Supporting Information
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An NHC-catalyzed Cross-benzoin/esterification Sequential Reaction for Synthesis of Trifluoromethyl-substituted α,β-Unsaturated Esters

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Supporting Information

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1. General methods

NMR data was obtained for $^1$H at 400 MHz, and for $^{13}$C at 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane using solvent resonance in CDCl$_3$ solution as the internal standard. ESI HRMS was performed on a Waters SYNAPT G2. Column chromatography was performed on silica gel (200-300 mesh) using an eluent of ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates; products were visualized using UV light and I$_2$. Melting points were determined on a Mel-Temp apparatus and were not corrected. All chemicals were used from Adamas-beta without purification unless otherwise noted.

2. General procedure for the synthesis of CF$_3$-substituted $\alpha,\beta$-unsaturated esters 5

![Reaction Scheme]

The reaction was carried out with aromatic aldehyde 1 (0.5 mmol), CF$_3$CH(OH)OEt 2 (1.0 mmol), precatalyst A (0.05 mmol, 13.7 mg) and DBU (0.1 mmol, 15 µL) in THF (2.0 mL) at 60 °C under argon to afford the acyloin 3, after which $\alpha$-bromo-enal 4 (0.3 mmol) was added in one-pot. The reaction mixture was stirred at 60 °C for a specified reaction time until the reaction completed (monitored by TLC). Then the reaction mixture was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 40:1) to give the final product 5.

5a: Obtained as a white solid; yield: 65% (65.3 mg) for two steps after flash chromatography. m.p. 58-60 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.03-8.01 (m, 2H), 7.82 (d, $J = 16.0$ Hz, 2H), 7.57-7.51 (m, 4H), 7.44-7.38 (m, 3H), 6.57 (d, $J = 16.0$ Hz, 1H), 6.45 (q, $J = 6.8$ Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 188.6, 164.8, 148.2, 134.6, 133.7, 131.2, 129.0, 128.9, 128.5, 121.9 (d, $J_{CF} = 280$ Hz), 115.2, 70.9 (q, $J_{CF} = 31$ Hz) ppm; ESI HRMS: calcd. For C$_{18}$H$_{15}$F$_3$O$_3$+Na 357.0714, found 357.0717.
**5b:** Obtained as a white solid; yield: 74% (82.3 mg) for two steps after flash chromatography. m.p. 46-48 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.00$ (m, 1H), 7.90-7.88 (m, 1H), 7.82 (d, $J = 16.0$ Hz, 1H), 7.63 (ddd, $J_1 = 2.8$ Hz, $J_2 = 2.0$ Hz, $J_3 = 0.8$ Hz, 1H), 7.57-7.55 (m, 2H), 7.50-7.39 (m, 4H), 6.56 (d, $J = 16.0$ Hz, 1H), 6.34 (q, $J = 6.8$ Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 187.7, 164.8, 148.5, 136.0, 135.4, 134.5, 133.7, 131.3, 130.3, 129.1, 129.0, 128.6, 127.0, 121.7$ (d, $J_{CF} = 280$ Hz), 115.0, 71.1 (q, $J_{CF} = 32$ Hz) ppm; ESI HRMS: calcd. For C$_{18}$H$_{12}$ClF$_3$O$_3$+Na 391.0325, found 391.0322.

**5c:** Obtained as a white solid; yield: 80% (88.1 mg) for two steps after flash chromatography. m.p. 73-74 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.98-7.95$ (m, 2H), 7.82 (d, $J = 16.0$ Hz, 1H), 7.57-7.55 (m, 2H), 7.52-7.50 (m, 2H), 7.44-7.41 (m, 3H), 6.55 (d, $J = 16.0$ Hz, 1H), 6.36 (q, $J = 6.8$ Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 187.6, 164.8, 148.4, 141.3, 133.7, 132.8, 131.2, 130.3, 129.4, 129.1, 128.5, 121.8$ (d, $J_{CF} = 280$ Hz), 115.0, 71.0 (q, $J_{CF} = 32$ Hz) ppm; ESI HRMS: calcd. For C$_{18}$H$_{12}$ClF$_3$O$_3$+Na 391.0325, found 391.0320.

