

Supporting Information

Polycatenar unsymmetrical β -diketonate ligands as a useful tool to induce columnar mesomorphism on highly luminescent boron difluoride complexes

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Characterisation of the compounds

Boron derivatives

Boron difluoride β -diketonate complexes of the type $[\text{BF}_2]_{1,2}(n/m)$; $n = m = 12, 14, 16, 18$ (1-4); $n = 12, m = 14, 16, 18$ (5-7)

$[\text{BF}_2]_{1,2}(12/12)$ (1): yellow solid (68%). Mp 60 °C. Elemental analysis: Found: C, 74.6; H, 9.8%. $\text{C}_{51}\text{H}_{83}\text{BF}_2\text{O}_5$ requires C, 74.3; H, 10.1%. $\nu_{\text{max}}(\text{solid})/\text{cm}^{-1}$: 2922vs, 2851vs $\nu(\text{C-H})$, 1607s $\nu(\text{C=C})$, 1550vs $\nu(\text{C=O})$, 1387m $\nu(\text{B-O})$, 1039s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl_3 ; Me_4Si)/ppm: 0.88 (9 H, t, 3J 6.6, CH_3), 1.26-1.48 (54 H, m, CH_2), 1.80 (6 H, q, CH_2), 4.01 (4 H, t, 3J 6.5, OCH_2), 4.07 (2 H, t, 3J 6.5, OCH_2), 6.71 (1 H, t, 4J 2.1, $\text{H}4''$), 7.00 (2 H, AA'XX' system, N 9.0, $\text{H}3'$ and $\text{H}5'$), 7.03 (1 H, s, $\text{H}2$), 7.19 (2 H, d, 4J 2.1, $\text{H}2''$ and $\text{H}6''$), 8.12 (2 H, AA'XX' system, N 9.0, $\text{H}2'$ and $\text{H}6'$).

$[\text{BF}_2]_{1,2}(14/14)$ (2): yellow solid (62%). Mp 72 °C. Elemental analysis: Found: C, 74.8; H, 10.0%. $\text{C}_{57}\text{H}_{95}\text{BF}_2\text{O}_5$ requires C, 75.3; H, 10.5%. $\nu_{\text{max}}(\text{solid})/\text{cm}^{-1}$: 2922vs, 2849vs $\nu(\text{C-H})$, 1606s $\nu(\text{C=C})$, 1548vs $\nu(\text{C=O})$, 1390m $\nu(\text{B-O})$, 1036s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl_3 ; Me_4Si)/ppm: 0.88 (9 H, t, 3J 6.7, CH_3), 1.26-1.48 (66 H, m, CH_2), 1.80 (6 H, m, CH_2), 4.00 (4 H, t, 3J 6.5, OCH_2), 4.06 (2 H, t, 3J 6.5, OCH_2), 6.70 (1 H, t, 4J 2.1, $\text{H}4''$), 6.98 (2 H, AA'XX' system, N 9.0, $\text{H}3'$ and $\text{H}5'$), 7.02 (1 H, s, $\text{H}2$), 7.17 (2 H, d, 4J 2.1, $\text{H}2''$ and $\text{H}6''$), 8.10 (2 H, AA'XX' system, N 9.0, $\text{H}2'$ and $\text{H}6'$).

[BF₂]_{1,2}(16/16) (3): yellow solid (70%). Mp 80 °C. Elemental analysis: Found: C, 76.6; H, 10.5%. C₆₃H₁₀₇BF₂O₅ requires C, 76.2; H, 10.8%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2922vs, 2849vs $\nu(\text{C-H})$, 1607s $\nu(\text{C=C})$, 1549vs $\nu(\text{C=O})$, 1387m $\nu(\text{B-O})$, 1038s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (9 H, t, ³J 6.6, CH₃), 1.26-1.48 (78 H, m, CH₂), 1.80 (6 H, m, CH₂), 4.01 (4 H, t, ³J 6.6, OCH₂), 4.08 (2 H, t, ³J 6.6, OCH₂), 6.72 (1 H, t, ⁴J 2.1, H4''), 7.00 (2 H, AA'XX' system, *N* 9.0, H3' and H5'), 7.03 (1 H, s, H2), 7.20 (2 H, d, ⁴J 2.1, H2'' and H6''), 8.13 (2 H, AA'XX' system, *N* 9.0, H2' and H6').

[BF₂]_{1,2}(18/18) (4): yellow solid (67%). Mp 80 °C. Elemental analysis: Found: C, 75.9; H, 10.5%. C₆₉H₁₁₉BF₂O₅(CH₂Cl₂)_{0.25} requires C, 75.7; H, 10.9%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2920vs, 2850vs $\nu(\text{C-H})$, 1608s $\nu(\text{C=C})$, 1551vs $\nu(\text{C=O})$, 1382m $\nu(\text{B-O})$, 1037s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (9 H, t, ³J 6.7, CH₃), 1.26-1.48 (90 H, m, CH₂), 1.80 (6 H, m, CH₂), 4.00 (4 H, t, ³J 6.5, OCH₂), 4.07 (2 H, t, ³J 6.6, OCH₂), 6.71 (1 H, t, ⁴J 2.1, H4''), 7.00 (2 H, AA'XX' system, *N* 9.0, H3' and H5'), 7.03 (1 H, s, H2), 7.19 (2 H, d, ⁴J 2.1, H2'' and H6''), 8.13 (2 H, AA'XX' system, *N* 9.0, H2' and H6').

[BF₂]_{1,2}(12/14) (5): yellow viscous solid (68%). Mp 64 °C. Elemental analysis: Found: C, 72.7; H, 9.7%. C₅₅H₉₁BF₂O₅(CH₂Cl₂)_{0.5} requires C, 72.2; H, 10.0%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2850vs $\nu(\text{C-H})$, 1607s $\nu(\text{C=C})$, 1563vs $\nu(\text{C=O})$, 1377m $\nu(\text{B-O})$, 1050s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (9 H, t, ³J 6.6, CH₃), 1.26-1.48 (62 H, m, CH₂), 1.80 (6 H, m, CH₂), 4.01 (4 H, t, ³J 6.5, OCH₂), 4.08 (2 H, t, ³J 6.5, OCH₂), 6.72 (1 H, t, ⁴J 2.1, H4''), 7.00 (2 H, AA'XX' system, *N* 9.0, H3' and H5'), 7.03 (1 H, s, H2), 7.20 (2 H, d, ⁴J 2.1, H2'' and H6''), 8.13 (2 H, AA'XX' system, *N* 9.0, H2' and H6').

