

Supporting Information

Ruthenium-catalyzed coupling of α -carbonyl phosphoniums with sulfoxonium ylides *via* C-H activation/Wittig reaction sequences

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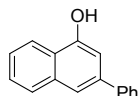
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I. General Information

All reagents and solvents used in this work were obtained from commercial sources and were used without further purification. Thin-layer chromatography (TLC) was performed on silica gel GF254 (0.25 mm thickness) plates and visualized under UV light. Organic solutions were concentrated under reduced pressure at 40 °C (water bath temperature) using a Büchi rotary evaporator, unless otherwise noted. Column chromatography was performed on silica gel (200-300 mesh). ¹H, ¹³C and ¹⁹F NMR spectra were recorded with Bruker Avance III HD (400 MHz, 101 MHz and 376 MHz respectively) spectrometers. NMR spectra are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quarter, m = multiplet, br = broad), coupling (*J*) constant and integration. High resolution mass spectra (HRMS) were recorded on a Waters TOFMS GCT Premier using ESI ionization. All phosphonium salts **1** were prepared according to literature reports¹.

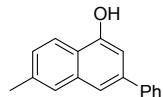
II. General Procedures for the Synthesis of **3**

A suspension of arylacyl phosphonium salts **1** (0.10 mmol), sulfoxonium ylides **2** (0.15 mmol), [RuCl₂(*p*-cymene)]₂ (3.1 mg, 5.0 mol %), and NaOAc (2.0 equiv.) in EtOH (1.0 mL) was stirred at 120 °C for 10 h under an ambient atmosphere of N₂. After completion, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (n-hexane/EtOAc: 30/1~10/1) to yield the corresponding products.



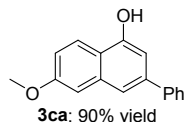
3aa: 96% yield

3-Phenyl-1-naphthol (3aa): known compound², 21.1 mg, 96% yield, yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 7.7 Hz, 1H), 7.92 – 7.85 (m, 1H), 7.70 – 7.66 (m, 3H), 7.53 – 7.45 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 1.5 Hz, 1H), 5.43 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 151.7, 140.9, 138.9, 134.9, 128.8, 128.0, 127.4, 127.3, 126.9, 125.3, 123.5, 121.5, 118.7, 108.4.

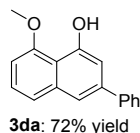


3ba: 94% yield

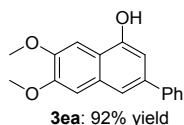
6-Methyl-3-phenyl-1-naphthol (3ba): unknown compound, 22.0 mg, 94% yield, yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.6 Hz, 1H), 7.69-7.66 (m, 2H), 7.64 (s, 1H), 7.57 (s, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.02 (s, 1H), 5.43 (s, 1H), 2.53 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151.7, 141.0, 138.9, 136.6, 135.2, 128.8, 127.6, 127.3, 127.3, 127.0, 121.7, 121.3, 118.2, 107.6, 21.7. HRMS (ESI) *m/z*: calcd for C₁₇H₁₄NaO [M+Na]⁺: 257.0937, found: 257.0921.



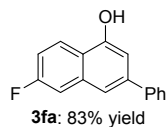
6-Methoxy-3-phenylnaphthalen-1-ol (3ca): unknown compound, 22.5 mg, 90% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.9$ Hz, 1H), 7.67 (d, $J = 7.2$ Hz, 2H), 7.55 (s, 1H), 7.51-7.44 (m, 2H), 7.42-7.34 (m, 1H), 7.14 (d, $J = 13.2$ Hz, 2H), 6.94 (s, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.5, 151.9, 141.0, 139.7, 136.4, 128.8, 127.4, 127.3, 123.3, 118.8, 117.8, 117.8, 106.5, 106.1, 55.3. HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{14}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 273.0886, found: 273.0875.



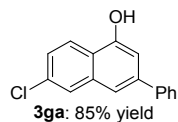
8-Methoxy-3-phenylnaphthalen-1-ol (3da): known compound³, 18.0 mg, 72% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 9.36 (s, 1H), 7.72 (d, $J = 7.1$ Hz, 2H), 7.53 (d, $J = 1.7$ Hz, 1H), 7.50-7.45 (m, 3H), 7.35 (dt, $J = 16.0$, 7.7 Hz, 2H), 7.19 (d, $J = 1.7$ Hz, 1H), 6.78 (d, $J = 7.7$ Hz, 1H), 4.08 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.1, 154.8, 140.6, 140.4, 136.9, 128.7, 127.5, 127.3, 126.1, 122.1, 116.9, 114.2, 109.8, 103.9, 56.1.



