Supporting Information

**Photoinduced Successive Oxidative Ring-Opening and Borylation of Indolizines with NHC-Boranes**

Guangdong Cosmetics Engineering & Technology Research Center, School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Zhongshan 528458, China

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1. General considerations

Unless otherwise noted, commercial reagents were purchased from Adamas, Alfa Aesar, TCI, or Maclin and used without further purification. All reactions were carried out using oven-dried glassware and all catalytic reactions proceeded without special care. Column chromatography was performed on 200-300 mesh silica gel (Huanghai, China).

$^1$H, $^{19}$F and $^{13}$C($^1$H) NMR spectra were recorded on an Bruker Ascend 400MHz spectrometer and Bruker Ultrashield 300MHz at ambient temperature. $^1$H NMR spectra are referred to the TMS signal (δ = 0 ppm) and $^{13}$C NMR spectra are referred to the residual solvent signal (δ = 77.16 ppm). Data for $^1$H NMR are reported as follows: chemical shifts (δ ppm), multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration.

Photochemical reaction experiments were carried out on a PL-SX100A Model Multi-channel photochemical reaction instrument (the light source is 20 W blue LED, the working current is 0.5-1.7 A, the input power is 120 W, the temperature is controlled by circulating water cooling, and the stirring speed is 0-1500 r/min). The material of the irradiation vessel is borosilicate glass and it is 3 cm away from the light source. The data of HRMS was carried out on a waters G2-XS high-resolution mass spectrometer (HR-ESI-MS) or Agilent 7250 GC/QTOF.

Note: In the $^{13}$C NMR spectral data, the carbons connected to boron are not listed due to quadrupole broadening and spin–spin coupling with boron.
2. Experimental procedures and characterization data

2.1 Experimental procedures

Synthesis of compounds 1 according to the following procedure1-2:

As exemplified for 1a:

\[
\text{A solution of 2-picoline (0.93 g, 10 mmol, 1.0 equiv.) and 2 bromoacetophenone (1.99 g, 10 mmol, 1.0 equiv.) in acetone (50 mL) were added to a 100 mL round bottom flask and heated with a heating mantle at 60 °C for 5 hours. The precipitate obtained by filtration separation was redissolved in 20 mL of hot water (60 °C). Then, K}_2\text{CO}_3 (1.38 g, 10 mmol, 1.0 equiv.) was added and heated at 60 °C for 5 hours. After filtration and drying in vacuo, a white solid compound was obtained in 50% overall yield (0.965 g, 5 mmol) without further purification.}
\]

Synthesis of NHC-BH\textsubscript{3} compounds 2 according to the following procedure3:

As exemplified for 2a:

\[
\text{To a mixture of 1-methylimidazole (50 mmol, 1.0 equiv.) in CH}_2\text{Cl}_2 (10 mL) was added methyl iodide (60 mmol, 1.2 equiv.) dropwise over 15 min at 0 °C. The mixture was allowed to stir for 2 h at room temperature. The crude product was then obtained after removing the solvent, and directly used for next step without further purification. To a mixture of imidazolium salt (40 mmol, 1.0 equiv) in toluene (40 mL) was added sodium borohydride (48 mmol, 1.2 equiv). The flask was fitted with a cold water condenser and placed in an oil bath at 125-130 °C for 24 h. The hot reaction solvent was cautiously decanted from the insoluble mixture, and the remaining residue was extracted with hot toluene (20 mL × 2 times). The organic extracts were combined, concentrated, and further recrystallized over water to give the pure product as a fine white crystal (3.7 g).}
\]

Synthesis of products 3 and 4 according to the following procedure:

As exemplified for 3a:

S3
A 25 mL sealed tube was charged with a stirring bar, and added 2-phenylindolizine (1a, 38.6 mg, 0.2 mmol), NHC-borane (2a, 44 mg, 0.4 mmol), NaOAc(32.8 mg, 0.4 mmol), rose bengal (10 mg, 0.01 mmol), and MeCN (2.0 mL). The reaction was irradiated with a 20W blue LED at room temperature stirring for 12 h and monitored by TLC. The reaction mixture was then diluted with EtOAc and water, extracted with EtOAc. The organic layers were washed with brine and dried over MgSO$_4$, evaporated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 1 : 1) to give 3a in 72% yield (47.9 mg).

**Scale-up reaction for 3a:**
A 50 mL round bottom flask was charged with a stirring bar, and added 2-phenylindolizine (1a, 193 mg, 1 mmol), NHC-borane (2a, 220 mg, 2 mmol), NaOAc (164 mg, 2 mmol), rose bengal (50 mg, 0.05 mmol), and MeCN (10.0 mL). The reaction was irradiated with a 20W blue LED at room temperature stirring for 12 h and monitored by TLC. The reaction mixture was then diluted with EtOAc and water, extracted with EtOAc. The organic layers were washed with brine and dried over MgSO$_4$, evaporated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 1 : 1) to give 3a in 70% yield (222.6 mg).

