Synthesis of Benzannulated Heterocycles by Twofold Suzuki–Miyaura Couplings of Cyclic Diarylborinic Acids

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Electronic Supplementary Information

**General.** All reactions were performed under an inert Argon atmosphere. Stainless steel syringes were used to transfer air- and moisture-sensitive liquids. Flash chromatography was carried out using neutral silica gel from Silicycle.

**Materials.** All reagents and solvents were purchased from Sigma Aldrich, Caledon, Carbosynth or Alfa Aesar and used without further purification. Toluene was purified by passing through two columns of activated alumina under argon (Innovative Technology, Inc.). Nuclear magnetic resonance (NMR) solvents were purchased from Cambridge Isotope Laboratories.

**Instrumentation.** $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ using either a Bruker Avance III 400 MHz, Varian Mercury 300 or 400 MHz, or Agilent 500 or 600 MHz spectrometer. $^1$H NMR are reported in parts per million (ppm) relative to tetramethylsilane and referenced to residual protium in the solvent. Spectral features are tabulated in the following order: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet); number of protons; coupling constants (J, Hz). High-resolution mass spectra (HRMS) were obtained on a VS 70-250S (double focusing) mass spectrometer at 70 eV. Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum 100 instrument equipped with a single-bounce diamond / ZnSe ATR accessory, either in the solid state or as neat liquids, as indicated. Spectral features are tabulated as follows: wavenumber (cm$^{-1}$); intensity (s-strong, m-medium, w-weak, br-broad).
I. Experimental and Characterization Data

Standard conditions for biscoupling with aryl halides (Table 1)

General procedure A. 10H-Dibenzo[b,e][1,4]oxaborinin-10-ol (19.6 mg, 0.1 mmol), Pd3(dba)3 (1.4 mg, 0.0015 mmol), t-Bu3PH(BF4) (1.0 mg, 0.003 mmol) and Cs2CO3 (107.5 mg, 0.33 mmol) were added to an oven-dried Schlenk tube equipped with a magnetic stirring bar. Please note, the Cs2CO3 used was from an older bottle and was likely hydrated (See Table SI-1 for water effects). The flask was evacuated and refilled with argon three times. Toluene (2 mL) and the aryl halide (0.3 mmol) were added. The reaction was allowed to stir for 1 h at room temperature prior to heating to 100 °C for 16 h. The reaction was cooled to room temperature, diluted with EtOA and purified by silica gel chromatography.

2,2''-oxydi-1,1'-biphenyl (2a). Synthesized according to general procedure A. The resulting crude material was purified by silica gel chromatography (5-10% DCM/pentane; Rf = 0.56 in 20% DCM/pentane), white solid. 1H-NMR (400 MHz; CDCl3): δ 7.35 (app dt, J = 6.5, 1.6 Hz, 4H), 7.30 (dd, J = 7.6, 1.7 Hz, 2H), 7.27-7.20 (m, 6H), 7.17-7.13 (m, 2H), 7.04 (app td, J = 7.5, 1.1 Hz, 2H), 6.83 (dd, J = 8.1, 1.0 Hz, 2H). 13C-NMR (100 MHz; CDCl3): δ 154.10, 138.02, 133.30, 131.30, 129.50, 128.62, 128.05, 127.21, 123.48, 118.91. IR (powder, cm−1): 1579 (m), 1498 (m), 1474 (m), 1427 (s), 1246 (s), 1223 (s), 1113 (m), 1077 (m), 1047 (m), 1009 (m), 877 (m), 739 (s), 697 (s). HRMS (DART, m/z): Calculated for C24H22NO [(M+NH4)+]: 340.17014. Found: 340.17030.

2-phenoxy-1,1'-biphenyl (2b). Synthesized according to general procedure A. The resulting crude material was purified by silica gel chromatography (5-10% DCM/pentane; Rf = 0.69 in 20% DCM/pentane), colorless oil. Spectral data are in agreement with previous reports. 1H-NMR (300 MHz; CDCl3): δ 7.55 (app dt, J = 6.9, 1.7 Hz, 2H), 7.46 (dd, J = 7.5, 1.8 Hz, 1H), 7.39-7.21 (m, 7H), 7.05-6.99 (m, 2H), 6.93 (dd, J = 8.7, 1.1 Hz, 2H). HRMS (DART, m/z): Calculated for C18H18NO [(M+NH4)+]: 264.13884. Found: 264.13853.

