Electronic Supplementary Information for
Rhodium(III)-Catalyzed Annulation of Arenes with Alkynes Assisted by an Internal Oxidizing N-O Bond

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CONCENTS

I. General Information ..........................................................S2
II. Typical Experimental Procedure for the Synthesis of 3. ........................................S2
III. KIE Studies ........................................................................S15
IV. NMR Spectra .......................................................................S18
I. General Information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. Diphenylacetylene was obtained from commercial sources. Other diarylacetylenes\(^1\) and dihydroisoxazoles\(^2\) were prepared by following literature reports. \([\text{RhCp}^\ast\text{Cl}_2]\)_2 was prepared from \(\text{RhCl}_3\cdot\text{H}_2\text{O}\) according to a literature procedure.\(^3\) All reactions were carried out using Schlenk techniques or in a nitrogen-filled glove box. NMR spectra were recorded on a 400 MHz or 500 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless \(\delta\) values and is frequency referenced relative to TMS in \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy. HRMS data were obtained on a Q-TOF analyzer. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

II. Typical Experimental Procedure for the Synthesis of 3.

Heterocycle 1 (0.20 mmol), alkyne 2 (0.24 mmol), \([\text{RhCp}^\ast\text{Cl}_2]\)_2 (4 mol %), CsOAc (30 mol %), and HFIP (2 mL) were charged into a pressure tube. The reaction mixture was stirred at 60 °C for 12 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the desired product 3. The substrates and products are cis.

2-(3,4-Diphenylisoquinolin-1-yl)cyclohexanol (3aa): White solid (57.6 mg, 76%); mp 110-111 °C; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.24 – 8.18 (m, 1H), 7.70 (dt, \(J = 6.9, 3.0\))
Hz, 1H), 7.63 – 7.57 (m, 2H), 7.40 – 7.32 (m, 5H), 7.29 – 7.25 (m, 1H), 7.24 – 7.14 (m, 5H), 4.56 (s, 1H), 3.65 (d, J = 11.6 Hz, 1H), 2.26 – 2.14 (m, 1H), 2.10 (d, J = 13.2 Hz, 1H), 2.00 – 1.82 (m, 3H), 1.71 – 1.57 (m, 3H); 13C NMR (100 MHz, CDCl3) δ 164.9, 148.0, 140.6, 137.4, 136.8, 131.6, 131.5, 130.4, 130.3, 129.6, 128.6, 128.5, 127.9, 127.6, 127.3, 127.1, 126.9, 125.1, 124.7, 68.3, 43.5, 33.2, 28.2, 26.8, 19.9; HRMS: [M + H]+ calculated for C27H26NO: 380.2014, found 380.2018.

![Image of compound 3ba](image)

2-(3,4-Diphenylisoquinolin-1-yl)cyclopentanol (3ba): White solid (48.9 mg, 67%); mp 99-100 °C; 1H NMR (400 MHz, CDCl3) δ 8.25 – 8.20 (m, 1H), 7.72 – 7.67 (m, 1H), 7.62 – 7.57 (m, 3H), 7.39 – 7.31 (m, 5H), 7.26 – 7.22 (m, 2H), 7.20 – 7.13 (m, 3H), 4.81 (s, 1H), 3.80 (ddd, J = 11.3, 8.3, 3.1 Hz, 1H), 2.42 – 2.31 (m, 1H), 2.28 – 2.12 (m, 2H), 2.07 – 1.87 (m, 3H); 13C NMR (100 MHz, CDCl3) δ 163.0, 147.9, 140.4, 137.3, 136.7, 131.6, 131.4, 130.5, 130.3, 129.6, 128.6, 128.5, 127.9, 127.6, 127.3, 127.1, 126.7, 126.3, 125.0, 75.9, 46.0, 34.8, 31.2, 22.8; HRMS: [M + H]+ calculated for C26H24NO: 366.1858, found 366.1856.

![Image of compound 3ca](image)