**On/Off experiment**
Standard reactions were set up parallel on a 0.20 mmol scale. After being irradiated for 2 h, an aliquot (150 μL) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.5 mL of CDCl$_3$. The yield of product 3a was determined by $^1$H NMR. Then the reaction mixture was stirred for 2 h with light-off. All of the following yields were analyzed in the identical way after a 2 h light on or off.
2.2 Characterization data

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-phenyl-3-(pyridin-2-yl)acryloyloxy)dihydroborate (3a)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3a.
Brown liquid (47.9 mg, 72%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.39 (d, $J = 3.9$ Hz, 1H), 7.54 (d, $J = 8.3$ Hz, 3H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.33 – 7.27 (m, 3H), 7.07 – 7.03 (m, 1H), 6.87 (s, 1H), 6.85 (s, 2H), 3.74 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.2, 155.0, 149.1, 141.9, 137.2, 136.2, 128.6, 128.3, 126.5, 125.2, 123.1, 121.8, 120.8, 36.2. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -13.51. IR (KBr): 3416, 3125, 2954, 1672, 1382, 1113, 778, cm$^{-1}$. HR-ESI-MS (m/z): calcd for C$_{19}$H$_{21}$BN$_3$O$_2$ [M + H]$^+$: 334.1722, found: 334.1728.

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(3-(3-methylpyridin-2-yl)-2-phenylacryloyloxy)dihydroborate (3b)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3b.
Brown liquid (48.6 mg, 70%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J = 3.1$ Hz, 1H), 7.64 – 7.54 (m, 2H), 7.41 – 7.25 (m, 4H), 6.99 – 6.93 (m, 1H), 6.92 (s, 1H), 6.86 (s, 2H), 3.79 (s, 6H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.3, 153.2, 146.2, 142.4, 137.9, 137.5, 131.4, 128.4, 128.1, 126.8, 122.2, 121.7, 120.6, 36.1, 19.0. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -15.51 (t, $J = 134.7$ Hz). IR (KBr): 3416, 3121, 2925, 1671, 1377, 1113, 764, cm$^{-1}$. HR-ESI-MS (m/z): calcd for C$_{20}$H$_{23}$BN$_3$O$_2$ [M + H]$^+$: 348.1877, found: 348.1865.

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl) (3-(4-methylpyridin-2-yl)-2-phenylacryloyloxy)dihydroborate (3c)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3c.
Red brown liquid (50.6 mg, 73%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 (d, $J = 5.0$ Hz, 1H), 7.57 – 7.50 (m, 2H), 7.37 – 7.27 (m, 5H), 6.90 (d, $J = 4.5$ Hz, 1H), 6.85 (s, 2H), 3.75 (s, 6H), 2.31 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.1, 154.7, 148.7, 147.1, 141.5, 137.3, 128.5, 128.1, 126.4, 125.3, 124.0, 122.8, 120.8, 36., 21.1. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -17.23. IR (KBr): 3416, 3163, 2956, 1671, 1301, 1113, 699, cm$^{-1}$. HR-ESI-MS (m/z): calcd for C$_{20}$H$_{23}$BN$_3$O$_2$ [M + H]$^+$: 348.1877, found: 348.1891.
(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)((3-(3,5-dimethylpyridin-2-yl)-2-phenylacryloyl)oxy)dihydroborate (3d)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3d. Brown liquid (49.1 mg, 68%). 1H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 2.1 Hz, 1H), 7.55 (d, J = 7.0 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.19 (s, 1H), 6.89 (s, 1H), 6.85 (s, 2H), 3.77 (s, 6H), 2.33 (s, 3H), 2.23 (s, 3H). 13C NMR (100 MHz, CDCl₃) δ 172.5, 150.5, 146.7, 141.6, 138.1, 138.0, 131.1, 130.9, 128.4, 127.9, 126.8, 122.4, 120.6, 36.1, 18.8, 18.2. 11B NMR (128 MHz, CDCl₃) δ -14.84. IR (KBr): 3409, 3158, 2958, 1694, 1401, 1082, 771, cm⁻¹. HR-ESI-MS (m/z): calcd for C₂₁H₂₅BN₃O₂ [M + H]^⁺: 362.2034, found: 362.2025.

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)((3-(3,5-dimethylpyridin-2-yl)-2-phenylacryloyl)oxy)dihydroborate (3e)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3e. Brown liquid (46.2 mg, 64%). 1H NMR (400 MHz, CDCl₃) δ 8.28 (s, 1H), 7.53 (d, J = 7.3 Hz, 2H), 7.39 (s, 2H), 7.36 – 7.27 (m, 3H), 6.87 (s, 1H), 6.85 (s, 2H), 3.74 (s, 6H), 2.61 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H). 13C NMR (100 MHz, CDCl₃) δ 172.2, 152.4, 148.8, 140.8, 137.4, 137.2, 135.5, 128.5, 128.1, 126.3, 125.2, 122.6, 120.8, 36.0, 25.9, 15.4. 11B NMR (128 MHz, CDCl₃) δ -13.76. IR (KBr): 3393, 3117, 2965, 1671, 1380, 1112, 759, cm⁻¹. HR-ESI-MS (m/z): calcd for C₂₁H₂₅BN₃O₂ [M + H]^⁺: 362.2034, found: 362.2041.

