Supporting Information

Photochemically Induced Coupling Reaction of C(sp³)–H Bonds and 4-Cyanopyridine
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General Information
All reactions sensitive to air or moisture were carried out under argon atmosphere and anhydrous conditions unless otherwise noted. Reagents were used as supplied unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed using E. Merck Silica gel 60 F254 pre-coated plates. Flash column chromatography was generally performed using 40-50 μm Silicagel 60N (Kanto) or 75 μm Activated Alumina (Wako). ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-ECX-500 (500 MHz), JNM-ECA-500 (500 MHz), or a JNM-ECS-400 (400 MHz) spectrometer. Chemical shifts are reported in δ (ppm) with reference to residual solvent signals [¹H-NMR: CDCl₃ (7.26); ¹³C-NMR: CDCl₃ (77.0)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. ESI-TOF mass spectra were recorded on a BRUKER DALTONICS micrOTOF II or JEOL JMS-T100LP instrument (HRMS). UV irradiation was carried out by using a Riko 100 W medium-pressure mercury lamp.

Procedure for Photochemically-Induced Coupling Reaction with 4-Cyanopyridine
To a MeCN/H₂O (2:1, 0.04 M) solution of 4-cyanopyridine 2 (16.3 mg, 157 μmol) in a test tube were added benzophenone (14.3 mg, 78.5 μmol) and cumene 1a (44 μL, 313 μmol) at room temperature. The mixture was degassed by freeze-thaw procedure for 3 times. The test tube was placed at 5 cm distance from a UV-lamp and irradiated with a Riko 100 W medium-pressure mercury lamp at room temperature for 12 h. Then, the reaction mixture was treated with saturated aqueous sodium bicarbonate. The mixture was extracted with AcOEt (20 mL x 3), washed with brine, dried over Na₂SO₄, and concentrated. The analysis of crude's ¹H NMR chart indicated that the desired product 3a was formed in 92% yield along with the formation of α,α-diphenyl-4-pyridylmethanol 4 in 7% yield. The residue was purified with flash column chromatography (hexane/AcOEt 5:1) to give the
pyridine derivative 3a in 90% yield (27.7 mg).

**Procedure for Photochemically-Induced Coupling Reaction on a Gram Scale**

To a MeCN/H2O (2:1, 0.4 M) solution of 4-cyanopyridine \(2\) (1.03 g, 9.89 mmol) in a 50 mL flask were added benzophenone (180 mg, 0.989 mmol) and cumene \(1a\) (2.76 mL, 19.8 mmol) at room temperature. The mixture was degassed by freeze-thaw procedure for 3 times. The flask was placed at 5 cm distance from a UV-lamp and irradiated with a Riko 100 W medium-pressure mercury lamp at room temperature for 160 h. Then, the reaction mixture was treated with saturated aqueous sodium bicarbonate. The mixture was extracted with AcOEt (40 mL x 3), washed with brine, dried over Na2SO4, and concentrated. The residue was purified with flash column chromatography (hexane/AcOEt 5:1) to give the pyridine derivative 3a in 78% yield (1.52 g) along with the recovery of 4-cyanopyridine \(2\) in 10% yield (100 mg).

**Analytical Data**

**4-(2-phenylpropan-2-yl)pyridine (3a):**
90% yield (27.7 mg); colorless oil; IR (neat) 1596, 1491, 1410, 765, 700 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.68 (6H, s), 7.13 (2H, dd, \(J = 1.4, 4.6\) Hz), 7.29 (2H, m), 8.48 (2H, d, \(J = 6.0\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 29.9, 42.8, 122.1, 126.2, 126.6, 148.6, 149.5, 159.6; HRMS (ESI-TOF) calcd for C\(_{14}\)H\(_{16}\)N (M+H\(^+\)) 198.1277, found 198.1301.

**4-(1-phenylbutyl)pyridine (3b):**
72% yield (23.8 mg); colorless oil; IR (neat) 1596, 1494, 1452, 1414, 743, 700 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.93 (3H, t, \(J = 7.4\) Hz), 1.28 (2H, m), 3.88 (1H, t, \(J = 7.8\) Hz), 7.15 (2H, dd, \(J = 1.4, 4.6\) Hz), 7.18-7.24 (3H, m), 8.47 (2H, d, \(J = 6.0\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 13.9, 20.9, 37.1, 50.5, 123.3, 126.6, 127.9, 128.6, 143.3, 149.7, 154.2; HRMS (ESI-TOF) calcd for C\(_{15}\)H\(_{18}\)N (M+H\(^+\)) 212.1434, found 212.1435.

