Supplementary Information

Rh(III)-catalyzed C-H activation-cyclization of benzamides and diazo compounds to form isocoumarins and α-pyrones

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1. General information

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were dehydrated and distilled under nitrogen. Phenyl(pyrrolidin-1-yl)methanone and its derivitives,\(^1\) diazo compounds\(^2,3\) and \([\text{Cp}^*\text{RhCl}_2]_2\)^4 were prepared according to the literature methods. Other chemicals were purchased from Adams-beta, TCI, Alfa-Aesar, J&K and other commercial places, and were used without further purification. \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on Bruker 400 MHz Spectrometer at 298 K. Chemical shifts (\(\delta\), ppm) in the \(^1\)H NMR spectra were recorded using TMS as internal standard. Chemical shifts in \(^{13}\)C \{\(^1\)H\} NMR spectra were internally referenced to CHCl\(_3\) (\(\delta = 77.16\) ppm). Chemical shift of water in \(^1\)H NMR was found in 1.54-1.56 ppm. HRMS were obtained by EI-TOF or ESI-TOF mass spectrometer.

2. Typical procedure for the synthesis of isocoumarins and \(\alpha\)-pyrones

To a mixture of \([\text{Cp}^*\text{RhCl}_2]_2\) (4.6 mg, 0.0075 mmol, 2.5 mol\%) and AgSbF\(_6\) (10.3 mg, 0.03 mmol, 10 mol\%) in 1, 2-dichloroethane (2 mL) was added phenyl(pyrrolidin-1-yl)methanone \(1\) (0.6 mmol), diazo compounds \(2\) (0.3 mmol), HOAc (10.8 mg, 0.18 mmol, 0.6 equiv) and Ac\(_2\)O (42.9 mg, 0.42 mmol, 1.4 equiv). The reaction mixture was stirred at 60 °C for 12 hours and the progress was monitored using TLC detection. After completion of present reaction, the solvent was evaporated under reduced pressure and the residue passed through flash column chromatography on silica gel to afford the desired products \(3\).

3. Analytical data for the products

\(\text{tert-Butyl 3-methyl-1-oxo-1H-isochromene-4-carboxylate (3a).}\) The compound was prepared from phenyl(pyrrolidin-1-yl)methanone \(1\) (105.1 mg, 0.6 mmol) and
tert-butyl 2-diazo-3-oxobutanoate 2a (55.3 mg, 0.3 mmol) following the typical procedure. The product 3a was obtained in 84% yield (65 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 83.0-85.5 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.64 (s, 9H), 2.44 (s, 3H), 7.49-7.52 (m, 1H), 7.70-7.72 (m, 2H), 8.28 (d, $J = 7.8$ Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 19.1, 28.3, 83.2, 111.8, 119.7, 123.9, 128.1, 129.8, 135.0, 135.1, 156.4, 161.5, 165.1; HRMS (EI, TOF) calcd for C$_{15}$H$_{16}$O$_4$ $^+$ [M$^+$]: 260.1049, found: 260.1050.

![Image of tert-Butyl 3,6-dimethyl-1-oxo-1H-isochromene-4-carboxylate (3b).](image)

**tert-Butyl 3,6-dimethyl-1-oxo-1H-isochromene-4-carboxylate (3b).** The compound was prepared from pyrrolidin-1-yl(p-tolyl)methanone 1b (113.6 mg, 0.6 mmol) and tert-butyl 2-diazo-3-oxobutanoate 2a (55.3 mg, 0.3 mmol) following the typical procedure. The product 3b was obtained in 85% yield (70 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 113.0-114.8 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.64 (s, 9H), 2.42 (s, 3H), 2.48 (s, 3H), 7.30-7.33 (m, 1H), 7.45 (s, 1H), 8.17 (d, $J = 8.1$ Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 19.1, 22.4, 28.4, 83.1, 111.7, 117.3, 123.9, 129.5, 129.7, 135.0, 146.3, 156.3, 161.6, 165.3; HRMS (ESI, TOF) calcd for C$_{16}$H$_{19}$O$_4$ $^+$ [M+H]$^+$: 275.1283, found: 275.1287.

![Image of tert-Butyl 6-methoxy-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3c).](image)

**tert-Butyl 6-methoxy-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3c).** The compound was prepared from (4-methoxyphenyl)(pyrrolidin-1-yl)methanone 1c (123.2 mg, 0.6 mmol) and tert-butyl 2-diazo-3-oxobutanoate 2a (55.3 mg, 0.3 mmol) following the typical procedure. The product 3c was obtained in 93% yield (81 mg) as
white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 144.5-146.5 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.64 (s, 9H), 2.42 (s, 3H), 3.91 (s, 3H), 7.03 (dd, \(J_1 = 2.4\) Hz, \(J_2 = 8.8\) Hz, 1H), 7.16 (d, \(J = 2.4\) Hz, 1H), 8.20 (d, \(J = 8.8\) Hz, 1H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 19.3, 28.4, 55.7, 83.0, 106.7, 111.5, 112.7, 116.2, 132.0, 137.2, 157.4, 161.2, 164.9, 165.2; HRMS (ESI, TOF) calcd for C\(_{18}\)H\(_{19}\)O\(_5\), [M+H]\(^+\): 291.1232, found: 291.1233.

![Image of tert-Butyl 6-(dimethylamino)-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3d).](image)

**tert-Butyl 6-(dimethylamino)-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3d).** The compound was prepared from (4-(dimethylamino)phenyl)(pyrrolidin-1-yl)methanone \(1d\) (131.0 mg, 0.6 mmol) and \textit{tert}-butyl 2-diazo-3-oxobutanoate \(2a\) (55.3 mg, 0.3 mmol) following the typical procedure. The product \(3d\) was obtained in 83% yield (75 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 145.4-148.2 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.63 (s, 9H), 2.37 (s, 3H), 3.10 (s, 6H), 6.73 (d, \(J = 2.5\) Hz, 1H), 6.80 (dd, \(J_1 = 2.5\) Hz, \(J_2 = 9.0\) Hz, 1H), 8.08 (d, \(J = 9.0\) Hz, 1H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 19.1, 28.4, 40.2, 82.6, 103.5, 107.5, 111.9, 112.6, 131.5, 136.6, 154.4, 156.2, 161.9, 165.9; HRMS (ESI, TOF) calcd for C\(_{17}\)H\(_{22}\)NO\(_4\), [M+H]\(^+\): 304.1549, found: 304.1546.

