Cooperative NHC/Photoredox Catalyzed Ring-Opening of Aryl Cyclopropanes to 1-Aroyloxylated-3-Acylated Alkanes

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Supporting Information

Table of Contents:

A. General information: ........................................................................................................... S2
B. Preparation of substrates: ............................................................................................... S3
C. Results: ............................................................................................................................ S9
D. Large-scale preparation of 3a and its derivatization: ...................................................... S28
E. Mechanistic studies: ......................................................................................................... S31
F. X-ray data for 3s: .............................................................................................................. S35
G. References: ..................................................................................................................... S43
H. NMR spectrum: ................................................................................................................ S44
A. General information:

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware using standard Schlenk techniques. All commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI Chemicals, Acros Organics or ABCR in the highest purity grade and used without further purification. DCE (99.8%, extra dry, AcroSeal) was used as received from Acros Organics.

Thin layer chromatography (TLC) was performed on Merck silica gel 60 F-254 plates and visualized by fluorescence quenching under UV light.

Column chromatography was performed on Merck or Fluka silica gel 60 (40-63 μm).

Melting points were measured on a Büchi M560 and are uncorrected.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker DPX 300, a Bruker AV 400 at 300 K, a Varian INOVA 500 or a Varian 600 UNITY plus spectrometer at 299 K. Spectra were calibrated relative to solvent’s residual proton and carbon chemical shift: CDCl₃ (δ = 7.27 ppm for ¹H NMR and δ = 77.0 ppm for ¹³C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constants (Hz) and integration.

Infrared spectra (IR) were measured on a Digilab 3100 FT-IR Excalibur Series spectrometer and the position of the absorption bands is given in wave numbers ν (cm⁻¹).

HRMS ESI (m/z) spectra were recorded on a Bruker MicroTof or an Orbitrap LTQ XL (Nanospray) of Thermo Scientific.

Chiral HPLC analysis was performed on a Hewlett Packard HP 1100 Series HPLC System using AD-H (0.46*25 cm, 5 μm silica-gel, DaicelTM) and IC (0.46*25 cm, 5 μm silica-gel, DaicelTM) chiral columns eluting with a mixture of cyclohexane and isopropyl alcohol.
B. Preparation of substrates:

General procedure for preparation of acyl fluorides:

To a 100-mL Schlenk tube with a magnetic stir bar, were successively added an acyl chloride (1.0 equiv.), 18-crown-6 (5.0 mol %), KF (10.0 equiv.) and THF (0.2 M). After the reaction was stirred at 40 °C for 24 hours, the insoluble inorganic solid was filtered, and the volatiles were removed using a
rotary evaporator. The crude product was purified by bulb-to-bulb distillation to afford the corresponding acyl fluorides.

All acyl fluorides are known compounds and spectroscopic data are in accordance with those described in literature.\textsuperscript{[1]}

**Preparation of cyclopropanes:**

**General procedure A:**\textsuperscript{[2]}

\[
\text{Ar} - \underset{\text{Br}}{\text{CH}_2} + \text{Pd(OAc)}_2 (5.0 \text{ mol\%}) \quad \text{PCy}_3 (10.0 \text{ mol\%}) \quad \text{K}_{3}\text{P}_{2}\text{O}_{7} (3.0 \text{ equiv}) \rightarrow \text{Ar} - \text{CH}_2 - \underset{\Delta}{\text{H}} \quad \text{Toluene/H}_2\text{O}, 110 ^\circ \text{C}, \text{24-48 h}
\]

In a 50 mL Schlenk tube with magnetic stirring bar were added the corresponding aryl bromide (3.0 mmol, 1 equiv.), tricyclohexylphosphine (84.0 mg, 0.30 mmol, 0.1 equiv.), palladium acetate (33.7 mg, 0.15 mol, 0.05 equiv.), tripotassium phosphate (1.9 g, 9.0 mmol, 3.0 equiv.) and cyclopropylboronic acid (387.0 mg, 4.5 mmol, 1.5 equiv.). Then, toluene (10 mL) and 0.5 mL of water were added, and the tube was closed. The reaction mixture was shaken briefly and set under inert atmosphere by bubbling nitrogen gas through the vial for 5 minutes. Afterwards, the tube was placed into an oil bath and stirred at 110 °C for 24-48 h. Upon completion, the reaction mixture was poured into a separatory funnel, diluted with ethyl acetate and washed with 15 mL water twice. The organic layer was dried with \( \text{Na}_2\text{SO}_4 \), concentrated \textit{in vacuo} and purified by column chromatography to give the title compound. Compounds 2a, 2d-\textit{j} were prepared following the General Procedure A.

**General procedure B:**\textsuperscript{[3]}

In a 100 mL oven-dried round-bottom flask with a stir bar, was added 2,4,6-trichlorophenol (1.18 g, 6.0 mmol, 2.5 equiv.) under nitrogen atmosphere. DCM (60 mL, 0.1 M) was added into the flask and the reaction mixture was cooled to -40 °C. \( \text{ZnEt}_2 \) (1.0 M, 6.0 mL, 6.0 mmol, 2.5 equiv.) was added slowly into the flask by syringe and the reaction mixture was stirred at this temperature for 15 min. \( \text{CH}_3\text{J}_2 \) (2.57 g, 9.6 mmol, 4.0 equiv.) was added slowly by syringe and the reaction mixture was stirred at this temperature for another 15 min. Next, the corresponding solution of alkene (2.4 mmol, 1.0 equiv.) in DCM (10 mL) was added by syringe and the reaction mixture was allowed to warm to room temperature and stirred for 16 h. After the reaction reached completion, the reaction mixture was
quenched with sat. NH₄Cl (30 mL) and extracted with DCM (100 mL) for 3 times. The combined organic layers were washed with aq. NaOH (1.0 M, 30 mL) and brine (20 mL), dried over Na₂SO₄ and filtered. After the volatile materials were removed under reduced pressure, the crude residue was purified by column chromatography to give the title compound. Compounds 2b, 2c, 2k, 2s were prepared following the General Procedure B.

**General procedure C:**

To a 50 mL oven-dried round-bottom flask equipped with a stir bar was added a solution of (4-methoxyphenyl)(tributylstanny1)methyl methyl carbonate (972 mg, 2.0 mmol, 1.0 equiv) and the corresponding alkene (2.2 mmol, 1.1 equiv) in toluene (10 mL) under nitrogen atmosphere at room temperature. The reaction vessel was cooled to -23 °C. BF₃·OEt₂ (312 mg, 2.2 mmol, 1.1 equiv) was added by syringe and the mixture was stirred at this temperature for 2 h. After the reaction reached completion according to the TLC analysis, the reaction mixture was quenched with sat. NaHCO₃ (10 mL) and extracted with EtOAc (30 mL) for 3 times. The combined organic layers were washed with brine (20 mL), dried over Na₂SO₄ and filtered. After the volatile materials were removed under reduced pressure, the crude residue was purified by column chromatography to afford the desired compound.

Compounds 2l-r, 2t-u were prepared following the General Procedure C.

The spectroscopic data of all known cyclopropanes are in accordance with those described in literature.[3-4]

\[(8S,9R,13R,14R)-3-(2-(4-Methoxyphenyl)cyclopropoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one + (8S,9R,13R,14R)-3-((1S,2S)-2-(4-methoxyphenyl)cyclopropoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (2t)\]

Following procedure C to afford a white solid (668.1 mg, 73% yield).

MP: 54-55 °C.

\(^1\)H NMR (300 MHz, CDCl₃): δ 7.20 – 7.14 (m, 3H), 6.86 – 6.75 (m, 3H), 6.71 (dd, J = 4.9, 2.8 Hz, 1H),
3.92 (td, J = 6.5, 3.7 Hz, 1H), 3.79 (s, 3H), 2.96 – 2.77 (m, 2H), 2.59 – 2.34 (m, 2H), 2.30 – 1.93 (m, 7H), 1.55 – 1.34 (m, 6H), 1.14 (dd, J = 6.9, 3.1 Hz, 1H), 0.92 (s, 3H).

13C NMR (76 MHz, CDCl3): δ 221.1, 157.9, 156.7, 137.5, 132.4, 129.2, 128.9, 126.1, 115.4, 113.4, 112.7, 55.6, 55.2, 50.4, 48.0, 44.0, 38.3, 35.9, 31.6, 29.7, 26.6, 25.9, 22.2, 21.6, 13.9, 12.8.

FTIR (neat): υ (cm⁻¹) 3053, 2935, 1736, 1515, 1265, 1246, 732.

HRMS (ESI-TOF) m/z: [M+Na⁺] Caled for C28H32NaO3 439.2249; found: 439.2238.

**Synthesis of enantioenriched cyclopropane (S,S)-2s**

a) To an oven-dried 100 mL round-bottom flask equipped with a stir bar, succinimidyl diazocetate (183.0 mg, 1.0 mmol), 1-methoxy-4-vinylbenzene (114.6 μL, 5.0 mmol), chiral Ru(II)-Pheox catalyst (12.6 mg, 0.02 mmol) and CH₂Cl₂ (10.0 mL) were added at room temperature. After that we checked the TLC in less than 1 min, and we noticed the disappearance of the diazo compound. The residue was purified by column chromatography on silica gel (eluting with pentane/ethyl acetate = 3/1) to afford the white solid (263.0 mg, 91% yield).

b) To the solution of succinimidyl cyclopropyl carboxylate derivatives (231.1 mg, 0.8 mmol) in Et₂O (10.0 mL) was added lithium aluminium hydride (60.8 mg, 1.6 mmol) at 0 ºC. After stirring for 2 h at same temperature, the reaction solution was quenched with water (0.5 mL), filtered, and evaporated under reduced pressure. The crude alcohol was used without further purification.

c) A solution of crude alcohol in CH₂Cl₂ (10.0 mL) was treated with Ac₂O (244.8 mg, 3.0 equiv.), Et₃N (242.4 mg, 3.0 equiv.), and 4-DMAP (10.0 mg, 0.1 equiv.) at 0 ºC. The mixture was allowed to warm up to room temperature overnight. The volatile materials of the reaction mixture were removed under reduced pressure, the crude residue was purified by column chromatography (pentane/ethyl acetate = 10:1) to afford ((S,S)-2S)-(4-methoxyphenyl)cyclopropyl)methyl acetate as colorless oil (136.0 mg, 77% yield over 2 steps, 90% ee). HPLC Analysis: Chiralpak AD-H (Cyclohexane/iPrOH = 99/1, 1.0 mL/min, 25 ºC).

Racemic sample:
Chiral sample:

Synthesis of enantioenriched cyclopropane (R,R)-21[^4]

a) To an oven-dried 100mL round-bottom flask equipped with a stir bar, (E)-(4-methoxystyryl)boronic acid (0.86 g, 5 mmol, 1.0 equiv.), (+)-N,N,N',N'-Tetramethyl-L-tartaric acid diamide (1.05 g, 5 mmol, 1.0 equiv.) and dry DCM (20 mL) were added at room temperature. The reaction mixture was stirred for 2 h and then cooled to -78 °C. In a separate oven-dried 100 mL flask, Et₂Zn (1.0 M, 15 mL, 15 mmol, 3.0 equiv.) was dissolved in dry DCM (20 mL), cooled to -78 °C and treated dropwise with CH₃I₂ (1.0 mL, 12 mmol, 4.8 equiv.), then stirred vigorously for 10 min to generate the carbenoid.
(ineffective stirring due to precipitation of zinc salt or CH$_3$I did not affect the reaction). The pre-chilled -78 °C solution was then quickly added via syringe over 2 min. The mixture was stirred at -78 °C for 8 h. 20 mL of saturated aqueous NH$_4$Cl solution was carefully added to quench the reaction. After addition of NH$_4$Cl, the mixture was stirred at -78 °C for 5 min, taken out of the cooling bath and warmed to ambient temperature. After phase separation, 1M HCl was added just to dissolve precipitate in the aqueous phase (pH was 5-6 at this point). The aqueous phase was extracted with 50 mL of DCM three times. The combined organic phases were dried with MgSO$_4$, filtered and concentrated and pumped to afford crude \( (1R,2R)-2-(4$-$methoxyphenyl)cyclopropyl)boronic acid \) (directly used for the next step).

b) To an oven-dried 50 mL round-bottom flask equipped with a stir bar, crude \( (1R,2R)-2-(4$-$methoxyphenyl)cyclopropyl)boronic acid, 4-bromoanisole (864 mg, 4.5 mmol, 0.9 equiv.), K$_3$PO$_4$ (3.2 g, 15 mmol, 3.3 equiv.), Pd(PPh$_3$)$_4$ (156 mg, 0.03 equiv.) and toluene (20 mL) were added under nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 16 h. Once the reaction was judged to be complete by TLC analysis, the reaction mixture was filtered to remove the solids and the volatile materials of the reaction mixture were removed under reduced pressure, the crude residue was purified by column chromatography (pentane:EA = 40:1) to \( (1R,2R)$-$1,2$-$bis(4$-$methoxyphenyl)cyclopropane \) as a white solid (381 mg, 30% yield over two steps, ee 78%). HPLC Analysis: Chiralpak AD-H (Cyclohexane/iPrOH = 98/2, 1.0 mL/min, 25 °C).

