Supporting Information

General Procedure for Metalation of *N*-cumylbenzamide and *N*-1,1-ethyldiphenylbenzamide (2a,b).
To a solution of **2a** (120 mg, 0.5 mmol) and TMEDA (0.24 mL, 1.6 mmol, 3.2 equiv) in THF (5 mL) at –78 °C under Ar was slowly added *s*-BuLi (1.6 mmol, 3.2 equiv) via syringe. The resulting yellow solution was stirred for 2 h and the electrophile (1.1 mmol, 2.2 equiv) was added. The reaction mixture was stirred for 1 h at –78 °C, or allowed to warm slowly to rt before satd NH_4Cl was added. The product was extracted with ether or EtOAc, and the combined organic extract was dried ($MgSO_4$) and concentrated in vacuo to give the crude product.

***N*-cumyl-2-(trimethylsilyl)benzamide (3a).**
Flash chromatography (hexane/EtOAc 9:1) afforded **3a** (Table 1, entry 7) as a colorless solid (147 mg, 94%), mp 75-77 °C.
IR ν_{max} (KBr) 3352, 1657 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.64 (dd, J = 6.0, 2.0Hz, 1H, ArH), 7.52-7.22 (m, 8H), 6.16 (s, 1H), 1.85 (s, 6H), 0.30 (s, 9H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 170.1, 146.8, 143.2, 140.1, 135.5, 129.4, 128.6, 125.5, 126.9, 126.1, 124.9, 56.3, 28.8, 0.3; HRMS calcd for $C_{19}H_{26}NOSi$: 312.1784; found 312.1780.

***N*-1,1-diphenylethyl-2-(trimethylsilyl)benzamide (3b).**
Flash chromatography (hexane/EtOAc 13:1) afforded **3b** (Table 1, entry 7) as a colorless solid (170 mg, 91%), mp 99-101 °C.
IR ν_{max} (KBr) 3426, 1665 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.67-7.56 (m, 2H), 7.42-7.25 (m, 12H), 6.57 (brs, 1H), 2.37 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 146.2, 142.9, 140.5, 135.6, 129.5, 128.4, 127.1, 126.6, 126.0, 62.7, 27.1, 0.3; HRMS calcd for $C_{24}H_{28}NOSi$ (M^++1): 374.1943; found 374.1940.

2-Trimethylsilylbenzamide (4a) from 3a.
To a solution of $BF_3{\cdot}OEt_2$ (0.13 mL, 1.0 mmol) in CH_2Cl_2 (5 mL) at 0 °C under Ar was added **3a** (245 mg, 0.788 mmol) in CH_2Cl_2 (10 mL). The resulting brown solution was stirred for 2 h at rt before water was added, and the product was extracted with CH_2Cl_2. The combined organic extract was dried ($MgSO_4$) and concentrated in vacuo to give the crude product. Flash chromatography (hexane/ethyl acetate 5:2) afforded **4a** as a colorless solid (130 mg, 86%).
IR ν_{max} (KBr) 3453, 3288, 1654 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.65 (dd, 1H, J = 1.8, 7.0Hz), 7.51-7.24 (m, 3H), 6.68 (brs, 1H), 6.13 (brs, 1H), 0.33 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.4, 140.9, 140.1, 135.4, 129.8, 128.6, 126.2, 0.1.

2-Trimethylsilylbenzamide (4a) from 3b.
To **3b** (345 mg, 0.924 mmol) was added ice-cooled TFA (4 mL) and the resulting green solution was stirred for at rt for 15 min. The solvent was removed in vacuo to give the crude product. Flash chromatography (hexane/EtOAc 2:1) afforded **4a** as a colorless solid (148 mg, 83%).

2-Trimethylsilylbenzonitrile (4b).

