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EXPERIMENTAL DETAILS



Content:

1.	General1				
2.	Synthesis of starting materials2				
3.	Photo-oxidation reactions in flow and batch13				
4.	Oxidation of phenylcyclohexene in acetonitrile14				
5.	Oxidation of phenylcyclohexene in methanol16				
6.	Oxidation of special compounds17				
7.	Conversion and Product formation kinetics of 4-chloro-1-phenyl-1- cyclohexene				
8.	Microreactor productivity and performance20				
9.	Isolated and clean products20				
10.	Hammett study28				
11.	Relative Rate Comparison: phenylcyclohexene				
12 .	Computational part32				
13.	References				
14.	Selected spectra45				
15.	Page count				

1. General

Commercial chemicals (\geq 98 % purity), especially phenylcyclohexene (95 % purity), were used as obtained without further purification. Oxygen gas (GA 201) was obtained by a 50 L pressure cylinder. Methylene blue hydrate (CAS 122965-43-9) was obtained from Alfa Aesar (high purity biological stain, >98 % purity). TLC was performed using commercial silica gel coated aluminum plates (DC Kieselgel 60 F254, Merck); visualization was done using UV light. Staining was realized with a solution of phosphomolybdic acid in ethanol (7 wt%). Product yields were determined from isolated materials after normal or flash column chromatography on silica gel (mesh 230-400) or for optimization and screening purposes by quantitative GC-FID measurements, with dodecanenitrile as internal standard on an Agilent 7820A GC-System with N_2 as carrier gas. HPLC separation was conducted on a Bischoff HPLC system in combination with the DAD-4L UV-Vis detector. Infrared spectra were recorded on an Agilent Cary 630 FTIR spectrometer equipped with an ATR unit; abbreviations: s - strong, m - medium, w - weak. Purity and structure were confirmed by ¹H-NMR, ¹³C-NMR, and MS. Low-resolution mass spectrometry (LRMS) was carried out on an Agilent 6890N GC-System coupled to a 5975 MSD unit and H₂ as carrier gas. High resolution mass spectrometry (HRMS) was carried out by the Central Analytics at the department of chemistry, University of Regensburg, on various machines. Abbreviations used in MS spectra: M – molar mass of target compound, r.I. - relative intensity, EI - electron impact, ESI - electrospray ionization. NMR spectral data were collected on a Bruker Avance 300 (300 MHz for ¹H; 75 MHz for ¹³C) and a Bruker Avance 400 (400 MHz for ¹H; 100 MHz for ¹³C) spectrometer at 25 °C. Solvent residual peaks or TMS from TMS-containing deuterated solvents were used as internal standard for NMR measurements. The quantification of ¹H cores was obtained by integration of resonance signals. Abbreviations used in ¹³C-NMR spectra: C_p – primary carbon, C_s – secondary carbon, C_t – tertiary carbon, C_q – quaternary carbon, C_{sp2} – sp^2 hybridization at this atom, C_{sp3} – sp^3 hybridization at this atom. Abbreviations used in ¹H-NMR spectra: s - singlet, bs - broad singlet, d - doublet, t - triplet, q - quartet, m - multiplet, R - organic rest, not hydrogen.

In case of literature-known compounds, at least one source of available spectroscopic data is cited. For literature-known syntheses, the source for preparation is cited in conjunction to the compound name.

2. Synthesis of starting materials

1-phenyl-1-cyclohexene

This starting material which was used as obtained and contained about 5 % further oxidized / unsaturated (like biphenyl) compounds which are hard to separate, however they do not interfere in the oxidation process.



4'-chloro-2,3,4,5-tetrahydro-1,1'-biphenyl [S1]



First, the Grignard was synthesized by addition of 1-bromo-4-chlorobenzene (6.1 g, 31.9 mmol, 1.8 equiv.) to a mixture of Mg turnings (0.88 g, 36.2 mmol, 2.1 equiv.) in dry diethylether (20 mL) at room temperature, with slight cooling when boiling. After 12 h of stirring, the Grignard reagent solution was added to a solution of cyclohexanone (1.70 g, 1.79 mL, 17.3 mmol, 1.0 equiv.) in diethylether (40 mL) at 0 °C. After stirring for 20 more hours, the reaction mixture was quenched on ice. Hydrochloric acid (ca. 30 mL) was added until a homogeneous aqueous layer was obtained. The aqueous layer was separated, extracted twice with ether (20 mL each), and washed with sodium bicarbonate (aq. sat., 20 mL) and brine (sat., 20 mL). After removal of solvents in vacuo, an orange oil (4.97 g) was afforded. The resulting oil was dissolved in toluene (60 mL) and heated to reflux under Dean Stark conditions together with p-toluenesulfonic acid (0.1 g) for 3 h. The solvent was removed in vacuo to yield a brown mixture (3.85 g). The crude product was purified by column chromatography with pure PE to give the product (2.33 g, 69.9 %) as white crystals.

 $\begin{array}{l} {\sf R}_{\sf f} \left({\sf PE}\right) = 0.62. \ ^1{\sf H}-{\sf NMR} \ (400 \ {\sf MHz}, {\sf CDCI}_3); \ \delta \left[{\sf ppm}\right] = 7.33 - 7.26 \ ({\sf m}, \ 4{\sf H}), \ 6.13 - 6.07 \ ({\sf m}, \ 1{\sf H}), \ 2.40 - 2.32 \ ({\sf m}, \ 1{\sf H}), \ 2.23 - 2.15 \ ({\sf m}, \ 2{\sf H}), \ 1.82 - 1.73 \ ({\sf m}, \ 2{\sf H}), \ 1.69 - 1.60 \ ({\sf m}, \ 2{\sf H}), \ ^{13}{\sf C}-{\sf NMR} \ (100 \ {\sf MHz}, \ {\sf CDCI}_3); \ \delta \left[{\sf ppm}\right] = 141.1 \ ({\sf C}), \ 135.6 \ ({\sf C}), \ 132.2 \ ({\sf C}), \ 128.3 \ ({\sf CH}), \ 126.2 \ ({\sf CH}), \ 125.4 \ ({\sf CH}), \ 27.3 \ ({\sf CH}_2), \ 25.9 \ ({\sf CH}_2), \ 23.0 \ ({\sf$

4'-bromo-2,3,4,5-tetrahydro-1,1'-biphenyl [52]



1,4-dibromobenzene (7.44 g, 31.5 mmol, 1.0 equiv.) was dissolved in dry diethylether (60 mL) in a dry Schlenk flask. At - 78 °C, n-BuLi (21.7 mL, 34.7 mmol, 1.6 M, 1.1 equiv.) was slowly added while stirring, whereby the inhomogeneous mixture was warmed to about 0 °C after 2 h to get all compounds in solution. Lithiation was monitored via GC-MS. After 3 h, cyclohexanone (4.23 mL, 4.02 g, 41.0 mmol, 1.3 equiv.) was added dropwise to the slurry mixture at - 78 °C. Subsequently, the reaction mixture was stirred overnight at room temperature. After quenching on ice, the aqueous layer was separated and extracted with ethyl acetate twice. The combined organic phases were washed with brine (sat.), dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure to yield a slightly yellow oil (9.223 g). The resulting oil was dissolved in toluene (100 mL) and heated to reflux under Dean Stark conditions together with p-toluenesulfonic acid (0.5 g) for 3 h. The solvent of the mixture was removed in vacuo to yield a yellow solid (9.448 g). The crude product was purified by column chromatography with pure PE to yield the title compound (6.1 g, 81.7 %) as white crystals.

 $\begin{array}{l} \mathsf{R_{f}} \ (\mathsf{PE}) = 0.61. \ ^{1}\mathsf{H}-\mathsf{NMR} \ (300 \ \mathsf{MHz}, \mathsf{CDCl}_3): \ \delta \ [\mathsf{ppm}] = 7.45 - 7.36 \ (\mathsf{m}, \ 2\mathsf{H}), \ 7.25 - 7.21 \ (\mathsf{m}, \ 2\mathsf{H}), \ 6.14 - 6.06 \ (\mathsf{m}, \ 1\mathsf{H}), \ 2.41 - 2.29 \ (\mathsf{m}, \ 2\mathsf{H}), \ 2.24 - 2.13 \ (\mathsf{m}, \ 2\mathsf{H}), \ 1.81 - 1.72 \ (\mathsf{m}, \ 2\mathsf{H}), \ 1.70 - 1.60 \ (\mathsf{m}, \ 2\mathsf{H}). \ ^{13}\mathsf{C}-\mathsf{NMR} \ (100 \ \mathsf{MHz}, \mathsf{CDCl}_3): \ \delta \ [\mathsf{ppm}] = 141.6 \ (\mathsf{C}), \ 135.6 \ (\mathsf{C}), \ 131.2 \ (\mathsf{CH}), \ 126.6 \ (\mathsf{CH}), \ 125.5 \ (\mathsf{CH}), \ 120.3 \ (\mathsf{C}), \ 27.3 \ (\mathsf{CH}_2), \ 25.9 \ (\mathsf{CH}_2), \ 23.0 \ (\mathsf{CH}_2), \ 22.0 \ (\mathsf{CH}_2). \ \mathsf{LRMS} \ (\mathsf{El}): \ \mathsf{m/z} \ (\mathsf{r.l.}) = 236 \ (33) \ [\mathsf{M}]^+, \ 129 \ (100), \ 128 \ (55), \ 115 \ (40). \ \mathsf{Spectral} \ \mathsf{data} \ \mathsf{were} \ \mathsf{consistent} \ \mathsf{with} \ \mathsf{literature}.^{[S2]} \end{array}$

2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile [53]



1-(4-bromophenyl)-1-cyclohexene (1.19 g, 5.0 mmol, 1.0 equiv.) and CuCN (895 mg, 10.0 mmol, 2.0 equiv.) were heated to reflux in degassed DMF (16 mL) for 7 h. CuCN (300 mg, 3.4 mmol, 0.67 equiv.) in 5 mL degassed DMF were added and the reaction was heated to reflux for one more hour. Afterwards, the mixture was cooled to r.t., and a solution of FeCl₃ (4.3 g, 26.5 mmol, 5.3 equiv.) and HCl (2.0 mL, conc. aq.) in water (20 mL) was added. After heating to 70 °C for 30 minutes, the mixture was extracted with toluene and DCM three times, and washed thoroughly with water. The organic phase was washed with brine (sat.) and dried over MgSO₄ to yield a brown liquid (1.19 g) after solvent removal under reduced pressure. The crude product was purified by column chromatography with 5 % EA in PE to give the desired compound (713 mg, 77.9 %) as yellow needles.

 $\begin{array}{l} \mathsf{R_f} \left(\mathsf{PE/EA}\ 15/1\right) = 0.62.\ ^1\mathsf{H}-\mathsf{NMR}\ (300\ \mathsf{MHz}, \mathsf{CDCl}_3): \delta\ [\mathsf{ppm}] = 7.61 - 7.54\ (\mathsf{m},\ 2\mathsf{H}),\ 7.48 - 7.42\ (\mathsf{m},\ 2\mathsf{H}),\ 6.29 \\ - \ 6.23\ (\mathsf{m},\ 1\mathsf{H}),\ 2.43 - 2.33\ (\mathsf{m},\ 2\mathsf{H}),\ 2.29 - 2.18\ (\mathsf{m},\ 2\mathsf{H}),\ 1.85 - 1.73\ (\mathsf{m},\ 2\mathsf{H}),\ 1.72 - 1.61\ (\mathsf{m},\ 2\mathsf{H}).\ ^{13}\mathsf{C}-\mathsf{NMR} \\ (100\ \mathsf{MHz},\ \mathsf{CDCl}_3): \delta\ [\mathsf{ppm}] = 147.0\ (\mathsf{C}),\ 135.4\ (\mathsf{C}),\ 132.1\ (\mathsf{CH}),\ 128.4\ (\mathsf{CH}),\ 125.4\ (\mathsf{CH}),\ 27.0\ (\mathsf{CH}_2),\ 26.0\ (\mathsf{CH}_2),\ 22.8\ (\mathsf{CH}_2),\ 21.9\ (\mathsf{CH}_2).\ \mathsf{LRMS}\ (\mathsf{EI}):\ \mathsf{m/z}\ (\mathsf{r.I.}) = 183\ (100)\ [\mathsf{M}]^+,\ 168\ (81),\ 154\ (73),\ 155\ (61).\ \mathsf{Spectral} \\ \mathsf{data} \ \mathsf{were} \ \mathsf{consistent} \ \mathsf{with} \ \mathsf{literature}.^{[\mathsf{S4}]} \end{array}$

3'-bromo-2,3,4,5-tetrahydro-1,1'-biphenyl [52]



1,3-dibromobenzene (7.44 g, 31.5 mmol, 1.0 equiv.) was dissolved in dry diethylether (60 mL) in a dry Schlenk flask. At - 78 °C, n-BuLi (21.7 mL, 34.7 mmol, 1.6 M, 1.1 equiv.) was slowly added while stirring, whereby the inhomogeneous mixture was warmed to about 0 °C after 2 h to get all compounds in solution. Lithiation was monitored via GC-MS. After 3 h, cyclohexanone (4.23 mL, 4.02 g, 41.0 mmol, 1.3 equiv.) was added dropwise to the slurry mixture at - 78 °C. Subsequently, the reaction mixture was stirred overnight at room temperature. After quenching on ice, the aqueous layer was separated and extracted with ethyl acetate twice. The combined organic phases were washed with brine (sat.), dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure to yield a slightly yellow oil (9.223 g). The resulting oil was dissolved in toluene (100 mL) and heated to reflux under Dean Stark conditions together with p-toluenesulfonic acid (0.5 g) for 3 h. The solvent of the mixture was removed in vacuo. The crude product was purified by column chromatography with pure PE to yield the desired compound (1.76 g, 23.6 %) as colorless liquid.