6,7-Dimethoxy-3-phenylnaphthalen-1-ol (3ea): unknown compound, 25.8 mg, 92% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 12.0$ Hz, 2H), 7.43 (t, $J = 7.5$ Hz, 2H), 7.34 (t, $J = 7.2$ Hz, 1H), 7.16 (s, 1H), 6.97 (s, 1H), 4.05 (br, 1H), 4.02 (s, 3H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.0, 150.0, 148.9, 141.1, 137.3, 130.9, 128.7, 127.0, 124.9, 118.8, 117.1, 107.0, 106.6, 100.7, 55.8, 55.8. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$: 281.1172, found: 281.1190.

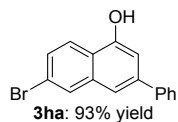


6-Fluoro-3-phenylnaphthalen-1-ol (3fa): known compound⁴, 20.0 mg, 83% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.19-8.15 (m, 1H), 7.62 (d, $J = 8.0$ Hz, 2H), 7.53 (s, 1H), 7.46-7.42 (m, 3H), 7.38-7.33 (m, 1H), 7.24-7.19 (m, 1H), 6.97 (s, 1H), 5.54 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.5 ($J = 246.6$ Hz), 151.9, 140.4 ($J = 23.0$ Hz), 136.0 ($J = 9.7$ Hz), 128.8, 127.7, 127.3, 124.5 ($J = 9.3$ Hz), 120.6, 118.0, 118.0, 115.4 ($J = 25.2$ Hz), 111.0 ($J = 20.6$ Hz), 107.7 ($J = 2.2$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -114.0.

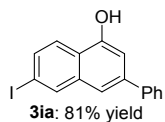


6-Chloro-3-phenylnaphthalen-1-ol (3ga): unknown compound, 21.6 mg, 85% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.9$ Hz, 1H), 7.84-7.82 (m, 1H), 7.65 (d, $J = 7.4$ Hz, 2H), 7.54 (s, 1H), 7.49-7.45 (m, 2H), 7.43-7.30 (m, 2H), 7.04 (s, 1H), 5.52 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.8, 140.4, 140.3, 135.7, 132.8,

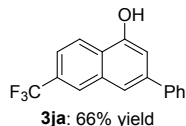
128.9, 127.7, 127.3, 126.5, 126.0, 123.5, 121.8, 117.8, 108.6. HRMS (ESI) m/z : calcd for $C_{16}H_{13}ClO$ $[M+H]^+$: 255.0571, found: 255.0580.



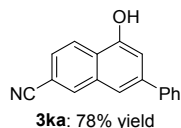
6-Bromo-3-phenylnaphthalen-1-ol (3ha): known compound⁴, 28.0 mg, 93% yield, yellow solid; 1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, $J = 8.9$ Hz, 1H), 8.01 (d, $J = 2.0$ Hz, 1H), 7.66-7.64 (m, 2H), 7.56-7.52 (m, 2H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.42-7.36 (m, 1H), 7.08 (d, $J = 1.6$ Hz, 1H), 5.46 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 140.5, 140.3, 136.1, 129.9, 128.9, 128.5, 127.8, 127.3, 123.6, 122.0, 121.2, 117.7, 108.8.



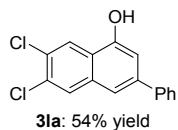
6-Iodo-3-phenylnaphthalen-1-ol (3ia): unknown compound, 28.0 mg, 81% yield, yellow solid; 1H NMR (400 MHz, $CDCl_3$) δ 8.26-8.23 (m, 1H), 7.92 (d, $J = 8.8$ Hz, 1H), 7.71 (dd, $J = 8.8, 1.7$ Hz, 1H), 7.67-7.62 (m, 2H), 7.51-7.44 (m, 3H), 7.41-7.36 (m, 1H), 7.08 (d, $J = 1.5$ Hz, 1H), 5.47 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 140.4, 140.0, 136.5, 136.5, 133.7, 128.9, 127.7, 127.3, 123.4, 122.3, 117.5, 108.9, 93.1. HRMS (ESI) m/z : calcd for $C_{16}H_{12}IO$ $[M+H]^+$: 346.9927, found: 346.9939.