**4-(1-(4-methoxyphenyl)butyl)pyridine (3c):**
83% yield (29.4 mg); colorless oil; IR (neat) 1598, 1511, 1462, 1415, 1249, 1035, 824 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.92 (3H, t, \(J = 7.3\) Hz), 1.26 (2H, m), 1.98 (2H, m), 3.77 (3H, s), 3.83 (1H, t, \(J = 7.8\) Hz), 6.83 (2H, dd, \(J = 2.3, 6.4\) Hz), 7.10-7.15 (4H, m), 8.46 (2H, dd, \(J = 1.6, 4.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 13.9, 20.9, 37.2, 49.6, 55.2, 113.9, 123.1, 128.7, 135.3, 149.6, 154.7, 158.2; HRMS (ESI-TOF) calcd for C\(_{16}\)H\(_{20}\)NO (M+H\(^+\)) 242.1539, found 242.1537.
4-(1-(pyridin-4-yl)butyl)phenyl acetate (3d):
71% yield (35.7 mg); colorless oil; IR (neat) 1761, 1597, 1504, 1415, 1201, 824 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.91 (3H, t, J = 7.3 Hz), 1.26 (2H, m), 1.98 (2H, q, J = 7.8 Hz), 2.27 (3H, s), 3.87 (1H, t, J = 7.8 Hz), 7.01 (2H, dd, J = 2.3, 6.9 Hz), 7.13 (2H, dd, J = 1.4, 4.6 Hz), 7.20 (2H, dd, J = 2.3, 6.9 Hz), 8.48 (2H, dd, J = 1.4, 4.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 20.8, 21.1, 37.1, 49.8, 121.6, 123.2, 128.7, 140.8, 149.2, 149.8, 153.8, 169.4; HRMS (ESI-TOF) calcd for C₁₇H₂₀NO₂ (M+H)⁺ 270.1489, found 270.1484.

N-(4-(1-(pyridin-4-yl)butyl)phenyl)acetamide (3e):
63% yield (28.1 mg); colorless oil; IR (neat) 3254, 1668, 1602, 1538, 1513, 1413, 1296 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (3H, t, J = 7.3 Hz), 1.26 (2H, m), 1.98 (2H, q, J = 7.8 Hz), 2.15 (3H, s), 3.86 (1H, t, J = 7.8 Hz), 7.10-7.20 (4H, m), 7.35 (1H, brs), 7.43 (2H, d, J = 8.2 Hz), 8.48 (2H, d, J = 5.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 20.8, 24.4, 37.0, 49.8, 120.2, 123.3, 128.3, 136.6, 138.9, 149.4, 154.5, 168.5; HRMS (ESI-TOF) calcd for C₁₇H₂₁N₂O (M+H)⁺ 269.1648, found 269.1633.

Methyl 4-(1-(pyridin-4-yl)butyl)benzoate (3f):
65% yield (27.6 mg); colorless oil; IR (neat) 1721, 1596, 1436, 1415, 1281, 1112 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.93 (3H, t, J = 7.8 Hz), 1.27 (2H, sextet, J = 7.8 Hz), 2.02 (2H, q, J = 7.8 Hz), 3.89 (3H, s), 3.94 (1H, t, J = 7.8 Hz), 7.13 (2H, d, J = 5.8 Hz), 7.27 (2H, d, J = 8.0 Hz), 7.26 (2H, d, J = 8.0 Hz), 8.49 (2H, d, J = 5.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 13.9, 20.9, 36.9, 50.5, 52.1, 123.2, 127.9, 128.7, 130.0, 148.5, 149.8, 153.3, 166.8; HRMS (ESI-TOF) calcd for C₁₇H₂₀NO₂ (M+H)⁺ 270.1489, found 270.1481.

4-(1-(4-bromophenyl)butyl)pyridine (3g):
68% yield (29.7 mg); yellow oil; IR (neat) 1596, 1485, 1412, 1072, 811 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (3H, t, J = 7.3 Hz), 1.27 (2H, sextet, J = 7.8 Hz), 2.02 (2H, q, J = 7.8 Hz), 3.89 (3H, s), 3.94 (1H, t, J = 7.8 Hz), 7.07 (2H, d, J = 8.7 Hz), 7.11 (2H, d, J = 6.0 Hz), 7.41 (2H, d, J = 8.7 Hz), 8.48 (2H, d, J = 6.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 20.9, 36.9, 49.8, 120.5, 123.2, 127.9, 128.7, 130.0, 148.5, 149.8, 153.5; HRMS (ESI-TOF) calcd for C₁₅H₁₇NBr (M+H)⁺ 290.0539, found 290.0532.

4-(1-(4-chlorophenyl)butyl)pyridine (3h):
70% yield (25.1 mg); yellow oil; IR (neat) 1596, 1490, 1462, 1412, 1092, 814 cm⁻¹; ¹H NMR
(400 MHz, CDCl3) δ 0.92 (3H, t, J = 7.3 Hz), 1.26 (2H, m), 1.98 (2H, m), 3.85 (1H, t, J = 7.8 Hz), 7.10-7.15 (4H, m), 7.27 (2H, m), 8.48 (2H, d, J = 1.4, 4.6 Hz); 13C NMR (100 MHz, CDCl3) δ 13.9, 20.8, 37.0, 49.8, 123.1, 128.7, 129.2, 132.4, 141.7, 149.8, 153.6; HRMS (ESI-TOF) calcd for C15H17NCl (M+H)+ 246.1044, found 246.1035.