Racemic sample:

Chiral sample:
C. Results:

**General procedure D for the reactions with acyl fluorides:**

\[
\text{Ar}-\text{O}^+ + \text{R}^2\text{C=C} + \text{Ph} \rightarrow \text{Ar}^+\text{O}^+ + \text{R}^2\text{C} + \text{Ph}
\]

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, an acyl fluoride 1 (0.50 mmol, 2.5 equiv.), an aryl cyclopropane 2 (0.20 mmol, 1.0 equiv.), photocatalyst 4CzIPN (7.9 mg, 5.0 mol%), N1 (6.3 mg, 10.0 mol%) and Cs2CO3 (130.4 mg, 2.0 equiv.) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, anhydrous DCE (2.0 mL, 0.1 M) was added. The resulting mixture was irradiated with blue LED at room temperature for 12 h. After solvent evaporation, the residue was purified by silica gel chromatography to afford the desired product 3.

**General procedure E for reactions with aryl anhydrides:**

\[
\text{Ar}^+\text{O}^+\text{O}^- + \text{R}^2\text{C} + \text{MeO}^- \rightarrow \text{Ar}^+\text{O}^+\text{O}^- + \text{R}^2\text{C} + \text{MeO}^-
\]

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, an aryl anhydride 8 (0.20 mmol, 1.0 equiv.), the aryl cyclopropane 2a (29.6 mg, 0.20 mmol, 1.0 equiv.), photocatalyst [Ir(dF(CFppy)2(dtbppy))PF6 (5.6 mg, 2.5 mol%), N1 (6.3 mg, 10.0 mol%) and Cs2CO3 (130.4 mg, 2.0 equiv.) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, anhydrous DCE (2.0 mL, 0.1 M) was added. The resulting mixture was irradiated under
blue LEDs at room temperature for 12 h. After solvent evaporation, the residue was purified by silica gel chromatography to afford the desired product 3.

3-(4-Methoxyphenyl)-4-oxo-4-phenylbutyl benzoate (3a)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (60.6 mg, 81% yield)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.98 (ddt, $J = 16.3, 7.1, 1.4$ Hz, 4H), 7.59 – 7.53 (m, 1H), 7.50 – 7.43 (m, 3H), 7.41 – 7.35 (m, 2H), 7.29 – 7.21 (m, 2H), 6.85 – 6.79 (m, 2H), 4.76 (t, $J = 7.3$ Hz, 1H), 4.36 (dt, $J = 11.6, 5.9$ Hz, 1H), 4.29 (ddd, $J = 11.2, 7.8, 5.5$ Hz, 1H), 3.75 (s, 3H), 2.70 – 2.60 (m, 1H), 2.30 (ddt, $J = 13.9, 7.8, 5.8$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 199.1, 166.4, 158.9, 136.5, 132.9, 130.5, 130.2, 129.6, 129.3, 128.8, 128.5, 128.4, 114.6, 63.0, 55.2, 49.5, 32.7.

FTIR (neat): $\nu$ (cm$^{-1}$) 3066, 2837, 1714, 1680, 1511, 1449, 1266, 1248, 1110, 711.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{24}$H$_{22}$NaO$_3$ 397.1415; found: 397.1405.

4-(2-Fluorophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 2-fluorobenzoate (3b)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (41.8 mg, 51% yield)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.91 (td, $J = 7.5, 1.9$ Hz, 1H), 7.74 (td, $J = 7.5, 1.9$ Hz, 1H), 7.56 – 7.50 (m, 1H), 7.42 (dddt, $J = 8.0, 5.9, 5.0, 1.3$ Hz, 1H), 7.22 – 7.12 (m, 5H), 7.03 (dddt, $J = 11.3, 8.3, 1.1$ Hz, 1H), 6.81 (dd, $J = 8.1, 1.3$ Hz, 2H), 4.77 (dd, $J = 8.3, 6.4$ Hz, 1H), 4.41 (dt, $J = 11.3, 5.7$ Hz, 1H), 4.21 (ddd, $J = 11.3, 8.1, 5.2$ Hz, 1H), 3.75 (d, $J = 0.8$ Hz, 3H), 2.71 – 2.61 (m, 1H), 2.28 – 2.19 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $^{19}$F: $\delta$ 198.3, 164.4, 161.9, 160.9, 158.9, 134.4, 134.2, 132.2, 131.1, 129.7, 129.4, 125.9, 124.4, 123.9, 118.8, 116.9, 116.6, 114.3, 63.1, 55.2, 53.2, 32.1.
19F NMR (282 MHz, CDCl3): δ -109.18 (d, J = 4.1 Hz), -109.65 (d, J = 4.5 Hz).

FTIR (neat): ν (cm⁻¹) 2904, 1717, 1685, 1610, 1511, 1452, 1249, 755.

HRMS (ESI-TOF) m/z: [M+Na⁺] Calcd for C24H20F2NaO4 433.1227, found: 433.1216.

4-(2-Chlorophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 2-chlorobenzoate (3c)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (67.2 mg, 76% yield)

1H NMR (300 MHz, CDCl3): δ 7.73 – 7.67 (m, 1H), 7.39 – 7.33 (m, 2H), 7.28 – 7.14 (m, 4H), 7.06 – 7.00 (m, 3H), 6.75 – 6.69 (m, 2H), 4.56 (dd, J = 8.4, 6.3 Hz, 1H), 4.34 (dt, J = 11.6, 5.9 Hz, 1H), 4.19 (ddd, J = 11.1, 7.7, 5.3 Hz, 1H), 3.68 (s, 3H), 2.73 – 2.47 (m, 1H), 2.23 (ddt, J = 14.3, 8.4, 5.8 Hz, 1H).

13C NMR (76 MHz, CDCl3): δ 202.6, 165.7, 159.1, 139.4, 133.6, 132.6, 131.5, 131.2, 131.1, 130.4, 130.2, 129.8, 128.9, 128.5, 126.5, 126.5, 114.5, 63.4, 55.2, 53.7, 31.2.

FTIR (neat): ν (cm⁻¹) 2962, 2837, 1728, 1700, 1510, 1434, 1246, 746.

HRMS (ESI-TOF) m/z: [M+Na⁺] Calcd for C24H20Cl2NaO4 465.0636, found: 465.0629.

4-(2-Bromophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 2-bromobenzoate (3d)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (75.5 mg, 71% yield)

1H NMR (300 MHz, CDCl3): δ 7.81 – 7.73 (m, 1H), 7.73 – 7.64 (m, 1H), 7.56 – 7.48 (m, 1H), 7.41 – 7.33 (m, 2H), 7.23 – 7.10 (m, 4H), 7.02 – 6.96 (m, 1H), 6.85 – 6.78 (m, 2H), 4.62 (dd, J = 8.5, 6.3 Hz, 1H), 4.45 (dt, J = 11.5, 5.9 Hz, 1H), 4.28 (ddd, J = 11.2, 7.8, 5.4 Hz, 1H), 3.78 (s, 3H), 2.73 (ddt, J = 13.9, 7.6, 5.9 Hz, 1H), 2.35 (ddt, J = 14.4, 8.6, 5.8 Hz, 1H).

13C NMR (76 MHz, CDCl3): δ 203.2, 166.1, 159.2, 141.5, 134.4, 133.3, 132.6, 132.3, 131.4, 131.1, 129.9, 128.8, 128.3, 127.2, 127.0, 121.6, 118.6, 114.5, 63.5, 55.2, 53.7, 31.0.
FTIR (neat): $\nu$ (cm$^{-1}$) 3059, 2839, 1728, 1701, 1511, 1465, 1248, 732.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{24}$H$_{20}$Br$_2$NaO$_4$ 552.9626, found: 552.9622.

3-(4-Methoxyphenyl)-4-oxo-4-(m-tolyl)butyl 3-methylbenzoate (3e)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (54.7 mg, 81% yield)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.82 – 7.73 (m, 4H), 7.40 – 7.27 (m, 4H), 7.26 – 7.22 (m, 2H), 6.86 – 6.80 (m, 2H), 4.74 (t, $J$ = 7.3 Hz, 1H), 4.38 – 4.23 (m, 2H), 3.75 (s, 3H), 2.75 – 2.56 (m, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 2.31 – 2.24 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 199.4, 166.6, 158.8, 138.3, 138.1, 136.6, 133.7, 133.7, 130.7, 130.2, 130.1, 129.3, 128.4, 128.2, 126.7, 125.9, 114.5, 63.0, 55.2, 49.5, 32.7, 21.3, 21.2.

FTIR (neat): $\nu$ (cm$^{-1}$) 2958, 1715, 1678, 1510, 1462, 1276, 1197, 744.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{26}$H$_{26}$NaO$_4$ 425.1728, found: 425.1717.

4-(3-Bromophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 3-bromobenzoate (3f)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (72.4 mg, 68% yield)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.09 (dt, $J$ = 3.4, 1.8 Hz, 2H), 7.88 (ddt, $J$ = 14.3, 7.8, 1.4 Hz, 2H), 7.71 – 7.57 (m, 2H), 7.39 – 7.20 (m, 4H), 6.89 – 6.77 (m, 2H), 4.65 (t, $J$ = 7.2 Hz, 1H), 4.34 (td, $J$ = 11.2, 9.6, 5.7 Hz, 2H), 3.76 (s, 3H), 2.72 – 2.61 (m, 1H), 2.37 – 2.20 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): $\delta$ 197.6, 165.1, 159.0, 138.1, 135.9, 135.8, 132.5, 132.0, 131.8, 130.1, 129.9, 129.8, 129.3, 128.1, 127.2, 122.9, 122.5, 114.8, 63.5, 55.2, 49.9, 32.6.

FTIR (neat): $\nu$ (cm$^{-1}$) 2837, 1719, 1683, 1510, 1247, 745.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{24}$H$_{20}$Br$_2$NaO$_4$ 552.9626, found: 552.9623.
3,4-Bis(4-methoxyphenyl)-4-oxobutyl 4-methoxybenzoate (3g)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 5:1)

Colorless oil (68.6 mg, 79% yield)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.52 – 7.38 (m, 4H), 7.29 – 7.23 (m, 1H), 7.20 – 7.12 (m, 3H), 7.02 (ddd, $J_1 = 8.2$, $J_2 = 2.7$, 1.0 Hz, 1H), 6.94 (ddd, $J_1 = 8.2$, $J_2 = 2.7$, 0.9 Hz, 1H), 6.79 – 6.72 (m, 2H), 4.64 (t, $J_1 = 7.3$ Hz, 1H), 4.33 – 4.14 (m, 2H), 3.77 (s, 3H), 3.71 (s, 3H), 3.67 (s, 3H), 2.63 – 2.50 (m, 1H), 2.23 – 2.16 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): $\delta$ 198.9, 166.3, 159.7, 159.6, 158.8, 137.9, 131.5, 130.5, 129.5, 129.4, 129.3, 121.9, 121.3, 119.4, 114.6, 114.1, 113.1, 63.2, 55.4, 55.3, 55.2, 49.6, 32.7.

FTIR (neat): $\nu$ (cm$^{-1}$) 2963, 1715, 1679, 1449, 1269, 1111, 710.