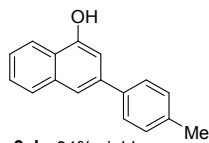
3-Phenyl-6-(trifluoromethyl)naphthalen-1-ol (3ja): unknown compound, 19.0 mg, 66% yield, yellow solid; 1H NMR (400 MHz, $DMSO-d_6$) δ 8.31 (d, $J = 8.5$ Hz, 1H), 8.16 (s, 1H), 7.72 (s, 1H), 7.69-7.60 (m, 3H), 7.52-7.47 (m, 2H), 7.43-7.39 (m, 1H), 7.19-7.17 (m, 1H), 5.55 (s, 1H). ^{13}C NMR (101 MHz, $DMSO-d_6$) δ 151.7, 140.4, 140.2, 133.8, 129.0, 128.6, 127.9, 127.3, 125.7, 125.57 (q, $J = 4.6$ Hz), 124.7, 123.1, 120.74 (q, $J = 3.0$ Hz), 119.3, 110.3. HRMS (ESI) m/z : calcd for $C_{17}H_{12}F_3O$ $[M+H]^+$: 289.0835, found: 289.0834.



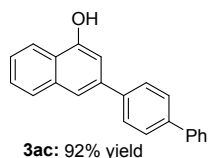
5-Hydroxy-7-phenyl-2-naphthonitrile (3ka): unknown compound, 19.1 mg, 78% yield, yellow solid; 1H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 8.53 (s, 1H), 8.26 (d, $J = 8.9$ Hz, 1H), 7.80 (s, 1H), 7.73-7.68 (m, 3H), 7.55-7.49 (m, 2H), 7.44 (d, $J = 6.8$ Hz, 1H), 7.34 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 140.2, 139.7, 134.3, 133.6, 129.1, 128.0, 126.9, 125.1, 125.0, 123.6, 119.3, 116.7, 110.2, 109.1. HRMS (ESI) m/z : calcd for $C_{17}H_{12}NO$ $[M+H]^+$: 246.0913, found: 246.0912.



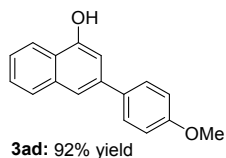
6,7-Dichloro-3-phenylnaphthalen-1-ol (3la): unknown compound, 15.6 mg, 54% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 9.0$ Hz, 1H), 8.06 (s, 1H), 7.70 (d, $J = 7.4$ Hz, 2H), 7.52-7.46 (m, 3H), 7.41 (t, $J = 7.3$ Hz, 1H), 7.13 (s, 1H), 5.46 (br, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.0, 140.3, 139.4, 132.4, 130.7, 128.4, 128.0, 127.0, 126.5, 125.4, 121.9, 120.8, 114.6, 108.2. HRMS (ESI) m/z : calcd for $\text{C}_{16}\text{H}_9\text{Cl}_2\text{O}$ [$\text{M}-\text{H}$] $^-$: 287.0030, found: 287.0036.



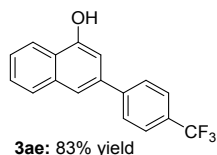
3-(p-Tolyl)naphthalen-1-ol (3ab): known compound², 22.0 mg, 94% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.18-8.15 (m, 1H), 7.87-7.83 (m, 1H), 7.64-7.64 (m, 1H), 7.61-7.56 (m, 2H), 7.54-7.45 (m, 2H), 7.32-7.26 (m, 2H), 7.09 (d, $J = 1.6$ Hz, 1H), 5.36 (br, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.7, 138.8, 138.0, 137.3, 135.0, 129.5, 127.9, 127.1, 126.8, 125.1, 123.4, 121.4, 118.4, 108.3, 21.1.



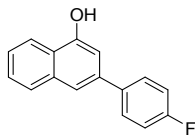
3-([1,1'-Biphenyl]-4-yl)naphthalen-1-ol (3ac): known compound⁴, 27.3 mg, 92% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.0$ Hz, 1H), 7.92-7.84 (m, 1H), 7.79-7.74 (m, 2H), 7.73-7.64 (m, 5H), 7.56-7.45 (m, 4H), 7.39-7.35 (m, 1H), 7.15 (s, 1H), 5.49 (br, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.8, 140.6, 140.3, 139.8, 138.3, 135.0, 128.8, 128.0, 127.6, 127.5, 127.4, 127.0, 126.9, 125.3, 123.6, 121.5, 118.6, 108.2.



