Iron catalysis and water, a synergy for refunctionalisation of boron

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1. Techniques

GC-MS analysis were performed with a HP 6890 series GC-system equipped with a J&W Scientific DB-1701 capillary column, a HP 5973 mass selective detector (EI) using the following method: 70°C for 1 min then 20°C.min⁻¹ until 230 °C then 6 min at 230 °C. MS analysis were performed on a Shimadzu LCMS-2020 with direct inject (CH₃CN/H₂O 1/1) equipped with APCI and electrospray dual source with simultaneous detection of positive and negative ions. ¹H, ¹¹B, ¹³C, ¹⁹F and ³¹P NMR were recorded on 300 MHz Avance I and 400 MHz Avance II spectrometers. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and hertz respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, m = multiplet.

Chemicals were purchased from Sigma-Aldrich or Alfa Aesar. All catalytic reactions were carried out under argon atmosphere unless specified. All chemicals were stored under argon. Acetonitrile were distilled over CaH₂. Silica gel (230-400 mesh) purchased from Merck was used for flash chromatography. Analytical TLC silica gel 60 F254 were used

2. General Procedures

2.1. General Procedure A : Transformation of Potassium Trifluoro(organo)borates into Boronic Acids

To a solution of potassium aryltrifluoroborate (1 mmol) in distilled H₂O (4 mL) was added, sequentially, a solution of FeCl₃ (8 mg, 0.05 mmol, 5 mol%) in H₂O (1 mL) and imidazole (204 mg, 3 mmol). The resulting colourless solution was stirred at room temperature for 15 min. The reaction was then diluted with H₂O (5 mL) and extracted with Et₂O (3 x 8 mL). The combined organic extracts were dried (Na₂SO₄) and concentrated in vacuo, affording pure product without the requirement for further purification.

2.2. General Procedure B : Transformation of Boronic Acids into Boronates

To a solution of aryl boronic acid (1 mmol) in MeCN (4 mL) was added, sequentially, a solution of FeCl₃ (8 mg, 0.05 mmol, 5 mol%) in H₂O (1 mL), imidazole (204 mg, 3 mmol) and pinacol (118 mg, 1 mmol). The resulting cloudy orange mixture was stirred at room temperature for 30 min. The reaction was then diluted with H₂O (5 mL) and extracted with Et₂O (3 x 8 mL). The combined organic extracts were dried (Na₂SO₄) and concentrated in vacuo. The resulting oil was then purified by a filtration through a silica gel plug (eluting with Et₂O), affording the title compound.

2.3. General Procedure C : Synthesis of Diazaborinane from Boronic Acids

To a solution of aryl boronic acid (1 mmol) in MeCN (4 mL) was added, sequentially, a solution of FeCl₃ (8 mg, 0.05 mmol, 5 mol%) in H₂O (1 mL), imidazole (204 mg, 3 mmol) and 1,8-diaminonaphthalene (159 mg, 1 mmol). The resulting cloudy, dark purple mixture was stirred at room temperature for 2h. The reaction was then diluted with H₂O (5 mL) and extracted with EtOAc (3 x 8 mL). The combined organic extracts were dried (Na₂SO₄) and
concentrated *in vacuo*. The resultant viscous purple oil was then purified by a filtration through a silica gel plug (eluting with Et₂O), affording the title compound.

2.4. General Procedure D: Synthesis of Diazaborolane from trifluoroborates

To a solution of potassium trifluorophenylborate (184 mg, 1 mmol) in distilled H₂O (4 mL) was added, sequentially, a solution of FeCl₃ (8 mg, 0.05 mmol, 5 mol%) in H₂O (1 mL), imidazole (204 mg, 3 mmol) and pinacol (118 mg, 1 mmol). The resulting dark yellow solution was vigorously stirred at room temperature for 15 min. The reaction was then diluted with H₂O (5 mL) and extracted with Et₂O (3 x 8 mL). The combined organic extracts were dried (Na₂SO₄) and concentrated *in vacuo*. The resulting oil was then purified by a filtration through a silica gel plug (eluting with Et₂O), affording 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane.