HRMS (ESI-TOF) m/z: [M+Na$^+$]$^+$ Caled for C$_{26}$H$_{26}$NaO$_6$ 457.1627, found: 457.1618.

4-(4-Bromophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 4-bromobenzoate (3h)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (72.4 mg, 68% yield)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.76 – 7.63 (m, 4H), 7.49 – 7.32 (m, 4H), 7.14 – 7.03 (m, 2H), 6.77 – 6.70 (m, 2H), 4.53 (t, $J_1 = 7.2$ Hz, 1H), 4.28 – 4.11 (m, 2H), 3.65 (s, 3H), 2.62 – 2.44 (m, 1H), 2.29 – 2.10 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$) $\delta$ 197.9, 165.7, 158.9, 135.1, 131.9, 131.7, 131.1, 130.3, 130.1, 129.2, 129.0, 128.2, 128.1, 114.8, 63.3, 55.2, 49.8, 32.5.

FTIR (neat): $\nu$ (cm$^{-1}$) 2908, 1717, 1680, 1585, 1397, 1267, 1173, 755.

HRMS (ESI-TOF) m/z: [M+Na$^+$]$^+$ Caled for C$_{24}$H$_{20}$Br$_2$NaO$_4$ 552.9626, found: 552.9622.
4-(4-Iodophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 4-iodobenzoate (3i)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (73.9 mg, 59% yield)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.75 – 7.49 (m, 8H), 7.12 – 7.05 (m, 2H), 6.78 – 6.69 (m, 2H), 4.52 (t, $J$ = 7.2 Hz, 1H), 4.28 – 4.12 (m, 2H), 3.66 (s, 3H), 2.60 – 2.45 (m, 1H), 2.27 – 2.09 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): $\delta$ 198.2, 165.9, 158.9, 137.9, 137.7, 135.6, 130.9, 130.1, 130.1, 129.6, 129.2, 114.7, 101.0, 100.8, 63.3, 55.2, 49.7, 32.5.

FTIR (neat): $\nu$ (cm$^{-1}$) 2906, 1716, 1680, 1580, 1392, 1264, 1007, 817.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{24}$H$_{20}$I$_2$NaO$_4$ 648.9348, found: 648.9345.

3-(4-Methoxyphenyl)-4-oxo-4-(4-(trifluoromethoxy)phenyl)butyl 4-(trifluoromethoxy)benzoate (3j)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (74.8 mg, 69% yield)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.12 – 7.88 (m, 4H), 7.36 – 7.12 (m, 6H), 6.97 – 6.73 (m, 2H), 4.67 (t, $J$ = 7.2 Hz, 1H), 4.43 – 4.27 (m, 2H), 3.76 (s, 3H), 2.75 – 2.60 (m, 1H), 2.35 – 2.22 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): $\delta$ 197.3, 165.2, 159.0, 152.7, 152.4, 152.4, 134.5, 131.5, 130.8, 130.1, 129.2, 128.5, 122.0, 120.2, 118.6, 114.8, 63.4, 55.2, 49.9, 32.6.

$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -57.65, -57.67.

FTIR (neat): $\nu$ (cm$^{-1}$) 2839, 1720, 1684, 1608, 1511, 1247, 1109, 738.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{26}$H$_{20}$F$_6$NaO$_6$ 565.1061, found: 565.1052.

3-(4-Methoxyphenyl)-4-oxo-4-(4-(trifluoromethyl)phenyl)butyl 4-(trifluoromethyl)benzoate (3k)

Performed with general procedure D and purified by flash silica column chromatography
(pentane/ethyl acetate = 20:1)

Colorless oil (67.3 mg, 66% yield)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.04 – 7.88 (m, 4H), 7.57 (dd, $J$ = 19.1, 8.2 Hz, 4H), 7.16 – 7.05 (m, 2H), 6.79 – 6.69 (m, 2H), 4.60 (q, $J$ = 7.6 Hz, 1H), 4.38 – 4.19 (m, 2H), 3.66 (s, 3H), 2.68 – 2.46 (m, 1H), 2.32 – 2.16 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): $\delta$ 197.8, 165.2, 159.1, 139.1, 134.7, 134.4, 133.9, 133.3, 129.9, 129.7, 129.3, 129.0, 125.6, 125.4, 121.7, 114.9, 63.6, 55.2, 50.2, 32.5.

$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -63.15, -63.24.

FTIR (neat): $\nu$ (cm$^{-1}$) 3044, 2961, 1722, 1686, 1511, 1323, 1122, 775.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{20}$H$_{26}$F$_6$NaO$_4$ 533.1163, found: 533.1155.

4-(4-Cyanophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 4-cyanobenzoate (3l)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 5:1)

Colorless oil (45.0 mg, 53% yield)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.01 – 7.87 (m, 4H), 7.68 – 7.57 (m, 4H), 7.12 – 7.03 (m, 2H), 6.79 – 6.71 (m, 2H), 4.53 (t, $J$ = 7.2 Hz, 1H), 4.37 – 4.21 (m, 2H), 3.67 (s, 3H), 2.56 (dt, $J$ = 13.6, 7.0 Hz, 1H), 2.22 (dt, $J$ = 13.9, 7.1 Hz, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): $\delta$ 197.4, 164.8, 159.2, 139.4, 133.8, 132.4, 132.2, 130.0, 129.3, 129.2, 129.1, 117.9, 117.8, 116.5, 116.2, 114.9, 63.8, 55.3, 50.4, 32.3.

FTIR (neat): $\nu$ (cm$^{-1}$) 2837, 2232, 1721, 1686, 1511, 1325, 1249, 1108, 767.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{29}$H$_{20}$N$_2$NaO$_4$ 447.1320, found: 447.1314.

3-(4-Methoxyphenyl)-4-(naphthalen-2-yl)-4-oxobutyl 2-naphthoate (3m)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)
Colorless oil (70.2 mg, 74% yield)

$^1$H NMR (300 MHz, CDCl$_3$): δ 8.60 – 8.47 (m, 2H), 8.05 (dt, $J = 8.6, 2.1$ Hz, 2H), 7.93 – 7.79 (m, 6H), 7.63 – 7.46 (m, 4H), 7.40 – 7.32 (m, 2H), 6.89 – 6.80 (m, 2H), 4.97 (t, $J = 7.2$ Hz, 1H), 4.52 – 4.38 (m, 2H), 3.73 (s, 3H), 2.87 – 2.72 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): δ 199.1, 166.6, 158.9, 135.5, 135.5, 133.9, 132.4, 131.1, 130.8, 130.5, 129.6, 129.4, 128.5, 128.4, 128.3, 128.1, 127.8, 127.7, 127.5, 126.7, 126.6, 125.2, 124.5, 114.7, 63.4, 55.2, 49.7, 32.9.

FTIR (neat): ν (cm$^{-1}$) 3058, 2936, 1712, 1675, 1510, 1465, 1249, 779.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{32}$H$_{26}$NaO$_4$ 497.1728, found: 497.1721.

4-(Furan-2-yl)-3-(4-methoxyphenyl)-4-oxobutyl furan-2-carboxylate (3n)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

Colorless oil (31.9 mg, 45% yield)

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.60 – 7.49 (m, 2H), 7.29 – 7.24 (m, 2H), 7.18 – 7.10 (m, 2H), 6.84 – 6.81 (m, 2H), 6.52 – 6.43 (m, 2H), 4.52 (q, $J = 7.8$ Hz, 1H), 4.35 – 4.18 (m, 2H), 3.77 (s, 3H), 2.66 – 2.58 (m, 1H), 2.30 – 2.22 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 188.1, 158.9, 158.6, 152.2, 146.4, 146.3, 144.6, 130.0, 129.4, 117.9, 117.8, 114.4, 112.3, 111.8, 62.9, 55.2, 49.5, 31.6.

FTIR (neat): ν (cm$^{-1}$) 2837, 1718, 1671, 1511, 1465, 1295, 1115, 734.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{20}$H$_{18}$NaO$_6$ 377.1001, found: 377.0994.

3-(4-Methoxyphenyl)-4-oxo-4-(thiophen-2-yl)butyl thiophene-2-carboxylate (3o)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

Yellow oil (47.1 mg, 61% yield)
\[^1\]H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.66\) (ddd, \(J = 16.9, 3.8, 1.2 \text{ Hz}, 2\text{H}\)), \(7.48\) (dt, \(J = 5.0, 1.0 \text{ Hz}, 2\text{H}\)), \(7.19\) (d, \(J = 8.7 \text{ Hz}, 2\text{H}\)), \(7.00\) (ddd, \(J = 18.1, 5.0, 3.8 \text{ Hz}, 2\text{H}\)), \(6.82 – 6.69\) (m, 2H), \(4.48\) (t, \(J = 7.4 \text{ Hz}, 1\text{H}\)), \(4.31 – 4.07\) (m, 2H), \(3.68\) (s, 3H), \(2.66 – 2.44\) (m, 1H), \(2.29 – 2.24\) (m, 1H).

\[^1\]C NMR (76 MHz, CDCl\(_3\)): \(\delta 192.0, 162.0, 159.0, 143.7, 133.8, 133.7, 133.5, 132.5, 132.4, 130.5, 129.3, 128.1, 127.8, 114.5, 62.9, 55.2, 50.9, 32.4\).

FTIR (neat): \(\nu (\text{cm}^{-1})\) 2997, 2836, 1703, 1656, 1510, 1414, 1247, 1099, 721.

HRMS (ESI-TOF) m/z: \([\text{M+Na}^+]\) Caled for C\(_{20}\)H\(_{18}\)NaO\(_4\)S\(_4\) 409.0544, found: 409.0538.

4-(4-Methoxyphenyl)-2-methyl-5-oxo-5-phenylpentan-2-yl benzoate (3p)

Purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (68.3 mg, 85% yield)

\[^1\]H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.90 – 7.84\) (m, 2H), \(7.81 – 7.72\) (m, 2H), \(7.45 – 7.32\) (m, 2H), \(7.27\) (td, \(J = 7.6, 3.3 \text{ Hz}, 4\text{H}\)), \(7.17 – 7.09\) (m, 2H), \(6.74 – 6.65\) (m, 2H), \(4.82\) (dd, \(J = 8.1, 4.1 \text{ Hz}, 1\text{H}\)), \(3.62\) (s, 3H), \(2.96\) (dd, \(J = 14.6, 8.0 \text{ Hz}, 1\text{H}\)), \(2.29\) (dd, \(J = 14.6, 4.1 \text{ Hz}, 1\text{H}\)), \(1.56\) (s, 3H), \(1.47\) (s, 3H).

\[^1\]C NMR (76 MHz, CDCl\(_3\)): \(\delta 199.4, 165.7, 158.6, 136.7, 132.9, 132.5, 132.0, 131.7, 129.4, 129.3, 128.7, 128.6, 128.1, 114.5, 82.7, 55.2, 47.9, 44.9, 26.7, 26.6.

FTIR (neat): \(\nu (\text{cm}^{-1})\) 3035, 1709, 1685, 1511, 1421, 1292, 1114, 833.

HRMS (ESI-TOF) m/z: \([\text{M+Na}^+]\) Caled for C\(_{26}\)H\(_{26}\)NaO\(_4\)S\(_4\) 425.1728, found: 425.1719.

3-Ethyl-5-(4-methoxyphenyl)-6-oxo-6-phenylhexan-3-yl benzoate (3q)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (49.1 mg, 57% yield)

\[^1\]H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.87 – 7.73\) (m, 4H), \(7.45 – 7.34\) (m, 3H), \(7.27\) (dd, \(J = 7.1, 1.3 \text{ Hz}, 3\text{H}\)), \(7.13\) (d, \(J = 8.7 \text{ Hz}, 2\text{H}\)), \(6.67\) (d, \(J = 8.7 \text{ Hz}, 2\text{H}\)), \(4.75\) (dd, \(J = 7.8, 4.3 \text{ Hz}, 1\text{H}\)), \(3.61\) (s, 3H), \(2.99\) (dd, \(J = 14.3, 6.6 \text{ Hz}, 1\text{H}\)), \(2.36\) (dd, \(J = 14.9, 4.3 \text{ Hz}, 1\text{H}\)), \(2.04 – 1.81\) (m, 4H), \(0.82\) (t, \(J = 7.5, 3\text{H}\)), \(0.78\) (t, \(J = 7.5, 3\text{H}\))
$^{13}$C NMR (76 MHz, CDCl$_3$): δ 199.2, 165.4, 158.5, 136.7, 132.8, 132.4, 131.9, 131.6, 129.4, 129.3, 128.7, 128.5, 128.1, 114.4, 88.4, 55.2, 47.4, 38.4, 27.9, 27.8, 8.0, 7.8.