2-(3,4-Diphenylisoquinolin-1-yl)cycloheptanol (3ca): White solid (61.3 mg, 78%); mp 100-101 °C; 1H NMR (400 MHz, CDCl3) δ 8.24 – 8.13 (m, 1H), 7.73 – 7.66 (m, 1H), 7.66 – 7.55 (m, 2H), 7.35 (s, 5H), 7.30 – 7.23 (m, 1H), 7.22 – 7.13 (m, 4H), 6.67 (s, 1H), 4.65 (s, 1H), 3.74 (d, J = 10.5 Hz, 1H), 2.54 – 2.37 (m, 1H), 2.21 – 2.06 (m, 1H), 2.03 – 1.74 (m, 7H), 1.73 – 1.59 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 166.0, 148.0, 140.7, 137.4, 136.9, 131.6, 131.5, 130.34, 130.29, 129.4, 128.6, 128.5, 127.9, 127.5, 127.3, 127.1, 126.9, 124.7, 124.5, 71.3, 45.8, 36.1, 28.5, 27.9, 27.4, 21.9; HRMS: [M
2-(3,4-Diphenylisoquinolin-1-yl)cyclooctanol (3da): Pale yellow solid (60.2 mg, 74%); mp 99-100 °C; 1H NMR (400 MHz, CDCl$_3$) δ 8.26 – 8.20 (m, 1H), 7.70 (dt, J = 6.7, 2.9 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.40 – 7.30 (m, 5H), 7.26 (dd, J = 6.7, 1.3 Hz, 1H), 7.23 – 7.12 (m, 4H), 7.07 (s, 1H), 4.51 – 4.43 (m, 1H), 4.01 (d, J = 9.2 Hz, 1H), 2.64 – 2.53 (m, 1H), 2.08 – 1.97 (m, 3H), 1.95 – 1.80 (m, 5H), 1.74 – 1.52 (m, 3H); 13C NMR (100 MHz, CDCl$_3$) δ 166.6, 147.9, 140.6, 137.4, 137.0, 131.5, 130.34, 130.26, 129.4, 128.54, 128.49, 127.9, 127.5, 127.3, 127.1, 126.9, 124.8, 124.7, 71.8, 40.4, 32.7, 29.6, 27.8, 27.4, 25.0, 21.2; HRMS: [M + H]$^+$ calculated for C$_{28}$H$_{28}$NO: 394.2171, found 394.2172.

1-(3,4-Diphenylisoquinolin-1-yl)hexan-2-ol (3ea): White solid (50.3 mg, 66%); mp 62-64 °C; 1H NMR (400 MHz, CDCl$_3$) δ 8.15 – 8.05 (m, 1H), 7.64 – 7.55 (m, 1H), 7.54 – 7.46 (m, 2H), 7.30 – 7.21 (m, 5H), 7.17 – 7.05 (m, 5H), 5.88 (s, 1H), 4.37 – 4.25 (m, 1H), 3.53 (dd, 16.5, 1.8 Hz, 1H), 3.19 (dd, 16.5, 9.7 Hz, 1H), 1.77 – 1.65 (m, 1H), 1.64 – 1.56 (m, 1H), 1.55 – 1.39 (m, 2H), 1.39 – 1.28 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl$_3$) δ 159.7, 148.3, 140.6, 137.3, 136.3, 131.4, 130.3, 130.2, 129.5, 128.38, 128.35, 127.7, 127.4, 127.2, 126.9, 126.5, 126.0, 124.7, 70.0, 39.2, 37.0, 28.1, 22.9, 14.2; HRMS: [M + H]$^+$ calculated for C$_{27}$H$_{28}$NO: 382.2171, found 382.2169.
2-(3,4-Diphenylisoquinolin-1-yl)-1-phenylethanol (3fa): Pale yellow solid (38.5 mg, 48%); mp 171-172 °C; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.18 – 8.10 (m, 1H), 7.74 – 7.67 (m, 1H), 7.59 (dd, \(J = 11.1, 7.0, 5.3\) Hz, 4H), 7.45 – 7.29 (m, 8H), 7.27 – 7.18 (m, 5H), 6.51 (s, 1H), 5.58 – 5.49 (m, 1H), 3.83 (dd, \(J = 16.7, 2.1\) Hz, 1H), 3.58 (dd, \(J = 16.7, 10.0\) Hz, 1H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.2, 148.5, 144.4, 140.6, 137.3, 136.57, 131.6, 131.5, 130.6, 130.3, 130.0, 128.6, 128.56, 128.55, 127.9, 127.6, 127.5, 127.4, 127.2, 126.7, 126.2, 126.1, 124.8, 72.5, 42.0; HRMS: [M + H]\(^+\) calculated for C\(_{29}\)H\(_{24}\)NO: 402.1858, found 402.1861.

