Supporting Information

Transition-metal free alkylation of acrylamides initiated by radical C–C bond cleavage of the tertiary cycloalkanols

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**General Information**

All reactions were carried out in Schlenk-tubes filled with nitrogen. 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 TMS with the solvent resonance as internal standard ($\text{CDCl}_3$: $^1$H-NMR: $\delta = 7.26$; $^{13}$C-NMR: $\delta = 77.0$). 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 measured on a microscopic apparatus and are uncorrected.

**Starting Materials**

All of acrylamides 1 were synthesized according to the literature, and the NMR spectroscopies were in full accordance with the data in the literature.$^1$ Tertiary cyclopropanols 4 were prepared by the addition of Grignard reagent to the precursor esters according to the reported procedure.$^2$ Tertiary cyclobutanols were prepared by the addition of Grignard reagent to cyclobutanone according to the reported procedure.$^3$ All of the NMR spectroscopy were in full accordance with the data in the literatures.
General Procedure for the Cyclization of Acrylamides with Cyclopropanols

Acrylamides 1 (0.2 mmol, 1.0 equiv), and Na$_2$S$_2$O$_8$ (71.4 mg, 1.5 equiv) were added into an oven-dried Schlenk-tube. The tube was evacuated and backfilled with nitrogen (3 times). Then, a solution of tertiary cyclopropanols 2 (0.3 mmol, 1.5 equiv) in HOAc/H$_2$O (1:1, 2 mL) was injected into the tube by syringe. The tube was then sealed with a Teflon lined cap and the mixture was stirred at 50 °C for 24 h. The resulting mixture was diluted with EtOAc, and the organic phase was washed successively with H$_2$O, NaHCO$_3$ (3 times) and brine then dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether: 1/10 to 1/5) to give the corresponding products 3 and 4 in yields listed in Table 2 and Table 3.
Characterization of Products 3

3a: Colorless liquid (82%, 50.3 mg); R$_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.85 (d, $J$ = 7.6 Hz, 2H), 7.52 (t, $J$ = 7.6 Hz, 1H), 7.42 (t, $J$ = 7.6 Hz, 2H), 7.26 (t, $J$ = 7.6 Hz, 1H), 7.21 (d, $J$ = 7.2 Hz, 1H), 7.07 (t, $J$ = 7.2 Hz, 1H), 6.84 (d, $J$ = 7.6 Hz, 1H), 3.22 (s, 3H), 2.90-2.77 (m, 2H), 2.01-1.84 (m, 2H), 1.43-1.34 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 199.5, 180.6, 143.2, 136.8, 133.7, 132.9, 128.5, 127.9, 127.8, 122.6, 108.0, 48.3, 38.3, 37.8, 26.2, 23.9, 19.2 ppm; IR (KBr): $\nu_{max}$ 1711, 1608, 1460, 1346, 1246 cm$^{-1}$; HRMS (ESI) calcd for C$_{20}$H$_{21}$NNaO$_2$ [M+Na]$^+$ 330.1464, found 330.1460.

3b: Pale yellow liquid (80%, 51.4 mg); R$_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.75 (d, $J$ = 8.0 Hz, 2H), 7.27-7.19 (m, 4H), 7.06 (t, $J$ = 7.6 Hz, 1H), 6.84 (d, $J$ = 7.6 Hz, 1H), 3.21 (s, 3H), 2.89-2.74 (m, 2H), 2.38 (s, 3H), 2.00-1.84 (m, 2H), 1.42-1.36 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 199.2, 180.5, 143.6, 143.2, 134.3, 133.7, 129.1, 128.0, 127.9, 127.7, 122.6, 122.5, 108.0, 48.3, 38.2, 37.8, 26.1, 23.9, 21.5, 19.3 ppm; IR (KBr): $\nu_{max}$ 1712, 1610, 1462, 1347, 1256 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{23}$NNaO$_2$ [M+Na]$^+$ 344.1621, found 344.1615.

3c: Pale yellow liquid (70%, 47.2 mg); R$_f$ 0.3 (EtOAc/petroleum ether = 1:2); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.85-7.82 (m, 2H), 7.27-7.19 (m, 2H), 7.06 (t, $J$ = 7.6 Hz, 1H), 6.90-6.86 (m, 2H), 6.84 (d, $J$ = 7.6 Hz, 1H), 3.84 (s, 3H), 3.21 (s, 3H), 2.86-2.71 (m, 2H), 2.00-1.83 (m, 2H), 1.41-1.32 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 198.1, 180.6, 163.3, 143.2, 133.7, 130.1, 129.9, 127.7, 122.6, 122.5, 113.6, 108.0,
55.4, 48.4, 38.0, 37.8, 26.1, 23.9, 19.4 ppm; IR (KBr): $\nu_{\text{max}}$ 1711, 1604, 1462, 1347, 1254, 1172 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{23}$NNaO$_3$ [M+Na]$^+$ 360.1570, found 360.1561.

