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***o*-Iodoxybenzoic Acid (IBX) as a Viable Reagent in the Manipulation of Nitrogen- and Sulfur-Containing Substrates: Scope, Generality and Mechanism of IBX-Mediated Amine Oxidations and Dithiane Deprotections**

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Supporting Information

General Procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), toluene, diethyl ether (ether) and methylene chloride (CH_2Cl_2) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Anhydrous dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were purchased commercially and used without further purification. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. *o*-Iodoxybenzoic acid (IBX) was prepared via the method of Santagostino.¹ **Caution!** IBX has been proven to be both shock-sensitive, and explosive when subjected to elevated temperatures.² Therefore, appropriate precautions should be taken when working with IBX, especially when conducting procedures on large scale and/or when heating is employed. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. E. Merck silica gel

(60, particle size 0.040–0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on 0.25 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Bruker DRX-600, DRX-500, or AMX-400 instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, b = broad, app = apparent. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Electrospray ionization mass spectrometry (ESIMS) experiments were performed on an API 100 Perkin Elmer SCIEX single quadrupole mass spectrometer at 4000V emitter voltage. High-resolution mass spectra (HRMS) were recorded on a VG ZAB-ZSE mass spectrometer under fast atom bombardment (FAB) conditions with NBA as the matrix or using MALDI. Molecular rotations were recorded on a Model 343 Perkin Elmer polarimeter. Melting points (m.p.) are uncorrected and were recorded on a Thomas-Hoover Unimelt capillary melting point apparatus.

Experimental Data for Compounds

General procedure for IBX-induced oxidation of amines at room temperature (Procedure A). IBX (92 mg, 0.33 mmol) was dissolved in DMSO (0.5 mL) with vigorous stirring for approximately 30 min at ambient temperature. This IBX solution was then added to a solution of amine (0.30 mmol) in DMSO (0.5 mL) and allowed to stir at room temperature for 10–20 min. The mixture was quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL) and then basified with saturated aqueous NaHCO_3 (1 mL). Following extraction with EtOAc (5 mL), the organic phase was washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated to yield the corresponding imine which, generally, needed no further purification.

General procedure for IBX-induced oxidation of amines at elevated temperatures (Procedure B). IBX (92 mg, 0.33 mmol) was added as a solid to a solution of amine (0.30 mmol) in DMSO (1 mL) and allowed to stir at 45 °C for 0.3–14 h. The mixture was cooled to

room temperature and quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL) and then basified with saturated aqueous NaHCO_3 (1 mL). Following extraction with EtOAc (5 mL), the organic phase was washed with water (2×10 mL) and brine (10 mL) and then dried (MgSO_4) and concentrated to yield the corresponding imine which, generally, needed no further purification.

4,4'-Dibromodibenzylamine (3). 4-Bromobenzylbromide (0.70 g, 2.8 mmol) was added to a solution of 4-bromobenzylamine (1.0 g, 5.6 mmol) and potassium carbonate (1.9 g, 14 mmol) in DMF (20 mL). The reaction mixture was allowed to stir at room temperature for 48 h, and then quenched by addition of water (10 mL). The mixture was then extracted with ether (30 mL) and washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated. The residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 4:1 to 2:1) to give the corresponding secondary amine (0.81 g, 81% yield). **3:** white crystalline solid, m.p. 48–49 °C; $R_f = 0.33$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3040, 2827, 1590, 1486, 1403, 1103, 1070, 1010, 806, 483 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.45 (d, $J = 8.1$ Hz, 4 H), 7.21 (d, $J = 8.1$ Hz, 4 H), 3.73 (s, 4 H), 1.62 (bs, 1 H); ^{13}C NMR (500 MHz, CDCl_3) δ 139.06, 131.42, 129.77, 120.71, 52.28; HRMS (MALDI-FTMS) calcd for $\text{C}_{14}\text{H}_{13}\text{Br}_2\text{NH}^+$ [$\text{M} + \text{H}^+$] 353.9487, found 353.9488.

4-Bromo-N-[(4-bromophenyl)methylene]-benzenemethanamine (4). Procedure A (91% yield); white solid, m.p. 89–92 °C; $R_f = 0.71$ (silica gel, hexanes:EtOAc, 2:1); IR (KBr pellet) ν_{max} 3084, 2849, 1637, 1584, 1484, 1396, 1067, 1008, 820, 509 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.33 (s, 1 H), 7.65 (d, $J = 8.4$ Hz, 2 H), 7.56 (d, $J = 8.4$ Hz, 2 H), 7.47 (d, $J = 8.4$ Hz, 2 H), 7.21 (d, $J = 8.4$ Hz, 2 H), 4.75 (s, 2 H); ^{13}C NMR (500 MHz, CDCl_3) δ 161.00, 138.03, 134.81, 131.88, 131.58, 129.66, 129.62, 125.35, 120.92, 64.21; HRMS (MALDI-FTMS) calcd for $\text{C}_{14}\text{H}_{11}\text{Br}_2\text{NH}^+$ [$\text{M} + \text{H}^+$] 351.9331, found 351.9340.

4,4'-Dimethoxydibenzylamine (5). 4-Methoxybenzylbromide (1.1 mL, 8.3 mmol) was added to a solution of 4-methoxybenzylamine (1.1 mL, 8.3 mmol) and potassium carbonate (1.5 g, 11 mmol) in DMF (30 mL). The reaction mixture was allowed to stir at 70 °C for 14 h, and

then quenched by addition of water (10 mL). The mixture was then extracted with ether (30 mL) and washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated. The residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 2:1 to 1:1) to give the corresponding secondary amine (0.54 g, 25% yield). **5**: light yellow oil; $R_f = 0.21$ (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2934, 2833, 1611, 1512, 1461, 1299, 1246, 1175, 1034, 820 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.27 (d, $J = 8.8$ Hz, 4 H), 6.87 (d, $J = 8.8$ Hz, 4 H), 3.79 (s, 6 H), 3.73 (s, 4 H); ^{13}C NMR (500 MHz, CDCl_3) δ 158.74, 129.57, 113.82, 113.80, 55.25, 51.97; HRMS (MALDI-FTMS) calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2\text{H}^+$ $[\text{M} + \text{H}^+]$ 258.1488, found 258.1487.

4-Methoxy-*N*-[(4-methoxyphenyl)methylene]-benzenemethanamine (6). Procedure B (99% yield); Procedure A (61% yield based on recovered starting material: 31% product; 49% recovered **5**); light yellow oil; $R_f = 0.52$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2933, 2835, 1606, 1512, 1460, 1249, 1169, 1031, 832, 524 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1 H), 7.72 (d, $J = 9.1$ Hz, 2 H), 7.25 (d, $J = 9.1$ Hz, 2 H), 6.92 (d, $J = 8.8$ Hz, 2 H), 6.88 (d, $J = 8.8$ Hz, 2 H), 4.73 (s, 2 H), 3.84 (s, 3 H), 3.80 (s, 3 H); ^{13}C NMR (500 MHz, CDCl_3) δ 161.61, 160.87, 159.46, 158.58, 131.59, 129.75, 129.09, 113.90, 113.84, 64.30, 55.27, 55.21; HRMS (MALDI-FTMS) calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_2\text{H}^+$ $[\text{M} + \text{H}^+]$ 256.1332, found 256.1332.

