Supporting Information

Synthesis of 2,2'-biphenols through direct C(sp²)–H hydroxylation of [1,1'-biphenyl]-2-ols

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I. General Experimental Information

All the commercial reagents were used without further purification. 2-Phenylphenol (1a) is commercially available and used as received. Other 2-arylphenol substrates were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The $^1$H NMR spectra were recorded at 400 MHz or 600 MHz. The $^{13}$C NMR spectra were recorded at 100 MHz or 150 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), quint (quintuplet), dd (doublet of doublet), m (multiplet), etc. The coupling constants $J$ were given in Hz. High resolution mass spectra (HRMS) were obtained via ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).
II. Experimental Procedures and Spectroscopic Data

1. Preparation of 2-arylphenols (1)

   (1) General procedure for the preparation of 2-arylphenols 1b-1w

   To a tube were added 2-bromophenol or substituted 2-bromophenol (1 mmol), arylboronic acid (1.5 mmol), iPr₂NH (202 mg, 2 mmol), Pd(OAc)₂ (0.6 mg, 0.0025 mmol) and H₂O (2 mL). The tube was then sealed, and stirred at 100 ºC for 10 min-2 h. Upon completion, it was quenched with brine (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as eluent to afford 2-arylphenols 1b-1w.

4'-Fluoro-[1,1'-biphenyl]-2-ol (1b)
White solid (169 mg, 90%), mp 44-45 ºC (lit.² 45-46 ºC); ¹H NMR (600 MHz, CDCl₃) δ: 5.13-5.16 (m, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.97 (td, J₁ = 7.8 Hz, J₂ = 1.2 Hz, 1H), 7.11-7.15 (m, 2H), 7.20 (dd, J₁ = 7.8 Hz, J₂ = 1.8 Hz, 1H), 7.23 (td, J₁ = 7.8 Hz, J₂ = 1.8 Hz, 1H), 7.41-7.43 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ: 116.1 (d, J₅₋₋₋₁C-F = 20.7 Hz), 121.1, 127.3, 129.3, 130.5, 131.0 (d, J₅₋₋₋₁C-F = 7.65 Hz), 133.2, 152.4, 162.5 (d, J₅₋₋₋₁C-F = 244.95 Hz). MS: m/z 187 [M-H]-.

4'-Chloro-[1,1'-biphenyl]-2-ol (1c)
White solid (182 mg, 89%), mp 52-53 ºC (lit.² 51-53 ºC); ¹H NMR (600 MHz, CDCl₃) δ: 4.84 (br s, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.98 (t, J = 7.8 Hz, 1H), 7.20-7.25 (m, 2H), 7.40-7.43 (m, 4H). ¹³C NMR (150 MHz, CDCl₃) δ: 116.1, 121.1, 127.1, 129.3, 129.4, 130.4, 130.6, 133.8, 135.8, 152.4. MS: m/z 203 [M-H]-.

4'-Methyl-[1,1'-biphenyl]-2-ol (1d)²
Colorless syrup (152 mg, 86%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 2.40 (s, 3H), 5.24 (s, 1H), 6.96-6.98 (m, 2H), 7.21-7.25 (m, 2H), 7.28 (d, $J = 7.8$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 21.2, 115.8, 120.8, 128.1, 128.99, 129.0, 130.1, 130.3, 134.1, 137.8, 152.5. MS: m/z 183 [M-H]$^-$.  

4'-Ethyl-[1,1'-biphenyl]-2-ol (1e)  

Colorless syrup (174 mg, 88%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.28 (t, $J = 7.6$ Hz, 3H), 2.70 (q, $J = 7.6$ Hz, 2H), 5.27 (br s, 1H), 6.96-7.00 (m, 2H), 7.22-7.26 (m, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.37-7.39 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 15.6, 28.6, 115.7, 120.8, 128.1, 128.9, 129.0, 129.1, 130.3, 134.3, 144.1, 152.5. HRMS calcd for C$_{14}$H$_{13}$O: 197.0972 [M-H]$^-$, found: 197.0961.  

4'-Pentyl-[1,1'-biphenyl]-2-ol (1f)  

Colorless syrup (211 mg, 88%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 0.91 (t, $J = 6.8$ Hz, 3H), 1.33-1.36 (m, 4H), 1.61-1.68 (m, 2H), 2.63 (t, $J = 7.6$ Hz, 2H), 4.98 (br s, 1H), 6.93-6.97 (m, 2H), 7.19-7.22 (m, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.35 (dd, $J_1 = 6.4$ Hz, $J_2 = 1.6$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 22.7, 31.3, 31.7, 35.8, 115.8, 120.9, 128.2, 129.01, 129.04, 129.4, 130.3, 134.4, 142.8, 152.6. HRMS calcd for C$_{17}$H$_{19}$O: 239.1441 [M-H]$^-$, found: 239.1432.  

4'-(tert-Butyl)-[1,1'-biphenyl]-2-ol (1g)  

Colorless syrup (208 mg, 92%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.36 (s, 9H), 4.87 (br s, 1H), 6.96-7.00 (m, 2H), 7.22-7.26 (m, 2H), 7.38-7.42 (m, 2H), 7.50-7.52 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 31.4, 34.7, 115.8, 120.8, 126.3, 128.1, 128.8, 129.0, 130.3, 134.1, 150.9, 152.6. HRMS calcd for C$_{16}$H$_{17}$O: 225.1285 [M-H]$^-$, found: 225.1272.  

4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-ol (1h)  

White solid (202 mg, 85%), mp 112-113 ºC (lit. 112-114 ºC); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 4.94 (s, 1H), 6.89 (d, $J = 7.8$ Hz, 1H), 6.95 (t, $J = 7.8$ Hz, 1H), 7.17-7.23 (m, 2H), 7.55 (d, $J = 7.8$ Hz, 2H), 7.65 (d, $J = 7.8$ Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 116.3, 121.3, 124.2 (q, $^1$J$_{C-F} = 271.35$ Hz), 125.9 (q, 2H).
$J_{C-F} = 3.3$ Hz), 127.0, 129.6, 129.79 (q, $J_{C-F} = 32.7$ Hz), 129.83, 130.4, 141.2, 152.3. MS: m/z 237 [M-H]$^-$.

**[1,1':4',1''-Terphenyl]-2-ol (1i)**

White solid (197 mg, 80%), mp 175-176 ºC (lit.$^3$ 176-177 ºC); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 5.28 (br s, 1H), 6.99-7.03 (m, 2H), 7.25-7.31 (m, 2H), 7.35-7.39 (m, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.54-7.56 (m, 2H), 7.63-7.65 (m, 2H), 7.70-7.72 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 116.0, 121.0, 127.2, 127.6, 127.8, 128.0, 128.9, 129.3, 129.5, 130.3, 136.1, 140.5, 140.8, 152.5. MS: m/z 245 [M-H]$^-$.

**4'-Methoxy-[1,1'-biphenyl]-2-ol (1j)**

White solid (180 mg, 90%), mp 67-68 ºC (lit.$^2$ 66-67 ºC); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 3.81 (s, 3H), 5.35 (s, 1H), 6.93-6.95 (m, 2H), 6.96-6.98 (m, 2H), 7.19-7.22 (m, 2H), 7.36-7.38 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 55.4, 114.7, 115.8, 120.9, 128.0, 128.8, 129.4, 130.4, 152.6, 159.3. MS: m/z 199 [M-H]$^-$.

