The Switch-Off Method: Rapid Investigation of Flow Photochemical Reactions

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Supporting Information

Table of contents

1. Materials and methods ... 1
1. 1. Materials ... 1
1. 2. Methods ... 1
1. 3. Inhomogeneity of the light and effective exposure time ... 2
1. 3. 1. Correction by light source output amendment ... 2
1. 3. 2. Correction by exclusion of start- and endpoint data ... 4
1. 3. 3. Comparison of both methods ... 5
2. Experimental procedures ... 9
2. 1. General procedure for switch off experiment performed herein: ... 9
2. 2. [2+2] photocycloaddition of 3,4-dihydro-2*H*-pyran an diphenylacetylene ... 9
2. 2. 1. Calibration curve for determination of reaction product yield using GC-FID monitoring: 10
2. 2. 2. Diphenylacetylene and 3,4-dihydro-2*H*-pyran [2+2] photoreaction Switch-Off optimisations results: ... 12
2. 2. 3. Validation of Switch-Off results obtained in [2+2] photocycloaddition of 3,4-dihydro-2*H*-pyran an diphenylacetylene ... 20
2. 3. [2+2] photocycloaddition of cyclohex-2-enone and 1,1,2,2-tetramethylethylene ... 20
2. 3. 1. Calibration curve for determination of compounds 5 and 6 yields using GC-FID monitoring: ... 21
2. 3. 2. Cyclohex-2-enone and tetramethylethylene [2+2] photoreaction Switch-Off optimisations results ... 23
2. 3. 3. Validation of Switch-Off results obtained in [2+2] photocycloaddition cyclohex-2-enone and tetramethylethylene ... 37
2. 4. Mallory photocyclization of *cis*-stilbene ... 37
2. 4. 1. Calibration curve for determination of phenanthrene yield using GC-FID monitoring: ... 38
2. 4. 2. Mallory photoreaction Switch-Off optimisations results ... 40

2. 4. 3. Validation of Switch-Off results obtained in Mallory photocyclisation of *cis*-stilbene 67

3. Syntheses and characterization data 68

3. 1. Procedures for synthesis of compounds 1, 2, 3, and 4: 68

3. 1. 1. *cis*-7,8-Diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (1): 68

3. 1. 2. 3,4-Dihydro-6,7-diphenyl-2*H*-oxocin (2): 68

3. 1. 3. *cis*-8*c*,11,12,12*a*-Tetrahydro-10*H*-phenanthro[9′,10′:3,4]cyclobuta[1,2-*b*]pyran (3): 69

3. 1. 4. (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (4): 70

3. 2. Procedure for synthesis of compounds 5, 6, 7, 8, and 9: 73

3. 2. 1. *trans*-7,7,8,8-Tetramethylbicyclo[4.2.0]octan-2-one (5): 73

3. 2. 2. *cis*-7,7,8,8-Tetramethylbicyclo[4.2.0]octan-2-one (6): 73

3. 2. 3. Structural assignment of the *trans*- and *cis*-bicyclo[4.2.0]octan-2-ones 5 and 6: 74

3. 2. 4. *cis*-*anti*-*cis*-Tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (7): 75

3. 2. 5. *cis*-*anti*-*cis*-Tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (8): 76

3. 2. 6. 3-(1,1,2-Trimethyl-2-propen-1-yl)cyclohexanone (9): 76

3. 3. Procedure for synthesis of compounds 10, 11, 12, and 13: 76

3. 3. 1. Phenanthrene (10): 77

3. 3. 2. (1α,2α,3β,4β)-1,2,3,4-Tetraphenylcyclobutane (11): 77

3. 3. 3. (1α,2β,3α,4β)-1,2,3,4-Tetraphenylcyclobutane (12): 77

3. 3. 4. (1α,2β,2aR,10bS)-1,2-Diphenyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene (13): 77

4. NMR, UV-Vis, IR, and MS spectra 78

5. References 115

1. Materials and methods

1. 1. Materials

Acetonitrile was distilled from CaH_2 and was stored in a closed RBF containing freshly dried 3Å molecular sieves. All other solvents and commercially available chemicals were used as received.

1. 2. Methods

NMR spectra were obtained on a Bruker DPX400 or Bruker AvanceCore AVII 400 spectrometers. ^{1}H chemical shifts are reported as values in ppm referenced to the deuterated solvent main peak. The following abbreviations are used to assign multiplicity: s = singlet, d = doublet, t=triplet, q = quartet, qu = quintet, sx = sextet, hpt = heptet, oct = octet, br = broad. Coupling constants, J, are measured in Hertz (Hz) and if indicated are reported as $^{X}J_{Y\text{-}Z}$, where X indicates number of bonds between coupled nuclei and Y-Z indicates the nuclei. ^{13}C chemical shifts are reported as values in ppm referenced to the main peak of deuterated solvent and are proton decoupled. If indicated, in the ^{13}C NMR spectra the nature of carbons (CH, CH_2 or CH_3) was determined by DEPT-135 experiment. Two-dimensional NMR (HSQC, HMBC, NOESY, COSY, and TOCSY) was used for signals assignment. Chloroform-d_1 was passed through K_2CO_3 directly prior to the measurement.

High resolution positive/negative ion electrospray ionisation (ESI) mass spectra were recorded using a MaXis (Bruker Daltonics, Bremen, Germany) time of flight (TOF) mass spectrometer. Samples were introduced to the mass spectrometer via a Dionex Ultimate 3000 autosampler and uHPLC pump. Ultrahigh performance liquid chromatography was performed using a Waters, Acquity UPLC BEH C18 (50 mm x 2.1 mm 1.7um) column. Gradient elution from 5% acetonitrile (0.2% formic acid) to 100% acetonitrile (0.2% formic acid) was performed in five minutes at 0.6 mL/min. High resolution electron ionization mass spectra were recorded using LECO Pegasus High-Resolution Gas Chromatography Time-of-Flight Mass Spectrometer.

Analytical HPLC measurement of Mallory photoreactions were performed on an Agilent 1100 series HPLC using Cosmosil Buckyprep column (4.6 mm I.D. x 250 mm, 5 µm particle size, pyrenylpropyl bonded silica as stationary phase) and *n*-hexane:toluene 9:1 (v/v) as eluent with 1.0 $mL\cdot min^{-1}$ flow rate at 30 °C. Preparative HPLC separations of Mallory photoreactions were performed on a Shimadzu Prominence modular preparative HPLC system, using Cosmosil Buckyprep column (2 columns connected in series, 20 mm I.D. x 250 mm, 5 µm particle size, pyrenylpropyl bonded silica as stationary phase) and *n*-hexane:toluene 9:1 (v/v) as eluent with 10.0 $mL\cdot min^{-1}$ flow rate at 30 °C.

GC measurements were performed on a Hewlett Packard HP 6890 series GC system, using a HP-5 (cross-linked 5% Ph Me siloxane) 30 m column, with a film thickness of 0.25 µm and 0.32 mm internal diameter. The carrier gas was helium and the flow rate was 2.7 $mL\cdot min^{-1}$. The injector was maintained at 300 °C with 1.0 µL injection. The run started at 80 °C with a gradient of 25 °C/min until 275 °C which was held for 3 min.

Infrared spectra were run as neat films on a Thermo Nicolet 380 FT-IR spectrometer with a Smart Orbit Goldengate ATR attachment.

UV-Vis measurements were recorded with the Ocean Optics DH-2000-BAL light source and USB 2000+ fibre optic spectrometer at room temperature using SpectraSuite Software. All flow *in situ* UV-Vis measurements were performed with a Type 583-F Starna® fluorimeter flow cell (path length: 1 mm, volume: 0.011 mL). The other UV-Vis measurements were run with UV Fused Quartz cuvette (path length: 10 mm, volume: 3.5 mL). The wavelengths are given in nanometres and the corresponding extinction coefficients in $M^{-1}\cdot cm^{-1}$.

Melting points were recorded on a GallenKamp or Stuart SMP20 melting point apparatus and are uncorrected.

Thin-layer chromatography was carried out on Merck silica gel plates, which were visualised under UV irradiation of 254 nm and/or by staining with aqueous $KMnO_4$, methanolic H_2SO_4, PMA or iodine. Column chromatography was performed with Merck silica gel 60 using solvent ratios as volumes before mixing described in the method.

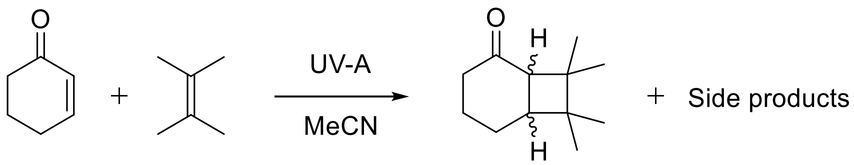
The Vapourtec® R series Integrated Flow Chemistry System (R2+) was the platform used for the flow experiments.

1. 3. Inhomogeneity of the light and effective exposure time

During a photoflow chemical reaction, the intensity of the light is not homogeneous throughout the whole photoreactor volume. Indeed, the photon flux is higher in the middle of the reactor than at the entrance and the end. With the switch-off method this means that the total exposure of each fraction of the reaction mixture as it leaves the reactor is not exactly the time it was in the reactor before the light was switched off (multiplied by average light intensity). The difference is specific for each photoreactor and varies for various designs and light sources used.

1. 3. 1. Correction by light source output amendment

To assess this difference of light irradiation intensity, the reaction between the cyclohex-2-enone and the tetramethylethylene was used as a model (Scheme S 1. [2+2] photocycloaddition used as a model reaction for determination of light irradiation efficiency). The reaction mixture was injected into the photoreactor (light source turned off), then once the reactor was entirely filled up, the pump was turned off, the light source was turned on, and the reaction was left to proceed. After the indicated reaction time the light was turned off and the content of the photoreactor was eluted and analysed.



Scheme S 1. [2+2] photocycloaddition used as a model reaction for determination of light irradiation efficiency

Experimental procedure for determination of light source efficiency:

In a 50 mL flask, cyclohex-2-enone (98.0 mg, 98.7 µL, 1.02 mmol, 1.00 equiv.) was mixed with tetramethylethylene (1.68 g, 2.38 mL, 20.0 mmol, 19.6 equiv.), dibutyl ether (115.5 mg, 150.0 µL, 0.89 mmol, 0.87 eq.) acting as an internal standard, and anhydrous MeCN (37.5 mL, 382.7 vol.). The reaction mixture was degassed by sonication whilst being saturated with nitrogen for 15 minutes. The reaction mixture was injected into the photoflow reactor (UV lamp switched off) until it was entirely filled up. Then, the pump was turned off, the water cooling system was turned on, the UV-A lamp (Philips PL-L 36W/09/4P) was switched on and the reaction was left to proceed for 60 minutes. Once the time has passed, the UV lamp was turned off, the feeding valve was returned to the stock solvent, the content of the UV reactor was pushed out (1 mL/min) and it was collected in GC vials. The sampling rate was precisely determined (30 seconds collection per vial with addition of 1 mL of MeCN).

The samples were then analysed via off-line GC measurements. Light output at each point was calculated as inversion of the ratio of the peak area of cyclohex-2-enone to the peak area of internal standard, which was then normalised to the arithmetic mean value of all datapoints, which was set as 100% (Figure S 1. Graph of relative light output at each point obtained from [2+2] photocycloaddition experiment between cyclohex-2-enone and tetramethylethylene using UV-A light source and 31.8 mL photoreactor..

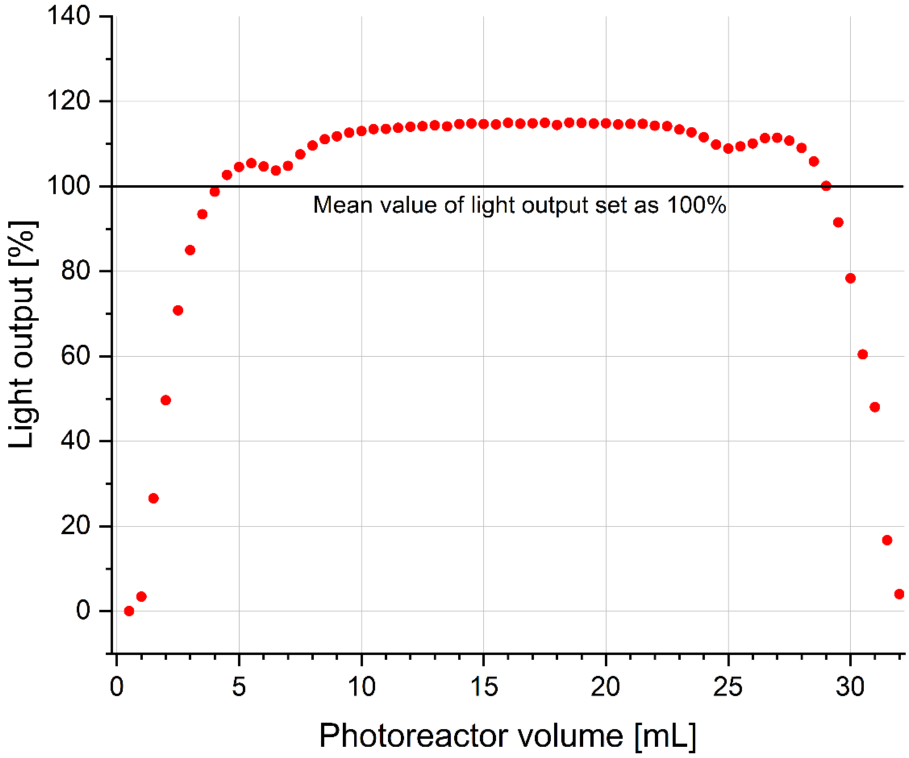


Figure S 1. Graph of relative light output at each point obtained from [2+2] photocycloaddition experiment between cyclohex-2-enone and tetramethylethylene using UV-A light source and 31.8 mL photoreactor.

In general, reaction time in flow reactions (described as residence time) is determined by the total flow rate and reactor volume, by the equation given below:

$$Rt = \frac{V_{reactor}}{FR}$$

where: Rt – reaction/residence time
$V_{reactor}$ – reactor internal volume
FR – total flow rate

In thermal reactions, the flow reaction time is often corrected for the thermal expansion of liquids, but in experiments described herein this step is omitted, due to the experiments being performed at room temperatures. In flow photoreactions, previously discussed light irradiation intensity takes crucial part as it effectively changes the total light exposure for a given reaction time at each point of the photoreactor, accordingly to the determined light source output.

The effective exposure time for each fraction of the photoreactor can then be calculated as a residence time of a fraction in the photoreactor before the light was switched off multiplied by an arithmetic mean of a sum of light outputs of all previous and current fractions, as described in equation below:

$$EET_{fraction\,n} = Rt_{fraction\,n} \cdot \left(\sum_{i=1}^{n} \frac{LightOutput\%_{fraction\,i}}{n \cdot 100} \right)$$

where: $EET_{fraction\,n}$ – effective exposure time for fraction n

$Rt_{fraction\,n}$ – residence time in photoreactor for fraction n before the light was switched off

$LightOutput\%_{fraction\,n}$ – output of UV light source for fraction n [%]

In order to convert the effective exposure time back to residence time, that could be further used in calculation of the flow rate needed in the experimental procedure, a following equation can be used:

$$Rt_{fraction\,n} = \frac{EET_{fraction\,n}}{\left(\sum_{i=1}^{n} \frac{LightOutput\%_{fraction\,i}}{n \cdot 100} \right)}$$

Flow rate for the experimental procedure can then be calculated using the following equation:

$$FR = \frac{V_{reactor}}{Rt}$$

Note that the multiplication or division by 100 in formulas presented above comes from the fact that *Light Output* values used herein are in percent. This correction method has been used in the analysis of results obtained from experiments utilizing UV-A light source.

1. 3. 2. Correction by exclusion of start- and endpoint data

A different approach would be to only use approximately 90% of the data from the region were the light irradiation intensity is relatively homogeneous, i.e. the central portion of the data. In an example below (Figure S 2. Graph of relative light output at each point obtained from [2+2] photocycloaddition experiment between cyclohex-2-enone and tetramethylethylene using UV-A light source and 31.8 mL photoreactor, with the datapoints excluded from Switch-Off calculations due to light irradiation inhomogeneity (blue points and area) and with datapoints included in the analysis of results (red points and area).), where UV-A lamp was used, only the datapoints laying in the red area would be used for analysis, which results in restricting the range of reactor volume used down to effective photoreactor volume. In the example below, the effective total photoreactor volume used in data analysis would be 28.5 mL (datapoints included in the analysis start at 2.0 mL and end at 30.5 mL) out of total internal photoreactor volume of 31.8 mL.

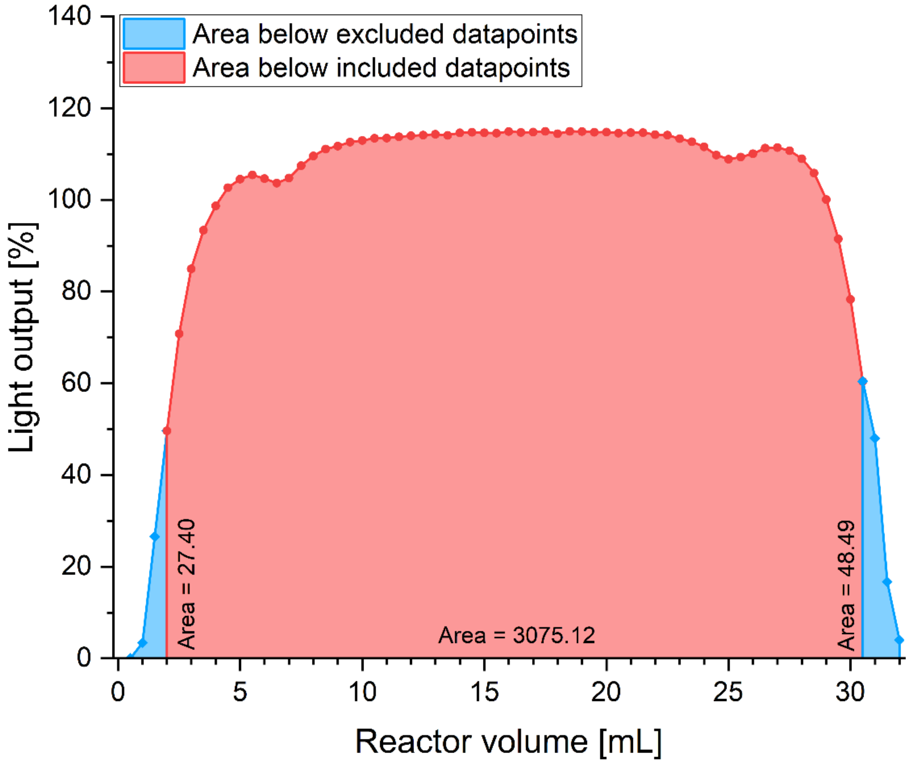


Figure S 2. Graph of relative light output at each point obtained from [2+2] photocycloaddition experiment between cyclohex-2-enone and tetramethylethylene using UV-A light source and 31.8 mL photoreactor, with the datapoints excluded from Switch-Off calculations due to light irradiation inhomogeneity (blue points and area) and with datapoints included in the analysis of results (red points and area).

Such approach minimizes the error caused by the uneven light irradiation intensity without the need for measurement of the light source output, but also results in slight overestimation of the results for the first few datapoints, i.e. the first datapoint analysed for which a set reaction time of zero would be assumed, had actually experienced slight irradiation, thus would show positive reaction output (e.g. conversion or yield). Table S 1. Values of areas from the Figure S 2. obtained from integration of datapoints.contains values of the areas generated by the curves obtained from excluded and included datapoints from the Figure S 2. Graph of relative light output at each point obtained from [2+2] photocycloaddition experiment between cyclohex-2-enone and tetramethylethylene using UV-A light source and 31.8 mL photoreactor, with the datapoints excluded from Switch-Off calculations due to light irradiation inhomogeneity (blue points and area) and with datapoints included in the analysis of results (red points and area). Analysis of the areas shows, that by using the central 90% of the datapoints obtained in experiment, only approx. 2.4% of the data is excluded from analysis, for this particular example.

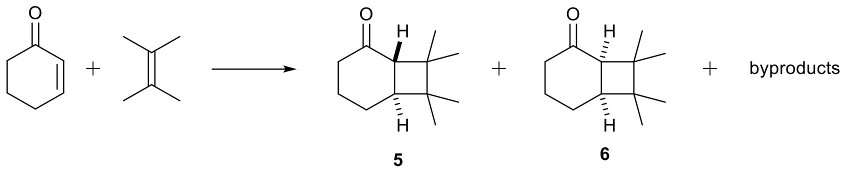
Table S 1. Values of areas from the Figure S 2. obtained from integration of datapoints.

	Area value	Percentage of total area [%]
Total area	3151.01	100.0
Excluded datapoints area	75.89	2.4
Reactor inlet excluded datapoints	27.40	0.9
Reactor outlet excluded datapoints	48.49	1.5
Included datapoints area	3075.12	97.6

The datapoints exclusion methodology has been used in the experiments performed with UV-B and UV-C light sources performed herein.

1. 3. 3. Comparison of both methods

In order to compare both light intensity inhomogeneity correction methodologies, experimental data from one of the Switch Off experiments performed herein (experimental procedure described in section 2. 3. 2. 1. Switch-Off experiment results using UV-A light) was used with both correction methods, and the results are presented below.



Scheme S 2. Switch-Off [2+2] photocycloaddition reaction experiment used for comparison of light intensity inhomogeneity correction methodologies.

Table S 2. Calculated data for the [2+2] photocycloaddition between cyclohex-2-enone and tetramethylethylene used in comparison of both correction methodologies.contains calculated values of effective exposure times and reaction yields for both methods, which were used for generation of Figure S 3. Comparison of Switch-Off experimental data obtained by not using any corrections for light inhomogeneity (black line/symbols), by using light output amendment (red line/symbols), and by excluding 10% of the endpoint data (green line/symbols).

Table S 2. Calculated data for the [2+2] photocycloaddition between cyclohex-2-enone and tetramethylethylene used in comparison of both correction methodologies.

Vial	**Light Output Amendment Method**			**Datapoints Exclusion Method**			Diastereo isomers **5** and **6** yield [%]
	Residence time [min]	Light output [%]	Effective exposure time [min]	Datapoint included or excluded from analysis	Effective Reactor Volume [mL]	Effective exposure time [min]	
1	239.1	0.0	235.7	Excluded			47.7%
2	236.3	3.4	235.7	Excluded			47.8%
3	233.5	15.0	235.5	Excluded			48.0%
4	230.6	26.6	235.1	Excluded			45.5%
5	227.8	49.7	234.3	Excluded			43.8%
6	225.0	70.8	232.9	Included	28.500	214.3	43.5%
7	222.2	77.9	230.9	Included	28.125	211.5	44.7%
8	219.4	85.0	228.7	Included	27.750	208.6	44.6%
9	216.5	93.4	226.3	Included	27.375	205.8	44.7%
10	213.7	98.7	223.6	Included	27.000	203.0	45.3%
11	210.9	100.7	220.8	Included	26.625	200.2	48.3%
12	208.1	102.7	218.0	Included	26.250	197.4	48.2%
13	205.3	104.5	215.1	Included	25.875	194.5	48.7%
14	202.4	105.5	212.2	Included	25.500	191.7	49.0%
15	199.6	105.1	209.2	Included	25.125	188.9	49.6%
16	196.8	104.7	206.2	Included	24.750	186.1	48.6%

17	194.0	103.7	203.3	Included	24.375	183.3	50.0%
18	191.2	104.8	200.3	Included	24.000	180.5	50.1%
19	188.3	106.2	197.4	Included	23.625	177.6	49.6%
20	185.5	107.5	194.4	Included	23.250	174.8	50.1%
21	182.7	109.6	191.4	Included	22.875	172.0	50.4%
22	179.9	111.1	188.3	Included	22.500	169.2	50.5%
23	177.1	111.4	185.1	Included	22.125	166.4	48.3%
24	174.2	111.8	182.0	Included	21.750	163.5	49.2%
25	171.4	112.6	178.9	Included	21.375	160.7	49.2%
26	168.6	113.0	175.7	Included	21.000	157.9	48.6%
27	165.8	113.2	172.5	Included	20.625	155.1	49.3%
28	163.0	113.4	169.3	Included	20.250	152.3	48.9%
29	160.2	113.5	166.1	Included	19.875	149.4	49.5%
30	157.3	113.6	162.9	Included	19.500	146.6	50.1%
31	154.5	113.8	159.7	Included	19.125	143.8	50.4%
32	151.7	114.0	156.5	Included	18.750	141.0	50.6%
33	148.9	114.1	153.3	Included	18.375	138.2	51.1%
34	146.1	114.2	150.1	Included	18.000	135.3	51.2%
35	143.2	114.3	146.9	Included	17.625	132.5	51.2%
36	140.4	114.1	143.7	Included	17.250	129.7	51.9%
37	137.6	114.7	140.5	Included	16.875	126.9	52.3%
38	134.8	114.7	137.3	Included	16.500	124.1	52.8%
39	132.0	114.8	134.0	Included	16.125	121.2	52.5%
40	129.1	114.6	130.8	Included	15.750	118.4	53.2%
41	126.3	114.6	127.6	Included	15.375	115.6	54.2%
42	123.5	114.8	124.4	Included	15.000	112.8	54.6%
43	120.7	114.9	121.1	Included	14.625	110.0	54.3%
44	117.9	114.8	117.9	Included	14.250	107.1	55.3%
45	115.0	114.8	114.7	Included	13.875	104.3	54.7%
46	112.2	114.9	111.5	Included	13.500	101.5	55.8%
47	109.4	115.0	108.2	Included	13.125	98.7	56.2%
48	106.6	114.4	105.0	Included	12.750	95.9	56.8%
49	103.8	115.0	101.8	Included	12.375	93.0	57.0%
50	100.9	115.0	98.6	Included	12.000	90.2	57.4%
51	98.1	114.9	95.3	Included	11.625	87.4	58.7%
52	95.3	114.8	92.1	Included	11.250	84.6	58.7%
53	92.5	114.8	88.9	Included	10.875	81.8	60.1%
54	89.7	114.7	85.7	Included	10.500	78.9	60.8%
55	86.8	114.6	82.5	Included	10.125	76.1	61.0%
56	84.0	114.7	79.3	Included	9.750	73.3	61.3%
57	81.2	114.7	76.0	Included	9.375	70.5	61.5%
58	78.4	114.5	72.8	Included	9.000	67.7	62.6%
59	75.6	114.3	69.6	Included	8.625	64.8	63.0%

60	72.7	114.1	66.4	Included	8.250	62.0	64.5%
61	69.9	113.8	63.3	Included	7.875	59.2	64.5%
62	67.1	113.4	60.1	Included	7.500	56.4	64.0%
63	64.3	112.7	56.9	Included	7.125	53.6	64.6%
64	61.5	111.6	53.8	Included	6.750	50.8	65.6%
65	58.6	110.7	50.7	Included	6.375	47.9	66.4%
66	55.8	109.8	47.6	Included	6.000	45.1	64.5%
67	53.0	108.9	44.5	Included	5.625	42.3	65.7%
68	50.2	109.4	41.5	Included	5.250	39.5	65.6%
69	47.4	110.4	38.5	Included	4.875	36.7	63.7%
70	44.5	110.1	35.4	Included	4.500	33.8	62.5%
71	41.7	111.3	32.4	Included	4.125	31.0	58.6%
72	38.9	111.4	29.3	Included	3.750	28.2	57.5%
73	36.1	111.1	26.3	Included	3.375	25.4	53.3%
74	33.3	110.7	23.2	Included	3.000	22.6	49.5%
75	30.5	109.0	20.2	Included	2.625	19.7	43.7%
76	27.6	105.9	17.3	Included	2.250	16.9	37.6%
77	24.8	103.0	14.4	Included	1.875	14.1	31.8%
78	22.0	100.1	11.7	Included	1.500	11.3	28.3%
79	19.2	91.5	9.1	Included	1.125	8.5	19.9%
80	16.4	78.3	6.7	Included	0.750	5.6	15.0%
81	13.5	69.4	4.7	Included	0.375	2.8	9.5%
82	10.7	60.5	3.0	Included	0.000	0.0	5.8%
83	7.9	48.0	1.6	Excluded			2.9%
84	5.1	16.7	0.5	Excluded			1.5%
85	2.3	10.4	0.2	Excluded			0.4%
86	0.0	4.0	0.0	Excluded			0.0%

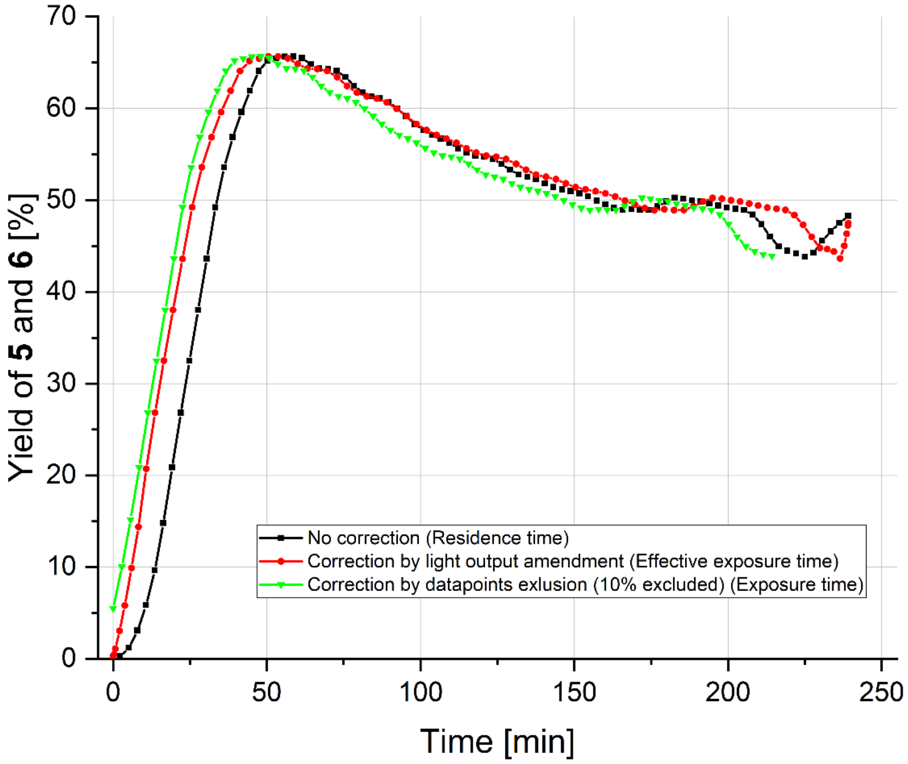


Figure S 3. Comparison of Switch-Off experimental data obtained by not using any corrections for light inhomogeneity (black line/symbols), by using light output amendment (red line/symbols), and by excluding 10% of the endpoint data (green line/symbols).

Correction performed by using light output amendment shows similar results to uncorrected data for the middle part of the data, however the front- and endpoints differ significantly, as expected due to the light irradiation inhomogeneity at the ends of the photoreactor. Second correction method, by exclusion of 10% of the data, is in a good agreement with the first correction method, however some differences are visible, especially at the end of analysed data. Both methods are viable for use, however the correction by light output amendment seems more precise, whereas the disadvantage is that it needs separate experiment for determination of the light output.

