Supporting Information

Efficient Synthetic Method of 2,4,5-Trisubstituted 2,5-Chiral Tetrahydropyridines by One-pot Asymmetric Azaelectrocyclization Protocol

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Experimental section

All commercially available reagents were used without further purification. All solvents were used after distillation. Diethylether, Dioxane, and benzene were refluxed over and distilled from sodium. Dichloromethane and acetonitrile were refluxed over and distilled from P₂O₅. Dimethylformamide (DMF) was distilled from CaH₂ under reduced pressure. Preparative separation was usually performed by column chromatography on silica gel and on aluminum oxide deactivated with 5 w/% of H₂O. ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz spectrometer and chemical shifts were represented as δ-values relative to the internal standard TMS. IR spectra were recorded on a FT/IR Spectrometer. High resolution mass spectra (HRMS) were measured on an ESI-TOF MS. Melting point was uncorrected.

**Data for (Z)-methyl 3-formyl-2-iodopent-2-enoate 5**: IR (KBr disk, cm⁻¹) 2976, 1730, 1689, 1593, 1435, 1265, 1205, 1086; ¹H NMR (400 MHz CDCl₃) δ 9.60 (s, 1H), 3.87 (s, 3H), 2.41 (q, J = 7.5 Hz, 2H), 0.96 (t, J = 7.5, 3H); ¹³C NMR (100 MHz, CDCl₃) 196.5, 165.6, 146.7, 101.8, 53.5, 23.9, 12.6.

**One-pot reaction by using (a), 5 and 6**: To a suspension of the vinyliodide 5 (70 mg, 0.261 mmol) and molecular sieve 4Å (162 mg) in 1,4-dioxane (2 mL) was added cis-1-amino-7-isopropylindan-2-ol (a) (50 mg, 0.261 mmol) at room temperature, and the mixture was stirred for 30 min at 80 °C. Then to this suspension was added lithium chloride (22 mg, 0.523 mmol), Tri(2-furyl)phosphine (5 mg, 0.021 mmol) and Tris(dibenzylideneacetone)dipalladium(0) (5 mg, 0.005 mmol) and the mixture was stirred for 10 min at this temperature then vinyl stannane 6 (206 mg, 0.523 mmol) in 1,4-dioxane (2.0 mL) was added to this suspension. After the reaction mixture was stirred at reflux for 5 h, the reaction mixture was cooled to room temperature, filtered and concentrated in vacuo to give a crude products which were purified by column chromatography on silica gel (from 5% to 9% ethyl acetate in hexane) gave the 1,2,5,6-tetrahydropyridine derivative 8 (84 mg, 77%) as a yellow oil; IR (neat, cm⁻¹) 1755, 1595, 1377, 1289, 1053; ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.33 (m, 5H), 7.18 (dd, 1H, J = 7.6, 7.6 Hz), 7.01 (d, 1H, J = 8.0), 6.99 (d, 1H, J = 7.6 Hz), 6.80 (d, 1H, J = 2.5 Hz), 4.95-4.92 (m, 1H), 4.89-4.88 (m, 1H), 4.26 (brs, 1H), 3.72 (s, 3H), 3.19 (d, 2H,
$J = 3.2$ Hz), 2.95-2.92 (m, 1H), 2.69 (qq, 1H, 6.9, 6.9 Hz), 1.65-1.57 (m, 3H), 1.01 (d, 3H, $J = 6.9$ Hz), 0.86 (t, 3H, $J = 7.6$ Hz), 0.61 (d, 3H, $J = 7.1$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.7, 147.7, 143.1, 141.0, 138.6, 136.0, 129.1, 128.7, 128.4, 127.9, 127.3, 123.5, 121.6, 91.0 74.8, 74.7, 57.1, 39.5, 35.9, 27.9, 26.7, 23.5.

**One-pot reaction by using (a), 5 and 9:** To a suspension of the vinyl iodide 5 (100 mg, 0.373 mmol) and molecular sieve 4Å (373 mg) in 1,4-dioxane (3 mL) was added cis-1-amino-7-isopropylindan-2-ol (a) (78 mg, 0.410 mmol) at room temperature, and the mixture was stirred for 30 min at 80 °C. Then to this suspension was added lithium chloride (32 mg, 0.746 mmol), Tri(2-furyl)phosphine (7 mg, 0.03 mmol) and Tris(dibenzylideneacetone)dipalladium(0) (7 mg, 0.007 mmol) and the mixture was stirred for 10 min at this temperature then vinyl stannane 9 (427 mg, 0.746 mmol) in 1,4-dioxane (3.0 mL) was added to this suspension. After the reaction mixture was stirred at reflux for 5 h, the reaction mixture was cooled to room temperature, filtered and concentrated in vacuo to give a crude products which were purified by column chromatography on silica gel (from 5% to 25% ethyl acetate in hexane) gave the 1,2,5,6-tetrahydropyridine derivative 10 (108 mg, 48%) as a yellow oil and 11 (58 mg, 28%) as a yellow oil: Data for 10; IR (KBr disk, cm$^{-1}$) 1719, 1449, 1371, 1256, 1173, 1022; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.33 (d, 1H, $J = 8.2$ Hz), 7.72-7.69 (m, 2H), 7.54-7.50 (m, 2H), 7.42-7.37 (m, 3H), 7.34-7.30 (m, 1H), 7.19 (dd, 1H, $J = 7.6, 7.6$ Hz), 7.02 (d, 1H, $J = 7.6$ Hz), 6.99 (d, 1H, $J = 7.6$ Hz), 6.91 (brs, 1H), 6.86 (d, 1H, $J = 3.0$ Hz), 5.13 (dd, 1H, $J = 2.6, 2.6$ Hz), 4.86-4.83 (m, 1H), 4.62 (d, 1H, $J = 5.3$ Hz), 4.25 (brs, 1H), 3.71 (s, 3H), 3.16-3.14 (m, 2H), 3.05 (qq, 1H, $J = 6.9$ Hz), 2.90 (dd, 1H, $J = 5.8, 5.8$ Hz), 1.59-1.51 (m, 3H), 1.05 (d, 3H, $J = 6.6$ Hz), 0.81 (t, 3H, $J = 7.6$), 0.59 (d, 3H, $J = 7.1$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.5, 147.4, 143.2, 141.1, 139.1, 137.9, 136.3, 135.8, 134.1, 129.5, 129.3, 128.9, 127.3, 126.1, 126.0, 125.0, 124.2, 123.5, 121.8, 120.7, 115.4, 113.6, 91.1, 76.0, 75.3, 55.5, 51.7, 39.2, 35.8, 28.0, 26.4, 23.5, 21.0, 11.4.