 R_f (PE) = 0.58. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.54 – 7.48 (m, 1H), 7.35 – 7.27 (m, 2H), 7.19 – 7.12 (m, 1H), 6.17 – 6.08 (m, 1H), 2.42 – 2.32 (m, 2H), 2.27 – 2.14 (m, 2H), 1.83 – 1.73 (m, 2H), 1.70 – 1.61 (m, 2H). LRMS (EI): m/z (r.I.) = 236 (64) [M]⁺, 129 (100), 128 (78), 157 (67). Spectral data were consistent with literature.^[S5]

2',3',4',5'-tetrahydro-[1,1'-biphenyl]-3-carbonitrile [S3]



1-(3-bromophenyl)-1-cyclohexene (0.4 g, 1.7 mmol, 1.0 equiv.) and CuCN (380 mg, 4.3 mmol, 2.5 equiv.) were heated to reflux in dry, degassed DMF for 20 h, whereby the starting materials precipitated first, but were in solution at the end. Afterwards, the mixture was cooled to r.t. under slight precipitation, and a solution of FeCl₃ (1.46 g, 9.0 mmol, 5.3 equiv.) and HCl (0.5 mL, conc. aq.) in water (8 mL) was added. After heating to 70 °C for 30 minutes, the mixture was extracted with DCM three times, washed thoroughly with water and brine (sat.), and dried over MgSO₄ to yield a brown oil (210 mg) after filtration and removal of solvent in vacuo. The crude product was purified by column chromatography with 7 % EA in PE to yield the title compound (205 mg, 66 %) as slightly yellow oil.

 $\begin{array}{l} \mathsf{R_{f}} \left(\mathsf{PE/EA} \ 15/1\right) = 0.38.\,^{1}\mathsf{H}-\mathsf{NMR} \ (300 \ \mathsf{MHz}, \mathsf{CDCI}_{3}) : \ \delta \ [\mathsf{ppm}] = 7.66 - 7.38 \ (\mathsf{m}, 4\mathsf{H}), \ 6.22 - 6.13 \ (\mathsf{m}, 1\mathsf{H}), \ 2.43 - 2.31 \ (\mathsf{m}, 2\mathsf{H}), \ 2.28 - 2.15 \ (\mathsf{m}, 2\mathsf{H}), \ 1.85 - 1.72 \ (\mathsf{m}, 2\mathsf{H}), \ 1.71 - 1.59 \ (\mathsf{m}, 2\mathsf{H}). \ ^{13}\mathsf{C}-\mathsf{NMR} \ (100 \ \mathsf{MHz}, \mathsf{CDCI}_{3}) : \\ \delta \ [\mathsf{ppm}] = 143.8 \ (\mathsf{C}), \ 134.9 \ (\mathsf{C}), \ 129.9 \ (\mathsf{CH}), \ 129.3 \ (\mathsf{CH}), \ 129.0 \ (\mathsf{CH}), \ 128.7 \ (\mathsf{CH}), \ 127.26 \ (\mathsf{CH}), \ 119.2 \ (\mathsf{CN}), \\ 112.3 \ (\mathsf{C}), \ 27.2 \ (\mathsf{CH}_{2}), \ 25.9 \ (\mathsf{CH}_{2}), \ 22.9 \ (\mathsf{CH}_{2}), \ 21.9 \ (\mathsf{CH}_{2}). \ \mathsf{HRMS} \ (\mathsf{EI}) : \ \mathsf{m/z} = 183.1043 \ [\mathsf{M}]^{+}, \ \mathsf{calc.:} \ 183.1043. \end{array}$

2,3,4,5-tetrahydro-1,1':2',1"-terphenyl



The Grignard reagent was synthesized by addition of 2-bromobiphenyl (4.65 g, 3.42 mL, 20.0 mmol, 1.0 equiv.) to a mixture of Mg turnings (0.58 g, 24.4 mmol, 1.2 equiv.) in dry THF (20 mL) at room temperature with slight cooling when necessary / boiling. After 15 h of stirring, a solution of cyclohexanone (1.96 g, 2.07 mL, 20.0 mmol, 1.0 equiv.) in THF (20 mL) was added to the slurry Grignard solution at 0 °C. After stirring for 4 more hours, the reaction mixture was quenched on ice. Hydrochloric acid (conc. aq.) was added until a homogeneous aqueous layer was obtained. The aqueous layer was separated, extracted with ether (2 x 20 mL), and the combined organic phases were washed with sodium bicarbonate (20 mL, sat. aq.) and brine (20 mL, sat.). After removal of solvents in vacuo, a brown oil was obtained.

The resulting oil was dissolved in toluene (80 mL) and heated to reflux under Dean Stark conditions together with p-toluenesulfonic acid (0.15 g) for 24 h. The solvent of the mixture was again removed in vacuo, ethyl acetate was added, and the organic phase was washed with water, the aqueous phase was separated and extracted with EtOAc two times, the organic layers were combined and dried with brine (sat.) and over MgSO₄ to yield a brown mixture. After distillation under reduced pressure (12 mbar), the low-boiling side products like biphenyl were separated and distilled off at a boiling point of up to 170 °C. The residual crude product was purified via column chromatography with pure pentane to yield the desired compound (1.02 g, 22 %) as colorless oil.

 $\begin{array}{l} \mathsf{R_f} \ (\text{pentane}) = 0.60. \ 1\text{H-NMR} \ (400 \ \text{MHz}, \ \text{CDCl}_3): \ \delta \ [\text{ppm}] = 7.47 - 7.22 \ (\text{m}, 9\text{H}), \ 5.71 - 5.65 \ (\text{m}, 1\text{H}), \ 2.14 \\ - 2.04 \ (\text{m}, 2\text{H}), \ 1.87 - 1.78 \ (\text{m}, 2\text{H}), \ 1.58 - 1.42 \ (\text{m}, 4\text{H}). \ ^{13}\text{C-NMR} \ (100 \ \text{MHz}, \ \text{CDCl}_3): \ \delta \ [\text{ppm}] = 143.7 \ (\text{C}), \\ 142.3 \ (\text{C}), \ 139.7 \ (\text{C}), \ 139.4 \ (\text{C}), \ 130.0 \ (\text{CH}), \ 129.3 \ (\text{CH}), \ 127.9 \ (\text{CH}), \ 127.6 \ (\text{CH}), \ 127.2 \ (\text{CH}), \\ 126.8 \ (\text{CH}), \ 126.7 \ (\text{CH}), \ 29.5 \ (\text{CH}_2), \ 23.0 \ (\text{CH}_2), \ 22.0 \ (\text{CH}_2). \ \text{HRMS} \ (\text{El}): \ \text{m/z} = 234.1409 \ [\text{M}]^+, \\ \text{calc.:} \ 234.1403. \end{array}$

2',3',4',5',6'-pentamethyl-2,3,4,5-tetrahydro-1,1'-biphenyl



The Grignard reagent was synthesized by addition of pentamethylphenylbromide (10 g, 44 mmol, 1.0 equiv.) to a mixture of Mg (chips; 1.28 g, 53 mmol, 1.2 equiv.) in dry THF (80 mL) in a dry 100 mL Schlenk flask under nitrogen and cooling if necessary. The synthesis of the Grignard started after addition of ca. 500 mg iodine, followed by stirring for 24 h. Cyclohexanone (4.1 mL, 3.88 g, 39.6 mmol, 0.9 equiv.) was added. After 48 h of stirring at room temperature, the mixture was quenched on ice, EtOAc and 12M HCl were added until two distinct phases were visible, the organic phase was separated, and the aqueous phase was extracted twice with EtOAc. The combined organic phases were washed with NaHCO₃ (aq. sat.) & brine (sat.) to yield the crude alcohol after solvent removal *in vacuo* and column chromatography of the crude mixture with EA/pentane as eluent (5 to 15 % EA).

The resulting oil was dissolved in toluene (150 mL) and refluxed under Dean Stark conditions together with *p*-toluenesulfonic acid (0.3 g) for 48 h. The solvent of the mixture was removed *in vacuo*. The crude product was purified *via* column chromatography with pentane and recrystallization from ethanol to yield colorless plates (470 mg, 2.06 mmol, 5 %).

1H-NMR (300 MHz, CDCl₃): δ [ppm] = 5.46-5.38 (m, 1H), 2.25-2.22 (s, 6H), 2.22-2.15 (s, 6H), 2.08-1.99 (m, 2H), 1.81-1.65 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 141.6, 139.2, 133.1, 132.3, 130.1, 125.3, 30.4, 25.5, 23.2, 22.3, 17.4, 16.7, 16.6. HRMS (EI): m/z = 228.1873 [M]⁺, calc.: 228.1873.

General procedure GP-1:

Mg (607 mg, 25 mmol, 1.25 equiv.) was suspended in dry THF (20 mL) under inert conditions. The bromoarene (22 mmol, 1.1 equiv.) was added at room temperature. After boiling subsided, the reaction mixture was stirred for an additional hour at room temperature. The reaction mixture was cooled to 0 °C, the cyclic ketone (20 mmol, 1.0 equiv.), dissolved in dry THF (15 mL), was added at 0 °C and the reaction mixture was stirred at 95 °C for 1 h. The reaction mixture was cooled to 0 °C, and 1 M aqueous HCl (10 mL) was added dropwise. The mixture was stirred for 30 min at room temperature and extracted with EA (50 mL). The phases were separated and the organic phase was washed with brine (50 mL). The organic phase was dried over Na₂SO₄, the drying agent was filtered off, the solvent was removed under reduced pressure. The reaction mixture was stirred over night at 140 °C using a *Dean-Stark* apparatus. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using mixtures of petroleum ether and ethyl acetate.

4'-Methyl-2,3,4,5-tetrahydro-1,1'-biphenyl



The product was synthesized according to GP-1 (94 %, colourless liquid). Pure PE was used as an eluent for column chromatography.

R_f (PE) = 0.57. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.38 – 7.19 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.11 (tt, *J* = 3.9, 1.7 Hz, 1H), 2.48 – 2.38 (m, 2H), 2.36 (s, 3H), 2.29 – 2.15 (m, 2H), 1.88 – 1.73 (m, 2H), 1.73 – 1.59 (m, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ [ppm] = 140.0, 136.5, 136.2, 129.0, 124.9, 124.0, 27.5, 26.0, 23.2, 22.3, 21.2. LR-MS (EI, 70 eV): m/z (r.I.) = 172 [M]⁺, 158, 142, 127, 105, 79, 51. Spectral data were consistent with literature.^[S6]

4'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl



The product was synthesized according to GP-1 (53 %, colourless liquid). Reaction was performed using 30 mmol of starting material. A mixture of PE and EA (0 --> 2 % EA) was used as an eluent for column chromatography.

 R_{f} (PE) = 0.72. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.37 – 7.30 (m, 2H), 7.05 – 6.92 (m, 2H), 6.06 (tt, *J* = 3.9, 1.7 Hz, 1H), 2.43 – 2.26 (m, 2H), 2.27 – 2.13 (m, 2H), 1.85 – 1.71 (m, 2H), 1.72 – 1.59 (m, 2H). LR-MS (EI, 70 eV): m/z (r.l.) = 176 [M]⁺, 55, 133, 109, 101, 75, 51. Spectral data were consistent with literature.^[S6]

N,N-Dimethyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-amine



The product was synthesized according to GP-1 (82 %, colourless liquid). Reaction was performed using 10 mmol of starting material. A mixture of PE and EA (0 --> 2 % EA) was used as an eluent for column chromatography.

R_f (PE) = 0.82. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.41 – 7.19 (m, 2H), 6.76 (ddd, *J* = 13.1, 6.8, 2.8 Hz, 2H), 6.06 – 6.00 (m, 1H), 2.96 (d, *J* = 2.8 Hz, 6H), 2.35 – 2.49 (m, 2H), 2.27 – 2.14 (m, 2H), 1.87 – 1.73 (m, 2H), 1.61 – 1.72 (m, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ [ppm] = 149.4, 136.0, 129.1, 125.6, 121.7, 116.7, 112.7, 112.6, 40.8, 40.7, 27.4, 25.9, 23.2, 22.4. LR-MS (EI, 70 eV): m/z (r.l.) = 202 [M]⁺, 180, 157, 129, 101, 77, 51. Spectral data were consistent with literature.^[S6]

3'-Methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl



Product was synthesized according to GP-1 (91 %, colourless liquid). Reaction was performed using 10 mmol of starting material. A mixture of PE and EA (0 --> 5 % EA) was used as an eluent for column chromatography.

