Supplementary Information for:

**Photo-Organocatalytic Enantioselective Perfluoroalkylation of β-Ketoesters**

Łukasz Woźniak,† John J. Murphy,† and Paolo Melchiorre*†‡

†ICIQ - Institute of Chemical Research of Catalonia, Av. Països Catalans 16, 43007 Tarragona, Spain
‡ICREA - Catalan Institution for Research and Advanced Studies, Pg. Lluís Companys 23, 08010 Barcelona, Spain
*Correspondence to: pmelchiorre@iciq.es
**Table of Contents**

A. General Information  
General Procedures and Materials  
Determination of Diastereomeric and Enantiomeric Ratios  
page S3

B. Representative Procedure for the Synthesis of Cyclic tert-Butyl-Ketoesters  
page S4

C. Synthesis of the PTC Catalysts  
page S4

D. Catalyst Screening and Optimization Studies  
page S7

E. General Procedure for the Photochemical Enantioselective Perfluoroalkylation  
page S9

F. Quantum Yield Measurement  
page S15

G. X-ray Crystallographic Data  
page S18

H. NMR spectra  
page S21

I. HPLC traces  
page S69

J. References  
page S84
A. General Information

The NMR spectra were recorded at 400 MHz and 500 MHz for $^1$H and 100 or 125 MHz for $^{13}$C. The chemical shift (δ) for $^1$H and $^{13}$C are given in ppm relative to residual signals of the solvents (CHCl$_3$ @ 7.26 ppm $^1$H NMR and 77.16 ppm $^{13}$C NMR, and tetramethylsilane @ 0 ppm). Coupling constants are given in Hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; m, multiplet; bs, broad signal.

High resolution mass spectra (HRMS) were obtained from the ICIQ HRMS unit on Waters GCT gas chromatograph coupled time-of-flight mass spectrometer (GC/MS-TOF) with electrospray ionization (ESI). X-ray data were obtained from the ICIQ X-Ray unit using a Brucker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector. Optical rotations are reported as follows: [α]°$_D$ (c in g per 100 mL, solvent).

UV-vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with photomultiplier detector, double beam optics and D$_2$ and W light sources.

Cut off and band-pass photochemical experiments have been performed using a 300 W xenon lamp (Asahi Spectra Co., Ltd.) to irradiate the reaction mixture.

The authors are indebted to the team of the Research Support Area at ICIQ and to Grace Fox for proof-reading the manuscript.

General Procedures.

All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques, unless otherwise stated. Synthesis grade solvents were used as purchased and the reaction mixtures were degassed by three cycles of freeze-pump-thaw. Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF$_{254}$, 0.25 mm) were employed, using UV light as the visualizing agent and basic aqueous potassium permanganate (KMnO$_4$) stain solutions, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator.

The light source used for illuminating the reaction vessel consisted of white LED light strips (19.2 W/m, 240 LEDs per meter) purchased from Farnell (http://www.farnell.com/). More information [here].

Determination of Enantiomeric Purity: HPLC analysis on chiral stationary phase was performed on an Agilent 1200-series instrument using a Daicel Chiralpak AD-H column and hexane, tPr-OH and/or DCM as the eluents. GC analysis was performed using a chiral Alphadex column. HPLC and GC traces were compared to racemic samples prepared using a superstechiometric amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 2 equiv) as the promoter of the photochemical perfluoroalkylation (products 3).

Materials. Commercial grade reagents and solvents were purchased from Sigma-Aldrich, Fluka, Alfa Aesar, Fluorochem, SynQuest and used as received, without further purifications.
B. Representative Procedure for the Synthesis of the Cyclic tert-Butyl-Ketoesters 1

NaH (5.2 mmol, 210 mg, 2.2 eq., 60% dispersion in mineral oil) and anhydrous dimethyl carbonate (DMC, 10 mL) were added sequentially to a dry three-necked flask equipped with a septum, condenser, argon inlet, and a large stirring egg. The indan-1-one derivative A (2.37 mmol, 1 eq), partially solubilized in anhydrous dimethyl carbonate (10 mL), was added via a syringe pump over the course of 30 minutes (Scheme S1). The heterogeneous mixture was brought to reflux (80 ºC), and heated overnight at this temperature. The reaction was allowed to cool and cautiously quenched at 0ºC under an argon atmosphere with H2O (10 mL). The mixture was transferred to a separative funnel with EtOAc while adding additional 50 mL of 1M HCl. The reaction was extracted with EtOAc (50 mL x 3) and the combined organic layers washed with a saturated brine solution before being dried over solid anhydrous magnesium sulfate and concentrated. The crude material was then dissolved in toluene (20 mL), and tBuOH (30 eq, 71.1 mmol, 6.5 mL), and dibutyl-tin oxide (0.2 eq, 118 mg) was added. The flask was fitted with an air condenser and the heterogeneous mixture was heated at 115ºC until the starting methyl ester B was fully consumed (12-36 h), as judged by TLC. The mixture was allowed to cool to room temperature and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent Et₂O/Hexane1:9 to 2:8) to yield the pure keto-ester 2.

Scheme S1: Synthesis of cyclic tert-butyl-ketoesters 1.

C. Synthesis of the PTC Catalysts

Based on the procedure reported by Hintermann.1 Cinchonine (1.5 g, 5.1 mmol) was suspended in 25 ml of dry MTBE (dried over molecular sieves) and cooled to -10ºC (ice/EtOH bath) under an argon atmosphere. The organo-lithium compound was prepared in a separate flask by adding nBuLi (5.1 mL, 12.75 mmol, 2.5 M) to a 5 mL MTBE solution of 4-bromobenzotrifluoride C (1.785 mL, 2.869 g, 12.75 mmol). The organo-lithium compound was added at once to the vigorously stirred MTBE solution of cinchonine and stirred at -10ºC for 20 min. Then the mixture was warmed to ambient temperature and stirred over 2 h. The reaction was quenched by dropwise addition of HOAc (2.5 mL) with rapid stirring and cooling, followed by the addition of water (30 mL) and EtOAc (30 mL).
Solid iodine (1.25 g) was added in several portions and the mixture shaken vigorously after each addition until all the solids had dissolved. A solution of sodium metabisulfite (Na$_2$S$_2$O$_5$; 0.500 g) in water (10 mL) was added to quench the excess of iodine. The mixture was made basic with the addition of aqueous ammonia (concentrated, 28%) and shaken thoroughly. The aqueous phase was extracted with AcOEt twice and the collected organic phases were washed with brine and dried over sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (30% MeOH-EtOAc) to give the reaction product D as an orange solid in 51% yield (1.129 g, 2.57 mmol). [α]$_D^{5h}$ = +70.0 (c= 0.55 DMSO).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.28 (d, $J$ = 8.0 Hz, 2H), 8.24 – 8.17 (m, 1H), 8.08 (s, 1H), 8.01 (d, $J$ = 7.9 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.75 – 7.70 (m, 1H), 7.54 (ddd, $J$ = 8.3, 6.9, 1.3 Hz, 1H), 5.99 (ddd, $J$ = 17.1, 10.5, 7.4 Hz, 1H), 5.72 (d, $J$ = 4.8 Hz, 1H), 5.07 – 4.97 (m, 2H), 3.26 – 3.12 (m, 2H), 2.92 (dd, $J$ = 13.9, 9.7 Hz, 2H), 2.84 – 2.71 (m, 1H), 2.24 (q, $J$ = 8.4 Hz, 1H), 2.07 – 1.96 (m, 1H), 1.82 – 1.75 (m, 1H), 1.58 – 1.48 (m, 2H), 1.35 – 1.27 (m, 1H).

$^{19}$F NMR decoupled $^1$H (376 MHz, chloroform-d + TFA) $\delta$ -62.68 (s, 3F).