2. Experimental procedures

2. 1. General procedure for switch off experiment performed herein:

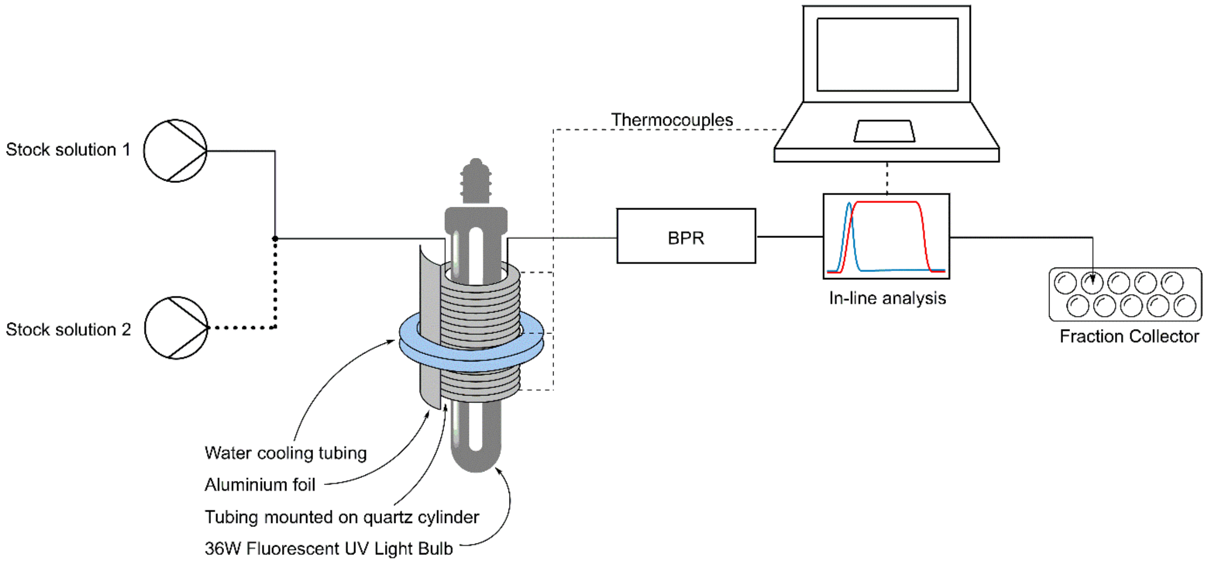


Figure S 4. Flow setup for the Switch Off experiments performed herein.

In a flask, the reagent A or the reagents A + B were mixed with an internal standard and the corresponding solvent (Stock solution 1). When indicated, in another flask, the reagent C was mixed with the corresponding solvent (Stock solution 2). Each flask was degassed by sonication whilst being saturated with nitrogen or, when indicated, with O_2. Before starting the reaction, solvent was pumped at the indicated flow rate and the indicated UV light source was switched on and left to warm up for 30 minutes. The water cooling system was turned on. Once the system was stable, the feeding valves (pump A or, when indicated, pump A and B) were switched to the stock solutions. Once the UV reactor was entirely filled up with the stock solutions, the UV lamp was switched off, the feeding valves were returned to the solvent feed, the content of the UV reactor was pushed out and collected in vials, and then analysed via off-line GC experiments.

2. 2. [2+2] photocycloaddition of 3,4-dihydro-2*H*-pyran an diphenylacetylene

An example of GC chromatogram containing all studied components of the [2+2] photocycloaddition between 3,4-dihydro-2*H*-pyran and diphenylacetylene with their respective retention times is presented below (Figure S 5. GC chromatogram of a [2+2] photoreaction between 3,4-dihydro-2H-pyran and diphenylacetylene with studied components and their respective retention times.). Injection of pure **4** into GC gives the same shaped peak as observed on the GC chromatogram presented below, which may indicate isomerisation occurring at the injection port of the GC (which is heated to 300 °C during the measurement).

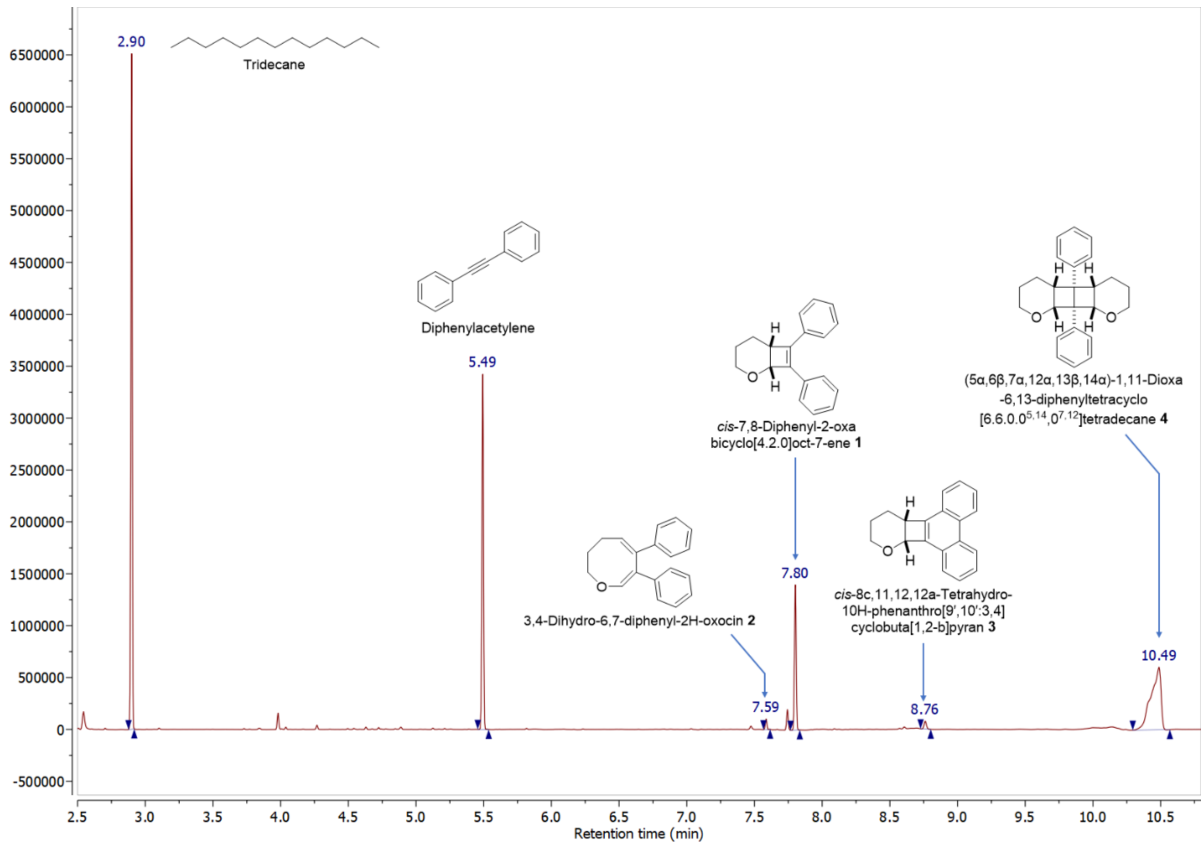


Figure S 5. GC chromatogram of a [2+2] photoreaction between 3,4-dihydro-2H-pyran and diphenylacetylene with studied components and their respective retention times.

2. 2. 1. Calibration curve for determination of reaction product yield using GC-FID monitoring:

Sample solutions of tridecane (internal standard) and 7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (referred to as cyclobutene **1**, photocycloaddition product) were prepared accordingly to the table below and were then measured using GC-FID. Calibration curve was then prepared by plotting the ratios of cyclobutene **1** and IS areas against molar ratios of cyclobutene **1** and IS.

Table S 3. Calibration table of GC-FID for [2+2] photoreaction between 3,4-dihydro-2H-pyran and diphenylacetylene.

Sample	Mass of cyclobutene **1** [mg]	Mass of IS (tridecane) [mg]	Moles of cyclobutene **1** [mol]	Moles of IS (tridecane) [mol]	**Molar ratio of cyclobutene 1 /IS**	Area of cyclobutene **1** peak	Area of IS peak (tridecane)	**Area ratio of cyclobutene 1 /IS**
1	4.1	8.5	$1.56 \cdot 10^{-5}$	$4.61 \cdot 10^{-5}$	**0.338980**	361.4	1405.0	**0.257224**
2	3.2	17.0	$1.22 \cdot 10^{-5}$	$9.22 \cdot 10^{-5}$	**0.132285**	257.6	2520.9	**0.102186**
3	2.9	3.4	$1.11 \cdot 10^{-5}$	$1.84 \cdot 10^{-5}$	**0.599416**	248.1	485.7	**0.510809**
4	8.9	65.4	$3.39 \cdot 10^{-5}$	$3.55 \cdot 10^{-4}$	**0.095636**	658.9	9383	**0.070223**

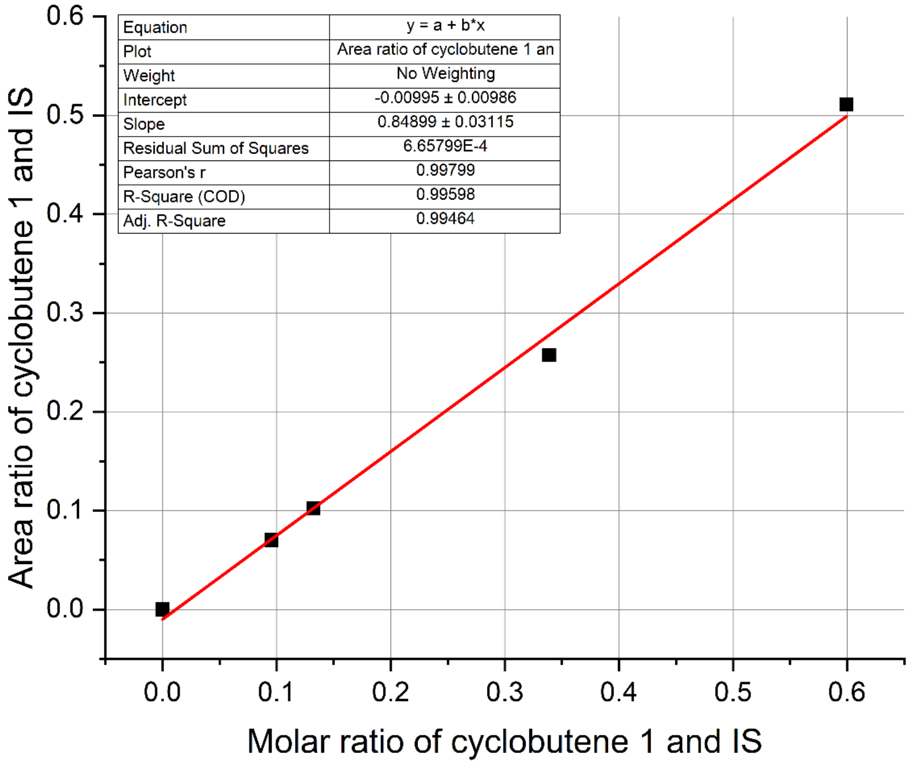


Figure S 6. GC-FID calibration curve of 7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene.

2. 2. 2. Diphenylacetylene and 3,4-dihydro-2*H*-pyran [2+2] photoreaction Switch-Off optimisations results:

2. 2. 2. 1. Switch-Off experiment results using UV-B light:

Diphenylacetylene (750.0 mg, 4.2 mmol, 1.0 eq., 56.1 mM solution) and veratrole (IS, 607.0 mg, 0.56 mL, 4.4 mmol, 1.05 eq., 58.6 mM solution) were dissolved in 3,4-dihydro-2*H*-pyran (75.0 mL, 100.0 vol.) and connected to a flow reagent stream. 3,4-Dihydro-2*H*-pyran was connected to a flow solvent stream. The UV-B lamp (Philips PL-L 36W/01/4P) and water cooling were then turned on and system was allowed to equilibrate for 30 minutes. Then reaction mixture was injected into the photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA). Effective exposure time was set to 290 minutes (which corresponds to 0.100 mL/min flow rate). Once the photoreactor was filled with reaction mixture, the UV lamp was switched off, the pump was switched to solvent stream, the reaction mixture was eluted from the photoreactor via the flow UV-Vis monitoring cell and was collected into vials (0.5 mL of reaction mixture, diluted to 1.0 mL with acetone). Collected samples were then analysed using off-line GC.

Table S 4. Results of Switch-Off optimisation performed for [2+2] photocycloaddition of diphenylacetylene and 3,4-dihydro-2H-pyran using UV-B light.

Vial	Residence time [min]	IS GC Area	Diphenylacetylene GC Area	Mono addition 1 GC Area	Phenanthrene 3 GC Area	Bisaddition 4 GC Area	Diphenyl acetylene/IS Area Ratio	Mono addition 1/IS Area Ratio	Phenanthrene /IS Area Ratio	Bis addition 4/IS Area Ratio	Datapoint included or excluded from analysis	Reactor volume [mL]	Effective reactor volume [mL]	Effective exposure time [min]	Conversion [%]	Yield [%]
1	320	560.9	4.0	21.3	18.8	769.8	0.00713	0.0380	0.0335	1.37	Excluded	32.0	N/A	N/A	99.7	4.8
2	315	587.3	4.2	22.6	19.6	786.4	0.00715	0.0385	0.0334	1.34	Excluded	31.5	N/A	N/A	99.7	4.9
3	310	588.7	4.4	22.4	19.8	798.2	0.00747	0.0380	0.0336	1.36	Excluded	31.0	N/A	N/A	99.6	4.8
4	305	579.6	4.5	21.8	19.6	789.5	0.00776	0.0376	0.0338	1.36	Included	30.5	28.5	285.0	99.6	4.8
5	300	597.4	5.0	22.4	20.3	805.3	0.00837	0.0375	0.0340	1.35	Included	30.0	28.0	280.0	99.6	4.7
6	295	649.9	5.9	24.0	21.2	861.0	0.00908	0.0369	0.0326	1.32	Included	29.5	27.5	275.0	99.6	4.7
7	290	648.0	6.6	25.2	21.2	871.0	0.0102	0.0389	0.0327	1.34	Included	29.0	27.0	270.0	99.5	4.9
8	285	655.3	7.6	24.6	21.3	881.0	0.0116	0.0375	0.0325	1.34	Included	28.5	26.5	265.0	99.4	4.7
9	280	638.0	8.6	23.8	20.8	853.2	0.0135	0.0373	0.0326	1.34	Included	28.0	26.0	260.0	99.3	4.7
10	275	642.0	10.0	23.9	21.1	845.1	0.0156	0.0372	0.0329	1.32	Included	27.5	25.5	255.0	99.2	4.7
11	270	649.5	11.7	24.2	20.9	854.8	0.0180	0.0373	0.0322	1.32	Included	27.0	25.0	250.0	99.1	4.7
12	265	651.9	13.6	24.3	20.6	851.2	0.0209	0.0373	0.0316	1.31	Included	26.5	24.5	245.0	99.0	4.7
13	260	739.7	17.7	27.4	22.9	951.9	0.0239	0.0370	0.0310	1.29	Included	26.0	24.0	240.0	98.8	4.7
14	255	643.9	17.7	26.3	20.4	824.8	0.0275	0.0408	0.0317	1.28	Included	25.5	23.5	235.0	98.7	5.2

15	250	650.5	20.6	29.6	20.2	828.6	0.0317	0.0455	0.0311	1.27	Included	25.0	23.0	230.0	98.5	5.8
16	245	664.2	24.0	33.7	20.5	839.3	0.0361	0.0507	0.0309	1.26	Included	24.5	22.5	225.0	98.3	6.4
17	240	679.3	27.7	38.1	20.9	848.7	0.0408	0.0561	0.0308	1.25	Included	24.0	22.0	220.0	98.0	7.1
18	235	680.0	31.6	42.2	20.9	845.6	0.0465	0.0621	0.0307	1.24	Included	23.5	21.5	215.0	97.8	7.8
19	230	663.6	34.8	45.3	20.1	814.0	0.0524	0.0683	0.0303	1.23	Included	23.0	21.0	210.0	97.5	8.6
20	225	710.4	42.1	53.0	21.5	860.8	0.0593	0.0746	0.0303	1.21	Included	22.5	20.5	205.0	97.1	9.4
21	220	705.7	47.0	57.4	20.7	841.9	0.0666	0.0813	0.0293	1.19	Included	22.0	20.0	200.0	96.8	10.3
22	215	691.3	51.8	61.4	20.4	813.1	0.0749	0.0888	0.0295	1.18	Included	21.5	19.5	195.0	96.4	11.2
23	210	726.8	60.8	69.5	20.8	841.5	0.0837	0.0956	0.0286	1.16	Included	21.0	19.0	190.0	96.0	12.1
24	205	756.0	70.6	78.2	21.7	857.9	0.0934	0.103	0.0287	1.13	Included	20.5	18.5	185.0	95.5	13.1
25	200	728.7	76.0	81.2	20.1	816.4	0.104	0.111	0.0276	1.12	Included	20.0	18.0	180.0	95.0	14.1
26	195	797.5	91.6	94.4	21.9	873.4	0.115	0.118	0.0275	1.10	Included	19.5	17.5	175.0	94.5	15.0
27	190	762.6	98.0	97.4	21.0	825.5	0.129	0.128	0.0275	1.08	Included	19.0	17.0	170.0	93.8	16.1
28	185	839.7	118.8	113.6	22.3	884.8	0.141	0.135	0.0266	1.05	Included	18.5	16.5	165.0	93.2	17.1
29	180	794.4	124.4	114.2	20.4	823.9	0.157	0.144	0.0257	1.04	Included	18.0	16.0	160.0	92.4	18.2
30	175	698.1	132.3	115.4	18.5	762.2	0.190	0.165	0.0265	1.09	Included	17.5	15.5	155.0	90.9	20.9
31	170	728.4	144.4	121.9	18.9	748.9	0.198	0.167	0.0259	1.03	Included	17.0	15.0	150.0	90.4	21.2
32	165	519.0	115.0	94.6	14.0	541.2	0.222	0.182	0.0270	1.04	Included	16.5	14.5	145.0	89.3	23.0
33	160	509.7	123.8	97.6	14.0	520.0	0.243	0.191	0.0275	1.02	Included	16.0	14.0	140.0	88.3	24.2
34	155	531.1	136.9	102.8	13.5	510.1	0.258	0.194	0.0254	0.960	Included	15.5	13.5	135.0	87.6	24.5
35	150	527.8	150.5	108.7	13.3	506.1	0.285	0.206	0.0252	0.959	Included	15.0	13.0	130.0	86.2	26.0
36	145	526.9	159.5	110.4	12.7	480.6	0.303	0.210	0.0241	0.912	Included	14.5	12.5	125.0	85.4	26.5
37	140	518.4	172.0	114.2	12.3	470.5	0.332	0.220	0.0237	0.908	Included	14.0	12.0	120.0	84.0	27.9
38	135	528.6	187.8	119.2	12.3	458.0	0.355	0.226	0.0233	0.866	Included	13.5	11.5	115.0	82.9	28.5
39	130	545.6	209.2	126.4	12.2	453.0	0.383	0.232	0.0224	0.830	Included	13.0	11.0	110.0	81.5	29.3
40	125	522.0	217.4	126.0	11.8	422.4	0.416	0.241	0.0226	0.809	Included	12.5	10.5	105.0	79.9	30.5
41	120	544.7	238.8	131.8	11.5	416.6	0.438	0.242	0.0211	0.765	Included	12.0	10.0	100.0	78.8	30.6

42	115	513.9	242.8	127.5	10.6	377.9	0.472	0.248	0.0206	0.735	Included	11.5	9.5	95.0	77.2	31.4
43	110	527.8	269.1	134.7	10.7	378.0	0.510	0.255	0.0203	0.716	Included	11.0	9.0	90.0	75.4	32.3
44	105	577.5	310.4	147.3	11.1	386.3	0.537	0.255	0.0192	0.669	Included	10.5	8.5	85.0	74.1	32.2
45	100	615.8	358.5	161.6	11.7	398.8	0.582	0.262	0.0190	0.648	Included	10.0	8.0	80.0	71.9	33.2
46	95	584.5	365.5	154.7	10.8	355.5	0.625	0.265	0.0185	0.608	Included	9.5	7.5	75.0	69.8	33.5
47	90	559.8	373.0	149.2	10.0	321.0	0.666	0.267	0.0179	0.573	Included	9.0	7.0	70.0	67.8	33.7
48	85	547.9	389.6	145.8	9.3	294.1	0.711	0.266	0.0170	0.537	Included	8.5	6.5	65.0	65.7	33.6
49	80	547.2	419.8	147.3	8.9	276.7	0.767	0.269	0.0163	0.506	Included	8.0	6.0	60.0	63.0	34.0
50	75	561.7	460.9	151.4	8.8	264.6	0.821	0.270	0.0157	0.471	Included	7.5	5.5	55.0	60.4	34.1
51	70	568.5	507.6	154.3	8.5	248.5	0.893	0.271	0.0150	0.437	Included	7.0	5.0	50.0	56.9	34.3
52	65	554.5	522.4	145.9	7.5	218.6	0.942	0.263	0.0135	0.394	Included	6.5	4.5	45.0	54.5	33.3
53	60	568.1	574.1	147.7	7.2	200.9	1.01	0.260	0.0127	0.354	Included	6.0	4.0	40.0	51.2	32.9
54	55	584.9	649.0	152.8	6.9	189.4	1.11	0.261	0.0118	0.324	Included	5.5	3.5	35.0	46.4	33.0
55	50	562.4	677.3	143.9	6.0	161.7	1.20	0.256	0.0107	0.288	Included	5.0	3.0	30.0	41.9	32.3
56	45	591.9	761.3	143.2	5.5	141.4	1.29	0.242	0.0093	0.239	Included	4.5	2.5	25.0	37.9	30.6
57	40	560.9	782.7	129.8	4.5	111.6	1.40	0.231	0.0080	0.199	Included	4.0	2.0	20.0	32.6	29.3
58	35	547.0	824.5	119.3	3.7	87.1	1.51	0.218	0.0068	0.159	Included	3.5	1.5	15.0	27.2	27.6
59	30	568.4	916.8	112.2	2.9	68.6	1.61	0.197	0.0051	0.121	Included	3.0	1.0	10.0	22.1	25.0
60	25	557.8	969.1	96.8	2.6	48.8	1.74	0.174	0.0047	0.0875	Included	2.5	0.5	5.0	16.1	21.9
61	20	758.3	1380.7	105.4	2.5	42.4	1.82	0.139	0.0033	0.0559	Included	2.0	0.0	0.0	12.1	17.6
62	15	770.7	1481.1	79.1	1.3	25.3	1.92	0.103	0.0017	0.0328	Excluded	1.5	N/A	N/A	7.2	13.0
63	10	709.9	1437.4	47.9	0.0	0.0	2.02	0.0675	0.00	0.00	Excluded	1.0	N/A	N/A	2.3	8.5
64	5	583.1	1256.4	21.6	0.0	0.0	2.15	0.0370	0.00	0.00	Excluded	0.5	N/A	N/A	-4.0	4.7
65	0	571.0	1212.7	8.8	0.0	0.0	2.12	0.0154	0.00	0.00	Excluded	0.0	N/A	N/A	-2.5	1.9

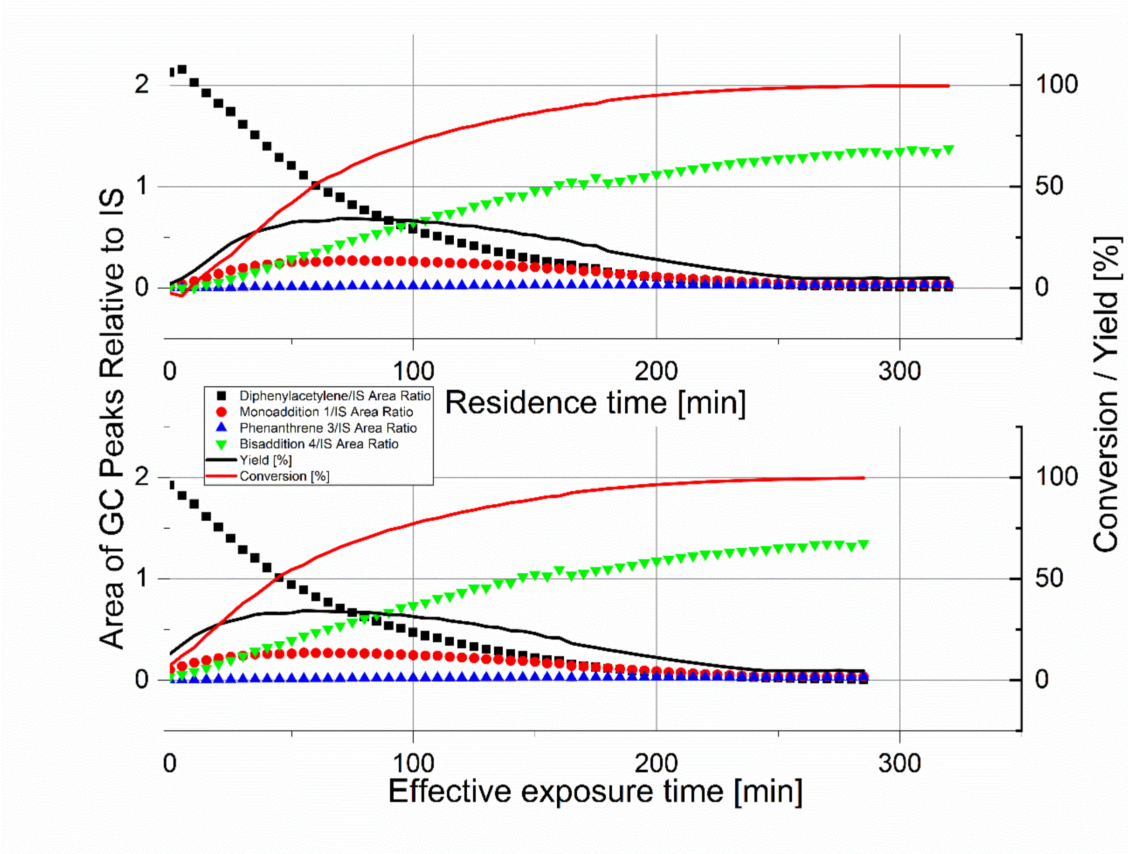


Figure S 7. Results of Switch-Off optimisation of [2+2] photoreaction using UV-B light. Top: Reaction components relative GC areas, conversion, and yield plotted against uncorrected residence time. Bottom: Reaction components GC areas, conversion, and yield plotted against exposure time, corrected for light inhomogeneity.

2. 2. 2. 2. Switch-Off experiment results using UV-C light:

Diphenylacetylene (750.0 mg, 4.2 mmol, 1.0 eq., 56.1 mM solution) and veratrole (IS, 607.0 mg, 0.56 mL, 4.4 mmol, 1.05 eq., 58.6 mM solution) were dissolved in 3,4-dihydro-2*H*-pyran (75.0 mL, 100.0 vol.) and connected to a flow reagent stream. 3,4-Dihydro-2*H*-pyran was connected to a flow solvent stream. The UV-C lamp (PISCES PLL 36W) and water cooling were then turned on and system was allowed to equilibrate for 30 minutes. Then reaction mixture was injected into the photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA). Effective exposure time was set to 105 minutes (which corresponds to 0.277 mL/min flow rate). Once the photoreactor was filled with reaction mixture, the UV lamp was switched off, the pump was switched to solvent stream, the reaction mixture was eluted from the photoreactor, and was collected into vials (0.5 mL of reaction mixture, diluted to 1.0 mL with acetone). Collected samples were then analysed using off-line GC.

Table S 5. Results of Switch-Off optimisation performed for [2+2] photocycloaddition of diphenylacetylene and 3,4-dihydro-2H-pyran using UV-C light.

