Supporting Information

Complex Carbocyclic Skeletons from Aryl Ketones through a Three-Photon Cascade Reaction
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Contents
1. General Methods ......................................................................................................................... 2
2. General Procedure 1 for the formation of 7-hydroxy-1-indanone derivatives ............................... 3
3. General Procedure 2 for the alkylation of 7-hydroxy-1-indanone derivatives ............................... 3
4. Characterization of starting materials ........................................................................................... 4
5. Optimization of the photocascade reaction .................................................................................... 10
6. Emission spectra of the light source ............................................................................................. 11
7. General Procedure 3 for the photocascade sequence .................................................................... 13
8. Characterization of photoproducts ................................................................................................ 13
9. Identification of 13b as an intermediate in the photocascade ......................................................... 17
10. Opening the cyclopropane moiety of the photo-adducts in selective transformations ................. 18
11. Determination of relative configuration by NOE interactions ..................................................... 21
12. Deuteration experiments ............................................................................................................. 23
13. X-ray Crystallographic Details .................................................................................................. 26
14. Spectra ......................................................................................................................................... 33
1. General Methods

Air- and moisture-sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Irradiation experiments were conducted in a photochemical reactor equipped with 16 fluorescence lamps ($\lambda_{\text{max}} = 350 \text{ nm}$). Dry tetrahydrofuran (THF), dichloromethane ($\text{CH}_2\text{Cl}_2$), and diethyl ether ($\text{Et}_2\text{O}$) were obtained from a solvent purification system. Other dry solvents, e.g., methanol ($\text{MeOH}$), were obtained in the highest purity available and were stored over molecular sieves. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 (F254) glass plates. The TLC plates were visualized by either ultraviolet (UV) light ($\lambda = 254 \text{ nm}$) or treatment with $\text{KMnO}_4$ stain followed by gentle heating. Purification of products was accomplished by either flash chromatography on silica gel 60 (230–400 mesh) or with preparative TLC on silica gel 60 (F254) glass plates. All solvents for chromatography, e.g., ethyl acetate ($\text{EtOAc}$), were distilled prior to use. NMR spectra were measured on a 300, 400, or 500 MHz nuclear magnetic resonance spectrometer. The $^1\text{H}$ NMR spectra were calibrated against the residual solvent peak of chloroform (7.26 ppm), and the $^{13}\text{C}$ NMR spectra were calibrated either against the central peak of $\text{CDCl}_3$ (77.16 ppm). Data for $^1\text{H}$ NMR spectra were reported as follows: chemical shift in parts per million (ppm), peak shape ($s = \text{singlet}$, $d = \text{doublet}$, $t = \text{triplet}$, $q = \text{quartet}$, $p = \text{quintet}$, $h = \text{sextet}$, $\text{hept} = \text{heptet}$, $m = \text{multiplet}$), coupling constant in hertz (Hz), and integration. The assignment of signals to diastereoisomers are based on integration of the signals in the NMR of the mixture of isomers unless otherwise indicated. The relative configuration of products was determined by two-dimensional NMR spectra (COSY, HSQC, HMBC, NOESY). High resolution mass spectroscopy (HR-MS) was performed on a Thermo Scientific LTQ-FT Ultra (ESI) or on a double focusing magnetic sector instrument (EI, 70 eV).
2. General Procedure 1 for the formation of 7-hydroxy-1-indanone derivatives

**Step 1**: AlCl$_3$ was added to a flame-dried flask containing a magnetic stirring bar under argon atmosphere. To the flask was added CH$_2$Cl$_2$ (0.2M) followed by the respective anisole derivative. The reaction mixture was cooled to 0 °C, whereafter the acid chloride derivative was added. The resulting mixture was allowed to slowly reach room temperature and was stirred for 16h. At this point, the reaction mixture was poured slowly into an Erlenmeyer flask containing a saturated solution of Rochelle salts (5 g Rochelle salt per 1 g AlCl$_3$ used in the reaction in 2.5 mL water per 1 g Rochelle salt). Subsequently, Na$_2$CO$_3$ (aq.) was added (5 mL per 1 g AlCl$_3$ used in the reaction). The mixture was left stirring until satisfactory phase separation could be observed. The aqueous phase was extracted 3 times with CH$_2$Cl$_2$, and the combined organic layers were dried using Na$_2$SO$_4$ and concentrated in vacuo. The resulting crude intermediate was used in the next step without further purification.

**Step 2**: AlCl$_3$ and crude intermediate (from step 1) were added to a flame-dried flask containing a magnetic stirring bar under argon atmosphere. The flask was connected via tubing to a neutralizing solution (NaOH (aq.)) with two intermediary empty flasks to secure against backflow of the basic solution into the reaction mixture. The neat reaction was carefully heated to 180°C and stirred at this temperature for 2h. At this point, the reaction mixture was allowed to cool to room temperature, whereafter saturated solution of Rochelle salt and Na$_2$CO$_3$ (aq.) were added (amounts as in step 1). The mixture was allowed to stir until the layers could be easily separated. The mixture was diluted with water and CH$_2$Cl$_2$ until a clearer biphasic mixture was observed. The aqueous phase was extracted 3 times with CH$_2$Cl$_2$. The combined organic layers were dried using Na$_2$SO$_4$ and concentrated in vacuo. The crude 7-hydroxy-1-indanone derivative was purified by FC.

3. General Procedure 2 for the alkylation of 7-hydroxy-1-indanone derivatives

7-hydroxy-1-indanone (1.0 equiv.) was added to a flame-dried flask and dissolved in dry DMF (1.0 M) under argon atmosphere. Alkenyl bromide (1.5 equiv.) was added followed by cesium carbonate (1.2 equiv.). The resulting mixture was stirred at room temperature for 16h. Hereafter, the reaction mixture was diluted with ammonium chloride (aq.) and CH$_2$Cl$_2$. The aqueous phase was extracted 3 times with CH$_2$Cl$_2$. The combined organic phase was dried using Na$_2$SO$_4$ and concentrated in vacuo. The crude product was purified by FC.
4. Characterization of starting materials

**Compound 5a** was synthesized according to General Procedure 2, using 7-hydroxy-1-indanone (600 mg, 4.05 mmol, 1.0 equiv.), 5-bromopent-1-ene (0.72 mL, 6.08 mmol, 1.5 equiv.), and cesium carbonate (1.58 g, 4.86 mmol, 1.2 equiv.). Purification by FC using an EtOAc/pentane gradient (3:97 EtOAc to 12:88 EtOAc in pentane) to provide 7-(pent-4-en-1-yl)-2,3-dihydro-1H-inden-1-one 5a as a colorless oil (820 mg, 94%).

$^{1}$H NMR (400 MHz, CDCl$_3$, 300 K): δ = 7.47 (t, $J$ = 7.9 Hz, 1H), 6.98, (d, $J$ = 8.2 Hz, 1H), 6.75 (d, $J$ = 8.2 Hz, 1H), 5.87 (ddt, $J$ = 17.1, 10.2, 6.6 Hz, 1H), 5.07 (dq, $J$ = 17.1, 1.7 Hz, 1H), 4.99 (ddt, $J$ = 10.2, 2.1, 1.3 Hz, 1H), 4.11 (t, $J$ = 6.6 Hz, 2H), 3.08-3.05 (m, 2H), 2.66-2.63 (m, 2H), 2.32-2.26 (m, 2H), 2.02-1.95 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$, 300 K): δ = 204.5, 158.0, 157.8, 137.9, 136.3, 125.7, 118.4, 115.4, 110.1, 68.0, 37.0, 30.1, 28.2, 25.7.

HRMS (ESI): calcd for C$_{14}$H$_{17}$O$_2$: [M + H$^+$] = 217.1223, found = 217.1223.

**Compound 5b** was synthesized according to General Procedure 2, using 7-hydroxy-4-methyl-1-indanone (810 mg, 5.00 mmol, 1.0 equiv.), 5-bromopent-1-ene (0.89 mL, 7.50 mmol, 1.5 equiv.), and cesium carbonate (1.95 g, 6.00 mmol, 1.2 equiv.). Purification by FC using an EtOAc/pentane gradient (3:97 EtOAc to 11:89 EtOAc in pentane) to provide 4-methyl-7-(pent-4-en-1-yl)-2,3-dihydro-1H-inden-1-one 5b as a colorless oil (1.07 g, 93%).

$^{1}$H NMR (400 MHz, CDCl$_3$, 300 K): δ = 7.28 (d, $J$ = 8.3 Hz, 1H), 6.69 (d, $J$ = 8.3 Hz, 1H), 5.86 (ddt, $J$ = 17.1, 10.2, 6.6 Hz, 1H), 5.06 (dq, $J$ = 17.1, 1.7 Hz, 1H), 4.98 (ddt, $J$ = 10.2, 2.1, 1.2 Hz, 1H), 4.08 (t, $J$ = 6.6 Hz, 2H), 2.95-2.92 (m, 2H), 2.67-2.64 (m, 2H), 2.31-2.25 (m, 2H), 2.25 (s, 3H), 2.00-1.93 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$, 300 K): δ = 204.9, 156.3, 155.9, 138.0, 136.5, 126.9, 125.4, 115.3, 110.3, 68.0, 36.9, 30.1, 28.2, 24.7, 17.1.

HRMS (ESI): calcd for C$_{15}$H$_{18}$O$_2$: [M + H$^+$] = 231.1380, found = 231.1380.

**Compound 5c** was synthesized according to General Procedure 2, using 7-hydroxy-1-indanone (619 mg, 4.18 mmol, 1.0 equiv.), 3-(chloromethoxy)prop-1-ene ether (0.89 mL$^{-1}$, 8.36 mmol, 2.0 equiv.$^{-1}$) and sodium carbonate (527 mg, 4.99 mmol, 1.2 equiv.). Purification by FC using an EtOAc/pentane 1:20 to provide 7-((allyloxy)methoxy)-2,3-dihydro-1H-inden-1-one 5c as a white solid (603 mg, 66%).

