Supporting Information

Regioselective Palladium-Catalyzed Olefination of Coumarins via Aerobic Oxidative Heck Reactions

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I. General Methods and Materials
II. Optimization Study
III. Experimental Procedures
IV. Compound characterizations

Appendix I

Spectral Copies of ^1^H- and ^13^C-NMR Data Obtained in this Study
I. General Methods and Materials. Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates and visualization on TLC was achieved by UV light (254 and 354 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). \(^1\)H NMR was recorded on 400 MHz or 300 MHz and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethyilsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, \(J\), were reported in hertz unit (Hz). \(^{13}\)C NMR was recorded on 75 MHz and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-\(d\). Mass spectral data were obtained from the KAIST Basic Science Institute by using EI method. Commercial grade reagents and solvents were used without further purification except as indicated below. Dichloromethane was distilled from calcium hydride. Unless otherwise stated, all commercial reagents and solvents were used without additional purification.

II. Optimization Study

Table S1. Optimization of the Dehydrogenation/Alkenylations of chromanone.\(^a\)

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Reactions were conducted with coumarin, tert-butyl acrylate (2.0 equiv), Pd(OPiv)₂ (0.2 equiv), and base (3 equiv) in PivOH at 100 °C for 9 h. Yields are reported after isolation and purification by flash silica gel chromatography.
III. Experimental Procedures

**General Procedure for Coumarin Alkenylation:**

Coumarin derivative (0.1 mmol), Pd(OPiv)$_2$ (0.2 equiv), K$_2$CO$_3$ (3.0 equiv) were combined in PivOH (1.0 mL) under O$_2$ (balloon). The alkene (2.0 equiv) was added and the reaction mixture was heated to 100 °C for 3–9 h. The reaction mixture was monitored by TLC using (Tetrahydrofuran:n-Hexane = 1:5) as the mobile phase. The reaction mixture was diluted with CH$_2$Cl$_2$ and the excess NaHCO$_3$ was added to neutralize PivOH. After stirring the mixture for 10 min, the residue was washed with sequentially aqueous NaHCO$_3$ and NH$_4$Cl. The organic layer was dried over MgSO$_4$. After removal of solvent, the residue was purified by flash chromatography on silica gel to give desired product.

**General Procedure for the H/D Exchange Experiments:**

7-Methoxycoumarin (0.1 mmol), Pd(OPiv)$_2$ (0.2 equiv), K$_2$CO$_3$ (3.0 equiv) were combined in PivOH (1.0 mL) under O$_2$ (balloon). The D$_2$O (20 equiv) was added and the reaction mixture was heated to 95 °C. The reaction mixture was diluted with CH$_2$Cl$_2$ and the excess NaHCO$_3$ was added to neutralize PivOH. After stirring the mixture for 10 min, the residue was washed with sequentially aqueous NaHCO$_3$ and NH$_4$Cl. The organic layer was dried over MgSO$_4$. The residue was concentrated, and evaporated to dryness under high vacuum. The extent of H/D exchange was determined by integration of $^1$H-NMR.

IV. Compound characterizations

(E)-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3a). Yield 81%. mp 120–122 °C. δ 7.79 (s, 1H), 7.51 (dd, $J$ = 15.9, 0.6 Hz, 1H), 7.42 (d, $J$ = 8.6 Hz, 1H), 7.02 (d, $J$ = 15.8 Hz, 1H), 6.86 (dd, $J$ = 8.6, 2.4 Hz, 1H), 6.81
(d, J = 2.5 Hz, 1H), 4.18 (t, J = 6.6 Hz, 2H), 3.88 (s, 3H), 1.70 – 1.62 (m, 2H), 1.46 – 1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.3, 163.9, 159.3, 155.6, 143.7, 138.2, 129.6, 122.3, 118.9, 113.4, 112.7, 100.5, 64.5, 55.9, 30.8, 19.2, 13.7. HRMS (ESI+) m/z calcd. for C$_{17}$H$_{18}$NaO$_5$$^+$/[M+Na]$^+$: 325.1046, found: 325.1048.

