Table S1. Crystal data and structure refinement for **2**, **3a**, **3b** and **4**

| | **2** | **3a** | **3b** | **4** |
|---|---|---|---|---|
| CCDC number | 915146 | 915147 | 915149 | 915148 |
| Empirical formula | $C_9H_8BF_2N_3$ | $C_{12}H_{14}BF_2N_3$ | $C_{13}H_{16}BF_2N_3$ | $C_{13}H_{16}BF_2N_3$ |
| Formula weight | 206.99 | 249.07 | 263.10 | 263.10 |
| Temperature | 296(2) | | | |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/c$ | C2/c | P-1 | $P2_1/c$ |
| a (Å) | 7.482(5) | 18.23(3) | 9.524(4) | 8.259(11) Å |
| b (Å) | 10.727(8) | 17.42(3) | 11.707(5) | 9.659(13) Å |
| c (Å) | 11.941(9) | 15.14(2) | 12.978(5) | 16.43(2) Å |
| $\alpha$(°) | 90 | 90 | 88.450(6) | 90°. |
| $\beta$(°) | 102.161(13) | 98.19(3) | 85.147(6) | 96.114(18)°. |
| $\gamma$ (°). | 90 | 90 | 71.671(6) | 90°. |
| Volume ($Å^3$) | 936.9(12) | 4758(13) | 1368.7(10) Å3 | 1303(3) |
| Z | 4 | 16 | 4 | 4 |
| Density calc. ($Mg/m^3$ | 1.467 | 1.391 | 1.277 | 1.341 |
| Absorption coefficient ($mm^{-1}$) | 0.118 | 0.106 | 0.096 | 0.101 |
| Theta range for data collection (°) | 2.58 to 25.00 | 2.22 to 25.00 | 1.57 to 24.99 | 2.45 to 25.99 |
| Reflections collected | 15593 | 17079 | 14137 | 13451 |
| Independent reflections | 1649 (0.1110) | 4111 (0.1627) | 4805 (0.2451) | 2563 (0.1056) |
| Completeness (%) | 100.0 | 98.2 | 99.8 | 100.0 |
| Absorption correction | Semi-empirical from equivalents | | | |
| Data / restraints / parameters | 1649 / 1 / 168 | 4111 / 0 / 338 | 4805 / 0 / 355 | 2563 / 0 / 174 |
| Goodness-of-fit on F2 | 0.888 | 0.893 | 0.921 | 0.838 |
| Final R indices [I>2sigma(I)] | R1 = 0.0509 wR2 = 0.1230 | R1 = 0.0638, wR2 = 0.1406 | R1 = 0.0699 wR2 = 0.0476 | R1 = 0.0540 wR2 = 0.1292 |
| peak and hole ($e.Å^{-3}$) | 0.146 and -0.234 | 0.224 and -0.216 | 0.199 and -0.252 | 0.184 and -0.189 |