Supporting Information

A Strategy for Site- and Chemoselective C–H Alkenylation through Osmaelectrooxidative Catalysis

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**General Remarks**

Osmium(II)-catalyzed electrooxidative C–H annulations were performed under a N₂ atmosphere in Schlenk tubes. The osmium catalysts[1] and starting materials[2] were synthesized according to previously described methods. Other chemicals and solvents were obtained from commercial sources, and were used without further purification. Platinum electrodes (10 mm × 15 mm × 0.125 mm, 99.95%; obtained from ESG-Edelmetall-Handel GmbH & Co. KG) and graphite felt electrodes (10 mm × 10 mm × 6 mm, SIGRACELL® GFA 6 EA, obtained from SGL Carbon, Wiesbaden, Germany) were connected using stainless steel adapters. Electrocatalysis was conducted using an AXIOMET AX-3003P potentiostat in constant current mode. Cyclic voltammetry studies were performed using a Metrohm Autolab PGSTAT204 workstation and Nova 2.1 software. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ¹H NMR. TLC: Macherey-Nagel, TLC plates Alugram® Sil G/UV254, detection under UV light at 254 nm. Chromatography: Separations were carried on Merck Silica 60 (0.040-0.063 mm, 70-230 mesh ASTM). NMR: ¹H-, ¹³C-, and ¹⁹F-NMR spectra were recorded on Varian 300 MHz, Bruker 400 MHz, and Varian 500 MHz spectrometers in CDCl₃ solutions, chemical shifts (δ) are given in ppm. IR: All spectra were recorded on a Bruker FT-IR Alpha device. MS: EI-MS: Finnigan MAT 95, 70 eV; DCI-MS: Finnigan MAT 95, 200 eV, reactant gas NH₃; ESI-MS: Finnigan LCQ. High resolution mass spectrometry (HRMS): APEX IV 7T FTICR, Bruker Daltonic. M.p.: Stuart® SMP3 melting point apparatus, all values are uncorrected.
General Procedures

1) General procedure 1 (GP1) for osmium-catalyzed electrooxidative [4+1] C–H annulation
A suspension of benzoic acid (0.20 mmol), olefin (3.0 equiv), [OsCl$_2$(p-cymene)]$_2$ (5.0 mol %), KI (2.0 equiv), and KOAc (2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL) was stirred at 100 °C for 16 h at 4.0 mA of a constant current under N$_2$. After cooling to ambient temperature, the electrodes were washed with ethyl acetate (3 × 10 mL). The reaction mixtures were extracted with brine (20 mL), dried over Na$_2$SO$_4$, and concentrated under reduced pressure. Purification by column chromatography on silica gel afforded the desired products.

\[
\text{RCO}_2\text{H} + \underset{\text{GF}}{\text{R}}\underset{\text{Pt}}{\text{CH}_2\text{OR}} \xrightarrow{\text{[OsCl}_2(p\text{-cymene})]_2 (5.0 \text{ mol }%)} \text{RCO}_2\text{R}^2
\]

2) General procedure 2 (GP2) for osmium-catalyzed electrooxidative [4+2] C–H annulation
A suspension of benzoic acid (0.20 mmol), alkyne (3.0 equiv), [OsCl$_2$(p-cymene)]$_2$ (5.0 mol %), KI (2.0 equiv), and KOAc (2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL) was stirred at 100 °C for 16 h at 4.0 mA of a constant current under N$_2$. After cooling to ambient temperature, the electrodes were washed with ethyl acetate (3 × 10 mL). The reaction mixtures were extracted with brine (20 mL), dried over Na$_2$SO$_4$, and concentrated under reduced pressure. Purification by column chromatography on silica gel afforded the desired products.

\[
\text{RCO}_2\text{H} + \underset{\text{GF}}{\text{R}}\underset{\text{Pt}}{\text{C} = \text{C} \text{R}^2} \xrightarrow{\text{[OsCl}_2(p\text{-cymene})]_2 (5.0 \text{ mol }%)} \text{RCO}_2\text{R}^2
\]
## Optimization Studies

**Table S1.** Optimization studies for osmaelectro-catalyzed C–H annulation.[a]

| Entry | Deviation from the standard reaction conditions | Yield (%) |
|-------|-----------------------------------------------|-----------|
| 1     | None                                          | 77 (75)   |
| 2     | NaI instead of KI                             | 29        |
| 3     | BQ instead of KI                              | 0         |
| 4     | Fc instead of KI                              | 0         |
| 5     | HOBt instead of KI                            | 0         |
| 6     | 4.0 equiv of KI instead of 2.0 equiv          | 76        |
| 7     | NaOAc instead of KOAc                        | 36        |
| 8     | NaOPiv instead of KOAc                        | 38        |
| 9     | Reaction temperature at 60 °C instead of 100 °C| 35        |
| 10    | Reaction temperature at 25 °C instead of 100 °C| 0         |
| 11    | HFIP (3.0 mL) and H2O (1.0 mL)                | 59        |
| 12    | [Cp*RhCl2]2 (2.5 mol %) instead of [OsCl2(p-cymene)]2 | 7         |
| 13    | [Cp*IrCl2]2 (2.5 mol %) instead of [OsCl2(p-cymene)]2 | 16        |
| 14    | [RuCl2(p-cymene)]2 (5.0 mol %) instead of [OsCl2(p-cymene)]2 | 90        |
| 15    | Without catalyst                              | 0         |
| 16[b] | Without electricity                           | 6         |
| 17    | Without KI                                    | 11        |
| 18[c] | [OsI2(p-cymene)]2 instead of [OsCl2(p-cymene)]2 | 24        |

[a] Reaction conditions: I (0.20 mmol), II (3.0 equiv), [OsCl2(p-cymene)]2 (5.0 mol %), KI (2.0 equiv), KOAc (2.0 equiv), HFIP (2.0 mL), H2O (2.0 mL), 100 °C, 16 h. Yield was determined by 1H NMR with CH2Br2 as the internal standard. Yield in the parenthesis is isolated yield. [b] The reaction was equipped with electrodes, but no electricity. [c] Without KI. GF = Graphite Felt. HFIP = Hexafluoroisopropyl alcohol. BQ = Benzoquinone. Fc = Ferrocene. HOBt = Hydroxybenzotriazole.
Electrochemical Setup

Figure S1. Detailed electrochemical setup. 1) A graphite felt and a platinum plate should be tightly held by stainless steel adaptor. 2) Schlenk tube and septa used for the electrochemical reactions. 3) Current should be checked by an electrical multimeter although a potentiostat is set. 4) Chemicals in the sealed Schlenk tube with electrodes. 5) During the course of the reaction, two electrodes should not be in contact. The electrodes should be surely dipped into the solution with the same height.
Reactions Comparisons with Different Additives

1) Procedure for the reaction with different additives

A suspension of o-toluic acid I (0.20 mmol), n-butyl acrylate II (3.0 equiv), \([\text{OsCl}_2(p\text{-cymene})]_2\) (5.0 mol %), additives (2.0 equiv), and KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL) was stirred at 100 °C for 16 h under N₂. The additives used were KPF₆, KSbF₆, NaSbF₆, nBu₄NI, and I₂.

![Diagram of the reaction](image)

**Figure S2.** Examination of various additives.
Reaction Comparisons with External Chemical Oxidants

1) Procedure for the reaction with chemical oxidants

A suspension of o-toluic acid I (0.20 mmol), n-butyl acrylate II (3.0 equiv), [OsCl₂(ρ-cymene)]₂ (5.0 mol %), oxidant (2.0 equiv), and KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL) was stirred at 100 °C for 16 h under N₂. Chemical oxidants used were AgOAc, Cu(OAc)₂, Mn(OAc)₃, Phl(OAc)₂, and K₂S₂O₈. Additionally, the same reaction was performed under air as a terminal oxidant.

Figure S3. Examination of chemical oxidants.
Reaction Comparisons with Different Catalysis

1) Procedure for the reaction with [Cp*RhCl₂]₂

The reaction was performed according to the reported procedure. A suspension of benzoic acid III (48.8 mg, 2.0 equiv), n-butyl acrylate II (25.6 mg, 0.20 mmol), [Cp*RhCl₂]₂ (3.1 mg, 2.5 mol %), and KOAc (39.3 mg, 2.0 equiv) in tAmOH (3.0 mL) and H₂O (1.0 mL) was stirred at 100 °C for 8 h at 4.0 mA of constant current under air.

2) Procedure for the reaction with [Cp*IrCl₂]₂

The reaction was performed according to the reported procedure. A suspension of benzoic acid III (24.4 mg, 0.20 mmol), n-butyl acrylate II (51.2 mg, 2.0 equiv), [Cp*IrCl₂]₂ (4.0 mg, 2.5 mol %), benzoquinone (2.2 mg, 10 mol %), KOAc (39.3 mg, 2.0 equiv) in tAmOH (3.0 mL) and H₂O (1.0 mL) was stirred at 100 °C for 18 h at 4.0 mA of constant current under air.
3) Procedure for the reaction with $[\text{RuCl}_2(p\text{-cymene})]_2$ 

The reaction was performed according to the reported procedure.$^5$ A suspension of benzoic acid $\text{III}$ (48.8 mg, 2.0 equiv), $n$-butyl acrylate $\text{II}$ (25.6 mg, 0.20 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (6.1 mg, 5.0 mol %), and NaOPiv (49.6 mg, 2.0 equiv) in $t$AmOH (3.0 mL) and $\text{H}_2\text{O}$ (1.0 mL) was stirred at 100 °C for 18 h at 4.0 mA of constant current under air.

![Chemical reaction diagram]

4) Procedure for the reaction with $[\text{OsCl}_2(p\text{-cymene})]_2$

GP1 was followed using benzoic acid $\text{III}$ (24.4 mg, 0.20 mmol), $n$-butyl acrylate $\text{II}$ (76.9 mg, 3.0 equiv), $[\text{OsCl}_2(p\text{-cymene})]_2$ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and $\text{H}_2\text{O}$ (2.0 mL) at 100 °C for 16 h at 4.0 mA of constant current under $\text{N}_2$.

![Chemical reaction diagram]
H/D Exchange Studies with Different Catalysis

1) Procedure for H/D exchange studies: Ruthenium catalysis (1)

GP1 was followed using 3-(trifluoromethyl)benzoic acid IV (38.0 mg, 0.20 mmol), n-butyl acrylate II (76.9 mg, 3.0 equiv), [RuCl₂(p-cymene)]₂ (6.1 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (1.0 mL) and D₂O (3.0 mL) at 100 °C for 2 h at 4.0 mA of constant current under N₂.

Figure S4. Ruthenium-catalyzed H/D exchange.
2) Procedure for H/D exchange studies: Ruthenium catalysis (2)

**GP1** was followed using 3-(trifluoromethyl)benzoic acid **IV** (38.0 mg, 0.20 mmol), [RuCl₂(p-cymene)]₂ (6.1 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (1.0 mL) and D₂O (3.0 mL) at 100 °C for 2 h at 4.0 mA of constant current under N₂.

![Diagram of H/D exchange process](image)

**Figure S5.** Ruthenium-catalyzed H/D exchange without acrylates.
3) H/D exchange study with product 4 by electro-ruthenium catalysis

**Figure S6.** H/D exchange study with product 4 by electro-ruthenium catalysis.
4) Procedure for H/D exchange studies: Osmium catalysis (1)

**GP1** was followed using 3-(trifluoromethyl)benzoic acid **IV** (38.0 mg, 0.20 mmol), *n*-butyl acrylate **II** (76.9 mg, 3.0 equiv), \([\text{OsCl}_2(\mu\text{-cymene})]_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (1.0 mL) and D_2O (3.0 mL) at 100 °C for 2 h at 4.0 mA of constant current under N_2.

![Diagram showing H/D exchange with GC/MS spectra](image)

**Figure S7.** Osmium-catalyzed H/D exchange.
5) Procedure for H/D exchange studies: Osmium catalysis (2)

**GP1** was followed using 3-((trifluoromethyl)benzoic acid **IV** (38.0 mg, 0.20 mmol), [OsCl$_2$(p-cymene)]$_2$ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (1.0 mL) and D$_2$O (3.0 mL) at 100 °C for 2 h at 4.0 mA of constant current under N$_2$.

![Chemical structure of IV](image)

**Figure S8.** Osmium-catalyzed H/D exchange without acrylates.
6) H/D exchange study with product 4 by electro-ruthenium catalysis

Figure S9. H/D exchange study with product 4 by electro-ruthenium catalysis.
The Preparation of Osmium Complexes

1) Procedure for the synthesis of $[\text{OsCl}_2(p\text{-cymene})]_2$

The reaction were performed under the condition of the reported procedure.\[1\] A suspension of $\text{OsCl}_3 \cdot x\text{H}_2\text{O}$ (1.0 mmol) and $\alpha$-terpinene (9.0 equiv) in isopropanol (5.0 mL) was stirred at 85 °C for 16 h under N$_2$. Filtration (Por 3) with MeOH (3 × 5 mL) gave yellow solid, which was dried in vacuo for 6 h.

\begin{align*}
\text{OsCl}_3 \cdot x\text{H}_2\text{O} & \xrightarrow{\alpha\text{-terpinene}} \text{PrOH, 85 °C, 16 h} [\text{OsCl}_2(p\text{-cymene})]_2 \\
\end{align*}

2) Procedure for the synthesis of $\text{OsCl}_2(\text{DMSO})(p\text{-cymene})$

The reactions were performed under the condition of the reported procedure.\[6\] A suspension of dimethyl sulfoxide (0.5 mL) and $[\text{OsCl}_2(p\text{-cymene})]_2$ (0.20 mmol) in dichloromethane (5.0 mL) was stirred at room temperature for 16 h under N$_2$. The reaction mixture was concentrated in vacuo for 24 h, giving reddish yellow solid.

\begin{align*}
[\text{OsCl}_2(p\text{-cymene})]_2 & \xrightarrow{\text{DMSO}} \text{CH}_2\text{Cl}_2, \text{RT, 16 h} \text{OsCl}_2(\text{DMSO})(p\text{-cymene}) \\
\end{align*}

3) Procedure for the synthesis of $\text{OsCl}($Me$)(\text{DMSO})(p\text{-cymene})$

The reactions were performed under the modified condition of the reported procedure.\[6\] To a solution of dimethyl sulfoxide (0.1 mL) and $\text{OsCl}_2(\text{DMSO})(p\text{-cymene})$ (0.20 mmol) in PhMe was added dropwise AlMe$_3$ (2.0 M solution in PhMe, 0.15 mL) in the glove box. After stirring at room temperature for 30 min, reaction vessel was taken out from the glove box. While stirring at room temperature for additional 20 min, acetone (1.0 mL) and H$_2$O (0.05 mL) were added dropwise (Caution: This step generates gas). Afterwards, diethyl ether (2.0 mL) was added, then forming the white solid. A short Na$_2$SO$_4$ packed filter followed by PTFE filter (Simplepure™, 0.22 μm) gave yellow solution which was vacuum evaporated for 16 h (Caution: Do not use rotary evaporator to remove solvents, which can give a color change of solution to dark brown). For spectra, see p. 68.

\begin{align*}
\text{OsCl}_2(\text{DMSO})(p\text{-cymene}) & \xrightarrow{\text{DMSO, AlMe}_3} \text{PhMe, RT, 1 h} \text{OsCl}($\text{Me}$)(\text{DMSO})(p\text{-cymene}) \\
\end{align*}
4) Procedure for the synthesis of Os-I

The reactions were performed under the modified condition of the reported procedure.[7] A suspension of OsCl(Me)(DMSO)(p-cymene) (0.20 mmol) and ((1-naphthoyl)oxy)silver (1.1 equiv) in C₆D₆ was stirred at room temperature for 16 h. During the course of reaction, the aliquot was taken to monitor the reaction. When OsCl(Me)(DMSO)(p-cymene) was fully consumed, the solution was filtered with benzene by PTFE filter (Simplepure™, 0.22 μm) to remove AgCl (Caution: Benzene is highly toxic. Please use it under ventilated condition). The filtrate was vacuum evaporated for 16 h, giving yellow solid (Caution: Do not use rotary evaporator to remove solvents, which may decompose the osmium complex). The crystal structure of Os-I was obtained in THF in the glove box. For spectra, see p. 69.