Data for 11 (R = iPr); IR (KBr disk, cm$^{-1}$) 1711, 1447, 1373, 1177, 1049; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.38 (d, 1H, $J = 16.3$ Hz, 1H), 8.24-8.22 (m, 1H), 7.86-7.83 (m, 2H), 7.52-7.45 (m, 2H), 7.41-7.37 (m, 2H), 7.34-7.30 (m, 1H), 7.25-7.21 (m, 2H), 7.09 (d, 1H, $J = 7.3$ Hz, 1H), 6.86 (s, 1H), 6.77 (d, 1H, $J = 16.3$ Hz, 1H), 5.75 (d, 1H, $J = 6.2$ Hz, 1H), 5.35 (s, 1H), 5.26 (ddd, 1H, $J = 6.0, 6.0, 3.0$ Hz, 1H), 3.65 (qq, 1H, $J = 6.9, 6.9$ Hz, 1H), 3.31-3.20 (m, 2H), 2.63 (q, 1H, $J = 7.6$ Hz, 2H), 1.33 (d, 1H, $J = 6.9$ Hz, 1H), 1.26 (d, 1H, $J = 6.9$ Hz, 3H), 1.23 (t,
$J = 7.6$ Hz, 3H)); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.9, 156.3, 147.9, 141.4, 139.4, 138.4, 137.6, 136.1, 133.7, 129.8, 129.6, 129.1, 128.6, 126.8, 126.1, 125.1, 124.5, 124.0, 123.8, 122.3, 120.8, 120.0, 115.1, 108.9, 91.1, 85.6, 62.6, 39.1, 28.8, 23.7, 20.8, 12.1; ESI-HRMS m/z calcd for C$_{34}$H$_{32}$N$_2$O$_4$S [M + H]$^+$ 587.1980, found 587.1985.

**One-pot reaction by using (b), 5 and 9:** To a suspension of the vinyliodide 5 (50 mg, 0.187 mmol) and molecular sieve 4Å (260 mg) in 1,4-dioxane (2 mL) was added cis-1-aminooindan-2-ol (-)-b (28 mg, 0.187 mmol) at room temperature, and the mixture was stirred for 30 min at 80 °C. Then to this solution was added lithium chloride (16 mg, 0.373 mmol), Tri(2-furyl)phosphine (4 mg, 0.015 mmol) and Tris(dibenzylideneacetone)dipalladium(0) (4 mg, 0.004 mmol) and the mixture was stirred for 10 min at this temperature then vinyl stannane 9 (243 mg, 0.373 mmol) in 1,4-dioxane (1.5 mL) was added to this suspension. After the reaction mixture was stirred at reflux for 5 h, the reaction mixture was cooled to room temperature, filtered and concentrated in vacuo to give a crude products which were purified by column chromatography on silica gel (from 5% to 25% ethyl acetate in hexane) gave the compound 11 (76 mg, 72%) as yellow oil: Data for 11 (R = H); IR (KBr disk, cm$^{-1}$) 1711, 1447, 1375, 1177, 1049; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.43 (d, $J = 16.3$ Hz, 1H), 8.25 (d, $J = 7.8$ Hz, 1H), 7.88-7.85 (m, 2H), 7.55-7.45 (m, 3H), 7.43-7.39 (m, 2H), 7.35-7.22 (m, 5H), 6.88 (s, 1H), 6.77 (d, $J = 16.1$ Hz, 1H), 5.68 (d, $J = 6.0$ Hz, 1H), 5.32 (s, 1H), 5.22 (ddd, $J = 6.0$, 6.0, 2.3 Hz, 1H), 3.31-3.19 (m, 2H), 2.66-2.56 (m, 2H), 1.21 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.5, 156.6, 141.4, 139.4, 139.3, 138.5, 137.6, 133.7, 129.7, 129.1, 128.9, 128.7, 127.6, 126.8, 126.1, 125.2, 125.1, 124.5, 124.0, 120.8, 119.8, 115.1, 108.7, 91.4, 85.8, 63.4, 39.0, 20.7, 12.2; ESI-HRMS m/z calcd for C$_{31}$H$_{26}$N$_2$O$_4$S [M + H]$^+$ 545.1511, found 545.1485.

