SUPPORTING INFORMATION

A NCS mediated oxidative C-H bond functionalization: direct esterification between C(sp³)–H bond and carboxylic acids

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General experimental: All reactions were carried out in air. Carboxylic acids, N-Chlorosuccinimide (NCS), base, and the solvent used in this reaction were were obtained from commercial sources and used without further purification. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in CDCl₃ on a Varian Inova-400 NMR spectrometer (400 MHz); chemical shifts were reported in ppm with the solvent signals as reference, and coupling constants (J) were given in Hertz. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. Products were characterized by comparison of ¹H NMR, ¹³C NMR and TOF-MS data in the literatures.

General Procedure for the NCS-Promoted Oxidative Coupling Esterfication.

To a Schlenk tube equipped with a magnetic stir bar was added carboxylic acids (1, 0.30 mmol), NCS (N-Chlorosuccinimide, 68.1 mg, 0.51 mmol), base (0.51 mmol), and ether 2 (2.0 mL). The reaction mixture was stirred at 80 °C for 12 hours. At the end of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 6:1) to afford the pure products.
Characterization of the Corresponding Products:

1,4-Dioxan-2-yl 3-phenylpropiolate

White oil; 53.8 mg; 77% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.61 (dd, $J = 8.3$ Hz, 1.3 Hz, 2H), 7.47 (ddd, $J = 6.6$ Hz, 3.9 Hz, 1.3 Hz, 1H), 7.41-7.37 (m, 2H), 5.99 (s, 1H), 4.26-4.20 (m, 2H), 3.85-3.80 (comp, 4H), 3.67 (dt, $J = 11.7$ Hz, 2.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 152.8, 133.1, 130.9, 128.6, 119.4, 90.7, 87.5, 80.3, 67.5, 66.0, 61.6; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{13}$O$_4$ [M+H]$: 233.0814, found 233.0817.

1,4-Dioxan-2-yl 3-(4-methoxyphenyl)propiolate

White oil; 56.0 mg; 71% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.57 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 5.98 (s, 1H), 4.26-4.20 (m, 1H), 3.87-3.80 (comp, 7H), 3.69-3.65 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 161.7, 153.0, 135.1, 114.3, 111.1, 90.5, 88.5, 79.8, 67.5, 66.0, 61.6, 55.4; HRMS (TOF MS Cl$^+$) calculated for C$_{14}$H$_{15}$O$_5$ [M+H]$: 263.0919, found 263.0928.

1,4-Dioxan-2-yl 3-$p$-tolylpropiolate

White oil; 54.0 mg; 73% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.52 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 5.99 (s, 1H), 4.27-4.21 (m, 1H), 3.85-3.81 (comp, 4H), 3.67 (dt, $J = 11.7$ Hz, 2.2 Hz, 1H), 2.40 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 152.9, 141.6, 133.2, 129.4, 116.3, 90.6, 88.1, 80.0, 67.5, 66.0, 61.6, 21.7; HRMS (TOF MS Cl$^+$) calculated for C$_{14}$H$_{15}$O$_4$ [M+H]$: 247.0970, found 247.0960.
1,4-Dioxan-2-yl 3-(4-tert-butylphenyl)propiolate

White oil; 72.0 mg; 83% yield; $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.58-7.55 (m, 2H), 7.43-7.41 (m, 2H), 6.00 (s, 1H), 4.28-4.22 (m, 1H), 3.86-3.82 (comp, 4H), 3.68 (dt, $J = 11.7$ Hz, 2.4 Hz, 1H), 1.34 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 154.6, 153.0, 133.1, 125.7, 116.3, 90.6, 88.1, 80.0, 67.5, 66.1, 61.6, 35.1, 31.0; HRMS (TOF MS Cl$^+$) calculated for C$_{17}$H$_{21}$O$_4$ [M+H]$^+$: 289.1440, found 289.1441.

1,4-Dioxan-2-yl 3-(4-fluorophenyl)propiolate

White oil; 48.9 mg; 65% yield; $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.65-7.61 (comp, 2H), 7.10 (t, $J=8.6$, 2H), 6.00 (s, 1H), 4.27-4.20 (m, 1H), 3.86-3.82 (comp, 4H), 3.68 (dt, $J = 11.8$ Hz, 2.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 164.0 (d, $J = 250.0$ Hz), 152.7, 135.5 (d, $J = 9.0$ Hz), 116.2 (d, $J = 23.0$ Hz), 115.5, 90.7, 86.4, 80.2, 67.5, 66.0, 61.6; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{12}$FO$_4$ [M+H]$^+$: 251.0720, found 251.0728.