 R_f (PE/EA = 15/1) = 0.26. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.23 (pt, *J* = 7.9 Hz, 1H), 6.99 (ddd, *J* = 7.8, 1.7, 1.0 Hz, 1H), 6.96 – 6.86 (m, *J* = 2.5, 1.7 Hz, 1H), 6.78 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 6.14 (tt, *J* = 3.9, 1.7 Hz, 1H), 3.84 – 3.80 (s, 3H), 2.45 – 2.36 (m, *J* = 6.3, 2.5, 2.1 Hz, 2H), 2.26 – 2.16 (m, 2H), 1.84 – 1.72 (m, *J* = 6.9, 4.8, 2.5 Hz, 2H), 1.72 – 1.60 (m, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ [ppm] = 159.6, 144.3, 136.5, 129.1, 125.1, 117.6, 111.8, 110.9, 55.2, 27.5, 25.9, 23.1, 22.2. LR-MS (EI, 70 eV): m/z (r.I.) = 188 [M]⁺, 160, 128, 91, 65. Spectral data were consistent with literature.^[57]

4'-Methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl



Product was synthesized according to GP-1 (81 %, colourless liquid). Reaction was performed using 10 mmol of starting material. A mixture of PE and EA (0 --> 20 % EA) was used as an eluent for column chromatography.

 R_f (PE/EA = 15/1) = 0.98. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.35 – 7.25 (m, 2H), 6.88 – 6.82 (m, 2H), 6.08 – 5.96 (m, 1H), 3.81 (d, J = 3.8 Hz, 3H), 2.38 (m, 1H), 2.25 – 2.14 (m, 1H), 1.85 – 1.73 (m, 1H), 1.71 – 1.58 (m, 1H). LR-MS (EI, 70 eV): m/z (r.I.) = 188 [M]⁺, 160, 129, 103, 80, 51. Spectral data were consistent with literature.^[S6]

4'-(Trifluoromethoxy)-2,3,4,5-tetrahydro-1,1'-biphenyl



Product was synthesized according to GP-1 (70 %, colourless liquid). Reaction was performed using 10 mmol of starting material. A mixture of PE and EA (0 --> 20 % EA) was used as an eluent for column chromatography.

 $\begin{array}{l} \mathsf{R_f} \left(\mathsf{PE/EA}=15/1\right)=0.80.\ ^1\mathsf{H}-\mathsf{NMR} \left(300\ \mathsf{MHz}, \mathsf{CDCI}_3\right): \delta \left[\mathsf{ppm}\right]=7.43-7.33 \ (\mathsf{m}, 2\mathsf{H}), 7.14 \ (\mathsf{ddt}, \textit{J}=7.7, 2.1, 1.0\ \mathsf{Hz}, 2\mathsf{H}), 6.11 \ (\mathsf{td}, \textit{J}=4.0, 1.9\ \mathsf{Hz}, 1\mathsf{H}), 2.43-2.33 \ (\mathsf{m}, 2\mathsf{H}), 2.27-2.15 \ (\mathsf{m}, 2\mathsf{H}), 1.84-1.73 \ (\mathsf{m}, 2\mathsf{H}), 1.73-1.61 \ (\mathsf{m}, 2\mathsf{H}).\ ^{13}\mathsf{C}-\mathsf{NMR} \ (75\ \mathsf{MHz}, \mathsf{CDCI}_3): \delta \left[\mathsf{ppm}\right]=141.4, 135.5, 126.2, 125.7, 120.7, 27.4, 25.9, 23.0, 22.0.\ \mathsf{FT-IR} \ (\mathsf{ATR}): \tilde{\nu} \ [\mathsf{cm}^{-1}]=2930 \ (\mathsf{w}), 2863 \ (\mathsf{w}), 2840 \ (\mathsf{w}), 1510 \ (\mathsf{m}), 1439 \ (\mathsf{w}), 1256 \ (\mathsf{s}), 1208 \ (\mathsf{s}), 1156 \ (\mathsf{s}), 1003 \ (\mathsf{m}), 921 \ (\mathsf{m}), 861 \ (\mathsf{m}), 831 \ (\mathsf{m}), 798 \ (\mathsf{s}), 746 \ (\mathsf{w}), 678 \ (\mathsf{w}).\ \mathsf{HR-MS} \ (\mathsf{EI}, 70\ \mathsf{eV}): \mathsf{m/z} = 242.0908 \ [\mathsf{M}^+]; \mathsf{calc}. 242.0913.\ \mathsf{LR-MS} \ (\mathsf{EI}, 70\ \mathsf{eV}): \mathsf{m/z} \ (\mathsf{r.l.}) = 243 \ [\mathsf{M}]^+, 214, 175, 141, 117, 80, 51. \end{array}$

2'-Methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl



Product was synthesized according to GP-1 (83 %, colourless liquid). Reaction was performed using 10 mmol of starting material. A mixture of PE and EA (0 --> 5 % EA) was used as an eluent for column chromatography.

 R_f (PE/EA = 15/1) = 0.90. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.33 - 7.14 (m, 2H), 7.03 - 6.88 (m, 2H), 5.85 (tt, *J* = 3.8, 1.7 Hz, 1H), 3.87 (s, 3H), 2.46 (tt, *J* = 6.2, 2.2 Hz, 2H), 2.34 - 2.21 (m, 2H), 1.90 - 1.66 (m, 4H). LR-MS (EI, 70 eV): m/z (r.l.) = 188 [M]⁺, 160, 129, 103, 80, 51. Spectral data were consistent with literature.^[S7]

4'-(Trifluoromethyl)-2,3,4,5-tetrahydro-1,1'-biphenyl



Product was synthesized according to GP-1 (78 %, colourless liquid). Reaction was performed using 10 mmol of starting material. A mixture of PE and EA (0 --> 20 % EA) was used as an eluent for column chromatography.

 $\begin{array}{l} \mathsf{R_f} \ (\mathsf{PE/EA} = 15/1) = 0.94. \ 1\mathsf{H}-\mathsf{NMR} \ (300 \ \mathsf{MHz}, \ \mathsf{CDCI3}): \ \delta \ [\mathsf{ppm}] = 7.58 \ (\mathsf{d}, \ \mathsf{J} = 8.3 \ \mathsf{Hz}, \ 2\mathsf{H}), \ 7.53 - 7.43 \ (\mathsf{m}, \ 2\mathsf{H}), \ 6.24 \ (\mathsf{tt}, \ \mathsf{J} = 4.0, \ 1.7 \ \mathsf{Hz}, \ 1\mathsf{H}), \ 2.50 - 2.37 \ (\mathsf{m}, \ 2\mathsf{H}), \ 2.31 - 2.19 \ (\mathsf{m}, \ 2\mathsf{H}), \ 1.90 - 1.76 \ (\mathsf{m}, \ 2\mathsf{H}), \ 1.76 - 1.64 \ (\mathsf{m}, \ 2\mathsf{H}). \ \mathsf{LR-MS} \ (\mathsf{EI}, \ 70 \ \mathsf{eV}): \ \mathsf{m/z} \ (\mathsf{r.I.}) = 227 \ [\mathsf{M}] +, \ 211, \ 185, \ 159, \ 130, \ 109, \ 80, \ 51. \ \mathsf{Spectral} \ \mathsf{data} \ \mathsf{were} \ \mathsf{consistent} \ \mathsf{with} \ \mathsf{literature.}^{[\mathsf{S8}]} \end{array}$

2,3,4,5-Tetrahydro-1,1':4',1"-terphenyl



Product was synthesized according to GP-1 (41 %, colourless liquid). Reaction was performed using 10 mmol of starting material. A mixture of PE and EA (0 --> 15 % EA) was used as an eluent for column chromatography.

 $\begin{array}{l} {\sf R_f} \left({\sf PE} \right) = 0.51. \ ^1 {\sf H} \cdot {\sf NMR} \left({\rm 300 \ MHz}, {\sf CDCl_3} \right) \delta \left[{\sf ppm} \right] = 7.65 - 7.48 \ ({\sf m}, \ 5{\sf H}), \ 7.48 - 7.39 \ ({\sf m}, \ 4{\sf H}), \ 6.22 - 6.16 \ ({\sf m}, \ 1{\sf H}), \ 2.51 - 2.40 \ ({\sf m}, \ 2{\sf H}), \ 2.30 - 2.16 \ ({\sf m}, \ 1{\sf H}), \ 1.88 - 1.74 \ ({\sf m}, \ 2{\sf H}), \ 1.74 - 1.62 \ ({\sf m}, \ 2{\sf H}). \ {\sf LR} \cdot {\sf MS} \ ({\sf EI}, \ 70 \ {\sf eV}): \ {\sf m/z} \ ({\sf r.l.}) = 234 \ [{\sf M}]^+, \ 205, \ 178. \end{array}$

4'-(*tert*-Butyl)-2,3,4,5-tetrahydro-1,1'-biphenyl



Product was synthesized according to GP-1 (82 %, colourless liquid). Reaction was performed using 10 mmol of starting material. A mixture of PE and EA (0 --> 2 % EA) was used as an eluent for column chromatography.

 $\begin{array}{l} \mathsf{R_{f}} \ (\mathsf{PE}) = 0.95. \ ^{1}\mathsf{H}-\mathsf{NMR} \ (300 \ \mathsf{MHz}, \mathsf{CDCl}_{3}): \ \delta \ [\mathsf{ppm}] = 7.37 - 7.29 \ (\mathsf{m}, \ 4\mathsf{H}), \ 6.16 - 6.04 \ (\mathsf{m}, \ 1\mathsf{H}), \ 2.51 - 2.32 \ (\mathsf{m}, \ 2\mathsf{H}), \ 2.27 - 2.11 \ (\mathsf{m}, \ 2\mathsf{H}), \ 1.81 - 1.71 \ (\mathsf{m}, \ 2\mathsf{H}), \ 1.71 - 1.59 \ (\mathsf{m}, \ 2\mathsf{H}), \ 1.32 \ (\mathsf{s}, \ 9\mathsf{H}). \ ^{13}\mathsf{C}-\mathsf{NMR} \ (75 \ \mathsf{MHz}, \ \mathsf{CDCl}_{3}): \ \delta \ [\mathsf{ppm}] = 149.4, \ 139.8, \ 136.2, \ 128.1, \ 125.4, \ 125.3, \ 125.1, \ 124.6, \ 124.1, \ 34.4, \ 31.4, \ 27.4, \ 25.9, \ 23.1, \ 22.3. \ \mathsf{LR}-\mathsf{MS} \ (\mathsf{EI}, \ 70 \ \mathsf{eV}): \ \mathsf{m/z} \ (\mathsf{r.l.}) = 215 \ [\mathsf{M}]^+, \ 198, \ 176, \ 141, \ 115, \ 91, \ 56. \ \mathsf{Spectral} \ \mathsf{data} \ \mathsf{were} \ \mathsf{consistent} \ \mathsf{with} \ \mathsf{literature.}^{[\mathsf{S8}]} \end{array}$

2',6'-Dimethyl-2,3,4,5-tetrahydro-1,1'-biphenyl



Product was synthesized according to GP-1 (14 %, colourless liquid). Reaction was performed using 10 mmol of starting material. A mixture of PE and EA (0 --> 2 % EA) was used as an eluent for column chromatography.

 $\begin{array}{l} {\sf R}_{\sf f} \,({\sf PE}) = 0.65.\,\,^1\text{H-NMR} \,(300 \;\text{MHz}, {\sf CDCl}_3) \colon \delta \,\,[{\sf ppm}] = 7.11 - 6.97 \,\,({\sf m}, \, 3\text{H}), \, 5.48 \,\,({\sf tt}, {\it J} = 3.7, \, 1.8 \; {\sf Hz}, \, 1\text{H}), \, 2.29 \\ - \, 2.23 \,\,({\sf m}, \, 6\text{H}), \, 2.23 - 2.13 \,\,({\sf m}, \, 2\text{H}), \, 2.13 - 2.02 \,\,({\sf m}, \, 2\text{H}), \, 1.86 - 1.66 \,\,({\sf m}, \, 4\text{H}).\,\,^{13}\text{C-NMR} \,\,(75 \;\,\text{MHz}, \, \text{CDCl}_3) \colon \delta \,\,\\ [{\sf ppm}] = 143.9, \,\, 137.5, \,\, 135.5, \,\, 127.1, \,\, 126.2, \,\, 126.1, \,\, 125.3, \,\, 29.2, \,\, 25.4, \,\, 23.1, \,\, 22.3, \,\, 21.4, \,\, 19.7. \,\, \text{LR-MS} \,\,(\text{EI}, \,\, 70 \; \text{eV}) \colon {\sf m/z} \,\,({\sf r.l.}) = 187 \,\,[\text{M}]^+, \,\, 158, \,\, 129, \,\, 105, \,\, 77, \,\, 51. \end{array}$

Cyclopent-1-en-1-ylbenzene



Product was synthesized according to a modified GP-1 (69 %, colourless liquid).

The reaction was performed using 20 mmol of starting material. Grignard reaction was executed as usual. For the elimination, the crude product was dissolved in acetic acid (80 mL). The reaction mixture was stirred for 3 h at 118 °C. After cooling down to room temperature 1 M aqueous NaOH (100 mL) was added and the aqueous phase was extracted with EA ($3 \cdot 100$ mL). The combined organic phases were washed with brine (75 mL). The organic phase was dried over Na₂SO₄, the drying agent was filtered off, the solvent was removed under reduced pressure. The crude product was purified by column chromatography using PE as an eluent.