3-(4-Methoxyphenyl)naphthalen-1-ol (3ad): known compound², 23.0 mg, 92% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 7.9$ Hz, 1H), 7.85 (d, $J = 7.7$ Hz, 1H), 7.61 (d, $J = 8.8$ Hz, 3H), 7.53-7.44 (m, 2H), 7.09-6.98 (m, 3H), 5.57 (br, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.2, 151.7, 138.5, 135.0, 133.4, 128.4, 127.9, 126.8, 125.0, 123.3, 121.4, 117.9, 114.3, 108.2, 55.4.

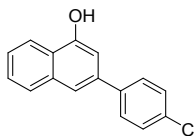


3-(4-(Trifluoromethyl)phenyl)naphthalen-1-ol (3ae): known compound², 23.9 mg, 83% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.23-8.17 (m, 1H), 7.90-7.85 (m, 1H), 7.78 (d, $J = 8.2$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H), 7.67 (s, 1H), 7.57-7.49 (m, 2H), 7.08 (d, $J = 1.6$ Hz, 1H), 5.43 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.0, 144.4, 137.3, 134.8, 129.4 (q, $J = 32.5$ Hz), 128.1, 127.5, 127.1, 125.9, 125.73 (q, $J = 3.8$ Hz), 123.9, 122.9, 121.5, 119.3, 108.0. ^{19}F NMR (377 MHz, CDCl_3) δ -62.4.



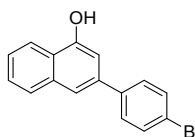
3af: 85% yield

3-(4-Fluorophenyl)naphthalen-1-ol (3af): known compound², 20.3 mg, 85% yield, yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.20-8.13 (m, 1H), 7.89-7.83 (m, 1H), 7.67-7.57 (m, 3H), 7.54-7.45 (m, 2H), 7.20-7.12 (m, 2H), 7.04 (d, *J* = 1.5 Hz, 1H), 5.40 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 162.5 (d, *J* = 246.7 Hz), 151.8, 137.9, 137.0, 134.9, 128.8, 128.8 (d, *J* = 8.1 Hz), 128.0, 127.0, 125.4, 123.5, 121.4, 118.6, 115.7 (d, *J* = 21.4 Hz), 108.2. ¹⁹F NMR (377 MHz, CDCl₃) δ -115.4.



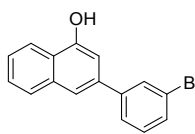
3ag: 87% yield

3-(4-Chlorophenyl)naphthalen-1-ol (3ag): known compound², 22.2 mg, 87% yield, yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 9.2 Hz, 3H), 7.55-7.47 (m, 2H), 7.46-7.40 (m, 2H), 7.03 (s, 1H), 5.46 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 151.9, 139.3, 137.6, 134.9, 133.5, 129.0, 128.5, 128.0, 127.1, 125.5, 123.6, 121.5, 118.7, 108.0.



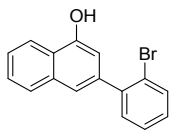
3ah: 86% yield

3-(4-Bromophenyl)naphthalen-1-ol (3ah): known compound⁴, 25.7 mg, 86% yield, yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.87-7.82 (m, 1H), 7.62-7.57 (m, 3H), 7.56-7.47 (m, 4H), 7.04 (d, *J* = 1.6 Hz, 1H), 5.37 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 151.9, 139.8, 137.6, 134.9, 131.9, 128.9, 128.0, 127.1, 125.6, 123.7, 121.7, 121.5, 118.7, 107.9.



3ai: 80% yield

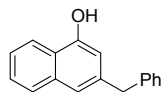
3-(3-Bromophenyl)naphthalen-1-ol (3ai): known compound², 23.9 mg, 80% yield, yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.22-8.14 (m, 1H), 7.89-7.79 (m, 2H), 7.66-7.44 (m, 5H), 7.37-7.29 (m, 1H), 7.05 (d, *J* = 1.6 Hz, 1H), 5.42 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 151.9, 143.1, 137.3, 134.8, 130.4, 130.3, 130.3, 128.1, 127.1, 125.9, 125.7, 123.8, 122.9, 121.5, 118.9, 108.0.



