Electronic Supplementary Information

A rapid construction of new boron heterocycles and evaluation for photophysical properties of iminoboronates

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Table of Contents
1. General Information. 2
2. Synthesis and Characterization of Amidoximes (1a-1e). 3
3. Synthesis and Characterization of the Oxadiazaborole Derivatives 3a–3k. 5
4. Synthesis and Characterization of α-Hydroxyl Oxime 4. 8
5. References 9
6. Synthesis and Characterization of Dioxazaborinine Derivatives 5a-5j. 10
7. Synthesis and Characterization of Oxadiazaborinine Derivatives 7a-7j. 14
8. Synthesis and Characterization of Iminoboronate 9a-9g. 18
9. NMR Spectra 21
10. High-resolution mass spectra of new compounds 150
11. Photophysical properties of 9a-9g. 182
1. General Information.
Commercial reagents were purchased from Meyer Reagent Co., Ltd., (Shanghai, China), Macklin Reagent Co., Ltd. (Shanghai, China), Chongqing Chuandong Chemical Co., Ltd. (Chongqing, China), etc., and used as received without further purification. $^1$H, $^{13}$C and $^{11}$B NMR spectra were recorded at Bruker Avance - III spectrometer (600 MHz, 151 MHz and 193 MHz) using TMS as internal standard. Chemical shifts were reported in ppm and coupling constants (J) in Hz. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets(dd), multiplet (m), triplet (t). UV-Vis spectra and fluorescence spectra were recorded on Shimadzu UV2600 and RF-5301PC, respectively. High-resolution mass spectra were recorded on a JEOL AccuTOF-MS or Agilent Q-TOF6550. TLC plates were visualized by exposing UV light. Purification of crude compounds and separation of reaction mixtures were carried out by column chromatography using silica gel (200-300 meshes, Shanghai, China).
2. Synthesis and Characterization of Amidoximes (1a-1e).  

**General procedure:** To a round-bottom flask was charged with benzonitrile (19.4 mmol, 1.0 equiv), hydroxylamine hydrochloride (29.1 mmol, 1.5 equiv), triethylamine (29.1 mmol, 1.5 equiv) and ethanol (15 mL). The resulting mixture was warmed to 70 °C under reflux for 5 h. When the reaction was completed, reduced the temperature to 25 °C, then, the solvent was removed under reduced pressure and a saturated solution of NaCl (25 mL) was added. Subsequently, the aqueous phase was extracted with ethyl acetate (4 × 20 mL), and dried over anhydrous Na₂SO₄ and concentrated in vacuum with silica gel added. The residue was purified by column chromatography (petroleum ether/ethyl acetate 4:1) obtain the target product 1a.

**Characterization data:**

**Amidoxime (1a).** White solid (2.20 g, 85% yield), PE/EA = 4:1, mp 67-69 °C. ¹H NMR (600 MHz, DMSO-d₆): δ 9.63 (1 H, s), 7.69 – 7.67 (2 H, m), 7.38 – 7.36 (3 H, m), 5.80 (2 H, s). ¹³C NMR (151 MHz, DMSO-d₆): δ 151.29, 133.84, 129.33, 128.56, 125.85.

**Amidoxime (1b).** White solid (2.20 g, 87% yield), PE/EA = 4:1, mp 124-127 °C. ¹H NMR (600 MHz, DMSO-d₆): δ 9.52 (1 H, s), 7.56 (2 H, d, J 8.2), 7.17 (2 H, d, J 8.0), 5.73 (1 H, s), 2.31 (3 H, s). ¹³C NMR (151 MHz, DMSO-d₆): δ 151.24, 138.71, 131.03, 129.10, 125.74, 21.28.

**Amidoxime (1c).** White solid (2.20 g, 90% yield), PE/EA = 4:1, mp 107-110 °C. ¹H NMR (600 MHz, DMSO-d₆): δ 9.44 (1 H, s), 7.61 (2 H, d, J 8.9), 6.92 (2 H, d, J 8.9), 5.71 (2 H, s), 3.77 (3 H, s). ¹³C NMR (151 MHz, DMSO-d₆): δ 160.27, 151.05, 127.17, 126.24, 113.91, 55.61.

**Amidoxime (1d).** White solid (2.00 g, 87% yield), PE/EA = 4:1, mp 157-160 °C. ¹H NMR (600 MHz, DMSO-d₆): δ 9.71 (1 H, s), 7.74 (2 H, d, J 8.3), 7.47 (2 H, d, J 8.1), 5.83 (2 H, s). ¹³C NMR (151 MHz, DMSO-d₆): δ 150.61, 137.36, 133.38, 127.90, 95.70.

S3
Amidoxime (1e). White solid (2.20 g, 85% yield), PE/EA = 4:1, mp 79-81 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 9.63 (1 H, s), 7.73 – 7.70 (2 H, m), 7.20 (2 H, t, $J$ 8.9), 5.83 (2 H, s). $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 163.79, 162.16, 150.52, 130.31, 130.29, 128.02, 127.96, 115.49, 115.34.

**General procedure:** Amidoxime 1 (1.1 mmol, 1.0 equiv), phenylboronic acid 2 (1.1 mmol, 1.0 equiv) derivatives and ethyl acetate (2 mL) were mixed together in round-bottom flask and stirred at room temperature for 5 min. Reaction progress was monitored with TLC. When the reaction was completed, excess of petroleum ether (5 mL) was added to round bottom flask, the product immediately precipitated from the reaction system. After filtration and washing with a mixed solvent of ethyl acetate and petroleum ether (15:1), the pure product was obtained.

**Characterization data:**

3,5-diphenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3a). White solid (0.22 g, 92% yield); mp 158-160 °C. \(^{1}H\) NMR (600 MHz, DMSO-\(d_{6}\)) \(\delta\) 10.46 (1 H, s), 8.00 (2 H, dd, \(J\) 6.5, 3.2), 7.96 (2 H, d, \(J\) 6.5), 7.59 (3 H, dd, \(J\) 7.0, 3.8), 7.55 (1 H, d, \(J\) 7.2), 7.52 (2 H, t, \(J\) 7.1). \(^{13}C\) NMR (151 MHz, DMSO-\(d_{6}\)) \(\delta\) 159.75, 134.38, 131.59, 131.24, 129.45, 128.73, 127.20, 126.78. \(^{11}B\) NMR (193 MHz, DMSO-\(d_{6}\)) \(\delta\) 32.07.

3-phenyl-5-(p-tolyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (3b). White solid (0.22 g, 85% yield); mp 143-146 °C. \(^{1}H\) NMR (600 MHz, DMSO-\(d_{6}\)) \(\delta\) 10.36 (1 H, s), 7.98 – 7.95 (2 H, m), 7.83 (2 H, d, \(J\) 7.9), 7.58 – 7.53 (4 H, m), 7.32 (2 H, d, \(J\) 7.5), 2.37 (4 H, s). \(^{13}C\) NMR (151 MHz, DMSO-\(d_{6}\)) \(\delta\) 159.66, 141.31, 134.42, 131.22, 129.45, 129.41, 127.22, 126.74, 21.77. \(^{11}B\) NMR (193 MHz, DMSO-\(d_{6}\)) \(\delta\) 33.74.

