Supporting Information for


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**General Section**

$^1$H and $^{13}$C NMR spectra were recorded on a Varian Gemini 200 (200 MHz) spectrometer in deuteriochloroform (CDCl3) with either tetramethylsilane (TMS) (0.00 ppm $^1$H, 0.00 ppm $^{13}$C) or chloroform (7.26 ppm $^1$H, 77.00 ppm $^{13}$C) as internal reference unless otherwise stated. Data are reported in the following order: chemical shift in ppm, multiplicities (br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), sex (sextet), hex (hextet), m (multiplet), exch (exchangeable), app (apparent)), coupling constants, $J$ (Hz), and integration. Infrared spectra were recorded on a Perkin-Elmer FTIR 1600 series spectrophotometer. Peaks are reported (cm$^{-1}$) with the following relative intensities: s (strong, 67-100%), m (medium 40-67%), and w (weak 20-40%). Melting points are not corrected. High-resolution mass spectra were obtained using a VG-70-250S (double focusing) mass spectrometer at 70 eV. Analytical thin-layer chromatography was performed on Merck silica gel plates with F-254 indicator. Visualization was accomplished by UV-light and 5% phosphomolybdic acid solution in ethanol. Medium pressure liquid chromatography (MPLC) was performed using gradient solutions with the indicated solvent systems. THF and acetonitrile were dried over activated 4Å molecular sieves. All reactions were performed under a dry N$_2$ atmosphere in oven- and or flame-dried glassware.

**Starting Materials**

$p$-Methoxybenzenethiol, triethylamine, (CH$_3$CN)$_2$PdCl$_2$, Pd(OAc)$_2$, $p$-iodoanisole, acetonitrile, tetrabutylammonium bromide, trifurlylphosphine, tris(dibenzylideneacetone)-dipalladium (0), and all of the boronic acids were commercially available and used as received. CuTC,$^1$ tributyl-$p$-tolylstannane,$^2$ tributyl-$p$-methoxyphenylstannane,$^2$ tributyl-$p$-
chlorophenylstannane, tributy1-3,4-(methylenedioxy)phenylstannane, were prepared as previously described.

**General Procedures.**

**Dione 2.** In a 100-mL two-necked round-bottomed flask equipped with a rubber septum, a nitrogen inlet, and a stir bar, dichlorocyclobutenedione (200 mg, 1.32 mmol) was dissolved in dry THF (50 mL) and the temperature was lowered to 0 °C (ice-bath). p-Methoxybenzenethiol (0.09 mL, 0.66 mmol) and triethylamine (0.08 mL, 0.66 mmol) were sequentially added. The mixture was stirred at 0 °C for 5 h whereupon the solvent was removed under reduced pressure. The remaining solid was extracted with a 5% EtOAc/hexanes (2 x 50 mL), the organic extracts were passed through a Celite pad and then the solvent was removed under reduced pressure to give a pale yellow solid (145 mg, 93%). TLC (Rf = 0.6, 30% EtOAc/hexanes, UV); mp 95-97 °C; IR (KBr, cm⁻¹): 1817 (m), 1782 (s), 1759 (s), 1592 (m), 1496 (s), 1480 (s), 1302 (m), 1256 (s), 1156 (s), 1057 (m), 1030 (m), 879 (m), 830 (i), 509 (m); ¹H NMR (200 MHz, CDCl₃): δ 7.5 (d, J = 8.8 Hz, 2H), 6.9 (d, J = 8.8 Hz, 2H), 3.8 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃): δ 196.3, 190.5, 187.7, 176.1, 162.1, 136.3, 115.4, 113.4, 55.7; HRMS (C₁₁H₇ClO₃S) calcd 253.9804 found 253.9809.