**5d:** Obtained as a white solid; yield: 73% (91.1 mg) for two steps after flash chromatography. m.p. 44-45 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.15$ (t, $J = 1.6$ Hz, 1H), 7.95-7.93 (m, 1H), 7.82 (d, $J = 16.0$ Hz, 1H), 7.80-7.77 (m, 1H), 7.58-7.55 (m, 2H), 7.43-7.39 (m, 4H), 6.56 (d, $J = 1.6$ Hz, 1H), 6.33 (q, $J = 6.8$ Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 187.6, 164.8, 148.5, 137.4, 136.2, 133.7, 131.9, 131.3, 130.5, 129.1, 128.6, 127.4, 123.3, 121.7$ (d, $J_{CF} = 280$ Hz), 114.9, 71.1 (q, $J_{CF} = 32$ Hz) ppm; ESI HRMS: calcd. For C$_{18}$H$_{12}$BrF$_3$O$_3$+Na 434.9820, found 434.9823.

**5e:** Obtained as a white solid; yield: 82% (102.1 mg) for two steps after flash chromatography. m.p. 80-81 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.90-7.86$ (m, 2H), 7.82 (d, $J = 16.4$ Hz, 1H), 7.69-7.66 (m, 2H), 7.57-7.55 (m, 2H), 7.44-7.39 (m, 3H), 6.55 (d, $J = 16.0$ Hz, 1H), 6.35 (q, $J = 6.8$ Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 187.8, 164.8, 148.5, 133.7, 133.3, 132.4, 131.3,$
130.4, 130.1, 129.1, 128.6, 121.7 (d, $J_{CF} = 280$ Hz), 115.0, 71.0 (q, $J_{CF} = 32$ Hz) ppm; ESI HRMS: calcd. For C$_{18}$H$_{12}$BrF$_3$O$_3$Na 434.9820, found 434.9817.

5f: Obtained as a white solid; yield: 70% (73.6 mg) for two steps after flash chromatography. m.p. 49-51 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.94-7.90 (m, 1H), 7.82 (d, $J = 16.0$ Hz, 1H), 7.64-7.55 (m, 3H), 7.43-7.41 (m, 3H), 7.32-7.28 (m, 1H), 7.24-7.19 (m, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 6.38 (qd, $J = 1.6$ Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 186.5, 164.8, 161.8 (d, $J_{CF} = 254$ Hz), 148.0, 136.3 (d, $J_{CF} = 10$ Hz), 133.8, 131.3 (d, $J_{CF} = 2$ Hz), 131.1, 129.0, 128.5, 125.0 (d, $J_{CF} = 3$ Hz), 121.8 (d, $J_{CF} = 280$ Hz), 116.9 (d, $J_{CF} = 24$ Hz), 115.4, 74.2 (q, $J_{CF} = 31$ Hz) ppm; ESI HRMS: calcd. For C$_{18}$H$_{12}$F$_4$O$_3$Na 375.0620, found 375.0617.

5g: Obtained as a white solid; yield: 76% (79.8 mg) for two steps after flash chromatography. m.p. 84-86 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.09-8.04 (m, 2H), 7.82 (d, $J = 16.0$ Hz, 1H), 7.58-7.55 (m, 2H), 7.44-7.39 (m, 3H), 7.23-7.18 (m, 2H), 6.56 (d, $J = 16.4$ Hz, 1H), 6.38 (q, $J = 6.8$ Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 187.0, 166.6 (d, $J_{CF} = 256$ Hz), 164.8, 148.4, 133.7, 131.8 (d, $J_{CF} = 9$ Hz), 131.2, 131.0, 129.1, 128.5, 121.8 (d, $J_{CF} = 280$ Hz), 116.3 (d, $J_{CF} = 22$ Hz), 115.0, 70.9 (q, $J_{CF} = 32$ Hz) ppm; ESI HRMS: calcd. For C$_{18}$H$_{12}$F$_4$O$_3$Na 375.0620, found 375.0616.