3aj: 51% yield

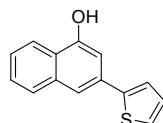
3-(2-Bromophenyl)naphthalen-1-ol (3aj): known compound⁵, 15.3 mg, 51% yield, yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.22-8.18 (m, 1H), 7.71-7.67 (m, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.54-7.50 (m, 2H), 7.44 (s, 1H),

7.42-7.35 (m, 2H), 7.25-7.20 (m, 1H), 6.92 (d, $J = 1.3$ Hz, 1H), 5.38 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.8, 142.2, 138.8, 134.4, 133.1, 131.4, 128.9, 128.0, 127.4, 126.8, 125.6, 123.6, 121.6, 121.2, 110.5.



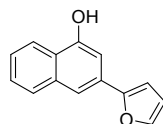
3ak: 84% yield

3-Benzyl-1-naphthol (3ak): known compound⁶, 19.7 mg, 84% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.12-8.09 (m, 1H), 7.76-7.7 (m, 1H), 7.50-7.41 (m, 2H), 7.32-7.27 (m, 3H), 7.24-7.20 (m, 3H), 6.63 (d, $J = 1.4$ Hz, 1H), 5.15 (s, 1H), 4.07 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.4, 140.8, 139.0, 134.8, 129.0, 128.5, 127.3, 126.6, 126.2, 124.8, 123.1, 121.4, 120.0, 110.1, 42.1.



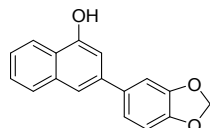
3al: 90% yield

3-(Thiophen-2-yl)naphthalen-1-ol (3al): known compound², 20.4 mg, 90% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 3H), 7.50 – 7.44 (m, 2H), 7.06 – 6.99 (m, 3H), 5.57 (br, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.2, 151.7, 138.5, 135.0, 133.4, 128.3, 127.9, 126.8, 125.0, 123.3, 121.4, 118.0, 114.3, 108.2, 55.4.



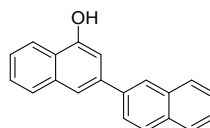
3am: 87% yield

3-(Furan-2-yl)naphthalen-1-ol (3am): known compound², 18.3 mg, 87% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 8.1$ Hz, 1H), 7.84-7.79 (m, 1H), 7.76 (s, 1H), 7.52-7.42 (m, 3H), 7.15-7.12 (m, 1H), 6.72 (d, $J = 3.4$ Hz, 1H), 6.53-6.49 (m, 1H), 5.38 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.8, 151.7, 142.3, 134.9, 128.4, 128.0, 127.0, 125.3, 123.8, 121.5, 115.3, 111.8, 105.6, 104.9.



3an: 88% yield

3-(Benzo[d][1,3]dioxol-5-yl)naphthalen-1-ol (3an): unknown compound, 23.3 mg, 88% yield, yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.59-7.43 (m, 3H), 7.16-7.13 (m, 2H), 7.04-6.98 (m, 1H), 6.91 (d, $J = 7.9$ Hz, 1H), 6.02 (s, 2H), 5.42 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.7, 148.1, 147.2, 138.6, 135.3, 134.9, 127.9, 126.9, 125.1, 123.4, 121.4, 120.8, 118.2, 108.6, 108.3, 107.8, 101.2. HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{11}\text{O}_3$ [$\text{M}-\text{H}$] $^-$: 263.0708, found: 263.0713.

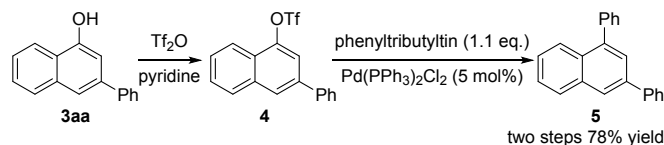


3ao: 90% yield

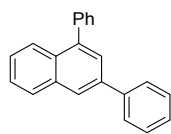
[2,2'-Binaphthalen]-4-ol (3aa): known compound², 24.3 mg, 90% yield, yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.22-8.19 (m, 1H), 8.13 (d, *J* = 1.7 Hz, 1H), 7.96-7.88 (m, 4H), 7.86-7.83 (m, 1H), 7.79 (s, 1H), 7.57-7.48 (m, 4H), 7.23 (d, *J* = 1.6 Hz, 1H), 5.49 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 151.8, 138.8, 138.2, 135.0, 133.7, 132.7, 128.5, 128.2, 128.1, 127.7, 127.0, 126.4, 126.0, 126.0, 125.6, 125.4, 123.6, 121.5, 119.1, 108.5.