**4'-Ethoxy-[1,1'-biphenyl]-2-ol (1k)**

White solid (184 mg, 86%), mp 55-56 ºC (lit.$^4$ 53.5-54.5 ºC); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.44 (t, $J = 6.8$ Hz, 3H), 4.06 (q, $J = 7.2$ Hz, 2H), 5.29 (br s, 1H), 6.94-7.01 (m, 4H), 7.20-7.24 (m, 2H), 7.35-7.39 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.9, 63.6, 115.3, 115.7, 120.8, 127.9, 128.8, 129.1, 130.3, 152.6, 158.7. MS: m/z 213 [M-H]$^-$.

**4'-(Trifluoromethoxy)-[1,1'-biphenyl]-2-ol (1l)**

White solid (229 mg, 90%), mp 88-89 ºC; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 4.85 (br s, 1H), 6.92 (d, $J = 8.4$ Hz, 1H), 6.99 (t, $J = 7.2$ Hz, 1H), 7.21-7.25 (m, 2H), 7.29 (d, $J = 7.8$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 116.2, 120.6 (q, $J_{C-F} = 254.85$ Hz), 121.2, 121.5, 127.0, 129.5, 130.5, 130.7, 136.1, 148.8, 152.4. HRMS calcd for C$_{13}$H$_8$F$_3$O$_2$: 253.0482 [M-H]$^-$, found: 253.0473.

**4'-Phenoxy-[1,1'-biphenyl]-2-ol (1m)**

4'-(Trifluoromethoxy)-[1,1'-biphenyl]-2-ol (1l)

White solid (229 mg, 90%), mp 88-89 ºC; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 4.85 (br s, 1H), 6.92 (d, $J = 8.4$ Hz, 1H), 6.99 (t, $J = 7.2$ Hz, 1H), 7.21-7.25 (m, 2H), 7.29 (d, $J = 7.8$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 116.2, 120.6 (q, $J_{C-F} = 254.85$ Hz), 121.2, 121.5, 127.0, 129.5, 130.5, 130.7, 136.1, 148.8, 152.4. HRMS calcd for C$_{13}$H$_8$F$_3$O$_2$: 253.0482 [M-H]$^-$, found: 253.0473.
White solid (225 mg, 86%), mp 102-103 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ: 5.17 (br s, 1H), 6.96-7.00 (m, 2H), 7.09 (t, $J = 8.0$ Hz, 4H), 7.15 (t, $J = 7.2$ Hz, 1H), 7.23-7.27 (m, 2H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 8.8$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 115.8, 119.2, 119.4, 120.9, 123.8, 127.6, 129.1, 129.9, 130.3, 130.6, 131.7, 152.5, 156.7, 157.3. MS: m/z 261 [M-H].

**1-(2'-Hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (1n)**

White solid (182 mg, 86%), mp 145-146 °C (lit. 145-148 °C); $^1$H NMR (400 MHz, CDCl$_3$) δ: 2.65 (s, 3H), 5.35 (br s, 1H), 6.98 (d, $J = 8.4$ Hz, 1H), 7.03 (t, $J = 7.6$ Hz, 1H), 7.26-7.30 (m, 2H), 7.63 (d, $J = 8.0$ Hz, 2H), 8.06 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 26.7, 116.3, 121.2, 127.2, 129.0, 129.4, 129.8, 130.4, 136.1, 142.5, 152.5, 198.0. MS: m/z 211 [M-H].

**3'-Fluoro-[1,1'-biphenyl]-2-ol (1o)**

Colorless syrup (162 mg, 86%); $^1$H NMR (600 MHz, CDCl$_3$) δ: 5.15 (br s, 1H), 6.96 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 6.98-7.01 (m, 1H), 7.06-7.10 (m, 1H), 7.19-7.21 (m, 1H), 7.24 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.25-7.28 (m, 2H), 7.42-7.45 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 114.7 (d, $^2J_{C-F} = 20.85$ Hz), 116.1, 116.3 (d, $^2J_{C-F} = 20.85$ Hz), 121.1, 124.7 (d, $^4J_{C-F} = 3.3$ Hz), 127.0, 129.6, 130.3, 130.7 (d, $^3J_{C-F} = 8.85$ Hz), 139.5 (d, $^3J_{C-F} = 7.65$ Hz), 152.3, 163.2 (d, $^1J_{C-F} = 246.15$ Hz). MS: m/z 187 [M-H].

**3'-Chloro-[1,1'-biphenyl]-2-ol (1p)**

White solid (189 mg, 92%), mp 142-143 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ: 5.21 (br s, 1H), 6.94 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H), 6.99 (td, $J_1 = 7.6$ Hz, $J_2 = 0.8$ Hz, 1H), 7.21-7.28 (m, 2H), 7.33-7.39 (m, 3H), 7.48 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 116.1, 121.1, 126.9, 127.3, 127.9, 129.4, 129.6, 130.3, 130.4, 134.9, 139.2, 152.3. MS: m/z 203 [M-H].

**3'-Methyl-[1,1'-biphenyl]-2-ol (1q)**

White solid (225 mg, 86%), mp 102-103 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ: 5.17 (br s, 1H), 6.96-7.00 (m, 2H), 7.09 (t, $J = 8.0$ Hz, 4H), 7.15 (t, $J = 7.2$ Hz, 1H), 7.23-7.27 (m, 2H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 8.8$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 115.8, 119.2, 119.4, 120.9, 123.8, 127.6, 129.1, 129.9, 130.3, 130.6, 131.7, 152.5, 156.7, 157.3. MS: m/z 261 [M-H].
Colorless syrup (158 mg, 86%); $^1$H NMR (600 MHz, CDCl$_3$) δ: 2.41 (s, 3H), 5.27 (br s, 1H), 6.96-6.99 (m, 2H), 7.20-7.27 (m, 5H), 7.37 (t, $J$ = 7.8 Hz, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 21.5, 115.8, 120.8, 126.1, 128.3, 128.7, 129.1, 129.3, 129.8, 130.2, 137.0, 139.2, 152.5. MS: m/z 183 [M-H]$^-$.

2'-Fluoro-[1,1'-biphenyl]-2-ol (1r)

Colorless syrup (165 mg, 88%); $^1$H NMR (600 MHz, CDCl$_3$) δ: 5.06 (br s, 1H), 6.97-7.02 (m, 2H), 7.19 (t, $J$ = 9.0 Hz, 1H), 7.23-7.25 (m, 2H), 7.29 (t, $J$ = 7.8 Hz, 1H), 7.37-7.38 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 116.2, 116.3 (d, $^2$J$_{C-F}$ = 21.9 Hz), 120.9, 122.4, 124.6 (d, $^2$J$_{C-F}$ = 15.3 Hz), 124.8 (d, $^4$J$_{C-F}$ = 3.3 Hz), 129.8, 130.0 (d, $^3$J$_{C-F}$ = 7.65 Hz), 131.2, 132.0 (d, $^4$J$_{C-F}$ = 3.3 Hz), 152.9, 160.0 (d, $^1$J$_{C-F}$ = 244.95 Hz). HRMS calcd for C$_{12}$H$_8$FO: 187.0565 [M-H]$^-$, found: 187.0558.

