# **Electronic Supplementary Information For**

# Regioselective Catalytic Carbonylation and Borylation of Alkynes with Aryldiazonium Salts Toward α-Unsubstituted β-Boryl Ketones

Fengxiang Zhu,\*a Pengpeng Yina and Xiao-Feng Wu\*b

<sup>a</sup> School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006 (China).

<sup>b</sup> Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 (China); Leibniz-Institut für Katalyse e.V., Rostock 18059 (Germany)

E-mail: zfx201989@sxu.edu.cn (Fengxiang Zhu); xwu2020@dicp.ac.cn; xiao-feng.wu@catalysis.de (Xiao-Feng Wu).

### **Table of Content**

1. General Methods	S2
2. Typical reaction procedure for the synthesis of $\beta$ -boryl ketones	S2
3. Characterization data for products	S2
4. References	S11
5. NMR Spectrum Copies	S12

#### 1. General Methods

NMR spectra were recorded on Bruker Avance NEO 600 M. Chemical shifts (ppm) are given relative to solvent: references for CDCl<sub>3</sub> were 7.26 ppm (<sup>1</sup>H-NMR) and 77.0 ppm (<sup>13</sup>C-NMR). <sup>13</sup>CNMR spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). All measurements were carried out at room temperature unless otherwise stated. Gas chromatography analysis was performed on a Shimadzu 2014 instrument with an FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using N<sub>2</sub> as carrier gas. HRMS was obtained on a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh. All reactions were carried out under air atmosphere. All the reagents were purchased from Heowns, Rhawn, infinity scientific, and Laajoo chemical company and used without further purification.

#### 2. Typical reaction procedure for the synthesis of β-boryl ketones:

General procedure: A 4 ml screw-cap vial was charged with Pd(acac)<sub>2</sub> (5 mol%), Cul (10 mol%), PPh<sub>3</sub> (20 mol%), alkyne (0.1 mmol), aryldiazonium salt (0.1 mmol), B<sub>2</sub>pin<sub>2</sub> (0.2 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.4 mmol), CH<sub>3</sub>COOEt (2 mL) and a stirring bar. The vial was closed by a Teflon septum and a phenolic cap and connected to the atmosphere through a needle. Then the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL). At room temperature, the autoclave is flushed with CO for three times and 20 bar of CO was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction was heated at 110 °C for 12 hours. Afterwards, the autoclave was cooled to room temperature and the pressure carefully released. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography using a petroleum ether/AcOEt (30:1) as the eluent to give the corresponding products.

#### 3. Characterization data for products

1-(4-methoxyphenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1one<sup>1</sup>

3aa

Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). Colorless oil (26.7 mg, 73%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 – 7.96 (m, 2H), 7.35 – 7.29 (m, 4H), 7.22 – 7.16 (m, 1H), 6.97 – 6.90 (m, 2H), 3.88 (s, 3H), 3.52 (dd, *J* = 18.0, 10.9 Hz, 1H), 3.41 (dd, *J* = 18.0, 5.1 Hz, 1H), 2.80 (dd, *J* = 10.9, 5.0 Hz, 1H), 1.27 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.25, 163.37, 142.14, 130.31, 129.89, 128.49, 128.41, 125.54, 113.62, 83.33, 55.46, 42.95, 24.58, 24.55. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.52. GC-MS (EI-70 eV): *m/z* (%) 366 (25), 308 (20), 283 (100), 266 (50), 239 (55), 135 (73).

# 1-(4-methoxyphenyl)-3-(4-propylphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propan-1-one

Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). Colorless oil (30.6 mg, 75%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 – 7.95 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.96 – 6.90 (m, 2H), 3.88 (s, 3H), 3.50 (dd, *J* = 18.0, 11.0 Hz, 1H), 3.39 (dd, *J* = 18.0, 5.0 Hz, 1H), 2.76 (dd, *J* = 11.0, 5.0 Hz, 1H), 2.60 – 2.54 (m, 2H), 1.65 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.27 (s, 6H), 1.19 (s, 6H), 0.96 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.37, 163.32, 139.78, 139.17, 130.30, 129.96, 128.58, 128.23, 113.59, 83.27, 55.45, 43.15, 37.66, 24.58, 24.56, 13.92. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.43. GC-MS (EI-70 eV): m/z (%) 408 (29) 350 (20), 325 (100), 281 (32), 264 (48). HRMS (ESI): calcd for C<sub>25</sub>H<sub>33</sub>BO<sub>4</sub> [M+Na]<sup>+</sup> : 431.2364, found: 431.2367.

# 3-(4-(*tert*-butyl)phenyl)-1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)propan-1-one



Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). Colorless oil (32.4 mg, 77%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (dd, J = 9.3, 2.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 6.94 – 6.91 (m, 2H), 3.88 (s, 3H), 3.50 (dd, J = 18.0, 11.0 Hz, 1H), 3.39 (dd, J = 18.0, 5.0 Hz, 1H), 2.77 (dd, J = 11.0, 4.9 Hz, 1H), 1.33 (s, 9H), 1.28 (s, 6H), 1.20 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.36, 163.31, 148.18, 138.89, 130.30, 129.98, 128.03, 125.39, 113.58, 83.28, 55.46, 43.23, 34.32, 31.43, 24.63, 24.60. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.47. GC-MS (EI-70 eV): m/z (%) 422(30), 365 (27), 339 (100), 322 (20), 278 (35), 221 (48). HRMS (ESI): calcd for C<sub>26</sub>H<sub>35</sub>BO<sub>4</sub> [M+Na]<sup>+</sup>: 445.2521, found: 445.2513.