III. Larger-scale Synthesis and Derivatization of 3aa.

Larger-scale synthesis. A suspension of arylacyl phosphonium salt **1b** (1.061 g, 2.00 mmol), sulfoxonium ylides **2a** (0.432 g, 2.2mmol), [RuCl₂(*p*-cymene)]₂ (61.2 mg, 5.0 mol %), and NaOAc (0.544 g, 2.0 equiv.) in EtOH (10.0 mL) was stirred at 120 °C for 10 h under an ambient atmosphere of N₂. After completion, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (n-hexane/EtOAc: 30/1~10/1) to yield the corresponding product **3aa** (400.9 mg, 91% yield).



Derivatization of 3aa.⁷ To a solution of 3-phenylnaphthalen-1-ol (**3aa**) (22 mg, 1 mmol, 1.0 eq.) in 2 mL DCM was added pyridine (0.16 mL, 2 mmol, 2.0 eq.) and the solution was cooled to 0 °C. Trifluoromethanesulfonic anhydride (0.2 mL, 1.2 mmol, 1.2 eq.) was added dropwise and the mixture was warmed to room temperature. The reaction was complete within 5 min as shown by TLC. The mixture was diluted with Et₂O, quenched with 1 M aq. HCl and washed successively with sat. NaHCO₃ and brine. After drying over Na₂SO₄, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the triflate as a light yellow liquid (35.2 mg, 100%). A 25-mL, one-necked, round-bottomed flask equipped with a rubber septum was charged with the obtained 3-phenylnaphthalen-1-yl trifluoromethanesulfonate (35.2 mg, 0.1 mmol) and tributylphenyltin (40 mg, 0.11 mmol) in 1 mL of DMF. Bis(triphenylphosphine)palladium(II) chloride (3.5 mg, 0.005 mmol) was added and the resulting yellow suspension was stirred at room temperature for 30 min. The reaction mixture was then heated at 60 °C for an additional 8 h. The reaction mixture was allowed to cool and then filtered through silica gel in a short column with the aid of Et₂O to remove the majority of the residual palladium. The filtrate was then washed with 1 N aq HCl solution, water, and saturated NaCl solution, dried over Na₂SO₄, filtered, and concentrated to afford a dark brown oily mixture. Column chromatography silica gel (elution with petroleum ether) furnished the desired compound as a colorless oily product.