![Scheme 4: Synthesis of Os-I](image)

5) Procedure for the synthesis of Os-II

A suspension of Os-I (0.20 mmol) and 1,2-di-p-tolylethyne VI (1.1 equiv) in CD₃OD was stirred at room temperature for 24 h. During the course of reaction, the aliquot was taken to monitor the reaction. The solution was concentrated under reduced pressure. Purification by column chromatography on silica gel afforded the desired products Os-II as a yellow solid. The crystal structure of Os-II was obtained in DCM/hexane. For spectra, see p. 70.

![Scheme 5: Synthesis of Os-II](image)
Table S2. Crystal structures of synthesized osmium complexes.

| Compound                        | CCDC Code   |
|---------------------------------|-------------|
| OsCl(Me)(DMSO)(p-cymene)        | CCDC 2085921|
| Os-I                            | CCDC 2085919|
| Os-II                           | CCDC 2085920|
Reactions with Osmium Complexes

1) Procedure for the stoichiometric reaction with **Os-I**

**GP1** was followed using **Os-I** (0.1 mmol), \( n \)-butyl acrylate **II** (3.0 equiv), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\(_2\)O (2.0 mL) at 100 °C for 16 h at 4.0 mA of constant current under N\(_2\).

![Reactions with Osmium Complexes](image)

2) Procedure for the stoichiometric reaction with **Os-II**

**GP2** was followed using **Os-II** (0.1 mmol), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\(_2\)O (2.0 mL) was stirred at 100 °C for 16 h at 4.0 mA of constant current under N\(_2\).

![Reactions with Osmium Complexes](image)

3) Procedure for the stoichiometric reaction with **Os-II**

**GP2** was followed using **Os-II** (0.1 mmol), NaSbF\(_6\) (2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\(_2\)O (2.0 mL) was stirred at 100 °C for 16 h at 4.0 mA of constant current under N\(_2\).

![Reactions with Osmium Complexes](image)
4) Procedure for the catalytic reaction with Os-I

GP1 was followed using naphthoic acid V (0.1 mmol), n-butyl acrylate II (3.0 equiv), Os-I (10 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL) at 100 °C for 16 h at 4.0 mA of constant current under N₂.

5) Procedure for the catalytic reaction with Os-II

GP2 was followed using naphthoic acid V (0.1 mmol), 1,2-di-\(p\)-tolylethyne VI (3.0 equiv), Os-II (10 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL) at 100 °C for 16 h at 4.0 mA of constant current under N₂.
**In-Operando NMR Study**

1) Procedure for *in-operando* NMR study

In a nitrogen filled glove box, a screw top NMR tube was loaded with **Os-I** (0.050 mmol), 1,3,5-trimethoxybenzene (500 mM stock solution in THF-d₈, 0.0125 mmol), and THF-d₈ (475.0 μL). An $^1$H NMR (400 MHz) spectrum of the resulted solution was then obtained. Subsequently, alkyne (0.050 mmol) was added and after homogenization, the progress of the reaction was monitored by $^1$H NMR (400 MHz) spectroscopy at 45 °C by collecting spectra every five minutes for a total period of 15 hours (18 data points out of the 180 collected spectra are only presented below for clarity). Color legend: Red = **Os-I**, Blue = **Os-II**, Green = VI (1,2-di-<i>p</i>-tolylethyne).

![Chemical Structures](image)

**Figure S10.** Data for in-operando NMR study.
HR-ESI-MS Monitoring Study

1) Procedure for HR-ESI-MS study

GP2 was followed using naphthoic acid V (0.1 mmol), 1,2-di-p-tolylethyne VI (3.0 equiv), [OsCl$_2$(p-cymene)]$_2$ (5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL) under N$_2$. The reaction mixture was then left to stir at 100 °C for 1 minute at which time a sample (t=0) was collected and analyzed by HR-ESI-MS. Subsequently, the reaction was initiated by passing a constant current of 4.0 mA through the reaction mixture followed by sampling at time intervals for a total length of 425 min. Each aliquot collected (~ 0.1 mL) was passed through a pipette filled with Na$_2$SO$_4$ and diluted with THF prior to analysis.

![Diagram of reaction](attachment:reaction_diagram.png)

**Figure S11.** Data for HR-ESI-MS study.
Figure S12. Plausible intermediates or product detected by HR-ESI-MS study.
Cyclovoltammetric Study

1) Procedure for cyclovoltammetric study

CV measurements were conducted with a Metrohm Autolab PGSTAT204 potentiostat and Nova 2.1 software. A glassy carbon working electrode (disk, diameter: 3mm), a coiled platinum wire counter electrode and a saturated calomel reference electrode (SCE) were employed. The voltammograms were recorded at room temperature in MeCN at a substrate concentration of 5.0 mM and with 0.1 M nBu4NPF6 as supporting electrolyte. MeCN was distilled to remove impurity prior to the use. All solutions were degassed with N2 prior to the measurement and an overpressure of protective gas was maintained throughout the experiment. The scan rate is 100 mV/s. Deviations from the general experimental conditions are indicated in the respective descriptions.

![Cyclic voltammograms of blank, V, VI, and [OsCl2(p-cymene)]2.](image)

**Figure S13.** Cyclic voltammograms of blank, V, VI, and [OsCl2(p-cymene)]2.
**Figure S14.** Cyclic voltammograms of Os-II, KI, and Os-II with KI.

**Figure S15.** Cyclic voltammograms of Os-I and Os-I with VI.
**Competition Experiments**

1) Procedure for competition experiment (1)

**GP1** was followed using 3-methyl benzoic acid VII (0.1 mmol), 3-trifluoromethyl benzoic acid IV (0.1 mmol), n-butyl acrylate II (3.0 equiv), [OsCl₂(p-cymene)]₂ (5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL) at 100 °C for 4 h at 4.0 mA of constant current under N₂. After cooling to ambient temperature, the electrodes were washed with ethyl acetate (3 × 10 mL). The reaction mixtures were extracted with brine (20 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The crude mixture was analyzed by ¹H NMR with CH₂Br₂ as the internal standard.

![Chemical Reaction Diagram](attachment:image.png)

**Figure S16.** Competition experiment with different benzoic acids.
2) Procedure for competition experiment (2)

**GP2** was followed using naphthoic acid **V** (0.20 mmol), 1,2-di-\textit{p}-tolylethyne **VI** (0.20 mmol), 1,2-bis(4-fluorophenyl)ethyne **VIII** (0.20 mmol), \([\text{OsCl}_2(\text{p-cymene})]_2\) (5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\textsubscript{2}O (2.0 mL) at 100 °C for 4 h at 4.0 mA of constant current under N\textsubscript{2}. After cooling to ambient temperature, the electrodes were washed with ethyl acetate (3 × 10 mL). The reaction mixture was extracted with brine (20 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated under reduced pressure. The crude mixture was analyzed by \textsuperscript{1}H NMR with CH\textsubscript{2}Br\textsubscript{2} as the internal standard.

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**Figure S17.** Competition experiment with different alkynes.
Hammett Correlations

A series of reactions were performed with electronically different substrates under standard reaction conditions.

![Diagram showing reactions](image)

Figure S18. Independent reactions for Hammett correlation study.
Table S3. Hammett Correlations.

| R_{meta} | H | Sub | k/k_0 | log(k/k_0) | σ_{meta} |
|----------|---|-----|-------|------------|----------|
| H        | 1 | 1   | 1.000 | 0.000      | 0        |
| OMe      | 37| 38  | 1.027 | 0.012      | 0.115    |
| Me       | 21| 27  | 1.286 | 0.109      | -0.069   |
| Br       | 26| 17  | 0.654 | -0.185     | 0.393    |
| F        | 24| 18  | 0.750 | -0.125     | 0.337    |

Figure S19. Hammett plot.
KIE Studies

1) Procedure for KIE study (Intermolecular competition reaction)

**GP1** was followed using \( I \) (0.1 mmol), \([D]_7-I\) (0.1 mmol), \( n\)-butyl acrylate **II** (3.0 equiv), \([\text{OsCl}_2(p\text{-cymene})]_2\) (5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\(_2\)O (2.0 mL) at 100 °C for 16 h at 4.0 mA of constant current under N\(_2\).

![Diagram](Diagram.png)

**Figure S20.** KIE study by intermolecular competition reaction. Note: CH\(_3\) of aromatic and CH\(_3\) of butyl group should be compared. Other C–H bonds were isotopically labelled by post-catalysis H/D exchange (See Figure S19).
Figure S21. H/D exchange study with isotopically labelled I.
2) Procedure for KIE study (Two parallel reactions)

**GP1** was followed for four independent reactions using substrate **I** (0.20 mmol) *n*-butyl acrylate **II** (3.0 equiv), and another four independent reactions using substrate [D]-**I** (0.20 mmol) and *n*-butyl acrylate **II** (3.0 equiv) for specified reaction time (30 min, 60 min, 90 min, and 120 min). The crude mixture was dried *in vacuo* for 6 h and analyzed by $^1$H NMR with CH$_2$Br$_2$ as the internal standard.

![Diagram](image)

**Figure S22.** KIE study by two parallel reactions.
Current Dependence of the Reaction Rate

GP1 was followed for five independent reactions using substrate I (0.20 mmol) n-butyl acrylate II (3.0 equiv) under five different currents (1.0 mA, 2.0 mA, 4.0 mA, 4.0 mA, 8.0 mA) for specified reaction time (30 min, 60 min, 90 min, and 120 min). The crude mixture was dried in vacuo for 1 h and analyzed by 1H NMR with CH2Br2 as the internal standard.

| Time (min) | 1.0 mA | 2.0 mA | 4.0 mA | 6.0 mA | 8.0 mA |
|-----------|--------|--------|--------|--------|--------|
| 0         | 0      | 0      | 0      | 0      | 0      |
| 30        | 4      | 6      | 8      | 10     | 9      |
| 60        | 7      | 13     | 18     | 20     | 25     |
| 90        | 13     | 19     | 28     | 31     | 35     |
| 120       | 16     | 28     | 35     | 40     | 46     |

Figure S23. Current dependence of the reaction rate.
Crystallographic Information

X-ray diffraction experiments for all of the compounds were carried out at 100(2) K on a Bruker D8 Venture four-circle-diffractometer from Bruker AXS GmbH equipped with a Photon II detector purchased from Bruker AXS GmbH and using microfocus IµS Cu/Mo radiation from Incoatec GmbH with HELIOS mirror optics and single-hole collimator from Bruker AXS GmbH. Intensities were integrated and absorption corrections based on equivalent reflections were applied using SADABS. The structures were all solved using SHELXT[8] and refined against all F2 in SHELXL[9] using Olex 2.[10] All of the non-hydrogen atoms were refined anisotropically while the carbon bond hydrogen atoms were located geometrically and refined using a riding model. Crystal structure and refinement data are given in Table S4, S5, and S6. Crystallographic data for the compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 2085919, 2085920 and 2085921. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk).

Table S4. Crystal data and structure refinement for OsCl(Me)(DMSO)(p-cymene).

| Compound | OsCl(Me)(DMSO)(p-cymene) |
|----------|---------------------------|
| Empirical formula | C\textsubscript{13}H\textsubscript{23}ClOOS |
| Formula weight | 453.02 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | Cc |
| a/Å | 11.2960(8) |
| b/Å | 15.1437(12) |
| c/Å | 9.2214(8) |
| α/° | 90 |
| β/° | 106.298(3) |
| γ/° | 90 |
| Volume/Å\textsuperscript{3} | 1514.1(2) |
| Z | 4 |
| \(\rho_{\text{calc}}\)/g/cm\textsuperscript{3} | 1.987 |
| \(\mu\)/mm\textsuperscript{-1} | 4.684 |
Table S5. Crystal data and structure refinement for Os-I.

| Compound                        | Os-I                                               |
|---------------------------------|----------------------------------------------------|
| Empirical formula               | C_{29}H_{38}O_{4.5}OsS                            |
| Formula weight                  | 680.85                                             |
| Temperature/K                   | 100                                                |
| Crystal system                  | monoclinic                                         |
| Space group                     | C2/c                                               |
| a/Å                             | 26.302(3)                                          |
| b/Å                             | 14.0767(14)                                        |
| c/Å                             | 15.6684(13)                                        |
| α/°                             | 90                                                 |
| β/°                             | 113.083(3)                                         |
| γ/°                             | 90                                                 |
| Volume/Å³                       | 5336.6(9)                                          |
| Z                               | 8                                                  |
| ρ_{calc}/g/cm³                  | 1.695                                              |
| μ/mm⁻¹                          | 4.892                                              |
| F(000)                          | 2720                                               |
| Crystal size/mm³                | 0.121 × 0.061 × 0.029                              |
Radiation: MoKα (λ = 0.71073)

2θ range for data collection/°: 5.326 to 61.174

Index ranges:
-37 ≤ h ≤ 37, -20 ≤ k ≤ 20, -22 ≤ l ≤ 22

Reflections collected: 83356

Independent reflections: 8195 [R(int) = 0.0394, R(sigma) = 0.0191]

Data/restraints/parameters: 8195/0/258

Goodness-of-fit on F²: 1.046

Final R indexes [I>=2σ (I)]: R₁ = 0.0309, wR₂ = 0.0793

Final R indexes [all data]: R₁ = 0.0356, wR₂ = 0.0824

Largest diff. peak/hole / e Å⁻³: 2.22/-0.60

Table S6. Crystal data and structure refinement for Os-II.