# 1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4 (trifluoromethoxy)phenyl)propan-1-one



Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). Colorless oil (36.4 mg, 81%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 – 7.95 (m, 2H), 7.35 – 7.32 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.95 – 6.92 (m, 2H), 3.88 (s, 3H), 3.44 (ddd, *J* = 23.4, 18.0, 7.9 Hz, 2H), 2.81 (dd, *J* = 10.3, 5.4 Hz, 1H), 1.27 (s, 6H), 1.20 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  197.88, 163.49, 147.22, 141.01, 130.34, 129.70, 129.61, 121.00, 120.54 (q, *J* = 256.70Hz), 113.67, 83.50, 55.48, 42.77, 24.57, 24.56. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -57.88. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.52. GC-MS (EI-70 eV): m/z (%) 450 (28), 392 (20), 367 (100), 349 (25), 306 (48), 265 (22), 190 (23). HRMS (ESI): calcd for C<sub>23</sub>H<sub>26</sub>BF<sub>3</sub>O<sub>5</sub> [M+Na]<sup>+</sup> : 473.1718, found: 473.1718.

# 3-(4-fluorophenyl)-1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propan-1-one



Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). White solid (24.1 mg, 63%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 – 7.95 (m, 2H), 7.27 (dd, *J* = 6.0, 2.6 Hz, 2H), 7.00 – 6.96 (m, 2H), 6.95 – 6.92 (m, 2H), 3.88 (s, 3H), 3.47 (dd, *J* = 17.9, 10.5 Hz, 1H), 3.39 (dd, *J* = 18.0, 5.4 Hz, 1H), 2.78 (dd, *J* = 10.4, 5.4 Hz, 1H), 1.26 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.05, 163.43, 161.14 (d, *J* = 243.11 Hz), 137.72 (d, *J* = 3.2 Hz), 130.32, 129.77 (d, *J* = 7.55 Hz), 129.69, 115.20 (d, *J* = 21.14 Hz), 113.64, 83.41, 55.47, 42.95, 24.58, 24.54. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -118.26. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.51. GC-MS (EI-70 eV): m/z (%) 384 (28), 326 (20), 301 (100), 257 (53), 135 (52). HRMS (ESI): calcd for C<sub>22</sub>H<sub>26</sub>BFO<sub>4</sub> [M+Na]<sup>+</sup> : 407.1800, found: 407.1790.

# 3-(4-chlorophenyl)-1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propan-1-one



Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). White solid (27.2 mg, 68%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d, *J* = 8.9 Hz, 2H), 7.26 (s, 4H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 3.47 (dd, *J* = 18.0, 10.4 Hz, 1H), 3.39 (dd, *J* = 17.9, 5.4 Hz, 1H), 2.77 (dd, *J* = 10.4, 5.4 Hz, 1H), 1.26 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  197.92, 163.47, 140.72, 131.24, 130.33, 129.74, 129.72, 128.55, 113.67, 83.46, 55.48, 42.65, 24.58, 24.55. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.55. GC-MS (EI-70 eV): m/z (%) 400 (28), 342 (20), 317 (100), 300 (45), 273 (49), 221 (30), 135 (55). HRMS (ESI): calcd for C<sub>22</sub>H<sub>26</sub>BClO<sub>4</sub> [M+Na]<sup>+</sup> : 423.1505, found: 423.1503.

# 1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(o-tolyl)propan-1-one



Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). Colorless oil (28.5 mg, 75%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (d, *J* = 8.9 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.16 (dd, *J* = 11.8, 7.4 Hz, 2H), 7.09 (t, *J* = 7.1 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 3.49 (dd, *J* = 18.0, 10.8 Hz, 1H), 3.33 (dd, *J* = 18.0, 4.8 Hz, 1H), 3.03 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.40 (s, 3H), 1.27 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.41, 163.34, 140.53, 136.43, 130.46, 130.30, 129.96, 127.77, 126.01, 125.44, 113.61, 83.27, 55.47, 42.30, 24.63, 24.56, 20.09. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.64. GC-MS (EI-70 eV): m/z (%) 380 (15), 297 (24), 236 (100), 221 (20), 121(23). HRMS (ESI): calcd for C<sub>23</sub>H<sub>29</sub>BO4 [M+Na]<sup>+</sup>: 403.2051, found: 403.2057.