(E)-tert-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3b). Yield 74%. mp 149–153 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (s, 1H), 7.44 – 7.38 (m, 2H), 6.92 (d, J = 15.8 Hz, 1H), 6.85 (dd, J = 8.6, 2.4 Hz, 1H), 6.80 (d, J = 2.4 Hz, 1H), 3.87 (s, 3H), 1.50 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.4, 163.7, 159.4, 155.5, 143.2, 137.1, 129.4, 124.2, 119.1, 113.3, 112.7, 100.5, 80.6, 55.7, 28.1. HRMS (ESI+) m/z calcd. for C$_{17}$H$_{18}$NaO$_5$$^+$/[M+Na]$^+$: 325.1046, found: 325.1051.

(E)-Ethyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3c). Yield 68%. mp 170–172 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.83 (s, 1H), 7.54 – 7.42 (m, 2H), 6.94 (s, J = 15.8 Hz, 1H), 6.88 (dd, J = 8.7, 2.4 Hz, 1H), 6.82 (d, J = 2.6 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 167.2, 164.3, 159.6, 156.0, 144.1, 138.6, 130.1, 122.2, 119.0, 113.5, 113.1, 100.8, 60.9, 56.4, 14.5. HRMS (ESI+) m/z calcd. for C$_{15}$H$_{14}$NaO$_5$$^+$/[M+Na]$^+$: 297.0733, found: 297.0742.
(E)-3-(7-Methoxy-2-oxo-2H-chromen-3-yl)-N,N-dimethylacrylamide (3d). Yield 50%. mp 228–231 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.80 (s, 1H), 7.61 (d, $J = 15.2$ Hz, 1H), 7.46 (d, $J = 8.7$ Hz, 1H), 7.39 (d, $J = 15.1$ Hz, 1H), 6.88 (dd, $J = 8.6$, 2.4 Hz, 1H), 6.83 (d, $J = 2.4$ Hz, 1H), 3.88 (s, 3H), 3.15 (s, 3H), 3.00 (s, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 166.8, 164.0, 159.9, 155.6, 144.1, 136.3, 129.8, 122.2, 119.8, 113.4, 113.3, 100.7, 56.3, 37.6, 35.9. HRMS (ESI+) m/z calcd. for C$_{15}$H$_{15}$NNaO$_4$ $^+$ [M+Na]$^+$: 296.0893, found: 296.0883.

(E)-Diethyl (2-(7-methoxy-2-oxo-2H-chromen-3-yl)vinyl)phosphonate (3e). Yield 42%. mp 120–124 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 (s, 1H), 7.41 (d, $J = 8.7$ Hz, 1H), 7.36 – 7.25 (m, 1H), 7.01 – 6.90 (m, 1H), 6.85 (dd, $J = 8.7$, 2.4 Hz, 1H), 6.79 (d, $J = 2.3$ Hz, 1H), 4.14 – 4.04 (m, 4H), 3.86 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.3, 159.7, 155.9, 144.3, 142.8 (d, $J_{CP} = 7.9$ Hz), 130.0, 119.2 (d, $J_{CP} = 186.5$ Hz), 119.1 (d, $J_{CP} = 23.5$ Hz), 113.8, 113.0, 100.8, 62.3 (d, $J_{CP} = 5.5$ Hz), 56.3, 16.8 (d, $J_{CP} = 6.4$ Hz). HRMS (ESI+) m/z calcd. for C$_{16}$H$_{19}$NaO$_6$P$^+$ [M+Na]$^+$: 361.0811, found: 361.0812.
(E)-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-methylacrylate (3g). Yield 27% (total yield 56%). mp 101–105 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67 (s, 1H), 7.63 – 7.60 (m, 1H), 7.40 (d, \(J = 8.6\) Hz, 1H), 6.86 (dd, \(J = 8.6, 2.5\) Hz, 1H), 6.81 (d, \(J = 2.4\) Hz, 1H), 4.19 (t, \(J = 6.7\) Hz, 2H), 3.87 (s, 3H), 2.11 (d, \(J = 1.6\) Hz, 3H), 1.73 – 1.63 (m, 2H), 1.48 – 1.36 (m, 2H), 0.94 (t, \(J = 7.4\) Hz, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.1, 163.6, 161.0, 155.7, 142.0, 131.8, 131.7, 129.6, 120.8, 113.4, 112.9, 101.0, 65.4, 56.2, 31.1, 19.6, 15.0, 14.1. HRMS (ESI+) \(m/z\) calcd. for C\(_{18}\)H\(_{20}\)NaO\(_5\)\([\text{M+Na}]^+\): 339.1203, found: 339.1206.

![Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-methylacrylate](image)

Butyl 2-((7-methoxy-2-oxo-2H-chromen-3-yl)methyl)acrylate (3g'). Yield 29% (total yield 56%). Colorless Oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.48 (s, 1H), 7.30 (d, \(J = 8.6\) Hz, 1H), 6.83 – 6.76 (m, 2H), 6.31 (d, \(J = 1.3\) Hz, 1H), 5.77 (d, \(J = 1.3\) Hz, 1H), 4.11 (t, \(J = 6.6\) Hz, 2H), 3.83 (s, 3H), 3.52 (s, 2H), 1.64 – 1.55 (m, 2H), 1.38 – 1.28 (m, 2H), 0.87 (t, \(J = 7.4\) Hz, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.8, 162.1, 161.7, 155.0, 140.2, 136.9, 128.3, 127.9, 123.0, 113.0, 112.4, 100.5, 64.8, 55.7, 32.7, 30.6, 19.2, 13.6. HRMS (ESI+) \(m/z\) calcd. for C\(_{18}\)H\(_{20}\)NaO\(_5\)\([\text{M+Na}]^+\): 339.1203, found: 339.1211.

![Butyl 2-((7-methoxy-2-oxo-2H-chromen-3-yl)methyl)acrylate](image)

(E)-Methyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)-3-phenylacrylate (3f). Yield 52%. mp 190–194 °C. \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.44 – 7.40 (m, 3H), 7.35 (s, 1H), 7.29 – 7.20 (m, 3H), 7.13 (s, 1H), 6.85 – 6.78 (m, 2H), 3.87 (s, 3H), 3.56 (s, 3H). \(^1^3\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 166.8, 164.1, 159.5, 155.7, 149.6, 144.7, 138.3, 130.1, 129.2, 128.5, 123.4, 121.3, 113.3, 112.9, 100.4, 56.3, 51.4. HRMS (ESI+) \(m/z\) calcd. for C\(_{20}\)H\(_{16}\)NaO\(_5\)\([\text{M+Na}]^+\): 359.0890, found: 359.0884.
(E)-7-Methoxy-3-styryl-2H-chromen-2-one (3h). Yield 62%. 
1H NMR (400 MHz, CDCl₃) δ 7.71 (s, 1H), 7.55 – 7.47 (m, 3H), 7.38 (d, J = 8.6 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.29 – 7.23 (m, 1H), 7.07 (d, J = 16.4 Hz, 1H), 6.83 (dd, J = 8.6, 2.4 Hz, 1H), 6.80 (d, J = 2.5 Hz, 1H), 3.85 (s, 3H). 13C NMR (100 MHz, CDCl₃) δ 162.4, 160.6, 154.6, 137.1, 137.1, 132.3, 128.7, 128.6, 128.1, 126.8, 122.3, 121.5, 113.3, 112.9, 100.4, 55.7. [Ref]. Org. Lett. 2011, 13, 5112-5115.

(E)-7-Methoxy-3-(4-methylstyryl)-2H-chromen-2-one (3i). Yield 56%. mp 188–191 °C. 
1H NMR (400 MHz, CDCl₃) δ 7.68 (s, 1H), 7.50 – 7.34 (m, 4H), 7.14 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 16.3 Hz, 1H), 6.82 (dd, J = 8.6, 2.4 Hz, 1H), 6.78 (d, J = 2.5 Hz, 1H), 3.84 (s, 3H), 2.33 (s, 3H). 13C NMR (100 MHz, CDCl₃) δ 162.3, 160.7, 154.5, 138.1, 136.7, 134.2, 132.1, 129.4, 128.5, 126.7, 121.7, 121.2, 113.4, 112.8, 100.4, 55.7, 21.3. HRMS (ESI+) m/z calcd. for C₁₉H₁₆NaO₃⁺[M+Na]⁺: 315.0992, found: 315.0993.