![Image of tert-Butyl 6-fluoro-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3e).](image)

**tert-Butyl 6-fluoro-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3e).** The compound was prepared from (4-fluorophenyl)(pyrrolidin-1-yl)methanone \(1e\) (115.9 mg, 0.6 mmol) and \textit{tert}-butyl 2-diazo-3-oxobutanoate \(2a\) (55.3 mg, 0.3 mmol) following the typical procedure. The product \(3e\) was obtained in 83% yield (69 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v).
tert-Butyl 6-chloro-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3f). The compound was prepared from (4-chlorophenyl)(pyrrolidin-1-yl)methanone 1f (125.8 mg, 0.6 mmol) and tert-butyl 2-diazo-3-oxobutanoate 2a (55.3 mg, 0.3 mmol) following the typical procedure. The product 3f was obtained in 90% yield (79 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 115.2-117.3 °C; 1H NMR (400 MHz, CDCl₃) δ 1.64 (s, 9H), 2.46 (s, 3H), 7.46 (dd, J₁ = 2.0 Hz, J₂ = 8.5 Hz, 1H), 7.79 (d, J = 1.9 Hz 1H), 8.21 (d, J = 8.5 Hz, 1H); 13C NMR (100.6 MHz, CDCl₃) δ 19.5, 28.4, 83.5, 110.7, 118.0, 124.1, 128.6, 131.3, 136.4, 142.0, 158.5, 160.6, 164.5; HRMS (ESI, TOF) calcd for C₁₅H₁₆O₄Cl, [M+H⁺]: 295.0737, found: 295.0742.

tert-Butyl 6-bromo-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3g). The compound was prepared from (4-bromophenyl)(pyrrolidin-1-yl)methanone 1g (152.5 mg, 0.6 mmol) and tert-butyl 2-diazo-3-oxobutanoate 2a (55.3 mg, 0.3 mmol) following the typical procedure. The product 3g was obtained in 78% yield (79 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 137.3-139.5 °C; 1H NMR (400 MHz, CDCl₃) δ 1.64 (s, 9H), 2.46 (s, 3H), 7.19 (td, J₁ = 2.4 Hz, J₂ = 8.4 Hz, 1H), 7.48 (dd, J₁ = 2.4 Hz, J₂ = 10.4 Hz, 1H), 8.30 (dd, J₁ = 5.8 Hz, J₂ = 8.8 Hz, 1H); 13C NMR (100.6 MHz, CDCl₃) δ 19.5, 28.3, 83.5, 110.5 (d, J = 25.0 Hz), 111.0 (d, J = 2.8 Hz), 116.1 (d, J = 23.4 Hz), 133.0 (d, J = 10.4 Hz), 137.8 (d, J = 11.1 Hz), 158.7, 160.5, 164.6, 165.7, 168.2; HRMS (ESI, TOF) calcd for C₁₅H₁₆O₄F, [M+H⁺]: 279.1033, found: 279.1031.
v/v). Mp: 114.2-115.9 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.64 (s, 9H), 2.46 (s, 3H), 7.62 (dd, \( J_1 = 1.8 \) Hz, \( J_2 = 8.5 \) Hz, 1H), 7.97 (d, \( J = 1.8 \) Hz 1H), 8.12 (d, \( J = 8.4 \) Hz, 1H); \( ^13C \) NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 19.5, 28.4, 83.6, 110.6, 118.3, 127.2, 130.9, 131.2, 131.5, 136.4, 158.5, 160.8, 164.5; HRMS (EI, TOF) calcd for C\(_{15}\)H\(_{15}\)O\(_4\)Br\(^+\) [M]+: 340.0133, found: 340.0136.

**tert-Butyl 3-methyl-1-oxo-6-(trifluoromethyl)-1\(H\)-isochromene-4-carboxylate (3h).** The compound was prepared from pyrrolidin-1-yl(4-(trifluoromethyl)phenyl)methanone \( 1h \) (145.9 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate \( 2a \) (55.3 mg, 0.3 mmol) following the typical procedure. The product 3h was obtained in 64% yield (63 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 111.4-113.5 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.65 (s, 9H), 2.50 (s, 3H), 7.72 (d, \( J = 8.3 \) Hz, 1H), 8.12 (s, 1H), 8.40 (d, \( J = 8.3 \) Hz, 1H); \( ^13C \) NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 19.5, 28.4, 83.8, 111.1, 121.7 (q, \( J = 4.1 \) Hz), 122.1, 123.4 (q, \( J = 273.1 \) Hz), 124.4 (q, \( J = 3.5 \) Hz), 130.7, 135.5, 136.4 (q, \( J = 32.8 \) Hz), 159.1, 160.3, 164.4; HRMS (ESI, TOF) calcd for C\(_{16}\)H\(_{16}\)O\(_3\)F\(_3\), [M+H]+: 329.1001, found: 329.1006.

**tert-Butyl 3-methyl-6-nitro-1-oxo-1\(H\)-isochromene-4-carboxylate (3i).** The compound was prepared from (4-nitrophenyl)(pyrrolidin-1-yl)methanone \( 1i \) (132.1 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate \( 2a \) (55.3 mg, 0.3 mmol) following the typical procedure. The product 3i was obtained in 63% yield (58 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 149.9-153.3°C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.68 (s, 9H), 2.53 (s, 3H),
8.27 (dd, $J_1 = 2.1$ Hz, $J_2 = 8.7$ Hz, 1H), 8.77 (d, $J = 2.1$ Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 19.7, 28.4, 84.2, 110.9, 120.1, 122.0, 123.6, 131.6, 136.4, 151.8, 159.7, 160.3, 164.0; HRMS (EI, TOF) calcd for C$_{15}$H$_{15}$NO$_6$ $^+ [M]^+$: 305.0899, found: 305.0892.