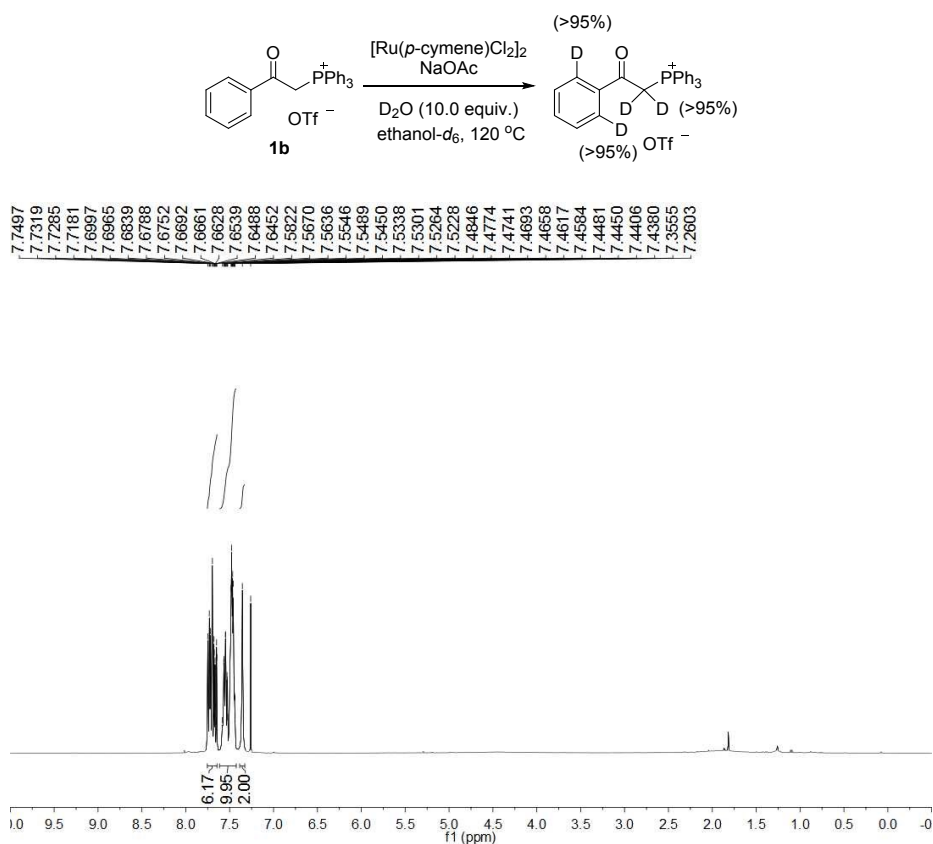


1,3-Diphenylnaphthalene (5): known compound⁸, 21.8 mg, 78% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.73 (s, 1H), 7.59-7.36 (m,

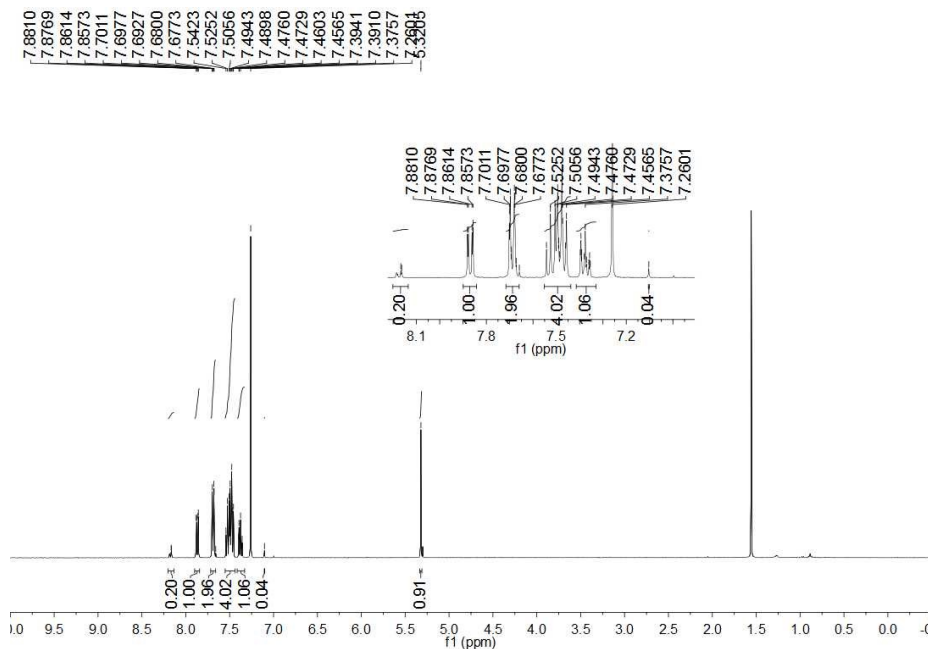
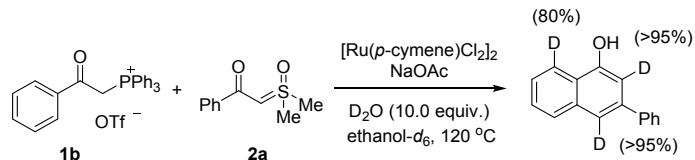
10H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.9, 140.8, 140.6, 138.0, 134.1, 130.8, 130.1, 128.9, 128.6, 128.3, 127.4, 127.4, 126.7, 126.7, 126.2, 126.1, 125.9, 125.4.