1,4-Dioxan-2-yl 3-(4-bromophenyl)propiolate

White oil; 60.6 mg; 65% yield; $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.55 (d, $J = 8.5$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 6.00 (s, 1H), 4.27-4.20 (m, 1H), 3.86-3.82 (comp, 4H), 3.68 (dt, $J = 11.7$ Hz, 2.1 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 152.6, 134.4, 132.1, 125.7, 118.3, 90.8, 86.2, 81.2, 67.4, 66.0, 61.6; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{12}$BrO$_4$ [M+H]$^+$: 310.9919, found 310.9921.
1,4-Dioxan-2-yl 3-(4-chlorophenyl)propiolate

White oil; 49.7 mg; 62% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.57-7.54 (m, 2H), 7.40-7.37 (m, 2H), 6.00 (s, 1H), 4.27-4.20 (m, 1H), 3.86-3.82 (comp, 4H), 3.68 (dt, $J = 11.8$ Hz, 2.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 152.6, 137.3, 134.3, 129.1, 117.9, 90.8, 86.1, 81.1, 67.4, 66.0, 61.6; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{12}$ClO$_4$ [M+H]$^+$: 267.0424, found 267.0429.

1,4-Dioxan-2-yl 3-(3-chlorophenyl)propiolate

White oil; 51.3 mg; 64% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.61 (t, $J = 1.7$ Hz, 1H), 7.51 (dt, $J = 7.6$ Hz, 1.3 Hz, 1H), 7.47-7.44 (m, 1H), 7.34 (t, $J = 7.9$ Hz, 1H), 6.00 (s, 1H), 4.27-4.20 (m, 1H), 3.86-3.82 (comp, 4H), 3.68 (dt, $J = 11.8$ Hz, 2.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 152.5, 134.6, 132.8, 131.2, 129.9, 121.1, 90.9, 85.5, 81.0, 67.4, 66.0, 61.6; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{12}$ClO$_4$ [M+H]$^+$: 267.0424, found 267.0425.

1,4-Dioxan-2-yl 3-(2-chlorophenyl)propiolate

White oil; 61.7 mg; 77% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.64-7.62 (m, 1H), 7.47-7.45 (m, 1H), 7.43-7.38 (m, 1H), 7.32-7.28 (m, 1H), 6.01 (s, 1H), 4.27-4.21 (m, 1H), 3.87-3.81 (comp, 4H), 3.68 (dt, $J = 11.9$ Hz, 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 152.5, 137.5, 134.8, 131.8, 129.7, 126.7, 119.8, 90.9, 84.4, 83.7, 67.4, 66.0, 61.7; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{12}$ClO$_4$ [M+H]$^+$: 267.0424, found 267.0414.
1,4-Dioxan-2-yl 3-(2-bromophenyl)propiolate

White oil; 66.1 mg; 71% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.65-7.61 (m, 2H), 7.37-7.30 (m, 2H), 6.01 (s, 1H), 4.27-4.20 (m, 1H), 3.90-3.78 (comp, 4H), 3.68 (dt, $J = 11.8$ Hz, 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 152.5, 134.9, 132.8, 131.9, 127.3, 126.6, 122.0, 90.9, 85.2, 83.8, 67.4, 66.0, 61.7; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{12}$BrO$_4$ [M+H]$^+$: 310.9919, found 310.9929.

1,4-Dioxan-2-yl 3-<o>-tolylpropiolate

White oil; 51.9 mg; 70% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.58 (d, $J = 7.1$ Hz, 1H), 7.37 (td, $J = 7.6$ Hz, 1.1 Hz, 1H), 7.24 (dt, $J = 15.1$ Hz, 5.4 Hz, 2H), 6.01 (s, 1H), 4.28-4.21 (m, 1H), 3.82-3.87 (comp, 4H), 3.69 (dt, $J = 11.8$ Hz, 2.4 Hz, 1H), 2.52 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 152.4, 142.0, 133.0, 130.4, 129.3, 125.3, 118.7, 90.2, 86.2, 83.5, 67.0, 65.5, 61.2, 20.1; HRMS (TOF MS Cl$^+$) calculated for C$_{14}$H$_{15}$O$_4$ [M+H]$^+$: 247.0970, found 247.0974.