[BF₂]_{1,2}(12/16) (6): yellow solid (65%). Mp 72 °C. Elemental analysis: Found: C, 75.4; H, 10.2%. C₅₉H₉₉BF₂O₅ requires C, 75.6; H, 10.6%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2919vs, 2849vs $\nu(\text{C-H})$, 1607s $\nu(\text{C=C})$, 1543vs $\nu(\text{C=O})$, 1389m $\nu(\text{B-O})$, 1026s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (9 H, t, ³J 6.6, CH₃), 1.26-1.48 (70 H, m, CH₂), 1.80 (6 H, m, CH₂), 4.01 (4 H, t, ³J 6.5, OCH₂), 4.07 (2 H, t, ³J 6.5, OCH₂), 6.72 (1 H, t, ⁴J 2.1, H4''), 7.00 (2 H, AA'XX' system, *N* 9.0, H3' and H5'), 7.03 (1 H, s, H2), 7.20 (2 H, d, ⁴J 2.1, H2'' and H6''), 8.13 (2 H, AA'XX' system, *N* 9.0, H2' and H6').

[BF₂]_{1,2}(12/18) (7): yellow viscous solid (53%). Mp 62 °C. Elemental analysis: Found: C, 76.6; H, 10.4%. C₆₃H₁₀₇BF₂O₅ requires C, 76.2; H, 10.9%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2919vs, 2849vs $\nu(\text{C-H})$, 1606s $\nu(\text{C=C})$, 1552vs $\nu(\text{C=O})$, 1389m $\nu(\text{B-O})$, 1022s $\nu(\text{B-F})$. δ_{H} (300

MHz; CDCl₃; Me₄Si)/ppm: 0.88 (9 H, t, ³J 6.6, CH₃), 1.26-1.48 (78 H, m, CH₂), 1.80 (6 H, m, CH₂), 4.01 (4 H, t, ³J 6.5, OCH₂), 4.08 (2 H, t, ³J 6.5, OCH₂), 6.72 (1 H, t, ⁴J 2.1, H4''), 7.00 (2 H, AA'XX' system, *N* 9.0, H3' and H5'), 7.03 (1 H, s, H2), 7.20 (2 H, d, ⁴J 2.1, H2'' and H6''), 8.13 (2 H, AA'XX' system, *N* 9.0, H2' and H6').

Boron difluoride β-diketonate complexes of the type [BF₂]_{1,3}(*n/m*); *n* = *m* = 12, 14, 16, 18 (8-11); *n* = 12, *m* = 14, 16, 18 (12-14)

[BF₂]_{1,3}(12/12) (8): yellow solid (36%). Mp 50 °C. Elemental analysis: Found: C, 74.9; H, 10.2%. C₆₃H₁₀₇BF₂O₆ requires C, 75.0; H, 10.7%. *v*_{max}(solid)/cm⁻¹: 2921vs, 2852vs *v*(C-H), 1606s *v*(C=C), 1564vs *v*(C=O), 1380m *v*(B-O), 1033s *v*(B-F). *δ*_H (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (12 H, t, ³J 6.6, CH₃), 1.27-1.48 (71 H, m, CH₂), 1.71-1.89 (8 H, m, CH₂), 4.04 (6 H, t, ³J 6.4, OCH₂), 4.09 (2 H, t, ³J 6.5, OCH₂), 6.94 (2 H, AA'XX' system, *N* 9.0, H3' and H5'), 6.96 (1 H, s, H2), 7.24 (2 H, s, H2'' and H6''), 8.04 (2 H, AA'XX' system, *N* 9.0, H2' and H6').

[BF₂]_{1,3}(14/14) (9): yellow solid (70%). Mp 62 °C. Elemental analysis: Found: C, 75.9; H, 10.6%. C₇₁H₁₂₃BF₂O₆ requires C, 76.0; H, 11.0%. *v*_{max}(solid)/cm⁻¹: 2920vs, 2851vs *v*(C-H), 1607s *v*(C=C), 1564vs *v*(C=O), 1381m *v*(B-O), 1033s *v*(B-F). *δ*_H (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (12 H, t, ³J 6.6, CH₃), 1.26-1.48 (88 H, m, CH₂), 1.71-1.89 (8 H, m, CH₂), 4.06 (4 H, t, ³J 6.4, OCH₂), 4.07 (2 H, t, ³J 6.5, OCH₂), 4.09 (2 H, t, ³J 6.5, OCH₂), 6.96 (1 H, s, H2), 7.01 (2 H, AA'XX' system, *N* 9.0, H3' and H5'), 7.30 (2 H, s, H2'' and H6''), 8.12 (2 H, AA'XX' system, *N* 9.0, H2' and H6').

[BF₂]_{1,3}(16/16) (10): yellow solid (65%). Mp 74 °C. Elemental analysis: Found: C, 77.3; H, 10.8%. C₇₉H₁₃₉BF₂O₆ requires C, 76.9; H, 11.3%. *v*_{max}(solid)/cm⁻¹: 2919vs, 2850vs *v*(C-H), 1606s *v*(C=C), 1563vs *v*(C=O), 1380m *v*(B-O), 1034s *v*(B-F). *δ*_H (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (12 H, t, ³J 6.6, CH₃), 1.26-1.48 (104 H, m, CH₂), 1.73-1.87 (8 H, m, CH₂), 4.05 (6 H, t, ³J 6.3, OCH₂), 4.09 (2 H, t, ³J 6.5, OCH₂), 6.96 (1 H, s, H2), 6.98 (2 H, AA'XX' system, *N* 9.0, H3' and H5'), 7.30 (2 H, s, H2'' and H6''), 8.09 (2 H, AA'XX' system, *N* 9.0, H2' and H6').