(E)-3-(4-Fluorostyryl)-7-methoxy-2H-chromen-2-one (3j). Yield 60%. mp 147–150 °C. 
1H NMR (400 MHz, CD₂Cl₂) δ 7.71 (s, 1H), 7.54 – 7.47 (m, 3H), 7.41 (d, J = 8.6 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.96 (d, J = 16.4 Hz,
1H), 6.85 (dd, J = 8.6, 2.5 Hz, 1H), 6.79 (d, J = 2.4 Hz, 1H), 3.85 (s, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 164.2, 163.0, 161.7, 160.6, 155.0, 137.9, 133.9, 133.9, 131.1, 129.1, 128.7, 128.6, 122.8, 121.5, 116.0, 115.8, 113.6, 113.1, 100.7, 56.2. HRMS (ESI+) m/z calcd. for C$_{18}$H$_{13}$FNaO$_3$+[M+Na]$^+$: 319.0741, found: 319.0740.

**E**-7-Methoxy-3-(4-nitrostyryl)-2H-chromen-2-one (3k). Yield 47%. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.20 – 8.18 (m, 2H), 7.83 (s, 1H), 7.71 – 7.64 (m, 3H), 7.47 (d, J = 8.6 Hz, 1H), 7.21 (dd, J = 16.3, 0.7 Hz, 1H), 6.89 (dd, J = 8.6, 2.4 Hz, 1H), 6.84 (d, J = 2.5 Hz, 1H), 3.88 (s, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) 163.7, 160.3, 155.5, 147.4, 144.2, 140.3, 130.1, 129.6, 127.7, 127.5, 124.4, 120.7, 113.5, 113.4, 100.8, 56.3. [Ref]. Org. Lett. 2011, 13, 5112-5115.

**E**-7-(Diethylamino)-3-styryl-2H-chromen-2-one (3l). Yield 70%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (s, 1H), 7.52 – 7.48 (m, 2H), 7.44 (d, J = 16.3 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.27 (d, J = 8.8 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.08 (d, J = 16.3 Hz, 1H), 6.57 (dd, J = 8.8, 2.5 Hz, 1H), 6.49 (d, J = 2.5 Hz, 1H), 3.40 (q, J = 7.1 Hz, 4H), 1.20 (t, J = 7.1 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.4, 155.6, 150.4, 137.9, 137.6, 130.0, 128.7, 128.6, 127.5, 126.5, 123.1, 117.8, 109.1, 97.2, 44.8, 12.5. [Ref]. Org. Lett. 2011, 13, 5112-5115.
(E)-Butyl 3-(2-oxo-2H-chromen-3-yl)acrylate (3m). Yield 53%. mp 105–108 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (s, 1H), 7.57 – 7.49 (m, 3H), 7.33 – 7.26 (m, 2H), 7.07 (d, $J = 15.9$ Hz, 1H), 4.18 (t, $J = 6.7$ Hz, 2H), 1.70 – 1.61 (m, 2H), 1.45 – 1.35 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.9, 159.0, 153.5, 143.4, 137.7, 132.8, 128.4, 124.8, 123.8, 122.4, 118.9, 116.6, 64.6, 30.7, 19.1, 13.7. HRMS (ESI+) m/z calcd. for C$_{16}$H$_{16}$NaO$_4^+$ [M+Na]$^+$: 295.0941, found: 295.0948.