| Compound                  | Os-II            |
|--------------------------|------------------|
| Empirical formula        | C₃₁H₃₄O₂Os      |
| Formula weight           | 700.84           |
| Temperature/K            | 100              |
| Crystal system           | monoclinic       |
| Space group              | P2₁/n            |
| a/Å                      | 16.0104(13)      |
| b/Å                      | 11.3652(9)       |
| c/Å                      | 16.2343(13)      |
| α/°                      | 90               |
| β/°                      | 108.231(2)       |
| γ/°                      | 90               |
| Volume/Å³                | 2805.7(4)        |
| Z                        | 4                |
| ρcalc/g/cm³              | 1.659            |
| μ/mm⁻¹                   | 4.578            |
| F(000)                   | 1392             |
| Crystal size/mm³         | 0.123 × 0.09 × 0.045 |
| Radiation                | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 4.31 to 61.158  |
| Description                                      | Value                                      |
|--------------------------------------------------|--------------------------------------------|
| Index ranges                                     | \(-22 \leq h \leq 22, -16 \leq k \leq 16, -23 \leq l \leq 23\) |
| Reflections collected                            | 84089                                      |
| Independent reflections                          | 8602 [\(R_{int} = 0.0424, R_{sigma} = 0.0221\)] |
| Data/restraints/parameters                        | 8602/0/366                                 |
| Goodness-of-fit on \(F^2\)                       | 1.041                                      |
| Final R indexes [\(I \geq 2\sigma (I)\)]       | \(R_1 = 0.0189, wR_2 = 0.0375\)           |
| Final R indexes [all data]                       | \(R_1 = 0.0248, wR_2 = 0.0395\)           |
| Largest diff. peak/hole / e Å\(^3\)              | 0.75/-0.57                                |
Deuteration Rate of Acrylate

1) Ruthenium

\[
\text{H} \quad \text{O} \quad \text{OnBu} \xrightarrow{\text{[RuCl}_2(\rho\text{-cymene})]_2 (5.0 \text{ mol \%})} \quad \text{H/D} \quad \text{O} \quad \text{OnBu}
\]

\[
\text{KOAc, D}_2\text{O} \quad 100 \degree \text{C}
\]

**Figure S24.** Deuteration rate of acrylate in ruthenium catalysis.

2) Osmium

\[
\text{H} \quad \text{O} \quad \text{OnBu} \xrightarrow{\text{[OsCl}_2(\rho\text{-cymene})]_2 (5.0 \text{ mol \%})} \quad \text{H/D} \quad \text{O} \quad \text{OnBu}
\]

\[
\text{KOAc, D}_2\text{O} \quad 100 \degree \text{C}
\]

**Figure S25.** Deuteration rate of acrylate in osmium catalysis.
Attempted Examples

Additional attempts on electrooxidative osmium-catalyzed C–H/O–H annulations are described below.
Characterization Data of Products

Butyl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (1)

**GPI** was followed using 2-methylbenzoic acid (27.2 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 1 (39.3 mg, 75%) as a colorless oil.

**¹H NMR** (400 MHz, CDCl₃) δ 7.49 (t, J = 7.6 Hz, 1H), 7.24 (ddd, J = 7.6, 3.8, 0.8 Hz, 2H), 5.77 (t, J = 6.5 Hz, 1H), 4.11 (t, J = 6.5 Hz, 2H), 2.83 (d, J = 6.5 Hz, 2H), 2.64 (s, 3H), 1.61 – 1.52 (m, 2H), 1.32 (dq, J = 14.6, 7.4 Hz, 2H), 0.88 (t, J = 7.4 Hz, 3H).

**¹³C NMR** (125 MHz, CDCl₃) δ 170.0 (C₄), 169.3 (C₄), 149.2 (C₄), 139.8 (C₄), 133.9 (CH), 131.0 (CH), 123.3 (C₄), 119.2 (CH), 76.0 (CH), 65.0 (CH₂), 39.7 (CH₂), 30.4 (CH₂), 19.0 (CH₂), 17.2 (CH₃), 13.6 (CH₃).

**IR** (ATR): 2960, 2927, 1745, 1711, 1519, 1371, 1321, 1065, 956, 608 cm⁻¹.

**MS** (ESI) m/z (relative intensity): 263 (40) [M+H]+, 285 (60) [M+Na]+.

**HR-MS** (ESI) C₁₅H₁₉O₄ [M+H]+: 263.1279, found: 263.1281.

The spectral data were in accordance with those reported in the literature.[³]
Butyl 2-(3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2)

GP1 was followed using benzoic acid (24.4 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl2(p-cymene)]2 (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H2O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 2 (35.3 mg, 71%) as a colorless oil.

1H NMR (400 MHz, CDCl3) δ 7.90 (d, J = 7.7 Hz, 1H), 7.66 (dd, J = 7.5, 1.1 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.48 (ddd, J = 7.7, 1.1, 0.8 Hz, 1H), 5.87 (t, J = 6.6 Hz, 1H), 4.14 (t, J = 6.6 Hz, 2H), 2.98 – 2.80 (m, 2H), 1.69 – 1.54 (m, 2H), 1.35 (dq, J = 14.7, 7.4 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H).

13C NMR (125 MHz, CDCl3) δ 169.8 (Cq), 169.3 (Cq), 148.8 (Cq), 134.2 (CH), 129.5 (CH), 126.0 (Cq), 125.8 (CH), 122.1 (CH), 77.0 (CH), 65.2 (CH2), 39.6 (CH2), 30.5 (CH2), 19.0 (CH2), 13.6 (CH3).

IR (ATR): 2959, 2933, 1759, 1599, 1466, 1288, 1172, 1059, 748, 571 cm⁻¹.

MS (ESI) m/z (relative intensity): 249 (40) [M+H]⁺, 271 (60) [M+Na]⁺.

HR-MS (ESI) C14H17O4 [M+H]⁺: 249.1124, found: 249.1121.

The spectral data were in accordance with those reported in the literature.[3]
Butyl 2-(3-oxo-4-phenyl-1,3-dihydroisobenzofuran-1-yl)acetate (9)

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{CO}_2\text{Bu}
\end{array}
\]

**GP1** was followed using 2-phenyl benzoic acid (39.6 mg, 0.20 mmol), *n*-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl\(_2\)(\(p\)-cymene)]\(_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\(_2\)O (2.0 mL). Purification by column chromatography on silica gel (\(n\)-hexane/EtOAc: 8/1) yielded 9 (42.2 mg, 65%) as a colorless oil.

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.72 (t, \(J = 7.6\) Hz, 1H), 7.59 – 7.43 (m, 7H), 5.89 (t, \(J = 6.5\) Hz, 1H), 4.20 (t, \(J = 6.5\) Hz, 2H), 2.96 (dd, \(J = 6.5, 1.5\) Hz, 2H), 1.71 – 1.55 (m, 2H), 1.47 – 1.32 (m, 2H), 0.96 (t, \(J = 7.3\) Hz, 3H).

**\(^{13}\)C NMR** (125 MHz, CDCl\(_3\)) \(\delta\) 169.4 (C\(_\text{q}\)), 168.6 (C\(_\text{q}\)), 150.1 (C\(_\text{q}\)), 143.0 (C\(_\text{q}\)), 136.2 (C\(_\text{q}\)), 134.0 (CH), 131.3 (CH), 129.5 (CH), 128.4 (CH), 128.0 (CH), 121.9 (C\(_\text{q}\)), 120.7 (CH), 75.6 (CH), 65.2 (CH\(_2\)), 39.8 (CH\(_2\)), 30.5 (CH\(_2\)), 19.1 (CH\(_2\)), 13.7 (CH\(_3\)).

**IR** (ATR): 2959, 2931, 1760, 1575, 1308, 1236, 1199, 1015, 944, 697 cm\(^-1\).

**MS** (ESI) \(m/z\) (relative intensity): 325 (66) [M+H]\(^+\), 347 (34) [M+Na]\(^+\).

**HR-MS** (ESI) C\(_{20}\)H\(_{21}\)O\(_4\) [M+H]\(^+\): 325.1435, found: 325.1434.

The spectral data were in accordance with those reported in the literature.\(^{[4]}\)
Butyl 2-(4-bromo-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (10)

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
\text{C}_9 & \quad \text{H} \quad \text{2nBu}
\end{align*}
\]

**GPI** was followed using 2-bromo benzoic acid (40.2 mg, 0.20 mmol), \(n\)-butyl acrylate (76.9 mg, 0.60 mmol), \([\text{OsCl}_2(p\text{-cymene})]_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\(_2\)O (2.0 mL). Purification by column chromatography on silica gel (\(n\)-hexane/EtOAc: 8/1) yielded 10 (32.1 mg, 49%) as a colorless oil.

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.69 (d, \(J = 7.7\) Hz, 1H), 7.49 (t, \(J = 7.7\) Hz, 1H), 7.43 (d, \(J = 7.6\) Hz, 1H), 5.79 (t, \(J = 6.5\) Hz, 1H), 4.13 (t, \(J = 6.7\) Hz, 2H), 2.99 – 2.81 (m, 2H), 1.64 – 1.52 (m, 2H), 1.34 (dq, \(J = 14.6, 7.4\) Hz, 2H), 0.91 (t, \(J = 7.4\) Hz, 3H).

**\(^{13}\)C NMR** (125 MHz, CDCl\(_3\)) \(\delta\) 169.1 (C\(_\text{q}\)), 167.1 (C\(_\text{q}\)), 151.2 (C\(_\text{q}\)), 135.1 (CH), 134.3 (CH), 124.4 (C\(_\text{q}\)), 121.2 (C\(_\text{q}\)), 121.1 (CH), 75.3 (CH), 65.3 (CH\(_2\)), 39.4 (CH\(_2\)), 30.5 (CH\(_2\)), 19.0 (CH\(_2\)), 13.6 (CH\(_3\)).

**IR** (ATR): 2959, 2932, 1763, 1722, 1582, 1343, 1207, 1173, 1011, 679 cm\(^{-1}\).

**MS** (ESI) \(m/z\) (relative intensity): 327 (66) \([^{79}\text{Br}]\text{[M+H]}^+\), 349 (34) \([^{79}\text{Br}]\text{[M+Na]}^+\).

**HR-MS** (ESI) \(C_{14}H_{16}^{79}\text{BrO}_4\) \([M+H]^+\): 327.0225, found: 327.0226.

The spectral data were in accordance with those reported in the literature.\(^{[11]}\)
Butyl 2-(5-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (7)

GP1 was followed using 3-methyl benzoic acid (27.2 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), \([\text{OsCl}_2(\text{p-cymene})]_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 7 (51.7 mg, 77%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (s, 1H), 7.46 (ddd, $J$ = 7.8, 1.6, 0.8 Hz, 1H), 7.35 (d, $J$ = 7.8 Hz, 1H), 5.82 (t, $J$ = 6.6 Hz, 1H), 4.14 (t, $J$ = 6.7 Hz, 2H), 2.94 – 2.76 (m, 2H), 2.44 (s, 3H), 1.64 – 1.55 (m, 2H), 1.40 – 1.29 (m, 2H), 0.91 (t, $J$ = 7.4 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.0 (C$_q$), 169.4 (C$_q$), 146.2 (C$_q$), 139.9 (C$_q$), 135.4 (CH), 126.1 (C$_q$), 125.8 (CH), 121.7 (CH), 76.9 (CH), 65.1 (CH$_2$), 39.7 (CH$_2$), 30.5 (CH$_2$), 21.2 (CH$_3$), 19.1 (CH$_2$), 13.7 (CH$_3$).

IR (ATR): 2960, 2929, 1771, 1733, 1495, 1290, 1154, 1009, 750, 557 cm$^{-1}$.

MS (ESI) $m/z$ (relative intensity): 263 (45) [M+H]$^+$, 285 (55) [M+Na]$^+$.  

HR-MS (ESI) C$_{15}$H$_{19}$O$_4$ [M+H]$^+$: 263.1281, found: 263.1278.

The spectral data were in accordance with those reported in the literature.$^{[3]}$
Butyl 2-(5-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (11)

GP1 was followed using 3-chloro benzoic acid (31.4 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 11 (24.3 mg, 43%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.02 (s, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 5.81 (t, J = 6.5 Hz, 1H), 4.14 (t, J = 6.7 Hz, 2H), 3.00 – 2.78 (m, 2H), 1.59 (dt, J = 14.6, 6.7 Hz, 2H), 1.34 (dq, J = 14.6, 7.4 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 169.1 (Cq), 168.2 (Cq), 147.4 (Cq), 137.3 (CH), 128.8 (CH), 128.1 (Cq), 123.8 (CH), 123.6 (Cq), 76.9 (CH), 65.3 (CH₂), 39.2 (CH₂), 30.5 (CH₂), 19.0 (CH₂), 13.6 (CH₃).

IR (ATR): 2959, 2932, 1654, 1710, 1418, 1287, 1174, 1071, 1006, 771 cm⁻¹.

MS (ESI) m/z (relative intensity): 283 (45) [M+H]⁺, 305 (55) [M+Na]⁺.

HR-MS (ESI) C₁₄H₁₆³⁵ClO₄ [M+H]⁺: 283.0733, found: 283.0732.
Butyl 2-(5-bromo-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (12)

GP1 was followed using 3-bromo benzoic acid (40.2 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 12 (34.0 mg, 52%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.86 (s, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 5.84 (t, J = 6.6 Hz, 1H), 4.14 (t, J = 6.7 Hz, 2H), 3.00 – 2.78 (m, 2H), 1.60 (dt, J = 14.6, 6.7 Hz, 2H), 1.34 (dq, J = 14.6, 7.4 Hz, 2H), 0.91 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 169.1 (Cₘ), 168.4 (Cₘ), 146.9 (Cₘ), 135.9 (Cₘ), 134.5 (CH), 127.9 (Cₘ), 125.8 (CH), 123.5 (CH), 76.8 (CH), 65.3 (CH₂), 39.3 (CH₂), 30.5 (CH₂), 19.0 (CH₂), 13.6 (CH₃).

IR (ATR): 2960, 2934, 1776, 1763, 1425, 1288, 1204, 1175, 1006, 832 cm⁻¹.

MS (ESI) m/z (relative intensity): 327 (50) (⁷⁹Br [M+H]⁺, 349 (50) (⁷⁹Br [M+Na]⁺).

HR-MS (ESI) C₁₄H₁₆⁷⁹BrO₄ [M+H]⁺: 327.0229, found: 327.0226.
Butyl 2-(3-oxo-5-(trifluoromethyl)-1,3-dihydroisobenzofuran-1-yl)acetate (4)

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{CO}_2\text{nBu} \\
& \quad \text{O}
\end{align*}
\]

**GP1** was followed using 3-trifluoromethyl benzoic acid (38.0 mg, 0.20 mmol), *n*-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl$_2$(p-cymene)]$_2$ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 8/1) yielded 4 (33.5 mg, 53%) as a white solid.

M. p. 94 °C

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 8.16 (s, 1H), 7.95 – 7.90 (m, 1H), 7.69 – 7.65 (m, 1H), 5.91 (t, $J = 6.5$ Hz, 1H), 4.14 (t, $J = 6.7$ Hz, 2H), 3.05 – 2.82 (m, 2H), 1.63 – 1.55 (m, 2H), 1.34 (dq, $J = 14.7$, 7.4 Hz, 2H), 0.91 (t, $J = 7.4$ Hz, 3H).