**tert-Butyl 3,8-dimethyl-1-oxo-1H-isochromene-4-carboxylate (3j).** The compound was prepared from pyrrolidin-1-yl(o-tolyl)methanone 1j (113.6 mg, 0.6 mmol) and tert-butyl 2-diazo-3-oxobutanoate 2a (55.3 mg, 0.3 mmol) following the typical procedure. The product 3j was obtained in 80% yield (66 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 105.0-107.1 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.63 (s, 9H), 2.42 (s, 3H), 2.46 (s, 3H), 7.55 (dd, $J_1 = 1.6$ Hz, $J_2 = 8.3$ Hz, 1H), 7.62 (d, $J = 8.3$ Hz 1H), 8.09 (s, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 19.0, 21.3, 28.4, 83.1, 111.7, 119.6, 123.9, 129.5, 132.5, 136.4, 138.4, 155.6, 161.8, 165.3; HRMS (ESI, TOF) calcd for C$_{16}$H$_{19}$O$_4$, [M+H]$^+$: 275.1283, found: 275.1287.

**tert-Butyl 7-fluoro-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3k).** The compound was prepared from (3-fluorophenyl)(pyrrolidin-1-yl)methanone 1k (115.9 mg, 0.6 mmol) and tert-butyl 2-diazo-3-oxobutanoate 2a (55.3 mg, 0.3 mmol) following the typical procedure. The product 3k was obtained in 68% yield (57 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 87.2-89.0 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.60 (s, 9H), 2.34 (s, 3H), 7.41-7.50 (m, 2H), 8.09-8.12 (m, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 17.8, 27.9,
83.3, 108.6, 121.6 (d, \( J = 21.2 \) Hz), 121.6 (d, \( J = 3.8 \) Hz), 123.7 (d, \( J = 14.0 \) Hz), 125.9 (d, \( J = 3.7 \) Hz), 129.0 (d, \( J = 8.2 \) Hz), 154.0, 155.1, 157.6, 160.4 (J = 3.5 Hz), 165.4; HRMS (ESI, TOF) calcd for C\(_{15}\)H\(_{16}\)O\(_4\)F, [M+H]\(^{+}\): 279.1033, found: 279.1034.

**tert-Butyl 6,7-dichloro-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3l).** The compound was prepared from (3,4-dichlorophenyl)(pyrrolidin-1-yl)methanone \( \text{1l} \) (146.5 mg, 0.6 mmol) and tert-butyl 2-diazo-3-oxobutanoate \( \text{2a} \) (55.3 mg, 0.3 mmol) following the typical procedure. The product \( \text{3l} \) was obtained in 22% yield (22 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 10:1 v/v). Mp: 134.9-137.8 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.64 (s, 9H), 2.47 (s, 3H), 7.97 (s, 1H), 8.33 (s, 1H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 19.7, 28.4, 83.8, 110.1, 119.2, 126.4, 131.1, 132.7, 134.4, 140.4, 159.1, 159.7, 164.2; HRMS (ESI, TOF) calcd for C\(_{15}\)H\(_{15}\)O\(_4\)Cl\(_2\), [M+H]\(^{+}\): 329.0347, found: 329.0347.

**tert-Butyl 3-methyl-1-oxo-1H-benzo[g]isochromene-4-carboxylate (3m).** The compound was prepared from naphthalen-2-yl(pyrrolidin-1-yl)methanone \( \text{1m} \) (135.2 mg, 0.6 mmol) and tert-butyl 2-diazo-3-oxobutanoate \( \text{2a} \) (55.3 mg, 0.3 mmol) following the typical procedure. The product \( \text{3m} \) was obtained in 78% yield (73 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 140.3-142.7 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.69 (s, 9H), 2.46 (s, 3H), 7.54-7.58 (m, 1H), 7.63-7.67 (m, 1H), 7.93 (d, \( J = 8.3 \) Hz, 1H), 8.01 (d, \( J = 8.2 \) Hz, 1H), 8.14 (s, 1H), 8.92 (s, 1H); \(^13\)C NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 19.1, 28.4, 83.1, 111.6, 118.0, 122.8, 127.0, 128.4, 129.5, 129.6, 132.0, 132.1, 136.6, 154.8.
tert-Butyl 5-methyl-7-oxo-7H-thieno[2,3-c]pyran-4-carboxylate (3n). The compound was prepared from pyrrolidin-1-yl(thiophen-2-yl)methanone 1n (108.8 mg, 0.6 mmol) and tert-butyl 2-diazo-3-oxobutanoate 2a (55.3 mg, 0.3 mmol) following the typical procedure. The product 3n was obtained in 64% yield (51 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 107.0-108.8 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.63 (s, 9H), 2.42 (s, 3H), 7.70 (d, $J$ = 5.2 Hz, 1H), 7.83 (d, $J$ = 5.2 Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 20.0, 28.4, 83.0, 109.7, 122.3, 126.1, 136.6, 145.7, 157.3, 163.4, 164.1; HRMS (ESI, TOF) calcd for C$_{13}$H$_{15}$O$_4$S, [M+H]$^+$: 267.0691, found: 267.0691.

Ethyl 3-methyl-1-oxo-1H-isochromene-4-carboxylate (3o). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone 1a (105.1 mg, 0.6 mmol) and ethyl 2-diazo-3-oxobutanoate 2b (46.8 mg, 0.3 mmol) following the typical procedure. The product 3o was obtained in 75% yield (52 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). $^1$H NMR (400 MHz, CDCl$_3$) δ 1.45 (d, $J$ = 7.1 Hz, 3H), 2.46 (s, 3H), 4.46 (d, $J$ = 7.1 Hz, 2H), 7.50-7.54 (m, 1H), 7.72-7.78 (m, 2H), 8.28-8.30 (m, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 14.3, 19.4, 61.8, 110.4, 119.6, 124.2, 128.3, 129.8, 134.7, 135.2, 157.8, 161.3, 165.9; HRMS (ESI, TOF) calcd for C$_{13}$H$_{13}$O$_4$, [M+H]$^+$: 233.0814, found: 233.0813.
**Ethyl 1-oxo-3-propyl-1H-isochromene-4-carboxylate (3p).** The compound was prepared from phenyl(pyrrolidin-1-yl)methanone 1a (105.1 mg, 0.6 mmol) and ethyl 2-diazo-3-oxohexanoate 2c (55.3 mg, 0.3 mmol) following the typical procedure. The product 3p was obtained in 81% yield (63 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). $^1$H NMR (400 MHz, CDCl$_3$) δ 1.00 (t, $J$ = 7.4 Hz, 3H), 1.43 (t, $J$ = 7.2 Hz, 3H), 1.76-1.85 (m, 2H), 2.66-2.70 (m, 2H), 4.45 (d, $J$ = 7.2 Hz, 2H), 7.50-7.54 (m, 1H), 7.68-7.76 (m, 2H), 8.21-8.31 (m, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 13.8, 14.3, 21.2, 34.6, 61.8, 110.5, 119.7, 124.2, 128.3, 129.8, 134.7, 135.2, 160.4, 161.5, 166.0; HRMS (EI, TOF) calcd for C$_{15}$H$_{16}$O$_4^+$ [M$^+$]: 260.1049, found: 260.1050.