$^{1}$H NMR (400 MHz, CDCl$_3$, 300 K): δ = 7.49 (t, $J$ = 7.8 Hz, 1H), 7.09-7.06 (m, 2H), 5.89 (ddt, $J$ = 17.1, 10.3, 5.6 Hz, 1H), 5.41 (s, 2H), 5.30 (dq, $J$ = 17.2, 1.6 Hz, 1H), 5.19 (dq, $J$ = 10.4, 1.4 Hz, 1H), 4.25 (dt, $J$ = 5.7, 1.4 Hz, 2H), 3.10-3.07 (m, 2H), 2.69-2.66 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$, 300 K): δ = 204.6, 157.8, 155.7, 136.3, 133.8, 126.1, 119.8, 117.8, 113.3, 92.8, 69.7, 37.0, 25.6.

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1 Assuming a density of 1.002 g/mL as reported in literature: A. A. Ozerov, A. K. Brel, *Chemistry of Heterocyclic Compounds (New York, NY, United States)*, 1993, 29, 945-948.

2 For the synthesis of 3-(chloromethoxy)prop-1-ene ether see: D. S. Connor, G. W. Klein, G. N. Taylor, R. K. Boeckman, Jr, J. B. Medwid, *Org. Synth.* 1972, 52, 16.
HRMS (ESI): calcd for C_{13}H_{14}O_{3}^{+} [M + H^+] = 219.1016, found = 219.1016.

Compound 5d was synthesized according to General Procedure 2, using 7-hydroxy-1-indanone (389 mg, 2.62 mmol, 1.0 equiv.), 4-bromobut-1-ene (0.40 mL, 3.90 mmol, 1.5 equiv.) and cesium carbonate (1.00 g, 3.14 mmol, 1.2 equiv.). Purification by FC using EtOAc/pentane 1:10 to provide 7-(but-3-en-1-ylxo)-2,3-dihydro-1H-inden-1-one 5d as a colorless oil (165 mg, 31%).

\[ \text{1H NMR (400 MHz, CDCl}_3, 300 K): \delta = 7.48 (t, J = 7.9 Hz, 1H), 6.99 (d, J = 7.9 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 5.95 (ddt, J = 17.1, 10.2, 6.8 Hz, 1H), 5.20 (dd, J = 17.1, 1.6 Hz, 1H), 5.13 (d, J = 10.2 Hz, 1H), 4.15 (t, J = 7.0 Hz, 2H), 3.08-3.05 (m, 2H), 2.66-2.64 (m, 4H). \]

\[ \text{13C NMR (101 MHz, CDCl}_3, 300 K): \delta = 204.3, 157.8, 157.4, 136.1, 118.4, 117.4, 110.0, 67.9, 36.8, 33.4, 25.5. \]

HRMS (ESI): calcd for C_{13}H_{14}O_{3}^{+} [M + H^+] = 203.1067, found = 203.1066.

4-Chloro-1-(2-hydroxy-5-methylphenyl)butan-1-one i5e was synthesized according to General Procedure 1 (step 1), using AlCl\(_3\) (11.46 g, 86.10 mmol, 3.5 equiv.), 4-methylanisole (3.00 g, 24.55 mmol, 1.0 equiv.), and 4-chlorobutyl chloride (4.12 mL, 36.82 mmol, 1.5 equiv.). The crude product was used in step 2 without further purification (5.46 g crude product was obtained).

7-Hydroxy-4,3'-dimethyl-1-indanone ii5e was synthesized according to General Procedure 1 (step 2), using AlCl\(_3\) (5.33 g, 40.0 mmol, 4.0 equiv.), crude i5e (2.13 g, 10.0 mmol, 1.0 equiv.). The resulting 7-hydroxy-4,3'-dimethyl-1-indanone ii5e was obtained as an orange solid (837 mg) and used without further purification.

\[ \text{1H NMR (400 MHz, CDCl}_3, 300 K): \delta = 9.04 (s, 1H), 7.27 (d, J = 8.3 Hz, 1H), 6.70 (d, J = 8.3 Hz, 1H), 3.47 (qd, J = 7.1, 1.9 Hz, 1H), 2.97 (dd, J = 19.1, 7.5 Hz, 1H), 2.34-2.30 (m, 4H), 1.34 (d, J = 7.1 Hz, 3H). \]

\[ \text{13C NMR (101 MHz, CDCl}_3, 300 K): \delta = 210.0, 157.6, 155.7, 139.3, 126.0, 121.6, 114.0, 45.7, 32.9, 21.0, 17.3. \]

HRMS (ESI): calcd for C_{11}H_{12}O_{3}^{+} [M + H^+] = 177.0910, found = 177.0910.

Compound 5e was synthesized according to General Procedure 2, using 7-hydroxy-4,3'-dimethyl-1-indanone (771 mg, 3.17 mmol, 1.0 equiv.), 5-bromopent-1-ene (0.56 mL, 4.73 mmol, 1.5 equiv.) and cesium carbonate (1.30 g, 3.80 mmol, 1.2 equiv.). Purification by FC using EtOAc/pentane 1:10 to provide 3,4-dimethyl-7-(pent-4-en-1-ylxyo)-2,3-dihydro-1H-inden-1-one 5e as a pale yellow oil (503 mg, 24% over 3 steps).

\[ \text{1H NMR (400 MHz, CDCl}_3, 300 K): \delta = 7.28 (d, J = 8.4 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 5.86, (ddt, J = 17.1, 10.2, 6.6 Hz, 1H), 5.06 (dq, J = 17.1, 1.9 Hz, 1H), 4.99 (ddt, J = 10.2, 1.9, 1.2 Hz, 1H), 4.12-4.03 (m, 2H), 3.43-3.37 (m, 1H), 2.89 (dd, J = 18.4, 7.7 Hz, 1H), 2.32 (s, 3H), 2.30-2.25 (m, 3H), 2.00-1.93 (m, 2H), 1.29 (s, 3H). \]

\[ \text{13C NMR (101 MHz, CDCl}_3, 300 K): \delta = 204.4, 160.5, 155.8, 138.0, 137.6, 126.5, 124.4, 115.3, 110.6, 68.0, 46.7, 32.0, 30.1, 28.2, 21.5, 17.3. \]
HRMS (ESI): calcd for C_{16}H_{20}O_{2}^{+} [M + H^{+}] = 245.1536, found = 245.1536.

3-Chloro-1-(2-hydroxy-4,5-dimethylphenyl)propan-1-one i5f was synthesized according to General Procedure 1 (step 1), using AlCl₃ (11.46 g, 86.10 mmol, 3.5 equiv.), 3,4-dimethylanisole (3.40 mL, 24.60 mmol, 1.0 equiv.), and 3-chloropropionyl chloride (3.52 mL, 36.90 mmol, 1.5 equiv.). The crude product was used in step 2 without further purification.

7-Hydroxy-4,5-dimethyl-1-indanone ii5f was synthesized according to General Procedure 1 (step 2), using AlCl₃ (13.10 g, 98.4 mmol, 4.0 equiv.), crude ii1c (assumed 24.6 mmol). Purification by FC using an EtOAc/pentane gradient (1:49 EtOAc to 1:9 EtOAc in pentane) to provide ii5f as a pale yellow solid (1.91 g, 44% over 2 steps).

1H NMR (400 MHz, CDCl₃, 300 K): δ = 8.84 (s, 1H), 6.61 (s, 1H), 3.01-2.98 (m, 2H), 2.72-2.70 (m, 2H), 2.30 (s, 3H), 2.14 (s, 3H).

13C NMR (101 MHz, CDCl₃, 300 K): δ = 209.8, 155.2, 153.5, 147.7, 125.0, 120.9, 115.1, 36.4, 25.4, 20.9, 13.8.

HRMS (ESI): calcd for C_{11}H_{12}O_{2}^{+} [M + H^{+}] = 177.0910, found = 177.0910.

Compound 5f was synthesized according to General Procedure 2, using 7-hydroxy-4,5-dimethyl-1-indanone (954 mg, 5.40 mmol, 1.0 equiv.), 5-bromopent-1-ene (0.96 mL, 8.12 mmol, 1.5 equiv.) and cesium carbonate (2.11 g, 5.40 mmol, 1.2 equiv.). Purification by FC using an EtOAc/pentane gradient (5% EtOAc to 15% EtOAc in pentane) afforded 4,5-dimethyl-7-(pent-4-en-1-yl oxy)-2,3-dihydro-1H-inden-1-one 5f as a pale yellow solid (0.47 g, 36%).

1H NMR (400 MHz, CDCl₃, 300 K): δ = 6.60 (s, 1H), 5.87 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.07 (dq, J = 17.0, 1.9 Hz, 1H), 4.99 (ddt, J = 10.2, 1.9, 1.2 Hz, 1H), 4.07 (t, J = 6.6 Hz, 2H), 2.95-2.92 (m, 2H), 2.66-2.63 (m, 2H), 2.33 (s, 3H), 2.31-2.25 (m, 2H), 2.15 (s, 3H), 2.00-1.93 (m, 2H).

13C NMR (101 MHz, CDCl₃, 300 K): δ = 204.4, 156.2, 155.2, 145.4, 137.9, 125.3, 123.5, 115.2, 112.2, 116.8, 37.1, 30.0, 28.1, 24.9, 20.8, 13.6.

HRMS (ESI): calcd for C_{16}H_{20}O_{2}^{+} [M + H^{+}] = 245.1536, found = 245.1536.