# 3-(2-chlorophenyl)-1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propan-1-one

3ha

Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). Colorless oil (25.2 mg, 63%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 – 7.92 (m, 2H), 7.44 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.36 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.19 (td, *J* = 7.5, 1.3 Hz, 1H), 7.13 – 7.10 (m, 1H), 6.95 – 6.90 (m, 2H), 3.88 (s, 3H), 3.50 – 3.38 (m, 2H), 3.29 (t, *J* = 7.2 Hz, 1H), 1.30 (s, 6H), 1.25 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  197.86, 163.37, 140.29, 134.32, 130.57, 130.34, 129.88, 129.61, 126.98, 126.82, 113.61, 83.56, 55.46, 41.30, 24.76, 24.67. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.50. GC-MS (EI-70 eV): m/z (%) 400 (35), 365 (20), 317 (100), 300 (48), 273 (72), 221 (30), 135 (90). HRMS (ESI): calcd for C<sub>22</sub>H<sub>26</sub>BClO<sub>4</sub> [M+Na]<sup>+</sup>: 423.1505, found: 423.1510.

# 1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(m-tolyl)propan-1-one



Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). Colorless oil (28.8 mg, 76%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (dd, *J* = 9.2, 2.2 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.12 (m, 2H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.95 – 6.91 (m, 2H), 3.88 (s, 3H), 3.51 (dd, *J* = 18.0, 11.1 Hz, 1H), 3.39 (dd, *J* = 18.0, 5.0 Hz, 1H), 2.76 (dd, *J* = 11.1, 4.9 Hz, 1H), 2.35 (s, 3H), 1.27 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.32, 163.35, 142.01, 138.01, 130.31, 129.92, 129.28, 128.37, 126.32, 125.35, 113.61, 83.30, 55.46, 43.06, 24.57, 24.55, 21.46. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.56. GC-MS (EI-70 eV): m/z (%) 380 (40), 322 (20), 297 (100), 236 (70), 135 (38). HRMS (ESI): calcd for C<sub>23</sub>H<sub>29</sub>BO<sub>4</sub> [M+Na]<sup>+</sup>: 403.2051, found: 403.2049.

# 3-(3-chlorophenyl)-1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propan-1-one

Bpin 3ja

Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). Colorless oil (26.4 mg, 66%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 – 7.94 (m, 2H), 7.32 (s, 1H), 7.28 – 7.13 (m, 3H), 6.97 – 6.92 (m, 2H), 3.89 (s, 3H), 3.49 (dd, *J* = 18.0, 10.6 Hz, 1H), 3.40 (dd, *J* = 18.0, 5.2 Hz, 1H), 2.78 (dd, *J* = 10.6, 5.2 Hz, 1H), 1.27 (s, 6H), 1.20 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  197.85, 163.49, 144.33, 134.17, 130.35, 129.68, 129.66,128.43, 126.68, 125.75, 113.67, 83.51, 55.48, 42.55, 24.55. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.53. GC-MS (EI-70 eV): m/z (%) 400 (30), 342 (23), 317 (100), 300 (63), 273 (56), 135 (90). HRMS (ESI): calcd for C<sub>22</sub>H<sub>26</sub>BClO<sub>4</sub> [M+Na]<sup>+</sup>: 423.1505, found: 423.1501.

# 1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(thiophen-3-yl) propan-1-one



Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). Yellow oil (25.2 mg, 68%). <sup>1</sup>HNMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 – 7.96 (m, 2H), 7.26 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.06 (dd, *J* = 21.2, 3.7 Hz, 2H), 6.95 – 6.92 (m, 2H), 3.89 (s, 3H), 3.51 – 3.41 (m, 2H), 2.90 (dd, *J* = 10.1, 5.5 Hz, 1H), 1.27 (s, 6H), 1.21 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.13, 163.41, 141.82, 130.33, 129.84, 128.34, 125.13, 119.69, 113.64, 83.38, 55.47, 42.24, 24.63, 24.55. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.46. GC-MS (EI-70 eV): m/z (%) 372 (65), 314 (40), 289 (100), 272 (35), 245 (46), 228 (48). HRMS (ESI): calcd for C<sub>20</sub>H<sub>25</sub>BO<sub>4</sub>S [M+Na]<sup>+</sup> : 395.1459, found: 395.1459.

# 1-(4-methoxyphenyl)-5-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-one



Purification by flash column chromatography (petroleum ether/EtOAc = 30:1). Colorless oil (29.5 mg, 75%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (d, *J* = 8.8 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.10 (dd, *J* = 11.7, 7.3 Hz, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 3.42 (s, 2H), 2.54 – 2.47 (m, 2H), 2.08 – 1.96 (m, 2H), 1.68 (s, 1H), 1.31 (s, 6H), 1.28 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.56, 163.22, 143.27,130.43, 130.26, 128.46, 128.04, 125.35, 113.49, 83.11, 55.45, 39.96, 34.44, 32.68, 24.91, 24.76. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.22. GC-MS (EI-70 eV): m/z (%) 394 (13), 311 (21), 289 (20), 232 (23), 189 (30), 150 (100). HRMS (ESI): calcd for C<sub>24</sub>H<sub>31</sub>BO<sub>4</sub> [M+Na]<sup>+</sup> : 417.2208, found: 417.2211.