**Ethyl 3-(chloromethyl)-1-oxo-1H-isochromene-4-carboxylate (3q).** The compound was prepared from phenyl(pyrrolidin-1-yl)methanone 1a (105.1 mg, 0.6 mmol) and ethyl 4-chloro-2-diazo-3-oxobutanoate 2d (57.2 mg, 0.3 mmol) following the typical procedure. The product 3q was obtained in 34% yield (21 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 55.6-58.1 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.47 (t, $J$ = 7.2 Hz, 3H), 4.51 (q, $J$ = 7.2 Hz, 2H), 4.59 (s, 2H), 7.59-7.63 (m, 1H), 7.77-7.86 (m, 2H), 8.33-8.35 (m, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 14.3, 40.3, 62.6, 112.6, 120.6, 125.3, 129.7, 130.1, 133.7, 135.4, 154.0, 160.3, 164.6; HRMS (ESI, TOF) calcd for C$_{13}$H$_{12}$O$_4$Cl, [M+H]$^+$: 267.0424, found: 267.0423.
Ethyl 3-isopropyl-1-oxo-1H-isochromene-4-carboxylate (3r). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone 1a (105.1 mg, 0.6 mmol) and ethyl 2-diazo-4-methyl-3-oxopentanoate 2e (55.3 mg, 0.3 mmol) following the typical procedure. The product 3r was obtained in 83% yield (65 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.32 (s, 3H), 1.33 (s, 3H), 1.43 (t, $J = 7.2$ Hz, 3H), 3.09-3.19 (m, 1H), 4.45 (q, $J = 7.1$ Hz, 2H), 7.49-7.53 (m, 1H), 7.59-7.61 (m, 1H), 7.71-7.75 (m, 1H), 8.29-8.31 (m, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 14.3, 20.2, 31.6, 61.9, 109.2, 119.8, 124.0, 128.2, 129.8, 134.8, 135.1, 161.5, 163.2, 166.1; HRMS (ESI, TOF) calcd for C$_{15}$H$_{17}$O$_4$, [M+H]$^+$: 261.1127, found: 261.1122.

Ethyl 3-cyclopropyl-1-oxo-1H-isochromene-4-carboxylate (3s). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone 1a (105.1 mg, 0.6 mmol) and ethyl 3-cyclopropyl-2-diazo-3-oxopropanoate 2f (54.7 mg, 0.3 mmol) following the typical procedure. The product 3s was obtained in 74% yield (57 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.00-1.05 (m, 2H), 1.26-1.30 (m, 2H), 1.44 (t, $J = 7.2$ Hz, 3H), 2.26-2.33 (m, 1H), 4.48 (q, $J = 7.1$ Hz, 2H), 7.44-7.48 (m, 1H), 7.67-7.74 (m, 2H), 8.23-8.26 (m, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 8.6, 12.6, 14.4, 61.8, 109.5, 119.2, 123.7, 127.7, 129.7, 135.1, 135.2, 160.4, 160.9, 166.3; HRMS (ESI, TOF) calcd for C$_{15}$H$_{15}$O$_4$, [M+H]$^+$: 259.0970, found: 259.0978.
**Ethyl 1-oxo-3-phenyl-1H-isochromene-4-carboxylate (3t).** The compound was prepared from phenyl(pyrrolidin-1-yl)methanone 1a (105.1 mg, 0.6 mmol) and ethyl 2-diazo-3-oxo-3-phenylpropanoate 2g (65.5 mg, 0.3 mmol) following the typical procedure. The product 3t was obtained in 85% yield (75 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 85.0-88.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.05 (t, $J$ = 7.1 Hz, 3H), 4.20 (q, $J$ = 7.2 Hz, 3H), 7.43-7.49 (m, 3H), 7.56-7.61 (m, 1H), 7.64-7.66 (m, 2H), 7.74-7.82 (m, 2H), 8.36-8.38 (m, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 13.7, 62.0, 111.1, 119.9, 124.3, 128.3, 128.6, 128.9, 130.0, 130.7, 132.7, 134.8, 135.4, 155.5, 161.2, 166.4; HRMS (ESI, TOF) calcd for C$_{18}$H$_{15}$O$_4$, [M+H]$^+$: 295.0970, found: 295.0966.

**Ethyl 3-(2,6-dichloro-5-fluoropyridin-3-yl)-1-oxo-1H-isochromene-4-carboxylate (3u).** The compound was prepared from phenyl(pyrrolidin-1-yl)methanone 1a (105.1 mg, 0.6 mmol) and ethyl 2-diazo-3-(2,6-dichloro-5-fluoropyridin-3-yl)-3-oxopropanoate 2h (92.0 mg, 0.3 mmol) following the typical procedure. The product 3u was obtained in 94% yield (108 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 95.8-97.6 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.08 (t, $J$ = 7.1 Hz, 3H), 4.22 (q, $J$ = 7.2 Hz, 3H), 7.67-7.71 (m, 2H), 7.85-7.89 (m, 1H), 8.14-8.36 (m, 1H), 8.39-8.41 (m, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 13.8, 62.2, 113.5, 120.4, 125.7, 127.9 (d, $J$ = 21.8 Hz), 129.7 (d, $J$ = 3.1 Hz), 130.1 (d, $J$ = 7.4 Hz), 133.4, 135.7, 139.1 (d, $J$ = 21.1 Hz), 143.2 (d, $J$ = 3.6 Hz), 151.2, 152.4, 155.0, 160.0, 163.9; HRMS (ESI, TOF) calcd for C$_{17}$H$_{11}$O$_4$NFCl$_2$,
4-Benzoyl-3-phenyl-1H-isochromen-1-one (3v). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone 1a (105.1 mg, 0.6 mmol) and 2-diazo-1,3-diphenylpropane-1,3-dione 2i (49.9 mg, 0.3 mmol) following the typical procedure. The product 3v was obtained in 38% yield (37 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 136.2-139.1 °C. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.23-7.29 (m, 3H), 7.33 (t, \( J = 8.0 \) Hz, 2H), 7.38 (d, \( J = 8.0 \) Hz, 1H), 7.46-7.50 (m, 1H), 7.56-7.59 (m, 3H), 7.67-7.71 (m, 1H), 7.84-7.86 (m, 1H); \( ^{13} \)C NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 115.7, 120.2, 124.6, 128.6, 128.7, 128.9, 129.0, 129.7, 130.1, 130.6, 132.0, 134.3, 135.4, 136.0, 137.0, 153.0, 161.6, 194.9; HRMS (EI, TOF) calcd for C\(_{22}\)H\(_{14}\)O\(_3\)\(^+\) [M]\(^+\): 326.0943, found: 326.0944.