**Data for (Z)-tert-butyl 3-formyl-2-iodopent-2-enoate 15:** IR (neat, cm$^{-1}$) 1720, 1688, 1460, 1372, 1261, 1152; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.60 (s, 1H), 2.53 (q, $J = 7.8$ Hz, 2H), 1.56 (s, 9H), 1.01 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.9, 164.4, 144.4, 105.1, 27.8, 23.2, 13.3, 10.9; ESI-HRMS m/z calcd for C$_{18}$H$_{15}$INNaO$_3$ [M + Na]$^+$ 332.9964, found 332.9951.

**One-pot reaction by using (a), 15 and 9.** To a suspension of the vinyl iodide 15 (50
mg, 0.162 mmol) and molecular sieve 5Å (162 mg) in Dioxane (1 mL) was added cis-1-amino-7-isopropylindan-2-ol (a) (31 mg, 0.162 mmol) at room temperature, and the mixture was stirred at 80 °C for 30 min. Then to this solution was added lithium chloride (14 mg, 0.324 mmol), Tri(2-furyl)phosphine (3 mg, 13 µmol) and Tris(dibenzylideneacetone)dipalladium(0) (3 mg, 3 µmol) at 80 °C, and the mixture was stirred for 10 min at this temperature then vinyl stannane 9 (185 mg, 0.324 mmol) in Dioxane (1 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 10 h, cooled to room temperature, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (from 3% to 9% ethyl acetate in hexane) to give the tetracyclic product 16T (79 mg, 77%) as a yellow amorphous: IR (KBr disk, cm⁻¹) 3449, 2964, 1709, 1448, 1369; ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.51 (dd, J = 7.6, 7.6 Hz, 2H), 7.41-7.36 (m, 3H), 7.31 (dd, J = 7.3 Hz, 1H), 7.17 (dd, J = 7.6, 7.6 Hz, 1H), 7.00 (dd, J = 7.8, 7.8 Hz, 2H), 6.89 (brs, 1H), 6.53 (d, J = 2.7 Hz, 1H), 5.14 (dd, J = 2.5, 2.5 Hz, 1H), 4.89-4.86 (m, 1H), 4.73 (d, J = 5.3 Hz, 1H), 4.23 (brs, 1H), 3.20-3.11 (m, 2H), 2.98 (qq, J = 6.9, 6.9 Hz, 1H), 2.86-2.83 (m, 1H), 1.55-1.47 (m, 2H), 1.44 (s, 9H), 1.01 (d, J = 6.9 Hz, 3H), 0.82 (t, J = 7.6 Hz, 3H), 0.58 (d, J = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.3, 147.9, 143.2, 141.5, 139.1, 137.9, 136.0, 134.9, 134.1, 129.7, 129.3, 129.0, 128.8, 126.1, 124.9, 124.2, 123.5, 121.8, 120.7, 115.5, 113.8, 91.3, 80.7, 75.7, 75.3, 55.3, 39.3, 35.9, 28.0, 26.7, 23.5, 23.0; ESI-HRMS m/z calcd for C₃₈H₄₂N₂NaO₃S [M + Na]^+ 661.2712, found 661.2729.

One-pot reaction by using (a), 15 and 17. To a suspension of the vinyl iodide 15 (100 mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added cis-1-amino-7-isopropylindan-2-ol (a) (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 °C for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 µmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 µmol) at 80 °C, and the mixture was stirred for 10 min at this temperature then vinyl stannane 17 (377 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 2.5 h, cooled to room temperature, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the tetracyclic product 17T (174 mg, 83%) as a yellow amorphous: IR (KBr disk, cm⁻¹) 3449, 2964,
1709, 1369, 1174; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.01 (d, \(J = 8.5\) Hz, 1H), 7.82 (d, \(J = 8.5\) Hz, 2H), 7.65 (s, 1H), 7.64 (d, \(J = 9.4\) Hz, 1H), 7.34 (td, \(J = 8.5, 1.0\) Hz, 1H), 7.24-7.20 (m, 3H), 7.14 (t, \(J = 7.5\) Hz, 1H), 6.98 (d, \(J = 7.0\)Hz, 1H), 6.92 (d, \(J = 7.5\)Hz, 1H), 6.68 (d, \(J = 2.0\) Hz, 1H), 4.97 (td, \(J = 5.0, 2.0\) Hz, 1H), 4.93 (d, \(J = 5.6\) Hz, 1H), 4.33 (t, \(J = 2.5\) Hz, 1H), 4.27 (d, \(J = 0.5\) Hz, 1H), 3.20 (m, 2H), 2.83-2.81 (m, 1H), 2.65 (sep, \(J = 7.0\) Hz, 1H), 2.31 (s, 3H), 1.70-1.55 (m, 2H), 1.45 (s, 9H), 0.88 (t, \(J = 7.5\) Hz, 3H), 0.63 (d, \(J = 7.0\) Hz, 3H), 0.15 (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.3, 161.3, 148.5, 147.2, 143.2, 136.5, 136.1, 135.3, 129.8, 128.7, 123.8, 122.7, 121.7, 90.9, 80.6, 75.0, 74.9, 65.6, 39.4, 36.0, 28.1, 28.0, 27.0, 23.5, 22.9, 11.7; ESI-HRMS m/z calcd for C\(_{39}\)H\(_{44}\)N\(_2\)O\(_5\)S \([\text{M} + \text{Na}]^+\) 675.2869, found 675.2848.