**$^{13}$C NMR** (125 MHz, CDCl$_3$) $\delta$ 168.9 (C$_q$), 168.3 (C$_q$), 151.9 (C$_q$), 132.6 (q, $J_{C-F} = 33.5$ Hz, C$_q$), 131.1 (q, $J_{C-F} = 3.5$ Hz, CH), 127.0 (C$_q$), 123.2 (CH), 123.2 (d, $J_{C-F} = 272.8$ Hz, C$_q$), 123.1 (q, $J_{C-F} = 4.1$ Hz, CH), 77.0 (CH), 65.4 (CH$_2$), 39.0 (CH$_2$), 30.5 (CH$_2$), 19.0 (CH$_2$), 13.6 (CH$_3$).

**$^{19}$F NMR** (282 MHz, CDCl$_3$) $\delta$ -62.6.

IR (ATR): 2962, 2935, 1779, 1734, 1398, 1329, 1168, 1126, 1007, 615 cm$^{-1}$.

**MS (ESI)** $m/z$ (relative intensity): 317 (30) [M+H]$^+$, 339 (70) [M+Na]$^+$.

**HR-MS (ESI)** C$_{15}$H$_{16}$F$_3$O$_4$ [M+H]$^+$: 317.0996, found: 317.0995.

The spectral data were in accordance with those reported in the literature.$^{[4]}$
Butyl 2-(5-(dimethylamino)-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (13)

\[
\text{Me}_2\text{N} \begin{array}{c} \text{C} \\ \text{O} \\ \text{CO}_2\text{nBu} \end{array} 
\]

GP1 was followed using 3-(dimethylamino)benzoic acid (33.0 mg, 0.20 mmol), \textit{n}-butyl acrylate (76.9 mg, 0.60 mmol), \([\text{OsCl}_2(\text{p-cymene})]_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\textsubscript{2}O (2.0 mL). Purification by column chromatography on silica gel (\textit{n}-hexane/EtOAc: 8/1) yielded 13 (39.6 mg, 68\%) as a colorless oil.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.27 (d, \(J = 8.5\ \text{Hz}, 1\text{H}\)), 7.08 (d, \(J = 2.4\ \text{Hz}, 1\text{H}\)), 6.98 (dd, \(J = 8.5, 2.4\ \text{Hz}, 1\text{H}\)), 5.77 (t, \(J = 6.6\ \text{Hz}, 1\text{H}\)), 4.14 (t, \(J = 6.7\ \text{Hz}, 2\text{H}\)), 3.00 (s, 6\text{H}), 2.91 – 2.72 (m, 2\text{H}), 1.65 – 1.55 (m, 2\text{H}), 1.35 (dq, \(J = 14.7, 7.4\ \text{Hz}, 2\text{H}\)), 0.91 (t, \(J = 7.4\ \text{Hz}, 3\text{H}\)).

\textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 170.9 (C\text{q}), 169.6 (C\text{q}), 151.5 (C\text{q}), 136.2 (C\text{q}), 126.9 (C\text{q}), 122.3 (CH), 118.7 (CH), 106.9 (CH), 76.9 (CH), 65.0 (CH\text{2}), 40.6 (CH\text{3}), 40.1 (CH\text{2}), 30.5 (CH\text{2}), 19.1 (CH\text{2}), 13.7 (CH\text{3}).

IR (ATR): 2959, 2930, 1767, 1758, 1625, 1510, 1345, 1166, 776, 567 cm\textsuperscript{-1}.

MS (ESI) \(m/\text{z}\) (relative intensity): 292 (70) [M+H]\textsuperscript{+}, 314 (30) [M+Na]\textsuperscript{+}.

HR-MS (ESI) \(\text{C}_{16}\text{H}_{22}\text{NO}_4\) [M+H]\textsuperscript{+} : 292.1545, found: 292.1543.
Butyl 2-(6-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (14)

GP1 was followed using 4-methyl benzoic acid (27.2 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 14 (43.0 mg, 82%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 7.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.28 – 7.22 (m, 1H), 5.80 (t, J = 6.6 Hz, 1H), 4.14 (t, J = 6.7 Hz, 2H), 2.93 – 2.77 (m, 2H), 2.46 (s, 3H), 1.64 – 1.56 (m, 2H), 1.35 (dq, J = 14.7, 7.4 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 169.9 (C₉), 169.4 (C₉), 149.4 (C₄₉), 145.6 (C₄₉), 130.7 (CH), 125.6 (CH), 123.4 (C₉), 122.4 (CH), 76.7 (CH), 65.2 (CH₂), 39.6 (CH₂), 30.5 (CH₂), 22.1 (CH₃), 19.1 (CH₂), 13.7 (CH₃).

IR (ATR): 2960, 2932, 1768, 1758, 1617, 1314, 1279, 1166, 1012, 687 cm⁻¹.

MS (ESI) m/z (relative intensity): 263 (60) [M+H]⁺, 285 (40) [M+Na]⁺.

HR-MS (ESI) C₁₅H₁₉O₄ [M+H]⁺: 263.1278, found: 263.1278.

The spectral data were in accordance with those reported in the literature.[3]
Butyl 2-(6-(tert-butyl)-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (15)

GP1 was followed using 4-tert-butyl benzoic acid (35.6 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 15 (40.8 mg, 67%) as a white solid.

M. p. 96°C

¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 8.2 Hz, 1H), 7.57 (dd, J = 8.2, 1.6 Hz, 1H), 7.47 – 7.42 (m, 1H), 5.84 (t, J = 6.7 Hz, 1H), 4.15 (td, J = 6.7, 2.7 Hz, 2H), 2.96 – 2.80 (m, 2H), 1.61 (dt, J = 14.6, 6.7 Hz, 2H), 1.38 – 1.32 (m, 2H), 1.34 (s, 9H), 0.91 (t, J = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 169.9 (Cₖ), 169.5 (Cₖ), 158.7 (Cₖ), 149.2 (Cₖ), 127.2 (CH), 125.4 (CH), 123.3 (Cₖ), 118.5 (CH), 77.0 (CH), 65.1 (CH₂), 39.8 (CH₂), 35.6 (Cₖ), 31.2 (CH₃), 30.6 (CH₂), 19.1 (CH₂), 13.7 (CH₃).

IR (ATR): 2967, 2935, 1771, 1750, 1697, 1315, 1280, 1005, 874, 666 cm⁻¹.

MS (ESI) m/z (relative intensity): 305 (60) [M+H]⁺, 327 (40) [M+Na]⁺.

HR-MS (ESI) C₁₈H₂₅O₄ [M+H]⁺: 305.1749, found: 305.1747.

The spectral data were in accordance with those reported in the literature.[³]
Butyl 2-(6-methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (16)

GP1 was followed using 4-methoxybenzoic acid (30.4 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl2(p-cymene)]2 (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H2O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 16 (47.3 mg, 85%) as a colorless oil.

1H NMR (400 MHz, CDCl3) δ 7.79 (d, J = 8.6 Hz, 1H), 7.03 (dd, J = 8.6, 2.2 Hz, 1H), 6.91 (d, J = 2.2 Hz, 1H), 5.78 (t, J = 6.6 Hz, 1H), 4.15 (t, J = 6.7 Hz, 2H), 3.87 (s, 3H), 2.95 – 2.77 (m, 2H), 1.64 – 1.56 (m, 2H), 1.35 (dq, J = 14.6, 7.4 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H).

13C NMR (125 MHz, CDCl3) δ 169.6 (Cq), 169.4 (Cq), 164.8 (Cq), 151.6 (Cq), 127.3 (CH), 118.2 (Cq), 116.7 (CH), 106.2 (CH), 76.2 (CH), 65.2 (CH2), 55.8 (CH3), 39.6 (CH2), 30.5 (CH2), 19.1 (CH2), 13.7 (CH3).

IR (ATR): 2960, 2935, 1759, 1731, 1605, 1460, 1359, 1281, 1253, 1007, 690 cm⁻¹.

MS (ESI) m/z (relative intensity): 279 (60) [M+H]+, 301 (40) [M+Na]+.

HR-MS (ESI) C15H19O5 [M+H]+: 279.1229, found: 279.1227.

The spectral data were in accordance with those reported in the literature.[4]
Butyl 2-(6-fluoro-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (17)

GPI was followed using 4-fluorobenzoic acid (28.0 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl$_2$(p-cymene)]$_2$ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 17 (24.5 mg, 46%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (dd, $J = 8.4$, 4.8 Hz, 1H), 7.25 – 7.17 (m, 2H), 5.81 (t, $J = 6.6$ Hz, 1H), 4.15 (t, $J = 6.7$ Hz, 2H), 3.02 – 2.78 (m, 2H), 1.65 – 1.57 (m, 2H), 1.35 (dq, $J = 14.7$, 7.4 Hz, 2H), 0.91 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 169.1 (C$_q$), 168.2 (d, $J = 75.8$ Hz, C$_q$), 165.3 (C$_q$), 151.6 (d, $J_{C-F} = 10.3$ Hz, C$_q$), 128.2 (d, $J_{C-F} = 10.4$ Hz, CH), 122.0 (d, $J_{C-F} = 2.0$ Hz, C$_q$), 117.8 (d, $J_{C-F} = 24.0$ Hz, CH), 109.8 (d, $J_{C-F} = 24.9$ Hz, CH), 76.2 (d, $J_{C-F} = 2.9$ Hz, CH), 65.3 (CH$_2$), 39.2 (CH$_2$), 30.5 (CH$_2$), 19.0 (CH$_2$), 13.6 (CH$_3$).

$^{19}$F NMR (282 MHz, CDCl$_3$) δ -102.13 (td, $J = 8.4$, 4.9 Hz).

IR (ATR): 2961, 1934, 1761, 1723, 1604, 1243, 1008, 882, 742, 682 cm$^{-1}$.

MS (ESI) $m/z$ (relative intensity): 267 (30) [M+H]$^+$, 289 (70) [M+Na]$^+$.

HR-MS (ESI) C$_{14}$H$_{16}$FO$_4$ [M+H]$^+$: 267.1030, found: 267.1027.

The spectral data were in accordance with those reported in the literature.$^{[4]}$
**Butyl 2-(6-chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (18)**

GP1 was followed using 4-chlorobenzoic acid (31.3 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl\(_2\)(p-cymene)]\(_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\(_2\)O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 18 (28.3 mg, 50%) as a colorless oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.81 (d, \(J = 8.6\) Hz, 1H), 7.53 – 7.49 (m, 2H), 5.81 (t, \(J = 6.6\) Hz, 1H), 4.14 (t, \(J = 6.7\) Hz, 2H), 3.01 – 2.78 (m, 2H), 1.64 – 1.56 (m, 2H), 1.35 (dq, \(J = 14.7, 7.4\) Hz, 2H), 0.91 (t, \(J = 7.4\) Hz, 3H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 169.1 (C\(_q\)), 168.7 (C\(_q\)), 150.4 (C\(_q\)), 141.0 (C\(_q\)), 130.3 (CH), 127.0 (CH), 124.5 (C\(_q\)), 122.8 (CH), 76.4 (CH), 65.3 (CH\(_2\)), 39.2 (CH\(_2\)), 30.5 (CH\(_2\)), 19.0 (CH\(_2\)), 13.6 (CH\(_3\)).

IR (ATR): 2960, 2932, 1768, 1722, 1617, 1314, 1166, 1012, 904, 687 cm\(^{-1}\).

MS (ESI) \(m/\epsilon\) (relative intensity): 283 (55) [M+H]\(^+\), 305 (45) [M+Na]\(^+\).

HR-MS (ESI) C\(_{14}\)H\(_{16}\)ClO\(_4\) [M+H]\(^+\): 283.0733, found: 283.0732.

The spectral data were in accordance with those reported in the literature.\(^{[4]}\)
Butyl 2-(6-bromo-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (19)

\[
\begin{align*}
&\text{Br} \\
&\text{CO}_2\text{Bu}
\end{align*}
\]

**GP1** was followed using 4-bromobenzoic acid (40.2 mg, 0.20 mmol), \textit{n}-butyl acrylate (76.9 mg, 0.60 mmol), \([\text{OsCl}_2(\text{p-cymene})]_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\textsubscript{2}O (2.0 mL). Purification by column chromatography on silica gel (\textit{n}-hexane/EtOAc: 8/1) yielded **19** (34.7 mg, 53\%) as a colorless oil.

\textbf{1H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.74 (d, \(J = 8.7\) Hz, 1H), 7.69 – 7.66 (m, 2H), 5.82 (t, \(J = 6.6\) Hz, 1H), 4.15 (t, \(J = 6.8\) Hz, 2H), 3.02 – 2.77 (m, 2H), 1.66 – 1.54 (m, 2H), 1.35 (dq, \(J = 14.7, 7.4\) Hz, 2H), 0.92 (t, \(J = 7.4\) Hz, 3H).

\textbf{13C NMR} (125 MHz, CDCl\textsubscript{3}) \(\delta\) 169.1 (C\textsubscript{q}), 168.8 (C\textsubscript{q}), 150.5 (C\textsubscript{q}), 133.2 (CH), 129.5 (C\textsubscript{q}), 127.1 (CH), 125.8 (CH), 125.0 (C\textsubscript{q}), 76.3 (CH), 65.3 (CH\textsubscript{2}), 39.2 (CH\textsubscript{2}), 30.5 (CH\textsubscript{2}), 19.1 (CH\textsubscript{2}), 13.6 (CH\textsubscript{3}).

**IR** (ATR): 2959, 2933, 1761, 1722, 1588, 1395, 1263, 1210, 1062, 781 cm\textsuperscript{-1}.

**MS** (ESI) \(m/\zeta\) (relative intensity): 327 (50) \([\text{M+H}]^+\), 349 (50) \([\text{M+Na}]^+\).

**HR-MS** (ESI) \(C_{14}H_{16}^{79}\text{BrO}_4\) \([\text{M+H}]^+\): 327.0231, found: 327.0226.

The spectral data were in accordance with those reported in the literature.\([4]\)
Butyl 2-(6-iodo-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (20)

GP1 was followed using 4-iodobenzoic acid (49.6 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 20 (45.6 mg, 61%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.87 (m, 2H), 7.62 – 7.59 (m, 1H), 5.80 (t, J = 6.6 Hz, 1H), 4.15 (td, J = 6.7, 1.6 Hz, 2H), 2.99 – 2.78 (m, 2H), 1.64 – 1.57 (m, 2H), 1.35 (dq, J = 14.8, 7.4 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 169.1 (Cₗ), 169.1 (Cₗ), 150.4 (Cₗ), 139.0 (CH), 131.7 (CH), 127.0 (CH), 125.5 (Cₗ), 102.1 (Cₗ), 76.2 (CH), 65.3 (CH₂), 39.2 (CH₂), 30.5 (CH₂), 19.1 (CH₂), 13.7 (CH₃).