**Stille couplings of 2 with organostannanes.**

**General Procedure.** In an oven-dried Schlenk tube, 2 (1 equiv.), and the arylstannane (1.2 equiv.) were dissolved in anhyd. CH₃CN (3 mL) under N₂. Then, the mixture was purged with N₂ for 5 min whereupon (CH₃CN)₂PdCl₂ (5%) was added and the reaction mixture was stirred at rt for 2 h. The mixture then was washed with hexanes (4 x 3 mL) to remove the tin by-products and the remaining CH₃CN phase was concentrated in vacuo. The final product was purified by Flash chromatography (SiO₂-gel, EtOAc/hexanes gradient).

**Dione 3.** Yellow solid. TLC (30% EtOAc/hexanes, Rf = 0.56); mp 180 °C; IR (KBr, cm⁻¹): 1766 (s), 1753 (s), 1601 (s), 1500 (m), 1482 (s), 1268 (s), 1258 (s), 1177 (s), 1019 (m), 838 (m), 828 (m); ¹H NMR (200 MHz, CDCl₃): δ 8.04 (d, J = 9.2 Hz, 2H), 7.55 (d, J = 9.2 Hz, 2H), 7.07 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 9.2 Hz, 2H), 3.91 (s, 3H), 3.86 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃): 192.8, 191.0, 187.4, 180.7, 163.6, 161.6, 135.7, 131.4, 131.4, 121.7, 115.7, 115.1, 115.1, 55.8, 55.6; HRMS (C₁₈H₁₄O₄S) calcd 326.0613 found 326.0597.
**Dione 4** 
\(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta 8.21\) (d, \(J = 7.0\) Hz, 2H), \(7.04\) (d, \(J = 7.0\) Hz, 2H), \(3.91\) (s, 3H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta 194.74, 190.35, 187.71, 176.86, 165.17, 131.35, 119.62, 115.14, 55.68.\(^4\)

**Dione 5.** yellow solid. TLC (30 % EtOAc/hexanes \(R_f = 0.65\)); mp 185 °C; IR (KBr, cm\(^{-1}\)): 1769.9 (s), 1751.6 (s), 1605.7 (m), 1591.8 (m), 1541.7 (m), 1484.8 (m) 1294.6 (m), 1252.5 (m), 1177.3 (m), 1086.7 (m), 1070.9 (m), 1021.6 (m), 908.0 (m), 846.5 (m), 507.8 (m), 4618 (m).\(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta 7.95\) (d, \(J = 8.2\) Hz, 2H), 7.56 (d, \(J = 8.6\) Hz, 2H), 7.38 (d, \(J = 8.2\) Hz, 2H), 6.96 (d, \(J = 8.4\) Hz, 2H), 3.86 (s, 3H), 2.47 (s, 3H). \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta 192.6, 191.2, 189.2, 181.2, 161.7, 144.3, 135.7, 130.2, 129.1, 126.1, 115.6, 115.1, 55.6, 22.2\); HRMS (C\(_{18}H_{14}O_4S\)) calcd 310.0664 found 310.0673.

**Dione 6.** Yellow solid. TLC (30 % EtOAc/hexanes \(R_f = 0.70\)); mp 178-179 °C; IR (KBr, cm\(^{-1}\)): 1768 (s), 1754 (s), 1469 (m), 1253 (m), 1095 (m), 828 (m); \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta 7.98\) (d, \(J = 8.2\) Hz, 2H), 7.55 (d, \(J = 8.6\) Hz, 4H), 6.97 (d, \(J = 8.2\) Hz, 2H), 3.87 (s, 3H), \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta 192.1, 191.0, 190.6, 179.5, 161.9, 139.4, 135.8, 130.2, 130.0, 127.0, 115.3, 115.1, 55.7\); HRMS (C\(_{17}H_{11}O_3SCl\)) calcd 330.0117 found 330.0102.