Compound 5g was synthesized according to General Procedure 2, using 7-hydroxy-1-indanone (296 mg, 2.0 mmol, 1.0 equiv.), 5-bromo-3-methylpent-1-ene (480 mg, 2.9 mmol, 1.5 equiv.) and cesium carbonate (800 mg, 2.4 mmol, 1.2 equiv.). Purification by FC using an EtOAc/pentane gradient (1:20 EtOAc to 1:5 EtOAc in pentane) to provide 7-((3-methylpent-4-en-1-yl)oxy)-2,3-dihydro-1H-inden-1-one 5g as a colorless oil (225 mg, 49%).

For the synthesis of 5-bromo-3-methylpent-1-ene: C. Brenninger, A. Pöthig, T. Bach, Angew. Chem. Int. Ed. 2017, 56, 4337 – 4341.
The reaction mixture was stirred for 20 min., quenched with NaBH₄ (56 mg, 1.2 equiv.) was dissolved in dry methanol (6.0 mL) and cooled to 0°C at which point NaBH₄ (772 mg, 20.4 mmol, 1.0 equiv.) was added. The mixture was stirred for 20 min., quenched with NH₄Cl (aq.) (40 mL) and extracted 3 times with Et₂O (25 mL). The combined organic layers were dried using Na₂SO₄ and concentrated in vacuo. The crude reaction mixture was passed through a short column using pentane/Et₂O 1:1 as eluent to provide the desired alcohol after careful evaporation (1.02 g, quant.). It should be noted, that residual ether is present and has been subtracted from the yield based on ¹H NMR. The alcohol containing ether was used directly in the next step.

¹H NMR (400 MHz, CDCl₃, 300 K): δ = 7.47 (t, J = 7.9 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 5.17-5.14 (m, 1H), 4.08 (t, J = 6.6 Hz, 2H), 3.07-3.05 (m, 2H), 2.66-2.63 (m, 2H), 2.21 (q, J = 7.3 Hz, 2H), 1.91 (p, J = 6.9, 2H), 1.69 (s, 3H), 1.61 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, 300 K): δ = 204.4, 157.92, 157.8, 143.7, 136.3, 125.6, 118.3, 113.7, 110.0, 68.0, 36.9, 29.1, 25.9, 25.7, 24.4, 17.8.

HRMS (EI): calcd for C₃₀H₂₀O₂: [M + H⁺] = 445.1458, found = 444.1458.

Hex-5-en-2-ol was obtained from the corresponding ketone (hex-5-en-2-one) by a sodium borohydride reduction. Hex-5-en-2-one (1.00 g, 10.2 mmol, 1.0 equiv.) was dissolved in dry methanol (6.0 mL) and cooled to 0°C at which point NaBH₄ (772 mg, 20.4 mmol, 2.0 equiv.) was added. The mixture was stirred for 20 min., quenched with NH₄Cl (aq.) (40 mL) and extracted 3 times with Et₂O (25 mL). The combined organic layers were dried using Na₂SO₄ and concentrated in vacuo. The crude reaction mixture was passed through a short column using pentane/Et₂O 1:1 as eluent to provide the desired alcohol after careful evaporation (1.02 g, quant.). It should be noted, that residual ether is present and has been subtracted from the yield based on ¹H NMR. The alcohol containing ether was used directly in the next step.

¹H NMR (400 MHz, CDCl₃, 300 K): δ = 7.40 (t, J = 7.9 Hz, 1H), 6.91 (d, J = 7.9 Hz, 1H), 6.70 (d, J = 7.9 Hz, 1H), 5.78 (ddt, J = 17.2, 10.2, 6.6 Hz, 1H), 4.94 (dq, J = 17.2, 1.9 Hz, 1H), 4.90 (ddt, J = 10.2, 1.9, 1.2 Hz, 

₄ Synthesis of 5-methylhex-4-en-1-ol: S. Peil, A. Guthertz, T. Biberger, A. Fürstner, Angew. Chem. Int. Ed. 2019, 58, 8851-8856.
1H), 4.45 (hept, J = 6.1 Hz, 1H), 3.02-2.95 (m, 2H), 2.60-2.57 (m, 2H), 2.26-2.11 (m, 2H), 2.93 (ddt, J = 13.4, 8.6, 6.7 Hz, 1H), 1.68 (ddddd, J = 14.0, 8.8, 6.7, 5.5 Hz, 1H), 1.34 (d, J = 6.1 Hz, 3H).

13C NMR (101 MHz, CDCl3, 300 K): δ = 204.2, 158.0, 157.3, 138.3, 136.1, 126.2, 118.2, 115.1, 111.6, 74.5, 37.0, 35.6, 29.8, 25.6, 19.7.

HRMS (ESI): calcd for C13H18O2+ [M + H+] = 231.1380, found = 231.1380.

To a flame-dried flask equipped with a magnetic stirring bar was added (E)-hex-4-en-1-ol (0.47 mL, 4.0 mmol, 1.0 equiv.) and dry pyridine (10 mL). Subsequently, TsCl (5.72 g, 30.0 mmol, 7.5 equiv.) was added and the reaction mixture was stirred at -20°C for 16h. At this point, HCl (10% in water) was added and the mixture was extracted 3 times with Et2O (10 mL). The combined organic layers were washed with HCl (10% in water) and NaHCO3 (aq.), whereafter they were dried using Na2SO4 and concentrated in vacuo. The crude tosylate i5j was purified by FC using pentane/EtOAc 97:3 as eluent to provide the desired product (E)-hex-4-en-1-yl 4-methylbenzenesulfonate i5j (910 mg, 89%).

1H NMR (400 MHz, CDCl3, 300 K): δ = 7.79 (d, J = 8.2 Hz, 2H), 7.34, (d, J = 8.2 Hz, 2H), 5.39-5.22 (m, 2H), 4.02 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H), 2.03-1.97 (m, 2H), 1.69 (dq, J = 8.2, 6.4 Hz, 2H), 1.59 (dd, J = 6.0, 1.2 Hz, 3H).

13C NMR (101 MHz, CDCl3, 300 K): δ = 144.8, 133.4, 129.9 (2C), 129.2, 128.1 (2C), 126.7, 70.0, 28.7, 28.3, 21.8, 18.0.

HRMS (ESI): calcd for C13H18O2S+ [M + Na+] = 277.0869, found = 277.0868.

In a flame-dried flask, 7-hydroxy-1-indanone (250 mg, 1.69 mmol, 1.0 equiv.) was dissolved in dry DMF (5.0 mL), and NaH (60% in mineral oil, 98 mg, 2.87 mmol, 1.5 equiv.) was added to the mixture in portions. The reaction was allowed to stir at room temperature for 2h. At this point, tosylate i5j was added dropwise (391 mg, 2.54 mmol, 1.5 equiv.) and the resulting mixture was heated to 60°C and stirred at this temperature for 24h. The reaction was quenched using NH4Cl (aq.) and extracted 3 times with Et2O (10 mL). The combined organic layers were dried using Na2SO4 and concentrated in vacuo. Purification by FC using an EtOAc/pentane gradient (1:10 EtOAc to 1:4 EtOAc in pentane) to provide (E)-7-(hex-4-en-1-ylxyloxy)-2,3-dihydro-1H-inden-1-one 5j as a colorless oil (167 mg, 43%).

1H NMR (400 MHz, CDCl3, 300 K): δ = 7.47 (t, J = 7.9 Hz, 1H), 6.98, (d, J = 7.9 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 5.49-5.46 (m, 2H), 4.09 (t, J = 6.7 Hz, 2H), 3.08-3.05 (m, 2H), 2.66-2.63 (m, 2H), 2.23-2.18 (m, 2H), 1.97-1.90 (m, 2H), 1.65-1.63 (m, 3H).

13C NMR (101 MHz, CDCl3, 300 K): δ = 204.4, 157.9, 157.8, 136.3, 130.3, 125.9, 125.6, 118.3, 110.0, 68.0, 36.9, 28.9, 28.8, 25.6, 18.0.

HRMS (ESI): calcd for C15H18O2S+ [M + H+] = 231.1380, found = 231.1380.

The alcohol (2-methylpent-4-en-1-ol i5k) was obtained from the corresponding ester (ethyl 2-methylpent-4-enoate) by a lithium aluminiumhydride reduction. Ethyl 2-methylpent-4-enoate (3.26 mL, 20.0 mmol, 1.0 equiv.) was dissolved in dry THF (10.0 mL) and cooled to 0°C at which point LiAlH4 (1.14 g, 30.0 mmol, 1.5 equiv.) was added dropwise as a solution in THF (10 mL). The mixture was allowed to reach room temperature and stirred for 2h. The reaction mixture was diluted with Et2O (20 mL) and quenched at 0°C with water (5.0 mL) and NaOH (15% in water, 1.5 mL). The resulting mixture was allowed to reach room
temperature and stirred for 15 min, whereafter the mixture was extracted three times with Et₂O (25 mL). The combined organic layers were dried using Na₂SO₄ and concentrated carefully in vacuo. The crude reaction mixture was passed through a short column using EtOAc/pentane as eluent to provide the desired crude alcohol (1.81 g corresponding to a crude yield of 90%) after careful evaporation. The crude alcohol was used without further purification in the next step.

Triphenylphosphine (540 mg, 3.33 mmol, 1.2 equiv.) was dissolved in dry THF (10.0 mL). To this solution was added 7-hydroxy-1-indanone (433 mg, 2.92 mmol, 1.05 equiv.) and 2-methylpent-4-en-1-ol i5k (278 mg, 2.78 mmol, 1.0 equiv.) followed by dropwise addition of diethyl azodicarboxylate as a solution (2.2 M) in toluene (1.0 mL). The reaction mixture was allowed to stir for 18 h, whereafter the solvent was removed in vacuo and the crude residue was purified by FC using an EtOAc/pentane 20:1 as eluent to provide 7-((2-methylpent-4-en-1-yl)oxy)-2,3-dihydro-1H-inden-1-one 5k as a white solid (374 mg, 58%).

