatography (hexane/acetone, 8:1) to afford **23** (458 mg, 90%) as a colorless oil: IR (neat) 1680 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, J = 7.5 Hz, 3 H), 1.35–1.48 (m, 3 H), 1.53–1.67 (m, 6 H), 1.72–1.95 (m, 5 H), 2.11 (qd, J = 7.4, 4.4 Hz, 1 H), 3.02 (tdd, J = 9.5, 8.2, 4.8 Hz, 1 H), 3.34–3.41 (br m, 1 H), 3.57–3.64 (m, 2 H), 4.45 and 4.52 (ABq, J = 11.9 Hz, 2 H), 7.25–7.35 (m, 5 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 18.68, 22.79, 25.40, 31.94, 32.34, 33.47, 35.37, 39.05, 44.73, 51.29, 53.04, 68.44, 71.79, 73.00, 127.49, 127.78 (2C), 128.33 (2C), 138.76, 176.44; HRMS (ESI–TOF) calcd for $C_{21}H_{30}NO_2$ ([M + H]$^+$) 328.2277, found 328.2295.

(2*R)-2-{(1*R**,5*S**,7*R**)-7-[2-(Benzyloxy)ethyl]-6-azaspiro[4.5]dec-1-yl}-1-propanol (26).** To an ice-cooled solution of **23** (150 mg, 0.458 mmol) in 1,2-dichloroethane (9.2 mL) was added dropwise methyl trifluoromethanesulfonate (0.16 mL, 1.37 mmol), and the mixture was heated at 60 °C for 1 h. The mixture was concentrated in vacuo and the residue was redissolved in THF (9.2 mL)/H_2O (0.9 mL). After being stirred at room temperature for 12 h, the mixture was dried ($MgSO_4$) and concentrated in vacuo to afford the triflate salt of **25**. Data for the free base **25**: IR (neat) 1736 cm^{-1}; HRMS (ESI–TOF) calcd for $C_{22}H_{34}NO_3$ ([M + H]$^+$) 360.2539, found 360.2534.

A solution of the above triflate salt of 25 in THF (2 mL) was added dropwise a suspension of lithium aluminum hydride (174 mg, 4.58 mmol) in THF (7.2 mL) at 0 °C, and the mixture was stirred at the same temperature for 30 min. The reaction was quenched with water (0.6 mL) and then 4 M aqueous NaOH (0.2 mL). The insoluble material was removed by filtration through Celite. The filtrate was diluted with $CHCl_3$ (50 mL), washed with brine (3 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography ($CHCl_3$/MeOH/ 29% NH_4OH, 100:9:1) to afford **26** (112 mg, 74% from **23**) as a colorless oil: IR (neat) 3312, 3254 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (d, J = 6.9 Hz, 3 H), 1.05–1.13 (m, 1 H), 1.17–1.41 (m, 5 H), 1.42–1.77 (m, 9 H), 1.78–1.93 (m, 3 H), 2.78–2.84 (m, 1 H), 3.47 (d, J = 2.1 Hz, 1

H), 3.49 (s, 1 H), 3.50–3.63 (m, 2 H), 4.44 and 4.50 (ABq, J = 11.7 Hz, 2 H), 7.26–7.37 (m, 5 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 18.60, 22.46, 23.49, 31.66, 32.64, 35.69, 36.39, 37.76, 37.92, 50.60, 58.45, 62.60, 68.93, 69.02, 73.13, 127.67, 127.78 (2C), 128.38 (2C), 138.30; HRMS (ESI–TOF) calcd for $C_{21}H_{34}NO_2$ ([M + H]$^+$) 332.2565, found 332.2577.

