Supporting Information

Silver-catalyzed oxidative coupling/cyclization of acrylamides with 1,3-dicarbonyl compounds

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Table of Contents

General Information S2
Starting Materials S2
General Procedure for the Oxidative Coupling of Acrylamides with 1,3-Dicarbonyl compounds S3
Characterization of Products 3 S4
Characterization of Products 4 S12
General Procedure for the Oxidative Coupling of Acrylamides with Ketones S16
Characterization of Products 6 S17
Investigation of the Reaction Mechanism S21
Isotope Labeling Experiment S23
Reference S25
1H NMR and 13C NMR Spectra of the Products 3 S26
1H NMR and 13C NMR Spectra of the Products 4 S43
1H NMR and 13C NMR Spectra of the Products 6 S51
General Information

All reactions were carried out under an atmosphere of nitrogen with strict exclusion of air. Column chromatography was carried out on silica gel. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Advance III-400 in solvents as indicated. Chemical shift are reported in ppm from CDCl$_3$ using TMS as internal standard. IR spectra were recorded on a Bruker Tensor 27 spectrometer and only major peaks are reported in cm$^{-1}$. HRMS were obtained on a Q-TOF micro spectrometer. Melting points were determined on a microscopic apparatus and were uncorrected.

Starting Materials

All of acrylamides 1 were synthesized according to the literature, and the NMR spectroscopy were in full accordance with the data in the literature.$^1$
General Procedure for the Oxidative Coupling of Acrylamides with 1,3-Dicarbonyl compounds

A 10 mL oven-dried Schlenk-tube was charged with AgNO₃ (1.7 mg, 5 mol %), acrylamide (1, 0.2 mmol, 1.0 equiv) and K₂S₂O₈ (54 mg, 0.2 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). 1,3-Dicarbonyl compounds (2, 0.4 mmol, 2.0 equiv) and H₂O 1 mL were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 28 h at 50 °C. The resulting mixture was then extracted with EtOAc. The combined organic phase was dried over anhydrous Na₂SO₄ and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/15 to 1/5) to give the corresponding products 3 or 4 in yields listed in Table 2 and Table 3.
Characterization of Products 3

3a: A pale yellow solid, $R_f$ 0.3 (EtOAc/petroleum ether = 1:3); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.30-7.25$ (m, 1H), 7.08-7.00 (m, 2H), 6.85-6.83 (d, $J = 8.0$ Hz, 1H), 3.28-3.25 (dd, $J = 7.2$, 4.4 Hz, 1H), 3.21 (s, 3H), 2.57-2.51 (dd, $J = 14.4$, 7.6 Hz, 1H), 2.40-2.35 (dd, $J = 14.0$, 4.4 Hz, 1H), 2.10 (s, 3H), 1.68 (s, 3H), 1.36 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 203.1$, 202.9, 179.4, 143.1, 132.1, 128.4, 123.9, 122.7, 108.1, 64.9, 47.2, 35.5, 29.4, 27.9, 26.2, 23.7 ppm; IR (KBr): $\nu_{\text{max}}$ 1704, 1613, 1471, 1355, 1255 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{19}$NNaO$_3$ [M+Na]$^+$ 296.1257, found 296.1270.

3b: A pale yellow oil, $R_f$ 0.3 (EtOAc/petroleum ether = 1:3); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.07-7.05$ (dd, $J = 8.0$, 0.8 Hz, 1H), 6.87 (s, 1H), 6.73-6.71 (d, $J = 8.0$ Hz, 1H), 3.29-3.26 (dd, $J = 7.2$, 4.8 Hz, 1H), 3.18 (s, 3H), 2.51-2.46 (dd, $J = 14.4$, 7.2 Hz, 1H), 2.39-2.34 (dd, $J = 14.4$, 4.8 Hz, 1H), 2.30 (s, 3H), 2.09 (s, 3H), 1.70 (s, 3H), 1.33 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 203.3$, 203.0, 179.4, 140.7, 132.3, 132.2, 128.5, 124.6, 107.9, 64.9, 47.1, 35.6, 29.4, 28.0, 26.2, 23.6, 21.0 ppm; IR (KBr): $\nu_{\text{max}}$ 1705, 1621, 1499, 1357 cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{21}$NNaO$_3$ [M+Na]$^+$ 310.1414, found 310.1420.
3c: A pale yellow oil, Rf 0.2 (EtOAc/petroleum ether = 1:3); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.78-6.77 (d, $J$ = 2.4 Hz, 1H), 6.74-6.72 (d, $J$ = 8.4 Hz, 1H), 6.67-6.66 (d, $J$ = 2.4 Hz, 1H), 3.75 (s, 3H), 3.30-3.27 (dd, $J$ = 7.2, 4.8 Hz, 1H), 3.16 (s, 3H), 2.50-2.44 (dd, $J$ = 14.4, 7.2 Hz, 1H), 2.38-2.33 (dd, $J$ = 14.4, 4.8 Hz, 1H), 2.09 (s, 3H), 1.72 (s, 3H), 1.33 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 203.2, 202.8, 179.0, 156.1, 136.5, 133.4, 112.9, 111.0, 108.5, 64.9, 55.8, 47.5, 35.4, 29.4, 27.9, 26.2, 23.7 ppm; IR (KBr): $\nu_{\text{max}}$ 1703, 1601, 1499, 1359, 1290, 1033 cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{21}$NNaO$_4$ [M+Na]$^+$ 326.1363, found 326.1372.

3d: A pale yellow solid, Rf 0.2 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.58-7.56 (dd, $J$ = 8.4, 0.8 Hz, 1H), 7.32 (d, $J$ = 1.6 Hz, 1H), 6.93-6.91 (d, $J$ = 8.0 Hz, 1H), 3.38-3.35 (dd, $J$ = 6.8, 5.2 Hz, 1H), 3.22 (s, 3H), 2.52-2.46 (dd, $J$ = 14.4, 6.8 Hz, 1H), 2.42-2.37 (dd, $J$ = 14.8, 5.2 Hz, 1H), 2.11 (s, 3H), 1.81 (s, 3H), 1.38 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 203.0, 202.4, 179.3, 146.1, 133.1, 126.1 (q, $J$ = 40.0 Hz), 124.9 (q, $J$ = 32.5 Hz), 124.2 (q, $J$ = 269.9 Hz), 120.6 (q, $J$ = 36.0 Hz), 108.0, 64.9, 46.9, 35.1, 29.1, 27.9, 26.4, 23.5 ppm; IR (KBr): $\nu_{\text{max}}$ 1722, 1624, 1505, 1460, 1328, 1118 cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{18}$F$_3$NNaO$_3$ [M+Na]$^+$ 364.1131, found 364.1141.