**One-pot reaction by using (a), 15 and 18.** To a suspension of the vinyl iodide 15 (100 mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added cis-1-amino-7-isopropylinden-2-ol (a) (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 °C for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 µmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 µmol) at 80 °C, and the mixture was stirred for 10 min at this temperature then vinyl stannane 18 (253 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 1 h, cooled to room temperature, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to gave the tetracyclic product 18T (94 mg, 63%) as a yellow amorphous: IR (KBr disk, cm\(^{-1}\)) 3416, 2964, 1668, 1591, 1473; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.56-8.54 (m, 1H), 7.76 (dt, \(J = 7.5, 1.5\) Hz, 1H), 7.52 (dt, \(J = 7.5, 1.0\)Hz, 1H), 7.28-7.25 (m, 1H), 7.16 (t, \(J = 7.5\)Hz, 1H), 6.99 (dd, \(J = 7.5, 7.5\) Hz, 2H), 6.76 (d, \(J = 2.5\) Hz, 1H), 5.09 (d, \(J = 5.5\) Hz, 1H), 4.98-4.95 (m, 1H), 4.38 (t, \(J = 3.0\) Hz, 1H), 4.25 (d, \(J = 1.0\) Hz, 1H), 3.17-3.16 (m, 2H), 2.89-2.88 (m, 1H), 2.57 (sep, \(J = 7.0\) Hz, 1H), 1.62-1.52 (m, 2H), 0.98 (d, \(J = 7.0\) Hz, 3H), 0.84 (t, \(J = 7.5\) Hz, 3H), 0.67 (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.3, 161.3, 148.5, 147.2, 143.2, 136.5, 136.1, 135.3, 129.8, 128.7, 123.8, 122.7, 121.7, 90.9, 80.6, 75.0, 74.9, 65.6, 39.4, 36.0, 28.1, 28.0, 27.0, 23.5, 22.9, 11.7; ESI-HRMS m/z calcd for C\(_{39}\)H\(_{44}\)N\(_2\)O\(_5\)S \([\text{M} + \text{Na}]^+\) 461.2804, found 461.2798.
One-pot reaction by using (a), 15 and 19. To a suspension of the vinyl iodide 15 (100 mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added cis-1-amino-7-isopropylindan-2-ol (a) (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 °C for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 µmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 µmol) at 80 °C, and the mixture was stirred for 10 min at this temperature then vinyl stannane 19 (253 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 4 h, cooled to room temperature, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the tetracyclic product 19T (130 mg, 88%) as a yellow amorphous: IR (KBr disk, cm⁻¹) 3449, 2964, 1709, 1255, 1163; ¹H NMR (400 MHz, CDCl₃) δ 8.66 (d, J = 2.0 Hz, 1H), 8.61 (dd, J = 5.0, 1.5 Hz, 1H), 7.77 (dt, J = 7.5, 2.0 Hz, 1H), 7.35 (dd, J = 8.0, 5.0 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.59 (d, J = 2.5 Hz, 1H), 4.96-4.93 (m, 2H), 4.81 (d, J = 5.0 Hz, 1H), 4.25 (d, J = 1.0 Hz, 1H), 4.13 (brt, J = 3.0 Hz, 1H), 3.19-3.18 (m, 2H), 2.89-2.86 (m, 1H), 2.58 (sep, J = 7.0 Hz, 1H), 1.64-1.53 (m, 2H), 1.02 (d, J = 7.0 Hz, 3H), 0.85 (t, J = 7.5 Hz, 3H), 0.64 (d, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.1, 150.1, 149.4, 147.4, 136.9, 136.8, 135.6, 130.0, 128.9, 123.5, 123.3, 121.7, 90.9, 80.8, 74.8, 74.8, 61.2, 39.4, 36.0, 28.1, 28.0, 27.0, 23.4, 22.7, 11.7; ESI-HRMS m/z calcd for C₂₉H₃₇N₂O₃ [M + H]⁺ 461.2804, found 461.2797.

