Supplementary Material (ESI) for Chemical Communications

Supporting Information

Pd-Catalyzed Oxidative Cross-Coupling of *N*-Tosylhydrazones with Arylboronic Acids

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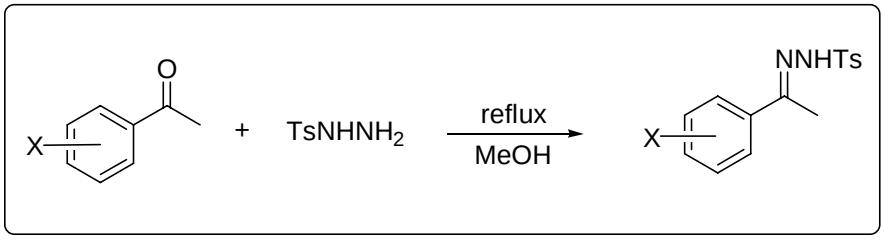
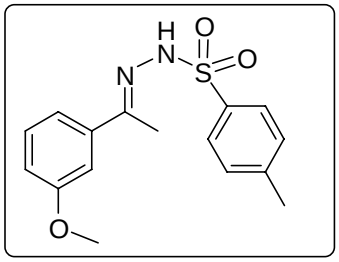
General All solvents were distilled prior to use. The solvents for reaction were distilled to remove water over Na, CaH_2 or K_2CO_3. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. 1H and 13C NMR spectra were recorded at 400 MHz (or 300 MHz, 200 MHz) and 100 MHz (or 75 MHz, 50 MHz) with Bruker ARX 400 spectrometer (Varian Mercury 300 spectrometer). Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded with a Thermo Electron Corporation Nicolet AVATAR 330 FT-IR spectrometer. Mass spectra were obtained on a VG ZAB-HS mass spectrometer, Bruker Apex IV FTMS spectrometer or on a GCT-MS Micromass UK mass spectrometer.



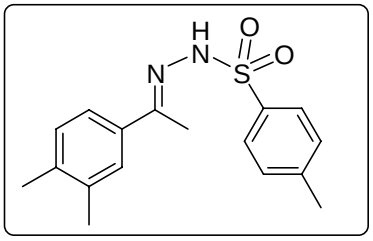
Typical Procedure for preparation of Tosylhydrazones[1]

The ketone (20 mmol) was added to the methanolic solution (30 mL) of *p*-toluenesulfonhydrazide (20 mmol). The reaction mixture was refluxed for 0.5-2 h. Then the mixture was allowed to cool

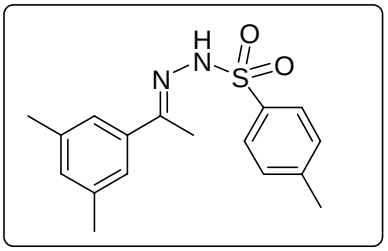
to room temperature and the product precipitated. The crystalline product was collected by filtration and washed thoroughly with cold ether.



(*E*)-N'-(1-(3-Methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide 1d: yield 67%, white solid; m.p. 116-117 ^{o}C; IR (film) 3218, 2948, 2834, 1598, 1578, 1304, 1232, 1164, 1043, 910.0, 859.9, 724.7 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.05 (s, br, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.13-7.27 (m, 3H), 6.87-6.91 (m, 1H), 3.81 (s, 3H), 2.40 (s, 3H), 2.14 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.4, 152.4; 144.2, 138.7, 135.3, 129.5, 129.2, 128.1, 118.8, 115.3, 111.5, 55.20, 21.56, 13.52; EI-MS (*m/z*, relative intensity): 318 (M^+, 3), 134 (100); HRMS calcd for $C_{16}H_{19}N_2O_3S$ [M+H$^+$] 319.1111, Found 319.1116.

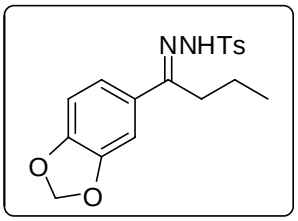


(*E*)-N'-(1-(3,4-Dimethylphenyl)ethylidene)-4-methylbenzenesulfonohydrazide 1f: yield 73%; white solid; m.p. 142-143 ^{o}C; IR (film) 3217, 2973, 2921, 1598, 1449, 1401, 1338, 1307, 1166, 910.9, 730.7, 718.0 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.37 (s, br, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.39 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 1H), 2.35 (s, 3H), 2.22 (s, 3H), 2.21 (s, 3H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.2, 143.8, 138.1, 136.2, 135.4, 134.9, 129.4, 128.0, 127.3, 123.7, 21.38, 19.69, 19.42, 13.46; EI-MS (*m/z*, relative intensity): 316 (M+, 8), 161 (100); HRMS calcd for $C_{17}H_{21}N_2O_2S$ [M+H]$^+$ 317.1318, Found 317.1309.

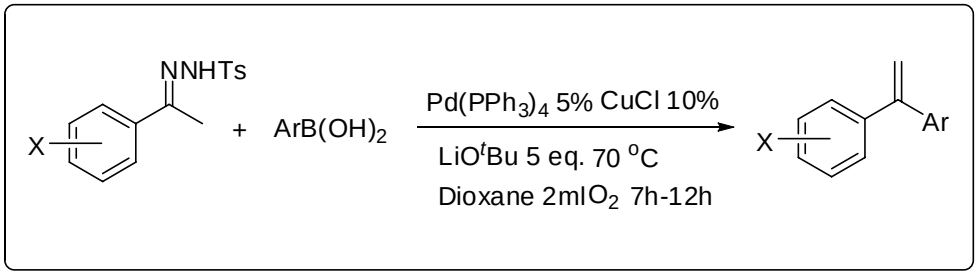


(*E*)-N'-(1-(3,5-dimethylphenyl)ethylidene)-4-methylbenzenesulfonohydrazide 1g: yield 70%; white solid; decomposed at 199 ^{o}C; IR (film) 3211, 2921, 1680, 1598, 1397, 1341, 1323, 1163, 1059, 918.9, 679.4 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.91 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.24 (s, 1H), 6.98 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.0, 144.0, 137.7, 137.3, 135.5, 131.2, 129.5, 128.1, 124.2, 21.56, 21.30, 13.59; EI-MS (*m/z*,

relative intensity): 316 (M^+, 2), 132 (100); HRMS calcd for $C_{17}H_{21}N_2O_2S$ [$M+H^+$] 317.1318, Found 317.1309.