Vial	Residence time [min]	IS GC Area	Diphenylacetylene GC Area	Mono addition 1 GC Area	Phenanthrene 3 GC Area	Bisaddition 4 GC Area	Diphenyl acetylene/IS Area Ratio	Mono addition 1/IS Area Ratio	Phenanthrene /IS Area Ratio	Bis addition 4/IS Area Ratio	Datapoint included or excluded from analysis	Reactor volume [mL]	Effective reactor volume [mL]	Effective exposure time [min]	Conversion [%]	Yield [%]
1	115.0	251.4	0.0	226.6	47.6	2.7	0.00	0.901	0.189	0.0107	Excluded	31.86	N/A	N/A	97.2	61.3
2	113.4	188.0	0.0	169.4	37.7	1.8	0.00	0.901	0.201	0.00957	Excluded	31.41	N/A	N/A	97.2	61.3
3	111.8	188.7	0.0	170.9	38.4	2.1	0.00	0.906	0.203	0.0111	Excluded	30.97	N/A	N/A	97.2	61.6
4	110.2	207.5	0.0	188.7	42.9	2.3	0.00	0.909	0.207	0.0111	Included	30.53	28.81	104.00	97.2	61.9
5	108.6	202.3	0.0	188.1	43.0	2.4	0.00	0.930	0.213	0.0119	Included	30.08	28.36	102.40	97.2	63.3
6	107.0	213.7	0.0	198.0	45.0	2.4	0.00	0.927	0.211	0.0112	Included	29.64	27.92	100.80	97.2	63.0
7	105.4	200.2	0.0	186.1	42.4	2.3	0.00	0.930	0.212	0.0115	Included	29.20	27.48	99.20	97.2	63.2
8	103.8	220.8	0.0	204.4	47.3	2.5	0.00	0.926	0.214	0.0113	Included	28.75	27.04	97.60	97.2	63.0
9	102.2	199.2	0.0	186.3	41.0	2.2	0.00	0.935	0.206	0.0110	Included	28.31	26.59	96.00	97.2	63.6
10	100.6	213.7	0.0	199.9	44.5	2.4	0.00	0.935	0.208	0.0112	Included	27.87	26.15	94.40	97.2	63.6
11	99.0	227.2	0.0	215.0	46.7	2.6	0.00	0.946	0.206	0.0114	Included	27.42	25.71	92.80	97.2	64.4
12	97.4	220.3	0.0	209.5	45.6	2.4	0.00	0.951	0.207	0.0109	Included	26.98	25.26	91.20	97.2	64.7
13	95.8	244.0	0.0	230.8	49.4	2.7	0.00	0.946	0.202	0.0111	Included	26.54	24.82	89.60	97.2	64.4
14	94.2	237.6	0.0	226.3	48.2	2.6	0.00	0.952	0.203	0.0109	Included	26.09	24.38	88.00	97.2	64.8
15	92.6	227.7	0.0	219.3	45.3	2.5	0.00	0.963	0.199	0.0110	Included	25.65	23.93	86.40	97.2	65.5
16	91.0	246.1	0.0	239.4	49.2	2.7	0.00	0.973	0.200	0.0110	Included	25.21	23.49	84.80	97.2	66.2
17	89.4	230.6	1.3	223.7	46.0	2.5	0.00564	0.970	0.199	0.0108	Included	24.76	23.05	83.20	96.7	66.0
18	87.8	238.6	1.5	232.9	46.7	2.5	0.00629	0.976	0.196	0.0105	Included	24.32	22.60	81.60	96.7	66.4
19	86.2	261.2	1.8	254.8	49.8	2.7	0.00689	0.975	0.191	0.0103	Included	23.88	22.16	80.00	96.6	66.4

20	84.6	254.3	1.9	251.0	48.4	2.6	0.00747	0.987	0.190	0.0102	Included	23.43	21.72	78.40	96.6	67.2
21	83.0	250.7	2.0	250.5	46.8	2.6	0.00798	0.999	0.187	0.0104	Included	22.99	21.27	76.80	96.5	68.0
22	81.4	243.3	2.4	243.9	43.4	2.4	0.00986	1.00	0.178	0.00986	Included	22.55	20.83	75.20	96.4	68.2
23	79.8	247.6	2.6	250.5	44.0	2.4	0.0105	1.01	0.178	0.00969	Included	22.10	20.39	73.60	96.3	68.8
24	78.2	273.4	3.3	279.6	46.1	2.6	0.0121	1.02	0.169	0.00951	Included	21.66	19.94	72.00	96.2	69.6
25	76.6	256.2	3.4	265.3	43.2	2.3	0.0133	1.04	0.169	0.00898	Included	21.22	19.50	70.40	96.1	70.5
26	75.0	264.8	4.0	274.9	42.7	2.4	0.0151	1.04	0.161	0.00906	Included	20.78	19.06	68.80	95.9	70.6
27	73.4	231.8	4.0	242.5	36.2	2.0	0.0173	1.05	0.156	0.00863	Included	20.33	18.61	67.20	95.7	71.2
28	71.8	229.9	4.4	240.3	34.6	1.9	0.0191	1.05	0.151	0.00826	Included	19.89	18.17	65.60	95.5	71.1
29	70.2	235.6	5.1	249.2	34.7	1.9	0.0216	1.06	0.147	0.00806	Included	19.45	17.73	64.00	95.3	72.0
30	68.6	238.5	6.2	254.9	33.8	1.9	0.0260	1.07	0.142	0.00797	Included	19.00	17.28	62.40	94.9	72.7
31	67.0	243.3	7.0	258.6	32.8	1.8	0.0288	1.06	0.135	0.00740	Included	18.56	16.84	60.80	94.7	72.3
32	65.4	259.6	8.5	277.9	33.6	1.9	0.0327	1.07	0.129	0.00732	Included	18.12	16.40	59.20	94.3	72.8
33	63.8	277.2	10.5	300.4	34.2	1.9	0.0379	1.08	0.123	0.00685	Included	17.67	15.96	57.60	93.9	73.7
34	62.2	263.7	11.4	286.7	32.1	1.7	0.0432	1.09	0.122	0.00645	Included	17.23	15.51	56.00	93.4	74.0
35	60.6	258.6	12.4	279.5	29.9	1.6	0.0480	1.08	0.116	0.00619	Included	16.79	15.07	54.40	93.0	73.5
36	59.0	242.6	13.3	262.2	26.3	1.5	0.0548	1.08	0.108	0.00618	Included	16.34	14.63	52.80	92.4	73.5
37	57.4	262.7	15.9	281.8	26.9	1.5	0.0605	1.07	0.102	0.00571	Included	15.90	14.18	51.20	91.9	73.0
38	55.8	256.0	17.4	271.4	24.6	1.2	0.0680	1.06	0.0961	0.00469	Included	15.46	13.74	49.60	91.2	72.1
39	54.2	302.3	23.2	328.2	29.3	1.6	0.0767	1.09	0.0969	0.00529	Included	15.01	13.30	48.00	90.5	73.9
40	52.6	324.1	27.9	353.6	29.8	1.6	0.0861	1.09	0.0919	0.00494	Included	14.57	12.85	46.40	89.7	74.2
41	51.0	320.5	31.8	351.7	28.0	1.5	0.0992	1.10	0.0874	0.00468	Included	14.13	12.41	44.80	88.5	74.7
42	49.4	294.5	31.9	317.3	24.4	1.4	0.108	1.08	0.0829	0.00475	Included	13.68	11.97	43.20	87.7	73.3
43	47.8	295.4	35.0	317.7	23.6	1.2	0.118	1.08	0.0799	0.00406	Included	13.24	11.52	41.60	86.8	73.2
44	46.2	322.5	41.8	343.8	24.4	1.3	0.130	1.07	0.0757	0.00403	Included	12.80	11.08	40.00	85.8	72.5
45	44.6	304.5	42.9	319.8	22.0	1.2	0.141	1.05	0.0722	0.00394	Included	12.35	10.64	38.40	84.8	71.5
46	43.0	339.9	52.9	357.2	23.3	1.3	0.156	1.05	0.0685	0.00382	Included	11.91	10.19	36.80	83.5	71.5

47	41.4	298.8	51.2	307.2	19.5	1.1	0.171	1.03	0.0653	0.00368	Included	11.47	9.75	35.20	82.1	69.9
48	39.8	290.0	54.2	295.7	17.6	0.0	0.187	1.02	0.0607	0.00	Included	11.02	9.31	33.60	80.8	69.4
49	38.2	311.2	63.9	311.1	17.7	0.0	0.205	1.000	0.0569	0.00	Included	10.58	8.86	32.00	79.2	68.0
50	36.6	332.4	76.2	327.1	17.3	0.0	0.229	0.984	0.0520	0.00	Included	10.14	8.42	30.40	77.1	67.0
51	35.0	302.0	75.3	294.0	14.8	0.0	0.249	0.974	0.0490	0.00	Included	9.70	7.98	28.80	75.3	66.2
52	33.4	330.8	89.5	312.8	13.8	0.0	0.271	0.946	0.0417	0.00	Included	9.25	7.53	27.20	73.4	64.3
53	31.8	299.3	89.4	277.4	11.9	0.0	0.299	0.927	0.0398	0.00	Included	8.81	7.09	25.60	70.9	63.1
54	30.2	334.3	108.1	304.4	12.4	0.0	0.323	0.911	0.0371	0.00	Included	8.37	6.65	24.00	68.8	62.0
55	28.6	327.4	114.0	284.3	10.9	0.0	0.348	0.868	0.0333	0.00	Included	7.92	6.20	22.40	66.6	59.1
56	27.0	330.1	124.8	279.4	10.1	0.0	0.378	0.846	0.0306	0.00	Included	7.48	5.76	20.80	64.0	57.6
57	25.4	334.9	137.0	271.2	9.4	0.0	0.409	0.810	0.0281	0.00	Included	7.04	5.32	19.20	61.2	55.1
58	23.8	309.6	138.8	244.1	7.5	0.0	0.448	0.788	0.0242	0.00	Included	6.59	4.88	17.60	57.8	53.6
59	22.2	304.9	147.2	225.3	7.1	0.0	0.483	0.739	0.0233	0.00	Included	6.15	4.43	16.00	54.7	50.3
60	20.6	312.6	161.6	216.7	6.2	0.0	0.517	0.693	0.0198	0.00	Included	5.71	3.99	14.40	51.7	47.2
61	19.0	336.2	192.1	223.7	5.6	0.0	0.571	0.665	0.0167	0.00	Included	5.26	3.55	12.80	46.9	45.3
62	17.4	339.5	206.5	205.7	4.8	0.0	0.608	0.606	0.0141	0.00	Included	4.82	3.10	11.20	43.7	41.22
63	15.8	351.1	230.0	196.4	4.4	0.0	0.655	0.559	0.0125	0.00	Included	4.38	2.66	9.60	39.6	38.06
64	14.2	320.0	222.1	160.9	3.2	0.0	0.694	0.503	0.0100	0.00	Included	3.93	2.22	8.00	36.1	34.21
65	12.6	374.8	278.9	168.3	2.5	0.0	0.744	0.449	0.00667	0.00	Included	3.49	1.77	6.40	31.7	30.55
66	11.0	308.6	247.2	122.8	2.0	0.0	0.801	0.398	0.00648	0.00	Included	3.05	1.33	4.80	26.7	27.07
67	9.4	326.7	274.6	109.9	1.7	0.0	0.841	0.336	0.00520	0.00	Included	2.60	0.89	3.20	23.2	22.89
68	7.8	328.9	294.0	90.7	1.2	0.0	0.894	0.276	0.00365	0.00	Included	2.16	0.44	1.60	18.5	18.76
69	6.2	338.10	321.30	72.70	0.00	0.00	0.95	0.22	0.00	0.00	Included	1.72	0.00	0.00	13.6	14.63
70	4.6	349.70	346.50	56.20	0.00	0.00	0.99	0.16	0.00	0.00	Excluded	1.27	N/A	N/A	10.0	10.93
71	3.0	390.50	407.80	43.30	0.00	0.00	1.04	0.11	0.00	0.00	Excluded	0.83	N/A	N/A	5.3	7.54
72	1.4	297.30	319.90	21.40	0.00	0.00	1.08	0.07	0.00	0.00	Excluded	0.39	N/A	N/A	2.5	4.90

73	-0.2	356.60	393.90	16.10	0.00	0.00	1.10	0.05	0.00	0.00	Excluded	-0.06	N/A	N/A	0.0	3.07

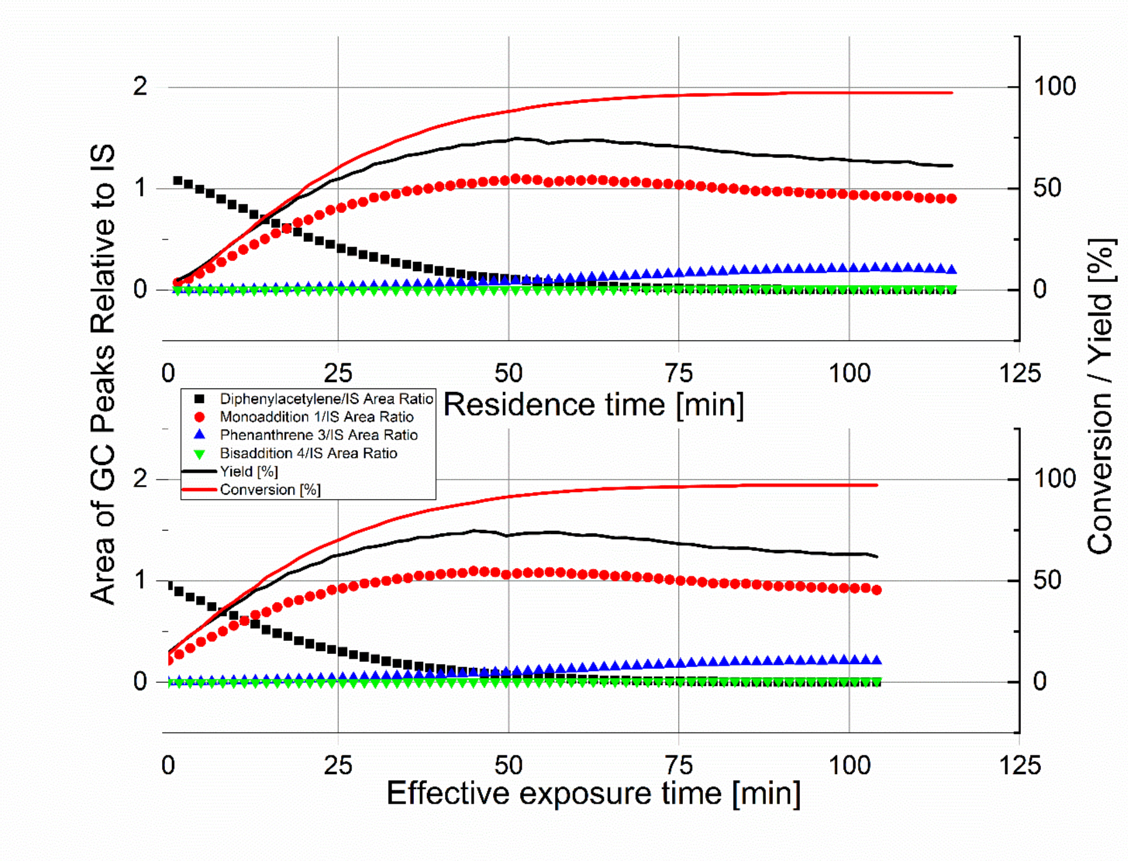


Figure S 8. Results of Switch-Off optimisation of [2+2] photoreaction using UV-C light. Top: Reaction components absolute GC areas, conversion, and yield plotted against uncorrected residence time. Bottom: Reaction components GC areas, conversion, and yield plotted against exposure time, corrected for light inhomogeneity.

2. 2. 3. Validation of Switch-Off results obtained in [2+2] photocycloaddition of 3,4-dihydro-2*H*-pyran an diphenylacetylene

Two validation experiments were performed, first utilizing UV-B light source and second utilizing UV-C light source with optimum effective exposure times of 50 minutes and 43 minutes, respectively, obtained from the switch-Off optimisation experiments.

2. 2. 3. 1. Irradiation over 50 minutes of effective exposure time under UV-B light

Diphenylacetylene (250.0 mg, 1.40 mmol, 56.1 mM solution) was dissolved in 3,4-dihydro-2*H*-pyran (25.0 mL, 100.0 vol.) and the mixture was injected into photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA) equipped with UV-B lamp (Philips PL-L 36W/01/4P). Irradiation over 50 minutes of effective exposure time was set (corresponding to 0.489 mL/min total flow rate). After injection of 20.0 mL, reaction mixture was eluted from photoreactor using pure 3,4-dihydro-2*H*-pyran, reaction mixture was then collected, solvent was removed, and obtained material was initially purified by column chromatography (SiO_2; *n*-hexane:AcOEt 10:0 to 9:1). Fractions containing product were combined, solvent was removed, remaining residue was dried *in vacuo,* and 7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene was obtained as a yellow dense oil (134.5 mg, 0.52 mmol, 36.8% yield). NMR data was consisted with literature.[1]

2. 2. 3. 2. Irradiation over 43 minutes of effective exposure time under UV-C light

Diphenylacetylene (1.51 g, 8.47 mmol, 0.056 M solution) was dissolved in 3,4-dihydro-2*H*-pyran (150.0 mL, 100.0 vol.) and the mixture was injected into photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA) equipped with UV-C lamp (DuraBulb 36W UV-C 253.7 nm). Irradiation over 43 minutes of effective exposure time was set (corresponding to 0.670 mL/min total flow rate). After injection of 145.0 mL, reaction mixture was eluted from photoreactor using pure 3,4-dihydro-2*H*-pyran, reaction mixture was then collected, solvent was removed, and obtained material was initially purified by flash chromatography (SiO_2; *n*-hexane:AcOEt 9:1), and then by automated column chromatography system (Biotage Selekt, Biotage HP-Sphere 25 micron). Fractions containing product were combined, solvent was removed, remaining residue was dried *in vacuo,* and 7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene was obtained as slightly yellow dense oil (1.521 g, 5.80 mmol, 70.8% yield). NMR data was consistent with literature.[1]

2. 3. [2+2] photocycloaddition of cyclohex-2-enone and 1,1,2,2-tetramethylethylene

An example of GC chromatogram containing all studied components of the [2+2] photocycloaddition between cyclohex-2-enone and tetramethylethylene with their respective retention times is presented below (Figure S 9. GC chromatogram of a [2+2] photoreaction between cyclohex-2-enone and tetramethylethylene with studied components and their respective retention times.).

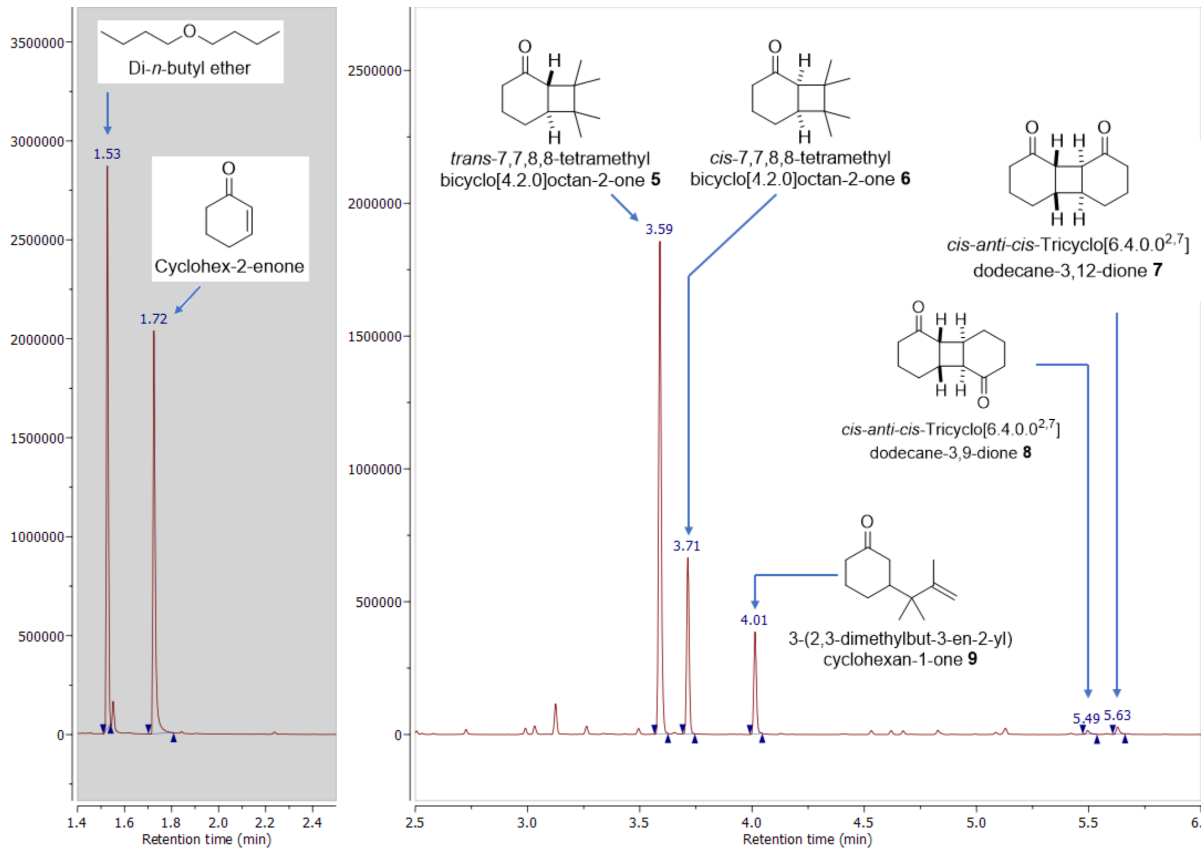


Figure S 9. GC chromatogram of a [2+2] photoreaction between cyclohex-2-enone and tetramethylethylene with studied components and their respective retention times.

2. 3. 1. Calibration curve for determination of compounds 5 and 6 yields using GC-FID monitoring:
Sample solutions of dibutyl ether (internal standard) and 7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (photocycloaddition products **5** and **6**) were prepared accordingly to the table below and were then measured using GC-FID. Calibration curve was then prepared by plotting the ratios of phenanthrene and IS areas against molar ratios of phenanthrene and IS.

Table S 6. Calibration table of GC-FID for [2+2] photoreaction between cyclohex-2-enone and tetramethylethylene.

Sample	Mass of diastereoisomers (**5** and **6**) [mg]	Mass of IS [mg]	Moles of diastereoisomers (**5** and **6**) [mol]		Moles of IS [mol]	**Molar ratio of diastereoisomers (5 and 6) and IS**	Area of diastereoisomers (**5** and **6**) peak	Area of IS peak	**Area ratio of diastereoisomers (5 and 6) and IS**
1	3.9	3.0	$2.15\cdot10^{-5}$		$2.33\cdot10^{-5}$	**1.53616**	1072.73	698.32	**0.92497**
2	3.6	1.6	$1.97\cdot10^{-5}$		$1.21\cdot10^{-5}$	**2.69157**	1004.28	373.12	**1.63331**
3	1.3	2.9	$7.38\cdot10^{-5}$		$2.22\cdot10^{-5}$	**0.50536**	373.32	738.72	**0.33242**
4	0.9	1.4	$4.71\cdot10^{-5}$		$1.04\cdot10^{-5}$	**0.75313**	246.53	327.34	**0.45480**

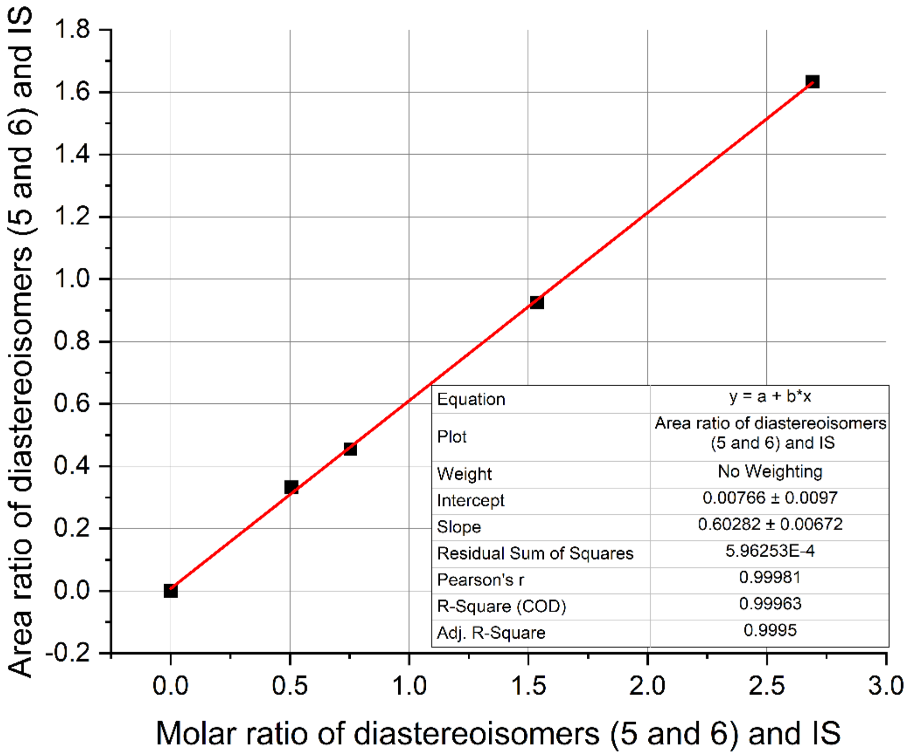


*Figure S 10. GC-FID calibration curve of 7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one **5** and **6**.*

2. 3. 2. Cyclohex-2-enone and tetramethylethylene [2+2] photoreaction Switch-Off optimisations results

2. 3. 2. 1. Switch-Off experiment results using UV-A light

Cyclohex-2-enone (125.0 µL, 124.0 mg, 1.3 mmol, 1.0 eq., 25.8 mM solution), dibutyl ether (0.19 mL, 146.0 mg, 1.1 mmol, 0.85 eq., 22.4 mmol solution), and tetramethylethylene (3.01 mL, 2.13 g, 25.3 mmol, 19.6 eq., 505.7 mM solution) were dissolved in anhydrous acetonitrile (47.9 mL, 386.3 vol.). Obtained solution was sonicated under high nitrogen flow for 30 minutes and was then connected to flow reagents stream. Anhydrous acetonitrile, sonicated under high nitrogen flow for 30 minutes, was connected to flow solvents stream. The UV-A lamp (Philips PLL 36W) and water cooling were then turned on and system was allowed to equilibrate for 30 minutes. Then reaction mixture was injected into the photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA). Effective exposure time was set to 239 minutes (which corresponds to 0.133 mL/min flow rate). Once the photoreactor was filled with reaction mixture, the UV lamp was switched off, the pump was switched to solvent stream, the reaction mixture was eluted from the photoreactor, and was collected into vials (0.375 mL of reaction mixture, diluted to 1.0 mL with acetone). Collected samples were then analysed using off-line GC.

Table S 7. Results of Switch-Off optimisation performed for [2+2] photocycloaddition of cyclohex-2-enone and tetramethylethylene using UV-A light.

Vial	Residence time	Cyclohex-2-enone GC Area	Diastereoisomer 5 GC Area	Diastereoisomer 6 GC Area	Norrish type II product 9 GC Area	Homodimers 7 and 8 GC Area	IS Area	Cyclohex-enone/IS Area ratio	Diastereoisomers 5 and 6/IS Area Ratio	Norrish type II product 9/IS Area Ratio	Homodimers 7 and 8/IS Area Ratio	Conversion [%]	Diastereoisomers 5 and 6 concentration [M]	Diastereoisomers 5 and 6 yield [%]	Lamp Efficiency [%]	Exposure time [min]
1	239.1	0.0	127.3	6.3	27.2	0.0	146.6	0.00	0.911	0.186	0.00	100.0	$3.28\cdot10^{-3}$	47.7	0.0	235.7
2	236.3	0.0	151.5	7.6	32.2	0.0	174.1	0.00	0.914	0.185	0.00	100.0	$3.29\cdot10^{-3}$	47.8	3.4	235.7
3	233.5	0.0	147.4	7.4	31.6	0.0	169.0	0.00	0.916	0.187	0.00	100.0	$3.30\cdot10^{-3}$	48.0	15.0	235.5
4	230.6	0.0	165.2	8.2	35.1	0.0	199.6	0.00	0.869	0.176	0.00	100.0	$3.13\cdot10^{-3}$	45.5	26.6	235.1
5	227.8	0.0	146.2	7.4	31.3	0.0	183.4	0.00	0.838	0.171	0.00	100.0	$3.02\cdot10^{-3}$	43.8	49.7	234.3
6	225.0	0.0	155.3	7.9	33.4	0.0	196.2	0.00	0.832	0.170	0.00	100.0	$2.99\cdot10^{-3}$	43.5	70.8	232.9
7	222.2	0.0	157.8	8.1	34.0	0.0	194.4	0.00	0.853	0.175	0.00	100.0	$3.07\cdot10^{-3}$	44.7	77.9	230.9
8	219.4	0.0	157.2	8.2	34.1	0.0	194.1	0.00	0.852	0.176	0.00	100.0	$3.07\cdot10^{-3}$	44.6	85.0	228.7
9	216.5	0.0	156.5	8.3	33.7	0.0	192.8	0.00	0.855	0.175	0.00	100.0	$3.08\cdot10^{-3}$	44.7	93.4	226.3
10	213.7	0.0	159.1	8.6	34.3	0.0	193.7	0.00	0.866	0.177	0.00	100.0	$3.12\cdot10^{-3}$	45.3	98.7	223.6
11	210.9	0.0	156.2	8.6	34.0	0.0	178.7	0.00	0.922	0.190	0.00	100.0	$3.32\cdot10^{-3}$	48.3	100.7	220.8
12	208.1	0.0	160.0	9.1	34.9	0.0	183.5	0.00	0.922	0.190	0.00	100.0	$3.32\cdot10^{-3}$	48.2	102.7	218.0
13	205.3	0.0	169.0	9.8	36.9	0.0	192.2	0.00	0.930	0.192	0.00	100.0	$3.35\cdot10^{-3}$	48.7	104.5	215.1
14	202.4	0.0	155.3	9.2	34.0	0.0	175.6	0.00	0.937	0.194	0.00	100.0	$3.37\cdot10^{-3}$	49.0	105.5	212.2
15	199.6	0.0	169.6	10.3	36.9	0.0	189.8	0.00	0.948	0.194	0.00	100.0	$3.41\cdot10^{-3}$	49.6	105.1	209.2
16	196.8	0.0	158.9	9.8	34.7	0.0	181.6	0.00	0.929	0.191	0.00	100.0	$3.34\cdot10^{-3}$	48.6	104.7	206.2

17	194.0	0.0	180.4	11.5	39.3	0.0	200.9	0.00	0.955	0.196	0.00	100.0	$3.44\cdot10^{-3}$	50.0	103.7	203.3
18	191.2	0.0	167.5	10.9	36.9	0.0	186.5	0.00	0.957	0.198	0.00	100.0	$3.44\cdot10^{-3}$	50.1	104.8	200.3
19	188.3	0.0	164.5	11.0	36.1	0.0	185.2	0.00	0.948	0.195	0.00	100.0	$3.41\cdot10^{-3}$	49.6	106.2	197.4
20	185.5	0.0	169.5	11.8	37.3	0.0	189.6	0.00	0.956	0.197	0.00	100.0	$3.44\cdot10^{-3}$	50.1	107.5	194.4
21	182.7	0.0	171.5	12.3	37.6	1.2	191.0	0.00	0.962	0.197	0.00628	100.0	$3.46\cdot10^{-3}$	50.4	109.6	191.4
22	179.9	0.0	170.6	12.6	37.7	1.3	189.9	0.00	0.965	0.199	0.00685	100.0	$3.47\cdot10^{-3}$	50.5	111.1	188.3
23	177.1	0.0	169.9	13.0	37.5	1.1	198.1	0.00	0.923	0.189	0.00555	100.0	$3.32\cdot10^{-3}$	48.3	111.4	185.1
24	174.2	0.0	191.7	15.2	42.1	1.4	220.0	0.00	0.940	0.191	0.00636	100.0	$3.39\cdot10^{-3}$	49.2	111.8	182.0
25	171.4	0.0	173.7	14.2	38.5	1.3	200.0	0.00	0.940	0.193	0.00650	100.0	$3.38\cdot10^{-3}$	49.2	112.6	178.9
26	168.6	0.0	163.5	13.8	36.1	1.2	191.0	0.00	0.928	0.189	0.00628	100.0	$3.34\cdot10^{-3}$	48.6	113.0	175.7
27	165.8	0.0	177.1	15.6	39.4	1.4	204.8	0.00	0.941	0.192	0.00684	100.0	$3.39\cdot10^{-3}$	49.3	113.2	172.5
28	163.0	0.0	178.2	16.2	39.3	1.4	208.2	0.00	0.934	0.189	0.00672	100.0	$3.36\cdot10^{-3}$	48.9	113.4	169.3
29	160.2	0.0	177.3	16.8	39.2	1.4	205.4	0.00	0.945	0.191	0.00682	100.0	$3.40\cdot10^{-3}$	49.5	113.5	166.1
30	157.3	0.0	174.3	17.1	38.6	1.4	200.0	0.00	0.957	0.193	0.00700	100.0	$3.45\cdot10^{-3}$	50.1	113.6	162.9
31	154.5	0.0	187.8	19.1	41.4	1.6	215.0	0.00	0.962	0.193	0.00744	100.0	$3.46\cdot10^{-3}$	50.4	113.8	159.7
32	151.7	0.0	175.7	18.5	38.8	1.6	201.1	0.00	0.966	0.193	0.00796	100.0	$3.48\cdot10^{-3}$	50.6	114.0	156.5
33	148.9	0.0	178.9	19.6	39.4	1.6	203.2	0.00	0.977	0.194	0.00787	100.0	$3.52\cdot10^{-3}$	51.1	114.1	153.3
34	146.1	0.0	180.0	20.5	39.9	1.7	205.0	0.00	0.978	0.195	0.00829	100.0	$3.52\cdot10^{-3}$	51.2	114.2	150.1
35	143.2	0.0	179.8	21.2	39.6	1.7	205.7	0.00	0.977	0.193	0.00826	100.0	$3.52\cdot10^{-3}$	51.2	114.3	146.9
36	140.4	0.0	189.7	23.4	41.7	1.9	215.0	0.00	0.991	0.194	0.00884	100.0	$3.57\cdot10^{-3}$	51.9	114.1	143.7
37	137.6	0.0	190.5	24.3	42.0	2.0	215.0	0.00	0.999	0.195	0.00930	100.0	$3.60\cdot10^{-3}$	52.3	114.7	140.5
38	134.8	0.0	182.4	24.2	40.1	1.9	205.0	0.00	1.01	0.196	0.00927	100.0	$3.63\cdot10^{-3}$	52.8	114.7	137.3
39	132.0	0.0	176.2	24.3	38.6	1.9	200.0	0.00	1.00	0.193	0.00950	100.0	$3.61\cdot10^{-3}$	52.5	114.8	134.0
40	129.1	0.0	190.9	27.4	41.7	2.0	215.0	0.00	1.02	0.194	0.00930	100.0	$3.66\cdot10^{-3}$	53.2	114.6	130.8
41	126.3	0.0	200.2	30.0	43.6	2.2	222.4	0.00	1.04	0.196	0.00989	100.0	$3.73\cdot10^{-3}$	54.2	114.6	127.6
42	123.5	0.0	193.2	30.1	42.0	2.2	214.0	0.00	1.04	0.196	0.0103	100.0	$3.76\cdot10^{-3}$	54.6	114.8	124.4
43	120.7	0.0	182.8	29.7	39.7	2.2	204.8	0.00	1.04	0.194	0.0107	100.0	$3.74\cdot10^{-3}$	54.3	114.9	121.1
44	117.9	0.0	195.1	33.0	42.2	2.3	216.0	0.00	1.06	0.195	0.0106	100.0	$3.80\cdot10^{-3}$	55.3	114.8	117.9
45	115.0	0.0	182.9	32.2	39.5	2.2	205.8	0.00	1.05	0.192	0.0107	100.0	$3.76\cdot10^{-3}$	54.7	114.8	114.7