¹H NMR (400 MHz, CDCl₃, 300 K): δ = 7.47 (t, J = 7.9 Hz, 1H), 6.98, (d, J = 7.9 Hz, 1H), 6.74 (d, J = 7.9 Hz, 1H), 5.83 (ddt, J = 17.0, 10.1, 7.0 Hz, 1H), 5.08-5.01 (m, 2H), 3.95 (dd, J = 9.2, 5.9 Hz, 1H), 3.86 (dd, J = 9.2, 6.4 Hz, 1H), 3.08-3.05 (m, 2H), 2.66-2.63 (m, 2H), 2.38-2.31 (m, 1H), 2.20-2.06 (m, 2H), 1.08 (d, J = 6.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, 300 K): δ = 204.1, 157.8, 157.7, 136.4, 136.1, 125.5, 118.2, 116.4, 109.9, 72.8, 37.7, 36.8, 32.8, 25.5, 16.7.

HRMS (ESI): calcd for C₁₅H₁₈O₂⁺ [M + H⁺] =231.1380, found = 231.1380.

Compound 5l was synthesized according to General Procedure 2, using 7-hydroxy-1-indanone (344 mg, 2.32 mmol, 1.0 equiv.), 7-bromohept-1-ene (0.53 mL, 3.48 mmol, 1.5 equiv.) and cesium carbonate (0.90 g, 2.78 mmol, 1.2 equiv.). Purification by FC using an EtOAc/pentane gradient (5% EtOAc to 10% EtOAc in pentane) to provide 7-(hept-6-en-1-yl)oxy)-2,3-dihydro-1H-inden-1-one 5l as a colorless oil (413 mg, 73%).

¹H NMR (400 MHz, CDCl₃, 300 K): δ = 7.47 (t, J = 7.9 Hz, 1H), 6.98 (d, J = 7.9 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 5.82 (ddt, J = 17.1, 10.2, 6.7 Hz, 1H), 5.01 (dq, J = 17.1, 1.7 Hz, 1H), 4.94 (ddt, J = 10.2, 2.2, 1.2 Hz, 1H), 4.09 (t, J = 6.7 Hz, 2H), 3.08-3.05 (m, 2H), 2.66-2.63 (m, 2H), 2.12-2.06 (m, 2H), 1.93-1.86 (m, 2H) 1.55-1.45 (m, 4H).

¹³C NMR (101 MHz, CDCl₃, 300 K): δ = 204.4, 157.8, 157.7, 138.9, 136.1, 125.5, 118.2, 114.4, 109.8, 68.5, 36.8, 33.6, 28.7, 28.6, 25.5, 25.4.

HRMS (ESI): calcd for C₁₆H₂₀O₂⁺ [M + H⁺] = 245.1536, found = 245.1536.
5. Optimization of the photocascade reaction

![Chemical structure diagram]

| Entry | Solvent | λ/nm | t/h | SM/% | 6a/% | 13a/% |
|-------|---------|------|-----|------|------|-------|
| 1     | CH₂Cl₂  | 300  | <2  | 0    | 38   | <3    |
| 2     | MeCN    | 300  | 3.5 | 0    | Complex mixture | 0 |
| 3     | MeOH    | 300  | <2.5| 0    | 55   | 0     |
| 4     | MeOH    | 350  | 16  | 0    | 68   | 0     |

Methanol was identified as the superior solvent (entries 1-3). At this point, a longer wavelength was tested providing a higher yield (68%, entry 4). The optimal conditions were employed to explore the scope of the reaction as demonstrated in the following sections.
6. Emission spectra of the light source

Datasheet FLT012

| Basic Information | Datasheet RPR3000 |
|-------------------|-------------------|
| Type              | Fluorescent light tube |
| Description       | Rayonet RPR-3000A |
| Manufacturer / Supplier | n/a / Southern New England Ultraviolet Company |
| Order number / Date of purch. | n/a / n/a |
| Internal lot / serial number | n/a / FLT012 |
| Specification Manufacturer | |
| Type / size       | T5 tube, G5 socket |
| Mechanical specification | 16 mm diameter, 288 mm length |
| Electrical specification | 8 W |
| Wavelength (range, typ.) | 300 nm |
| Spectral width (FWHM) | ~ 40 nm |
| Datasheet | n/a |

Characterization

| Description of measurement | Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). 
The cosine corrector was placed at 20 mm distance from a single fluorescent tube at half height. |
| Measured dominant wavelength / Int. | 313 nm 138 μW/mm²nm |
| Measured spectral width (FWHM) | 40 nm |
| Integral Reference intensity / range | 4725 μW/cm² 260-380 nm |

Spectrum
Datasheet FLT021

LZC-UVA

Basic Information
- Type: Fluorescent light tube
- Description: Luzchem LZC-UVA
- Manufacturer / Supplier: Hitachi / Luzchem
- Order number / Date of purch.: LZC-UVA / 09/2015
- Internal lot / serial number: 2015-09 / FLT021

Specification Manufacturer
- Type / size: TS tube, GS socket
- Mechanical specification: 16 mm diameter, 288 mm length
- Electrical specification: 8 W
- Wavelength (range, typ.): 300 - 400 nm, 350m nm, UV-A
- Spectral width (FWHM): ~ 40 nm
- Datasheet: Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre).
The cosine corrector was placed at 20 mm distance from a single fluorescent tube at half height.

Characterization
- Description of measurement: Measured dominant wavelength / Int.
  - 350 nm: 115 µW/mm²/nm
  - Measured spectral width (FWHM): 40 nm
  - Integral Reference intensity / range:
    - 5017 µW/cm²: 300-425 nm

Spectrum
7. General Procedure 3 for the photocascade sequence

Compound 5 was added to a flame-dried Duran phototube (diameter 1 cm, volume 12 mL) and dissolved in distilled MeOH (0.01M). The reaction mixture was purged with argon (ultrasound, 15 min.). The phototube was equipped with a balloon and subjected to irradiation (λ_max = 350 nm) for the indicated time period. At this point, the solvent was removed in vacuo and the crude residue was purified by FC to give the desired photocascade adducts.

8. Characterization of photoproducts

Compound 6a was synthesized according to General Procedure 5, using 5a (21.6 mg, 0.10 mmol, 1.0 equiv.) as the starting material and an irradiation time of 17 h. Purification by FC using an EtOAc/pentane 1:10 to provide 6a as a white solid (14.7 mg, 68%, >20:1 d.r.). It is noteworthy that a scale up experiment (0.6 mmol) using 60 mL distilled MeOH in a larger phototube provided the desired product 1,2,4a,5,6,7-hexahydro-3H,3a1H,4H-cyclopenta[1',2']cyclopropa[3,4]pentaleno[6a,1-b]pyran-3-one in 70% yield and the same excellent diastereoselectivity.

1H NMR (400 MHz, CDCl3, 300 K): δ = 6.05 (dd, J = 5.9, 1.3 Hz, 1H), 5.99, (d, J = 5.9 Hz, 1H), 3.89-3.85 (m, 1H), 3.76 (td, J = 12.3, 3.7 Hz, 1H), 2.94 (s, 1H), 2.37 (dd, J = 13.2, 8.1 Hz, 1H), 2.29-2.08 (m, 5H), 1.71-1.55 (m, 3H), 1.30 (q, J = 12.3, 4.5 Hz, 1H), 0.88 (dd, J = 13.2, 11.7 Hz, 1H).

13C NMR (101 MHz, CDCl3, 300 K): δ = 209.5, 132.3, 126.8, 93.4, 64.4, 54.5, 54.4, 53.1, 52.7, 34.6, 26.1, 24.4, 23.4, 22.5.

HRMS (ESI): calcd for C14H17O2+ [M+H+] = 217.1223, found = 217.1223.

Compound 6b was synthesized according to General Procedure 5, using 5b (23.0 mg, 0.10 mmol, 1.0 equiv.) as the starting material and an irradiation time of 16h. Purification by FC using an EtOAc/pentane 1:20 to provide 3a1-methyl-1,2,4a,5,6,7-hexahydro-3H,3a1H,4H-cyclopenta[1',2']cyclopropa[3,4]pentaleno[6a,1-b]pyran-3-one 6b as a white solid (14.8 mg, 64%, >20:1 d.r.).

1H NMR (400 MHz, CDCl3, 300 K): δ = 6.02 (d, J = 5.9 Hz, 1H), 5.94, (d, J = 5.9 Hz, 1H), 3.92-3.87 (m, 1H), 3.74 (td, J = 11.8, 3.9 Hz, 1H), 2.37-2.25 (m, 3H), 2.22-2.05 (m, 3H), 1.71-1.55 (m, 3H), 1.34-1.24 (m, 1H), 1.32 (s, 3H), 0.89 (dd, J = 13.2, 11.8 Hz, 1H).

13C NMR (101 MHz, CDCl3, 300 K): δ = 210.7, 132.7, 126.1, 94.2, 64.3, 59.1, 57.2, 56.5, 52.7, 37.1, 26.2, 24.3, 23.5, 20.9, 6.9.

HRMS (ESI): calcd for C15H18O2+ [M+H+] = 231.1380, found = 231.1380.