To **3a** (312 mg, 1.0 mmol) in CH_2Cl_2 (5mL) at –40 °C under Ar was sequentially added pyridine (0.25 mL, 3.0 mmol) and triflic anhydride (0.22 mL, 1.3 mmol) dropwise. The resulting solution was allowed to warm to 0 °C (2 h) and kept at this temperature for 5 h. Ethanol was added (2 mL, >30mmol) and the mixture was stirred at rt for 18 h. To the resulting pale yellow solution was added 1N HCl and the product was extracted with ether. The combined organic extract was washed once with 1N $KHCO_3$, dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (hexane/EtOAc 19:1) gave **4b** as a volatile colorless oil (89 mg, 51%).
IR ν_{max} (NaCl, neat) 2222 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.70-7.44 (m, 4H), 0.45 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.7, 134.4, 133.3, 131.5, 129.0, 119.8, 117.2, –1.5.

3-Thiomethylphthalimide (**7b**).
To a solution of *N*-cumylphthalimidine (**5**) (1.60 g, 6.0 mmol) and TMEDA (1.99 mL, 13.3 mmol, 2.2 equiv) in THF (60 mL) at –78 °C under Ar was slowly added *s*-BuLi (13.3 mmol, 2.2 equiv) via syringe. The resulting dark green, almost black solution was stirred for 2 h before methyl disulfide (0.65 mL, 7.2 mmol, 1.2 equiv) was added. The reaction mixture was allowed to warm slowly to rt and satd NH_4Cl was added. The product was extracted with EtOAc, and the combined organic extract dried ($MgSO_4$) and concentrated in vacuo with a bleach trap to give the crude product. Flash chromatography (hexane/EtOAc 3:2) gave *N*-cumyl-6-(thiomethyl)phthalimidine a pale yellow solid (1.68 g, 89%), mp 167-170 °C.
IR ν_{max} (KBr) 3413, 1671 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.42-7.06 (m, 8H), 5.98 (d, 1H, J=9.7 Hz), 3.35 (d, 1H, J=9.7 Hz), 2.35, (s, 3H), 1.89 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.4, 146.9, 144.6, 138.4, 132.1, 128.1, 127.1, 126.3, 125.1, 123.8, 118.1, 81.6, 58.9, 28.9, 27.9, 13.6; HRMS calcd for $C_{18}H_{19}NO_2S$: 313.1136; found 313.1149.
To a solution of *N*-cumyl-6-(thiomethyl)phthalimidine (940 mg, 3.0 mmol) in DMF (12 mL) under Ar at rt was added pyridinium dichromate (2.26 g, 6.0 mmol, 2.0 equiv) all at once and the dark mixture was stirred for 2 h. Water was added and the product was extracted with EtOAc. The combined organic extract was washed with water (3 times), brine, and dried ($MgSO_4$). Evaporation of solvent and flash chromatography (hexane/EtOAc 4:1) gave **6b** (840 mg, 89%) as a pale yellow solid, mp 168-169 °C.
IR ν_{max} (KBr) 1761, 1699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.61-7.20 (m, 8H), 2.53 (s, 3H), 2.04, (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 169.0, 147.1, 139.9, 134.3, 133.4, 128.8, 127.1, 126.7, 124.9, 121.1, 118.6, 62.1, 29.5, 14.4; HRMS calcd for $C_{18}H_{17}NO_2S$: 311.0981; found 311.0988.
To **6b** (312 mg, 1.0 mmol) was added TFA (4 mL) and the resulting solution was stirred for 16 h at 50 °C. The solvent was removed on a rotary evaporator to give the crude product. Gradient flash chromatography (hexane/EtOAc 19:1, then EtOAc) afforded **7b** as a bright yellow solid (168 mg, 87%), subl 195 °C.
IR ν_{max} (KBr) 3188, 1771, 1717 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 11.27 (brs, 1H), 7.73 (t, 1H, J=8.1 Hz), 7.60 (d, 1H, J=8.0 Hz), 7.51 (d, 1H, J=7.0 Hz), 2.53 (s, 3H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 168.9, 168.7, 139.0, 134.5, 133.6, 129.0,; 126.5, 118.1, 81.5; HRMS calcd for $C_9H_7NO_2S$: 193.0198; found 193.0207.