4-phenyl-4-(pyridin-4-yl)butyl benzoate (3i):
79% yield (38.8 mg); colorless oil; IR (neat) 1715, 1597, 1494, 1452, 1415, 1275, 1117, 713 cm−1; 1H NMR (400 MHz, CDCl3) δ 1.75 (2H, m), 1.27 (2H, m), 3.95 (1H, t, J = 7.8 Hz), 4.33 (2H, dt, J = 0.9, 6.0 Hz), 7.20 (2H, dd, J = 1.4, 4.6 Hz), 7.23 (3H, m), 7.32 (2H, m), 7.44 (2H, t, J = 7.3 Hz), 7.56 (1H, t, J = 7.3 Hz), 8.01 (2H, d, J = 7.3 Hz), 8.50 (2H, dd, J = 1.4, 4.6 Hz); 13C NMR (100 MHz, CDCl3) δ 27.1, 31.3, 50.3, 64.4, 123.1, 126.9, 127.8 128.3, 128.8, 129.5, 130.2, 132.9, 142.5, 149.8, 153.6, 166.5; HRMS (ESI-TOF) calcd for C22H22NO2 (M+H)+ 332.1645, found 332.1629.

methyl 5-phenyl-5-(pyridin-4-yl)pentanoate (3j):
83% yield (28.4 mg); colorless oil; IR (neat) 1735, 1596, 1494, 1452, 1415, 1200, 744, 701 cm−1; 1H NMR (400 MHz, CDCl3) δ 1.59 (2H, m), 2.07 (2H, m), 2.34 (2H, t, J = 7.3 Hz), 3.65 (3H, s), 3.88 (1H, t, J = 7.8 Hz), 7.15 (2H, d, J = 1.8, 4.6 Hz), 7.21 (3H, m), 7.30 (2H, m), 8.47 (2H, d, J = 1.8, 4.6 Hz); 13C NMR (100 MHz, CDCl3) δ 23.2, 33.7, 34.2, 50.6, 51.5, 123.1, 126.8, 127.8, 142.7, 149.8, 153.6, 173.6; HRMS (ESI-TOF) calcd for C17H20NO2 (M+H)+ 270.1489, found 270.1476.

4-(1-(4-bromophenyl)butyl)pyridine (3k):
62% yield (27.8 mg); yellow oil; IR (neat) 1595, 1494, 1452, 1415, 701 cm−1; 1H NMR (400 MHz, CDCl3) δ 1.82 (2H, m), 2.22 (2H, m), 3.40 (2H, t, J = 6.4 Hz), 3.89 (1H, t, J = 7.8 Hz), 7.16 (2H, dd, J = 1.8, 4.6 Hz), 7.22 (3H, m), 7.31 (2H, m), 8.50 (2H, d, J = 1.8, 4.6 Hz); 13C NMR (100 MHz, CDCl3) δ 30.8, 33.3, 33.4, 50.0, 123.0, 126.9, 127.8, 128.8, 142.4, 149.9, 153.4; HRMS (ESI-TOF) calcd for C15H17NBr (M+H)+ 290.0539, found 290.0525.

4-benzylpyridine (3l): [CAS: 2116-65-6]: 51% yield (17.0 mg); colorless oil; 1H NMR (400 MHz, CDCl3) δ 3.97 (2H, s), 7.10 (2H, d, J = 1.8, 4.6 Hz), 7.17 (2H, d, J = 7.3 Hz), 7.25 (1H, t, J = 7.3 Hz). [1] Wu, G. G.; Chen, F. X.; LaFrance, D.; Liu, Z.; Greene, S. G.; Wong, Y.-S.; Xie, J. Org. Lett. 2011, 13, 5220.
$J = 7.8$ Hz), 7.32 (2H, m), 8.49 (2H, dd, $J = 1.8, 4.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 41.2, 124.2, 126.7, 128.7, 129.0, 138.8, 149.7, 150.0.

4-(1-phenylcyclohexyl)pyridine (3m):
50% yield (23.5 mg); colorless oil; IR (neat) 1593, 1494, 1449, 1411, 810, 759, 699 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.45-1.65 (6H, m), 2.20-2.35 (4H, m), 7.15-7.20 (3H, m), 7.25-7.35 (4H, m), 8.47 (2H, d, $J = 6.4$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 22.6, 26.1, 36.3, 46.1, 122.4, 126.0, 127.0, 128.5, 146.5, 149.7, 157.8; HRMS (ESI-TOF) calcd for C$_{17}$H$_{20}$N (M+H)$^+$ 238.1596, found 238.1608.