Compound 6c was synthesized according to General Procedure 5, using 5c (21.8 mg, 0.10 mmol, 1.0 equiv.) as the starting material and an irradiation time of 25h. Purification by FC using an EtOAc/pentane gradient (1:10 to 1:5) to provide 1,2,4a,5-tetrahydro-3H,3a1H,4H-cyclopenta[1',2']cyclopropa[3,4]pentaleno[6a,1-d][1,3]dioxin-3-one 6c as a white solid (10.7 mg, 49%, >20:1 d.r.). On a 0.5 mmol scale the desired product could be obtained in 52% yield, >20:1 d.r. using a larger phototube (50 mL).
**1H NMR (400 MHz, CDCl₃, 300 K):** δ = 6.11 (dd, J = 6.0, 1.3 Hz, 1H), 6.07 (d, J = 6.0 Hz, 1H), 4.99 (d, J = 6.8 Hz, 1H), 4.95 (d, J = 6.8 Hz, 1H), 3.97 (dd, J = 11.0, 4.2 Hz, 1H), 3.53 (t, J = 11.0 Hz, 1H), 3.09, (s, 1H), 2.62 (td, J = 12.4, 8.0, 4.2 Hz, 1H), 2.39 (dd, J = 13.1, 8.0 Hz, 1H), 2.30-2.10 (m, 4H), 0.91 (t, J = 12.4 Hz, 1H).

**13C NMR (101 MHz, CDCl₃, 300 K):** δ = 208.6, 133.3, 125.3, 92.0, 89.7, 67.8, 54.3, 53.1, 52.9, 52.2, 34.5, 23.2, 19.1.

**HRMS (ESI):** calcd for C₁₃H₁₄O₂⁺ [M + H⁺] = 219.1016, found = 219.1015.

**Compound 6d was synthesized according to General Procedure 5, using 5d (20.0 mg, 0.10 mmol, 1.0 equiv.) as the starting material and an irradiation time of 18h. Purification by FC using an EtOAc/pentane 1:20 to provide 1,2,4,4a,5,6-hexahydro-3H,3a1H-cyclopenta[1',2']cyclopropa[3,4]pentaleno[6a,1-b]furan-3-one 6d as a white solid (10.0 mg, 50%, >20:1 d.r.).**

**1H NMR (400 MHz, CDCl₃, 300 K):** δ = 5.90 (d, J = 5.8 Hz, 1H), 5.62 (dd, J = 5.8, 1.2 Hz, 1H), 4.39-4.32 (m, 2H), 3.04 (s, 1H), 2.76 (dddd, J = 13.5, 11.9, 7.4, 6.2 Hz, 1H), 2.33 (dd, J = 12.6, 7.4 Hz, 1H), 2.26-2.07 (m, 4H), 1.75-1.68 (m, 1H), 1.65-1.54 (m, 1H), 1.00 (t, J = 12.6 Hz, 1H).

**13C NMR (101 MHz, CDCl₃, 300 K):** δ = 208.8, 130.5, 130.0, 101.5, 75.9, 61.6, 59.4, 53.2, 50.7, 34.5, 25.3, 16.6.

**HRMS (ESI):** calcd for C₁₃H₁₄O₂⁺ [M + H⁺] = 203.1067, found = 203.1066.

**Compound 6e was synthesized according to General Procedure 5, using 5e (24.4 mg, 0.10 mmol, 1.0 equiv.) as the starting material and an irradiation time of 16h. Purification by FC using an EtOAc/pentane 1:50 on a pipette column to provide 1,3α₁,1β-dimethyl-1,2,4a,5,6,7-hexahydro-3H,3α1H,4H-cyclopenta[1',2']cyclopropa[3,4]-pentaleno[6a,1-b]pyran-3-one 6e as a yellow oil (14.9 mg, 61%, 1.4:1 d.r.).**

**1H NMR (400 MHz, CDCl₃, 300 K):** Major diastereoisomer: δ = 6.07 (d, J = 6.0 Hz, 1H), 5.94 (d, J = 6.0 Hz, 1H), 2.77 (tq, J = 9.5, 7.0 Hz, 1H), 1.95 (dd, J = 18.7, 9.3 Hz, 1H), 1.47 (s, 3H).

Minor diastereoisomer: δ = 6.10 (d, J = 6.0 Hz, 1H), 6.05 (d, J = 6.0 Hz, 1H), 1.90-1.85 (m, 1H), 1.34 (s, 3H).

Overlapping signals: δ = 3.92-3.88 (m, 2H), 3.78-3.72 (m, 2H), 2.49-2.43 (m, 3H), 3.38-2.32 (m, 2H), 2.13-2.04 (m, 2H), 1.70-1.55 (m, 6H), 1.36-1.27 (m, 2H), 1.22-1.19 (m, 6H), 0.92-0.85 (m, 2H).

**13C NMR (101 MHz, CDCl₃, 300 K):**

Major diastereoisomer: δ = 209.7, 132.4, 126.8, 94.4, 64.4, 60.9, 59.8, 57.6, 52.3, 44.6, 30.9, 26.3, 24.3, 23.3, 16.8, 9.5.

Minor diastereoisomer: δ = 209.9, 129.9, 126.3, 94.2, 64.4, 62.2, 59.8, 56.7, 52.9, 46.2, 27.4, 26.2, 24.3, 23.5, 20.8, 7.2.

**HRMS (ESI):** calcd for C₁₆H₂₀O₂⁺ [M + H⁺] = 245.1536, found = 245.1536.
Compound 6f was synthesized according to General Procedure 5, using 5f (24.4 mg, 0.10 mmol, 1.0 equiv.) as the starting material and an irradiation time of 16h. Purification by FC using an EtOAc/pentane 1:20 to provide 3a1,10-dimethyl-1,2,4a,5,6,7-hexahydro-3H,3a1H,4H-cyclopenta[1',2']cyclopropa[3,4]pentaleno-[6a,1-b]pyran-3-one 6f as a white solid (16.4 mg, 67%, >20:1 d.r.).

\(^1\)H NMR (400 MHz, CDCl\(_3\), 300 K): \(\delta = 5.69 \) (d, \(J = 1.6 \) Hz, 1H), 3.90-3.85 (m, 1H), 3.72 (td, \(J = 11.9, 3.9 \) Hz, 1H), 2.37-2.00 (m, 6H), 1.84 (d, \(J = 1.6 \) Hz, 3H), 1.70-1.52 (m, 3H), 1.37-1.23 (m, 1H), 1.32 (s, 3H), 0.84-0.77 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\), 300 K): \(\delta = 210.8, 141.1, 119.7, 92.4, 64.2, 59.3, 58.5, 56.2, 53.1, 36.9, 26.3, 24.3, 23.8, 18.9, 14.8, 6.9.

HRMS (ESI): calcd for C\(_{16}\)H\(_{20}\)O\(_2\) [M + H\(^+\)] = 245.1536, found = 245.1536.

Compound 6g was synthesized according to General Procedure 5, using 5g (23.0 mg, 0.10 mmol, 1.0 equiv.) as the starting material and an irradiation time of 16h. Purification by FC using an EtOAc/pentane 1:20 to provide 5-methyl-1,2,4a,5,6,7-hexahydro-3H,3a1H,4H-cyclopenta[1',2']cyclopropa[3,4]pentaleno[6a,1-b]pyran-3-one 6g as a pale yellow oil (14.6 mg, 59%, >20:1 d.r.). The NMR contains <1% of the MeOH-opening adduct as well as <2% of the corresponding acetal adduct these have been subtracted from the yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\), 300 K): \(\delta = 6.02 \) (dd, \(J = 5.9, 1.3 \) Hz, 1H), 5.97, (d, \(J = 5.9 \) Hz, 1H), 3.90 (ddd, \(J = 12.3, 5.6, 1.3 \) Hz, 1H), 3.81 (td, \(J = 12.3, 2.7 \) Hz, 1H), 2.97 (s, 1H), 2.47 (dd, \(J = 13.3, 8.0 \) Hz, 1H), 2.27-2.10 (m, 4H), 1.87 (td, \(J = 11.6, 8.0 \) Hz, 1H), 1.58-1.53 (m, 2H), 1.29-1.18 (m, 1H), 0.90-0.84 (m, 4H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\), 300 K): \(\delta = 209.6, 132.1, 127.3, 93.5, 65.0, 61.5, 54.6, 53.1, 52.5, 34.8, 34.6, 30.8, 23.4, 20.8, 20.0.

HRMS (ESI): calcd for C\(_{15}\)H\(_{18}\)O\(_2\) [M + H\(^+\)] = 231.1380, found = 231.1379.

Compound 6h was synthesized according to General Procedure 5, with the exception that t-BuOH:MeOH 9:1 was used as a solvent. Starting material 5h (24.4 mg, 0.10 mmol, 1.0 equiv.) was used and an irradiation time of 24h was employed. Purification by FC using an EtOAc/pentane 1:20 to provide 4,4-dimethyl-1,2,4a,5,6,7-hexahydro-3H,3a1H,4H-cyclopenta[1',2']cyclopropa[3,4]pentaleno[6a,1-b]pyran-3-one 6h as an off-white solid (13.7 mg, 56%, >20:1 d.r.).

\(^1\)H NMR (400 MHz, CDCl\(_3\), 300 K): \(\delta = 6.17 \) (dd, \(J = 5.8, 1.3 \) Hz, 1H), 6.02, (d, \(J = 5.8 \) Hz, 1H), 3.92-3.87 (m, 1H), 3.86-3.79 (m, 1H), 3.05 (s, 1H), 2.23 (ddd, \(J = 12.4, 10.3, 8.7 \) Hz, 1H), 2.16-2.03 (m, 4H), 1.69-1.63 (m, 2H), 1.58-1.52 (m, 1H), 1.44 (s, 3H), 1.31-1.20 (m, 1H), 0.89 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\), 300 K): \(\delta = 209.1, 134.5, 129.6, 92.4, 64.7, 64.0, 58.9, 55.7, 54.3, 39.5, 35.3, 30.3, 26.6, 23.5, 21.3, 20.7.

