Supporting Information

*gem*-Dibromomethylarenes: A convenient substitute for noncommercial aldehydes in Knoevenagel-Doebner reaction for the synthesis of α,β-unsaturated carboxylic acids

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General Methods

1H and 13C NMR Spectra were recorded on 400-MHz and 100-MHz Bruker spectrometer respectively and elemental analysis was performed on Thermo Finnigan FLASH EA 1112 CHN analyzer. Melting points were recorded (uncorrected) on Buchi Melting Point B-545 instrument. Reactions were carried out in an oven dried three-necked round-bottomed flask. Yields in table refer to isolated yields of compounds with purity >95 % as determined by 1H NMR and HPLC analysis. Compounds previously described in the literature were characterized only by 1H and 13C NMR.
General procedure for the preparation of gem-dibromomethyl compounds

Representative procedure for the synthesis of 1h: To a solution of methyl-2-chloro-6-methylpyridine-4-carboxylate (27.9g, 0.151mol) in CCl4 (300ml) was added NBS (53.8g, 0.302mol) followed by benzoylperoxide (2.5g, 0.018mol). The mixture was gradually heated to reflux for 8h and cooled to room temperature. The succinimide was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography using petroleum ether/ethyl acetate (9/1) to afford 41.8g (81%) of methyl-2-chloro-6-dibromomethylpyridine-4-carboxylate (1h) as a colourless liquid.

This procedure was applied to the synthesis of gem-dibromides 1b, 1c, 1d, 1e, 1f, 1g, 1i, 1j, 1k, 1l, 1o and 1p. Substrate 1m was obtained by brominating the commercially available methyl-2-methylfuran-3-carboxylate with 2.8eq of NBS. Similarly compound 1n was prepared by brominating the commercially available 2-acetamido-4-methylthiazole with 2.8eq of NBS.

General procedure for the preparation of α,β-unsaturated carboxylic acids

Representative procedure for the synthesis of 2a: To a mixture of 1a (10g, 0.04mol) and malonic acid (8.35g, 0.08mol) in pyridine (30ml) was added piperidine (0.14ml, 0.0016mol) and the mixture was refluxed for 1.5h (entry 1, Table 1). The completion of reaction was confirmed by TLC. The brown reaction mixture was cooled and poured onto ice containing hydrochloric acid. The solid precipitated was collected by filtration, washed with water (3x75ml) and dried under suction to afford 5.5g (93%) of cinnamic acid 2a as a white solid.

Alternatively, the reaction mixture could be poured into water and extracted with ethyl acetate. The organic phase could be evaporated and directly loaded onto a silica gel column. This method is suitable for isolating α,β-unsaturated carboxylic acids obtained from nitrogen heterocycles.

The required time for refluxing was 1hour in the case of entries 4 and 15 (Table 1), 1.5 hours in the case of entries 1, 3, 6, 11 and 16 (Table 1), 2 hours in the case of entries 2, 7, 8, 9, 12 and 13 (Table 1) and 3 hours in all other entries.
Methyl-3-bromo-4-dibromomethylbenzoate (1b): Colorless liquid; 70% yield; $R_f = 0.65$ (petroleum ether/EtOAc, 9/1); $^1$H NMR (400MHz, DMSO-$d_6$): $\delta$ 8.09-8.06 (m, 2H), 8.03-8.00 (m, 1H), 7.32 (s, 1H), 3.86 (s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$): $\delta$ 164.58, 144.45, 133.77, 132.66, 131.59, 129.76, 120.15, 53.15, 40.69; Anal. Calcd for C$_9$H$_7$Br$_3$O$_2$: C, 27.94; H, 1.82%; Found: C, 27.98; H, 1.89%.