3-(1-(pyridin-4-yl)ethyl)phenyl acetate (3n):
83% yield (27.3 mg); colorless oil; IR (neat) 1765, 1595, 1486, 1442, 1414, 1203, 826, 801 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.62 (3H, d, $J = 7.3$ Hz), 2.28 (3H, s), 4.12 (1H, q, $J = 7.3$ Hz), 6.90 (1H, s), 6.96 (1H, d, $J = 8.0$ Hz), 7.05 (1H, d, $J = 8.0$ Hz), 7.12 (2H, d, $J = 6.0$ Hz), 7.31, (1H, t, $J = 8.0$ Hz), 8.49 (2H, d, $J = 6.0$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.9, 21.1, 43.9, 119.8, 120.7, 122.9, 125.1, 129.5, 146.0, 149.8, 150.8, 154.5, 169.4; HRMS (ESI-TOF) calcd for C$_{15}$H$_{15}$NO$_2$Na (M+Na)$^+$ 264.0995, found 264.0999.

2-(1-(pyridin-4-yl)ethyl)phenyl acetate (3o):
68% yield (21.9 mg); colorless oil; IR (neat) 1764, 1597, 1488, 1451, 1414, 1201, 829, 755 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.59 (3H, d, $J = 7.3$ Hz), 2.16 (3H, s), 4.23 (1H, q, $J = 7.3$ Hz), 7.04 (1H, dd, $J = 1.4, 7.8$ Hz), 7.09 (2H, dd, $J = 1.8, 4.6$ Hz), 7.20-7.30 (3H, m), 8.47 (2H, dd, $J = 1.8, 4.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.2, 20.8, 38.1, 122.7, 122.8, 126.3, 127.8, 128.3, 135.9, 148.4, 149.6, 154.4, 169.0; HRMS (ESI-TOF) calcd for C$_{15}$H$_{16}$NO$_2$ (M+H)$^+$ 242.1176, found 242.1175.

methyl 2-(4-(2-methyl-1-(pyridin-4-yl)propyl)phenyl)propanoate (3p):
75% yield based on the NMR analysis using CH$_2$Br$_2$ as an internal standard, 9.2 mg (20%) was isolated; colorless oil; IR (neat) 1736, 1595, 1459, 1415, 1210, 1166, 809 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.85 (3H, d, $J = 6.4$ Hz), 0.87 (3H, d, $J = 6.4$ Hz), 1.45 (3H, d, $J = 7.3$ Hz), 2.46 (1H, m), 3.37 (1H, d, $J = 10.5$ Hz), 3.64 (3H, s), 3.67 (1H, q, $J = 7.3$ Hz), 7.20 (6H, m), 8.46 (2H, d, $J = 1.4, 4.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 18.5, 21.5, 21.6, 31.4, 44.9, 52.0, 59.9, 123.5, 127.7, 128.2, 138.7, 141.7, 149.6, 153.8, 175.0; HRMS (ESI-TOF) calcd for C$_{19}$H$_{23}$NO$_2$Na (M+Na)$^+$ 320.1621, found 320.1607.
4-(butoxy(phenyl)methyl)pyridine (3q): 66% yield (28.6 mg); colorless oil; IR (neat) 1596, 1493, 1453, 1412, 1100, 790, 740, 700 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.92 (3H, t, \(J = 7.3\) Hz), 1.42 (2H, m), 1.63 (2H, m), 3.45 (2H, m), 5.29 (1H, s), 7.25-7.35 (7H, m), 8.53 (2H, dd, \(J = 1.4, 4.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 13.9, 19.4, 31.9, 69.1, 82.3, 121.6, 127.1, 128.0, 128.6, 141.0, 149.7, 151.6; HRMS (ESI-TOF) calcd for C\(_{16}\)H\(_{20}\)NO (M+H\(^+\)) 242.1539, found 242.1525.

4-benzhydrylpyridine (3r) [CAS: 3678-72-6]: 87% yield (38.5 mg); colorless solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.51 (1H, s), 7.05 (2H, dd, \(J = 1.4, 4.6\) Hz), 7.09 (4H, m), 7.20-7.35 (6H, m), 8.51 (2H, dd, \(J = 1.4, 4.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 56.2, 124.7, 126.9, 128.6, 129.3, 142.0, 149.6, 152.9.

4-(1,1-diphenylpropyl)pyridine (3s): 74% yield (31.0 mg); colorless oil; IR (neat) 1592, 1493, 1445, 1410, 815, 757, 702 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.78 (3H, t, \(J = 7.3\) Hz), 2.62 (2H, q, \(J = 7.3\) Hz), 7.20-7.35 (12H, m), 8.49 (1H, d, \(J = 8.2\) Hz), 7.11 (2H, dd, \(J = 1.6, 4.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 10.1, 32.1, 56.8, 124.4, 126.3, 128.0, 129.1, 145.5, 149.3, 156.6; HRMS (ESI-TOF) calcd for C\(_{20}\)H\(_{20}\)N (M+H\(^+\)) 274.1590, found 274.1576.