2',2''-oxybis(4-methoxy-1,1'-biphenyl) (3a). Synthesized according to general procedure A. The resulting crude material was purified by silica gel chromatography (gradient 10-70% DCM/pentane; Rf = 0.19 in 20% DCM/pentane), white solid. 1H-NMR (400 MHz; CDCl3): δ 7.41-7.36 (m, 6H), 7.20 (app td, J = 7.7, 1.8 Hz, 2H), 7.11 (app td, J = 7.5, 1.2 Hz, 2H), 6.90-6.87 (m, 6H), 3.82 (s, 6H). 13C-NMR (125 MHz; CDCl3): δ 158.89, 154.13, 132.87, 131.09, 130.55, 130.44, 128.18, 123.44, 118.97, 113.54, 55.36. IR (powder, cm−1): 1612 (m), 1514 (m), 1474 (m), 1439 (s), 1295 (m), 1243 (s), 1217 (s), 1174 (s), 1027 (m), 828 (s). HRMS (DART, m/z): Calculated for C26H23NO3 [(M+H)+]: 383.16472. Found: 383.16429.

4'-methoxy-2-Phenoxy-1,1'-biphenyl (3b). Synthesized according to general procedure A. The resulting crude material was purified by silica gel chromatography (gradient 10-70% DCM/pentane; Rf = 0.4 in 20% DCM/pentane), yellow oil. ¹H-NMR (400 MHz; CDCl₃): δ 7.50-7.47 (m, 2H), 7.44 (dd, J = 7.6, 1.8 Hz, 1H), 7.29-7.24 (m, 3H), 7.19 (app td, J = 7.4, 1.3 Hz, 1H), 7.04-6.98 (m, 2H), 6.94-6.89 (m, 4H), 3.81 (s, 3H). ¹³C-NMR (75 MHz; CDCl₃): δ 159.01, 158.01, 153.64, 131.20, 130.43, 129.73, 128.35, 124.22, 122.70, 120.37, 118.23, 113.76, 55.38. IR (powder, cm⁻¹): 1587 (m), 1479 (s), 1225 (s), 1036 (m), 752 (s). HRMS (DART, m/z): Calculated for C₁₉H₂₀NO₂ [(M+NH₄)⁺]: 294.14940. Found: 294.14928.

2',2'''-oxybis(4-nitro-1,1'-biphenyl) (4a). Synthesized according to general procedure A. The resulting crude material was purified by silica gel chromatography (gradient 30-70% DCM/pentane; Rf = 0.60 in 60% DCM/pentane), yellow solid. ¹H-NMR (300 MHz; CDCl₃): δ 8.18 (d, J = 8.9 Hz, 4H), 7.57-7.54 (m, 4H), 7.41-7.31 (m, 4H), 7.20 (app td, J = 7.5, 1.2 Hz, 2H), 6.95 (dd, J = 8.2, 1.1 Hz, 2H). ¹³C-NMR (125 MHz; CDCl₃): δ 153.68, 147.11, 144.45, 131.23, 130.92, 130.37, 130.15, 124.36, 123.46, 119.12. IR (powder, cm⁻¹): 1601 (m), 1509 (s), 1472 (s), 1444 (m), 1340 (s), 1218 (s), 1104 (m), 850 (s), 733 (s). HRMS (DART, m/z): Calculated for C₂₄H₂₀N₃O₅ [(M+NH₄)⁺]: 430.14030. Found: 430.14058.

4'-nitro-2-Phenoxy-1,1'-biphenyl (4b). Synthesized according to general procedure A. The resulting crude material was purified by silica gel chromatography (gradient 30-70% DCM/pentane; Rf = 0.13 in 20% DCM/pentane), yellow oil. Spectral data are in agreement with previous reports. ¹H-NMR (400 MHz; CDCl₃): δ 8.21 (d, J = 9.2 Hz, 2H), 7.72 (d, J = 9.2 Hz, 2H), 7.47 (dd, J = 7.6, 1.7 Hz, 1H), 7.38 (dd, J = 8, 7.2, 1.8 Hz, 1H), 7.31-7.25 (m, 3H), 7.08-7.02 (m, 2H), 6.92 (dd, J = 8.7, 1 Hz, 2H).

