Heterogeneously Catalyzed *Aerobic* Oxidative Biaryl Coupling of 2-Naphthols and Substituted Phenols *in Water*

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1,1'-Bi-2,2'-naphthol (1b): ¹H NMR (270 MHz, CD₃CN, 298 K): δ 6.65 (s, 2H), 6.99 (d, *J* = 8.6, 2H), 7.19-7.33 (m, 6H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.94 (d, *J* = 8.9 Hz, 2H). ¹³C{¹H} NMR (67.8 MHz, CD₃CN, 298 K): δ 114.5, 119.2, 124.1, 125.0, 127.5, 129.0, 130.1, 131.0, 135.2, 154.1.

6,6'-Dibromo-1,1'-bi-2,2'-naphthol (2b): ¹H NMR (270 MHz, CD₃CN, 298 K): δ 6.89 (d, *J* = 9.1 Hz, 2H), 6.92 (s, 2H), 7.28 (dd, *J* = 2.1, 9.0 Hz, 2H), 7.33 (d, *J* = 8.9 Hz, 2H), 7.86 (d, *J* = 8.9 Hz, 2H), 8.06 (d, *J* = 2.0 Hz, 2H). ¹³C{¹H} NMR (67.8 MHz, CD₃CN, 298 K): δ 114.5, 117.2, 120.5, 127.1, 130.3, 130.4, 130.9, 131.1, 133.7, 154.6.

6,6'-Dimethoxy-1,1'-bi-2,2'-naphthol (3b): ¹H NMR (270 MHz, CDCl₃, 298 K): δ 3.93 (s, 6H), 5.00 (s, 2H), 6.97 (dd, *J* = 2.3, 9.2 Hz, 2H), 7.05 (d, *J* = 9.2 Hz, 2H), 7.19 (d, *J* = 2.3 Hz, 2H), 7.33 (d, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 9.0 Hz, 2H). ¹³C{¹H} NMR (67.8 MHz, CDCl₃, 298 K): δ 55.3, 106.8, 111.4, 118.1, 119.7, 125.8, 128.5, 129.9, 130.3, 150.9, 156.3.

7,7'-Dimethoxy-1,1'-bi-2,2'-naphthol (4b): ¹H NMR (270 MHz, CDCl₃, 298 K): δ 3.57 (s, 6H), 5.14 (s, 2H), 6.48 (d, *J* = 2.5 Hz, 2H), 7.03 (dd, *J* = 2.6, 8.8 Hz, 2H), 7.22 (d, *J* = 8.9 Hz,

2H), 7.78 (d, $J = 9.1$ Hz, 2H), 7.87 (d, $J = 8.9$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3 , 298 K): δ 55.1, 103.1, 110.1, 115.1, 116.0, 124.7, 130.0, 131.1, 134.7, 153.3, 159.1.

7,7'-Dihydroxy-1,1'-bi-2,2'-naphthol (5b): ^1H NMR (270 MHz, CD_3CN , 298 K): δ 6.31 (d, $J=2.5$ Hz, 2H), 6.46 (s, 2H), 6.86 (d, $J = 2.5$ Hz, 2H), 6.89 (d, $J = 2.5$ Hz, 2H), 7.09 (d, $J = 2.5$ Hz, 2H), 7.75 (d, $J = 8.7$ Hz, 2H), 7.81 (d, $J = 8.7$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CD_3CN , 298 K): δ 106.9, 113.1, 115.9, 116.2, 125.0, 130.7, 130.8, 136.8, 154.5, 156.6.

10,10'-Bi-9,9'-phenanthrol (6b): ^1H NMR (270 MHz, CDCl_3 , 298 K): δ 5.78 (s, 2H), 7.26 (dd, $J = 1.4, 8.0$ Hz, 2H), 7.33 (td, $J = 1.2, 7.5$ Hz, 2H), 7.45-7.51 (m, 2H), 7.67-7.13 (m, 2H), 7.79 (td, $J = 1.4, 7.6$ Hz, 2H), 8.46 (dd, $J = 1.2, 8.0$ Hz, 2H), 8.71 (d, $J = 8.1$, 2H), 8.77 (d, $J = 8.1$ Hz, 2H).

1,1'-Bi-2,2'-naphthol-3,3',4,4',5,5',6,6',7,7',8,8'- d_{12} (7b): $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CD_3CN , 298 K): δ 110.8, 117.3 (t, $J = 24.0$ Hz), 123.5 (t, $J = 24.0$ Hz), 123.8 (t, $J = 24.0$ Hz), 126.9 (t, $J = 24.0$ Hz), 127.9 (t, $J = 24.0$ Hz), 129.2, 130.9 (t, $J = 24.0$ Hz), 133.3, 152.7. MS (70 eV, EI): m/z (%): 299 (23), 298 (100) [M^+], 297 (11), 268 (12), 125 (11).

3,3',5,5'-tetra-*tert*-butyl-2,2'-dihydroxybiphenyl (8b): ^1H NMR (270 MHz, CDCl_3 , 298 K): δ 1.32 (s, 18 H), 1.45 (s, 18H), 5.28 (s, 2H), 7.11 (d, $J = 2.5$ Hz, 2H), 7.40 (d, $J = 2.5$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3 , 298 K): δ 29.6, 31.5, 34.4, 35.1, 122.4, 124.8, 125.2, 136.2, 142.7, 149.7. MS (70 eV, EI): m/z (%): 411 (33), 410 (100) [M^+], 396 (30), 395 (89), 354 (29), 340 (25), 339 (96), 283 (41), 227 (22), 190 (46), 176 (12), 57 (100), 41 (19).

3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenquinone (9b): ^1H NMR (270 MHz, CDCl_3 , 298 K): δ 1.37 (s, 36H), 7.71 (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3 , 298 K): δ 29.6, 36.0, 126.0, 136.1, 150.4, 186.5.

3,3',5,5'-tetramethyl-4,4'-diphenquinone (10b): ^1H NMR (270 MHz, CDCl_3 , 298 K): δ 2.16 (s, 12H), 7.73 (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (67.8 MHz, CDCl_3 , 298 K): δ 17.1, 129.7, 135.6, 138.9, 187.3.

Figure S1. XPS spectra of Ru 3p region of (a) fresh Ru(OH)_x/Al₂O₃ and (b) Ru(OH)_x/Al₂O₃ recovered after the reaction with **1a** under argon.

Figure S2. Mass spectra of (a) **1b**, (b) **7b**, and the mixture of the isolated products of the competitive oxidation of **1a** and **7b** under the conditions in eq 4.

Figure S3. A $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the compound **7b**.