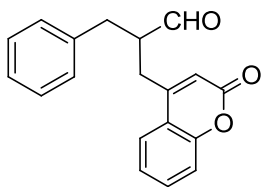
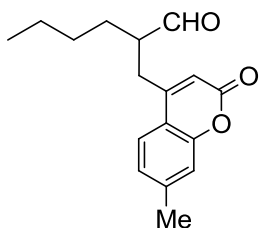


**Experimental:** All reactions were run in flame-dried glassware under an Ar atmosphere using standard Schlenk techniques. Commercially available reagents were used without additional purification. Compound purification was effected by flash chromatography using 230x400 mesh, 60 Å porosity silica gel. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a Bruker Avance 400 and 500 DRX spectrometer and referenced to residual protio solvent signals. Structural assignments are based on <sup>1</sup>H, <sup>13</sup>C, IR, and HRMS spectroscopies.

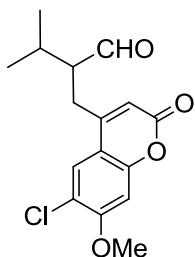
**General procedure:** A solution of coumarinyl(methyl) acetate (0.5 mmol), 5 mol % of palladium(II) acetylacetonate (7.6 mg) and 5.0 mol% of 1,1'-bis(diphenylphosphino)ferrocene (14.4 mg) was prepared in DMSO (3 mL). Next, aldehyde or ketone (1.5 mmol) and pyrrolidine (53 mg, 0.74 mmol) were added. After 12 h stirring at room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel to afford pure product.



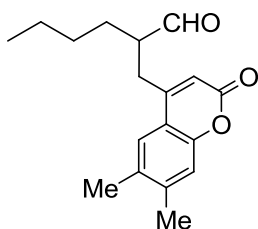
**2-benzyl-3-(2-oxo-2H-chromen-4-yl)propanal:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.81 (d, *J* = 1.3 Hz, 1H), 7.52 (m, 1H), 7.39 – 7.27 (m, 4H), 7.26 – 7.17 (m, 4H), 6.28 (s, 1H), 3.22 (dt, *J* = 13.8, 7.7 Hz, 2H), 3.13 – 3.06 (m, 1H), 2.81 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.65, 160.42, 153.78, 153.06, 137.25, 131.94, 129.15, 128.98, 127.20, 124.34, 124.08, 118.71, 117.47, 115.66, 51.92, 35.46, 29.54; IR (CH<sub>2</sub>Cl<sub>2</sub>): 1726, 1604, 1448 cm<sup>-1</sup>; Calcd. HRMS for C<sub>19</sub>H<sub>17</sub>O<sub>3</sub> (M+H), 293.1178; Found, 293.1183.



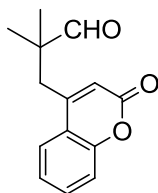
**2-((7-methyl-2-oxo-2H-chromen-4-yl)methyl)hexanal:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.72 (d, *J* = 1.8 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.19 – 7.01 (m, 2H), 6.21 (s, 1H), 3.25–3.19 (m, 1H), 2.77 – 2.69 (m, 2H), 2.45 (s, 3H), 1.81 – 1.72 (m, 1H), 1.68 – 1.60 (m, 1H), 1.45 – 1.28 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 202.56, 160.76, 153.88, 153.30, 143.24, 125.57, 123.83, 117.63, 116.45, 114.26, 50.10, 30.22, 28.86, 22.74, 21.58, 13.83; IR (CH<sub>2</sub>Cl<sub>2</sub>): 1724, 1620 cm<sup>-1</sup>; Calcd. HRMS for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub> (M+H), 273.1491; Found, 273.1498.