2'-Chloro-[1,1'-biphenyl]-2-ol (1s)

White solid (176 mg, 86%), mp 144-145 ºC (lit. 9 145.1-146.4 ºC); $^1$H NMR (600 MHz, CDCl$_3$) δ: 4.82 (br s, 1H), 6.98-7.01 (m, 2H), 7.16 (d, $J$ = 7.2 Hz, 1H), 7.30 (t, $J$ = 7.2 Hz, 1H), 7.34-7.35 (m, 3H), 7.51-7.52 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 115.9, 120.6, 126.0, 127.4, 129.7, 129.9, 130.2, 130.7, 132.2, 134.1, 135.7, 152.6. MS: m/z 203 [M-H]$^-$.

2'-Methyl-[1,1'-biphenyl]-2-ol (1t) 2

Colorless syrup (140 mg, 76%); $^1$H NMR (600 MHz, CDCl$_3$) δ: 2.15 (s, 3H), 4.80 (s, 1H), 6.94-6.97 (m, 2H), 7.09 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.2 Hz, 1H), 7.20-7.22 (m, 1H), 7.24-7.28 (m, 2H), 7.29-7.31 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 19.8, 115.4, 120.5, 126.5, 127.8, 128.6, 129.2, 130.2, 130.6, 130.7, 135.8, 137.5, 152.6. MS: m/z 183 [M-H]$^-$.

4-Fluoro-[1,1'-biphenyl]-2-ol (1b') 10

Colorless syrup (147 mg, 78%); $^1$H NMR (600 MHz, CDCl$_3$) δ: 5.46 (br s, 1H), 6.66-6.69 (m, 2H), 7.13-7.15 (m, 1H), 7.34-7.38 (m, 3H), 7.44 (t, $J$ = 7.8 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 103.4 (d, $^2$J$_{C-F}$
= 25.05 Hz), 107.9 (d, $2^1J_{C,F} = 20.85$ Hz), 124.4 (d, $4^1J_{C,F} = 2.1$ Hz), 128.1, 129.2, 129.5, 131.1 (d, $3^1J_{C,F} = 9.75$ Hz), 136.4, 153.6 (d, $2^1J_{C,F} = 12.15$ Hz), 163.2 (d, $1^1J_{C,F} = 243.9$ Hz). MS: m/z 187 [M-H].

4-Chloro-[1,1'-biphenyl]-2-ol (1c')

White solid (176 mg, 86%), mp 39-40 °C (lit.11 38.5-39 °C); $^1$H NMR (600 MHz, CDCl$_3$) δ: 5.37 (br s, 1H), 6.95-6.98 (m, 2H), 7.14 (d, $J = 8.4$ Hz, 1H), 7.37-7.41 (m, 3H), 7.47 (t, $J = 7.8$ Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 116.3, 121.2, 126.8, 128.3, 129.0, 129.5, 131.1, 134.3, 136.1, 153.1. MS: m/z 203 [M-H].

4-Methoxy-[1,1'-biphenyl]-2-ol (1j')

White solid (178 mg, 89%), mp 68-69 °C (lit.10 66-67 °C); $^1$H NMR (600 MHz, CDCl$_3$) δ: 3.78 (s, 3H), 5.39 (br s, 1H), 6.54-6.56 (m, 2H), 7.13 (d, $J = 8.4$ Hz, 1H), 7.33 (d, $J = 7.2$ Hz, 1H), 7.40-7.45 (m, 4H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 55.4, 101.5, 107.0, 121.0, 127.5, 129.2, 129.3, 130.9, 137.1, 153.5, 160.6. MS: m/z 199 [M-H].

5-Chloro-[1,1'-biphenyl]-2-ol (1p')

Colorless syrup (160 mg, 78%); $^1$H NMR (600 MHz, CDCl$_3$) δ: 5.07 (br s, 1H), 6.87 (d, $J = 8.4$ Hz, 1H), 7.17 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 1H), 7.20 (d, $J = 2.4$ Hz, 1H), 7.36-7.41 (m, 3H), 7.44-7.46 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 117.3, 125.6, 128.4, 128.9, 129.0, 129.4, 129.6, 129.9, 136.0, 151.1. MS: m/z 203 [M-H].

5-Methyl-[1,1'-biphenyl]-2-ol (1q')

White solid (156 mg, 85%), mp 70-71 °C (lit.13 68-69 °C); $^1$H NMR (600 MHz, CDCl$_3$) δ: 2.28 (s, 3H), 5.15 (s, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 7.01-7.02 (m, 2H), 7.32-7.33 (m, 1H), 7.40-7.42 (m, 4H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 20.6, 115.8, 127.8, 128.0, 129.22, 129.25, 129.7, 130.1, 130.8, 137.5, 150.3. MS: m/z 183 [M-H].

5-Methoxy-[1,1'-biphenyl]-2-ol (1u)
Colorless syrup (152 mg, 76%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.77 (s, 3H), 4.58 (br s, 1H), 6.80-6.83 (m, 2H), 6.90 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.36-7.41 (m, 1H), 7.46-7.47 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 55.9, 114.6, 115.3, 116.7, 128.0, 128.7, 129.1, 129.2, 137.3, 146.5, 153.6. MS: m/z 199 [M-H]$^-$.

2-(Naphthalen-2-yl)phenol (1v)

White solid (176 mg, 80%), mp 95-96 ºC (lit.$^{14}$ 96.2-96.8 ºC); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 4.73 (br s, 1H), 7.00-7.03 (m, 2H), 7.27 (t, $J = 7.8$ Hz, 1H), 7.33 (d, $J = 7.2$ Hz, 1H), 7.50-7.51 (m, 2H), 7.56 (d, $J = 8.4$ Hz, 1H), 7.84-7.85 (m, 2H), 7.92-7.93 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 116.0, 121.0, 126.5, 126.7, 127.2, 127.86, 127.93, 128.1, 128.2, 129.2, 129.3, 130.6, 132.8, 133.7, 134.6, 152.7. MS: m/z 219 [M-H]$^-$.

4-Fluoro-4'-methoxy-[1,1'-biphenyl]-2-ol (1w)

White solid (185 mg, 85%), mp 65-66 ºC (lit.$^{10}$ 63-65 ºC); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85 (s, 3H), 5.38 (br s, 1H), 6.66-6.72 (m, 2H), 6.99-7.03 (m, 2H), 7.12-7.16 (m, 1H), 7.31-7.35 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 55.4, 103.1 (d, $^2J_{C-F} = 24.8$ Hz), 107.7 (d, $^2J_{C-F} = 21.1$ Hz), 114.9, 124.0 (d, $^4J_{C-F} = 3.7$ Hz), 128.3, 130.3, 131.0 (d, $^3J_{C-F} = 9.5$ Hz), 153.7 (d, $^3J_{C-F} = 12.4$ Hz), 159.5, 162.9 (d, $^1J_{C-F} = 243.6$ Hz). MS: m/z 217 [M-H]$^-$.

(2) Procedure for the preparation of [1,1'-binaphthalen]-2-ol (1x)$^{15}$

To a Schlenk flask were added Pd(PPh$_3$)$_4$ (58 mg, 0.05 mmol), Na$_2$CO$_3$ (223 mg, 2.1 mmol), 1-bromonaphthalen-2-ol (223 mg, 1.0 mmol), naphthalen-1-ylboronic acid (344 mg, 2.0 mmol), toluene (5 mL), ethanol (1 mL) and water (1 mL). After the flask was evacuated and flushed with nitrogen, the mixture was stirred at 80 ºC for 20 h. Upon completion, it was quenched with saturated NH$_4$Cl (10 mL), and extracted with EtOAc (10 mL $\times$ 3). The combined organic phases were dried over anhydrous Na$_2$SO$_4$,
and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as eluent to afford 1x.