3d: Colorless liquid (73%, 49.8 mg); R$_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.77 (d, $J$ = 8.8 Hz, 2H), 7.37 (d, $J$ = 8.4 Hz, 2H), 7.27-7.23 (m, 1H), 7.19 (d, $J$ = 7.2 Hz, 1H), 7.05 (t, $J$ = 7.6 Hz, 1H), 6.84 (d, $J$ = 7.6 Hz, 1H), 3.21 (s, 3H), 2.87-2.72 (m, 2H), 1.99-1.82 (m, 2H), 1.41-1.31 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 198.2, 180.4, 143.2, 139.3, 135.0, 133.6, 129.3, 128.8, 127.8, 122.5, 108.0, 48.3, 38.3, 37.6, 26.1, 23.9, 19.1 ppm; IR (KBr): $\nu_{\text{max}}$ 1711, 1611, 1464, 1347, 1247 cm$^{-1}$; HRMS (ESI) calcd for C$_{20}$H$_{20}$ClKNO$_2$ [M+K]$^+$ 380.0814, found 380.0806.

3e: Colorless liquid (54%, 40.5 mg); R$_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.94 (d, $J$ = 8.4 Hz, 2H), 7.68 (d, $J$ = 8.4 Hz, 2H), 7.26 (t, $J$ = 8.0 Hz, 1H), 7.20 (d, $J$ = 6.8 Hz, 1H), 7.06 (t, $J$ = 7.6 Hz, 1H), 6.85 (d, $J$ = 7.6 Hz, 1H), 3.22 (s, 3H), 2.93-2.79 (m, 2H), 2.02-1.84 (m, 2H), 1.44-1.33 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 198.5, 180.4, 143.2, 139.4, 134.2 (q, $J$ = 32.5 Hz), 128.2, 127.8, 125.6 (q, $J$ = 3.6 Hz), 123.5 (q, $J$ = 271.2 Hz), 122.6, 122.5, 108.1, 48.3, 38.6, 37.6, 26.1, 24.0, 19.0 ppm; IR (KBr): $\nu_{\text{max}}$ 1711, 1612, 1469, 1325, 1169, 1130, 1067 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{20}$F$_3$NNaO$_2$ [M+Na]$^+$ 398.1338, found 398.1330.

3f: Pale yellow liquid (80%, 51.4 mg); R$_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.31-7.23 (m, 4H), 7.16-7.11 (m, 3H), 7.05 (td, $J$ = 7.6, 0.8 Hz, 1H), 6.82 (d, $J$ = 8.0 Hz, 1H), 3.57 (s, 2H), 3.19 (s, 3H), 2.41-2.27 (m, 2H), 1.42-1.31 (m, 5H); IR (KBr): $\nu_{\text{max}}$ 1711, 1604, 1462, 1347, 1254, 1172 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{23}$NNaO$_3$ [M+Na]$^+$ 360.1570, found 360.1561.
1.84-1.73 (m, 2H), 1.31 (s, 3H), 1.22-1.13 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 207.7, 180.5, 143.2, 134.1, 133.6, 129.3, 128.7, 127.7, 126.9, 122.5, 108.0, 50.0, 48.3, 41.7, 37.5, 26.1, 23.8, 18.7 ppm; IR (KBr): $\nu_{\text{max}}$ 1711, 1610, 1462, 1346 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{23}$NNaO$_2$ [M+Na]$^+$ 344.1621, found 344.1611.

3g: Pale yellow liquid (68%, 51.3 mg); R$_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.32 (d, $J =$ 8.4 Hz, 2H), 7.27-7.23 (m, 1H), 7.15 (d, $J =$ 7.2 Hz, 1H), 7.07-7.03 (m, 3H), 6.83 (d, $J =$ 8.0 Hz, 1H), 3.54 (s, 2H), 3.19 (s, 3H), 2.40-2.25 (m, 2H), 1.84-1.68 (m, 2H), 1.32 (s, 3H), 1.30 (s, 9H), 1.22-1.14 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 208.0, 180.5, 149.8, 143.2, 133.6, 131.0, 128.9, 127.7, 125.6, 122.5, 108.0, 49.5, 48.3, 41.6, 37.5, 34.4, 31.3, 26.1, 23.8, 18.7 ppm; IR (KBr): $\nu_{\text{max}}$ 1713, 1612, 1468, 1373, 1261 cm$^{-1}$; HRMS (ESI) calcd for C$_{25}$H$_{31}$KNO$_2$ [M+K]$^+$ 416.1986, found 416.1975.