3e: A white solid, Rf 0.2 (EtOAc/petroleum ether = 1:3); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.64-7.62 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.37 (d, $J$ = 1.2 Hz, 1H), 6.94-6.92 (d, $J$ = 8.0 Hz, 1H), 3.41-3.37 (t, $J$ = 6.4 Hz, 1H), 3.22 (s, 3H), 2.48-2.43 (dd, $J$ = 14.4, 6.4 Hz, 1H), 2.40-2.35 (dd, $J$ = 14.4, 5.6 Hz, 1H), 2.12 (s, 3H), 1.90 (s, 3H), 1.38 (s, 3H).
The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 203.0, 202.2, 179.1, 146.9, 133.8, 133.7, 126.6, 118.8, 108.7, 105.9, 65.0, 46.6, 34.9, 29.2, 27.9, 26.4, 23.5$ ppm; IR (KBr): $\nu_{\text{max}} 2223, 1723, 1615, 1497, 1346$ cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{18}$N$_2$NaO$_3$ [M+Na]$^+$ 321.1210, found 321.1214.

![Chemical Structure](image)

3f: A white solid, R$_f$ 0.2 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.02-7.99$ (dd, $J = 8.0, 1.2$ Hz, 1H), 7.75-7.74 (d, $J = 1.2$ Hz, 1H), 6.87-6.85 (d, $J = 8.0$ Hz, 1H), 4.35-4.30 (q, $J = 7.2$ Hz, 2H), 3.40-3.37 (t, $J = 6.4$ Hz, 1H), 1.82 (s, 3H), 1.37-1.34 (m, 6H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 203.1, 202.4, 179.6, 166.1, 147.0, 132.4, 131.0, 124.9, 124.3, 107.7, 65.0, 60.9, 46.5, 35.1, 29.0, 27.9, 26.3, 23.4, 14.3$ ppm; IR (KBr): $\nu_{\text{max}} 1718, 1616, 1499, 1353, 1284, 1259$ cm$^{-1}$; HRMS (ESI) calcd for C$_{19}$H$_{23}$NNaO$_5$ [M+Na]$^+$ 368.1468, found 368.1476.

![Chemical Structure](image)

3g: A pale yellow oil, R$_f$ 0.2 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.00-6.95$ (td, $J = 8.8, 2.4$ Hz, 1H), 6.85-6.83 (dd, $J = 8.0, 2.4$ Hz, 1H), 6.78-6.75 (dd, $J = 8.4, 4.0$ Hz, 1H), 3.34-3.31 (t, $J = 5.6$ Hz, 1H), 2.49-2.43 (dd, $J = 14.4, 7.2$ Hz, 1H), 2.39-2.34 (dd, $J = 14.4, 5.2$ Hz, 1H), 1.81 (s, 3H), 1.34 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 203.1, 202.6, 179.0, 159.3$ (d, $J = 240.0$ Hz), 139.0, 134.0 (d, $J = 8.0$ Hz), 114.6 (d, $J = 23.0$ Hz), 111.8 (d, $J = 25.0$ Hz), 108.7 (d, $J = 8.0$ Hz), 64.9, 47.5, 35.1, 29.3, 27.9, 26.3, 23.6 ppm; IR (KBr): $\nu_{\text{max}} 1709, 1621, 1495, 1356, 1275$ cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{18}$FNNaO$_3$ [M+Na]$^+$ 344.1539, found 344.1538.
314.1163, found 314.1168.

**3h:** A white solid, Rf 0.2 (EtOAc/petroleum ether = 1:5); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.26-7.24\ (dd, \ J = 8.4,\ 2.0\ Hz, \ 1H),\ 7.07-7.06\ (d, \ J = 2.0\ Hz, \ 1H),\ 6.78-6.76\ (d, \ J = 8.4\ Hz, \ 1H),\ 3.37-3.34\ (t, \ J = 6.0\ Hz, \ 1H),\ 3.17\ (s, \ 3H),\ 2.47-2.41\ (dd, \ J = 14.4,\ 6.8\ Hz, \ 1H),\ 2.39-2.34\ (dd, \ J = 14.4,\ 5.2\ Hz, \ 1H),\ 2.10\ (s, \ 3H),\ 1.84\ (s, \ 3H),\ 1.34\ (s, \ 3H).\) The \(^1\)H NMR spectrum also displayed a minor set of signals due to enol isomers; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 203.1,\ 202.6,\ 178.9,\ 141.6,\ 134.1,\ 128.3,\ 128.1,\ 124.0,\ 109.2,\ 65.0,\ 47.2,\ 35.1,\ 29.2,\ 27.9,\ 26.3,\ 23.5\ ppm;\) IR (KBr): \(\nu_{max}\ 1712,\ 1610,\ 1490,\ 1361\ cm^{-1};\) HRMS (ESI) calcd for C\(_{16}\)H\(_{18}\)ClNNaO\(_3\) [M+Na]\(^+\) 330.0867, found 330.0879.

**3i:** A white solid, Rf 0.2 (EtOAc/petroleum ether = 1:5); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.60-7.58\ (dd, \ J = 8.0,\ 1.6\ Hz, \ 1H),\ 7.37-7.36\ (d, \ J = 1.6\ Hz, \ 1H),\ 6.64-6.62\ (d, \ J = 8.4\ Hz, \ 1H),\ 3.37-3.34\ (t, \ J = 6.4\ Hz, \ 1H),\ 3.16\ (s, \ 3H),\ 2.45-2.40\ (dd, \ J = 14.4,\ 6.4\ Hz, \ 1H),\ 2.39-2.34\ (dd, \ J = 14.4,\ 5.2\ Hz, \ 1H),\ 2.10\ (s, \ 3H),\ 1.84\ (s, \ 3H),\ 1.33\ (s, \ 3H).\) The \(^1\)H NMR spectrum also displayed a minor set of signals due to enol isomers; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 203.1,\ 202.6,\ 178.6,\ 142.8,\ 137.2,\ 134.9,\ 132.3,\ 110.3,\ 85.1,\ 65.0,\ 46.9,\ 35.2,\ 29.2,\ 27.9,\ 26.2,\ 23.5\ ppm;\) IR (KBr): \(\nu_{max}\ 1711,\ 1603,\ 1486,\ 1416,\ 1360\ cm^{-1};\) HRMS (ESI) calcd for C\(_{16}\)H\(_{18}\)INaO\(_3\) [M+Na]\(^+\) 422.0224, found 422.0233.