#### 1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octan-1-one



Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (26.2 mg, 73%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 3H), 3.09 (qd, *J* = 17.8, 6.7 Hz, 2H), 1.42 – 1.35 (m, 4H), 1.34 – 1.26 (m, 11H), 1.25 (s, 6H), 0.89 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  199.03, 163.20, 130.26, 113.54, 82.87, 55.44, 40.72, 32.08, 30.62, 28.74, 24.81, 24.71, 22.60, 14.08. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.58. GC-MS (EI-70 eV): m/z (%) 360 (1), 345 (10), 231 (18), 189 (10), 150 (100), 133 (28). HRMS (ESI): calcd for C<sub>21</sub>H<sub>33</sub>BO<sub>4</sub> [M+Na]<sup>+</sup> : 383.2364, found: 383.2359.

1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonan-1-one



Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (28.5 mg, 76%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 – 7.97 (m, 2H), 6.95 – 6.89 (m, 2H), 3.88 (s, 3H), 3.34 (s, 2H), 1.27 (d, *J* = 12.0 Hz, 23H), 0.82 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.73, 163.14, 130.40, 130.35, 113.44, 82.98, 55.42, 39.71, 31.86, 30.09, 29.89, 27.76, 24.83, 24.75, 22.60, 14.06. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.52. GC-MS (EI-70 eV): m/z (%) 374 (1), 289 (5), 231 (18), 189 (15), 150 (100). HRMS (ESI): calcd for C<sub>22</sub>H<sub>35</sub>BO<sub>4</sub> [M+Na]<sup>+</sup>: 397.2521, found: 397.2517.

1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one<sup>2</sup>



3ab

Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (22.0 mg, 66%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.99 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.48 – 7.45 (m, 2H), 7.34 – 7.29 (m, 4H), 7.24 – 7.15 (m, 1H), 3.58 (dd, *J* = 18.2, 10.9 Hz, 1H), 3.49 – 3.39 (m, 1H), 2.83 (dd, *J* = 10.9, 4.9 Hz, 1H), 1.27 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>) δ 199.72, 141.96, 136.80, 132.94, 128.53, 128.50, 128.40, 128.07, 125.61, 83.41, 43.28, 24.58, 24.54. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 22.53. GC-MS (EI-70 eV): m/z (%) 336 (2), 278 (20), 236 (75), 209 (62), 115 (42),103 (100).

#### 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(o-tolyl)propan-1-one



3ac

Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (24.8 mg, 71%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.31 – 7.28 (m, 4H), 7.26 – 7.23 (m, 2H), 7.18 (ddd, *J* = 8.6, 6.2, 2.3 Hz, 1H), 3.50 (dd, *J* = 18.3, 10.9 Hz, 1H), 3.36 (dd, *J* = 18.3, 5.1 Hz, 1H), 2.82 (dd, *J* = 10.9, 5.1 Hz, 1H), 2.51 (s, 3H), 1.28 (s, 6H), 1.21 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  203.86, 141.89, 138.01, 137.71, 131.81, 131.13, 128.52, 128.50, 128.38, 125.58, 125.56, 83.41, 46.06, 24.61, 21.22. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.54. GC-MS (EI-70 eV): m/z (%) 350(6), 335 (100), 292 (23), 267 (32), 206 (50), 117 (56). HRMS (ESI): calcd for C<sub>22</sub>H<sub>27</sub>BO<sub>3</sub> [M+Na]<sup>+</sup>: 373.1945, found: 373.1949.

#### 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)propan-1-one<sup>3</sup>



3ad

Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (25.5 mg, 73%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 – 7.87 (m, 2H), 7.34 – 7.29 (m, 4H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.16 (m,

1H), 3.55 (dd, J = 18.2, 11.0 Hz, 1H), 3.43 (dd, J = 18.2, 5.0 Hz, 1H), 2.81 (dd, J = 10.9, 5.0 Hz, 1H), 2.42 (s, 3H), 1.27 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  199.34, 143.66, 142.07, 134.32, 129.17, 128.50, 128.41, 128.19, 125.56, 83.36, 43.17, 24.58, 24.55, 21.65. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.50. GC-MS (EI-70 eV): m/z (%) 350 (5), 335 (51), 292 (24), 267 (82), 223 (78), 117 (100).

### 1-(3,4-dimethylphenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propan-1-one

3ae

Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (22.9 mg, 63%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 – 7.71 (m, 2H), 7.32 (ddd, *J* = 22.2, 10.8, 4.8 Hz, 4H), 7.19 (ddd, *J* = 8.6, 6.5, 4.9 Hz, 2H), 3.54 (dd, *J* = 18.2, 11.0 Hz, 1H), 3.42 (dd, *J* = 18.2, 5.0 Hz, 1H), 2.80 (dd, *J* = 11.0, 4.9 Hz, 1H), 2.32 (d, *J* = 4.9 Hz, 6H), 1.27 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  199.57, 142.38, 142.15, 136.78, 134.72, 129.71, 129.21, 128.49, 128.42, 125.80, 125.54, 83.33, 43.24, 24.58, 24.56, 20.02, 19.75. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.50. GC-MS (EI-70 eV): m/z (%) 364 (3), 349 (100), 306 (20), 281 (50), 237 (48), 131 (50). HRMS (ESI): calcd for C<sub>23</sub>H<sub>29</sub>BO<sub>3</sub> [M+Na]<sup>+</sup> : 387.2102, found: 387.2107.

