Supporting Information for

How stable are 1,2-dihydro-1,2-azaborines toward water and oxygen?

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General

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk techniques or a glove box.

THF, Et_2O, CH_2Cl_2, and pentane were purified by passing through a neutral alumina column under argon. Cyclohexene was dried over CaH_2 and distilled under N_2 prior to use. Dimethyl sulfoxide-d6 (DMSO-d6) was refluxed with CaO, filtered through powdered molecular sieves, dried over CaH_2, and vacuum distilled prior to use.

Potassium hydride (Strem) was washed with pentane three times and pumped dry under vacuum prior to use. *N*-allyl-*N*-tert-butylamine was prepared according to an adapted procedure.[1] All other chemicals and solvents were purchased (Aldrich or Strem) and used as received.

Silica gel (230-400 mesh) was heated under vacuum in a 200 °C sand bath for 12 hours. Flash chromatography was performed with this silica gel under an inert atmosphere. Preparative TLC (1000 μm thickness) plates were purchased from Silicycle and heated to 120° C for 18 h in an oven before being brought into the glove box.

^{11}B NMR spectra were recorded on a Varian Unity/Inova 600 spectrometer at ambient temperature. ^{1}H NMR spectra were recorded on a Varian Unity/Inova 300 or Varian Unity/Inova 500 spectrometer. ^{13}C NMR spectra were recorded on a Varian Unity/Inova 300 or Varian Unity/Inova 500 spectrometer. ^{11}B NMR spectra were externally referenced to $BF_3 \bullet Et_2O$ (δ 0).

IR spectra were recorded on a Nicolet Magna 550 FT-IR instrument with OMNIC software.

High-resolution mass spectroscopy data were obtained at the Mass Spectroscopy Facilities and Services Core of the Environmental Health Sciences Center at Oregon State University. Financial support for this facility has been furnished in part by the National Institute of Environmental Health Sciences, NIH (P30 ES00210).

(1) Makino, T.; Itoh, K. *J. Org. Chem.* **2004**, *69*, 395-405.

Synthesis of BN Heterocycles 2 and 3 (Scheme 1)

Compound 2. In a glove box, a 250 mL Schlenk flask containing a stir bar was charged with **1**[2] (7.62 g, 44.5 mmol), Pd/C (0.944 g, 8.89 mmol), and cyclohexene (175 mL). The vessel was sealed and heated to 80 °C for 16 h. The cooled reaction mixture was filtered and the resulting filtrate was cooled to –78 °C. A solution of phenylethynylmagnesium bromide (1.0 M solution in THF; 6.4 mL, 6.4 mmol) was then added. The mixture was allowed to warm to room temperature and was concentrated under reduced pressure. Vacuum distillation (52-55 °C, 50 mTorr) gave 1,2-azaborine **2** as a clear, colorless liquid (4.77 g, 63 %).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.63 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 7.54 (dd, $^3J_{HH}$ = 10.3, 6.1 Hz, 1H), 6.46 (dd, $^3J_{HH}$ = 9.4, 1.4 Hz, 1H), 6.30 (t, $^3J_{HH}$ = 5.9 Hz, 1H), 1.62 (s, 9H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 143.9, 135.6, 129 (br), 110.0, 61.1, 30.7. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 33.0. FTIR (thin film) 3076, 3042, 3011, 2979, 1605, 1517, 1441, 1390, 1370, 1291, 1241, 1201, 1153, 1122, 1012, 742, 716, 680, 668, 628 cm^{-1}. HRMS (EI) calcd for $C_8H_{13}BNCl$ (M+) 169.08296, found 168.9888.

Compound 3. Br_2 (1.01 g, 6.31 mmol in 5.0 mL CH_2Cl_2) was added slowly to a 0 °C solution of **2** (1.00 g, 5.92 mmol in 15.0 mL CH_2Cl_2). The resulting solution was stirred at 0 °C for 10 minutes and at room temperature for 4 hours. The solvent was removed under reduced pressure, and pentane was added to the crude mixture. The suspension was then passed through an acrodisc and the resulting filtrate was concentrated under reduced pressure. Vacuum distillation (27-30 °C, 300 mTorr) gave desired **3** as a clear colorless liquid (1.08 g, 68%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.88 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 7.63 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 6.18 (t, $^3J_{HH}$ = 7.0, 1.4 Hz, 1H), 1.71 (s, 9H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 145.4, 135.5, 126 (br), 109.4, 62.5, 30.6. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 32.1. FTIR (thin film) 2979, 1602, 1505, 1484, 1436, 1399, 1372, 1345, 1285, 1237, 1192, 1134, 1100, 1050, 1010, 954, 759, 713, 669, 658 cm^{-1}. HRMS (EI) calcd for $C_8H_{12}BNBrCl$ (M+) 246.99347, found 246.99153.