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)((3-(4-methoxypyridin-2-yl)-2-phenylacryloyl)oxy)dihydroborate (3f)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3f. Yellow brown liquid (42.8 mg, 59%). 1H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 5.7 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.37 – 7.26 (m, 3H), 7.11 (d, J = 2.4 Hz, 1H), 6.86 (s, 1H), 6.85 (s, 2H), 6.65 – 6.61 (m, 1H), 3.87 (s, 3H), 3.74 (s, 6H). 13C NMR (100 MHz, CDCl₃) δ 172.0, 165.9, 156.6, 150.1, 141.9, 137.1, 128.5, 128.3, 126.5, 125.4, 120.9, 109.00, 108.1, 55.3, 36.1. 11B NMR (128 MHz, CDCl₃) δ -13.89. IR (KBr): 3323,
3-(3-Bromopyridin-2-yl)-2-phenylacryloyloxy)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (3g)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3g.
Brown liquid (46.0 mg, 56%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (d, $J = 3.1$ Hz, 1H), 7.78 (d, $J = 6.5$ Hz, 1H), 7.59 (d, $J = 6.4$ Hz, 2H), 7.37 – 7.29 (m, 3H), 7.20 (s, 1H), 6.92 (dd, $J = 8.1$, 4.6 Hz, 1H), 6.86 (s, 2H), 3.79 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.9, 152.6, 147.1, 144.2, 140.2, 137.2, 128.5, 127.4, 126.9, 122.8, 121.8, 121.1, 120.7, 36.1. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -14.72. IR (KBr): 3431, 3143, 2957, 1661, 1430, 1103, 781, cm$^{-1}$. HR-ESI-MS (m/z): calcd for C$_{19}$H$_{20}$BBrN$_3$O$_2$ [M + H]$^+$: 412.0827, found: 412.0837.

1,3-Dimethyl-1H-imidazol-3-ium-2-yl)((3-(pyridin-2-yl)-2-(p-toly)acryloyloxy)dihydroborate (3h)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3h.
Brown liquid (49.3 mg, 71%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.39 (d, $J = 4.9$ Hz, 1H), 7.57 – 7.53 (m, 1H), 7.46 – 7.41 (m, 3H), 7.14 (d, $J = 7.9$ Hz, 2H), 7.07 – 7.02 (m, 1H), 6.91 – 6.82 (m, 3H), 3.74 (s, 6H), 2.34 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.3, 155.1, 149.0, 141.7, 138.2, 136.1, 134.2, 129.2, 126.3, 124.1, 122.9, 121.5, 120.8, 36.1, 21.2. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -14.37. IR (KBr): 3416, 3121, 2925, 1671, 1301, 1180, 764, cm$^{-1}$. HR-ESI-MS (m/z): calcd for C$_{20}$H$_{23}$N$_3$O$_2$ [M + H]$^+$: 348.1877, found: 348.1887.

1,3-Dimethyl-1H-imidazol-3-ium-2-yl)((2-(4-methoxyphenyl)-3-(pyridin-2-yl)acryloyloxy)dihydroborate (3i)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3i. Brown liquid (45.7 mg, 63%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.37 (d, $J = 3.1$ Hz, 1H), 7.58 – 7.43 (m, 4H), 7.39 (d, $J = 8.0$ Hz, 1H), 7.03 (dd, $J = 7.5$, 5.0 Hz, 1H), 6.87 (d, $J = 5.9$ Hz, 3H), 6.79 (s, 1H), 3.80 (s, 3H), 3.73 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.3, 159.8, 155.1, 148.9, 141.3, 136.1, 129.6, 127.7,
123.1, 122.8, 121.4, 120.8, 113.9, 55.3, 36.0. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -13.65. IR (KBr): 3223, 3158, 2960, 1581, 1317, 1179, 777, cm$^{-1}$. HR-ESI-MS (m/z): calcd for C$_{20}$H$_{23}$BN$_3$O$_3$ [M + H]$^+$: 364.1827, found: 364.1838.