Isoindole (9). Obtained in trace amounts using Procedure A; HRMS (MALDI-FTMS) calcd for $\text{C}_8\text{H}_7\text{NH}^+$ $[\text{M} + \text{H}^+]$ 118.0651, found 118.0646.

2-(Benzylideneamino)-ethanol (11). Procedure B (79% yield); light yellow oil; $R_f = 0.16$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3378, 2877, 1697, 1648, 1450, 1205, 1063, 905, 866, 754, 693, 490 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.20 (s, 1 H), 7.65–7.63 (m, 2 H), 7.38–7.35 (m, 3 H), 3.87 (t, $J = 5.3$ Hz, 2 H), 3.69 (t, $J = 5.3$ Hz, 2 H), 3.56 (bs, 1 H); ^{13}C NMR (500 MHz, CDCl_3) δ 163.14, 135.52, 130.66, 128.40, 128.05, 63.31, 61.88; HRMS (MALDI-FTMS) calcd for $\text{C}_9\text{H}_{11}\text{NOH}^+$ $[\text{M} + \text{H}^+]$ 150.0913, found 150.0915.

***N'*-Benzylidene-*N,N*-dimethyl-ethylenediamine (13).** Procedure A (74% yield); light yellow oil; $R_f = 0.08$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2941, 2820, 2771, 1647,

1454, 1311, 1026, 754, 694, 494 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1 H), 7.72–7.70 (m, 2 H), 7.39–7.37 (m, 3 H), 3.73 (t, $J = 7.1$ Hz, 2 H), 2.64 (t, $J = 7.1$ Hz, 2 H), 2.30 (s, 6 H); ^{13}C NMR (600 MHz, CDCl_3) δ 161.77, 136.10, 130.50, 128.46, 128.02, 60.04, 59.80, 45.79; HRMS (MALDI-FTMS) calcd for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{H}^+$ $[\text{M} + \text{H}^+]$ 177.1386, found 177.1387.

3-(Benzylideneamino)-propionitrile (15). Procedure A (95% yield); light yellow oil; $R_f = 0.22$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3030, 2853, 2194, 1646, 1452, 1312, 1033, 756, 695 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.34 (s, 1 H), 7.75–7.73 (m, 2 H), 7.45–7.41 (m, 3 H), 3.82 (td, $J = 6.6, 1.3$ Hz, 2 H), 2.74 (t, $J = 6.6$ Hz, 2 H); ^{13}C NMR (600 MHz, CDCl_3) δ 163.49, 135.29, 131.16, 128.58, 128.28, 118.31, 56.05, 19.43; HRMS (MALDI-FTMS) calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{H}^+$ $[\text{M} + \text{H}^+]$ 159.0917, found 159.0918.

(R)-(-)-(α -[(Phenylmethoxy)methyl]-N-(phenylmethyl)-benzenemethanamine (16). Prepared from (R)-(-)-N-benzyl-2-phenyl glycinol using the procedure reported in ref. 3. **16:** 49% yield; colorless oil; $[\alpha]_D -43.0$ (c 1.15, MeOH); $R_f = 0.71$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3331, 3028, 2856, 1493, 1454, 1361, 1090, 738, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.46–7.44 (m, 2 H), 7.39–7.25 (m, 13 H), 4.55 (d, $J = 12.0$ Hz, 1 H), 4.50 (d, $J = 12.0$ Hz, 2 H), 4.02 (dd, $J = 7.9, 5.0$ Hz, 1 H), 3.74 (d, $J = 13.2$ Hz, 1 H), 3.60–3.57 (m, 3 H), 2.54 (bs, 1 H); ^{13}C NMR (500 MHz, CDCl_3) δ 140.32, 138.02, 128.43, 128.36, 128.33, 128.17, 127.80, 127.68, 127.63, 127.54, 126.84, 75.36, 73.13, 62.01, 51.22; HRMS (MALDI-FTMS) calcd for $\text{C}_{22}\text{H}_{23}\text{NOH}^+$ $[\text{M} + \text{H}^+]$ 318.1852, found 318.1848.

α -[(Phenylmethoxy)methyl]-N-(phenylmethylene)-benzenemethanamine (17). Procedure B (78% yield based on recovered starting material: 49% product; 37% recovered **16**); colorless oil; $R_f = 0.79$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2921, 1604, 1506, 1254, 1180, 1035, 709 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.41 (s, 1 H), 7.83–7.82 (m, 2 H), 7.49–7.25 (m, 12 H), 4.61–4.54 (m, 3 H), 3.82 (app d, $J = 6.2$ Hz, 2 H); ^{13}C NMR (500 MHz, CDCl_3) δ 161.57, 141.06, 140.08, 136.35, 130.62, 128.48, 128.41, 128.39, 128.28, 127.56, 127.47, 127.39, 127.31, 75.05, 74.66, 73.14; HRMS (MALDI-FTMS) calcd for $\text{C}_{22}\text{H}_{21}\text{NOH}^+$ $[\text{M} + \text{H}^+]$ 316.1696, found 316.1702.

***N*-Benzylidene-1-methyl-ethylamine (19).** Procedure B (88% yield); colorless oil; R_f = 0.72 (silica gel, hexanes:EtOAc, 2:1); IR (film) $\nu_{\max}$ 2968, 2836, 1703, 1646, 1453, 1204, 1164, 826, 751, 692 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.31 (s, 1 H), 7.75–7.73 (m, 2 H), 7.41–7.39 (m, 3 H), 3.55 (sep, J = 6.1 Hz, 1 H), 1.28 (d, J = 6.1 Hz, 6 H); ^{13}C NMR (600 MHz, CDCl_3) δ 158.14, 136.45, 130.24, 128.42, 127.96, 61.55, 24.08; HRMS (MALDI-FTMS) calcd for $\text{C}_{10}\text{H}_{13}\text{NH}^+$ [$\text{M} + \text{H}^+$] 148.1121, found 148.1123.

***N,O*-Dibenzylhydroxylamine (22).** Benzyl bromide (1.5 mL, 13 mmol) was added to a solution of *O*-benzylhydroxylamine hydrochloride (2.0 g, 13 mmol) and potassium carbonate (5.2 g, 38 mmol) in DMF (50 mL). The reaction mixture was allowed to stir at room temperature for 14 h, and then quenched by addition of water (10 mL). The resulting mixture was then extracted with chloroform (50 mL) and washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated. The residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 4:1 to 2:1) to give the corresponding secondary amine (0.61 g, 23% yield). **22:** colorless oil; R_f = 0.69 (silica gel, hexanes:EtOAc, 2:1); IR (film) $\nu_{\max}$ 3029, 2915, 1494, 1452, 987, 744, 695 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.38–7.29 (m, 10 H), 4.70 (s, 2 H), 4.07 (s, 2 H); ^{13}C NMR (500 MHz, CDCl_3) δ 137.38, 136.73, 129.14, 128.54, 128.42, 128.36, 127.91, 127.61, 76.31, 56.26; HRMS (MALDI-FTMS) calcd for $\text{C}_{14}\text{H}_{15}\text{NOH}^+$ [$\text{M} + \text{H}^+$] 214.1226, found 214.1225.