[BF₂]_{1,3}(18/18) (11): yellow solid (64%). Mp 77 °C. Elemental analysis: Found: C, 78.4; H, 11.2%. C₈₅H₁₅₁BF₂O₆ requires C, 77.7; H, 11.6%. *v*_{max}(solid)/cm⁻¹: 2919vs, 2850vs *v*(C-H), 1606s *v*(C=C), 1564vs *v*(C=O), 1380m *v*(B-O), 1034s *v*(B-F). *δ*_H (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (12 H, t, ³J 6.6, CH₃), 1.25-1.48 (116 H, m, CH₂), 1.71-1.87

(8 H, m, CH₂), 4.06 (4 H, t, ³J 6.4, OCH₂), 4.07 (2 H, t, ³J 6.5, OCH₂), 4.10 (2 H, t, ³J 6.5, OCH₂), 6.96 (1 H, s, H₂), 7.00 (2 H, AA'XX' system, *N* 9.0, H₃' and H₅'), 7.30 (2 H, s, H₂'' and H₆''), 8.11 (2 H, AA'XX' system, *N* 9.0, H₂' and H₆').

[BF₂]_{1,3}(12/14) (12): yellow solid (66%). Mp 60 °C. Elemental analysis: Found: C, 72.6; H, 10.2%. C₆₉H₁₁₉BF₂O₆(CH₂Cl₂)_{0.75} requires C, 72.4; H, 10.5%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2917vs, 2849vs $\nu(\text{C-H})$, 1606s $\nu(\text{C=C})$, 1556vs $\nu(\text{C=O})$, 1379m $\nu(\text{B-O})$, 1029s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (12 H, t, ³J 6.6, CH₃), 1.26-1.48 (84 H, m, CH₂), 1.73-1.87 (8 H, m, CH₂), 4.06 (4 H, t, ³J 6.4, OCH₂), 4.07 (2 H, t, ³J 6.4, OCH₂), 4.10 (2 H, t, ³J 6.4, OCH₂), 6.96 (1 H, s, H₂), 7.01 (2 H, AA'XX' system, *N* 9.0, H₃' and H₅'), 7.31 (2 H, s, H₂'' and H₆''), 8.11 (2 H, AA'XX' system, *N* 9.0, H₂' and H₆').

[BF₂]_{1,3}(12/16) (13): yellow solid (69%). Mp 70 °C. Elemental analysis: Found: C, 76.9; H, 10.9%. C₇₅H₁₃₁BF₂O₆ requires C, 76.5; H, 11.2%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2850vs $\nu(\text{C-H})$, 1605s $\nu(\text{C=C})$, 1555vs $\nu(\text{C=O})$, 1384m $\nu(\text{B-O})$, 1026s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (12 H, t, ³J 6.6, CH₃), 1.26-1.48 (96 H, m, CH₂), 1.78-1.89 (8 H, m, CH₂), 4.06 (4 H, t, ³J 6.4, OCH₂), 4.07 (2 H, t, ³J 6.4, OCH₂), 4.10 (2 H, t, ³J 6.4, OCH₂), 6.96 (1 H, s, H₂), 7.01 (2 H, AA'XX' system, *N* 9.0, H₃' and H₅'), 7.31 (2 H, s, H₂'' and H₆''), 8.11 (2 H, AA'XX' system, *N* 9.0, H₂' and H₆').

[BF₂]_{1,3}(12/18) (14): yellow solid (56%). Mp 65 °C. Elemental analysis: Found: C, 75.7; H, 10.7%. C₈₁H₁₄₃BF₂O₆(CH₂Cl₂)_{0.25} requires C, 76.0; H, 11.2%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2919vs, 2850vs $\nu(\text{C-H})$, 1606s $\nu(\text{C=C})$, 1557vs $\nu(\text{C=O})$, 1373m $\nu(\text{B-O})$, 1043s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (12 H, t, ³J 6.6, CH₃), 1.26-1.48 (108 H, m, CH₂), 1.79-1.87 (8 H, m, CH₂), 4.05 (6 H, t, ³J 6.4, OCH₂), 4.10 (2 H, t, ³J 6.5, OCH₂), 6.96 (1 H, s, H₂), 7.01 (2 H, AA'XX' system, *N* 9.0, H₃' and H₅'), 7.30 (2 H, s, H₂'' and H₆''), 8.11 (2 H, AA'XX' system, *N* 9.0, H₂' and H₆').

Boron difluoride β -diketonate complexes of the type [BF₂]_{2,3}(*n/m*); *n* = *m* = 12, 14, 16, 18 (15-18); *n* = 12, *m* = 14, 16, 18 (19-21); *n* = 14, *m* = 12, 16, 18 (22-24); *n* = 16, *m* = 12, 14, 18 (25-27)

Melting points of the compounds exhibiting liquid crystal behaviour at room temperature are omitted (see Table 4).