$^{13}$C NMR (101 MHz, chloroform-d) $\delta$ 162.2 (q, $J$ = 37.2 Hz, C=O, TFA), 154.5, 149.8, 144.9, 139.8, 135.7, 132.3 (q, $J$ = 32.7 Hz), 131.2, 128.6, 128.4, 128.0, 126.0 (q, $J$ = 3.7 Hz), 123.9 (q, $J$ = 272.5 Hz, CF$_3$) 123.5, 122.2, 118.1, 117.2, 116.20 (q, $J$ = 290.7 Hz, CF$_3$, TFA) 66.9, 60.7, 49.5, 48.7, 37.3, 27.3, 23.2, 18.0.

HRMS calculated for C$_{26}$H$_{22}$F$_3$N$_2$O (M+H): 439.1992, found: 439.1996.

5-(Bromomethyl)-1,2,3-trifluorobenzene E (0.27 mL, 457 mg, 2.03 mmol) was added to a MeCN-CHCl$_3$ (1:1, 34 ml) suspension of cinchonine derivative D (742 mg, 1.69 mmol). The reaction mixture was stirred for 16 h at 50 °C under an argon atmosphere. After complete consumption of D (inferred by TLC analysis) the solvent was evaporated under reduced pressure. DCM was added to the resulting orange solid followed by a small amount of MeOH in order to completely dissolve the crude product. Next Et$_2$O was added and the mixture was slowly concentrated under reduced pressure. When precipitation of a solid began, more Et$_2$O was added and the mixture was concentrated again. This procedure was repeated twice in order to remove traces of methanol and dichloromethane and the mixture was placed in a freezer. The precipitated yellow solid was filtered and washed with cold Et$_2$O to give the product 5b in 70% yield (789 mg, 1.19 mmol). [α]$_D^{5h}$ = +131.8 (c= 0.52 DMSO).

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.52 (d, $J$ = 8.2 Hz, 2H), 8.47 – 8.38 (m, 2H), 8.22 (d, $J$ = 8.3 Hz, 1H), 8.04 – 7.87 (m, 5H), 7.84 – 7.75 (m, 1H), 6.92 (d, $J$ = 3.6 Hz, 1H), 6.55 (s, 1H), 6.10 (ddd, $J$ = 17.4, 10.0, 7.2 Hz, 1H), 5.31 – 5.17 (m, 3H), 4.98 (d, $J$ = 12.4 Hz, 1H), 4.29 – 4.18 (m, 1H), 4.07 – 3.86 (m, 2H), 3.59 (t, $J$ = 11.4 Hz, 1H), 3.14 – 2.99 (m, 1H), 2.62 (q, $J$ = 8.3 Hz, 1H), 2.42 (t, $J$ = 11.8 Hz, 1H), 1.87 (s, 1H), 1.82 – 1.71 (m, 2H), 1.22 – 1.08 (m, 1H).

$^{19}$F NMR decoupled $^1$H (376 MHz, DMSO-d$_6$) $\delta$ -61.18 (s, 3F), -134.68 (d, $J$ = 21.7 Hz, 2F), -159.61 (t, $J$ = 21.7 Hz, 1F).

$^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta$ 154.6, 152.0 – 151.6 (m), 149.5 – 149.2 (m), 148.1, 147.1, 142.9, 139.3, 137.7, 130.7, 130.2 (q, $J$ = 31.8 Hz), 128.56, 128.2, 126.4 (q, $J$ = 3.9 Hz), 125.8 –

Supplementary Information
Supplementary Information

HRMS calculated for $\text{C}_{33}\text{H}_{29}\text{F}_6\text{N}_2\text{O}$ (M*): 583.2179, found: 583.2176

The relative and absolute configuration for 5b was unambiguously inferred by anomalous
dispersion X-ray crystallographic analysis, see X-ray Crystallographic Data section.

5c was purified by column chromatography (AcOEt, 30% MeOH-AcOEt) from reaction mixture
GP as violet solid (11 mg, 54% yield). $[\alpha]_D^{25} = +64.0$ (c= 0.80 DMSO).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.42 – 8.34 (m, 3H), 8.27 – 8.19 (m, 2H), 7.96 – 7.87 (m, 5H),
7.78 (dd, $J = 8.4$, 6.9, 1.3 Hz, 1H), 7.21 (d, $J = 3.8$ Hz, 1H), 6.71 (dd, $J = 16.1$, 5.4 Hz, 1H),
6.57 – 6.51 (m, 1H), 6.26 (dd, $J = 16.1$, 1.7 Hz, 1H), 5.19 (d, $J = 12.5$ Hz, 1H), 5.09 (d, $J = 12.5$ Hz,
1H), 4.48 – 4.37 (m, 1H), 3.94 (t, $J = 10.0$ Hz, 2H), 3.66 (t, $J = 11.6$ Hz, 1H), 3.09 (q, $J = 10.2$ Hz, 1H),
2.96 – 2.84 (m, 1H), 2.17 (t, $J = 11.6$ Hz, 1H), 2.12 – 2.04 (m, 1H), 1.90 – 1.73 (m, 2H), 1.23 – 1.17 (m,
1H).

$^{19}$F NMR decoupled $^1$H (376 MHz, DMSO-$d_6$) $\delta$ -61.63 (s, 3F), -80.47 (t, $J = 9.9$ Hz, 3F), -108.67 –
-112.29 (m, 2F), -121.23 – -121.62 (m, 2F), -122.28 – -122.95 (m, 4F), -125.74 – -126.18 (m, 2F),
-134.67 (d, $J = 21.8$ Hz, 2F), -159.54 (t, $J = 21.8$ Hz, 1F).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 154.7, 151.7 – 151.4 (m), 149.7 – 149.2 (m), 148.2, 147.1, 143.7
(t, $J = 9.6$ Hz), 143.1, 139.5, 130.7, 130.6, 130.2 (q, $J = 31.9$ Hz), 128.3, 128.2, 126.2 – 126.0 (m),
125.51 – 125.1 (m), 124.6 (q, $J = 272.0$ Hz), 124.3, 124.2, 119.4, 119.4 (d, $J = 20.9$ Hz), 119.3,
117.9, 117.7, 79.6, 68.0, 65.4, 61.2, 56.5, 53.8, 35.5, 31.4, 26.1, 23.1, 22.5, 21.0, 14.4.

HRMS calculated for $\text{C}_{39}\text{H}_{25}\text{F}_{19}\text{N}_2\text{O}$ (M*): 901.1893, found: 901.1883
D. Catalyst Screening and Optimization Studies

Figure S1: Catalysts Screening with Cinchonidine derived-PTC catalysts. NMR yield of 3a determined by $^{19}$F NMR analysis of the crude mixture using 1-fluoro-2-nitrobenzene as the internal standard.
Supplementary Information

Figure S2: Catalysts Screening with Cinchonine derived-PTC catalysts. NMR yield of 3a determined by $^{19}$F NMR analysis of the crude mixture using 1-fluoro-2-nitrobenzene as the internal standard.