***O*-Benzylbenzaldoxime (23).** Procedure A (99% yield); colorless oil; R_f = 0.81 (silica gel, hexanes:EtOAc, 2:1); IR (film) $\nu_{\max}$ 3029, 2926, 1450, 1366, 1210, 1019, 945, 754, 694, 510 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.15 (s, 1 H), 7.60–7.59 (m, 2 H), 7.44–7.32 (m, 8 H), 5.23 (s, 2 H); ^{13}C NMR (600 MHz, CDCl_3) δ 149.02, 137.45, 132.17, 129.81, 128.64, 128.42, 128.39, 127.95, 127.06, 76.38; HRMS (MALDI-FTMS) calcd for $\text{C}_{14}\text{H}_{13}\text{NOH}^+$ [$\text{M} + \text{H}^+$] 212.1070, found 212.1068.

3,4-Dihydro- β -carboline (25). Procedure A (99% yield based on recovered starting material: 40% product; 59% recovered **24**); orange oil; R_f = 0.09 (silica gel, EtOAc); IR (film) $\nu_{\max}$ 2924, 2849, 1631, 1549, 1453, 1326, 1161, 1020, 743 cm^{-1} ; ^1H NMR (600 MHz, DMSO-

δ 11.32 (s, 1 H), 8.36 (s, 1 H), 7.56 (d, $J = 7.7$ Hz, 1 H), 7.40 (d, $J = 8.8$ Hz, 1 H), 7.19 (app t, $J = 7.2$ Hz, 1 H), 7.04 (app t, $J = 7.2$ Hz, 1 H), 3.78 (t, $J = 8.8$ Hz, 2 H), 2.80 (t, $J = 8.8$ Hz, 2 H); ^{13}C NMR (500 MHz, DMSO- d_6) δ 151.62, 136.69, 128.41, 124.81, 123.73, 119.68, 119.57, 113.84, 112.50, 48.10, 18.71; HRMS (MALDI-FTMS) calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{H}^+$ [$\text{M} + \text{H}^+$] 171.0917, found 171.0921.

3,4-Dihydroisoquinoline (27). Procedure A (78% yield); orange oil; $R_f = 0.23$ (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 3020, 2935, 1627, 1575, 1454, 1210, 1005, 879, 755, 693, 590 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 8.31 (s, 1 H), 7.33 (app td, $J = 7.2, 1.8$ Hz, 1 H), 7.28–7.24 (m, 2 H), 7.13 (d, $J = 7.5$ Hz, 1 H), 3.76–3.73 (m, 2 H), 2.72 (t, $J = 7.5$ Hz, 2 H); ^{13}C NMR (600 MHz, CDCl_3) δ 160.28, 136.21, 130.98, 128.36, 127.32, 127.13, 126.97, 47.20, 24.89; HRMS (MALDI-FTMS) calcd for $\text{C}_9\text{H}_9\text{NH}^+$ [$\text{M} + \text{H}^+$] 132.0808, found 132.0812.

4-Bromodibenzylamine (31). Benzyl bromide (0.28 mL, 2.4 mmol) was slowly added to a solution of 4-bromobenzylamine (0.88 g, 4.7 mmol) and potassium carbonate (1.6 g, 12 mmol) in DMF (20 mL). The reaction mixture was allowed to stir at room temperature for 23 h, and then quenched by addition of water (10 mL). The resulting mixture was then extracted with ether (30 mL) and washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated. The residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 4:1 to 2:1) to give the corresponding secondary amine (0.55 g, 84% yield). **31:** light yellow oil; $R_f = 0.50$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3313, 3026, 2826, 1488, 1453, 1105, 1071, 1010, 794, 737, 588 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 8.5$ Hz, 2 H), 7.35–7.34 (m, 4 H), 7.29–7.26 (m, 1 H), 7.24 (d, $J = 8.5$ Hz, 2 H), 3.79 (s, 2 H), 3.76 (s, 2 H), 1.67 (bs, 1 H); ^{13}C NMR (400 MHz, CDCl_3) δ 140.03, 139.27, 131.40, 129.81, 128.40, 128.08, 127.00, 120.63, 53.04, 52.34; HRMS (MALDI-FTMS) calcd for $\text{C}_{14}\text{H}_{14}\text{BrNH}^+$ [$\text{M} + \text{H}^+$] 276.0382, found 276.0381.

N-Benzylidene-4-bromobenzylamine (32). Procedure B (99% crude yield; 32:2:33:4, 0.8:1.0:1.7:1.2); white solid, m.p. 48–50 $^\circ\text{C}$; $R_f = 0.73$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3060, 2841, 1701, 1648, 1578, 1487, 1450, 1378, 1221, 1071, 1011, 797, 754, 693 cm^{-1} ; ^1H

NMR (500 MHz, CDCl_3) δ 8.39 (s, 1 H), 7.82–7.80 (m, 2 H), 7.47–7.44 (m, 5 H), 7.24 (d, J = 8.4 Hz, 2 H), 4.77 (s, 2 H); ^{13}C NMR (500 MHz, CDCl_3) δ 162.25, 138.31, 135.87, 131.45, 130.85, 129.55, 128.56, 128.21, 120.72, 64.12; HRMS (MALDI-FTMS) calcd for $\text{C}_{14}\text{H}_{12}\text{BrNH}^+$ $[\text{M} + \text{H}^+]$ 274.0226, found 274.0224.

***N*-(4-Bromobenzylidene)-benzylamine (33).** Procedure B (99% crude yield; 33:2:32:4, 1.7:1.0:0.8:1.2); white solid, m.p. 40–41 °C (lit.⁴ 43–44 °C); R_f = 0.62 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3027, 2840, 1645, 1590, 1488, 1451, 1374, 1295, 1067, 1010, 823, 699 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.34 (s, 1 H), 7.67 (d, J = 8.4 Hz, 2 H), 7.56 (d, J = 8.4 Hz, 2 H), 7.39–7.35 (m, 4 H), 7.31–7.28 (m, 1 H), 4.83 (s, 2 H); ^{13}C NMR (500 MHz, CDCl_3) δ 160.56, 138.92, 134.95, 131.76, 129.61, 128.48, 127.92, 127.03, 125.09, 64.94; HRMS (MALDI-FTMS) calcd for $\text{C}_{14}\text{H}_{12}\text{BrNH}^+$ $[\text{M} + \text{H}^+]$ 274.0226, found 274.0219.