4-(2,3-dihydro-1H-inden-1-yl)pyridine (3t): 89% yield (23.0 mg); colorless oil; IR (neat) 1597, 1478, 1458, 1414, 819, 747 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.04 (1H, ddt, \(J = 8.2, 8.7, 12.8\) Hz), 2.61 (1H, dddd, \(J = 4.6, 8.2, 8.7, 12.8\) Hz), 2.95-3.15 (2H, m), 4.32 (1H, t, \(J = 8.2\) Hz), 6.94 (1H, d, \(J = 7.3\) Hz), 7.11 (2H, dd, \(J = 1.6, 4.6\) Hz), 7.15 (1H, t, \(J = 7.3\) Hz), 7.22 (1H, t, \(J = 7.3\) Hz), 7.31 (1H, d, \(J = 7.3\) Hz), 8.51 (2H, dd, \(J = 1.6, 4.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 31.8, 35.8, 50.8, 123.3, 124.6, 124.7, 126.6, 127.1, 144.3, 144.9, 149.8, 154.3; HRMS (ESI-TOF) calcd for C\(_{14}\)H\(_{14}\)N (M+H\(^+\)) 196.1121, found 196.1127.

4-(1,2,3,4-tetrahydronaphthalen-1-yl)pyridine (3u): 70% yield (28.4 mg); colorless oil; IR (neat) 1596, 1492, 1450, 1412, 815, 743 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.70-1.90 (3H, m), 2.17 (1H, m),

2.80-3.00 (2H, m), 4.12 (1H, dd, $J = 6.0, 6.9$ Hz), 6.78 (1H, d, $J = 7.8$ Hz), 7.02 (2H, dd, $J = 1.8, 4.6$ Hz), 7.06 (1H, dd, $J = 7.3, 7.8$ Hz), 7.16 (2H, d, $J = 7.3$ Hz), 8.49 (2H, dd, $J = 1.8, 4.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.5, 29.5, 32.5, 44.9, 124.1, 125.9, 126.4, 129.2, 130.0, 137.2, 137.6, 149.6, 156.3; HRMS (ESI-TOF) calcd for C$_{15}$H$_{16}$N (M+H)$^+$ 210.1277, found 210.1273.

4-(1,3-dihydroisobenzofuran-1-yl)pyridine (3v):
75% yield (30.3 mg); yellow oil; IR (neat) 1599, 1462, 1414, 1044, 802, 748 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.25 (1H, dd, $J = 1.8, 12.4$ Hz), 5.37 (1H, dd, $J = 2.8, 12.4$ Hz), 6.14 (1H, brs), 7.07 (1H, d, $J = 7.8$ Hz), 7.20-7.35 (5H, m), 8.58 (2H, dd, $J = 1.4, 4.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 73.7, 84.6, 121.16, 121.24, 121.9, 127.7, 128.1, 138.7, 140.4, 150.0, 151.1; HRMS (ESI-TOF) calcd for C$_{13}$H$_{12}$NO (M+H)$^+$ 198.0913, found 198.0908.

tert-butyl 1-(pyridin-4-yl)isoindoline-2-carboxylate (3w):
77% yield (32.0 mg), mixture of two rotamers; amorphous; IR (neat) 1699, 1598, 1475, 1391, 1170, 747 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.24 (45/8H, s), 1.47 (27/8H, s), 4.86 (6/8H, s), 4.91 (10/8H, s), 5.83 (5/8H, s), 5.96 (3/8H, s), 6.97 (5/8H, d, $J = 7.8$ Hz), 7.02 (3/8H, d, $J = 7.8$ Hz), 7.15-7.25 (3H, m), 7.29 (2H, m), 8.54 (2H, d, $J = 5.5$ Hz); Detectable signals of $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 28.1, 28.4, 52.7, 53.0, 66.2, 66.5, 80.4, 121.4, 121.5, 122.7, 123.0, 123.2, 123.3, 127.8, 128.2, 135.7, 140.0, 149.8, 152.9, 154.0; HRMS (ESI-TOF) calcd for C$_{18}$H$_{21}$N$_2$O$_2$ (M+H)$^+$ 297.1598, found 297.1584.

tert-butyl 1-(pyridin-4-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3x):
82% yield (40.3 mg), mixture of two rotamers; colorless oil; IR (neat) 1693, 1595, 1455, 1415, 1166, 750 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.48 (9H, s), 2.75 (1H, brs), 2.93 (1H, brs), 3.27 (1H, ddd, $J = 4.6, 9.6, 13.2$ Hz), 3.89 (1H, ddd, $J = 9.6$ Hz), 4.02 (1H, ddd, $J = 13.2, 16.0$ Hz), 6.12 (1H, d, $J = 6.0$ Hz), 6.34 (1H, brs), 6.42 (1H, brs), 7.08 (1H, brs), 7.13 (2H, d, $J = 6.0$ Hz), 7.17-7.30 (3H, m), 8.51 (2H, d, $J = 6.0$ Hz); Detectable signals of $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 28.3, 28.4, 38.4, 39.4, 56.3, 57.4, 80.5, 122.8, 126.3, 127.5, 128.2, 128.9, 134.1, 135.3, 149.6, 151.8, 154.9; HRMS (ESI-TOF) calcd for C$_{19}$H$_{23}$N$_2$O$_2$ (M+H)$^+$ 311.1754, found 311.1750.