Synthesis of B- and C(3)-Substituted 1,2-Azaborines **(Table 1)**

Compound 4a. In a glove box, a vial was charged with a solution of **2** (0.117 g, 0.687 mmols in 10.0 mL Et_2O) and cooled to –78 °C. *n*-BuMgCl (2.0 M in Et_2O; 0.34 mL, 0.69 mmol) was added to this stirring solution, and the reaction was allowed to warm to room temperature. After stirring for 8 h, approximately 75% of the solvent was removed. The crude material was subjected to silica gel chromatography using pentane as eluent, yielding **4a** (0.102 g, 77%) as a clear colorless oil.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.56 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 7.46 (dd, $^3J_{HH}$ = 6.2, 4.4 Hz, 1H), 6.77 (d, $^3J_{HH}$ = 9.4 Hz, 1H), 6.16 (t, $^3J_{HH}$ = 5.6 Hz, 1H), 1.65 (s, 9H), 1.59-1.46 (m, 6H), 1.02 (t, $^3J_{HH}$ = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 141.0, 134.8, 131 (br), 108.8, 59.9, 32.0, 30.8, 26.6, 22.6 (br), 14,2. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 39.4. FTIR (thin film) 3073, 3003, 2956, 2924, 2870, 2855, 1609, 1518, 1462, 1399, 1369, 1296, 1240, 1204, 1153, 1144, 1094, 1045, 1009, 739, 692 cm^{-1}. HRMS (EI) calcd for $C_{12}H_{22}BN$ (M+) 191.18453, found 191.18377.

(2) Abbey, E. R.; Zakharov, L. N.; Liu, S.-Y. *J. Am. Chem. Soc.* **2008**, *130*, 7250–7252.

Compound 4b. A vial was charged with a solution of **2** (0.250 g, 1.48 mmol in 10.0 mL Et_2O) and cooled to –78 °C. To this stirring solution, phenylmagnesium bromide (3.0 M solution in Et_2O; 0.51 mL, 1.5 mmol) was added dropwise. Then the reaction was allowed to warm to room temperature and stirred for 10 h. Approximately 75% of the solvent was then removed under reduced pressure, and the remaining crude material was subjected to silica gel chromatography using pentane/CH_2Cl_2 as eluent. Pure **4c** was obtained as a white crystalline solid (0.257 g, 82%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.70 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.54 (dd, $^3J_{HH}$ = 6.3, 4.2 Hz, 1H), 7.42 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 7.34 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 7.28 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.56 (d, $^3J_{HH}$ = 1.3 Hz, 1H), 6.40 (t, $^3J_{HH}$ = 1.7 Hz, 1H), 1.50 (s, 9H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 141.3, 135.7, 133 (br), 131.6, 127.1, 126.1, 110.8, 61.0, 33.1, $C_{ph(ipso)}$ not observed. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 36.5. FTIR (thin film) 2971, 1605, 1516, 1447, 1391, 1366, 1293, 1198, 1112, 969, 749, 702 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{18}BN$ (M^+) 211.15323, found 211.15280.

Compound 4c. In a glovebox, a round bottom flask was charged with **2** (0.050 g, 0.30 mmols) and 10.0 mL Et_2O. The flask was then cooled to –78 °C. Super Hydride (1.0 M solution in THF, 0.30 mL, 0.30 mmols) was added dropwise to the stirring reaction flask. The mixture was allowed to warm to room temperature. After 10 h of stirring, the mixture was passed through an acrodisc and concentrated under a stream of nitrogen. The crude material was subjected to silica gel chromatography using pentane as an eluent to afford **4b** as a clear colorless liquid (0.033 g, 83%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.69 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 7.61 (d, $^3J_{HH}$ = 6.1 Hz, 1H), 6.91 (d, $^3J_{HH}$ = 9.5 Hz, 1H), 6.44 (t, $^3J_{HH}$ = 5.45 Hz, 1H), 5.32 (q (br), $^1J_{BH}$ = 118 Hz, 1H), 1.61 (s, 9H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 141.9, 135.5, 130 (br), 111.5, 58.4, 32.0. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 30.7 (d, $^1J_{BH}$ = 127 Hz). FTIR (thin film) 2978, 2560, 1606, 1515, 1464, 1397, 1369, 1295, 1240, 1197, 1143, 1019, 954, 879, 797, 744, 714. HRMS (EI) calcd for $C_8H_{14}BN$ (M^+) 135.12193 found 135.12164.