1,3-Dimethyl-1H-imidazol-3-ium-2-yl)((2-(4-fluorophenyl)-3-(pyridin-2-yl)acryloyloxy)dihydroborate (3j)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3j. Brown liquid (47.1 mg, 67%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.38 (d, $J$ = 3.2 Hz, 1H), 7.61 – 7.50 (m, 3H), 7.40 (d, $J$ = 7.9 Hz, 1H), 7.09 – 6.98 (m, 3H), 6.87 (s, 2H), 6.80 (s, 1H), 3.75 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.9, 164.0, 161.5, 154.7, 149.0, 140.7, 136.1, 133.3 (d, $J$ = 3.3 Hz), 128.2 (d, $J$ = 8.2 Hz), 124.9, 123.0, 121.7, 120.7, 115.4 (d, $J$ = 21.6 Hz), 36.0. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -14.55. IR (KBr): 3400, 3159, 2927, 1579, 1320, 1171, 777, cm$^{-1}$. HR-ESI-MS (m/z): calcd for C$_{19}$H$_{20}$BFN$_3$O$_2$ [M + H]$^+$: 352.1627, found: 352.1638.

2-(4-Bromophenyl)-3-(pyridin-2-yl)acryloyloxy)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (3k)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3k. Brown liquid (57.5 mg, 70%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.38 (d, $J$ = 4.8 Hz, 1H), 7.57 (d, $J$ = 1.9 Hz, 1H), 7.48 – 7.39 (m, 5H), 7.08 (d, $J$ = 4.0 Hz, 1H), 6.87 (s, 2H), 6.85 (s, 1H), 3.74 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.6, 154.5, 149.0, 140.6, 136.2, 136.1, 131.6, 128.0, 125.4, 123.2, 122.3, 121.9, 120.8, 36.0. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -15.18. IR (KBr): 3431, 3143, 2925, 1661, 1315, 1179, 781, cm$^{-1}$. HR-ESI-MS (m/z): calcd for C$_{19}$H$_{20}$BrN$_3$O$_2$ [M + H]$^+$: 412.0826, found: 412.0837.

2-(4-Cyanophenyl)-3-(pyridin-2-yl)acryloyloxy)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (3l)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3l. Red brown liquid (56.2 mg, 73%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.38 (d, J
= 3.4 Hz, 1H), 7.71 – 7.56 (m, 5H), 7.41 (d, J = 7.9 Hz, 1H), 7.14 – 7.08 (m, 1H), 6.93 (s, 1H), 6.90 (s, 2H), 3.76 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 171.0, 154.0, 149.1, 141.7, 140.0, 136.2, 132.3, 127.6, 127.0, 123.6, 122.3, 120.8, 118.8, 111.4, 36.0. 11B NMR (128 MHz, CDCl3) δ -14.33. IR (KBr): 3368, 3161, 2227, 1580, 1398, 1176, 923, 776, cm−1. HR-ESI-MS (m/z): calcd for C20H19BF3NaO2 [M + Na]+: 381.1493, found: 381.1495.

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(3-(pyridin-2-yl)-2-(4-(trifluoromethyl)phenyl)acryloyl)oxy)dihydroborate (3m)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3m. Yellow brown liquid (60.1 mg, 75%). 1H NMR (400 MHz, CDCl3) δ 8.39 (d, J = 3.3 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.62 – 7.54 (m, 3H), 7.42 (d, J = 7.9 Hz, 1H), 7.14 – 7.05 (m, 1H), 6.92 (s, 1H), 6.88 (s, 2H), 3.74 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 171.4, 154.2, 149.0, 140.7, 140.4, 136.2, 129.9 (q, J = 32.4 Hz), 126.9, 126.7, 125.4 (q, J = 3.9 Hz), 123.4, 122.1, 120.8, 36.0. 11B NMR (128 MHz, CDCl3) δ -13.99. IR (KBr): 3338, 3161, 2862, 1582, 1326, 1198, 777, cm−1. HR-ESI-MS (m/z): calcd for C20H19BF3NaO2 [M + Na]+: 424.1415, found: 424.1410.

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(2-fluorophenyl)-3-(pyridin-2-yl)acryloyl)oxy)dihydroborate (3n)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3n. Brown liquid (51.2 mg, 73%). 1H NMR (400 MHz, CDCl3) δ 8.47 (d, J = 4.9 Hz, 1H), 7.62 (d, J = 1.8 Hz, 1H), 7.50 (d, J = 6.5 Hz, 2H), 7.15 – 7.08 (m, 2H), 7.07 – 6.96 (m, 3H), 6.85 (s, 2H), 3.76 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 171.2, 154.8, 148.9, 136.3, 136.0, 130.7 (d, J = 5.3 Hz), 130.2 (d, J = 3.4 Hz), 129.6 (d, J = 8.6 Hz), 124.2 (d, J = 3.5 Hz), 123.6, 122.0, 120.6, 115.9, 115.7, 36.0. 11B NMR (128 MHz, CDCl3) δ -13.19. IR (KBr): 3400, 3111, 2857, 1579, 1427, 1171, 777, cm−1. HR-ESI-MS (m/z): calcd for C19H20BF3NO2 [M + H]+: 352.1627, found: 352.1618.

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-(3-methoxyphenyl)-3-(pyridin-2-yl)acryloyl)oxy)dihydroborate (3o)
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3o.