Methyl-4-dibromomethyl-1-naphthoate (1c): White solid; 86% yield; mp = 90-91°C; $R_f = 0.6$ (petroleum ether/EtOAc, 9/1); $^1$H NMR (400MHz, DMSO-$d_6$): $\delta$ 8.73-8.71 (d, 1H, $J = 8.2$Hz), 8.50 (bs, 1H), 8.29-8.10 (m, 3H), 7.80-7.71 (m, 2H), 3.95 (s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$): $\delta$ 167.38, 141.08, 131.07, 129.90, 129.53, 128.69, 128.52, 127.43, 126.44, 124.69, 53.05, 40.96; Anal. Calcd for C$_{13}$H$_{10}$Br$_2$O$_2$: C, 43.61; H, 2.82%; Found: C, 43.68; H, 2.90%.

1-(Dibromomethyl)-4-methoxy-2-nitrobenzene (1d): Brown solid; $^1$H NMR (400MHz, CDCl$_3$) $\delta$ 8.15-8.13 (d, 1H, $J = 8.92$Hz), 7.43 (s, 1H), 7.38-7.37 (d, 1H, $J = 2.6$Hz), 7.27-7.24 (dd, 1H, $J_1 = 8.76$Hz, $J_2 = 2.56$Hz), 3.91 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$ 160.56, 144.85, 133.80, 128.21, 120.79, 108.49, 56.17, 34.36; Anal. Calcd for C$_8$H$_7$Br$_2$NO$_3$: C, 29.57; H, 2.17; N, 4.31. Found: C, 29.73; H, 2.28; N, 4.11.

Methyl-3-dibromomethyl-4-nitrobenzoate (1e): Yellow solid; 75% yield; mp = 121-123°C; $R_f = 0.70$ (petroleum ether/EtOAc, 9/1); $^1$H NMR (400MHz, DMSO-$d_6$): $\delta$ 8.63 (s, 1H), 8.14-8.07 (m, 2H), 7.48 (s, 1H), 3.94 (s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$): $\delta$ 164.45, 147.51, 135.85, 134.80, 132.66, 132.00, 125.69, 53.55, 35.8.

7-(Dibromomethyl)-2,2-dimethyl-4H-1,3-benzodioxin-4-one (1f): White solid; 76% yield; mp = 84.5-86.6°C; $R_f = 0.75$ (petroleum ether/EtOAc, 9/1); $^1$H NMR (400MHz, DMSO-$d_6$): $\delta$ 7.95-7.93 (d, 1H, $J = 8.16$Hz), 7.46-7.44 (dd, 1H, $J = 8.16$Hz and 1.72Hz), 7.39 (s, 1H), 7.29-7.28 (d, 1H, $J = 1.84$Hz), 1.68 (s, 6H); $^{13}$C NMR (100MHz, DMSO-$d_6$): $\delta$ 159.79, 155.51, 150.55, 130.63, 121.84, 115.31, 114.17, 107.36, 40.91, 25.71; Anal. Calcd for C$_{11}$H$_{10}$Br$_2$O$_3$: C, 37.75; H, 2.88%; Found: C, 37.72; H, 2.92%.
2-Bromo-4-(dibromomethyl)pyridine (1g): $^1$H NMR (400MHz, DMSO-$d_6$) $\delta$ 8.49-8.47 (d, 1H, $J = 5.16$Hz), 7.79-7.78 (d, 1H, $J = 1.24$Hz), 7.67-7.66 (dd, 1H, $J_1 = 5.16$Hz, $J_2 = 1.8$Hz), 7.30 (s, 1H); $^{13}$C NMR (100MHz, DMSO-$d_6$) $\delta$ 152.81, 151.60, 141.43, 124.66, 121.17, 38.04.

Methyl-2-chloro-6-dibromomethylpyridine-4-carboxylate (1h): Colorless liquid; 81% yield: $R_f = 0.70$ (petroleum ether/EtOAc, 9/1); $^1$H NMR (400MHz, DMSO-$d_6$): $\delta$ 8.07 (s, 1H), 7.88 (s, 1H), 7.46 (s, 1H), 3.91 (s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$): $\delta$ 163.61, 159.80, 151.48, 142.22, 125.06, 118.83, 53.73, 41.14; Anal. Calcd for C$_8$H$_6$Br$_2$ClNO$_2$: C, 27.98; H, 1.76%; N, 4.08; Found: C, 27.91; H, 1.72; N, 4.01%.