**3j:** A pale yellow oil, Rf 0.3 (EtOAc/petroleum ether = 1:5); \(^1\)H NMR (400 MHz,
CDCl$_3$): $\delta = 7.01-6.99$ (dd, $J = 7.2$, 1.6 Hz, 1H), 6.95-6.89 (m, 2H), 3.49 (s, 3H), 3.32-3.29 (dd, $J = 7.2$, 4.8 Hz, 1H), 2.58 (s, 3H), 2.51-2.45 (dd, $J = 14.4$, 7.2 Hz, 1H), 2.40-2.35 (dd, $J = 14.4$, 4.8 Hz, 1H), 2.11 (s, 3H), 1.74 (s, 3H), 1.34 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 203.4, 203.0, 180.2, 140.9, 132.9, 132.1, 122.7, 121.6, 119.9, 65.1, 46.5, 35.9, 29.5, 29.4, 28.0, 24.0, 19.0$ ppm; IR (KBr): $\nu_{\text{max}}$ 1702, 1601, 1461, 1363, 1245 cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{21}$NNaO$_3$ [M+Na]$^+$ 310.1414, found 310.1419.

![chem STRUCTURE](image1)

**3k:** A pale yellow oil, R$_f$ 0.3 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.03-6.95$ (m, 2H), 6.88-6.86 (m, 1H), 3.43-3.42 (d, $J = 2.8$ Hz, 3H), 3.35-3.33 (dd, $J = 6.8$, 4.8 Hz, 1H), 2.53-2.47 (dd, $J = 14.4$, 7.2 Hz, 1H), 2.40-2.35 (dd, $J = 14.4$, 4.8 Hz, 1H), 2.13 (s, 3H), 1.80 (s, 3H), 1.36 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 203.1, 202.7, 179.1, 147.6$ (d, $J = 243$ Hz), 135.3, 129.8, 123.3 (d, $J = 6$ Hz), 119.5 (d, $J = 3$ Hz), 116.3 (d, $J = 19$ Hz), 64.9, 47.5, 35.4, 29.5, 28.7, 28.1, 24.0 ppm; IR (KBr): $\nu_{\text{max}}$ 1709, 1631, 1481, 1359, 1237 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{18}$FNNaO$_3$ [M+Na]$^+$ 314.1163, found 314.1169.

![chem STRUCTURE](image2)

**3l:** A pale yellow oil, R$_f$ 0.3 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.35-7.28$ (m, 5H), 7.20-7.15 (td, $J = 7.6$, 1.2 Hz, 1H), 7.08-7.06 (dd, $J = 7.2$, 0.8 Hz, 1H), 7.03-7.01 (m, 1H), 6.80-6.78 (d, $J = 7.6$ Hz, 1H), 4.97-4.93 (d, $J = 15.6$ Hz, 1H), 4.88-4.84 (d, $J = 15.2$ Hz, 1H), 3.35-3.32 (dd, $J = 8.0$, 3.2 Hz, 1H), 2.64-2.58 (dd, $J = 14.0$, 8.0 Hz, 1H), 2.42-2.37 (dd, $J = 14.0$, 3.2 Hz, 1H), 2.08 (s, 3H), 1.57 (s, 3H), 1.42 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals
due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 202.8, 202.7, 179.7, 142.2, 136.0, 132.2, 128.8, 128.2, 127.8, 127.6, 127.0, 124.2, 122.7, 109.1, 64.5, 47.2, 43.8, 35.7, 29.5, 28.0, 23.8 ppm; IR (KBr): $\nu_{\text{max}}$ 1705, 1611, 1453, 1358, 1174 cm$^{-1}$; HRMS (ESI) calcd for C$_{22}$H$_{23}$NNaO$_3$ [M+Na]$^+$ 372.1570, found 372.1577.

3n: A pale yellow oil, R$_f$ 0.2 (EtOAc/petroleum ether = 1:3); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.20-7.15$ (m, 1H), 7.03-6.99 (m, 5H), 6.77-6.75 (dd, $J = 8.0, 1.6$ Hz, 2H), 6.58-6.56 (d, $J = 7.6$ Hz, 1H), 3.26-3.23 (dd, $J = 8.0, 4.0$ Hz, 1H), 3.15-3.12 (d, $J = 12.8$ Hz, 1H), 3.02-2.97 (d, $J = 12.8$ Hz, 1H), 2.94 (s, 3H), 2.76-2.71 (dd, $J = 14.4, 8.0$ Hz, 1H), 2.56-2.51 (dd, $J = 14.4, 4.0$ Hz, 1H), 2.13 (s, 3H), 1.64 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 203.0, 202.9, 178.0, 143.8, 135.0, 129.7, 129.1, 128.5, 127.5, 126.6, 125.0, 122.2, 107.8, 65.0, 53.7, 44.1, 34.2, 29.6, 27.9, 25.8 ppm; IR (KBr): $\nu_{\text{max}}$ 1705, 1611, 1494, 1470, 1357, 1255 cm$^{-1}$; HRMS (ESI) calcd for C$_{22}$H$_{23}$NNaO$_3$ [M+Na]$^+$ 372.1570, found 372.1574.