 R_{f} (PE) = 0.66. ¹H-NMR (300 MHz, CDCl₃) δ = 7.48 – 7.42 (m, 2H), 7.36 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 6.19 (h, *J* = 2.1 Hz, 1H), 2.82 – 2.61 (m, 2H), 2.54 (tq, *J* = 7.6, 2.5 Hz, 2H), 2.15 – 1.93 (m, 2H). LR-MS (EI, 70 eV): m/z (r.I.) = 144 [M]⁺, 129, 115, 103, 91, 77, 63, 51. Spectral data were consistent with literature.^[S9]

1-Phenylcyclohept-1-ene



Product was synthesized according to GP-1 (84 %, colourless liquid). Reaction was performed using 20 mmol of starting material. PE was used as an eluent for column chromatography.

 R_f (PE) = 0.69. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.42 – 7.16 (m, 5H), 6.13 (td, *J* = 6.8, 1.3 Hz, 1H), 2.75 – 2.52 (m, 2H), 2.43 – 2.25 (m, 2H), 1.94 – 1.80 (m, 2H), 1.74 – 1.50 (m, 4H). HR-MS (EI, 70 eV): m/z (r.I.) = 172.1249 [M⁺], calc: 72.1247. Spectral data were consistent with literature.^[S9]

2-methoxy-2-phenylcyclohexan-1-ol^[S10,S11]



Phenylcyclohexene (1.0 mL, 6.28 mmol, 1.0 equiv.) was dissolved in CHCl₃ (40 mL). *m*-CPBA (2.17 g, 8.79 mmol, 1.4 equiv.) was added over 15 min. After 2 h, the reaction was finished (GC-MS). Excess perbenzoic acid was reduced with Na₂S₂O₃ (100 g/L). The aqueous layer was extracted three times with DCM. The combined organic layers were washed with NaHCO₃ and brine, dried over Na₂SO₄, and concentrated in vacuo. The crude epoxide product (ca 1 g) was dissolved in DCM together with *p*-TsOH (110 mg) and MeOH (1.53 mL) (molar ratio epoxide/acid/methanol 1:0.1:6). The resulting mixture was stirred for 2 h at r.t. and washed with saturated NaHCO₃. Column chromatography (PE/EA 8/1 to 5/1) yielded the *syn* (white solid) and *anti* (slightly yellow oil) configured product. Product yields or purity were neither determined nor very important as the material was synthesized for characterization (GC-MS, NMR) only.

Trans-Isomer (with impurities): R_f (PE/EA 5/1) = 0.62. ¹H-NMR (300 MHz, CDCl₃, only characteristic peaks): δ [ppm] = 3.61 (dd, *J* = 12.1, 5.2 Hz, 1H), 2.97 (s, 3H, OCH₃). LR-MS (EI, 70 eV): m/z (r.I.) = 206 [M⁺], 191, 174, 147

Cis-Isomer: R_f (PE/EA 5/1) = 0.45. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.47-7.35 (m, 4H), 7.31-7.26 (m, 1H), 3.62-3.53 (m, 1H), 3.13 (s, 3H, OCH₃), 2.12-1.56 (m, 4H). LR-MS (EI, 70 eV): m/z (r.I.) = 206 [M⁺], 191, 174, 147

6-oxo-6-phenylhexanal^[S12]



To a suspension of LiAlH₄ (680 mg, 3.7 equiv.) in anhydrous THF (25 mL) was added dropwise a solution of the oxocarboxylic acid (1.00 g, 1.0 equiv.) in dry THF. The reaction was stirred for 1h at ambient temperature. The excess hydride was cautiously quenched by the sequential addition of water and NaOH (30 % aq.) at 0 °C. The resulting white suspension was stirred for 30 min at r.t, filtered, extracted with ethyl acetate and the organic phases were dried with brine and over magnesium sulfate. Concentration *in vacuo* provided the crude diol. To a solution of the crude alcohol in anhydrous DCM was added PCC (3.0 equiv.) at room temperature. The mixture was stirred for 20 h, concentrated under reduced pressure and the crude oil was directly purified by flash silica gel chromatography (EA/Pe 5/1) to give the ketoaldehyde after removal of solvents. Yields were not determined as the compound was only used as authentic sample.

 R_f (EA/Pe 5/1) = 0.43. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 9.79 (s, 1H), 8.01-7.88 (m, 2H), 7.62-5.51 (m, 1H), 7.51-7.40 (m, 2H), 3.01-2.95 (m, 2H), 2.56-2.45 (m, 2H), 1.85-1.65 (m, 4H). LR-MS (EI, 70 eV): m/z (r.l.) = 172 [M⁺-H₂O] (2), 162 (2), 146, 120, 105 (100). Spectral data were consistent with literature.^[S12]

3. Photo-oxidation reactions in flow and batch

Typically, reactions were conducted in our home-built photo-flow microreactor setup which is explained in detail in a preceding publication.^[S13] Usual reactions feature acetonitrile as solvent, irradiation with 24 water-cooled red high-power LEDs (Cree XP-E2 red, I = 700 mA, U = 2.43 V, P = 1.7 W; per lamp), a temperature of 0 °C, a reaction time of approximately 7 minutes, a 12 bar backpressure regulator, and oxygen gas at an inlet pressure of 30 bar (435 psi).



Batch reactions were conducted in u-tubes made from glass with a built-in frit, irradiated by six watercooled white high-power LEDs (Cree MK-R warm white; I = 700 mA, U = 11.6 V, P = 8.1 W; per lamp) at room temperature. Pure oxygen was bubbled through the solution during the irradiation, with near to atmospheric pressure.



Because of a maximum efficiency of the power adapters of 95 %, a minimum of 106 % of the given power (wattage) is consumed.

4. Oxidation of phenylcyclohexene in acetonitrile

When oxidizing phenylcyclohexene in the flow reactor^[513] (8 min, 0 °C, MeCN, 0.1 M substrate, 1mM MB), a variety of products was obtained and detected *via* ¹H-NMR spectroscopy. In the following, the crude spectrum after solvent removal *in vacuo* is shown:



The spectroscopic data on first stage products after oxidation of 1-phenyl-1-cyclohexene in the flow reactor is not obtained by pure and isolated compounds, but by mixtures of isomers with other / degradation products; the signals were decisively assignable to the respective compound after one or two silica-based column chromatography separation attempts.



6-hydroperoxy-1-phenyl-1-cyclohexene



R_f (pentane/EA 4/1) = 0.70. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.82-7.71 (m, 1H, OOH), 7.48-7.43 (m, 2H), 7.37-7.27 (m, 3H), 6.39-6.31 (m, 1H, C), 5.01-4.95 (m, 1H), 2.48-2.40 (m, 1H), 2.35-2.10 (m, 2H), 1.88-1.76 (m, 1H), 1.72-1.62 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 140.5, 133.9, 133.2 (CH), 128.4 (CH), 127.1 (CH), 125.8 (CH), 79.3 (COOH), 26.4 (CH₂), 26.2 (CH₂), 16.8 (CH₂). HRMS (ESI): m/z = 191.1067 [M+H]⁺, calc.: 191.1067.

3-hydroperoxy-3-phenyl-1-cyclohexene

 R_f (pentane/EA 4/1) = 0.70. ¹H-NMR (400 MHz, CDCl₃, only clearly identifiable signals are denoted): δ [ppm] = 6.23-6.15 (m, 1H), 6.09-6.04 (m, 1H).

After reduction with PPh_3 , the corresponding alcohol is formed which is also characterized in a different section.

1,4,4a,6a,7,8,9,10-octahydro-1,4-epidioxydibenzo[c,e][1,2]dioxine



R_f (PE/EA 4/1) = 0.32. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 6.80-6.70 (m, 1H), 6.69-6.60 (m, 1H), 5.29 (d, J = 5.7 Hz, 1H), 4.86 (dd, J = 6.3, 1.0 Hz, 1H), 4.61-4.54 (m, 1H), 4.29 (dd, J = 11.2, 5.3 Hz, 1H), 2.84-2.74 (m, 1H), 2.18-2.09 (m, 1H), 2.03-1.78 (m, 4H), 1.53-1.42 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 137.8, 132.2, 129.8, 118.5, 81.1 (CO), 78.0 (CO), 74.7 (CO), 68.9 (CO), 34.1 (CH₂), 28.9 (CH₂), 27.1 (CH₂), 24.7 (CH₂). HRMS (ESI): m/z = 223.0960 [M+H]⁺, calc.: 223.0965.

5. Oxidation of phenylcyclohexene in methanol

In methanol, the substrate is not completely converted under identical conditions as seen in chapter 4. However, a nucleophilic attack of MeOH is observed as an additional reaction pathway, see the following ¹H-NMR:



6. Oxidation of special compounds





7. Conversion and Product formation kinetics of 4-chloro-1-phenyl-1-cyclohexene

Standard added: dimethylsulfone, ca. 1 equiv. with respect to substrate, before reaction.

Kinetic experiment in microreactor: the reactor tubing was filled with reaction mixture (0.1 M substrate in MeCN together w/ 0.1 M dimethylsulfone and 0.001 M methylene blue) and oxygen, just as in a usual run. When the reactor was continuously running with this mixture, the red light-source (which was switched on already before the reaction but outside the vessel for reproducible LED irradiation) was added to the reactor setup for irradiation, and samples were taken at the outlet of the reactor after certain times (see timescale) which directly correspond to irradiation and reaction time.

8. Microreactor productivity and performance

We could determine the ideal conditions for the photooxygenation of the model substrate phenylcyclohexene in the photo-flow reactor varying a broad palette of reaction parameters. Applying an oxygen inlet pressure of 30 bar, a back-pressure regulator of 7 bar, red LEDs (24 × Cree XP-E 2), and acetonitrile at 0 °C, very good results regarding productivity and energy efficiency were achieved without exhausting the upper pressure limits of the reactor tubing. The sensitizer loading could be reduced to a minimum of 0.05 mol%. The production capacity of the flow system clearly stands out comparing batch and flow reaction, and especially the energy saving potential of up to more than 99.8 % with respect to the according batch reaction is a huge advantage comparing the best results of both systems:

Table. Productivity and power consumption of the model photo-oxygenation of 1-phenyl-1-cyclohexene.

Reactor	Ca	LEDs	Time ^b	Power ^c	Productivity ^d
batch	0.1	white	8 h	819	0.25
batch	1	white	> 48 h	491	< 0.42
flow	0.1	white	1.0 min	22.7	9
flow	0.1	red	4.3 min	9.6	4.5
flow	1	red	8.5 min	1.43	30

^aConcentration in mmol/L. ^bTime required for complete conversion of phenylcyclohexene. ^cConsumed power in Wh mmol⁻¹. ^dProductivity in mmol h⁻¹.

9. Isolated and clean products

The clean products were obtained by oxidation in the micro flow reactor and, in some cases, addition of an additive with a possible intermediate isolation of the hydroperoxide.

General procedure GP-2:



The starting material was dissolved in a solution of methylene blue (1 mM, in MeCN) in acetonitrile to give a 0.1 molar solution of the substrate (1 mol% of MB sensitizer with respect to the substrate), whereby ultrasonication was used to assure a homogeneous and particle-free solution. The solution was then injected to our micro flow reactor at 0 °C, and irradiated for 8 min with 24 red LEDs in an approximately 13 m long 1/16 inch (0.79 mm) inner diameter FEP^[S14] tubing, together with oxygen at a pressure of roughly 30 bar. The crude mixture was further treated as explained in the respective experimental details.

2-hydroperoxy-2'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl



The compound was synthesized according to GP-2 with 1-(*o*-methoxyphenyl)-1-cyclohexene (94.1 mg, 0.5 mmol) in 5 mL sensitizer solution. After oxidation, the solvent of the crude mixture was removed *in vacuo* and the crude product was purified via column chromatography with EA in pentane (15 to 30 % EA) as eluent to give the title compound (34.0 mg, 31 %) as white solid.

R_f (pentane/EA 4/1) = 0.61. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 8.00 (s, 1H), 7.28-7.23 (m, 1H), 7.14 (dd, J = 7.4 Hz, J = 1.7 Hz, 1H), 6.94 (td, J = 7.4 Hz, J = 0.9 Hz, 1H), 6.89 (d, J = 8.1 Hz, 1H), 6.0 (t, J = 3.8 Hz, 1H), 4.94 (t, J = 3.7 Hz, 1H), 3.83 (s, 3H), 2.35-2.15 (m, 3H), 1.94-1.80 (m, 2H), 1.75-1.64 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 156.8 (COMe), 134.7 (C), 134.2 (CH), 130.9 (C), 130.6 (CH), 128.5 (CH), 120.9 (CH), 110.8 (H), 80.4 (COOH), 55.6 (CH₃), 26.8 (CH₂), 25.8 (CH₂), 18.2 (CH₂). IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3381 (m), 2934 (m), 2837 (w), 1598 (w), 1489 (m), 1240 (s). HRMS (EI): m/z = 221.1172 [M+H]⁺, calc.: 221.1172.

2-hydroperoxy-2,3,4,5-tetrahydro-1,1':2',1"-terphenyl

The compound was synthesized according to GP-2 with 1-(*o*-biphenyl)-1-cyclohexene (93.7 mg, 0.4 mmol) in 4 mL sensitizer solution. After oxidation, the solvent of the crude mixture was removed *in vacuo* and the crude product was purified via column chromatography with EA in pentane (10 to 20 % EA) as eluent to give the title compound (51 mg, 48 %) as colorless oil.