1,4-Dioxan-2-yl 3-(naphthalen-1-yl)propiolate

White oil; 53.5 mg; 63% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 8.38 (d, $J = 8.4$ Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 1H), 7.93-7.87 (comp, 2H), 7.68-7.64 (m, 1H), 7.61-7.57 (m, 1H), 7.51-7.47 (m, 1H), 6.07 (s, 1H), 4.33-4.27 (m, 1H), 3.96-3.82 (comp, 4H), 3.72 (dt, $J = 11.7$ Hz, 2.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 152.4, 133.2, 132.9, 132.5, 131.1, 128.0, 127.3, 126.5, 125.3, 124.6, 116.5, 90.3, 85.5, 84.4, 67.0, 65.6, 61.2; HRMS (TOF MS Cl$^+$) calculated for C$_{17}$H$_{16}$O$_4$ [M+H]$^+$: 283.0970, found 283.0965.
1,4-Dioxan-2-yl 3-(naphthalen-2-yl)propiolate

White oil; 46.7 mg; 55% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 8.24 (s, 1H), 7.90-7.87 (comp, 3H), 7.66-7.57 (comp, 3H), 6.07 (s, 1H), 4.35-4.28 (m, 1H), 3.96-3.84 (comp, 4H), 3.74 (dt, $J = 11.7$ Hz, 2.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 152.4, 134.1, 133.5, 132.1, 128.0, 127.8, 127.7, 127.6, 127.4, 126.6, 116.1, 90.2, 87.6, 80.0, 67.0, 65.6, 61.1; HRMS (TOF MS Cl$^+$) calculated for C$_{17}$H$_{15}$O$_4$ [M+H]$^+$: 283.0970, found 283.0967.

1,4-Dioxan-2-yl but-2-ynoate

White oil; 31.8 mg; 62% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 5.90 (s, 1H), 4.20-4.14 (m, 1H), 3.80-3.78 (comp, 4H), 3.64 (dt, $J = 11.9$ Hz, 2.4 Hz, 1H), 2.02 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 151.9, 89.9, 86.6, 71.6, 66.9, 65.5, 61.1, 3.4; HRMS (TOF MS Cl$^+$) calculated for C$_8$H$_{10}$O$_4$ [M+H]$^+$: 171.0657, found 171.0660

1,4-Dioxan-2-yl benzoate

White oil; 46.4 mg; 74% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 8.19-8.17 (m, 2H), 7.66-7.62 (m, 1H), 7.53-7.49 (m, 2H), 6.15 (t, $J = 1.9$ Hz, 1H), 4.31-4.25 (m, 1H), 3.95 (d, $J = 2.0$ Hz, 2H), 3.88 (dd, $J = 6.8$ Hz, 2.6 Hz, 2H), 3.73 (dt, $J = 11.8$ Hz, 2.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 164.8, 132.9, 129.4, 129.2, 128.0, 89.3, 67.4, 65.7, 61.3; HRMS (TOF MS Cl$^+$) calculated for C$_{11}$H$_{13}$O$_4$ [M+H]$^+$: 209.0814, found 209.0810.
**1,4-Dioxan-2-yl 4-tert-butylbenzoate**

![Image of molecule 4b]

White oil; 74.7 mg; 94% yield; $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 8.12-8.09 (m, 2H), 7.54-7.51 (m, 2H), 6.14 (t, $J$ = 1.8 Hz, 1H), 4.30-4.23 (m, 1H), 3.94-3.93 (m, 2H), 3.87 (dd, $J$ = 6.7 Hz, 2.6 Hz, 2H), 3.72 (dt, $J$ = 11.7 Hz, 2.6 Hz, 1H), 1.39 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 164.7, 156.7, 129.3, 126.5, 124.9, 89.1, 67.4, 65.7, 61.3, 34.7, 30.6; HRMS (TOF MS Cl$^+$) calculated for C$_{15}$H$_{21}$O$_4$ [M+H]$^+$: 265.1440, found 265.1445.