**Substrate synthesis**

**General procedure B.** Procedure adapted from previous reports. ³ To an oven-dried Schlenk flask, equipped with a magnetic stirring bar, were added aryl alcohol (2 mmol), Pd(OAc)₂ (9.0 mg, 0.04 mmol), (t-Bu)X-Phos (25.5 mg, 0.06 mmol), K₃PO₄ (849.1 mg, 2 mmol). Aryl halide (2.4 mmol) and toluene (4 mL) were then added under argon. The reaction was stirred at 100°C overnight. Upon cooling to room temperature, the reaction was filtered over Celite, washed with EtOAc and concentrated _in vacuo_. The resulting crude material was purified by silica gel chromatography.

General procedure C. Procedure adapted from previous reports. To an oven-dried Schlenk flask, equipped with a magnetic stirring bar, n-butyllithium (2 M in hexanes, 2.11 equiv.) was dropwise added to a 1.26 M solution of diphenyl ether (1 equiv) in anhydrous THF under argon, at –30 °C. After stirring the resulting suspension overnight (–30 °C - 23 °C), tributyl borate (1.5 equiv) was added. The resulting solution was heated to reflux for 2 h. Upon cooling to room temperature, 4 N HCl was added, and the mixture was stirred for 30 minutes at 23 °C. The two phases were separated and the organic phase was washed with water, dried over MgSO₄ and concentrated in vacuo. The resulting crude material was purified by recrystallization or silica gel chromatography.

General procedure D. Procedure adapted from previous reports. CBr₄ (1 equiv.) and PPh₃ (2 equiv.) were added to a round bottom flask equipped with a magnetic stirring bar under argon. DCM was added (0.45 M) and the reaction was cooled to –10 °C and stirred for 40 mins. The aldehyde was added dropwise and mixture stirred for another 2.5 h, allowing to warm to 23 °C. Solvents were removed in vacuo, and the solid was extracted with pentane/DCM and filtered over a silica plug. The resulting crude material was purified using silica gel chromatography.

1,1'-oxydinaphthalene. Synthesized according to general procedure B from 1-naphthol and 1-bromonaphthalene. The resulting crude material was purified by silica gel chromatography (pentane; Rf = 0.46 in pentane), 63% yield, white solid. Spectral data are in agreement with previous reports. ¹H-NMR (300 MHz; CDCl₃): δ 8.32 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.58-7.48 (m, 4H), 7.36 (t, J = 7.9 Hz, 2H), 6.91 (d, J = 7.6 Hz, 2H). HRMS (DART, m/z): Calculated for C₂₀H₁₅O [(M+H)⁺]: 271.11229. Found: 271.11308.

1-methoxy-3-phenoxybenzene. Synthesized according to general procedure B from phenol and 3-bromoanisole. The resulting crude material was purified by silica gel chromatography (20-40% DCM/pentane; Rf = 0.74 in 50% DCM/pentane), 28% yield, pale yellow oil. Spectral data are in agreement with previous reports. ¹H-NMR (400 MHz; CDCl₃): δ 7.34 (app, J = 8.0 Hz, 2H), 7.22 (app t, J = 8.4 Hz, 1H), 7.11 (tt, J = 7.6, 0.8 Hz, 1H), 7.03 (dd, J = 8.6, 1.0 Hz, 2H), 6.67-6.64 (m, 1H), 6.60-6.57 (m, 2H), 3.78 (s, 3H).

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10H-Dibenzo[\(b,e\)][1,4]oxaborinin-10-ol (1a). Synthesized according to general procedure C from diphenyl ether. Recrystallization from hot toluene yielded the title compound as a white, fluffy solid, 61% yield. Spectral data are in agreement with previous reports.\(^4\) \(^1\)H NMR (300 MHz; DMSO-\(\text{d}_6\)): \(\delta\) 9.85 (s, 1H, BOH), 8.14 (dd, 2H, \(J = 7.5, 1.8, 0.3\) Hz, 2H), 7.67 (ddd, \(J = 8.4, 7.2, 1.8\) Hz, 2H), 7.42 (ddd, \(J = 8.4, 0.9, 0.3\) Hz, 2H), 7.28 (ddd, \(J = 7.5, 7.2, 0.9\) Hz, 2H).