5-(4-ethylphenyl)-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3c). White solid (0.23 g, 82% yield); mp 116-119 °C. \(^{1}H\) NMR (600 MHz, DMSO-\(d_{6}\)) \(\delta\) 10.37 (1 H, s), 7.97 (2 H, m), 7.83 (2 H, d, \(J\) 7.9), 7.58 – 7.57 (3 H, m), 7.35 (2 H, d, \(J\) 7.8), 2.67 (2 H, q, \(J\) 7.6), 1.22 (4 H, t, \(J\) 7.6). \(^{13}C\) NMR (151 MHz, DMSO-\(d_{6}\)) \(\delta\) 159.67, 147.51, 134.51, 131.22, 129.44, 128.22, 127.23, 126.75, 28.83, 15.80. \(^{11}B\) NMR (193 MHz, DMSO-\(d_{6}\)) \(\delta\) 32.86. HRMS (ESI): m/z [M + H]\(^{+}\) calculated for C\(_{15}\)H\(_{16}\)BN\(_2\)O: 251.1350, found: 251.1344.
5-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3d). White solid (0.24 g, 90% yield); mp 192-194 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) δ 10.46 (1 H, s), 8.03 – 8.00 (2 H, m), 7.99 – 7.97 (2 H, m), 7.60 – 7.58 (3 H, m), 7.36 (2 H, t, J 8.9). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 165.49, 163.84, 159.75, 136.91, 136.85, 131.27, 129.46, 127.12, 126.74, 115.99, 115.86. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 33.62. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{13}$H$_{11}$BN$_2$OF: 241.0943, found: 241.0939.

5-(4-nitrophenyl)-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3e). White solid (0.27 g, 93% yield); mp 254-256 °C, $^1$H NMR (600 MHz, DMSO-$d_6$) δ 10.71 (1 H, s), 8.35 (2 H, d, J 8.5), 8.18 (2 H, d, J 8.5), 7.97 (2 H, dd, J 6.4, 2.9), 7.61 – 7.57 (3 H, m). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 159.96, 149.60, 135.57, 131.40, 129.49, 126.87, 126.75. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 34.03.

5-(2,6-dimethylphenyl)-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3f). White solid (0.21 g, 80% yield); mp 148-151 °C, $^1$H NMR (600 MHz, DMSO-$d_6$) δ 10.26 (1 H, s), 7.95 (3 H, dd, J 6.6, 3.0), 7.58 – 7.53 (4 H, m), 7.25 (2 H, t, J 7.6), 7.07 (3 H, d, J 7.6), 2.31 (9 H, s). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 159.34, 141.91, 131.25, 130.05, 129.48, 127.10, 126.89, 22.89. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 33.97. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{15}$H$_{16}$BN$_2$O: 251.1350, found: 251.1345.

5-(naphthalen-1-yl)-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3g). White solid (0.25 g, 84% yield); mp 134-136 °C, $^1$H NMR (600 MHz, DMSO-$d_6$) δ 10.58 (1 H, s), 8.66 (1 H, d, J 8.4), 8.23 (1 H, d, J 6.8), 8.12 (1 H, d, J 8.1), 8.06 (3 H, d, J 4.6), 8.01 (1 H, d, J 8.1), 7.67 (3 H, dd, J 13.0, 6.3), 7.60 (5 H, t, J 6.2). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 159.70, 136.00, 135.73, 133.44, 131.80, 131.32, 129.47, 129.08, 128.37, 127.34, 127.13, 126.97, 126.46, 125.81. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 34.99. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{17}$H$_{14}$BN$_2$O: 273.1193, found: 273.1196.
3-(4-methoxyphenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3h). White solid (0.21 g, 92% yield); mp 176-179 °C, $^1$H NMR (600 MHz, DMSO-$d_6$) δ 10.33 (1 H, s), 7.94 (5 H, t, $J$ 7.4), 7.55 (1 H, t, $J$ 7.2), 7.51 (2 H, t, $J$ 7.2), 7.13 (3 H, d, $J$ 8.7), 3.85 (4 H, s). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 161.60, 159.41, 134.35, 131.52, 128.71, 128.34, 119.46, 114.85, 55.82. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 33.27.

5-phenyl-3-(p-tolyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (3i). White solid (0.21 g, 90% yield); mp 151-154 °C, $^1$H NMR (600 MHz, DMSO-$d_6$) δ 10.37 (1 H, s), 7.94 (2 H, d, $J$ 6.7), 7.87 (2 H, d, $J$ 8.1), 7.55 (1 H, t, $J$ 7.3), 7.51 (2 H, t, $J$ 7.2), 7.38 (2 H, d, $J$ 8.0), 2.39 (3 H, s). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 159.67, 141.05, 134.36, 131.55, 129.99, 128.72, 126.67, 124.38, 21.46. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 33.27.

3-(4-iodophenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3j). White solid (0.16 g, 83% yield); mp 219-221 °C, $^1$H NMR (600 MHz, DMSO-$d_6$) δ 10.49 (1 H, s), 7.97 (2 H, d, $J$ 6.7), 7.76 (2 H, d, $J$ 7.9), 7.55 (1 H, t, $J$ 7.3), 7.50 (2 H, t, $J$ 7.1). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 159.22, 138.35, 134.36, 131.67, 128.76, 128.56, 126.63, 98.39. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 33.67.

3-(4-fluorophenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3k). White solid (0.19 g, 82% yield); mp 192-195 °C, $^1$H NMR (600 MHz, DMSO-$d_6$) δ 10.48 (1 H, s), 8.04 (2 H, dd, $J$ 8.7, 5.4), 7.94 (2 H, d, $J$ 6.7), 7.56 (1 H, t, $J$ 7.3), 7.52 (2 H, t, $J$ 7.4), 7.44 (2 H, t, $J$ 8.8). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 164.79, 163.15, 158.96, 134.35, 131.62, 129.24, 129.19, 128.74, 123.76, 123.74, 116.65, 116.50. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 33.47. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{13}$H$_{11}$BN$_2$OF: 241.0943, found: 249.0941.

**General procedure:** To a round-bottom flask was charged with 2-hydroxyacetophenone (14.7 mmol, 1.0 equiv), hydroxylamine hydrochloride (22.0 mmol, 1.5 equiv), triethylamine (22.0 mmol, 1.5 equiv) and ethanol (15 mL). The resulting mixture was warmed to 70 °C under reflux for 2 h. When the reaction was completed, reduced the temperature to 25 °C, then, the solvent was removed under reduced pressure and a saturated solution of NaCl (25 mL) was added. Subsequently, the aqueous phase was extracted with ethyl acetate (4 × 20 mL), and dried over anhydrous Na₂SO₄ and concentrated in vacuum with silica gel added. The residue was purified by column chromatography (petroleum ether/ethyl acetate 3:1) obtain the target product 4.

**Characterization data:**

α-hydroxyl oxime 4. White solid (1.20 g, 55% yield); PE/EA = 3:1, mp 48-51 °C. ¹H NMR (600 MHz, DMSO-\(d_6\)) δ 11.31 (1 H, s), 7.65 (2 H, dd, \(J = 8.1, 1.5\)), 7.39 – 7.33 (3 H, m), 5.00 (1 H, t, \(J = 5.8\)), 4.60 (2 H, d, \(J = 5.8\)). ¹³C NMR (151 MHz, DMSO-\(d_6\)) δ 157.35, 135.78, 128.81, 128.48, 127.23, 53.46.
5. References


General procedure: $\alpha$-hydroxyl oxime 4 (1.0 mmol, 1.0 equiv), phenylboronic acid 2 (1.0 mmol, 1.0 equiv) derivatives and ethyl acetate (2 mL) were mixed together in round-bottom flask and stirred at room temperature for 5 min. Reaction progress was monitored with TLC. When the reaction was completed, excess of petroleum ether (5 mL) was added to round bottom flask, the product immediately precipitated from the reaction system. After filtration and washing with a mixed solvent of ethyl acetate and petroleum ether (15:1), the pure product was obtained.