3o: A white solid, R$_f$ 0.2 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.34-7.25$ (m, 6H), 7.14-7.06 (m, 2H), 6.92-6.90 (d, $J = 8.0$ Hz, 1H), 3.38-3.35 (dd, $J = 6.8, 4.4$ Hz, 1H), 3.26 (s, 3H), 3.02-2.96 (dd, $J = 14.4, 7.2$ Hz, 1H), 2.95-2.90 (dd, $J = 14.0, 4.4$ Hz, 1H), 2.11 (s, 3H), 1.73 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 203.2, 202.7, 177.6, 143.6, 139.2, 130.7, 128.8, 128.7, 127.6, 126.7, 125.9, 122.9, 108.5, 65.0, 55.4, 35.2, 29.6, 28.1, 26.5 ppm; IR (KBr): $\nu_{\text{max}}$ 1701, 1611, 1469, 1353, 1258 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{21}$NNaO$_3$ [M+Na]$^+$ 358.1414, found 358.1422.
3p: A pale yellow oil, R$_f$ 0.2 (EtOAc/petroleum ether = 1:2); $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.79-7.77 (m, 2H), 7.69-7.67 (m, 2H), 7.28-7.23 (m, 1H), 7.06-7.04 (d, J = 7.6 Hz, 1H), 6.98-6.95 (t, J = 7.6, 1H), 6.81-6.79 (d, J = 7.6 Hz, 1H), 4.09-4.01 (m, 2H), 3.23-3.20 (m, 4H), 2.87-2.81 (dd, J = 14.4, 8.4 Hz, 1H), 2.57-2.53 (dd, J = 14.4, 3.6 Hz, 1H), 2.13 (s, 3H), 1.66 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 202.8, 202.6, 176.7, 167.8, 143.9, 134.0, 131.5, 129.2, 127.3, 125.3, 123.4, 122.5, 108.2, 64.8, 51.7, 43.1, 32.9, 29.5, 27.9, 26.4 ppm; IR (KBr): $\nu_{max}$ 1776, 1720, 1611, 1424, 1395 cm$^{-1}$; HRMS (ESI) calcd for C$_{24}$H$_{22}$N$_2$NaO$_5$ [M+Na]$^+$ 441.1421, found 441.1420.

3q/3q' (1.25:1): A white solid, R$_f$ 0.3 (EtOAc/petroleum ether = 1:5); 3q: $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.75-7.73 (d, J = 8.4 Hz, 1H), 7.56-7.42 (m, 3H), 7.37-7.35 (d, J = 7.2 Hz, 1H), 7.00-6.98 (d, J = 7.6 Hz, 1H), 3.54-3.48 (m, 4H), 2.71-2.66 (dd, J = 14.0, 5.2 Hz, 1H), 2.64-2.59 (dd, J = 14.4, 6.0 Hz, 1H), 2.07 (s, 3H), 2.13 (s, 3H), 1.69 (s, 3H), 1.39 (s, 3H); 3q': $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.79-7.77 (d, J = 8.0 Hz, 1H), 7.56-7.42 (m, 3H), 7.37-7.35 (d, J = 7.2 Hz, 1H), 6.93-6.92 (d, J = 7.6 Hz, 1H), 3.48 (s, 3H), 2.90-2.86 (d, J = 17.2 Hz, 1H), 2.58-2.54 (d, J = 17.2 Hz, 1H), 1.88 (s, 3H), 1.73 (s, 3H), 1.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 203.4, 202.8, 192.0, 172.2, 136.8, 136.6, 136.4, 136.1, 133.2, 132.9, 127.0, 126.7, 126.6, 123.5, 123.3, 122.7, 122.3, 120.5, 119.4, 108.8, 108.7, 105.3, 66.3, 49.0, 46.6, 44.0, 41.8, 29.8, 29.6, 29.3, 29.2, 27.8, 22.6, 22.3 ppm; IR (KBr): $\nu_{max}$ 3500, 1699, 1658, 1585, 1465, 1380, 1314 cm$^{-1}$; HRMS (ESI) calcd for C$_{20}$H$_{21}$NNaO$_3$ [M+Na]$^+$ 346.1414, found 346.1422.
3r: $R_f$ 0.2 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.24-7.22 (d, $J = 8.0$, 1H), 7.02-7.00 (d, $J = 6.0$ Hz, 1H), 6.85 (s, 1H), 3.30-3.27 (t, $J = 6.0$ Hz, 1H), 3.19 (s, 3H), 2.52-2.47 (dd, $J = 14.4$, 6.8 Hz, 1H), 2.39-2.34 (dd, $J = 14.4$, 5.2 Hz, 1H), 2.11 (s, 3H), 1.79 (s, 3H), 1.34 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 203.1, 202.7, 179.4, 144.3, 134.2, 130.5, 124.7, 122.5, 109.0, 65.0, 46.9, 35.1, 29.7, 28.0, 26.3, 23.8 ppm.

3r': $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.26-7.24 (d, $J = 8.4$, 1H), 7.00-6.98 (d, $J = 8.4$ Hz, 1H), 6.77-6.75 (d, $J = 7.6$ Hz, 1H), 3.30-3.27 (t, $J = 6.4$ Hz, 1H), 3.18 (s, 3H), 2.81-2.75 (dd, $J = 14.4$, 6.4 Hz, 1H), 2.52-2.47 (dd, $J = 14.4$, 6.4 Hz, 1H), 2.06 (s, 3H), 1.89 (s, 3H), 1.52 (s, 3H). The $^1$H NMR spectrum also displayed a minor set of signals due to enol isomers; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 203.5, 202.5, 178.7, 145.1, 130.9, 129.8, 128.4, 123.8, 106.8, 65.6, 48.4, 32.9, 28.8, 27.8, 26.4, 21.2 ppm; IR (KBr): $\nu_{\text{max}}$ 1715, 1609, 1460, 1360 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{18}$ClINaO$_3$ [M+Na]$^+$ 330.0867, found 330.0869.
Characterization of Products 4