Methyl-6-dibromomethylpyridine-3-carboxylate (1i): Colorless liquid; 75% yield; $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 9.12 (s, 1H), 8.40-8.37 (dd, 1H, $J = 8.24$Hz and 2.04Hz), 7.89-7.87 (d, 1H, $J = 8.24$Hz), 6.68 (s, 1H), 3.97 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 164.79, 162.30, 149.75, 138.82, 126.27, 121.57, 52.64, 40.47.

2-Cyano-3-(dibromomethyl)pyridine (1j): White solid; mp = 103.5-104.9°C; $^1$H NMR (400MHz, DMSO-$d_6$) $\delta$ 8.74-8.73 (dd, 1H, $J_1 = 4.72$Hz, $J_2 = 1.44$Hz), 8.37-8.35 (dd, 1H, $J_1 = 8.24$Hz, $J_2 = 1.36$Hz), 7.86-7.83 (dd, 1H, $J_1 = 8.2$Hz, $J_2 = 4.72$Hz), 7.46 (s, 1H); $^{13}$C NMR (100MHz, DMSO-$d_6$) $\delta$ 152.30, 141.72, 137.30, 130.01, 128.81, 115.47, 35.98; Anal.Calc’d for C$_7$H$_4$Br$_2$N$_2$: C, 30.47; H, 1.46; N, 10.15. Found: C, 30.54; H, 1.53; N, 10.03.

2-Bromo-5-(dibromomethyl)pyridine (1k): White solid; mp = 90-91.5°C; $^1$H NMR (400MHz, DMSO-$d_6$) $\delta$ 8.58-8.57 (d, 1H, $J = 2.48$Hz), 8.04-8.01 (dd, 1H, $J_1 = 8.4$Hz, $J_2 = 2.68$Hz), 7.77-7.75 (d, 1H, $J = 8.36$Hz), 7.43 (s, 1H); $^{13}$C NMR (100MHz, DMSO-$d_6$) $\delta$ 150.76, 145.89, 141.96, 141.78, 132.27, 41.33.
Methyl-5-dibromomethylthiophene-2-carboxylate (1l): Brown solid; 82% yield; mp = 68-69.5°C; $R_f = 0.7$ (petroleum ether/EtOAc, 9/1); $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.64-7.63(d, 1H, $J = 4.0$Hz), 7.24-7.23 (dd, 1H, $J = 4.0$Hz and 0.44Hz), 6.86 (s, 1H), 3.89 (s, 3H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 162.10, 151.93, 134.83, 132.68, 127.13, 52.47, 31.10.

Methyl-5-bromo-2-dibromomethylfuran-3-carboxylate (1m): White solid; 72% yield; mp = 147-149°C; $R_f = 0.55$ (petroleum ether/EtOAc, 9/1); $^1$H NMR (400MHz, DMSO-d$_6$): $\delta$ 7.43 (s, 1H), 6.99 (s, 1H), 3.81 (s, 3H); $^{13}$C NMR (100MHz, DMSO-d$_6$): $\delta$ 160.96, 155.70, 125.49, 114.51, 112.81, 52.59, 25.23.

$N$-[5-Bromo-4-(dibromomethyl)-1,3-thiazol-2-yl]acetamide (1n): brown solid; $^1$H NMR (400MHz, DMSO-d$_6$) $\delta$ 12.83 (bs, 1H), 7.20 (s, 1H), 2.15 (s, 3H); $^{13}$C NMR (100MHz, DMSO-d$_6$) $\delta$ 169.59, 158.03, 146.24, 97.62, 33.60, 22.24.