[BF₂]_{2,3}(12/12) (15): dark yellow viscous solid (48%). Mp 45 °C. Elemental analysis: Found: C, 75.5; H, 10.6%. C₇₅H₁₃₁BF₂O₇ requires C, 75.5; H, 11.0%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2851vs $\nu(\text{C-H})$, 1607s $\nu(\text{C=C})$, 1555vs $\nu(\text{C=O})$, 1373m $\nu(\text{B-O})$, 1061s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.7, CH₃), 1.26-1.47 (90 H, m, CH₂), 1.71-1.95 (10 H, m, CH₂), 4.02 (4 H, t, ³J 6.5, OCH₂), 4.07 (4 H, t, ³J 6.5, OCH₂), 4.12 (2 H, t, ³J 6.5, OCH₂), 6.74 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.33 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(14/14) (16): dark yellow viscous solid (54%). Mp 48 °C. Elemental analysis: Found: C, 76.3; H, 11.0%. C₈₅H₁₅₁BF₂O₇ requires C, 76.5; H, 11.4%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2917vs, 2850vs $\nu(\text{C-H})$, 1607s $\nu(\text{C=C})$, 1556vs $\nu(\text{C=O})$, 1372m $\nu(\text{B-O})$, 1066s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.7, CH₃), 1.26-1.47 (110 H, m, CH₂), 1.74-1.86 (10 H, m, CH₂), 4.02 (4 H, t, ³J 6.5, OCH₂), 4.07 (4 H, t, ³J 6.5, OCH₂), 4.13 (2 H, t, ³J 6.5, OCH₂), 6.73 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.33 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(16/16) (17): yellow solid (64%). Mp 54 °C. Elemental analysis: Found: C, 77.7; H, 11.2%. C₉₅H₁₇₁BF₂O₇ requires C, 77.4; H, 11.6%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2920vs, 2851vs $\nu(\text{C-H})$, 1608s $\nu(\text{C=C})$, 1561vs $\nu(\text{C=O})$, 1384m $\nu(\text{B-O})$, 1048s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.87 (15 H, t, ³J 6.7, CH₃), 1.25-1.47 (130 H, m, CH₂), 1.70-1.89 (10 H, m, CH₂), 4.01 (4 H, t, ³J 6.5, OCH₂), 4.06 (4 H, t, ³J 6.5, OCH₂), 4.11 (2 H, t, ³J 6.6, OCH₂), 6.73 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.32 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(18/18) (18): yellow solid (59%). Mp 60 °C. Elemental analysis: Found: C, 78.7; H, 11.4%. C₁₀₅H₁₉₁BF₂O₇ requires C, 78.2; H, 11.9%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2850vs $\nu(\text{C-H})$, 1604s $\nu(\text{C=C})$, 1563vs $\nu(\text{C=O})$, 1366m $\nu(\text{B-O})$, 1048s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.7, CH₃), 1.25-1.47 (150 H, m, CH₂), 1.78-1.90 (10 H, m, CH₂), 4.01 (4 H, t, ³J 6.5, OCH₂), 4.07 (4 H, t, ³J 6.6, OCH₂), 4.12 (2 H, t, ³J 6.6, OCH₂), 6.74 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.33 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(12/14) (19): dark yellow viscous (36%). Elemental analysis: Found: C, 75.3; H, 11.2%. C₈₁H₁₄₃BF₂O₇(CH₂Cl₂)_{0.2} requires C, 75.3; H, 11.1%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2850vs $\nu(\text{C-H})$, 1608s $\nu(\text{C=C})$, 1555vs $\nu(\text{C=O})$, 1371m $\nu(\text{B-O})$, 1066s $\nu(\text{B-F})$. δ_{H} (300

MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.7, CH₃), 1.26-1.47 (102 H, m, CH₂), 1.71-1.90 (10 H, m, CH₂), 4.02 (4 H, t, ³J 6.5, OCH₂), 4.06 (2 H, t, ³J 6.5, OCH₂), 4.12 (2 H, t, ³J 6.6, OCH₂), 6.73 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.20 (2 H, d, ⁴J 2.1, H2' and H6'), 7.32 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(12/16) (20): dark yellow viscous (42%). Elemental analysis: Found: C, 76.8; H, 11.1%. C₈₇H₁₅₅BF₂O₇ requires C, 76.7; H, 11.4%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2850vs $\nu(\text{C-H})$, 1606s $\nu(\text{C=C})$, 1562vs $\nu(\text{C=O})$, 1377m $\nu(\text{B-O})$, 1047s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.7, CH₃), 1.25-1.47 (114 H, m, CH₂), 1.73-1.90 (10 H, m, CH₂), 4.02 (4 H, t, ³J 6.5, OCH₂), 4.07 (2 H, t, ³J 6.5, OCH₂), 4.12 (2 H, t, ³J 6.5, OCH₂), 6.74 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.33 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(12/18) (21): dark yellow viscous (47%). Elemental analysis: Found: C, 77.3; H, 11.2%. C₉₃H₁₆₇BF₂O₇ requires C, 77.2; H, 11.6%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2850vs $\nu(\text{C-H})$, 1606s $\nu(\text{C=C})$, 1560vs $\nu(\text{C=O})$, 1377m $\nu(\text{B-O})$, 1053s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.7, CH₃), 1.25-1.47 (126 H, m, CH₂), 1.75-1.90 (10 H, m, CH₂), 4.02 (4 H, t, ³J 6.5, OCH₂), 4.07 (2 H, t, ³J 6.5, OCH₂), 4.12 (2 H, t, ³J 6.5, OCH₂), 6.74 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.33 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(14/12) (22): dark yellow viscous (43%). Elemental analysis: Found: C, 76.4; H, 10.4%. C₇₉H₁₃₉BF₂O₇ requires C, 75.9; H, 11.2%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2920vs, 2821vs $\nu(\text{C-H})$, 1606s $\nu(\text{C=C})$, 1555vs $\nu(\text{C=O})$, 1376m $\nu(\text{B-O})$, 1066s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.7, CH₃), 1.26-1.47 (98 H, m, CH₂), 1.71-1.90 (10 H, m, CH₂), 4.02 (4 H, t, ³J 6.5, OCH₂), 4.07 (2 H, t, ³J 6.5, OCH₂), 4.12 (2 H, t, ³J 6.5, OCH₂), 6.74 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.33 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(14/16) (23): dark yellow viscous (52%). Elemental analysis: Found: C, 77.4; H, 11.2%. C₉₁H₁₆₃BF₂O₇ requires C, 77.1; H, 11.6%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2850vs $\nu(\text{C-H})$, 1607s $\nu(\text{C=C})$, 1559vs $\nu(\text{C=O})$, 1373m $\nu(\text{B-O})$, 1052s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.87 (15 H, t, ³J 6.7, CH₃), 1.27-1.47 (122 H, m, CH₂), 1.73-1.88 (10 H, m, CH₂), 4.01 (4 H, t, ³J 6.5, OCH₂), 4.07 (2 H, t, ³J 6.5, OCH₂), 4.12 (2 H, t, ³J 6.5,