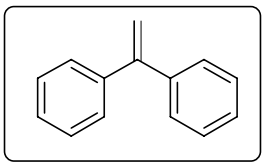


***N'*-(1-(Benzo[d][1,3]dioxol-5-yl)butylidene)-4-methylbenzenesulfonohydrazide 4g:** yield 77%; white solid; m.p. = 182-183 ^oC; IR (film) 3209, 2976, 2964, 2916, 2849, 1597, 1437, 1386, 1335, 1263, 1243, 1164, 1039, 934.3, 900.6, 874.0, 811.9, 738.5, 705.5 cm^{-1}; ^1H NMR (CD_3SOCD_3, 400 MHz) δ 10.56 (s, br, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.12-7.10 (m, 2H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.03 (s, 2H), 2.62-2.58 (m, 2H), 2.37 (s, 3H), 1.39-1.33 (m, 2H), 0.90-0.86 (m, 3H); ^{13}C NMR (CD_3SOCD_3, 100 MHz) δ 155.5, 148.1, 147.3, 143.0, 136.6, 130.8, 129.2, 127.2, 120.4, 107.6, 105.7, 101.1, 28.21, 20.72, 18.91, 13.40; EI-MS (*m/z*, relative intensity): 282 (M^+, 8), 205 (100); HRMS calcd for $C_{18}H_{21}N_2O_4S$ [$M+H]^+$ 361.1217, Found 361.1217.



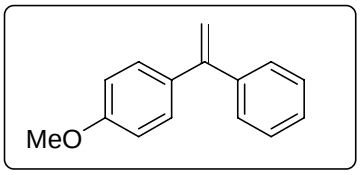
Typical Procedure for Pd-catalyzed Reactions

Tosylhyrazone (0.25 mmol), phenylboronic acid (0.75 mmol). CuCl (0.025 mmol, 10 mol %), tetrakistriphenylphosphine palladium (0.0125 mmol, 5 mol %), lithium *t*-butoxide (1.25 mmol) and 2 ml dioxane were mixed in a reaction tube. The mixture was stirred at 70 ^oC until the reaction completed by TLC analysis. The crude reaction mixture was allowed to cool to room temperature. Pentane was added to the mixture, which was filtered through *celite*. The solvents were evaporated under reduced pressure and the crude residue was purified by flash chromatography on silica gel.

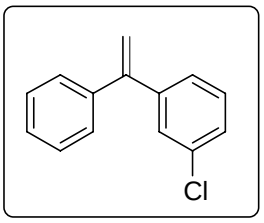


Ethene-1,1-diyldibenzene 3a: yield 71%; colorless oil; IR (film) 3057, 3029, 2927, 2843, 1665, 1495, 1443, 1272, 901.0, 777.3, 696.9 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.36-7.23 (m, 10H), 5.46 (s, 2H); ^{13}C NMR

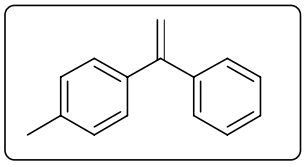
($CDCl_3$, 75 MHz) δ 150.0, 141.4, 128.2, 128.1, 127.7, 114.3; EI-MS (*m/z*, relative intensity): 180 (M^+, 100); HRMS calcd for $C_{14}H_{13}$ $[M+H]^+$ 181.1012, Found 181.1011.



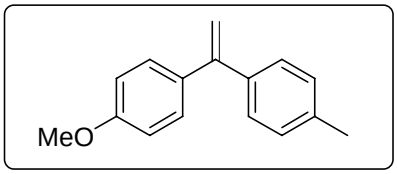
1-Methoxy-4-(1-phenylvinyl)benzene 3b: yield 67%; white solid; m.p. 71-73 ^oC; IR (film) 3084, 2955, 2927, 2837, 1607, 1509, 1248, 1034, 835.6, 777.4, 702.9 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.34-7.32 (m, 5H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.39 (d, *J* = 1.2 Hz, 1H), 5.35 (d, *J* = 1.2 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.3, 149.5, 141.8, 134.0, 129.4, 128.3, 128.1, 127.6, 113.5, 112.9, 55.26; EI-MS (*m/z*, relative intensity): 210 (M^+, 100); HRMS calcd for $C_{15}H_{15}O$ $[M+H]^+$ 211.1117, Found 211.1118.



1-Chloro-3-(1-phenylvinyl)benzene 3c: yield 47%; colorless oil; IR (film) 3063, 3023, 2924, 2849, 1664, 1594, 1564, 1474, 1447, 1271, 802.2, 698.5. cm^{-1} ; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.22 (m, 9H), 5.49 (s, 1H), 5.47 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ148.9, 143.4, 140.8, 134.1, 129.4, 128.3, 128.3, 128.2, 128.0, 127.8, 126.4, 115.2; EI-MS (*m/z*, relative intensity): 214 (M^+, 70), 179 (100); HRMS calcd for $C_{14}H_{11}Cl$ $[M^+]$ 214.0549, Found 214.0552.

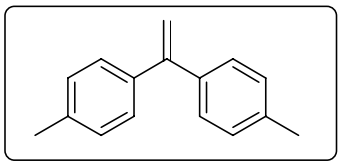


1-Methyl-4-(1-phenylvinyl)benzene 3d: yield 70%; colorless oil; IR (film) 3081, 3054, 3023, 2914, 1609, 1507, 1489, 1445, 1328, 1028, 1022, 829.9, 777.3, 740.2, 700.0 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.24-7.34 (m ,5H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.41 (dd, *J* = 1.2, 11.2 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.9, 141.7, 141.2, 138.6, 137.5, 128.8, 128.3, 128.13, 128.10, 127.6, 113.6, 21.15; EI-MS (*m/z*, relative intensity): 194 (M^+, 46), 154 (100); HRMS calcd for $C_{15}H_{14}$ $[M+H]^+$ 195.1168, Found 195.1165.