One-pot reaction by using (a), 15 and 20. To a suspension of the vinyl iodide 15 (100 mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added cis-1-amino-7-isopropylindan-2-ol (a) (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 °C for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 µmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 µmol) at 80 °C, and the mixture was stirred for 10 min at this temperature then vinyl stannane 20 (285 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 4.5 h, cooled to room temperature, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the tetracyclic product 20T (133 mg, 81%) as a yellow amorphous: IR (KBr disk, cm⁻¹) 3449, 2964,
One-pot reaction by using (a), 15 and 21. To a suspension of the vinyl iodide 15 (100 mg, 0.322 mmol) and molecular sieve 5 Å (483 mg) in Dioxane (3 mL) was added 
cis-1-amo-7-isopropylindan-2-ol (a) (62 mg, 0.322 mmol) at room temperature,
and the mixture was stirred at 80 °C for 30 min. Then to this solution was added lithium
chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 µmol) and
Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 µmol) at 80 °C, and the
mixture was stirred for 10 min at this temperature then vinyl stannane 21 (257 mg, 0.644 mmol)
in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred
under reflux for 4 h, cooled to room temperature, filtered and concentrated in vacuo.
The residue was purified by column chromatography on silica gel to gave the
tetracyclic product 21T (109 mg, 73%) as a yellow amorphous: IR (KBr disk, cm⁻¹) 3449, 2964,
1709, 1253, 1167 ; ¹H NMR (400 MHz, CDCl₃) δ 9.00 (d, J = 2.5 Hz, 1H), 8.19 (d, J
= 1.5 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.75 (dt, J = 7.0, 1.5
Hz, 1H), 7.59 (dt, J = 8.0, 1.0Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.98 (t, J = 6.5 Hz, 2H),
6.69 (d, J = 3.0 Hz, 1H), 5.02-4.99 (m, 1H), 4.88 (d, J = 5.5 Hz, 1H), 4.33 (t, J = 3.0 Hz,
1H), 4.31 (s, 1H), 3.22-3.21 (m, 1H), 2.94 (m, 1H), 2.55 (sep, J = 7.0 Hz, 1H),
1.67-1.61 (m, 2H), 1.01(d, J = 7.0 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H), 0.35 (d, J = 7.0 Hz,
3H) ; ¹³C NMR (100 MHz, CDCl₃) δ 165.3, 147.7, 143.0, 142.2, 136.6, 136.1, 129.0,
128.7, 128.0, 125.8, 123.5, 122.9, 121.6, 91.1, 80.5, 74.9, 74.6, 58.6, 39.5, 35.9, 28.0,
26.8, 23.6, 23.0, 11.5 ; ESI-HRMS m/z calcd for C₃₃H₃₅N₂O₃ [M + H]^+ 511.2961, found
511.2953.

One-pot reaction by using (a), 15 and 6. To a suspension of the vinyl iodide 15 (100
mg, 0.322 mmol) and molecular sieve 5 Å (483 mg) in Dioxane (3 mL) was added

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mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added cis-1-amino-7-isopropylindan-2-ol (a) (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 °C for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 µmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 µmol) at 80 °C, and the mixture was stirred for 10 min at this temperature then vinyl stannane 6 (253 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 4 h, cooled to room temperature, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the tetracyclic product 22T (120 mg, 81%) as a yellow amorphous: IR (KBr disk, cm⁻¹) 3462, 2928, 1664, 1454, 1369; ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.33 (m, 5H), 7.18 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.69 (d, J = 2.5 Hz, 1H), 4.97-4.93 (m, 1H), 4.89 (d, J = 5.0 Hz, 1H), 4.26 (s, 1H), 4.10 (t, J = 2.0 Hz, 1H), 3.20-3.19 (m, 2H), 2.88 (m, 1H), 2.68 (sep, J = 7.0 Hz, 1H), 1.65-1.55 (m, 2H), 1.47 (s, 9H), 1.02 (d, J = 7.0 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H), 0.63 (d, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.4, 147.7, 143.0, 141.2, 137.1, 136.1, 129.2, 128.9, 128.7, 128.3, 127.8, 123.5, 121.6, 91.1, 80.4, 74.7, 74.7, 63.6, 39.5, 36.0, 28.0, 27.8, 27.1, 23.5, 22.8, 11.7; ESI-HRMS m/z calcd for C₃₀H₃₇NNaO₃ [M + Na]⁺ 482.2695, found 482.2671.

One-pot reaction by using (a), 15 and 23. To a suspension of the vinyl iodide 15 (100 mg, 0.322 mmol) and molecular sieve 5Å (483 mg) in Dioxane (3 mL) was added cis-1-amino-7-isopropylindan-2-ol (a) (62 mg, 0.322 mmol) at room temperature, and the mixture was stirred at 80 °C for 30 min. Then to this solution was added lithium chloride (27 mg, 0.644 mmol), Tri(2-furyl)phosphine (6 mg, 25 µmol) and Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 6 µmol) at 80 °C, and the mixture was stirred for 10 min at this temperature then vinyl stannane 6 (253 mg, 0.644 mmol) in Dioxane (3 mL) was added to this suspension. After the reaction mixture was stirred under reflux for 1.5 h, cooled to room temperature, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the tetracyclic product 23T (118 mg, 66%) as a yellow amorphous: IR (KBr disk, cm⁻¹) 3508, 2959, 2858, 1711, 1253; ¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.61 (d, J = 3.0 Hz, 1H), 5.85 (dt, J = 15.0, 4.5 Hz,
1H), 5.72 (ddt, J = 15.0, 9.0, 1.5 Hz, 1H), 4.88 (d, J = 5.0 Hz, 1H), 4.79-4.77 (m, 1H), 4.25 (dd, J = 5.0, 1.5 Hz, 2H), 4.14 (d, J = 1.0 Hz, 1H), 3.63-3.56 (m, 2H), 3.15 (m, 1H), 2.82-2.80 (m, 1H), 1.25 (m, 1H), 1.21 (d, J = 7.0 Hz, 3H), 0.15 (d, J = 7.0 Hz, 3H), 0.93 (s, 9H), 0.74 (t, J = 7.5 Hz, 3H), 0.10 (s, 6H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.4, 147.6, 143.1, 136.9, 132.4, 130.0, 129.2, 128.7, 123.5, 121.7, 91.0, 80.4, 74.4, 74.7, 63.0, 61.6, 39.4, 35.8, 28.4, 26.4, 25.9, 23.5, 23.5, 11.1, -5.2, -5.2; ESI-HRMS m/z calcd for C$_{33}$H$_{52}$NO$_4$Si [M + H]$^+$ 554.3666, found 554.3652.