FTIR (neat): ν (cm$^{-1}$) 2960, 1713, 1679, 1511, 1428, 1269, 1113, 711.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{28}$H$_{30}$NaO$_4$ 453.2042, found: 453.2035.

3-([4-(Benzyloxy)phenyl]-4-oxo-4-phenylbutyl benzoate (3r)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

White solid (71.1 mg, 79% yield)

MP: 127-128 °C

$^1$H NMR (300 MHz, CDCl$_3$): δ 8.05 – 7.89 (m, 4H), 7.64 – 7.33 (m, 11H), 7.33 – 7.22 (m, 2H), 7.02 – 6.89 (m, 2H), 5.01 (s, 2H), 4.78 (t, $J = 7.3$ Hz, 1H), 4.51 – 4.24 (m, 2H), 2.69 – 2.65 (m, 1H), 2.36 – 2.29 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): δ 199.1, 166.5, 158.2, 136.9, 136.5, 132.9, 130.8, 130.2, 129.6, 129.4, 128.8, 128.6, 128.5, 128.4, 128.0, 127.5, 115.5, 70.0, 63.1, 49.5, 32.7.

FTIR (neat): ν (cm$^{-1}$) 3055, 2920, 1737, 1612, 1515, 1496, 1245, 732.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{30}$H$_{26}$NaO$_4$ 473.1728, found: 473.1719.

3-([4-Cyclopropylphenyl]-4-oxo-4-phenylbutyl benzoate (3s)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 30:1)

White solid (49.2 mg, 64% yield)

MP: 108-109 °C

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.88 (ddd, $J = 8.6, 6.1, 1.4$ Hz, 4H), 7.49 – 7.26 (m, 6H), 7.12 (d, $J = 6.2$ Hz, 2H), 6.99 – 6.86 (m, 2H), 4.67 (t, $J = 7.3$ Hz, 1H), 4.35 – 4.16 (m, 2H), 2.69 – 2.45 (m, 1H), 2.21 (ddt, $J = 13.8, 7.8, 5.8$ Hz, 1H), 1.72 (td, $J = 8.4, 4.2$ Hz, 1H), 0.83 (ddd, $J = 8.6, 4.2, 1.5$ Hz, 2H), 0.57 – 0.51 (m, 2H).
$^{13}$C NMR (76 MHz, CDCl$_3$): δ 198.9, 166.5, 143.2, 136.5, 135.5, 132.9, 132.9, 130.2, 129.6, 128.8, 128.5, 128.4, 128.2, 126.4, 63.1, 50.0, 32.7, 15.0, 9.3, 9.2.

FTIR (neat): ν (cm$^{-1}$) 2837, 1721, 1686, 1511, 1375, 1249, 1108, 767.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{26}$H$_{24}$NaO$_{4}$ 407.1623, found: 407.1618.

3-((1,1'-Biphenyl)-4-yl)-4-oxo-4-phenylbutyl benzoate (3t)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 30:1)

White solid (57.2 mg, 68% yield)

MP: 113-114 °C.

$^1$H NMR (599 MHz, CDCl$_3$): δ 8.03 – 7.93 (m, 4H), 7.56 – 7.47 (m, 6H), 7.44 – 7.36 (m, 8H), 7.36 – 7.28 (m, 1H), 6.84 (t, J = 7.2 Hz, 1H), 4.42 – 4.28 (m, 2H), 2.68 – 2.65 (m, 1H), 2.45 – 2.30 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 198.8, 166.4, 140.5, 140.3, 137.6, 136.4, 133.1, 132.9, 130.2, 129.5, 128.8, 128.7, 128.6, 128.5, 128.4, 127.9, 127.3, 126.9, 63.1, 50.1, 32.8.

FTIR (neat): ν (cm$^{-1}$) 3061, 3026, 2928, 1715, 1680, 1486, 1449, 1270, 1113, 710.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{29}$H$_{24}$NaO$_{3}$ 443.1623, found: 443.1616.

3-(3,4-Dimethoxyphenyl)-4-oxo-4-phenylbutyl benzoate (3u)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

Colorless oil (49.3 mg, 61% yield)

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.97 – 7.82 (m, 4H), 7.50 – 7.29 (m, 6H), 6.82 – 6.59 (m, 3H), 4.65 (t, J = 7.3 Hz, 1H), 4.31 – 4.16 (m, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 2.61 – 2.54 (m, 1H), 2.40 – 2.04 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): δ 199.1, 166.4, 149.5, 148.4, 136.5, 132.9, 132.9, 129.7, 129.6, 129.5, 128.7, 128.5, 128.4, 120.9, 111.6, 110.8, 63.0, 55.9, 55.8, 50.0, 32.7.

FTIR (neat): ν (cm$^{-1}$) 2935, 1715, 1679, 1515, 1450, 1262, 1155, 712.
3-(2-Methoxyphenyl)-4-oxo-4-phenylbutyl benzoate (3v)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

Colorless oil (53.9 mg, 72% yield)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.07 – 7.91 (m, 4H), 7.61 – 7.53 (m, 1H), 7.49 – 7.41 (m, 3H), 7.38 – 7.33 (m, 2H), 7.22 – 7.12 (m, 2H), 6.87 (ddd, $J = 8.4$, 5.9, 1.2 Hz, 2H), 5.32 (dd, $J = 7.8$, 6.4 Hz, 1H), 4.36 – 4.24 (m, 2H), 3.81 (s, 3H), 2.71 – 2.62 (m, 1H), 2.29 – 2.21 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 199.7, 166.5, 156.1, 136.4, 132.8, 132.7, 130.4, 129.5, 128.6, 128.5, 128.4, 128.3, 128.2, 127.4, 121.2, 110.9, 63.2, 55.5, 42.3, 31.8.

FTIR (neat): $\nu$ (cm$^{-1}$) 3066, 2837, 1721, 1682, 1603, 1511, 1249, 1176, 711.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{25}$H$_{24}$NaO$_5$ 427.1521, found: 427.1512.

4-(3-Chloro-4-methoxyphenyl)-2-methyl-5-oxo-5-phenylpentan-2-yl benzoate (3y)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (51.6 mg, 59% yield)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.01 – 7.89 (m, 2H), 7.89 – 7.79 (m, 2H), 7.61 – 7.46 (m, 2H), 7.46 – 7.33 (m, 5H), 7.17 (dd, $J = 8.5$, 2.3 Hz, 1H), 6.78 (d, $J = 8.6$ Hz, 1H), 4.88 (dd, $J = 7.7$, 4.5 Hz, 1H), 3.80 (s, 3H), 2.98 (dd, $J = 14.7$, 7.8 Hz, 1H), 2.44 (dd, $J = 14.7$, 4.5 Hz, 1H), 1.66 (s, 3H), 1.57 (s, 3H).

$^{13}$C NMR (76 MHz, CDCl$_3$): $\delta$ 198.9, 165.6, 154.0, 136.3, 133.1, 132.9, 132.6, 131.5, 130.2, 129.9, 129.4, 128.7, 128.5, 127.5, 122.8, 112.5, 82.5, 56.1, 47.5, 44.6, 26.8, 26.6.

FTIR (neat): $\nu$ (cm$^{-1}$) 3062, 2975, 1709, 1682, 1501, 1283, 1111, 771.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{26}$H$_{25}$ClNaO$_4$ 459.1339, found: 459.1330.
7-Methoxy-2-(4-methoxyphenyl)-1,7-dioxo-1-phenyleth-4-yl benzoate (3z)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 5:1) as inseparable mixture of diastereoisomers (dr = 1:1:1)

Yellow oil (50.7 mg, 55% yield)

$^1$H NMR (300 MHz, CDCl$_3$): (mixture of diastereoisomers) $\delta$ 8.03 – 7.82 (m, 4H), 7.61 – 7.53 (m, 1H), 7.47 – 7.30 (m, 5H), 7.23 – 7.15 (m, 2H), 6.87 – 6.78 (m, 1H), 6.79 – 6.71 (m, 1H), 5.26 – 5.07 (m, 1H), 4.67 (dt, $J$ = 8.5, 5.8 Hz, 1H), [3.76 (s) + 3.69 (s), 3H] + [3.61 (s) + 3.58 (s), 3H], 2.72 – 2.55 (m, 1H), 2.47 – 2.33 (m, 2H), 2.26 – 1.99 (m, 3H).

$^{13}$C NMR (76 MHz, CDCl$_3$): (mixture of diastereoisomers) $\delta$ 199.1, 198.9, 173.4, 173.3, 166.1, 166.0, 158.8, 158.7, 136.5, 136.2, 133.0, 132.9, 132.8, 130.9, 130.4, 130.0, 129.9, 129.6, 129.5, 129.4, 129.1, 128.7, 128.5, 128.4, 128.3, 128.2, 114.6, 114.5, 72.8, 72.0, 55.2, 55.1, 51.7, 51.6, 49.2, 49.1, 38.5, 38.2, 30.0, 29.9, 29.8.

FTIR (neat): $\nu$ (cm$^{-1}$) 2983, 1737, 1681, 1448, 1373, 1233, 1044, 711.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{28}$H$_{28}$NaO$_4$ 483.1783, found: 483.1778.

7-Bromo-2-(4-methoxyphenyl)-1-oxo-1-phenyleth-4-yl benzoate (3aa)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1) as inseparable mixture of diastereoisomers (dr = 1.3:1)

Colorless oil (56.5 mg, 57% yield)

$^1$H NMR (300 MHz, CDCl$_3$): (mixture of diastereoisomers) $\delta$ 7.99 – 7.74 (m, 4H), 7.53 – 7.17 (m, 6H), 7.15 – 7.04 (m, 2H), 6.75 – 6.62 (m, 2H), 5.18 – 4.95 (m, 1H), 4.62 – 4.56 (m, 1H), [3.66 (s) + 3.59 (s), 3H], 3.36 – 3.24 (m, 2H), 2.64 – 2.44 (m, 1H), 2.22 – 2.02 (m, 1H), 1.91 – 1.62 (m, 4H).

$^{13}$C NMR (76 MHz, CDCl$_3$): (mixture of diastereoisomers) $\delta$ 199.2, 199.0, 166.2, 166.1, 158.9, 158.7, 136.5, 136.2, 133.1, 132.9, 132.8, 131.1, 130.4, 130.2, 130.1, 129.6, 129.5, 129.4, 129.1, 128.7, 128.5, 128.4, 128.3, 114.6, 114.5, 72.7, 72.1, 55.2, 55.1, 49.3, 49.2, 38.6, 38.3, 33.6, 33.5, 33.4, 33.3, 28.4, 28.3.

FTIR (neat): $\nu$ (cm$^{-1}$) 2837, 1712, 1678, 1510, 1269, 1178, 711.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{28}$H$_{28}$BrNaO$_4$ 517.0990, found: 517.0984.
1-Acetoxy-4-(4-methoxyphenyl)-5-oxo-5-phenylpentan-2-yl benzoate (3ab)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) as inseparable mixture of diastereoisomers (dr = 1.4:1)

Yellow oil (36.6 mg, 41% yield)

$^1$H NMR (300 MHz, CDCl$_3$): (mixture of diastereoisomers) $\delta$ 7.95 – 7.78 (m, 5H), 7.34 – 7.28 (m, 5H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.76 – 6.67 (m, 2H), 5.33 – 5.08 (m, 1H), 4.62 (dt, $J = 14.1$, 7.7 Hz, 1H), 4.26 – 4.08 (m, 2H), 3.68 – 3.60 (m, 3H), 2.57 (dd, $J = 13.0$, 5.9 Hz, 1H), 2.23 – 2.08 (m, 1H), 1.96 – 1.91 (m, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): (mixture of diastereoisomers) $\delta$ 198.9, 198.7, 170.7, 170.6, 165.9, 165.8, 158.9, 158.8, 136.3, 136.1, 133.1, 133.0, 132.9, 132.8, 130.7, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 114.7, 114.6, 114.5, 71.0, 70.3, 65.3, 65.1, 55.2, 55.1, 49.1, 48.9, 35.0, 34.9, 20.8, 20.7.