2-(6-Methyl-3,4-diphenylisoquinolin-1-yl)cyclohexanol (3ga): Pale yellow solid (62.9 mg, 80%); mp 125-126 °C; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.10 (d, \(J = 8.6\) Hz, 1H), 7.45 (s, 1H), 7.43 – 7.40 (m, 1H), 7.39 – 7.29 (m, 6H), 7.25 (dd, \(J = 6.2, 1.8\) Hz, 1H), 7.22 – 7.18 (m, 1H), 7.18 – 7.14 (m, 3H), 4.55 (s, 1H), 3.61 (dd, \(J = 7.2, 5.6\) Hz, 1H), 2.43 (s, 3H), 2.25 – 2.13 (m, 1H), 2.09 (d, \(J = 13.2\) Hz, 1H), 1.99 – 1.83 (m, 3H), 1.71 – 1.55 (m, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.5, 148.1, 140.8, 140.7, 137.5, 137.1, 131.6, 131.5, 130.3, 129.2, 129.1, 128.5, 128.5, 127.8, 127.5, 127.2, 125.7, 124.6, 123.4, 68.3, 43.5, 33.2, 28.2, 26.8, 22.3, 20.0; HRMS: [M + H]\(^+\) calculated for C\(_{28}\)H\(_{28}\)NO: 394.2171, found 394.2169.
2-(6-Fluoro-3,4-diphenylisoquinolin-1-yl)cyclohexanol (3ha): White solid (54.8 mg, 69%); mp 208-209 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23 (dd, $J = 9.2$, 5.6 Hz, 1H), 7.41 – 7.28 (m, 7H), 7.24 (dd, $J = 6.7$, 1.9 Hz, 1H), 7.22 – 7.16 (m, 4H), 7.13 (s, 1H), 4.55 (s, 1H), 3.63 – 3.55 (m, 1H), 2.21 (qd, $J = 13.0$, 3.3 Hz, 1H), 2.10 (d, $J = 12.9$ Hz, 1H), 2.00 – 1.82 (m, 3H), 1.70 – 1.55 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.7, 163.5 (d, $J_{C-F} = 251.1$ Hz), 149.0, 140.2, 139.0 (d, $J_{C-F} = 9.7$ Hz), 136.9, 131.4, 131.3, 130.2, 129.3 (d, $J_{C-F} = 5.2$ Hz), 128.8, 128.7, 127.98, 127.95, 127.9, 127.8, 127.6, 122.3 (d, $J_{C-F} = 0.8$ Hz), 117.3 (d, $J_{C-F} = 25.1$ Hz), 110.6 (d, $J_{C-F} = 22.1$ Hz), 68.2, 43.8, 33.1, 28.3, 26.8, 19.9; HRMS: [M + H]$^+$ calculated for C$_{27}$H$_{25}$FNO: 398.1920, found 398.1921.

2-(6-Chloro-3,4-diphenylisoquinolin-1-yl)cyclohexanol (3ia): White solid (57.8 mg, 70%); mp 129-130 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (d, $J = 9.0$ Hz, 1H), 7.67 (d, $J = 2.0$ Hz, 1H), 7.53 (dd, $J = 9.0$, 2.1 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.31 (ddd, $J = 6.3$, 3.7, 1.3 Hz, 2H), 7.24 (dd, $J = 5.9$, 2.0 Hz, 1H), 7.21 – 7.16 (m, 4H), 7.12 (s, 1H), 4.55 (s, 1H), 3.64 – 3.53 (m, 1H), 2.19 (qd, $J = 13.0$, 3.3 Hz, 1H), 2.09 (d, $J = 12.1$ Hz, 1H), 2.00 – 1.79 (m, 3H), 1.72 – 1.56 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.8, 149.2, 140.2, 137.9, 137.0, 136.6, 131.41, 131.35, 130.2, 128.81, 128.76, 128.7, 128.00, 127.95, 127.9, 127.60, 126.57, 125.7, 123.3, 68.2, 43.7, 33.0, 28.2, 26.7, 19.8; HRMS: [M + H]$^+$ calculated for C$_{27}$H$_{25}$ClNO: 414.1625, found 414.1623.
2-(6-Bromo-3,4-diphenylisoquinolin-1-yl)cyclohexanol (3ja): Pale yellow solid (67.8 mg, 74%); mp 133-134 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06 (d, \(J = 9.0\) Hz, 1H), 7.85 (d, \(J = 1.9\) Hz, 1H), 7.66 (dd, \(J = 9.0, 1.9\) Hz, 1H), 7.42 – 7.34 (m, 3H), 7.34 – 7.29 (m, 2H), 7.23 (dd, \(J = 5.9, 1.9\) Hz, 1H), 7.21 – 7.14 (m, 4H), 7.01 (s, 1H), 4.54 (s, 1H), 3.58 (d, \(J = 11.2\) Hz, 1H), 2.19 (qd, \(J = 13.0, 3.2\) Hz, 1H), 2.09 (d, \(J = 12.4\) Hz, 1H), 2.00 – 1.88 (m, 2H), 1.84 (d, \(J = 12.2\) Hz, 1H), 1.70 – 1.54 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.9, 149.2, 140.2, 138.2, 136.6, 131.41, 131.35, 130.6, 130.2, 129.1, 128.8, 128.7, 128.6, 127.94, 127.89, 127.6, 126.5, 125.6, 123.5, 68.2, 43.7, 33.1, 28.2, 26.7, 19.8; HRMS: [M + H]\(^+\) calculated for C\(_{27}\)H\(_{25}\)BrNO: 458.1120, found 458.1118.