4a: A pale yellow oil, R_f 0.2 (EtOAc/petroleum ether = 1:5); The mixture of isomers cannot be separated by column chromatography on silica gel. The NMR spectroscopy of mixture (d.r.= 1.3:1), ^1^H NMR (400 MHz, CDCl_3): δ = 7.85-7.83 (d, J = 7.6 Hz, 1H), 7.56-7.41 (m, 3H), 7.30-7.16 (m, 2H), 7.07-6.89 (m, 2H), 6.75-6.73 (d, J = 8.0 Hz, 0.42H), 6.49-6.47 (d, J = 8.0 Hz, 0.55H), 4.48-4.44 (t, J = 6.0 Hz, 0.43H), 4.26-4.22 (dd, J = 7.6, 5.2 Hz, 0.57H), 3.10 (s, 1.7H), 2.97 (s, 1.3H), 2.67-2.48 (m, 2H), 2.06 (s, 1.7H), 1.84 (s, 1.3H), 1.36 (s, 1.7H), 1.32 (s, 1.3H). The ^1^H NMR spectrum also displayed a minor set of signals due to enol isomers; ^13^C NMR (100 MHz, CDCl_3): δ = 202.5, 202.1, 195.5, 195.3, 179.5, 179.3, 142.9, 142.8, 136.0, 135.8, 133.6, 133.3, 132.7, 131.8, 128.7, 128.3, 128.2, 123.7, 123.2, 122.7, 122.5, 108.1, 107.8, 58.7, 58.2, 47.2, 46.8, 36.4, 36.3, 28.5, 27.9, 26.0, 25.8, 24.3, 23.6 ppm; IR (KBr): v_max 1711, 1612, 1471, 1352, 1256 cm^{-1}; HRMS (ESI) calcd for C_{21}H_{21}NNaO_3 [M+Na]^+ 358.1414, found 358.1425.

4b: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^1^H NMR (400 MHz, CDCl_3): δ = 7.97-7.95 (d, J = 7.2 Hz, 2H), 7.72-7.70 (d, J = 7.2 Hz, 2H), 7.55-7.51 (t, J = 7.2 Hz, 1H), 7.48-7.41 (m, 3H), 7.34-7.30 (t, J = 7.6 Hz, 2H), 7.19-7.12 (m, 2H), 7.02-6.98 (t, J = 7.6 Hz, 1H), 6.63-6.61 (d, J = 7.6 Hz, 1H), 5.59-5.56 (t, J = 5.6 Hz, 1H), 3.12 (s, 3H), 2.88-2.83 (dd, J = 14.4, 6.0 Hz, 1H), 2.55-2.50 (dd, J = 14.4, 6.0 Hz, 1H), 1.36 (s, 3H). The ^1^H NMR spectrum also displayed a minor set of signals due to enol isomers; ^13^C NMR (100 MHz, CDCl_3): δ = 195.0, 194.8, 179.9, 142.6, 136.0, 135.7, 133.4, 133.2, 132.9, 128.7, 128.5, 128.4, 128.1, 123.6, 122.7, 107.9, 52.1, 47.1, 36.6, 26.0, 23.5 ppm; IR (KBr): v_max 1703, 1613, 1449, 1379, 1266 cm^{-1}; HRMS (ESI)
calcd for C_{26}H_{23}NNaO_3 [M+Na]^+ 420.1570, found 420.1577.

**4c:** A white solid, R_f 0.3 (EtOAc/petroleum ether = 1:3); ^1^H NMR (400 MHz, CDCl_3): δ = 12.20 (s, 1H), 7.44-7.42 (d, J = 7.2 Hz, 1H), 7.31-7.23 (t, J = 7.6 Hz, 1H), 7.18-7.14 (t, J = 7.6 Hz, 1H), 6.91-6.89 (d, J = 7.6 Hz, 1H), 3.28 (s, 3H), 3.02-2.98 (d, J = 16.0 Hz, 1H), 2.56-2.44 (m, 4H), 2.24-2.20 (d, J = 15.6 Hz, 1H), 1.23 (s, 3H); ^1^C NMR (100 MHz, CDCl_3): δ = 196.5, 184.9, 141.6, 135.4, 128.1, 124.1, 123.4, 112.1, 108.7, 48.4, 33.2, 27.7, 27.2, 26.7, 22.2 ppm; IR (KBr): \upsilon_{max} 3446, 1704, 1613, 1384, 1124 cm\(^{-1}\); HRMS (ESI) calcd for C_{16}H_{17}NNaO_3 [M+Na]^+ 294.1101, found 294.1107.

**4d:** A white solid, R_f 0.3 (EtOAc/petroleum ether = 1:3); ^1^H NMR (400 MHz, CDCl_3): δ = 10.06 (s, 1H), 7.51-7.49 (d, J = 7.2 Hz, 1H), 7.27-7.23 (m, 1H), 7.15-7.11 (m, 1H), 6.85-6.84 (d, J = 7.6 Hz, 1H), 3.24 (s, 3H), 3.12-3.08 (d, J = 14.8 Hz, 1H), 2.63-2.59 (d, J = 14.8 Hz, 1H), 2.51-2.40 (m, 2H), 2.25-2.24 (m, 2H), 1.90-1.76 (m, 2H), 1.22 (s, 3H); ^1^C NMR (100 MHz, CDCl_3): δ = 198.6, 185.5, 174.3, 142.0, 135.4, 127.7, 124.2, 123.7, 111.4, 108.2, 48.9, 36.4, 29.7, 27.6, 26.6, 23.3, 20.5 ppm; IR (KBr): \upsilon_{max} 3056, 1710, 1611, 1493, 1380, 1274, 1107 cm\(^{-1}\); HRMS (ESI) calcd for C_{17}H_{19}NNaO_3 [M+Na]^+ 308.1257, found 308.1268.

**4e:** A white solid, R_f 0.3 (EtOAc/petroleum ether = 1:3); ^1^H NMR (400 MHz, CDCl_3): δ = 9.56 (s, 1H), 7.49-7.47 (dd, J = 7.6, 0.8 Hz, 1H), 7.26-7.22 (td, J = 7.6, 1.2 Hz,
1H), 7.14-7.10 (td, J = 7.6, 0.8 Hz, 1H), 6.84-6.82 (d, J = 8.0 Hz, 1H), 3.23 (s, 3H), 3.06-3.02 (d, J = 14.8 Hz, 1H), 2.77-2.74 (d, J = 14.8 Hz, 1H), 2.35-2.31 (d, J = 17.6 Hz, 1H), 2.26-2.22 (d, J = 17.2 Hz, 1H), 2.14-2.10 (d, J = 16.0 Hz, 1H), 2.04-2.00 (d, J = 16.0 Hz, 1H), 1.26 (s, 3H), 0.99 (s, 3H) 0.80 (s, 3H); 13C NMR (100 MHz, CDCl3): δ = 197.9, 185.3, 172.1, 142.0, 134.8, 127.8, 124.4, 123.6, 110.1, 108.2, 50.2, 49.1, 43.3, 31.2, 28.7, 27.7, 27.3, 26.6, 23.7 ppm; IR (KBr): υmax 3476, 1694, 1613, 1470, 1381, 1256 cm⁻¹; HRMS (ESI) calcd for C19H23NNaO3 [M+Na⁺] 336.1570, found 336.1575.

