General methods. All reagents were either commercially obtained or purified prior to use, or prepared according to literature. Air and moisture-sensitive liquids were transferred via syringe. Organic solutions were concentrated by rotary evaporation below 35 °C using a rotary evaporator. Dichloromethane was distilled from calcium hydride prior to use. Chromatographic purification of products was accomplished using forced-flow chromatography on Baker 7024–R silica gel or by Chromatotron. Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60F plates (230-400 mesh). Visualization of the developed chromatogram was performed by either fluorescence quenching, or by staining with aqueous ceric ammonium molybdate (CAM), aqueous potassium permanganate, or ethanolic *p*-anisaldehyde.

NMR spectra were recorded on either a Delta 400 operating at 400 and 100 MHz or a General Electric 300 operating at 300 MHz for ^{1}H, 470 MHz for ^{19}F, and 75 MHz, for ^{13}C as indicated. ^{1}H NMR spectra are referenced internally to residual protio solvent signals. Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet), integration, and coupling constant (Hz). Data for ^{13}C are reported in terms of chemical shift. ^{19}F NMR are externally referenced to trichlorofluoromethane. Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 with samples prepared as either thin films on NaCl salt plates or as a KBr pellet (as indicated) and reported in cm^{-1}. Combustion analysis was performed by the analytical laboratory at the California Institute of Technology. High resolution mass spectra were obtained from the UC Irvine Mass Spectral facility.

Lithium N,O-bis(trifluoroacetyl)hydroxylamine **1**. To a solution of **3** (8.00 g, 35.5 mmol) in diethyl ether (16 mL) at –78 C was added *tert*-BuLi (1.7 M in pentane, 21.0 mL, 35.5 mmol) over ten minutes. The resulting suspension was allowed to warm to room temperature at which time pentane (20 mL) was added. After stirring for 2 h, the solvent was removed via cannula and the remaining solvent was evaporated *in vacuo* to afford **1** as a colorless powder (7.46 g, 91%): ^{19}F NMR (CD_2Cl_2) δ –70.3, -75.2 ppm; IR (KBr) ν 1786, 1655; mp 195 °C (dec). Anal. Calcd for $C_4F_6LiNO_3$: C, 20.80; N, 6.06. Found: C, 20.67; N, 6.02.

The sulfides used in this study are either commercially available or prepared utilizing known procedures:

Methyl isopropylsulfide: McAllan, D. T.; Cullum, T. V.; Dean, R. A.; Fidler, F. A. *J. Am. Chem. Soc.* **1951**, *73*, 3627.

Thiochromane: Zahalka, H. A.; Robillard, B.; Hughes, L.; Lusztyk, J.; Burton, G. W.; Janzen, E. G.; Kotake, Y.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 3739.

2,3-Dihydrobenzothiophene: Fricke, R.; Spilker, G. *Ber.* **1925**, *58*, 1589.

Representative Experimental Procedure. A solution of **1** (0.462 g, 2.00 mmol), $Cu(OTf)_2$, (0.025 g, 0.070 mmol) and methyl *p*-tolylsulfide (0.135 mL, 1.00 mmol) in DME (10 mL) was heated to 60 °C for 15 h, after which time the green solution was concentrated in vacuo and subjected to chromatography (1:2 hexanes/ethyl acetate) to afford N-trifluoroacetyl-methyl *p*-tolylsulfilimine (0.191 g, 78%) as a white solid.

N-Trifluoroacetyl-methyl *p*-tolylsulfilimine. TLC R_f = 0.34 (1:2 hexanes/EtOAc); mp = 70-72 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69 (dm, 2H, *J* = 8.4 Hz), 7.38 (d, 2H, *J* = 8.1 Hz), 2.93 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.7 (q, *J* = 37 Hz), 144.3, 131.0, 129.7, 127.1, 117.0 (q, *J* = 286 Hz), 34.7, 21.5 ppm; ^{19}F NMR ($CDCl_3$, 400 MHz) δ -73.4 ppm; IR (thin film) ν 1633, 1179, 1141, 978, 876, 810, 773 cm^{-1}; Anal. Calcd for $C_{10}H_{10}F_3NOS$: C, 48.19; H, 4.04; N, 5.62. Found: C, 47.93; H, 3.92; N, 5.90.