2-(3,4-Diphenyl-6-(trifluoromethyl)isoquinolin-1-yl)cyclohexanol (3ka): White solid (54.5 mg, 61%); mp 128-129 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.34 (d, \(J = 8.9\) Hz, 1H), 8.02 (s, 1H), 7.77 (dd, \(J = 8.8, 1.6\) Hz, 1H), 7.44 – 7.37 (m, 3H), 7.36 – 7.30 (m, 2H), 7.28 – 7.23 (m, 1H), 7.23 – 7.16 (m, 4H), 6.92 (s, 1H), 4.58 (s, 1H), 3.66 (d, \(J = 11.2\) Hz, 1H), 2.21 (qd, \(J = 12.8, 3.1\) Hz, 1H), 2.11 (d, \(J = 13.0\) Hz, 1H), 2.00 – 1.82 (m, 3H), 1.74 – 1.54 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.0, 149.5, 140.0, 136.3, 136.2, 132.0 (q, \(J_{C-F} = 32.4\) Hz), 131.4, 131.3, 130.23, 130.19, 128.9, 128.8, 128.13, 128.05, 127.8, 126.2, 126.0, 123.9 (q, \(J_{C-F} = 271.2\) Hz), 124.5 (q, \(J_{C-F} = 4.5\) Hz), 122.7 (q, \(J_{C-F} = 3.0\) Hz), 68.2, 43.9, 33.1, 28.2, 26.8, 19.8; HRMS: [M + H]\(^+\) calculated for C\(_{28}\)H\(_{25}\)F\(_3\)NO: 448.1888, found 448.1888.
**1-(2-Hydroxycyclohexyl)-3,4-diphenylisoquinoline-6-carbonitrile (3la):** White solid (49.3 mg, 61%); mp 167-168 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.31 (d, \(J = 8.8\) Hz, 1H), 8.09 (s, 1H), 7.78 – 7.71 (m, 1H), 7.42 (s, 3H), 7.33 (dd, \(J = 6.5, 2.9\) Hz, 2H), 7.28 – 7.17 (m, 5H), 6.74 (s, 1H), 4.56 (s, 1H), 3.63 (d, \(J = 11.5\) Hz, 1H), 2.28 – 2.14 (m, 1H), 2.11 (d, \(J = 12.5\) Hz, 1H), 2.00 – 1.80 (m, 3H), 1.71 – 1.57 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.2, 150.0, 139.6, 136.2, 135.8, 133.1, 131.3, 131.26, 130.2, 129.5, 129.01, 128.99, 128.3, 128.1, 128.0, 127.5, 126.3, 125.7, 118.5, 114.1, 68.1, 43.9, 33.0, 28.2, 26.7, 19.8; HRMS: [M + H]\(^+\) calculated for C\(_{28}\)H\(_{25}\)N\(_2\)O: 405.1967, found 405.1965.

**2-(3,4,6-Triphenylisoquinolin-1-yl)cyclohexanol (3ma):** White solid (70.0 mg, 67%); mp 166-167 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.28 (d, \(J = 8.8\) Hz, 1H), 7.89 (d, \(J = 1.4\) Hz, 1H), 7.85 (dd, \(J = 8.7, 1.7\) Hz, 1H), 7.58 – 7.51 (m, 2H), 7.46 – 7.40 (m, 2H), 7.40 – 7.32 (m, 6H), 7.30 (d, \(J = 7.8\) Hz, 1H), 7.27 – 7.22 (m, 2H), 7.22 – 7.15 (m, 3H), 4.58 (s, 1H), 3.67 (d, \(J = 11.6\) Hz, 1H), 2.31 – 2.15 (m, 1H), 2.11 (d, \(J = 13.3\) Hz, 1H), 2.01 – 1.87 (m, 3H), 1.71 – 1.57 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.7, 148.5, 143.0, 140.6, 140.4, 137.3, 137.2, 131.6, 131.5, 130.3, 129.8, 129.1, 128.63, 128.59, 128.3, 127.9, 127.68, 127.65, 127.4, 126.7, 125.4, 124.6, 124.1, 68.3, 43.6, 33.2, 28.2, 26.8, 20.0; HRMS: [M + H]\(^+\) calculated for C\(_{33}\)H\(_{30}\)NO: 456.2327, found 456.2326.
2-(7-Methyl-3,4-diphenylisoquinolin-1-yl)cyclohexanol (3na): White solid (56.6 mg, 72%); mp 131-132 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.40 – 7.30 (m, 6H), 7.25 (d, J = 5.7 Hz, 1H), 7.23 – 7.13 (m, 4H), 4.54 (s, 1H), 3.62 (d, J = 12.0 Hz, 1H), 2.58 (s, 3H), 2.25 – 2.13 (m, 1H), 2.10 (d, J = 13.5 Hz, 1H), 2.00 – 1.84 (m, 3H), 1.72 – 1.53 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.1, 147.2, 140.6, 137.5, 137.0, 135.0, 132.6, 131.51, 131.47, 130.3, 129.4, 128.50, 128.46, 127.9, 127.5, 127.2, 126.8, 125.2, 123.6, 68.3, 43.3, 33.2, 28.1, 26.8, 22.2, 19.9; HRMS: [M + H]⁺ calculated for C₂₈H₂₈NO: 394.2171, found 394.2171.