### 1-(4-(methylthio)phenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one

Bpin C

3af

Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Yellow oil (30.9 mg, 81%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 – 7.88 (m, 2H), 7.34 – 7.28 (m, 4H), 7.28 – 7.25 (m, 2H), 7.21 – 7.17 (m, 1H), 3.53 (dd, *J* = 18.1, 10.9 Hz, 1H), 3.40 (dd, *J* = 18.1, 5.0 Hz, 1H), 2.81 (dd, *J* = 10.9, 5.0 Hz, 1H), 2.53 (s, 3H), 1.27 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.69, 145.58, 142.00, 133.13, 128.52, 128.49,128.40, 125.60, 124.96, 83.38, 43.06, 24.58, 24.55, 14.83. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.50. GC-MS (EI-70 eV): m/z (%) 382 (38), 335 (52), 324 (25), 299 (81), 238 (60), 191 (62),151 (100). HRMS (ESI): calcd for C<sub>22</sub>H<sub>27</sub>BO<sub>3</sub>S [M+Na]<sup>+</sup> : 405.1666, found: 405.1661.

### 1-([1,1'-biphenyl]-4-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1one

3ag

Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (35.4 mg, 86%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (d, *J* = 8.3 Hz, 2H), 7.70 – 7.64 (m, 4H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.33 (dt, *J* = 15.2, 7.7 Hz, 4H), 7.20 (t, *J* = 7.2 Hz, 1H), 3.61 (dd, *J* = 18.2, 10.9 Hz, 1H), 3.48 (dd, *J* = 18.2, 5.0 Hz, 1H), 2.85 (dd, *J* = 10.9, 4.9 Hz, 1H), 1.28 (s, 6H), 1.21 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  199.32, 145.63, 141.99, 139.99, 135.50, 128.95, 128.66, 128.55, 128.42, 128.18, 127.29, 127.17, 125.62, 83.42,

43.34, 24.60, 24.56. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.53. GC-MS (EI-70 eV): m/z (%) 412 (28), 354 (20), 329 (100), 312 (52), 285 (60), 268 (58), 152 (32). HRMS (ESI): calcd for C<sub>27</sub>H<sub>29</sub>BO<sub>3</sub> [M+Na]<sup>+</sup>: 435.2102, found: 435.2096.

### 1-([1,1'-biphenyl]-3-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1one

Bpin

3ah

Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (33.3 mg, 81%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.21 (t, *J* = 1.7 Hz, 1H), 7.99 – 7.95 (m, 1H), 7.80 (ddd, *J* = 7.7, 1.7, 1.1 Hz, 1H), 7.63 (dt, *J* = 8.1, 1.6 Hz, 2H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.42 – 7.39 (m, 1H), 7.36 – 7.30 (m, 4H), 7.22 – 7.17 (m, 1H), 3.63 (dd, *J* = 18.2, 10.9 Hz, 1H), 3.50 (dd, *J* = 18.2, 4.9 Hz, 1H), 2.85 (dd, *J* = 10.9, 4.9 Hz, 1H), 1.28 (s, 6H), 1.20 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  199.64, 141.96, 141.65, 140.27, 137.30, 131.59, 128.99, 128.91,128.56, 128.44, 127.77, 127.23, 126.91, 126.80, 125.65, 83.44, 43.50, 24.60, 24.57. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.57. GC-MS (EI-70 eV): m/z (%) 412 (48), 329 (90), 312 (100), 285 (75), 268 (77), 179 (68), 152 (70). HRMS (ESI): calcd for C<sub>27</sub>H<sub>29</sub>BO<sub>3</sub> [M+Na]<sup>\*</sup> : 435.2102, found: 435.2100.

1-(naphthalen-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one



3ai Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (25.0 mg, 65%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.64 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.90 (t, *J* = 6.9 Hz, 2H), 7.61 – 7.53 (m, 2H), 7.50 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.33 (ddd, *J* = 26.2, 10.8, 4.6 Hz, 4H), 7.23 – 7.18 (m, 1H), 3.70 (dd, *J* = 18.2, 10.9 Hz, 1H), 3.50 (dd, *J* = 18.2, 5.0 Hz, 1H), 2.95 (dd, *J* = 10.9, 5.0 Hz, 1H), 1.31 (s, 6H), 1.25 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>) δ 204.24, 141.83, 135.92, 133.92, 132.36, 130.12, 128.56, 128.43, 128.34, 127.70, 127.37, 126.37, 125.93, 125.64, 124.42, 83.53, 46.63, 24.67. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 22.52. GC-MS (EI-70 eV): m/z (%) 386 (76), 342 (100), 328 (23), 285(26), 259 (25), 153 (49), 127 (70). HRMS (ESI): calcd for C<sub>25</sub>H<sub>27</sub>BO<sub>3</sub> [M+Na]<sup>\*</sup> : 409.1945, found: 409.1940.

#### 1-(4-fluorophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one<sup>3</sup>

3aj

Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (26.5 mg, 75%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 – 7.97 (m, 2H), 7.34 – 7.29 (m, 4H), 7.21 – 7.10 (m, 3H), 3.54 (dd, *J* = 18.2, 10.9 Hz, 1H), 3.41 (dd, *J* = 18.2, 5.0 Hz, 1H), 2.82 (dd, *J* = 10.9, 5.0 Hz, 1H), 1.27 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.14, 165.69 (d, *J* = 253.68 Hz), 141.81, 133.22 (d, *J* = 3.0 Hz), 130.67 (d, *J* = 9.3 Hz), 128.57, 128.38, 125.68, 115.58 (d, *J* = 22.65 Hz), 83.45, 43.16, 24.57, 24.53. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -

105.65. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 22.50. GC-MS (EI-70 eV): m/z (%) 354 (2), 339 (10), 296 (20), 254 (100), 210 (51), 123 (53).