Table S1. Refinement of the Reaction Conditions

| 1a (equiv) | 2a (equiv) | solvent                  | % yield$^b$ | % ee$^c$ |
|-----------|-----------|--------------------------|-------------|---------|
| 1,2       | 1         | C$_6$H$_5$Cl             | 35          | 92      |
| 1         | 3         | C$_6$H$_5$Cl             | 41          | 92      |
| 1         | 3         | C$_6$H$_5$Cl/C$_6$F$_4$ 1:1 | 58          | 89      |
| 1         | 3         | C$_6$H$_5$Cl/C$_6$F$_4$ 2:1 | 49          | 92      |
| 1         | 3         | C$_6$H$_5$Cl/C$_6$F$_4$ 2:1 | 56          | 92      |
| 1         | 3         | C$_6$H$_5$Cl/C$_6$F$_4$ 2:1 | 59          | 93      |

$^a$ Reactions performed over 16 h on a 0.1 mmol scale using a white LED strip to illuminate the reaction vessel.
$^b$ Yield of 3a determined after isolation by chromatography.
$^c$ Enantiomeric excess determined by HPLC analysis on a chiral stationary phase.
E. General Procedures for the Photochemical Enantioselective Perfluoroalkylation of β-Ketoesters under PTC Conditions

A 15 mL Schlenk tube was charged with β-ketoester 1 (0.1 mmol), the PTC catalyst 5b (0.02 mmol), chlorobenzene (0.25 mL), perfluoroctane (0.125 mL), the perfluoroalkyl iodide 2 (0.3 mmol, 3 equiv) and cesium carbonate (0.2 mmol). The reaction mixture was degassed via freeze pump thaw (x3), and the vessel refilled with argon. After the reaction mixture was thoroughly degassed, the Schlenk tube was sealed and positioned in the middle of a 250 mL evaporation bath surrounded by 1 m strip containing white LEDs. A small fan was installed directly above the Schlenk tube so as to keep the temperature constant. After stirring (1000 rpm) for 64 hours, reaction was quenched by adding an aqueous 1M HCl solution and extracted 3 times with DCM. The organic phase was dried over Na2SO4, the solvent was removed under reduced pressure and the crude mixture was purified by column chromatography to give the product in the stated yield and optical purity.

Methyl \((S)-1\text{-oxo-2-(perfluorohexyl)-2,3-dihydro-1H-indene-2-carboxylate}\) (3a). Prepared according to general procedure using methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.1 mmol, 19 mg), perfluorohexyl iodide (0.3 mmol, 134 mg, 0.065 mL), the phase transfer catalyst 5b (0.002 mmol, 13 mg) and cesium carbonate (0.2 mmol, 65 mg). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 5:95) to afford the product as a white solid (21 mg, 41% yield, 92% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99:1 hexane:iPrOH, flow rate 0.50 mL/min, \(\lambda = 254\) nm: \(\tau\) minor = 9.8 min, \(\tau\) major = 10.8 min (90% ee); \([\alpha]_D^{25} = +38.9\) (c= 0.83, CHCl3, 92% ee).

3H NMR (400 MHz, Chloroform-d) \(\delta 7.82\) (d, \(J = 7.7\) Hz, 1H), 7.69 (td, \(J = 7.6, 1.2\) Hz, 1H), 7.53 (d, \(J = 7.7\) Hz, 0H), 7.44 (t, \(J = 7.1\) Hz, 1H), 3.94 (d, \(J = 17.9\) Hz, 1H), 3.80 (s, 3H), 3.61 (d, \(J = 17.6\) Hz, 1H).

3F NMR decoupled 3H (376 MHz, Chloroform-d) \(\delta -80.77\) to -81.06 (m, 2F), -109.21 to -111.91 (m, 2F), -116.22 to -116.74 (m, 2F), -122.16 (m, 2F), -122.59 (m, 2F), -126.09 to -126. (m, 2F).

19F NMR (126 MHz, Chloroform-d) \(\delta 192.1, 164.8\) (d, \(J = 8.7\) Hz), 151.7, 136.3, 133.9, 128.4, 126.2, 125.5, 63.1 (dd, \(J = 24.2, 18.5\) Hz), 53.9, 33.4 – 33.2 (m).

HRMS calculated for C17H2F13NaO3 (M+Na): 531.0236, found: 531.0222

tert-Butyl \((S)-1\text{-oxo-2-(perfluorohexyl)-2,3-dihydro-1H-indene-2-carboxylate}\) (3b) Prepared according to general procedure using tert-butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.1 mmol, 23 mg), perfluorohexyl iodide (0.3 mmol, 134 mg, 0.065 mL), phase transfer catalyst 5b (0.002 mmol, 13 mg) and cesium carbonate (0.2 mmol, 65 mg). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 5:95) to give the product as a white solid (39 mg, 71% yield, 93% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99:5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, \(\lambda = 254\) nm: \(\tau\) minor = 6.7 min, \(\tau\) major = 7.6 min (94% ee); \([\alpha]_D^{25} = +28.2\) (c= 1.08 CHCl3, 93% ee).
**Supplementary Information**

**HRMS**
- 126.4, 126.3 (m, 2F), -115.68 – 115.89 (m, 2F), -122.08 – -122.38 (m, 2F), -122.41 – -122.73 (m, 2F), -126.11 – -126.33 (m, 2F).
- 13C NMR (75 MHz, Chloroform-d) δ 192.7, 163.0 (d, J = 8.9 Hz), 151.9, 136.0, 134.1, 128.2, 126.1, 125.3, 84.6, 64.9 – 63.6 (m), 33.9 – 32.1 (m), 27.5.

HRMS calculated for C_{20}H_{13}F_{14}NaO_3 (M+Na): 573.0706, found: 573.0697

**tert-Butyl** (S)-5-fluoro-1-oxo-2-(perfluorohexyl)-2,3-dihydro-1H-indene-2-carboxylate (3c)
Prepared according to general procedure using tert-butyl 5-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.1 mmol, 25 mg), perfluorohexyl iodide (0.3 mmol, 134 mg, 0.065 ml), phase transfer catalyst 5b (0.002 mmol, 13 mg) and cesium carbonate (0.2 mmol, 65 mg). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 5:95) to give the product as a yellow solid (36 mg, 63% yield, 87% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99:5:0.5 hexane:iPrOH, flow rate 0.60 ml/min, λ = 254 nm: τ_{minor} = 7.1 min, τ_{major} = 11.3 min (87% ee); [α]_{D}^{25} = +29.71 (c= 1.00, CHCl_{3} 87% ee).

**H NMR** (400 MHz, Chloroform-d) δ 7.81 (d, J = 7.2 Hz, 1H), 7.71 – 7.62 (m, 1H), 7.56 – 7.48 (m, 1H), 7.48 – 7.40 (m, 1H), 3.85 (d, J = 17.5 Hz, 1H), 3.55 (d, J = 17.5 Hz, 1H), 1.44 (s, 9H).

**19F NMR** decoupled 1H (376 MHz, Chloroform-d) δ -0.088 (t, J = 10.0 Hz, 3F), -108.19 – -111.48 (m, 2F), -115.68 – -115.89 (m, 2F), -122.08 – -122.38 (m, 2F), -122.41 – -122.73 (m, 2F), -126.11 – -126.33 (m, 2F).

**13C NMR** (75 MHz, Chloroform-d) δ 126.12 (m, 2F), 126.34 (m, 2F).

**tert-Butyl** (S)-5-chloro-1-oxo-2-(perfluorohexyl)-2,3-dihydro-1H-indene-2-carboxylate (3d)
Prepared according to general procedure using tert-butyl 5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.1 mmol, 27 mg), perfluorohexyl iodide (0.3 mmol, 134 mg, 0.065 ml), phase transfer catalyst 5b (0.002 mmol, 13 mg) and cesium carbonate (0.2 mmol, 65 mg). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 5:95) to give the product as a yellow solid (41 mg, 70% yield, 86% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99:5:0.5 hexane:iPrOH, flow rate 0.60 ml/min, λ = 254 nm: τ_{minor} = 8.1 min, τ_{major} = 12.4 min (86% ee); [α]_{D}^{25} = +46.74 (c= 0.88, CHCl_{3} 86% ee).

**H NMR** (400 MHz, Chloroform-d) δ 7.74 (d, J = 8.3 Hz, 1H), 7.52 (d, J = 1.0 Hz, 1H), 7.41 (dd, J = 8.3, 1.8 Hz, 1H), 3.83 (d, J = 17.5 Hz, 1H), 3.51 (d, J = 17.6 Hz, 1H), 1.44 (s, 9H).

**19F NMR** decoupled 1H (376 MHz, Chloroform-d) δ -80.89 (t, J = 10.0 Hz, 3F), -108.16 – -111.52 (m, 2F), -115.70 – -115.97 (m, 2F), -122.05 – -122.41 (m, 2F), -122.42 – -122.71 (m, 2F), -126.12 – -126.34 (m, 2F).