3-Dibromomethyl-4-fluorobenzeneboronicacid pinacol ester (1o): Colourless liquid; 82% yield; $R_f = 0.65$ (petroleum ether/EtOAc, 9/1); $^1$H NMR (400MHz, DMSO-d$_6$): $\delta$ 8.01-7.99 (dd, 1H, $J = 8.16$Hz and 1.48Hz), 7.73-7.69 (m, 1H), 7.46 (s, 1H), 7.29-7.24 (dd, 1H, $J = 10.96$Hz and 8.28Hz), 1.27 (s, 12H); $^{13}$C NMR (100MHz, DMSO-d$_6$): $\delta$ 161.90, 159.35, 138.91, 138.82, 135.50, 135.48, 129.26, 129.15, 116.51, 116.31, 84.54, 34.77, 34.73, 25.09; Anal. Calcd for C$_{13}$H$_{16}$BBr$_2$FO$_2$: C, 39.64; H, 4.09%; Found: C, 39.69; H, 4.13%.

5-Dibromomethylbenzo[b]thiophene-2-boronic acid pinacol ester (1p): White solid; 81% yield; mp = 178-179.9°C; $R_f = 0.70$ (petroleum ether/EtOAc, 9/1); $^1$H NMR (400MHz, DMSO-d$_6$): $\delta$ 8.16-8.15 (d, 1H, $J = 1.52$Hz), 8.10-8.08 (d, 1H, $J = 8.56$Hz), 7.97 (s, 1H), 7.71-7.68 (dd, 1H, $J = 8.56$Hz and 1.84Hz), 7.55 (s, 1H), 1.31 (s, 12H); $^{13}$C NMR (100MHz, DMSO-d$_6$): $\delta$ 144.17, 139.96, 139.22, 135.29, 125.01, 123.76, 122.21, 85.02, 43.52, 25.06; Anal. Calcd for C$_{15}$H$_{17}$BBr$_2$O$_2$S: C, 41.71; H, 3.97%; Found: C, 41.76; H, 3.93%.
3-[2-Bromo-4-(methoxycarbonyl)phenyl]acrylic acid (2b): White solid; mp.= 222.5-224°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.84 (bs, 1H), 8.12-8.12 (d, 1H, $J = 1.52$Hz), 8.02-8.00 (d, 1H, $J = 8.2$Hz), 7.91-7.89 (dd, 1H, $J_1 = 8.2$Hz, $J_2 = 1.2$Hz), 7.81-7.77 (d, 1H, $J = 15.88$Hz), 6.67-6.63 (d, 1H, $J = 15.92$Hz), 3.85 (s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.24, 164.94, 140.63, 138.45, 133.83, 132.46, 129.12, 128.96, 125.21, 124.74, 53.07; Anal.Calc’d for C$_{11}$H$_9$BrO$_4$: C, 46.34; H, 3.18. Found: C, 46.43; H, 3.24.

3-[4-(Methoxycarbonyl)-1-naphthyl]acrylic acid (2c): White solid; mp.= 223-225°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.81 (bs, 1H), 8.76-8.74 (dd, 1H, $J_1 = 6.48$Hz, $J_2 = 2.2$Hz), 8.39-8.35 (d, 1H, $J = 15.76$Hz), 8.26-8.24 (dd, 1H, $J_1 = 7.32$Hz, $J_2 = 3.04$Hz), 8.09-8.07 (d, 1H, $J = 7.68$Hz), 7.96-7.94 (d, 1H, $J = 7.68$Hz), 7.71-7.67 (m, 2H), 6.66-6.62 (d, 1H, $J = 15.72$Hz), 3.93 (s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.54, 167.52, 140.04, 136.42, 131.43, 130.99, 129.60, 128.80, 128.39, 127.78, 126.23, 124.85, 124.56, 124.34, 52.89; Anal.Calc’d for C$_{15}$H$_{12}$O$_4$: C, 70.31; H, 4.72. Found: C, 70.40; H, 4.77.