3h: Pale yellow liquid (66%, 46.3 mg); R$_f$ 0.3 (EtOAc/petroleum ether = 1:2); $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.27-7.23 (m, 1H), 7.15 (d, $J =$ 7.2 Hz, 1H), 7.07-7.02 (m, 3H), 6.85-6.82 (m, 3H), 3.78 (s, 3H), 3.50 (s, 2H), 3.19 (s, 3H), 2.37-2.23 (m, 2H), 1.83-1.67 (m, 2H), 1.31 (s, 3H), 1.21-1.12 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 208.1, 180.5, 158.5, 143.2, 130.3, 127.7, 126.2, 122.5, 114.1, 108.0, 55.2, 49.1, 48.2, 41.5, 37.5, 26.1, 23.8, 18.7 ppm; IR (KBr): $\nu_{\text{max}}$ 1711, 1612, 1512, 1465, 1348, 1252 cm$^{-1}$; HRMS (ESI) calcd for C$_{22}$H$_{25}$KNO$_3$ [M+K]$^+$ 390.1466, found 390.1457.

3i: Pale yellow liquid (62%, 49.5 mg); R$_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.43 (d, $J =$ 8.0 Hz, 2H), 7.30-7.26 (m, 1H), 7.17 (d, $J =$ 6.8 Hz, 1H), 7.08 (t, $J =$ 7.2 Hz, 1H), 7.01 (d, $J =$ 8.4 Hz, 2H), 6.85 (d, $J =$ 8.0 Hz,
1H), 3.55 (s, 2H), 3.22 (s, 3H), 2.41-2.27 (m, 2H), 1.84-1.73 (m, 2H), 1.34 (s, 3H), 1.24-1.17 (m, 2H); 13C NMR (100 MHz, CDCl₃): δ = 206.9, 180.4, 143.1, 133.5, 133.0, 131.7, 131.0, 127.8, 122.5, 121.0, 108.0, 49.0, 48.2, 41.9, 37.4, 26.1, 23.8, 18.7 ppm; IR (KBr): νmax 1711, 1612, 1490, 1469, 1376, 1348; HRMS (ESI) calcd for C₂₁H₂₂BrNNaO₂ [M+Na]+ 422.0726, found 422.0713.

3j: Colorless liquid (73%, 48.9 mg); Rf 0.25 (EtOAc/petroleum ether = 1:5); 1H NMR (400 MHz, CDCl₃): δ = 7.28-7.24 (m, 3H), 7.19-7.12 (m, 4H), 7.06 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 3.21 (s, 3H), 2.82 (t, J = 7.6 Hz, 2H), 2.62 (t, J = 7.6 Hz, 2H), 2.33-2.19 (m, 2H), 1.87-1.69 (m, 2H), 1.33 (s, 3H), 1.24-1.16 (m, 2H); 13C NMR (100 MHz, CDCl₃): δ = 209.4, 180.4, 143.1, 140.9, 133.6, 128.4, 128.2, 127.7, 126.0, 122.5, 108.0, 48.2, 44.0, 42.6, 37.5, 29.5, 26.1, 23.8, 18.7 ppm; IR (KBr): νmax 1711, 1612, 1493, 1469, 1348 cm⁻¹; HRMS (ESI) calcd for C₂₂H₂₅NNaO₂ [M+Na]+ 358.1777, found 358.1782.

3k: Colorless liquid (40%, 25 mg); Rf 0.25 (EtOAc/petroleum ether = 1:5); 1H NMR (400 MHz, CDCl₃): δ = 7.25 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.2 Hz, 1H), 7.06 (t, J = 7.2 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 3.21 (s, 3H), 2.38-2.21 (m, 3H), 1.86-1.71 (m, 6H), 1.34 (s, 3H), 1.25-1.13 (m, 8H); 13C NMR (100 MHz, CDCl₃): δ = 213.6, 180.6, 143.2, 133.7, 127.7, 122.6, 122.5, 108.0, 50.6, 48.3, 40.3, 37.7, 28.4, 26.1, 25.8, 25.6, 23.9, 18.6 ppm; IR (KBr): νmax 1711, 1612, 1492, 1452, 1375, 1347 cm⁻¹; HRMS (ESI) calcd for C₂₀H₂₇NNaO₂ [M+Na]+ 336.1934, found 336.1936.