4-(pyridin-4-yl)chroman-2-one (3y):
84% yield (31.3 mg); yellow oil; IR (neat) 1770, 1597, 1486, 1455, 1416, 1216, 824, 759 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.03 (1H, ddd, $J = 6.4, 16.0$ Hz), 3.11 (1H, dd, $J = 6.4, 16.0$ Hz), 4.34 (1H, $t$, $J = 6.4$ Hz), 7.00 (1H, 13N publication not provided.}
d, \( J = 6.8 \text{ Hz} \), 7.05-7.20 (4H, m), 7.35 (1H, m), 8.57 (2H, dd, \( J = 1.4, 4.6 \text{ Hz} \)); \(^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 36.1, 40.1, 117.5, 122.6, 123.7, 124.9, 128.1, 129.5, 149.2, 150.5, 151.7, 166.6; \) HRMS (ESI-TOF) calcd for C\(_{14}\)H\(_{12}\)NO\(_2\) (M+H)\(^+\) 226.0863, found 226.0857.

**4-(pyridin-4-yl)-3,4-dihydroquinolin-2(1H)-one (3z):**

84% yield (29.2 mg); colorless solid; m.p. 210-213 °C; IR (neat) 3208, 1681, 1488, 1417, 825, 756 cm\(^{-1}\); \(^{1}\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 2.90 (1H, dd, \( J = 7.3, 16.5 \text{ Hz} \)), 3.00 (1H, dd, \( J = 6.4, 16.5 \text{ Hz} \)), 4.29 (1H, dd, \( J = 6.4, 7.3 \text{ Hz} \)), 6.90-7.05 (3H, m), 7.13 (2H, d, \( J = 6.0 \text{ Hz} \)), 7.25 (1H, \( t, J = 7.8 \text{ Hz} \)), 8.57 (2H, d, \( J = 6.0 \text{ Hz} \)), 9.11 (1H, brs); \(^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 37.5, 41.3, 116.1, 122.9, 123.6, 124.4, 128.3, 128.7, 137.1, 150.1, 150.7, 170.0; \) HRMS (ESI-TOF) calcd for C\(_{14}\)H\(_{13}\)N\(_2\)O (M+H)\(^+\) 225.1022, found 225.1041.

**Pyridinyl O-acetoxy podocarpic acid methyl ester (3aa):**

71% (45.3 mg); \( \text{3aa-} \alpha / \text{3aa-} \beta = 2:1 \); amorphous.

\(^{1}\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 0.81 (2H, s), 0.86 (2/3H, dt, \( J = 4.6, 13.7 \text{ Hz} \)), 1.05 (2H, s), 1.10 (1/3H, dt, \( J = 4.1, 13.7 \text{ Hz} \)), 1.16 (1H, s), 1.20-1.50 (10/3H, m), 1.62 (2/3H, m), 1.73 (2/3H, dd, \( J = 1.4, 12.4 \text{ Hz} \)), 1.85-2.25 (10/3H, m), 2.27 (1H, s), 2.30 (2H, s), 2.38 (1/3H, dd, \( J = 6.0, 14.2 \text{ Hz} \)), 2.52 (2/3H, ddd, \( J = 6.0, 12.8, 12.8 \text{ Hz} \)), 3.63 (1H, s), 3.65 (2H, s), 3.99 (1/3H, dd, \( J = 6.0, 12.4 \text{ Hz} \)), 4.31 (2/3H, d, \( J = 6.0 \text{ Hz} \)), 6.66 (1/3H, d, \( J = 8.7 \text{ Hz} \)), 6.74 (1/3H, dd, \( J = 2.3, 8.7 \text{ Hz} \)), 6.80-7.00 (8/3H, m), 7.03 (1/3H, d, \( J = 2.3 \text{ Hz} \)), 7.07 (2/3H, d, \( J = 1.8 \text{ Hz} \)), 7.11 (2/3H, dd, \( J = 1.4, 4.6 \text{ Hz} \)), 8.48 (4/3H, d, \( J = 6.0 \text{ Hz} \)), 8.53 (2/3H, d, \( J = 6.0 \text{ Hz} \)); Detectable signals of \(^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 19.7, 19.8, 21.1, 21.2, 22.6, 23.4, 27.9, 28.4, 28.8, 31.5, 37.0, 37.4, 38.8, 38.9, 39.3, 43.1, 43.9, 44.5, 45.9, 48.3, 51.39, 51.44, 51.7, 118.3, 118.8, 119.1, 119.5, 124.07, 124.13, 130.6, 131.6, 131.7, 134.0, 149.4, 149.5, 149.7, 149.9, 150.3, 150.6, 156.2, 156.3, 169.5, 169.6, 177.3, 177.5; \) HRMS (ESI-TOF) calcd for C\(_{25}\)H\(_{30}\)NO\(_4\) (M+H)\(^+\) 408.2169, found 408.2159.