5-Methyldibenzo[\(b,e\)][1,4]azaborinin-10(5H)-ol (1b). Synthesized according to general procedure C from 2-bromo-N-(2-bromophenyl)-N-methylaniline. Recrystallization from 2:1 pentane:dichloromethane yielded the title compound as a white solid, 55% yield. Spectral data are in agreement with previous reports.\(^4\) \(^1\)H NMR (300 MHz; DMSO-\(\text{d}_6\)): \(\delta\) 9.00 (s, 1H, BOH), 8.22 (ddd, \(J = 7.5, 1.8, 0.6\) Hz, 2H), 7.64 (ddd, \(J = 8.7, 6.8, 1.8\) Hz, 2H), 7.57 (d, \(J = 8.5\) Hz, 2H), 7.12 (ddd, \(J = 7.5, 6.8, 0.9\) Hz, 2H), 3.79 (s, 3H).

1-methoxy-10H-dibenzo[\(b,e\)][1,4]oxaborinin-10-ol. Synthesized according to general procedure C from 1-methoxy-3-phenoxybenzene. The resulting crude material was purified by silica gel chromatography (gradient 20-50% DCM/pentane; \(R_f = 0.26\) in 20% DCM/pentane), 34% yield, white solid. \(^1\)H-NMR (300 MHz; CDCl\(_3\)): \(\delta\) 8.09 (dd, \(J = 7.5, 1.5\) Hz, 1H), 7.68 (s, 1H, BOH), 7.60 (ddd, \(J = 8.4, 7.1, 1.8\) Hz, 1H), 7.53 (app t, \(J = 8.3\) Hz, 1H), 7.37 (ddd, \(J = 8.4, 0.9, 0.3\) Hz, 1H), 7.26 (app td, \(J = 7.5, 0.9\) Hz, 1H), 7.05 (ddd, \(J = 8.4, 0.7, 1.6\) Hz, 1H), 6.67 (d, \(J = 8.1\) Hz, 1H), 4.00 (s, 3H). \(^{13}\)C-NMR (75 MHz; CDCl\(_3\)): \(\delta\) 164.77, 162.23, 161.14, 133.76, 133.14, 131.57, 122.42, 117.13, 111.26, 102.74, 55.99. IR (powder, cm\(^{-1}\)) \(\mid\): 3502 (m), 1604 (m), 1432 (s), 1346 (s), 1304 (s), 1229 (m), 1075 (s), 758 (s). HRMS (DART, m/z): Calculated for C\(_{13}\)H\(_{12}\)BO\(_3\) [(M+H\(^+\)]: 227.08795. Found: 227.08859.

7H-dinaphtho[1,2-b;2',1'-e][1,4]oxaborinin-7-ol. Synthesized according to general procedure C from 1,1'-oxydinaphthalene. The resulting crude material was purified by silica gel chromatography (0-5% DCM/pentane; \(R_f = 0.66\) in 20% DCM/pentane), 24% yield, off-white solid. \(^1\)H-NMR (400 MHz; DMSO-\(\text{d}_6\)): \(\delta\) 9.89 (s, 1H, BOH), 8.95 (d, \(J = 8.0\) Hz, 2H), 8.19 (d, \(J = 8.3\) Hz, 2H), 8.08 (dd, \(J = 7.7, 0.8\) Hz, 2H), 7.84-7.75 (m, 6H). \(^{13}\)C-NMR (125 MHz; DMSO-\(\text{d}_6\)): \(\delta\) 156.92, 135.77, 128.36, 128.04, 127.08, 126.76, 124.33, 122.36, 122.26, 116.2; IR (powder, cm\(^{-1}\)) \(\mid\): 3302 (br), 1633 (w), 1577 (w), 1384 (s), 1318 (m), 1260 (m), 1131 (m), 814 (m), 747 (s). HRMS (DART, m/z): Calculated for C\(_{20}\)H\(_{14}\)BO\(_2\) [(M+H\(^+\)]: 297.10868. Found: 297.10879.