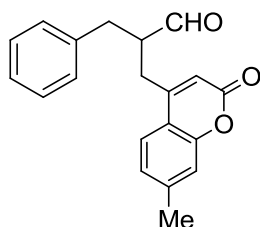
**2-((6-chloro-7-methoxy-2-oxo-2H-chromen-4-yl)methyl)-3-methylbutanal:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.77 (d,  $J = 1.4$  Hz, 1H), 7.60 (s, 1H), 6.88 (s, 1H), 6.15 (s, 1H), 3.98 (s, 3H), 3.17 (dd,  $J = 16.3, 10.0$  Hz, 1H), 2.75 – 2.68 (m, 2H), 2.29 – 2.23 (m, 1H), 1.15 (d,  $J = 8.0$  Hz, 3H), 1.13 (d,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.37, 160.33, 157.68, 153.96, 153.13, 124.98, 119.11, 113.05, 112.82, 100.75, 56.69, 55.93, 28.65, 26.90, 19.81, 19.62; IR ( $\text{CH}_2\text{Cl}_2$ ): 1728, 1608  $\text{cm}^{-1}$ ; Calcd. HRMS for  $\text{C}_{16}\text{H}_{18}\text{ClO}_4$  (M+H), 309.0894; Found, 309.0890



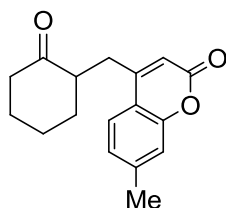
**2-((6,7-dimethyl-2-oxo-2H-chromen-4-yl)methyl)hexanal:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.74 (d,  $J = 0.9$  Hz, 1H), 7.31 (s, 1H), 7.13 (s, 1H), 6.19 (s, 1H), 3.22 (dd,  $J = 14.2, 6.2$  Hz, 1H), 2.79 – 2.69 (m, 2H), 2.35 (s, 3H), 2.34 (s, 3H), 1.79 – 1.72 (m, 1H), 1.69 – 1.61 (m, 1H), 1.43 – 1.32 (m, 5H), 0.92 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.63, 160.96, 153.19, 152.18, 142.05, 133.09, 124.19, 117.98, 116.54, 114.20, 50.00, 30.14, 28.85, 28.79, 22.75, 20.18, 19.54, 13.84; IR ( $\text{CH}_2\text{Cl}_2$ ): 1724, 1622  $\text{cm}^{-1}$ ; Calcd. HRMS for  $\text{C}_{18}\text{H}_{23}\text{O}_3$  (M+H), 287.1647; Found, 287.1644.



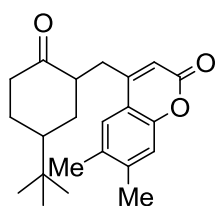
**2,2-dimethyl-3-(2-oxo-2H-chromen-4-yl)propanal:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.55 (s, 1H), 7.63 (d,  $J = 8.0$  Hz, 1H), 7.55 – 7.51 (m, 1H), 7.34 – 7.27 (m, 2H), 6.25 (s, 1H), 2.98 (s, 2H), 1.15 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  203.91, 160.18, 153.70, 152.00, 132.01, 125.11, 124.20, 119.74, 117.49, 117.32, 46.66, 36.52, 22.18; IR ( $\text{CH}_2\text{Cl}_2$ ): 2976, 1722,  $\text{cm}^{-1}$ ; Calcd. HRMS for  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{Na}$  (M+Na), 253.0841; Found, 253.0847.



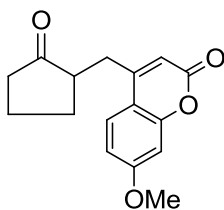
**2-benzyl-3-(7-methyl-2-oxo-2H-chromen-4-yl)propanal :**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.80 (d,  $J = 1.2$  Hz, 1H), 7.38-7.28 (m, 3H), 7.22 – 7.20 (m, 2H), 7.10 (d,  $J = 8.9$  Hz, 2H), 7.00 (d,  $J = 8.1$  Hz, 1H), 6.21 (s, 1H), 3.22 – 3.14 (m, 2H), 3.10 – 3.05 (m, 1H), 2.85-2.27 (m, 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.78, 160.76, 153.86, 153.16, 143.21, 137.34, 129.16, 128.95, 127.15, 125.52, 123.79, 117.57, 116.29, 114.50, 52.00, 35.43, 29.59, 21.57; IR ( $\text{CH}_2\text{Cl}_2$ ): 1725.36, 1617  $\text{cm}^{-1}$ ; Calcd. HRMS for  $\text{C}_{20}\text{H}_{19}\text{O}_3$  (M+H), 307.1334; Found, 307.1338.