3l: Colorless liquid (80%, 53.9 mg); Rf 0.25 (EtOAc/petroleum ether = 1:5); 1H NMR (400 MHz, CDCl₃): δ = 7.30-7.24 (m, 3H), 7.18 (d, J = 6.8 Hz, 1H), 7.06 (t, J = 7.6
Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.85-6.81 (m, 3H), 4.44 (s, 2H), 3.20 (s, 3H), 2.48 (td, J = 7.6, 1.2 Hz, 2H), 1.92-1.75 (m, 2H), 1.34 (s, 3H), 1.30-1.21 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 207.2, 180.4, 157.6, 143.2, 133.5, 129.6, 127.8, 122.5, 121.6, 114.4, 108.0, 72.6, 48.2, 38.8, 37.5, 26.1, 23.9, 18.1 ppm; IR (KBr): $\nu_{\text{max}}$ 1707, 1608, 1491, 1463, 1375, 1241 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{23}$NNaO$_3$ [M+Na]$^+$ 360.1570, found 360.1573.
Characterization of Products 4

4b: Pale yellow solid (73%, 46.9 mg), mp = 93-95 °C; Rf 0.25 (EtOAc/petroleum ether = 1:5); ¹H NMR (400 MHz, CDCl₃): δ = 7.86-7.84 (m, 2H), 7.55-7.51 (m, 1H), 7.44-7.40 (m, 2H), 7.06-7.01 (m, 2H), 6.73 (d, J = 7.6 Hz, 1H), 3.20 (s, 3H), 2.88-2.78 (m, 2H), 2.33 (s, 3H), 2.01-1.82 (m, 2H), 1.42-1.35 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 199.7, 180.5, 140.9, 136.8, 133.8, 132.9, 132.1, 128.5, 128.0, 127.9, 123.4, 107.8, 48.4, 38.4, 37.8, 26.2, 24.0, 21.1, 19.3 ppm; IR (KBr): υmax 1710, 1601, 1498, 1454, 1351, 1260 cm⁻¹; HRMS (ESI) calcd for C₂₁H₂₃N₂NaO₂ [M+Na]+ 344.1621, found 344.1624.

4c: Pale yellow solid (60%, 40.4 mg), mp = 87-89 °C; Rf 0.3 (EtOAc/petroleum ether = 1:2); ¹H NMR (400 MHz, CDCl₃): δ = 7.86 (dd, J = 7.2, 1.2 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.43-7.39 (m, 2H), 6.82-6.73 (m, 3H), 3.79 (s, 3H), 3.19 (s, 3H), 2.92-2.77 (m, 2H), 2.01-1.80 (m, 2H), 1.41-1.35 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 199.5, 180.1, 156.1, 136.8, 135.1, 132.9, 128.5, 127.9, 111.7, 110.3, 108.2, 55.7, 48.8, 38.3, 37.8, 26.2, 24.0, 19.3 ppm; IR (KBr): υmax 1707, 1600, 1496, 1356, 1287, 1214 cm⁻¹; HRMS (ESI) calcd for C₂₁H₂₃N₂NaO₃ [M+Na]+ 360.1570, found 360.1572.

4d: Pale yellow liquid (80%, 60 mg); Rf 0.2 (EtOAc/petroleum ether = 1:5); ¹H NMR (400 MHz, CDCl₃): δ = 7.85 (dd, J = 7.2, 1.2 Hz, 2H), 7.56-7.50 (m, 2H), 7.43-7.39 (m, 3H), 6.91 (d, J = 8.0 Hz, 1H), 3.25 (s, 3H), 2.90-2.83 (m, 2H), 2.06-1.85 (m, 2H), 1.43-1.30 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 199.2, 180.4, 146.3, 136.7, 134.3, 133.0, 128.5, 127.8, 125.7 (q, J_C-F = 4.0 Hz), 124.8 (q, J_C-F = 3.25 Hz), 124.4 (q,
$J_{C,F} = 271.2$ Hz), 119.5 (q, $J = 3.6$ Hz), 107.8, 48.4, 38.2, 37.7, 26.3, 23.8, 19.0 ppm; IR (KBr): $\nu_{\text{max}}$ 1723, 1619, 1455, 1332, 1279, 1118 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{20}$F$_3$NNaO$_2$ [M+Na]$^+$ 398.1338, found 398.1337.

4e: Pale yellow liquid (68%, 45.2 mg); $R_f$ 0.2 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.86$ (dd, $J = 7.2$, 1.2 Hz, 2H), 7.60 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.56-7.52 (m, 1H), 7.45-7.41 (m, 3H), 6.91 (d, $J = 8.0$ Hz, 1H), 3.25 (s, 3H), 2.91-2.85 (m, 2H), 2.01-1.83 (m, 2H), 1.41-1.29 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 199.1$, 180.1, 147.2, 136.7, 134.8, 133.3, 133.1, 128.6, 127.9, 125.9, 119.2, 108.5, 105.7, 48.3, 38.1, 37.6, 26.4, 23.8, 19.0 ppm; IR (KBr): $\nu_{\text{max}}$ 2221, 1722, 1611, 1496, 1453, 1344, 1256 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{20}$N$_2$NaO$_4$ [M+Na]$^+$ 355.1412, found 355.1417.