**[1,1'-Binaphthalen]-2-ol (1x)**

White solid (232 mg, 86%), mp 95-96 °C (lit. 90-93 °C); ¹H NMR (400 MHz, CDCl₃) δ: 4.93 (s, 1H), 7.08 (d, J = 8.4 Hz, 1H), 7.17-7.21 (m, 1H), 7.27-7.32 (m, 3H), 7.37 (d, J = 8.0 Hz, 1H), 7.45-7.50 (m, 2H), 7.56-7.60 (m, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.91-7.96 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 117.6, 118.8, 123.5, 125.1, 125.9, 126.1, 126.7, 127.0, 128.1, 128.6, 129.0, 129.3, 129.7, 130.0, 131.6, 132.9, 134.0, 134.3, 151.1. MS: m/z 269 [M-H]⁻.

(3) Procedure for the preparation of [1,1'-biphenyl]-2',3',4',5',6'-d₅-2-ol (1a-d₅)

To a tube were added 1-bromobenzene-2,3,4,5,6-d₅ (162 mg, 1 mmol), (2-hydroxyphenyl)boronic acid (207 mg, 1.5 mmol), iPr₂NH (202 mg, 2 mmol), Pd(OAc)₂ (0.56 mg, 0.0025 mmol) and H₂O (2 mL). The tube was then sealed, and the mixture was stirred at 100 °C for 30 min. Upon completion, it was quenched with brine (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as eluent to afford 1a-d₅.

**[1,1'-Biphenyl]-2',3',4',5',6'-d₅-2-ol (1a-d₅)**

White solid (168 mg, 96%), mp 85-86 °C; ¹H NMR (600 MHz, CDCl₃) δ: 5.28 (br s, 1H), 6.95-6.98 (m, 2H), 7.22-7.24 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ: 116.0, 121.0, 127.4 (t, J = 24.0 Hz, 1C), 128.2, 128.77 (t, J = 24.0 Hz, 2C), 128.80 (t, J = 24.0 Hz, 2C), 129.2, 130.4, 137.0, 152.5. MS: m/z 174 [M-H]⁻.

(4) Procedure for the preparation of [1,1'-biphenyl]-2'-d₂-2-ol (1a-d₁)

To a Schlenk tube were added 2'-bromo-[1,1'-biphenyl]-2-ol (249 mg, 1 mmol) and Et₂O (6 mL). The solution was cooled to -78 °C, followed by dropwise addition of n-BuLi (1.6 M in hexane, 3 mL) under nitrogen. The resulting mixture was stirred at -78 °C for 15 min, then at 0 °C for additional 2 h. The
reaction was quenched with careful addition of D$_2$O (1 mL), followed by vigorous stirring at room temperature for 1 h. Then, the reaction mixture was diluted with EtOAc (30 mL), and the organic phase was dried over anhydrous Na$_2$SO$_4$, filtered, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as eluent to afford 1a-d$_1$.

[1,1'-Biphenyl]-2'-d-2-ol (1a-d$_1$)

White solid (164 mg, 96%), mp 58-59 ºC (lit. $^6$ 56-57 ºC); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 5.16 (s, 1H), 6.87-6.90 (m, 2H), 7.13-7.16 (m, 2H), 7.28 (td, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.35-7.38 (m, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 115.9, 120.9, 127.9, 128.2, 128.9 (t, $J = 24.0$ Hz, 1C), 129.18, 129.21, 129.23, 129.3, 130.3, 137.1, 152.5. MS: m/z 170 [M-H]$.^-$.

2. Preparation of 2,2'-biphenols (2)

A typical procedure for the preparation of [1,1'-biphenyl]-2,2'-diol (2a)

To a tube containing 2-phenylphenol (1a, 85 mg, 0.5 mmol) were added Pd(OAc)$_2$ (5.6 mg, 0.025 mmol), Cs$_2$CO$_3$ (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH$_3$CN (2 mL) and TBHP (0.27 mL, 70% aqueous solution, 2 mmol) under air. The tube was then sealed, and stirred at 80 ºC for 18 h. Afterwards, the reaction was quenched with saturated NH$_4$Cl (10 mL), and extracted with EtOAc (6 mL $\times$ 3). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to afford 2a (71 mg, 76%) and recover 1a (5 mg, 6%). 2b-2w were obtained in a similar manner.

[1,1'-Biphenyl]-2,2'-diol (2a)$^{17}$

Colorless syrup (71 mg, 76%); $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 6.79 (t, $J = 7.8$ Hz, 2H), 6.88 (d, $J = 8.4$ Hz, 2H), 7.09-7.13 (m, 4H), 9.16 (br s, 2H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 116.2, 119.4, 126.4,
128.6, 132.0, 154.9. FT-IR (KBr) \( \nu \) (cm\(^{-1}\)): 744, 840, 1094, 1224, 1440, 1483, 3150. HRMS calcd for C\(_{12}\)H\(_{10}\)NaO\(_2\): 209.0573 [M+Na]\(^+\), found: 209.0578.

4-Fluoro-[1,1'-biphenyl]-2,2'-diol (2b) \(^{17}\)

Colorless solid (82 mg, 80%), mp 80-81 °C. \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \( \delta \): 6.65 (td, J\(_1\) = 8.4 Hz, J\(_2\) = 2.4 Hz, 1H), 6.72 (dd, J\(_1\) = 10.8 Hz, J\(_2\) = 2.4 Hz, 1H), 6.83 (td, J\(_1\) = 7.2 Hz, J\(_2\) = 1.2 Hz, 1H), 6.92 (dd, J\(_1\) = 7.8 Hz, J\(_2\) = 0.6 Hz, 1H), 7.12-7.17 (m, 3H), 9.47 (br s, 2H). \(^{13}\)C NMR (150 MHz, DMSO-\(d_6\)) \( \delta \): 103.0 (d, \( ^2\)J\(_{C-F}\) = 24.0 Hz), 105.7 (d, \( ^2\)J\(_{C-F}\) = 20.85 Hz), 116.1, 119.2, 122.9 (d, \( ^4\)J\(_{C-F}\) = 3.15 Hz), 125.4, 128.6, 132.0, 133.0 (d, \( ^3\)J\(_{C-F}\) = 9.9 Hz), 155.1, 156.5 (d, \( ^3\)J\(_{C-F}\) = 10.95 Hz), 162.3 (d, \( ^1\)J\(_{C-F}\) = 240.6 Hz). FT-IR (KBr) \( \nu \) (cm\(^{-1}\)): 743, 831, 970, 1089, 1139, 1278, 1482, 1604, 3277. HRMS calcd for C\(_{12}\)H\(_8\)FO\(_2\): 203.0514 [M-H], found: 203.0508.