FTIR (neat): $\nu$ (cm$^{-1}$) 2837, 1741, 1717, 1660, 1510, 1449, 1248, 1109, 712.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{27}$H$_{26}$NaO$_4$ 469.1627, found: 469.1620.

4-(4-Methoxyphenyl)-2-methyl-5-oxo-5-phenylpentan-2-yl benzoate (3ac)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) as inseparable mixture of diastereoisomers (dr = 1.2:1)

Colorless oil (42.9 mg, 53% yield)

$^1$H NMR (300 MHz, CDCl$_3$): (mixture of diastereoisomers) $\delta$ 8.03 – 7.76 (m, 4H), 7.57 – 7.24 (m, 6H), 7.16 – 7.08 (m, 2H), 6.89 – 6.62 (m, 2H), [5.95 (t, $J = 5.3$ Hz, minor diastereoisomers) + 5.76 (dd, $J = 7.0$, 4.0 Hz, major diastereoisomers) 1H], 4.75 (dt, $J = 7.7$, 6.1 Hz, 1H), 3.66 (s, 3H), [3.37 (s) + 3.32 (s) 3H), 2.85 – 2.50 (m, 1H), 2.38 – 2.20 (m, 1H).

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$+CDCl$_3$): (mixture of diastereoisomers) $\delta$ 198.8, 198.7, 165.9, 158.9, 143.4, 133.2, 132.8, 132.7, 130.9, 130.3, 130.0, 129.9, 129.7, 129.6, 129.4, 129.3, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 114.4, 114.3, 99.1, 98.5, 56.7, 56.6, 48.3, 47.7, 47.6, 46.8, 38.3, 37.8.
FTIR (neat): $\nu$ (cm$^{-1}$) 3063, 2938, 1717, 1680, 1510, 1449, 1248, 1176, 711.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{25}$H$_{24}$NaO$_5$ 427.1521, found: 427.1509.

1,3-Bis(4-methoxyphenyl)-4-oxo-4-phenylbutyl benzoate (3ad)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) as inseparable mixture of diastereoisomers (1.3:1 dr)

Colorless oil (63.4 mg, 66% yield)

$^1$H NMR (300 MHz, CDCl$_3$): (mixture of diastereoisomers) $\delta$ 8.09 – 7.93 (m, 2H), 7.87 (ddt, $J = 11.3$, 7.1, 1.4 Hz, 2H), 7.60 – 7.50 (m, 1H), 7.49 – 7.30 (m, 7H), 7.23 – 7.17 (m, 2H), 6.95 – 6.78 (m, 4H), 5.97 – 5.73 (m, 1H), 4.80 – 4.40 (m, 1H), [3.83 (s) + 3.79 (s), 3H], [3.77 (s) + 3.74 (s), 3H], 3.08 – 2.77 (m, 1H), 2.68 – 2.33 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): (mixture of diastereoisomers) $\delta$ 199.1, 198.9, 165.7, 165.6, 159.5, 159.4, 158.8, 158.7, 136.4, 132.9, 132.9, 132.8, 132.7, 132.2, 130.5, 130.4, 130.3, 129.6, 129.6, 129.4, 128.7, 128.5, 128.3, 128.2, 128.1, 127.8, 114.6, 114.5, 114.0, 113.9, 74.9, 74.5, 55.3, 55.2, 55.1, 55.0, 49.4, 49.1, 40.6, 40.0.

FTIR (neat): $\nu$ (cm$^{-1}$) 3061, 2837, 1715, 1679, 1510, 1449, 1245, 711.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{31}$H$_{28}$NaO$_5$ 503.1834, found: 503.1830.

1-(4-Methoxyphenyl)-4-oxo-3,4-diphenylbutyl benzoate (3ae)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1) as inseparable diastereoisomeric (1.3:1 dr) and regioisomeric (3:1 rr) mixture.

Colorless oil (53.2 mg, 59% yield)

$^1$H NMR (300 MHz, CDCl$_3$): (mixture of diastereoisomers and regioisomer) $\delta$ 8.23 – 7.63 (m, 5H), 7.59 – 7.30 (m, 10H), 7.24 – 6.77 (m, 4H), 6.02 – 5.73 (m, 1H), 4.78 – 4.59 (m, 1H), [3.83 (s, major diastereoisomer) + 3.79 (s, minor diastereoisomer) + 3.77 (s, regioisomer) + 3.74 (s, regioisomer), 3H], 3.13 – 2.81 (m, 1H), 2.67 – 2.30 (m, 1H).
$^{13}$C NMR (76 MHz, CDCl$_3$): (mixture of diastereoisomers and regioisomer) δ 198.9, 198.8, 165.7, 165.6, 159.5, 159.4, 138.7, 136.4, 132.9, 132.8, 132.5, 132.2, 130.3, 129.7, 129.6, 129.4, 129.3, 129.2, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.4, 127.3, 126.6, 114.5, 114.0, 113.9, 74.9, 74.6, 55.3, 55.2, 50.3, 49.9, 40.6, 40.2.

FTIR (neat): $\nu$ (cm$^{-1}$) 3062, 1715, 1679, 1513, 1448, 1247, 1175, 699.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{31}$H$_{26}$F$_3$NaO$_4$ 541.1603, found: 541.1597.

1-(4-Methoxyphenyl)-4-oxo-4-phenyl-3-(4-(trifluoromethyl)phenyl)butyl benzoate (3af)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1) as inseparable diastereoisomeric (1.2:1 dr) and regioisomeric (7:1 rr) mixture.

Yellow oil (63.2 mg, 61% yield)

$^1$H NMR (300 MHz, CDCl$_3$): (mixture of diastereoisomers and regioisomer) δ 7.94 – 7.74 (m, 4H), 7.49 – 7.17 (m, 12H), 6.89 – 6.71 (m, 2H), 5.97 – 5.71 (m, 1H), 4.68 (dt, J = 22.3, 7.0 Hz, 1H), [3.72 (s, major diastereoisomer) + 3.68 (s, minor diastereoisomer) + 3.66 (s, regioisomer) + 3.62 (s, regioisomer), 3H], 3.07 – 2.71 (m, 1H), 2.62 – 2.27 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$) [19F]: (mixture of diastereoisomers and regioisomer) δ 198.3, 198.2, 165.7, 165.6, 159.6, 159.5, 142.7, 135.9, 133.4, 133.3, 133.1, 133.0, 132.1, 131.8, 130.1, 130.0, 129.7, 129.6, 129.5, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.0, 127.8, 126.1, 126.0, 125.9, 114.1, 114.0, 74.8, 74.4, 55.3, 55.2, 49.9, 40.5, 40.1.

$^{19}$F NMR (282 MHz, CDCl$_3$): (mixture of diastereoisomers) δ -62.54, -62.56.

FTIR (neat): $\nu$ (cm$^{-1}$) 2963, 1717, 1681, 1514, 1450, 1327, 1247, 1109, 711.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{31}$H$_{23}$F$_3$NaO$_4$ 541.1603, found: 541.1597.

1-(4-Methoxyphenyl)-3-(naphthalen-2-yl)-4-oxo-4-phenylbutyl benzoate (3ag)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1) as inseparable diastereoisomeric (dr = 1.2:1) and regioisomeric (4:1 rr)
mixture.

Yellow oil (55.1 mg, 55% yield)

$^1$H NMR (300 MHz, CDCl$_3$): (mixture of diastereoisomers and regioisomer) $\delta$ 7.93 – 7.88 (m, 1H), 7.84 – 7.66 (m, 6H), 7.47 – 7.19 (m, 12H), 6.85 – 6.79 (m, 1H), 6.77 – 6.70 (m, 1H), 5.83 (dd, $J = 13.9, 8.6, 5.2$ Hz, 1H), 4.75 (dt, $J = 23.5, 7.0$ Hz, 1H), [3.71 (s, major diastereoisomer) + 3.66 (s, minor diastereoisomer) + 3.65 (s, regioisomer) + 3.62 (s, regioisomer) 3H], 3.11 – 2.81 (m, 1H), 2.70 – 2.34 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): (mixture of diastereoisomers and regioisomer) $\delta$ 198.9, 198.7, 165.7, 165.6, 159.5, 159.4, 136.4, 136.2, 136.1, 133.7, 133.6, 133.0, 132.9, 132.6, 132.5, 132.9, 132.2, 130.3, 130.2, 129.7, 129.6, 129.5, 129.4, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 126.3, 126.2, 126.1, 126.0, 126.0, 114.6, 114.0, 113.9, 75.0, 74.6, 55.3, 55.3, 50.4, 50.3, 40.6, 40.2.

FTIR (neat): $\nu$ (cm$^{-1}$) 3061, 2962, 1716, 1680, 1513, 1267, 711.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{34}$H$_{28}$NaO$_5$ 523.1885, found: 523.1881.

3-(4-Methoxyphenyl)-1-((8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)-4-oxo-4-phenylbutyl benzoate (3ah)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 5:1) as inseparable mixture of diastereoisomers (dr = 1:1)

Brown oil (66.8 mg, 52% yield)

$^1$H NMR (300 MHz, CDCl$_3$): (mixture of diastereoisomers) $\delta$ 8.04 (dt, $J = 7.1, 1.4$ Hz, 1H), 7.92 – 7.85 (m, 2H), 7.68 – 7.46 (m, 1H), 7.49 – 7.26 (m, 4H), 7.18 – 7.05 (m, 4H), 6.84 – 6.45 (m, 5H), [5.72 (td, $J = 5.2, 1.9$ Hz) + 5.50 (td, $J = 5.2, 1.6$ Hz) 1H], 4.80 (q, $J = 7.5$ Hz, 1H), [3.67 (s) + 3.66 (s) 3H], 2.76 (dq, $J = 9.4, 4.3$ Hz, 3H), 2.41 – 1.88 (m, 9H), 1.49 – 1.37 (m, 5H), 0.82 (d, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (76 MHz, CDCl$_3$): (mixture of diastereoisomers) $\delta$ 221.2, 221.1, 221.0, 198.8, 198.7, 158.9, 154.4, 154.3, 138.1, 138.0, 138.0, 137.9, 136.3, 136.2, 134.9, 134.8, 133.7, 133.1, 133.0, 130.2, 130.1, 129.4, 129.3, 128.9, 128.8, 128.6, 128.5, 128.4, 126.5, 126.4, 117.3, 117.2, 115.3, 114.7, 114.6, 114.5, 112.9, 110.6, 107.7, 55.2, 50.4, 50.3, 48.1, 48.0, 48.0, 47.6, 47.5, 47.4, 44.1, 44.0, 43.9, 38.4, 38.2, 35.9, 31.6, 31.5, 29.6, 29.5, 29.5, 26.5, 26.4, 26.4, 25.9, 25.9, 25.8, 21.6, 21.6, 13.9, 13.8.
FTIR (neat): $\nu$ (cm$^{-1}$) 2931, 2837, 1722, 1680, 1511, 1448, 1246, 1176, 695.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{42}$H$_{42}$NaO$_6$ 665.2879, found: 665.2879.

1-(4-Methoxyphenyl)-4-oxo-3-(11-oxo-6,11-dihydrodibenzo[b,c]oxepin-2-yl)-4-phenylbutyl benzoate (3ai)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) as inseparable inseparable diastereoisomeric (dr = 1.1:1) and regioisomeric (1.7:1 rr) mixture.

Yellow oil (66.8 mg, 61% yield)

$^1$H NMR (300 MHz, CDCl$_3$): (mixture of diastereoisomers and regioisomer) $\delta$ 8.39 – 7.86 (m, 6H), 7.61 – 7.31 (m, 12H), 7.07 – 6.77 (m, 3H), 6.01 – 5.79 (m, 1H), 5.16 (dd, $J$ = 14.1, 7.7 Hz, 2H), 4.89 – 4.55 (m, 1H), [3.83 (s, major diastereoisomer) + 3.78 (s, minor diastereoisomer) + 3.76 (s, regioisomer) + 3.74 (s, regioisomer) 3H), 3.14 – 2.79 (m, 1H), 2.69 – 2.39 (m, 1H).