2-[(1*R,5*S**,7*R**)-1-((1*R**)-2-{[*tert*-Butyl(diphenyl)silyl]oxy}-1-methylethyl)-6-(trifluoroacetyl)-6-azaspiro[4.5]dec-7-yl]ethanol (27).** A solution containing **26** (112 mg, 0.338 mmol), triethylamine (513 mg, 0.507 mmol), 4-(dimethylamino)pyridine (4.13 mg, 0.0338 mmol), and *tert*-butylchlorodiphenylsilane (139 mg, 0.506 mmol) in CH_2Cl_2 (6.8 mL) was stirred at room temperature for 1 h. The mixture was diluted with Et_2O (70 mL) and washed with saturated aqueous $NaHCO_3$ (3 mL) and brine (3 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography (NH silica gel, hexane/AcOEt, 20:1) to afford (1*R**,5*S**,7*R**)-7-[2-(benzyloxy)ethyl]-1-((1*R**)-2-{[*tert*-butyl(diphenyl)silyl]oxy}-1-methylethyl)-6-azaspiro[4.5]decane (183 mg, 95%) as a colorless oil: IR (neat) 3343 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (d, J = 6.8 Hz, 3 H), 1.08 (s, 9 H), 1.12–1.23 (m, 2 H), 1.25–1.65 (m, 13 H), 1.72–1.77 (m, 1 H), 1.86–2.00 (m, 1 H), 2.72–2.80 (br m, 1 H), 3.48–3.59 (m, 3 H), 3.66 (dd, J = 9.4, 6.1 Hz, 1H), 4.49 (s, 2 H), 7.26–7.43 (m, 11 H), 7.68 (d, J = 7.2 Hz, 4 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 15.60, 19.35, 22.49, 22.84, 26.75, 27.00 (3C), 33.18, 34.36, 35.91, 36.49, 37.46, 49.45, 50.92, 63.13, 68.35, 69.09, 73.04, 127.54 (4C), 127.67 (2C), 128.35 (2C), 129.43 (3C), 134.30 (2C), 135.72 (4C), 138.64; HRMS (ESI–TOF) calcd for $C_{37}H_{52}NO_2Si$ ([M + H]$^+$) 570.3767, found 570.3752.

To an ice-cooled solution of the above silyl ether (183 mg, 0.321 mmol) and *N*,*N*-diisopropylethylamine (2.08 mg, 1.61 mmol) in 1,2-dichloroethane (6.4 mL) was added dropwise trifluoroacetic anhydride (338 mg, 1.61 mmol), and the mixture was stirred for 15 min. The mixture was poured into saturated aqueous $NaHCO_3$ (10 mL) and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 15 mL) and the combined organic layers were dried

($MgSO_4$) and concentrated in vacuo. The residue was purified by chromatography (hexane/AcOEt, 20:1) to afford (1*R**,5*S**,7*R**)-7-[2-(benzyloxy)ethyl]-1-((1*R**)-2-{[*tert*-butyl(diphenyl)silyl]-oxy}-1-methylethyl)-6-trifluoroacetyl)-6-azaspiro[4.5]decane (212 mg, 99%) as a colorless oil: IR (neat) 1687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (d, *J* = 6.8 Hz, 3 H), 1.08 (s, 9 H), 1.36 (tt, *J* = 19.4, 6.4 Hz, 1 H), 1.45–1.93 (m, 13 H), 2.13–2.31 (m, 2 H), 3.27 (t, *J* = 5.7 Hz, 2 H), 3.50 (A part of ABX, *J* = 9.6, 7.5 Hz, 1 H), 3.64 (B part of ABX, *J* = 9.6, 5.2 Hz, 1 H), 4.03 (br d, *J* = 9.8 Hz, 1 H), 4.40 and 4.47 (ABq, *J* = 12.1 Hz, 2 H), 7.29–7.40 (m, 11 H), 7.62 (d, *J* = 7.7 Hz, 1 H), 7.63 (d, *J* = 7.7 Hz, 1 H), 7.66 (d, *J* = 7.5 Hz, 1 H), 7.67 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.13, 16.51, 19.37, 23.42, 24.75, 27.02 (3C), 30.75, 34.45, 34.90, 35.21, 35.92, 52.17, 53.60, 67.60, 68.42, 69.15, 72.86, 117.00, 127.37 (2 C), 127.59 (4 C), 127.76, 128.38 (2C), 129.57, 129.62, 133.85, 134.02, 135.77 (2C), 135.86 (2C), 138.38, 157.45; HRMS (ESI–TOF) calcd for $C_{39}H_{50}F_3NNaO_3Si$ ([M + Na]$^+$) 688.3410, found 688.3427.