R_f (pentane/EA 7/1) = 0.46. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.53 (s, 1H), 7.44-7.27 (9H), 5.99 (t, *J* = 3.7 Hz, 1H), 4.1 (t, *J* = 3.4 Hz, 1H), 2.17-1.99 (m, 3H), 1.81-1.64 (m, 1H), 1.61-1.47 (m, 1H), 1.43-1.25 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 141.9 (C), 140.5 (C), 140.0 (C), 136.1 (C), 135.9 (CH), 130.1 (CH), 130.0 (CH), 129.3 (CH), 128.0 (CH), 127.5 (CH), 127.4 (CH), 126.8 (CH), 80.3 (CO), 26.1 (CH₂), 26.0 (CH₂), 17.0(CH₂). IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3400 (broad, m), 2934 (m), 1478 (m), 1437 (m), 909 (s). HRMS (EI): *m/z* = 267.1365 [M+H]⁺, calc.: 267.1380.

2'-hydroxy-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile



The compound was synthesized according to GP-2 with 1-(*p*-cyanophenyl)-1-cyclohexene (73.3 mg, 0.4 mmol, 1.0 equiv.) in 4 mL sensitizer solution. When leaving the microreactor, the crude mixture was directly dropping into a solution of PPh₃ (105 mg, 0.4 mmol, 1.0 equiv.) in MeCN (5.0 mL). Ten minutes after the irradiation, the solvent was removed under reduced pressure, and the crude product was purified via column chromatography with EA in pentane (18 to 25 % EA) as eluent to yield the desired compound (34.7 mg, 44 %) as slightly green oil.

R_f (pentane/EA 4/1) = 0.25. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.64-7.54 (m, 4H), 6.32 (dd, J = 4.6 Hz, J = 3.4 Hz, 1H), 4.67 (t, J = 3.8 Hz, 1H), 2.38-2.27 (m, 1H), 2.26-2.15 (m, 1H), 2.01-1.93 (m, 1H), 1.91-1.67 (m, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 145.1 (C), 137.7 (C), 132.2 (CH), 132.0 (CH), 126.5 (CH), 119.1 (C), 110.2 (C), 65.2 (CO), 31.8 (CH₂), 26.1 (CH₂), 17.0 (CH₂). HRMS (EI): m/z = 199.0996 [M]⁺, calc.: 199.0992.

4'-(trifluoromethyl)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-ol



The compound was synthesized according to GP-2 with 1-(*p*-(trifluoromethyl)phenyl)-1-cyclohexene (90.4 mg, 0.4 mmol, 1.0 equiv.) in 4 mL sensitizer solution. When leaving the microreactor, the crude mixture was directly dropping into a solution of PPh₃ (105 mg, 0.4 mmol, 1.0 equiv.) in MeCN (5.0 mL). Ten minutes after the irradiation, the solvent was removed under reduced pressure, and the crude product was purified via column chromatography with EA in pentane (18 to 25 % EA) as eluent to yield the desired compound (10 mg, 10 %) as slightly green oil.

R_f (pentane/EA 7/1) = 0.42. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.61-7.55 (m, 4H), 6.30-6.23 (m, 1H), 4.70 (s, 1H), 2.37-2.17 (m, 2H), 2.01-1.70 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 143.9, 138.2, 130.8, 126.2, 125.4, 125.4, 65.4 (CO), 31.8 (CH₂), 26.0 (CH₂), 17.1 (CH₂). HRMS (EI): m/z = 242.0913 [M]⁺, calc.: 242.0913.

4'-chloro-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-ol



The compound was synthesized according to GP-2 with 1-(*p*-chlorophenyl)-1-cyclohexene (96.4 mg, 0.5 mmol, 1.0 equiv.) in 5 mL sensitizer solution. When leaving the microreactor, the crude mixture was directly dropping into a solution of PPh₃ (105 mg, 0.4 mmol, 0.8 equiv.) in MeCN (5.0 mL). Ten minutes after the irradiation, the solvent was removed under reduced pressure, and the crude product was purified via column chromatography with EA in pentane (12 to 40 % EA) as eluent to yield the title compound (32 mg, 31 %) as yellow crystals.

R_f (PE/EA 4/1) = 0.63. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.43-7.38 (m, 2H), 7.32-7.27 (m, 2H), 6.17 (dd, J = 4.5 Hz, J = 3.3 Hz, 1H), 4.65 (t, J = 3.9 Hz, 1H), 2.33-2.10 (m, 2H), 2.00-1.64 (m, 4H). ¹³C-NMR (75 MHz, CDCl₃): δ [ppm] = 138.7 (C), 138.0 (C), 132.8 (C), 129.3 (CH), 128.6 (CH), 127.3 (CH), 65.5 (CO), 31.7 (CH₂), 26.0 (CH₂), 17.2 (CH₂). HRMS (EI): m/z = 208.0647 [M]⁺, calc.: 208.0649.

The byproduct 4'-chloro-3,4-dihydro-[1,1'-biphenyl]-1(2H)-ol (5 mg, 5 %) was isolated as slightly orange oil; it could not be perfectly separated from the main title compound.



R_f (PE/EA 4/1) = 0.74. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.45-7.38 (m, 2H), 7.33-7.27 (m, 2H), 6.05 (dt, J = 9.9 Hz, J = 3.8 Hz, 1H), 5.74 (d, J = 9.9 Hz, 1H), 2.30-1.60 (m, 4H).

2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-ol



The compound was synthesized according to GP-2 with phenylcyclohexene (31.3 mg, 0.2 mmol, 1.0 equiv.) in 2 mL sensitizer solution. When leaving the microreactor, the crude mixture was directly dropping into a solution of PPh₃ (58 mg, 0.2 mmol, 1.0 equiv.) in MeCN (5.0 mL). Ten minutes after the irradiation, the solvent was removed under reduced pressure, and the crude product was purified via column chromatography with 15 % EA in pentane as eluent to yield the title compound (11 mg, 33 %) as colorless oil.

R_f (PE/EA 4/1) = 0.71. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.50-7.43 (m, 2H), 7.39-7.30 (m, 2H), 7.29-7.24 (m, 1H), 6.17 (dd, *J* = 4.4 Hz, *J* = 3.6 Hz, 1H), 4.74-4.68 (m, 1H), 2.34-2.13 (m, 2H), 1.99-1.73 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 140.2 (C), 139.1 (C), 128.7 (CH), 128.6 (CH), 127.1 (CH), 126.0 (CH), 65.5 (CO), 31.6 (CH₂), 26.1 (CH₂), 17.4 (CH₂). HRMS (EI): m/z = 174.1041 [M]⁺, calc.: 174.1039. Spectral data were consistent with literature.^[S15]

The byproduct 3,4-dihydro-[1,1'-biphenyl]-1(2H)-ol (2 mg, 5 %) was isolated as colorless oil.



R_f (PE/EA 4/1) = 0.74. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.51-7.46 (m, 2H), 7.38-7.29 (m, 3H), 7.28-7.24 (m, 1H), 6.04 (dt, J = 10.0 Hz, J = 3.8 Hz, 1H), 5.79 (d, J = 10.0 Hz, 1H), 2.13-1.79 (m, 6H). ¹³C-NMR (75 MHz, CDCl₃): δ [ppm] = 132.2, 130.8, 128.1 (CH), 126.9, 125.5 (CH), 77.23 (CO), 39.6 (CH₂), 25.0 (CH₂), 19.2 (CH₂). LRMS (EI): m/z = 174 (80) [M]⁺, 145 (100), 146 (90), 77 (78). Spectral data were consistent with literature.^[S16]

Cis 1-([1,1'-biphenyl]-2-yl)-7-oxabicyclo[4.1.0]heptan-2-ol + determination of diastereomeric ratio



The compound was synthesized according to GP-2 with phenylcyclohexene (79.1 mg, 0.5 mmol) in 5 mL sensitizer solution. After oxidation, the solvent was removed under reduced pressure, and the crude product was purified via column chromatography with 15 % EA in pentane as eluent to yield the hydroperoxide (35 mg, 37 %) (together with approximately 13 % regioisomer featuring the hydroperoxyl group at the tertiary carbon) as slightly yellow oil. 110 mg of hydroperoxide synthesized this way (0.58 mmol, 1 equiv.) was added to a solution of $Ti(O'Pr)_4$ (30 µL, 28 mg, 0.1 mmol, 20 mol%) in DCM (5 mL) at 0 °C, and stirred for 1 h. The reaction was quenched with water (0.5 mL). The organic phase was extracted with DCM twice. The organic phases were dried over sodium sulfate. The solvent was removed under reduced pressure, and the crude product (containing amongst other substances 0.3 % of the trans diastereomer) was purified via column chromatography with 20 % EA in PE to yield the title compound (95 mg, 32 % overall yield) as white solid. For the detection of *d.r.*, the same reaction was conducted, while dibromomethane (DBM; 111.4 mg) was added before addition of the crude product mixture (without applying the final column chromatography) to the NMR tube.

R_f (PE/EA 4/1) = 0.26. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.45-7.40 (m, 2H), 7.39-7.33 (m, 2H), 7.32-7.27 (m, 1H), 4.53-4.44 (m, 1H), 3.25 (d, *J* = 3.1 Hz, 1H), 2.03-1.86 (m, 3H), 1.81-1.60 (m, 3H). ¹³C-NMR

(100 MHz, CDCl₃): δ [ppm] = 139.3 (C), 128.5 (CH), 127.7 (CH), 125.8 (CH), 69.0 (CO), 65.2 (CO), 63.3 (CO), 29.6 (CH₂), 24.0 (CH₂), 17.8 (CH₂). LRMS (EI): m/z = 190 (6) [M]⁺, 105 (100), 77 (100), 133 (77), 91 (64). Spectral data were consistent with literature.^[S17]

The byproduct 2-phenyl-7-oxabicyclo[4.1.0]heptan-2-ol (6 mg, 2 % overall yield) was isolated as white solid.



R_f (PE/EA 4/1) = 0.30. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.53-7.47 (m, 2H), 7.42-7.35 (m, 2H), 7.33-7.26 (m, 1H), 3.60-2.55 (m, 1H), 3.34 (d, J = 3.9 Hz, 1H), 2.96-2.53 (bs, 1H), 2.20-2.01 (m, 1H), 1.97-1.71 (m, 2H), 1.63-1.56 (m, 1H), 1.43-1.18 (m, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ [ppm] = 145.3 (C), 128.3 (CH), 127.2 (CH), 125.1 (CH), 71.6 (CO), 59.0 (CO), 56.2 (CO), 37.8 (CH₂), 23.5 (CH₂), 15.8 (CH₂). LRMS (EI): m/z = 190 (6) [M]⁺, 105 (100), 77 (72), 121 (32). Spectral data were consistent with literature.^[518]

Cis and trans stereoisomers of 1-([1,1'-biphenyl]-2-yl)-7-oxabicyclo[4.1.0]heptan-2-ol



The alcohol (obtained by PCH oxidation and subsequent reduction with triphenylphosphine) (26 mg, 0.15 mmol, 1.0 equiv) and *m*-CPBA (48.8 mg, containing 75 % active *meta*-chloroperbenzoic acid, 1.4 equiv) were stirred in DCM (3 mL) for 18 h at r.t. The mixture was quenched with Na_2SO_3 , washed with $NaHCO_3$ and brine, and separated by column chromatography (20 % EA in Pe). The *cis*-diastereomer was isolated as a white solid (10 mg, 0.053 mmol, 35 %) while the trans-configured stereoisomer was isolated as brown oil with small impurities of the *cis* configured isomer (3 mg, 0.0158 mmol, 11 %).

Cis-isomer: R_f (PE/EA 4/1) = 0.26. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.45-7.40 (m, 2H), 7.39-7.33 (m, 2H), 7.32-7.27 (m, 1H), 4.53-4.44 (m, 1H), 3.25 (d, *J* = 3.1 Hz, 1H), 2.03-1.86 (m, 3H), 1.81-1.60 (m, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 139.3 (C), 128.5 (CH), 127.7 (CH), 125.8 (CH), 69.0 (CO), 65.2 (CO), 63.3 (CO), 29.6 (CH₂), 24.0 (CH₂), 17.8 (CH₂). LRMS (EI): *m/z* = 190 (6) [M]⁺, 105 (100), 77 (100), 133 (77), 91 (64). HRMS (EI): *m/z* = 190.0985 [M]⁺, calc.: 190.0988. Spectral data were consistent with literature.^[S17]

Trans-isomer: R_f (Pe/EA 4/1) = 0.44. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.50-7.48 (m, 2H), 7.40-7.32 (m, 3H), 4.31-4.26 (m, 1H), 3.39 (pst, *J* = 2.9 Hz, 1H), 2.07-2.02 (m, 2H), 2.01-1.81 (m, 2H), 1.75-1.61 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 138.6 (C), 128.4 (CH), 128.3 (CH), 127.9 (CH), 68.4 (CO), 63.3 (CO), 59.9 (CO), 28.3 (CH₂), 23.8 (CH₂), 14.4(CH₂). HRMS (EI): m/z = 190.0984 [M]⁺, calc.: 190.0988

1-([1,1'-biphenyl]-2-yl)-7-oxabicyclo[4.1.0]heptan-2-ol



The compound was synthesized according to GP-2 with 1-(*o*-biphenyl)-1-cyclohexene (585 mg, 2.5 mmol) in 25 mL sensitizer solution, irradiating for 11 min instead of 8 min. After oxidation, the solvent

was removed under reduced pressure, and the crude product was purified via column chromatography with EA in pentane (10 to 20 % EA) as eluent to yield the hydroperoxide (421 mg, 1.58 mmol, 63 %) as colorless oil which was added to a solution of $Ti(O'Pr)_4$ (90 µL, 86 mg, 0.3 mmol, 20 mol%) in DCM (5 mL) at 0 °C, and stirred for 1 h. The reaction was quenched with water (2 mL), the organic phase was extracted with DCM twice and dried with brine (sat.). The solvent was removed under reduced pressure, and the crude product was purified via column chromatography with EA in PE (5 to 18 % EA) to yield the title compound (267 mg, 40 % overall yield) as white crystals.