**13C NMR** (101 MHz, Chloroform-d) δ 191.3, 162.7 (d, J = 8.7 Hz), 153.3, 142.8, 132.5, 129.2, 126.4, 126.34, 85.0, 64.5 – 63.9 (m), 33.3 – 32.8 (m), 27.5.

HRMS calculated for C_{20}H_{13}ClF_{13}NaO_3 (M+Na): 607.0316, found: 607.0331

**tert-Butyl** 6-bromo-1-oxo-2-(perfluorohexyl)-2,3-dihydro-1H-indene-2-carboxylate (3e)
Prepared according to general procedure using tert-butyl 6-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.1 mmol, 31 mg), perfluorohexyl iodide (0.3 mmol, 134 mg, 0.065 ml), phase transfer catalyst
(0.002 mmol, 13 mg) and cesium carbonate (0.2 mmol, 65 mg). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 5:95) to give the product as a yellow solid (38 mg, 60% yield, 82% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm: \( \tau_{\text{minor}} = 6.2 \text{ min}, \tau_{\text{major}} = 7.4 \text{ min (82% ee)}; [\alpha]_D^{28} = +11.53 \text{ (c= 1.00, CHCl}_3, 82\% \text{ ee)}.\)

\(^1\)H NMR (400 MHz, Chloroform-\(d\)): \( \delta 7.93 \text{ (d, } J = 1.8 \text{ Hz, 1H)}, 7.77 \text{ (dd, } J = 8.2, 1.9 \text{ Hz, 1H}), 7.41 \text{ (d, } J = 8.2 \text{ Hz, 1H}), 3.80 \text{ (d, } J = 17.5 \text{ Hz, 1H}), 3.48 \text{ (d, } J = 17.6 \text{ Hz, 1H}), 1.44 \text{ (s, 9H).}\)

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)): \( \delta \text{ 126.33 (m, 2F), 115.93 (m, 2F), 115.94 (m, 2F), 63.6 (m), 33.3 (m).}\)

HRMS calculated for \( \text{C}_{20}\text{H}_{14}\text{BrF}_{13}\text{NaO}_{3} \) (M+Na): 650.9811, found: 650.9799

**tert-Butyl \((S)-5\)-bromo-1-oxo-2-(perfluorohexyl)-2,3-dihydro-1H-indene-2-carboxylate**: (3f) Prepared according to general procedure using tert-butyl 5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.1 mmol, 31 mg), perfluorohexyl iodide (0.3 mmol, 134 mg, 0.065 ml), phase transfer catalyst 5b (0.002 mmol, 13 mg) and cesium carbonate (0.2 mmol, 65 mg). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 5:95) to give the product as a yellow solid (38 mg, 60% yield, 82% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm: \( \tau_{\text{minor}} = 6.5 \text{ min, } \tau_{\text{major}} = 8.9 \text{ min (88% ee)}; [\alpha]_D^{28} = +45.52 \text{ (c= 0.41, CHCl}_3, 88\% \text{ ee)}.\)

\(^1\)H NMR (400 MHz, Chloroform-\(d\)): \( \delta 7.74 – 7.67 \text{ (m, 1H)}, 7.66 \text{ (d, } J = 8.2 \text{ Hz, 1H}), 7.61 – 7.54 \text{ (m, 1H)}, 3.84 \text{ (d, } J = 17.6 \text{ Hz, 1H}), 3.52 \text{ (d, } J = 17.7 \text{ Hz, 1H}), 1.44 \text{ (s, 9H).}\)

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)): \( \delta 191.5, 162.5 \text{ (d, } J = 8.7 \text{ Hz}), 150.4, 138.8, 135.8, 128.1, 127.6, 122.4, 85.0, 65.1 – 63.6 \text{ (m), 33.3 – 32.7 (m), 27.5.}\)

HRMS calculated for \( \text{C}_{20}\text{H}_{14}\text{BrF}_{13}\text{NaO}_{3} \) (M+Na): 650.9811, found: 650.9811

The absolute configuration for 3f was unambiguously inferred by anomalous dispersion X-ray crystallographic analysis, see X-ray Crystallographic Data section.

**tert-Butyl \((S)-1\)-oxo-2-(perfluorohexyl)-4-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate**: (3g) Prepared according to general procedure using tert-butyl 1-oxo-4-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate (0.1 mmol, 30 mg), perfluorohexyl iodide (0.3 mmol, 134 mg, 0.065 ml), phase transfer catalyst 5b (0.002 mmol, 13 mg) and cesium carbonate (0.2 mmol, 65 mg). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 3:97) to give the product as a yellow oil (38 mg, 61% yield, 94% ee) The enantiomeric excess was determined by GC analysis on an Alphadex column (120 30x0.25mm, 0.25µm, Tijin/aux 280 Flow 1.5mL/min split 50:1 (1µL) Isomer 80°C, FID detector) \( \tau_{\text{minor}} = 486.0,1 \text{ min, } \tau_{\text{major}} = 495.9 \text{ min (90% ee)}.\) \([\alpha]_D^{28} = +22.6 \text{ (c= 0.40, CHCl}_3, 90\% \text{ ee}).\)

\(^1\)H NMR (400 MHz, Chloroform-\(d\)): \( \delta 8.00 \text{ (d, } J = 8.2 \text{ Hz, 1H}), 7.96 – 7.92 \text{ (m, 1H)}, 7.64 – 7.24 \text{ (m, 1H)}, 4.03 \text{ (d, } J = 18.2 \text{ Hz, 1H}), 3.67 \text{ (d, } J = 18.2 \text{ Hz, 1H}), 1.44 \text{ (s, 9H).}\)

\(^{13}\)C NMR decoupled \(^1\)H (376 MHz, Chloroform-\(d\)): \( \delta -62.45 \text{ (s, 3F), -80.88 (t, } J = 8.9 \text{ Hz, 3F), -107.99 – -111.60 \text{ (m, 2F), -115.63 – -115.88 (m, 2F), -122.05 – -122.39 (m, 2F), -126.22 – -126.35 (m, 2F).}\)

Supplementary Information S11
the product as a yellow solid (31 mg, 55% yield, 83% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99:5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm: [α] D 28 = +22.98 (c= 0.95, CHCl₃, 83% ee).

1H NMR (400 MHz, Chloroform-d) δ 7.60 (d, J = 7.9 Hz, 1H), 7.48 (dd, J = 7.6, 1.5 Hz, 1H), 7.40 (d, J = 7.9 Hz, 1H), 3.78 (d, J = 17.4 Hz, 1H), 3.49 (d, J = 17.4 Hz, 1H), 2.41 (s, 3H), 1.43 (s, 9H).

1F NMR decoupled 1H (376 MHz, Chloroform-d) δ -80.90 (t, J = 9.8 Hz, 3F), -108.25 – -111.39 (m, 2F), -115.66 – -115.94 (m, 2F), -122.04 – -122.40 (m, 2F), -122.41 – -122.72 (m, 2F), -126.11 – -126.36 (m, 2F).

13C NMR (101 MHz, Chloroform-d) δ 190.6, 166.3, 163.3 (d, J = 9.4 Hz), 155.1, 127.1, 127.1, 116.5, 109.1, 84.4, 65.0 – 63.2 (m), 55.82, 33.4 – 33.1 (m), 27.56.

HRMS calculated for C₂₁H₂₁F₁₈NaO₃ (M+Na): 587.0862, found: 587.0855

**tert-Butyl (S)-5-methoxy-1-oxo-2-(perfluorohexyl)-2,3-dihydro-1H-indene-2-carboxylate (3i)**

Prepared according to general procedure using tert-butyl 5-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.1 mmol, 26 mg), perfluorohexyl iodide (0.3 mmol, 134 mg, 0.065 ml), phase transfer catalyst 5b (0.002 mmol, 13 mg) and cesium carbonate (0.2 mmol, 65 mg). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 5:95) to give the product as a yellow solid (22 mg, 38% yield, 86% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99:5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm: [α] D 28 = +57.76 (c= 0.52, CHCl₃, 86% ee).