To a solution of the above trifluoroacetamide (212 mg, 0.318 mmol) in MeOH (6.4 mL) was added 20% palladium hydroxide on carbon (42.4 mg), and the resulting suspension was stirred under hydrogen at a balloon pressure for 2 h. The catalyst was removed by filtration and the filtrate was concentrated in vacuo. The residue was purified by chromatography (hexane/AcOEt, 8:1) to afford **27** (181 mg, 99%) as a colorless oil: IR (neat) 3461, 1685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (d, *J* = 6.7 Hz, 3 H), 1.07 (s, 9 H), 1.19–1.57 (m, 6 H), 1.59–1.90 (m, 9 H), 2.12–2.29 (m, 2 H), 3.34–3.45 (m, 2 H), 3.46 (A part of ABX, *J* = 9.6, 5.4 Hz, 1 H), 3.65 (B part of ABX, *J* = 9.5, 3.7 Hz, 1 H), 3.96 (br d, *J* = 9.5 Hz, 1 H), 7.37–7.43 (m, 6 H), 7.62 (d, *J* = 7.8 Hz, 1 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 7.67 (d, *J* = 7.8 Hz, 1 H), 7.68 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.05, 16.52, 19.37, 23.28, 24.72, 26.99 (3C), 30.80, 34.38, 35.31, 35.92, 37.82, 51.38, 53.74, 60.24, 68.41, 69.12, 115.53, 127.59 (2C), 127.63 (2C), 129.57, 129.61, 133.98, 134.11, 135.83 (2C), 135.95 (2C), 157.34; HRMS (ESI–TOF) calcd for $C_{32}H_{44}F_3NNaO_3Si$ ([M + Na]$^+$) 598.2940, found 598.2912.

[(1*R,5*S**,7*R**)-1-((1*R**)-2-{[*tert*-Butyl(diphenyl)silyl]oxy}-1-methylethyl)-6-(trifluoroacetyl)-6-azaspiro[4.5]dec-7-yl]acetaldehyde (12).** To a solution of **27** (181 mg, 0.314 mmol) in CH_2Cl_2 (6.3 mL) was added Dess–Martin periodinane (400 mg, 0.943 mmol) at room temperature, and the mixture was stirred for 30 min. The reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL) and the mixture was extracted with Et_2O (3 x 15 mL). The combined extracts were washed with brine (3 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by chromatography (hexane/AcOEt, 20:1) to afford **12** (171 mg, 95%) as a colorless oil: IR (neat) 1727, 1693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (d, J = 6.7 Hz, 3 H), 1.09 (s, 9 H), 1.24–1.45 (m, 2 H), 1.49–1.89 (m, 10 H), 2.10–2.28 (m, 4 H), 3.47 (A part of ABX, J = 9.5, 5.3 Hz, 1 H), 3.67 (ABX, J = 9.5, 3.7 Hz, 1 H), 4.39 (br d, J = 9.3 Hz, 1 H), 7.37–7.45 (m, 6 H), 7.63 (d, J = 7.9 Hz, 1 H), 7.64 (d, J = 7.9, Hz, 1 H), 7.70 (d, J = 7.8 Hz, 1 H), 7.71 (d, J = 7.8 Hz, 1 H), 9.28 (s, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.67, 16.74, 19.32, 24.11, 24.75, 26.98 (3C), 30.95, 34.29, 35.48, 35.81, 47.36, 48.61, 53.67, 68.15, 68.95, 116.78, 127.72 (2C), 127.76 (2C), 129.77, 129.82, 133.64, 134.06, 135.80 (2C), 136.02 (2C), 157.51, 198.13; HRMS (ESI–TOF) calcd for $C_{32}H_{43}F_3NO_3Si$ ($[M + H]^+$) 574.2964, found 574.2921.

Ethyl (2*E*)-4-[(1*R,5*S**,7*R**)-1-((1*R**)-2-{[*tert*-Butyl(diphenyl)silyl]oxy}-1-methylethyl)]-6-(trifluoroacetyl)-6-azaspiro[4.5]dec-7-yl]-2-methyl-2-butenoate (6).** To an ice-cooled suspension of sodium hydride (60% dispersion in mineral oil, 2.4 mg, 0.060 mmol) in THF (0.6 mL) was added dropwise a solution of triethyl 2-phosphonopropionate (14.7 mg, 0.0617 mmol) in THF (0.1 mL). After being stirred at 0 ℃ for 30 min, the mixture was cooled to –78 ℃. To this was added a solution of **12** (23.6 mg, 0.0411 mmol) in THF (0.2 mL) and the mixture was stirred at the same temperature for 30 min. The reaction was quenched with water (3 mL) and the mixture was extracted with Et_2O (3 x 10 mL). The combined extracts were washed with water (1 mL), brine (1 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by chromatography (hexane/AcOEt, 20:1) to afford **6** (20.5 mg, 76%) as a