4-Hydroxymethyl-2-(N-benzensulfonylindol-2-yl)-1,2,5,6-tetrahydropyridine 16P:

To a solution of compound 16T (22 mg, 34.4 µmol) in CH$_2$Cl$_2$ (3 mL) was slowly added diisobutylaluminium hydride (0.44 mL, 0.44 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 30 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 30 min. The organic layers were extracted with ethyl acetate, washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (20% to 50% ethyl acetate in hexane) gave the diol (15 mg, 76%).

To a solution of diol obtained above (15 mg, 26.3 µmol) in CHCl$_3$ (2 mL) was added n-propylamine (22 µL, 0.263 mmol) and lead tetraacetate (70 mg, 0.158 mmol) at -50 °C. After the mixture was stirred at this temperature for 43 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (from 0% to 5% methanol in chloroform containing 0.5% triethylamine) gave the 16P (8 mg, 77%) as a pale yellow amorphous: IR (thin film) 3339, 2963, 2929, 2874, 1655, 1449, 1368, 1173, 1092, 1046 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.16 (d, J = 8.0 Hz, 1H), 7.74-7.77 (m, 2H), 7.50 (td, J = 7.5, 1.5 Hz, 1H), 7.19-7.44 (m, 5H), 6.49 (s, 1H), 5.79 (d, J = 2.5 Hz, 1H), 5.11 (s, 1H), 4.74 (s, 1H), 4.19 (d, J = 14.0 Hz, 1H), 4.13 (d, J = 14.0 Hz, 1H), 2.95 (dd, J = 12.0, 5.0 Hz, 1H), 2.66 (dd, J = 12.0, 8.0 Hz, 1H), 2.20 (m, 1H), 1.60-1.70 (m, 1H), 1.28-1.41 (m, 1H), 0.87 (t, J = 7.5 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 142.7, 141.1, 138.8, 137.6, 133.8, 129.7, 129.3, 129.0, 128.5, 126.2, 124.9, 123.8, 121.7, 120.9, 115.0, 64.6, 50.5, 43.0, 36.7, 23.5, 11.3; ESI-HRMS m/z calcd for C$_{22}$H$_{25}$N$_2$O$_3$S (M + H)$^+$ 397.1586, found 397.1587
4-Hydroxymethyl-2-(N-p-toluenesulfonylindol-3-yl)-1,2,5,6-tetrahydropyridine

17P: To a solution of compound 17T (30 mg, 46.0 µmol) in CH₂Cl₂ (3 mL) was slowly added diisobutylaluminium hydride (0.46 mL, 0.46 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 40 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 1 h. The organic layers were extracted with ethyl acetate, washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (20% to 50% ethyl acetate in hexane) gave the diol (19 mg, 79%).

To a solution of diol obtained above (12 mg, 20.5 µmol) in CHCl₃ (1.8 mL) was added n-propylamine (25 µL, 0.308 mmol) and lead tetraacetate (82 mg, 0.185 mmol) at –50 °C. After the mixture was stirred at this temperature for 42 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (from 0% to 5% methanol in chloroform containing 0.5% triethylamine) gave the 17P (7 mg, 83%) as a pale yellow amorphous: IR (thin film) 3318, 2965, 2932, 2874, 1655, 1447, 1373, 1175, 1125, 1096 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.95 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.41 (s, 1H), 7.17-7.33 (m, 5H), 5.81 (s, 1H), 4.73 (s, 1H), 4.18 (d, J = 13.0 Hz, 1H), 4.12 (d, J = 13.0 Hz, 1H), 2.88-2.98 (m, 2H), 2.32 (s, 3H), 2.11 (m, 1H), 1.62-1.75 (m, 1H), 1.45-1.57 (m, 1H), 0.94 (t, J = 7.0 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 144.9, 141.7, 135.6, 135.2, 129.8, 129.5, 126.8, 124.8, 124.1, 124.0, 123.4, 123.2, 120.1, 113.8, 65.0, 50.6, 44.6, 36.4, 23.9, 21.5, 11.9; ESI-HRMS m/z calcd for C₂₃H₂₇N₂O₅S (M + H)⁺ 411.1742, found 411.1755

4-Hydroxymethyl-2-(2-pyridyl)-1,2,5,6-tetrahydropyridine 18P: To a solution of compound 18T (35 mg, 76.0 µmol) in CH₂Cl₂ (4 mL) was slowly added diisobutylaluminium hydride (0.76 mL, 0.76 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 50 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 33 min. The organic layers were extracted...
with ethyl acetate, washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (67% to 100% ethyl acetate in hexane and then 17% methanol in chloroform) gave the diol (21 mg, 70%).