$^{13}$C NMR (76 MHz, CDCl$_3$): (mixture of diastereoisomers and regioisomer) $\delta$ 198.9, 198.8, 198.7, 190.8, 190.7, 165.7, 165.6, 165.6, 161.1, 160.9, 160.6, 160.5, 159.5, 159.4, 158.9, 158.8, 140.5, 140.4, 140.3, 136.3, 136.1, 135.4, 134.8, 134.7, 134.5, 134.1, 133.5, 133.1, 133.0, 132.9, 132.9, 132.8, 132.8, 132.7, 132.4, 132.3, 132.1, 131.9, 131.8, 130.6, 130.2, 130.1, 130.0, 129.9, 129.7, 129.7, 129.6, 129.6, 129.5, 129.4, 129.3, 129.3, 129.2, 128.9, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.9, 127.8, 127.7, 125.5, 125.4, 125.2, 125.1, 121.8, 121.7, 121.2, 121.1, 114.7, 114.6, 114.1, 114.0, 74.8, 74.7, 74.6, 74.1, 73.6, 73.5, 73.5, 73.5, 55.3, 55.2, 49.4, 49.2, 49.0, 48.9, 40.5, 40.4, 40.2, 40.1.

FTIR (neat): $\nu$ (cm$^{-1}$) 2831, 1711, 1680, 1648, 1513, 1486, 1360, 1265, 1248, 1109, 711.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{38}$H$_{30}$NaO$_6$ 605.1940, found: 605.1939.

3-(4-Methoxyphenyl)-4-oxo-4-phenylbutyl 2-methoxybenzoate (3aj)
Performed with general procedure E and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

Colorless oil (29.1 mg, 36% yield)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.99 – 7.93 (m, 2H), 7.74 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.50 – 7.45 (m, 2H), 7.38 (dd, $J = 8.3, 7.1$ Hz, 2H), 7.27 – 7.20 (m, 2H), 6.99 (d, $J = 7.9$ Hz, 2H), 6.87 – 6.82 (m, 2H), 4.81 (dd, $J = 8.0, 6.5$ Hz, 1H), 4.33 (dt, $J = 11.3, 5.7$ Hz, 1H), 4.25 – 4.22 (m, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 2.73 – 2.53 (m, 1H), 2.35 – 2.21 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 199.3, 166.3, 159.1, 158.8, 136.6, 133.5, 132.8, 131.6, 130.6, 129.4, 128.8, 128.5, 120.3, 120.2, 114.6, 112.0, 62.7, 55.9, 55.2, 49.3, 32.7.

FTIR (neat): $\nu$ (cm$^{-1}$) 2963, 2831, 1727, 1685, 1512, 1180, 757.

HRMS (ESI-TOF) m/z: [M+Na$^+$]+ Caled for C$_{23}$H$_{24}$NaO$_5$ 427.1521, found: 427.1509.

3-(4-Methoxyphenyl)-4-oxo-4-(4-(trifluoromethyl)phenyl)butyl 4-methoxybenzoate or 3,4-bis(4-methoxyphenyl)-4-oxobutyl 4-(trifluoromethyl)benzoate (3ak)

Performed with general procedure E and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) as inseparable mixture of regioisomer (1.8:1 rr).

Colorless oil (40.6 mg, 43% yield)

$^1$H NMR (300 MHz, CDCl$_3$): (mixture of regioisomer) $\delta$ 8.01 – 7.83 (m, 4H), 7.61 – 7.52 (m, 2H), 7.13 (t, $J = 8.7$ Hz, 2H), 6.86 – 6.73 (m, 4H), 4.60 (q, $J = 7.8$ Hz, 1H), 4.34 – 4.10 (m, 2H), [3.79 (s, major regioisomer) + 3.74 (s, minor regioisomer) + 3.67 (s, major regioisomer) + 3.66 (s, minor regioisomer), 6H], 2.61 – 2.54 (m, 1H), 2.25 – 2.51 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) ($^{19}$F): (mixture of regioisomer) $\delta$ 198.1, 197.4, 166.2, 165.2, 163.4, 163.3, 159.0, 158.8, 139.2, 134.4, 134.0, 133.4, 131.5, 131.0, 130.9, 129.9, 129.8, 129.8, 129.3, 129.2, 129.0, 125.5, 125.3, 125.2, 123.6, 123.5, 122.5, 114.8, 114.6, 113.7, 113.6, 63.9, 62.5, 55.4, 55.4, 55.2, 55.2, 50.1, 49.3, 32.7, 33.6.

$^{19}$F NMR (564 MHz, CDCl$_3$): (mixture of regioisomer) $\delta$ -63.13, -63.23.

FTIR (neat): $\nu$ (cm$^{-1}$) 2909, 1718, 1686, 1606, 1512, 1325, 1168, 771.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Caled for C$_{25}$H$_{24}$F$_3$NaO$_5$ 495.1395, found: 495.1387.
Regioselectivities Determination of Unsymmetrical Diaryl Cyclopropanes

The regioselectivities of 3ae-3ag was determine by further derivatization (see below) and confirmed by comparison with the $^1$H NMR of related known compounds or similar structures.[6-7]

Major regioisomer of 3ae-s

4-(4-Methoxyphenyl)-1,2-diphenylbutane-1,4-dione

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.11 – 8.00 (m, 4H), 7.55 – 7.34 (m, 8H), 7.01 – 6.90 (m, 2H), 5.38 – 5.33 (m, 1H), 4.30 – 4.18 (m, 1H), 3.90 (s, 3H), 3.35 – 3.26 (m, 1H).

Major regioisomer of 3af-s

4-(4-Methoxyphenyl)-1-phenyl-2-(4-(trifluoromethyl)phenyl)butane-1,4-dione

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.97 (ddt, $J$ = 16.5, 6.9, 2.0 Hz, 4H), 7.54 – 7.36 (m, 7H), 6.91 (dd, $J$ = 9.1, 2.4 Hz, 2H), 5.39 (dd, $J$ = 9.8, 4.0 Hz, 1H), 4.18 – 4.06 (m, 1H), 3.85 (s, 3H), 3.31 – 3.23 (m, 1H).

Major regioisomer of 3ag-s

4-(4-methoxyphenyl)-2-(naphthalen-2-yl)-1-phenylbutane-1,4-dione

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.04 – 7.98 (m, 2H), 7.92 – 7.89 (m, 2H), 7.72 (d, $J$ = 5.3 Hz, 3H), 7.44 – 7.30 (m, 7H), 6.85 (d, $J$ = 8.9 Hz, 2H), 5.41 (dd, $J$ = 10.0, 3.7 Hz, 1H), 4.19 (dd, $J$ = 17.9, 10.1 Hz, 1H), 3.79 (s, 3H), 3.28 (dd, $J$ = 17.9, 3.8 Hz, 1H).

D. Large-scale preparation of 3a and its derivatization:

(a) Large-scale preparation of 3a
To an oven-dried 50 mL Schlenk tube equipped with a stir bar, acyl fluoride 1a (620 mg, 5.0 mmol, 2.5 equiv.), aryl cyclopropane 2a (370.5 mg, 2.0 mmol, 1.0 equiv.), photocatalyst 4CzIPN (39.5 mg, 2.5 mol%), NaI (31.0 mg, 5.0 mol%) and Cs2CO3 (1.3 g, 2.0 equiv.) were added. Then, the reaction tube was evacuated and backfilled with argon for two times. Subsequently, anhydrous DCE (10.0 mL, 0.2 M) was added. The resulting mixture was irradiated with blue LED at room temperature for 12 h. The residue was purified by silica gel chromatography to afford the desired product 3a (554 mg, 74% yield).

(b) Deprotection of 3a

4-Hydroxy-2-(4-methoxyphenyl)-1-phenylbutan-1-one (4a)

The NaOH aq (1 mL, 1 M) solution was added to a solution of 3a (37.4 mg, 0.10 mmol) in THF (1.0 mL). The reaction mixture was stirred at 80 °C for 6 h. After completion, the mixture was extracted with ethyl acetate (3 × 3 mL). The organic layer was dried by Na2SO4, after filtration and evaporated under reduced pressure. Then, the residue was purified by column chromatography on silica gel (pentane/ethyl acetate = 6:1) to afford the desired product 4a as colorless oil (20.5 mg, 76% yield).

1H NMR (300 MHz, CDCl3): δ 7.94 – 7.86 (m, 2H), 7.45 – 7.35 (m, 1H), 7.31 (dd, J = 8.3, 6.6 Hz, 2H), 7.18 – 7.09 (m, 2H), 6.83 – 6.68 (m, 2H), 4.74 (t, J = 7.2 Hz, 1H), 3.68 (s, 3H), 3.64 – 3.45 (m, 2H), 2.33 (ddd, J = 14.5, 7.2, 5.2 Hz, 1H), 1.99 (ddd, J = 7.4, 6.1, 4.9 Hz, 1H).

13C NMR (76 MHz, CDCl3): δ 200.3, 158.7, 136.7, 132.9, 131.0, 129.4, 128.8, 128.5, 114.5, 60.5, 55.2, 49.1, 36.4.

FTIR (neat): ν (cm⁻¹) 2957, 2930, 1710, 1512, 1248, 1178.

HRMS (ESI-TOF) m/z: [M+Na⁺] Caled for C17H18NaO3 293.1154, found: 293.1148.

(c) Reduction of 3a

2-(4-Methoxyphenyl)-1-phenylbutane-1,4-diol (4b)
A solution of LiAlH$_4$ (19.0 mg, 0.50 mmol, 5.0 equiv.) in dry THF (3 mL) was stirred at 0 °C under N$_2$ atmosphere. Then, a solution of 3a (37.4 mg, 0.10 mmol, 1.0 equiv.) in dry THF (2 mL) was added slowly. The reaction mixture was stirred at room temperature for 3 h and quenched with aqueous NaOH (2 mL, 2.5 M) solution. The mixture was extracted with ethyl acetate (3 × 3 mL). The organic layer was dried by Na$_2$SO$_4$, after filtration and evaporated under reduced pressure. The diastereoselectivity was determined by $^1$H NMR on the crude product (>19:1 dr). Then, the residue was purified by column chromatography on silica gel (pentane/ethyl acetate = 2:1) to afford the desired product 4b as colorless oil (26.4 mg, 97% yield). The relative configuration was confirmed by comparison with a related known compound.$^8$

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.38 – 7.24 (m, 5H), 7.20 – 7.12 (m, 2H), 6.92 – 6.86 (m, 2H), 4.72 (d, $J$ = 8.1 Hz, 1H), 3.82 (s, 3H), 3.43 (ddd, $J$ = 11.7, 6.9, 5.0 Hz, 1H), 3.32 (ddd, $J$ = 10.6, 8.0, 6.3 Hz, 1H), 3.00 (ddd, $J$ = 12.4, 8.1, 4.5 Hz, 1H), 1.81 – 1.62 (m, 2H).

$^{13}$C NMR (76 MHz, CDCl$_3$): δ 158.7, 142.4, 132.4, 129.7, 128.3, 127.8, 127.0, 114.2, 78.7, 60.9, 55.3, 49.9, 34.9.

FTIR (neat): $\nu$ (cm$^{-1}$) 3057, 1512, 1420, 1265, 702.

HRMS (ESI-TOF) m/z [M+Na$^+$] Calcd for C$_{17}$H$_{20}$NaO$_3$ 295.1310, found: 295.1302.