5h: Obtained as a white solid; yield: 58% (65.5 mg) for two steps after flash chromatography. m.p. 48-50 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.97-7.95 (m, 2H), 7.82 (d, $J = 16.0$ Hz, 1H), 7.57-7.55 (m, 2H), 7.43-7.36 (m, 5H), 6.57 (d, $J = 16.0$ Hz, 1H), 6.44 (q, $J = 6.8$ Hz, 1H), 3.02-2.95 (m, 1H), 1.29 (s, 3H), 1.27 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 187.9, 164.8, 156.5, 148.1, 133.8, 132.4, 131.1, 129.3, 129.0, 128.5, 127.1, 121.9 (d, $J_{CF} = 280$ Hz), 115.3, 70.7 (q, $J_{CF} = 32$ Hz), 34.4, 23.54, 23.53 ppm; ESI HRMS: calcd. For C$_{21}$H$_{19}$F$_3$O$_3$Na 399.1184, found 399.1187.
5i: Obtained as a white solid; yield: 50% (48.7 mg) for two steps after flash chromatography. m.p. 64-65 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.83\) (d, \(J = 16.0\) Hz, 1H), 7.72 (d, \(J = 1.2\) Hz, 1H), 7.58-7.55 (m, 2H), 7.46-7.40 (m, 4H), 6.64 (dd, \(J_1 = 3.6\) Hz, \(J_2 = 1.6\) Hz, 1H), 6.57 (d, \(J = 16.0\) Hz, 1H), 6.26 (q, \(J = 6.8\) Hz, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 176.2, 164.7, 150.6, 148.3, 148.2, 133.7, 131.2, 129.1, 128.5, 121.8\) (d, \(J_{CF} = 280\) Hz), 120.6, 115.2, 113.1, 71.2 (q, \(J_{CF} = 32\) Hz) ppm; ESI HRMS: calcd. For C\(_{16}\)H\(_{11}\)F\(_3\)O\(_4\)+Na 347.0507, found 347.0501.

5j: Obtained as a white solid; yield: 53% (53.7 mg) for two steps after flash chromatography. m.p. 39-41 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.95\) (d, \(J = 4.0\) Hz, 1H), 7.84 (d, \(J = 16.0\) Hz, 1H), 7.80 (dd, \(J_1 = 5.2\) Hz, \(J_2 = 1.2\) Hz, 1H), 7.60-7.56 (m, 2H), 7.44-7.40 (m, 3H), 7.21 (dd, \(J_1 = 4.8\) Hz, \(J_2 = 4.0\) Hz, 1H), 6.58 (d, \(J = 16.0\) Hz, 1H), 6.20 (q, \(J = 6.8\) Hz, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 180.7, 164.8, 148.4, 140.7, 136.5, 134.5, 133.7, 131.2, 129.1, 128.7, 128.5, 121.7\) (d, \(J_{CF} = 280\) Hz), 115.1, 72.2 (q, \(J_{CF} = 32\) Hz) ppm; ESI HRMS: calcd. For C\(_{16}\)H\(_{11}\)F\(_3\)S+Na 363.0279, found 363.0282.

5k: Obtained as a white solid; yield: 55% (59.3 mg) for two steps after flash chromatography. m.p. 56-57 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.86\) (d, \(J = 16.0\) Hz, 1H), 7.85 (d, \(J = 16.0\) Hz, 1H), 7.62-7.57 (m, 4H), 7.45-7.39 (m, 6H), 7.00 (d, \(J = 16.0\) Hz, 1H), 6.60 (d, \(J = 16.0\) Hz, 1H), 5.82 (q, \(J = 7.2\) Hz, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 187.0, 164.7, 148.2, 146.9, 133.8, 131.6, 131.2, 129.1, 129.06, 129.00, 128.5, 121.9\) (d, \(J_{CF} = 279\) Hz), 120.2, 120.1, 115.3, 74.0 (q, \(J_{CF} = 31\) Hz) ppm; ESI HRMS: calcd. For C\(_{20}\)H\(_{15}\)F\(_3\)O\(_3\)+Na 383.0871, found 383.0867.