4-Methoxydibenzylamine (34). Benzyl bromide (0.30 mL, 2.5 mmol) was slowly added to a solution of 4-bromobenzylamine (0.65 mL, 5.0 mmol) and potassium carbonate (1.7 g, 13 mmol) in DMF (20 mL). The reaction mixture was allowed to stir at room temperature for 23 h, and then quenched by addition of water (10 mL). The mixture was then extracted with ether (30 mL) and washed with water (2 $\times$ 10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated. The residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 2:1 to 1:2) to give the corresponding secondary amine (0.37 g, 65% yield). 34: light yellow oil; R_f = 0.25 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3328, 2908, 2832, 1611, 1512, 1455, 1299, 1246, 1175, 1106, 1034, 822 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.38–7.34 (m, 4 H), 7.30–7.27 (m, 3 H), 6.90 (d, J = 8.4 Hz, 2 H), 3.82 (s, 5 H), 3.77 (s, 2 H), 1.73 (bs, 1 H); ^{13}C NMR (500 MHz, CDCl_3) δ 158.54, 140.27, 132.34, 129.26, 128.31, 128.08, 126.84, 113.69, 55.18, 52.97, 52.46; HRMS (MALDI-FTMS) calcd for $\text{C}_{15}\text{H}_{17}\text{NOH}^+$ $[\text{M} + \text{H}^+]$ 228.1383, found 228.1379.

***N*-Benzylidene-4-methoxybenzylamine (35).** Procedure B (99% crude yield; 35:2:36:6, 1.6:1.0:0.7:1.0); light yellow oil; R_f = 0.66 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3001, 2834, 1645, 1609, 1512, 1451, 1300, 1247, 1175, 1035, 817, 761, 694, 575 cm^{-1} ; ^1H NMR (400

MHz, CDCl₃) δ 8.38 (s, 1 H), 7.80–7.78 (m, 2 H), 7.44–7.41 (m, 3 H), 7.27 (d, J = 8.8 Hz, 2 H), 6.90 (d, J = 8.5 Hz, 2 H), 4.78 (s, 2 H), 3.81 (s, 3 H); ¹³C NMR (400 MHz, CDCl₃) δ 161.59, 158.62, 136.10, 131.26, 130.67, 129.15, 128.53, 128.20, 113.85, 64.41, 55.22; HRMS (MALDI-FTMS) calcd for C₁₅H₁₅NOH⁺ [M + H⁺] 226.1226, found 226.1226.

***N*-(4-Methoxybenzylidene)-benzylamine (36).** Procedure B (99% crude yield; 36:2:35:6, 0.7:1.0:1.6:1.0); light yellow oil; R_f = 0.53 (silica gel, hexanes:EtOAc, 2:1); IR (film) $\nu_{\max}$ 3027, 2836, 1604, 1512, 1455, 1306, 1251, 1165, 1030, 834, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.34 (s, 1 H), 7.75 (d, J = 8.8 Hz, 2 H), 7.36–7.35 (m, 4 H), 7.29–7.27 (m, 1 H), 6.96 (d, J = 8.8 Hz, 2 H), 4.81 (d, J = 1.1 Hz, 2 H), 3.85 (s, 3 H); ¹³C NMR (500 MHz, CDCl₃) δ 161.63, 161.26, 139.50, 129.77, 129.04, 128.39, 127.88, 126.83, 113.90, 64.89, 55.27; HRMS (MALDI-FTMS) calcd for C₁₅H₁₅NOH⁺ [M + H⁺] 226.1226, found 226.1225.

IBX•*tert*-Butylamine complex (47). 99% conversion by ¹H NMR (compound not isolated from DMSO); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.10 (d, J = 7.4 Hz, 1 H), 8.05 (bs, 2 H), 7.94 (dd, J = 7.4, 1.5 Hz, 1 H), 7.78 (app t, J = 8.2 Hz, 1 H), 7.63 (app t, J = 7.4 Hz, 1 H), 1.26 (s, 9 H); ¹³C NMR (400 MHz, DMSO-*d*₆) δ 167.32, 148.14, 134.65, 131.45, 130.76, 129.33, 122.45, 50.92, 27.27; HRMS (ESI) calcd for C₁₁H₁₆INO₄H⁺ [M + H⁺] 354.0, found 354.0.

***N*-Benzylcyclopropylamine (52).** Benzyl bromide (0.35 mL, 2.9 mmol) was slowly added to a solution of cyclopropylamine (0.41 mL, 5.8 mmol) and potassium carbonate (2.0 g, 15 mmol) in DMF (20 mL). The reaction mixture was allowed to stir at room temperature for 21 h, and then quenched by addition of water (10 mL). The mixture was then extracted with ether (30 mL) and washed with water (2 × 10 mL) and brine (10 mL), and then dried (MgSO₄) and concentrated. The residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 4:1 to 2:1) to give the corresponding secondary amine (0.21 g, 48% yield). **52:** light yellow oil; R_f = 0.32 (silica gel, hexanes:EtOAc, 1:1); IR (film) $\nu_{\max}$ 3318, 3084, 3007, 2932, 2819, 1494, 1452, 1372, 1346, 1212, 1015, 829, 732, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.27–7.25 (m, 5 H), 3.85 (s, 2 H), 2.19–2.14 (m, 1 H), 1.99 (bs, 1 H), 0.47–0.39 (m, 4

H); ^{13}C NMR (500 MHz, CDCl_3) δ 140.43, 128.31, 128.17, 126.81, 53.65, 29.96, 6.38; HRMS (MALDI-FTMS) calcd for $\text{C}_{10}\text{H}_{13}\text{NH}^+$ $[\text{M} + \text{H}^+]$ 148.1121, found 148.1119.

***N*-Benzylidene-cyclopropylamine (53).** Procedure A (96% yield); light yellow oil; R_f = 0.85 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3010, 2960, 2867, 1635, 1451, 1308, 1172, 1018, 954, 886, 754, 693 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.45 (s, 1 H), 7.69–7.67 (m, 2 H), 7.39–7.38 (m, 3 H), 3.06–3.01 (m, 1 H), 1.00–0.92 (m, 4 H); ^{13}C NMR (400 MHz, CDCl_3) δ 158.36, 136.39, 129.99, 128.46, 127.46, 41.88, 8.72; HRMS (MALDI-FTMS) calcd for $\text{C}_{10}\text{H}_{11}\text{NH}^+$ $[\text{M} + \text{H}^+]$ 146.0964, found 146.0963.

2-(Methylthio)-imidazole (57). IBX (167 mg, 0.598 mmol) was added to a solution of 2-methylthio-2-imidazoline (46.3 mg, 0.399 mmol; obtained from the commercially available hydrobromide salt) in DMSO (1 mL). The reaction mixture was allowed to stir at 45 °C for 16 h, and then quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL). The resulting mixture was basified with 1 M KOH (1 mL) and extracted with EtOAc (5 $\times$ 5 mL), and then dried (MgSO_4) and concentrated to give the corresponding imidazole (36.9 mg, 81% yield). **57**: white solid, m.p. 134–135 °C (lit.⁵ 136–138 °C); R_f = 0.11 (silica gel, hexanes:EtOAc, 1:2); IR (film) ν_{max} 2628, 1549, 1414, 1330, 1099, 962, 770 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.13 (s, 2 H), 2.64 (s, 3 H); ^{13}C NMR (500 MHz, CDCl_3) δ 141.86, 122.66, 17.00; HRMS (MALDI-FTMS) calcd for $\text{C}_4\text{H}_6\text{N}_2\text{SH}^+$ $[\text{M} + \text{H}^+]$ 115.0324, found 115.0323.