R_f (pentane/EA 4/1) = 0.46. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.60-7.57 (m, 1H), 7.46-7.26 (m, 8H), 3.73 (t, J = 4.8 Hz, 1H), 3.33 (m, 1H), 1.98-1.89 (m, 1H), 1.61-1.51 (m, 1H), 1.42-1.27 (m, 2H), 1.03-0.78 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 141.3 (C), 140.1 (C), 138.3 (C), 129.7 (CH), 129.3 (CH), 128.4 (CH), 127.8 (CH), 127.5 (CH), 127.4 (CH), 127.0 (CH), 68.8 (CO), 65.1 (CO), 63.1 (CO), 29.4 (CH₂), 23.7 (CH₂), 14.8 (CH₂). HRMS (EI): m/z = 266.1300 [M]⁺, calc.: 266.1301.

7-Hydroperoxy-1-phenylcyclohept-1-ene



The compound was synthesized according to GP-2 with 1-phenyl-1-cycloheptene (430 mg, 2.5 mmol) in 10 mL sensitizer solution, irradiated for 7 min instead of 8 min. After oxidation, the solvent was removed under reduced pressure, and the crude product was purified via column chromatography with EA in PE (0 to 10 % EA) as eluent to yield the hydroperoxide (330 mg, 1.6 mmol, 65 %) as colorless oil.

 $\begin{array}{l} \mathsf{R}_{\mathsf{f}} \left(\mathsf{PE/EA}=9/1\right)=0.40.\ ^{1}\mathsf{H}-\mathsf{NMR} \left(300\ \mathsf{MHz},\mathsf{CDCl}_{3}\right): \delta \left[\mathsf{ppm}\right]=7.99-7.81 \left(\mathsf{s},\mathsf{1H}\right), 7.47-7.17 \left(\mathsf{m},\mathsf{5H}\right), 6.19 \\ \left(\mathsf{dd},\mathit{J}=7.8,\ 5.7\ \mathsf{Hz},\ \mathsf{1H}\right), 5.06 \left(\mathsf{dd},\mathit{J}=7.0,\ 1.4\ \mathsf{Hz},\ \mathsf{1H}\right), 2.49 \left(\mathsf{dddd},\mathit{J}=\mathsf{16.0},\ 10.4,\ 5.7,\ 2.3\ \mathsf{Hz},\ \mathsf{1H}\right), 2.33-2.16 \left(\mathsf{m},\ 2\mathsf{H}\right), 2.10-1.94 \left(\mathsf{m},\ \mathsf{1H}\right),\ 1.89-1.67 \left(\mathsf{m},\ 3\mathsf{H}\right),\ 1.64-1.44 \left(\mathsf{m},\ \mathsf{1H}\right).\ ^{13}\mathsf{C}-\mathsf{NMR} \left(75\ \mathsf{MHz},\ \mathsf{CDCl}_{3}\right): \delta \\ \left[\mathsf{ppm}\right]=143.0,\ 142.2,\ 135.3,\ 128.3,\ 126.9,\ 126.6,\ 86.2,\ 29.6,\ 27.9,\ 26.9,\ 25.4,\ 23.9.\ \mathsf{FT-IR} \left(\mathsf{ATR}\right): \widetilde{\nu} \left[\mathsf{cm}^{-1}\right]=3384 \left(\mathsf{b}\right),\ 2930 \left(\mathsf{m}\right),\ 2855 \left(\mathsf{w}\right),\ 2599 \left(\mathsf{w}\right),\ 1491 \left(\mathsf{w}\right),\ 1364 \left(\mathsf{w}\right),\ 1264 \left(\mathsf{w}\right),\ 1174 \left(\mathsf{w}\right),\ 1118 \left(\mathsf{w}\right),\ 1074 \\ \left(\mathsf{m}\right),\ 1033 \left(\mathsf{w}\right),\ 988 \left(\mathsf{m}\right),\ 932 \left(\mathsf{w}\right),\ 891 \left(\mathsf{m}\right),\ 842 \left(\mathsf{m}\right),\ 757 \left(\mathsf{s}\right),\ 697 \left(\mathsf{s}\right).\ \mathsf{HR-MS} \left(\mathsf{ESI}\right):\ m/z=205.1223 \left[\mathsf{M+H}]^{+}; \\ \mathsf{calc:}\ 205.1223. \end{array}$

(5-Hydroperoxycyclopent-1-en-1-yl)benzene



The compound was synthesized according to GP-2 with 1-phenyl-1-cyclopentene (360 mg, 2.5 mmol) in 10 mL sensitizer solution, irradiated for 7 min instead of 8 min. After oxidation, the solvent was removed under reduced pressure, and the crude product was purified via column chromatography with EA in PE (0 to 15 % EA) as eluent to yield the hydroperoxide (189 mg, 1.07 mmol, 43 %) as colorless oil.

R_f (PE/EA = 6.5/1) = 0.40. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.71 − 7.59 (m, 1H), 7.59 − 7.48 (m, 2H), 7.40 − 7.19 (m, 3H), 6.59 − 6.47 (m, 1H), 5.53 (dt, *J* = 7.0, 2.4 Hz, 1H), 2.79 − 2.59 (m, 1H), 2.56 − 2.24 (m, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ [ppm] = 139.3, 134.8, 134.6, 128.7, 127.6, 126.1, 90.8, 31.3, 29.2. FT-IR (ATR): \tilde{v} [cm⁻¹] = 3366 (b), 3056 (w), 2930 (w), 2848 (w), 1722 (w), 1625 (w), 1599 (w), 1495 (m), 1446 (m), 1379 (w), 1327 (m), 1249 (w), 1185 (w), 1156 (w), 1036 (m), 980 (m), 939 (m), 828 (m), 753 (s), 693 (s). HR-MS (ESI): *m/z* = 177.0910 [M+H]⁺; calc: 177.0910. Spectral data were consistent with literature.^[S19]

3-bromo-1,4,4a,6a,7,8,9,10-octahydro-1,4-epidioxydibenzo[c,e][1,2]dioxine



The compound was synthesized according to GP-2 with 1-(*p*-bromophenyl)-1-cyclohexene (500 mg, 2.1 mmol) in 21 mL sensitizer solution. After oxidation, the solvent of the crude mixture was removed *in vacuo* and the crude product was purified *via* column chromatography with EA in pentane (12 % EA) as eluent to yield the title compound as yellow solid.

A yield was not determined, as only small fractions after column chromatography were used to obtain semi-pure material suitable for analysis.



 R_f (Pe/EA 10/1) = 0.38. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 6.89 (dd, J = 6.4, 2.1 Hz, 1H), 5.37 (d, J = 6.4 Hz, 1H), 4.93-4.88 (m, 1H), 4.77-4.73 (m, 1H), 4.34-

4.26 (m, 1H), 2.80-2.71 (m, 1H), 2.20-1.40 (m, 7H). 13 C-NMR (150 MHz, CDCl₃): δ [ppm] = 138.4, 133.7, 132.1, 118.6, 117.8, 81.8, 81.0, 77.6, 71.0, 34.0, 28.9, 27.0, 24.6.

The nearly co-eluting 4'-bromo-2-hydroperoxy-2,3,4,5-tetrahydro-1,1'-biphenyl was isolated as yellow oil.



 $\begin{array}{l} \mathsf{R_f} \ (\mathsf{Pe/EA} \ 10/1) = 0.32. \ ^1 \mathsf{H}-\mathsf{NMR} \ (300 \ \mathsf{MHz}, \mathsf{CDCl}_3): \ \delta \ [\mathsf{ppm}] = 7.89 \ (\mathsf{s}, \ 1\mathsf{H}, \ \mathsf{OOH}), \ 7.46-7.41 \ (\mathsf{m}, \ 2\mathsf{H}), \ 7.35-7.28 \ (2\mathsf{H}), \ 6.37-6.32 \ (\mathsf{m}, \ 1\mathsf{H}), \ 4.92-4.85 \ (\mathsf{m}, \ 1\mathsf{H}), \ 2.47-1.56 \ (\mathsf{m}, \ 6\mathsf{H}). \ ^{13}\mathsf{C}-\mathsf{NMR} \ (150 \ \mathsf{MHz}, \ \mathsf{CDCl}_3): \ \delta \ [\mathsf{ppm}] = 139.3, \ 133.6, \ 132.8, \ 131.4, \ 127.4, \ 120.9, \ 97.0, \ 26.2, \ 26.1, \ 16.5. \end{array}$

1,4,4a,6a,7,8,9,10-octahydro-1,4-epidioxydibenzo[c,e][1,2]dioxine-3-carbonitrile



The compound was synthesized according to GP-2 with 1-(*p*-cyanophenyl)-1-cyclohexene (500 mg, 2.7 mmol) in 27 mL sensitizer solution. After oxidation, the solvent of the crude mixture was removed *in vacuo* and the crude product was purified *via* column chromatography with EA in pentane (20 % EA) as eluent to yield the title compound as colorless solid.

A yield was not determined, as only small fractions after column chromatography were used to obtain semi-pure material suitable for analysis.



 R_{f} (Pe/EA 4/1) = 0.31. ¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.47 (dd, J = 6.0, 1.8

Hz, 1H), 6.52-6.48 (m, 1H), 5.44 (dd, J = 6.0, 1.1 Hz, 1H), 5.04-5.00 (m, 1H), 4.67-5.63 (m, 1H), 4.37-4.29 (m, 1H), 2.81-2.71 (m, 1H), 2.20-1.48 (m, 7H). ¹³C-NMR (75 MHz, CDCl₃): δ [ppm] = 145.6, 141.3, 115.4, 115.1, 113.7, 81.2, 76.9, 75.4, 68.4, 34.0, 29.0, 27.1, 24.4.

The nearly co-eluting 2'-hydroperoxy-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile was isolated as yellow crystals.

C₁₃H₁₃NO₂ 215.25 он NC

 $\begin{array}{l} \mathsf{R_f} \ (\mathsf{Pe/EA} \ 4/1) = 0.43. \ ^1\mathrm{H}\text{-}\mathsf{NMR} \ (300 \ \mathsf{MHz}, \mathsf{CDCl}_3) \text{: } \delta \ [\mathsf{ppm}] = 8.64 \ (\mathsf{s}, \ 1\mathrm{H}, \ \mathsf{OOH}), \ 7.61\text{-}7.55 \ (\mathsf{m}, \ 4\mathrm{H}), \ 6.53\text{-} 6.48 \ (\mathsf{m}, \ 1\mathrm{H}), \ 4.93\text{-}4.89 \ (\mathsf{m}, \ 1\mathrm{H}), \ 2.53\text{-}2.12 \ (\mathsf{m}, \ 3\mathrm{H}), \ 1.91\text{-}1.58 \ (\mathsf{m}, \ 3\mathrm{H}). \ ^{13}\text{C}\text{-}\mathsf{NMR} \ (100 \ \mathsf{MHz}, \ \mathsf{CDCl}_3) \text{: } \delta \ [\mathsf{ppm}] = 145.0, \ 136.2, \ 132.5, \ 132.2, \ 126.3, \ 119.1, \ 110.1, \ 78.5, \ 26.3, \ 26.0, \ 16.4. \end{array}$

10. Hammett study

For the product ratios regarding the Hammett study, signals of clearly assignable protons of the two products in ¹H-NMR of the crude mixture after solvent removal were integrated. The crude NMR after the oxidation of phenylcyclohexenes shows a clear pattern of signals which makes an assignment possible without the necessity of isolating all products: the signals of the starting materials are known because of their synthesis, the hydroperoxide features a non-aromatic sp²-proton slightly low-field shifted with respect to the starting material and one allylic proton in the middle of the signals of the endoperoxide. The shifts of the protons of the endoperoxide at carbon atoms attached to oxygen can be clearly assigned by four signals with equal integrals being high-field shifted with respect to the starting material; one more proton signal is a low-field shifted multiplet with integral 2, or 1 in the case of substitution in *para* position, which again arises because of one or two non-aromatic sp²-proton(s).

In many cases, endoperoxide and hydroperoxide product could be identified via ¹H-NMR in a precedent oxidation of the starting material and subsequent column chromatography (whereby they are not isolable in most cases).

The following two spectra show how integration was performed. The typical, empirically determined error is in the region of approximately 8 % or an uncertainty of about \pm 0.3 regarding the ratio. As relaxation times at the used NMR machines were set to 2 min in all experiments, the signal of the hydrogen atom attached to the carbon featuring the hydroperoxy group has the tendency to show an integral being too low.^[S20]





11. Relative Rate Comparison: phenylcyclohexene



Reaction in microreactor environment, determination of relative reaction rate by one-pot oxidation of two substrates where one is literature-known.^[S21–S23] Relative amounts were measured via GC-FID against the internal standard dodecanenitrile.