4f: A pale yellow oil, Rf 0.3 (EtOAc/petroleum ether = 1:5); The mixture of isomers cannot be separated by column chromatography on silica gel. The NMR spectroscopy of mixture (d.r.= 1:1), 1H NMR (400 MHz, CDCl3): δ = 7.25-7.23 (m, 1H), 7.14-7.12 (d, J = 7.6 Hz, 0.6H), 7.09-7.07 (d, J = 6.8 Hz, 0.4H), 7.04-7.00 (m, 1H), 6.84-6.82 (d, J = 7.6 Hz, 1H), 4.13-4.08 (q, J = 7.2 Hz, 1H), 3.82-3.62 (m, 1H), 3.24-3.04 (m, 4H), 2.48-2.44 (m, 2H), 2.11 (s, 1.5H), 1.83 (s, 1.5H), 1.35 (s, 3H), 1.23-1.19 (t, J = 7.2 Hz, 1.5H), 0.51-1.01 (t, J = 7.2 Hz, 1.5H); 13C NMR (100 MHz, CDCl3): δ = 201.9, 201.7, 179.5, 179.4, 169.0, 143.3, 143.1, 132.6, 132.1, 128.2, 128.2, 123.6, 122.6, 122.4, 108.1, 108.0, 61.6, 61.3, 56.5, 55.4, 47.2, 46.7, 35.4, 34.9, 29.2, 28.1, 26.1, 24.5, 23.5, 13.9, 13.7 ppm; IR (KBr): υmax 1712, 1694, 1613, 1493, 1378, 1351, 1250 cm⁻¹; HRMS (ESI) calcd for C17H21NNaO4 [M+Na⁺] 326.1363, found 326.1370.

4g: A pale yellow oil, Rf 0.3 (EtOAc/petroleum ether = 1:5); The mixture of isomers cannot be separated by column chromatography on silica gel. The NMR spectroscopy of mixture (d.r.= 1.2:1), 1H NMR (400 MHz, CDCl3): δ = 7.88-7.86 (dd, J = 8.4, 1.2 Hz, 1H), 7.59-7.57 (dd, J = 8.4, 1.2 Hz, 1H), 7.56-7.40 (m, 2H), 7.31-7.20 (m, 2H),
7.08-6.91 (m, 2H), 6.79-6.77 (d, J = 7.6 Hz, 0.45H), 6.46-6.44 (d, J = 7.6 Hz, 0.55H),
4.21-4.17 (m, 1H), 4.10-4.01 (m, 1H), 3.75-3.61 (m, 1H), 3.08 (s, 3H), 2.67-2.60 (m,
2H), 1.38 (s, 1.5H), 1.35 (s, 1.5H), 1.12-1.08 (t, J = 7.2 Hz, 1.5H), 0.96-0.93 (t, J =
7.2 Hz, 1.5H); 13C NMR (100 MHz, CDCl3): δ = 194.7, 194.4, 179.6, 179.4, 169.1,
168.9, 143.1, 142.8, 135.9, 135.7, 133.4, 133.0, 132.4, 132.1, 128.8, 128.5, 128.3,
128.2, 128.1, 123.8, 123.5, 122.6, 122.5, 108.0, 107.8, 61.6, 61.3, 50.2, 49.4, 47.1,
47.0, 36.6, 36.1, 26.0, 24.5, 24.1, 13.8, 13.6; IR (KBr): v_{max} 1710, 1613, 1450,
1383 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{22}\)H\(_{23}\)NNaO\(_4\) [M+Na]+ 388.1519, found 388.1537.

4h: A pale yellow oil, R\(_f\) 0.3 (EtOAc/petroleum ether = 1:5); \(^1\)H NMR (400 MHz,
CDCl\(_3\)): δ = 7.39-7.35 (td, J = 7.6, 1.2 Hz, 1H), 7.24-7.22 (dd, J = 7.6, 0.8 Hz, 1H),
7.17-7.13 (td, J = 7.6, 0.8 Hz, 1H), 6.94-6.92 (d, J = 8.0 Hz, 1H), 3.81-3.78 (dd, J =
9.2, 5.6 Hz, 1H), 3.24 (s, 3H), 2.78-2.72 (dd, J = 14.4, 9.2 Hz, 1H), 2.38-2.33 (dd, J =
14.4, 5.6 Hz, 1H), 1.48 (s, 3H); 13C NMR (100 MHz, CDCl\(_3\)): δ = 177.8, 143.1, 130.0,
129.5, 123.3, 122.9, 112.0, 109.1, 46.1, 37.6, 30.9, 26.5, 18.4 ppm; IR (KBr): v_{max}
2256, 1714, 1613, 1471, 1382 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{14}\)H\(_{13}\)N\(_3\)NaO [M+Na]+
262.0951, found 262.0961.
General Procedure for the Oxidative Coupling of Acrylamides with Ketones

A 10 mL oven-dried Schlenk-tube was charged with AgNO₃ (3.4 mg, 10 mol %), acrylamide (1, 0.2 mmol, 1.0 equiv) and K₂S₂O₈ (54 mg, 0.2 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). Acetone/H₂O (1:1) 1 mL were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 28 h at 50 °C. The resulting mixture was then extracted with EtOAc. The combined organic phase was dried over anhydrous Na₂SO₄ and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/20 to 1/5) to give the corresponding products 6 in yields listed in Table 4.
Characterization of Products 6

6a: A pale yellow oil, Rf 0.3 (EtOAc/petroleum ether = 1:3); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.29-7.26 (m, 1H), 7.16-7.14 (d, $J$ = 7.2 Hz, 1H), 7.08-7.04 (t, $J$ = 7.2 Hz, 1H), 6.86-6.84 (d, $J$ = 7.6 Hz, 1H), 3.22 (s, 3H), 2.24-2.05 (m, 3H), 2.02 (s, 3H), 1.96-1.89 (m, 1H), 1.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 207.7, 180.0, 143.1, 133.2, 128.0, 122.7, 122.6, 108.0, 47.3, 38.5, 31.7, 29.8, 26.1, 23.6 ppm; IR (KBr): $\nu_{\text{max}}$ 1712, 1613, 1470, 1453, 1384, 1129 cm$^{-1}$; HRMS (ESI) calcd for C$_{14}$H$_{17}$NNaO$_2$ [M+Na]$^+$ 254.1151, found 254.1161.