IR (ATR): 2958, 2931, 1765, 1728, 1584, 1395, 1264, 1178, 1007, 678 cm⁻¹.

MS (ESI) m/z (relative intensity): 375 (60) [M+H]⁺, 397 (40) [M+Na]⁺.

HR-MS (ESI) C₁₄H₁₆IO₄ [M+H]⁺: 375.0088, found: 375.0089. C₁₄H₁₅IO₄Na [M+Na]⁺: 396.9909, found: 396.9907.

The spectral data were in accordance with those reported in the literature.⁴
Butyl 2-(6-(dimethylamino)-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (21)

GP1 was followed using 4-(dimethylamino)benzoic acid (33.0 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 21 (48.9 mg, 84%) as a colorless oil.

^1H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.7 Hz, 1H), 6.72 (dd, J = 8.7, 2.2 Hz, 1H), 6.51 (d, J = 2.2 Hz, 1H), 5.70 (t, J = 6.6 Hz, 1H), 4.12 (t, J = 6.7 Hz, 2H), 3.05 (s, 6H), 2.82 (dd, J = 6.6, 4.2 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.34 (dq, J = 14.7, 7.4 Hz, 2H), 0.89 (t, J = 7.4 Hz, 3H).

^13C NMR (125 MHz, CDCl₃) δ 170.4 (Cₗ), 169.7 (Cₗ), 154.4 (Cₗ), 151.7 (Cₗ), 126.7 (CH), 113.0 (CH), 112.3 (Cₗ), 102.4 (CH), 76.2 (CH), 65.0 (CH₂), 40.3 (CH₃), 40.0 (CH₂), 30.5 (CH₂), 19.0 (CH₂), 13.6 (CH₃).

IR (ATR): 2958, 2931, 1723, 1605, 1519, 1351, 1116, 1005, 791, 692 cm⁻¹.

MS (ESI) m/z (relative intensity): 292 (60) [M+H]^+, 314 (40) [M+Na]^+.

HR-MS (ESI) C₁₆H₂₂NO₄ [M+H]^+: 292.1544, found: 292.1543.

The spectral data were in accordance with those reported in the literature.[11]
Butyl 2-(4,5-dimethyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (22)

\[
\text{Butyl 2-(4,5-dimethyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (22)}
\]

\[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{Me} \\
\text{CO}_2\text{nBu}
\end{array}
\]

**GPI** was followed using 2,3-dimethylbenzoic acid (30.0 mg, 0.20 mmol), *n*-butyl acrylate (76.9 mg, 0.60 mmol), \([\text{OsCl}_2(\rho\text{-cymene})]_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (\(n\)-hexane/EtOAc: 8/1) yielded 22 (36.5 mg, 66\%) as a colorless oil.

**¹H NMR** (400 MHz, CDCl₃) δ 7.38 (d, \(J = 7.7\) Hz, 1H), 7.13 (d, \(J = 7.7\) Hz, 1H), 5.72 (t, \(J = 6.5\) Hz, 1H), 4.12 (t, \(J = 6.7\) Hz, 2H), 2.81 (d, \(J = 6.5\) Hz, 2H), 2.60 (s, 3H), 2.32 (s, 3H), 1.62 – 1.54 (m, 2H), 1.33 (dq, \(J = 14.7, 7.4\) Hz, 2H), 0.90 (t, \(J = 7.4\) Hz, 3H).

**¹³C NMR** (125 MHz, CDCl₃) δ 170.4 (Cₓ), 169.5 (Cₓ), 147.0 (Cₓ), 138.7 (Cₓ), 138.4 (Cₓ), 135.5 (CH), 123.3 (Cₓ), 118.6 (CH), 75.3 (CH), 65.0 (CH₂), 39.9 (CH₂), 30.5 (CH₂), 19.1 (CH₃), 19.0 (CH₂), 13.6 (CH₃), 13.2 (CH₃).

**IR** (ATR): 2959, 2933, 1761, 1726, 1457, 1288, 1210, 1173, 1008, 910, 699 cm⁻¹.

**MS** (ESI) \(m/z\) (relative intensity): 277 (60) [M+H]⁺, 299 (40) [M+Na]⁺.

**HR-MS** (ESI) C₁₆H₂₁O₄ [M+H]⁺: 277.1436, found: 277.1434.
Butyl 2-(4,6-dimethyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (23)

GPI was followed using 2,4-dimethylbenzoic acid (30.0 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 23 (42.0 mg, 76%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.07 (s, 1H), 7.03 (s, 1H), 5.73 (t, J = 6.5 Hz, 1H), 4.13 (t, J = 6.6 Hz, 2H), 2.82 (d, J = 6.5 Hz, 2H), 2.61 (s, 3H), 2.40 (s, 3H), 1.63 – 1.57 (m, 2H), 1.34 (dq, J = 14.7, 7.4 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 170.0 (C₉), 169.5 (C₉), 149.8 (C₉), 145.1 (C₉), 139.5 (C₉), 132.2 (CH), 120.9 (C₉), 119.6 (CH), 75.8 (CH), 65.1 (CH₂), 39.8 (CH₂), 30.5 (CH₂), 21.9 (CH₃), 19.0 (CH₂), 17.2 (CH₃), 13.6 (CH₃).

IR (ATR): 2959, 2931, 1762, 1729, 1604, 1343, 1271, 1172, 1014, 686 cm⁻¹.

MS (ESI) m/z (relative intensity): 277 (70) [M+H]⁺, 299 (30) [M+Na]⁺.

HR-MS (ESI) C₁₆H₂₁O₄ [M+H]⁺: 277.1435, found: 277.1434.

The spectral data were in accordance with those reported in the literature.[⁴]
Butyl 2-(4,5-dimethoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (24)

\[
\text{MeO} \quad \text{OMe} \quad \text{CO}_2nBu
\]

GPI was followed using 2,3-dimethoxybenzoic acid (36.4 mg, 0.20 mmol), \textit{n}-butyl acrylate (76.9 mg, 0.60 mmol), \([\text{OsCl}_2(\text{p-cymene})]_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\textsubscript{2}O (2.0 mL). Purification by column chromatography on silica gel (\textit{n}-hexane/EtOAc: 8/1) yielded 24 (39.5 mg, 64\%) as a colorless oil.

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.18 (d, \(J = 8.3\) Hz, 1H), 7.05 (d, \(J = 8.3\) Hz, 1H), 5.72 (d, \(J = 7.0\) Hz, 1H), 4.12 (t, \(J = 6.7\) Hz, 2H), 4.06 (s, 3H), 3.88 (s, 3H), 2.90 – 2.73 (m, 2H), 1.63 – 1.54 (m, 2H), 1.34 (dq, \(J = 14.6, 7.4\) Hz, 2H), 0.90 (t, \(J = 7.4\) Hz, 3H).

\textbf{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}) \(\delta\) 169.4 (C\textsubscript{q}), 167.3 (C\textsubscript{q}), 152.8 (C\textsubscript{q}), 148.4 (C\textsubscript{q}), 141.7 (C\textsubscript{q}), 119.4 (CH), 118.1 (C\textsubscript{q}), 116.5 (CH), 75.7 (CH), 65.1 (CH\textsubscript{2}), 62.4 (CH\textsubscript{3}), 56.8 (CH\textsubscript{3}), 40.0 (CH\textsubscript{2}), 30.5 (CH\textsubscript{3}), 19.0 (CH\textsubscript{2}), 13.6 (CH\textsubscript{3}).

\textbf{IR} (ATR): 2960, 2934, 1759, 1729, 1497, 1270, 1175, 1113, 1010, 825 cm\textsuperscript{-1}.

\textbf{MS} (ESI) \textit{m/z} (relative intensity): 309 (70) [M+H]\textsuperscript{+}, 331 (30) [M+Na]\textsuperscript{+}.

\textbf{HR-MS} (ESI) \textit{C}_{16}\textit{H}_{21}\textit{O}_{6} [M+H]\textsuperscript{+}: 309.1335, found: 309.1333.

The spectral data were in accordance with those reported in the literature.\textsuperscript{[4]}
Butyl 2-(4,6-dimethoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (25)

\[
\text{GPI was followed using 2,4-dimethoxybenzoic acid (36.4 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl}_2(p\text{-cymene})_2 (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H}_2\text{O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 25 (45.0 mg, 73\%) as a colorless oil.}
\]

\[\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) \delta 6.47 (d, J = 1.8 Hz, 1H), 6.42 (d, J = 1.8 Hz, 1H), 5.69 (t, J = 6.6 Hz, 1H), 4.14 (t, J = 6.7 Hz, 2H), 3.93 (s, 3H), 3.86 (s, 3H), 2.92 – 2.74 (m, 2H), 1.67 – 1.55 (m, 2H), 1.36 (dq, J = 14.7, 7.4 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H).}
\]

\[\text{\textsuperscript{13}C NMR (125 MHz, CDCl}_3) \delta 169.5 (C}_q, 167.7 (C}_q, 166.9 (C}_q, 159.7 (C}_q, 153.9 (C}_q, 106.6 (C}_q, 99.1 (CH), 97.8 (CH), 75.6 (CH), 65.1 (CH}_2, 56.0 (CH}_3, 55.9 (CH}_3, 39.8 (CH}_2, 30.5 (CH}_2, 19.1 (CH}_2, 13.7 (CH}_3).}
\]

\[\text{IR (ATR): 2960, 2874, 1754, 1731, 1614, 1457, 1337, 1158, 1011, 689 cm}^{-1}.\]

\[\text{MS (ESI) m/z (relative intensity): 309 (80) [M+H]}^+, 331 (20) [M+Na]^+.
\]

\[\text{HR-MS (ESI) C}_{16}\text{H}_{21}\text{O}_6 [M+H]^+: 309.1335, found: 309.1333.}
\]

The spectral data were in accordance with those reported in the literature.\textsuperscript{[12]}
Butyl 2-(5,7-dimethoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (26)

GP1 was followed using 3,5-dimethoxybenzoic acid (36.4 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 26 (43.8 mg, 71%) as a colorless oil.

**¹H NMR** (400 MHz, CDCl₃) δ 6.89 (d, J = 1.9 Hz, 1H), 6.65 (d, J = 1.9 Hz, 1H), 5.79 (dd, J = 8.8, 3.2 Hz, 1H), 4.10 (t, J = 6.7 Hz, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.23 (dd, J = 16.3, 3.2 Hz, 2H), 2.58 (dd, J = 16.3, 8.8 Hz, 2H), 1.33 (dq, J = 14.6, 7.4 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H).

**¹³C NMR** (125 MHz, CDCl₃) δ 170.0 (C₆), 169.5 (C₆), 162.8 (C₆), 154.8 (C₆), 129.5 (C₆), 128.6 (C₆), 104.9 (CH), 98.7 (CH), 76.2 (CH), 64.9 (CH₂), 55.9 (CH₃), 55.7 (CH₃), 38.1 (CH₂), 30.5 (CH₂), 19.1 (CH₂), 13.7 (CH₃).

**IR** (ATR): 2960, 2933, 1767, 1607, 1503, 1332, 1173, 1005, 634 cm⁻¹.

**MS** (ESI) m/z (relative intensity): 309 (40) [M+H]⁺, 331 (60) [M+Na]⁺.

**HR-MS** (ESI) C₁₆H₂₁O₆ [M+H]⁺: 309.1334, found: 309.1333.

The spectral data were in accordance with those reported in the literature.^[4]
Butyl 2-(5,6,7-trimethoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (27)

**GP1** was followed using 3,4,5-trimethoxybenzoic acid (42.4 mg, 0.20 mmol), \(n\)-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl\(_2\)(p-cymene)]\(_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\(_2\)O (2.0 mL). Purification by column chromatography on silica gel (\(n\)-hexane/EtOAc: 8/1) yielded **27** (39.9 mg, 59%) as a colorless oil.

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.10 (s, 1H), 5.80 (dd, \(J = 8.5, 3.4\) Hz, 1H), 4.10 (t, \(J = 6.7\) Hz, 2H), 3.97 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H), 3.17 (dd, \(J = 16.2, 3.4\) Hz, 1H), 2.63 (dd, \(J = 16.2, 8.6\) Hz, 1H), 1.62 – 1.53 (m, 2H), 1.39 – 1.28 (m, 2H), 0.90 (t, \(J = 7.4\) Hz, 3H).

**\(^{13}\)C NMR** (125 MHz, CDCl\(_3\)) \(\delta\) 169.8 (C\(\alpha\)), 169.4 (C\(\alpha\)), 156.0 (C\(\alpha\)), 147.4 (C\(\alpha\)), 146.7 (C\(\alpha\)), 133.7 (C\(\alpha\)), 121.3 (C\(\alpha\)), 102.6 (CH), 75.8 (CH), 65.0 (CH\(_2\)), 61.1 (CH\(_3\)), 60.9 (CH\(_3\)), 56.4 (CH\(_3\)), 38.4 (CH\(_2\)), 30.5 (CH\(_2\)), 19.0 (CH\(_2\)), 13.7 (CH\(_3\)).

**IR** (ATR): 2960, 2936, 1771, 1733, 1615, 1478, 1340, 1250, 1105, 765 cm\(^{-1}\).

**MS** (ESI) \(m/z\) (relative intensity): 339 (60) [M+H]\(^+\), 361 (40) [M+Na]\(^+\).

**HR-MS** (ESI) \(C_{17}H_{23}O_7\) [M+H]\(^+\): 339.1441, found: 339.1438.

The spectral data were in accordance with those reported in the literature.\(^{[4]}\)
Butyl 2-(1-oxo-1,3-dihyronaphtho[1,2-c]furan-3-yl)acetate (5)

GPI was followed using naphthoic acid (34.4 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl$_2$(p-cymene)]$_2$ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 5 (35.2 mg, 74%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.99 (d, $J = 8.3$ Hz, 1H), 8.13 (d, $J = 8.3$ Hz, 1H), 7.95 (d, $J = 8.3$ Hz, 1H), 7.72 (ddd, $J = 8.3$, 7.0, 1.3 Hz, 1H), 7.63 (ddd, $J = 8.3$, 7.0, 1.3 Hz, 1H), 7.51 (d, $J = 8.3$ Hz, 1H), 5.94 (t, $J = 6.6$ Hz, 1H), 4.16 (t, $J = 6.7$ Hz, 2H), 2.94 (d, $J = 6.6$ Hz, 2H), 1.64–1.56 (m, 2H), 1.34 (dq, $J = 14.9$, 7.4 Hz, 2H), 0.89 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.1 (C$_q$), 169.4 (C$_q$), 150.4 (C$_q$), 135.7 (CH), 133.5 (C$_q$), 129.2 (CH), 129.1 (C$_q$), 128.4 (CH), 127.5 (CH), 123.6 (CH), 120.3 (C$_q$), 118.4 (CH), 76.4 (CH), 65.2 (CH$_2$), 39.4 (CH$_2$), 30.5 (CH$_2$), 19.1 (CH$_2$), 13.6 (CH$_3$).