1-(2,2-dibromovinyl)-4-methoxybenzene. Synthesized according to general procedure D. The resulting crude material was purified by silica gel chromatography (1-2.5% EtOAc/pentane; \(R_f = 0.30\) in 1% EtOAc/pentane), 83%, pale yellow solid. Spectral data are in agreement
with previous reports.\textsuperscript{9} \textsuperscript{1}H-NMR (400 MHz; CDCl\textsubscript{3}): \(\delta\) 7.50 (d, \(J = 8.7\) Hz, 2H), 7.40 (s, 1H), 6.89 (d, \(J = 8.7\) Hz, 2H), 3.82 (s, 3H).

1-(2,2-dibromovinyl)-4-nitrobenzene. Synthesized according to general procedure D. The resulting crude material was purified by silica gel chromatography (5-7\% EtOAc/pentane; \(R_f = 0.50\) in 5\% DCM/pentane), 81\%, yellow solid. Spectral data are in agreement with previous reports.\textsuperscript{10} \textsuperscript{1}H-NMR (500 MHz; CDCl\textsubscript{3}): \(\delta\) 8.23 (d, \(J = 8.9\) Hz, 2H), 7.70 (d, \(J = 8.9\) Hz, 2H), 7.56 (s, 1H).

**Standard conditions for Suzuki–Miyaura couplings with dihalides (Scheme 4)**

**General procedure D.** Borinic acid (0.1 mmol), Pd\textsubscript{2}(dba)\textsubscript{3} (1.4 mg, 0.0015 mmol), t-Bu\textsubscript{3}PH(BF\textsubscript{4}) (1.0 mg, 0.003 mmol) and Cs\textsubscript{2}CO\textsubscript{3} (107.5 mg, 0.33 mmol) were added to an oven-dried Schlenk tube equipped with a magnetic stirring bar. Please note, the Cs\textsubscript{2}CO\textsubscript{3} used was from an older bottle and was likely hydrated (See Table SI-1 for water effects). The flask was evacuated and refilled with argon three times. t-BuOH or t-AmOH (2 mL) and the dihalide (0.2 mmol) were added. The reaction was allowed to stir for 1 h at room temperature prior to heating to 80 or 100 °C for 16 h. The reaction was cooled to room temperature, diluted with EtOAc, filtered over Celite, concentrated \textit{in vacuo} and purified by silica gel chromatography.

2,3-dimethoxytribenzo\textsubscript{[b,d,f]}oxepine (5a). Synthesized according to general procedure D from 4,5-dibromoveratrole and 10H-dibenzo[b,e][1,4]oxaborinin-10-ol in t-BuOH at 80 °C. The resulting crude material was purified by silica gel chromatography (5-10\% EtOAc/pentane; \(R_f = 0.53\) in 20\% EtOAc/pentane), 90\%, yellow solid. \textsuperscript{1}H-NMR (300 MHz; CDCl\textsubscript{3}): \(\delta\) 7.54-7.52 (m, 2H), 7.33-7.31 (m, 4H), 7.25-7.20 (m, 2H), 7.12 (s, 2H), 4.01 (s, 6H). \textsuperscript{13}C-NMR (100 MHz; CDCl\textsubscript{3}): \(\delta\) 159.66, 149.00, 132.77, 129.36, 129.18, 128.89, 125.43, 120.88, 112.04, 56.12. IR (powder, cm\textsuperscript{-1}): 1603 (m), 1513 (m), 1484 (m), 1442 (m), 1386 (m), 1356 (m), 1267 (m), 1230 (m), 1206 (m), 1163 (m), 1020 (m), 740 (s). HRMS (DART, m/z): Calculated for C\textsubscript{20}H\textsubscript{17}NO\textsubscript{3} [(M+H)\textsuperscript{+}]: 305.11777. Found: 305.11763.