3-(4-Methoxy-2-nitrophenyl)acrylic acid (2d): Off-white solid; mp.= 237.5-239.4°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.59 (bs, 1H), 7.92-7.90 (d, 1H, $J = 8.8$Hz), 7.72-7.68 (d, 1H, $J = 16$Hz), 7.56 (s, 1H), 7.33-7.30 (dd, 1H, $J_1 = 8.8$Hz, $J_2 = 2.8$Hz), 6.49-6.45 (d, 1H, $J = 16$Hz), 3.87 (s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.52, 161.04, 150.05, 138.22, 130.64, 122.32, 121.30, 120.25, 109.78, 56.71; Anal.Calc’d for C$_{10}$H$_9$NO$_5$: C, 53.82; H, 4.06; N, 6.28. Found: C, 53.88; H, 4.11; N, 6.21.

3-[5-(Methoxycarbonyl)-2-nitrophenyl]acrylic acid (2e): Pale yellow solid; mp.= 170-172°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.80 (bs, 1H), 8.30-8.29 (d, 1H, $J = 1.12$Hz), 8.20-8.12 (m, 2H), 7.84-7.80 (d, 1H, $J = 15.84$Hz), 6.60-6.56 (d, 1H, $J = 15.80$Hz), 3.91 (s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.08, 164.93, 150.96, 138.56, 134.40, 131.48, 130.39, 130.32, 125.80, 125.32, 53.38; Anal.Calc’d for C$_{11}$H$_9$NO$_6$: C, 52.60; H, 3.61; N, 5.58. Found: C, 52.66; H, 3.69; N, 5.47.
3-(2,2-Dimethyl-4-oxo-4H-1,3-benzodioxin-7-yl)acrylic acid (2f): White solid; mp. = 253-255°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.76 (bs, 1H), 7.87-7.85 (d, 1H, $J = 8.04$Hz), 7.62-7.58 (d, 1H, $J = 16$Hz), 7.54-7.52 (d, 1H, $J = 8.04$Hz), 7.48 (s, 1H), 6.73-6.69 (d, 1H, $J = 16$Hz), 1.64 (s, 6H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.57, 160.27, 156.13, 143.04, 142.23, 130.01, 123.80, 122.89, 117.11, 114.16, 107.03, 25.72; Anal.Calc’d for C$_{13}$H$_{12}$O$_5$: C, 62.90; H, 4.87. Found: C, 62.93; H, 4.91.

3-(2-Bromopyridin-4-yl)acrylic acid (2g): White solid; mp. = 229-230°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.86 (bs, 1H), 8.41-8.40 (d, 1H, $J = 5.08$Hz), 7.97 (s, 1H), 7.74-7.73 (d, 1H, $J = 5.08$Hz), 7.53-7.49 (d, 1H, $J = 16.08$Hz), 6.88-6.84 (d, 1H, $J = 16.08$Hz); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.26, 151.38, 145.49, 142.73, 139.97, 126.85, 126.12, 122.03; Anal.Calc’d for C$_8$H$_6$BrNO$_2$: C, 42.14; H, 2.65; N, 6.14. Found: C, 42.18; H, 2.73; N, 6.05.

3-[6-Chloro-4-(methoxycarbonyl)pyridin-2-yl]acrylic acid (2h): White solid; mp. = 183-185°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.77 (bs, 1H), 8.14-8.13 (d, 1H, $J = 1.08$Hz), 7.84 (d, 1H, $J = 1.08$Hz), 7.67-7.63 (d, 1H, $J = 15.64$Hz), 6.86-6.82 (d, 1H, $J = 15.64$Hz), 3.89 (s, 1H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.18, 164.08, 154.81, 151.63, 141.87, 140.84, 125.60, 124.40, 123.13, 53.60; Anal.Calc’d for C$_{10}$H$_8$ClNO$_4$: C, 49.71; H, 3.34; N, 5.80. Found: C, 49.76; H, 3.39; N, 5.72.