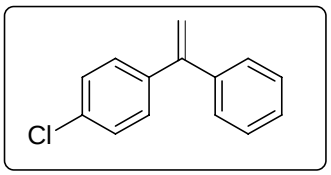


1-Methoxy-4-(1-p-tolylvinyl)benzene 3e: yield 71%; white solid; m.p. 73-74 ^oC; IR (film) 3088, 3026, 2998, 2955, 2930, 2834, 1067, 1510, 1247, 1177, 1034, 826.6 cm^{-1}; ^1H

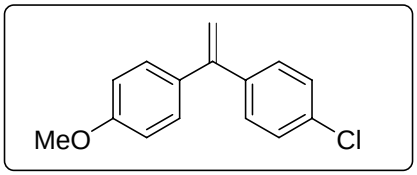
NMR ($CDCl_3$, 300 MHz) δ 7.29-7.22 (m, 4H), 7.15-7.12 (m, 2H), 6.87-6.84 (m, 2H), 5.34 (d, *J* = 1.5 Hz, 1H), 5.31 (d, *J* = 1.5 Hz, 1H), 3.81 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ159.2, 149.3, 137.4, 134.2, 129.4, 128.8, 128.2, 113.4, 112.3, 55.24, 21.13; EI-MS (*m/z*, relative intensity): 224 (M^+, 100); HRMS calcd for $C_{16}H_{17}O$ $[M+H]^+$ 225.1274, Found 225.1270.



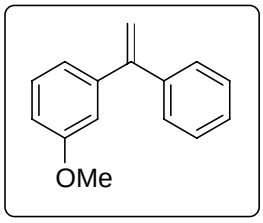
4,4'-(Ethane-1,1-diyl)bis(methylbenzene) 3f: yield 67%; colorless oil; IR (film) 3088, 3029,2927, 2843, 1665, 1495, 1443, 1272, 901.0, 777.3, 696.9 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.23 (d, *J* = 8.0 Hz, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.37 (s, 2H), 2.35 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.7, 138.8, 137.4, 128.8, 128.1, 127.3, 21.14; EI-MS (*m/z*, relative intensity): 208 (M^+, 100); HRMS calcd for $C_{16}H_{17}$ $[M+H]^+$ 209.1325, Found 209.1321.



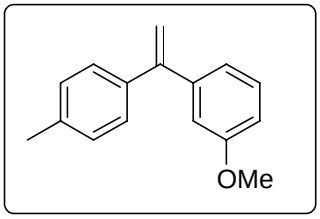
1-Chloro-4-(1-phenylvinyl)benzene 3g: yield 52%; colorless oil; IR (film) 3088, 3057, 3029, 2924, 2849, 1488, 1092, 1013, 901.8, 834.1, 777.3, 702.0 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.24 (m, 9H), 5.46 (d, *J* = 0.7 Hz, 1H), 5.44 (d, *J* = 0.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.0, 141.0, 140.0, 133.6, 129.5, 128.3, 128.2, 128.2, 127.9, 114.6; EI-MS (*m/z*, relative intensity): 214 (M^+, 65), 179 (100); HRMS calcd for $C_{14}H_{11}Cl$ [M] 214.0549, Found 214.0553.



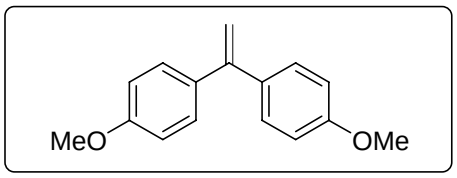
1-Chloro-4-(1-(4-methoxyphenyl)vinyl)benzene 3h: yield 67%; White solid; m.p. 67-69 ^oC; IR (film) 2955, 2926, 2837, 1607, 1510, 1487, 1250, 1027, 842.0 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.31-7.26 (m, 4H), 7.24 (dd, *J* = 2.1, 6.7 Hz, 2H), 6.86 (dd, *J*= 2.1, 6.7 Hz, 2H), 5.39 (d, *J* = 0.9 Hz, 1H), 5.31 (d, *J* = 0.9 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.5, 148.4, 140.3, 133.5, 129.6, 129.3, 128.3, 113.6, 113.3, 55.28; EI-MS (*m/z*, relative intensity): 244 (M^+, 100); HRMS calcd for $C_{15}H_{14}ClO$ $[M+H]^+$ 245.0728, Found 245.0727.



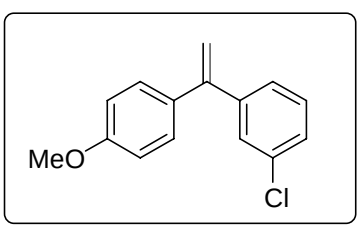
1-Methoxy-3-(1-phenylvinyl)benzene 3i: yield 57%; colorless oil; IR (film) 3081, 3054. 3023, 2930, 1676, 1612, 1445, 1184, 755.7, 687.9 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.35-7.30 (m, 5H), 7.27-7.22 (m, 1H), 6.94-6.85 (m, 3H), 5.46 (s, 2H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.4, 149.9, 142.9, 141.3, 129.1, 128.2, 128.1, 127.7, 120.9, 114.4, 113.9, 113.1, 55.21; EI-MS (*m/z*, relative intensity): 210 (M^+, 100); HRMS calcd for $C_{15}H_{15}O$ $[M+H]^+$ 211.1117, Found 211.1116.