2,3-dimethoxy-9-methyl-9H-tribenzo\textsubscript{[b,d,f]}azepine (5b). Synthesized according to general procedure D from 4,5-dibromoveratrole and 5-Methyldibenzo[b,e][1,4]azaborinin-10(5H)-ol in t-AmOH at 100 °C. The resulting crude material was purified by silica gel chromatography (5-20\% EtOAc/pentane; \(R_f = 0.44\) in 20\% EtOAc/pentane), 89\% yield, white solid. \textsuperscript{1}H-NMR (500 MHz; CDCl\textsubscript{3}): \(\delta\) 7.43 (dd, \(J = 7.7, 1.6\) Hz, 2H), 7.30 (ddd, \(J = 8.1, 7.3, 1.6\) Hz, 2H), 7.19 (dd, \(J = 8.1, 1.1\) Hz, 2H), 7.13


tribenzo[\textit{b,d,f}]oxepine (5c). Synthesized according to general procedure D from 1,2-dibromobenzene and 10\textit{H}-dibenzo[\textit{b,e}][1,4]oxaborinin-10-ol in \textit{t}-AmOH
at 100 °C. The resulting crude material was purified by silica gel chromatography (10-20% DCM/pentane; \textit{R} \textit{f} = 0.38 in 20% DCM/pentane), 89% yield, white solid. Spectral data are in agreement with previous reports.\textsuperscript{11} \textsuperscript{1}H-NMR (400 MHz; CDCl\textsubscript{3}): \textit{\delta} 7.57 (dd, \textit{J} = 5.8, 3.4 Hz, 2H), 7.50 (dd, \textit{J} = 7.6, 1.5 Hz, 2H), 7.42 (dd, \textit{J} = 5.9, 3.3 Hz, 2H), 7.30-7.23 (m, 4H), 7.20-7.16 (m, 2H). HRMS (DART, m/z): Calculated for C\textsubscript{18}H\textsubscript{16}NO [(M+\textit{NH}_\textsubscript{4})\textsuperscript{+}]: 262.12319. Found: 262.12378.

\textbf{2,3,5-trimethoxytribenzo[\textit{b,d,f}]oxepine (5d).} Synthesized according to general procedure D from 4,5-dibromoveratrole and 1-methoxy-10\textit{H}-dibenzo[\textit{b,e}][1,4]oxaborinin-10-ol in \textit{t}-AmOH at 100 °C. The resulting crude material was purified by silica gel chromatography (10-30% EtOAc/pentane; \textit{R} \textit{f} = 0.34 in 20% EtOAc/pentane), 27% yield, yellow solid. \textsuperscript{1}H-NMR (300 MHz; CDCl\textsubscript{3}): \textit{\delta} 7.56-7.53 (m, 1H), 7.42 (s, 1H), 7.28-7.22 (m, 4H), 7.06 (s, 1H), 6.99 (dd, \textit{J} = 8.1, 1.1 Hz, 1H), 6.81 (dd, \textit{J} = 8.4, 0.9 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H), 3.81 (s, 3H). \textsuperscript{13}C-NMR (125 MHz; CDCl\textsubscript{3}): \textit{\delta} 161.69, 160.15, 157.49, 148.66, 147.57, 133.30, 130.22, 128.97, 128.97, 128.86, 125.59, 125.33, 121.36, 120.73, 114.78, 113.76, 112.06, 108.60, 56.19, 56.15, 56.14. IR (powder, cm\textsuperscript{-1}): 1602 (m), 1518 (m), 1462 (s), 1436 (m), 1384 (m), 1352 (m), 1261 (m), 1126 (m), 1073 (s), 1052 (s), 734 (s). HRMS (DART, m/z): Calculated for C\textsubscript{21}H\textsubscript{19}O\textsubscript{4} [(M+H)\textsuperscript{+}]: 335.12833. Found: 335.12857.