1H NMR (400 MHz, Chloroform-d) δ 7.73 (d, J = 8.5 Hz, 1H), 6.97 – 6.91 (m, 2H), 3.91 (s, 3H), 3.79 (d, J = 17.5 Hz, 1H), 3.46 (d, J = 17.5 Hz, 1H), 1.44 (s, 3H).

1F NMR decoupled 1H (376 MHz, Chloroform-d) δ -80.88 (t, J = 10.0 Hz, 3F), -108.29 – -111.88 (m, 2F), -115.71 – -115.93 (m, 2F), -122.08 – -122.40 (m, 2F), -122.41 – -122.69 (m, 2F), -126.10 – -126.35 (m, 2F).

13C NMR (101 MHz, Chloroform-d) δ 190.6, 166.3, 163.3 (d, J = 9.4 Hz), 155.1, 127.1, 127.1, 116.5, 109.1, 84.4, 65.0 – 63.2 (m), 55.82, 33.4 – 33.1 (m), 27.56.

HRMS calculated for C₂₁H₂₁F₁₈NaO₃ (M+Na): 603.0811, found: 603.0827

**tert-Butyl (S)-1-oxo-2-(perfluorobutyl)-2,3-dihydro-1H-indene-2-carboxylate (3j)**

Prepared according to general procedure using tert-butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.1 mmol, 23 mg), perfluorobutyl iodide (0.002 mmol, 104 mg, 0.052 ml), phase transfer catalyst 5b (0.002 mmol, 13 mg) and cesium carbonate (0.2 mmol, 65 mg). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 5:95) to give the product as a yellow solid (28 mg, 62% yield, 90% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99:5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm: [α] D 28 = 22.98 (c= 0.95, CHCl₃, 83% ee).
excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm: τ_{minor} = 7.8 min, τ_{major} = 9.0 min (90% ee); [α]_D^{25} = +32.23 (c = 0.40, CHCl_3, 90% ee).

^{1}H NMR (400 MHz, Chloroform- d) δ 7.81 (d, J = 7.7 Hz, 1H), 7.67 (td, J = 7.6, 1.2 Hz, 1H), 7.52 (dt, J = 7.7, 0.9 Hz, 1H), 7.48 – 7.39 (m, 1H), 3.85 (d, J = 17.5 Hz, 1H), 3.55 (d, J = 17.5 Hz, 1H), 1.44 (s, 9H).

^{19}F NMR decoupled ^{1}H (376 MHz, Chloroform- d) δ -108.46 – -111.60 (m, 2F), -116.56 – -116.87 (m, 2F), -126.49 (m, 2F).

^{13}C NMR (101 MHz, Chloroform- d) δ 126.49 (m, 2F).

HRMS calculated for C_{18}H_{18}F_{7}NaO_{3} (M+Na): 473.0770, found: 473.0761

**tert-Butyl (S)-1-oxo-2-(perfluorooctyl)-2,3-dihydro-1H-indene-2-carboxylate (3k)**

Prepared according to general procedure using tert-butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.1 mmol, 23 mg), perfluorooctyl iodide (0.3 mmol, 164 mg, 0.079 ml), phase transfer catalyst 5b (0.002 mmol, 13 mg) and cesium carbonate (0.2 mmol, 65 mg). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 4:96) to give the product as a yellow solid (44 mg, 68% yield, 93% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm: τ_{minor} = 6.8 min, τ_{major} = 6.5 min (93% ee); [α]_D^{25} = +29.6 (c= 1.17, CHCl_3, 93% ee)

^{1}H NMR (400 MHz, Chloroform- d) δ 7.37 (d, J = 7.7 Hz, 1H), 7.30 – 7.62 (m, 1H), 7.40 (t, J = 7.7 Hz, 1H), 3.73 (d, J = 17.4 Hz, 1H), 3.55 (d, J = 17.5 Hz, 1H), 1.44 (s, 9H).

^{19}F NMR decoupled ^{1}H (376 MHz, Chloroform- d) δ -108.19 – -111.62 (m, 2F), -112.14 – -112.75 (m, 2F), -122.03 (s, 4F), -122.64 – -122.94 (m, 2F), -126.13 – -126.32 (m, 2F).

^{13}C NMR (101 MHz, Chloroform- d) δ 126.53 (m, 2F).

HRMS calculated for C_{22}H_{22}F_{7}NaO_{3} (M+Na): 673.0642, found: 673.0638

**tert-Butyl (S)-1-oxo-2-(perfluorodecyl)-2,3-dihydro-1H-indene-2-carboxylate (3l)**

Prepared according to general procedure using tert-butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.002 mmol, 13 mg) and cesium carbonate (0.002 mmol, 65 mg). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 5:95) to give the product as a yellow solid (44 mg, 68% yield, 93% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm: τ_{minor} = 6.4 min, τ_{major} = 7.3 min (94% ee); [α]_D^{25} = +25.3 (c= 1.12, CHCl_3, 94% ee).

^{1}H NMR (400 MHz, Chloroform- d) δ 7.17 (d, J = 7.6 Hz, 1H), 7.66 (td, J = 7.5, 1.2 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 3.85 (d, J = 17.5 Hz, 1H), 3.54 (d, J = 17.5 Hz, 1H), 1.44 (s, 9H).

^{19}F NMR decoupled ^{1}H (376 MHz, Chloroform- d) δ -80.88 (d, J = 9.9 Hz, 3F), -108.12 – -111.41 (m, 2F), -115.62 – -115.88 (m, 2F), -121.56 (m, 2F), -121.69 – -122.22 (m, 8F), -122.67 – -122.97 (m, 2F), -126.10 – -126.53 (m, 2F).

^{13}C NMR (101 MHz, Chloroform- d) δ 192.73, 163.01 (d, J = 8.7 Hz), 151.90, 136.01, 134.06,
tert-Butyl (S)-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate (3m). Prepared according to general procedure using tert-butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0,1 mmol, 23 mg), phase transfer catalyst 5b (0,002 mmol, 13 mg) and cesium carbonate (0,2 mmol, 65 mg). Trifluoriodomethane (0,3 mmol, 7,5 mL, gas) was added after the 3 cycles of freeze pump thaw via gas syringe at -196 °C (nitrogen bath). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, EtOAc:hex 99,5:0,5) to give the product as a white solid (15 mg, 50% yield, 96% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99,5:0,5 hexane:iPrOH, flow rate 0,60 mL/min, λ = 254 nm: τ minor = 9,4 min, τ major = 10,7 min (96% ee); [α]D 25 = +27,2 (c = 0,25, CHCl3, 96% ee). Lit. 2 \[ \alpha \] 25 = +12,7 (c = 1,05, CHCl3, 78% ee).

1H NMR (400 MHz, Chloroform-d) δ 7.83 (d, J = 7,6 Hz, 1H), 7,72 – 7,63 (m, 1H), 7,52 (dt, J = 7,7, 0,9 Hz, 1H), 7,49 – 7,40 (m, 1H), 3,68 (d, J = 17,6 Hz, 1H), 3,56 (d, J = 17,6 Hz, 1H), 1,43 (s, 9H).

19F NMR decoupled 1H (376 MHz, Chloroform-d) δ -69,19 (s, 3F).