***N*-(1,1-Dimethylethyl)-3-isoquinolinecarboxamide (60).** IBX (76.0 mg, 0.270 mmol) was added to a solution of [(3*S*)-(3-1,2,3,4-tetrahydroisoquinolyl)]-*N*-(*tert*-butyl)carboxamide (41.7 mg, 0.180 mmol) in DMSO (0.6 mL). The reaction mixture was allowed to stir at 45 °C for 6.5 h, and then quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL). The resulting mixture was then basified with 1 M KOH (1 mL) and extracted with EtOAc (5 mL). The organic phase was washed with water (2 $\times$ 10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated to give the corresponding isoquinoline (39.1 mg, 95% yield). **60**: light yellow solid, m.p. 104–106 °C; R_f = 0.68 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3370, 2967, 1671, 1522, 1444, 1390, 1287, 1226, 764, 499 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 9.13 (s, 1 H), 8.59

(s, 1 H), 8.22 (bs, 1 H), 8.02 (d, $J = 8.1$ Hz, 1 H), 7.96 (d, $J = 8.1$ Hz, 1 H), 7.75 (ddd, $J = 8.1$, 7.0, 1.1 Hz, 1 H), 7.68 (ddd, $J = 8.1$, 7.0, 1.1 Hz, 1 H), 1.54 (s, 9 H); ^{13}C NMR (500 MHz, CDCl_3) δ 163.67, 150.53, 144.24, 136.16, 131.11, 129.41, 128.70, 128.09, 127.62, 119.88, 51.03, 28.80; HRMS (MALDI-FTMS) calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{OH}^+$ [$\text{M} + \text{H}^+$] 229.1335, found 229.1334.

4-(4-Chlorophenyl)-pyridine (62). IBX (79.0 mg, 0.284 mmol) was added to a solution of 4-(4-chlorophenyl)-1,2,3,6-tetrahydropyridine hydrochloride (43.5 mg, 0.189 mmol) in DMSO (0.5 mL). The reaction mixture was allowed to stir at 45 °C for 48 h, and then quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL). The resulting mixture was then basified with 1 M KOH (1 mL) and extracted with EtOAc (5 mL). The organic phase was washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated to give the corresponding pyridine (32.3 mg, 90% yield). **62**: off-white solid, m.p. 67–69 °C (lit.⁶ 71–72 °C); $R_f = 0.43$ (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 3052, 1596, 1479, 1396, 1092, 801, 478, 499 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.68 (bs, 2 H), 7.58 (d, $J = 11.0$ Hz, 2 H), 7.53 (d, $J = 7.7$ Hz, 2 H), 7.47 (d, $J = 11.0$ Hz, 2 H); ^{13}C NMR (500 MHz, CDCl_3) δ 149.37, 148.06, 136.13, 135.71, 129.44, 128.31, 121.68; HRMS (MALDI-FTMS) calcd for $\text{C}_{11}\text{H}_8\text{ClNH}^+$ [$\text{M} + \text{H}^+$] 190.0418, found 190.0417.

Benzophenone azine (69). IBX (142 mg, 0.509 mmol) was carefully added as a solid to a solution of benzophenone hydrazone (49.9 mg, 0.254 mmol) in DMSO (0.8 mL) at ambient temperature. The reaction mixture was allowed to stir at room temperature for approximately 10 min until initial vigorous gas evolution had ceased, and was then heated to 45 °C for 15 min. The resulting mixture was quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL) and then basified with 1 M KOH (1 mL). Following extraction with EtOAc (5 mL), the organic phase was washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated to yield the corresponding azine (45.3 mg, 99%). **69**: colorless oil; $R_f = 0.79$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3060, 1730, 1659, 1598, 1447, 1315, 1278, 1177, 919, 764, 701, 639 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.6$ Hz, 8 H), 7.59 (app t, $J = 7.6$ Hz, 4

H), 7.48 (app t, $J = 7.6$ Hz, 8 H); ^{13}C NMR (500 MHz, CDCl_3) δ 196.76, 137.55, 132.39, 130.03, 128.24; HRMS (MALDI-FTMS) calcd for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{H}^+$ [$\text{M} + \text{H}^+$] 361.1699, found 361.1700.

Salicylaldehyde azine (71). IBX (98.0 mg, 0.349 mmol) was carefully added as a solid to a solution of salicylaldehyde hydrazone (47.5 mg, 0.349 mmol) in DMSO (1.2 mL) at ambient temperature. The reaction mixture was allowed to stir at room temperature for approximately 20 min until gas evolution had ceased, and then quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL). Following extraction with EtOAc (5 mL), the organic phase was washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated to yield the corresponding azine (35.4 mg, 84%). **71:** light yellow solid, m.p. 200–202 °C (lit.⁷ 211 °C); $R_f = 0.73$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2932, 1617, 1484, 1269, 1194, 748 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.72 (s, 2 H), 7.42–7.35 (m, 4 H), 7.04 (d, $J = 8.2$ Hz, 2 H), 7.98 (app t, $J = 7.6$ Hz, 2 H); ^{13}C NMR (500 MHz, CDCl_3) δ 164.71, 159.78, 133.45, 132.56, 119.74, 117.15, 117.26; HRMS (MALDI-FTMS) calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2\text{H}^+$ [$\text{M} + \text{H}^+$] 241.0971, found 241.0969.

Diazodiphenylethanone (73). IBX (126 mg, 0.450 mmol) dissolved in DMSO (0.5 mL) was added to a solution of benzil monohydrazone (67.3 mg, 0.300) in DMSO (0.5 mL) at ambient temperature. The reaction mixture was allowed to stir at room temperature for 4 h, and then quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL). The resulting mixture was then basified with saturated aqueous NaHCO_3 (1 mL) and extracted with EtOAc (5 mL). The organic phase was washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated to give the corresponding diazo compound (65.9 mg, 99% yield). **73:** orange amorphous solid; $R_f = 0.73$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3060, 2076, 1679, 1621, 1496, 1448, 1350, 1244, 1183, 1072, 849, 756, 698, 645 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.62 (d, $J = 7.0$ Hz, 2 H), 7.50–7.47 (m, 3 H), 7.41 (app q, $J = 7.5, 7.9$ Hz, 4 H), 7.26 (app t, $J = 7.5$ Hz, 1 H); ^{13}C NMR (600 MHz, CDCl_3) δ 188.27, 137.93, 131.61, 128.96, 128.46, 127.66, 126.92, 126.08, 125.98, 42.84; HRMS (MALDI-FTMS) calcd for $\text{C}_{14}\text{H}_{10}\text{O}$ [$\text{M} - \text{N}_2$] 194.0732, found 194.0727.