IV Mechanistic Studies

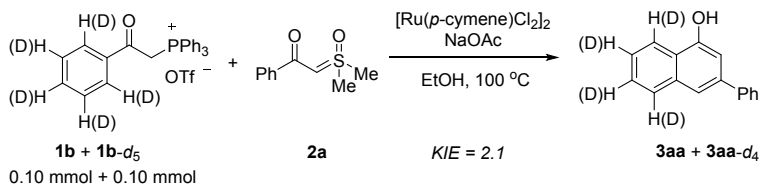
H/D Exchange Experiments. Under N_2 , a suspension of phenacyl phosphonium salt **1b** (53.0 mg, 0.10 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), D_2O (18 μL , 1.0 mmol), and NaOAc (27.2 mg, 0.2 mmol) in ethanol- d_6 (1.0 mL) was stirred at 120 $^\circ\text{C}$ for 10 h. At ambient temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using n-hexane/EtOAc to afford a yellow solid product, which was characterized by ^1H NMR spectroscopy.

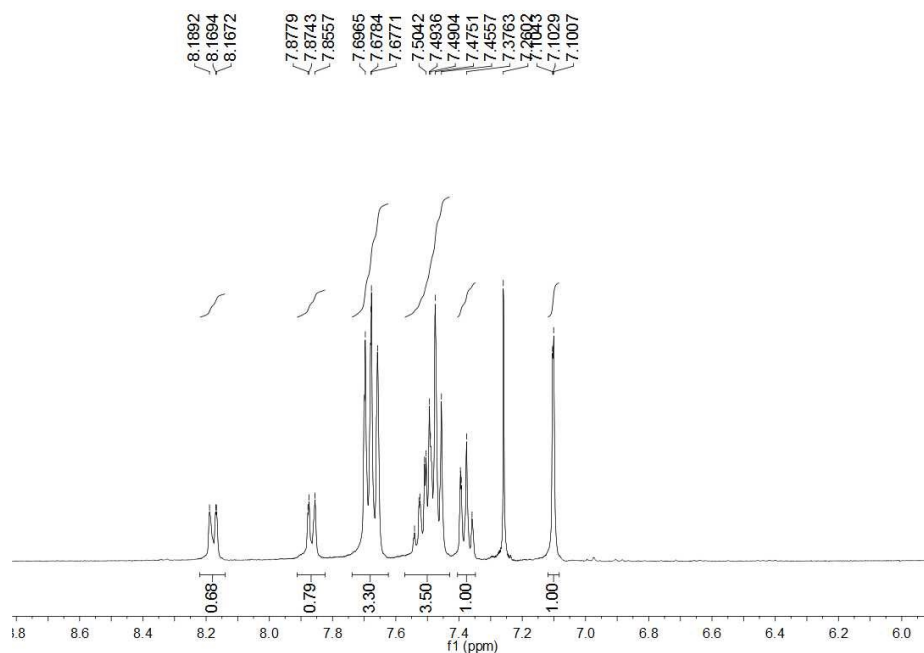


A suspension of phenacyl phosphonium salt **1b** (53.0 mg, 0.10 mmol), sulfoxonium ylides **2** (29.4 mg, 0.15 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), D_2O (18 μL , 1.0 mmol), and NaOAc (27.2 mg, 0.2 mmol) in ethanol- d_6 (1.0 mL) was stirred at 120 $^\circ\text{C}$ for 10 h under an ambient atmosphere of N_2 . At ambient temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using n-hexane/EtOAc to afford a white solid product, which was characterized by ^1H NMR spectroscopy.



Kinetic Isotope Effect Experiments. Two pressure tubes were separately charged with **1b** (0.10 mmol) and **1b-d₅** (0.1 mmol), and to each tube was added sulfoxonium ylides **2** (0.15 mmol), [RuCl₂(*p*-cymene)]₂ (3.1 mg, 5.0 mol %), NaOAc (2.0 equiv.), and EtOH (1.0 mL). The two reaction mixtures were stirred side by side in an oil bath preheated at 100 °C for 30 min. After that, the reaction was quenched in an ice bath and n-hexane was rapidly added to each tube. The two mixtures were combined and the solvent was removed under vacuum and the residue was purified by silica gel chromatography using n-hexane/EtOAc: 30/1~10/1 to yield the product **3aa** and **3aa-d₄** as white solid (2.6 mg, 12% yield). The KIE value was determined to be $k_H/k_D = 2.1$ on the basis of ¹H NMR analysis.





V. References

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VI. Spectral Data for Representative Compounds