3. Analyses

3.1. Phenylboronic acid CAS = [98-80-6]¹

Phenylboronic acid was prepared according to the general procedure A, affording the title compound as a white solid; 87% yield,

mp 215-217 °C (lit.⁰ ref mp 216-219 °C),
Rₓ (DCM-EtOAc; 3:1): 0.66.
¹H NMR (300 MHz, DMSO-d₆) δ 7.32-7.43 (3H, m), 7.80 (2H, dd, J 1.6 Hz, 8.0 Hz), 8.04 (2H, broad s).
¹³C NMR (50 MHz, DMSO-d₆) δ 127.9, 130.5, 134.6.
¹¹B NMR (96 MHz, DMSO-d₆) δ 27.6.

3.2. 4-Chlorophenylboronic acid CAS = [1679-18-1]²

4-Chlorophenylboronic acid was prepared according to the general procedure A, affording the title compound as a white solid; 85% yield,

mp 271-273 °C (lit.⁰ ref mp 278-280 °C),
Rₓ (DCM-EtOAc; 3:1): 0.70.
¹H NMR (300 MHz, DMSO-d₆) δ 7.40 (2H, d, J 8.4 Hz), 7.80 (2H, d, J 8.4 Hz), 8.19 (2H, broad s).
¹³C NMR (50 MHz, DMSO-d₆) δ 127.9, 135.6, 136.4.
¹¹B NMR (96 MHz, DMSO-d₆) δ 27.4.

3.3. 4-(tert-Butyl)phenylboronic acid CAS = [123324-71-0]³

4-(tert-Butyl)phenylboronic acid was prepared according to the general procedure A, affording the title compound as a grey solid; 85% yield,

mp 191-193 °C (lit. ref mp 194 °C),
Rf (DCM-EtOAc; 3:1): 0.78.

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 1.28 (9H, s), 7.36 (2H, d, $J$ 8.3 Hz), 7.75 (2H, d, $J$ 8.3 Hz), 7.94 (2H, broad s).

$^{13}$C NMR (50 MHz, DMSO-$d_6$) δ 31.56, 34.9, 124.6, 134.5, 152.9

$^{11}$B NMR (96 MHz, DMSO-$d_6$) δ 27.9.

3.4. 4-Methylphenylboronic acid CAS = [5720-05-8]$^4$

4-Methylphenylboronic acid was prepared via a method similar to that of the general procedure A albeit using a 0.1 M solution in H$_2$O; affording the title compound as a white solid; 76% yield,

mp 246-248 °C (lit. ref mp 242-243/252-253 °C),
Rf (DCM-EtOAc; 3:1): 0.70.

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 2.31 (3H, s), 7.16 (2H, d, $J$ 7.7 Hz), 7.70 (2H, d, $J$ 7.7 Hz), 7.94 (2H, broad s).

$^{13}$C NMR (50 MHz, DMSO-$d_6$) δ 21.6, 128.5, 130.01, 131.7, 140.0.

$^{11}$B NMR (96 MHz, DMSO-$d_6$) δ 29.9.

3.5. 4-Methoxyphenylboronic acid CAS = [5720-07-0]$^4$

4-Methoxyphenylboronic acid was prepared according to the general procedure A, affording the title compound as an orange solid; 81% yield,

mp 271-273 °C (lit. ref mp 200-202 °C),
Rf (DCM-EtOAc; 3:1): 0.59

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 3.70 (3H, s), 6.91 (2H, d, $J$ 8.6 Hz), 7.78 (2H, d, $J$ 8.6 Hz), 7.86 (2H, broad s).

$^{13}$C NMR (75 MHz, DMSO-$d_6$) 55.3, 113.4, 136.3, 161.4.

$^{11}$B NMR (96 MHz, DMSO-$d_6$) δ 29.3.

3.6. 4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane CAS = [24388-23-6]$^5$

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane was prepared according to the general procedure B, affording the title compound as a pale yellow oil, which solidified upon standing; 86% yield,

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane was prepared according to the general procedure D, affording the title compound as a pale yellow oil, which solidified upon standing; 65% yield,


\textbf{3.7. 5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane CAS = \textit{[5123-13-7]}^{6}\text{\textit{\textsuperscript{}}}}

5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane was prepared according to the general procedure B, affording the title compound as an orange solid; 77\% yield,

mp 63-65 °C (lit.\textsuperscript{ref} mp 62-64 °C),

R\text{\textsubscript{f}} (petroleum ether-PhMe; 10:1): 0.70

\textit{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 1.08 (6H, s), 3.83 (4H, s), 7.37-7.52 (3H, m), 7.87 (2H, dd, \(J\) 1.5Hz, 8.0 Hz).