Compound 4d. To a stirring solution of **2** (0.250 g, 1.50 mmol in 5.0 mL Et_2O) at –78 °C was added phenylethynylmagnesium bromide (1.0 M solution in THF; 1.55 mL, 1.55 mmol). The solution was allowed to warm to room temperature and stirred for 12 h. Approximately 75% of the solvent was removed, and the remaining mixture was passed through an acrodisc. This material was then subjected to silica gel chromatography using a mixture pentane/CH_2Cl_2 (9:1) as eluent to afford **4d** as a light yellow crystalline solid (0.330 g, 93%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.68 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.54-7.51 (m, 3H), 7.38-7.36 (m, 3H), 6.98 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 6.36 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 1.82 (s, 9H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 142.3, 135.6, 133 (br), 131.5, 128.6, 124.5, 110.7, 109.3, 104.4, 60.7, 31.4, $C_{B\underline{C}C}$ not observed. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 26.8. FTIR (thin film) 2967, 2171, 1598, 1514, 1488, 1440, 1397, 1370, 1294, 1258, 1227, 1198, 1173, 1160, 1128, 1089, 1070, 1044, 755, 743, 690 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{18}BN$ (M^+) 235.15323 found 235.15325.

Compound 4e. In a glovebox, a round bottom flask was charged with triethylamine (0.120 mL, 0.840 mmols in 5.0 mL THF) and EtOH (0.043 mL, 0.84 mmols). The flask was then cooled to –78 °C. In a separate round bottom flask, compound **2** (0.135 g, 0.803 mmols) in 10.0 mL THF was cooled to –78 °C. The ethanol solution was slowly added to the flask containing compound

2. The combined mixture was allowed to warm to room temperature. After 10 h of stirring, the mixture was passed through an acrodisc and concentrated under vacuum. The crude material was subjected to silica gel chromatography using pentane as eluent to afford **4e** as a yellow liquid (0.103 g, 72%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.48 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.37 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 6.25 (d, $^3J_{HH}$ = 11 Hz, 1H), 5.86 (t, $^3J_{HH}$ = 5.9 Hz, 1H), 4.10 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 1.60 (s, 9H) 1.37 (t, $^3J_{HH}$ = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 144.5, 135.1, 116 (br), 104.2, 60.5, 58.2, 30.4, 17.4. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 29.6. FTIR (thin film) 3076, 2973, 2197, 1652, 1635, 1609, 1576, 1538, 1521, 1487, 1464, 1412, 1363, 1310, 1268, 1204, 1135, 1056, 1005, 832, 803, 769, 732, 708, 693, 667. HRMS (EI) calcd for $C_{10}H_{18}BNO$ (M^+) 179.14815 found 179.14769.

Compound 5a. In a glove box, a vial was charged with a solution of **3** (0.498 g, 2.02 mmols in 20.0 mL Et_2O) and cooled to –78 °C. *n*-BuMgCl (2.0 M in Et_2O; 1.01 mL, 2.02 mmol) was added to this stirring solution, and the reaction was allowed to warm to room temperature. After stirring for 8 h, approximately 75% of the solvent was removed. The crude material was subjected to silica gel chromatography using pentane as eluent, yielding **5a** (0.417 g, 76%) as a clear colorless oil.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.76 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 7.58 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 6.06 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 1.63 (s, 9H) 1.54-1.51 (m, 6H), 1.03 (t, $^3J_{HH}$ = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 143.7, 135.0, 132 (br), 108.3, 61.2, 32.1, 28.3, 26.7, 22 (br) 13.8. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 37.7. FTIR (thin film) 3133, 3074, 2958, 2856, 1605, 1505, 1464, 1398, 1351, 1285, 1237, 1195, 1161, 1122, 1085, 1063, 1035, 1010, 950, 921, 888, 752, 725, 698, 672, 592 cm^{-1}. HRMS (EI) calcd for $C_{12}H_{21}BNBr$ (M^+) 269.09504, found 269.09397.

Compound 5b. To a stirring solution of **3** (0.137 g, 0.549 mmol in 15.0 mL Et_2O) at –78 °C was added phenylmagnesium bromide (3.0 M solution in Et_2O; 0.219 mL, 0.658 mmol). The solution was allowed to warm to room temperature and stirred for 10 h. Approximately 75% of the solvent was removed, and the remaining mixture was passed through an acrodisc. This material was then subjected to silica gel chromatography using a mixture pentane/CH_2Cl_2 as eluent to afford **5c** as a white crystalline solid (0.146 g, 92%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.94 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.72 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 7.34-7.32 (m, 5H), 6.28 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 143.7, 135.7, C(3) not observed, 132.2, 127.3, 126.8, 110.4, $C_{ph(ipso)}$ not observed, 62.3, 33.9. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 35.9. FTIR (thin film) 2963, 1605, 1506, 1428, 1369, 1349, 1260, 1193, 1121, 1013, 755, 703, 692 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{17}BNBr$ (M^+) 289.06374, found 289.06254.