2-(7-Bromo-3,4-diphenylisoquinolin-1-yl)cyclohexanol (3oa): White solid (55.8 mg, 61%); mp 148-149 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.32 (s, 1H), 7.65 (dd, J = 9.1, 1.3 Hz, 1H), 7.58 (d, J = 9.1 Hz, 1H), 7.40 – 7.29 (m, 5H), 7.28 – 7.15 (m, 5H), 7.00 (s, 1H), 4.53 (s, 1H), 3.55 (d, J = 11.8 Hz, 1H), 2.18 (tt, J = 13.1, 6.6 Hz, 1H), 2.09 (d, J = 12.5 Hz, 1H), 1.99 – 1.80 (m, 3H), 1.74 – 1.57 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 148.5, 140.1, 136.7, 135.4, 133.8, 131.41, 131.36, 130.2, 129.5, 128.9, 128.69, 128.65, 128.0, 127.8, 127.6, 127.0, 126.2, 121.3, 68.2, 43.6, 33.1, 28.1, 26.7, 19.8; HRMS: [M + H]⁺ calculated for C₂₇H₂₅BrNO: 458.1120, found 458.1122.
2-(3,4-Diphenyl-7-(trifluoromethyl)isoquinolin-1-yl)cyclohexanol (3pa): White solid (55.4 mg, 62%); mp 137-138 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.47 (s, 1H), 7.84 (d, $J = 8.9$ Hz, 1H), 7.75 (dd, $J = 9.0$, 1.5 Hz, 1H), 7.44 – 7.31 (m, 5H), 7.29 – 7.17 (m, 5H), 6.91 (d, $J = 1.3$ Hz, 1H), 4.57 (s, 1H), 3.66 (d, $J = 11.2$ Hz, 1H), 2.23 (qd, $J = 12.9$, 3.1 Hz, 1H), 2.11 (d, $J = 13.2$ Hz, 1H), 2.02 – 1.82 (m, 3H), 1.67 (dd, $J = 27.1$, 13.7 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.8, 150.1, 139.9, 138.4, 136.6, 131.41, 131.35, 130.3, 129.5, 128.80 (q, $J_{C-F} = 32.4$ Hz), 128.78, 128.75, 128.3, 128.04, 127.98, 127.8, 125.93 (q, $J_{C-F} = 3.0$ Hz), 125.10 (q, $J_{C-F} = 270.8$ Hz), 124.05, 122.5 (q, $J_{C-F} = 4.5$ Hz), 68.2, 43.7, 33.0, 28.4, 26.7, 19.8; HRMS: [M + H]$^+$ calculated for C$_{28}$H$_{25}$F$_3$NO: 448.1888, found 448.1896.

2-(8-Fluoro-3,4-diphenylisoquinolin-1-yl)cyclohexanol (3qa): White solid (42.9 mg, 54%); mp 108-109 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.54 – 7.45 (m, 2H), 7.40 – 7.29 (m, 5H), 7.28 – 7.22 (m, 2H), 7.22 – 7.16 (m, 4H), 6.91 (s, 1H), 4.57 (s, 1H), 3.84 (d, $J = 11.6$ Hz, 1H), 2.19 – 2.01 (m, 2H), 1.99 – 1.86 (m, 3H), 1.68 – 1.53 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.4 (d, $J_{C-F} = 7.6$ Hz), 159.8 (d, $J_{C-F} = 254.8$ Hz), 148.7, 140.1, 139.5 (d, $J_{C-F} = 3.1$ Hz), 137.2, 131.4, 130.5, 130.4, 130.2, 128.9 (d, $J_{C-F} = 3.1$ Hz), 128.7, 128.6, 128.0, 127.8, 127.6, 123.1 (d, $J_{C-F} = 4.1$ Hz), 116.2 (d, $J_{C-F} = 12.5$ Hz), 112.7 (d, $J_{C-F} = 24.3$ Hz), 68.4, 47.5 (d, $J_{C-F} = 11.7$ Hz), 33.2, 28.3, 27.0, 20.0; HRMS: [M + H]$^+$ calculated for C$_{27}$H$_{25}$F$_3$NO: 398.1920, found 398.1922.
2-(3,4-Diphenylbenzo[g]isoquinolin-1-yl)cyclohexanol (3ra): White solid (27.4 mg, 32%); mp 90-91 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (s, 1H), 7.91 – 7.84 (m, 1H), 7.79 (dd, $J = 9.8$, 3.7 Hz, 2H), 7.56 – 7.48 (m, 2H), 7.25 – 7.11 (m, 10H), 6.85 (s, 1H), 4.13 (dt, $J = 7.5$, 3.9 Hz, 1H), 3.30 (dd, $J = 16.5$, 7.4 Hz, 1H), 2.03 – 1.90 (m, 1H), 1.64 – 1.54 (m, 3H), 1.46 (s, 3H), 1.19 – 1.03 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.6, 141.9, 141.1, 139.9, 137.4, 133.7, 132.5, 131.5, 130.9, 130.5, 130.1, 129.5, 128.5, 128.32, 128.26, 128.0, 127.8, 127.7, 127.4, 127.3, 126.9, 79.8, 47.4, 25.60, 25.58, 22.3, 20.3; HRMS: [M + H]$^+$ calculated for C$_{31}$H$_{28}$NO: 430.2171, found 430.2170.