Characterization data:

2,5-diphenyl-6H-1,3,4,2-dioxazaborinine (5a). White solid (0.21 g, 91% yield); mp 130-133 °C, $^1$H NMR (600 MHz, CDCl$_3$) δ 7.94 (1 H, d, J 7.8), 7.68 (1 H, d, J 7.0), 7.50 (1 H, dd, J 15.9, 7.3), 7.45 (1 H, t, J 7.3), 7.41 (1 H, t, J 7.5), 4.94 (1 H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 157.82, 134.27, 131.88, 131.66, 131.14, 128.98, 127.90, 125.65, 57.40. $^{11}$B NMR (193 MHz, DMSO-d$_6$) δ 24.13. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{14}$H$_{11}$BNO$_2$: 238.1033, found: 238.1030.

5-phenyl-2-(p-tolyl)-6H-1,3,4,2-dioxazaborinine (5b). White solid (0.21 g, 85% yield); mp 154-156 °C, $^1$H NMR (600 MHz, CDCl$_3$) δ 7.84 (1 H, d, J 7.9), 7.67 (1 H, d, J 7.0), 7.48 (0 H, t, J 7.2), 7.44 (1 H, t, J 7.3), 7.23 (1 H, d, J 7.8), 4.91 (1 H, s), 2.38 (2 H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 157.79, 142.14, 134.34, 131.74, 131.07, 128.95, 128.74, 125.63, 57.33, 21.83. $^{11}$B NMR (193 MHz, DMSO-d$_6$) δ 24.77. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{15}$H$_{15}$BNO$_2$: 252.1190, found: 252.1189.
2-(4-ethylphenyl)-5-phenyl-6H-1,3,4,2-dioxazaborinine (5c). White solid (0.22 g, 83% yield); mp 107-110 °C, $^1$H NMR (600 MHz, DMSO-$d_6$) δ 7.72 (1 H, t, J 7.7), 7.54 – 7.51 (1 H, m), 7.49 (0 H, t, J 7.2), 7.26 (0 H, d, J 8.0), 5.00 (0 H, s), 2.64 (0 H, q, J 7.6), 1.19 (1 H, t, J 7.6). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 158.79, 147.48, 134.08, 132.47, 131.20, 129.27, 127.80, 126.15, 57.57, 28.82, 15.81. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 27.10. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{16}$H$_{17}$BNO$_2$: 266.1346, found: 266.1343.

1-(4-(5-phenyl-6H-1,3,4,2-dioxazaborinin-2-yl) phenyl) ethan-1-one (5d). White solid (0.24 g, 87% yield); mp 226-228 °C, $^1$H NMR (600 MHz, CDCl$_3$) δ 8.03 (1 H, d, J 8.2), 7.98 (1 H, d, J 8.2), 7.68 (1 H, d, J 7.1), 7.51 (1 H, t, J 7.3), 7.47 (1 H, t, J 7.3), 4.98 (1 H, s), 2.63 (2 H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 198.39, 157.89, 139.51, 134.44, 131.42, 131.30, 129.02, 127.45, 125.67, 57.53, 26.79. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 28.34. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{16}$H$_{15}$BNO$_3$: 280.1139, found: 280.1137.

2-(4-nitrophenyl)-5-phenyl-6H-1,3,4,2-dioxazaborinine (5e). White solid (0.25 g, 90% yield); mp 218-220 °C, $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.12 (1 H, d, J 8.6), 7.78 (1 H, d, J 8.6), 7.66 (1 H, dd, J 6.7, 2.9), 7.43 (1 H, s), 4.64 (1 H, s). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 158.21, 147.45, 135.70, 134.55, 133.14, 129.88, 129.04, 125.41, 122.32, 57.36. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 27.75. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{14}$H$_{12}$BN$_2$O$_4$: 283.0884, found: 283.0876.

2-(4-bromophenyl)-5-phenyl-6H-1,3,4,2-dioxazaborinine (5f). White solid (0.25 g, 90% yield); mp 164-166 °C, $^1$H NMR (600 MHz, CDCl$_3$) δ 7.79 (1 H, d, J 8.2), 7.67 (1 H, d, J 7.1), 7.55 (1 H,
5-phenyl-2-(4-(trifluoromethyl) phenyl)-6H-1,3,4,2-dioxazaborinine (5g). White solid (0.25 g, 84% yield); mp 164-167 °C, $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$ 8.04 (1 H, d, J 7.9), 7.67 (2 H, t, J 8.8), 7.51 (1 H, t, J 7.3), 7.47 (1 H, t, J 7.4), 4.98 (1 H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 157.91, 140.80, 136.84, 134.55, 131.67, 131.12, 128.97, 125.71, 125.64, 115.22, 57.39. $^{11}$B NMR (193 MHz, DMSO-d$_6$) $\delta$ 21.10. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{15}$H$_{12}$BNO$_2$F$_3$: 306.0905, found: 306.0907.

5-phenyl-2-(4-vinylphenyl)-6H-1,3,4,2-dioxazaborinine (5h). White solid (0.21 g, 80% yield); mp 129-132 °C, $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$ 7.90 (1 H, d, J 8.1), 7.67 (1 H, d, J 7.0), 7.49 (0 H, t, J 7.2), 7.45 (2 H, dd, J 7.8, 4.7), 6.75 (1 H, dd, J 17.6, 10.9), 5.83 (1 H, d, J 17.6), 5.31 (1 H, d, J 10.9), 4.94 (1 H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 157.82, 140.80, 136.84, 134.55, 131.67, 131.12, 128.97, 125.71, 125.64, 115.22, 57.39. $^{11}$B NMR (193 MHz, DMSO-d$_6$) $\delta$ 21.10. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{16}$H$_{15}$BNO$_2$: 264.1190, found: 264.1187.

4-(5-phenyl-6H-1,3,4,2-dioxazaborinin-2-yl) benzonitrile (5i). White solid (0.21 g, 82% yield); mp 169-171 °C, $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$ 8.02 (1 H, d, J 8.2), 7.70 – 7.66 (2 H, m), 7.51 (0 H, t, J 7.3), 7.47 (1 H, t, J 7.4), 4.98 (1 H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 157.94, 134.57, 131.42, 131.34, 131.23, 129.06, 125.67, 118.76, 115.15, 57.63. $^{11}$B NMR (193 MHz, DMSO-d$_6$) $\delta$ 28.23. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{15}$H$_{12}$BN$_2$O$_2$: 263.0986, found: 263.0982.
2-(3,5-dimethylphenyl)-5-phenyl-6H-1,3,4,2-dioxazaborinine (5j). White solid (0.21 g, 81% yield); mp 80-82 °C, $^1$H NMR (600 MHz, CDCl$_3$) δ 7.67 (1 H, d, J 7.0), 7.56 (1 H, s), 7.48 (0 H, t, J 7.2), 7.44 (1 H, t, J 7.2), 7.14 (0 H, s), 4.92 (1 H, s), 2.34 (3 H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 157.74, 137.24, 133.61, 131.99, 131.73, 131.07, 128.95, 125.64, 57.36, 21.27. $^{11}$B NMR (193 MHz, DMSO-d$_6$) δ 25.06. HRMS (ESI): HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{16}$H$_{16}$BNO$_2$: 266.1322, found: 266.1357.