Compound 5c. In a glovebox, a round bottom flask was charged with **3** (0.288 g, 1.15 mmols) and 10.0 mL Et_2O. The flask was then cooled to –78 °C. Super Hydride (1.0 Mol solution in THF, 1.17 mL, 1.17 mmols) was added dropwise to the stirring reaction flask. The mixture was allowed to warm to room temperature. After 10 h of stirring, the mixture was passed through an acrodisc and concentrated under vacuum. The crude material was subjected to silica gel chromatography using pentane as an eluent to afford **5b** as a clear colorless liquid (0.200 g, 81%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.79 (d, $^{3}J_{HH}$ = 6.9 Hz, 1H), 7.65 (d, $^{3}J_{HH}$ = 6.9 Hz, 1H), 6.33 (t, $^{3}J_{HH}$ = 7.05 Hz, 1H), 5.41 (q (br), $^{1}J_{BH}$ = 150 Hz, 1H), 1.58 (s, 9H). ^{13}C NMR (125 MHz, CD_2Cl_2): 142.8, 134.7, 129 (br), 111.3, 59.1, 31.8. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 31.5 (d, $^{1}J_{BH}$ = 137 Hz). FTIR (thin film) 2977, 2594, 1602, 1501, 1471, 1397, 1373, 1347, 1286, 1214, 1192, 1038, 1018, 1003, 834, 763, 682, 646, 611. HRMS (EI) calcd for $C_8H_{13}BNBr$? (M^+) 213.03244 found 213.02174.

Compound 5d. To a stirring solution of **3** (0.373 g, 1.50 mmol in 5.0 mL Et_2O) at –78 °C was added phenylethynylmagnesium bromide (1.0 M solution in THF; 1.55 mL, 1.55 mmol). The solution was allowed to warm to room temperature and stirred for 12 h. Approximately 75% of the solvent was removed, and the remaining mixture was passed through an acrodisc. This material was then subjected to silica gel chromatography using a mixture pentane/CH_2Cl_2 (9:1) as eluent to afford **5d** as a white crystalline solid (0.349 g, 74%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.91 (d, $^{3}J_{HH}$ = 7.1 Hz, 1H), 7.68 (d, $^{3}J_{HH}$ = 7.1 Hz, 1H), 7.62-7.60 (m, 2H), 7.42-7.40 (m, 3H), 6.26 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 1.84 (s, 9H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 143.8, 137 (br), 135.1, 131.7, 128.9, 128.6, 112.6, 110.0, 93.3, 61.7, 31.3, $C_{B\underline{C}C}$ not observed. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 26.6. FTIR (thin film) 2976, 2181, 1597, 1558 1503, 1489, 1457, 1437, 1370, 1357, 1194, 1027, 757, 690, 678. HRMS (EI) calcd for $C_{16}H_{17}BNBr$ (M^+) 313.06374 found 313.06374.

Compound 5e. In a glovebox, a round bottom flask was charged with triethylamine (0.120 mL, 0.840 mmols in 5.0 mL THF) and EtOH (0.043 mL, 0.84 mmols). In a separate round bottom flask, compound **3** (0.200 g, 0.803 mmols) in 10.0 mL THF was cooled to –78 °C. The ethanol solution was slowly added to the flask containing compound **3**. The combined mixture was allowed to warm to room temperature. After 10 h of stirring, the mixture was passed through an acrodisc and concentrated under vacuum. The crude material was subjected to silica gel chromatography using pentane as and eluent to afford **5e** as a yellow liquid (0.139 g, 65%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.73 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H) 7.39 (d, $^{3}J_{HH}$ = 6.8 Hz, 1H), 7.75 (t, $^{3}J_{HH}$ = 6.9 Hz, 1H), 4.55 (q, $^{3}J_{HH}$ = 6.9 Hz, 2H), 1.59 (s, 9H), 1.39 (t, $^{3}J_{HH}$ = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 147.5, 135.2, 116 (br), 103.9, 62.1, 59.4, 30.4, 17.9. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 28.4. FTIR (thin film) 2977, 1606, 1504, 1410, 1378, 1351, 1296, 1233, 1194, 1020, 954, 800, 714, 680. HRMS (EI) calcd for $C_{10}H_{17}BBrNO$ (M^+) 257.05866 found 257.0009.