6b: A pale yellow solid, Rf 0.3 (EtOAc/petroleum ether = 1:3), mp = 96-98 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.26-7.23 (dd, $J$ = 8.4, 2.4 Hz, 1H), 7.13-7.12 (d, $J$ = 2.0 Hz, 1H), 6.78-6.76 (d, $J$ = 8.4 Hz, 1H), 3.20 (s, 3H), 2.24-1.93 (m, 7H), 1.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 207.2, 179.5, 141.7, 135.1, 128.1, 127.9, 123.2, 109.0, 47.5, 38.4, 31.6, 29.8, 26.3, 23.5 ppm; IR (KBr): $\nu_{\text{max}}$ 1716, 1610, 1490, 1364, 1345, 1270 cm$^{-1}$; HRMS (ESI) calcd for C$_{14}$H$_{16}$ClNNaO$_2$ [M+Na]$^+$ 288.0762, found 288.0766.

6c: A pale yellow solid, Rf 0.3 (EtOAc/petroleum ether = 1:3), mp = 100-102 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.58-7.56 (dd, $J$ = 8.0, 1.6 Hz, 1H), 7.41 (d, $J$ = 1.6 Hz, 1H), 6.64-6.62 (d, $J$ = 8.4 Hz, 1H), 3.17 (s, 3H), 2.20-2.10 (m, 2H), 2.08-1.94 (m, 5H), 1.33 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 207.2, 179.2, 142.8, 136.8, 135.7, 131.4, 110.1, 85.3, 47.3, 38.3, 31.5, 29.8, 26.2, 23.5 ppm; IR (KBr): $\nu_{\text{max}}$ 1715, 1603,
1487, 1362, 1242 cm⁻¹; HRMS (ESI) calcd for C₁₄H₁₆INaO₂ [M+Na]^+ 380.0118, found 380.0129.

**6d:** A pale yellow solid, Rf 0.2 (EtOAc/petroleum ether = 1:3), mp = 122-123 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.63-7.61 (dd, J = 8.0, 1.6 Hz, 1H), 7.41 (d, J = 1.6 Hz, 1H), 6.94-6.91 (d, J = 8.4 Hz, 1H), 3.25 (s, 3H), 2.26-1.98 (m, 7H), 1.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 206.8, 179.7, 146.9, 134.5, 133.5, 126.0, 119.0, 108.5, 105.9, 47.1, 38.2, 31.5, 29.8, 26.4, 23.3 ppm; IR (KBr): ν max 2222, 1720, 1614, 1455, 1384, 1062 cm⁻¹; HRMS (ESI) calcd for C₁₅H₁₆N₂NaO₂ [M+Na]^+ 279.1104, found 279.1115.

**6e:** A pale yellow oil, Rf 0.1 (EtOAc/petroleum ether = 1:3); ¹H NMR (400 MHz, CDCl₃): δ = 8.27-8.25 (dd, J = 8.4, 2.4 Hz, 1H), 8.05-8.04 (d, J = 2.4 Hz, 1H), 6.95-6.93 (d, J = 8.4 Hz, 1H), 3.28 (s, 3H), 2.28-2.05 (m, 4H), 2.04 (s, 3H), 1.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 206.7, 180.0, 148.7, 143.5, 134.3, 125.4, 118.5, 107.7, 47.2, 38.1, 31.4, 29.8, 26.6, 23.2 ppm; IR (KBr): ν max 1723, 1613, 1495, 1335, 1108, 1052 cm⁻¹; HRMS (ESI) calcd for C₁₄H₁₆N₂NaO₄ [M+Na]^+ 299.1002, found 299.1013.

**6f:** A pale yellow oil, Rf 0.3 (EtOAc/petroleum ether = 1:3); ¹H NMR (400 MHz, CDCl₃): δ = 7.74-7.72 (d, J = 8.0 Hz, 1H), 7.55-7.52 (m, 2H), 7.47-7.41 (m, 2H), 6.98-6.96 (d, J = 7.6 Hz, 1H), 3.54 (s, 3H), 2.61-2.54 (m, 1H), 2.36-2.19 (m, 2H), 2.08-2.00 (m, 4H), 1.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 207.9, 172.8,
137.3, 136.6, 133.3, 127.2, 126.4, 126.2, 122.6, 119.5, 108.5, 46.7, 39.7, 37.0, 31.0, 29.8, 29.6 ppm; IR (KBr): \( \nu_{\text{max}} \) 1715, 1660, 1585, 1465, 1383, 1315 cm\(^{-1}\); HRMS (ESI) calcd for \( \text{C}_{18}\text{H}_{19}\text{NNaO}_2 \) [M+Na]\(^+\) 304.1308, found 304.1317.

**6g:** A pale yellow oil, \( R_f \) 0.3 (EtOAc/petroleum ether = 1:3); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) = 7.21-7.17 (td, \( J = 7.6, 0.8 \) Hz, 1H), 7.13-7.12 (d, \( J = 6.8 \) Hz, 1H), 7.06-6.99 (m, 4H), 6.80-6.77 (m, 2H), 6.60-6.58 (d, \( J = 7.6 \) Hz, 1H), 3.16-3.13 (d, \( J = 12.8 \) Hz, 1H), 3.03-2.99 (d, \( J = 13.2 \) Hz, 1H), 2.96 (s, 3H), 2.34-2.20 (m, 3H), 1.97-1.87 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) = 207.6, 178.6, 143.7, 135.5, 130.3, 129.7, 128.1, 127.4, 126.4, 123.6, 122.3, 107.7, 53.8, 44.3, 38.6, 30.3, 29.9, 25.8 ppm; IR (KBr): \( \nu_{\text{max}} \) 1710, 1612, 1494, 1377, 1259, 1164 cm\(^{-1}\); HRMS (ESI) calcd for \( \text{C}_{20}\text{H}_{21}\text{NNaO}_2 \) [M+Na]\(^+\) 330.1464, found 330.1479.