colorless oil: IR (neat) 1714, 1693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (d, J = 6.7 Hz, 3 H), 1.13 (s, 9 H), 1.26–1.43 (m, 1 H), 1.32 (t, J = 7.1 Hz, 3 H), 1.50–2.00 (m, 11 H), 1.67 (s, 3 H), 2.12–2.28 (m, 4 H), 3.49 (A part of ABX, J = 9.6, 5.4 Hz, 1 H), 3.64 (B part of ABX, J = 9.6, 3.9 Hz, 1 H), 3.82 (br s, 1 H), 4.22 (q, J = 7.1 Hz, 2 H), 6.43 (br t, J = 7.3 Hz, 1 H), 7.32–7.41 (m, 6 H), 7.60–7.65 (m, 4 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.59, 14.15, 14.32, 16.49, 19.40, 23.18, 24.72, 27.01 (3C), 30.75, 34.53, 34.73, 35.40, 35.87, 53.11, 53.86, 60.78, 68.55, 69.20, 118.38, 127.62 (4C), 129.69, 129.76, 130.15, 133.76, 133.88, 135.71 (2C), 135.79 (2C), 136.51, 157.48, 167.77; HRMS (ESI–TOF) calcd for $C_{37}H_{51}F_3NO_4Si$ ([M + H]$^+$) 658.3539, found 658.3491.

(1*R,5*S**,7*R**)-7-Allyl-1-((1*R**)-2-{[*tert*-butyl(diphenyl)silyl]oxy}-1-methylethyl)-6-(trifluoroacetyl)-6-azaspiro[4.5]decane (28).** To an ice-cooled suspention of (methyl)triphenylphosphonium iodide (128 mg, 0.358 mmol) in THF (4 mL) was added dropwise a 1.58 M solution of butyllithium in hexane (0.208 mL, 0.329 mmol). The ice bath was removed and the mixture was stirred at room temperature for 30 min and then cooled to 0 ℃. After addition of a solution of **12** (171 mg, 0.298 mmol) in THF (2 mL), the resulting mixture was stirred at 0 ℃ for 30 min. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) and the mixture was extracted with Et_2O (3 x 15 mL). The combined extracts were washed with water (3 mL) and brine (3 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography (hexane/AcOEt, 20:1) to afford **27** (136 mg, 80%) as a colorless oil: IR (neat) 3070, 3052, 1689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (d, J = 6.7 Hz, 3 H), 1.08 (s, 9 H), 1.30–1.40 (m, 1 H), 1.42–1.94 (m, 11 H), 1.99–2.07 (m, 1 H), 2.11–2.29 (m, 3 H), 3.48 (A part of ABX, J = 9.6, 5.3 Hz, 1 H), 3.63 (B part of ABX, J = 9.7, 3.7 Hz, 1 H), 3.71–3.79 (br m, 1 H), 4.95 (d, J = 17.1 Hz, 1 H), 5.05 (d, J = 10.1 Hz, 1 H), 5.55 (dddd, J = 17.2, 9.9, 7.7, 6.7 Hz, 1 H), 7.29–7.44 (m, 6 H), 7.61 (d, J = 7.8 Hz, 1 H), 7.62 (d, J = 7.8 Hz, 1 H), 7.66 (d, J = 7.9 Hz, 1 H), 7.67 (d, J = 7.9 Hz, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.87, 16.56, 19.38, 22.36, 24.75, 27.01 (3C), 30.79, 34.46, 35.27, 35.88, 40.00, 53.65 (2C), 68.40, 69.12, 117.99,

118.44, 127.63 (4C), 129.62, 129.71, 133.68, 133.82, 134.34, 135.78 (2C), 135.86 (2C), 157.19; HRMS (ESI–TOF) calcd for $C_{33}H_{45}F_3NO_2Si$ ([M + H]$^+$) 572.3172, found 572.3205.