2-(3,4-Di-p-tolylisoquinolin-1-yl)cyclohexanol (3ab): White solid (56.1 mg, 69%); mp 143-144 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (dd, $J = 6.6$, 3.0 Hz, 1H), 7.69 (dt, $J = 6.8$, 3.2 Hz, 1H), 7.56 (dq, $J = 6.6$, 3.3 Hz, 2H), 7.33 (s, 1H), 7.26 (d, $J = 8.1$ Hz, 2H), 7.21 – 7.08 (m, 4H), 6.99 (d, $J = 7.9$ Hz, 2H), 4.55 (s, 1H), 3.62 (d, $J = 11.7$ Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H), 2.24 – 2.13 (m, 1H), 2.13 – 2.05 (m, 1H), 1.99 – 1.82 (m, 3H), 1.70 – 1.54 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.5, 147.9, 137.8, 137.10, 137.05, 137.0, 134.4, 131.32, 131.28, 130.20, 130.15, 129.29, 129.27, 129.25, 128.7, 126.9, 126.8, 124.9, 124.7, 68.3, 43.4, 33.1, 28.1, 26.8, 21.5, 21.3, 19.9; HRMS: [M + H]$^+$ calculated for C$_{29}$H$_{30}$NO: 408.2327, found 408.2325.
2-(3,4-Bis(4-methoxyphenyl)isoquinolin-1-yl)cyclohexanol (3ac): White solid (59.7 mg, 68%); mp 125-126 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.24 – 8.10 (m, 1H), 7.77 – 7.66 (m, 1H), 7.62 – 7.51 (m, 2H), 7.36 – 7.27 (m, 3H), 7.17 (d, \(J = 8.0\) Hz, 1H), 7.13 (d, \(J = 8.0\) Hz, 1H), 6.92 (t, \(J = 6.1\) Hz, 2H), 6.74 (d, \(J = 8.6\) Hz, 2H), 4.55 (s, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 3.62 (d, \(J = 12.0\) Hz, 1H), 2.25 – 2.03 (m, 2H), 2.00 – 1.82 (m, 3H), 1.72 – 1.52 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 164.5, 159.0, 158.8, 147.7, 137.2, 133.2, 132.5, 132.5, 131.5, 130.2, 129.6, 128.6, 126.8, 126.7, 124.8, 124.7, 114.11, 114.07, 113.4, 68.3, 55.4, 55.3, 43.4, 33.1, 28.1, 26.8, 19.9; HRMS: [M + H]\(^+\) calculated for C\(_{29}\)H\(_{30}\)NO\(_3\): 440.2226, found 440.2227.

2-(3,4-Bis(4-fluorophenyl)isoquinolin-1-yl)cyclohexanol (3ad): White solid (60.6 mg, 73%); mp 236-237 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.22 (dd, \(J = 6.1, 3.3\) Hz, 1H), 7.71 – 7.58 (m, 3H), 7.29 (dd, \(J = 8.6, 5.5\) Hz, 2H), 7.25 – 7.15 (m, 2H), 7.14 – 7.04 (m, 3H), 6.90 (t, \(J = 8.7\) Hz, 2H), 4.55 (s, 1H), 3.65 (d, \(J = 12.1\) Hz, 1H), 2.26 – 2.05 (m, 2H), 2.01 – 1.83 (m, 3H), 1.74 – 1.57 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 165.2, 162.4 (d, \(J_{C,F} = 246.0\) Hz), 162.2 (d, \(J_{C,F} = 246.2\) Hz), 147.2, 136.8, 136.5 (d, \(J_{C,F} = 3.3\) Hz), 133.09 (d, \(J_{C,F} = 9.4\) Hz), 133.08 (d, \(J_{C,F} = 7.1\) Hz), 133.06, 132.0, 131.9, 130.7, 128.5, 127.3, 126.6, 125.1, 124.9, 115.9 (d, \(J_{C,F} = 21.3\) Hz), 115.8 (d, \(J_{C,F} = 21.3\) Hz), 115.8 (d, \(J_{C,F} = 21.3\) Hz).
\( f = 21.3 \text{ Hz}, 115.0 (d, J_{C,F} = 21.3 \text{ Hz}), 68.3, 43.6, 33.1, 28.2, 26.8, 19.9. \) HRMS: [M + H]⁺ calculated for C\(_{27}H_{24}\)F\(_2\)NO: 416.1826, found 416.1825.