13C NMR (101 MHz, Chloroform-d) δ 193,4, 164,1 (q, J = 2,0 Hz), 151,7, 136,0, 134,7 – 134,5 (m), 128,3, 126,2, 125,4, 123,6 (q, J = 281,3 Hz), 84,3, 63,9 (q, J = 25,8 Hz), 34,3 (q, J = 1,9 Hz), 27,7.

tert-Butyl (S)-5-bromo-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate (3n). Prepared according to general procedure using tert-butyl 6-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0,1 mmol, 31 mg), phase transfer catalyst 5b (0,002 mmol, 13 mg) and cesium carbonate (0,2 mmol, 65 mg). Trifluoriodomethane (0,3 mmol, 7,5 mL, gas) was added after the 3 cycles of freeze pump thaw via gas syringe at -196 °C (nitrogen bath). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, DCM:hex 4:6) to give the product as a white solid (20 mg, 53% yield, 84% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99,5:0,5 hexane:iPrOH, flow rate 0,60 mL/min, λ = 254 nm: τ minor = 15,3 min, τ major = 22,6 min (84% ee); [α]D 25 = +47,8 (c = 0,83, CHCl3, 84% ee). Lit. 2 \[ \alpha \] 25 = -45,9 (c = 1,23, CHCl3, -92% ee).

1H NMR (400 MHz, Chloroform-d) δ 7,73 – 7,66 (m, 2H), 7,62 – 7,56 (m, 1H), 3,67 (d, J = 17,8 Hz, 1H), 3,53 (d, J = 17,8 Hz, 1H), 1,44 (s, 9H).

19F NMR decoupled 1H (376 MHz, Chloroform-d) δ -69,20 (s, 3F).

13C NMR (101 MHz, Chloroform-d) δ 192,1, 163,6 (q, J = 2,2 Hz), 153,1, 133,5 (t, J = 1,8 Hz), 132,1, 131,6, 129,6, 126,5, 123,4 (q, J = 281,5 Hz), 84,6, 63,94 (q, J = 26,0 Hz), 33,9 – 33,7 (m), 27,7.

tert-Butyl (S)-6-methyl-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate (3o). Prepared according to general procedure using tert-butyl 6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0,1 mmol, 25 mg), phase transfer catalyst 5b (0,002 mmol, 13 mg) and cesium carbonate (0,2 mmol, 65 mg). Trifluoriodomethane (0,3 mmol, 7,5 mL, gas) was added after the 3 cycles of freeze pump thaw via gas syringe at -196 °C (nitrogen bath). Time of irradiation: 64 hours. The crude mixture was purified by flash column chromatography (hexane, DCM:hex 4:6) to give the product as a white solid (12 mg, 38% yield, 78% ee). The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 99,5:0,5 hexane:iPrOH, flow rate 0,60 mL/min, λ = 254 nm: τ minor = 12,7 min, τ major = 13,9 min (78% ee); [α]D 25 = +12,7 (c = 1,05, CHCl3, 78% ee).
$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.62 (s, 1H), 7.48 (dd, $J = 7.9$, 1.1 Hz, 1H), 7.39 (d, $J = 7.8$ Hz, 1H), 3.62 (d, $J = 17.5$ Hz, 1H), 3.50 (d, $J = 17.4$ Hz, 1H), 2.42 (s, 1H), 1.43 (s, 9H).

$^{19}$F NMR decoupled $^1$H (376 MHz, Chloroform-$d$) $\delta$ -69.23 (s, 3F).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 193.4, 164.2 (d, $J = 2.4$ Hz), 149.1, 138.5, 137.3, 134.8 (d, $J = 1.7$ Hz), 125.9, 125.2, 123.7 (q, $J = 281.3$ Hz), 64.2 (d, $J = 25.8$ Hz), 34.0 – 33.8 (m), 27.7, 21.0.

F. Quantum Yield Measurement

A ferrioxalate actinometry solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in Handbook of Photochemistry$^3$. Ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed.

The solutions were prepared and stored in the dark (red light):

1. Potassium ferrioxalate solution: 589.5 mg of potassium ferrioxalate (commercially available from Alfa Aesar) and 278 $\mu$L of sulfuric acid (96%) were added to a 100 mL volumetric flask, and filled to the mark with water (HPLC grade).
2. Phenanthroline solution: 0,2% by weight of 1,10-phenanthroline in water (200 mg in 100 mL volumetric flask).
3. Buffer solution: to a 100 mL volumetric flask 4.94 g of NaOAc and 1 mL of sulfuric acid (96%) were added and filled to the mark with water (HPLC grade).
4. Model reaction solution: tert-butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate 1b (0,2 mmol, 46 mg), perfluorohexyl iodide 2a (0.6 mmol, 0,130 ml) tetradecane (0,1 mmol, 0,026ml) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (0,4 mmol, 0,06 ml) were added to a 5 mL volumetric flask 442 $\mu$L and filled to the mark with chlorobenzene.

The actinometry measurements were done as follows:

1. 1 mL of the actinometer solution was added to a quartz cuvette (l = 10 mm). The cuvette was placed along with a sample solution (1 mL in a similar cuvette) whose quantum yield has to be measured (our model reaction). The sample and actinometry solutions (placed 10 cm away from the lamp) were irradiated with 300 W Xenon Lamp (50% of light intensity, 400 ± 5 nm bandpass filter high transmittance) for specified time intervals (5, 7.5, 10, 12.5) min.
2. After irradiation all the actinometer solution was removed and placed in a 10 mL volumetric flask. 0.5mL of 1,10-phenanthroline solution and 2 mL of buffer solution was added to this flask and filled to the mark with water (HPLC grade).
3. The UV-Vis spectra of actinometry samples were recorded for each time interval. The absorbance of the actinometry solution was monitored at 510 nm.
4. The moles of Fe$^{2+}$ formed for each sample is determined according to the Beers’ Law:
Supplementary Information

\[ \text{moles } Fe^{2+} = \frac{V_1 \cdot V_3 \cdot \Delta A(510 \text{ nm})}{10^3 \cdot V_2 \cdot l \cdot \varepsilon(510 \text{ nm})} \]

where \( V_1 \) is the irradiated volume (1 mL), \( V_2 \) is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), \( V_3 \) is the final volume after complexation with phenanthroline (10 mL), \( l \) is the optical path-length of the irradiation cell (1 cm), \( \Delta A(510 \text{ nm}) \) the optical difference in absorbance between the irradiated solution and the one stored in the dark, \( \varepsilon(510 \text{ nm}) \) is that of the complex \( \text{Fe}^{2+} \)(phen) \[3+ \] (11100 L mol\(^{-1}\)cm\(^{-1}\)).

5. The moles of \( Fe^{2+} \) formed (\( dx \)) are plotted as a function of time (\( dt \)). The slope of this line was correlated to the moles of incident photons by unit of time (\( q_{n,p}^0 \)) by the use of the following equation (6):

\[ \Phi(\lambda) = \frac{dx/dt}{q_{n,p}^0 \cdot [1 - 10^{-A(\lambda)}]} \quad (6) \]

where \( dx/dt \) is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (\( \Phi \)) for \( Fe^{2+} \) at 400 nm is 1.13 (2) and \( A(\lambda) \) is the absorbance at the excitation wavelength (400 nm). The absorbance at this wavelength, \( A(400) \), was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in 1 mm path quartz cuvettes in the presence of the bandpass filter of 400 nm employed to carry out the measurements, obtaining an absorbance of 0.256. \( q_{n,p}^0 \) was determined to be 5.25 \( 10^9 \) einstein s\(^{-1}\).

The moles of products formed for the reaction of interest (performed by irradiating the sample alongside with the actinometer solution) are described below.

6. The moles of products formed were determined by GC measurement (FID detector) using tetradecane as reference standard. The number of moles of product per unit time is related to the number of photons absorbed. The number of photons absorbed is correlated to the number of incident photons by the use of the equation displayed in the previous point.

According to the equation the slope \( (dx/dt) \) is equal to: \( \Phi \cdot (1 - 10^{-A(400 \text{ nm})}) \cdot q_{n,p}^0 \).
were (1-10^{-(A/400\text{ nm})}) was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in 1 mm path quartz cuvettes in the presence of the bandpass filter of 400 nm employed to carry out the measurements, obtaining an absorbance of 0,302. The calculation yields the quantum yield ($\Phi$) of the photoreaction = 1,2.
G. X-ray Crystallographic Data

Single Crystal X-ray Diffraction Data for compound 3f (Synthesized from 1f using GP)

X-ray structure determinations: Crystals of compound 3f were obtained by slow diffusion of hexane into a saturated ethyl acetate solution. Data Collection. Measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoKα radiation, Montel mirrors and a Cryostream Plus low temperature device (T = 100K). Full-sphere data collection was used with ω and φ scans.