3,3-Dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (3w). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone 1a (105.1 mg, 0.6 mmol) and 2-diazo-5,5-dimethylcyclohexane-1,3-dione 2j (49.9 mg, 0.3 mmol) following the typical procedure. The product 3w was obtained in 93% yield (80 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 143.2-144.9 °C. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.18 (s, 6H), 2.53 (s, 2H), 2.81 (s, 2H), 7.52-7.56 (m, 1H), 7.78-7.82 (m, 1H), 8.29 (dd, \( J_1 = 1.5 \) Hz, \( J_2 = 8.0 \) Hz, 1H), 9.05 (d, \( J = 8.4 \) Hz, 1H); \( ^{13} \)C NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 28.2, 32.1, 42.6, 52.9, 110.7, 119.9, 125.9, 128.5, 129.7, 133.9, 135.7, 160.8, 168.1, 197.0;

**tert-Butyl-3,6-dimethyl-2-oxo-2H-pyran-5-carboxylate (4a).** The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one 1o (83.5 mg, 0.6 mmol) and tert-butyl 2-diazo-3-oxobutanoate 2a (55.3 mg, 0.3 mmol) following the typical procedure. The product 4a was obtained in 76% yield (51 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). $^1$H NMR (400 MHz, CDCl$_3$) δ 1.56 (s, 9H), 2.10 (s, 3H), 2.60 (s, 3H), 7.55 (d, $J$ = 0.9 Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 16.3, 20.1, 28.3, 82.4, 110.6, 121.6, 140.3, 162.7, 163.5, 167.2; HRMS (ESI, TOF) calcd for C$_{12}$H$_{16}$O$_4$Na, [M+Na]$^+$: 247.0946, found: 247.0949.

Ethyl-3,6-dimethyl-2-oxo-2H-pyran-5-carboxylate (4b). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one 1o (83.5 mg, 0.6 mmol) and ethyl 2-diazo-3-oxobutanoate 2b (46.8 mg, 0.3 mmol) following the typical procedure. The product 4b was obtained in 68% yield (40 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 45.7-47.8 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.37 (t, $J$ = 7.2 Hz, 3H), 2.11 (s, 3H), 2.63 (s, 3H), 4.32 (q, $J$ = 7.1 Hz, 2H), 7.62 (d, $J$ = 1.0 Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ 14.4, 16.4, 20.1, 61.4, 109.3, 121.8, 139.8, 162.5, 164.4, 168.0; HRMS (EI, TOF) calcd for C$_{10}$H$_{12}$O$_4$, [M]$^+$: 196.0736, found: 196.0737.
Ethyl-3-methyl-6-propyl-2-oxo-2H-pyran-5-carboxylate (4c). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one \(1o\) (83.5 mg, 0.6 mmol) and ethyl ethyl 2-diazo-3-oxohexanoate \(2c\) (55.3 mg, 0.3 mmol) following the typical procedure. The product \(4c\) was obtained in 82% yield (55 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 30.2-31.9 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.99 (t, \(J = 7.1\) Hz, 3H), 1.37 (t, \(J = 7.2\) Hz, 3H), 1.69-1.79 (m, 2H), 2.10 (s, 3H), 2.94-2.98 (m, 2H), 4.32 (q, \(J = 7.1\) Hz, 2H), 7.61 (d, \(J = 1.1\) Hz, 1H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 13.9, 14.3, 16.4, 21.4, 34.7, 61.4, 109.1, 121.9, 139.9, 162.6, 164.3, 171.5; HRMS (EI, TOF) calcd for C\(_{12}\)H\(_{16}\)O\(_4\), [M]\(^+\): 224.1049, found: 224.1048.

Ethyl-6-isopropyl-3-methyl-2-oxo-2H-pyran-5-carboxylate (4d). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one \(1o\) (83.5 mg, 0.6 mmol) and ethyl 2-diazo-4-methyl-3-oxopentanoate \(2e\) (55.3 mg, 0.3 mmol) following the typical procedure. The product \(4d\) was obtained in 73% yield (49 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 71.6-73.8 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.26 (s, 3H), 1.27 (s, 3H), 1.37 (t, \(J = 7.2\) Hz, 3H), 2.10 (d, \(J = 1.2\) Hz, 3H), 3.92-4.02 (m, 2H), 4.31 (q, \(J = 7.2\) Hz, 2H), 7.59 (d, \(J = 1.2\) Hz, 1H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 14.3, 16.4, 20.1, 30.4, 61.4, 107.8, 121.7, 140.1, 162.5, 164.4, 175.0; HRMS (EI, TOF) calcd for C\(_{12}\)H\(_{16}\)O\(_4\), [M]\(^+\): 224.1049, found: 224.1052.
Ethyl-3-methyl-2-oxo-6-phenyl-2H-pyran-5-carboxylate (4e). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one 1o (83.5 mg, 0.6 mmol) and ethyl 2-diazo-3-oxo-3-phenylpropanoate 2g (65.5 mg, 0.3 mmol) following the typical procedure. The product 4e was obtained in 61% yield (47 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.08 (t, $J$ = 7.2 Hz, 3H), 2.18 (d, $J$ = 1.2 Hz, 3H), 4.14 (q, $J$ = 7.1 Hz, 2H), 7.40-7.53 (m, 5H), 7.64 (d, $J$ = 1.2 Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 13.8, 16.6, 61.6, 110.0, 123.3, 128.1, 129.1, 130.9, 132.4, 140.1, 162.2, 164.4, 165.1; HRMS (EI, TOF) calcd for C$_{15}$H$_{14}$O$_4$, [M$^+$]: 258.0892, found: 258.0893.