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\begin{align*}
&\text{2-(3,4-Bis(4-chlorophenyl)isoquinolin-1-yl)cyclohexanol (3ae): White solid (64.5 mg, 72\%); mp 260-261 °C; }^{1}\text{H NMR (400 MHz, CDCl}_3\text{) }\delta 8.28 – 8.16 (m, 1H), 7.71 – 7.58 (m, 3H), 7.37 (t, J = 6.0 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.22 – 7.11 (m, 4H), 6.98 (s, 1H), 4.53 (s, 1H), 3.65 (d, J = 12.3 Hz, 1H), 2.27 – 2.01 (m, 2H), 2.00 – 1.81 (m, 3H), 1.72 – 1.54 (m, 3H); \text{ }^{13}\text{C NMR (100 MHz, CDCl}_3\text{) }\delta 165.5, 146.9, 138.8, 136.5, 135.5, 133.9, 133.7, 132.8, 132.7, 131.5, 130.8, 129.1, 129.0, 128.5, 128.3, 127.5, 126.5, 125.2, 124.9, 68.3, 43.6, 33.1, 28.1, 26.7, 19.9; \text{ HRMS: [M + H]}^+ \text{ calculated for C}_{27}H_{24}Cl_2NO: 448.1236, \text{ found 448.1236.}
\end{align*}
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\begin{align*}
&\text{2-(3,4-Bis(4-(trifluoromethyl)phenyl)isoquinolin-1-yl)cyclohexanol (3af): White solid (71.1 mg, 69\%); mp 136-137 °C; }^{1}\text{H NMR (400 MHz, CDCl}_3\text{) }\delta 8.33 – 8.21 (m, 1H), 7.74 – 7.64 (m, 4H), 7.64 – 7.58 (m, 1H), 7.51 – 7.35 (m, 6H), 6.85 (s, 1H), 4.55 (s, 1H), 3.69 (d, J = 11.9 Hz, 1H), 2.20 (qd, J = 13.4, 3.3 Hz, 1H), 2.10 (d, J = 11.9 Hz, 1H), 2.02 – 1.86 (m, 3H), 1.73 – 1.57 (m, 3H); \text{ }^{13}\text{C NMR (100 MHz, CDCl}_3\text{) }\delta 166.0, 146.6, 143.7, 140.8, 136.3, 131.9, 131.8, 131.2, 130.5, 130.3 (q, J_{C,F} = 32.5 \text{ Hz}), 129.7 (q, J_{C,F} = 32.4 \text{ Hz}), 128.77, 127.9, 126.5, 125.8 (q, J_{C,F} = 3.6 \text{ Hz}), 125.4, 125.12
\end{align*}
\]
(q, $J_{C-F} = 3.8$ Hz), 125.06, 124.2 (q, $J_{C-F} = 270.3$ Hz), 68.3, 43.8, 33.1, 28.2, 26.7, 19.9; HRMS: [M + H]$^+$ calculated for C$_{29}$H$_{24}$F$_6$NO: 516.1762, found 516.1756.

2-(3,4-Bis(3-chlorophenyl)isoquinolin-1-yl)cyclohexanol (3ag): White solid (59.1 mg, 66%); mp 135-136 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.28 – 8.18 (m, 1H), 7.69 – 7.61 (m, 3H), 7.40 – 7.23 (m, 5H), 7.23 – 7.05 (m, 5H), 6.85 (s, 1H), 4.54 (s, 1H), 3.66 (d, $J = 11.4$ Hz, 1H), 2.28 – 2.04 (m, 2H), 1.99 – 1.82 (m, 3H), 1.69 – 1.58 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.6, 146.7, 142.0, 138.8, 136.4, 134.6, 134.0, 131.33, 131.28, 130.9, 130.2, 130.0, 129.72, 129.66, 129.3, 128.6, 128.4, 128.1, 127.8, 127.6, 126.6, 125.2, 124.9, 68.2, 43.7, 33.1, 28.1, 26.8, 19.9; HRMS: [M + H]$^+$ calculated for C$_{27}$H$_{24}$Cl$_2$NO: 448.1235, found 448.1238.