5l: Obtained as a white solid; yield: 67% (73.6 mg) for two steps after flash chromatography. m.p. 99-101 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.25\) (d, \(J = 16.0\) Hz, 1H), 8.04-8.01 (m, 2H), 7.68-7.64 (m, 2H), 7.55-7.52 (m, 2H), 7.45-7.42 (m, 1H), 7.37-7.28 (m, 2H), 6.58 (d, \(J = 16.0\) Hz, 1H), 6.45 (q, \(J = 6.8\) Hz, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 188.5, 164.4, 143.9, 135.4, 134.6, 134.5, 132.0, 131.9, 130.4, 129.0, 127.9, 127.2, 121.8\) (d, \(J_{CF} = 280\) Hz), 117.7, 71.0 (q, \(J_{CF} = 32\) Hz) ppm; ESI HRMS: calcd. For C\(_{18}\)H\(_{12}\)ClF\(_3\)O\(_3\)+Na 391.0325, found 391.0320.
5m: Obtained as a white solid; yield: 70% (77.5 mg) for two steps after flash chromatography. m.p. 60-62 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.02-8.00\) (m, 2H), 7.74 (d, \(J = 16.0\) Hz, 1H), 7.68-7.65 (m, 1H), 7.55-7.51 (m, 3H), 7.44-7.33 (m, 3H), 6.57 (d, \(J = 16.0\) Hz, 1H), 6.44 (q, \(J = 6.8\) Hz, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 188.4, 164.4, 146.4, 135.5, 135.1, 134.6, 134.5, 131.0, 130.3, 129.0, 128.9, 128.2, 126.6, 121.8\) (d, \(J_{CF} = 280\) Hz), 116.8, 71.0 (q, \(J_{CF} = 32\) Hz) ppm; ESI HRMS: calcd. For C\(_{18}\)H\(_{12}\)ClF\(_3\)O\(_3\)+Na 391.0325, found 391.0328.

5n: Obtained as a white solid; yield: 73% (80.4 mg) for two steps after flash chromatography. m.p. 90-92 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.02-8.00\) (m, 2H), 7.76 (d, \(J = 16.0\) Hz, 1H), 7.68-7.64 (m, 1H), 7.55-7.47 (m, 4H), 7.40-7.37 (m, 2H), 6.54 (d, \(J = 16.0\) Hz, 1H), 6.45 (q, \(J = 6.8\) Hz, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 188.4, 164.6, 146.6, 137.2, 134.6, 134.5, 132.2, 129.7, 129.4, 129.0, 121.8\) (d, \(J_{CF} = 280\) Hz), 115.8, 70.9 (q, \(J_{CF} = 32\) Hz) ppm; ESI HRMS: calcd. For C\(_{18}\)H\(_{12}\)ClF\(_3\)O\(_3\)+Na 391.0325, found 391.0329.

5o: Obtained as a white solid; yield: 66% (69.5 mg) for two steps after flash chromatography. m.p. 45-46 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.03-8.01\) (m, 2H), 7.94 (d, \(J = 16.0\) Hz, 1H), 7.68-7.64 (m, 1H), 7.58-7.51 (m, 3H), 7.43-7.38 (m, 1H), 7.21-7.10 (m, 2H), 6.68 (d, \(J = 16.4\) Hz, 1H), 6.45 (q, \(J = 6.8\) Hz, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 188.5, 164.7, 161.6\) (d, \(J_{CF} = 254\) Hz), 140.8 (d, \(J_{CF} = 2\) Hz), 134.6, 132.6 (d, \(J_{CF} = 8\) Hz), 129.5 (d, \(J_{CF} = 2\) Hz), 129.0, 124.6 (d, \(J_{CF} = 4\) Hz), 121.9 (d, \(J_{CF} = 12\) Hz), 121.8 (d, \(J_{CF} = 280\) Hz), 117.8 (d, \(J_{CF} = 7\) Hz), 116.4 (d, \(J_{CF} = 22\) Hz), 71.0 (q, \(J_{CF} = 32\) Hz) ppm; ESI HRMS: calcd. For C\(_{18}\)H\(_{12}\)F\(_4\)O\(_3\)+Na 375.0620, found 375.0617.