Conditions:



 k_A/k_B (MeCN) = 0.5476



Conditions analogue to the reaction conducted in MeCN. Reactivity of the substrates is much lower in methanol, likely due to singlet oxygen quenching by MeOH. The curve fitting for relative rate determination is very good:



k_A/k_B (MeOH) = 0.4936

12. Computational part

DFT and MP2 calculations were performed with the Gaussian G09 software package.^[S24] Vibrational analyses were performed on all optimized geometries to ascertain the types of minima obtained. Energies E are total electronic energies and usually given in Hartree, zero-point energy calculations are included. Three-dimensional molecular graphics were obtained using the Avogadro molecular visualization software, v 1.1.1.^[S25]

Calculations were usually performed on the Athene HPC-Cluster at the University of Regensburg.

Stabilization / destabilization of zwitterionic intermediates

Optimization of geometries and single point calculations were performed using the PCM solvation model (in acetonitrile) using the DFT method with B3LYP functional and 6-311++G(2d,p) basis set.



The relative stabilization energy was calculated by comparison of difference of substrate energy vs reaction intermediate energy.

Structure	E	ZPE	E+ZPE	ΔΕ	ΔΔΕ	ΔΔΕ / kcal mol ⁻¹
A1	-465.8400	0.2264	-465.6136	150 2210	0	0
B1	-616.1790	0.2336	-615.9454	-130.3318	0	0
A2	-580.4010	0.2585	-580.1425	150 2271		-3.33
B2	-730.7455	0.2659	-730.4796	-130.3371	-0.0055	(stabilization)
A3	-803.0001	0.2305	-802.7696	150 2202	10.0025	+2.20
B3	-953.3355	0.2376	-953.0979	-130.3285	+0.0055	(destabilization)

XYZ geometry data of Structure A1

С	3.02323	1.13556	0.35468
С	3.70480	-0.01707	-0.02973
С	2.97741	-1.14735	-0.38937
С	1.58616	-1.12454	-0.36879
С	0.88243	0.03236	-0.00166
С	1.63378	1.15757	0.37196
С	-0.60386	0.05303	-0.00505
С	-1.32748	-1.24547	0.30484
С	-2.80152	-1.03302	0.66417
С	-3.47709	-0.09068	-0.33212
С	-2.78732	1.27652	-0.32848
С	-1.28714	1.17162	-0.28647
н	3.57619	2.01830	0.65471

Н	4.78806	-0.03592	-0.03921	
Н	3.49315	-2.05297	-0.68739	
Н	1.04381	-2.01623	-0.65711	
Н	1.12352	2.05524	0.69915	
Н	-0.81386	-1.75884	1.12354	
Н	-1.25674	-1.91972	-0.55766	
Н	-3.31600	-1.99707	0.69516	
Н	-2.87135	-0.60467	1.67041	
Н	-4.53939	0.02240	-0.10082	
Н	-3.41593	-0.52628	-1.33570	
Н	-3.08441	1.85698	-1.20835	
Н	-3.12653	1.86590	0.53467	
Н	-0.74076	2.08177	-0.51530	
XYZ	geometry dat	a of Structure	B1	
С	1.75725	-1.41063	-0.20680	
С	3.13570	-1.37293	-0.20362	
С	3.80701	-0.20159	0.16437	
С	3.08321	0.92168	0.53950	
С	1.69351	0.88930	0.55668	
С	0.99093	-0.27956	0.17848	
С	-0.44117	-0.32330	0.14578	
С	-1.24377	0.87780	0.45222	
0	-1.11179	1.29733	-0.96550	
С	-2.70875	0.73807	0.84970	
С	-3.30234	-0.66428	0.65361	
С	-2.66985	-1.35948	-0.54754	
0	-0.16503	2.28594	-1.13512	
Н	1.26238	-2.32624	-0.49727	
Н	3.69888	-2.25233	-0.49038	
Н	4.89005	-0.17564	0.16277	
Н	3.59896	1.82823	0.83103	
Н	1.16117	1.76938	0.87438	
Н	-0.74818	1.63560	1.04680	
Н	-2.80945	1.05050	1.89106	
Н	-3.25877	1.47182	0.25295	
Н	-4.38540	-0.59103	0.53726	
Н	-3.12392	-1.27093	1.54755	
Н	-3.12606	-2.33692	-0.71620	
Н	-2.83491	-0.77062	-1.45445	
С	-1.16707	-1.55278	-0.31947	
н	-1.02462	-2.31645	0.45936	
Н	-0.69349	-1.95548	-1.21730	
XYZ geometry data of Structure A2				
С	-2.21048	0.94803	-0.28253	

С	-2.21048	0.94803	-0.28253
С	-2.82566	-0.25062	0.07999
С	-2.03040	-1.35282	0.40290
С	-0.64889	-1.25319	0.36842
С	-0.00261	-0.05335	0.02636
С	-0.82083	1.03098	-0.30802

С	1.47948	0.04583	0.01682		
С	2.26493	-1.20692	-0.33067		
С	3.71999	-0.91237	-0.70868		
С	4.36362	0.04487	0.29452		
С	3.60418	1.37450	0.32776		
С	2.11055	1.19139	0.31238		
Н	-2.79480	1.81407	-0.56005		
Н	-2.51106	-2.28376	0.67903		
Н	-0.06393	-2.12649	0.62864		
Н	-0.36882	1.96567	-0.61705		
Н	1.76528	-1.73077	-1.15140		
Н	2.24311	-1.90053	0.51938		
Н	4.28284	-1.84779	-0.76754		
Н	3.75045	-0.46181	-1.70723		
Н	5.41486	0.21627	0.04858		
Н	4.34121	-0.41147	1.29048		
Н	3.88895	1.95405	1.21241		
Н	3.89768	1.99429	-0.53097		
Н	1.52231	2.06699	0.57117		
0	-4.17636	-0.44483	0.13551		
С	-5.03079	0.65253	-0.18468		
Н	-4.87903	0.98432	-1.21493		
Н	-6.04647	0.28151	-0.06986		
Н	-4.87013	1.49098	0.49783		
XYZ geometry data of Structure B2					
С	1.09288	-1.22302	-0.20115		

С	1.09288	-1.22302	-0.20115
С	2.46169	-1.09388	-0.19429
С	3.04340	0.13246	0.17931
С	2.22180	1.20313	0.55182
С	0.85163	1.06318	0.55594
С	0.22973	-0.15941	0.17704
С	-1.18052	-0.31748	0.14766
С	-2.08065	0.82731	0.42077
0	-2.03305	1.27811	-0.98317
С	-3.52121	0.56085	0.85396
С	-4.00598	-0.88358	0.65946
С	-3.31977	-1.53025	-0.53878
0	-1.12814	2.32135	-1.16062
Н	0.67761	-2.17644	-0.49505
Н	3.07634	-1.93470	-0.48043
Н	2.68449	2.13800	0.84146
Н	0.25296	1.90530	0.85843
Н	-1.64689	1.62329	1.01560
Н	-3.62240	0.85560	1.90057
Н	-4.14316	1.25163	0.27699
Н	-5.09146	-0.89479	0.54183
Н	-3.78273	-1.47440	1.55407
Н	-3.70044	-2.53981	-0.70700
Н	-3.52578	-0.95597	-1.44664
С	-1.80842	-1.60785	-0.30332

Н	-1.61424	-2.35172	0.48279
Н	-1.30448	-1.98262	-1.19667
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С	-0.64918	0.04853	-0.00357
С	0.09506	1.18242	0.35844
С	-2.13300	0.05581	-0.00202
С	-2.84492	-1.25136	0.29642
С	-4.31989	-1.05112	0.65863
С	-5.00278	-0.10795	-0.33181
С	-4.32313	1.26429	-0.32162
С	-2.82341	1,17219	-0.27562
н	2 02820	2 06202	0.62709
ц	1 07133	2.00202	0.68268
н Ц	0 47124	-2.02371	-0.00200
	-0.47134	-2.00432	-0.04439
п	-0.41707	2.08045	0.07805
н	-2.32747	-1.76786	1.11064
Н	-2.77050	-1.91682	-0.57245
Н	-4.82686	-2.01911	0.68379
Н	-4.39164	-0.62985	1.66758
Н	-6.06536	-0.00319	-0.09869
Н	-4.94008	-0.53742	-1.33780
Н	-4.62150	1.84713	-1.19931
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F	4.21149	1,19883	-0.26777
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•	4.10240	-0.07007	-0.00002
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C C	-1.70101	-1.29009	0.23410
	-2.42766	-0.09822	-0.10233
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С	-0.30063	0.94138	-0.52334
С	0.37758	-0.24607	-0.17444
С	1.81256	-0.31954	-0.15281
С	2.63172	0.86634	-0.46764
0	2.47773	1.27604	0.95682
С	4.10012	0.71046	-0.84123
С	4.66484	-0.70554	-0.66285
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0	1.55469	2.27507	1.12352
Н	0.06666	-2.29698	0.47304
Н	-2.35890	-2.16576	0.51887
Н	-2.18655	1.93371	-0.74684
Н	0.24060	1.81217	-0.84905
Н	2.15030	1.63198	-1.06356
Н	4.22377	1.04231	-1.87388
Н	4.65252	1.42224	-0.22064
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Н	4.47339	-1.29757	-1.56378
Н	4.45831	-2.38898	0.68899
Н	4.19934	-0.82583	1.44488
С	2.51398	-1.56404	0.30614
Н	2.35460	-2.32049	-0.47675
Н	2.03399	-1.96099	1.20307
С	-3.92800	-0.05026	-0.04721
F	-4.43107	1.13053	-0.45383
F	-4.49262	-1.00737	-0.82309
F	-4.39118	-0.26284	1.20917

DFT-calculated charges

Optimization of geometries was performed using the DFT method with B3LYP functional and 6-311+G(d,p) basis set. The indicated numbers are computed Mulliken charges.





XYZ geometry data of Structure R=H

С	3.34346	-0.63214	-0.57858
С	2.73558	0.76466	-0.78244
С	1.24347	0.86982	-0.47037
С	0.45618	-0.34637	-0.19430
С	1.18442	-1.57522	0.28982
С	2.67093	-1.34586	0.59235
Н	0.76067	1.60765	-1.10432
Н	3.21096	-1.23450	-1.48558
Н	4.42146	-0.54453	-0.41914
Н	0.68310	-1.98561	1.17057
Н	1.09998	-2.34573	-0.49287
Н	3.14803	-2.31032	0.78719
Н	2.77260	-0.74795	1.50392
Н	3.23398	1.49253	-0.13371
Н	2.89980	1.10368	-1.80893
С	-0.97358	-0.30343	-0.22027
С	-1.68108	0.88968	-0.52283
С	-1.74499	-1.44874	0.12974
С	-3.07423	0.92959	-0.45524
Н	-1.15663	1.78142	-0.82059
С	-3.12281	-1.40128	0.16827
Н	-1.24899	-2.38188	0.36121
С	-3.79799	-0.20374	-0.11577
Н	-3.58822	1.85708	-0.67934
Н	-3.68540	-2.29141	0.42610
Н	-4.88094	-0.16958	-0.07633
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0	0.06820	2.27287	1.03320
XYZ	aeometrv dat	a of Structure	R=OMe
С	-4.06198	-0.83840	0.56889
С	-3.56281	0.60250	0.76244