**1,4-Dioxan-2-yl 4-methoxybenzoate**

![Image of molecule 4c]

White oil; 43.1 mg; 60% yield; $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 8.11-8.08 (m, 2H), 6.97-6.93 (m, 2H), 6.09 (t, $J$ = 1.9 Hz, 1H), 4.26-4.19 (m, 1H), 3.90-3.82 (comp, 7H), 3.69 (dt, $J$ = 11.8 Hz, 2.7 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 164.9, 163.8, 132.0, 122.0, 113.7, 89.5, 67.9, 66.2, 61.8, 55.5; HRMS (TOF MS Cl$^+$) calculated for C$_{12}$H$_{15}$O$_5$ [M+H]$^+$: 239.0919, found 239.0918.

**1,4-Dioxan-2-yl 4-methylbenzoate**

![Image of molecule 4d]

White oil; 53.5 mg; 80% yield; $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 8.07 (d, $J$ = 8.2 Hz, 2H), 7.32-7.30 (m, 2H), 6.14 (t, $J$ = 1.9 Hz, 1H), 4.30-4.24 (m, 1H), 3.94 (m, 2H), 3.88 (dd, $J$ = 6.8 Hz, 2.6 Hz, 2H), 3.73 (dt, $J$ = 11.7 Hz, 2.7 Hz, 1H), 2.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 164.8, 143.7, 129.5, 128.7, 126.5, 89.2, 67.4, 65.7, 61.3, 21.2; HRMS (TOF MS Cl$^+$) calculated for C$_{12}$H$_{15}$O$_4$ [M+H]$^+$: 223.0970, found 223.0973.

**1,4-Dioxan-2-yl 4-(trifluoromethyl)benzoate**

![Image of molecule 4e]
White oil; 70.6 mg; 85% yield; $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 8.25 (d, $J = 8.1$ Hz, 2H), 7.74 (d, $J = 8.2$ Hz, 2H), 6.13 (s, 1H), 4.26-4.20 (m, 1H), 3.92 (d, $J = 1.8$ Hz, 2H), 3.86 (dd, $J = 6.8$ Hz, 2.3, 2H), 3.71 (dt, $J = 11.8$ Hz, 2.4, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 164.1, 134.9 (d, $J = 33.0$ Hz), 133.0, 130.3, 125.5 (q, $J = 3.7$ Hz), 122.2, 90.4, 67.1, 66.1, 61.8; HRMS (TOF MS Cl$^+$) calculated for C$_{12}$H$_{12}$F$_3$O$_4$ [M+H]$^+$: 277.0688, found 277.0685.

1,4-Dioxan-2-yl 2-benzoylbenzoate

White oil; 77.0 mg; 82% yield; $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 8.18 (dd, $J = 7.8$ Hz, 1.0 Hz, 1H), 7.81-7.79 (m, 2H), 7.67 (td, $J = 7.5$ Hz, 1.3 Hz, 1H), 7.62-7.53 (m, 2H), 7.47-7.39 (m, 3H), 5.85 (s, 1H), 3.88-3.82(m, 1H), 3.70-3.60 (comp, 3H), 3.51-3.47 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 196.2, 164.1, 141.6, 136.4, 132.8, 132.2, 130.2, 129.3, 129.0, 128.1, 127.9, 127.1, 90.1, 66.7, 65.3, 61.1; HRMS (TOF MS Cl$^+$) calculated for C$_{18}$H$_{17}$O$_5$ [M+H]$^+$: 313.1076, found 313.1077.

1,4-Dioxan-2-yl 4-fluorobenzoate

White oil; 68.1 mg; 65% yield; $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 8.18-8.13 (m, 2H), 7.17-7.12 (m, 2H), 6.10 (s, 1H), 4.25-4.19 (m, 1H), 3.90 (d, $J = 1.9$ Hz, 2H), 3.84 (dd, $J = 6.8$ Hz, 2.5 Hz, 2H), 3.70 (dt, $J = 11.8$ Hz, 2.5 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 166.0 (d, $J = 250.0$ Hz), 164.3, 132.5 (d, $J = 9.4$ Hz), 126.0 (d, $J = 2.9$ Hz), 115.7 (d, $J = 21.9$ Hz), 89.9, 67.8, 66.1, 61.8; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{17}$O$_5$ [M+H]$^+$: 313.1076, found 313.1077.