1-Methoxy-3-(1-*p*-tolylvinyl)benzene 3j : yield 68%; colorless oil; IR (film) 3091, 3026. 3004, 2952, 2923, 2834, 1607, 1576, 1510, 1241, 894.7, 826.9, 791.8 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.25-7.22 (m, 3H), 7.14-7.12 (m, 2H), 6.93-6.85 (m, 3H), 5.43 (d, *J* = 1.2 Hz, 1H), 5.40 (d, *J* = 1.2 Hz, 1H), 3.78 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.4, 149.8, 143.2, 138.4, 137.5, 129.0, 128.8, 128.1, 120.9, 114.0, 113.7, 113.2, 55.22, 21.14; EI-MS (*m/z*, relativeintensity): 224 (M^+, 100); HRMS calcd for $C_{16}H_{17}O$ $[M+H]^+$ 225.1274, Found 225.1270.

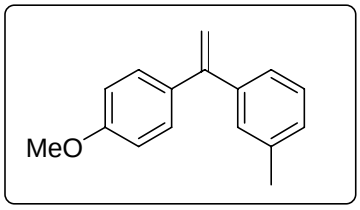


4,4'-(Ethene-1,1-diyl)bis(methoxybenzene) 3k: yield 76%; white solid; m.p. 136-138 ^oC; IR (film) 3016, 2954, 2837, 1605, 1509, 1250, 1182, 1027, 841.2 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.28 (dd, *J* = 2.0, 6.8 Hz ,4H), 6.86 (dd, *J* = 2.0, 6.8 Hz ,4H), 5.29 (s, 2H), 3.83 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 149.0, 134.3, 129.4, 113.5, 111.7, 55.29; EI-MS (*m/z*, relative intensity): 240 (M^+, 100); HRMS calcd for $C_{16}H_{17}O_2$ $[M+H]^+$ 241.1223, Found 241.1221.

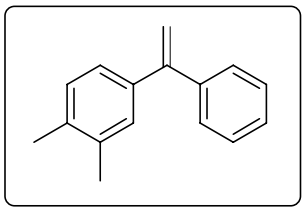


1-Chloro-3-(1-(4-methoxyphenyl)vinyl)benzene 3l: yield 40%; colorless oil; IR (film) 3001, 2929, 2837, 1608, 1509, 1248, 867.9, 835.8 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.21 (m, 6H), 6.89-6.85 (m, 2H), 5.42 (d, *J* = 1.0 Hz, 1H), 5.35 (d, *J* = 1.0 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.5, 148.4, 143.7, 134.1,

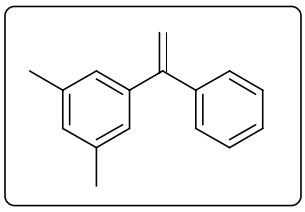
133.3, 129.4, 129.3, 128.3, 127.7, 126.5, 113.9, 113.7, 55.29; EI-MS (*m/z*, relative intensity): 244 (M^+, 100); HRMS calcd for $C_{15}H_{14}ClO$ $[M+H]^+$ 245.0728, Found 245.0726.



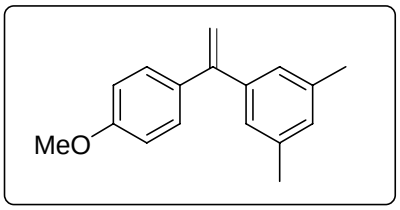
1-(1-(4-Methoxyphenyl)vinyl)-3-methylbenzene 3m: yield 70%; white solid; m.p. 45-47 ^oC; IR (film) 3032, 3001, 2959, 2927, 2831, 1608, 1509, 1248, 1177, 1034, 890.6, 836.2, 793.5 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.28-7.11 (m, 6H), 6.86-6.84 (m, 2H), 5.37 (d, *J* = 0.9 Hz, 1H), 5.33 (d, *J* = 0.9 Hz, 1H), 3.81 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ159.3, 149.6, 141.8, 137.6, 134.1, 129.4, 129.0, 128.4, 128.0, 125.5, 113.5, 112.8, 55.24, 21.40; EI-MS (*m/z*, relative intensity): 224 (M^+, 100); HRMS calcd for $C_{16}H_{17}O$ $[M+H]^+$ 225.1274, Found 225.1271.



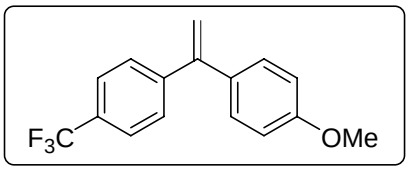
1,2-Dimethyl-4-(1-phenylvinyl)benzene 3n: yield 57%; colorless oil; IR (film) 3085, 3057. 3026, 2922, 1656, 1603, 1502, 1492, 1445, 889.9, 827.6, 777.5,701.0 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.35-7.29 (m, 5H), 7.12-7.07 (m, 3H), 5.41 (d, *J* = 1.2 Hz, 1H), 5.38 (d, *J* = 1.2 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.0, 141.7, 139.1, 136.2, 136.2, 129.4, 128.3, 128.1, 127.6, 125.7, 113.5, 19.78, 19.48; EI-MS (*m/z*, relative intensity): 208 (M^+, 100); HRMS calcd for $C_{16}H_{16}$ $[M+H]^+$ 209.1325, Found 209.1317.



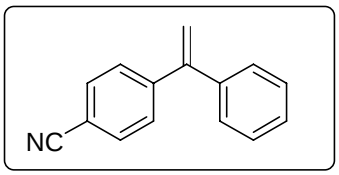
1,3-Dimethyl-5-(1-phenylvinyl)benzene 3o: yield 63%; colorless oil; IR (film) 3081, 3054. 3029, 2918, 1597, 1483, 1444, 894.8, 853.6, 778.2, 737.4, 696.0 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.30 (m, 5H), 6.95 (s, 3H), 5.42 (d, *J* = 1.2 Hz, 1H), 5.41 (d, *J* = 1.2 Hz, 1H), 2.29 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.2, 141.7, 141.5, 137.6, 129.4, 128.2, 128.1, 127.6, 126.1, 114.0, 21.27; EI-MS (*m/z*, relative intensity): 208 (M^+, 100); HRMS calcd for $C_{16}H_{17}$ $[M+H]^+$ 209.1325, Found 209.1318.