4f: Colorless liquid (83%, 62.9 mg); $R_f$ 0.2 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.02$ (dd, $J = 8.4$, 1.6 Hz, 1H), 7.86-7.83 (m, 3H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.41(t, $J = 7.6$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 1H), 4.42-4.31 (m, 2H), 3.25 (s, 3H), 2.93-2.77 (m, 2H), 2.06-1.86 (m, 2H), 1.44-1.27 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 199.3$, 180.8, 166.5, 147.4, 136.7, 133.6, 133.0, 130.6, 128.5, 127.9, 124.9, 123.7, 107.5, 60.9, 48.3, 38.3, 37.7, 26.4, 23.9, 19.1, 14.4 ppm; IR (KBr): $\nu_{\text{max}}$ 1709, 1615, 1498, 1454, 1372, 1276 cm$^{-1}$; HRMS (ESI) calcd for C$_{23}$H$_{25}$NNaO$_4$ [M+Na]$^+$ 402.1676, found 402.1671.

4g: Pale yellow liquid (87%, 75.3 mg); $R_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.87$ (dd, $J = 7.2$, 1.6 Hz, 2H), 7.59-7.54 (m, 2H), 7.52-7.41 (m, 3H), 6.63 (d, $J = 8.0$ Hz, 1H), 3.19 (s, 3H), 2.90-2.83 (m, 2H), 1.99-1.79 (m,
2H), 1.41-1.33 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 199.4, 179.7, 143.0, 136.8, 136.7, 136.2, 133.0, 131.4, 128.6, 127.9, 110.1, 85.2, 48.5, 38.3, 37.7, 26.2, 23.9, 19.1 ppm; IR (KBr): $\nu_{\text{max}}$ 1714, 1602, 1484, 1341 cm$^{-1}$; HRMS (ESI) calcd for C$_{20}$H$_{20}$INNaO$_2$ [M+Na]$^+$ 456.0431, found 456.0423.

4h: White solid (62%, 39.8 mg), mp = 97-99 °C; $R_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.86 (dd, $J$ = 7.2, 1.2 Hz, 2H), 7.55-7.51 (m, 1H), 7.42 (td, $J$ = 7.6, 1.6 Hz, 2H), 7.04-6.92 (m, 3H), 3.50 (s, 3H), 2.88-2.81 (m, 2H), 2.58 (s, 3H), 1.97-1.83 (m, 2H), 1.39-1.31 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 199.6, 181.3, 141.0, 136.8, 134.3, 132.9, 131.5, 128.5, 127.9, 122.5, 120.5, 119.6, 47.7, 38.4, 38.1, 29.5, 24.5, 19.3, 19.1 ppm; IR (KBr): $\nu_{\text{max}}$ 1708, 1600, 1459, 1364, 1337 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{23}$NNaO$_3$ [M+Na]$^+$ 344.1621, found 344.1614.

4i: Colorless liquid (45%, 30.3 mg); $R_f$ 0.3 (EtOAc/petroleum ether = 1:2); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.85 (dd, $J$ = 7.2, 1.6 Hz, 2H), 7.54-7.50 (m, 1H), 7.44-7.40 (m, 2H), 7.02-6.98 (m, 1H), 6.82 (dd, $J$ = 8.0, 0.8 Hz, 2H), 3.86 (s, 3H), 3.49 (s, 3H), 2.88-2.81 (m, 2H), 1.97-1.83 (m, 2H), 1.39-1.32 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 199.6, 180.8, 145.3, 136.8, 135.4, 132.9, 131.0, 128.5, 127.9, 123.1, 115.3, 111.6, 55.8, 48.4, 38.4, 38.0, 29.4, 24.3, 19.3 ppm; IR (KBr): $\nu_{\text{max}}$ 1707, 1605, 1464, 1336, 1249 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{23}$NNaO$_3$ [M+Na]$^+$ 360.1570, found 360.1565.

4j: Colorless liquid (63%, 41 mg); $R_f$ 0.3 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.86 (dd, $J$ = 7.2, 1.2 Hz, 2H), 7.55-7.51 (m, 1H), 7.44-7.41 (m, 2H), 6.99-6.96 (m, 3H), 3.43 (d, $J$ = 2.8 Hz, 3H), 2.94-2.79 (m, 2H), 2.01-1.83 (m,
2H), 1.42-1.37 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 199.4, 180.1, 147.7 (d, $J_{C\text{-}F}$ = 242.0 Hz), 146.8, 136.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 133.0, 129.8 (d, $J_{C\text{-}F}$ = 7.7 Hz), 128.5, 127.9, 123.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 118.4 (d, $J_{C\text{-}F}$ = 3.2 Hz), 115.8 (d, $J_{C\text{-}F}$ = 19.2 Hz), 48.8 (d, $J_{C\text{-}F}$ = 1.4 Hz), 38.2, 37.9, 28.6 (d, $J_{C\text{-}F}$ = 5.6 Hz), 24.2, 19.1 ppm; IR (KBr): $\nu_{\text{max}}$ 1718, 1630, 1483, 1371, 1336, 1237 cm$^{-1}$; HRMS (ESI) calcd for C$_{20}$H$_{20}$FNNaO$_2$ [M+Na]$^+$ 348.1370, found 348.1365.

**4k:** White solid (72%, 55.2 mg), mp = 128-130 ºC; R$_f$ 0.3 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.88 (dd, $J$ = 7.2, 1.2 Hz, 2H), 7.54 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.45-7.35 (m, 7H), 7.22-7.20 (m, 1H), 7.10-7.05 (m, 2H), 2.91-2.87 (m, 2H), 2.85 (s, 3H), 2.02-1.91 (m, 2H), 1.49-1.26 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 199.6, 181.5, 140.1, 139.0, 136.8, 134.7, 132.9, 130.8, 130.0, 128.5, 127.9, 127.7, 127.5, 125.4, 121.9, 121.6, 47.6, 38.3, 38.1, 30.1, 24.4, 19.2 ppm; IR (KBr): $\nu_{\text{max}}$ 1712, 1598, 1454, 1367, 1336, 1065 cm$^{-1}$; HRMS (ESI) calcd for C$_{26}$H$_{25}$NNaO$_2$ [M+Na]$^+$ 406.1777, found 406.1773.

**4l:** Pale yellow liquid (67%, 44.9 mg); R$_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.84 (dd, $J$ = 7.2, 1.2 Hz, 2H), 7.52 (t, $J$ = 7.2 Hz, 1H), 7.43-7.39 (m, 2H), 6.65 (s, 1H), 6.52 (s, 1H), 3.19 (s, 3H), 2.87-2.79 (m, 2H), 2.35 (s, 3H), 2.33 (s, 3H), 2.17-1.96 (m, 2H), 1.41 (s, 3H), 1.35-1.19 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 199.6, 180.9, 143.6, 137.6, 136.8, 134.0, 132.9, 128.5, 127.9, 127.2, 125.7, 106.8, 49.2, 38.2, 35.9, 26.2, 22.6, 21.5, 19.7, 18.0 ppm; IR (KBr): $\nu_{\text{max}}$ 1711, 1619, 1452, 1378, 1334, 1240 cm$^{-1}$; HRMS (ESI) calcd for C$_{22}$H$_{25}$NNaO$_2$ [M+Na]$^+$ 358.1777, found 358.1768.
4m: Solid (29%, 21.3 mg), \( mp = 123-125 \^\circ C \); \( R_f \) 0.35 (EtOAc/petroleum ether = 1:2); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.86 \) (dd, \( J = 6.8, 1.6 \text{ Hz}, 2\text{H} \)), 7.55-7.51 (m, 1H), 7.44-7.40 (m, 2H), 6.41-6.39 (m, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 3.44 (s, 3H), 2.92-2.78 (m, 2H), 1.98-1.77 (m, 2H), 1.39-1.33 (m, 5H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 199.7, 180.4, 156.7, 145.9, 136.8, 136.0, 132.9, 128.5, 127.9, 124.5, 100.4, 98.9, 55.8, 49.0, 38.4, 38.0, 29.3, 24.4, 19.3 \text{ ppm}; \) IR (KBr): \( \nu_{\text{max}} \) 1702, 1605, 1496, 1456, 1363, 1270,1210, 1153 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{22}\)H\(_{25}\)NNaO\(_4\) [M+Na]\(^+\) 390.1676, found 390.1671.

4n: White solid (75%, 57.5 mg), \( mp = 154-156 \^\circ C \); \( R_f \) 0.35 (EtOAc/petroleum ether = 1:5); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.86 \) (dd, \( J = 7.2, 1.6 \text{ Hz}, 2\text{H} \)), 7.53 (t, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 7.42 (t, \( J = 7.2 \text{ Hz}, 2\text{H} \)), 7.17 (t, \( J = 7.2 \text{ Hz}, 2\text{H} \)), 7.06-6.99 (m, 4H), 6.82-6.80 (m, 2H), 6.58 (d, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 3.13 (d, \( J = 12.8 \text{ Hz}, 1\text{H} \)), 3.02 (d, \( J = 12.8 \text{ Hz}, 1\text{H} \)), 2.95-2.80 (m, 5H), 2.18-1.99 (m, 2H), 1.46-1.38 (m, 2H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 199.5, 179.0, 143.8, 136.8, 135.7, 132.9, 130.8, 129.8, 128.5, 127.9, 127.8, 127.4, 126.4, 123.5, 122.2, 107.8, 54.7, 44.5, 38.4, 36.3, 25.8, 19.2 \text{ ppm}; \) IR (KBr): \( \nu_{\text{max}} \) 1703, 1611, 1493, 1450, 1375, 1261 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{26}\)H\(_{25}\)NNaO\(_2\) [M+Na]\(^+\) 406.1777, found 406.1763.

4o: Colorless liquid (70%, 53.6 mg); \( R_f \) 0.25 (EtOAc/petroleum ether = 1:5); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.86 \) (d, \( J = 7.6 \text{ Hz}, 2\text{H} \)), 7.53 (t, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 7.42 (t, \( J = 7.6 \text{ Hz}, 2\text{H} \)), 7.29-7.21 (m, 6H), 7.14 (td, \( J = 7.6, 0.8 \text{ Hz}, 1\text{H} \)), 7.04 (t, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 6.73 (d, \( J = 7.6 \text{ Hz}, 1\text{H} \)), 4.96 (d, \( J = 15.6 \text{ Hz}, 1\text{H} \)), 4.91 (d, \( J = 16.0 \text{ Hz}, 1\text{H} \)), 2.94-2.79 (m, 2H), 2.08-1.91 (m, 2H), 1.54-1.38 (m, 5H); \(^1^3\)C NMR (100 MHz,
**4p:** White solid (76%, 56.1 mg), mp = 125-126 °C; Rf 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.87$ (dd, $J = 7.6$, 1.2 Hz, 2H), 7.55-7.50 (m, 3H), 7.44-7.38 (m, 5H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.19 (td, $J = 7.6$, 1.2 Hz, 1H), 7.11 (t, $J = 7.2$ Hz, 1H), 6.84 (d, $J = 8.0$ Hz, 1H), 2.93-2.87 (m, 2H), 2.08-1.97 (m, 2H), 1.57-1.50 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 199.5$, 180.0, 143.2, 136.8, 134.6, 133.5, 132.9, 129.5, 128.5, 127.9, 127.7, 126.6, 123.1, 122.9, 109.4, 48.5, 38.3, 38.2, 24.2, 19.3 ppm; IR (KBr): $\nu_{\text{max}}$ 1721, 1603, 1497, 1456, 1371, 1203 cm$^{-1}$; HRMS (ESI) calcd for C$_{25}$H$_{23}$NNaO$_2$ [M+Na]$^+$ 392.1621, found 392.1607.
General Procedure for the Cyclization of Acrylamide 1a with Cyclobutanols

Acrylamide 1a (0.2 mmol, 1.0 equiv), and Na$_2$S$_2$O$_8$ (71.4 mg, 1.5 equiv) were added into an oven-dried Schlenk-tube. The tube was evacuated and backfilled with nitrogen (3 times). Then, a solution of tertiary cyclobutanols 5 (0.4 mmol, 2.0 equiv) in HOAc/H$_2$O (1:1, 2 mL) was injected into the tube by syringe. The tube was then sealed with a Teflon lined cap and the mixture was stirred at 65 °C for 24 h. The resulting mixture was diluted with EtOAc, and the organic phase was washed successively with H$_2$O, NaHCO$_3$ (2 times) and brine then dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (gradient eluent of EtOAc/petroleum ether: 1/10 to 1/5) to give the corresponding products 6 in yields listed in equation 1.
Characterization of Products 6

6a: Colorless liquid (40%, 25.7 mg); R$_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.89-7.87 (m, 2H), 7.52 (t, $J$ = 7.2 Hz, 1H), 7.44-7.40 (m, 2H), 7.26 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.17 (dd, $J$ = 7.2, 0.8 Hz, 1H), 7.06 (td, $J$ = 7.6, 0.4 Hz, 1H), 6.84 (d, $J$ = 8.0 Hz, 1H), 3.21 (s, 3H), 2.87-2.76 (m, 2H), 2.00-1.74 (m, 2H), 1.65-1.58 (m, 2H), 1.35 (s, 3H), 1.10-0.93 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 200.0, 180.6, 143.2, 136.8, 134.0, 128.5, 127.9, 127.6, 122.4, 107.9, 48.3, 38.2, 26.1, 24.2, 23.8 ppm; IR (KBr): $\nu_{\text{max}}$ 1712, 1610, 1468, 1375, 1253, 1125 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{23}$NNaO$_2$ [M+Na]$^+$ 344.1621, found 344.1624.