Ethyl-6-(2,6-dichloro-5-fluoropyridin-3-yl)-3-methyl-2-oxo-2H-pyran-5-carboxylate (4f). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one 1o (83.5 mg, 0.6 mmol) and ethyl 2-diazo-3-(2,6-dichloro-5-fluoropyridin-3-yl)-3-oxopropanoate 2h (92.0 mg, 0.3 mmol) following the typical procedure. The product 4f was obtained in 86% yield (89 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 10:1 v/v). Mp: 116.2-118.5 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.15 (t, $J$ = 7.1 Hz, 3H), 2.22 (d, $J$ = 1.2 Hz, 3H), 4.19 (q, $J$ = 7.1 Hz, 2H), 7.59 (d, $J$ = 7.1 Hz, 1H), 7.73 (d, $J$ = 1.2 Hz, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ 13.9, 16.6, 62.2, 112.4, 126.0, 127.5 (d, $J$ = 21.9 Hz), 129.2 (d, $J$ = 3.5 Hz), 138.6, 139.2 (d, $J$ = 20.8 Hz), 142.9 (d, $J$ = 3.7 Hz), 152.4, 155.0, 157.4, 160.9, 162.7; HRMS (EI, TOF) calcd for C$_{14}$H$_{10}$O$_4$ClNF, [M-Cl$^+$]: 310.0277, found: 310.0277.
3,7,7-Trimethyl-7,8-dihydro-2H-chromene-2,5(6H)-dione (4g). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one 1o (83.5 mg, 0.6 mmol) and 2-diazo-1,3-diphenylpropane-1,3-dione 2i (49.9 mg, 0.3 mmol) following the typical procedure. The product 4g was obtained in 87% yield (54 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 109.3-111.6 °C; 1H NMR (400 MHz, CDCl3) δ 1.14 (s, 6H), 2.12 (s, 3H), 2.40 (s, 2H), 2.70 (s, 2H), 7.62 (d, J = 1.0 Hz, 1H); 13C NMR (100.6 MHz, CDCl3) δ 16.7, 28.4, 32.8, 41.5, 50.6, 113.7, 123.4, 135.2, 162.2, 170.6, 194.2; HRMS (EI, TOF) calcd for C12H14O3, [M]+: 206.0943, found: 206.0946.

4. Compete experiments and mechanistic studies

Kinetic isotope effect experiment

To a mixture of [Cp*RhCl2]2 (4.6 mg, 0.0075 mmol, 2.5 mol%) and AgSbF6 (10.3 mg, 0.03 mmol, 10 mol%) in 1, 2-dichloroethane (2 mL) was added 1a (105.1 mg, 0.6 mmol), 1a-d5 (108.2 mg, 0.6 mmol) and tert-butyl 2-diazo-3-oxobutanoate 2a (55.3 mg, 0.3 mmol), HOAc (10.8 mg, 0.18 mmol, 0.6 equiv) and Ac2O (42.9 mg, 0.42 mmol, 1.4 equiv). The reaction mixture was stirred at 60 °C for 30 min. After cooling to ambient temperature by the ice-water bath, the solvent was evaporated under reduced pressure and the residue passed through flash column chromatography on silica gel to afford the mixture of products 3a and 3a-d4 with 13.0 mg (16 % yield).
Parallel reactions using 1a and 1a-d₅ under the optimal conditions for 30 min

1a + \(\text{2a}^{\text{D}}\) & \[\text{[Cp*RhCl₂]}_2 \text{(2.5 mol\%)}\] & \[\text{AgSbF₆ (10 mol\%)}\] & \[\text{(Ac}_2\text{O, AcOH)}\] & \[\text{DCE, 60 °C, 30 min}\] & \(\text{3a}^{\text{D}}: 15.4\%\) \\
1a-d₅ + \(\text{2a}^{\text{D}}\) & \[\text{[Cp*RhCl₂]}_2 \text{(2.5 mol\%)}\] & \[\text{AgSbF₆ (10 mol\%)}\] & \[\text{(Ac}_2\text{O, AcOH)}\] & \[\text{DCE, 60 °C, 30 min}\] & \(\text{3a-d₅}^{\text{D}}: 5.7\%\)

To a mixture of [Cp*RhCl₂]₂ (4.6 mg, 0.0075 mmol, 2.5 mol%) and AgSbF₆ (10.3 mg, 0.03 mmol, 10 mol%) in 1, 2-dichloroethane (2 mL) was added 1a (105.1 mg, 0.6 mmol) or 1a-d₅ (108.2 mg, 0.6 mmol) and \text{t}\text{e}r\text{t}-\text{b}ut\text{y}l 2-diaz\text{o}-3-oxobutanoate 2a (55.3 mg, 0.3 mmol), HOAc (10.8 mg, 0.18 mmol, 0.6 equiv) and Ac₂O (42.9 mg, 0.42 mmol, 1.4 equiv). The reaction mixture was stirred at 60 °C for 30 min. After cooling to ambient temperature by the ice-water bath, the solvent was evaporated under reduced pressure and the residue passed through flash column chromatography on silica gel to afford the product 3a (4.5 mg, 5.7%) or 3a-d₄ (12.0 mg, 15.4%).
Reaction of 1a and diethyl 2-diazomalonate under standard conditions

To a mixture of [Cp*RhCl₂]₂ (4.6 mg, 0.0075 mmol, 2.5 mol%) and AgSbF₆ (10.3 mg, 0.03 mmol, 10 mol%) in 1, 2-dichloroethane (2 mL) was added 1a (105.1 mg, 0.6 mmol) and diethyl 2-diazomalonate (55.9 mg, 0.3 mmol), HOAc (10.8 mg, 0.18 mmol, 0.6 equiv) and Ac₂O (42.9 mg, 0.42 mmol, 1.4 equiv). The reaction mixture was stirred at 60 °C and the progress was monitored using TLC detection.

5. Crystal data and structure refinement of product 3a

Table 1. Crystal data and structure refinement for 3a.