![Chemical structure of compound 3f](image)

**Table S2.** Crystal data and structure refinement for 3f at 100 K: CCDC 1055351

| Property                              | Value                        |
|---------------------------------------|------------------------------|
| Identification code                   | mo_LW3021_0m                 |
| Empirical formula                     | C20 H14 Br1 F13 O3           |
| Formula weight                        | 629.22                       |
| Temperature                           | 100(2) K                     |
| Wavelength                            | 0.71073 Å                    |
| Crystal system                        | Triclinic                    |
| Space group                           | P1                           |
| Unit cell dimensions                  | a = 6.7268(7)Å, α = 75.871(2)° |
|                                       | b = 12.1525(10)Å, β = 85.192(4)° |
|                                       | c = 14.3989(15)Å, γ = 89.437(3)° |
| Volume                                | 1137.38(19) Å³               |
| Z                                      | 2                            |
| Density (calculated)                  | 1.837 Mg/m³                  |
| Absorption coefficient                | 1.935 mm⁻¹                   |
| F(000)                                | 620                          |
| Crystal size                          | 0.40 x 0.10 x 0.10 mm³       |
| Theta range for data collection       | 1.463 to 31.632°             |
| Index ranges                          | -9 ≤ h ≤ 9, -17 ≤ k ≤ 17, -12 ≤ l ≤ 21 |
| Reflections collected                 | 14059                        |
| Independent reflections               | 8670[R(int) = 0.0208]        |
| Completeness to theta =31.632°        | 91.1%                        |
| Absorption correction                 | Empirical                    |
| Max. and min. transmission            | 0.830 and 0.625              |
| Refinement method                     | Full-matrix least-squares on F²|
| Data / restraints / parameters        | 8670/ 3/ 673                 |
| Goodness-of-fit on F²                 | 1.087                        |
| Final R indices [I>2sigma(I)]         | R1 = 0.0285, wR2 = 0.0778    |
| R indices (all data)                  | R1 = 0.0307, wR2 = 0.0869    |
| Flack parameter                       | x =0.000(4)                  |
| Largest diff. peak and hole           | 0.915 and -0.549 e Å⁻³       |
Single Crystal X-ray Diffraction Data for compound 5b (Synthesised as in S4+S5)

X-ray structure determinations: Crystals of compound 5b were obtained by slow diffusion of hexane into a saturated methanol, diethyl ether solution. Measurements were made on a Rigaku XtaLab P200 diffractometer equipped with a Pilatus 200K area detector, a Microfocus-HF007 rotating anode with MoKα radiation, Confocal Max Flux optic and a Cryostream Plus low temperature device (T = 100K). Full-sphere data collection was used with ω and φ scans.

For the absolute configuration determination of the light-atom molecule 5b the methodology described in the following work has been followed:

*The use of Mo Kα radiation in the assignment of the absolute configuration of light-atom molecules; the importance of high-resolution data*
E. C. Escudero-Adán, J. Benet-Buchholz, P. Ballester
*Acta Cryst. B, 2014, 70, 660-668*

**Table S3.** Crystal data and structure refinement for 5b at 100 K: **CCDC 1056560**

| Identification code       | mo_LWCN13_0m               |
|---------------------------|----------------------------|
| Empirical formula         | C35 H34 Br F6 N2 O1.50     |
| Formula weight            | 700.55                     |
| Temperature               | 100(2) K                   |
| Wavelength                | 0.71073 Å                  |
| Crystal system            | Monoclinic                 |
| Space group               | P2(1)                      |
| Unit cell dimensions      | a = 12.0338(6)Å            |
|                          | α = 90°                    |
|                          | b = 8.9481(6)Å             |
|                          | β = 100.6910(17)°          |
|                          | c = 15.3554(9)Å            |
|                          | γ = 90°                    |
| Volume                    | 1624.76(17) Å³             |
| Z                         | 2                          |
| Density (calculated)      | 1.432 Mg/m³                |
| Absorption coefficient    | 1.332 mm⁻¹                 |
| F(000)                    | 718                        |
| Crystal size              | 0.20 x 0.05 x 0.01 mm³     |
| Theta range for data collection | 1.722 to 28.095°   |
| Index ranges              | -13<=h<=15,-11<=k<=11,-19<=l<=14 |
| Reflections collected     | 13252                      |
| Independent reflections   | 6279[R(int) = 0.0338]       |
| Completeness to theta     | 87.5%                      |
| Absorption correction     | Empirical                  |
| Max. and min. transmission| 0.987 and 0.651            |
| Refinement method         | Full-matrix least-squares on F² |
| Data / restraints / parameters | 6279/ 220/ 525           |
| Goodness-of-fit on $F^2$ | 1.064 |
|--------------------------|-------|
| Final $R$ indices [$I>2\sigma(I)$] | $R_1 = 0.0564$, $wR_2 = 0.1612$ |
| $R$ indices (all data) | $R_1 = 0.0699$, $wR_2 = 0.1746$ |
| Flack parameter | $x = 0.015(7)$ |
| Largest diff. peak and hole | 1.118 and $-0.523$ e.$\text{Å}^{-3}$ |
H. NMR spectra

Supplementary Information
$^{19}$F (1H) NMR, CDCl$_3$ + TFA
$^{13}$C NMR, CDCl₃ + TFA
$^1$H NMR, DMSO-$d_6$
$^{19}\text{F} \{^1\text{H}\} \text{ NMR, DMSO-}d_6$
$^{13}$C NMR, DMSO-$d_6$
Supplementary Information
Supplementary Information
$^{13}$C NMR, DMSO-$d_6$
Supplementary Information
$^{19}$F \{(H) NMR, CDCl$_3$\}
$^{13}$C NMR, CDCl$_3$
$^{1}$H NMR, CDCl$_3$
Supplementary Information
$^{13}$C NMR, CDCl$_3$
$^{1}H$ NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
Supplementary Information
Supplementary Information

$^1$H NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
Supplementary Information

$^1$H NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
$^{13}$C NMR, CDCl$_3$
Supplementary Information
I. HPLC traces

**Racemic sample 3a:** HPLC (Daicel Chiralpak AD-H column, 99:1 hexane:iPrOH, flow rate 0.50 mL/min, λ = 254 nm)

| Peak RetTime Type | Width | Area     | Height  | Area % |
|-------------------|-------|----------|---------|--------|
| #                 | [min] | [min]    | [mAU*]  | [mAU]  |
| 1                 | 9.931 | 0.2221   | 484.045 | 32.808 | 50.4019 |
| 2                 | 12.404| 0.3052   | 476.325 | 23.827 | 49.5981 |

**Enantioenriched sample 3a:** HPLC (Daicel Chiralpak AD-H column, 99:1 hexane:iPrOH, flow rate 0.50 mL/min, λ = 254 nm)

| Peak RetTime Type | Width | Area     | Height  | Area % |
|-------------------|-------|----------|---------|--------|
| #                 | [min] | [min]    | [mAU*]  | [mAU]  |
| 1                 | 9.980 | 0.2315   | 128.457 | 8.256 | 3.0739 |
| 2                 | 11.082| 0.2635   | 3187.479 | 184.515 | 96.1261 |
**Racemic sample 3b:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC chromatogram for racemic sample 3b](image1)

| Peak Ret Time Type Width Area Height Area | % |
|-----------------------------------------|---|
| 1 6.485 MM 0.1385 270.01233 32.49933 50.0458 |   |
| 2 7.191 MM 0.1561 269.51859 28.77462 49.9542 |   |