2-([1,1'-biphenyl]-4-yl)-5-phenyl-6H-1,3,4,2-dioxazaborinine (5l). White solid (0.09 g, 60% yield); mp 208-210 °C, $^1$H NMR (600 MHz, CDCl$_3$) δ 8.01 (1 H, d, J 8.2), 7.69 (1 H, d, J 6.9), 7.66 – 7.63 (2 H, m), 7.52 – 7.48 (1 H, m), 7.46 (2 H, dd, J 14.8, 7.6), 7.36 (1 H, t, J 7.4), 4.97 (1 H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 157.84, 144.45, 140.90, 134.76, 131.70, 131.08, 128.94, 128.78, 127.65, 127.22, 126.58, 125.65, 57.42. $^{11}$B NMR (193 MHz, DMSO-d$_6$) δ 28.76. APCI-MS[M+H]$^-$ = 313.7.
7. Synthesis and Characterization of Oxadiazaborinine Derivatives 7a-7j.

**General procedure:** α-hydroxyl hydrazone \( 6 \) (1.0 mmol, 1.0 equiv), phenylboronic acid \( 2 \) (1.0 mmol, 1.0 equiv) derivatives and ethyl acetate (2 mL) were mixed together in round-bottom flask and stirred at room temperature for 5 min. Reaction progress was monitored with TLC. When the reaction was completed, excess of petroleum ether (5 mL) was added to round bottom flask, the product immediately precipitated from the reaction system. After filtration and washing with a mixed solvent of ethyl acetate and petroleum ether (15:1), the pure product was obtained.

**Characterization data:**

2,5-diphenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7a). White solid (0.21 g, 90% yield); mp 185-188 °C, \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \( \delta \) 9.75 (1 H, s), 7.82 (2 H, d, \( J \) 6.7), 7.70 (3 H, d, \( J \) 6.9), 7.48 – 7.37 (8 H, m), 5.04 (3 H, s). \(^{13}\)C NMR (151 MHz, DMSO-\(d_6\)) \( \delta \) 145.44, 135.35, 133.54, 131.19, 129.49, 128.99, 128.21, 125.22, 59.57. \(^{11}\)B NMR (193 MHz, DMSO-\(d_6\)) \( \delta \) 27.22. HRMS (ESI): m/z [M + H]+ calculated for C\(_{14}\)H\(_{14}\)BN\(_2\)O: 237.1193, found: 237.1198.

5-phenyl-2-(p-tolyl)-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7b). White solid (0.21 g, 84% yield); mp 135-138 °C, \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \( \delta \) 9.69 (1 H, s), 7.70 (4 H, dd, \( J \) 18.4, 7.4), 7.46 – 7.39 (3 H, m), 7.21 (2 H, d, \( J \) 7.6), 5.02 (2 H, s), 2.33 (1 H, s). \(^{13}\)C NMR (151 MHz, DMSO-\(d_6\)) \( \delta \) 150.04, 145.52, 140.16, 138.38, 134.18, 133.73, 133.65, 129.95, 64.24, 26.47. \(^{11}\)B NMR (193 MHz, DMSO-\(d_6\)) \( \delta \) 27.45. HRMS (ESI): m/z [M + H]+ calculated for C\(_{15}\)H\(_{15}\)BN\(_2\)O: 251.1360, found: 251.1360.
2-(4-ethylphenyl)-5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7c). White solid (0.22 g, 82% yield); mp 122-125 °C, ¹H NMR (600 MHz, DMSO-δ6) δ 9.69 (1 H, s), 7.74 (2 H, d, J 8.0), 7.69 (2 H, d, J 6.9), 7.45 – 7.38 (3 H, m), 7.23 (2 H, d, J 8.0), 5.02 (2 H, s), 2.62 (2 H, q, J 7.6), 1.19 (3 H, t, J 7.6). ¹³C NMR (151 MHz, DMSO-δ6) δ 147.02, 145.30, 135.41, 133.70, 129.43, 128.98, 127.70, 125.20, 59.49, 28.78, 15.86. ¹¹B NMR (193 MHz, DMSO-δ6) δ 27.46. HRMS (ESI): m/z [M + H]⁺ calculated for C₁₆H₁₈BN₂O: 265.1506, found: 265.1504.

2-(4-isopropylphenyl)-5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7d). White solid (0.22 g, 81% yield); mp 119-121 °C, ¹H NMR (600 MHz, CDCl₃) δ 7.63 (1 H, t, J 7.8), 7.54 (0 H, s), 7.41 – 7.34 (1 H, m), 7.26 (0 H, d, J 7.8), 5.02 (1 H, s), 2.96 – 2.88 (0 H, m), 1.26 (1 H, d, J 6.9). ¹³C NMR (151 MHz, CDCl₃) δ 152.01, 145.76, 134.99, 132.89, 129.28, 128.62, 126.22, 124.95, 59.80, 34.29, 23.85. ¹¹B NMR (193 MHz, DMSO-δ6) δ 27.64. HRMS (ESI): m/z [M + H]⁺ calculated for C₁₇H₂₀BN₂O: 279.1663, found: 279.1662.

2-(4-methoxyphenyl)-5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7e). White solid (0.22 g, 84% yield); mp 183-185 °C, ¹H NMR (600 MHz, DMSO-δ6) δ 9.65 (1 H, s), 7.77 (2 H, d, J 8.5), 7.68 (2 H, d, J 7.2), 7.41 (3 H, dt, J 21.3, 7.0), 6.95 (2 H, d, J 8.5), 5.00 (2 H, s), 3.79 (3 H, s). ¹³C NMR (151 MHz, DMSO-δ6) δ 166.68, 149.87, 140.21, 140.07, 134.13, 133.72, 129.92, 118.61, 64.19, 60.16. ¹¹B NMR (193 MHz, DMSO-δ6) δ 27.27. HRMS (ESI): m/z [M + H]⁺ calculated for C₁₅H₁₆BN₂O₂: 267.1299, found: 267.1300.

2-(4-chlorophenyl)-5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7f). White solid (0.24 g, 88% yield); mp 179-181 °C, ¹H NMR (600 MHz, DMSO-δ6) δ 9.80 (1 H, s), 7.82 (2 H, d, J 8.3), 7.69 (2 H, d, J 6.7), 7.47 (2 H, d, J 8.3), 7.45 – 7.39 (3 H, m), 5.04 (2 H, s). ¹³C NMR (151 MHz, DMSO-δ6) δ 145.62, 136.23, 135.36, 135.25, 129.56, 128.98, 128.34, 125.25, 59.67. ¹¹B NMR (193 MHz, DMSO-δ6) δ 27.93. HRMS (ESI): m/z [M + H]⁺ calculated for C₁₄H₁₃BN₂OCl: 271.0804, found: 271.0798.
2-(4-nitrophenyl)-5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7g). Yellow solid (0.24 g, 86%); mp 191-194 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 9.97 (1 H, s), 8.23 (2 H, d, $J$ 8.6), 8.06 (2 H, d, $J$ 8.6), 7.71 (2 H, d, $J$ 6.4), 7.49 – 7.34 (3 H, m), 5.09 (2 H, s). $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 149.51, 146.08, 135.08, 134.71, 129.73, 129.00, 125.34, 122.87, 59.90. $^{11}$B NMR (193 MHz, DMSO-$d_6$) $\delta$ 27.68. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{14}$H$_{13}$BN$_3$O$_3$: 282.1044, found: 282.1040.