**7-methyl-4-((2-oxocyclohexyl)methyl)-2H-chromen-2-one:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 8.1$  Hz, 1H), 7.21 – 7.04 (m, 2H), 6.18 (s, 1H), 3.50 (dd,  $J = 14.8$ , 4.6 Hz, 1H), 2.66 (m, 1H), 2.56 – 2.33 (m, 6H), 2.15 (tdd,  $J = 12.0$ , 5.7, 2.8 Hz, 2H), 1.92 – 1.89 (m, 1H), 1.75 – 1.58 (m, 2H), 1.50 – 1.38 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  210.63, 160.95, 154.48, 153.89, 143.04, 125.48, 124.04, 117.56, 116.75, 114.10, 49.28, 42.13, 34.07, 31.35, 27.81, 25.13, 21.58; IR ( $\text{CH}_2\text{Cl}_2$ ): 1724, 1710, 1620  $\text{cm}^{-1}$ ; Calcd. HRMS for  $\text{C}_{17}\text{H}_{19}\text{O}_3$  (M+H) 271.1334; Found, 271.1324.



**4-((5-tert-butyl-2-oxocyclohexyl)methyl)-6,7-dimethyl-2H-chromen-2-one:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (d,  $J = 2.7$  Hz, 1H), 7.12 (s, 1H), 6.14 (s, 1H), 3.53 (dd,  $J = 15.1$ , 4.7 Hz, 1H), 2.69 (td,  $J = 12.7$ , 5.0 Hz, 1H), 2.59 – 2.35 (m, 3H), 2.34 (s, 3H), 2.31 (s, 3H), 2.22 – 2.11 (m, 2H), 1.64 – 1.41 (m, 2H), 1.26 (q,  $J = 12.7$  Hz, 1H), 0.89 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  211.04, 161.18, 154.48, 152.14, 141.83, 132.98, 124.38, 117.87, 116.86, 113.70, 48.16, 46.86, 41.44, 35.25, 32.51, 31.40, 28.61, 27.61, 20.17, 19.50; IR ( $\text{CH}_2\text{Cl}_2$ ): 1724, 1712, 1622  $\text{cm}^{-1}$ ; Calcd. HRMS for  $\text{C}_{22}\text{H}_{29}\text{O}_3$  (M+H), 341.2117; Found, 341.2119



**7-methoxy-4-((2-oxocyclopentyl)methyl)-2H-chromen-2-one:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 8.8$  Hz, 1H), 6.83 – 6.78 (m, 2H), 6.09 (s, 1H), 3.84 (s, 3H), 3.39 (d,  $J = 11.4$  Hz, 1H), 2.44 – 2.34 (m, 3H), 2.23 – 2.12 (m, 2H), 2.07 – 2.00 (m, 1H), 1.84 – 1.73 (m, 1H), 1.59–1.51 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  218.54, 162.71, 161.04, 155.59, 154.46, 125.31, 112.40, 112.33, 111.45, 101.14, 55.78, 48.29, 37.59, 32.10, 29.92, 20.43; IR ( $\text{CH}_2\text{Cl}_2$ ): 1724, 1612  $\text{cm}^{-1}$ ; Calcd. HRMS for  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{Na}$  ( $\text{M}+\text{Na}$ ), 295.0946; Found, 295.0928.