**6h:** A pale yellow oil, \( R_f \) 0.3 (EtOAc/petroleum ether = 1:5); The mixture of isomers cannot be separated by column chromatography on silica gel. The NMR spectroscopy of mixture (d.r.= 1.5:1), \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) = 7.25-7.22 (m, 1H), 7.18-7.13 (m, 1H), 7.04-7.02 (m, 1H), 6.84-6.82 (d, \( J = 8.0 \) Hz, 1H), 3.21 (s, 1.7H), 3.19 (s, 1.3H), 2.73-2.63 (m, 1H), 2.42-2.39 (m, 1H), 2.26-2.22 (m, 1H), 2.06-1.98 (m, 1H), 1.91-1.82 (m, 3H), 1.76-1.46 (m, 4H), 1.34 (s, 1.7H), 1.31 (s, 1.3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) = 212.4, 211.5, 180.7, 180.3, 143.0, 142.9, 134.5, 133.2, 127.8, 123.1, 122.5, 122.4, 108.0, 107.9, 47.3, 47.1, 46.9, 41.7, 41.5, 37.0, 36.0, 35.6, 35.0, 28.1, 27.9, 26.2, 26.1, 25.1, 25.0, 24.5, 24.3 ppm; IR (KBr): \( \nu_{\text{max}} \) 1712, 1613, 1493, 1378, 1253, 1127 cm\(^{-1}\); HRMS (ESI) calcd for \( \text{C}_{17}\text{H}_{21}\text{NNaO}_2 \) [M+Na]\(^+\) 294.1465, found 294.1475.

Electronic Supplementary Material (ESI) for Chemical Communications
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6i: A pale yellow oil, R\textsubscript{f} 0.3 (EtOAc/petroleum ether = 1:5); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 7.79-7.77\) (m, 2H), 7.52-7.48 (m, 1H), 7.39-7.37 (m, 2H), 7.30-7.20 (m, 2H), 7.10-7.09 (m, 1H), 7.08-7.06 (m, 1H), 6.87-6.85 (d, \(J = 7.6\) Hz, 1H), 3.25 (s, 3H), 2.80-2.76 (m, 1H), 2.52-2.45 (m, 1H), 2.34-2.30 (m, 1H), 2.27-2.23 (m, 1H), 1.43 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 199.3, 180.2, 143.2, 136.6, 133.4, 133.0, 128.5, 128.0, 122.8, 122.7, 108.1, 47.6, 33.6, 32.4, 26.2, 23.8\) ppm; IR (KBr): \(\nu_{\text{max}} = 1710, 1639, 1493, 1377, 1260, 1126\) cm\(^{-1}\); HRMS (ESI) calcd for C\textsubscript{19}H\textsubscript{19}NNaO\textsubscript{2} \([\text{M+Na}]^+ = 316.1308\), found 316.1315.
Investigation of the Reaction Mechanism

When the TEMPO was added to the reaction of 1a with 2a under the standard conditions, the desired product 3a was only isolated in 26% yield. The result indicates that the radical intermediate should be involved in the catalytic cycle of the reaction.
Investigation of the Reaction Mechanism

\[
\text{1a} + \text{2a} \xrightarrow{\text{Mn(OAc)}_3 (2.5 \text{ equiv})} \text{HOAc/H}_2\text{O (1:1), 50 °C}} \rightarrow \text{3a, 29%}
\]

A 10 mL oven-dried Schlenk-tube was charged with Mn(OAc)$_3$·2H$_2$O (134 mg, 0.5 mmol, 2.5 equiv) and acrylamide (1a, 0.2 mmol, 1.0 equiv). The tube was evacuated backfilled with nitrogen (three times). 2,4-pentadione (2a, 0.4 mmol, 2.0 equiv) and HOAc/H$_2$O (1:1) 1 mL were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 24 h at 50 °C. The resulting mixture was then extracted with EtOAc. The combined organic phase was dried over anhydrous Na$_2$SO$_4$ and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/15 to 1/5) to give the corresponding products 3a in 29% yield.
Isotope Labeling Experiment

a) Intramolecular Kinetic Isotope Effect (KIE) Experiment:

[D₁]-1a was synthesized according the literature procedure. A 10 mL oven-dried Schlenk-tube was charged with AgNO₃ (1.7 mg, 5 mol %), [D₁]-1a (0.2 mmol, 1.0 equiv) and K₂S₂O₈ (54 mg, 0.2 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). 2,4-pentadione (2a, 0.4 mmol, 2.0 equiv) and H₂O 1 mL were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred at 50 °C for 28 h. Upon completion of the reaction, the mixture was extracted with EtOAc, dried over Na₂SO₄ and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel to give the corresponding product. The product was analysed by ¹H NMR (Figure 1).

![Diagram of chemical reaction]

Figure 1. ¹H NMR spectra of the mixture of the product 3a and [D₁]-3a.
b) Intermolecular Kinetic Isotope Effect (KIE) Experiment:

Aniline (ring-D$_5$, 98%, cat. No. DLM-862-0) was purchased from Cambridge Isotope Laboratories. The isotope reagent was used without further purification. [D$_5$]-1a was synthesized according the literature procedure using D$_5$-aniline as starting material.$^1$ A 10 mL oven-dried Schlenk-tube was charged with AgNO$_3$ (1.7 mg, 5 mol %), [D$_5$]-1a (0.1 mmol), 1a (0.1 mmol) and K$_2$S$_2$O$_8$ (54 mg, 0.2 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). 2,4-pentadione (2a, 0.4 mmol, 2.0 equiv) and H$_2$O 1 mL were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred at 50 °C for 28 h. Upon completion of the reaction, the mixture was extracted with EtOAc, dried over Na$_2$SO$_4$ and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel to give the corresponding product. The product was analysed by $^1$H NMR (Figure 2).

![Diagram of reaction](image)

Figure 2. $^1$H NMR spectra of the mixture of the product 3a and [D$_4$]-3a.
References

$^1$H NMR and $^{13}$C NMR Spectra of the Products 3
$^1$H NMR and $^{13}$C NMR Spectra of the Products 4
$^1$H NMR and $^{13}$C NMR Spectra of the Products 6

6a

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