HRMS (EI): calcd for C\(_{16}\)H\(_{20}\)O\(_2\) = 244.1458, found = 244.1458.
Compound 7i was synthesized according to General Procedure 5, using 5i (22.9 mg, 0.10 mmol, 1.0 equiv.) as the starting material and an irradiation time of 19 h.

Purification by FC using an EtOAc/pentane 1:10 to provide 8a-methoxy-2-methyl-2,3,4,4a,5,5a,5a1,7,8,8a-decachydro-6H-cyclopenta[7,1]indenol[1,2-b]pyran-6-one 7i as a white solid (9.6 mg, 37%, 15:1 d.r.).

$^1$H NMR (400 MHz, CDCl$_3$, 300 K): $\delta$ = 6.09 (d, $J$ = 5.7 Hz, 1H), 5.81 (d, $J$ = 5.7 Hz, 1H), 4.22-4.14 (m, 1H), 3.28 (s, 3H), 2.93-2.85 (m, 1H), 2.51 (d, $J$ = 10.9 Hz, 1H), 2.43-2.31 (m, 2H), 2.25-2.12 (m, 3H), 2.00-1.90 (m, 2H), 1.83-1.76 (m, 1H), 1.71-1.60 (m, 1H), 1.52 (tdd, $J$ = 12.7, 9.5, 2.8 Hz, 1H), 1.19-1.06 (m, 1H), 1.17 (d, $J$ = 6.1 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$, 300 K): $\delta$ = 212.5, 139.6, 137.6, 96.7, 85.8, 68.4, 54.8, 51.5, 48.9, 40.5, 34.51, 34.45, 33.1, 29.5, 22.9, 21.0.

HRMS (ESI): calcd for C$_{16}$H$_{22}$O$_3$ $^+$ [M-MeO]$^+$ (the fragment fitting this mass is shown to the right) = 231.1380, found = 231.1379.

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![Observed by HRMS](image)

Compound 7j was synthesized according to General Procedure 5, using 5j (23.2 mg, 0.10 mmol, 1.0 equiv.) as the starting material and an irradiation time of 23 h.

Purification by FC using an EtOAc/pentane 1:10 to provide 8a-methoxy-5-methyl-2,3,4,4a,5,5a,5a1,7,8,8a-decachydro-6H-cyclopenta[7,1]indenol[1,2-b]pyran-6-one 7j as a white solid (9.7 mg of the major diastereoisomer and 3.6 mg of the minor diastereoisomer, 51%, 3:1 d.r.). The diastereoisomers could be separated on the column and characterized separately.

$^1$H NMR (400 MHz, CDCl$_3$, 300 K):

Major diastereoisomer: $\delta$ = 6.63 (d, $J$ = 5.8 Hz, 1H), 6.01 (d, $J$ = 5.8 Hz, 1H), 3.90-3.85 (m, 1H), 3.82-3.75 (m, 1H), 3.26 (s, 3H), 2.59 (d, $J$ = 11.1 Hz, 1H), 2.38-2.26 (m, 3H), 2.21-2.08 (m, 2H), 1.90-1.86 (m, 1H), 1.76-1.70 (m, 2H), 1.57-1.47 (m, 2H), 1.37-1.26 (m, 1H), 0.94 (d, $J$ = 6.3 Hz, 3H).

Minor diastereoisomer: $\delta$ = 6.72 (d, $J$ = 5.8 Hz, 1H), 6.93 (d, $J$ = 5.8 Hz, 1H), 3.89-3.83 (m, 1H), 3.81-3.74 (m, 1H), 3.28 (s, 3H), 3.18-3.11 (m, 1H), 2.59 (d, $J$ = 11.1 Hz, 1H), 2.56-2.46 (m, 1H), 2.44-2.38 (m, 1H), 2.19-2.03 (m, 4H), 1.83-1.68 (m, 4H), 0.70 (d, $J$ = 7.7 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$, 300 K):

Major diastereoisomer: $\delta$ = 211.2, 140.4, 135.3, 95.3, 85.9, 64.3, 56.4, 54.3, 53.2, 51.7, 40.2, 35.0, 32.8, 26.5, 23.2, 15.7.

Minor diastereoisomer: $\delta$ = 212.7, 138.3, 137.4, 96.0, 86.2, 64.2, 54.3, 51.64, 51.55, 49.5, 38.9, 38.6, 31.2, 27.0, 22.7, 11.9.

HRMS (ESI): calcd for C$_{16}$H$_{22}$O$_3$ $^+$ [M + H$^+$] = 263.1642, found = 263.1640.
Compound 7k was synthesized according to General Procedure 5, using 5k (22.4 mg, 0.10 mmol, 1.0 equiv.) as the starting material and an irradiation time of 24h. Purification by FC using an EtOAc/pentane 1:10 to provide 8α-methoxy-3-methyl-2,3,4,4a,5,5a,5a1,7,8,8α-decahydro-6H-cyclopenta[7,1]indenol[1,2-b]pyran-6-one 7k as a white solid (16.2 mg, 64%, 19:1 d.r.).

1H NMR (400 MHz, CDCl3, 300 K): δ = 6.57 (d, J = 5.9 Hz, 1H), 6.04 (d, J = 5.9 Hz, 1H), 3.77 (ddd, J = 11.7, 5.0, 1.5 Hz, 1H), 3.38 (t, J = 11.7 Hz, 1H), 3.27 (s, 3H), 2.87 (tdd, J = 11.2, 7.3, 1.5 Hz, 1H), 2.54 (d, J = 11.2 Hz, 1H), 2.40-2.09 (m, 4H), 1.98 (tdd, J = 13.2, 5.2, 2.9 Hz, 1H), 1.92-1.80 (m, 3H), 1.30-1.17 (m, 1H), 1.07 (dt, J = 13.4, 11.7 Hz, 1H), 0.89 (d, J = 6.3 Hz, 3H).

13C NMR (101 MHz, CDCl3, 300 K): δ = 212.2, 141.0, 134.8, 95.8, 85.9, 70.8, 53.5, 51.7, 48.7, 45.9, 34.7, 33.9, 33.2, 32.1, 32.0, 17.2.

HRMS (ESI): calcd for C16H20O3+ [M + H+] = 263.1642, found = 263.1640.

Compound 15 was synthesized according to General Procedure 5, using 5l (24.4 mg, 0.10 mmol, 1.0 equiv.) as the starting material and an irradiation time of 17h. Purification by FC using an EtOAc/pentane 1:10 to provide 7-(hepta-1,6-dien-1-ylxy)-2,3-dihydro-1H-inden-1-ol 15 as a colourless oil (4.1 mg of the E-isomer and 2.8 mg of the Z-isomer, 28%, 1.5:1 E/Z). The isomers could be separated on the column and the major E-isomer has been characterized.

1H NMR (400 MHz, CDCl3, 300 K):

E-isomer: δ = 7.21 (t, J = 7.8 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 6.47 (d, J = 12.1 Hz, 1H), 5.82 (ddt, J = 17.1, 10.1, 6.7 Hz, 1H), 5.51-5.45 (m, 1H), 5.41 (dt, J = 12.1, 7.5 Hz, 1H), 5.03 (dq, J = 17.1, 1.5 Hz, 1H), 4.98 (dt, J = 10.1, 1.5 Hz, 1H), 3.14-3.08 (m, 1H), 2.83 (tdd, J = 15.7, 8.8, 5.7 Hz, 1H), 2.48-2.41 (m, 2H), 2.14-2.02 (m, 5H), 1.53-1.49 (m, 2H).

13C NMR (101 MHz, CDCl3, 300 K): δ = 154.2, 146.2, 141.3, 138.5, 133.1, 129.9, 119.2, 114.8, 114.0, 112.3, 74.2, 34.0, 33.1, 30.4, 29.1, 26.6.

HRMS (ESI): calcd for C16H20O3+ [M + H+] = 245.1536, found = 245.1536.

9. Identification of 13b as an intermediate in the photocascade

Starting material 5b was submitted to irradiation for 2.5h following general procedure 5. Purification by FC using EtOAc/pentane 1:5 as the eluent, afforded 10b-methyl-4,5,6,6a,7,9,10,10b-octahydro-8H-cyclobuta[j]cyclopenta[g]chromen-8-one 13b as a colourless semi-solid in 27% yield, >20:1 d.r. The title compound could be resubmitted to irradiation for 5h under otherwise identical reaction conditions to give the final product 6b (72% yield, >20:1 d.r.). This result indicates that 13b is indeed an intermediate product in the three-photon reaction cascade.

1H NMR (400 MHz, CDCl3, 300 K): δ = 6.68 (d, J = 3.0 Hz, 1H), 6.21 (d, J = 3.0 Hz, 1H), 3.93 (ddt, J = 11.6, 5.0, 1.6 Hz, 1H), 3.62 (ddd, J = 12.6, 11.6, 2.8 Hz, 1H), 2.62-2.56 (m, 1H), 2.51-2.45 (m, 1H), 2.40-2.37 (m, 3H), 1.82-1.78 (m, 1H), 1.75-1.65 (m, 1H), 1.63-1.58 (m, 1H), 1.50-1.38 (m, 3H), 1.33 (s, 3H).

13C NMR (101 MHz, CDCl3, 300 K): δ = 208.0, 175.8, 143.7, 137.9, 134.5, 86.4, 65.2, 53.8, 38.4, 34.9, 27.3, 26.6, 26.5, 24.1, 15.2.
HRMS (ESI): calcd for C_{15}H_{18}O_2^+ [M + H^+] = 231.1380, found = 231.1380.