4-Chloro-[1,1'-biphenyl]-2,2'-diol (2c) \(^{18}\)

Colorless solid (85 mg, 77%), mp 119-120 °C. \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \( \delta \): 6.83 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.97 (s, 1H), 7.13-7.17 (m, 3H), 9.49 (br s, 2H). \(^{13}\)C NMR (150 MHz, DMSO-\(d_6\)) \( \delta \): 115.8, 116.1, 119.0, 119.2, 125.1, 125.5, 128.8, 131.8, 132.2, 133.2, 155.0, 156.2. FT-IR (KBr) \( \nu \) (cm\(^{-1}\)): 757, 900, 1005, 1191, 1290, 1481, 1599, 3280. HRMS calcd for C\(_{12}\)H\(_8\)ClO\(_2\): 219.0218 [M-H], found: 219.0219.

4-Methyl-[1,1'-biphenyl]-2,2'-diol (2d)

Colorless solid (77 mg, 77%), mp 78-79 °C. \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \( \delta \): 2.25 (s, 3H), 6.64 (d, J = 7.2 Hz, 1H), 6.71 (s, 1H), 6.81 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 7.02 (d, J = 7.2 Hz, 1H), 7.10-7.13(m, 2H), 9.10 (br s, 2H). \(^{13}\)C NMR (150 MHz, DMSO-\(d_6\)) \( \delta \): 21.3, 116.2, 116.8, 119.3, 120.2, 123.4, 126.4, 128.3, 131.8, 132.0, 137.8, 154.7, 154.9. FT-IR (KBr) \( \nu \) (cm\(^{-1}\)): 750, 941, 1043, 1225, 1279, 1483, 1703, 3203. HRMS calcd for C\(_{13}\)H\(_{11}\)O\(_2\): 199.0765 [M-H], found: 199.0766.

4-Ethyl-[1,1'-biphenyl]-2,2'-diol (2e)
Colorless syrup (83 mg, 78%). $^1$H NMR (400 MHz, DMSO-\textit{d}_6) $\delta$: 1.15 (t, $J = 7.6$ Hz, 3H), 2.51 (q, $J = 7.6$ Hz, 2H), 6.65 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 6.73 (d, $J = 1.6$ Hz, 1H), 6.78 (td, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 6.87 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H), 7.03 (d, $J = 7.6$ Hz, 1H), 7.06-7.12 (m, 2H), 9.13 (br s, 2H). $^{13}$C NMR (100 MHz, DMSO-\textit{d}_6) $\delta$: 15.5, 27.9, 115.1, 115.7, 118.5, 118.9, 123.2, 125.9, 127.9, 131.3, 131.5, 143.8, 154.2, 154.4. FT-IR (KBr) $\nu$ (cm$^{-1}$): 752, 935, 1039, 1226, 1289, 1491, 1723, 3233. HRMS calcd for C$_{14}$H$_{13}$O$_2$: 213.0921 [M-H], found: 213.0923.

4-Pentyl-[1,1'-biphenyl]-2,2'-diol (2f)

Colorless syrup (96 mg, 75%). $^1$H NMR (400 MHz, DMSO-\textit{d}_6) $\delta$: 0.91 (t, $J = 6.8$ Hz, 3H), 1.29-1.38 (m, 4H), 1.61 (quint, $J = 7.2$ Hz, 2H), 2.54 (t, $J = 7.6$ Hz, 2H), 6.69 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 6.78 (d, $J = 1.2$ Hz, 1H), 6.84 (td, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 6.93-6.95 (m, 1H), 7.09 (d, $J = 8.0$ Hz, 1H), 7.14 (td, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.18 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz, 1H), 9.20 (br s, 2H). $^{13}$C NMR (100 MHz, DMSO-\textit{d}_6) $\delta$: 13.9, 22.1, 30.6, 31.0, 34.9, 115.6, 115.8, 118.9, 119.1, 123.2, 126.0, 127.8, 131.3, 131.5, 142.4, 154.1, 154.4. FT-IR (KBr) $\nu$ (cm$^{-1}$): 755, 945, 1049, 1228, 1288, 1412, 1493, 1705, 3212. HRMS calcd for C$_{17}$H$_{19}$O$_2$: 255.1391 [M-H], found: 255.1403.

4-(tert-Butyl)-[1,1'-biphenyl]-2,2'-diol (2g)

Colorless solid (91 mg, 75%), mp 116-117 °C. $^1$H NMR (600 MHz, DMSO-\textit{d}_6) $\delta$: 1.30 (s, 9H), 6.84 (t, $J = 7.8$ Hz, 1H), 6.89 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.8$ Hz, 1H), 6.92 (d, $J = 7.8$ Hz, 1H), 6.95 (d, $J = 1.8$ Hz, 1H), 7.11 (d, $J = 7.8$ Hz, 1H), 7.12-7.15 (m, 1H), 7.17 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 9.07 (br s, 1H), 9.19 (br s, 1H). $^{13}$C NMR (150 MHz, DMSO-\textit{d}_6) $\delta$: 31.6, 34.6, 113.3, 116.2, 116.4, 119.4, 123.4, 126.3, 128.4, 131.5, 132.0, 151.3, 154.4, 154.9. FT-IR (KBr) $\nu$ (cm$^{-1}$): 748, 863, 930, 1099, 1223, 1408, 1483, 2961, 3198. HRMS calcd for C$_{16}$H$_{17}$O$_2$: 241.1234 [M-H], found: 241.1251.

4-(Trifluoromethyl)-[1,1'-biphenyl]-2,2'-diol (2h)
Colorless solid (102 mg, 80%), mp 101-102 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 6.84 (td, $J_1 = 7.2$ Hz, $J_2 = 0.6$ Hz, 1H), 6.94 (d, $J = 7.2$ Hz, 1H), 7.15-7.19 (m, 3H), 7.21 (d, $J = 1.2$ Hz, 1H), 7.36 (d, $J = 7.8$ Hz, 1H), 9.65 (br s, 2H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 112.3 (q, $J_{C-F} = 3.3$ Hz), 115.5 (q, $J_{C-F} = 3.15$ Hz), 116.2, 119.2, 124.7 (q, $J_{C-F} = 270.15$ Hz), 124.9, 129.0 (q, $J_{C-F} = 31.65$ Hz), 129.2, 130.7, 131.7, 132.9, 155.1, 155.7. FT-IR (KBr) $\nu$(cm$^{-1}$): 754, 822, 914, 1004, 1119, 1331, 1422, 3071. HRMS calcd for C$_{13}$H$_8$F$_3$O$_2$: 253.0482 [M-H], found: 253.0502.

[1,1′:4′,1″-Terphenyl]-2,2'-diol (2i)

Colorless solid (101 mg, 77%), mp 139-140 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 6.88 (t, $J = 7.2$ Hz, 1H), 6.98 (d, $J = 7.8$ Hz, 1H), 7.15-7.20(m, 2H), 7.24-7.25(m, 2H), 7.29 (d, $J = 7.2$ Hz, 1H), 7.37 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.2$ Hz, 2H), 7.65 (d, $J = 7.8$ Hz, 2H), 9.41 (br s, 2H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 114.4, 116.3, 117.9, 119.4, 125.7, 126.0, 127.0, 127.8, 128.7, 129.4, 132.0, 132.6, 140.72, 140.74, 155.0, 155.4. FT-IR (KBr) $\nu$(cm$^{-1}$): 759, 820, 895, 1172, 1404, 1476, 2922, 3515. HRMS calcd for C$_{18}$H$_{13}$O$_2$: 261.0921 [M-H], found: 261.0919.