46	112.2	0.0	183.0	33.6	39.3	2.3	203.2	0.00	1.07	0.193	0.0113	100.0	$3.84\cdot10^{-3}$	55.8	114.9	111.5
47	109.4	0.0	186.9	35.7	40.0	2.4	207.3	0.00	1.07	0.193	0.0116	100.0	$3.87\cdot10^{-3}$	56.2	115.0	108.2
48	106.6	0.0	193.0	38.4	41.4	4.2	213.1	0.00	1.09	0.194	0.0197	100.0	$3.91\cdot10^{-3}$	56.8	114.4	105.0
49	103.8	0.0	184.9	38.3	39.1	4.0	205.1	0.00	1.09	0.191	0.0195	100.0	$3.92\cdot10^{-3}$	57.0	115.0	101.8
50	100.9	0.0	180.6	39.0	38.4	2.5	200.3	0.00	1.10	0.192	0.0125	100.0	$3.95\cdot10^{-3}$	57.4	115.0	98.6
51	98.1	0.0	198.4	44.6	42.1	4.4	216.6	0.00	1.12	0.194	0.0203	100.0	$4.04\cdot10^{-3}$	58.7	114.9	95.3
52	95.3	0.0	182.5	42.7	38.2	4.2	200.9	0.00	1.12	0.190	0.0209	100.0	$4.04\cdot10^{-3}$	58.7	114.8	92.1
53	92.5	0.0	189.3	46.1	40.0	4.6	205.0	0.00	1.15	0.195	0.0224	100.0	$4.13\cdot10^{-3}$	60.1	114.8	88.9
54	89.7	0.0	199.2	50.6	41.7	4.9	215.0	0.00	1.16	0.194	0.0228	100.0	$4.18\cdot10^{-3}$	60.8	114.7	85.7
55	86.8	0.0	188.1	49.9	39.7	4.7	204.3	0.00	1.16	0.194	0.0230	100.0	$4.19\cdot10^{-3}$	61.0	114.6	82.5
56	84.0	0.0	184.8	51.1	39.1	4.7	201.4	0.00	1.17	0.194	0.0233	100.0	$4.22\cdot10^{-3}$	61.3	114.7	79.3
57	81.2	0.0	192.3	55.3	39.4	5.0	210.7	0.00	1.18	0.187	0.0237	100.0	$4.23\cdot10^{-3}$	61.5	114.7	76.0
58	78.4	0.0	189.9	56.9	39.0	5.0	206.3	0.00	1.20	0.189	0.0242	100.0	$4.31\cdot10^{-3}$	62.6	114.5	72.8
59	75.6	0.0	191.3	59.6	39.8	5.3	208.4	0.00	1.20	0.191	0.0254	100.0	$4.33\cdot10^{-3}$	63.0	114.3	69.6
60	72.7	0.0	192.5	62.6	39.8	5.3	207.0	0.00	1.23	0.192	0.0256	100.0	$4.44\cdot10^{-3}$	64.5	114.1	66.4
61	69.9	0.0	195.7	66.3	40.2	5.6	212.8	0.00	1.23	0.189	0.0263	100.0	$4.43\cdot10^{-3}$	64.5	113.8	63.3
62	67.1	0.0	187.1	65.7	38.1	5.4	206.8	0.00	1.22	0.184	0.0261	100.0	$4.40\cdot10^{-3}$	64.0	113.4	60.1
63	64.3	2.4	192.9	70.5	39.2	5.8	213.6	0.0112	1.23	0.184	0.0272	98.8	$4.44\cdot10^{-3}$	64.6	112.7	56.9
64	61.5	3.3	190.7	72.2	38.4	5.8	209.7	0.0157	1.25	0.183	0.0277	98.3	$4.51\cdot10^{-3}$	65.6	111.6	53.8
65	58.6	4.2	182.4	71.4	36.6	5.8	200.0	0.0210	1.27	0.183	0.0290	97.7	$4.57\cdot10^{-3}$	66.4	110.7	50.7
66	55.8	6.2	189.9	76.7	37.9	6.3	216.4	0.0287	1.23	0.175	0.0291	96.8	$4.44\cdot10^{-3}$	64.5	109.8	47.6
67	53.0	8.1	186.0	77.5	36.9	6.3	209.9	0.0386	1.26	0.176	0.0300	95.7	$4.52\cdot10^{-3}$	65.7	108.9	44.5
68	50.2	11.8	201.9	86.4	40.0	7.3	230.0	0.0513	1.25	0.174	0.0317	94.3	$4.51\cdot10^{-3}$	65.6	109.4	41.5
69	47.4	14.3	180.6	79.0	35.5	6.8	213.5	0.0670	1.22	0.166	0.0319	92.6	$4.38\cdot10^{-3}$	63.7	110.4	38.5
70	44.5	18.2	171.1	76.7	33.6	6.5	207.4	0.0878	1.19	0.162	0.0313	90.3	$4.30\cdot10^{-3}$	62.5	110.1	35.4
71	41.7	24.1	167.1	76.5	32.7	6.6	217.7	0.111	1.12	0.150	0.0303	87.7	$4.03\cdot10^{-3}$	58.6	111.3	32.4
72	38.9	34.1	171.9	80.3	33.9	7.2	229.5	0.149	1.10	0.148	0.0314	83.5	$3.96\cdot10^{-3}$	57.5	111.4	29.3
73	36.1	37.9	141.5	67.1	27.6	6.0	205.0	0.185	1.02	0.135	0.0293	79.5	$3.66\cdot10^{-3}$	53.3	111.1	26.3
74	33.3	48.1	130.9	63.1	25.7	6.0	205.0	0.235	0.946	0.125	0.0293	73.9	$3.41\cdot10^{-3}$	49.5	110.7	23.2

75	30.5	62.9	119.4	58.2	23.2	5.5	212.6	0.296	0.835	0.109	0.0259	67.1	$3.01 \cdot 10^{-3}$	43.7	109.0	20.2
76	27.6	73.1	100.7	49.7	19.7	4.8	209.2	0.349	0.719	0.0942	0.0229	61.2	$2.59 \cdot 10^{-3}$	37.6	105.9	17.3
77	24.8	86.8	83.9	41.6	16.6	2.6	206.4	0.421	0.608	0.0804	0.0126	53.3	$2.19 \cdot 10^{-3}$	31.8	103.0	14.4
78	22.0	106.3	71.6	35.7	14.2	2.3	198.3	0.536	0.541	0.0716	0.0116	40.5	$1.95 \cdot 10^{-3}$	28.3	100.1	11.7
79	19.2	127.5	56.9	28.6	11.2	1.8	224.6	0.568	0.381	0.0499	0.00801	36.9	$1.37 \cdot 10^{-3}$	19.9	91.5	9.1
80	16.4	140.0	41.0	20.8	8.2	0.0	216.1	0.648	0.286	0.0379	0.00	28.0	$1.03 \cdot 10^{-3}$	15.0	78.3	6.7
81	13.5	141.1	24.7	12.5	4.8	0.0	204.6	0.690	0.182	0.0235	0.00	23.4	$6.55 \cdot 10^{-4}$	9.5	69.4	4.7
82	10.7	162.4	15.8	8.0	3.2	0.0	213.7	0.760	0.111	0.0150	0.00	15.6	$4.01 \cdot 10^{-4}$	5.8	60.5	3.0
83	7.9	173.6	8.3	4.2	1.7	0.0	222.2	0.781	0.0563	0.00765	0.00	13.2	$2.03 \cdot 10^{-4}$	2.9	48.0	1.6
84	5.1	165.7	3.6	1.8	0.0	0.0	191.7	0.864	0.0282	0.00	0.00	4.0	$1.01 \cdot 10^{-4}$	1.5	16.7	0.5
85	2.3	175.4	1.5	0.0	0.0	0.0	212.7	0.825	0.00705	0.00	0.00	8.4	$2.54 \cdot 10^{-5}$	0.4	10.4	0.2
86	-0.6	168.1	0.0	0.0	0.0	0.0	204.9	0.820	0.00	0.00	0.00	8.9	0.00	0.0	4.0	0.0

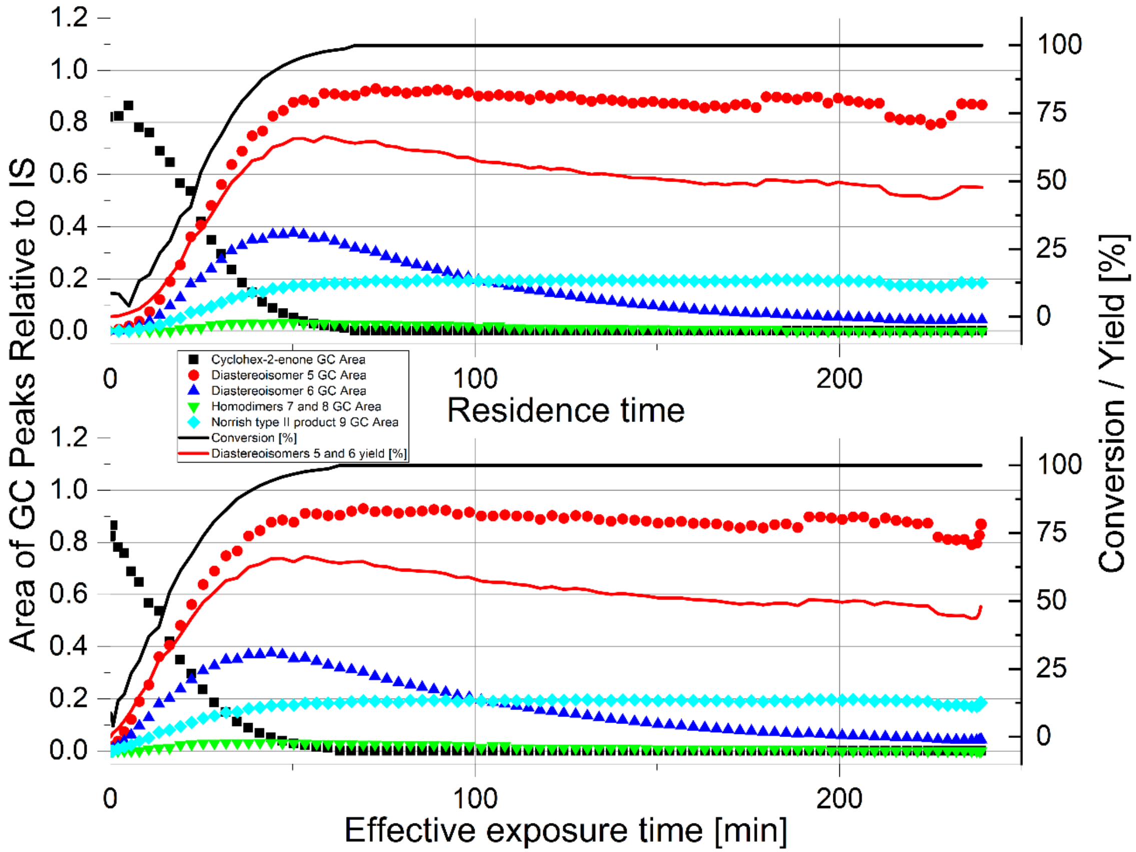


Figure S 11. Results of Switch-Off optimisation of [2+2] photoreaction using UV-A light. Top: Reaction components absolute GC areas, conversion, and yield plotted against uncorrected residence time. Bottom: Reaction components GC areas, conversion, and yield plotted against exposure time, corrected for light inhomogeneity.

2. 3. 2. 2. Switch-Off experiment results using UV-B light

Cyclohex-2-enone (125.0 µL, 124.0 mg, 1.3 mmol, 1.0 eq., 25.8 mM solution), dibutyl ether (0.19 mL, 146.0 mg, 1.1 mmol, 0.85 eq., 22.4 mmol solution), and tetramethylethylene (3.01 mL, 2.13 g, 25.3 mmol, 19.6 eq., 505.7 mM solution) were dissolved in anhydrous acetonitrile (47.9 mL, 386.3 vol.). Obtained solution was sonicated under high nitrogen flow for 30 minutes and was then connected to flow reagents stream. Anhydrous acetonitrile, sonicated under high nitrogen flow for 30 minutes, was connected to flow solvents stream. The UV-B lamp (Philips PL-L 36W/01/4P) and water cooling were then turned on and system was allowed to equilibrate for 30 minutes. Then reaction mixture was injected into the photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA). Effective exposure time was set to 239 minutes (which corresponds to 0.133 mL/min flow rate). Once the photoreactor was filled with reaction mixture, the UV lamp was switched off, the pump was switched to solvent stream, the reaction mixture was eluted from the photoreactor, and was collected into vials (0.375 mL of reaction mixture, diluted to 1.0 mL with acetone). Collected samples were then analysed using off-line GC.

Table S 8. Results of Switch-Off optimisation performed for [2+2] photocycloaddition of cyclohex-2-enone and tetramethylethylene using UV-B light.

Vial	Residence time	Cyclohex-2-enone GC Area	Diastereoisomer 5 GC Area	Diastereoisomer 6 GC Area	Norrish type II product 9 GC Area	Homodimers 7 and 8 GC Area	IS Area	Cyclohex-enone/IS Area ratio	Diastereoisomers 5 and 6/IS Area Ratio	Norrish type II product 9/IS Area Ratio	Homodimers 7 and 8/IS Area Ratio	Conversion [%]	Diastereoisomers 5 and 6 concentration [M]	Diastereoisomers 5 and 6 yield [%]	Datapoint included or excluded from analysis	Reactor Volume [mL]	Effective Reactor Volume [mL]	Effective Exposure Time [min]
1	239.1	0.0	0.0	0.0	0.0	0.0	145.6	0.00	0.00	0.00	0.00	100.0	0.00	0.0	Excluded	31.80	N/A	N/A
2	236.3	0.0	0.0	0.0	1.2	0.0	199.7	0.00	0.00	0.00601	0.00	100.0	0.00	0.0	Excluded	31.43	N/A	N/A
3	233.5	0.0	0.0	0.0	0.0	0.0	191.6	0.00	0.00	0.00	0.00	100.0	0.00	0.0	Excluded	31.05	N/A	N/A
4	230.6	0.0	0.0	0.0	1.2	0.0	190.7	0.00	0.00	0.00629	0.00	100.0	0.00	0.0	Excluded	30.68	N/A	N/A
5	227.8	0.0	0.0	0.0	1.2	0.0	189.9	0.00	0.00	0.00632	0.00	100.0	0.00	0.0	Excluded	30.30	N/A	N/A
6	225.0	0.0	0.0	0.0	1.3	0.0	197.1	0.00	0.00	0.00660	0.00	100.0	0.00	0.0	Included	29.93	28.500	214.3
7	222.2	0.0	0.0	0.0	1.4	0.0	192.3	0.00	0.00	0.00728	0.00	100.0	0.00	0.0	Included	29.55	28.125	211.5
8	219.4	0.0	0.0	0.0	1.4	0.0	189.8	0.00	0.00	0.00738	0.00	100.0	0.00	0.0	Included	29.18	27.750	208.6
9	216.5	0.0	0.0	0.0	1.5	0.0	188.1	0.00	0.00	0.00797	0.00	100.0	0.00	0.0	Included	28.80	27.375	205.8
10	213.7	0.0	0.0	0.0	1.8	0.0	201.3	0.00	0.00	0.00894	0.00	100.0	0.00	0.0	Included	28.43	27.000	203.0
11	210.9	0.0	0.0	0.0	1.8	0.0	192.4	0.00	0.00	0.00936	0.00	100.0	0.00	0.0	Included	28.05	26.625	200.2
12	208.1	0.0	0.0	0.0	2.0	0.0	196.9	0.00	0.00	0.0102	0.00	100.0	0.00	0.0	Included	27.68	26.250	197.4
13	205.3	0.0	0.0	0.0	2.1	0.0	198.1	0.00	0.00	0.0106	0.00	100.0	0.00	0.0	Included	27.30	25.875	194.5
14	202.4	0.0	0.0	0.0	2.1	0.0	183.5	0.00	0.00	0.0114	0.00	100.0	0.00	0.0	Included	26.93	25.500	191.7
15	199.6	0.0	0.0	0.0	2.4	0.0	202.0	0.00	0.00	0.0119	0.00	100.0	0.00	0.0	Included	26.55	25.125	188.9
16	196.8	0.0	0.0	0.0	2.3	0.0	190.6	0.00	0.00	0.0121	0.00	100.0	0.00	0.0	Included	26.18	24.750	186.1
17	194.0	0.0	0.0	0.0	2.7	0.0	205.7	0.00	0.00	0.0131	0.00	100.0	0.00	0.0	Included	25.80	24.375	183.3
18	191.2	0.0	0.0	0.0	2.6	0.0	194.2	0.00	0.00	0.0134	0.00	100.0	0.00	0.0	Included	25.43	24.000	180.5
19	188.3	0.0	0.0	0.0	2.8	0.0	195.0	0.00	0.00	0.0144	0.00	100.0	0.00	0.0	Included	25.05	23.625	177.6
20	185.5	0.0	0.0	0.0	2.9	0.0	199.4	0.00	0.00	0.0145	0.00	100.0	0.00	0.0	Included	24.68	23.250	174.8
21	182.7	0.0	0.0	0.0	3.3	0.0	194.2	0.00	0.00	0.0170	0.00	100.0	0.00	0.0	Included	24.30	22.875	172.0
22	179.9	0.0	0.0	0.0	3.4	0.0	205.5	0.00	0.00	0.0165	0.00	100.0	0.00	0.0	Included	23.93	22.500	169.2
23	177.1	0.0	0.0	0.0	3.4	0.0	195.9	0.00	0.00	0.0174	0.00	100.0	0.00	0.0	Included	23.55	22.125	166.4

24	174.2	0.0	0.0	0.0	3.6	0.0	203.7	0.00	0.00	0.0177	0.00	100.0	0.00	0.0	Included	23.18	21.750	163.5
25	171.4	0.0	0.0	0.0	3.8	0.0	198.0	0.00	0.00	0.0192	0.00	100.0	0.00	0.0	Included	22.80	21.375	160.7
26	168.6	0.0	0.0	0.0	3.9	0.0	203.5	0.00	0.00	0.0192	0.00	100.0	0.00	0.0	Included	22.43	21.000	157.9
27	165.8	0.0	0.0	0.0	3.9	0.0	198.7	0.00	0.00	0.0196	0.00	100.0	0.00	0.0	Included	22.05	20.625	155.1
28	163.0	0.0	0.0	0.0	4.5	0.0	206.1	0.00	0.00	0.0218	0.00	100.0	0.00	0.0	Included	21.68	20.250	152.3
29	160.2	0.0	0.0	0.0	4.2	0.0	196.6	0.00	0.00	0.0214	0.00	100.0	0.00	0.0	Included	21.30	19.875	149.4
30	157.3	0.0	0.0	0.0	4.5	0.0	203.9	0.00	0.00	0.0221	0.00	100.0	0.00	0.0	Included	20.93	19.500	146.6
31	154.5	0.0	0.0	0.0	4.5	0.0	197.8	0.00	0.00	0.0228	0.00	100.0	0.00	0.0	Included	20.55	19.125	143.8
32	151.7	0.0	0.0	0.0	4.8	0.0	199.4	0.00	0.00	0.0241	0.00	100.0	0.00	0.0	Included	20.18	18.750	141.0
33	148.9	0.0	0.0	0.0	5.1	0.0	201.7	0.00	0.00	0.0253	0.00	100.0	0.00	0.0	Included	19.80	18.375	138.2
34	146.1	0.0	0.0	0.0	5.6	0.0	214.9	0.00	0.00	0.0261	0.00	100.0	0.00	0.0	Included	19.43	18.000	135.3
35	143.2	0.0	0.0	0.0	5.4	0.0	201.8	0.00	0.00	0.0268	0.00	100.0	0.00	0.0	Included	19.05	17.625	132.5
36	140.4	0.0	0.0	0.0	5.7	0.0	206.9	0.00	0.00	0.0275	0.00	100.0	0.00	0.0	Included	18.68	17.250	129.7
37	137.6	0.0	0.0	0.0	6.3	0.0	211.4	0.00	0.00	0.0298	0.00	100.0	0.00	0.0	Included	18.30	16.875	126.9
38	134.8	0.0	0.0	0.0	5.9	0.0	198.7	0.00	0.00	0.0297	0.00	100.0	0.00	0.0	Included	17.93	16.500	124.1
39	132.0	0.0	0.0	0.0	6.5	0.0	203.2	0.00	0.00	0.0320	0.00	100.0	0.00	0.0	Included	17.55	16.125	121.2
40	129.1	0.0	0.0	0.0	6.5	0.0	201.3	0.00	0.00	0.0323	0.00	100.0	0.00	0.0	Included	17.18	15.750	118.4
41	126.3	0.0	5.0	0.0	7.1	0.0	204.9	0.00	0.0244	0.0347	0.00	100.0	$8.78\cdot10^{-5}$	1.3	Included	16.80	15.375	115.6
42	123.5	0.0	5.3	0.0	7.8	0.0	218.3	0.00	0.0243	0.0357	0.00	100.0	$8.74\cdot10^{-5}$	1.3	Included	16.43	15.000	112.8
43	120.7	0.0	2.2	0.0	7.6	0.0	200.9	0.00	0.0110	0.0378	0.00	100.0	$3.94\cdot10^{-5}$	0.6	Included	16.05	14.625	110.0
44	117.9	0.0	2.5	0.0	7.8	0.0	200.3	0.00	0.0125	0.0389	0.00	100.0	$4.49\cdot10^{-5}$	0.7	Included	15.68	14.250	107.1
45	115.0	0.0	6.2	0.0	9.2	0.0	216.8	0.00	0.0286	0.0424	0.00	100.0	$1.03\cdot10^{-4}$	1.5	Included	15.30	13.875	104.3
46	112.2	0.0	3.3	0.0	8.6	0.0	208.9	0.00	0.0158	0.0412	0.00	100.0	$5.69\cdot10^{-5}$	0.8	Included	14.93	13.500	101.5
47	109.4	0.0	7.3	0.0	10.1	0.0	217.6	0.00	0.0335	0.0464	0.00	100.0	$1.21\cdot10^{-4}$	1.8	Included	14.55	13.125	98.7
48	106.6	0.0	4.1	1.6	10.2	0.0	214.5	0.00	0.0266	0.0476	0.00	100.0	$9.57\cdot10^{-5}$	1.4	Included	14.18	12.750	95.9
49	103.8	0.0	5.1	1.8	10.9	0.0	198.7	0.00	0.0347	0.0549	0.00	100.0	$1.25\cdot10^{-4}$	1.8	Included	13.80	12.375	93.0
50	100.9	0.0	5.7	1.9	10.8	0.0	194.2	0.00	0.0391	0.0556	0.00	100.0	$1.41\cdot10^{-4}$	2.0	Included	13.43	12.000	90.2
51	98.1	0.0	6.9	1.7	11.8	0.0	205.3	0.00	0.0419	0.0575	0.00	100.0	$1.51\cdot10^{-4}$	2.2	Included	13.05	11.625	87.4
52	95.3	0.0	9.2	2.6	12.7	0.0	209.7	0.00	0.0563	0.0606	0.00	100.0	$2.03\cdot10^{-4}$	2.9	Included	12.68	11.250	84.6

53	92.5	0.0	9.4	2.3	13.2	0.0	193.2	0.00	0.0606	0.0683	0.00	100.0	$2.18 \cdot 10^{-4}$	3.2	Included	12.30	10.875	81.8
54	89.7	0.0	14.3	3.0	14.8	0.0	215.6	0.00	0.0802	0.0686	0.00	100.0	$2.89 \cdot 10^{-4}$	4.2	Included	11.93	10.500	78.9
55	86.8	0.0	14.1	4.0	14.6	0.0	201.4	0.00	0.0899	0.0725	0.00	100.0	$3.24 \cdot 10^{-4}$	4.7	Included	11.55	10.125	76.1
56	84.0	1.6	16.1	4.7	15.2	0.0	191.1	0.00837	0.109	0.0795	0.00	99.1	$3.92 \cdot 10^{-4}$	5.7	Included	11.18	9.750	73.3
57	81.2	2.3	19.2	5.3	18.1	0.0	216.2	0.0106	0.113	0.0837	0.00	98.9	$4.08 \cdot 10^{-4}$	5.9	Included	10.80	9.375	70.5
58	78.4	3.3	25.8	7.2	20.6	0.0	233.3	0.0141	0.141	0.0883	0.00	98.5	$5.09 \cdot 10^{-4}$	7.4	Included	10.43	9.000	67.7
59	75.6	3.2	24.0	6.9	17.8	0.0	190.6	0.0168	0.162	0.0934	0.00	98.2	$5.84 \cdot 10^{-4}$	8.5	Included	10.05	8.625	64.8
60	72.7	4.4	28.4	9.1	20.0	0.0	201.1	0.0219	0.186	0.0995	0.00	97.7	$6.71 \cdot 10^{-4}$	9.8	Included	9.68	8.250	62.0
61	69.9	5.2	30.5	10.3	19.4	0.0	189.5	0.0274	0.215	0.102	0.00	97.1	$7.75 \cdot 10^{-4}$	11.3	Included	9.30	7.875	59.2
62	67.1	7.5	39.0	13.3	22.2	0.0	206.4	0.0363	0.253	0.108	0.00	96.2	$9.12 \cdot 10^{-4}$	13.3	Included	8.93	7.500	56.4
63	64.3	9.3	42.9	15.8	22.5	0.0	199.5	0.0466	0.294	0.113	0.00	95.1	$1.06 \cdot 10^{-3}$	15.4	Included	8.55	7.125	53.6
64	61.5	11.7	48.2	18.6	23.5	0.0	210.4	0.0556	0.317	0.112	0.00	94.1	$1.14 \cdot 10^{-3}$	16.6	Included	8.18	6.750	50.8
65	58.6	13.8	50.0	20.6	23.0	0.0	196.0	0.0704	0.360	0.117	0.00	92.6	$1.30 \cdot 10^{-3}$	18.9	Included	7.80	6.375	47.9
66	55.8	17.5	56.0	24.1	23.7	0.0	196.5	0.0891	0.408	0.121	0.00	90.6	$1.47 \cdot 10^{-3}$	21.3	Included	7.43	6.000	45.1
67	53.0	20.5	58.7	26.2	23.0	0.0	192.7	0.106	0.441	0.119	0.00	88.8	$1.59 \cdot 10^{-3}$	23.1	Included	7.05	5.625	42.3
68	50.2	25.0	63.8	29.5	23.4	0.0	195.3	0.128	0.478	0.120	0.00	86.5	$1.72 \cdot 10^{-3}$	25.0	Included	6.68	5.250	39.5
69	47.4	31.0	69.6	33.4	24.1	0.0	196.6	0.158	0.524	0.123	0.00	83.4	$1.89 \cdot 10^{-3}$	27.4	Included	6.30	4.875	36.7
70	44.5	33.2	66.6	32.9	21.9	0.0	178.6	0.186	0.557	0.123	0.00	80.4	$2.01 \cdot 10^{-3}$	29.2	Included	5.93	4.500	33.8
71	41.7	43.5	75.1	38.2	23.3	0.0	197.5	0.220	0.574	0.118	0.00	76.8	$2.07 \cdot 10^{-3}$	30.0	Included	5.55	4.125	31.0
72	38.9	48.7	72.6	37.7	21.4	0.0	192.0	0.254	0.574	0.111	0.00	73.3	$2.07 \cdot 10^{-3}$	30.1	Included	5.18	3.750	28.2
73	36.1	62.3	77.8	41.5	21.9	0.0	205.0	0.304	0.582	0.107	0.00	68.0	$2.10 \cdot 10^{-3}$	30.5	Included	4.80	3.375	25.4
74	33.3	66.2	69.3	37.3	18.6	0.0	186.6	0.355	0.571	0.0997	0.00	62.6	$2.06 \cdot 10^{-3}$	29.9	Included	4.43	3.000	22.6
75	30.5	81.5	69.5	37.7	17.6	0.0	198.6	0.410	0.540	0.0886	0.00	56.8	$1.94 \cdot 10^{-3}$	28.3	Included	4.05	2.625	19.7
76	27.6	92.3	62.4	34.1	15.4	0.0	193.3	0.477	0.499	0.0797	0.00	49.7	$1.80 \cdot 10^{-3}$	26.1	Included	3.68	2.250	16.9
77	24.8	109.1	57.2	31.2	13.4	0.0	192.8	0.566	0.459	0.0695	0.00	40.4	$1.65 \cdot 10^{-3}$	24.0	Included	3.30	1.875	14.1
78	22.0	126.0	50.1	27.1	11.4	0.0	203.0	0.621	0.380	0.0562	0.00	34.6	$1.37 \cdot 10^{-3}$	19.9	Included	2.93	1.500	11.3
79	19.2	127.2	36.8	19.7	8.1	0.0	191.1	0.666	0.296	0.0424	0.00	29.9	$1.06 \cdot 10^{-3}$	15.5	Included	2.55	1.125	8.5
80	16.4	143.0	28.5	15.2	6.1	0.0	195.0	0.733	0.224	0.0313	0.00	22.8	$8.07 \cdot 10^{-3}$	11.7	Included	2.18	0.750	5.6
81	13.5	153.6	19.8	10.4	4.3	0.0	199.2	0.771	0.152	0.0216	0.00	18.8	$5.46 \cdot 10^{-3}$	7.9	Included	1.80	0.375	2.8

82	10.7	157.2	12.1	6.4	2.6	0.0	186.8	0.842	0.0990	0.0139	0.00	11.4	$3.57 \cdot 10^{-3}$	5.2	Included	1.43	0.000	0.0
83	7.9	148.8	6.5	3.4	1.4	0.0	175.5	0.848	0.0564	0.00798	0.00	10.7	$2.03 \cdot 10^{-3}$	3.0	Excluded	1.05	N/A	N/A
84	5.1	162.9	3.7	1.9	0.0	0.0	177.6	0.917	0.0315	0.00	0.00	3.4	$1.14 \cdot 10^{-3}$	1.7	Excluded	0.68	N/A	N/A
85	2.3	198.6	1.9	0.0	0.0	0.0	213.2	0.932	0.00891	0.00	0.00	1.9	$3.21 \cdot 10^{-3}$	0.5	Excluded	0.30	N/A	N/A
86	-0.6	180.8	0.0	0.0	0.0	0.0	198.3	0.912	0.00	0.00	0.00	4.0	0.00	0.0	Excluded	-0.07	N/A	N/A

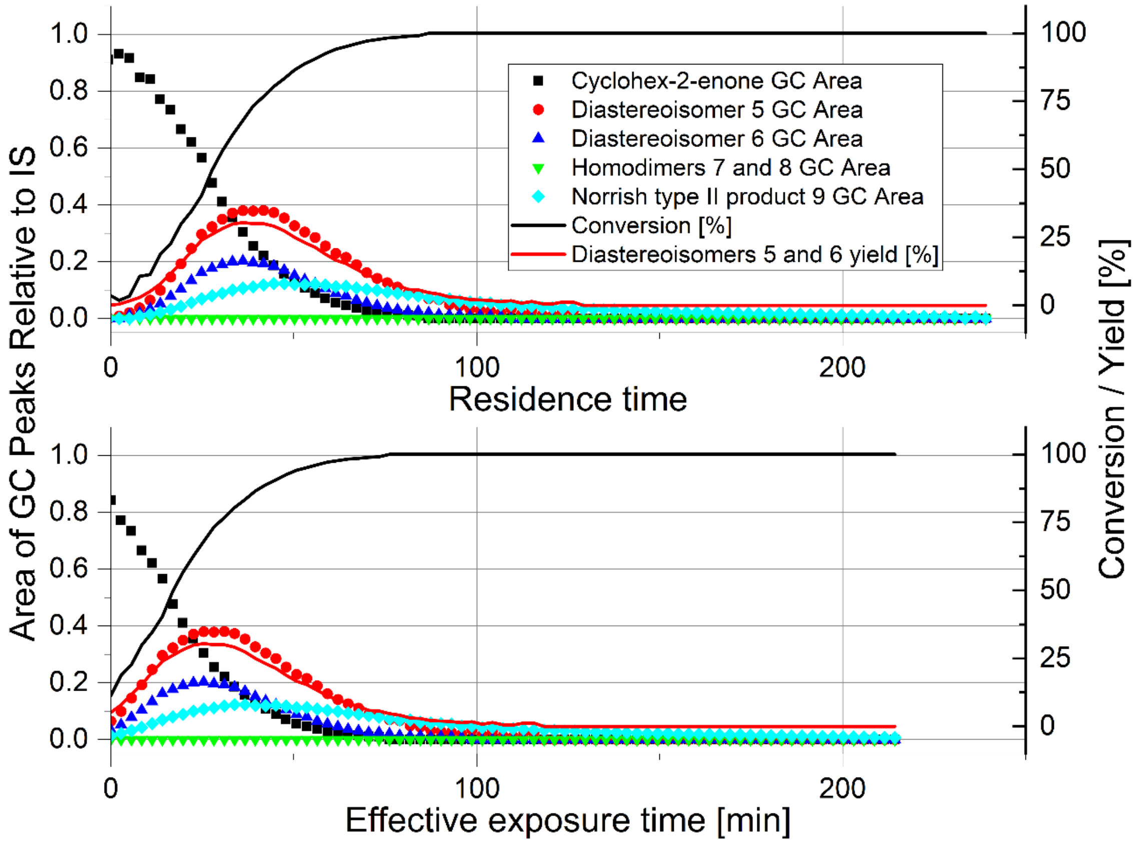


Figure S 12. Results of Switch-Off optimisation of [2+2] photoreaction using UV-B light. Top: Reaction components absolute GC areas, conversion, and yield plotted against uncorrected residence time. Bottom: Reaction components GC areas, conversion, and yield plotted against exposure time, corrected for light inhomogeneity.