3-[5-(Methoxycarbonyl)pyridin-2-yl]acrylic acid (2i): White solid; mp. = 224-225°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.79 (bs, 1H), 9.08 (s, 1H), 8.32-8.30 (dd, 1H, $J_1 = 8.08$Hz, $J_2 = 1.72$Hz), 7.87-7.85 (d, 1H, $J = 8.12$Hz), 7.66-7.62 (d, 1H, $J = 15.72$Hz), 6.94-6.90 (d, 1H, $J = 15.72$Hz), 3.88 (s, 1H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.41, 165.27, 156.54, 150.72, 142.15, 138.37, 125.98, 125.66, 124.67, 52.93; Anal.Calc’d for C$_{10}$H$_9$NO$_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 58.02; H, 4.44; N, 6.67.
3-(2-Cyanopyridin-3-yl)acrylic acid (2j): White solid; mp. = 243-244°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.96 (bs, 1H), 8.74-8.73 (dd, 1H, $J_1 = 4.48$Hz, $J_2 = 0.8$Hz), 8.55-8.52 (dd, 1H, $J_1 = 8.24$Hz, $J_2 = 0.72$Hz), 7.80-7.77 (m, 1H), 7.74-7.70 (d, 1H, $J = 15.92$Hz), 6.92-6.88 (d, 1H, $J = 15.88$Hz); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.00, 152.32, 136.44, 135.68, 134.61, 132.75, 128.32, 126.72, 116.46; Anal.Calc’d for C$_9$H$_6$N$_2$O$_2$: C, 62.07; H, 3.47; N, 16.08. Found: C, 62.11; H, 3.49; N, 16.01.

3-(6-Bromopyridin-3-yl)acrylic acid (2k): White solid; mp. = 231-232°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.62 (bs, 1H), 8.68-8.67 (d, 1H, $J = 2.16$Hz), 8.13-8.10 (dd, 1H, $J_1 = 8.36$Hz, $J_2 = 2.36$Hz), 7.71-7.69 (d, 1H, $J = 8.32$Hz), 7.61-7.57 (d, 1H, $J = 16.16$Hz), 6.74-6.70 (d, 1H, $J = 16.12$Hz); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.53, 150.90, 142.93, 139.67, 138.16, 130.39, 128.70, 122.73; Anal.Calc’d for C$_8$H$_6$BrNO$_2$: C, 42.14; H, 2.65; N, 6.14. Found: C, 42.18; H, 2.73; N, 6.05.

3-[5-(Methoxycarbonyl)-2-thienyl]acrylic acid (2l): Pale yellow solid; mp. = 182-184°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.64 (bs, 1H), 7.76-7.71 (m, 2H), 7.57-7.56 (d, 1H, $J = 3.6$Hz), 6.41-6.38 (d, 1H, $J = 15.84$Hz), 3.82 (s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.28, 161.95, 145.55, 136.14, 134.79, 134.47, 131.87, 121.41, 52.94; Anal.Calc’d for C$_9$H$_8$O$_4$S: C, 50.94; H, 3.80. Found: C, 50.99; H, 3.86.

3-[5-Bromo-3-(methoxycarbonyl)-2-furyl]acrylic acid (2m): White solid; mp. = 213-214°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.81 (bs, 1H), 7.79-7.75 (m, 2H), 7.57-7.56 (d, 1H, $J = 15.96$Hz), 7.05 (s, 1H), 6.40-6.36 (d, 1H, $J = 16$Hz), 3.81 (s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.05, 161.89, 154.82, 127.82, 126.53, 122.36, 120.92, 114.71, 52.75; Anal.Calc’d for C$_9$H$_7$BrO$_5$: C, 39.30; H, 2.57. Found: C, 39.34; H, 2.62.