2-Imino-3-methyl-benzothiazolidine (75). IBX (128 mg, 0.458 mmol) was carefully added as a solid to a solution of 3-methyl-2-benzothiazolinone hydrazone hydrochloride hydrate (71.3 mg, 0.305 mmol) in DMSO (1 mL) at ambient temperature. The reaction mixture was allowed to stir at room temperature for approximately 20 min until gas evolution had ceased. The resulting mixture was quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL) and then basified with 1 M KOH (1 mL). Following extraction with EtOAc (5 mL), the organic phase was washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated to yield the corresponding imine **75** and thiourea **76** in a ratio of 1.0:0.2 (49.7 mg, 99% total yield). **75**: light orange solid, m.p. 114–116 °C (lit.⁸ 120–122 °C); R_f = 0.15 (silica gel, hexanes:EtOAc, 1:2); IR (film) ν_{max} 3248, 1603, 1476, 1333, 1300, 1218, 1115, 1022, 985, 738 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.28–7.23 (m, 2 H), 7.02 (app td, J = 7.7, 1.1 Hz, 1 H), 6.86 (d, J = 8.1 Hz, 1 H), 3.44 (s, 3 H); ^{13}C NMR (500 MHz, CDCl_3) δ 162.50, 141.15, 126.20, 122.57, 121.60, 121.41, 109.17, 29.24; HRMS (MALDI-FTMS) calcd for $\text{C}_8\text{H}_8\text{N}_2\text{SH}^+$ [$\text{M} + \text{H}^+$] 165.0481, found 165.0477. **3-Methyl-2-benzothiazolinone (76)**: colorless oil; R_f = 0.75 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2931, 1679, 1590, 1474, 1325, 1243, 1125, 745, 532 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.43 (d, J = 7.7, Hz, 1 H), 7.35–7.32 (m, 1 H), 7.17 (app td, J = 7.7, 1.1 Hz, 1 H), 7.04 (d, J = 8.1 Hz, 1 H), 3.46 (s, 3 H); ^{13}C NMR (600 MHz, CDCl_3) δ 170.03, 137.70, 126.33, 123.18, 122.55, 122.49, 110.37, 28.96; HRMS (MALDI-FTMS) calcd for $\text{C}_8\text{H}_7\text{NOSH}^+$ [$\text{M} + \text{H}^+$] 166.0321, found 166.0321.

Trifluoromethylpyrimidine hydrazine dimer (78). IBX (71.0 mg, 0.255 mmol) was carefully added as a solid to a solution of 2-hydrazino-4-(trifluoromethyl)pyrimidine (30.3 mg, 0.170 mmol) in DMSO (0.6 mL) at ambient temperature. The reaction mixture was allowed to stir at room temperature for approximately 20 min until gas evolution had ceased. The resulting mixture was quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL) and then basified with 1 M KOH (1 mL). Following extraction with EtOAc (5 mL), the organic phase was washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated to yield the corresponding hydrazine (23.3 mg, 94%). **78**: light yellow foam; R_f = 0.67 (silica gel,

hexanes:EtOAc, 1:1); IR (film) $\nu_{\max}$ 3256, 1590, 1457, 1385, 1327, 1192, 1149, 989, 926, 829, 670 cm^{-1} ; ^1H NMR (500 MHz, CD_3CN) δ 8.62 (bs, 2 H), 8.03 (bs, 2 H), 7.12 (d, $J = 5.1$ Hz, 2 H); ^{13}C NMR (600 MHz, CD_3CN) δ 164.58, 162.48, 122.48, 120.66, 109.28; HRMS (MALDI-FTMS) calcd for $\text{C}_{10}\text{H}_6\text{F}_6\text{N}_6\text{H}^+$ [$\text{M} + \text{H}^+$] 325.0631, found 325.0629.

2-Phenyl-1,3-dithiane (83). Prepared from benzaldehyde as reported in ref. 9. **83:** 88% yield; white needles, m.p. 69–70 °C (lit.¹⁰ 71–72 °C); $R_f = 0.72$ (silica gel, hexanes:EtOAc, 2:1); IR (film) $\nu_{\max}$ 2893, 1483, 1418, 1272, 1173, 909, 726, 695 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.50–7.48 (m, 2 H), 7.37–7.28 (m, 3 H), 5.18 (s, 1 H), 3.09–3.02 (m, 2 H), 2.92 (app t, $J = 4.1$ Hz, 1 H), 2.88 (app t, $J = 3.7$ Hz, 1 H), 2.19–2.12 (m, 1 H), 2.00–1.87 (m, 1 H); ^{13}C NMR (400 MHz, CDCl_3) δ 139.00, 128.59, 128.31, 127.62, 51.32, 31.96, 24.97; HRMS (MALDI-FTMS) calcd for $\text{C}_{10}\text{H}_{12}\text{S}_2\text{H}^+$ [$\text{M} + \text{H}^+$] 197.0453, found 197.0458.

Dithiane 84. Prepared from aldehyde **85** as reported in ref. 11. **84:** light yellow oil; $R_f = 0.53$ (silica gel, hexanes:EtOAc, 2:1); IR (film) $\nu_{\max}$ 2982, 2931, 2858, 1732, 1710, 1454, 1258, 1177, 1093, 1026, 965, 749 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.62–7.60 (m, 1 H), 7.21–7.19 (m, 2 H), 7.15–7.13 (m, 1 H), 6.77–6.74 (m, 1 H), 5.33 (s, 1 H), 4.19 (q, $J = 7.0$ Hz, 2 H), 3.08 (t, $J = 12.5$ Hz, 2 H), 2.94–2.90 (m, 2 H), 2.72 (t, $J = 7.7$ Hz, 2 H), 2.20–2.15 (m, 3 H), 1.98–1.90 (m, 1 H), 1.82 (s, 3 H), 1.66–1.62 (m, 2 H), 1.48–1.40 (m, 6 H), 1.29 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR (500 MHz, CDCl_3) δ 168.29, 142.28, 139.50, 136.77, 129.56, 128.52, 128.17, 127.72, 126.61, 60.38, 47.89, 32.91, 32.55, 31.24, 29.34, 29.18, 28.62, 28.48, 25.22, 14.29, 12.35; HRMS (MALDI-FTMS) calcd for $\text{C}_{22}\text{H}_{31}\text{S}_2\text{O}_2^+$ [M^+] 391.1760, found 391.1770.

Aldehyde 85. See ref. 11.

3-Phenylbutyraldehyde S,S' -dipropylacetal (86). Prepared from 3-phenylbutyraldehyde as reported in ref. 9. **86:** 92% yield; colorless oil; $R_f = 0.85$ (silica gel, hexanes:EtOAc, 3:1); IR (film) $\nu_{\max}$ 2980, 2870, 1603, 1455, 1376, 1239, 1088, 898 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.33–7.30 (m, 2 H), 7.26–7.19 (m, 3 H), 3.48 (dd, $J = 9.6, 5.5$ Hz, 1 H), 3.20–3.13 (m, 1 H), 2.67–2.61 (m, 1 H), 2.59–2.45 (m, 3 H), 2.13–2.07 (m, 1 H), 2.02–1.96 (m, 1 H), 1.61–1.48 (m, 4 H), 1.27 (d, $J = 7.0$ Hz, 3 H), 0.99 (t, $J = 7.4$ Hz, 3 H), 0.95 (t, $J = 7.4$

Hz, 3 H); ^{13}C NMR (500 MHz, CDCl_3) δ 145.97, 128.41, 127.04, 126.20, 49.57, 44.54, 37.43, 31.79, 22.70, 22.67, 22.14, 13.63; MS (GC/MS) calcd for $\text{C}_{16}\text{H}_{26}\text{S}_2^+$ [M^+] 282, found 282 [M^+], 207 [$\text{M}^+ - \text{S}(\text{CH}_2)_2\text{CH}_3$], 131 [$\text{M}^+ - 2\text{S}(\text{CH}_2)_2\text{CH}_3$], 105.