1,4-Dioxan-2-yl furan-2-carboxylate

White oil; 44.2 mg; 74% yield; $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.66 (m, 1H), 7.35-7.33 (m, 1H), 6.58-6.57 (m, 1H), 6.11 (s, 1H), 4.28-4.21 (m, 1H), 3.91 (d, $J = 1.9$ Hz, 2H), 3.87-3.85 (m, 2H), 3.71 (dt, $J = 11.7$ Hz, 2.5 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 156.8, 146.4, 143.6, 118.5, 111.5, 89.3, 67.2, 65.6, 61.3; HRMS (TOF MS Cl$^+$) calculated for C$_{9}$H$_{11}$O$_5$ [M+H]$^+$: 199.0606, found 199.0609.
1,4-Dioxan-2-yl 2-naphthoate

![Image](4i)

White oil; 55.2 mg; 71% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 8.76 (s, 1H), 8.19 (dd, $J$ = 8.6 Hz, 1.7 Hz, 1H), 8.04 (d, $J$ = 8.0 Hz, 1H), 7.96-7.93 (m, 2H), 7.68-7.59 (m, 2H), 6.23 (t, $J$ = 1.9 Hz, 1H), 4.37-4.31 (m, 1H), 4.01-4.00 (m, 2H), 3.93-3.91 (m, 2H), 3.77 (dt, $J$ = 11.8 Hz, 2.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 164.9, 135.3, 132.0, 131.1, 129.0, 128.0, 127.8, 127.3, 126.5, 126.3, 124.9, 89.4, 67.5, 65.7, 61.4; HRMS (TOF MS Cl$^+$) calculated for C$_{15}$H$_{15}$O$_4$ [M+H]$^+$: 259.0970, found 259.0961.

1,4-Dioxan-2-yl 3-phenylpropanoate

![Image](4j)

White oil; 59.0 mg; 83% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.37-7.31 (m, 2H), 7.28-7.24 (comp, 3H), 5.91 (t, $J$ = 2.0 Hz, 1H), 4.12-4.04 (m, 1H), 3.84-3.71 (m, 4H), 3.64 (dt, $J$ = 11.8 Hz, 2.7 Hz, 1H), 3.05 (t, $J$ = 7.8 Hz, 2H), 2.81-2.77 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 171.2, 139.7, 128.1, 127.8, 125.9, 88.8, 67.2, 65.6, 61.2, 35.4, 30.3; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{17}$O$_4$ [M+H]$^+$: 237.1127, found 237.1124.

(E)-1,4-Dioxan-2-yl 3-(3-nitrophenyl)acrylate

![Image](4k)

Yellow oil; 69.7 mg; 83% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 8.41 (s, 1H), 8.26 (dd, $J$ = 8.2 Hz, 1.3, 1H), 7.87-7.80 (m, 2H), 7.61 (t, $J$ = 8.0 Hz, 1H), 6.65 (d, $J$ = 16.0 Hz, 1H), 6.01 (s, 1H), 4.24-4.18 (m, 1H), 3.90-3.82 (comp, 4H), 3.69 (dt, $J$ = 11.8 Hz, 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 164.2, 148.2, 142.6, 135.4, 133.2, 129.6, 124.3, 122.1, 120.2, 89.3, 67.3, 65.6, 61.2; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{14}$NO$_6$ [M+H]$^+$: 280.0821, found 280.0824.
**1,4-Dioxan-2-yl cinnamate**

![Image](image1.png)

White oil; 42.3 mg; 60% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) (δ, ppm) 7.81 (d, \(J = 16.0\) Hz, 1H), 7.58-7.56 (m, 2H), 7.43-7.42 (comp, 3H), 6.54 (d, \(J = 16.0\) Hz, 1H), 6.02 (t, \(J = 1.8\) Hz, 1H), 4.25-4.19 (m, 1H), 3.91-3.83 (comp, 4H), 3.69 (dt, \(J = 11.7\) Hz, 2.6 Hz, 1H); \(^1\)\(^3\)C NMR (100 MHz, CDCl\(_3\)) (δ, ppm) 165.6, 146.2, 134.2, 130.6, 129.0, 128.3, 117.4, 89.4, 67.9, 66.2, 61.7; HRMS (TOF MS Cl\(^+\)) calculated for C\(_{13}\)H\(_{15}\)O\(_4\) [M+H]\(^+\): 235.0970, found 235.0979.