Brown liquid (47.2 mg, 65%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.42 (d, $J = 4.8$ Hz, 1H), 7.58 (t, $J = 7.7$ Hz, 1H), 7.46 (d, $J = 7.9$ Hz, 1H), 7.23 (d, $J = 8.0$ Hz, 1H), 7.17 – 7.03 (m, 4H), 6.90 – 6.83 (m, 4H), 3.81 (s, 3H), 3.77 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.9, 159.6, 154.8, 149.0, 141.7, 136.1, 129.4, 125.3, 123.0, 121.7, 120.7, 120.7, 119.1, 114.2, 111.6, 55.3, 36.0. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -13.81 (d, $J = 79.0$ Hz). IR (KBr): 3223, 3111, 2960, 1581, 1248, 1179, 777, cm$^{-1}$. HR-ESI-MS (m/z): calcd for C$_{26}$H$_{33}$BN$_3$O$_3$ [M + H]$^+$: 364.1827, found: 364.1839.

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)((2-(3-fluorophenyl)-3-(pyridin-2-yl)acryloyloxy)dihydroborate (3p)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3p.

Brown liquid (46.3 mg, 66%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.41 (d, $J = 5.4$ Hz, 1H), 7.63 – 7.53 (m, 1H), 7.43 (d, $J = 6.9$ Hz, 1H), 7.39 – 7.30 (m, 2H), 7.22 (d, $J = 10.5$ Hz, 1H), 7.13 – 7.05 (m, 1H), 7.02 – 6.94 (m, 1H), 6.88 (s, 2H), 6.87 (s, 1H), 3.77 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.6, 164.0, 161.6, 154.4, 149.1, 140.5 (d, $J = 2.7$ Hz), 139.4 (d, $J = 7.8$ Hz), 136.2, 129.9 (d, $J = 8.4$ Hz), 125.9, 123.2, 122.1 (d, $J = 2.8$ Hz), 121.9, 120.8, 115.1, 114.9, 113.4, 113.1, 36.0. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -14.10. IR (KBr): 3400, 3159, 2857, 1579, 1395, 1171, 777, cm$^{-1}$. HR-ESI-MS (m/z): calcd for C$_{19}$H$_{26}$BF$_3$O$_2$ [M + H]$^+$: 352.1627, found: 352.1632.

((2-(3-chlorophenyl)-3-(pyridin-2-yl)acryloyloxy)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (3q)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3q. Yellow brown liquid (52.1mg, 71%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.42 (d, $J = 3.9$ Hz, 1H), 7.67 – 7.53 (m, 1H), 7.51 – 7.40 (m, 3H), 7.27 (d, $J = 2.8$ Hz, 2H), 7.12 – 7.06 (m, 1H), 6.89 (s, 2H), 6.86 (s, 1H), 3.78 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.5, 154.4, 149.1, 140.3, 139.0, 136.2, 134.3, 129.7, 128.1, 126.4, 126.1, 124.6, 123.2, 122.0, 120.8, 36.1. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -15.02. IR (KBr): 3413, 3050,
2925, 1661, 1381, 1179, 781, cm⁻¹. HR-ESI-MS (m/z): calcld for C₁₉H₁₉BCl₁₂NaO₂ [M + H]⁺: 390.1151, found: 390.1168.

((2-(3-Bromophenyl)-3-(pyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborat-e (3r)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3r. Yellow brown liquid (60.0 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, J = 4.1 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.51 (d, J = 7.9 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.21 (t, J = 7.9 Hz, 1H), 7.13 – 7.02 (m, 1H), 6.88 (s, 2H), 6.85 (s, 1H), 3.77 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 154.3, 149.1, 140.2, 139.4, 136.2, 131.0, 130.0, 129.3, 126.2, 125.0, 123.2, 122.5, 122.0, 120.8, 36.0. ¹¹B NMR (128 MHz, CDCl₃) δ -13.83. IR (KBr): 3431, 3143, 2957, 1661, 1381, 1103, 781, cm⁻¹. HR-ESI-MS (m/z): calcld for C₁₀H₂₀BBrN₃O₂ [M + H]⁺: 412.0826, found: 412.0825.

((2-(3,4-Dichlorophenyl)-3-(pyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroboro-rate (3s)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3s. Brown liquid (56.1 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, J = 5.0 Hz, 1H), 7.66 – 7.51 (m, 2H), 7.47 – 7.35 (m, 3H), 7.16 – 7.03 (m, 1H), 6.89 (s, 2H), 6.84 (s, 1H), 3.78 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 171.2, 154.1, 149.1, 139.3, 137.3, 136.2, 132.5, 132.0, 130.4, 128.2, 126.4, 125.7, 123.3, 122.1, 120.8, 36.1. ¹¹B NMR (128 MHz, CDCl₃) δ -14.39. IR (KBr): 3119, 2956, 1672, 1473, 1112, 743, cm⁻¹. HR-ESI-MS (m/z): calcld for C₁₀H₁₉BCl₂N₃O₂ [M + H]⁺: 402.0942, found: 402.0942.