3,3-Diphenyl-1,2-benzisothiazole-1,1-dioxide (10b).
To a solution of *N*-cumylbenzenesulfonamide (**8**) (551 mg, 2.0 mmol) and TMEDA (0.66 mL, 4.4 mmol, 2.2 equiv) in THF (20 mL) at –78 °C under Ar was slowly added *s*-BuLi (4.4 mmol, 2.2 equiv) via syringe. The resulting mixture was stirred for 2 h before benzophenone (437 mg, 2.4 mmol, 1.2 equiv) in THF (10mL) was slowly added. The reaction mixture was left to warm slowly to rt and satd NH_4Cl was added. The product was extracted with ether, and the combined organic extract dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (hexane/EtOAc 6:1) gave *N*-cumyl-2-(hydroxydiphenylmethyl)benzenesulfonamide (**9b**) as a colorless solid (868 mg, 95%), mp 143-145 °C.
IR ν_{max} (KBr) 3451, 3257 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, 330K) δ 7.83-7.78 (m, 1H), 7.22-7.09 (m, 17H), 6.89-6.84 (m, 1H), 6.12 (s, 1H), 5.16 (s, 1H), 1.46 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$, 330K) δ 146.2, 146.2, 145.4, 144.1, 141.9, 132.5, 130.6, 130.5, 127.9, 127.8, 127.5, 127.4, 126.6, 125.2, 82.9, 59.3, 30.0; HRMS calcd for $C_{28}H_{27}NO_3S$: 457.1712; found 457.1685.
To **9b** (114 mg, 0.25 mmol) was added ice-cooled TFA (2 mL) and the resulting solution was stirred for 10 min at rt. The solvent was removed in vacuo to give the crude product. Flash chromatography (hexane/EtOAc 2:1) afforded **10b** as a colorless solid (79 mg, 99%).
^1H NMR (200 MHz, $CDCl_3$) δ 7.79 (dd, 1H, J=1.6, 7.0 Hz), 7.61-7.50 (m, 2H), 7.44-7.25 (m, 11H), 5.04 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.0, 142.9, 135.1, 133.2, 129.5, 128.7, 128.4, 127.7, 126.6, 121.4, 72.4.

2-Trimethylsilylphenol (13a).
To a solution of *N*-cumyl-*N*-methyl benzene-*O*-carbamate (**11**) (453 mg, 1.68 mmol) and TMEDA (0.30 mL, 2.0 mmol, 1.2 equiv) in THF (17 mL) at –78 °C under Ar was slowly added *s*-BuLi (2.0 mmol, 1.2 equiv) via syringe. The resulting mixture was stirred for 2 h before TMSCl (0.26 mL, 2.0 mmol, 1.2 equiv) was added. The reaction mixture was stirred for 1.5 h before satd NH_4Cl was added, and the mixture was allowed to warm to rt. The product was extracted with ether, and the combined organic extract dried ($MgSO_4$) in vacuo. Flash chromatography (hexane/EtOAc 9:1) gave *N*-cumyl-*N*-methyl-2-(trimethylsilyl)benzene-*O*-carbamate (**12a**) as a colorless oil (402 mg, 70%).
IR ν_{max} (NaCl, neat) 1728 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, 330K) δ 7.49-7.12 (m, 8H), 6.89 (d, 1H, J=8.4 Hz), 3.15 (s, 3H), 1.84 (s, 6H), 0.35 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$, 330K) δ 156.4, 154.5, 148.2, 134.6, 131.6, 130.1, 128.3, 126.3, 124.8, 124.6, 122.3, 61.6, 32.9, 28.4, -0.7; HRMS calcd for $C_{20}H_{27}NO_2Si$: 341.1811; found 341.1826.
To **12a** (338 mg, 0.99 mmol) was added ice-cooled TFA (4 mL) and the resulting solution was stirred for 6 min at rt. The solvent was removed in vacuo to give the crude product. Flash chromatography (hexane/EtOAc 3:1) afforded *N*-methyl-2-(trimethylsilyl)benzene-*O*-carbamate as a colorless oil (177 mg, 80%).
IR ν_{max} (KBr) 3310, 1707 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.45-7.31 (m, 2H), 7.20-7.06 (m, 2H), 5.25 (br, 1H), 2.87 (d, 0.5H, J=4.7 Hz), 2.75 (d, 2.5H, J=4.7Hz), 0.26 (s,