2. 3. 2. 3. Switch-Off experiment results using UV-C light

Cyclohex-2-enone (125.0 µL, 124.0 mg, 1.3 mmol, 1.0 eq., 25.8 mM solution), dibutyl ether (0.19 mL, 146.0 mg, 1.1 mmol, 0.85 eq., 22.4 mmol solution), and tetramethylethylene (3.01 mL, 2.13 g, 25.3 mmol, 19.6 eq., 505.7 mM solution) were dissolved in anhydrous acetonitrile (47.9 mL, 386.3 vol.). Obtained solution was sonicated under high nitrogen flow for 30 minutes and was then connected to flow reagents stream. Anhydrous acetonitrile, sonicated under high nitrogen flow for 30 minutes, was connected to flow solvents stream. The UV-C lamp (PISCES PLL 36W) and water cooling were then turned on and system was allowed to equilibrate for 30 minutes. Then reaction mixture was injected into the photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA). Effective exposure time was set to 239 minutes (which corresponds to 0.133 mL/min flow rate). Once the photoreactor was filled with reaction mixture, the UV lamp was switched off, the pump was switched to solvent stream, the reaction mixture was eluted from the photoreactor, and was collected into vials (0.375 mL of reaction mixture, diluted to 1.0 mL with acetone). Collected samples were then analysed using off-line GC.

Table S 9. Results of Switch-Off optimisation performed for [2+2] photocycloaddition of cyclohex-2-enone and tetramethylethylene using UV-C light.

Vial	Residence time	Cyclohex-2-enone GC Area	Diastereoisomer 5 GC Area	Diastereoisomer 6 GC Area	Norrish type II product 9 GC Area	Homodimers 7 and 8 GC Area	IS Area	Cyclohex-enone/IS Area ratio	Diastereoisomers 5 and 6/IS Area Ratio	Norrish type II product 9/IS Area Ratio	Homodimers 7 and 8/IS Area Ratio	Conversion [%]	Diastereoisomers 5 and 6 concentration [M]	Diastereoisomers 5 and 6 yield [%]	Datapoint included or excluded from analysis	Reactor Volume [mL]	Effective Reactor Volume [mL]	Effective Exposure Time [min]
1	239.1	0.0	4.0	0.0	3.5	0.0	196.1	0.00	0.0204	0.0178	0.00	100.0%	$7.43\cdot10^{-5}$	1.1	Excluded	31.80	N/A	N/A
2	236.3	0.0	4.0	0.0	4.3	0.0	246.3	0.00	0.0162	0.0175	0.00	100.0%	$5.91\cdot10^{-5}$	0.8	Excluded	31.43	N/A	N/A
3	233.5	0.0	6.8	0.0	4.7	0.0	257.4	0.00	0.0264	0.0183	0.00	100.0%	$9.62\cdot10^{-5}$	1.4	Excluded	31.05	N/A	N/A
4	230.6	0.0	5.8	0.0	4.6	0.0	249.5	0.00	0.0232	0.0184	0.00	100.0%	$8.47\cdot10^{-5}$	1.2	Excluded	30.68	N/A	N/A
5	227.8	0.0	6.1	0.0	6.2	0.0	258.2	0.00	0.0236	0.0240	0.00	100.0%	$8.60\cdot10^{-5}$	1.2	Excluded	30.30	N/A	N/A
6	225.0	0.0	6.0	0.0	6.1	0.0	251.5	0.00	0.0239	0.0243	0.00	100.0%	$8.69\cdot10^{-5}$	1.2	Included	29.93	28.500	214.3
7	222.2	0.0	6.7	0.0	6.6	0.0	265.0	0.00	0.0253	0.0249	0.00	100.0%	$9.21\cdot10^{-5}$	1.3	Included	29.55	28.125	211.5
8	219.4	0.0	6.8	0.0	6.7	0.0	264.7	0.00	0.0257	0.0253	0.00	100.0%	$9.36\cdot10^{-5}$	1.3	Included	29.18	27.750	208.6
9	216.5	0.0	7.8	0.0	7.1	0.0	280.8	0.00	0.0278	0.0253	0.00	100.0%	$1.01\cdot10^{-4}$	1.4	Included	28.80	27.375	205.8
10	213.7	0.0	7.9	0.0	7.2	0.0	273.8	0.00	0.0289	0.0263	0.00	100.0%	$1.05\cdot10^{-4}$	1.5	Included	28.43	27.000	203.0
11	210.9	0.0	7.8	0.0	7.4	0.0	276.0	0.00	0.0283	0.0268	0.00	100.0%	$1.03\cdot10^{-4}$	1.5	Included	28.05	26.625	200.2
12	208.1	0.0	8.7	0.0	7.9	0.0	294.0	0.00	0.0296	0.0269	0.00	100.0%	$1.08\cdot10^{-4}$	1.5	Included	27.68	26.250	197.4
13	205.3	0.0	8.5	0.0	7.5	0.0	275.1	0.00	0.0309	0.0273	0.00	100.0%	$1.13\cdot10^{-4}$	1.6	Included	27.30	25.875	194.5
14	202.4	0.0	9.8	0.0	8.1	0.0	282.7	0.00	0.0347	0.0287	0.00	100.0%	$1.26\cdot10^{-4}$	1.8	Included	26.93	25.500	191.7
15	199.6	0.0	9.7	0.0	8.7	0.0	290.1	0.00	0.0334	0.0300	0.00	100.0%	$1.22\cdot10^{-4}$	1.7	Included	26.55	25.125	188.9
16	196.8	0.0	9.7	0.0	8.6	0.0	280.9	0.00	0.0345	0.0306	0.00	100.0%	$1.26\cdot10^{-4}$	1.8	Included	26.18	24.750	186.1
17	194.0	0.0	11.8	0.0	9.3	0.0	294.9	0.00	0.0400	0.0315	0.00	100.0%	$1.46\cdot10^{-4}$	2.1	Included	25.80	24.375	183.3

18	191.2	0.0	12.2	0.0	9.3	0.0	295.4	0.00	0.0413	0.0315	0.00	100.0%	$1.50 \cdot 10^{-4}$	2.1	Included	25.43	24.000	180.5
19	188.3	0.0	12.7	0.0	9.4	0.0	287.7	0.00	0.0441	0.0327	0.00	100.0%	$1.61 \cdot 10^{-4}$	2.3	Included	25.05	23.625	177.6
20	185.5	0.0	12.2	0.0	10.1	0.0	302.8	0.00	0.0403	0.0334	0.00	100.0%	$1.47 \cdot 10^{-4}$	2.1	Included	24.68	23.250	174.8
21	182.7	0.0	13.0	0.0	8.4	0.0	285.3	0.00	0.0456	0.0294	0.00	100.0%	$1.66 \cdot 10^{-4}$	2.4	Included	24.30	22.875	172.0
22	179.9	0.0	14.1	0.0	11.0	0.0	304.3	0.00	0.0463	0.0361	0.00	100.0%	$1.69 \cdot 10^{-4}$	2.4	Included	23.93	22.500	169.2
23	177.1	0.0	13.8	0.0	10.8	0.0	289.9	0.00	0.0476	0.0373	0.00	100.0%	$1.73 \cdot 10^{-4}$	2.5	Included	23.55	22.125	166.4
24	174.2	0.0	13.1	0.0	10.7	0.0	287.3	0.00	0.0456	0.0372	0.00	100.0%	$1.66 \cdot 10^{-4}$	2.4	Included	23.18	21.750	163.5
25	171.4	0.0	14.6	0.0	9.6	0.0	288.5	0.00	0.0506	0.0333	0.00	100.0%	$1.84 \cdot 10^{-4}$	2.6	Included	22.80	21.375	160.7
26	168.6	0.0	15.0	0.0	11.6	0.0	289.0	0.00	0.0519	0.0401	0.00	100.0%	$1.89 \cdot 10^{-4}$	2.7	Included	22.43	21.000	157.9
27	165.8	0.0	16.4	0.0	12.7	0.0	306.2	0.00	0.0536	0.0415	0.00	100.0%	$1.95 \cdot 10^{-4}$	2.8	Included	22.05	20.625	155.1
28	163.0	0.0	16.4	0.0	12.4	0.0	285.2	0.00	0.0575	0.0435	0.00	100.0%	$2.09 \cdot 10^{-4}$	3.0	Included	21.68	20.250	152.3
29	160.2	0.0	16.2	0.0	12.8	0.0	283.4	0.00	0.0572	0.0452	0.00	100.0%	$2.08 \cdot 10^{-4}$	3.0	Included	21.30	19.875	149.4
30	157.3	0.0	17.7	0.0	13.7	0.0	296.5	0.00	0.0597	0.0462	0.00	100.0%	$2.17 \cdot 10^{-4}$	3.1	Included	20.93	19.500	146.6
31	154.5	0.0	17.8	1.1	13.4	0.0	286.5	0.00	0.0660	0.0468	0.00	100.0%	$2.40 \cdot 10^{-4}$	3.4	Included	20.55	19.125	143.8
32	151.7	0.0	18.9	1.1	14.1	0.0	297.3	0.00	0.0673	0.0474	0.00	100.0%	$2.45 \cdot 10^{-4}$	3.5	Included	20.18	18.750	141.0
33	148.9	0.0	18.3	1.3	14.6	0.0	296.0	0.00	0.0662	0.0493	0.00	100.0%	$2.41 \cdot 10^{-4}$	3.4	Included	19.80	18.375	138.2
34	146.1	0.0	20.1	1.4	15.3	0.0	300.6	0.00	0.0715	0.0509	0.00	100.0%	$2.60 \cdot 10^{-4}$	3.7	Included	19.43	18.000	135.3
35	143.2	0.0	18.8	1.4	14.8	0.0	289.6	0.00	0.0698	0.0511	0.00	100.0%	$2.54 \cdot 10^{-4}$	3.6	Included	19.05	17.625	132.5
36	140.4	0.0	20.0	1.6	15.7	0.0	294.9	0.00	0.0732	0.0532	0.00	100.0%	$2.67 \cdot 10^{-4}$	3.8	Included	18.68	17.250	129.7
37	137.6	0.0	20.7	1.8	15.7	0.0	281.4	0.00	0.0800	0.0558	0.00	100.0%	$2.91 \cdot 10^{-4}$	4.1	Included	18.30	16.875	126.9
38	134.8	0.0	21.6	1.9	16.2	0.0	288.2	0.00	0.0815	0.0562	0.00	100.0%	$2.97 \cdot 10^{-4}$	4.2	Included	17.93	16.500	124.1
39	132.0	0.0	21.7	2.1	16.6	0.0	288.0	0.00	0.0826	0.0576	0.00	100.0%	$3.01 \cdot 10^{-4}$	4.3	Included	17.55	16.125	121.2
40	129.1	0.0	21.1	2.2	16.0	0.0	274.3	0.00	0.0849	0.0583	0.00	100.0%	$3.09 \cdot 10^{-4}$	4.4	Included	17.18	15.750	118.4
41	126.3	0.0	24.3	2.7	18.3	0.0	309.8	0.00	0.0872	0.0591	0.00	100.0%	$3.17 \cdot 10^{-4}$	4.5	Included	16.80	15.375	115.6
42	123.5	0.0	22.8	2.7	17.5	0.0	279.6	0.00	0.0912	0.0626	0.00	100.0%	$3.32 \cdot 10^{-4}$	4.7	Included	16.43	15.000	112.8
43	120.7	0.0	22.8	2.9	14.8	0.0	245.6	0.00	0.105	0.0603	0.00	100.0%	$3.81 \cdot 10^{-4}$	5.4	Included	16.05	14.625	110.0
44	117.9	0.0	25.0	3.4	18.6	0.0	292.2	0.00	0.0972	0.0637	0.00	100.0%	$3.54 \cdot 10^{-4}$	5.0	Included	15.68	14.250	107.1
45	115.0	0.0	25.5	3.7	18.8	0.0	283.9	0.00	0.103	0.0662	0.00	100.0%	$3.75 \cdot 10^{-4}$	5.3	Included	15.30	13.875	104.3
46	112.2	0.0	26.0	4.0	19.0	0.0	281.4	0.00	0.107	0.0675	0.00	100.0%	$3.88 \cdot 10^{-4}$	5.5	Included	14.93	13.500	101.5

47	109.4	0.0	30.1	4.9	22.3	0.0	317.1	0.00	0.110	0.0703	0.00	100.0%	$4.02\cdot10^{-4}$	5.7	Included	14.55	13.125	98.7
48	106.6	0.0	28.4	5.0	20.5	0.0	288.0	0.00	0.116	0.0712	0.00	100.0%	$4.22\cdot10^{-4}$	6.0	Included	14.18	12.750	95.9
49	103.8	0.0	28.8	5.4	20.5	0.0	283.2	0.00	0.121	0.0724	0.00	100.0%	$4.40\cdot10^{-4}$	6.2	Included	13.80	12.375	93.0
50	100.9	0.0	28.1	5.6	19.7	0.0	262.7	0.00	0.128	0.0750	0.00	100.0%	$4.67\cdot10^{-4}$	6.6	Included	13.43	12.000	90.2
51	98.1	0.0	32.4	6.8	22.4	0.0	298.1	0.00	0.131	0.0751	0.00	100.0%	$4.79\cdot10^{-4}$	6.8	Included	13.05	11.625	87.4
52	95.3	0.0	32.1	7.2	22.1	0.0	290.2	0.00	0.135	0.0762	0.00	100.0%	$4.93\cdot10^{-4}$	7.0	Included	12.68	11.250	84.6
53	92.5	0.0	34.0	8.0	22.5	0.0	289.8	0.00	0.145	0.0776	0.00	100.0%	$5.28\cdot10^{-4}$	7.5	Included	12.30	10.875	81.8
54	89.7	0.0	36.2	9.1	25.1	0.0	299.1	0.00	0.151	0.0839	0.00	100.0%	$5.52\cdot10^{-4}$	7.8	Included	11.93	10.500	78.9
55	86.8	0.0	34.1	9.2	20.9	0.0	276.6	0.00	0.157	0.0756	0.00	100.0%	$5.70\cdot10^{-4}$	8.1	Included	11.55	10.125	76.1
56	84.0	0.0	37.1	10.5	24.1	0.0	285.8	0.00	0.167	0.0843	0.00	100.0%	$6.07\cdot10^{-4}$	8.6	Included	11.18	9.750	73.3
57	81.2	0.0	38.6	11.5	25.6	0.0	286.5	0.00	0.175	0.0894	0.00	100.0%	$6.37\cdot10^{-4}$	9.0	Included	10.80	9.375	70.5
58	78.4	0.0	39.5	12.5	25.6	0.0	292.6	0.00	0.178	0.0875	0.00	100.0%	$6.47\cdot10^{-4}$	9.2	Included	10.43	9.000	67.7
59	75.6	0.0	41.6	13.9	27.4	0.0	293.2	0.00	0.189	0.0935	0.00	100.0%	$6.89\cdot10^{-4}$	9.8	Included	10.05	8.625	64.8
60	72.7	0.0	41.5	14.7	25.0	0.0	287.6	0.00	0.195	0.0869	0.00	100.0%	$7.12\cdot10^{-4}$	10.1	Included	9.68	8.250	62.0
61	69.9	0.0	43.9	16.5	25.9	0.0	292.2	0.00	0.207	0.0886	0.00	100.0%	$7.53\cdot10^{-4}$	10.7	Included	9.30	7.875	59.2
62	67.1	0.0	44.8	17.5	26.8	0.0	281.3	0.00	0.221	0.0953	0.00	100.0%	$8.07\cdot10^{-4}$	11.5	Included	8.93	7.500	56.4
63	64.3	0.0	38.2	16.2	22.2	0.0	233.3	0.00	0.233	0.0952	0.00	100.0%	$8.49\cdot10^{-4}$	12.1	Included	8.55	7.125	53.6
64	61.5	0.0	51.8	22.6	29.2	0.0	292.6	0.00	0.254	0.0998	0.00	100.0%	$9.26\cdot10^{-4}$	13.2	Included	8.18	6.750	50.8
65	58.6	0.0	40.6	18.9	21.5	0.0	232.0	0.00	0.256	0.0927	0.00	100.0%	$9.34\cdot10^{-4}$	13.3	Included	7.80	6.375	47.9
66	55.8	0.0	52.3	25.2	28.0	0.0	285.3	0.00	0.272	0.0981	0.00	99.2%	$9.89\cdot10^{-4}$	14.1	Included	7.43	6.000	45.1
67	53.0	1.9	53.4	27.3	27.3	0.0	282.2	0.00673	0.286	0.0967	0.00	99.3%	$1.04\cdot10^{-3}$	14.8	Included	7.05	5.625	42.3
68	50.2	1.7	52.1	27.8	27.1	0.0	261.0	0.00651	0.306	0.104	0.00	99.0%	$1.11\cdot10^{-3}$	15.8	Included	6.68	5.250	39.5
69	47.4	2.2	48.8	27.2	24.0	0.0	239.3	0.00919	0.318	0.100	0.00	99.1%	$1.16\cdot10^{-3}$	16.4	Included	6.30	4.875	36.7
70	44.5	2.3	61.3	35.3	28.3	0.0	290.3	0.00792	0.333	0.0975	0.00	98.4%	$1.21\cdot10^{-3}$	17.2	Included	5.93	4.500	33.8
71	41.7	4.0	62.7	37.2	28.0	0.0	281.8	0.0142	0.355	0.0994	0.00	97.4%	$1.29\cdot10^{-3}$	18.3	Included	5.55	4.125	31.0
72	38.9	5.4	54.8	33.3	23.8	0.0	231.5	0.0233	0.381	0.103	0.00	96.0%	$1.39\cdot10^{-3}$	19.7	Included	5.18	3.750	28.2
73	36.1	10.1	68.6	42.1	28.7	0.0	282.3	0.0358	0.392	0.102	0.00	93.3%	$1.43\cdot10^{-3}$	20.3	Included	4.80	3.375	25.4
74	33.3	16.5	67.5	41.5	27.4	0.0	275.7	0.0598	0.395	0.0994	0.00	88.0%	$1.44\cdot10^{-3}$	20.5	Included	4.43	3.000	22.6
75	30.5	25.2	61.8	37.9	24.8	0.0	234.1	0.108	0.426	0.106	0.00	82.2%	$1.55\cdot10^{-3}$	22.0	Included	4.05	2.625	19.7

76	27.6	42.9	70.4	42.5	27.7	0.0	269.9	0.159	0.418	0.103	0.00	75.5%	$1.52\cdot10^{-3}$	21.6	Included	3.68	2.250	16.9
77	24.8	61.1	65.4	38.8	25.4	0.0	278.6	0.219	0.374	0.0912	0.00	65.7%	$1.36\cdot10^{-3}$	19.3	Included	3.30	1.875	14.1
78	22.0	80.7	58.0	33.8	21.7	0.0	263.3	0.306	0.349	0.0824	0.00	54.8%	$1.27\cdot10^{-3}$	18.0	Included	2.93	1.500	11.3
79	19.2	101.7	50.1	28.7	18.4	0.0	252.0	0.404	0.313	0.0730	0.00	43.7%	$1.14\cdot10^{-3}$	16.2	Included	2.55	1.125	8.5
80	16.4	154.5	57.8	28.9	19.0	0.0	307.1	0.503	0.282	0.0619	0.00	33.5%	$1.03\cdot10^{-3}$	14.6	Included	2.18	0.750	5.6
81	13.5	164.2	37.0	20.5	13.7	0.0	276.3	0.594	0.208	0.0496	0.00	22.0%	$7.58\cdot10^{-4}$	10.8	Included	1.80	0.375	2.8
82	10.7	156.5	23.7	13.0	8.7	0.0	224.5	0.697	0.163	0.0388	0.00	13.2%	$5.95\cdot10^{-4}$	8.5	Included	1.43	0.000	0.0
83	7.9	219.8	23.6	11.4	7.3	0.0	283.5	0.775	0.123	0.0257	0.00	9.5%	$4.50\cdot10^{-4}$	6.4	Excluded	1.05	N/A	N/A
84	5.1	241.8	15.2	7.3	4.7	0.0	299.0	0.809	0.0753	0.0157	0.00	2.5%	$2.74\cdot10^{-4}$	3.9	Excluded	0.68	N/A	N/A
85	2.3	267.8	9.3	4.4	2.9	0.0	307.5	0.871	0.0446	0.00943	0.00	2.9%	$1.62\cdot10^{-4}$	2.3	Excluded	0.30	N/A	N/A
86	-0.6	255.4	4.1	2.0	1.3	0.0	294.2	0.868	0.0207	0.00442	0.00	1.1%	$7.55\cdot10^{-5}$	1.1	Excluded	0.00	N/A	N/A

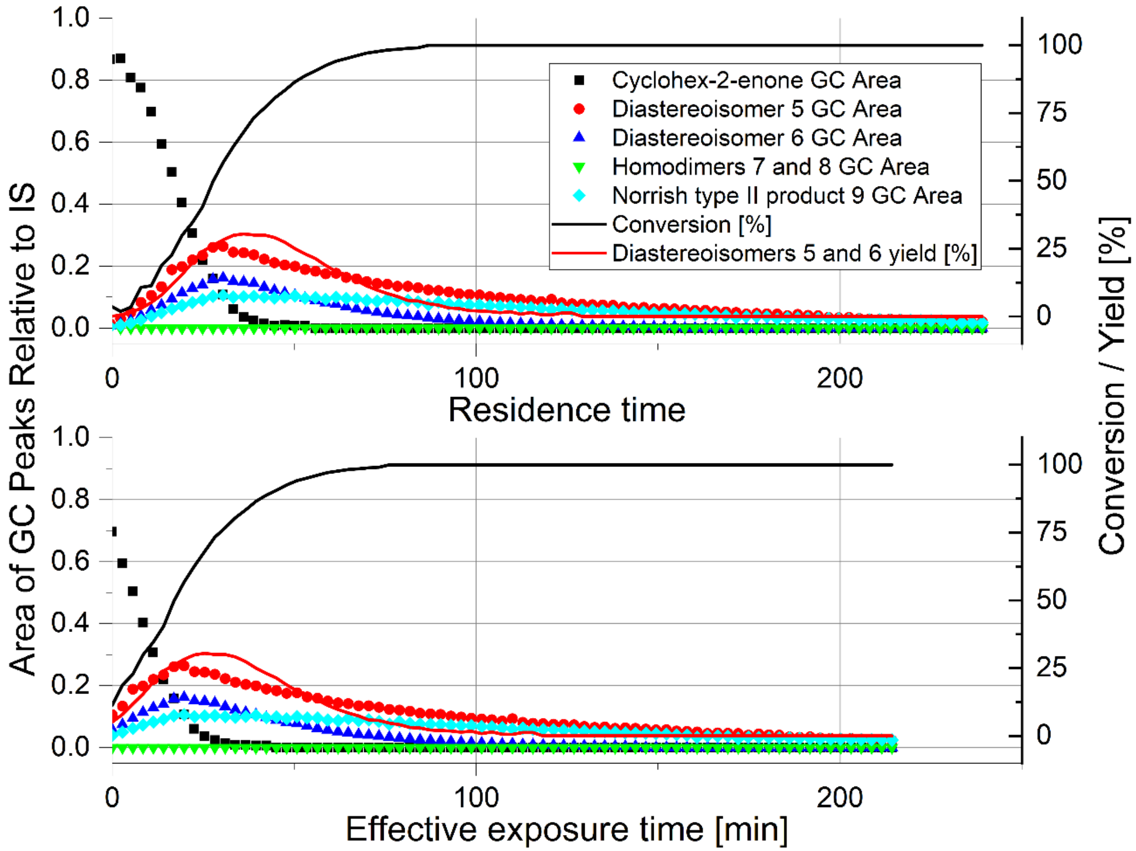


Figure S 13. Results of Switch-Off optimisation of [2+2] photoreaction using UV-C light. Top: Reaction components absolute GC areas, conversion, and yield plotted against uncorrected residence time. Bottom: Reaction components GC areas, conversion, and yield plotted against exposure time, corrected for light inhomogeneity.

2. 3. 3. Validation of Switch-Off results obtained in [2+2] photocycloaddition cyclohex-2-enone and tetramethylethylene

A reaction utilizing UV-A irradiation and 50 minutes of effective exposure time was performed in order to validate results obtained from the Switch-Off optimisation and perform full characterisation of reaction products.

To a 250.0 mL round-bottom flask flushed with nitrogen, cyclohex-2-enone (536.5 mg, 532.4 µL, 5.58 mmol, 1.0 eq., 25.4 mM solution), tetramethylethylene (9.2451 g, 13.0673 mL, 109.85 mmol, 19.7 eq., 499.3 mM solution), dibutyl ether (internal standard, 628.9 mg, 816.8 µL, 4.83 mmol, 0.87 eq., 22.0 mM solution) and anhydrous acetonitrile (205.6 mL, 383.2 vol.) were added and resulting mixture was sonicated under high nitrogen flow for 15 minutes in order to remove oxygen from solution. Effective exposure time of 50 minutes was set (corresponding to 0.569 mL/min total flow rate) and mixture was injected into the photoreactor (31.8 mL internal volume, 1.00 mm ID, 1.60 mm OD, PFA) equipped with UV-A lamp (Philips PLL 36W). Once the 195.0 mL of the mixture was entirely injected, it was eluted using acetonitrile (anhydrous and deoxygenated) out of the flow system. After collection of reaction mixture, solvent was removed, obtained residue was purified by column chromatography (SiO_2; toluene:Et_2O 100:0 to 75:25 then Et_2O, then pure Et_2O) and then by automated column chromatography system (Biotage Selekt, Biotage HP-Sphere 25 micron). Following products were obtained:

- *trans*-7,7,8,8-Tetramethylbicyclo[4.2.0]octan-2-one (**5**): 404.1 mg (2.24 mmol, 45.3% yield)
- *cis*-7,7,8,8-Tetramethylbicyclo[4.2.0]octan-2-one (**6**): 153.1 mg (0.85 mmol, 17.1% yield)
- *cis-anti-cis*-Tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (**7**): 27.9 mg (0.15 mmol, 2.9% yield)
- *cis-anti-cis*-Tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (**8**): 17.2 mg (0.09 mmol, 1.8% yield)
- 3-(1,1,2-Trimethyl-2-propen-1-yl)cyclohexanone (**9**): 67.4 mg (0.37 mmol, 7.5% yield)

Additionally, crude ^{1}H NMR showed traces of Norrish type I products and traces of additional unknown byproducts. Full characterisation data of the compounds **5**, **6**, **7**, **8**, and **9** can be found in section 3. 2. Procedure for synthesis of compounds 5, 6, 7, 8, and 9: of this document.

2. 4. Mallory photocyclization of *cis*-stilbene

An example of GC chromatogram containing all studied Mallory photoreaction components with their respective retention times is presented below (Figure S 14. GC chromatogram of a Mallory photoreaction components with their respective retention times.).

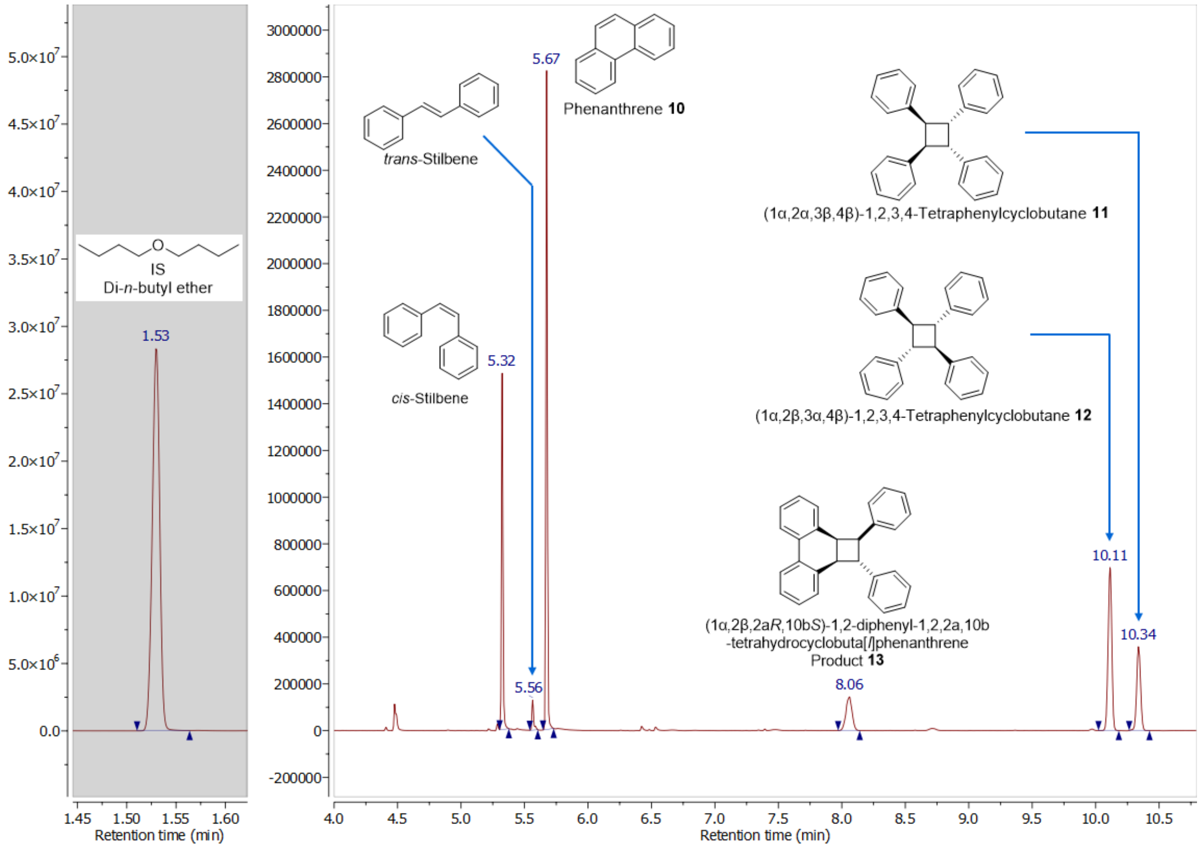


Figure S 14. GC chromatogram of a Mallory photoreaction components with their respective retention times.