10. Opening the cyclopropane moiety of the photo-adducts in chemo-selective transformations

Compound 6a (21.8 mg, 0.1 mmol, 1 equiv.) was dissolved in MeOH (0.5 mL) and trimethyl orthoformate (0.83 mL, 0.76 mmol, 7.6 equiv.) whereafter p-TsOH (0.8 mg, 0.004 mmol, 4mol%) was added and the reaction was stirred at rt for 20 h. Upon full conversion the reaction mixture was diluted with CH_{2}Cl_{2} and washed with NaHCO_{3} (aq.). The aqueous phase was extracted with CH_{2}Cl_{2} and the combined organic layers were dried using Na_{2}SO_{4} and the volatiles were removed in vacuo. The crude product was purified by FC to obtain the desired product 6a-1,6,8a-trimethoxy-3,4,4a,5,5a,5a1,6,7,8,8a-decahydro-2H-cyclopenta[7,1]-indeno[1,2-b]pyran 8 as a pale yellow solid (19.6 mg, 66% yield, >20:1 d.r.).

^{1}H NMR (400 MHz, CDCl_{3}, 300 K): δ = 6.48 (d, J = 5.9 Hz, 1H), 5.80, (d, J = 5.9 Hz, 1H), 3.87-3.77 (m, 2H), 3.20 (s, 3H), 3.18 (s, 3H), 3.16 (s, 3H), 2.45 (dddd, J = 12.2, 10.8, 5.9, 2.3 Hz, 1H), 2.30 (d, J = 10.8 Hz, 1H), 1.91-1.64 (m, 7H), 1.58 (dd, J = 12.2, 4.0 Hz, 1H), 1.52-1.47 (m, 1H), 1.25 (dd, J = 14.2, 11.8, 6.4 Hz, 1H), 0.89 (dt, J = 13.2, 12.2 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_{3}, 300 K): δ = 141.9, 133.2, 101.1, 95.8, 86.7, 64.2, 51.2, 50.4, 48.2, 47.6, 45.2, 43.6, 30.8, 30.6, 26.9, 24.6, 24.4.

HRMS (ESI): calcd for C_{16}H_{23}O_3^+ [(M-MeO)] = 263.1642, found = 263.1642. The mass fits the drawn structure shown to the left.

Compound 6a (43.2 mg, 0.2 mmol, 1 equiv.) was dissolved in CH_{2}Cl_{2} (1.0 mL) and cooled to -78°C, whereafter bromine (10.3 µL, 0.2 mmol, 2 equiv.) was added as a solution in CH_{2}Cl_{2} (0.5 mL). The reaction was stirred at -78°C for 4h. At this point, the reaction mixture was moved to -20 and left overnight. To obtain full cyclopropane opening the reaction mixture was allowed to reach 0°C for 2h. Work up using Na_{2}SO_{4} (aq.), evaporation of the volatiles and subsequent purification by GC gave the desired product 5a,9,10,11-tetrabromodecahydro-6H-8a,10a-methanoazuleno[6,5-b]pyran-6-one 10 as a crystalline, white solid (55.8 mg, 46%, >20:1 d.r.).

^{1}H NMR (400 MHz, CDCl_{3}, 300 K): δ = 5.11 (d, J = 5.6 Hz, 1H), 4.89, (d, J = 2.0 Hz, 1H), 4.17 (d, J = 5.6, 2.0 Hz, 1H), 3.96 (ddt, J = 12.6, 3.7, 1.8 Hz, 1H), 3.77 (td, J = 12.4, 2.6 Hz, 1H), 2.81-2.66 (m, 2H), 2.49-2.37 (m, 2H), 2.31 (dd, J = 16.1, 4.5, 1H), 2.01 (ddd, J = 14.0, 9.0, 2.4, 1H), 1.90 (dd, J = 16.1, 12.8 Hz, 1H), 1.81-1.76 (m, 1H), 1.71 (tt, J = 12.8, 4.3 Hz, 1H), 1.65-1.61 (m, 1H), 1.41 (qd, J = 12.8, 3.7 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_{3}, 300 K): δ = 204.1, 81.4, 78.9, 78.9, 65.0, 63.5, 61.2, 59.4, 54.6, 42.3, 35.1, 33.3, 28.7, 25.6, 24.8.

HRMS (EI): calcd for C_{44}H_{36}O_2Br_7, found = 537.7800.

The structure was confirmed by X-ray analysis.
Figure 1. Structure confirmation of 10 by X-ray analysis.

Figure 2. Structure confirmation of 9 by X-ray analysis.

Compound 6a (21.6 mg, 0.1 mmol, 1 equiv.) was dissolved in CH₂Cl₂ (1.0 mL) and cooled to -78°C, where after bromine (10.3 µL, 0.2 mmol, 2 equiv.) was added as a solution in CH₂Cl₂ (0.5 mL). The reaction was stirred at -78°C for 4h. Work up using Na₂S₂O₃ (aq.), evaporation of the volatiles and subsequent purification by FC gave the desired product 9,10-dibromo-octahydro-3H,3a1H,4H-cyclopenta-[1',2':]cyclopropa[3,4]pentaleno[6a,1-b]pyran-3-one 9 as a crystalline, white solid (23.2 mg, 79%, >20:1 d.r.).

¹H NMR (400 MHz, CDCl₃, 300 K): δ = 5.20 (d, J = 2.1 Hz, 1H), 4.43, (d, J = 2.1 Hz, 1H), 3.77-3.74 (m, 2H), 2.73 (s, 1H), 2.47-2.35 (m, 2H), 2.26-2.17 (m, 2H), 2.14-2.04 (m, 2H), 1.82 (tq, J = 13.3, 3.5 Hz, 1H), 1.74 (dd, J = 13.3, 11.6 Hz, 1H), 1.64-1.54 (m, 2H), 1.33 (tdd, J =12.9, 10.9, 4.8 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃, 300 K): δ = 208.9, 88.8, 64.7, 62.7, 61.5, 54.1, 51.3, 50.8, 49.3, 33.7, 25.2, 23.8, 22.6, 21.4.

HRMS (El): calcd for C₁₄H₁₆O₂⁷⁹Br = 295.0324, found = 295.0328.

The structure was confirmed by X-ray analysis (figure 2).
Compound 7k provided structural confirmation for the MeOH-opened adducts as well as the relative configuration.

Figure 3. Structure confirmation of 7k by X-ray analysis.
11. Determination of relative configuration by NOE interactions

In the NOESY-spectrum of compound 7i there are NOE interactions between H and H which supports the relative configuration within the five-membered ring. Additionally, NOE interactions can be found between the methoxy group (H) and the H. Finally, NOE interactions can be observed between the H and H which establishes the relative configuration of the methyl group. The key interactions are marked with a blue circle in the NOESY-spectrum shown below and highlighted with double sided arrows on the depicted compound structure.

Figure 4. NOESY-spectrum of compound 7i.
NOE-interactions between H and H were observed as indicated in the figure. Additionally, NOE-interactions between H and the methyl group were observed leading us to propose the relative configuration drawn below.

Figure 5. NOESY-spectrum of compound 6g.
12. Deuteration experiments

It can be seen from the spectrum below that a 20% deuterium incorporation could be observed in the product 6a when the reaction was performed in MeOD as a solvent under otherwise identical reaction conditions (spectrum A). The $^1$H NMR is shown with a zoom of the relevant area. It is noteworthy that using CD$_3$OH gave no deuterium incorporation indicating that the proton is incorporated via deprotonation as opposed to proton abstraction. Additionally, the isolated product 6a was submitted to the reaction conditions using MeOD as a solvent to verify that deuterium incorporation takes place during the reaction cascade and not after product formation (spectrum B). In addition to these experiments, an experiment was also conducted in MeOD, but stopped after 30 mins reaction time. The goal was to see if the incorporation of deuterium happens prior to the photocascade reaction. Therefore, the remaining starting material was recovered wherein a 20% deuterium incorporation was observed (spectrum C). The integral for the indicated protons shows an integral of 1.59H as opposed to 2H, corresponding to a 20% incorporation.

HRMS (ESI) of 6a formed in MeOD showed a significantly higher peak corresponding to the 6a-D at the expected 218.1287 (calc. 218.1286) as well as the 6a-D$_2$ at 219.1350 (calc. 219.1349).
Spectrum A: $^1$H NMR of compound 6a with deuterium incorporation from MeOD.
Spectrum B: $^1$H NMR of compound 6a with no deuterium incorporation from MeOD.

Spectrum C: $^1$H NMR of compound 5a with 20% deuterium incorporation from MeOD.
13. X-ray Crystallographic Details

Data were collected on a single crystal x-ray diffractometer equipped with a CMOS detector (Bruker APEX III, κ-CMOS), an IMS microsource with MoK̇ radiation (λ = 0.71073 Å) and a Helios optic using the APEX3 software package. Measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT. Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS. Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. The structures were solved using SHELXT with the aid of successive difference Fourier maps, and were refined against all data using SHELXL in conjunction with SHELXLE. Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and Uiso(H) = 1.5·Ueq(C). Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, other C–H distances of 1.00 Å, all with Uiso(H) = 1.2·Ueq(C). Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing Σw(Fo2 - Fc2)2 with the SHELXL weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography. Images of the crystal structures were generated with PLATON. CCDC 1970234-1970236 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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5 APEX suite of crystallographic software, APEX 3, Version 2016-9.0, Bruker AXS Inc., Madison, Wisconsin, USA, 2016.
6 SAINT, Version 8.38A and SADABS, Version 2016/2, Bruker AXS Inc., Madison, Wisconsin, USA, 2016/2017.
7 G. M. Sheldrick, Acta Crystallogr. Sect. A 2015, 71, 3–8.
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10 International Tables for Crystallography, Vol. C (Ed.: A. J. Wilson), Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992, Tables 6.1.1.4 (pp. 500–502), 4.2.6.8 (pp. 219–222), and 4.2.4.2 (pp. 193–199).
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Compound 10 (CCDC 1970234)