\textit{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\) 22.0, 31.9, 72.4, 127.6, 130.7, 133.9.

\textit{11}B NMR (96 MHz, CDCl\textsubscript{3}) \(\delta\) 26.6.

\textbf{3.8. 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenol}

Following the general procedure B using 138mg of (4-hydroxyphenyl)boronic acid, 145 mg of 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenol were obtained as a white solid. 70\% yield.

\textit{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.70 (d, \(J\) = 8.5 Hz, 1H), 6.81 (d, \(J\) = 8.6 Hz, 1H), 5.10 (s, 1H), 3.75 (s, 2H), 1.02 (s, 3H).

\textit{11}B NMR (96 MHz, CDCl\textsubscript{3}) \(\delta\) 27.2 (s).

\textit{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 158.0, 135.9, 114.8, 72.4, 32.0, 22.0.

MS : (APCI/ES) : M- H\textsuperscript{+} = 206 (M, 100\%), 120 (M-C\textsubscript{5}H\textsubscript{10}, 70\%)

\textbf{3.9. methyl 3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-5-nitrobenzoate}

Following the general procedure B using 225mg of (3-(methoxycarbonyl)-5-nitrophenyl)boronic acid, 239mg of methyl 3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-5-nitrobenzoate were obtained as a white solid. 82\% yield.

\textit{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 8.88 (s, 1H), 8.76 (d, \(J\) = 15.6 Hz, 2H), 3.98 (s, 3H), 3.82 (s, 4H), 1.04 (s, 7H).

\textit{11}B NMR (96 MHz, CDCl\textsubscript{3}) \(\delta\) 26.3 (s).

\textit{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 140.6, 132.6, 131.2, 126.5, 72.7, 52.8, 32.1, 22.0.

MS : (EI) : M= 293 (M, 100\%), 262 (M-OCH\textsubscript{3}, 100\%), 250 (M-2CH\textsubscript{3}-H\textsuperscript{+}, 26\%)

\textbf{3.10. 4,4,6-Trimethyl-2-phenyl-1,3,2-dioxaborinane CAS = \textit{[15961-35-0]}^{7\text{\textsuperscript{}}}}

4,4,6-Trimethyl-2-phenyl-1,3,2-dioxaborinane was prepared according to the general procedure B, affording the title compound as a light orange oil; 82\% yield.


Rf (petroleum ether-PhMe; 10:1): 0.70.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.43 (3H, d, \(J = 6.2\) Hz), 1.45 (3H, s), 1.46 (3H, s), 1.66 (1H, dd, \(J = 11.7\) Hz, 13.8 Hz), 1.93 (1H, dd, \(J = 3.0\) Hz, 13.8 Hz), 4.37–4.48 (1H, m), 7.39–7.52 (3H, m), 7.91 (2H, dd, \(J = 1.6\) Hz, 7.9 Hz).

\(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\) 23.3, 28.2, 31.4, 46.1, 65.0, 71.0, 127.5, 130.4, 133.8.

\(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) 26.6.

3.11. (3aS,4S,6S,7aR)-3a,5,5-Trimethyl-2-phenylhexahydro-4,6-methanobenzo\([d]\)[1,3,2]dioxaborole CAS = [76110-78-6]\(^8\)

(3aS,4S,6S,7aR)-3a,5,5-Trimethyl-2-phenylhexahydro-4,6-methanobenzo\([d]\)[1,3,2]dioxaborole was prepared according to the general procedure B, affording the title compound as a white solid; 90% yield

mp 75–78 °C

Rf (petroleum ether-PhMe; 10:1): 0.67.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.96 (3H, s), 1.31 (1H, d, \(J = 10.7\) Hz), 1.39 (3H, s), 1.56 (3H, s), 1.98–2.09 (2H, m), 2.22–2.25 (1H, m), 2.27–2.35 (1H, m), 2.45–2.53 (1H, m), 4.53 (1H, dd, \(J = 2.0\) Hz, 8.8 Hz), 7.43–7.57 (3H, m), 7.91 (2H, dd, \(J = 1.5\) Hz, 8.0 Hz).

\(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\) 24.1, 26.6, 27.2, 28.8, 35.6, 38.2, 39.6, 51.5, 78.3, 86.3, 127.8, 131.3, 134.9.