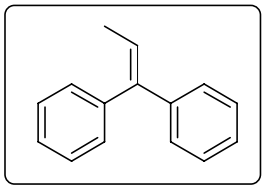
1-(1-(4-Methoxyphenyl)vinyl)-3,5-dimethylbenzene 3p: yield 30%; white Solid; m.p.72-73 ^{o}C; IR (film) 3004, 2958, 2921, 2859, 2834, 1608, 1509, 1250, 1177, 1035, 835.9 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27 (dd, *J* = 2.0, 6.8 Hz ,2H), 6.95 (s, 3H), 6.86 (dd, *J* = 2.0, 6.8 Hz ,2H), 5.35 (d, *J* = 1.2 Hz, 1H), 5.31 (d, *J* = 1.2 Hz, 1H), 3.82 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.2, 149.7, 141.8, 137.5, 134.2, 129.4, 129.3, 126.2, 113.4, 112.6, 55.25, 21.27; EI-MS (*m/z*, relative intensity): 238 (M^+, 100); HRMS calcd for $C_{17}H_{19}O$ $[M+H]^+$ 239.1430, Found 239.1427.



1-Methoxy-4-(1-(4-(trifluoromethyl)phenyl)vinyl)benzene 3q : yield 64%; white solid; m.p.: 79-80 ^{o}C; IR (film) 2977, 2864, 1606, 1510, 1324, 1251, 1169, 1122, 1077, 857, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.25-7.23 (m, 2H), 6.89-6.86 (m, 2H), 5.49 (s, 1H), 5.39 (s, 1H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.6, 148.4, 145.4, 133.1, 129.6 (q, *J*=32.3 Hz, 1C), 129.3, 128.6, 124.2 (q, *J*=270 Hz, 1C), 125.1 (q, *J*=3.7 Hz, 1C), 114.5, 113.7, 55.27; EI-MS (*m/z*, relative intensity): 278 (M^+, 100); HRMS calcd for $C_{16}H_{14}F_3O$ $[M+H]^+$ 279.0991, Found 279.0990.

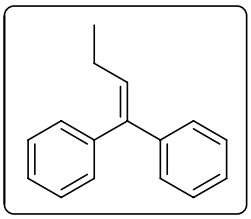


4-(1-Phenylvinyl)benzonitrile 3r: yield 51%; colorless oil; IR (film) 2916, 2849, 2228, 1606, 1504, 1492, 908.8, 849.8, 778.8, 703.9 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63-7.61 (m, 2H), 7.45-7.42 (m, 2H), 7.36-7.35 (m, 3H), 7.29-7.27 (m, 2H), 5.58 (s, 1H), 5.54 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.7, 146.0, 140.2, 132.0, 128.8, 128.4, 128.2, 128.1, 118.8,116.7, 111.3; EI-MS (*m/z*, relative intensity): 205 (M^+, 100); HRMS calcd for $C_{15}H_{11}NNa$ $[M+Na]^+$ 228.0784, Found 228.0781.

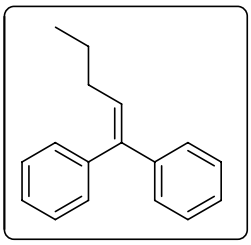


1,1-Diphenylpropene 5a: yield 69%; colorless oil; IR (film) 3078, 3054, 3029, 1598, 1494, 1441, 1355,769.5, 757.4, 737.6, 697.8 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.17 (m, 10H), 6.17 (t, *J* = 7.0 Hz, 1H),

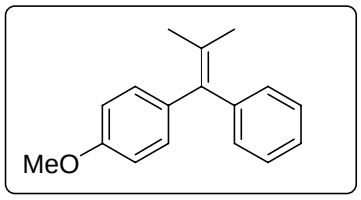
1.75 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.9, 142.4, 140.0, 130.0, 128.1, 128.0, 127.1, 126.8, 126.7, 124.1, 15.68; EI-MS (*m/z*, relative intensity): 194 (M^+, 100); HRMS calcd for $C_{15}H_{15}$ $[M+H]^+$ 195.1168, Found 195.1164.



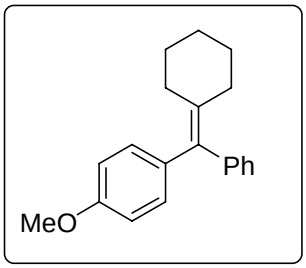
But-1-ene-1,1-diyldibenzene 5b: yield 75%; colorless oil; IR (film) 3057, 3023, 2963, 2927, 1597, 1494, 1443, 1073, 1030, 867.2, 763.2, 737.9, 698.3 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.17 (m, 10H), 6.07 (t, *J* = 7.5 Hz, 1H), 2.12 (m, 2H), 1.03 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.8, 140.9, 140.2, 131.7, 129.9, 128.1, 128.0, 127.1, 126.8, 126.7, 23.18, 14.50; EI-MS (*m/z*, relative intensity): 208 (M^+, 100); HRMS calcd for $C_{16}H_{17}$ $[M+H]^+$ 209.1325, Found 209.1324.



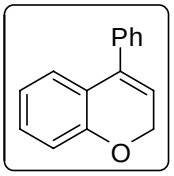
Pent-1-ene-1,1-diyldibenzene 5c: yield 73%; colorless oil; IR (film) 3060, 3026, 2959, 2924, 2868, 1494, 1444, 1073, 1030, 894.8, 760.0, 737.6, 698.3 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.16 (m, 10H), 6.08 (t, *J* = 7.5 Hz, 1H), 2.11-2.06 (m, 2H), 1.50-1.41 (m, 2H), 0.95-0.70 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.9, 141.5, 140.3, 130.1, 129.9, 128.1, 128.0, 127.1, 126.8, 126.7, 31.81, 23.15, 13.86; EI-MS (*m/z*, relative intensity): 222 (M+, 55), 193 (100); HRMS calcd for $C_{17}H_{19}$ $[M+H]^+$ 223.1481, Found 223.1483.