Compound 6a. Compound **4a** (0.116 g, 0.607 mmols in 5.0 mL CH_2Cl_2) was added to a solution of *N*-chlorosuccinimide (0.283 g, 1.80 mmols in 20.0 mL CH_2Cl_2). The mixture was stirred for 8 hours at room temperature. The solvent was removed under reduced pressure. The crude material was subjected to silica gel chromatography using pentane/CH_2Cl_2 (7:1) as eluent to yield **6a** as a yellow liquid (0.075 g, 55%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.74 (app. t, $^{3}J_{HH}$ = 7.0 Hz, 2H), 6.07 (t, $^{3}J_{HH}$ = 7.0, 1.39 Hz, 1H), 1.62 (s, 9H), 1.55 (m, 6H), 0.97 (t, $^{3}J_{HH}$ = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 140.9, 132.4, 130 (br), 107.3, 61.9, 32.1, 30.2, 26.7, 20 (br), 14.0. ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 37.7. FTIR (thin film) 2959, 2926, 1695, 1652, 1607, 1456, 1436, 1419, 1363, 1336, 1263, 1195, 763, 742 cm^{-1}. HRMS (EI) calcd for $C_{12}H_{21}BNCl$ (M^+) 225.14556, found 225.14535.

Oxygen Stability Studies (Table 2)

General procedure: 1,2-Azaborine (0.052 mmols) was weighed into a vial, 0.50 mL stock solution of 0.006 M hexamethyl benzene (HMB) in benzene-d_6 was added to vial. The solution was then transferred to a J Young valve NMR tube and degassed via freeze-pump-thaw. 2.5 mL pure oxygen was then introduced to the sample. The NMR tube was sealed and vigorously shaken. The reaction progress was monitored by ^{1}H NMR at 50 °C. Each compound was tested in duplicate. The conversion (i.e., % SM remaining) was plotted against the time, and the data was fitted to an exponential function to obtain the observed rate constant k_{obs}.

Table 2, entry 1: average $k_{obs} = 52 \times 10^{-6}\ s^{-1}$

Compound 4a

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	96.0	97.9
0.05	93.0	92.2
0.10	89.6	88.8
0.17	83.3	84.8
0.25	82.2	81.2
0.35	80.0	84.8
0.47	78.4	75.4
0.60	76.9	72.0
0.75	76.4	68.8
0.92	75.9	66.0
1.10	74.1	62.9
1.30	70.6	59.7
1.52	69.0	56.9
1.75	66.3	54.0
2.00	63.8	50.5
2.27	61.2	49.7
2.55	58.8	48.7
2.85	55.3	47.7
3.17	53.3	47.3
3.50	50.6	45.5
3.85	47.6	44.8

Table 2, entry 2: average $k_{obs} = 13 \times 10^{-6}\ s^{-1}$

Compound 4b

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	99.2	99.7
0.05	98.3	99.4
0.10	97.5	97.5

0.17	95.9	97.3
0.25	93.7	96.2
0.35	91.5	95.5
0.47	90.1	94.4
0.60	88.7	93.9
0.75	86.8	92.7
0.92	86.8	92.5
1.10	84.9	91.3
1.30	84.3	90.8
1.52	83.7	90.2
1.75	83.1	89.9
2.00	83.1	89.3
2.27	82.5	88.1
2.55	82.5	87.5
2.85	81.9	87.3
3.17	81.9	86.2
3.50	81.4	86.0
3.85	80.8	84.8

Table 2, entry 3: average $k_{obs} = 9 \times 10^{-6}\ s^{-1}$

Compound 4c

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	98.5	98.2
0.05	98.5	98.2
0.10	97.7	96.4
0.17	97.0	96.4
0.25	96.3	94.7
0.35	95.6	94.7
0.47	95.6	91.5
0.60	94.2	91.5
0.75	94.2	91.5
0.92	92.9	90.0
1.10	92.9	90.0
1.30	91.5	90.0
1.52	91.5	90.0
1.75	90.9	90.0
2.00	90.3	88.5
2.27	89.7	88.5
2.55	89.0	88.5
2.85	88.4	87.1
3.17	88.4	87.1
3.50	87.2	85.7
3.85	87.2	85.7

Table 2, entry 4: average $k_{obs} = 5 \times 10^{-6}\ s^{-1}$

Compound 4d		
Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	100.0	99.2
0.05	100.0	99.2
0.10	100.0	98.4
0.17	100.0	98.4
0.25	100.0	97.7
0.35	98.7	96.9
0.47	98.7	96.2
0.60	98.7	96.2
0.75	98.7	95.5
0.92	98.7	95.5
1.10	98.7	95.5
1.30	97.4	94.8
1.52	97.4	94.8
1.75	97.4	94.1
2.00	96.2	94.1
2.27	96.2	93.4
2.55	96.2	93.4
2.85	95.0	92.7
3.17	95.0	92.0
3.50	95.0	91.4
3.85	93.8	90.7

Table 2, entry 5: average $k_{obs} = 5 \times 10^{-6}\ s^{-1}$

Compound 2		
Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	99.3	99.7
0.05	97.9	99.7
0.10	96.5	99.4
0.17	95.8	99.1
0.25	95.1	98.5
0.35	94.5	98.5
0.47	94.5	97.7
0.60	93.8	97.4
0.75	93.8	97.4
0.92	93.2	96.8
1.10	93.2	96.8
1.30	93.2	96.6
1.52	92.6	96.3