\(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) 30.0.

3.12. (3aS,4S,6S,7aR)-3a,5,5-trimethyl-2-(4-nitrophenyl)hexahydro-4,6 methanobenzo\([d]\)[1,3,2]dioxaborole

292mg of (3aS,4S,6S,7aR)-3a,5,5-trimethyl-2-(4-nitrophenyl)hexahydro-4,6 methanobenzo\([d]\)[1,3,2]dioxaborole were prepared according to the general procedure B, using 167mg of 4-nitrobenzene boronic acid affording the title compound as a white solid; 97% yield

\(^1\)H NMR (300 MHz, DMSO) \(\delta\) 8.23 (d, \(J = 8.7\) Hz, 1H), 7.94 (d, \(J = 8.7\) Hz, 1H), 4.59 (dd, \(J = 8.7, 1.6\) Hz, 1H), 2.41 (ddd, \(J = 14.2, 8.7, 2.3\) Hz, 1H), 2.22 (ddd, \(J = 10.5, 6.1, 3.1\) Hz, 1H), 2.10 (t, \(J = 5.4\) Hz, 1H), 1.95 – 1.80 (m, 1H), 1.46 (s, 1H), 1.27 (s, 2H), 1.04 (d, \(J = 10.7\) Hz, 1H), 0.86 (s, 1H).

\(^{11}\)B NMR (100 MHz, CDCl\(_3\)) \(\delta\) 31.1

\(^{13}\)C NMR (75 MHz, DMSO) \(\delta\) 149.4, 135.7, 122.6, 86.6, 77.7, 50.8, 37.8, 34.9, 28.2, 26.8, 26.0, 23.6.

MS : (ESI) : 320 (M+H\(^+\)+H\(_2\)O, 100%).

3.13. 4-((3aS,4S,6S,7aR)-3a,5,5-trimethylhexahydro-4,6 methanobenzo\([d]\)[1,3,2]dioxaborol-2-yl)benzamide

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299 mg of 4-((3aS,4S,6S,7aR)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)benzamide were prepared according to the general procedure B, using 165 mg of (4-carbamoylphenyl)boronic acid affording the title compound as a white solid; 99% yield.

\[\text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) } \delta 7.89 (d, \textit{J} = 8.3 \text{ Hz}, 1\text{H}), 7.80 (d, \textit{J} = 8.3 \text{ Hz}, 1\text{H}), 2.49 – 2.36 (m, 1\text{H}), 2.23 (dd, \textit{J} = 10.8, 6.3, 2.1 \text{ Hz}, 1\text{H}), 2.15 (t, \textit{J} = 5.5 \text{ Hz}, 1\text{H}), 2.02 – 1.90 (m, 1\text{H}), 1.49 (s, 2\text{H}), 1.31 (s, 2\text{H}), 1.19 (d, \textit{J} = 10.9 \text{ Hz}, 1\text{H}), 0.89 (s, 2\text{H}).\]

\[\text{\textsuperscript{11}B NMR (96 MHz, CDCl\textsubscript{3}) } \delta 31.32 (s).\]

\[\text{\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) } \delta 169.6, 135.6, 135.2, 126.6, 86.8, 78.6, 51.5, 39.6, 38.3, 35.6, 28.8, 27.2, 26.6, 24.2.\]

MS: (ESI) : 300 (M+H\textsuperscript{+}, 1%), 338 (M+K\textsuperscript{+}, 100%).

3.14. 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane CAS=[195062-61-4] \textsuperscript{9}

2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the general procedure B, affording the title compound as a white solid; 78% yield, mp 56-58 °C,

\[\text{R_f (petroleum ether-PhMe; 10:1): 0.55.}\]

\[\text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) } \delta 1.38 (12H, s), 7.38 (2\text{H}, d, \textit{J} 8.4 \text{ Hz}), 7.77 (2\text{H}, d, J 8.4 \text{ Hz}).\]

\[\text{\textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) } \delta 24.9, 84.0, 128.0, 136.1, 137.5.\]

\[\text{\textsuperscript{11}B NMR (96 MHz, CDCl\textsubscript{3}) } \delta 30.6.\]

3.15. 2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane CAS=[214360-66-4] \textsuperscript{10}