2. 4. 1. Calibration curve for determination of phenanthrene yield using GC-FID monitoring:

Sample solutions of dibutyl ether (internal standard) and phenanthrene **10** (photocycloaddition product) were prepared accordingly to the table below and were then measured using GC-FID. Calibration curve was then prepared by plotting the ratios of phenanthrene and IS areas against molar ratios of phenanthrene and IS.

Table S 10. Calibration table of GC-FID for Mallory photoreaction.

Sample	Mass of phenanthrene [mg]	Mass of IS [mg]	Moles of phenanthrene [mol]	Moles of IS [mol]	**Molar ratio of phenanthrene /IS**	Area of phenanthrene peak	Area of IS peak	**Area ratio of phenanthrene /IS**
1	1.00	3.10	$5.61 \cdot 10^{-6}$	$2.38 \cdot 10^{-5}$	**0.235705**	174.80	481.70	**0.362881**
2	1.02	5.45	$5.72 \cdot 10^{-6}$	$4.18 \cdot 10^{-5}$	**0.136752**	253.90	1233.70	**0.205804**
3	1.40	5.57	$7.86 \cdot 10^{-6}$	$4.28 \cdot 10^{-5}$	**0.183655**	365.00	1336.20	**0.273163**
4	1.00	3.50	$5.61 \cdot 10^{-6}$	$2.69 \cdot 10^{-5}$	**0.208767**	207.50	654.70	**0.316939**

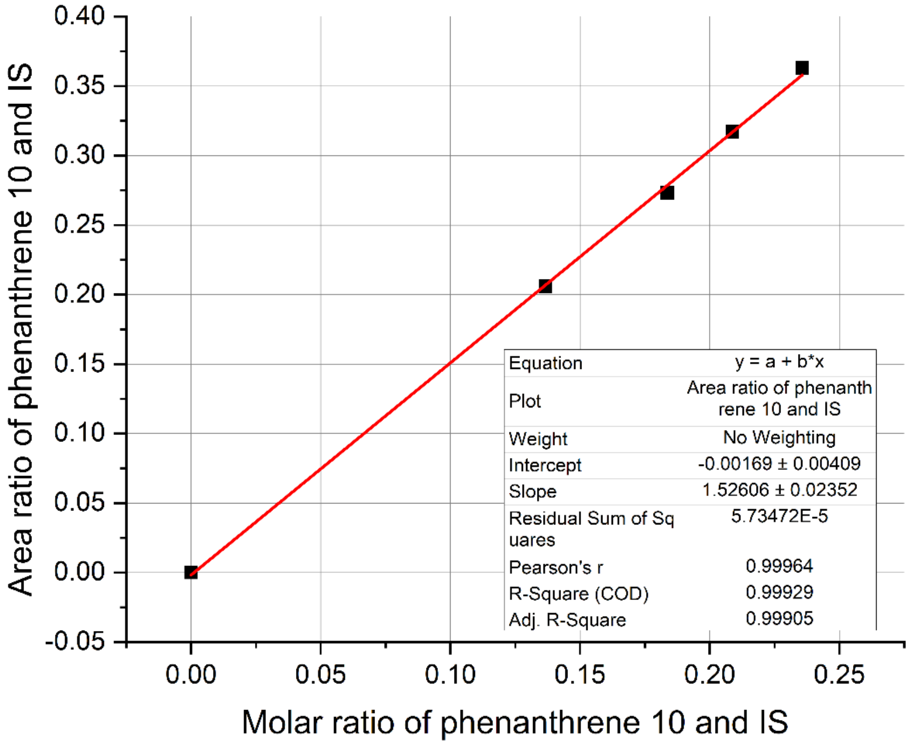


Figure S 15. GC-FID calibration curve of phenanthrene.

The FID detector is a mass sensitive detector and it's response factor for simple hydrocarbons is generally proportional to the number of carbons in the measured molecule, thus the yields of dimers **11**, **12** and phenanthrene-stilbene photoaddition product **13** were determined using the phenanthrene **10** calibration curve, but since the compounds **11**, **12**, and **13** possess twice the number of carbons, the calculated dimers concentrations were additionally divided by half.

2. 4. 2. Mallory photoreaction Switch-Off optimisations results

2. 4. 2. 1. Switch-Off experiment results using UV-A light and 5.0 mM stilbene concentration

Cis-stilbene (44.5 µL, 45.0 mg, 0.25 mmol, 1.0 eq., 5.0 mM solution), iodine (6.3 mg, 0.025 mmol, 0.1 eq., 0.5 mM solution), and dibutyl ether (0.15 mL, 117.1 mg, 0.90 mmol, 3.6 eq., 18.0 mM solution) were dissolved in cyclohexane (50.0 mL, 1111.1 vol.), obtained solution was saturated with oxygen by bubbling gaseous O_2 for 15 minutes, and then connected to flow reagents stream. Cyclohexane was connected to flow solvents stream. The UV-A lamp (Philips PLL 36W) and water cooling were then turned on and system was allowed to equilibrate for 30 minutes. Then reaction mixture was injected into the photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA). Effective exposure time was set to 45 minutes (which corresponds to 0.707 mL/min flow rate). Once the photoreactor was filled with reaction mixture, the UV lamp was switched off, the pump was switched to solvent stream, the reaction mixture was eluted from the photoreactor, and was collected into vials (0.375 mL of reaction mixture, diluted to 1.0 mL with acetone). Collected samples were then analysed using off-line GC.

Table S 11. Results of Switch-Off optimisation performed for Mallory reaction of cis-stilbene using UV-A light and 5.0 mM stilbene concentration.

#	Residence time [min]	Light output [%]	Effective exposure time [min]	IS GC Area	Area Ratio *cis*-Stilbene/IS	Area Ratio *trans*-Stilbene/IS	Area Ratio Phenanthrene 10/IS	Area Ratio Dimer ABAB 12/IS	Area Ratio Dimer AABB 11/IS	Area Ratio Product 13/IS	Phenanthrene yield [%]	Dimer 12 yield [%]	Dimer 11 yield [%]	Product 13 yield [%]	*trans*-Stilbene yield [%]	Remaining *cis*-Stilbene [%]
1	45.0	0.0	44.3	48403	$1.45\cdot10^{-4}$	0.00	$4.49\cdot10^{-1}$	$3.33\cdot10^{-3}$	$1.45\cdot10^{-3}$	$7.65\cdot10^{-5}$	98.5%	0.77%	0.34%	0.02%	0.00%	0.03%
2	44.4	3.4	44.3	46903	$1.07\cdot10^{-4}$	0.00	$4.53\cdot10^{-1}$	$3.39\cdot10^{-3}$	$1.51\cdot10^{-3}$	0.00	99.2%	0.79%	0.35%	0.00%	0.00%	0.02%
3	43.9	15.0	44.3	47070	$1.49\cdot10^{-4}$	0.00	$4.51\cdot10^{-1}$	$3.42\cdot10^{-3}$	$1.59\cdot10^{-3}$	$2.36\cdot10^{-4}$	98.8%	0.79%	0.37%	0.05%	0.00%	0.03%
4	43.4	26.6	44.2	47110	$2.12\cdot10^{-4}$	0.00	$4.51\cdot10^{-1}$	$3.31\cdot10^{-3}$	$1.42\cdot10^{-3}$	0.00	98.9%	0.77%	0.33%	0.00%	0.00%	0.05%
5	42.9	49.7	44.1	49412	$2.02\cdot10^{-4}$	0.00	$4.52\cdot10^{-1}$	$3.3\cdot10^{-3}$	$1.48\cdot10^{-3}$	$1.50\cdot10^{-4}$	99.0%	0.78%	0.34%	0.03%	0.00%	0.04%
6	42.3	70.8	43.8	46756	$1.92\cdot10^{-4}$	0.00	$4.49\cdot10^{-1}$	$3.38\cdot10^{-3}$	$1.60\cdot10^{-3}$	$1.58\cdot10^{-4}$	98.4%	0.78%	0.37%	0.04%	0.00%	0.04%
7	41.8	77.9	43.4	50112	$2.79\cdot10^{-4}$	0.00	$4.51\cdot10^{-1}$	$3.31\cdot10^{-3}$	$1.52\cdot10^{-3}$	$2.22\cdot10^{-4}$	98.9%	0.77%	0.35%	0.05%	0.00%	0.06%
8	41.3	85.0	43.0	47022	$2.55\cdot10^{-4}$	0.00	$4.48\cdot10^{-1}$	$3.32\cdot10^{-3}$	$1.45\cdot10^{-3}$	$3.15\cdot10^{-4}$	98.2%	0.77%	0.34%	0.07%	0.00%	0.05%
9	40.7	93.4	42.6	49078	$1.83\cdot10^{-4}$	0.00	$4.51\cdot10^{-1}$	$3.44\cdot10^{-3}$	$1.69\cdot10^{-3}$	$1.51\cdot10^{-4}$	98.8%	0.80%	0.39%	0.04%	0.00%	0.04%
10	40.2	98.7	42.1	49104	$2.24\cdot10^{-4}$	0.00	$4.52\cdot10^{-1}$	$3.32\cdot10^{-3}$	$1.61\cdot10^{-3}$	$7.54\cdot10^{-5}$	99.0%	0.77%	0.37%	0.02%	0.00%	0.05%
11	39.7	100.7	41.5	51079	$1.76\cdot10^{-4}$	0.00	$4.50\cdot10^{-1}$	$3.31\cdot10^{-3}$	$1.51\cdot10^{-3}$	$3.63\cdot10^{-4}$	98.6%	0.77%	0.35%	0.08%	0.00%	0.04%
12	39.1	102.7	41.0	49857	$2.41\cdot10^{-4}$	0.00	$4.51\cdot10^{-1}$	$3.59\cdot10^{-3}$	$1.58\cdot10^{-3}$	$5.20\cdot10^{-4}$	98.9%	0.83%	0.37%	0.12%	0.00%	0.05%
13	38.6	104.5	40.5	49520	$2.83\cdot10^{-4}$	0.00	$4.52\cdot10^{-1}$	$3.63\cdot10^{-3}$	$1.55\cdot10^{-3}$	$4.49\cdot10^{-4}$	99.0%	0.84%	0.36%	0.10%	0.00%	0.06%
14	38.1	105.5	39.9	51819	$1.54\cdot10^{-4}$	0.00	$4.54\cdot10^{-1}$	$3.45\cdot10^{-3}$	$1.52\cdot10^{-3}$	$1.43\cdot10^{-4}$	99.5%	0.80%	0.35%	0.03%	0.00%	0.03%

15	37.6	105.1	39.4	49709	$1.41\cdot10^{-4}$	0.00	$4.49\cdot10^{-1}$	$3.40\cdot10^{-3}$	$1.55\cdot10^{-3}$	$2.24\cdot10^{-4}$	98.5%	0.79%	0.36%	0.05%	0.00%	0.03%
16	37.0	104.7	38.8	52539	$3.81\cdot10^{-4}$	0.00	$4.54\cdot10^{-1}$	$3.52\cdot10^{-3}$	$1.75\cdot10^{-3}$	$2.11\cdot10^{-4}$	99.4%	0.82%	0.41%	0.05%	0.00%	0.08%
17	36.5	103.7	38.2	53398	$2.81\cdot10^{-4}$	0.00	$4.53\cdot10^{-1}$	$3.52\cdot10^{-3}$	$1.48\cdot10^{-3}$	$2.77\cdot10^{-4}$	99.3%	0.82%	0.34%	0.06%	0.00%	0.06%
18	36.0	104.8	37.7	52033	$2.69\cdot10^{-4}$	0.00	$4.54\cdot10^{-1}$	$3.40\cdot10^{-3}$	$1.69\cdot10^{-3}$	$7.12\cdot10^{-5}$	99.5%	0.79%	0.39%	0.02%	0.00%	0.06%
19	35.4	106.2	37.1	50800	$2.95\cdot10^{-4}$	0.00	$4.52\cdot10^{-1}$	$3.44\cdot10^{-3}$	$1.44\cdot10^{-3}$	$3.65\cdot10^{-4}$	99.0%	0.80%	0.33%	0.08%	0.00%	0.06%
20	34.9	107.5	36.6	53892	$2.78\cdot10^{-4}$	0.00	$4.56\cdot10^{-1}$	$3.27\cdot10^{-3}$	$1.47\cdot10^{-3}$	$6.87\cdot10^{-5}$	99.8%	0.76%	0.34%	0.02%	0.00%	0.06%
21	34.4	109.6	36.0	49351	$4.26\cdot10^{-4}$	0.00	$4.51\cdot10^{-1}$	$3.55\cdot10^{-3}$	$1.60\cdot10^{-3}$	$7.50\cdot10^{-4}$	98.7%	0.82%	0.37%	0.17%	0.00%	0.09%
22	33.8	111.1	35.4	55057	$3.27\cdot10^{-4}$	0.00	$4.44\cdot10^{-1}$	$3.51\cdot10^{-3}$	$1.69\cdot10^{-3}$	$1.28\cdot10^{-3}$	97.4%	0.81%	0.39%	0.30%	0.00%	0.07%
23	33.3	111.4	34.8	59990	$3.33\cdot10^{-4}$	0.00	$4.50\cdot10^{-1}$	$3.50\cdot10^{-3}$	$1.52\cdot10^{-3}$	$9.88\cdot10^{-4}$	98.6%	0.81%	0.35%	0.23%	0.00%	0.07%
24	32.8	111.8	34.2	57889	$3.80\cdot10^{-4}$	0.00	$4.50\cdot10^{-1}$	$3.30\cdot10^{-3}$	$1.55\cdot10^{-3}$	$7.68\cdot10^{-4}$	98.6%	0.77%	0.36%	0.18%	0.00%	0.08%
25	32.2	112.6	33.6	57054	$3.15\cdot10^{-4}$	0.00	$4.53\cdot10^{-1}$	$3.51\cdot10^{-3}$	$1.65\cdot10^{-3}$	$1.49\cdot10^{-3}$	99.3%	0.81%	0.38%	0.35%	0.00%	0.07%
26	31.7	113.0	33.1	52932	$4.35\cdot10^{-4}$	0.00	$4.51\cdot10^{-1}$	$3.40\cdot10^{-3}$	$1.68\cdot10^{-3}$	$1.47\cdot10^{-3}$	98.9%	0.79%	0.39%	0.34%	0.00%	0.09%
27	31.2	113.2	32.5	57162	$3.15\cdot10^{-4}$	0.00	$4.56\cdot10^{-1}$	$3.43\cdot10^{-3}$	$1.61\cdot10^{-3}$	$1.62\cdot10^{-3}$	100%	0.80%	0.37%	0.38%	0.00%	0.07%
28	30.7	113.4	31.9	56929	$4.04\cdot10^{-4}$	0.00	$4.52\cdot10^{-1}$	$3.58\cdot10^{-3}$	$1.60\cdot10^{-3}$	$1.95\cdot10^{-3}$	99.0%	0.83%	0.37%	0.45%	0.00%	0.08%
29	30.1	113.5	31.3	52722	$4.93\cdot10^{-4}$	0.00	$4.55\cdot10^{-1}$	$3.47\cdot10^{-3}$	$1.65\cdot10^{-3}$	$2.81\cdot10^{-3}$	99.7%	0.81%	0.38%	0.65%	0.00%	0.10%
30	29.6	113.6	30.7	53077	$5.46\cdot10^{-4}$	0.00	$4.46\cdot10^{-1}$	$3.39\cdot10^{-3}$	$1.53\cdot10^{-3}$	$2.16\cdot10^{-3}$	97.7%	0.79%	0.35%	0.50%	0.00%	0.11%
31	29.1	113.8	30.0	59100	$5.75\cdot10^{-4}$	0.00	$4.53\cdot10^{-1}$	$3.42\cdot10^{-3}$	$1.68\cdot10^{-3}$	$2.69\cdot10^{-3}$	99.3%	0.79%	0.39%	0.63%	0.00%	0.12%
32	28.5	114.0	29.4	51767	$5.99\cdot10^{-4}$	0.00	$4.54\cdot10^{-1}$	$3.42\cdot10^{-3}$	$1.64\cdot10^{-3}$	$3.79\cdot10^{-3}$	99.5%	0.79%	0.38%	0.88%	0.00%	0.12%
33	28.0	114.1	28.8	51488	$5.24\cdot10^{-4}$	0.00	$4.50\cdot10^{-1}$	$3.65\cdot10^{-3}$	$1.67\cdot10^{-3}$	$3.38\cdot10^{-3}$	98.5%	0.85%	0.39%	0.78%	0.00%	0.11%
34	27.5	114.2	28.2	54492	$7.71\cdot10^{-4}$	0.00	$4.49\cdot10^{-1}$	$3.58\cdot10^{-3}$	$1.61\cdot10^{-3}$	$3.67\cdot10^{-3}$	98.5%	0.83%	0.37%	0.85%	0.00%	0.16%
35	26.9	114.3	27.6	54503	$7.71\cdot10^{-4}$	0.00	$4.47\cdot10^{-1}$	$3.56\cdot10^{-3}$	$1.67\cdot10^{-3}$	$4.62\cdot10^{-3}$	97.9%	0.83%	0.39%	1.07%	0.00%	0.16%
36	26.4	114.1	27.0	52996	$3.40\cdot10^{-4}$	0.00	$4.49\cdot10^{-1}$	$3.70\cdot10^{-3}$	$1.72\cdot10^{-3}$	$5.10\cdot10^{-3}$	98.5%	0.86%	0.40%	1.18%	0.00%	0.07%
37	25.9	114.7	26.4	53263	$1.07\cdot10^{-3}$	0.00	$4.50\cdot10^{-1}$	$3.68\cdot10^{-3}$	$1.50\cdot10^{-3}$	$5.08\cdot10^{-3}$	98.5%	0.85%	0.35%	1.18%	0.00%	0.22%
38	25.4	114.7	25.8	57265	$1.33\cdot10^{-3}$	0.00	$4.50\cdot10^{-1}$	$3.54\cdot10^{-3}$	$1.61\cdot10^{-3}$	$5.82\cdot10^{-3}$	98.5%	0.82%	0.37%	1.35%	0.00%	0.27%
39	24.8	114.8	25.2	55861	$1.58\cdot10^{-3}$	0.00	$4.53\cdot10^{-1}$	$3.63\cdot10^{-3}$	$1.63\cdot10^{-3}$	$6.83\cdot10^{-3}$	99.3%	0.84%	0.38%	1.59%	0.00%	0.32%
40	24.3	114.6	24.6	61756	$1.75\cdot10^{-3}$	0.00	$4.52\cdot10^{-1}$	$3.53\cdot10^{-3}$	$1.64\cdot10^{-3}$	$7.26\cdot10^{-3}$	99.0%	0.82%	0.38%	1.68%	0.00%	0.36%
41	23.8	114.6	24.0	62196	$2.04\cdot10^{-3}$	0.00	$4.52\cdot10^{-1}$	$3.52\cdot10^{-3}$	$1.74\cdot10^{-3}$	$8.04\cdot10^{-3}$	99.1%	0.82%	0.40%	1.87%	0.00%	0.42%
42	23.2	114.8	23.4	65062	$2.31\cdot10^{-3}$	0.00	$4.49\cdot10^{-1}$	$3.43\cdot10^{-3}$	$1.64\cdot10^{-3}$	$9.22\cdot10^{-3}$	98.3%	0.80%	0.38%	2.14%	0.00%	0.47%
43	22.7	114.9	22.8	68364	$2.72\cdot10^{-3}$	0.00	$4.49\cdot10^{-1}$	$3.60\cdot10^{-3}$	$1.70\cdot10^{-3}$	$9.97\cdot10^{-3}$	98.4%	0.84%	0.39%	2.31%	0.00%	0.55%
44	22.2	114.8	22.2	62834	$3.14\cdot10^{-3}$	0.00	$4.49\cdot10^{-1}$	$3.60\cdot10^{-3}$	$1.54\cdot10^{-3}$	$1.18\cdot10^{-2}$	98.4%	0.84%	0.36%	2.74%	0.00%	0.64%

45	21.6	114.8	21.6	59440	$3.57\cdot10^{-3}$	0.00	$4.47\cdot10^{-1}$	$3.68\cdot10^{-3}$	$1.70\cdot10^{-3}$	$1.37\cdot10^{-2}$	98.0%	0.86%	0.39%	3.18%	0.00%	0.73%
46	21.1	114.9	21.0	63840	$4.14\cdot10^{-3}$	0.00	$4.44\cdot10^{-1}$	$3.68\cdot10^{-3}$	$1.71\cdot10^{-3}$	$1.28\cdot10^{-2}$	97.2%	0.85%	0.40%	2.96%	0.00%	0.84%
47	20.6	115.0	20.4	61408	$4.79\cdot10^{-3}$	0.00	$4.44\cdot10^{-1}$	$3.76\cdot10^{-3}$	$1.6\cdot10^{-3}$	$1.56\cdot10^{-2}$	97.3%	0.87%	0.39%	3.61%	0.00%	0.97%
48	20.0	114.4	19.8	70740	$5.63\cdot10^{-3}$	0.00	$4.49\cdot10^{-1}$	$3.77\cdot10^{-3}$	$1.68\cdot10^{-3}$	$1.40\cdot10^{-2}$	98.5%	0.88%	0.39%	3.26%	0.00%	1.14%
49	19.5	115.0	19.1	61459	$6.49\cdot10^{-3}$	0.00	$4.38\cdot10^{-1}$	$3.63\cdot10^{-3}$	$1.74\cdot10^{-3}$	$2.02\cdot10^{-2}$	95.9%	0.84%	0.40%	4.70%	0.00%	1.32%
50	19.0	115.0	18.5	57916	$7.32\cdot10^{-3}$	0.00	$4.37\cdot10^{-1}$	$3.70\cdot10^{-3}$	$1.69\cdot10^{-3}$	$2.03\cdot10^{-2}$	95.8%	0.86%	0.39%	4.72%	0.00%	1.48%
51	18.5	114.9	17.9	65937	$8.93\cdot10^{-3}$	0.00	$4.44\cdot10^{-1}$	$3.72\cdot10^{-3}$	$1.70\cdot10^{-3}$	$1.79\cdot10^{-2}$	97.4%	0.86%	0.39%	4.16%	0.00%	1.81%
52	17.9	114.8	17.3	60322	$1.03\cdot10^{-2}$	0.00	$4.34\cdot10^{-1}$	$3.75\cdot10^{-3}$	$1.61\cdot10^{-3}$	$2.53\cdot10^{-2}$	95.1%	0.87%	0.37%	5.87%	0.00%	2.09%
53	17.4	114.8	16.7	57789	$1.20\cdot10^{-2}$	0.00	$4.28\cdot10^{-1}$	$3.82\cdot10^{-3}$	$1.71\cdot10^{-3}$	$2.55\cdot10^{-2}$	93.8%	0.89%	0.40%	5.92%	0.00%	2.44%
54	16.9	114.7	16.1	62647	$1.44\cdot10^{-2}$	0.00	$4.29\cdot10^{-1}$	$3.54\cdot10^{-3}$	$1.55\cdot10^{-3}$	$2.39\cdot10^{-2}$	94.0%	0.82%	0.36%	5.56%	0.00%	2.93%
55	16.3	114.6	15.5	68150	$1.78\cdot10^{-2}$	0.00	$4.33\cdot10^{-1}$	$3.82\cdot10^{-3}$	$1.67\cdot10^{-3}$	$2.50\cdot10^{-2}$	94.9%	0.89%	0.39%	5.80%	0.00%	3.61%
56	15.8	114.7	14.9	59007	$2.06\cdot10^{-2}$	0.00	$4.21\cdot10^{-1}$	$3.53\cdot10^{-3}$	$1.71\cdot10^{-3}$	$3.31\cdot10^{-2}$	92.3%	0.82%	0.40%	7.69%	0.00%	4.17%
57	15.3	114.7	14.3	71837	$2.42\cdot10^{-2}$	0.00	$4.24\cdot10^{-1}$	$3.79\cdot10^{-3}$	$1.66\cdot10^{-3}$	$2.45\cdot10^{-2}$	93.0%	0.88%	0.38%	5.70%	0.00%	4.91%
58	14.7	114.5	13.7	55471	$2.89\cdot10^{-2}$	0.00	$4.13\cdot10^{-1}$	$3.77\cdot10^{-3}$	$1.57\cdot10^{-3}$	$4.01\cdot10^{-2}$	90.6%	0.87%	0.36%	9.30%	0.00%	5.84%
59	14.2	114.3	13.1	57730	$3.19\cdot10^{-2}$	0.00	$4.10\cdot10^{-1}$	$3.71\cdot10^{-3}$	$1.73\cdot10^{-3}$	$3.10\cdot10^{-2}$	89.8%	0.86%	0.40%	7.19%	0.00%	6.45%
60	13.7	114.1	12.5	87754	$3.74\cdot10^{-2}$	0.00	$4.15\cdot10^{-1}$	$3.73\cdot10^{-3}$	$1.83\cdot10^{-3}$	$2.22\cdot10^{-2}$	91.0%	0.87%	0.43%	5.16%	0.00%	7.57%
61	13.2	113.8	11.9	61657	$4.00\cdot10^{-2}$	0.00	$3.99\cdot10^{-1}$	$3.67\cdot10^{-3}$	$1.67\cdot10^{-3}$	$4.95\cdot10^{-2}$	87.5%	0.85%	0.39%	11.5%	0.00%	8.09%
62	12.6	113.4	11.3	68217	$5.27\cdot10^{-2}$	0.00	$3.91\cdot10^{-1}$	$3.87\cdot10^{-3}$	$1.64\cdot10^{-3}$	$3.14\cdot10^{-2}$	85.7%	0.90%	0.38%	7.29%	0.00%	10.7%
63	12.1	112.7	10.7	25380	$5.85\cdot10^{-2}$	0.00	$3.82\cdot10^{-1}$	$3.78\cdot10^{-3}$	$2.01\cdot10^{-3}$	$9.49\cdot10^{-2}$	83.8%	0.88%	0.47%	22.0%	0.00%	11.8%
64	11.6	111.6	10.1	95461	$5.85\cdot10^{-2}$	0.00	$3.81\cdot10^{-1}$	$3.75\cdot10^{-3}$	$1.66\cdot10^{-3}$	$9.47\cdot10^{-3}$	83.6%	0.87%	0.38%	2.20%	0.00%	11.9%
65	11.0	110.7	9.5	57755	$6.51\cdot10^{-2}$	0.00	$3.62\cdot10^{-1}$	$3.64\cdot10^{-3}$	$1.66\cdot10^{-3}$	$5.76\cdot10^{-2}$	79.4%	0.84%	0.39%	13.4%	0.00%	13.2%
66	10.5	109.8	9.0	61381	$7.90\cdot10^{-2}$	0.00	$3.53\cdot10^{-1}$	$3.60\cdot10^{-3}$	$1.76\cdot10^{-3}$	$3.28\cdot10^{-2}$	77.4%	0.84%	0.41%	7.62%	0.00%	16.0%
67	10.0	108.9	8.4	56826	$8.02\cdot10^{-2}$	0.00	$3.38\cdot10^{-1}$	$3.45\cdot10^{-3}$	$1.67\cdot10^{-3}$	$3.69\cdot10^{-2}$	74.1%	0.80%	0.39%	8.56%	0.00%	16.2%
68	9.4	109.4	7.8	62722	$8.67\cdot10^{-2}$	0.00	$3.27\cdot10^{-1}$	$3.59\cdot10^{-3}$	$1.64\cdot10^{-3}$	$2.98\cdot10^{-2}$	71.6%	0.83%	0.38%	6.91%	0.00%	17.5%
69	8.9	110.4	7.2	72433	$1.43\cdot10^{-1}$	0.00	$3.07\cdot10^{-1}$	$3.48\cdot10^{-3}$	$1.70\cdot10^{-3}$	$2.74\cdot10^{-2}$	67.3%	0.81%	0.39%	6.36%	0.00%	29.0%
70	8.4	110.1	6.7	80708	$1.68\cdot10^{-1}$	0.00	$2.92\cdot10^{-1}$	$3.64\cdot10^{-3}$	$1.67\cdot10^{-3}$	$2.55\cdot10^{-2}$	64.0%	0.85%	0.39%	5.92%	0.00%	34.1%
71	7.9	111.3	6.1	81057	$1.96\cdot10^{-1}$	0.00	$2.70\cdot10^{-1}$	$3.53\cdot10^{-3}$	$1.57\cdot10^{-3}$	$2.70\cdot10^{-2}$	59.2%	0.82%	0.36%	6.27%	0.00%	39.6%
72	7.3	111.4	5.5	82470	$2.19\cdot10^{-1}$	0.00	$2.44\cdot10^{-1}$	$3.48\cdot10^{-3}$	$1.46\cdot10^{-3}$	$2.40\cdot10^{-2}$	53.6%	0.81%	0.34%	5.57%	0.00%	44.3%
73	6.8	111.1	4.9	87451	$2.52\cdot10^{-1}$	0.00	$2.17\cdot10^{-1}$	$3.14\cdot10^{-3}$	$1.50\cdot10^{-3}$	$2.10\cdot10^{-2}$	47.6%	0.73%	0.35%	4.89%	0.00%	51.0%
74	6.3	110.7	4.4	55707	$2.75\cdot10^{-1}$	0.00	$1.83\cdot10^{-1}$	$2.96\cdot10^{-3}$	$1.42\cdot10^{-3}$	$2.94\cdot10^{-2}$	40.3%	0.69%	0.33%	6.82%	0.00%	55.7%