N-Trifluoroacetyl-methyl isopropylsulfilimine. TLC R_f = 0.14 (1:2 hexanes/ethyl acetate); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.38 (hept, 1H, *J* = 6.9 Hz), 2.62 (s, 3H), 1.37

(dd, 6H, *J* = 6.8, 3.8 Hz) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.37 (q, *J* = 34 Hz), 116.7 (q, *J* = 286 Hz), 47.5, 24.9, 16.1, 15.3 ppm; ^{19}F ($CDCl_3$, 400 MHz) δ -73.6 ppm; IR (thin film) ν 1634, 1184, 1139, 1070, 966, 877, 797, 773 cm^{-1}; HRMS calcd for $C_6H_{11}F_3NOS$ (MH+) 202.0513, found 202.0513.

N-Trifluoroacetyl-methyl cyclohexylsulfilimine. TLC R_f = 0.18 (1:2 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.18 (tt, 1H, *J* = 12.0, 6.0 Hz), 2.69 (s, 3H), 2.17 (dm, 1H, *J* = 10.8 Hz), 2.05 (dm, 1H, *J* = 12.3 Hz), 1.93 (dm, 2H, *J* = 12.0 Hz), 1.75 (dm, 1H, *J* = 9.9 Hz), 1.56-1.24 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.3 (q, *J* = 34 Hz), 117.1 (q, *J* = 286 Hz), 56.4, 26.7, 26.2, 25.2 ppm; ^{19}F ($CDCl_3$, 400 MHz) δ -73.6 ppm; IR (thin film) ν 1630, 1178, 1138, 967, 874, 795, 772 cm^{-1}; HRMS calcd for $C_9H_{15}F_3NOS$ (MH+) 242.0826, found 242.0821.

S-Trifluoroacetamide thiobenzopyran. TLC R_f = 0.34 (1:2 hexanes/EtOAc); mp = 100-102 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89 (dd, 1H, *J* = 7.8, 1.2 Hz), 7.51 (td, 1H, *J* = 7.5, 1.4 Hz), 7.39 (tm, 1H, *J* = 4.4 Hz), 7.31 (dm, 1H, *J* = 7.5 Hz), 3.55 (ddd, 1H, *J* = 13.5, 5.7, 2.4 Hz), 3.25 (ddd, 1H, *J* = 14.4, 11.4, 3.0 Hz), 3.16 (td, 1H, *J* = 17.6, 4.9 Hz) 2.95 (ddd, 1H, *J* = 17.6, 10.8, 5.4), 2.76-2.61 (m, 1H), 2.28-2.17 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.3 (q, *J* = 34 Hz), 137.1, 132.8, 132.7, 131.3, 128.0, 126.5, 117.1 (q, *J* = 286 Hz), 39.2, 27.6, 15.6 ppm; ^{19}F NMR ($CDCl_3$, 400 MHz) δ -73.4 ppm; IR (thin film) ν 1633, 1179, 1139, 880, 760 cm^{-1}; Anal. Calcd for $C_{11}H_{10}F_3NOS$: C, 50.57; H, 3.86; N, 5.36. Found: C, 50.30; H, 4.01; N, 5.37.

S-Trifluoroacetamide benzothiophene. TLC R_f = 0.32 (1:2 hexanes/EtOAc); mp = 96-97 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, 1H, *J* = 8.0 Hz), 7.56 (t, 1H, *J* = 7.5 Hz), 7.56-7.42 (m, 2H), 3.92 (dt, 1H, *J* = 16.1, 8.4 Hz), 3.73-3.61 (m, 2H), 3.44 (ddd, 1H, *J* = 16.1, 7.3, 3.3 Hz), ^{13}C NMR (d6-acetone, 100 MHz) δ 171.4 (q, *J* = 34 Hz), 150.2, 140.4, 138.4, 133.8, 133.7, 131.8, 122.6 (q, *J* = 358 Hz), 50.2, 37.3, ppm; ^{19}F NMR ($CDCl_3$, 400 MHz) δ -73.4 ppm; IR (thin film) ν 1622, 1185, 1133, 884, 796, 764 cm^{-1}; Anal. Calcd for $C_{10}H_{18}F_3NOS$: C, 48.58; H, 3.26; N, 5.67. Found: C, 48.48; H, 3.07; N, 5.48.