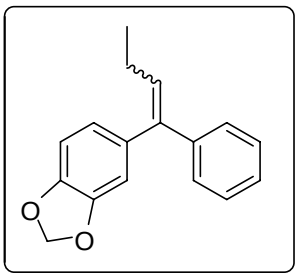
1-Methoxy-4-(2-methyl-1-phenylprop-1-enyl)benzene 5d: yield 72%; colorless oil; IR (film) 2925, 2853, 1606, 1508, 1243, 1174, 1036, 828.6, 759.2, 701.1 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31-7.26 (m, 2H), 7.21-7.20 (m, 1H), 7.16-7.14 (m, 2H), 7.09-7.06 (m, 2H), 6.85-6.83 (m, 2H), 3.80 (s, 3H), 1.84 (s, 3H), 1.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.8, 143.6, 136.5, 135.8, 130.9, 130.5, 129.8, 127.8, 125.9, 113.2, 55.13, 22.50; EI-MS (*m/z*, relative intensity): 238 (M^+, 100); HRMS calcd for $C_{17}H_{19}O$ $[M+H]^+$ 239.1430, Found 239.1430.



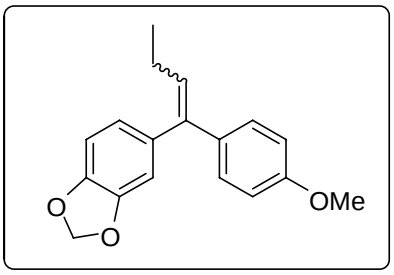
1-(Cyclohexylidene(phenyl)methyl)-4-methoxybenzene 5e: yield 61%; white solid; m.p.: 90-91 ^{o}C; IR (film) 2924, 2852, 1605, 1507, 1465, 1442, 1243, 1236, 1036, 833.0, 803.3, 761.1, 705.0 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30-7.26 (m, 2H), 7.21-7.20 (m, 1H), 7.14-7.12 (m, 2H), 7.07-7.05 (m, 2H), 6.84-6.82 (m, 2H), 3.80 (s, 3H), 2.30-2.36 (m, 4H), 1.62-1.58 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.8, 143.4, 138.7, 135.6, 134.0, 130.9, 129.8, 127.8, 125.9, 113.2, 55.13, 32.46, 32.40, 28.66, 26.82; EI-MS (*m/z*, relative intensity): 278 (M^+, 100); HRMS Calcd for $C_{20}H_{23}O$ $[M+H]^+$ 279.1743, Found 239.1744.



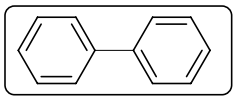
4-Phenyl-2*H*-chromene 5f: yield 30%; colorless oil; IR (film) 3063, 3026, 1594, 1492, 1445, 1347, 1160, 1092, 763.8, 742.8, 696.3, 655.3 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.33 (m, 5H), 7.16-7.16 (m, 1H), 7.00-7.00 (m, 1H), 6.91-6.85 (m, 2H), 5.80 (t, *J* = 3.9 Hz, 1H), 4.86 (d, *J* = 3.9, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.7, 138.2, 137.1, 129.2, 128.6, 128.3, 127.8, 125.8, 123.7, 121.1, 119.9, 116.2, 65.22; EI-MS (*m/z*, relative intensity): 208 (M^+, 100); HRMS Calcd for $C_{15}H_{13}O$ $[M+H]^+$ 209.0961, Found 209.0958.



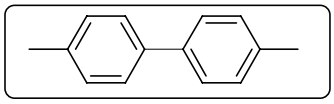
5-(1-Phenylbut-1-enyl)benzo[d][1,3]dioxole 5g: yield 75%; colorless oil; IR (film) 2963, 2917, 1502, 1486, 1246, 1227, 1040, 937.2, 809.5, 700.6 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.15 (m, 5H), 6.82-6.64 (m, 3H), 6.01 (t, *J* = 7.5 Hz, 0.5H), 5.95 (t, *J* = 8.1, 0.5H), 5.96 (s, 1H), 5.90 (s, 1H), 2.18-2.10 (m, 1H), 2.11-2.04 (m, 1H), 1.05-0.99 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.5, 147.4, 146.5, 146.4, 142.9, 140.5, 140.3, 137.4, 134.0, 131.7, 130.6, 129.8, 128.1, 128.1, 128.0, 127.2, 127.2, 126.8, 126.8, 123.2, 121.0, 110.3, 108.0, 107.8, 107.6, 100.9, 23.19, 23.12, 14.53, 14.48; EI-MS (*m/z*, relative intensity): 252 (M+, 100); HRMS calcd for $C_{17}H_{17}O_2$ $[M+H]^+$ 253.1223, Found 253.1224.



5-(1-(4-Methoxyphenyl)but-1-enyl)benzo[d][1,3]dioxole 5h: yield 84%; white solid; IR (film) 2962, 2916, 2849, 1607, 1509, 1486, 1435, 1288, 1244, 1231, 1038, 936.5, 829.8, 809.9 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.15 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.82-6.80 (m, 1.5H), 6.78 (s, 0.5H), 6.75-6.64 (m, 2H), 5.96 (s, 1H), 5.93-5.89 (m, 2H), 3.82 (s, 1.5H), 3.78 (s, 1.5H), 2.15-2.04 (m, 2H), 1.04-1.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.6, 158.5, 147.4, 147.3, 146.4, 146.3, 140.1, 139.9, 137.8, 135.6, 134.3, 132.6, 130.9, 130.4, 130.1, 128.2, 123.1, 121.0, 113.4, 113.4, 110.3, 108.0, 107.7, 107.7, 100.9, 100.9, 55.22, 55.19, 23.16, 23.14; EI-MS (*m/z*, relative intensity): 282 (M^+, 100); HRMS Calcd for $C_{18}H_{19}O_3$ [$M+H^+$] 283.1329, Found 283.1328.