2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the general procedure B, affording the title compound as an orange solid; 80% yield, mp 140-141 °C (lit.\textsuperscript{ref} 139.9-140.9 °C)

\[\text{R_f (petroleum ether-PhMe; 10:1): 0.78.}\]

\[\text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) } \delta 1.37-1.40 (21H, m), 7.47 (2\text{H}, d, J 8.2 \text{ Hz}), 7.83 (2\text{H}, d, J 8.2 \text{ Hz}).\]

\[\text{\textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) } \delta 24.9, 31.2, 34.9, 83.6, 124.7, 134.7, 154.5.\]

\[\text{\textsuperscript{11}B NMR (96 MHz, CDCl\textsubscript{3}) } \delta 31.1.\]

3.16. 4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane CAS = [195062-57-8]\textsuperscript{11}

4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane was prepared according to the general procedure B, affording the title compound as a colourless oil; 77% yield,

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\textsuperscript{10} T. Yamamoto, T. Morita, J. Takagi and T. Yamakawa, Org. Lett., 2011, 13, 5766-5769

R<sub>f</sub> (petroleum ether-PhMe; 10:1): 0.52

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.42 (12H, s), 2.45 (3H, s), 7.27 (2H, d, J 7.8 Hz), 7.81 (2H, d, J 7.8 Hz).

<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 21.8, 24.9, 83.7, 128.6, 134.9, 141.4.

<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>) δ 30.9.

3.17.  (E)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane CAS = [83947-56-2]<sup>12</sup>

(E)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane was prepared according to the general procedure B, affording the title compound as a slightly brown oil; 76% yield,

R<sub>f</sub> (petroleum ether-PhMe; 10:1): 0.28.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.36 (12H, s), 6.24 (1H, d, J 18.4 Hz), 7.30-7.41 (3H, m), 7.46 (1H, d, J 18.4 Hz), 7.54 (2H, d, J 1.5 Hz, 8.0 Hz).

<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 24.9, 83.4, 127.1, 128.6, 128.9, 137.5, 149.5.

<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>) δ 30.3.

3.18.  4,4,5,5-tetramethyl-2-(4-methyl-3-nitrophenyl)-1,3,2-dioxaborolane
[1072945-06-2]

213mg of 4,4,5,5-tetramethyl-2-(4-methyl-3-nitrophenyl)-1,3,2-dioxaborolane were prepared according to the general procedure B, using 181mg of (4-methyl-3-nitrophenyl)boronic acid affording the title compound as a white solid; 81% yield

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.35 (s, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 2.60 (s, 3H), 1.35 (s, 13H).

<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>) δ 30.5 (s).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 149.3, 139.0, 136.4, 132.3, 130.8, 84.6, 25.0, 20.7.

MS : (EI) : 263 (M, 19%), 248 (M-CH<sub>3</sub>, 67%), 203 (M-CH<sub>3</sub>-NO<sub>2</sub>+H<sup>+</sup>, 26%), 164 (M-C<sub>6</sub>H<sub>13</sub>O+H<sup>+</sup>, 100%)  

3.19.  tert-butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate [1409999-54-7]

303mg of tert-butyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate were prepared according to the general procedure B, using 221mg of (4-((tert-butoxycarbonyl)amino)phenyl)borynic acid affording the title compound as a white solid; 81% yield

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.71 (dd, J = 10.0, 8.3 Hz, 1H), 7.36 (dd, J = 8.5 Hz, 1H), 1.51 (s, 3H), 1.33 (s, 5H).

<sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>) δ 30.8 (s).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 152.6, 141.3, 136.0, 135.2, 122.1, 117.4, 83.8, 80.8, 28.4, 25.0.

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MS : (ESI) : 320 (M+ H\(^+\), 8%), 337 (M+H\(_2\)O, 54%), 364 (M+HCOO\(^-\), 100%), 388 (M+HCOOH+Na\(^+\), 100%)

3.20. 2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid

123mg of 2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid were prepared according to the general procedure B, using 184mg of 5-borono-2-fluorobenzoic acid affording the title compound as a white solid; 46% yield

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.51 (dd, \(J = 7.8, 1.2\) Hz, 1H), 8.01 (ddd, \(J = 8.1, 5.0, 1.3\) Hz, 1H), 7.16 (dd, \(J = 10.9, 8.4\) Hz, 1H), 1.36 (s, 12H).