75	5.7	109.0	3.8	75364	$3.17\cdot10^{-1}$	0.00	$1.59\cdot10^{-1}$	$2.72\cdot10^{-3}$	$1.35\cdot10^{-3}$	$1.21\cdot10^{-2}$	35.1%	0.63%	0.31%	2.82%	0.00%	64.2%
76	5.2	105.9	3.2	68641	$3.41\cdot10^{-1}$	0.00	$1.28\cdot10^{-1}$	$2.36\cdot10^{-3}$	$1.34\cdot10^{-3}$	$1.46\cdot10^{-2}$	28.1%	0.55%	0.31%	3.38%	0.00%	69.0%
77	4.7	103.0	2.7	100513	$3.79\cdot10^{-1}$	0.00	$1.06\cdot10^{-1}$	$2.11\cdot10^{-3}$	$1.06\cdot10^{-3}$	$7.74\cdot10^{-3}$	23.3%	0.49%	0.25%	1.80%	0.00%	76.7%
78	4.1	100.1	2.2	57436	$3.92\cdot10^{-1}$	0.00	$8.04\cdot10^{-2}$	$1.93\cdot10^{-3}$	$8.18\cdot10^{-3}$	$1.39\cdot10^{-2}$	17.8%	0.45%	0.19%	3.22%	0.00%	79.4%
79	3.6	91.5	1.7	74038	$4.18\cdot10^{-1}$	0.00	$6.28\cdot10^{-2}$	$1.66\cdot10^{-3}$	$1.04\cdot10^{-4}$	$4.65\cdot10^{-3}$	13.9%	0.39%	0.24%	1.08%	0.00%	84.7%
80	3.1	78.3	1.3	72249	$4.37\cdot10^{-1}$	0.00	$4.87\cdot10^{-2}$	$1.38\cdot10^{-3}$	$7.47\cdot10^{-4}$	$4.97\cdot10^{-2}$	10.8%	0.32%	0.17%	1.15%	0.00%	88.5%
81	2.5	69.4	0.9	63430	$4.51\cdot10^{-1}$	0.00	$3.74\cdot10^{-2}$	$1.25\cdot10^{-3}$	$6.78\cdot10^{-4}$	$4.32\cdot10^{-2}$	8.36%	0.29%	0.16%	1.00%	0.00%	91.2%
82	2.0	60.5	0.6	38607	$4.48\cdot10^{-1}$	0.00	$2.73\cdot10^{-2}$	$1.24\cdot10^{-3}$	$4.92\cdot10^{-4}$	$4.22\cdot10^{-2}$	6.16%	0.29%	0.11%	0.98%	0.00%	90.7%
83	1.5	48.0	0.3	32956	$4.62\cdot10^{-1}$	0.00	$2.17\cdot10^{-2}$	$1.03\cdot10^{-3}$	$3.94\cdot10^{-4}$	$3.15\cdot10^{-2}$	4.92%	0.24%	0.09%	0.73%	0.00%	93.6%
84	1.0	16.7	0.1	36695	$4.93\cdot10^{-1}$	0.00	$1.80\cdot10^{-2}$	$9.81\cdot10^{-4}$	$4.63\cdot10^{-4}$	$2.22\cdot10^{-2}$	4.11%	0.23%	0.11%	0.52%	0.00%	99.8%
85	0.4	10.4	0.0	16720	$4.94\cdot10^{-1}$	0.00	$1.34\cdot10^{-2}$	$1.38\cdot10^{-3}$	$4.78\cdot10^{-4}$	$5.76\cdot10^{-2}$	3.11%	0.32%	0.11%	1.34%	0.00%	100.0%

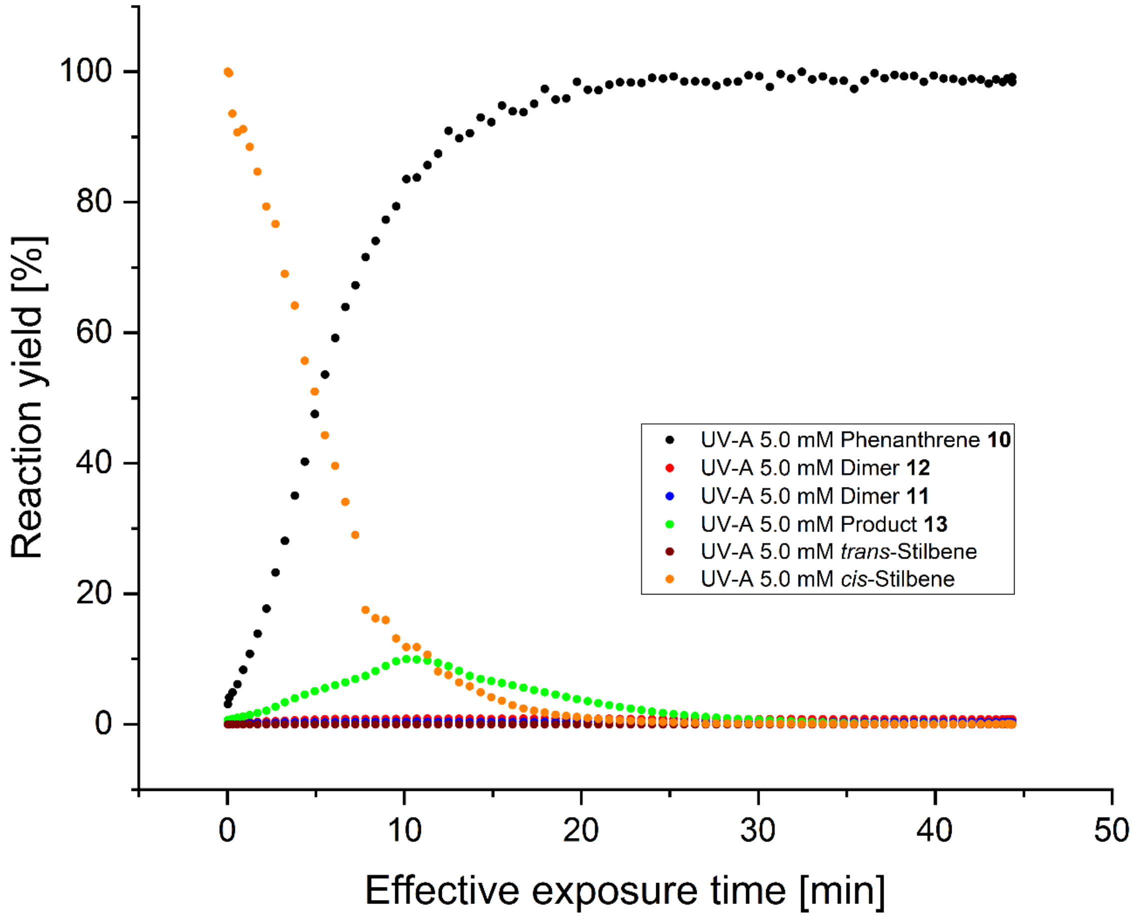


Figure S 16. Results of Switch-Off optimisation of Mallory photoreaction using UV-A light and 5.0 mM stilbene concentration. Top: Reaction components GC areas, conversion, and yield plotted against uncorrected residence time. Bottom: Reaction components GC areas, conversion, and yield plotted against exposure time, corrected for light inhomogeneity.

2. 4. 2. 2. Switch-Off experiment results using UV-A light and 50.0 mM stilbene concentration

Cis-stilbene (445.0 µL, 450.2 mg, 2.50 mmol, 1.0 eq., 50.0 mM solution), iodine (63.0 mg, 0.25 mmol, 0.1 eq., 5.0 mM solution), and dibutyl ether (1.5 mL, 1.17 g, 9.0 mmol, 3.6 eq., 180.0 mM solution) were dissolved in cyclohexane (48.0 mL, 106.6 vol.), obtained solution was saturated with oxygen by bubbling gaseous O_2 for 15 minutes, and then connected to flow reagents stream. Cyclohexane was connected to flow solvents stream. The UV-A lamp (Philips PLL 36W) and water cooling were then turned on and system was allowed to equilibrate for 30 minutes. Then reaction mixture was injected into the photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA). Effective exposure time was set to 180 minutes (which corresponds to 0.177 mL/min flow rate). Once the photoreactor was filled with reaction mixture, the UV lamp was switched off, the pump was switched to solvent stream, the reaction mixture was eluted from the photoreactor, and was collected into vials (0.375 mL of reaction mixture, diluted to 1.0 mL with acetone). Collected samples were then analysed using off-line GC.

Table S 12. Results of Switch-Off optimisation performed for Mallory reaction of cis-stilbene using UV-A light and 50.0 mM stilbene concentration.

#	Residence time [min]	Light output [%]	Effective exposure time [min]	IS GC Area	Area Ratio *cis*-Stilbene/IS	Area Ratio *trans*-Stilbene/IS	Area Ratio Phenanthrene 10/IS	Area Ratio Dimer ABAB 12/IS	Area Ratio Dimer AABB 11/IS	Area Ratio Product 13/IS	Phenanthrene yield [%]	Dimer 12 yield [%]	Dimer 11 yield [%]	Product 13 yield [%]	*trans*-Stilbene yield [%]	Remaining *cis*-Stilbene [%]
1	179.7	0.0	177.4	109081	$1.92\cdot10^{-3}$	$1.92\cdot10^{-2}$	$2.54\cdot10^{-1}$	$8.62\cdot10^{-2}$	$4.70\cdot10^{-2}$	$2.36\cdot10^{-2}$	59.0%	10.0%	5.45%	3.21%	4.47%	0.44%
2	177.5	3.4	177.3	154826	$2.38\cdot10^{-3}$	$1.94\cdot10^{-2}$	$2.56\cdot10^{-1}$	$8.78\cdot10^{-2}$	$4.81\cdot10^{-2}$	$1.66\cdot10^{-2}$	59.3%	10.2%	5.58%	2.26%	4.50%	0.54%
3	175.4	15.0	177.2	209235	$2.57\cdot10^{-3}$	$1.93\cdot10^{-2}$	$2.55\cdot10^{-1}$	$8.98\cdot10^{-2}$	$4.93\cdot10^{-2}$	$1.97\cdot10^{-2}$	59.2%	10.4%	5.72%	2.68%	4.48%	0.57%
4	173.3	26.6	176.9	195908	$2.74\cdot10^{-3}$	$1.92\cdot10^{-2}$	$2.54\cdot10^{-1}$	$8.86\cdot10^{-2}$	$4.83\cdot10^{-2}$	$2.96\cdot10^{-2}$	58.9%	10.3%	5.61%	4.04%	4.46%	0.61%
5	171.2	49.7	176.3	210482	$2.79\cdot10^{-3}$	$1.93\cdot10^{-2}$	$2.55\cdot10^{-1}$	$9.01\cdot10^{-2}$	$4.93\cdot10^{-2}$	$2.58\cdot10^{-2}$	59.3%	10.5%	5.72%	3.52%	4.49%	0.62%
6	169.1	70.8	175.2	200347	$2.73\cdot10^{-3}$	$1.94\cdot10^{-2}$	$2.57\cdot10^{-1}$	$9.02\cdot10^{-2}$	$4.95\cdot10^{-2}$	$3.01\cdot10^{-2}$	59.6%	10.5%	5.75%	4.10%	4.51%	0.60%
7	166.9	77.9	173.7	212641	$2.86\cdot10^{-3}$	$1.95\cdot10^{-2}$	$2.56\cdot10^{-1}$	$8.94\cdot10^{-2}$	$4.91\cdot10^{-2}$	$2.75\cdot10^{-2}$	59.4%	10.4%	5.69%	3.74%	4.52%	0.63%
8	164.8	85.0	172.1	214566	$2.84\cdot10^{-3}$	$1.95\cdot10^{-2}$	$2.55\cdot10^{-1}$	$9.09\cdot10^{-2}$	$4.98\cdot10^{-2}$	$2.92\cdot10^{-2}$	59.1%	10.5%	5.77%	3.98%	4.53%	0.63%
9	162.7	93.4	170.2	209322	$2.92\cdot10^{-3}$	$1.96\cdot10^{-2}$	$2.55\cdot10^{-1}$	$9.10\cdot10^{-2}$	$4.99\cdot10^{-2}$	$3.21\cdot10^{-2}$	59.3%	10.6%	5.79%	4.38%	4.56%	0.64%
10	160.6	98.7	168.3	213270	$2.98\cdot10^{-3}$	$1.95\cdot10^{-2}$	$2.52\cdot10^{-1}$	$9.07\cdot10^{-2}$	$4.97\cdot10^{-2}$	$3.21\cdot10^{-2}$	58.6%	10.5%	5.77%	4.38%	4.53%	0.65%
11	158.5	100.7	166.2	206376	$3.10\cdot10^{-3}$	$1.98\cdot10^{-2}$	$2.54\cdot10^{-1}$	$9.17\cdot10^{-2}$	$5.00\cdot10^{-2}$	$3.54\cdot10^{-2}$	59.0%	10.6%	5.80%	4.82%	4.60%	0.68%
12	156.4	102.7	164.0	206074	$3.26\cdot10^{-3}$	$1.99\cdot10^{-2}$	$2.53\cdot10^{-1}$	$9.09\cdot10^{-2}$	$4.97\cdot10^{-2}$	$3.62\cdot10^{-2}$	58.7%	10.6%	5.77%	4.93%	4.63%	0.71%
13	154.2	104.5	161.8	232378	$3.45\cdot10^{-3}$	$1.99\cdot10^{-2}$	$2.50\cdot10^{-1}$	$9.17\cdot10^{-2}$	$5.00\cdot10^{-2}$	$3.38\cdot10^{-2}$	57.9%	10.6%	5.80%	4.60%	4.61%	0.75%
14	152.1	105.5	159.6	264955	$3.69\cdot10^{-3}$	$2.01\cdot10^{-2}$	$2.49\cdot10^{-1}$	$9.40\cdot10^{-2}$	$5.15\cdot10^{-2}$	$3.57\cdot10^{-2}$	57.9%	10.9%	5.97%	4.86%	4.67%	0.79%
15	150.0	105.1	157.4	220090	$3.91\cdot10^{-3}$	$2.03\cdot10^{-2}$	$2.49\cdot10^{-1}$	$9.31\cdot10^{-2}$	$5.09\cdot10^{-2}$	$5.39\cdot10^{-2}$	57.7%	10.8%	5.90%	7.34%	4.71%	0.84%
16	147.9	104.7	155.2	213868	$4.21\cdot10^{-3}$	$2.05\cdot10^{-2}$	$2.48\cdot10^{-1}$	$9.31\cdot10^{-2}$	$5.07\cdot10^{-2}$	$4.87\cdot10^{-2}$	57.5%	10.8%	5.89%	6.63%	4.75%	0.89%
17	145.8	103.7	152.9	227018	$4.51\cdot10^{-3}$	$2.05\cdot10^{-2}$	$2.44\cdot10^{-1}$	$9.24\cdot10^{-2}$	$5.05\cdot10^{-2}$	$4.68\cdot10^{-2}$	56.6%	10.7%	5.86%	6.38%	4.75%	0.95%
18	143.6	104.8	150.7	208912	$4.80\cdot10^{-3}$	$2.05\cdot10^{-2}$	$2.42\cdot10^{-1}$	$9.15\cdot10^{-2}$	$4.99\cdot10^{-2}$	$5.73\cdot10^{-2}$	56.1%	10.6%	5.80%	7.80%	4.76%	1.01%
19	141.5	106.2	148.5	219769	$5.05\cdot10^{-3}$	$2.05\cdot10^{-2}$	$2.39\cdot10^{-1}$	$9.18\cdot10^{-2}$	$5.01\cdot10^{-2}$	$5.23\cdot10^{-2}$	55.6%	10.7%	5.81%	7.13%	4.77%	1.06%
20	139.4	107.5	146.3	226213	$5.37\cdot10^{-3}$	$2.08\cdot10^{-2}$	$2.39\cdot10^{-1}$	$9.29\cdot10^{-2}$	$5.08\cdot10^{-2}$	$5.67\cdot10^{-2}$	55.6%	10.8%	5.90%	7.72%	4.82%	1.12%
21	137.3	109.6	144.0	234498	$5.74\cdot10^{-3}$	$2.09\cdot10^{-2}$	$2.38\cdot10^{-1}$	$9.20\cdot10^{-2}$	$5.03\cdot10^{-2}$	$5.99\cdot10^{-2}$	55.2%	10.7%	5.84%	8.15%	4.85%	1.20%
22	135.2	111.1	141.7	62733	$4.53\cdot10^{-3}$	$2.07\cdot10^{-2}$	$2.35\cdot10^{-1}$	$8.90\cdot10^{-2}$	$4.85\cdot10^{-2}$	$2.41\cdot10^{-1}$	54.7%	10.3%	5.63%	-	4.81%	0.96%

23	133.1	111.4	139.3	220717	$6.01\cdot10^{-3}$	$2.11\cdot10^{-2}$	$2.34\cdot10^{-1}$	$9.26\cdot10^{-2}$	$5.05\cdot10^{-2}$	$1.83\cdot10^{-2}$	54.3%	10.7%	5.87%	-	4.89%	1.25%
24	130.9	111.8	136.9	225538	$6.50\cdot10^{-3}$	$2.12\cdot10^{-2}$	$2.33\cdot10^{-1}$	$9.26\cdot10^{-2}$	$5.05\cdot10^{-2}$	$7.05\cdot10^{-2}$	54.1%	10.7%	5.86%	9.60%	4.92%	1.34%
25	128.8	112.6	134.6	228320	$6.75\cdot10^{-3}$	$2.10\cdot10^{-2}$	$2.29\cdot10^{-1}$	$9.29\cdot10^{-2}$	$5.06\cdot10^{-2}$	$7.46\cdot10^{-2}$	53.1%	10.8%	5.87%	10.2%	4.88%	1.39%
26	126.7	113.0	132.2	252598	$7.30\cdot10^{-3}$	$2.12\cdot10^{-2}$	$2.28\cdot10^{-1}$	$9.33\cdot10^{-2}$	$5.09\cdot10^{-2}$	$7.20\cdot10^{-2}$	53.0%	10.8%	5.91%	9.81%	4.92%	1.50%
27	124.6	113.2	129.8	233113	$7.78\cdot10^{-3}$	$2.12\cdot10^{-2}$	$2.26\cdot10^{-1}$	$9.33\cdot10^{-2}$	$5.10\cdot10^{-2}$	$9.11\cdot10^{-2}$	52.5%	10.8%	5.92%	12.4%	4.92%	1.60%
28	122.5	113.4	127.4	238504	$8.26\cdot10^{-3}$	$2.10\cdot10^{-2}$	$2.23\cdot10^{-1}$	$9.22\cdot10^{-2}$	$5.03\cdot10^{-2}$	$8.59\cdot10^{-2}$	51.7%	10.7%	5.84%	11.7%	4.88%	1.69%
29	120.3	113.5	125.0	227079	$9.10\cdot10^{-3}$	$2.08\cdot10^{-2}$	$2.19\cdot10^{-1}$	$9.15\cdot10^{-2}$	$4.99\cdot10^{-2}$	$9.48\cdot10^{-2}$	50.7%	10.6%	5.79%	12.9%	4.84%	1.86%
30	118.2	113.6	122.6	235982	$9.48\cdot10^{-3}$	$2.08\cdot10^{-2}$	$2.17\cdot10^{-1}$	$9.24\cdot10^{-2}$	$5.04\cdot10^{-2}$	$8.95\cdot10^{-2}$	50.4%	10.7%	5.85%	12.2%	4.82%	1.93%
31	116.1	113.8	120.2	246683	$1.16\cdot10^{-2}$	$2.04\cdot10^{-2}$	$2.12\cdot10^{-1}$	$9.41\cdot10^{-2}$	$5.12\cdot10^{-2}$	$9.35\cdot10^{-2}$	49.2%	10.9%	5.94%	12.7%	4.74%	2.34%
32	114.0	114.0	117.8	236289	$1.03\cdot10^{-2}$	$2.08\cdot10^{-2}$	$2.16\cdot10^{-1}$	$9.36\cdot10^{-2}$	$5.11\cdot10^{-2}$	$1.12\cdot10^{-1}$	50.2%	10.9%	5.93%	15.2%	4.83%	2.10%
33	111.9	114.1	115.4	220826	$1.31\cdot10^{-2}$	$2.03\cdot10^{-2}$	$2.10\cdot10^{-1}$	$9.23\cdot10^{-2}$	$5.02\cdot10^{-2}$	$1.10\cdot10^{-1}$	48.7%	10.7%	5.83%	15.0%	4.70%	2.64%
34	109.7	114.2	112.9	254450	$1.43\cdot10^{-2}$	$2.00\cdot10^{-2}$	$2.08\cdot10^{-1}$	$9.36\cdot10^{-2}$	$5.11\cdot10^{-2}$	$9.34\cdot10^{-2}$	48.3%	10.9%	5.93%	12.7%	4.64%	2.87%
35	107.6	114.3	110.5	221751	$1.56\cdot10^{-2}$	$1.95\cdot10^{-2}$	$2.05\cdot10^{-1}$	$9.28\cdot10^{-2}$	$5.05\cdot10^{-2}$	$1.30\cdot10^{-1}$	47.6%	10.8%	5.86%	17.7%	4.52%	3.12%
36	105.5	114.1	108.1	233204	$1.68\cdot10^{-2}$	$1.91\cdot10^{-2}$	$2.03\cdot10^{-1}$	$9.31\cdot10^{-2}$	$5.06\cdot10^{-2}$	$1.09\cdot10^{-1}$	47.1%	10.8%	5.87%	14.8%	4.44%	3.36%
37	103.4	114.7	105.7	259630	$2.00\cdot10^{-2}$	$1.86\cdot10^{-2}$	$2.01\cdot10^{-1}$	$9.57\cdot10^{-2}$	$5.21\cdot10^{-2}$	$1.06\cdot10^{-1}$	46.7%	11.1%	6.05%	14.4%	4.32%	3.99%
38	101.3	114.7	103.3	243198	$2.50\cdot10^{-2}$	$1.78\cdot10^{-2}$	$1.96\cdot10^{-1}$	$9.50\cdot10^{-2}$	$5.18\cdot10^{-2}$	$1.33\cdot10^{-1}$	45.5%	11.0%	6.01%	18.1%	4.12%	4.98%
39	99.2	114.8	100.8	227043	$3.02\cdot10^{-2}$	$1.69\cdot10^{-2}$	$1.92\cdot10^{-1}$	$9.39\cdot10^{-2}$	$5.11\cdot10^{-2}$	$1.34\cdot10^{-1}$	44.6%	10.9%	5.93%	18.3%	3.92%	5.99%
40	97.0	114.6	98.4	220435	$3.52\cdot10^{-2}$	$1.60\cdot10^{-2}$	$1.88\cdot10^{-1}$	$9.45\cdot10^{-2}$	$5.14\cdot10^{-2}$	$1.29\cdot10^{-1}$	43.7%	11.0%	5.96%	17.6%	3.71%	6.99%
41	94.9	114.6	96.0	231694	$3.98\cdot10^{-2}$	$1.51\cdot10^{-2}$	$1.84\cdot10^{-1}$	$9.35\cdot10^{-2}$	$5.07\cdot10^{-2}$	$1.22\cdot10^{-1}$	42.7%	10.8%	5.89%	16.6%	3.50%	7.88%
42	92.8	114.8	93.6	281435	$4.75\cdot10^{-2}$	$1.40\cdot10^{-2}$	$1.81\cdot10^{-1}$	$9.69\cdot10^{-2}$	$5.29\cdot10^{-2}$	$1.05\cdot10^{-1}$	42.0%	11.2%	6.14%	14.4%	3.25%	9.40%
43	90.7	114.9	91.1	239149	$5.64\cdot10^{-2}$	$1.20\cdot10^{-2}$	$1.71\cdot10^{-1}$	$9.25\cdot10^{-2}$	$5.03\cdot10^{-2}$	$1.58\cdot10^{-1}$	39.8%	10.7%	5.84%	21.5%	2.79%	11.2%
44	88.6	114.8	88.7	255763	$6.39\cdot10^{-2}$	$1.11\cdot10^{-2}$	$1.70\cdot10^{-1}$	$9.56\cdot10^{-2}$	$5.21\cdot10^{-2}$	$1.20\cdot10^{-1}$	39.5%	11.1%	6.04%	16.3%	2.58%	12.6%
45	86.4	114.8	86.3	229396	$7.19\cdot10^{-2}$	$9.70\cdot10^{-3}$	$1.64\cdot10^{-1}$	$9.42\cdot10^{-2}$	$5.12\cdot10^{-2}$	$1.48\cdot10^{-1}$	38.0%	10.9%	5.94%	20.1%	2.25%	14.2%
46	84.3	114.9	83.8	249088	$8.21\cdot10^{-2}$	$8.21\cdot10^{-3}$	$1.59\cdot10^{-1}$	$9.49\cdot10^{-2}$	$5.17\cdot10^{-2}$	$1.20\cdot10^{-1}$	36.9%	11.0%	5.99%	16.3%	1.90%	16.2%
47	82.2	115.0	81.4	244605	$9.53\cdot10^{-2}$	$6.57\cdot10^{-3}$	$1.53\cdot10^{-1}$	$9.54\cdot10^{-2}$	$5.20\cdot10^{-2}$	$1.32\cdot10^{-1}$	35.5%	11.1%	6.03%	18.0%	1.52%	18.8%
48	80.1	114.4	79.0	225833	$1.04\cdot10^{-1}$	$5.43\cdot10^{-3}$	$1.45\cdot10^{-1}$	$9.19\cdot10^{-2}$	$4.99\cdot10^{-2}$	$1.38\cdot10^{-1}$	33.7%	10.7%	5.79%	18.8%	1.26%	20.5%
49	78.0	115.0	76.6	286773	$1.17\cdot10^{-1}$	$4.45\cdot10^{-3}$	$1.42\cdot10^{-1}$	$9.69\cdot10^{-2}$	$5.28\cdot10^{-2}$	$9.52\cdot10^{-2}$	32.9%	11.2%	6.12%	13.0%	1.03%	23.1%
50	75.8	115.0	74.1	250257	$1.35\cdot10^{-1}$	$2.99\cdot10^{-3}$	$1.32\cdot10^{-1}$	$9.38\cdot10^{-2}$	$5.09\cdot10^{-2}$	$1.46\cdot10^{-1}$	30.7%	10.9%	5.91%	19.8%	0.69%	26.5%
51	73.7	114.9	71.7	237633	$1.55\cdot10^{-1}$	$1.56\cdot10^{-3}$	$1.21\cdot10^{-1}$	$9.24\cdot10^{-2}$	$5.02\cdot10^{-2}$	$1.26\cdot10^{-1}$	28.1%	10.7%	5.82%	17.1%	0.36%	30.5%
52	71.6	114.8	69.3	253777	$1.66\cdot10^{-1}$	$1.12\cdot10^{-3}$	$1.15\cdot10^{-1}$	$9.33\cdot10^{-2}$	$5.08\cdot10^{-2}$	$1.05\cdot10^{-1}$	26.8%	10.8%	5.89%	14.3%	0.26%	32.6%

53	69.5	114.8	66.9	278634	$1.77\cdot10^{-1}$	$6.89\cdot10^{-4}$	$1.09\cdot10^{-1}$	$9.43\cdot10^{-2}$	$5.13\cdot10^{-2}$	$1.03\cdot10^{-1}$	25.3%	10.9%	5.95%	14.0%	0.16%	34.9%
54	67.4	114.7	64.4	276581	$1.91\cdot10^{-1}$	$3.58\cdot10^{-4}$	$1.02\cdot10^{-1}$	$9.34\cdot10^{-2}$	$5.08\cdot10^{-2}$	$1.13\cdot10^{-1}$	23.8%	10.8%	5.90%	15.4%	0.08%	37.5%
55	65.3	114.6	62.0	237512	$1.92\cdot10^{-1}$	$2.53\cdot10^{-4}$	$9.79\cdot10^{-2}$	$9.25\cdot10^{-2}$	$5.02\cdot10^{-2}$	$1.26\cdot10^{-1}$	22.7%	10.7%	5.83%	17.2%	0.06%	37.8%
56	63.1	114.7	59.6	236712	$2.03\cdot10^{-1}$	$1.44\cdot10^{-4}$	$9.24\cdot10^{-2}$	$9.15\cdot10^{-2}$	$4.97\cdot10^{-2}$	$1.07\cdot10^{-1}$	21.4%	10.6%	5.76%	14.6%	0.03%	40.0%
57	61.0	114.7	57.2	238023	$2.09\cdot10^{-1}$	$3.36\cdot10^{-5}$	$8.63\cdot10^{-2}$	$8.97\cdot10^{-2}$	$4.86\cdot10^{-2}$	$1.03\cdot10^{-1}$	20.0%	10.4%	5.64%	14.0%	0.01%	41.1%
58	58.9	114.5	54.8	268091	$2.24\cdot10^{-1}$	$2.61\cdot10^{-5}$	$8.08\cdot10^{-2}$	$8.99\cdot10^{-2}$	$4.88\cdot10^{-2}$	$8.86\cdot10^{-2}$	18.8%	10.4%	5.66%	12.1%	0.01%	44.1%
59	56.8	114.3	52.4	250037	$2.27\cdot10^{-1}$	$1.20\cdot10^{-5}$	$7.64\cdot10^{-2}$	$8.77\cdot10^{-2}$	$4.76\cdot10^{-2}$	$1.04\cdot10^{-1}$	17.7%	10.2%	5.52%	14.2%	0.00%	44.6%
60	54.7	114.1	50.0	260607	$2.34\cdot10^{-1}$	$1.15\cdot10^{-5}$	$7.51\cdot10^{-2}$	$8.84\cdot10^{-2}$	$4.81\cdot10^{-2}$	$8.95\cdot10^{-2}$	17.4%	10.3%	5.58%	12.2%	0.00%	46.0%
61	52.5	113.8	47.6	276793	$2.43\cdot10^{-1}$	$3.61\cdot10^{-6}$	$7.14\cdot10^{-2}$	$8.62\cdot10^{-2}$	$4.68\cdot10^{-2}$	$8.80\cdot10^{-2}$	16.6%	10.0%	5.43%	12.0%	0.00%	47.8%
62	50.4	113.4	45.2	238283	$2.47\cdot10^{-1}$	0.00	$6.84\cdot10^{-2}$	$8.27\cdot10^{-2}$	$4.50\cdot10^{-2}$	$1.01\cdot10^{-1}$	15.9%	9.60%	5.22%	13.8%	0.00%	48.6%
63	48.3	112.7	42.8	226196	$2.61\cdot10^{-1}$	0.00	$6.48\cdot10^{-2}$	$8.02\cdot10^{-2}$	$4.36\cdot10^{-2}$	$8.57\cdot10^{-2}$	15.0%	9.30%	5.06%	11.7%	0.00%	51.3%
64	46.2	111.6	40.4	285215	$2.67\cdot10^{-1}$	0.00	$6.29\cdot10^{-2}$	$8.01\cdot10^{-2}$	$4.37\cdot10^{-2}$	$5.92\cdot10^{-2}$	14.6%	9.29%	5.07%	8.07%	0.00%	52.6%
65	44.1	110.7	38.1	294821	$2.77\cdot10^{-1}$	0.00	$6.29\cdot10^{-2}$	$8.04\cdot10^{-2}$	$4.39\cdot10^{-2}$	$7.00\cdot10^{-2}$	14.6%	9.34%	5.09%	9.54%	0.00%	54.5%
66	41.9	109.8	35.8	316725	$2.83\cdot10^{-1}$	0.00	$5.77\cdot10^{-2}$	$7.34\cdot10^{-2}$	$4.01\cdot10^{-2}$	$6.59\cdot10^{-2}$	13.4%	8.51%	4.65%	8.98%	0.00%	55.7%
67	39.8	108.9	33.5	270764	$3.00\cdot10^{-1}$	0.00	$5.58\cdot10^{-2}$	$7.22\cdot10^{-2}$	$3.94\cdot10^{-2}$	$6.94\cdot10^{-2}$	13.0%	8.38%	4.58%	9.45%	0.00%	58.9%
68	37.7	109.4	31.2	231788	$3.05\cdot10^{-1}$	0.00	$5.27\cdot10^{-2}$	$6.88\cdot10^{-2}$	$3.76\cdot10^{-2}$	$6.36\cdot10^{-2}$	12.2%	7.98%	4.37%	8.67%	0.00%	60.0%
69	35.6	110.4	28.9	254380	$3.13\cdot10^{-1}$	0.00	$4.98\cdot10^{-2}$	$6.58\cdot10^{-2}$	$3.61\cdot10^{-2}$	$4.57\cdot10^{-2}$	11.6%	7.64%	4.19%	6.23%	0.00%	61.6%
70	33.5	110.1	26.6	273213	$3.26\cdot10^{-1}$	0.00	$4.72\cdot10^{-2}$	$6.36\cdot10^{-2}$	$3.49\cdot10^{-2}$	$4.26\cdot10^{-2}$	11.0%	7.38%	4.05%	5.80%	0.00%	64.2%
71	31.4	111.3	24.3	266261	$3.39\cdot10^{-1}$	0.00	$4.37\cdot10^{-2}$	$5.95\cdot10^{-2}$	$3.27\cdot10^{-2}$	$4.23\cdot10^{-2}$	10.1%	6.90%	3.80%	5.76%	0.00%	66.6%
72	29.2	111.4	22.0	258217	$3.49\cdot10^{-1}$	0.00	$4.00\cdot10^{-2}$	$5.58\cdot10^{-2}$	$3.07\cdot10^{-2}$	$3.68\cdot10^{-2}$	9.29%	6.48%	3.56%	5.01%	0.00%	68.7%
73	27.1	111.1	19.7	287101	$3.62\cdot10^{-1}$	0.00	$3.60\cdot10^{-2}$	$5.15\cdot10^{-2}$	$2.84\cdot10^{-2}$	$2.84\cdot10^{-2}$	8.35%	5.98%	3.30%	3.87%	0.00%	71.3%
74	25.0	110.7	17.5	283057	$3.80\cdot10^{-1}$	0.00	$3.22\cdot10^{-2}$	$4.80\cdot10^{-2}$	$2.65\cdot10^{-2}$	$2.69\cdot10^{-2}$	7.47%	5.57%	3.08%	3.67%	0.00%	74.6%
75	22.9	109.0	15.2	239673	$3.90\cdot10^{-1}$	0.00	$2.80\cdot10^{-2}$	$4.34\cdot10^{-2}$	$2.41\cdot10^{-2}$	$2.65\cdot10^{-2}$	6.49%	5.04%	2.79%	3.61%	0.00%	76.7%
76	20.8	105.9	13.0	238391	$4.11\cdot10^{-1}$	0.00	$2.23\cdot10^{-2}$	$3.63\cdot10^{-2}$	$2.02\cdot10^{-2}$	$1.86\cdot10^{-2}$	5.17%	4.21%	2.34%	2.53%	0.00%	80.7%
77	18.6	103.0	10.9	237222	$4.25\cdot10^{-1}$	0.00	$1.75\cdot10^{-2}$	$3.05\cdot10^{-2}$	$1.70\cdot10^{-2}$	$1.34\cdot10^{-2}$	4.06%	3.53%	1.98%	1.82%	0.00%	83.6%
78	16.5	100.1	8.8	276563	$4.38\cdot10^{-1}$	0.00	$1.40\cdot10^{-2}$	$2.61\cdot10^{-2}$	$1.46\cdot10^{-2}$	$8.37\cdot10^{-3}$	3.26%	3.03%	1.70%	1.14%	0.00%	86.1%
79	14.4	91.5	6.8	319017	$4.44\cdot10^{-1}$	0.00	$1.05\cdot10^{-2}$	$2.13\cdot10^{-2}$	$1.20\cdot10^{-2}$	$6.46\cdot10^{-3}$	2.43%	2.48%	1.39%	0.88%	0.00%	87.2%
80	12.3	78.3	5.0	318741	$4.60\cdot10^{-1}$	0.00	$7.56\cdot10^{-3}$	$1.77\cdot10^{-2}$	$9.96\cdot10^{-3}$	$5.21\cdot10^{-3}$	1.75%	2.05%	1.16%	0.71%	0.00%	90.5%
81	10.2	69.4	3.5	243650	$4.76\cdot10^{-1}$	0.00	$5.09\cdot10^{-3}$	$1.40\cdot10^{-2}$	$7.96\cdot10^{-3}$	$4.89\cdot10^{-3}$	1.18%	1.62%	0.92%	0.67%	0.00%	93.6%
82	8.1	60.5	2.2	255433	$4.87\cdot10^{-1}$	0.00	$3.23\cdot10^{-3}$	$1.07\cdot10^{-2}$	$6.08\cdot10^{-3}$	$2.52\cdot10^{-3}$	0.75%	1.24%	0.71%	0.34%	0.00%	95.8%