5p: Obtained as a white solid; yield: 71% (74.6 mg) for two steps after flash chromatography. m.p. 41-42 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.03-8.01\) (m, 2H), 7.77 (d, \(J = 16.0\) Hz, 1H), 7.68-7.64 (m,1H), 7.55-7.51 (m, 2H), 7.41-7.32 (m, 2H), 7.27-7.24 (m, 1H), 7.15-7.10 (m, 1H), 6.56 (d, \(J = 16.0\) Hz, 1H), 6.45 (q, \(J = 6.8\) Hz, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 188.4, 164.5, 163.0\) (d, \(J_{CF} = 246\) Hz), 146.7 (d, \(J_{CF} = 2\) Hz), 135.9 (d, \(J_{CF} = 8\) Hz), 134.6, 134.5, 130.6 (d, \(J_{CF} = 1465\) Hz, 1H), 116.4 (d, \(J_{CF} = 22\) Hz), 71.0 (q, \(J_{CF} = 32\) Hz) ppm; ESI HRMS: calcd. For C\(_{18}\)H\(_{12}\)F\(_4\)O\(_3\)+Na 375.0620, found 375.0617.
$J_{CF} = 9 \text{ Hz}$), 129.0, 128.9, 124.5 (d, $J_{CF} = 2 \text{ Hz}$), 121.8 (d, $J_{CF} = 280 \text{ Hz}$), 118.0 (d, $J_{CF} = 21 \text{ Hz}$), 116.7, 114.7 (d, $J_{CF} = 22 \text{ Hz}$), 71.0 (q, $J_{CF} = 31 \text{ Hz}$) ppm; ESI HRMS: calcd. For $C_{18}H_{12}F_{4}O_{3}$+Na 375.0620, found 375.0624.

5q: Obtained as a white solid; yield: 72% (88.7 mg) for two steps after flash chromatography. m.p. 46-48 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.02-8.00 (m, 2H), 7.75-7.65 (m, 3H), 7.55-7.46 (m, 4H), 7.31-7.27 (m, 1H), 6.56 (d, $J = 16.0 \text{ Hz}$, 1H), 6.44 (q, $J = 6.4 \text{ Hz}$, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 188.4, 164.4, 146.4, 135.8, 134.7, 134.5, 133.9, 131.2, 130.5, 129.0, 128.9, 127.1, 123.2, 121.8 (d, $J_{CF} = 283 \text{ Hz}$), 116.8, 71.0 (q, $J_{CF} = 32 \text{ Hz}$) ppm; ESI HRMS: calcd. For $C_{18}H_{12}BrF_{3}O_{3}$+Na 434.9820, found 434.9816.

5r: Obtained as a white solid; yield: 75% (92.5 mg) for two steps after flash chromatography. m.p. 114-116 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.02-8.00 (m, 2H), 7.75 (d, $J = 16.0 \text{ Hz}$, 1H), 7.69-7.64 (m, 1H), 7.56-7.51 (m, 4H), 7.43-7.41 (m, 2H), 6.55 (d, $J = 16.0 \text{ Hz}$, 1H), 6.44 (q, $J = 6.8 \text{ Hz}$, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 188.4, 164.6, 146.7, 134.6, 134.5, 132.6, 132.3, 129.8, 129.0, 125.6, 121.8 (d, $J_{CF} = 280 \text{ Hz}$), 115.9, 70.9 (q, $J_{CF} = 32 \text{ Hz}$) ppm; ESI HRMS: calcd. For $C_{18}H_{12}BrF_{3}O_{3}$+Na 434.9820, found 434.9816.

5s: Obtained as a white solid; yield: 63% (71.5 mg) for two steps after flash chromatography. m.p. 82-83 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.29-8.26 (m, 2H), 8.03-8.01 (m, 2H), 7.85 (d, $J = 16.0 \text{ Hz}$, 1H), 7.74-7.66 (m, 3H), 7.57-7.53 (m, 2H), 6.70 (d, $J = 16.0 \text{ Hz}$, 1H), 6.47 (q, $J = 6.8 \text{ Hz}$, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 188.1, 163.9, 149.0, 144.9, 139.7, 134.8, 134.5, 129.1, 129.0, 128.9, 124.3, 121.7 (d, $J_{CF} = 280 \text{ Hz}$), 119.6, 71.1 (q, $J_{CF} = 32 \text{ Hz}$) ppm; ESI HRMS: calcd. For $C_{18}H_{12}F_{5}NO_{3}$+Na 402.0565, found 402.0571.