(c) Acid-catalyzed cyclization of 4b

3-(4-Methoxyphenyl)-2-phenyltetrahydrofuran (4c)

To a stirred solution of diol 4b (27.2 mg, 0.10 mmol) in 1.0 mL dry 1,2-dichloroethane in a 5.0 mL reaction tube, TfOH (10.0 mol%) was added under inert atmosphere. The reaction vial was capped and put into an oil bath pre heated at 40 °C for overnight. After completion, the mixture was concentrated under reduced pressure and a column chromatographic purification was performed using silica gel (pentane/ethyl acetate = 50:1) to afford the desired product 4c as colorless oil (22.6 mg, 89% yield). The relative configuration was confirmed by comparison with a related known compound.$^9$–$^{10}$

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.21 – 7.06 (m, 5H), 7.06 – 6.94 (m, 2H), 6.83 – 6.73 (m, 2H), 4.70 (d, $J$ = 8.5 Hz, 1H), 4.17 (dd, $J$ = 8.3, 5.8 Hz, 2H), 3.72 (s, 3H), 3.09 (dt, $J$ = 9.6, 8.2 Hz, 1H), 2.42 – 2.30 (m, 1H), 2.23 – 2.10 (m, 1H).
$^{13}$C NMR (76 MHz, CDCl$_3$): $\delta$ 158.4, 141.8, 132.7, 128.7, 128.2, 127.4, 125.8, 113.9, 87.7, 68.5, 55.3, 53.5, 35.6.

FTIR (neat): $\nu$ (cm$^{-1}$) 2968, 1582, 1514, 1339, 1215, 701.

HRMS (ESI-TOF) m/z: [M+Na$^+$] Calcd for C$_{17}$H$_{18}$NaO$_2$ 277.1204, found: 277.1196.

E. Mechanistic studies:

(a) Radical trapping experiment:

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, acyl fluoride 1a (62.1 mg, 0.50 mmol, 2.5 equiv), aryl cyclopropane 2a (29.6 mg, 0.20 mmol, 1.0 equiv.), photocatalyst 4CzIPN (7.9 mg, 5.0 mol%), N1 (6.2 mg, 10.0 mol%), Cs$_2$CO$_3$ (130.4 mg, 2.0 equiv.) and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (62.5 mg, 2.0 equiv.) were added. Then, the reaction tube was evacuated and backfilled with argon for two times. Subsequently, anhydrous DCE (2.0 mL, 0.1 M) was added. The resulting mixture was irradiated with blue LED at room temperature for 12 h. The mixture was analyzed by HRMS (see below).

(b) The acyl azolium salt 5 as and Na-benzoate as competent substrates:

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, aryl cyclopropane 2a (29.6 mg, 0.20 mmol, 1.0 equiv.), acylazolium ion 5 (40.3 mg, 0.20 mmol, 1.0 equiv.), sodium benzoate 6 (28.8 mg, 0.20 mmol, 1.0 equiv.), photocatalyst 4CzIPN (7.9 mg, 5.0 mol%) and Cs$_2$CO$_3$ (130.4 mg, 2.0 equiv.)
were added. Then, the reaction tube was evacuated and backfilled with argon for two times. Subsequently, anhydrous DCE (2.0 mL, 0.1 M) was added. The resulting mixture was irradiated with blue LEDs at room temperature for 12 h. The residue was purified by silica gel chromatography to afford the desired product 3a in 52% yield.

(c) The benzyl anion trapping experiment by acetone:

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, aryl cyclopropane 2a (29.6 mg, 0.20 mmol, 1.0 equiv.), sodium benzoate 6 (28.8 mg, 0.20 mmol, 1.0 equiv.), dry acetone (116 mg, 2.0 mmol, 10.0 equiv.) and photocatalyst 4CzIPN (7.9 mg, 5.0 mol%) were added. Then, the reaction tube was evacuated and backfilled with argon for two times. Subsequently, anhydrous DCE (2.0 mL, 0.1 M) was added. The resulting mixture was irradiated with blue LEDs at room temperature for 12 h. The alcohol 7 was not formed by HRMS measurement.

(d) Experiments with enantiomerically enriched 2s:

The reaction of (1S,2S)-2s with 90% ee was performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) to afford the product 3ab in 45% yield with 83%/82% ee and 1.2:1 dr. HPLC Analysis: Chiralpak IC (Cyclohexane/iPrOH = 93/7, 1.0 mL/min, 25 °C).

Racemic sample:
Chiral sample:

(e) Experiments with enantiomerically enriched 2l:

The reaction of (1R,2R)-2l with 78% ee was performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) to afford the product 3ad in 59% yield with 14%/14% ee and 1.2:1 dr. HPLC Analysis: Chiralpak AD-H (Cyclohexane/iPrOH = 90/10, 1.0 mL/min, 25 °C).

Racemic sample:
Chiral sample:

To our hypothesis of the erosion of stereochemistry due to the rapid ring opening/closing process of the diaryl radical cation, we treated the enantiomerically enriched 2s and 2l with blue LED irritation (see below). After one hour, the ee of 2s would be retained but the diaryl cyclopropane 2l would be racemization totally. These experimental results could support our assumption.

(f) Luminescence quenching experiments
Emission intensities were recorded using a Jasco FP-8300 spectrofluorometer. 4-CzIPN solutions were excited at 435 nm and the emission intensity was recorded at 590 nm. In a typical experiment, to a certain amount of a solution of 4-CzIPN in DCE (5 mL), the appropriate amount of quencher (1-cyclopropyl-4-methoxybenzene 2a, acylazolium ion 5) was added in a screw-top quartz cuvette, and the emission of the sample was recorded.

F. X-ray data for 3s:

X-Ray diffraction: Data sets for compound 3s were collected with a Bruker APEXII Kappa CCD diffractometer. Programs used: data collection: APEX3 V2019.1-0\(^1\) (Bruker AXS Inc., 2019); cell refinement: SAINT V8.40A (Bruker AXS Inc., 2019); data reduction: SAINT V8.40A (Bruker AXS Inc., 2019); absorption correction, SADABS V2016/2 (Bruker AXS Inc., 2019); structure solution SHELXT-2015\(^2\) (Sheldrick, G. M. Acta Cryst., 2015, A71, 3-8); structure refinement SHELXL-2015\(^3\) (Sheldrick, G. M. Acta Cryst., 2015, C71 (1), 3-8) and graphics, XP\(^4\) (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, 1998). R-values are given for observed reflections, and \(wR^2\) values are given for all reflections.

X-ray crystal structure analysis of 3s: A colorless plate-like specimen of C\(_{26}\)H\(_{24}\)O\(_3\), approximate dimensions 0.050 mm x 0.140 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Kappa CCD APEXII Bruker APEXII Diffractometer system equipped with a fine-focus sealed tube Cu sealed tube (CuKa, \(\lambda = 1.54178\) Å) and a graphite monochromator. A total of 1558 frames were collected. The total exposure time was 21.01 hours. The
frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 12124 reflections to a maximum θ angle of 66.68° (0.84 Å resolution), of which 3457 were independent (average redundancy 3.507, completeness = 99.2%, R_int = 4.24%, R_sig = 3.80%) and 2728 (78.91%) were greater than 2σ(F²). The final cell constants of a = 5.7053(2) Å, b = 9.3059(4) Å, c = 19.1323(7) Å, α = 89.576(2)°, β = 89.233(2)°, γ = 75.384(2)°, volume = 982.82(7) Å³, are based upon the refinement of the XYZ-centroids of 2945 reflections above 20 σ(I) with 9.245° < 2θ < 132.9°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.906. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9130 and 0.9680. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, C₂₆H₂₄O₃. The final anisotropic full-matrix least-squares refinement on F² with 281 variables converged at R1 = 3.97%, for the observed data and wR2 = 10.31% for all data. The goodness-of-fit was 1.051. The largest peak in the final difference electron density synthesis was 0.170 e/Å³ and the largest hole was -0.255 e/Å³ with an RMS deviation of 0.044 e/Å³. On the basis of the final model, the calculated density was 1.299 g/cm³ and F(000), 408 e-. CCDC Nr.: 2094400.

![Crystal structure](image)

**Figure 1:** Crystal structure of compound 3s. Thermal ellipsoids are shown at 30% probability.

| Table 1. Sample and crystal data for 3s. |
|----------------------------------------|
| **Identification code** | 3s |

S36
Chemical formula \[ \text{C}_2\text{H}_4\text{O}_3 \]

Formula weight \( 384.45 \text{ g/mol} \)

Temperature \( 103(2) \text{ K} \)

Wavelength \( 1.54178 \text{ Å} \)

Crystal size \( 0.050 \times 0.140 \times 0.140 \text{ mm} \)

Crystal habit colorless plate

Crystal system triclinic

Space group \( P -1 \)

Unit cell dimensions
\[
\begin{align*}
a &= 5.7053(2) \text{ Å} \\
b &= 9.3059(4) \text{ Å} \\
c &= 19.1323(7) \text{ Å}
\end{align*}
\]

\( \alpha = 89.576(2)^\circ \)

\( \beta = 89.233(2)^\circ \)

\( \gamma = 75.384(2)^\circ \)

Volume \( 982.82(7) \text{ Å}^3 \)

\( Z = 2 \)

Density (calculated) \( 1.299 \text{ g/cm}^3 \)

Absorption coefficient \( 0.664 \text{ mm}^{-1} \)

\( F(000) = 408 \)

---

Table 2. Data collection and structure refinement for 3s.

|                     |     |
|---------------------|-----|
| **Diffractometer**  | Kappa CCD APEXII Bruker APEXII Diffractometer |
| **Radiation source**| fine-focus sealed tube Cu sealed tube (CuK\( \alpha \), \( \lambda = 1.54178 \text{ Å} \)) |
| **Theta range for data collection** | 4.62 to 66.68° |
| **Index ranges**    | \(-6 \leq h \leq 6, -11 \leq k \leq 11, -22 \leq l \leq 22\) |
| **Reflections collected** | 12124 |
| **Independent reflections** | 3457 [R(int) = 0.0424] |
| **Coverage of independent reflections** | 99.2% |

S37
Absorption correction          Multi-Scan
Max. and min. transmission     0.9680 and 0.9130
Structure solution technique   direct methods
Structure solution program    SHELXT 2018/2 (Sheldrick, 2018)
Refinement method             Full-matrix least-squares on F^2
Refinement program            SHELXL-2018/3 (Sheldrick, 2018)
Function minimized             \[ \Sigma w(F_o^2 - F_c^2)^2 \]
Data / restraints / parameters 3457 / 49 / 281
Goodness-of-fit on F^2        1.051
Final R indices               
2728 data; I>2\(\sigma(I)\)   R1 = 0.0397, wR2 = 0.0964
all data                      R1 = 0.0528, wR2 = 0.1031
Weighting scheme              \[ w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 0.1073P] \] where \( P = (F_o^2 + 2F_c^2)/3 \)
Largest diff. peak and hole    0.170 and -0.255 eÅ^{-3}
R.M.S. deviation from mean     0.044 eÅ^{-3}

Table 3. Bond lengths (Å) for 3s.