To a solution of diol obtained above (18 mg, 45.9 µmol) in CHCl₃ (3.0 mL) was added n-propylamine (57 µL, 0.688 mmol) and lead tetraacetate (122 mg, 0.275 mmol) at −50 °C. After the mixture was stirred at this temperature for 50 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (from 0% to 33% methanol in chloroform containing 0.5% triethylamine) gave the 18P (6 mg, 60%) as a yellow amorphous: IR (thin film) 3373, 2965, 2926, 1655, 1590, 1460, 1437, 1380, 1050 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.52 (d, J = 4.5 Hz, 1H), 7.64 (td, J = 7.5, 2.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.16 (dd, J = 7.5, 4.5 Hz, 1H), 5.80 (s, 1H), 4.68 (s, 1H), 4.14 (d, J = 13.0 Hz, 1H), 4.09 (d, J = 13.0 Hz, 1H), 3.07 (dd, J = 12.5, 3.0 Hz, 1H), 3.02 (dd, J = 12.5, 4.0 Hz, 1H), 2.07 (m, 1H), 1.48-1.71 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 149.2, 141.6, 136.9, 122.5, 122.4 122.0, 65.0, 59.2, 44.3, 35.9, 24.3, 12.1; ESI-HRMS m/z calcd for C₁₃H₁₉N₂O (M + H)+ 219.1497, found 219.1499

4-Hydroxymethyl-2-(3-pyridyl)-1,2,5,6-tetrahydropyridine 19P: To a solution of compound 19T (33 mg, 71.6 µmol) in CH₂Cl₂ (4 mL) was slowly added diisobutylaluminium hydride (0.716 mL, 0.716 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 30 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 34 min. The organic layers were extracted with ethyl acetate, washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (50% to 100% ethyl acetate in hexane) gave the diol (22 mg, 78%).

To a solution of diol obtained above (12 mg, 30.6 µmol) in CHCl₃ (2.5 mL) was added n-propylamine (25 µL, 0.306 mmol) and lead tetraacetate (81 mg, 0.183 mmol) at −50 °C. After the mixture was stirred at this temperature for 23 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The
organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (from 0% to 9% methanol in chloroform containing 0.5% triethylamine) gave the 19P (5 mg, 75%) as a pale yellow amorphous: IR (thin film) 3350, 2963, 2928, 1458, 1428, 1217, 1030, 874 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.58 (s, 1H), 8.49 (brs, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.23-7.27 (m, 1H), 5.67 (s, 1H), 4.62 (s, 1H), 4.11-4.19 (m, 2H), 3.01 (d, J = 4.0 Hz, 2H), 2.14 (m, 1H), 1.52-1.73 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 149.7, 149.2, 142.4, 136.9, 136.2, 123.6, 121.9, 64.5, 55.8, 43.9, 35.8, 24.1, 11.9; ESI-HRMS m/z calcd for C₁₃H₁₉N₂O (M + H)+ 219.1497, found 219.1487

4-Hydroxymethyl-2-(3-quinolyl)-1,2,5,6-tetrahydropyridine 20P: To a solution of compound 20T (28 mg, 54.8 µmol) in CH₂Cl₂ (4 mL) was slowly added diisobutylaluminium hydride (0.548 mL, 0.548 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 30 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 45 min. The organic layers were extracted with ethyl acetate, washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (33% to 100% ethyl acetate in hexane) gave the diol (20 mg, 82%).

To a solution of diol obtained above (20 mg, 45.2 µmol) in CHCl₃ (3 mL) was added n-propylamine (37 µL, 0.451 mmol) and lead tetraacetate (120 mg, 0.271 mmol) at –50 °C. After the mixture was stirred at this temperature for 40 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (from 0% to 17% methanol in chloroform containing 0.5% triethylamine) gave the 20P (8 mg, 66%) as a yellow amorphous: IR (thin film) 3390, 2965, 2928, 1622, 1499, 1462, 1379, 1217, 1046 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.89 (d, J = 2.0 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 2.0 Hz, 1H), 7.77 (dd, J = 8.0, 1.0 Hz, 1H), 7.66 (td, J = 8.5, 1.5 Hz, 1H), 7.51 (td, J = 8.0, 1.0 Hz, 1H), 5.73 (s, 1H), 4.68 (s, 1H), 4.12-4.21 (m, 2H), 3.07 (dd, J = 12.5, 3.0 Hz, 1H), 3.00 (dd, J = 12.5, 4.5 Hz, 1H) 2.05 (m, 1H), 1.60-1.70 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 151.4, 147.6,
4-Hydroxymethyl-2-(3-thienyl)-1,2,5,6-tetrahydropyridine 21P : To a solution of compound 21T (35 mg, 75.2 µmol) in CH₂Cl₂ (4 mL) was slowly added diisobutylaluminium hydride (0.752 mL, 0.752 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 31 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 36 min. The organic layers were extracted with ethyl acetate, washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (25% to 40% ethyl acetate in hexane) gave the diol (23 mg, 77%).