С

С

С

С

-2.08391

-1.20124

-1.82949

-3.32524

-1.62622	-0.26479
-1.51275	-0.58649

0.44192

0.20131

0.82415

-0.33509

	-1.00450	1.60087	1.00815
Н	-3.89459	-1.41987	1.48391
Н	-5.14183	-0.83454	0.39766
Н	-1.29152	-2.01314	-1.13458
Н	-1.69867	-2.37547	0.53196
Н	-3.72693	-2.51252	-0.77426
н	-3.46052	-0.93366	-1.50567
Н	-4 11819	1 28566	0 11143
н	-3 74946	0.93335	1 78785
C	0 21424	-0 18017	0 23391
C	0.23868	1 06532	0.53359
C C	1 07871	1.00002	0.00773
C C	2 21510	1 20018	-0.09775
С Ц	0.24621	1.20910	0.49221
	0.24031	1.92300	0.00101
	2.45079	-1.12295	-0.12103
Н	0.66239	-2.23075	-0.32998
0	3.03397	0.12714	0.16605
н	2.67896	2.16269	0.71270
Н	3.06445	-1.97829	-0.37012
0	-1.93325	1.30535	-0.96018
0	-1.01144	2.29055	-1.07111
0	4.36806	0.36397	0.15985
С	5.26299	-0.69417	-0.17124
Н	5.08354	-1.06285	-1.18596
Н	6.26068	-0.26314	-0.11494
Н	5.18353	-1.52050	0.54227
XYZ	geometry dat	a of Structure	R=CF₃
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С	4.12850	0.73970	-0.75094
С	2 63143	0 86027	-0 47288
	2.00170	0.00021	0.11200
С	1.82415	-0.34547	-0.20952
C C	1.82415	-0.34547	-0.20952 0.26848
C C C	1.82415 2.52611 4.01332	-0.34547 -1.59111 -1.39065	-0.20952 0.26848 0.58867
С С С Н	1.82415 2.52611 4.01332 2.16958	-0.34547 -1.59111 -1.39065 1 60778	-0.20952 0.26848 0.58867 -1 11097
С С С Н Н	1.82415 2.52611 4.01332 2.16958 4.57758	-0.34547 -1.59111 -1.39065 1.60778 -1.25516	-0.20952 0.26848 0.58867 -1.11097 -1.48211
С С С Н Н Н	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284	-0.20952 0.26848 0.58867 -1.11097 -1.48211
С С Н Н Н Н	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 2.00316	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1 13922
СССНННЫ	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922
С С С Н Н Н Н Н Н	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463
СССННННН	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665 4.47176	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038 -2.36585	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463 0.77320
СССНННННН	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665 4.47176 4.11587	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038 -2.36585 -0.80942	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463 0.77320 1.51094
СССНННННН	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665 4.47176 4.11587 4.62262	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038 -2.36585 -0.80942 1.44517	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463 0.77320 1.51094 -0.07482
СССННННННН	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665 4.47176 4.11587 4.62262 4.32191	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038 -2.36585 -0.80942 1.44517 1.09923	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463 0.77320 1.51094 -0.07482 -1.76508
СССНННННННС	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665 4.47176 4.11587 4.62262 4.32191 0.39490	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038 -2.36585 -0.80942 1.44517 1.09923 -0.27304	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463 0.77320 1.51094 -0.07482 -1.76508 -0.23821
СССНННННННСС	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665 4.47176 4.11587 4.62262 4.32191 0.39490 -0.28559	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038 -2.36585 -0.80942 1.44517 1.09923 -0.27304 0.93550	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463 0.77320 1.51094 -0.07482 -1.76508 -0.23821 -0.52998
СССНННННННССС	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665 4.47176 4.11587 4.62262 4.32191 0.39490 -0.28559 -0.40178	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038 -2.36585 -0.80942 1.44517 1.09923 -0.27304 0.93550 -1.40210	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463 0.77320 1.51094 -0.07482 -1.76508 -0.23821 -0.52998 0.11015
СССНННННННСССС	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665 4.47176 4.11587 4.62262 4.32191 0.39490 -0.28559 -0.40178 -1.67757	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038 -2.36585 -0.80942 1.44517 1.09923 -0.27304 0.93550 -1.40210 1.01340	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463 0.77320 1.51094 -0.07482 -1.76508 -0.23821 -0.52998 0.11015 -0.44813
СССНННННННССССН	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665 4.47176 4.11587 4.62262 4.32191 0.39490 -0.28559 -0.40178 -1.67757 0.25037	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038 -2.36585 -0.80942 1.44517 1.09923 -0.27304 0.93550 -1.40210 1.01340 1.81390	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463 0.77320 1.51094 -0.07482 -1.76508 -0.23821 -0.52998 0.11015 -0.44813 -0.84439
СССНННННННССССНС	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665 4.47176 4.11587 4.62262 4.32191 0.39490 -0.28559 -0.40178 -1.67757 0.25037 -1.77401	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038 -2.36585 -0.80942 1.44517 1.09923 -0.27304 0.93550 -1.40210 1.01340 1.81390 -1.32441	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463 0.77320 1.51094 -0.07482 -1.76508 -0.23821 -0.52998 0.11015 -0.44813 -0.84439 0.16425
СССННННННННССССНСН	1.82415 2.52611 4.01332 2.16958 4.57758 5.78710 2.00921 2.43665 4.47176 4.11587 4.62262 4.32191 0.39490 -0.28559 -0.40178 -1.67757 0.25037 -1.77401 0.07079	-0.34547 -1.59111 -1.39065 1.60778 -1.25516 -0.60284 -2.00316 -2.35038 -2.36585 -0.80942 1.44517 1.09923 -0.27304 0.93550 -1.40210 1.01340 1.81390 -1.32441 -2.34960	-0.20952 0.26848 0.58867 -1.11097 -1.48211 -0.39138 1.13922 -0.52463 0.77320 1.51094 -0.07482 -1.76508 -0.23821 -0.52998 0.11015 -0.44813 -0.84439 0.16425 0.32980

Н	-2.17310	1.95060	-0.66430
Н	-2.35757	-2.20033	0.42083
0	2.40267	1.33382	0.93337
0	1.44274	2.26495	1.02092
С	-3.92109	-0.04829	-0.02093
F	-4.36223	-0.34251	1.22700
F	-4.50322	-0.94989	-0.85195
F	-4.41822	1.16283	-0.34167

Epoxy alcohol diastereoisomers

The compounds showed to be too complex for evaluation of NMR coupling constants or NOE effects for structure determination. The gained NMR data set showed to be too complex for reasonable interpretation.

The following graphics show one enantiomer per diastereomer as the discussed physical properties of the respective enantiomers are equal.

Optimization of geometries and single point calculations were performed using the MP2 method with 6-311++G(2d,p) basis set combined with the PCM solvation model (in chloroform). Higher energy conformers were also computed using the same method. NMR shielding was computed by the GIAO method against the magnetic shielding of TMS as reference using the PCM solvation model (in chloroform), the MP2 method which is reported to be superior to HF or DFT calculations of NMR shieldings,^[526] and 6-311++G(2d,p) basis set.

Calculations using the DFT method (not explicitly listed) list analogue results pointing towards the shown structure correlation. The shifts calculated *via* DFT model are, as assumed, less precise than MP2 results. The higher energy conformers show equal shifts.



Structure	E	ZPE	E+ZPE	$\delta_{exp} \mid \delta_{calc} (1-H)$	δ _{exp} δ _{calc} (2-Η)	Dipole / D
ST-1	-614.6420	0.2365	-614.4055	3.24 3.02	4.48 4.65	4.36
ST-2	-614.6399	0.2367	-614.4032	3.24 3.03	4.48 4.78	4.38
ST-3	-614.6408	0.2365	-614.4043	3.40 3.38	4.28 4.38	2.46
ST-4	-614.6393	0.2363	-614.4030	3.40 3.30	4.28 4.04	3.28

XYZ geometry data of Structure ST-1

	U		
С	-1.87980	-0.49868	-1.04017
С	-3.26578	-0.45693	-0.87200
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C C	2 64130	-0.96461	1 06737
C	1 17928	-1 17600	0.76600
0	0.87097	-1 62589	-0 58950
ц	1 46634	1 20146	1 85005
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XYZ	geometry dat	a of Structure	e ST-4
XYZ C	geometry dat -1.84866	a of Structure -0.61067	ST-4 -1.05763
XYZ C C	2 geometry dat -1.84866 -3.23530	a of Structure -0.61067 -0.52992	ST-4 -1.05763 -0.91480
XYZ C C C	geometry dat -1.84866 -3.23530 -3.78929	a of Structure -0.61067 -0.52992 -0.00947	ST-4 -1.05763 -0.91480 0.25701
XYZ C C C C	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150	a of Structure -0.61067 -0.52992 -0.00947 0.42741	e ST-4 -1.05763 -0.91480 0.25701 1.28707
XYZ C C C C C	geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229
XYZ C C C C C C C	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078
XYZ C C C C C C C	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815
XYZ C C C C C C C C	geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517
XYZ C C C C C C C C C O	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972
XYZ C C C C C C C C C C C C C C C C C C C	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1 18131	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921
XYZ C C C C C C C C C C C C C C C C C C C	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0 11289	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805
XYZ C C C C C C C C C C C C C C C C C C C	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1 14379	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112
XYZ C C C C C C C C C C C C C C C C C C C	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694
XYZ C C C C C C C C C C C C C C C C C C C	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163 0.93612	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689 -1.44592	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694 -0.87444
XYZ C C C C C C C C C C C C C C C C C C C	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163 0.93612 1.41002	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689 -1.44592 1.02688	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694 -0.87444 1.96023
XYZ C C C C C C C C C C C C C C C C C C C	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163 0.93612 -1.41092 2.88216	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689 -1.44592 -1.02688 0.87527	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694 -0.87444 -1.96033 1.71562
хүz ссссссоссонн н	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163 0.93612 -1.41092 -3.88216 4.26726	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689 -1.44592 -1.02688 -0.87537	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694 -0.87444 -1.96033 -1.71562 0.26000
хүz ссссссоссоннн н	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163 0.93612 -1.41092 -3.88216 -4.86736 2.97704	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689 -1.44592 -1.02688 -0.87537 0.05048	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694 -0.87444 -1.96033 -1.71562 0.36999 2.20227
хүz ссссссссссонннн:	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163 0.93612 -1.41092 -3.88216 -4.86736 -3.37781 2.0100	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689 -1.44592 -1.02688 -0.87537 0.05048 0.82704	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694 -0.87444 -1.96033 -1.71562 0.36999 2.20227
хүz ссссссосссонннн:	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163 0.93612 -1.41092 -3.88216 -4.86736 -3.37781 -0.91238 1.2025	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689 -1.44592 -1.02688 -0.87537 0.05048 0.82704 0.68916	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694 -0.87444 -1.96033 -1.71562 0.36999 2.20227 1.94044
хүz ссссссссссоннннн:	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163 0.93612 -1.41092 -3.88216 -4.86736 -3.37781 -0.91238 1.33455 0.9255	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689 -1.44592 -1.02688 -0.87537 0.05048 0.82704 0.68916 0.88046	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694 -0.87444 -1.96033 -1.71562 0.36999 2.20227 1.94044 -1.74866
ХҮZ С С С С С С С С С С С О Н Н Н Н Н Н Н Н	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163 0.93612 -1.41092 -3.88216 -4.86736 -3.37781 -0.91238 1.33455 0.82376	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689 -1.44592 -1.02688 -0.87537 0.05048 0.82704 0.68916 0.88046 2.91291	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694 -0.87444 -1.96033 -1.71562 0.36999 2.20227 1.94044 -1.74866 -0.69254
XYZ ССССССССССОННННННН Н	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163 0.93612 -1.41092 -3.88216 -4.86736 -3.37781 -0.91238 1.33455 0.82376 2.36817	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689 -1.44592 -1.02688 -0.87537 0.05048 0.82704 0.68916 0.88046 2.91291 1.51354	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694 -0.87444 -1.96033 -1.71562 0.36999 2.20227 1.94044 -1.74866 -0.69254 1.03815
ХҮ С С С С С С С С С С С О Н Н Н Н Н Н Н Н	2 geometry dat -1.84866 -3.23530 -3.78929 -2.95150 -1.56643 -1.00944 0.47011 1.19778 0.34308 2.55128 3.35796 2.65934 1.21163 0.93612 -1.41092 -3.88216 -4.86736 -3.37781 -0.91238 1.33455 0.82376 2.36817 3.10108	a of Structure -0.61067 -0.52992 -0.00947 0.42741 0.34800 -0.17092 -0.25240 1.00175 2.12170 1.18131 -0.11289 -1.14379 -1.29689 -1.44592 -1.02688 -0.87537 0.05048 0.82704 0.68916 0.88046 2.91291 1.51354 1.97825	e ST-4 -1.05763 -0.91480 0.25701 1.28707 1.14229 -0.03078 -0.18815 -0.66517 -0.40972 0.00921 0.02805 0.91112 0.54694 -0.87444 -1.96033 -1.71562 0.36999 2.20227 1.94044 -1.74866 -0.69254 1.03815 -0.50240

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14. Selected spectra









































































		Consula	Score	Mass	Mass (MFG)	Diff (ppm)	Diff (abs. ppm)	Diff (mDa)	ID Source	Score (MFC
here	Best	Pormula	99.28	220.11	220.1099	-0.31	0.31	-0.07	мга	1
	Species	Ion Formula	míz	Heighi	Score (MFG)	Score (MS)	Score (MFG, MS/MS)	Score (mass) 99.97	Score (iso, abund) 99.31	Score (iso. spi 97.85
8	(M+H)+	C13 H17 O3	221.1172	10200.1	100110	List in stations	Luciant M	Height % (Calc)	Height Sum %	Height Sum%
	m/z	m/z (Calc)	Diff (ppm)	Diff (mDa)	Heighi	Height (Calc)	100	100	85.8	86.2
	221.1172	221.1172	-0.02	0	38006.7	55200.7	15.1	14.4	13	12.4
	222.1205	222.1206	0.74	0.2	5/49.6	5490.4	13.1	16	1.2	1.4
							C ₁₃ H ₁₆ O ₃	4		







2-1	Earmula	Score	Mass	Mass (MFG)	Diff (ppm)	Diff (abs. ppm)	Diff (mDa)	ID Source	Score (MFC
Best	C18 H18 O2	82.84	266.1289	266.1307	6.51	6.51	1.73	MFG	82.04
	lon Formula	Tm/z	Height	Score (MFG)	Score (MS)	Score (MFG, MS/MS)	Score (mass)	Score (iso. abund)	Score (iso. spa
(M+H)+	C18 H19 O2	267.138	8711.3	82.84	82.84		87.14	81.13	76.98
	inia (Cala)	Diff (opm)	Diff (mDa)	Height	Height (Calc)	Height %	Height % (Calc)	Height Sum %	Height Sunt%
267.1365	267.138	5.41	1.4	8217.7	8711.3	100	100	77.3	82
268.1402	268.1413	4.19	1.1	1899	1721.6	23.1	19.8	17.9	16.2
269.1357	269.1443	32.04	8.6	513	196.8	6.2	2.3	4.8	1.9
					Ŷ	$\hat{\Box}$			
























































Supplementary Information





Supplementary Information

15. Page count