2-(3,4-Bis(2-fluorophenyl)isoquinolin-1-yl)cyclohexanol (3ah): White solid (58.9 mg, 71%); mp 113-114 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 – 7.50 (m, 1H), 7.38 – 7.32 (m, 2H), 7.30 – 7.23 (m, 1H), 7.21 – 7.12 (m, 2H), 7.09 (td, $J = 7.4$, 1.7 Hz, 1H), 7.05 – 6.85 (m, 6H), 4.20 (dt, $J = 7.2$, 3.6 Hz, 1H), 3.42 (dt, $J = 9.5$, 7.2 Hz, 1H), 2.05 (dd, $J = 14.7$, 3.2 Hz, 1H), 1.67 – 1.44 (m, 5H), 1.21 – 1.07 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.6, 160.5 (d, $J_{C-F} = 247.7$ Hz), 160.3 (d, $J_{C-F} = 247.3$ Hz), 142.2, 137.7, 132.6 (d, $J_{C-F} = 3.5$ Hz), 130.7, 130.1 (d, $J_{C-F} = 8.2$ Hz), 129.9, 129.7 (d, $J_{C-F} = 3.0$ Hz), 129.5, 129.4 (d, $J_{C-F} = 8.3$ Hz), 129.1, 128.0, 127.6 (d, $J_{C-F} = 14.1$ Hz), 127.2 (d, $J_{C-F} = 3.0$ Hz), 125.0 (d, $J_{C-F} = 14.0$ Hz), 124.3 (d, $J_{C-F} = 3.4$ Hz), 123.8 (d, $J_{C-F} = 3.4$ Hz), 123.8 (d, $J_{C-F} =$...
3.5 Hz), 116.2 (d, $J_{C-F} = 21.8$ Hz), 115.7 (d, $J_{C-F} = 21.8$ Hz), 80.0, 47.3, 25.8, 25.4, 22.3, 20.4; HRMS: [M + H]$^+$ calculated for $C_{27}H_{24}F_2NO$: 416.1826, found 416.1827.

2-(4-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)isoquinolin-1-yl)cyclohexanol (3ai): White solid (58.2 mg, 61%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 (dd, $J = 6.7$, 3.0 Hz, 1H), 7.76 (dt, $J = 6.9$, 3.2 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.46 (s, 4H), 7.19 – 7.10 (m, 2H), 7.02 (s, 1H), 6.97 – 6.90 (m, 2H), 4.54 (s, 1H), 3.86 (s, 3H), 3.69 – 3.61 (m, 1H), 2.24 – 2.13 (m, 1H), 2.13 – 2.05 (m, 1H), 2.01 – 1.84 (m, 3H), 1.69 – 1.59 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.0, 159.4, 146.7, 144.5, 137.1, 132.6, 132.5, 130.6, 130.5, 130.0, 129.2 (q, $J_{C-F} = 32.2$ Hz), 128.8, 127.5, 127.1, 124.9 (q, $J_{C-F} = 3.8$ Hz), 124.8, 124.4 (q, $J_{C-F} = 273.9$ Hz), 114.3, 68.4, 55.5, 43.6, 33.2, 28.2, 26.8, 19.9. HRMS: [M + H]$^+$ calculated for $C_{29}H_{27}F_3NO_2$: 478.1994, found 478.1992.

### III. KIE Studies

KIE determined from an intermolecular competition

A mixture of 1d and 1d-$d_5$ (1:1 ratio, 0.4 mmol in total), diphenylacetylene (0.2 mmol), [Cp*RhCl$_2$]$_2$ (4 mol%), and CsOAc (30 mol%) were charged into a pressure tube, to which was added HFIP (2 mL) under N$_2$. The reaction mixture was stirred at 60 °C for 90 min. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE to afford the product mixture. KIE value ($k_H/k_D = 0.82/(1-0.82) = 4.6$) was determined by $^1$H NMR analysis.
KIE determined from two parallel reactions

A mixture of 1d (0.2 mmol), diphenylacetylene (0.2 mmol), [Cp*RhCl₂]₂ (4 mol%), and CsOAc (30 mol%) were charged into a pressure tube, to which was added HFIP (2 mL) under N₂. The reaction mixture was stirred at 60 °C for 60 min. A parallel reaction, 1d-d₅ instead of 1d, was carried out at same conditions. After cooled to room temperature, combined the two parallel reactions, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE to afford the product mixture. KIE value ($k_{\text{H}}/k_{\text{D}} = 0.74/(1-0.74) = 2.8$) was determined by ¹H NMR analysis.
Reference


IV. NMR Spectra

[Diagram of NMR spectra with peaks and chemical structures labeled 3aa]
NOESY of 3ai

in NOESY sample q2015092301 in CDCl3
HSQC of 3ai

HMBC of 3ai