4-(5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinin-2-yl) benzonitrile (7h). White solid (0.22 g, 83%); mp 161-163 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 9.97 (1 H, s), 8.23 (2 H, d, $J$ 8.6), 8.06 (2 H, d, $J$ 8.6), 7.71 (2 H, d, $J$ 6.4), 7.49 – 7.34 (3 H, m), 5.09 (2 H, s). $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 146.00, 135.11, 134.06, 131.81, 129.70, 129.00, 125.32, 119.31, 113.49, 59.85. $^{11}$B NMR (193 MHz, DMSO-$d_6$) $\delta$ 28.17. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{15}$H$_{13}$BN$_3$O: 262.1146, found: 262.1141.

1-(4-(5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinin-2-yl) phenyl) ethan-1-one (7i). White solid (0.24 g, 85%); mp 205-207 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 14.61 (1 H, s), 12.69 (4 H, s), 12.44 (2 H, d, $J$ 6.7), 12.20 – 12.12 (3 H, m), 9.80 (2 H, s), 7.34 (3 H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 203.35, 150.55, 143.55, 139.97, 138.48, 134.37, 133.75, 132.47, 130.04, 64.48, 32.03. $^{11}$B NMR (193 MHz, DMSO-$d_6$) $\delta$ 28.57. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{16}$H$_{16}$BN$_2$O$_2$: 279.1299, found: 279.1303.
2-(3,5-dimethylphenyl)-5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7j). White solid (0.21 g, 80%); mp 69-71 °C, $^1$H NMR (600 MHz, CDCl$_3$) δ 7.63 (1 H, dd, $J$ 8.1, 1.5), 7.56 (0 H, s), 7.42 – 7.35 (2 H, m), 7.32 (1 H, s), 7.10 (0 H, s), 5.02 (1 H, s), 2.33 (3 H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 145.71, 137.38, 134.98, 132.70, 130.47, 129.29, 128.62, 124.96, 59.83, 21.33. $^{11}$B NMR (193 MHz, DMSO-$d_6$) δ 28.54. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{16}$H$_{18}$BN$_2$O: 265.1506, found: 265.1500.
8. Synthesis and Characterization of Iminoboronate 9a-9g.

**General procedure:** α-hydroxyl hydrazine 6 (1.0 mmol, 1.0 equiv), salicylaldehyde 8 (1.0 mmol, 1.0equiv), phenylboronic acid 2 (1.2 mmol, 1.2 equiv) derivatives and acetonitrile (2 mL) were mixed together in round-bottom flask and stirred and stirred at 80 °C for 1 h. Reaction progress was monitored with TLC. As soon as the reaction was complete, it was cooled to room temperature. After filtration and washing with methanol, the pure product was obtained.

**Characterization data:**

**Iminoboronate 9a.** light green solid (0.21 g, 61% yield); mp 249-251 °C, $^1$H NMR (600 MHz, CDCl$_3$) δ 8.53 (1 H, s), 7.76 (2 H, d, J 7.3), 7.48 (1 H, t, J 7.4), 7.44 – 7.39 (5 H, m), 7.36 (1 H, dd, J 7.8, 1.6), 7.23 (2 H, t, J 7.1), 7.19 (1 H, t, J 7.2), 6.97 (1 H, d, J 8.4), 6.85 (1 H, t, J 7.5), 5.16 (1 H, d, J 19.2), 4.85 (1 H, d, J 19.2). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 169.87, 160.31, 156.17, 138.05, 132.87, 132.01, 131.81, 130.84, 128.82, 127.65, 127.43, 126.46, 120.02, 119.63, 116.14, 63.89. $^{11}$B NMR (193 MHz, CDCl$_3$) δ 4.40. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{21}$H$_{18}$BN$_2$O$_2$: 341.1455, found: 341.1450.

**Iminoboronate 9b.** light green solid (0.20 g, 57% yield); mp 265-267 °C, $^1$H NMR (600 MHz, CDCl$_3$) δ 8.52 (1 H, s), 7.76 (2 H, d, J 7.2), 7.48 (1 H, t, J 7.4), 7.44 – 7.39 (3 H, m), 7.36 (1 H, dd, J 7.8, 1.6), 7.32 (2 H, d, J 7.8), 7.05 (2 H, d, J 7.6), 6.96 (1 H, d, J 8.4), 6.84 (1 H, t, J 7.5), 5.16 (1 H, d, J 19.2), 4.85 (1 H, d, J 19.2), 2.25 (4 H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 169.82, 160.35, 156.10, 137.98, 136.89, 132.91, 131.97, 131.78, 130.90, 128.80, 128.46, 126.45, 120.05, 119.57, 116.16, 63.90, 21.29. $^{11}$B NMR (193 MHz, CDCl$_3$) δ 4.44. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{22}$H$_{20}$BN$_2$O$_2$: 355.1612, found: 355.1614.
**Iminoboronate 9c.** light green solid (0.20 g, 55% yield); mp 234-236 °C, $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.52 (1 H, s), 7.76 (2 H, d, $J$ 7.3), 7.48 (1 H, t, $J$ 7.4), 7.44 – 7.39 (3 H, m), 7.35 (3 H, dd, $J$ 14.1, 4.8), 7.07 (2 H, d, $J$ 8.0), 6.96 (1 H, d, $J$ 8.4), 6.84 (1 H, t, $J$ 7.5), 5.16 (1 H, d, $J$ 19.2), 4.86 (1 H, d, $J$ 19.2), 2.56 (2 H, q, $J$ 7.6), 1.17 (3 H, t, $J$ 7.6). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 169.80, 160.38, 156.07, 143.14, 137.96, 132.93, 131.96, 131.78, 130.88, 128.80, 127.21, 126.46, 120.05, 119.54, 116.16, 63.90, 28.65, 15.30. $^{11}$B NMR (193 MHz, CDCl$_3$) $\delta$ 4.52. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{23}$H$_{22}$BN$_2$O$_2$: 369.1768, found: 369.1771.

**Iminoboronate 9d.** light green solid (0.25 g, 60% yield); mp 263-265 °C, $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.52 (1 H, s), 7.74 (2 H, d, $J$ 7.4), 7.48 (1 H, t, $J$ 7.4), 7.44 (1 H, t, $J$ 7.8), 7.40 (2 H, t, $J$ 7.7), 7.37 (1 H, d, $J$ 6.3), 7.33 (2 H, d, $J$ 8.2), 7.26 (2 H, d, $J$ 8.1), 6.95 (1 H, d, $J$ 8.4), 6.86 (1 H, t, $J$ 7.5), 5.14 (1 H, d, $J$ 19.3), 4.78 (1 H, d, $J$ 19.2). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 169.92, 160.09, 156.26, 138.27, 132.67, 132.16, 131.86, 130.75, 128.88, 126.43, 121.78, 119.95, 119.87, 116.01, 63.78. $^{11}$B NMR (193 MHz, CDCl$_3$) $\delta$ 4.18. HRMS (ESI): m/z [M + H]$^+$ calculated for C$_{21}$H$_{17}$BN$_2$O$_2$Br: 419.0561, found: 419.0566.