3-[2-(Acetylamino)-5-bromo-1,3-thiazol-4-yl]acrylic acid (2n): Brown solid; mp. >350°C; $^1$H NMR (400MHz, DMSO-$d_6$) δ 12.70 (bs, 1H), 12.57 (bs, 1H), 7.43-7.39 (d, 1H, $J = 15.32$Hz), 6.45-6.41(d, 1H, $J = 15.36$Hz), 2.15 (s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 169.66, 167.30, 157.33, 143.19, 132.56, 122.09, 107.13, 22.31.
3-[2-Fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]acrylic acid (2o): White solid; mp. = 187-189°C; \(^1\)H NMR (400MHz, DMSO-\(d_6\)) \(\delta\) 12.60 (bs, 1H), 7.98-7.96 (d, 1H, \(J = 7.84\)Hz), 7.74-7.71 (m, 1H), 7.65-7.61(d, 1H, \(J = 16.2\)Hz), 7.32-7.27 (m, 1H), 6.57-6.53 (d, 1H, \(J = 16.2\)Hz), 1.29 (s, 12H); \(^1^3\)C NMR (100MHz, DMSO-\(d_6\)) \(\delta\) 167.60, 164.30, 161.76, 159.96, 138.72, 138.63, 135.98, 135.95, 135.86, 135.83, 122.91, 122.86, 122.18, 122.07, 116.49, 116.28, 84.51, 25.09; Anal.Calc’d for C\(_{15}\)H\(_{18}\)BFO\(_4\): C, 61.68; H, 6.21. Found: C, 61.73; H, 6.24.

3-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-benzothien-5-yl]acrylic acid (2p): White solid; mp. = 172-174°C; \(^1\)H NMR (400MHz, CDCl\(_3\)) \(\delta\) 7.99 (s, 1H), 7.94-9.11 (m, 3H), 7.62-7.59 (dd, 1H, \(J_1 = 8.48\)Hz, \(J_2 = 1.56\)Hz), 6.55-6.51(d, 1H, \(J = 15.96\)Hz), 1.39 (s, 12H); \(^1^3\)C NMR (100MHz, CDCl\(_3\)) \(\delta\) 171.89, 147.14, 145.87, 140.86, 134.56, 130.45, 125.42, 124.09, 123.07, 116.80, 84.66, 24.81; Anal.Calc’d for C\(_{17}\)H\(_{19}\)BO\(_4\)S: C, 61.84; H, 5.80. Found: C, 61.89; H, 5.84.