N-Trifluoroacetyl-methyl *p*-methoxyphenylsulfilimine. TLC R_f = 0.28 (1:2 hexanes/EtOAc); mp = 80-82 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80 (d, 2H, *J* = 8.7 Hz), 7.11 (d, 2H, *J* = 8.7 Hz), 3.92 (s, 3H), 2.98 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.3 (q, *J* = 38 Hz), 163.3, 129.1, 122.9, 116.7 (q, *J* = 286 Hz), 115.6, 55.5, 34.5 ppm; ^{19}F ($CDCl_3$, 400 MHz) δ -73.5 ppm; IR (thin film) ν 1634, 1594, 1498, 1307, 1263, 1182, 1140, 1086, 1025, 977, 876, 832, 799, 773 cm^{-1}; Anal. Calcd for $C_{10}H_{10}F_3NO_2S$: C, 45.28; H, 3.80; N, 5.28. Found: C, 45.28; H, 3.88; N, 5.22.

N-Trifluoroacetyl-methyl *p*-chlorophenylsulfilimine. TLC R_f = 0.32 (1:2 hexanes/EtOAc); mp = 82-84 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 (dm, 2H, *J* = 8.7 Hz), 7.58 (dm, 2H, *J* = 8.7 Hz), 2.96 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9 (q, *J* = 35 Hz), 139.9, 131.7, 130.7, 128.6, 116.9 (q, *J* = 286 Hz), 34.8 ppm; ^{19}F ($CDCl_3$, 400 MHz) δ -73.5 ppm; IR (thin film) ν 1631, 1183, 1140, 978, 824, 773 cm^{-1}; Anal. Calcd for $C_9H_7ClF_3NOS$: C, 40.09; H, 2.77; N, 5.19. Found: C, 39.94; H, 2.77; N, 5.17.

N-Trifluoroacetyl-methyl *p*-bromophenylsulfilimine. TLC R_f = 0.44 (1:2 hexanes/EtOAc); mp = 94-96 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.72 (dm, 2H, *J* = 8.7 Hz), 7.67 (dm, 2H, *J* = 8.7 Hz), 2.94 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9 (q, *J* = 35 Hz), 133.7, 132.1, 128.5, 128.2, 116.9 (q, *J* = 288 Hz), 34.8 (q, *J* = 11 Hz) ppm; ^{19}F ($CDCl_3$, 400 MHz) δ -73.6 ppm; IR (thin film) ν 1631, 1177, 1153, 1070, 1010, 975, 962, 912, 878, 818 cm^{-1}; Anal. Calcd for $C_9H_7BrF_3NOS$: C, 34.41; H, 2.25; N, 4.46. Found: C, 34.41; H, 2.36; N, 4.43.

N-Trifluoroacetyl-ethyl phenylsulfilimine. TLC R_f = 0.40 (1:2 hexanes/EtOAc); mp = 62-64 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80-7.75 (m, 2H), 7.64-7.57 (m, 3H), 3.32-3.18 (m, 2H), 1.26 (t, 3H, *J* = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.7 (q, *J* = 37 Hz), 132.9, 130.5, 129.9, 127.3, 116.8 (q, *J* = 285 Hz) 43.8, 7.2 ppm; ^{19}F NMR ($CDCl_3$, 400 MHz) δ -73.4 ppm; IR (thin film) ν 1634, 1180, 1140, 882, 802, 775, 748, 688 cm^{-1}; Anal. Calcd for $C_{10}H_{10}F_3NOS$: C, 48.19; H, 4.04; N, 5.62. Found: C, 47.86; H, 4.20; N, 5.58.