\textbf{2,3-dimethoxybenzo[\textit{d}]dinaphtho[1,2-\textit{b}:2',1'-\textit{f}]oxepine (5e).} Synthesized according to general procedure D from 4,5-dibromoveratrole and 7\textit{H}-dinaphtho[1,2-\textit{b}:2',1'-\textit{e}][1,4]oxaborinin-7-ol in \textit{t}-AmOH at 100 °C. The resulting crude material was purified by silica gel chromatography (gradient 30-70% DCM/pentane; \textit{R} \textit{f} = 0.11 in 20% DCM/pentane), 23% yield, white solid. \textsuperscript{1}H-NMR (300 MHz; CDCl\textsubscript{3}): \textit{\delta} 9.02 (d, \textit{J} = 8.1 Hz, 2H), 7.83 (dd, \textit{J} = 8.0, 0.4 Hz, 2H), 7.74-7.69 (m, 2H), 7.67-7.62 (m, 4H), 7.50 (ddd, \textit{J} = 8.1, 6.9, 1.1 Hz, 2H), 7.13 (s, 2H), 4.03 (s, 6H). \textsuperscript{13}C-NMR (125 MHz; CDCl\textsubscript{3}): \textit{\delta} 156.45, 149.11, 134.19, 130.43, 128.20, 127.85, 127.51, 127.01, 126.48, 126.36, 125.50, 122.66, 112.54, 56.36. IR (powder, cm\textsuperscript{-1}): 1606 (m), 1523 (m), 1498 (m), 1399 (s), 1255 (s), 1185 (m), 1036 (s), 815 (s), 733 (s). HRMS (DART, m/z): Calculated for C\textsubscript{28}H\textsubscript{23}O\textsubscript{3} [(M+H)\textsuperscript{+}]: 405.14907. Found: 405.14910.

\textsuperscript{11} Kumar, S.; Ila, H.; Junjappa, H.; 	extit{Tetrahedron} 2007, 63, 10067–10076.
14-methyl-14H-dibenzo[2,3:6,7]oxepino[4,5-b]indole (5f). Synthesized according to general procedure D from 2,3-dibromo-1-methyl-1H-indole\textsuperscript{12} and 10H-dibenzo[b,e][1,4]oxaborinin-10-ol in t-AmOH at 100 °C, for 40 h. The resulting crude material was purified by silica gel chromatography (20-25% DCM/pentane; \( R_f = 0.31 \) in 20% DCM/pentane), 28% yield, yellow solid. \(^1\)H-NMR (300 MHz; CDCl\textsubscript{3}): \( \delta \) 8.04 (dd, \( J = 7.9, 0.9 \) Hz, 1H), 7.93-7.90 (m, 1H), 7.53-7.34 (m, 6H), 7.32-7.26 (m, 4H), 3.97 (s, 3H). \(^13\)C-NMR (125 MHz; CDCl\textsubscript{3}): \( \delta \) 158.55, 157.70, 139.30, 135.70, 129.79, 128.76, 128.54, 128.31, 127.68, 125.63, 125.47, 124.95, 124.90, 123.18, 122.45, 121.48, 120.86, 119.82, 113.13, 110.17, 32.45. HRMS (DART, m/z): Calculated for C\(_{21}\)H\(_{16}\)NO [(M+H)\(^+\)]: 298.1239. Found: 298.1239.

9-(4-methoxybenzylidene)-9H-xanthene (5g). Synthesized according to general procedure D from 1-(2,2-dibromovinyl)-4-methoxybenzene and 10H-dibenzo[b,e][1,4]oxaborinin-10-ol in t-BuOH at 80 °C. The resulting crude material was purified by silica gel chromatography (0-2% EtOAc/pentane; \( R_f = 0.72 \) in 5% EtOAc/pentane), 71% yield, yellow solid. \(^1\)H-NMR (400 MHz; CDCl\textsubscript{3}): \( \delta \) 7.73 (dd, \( J = 8.3, 1.6 \) Hz, 1H), 7.36 (dd, \( J = 8.0, 1.5 \) Hz, 1H), 7.31-7.26 (m, 3H), 7.22 (ddd, \( J = 8.3, 7.0, 1.5 \) Hz, 1H), 7.17-7.15 (m, 3H), 6.89 (s, 1H), 6.85-6.83 (m, 3H), 3.83 (s, 3H). \(^13\)C-NMR (100 MHz; CDCl\textsubscript{3}): \( \delta \) 158.77, 153.19, 151.75, 130.25, 130.06, 129.99, 129.09, 128.58, 128.55, 128.01, 126.01, 125.32, 123.89, 123.25, 122.52, 122.45, 121.73, 117.29, 116.98, 114.02, 55.39. IR (powder, cm\(^{-1}\)): 1603 (m), 1506 (m), 1449 (s), 1236 (s), 1173 (m), 1099 (m), 1032 (m), 748 (s). HRMS (DART, m/z): Calculated for C\(_{21}\)H\(_{17}\)O\(_2\) [(M+H)\(^+\)]: 301.12285. Found: 301.12312.