9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.7, 155.3, 134.7, 131.4, 130.2, 124.8, 121.9, 27.4, -1.1; HRMS calcd for $C_{11}H_{17}NO_2Si$: 223.1029; found 223.1032.
To *N*-methyl-2-(trimethylsilyl)benzene-*O*-carbamate (91 mg, 0.40mmol) in EtOH (1mL) was added 10% NaOH (1mL). The mixture was stirred for 4 h at rt and then neutralized with 1N HCl. . The product was extracted with ether, and the combined organic extract dried ($MgSO_4$) and concentrated in vacuo. Bulb-to-bulb distillation gave **13a** as a volatile colorless oil (66 mg, 99%), bp 89 °C (14 mmHg).
IR ν_{max} (NaCl, neat) 3414 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36 (d, 7.2 Hz), 7.21 (m, 1H), 6.90 (t, 1H, J=7.2 Hz), 6.67 (d, 1H, J=8.1 Hz), 5.54 (brs, 1H), 0.30 (s, 9H).

***N*-methyl-2-(hydroxy)benzamide (13b).**
To a solution of **11** (269 mg, 1.0 mmol) and TMEDA (0.17 mL, 1.1 mmol, 1.1 equiv) in THF (10 mL) at –78 °C under Ar was slowly added *s*-BuLi (1.1 mmol, 1.1 equiv) via syringe. The resulting mixture was stirred for >2 h and then allowed to warm slowly to rt before satd NH_4Cl was added. The product was extracted with ether, and the combined organic extract was washed with 1N NaOH (30 mL). The aqueous extract was acidified with 1N HCl to pH 2, extracted with CH_2Cl_2 and dried ($MgSO_4$). Removal of solvent in vacuo gave a solid (**12b**) which was recrystallized to give a colorless solid (220 mg, 82%), mp 183-185 °C (hexane/CH_2Cl_2).
IR ν_{max} (KBr) 3082, 1612 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ 9.84 (s, 1H), 7.43 (d, 2H, J=8.6 Hz), 7.32-7.06 (m, 5H), 6.89-6.82 (m, 2H), 2.92 (s, 3H), 1.66 (s, 6H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 169.0, 153.3, 149.0, 129.8, 127.9, 127.7, 126.3, 125.3, 124.3, 119.0, 115.7, 60.7, 33.9, 28.1; HRMS calcd for $C_{17}H_{19}NO_2$: 269.1416; found 269.1426.
To **12b** (76 mg, 0.28 mmol) was added 2,2,2-trifluoroethanol (3 mL) and the resulting solution was heated to reflux for 11 h under a $CaCl_2$ drying tube attachment. The solvent was removed in vacuo to give the crude product. Flash chromatography (hexane/EtOAc 7:3) afforded **13b** as a colorless solid (37 mg, 87%).
IR ν_{max} (KBr) 3406, 1645 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 12.42 (s, 1H), 7.40-7.34 (m, 2H), 6.97 (d, 1H, J=8.4 Hz), 6.82 (t, 1H, J=8.4 Hz), 6.63 (brs, 1H), 2.99 (d, 3H, J=4.6 Hz).