Biphenyl: white Solid; IR (film) 3062, 3035, 1597, 1482, 1431, 907.2, 732.2, 698.3 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.60-7.57 (m, 4H), 7.45-7.41 (m, 4H), 7.36-7.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.2, 128.7, 127.2, 127.2.



4,4'-dimethylbiphenyl: White Solid; IR (film) 3025, 2918, 1502, 1449, 802.5, 731.0 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.47 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 4H), 2.37 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 138.3, 136.7, 129.4, 126.8, 21.04.

Mechanistic investigation.

(1) Preparation of the starting material.

Acetophenone-*methyl-d*$_3$: Similar procedures as reported in reference was followed.[2] A mixture of acetophenone (2.88 g, 24 mmol), NaOH (0.08 g, 2 mmol) and D_2O (99.9% D) (16.0 ml, 800 mmol) was stirred at room temperature for 24 h under N_2. The reaction mixture was diluted with dry diethyl ether (10 mL). The aqueous layer was extracted with diethyl ether (10 x 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. Then, the crude product was deuterated again using the same procedure. The final residue was chromatographed using hexane/EtOAc (60/1) to afford acetophenone-*methyl-d*$_3$ (99% atom D, yield 80%). 1H NMR (400

MHz, CDCl3) δ 7.96 (dd, *J* = 7.2, 1.3 Hz, 2H), 7.58-7.54 (m, 1H), 7.40-7.50 (dd, *J* = 7.9, 7.3Hz, 2H).

Acetophenone-*methyl*--d_1: Similar procedures as reported in reference was followed.[2] A solution of MeLi (3.36 mL, 1.6 M in ether, 5.37 mmol) was added dropwise to the trimethyl(1-phenyl vinyloxy)silane (0.938 g, 4.9 mmol) at room temperature. This resulting solution was stirred for 1 h at room temperature and then cooled at -78 ^{o}C. Acetic acid-d_4 (0.8 ml, 14.7 mmol) in THF (10 mL) was added dropwise to this solution and the mixture stirred for another 30 min at -78 ^{o}C. The reaction mixture was diluted with the addition of water (100 mL) and extracted with ether (3 x 20 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography on silica gel eluting with petroleum/EtOAc (60/1) to give the acetophenone-*methyl*-d_1 (85% atom D, yield 70%) as an oil. 1H NMR (300 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.2, 1.3 Hz, 2H), 7.59-7.54 (dt, *J* = 7.6, 1.8 Hz, 1H), 7.49-7.44 (m, 2H), 2.61 (s, 0.38 H), 2.60 (t, *J* = 2.1 Hz, 1.36H).

Typical Procedure for preparation of D-Tosylhydrazones

The Deuterated acetophenone (10 mmol) was added to the methanolic solution (15 mL) of *p*-toluenesulfonhydrazide (10 mmol). The reaction mixture was refluxed for 0.5h. After cooling to room temperature, the product precipitated and the crystalline product was collected by filtration and washed with cold ether to give D-Tosylhydrazones.

(E)-N'-(1-(3-methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide-d_3(8): δ ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.78 (s, br, 1H), 7.65-7.63 (m, 2H), 7.35-7.31 (m, 5H), 2.41 (s, 3H). (99% atom D, yield 80%) **(*E*)-N'-(1-(3-methoxyphenyl)ethylidene)-4-methyl benzenesulfonohydrazide-d_1 (10):** δ ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (s, br, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.65-7.63 (m, 2H), 7.34-7.31 (m, 5H), 2.41 (s, 3H), 2.16 (s, 0.46H), 2.60 (t, *J* = 2.2 Hz, 1.56H). (83.6% atom D, yield 80%)

(2) The kinetic isotope effect experiment

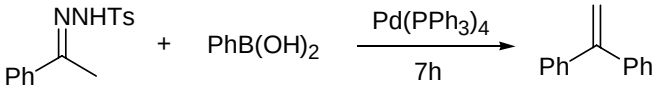
Intermolecular reaction: **8** (36.4mg, 0.125mmol), **1a** (36 mg, 0.125 mmol), phenylboronic acid **2b** (114 mg, 0.75 mmol). CuCl (2.5 mg, 0.025 mmol, 10 mol %), tetrakistriphenylphosphine palladium (15 mg, 0.0125 mmol, 5 mol %), lithium *t*-butoxide (100 mg, 1.25 mmol) and 2 mL dioxane were mixed in a reaction tube. The mixture was stirred at 70 ^{o}C for 3 h. The hydrazones

still remained in the reaction system. Then, the crude reaction mixture was allowed to cool down to room temperature. Pentane was added to the mixture, which was filtered through *celite*. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel with petroleum, affording the product. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.25 (m, 7H), 6.86 (dd, *J* = 6.8, 2.0 Hz, 2H), 5.39 (d, *J* = 1.2 Hz, 0.5H), 5.35 (d, *J* = 1.2 Hz, 0.5 H), 3.82 (s, 3H); (**3b**: **9** = 1:1).

Intramolecular reaction: **10** (72.3 mg, 0. 25 mmol, 85% atom D), phenylboronic acid **2b** (114 mg, 0.75 mmol). CuCl (2.5 mg, 0.025 mmol, 10 mol %), tetrakistriphenylphosphine palladium (15 mg, 0.0125 mmol, 5 mol %), lithium *t*-butoxide (100 mg, 1.25 mmol) and 2 mL dioxane were mixed in a reaction tube. The mixture was stirred at 70 ^{o}C for 5 h. The crude reaction mixture was allowed to cool down to room temperature, Pentane was added to the mixture, which was filtered through *celite*. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel with petroleum, giving the product. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.24 (m, 7H), 6.86 (dd, *J* = 6.8, 2.1 Hz, 2H), 5.39 (d, *J* = 1.2 Hz, 0.31 H), 5.38 (s, 0.34 H), 5.35 (d, *J* = 1.2 Hz, 0.32 H), 5.34 (s, 0.35 H), 3.82 (s, 3H).