**(E)-1,4-Dioxan-2-yl 3-(4-isopropylphenyl)acrylate**

![Image](image2.png)

White oil; 59.0 mg; 71% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) (δ, ppm) 7.82 (d, \(J = 16.0\) Hz, 1H), 7.31 (d, \(J = 8.2\) Hz, 2H), 7.31 (d, \(J = 8.2\) Hz, 2H), 6.53 (d, \(J = 16.0\) Hz, 1H), 6.04 (t, \(J = 1.9\) Hz, 1H), 4.27-4.21 (m, 1H), 3.93-3.85 (comp, 4H), 3.72 (dt, \(J = 11.7\) Hz, 2.7 Hz, 1H), 3.03-2.93 (m, 1H), 1.32-1.30 (comp, 6H); \(^1\)\(^3\)C NMR (100 MHz, CDCl\(_3\)) (δ, ppm) 165.3, 151.5, 145.7, 131.4, 127.9, 126.6, 115.9, 88.8, 67.4, 65.7, 61.3, 33.6, 23.3; HRMS (TOF MS Cl\(^+\)) calculated for C\(_{16}\)H\(_{21}\)O\(_4\) [M+H]\(^+\): 277.1440, found 277.1437.

**(E)-1,4-Dioxan-2-yl 3-(3-chlorophenyl)acrylate**

![Image](image3.png)

White oil; 51.6 mg; 64% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) (δ, ppm) 7.75 (d, \(J = 16.0\) Hz, 1H), 7.57 (m, 1H), 7.46 (dt, \(J = 7.1\) Hz, 1.5 Hz, 1H), 7.43-7.36 (m, 2H), 6.56 (d, \(J = 16.0\) Hz, 1H), 6.03 (t, \(J = 1.9\) Hz, 1H), 4.26-4.20 (m, 1H), 3.93-3.85 (comp, 4H), 3.71 (dt, \(J = 11.7\) Hz, 2.6 Hz, 1H); \(^1\)\(^3\)C NMR (100 MHz, CDCl\(_3\)) (δ, ppm) 164.6, 143.9, 135.5, 134.5, 129.9, 129.7, 127.5, 125.9, 118.5, 89.1, 67.3, 65.6, 61.2; HRMS (TOF MS Cl\(^+\)) calculated for C\(_{13}\)H\(_{14}\)ClO\(_4\) [M+H]\(^+\): 269.0581, found 269.0584.
**1,3-Dioxolan-4-yl 3-phenylpropiolate**

![Structure 1](image1)

White oil; 19.7 mg; 30% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.66-7.64 (m, 2H), 7.55-7.50 (m, 1H), 7.46-7.42 (m, 2H), 6.51 (dd, $J = 3.9$ Hz, 2.0 Hz, 1H), 5.25 (s, 1H), 5.19 (s, 1H), 4.19-4.12 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 152.6, 132.7, 130.5, 128.2, 118.7, 95.7, 94.7, 87.3, 79.6, 70.0; HRMS (TOF MS Cl$^+$) calculated for C$_{12}$H$_{11}$O$_4$ [M+H]$^+$: 219.0657, found 219.0655.

**1,2-Dimethoxyethyl 3-phenylpropiolate**

![Structure 2](image2)

White oil; 26.5 mg; 37% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.61-7.59 (m, 2H), 7.49-7.45 (m, 1H), 7.39 (t, $J = 7.4$ Hz, 2H), 6.01 (t, $J = 4.9$ Hz, 1H), 3.59-3.57 (m, 2H), 3.55 (s, 3H), 3.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 153.6, 133.1, 130.9, 128.6, 119.4, 98.4, 87.6, 80.0, 72.4, 59.6, 57.5; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{15}$O$_4$ [M+H]$^+$: 235.0970, found 239.0962.

**2-Methoxyethoxy)methyl 3-phenylpropiolate**

![Structure 3](image3)

White oil; 24.7 mg; 35% yield; $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.62-7.60 (m, 2H), 7.48 (ddd, $J = 6.6$ Hz, 3.9 Hz, 1.3 Hz, 1H), 7.40 (t, $J = 7.4$ Hz, 2H), 5.48 (s, 2H), 3.90-3.88 (m, 2H), 3.62-3.60 (m, 2H), 3.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 153.4, 133.1, 130.8, 128.6, 119.4, 90.6, 87.2, 80.3, 71.4, 69.9, 59.1; HRMS (TOF MS Cl$^+$) calculated for C$_{13}$H$_{15}$O$_4$ [M+H]$^+$: 235.0970, found 235.0969.
Copy of HR-MS Spectra:

Proton NMR Observation of Intermediates A and D: