

Supporting Information

Metal-free Desulfurizing Radical Reductive C-C Coupling of Thiols and Alkenes

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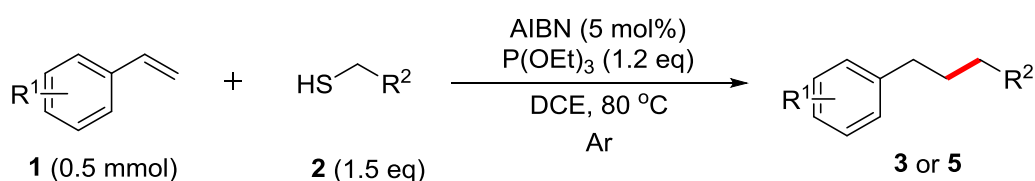
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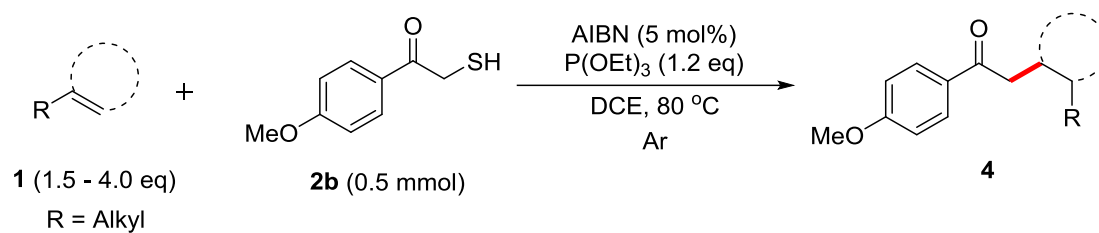
1. General information

All manipulations were conducted with a standard Schlenk technique under argon atmosphere (1 atm). ^1H -NMR spectra were recorded with a Bruker AVIII-400 spectrometer. Chemical shifts (in ppm) were referenced to CDCl_3 ($\delta = 7.26$ ppm) or TMS ($\delta = 0.00$ ppm) as an internal standard. ^{13}C -NMR spectra were obtained by the same NMR spectrometer and were calibrated with CDCl_3 ($\delta = 77.00$ ppm). Mass spectra were recorded by PE SCLEX QSTAR spectrometer. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. General procedure of reductive C-C coupling of styrenes and thiols

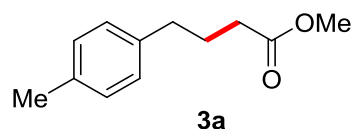


General procedure A (for styrenes substrates): a 25 mL Schlenk tube was equipped with a rubber septum and magnetic stir bar and was charged with AIBN (4.5 mg, 5.0 mol %). The tube was evacuated and backfilled with Ar for 3 times. Styrene 1 (0.5 mmol, 1.0 equiv), thiol 2 (0.75 mmol, 1.5 equiv), DCE (4.0 mL), $\text{P}(\text{OEt})_3$ (105 μL , 1.2 equiv) were added respectively with syringe under Ar. The mixture was stirred at 80 °C under Ar for 12 h. The mixture was diluted with water (10 mL) and extracted with DCM (3×10 mL). The combined organic extracts were washed with a saturated solution of NaCl (15 mL), dried over MgSO_4 , and evaporated in vacuo. The residue was purified by chromatography on silica gel (PE/EA = 50:1) to afford product 3 or 5.

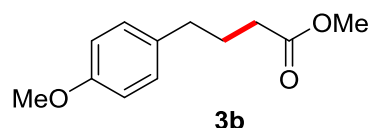


General procedure B (for aliphatic olefins): a 25 mL Schlenk tube was equipped with a rubber septum and magnetic stir bar and was charged with AIBN (4.5 mg, 5.0 mol %) and Thiol **2b** (0.5 mmol, 1.0 equiv). The tube was evacuated and backfilled with Ar for 3 times. Then aliphatic olefins **1** (0.75 mmol, 1.5 equiv), DCE (4.0 mL), P(OEt)_3 (105 μL , 1.2 equiv) were added respectively with syringe under Ar. The mixture was stirred at 80 $^\circ\text{C}$ under Ar for 12 h. The mixture was diluted with water (10 mL) and extracted with DCM (3×10 mL). The combined organic extracts were washed with a saturated solution of NaCl (15 mL), dried over MgSO_4 , and evaporated in vacuo. The residue was purified by chromatography on silica gel (PE/EA = 50:1) to afford product **4**.

3. Analytical Data for All Products

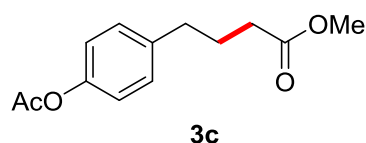


methyl 4-(p-tolyl)butanoate (3a)¹: According to general procedure A, a solution of **1a** (0.5 mmol, 59.1 mg), Methyl thioglycolate (0.75 mmol, 65 μL), AIBN (0.025 mmol, 4.5 mg), P(OEt)_3 (0.6 mmol, 105 μL) in DCE (4.0 mL) were stirred at 80 $^\circ\text{C}$ under Ar for 12 h to afford **3a** (79.7 mg, 83%) as colorless oil after purification on silica gel (PE:EA=50:1). ^1H NMR (400 MHz, CDCl_3) δ 7.17-7.06 (m, 4H), 3.70 (s, 3H), 2.65 (t, $J = 7.6$ Hz, 2H), 2.37 (t, $J = 7.2$ Hz, 2H), 2.36 (s, 3H), 2.05-1.92 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.0, 138.3, 135.4, 129.1, 128.4, 51.5, 34.7, 33.4, 26.6, 21.0. MS (70 ev): m/z (%): 58.8 (85), 104.9 (100), 117.8 (55), 191.9 (M^+ , 15).

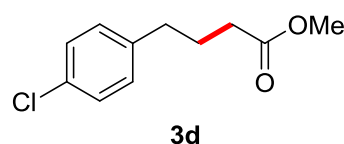


methyl 4-(4-methoxyphenyl)butanoate (3b): According to general procedure A, a solution of **1b** (0.5 mmol, 67.1 mg), Methyl thioglycolate (0.75 mmol, 65 μL), AIBN

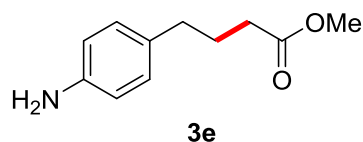
(0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3b** (95.7 mg, 92%) as colorless oil after purification on silica gel (PE:EA=50:1). ¹H NMR (400 MHz, CDCl₃) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.69 (s, 3H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.98-1.91 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 157.9, 133.5, 129.4, 113.8, 55.3, 51.5, 34.2, 33.4, 26.7. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₂H₁₇O₃: 209.1178; found: 209.1178.



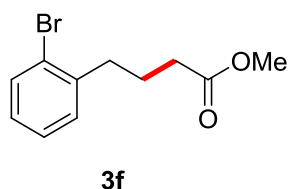
methyl 4-(4-acetoxyphenyl)butanoate (3c): According to general procedure A, a solution of **1c** (0.5 mmol, 81.1 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3c** (89.7 mg, 76%) as colorless oil after purification on silica gel (PE:EA=15:1). ¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 3.69 (s, 3H), 2.69-2.63 (m, 2H), 2.36 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 2.05-1.92 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 169.7, 148.9, 138.9, 129.4, 121.4, 51.6, 34.5, 33.3, 26.4, 21.2. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₃H₁₇O₄: 237.1127; found: 237.1131.



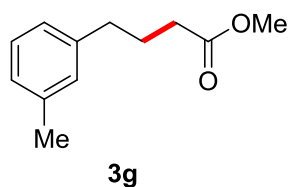
methyl 4-(4-chlorophenyl)butanoate (3d)¹: According to general procedure A, a solution of **1d** (0.5 mmol, 69.2 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3d** (71.1 mg, 67%) as colorless oil after purification on silica gel (PE:EA=30:1). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.69 (s, 3H), 2.72-2.57 (m, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.99-1.91 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 173.8, 139.8, 131.7, 129.8, 128.5, 51.6, 34.4, 33.2, 26.4. MS (70 ev): *m/z* (%): 58.8 (95), 88.7 (50), 124.8 (100), 211.7 (M⁺, 10).



methyl 4-(4-aminophenyl)butanoate (3e): According to general procedure A , a solution of **1e** (0.5 mmol, 59.6 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3e** (72.4 mg, 75%) as colorless oil after purification on silica gel (PE:EA=3:1). ¹H NMR (400 MHz, CDCl₃) δ 6.99 (d, *J* = 8.3 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 3.68 (s, 3H), 3.54 (s, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.96-1.88 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 144.5, 131.4, 129.3, 115.3, 51.5, 34.3, 33.4, 26.8. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₁H₁₆NO₂: 194.1181; found: 194.1182.

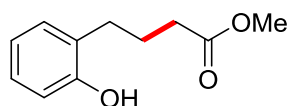


methyl 4-(2-bromophenyl)butanoate (3f)¹: According to general procedure A , a solution of **1f** (0.5 mmol, 91.5 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3f** (91.0 mg, 71%) as colorless oil after purification on silica gel (PE:EA=50:1). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.32-7.21 (m, 2H), 7.10-7.05 (m, 1H), 3.70 (s, 3H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.47-2.37 (m, 2H), 2.09-1.91 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 173.8, 140.7, 132.9, 130.5, 127.8, 127.5, 124.5, 51.6, 35.3, 33.4, 25.0. GC-MS (EI) ([M]) Calcd. for C₁₁H₁₃BrO₂: 212.1; found: 211.7. MS (70 ev): *m/z* (%): 58.9 (100), 88.8 (85), 168.8 (60), 255.8 (M⁺, 5).



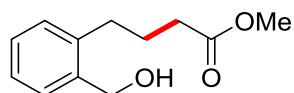
methyl 4-(m-tolyl)butanoate (3g)²: According to general procedure A , a solution of **1g** (0.5 mmol, 59.1 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3g** (86.4 mg, 90%) as colorless oil after purification on

silica gel (PE:EA=50:1). ^1H NMR (400 MHz, CDCl_3) δ 7.21 (t, J = 7.9 Hz, 1H), 7.08-6.99 (m, 3H), 3.70 (s, 3H), 2.65 (t, J = 7.2 Hz, 2H), 2.37 (s, 3H), 2.36 (t, J = 7.4 Hz, 2H) 2.02-1.95 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.9, 141.3, 137.9, 129.3, 128.3, 126.7, 125.5, 51.5, 35.1, 33.5, 26.5, 21.4. MS (70 ev): m/z (%): 58.8 (100), 104.9 (85), 117.8 (55), 191.9 (M^+ , 10).



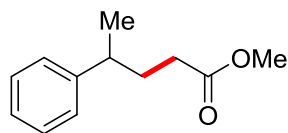
3h

methyl 4-(2-hydroxyphenyl)butanoate (3h): According to general procedure A, a solution of **1a** (0.5 mmol, 60.0 mg), Methyl thioglycolate (0.75 mmol, 65 μL), AIBN (0.025 mmol, 4.5 mg), $\text{P}(\text{OEt})_3$ (0.6 mmol, 105 μL) in DCE (4.0 mL) were stirred at 80 $^\circ\text{C}$ under Ar for 12 h to afford **3h** (62.1 mg, 64%) as colorless oil after purification on silica gel (PE:EA=15:1). ^1H NMR (400 MHz, CDCl_3) δ 7.17 – 7.09 (m, 2H), 6.91 – 6.83 (m, 2H), 6.49 (s, 1H), 3.74 (s, 3H), 2.69 (t, J = 7.6 Hz, 2H), 2.43 (t, J = 6.9 Hz, 2H), 1.99-1.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 175.4, 154.3, 130.2, 127.6, 127.2, 120.4, 115.8, 51.9, 32.9, 29.4, 24.9. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{11}\text{H}_{15}\text{O}_3$: 195.1021; found: 195.1024.



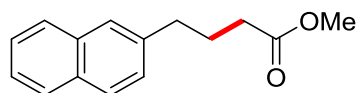
3i

methyl 4-(2-(hydroxymethyl)phenyl)butanoate (3i): According to general procedure A, a solution of **1i** (0.5 mmol, 67.1 mg), Methyl thioglycolate (0.75 mmol, 65 μL), AIBN (0.025 mmol, 4.5 mg), $\text{P}(\text{OEt})_3$ (0.6 mmol, 105 μL) in DCE (4.0 mL) were stirred at 80 $^\circ\text{C}$ under Ar for 12 h to afford **3i** (55.1 mg, 53%) as colorless oil after purification on silica gel (PE:EA=5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.38 (m, 1H), 7.31-7.17 (m, 3H), 4.72 (s, 2H), 3.68 (s, 3H), 2.74 (t, J = 8.0 Hz, 2H), 2.41 (t, J = 7.1 Hz, 2H), 2.23 (s, 1H), 2.08-1.86 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.2, 139.7, 138.5, 129.5, 128.7, 127.9, 126.5, 63.1, 51.6, 33.5, 31.6, 26.2. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{12}\text{H}_{17}\text{O}_3$: 209.1178; found: 209.1176.



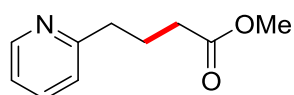
3j

methyl 4-phenylpentanoate (3j)¹: According to general procedure A, a solution of **1j** (0.5 mmol, 59.1 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3j** (83.5 mg, 87%) as colorless oil after purification on silica gel (PE:EA=50:1). ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.30 (m, 2H), 7.25-7.18 (m, 3H), 3.65 (s, 3H), 2.87-2.67 (m, 1H), 2.37-2.12 (m, 2H), 2.07-1.84 (m, 2H), 1.31 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 146.2, 128.4, 127.0, 126.2, 51.5, 39.4, 33.2, 32.3, 22.2. MS (70 ev): *m/z* (%): 58.8 (65), 76.8 (55), 104.9 (100), 191.9 (M⁺, 10).



3k

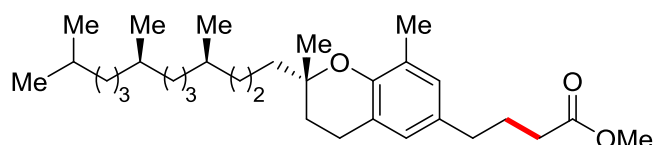
methyl 4-(naphthalen-2-yl)butanoate (3k)¹: According to general procedure A, a solution of **1k** (0.5 mmol, 77.1 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3k** (87.8 mg, 77%) as colorless oil after purification on silica gel (PE:EA=50:1). ¹H NMR (400 MHz, CDCl₃) δ 7.90-7.77 (m, 3H), 7.66 (s, 1H), 7.56-7.42 (m, 2H), 7.37 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.71 (s, 3H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.18-2.04 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 174.0, 138.9, 133.6, 132.1, 128.0, 127.6, 127.5, 127.3, 126.6, 126.0, 125.3, 51.5, 35.3, 33.4, 26.4. MS (70 ev): *m/z* (%): 62.9 (100), 115.9 (100), 197.0 (100), 228.1 (M⁺, 100).



3l

methyl 4-(pyridin-2-yl)butanoate (3l): According to general procedure A, a solution of **1l** (0.5 mmol, 53.1 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025

mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3l** (50.1 mg, 56%) as colorless oil after purification on silica gel (PE:EA=20:1). ¹H NMR (400 MHz, CDCl₃) δ 8.54-8.51 (m, 1H), 7.59 (td, *J* = 7.7, 1.9 Hz, 1H), 7.19-7.06 (m, 2H), 3.67 (s, 3H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.38 (t, *J* = 7.5 Hz, 2H), 2.12-2.04 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 173.8, 161.1, 149.3, 136.3, 122.9, 121.2, 51.5, 37.4, 33.4, 24.8. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₀H₁₄NO₂: 180.1025; found: 180.1024.

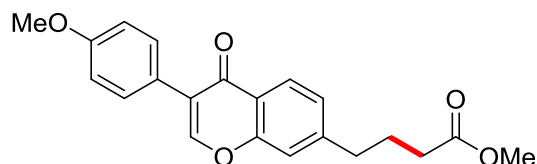


3m

methyl

4-((S)-2,8-dimethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)butanoate

(3m): According to general procedure A, a solution of **1m** (0.5 mmol, 206.3 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3m** (141.0 mg, 58%) as colorless oil after purification on silica gel (PE:EA=50:1). ¹H NMR (400 MHz, CDCl₃) δ 6.79 (s, 1H), 6.73 (s, 1H), 3.69 (s, 3H), 2.76-2.71 (m, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 2.16 (s, 3H), 1.97-1.89 (m, 2H), 1.86-1.72 (m, 2H), 1.67-1.02 (m, 21H), 1.28 (s, 3H), 0.90-0.86 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 174.2, 150.3, 131.4, 128.5, 126.6, 126.0, 120.2, 75.8, 51.5, 40.2, 39.4, 37.5, 37.4, 37.3, 34.4, 33.6, 32.8, 32.7, 31.3, 28.0, 26.8, 24.8, 24.5, 24.3, 22.74, 22.65, 22.4, 21.0, 19.8, 19.7, 16.1. HRMS (ESI) ([M+NH₄]⁺) Calcd. for C₃₂H₅₈NO₃: 504.4417; found: 504.4425.

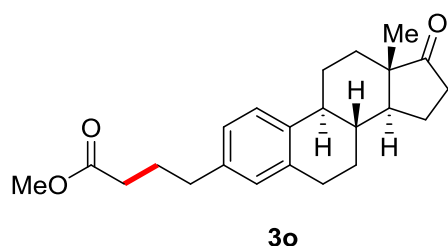


3n

methyl 4-(3-(4-methoxyphenyl)-4-oxo-4H-chromen-7-yl)butanoate (3n):

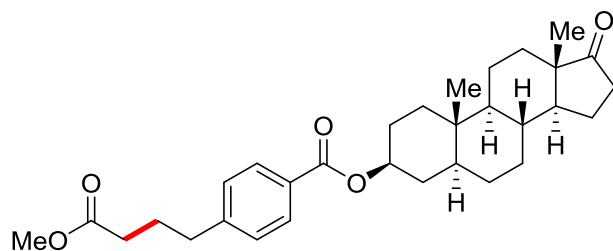
According to general procedure A, a solution of **1n** (0.5 mmol, 139.2 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol,

105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3n** (87.3 mg, 50%) as white solid after purification on silica gel (PE:EA=4:1). ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.1 Hz, 1H), 7.98 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.33-7.24 (m, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 3.70 (s, 3H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 2.17-1.97 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 176.3, 173.6, 159.6, 156.3, 152.4, 148.2, 130.1, 126.4, 125.9, 124.9, 124.2, 122.8, 117.3, 113.9, 55.4, 51.7, 35.1, 33.2, 25.9. HRMS (ESI) ([M+H]⁺) Calcd. for C₂₁H₂₁O₅: 353.1389; found: 353.1388.



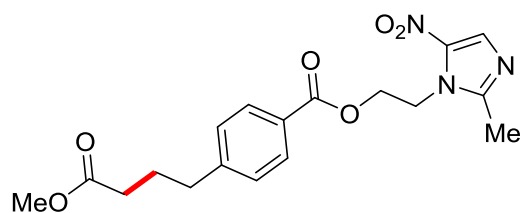
methyl

4-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)butanoate (3o): According to general procedure A, a solution of **1o** (0.5 mmol, 140.0 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3o** (128.2 mg, 72%) as white solid after purification on silica gel (PE:EA=10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 1.0 Hz, 1H), 7.02-6.98 (m, 1H), 6.95 (s, 1H), 3.69 (s, 3H), 2.94-2.90 (m, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.53 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.47-2.41 (m, 1H), 2.37 (t, *J* = 7.5 Hz, 2H), 2.33-2.26 (m, 1H), 2.21-2.11 (m, 1H), 2.12-2.01 (m, 2H), 2.01-1.91 (m, 3H), 1.76-1.38 (m, 6H), 0.93 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 220.9, 174.0, 138.9, 137.4, 136.4, 129.1, 125.9, 125.4, 51.5, 50.5, 48.0, 44.3, 38.2, 35.9, 34.6, 33.5, 31.6, 29.4, 26.6, 26.5, 25.8, 21.6, 13.9. HRMS (ESI) ([M+Na]⁺) Calcd. for C₂₃H₃₀NaO₃: 377.2093; found: 377.2094.



3p

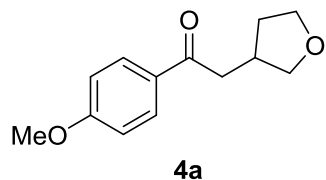
(3S,5S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(4-methoxy-4-oxobutyl)benzoate (3p): According to general procedure A , a solution of **1p** (0.5 mmol, 210.0 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3p** (137.1 mg, 55%) as white solid after purification on silica gel (PE:EA=5:1). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 4.98-4.89 (m, 1H), 3.67 (s, 3H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.54 – 2.40 (m, 1H), 2.33 (t, *J* = 7.4 Hz, 2H), 2.13-2.03 (m, 1H), 2.02-1.89 (m, 4H), 1.86-1.21 (m, 16H), 1.18-0.95 (m, 2H), 0.91 (s, 3H), 0.87 (s, 3H), 0.82-0.70 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 221.2, 173.7, 166.1, 146.7, 129.7, 128.8, 128.4, 73.9, 54.3, 51.6, 51.4, 47.8, 44.7, 36.8, 35.9, 35.7, 35.2, 35.1, 34.1, 33.2, 31.5, 30.8, 28.3, 27.5, 26.2, 21.8, 20.5, 13.8, 12.3. HRMS (ESI) ([M+Na]⁺) Calcd. for C₃₁H₄₃O₅: 495.3110; found: 495.3121.



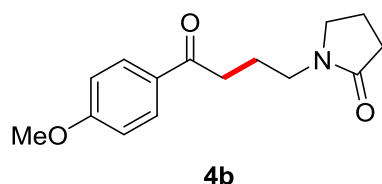
3q

2-(2-methyl-5-nitro-1H-imidazol-1-yl)ethyl 4-(4-methoxy-4-oxobutyl)benzoate (3q): According to general procedure A , a solution of **1q** (0.5 mmol, 150.0 mg), Methyl thioglycolate (0.75 mmol, 65 uL), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **3q** (92.1 mg, 50%) as white solid after purification on silica gel (PE:EA=1:1). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 9.7 Hz, 2H), 4.73-4.69 (m, 2H), 4.68-4.65 (m, 2H), 3.69 (s, 3H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.50 (s, 3H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.99 (p, *J* = 7.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ

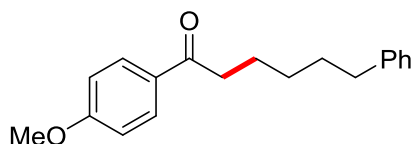
173.6, 166.0, 150.9, 147.8, 133.3, 129.8, 128.8, 126.9, 62.7, 51.6, 45.3, 35.1, 33.2, 26.0, 14.4. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{22}N_3O_6$: 376.1509; found: 376.1506.



1-(4-methoxyphenyl)-2-(tetrahydrofuran-3-yl)ethan-1-one (4a): According to general procedure B, a solution of **1r** (1.5 mmol, 105.1 mg), **2b** (0.5 mmol, 92.1 mg), AIBN (0.025 mmol, 4.5 mg), $P(OEt)_3$ (0.6 mmol, 105 μ L) in DCE (4.0 mL) were stirred at 80 $^{\circ}C$ under Ar for 12 h to afford **4a** (69.3 mg, 63%) as colorless oil after purification on silica gel (PE:EA=5:1). 1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 4.03 (dd, J = 8.6, 7.1 Hz, 1H), 3.91-3.86 (m, 1H), 3.88 (s, 3H), 3.83-3.72 (m, 1H), 3.45 (dd, J = 8.6, 6.3 Hz, 1H), 3.14-2.98 (m, 2H), 2.86-2.76 (m, 1H), 2.23-2.15 (m, 1H), 1.64-1.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 163.5, 130.3, 130.0, 113.8, 73.3, 67.7, 55.5, 42.1, 34.8, 32.3. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{17}O_3$: 221.1178; found: 221.1178.

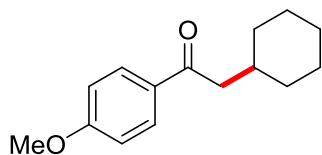


1-(4-(4-methoxyphenyl)-4-oxobutyl)pyrrolidin-2-one (4b): According to general procedure B, a solution of **1s** (0.75 mmol, 83.5 mg), **2b** (0.5 mmol, 92.1 mg), AIBN (0.025 mmol, 4.5 mg), $P(OEt)_3$ (0.6 mmol, 105 μ L) in DCE (4.0 mL) were stirred at 80 $^{\circ}C$ under Ar for 12 h to afford **4b** (106.3 mg, 82%) as colorless oil after purification on silica gel (PE:EA=50:1). 1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H), 3.40-3.33 (m, 4H), 2.91 (t, J = 7.2 Hz, 2H), 2.30 (t, J = 8.1 Hz, 2H), 2.09-1.87 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 175.1, 163.5, 130.3, 129.8, 113.7, 55.4, 47.0, 42.0, 35.2, 31.0, 21.9, 17.9. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{15}H_{20}NO_3$: 262.1443; found: 262.1441.



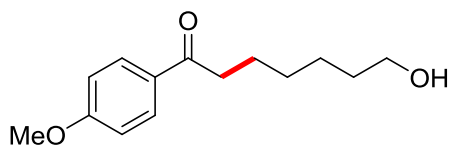
4c

1-(4-methoxyphenyl)-6-phenylhexan-1-one (4c): According to general procedure B, a solution of **1t** (1.5 mmol, 198.1 mg), **2b** (0.5 mmol, 92.1 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **4c** (70.4 mg, 50%) as colorless oil after purification on silica gel (PE:EA=10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.9 Hz, 2H), 7.38 – 7.26 (m, 2H), 7.22-7.18 (m, 3H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.79 (p, *J* = 7.5 Hz, 2H), 1.75-1.65 (m, 2H), 1.53-1.40 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 199.1, 163.3, 142.6, 130.3, 130.2, 128.4, 128.3, 125.7, 113.7, 55.5, 38.2, 35.8, 31.4, 29.1, 24.4. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₉H₂₃O₂: 283.1698; found: 283.1696.



4d

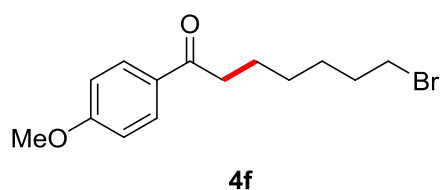
2-cyclohexyl-1-(4-methoxyphenyl)ethan-1-one (4d): According to general procedure B, a solution of **1u** (3.0 mmol, 246.4 mg), **2b** (0.5 mmol, 92.1 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **4d** (30.1 mg, 25%) as colorless oil after purification on silica gel (PE:EA=20:1). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 9.1 Hz, 2H), 6.95 (d, *J* = 9.1 Hz, 2H), 3.89 (s, 3H), 2.78 (d, *J* = 6.9 Hz, 2H), 2.02-1.94 (m, 1H), 1.84-1.61 (m, 5H), 1.39-1.11 (m, 3H), 1.08-0.94 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 198.9, 163.3, 130.6, 130.4, 113.6, 55.5, 45.9, 34.8, 33.5, 26.3, 26.2. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₅H₂₁O₂: 233.1542; found: 233.1543.



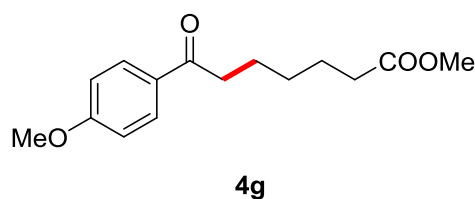
4e

7-hydroxy-1-(4-methoxyphenyl)heptan-1-one (4e): According to general procedure

B , a solution of **1v** (0.75 mmol, 64.6 mg), **2b** (0.5 mmol, 92.1 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 μ L) in DCE (4.0 mL) were stirred at 80 $^{\circ}$ C under Ar for 12 h to afford **4e** (33.3 mg, 28%) as white solid after purification on silica gel (PE:EA=5:1). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 1.78-1.70 (m, 2H), 1.64-1.56 (m, 3H), 1.46-1.40 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 199.1, 163.3, 130.3, 130.1, 113.7, 62.9, 55.5, 38.1, 32.6, 29.1, 25.6, 24.5. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₄H₂₁O₃: 237.1491; found: 237.1484.

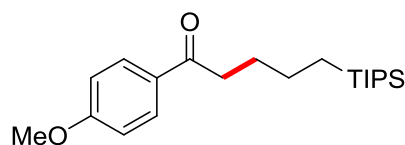


7-bromo-1-(4-methoxyphenyl)heptan-1-one (4f): According to general procedure B , a solution of **1w** (0.75 mmol, 111.8 mg), **2b** (0.5 mmol, 92.1 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 μ L) in DCE (4.0 mL) were stirred at 80 $^{\circ}$ C under Ar for 12 h to afford **4f** (77.5 mg, 52%) as white solid after purification on silica gel (PE:EA=10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.43 (t, *J* = 6.8 Hz, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 1.93-1.86 (m, 2H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.59-1.37 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 198.9, 163.4, 130.3, 130.1, 113.7, 55.5, 38.0, 33.9, 32.6, 28.5, 28.0, 24.3. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₄H₂₀BrO₂: 299.0647; found: 299.0637.



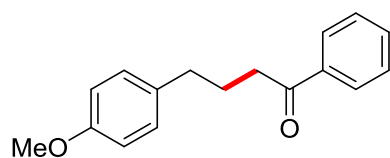
methyl 7-(4-methoxyphenyl)-7-oxoheptanoate (4g): According to general procedure B, a solution of **1x** (2.0 mmol, 228.2 mg), **2b** (0.5 mmol, 92.1 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 μ L) in DCE (4.0 mL) were stirred at 80 $^{\circ}$ C under Ar for 12 h to afford **4g** (59.7 mg, 45%) as white solid after purification on silica gel (PE:EA=10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 3.68 (s, 3H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.34 (t, *J* = 7.5

Hz, 2H), 1.80-1.66 (m, 4H), 1.49-1.35 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 174.1, 163.4, 130.3, 130.1, 113.7, 55.5, 51.5, 37.9, 33.9, 28.9, 24.8, 24.1. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{21}\text{O}_4$: 265.1440; found: 265.1434.



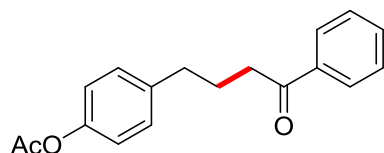
4h

1-(4-methoxyphenyl)-5-(triisopropylsilyl)pentan-1-one (4h): According to general procedure B, a solution of **1y** (1.0 mmol, 198.0 mg), **2b** (0.5 mmol, 92.1 mg), AIBN (0.025 mmol, 4.5 mg), $\text{P}(\text{OEt})_3$ (0.6 mmol, 105 μL) in DCE (4.0 mL) were stirred at 80 $^\circ\text{C}$ under Ar for 12 h to afford **4h** (103.1 mg, 59%) as colorless oil after purification on silica gel (PE:EA=50:1). ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 3.89 (s, 3H), 2.94 (t, J = 7.5 Hz, 2H), 1.77 (p, J = 7.5 Hz, 2H), 1.50-1.42 (m, 2H), 1.05 (s, 21H), 0.78-0.55 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 199.3, 163.3, 130.3, 130.2, 113.7, 55.4, 38.0, 29.3, 24.3, 18.9, 10.9, 9.4. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{21}\text{H}_{37}\text{O}_2\text{Si}$: 349.2563; found: 349.2557.



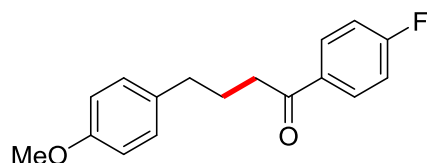
5a

4-(4-methoxyphenyl)-1-phenylbutan-1-one (5a): According to general procedure A, a solution of **1b** (0.5 mmol, 67.1 mg), **2c** (0.75 mmol, 112.5 mg), AIBN (0.025 mmol, 4.5 mg), $\text{P}(\text{OEt})_3$ (0.6 mmol, 105 μL) in DCE (4.0 mL) were stirred at 80 $^\circ\text{C}$ under Ar for 12 h to afford **5a** (112.1 mg, 88%) as white solid after purification on silica gel (PE:EA=40:1). ^1H NMR (400 MHz, CDCl_3) δ 8.03-7.89 (m, 2H), 7.64-7.53 (m, 1H), 7.49-7.45 (m, 2H), 7.16 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H), 3.00 (t, J = 7.3 Hz, 2H), 2.70 (t, J = 7.5 Hz, 2H), 2.12-2.04 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 200.2, 157.9, 137.1, 133.8, 132.9, 129.4, 128.6, 128.0, 113.9, 55.3, 37.7, 34.3, 25.9. MS (70 ev): m/z (%): 76.8 (100), 120.9 (50), 253.9 (M^+ , 3).



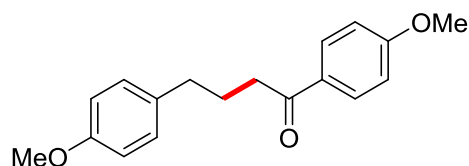
5b

4-(4-oxo-4-phenylbutyl)phenyl acetate (5b): According to general procedure A, a solution of **1c** (0.5 mmol, 81.1 mg), **2c** (0.75 mmol, 112.5 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **5b** (117.0 mg, 83%) as white solid after purification on silica gel (PE:EA=15:1). ¹H NMR (400 MHz, CDCl₃) δ 8.01-7.90 (m, 2H), 7.63-7.53 (m, 1H), 7.51-7.42 (m, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.30 (s, 3H), 2.18-2.02 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 199.9, 169.6, 148.9, 139.3, 136.9, 133.0, 129.4, 128.6, 128.0, 121.4, 37.6, 34.6, 25.6, 21.1. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₈H₁₉O₃: 283.1334; found: 283.1334.



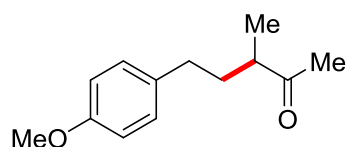
5c

1-(4-fluorophenyl)-4-(4-methoxyphenyl)butan-1-one (5c)³: According to general procedure A, a solution of **1b** (0.5 mmol, 67.1 mg), **2d** (0.6 mmol, 102.6 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **5c** (113.2 mg, 83%) as white solid after purification on silica gel (PE:EA=30:1). ¹H NMR (400 MHz, CDCl₃) δ 8.01-7.92 (m, 2H), 7.20-7.06 (m, 4H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.18-1.97 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 198.6, 165.7 (d, *J*_{C-F} = 255.2 Hz), 157.9, 133.7, 133.4 (d, *J*_{C-F} = 3.0 Hz), 130.6 (d, *J*_{C-F} = 9.2 Hz), 129.3, 115.7 (d, *J*_{C-F} = 21.8 Hz), 113.9, 55.3, 37.6, 34.3, 26.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -105.6. MS (70 ev): *m/z* (%): 94.8 (88), 122.8 (100), 271.9 (M⁺, 1).



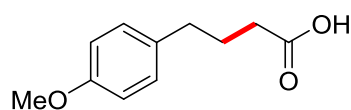
5d

1,4-bis(4-methoxyphenyl)butan-1-one (5d)³: According to general procedure A, a solution of **1b** (0.5 mmol, 67.1 mg), **2b** (0.6 mmol, 109.8 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **5d** (121.3 mg, 85%) as white solid after purification on silica gel (PE:EA=20:1). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.13-2.01 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 198.8, 163.4, 157.9, 133.9, 130.3, 130.1, 129.4, 113.8, 113.7, 55.5, 55.3, 37.3, 34.4, 26.2. MS (70 ev): *m/z* (%): 76.8 (60), 134.8 (100), 284.1 (M⁺, 3).



5e

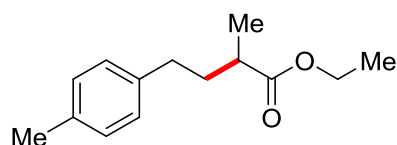
5-(4-methoxyphenyl)-3-methylpentan-2-one (5e)⁴: According to general procedure A, a solution of **1b** (0.5 mmol, 67.1 mg), **2e** (0.75 mmol, 78.1 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **5e** (63.9 mg, 62%) as colorless oil after purification on silica gel (PE:EA=20:1). ¹H NMR (400 MHz, CDCl₃) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 2.67-2.45 (m, 3H), 2.14 (s, 3H), 2.04-1.95 (m, 1H), 1.67-1.58 (m, 1H), 1.15 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 212.5, 157.9, 133.7, 129.3, 113.9, 55.3, 46.4, 34.6, 32.5, 28.1, 16.3. MS (70 ev): *m/z* (%): 77.8 (60), 120.8 (90), 133.8 (100), 206.0 (M⁺, 5).



5f

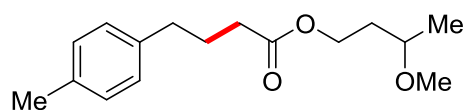
4-(4-methoxyphenyl)butanoic acid (5f)⁵: According to general procedure A, a

solution of **1a** (0.5 mmol, 59.1 mg), **2f** (0.75 mmol, 69.1 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **5f** (55.7 mg, 57%) as white solid after purification on silica gel (PE:EA=4:1). ¹H NMR (400 MHz, CDCl₃) δ 11.12 (s, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 1.96 (p, *J* = 7.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 180.0, 157.9, 133.3, 129.4, 113.9, 55.3, 34.1, 33.3, 26.5. MS (70 ev): *m/z* (%): 77.9 (82), 120.8 (100), 194.0 (M⁺, 15).



5g

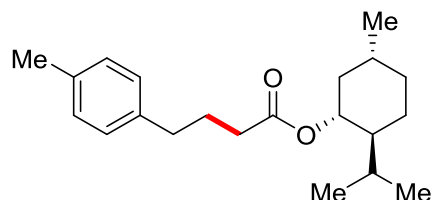
ethyl 2-methyl-4-(p-tolyl)butanoate (5g): According to general procedure A, a solution of **1a** (0.5 mmol, 59.1 mg), **2g** (0.75 mmol, 101.2 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **5g** (69.3 mg, 63%) as colorless oil after purification on silica gel (PE:EA=100:1). ¹H NMR (400 MHz, CDCl₃) δ 7.12-7.08 (m, 4H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.52-2.43 (m, 1H), 2.34 (s, 3H), 2.06-1.96 (m, 1H), 1.80-1.64 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.21 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.6, 138.7, 135.3, 129.1, 128.3, 60.2, 39.1, 35.6, 33.0, 20.9, 17.1, 14.3. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₄H₂₁O₂: 221.1542; found: 221.1543.



5h

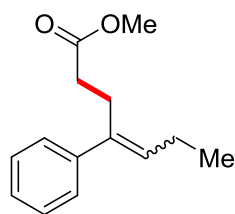
3-methoxybutyl 4-(p-tolyl)butanoate (5h): According to general procedure A, a solution of **1a** (0.5 mmol, 59.1 mg), **2h** (0.75 mmol, 133.7 mg), AIBN (0.025 mmol, 4.5 mg), P(OEt)₃ (0.6 mmol, 105 uL) in DCE (4.0 mL) were stirred at 80 °C under Ar for 12 h to afford **5h** (110.9 mg, 84%) as colorless oil after purification on silica gel (PE:EA=20:1). ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 4.19 (t, *J* = 6.8 Hz, 2H), 3.47-3.39 (m, 1H), 3.34 (s, 3H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.35 (s, 3H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.96 (p, *J* = 7.6 Hz, 2H), 1.90-1.69 (m,

2H), 1.19 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 138.3, 135.4, 129.1, 128.4, 73.7, 61.4, 56.1, 35.6, 34.7, 33.7, 26.7, 21.0, 19.1. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{16}\text{H}_{25}\text{O}_3$: 265.1804; found: 265.1796.



5i

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(p-tolyl)butanoate (5i): According to general procedure A, a solution of **1a** (0.5 mmol, 59.1 mg), **2i** (0.75 mmol, 172.5 mg), AIBN (0.025 mmol, 4.5 mg), $\text{P}(\text{OEt})_3$ (0.6 mmol, 105 μL) in DCE (4.0 mL) were stirred at 80 $^\circ\text{C}$ under Ar for 12 h to afford **5i** (120.1 mg, 76%) as colorless oil after purification on silica gel (PE:EA=100:1). ^1H NMR (400 MHz, CDCl_3) δ 7.13 (d, $J = 8.3$ Hz, 2H), 7.10 (d, $J = 8.3$ Hz, 2H), 4.73 (td, $J = 10.9, 4.4$ Hz, 1H), 2.64 (t, $J = 7.6$ Hz, 2H), 2.35 (s, 3H), 2.34 (t, $J = 7.6$ Hz, 2H), 2.12-1.84 (m, 4H), 1.74-1.67 (m, 2H), 1.57-1.47 (m, 1H), 1.45-1.33 (m, 1H), 1.18-1.02 (m, 1H), 0.94 (d, $J = 2.8$ Hz, 3H), 0.92 (d, $J = 3.3$ Hz, 3H), 1.02-0.84 (m, 2H), 0.80 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 138.5, 135.4, 129.1, 128.4, 74.0, 47.1, 41.0, 34.8, 34.3, 34.1, 31.4, 26.9, 26.3, 23.4, 22.1, 21.0, 20.8, 16.3. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{21}\text{H}_{33}\text{O}_2$: 317.2481; found: 317.2476.



6

$E/Z = 3:1$

methyl 4-phenylhept-4-enoate (6): According to general procedure A, a solution of **1z** (0.5 mmol, 72.0 mg), **1b** (0.75 mmol, 65 μL), AIBN (0.025 mmol, 4.5 mg), $\text{P}(\text{OEt})_3$ (0.6 mmol, 105 μL) in DCE (4.0 mL) were stirred at 80 $^\circ\text{C}$ under Ar for 12 h to afford **6** (68.4 mg, 63%, a mixture of E/Z) as colorless oil after purification on silica gel (PE:EA=150:1). E : ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.21 (m, 5H), 5.72

(t, $J = 7.3$ Hz, 1H), 3.65 (s, 3H), 2.87 (t, $J = 8.0$ Hz, 2H), 2.35 (t, $J = 8.4$ Hz, 2H), 2.26 (p, $J = 7.4$ Hz, 2H), 1.09 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 142.2, 137.6, 132.0, 128.3, 128.1, 126.8, 126.4, 51.5, 33.3, 25.1, 21.8, 14.4. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{14}\text{H}_{19}\text{O}_2$: 219.1385; found: 219.1385.

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4. NMR Spectra for All Compound