(E)-Butyl 3-(7-ethoxy-2-oxo-2H-chromen-3-yl)acrylate (3n). Yield 74%. mp 149–151 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (s, 1H), 7.49 (d, $J = 15.7$ Hz, 1H), 7.40 (d, $J = 8.7$ Hz, 1H), 7.00 (d, $J = 15.8$ Hz, 1H), 6.83 (dd, $J = 8.7$, 2.4 Hz, 1H), 6.77 (d, $J = 2.4$ Hz, 1H), 4.17 (t, $J = 6.7$ Hz, 2H), 4.08 (q, $J = 7.0$ Hz, 2H), 1.69 – 1.61 (m, 2H), 1.46 – 1.33 (m, 5H), 0.93 (t, $J = 7.7$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.7, 163.7, 159.8, 156.0, 144.1, 138.6, 129.9, 122.5, 119.0, 114.1, 112.9, 101.3, 64.9, 64.8, 31.1, 19.5, 14.9, 14.1. HRMS (ESI+) m/z calcd. for C$_{18}$H$_{20}$NaO$_5^+$[M+Na]$^+$: 339.1203, found: 339.1208.
(E)-Butyl 3-(7-(benzyloxy)-2-oxo-2H-chromen-3-yl)acrylate (3o). Yield 75%. mp 155–159 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.84 (s, 1H), 7.53 – 7.33 (m, 7H), 7.00 – 6.88 (m, 3H), 5.15 (s, 2H), 4.17 (t, $J = 6.6$ Hz, 2H), 1.72 – 1.62 (m, 2H), 1.49 – 1.37 (m, 2H), 0.96 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 167.3, 163.3, 159.6, 155.9, 144.1, 138.5, 136.2, 130.1, 129.0, 128.7, 128.0, 122.3, 119.2, 114.1, 113.3, 101.7, 71.0, 64.8, 31.1, 19.6, 13.9. HRMS (ESI+) m/z calcd. for C$_{23}$H$_{22}$NaO$_5$ $^+ [M+Na]^+$: 401.1359, found: 401.1360.

(E)-Butyl 3-(6,7-dimethoxy-2-oxo-2H-chromen-3-yl)acrylate (3p). Yield 77%. mp 152–155 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.81 (s, 1H), 7.50 (dd, $J = 15.9$, 0.7 Hz, 1H), 6.96 (dd, $J = 15.9$, 0.4 Hz, 1H), 6.87 (d, $J = 26.9$ Hz, 2H), 4.17 (t, $J = 6.7$ Hz, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 1.71 – 1.63 (m, 2H), 1.48 – 1.37 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) 167.4, 159.8, 154.8, 150.4, 147.3, 144.1, 138.7, 122.1, 119.3, 112.1, 108.8, 100.0, 64.8, 56.8, 56.7, 31.2, 19.6, 13.9. HRMS (ESI+) m/z calcd. for C$_{18}$H$_{20}$NaO$_6$ $^+ [M+Na]^+$: 355.1152, found: 355.1147.

(E)-Butyl 3-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)acrylate (3q). Yield 66%. mp 111–114 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.67 (s, 1H), 7.50 (d, $J = 15.8$ Hz, 1H), 7.27 (d, $J = 8.9$ Hz, 1H), 6.92 (d, $J = 15.8$ Hz, 1H), 6.57 (dd, $J = 8.9$, 2.5 Hz, 1H), 6.46 (d, $J = 2.5$ Hz, 1H), 4.16 (t, $J = 6.7$ Hz, 2H), 3.41 (q, $J = 7.1$ Hz, 4H), 1.68 – 1.61 (m, 2H), 1.46 – 1.34 (m, 2H), 1.20 (t, $J = 7.1$ Hz, 6H), 0.93 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.8, 160.2, 156.5, 151.7, 144.2, 139.3, 129.8, 119.5, 114.7, 109.4, 108.6, 97.0, 64.2, 45.0, 30.8, 19.2, 13.7, 12.5. HRMS (ESI+) m/z calcd. for C$_{20}$H$_{23}$NNaO$_4$ $^+ [M+Na]^+$: 366.1676, found: 366.1662.
(E)-Butyl 3-(2-oxo-7-(((trifluoromethyl)sulfonyl)oxy)-2H-chromen-3-yl)acrylate (3r). Yield 51%. mp 163–166 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.91 (s, 1H), 7.68 (d, $J$ = 8.6 Hz, 1H), 7.52 (dd, $J$ = 15.9, 0.7 Hz, 1H), 7.32 (d, $J$ = 2.4 Hz, 1H), 7.27 (dd, $J$ = 8.6, 2.4 Hz, 1H), 7.04 (d, $J$ = 15.9 Hz, 1H), 4.19 (t, $J$ = 6.6 Hz, 2H), 1.73 – 1.63 (m, 2H), 1.49 – 1.40 (m, 2H), 0.96 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 166.7, 158.3, 154.3, 151.6, 142.1, 137.2, 130.6, 125.1, 123.7, 119.4, 119.0 (q, $J_{CF}$ = 318.9 Hz), 118.4, 110.5, 65.0, 31.1, 19.5, 13.8. HRMS (ESI+) m/z calcd. for C$_{17}$H$_{15}$F$_3$NaO$_7$S$^+[M+Na]^+$: 443.0383, found: 443.0377.