((2-(2,4-Dichlorophenyl)-3-(pyridin-2-yl)acryloyl)oxy)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroboro-rate (3t)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3t. Brown liquid (57.7 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 8.54 – 8.47 (m, 1H), 7.67 – 7.54 (m, 2H), 7.44 (d, J = 8.3 Hz, 1H), 7.36 (d, J = 2.1 Hz, 1H), 7.24
(dd, J = 8.3, 2.2 Hz, 1H), 7.18 – 7.10 (m, 1H), 6.82 (s, 2H), 6.79 (s, 1H), 3.71 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 169.7, 154.4, 148.9, 138.1, 137.2, 135.8, 134.2, 134.0, 133.7, 132.0, 129.3, 127.1, 124.0, 122.3, 120.7, 36.0. 11B NMR (128 MHz, CDCl3) δ -13.92. IR (KBr): 3162, 2926, 1672, 1368, 1112, 776, cm−1. HR-ESI-MS (m/z): calcd for C19H19BCl2N3O2 [M + H]+: 402.0942, found: 402.0941.

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)((2-(4-fluorophenyl)-3-(3-methylpyridin-2-yl)acryloyloxy)dihydroroborate (3u)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3u. Brown liquid (45.2mg, 62%). 1H NMR (400 MHz, CDCl3) δ 8.02 (d, J = 3.1 Hz, 1H), 7.61 – 7.50 (m, 2H), 7.38 (d, J = 6.7 Hz, 1H), 7.03 (t, J = 8.7 Hz, 2H), 6.95 (dd, J = 7.6, 4.7 Hz, 1H), 6.87 (s, 2H), 6.86 (s, 1H), 3.77 (s, 6H), 2.37 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 172.1, 163.9, 161.5, 153.0, 146.1, 141.3, 137.5, 134.1 (d, J = 3.2 Hz), 131.4, 128.5 (d, J = 8.1 Hz), 122.1 (d, J = 1.7 Hz), 121.7, 120.6, 115.4, 115.2, 36.0, 18.9. 11B NMR (128 MHz, CDCl3) δ -15.27. IR (KBr): 3382, 3161, 2927, 1576, 1397, 1167, 778, cm−1. HR-ESI-MS (m/z): calcd for C20H22BF3N2O2 [M + H]+: 366.1784, found: 366.1779.

((2-(4-Chlorophenyl)-3-(3-methylpyridin-2-yl)acryloyloxy)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydropoborate (3v)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3v. Red brown liquid (48.7mg, 64%). 1H NMR (400 MHz, CDCl3) δ 8.03 (d, J = 4.0 Hz, 1H), 7.52 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 7.6 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.00 – 6.92 (m, 1H), 6.90 (s, 1H), 6.87 (s, 2H), 3.78 (s, 6H), 2.37 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 171.9, 152.9, 146.1, 141.2, 137.5, 136.4, 133.9, 131.5, 128.5, 128.1, 122.6, 121.9, 120.6, 36., 18.9. 11B NMR (128 MHz, CDCl3) δ -15.46. IR (KBr): 3400, 3120, 2956, 1671, 1376, 1113, 831, cm−1. HR-ESI-MS (m/z): calcd for C20H22ClBClN3NaO2 [M + Na]+: 404.1308, found: 404.1303.

((2-(3-Chlorophenyl)-3-(4-methylpyridin-2-yl)acryloyloxy)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydropoborate (3w)
Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3w. Brown solid (52.5mg, 69%). ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 5.0 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.36 – 7.25 (m, 3H), 6.91 (d, J = 5.1 Hz, 1H), 6.87 (s, 2H), 6.83 (s, 1H), 3.75 (s, 6H), 2.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 154.1, 148.8, 147.2, 140.0, 139.1, 134.2, 129.7, 128.0, 126.4, 126.3, 124.5, 124.2, 123.1, 120.8, 36.0, 21.0. ¹¹B NMR (128 MHz, CDCl₃) δ -13.72. IR (KBr): 3400, 3120, 2926, 1671, 1299, 1113, 800, cm⁻¹. HR-ESI-MS (m/z): calcd for C₂₀H₂₂BCl₅N₆O₂ [M + H]⁺: 442.0932, found: 442.0940.

((2-(3-Bromophenyl)-3-(4-methoxypyridin-2-yl)acryloyloxy)(1,3-dimethyl-1H-imidazol-3-iium-2-yl)dihydroborate (3x)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3x. Brown liquid (52.0mg, 59%). ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 5.7 Hz, 1H), 7.57 (d, J = 1.9 Hz, 1H), 7.50 (d, J = 7.0 Hz, 1H), 7.41 (d, J = 6.9 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.10 (d, J = 2.3 Hz, 1H), 6.88 (s, 2H), 6.84 (s, 1H), 6.65 (d, J = 3.4 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 165.9, 156.0, 150.1, 140.3, 139.2, 131.0, 130.0, 129.3, 126.5, 125.0, 122.5, 120.8, 109.2, 108.3, 55.2, 36.0. ¹¹B NMR (128 MHz, CDCl₃) δ -14.43. IR (KBr): 3423, 3124, 2956, 1671, 1309, 1112, 786, cm⁻¹. HR-ESI-MS (m/z): calcd for C₂₀H₂₂BrCl₅N₆O₂ [M + H]⁺: 442.0932, found: 442.0940.