\(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 30.7 (s).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 169.1, 166.1, 163.5, 142.2, 142.1, 140.0, 117.3, 116.9, 116.7, 84.7, 25.0.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -105.5 (s).

3.21. 2-Phenyl-2,3-dihydro-1\(H\)-naphtho[1,8-de][1,3,2]diazaborinine CAS = [24341-81-9]

2-Phenyl-2,3-dihydro-1\(H\)-naphtho[1,8-de][1,3,2]diazaborinine was prepared according to the general procedure C, affording the title compound as a lilac solid; 93% yield,

mp 97-98 °C (lit. ref mp 92-93.5 °C),

R\(_f\) (EtOAc-petroleum ether; 1:10): 0.74.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.07 (2H, broad s), 6.48 (2H, d, \(J = 7.2\) Hz), 7.19 (2H, d, \(J = 8.2\) Hz), 7.26 (2H, t, \(J = 7.7\) Hz), 7.51-7.60 (3H, m), 7.70 (2H, dd, \(J = 1.6\) Hz, 7.8 Hz).

\(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\) 106.2, 118.0, 130.0, 128.0, 128.4, 130.4, 131.6, 136.5, 141.2.

\(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) 29.2.

3.22. 2-(4-chlorophenyl)-2,3-dihydro-1\(H\)-naphtho[1,8-de][1,3,2]diazaborinine CAS = [1336918-65-0]

2-(4-chlorophenyl)-2,3-dihydro-1\(H\)-naphtho[1,8-de][1,3,2]diazaborinine was prepared via a method similar to that of the general procedure C albeit using a 0.1 M solution in MeCN-H\(_2\)O 4:1, affording the title compound after 2h as a rose solid; 87% yield

mp 155-157 °C

R\(_f\) (EtOAc-petroleum ether; 1:10): 0.69.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.98 (2H, broad s), 6.44 (2H, d, \(J = 1.1\) Hz, 7.1 Hz), 7.13 (2H, dd, \(J = 1.1\) Hz, 8.4 Hz), 7.21 (2H, dd, \(J = 7.1\) Hz, 8.4 Hz), 7.45 (2H, apparent dt, \(J = 2.0\) Hz, 8.4 Hz), 7.56 (2H, apparent dt, \(J = 1.9\) Hz, 8.4 Hz).

13C NMR (50 MHz, CDCl3) δ 106.2, 118.1, 120.0, 127.7, 128.5, 132.9, 136.39, 136.45, 140.9.
11B NMR (96 MHz, CDCl3) δ 29.0.

3.23. 2-(tert-Butyl)phenyl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine

2-(tert-Butyl)phenyl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine was prepared via a method similar to that of the general procedure (0.1 M MeCN-H2O 4:1, rt, 5h), affording the title compound as a brown solid; 94% yield

mp 140-142 °C
Rf (EtOAc-petroleum ether; 1:10): 0.87.
1H NMR (300 MHz, CDCl3) δ 1.47 (9H, s), 6.11 (2H, broad s), 6.50 (2H, dd, J 1.0 Hz, 7.2 Hz), 7.16 (2H, dd, J 1.0 Hz, 8.3 Hz), 7.26 (2H, dd, J 7.2 Hz, 8.3 Hz), 7.57 (2H, d, J 8.3 Hz), 7.68 (2H, d, J 8.3 Hz).
13C NMR (50 MHz, CDCl3) δ 31.3, 34.9, 106.1, 117.8, 119.9, 125.3, 127.7, 131.5, 136.5, 141.3, 153.6.
11B NMR (96 MHz, CDCl3) δ 29.2.

3.24. 2-(p-Tolyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine

CAS= [1159803-47-0]14

2-(p-Tolyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine was prepared via a method similar to that of the general procedure C albeit using a 0.1 M solution in MeCN-H2O 4:1 affording the title compound after 5h as a pink/orange solid; 94% yield

mp 201-203 °C
Rf (EtOAc-petroleum ether; 1:10): 0.76.
1H NMR (300 MHz, CDCl3) δ 2.46 (3H, s), 6.07 (2H, broad s), 6.46 (2H, d, J 1.0 Hz, 7.2 Hz), 7.11 (2H, dd, J 1.0 Hz, 8.3 Hz), 7.20 (2H, dd, J 7.2 Hz, 8.3 Hz), 7.30-7.33 (2H, m), 7.60 (2H, d, J 7.9 Hz).
13C NMR (50 MHz, CDCl3) δ 21.6, 106.0, 117.8, 117.9, 127.7, 129.1, 131.5, 136.4, 140.4, 141.2.
11B NMR (96 MHz, CDCl3) δ 28.5.