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F(000) 276
Crystal size 0.211 x 0.156 x 0.112 mm³
Theta range for data collection 1.945 to 25.998°.
Index ranges -10<=h<=9, -10<=k<=7, -13<=l<=12
Reflections collected 4021
Independent reflections 2687 [R(int) = 0.0238]
Completeness to theta = 25.242° 99.2 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7457 and 0.6689
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 2687 / 0 / 176
Goodness-of-fit on F² 0.898
Final R indices [I>2sigma(I)] R1 = 0.0468, wR2 = 0.1120
R indices (all data) R1 = 0.1073, wR2 = 0.1336
Extinction coefficient n/a
Largest diff. peak and hole 0.127 and -0.116 e.Å⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for 3a. U(eq) is defined as one third of the trace of the orthogonalized Uᵢⱼ tensor.

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Table 3. Bond lengths [Å] and angles [°] for 3a.

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O(1)-C(1)-O(2) 116.3(2)
O(1)-C(1)-C(2) 126.1(3)
O(2)-C(1)-C(2) 117.6(2)
C(3)-C(2)-C(7) 121.1(2)
C(3)-C(2)-C(1) 118.8(2)
C(7)-C(2)-C(1) 120.1(2)
C(4)-C(3)-C(2) 120.4(2)
C(4)-C(3)-H(3) 119.8
C(2)-C(3)-H(3) 119.8
C(3)-C(4)-C(5) 120.2(3)
C(3)-C(4)-H(4) 119.9
C(5)-C(4)-H(4) 119.9
C(4)-C(5)-C(6) 120.6(2)
C(4)-C(5)-H(5) 119.7
C(6)-C(5)-H(5) 119.7
C(5)-C(6)-C(7) 121.2(2)
C(5)-C(6)-H(6) 119.4
C(7)-C(6)-H(6) 119.4
C(2)-C(7)-C(6) 116.5(2)
C(2)-C(7)-C(8) 118.0(2)
C(6)-C(7)-C(8) 125.4(2)
C(9)-C(8)-C(7) 120.3(2)
C(9)-C(8)-C(11) 121.2(2)
C(7)-C(8)-C(11) 118.5(2)
C(8)-C(9)-O(2) 121.5(2)
C(8)-C(9)-C(10) 129.7(2)
O(2)-C(9)-C(10) 108.7(2)
C(9)-C(10)-H(10A) 109.5
C(9)-C(10)-H(10B) 109.5
H(10A)-C(10)-H(10B) 109.5
C(9)-C(10)-H(10C) 109.5
O(3)-C(11)-O(4) 125.1(2)
O(3)-C(11)-C(8) 124.1(2)
O(4)-C(11)-C(8) 110.7(2)
O(4)-C(12)-C(14) 109.91(18)
O(4)-C(12)-C(15) 102.06(19)
C(14)-C(12)-C(15) 111.5(2)
O(4)-C(12)-C(13) 109.19(18)
C(14)-C(12)-C(13) 113.1(2)
C(15)-C(12)-C(13) 110.5(2)
C(12)-C(13)-H(13A) 109.5
C(12)-C(13)-H(13B) 109.5
H(13A)-C(13)-H(13B) 109.5
C(12)-C(13)-H(13C) 109.5
H(13A)-C(13)-H(13C) 109.5
H(13B)-C(13)-H(13C) 109.5
C(12)-C(14)-H(14A) 109.5
C(12)-C(14)-H(14B) 109.5
H(14A)-C(14)-H(14B) 109.5
C(12)-C(14)-H(14C) 109.5
H(14A)-C(14)-H(14C) 109.5
H(14B)-C(14)-H(14C) 109.5
C(12)-C(15)-H(15A)  109.5
C(12)-C(15)-H(15B)  109.5
H(15A)-C(15)-H(15B)  109.5
C(12)-C(15)-H(15C)  109.5
H(15A)-C(15)-H(15C)  109.5
H(15B)-C(15)-H(15C)  109.5

Symmetry transformations used to generate equivalent atoms:

6. References
7. Copies of $^1$H NMR, $^{13}$C NMR for the products

$^1$H NMR spectra of tert-Butyl 3-methyl-1-oxo-$^1$H-isochromene-4-carboxylate (3a).

$^{13}$C NMR spectra of tert-Butyl 3-methyl-1-oxo-$^1$H-isochromene-4-carboxylate (3a).
$^1$H NMR spectra of tert-Butyl 3,6-dimethyl-1-oxo-$^1$H-isochromene-4-carboxylate (3b).

$^{13}$C NMR spectra of tert-Butyl 3,6-dimethyl-1-oxo-$^1$H-isochromene-4-carboxylate (3b).
$^1$H NMR spectra of tert-Butyl 6-methoxy-3-methyl-1-oxo-$^1$H-isochromene-4-carboxylate (3c).

$^{13}$C NMR spectra of tert-Butyl 6-methoxy-3-methyl-1-oxo-$^1$H-isochromene-4-carboxylate (3c).
$^1$H NMR spectra of tert-Butyl 6-(dimethylamino)-3-methyl-1-oxo-$^1$H-isochromene-4-carboxylate (3d).

$^{13}$C NMR spectra of tert-Butyl 6-(dimethylamino)-3-methyl-1-oxo-$^1$H-isochromene-4-carboxylate (3d).
$^1$H NMR spectra of *tert*-Butyl 6-fluoro-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3e).

$^{13}$C NMR spectra of *tert*-Butyl 6-fluoro-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3e).
$^1$H NMR spectra of tert-Butyl 6-chloro-3-methyl-1-oxo-$^1$H-isochromene-4-carboxylate (3f).

$^{13}$C NMR spectra of tert-Butyl 6-chloro-3-methyl-1-oxo-$^1$H-isochromene-4-carboxylate (3f).
$^1$H NMR spectra of tert-Butyl 6-bromo-3-methyl-1-oxo-$^1$H-isochromene-4-carboxylate (3g).

$^{13}$C NMR spectra of tert-Butyl 6-bromo-3-methyl-1-oxo-$^1$H-isochromene-4-carboxylate (3g).
$^1$H NMR spectra of tert-Butyl 3-methyl-1-oxo-6-(trifluoromethyl)-1H-isochromene-4-carboxylate (3h).

$^{13}$C NMR spectra of tert-Butyl 3-methyl-1-oxo-6-(trifluoromethyl)-1H-isochromene-4-carboxylate (3h).
$^1$H NMR spectra of tert-Butyl 3-methyl-6-nitro-1-oxo-$^1$H-isochromene-4-carboxylate (3i).

$^{13}$C NMR spectra of tert-Butyl 3-methyl-6-nitro-1-oxo-$^1$H-isochromene-4-carboxylate (3i).
$^1$H NMR spectra of tert-Butyl 3,8-dimethyl-1-oxo-$1H$-isochromene-4-carboxylate (3j).