((2-(3,4-Dichlorophenyl)-3-(3-methylpyridin-2-yl)acryloyloxy)(1,3-dimethyl-1H-imidazol-3-iium-2-yl)dihydroborate (3y)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3y. Brown liquid (52.3mg, 63%). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 4.6 Hz, 1H), 7.61 (d, J = 2.1 Hz, 1H), 7.47 – 7.35 (m, 3H), 7.02 – 6.95 (m, 1H), 6.91 (s, 1H), 6.89 (s, 2H), 3.79 (s, 6H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 152.5, 146.2, 140.0, 138.1, 137.6, 132.4, 131.8, 131.7, 130.3, 128.5, 126.2, 123.7, 122.1, 120.7, 36.1, 18.9. ¹¹B NMR (128 MHz, CDCl₃) δ -14.38. IR (KBr): 3400, 3163, 2956, 1671, 1376, 1113, 775, cm⁻¹. HR-ESI-MS (m/z): calcd for C₂₀H₂₁BCl₂N₆O₂ [M + H]⁺: 416.1098, found: 416.1113.
(1,3-Dimethyl-1H-imidazol-3-i um-2-yl)((3-(3,5-dimethylpyridin-2-yl)-2-(4-fluorophenyl)acryloyloxy)dihydroborate (3z)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3z. Brown liquid (50.8mg, 67%). 1H NMR (400 MHz, CDCl3) δ 7.88 (d, J = 2.1 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.22 – 7.16 (m, 1H), 7.02 (t, J = 8.6 Hz, 2H), 6.87 (s, 2H), 6.83 (s, 1H), 3.78 (s, 6H), 2.33 (s, 3H), 2.23 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 172.3, 163.8, 161.4, 150.3, 146.6, 140.4, 138.1, 134.2 (d, J = 3.4 Hz), 131.2, 130.8, 128.4 (d, J = 8.1 Hz), 122.3, 120.6, 115.4, 115.1. 11B NMR (128 MHz, CDCl3) δ -15.09. IR (KBr): 3388, 3165, 2926, 1671, 1380, 1231, 841, cm−1. HR-ESI-MS (m/z): calcd for C21H24BFN3O2 [M + H]^+: 380.1940, found: 380.1938.

(1,3-Dimethyl-1H-imidazol-3-i um-2-yl)((2-(naphthalen-2-yl)-3-(pyridin-2-yl)acryloyloxy)dihydroborate -e (3aa)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 3aa. Brown liquid (53.6mg, 70%). 1H NMR (400 MHz, CDCl3) δ 8.44 (d, J = 4.0 Hz, 1H), 7.94 – 7.90 (m, 1H), 7.84 – 7.76 (m, 3H), 7.74 (d, J = 8.7 Hz, 1H), 7.60 (t, J = 8.6 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.13 – 7.04 (m, 1H), 7.03 (s, 1H), 6.86 (s, 2H), 3.75 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 172.1, 154.89, 149.1, 141.6, 136.2, 134.3, 133.3, 133.1, 128.4, 128.1, 127.5, 126.3 – 126.0 (m), 125.4, 123.9, 123.1, 121.7, 120.7, 36.1. 11B NMR (128 MHz, CDCl3) δ -14.20. IR (KBr): 3417, 3160, 2923, 1581, 1381, 1175, 756, cm−1. HR-ESI-MS (m/z): calcd for C23H26BFN3O2 [M + H]^+: 384.1878, found: 384.1870.

(1-Isopropyl-3-methyl-1H-imidazol-3-i um-2-yl)((2-phenyl-3-(pyridin-2-yl)acryloyloxy)dihydroborate (4a)

Flash column chromatography on silica gel (eluent: PE/EA = 1/1, v/v) to afford 4a. Brown liquid (52.7mg, 73%). 1H NMR (400 MHz, CDCl3) δ 8.45 (d, J = 5.6 Hz, 1H), 7.56 (d, J = 7.9 Hz, 3H), 7.50 (d, J = 7.9 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.11 – 7.03 (m, 1H), 6.96 (d, J = 1.9 Hz, 1H), 6.89 (s, 1H), 6.87 (s, 1H), 5.22 – 5.06 (m,
1H), 3.72 (s, 3H), 1.29 (d, J = 6.7 Hz, 6H). 13C NMR (100 MHz, CDCl3) δ 171.9, 154.8, 149.1, 141.8, 137.0, 136.1, 128.4, 128.2, 126.4, 125.2, 122.8, 121.7, 121.3, 115.4, 50.0, 35.9, 23.02. 11B NMR (128 MHz, CDCl3) δ -15.17. IR (KBr): 3457, 2925, 1672, 1378, 1109, 778, cm⁻¹. HR-ESI-MS (m/z): calcd for C21H25BN3O2 [M + H]+: 362.2034, found: 362.2030.
3. NMR spectra for new compounds