Ethyl 2-{[(1*R,5*S**,7*R**)-7-Allyl-1-((1*R**)-2-{[*tert*-butyl(diphenyl)silyl]oxy}-1-methylethyl)-6-azaspiro[4.5]dec-6-yl]methyl}acrylate (11).** To a solution of **28** (136 mg, 0.238 mmol) in EtOH (4.8 mL) was added sodium borohydride (45.0 mg, 1.19 mmol), and the mixture was stirred at room temperature for 15 h. The reaction mixture was quenched with water (5 mL) and extracted with $CHCl_3$ (3 x 15 mL). The combined extracts were washed with water (3 mL) and brine (3 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography ($CHCl_3$/MeOH/29% NH_4OH, 500:9:1) to afford (1*R**,5*S**,7*R**)-7-allyl-1-((1*R**)-2-{[*tert*-butyl(diphenyl)silyl]oxy}-1-methylethyl)-6-azaspiro[4.5]decane (93.9 mg, 83%) as a colorless oil: IR (neat) 3070, 3048 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78–0.97 (m, 1 H), 0.95 (d, *J* = 6.9 Hz, 3 H), 1.07 (s, 9 H), 1.08–1.19 (m, 1 H), 1.27–1.75 (m, 12 H), 1.93–2.01 (m, 2 H), 2.06–2.12 (m, 1 H), 2.59–2.65 (br m, 1 H), 3.50 (A part of ABX, *J* = 9.4, 6.8 Hz, 1 H), 3.68 (B part of ABX, *J* = 9.4, 6.0 Hz, 1 H), 5.02 (d, *J* = 10.1 Hz, 1 H), 5.04 (d, *J* = 17.2 Hz, 1 H), 5.74 (dddd, *J* = 17.2, 10.0, 7.5, 6.9 Hz, 1 H), 7.36–7.42 (m, 6 H), 7.67–7.71 (m, 4 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 15.66, 19.37, 22.45, 22.82, 26.80, 27.01 (3C), 32.69, 34.43, 35.97, 36.47, 42.17, 50.56, 50.95, 63.24, 69.11, 116.62, 127.55 (4C), 129.44 (2C), 134.32 (2C), 135.73 (4C), 136.27; HRMS (ESI–TOF) calcd for $C_{31}H_{46}NOSi$ ([M + H]$^+$) 476.3349, found 476.3372.

To a mixture of the above amine (93.9 mg, 0.197 mmol) and potassium carbonate (136 mg, 0.987 mmol) in acetonitrile (2 mL) was added 2-(bromomethyl)acrylic acid ethyl ester (190 mg, 0.984 mmol), and the mixture was heated at 60 ℃ for 12 h. After the mixture was diluted with $CHCl_3$ (50 mL), and the resulting solution was washed with water (2 mL) and brine (2 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography (hexane/AcOEt, 50:1) to afford **11** (102 mg, 88%) as a colorless oil: IR (neat) 3072, 3050, 1712

cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (d, J = 6.7 Hz, 3 H), 1.06 (s, 9 H), 1.22–1.54 (m, 9 H), 1.28 (t, J = 7.2 Hz, 3 H), 1.60–1.77 (m, 4 H), 1.78–1.91 (m, 2 H), 2.03–2.12 (m, 1 H), 2.28–2.40 (m, 1 H), 3.06 and 3.36 (ABq, J = 18.9 Hz, 2 H), 3.57 (A part of ABX, J = 9.1, 6.3 Hz, 1 H), 3.79 (B part of ABX, J = 9.0, 4.6 Hz, 1 H), 4.17 (q, J = 7.1 Hz, 2 H), 4.90 (d, J = 17.1 Hz, 1 H), 4.93 (d, J = 9.7 Hz, 1 H), 5.57 (dddd, J = 17.3, 9.9, 8.4, 5.2 Hz, 1 H), 5.93 (d, J = 1.6 Hz, 1 H), 6.25 (d, J = 1.9 Hz, 1 H), 7.35–7.44 (m, 6 H), 7.64–7.68 (m, 4 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.24, 19.30, 21.88, 23.34, 26.98 (3 C), 28.47, 29.40, 29.73, 30.36, 31.09, 34.41, 40.48, 51.31, 53.15, 60.43, 61.18, 68.02, 69.94, 116.01, 126.54, 127.54 (2C), 127.56 (2C), 129.45, 129.48, 134.15 (2C), 135.83 (2C), 135.86 (2C), 137.48, 140.93, 167.04; HRMS (ESI–TOF) calcd for $C_{37}H_{54}NO_3Si$ ($[M + H]^+$) 588.3873, found 588.3857.