**Iminoboronate 9e.** light green solid (0.22 g, 58% yield); mp 235-238 °C, $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.61 (1 H, s), 8.05 (2 H, d, $J$ 8.7), 7.76 (2 H, d, $J$ 7.2), 7.56 (2 H, d, $J$ 8.6), 7.49 (2 H, dt, $J$ 8.7, 4.6), 7.43 (3 H, t, $J$ 7.5), 6.98 (1 H, d, $J$ 8.4), 6.92 (1 H, t, $J$ 7.5), 5.18 (1 H, d, $J$ 19.3), 4.77 (1 H, d, $J$ 19.4). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 169.96, 159.81, 156.58, 147.73, 138.61, 132.41, 132.38, 132.02, 131.66, 128.96, 126.44, 122.58, 120.23, 119.88, 115.87, 63.62. $^{11}$B NMR (193 MHz,
CDCl₃ δ 3.66. **HRMS** (ESI): m/z [M + H]⁺ calculated for C₂₁H₁₇BN₃O₄: 386.1306, found: 386.1308.

![Iminoboronate 9f](image)

**Iminoboronate 9f**. light green solid (0.21 g, 57% yield); mp 257-259 °C, **¹H NMR** (600 MHz, CDCl₃) δ 8.40 (1 H, s), 7.71 (2 H, d, J 7.3), 7.44 (1 H, t, J 7.4), 7.41 (1 H, d, J 6.7), 7.37 (2 H, t, J 7.6), 7.22 (3 H, dd, J 14.2, 6.2), 7.17 (1 H, t, J 7.2), 6.44 – 6.39 (2 H, m), 5.10 (1 H, d, J 19.0), 4.79 (1 H, d, J 19.0), 3.77 (3 H, s). **¹³C NMR** (151 MHz, CDCl₃) δ 168.27, 167.77, 162.95, 154.98, 133.20, 133.06, 131.59, 130.88, 128.74, 127.64, 127.35, 126.26, 109.97, 109.68, 102.48, 63.79, 55.68. **¹¹B NMR** (193 MHz, CDCl₃) δ 4.11. **HRMS** (ESI): m/z [M + H]⁺ calculated for C₂₂H₂₀BN₂O₃: 371.1561, found: 371.1565.

![Iminoboronate 9g](image)

**Iminoboronate 9g**. light green solid (0.25 g, 62% yield); mp 251-253 °C, **¹H NMR** (600 MHz, CDCl₃) δ 8.23 (1 H, s), 7.71 (2 H, d, J 7.2), 7.45 (2 H, d, J 6.7), 7.41 (1 H, t, J 7.3), 7.36 (2 H, t, J 7.4), 7.22 (2 H, t, J 7.2), 7.16 (1 H, t, J 7.3), 7.12 (1 H, d, J 9.0), 6.21 (1 H, d, J 6.8), 6.12 (1 H, s), 5.07 (1 H, d, J 18.7), 4.76 (1 H, d, J 18.7), 3.39 (2 H, dq, J 14.3, 7.1), 1.16 (6 H, t, J 7.1). **¹³C NMR** (151 MHz, CDCl₃) δ 164.63, 162.19, 155.45, 153.38, 133.87, 133.54, 131.08, 130.89, 128.61, 127.48, 126.95, 125.99, 106.47, 105.72, 99.37, 63.53, 44.99, 12.68. **¹¹B NMR** (193 MHz, CDCl₃) δ 3.68. **HRMS** (ESI): m/z [M + H]⁺ calculated for C₂₅H₂₅BN₃O₂: 412.2190, found: 412.2193.
9. NMR Spectra