To a solution of diol obtained above (21 mg, 52.8 µmol) in CHCl₃ (3.5 mL) was added n-propylamine (43 µL, 0.528 mmol) and lead tetraacetate (141 mg, 0.317 mmol) at -50 °C. After the mixture was stirred at this temperature for 20 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (from 0% to 9% methanol in chloroform containing 0.5% triethylamine) gave the 21P (9 mg, 76%) as a yellow amorphous: IR (thin film) 3384, 2963, 2928, 1649, 1458, 1217, 1046, 857 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.26 (dd, J = 5.0, 3.0 Hz, 1H), 7.12 (d, J = 3.0 Hz, 1H), 7.05 (d, J = 5.0 Hz, 1H), 5.77 (s, 1H), 4.59 (s, 1H), 4.14 (d, J = 13.5 Hz, 1H), 4.08 (d, J = 13.5 Hz, 1H), 2.90-3.00 (m, 2H), 2.06 (m, 1H), 1.58-1.69 (m, 1H), 1.40-1.53 (m, 1H), 0.93 (t, J = 7.5 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 144.0, 141.1, 128.5, 127.1, 126.0, 124.4, 121.9, 65.0, 53.8, 44.5, 36.1, 24.2, 12.0; ESI-HRMS m/z calcd for C₁₇H₂₁N₂O (M + H)⁺ 269.1654, found 269.1659

4-Hydroxymethyl-2-phenyl-1,2,5,6-tetrahydropyridine 22P: To a solution of compound 22T (65 mg, 0.141 mmol) in CH₂Cl₂ (5 mL) was slowly added diisobutylaluminium hydride (1.13 mL, 1.13 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 34 min, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 30 min. The organic layers were extracted
with ethyl acetate, washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (17% to 25% ethyl acetate in hexane) gave the diol (45 mg, 81%).

To a solution of diol obtained above (19 mg, 39.1 µmol) in CHCl$_3$ (3 mL) was added $n$-propylamine (48 µL, 0.587 mmol) and lead tetraacetate (104 mg, 0.235 mmol) at –50 °C. After the mixture was stirred at this temperature for 30 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (from 0% to 9% methanol in chloroform containing 0.5% triethylamine) gave the diol (9 mg, 86%) as a pale yellow amorphous: IR (thin film) 3377, 2961, 1637, 1491, 1217, 1121, 1028, 874 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.14-7.26 (m, 5H), 5.60 (s, 1H), 4.39 (s, 1H), 4.07 (d, $J=13.0$ Hz, 1H), 4.01 (d, $J=13.0$ Hz, 1H), 2.96 (dd, $J=12.0$, 2.5 Hz, 1H), 2.87 (dd, $J=12.0$, 4.0 Hz, 1H), 1.95 (m, 1H), 1.42-1.64 (m, 2H), 0.89 (t, $J=7.5$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 143.5, 141.1, 128.5, 127.7, 127.4, 125.2, 65.2, 58.9, 45.1, 36.3, 24.5, 12.3; ESI-HRMS m/z calcd for C$_{14}$H$_{20}$NO (M + H)$^+$ 218.1545, found 218.1539.

**4-Hydroxymethyl-2-(3-tert-butyldimethylsilyloxy)prop-1-enyl-1,2,5,6-tetrahydropyridine (23P):** To a solution of compound 23T (31 mg, 56.0 µmol) in CH$_2$Cl$_2$ (3 mL) was slowly added diisobutylaluminium hydride (0.560 mL, 0.560 mmol, 1M in toluene) at -78 °C. After the mixture was stirred at this temperature for 1 h, quenched with ethyl acetate and saturated aqueous potassium sodium tartrate tetrahydrate solution, and the resulting mixture was stirred at room temperature for 33 min. The organic layers were extracted with ethyl acetate, washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel (17% to 33% ethyl acetate in hexane) gave the diol (19 mg, 70%).

To a solution of diol obtained above (15 mg, 30.9 µmol) in CHCl$_3$ (2.5 mL) was added $n$-propylamine (38 µL, 0.463 mmol) and lead tetraacetate (82 mg, 0.185 mmol) at –50 °C. After the mixture was stirred at this temperature for 28 min, added to ice-1N aqueous NaOH solution and the resulting mixture was extracted with chloroform. The organic layers were combined, washed with brine, dried over MgSO$_4$, filtered, and concentrated in vacuo to give the crude products. Column chromatography on silica gel...
(from 0% to 17% methanol in chloroform containing 0.5% triethylamine) gave the 23P (7 mg, 73%) as a brown amorphous: IR (thin film) 3423, 2959, 2930, 2855, 1671, 1472, 1256, 1123, 837 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 5.64-5.76 (m, 2H), 5.62 (s, 1H), 3.96-4.15 (m, 5H), 2.72-3.13 (m, 2H), 2.12 (m, 1H), 1.54-1.65 (m, 1H), 1.34-1.44 (m, 1H), 0.90 (t, J = 7.5 Hz, 3H), 0.88 (s, 9H), 0.041 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 141.1, 133.0, 129.3, 123.2, 64.7, 63.2, 54.7, 43.3, 35.5, 29.7, 25.9, 23.6, 18.4, 11.4, -5.2; ESI-HRMS m/z calcd for C₁₇H₃₄NO₂Si (M + H)⁺ 312.2359, found 312.2347