**Enantioenriched sample 3b:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC chromatogram for enantioenriched sample 3b](image2)

| Peak Ret Time Type Width Area Height Area | % |
|-----------------------------------------|---|
| 1 6.768 MM 0.1536 17.66068 1.91641 3.2682 |   |
| 2 7.741 MM 0.1833 522.71143 47.53526 96.7318 |   |
**Racemic sample 3c:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC chromatogram of racemic sample 3c.](image)

| Peak RetTime Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|-------------------|-------------|--------------|--------------|--------|
| 1                 | 7.058       | 0.1787       | 986.49072    | 49.8348|
| 2                 | 11.140      | 0.5993       | 295.37082    | 50.0652|

**Enantioenriched sample 3c:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC chromatogram of enantioenriched sample 3c.](image)

| Peak RetTime Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|-------------------|-------------|--------------|--------------|--------|
| 1                 | 7.114       | 0.2048       | 100.63689    | 8.18921|
| 2                 | 11.277      | 0.5424       | 1451.22192   | 93.5151|
Racemic sample 3d: HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

Enantioenriched sample 3d: HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)
**Racemic sample 3e:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm)

![HPLC Chromatogram of Racemic Sample 3e]

**Enantioenriched sample 3e:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm)

![HPLC Chromatogram of Enantioenriched Sample 3e]
**Racemic sample 3f:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC Racemic sample 3f](image)

| Peak RetTime Type | Width | Area  | Height | Area % |
|-------------------|-------|-------|--------|--------|
| # | [min] | [min] | [mA°s] | [mA] |
| 1 | 6.429 | 0.1789 | 833.13019 | 77.63042 | 49.5972 |
| 2 | 8.924 | 0.4336 | 846.66174 | 30.15081 | 50.4028 |

**Enantioenriched sample 3f:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC Enantioenriched sample 3f](image)

| Peak RetTime Type | Width | Area  | Height | Area % |
|-------------------|-------|-------|--------|--------|
| # | [min] | [min] | [mA°s] | [mA] |
| 1 | 6.465 | 0.1737 | 79.87282 | 7.66278 | 6.0697 |
| 2 | 8.872 | 0.4945 | 1236.05933 | 41.65729 | 93.9303 |
Racemic sample sample 3g. GC (Alphadex 120 30x0.25mm, 0.25µm) Tinj/aux 280 Flow 1.5mL/min split 50:1 (1µL) Isotherm 80°C

Enantioenriched sample sample 3g. GC (Alphadex 120 30x0.25mm, 0.25µm) Tinj/aux 280 Flow 1.5mL/min split 50:1 (1µL) Isotherm 80°C
**Racemic sample sample 3h:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC chromatogram for racemic sample 3h](image)

| Peak RetTime Type | Width | Area   | Height | Area   | %     |
|------------------|-------|--------|--------|--------|-------|
| 1                | 6.265 | 0.1620 | 3759.70532 | 386.70343 | 50.0338 |
| 2                | 6.967 | 0.1944 | 3754.62793 | 321.07534 | 49.9662 |

**Enantioenriched sample 3h:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC chromatogram for enantioenriched sample 3h](image)

| Peak RetTime Type | Width | Area   | Height | Area   | %     |
|------------------|-------|--------|--------|--------|-------|
| 1                | 6.206 | 0.1578 | 2698.13501 | 285.05072 | 8.5436 |
| 2                | 6.846 | 0.2219 | 2688.26264 | 2169.68188 | 91.4564 |
**Racemic sample 3i:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm)

![HPLC graph for racemic sample 3i](image)

| Peak | RetTime | Type | Width | Area    | Height | Area %  |
|------|---------|------|-------|---------|--------|---------|
| 1    | 7.739   | MM   | 0.1714| 852.49194 | 82.90517 | 50.0874 |
| 2    | 8.547   | MM   | 0.1891| 849.51660 | 74.87140 | 49.9126 |

**Enantioenriched sample 3i:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, λ = 254 nm)

![HPLC graph for enantioenriched sample 3i](image)

| Peak | RetTime | Type | Width | Area    | Height | Area %  |
|------|---------|------|-------|---------|--------|---------|
| 1    | 7.734   | MM   | 0.1699| 139.74759 | 13.70889 | 7.2358  |
| 2    | 8.540   | MM   | 0.1920| 1791.59094 | 155.50139 | 92.7642 |
**Racemic sample sample 3j:** HPLC (Daicel Chiralpak AD-H column, 99:5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC chromatogram of racemic sample 3j](image)

| Peak | RetTime | Type | Width | Area | Height | Area % |
|------|---------|------|-------|------|--------|--------|
| 1    | 7.966   | MM   | 0.1738| 829.03094 | 79.49958 | 49.9810 |
| 2    | 9.208   | MM   | 0.2027| 829.66229 | 68.22765 | 50.0190 |

**Enantioenriched sample 3j:** HPLC (Daicel Chiralpak AD-H column, 99:5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC chromatogram of enantioenriched sample 3j](image)

| Peak | RetTime | Type | Width | Area | Height | Area % |
|------|---------|------|-------|------|--------|--------|
| 1    | 7.839   | MM   | 0.1559| 211.34802 | 22.58916 | 5.2246  |
| 2    | 8.993   | MM   | 0.2082| 3833.92236 | 306.91364 | 94.7754 |
**Racemic sample sample 3k:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, \( \lambda = 254 \) nm)

**Enantioenriched sample 3k:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, \( \lambda = 254 \) nm)
Supplementary Information

**Racemic sample 3l**: HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC Chromatogram](image1)

| Peak | Ret Time Type | Width | Area      | Height | Area % |
|------|---------------|-------|-----------|--------|--------|
| #    | [min]         | [min] | [mAU*s]   | [mAU]  | %      |
| 1    | 6.405 MM      | 0.1855| 888.89520 | 79.86377| 49.7812|
| 2    | 7.179 MM      | 0.2303| 896.71002 | 64.89669| 50.2188|

**Enantioenriched sample 3l**: HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![HPLC Chromatogram](image2)

| Peak | Ret Time Type | Width | Area      | Height | Area % |
|------|---------------|-------|-----------|--------|--------|
| #    | [min]         | [min] | [mAU*s]   | [mAU]  | %      |
| 1    | 6.442 MM      | 0.1917| 39.11406  | 3.40087 | 2.8130 |
| 2    | 7.269 MM      | 0.2396| 1351.38049| 94.00900| 97.1870|
**Racemic sample 3m**: HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

**Enantioenriched sample 3m**: HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)
**Racemic sample 3n:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

**Enantioenriched sample 3n:** HPLC (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)
**Racemic sample 3o: HPLC** (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![Racemic sample 3o HPLC graph]

| Peak RetTime | Type | Width | Area | Height | Area % |
|-------------|------|-------|------|--------|--------|
| 12.196      | MM   | 0.3959| 755.55182 | 31.80774 | 49.6551 |
| 13.582      | MM   | 0.3384| 766.04694 | 37.72651 | 50.3449 |

**Enantioenriched sample 3o: HPLC** (Daicel Chiralpak AD-H column, 99.5:0.5 hexane:iPrOH, flow rate 0.60 mL/min, $\lambda = 254$ nm)

![Enantioenriched sample 3o HPLC graph]

| Peak RetTime | Type | Width | Area | Height | Area % |
|-------------|------|-------|------|--------|--------|
| 12.713      | MM   | 0.5786| 168.05351 | 4.84093 | 10.7591 |
| 13.871      | MM   | 0.4647| 1393.91760 | 49.99504 | 89.2409 |
J. References

1. L. Hintermann, M. Schmitz, U. Englert, Angew. Chem. Int. Ed. 2007, 46, 5164–5167

2. Q-H. Deng, H. Wadepohl, L. H. Gade, J. Am. Chem. Soc., 2012, 134, 10769–10772.

3. S. Murov, L., Handbook of Photochemistry, Marcel Dekker, New York, 1973