Ethyl [(1*S,2*R**,9′a*R**)-1′,2′,3′,6′,9′,9′a-Hexahydro-2-[(1*R**)-2-{[*tert*-butyl(diphenyl)silyl]oxy}-1-methylethyl]spirocyclopentane-1,4′-[4*H*]quinolizine-7′-carboxylate (30).** A solution of **11** (102 mg, 0.173 mmol) and ruthenium complex **29** (7.36 mg, 0.00867 mmol) in CH_2Cl_2 (8.7 mL) was heated at reflux for 1 h. After being cooled to room temperature, the mixture was concentrated in vacuo and the residue was purified by chromatography (hexane/AcOEt, 20:1) to afford **30** (96.2 mg, 99%) as a colorless oil: IR (neat) 3070, 3048, 1712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (d, J = 6.7 Hz, 3 H), 1.06 (s, 9 H), 1.23–1.68 (m, 8 H), 1.28 (t, J = 7.1 Hz, 3 H), 1.75–1.86 (m, 4 H), 1.92–2.04 (m, 3 H), 2.13 (dq, J = 19.2, 3.7 Hz, 1 H), 2.21–2.27 (m, 1 H), 2.89 (dq, J = 16.5, 3.2 Hz, 1 H), 3.42 (d, J = 16.3 Hz, 1 H), 3.68 (A part of ABX, J = 9.2, 6.5 Hz, 1 H), 3.93 (B part of ABX, J = 9.2, 3.9 Hz, 1 H), 4.18 (dq, J = 8.4, 7.2 Hz, 2 H), 6.75–6.81 (br m, 1 H), 7.32–7.42 (m, 6 H), 7.62–7.68 (m, 4 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.30, 17.26, 19.41, 21.73, 23.87, 27.07 (3C), 28.89, 29.74, 32.31, 33.28, 35.87, 35.93, 47.30, 52.55, 53.90, 60.16, 67.20, 68.51, 127.45 (4C), 129.19, 129.35, 129.37, 134.44, 134.51, 135.75 (2C), 135.79 (2C), 136.53, 166.13; HRMS (ESI–TOF) calcd for $C_{35}H_{50}NO_3Si$ ($[M + H]^+$) 560.3560, found 560.3561.

Ethyl [(1*S,2*R**,9′a*R**)-1′,2′,3′,6′,9′,9′a-Hexahydro-2-[(1*R**)-2-hydroxy-1-methylethyl]spirocyclopentane-1,4′-[4*H*]quinolizine-7′-carboxylate (5).** A solution containing **30** (96.2 mg, 0.172 mmol), triethylamine trihydrofluoride (277 mg, 17.2 mmol) and triethylamine (203 mg, 2.01 mmol) in acetonitrile (29 mL) was stirred at room temperature for 1 h. Saturated aqueous $NaHCO_3$ (30 mL) was added and the mixture was extracted with $CHCl_3$ (3 x 50 mL). The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by chromatography ($CHCl_3$/MeOH/ 29% NH_4OH, 200:9:1) to afford **5** (51.9 mg, 94%) as a colorless oil: IR (neat) 3376, 3135, 2931, 2871, 2817, 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, J = 6.7 Hz, 3 H), 1.26 (t, J = 7.2 Hz, 3 H), 1.29–1.64 (m, 8 H), 1.72 (br dt, J = 12.8, 2.7 Hz, 1 H), 1.76–1.86 (m, 1 H), 1.86–2.03 (m, 2 H), 2.04–2.18 (m, 3 H), 2.17–2.32 (m, 1 H), 2.34–2.41 (m, 1 H), 2.97 (dq, J = 16.4, 3.2 Hz, 1 H), 3.44 (dd, J = 10.8, 2.2 Hz, 1 H), 3.52–3.59 (m, 1 H), 3.56 (d, J = 10.6 Hz, 1 H), 4.15 (q, J = 7.1 Hz, 2 H), 6.82–6.85 (m, 1 H), 7.40–8.30 (br s, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.21, 19.21, 21.48, 24.15, 29.65, 32.81, 34.16, 34.93, 39.24, 41.15, 46.39, 52.44, 60.35, 61.82, 68.34, 68.71, 127.94, 136.12, 165.50; HRMS (ESI–TOF) calcd for $C_{19}H_{32}NO_3$ ($[M + H]^+$) 322.2382, found 322.2375.