IR (ATR): 2961, 2933, 1760, 1734, 1610, 1699, 1340, 1291, 1154, 1009, 844, 596 cm$^{-1}$.

MS (ESI) $m/z$ (relative intensity): 299 (70) [M+H]$^+$, 321 (30) [M+Na]$^+$.

HR-MS (ESI) C$_{18}$H$_{19}$O$_4$ [M+H]$^+$: 299.1278, found: 299.1278.

The spectral data were in accordance with those reported in the literature.$^{[13]}$
**tert-Butyl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (28)**

![Chemical Structure]

**GPI** was followed using 2-methylbenzoic acid (27.2 mg, 0.20 mmol), tert-butyl acrylate (76.9 mg, 0.60 mmol), \([\text{OsCl}_2(p\text{-cymene})]_2\) (7.9 mg, 5.0 mol%), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 28 (19.9 mg, 38%) as a colorless oil.

**¹H NMR** (400 MHz, CDCl₃) δ 7.50 (t, J = 7.6 Hz, 1H), 7.30 – 7.22 (m, 2H), 5.74 (t, J = 6.4 Hz, 1H), 2.79 (dd, J = 6.4, 2.7 Hz, 2H), 2.67 (s, 3H), 1.42 (s, 9H).

**¹³C NMR** (125 MHz, CDCl₃) δ 170.2 (C₉), 168.5 (C₉), 149.5 (C₉), 139.8 (C₉), 133.8 (CH), 131.0 (CH), 123.6 (C₉), 119.2 (CH), 81.9 (C₉), 40.8 (CH), 29.7 (CH₂), 28.0 (CH₃), 17.3 (CH₃).

**IR** (ATR): 2959, 2931, 1760, 1722, 1486, 1304, 1210, 1157, 1005, 627 cm⁻¹.

**MS** (ESI) m/z (relative intensity): 263 (45) [M+H]⁺, 285 (55) [M+Na]⁺.

**HR-MS** (ESI) C₁₅H₁₉O₄ [M+H]⁺: 263.1278, found: 263.1278.

The spectral data were in accordance with those reported in the literature.⁴
Hexyl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (29)

**GPI** was followed using 2-methylbenzoic acid (27.2 mg, 0.20 mmol), *n*-hexyl acrylate (93.7 mg, 0.60 mmol), [OsCl$_2$(*p*-cymene)]$_2$ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 8/1) yielded **29** (46.5 mg, 80%) as a colorless oil.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.50 (t, $J = 7.6$ Hz, 1H), 7.30 – 7.21 (m, 2H), 5.79 (t, $J = 6.6$ Hz, 1H), 4.12 (t, $J = 6.8$ Hz, 2H), 2.85 (d, $J = 6.6$ Hz, 2H), 2.66 (s, 3H), 1.66 – 1.54 (m, 2H), 1.37 – 1.22 (m, 6H), 0.86 (t, $J = 6.9$ Hz, 3H).

**$^{13}$C NMR** (125 MHz, CDCl$_3$) $\delta$ 170.0 (C$_q$), 169.4 (C$_q$), 149.3 (C$_q$), 139.9 (C$_q$), 133.9 (CH), 131.1 (CH), 123.4 (C$_q$), 119.2 (CH), 76.0 (CH), 65.4 (CH$_2$), 39.8 (CH$_2$), 31.4 (CH$_2$), 28.4 (CH$_2$), 25.5 (CH$_2$), 22.5 (CH$_2$), 17.3 (CH$_3$), 14.0 (CH$_3$).

**IR** (ATR): 2960, 2935, 1763, 1739, 1601, 1448, 1328, 1175, 1057, 691 cm$^{-1}$.

**MS** (ESI) $m$/z (relative intensity): 291 (70) [M+H]$^+$, 313 (30) [M+Na]$^+$.

**HR-MS** (ESI) C$_{17}$H$_{23}$O$_4$ [M+H]$^+$: 291.1594, found: 291.1591.
Pentan-3-yl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (30)

![Chemical structure of the compound](image)

GP1 was followed using 2-methylbenzoic acid (27.2 mg, 0.20 mmol), pentan-3-yl acrylate (85.3 mg, 0.60 mmol), [OsCl$_2$(p-cymene)]$_2$ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL). Purification by column chromatography on silica gel ($n$-hexane/EtOAc: 8/1) yielded 30 (35.9 mg, 65%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 7.6$ Hz, 1H), 7.30 – 7.23 (m, 2H), 5.79 (t, $J = 6.6$ Hz, 1H), 4.06 (dd, $J = 5.8$, 2.4 Hz, 2H), 2.86 (d, $J = 6.6$ Hz, 2H), 2.67 (s, 3H), 1.50 (dt, $J = 12.6$, 6.4 Hz, 1H), 1.38 – 1.25 (m, 4H), 0.86 (t, $J = 7.4$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.0 (C$_q$), 169.5 (C$_q$), 149.3 (C$_q$), 139.9 (C$_q$), 133.9 (CH), 131.1 (CH), 123.4 (C$_q$), 119.2 (CH), 76.0 (CH), 67.3 (CH$_2$), 40.2 (CH), 39.8 (CH$_2$), 23.2 (CH$_2$), 23.2 (CH$_2$), 17.3 (CH$_3$), 11.0 (CH$_3$), 10.9 (CH$_3$).

IR (ATR): 2960, 2933, 1758, 1730, 1495, 1453, 1310, 1277, 1005, 690 cm$^{-1}$.

MS (ESI) $m/z$ (relative intensity): 291 (60) [M+H]$^+$, 313 (40) [M+Na]$^+$.

HR-MS (ESI) $C_{17}H_{23}O_4$ [M+H]$^+$: 291.1595, found: 291.1591.
3-Methylbut-3-en-1-yl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (31)

GPI was followed using 2-methylbenzoic acid (27.2 mg, 0.20 mmol), 3-methylbut-3-en-1-yl acrylate (84.1 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 31 (42.8 mg, 78%) as a colorless oil.

_¹H NMR_ (400 MHz, CDCl₃) δ 7.51 (d, J = 7.6 Hz, 1H), 7.30 – 7.23 (m, 2H), 5.79 (t, J = 6.6 Hz, 1H), 4.82 – 4.76 (m, 1H), 4.75 – 4.68 (m, 1H), 4.26 (t, J = 6.9 Hz, 2H), 2.85 (d, J = 6.6 Hz, 2H), 2.67 (s, 3H), 2.34 (t, J = 6.9 Hz, 2H), 1.74 (s, 3H).

_¹³C NMR_ (125 MHz, CDCl₃) δ 170.0 (Cₜ), 169.3 (Cₜ), 149.2 (Cₜ), 141.3 (Cₜ), 140.0 (Cₜ), 133.9 (CH), 131.1(CH), 123.4 (Cₜ), 119.2 (CH), 112.5 (CH₂), 76.0 (CH), 63.3 (CH₂), 39.8 (CH₂), 36.6 (CH₂), 22.4 (CH₃), 17.3 (CH₃).

_IR_ (ATR): 2959, 2933, 1760, 1735, 1599, 1467, 1345, 1170, 1005, 784, 698 cm⁻¹.

_MS_ (ESI) m/z (relative intensity): 275 (55) [M+H]⁺, 297 (45) [M+Na]⁺.

_HR-MS_ (ESI) C₁₆H₁₉O₄ [M+H]⁺: 275.1282, found: 275.1278.
Phenethyl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (32)

\[
\text{Phenethyl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (32)}
\]

**GPI** was followed using 2-methylbenzoic acid (27.2 mg, 0.20 mmol), phenethyl acrylate (85.9 mg, 0.60 mmol), \([\text{OsCl}_2(p\text{-cymene})]_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\textsubscript{2}O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 8/1) yielded 32 (44.1 mg, 71%) as a colorless oil.

\[ ^{1}\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.48 \ (d, J = 7.6 \text{ Hz, 1H}), 7.31 - 7.24 \ (m, 3H), 7.24 - 7.15 \ (m, 4H), 5.76 \ (t, J = 7.0 \text{ Hz, 1H}), 4.39 - 4.34 \ (m, 2H), 2.94 \ (d, J = 7.0 \text{ Hz, 2H}), 2.83 \ (dd, J = 6.6, 4.6 \text{ Hz, 2H}), 2.67 \ (s, 3H). \]

\[ ^{13}\text{C NMR} \ (125 \text{ MHz, CDCl}_3) \delta 170.0 \ (C_q), 169.2 \ (C_q), 149.2 \ (C_q), 140.0 \ (C_q), 137.4 \ (C_q), 133.9 \ (CH), 131.1 \ (CH), 128.8 \ (CH), 128.5 \ (CH), 126.6 \ (CH), 123.3 \ (C_q), 119.2 \ (CH), 75.9 \ (CH), 65.6 \ (CH_2), 39.8 \ (CH_2), 34.9 \ (CH_2), 17.3 \ (CH_3). \]

**IR** (ATR): 2959, 2931, 1765, 1730, 1605, 1344, 1277, 1137, 1010, 905, 686 cm\(^{-1}\).

**MS** (ESI) \( m/\text{z } \) (relative intensity): 311 (30) [M+H]\(^+\), 333 (70) [M+Na]\(^+\).

**HR-MS** (ESI) \( \text{C}_{19}\text{H}_{19}\text{O}_4 \) [M+H]\(^+\): 311.1280, found: 311.1278.
3.4-Bis(4-methoxyphenyl)-8-methyl-1H-isochromen-1-one (33)

GP2 was followed using 2-methylbenzoic acid (27.2 mg, 0.20 mmol), 1,2-bis(4-methoxyphenyl)ethyne (142.9 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded 33 (58.8 mg, 79%) as a yellow solid.

M. p. 143 °C

¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 2.0, 0.6 Hz, 1H), 7.41 (ddd, J = 8.3, 2.0, 0.6 Hz, 1H), 7.26 (d, J = 9.1 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.3 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 9.1 Hz, 2H), 3.84 (s, 3H), 3.74 (s, 3H), 2.44 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 162.6 (Cq), 159.7 (Cq), 159.2 (Cq), 150.0 (Cq), 137.9 (Cq), 137.0 (Cq), 135.8 (CH), 132.3 (CH), 130.5 (CH), 129.1 (CH), 126.8 (Cq), 125.5 (Cq), 125.1 (CH), 120.0 (Cq), 115.3 (Cq), 114.5 (CH), 113.3 (CH), 55.3 (CH₃), 55.2 (CH₃), 21.2 (CH₃).

IR (ATR): 2930, 1720, 1629, 1251, 1110, 1052, 964, 715, 631 cm⁻¹.

MS (ESI) m/z (relative intensity): 373 (55) [M+H]+, 395 (45) [M+Na]+.

HR-MS (ESI) C₂₇H₂₁O₂ [M+H]+: 377.1430, found: 377.1434.

The spectral data were in accordance with those reported in the literature. [⁵]
3,4-Bis(4-methoxyphenyl)-6,7-dimethyl-1H-isochromen-1-one (34)

GP2 was followed using 3,4-dimethylbenzoic acid (30.0 mg, 0.20 mmol), 1,2-bis(4-methoxyphenyl)ethyne (142.9 mg, 0.60 mmol), [OsCl$_2$(p-cymene)]$_2$ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded 34 (51.8 mg, 67%) as a yellow solid.

**M. p.** 172 °C

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (s, 1H), 7.29 (d, $J = 8.7$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.99 (d, $J = 8.5$ Hz, 2H), 6.96 (s, 1H), 6.73 (d, $J = 8.8$ Hz, 2H), 3.89 (s, 3H), 3.78 (s, 9H), 2.39 (s, 3H), 2.30 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.7 (C$_q$), 159.7(C$_q$), 159.2(C$_q$), 150.2(C$_q$), 144.8(C$_q$), 137.5 (C$_q$), 137.2 (C$_q$), 132.3 (CH), 130.6 (CH), 129.7 (CH), 126.9 (C$_q$), 125.7 (C$_q$), 125.6 (CH), 118.0 (C$_q$), 115.2 (C$_q$), 114.5 (CH), 113.2 (CH), 55.3 (CH$_3$), 55.2 (CH$_3$), 20.6 (CH$_3$), 19.6 (CH$_3$).

**IR** (ATR): 2951, 2712, 1719, 1570, 1201, 1109, 1059, 955, 720, 627 cm$^{-1}$.

**MS** (ESI) $m/z$ (relative intensity): 387 (100) [M+H]$^+$.

**HR-MS** (ESI) C$_{27}$H$_{21}$O$_2$ [M+H]$^+$: 387.1577, found: 387.1591.
3.4-Di-p-tolyl-7-(trifluoromethyl)-1H-isochromen-1-one (35)

\[ \text{F}_3\text{C} \quad \text{O} \quad \text{O} \quad \text{Me} \]

GP2 was followed using 3-trifluoromethyl benzoic acid (38.0 mg, 0.20 mmol), 1,2-di-p-tolylethyne (123.8 mg, 0.60 mmol), \([\text{OsCl}_2(\text{p-cymene})]_2\) (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\(_2\)O (2.0 mL). Purification by column chromatography on silica gel (\(n\)-hexane/EtOAc: 20/1) yielded 35 (43.4 mg, 55%) as a yellow solid.

**M. p.** 150 °C

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\): 8.68 (s, 1H), 7.82 (d, \(J = 8.3\) Hz, 1H), 7.44 (d, \(J = 8.3\) Hz, 1H), 7.34 (d, \(J = 8.1\) Hz, 1H), 7.30 – 7.28 (m, 2H), 7.20 – 7.12 (m, 1H), 7.15, (d, \(J = 8.2\) Hz, 2H), 7.05 (d, \(J = 8.2\) Hz, 2H), 2.45 (s, 3H), 2.32 (s, 3H).

\(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)) \(\delta\): 161.4 (C\(_q\)), 153.0 (C\(_q\)), 142.0 (C\(_q\)), 139.71 (C\(_q\)), 138.3 (C\(_q\)), 131.4 (CH), 130.9, 130.7 (q, \(J = 3.5\) Hz, CH), 130.5 (d, \(J = 61.7\) Hz), 129.6 (CH), 129.5 (CH), 129.1 (CH), 129.1 (CH), 128.7 (CH), 127.0 (q, \(J = 3.9\) Hz, CH)), 126.2 (CH), 123.5 (d, \(J = 272.2\) Hz, C\(_q\)), 120.3 (C\(_q\)), 115.7 (C\(_q\)), 21.4 (CH\(_3\)), 21.3 (CH\(_3\)).

\(^{19}\text{F NMR}\) (282 MHz, CDCl\(_3\)) \(\delta\): -62.69.

**IR** (ATR): 3013, 2949, 2704, 1701, 1519, 1212, 1106, 736, 570 cm\(^{-1}\).

**MS** (ESI) \(m/z\) (relative intensity): 395 (100) [M+H]\(^+\).

**HR-MS** (ESI) \(C_{27}H_{21}O_2\) [M+H]\(^+\): 395.1250, found: 395.1253.
3,4-Di-p-tolyl-1H-benzo[h]isochromen-1-one (6)

GP2 was followed using naphthoic acid (34.4 mg, 0.20 mmol), 1,2-di-p-tolylethylene (123.8 mg, 0.60 mmol), [OsCl$_2$(p-cymene)]$_2$ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded 6 (61.0 mg, 81%) as a yellow solid.

M. p. 197 °C

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.84 (d, $J$ = 8.7 Hz, 1H), 7.95 (d, $J$ = 8.7 Hz, 1H), 7.84 (d, $J$ = 8.0 Hz, 1H), 7.76 (ddd, $J$ = 8.7, 6.9, 1.4 Hz, 1H), 7.59 (ddd, $J$ = 8.0, 6.9, 1.1 Hz, 1H), 7.29 (d, $J$ = 8.0 Hz, 2H), 7.25 (d, $J$ = 6.9 Hz, 3H), 7.16 (d, $J$ = 8.0 Hz, 2H), 7.01 (d, $J$ = 8.0 Hz, 2H), 2.43 (s, 3H), 2.28 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.5 (C$_q$), 152.5 (C$_q$), 141.4 (C$_q$), 139.1 (C$_q$), 137.8 (C$_q$), 135.6 (CH), 132.5 (C$_q$), 131.8 (C$_q$), 131.5 (C$_q$), 131.2 (CH), 130.0 (C$_q$), 129.9 (CH), 129.3 (CH), 129.0 (CH), 128.6 (CH), 128.4 (CH), 130.0 (CH), 126.8 (CH), 122.7 (CH), 116.8 (C$_q$), 113.7 (C$_q$), 21.3 (CH$_3$), 21.3 (CH$_3$).

IR (ATR): 3057, 1712, 1591, 1508, 1216, 1105, 921, 753, 636, 503 cm$^{-1}$.

MS (ESI) $m/z$ (relative intensity): 377 (100) [M+H]$^+$.

HR-MS (ESI) C$_{27}$H$_{21}$O$_2$ [M+H]$^+$: 377.1535, found: 377.1536.
3,4-Diphenyl-1\textit{H}-benzo[\textit{h}]isochromen-1-one (36)

\begin{center}
\includegraphics[width=0.3\textwidth]{structure.png}
\end{center}

\textbf{GP2} was followed using 2-methyl benzoic acid (34.4 mg, 0.20 mmol), 1,2-diphenylethyne (106.9 mg, 0.60 mmol), [OsCl\textsubscript{2}(p-cymene)]\textsubscript{2} (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\textsubscript{2}O (2.0 mL). Purification by column chromatography on silica gel (\textit{n}-hexane/EtOAc: 20/1) yielded \textbf{36} (61.3 mg, 88\%) as a white solid.

\textbf{M. p.} 192 °C

\textbf{\textit{^1H} NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.85 (d, \(J = 8.7\) Hz, 1H), 7.99 (d, \(J = 8.7\) Hz, 1H), 7.87 (d, \(J = 7.9\) Hz, 1H), 7.78 (ddd, \(J = 8.6, 6.9, 1.4\) Hz, 1H), 7.62 (ddd, \(J = 8.0, 7.0, 1.1\) Hz, 1H), 7.47 – 7.41 (m, 3H), 7.40 – 7.34 (m, 2H), 7.31 – 7.27 (m, 2H), 7.26 – 7.17 (m, 4H).

\textbf{\textit{^{13}C} NMR} (125 MHz, CDCl\textsubscript{3}) \(\delta\) 161.4 (C\textsubscript{q}), 152.5 (C\textsubscript{q}), 141.0 (C\textsubscript{q}), 135.8 (CH), 134.8 (C\textsubscript{q}), 132.8 (C\textsubscript{q}), 132.6 (C\textsubscript{q}), 131.5 (C\textsubscript{q}), 131.5 (CH), 129.5 (CH), 129.2 (CH), 129.1 (CH), 129.1 (CH), 128.4 (CH), 128.2 (CH), 127.9 (CH), 127.1 (CH), 127.0 (CH), 122.7 (CH), 117.4 (C\textsubscript{q}), 114.0 (C\textsubscript{q}).

\textbf{IR} (ATR): 3026, 1702, 1590, 1510, 1430, 1215, 1105, 1019, 820, 503 cm\textsuperscript{-1}.

\textbf{MS (ESI) }\textit{m/z} (relative intensity): 349 (100) [M+H]\textsuperscript{+}.

\textbf{HR-MS (ESI) }C\textsubscript{25}H\textsubscript{17}O\textsubscript{2} [M+H]\textsuperscript{+}: 349.1225, found: 349.1223.
3.4-Bis(4-methoxyphenyl)-1H-benzo[\textit{h}]isochromen-1-one (37)

GP2 was followed using 2-methyl benzoic acid (34.4 mg, 0.20 mmol), 1,2-bis(4-methoxyphenyl)ethyne (142.9 mg, 0.60 mmol), [OsCl\textsubscript{2}(\textit{p}-cymene)]\textsubscript{2} (7.9 mg, 5.0 mol%), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H\textsubscript{2}O (2.0 mL). Purification by column chromatography on silica gel (\textit{n}-hexane/EtOAc: 20/1) yielded 37 (67.0 mg, 82%) as an orange solid.

\textbf{M. p.} 217 °C

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.82 (d, \(J = 8.6\) Hz, 1H), 7.96 (d, \(J = 8.6\) Hz, 1H), 7.84 (d, \(J = 8.0\) Hz, 1H), 7.73 (ddd, \(J = 8.6, 6.9, 1.4\) Hz, 1H), 7.59 (ddd, \(J = 8.0, 6.9, 1.1\) Hz, 1H), 7.33 (d, \(J = 8.6\) Hz, 2H), 7.24 (d, \(J = 8.6\) Hz, 1H), 7.18 (d, \(J = 8.6\) Hz, 2H), 6.99 (d, \(J = 8.6\) Hz, 2H), 6.73 (d, \(J = 8.6\) Hz, 2H), 3.86 (s, 3H), 3.75 (s, 3H).

\textbf{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}) \(\delta\) 161.5 (C\textsubscript{q}), 160.0 (C\textsubscript{q}), 159.3 (C\textsubscript{q}), 152.5 (C\textsubscript{q}), 141.7 (C\textsubscript{q}), 135.7 (CH), 132.5 (CH), 132.4 (C\textsubscript{q}), 131.6 (C\textsubscript{q}), 130.6 (CH), 129.3 (CH), 128.4 (CH), 127.0 (C\textsubscript{q}), 126.9 (CH), 126.8 (CH), 125.3 (C\textsubscript{q}), 122.6 (CH), 115.8 (C\textsubscript{q}), 114.7 (CH), 113.5 (C\textsubscript{q}), 113.3 (CH), 55.3 (CH\textsubscript{3}), 55.2 (CH\textsubscript{3}).

\textbf{IR} (ATR): 3203, 1703, 1510, 1441, 1247, 1177, 1091, 831, 765, 570 cm\(^{-1}\).

\textbf{MS} (ESI) \textit{m/z} (relative intensity): 409 (100) [M+H]\textsuperscript{+}.

\textbf{HR-MS} (ESI) C\textsubscript{27}H\textsubscript{21}O\textsubscript{4} [M+H]\textsuperscript{+}: 409.1435, found: 409.1434.
3.4-Bis(4-fluorophenyl)-1H-benzo[h]isochromen-1-one (8)

GP2 was followed using 2-methyl benzoic acid (34.4 mg, 0.20 mmol), 1,2-bis(4-fluorophenyl)ethyne (128.5 mg, 0.60 mmol), [OsCl₂(p-cymene)]₂ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded 8 (65.3 mg, 85%) as a yellow solid.

**M. p.** 196 °C

**¹H NMR** (400 MHz, CDCl₃) δ 9.85 (dd, J = 8.7, 1.0 Hz, 1H), 8.05 (d, J = 8.7 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.82 (ddd, J = 8.7, 6.9, 1.4 Hz, 1H), 7.67 (ddd, J = 8.0, 6.9, 1.4 Hz, 1H), 7.38 (dd, J = 9.0, 5.3 Hz, 2H), 7.30 (dd, J = 9.0, 5.3 Hz, 2H), 7.23 (d, J = 8.7 Hz, 1H), 7.25 – 7.22 (m, 2H), 6.99 – 6.93 (m, 2H).

**¹³C NMR** (125 MHz, CDCl₃) δ 163.6 (d, J_C–F = 44.6 Hz, C_q), 161.9 (d, J_C–F = 42.2 Hz, C_q), 161.0 (C_q), 151.8 (C_q), 140.7 (C_q), 136.1 (CH), 133.2 (d, J_C–F = 8.0 Hz, CH), 132.6 (C_q), 131.5 (C_q), 131.2 (d, J_C–F = 8.5 Hz, CH), 130.5 (d, J_C–F = 3.6 Hz, C_q), 129.6 (CH), 128.8 (d, J_C–F = 3.4 Hz, C_q), 128.5 (CH), 127.2 (CH), 127.0 (CH), 122.3 (CH), 116.5 (d, J_C–F = 21.5 Hz, CH), 116.3 (C_q), 115.2 (d, J_C–F = 21.8 Hz, CH), 113.9 (C_q).

**¹⁹F NMR** (282 MHz, CDCl₃) δ -110.52, -112.72.

**IR** (ATR): 3501, 1720, 1595, 1510, 1330, 1229, 1106, 833, 730, 530, cm⁻¹.

**MS** (ESI) m/z (relative intensity): 385 (100) [M+H]⁺.

**HR-MS** (ESI) C₂₅H₁₅F₂O₂ [M+H]⁺: 385.1037, found: 385.1035.
3.4-Di-p-tolyl-1H-benzo[g]isochromen-1-one (38)

\[
\text{GP2 was followed using 2-naphthoic acid (70 mg, 0.40 mmol), 1,2-di-p-tolylethynne (246 mg, 1.20 mmol), [OsCl}_2(p\text{-cymene})]_2 (28.5 mg, 10.0 mol %), KI (134 mg, 2.0 equiv), KOAc (80 mg, 2.0 equiv) in HFIP (2.0 mL) and H}_2\text{O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded 38 (25.6 mg, 17\%) as a yellow solid.}
\]

**M. p.** 233 °C

**¹H NMR** (300 MHz, CDCl₃) \(\delta\) 9.02 (s, 1H), 8.04 (d, \(J = 8.0\) Hz, 1H), 7.76 (d, \(J = 8.0\) Hz, 1H), 7.61 – 7.49 (m, 3H), 7.27 (d, \(J = 7.4\) Hz, 4H), 7.22 (d, \(J = 7.4\) Hz, 2H), 7.02 (d, \(J = 8.0\) Hz, 2H), 2.46 (s, 3H), 2.30 (s, 3H).

**¹³C NMR** (75 MHz, CDCl₃) \(\delta\) 162.7 (Cq), 149.4 (Cq), 138.8 (Cq), 137.8 (Cq), 136.4 (Cq), 134.3 (Cq), 132.0 (Cq), 131.8 (Cq), 131.7 (CH), 131.1 (CH), 130.3 (Cq), 129.9 (CH), 129.4 (CH), 129.1 (CH), 129.1 (CH), 128.6 (CH), 128.2 (CH), 126.7 (CH), 124.3 (CH), 118.9 (Cq), 116.3 (Cq), 21.4 (CH₃), 21.3 (CH₃).

**IR** (ATR): 2927, 1720, 1620, 1504, 1363, 1172, 763, 624 cm\(^{-1}\).

**MS** (ESI) \(m/z\) (relative intensity): 377 (100) [M+H]^+, 399 (40) [M+Na]^+.

**HR-MS** (ESI) \(C_{27}H_{20}O_2\) [M+H]^+: 377.1536, found: 377.1536.
1,2-Di-p-tolyl-4H-benzo[f]isochromen-4-one (39)

GP2 was followed using 2-naphthoic acid (70 mg, 0.40 mmol), 1,2-di-p-tolylethyne (246 mg, 1.20 mmol), [OsCl₂(p-cymene)]₂ (28.5 mg, 10.0 mol %), KI (134 mg, 2.0 equiv), KOAc (80 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded 39 (54.2 mg, 36%) as a yellow solid.

M. p. 209 °C

¹H NMR (300 MHz, CDCl₃) δ 8.38 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 8.7 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 9.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.15 – 7.05 (m, 5H), 7.00 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H), 2.30 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 162.8 (Cₗ), 153.2 (Cₗ), 138.6 (Cₗ), 137.8 (Cₗ), 137.5 (Cₗ), 137.2 (Cₗ), 134.6 (Cₗ), 131.3 (CH), 130.9 (Cₗ), 129.9 (CH), 129.8 (CH), 129.5 (CH), 128.9 (CH), 128.9 (Cₗ), 128.4 (CH), 128.4 (CH), 128.2 (CH), 125.6 (CH), 124.4 (CH), 119.0 (Cₗ), 117.2 (Cₗ), 21.4 (CH₃), 21.3 (CH₃).

IR (ATR): 2920, 2105, 1609, 1542, 1340, 1261, 1188, 822, 533 cm⁻¹.

MS (ESI) m/z (relative intensity): 377 (100) [M+H]⁺, 399 (40) [M+Na]⁺.

HR-MS (ESI) C₂₇H₂₀O₂ [M+H]⁺: 377.1536, found: 377.1532.
3,4-diphenyl-6-vinyl-1H-isochromen-1-one (40)

GP2 was followed using 4-vinyl benzoic acid (148 mg, 1.00 mmol), 1,2-diphenylethyne (535 mg, 3.00 mmol), [OsCl$_2$(p-cymene)]$_2$ (39.5 mg, 5.0 mol%), KI (332 mg, 2.0 equiv), KOAc (197 mg, 2.0 equiv) in HFIP (2.5 mL) and H$_2$O (2.5 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded 40 (214 mg, 66%) as a white solid.

M. p. 82 °C

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.38 (d, $J$ = 8.2 Hz, 1H), 7.62 (d, $J$ = 8.2 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.35 (d, $J$ = 7.3 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.22 (d, $J$ = 7.3 Hz, 2H), 7.17 – 7.13 (m, 1H), 6.69 (dd, $J$ = 17.6, 10.8 Hz, 1H), 5.83 (d, $J$ = 17.6 Hz, 1H), 5.41 (d, $J$ = 10.8 Hz, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 162.0 (C$_q$), 151.3 (C$_q$), 143.6 (C$_q$), 139.2 (C$_q$), 135.9 (CH), 134.2 (C$_q$), 132.9 (C$_q$), 131.3 (CH), 129.9 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.2 (CH), 127.9 (CH), 125.3 (CH), 123.4 (CH), 119.5 (CH$_2$), 118.0 (C$_q$), 116.9 (C$_q$).

IR (ATR): 3059, 2924, 1719, 1651, 1445, 1204, 1166, 734, 505 cm$^{-1}$.

MS (ESI) m/z (relative intensity): 325 (90) [M+H]$^+$, 347 (10) [M+Na]$^+$.