4-Methoxy-[1,1'-biphenyl]-2,2'-diol (2j)

Colorless syrup (81 mg, 75%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 3.72 (s, 3H), 6.45 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 1H), 6.49 (d, $J = 2.8$ Hz, 1H), 6.81 (td, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 6.89 (dd, $J_1 = 7.6$ Hz, $J_2 = 0.8$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 1H), 7.09-7.14 (m, 2H), 9.24 (br s, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 54.9, 101.5, 104.5, 115.6, 118.5, 118.8, 125.7, 127.7, 131.6, 132.0, 154.4, 155.3, 159.3. FT-IR (KBr) $\nu$(cm$^{-1}$): 755, 829, 1037, 1157, 1284, 1484, 1573, 1619, 2928, 3280. HRMS calcd for C$_{13}$H$_{11}$O$_3$: 215.0714 [M-H], found: 215.0709.

4-Ethoxy-[1,1'-biphenyl]-2,2'-diol (2k)

Colorless solid (86 mg, 75%), mp 99-100 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 1.32 (t, $J = 7.2$ Hz, 3H), 3.98 (q, $J = 7.2$ Hz, 2H), 6.41 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 1H), 6.45 (d, $J = 2.4$ Hz, 1H), 6.80 (t, $J = 7.2$ Hz, 1H).
Hz, 1H), 6.86 (d, \( J = 7.8 \) Hz, 1H), 7.03 (d, \( J = 8.4 \) Hz, 1H), 7.08-7.11(m, 2H), 9.15 (br s, 2H). \(^{13}\)C NMR (150 MHz, DMSO-\( d_6 \)) \( \delta \): 15.2, 63.3, 102.5, 105.5, 116.1, 118.8, 119.3, 126.2, 128.1, 132.1, 132.4, 154.9, 155.8, 159.1. FT-IR (KBr) \( \nu \) (cm\(^{-1}\)): 759, 843, 982, 1103, 1176, 1293, 1480, 1618, 2925, 2983, 3156.

HRMS calcd for \( C_{14}H_{13}O_{3} \): 229.0870 [M-H], found: 229.0872.

4-(Trifluoromethoxy)-[1,1'-biphenyl]-2,2'-diol (2l)

Colorless solid (101 mg, 75%), mp 75-76 °C. \(^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \): 6.78-6.84(m, 2H), 6.86 (d, \( J = 1.2 \) Hz, 1H), 7.13-7.17 (m, 2H), 7.24 (d, \( J = 8.4 \) Hz, 1H), 9.60 (br s, 2H). \(^{13}\)C NMR (100 MHz, DMSO-\( d_6 \)) \( \delta \): 107.8, 110.6, 115.6, 118.6, 120.1 (q, \( J_{C-F} = 254.6 \) Hz), 124.4, 125.3, 128.4, 131.4, 132.6, 147.8, 154.6, 155.8. FT-IR (KBr) \( \nu \) (cm\(^{-1}\)): 752, 868, 986, 1095, 1147, 1482, 1569, 1572. HRMS calcd for \( C_{13}H_{8}F_{3}O_{3} \): 269.0431 [M-H], found: 269.0429.

4-Phenoxy-[1,1'-biphenyl]-2,2'-diol (2m)

Colorless syrup (106 mg, 76%). \(^1\)H NMR (600 MHz, DMSO-\( d_6 \)) \( \delta \): 6.47 (dd, \( J_1 = 8.4 \) Hz, \( J_2 = 2.4 \) Hz, 1H), 6.52 (d, \( J = 2.4 \) Hz, 1H), 6.81(t, \( J = 7.8 \) Hz, 1H), 6.88 (d, \( J = 7.8 \) Hz, 1H), 7.08 (d, \( J = 8.4 \) Hz, 2H), 7.10-7.17(m, 4H), 7.42 (t, \( J = 8.4 \) Hz, 2H), 9.14(br s, 1H) , 9.40(br s, 1H). \(^{13}\)C NMR (150 MHz, DMSO-\( d_6 \)) \( \delta \): 105.9, 109.1, 116.1, 119.2, 119.6, 121.5, 124.0, 125.7, 128.4, 130.5, 132.1, 132.9, 155.0, 156.2, 156.9, 157.2. FT-IR (KBr) \( \nu \) (cm\(^{-1}\)): 753, 829, 974, 1097, 1211, 1483, 1589, 2853, 2923, 3288. HRMS calcd for \( C_{18}H_{13}O_{3} \): 277.0870 [M-H], found: 277.0863.

1-(2,2'-Dihydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (2n)

Colorless solid (88 mg, 77%), mp 149-150 °C. \(^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \): 2.54 (s, 3H), 6.83 (td, \( J_1 = 7.2 \) Hz, \( J_2 = 0.8 \) Hz, 1H), 6.90 (d, \( J = 7.6 \) Hz, 1H), 7.14-7.18 (m, 2H), 7.28 (dd, \( J_1 = 6.8 \) Hz, \( J_2 = 1.6 \) Hz, 1H), 7.44-7.46 (m, 2H), 9.50 (br s, 2H). \(^{13}\)C NMR (100 MHz, DMSO-\( d_6 \)) \( \delta \): 26.7, 114.4, 115.6, 118.6, 119.1, 124.8, 128.6, 131.10, 131.15, 131.8, 136.6, 154.5, 154.8, 197.5. FT-IR (KBr) \( \nu \) (cm\(^{-1}\)): 757, 825,
1005, 1154, 1291, 1415, 1483, 1571, 1652, 2923, 3327. HRMS calcd for C_{14}H_{11}O_3: 227.0714 [M-H], found: 227.0720.

5-Fluoro-[1,1'-biphenyl]-2,2'-diol (2o)

Colorless solid (77 mg, 75%), mp 76-77 °C. ¹H NMR (400 MHz, DMSO-δ6) δ: 6.83 (td, J₁ = 7.6 Hz, J₂ = 1.2 Hz, 1H), 6.86-6.92 (m, 2H), 6.95-6.98 (m, 2H), 7.13-7.19 (m, 2H), 9.30 (br s, 2H). ¹³C NMR (100 MHz, DMSO-δ6) δ: 114.1 (d, ²J_{C-F} = 22.5 Hz), 115.7, 116.3 (d, ³J_{C-F} = 8.0 Hz), 117.4 (d, ²J_{C-F} = 22.5 Hz), 118.7, 124.6, 126.8 (d, ³J_{C-F} = 8.0 Hz), 128.5, 131.4, 150.8 (d, ⁴J_{C-F} = 1.4 Hz), 154.4, 155.1 (d, ¹J_{C-F} = 232.0 Hz). FT-IR (KBr) ν (cm⁻¹): 753, 822, 877, 1170, 1219, 1419, 1592, 3166. HRMS calcd for C_{12}H_{8}FO_2: 203.0514 [M-H], found: 203.0496.

5-Chloro-[1,1'-biphenyl]-2,2'-diol (2p)

Colorless solid (80 mg, 73%), mp 105-106 °C (lit.¹⁹ 109.2-109.7 °C). ¹H NMR (400 MHz, DMSO-δ6) δ: 6.80-6.84 (m, 1H), 6.91 (d, J = 8.0 Hz, 2H), 7.13-7.18 (m, 4H), 9.46 (br s, 2H). ¹³C NMR (100 MHz, DMSO-δ6) δ: 115.6, 117.1, 118.7, 121.9, 124.3, 127.5, 127.6, 128.5, 130.8, 131.3, 153.6, 154.4. FT-IR (KBr) ν (cm⁻¹): 755, 905, 1021, 1201, 1285, 1483, 1601, 3273. HRMS calcd for C_{12}H_{8}ClO_2: 219.0218 [M-H], found: 219.0223.