1.75	92.6	96.0
2.00	92.6	96.0
2.27	92.6	95.7
2.55	91.9	95.7
2.85	91.9	94.9
3.17	91.9	93.6
3.50	91.3	91.6
3.85	91.3	91.1

Table 2, entry 6: average $k_{obs} = 11 \times 10^{-6}\ s^{-1}$

Compound 4e

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	99.2	100.0
0.05	99.2	100.0
0.10	99.2	99.2
0.17	99.2	99.2
0.25	99.2	98.5
0.35	98.3	98.5
0.47	97.5	98.5
0.60	96.7	98.5
0.75	95.2	98.5
0.92	94.4	97.0
1.10	93.0	97.0
1.30	92.2	96.2
1.52	91.5	95.5
1.75	90.2	94.8
2.00	89.5	94.1
2.27	87.5	93.4
2.55	87.5	92.8
2.85	86.9	91.4
3.17	86.2	90.1
3.50	85.6	88.9
3.85	85.0	87.7

Table 2, entry 7:

Compound 5a

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	99.4	99.5
0.05	97.1	97.9
0.10	96.0	96.4
0.17	95.0	94.0
0.25	93.4	92.1

0.35	91.9	90.8
0.47	90.4	89.5
0.60	88.5	86.6
0.75	86.3	83.5
0.92	84.2	82.4
1.10	82.1	81.3
1.30	80.2	79.9
1.52	77.6	77.9
1.75	75.6	74.5
2.00	73.0	71.1
2.27	71.1	68.2
2.55	68.8	65.2
2.85	66.7	63.0
3.17	64.2	62.3
3.50	61.6	60.3
3.85	59.4	59.7

Table 2, entry 8:

Compound 5b

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	99.7	99.7
0.05	99.5	99.1
0.10	99.5	99.1
0.17	99.2	98.8
0.25	98.9	98.8
0.35	99.2	98.5
0.47	98.6	98.2
0.60	98.6	97.9
0.75	98.6	97.9
0.92	98.4	97.9
1.10	98.4	97.4
1.30	97.6	97.4
1.52	97.3	96.5
1.75	97.3	96.2
2.00	96.5	96.0
2.27	96.0	95.7
2.55	96.0	95.4
2.85	94.3	94.9
3.17	94.3	95.1
3.50	93.8	94.6
3.85	93.1	94.6

Table 2, entry 9:

Compound 5c		
Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	100.0	100.0
0.05	100.0	99.4
0.10	100.0	99.4
0.17	100.0	99.4
0.25	100.0	97.7
0.35	100.0	97.7
0.47	99.4	96.6
0.60	98.8	95.5
0.75	98.2	94.4
0.92	98.2	93.9
1.10	98.2	93.9
1.30	98.2	93.9
1.52	96.5	93.3
1.75	95.9	93.3
2.00	95.3	92.8
2.27	94.3	92.8
2.55	93.7	92.3
2.85	92.7	91.8
3.17	92.1	91.3
3.50	91.6	90.8
3.85	91.1	90.3

Table 2, entry 10:

Compound 5d		
Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	99.5	99.5
0.05	99.5	99.5
0.10	99.5	99.5
0.17	99.5	99.5
0.25	99.5	99.2
0.35	99.5	99.2
0.47	99.5	99.2
0.60	99.5	99.2
0.75	99.5	99.2
0.92	99.5	99.2
1.10	99.1	98.9
1.30	99.1	98.9
1.52	99.1	98.9
1.75	99.3	98.9
2.00	99.1	98.7

2.27	99.1	98.7
2.55	98.8	98.7
2.85	98.8	98.7
3.17	98.8	98.4
3.50	98.6	98.4
3.85	98.4	98.4

Table 2, entry 11:

Compound 3		
Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	98.3	97.8
0.05	96.7	97.1
0.10	94.3	96.0
0.17	92.8	95.4
0.25	92.0	94.0
0.35	91.3	93.0
0.47	90.9	91.8
0.60	90.6	91.1
0.75	90.2	90.5
0.92	90.2	90.5
1.10	90.2	90.5
1.30	89.5	89.9
1.52	89.2	89.9
1.75	88.2	89.0
2.00	88.5	88.7
2.27	88.2	88.4
2.55	86.5	88.1
2.85	85.6	87.8
3.17	84.6	87.5
3.50	84.3	87.3
3.85	84.0	87.0

Table 2, entry 12:

Compound 5e		
Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	99.7	99.8
0.05	99.4	99.8
0.10	99.4	99.6
0.17	99.1	99.3
0.25	99.1	99.3
0.35	98.8	99.3
0.47	98.8	99.3
0.60	98.5	99.1