3.25. (E)-2-Styryl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine

CAS= [1147458-75-0]15

(E)-2-Styryl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine was prepared via a method similar to that of the general procedure C albeit using a 0.2 M solution in MeCN-H2O 4:1. After 6h reaction time, filtration of the crude material through a silica gel column (eluting with Et2O-petroleum ether-EtOAc; 7:6:1) yielded the title compound as a slightly orange oil, which solidified upon standing; 95% yield

mp 105-107 °C
Rf (EtOAc-petroleum ether; 1:10): 0.65.
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.87 (2H, broad s), 6.36 (1H, d, $J$ 18.6 Hz), 6.42 (2H, dd, $J$ 0.9 Hz, 7.2 Hz), 7.13 (2H, dd, $J$ 0.9 Hz, 8.3 Hz), 7.16-7.24 (3H, m), 7.38-7.50 (3H, m), 7.59 (2H, dd, $J$ 1.6 Hz, 8.5 Hz).
$^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ 105.9, 117.7, 120.0, 126.9, 127.7, 128.8, 136.5, 137.7, 141.2, 143.7.
$^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ 27.8.

3.26. 2-(4-nitrophenyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine

289mg of 2-(4-nitrophenyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine were prepared according to the general procedure B, using 167mg of 4-nitrobenzene boronic acid affording the title compound as a white solid; 99% yield

$^1$H NMR (300 MHz, DMSO) $\delta$ 8.49 (s, 1H), 8.30 (d, $J$ = 8.7 Hz, 1H), 8.19 (d, $J$ = 8.7 Hz, 1H), 7.15 – 7.06 (m, 1H), 6.94 (d, $J$ = 7.7 Hz, 1H), 6.60 (d, $J$ = 6.8 Hz, 1H).
$^{11}$B NMR (128 MHz, DMSO) $\delta$ 29.5 (s).
$^{13}$C NMR (75 MHz, DMSO) $\delta$ 148.6, 142.0, 135.9, 133.9, 127.7, 122.3, 119.9, 116.7, 105.9.
MS : (ESI) : 334 (M+HCO$_2$-, 100%), 288 (M-H, 18%).

3.27. 3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)phenol

238mg of 3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)phenol were prepared according to the general procedure B, using 138mg of (3-hydroxyphenyl)boronic acid affording the title compound as a white solid; 92% yield

$^1$H NMR (300 MHz, DMSO) $\delta$ 9.30 (s, 1H), 8.19 (s, 2H), 7.32 (t, $J$ = 5.2 Hz, 2H), 7.24 (t, $J$ = 7.6 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.94 – 6.85 (m, 3H), 6.63 – 6.56 (m, 2H).
$^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ 29.1 (s).
$^{13}$C NMR (75 MHz, DMSO) $\delta$ 156.8, 142.4, 135.9, 135.2, 128.7, 127.6, 123.3, 119.7, 119.5, 116.9, 116.1, 105.6.
MS : (ESI) : 259 (M-H, 66%), 519 (2M-H, 100%).

3.28. 1-(4-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)phenyl)ethanone

286mg of 1-(4-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)phenyl)ethanone were prepared according to the general procedure B, using 164mg of (4-acetylphenyl)boronic acid affording the title compound as a white solid; 99% yield

$^1$H NMR (300 MHz, DMSO) $\delta$ 8.39 (s, 1H), 8.08 (d, $J$ = 8.3 Hz, 1H), 8.01 (d, $J$ = 8.3 Hz, 1H), 7.10 (t, 1H), 6.92 (d, $J$ = 7.6 Hz, 1H), 6.61 (dd, $J$ = 7.3, 0.6 Hz, 1H), 2.63 (s, 2H).
$^{11}$B NMR (100 MHz, CDCl$_3$) $\delta$ 29.4
$^{13}$C NMR (75 MHz, DMSO) $\delta$ 198.2, 142.1, 137.8, 135.9, 132.9, 127.6, 127.2, 119.8, 116.5, 105.8, 26.8.
MS : (ESI) : 287 (M+H$^+$, 100%), 397 (M+HCOOH+Na$^+$+CH$_3$CN, 85%).