Diffractometer operator C. Jandl
scanspeed 1-2 s per frame
dx 37 mm
1804 frames measured in 10 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

\[ \text{C}_{14}\text{H}_{16}\text{Br}_4\text{O}_2 \]

\[ M_r = 535.87 \]

Monoclinic, \( P2_1/c \)

Hall symbol: \( -P 2ybc \)

\[ a = 12.4119 \ (11) \ \text{Å} \]
\[ b = 7.9029 \ (6) \ \text{Å} \]
\[ c = 16.1893 \ (14) \ \text{Å} \]
\[ \beta = 102.172 \ (3) \ ^\circ \]
\[ V = 1552.3 \ (2) \ \text{Å}^3 \]
\[ Z = 4 \]
\[ F(000) = 1024 \]

\[ D_x = 2.293 \ \text{Mg m}^{-3} \]

Melting point: 2 K

Mo K\( \alpha \) radiation, \( \lambda = 0.71073 \ \text{Å} \)

Cell parameters from 9779 reflections

\[ \theta = 2.6-26.7^\circ \]
\[ \mu = 10.37 \ \text{mm}^{-1} \]
\[ T = 100 \ \text{K} \]

Fragment, colourless

\[ 0.45 \times 0.41 \times 0.27 \ \text{mm} \]
Data collection

Bruker Photon CMOS diffractometer
3182 independent reflections

Radiation source: IMS microsource
2977 reflections with I > 2σ(I)

Helios optic monochromator
Rint = 0.162

Detector resolution: 16 pixels mm−1
θmax = 26.4°, θmin = 2.6°

phi– and ω–rotation scans

Absorption correction: multi-scan
SADABS 2016/2, Bruker

k = −9  9
h = −15  15

Tmin = 0.251, Tmax = 0.745
l = −20  20

51641 measured reflections

Refinement

Refinement on F²

Least-squares matrix: full

R(F² > 2σ(F²)) = 0.035

wR(F²) = 0.087

S = 1.06

3182 reflections

181 parameters

0 restraints

0 constraints

Primary atom site location: iterative

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

W = 1/[Σ²(FO²) + (0.0469P)² + 3.2221P]
WHERE P = (FO² + 2FC²)/3

(Δ/σ)max = 0.001

Δρmax = 1.20 e Å⁻³

Δρmin = −1.19 e Å⁻³

Extinction correction: none

Extinction coefficient: −

Compound 9 (CCDC 1970235)

Diffractometer operator C. Jandl
scanspeed 2-10 s per frame
dx 50 mm
2227 frames measured in 8 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

C_{14}H_{16}Br_{2}O_{2}

$M_r = 376.07$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$\alpha = 12.9911$ (10) Å

$\beta = 9.5719$ (9) Å

$\gamma = 21.689$ (2) Å

$\beta = 95.456$ (3)$^\circ$

$V = 2684.8$ (4) Å$^3$

$Z = 8$

$F(000) = 1488$

$\mu = 6.03$ mm$^{-1}$

$\lambda = 0.71073$ Å

Cell parameters from 9953 reflections

$\theta = 2.3$–26.7$^\circ$

$T = 100$ K

Fragment, colourless

Melting point: 2 K

$D_x = 1.861$ Mg m$^{-3}$

$0.31 \times 0.24 \times 0.04$ mm
**Data collection**

Bruker Photon CMOS diffractometer  5476 independent reflections

Radiation source: **IMS microsource**  4823 reflections with $I > 2\sigma(I)$

Helios optic monochromator  $R_{int} = 0.043$

Detector resolution: 16 pixels mm$^{-1}$  $\theta_{\text{max}} = 26.4^\circ$, $\theta_{\text{min}} = 2.3^\circ$

phi– and $\omega$–rotation scans  $h = -15$  $16$

Absorption correction: **multi-scan**  $k = -11$  $11$

$T_{\text{min}} = 0.520$, $T_{\text{max}} = 0.745$  $l = -27$  $27$

75640 measured reflections

**Refinement**

Refinement on $F^2$  Secondary atom site location: **difference** Fourier map

Least-squares matrix: **full**  Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.023$  H-atom parameters constrained

$wR(F^2) = 0.050$  $W = 1/[\Sigma^2(FO^2) + (0.0146P)^2 + 3.7955P]$

WHERE $P = (FO^2 + 2FC^2)/3$

$S = 1.07$  $(\Delta/\sigma)_{\text{max}} = 0.002$

5476 reflections  $\Delta\rho_{\text{max}} = 0.38$ e Å$^{-3}$

325 parameters  $\Delta\rho_{\text{min}} = -0.40$ e Å$^{-3}$

0 restraints  Extinction correction: **none**

0 constraints  Extinction coefficient: -

Primary atom site location: **iterative**
Compound 7k (CCDC 1970236)

Diffractometer operator C. Jandl
scanspeed 1-2 s per frame
dx 37 mm
3405 frames measured in 13 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

\( \text{C}_{16}\text{H}_{22}\text{O}_3 \)

\( M_r = 262.34 \quad D_x = 1.311 \text{ Mg m}^{-3} \)

Monoclinic, \( P2_1/c \)

Hall symbol: -P 2ybc

Melting point: 2 K

Mo K\( \alpha \) radiation, \( \lambda = 0.71073 \) Å

\( a = 11.068 (1) \) Å

Cell parameters from 9605 reflections

\( b = 11.4032 (10) \) Å

\( \theta = 2.6–26.7^\circ \)

\( c = 11.7717 (12) \) Å

\( \mu = 0.09 \) mm\(^{-1} \)

\( \beta = 116.539 (3)^\circ \)

\( T = 100 \) K

\( V = 1329.2 (2) \) Å\(^3\)

Fragment, colourless

\( Z = 4 \)

\( 0.55 \times 0.36 \times 0.29 \) mm

\( F(000) = 568 \)
**Data collection**

Bruker Photon CMOS diffractometer

2817 independent reflections

Radiation source: **IMS microsource**

2592 reflections with \( I > 2\sigma(I) \)

Helios optic monochromator

\( R_{int} = 0.042 \)

Detector resolution: 16 pixels mm\(^{-1}\)

\( \theta_{\text{max}} = 26.8^\circ, \theta_{\text{min}} = 2.6^\circ \)

phi- and \( \omega \)-rotation scans

\( h = -14 \quad 14 \)

Absorption correction: multi-scan

**SADABS 2016/2, Bruker**

\( k = -14 \quad 14 \)

\( T_{\text{min}} = 0.722, \ T_{\text{max}} = 0.745 \)

\( l = -14 \quad 14 \)

80577 measured reflections

**Refinement**

Refinement on \( F^2 \)

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Secondary atom site location: inferred from neighbouring sites

\( R[F^2 > 2\sigma(F^2)] = 0.035 \)

H-atom parameters constrained

\( wR(F^2) = 0.092 \)

\( W = 1/[\Sigma^2(FO^2) + (0.0407P)^2 + 0.6991P] \)

\( \text{WHERE} \ P = (FO^2 + 2FC^2)/3 \)

\( (\Delta/\sigma)_{\text{max}} < 0.001 \)

\( (\Delta/\sigma)_{\text{max}} < 0.001 \)

2817 reflections

\( \Delta\rho_{\text{max}} = 0.39 \text{ e Å}^{-3} \)

174 parameters

\( \Delta\rho_{\text{min}} = -0.20 \text{ e Å}^{-3} \)

0 restraints

Extinction correction: none

0 constraints

Extinction coefficient: -

Primary atom site location: iterative
14. Spectra

\[ ^1\text{H NMR of compound 5a} \]

\[ ^13\text{C NMR of compound 5a} \]
$^1$H NMR of compound 5b

$^{13}$C NMR of compound 5b
$^1$H NMR of compound 5c

$^{13}$C NMR of compound 5c
$^1$H NMR of compound 5d

$^{13}$C NMR of compound 5d
$^1$H NMR of compound ii5e

$^{13}$C NMR of compound ii5e
$^1$H NMR of compound ii5f

$^{13}$C NMR of compound ii5f
$^{1}H$ NMR of compound 5f

$^{13}C$ NMR of compound 5f
$^1$H NMR of compound 5g

$^{13}$C NMR of compound 5g
$^1$H NMR of compound 5j

$^{13}$C NMR of compound 5j
$^1$H NMR of compound 5k

$^{13}$C NMR of compound 5k
$^1$H NMR of compound 6a

$^{13}$C NMR of compound 6a
$^1$H NMR of compound 6b

$^{13}$C NMR of compound 6b
$^1$H NMR of compound 6c

$^{13}$C NMR of compound 6c
$^{1}H$ NMR of compound 6d

$^{13}C$ NMR of compound 6d
$^1$H NMR of compound 6e

$^{13}$C NMR of compound 6e
$^1$H NMR of compound 6f

$^{13}$C NMR of compound 6f
$^1$H NMR of compound 6g (contains 2% acetal opened adduct)

$^{13}$C NMR of compound 6g
$^{1}H$ NMR of compound 7i

$^{13}C$ NMR of compound 7i
$^1$H NMR of compound 7j (major diastereoisomer)

$^{13}$C NMR of compound 7j (major diastereoisomer)
$^1$H NMR of compound 7j (minor diastereoisomer)

$^{13}$C NMR of compound 7i (minor diastereoisomer)
$^1$H NMR of compound 7k

$^{13}$C NMR of compound 7k
$^1$H NMR of compound 15

$^{13}$C NMR of compound 15
$^1$H NMR of compound 13b

$^{13}$C NMR of compound 13b
$^1$H NMR of compound 10

$^{13}$C NMR of compound 10
$^1$H NMR of compound 9

$^{13}$C NMR of compound 9