6b: Colorless liquid (40%, 26.8 mg); R$_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.78 (d, $J$ = 8.0 Hz, 2H), 7.28-7.21 (m, 3H), 7.17 (d, $J$ = 7.2 Hz, 1H), 7.06 (t, $J$ = 7.2 Hz, 1H), 6.84 (d, $J$ = 7.6 Hz, 1H), 3.21 (s, 3H), 2.84-2.69 (m, 2H), 2.39 (s, 3H), 1.99-1.74 (m, 2H), 1.64-1.56 (m, 2H), 1.35 (s, 3H), 1.09-0.92 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 199.7, 180.7, 143.6, 143.2, 134.3, 134.0, 129.2, 128.1, 127.6, 122.5, 107.9, 48.3, 38.2, 26.1, 24.3, 23.8, 21.6 ppm; IR (KBr): $\nu_{\text{max}}$ 1712, 1608, 1461, 1366, 1252, 1185, 1021 cm$^{-1}$; HRMS (ESI) calcd for C$_{22}$H$_{25}$NNaO$_2$ [M+Na]$^+$ 358.1777, found 358.1780.

6c: Pale yellow liquid (44%, 28.8 mg); R$_f$ 0.25 (EtOAc/petroleum ether = 1:5); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.63 (d, $J$ = 4.0 Hz, 1H), 7.59 (d, $J$ = 4.8 Hz, 1H), 7.26 (t, $J$ = 7.6 Hz, 1H), 7.16 (d, $J$ = 6.8 Hz, 1H), 7.10-7.04 (m, 2H), 6.84 (d, $J$ = 7.6 Hz,
1H), 3.21 (s, 3H), 2.84-2.69 (m, 2H), 1.99-1.74 (m, 2H), 1.65-1.58 (m, 2H), 1.35 (s, 3H), 1.09-0.95 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 193.0, 180.6, 144.2, 143.2, 133.9, 133.4, 131.7, 128.0, 127.7, 122.5, 122.4, 107.9, 48.3, 39.0, 38.1, 26.1, 24.5, 24.2, 23.8 ppm; IR (KBr): $\nu_{\text{max}}$ 1706, 1608, 1465, 1356, 1248, 1080 cm$^{-1}$; HRMS (ESI) calcd for C$_{19}$H$_{21}$NNaO$_2$S [M+Na]$^+$ 350.1185, found 350.1187.
Investigation of the Reaction Mechanism

When 1.0 equiv of TEMPO was added to the reaction of 1a with 2a under the standard conditions, no desired product 3a was detected along with a coupling product 7 isolated in 60%. The result indicates that the radical intermediate probably be involved in the catalytic cycle of the reaction.

When 1.0 equiv of BHT was added to the reaction of 1a with 2a under the standard conditions, 52% yield of desired product 3a was isolated along with 38% 1a recovered. The result indicates that the radical intermediate probably be involved in the catalytic cycle of the reaction.
Isotope Labeling Experiment

a) Intramolecular Kinetic Isotope Effect (KIE) Experiment:
An oven-dried Schlenk-tube was charged with [D$_1$]-1a (0.1 mmol, 1.0 equiv) and Na$_2$S$_2$O$_8$ (35.7 mg, 1.5 equiv). The tube was evacuated and backfilled with nitrogen (3 times). Then, a solution of tertiary cycloalkanol 2a (0.15 mmol, 1.5 equiv) in HOAc/H$_2$O (1:1, 1 mL) was injected into the tube by syringe. The tube was then sealed with a Teflon lined cap and the mixture was stirred at 50 °C for 3.5 h. The resulting mixture was diluted with EtOAc, and the organic phase was washed successively with H$_2$O (1 time), NaHCO$_3$ (3 times) and brine (1 time) then dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product in 60% yield. The product was analyzed by $^1$H NMR (Figure 1).

![Chemical reaction diagram](attachment:reaction_diagram.png)

Figure 1. $^1$H NMR spectra of the mixture of the product 3a and [D$_1$]-3a.
b) Intermolecular Kinetic Isotope Effect (KIE) Experiment:
An oven-dried Schlenk-tube was charged with 1a (0.05 mmol), [D₅]-1a (0.05 mmol) and Na₂S₂O₅ (35.7 mg, 1.5 equiv). The tube was evacuated and backfilled with nitrogen (3 times). Then, a solution of tertiary cycloalkanol 2a (0.15 mmol, 1.5 equiv) in HOAc/H₂O (1:1, 1 mL) was injected into the tube by syringe. The tube was then sealed with a Teflon lined cap and the mixture was stirred at 50 °C for 3.5 h. The resulting mixture was diluted with EtOAc, and the organic phase was washed successively with H₂O (1 time), NaHCO₃ (2 times) and brine (1 time) then dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product in 65% yield. The product was analyzed by ¹H NMR (Figure 2).

![Chemical Structures](image)

Figure 2. ¹H NMR spectra of the mixture of the product 3a and [D₄]-3a.
References


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

3a

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

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

**4b**
$^{1} \text{H NMR}$ and $^{13} \text{C NMR}$ Spectra of Products 6

6a