(E)-Butyl 3-(6-chloro-2-oxo-2H-chromen-3-yl)acrylate (3s). Yield 43%. mp 161–164 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.83 (s, 1H), 7.58 – 7.49 (m, 3H), 7.30 (dd, $J$ = 8.7, 0.6 Hz, 1H), 7.03 (d, $J$ = 15.9 Hz, 1H), 4.19 (t, $J$ = 6.6 Hz, 2H), 1.72 – 1.63 (m, 2H), 1.49 – 1.35 (m, 2H), 0.95 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) 166.9, 158.8, 152.3, 142.3, 137.5, 132.9, 130.2, 128.0, 124.7, 123.8, 120.5, 118.4, 65.0, 31.1, 19.6, 13.9. HRMS (ESI+) m/z calcd. for C$_{16}$H$_{15}$ClNaO$_4$$^+[M+Na]^+$: 329.0551, found: 329.0545.
(E)-Butyl 3-(7-methyl-2-oxo-2H-chromen-3-yl)acrylate (3t). Yield 70%. mp 127–130 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.86 (s, 1H), 7.55 – 7.42 (m, 2H), 7.16 – 7.11 (m, 2H), 6.99 (d, $J$ = 15.9 Hz, 1H), 4.17 (t, $J$ = 6.6 Hz, 2H), 2.45 (s, 3H), 1.73 – 1.61 (m, 2H), 1.49 – 1.37 (m, 2H), 0.95 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 167.2, 159.6, 154.1, 145.1, 144.0, 138.3, 128.6, 126.4, 123.1, 121.4, 117.0, 116.9, 64.8, 31.1, 22.1, 19.6, 13.9. HRMS (ESI+) m/z calcd. for C$_{17}$H$_{18}$NaO$_4$[M+Na]$^+$ : 309.1097, found: 309.1103.

(E)-Butyl 3-(1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acrylate (3u). Yield 52%. mp 77–81 °C. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.91 (s, 1H), 7.71 (dd, $J$ = 16.0, 0.6 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.38 – 7.33 (m, 1H), 7.28 – 7.22 (m, 1H), 7.05 (d, $J$ = 15.9 Hz, 1H), 4.18 (t, $J$ = 6.7 Hz, 2H), 3.71 (s, 3H), 1.72 – 1.63 (m, 2H), 1.51 – 1.38 (m, 2H), 0.96 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 167.5, 161.0, 140.4, 139.9, 139.7, 132.0, 129.8, 126.1, 122.7, 122.1, 120.3, 114.5, 64.7, 31.2, 29.9, 19.6, 13.9. HRMS (ESI+) m/z calcd. for C$_{17}$H$_{19}$NNaO$_3$[M+Na]$^+$ : 308.1257, found: 308.1253.

(E)-Butyl 3-(7-methoxy-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acrylate (3v). Yield 59%. mp 83–87 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (s, 1H), 7.71 (dd, $J$ = 15.9, 0.7 Hz, 1H), 7.48 (d, $J$ = 8.7 Hz, 1H), 7.01 (d, $J$ = 15.9 Hz, 1H), 6.82 (dd, $J$ = 8.7, 2.3 Hz, 1H), 6.73 (d, $J$ = 2.3 Hz, 1H), 4.17 (t, $J$ = 6.6 Hz, 2H), 3.91 (s, 3H), 3.69 (s, 3H), 1.70 – 1.61 (m, 2H), 1.47 – 1.35 (m, 2H), 0.93 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.7, 162.8,
161.1, 141.7, 139.9, 139.3, 131.0, 122.7, 120.6, 114.3, 110.5, 98.4, 64.2, 55.7, 30.7, 29.7, 19.2, 13.7. HRMS (ESI+) m/z calcd. for C_{18}H_{21}NNaO_{4}^[M+Na]^+: 338.1363, found: 338.1366.