**Dione 7.** yellow solid. TLC (30 % EtOAc/hexanes \(R_f = 0.53\)); mp 160-163 °C; IR (KBr, cm\(^{-1}\)): 1764 (s), 1740 (s), 1498 (m), 1467 (s), 1263 (s), 1249 (s), 1237 (s), 1085 (m), 1027 (m), 840 (m); \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta 7.68\) (d, \(J = 8.4\) Hz, 1 H), 7.55 (d, \(J = 9.2\) Hz, 3H), 6.98 (t, \(J = 8.4\) Hz, 3H), 6.10 (s, 2H), 3.9 (s, 3H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta 192.5, 190.9, 187.8, 180.4, 161.7, 151.9, 148.7, 135.7, 125.6, 122.9, 119.5, 115.5, 115.1, 109.5, 108.4, 102.3, 55.6; HRMS (C\(_{18}H_{12}O_5S\)) calcd 340.0405 found 340.0399.

**Liebeskind/Srögl cross-couplings of 3, 5-7 with boronic acids**

**General procedure:** In an oven-dried Schlenk tube, the thiocyclobutenedione (1 equiv.) and the arylboronic acid (2.5 equiv.) were dissolved in dry THF (4 mL) under N\(_2\). Then, the mixture was purged with N\(_2\) for 5 min whereupon, Pd\(_2\)bda\(_3\) (1%), TFP (3%) and CuTC (3 equiv.), were added. The reaction mixture was heated at 50 °C for 20 h, cooled to rt, and then quenched with satd. aq. NH\(_4\)Cl. Then, it was extracted with EtOAc (3 x 10 mL), dried over CaCl\(_2\), filtered and the volatiles removed under reduced pressure. The product was purified by Flash chromatography (SiO\(_2\)-gel, EtOAc/hexanes gradient).
Dione 8. yellow solid. TLC (30 % EtOAc/hexanes \( R_f = 0.65 \)); mp 157-159 °C; IR (KBr, cm\(^{-1}\)): 1776 (s), 1755 (s), 1601 (s), 1562 (m), 1492 (m), 1361 (m), 1273 (m), 1176 (m), 1071 (m), 1026 (m), 836 (m); \(^1\)H NMR (200 MHz, CDCl\(_3\)): \( \delta \) 8.15 (d, \( J = 8.8 \) Hz, 2H), 8.04 (d, \( J = 8.4 \) Hz, 2H), 7.57 (d, \( J = 8.6 \) Hz, 2H), 7.04 (dd, \( J = 7.0 \) Hz, \( J = 1.0 \) Hz, 2H), 6.78 (dd, \( J = 17.4 \) Hz, \( J = 11.0 \) Hz, 1H), 5.9 (d, \( J = 17.6 \) Hz, 1H), 3.92 (s, 3H); \(^13\)C NMR (75.5 MHz, CDCl\(_3\)): \( \delta \) 196.8, 196.0, 184.7, 164.1, 142.2, 136.1, 131.0, 128.6, 127.9, 127.1, 121.3, 117.3, 115.0, 55.8; HRMS (C\(_{19}\)H\(_{14}\)O\(_3\)) calcd 290.0943 found 290.0931.

Dione 9. brown solid. TLC (30 % EtOAc/hexanes \( R_f = 0.31 \)); mp 178-180 °C; IR (KBr, cm\(^{-1}\)): 1750 (m), 1736 (m), 1602 (s), 1355 (s), 1234 (m), 1175 (m), 1076 (m), 824 (m); \(^1\)H NMR (200 MHz, CDCl\(_3\)): \( \delta \) 8.10 (dd, \( J = 13.4 \) Hz, \( J = 9.0 \) Hz, 4H), 7.06 (d, \( J = 8.0 \) Hz, 2H), 6.74 (d, \( J = 8.6 \) Hz, 2H), 3.91 (s, 3H), 3.13 (s, 6H); \(^13\)C NMR (75.5 MHz, CDCl\(_3\)): \( \delta \) 197.4, 195.9, 184.3, 181.7, 163.0, 153.5, 130.9, 130.3, 122.2, 116.6, 114.8, 111.9, 55.7, 40.4; HRMS (C\(_{19}\)H\(_{17}\)NO\(_3\)) calcd 307.1208 found 307.1206.