5-Methyl-[1,1'-biphenyl]-2,2'-diol (2q)

Colorless solid (71 mg, 71%), mp 83-84 °C (lit.²⁰ 81-83 °C). ¹H NMR (600 MHz, DMSO-δ6) δ: 2.23 (s, 3H), 6.81 (d, J = 7.8 Hz, 1H), 6.84 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.95-6.96 (m, 2H), 7.13-7.16(m, 2H), 9.07 (br s, 2H). ¹³C NMR (150 MHz, DMSO-δ6) δ: 20.6, 116.1, 116.2, 119.3, 126.2, 126.6, 127.7, 128.5, 128.9, 132.0, 132.4, 152.6, 154.9. FT-IR (KBr) ν (cm⁻¹): 756, 943, 1055, 1216, 1285, 1476, 1711, 3205. HRMS calcd for C_{13}H_{11}O_2: 199.0765 [M-H], found: 199.0767.

6-Fluoro-[1,1'-biphenyl]-2,2'-diol (2r)
Colorless solid (59 mg, 58%), mp 75-76 °C. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$: 6.60-6.65 (m, 1H), 6.72 (d, $J = 8.0$ Hz, 1H), 6.80 (td, $J_1 = 7.2$ Hz, $J_2 = 0.8$ Hz, 1H), 6.87-6.89 (m, 1H), 7.05 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz, 1H), 7.10-7.17 (m, 2H), 9.43 (br s, 2H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$: 105.4 (d, $^2$J$_{C-F}$ = 22.5 Hz), 111.2 (d, $^4$J$_{C-F}$ = 2.2 Hz), 114.0 (d, $^2$J$_{C-F}$ = 19.7 Hz), 115.3, 118.4, 119.1, 128.4 (d, $^3$J$_{C-F}$ = 10.9 Hz), 128.6, 131.9, 155.2, 156.5 (d, $^3$J$_{C-F}$ = 7.3 Hz), 160.6 (d, $^1$J$_{C-F}$ = 240.0 Hz). FT-IR (KBr) $\nu$ (cm$^{-1}$): 756, 831, 1003, 1111, 1449, 1465, 1607, 3359, 3561. HRMS calcd for C$_{12}$H$_8$FO$_2$: 203.0514 [M-H], found: 203.0497.

6-Chloro-[1,1'-biphenyl]-2,2'-diol (2s)

Colorless solid (61 mg, 55%), mp 115-116 °C (lit.$^{19}$ 117.2-117.7 °C). $^1$H NMR (600 MHz, DMSO-d$_6$) $\delta$: 6.80 (t, $J = 7.8$ Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 6.91 (d, $J = 7.8$ Hz, 1H), 6.95 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.8$ Hz, 1H), 7.11-7.16 (m, 2H), 9.16 (br s, 1H), 9.49 (br s, 1H). $^{13}$C NMR (150 MHz, DMSO-d$_6$) $\delta$: 114.4, 115.8, 118.9, 119.7, 123.4, 125.8, 129.0, 129.2, 131.9, 134.6, 155.4, 157.0. FT-IR (KBr) $\nu$ (cm$^{-1}$): 750, 941, 1043, 1225, 1279, 1483, 1703, 3203. HRMS calcd for C$_{12}$H$_8$ClO$_2$: 219.0218 [M-H], found: 219.0197.

6-Methyl-[1,1'-biphenyl]-2,2'-diol (2t)

Colorless solid (50 mg, 50%), mp 99-100 °C (lit.$^{21}$ 101-102 °C). $^1$H NMR (600 MHz, DMSO-d$_6$) $\delta$: 1.95 (s, 3H), 6.68 (d, $J = 7.8$ Hz, 1H), 6.70 (d, $J = 7.8$ Hz, 1H), 6.80 (t, $J = 7.8$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 6.93 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.8$ Hz, 1H), 7.00 (t, $J = 7.8$ Hz, 1H), 7.11-7.13 (m, 1H), 8.84 (br s, 1H), 9.02 (br s, 1H). $^{13}$C NMR (150 MHz, DMSO-d$_6$) $\delta$: 20.4, 113.1, 115.8, 119.1, 120.5, 125.1, 126.3, 127.8, 128.3, 131.9, 138.2, 155.2, 155.3. FT-IR (KBr) $\nu$ (cm$^{-1}$): 750, 941, 1043, 1225, 1279, 1483, 1703, 3203. HRMS calcd for C$_{13}$H$_{11}$O$_2$: 199.0765 [M-H], found: 199.0767.

5-Methoxy-[1,1'-biphenyl]-2,2'-diol (2u)
Colorless syrup (81 mg, 75%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 3.70 (s, 3H), 6.77-6.78 (m, 2H), 6.86 (d, $J = 7.2$ Hz, 2H), 6.94 (d, $J = 7.8$ Hz, 1H), 7.17 (t, $J = 7.8$ Hz, 1H), 7.21 (d, $J = 7.8$ Hz, 1H), 9.02 (br s, 2H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 55.8, 114.0, 116.4, 116.9, 117.1, 119.5, 126.3, 127.0, 128.7, 132.0, 148.7, 152.5, 154.8. FT-IR (KBr) $\nu$ (cm$^{-1}$): 756, 835, 1039, 1163, 1292, 1492, 1575, 1622, 2925, 3285. HRMS calcd for C$_{13}$H$_{11}$O$_3$: 215.0714 [M-H]$^-$; found: 215.0694.

3-(2-Hydroxyphenyl)naphthalen-2-ol (2v) $^{22}$

Colorless syrup (68 mg, 58%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 6.85 (t, $J = 7.8$ Hz, 1H), 6.92 (d, $J = 8.4$ Hz, 1H), 7.17-7.21 (m, 3H), 7.26 (t, $J = 7.8$ Hz, 1H), 7.38 (t, $J = 8.4$ Hz, 1H), 7.67-7.69 (m, 2H), 7.76 (d, $J = 7.8$ Hz, 1H), 9.22 (br s, 1H), 9.61 (br s, 1H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 109.3, 116.0, 119.1, 123.2, 125.9, 126.2, 126.3, 128.0, 128.1, 128.8, 129.6, 130.8, 132.0, 134.3, 154.2, 155.3. FT-IR (KBr) $\nu$ (cm$^{-1}$): 745, 839, 1102, 1167, 1279, 1443, 1632, 1703, 2923, 3281. HRMS calcd for C$_{16}$H$_{11}$O$_2$: 235.0765 [M-H]$^-$; found: 235.0761.