Additional Data for Optimization of Reaction Conditions

(1) The effects of oxidant and base[a]



1a **2a** **3a**

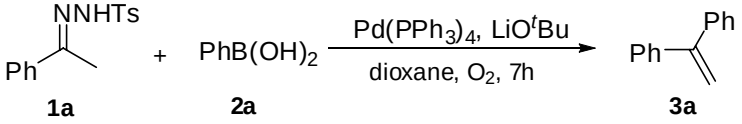
entry	oxidant	base	*T* (^{o}C)	solvent	yield (%)[b]
1	Ag_2CO_3 2eq.	^{t}BuOLi 3eq.	70	dioxane	16
2[c]	^{t}BuOO^{t}Bu 2eq.	^{t}BuOLi 3eq.	70	dioxane	10
3[c]	^{t}BuOO^{t}Bu 3eq.	^{t}BuOLi 3eq.	70	dioxane	13
4	$Cu(OAc)_2$ 2eq.	^{t}BuOLi 4eq.	70	dioxane	*trace*
5	$CuCl_2$ 2eq.	^{t}BuOLi 4eq.	70	dioxane	*trace*
6	$KBrO_3$ 1.5eq.	^{t}BuOLi 5eq.	70	dioxane	8
7	O_2, CuCl 20%	^{t}BuOLi 4eq.	70	dioxane	47
8	O_2, CuCl 20%	^{t}BuOLi 4eq.	70	toluene	34
9	O_2, CuCl 20%	^{t}BuOLi 4eq.	70	CH_3CN	22
10	O_2, CuCl 10%	^{t}BuOLi 5eq.	70	DMSO	7.5
11	O_2, CuCl 20%	^{t}BuOLi 5eq.	70	dioxane	68
12	O_2, CuCl 20%	^{t}BuOLi 5eq.	80	dioxane	24

13	O_2, CuCl 20%	^{t}BuOLi 5eq.	60	dioxane	66
14	O_2, CuCl 20%	^{t}BuOLi 5eq., ^{i}Pr$_2$NH 1.5eq.	70	dioxane	68
15	O_2, CuCl 10%	^{t}BuOLi 3eq., K_2CO_3 1eq.	70	dioxane	23
16	O_2, CuCl 10%	^{t}BuOLi 3eq., K_3PO_4 1eq.	70	dioxane	53
17	O_2, CuCl 10%	^{t}BuOLi 3eq.	70	dioxane	20
18	O_2, CuCl 10%	^{t}BuOLi 6eq.	70	dioxane	43

[a] Reaction conditions: **1a** (0.25 mmol), **1b** (0.75 mmol), $Pd(PPh_3)_4$ (5 mol %), solvent (2 mL)

[b] Yield of isolated product after chromatography

[c] **1b** (1.2 eq) was employed.



1a **2a** **3a**

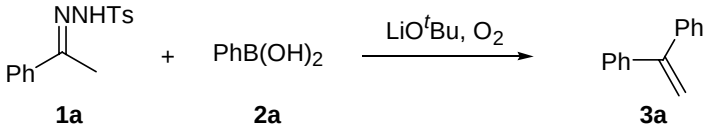
entry[a]	copper	yield (%)[b]	entry	copper	yield (%)[b]
1	CuOTf 10%	26	10[c]	$CuCl_2$ 20%	64
2	$Cu(OTf)_2$ 20%	15	11	$CuCl_2$ 10%	56
3	$Cu(OTf)_2$ 2.2eq.	<10	12	NaI 20%	16
4	Cu_2S 10%	36	13	CuI 20%	13
5	CuF_2 20%	39	14	$Cu(acac)_2$ 20%	29
6	CuSCN 10%	20	15	CuBr 20%	60
7	$Cu(IO_3)_2$ 10%	41	16	$CuCl_2$ 20%	70
8	$CuSO_4$ 10%	42	17	$Cu(OAc)_2$ 20%	42
9	$CuCl_2$ 20%	70	18	CuCl 10%	71

[a]Reaction conditions: **1a** (0.25 mmol), **1b** (0.75 mmol), $Pd(PPh_3)_4$ (5 mol %), LiO^{t}Bu (1.25 mmol), dioxane (2 mL), 70 ^{o}C.

[b]Yield of isolated product after chromatography.

[c]In the atmosphere of O_2 : N_2 = 1 : 4.

(2) The effect of Pd catalysts[a]



1a **2a** **3a**

entry	catalyst	copper	yield (%)[b]
1	$Pd_2(dba)_3$ 2.5%, $(4\text{-}MeOC_6H_4)_3P$ 10%	CuCl 10%	46
2	$PdCl_2(PPh_3)_2$ 5%, PPh_3 5%	CuCl 10%	68
3	$Pd(OAc)_2$ 5%, $(4\text{-}MeC_6H_4)_3P$ 10%	CuCl 10%	63
4	$Pd(O_2CF_3)_2$ 5%, PPh_3 10%	CuCl 20%	48
5	$Pd(OAc)_2$ 5%, $(4\text{-}MeOC_6H_4)_3P$ 10%	CuCl 20%	55

6	$Pd(OAc)_2$ 5%, PPh_3 10%	CuCl 20%	60
7	$PdCl_2$dppf CH_2Cl_2 5%	CuCl 20%	44
8	$Pd(PPh_3)_4$ 5%	CuCl 10%	71
9	$PdCl_2(PhCN)_2$ 5%	CuCl 10%	<10
10	$Pd(OAc)_2$ 5% PPh_3 20%	CuCl 10%	64
11	$[Pd(C_3H_5)Cl]_2$ 5% XPhos 10%	CuCl 10%	25
12	$Pd(PPh_3)_4$ 5% PPh_3 10%	CuCl 10%	61

[a]Reaction conditions: **1a** (0.25 mmol), **1b** (0.75 mmol), LiO^tBu (1.25 mmol), dioxane (2 mL), 70 ^oC.

[b]Yield of isolated product after chromatography.

References

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