Dione 10. yellow solid. TLC (30 % EtOAc/hexanes \( R_f = 0.65 \)); mp 181-184 °C; IR (KBr, cm\(^{-1}\)): 1779 (m), 1735 (m), 1602 (s), 1554 (m), 1500 (m), 1476 (m), 1355 (s), 1269 (m), 1225 (m), 1081 (m), 1023 (m); \(^1\)H NMR (200 MHz, CDCl\(_3\)): \( \delta \) 8.68 (s, 1H), 7.36 (d, \( J = 1.8 \) Hz, 2H), 7.26-7.17 (m, 2H), 3.97 (s, 3H), 2.48 (s, 3H); \(^13\)C NMR (200 MHz, CDCl\(_3\)): \( \delta \) 196.8, 196.5, 186.5, 160.5, 144.5, 137.4, 131.5, 130.2, 128.5, 127.9, 126.0, 124.5, 123.7, 120.4, 106.4, 55.7, 22.1; HRMS (C\(_{22}\)H\(_{16}\)O\(_3\)) calcd 328.1099 found 328.1115.

Dione 11. yellow solid. TLC (30 % EtOAc/hexanes \( R_f = 0.37 \)); mp 193-195 °C; IR (KBr, cm\(^{-1}\)): 1778 (s), 1756 (s), 1593 (m), 1569 (m), 1498 (s), 1360 (s), 1270 (s), 1241 (m), 1080 (m), 1017 (m); \(^1\)H NMR (200 MHz, CDCl\(_3\)): \( \delta \) 8.00 (d, \( J = 8.0 \) Hz, 2H), 7.86 (dd, \( J = 8.2 \) Hz, \( J = 1.8 \) Hz, 1H), 7.65 (d, \( J = 1.8 \) Hz, 1H), 7.36 (d, \( J = 8.0 \) Hz, 2H), 7.00 (d, \( J = 8.4 \) Hz, 1H), 3.99 (s, 3H), 3.90 (s, 3H), 2.47 (s, 3H); \(^13\)C NMR (200 MHz, CDCl\(_3\)): \( \delta \) 196.8, 196.1, 185.8, 185.4, 153.7, 149.4, 144.2, 130.1, 128.3, 126.0, 123.4, 121.4, 111.5, 110.8, 56.3, 22.1; HRMS (C\(_{19}\)H\(_{16}\)O\(_4\)) calcd 308.1049 found 308.1061.

Dione 12. yellow solid. TLC (30 % EtOAc/hexanes \( R_f = 0.30 \)); mp 174 °C; IR (KBr, cm\(^{-1}\)): 1782 (s), 1771 (s), 1704 (s), 1587 (m), 1349 (m), 1207 (m), 826 (m); \(^1\)H NMR (200 MHz, CDCl\(_3\)): \( \delta \) 10.13 (s, 1H), 8.19-8.01 (m, 4H), 7.56 (d, \( J = 8.6 \) Hz, 2H), \(^13\)C NMR (75.5 MHz, CDCl\(_3\)): \( \delta \) 195.6, 194.9, 191.21, 187.5, 186.0, 140.8, 139.1, 133.1, 130.6, 130.3, 129.9, 128.9, 126.3; HRMS (C\(_{17}\)H\(_5\)ClO\(_3\)) calcd 296.0240 found 296.0245.
Dione 13. yellow solid. TLC (30 % EtOAc/hexanes $R_f = 0.85$), mp 153 -156 °C; IR (KBr, cm$^{-1}$): 1782 (s), 1768 (s), 1586 (m), 1348 (m), 1067 (m), 826 (m); $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 8.00 (d, $J = 8.6$ Hz, 2H), 7.91 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ 195.6, 195.5, 186.2, 140.2, 133.1, 130.1, 129.7, 128.8, 126.9, 126.5; HRMS (C$_{16}$H$_8$BrClO$_2$) calcd 345.9396 found 345.9394.