1-(3-fluorophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one



3ak

Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (26.9 mg, 76%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 – 7.73 (m, 1H), 7.71 – 7.62 (m, 1H), 7.44 (td, *J* = 8.0, 5.5 Hz, 1H), 7.33 – 7.25 (m, 5H), 7.20 (ddd, *J* = 8.6, 5.8, 2.6 Hz, 1H), 3.55 (dd, *J* = 18.3, 10.9 Hz, 1H), 3.41 (dd, *J* = 18.3, 5.0 Hz, 1H), 2.83 (dd, *J* = 10.9, 4.9 Hz, 1H), 1.27 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.49 (d, *J* = 2.0 Hz), 162.84 (d, *J* = 247.64 Hz), 141.68, 138.88 (d, *J* = 6.1 Hz), 130.17 (d, *J* = 7.6 Hz), 128.59, 128.37, 125.72, 123.83 (d, *J* = 2.9 Hz), 119.95 (d, *J* = 21.14 Hz), 114.79 (d, *J* = 21.24 Hz), 83.50, 43.37, 24.57, 24.53. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -112.08. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.54. GC-MS (EI-70 eV): m/z (%) 354 (3), 296 (23), 254 (100), 210 (50), 123 (48). HRMS (ESI): calcd for C<sub>21</sub>H<sub>24</sub>BFO<sub>3</sub> [M+Na]<sup>+</sup> : 377.1695, found: 377.1699.

#### 1-(4-chlorophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one<sup>1</sup>



Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). White solid (27.0 mg, 73%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 – 7.91 (m, 2H), 7.46 – 7.40 (m, 3H), 7.30 (dd, *J* = 5.9, 2.5 Hz, 3H), 7.19 (ddd, *J* = 8.6, 5.8, 2.6 Hz, 1H), 3.54 (dd, *J* = 18.2, 10.9 Hz, 1H), 3.41 – 3.35 (m, 1H), 2.82 (dd, *J* = 10.9, 5.0 Hz, 1H), 1.26 (s, 6H), 1.18 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.54, 141.72, 139.36, 135.09, 129.49, 128.82, 128.57, 128.37, 125.70, 83.48, 43.19, 24.56, 24.52. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.53. GC-MS (EI-70 eV): m/z (%) 370 (1), 312 (20), 287 (50), 270 (78), 243 (40), 139 (48), 84 (100).

#### 1-(2-chlorophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one



#### 3am

Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (22.5 mg, 61%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (t, *J* = 1.8 Hz, 1H), 7.88 – 7.83 (m, 1H), 7.54 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.33 – 7.29 (m, 4H), 7.20 (ddd, *J* = 8.6, 5.8, 2.9 Hz, 1H), 3.55 (dd, *J* = 18.3, 10.9 Hz, 1H), 3.40 (dd, *J* = 18.3, 5.0 Hz, 1H), 2.83 (dd, *J* = 10.9, 4.9 Hz, 1H), 1.27 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.45, 141.67, 138.32, 134.86, 132.88, 129.86, 128.60, 128.38, 128.20, 126.15, 125.73, 83.51, 43.35, 24.57, 24.54. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.40. GC-MS (EI-70 eV): m/z (%) 370 (1), 312 (20), 287 (28), 243 (42), 139 (32), 84 (100). HRMS (ESI): calcd for C<sub>21</sub>H<sub>24</sub>BClO<sub>3</sub> [M+Na]<sup>+</sup> : 393.1399, found: 393.1392.

#### 1-(4-bromophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one

#### 3an

Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (24.4 mg, 59%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.11 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.36 – 7.27 (m, 6H), 3.54 (dd, *J* = 18.3, 10.8 Hz, 1H), 3.39 (dd, *J* = 18.3, 4.9 Hz, 1H), 2.82 (dd, *J* = 10.8, 4.8 Hz, 1H), 1.27 (s, 6H), 1.19 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.36, 141.65, 138.51, 135.79, 131.15, 130.13, 128.60, 128.37, 126.59, 125.73, 122.90, 83.51, 43.32, 24.56, 24.53. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  22.54. GC-MS (EI-70 eV): m/z (%) 414 (1), 358 (20), 314 (52), 287 (25), 191 (40), 84 (100). HRMS (ESI): calcd for C<sub>21</sub>H<sub>24</sub>BBrO<sub>3</sub> [M+Na]<sup>+</sup> : 437.0894, found: 437.0892.

#### 4. References

(1) X. Huang, J. Hu, M. Wu, J. Wang, Y. Peng, G. Song, Green Chem., 2018, 20, 255-260.

(2) M. L. Shegavi, S. Saini, R. Bhawar, M. D. Vishwantha, S. K. Bose, *Adv. Synth. Catal.*, 2021, **363**, 2408-2416.