9-(4-nitrobenzylidene)-9H-xanthene (5h). Synthesized according to general procedure D from 1-(2,2-dibromovinyl)-4-nitrobenzene and 10H-dibenzo[b,e][1,4]oxaborinin-10-ol in t-AmOH at 100 °C, 40 h. The resulting crude material was purified by silica gel chromatography (12-30% DCM/pentane; \( R_f = 0.24 \) in 20% DCM/pentane), 64% yield, yellow solid. \(^1\)H-NMR (500 MHz; CDCl\textsubscript{3}): \( \delta \) 8.15 (d, \( J = 8.6 \) Hz, 2H), 7.78 (ddd, \( J = 8.1, 1.3, 0.4 \) Hz, 1H), 7.51 (ddd, \( J = 9.0, 0.8 \) Hz, 2H), 7.37 (ddd, \( J = 8.3, 7.1, 1.5 \) Hz, 1H), 7.31 (ddd, \( J = 8.3, 7.1, 1.6 \) Hz, 1H), 7.25-7.20 (m, 4H), 6.89-6.85 (m, 2H). \(^13\)C-NMR (125 MHz; CDCl\textsubscript{3}): \( \delta \) 153.15, 151.57, 146.47, 145.53, 130.33, 130.30, 129.62, 129.52, 128.51, 124.20, 124.12, 123.96, 123.30, 122.82, 120.22, 119.60, 117.78, 117.28. IR (powder, cm\(^{-1}\)): 1617 (w), 1588 (m), 1508 (s), 1451 (s), 1338 (s), 1109 (m), 857 (s). HRMS (DART, m/z): Calculated for C\(_{26}\)H\(_{14}\)NO\(_3\) [(M+H)\(^+\)]: 316.09737. Found: 316.09727.

tetramelze\[b,d,f,h\]oxonine (5i). Synthesized according to general procedure D from 2,2'-dibromo-1,1'-biphenyl and 10H-dibenzo\[b,e\][1,4]oxaborinin-10-ol in t-AmOH at 100 °C, 40 h. The resulting crude material was purified by silica gel chromatography (10-30% DCM/pentane; Rf = 0.44 in 20% DCM/pentane), 61% yield, white solid. 1H-NMR (500 MHz; CDCl3): δ 7.26-7.25 (m, 4H), 7.20-7.17 (m, 2H), 7.12 (ddd, J = 8.2, 6.5, 2.6 Hz, 2H), 7.01 (app dt, J = 7.4, 1.0 Hz, 2H), 6.95-6.90 (m, 6H). 13C-NMR (125 MHz; CDCl3): δ 153.75, 142.18, 138.60, 132.13, 131.77, 128.73, 128.67, 128.02, 127.30, 127.09, 122.84, 120.27. IR (powder, cm\(^{-1}\)): 1565 (m), 1489 (m), 1462 (m), 1427 (s), 1280 (m), 1219 (m), 748 (s). HRMS (DART, m/z): Calculated for C\(_{24}\)H\(_{20}\)NO \([(M+NH_4)^+\]: 338.15449. Found: 338.15484.

Investigating the effects of water

Table SI-1. The role of water was evaluated using anhydrous Cs\(_2\)CO\(_3\).

<table>
<thead>
<tr>
<th>entry</th>
<th>X equiv. H(_2)O</th>
<th>NMR yield (%)(^a)</th>
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<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>35(^b)</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>74</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
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<td>75</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>77</td>
</tr>
</tbody>
</table>

\(^a\) Yields determined by 1H NMR with 1,3,5-trimethoxybenzene as a quantitative internal standard. \(^b\) Isolated yield.
II. $^1$H and $^{13}$C NMR Spectra