Fig. S1 $^1$H NMR for compound 1a (600 MHz, DMSO-$d_6$)
Fig. S2 $^{13}$C NMR for compound 1a (151 MHz, DMSO-$d_6$)
Fig. S3 $^1$H NMR for compound 1b (600 MHz, DMSO-$d_6$)
Fig. S4 $^{13}$C NMR for compound 1b (151 MHz, DMSO-$d_6$)
Fig. S5 $^1$H NMR for compound 1c (600 MHz, DMSO-$d_6$)
Fig. S6 $^{13}$C NMR for compound 1c (151 MHz, DMSO-$d_6$)
Fig. S7 $^1$H NMR for compound 1d (600 MHz, DMSO-$d_6$)
Fig. S8 $^{13}$C NMR for compound 1d (151 MHz, DMSO-$d_6$)
Fig. S9 $^1$H NMR for compound 1e (600 MHz, DMSO-$d_6$)
Fig. S10 $^{13}$C NMR for compound 1e (151 MHz, DMSO-$d_6$)
Fig. S11 $^1$H NMR for compound 3a (600 MHz, DMSO-$d_6$)
Fig. S12 $^{13}$C NMR for compound 3a (151 MHz, DMSO-$d_6$)
Fig. S13 $^{11}$B NMR for compound 3a (193 MHz, DMSO-$d_6$)
Fig. S14 $^1$H NMR for compound 3b (600 MHz, DMSO-$d_6$)
Fig. S15 $^{13}$C NMR for compound 3b (151 MHz, DMSO-$d_6$)
Fig. S16 $^{11}$B NMR for compound 3b (193 MHz, DMSO-$d_6$)
Fig. S17 $^1$H NMR for compound 3c (600 MHz, DMSO-$d_6$)
Fig. S18 $^{13}$C NMR for compound 3c (151 MHz, DMSO-$d_6$)
Fig. S19 $^{11}$B NMR for compound 3c (193 MHz, DMSO-$d_6$)
Fig. S20 $^1$H NMR for compound 3d (600 MHz, DMSO-$d_6$)
Fig. S21 $^{13}$C NMR for compound 3d (151 MHz, DMSO-$d_6$)
Fig. S22 $^{11}$B NMR for compound 3d (193 MHz, DMSO-$d_6$)
Fig. S23 $^1$H NMR for compound 3e (600 MHz, DMSO-$d_6$)
Fig. S24 $^{13}$C NMR for compound 3e (151 MHz, DMSO-\textit{d}_6)
Fig. S25 $^{11}$B NMR for compound 3e (193 MHz, DMSO-$d_6$)
Fig. S26 $^1$H NMR for compound 3f (600 MHz, DMSO-$d_6$)
Fig. S27 $^{13}$C NMR for compound 3f (151 MHz, DMSO-$d_6$)
Fig. S28 $^{11}$B NMR for compound 3f (193 MHz, DMSO-$d_6$)
Fig. S29 $^1$H NMR for compound 3g (600 MHz, DMSO-$d_6$)
Fig. S30 $^{13}$C NMR for compound 3g (151 MHz, DMSO-$d_6$)
Fig. S31 \(^{11}\text{B} \text{NMR for compound 3g (193 MHz, DMSO-}d_6\text{)}\)
Fig. S32 $^1$H NMR for compound 3h (600 MHz, DMSO-$d_6$)
Fig. S33 $^{13}$C NMR for compound 3h (151 MHz, DMSO-$d_6$)
Fig. S34 $^{11}$B NMR for compound 3h (193 MHz, DMSO-$d_6$)
Fig. S35 $^1$H NMR for compound 3i (600 MHz, DMSO-$d_6$)
Fig. S36 $^{13}$C NMR for compound 3i (151 MHz, DMSO-$d_6$)
Fig. S37 $^{11}$B NMR for compound 3l (193 MHz, DMSO-$d_6$)
Fig. S38 $^1$H NMR for compound 3j (600 MHz, DMSO-$d_6$)
Fig. S39 $^{13}$C NMR for compound 3j (151 MHz, DMSO-$d_6$)
Fig. S40 $^{11}$B NMR for compound 3j (193 MHz, DMSO-$d_6$)
Fig. S41 $^1$H NMR for compound 3k (600 MHz, DMSO-$d_6$)
Fig. S42 $^{13}$C NMR for compound 3k (151 MHz, DMSO-$d_6$)
Fig. S43 $^{11}$B NMR for compound 3k (193 MHz, DMSO-$d_6$)
Fig. S44 $^1$H NMR for compound 4a (600 MHz, DMSO-$d_6$)
Fig. S45 $^{13}$C NMR for compound 4a (151 MHz, DMSO-$d_6$)
Fig. S46 $^1$H NMR for compound 5a (600 MHz, CDCl$_3$)
Fig. S47 $^{13}$C NMR for compound 5a (151 MHz, CDCl$_3$)
Fig. S48 $^{11}$B NMR for compound 5a (193 MHz, DMSO-$d_6$)
Fig. S49 $^1$H NMR for compound 5b (600 MHz, CDCl$_3$)
Fig. S50 $^{13}$C NMR for compound 5b (151 MHz, CDCl$_3$)
Fig. S51 $^{11}$B NMR for compound 5b (193 MHz, DMSO-$d_6$)
Fig. S52 $^1$H NMR for compound 5c (600 MHz, DMSO-$d_6$)
Fig. S53 $^{13}$C NMR for compound 5c (151 MHz, DMSO-$d_6$)
Fig. S54 ¹¹B NMR for compound 5c (193 MHz, DMSO-d₆)
Fig. S55 $^1$H NMR for compound 5d (600 MHz, CDCl$_3$)
Fig. S56 $^{13}$C NMR for compound 5d (151 MHz, CDCl$_3$)
Fig. S57 $^{11}$B NMR for compound 5d (193 MHz, DMSO-$d_6$)
Fig. S58 \(^1\)H NMR for compound 5e (600 MHz, DMSO-\(d_6\))
Fig. S59 $^{13}$C NMR for compound 5e (151 MHz, DMSO-$d_6$)
Fig. S60 $^{11}$B NMR for compound 5e (193 MHz, DMSO-$d_6$)
Fig. S61 $^1$H NMR for compound 5f (600 MHz, CDCl$_3$)
Fig. S62 ¹³C NMR for compound 5f (151 MHz, CDCl₃)
Fig. S63 $^{11}$B NMR for compound 5f (193 MHz, DMSO-$d_6$)
Fig. S64 $^1$H NMR for compound 5g (600 MHz, CDCl$_3$)
Fig. S65 $^{13}$C NMR for compound 5g (151 MHz, CDCl$_3$)
Fig. S66 $^{11}$B NMR for compound 5g (193 MHz, DMSO-$d_6$)
Fig. S67 $^1$H NMR for compound 5h (600 MHz, CDCl$_3$)
Fig. S68 $^{13}$C NMR for compound 5h (151 MHz, CDCl$_3$)
Fig. S69 $^{11}$B NMR for compound 5h (193 MHz, DMSO-$d_6$)
Fig. S70 $^1$H NMR for compound 5i (600 MHz, CDCl$_3$)
**Fig. S71** $^{13}$C NMR for compound 5i (151 MHz, CDCl$_3$)
Fig. S72 $^{11}$B NMR for compound 5i (193 MHz, DMSO-$d_6$)
Fig. S73 $^1$H NMR for compound 5j (600 MHz, CDCl$_3$)
Fig. S74 $^{13}$C NMR for compound 5j (151 MHz, CDCl$_3$)
Fig. S75 $^{11}$B NMR for compound 5j (193 MHz, DMSO-$d_6$)
Fig. S76 $^1$H NMR for compound 5l (600 MHz, CDCl$_3$)
Fig. S77 $^{13}$C NMR for compound 51 (151 MHz, CDCl$_3$)
Fig. S78 $^{11}$B NMR for compound 5l (193 MHz, DMSO-$d_6$)
Fig. S79 $^1$H NMR for compound 7a (600 MHz, DMSO-$d_6$)
Fig. S80 $^{13}$C NMR for compound 7a (151 MHz, DMSO-$d_6$)
Fig. S81 $^{11}$B NMR for compound 7a (193 MHz, DMSO-$d_6$)
Fig. S82 $^1$H NMR for compound 7b (600 MHz, DMSO-$d_6$)
Fig. S83 $^{13}$C NMR for compound 7b (151 MHz, DMSO-$d_6$)
Fig. S84 $^{11}$B NMR for compound 7b (193 MHz, DMSO-$d_6$)
Fig. S85 $^1$H NMR for compound 7c (600 MHz, DMSO-$d_6$)
Fig. S86 $^{13}$C NMR for compound 7c (151 MHz, DMSO-$d_6$)
Fig. S87 $^{11}$B NMR for compound 7c (193 MHz, DMSO-$d_6$)
Fig. S88 $^1$H NMR for compound 7d (600 MHz, CDCl$_3$)
Fig. S89 $^{13}$C NMR for compound 7d (151 MHz, CDCl$_3$)
Fig. S90 $^{11}$B NMR for compound 7d (193 MHz, DMSO-$d_6$)
Fig. S91 $^1$H NMR for compound 7e (600 MHz, DMSO-$d_6$)
Fig. S92 $^{13}$C NMR for compound 7e (151 MHz, DMSO-$d_6$)
Fig. S93 $^{11}B$ NMR for compound 7e (193 MHz, DMSO-$d_6$)
Fig. S94 $^1$H NMR for compound 7f (600 MHz, DMSO-$d_6$)
Fig. S95 $^{13}$C NMR for compound 7f (151 MHz, DMSO-$d_6$)
Fig. S96 $^{11}$B NMR for compound 7f (193 MHz, DMSO-$d_6$)
Fig. S97 $^1$H NMR for compound 7g (600 MHz, DMSO-$d_6$)
Fig. S98 $^{13}$C NMR for compound 7g (151 MHz, DMSO-$d_6$)
Fig. S99 $^{11}$B NMR for compound 7g (193 MHz, DMSO-$d_6$)
Fig. S100 $^1$H NMR for compound 7h (600 MHz, CDCl$_3$)
Fig. S101 $^{13}$C NMR for compound 7h (151 MHz, CDCl$_3$)
Fig. S102 $^{11}$B NMR for compound 7h (193 MHz, DMSO-$d_6$)
Fig. S103 $^1$H NMR for compound 71 (600 MHz, CDCl$_3$)
**Fig. S104** $^{13}$C NMR for compound 7i (151 MHz, CDCl$_3$)
Fig. S105 $^{11}$B NMR for compound 7i (193 MHz, DMSO-$d_6$)
Fig. S106 $^1$H NMR for compound 7j (600 MHz, CDCl$_3$)
Fig. S107 $^{13}$C NMR for compound 7j (151 MHz, CDCl$_3$)
Fig. S108 $^{11}$B NMR for compound 7j (193 MHz, DMSO-$d_6$)
Fig. S109 $^1$H NMR for compound 9a (600 MHz, CDCl$_3$)
Fig. S110 $^{13}$C NMR for compound 9a (151 MHz, CDCl$_3$)
Fig. S111 $^1$B NMR for compound 9a (193 MHz, CDCl$_3$)
Fig. S112 $^1$H NMR for compound 9b (600 MHz, CDCl$_3$)
Fig. S113 $^{13}$C NMR for compound 9b (151 MHz, CDCl$_3$)
Fig. S114 $^{11}$B NMR for compound 9b (193 MHz, CDCl$_3$)
Fig. S115 $^1$H NMR for compound 9c (600 MHz, CDCl$_3$)
Fig. S116 $^{13}$C NMR for compound 9c (151 MHz, CDCl$_3$)
Fig. S117 $^{11}$B NMR for compound 9c (193 MHz, CDCl$_3$)
Fig. S118 $^1$H NMR for compound 9d (600 MHz, CDCl$_3$)
Fig. S119 $^{13}\text{C}$ NMR for compound 9d (151 MHz, CDCl$_3$)
Fig. S120 $^{11}$B NMR for compound 9d (193 MHz, CDCl$_3$)
Fig. S121 $^1$H NMR for compound 9e (600 MHz, CDCl$_3$)
Fig. S122 $^{13}$C NMR for compound 9e (151 MHz, CDCl$_3$)
Fig. S123 $^{11}$B NMR for compound 9e (193 MHz, CDCl$_3$)
Fig. S124 $^1$H NMR for compound 9f (600 MHz, CDCl$_3$)
Fig. S125 $^{13}$C NMR for compound 9f (151 MHz, CDCl$_3$)
Fig. S126 $^{11}$B NMR for compound 9f (193 MHz, CDCl$_3$)
Fig. S127 $^1$H NMR for compound 9g (600 MHz, CDCl$_3$)
Fig. S128 $^{13}$C NMR for compound 9g (151 MHz, CDCl$_3$)
Fig. S129 $^{11}$B NMR for compound 9g (193 MHz, CDCl$_3$)
10. High-resolution mass spectra of new compounds