Dione 14. yellow solid. TLC (30 % EtOAc/hexanes $R_f = 0.38$); mp 167-167 °C; IR (KBr, cm$^{-1}$): 1751 (s), 1562 (m), 1442 (m), 1272 (m), 1039 (m); $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 8.56 (dd, $J = 2.8$ Hz, $J = 1.2$ Hz, 1H), 7.81 (dd, $J = 8.2$ Hz, $J = 1.8$ Hz, 1H), 7.4 (d, $J = 5.0$ Hz, $J = 1.2$ Hz, 1H), 7.57-7.53 (m, 2H), 7.00 (d, $J = 8.2$ Hz, 1H), 6.12 (s, 2H) $^{13}$C NMR (75.5 MHz, CDCl$_3$): 196.0, 195.8, 183.6, 179.4, 152.2, 148.7, 132.5, 129.6, 127.9, 126.2, 125.2, 122.6, 109.5, 108.0, 102.4; HRMS (C$_{15}$H$_8$O$_4$S) calcd 284.0143 found 284.0141.

Dione 15. Yellow solid. TLC (20 % EtOAc/hexanes $R_f = 0.27$); mp 199-200 °C; IR (KBr, cm$^{-1}$): 1754 (s), 1600 (m), 1452 (s), 1034 (m), 1256 (m), 1034 (m); $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 8.26 (dd, $J = 8.4$ Hz, $J = 1.8$ Hz, 1H), 8.05 (d, $J = 1.6$ Hz, 1H), 7.96 (d, $J = 3.6$ Hz, 1H), 7.81 (d, $J = 3.6$ Hz, 1H), 7.02 (d, $J = 8.2$ Hz, 1H), 6.79 (dd, $J = 3.8$ Hz, $J = 2.0$ Hz, 1H), 6.13 (s, 2H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ 194.7, 192.6, 178.8, 178.8, 169.5, 152.6, 148.8, 148.6, 144.5, 127.0, 122.9, 121.4, 114.1, 109.5, 109.3, 102.3; HRMS (C$_{15}$H$_8$O$_5$) calcd 268.0372 found 268.0369.

Dione 16. A Schlenk tube was charged with p-iodoanisole (24.2 mg, 0.10 mmol), Na$_2$CO$_3$ (22.0 mg, 0.20 mmol), Bu$_4$NBr (33.3 mg, 0.1 mmol) and Pd(OAc)$_2$ (0.8 mg, 0.003 mmol), and dry DMF (2 mL). The reaction mixture was purged with N$_2$ for 5 min whereupon dione 8 (20 mg, 0.07 mmol) was added. The reaction vessel was heated at 80 °C for 1h, cooled to rt and diluted with EtOAc (5 mL). The organic phase was washed with water (5 x 5 mL), dried over MgSO4 and filtered. The product (yellow solid, 20.3 mg, 73%) was purified by Flash chromatography (SiO2-gel, EtOAc/hexanes gradient) and further crystallized (CH$_2$Cl$_2$/petroleum ether). TLC (15% EtOAc/hexanes $R_f = 0.2$); mp 229-230 °C; IR (KBr, cm$^{-1}$): 1747 (s), 158 (s), 1357 (s), 1269 (m), 1254 (m), 1174 (m), 838 (m); $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 8.16 (d, $J = 9.0$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 8.2$ Hz, 2H), 7.51 (d, $J = 8.8$ Hz, 2H), 7.13 (d, $J = 16.4$ Hz, 1H), 7.13 (d, $J = 8.8$ Hz, 2H), 7.05 (d, $J = 16.4$ Hz, 1H), 6.93 (d, $J = 8.8$ Hz, 2H), 3.88 (s, 3H), 3.82 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ 196.8, 196.2, 185.6, 184.6, 164.0, 160.2, 142.7, 131.7, 131.0, 129.5, 128.8, 128.5, 127.1, 127.0, 125.4, 121.4, 115.0, 114.2, 55.8, 55.6; HRMS (C$_{26}$H$_{26}$O$_4$) calcd 396.1361 found 396.1370.
References


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