0.75	97.9	99.1
0.92	97.6	99.1
1.10	97.6	98.9
1.30	97.4	98.9
1.52	97.1	98.7
1.75	97.1	98.7
2.00	96.2	98.4
2.27	95.7	97.8
2.55	94.3	97.4
2.85	94.9	95.5
3.17	94.6	94.7
3.50	94.3	94.3
3.85	94.3	93.7

Table 2, entry 13:

Compound 6a		
Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	95.4	98.1
0.05	94.5	97.5
0.10	94.3	95.5
0.17	92.7	93.3
0.25	90.6	91.1
0.35	90.4	90.1
0.47	89.6	88.1
0.60	89.2	87.1
0.75	85.7	85.3
0.92	84.1	82.8
1.10	83.5	80.7
1.30	80.8	79.7
1.52	79.5	77.2
1.75	77.6	75.9
2.00	77.6	74.3
2.27	72.8	73.1
2.55	72.1	68.4
2.85	70.9	65.3
3.17	69.4	64.2
3.50	66.7	62.0
3.85	65.9	60.7

Water Stability Studies (Table 3)

General procedure: 1,2-Azaborine (0.052 mmols) was weighed into vial. A solution of DMSO (0.3 mL) containing tetramethylsilane as an internal standard was added. The solution was then transferred to a Norell screw cap NMR tube and sealed. Degassed D_2O (2.0 μL, 0.11 mmols) was added, and the reaction mixture was vigorously shaken. The reaction progress was monitored by ^1H NMR at 25 °C. Each compound was tested in duplicate.

Table 3, entry 1:

Compound 4a

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	100.0	100.0
0.05	100.0	100.0
0.10	100.0	100.0
0.17	100.0	100.0
0.25	100.0	100.0
0.35	100.0	100.0
0.47	100.0	100.0
0.60	100.0	100.0
0.75	100.0	99.4
0.92	100.0	99.4
1.30	100.0	100.0
1.70	100.0	100.0
2.18	100.0	100.0
2.75	96.2	100.0
3.48	96.2	99.4

Table 3, entry 2:

Compound 4b

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	97.0	100.0
0.05	98.8	99.8
0.10	100.0	100.0
0.17	100.0	100.0
0.25	100.0	98.6
0.35	100.0	98.8
0.47	100.0	97.8
0.60	100.0	99.0
0.75	100.0	99.0
0.92	100.0	99.2
1.30	100.0	99.2
1.70	100.0	99.0
2.18	100.0	98.2

2.75	100.0	97.8
3.48	100.0	97.1

Table 3, entry 3:

Compound 4c

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	96.5	100.0
0.05	98.9	99.8
0.10	96.7	99.6
0.17	97.4	99.6
0.25	98.9	99.4
0.35	100.0	99.2
0.47	99.8	99.2
0.60	97.8	99.0
0.75	96.7	99.0
0.92	95.6	98.8
1.30	96.5	98.6
1.70	98.0	98.6
2.18	95.6	98.4
2.75	95.6	98.2
3.48	95.6	98.2

Table 3, entry 4:

Compound 4d

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	98.0	99.8
0.05	97.6	98.9
0.10	100.0	99.7
0.17	100.2	98.1
0.25	96.5	98.7
0.35	100.0	98.4
0.47	97.0	98.1
0.60	97.0	97.4
0.75	98.1	97.2
0.92	100.0	98.7
1.30	99.0	96.8
1.70	96.2	99.0
2.18	98.3	96.7
2.75	98.3	96.7
3.48	97.0	96.4

Table 3, entry 5:

Compound 4e

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	100.0	99.3
0.05	99.0	99.2
0.10	98.3	100.0
0.17	99.9	99.5
0.25	99.9	98.4
0.35	98.6	99.9
0.47	98.2	99.5
0.60	97.5	99.0
0.75	97.4	99.5
0.92	97.3	98.8
1.30	97.8	98.1
1.70	97.8	97.8
2.18	97.3	97.5
2.75	97.4	97.5
3.48	97.4	97.5

Table 3, entry 6: Compound **2** reacted rapidly with water to furnish *B*-OR containing 1,2-azaborines.