1,1’-(Phenylmethylene)bis-pyridinium dibromide (1) (Scheme 2): Yellow solid; \(^1\)H NMR (400MHz, DMSO-\(d_6\)) \(\delta\) 9.55 (s, 1H), 9.42-9.40 (m, 4H), 8.92-8.88 (m, 2H), 8.40-8.36 (m, 4H), 7.69-7.61 (m, 3H), 7.42-7.40 (m, 2H); \(^1^3\)C NMR (100MHz, DMSO-\(d_6\)) \(\delta\) 149.60, 145.02, 132.02, 130.03, 129.37, 128.96, 128.73, 86.98.
$^1$H NMR in DMSO-$d_6$ (1b)
^1H NMR in DMSO-\textsubscript{d} \textit{d} (1b) - (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (1b)
$^1$H NMR in DMSO-$d_6$ (1c)
$^{13}$C NMR in DMSO-$d_6$ (1c)
$^1$H NMR in CDCl$_3$(1d)
$^1$H NMR in CDCl$_3$(1d) (inset is the expanded aromatic region)
$^{13}$C NMR in CDCl$_3$ (1d)
$^1$H NMR in DMSO-$d_6$ (1e)
¹H NMR in DMSO-$d_6$ (1e) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (1e)
$^1$H NMR in DMSO-$d_6$ (I)
$^1$H NMR in DMSO-$d_6$ (1f) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (1f)
$^1$H NMR in DMSO-$d_6$ (1g)
$^{13}\text{C}$ NMR in DMSO-$d_6$ (Ig)
$^1$H NMR in DMSO-$d_6$ (1h)
$^1$H NMR in DMSO-$d_6$ (1h) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (1h)
$^1$H NMR in CDCl$_3$ (II)
$^1$H NMR in CDCl$_3$ (II) (inset is the expanded aromatic region)
$^{13}$C NMR in CDCl$_3$ (II)
$^1$H NMR in DMSO-$d_6$ (1j)
$^1$H NMR in DMSO-$d_6$ (1j) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (1j)
$^1$H NMR in DMSO-$d_6$ (1k)
$^1$H NMR in DMSO-$d_6$ (1k) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (1k)
$^1$H NMR in CDCl$_3$ (II)
$^1$H NMR in CDCl$_3$ (II) (inset is the expanded aromatic region)
$^{13}$C NMR in CDCl$_3$ (II)
$^1$H NMR in DMSO-$d_6$ (1m)
$^{13}$C NMR in DMSO-$d_6$ (1m)
$^1$H NMR in DMSO-$d_6$ (1n)
$^{13}\text{C NMR in DMSO-d}_6$ (1n)
$^1$H NMR in DMSO-$d_6$ (1o)
$^1$H NMR in DMSO-$d_6$ (1o) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (1o)
$^{1}$H NMR in DMSO-$d_6$ (1p)
$^1$H NMR in DMSO-$d_6$ (1p) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-<i>d</i><sub>6</sub> (1p)
$^1$H NMR in DMSO-$_d_6$ (2b)
$^1$H NMR in DMSO-$d_6$ (2b) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2b)
$^1$H NMR in DMSO-$d_6$ (2e)
$^1$H NMR in DMSO-$d_6$ (2c) (inset is the expanded aromatic region)
$^1$H NMR in DMSO-$_d_6$ (2c)
$^1$H NMR in DMSO-$d_6$ (2d)
$^1$H NMR in DMSO-$d_6$ (2d) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2d)
$^1$H NMR in DMSO-$d_6$ (2e)
$^1$H NMR in DMSO-$d_6$ (2e) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2e)
$^1$H NMR in DMSO-$d_6$ (2f)
$^1$H NMR in DMSO-$d_6$ (2f) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2f)
$^1$H NMR in DMSO-$d_6$ (2g)
\(^1\)H NMR in DMSO-\(d_6\) (2g) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2g)
$^1$H NMR in DMSO-$d_6$ (2h)
$^1$H NMR in DMSO-$d_6$ (2h) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2h)
$^1$H NMR in DMSO-$d_6$ (2i)
$^1$H NMR in DMSO-$d_6$ (2i) (inset is the expanded aromatic region)
$^{13}\text{C NMR in DMSO-d}_6$ (2i)
$^1$H NMR in DMSO-$d_6$ (2j)
$^1$H NMR in DMSO-$d_6$ (2j) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2j)
$^1$H NMR in DMSO-$d_6$ (2k)
$^1$H NMR in DMSO-$d_6$ (2k) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2k)
$^1$H NMR in DMSO-$d_6$ (2l)
$^1$H NMR in DMSO-$d_6$ (2l) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2l)
$^1$H NMR in DMSO-$d_6$ (2m)
$^1$H NMR in DMSO-$_d_6$ (2m) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2m)
$^1$H NMR in DMSO-$d_6$ (2n)
$^1$H NMR in DMSO-$d_6$ (2n) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2n)
$^1$H NMR in DMSO-$d_6$ (2o)
$^1$H NMR in DMSO-$d_6$ (2o) (inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (2o)
$^1\text{H NMR in CDCl}_3(2p)$
$^1$H NMR in CDCl$_3$ (2p) (inset is the expanded aromatic region)
$^{13}$C NMR in CDCl$_3$ (2p)
$^1$H NMR in DMSO-$_d_6$ (Compound 1 in Scheme 2)
\(^1\)H NMR in DMSO-\(d_6\) (Compound 1 in Scheme 2)

(inset is the expanded aromatic region)
$^{13}$C NMR in DMSO-$d_6$ (Compound 1 in Scheme 2)