[Diagram of tert-Butyl 3,8-dimethyl-1-oxo-$1H$-isochromene-4-carboxylate]

$^{13}$C NMR spectra of tert-Butyl 3,8-dimethyl-1-oxo-$1H$-isochromene-4-carboxylate (3j).

[Diagram of tert-Butyl 3,8-dimethyl-1-oxo-$1H$-isochromene-4-carboxylate]
$^{1}$H NMR spectra of tert-Butyl 7-fluoro-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3k).

$^{13}$C NMR spectra of tert-Butyl 7-fluoro-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3k).
$^1$H NMR spectra of tert-Butyl 6,7-dichloro-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3l).

$^{13}$C NMR spectra of tert-Butyl 6,7-dichloro-3-methyl-1-oxo-1H-isochromene-4-carboxylate (3l).

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$^1$H NMR spectra of tert-Butyl 3-methyl-1-oxo-1$H$-benzo[g]isochromene-4-carboxylate (3m).

$^{13}$C NMR spectra of tert-Butyl 3-methyl-1-oxo-1$H$-benzo[g]isochromene-4-carboxylate (3m).
$^1$H NMR spectra of tert-Butyl 5-methyl-7-oxo-7$H$-thieno[2,3-c]pyran-4-carboxylate (3n).

$^{13}$C NMR spectra of tert-Butyl 5-methyl-7-oxo-7$H$-thieno[2,3-c]pyran-4-carboxylate (3n).
$^1\text{H NMR spectra of Ethyl 3-methyl-1-oxo-1H-isochromene-4-carboxylate (3o).}$

$^{13}\text{C NMR spectra of Ethyl 3-methyl-1-oxo-1H-isochromene-4-carboxylate (3o).}$
$^1$H NMR spectra of Ethyl 1-oxo-3-propyl-$^1$H-isochromene-4-carboxylate (3p).

$^{13}$C NMR spectra of Ethyl 1-oxo-3-propyl-$^1$H-isochromene-4-carboxylate (3p).
$^1$H NMR spectra of Ethyl 3-(chloromethyl)-1-oxo-1H-isochromene-4-carboxylate (3q).

$^{13}$C NMR spectra of Ethyl 3-(chloromethyl)-1-oxo-1H-isochromene-4-carboxylate (3q).
\[ ^1H \text{ NMR spectra of Ethyl-3-isopropyl-1-oxo-1H-isochromene-4-carboxylate (3r).} \]

\[ ^{13}C \text{ NMR spectra of Ethyl-3-isopropyl-1-oxo-1H-isochromene-4-carboxylate (3r).} \]
$^1$H NMR spectra of Ethyl-3-cyclopropyl-1-oxo-1H-isochromene-4-carboxylate (3s).

$^{13}$C NMR spectra of Ethyl 3-cyclopropyl-1-oxo-1H-isochromene-4-carboxylate (3s).
$^1$H NMR spectra of Ethyl 1-oxo-3-phenyl-$1H$-isochromene-4-carboxylate (3t).

$^{13}$C NMR spectra of Ethyl 1-oxo-3-phenyl-$1H$-isochromene-4-carboxylate (3t).
$^1$H NMR spectra of Ethyl 3-(2,6-dichloro-5-fluoropyridin-3-yl)-1-oxo-1H-isochromene-4-carboxylate (3u).

$^{13}$C NMR spectra of Ethyl 3-(2,6-dichloro-5-fluoropyridin-3-yl)-1-oxo-1H-isochromene-4-carboxylate (3u).
\(^1\)H NMR spectra of 4-Benzoyl-3-phenyl-1\(H\)-isochroman-1-one (3v).

\(^{13}\)C NMR spectra of 4-Benzoyl-3-phenyl-1\(H\)-isochroman-1-one (3v).
$^1$H NMR spectra of 3,3-Dimethyl-3,4-dihydro-$1H$-benzo[c]chromene-1,6-($2H$)-dione (3w).

$^{13}$C NMR spectra of 3,3-Dimethyl-3,4-dihydro-$1H$-benzo[c]chromene-1,6-($2H$)-dione (3w).
$^1$H NMR spectra of tert-Butyl 3,6-dimethyl-2-oxo-2H-pyran-5-carboxylate (4a).

$^{13}$C NMR spectra of tert-Butyl 3,6-dimethyl-2-oxo-2H-pyran-5-carboxylate (4a).
\(^1\)H NMR spectra of Ethyl-3,6-dimethyl-2-oxo-2\(H\)-pyran-5-carboxylate (4b).

\(^{13}\)C NMR spectra of Ethyl 3,6-dimethyl-2-oxo-2\(H\)-pyran-5-carboxylate (4b).
$^1$H NMR spectra of Ethyl-3-methyl-6-propyl-2-oxo-2$H$-pyran-5-carboxylate (4c).

$^{13}$C NMR spectra of Ethyl-3-methyl-6-propyl-2-oxo-2$H$-pyran-5-carboxylate (4c).
$^1$H NMR spectra of Ethyl-6-isopropyl-3-methyl-2-oxo-2$H$-pyran-5-carboxylate (4d).

$^{13}$C NMR spectra of Ethyl-6-isopropyl-3-methyl-2-oxo-2$H$-pyran-5-carboxylate (4d).
$^1$H NMR spectra of Ethyl-3-methyl-2-oxo-6-phenyl-2H-pyran-5-carboxylate (4e).

$^{13}$C NMR spectra of Ethyl-3-methyl-2-oxo-6-phenyl-2H-pyran-5-carboxylate (4e).
$^1$H NMR spectra of Ethyl-6-(2,6-dichloro-5-fluoropyridin-3-yl)-3-methyl-2-oxo-$2H$-pyran-5-carboxylate (4f).

$^{13}$C NMR spectra of Ethyl-6-(2,6-dichloro-5-fluoropyridin-3-yl)-3-methyl-2-oxo-$2H$-pyran-5-carboxylate (4f).
$^1$H NMR spectra of 3,7,7-trimethyl-7,8-dihydro-$2H$-chromene-2,5-($6H$)-dione (4g).

$^{13}$C NMR spectra of 3,7,7-trimethyl-7,8-dihydro-$2H$-chromene-2,5-($6H$)-dione (4g).