(3) L. Zhao, Y. Ma, F. He, W. Duan, J. Chen, C. Song, J. Org. Chem., 2013, 78, 1677-1681.

### 5. NMR Spectrum Copies



<sup>1</sup>H NMR (600 MHz) Spectrum of **3aa** in CDCl<sub>3</sub>

## $^{\mbox{\tiny 13}}\mbox{C}\{^{\mbox{\tiny 1}}\mbox{H}\}$ NMR (151 MHz) Spectrum of 3aa in CDCl\_3



 $^{\rm 11}\text{B}$  NMR (160 MHz) Spectrum of 3aa in CDCl3



## $^1\text{H}$ NMR (600 MHz) Spectrum of **3ba** in CDCl\_3



# $^{\rm 13}\text{C}\{^{\rm 1}\text{H}\}$ NMR (151 MHz) Spectrum of 3ba in CDCl\_3



 $^{\rm 11}{\rm B}$  NMR (160 MHz) Spectrum of  ${\bf 3ba}$  in CDCl3



<sup>1</sup>H NMR (600 MHz) Spectrum of **3ca** in CDCl<sub>3</sub>



 $^{\scriptscriptstyle 13}\text{C}\{^{\scriptscriptstyle 1}\text{H}\}$  NMR (151 MHz) Spectrum of **3ca** in CDCl\_{\scriptscriptstyle 3}



 $^{\scriptscriptstyle 11}\text{B}$  NMR (160 MHz) Spectrum of 3ca in CDCl\_3







 $^{\scriptscriptstyle 13}\text{C}\{^{\scriptscriptstyle 1}\text{H}\}$  NMR (151 MHz) Spectrum of 3da in CDCl\_3



 $^{\rm 19}{\rm F}$  NMR (471 MHz) Spectrum of  ${\rm 3da}$  in CDCl3









 $^{\rm 13}\text{C}\{^{\rm 1}\text{H}\}$  NMR (151 MHz) Spectrum of 3ea in CDCl\_3



 $^{\rm 19}{\rm F}$  NMR (471 MHz) Spectrum of 3ea in CDCl3



 $^{\scriptscriptstyle 11}\text{B}$  NMR (160 MHz) Spectrum of **3ea** in CDCl<sub>3</sub>



<sup>1</sup>H NMR (600 MHz) Spectrum of **3fa** in CDCI<sub>3</sub>



 $^{\rm 13}\text{C}\{^{\rm 1}\text{H}\}$  NMR (151 MHz) Spectrum of 3fa in CDCl\_3



 $^{\rm 11}\text{B}$  NMR (160 MHz) Spectrum of 3fa in CDCl3







 $^{\scriptscriptstyle 13}\text{C}\{^{\scriptscriptstyle 1}\text{H}\}$  NMR (151 MHz) Spectrum of 3ga in CDCl\_ ${\scriptscriptstyle 3}$ 



 $^{\rm 11}\text{B}$  NMR (160 MHz) Spectrum of 3ga in CDCl3



<sup>1</sup>H NMR (600 MHz) Spectrum of **3ha** in CDCl<sub>3</sub>



 $^{\scriptscriptstyle 13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) Spectrum of 3ha in CDCl\_3



 $^{\scriptscriptstyle 11}\text{B}$  NMR (160 MHz) Spectrum of 3ha in CDCl3







 $^{\rm 13}\text{C}\{^{\rm 1}\text{H}\}$  NMR (151 MHz) Spectrum of 3ia in CDCl\_3



 $^{\rm 11}\text{B}$  NMR (160 MHz) Spectrum of 3ia in CDCl3





 $^1\text{H}$  NMR (600 MHz) Spectrum of 3ja in CDCl $_3$ 

0 10.5 10.0 9.5 9.0 18.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1 fl(ppm)

 $^{\rm 13}\text{C}\{^{\rm 1}\text{H}\}$  NMR (151 MHz) Spectrum of 3ja in CDCl $_{\rm 3}$ 



 $^{\rm 11}{\rm B}$  NMR (160 MHz) Spectrum of  ${\bf 3ja}$  in CDCl<sub>3</sub>



## $^1\text{H}$ NMR (600 MHz) Spectrum of 3ka in CDCl\_3



 $^{\scriptscriptstyle 13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) Spectrum of  $\boldsymbol{3ka}$  in CDCl\_ ${\scriptscriptstyle 3}$ 



S32

 $^{\rm 11}{\rm B}$  NMR (160 MHz) Spectrum of 3ka in CDCl3



## $^1\text{H}$ NMR (600 MHz) Spectrum of 3Ia in CDCl\_3



 $^{\scriptscriptstyle 13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) Spectrum of 3la in CDCl\_3



 $^{\scriptscriptstyle 11}\text{B}$  NMR (160 MHz) Spectrum of 3Ia in CDCl\_3



 $^1\text{H}$  NMR (600 MHz) Spectrum of **3ma** in CDCl\_3



 $^{\rm 13}\text{C}\{^{\rm 1}\text{H}\}$  NMR (151 MHz) Spectrum of 3ma in CDCl $_{\rm 3}$ 