| Bond                  | Length (Å)  | Bond                  | Length (Å)  | Bond                  | Length (Å) 
|-----------------------|-------------|-----------------------|-------------|-----------------------|-------------
| C1-C31                | 1.528(2)    | C1-C5                 | 1.530(2)    | C1-C2                 | 1.5372(19)  
| C1-C2                 | 1.5372(19)  | C1-H1                 | 1.0         | C2-C3                 | 1.514(2)    
| C2-C3                 | 1.514(2)    | C2-H2A                | 0.99        | C2-H2B                | 0.99        
| C2-H2B                | 0.99        | C3-O1                 | 1.4470(17)  | C3-H3A                | 0.99        
| C3-H3A                | 0.99        | C3-H3B                | 0.99        | C4-O2                 | 1.2069(18)  
| C4-O2                 | 1.2069(18)  | C4-O1                 | 1.3448(19)  | C4-C11                | 1.490(2)    
| C4-C11                | 1.490(2)    | C5-O3                 | 1.2187(18)  | C5-C21                | 1.502(2)    
| C5-C21                | 1.502(2)    | C11-C12               | 1.388(2)    | C11-C16               | 1.393(2)    
| C11-C16               | 1.393(2)    | C12-C13               | 1.388(2)    | C12-H12               | 0.95        
| C12-H12               | 0.95        | C13-C14               | 1.386(2)    | C13-H13               | 0.95        
| C13-H13               | 0.95        | C14-C15               | 1.389(2)    |
| Bond          | Distance | Bond          | Distance |
|---------------|----------|---------------|----------|
| C14-H14       | 0.95     | C15-C16       | 1.386(2) |
| C15-H15       | 0.95     | C16-H16       | 0.95     |
| C21-C22       | 1.394(2) | C21-C26       | 1.396(2) |
| C22-C23       | 1.386(2) | C22-H22       | 0.95     |
| C23-C24       | 1.388(2) | C23-H23       | 0.95     |
| C24-C25       | 1.388(2) | C24-H24       | 0.95     |
| C25-C26       | 1.385(2) | C25-H25       | 0.95     |
| C26-H26       | 0.95     | C31-C36       | 1.392(2) |
| C31-C32       | 1.393(2) | C32-C33       | 1.386(2) |
| C32-H32       | 0.95     | C33-C34       | 1.397(2) |
| C33-H33       | 0.95     | C34-C35       | 1.397(2) |
| C34-C41       | 1.486(2) | C35-C36       | 1.387(2) |
| C35-H35       | 0.95     | C36-H36       | 0.95     |
| C41-C42A      | 1.497(10)| C41-C43       | 1.506(5) |
| C41-C42       | 1.516(5) | C41-C43A      | 1.528(11)|
| C41-H41       | 1.0      | C41-H41A      | 1.0      |
| C42-C43       | 1.490(6) | C42-H42A      | 0.99     |
| C42-H42B      | 0.99     | C43-H43A      | 0.99     |
| C43-H43B      | 0.99     | C42A-C43A     | 1.471(11)|
| C42A-H42C     | 0.99     | C42A-H42D     | 0.99     |
| C43A-H43C     | 0.99     | C43A-H43D     | 0.99     |
Table 4. Bond angles (°) for 3s.

| Bond 1         | Bond 2         | Bond 3         | Angle 1       | Angle 2       |
|----------------|----------------|----------------|---------------|---------------|
| C31-C1-C5      | 107.88(12)     | C31-C1-C2      | 111.92(12)    |
| C5-C1-C2       | 111.15(12)     | C31-C1-H1      | 108.6         |
| C5-C1-H1       | 108.6          | C2-C1-H1       | 108.6         |
| C3-C2-C1       | 110.13(12)     | C3-C2-H2A      | 109.6         |
| C1-C2-H2A      | 109.6          | C3-C2-H2B      | 109.6         |
| C1-C2-H2B      | 109.6          | H2A-C2-H2B     | 108.1         |
| O1-C3-C2       | 107.52(11)     | O1-C3-H3A      | 110.2         |
| C2-C3-H3A      | 110.2          | O1-C3-H3B      | 110.2         |
| C2-C3-H3B      | 110.2          | H3A-C3-H3B     | 108.5         |
| O2-C4-O1       | 123.26(13)     | O2-C4-C11      | 124.78(14)    |
| O1-C4-C11      | 111.96(12)     | O3-C5-C21      | 120.53(14)    |
| O3-C5-C1       | 120.70(13)     | C21-C5-C1      | 118.68(12)    |
| C4-O1-C3       | 115.39(11)     | C12-C11-C16    | 119.63(14)    |
| C12-C11-C4     | 121.88(14)     | C16-C11-C4     | 118.49(13)    |
| C11-C12-C13    | 120.08(15)     | C11-C12-H12    | 120.0         |
| C13-C12-H12    | 120.0          | C14-C13-C12    | 120.31(15)    |
| C14-C13-H13    | 119.8          | C12-C13-H13    | 119.8         |
| C13-C14-C15    | 119.64(14)     | C13-C14-H14    | 120.2         |
| C15-C14-H14    | 120.2          | C16-C15-C14    | 120.23(15)    |
| C16-C15-H15    | 119.9          | C14-C15-H15    | 119.9         |
| C15-C16-C11    | 120.09(14)     | C15-C16-H16    | 120.0         |
| C11-C16-H16    | 120.0          | C22-C21-C26    | 118.77(14)    |
| C22-C21-C5     | 118.00(13)     | C26-C21-C5     | 123.23(14)    |
| C23-C22-C21    | 120.96(14)     | C23-C22-H22    | 119.5         |
| C21-C22-H22    | 119.5          | C22-C23-C24    | 119.62(15)    |
| C22-C23-H23    | 120.2          | C24-C23-H23    | 120.2         |
C25-C24-C23 120.07(14)  C25-C24-H24 120.0
C23-C24-H24 120.0  C26-C25-C24 120.17(14)
C26-C25-H25 119.9  C24-C25-H25 119.9
C25-C26-C21 120.40(14)  C25-C26-H26 119.8
C21-C26-H26 119.8  C36-C31-C32 117.50(14)
C36-C31-C1 122.18(13)  C32-C31-C1 120.32(13)
C33-C32-C31 121.27(14)  C33-C32-H32 119.4
C31-C32-H32 119.4  C32-C33-C34 121.33(14)
C32-C33-H33 119.3  C34-C33-H33 119.3
C35-C34-C33 117.33(14)  C35-C34-C41 122.67(14)
C33-C34-C41 120.00(14)  C36-C35-C34 121.11(13)
C36-C35-H35 119.4  C34-C35-H35 119.4
C35-C36-C31 121.46(14)  C35-C36-H36 119.3
C31-C36-H36 119.3  C34-C41-C42A 123.8(5)
C34-C41-C43 121.4(3)  C34-C41-C42 118.2(3)
C43-C41-C42 59.1(2)  C34-C41-C43A 119.5(6)
C42A-C41-C43A 58.2(5)  C34-C41-H41 115.5
C43-C41-H41 115.5  C42-C41-H41 115.5
C34-C41-H41A 114.6  C42A-C41-H41A 114.6
C43A-C41-H41A 114.6  C43-C42-C41 60.2(3)
C43-C42-H42A 117.8  C41-C42-H42A 117.8
C43-C42-H42B 117.8  C41-C42-H42B 117.8
H42A-C42-H42B 114.9  C42-C43-C41 60.8(3)
C42-C43-H43A 117.7  C41-C43-H43A 117.7
C42-C43-H43B 117.7  C41-C43-H43B 117.7
H43A-C43-H43B 114.8  C43A-C42A-C41 62.0(6)
C43A-C42A-H42C 117.6  C41-C42A-H42C 117.6
Table 5. Torsion angles (°) for 3s.

| Bond Ranges | Angle |
|-------------|-------|
| C31-C1-C2-C3 | -68.75(16) |
| C1-C2-C3-O1 | 169.26(12) |
| C2-C1-C5-O3 | 17.9(2) |
| C2-C1-C5-C21 | -165.46(12) |
| C11-C4-O1-C3 | 178.12(12) |
| O2-C4-C11-C12 | 177.08(15) |
| O2-C4-C11-C16 | -3.7(2) |
| C16-C11-C12-C13 | -1.6(2) |
| C11-C12-C13-C14 | 1.1(2) |
| C13-C14-C15-C16 | -1.0(2) |
| C12-C11-C16-C15 | 0.8(2) |
| C3-C5-C21-C22 | 3.9(2) |
| C3-C5-C21-C26 | -176.41(15) |
| C26-C21-C22-C23 | -0.3(2) |
| C21-C22-C23-C24 | -1.0(2) |
| C23-C24-C25-C26 | -0.6(2) |
| C22-C21-C26-C25 | 1.1(2) |
| C5-C1-C31-C36 | -119.40(15) |
| C5-C1-C31-C32 | 60.20(17) |
| C36-C31-C32-C33 | 0.1(2) |
| Bond Pair                  | Distance  | Bond Angle  |
|---------------------------|-----------|-------------|
| C31-C32-C33-C34           | 0.3(2)    | C32-C33-C34-C35 -0.6(2) |
| C32-C33-C34-C41           | 179.47(14)| C33-C34-C35-C36 0.5(2)  |
| C41-C34-C35-C36           | -179.59(15)| C34-C35-C36-C31 -0.1(2)  |
| C32-C31-C36-C35           | -0.2(2)   | C1-C31-C36-C35 179.38(14)  |
| C35-C34-C41-C42A          | 27.3(11)  | C33-C34-C41-C42A -152.8(11)  |
| C35-C34-C41-C43           | -22.0(6)  | C33-C34-C41-C43 157.9(5)  |
| C35-C34-C41-C42           | 47.1(4)   | C33-C34-C41-C42 -133.0(4)  |
| C35-C34-C41-C43A          | -42.3(9)  | C33-C34-C41-C43A 137.6(8)  |
| C34-C41-C42-C43           | -111.6(3) | C34-C41-C43-C42 106.3(4)  |
| C34-C41-C42A-C43A         | -106.4(9) | C34-C41-C43A-C42A 113.6(7)  |

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H. NMR spectrum:

300 MHz in CDCl₃

75 MHz in CDCl₃
500 MHz in CDCl$_3$

126 MHz in CDCl$_3$
500 MHz in CDCl₃

126 MHz in CDCl₃
286 MHz in CDCl₃
300 MHz in CDCl$_3$ (3c)

76 MHz in CDCl$_3$
500 MHz in CDCl$_3$

126 MHz in CDCl$_3$
300 MHz in CDCl₃

76 MHz in CDCl₃
300 MHz in CDCl₃

76 MHz in CDCl₃
300 MHz in CDCl$_3$

76 MHz in CDCl$_3$
300 MHz in CDCl$_3$

76 MHz in CDCl$_3$
282 MHz in CDCl₃
300 MHz in CDCl$_3$

76 MHz in CDCl$_3$
282 MHz in CDCl₃
300 MHz in CDCl₃

76 MHz in CDCl₃
300 MHz in CDCl₃

76 MHz in CDCl₃
$^{300\text{ MHz in CDCl}_3}$

$^{76\text{ MHz in CDCl}_3}$
$^{1}H$ NMR spectra of compound (3o):

- 500 MHz in CDCl$_3$
- 126 MHz in CDCl$_3$
300 MHz in CDCl₃

76 MHz in CDCl₃
300 MHz in CDCl$_3$

76 MHz in CDCl$_3$
300 MHz in CDCl$_3$

76 MHz in CDCl$_3$
300 MHz in CDCl$_3$

(3s)

76 MHz in CDCl$_3$
600 MHz in CDCl₃

151 MHz in CDCl₃
300 MHz in CDCl$_3$

76 MHz in CDCl$_3$
500 MHz in CDCl$_3$

126 MHz in CDCl$_3$
$300 \text{ MHz in CDCl}_3$

$76 \text{ MHz in CDCl}_3$
Mixture of diastereomer

300 MHz in CDCl$_3$

Mixture of diastereomer

76 MHz in CDCl$_3$

Mixture of diastereomer
(3aa)

Mixture of diastereomer

300 MHz in CDCl₃

Mixture of diastereomer

76 MHz in CDCl₃
Mixture of diastereomer

300 MHz in CDCl₃

Mixture of diastereomer

151 MHz in CDCl₃

Mixture of diastereomer
Mixture of diastereomer

300 MHz in CDCl₃

126 MHz in CD₂Cl₂+CDCl₃
Mixture of diastereomer

300 MHz in CDCl₃

76 MHz in CDCl₃
Mixture of diastereomer and regioisomer

Mixture of diastereomer and regioisomer
Mixture of diastereomer and regioisomer

Mixture of diastereomer and regioisomer

Mixture of diastereomer and regioisomer
282 MHz in CDCl$_3$  
Mixture of diastereomer and regioisomer
Mixture of diastereomer and regioisomer

300 MHz in CDCl₃

Mixture of diastereomer and regioisomer

76 MHz in CDCl₃
Mixture of diastereomer

Mixture of diastereomer

300 MHz in CDCl$_3$

76 MHz in CDCl$_3$
Mixture of diastereomer and regioisomer

300 MHz in CDCl₃

76 MHz in CDCl₃

Mixture of diastereomer and regioisomer
500 MHz in CDCl₃

126 MHz in CDCl₃
Mixture of regioisomer

(3ak)

Mixture of regioisomer
564 MHz in CDCl₃

Mixture of regioisomer
300 MHz in CDCl₃

75 MHz in CDCl₃
500 MHz in CDCl$_3$

76 MHz in CDCl$_3$
300 MHz in CDCl₃

76 MHz in CDCl₃