$^1$H NMR and $^{13}$C NMR spectrum of compound 3a

$^{11}$B NMR spectrum of compound 3a
$^{1}H$ NMR and $^{13}C$ NMR spectrum of compound 3b
$^{11}$B NMR spectrum of compound 3b

$^1$H NMR and $^{13}$C NMR spectrum of compound 3c
$\text{S19}$

$^{11}$B NMR spectrum of compound 3c
$^1$H NMR and $^{13}$C NMR spectrum of compound 3d
$^{11}$B NMR spectrum of compound 3d

$^1$H NMR and $^{13}$C NMR spectrum of compound 3e
$^{11}$B NMR spectrum of compound 3e
$^1$H NMR and $^{13}$C NMR spectrum of compound 3f
$1^1$B NMR spectrum of compound 3f

$1^1$H NMR and $1^3$C NMR spectrum of compound 3g
$^{11}$B NMR spectrum of compound 3g
$^{1}H$ NMR and $^{13}C$ NMR spectrum of compound 3h
$^{11}$B NMR spectrum of compound 3h

$^1$H NMR and $^{13}$C NMR spectrum of compound 3i
$^{11}$B NMR spectrum of compound 3i
$^1$H NMR and $^{13}$C NMR spectrum of compound 3j

![NMR Spectrum](image)
$^{11}$B NMR spectrum of compound 3j

$^1$H NMR and $^{13}$C NMR spectrum of compound 3k
$^{11}$B NMR spectrum of compound 3k
$^1$H NMR and $^{13}$C NMR spectrum of compound 3l
$^{11}$B NMR spectrum of compound 3l

$^1$H NMR and $^{13}$C NMR spectrum of compound 3m
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$^{1}$H NMR and $^{13}$C NMR spectrum of compound 3n
$^{11}$B NMR spectrum of compound 3n

$^1$H NMR and $^{13}$C NMR spectrum of compound 3o
$^{11}$B NMR spectrum of compound 30

S37
$^1$H NMR and $^{13}$C NMR spectrum of compound 3p
$^1$H NMR and $^{13}$C NMR spectrum of compound 3q
$^{11}$B NMR spectrum of compound 3q
$^1$H NMR and $^{13}$C NMR spectrum of compound 3r
$^{11}$B NMR spectrum of compound 3r

$^{1}$H NMR and $^{13}$C NMR spectrum of compound 3s
$^{11}$B NMR spectrum of compound 3s
$^1$H NMR and $^{13}$C NMR spectrum of compound 3t
$\text{1}^1\text{B NMR spectrum of compound 3t}$

$\text{1}^1\text{H NMR and 13}^\text{C NMR spectrum of compound 3u}$
$^{11}$B NMR spectrum of compound 3u
$^{1}H$ NMR and $^{13}C$ NMR spectrum of compound 3v
$^{11}$B NMR spectrum of compound 3v
\( ^1 \text{H NMR and } ^{13} \text{C NMR spectrum of compound } 3w \)

![NMR spectrum image](image_url)

\( ^{11} \text{B NMR spectrum of compound } 3w \)

![B NMR spectrum image](image_url)
$^1$H NMR and $^{13}$C NMR spectrum of compound 3x.
$^{11}$B NMR spectrum of compound 3x

$^1$H NMR and $^{13}$C NMR spectrum of compound 3y
$^{11}$B NMR spectrum of compound 3y
$^1$H NMR and $^{13}$C NMR spectrum of compound 3z
$^{11}$B NMR spectrum of compound 3z
$^1$H NMR and $^{13}$C NMR spectrum of compound 3aa

$^{11}$B NMR spectrum of compound 3aa
$^1$H NMR and $^{13}$C NMR spectrum of compound 4a
$^{11}$B NMR spectrum of compound 4a
4. X-ray crystallographic data

**Figure S1** X-ray single crystal structure of 3w

Single crystals of 3w were grown by slow evaporation of its DCM/PE solution. Single-crystal X-ray diffraction data were collected with a 'multiwire proportional' diffractometer. The crystal was kept at 149.99 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Least Squares minimization. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2116778).

**Table S1** Crystal data and structure refinement for 3w

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Reflections collected 3641
Independent reflections 2528 [R(int) = 0.0275, R(sigma) = 0.0389]
Data/restraints/parameters 2528/2/248
Goodness-of-fit on F² 1.073
Final R indexes [I>=2σ (I)] R₁ = 0.0346, wR₂ = 0.0857
Final R index [all data] R₁ = 0.0361, wR₂ = 0.0880
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5. **References**