(E)-7-Methoxy-1-methyl-3-styrylquinolin-2(1H)-one. Yield 71%. Yellow Oil. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.80 (s, 1H), 7.58 – 7.47 (m, 4H), 7.39 – 7.23 (m, 4H), 6.83 (dd, $J = 8.6, 2.3$ Hz, 1H), 6.75 (d, $J = 2.3$ Hz, 1H), 3.90 (s, 3H), 3.68 (s, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) $\delta$ 162.0, 161.9, 141.3, 138.1, 133.8, 130.5, 130.4, 129.0, 128.0, 127.0, 125.6, 124.4, 115.2, 110.3, 98.7, 55.9, 30.0. HRMS (ESI+) m/z calcd. for C_{19}H_{17}NNaO_{2}^[M+Na]^+: 314.1151, found: 314.1161.
Appendix I

Spectral Copies of $^1$H and $^{13}$C NMR Data Obtained in this Study
(E)-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3a).

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
(E)-tert-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3b).

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
(E)-Ethyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3c).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
(E)-3-(7-Methoxy-2-oxo-2H-chromen-3-yl)-N,N-dimethylacrylamide (3d).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
(E)-3-(7-Methoxy-2-oxo-2H-chromen-3-yl)-N,N-dimethylacrylamide (3e).

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
(E)-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-methylacrylate (3g).

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
Butyl 2-((7-methoxy-2-oxo-2H-chromen-3-yl)methyl)acrylate (3g').

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
(E)-Methyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)-3-phenylacrylate (3f).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
(E)-7-Methoxy-3-styryl-2H-chromen-2-one (3h).

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
(E)-7-Methoxy-3-(4-methylstyril)-2H-chromen-2-one (3i).

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
(E)-3-(4-Fluorostyryl)-7-methoxy-2H-chromen-2-one (3j).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
(E)-7-Methoxy-3-(4-nitrostyryl)-2H-chromen-2-one (3k).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
(E)-7-(Diethylamino)-3-styryl-2H-chromen-2-one (3l).

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
(E)-Butyl 3-(2-oxo-2H-chromen-3-yl)acrylate (3m).

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
(E)-Butyl 3-(7-ethoxy-2-oxo-2H-chromen-3-yl)acrylate (3n).

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
(E)-Butyl 3-(7-(benzyloxy)-2-oxo-2H-chromen-3-yl)acrylate (3o).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
(E)-Butyl 3-(6,7-dimethoxy-2-oxo-2H-chromen-3-yl)acrylate (3p).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
(E)-Butyl 3-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)acrylate (3q).

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
(E)-Butyl 3-(2-oxo-7-(((trifluoromethyl)sulfonyl)oxy)-2H-chromen-3-yl)acrylate (3r).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
(E)-Butyl 3-(6-chloro-2-oxo-2H-chromen-3-yl)acrylate (3s).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
(E)-Butyl 3-(7-methyl-2-oxo-2H-chromen-3-yl)acrylate (3t).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
(E)-Butyl 3-(1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acrylate (3u).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
(E)-Butyl 3-(7-methoxy-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acrylate (3v).

400 MHz, $^1$H NMR in CDCl$_3$

100 MHz, $^{13}$C NMR in CDCl$_3$
(E)-7-Methoxy-1-methyl-3-styrylquinolin-2(1H)-one (3w).

400 MHz, $^1$H NMR in CD$_2$Cl$_2$

100 MHz, $^{13}$C NMR in CD$_2$Cl$_2$
H/D Exchange Experiment:

$^1$H-NMR spectra observed from H/D exchange experiment (after 3h)

$^1$H-NMR spectra observed from H/D exchange experiment (after 12h)