OCH₂), 6.74 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.33 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(14/18) (24): dark yellow viscous (39%). Elemental analysis: Found: C, 78.1; H, 11.4%. C₉₇H₁₇₅BF₂O₇ requires C, 77.6; H, 11.7%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2850vs $\nu(\text{C-H})$, 1607s $\nu(\text{C=C})$, 1562vs $\nu(\text{C=O})$, 1377m $\nu(\text{B-O})$, 1050s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.7, CH₃), 1.26-1.47 (134 H, m, CH₂), 1.76-1.90 (10 H, m, CH₂), 4.02 (4 H, t, ³J 6.5, OCH₂), 4.07 (2 H, t, ³J 6.5, OCH₂), 4.12 (2 H, t, ³J 6.5, OCH₂), 6.74 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.33 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(16/12) (25): dark yellow viscous (42%). Elemental analysis: Found: C, 75.0; H, 10.7%. C₈₃H₁₄₇BF₂O₇(CH₂Cl₂)_{0.25} requires C, 75.3; H, 11.2%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2850vs $\nu(\text{C-H})$, 1607s $\nu(\text{C=C})$, 1556vs $\nu(\text{C=O})$, 1371m $\nu(\text{B-O})$, 1063s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.7, CH₃), 1.26-1.47 (106 H, m, CH₂), 1.73-1.83 (10 H, m, CH₂), 4.01 (4 H, t, ³J 6.5, OCH₂), 4.06 (2 H, t, ³J 6.5, OCH₂), 4.11 (2 H, t, ³J 6.5, OCH₂), 6.74 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.33 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(16/14) (26): dark yellow viscous (50%). Elemental analysis: Found: C, 77.3; H, 11.2%. C₈₉H₁₅₉BF₂O₇ requires C, 76.9; H, 11.5%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2850vs $\nu(\text{C-H})$, 1604s $\nu(\text{C=C})$, 1562vs $\nu(\text{C=O})$, 1371m $\nu(\text{B-O})$, 1063s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.87 (15 H, t, ³J 6.7, CH₃), 1.26-1.47 (118 H, m, CH₂), 1.71-1.88 (10 H, m, CH₂), 4.02 (4 H, t, ³J 6.5, OCH₂), 4.07 (2 H, t, ³J 6.5, OCH₂), 4.12 (2 H, t, ³J 6.5, OCH₂), 6.73 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.32 (2 H, s, H2'' and H6'').

[BF₂]_{2,3}(16/18) (27): dark yellow viscous (41%). Elemental analysis: Found: C, 77.8; H, 11.4%. C₁₀₁H₁₈₃BF₂O₇ requires C, 77.8; H, 11.8%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2918vs, 2850vs $\nu(\text{C-H})$, 1605s $\nu(\text{C=C})$, 1561vs $\nu(\text{C=O})$, 1377m $\nu(\text{B-O})$, 1052s $\nu(\text{B-F})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.7, CH₃), 1.26-1.47 (142 H, m, CH₂), 1.78-1.87 (10 H, m, CH₂), 4.02 (4 H, t, ³J 6.5, OCH₂), 4.07 (2 H, t, ³J 6.5, OCH₂), 4.12 (2 H, t, ³J 6.5, OCH₂), 6.74 (1 H, t, ⁴J 2.1, H4'), 6.99 (1 H, s, H2), 7.21 (2 H, d, ⁴J 2.1, H2' and H6'), 7.33 (2 H, s, H2'' and H6'').

Precursor β -diketone ligands

The β -diketones were synthesised by adapting literature methods and fully characterised according to the previous results when corresponding.³⁴⁻³⁷ Specifically, compounds D_{1,2}(12/12), D_{1,2}(12/14), D_{2,3}(12/12), D_{2,3}(14/14), D_{2,3}(12/14), D_{2,3}(14/12), D_{2,3}(14/16), D_{2,3}(14/18), D_{2,3}(16/12), D_{2,3}(16/14) and D_{2,3}(16/18) needed an additional procedure in order to be purified. The reaction crude was neutralised with diluted HCl and extracted with diethyl ether (2 x 50 mL). The ethereal fraction was washed with water (4 x 50 mL) and dried under anhydrous MgSO₄. For the diketones D_{1,2}(12/12), D_{1,2}(12/14), D_{2,3}(12/12), D_{2,3}(14/14), and D_{2,3}(12/14), the ethereal solution was evaporated to give a waxy yellow solid.

However, for D_{2,3}(14/12), D_{2,3}(14/16), D_{2,3}(14/18), D_{2,3}(16/12), D_{2,3}(16/14) and D_{2,3}(16/18), the oily residue after removing the solvent was purified by silica chromatography with a 10/1 hexane-ethyl acetate mixture as an eluent. The final yellow solids were crystallised from dichloromethane/methanol.

Full characterisation of the new ligands is given as follows. In general, the β -diketone ligands tend to crystallise with a variable amount of water as it may be observed in the analytical data.

Diketones of the type D_{1,2}(*n/m*); *n* = *m* = 18; *n* = 12, *m* = 14, 16, 18

D_{1,2}(18/18): pale yellow solid (45%). Mp 65 °C. Elemental analysis: Found: C, 74.9; H, 11.3%. C₆₉H₁₂₀O₅·4H₂O requires C, 75.2; H, 11.7%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3380w $\nu(\text{O-H})$, 2917vs, 2850vs $\nu(\text{C-H})$, 1687w $\nu(\text{C=O})$, 1604s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (9 H, t, ³J 6.6, CH₃), 1.25-1.48 (90 H, m, CH₂), 1.80 (6 H, m, CH₂), 3.97-4.04 (6 H, m, OCH₂), 6.62 (1 H, t, ⁴J 2.1, H4''), 6.73 (1 H, s, H2), 6.96 (2 H, AA'XX' system, *N* 8.9, H3' and H5'), 7.08 (2 H, d, ⁴J 2.1, H2'' and H6''), 7.95 (2 H, AA'XX' system, *N* 8.9, H2' and H6'), 16.97 (1 H, s, OH).

D_{1,2}(12/14): pale yellow solid (45%). Mp 52 °C. Elemental analysis: Found: C, 77.6; H, 10.7%. C₅₅H₉₂O₅·H₂O requires C, 77.6; H, 11.1%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3378w $\nu(\text{O-H})$, 2917vs, 2850vs $\nu(\text{C-H})$, 1687w $\nu(\text{C=O})$, 1604s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.87 (9 H, t, ³J 6.6, CH₃), 1.26-1.48 (52 H, m, CH₂), 1.78 (6 H, m, CH₂), 3.95-4.02 (6 H, m, OCH₂), 6.61 (1 H, t, ⁴J 2.1, H4''), 6.73 (1 H, s, H2), 6.96 (2 H,

AA'XX' system, *N* 8.9, H3' and H5'), 7.08 (2 H, d, ⁴*J* 2.1, H2'' and H6''), 7.94 (2 H, AA'XX' system, *N* 8.9, H2' and H6'), 16.97 (1 H, s, OH).

D_{1,2}(12/16): pale yellow solid (58%). Mp 62 °C. Elemental analysis: Found: C, 76.6; H, 10.9%. C₅₉H₁₀₀O₅·2H₂O requires C, 76.6; H, 11.3%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3377w $\nu(\text{O-H})$, 2917vs, 2850vs $\nu(\text{C-H})$, 1689w $\nu(\text{C=O})$, 1603s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (9 H, t, ³*J* 6.6, CH₃), 1.26-1.48 (70 H, m, CH₂), 1.79 (6 H, m, CH₂), 3.97-4.05 (6 H, m, OCH₂), 6.63 (1 H, t, ⁴*J* 2.1, H4''), 6.73 (1 H, s, H2), 6.92 (2 H, AA'XX' system, *N* 8.9, H3' and H5'), 7.06 (2 H, d, ⁴*J* 2.1, H2'' and H6''), 8.00 (2 H, AA'XX' system, *N* 8.9, H2' and H6'), 17.01 (1 H, s, OH).

D_{1,2}(12/18): pale yellow solid (53%). Mp 56 °C. Elemental analysis: Found: C, 78.8; H, 11.2%. C₆₃H₁₀₈O₅·H₂O requires C, 78.6; H, 11.5%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3357w $\nu(\text{O-H})$, 2917vs, 2850vs $\nu(\text{C-H})$, 1688w $\nu(\text{C=O})$, 1605s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (9 H, t, ³*J* 6.6, CH₃), 1.26-1.48 (78 H, m, CH₂), 1.79 (6 H, m, CH₂), 3.97-4.05 (6 H, m, OCH₂), 6.62 (1 H, t, ⁴*J* 2.1, H4''), 6.73 (1 H, s, H2), 6.94 (2 H, AA'XX' system, *N* 8.9, H3' and H5'), 7.08 (2 H, d, ⁴*J* 2.1, H2'' and H6''), 7.95 (2 H, AA'XX' system, *N* 8.9, H2' and H6'), 16.97 (1 H, s, OH).

Diketones of the type D_{1,3}(*n/m*); *n* = *m* = 18; *n* = 12, *m* = 14, 16, 18

D_{1,3}(18/18): pale yellow solid (52%). Mp 80 °C. Elemental analysis: Found: C, 78.2; H, 11.6%. C₈₅H₁₅₂O₆·2H₂O requires C, 78.3; H, 12.0%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3376w $\nu(\text{O-H})$, 2917vs, 2849vs $\nu(\text{C-H})$, 1683w $\nu(\text{C=O})$, 1605s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.87 (12 H, t, ³*J* 6.7, CH₃), 1.25-1.47 (116 H, m, CH₂), 1.75-1.86 (8 H, m, CH₂), 4.00-4.08 (8 H, m, OCH₂), 6.68 (1 H, s, H2), 6.96 (2 H, AA'XX' system, *N* 8.9, H3' and H5'), 7.17 (2 H, s, H2'' and H6''), 7.95 (2 H, AA'XX' system, *N* 8.9, H2' and H6'), 17.17 (1 H, s, OH).

D_{1,3}(12/14): pale yellow solid (54%). Mp 67 °C. Elemental analysis: Found: C, 77.4; H, 11.0%. C₆₉H₁₂₀O₆·H₂O requires C, 77.9; H, 11.5%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3386w $\nu(\text{O-H})$, 2918vs, 2850vs $\nu(\text{C-H})$, 1681w $\nu(\text{C=O})$, 1605s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (12 H, t, ³*J* 6.7, CH₃), 1.26-1.47 (84 H, m, CH₂), 1.70-1.86 (8 H, m, CH₂), 4.00-4.06 (8 H, m, OCH₂), 6.68 (1 H, s, H2), 6.96 (2 H, AA'XX' system, *N* 8.9, H3' and H5'), 7.17 (2 H, s, H2'' and H6''), 7.95 (2 H, AA'XX' system, *N* 8.9, H2' and H6'), 17.11 (1 H, s, OH).

D_{1,3}(12/16): pale yellow solid (72%). Mp 76 °C. Elemental analysis: Found: C, 78.3; H, 11.3%. C₇₅H₁₃₂O₆·H₂O requires C, 78.5; H, 11.7%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3392w $\nu(\text{O-H})$, 2917vs, 2850vs $\nu(\text{C-H})$, 1682w $\nu(\text{C=O})$, 1605s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.87 (12 H, t, ³J 6.7, CH₃), 1.25-1.47 (96 H, m, CH₂), 1.77-1.86 (8 H, m, CH₂), 3.99-4.05 (8 H, m, OCH₂), 6.68 (1 H, s, H₂), 6.96 (2 H, AA'XX' system, N 8.9, H₃' and H₅'), 7.17 (2 H, s, H₂'' and H₆''), 7.95 (2 H, AA'XX' system, N 8.9, H₂' and H₆'), 17.12 (1 H, s, OH).

D_{1,3}(12/18): pale yellow solid (68%). Mp 79 °C. Elemental analysis: Found: C, 78.6; H, 11.5%. C₈₁H₁₄₄O₆·H₂O requires C, 78.9; H, 11.9%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3387w $\nu(\text{O-H})$, 2917vs, 2850vs $\nu(\text{C-H})$, 1683w $\nu(\text{C=O})$, 1606s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.87 (12 H, t, ³J 6.7, CH₃), 1.25-1.47 (108 H, m, CH₂), 1.77-1.85 (8 H, m, CH₂), 3.99-4.05 (8 H, m, OCH₂), 6.68 (1 H, s, H₂), 6.96 (2 H, AA'XX' system, N 8.9, H₃' and H₅'), 7.17 (2 H, s, H₂'' and H₆''), 7.95 (2 H, AA'XX' system, N 8.9, H₂' and H₆'), 17.11 (1 H, s, OH).

Diketones of the type D_{2,3}(n/m); n = m = 12, 14, 16, 18; n = 12, m = 14, 16, 18; n = 14, m = 12, 16, 18; n = 16, m = 12, 14, 18

D_{2,3}(12/12): dark yellow viscous solid (45%). Mp 52 °C. Elemental analysis: Found: C, 79.0; H, 11.1%. C₇₅H₁₃₂O₇ requires C, 78.6; H, 11.6%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3362w $\nu(\text{O-H})$, 2918vs, 2850vs $\nu(\text{C-H})$, 1682w $\nu(\text{C=O})$, 1591s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.6, CH₃), 1.26-1.47 (90 H, m, CH₂), 1.78-1.88 (10 H, m, CH₂), 3.98-4.08 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H₄'), 6.69 (1 H, s, H₂), 7.08 (2 H, d, ⁴J 2.0, H₂' and H₆'), 7.18 (2 H, s, H₂'' and H₆''), 16.99 (1 H, s, OH).

D_{2,3}(14/14): pale yellow solid (58%). Mp 63 °C. Elemental analysis: Found: C, 78.9; H, 11.3%. C₈₅H₁₅₂O₇·0.5H₂O requires C, 78.8; H, 11.9%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3382w $\nu(\text{O-H})$, 2917vs, 2849vs $\nu(\text{C-H})$, 1683w $\nu(\text{C=O})$, 1588s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.6, CH₃), 1.26-1.47 (110 H, m, CH₂), 1.75-1.82 (10 H, m, CH₂), 4.00-4.06 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H₄'), 6.69 (1 H, s, H₂), 7.08 (2 H, d, ⁴J 2.0, H₂' and H₆'), 7.18 (2 H, s, H₂'' and H₆''), 16.97 (1 H, s, OH).

D_{2,3}(16/16): pale yellow solid (53%). Mp 75 °C. Elemental analysis: Found: C, 78.8; H, 11.7%. C₉₅H₁₇₂O₇·H₂O requires C, 79.0; H, 12.1%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3402w $\nu(\text{O-H})$, 2917vs, 2849vs $\nu(\text{C-H})$, 1683w $\nu(\text{C=O})$, 1587s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃;

Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.6, CH₃), 1.25-1.47 (130 H, m, CH₂), 1.78-1.84 (10 H, m, CH₂), 3.98-4.08 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H₄'), 6.68 (1 H, s, H₂), 7.08 (2 H, d, ⁴J 2.0, H₂' and H₆'), 7.18 (2 H, s, H₂'' and H₆''), 16.97 (1 H, s, OH).

D_{2,3}(18/18): pale yellow solid (61%). Mp 80 °C. Elemental analysis: Found: C, 77.6; H, 11.8%. C₁₀₅H₁₉₂O₇·3H₂O requires C, 77.8; H, 12.2%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3377w $\nu(\text{O-H})$, 2917vs, 2850vs $\nu(\text{C-H})$, 1683w $\nu(\text{C=O})$, 1588s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.87 (15 H, t, ³J 6.6, CH₃), 1.25-1.47 (150 H, m, CH₂), 1.73-1.86 (10 H, m, CH₂), 3.98-4.08 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H₄'), 6.68 (1 H, s, H₂), 7.08 (2 H, d, ⁴J 2.0, H₂' and H₆'), 7.18 (2 H, s, H₂'' and H₆''), 16.97 (1 H, s, OH).

D_{2,3}(12/14): pale yellow solid (52%). Mp 64 °C. Elemental analysis: Found: C, 78.7; H, 11.1%. C₈₁H₁₄₄O₇ requires C, 79.0; H, 11.2%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3377w $\nu(\text{O-H})$, 2918vs, 2850vs $\nu(\text{C-H})$, 1683w $\nu(\text{C=O})$, 1589s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.6, CH₃), 1.25-1.47 (102 H, m, CH₂), 1.73-1.86 (10 H, m, CH₂), 3.98-4.08 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H₄'), 6.68 (1 H, s, H₂), 7.08 (2 H, d, ⁴J 2.0, H₂' and H₆'), 7.18 (2 H, s, H₂'' and H₆''), 16.98 (1 H, s, OH).

D_{2,3}(12/16): pale yellow solid (60%). Mp 77 °C. Elemental analysis: Found: C, 77.9; H, 11.2%. C₈₇H₁₅₆O₇·H₂O requires C, 77.6; H, 11.7%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3378w $\nu(\text{O-H})$, 2918vs, 2849vs $\nu(\text{C-H})$, 1683w $\nu(\text{C=O})$, 1588s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.6, CH₃), 1.25-1.47 (114 H, m, CH₂), 1.73-1.86 (10 H, m, CH₂), 3.98-4.08 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H₄'), 6.68 (1 H, s, H₂), 7.08 (2 H, d, ⁴J 2.0, H₂' and H₆'), 7.18 (2 H, s, H₂'' and H₆''), 16.99 (1 H, s, OH).

D_{2,3}(12/18): dark yellow viscous solid (67%). Mp 82 °C. Elemental analysis: Found: C, 78.1; H, 11.4%. C₉₃H₁₆₈O₇·H₂O requires C, 78.0; H, 11.9%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3376w $\nu(\text{O-H})$, 2918vs, 2850vs $\nu(\text{C-H})$, 1683w $\nu(\text{C=O})$, 1587s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.6, CH₃), 1.25-1.47 (126 H, m, CH₂), 1.75-1.86 (10 H, m, CH₂), 3.98-4.08 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H₄'), 6.68 (1 H, s, H₂), 7.08 (2 H, d, ⁴J 2.0, H₂' and H₆'), 7.18 (2 H, s, H₂'' and H₆''), 17.00 (1 H, s, OH).

D_{2,3}(14/12): dark yellow viscous solid (42%). Mp 44 °C. Elemental analysis: Found: C, 78.6; H, 11.2%. C₇₉H₁₄₀O₇ requires C, 78.9; H, 11.7%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3383w $\nu(\text{O-H})$, 2920vs, 2851vs $\nu(\text{C-H})$, 1697w $\nu(\text{C=O})$, 1592s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.6, CH₃), 1.27-1.47 (98 H, m, CH₂), 1.71-1.86 (10 H, m,

CH₂), 3.99-4.08 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H4'), 6.69 (1 H, s, H2), 7.08 (2 H, d, ⁴J 2.0, H2' and H6'), 7.18 (2 H, s, H2'' and H6''), 17.00 (1 H, s, OH).

D_{2,3}(14/16): yellow solid (50%). Mp 57 °C. Elemental analysis: Found: C, 79.6; H, 11.5%. C₉₁H₁₆₄O₇ requires C, 79.8; H, 12.0%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3376w $\nu(\text{O-H})$, 2920vs, 2851vs $\nu(\text{C-H})$, 1704w $\nu(\text{C=O})$, 1590s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.6, CH₃), 1.26-1.47 (122 H, m, CH₂), 1.69-1.89 (10 H, m, CH₂), 3.98-4.08 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H4'), 6.69 (1 H, s, H2), 7.08 (2 H, d, ⁴J 2.0, H2' and H6'), 7.18 (2 H, s, H2'' and H6''), 17.00 (1 H, s, OH).

D_{2,3}(14/18): pale yellow solid (66%). Mp 50 °C. Elemental analysis: Found: C, 79.9; H, 11.6%. C₉₇H₁₇₆O₇ requires C, 80.1; H, 12.2%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3369w $\nu(\text{O-H})$, 2919vs, 2851vs $\nu(\text{C-H})$, 1697w $\nu(\text{C=O})$, 1591s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.89 (15 H, t, ³J 6.6, CH₃), 1.26-1.47 (134 H, m, CH₂), 1.74-1.87 (10 H, m, CH₂), 3.99-4.08 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H4'), 6.69 (1 H, s, H2), 7.09 (2 H, d, ⁴J 2.0, H2' and H6'), 7.19 (2 H, s, H2'' and H6''), 16.99 (1 H, s, OH).

D_{2,3}(16/12): dark yellow viscous solid (35%). Mp 43 °C. Elemental analysis: Found: C, 79.5; H, 11.4%. C₈₃H₁₄₈O₇ requires C, 79.2; H, 11.8%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3389w $\nu(\text{O-H})$, 2920vs, 2852vs $\nu(\text{C-H})$, 1697w $\nu(\text{C=O})$, 1594s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.89 (15 H, t, ³J 6.6, CH₃), 1.26-1.47 (106 H, m, CH₂), 1.69-1.87 (10 H, m, CH₂), 3.99-4.09 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H4'), 6.69 (1 H, s, H2), 7.09 (2 H, d, ⁴J 2.0, H2' and H6'), 7.19 (2 H, s, H2'' and H6''), 16.99 (1 H, s, OH).

D_{2,3}(16/14): yellow solid (48%). Mp 54 °C. Elemental analysis: Found: C, 79.8; H, 11.6%. C₈₉H₁₆₀O₇ requires C, 79.6; H, 12.0%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3369w $\nu(\text{O-H})$, 2919vs, 2851vs $\nu(\text{C-H})$, 1690w $\nu(\text{C=O})$, 1596s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.89 (15 H, t, ³J 6.6, CH₃), 1.27-1.47 (138 H, m, CH₂), 1.67-1.87 (10 H, m, CH₂), 3.99-4.09 (10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H4'), 6.69 (1 H, s, H2), 7.09 (2 H, d, ⁴J 2.0, H2' and H6'), 7.19 (2 H, s, H2'' and H6''), 16.99 (1 H, s, OH).

D_{2,3}(16/18): pale yellow solid (70%). Mp 46 °C. Elemental analysis: Found: C, 79.8; H, 11.8%. C₁₀₁H₁₈₄O₇ requires C, 80.3; H, 12.2%. $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3376w $\nu(\text{O-H})$, 2919vs, 2851vs $\nu(\text{C-H})$, 1704w $\nu(\text{C=O})$, 1599s $\nu(\text{C=C})$. δ_{H} (300 MHz; CDCl₃; Me₄Si)/ppm: 0.88 (15 H, t, ³J 6.6, CH₃), 1.26-1.47 (142 H, m, CH₂), 1.69-1.89 (10 H, m, CH₂), 3.99-4.08

(10 H, m, OCH₂), 6.63 (1 H, t, ⁴J 2.0, H4'), 6.69 (1 H, s, H2), 7.08 (2 H, d, ⁴J 2.0, H2' and H6'), 7.18 (2 H, s, H2'' and H6''), 16.99 (1 H, s, OH).

Table S1. Selected bond distances (Å) and angles (°) for difluoride 1-(4'-methoxyphenyl) propane-1,3-dionate boron [BF₂]_{1,0}(1)

B – F1	1.362(2)	F1 – B – F1' ^a	109.6(2)
B – F1' ^a	1.362(2)	F1 – B – O1	109.0(2)
B – O1	1.481(4)	F1 – B – O2	108.8(2)
B – O2	1.471(4)	F1' – B – O1 ^a	109.0(2)
C1 – O1	1.301(3)	F1' – B – O2 ^a	108.8(2)
C3 – O2	1.299(3)	O1 – B – O2	111.8(2)
C1 – C2	1.390(3)		
C2 – C3	1.337(3)		

^a Symmetry operation ('): $x, -y + \frac{1}{2}, z$