Table 3, entry 7:

Compound 5a

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	99.2	100.0
0.05	99.5	99.9
0.10	99.7	99.9
0.17	98.7	99.9
0.25	98.8	100.0
0.35	98.7	99.9
0.47	99.2	99.8
0.60	98.2	99.8
0.75	98.4	99.7
0.92	97.5	99.6
1.30	97.5	99.5
1.70	98.6	99.5
2.18	98.9	99.6
2.75	98.9	99.5
3.48	98.9	99.4

Table 3, entry 8:

Compound 5b

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	100.0	96.9
0.05	100.0	97.4
0.10	99.4	97.4
0.17	100.0	97.6
0.25	100.0	98.9
0.35	99.0	98.5
0.47	100.0	100.0
0.60	100.0	99.3
0.75	100.0	100.0
0.92	99.1	100.0
1.30	99.7	100.0
1.70	99.6	98.4
2.18	100.0	98.2
2.75	97.9	96.6
3.48	96.4	96.6

Table 3, entry 9:

Compound 5c

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	100.0	99.5
0.05	100.0	100.9
0.10	99.5	99.1
0.17	99.5	99.5
0.25	99.5	100.0
0.35	98.9	100.9
0.47	98.9	100.0
0.60	98.9	100.0
0.75	97.4	99.5
0.92	98.9	99.5
1.30	95.4	100.0
1.70	96.4	99.1
2.18	98.4	99.5
2.75	95.4	98.6
3.48	97.9	99.5

Table 3, entry 10:

Compound 5d

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	97.2	99.0
0.05	99.0	99.1
0.10	96.9	98.5
0.17	96.9	98.3
0.25	96.9	97.8
0.35	95.6	98.5
0.47	95.3	97.6
0.60	95.9	98.0
0.75	100.4	97.2
0.92	100.4	96.9
1.30	99.1	98.1
1.70	97.0	96.3
2.18	99.8	96.1
2.75	98.9	96.1
3.48	96.9	96.1

Table 3, entry 11:

Compound 5e

Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	98.2	100.3
0.05	96.7	99.7
0.10	96.7	99.4
0.17	97.4	99.6
0.25	99.5	99.1
0.35	99.3	99.7
0.47	98.4	98.4
0.60	99.3	98.5
0.75	98.6	97.8
0.92	98.9	98.3
1.30	99.4	98.6
1.70	96.8	98.0
2.18	97.0	97.9
2.75	96.6	97.5
3.48	96.0	97.8

Table 3, entry 12:

Compound 6a		
Time (h)	% SM remaining Trial 1	% SM remaining Trial 2
0	100.0	100.0
0.02	99.6	97.0
0.05	99.6	98.8
0.10	100.0	100.0
0.17	99.9	100.0
0.25	98.9	100.0
0.35	100.0	100.0
0.47	99.9	100.0
0.60	99.4	100.0
0.75	99.8	99.9
0.92	99.2	100.0
1.30	98.5	100.0
1.70	98.2	100.0
2.18	97.9	100.0
2.75	97.8	100.0
3.48	97.7	100.0

Table 3, entry 13: Compound **3** reacted rapidly with water to furnish *B*-OR containing 1,2-azaborines.

Procedure with 10 equiv. of H_2O and prolonged reaction time: 1,2-Azaborine (0.052 mmols) was weighed into vial. A solution of DMSO (0.3 mL) containing tetramethylsilane as an internal standard was added. The solution was then transferred to a Norell screw cap NMR tube and sealed. Degassed D_2O (10 μL, 0.56 mmols) was added, and the reaction mixture was vigorously shaken. The reaction progress was monitored by ^1H NMR at 25 °C. Compounds **4a**, **4c** and **4e** were each tested.

Time (h)	% **4a** remaining	**% 4c** remaining	**% 4e** remaining
0	100.0	100.0	100.0
0.02	100.0	100.0	100.0
0.05	100.0	100.0	100.0
0.10	100.0	100.0	100.0
0.17	100.0	100.0	100.0
0.25	99.7	100.0	100.0
0.35	100.0	100.0	100.0
0.47	99.5	100.0	100.0
0.60	99.7	100.0	100.0
0.75	100.0	100.0	100.0
0.92	100.3	100.0	100.0
1.10	100.0	100.0	100.0
1.30	100.0	100.9	98.9
1.52	100.3	100.0	98.9

1.75	100.0	100.0	98.9
2.00	99.5	100.0	98.9
2.27	100.0	100.0	98.9
2.55	100.0	100.0	98.9
2.85	101.4	100.0	100.0
3.17	101.4	100.9	100.0
3.50	101.4	100.9	98.9
3.85	100.3	100.9	98.9
4.22	100.0	100.9	100.0
4.60	99.7	99.1	98.9
5.00	99.5	100.9	98.9
5.42	99.5	100.0	101.1
5.85	100.0	100.9	100.0
6.30	99.5	100.9	100.0
6.77	99.5	100.0	100.0
7.25	99.5	100.0	100.0
7.75	98.9	100.0	100.0
8.27	99.2	101.9	101.1
8.80	98.9	100.0	100.0
9.35	98.9	100.0	100.0
9.92	100.3	100.0	98.9
10.50	100.0	100.9	100.0
11.10	100.0	101.9	100.0
11.72	98.7	100.0	101.1
12.35	98.4	99.1	98.9