5t: Obtained as a white solid; yield: 60% (62.6 mg) for two steps after flash chromatography. m.p. 44-46 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.03-8.01 (m, 2H), 7.79 (d, $J = 16.0 \text{ Hz}$, 1H),
7.67-7.63 (m, 1H), 7.54-7.50 (m, 2H), 7.46-7.44 (m, 2H), 7.22-7.20 (m, 2H), 6.51 (d, J = 16.0 Hz, 1H), 6.47 (q, J = 6.8 Hz, 1H), 2.38 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 188.7, 165.0, 148.2, 141.8, 134.5, 131.1, 129.8, 129.6, 129.0, 128.9, 128.5, 121.9 (d, $J_{CF} = 280$ Hz), 114.0, 70.8 ppm; ESI HRMS: calcd. For C$_{19}$H$_{15}$F$_3$O$_3$+Na 371.0871, found 371.0867.

5u: Obtained as a white solid; yield: 54% (58.6 mg) for two steps after flash chromatography. m.p. 62-63 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.03-8.01 (m, 2H), 7.77 (d, J = 16.0 Hz, 1H), 7.67-7.63 (m, 1H), 7.54-7.50 (m, 4H), 6.94-6.90 (m, 2H), 6.47-6.40 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 188.8, 165.1, 162.1, 147.9, 134.6, 134.5, 130.3, 129.0, 128.9, 126.5, 121.9 (d, $J_{CF} = 280$ Hz), 114.5, 112.5, 70.7 ppm; ESI HRMS: calcd. For C$_{19}$H$_{15}$F$_3$O$_3$+Na 387.0820, found 387.0825.

5v: Obtained as a white solid; yield: 38% (37.4 mg) for two steps after flash chromatography. m.p. 76-77 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.01 (d, J = 7.6 Hz, 2H), 7.67-7.63 (m, 1H), 7.56-7.50 (m, 4H), 6.71 (d, J = 3.6 Hz, 1H), 6.50 (dd, J$_1$ = 3.6 Hz, J$_2$ = 2.0 Hz, 1H), 6.44-6.39 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 188.6, 164.8, 150.4, 145.7, 134.6, 134.5, 133.8, 129.0, 128.9, 121.9 (d, $J_{CF} = 280$ Hz), 116.6, 112.7, 112.6, 70.9 ppm; ESI HRMS: calcd. For C$_{16}$H$_{11}$F$_3$O$_4$+Na 347.0507, found 347.0504.

5w: Obtained as a white solid; yield: 51% (41.5 mg) for two steps after flash chromatography. m.p. 59-61 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.00-7.97 (m, 2H), 7.67-7.63 (m, 1H), 7.53-7.49 (m, 2H), 7.21-7.12 (m, 1H), 6.36 (q, J = 6.8 Hz, 1H), 5.99 (dq, J$_1$ = 15.6 Hz, J$_2$ = 1.6 Hz, 1H), 1.94 (dd, J$_1$ = 7.2 Hz, J$_2$ = 1.6 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 188.6, 164.1, 149.0, 134.6, 134.5, 128.94, 128.92, 121.8 (d, $J_{CF} = 280$ Hz), 120.3, 70.7 ppm; ESI HRMS: calcd. For C$_{13}$H$_{11}$F$_3$O$_3$+Na 295.0558, found 295.0562.
3. Synthetic transformations to access multi-functionalized oxazole 7

To a solution of 5a (50.0 mg, 0.15 mmol) in DMF (2.0 mL) was added thiourea (22.8 mg, 0.30 mmol). The mixture was stirring at 150 ºC (oil bath) under a nitrogen atmosphere for 16h. The reaction was then extracted with ethyl acetate, and the organic layer was dried over Na₂SO₄ and concentrated. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). The oxazole 7 was obtained as a yellow solid in 72% yield (34.1 mg) after flash chromatography. m.p. 182-184 ºC; ¹H NMR (400 MHz, CDCl₃): δ = 7.53-7.52 (m, 2H), 7.48-7.43 (m, 5H), 7.39-7.31 (m, 4H), 6.95 (d, J = 16.4 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 145.6, 135.6, 133.4, 129.3, 128.94, 128.91, 128.8, 128.4, 128.3, 126.9, 126.1, 122.1 (d, J_CF = 266 Hz), 115.2 ppm; ESI HRMS: calcd. For C₁₈H₁₂F₃NO₃+Na 338.0769, found 338.0763.
4. NMR spectra