2-Methyl-*N,N*-bis(phenylmethyl)-1,3-dithiane-2-ethanamine (88). Prepared from 4-(dibenzylamino)-2-butanone (**89**) as reported in ref. 9. **88**: 84% yield; light yellow oil; R_f = 0.69 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3026, 2923, 2822, 1724, 1450, 1368, 1275, 1138, 1072, 972, 909 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.39–7.24 (m, 10 H), 3.63 (s, 4 H), 2.77–2.74 (m, 4 H), 2.68–2.64 (m, 2 H), 2.18–2.15 (m, 2 H), 1.98–1.84 (m, 2 H), 1.48 (s, 3 H); ^{13}C NMR (500 MHz, CDCl_3) δ 139.66, 128.73, 128.15, 126.84, 58.57, 49.09, 48.07, 38.30, 27.68, 26.47, 25.13; HRMS (MALDI-FTMS) calcd for $\text{C}_{21}\text{H}_{27}\text{NS}_2\text{H}^+$ [$\text{M} + \text{H}^+$] 358.1658, found 358.1651.

4-(Dibenzylamino)-2-butanone (89). Methyl vinyl ketone (1.3 mL, 16 mmol) was added to a solution of dibenzylamine (1.6 g, 8 mmol) in ether and the resulting mixture was stirred for 1 h at room temperature. Removal of the volatiles yielded **89** (1.5 g, 72% yield). **89**: orange solid, m.p. 49–51 °C (lit.¹² 52 °C); R_f = 0.48 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3027, 2925, 2801, 1711, 1450, 1361, 1227, 1126, 1028, 913 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.30 (m, 8 H), 7.26–7.23 (m, 2 H), 3.55 (s, 4 H), 2.77 (t, J = 7.0 Hz, 2 H), 2.59 (t, J = 7.0 Hz, 2 H), 1.99 (s, 3 H); ^{13}C NMR (500 MHz, CDCl_3) δ 208.29, 139.27, 128.87, 128.22, 126.98, 58.32, 48.52, 41.97, 29.64; HRMS (MALDI-FTMS) calcd for $\text{C}_{18}\text{H}_{21}\text{NOH}^+$ [$\text{M} + \text{H}^+$] 268.1696, found 268.1703.

2-Methyl-2-(2-phenylethyl)-1,3-dithiane (90). Prepared from benzylacetone as reported in ref. 9. **90**: 88% yield; colorless oil; R_f = 0.84 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3024, 2945, 1495, 1451, 1420, 1370, 1274, 1059, 907 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.31 (app t, J = 7.7 Hz, 2 H), 7.23–7.20 (m, 3 H), 2.93–2.89 (m, 2 H), 2.86–2.80 (m, 4 H), 2.26–2.23 (m, 2 H), 2.03–1.94 (m, 2 H), 1.69 (s, 3 H); ^{13}C NMR (600 MHz, CDCl_3) δ 141.75, 128.39, 125.85, 48.89, 43.31, 31.17, 27.74, 26.41, 25.15; HRMS (MALDI-FTMS) calcd for $\text{C}_{13}\text{H}_{18}\text{S}_2\text{H}^+$ [$\text{M} + \text{H}^+$] 239.0923, found 239.0924.

Benzylacetone *S,S'*-dipropylketal (92). Prepared from benzylacetone as reported in ref. 9. **92:** 53% yield; light yellow oil; $R_f = 0.77$ (silica gel, hexanes:EtOAc, 5:1); IR (film) $\nu_{\max}$ 2960, 2869, 1603, 1496, 1455, 1374, 1060 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.31–7.28 (m, 2 H), 7.20–7.18 (m, 3 H), 2.85–2.82 (m, 2 H), 2.61 (t, $J = 7.4$ Hz, 4 H), 2.05–2.02 (m, 2 H), 1.65–1.60 (m, 7 H), 1.02 (t, $J = 7.4$ Hz, 6 H); ^{13}C NMR (500 MHz, CDCl_3) δ 141.88, 128.43, 128.39, 125.87, 59.56, 43.73, 31.50, 31.18, 27.66, 13.95; MS (GC/MS) calcd for $\text{C}_{16}\text{H}_{26}\text{S}_2^+$ [M^+] 282, found 282 [M^+], 207 [$\text{M}^+ - \text{S}(\text{CH}_2)_2\text{CH}_3$], 131 [$\text{M}^+ - 2\text{S}(\text{CH}_2)_2\text{CH}_3$], 91.

2-(2,2-Dimethyl-5-hexenyl)-2-methyl-1,3-dithiane (93). Prepared from **95** as reported in ref. 9. **93:** 66% yield; light yellow oil; $R_f = 0.71$ (silica gel, hexanes:EtOAc, 4:1); IR (film) $\nu_{\max}$ 3072, 2932, 1446, 1421, 1370, 1276, 1063, 993, 910 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.84–5.76 (m, 1 H), 5.00 (dd, $J = 16.5, 1.5$ Hz, 1 H), 4.91 (d, $J = 10.3$ Hz, 1 H), 2.96 (ddd, $J = 14.3, 9.9, 2.9$ Hz, 2 H), 2.75 (ddd, $J = 14.7, 6.6, 2.9$ Hz, 2 H), 2.07–1.87 (m, 4 H), 1.94 (s, 2 H), 1.85 (s, 3 H), 1.47–1.44 (m, 2 H), 1.09 (s, 6 H); ^{13}C NMR (500 MHz, CDCl_3) δ 139.35, 113.90, 52.70, 49.86, 43.58, 35.76, 29.13, 28.73, 28.62, 27.14, 25.22; HRMS (MALDI-FTMS) calcd for $\text{C}_{13}\text{H}_{24}\text{S}_2\text{H}^+$ [$\text{M} + \text{H}^+$] 245.1392, found 245.1400.

Vinyl sulfide (94). IBX (85.1 mg, 0.304 mmol) was dissolved in DMSO (0.2 mL) with vigorous stirring for approximately 30 min at ambient temperature. This IBX solution was then added to a solution of dithiane **93** (37.2 mg, 0.152 mmol) in $\text{DMSO}:\text{H}_2\text{O}:\text{CH}_2\text{Cl}_2$ (4:1:1, 0.3 mL). The reaction was allowed to stir at room temperature for *ca* 5–10 min. The mixture was quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL) and then basified with saturated aqueous NaHCO_3 (1 mL). Following extraction with ether (5 mL), the organic phase was washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated to yield the crude compound. The crude material was purified using preparative thin-layer chromatography (silica gel, hexanes:EtOAc, 2:1) to afford the product in pure form (36.4 mg, 98% yield). **94:** colorless oil; $R_f = 0.77$ (silica gel, hexanes:EtOAc, 4:1); IR (film) $\nu_{\max}$ 3075, 2926, 1715, 1640, 1596, 1438, 1364, 1246, 1199, 995, 909, 847, 631 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.86–5.78 (m, 1 H), 5.01 (dd, $J = 17.2, 2.2$ Hz, 1 H), 4.97 (s, 1 H), 4.93–4.91 (m, 1 H), 4.79 (s, 1 H),

2.81–2.77 (m, 4 H), 2.14 (s, 2 H), 2.06–2.03 (m, 4 H), 1.37–1.34 (m, 2 H), 0.94 (s, 6 H); ^{13}C NMR (600 MHz, CDCl_3) δ 142.15, 139.56, 113.86, 108.23, 49.49, 41.46, 37.63, 33.68, 30.28, 28.68, 27.39, 27.17; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{24}\text{S}_2\text{H}^+$ [$\text{M} + \text{H}^+$] 245.1, found 245.1.