**Preparation of O-pivaloyl totarol (1bb):**

To a solution of (+)-totarol (94.0 mg, 328 \( \mu \text{mol} \)) in pyridine (1.6 mL, 0.2 M) were added pivaloyl chloride (480 \( \mu \text{L} \), 3.90 mmol) and DMAP (2.0 mg, 16.4 \( \mu \text{mol} \)) at room temperature. The mixture was refluxed on 110 °C for three days, then the reaction was quenched with water. The mixture was extracted with Et\(_2\)O (20 mL x 3), washed with brine,
dried over Na₂SO₄, and concentrated. The residue was purified with flash column chromatography (hexane/ACOEt 40:1) to afford O-pivaloyl totarol 1aa in 100% yield (122 mg): white solid; m.p. 113-115 °C; IR (neat) 1750, 1473, 1123, 733 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.93 (3H, s), 0.96 (3H, s), 1.21 (3H, s), 1.23-1.31 (9H, m), 1.39 (9H, s), 1.48 (1H, d, J = 13.8 Hz), 1.55-1.80 (3H, m), 1.93 (1H, dd, J = 7.8, 13.3 Hz), 2.25 (1H, d, J = 12.8 Hz), 2.78 (1H, m), 2.95 (1H, dd, J = 6.4, 17.4 Hz), 3.29 (1H, quintet, J = 7.3 Hz), 6.68 (1H, d, J = 8.7 Hz), 7.14 (1H, d, J = 8.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 19.2, 19.4, 20.69, 20.73, 21.6, 25.0, 27.0, 27.3, 28.8, 33.2, 33.3, 38.0, 39.1, 39.3, 41.4, 49.3, 120.5, 123.2, 134.0, 136.4, 147.6, 147.7, 177.5; HRMS (ESI-TOF) calcd for C₂₅H₃₈O₂Na (M+Na) + 393.2764, found 393.2772.

Pyridinyl O-pivaloyl totarol (3bb):
72% (52.8 mg); 3bb-α / 3bb-β = 2:3; colorless oil.
3bb-α: IR (neat) 1748, 1595, 1471, 1122, 732 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.39 (3H, s), 0.69 (3H, d, J = 6.8 Hz), 0.84 (3H, s), 1.06 (1H, m), 1.14 (3H, d, J = 6.8 Hz), 1.23-1.40 (15H, m), 1.50-1.85 (3H, m), 2.19 (1H, ddd, J = 6.0, 13.3, 13.3 Hz), 2.30 (1H, d, J = 13.3 Hz), 2.78 (1H, quintet, J = 6.8 Hz), 4.41 (1H, d, J = 6.0 Hz), 6.81 (1H, d, J = 9.1 Hz), 6.91 (2H, brs), 7.26 (1H, d, J = 9.1 Hz), 8.0 Hz, 46 (2H, d, J = 4.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 19.4, 19.7, 20.9, 21.6, 25.5, 27.3, 27.9, 28.1, 32.3, 32.5, 38.9, 39.1, 39.3, 40.9, 43.2, 43.6, 122.6, 123.8, 124.2, 133.3, 137.1, 148.2, 148.8, 149.3, 156.7, 177.4; HRMS (ESI-TOF) calcd for C₃₀H₄₂NO₂ (M+H)+ 448.3210, found 448.3197.

3bb-β: IR (neat) 1747, 1595, 1472, 1122, 732 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.55 (3H, d, J = 6.9 Hz), 0.83 (3H, s), 0.96 (3H, s), 1.08 (3H, d, J = 6.9 Hz), 1.15-1.90 (19H, m), 2.25-2.35 (2H, m), 2.86 (1H, quintet, J = 6.9 Hz), 4.37 (1H, dd, J = 9.6, 9.6 Hz), 6.78 (1H, d, J = 8.7 Hz), 6.94 (2H, brs), 7.24 (1H, d, J = 8.7 Hz), 8.47 (2H, d, J = 5.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 19.1, 19.2, 21.1, 21.3, 24.7, 27.3, 28.5, 31.5, 32.9, 33.3, 38.1, 39.1, 39.7, 41.4, 44.6, 48.8, 122.2, 122.5, 123.1, 134.4, 137.4, 148.9, 149.6, 149.8, 158.9, 177.4; HRMS (ESI-TOF) calcd for C₃₀H₄₂NO₂ (M+H)+ 448.3210, found 448.3190.