**Fig. S130** 5-(4-ethylphenyl)-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3c).
Fig. S131 5-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3d).
Fig. S132 5-(2,6-dimethylphenyl)-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3f).
**Fig. S133** 5-(naphthalen-1-yl)-3-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3g).
**Fig. S134** 3-(4-fluorophenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (3k).
Fig. S135 2,5-diphenyl-6H-1,3,4,2-dioxaazaborinine (5a).
Fig. S136 5-phenyl-2-(p-tolyl)-6H-1,3,4,2-dioxazaborinine (5b).
Fig. S137 2-(4-ethylphenyl)-5-phenyl-6H-1,3,4,2-dioxazaborinine (5c).
Fig. S138 1-(4-(5-phenyl-6H-1,3,4,2-dioxazaborinin-2-yl)phenyl)ethan-1-one (5d).
Fig. S139 2-(4-nitrophenyl)-5-phenyl-6H-1,3,4,2-dioxazaborinine (5e).
Fig. S140 2-(4-bromophenyl)-5-phenyl-6H-1,3,4,2-dioxazaborinine (5f).
Fig. S141 5-phenyl-2-(4-(trifluoromethyl) phenyl)-6H-1,3,4,2-dioxazaborinine (5g).
Fig. S142 5-phenyl-2-(4-vinylphenyl)-6H-1,3,4,2-dioxazaborinine (5h).
Fig. S143 4-(5-phenyl-6H-1,3,4,2-dioxazaborinin-2-yl) benzonitrile (5i).
Fig. S144 2-(3,5-dimethylphenyl)-5-phenyl-6H-1,3,4,2-dioxazaborinine (5j).
Fig. S145 2,5-diphenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7a).
Fig. S146 5-phenyl-2-(p-tolyl)-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7b).
Fig. S147 2-(4-ethylphenyl)-5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7c).
Fig. S148 2-(4-isopropylphenyl)-5-phenyl-3,6-dihydro-2H-1,3,4-oxadiazaborinine (7d).
Fig. S149 2-(4-methoxyphenyl)-5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7e).
Fig. S150 2-(4-chlorophenyl)-5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7f).
Fig. S151 2-(4-nitrophenyl)-5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7g).
Fig. S152 4-(5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinin-2-yl) benzonitrile (7h).
Fig. S153 1-(4-(5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinin-2-yl) phenyl) ethan-1-one (7i).
Fig. S154 2-(3,5-dimethylphenyl)-5-phenyl-3,6-dihydro-2H-1,3,4,2-oxadiazaborinine (7j).
Fig. S155 Iminoborones (9a).
Fig. S156 Iminoboronates (9b).
Fig. S157 Iminoboranes (9c).
Fig. S158 Iminoboranes (9d).

MS: 0.9589-1.0756 / 27 / ESI+ / / (849)
Fig. S159 Iminoboranes (9e).
Fig. S160 Iminoboronates (9f).
Fig. S161 Iminoboronates (9g).
11. Photophysical properties of 9a-9g.

**Fig. S162** (a) Absorption spectra of 9a-9e (1 × 10^{-5} M), 9f (4 × 10^{-5} M) and 9g (1 × 10^{-6} M) in acetonitrile; (b) Fluorescence spectra of 9a-9e (1 × 10^{-5} M), 9f (4 × 10^{-6} M) and 9g (1 × 10^{-6} M) in acetonitrile (λ_{ex} = 295 nm); (c) and (d) Normalized absorption and emission spectra of 9a-9g, respectively.

**Table S163.** Photophysical Data of 9a-9g in Acetonitrile$^a$

$^{a}$
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<tr>
<th>Entry</th>
<th>Compound</th>
<th>λ_{abs} (nm)</th>
<th>ε_{max} (M^{-1}cm^{-1})</th>
<th>λ_{ex} (nm)</th>
<th>Stokes shift (nm)</th>
<th>Φ_F^{b,c}</th>
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<td>47000</td>
<td>478</td>
<td>53</td>
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</table>

*a* Absorption and fluorescence spectra of 9a-9e (1 × 10^{-5} M), 9f (4 × 10^{-6} M) and 9g (1 × 10^{-6} M) in acetonitrile (λ_{ex} = 348 nm) at room temperature.

*b* Fluorescence quantum yields (Φ_F) were measured in acetonitrile at room temperature (9a-9e (1 × 10^{-5} M), 9f (4 × 10^{-6} M) and 9g (1 × 10^{-6} M)) and the reference standard is 1 × 10^{-6} M Rhodamine B (λ_{ex} = 348 nm, quantum yield = 0.7 in methanol).

*c* The Φ_F values of the compounds were calculated according to the following equation:

\[
Φ_F(s) = Φ_F(ref) \times \frac{F(s)}{F(ref)} \times \frac{Ab(ref)}{Ab(s)} \times \frac{n(ref)^2}{n(s)^2}
\]

where \(F\) is the area under the emission spectra with excitation at 348 nm, \(Ab\) is the absorbance at 348 nm (no more than 0.05), \(n\) is the index of the refractive index of the solvent (MeCN: 1.34 MeOH: 1.32), and the symbols s and ref in brackets represent the sample and reference, respectively.