HR-MS (ESI) C$_{23}$H$_{17}$O$_2$ [M+H]$^+$: 325.1225, found: 325.1223.
(R)-6-(1,2-dihydroxyethyl)-3,4-diphenyl-1H-isochromen-1-one (41)

GP2 was followed using 4-vinyl benzoic acid (148 mg, 1.00 mmol), 1,2-diphenylethyne (535 mg, 3.00 mmol), [OsCl₂(p-cymene)]₂ (39.5 mg, 5.0 mol %), KI (332 mg, 2.0 equiv), KOAc (197 mg, 2.0 equiv) in HFIP (2.5 mL) and H₂O (2.5 mL). Then, and without purification, K₂OsO₂(OH)₄ (0.7 mg, 0.2 mol %), (DHQD)₂PHAL (7.8 mg, 1 mol %), I₂ (25.4 mg, 10 mol %), and K₂CO₃ (414 mg, 3.0 equiv) were added and stirred at room temperature for 16 h at 4.0 mA of a constant current under N₂. Purification by column chromatography on silica gel (n-hexane/EtOAc: 1/1) yielded 41 (168 mg, 47%, 93:7 e.r.) as a white solid.

M. p. 107 °C

¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, J = 8.1 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.36 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 7.24 – 7.19 (m, 3H), 4.84 (dd, J = 8.0, 3.4 Hz, 1H), 3.76 (dd, J = 11.3, 3.4 Hz, 1H), 3.60 (dd, J = 11.3, 8.0 Hz, 1H), 2.77 (s, 1H), 2.18 (s, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 162.1 (C₉), 151.3 (C₉), 147.8 (C₉), 139.0 (C₉), 134.1 (C₉), 132.8 (C₉), 131.2 (CH), 129.9 (CH), 129.2 (CH), 129.2 (CH), 129.0 (CH), 128.3 (CH), 127.9 (CH), 125.8 (CH), 122.7 (CH), 119.8 (C₉), 116.9 (C₉), 74.2 (CH), 67.7 (CH₂).

IR (ATR): 3399, 1726, 1703, 1614, 1481, 1319, 1077, 787, 695 cm⁻¹.

MS (ESI) m/z (relative intensity): 359 (90) [M+H]+, 381 (10) [M+Na]+.

HR-MS (ESI) C₂₃H₁₉O₄ [M+H]+: 359.1280, found: 359.1278.
Signal 1: DAD1 A, Sig=250,4 Ref=off

| # | RetTime | Type | Width | Area  | Height | Area % |
|---|---------|------|-------|-------|--------|-------|
| 1 | 42.775  | BV   | 0.9157| 5.39222e4 | 886.42560 | 49.8450 |
| 2 | 45.316  | VB   | 0.9991| 5.42576e4 | 828.44061 | 50.1550 |

Totals: 1.08180e5 1714.86621

Signal 1: DAD1 A, Sig=250,4 Ref=off

| # | RetTime | Type | Width | Area  | Height | Area % |
|---|---------|------|-------|-------|--------|-------|
| 1 | 42.753  | BB   | 0.7525| 4312.72217 | 74.71085 | 6.7074 |
| 2 | 45.170  | BB   | 0.9822| 5.99851e4  | 918.15948 | 93.2926 |

Totals: 6.42978e4 992.87034
Butyl (E)-3-(1-(2-butoxy-2-oxoethyl)-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (3)

GP1 was followed using benzoic acid (24.4 mg, 0.20 mmol), n-butyl acrylate (76.9 mg, 0.60 mmol), [OsCl$_2$(p-cymene)$_2$ (7.9 mg, 5.0 mol %), KI (66.4 mg, 2.0 equiv), KOAc (39.3 mg, 2.0 equiv) in HFIP (2.0 mL) and H$_2$O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 4/1) yielded 3 (1.5 mg, 2%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.65 (d, $J = 16.3$ Hz, 1H), 7.73 (d, $J = 8.3$ Hz, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.46 (d, $J = 7.6$ Hz, 1H), 6.55 (d, $J = 16.3$ Hz, 1H), 5.80 (t, $J = 6.4$ Hz, 1H), 4.17 (t, $J = 6.7$ Hz, 2H), 4.09 (t, $J = 6.7$ Hz, 2H), 2.87 (d, $J = 6.4$ Hz, 2H), 1.69 – 1.61 (m, 2H), 1.59 – 1.50 (m, 2H), 1.39 (dq, $J = 15.2, 7.4$ Hz, 2H), 1.29 (dq, $J = 14.7, 7.4$ Hz, 2H), 0.91 (t, $J = 7.4$ Hz, 3H), 0.86 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 169.1 (C$_q$), 168.8 (C$_q$), 166.1 (C$_q$), 149.6 (C$_q$), 137.2 (CH), 134.9 (C$_q$), 134.2 (CH), 126.5 (CH), 123.1 (C$_q$), 123.0 (CH), 122.9 (CH), 76.0 (CH), 65.1 (CH$_2$), 64.6 (CH$_2$), 39.3 (CH$_2$), 30.6 (CH$_2$), 30.4 (CH$_2$), 19.1 (CH$_2$), 18.9 (CH$_2$), 13.6 (CH$_3$), 13.5 (CH$_3$).

IR (ATR): 2960, 2936, 1771, 1730, 1487, 1281, 1172, 1109, 1005, 747, 686 cm$^{-1}$.

MS (ESI) $m/z$ (relative intensity): 374 (60) [M+H]$^+$, 396 (40) [M+Na]$^+$.

HR-MS (ESI) C$_{21}$H$_{27}$O$_6$ [M+H]$^+$: 374.1729, found: 374.1731.

The spectral data were in accordance with those reported in the literature.$^{[14]}$
4,8-Dimethyl-3-phenyl-1H-isochromen-1-one (42)

GP2 was followed using 2-methyl benzoic acid (54 mg, 0.40 mmol), prop-1-yn-1-ylbenzene (140 mg, 1.20 mmol), [OsCl₂(p-cymene)]₂ (28.5 mg, 10.0 mol %), KI (134 mg, 2.0 equiv), KOAc (80 mg, 2.0 equiv) in HFIP (2.0 mL) and H₂O (2.0 mL). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded 42 (29 mg, 29%) as a white solid.

M. p. 133 °C

¹H NMR (300 MHz, CDCl₃) δ 7.70 – 7.63 (m, 1H), 7.64 – 7.59 (m, 2H), 7.48 (q, J = 8.1, 7.6 Hz, 4H), 7.36 (d, J = 7.5 Hz, 1H), 2.91 (s, 3H), 2.30 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 161.8 (C_q), 150.9 (C_q), 143.7 (C_q), 140.3 (C_q), 133.9 (CH), 133.4 (C_q), 130.9 (CH), 129.5 (CH), 129.2 (CH), 128.2 (CH), 121.4 (CH), 119.3 (C_q), 108.9 (C_q), 23.6 (CH₃), 14.1 (CH₃).

IR (ATR): 2995, 2926, 1718, 1592, 1472, 1229, 1183, 763, 693 cm⁻¹.

MS (ESI) m/z (relative intensity): 251 (100) [M+H]⁺, 273 (80) [M+Na]⁺.

HR-MS (ESI) C₁₇H₁₄O₂ [M+H]⁺: 251.1067, found: 251.1062.
OsCl(Me)(DMSO)(ρ-cymene)

1H NMR (400 MHz, Benzene-d6)  δ 5.06 (d, J = 5.5 Hz, 1H), 4.88 (d, J = 5.5 Hz, 1H), 4.84 (d, J = 5.5 Hz, 1H), 4.67 (d, J = 5.5 Hz, 1H), 3.01 (s, 3H), 2.66 – 2.59 (m, 1H), 2.56 (s, 3H), 1.86 (s, 3H), 1.43 (s, 3H), 1.05 (d, J = 7.0 Hz, 3H), 1.02 (d, J = 7.0 Hz, 3H).

13C NMR (125 MHz, Benzene-d6)  δ 99.7 (C₆), 92.9 (C₆), 84.5 (CH), 83.5 (CH), 76.2 (CH), 74.9 (CH), 49.2 (CH₃), 40.7 (CH₃), 37.3 (CH₃), 30.4 (CH), 23.2 (CH₃), 21.9 (CH₃), 17.7 (CH₃), -16.0 (CH₃).

HR-MS (ESI) C₁₃H₂₃ClO₅S [M]: 454.0755, found: 454.0764.
Os-I

\[ \text{Me-} \quad \begin{array}{c}
\text{iPr} \\
\text{DMSO-} \quad \text{Os-} \\
\text{O} \\
\text{O}
\end{array} \]

\(^1\text{H NMR\ (400 MHz, CD}_2\text{Cl}_2\) \(\delta 9.45\ (d, \ J = 8.2\ Hz, 1H), 7.92\ (d, \ J = 8.2\ Hz, 1H), 7.76\ (d, \ J = 8.2\ Hz, 1H), 7.67\ (d, \ J = 8.2\ Hz, 1H), 7.53 - 7.44\ (m, 1H), 7.39 - 7.30\ (m, 1H), 5.67 - 5.57\ (m, 3H), 5.51\ (d, \ J = 5.7\ Hz, 1H), 2.88 - 2.80\ (m, 1H), 2.82\ (s, 3H), 2.41\ (s, 3H), 2.30\ (s, 3H), 1.23\ (d, \ J = 6.9\ Hz, 3H), 1.12\ (d, \ J = 6.9\ Hz, 3H).\]

\(^{13}\text{C NMR\ (125 MHz, CD}_2\text{Cl}_2\) \(\delta 183.7\ (C_q), 160.1\ (C_q), 138.1\ (CH), 133.3\ (C_q), 132.3\ (C_q), 131.2\ (CH), 129.8\ (C_q), 128.1\ (CH), 126.7\ (CH), 124.2\ (CH), 123.1\ (CH), 108.3\ (C_q), 98.9\ (C_q), 81.7\ (CH), 80.8(CH), 80.2(CH), 79.7(CH), 46.3\ (CH_3), 42.3\ (CH_3), 30.9\ (CH), 22.6\ (CH_3), 22.5\ (CH_3), 18.5\ (CH_3).\]

**HR-MS (ESI) C\text{23H}_{27}O_3OsO [M+H]^+: 575.1290, found: 575.1285.**
Os-II

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (d, $J$ = 7.9 Hz, 1H), 7.52 – 7.40 (m, 2H), 7.36 (d, $J$ = 7.9 Hz, 1H), 7.29 (d, $J$ = 7.0 Hz, 1H), 7.24 – 7.15 (m, 1H), 7.09 (d, $J$ = 7.0 Hz, 1H), 7.01 (d, $J$ = 6.2 Hz, 1H), 7.02 – 6.98 (m, 2H), 6.93 (d, $J$ = 8.2 Hz, 2H), 6.84 (d, $J$ = 8.2 Hz, 2H), 5.45 (d, $J$ = 5.4 Hz, 1H), 5.39 (d, $J$ = 5.4 Hz, 1H), 3.91 (d, $J$ = 5.4 Hz, 1H), 3.40 (d, $J$ = 5.4 Hz, 1H), 2.37 (s, 3H), 2.20 (s, 3H), 1.67 – 1.59 (m, 1H), 1.64 (s, 3H), 1.13 (d, $J$ = 6.8 Hz, 3H), 0.95 (d, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 175.1 (C$_q$), 140.2 (C$_q$), 138.8 (C$_q$), 137.0 (C$_q$), 133.4 (C$_q$), 133.1 (C$_q$), 132.6 (CH), 131.5 (CH), 129.5 (CH), 129.3 (CH), 129.1 (C$_q$), 128.7 (CH), 128.7 (CH), 127.6 (CH), 127.6 (CH), 125.1 (CH), 125.0 (CH), 123.8 (CH), 110.0 (C$_q$), 103.0 (C$_q$), 92.2 (C$_q$), 85.1 (C$_q$), 79.0 (CH), 79.0 (CH), 76.3 (C$_q$), 74.2 (CH), 51.9 (C$_q$), 30.1 (CH), 24.8 (CH$_3$), 21.6 (CH$_3$), 21.3 (CH$_3$), 20.9 (CH$_3$), 17.5 (CH$_3$).

HR-MS (ESI) C$_{37}$H$_{35}$O$_2$Os [M+H]$^+$: 703.2249, found: 703.2236.
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$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra

1

(400 MHz, CDCl$_3$)

1

(125 MHz, CDCl$_3$)
(400 MHz, CDCl$_3$)

(125 MHz, CDCl$_3$)
(400 MHz, CDCl₃)

(125 MHz, CDCl₃)
(400 MHz, CDCl₃)

(125 MHz, CDCl₃)
$\text{Me}\begin{array}{c}\text{CO}_2\text{nBu} \\
\end{array}$

(400 MHz, CDCl$_3$)

$\text{Me}\begin{array}{c}\text{CO}_2\text{nBu} \\
\end{array}$

(125 MHz, CDCl$_3$)
(400 MHz, CDCl$_3$)

(125 MHz, CDCl$_3$)
12
(400 MHz, CDCl₃)

12
(125 MHz, CDCl₃)
$\text{F}_3\text{C}$

$\text{CO}_2\text{nBu}$

4

(282 MHz, CDCl$_3$)
$14$ (400 MHz, CDCl$_3$)

$14$ (125 MHz, CDCl$_3$)
16

(400 MHz, CDCl₃)

MeO

16

(125 MHz, CDCl₃)
(282 MHz, CDCl₃)
(400 MHz, CDCl₃)

(125 MHz, CDCl₃)
22
(400 MHz, CDCl$_3$)

22
(125 MHz, CDCl$_3$)
27
(400 MHz, CDCl₃)

27
(125 MHz, CDCl₃)
(400 MHz, CDCl₃)

(125 MHz, CDCl₃)
(400 MHz, CDCl₃)

(125 MHz, CDCl₃)
30
(400 MHz, CDCl₃)

30
(125 MHz, CDCl₃)
31
(400 MHz, CDCl₃)

31
(125 MHz, CDCl₃)
32
(400 MHz, CDCl₃)

32
(125 MHz, CDCl₃)
34
(300 MHz, CDCl₃)

34
(75 MHz, CDCl₃)
35
(300 MHz, CDCl₃)

35
(75 MHz, CDCl₃)
35
(282 MHz, CDCl$_3$)
38
(400 MHz, CDCl₃)

38
(125 MHz, CDCl₃)
36
(400 MHz, CDCl₃)

36
(125 MHz, CDCl₃)
37
(400 MHz, CDCl₃)

37
(125 MHz, CDCl₃)
8

(400 MHz, CDCl₃)

8

(125 MHz, CDCl₃)
8
(282 MHz, CDCl₃)
40

(300 MHz, CDCl₃)

40

(75 MHz, CDCl₃)
OsCl(Me)(DMSO)(\(p\)-cymene)  
(400 MHz, \(\text{C}_6\text{D}_6\))

OsCl(Me)(DMSO)(\(p\)-cymene)  
(125 MHz, \(\text{C}_6\text{D}_6\))