4-Fluoro-4’-methoxy-[1,1’-biphenyl]-2,2’-diol (2w)

Colorless solid (90 mg, 77%), mp 89-90 ºC. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 3.68 (s, 3H), 6.39 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 1H), 6.45 (d, $J = 2.4$ Hz, 1H), 6.59 (td, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz, 1H), 6.65 (dd, $J_1 = 10.8$ Hz, $J_2 = 2.4$ Hz, 1H), 7.00 (d, $J = 8.4$ Hz, 1H), 7.08 (t, $J = 7.6$ Hz, 1H), 9.41 (br s, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 54.8, 101.4, 102.4 (d, $^2$J$_{C-F} = 24.0$ Hz), 104.3, 105.1 (d, $^2$J$_{C-F} = 20.3$ Hz), 117.5, 122.1 (d, $^4$J$_{C-F} = 2.9$ Hz), 132.0, 132.6 (d, $^3$J$_{C-F} = 9.5$ Hz), 155.5, 156.0 (d, $^3$J$_{C-F} = 10.9$ Hz), 159.4, 161.6 (d, $^1$J$_{C-F} = 240.8$ Hz). FT-IR (KBr) $\nu$ (cm$^{-1}$): 730, 832, 971, 1151, 1264, 1418, 1496, 1606, 2923, 3335. HRMS calcd for C$_{16}$H$_{10}$FO$_3$: 233.0619 [M-H]$^-$; found: 233.0609.

3. Preparation of 1-hydroxy-[1,1’-binaphthalen]-2(1H)-one (3)

To a tube containing [1,1’-binaphthalen]-2-ol (1x, 135 mg, 0.5 mmol) were added Pd(OAc)$_2$ (5.6 mg, 0.025 mmol), Cs$_2$CO$_3$ (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH$_3$CN (2 mL) and TBHP (0.27
mL, 70% aqueous solution, 2 mmol) under air. The tube was then sealed, and stirred at 80 °C for 18 h. Afterwards, the reaction was quenched with saturated NH$_4$Cl (10 mL), and extracted with EtOAc (6 mL × 3). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, and concentrated under vacuum. The residue was separated by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to afford 1-hydroxy-[1,1’-binaphthalen]-2(1H)-one (3, 64 mg, 45%) and recover 1x (62 mg, 46%).

1-Hydroxy-[1,1’-binaphthalen]-2(1H)-one (3)

White solid (64 mg, 45%), mp 196-197 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ: 3.32 (s, 1H), 6.35 (d, $J = 10.2$ Hz, 1H), 7.18-7.19 (m, 1H), 7.22-7.25 (m, 2H), 7.32-7.38 (m, 3H), 7.43 (d, $J = 6.6$ Hz, 1H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.60 (d, $J = 10.2$ Hz, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.83 (d, $J = 8.4$ Hz, 1H), 8.00 (dd, $J_1 = 7.2$ Hz, $J_2 = 0.6$ Hz, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 77.4, 123.9, 124.45, 124.51, 125.0, 125.5, 126.4, 129.03, 129.05, 129.3, 129.37, 129.43, 129.8, 130.0, 130.9, 134.2, 138.0, 142.9, 145.2, 200.4. HRMS calcd for C$_{20}$H$_{14}$O$_2$Na: 309.0886 [M+Na]$^+$, found: 309.0882.
III. Mechanism studies

1. Control experiment 1

To a tube containing 2-phenylphenol (1a, 85 mg, 0.5 mmol) were added Pd(OAc)$_2$ (5.6 mg, 0.025 mmol), Cs$_2$CO$_3$ (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH$_3$CN (2 mL), TBHP (0.27 mL, 70% aqueous solution, 2 mmol) and TEMPO (156.3 mg, 1 mmol) under air (Scheme 1). The tube was then sealed, and stirred at 80 ºC for 18 h. Afterwards, the reaction was quenched with saturated NH$_4$Cl (10 mL), and extracted with EtOAc (6 mL × 3). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to afford 2a (33 mg, 35%).

To a tube containing 2-phenylphenol (1a, 85 mg, 0.5 mmol) were added Pd(OAc)$_2$ (5.6 mg, 0.025 mmol), Cs$_2$CO$_3$ (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH$_3$CN (2 mL), TBHP (0.27 mL, 70% aqueous solution, 2 mmol) and TEMPO (312.6 mg, 2 mmol) under air (Scheme 1). The tube was then sealed, and stirred at 80 ºC for 18 h. Afterwards, the reaction was quenched with saturated NH$_4$Cl (10 mL), and extracted with EtOAc (6 mL × 3). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, and concentrated under vacuum. The residue was separated by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to give trace amount of 2a and 72 mg of 1a.

![Scheme 1. Control experiment 1](image-url)

2. Control experiment 2

To a tube containing 2-methoxy-1,1′-biphenyl (A, 92 mg, 0.5 mmol) were added Pd(OAc)$_2$ (5.6 mg, 0.025 mmol), Cs$_2$CO$_3$ (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH$_3$CN (2 mL) and TBHP (0.27 mL, 70% aqueous solution, 2 mmol) under air (Scheme 2). The tube was then sealed, and stirred at 80 ºC for 18 h. Afterwards, the reaction was quenched with saturated NH$_4$Cl (10 mL), and extracted with
EtOAc (6 mL × 3). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, and concentrated under vacuum. The residue was separated by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to give 86 mg of A.

**Scheme 2.** Control experiment 2

### 3. The intermolecular KIE experiments

To two tubes, one containing 2-phenylphenol (1a, 85.1 mg, 0.5 mmol) and another one containing 2-phenylphenol-$d_5$ (1a-$d_5$, 87.6 mg, 0.5 mmol), were respectively added Pd(OAc)$_2$ (5.6 mg, 0.025 mmol), Cs$_2$CO$_3$ (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH$_3$CN (2 mL) and TBHP (0.27 mL, 70% aqueous solution, 2 mmol) under air. After being sealed, the two tubes were stirred side-by-side in an oil bath at 80 ºC for 3 h. Then, the reactions were quenched with saturated NH$_4$Cl (10 mL), and extracted with EtOAc (6 mL × 3). The following purifications via column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent afforded 2a (39 mg, 42%) and 2a-$d_5$ (22 mg, 23%), respectively. From these results, an intermolecular KIE ($k_{H}/k_{D}$) value of 1.8 is obtained.

**Scheme 3.** Intermolecular KIE experiments

### 4. The intramolecular KIE experiments

To a tube containing 2'-deuterio-biphenyl-2-ol (1a-$d_1$, 85.6 mg, 0.5 mmol) were added Pd(OAc)$_2$ (5.6 mg, 0.025 mmol), Cs$_2$CO$_3$ (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH$_3$CN (2 mL) and
TBHP (0.27 mL, 70% aqueous solution, 2 mmol) under air. After being sealed, the tube was stirred at 80 ºC for 3 h. Then, the reaction was quenched with saturated NH₄Cl (10 mL), and extracted with EtOAc (6 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to afford a mixture of 2a and 2a-d₁. Upon analyzing the corresponding ¹H NMR spectrum as shown in Fig 1, the ratio of 2a and 2a-d₁ in the resulting mixture was determined as 0.75:0.25. Accordingly, the intramolecular KIE (k_H/k_D) was calculated as 3.0.

**Scheme 4.** The intramolecular KIE experiment

**Fig 1.** The ¹H NMR spectrum of the products obtained from the intramolecular KIE experiment
IV. Copies of $^1$H and $^{13}$C NMR Spectra of 1b-1x
V. Copies of $^1$H and $^{13}$C NMR Spectra of 1a-$d_5$ and 1a-$d_1$
VI. Copies of $^1$H and $^{13}$C NMR spectra of 2a-2w
VII. Copies of $^1$H and $^{13}$C NMR Spectra of 3
VIII. References