4,4-Dimethyl-7-octen-2-one (95). Prepared from mesityl oxide and 4-bromo-1-butene using the procedure reported in ref. 13. **95:** 65% yield; colorless oil; R_f = 0.52 (silica gel, hexanes:EtOAc, 4:1); IR (film) ν_{max} 3075, 2955, 1712, 1641, 1468, 1360, 1211, 1152, 995, 910 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.84–5.78 (m, 1 H), 5.03–4.99 (m, 1 H), 4.95–4.92 (m, 1 H), 2.34 (s, 2 H), 2.13 (s, 3 H), 2.05–1.99 (m, 2 H), 1.44–1.40 (m, 2 H), 1.00 (s, 6 H); ^{13}C NMR (500 MHz, CDCl_3) δ 208.83, 139.16, 114.10, 53.87, 41.40, 33.43, 32.53, 28.62, 27.19; MS (GC/MS) calcd for $\text{C}_{10}\text{H}_{18}\text{O}^+$ [M^+] 154, found 154 [M^+], 139 [$\text{M}^+ - \text{CH}_3$], 111 [$\text{M}^+ - \text{CH}_3\text{CO}$], 96 [$\text{M}^+ - \text{CH}_3\text{CO} - \text{CH}_3$], 81 [$\text{M}^+ - \text{CH}_3\text{CO} - 2\text{CH}_3$], 55 [$\text{M}^+ - \text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2$], 43 [$\text{M}^+ - \text{CH}_2\text{CH}(\text{CH}_2)_2\text{C}(\text{CH}_3)_2$].

2-(4-Methoxybenzoyl)-thiophene dithiane (99). Prepared from 2-(4-methoxybenzoyl)-thiophene as reported in ref. 9. **99:** 98% yield; white solid, m.p. 91–94 °C; R_f = 0.77 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2904, 2832, 1604, 1504, 1422, 1252, 1176, 1033, 818, 707 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, J = 8.8 Hz, 2 H), 7.37 (d, J = 5.0 Hz, 1 H), 7.28 (d, J = 2.9 Hz, 1 H), 7.04 (app t, J = 4.4 Hz, 1 H), 6.84 (d, J = 8.0 Hz, 2 H), 3.78 (s, 3 H), 3.06–2.99 (m, 2 H), 2.82–2.76 (m, 2 H), 2.07–1.98 (m, 2 H); ^{13}C NMR (400 MHz, CDCl_3) δ 159.12, 149.19, 135.42, 129.34, 129.29, 127.23, 126.96, 113.38, 57.80, 29.85, 24.13; HRMS (MALDI-FTMS) calcd for $\text{C}_{15}\text{H}_{16}\text{OS}_3\text{H}^+$ [$\text{M} + \text{H}^+$] 309.0436, found 309.0439.

2-(4-Methoxybenzoyl)-thiophene dithiane disulfoxide (101) and monosulfoxide (102). IBX (63.0 mg, 0.226 mmol) was dissolved in DMSO (0.5 mL) with vigorous stirring for approximately 30 min at ambient temperature. This IBX solution was then added to a solution of dithiane (34.8 mg, 0.113 mmol) in DMSO:H₂O (4:1, 0.5 mL), followed by the addition of 10 mol% AcOH. The reaction mixture was allowed to stir at room temperature for 24 h. The mixture was quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL) and then basified with saturated aqueous NaHCO_3 (1 mL). Following extraction with ether (5 mL), the organic phase

was washed with water (2×10 mL) and brine (10 mL), and then dried (MgSO_4) and concentrated to yield 24.1 mg of the crude compound, which was then purified using preparative thin-layer chromatography (silica gel, hexanes:EtOAc, 2:1). **101**: 8% yield; colorless oil; $R_f = 0.47$ (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2924, 1604, 1506, 1299, 1259, 1179, 1134, 1029, 725, 541 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.81 (bs, 1 H), 7.55 (bd, $J = 8.4$ Hz, 2 H), 7.47 (dd, $J = 5.5, 1.5$ Hz, 1 H), 7.12 (dd, $J = 5.1, 3.7$ Hz, 1 H), 6.88 (d, $J = 9.2$ Hz, 2 H), 3.79 (s, 3 H), 3.43 (ddd, $J = 15.4, 12.1, 3.3$ Hz, 1 H), 3.19–3.14 (m, 1 H), 3.00 (app t, $J = 12.1$ Hz, 1 H), 2.85–2.77 (m, 1 H), 2.74–2.70 (m, 1 H), 2.47 (bd, $J = 15.0$ Hz, 1 H); ^{13}C NMR (600 MHz, CDCl_3) δ 160.52, 131.37, 131.16, 130.96, 128.58, 127.57, 124.61, 113.68, 64.36, 55.29, 49.75, 29.38, 28.30; HRMS (MALDI-FTMS) calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3\text{S}_3\text{H}^+$ [$\text{M} + \text{H}^+$] 341.0334, found 341.0338. **102**: Observed as an inseparable mixture of products; $R_f = 0.21$ (silica gel, hexanes:EtOAc, 1:1); HRMS (MALDI-FTMS) calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{S}_3\text{H}^+$ [$\text{M} + \text{H}^+$] 325.0385, found 325.0387.

9-(1,1-Dimethylethyl)-1,5-dithiaspiro[5.5]undecane (109). Prepared from 4-*tert*-butylcyclohexanone as reported in ref. 9. **109**: 88% yield; white solid, m.p. 67–68 °C; $R_f = 0.83$ (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2940, 1440, 1365, 1238 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 2.85–2.83 (m, 2 H), 2.70–2.68 (m, 2 H), 2.36 (app s, 1 H), 2.34 (app s, 1 H), 1.96–1.92 (m, 2 H), 1.62–1.53 (m, 4 H), 1.47 (dd, $J = 13.2, 3.1$ Hz, 1 H), 1.42 (dd, $J = 13.2, 3.5$ Hz, 1 H), 0.99 (tt, $J = 12.3, 3.5$ Hz, 1 H), 0.82 (s, 9 H); ^{13}C NMR (600 MHz, CDCl_3) δ 50.01, 47.82, 38.20, 32.28, 27.38, 26.16, 26.08, 25.55, 22.80; MS (GC/MS) calcd for $\text{C}_{13}\text{H}_{24}\text{S}_2^+$ [M^+] 244, found 244 [M^+], 170, 145, 81, 57.

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