4-(1-(thiophen-2-yl)butyl)pyridine (3cc):
67% yield (22.9 mg); yellow oil; IR (neat) 1597, 1414, 822, 697 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.93 (3H, t, J = 7.5 Hz), 1.20-1.40 (2H, m), 1.90-2.10 (2H, m), 4.12 (1H, t, J = 7.5 Hz), 6.83 (1H, d, J = 3.4 Hz), 6.93 (1H, dd, J = 3.4, 5.2 Hz), 7.10-7.20 (3H, m), 8.51 (2H, d, J = 6.3 Hz); ¹³C
NMR (125 MHz, CDCl₃) δ 13.8, 20.9, 38.9, 45.9, 123.0, 123.9, 124.3, 126.7, 147.2, 149.8, 153.6; HRMS (ESI-TOF) calcd for C₁₃H₁₆NS (M+H)+ 218.0998, found 218.1000.

4-(1-(thiophen-3-yl)butyl)pyridine (3dd):
47% yield (19.3 mg); yellow oil; IR (neat) 1598, 1415, 824, 775 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (3H, t, J = 7.8 Hz), 1.20-1.40 (2H, m), 1.90-2.10 (2H, m), 3.96 (1H, t, J = 7.8 Hz), 6.87 (1H, dd, J = 1.4, 5.0 Hz), 7.01 (1H, dd, J = 1.4, 2.7 Hz), 7.13 (2H, dd, J = 1.8, 4.6 Hz), 7.25 (1H, dd, J = 2.7, 5.0 Hz), 8.49 (2H, dd, J = 1.8, 4.6 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 13.9, 20.8, 37.6, 46.1, 120.6, 123.2, 125.8, 127.3, 144.1, 149.7, 153.9; HRMS (ESI-TOF) calcd for C₁₃H₁₆NS (M+H)+ 218.0998, found 218.0991.

4-(1-(furan-2-yl)pentyl)pyridine (3ee):
51% yield (14.2 mg); colorless oil; IR (neat) 1597, 1560, 1503, 1460, 1415, 1010, 801, 732 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.87 (3H, t, J = 7.3 Hz), 1.10-1.40 (4H, m), 1.87 (1H, m), 2.08 (1H, m), 3.89 (1H, t, J = 7.8 Hz), 6.10 (1H, d, J = 3.2 Hz), 6.30 (1H, dd, J = 1.8, 3.2 Hz), 7.15 (2H, dd, J = 1.4, 4.6 Hz), 7.32 (1H, d, J = 1.8 Hz), 8.51 (2H, dd, J = 1.4, 4.6 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 13.9, 22.4, 29.6, 33.8, 44.7, 105.9, 110.1, 123.2, 141.7, 149.8, 151.9, 156.1; HRMS (ESI-TOF) calcd for C₁₄H₁₈NO (M+H)+ 216.1383, found 216.1392.

4-(cyclohex-2-enyl)pyridine (3ff) [CAS: 78905-51-8]:
44% yield (9.8 mg); colorless oil; IR (neat) 1596, 1445, 1412, 832 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.50-1.80 (3H, m), 1.95-2.15 (3H, m), 3.39 (1H, m), 5.66 (1H, dd, J = 1.8, 10.0 Hz), 5.95 (1H, ddd, J = 2.3, 3.6, 10.0 Hz), 7.15 (2H, d, J = 6.0 Hz), 8.50 (2H, dd, J = 6.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 20.8, 24.8, 31.7, 41.1, 123.2, 128.1, 129.7, 149.6, 155.4.

4-cyclooctylpyridine (3gg):
35% yield (11.1 mg); yellow oil; IR (neat) 1596, 1445, 1412, 832 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.50-1.90 (14H, m), 2.74 (1H, m), 7.10 (2H, dd, J = 1.8, 4.6 Hz), 8.46 (2H, dd, J = 1.8, 4.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 25.7, 26.2, 26.8, 33.6, 44.0, 122.5, 149.6, 158.8; HRMS (ESI-TOF) calcd for C₁₃H₂₀N (M+H)+ 190.1590, found 190.1598.

4-methyl-4-(pyridin-4-yl)pentyl acetate (3hh):
43% yield (14.5 mg); colorless oil; IR (neat) 1738, 1597, 1411, 1240, 823 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.31 (6H, s), 1.37 (2H, m), 1.65 (2H, m), 2.01 (3H, s), 3.96 (2H, t, J = 6.9 Hz), 7.23 (2H, dd, J = 1.8, 4.6 Hz), 8.52 (2H, dd, J = 1.8, 4.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 20.9, 24.0, 28.0, 37.5, 39.7, 64.6, 121.3, 149.4, 158.4, 171.1; HRMS (ESI-TOF) calcd for C₁₃H₂₀NO₂ (M+H)⁺ 222.1489, found 222.1491.
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