 $^{\scriptscriptstyle 11}\text{B}$  NMR (160 MHz) Spectrum of 3ma in CDCl3



### <sup>1</sup>H NMR (600 MHz) Spectrum of **3na** in CDCl<sub>3</sub>



## $^{\scriptscriptstyle 13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) Spectrum of 3na in CDCl\_ ${\scriptscriptstyle 3}$



 $^{\rm 11}{\rm B}$  NMR (160 MHz) Spectrum of 3na in CDCl3







 $^{\scriptscriptstyle 13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) Spectrum of 3ab in CDCl\_ ${\scriptscriptstyle 3}$ 



 $^{\rm 11}{\rm B}$  NMR (160 MHz) Spectrum of  ${\bf 3ab}$  in CDCl3







 $^{\scriptscriptstyle 13}\text{C}\{^{^1}\text{H}\}$  NMR (151 MHz) Spectrum of 3ac in CDCl\_3



 $^{\rm 11}{\rm B}$  NMR (160 MHz) Spectrum of 3ac in CDCl3



 $^1\text{H}$  NMR (600 MHz) Spectrum of 3ad in CDCl\_3



 $^{\scriptscriptstyle 13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) Spectrum of 3ad in CDCl\_ ${\scriptscriptstyle 3}$ 



 $^{\rm 11}\text{B}$  NMR (160 MHz) Spectrum of 3ad in CDCl3







 $^{\mbox{\tiny 13}}\mbox{C}\{^1\mbox{H}\}$  NMR (151 MHz) Spectrum of 3ae in CDCl\_3



 $^{\rm 11}\text{B}$  NMR (160 MHz) Spectrum of 3ae in CDCl3



 $^1\text{H}$  NMR (600 MHz) Spectrum of 3af in CDCl\_3



 $^{\rm 13}\text{C}\{^{\rm 1}\text{H}\}$  NMR (151 MHz) Spectrum of 3af in CDCl\_3



 $^{\rm 11}{\rm B}$  NMR (160 MHz) Spectrum of  ${\bf 3af}$  in CDCl3



### <sup>1</sup>H NMR (600 MHz) Spectrum of **3ag** in CDCl<sub>3</sub>



 $^{\mbox{\tiny 13}}\mbox{C}\{^{\mbox{\tiny 1}}\mbox{H}\}$  NMR (151 MHz) Spectrum of  ${\bf 3ag}$  in CDCl\_{\mbox{\tiny 3}}



 $^{\rm 11}{\rm B}$  NMR (160 MHz) Spectrum of  ${\bf 3ag}$  in CDCl3



### <sup>1</sup>H NMR (600 MHz) Spectrum of **3ah** in CDCl<sub>3</sub>



 $^{\mbox{\tiny 13}}\mbox{C}\{^{\mbox{\tiny 1}}\mbox{H}\}$  NMR (151 MHz) Spectrum of  ${\bf 3ah}$  in CDCl $_{\mbox{\tiny 3}}$ 



 $^{\rm 11}{\rm B}$  NMR (160 MHz) Spectrum of  ${\bf 3ah}$  in CDCl3







 $^{\scriptscriptstyle 13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) Spectrum of 3ai in CDCl\_3



 $^{\scriptscriptstyle 11}\text{B}$  NMR (160 MHz) Spectrum of 3ai in CDCl\_3



<sup>1</sup>H NMR (600 MHz) Spectrum of **3aj** in CDCl<sub>3</sub>



 $^{\scriptscriptstyle 13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) Spectrum of 3aj in CDCl\_ ${\scriptscriptstyle 3}$ 



 $^{\rm 19}{\rm F}$  NMR (471 MHz) Spectrum of  ${\bf 3aj}$  in CDCl $_{\rm 3}$ 



### <sup>1</sup>H NMR (600 MHz) Spectrum of **3ak** in CDCl<sub>3</sub>



# $^{\rm 13}\text{C}\{^{\rm 1}\text{H}\}$ NMR (151 MHz) Spectrum of 3ak in CDCl $_{\rm 3}$



 $^{\rm 19}{\rm F}$  NMR (471 MHz) Spectrum of **3ak** in CDCl<sub>3</sub>



 $^1\text{H}$  NMR (600 MHz) Spectrum of **3al** in CDCl\_3



 $^{\scriptscriptstyle 13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) Spectrum of 3al in CDCl\_ ${\scriptscriptstyle 3}$ 



 $^{\rm 11}{\rm B}$  NMR (160 MHz) Spectrum of 3al in CDCl3







 $^{\mbox{\tiny 13}}\mbox{C}\{^{\mbox{\tiny 1}}\mbox{H}\}$  NMR (151 MHz) Spectrum of  ${\bf 3am}$  in CDCl\_{\mbox{\tiny 3}}



 $^{\scriptscriptstyle 11}\text{B}$  NMR (160 MHz) Spectrum of 3am in CDCl3



### <sup>1</sup>H NMR (600 MHz) Spectrum of **3an** in CDCl<sub>3</sub>



## $^{\scriptscriptstyle 13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) Spectrum of 3an in CDCl\_ ${\scriptscriptstyle 3}$



 $^{\rm 11}{\rm B}$  NMR (160 MHz) Spectrum of 3an in CDCl3