83	5.9	48.0	1.2	280209	$4.87\cdot10^{-1}$	0.00	$1.87\cdot10^{-3}$	$7.58\cdot10^{-3}$	$4.31\cdot10^{-3}$	$1.59\cdot10^{-3}$	0.43%	0.88%	0.50%	0.22%	0.00%	95.7%
84	3.8	16.7	0.4	304730	$4.97\cdot10^{-1}$	0.00	$1.14\cdot10^{-3}$	$5.48\cdot10^{-3}$	$3.16\cdot10^{-3}$	$1.08\cdot10^{-3}$	0.26%	0.64%	0.37%	0.15%	0.00%	97.7%
85	1.7	10.4	0.1	300733	$5.01\cdot10^{-1}$	0.00	$7.08\cdot10^{-4}$	$3.53\cdot10^{-3}$	$2.05\cdot10^{-3}$	$6.90\cdot10^{-4}$	0.16%	0.41%	0.24%	0.09%	0.00%	98.4%
86	0.0	4.0	0.0	267768	$5.09\cdot10^{-1}$	0.00	$3.77\cdot10^{-4}$	$2.22\cdot10^{-3}$	$1.29\cdot10^{-3}$	$5.39\cdot10^{-4}$	0.09%	0.26%	0.15%	0.07%	0.00%	99.3%

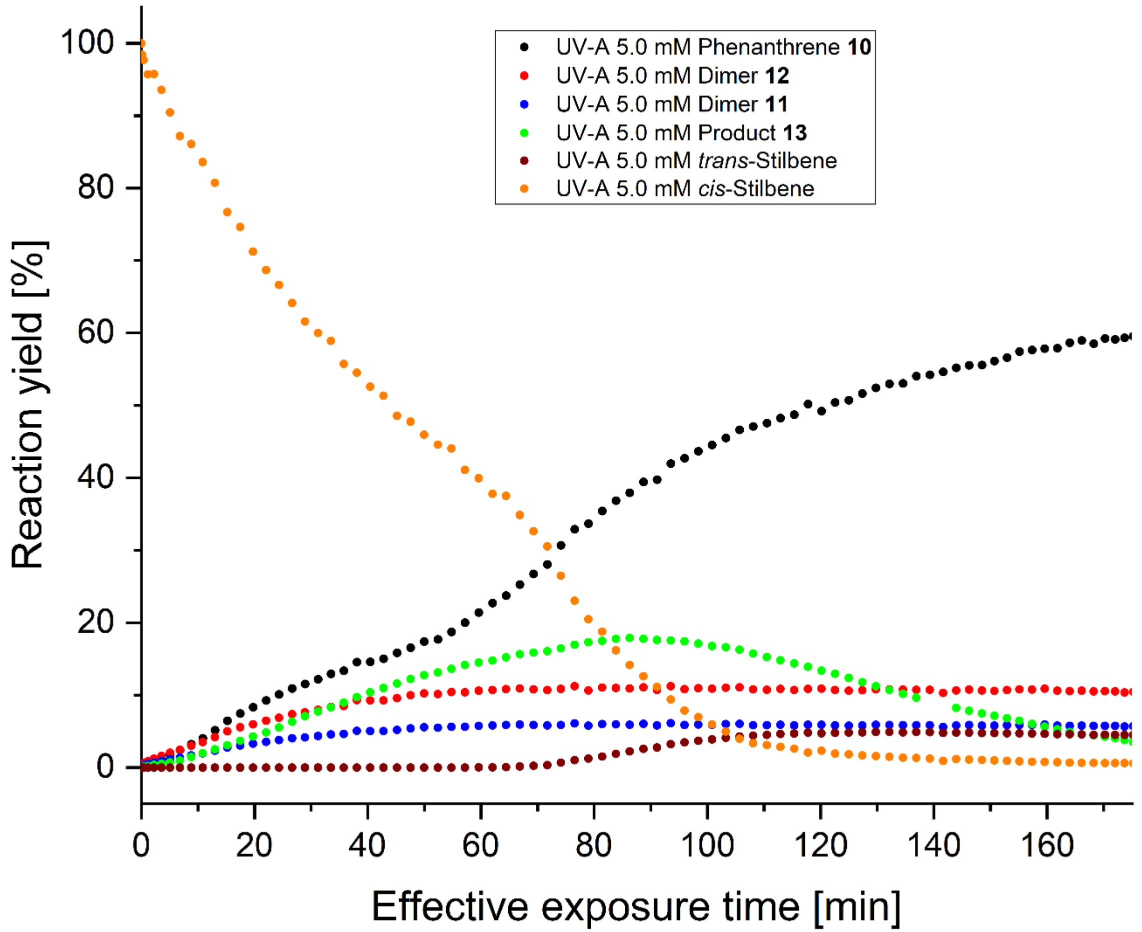


Figure S 17. Results of Switch-Off optimisation of Mallory photoreaction using UV-A light and 50.0 mM stilbene concentration. Top: Reaction components GC areas, conversion, and yield plotted against uncorrected residence time. Bottom: Reaction components GC areas, conversion, and yield plotted against exposure time, corrected for light inhomogeneity.

2. 4. 2. 3. Switch-Off experiment results using UV-B light and 5.0 mM stilbene concentration

Cis-stilbene (44.5 µL, 45.0 mg, 0.25 mmol, 1.0 eq., 5.0 mM solution), iodine (6.3 mg, 0.025 mmol, 0.1 eq., 0.5 mM solution), and dibutyl ether (0.15 mL, 117.1 mg, 0.90 mmol, 3.6 eq., 18.0 mM solution) were dissolved in cyclohexane (50.0 mL, 1111.1 vol.), obtained solution was saturated with oxygen by bubbling gaseous O_2 for 15 minutes, and then connected to flow reagents stream. Cyclohexane was connected to flow solvents stream. The UV-B lamp (Philips PL-L 36W/01/4P) and water cooling were then turned on and system was allowed to equilibrate for 30 minutes. Then reaction mixture was injected into the photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA). Effective exposure time was set to 45 minutes (which corresponds to 0.707 mL/min flow rate). Once the photoreactor was filled with reaction mixture, the UV lamp was switched off, the pump was switched to solvent stream, the reaction mixture was eluted from the photoreactor, and was collected into vials (0.375 mL of reaction mixture, diluted to 1.0 mL with acetone). Collected samples were then analysed using off-line GC.

Table S 13. Results of Switch-Off optimisation performed for Mallory reaction of cis-stilbene using UV-B light and 5.0 mM stilbene concentration.

#	Residence time [min]	Included/Excluded	Reactor volume [mL]	Effective Reactor Volume [mL]	Effective exposure time [min]	IS GC Area	Area Ratio *cis*-Stilbene/IS	Area Ratio *trans*-Stilbene/IS	Area Ratio Phenanthrene 10/IS	Area Ratio Dimer ABAB 12/IS	Area Ratio Dimer AABB 11/IS	Area Ratio Product 13/IS	Phenanthrene yield [%]	Dimer 12 yield [%]	Dimer 11 yield [%]	Product 13 yield [%]	*trans*-Stilbene yield [%]	Remaining *cis*-Stilbene [%]
1	45.0	Excluded	31.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	44.4	Excluded	31.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	43.9	Excluded	31.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	43.4	Excluded	30.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	42.9	Excluded	30.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	42.3	Included	29.9	28.5	40.3	214976	0.00	$5.65\cdot10^{-2}$	$3.08\cdot10^{-1}$	$4.14\cdot10^{-2}$	$2.05\cdot10^{-2}$	$1.90\cdot10^{-4}$	71.4%	4.80%	4.75%	0.04%	13.1%	0.00%
7	41.8	Included	29.6	28.1	39.8	208518	0.00	$5.61\cdot10^{-2}$	$3.06\cdot10^{-1}$	$4.08\cdot10^{-2}$	$2.02\cdot10^{-2}$	$2.13\cdot10^{-4}$	71.1%	4.73%	4.68%	0.05%	13.0%	0.00%
8	41.3	Included	29.2	27.8	39.3	215194	0.00	$5.65\cdot10^{-2}$	$3.06\cdot10^{-1}$	$4.05\cdot10^{-2}$	$2.01\cdot10^{-2}$	$3.44\cdot10^{-4}$	71.0%	4.70%	4.65%	0.08%	13.1%	0.00%
9	40.7	Included	28.8	27.4	38.7	210371	0.00	$5.52\cdot10^{-2}$	$3.04\cdot10^{-1}$	$4.00\cdot10^{-2}$	$1.98\cdot10^{-2}$	$1.76\cdot10^{-4}$	70.5%	4.64%	4.59%	0.04%	12.8%	0.00%
10	40.2	Included	28.4	27.0	38.2	204481	0.00	$5.69\cdot10^{-2}$	$3.09\cdot10^{-1}$	$4.12\cdot10^{-2}$	$2.04\cdot10^{-2}$	$1.81\cdot10^{-4}$	71.8%	4.78%	4.73%	0.04%	13.2%	0.00%
11	39.7	Included	28.1	26.6	37.7	210276	0.00	$5.76\cdot10^{-2}$	$3.12\cdot10^{-1}$	$4.18\cdot10^{-2}$	$2.06\cdot10^{-2}$	$2.99\cdot10^{-4}$	72.3%	4.85%	4.78%	0.07%	13.4%	0.00%
12	39.1	Included	27.7	26.3	37.1	208870	0.00	$5.68\cdot10^{-2}$	$3.07\cdot10^{-1}$	$4.09\cdot10^{-2}$	$2.02\cdot10^{-2}$	$2.31\cdot10^{-4}$	71.3%	4.75%	4.69%	0.05%	13.2%	0.00%
13	38.6	Included	27.3	25.9	36.6	283342	0.00	$5.80\cdot10^{-2}$	$3.09\cdot10^{-1}$	$4.19\cdot10^{-2}$	$2.07\cdot10^{-2}$	$2.09\cdot10^{-4}$	71.8%	4.86%	4.80%	0.05%	13.5%	0.00%
14	38.1	Included	26.9	25.5	36.1	212297	0.00	$5.80\cdot10^{-2}$	$3.06\cdot10^{-1}$	$4.06\cdot10^{-2}$	$2.01\cdot10^{-2}$	$4.01\cdot10^{-4}$	70.9%	4.71%	4.66%	0.09%	13.5%	0.00%
15	37.6	Included	26.6	25.1	35.5	201569	0.00	$5.92\cdot10^{-2}$	$3.18\cdot10^{-1}$	$4.20\cdot10^{-2}$	$2.07\cdot10^{-2}$	$3.67\cdot10^{-4}$	73.8%	4.88%	4.80%	0.09%	13.7%	0.00%
16	37.0	Included	26.2	24.8	35.0	226519	0.00	$5.99\cdot10^{-2}$	$3.14\cdot10^{-1}$	$4.18\cdot10^{-2}$	$2.06\cdot10^{-2}$	$3.11\cdot10^{-4}$	72.9%	4.85%	4.78%	0.07%	13.9%	0.00%

17	36.5	Included	25.8	24.4	34.5	211318	0.00	$5.89\cdot10^{-2}$	$3.09\cdot10^{-1}$	$4.11\cdot10^{-2}$	$2.03\cdot10^{-2}$	$8.76\cdot10^{-4}$	71.7%	0.48%	4.71%	0.02%	13.7%	0.00%
18	36.0	Included	25.4	24.0	33.9	204693	0.00	$5.86\cdot10^{-2}$	$3.06\cdot10^{-1}$	$4.08\cdot10^{-2}$	$2.01\cdot10^{-2}$	$2.90\cdot10^{-4}$	70.9%	4.74%	4.66%	0.07%	13.6%	0.00%
19	35.4	Included	25.1	23.6	33.4	210676	0.00	$5.95\cdot10^{-2}$	$3.07\cdot10^{-1}$	$4.11\cdot10^{-2}$	$2.02\cdot10^{-2}$	$1.23\cdot10^{-4}$	71.3%	4.76%	4.68%	0.03%	13.8%	0.00%
20	34.9	Included	24.7	23.3	32.9	254726	0.00	$5.89\cdot10^{-2}$	$3.06\cdot10^{-1}$	$4.09\cdot10^{-2}$	$2.02\cdot10^{-2}$	$2.76\cdot10^{-4}$	71.0%	4.74%	4.68%	0.06%	13.7%	0.00%
21	34.4	Included	24.3	22.9	32.4	223956	0.00	$5.97\cdot10^{-2}$	$3.06\cdot10^{-1}$	$4.14\cdot10^{-2}$	$2.04\cdot10^{-2}$	$1.16\cdot10^{-4}$	71.1%	4.81%	4.74%	0.03%	13.8%	0.00%
22	33.8	Included	23.9	22.5	31.8	179275	0.00	$6.05\cdot10^{-2}$	$3.07\cdot10^{-1}$	$4.09\cdot10^{-2}$	$2.02\cdot10^{-2}$	$2.27\cdot10^{-4}$	71.3%	4.75%	4.68%	0.05%	14.1%	0.00%
23	33.3	Included	23.6	22.1	31.3	325872	0.00	$6.06\cdot10^{-2}$	$3.05\cdot10^{-1}$	$4.21\cdot10^{-2}$	$2.08\cdot10^{-2}$	$6.82\cdot10^{-5}$	70.8%	4.89%	4.83%	0.02%	14.1%	0.00%
24	32.8	Included	23.2	21.8	30.8	185317	0.00	$6.03\cdot10^{-2}$	$3.00\cdot10^{-1}$	$3.96\cdot10^{-2}$	$1.95\cdot10^{-2}$	$7.99\cdot10^{-5}$	69.7%	4.59%	4.52%	0.02%	14.0%	0.00%
25	32.2	Included	22.8	21.4	30.2	207678	0.00	$6.19\cdot10^{-2}$	$3.07\cdot10^{-1}$	$4.11\cdot10^{-2}$	$2.02\cdot10^{-2}$	$3.39\cdot10^{-4}$	71.3%	4.77%	4.69%	0.08%	14.4%	0.00%
26	31.7	Included	22.4	21.0	29.7	211265	0.00	$6.15\cdot10^{-2}$	$3.04\cdot10^{-1}$	$4.08\cdot10^{-2}$	$2.01\cdot10^{-2}$	$1.40\cdot10^{-4}$	70.6%	4.73%	4.66%	0.03%	14.3%	0.00%
27	31.2	Included	22.1	20.6	29.2	215651	0.00	$6.19\cdot10^{-2}$	$3.04\cdot10^{-1}$	$4.06\cdot10^{-2}$	$2.00\cdot10^{-2}$	$4.12\cdot10^{-4}$	70.6%	4.72%	4.64%	0.10%	14.4%	0.00%
28	30.7	Included	21.7	20.3	28.6	216570	0.00	$6.18\cdot10^{-2}$	$3.04\cdot10^{-1}$	$4.08\cdot10^{-2}$	$2.01\cdot10^{-2}$	$3.08\cdot10^{-4}$	70.5%	4.73%	4.67%	0.07%	14.3%	0.00%
29	30.1	Included	21.3	19.9	28.1	221545	0.00	$6.23\cdot10^{-2}$	$3.03\cdot10^{-1}$	$4.06\cdot10^{-2}$	$1.99\cdot10^{-2}$	$2.51\cdot10^{-4}$	70.2%	4.71%	4.62%	0.06%	14.5%	0.00%
30	29.6	Included	20.9	19.5	27.6	237433	0.00	$6.41\cdot10^{-2}$	$3.11\cdot10^{-1}$	$4.18\cdot10^{-2}$	$2.06\cdot10^{-2}$	$2.96\cdot10^{-4}$	72.2%	4.85%	4.78%	0.07%	14.9%	0.00%
31	29.1	Included	20.6	19.1	27.1	244175	0.00	$6.26\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.03\cdot10^{-2}$	$1.99\cdot10^{-2}$	$9.10\cdot10^{-5}$	70.2%	4.68%	4.62%	0.02%	14.5%	0.00%
32	28.5	Included	20.2	18.8	26.5	225254	0.00	$6.27\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.03\cdot10^{-2}$	$1.98\cdot10^{-2}$	$2.14\cdot10^{-4}$	70.0%	4.67%	4.60%	0.05%	14.6%	0.00%
33	28.0	Included	19.8	18.4	26.0	223877	0.00	$6.41\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.01\cdot10^{-2}$	$1.97\cdot10^{-2}$	$3.64\cdot10^{-4}$	70.2%	4.66%	4.57%	0.08%	14.9%	0.00%
34	27.5	Included	19.4	18.0	25.5	244633	0.00	$6.46\cdot10^{-2}$	$3.03\cdot10^{-1}$	$4.04\cdot10^{-2}$	$1.98\cdot10^{-2}$	$1.97\cdot10^{-4}$	70.3%	4.69%	4.60%	0.05%	15.0%	0.00%
35	26.9	Included	19.1	17.6	24.9	227477	0.00	$6.73\cdot10^{-2}$	$3.09\cdot10^{-1}$	$4.14\cdot10^{-2}$	$2.03\cdot10^{-2}$	$1.30\cdot10^{-4}$	71.8%	4.81%	4.72%	0.03%	15.6%	0.00%
36	26.4	Included	18.7	17.3	24.4	225827	0.00	$6.55\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.07\cdot10^{-2}$	$2.00\cdot10^{-2}$	$9.84\cdot10^{-5}$	70.0%	4.72%	4.64%	0.02%	15.2%	0.00%
37	25.9	Included	18.3	16.9	23.9	230547	0.00	$6.47\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.03\cdot10^{-2}$	$1.98\cdot10^{-2}$	$2.73\cdot10^{-4}$	70.1%	4.67%	4.59%	0.06%	15.0%	0.00%
38	25.4	Included	17.9	16.5	23.3	264884	0.00	$6.64\cdot10^{-2}$	$3.03\cdot10^{-1}$	$4.09\cdot10^{-2}$	$2.01\cdot10^{-2}$	$2.52\cdot10^{-4}$	70.4%	4.75%	4.65%	0.06%	15.4%	0.00%
39	24.8	Included	17.6	16.1	22.8	281395	0.00	$6.64\cdot10^{-2}$	$3.03\cdot10^{-1}$	$4.14\cdot10^{-2}$	$2.03\cdot10^{-2}$	$2.50\cdot10^{-4}$	70.3%	4.80%	4.72%	0.06%	15.4%	0.00%
40	24.3	Included	17.2	15.8	22.3	229265	0.00	$6.71\cdot10^{-2}$	$3.03\cdot10^{-1}$	$3.97\cdot10^{-2}$	$1.95\cdot10^{-2}$	$2.26\cdot10^{-4}$	70.4%	4.60%	4.53%	0.05%	15.6%	0.00%
41	23.8	Included	16.8	15.4	21.7	207086	0.00	$6.86\cdot10^{-2}$	$3.06\cdot10^{-1}$	$3.91\cdot10^{-2}$	$1.93\cdot10^{-2}$	$5.19\cdot10^{-4}$	71.0%	4.54%	4.47%	0.12%	15.9%	0.00%
42	23.2	Included	16.4	15.0	21.2	230576	0.00	$6.74\cdot10^{-2}$	$3.02\cdot10^{-1}$	$3.90\cdot10^{-2}$	$1.92\cdot10^{-2}$	$2.57\cdot10^{-4}$	70.1%	4.53%	4.46%	0.06%	15.6%	0.00%
43	22.7	Included	16.1	14.6	20.7	278317	0.00	$6.91\cdot10^{-2}$	$3.04\cdot10^{-1}$	$3.94\cdot10^{-2}$	$1.94\cdot10^{-2}$	$3.19\cdot10^{-4}$	70.5%	4.57%	4.50%	0.07%	16.0%	0.00%
44	22.2	Included	15.7	14.3	20.2	225406	0.00	$6.98\cdot10^{-2}$	$3.03\cdot10^{-1}$	$3.95\cdot10^{-2}$	$1.94\cdot10^{-2}$	$3.61\cdot10^{-4}$	70.3%	4.58%	4.50%	0.08%	16.2%	0.00%
45	21.6	Included	15.3	13.9	19.6	226576	0.00	$6.81\cdot10^{-2}$	$3.00\cdot10^{-1}$	$3.91\cdot10^{-2}$	$1.92\cdot10^{-2}$	$1.63\cdot10^{-4}$	69.6%	4.54%	4.46%	0.04%	15.8%	0.00%
46	21.1	Included	14.9	13.5	19.1	245171	0.00	$7.01\cdot10^{-2}$	$3.02\cdot10^{-1}$	$3.97\cdot10^{-2}$	$1.95\cdot10^{-2}$	$3.17\cdot10^{-4}$	70.1%	4.61%	4.53%	0.07%	16.3%	0.00%

47	20.6	Included	14.6	13.1	18.6	240746	0.00	$6.92\cdot10^{-2}$	$2.98\cdot10^{-1}$	$3.93\cdot10^{-2}$	$1.93\cdot10^{-2}$	$2.46\cdot10^{-4}$	69.3%	4.56%	4.49%	0.06%	16.1%	0.00%
48	20.0	Included	14.2	12.8	18.0	227392	0.00	$6.88\cdot10^{-2}$	$2.98\cdot10^{-1}$	$3.90\cdot10^{-2}$	$1.92\cdot10^{-2}$	$3.09\cdot10^{-4}$	69.1%	4.53%	4.45%	0.07%	16.0%	0.00%
49	19.5	Included	13.8	12.4	17.5	257592	0.00	$7.01\cdot10^{-2}$	$2.99\cdot10^{-1}$	$3.96\cdot10^{-2}$	$1.94\cdot10^{-2}$	$8.63\cdot10^{-5}$	69.5%	4.59%	4.51%	0.02%	16.3%	0.00%
50	19.0	Included	13.4	12.0	17.0	229175	0.00	$7.04\cdot10^{-2}$	$3.05\cdot10^{-1}$	$4.05\cdot10^{-2}$	$1.98\cdot10^{-2}$	$1.78\cdot10^{-4}$	70.9%	4.70%	4.59%	0.04%	16.3%	0.00%
51	18.5	Included	13.1	11.6	16.4	236139	0.00	$6.96\cdot10^{-2}$	$2.97\cdot10^{-1}$	$3.91\cdot10^{-2}$	$1.92\cdot10^{-2}$	$1.57\cdot10^{-4}$	69.0%	4.53%	4.45%	0.04%	16.1%	0.00%
52	17.9	Included	12.7	11.3	15.9	252422	0.00	$7.05\cdot10^{-2}$	$3.01\cdot10^{-1}$	$3.98\cdot10^{-2}$	$1.95\cdot10^{-2}$	$3.08\cdot10^{-4}$	69.8%	4.62%	4.53%	0.07%	16.4%	0.00%
53	17.4	Included	12.3	10.9	15.4	230908	0.00	$7.00\cdot10^{-2}$	$2.98\cdot10^{-1}$	$3.93\cdot10^{-2}$	$1.93\cdot10^{-2}$	$2.25\cdot10^{-4}$	69.1%	4.57%	4.47%	0.05%	16.2%	0.00%
54	16.9	Included	11.9	10.5	14.9	231571	0.00	$6.88\cdot10^{-2}$	$2.96\cdot10^{-1}$	$3.96\cdot10^{-2}$	$1.94\cdot10^{-2}$	$1.44\cdot10^{-4}$	68.8%	4.59%	4.50%	0.03%	16.0%	0.00%
55	16.3	Included	11.6	10.1	14.3	225298	0.00	$6.98\cdot10^{-2}$	$2.97\cdot10^{-1}$	$3.92\cdot10^{-2}$	$1.91\cdot10^{-2}$	$3.12\cdot10^{-4}$	68.9%	4.54%	4.44%	0.07%	16.2%	0.00%
56	15.8	Included	11.2	9.8	13.8	242734	$2.06\cdot10^{-5}$	$7.13\cdot10^{-2}$	$3.03\cdot10^{-1}$	$4.00\cdot10^{-2}$	$1.95\cdot10^{-2}$	$3.20\cdot10^{-4}$	70.3%	4.64%	4.54%	0.07%	16.5%	0.00%
57	15.3	Included	10.8	9.4	13.3	240166	$7.08\cdot10^{-5}$	$7.05\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.01\cdot10^{-2}$	$1.96\cdot10^{-2}$	$3.08\cdot10^{-4}$	70.0%	4.66%	4.56%	0.07%	16.4%	0.02%
58	14.7	Included	10.4	9.0	12.7	238512	$2.05\cdot10^{-4}$	$6.88\cdot10^{-2}$	$2.97\cdot10^{-1}$	$3.89\cdot10^{-2}$	$1.89\cdot10^{-2}$	$2.95\cdot10^{-4}$	69.0%	4.51%	4.39%	0.07%	16.0%	0.04%
59	14.2	Included	10.1	8.6	12.2	243239	$6.50\cdot10^{-4}$	$7.03\cdot10^{-2}$	$3.07\cdot10^{-1}$	$4.07\cdot10^{-2}$	$1.98\cdot10^{-2}$	$4.42\cdot10^{-4}$	71.2%	4.73%	4.60%	0.10%	16.3%	0.14%
60	13.7	Included	9.7	8.3	11.7	231896	$1.63\cdot10^{-3}$	$6.81\cdot10^{-2}$	$3.00\cdot10^{-1}$	$3.96\cdot10^{-2}$	$1.93\cdot10^{-2}$	$3.99\cdot10^{-4}$	69.6%	4.60%	4.49%	0.09%	15.8%	0.35%
61	13.2	Included	9.3	7.9	11.1	221247	$3.57\cdot10^{-3}$	$6.68\cdot10^{-2}$	$2.97\cdot10^{-1}$	$3.96\cdot10^{-2}$	$1.92\cdot10^{-2}$	$5.52\cdot10^{-4}$	68.9%	4.60%	4.46%	0.13%	15.5%	0.77%
62	12.6	Included	8.9	7.5	10.6	282336	$7.83\cdot10^{-3}$	$6.40\cdot10^{-2}$	$2.95\cdot10^{-1}$	$3.94\cdot10^{-2}$	$1.91\cdot10^{-2}$	$6.95\cdot10^{-4}$	68.4%	4.57%	4.43%	0.16%	14.8%	1.70%
63	12.1	Included	8.6	7.1	10.1	246289	$1.46\cdot10^{-2}$	$6.01\cdot10^{-2}$	$2.89\cdot10^{-1}$	$3.92\cdot10^{-2}$	$3.11\cdot10^{-2}$	$1.14\cdot10^{-3}$	67.1%	4.55%	7.21%	0.27%	14.0%	3.17%
64	11.6	Included	8.2	6.8	9.5	239232	2.42	$5.66\cdot10^{-2}$	$2.83\cdot10^{-1}$	$3.92\cdot10^{-2}$	$1.88\cdot10^{-2}$	$1.63\cdot10^{-4}$	65.6%	4.55%	4.36%	0.38%	13.1%	5.25%
65	11.0	Included	7.8	6.4	9.0	220087	3.66	$5.17\cdot10^{-2}$	$2.73\cdot10^{-1}$	$3.94\cdot10^{-2}$	$1.89\cdot10^{-2}$	$2.17\cdot10^{-4}$	63.3%	4.57%	4.39%	0.50%	12.0%	7.92%
66	10.5	Included	7.4	6.0	8.5	228000	4.86	$4.71\cdot10^{-2}$	$2.66\cdot10^{-1}$	$3.99\cdot10^{-2}$	$1.91\cdot10^{-2}$	$2.65\cdot10^{-4}$	61.7%	4.63%	4.42%	0.61%	10.9%	10.5%
67	10.0	Included	7.1	5.6	8.0	242781	7.05	$4.14\cdot10^{-2}$	$2.54\cdot10^{-1}$	$4.04\cdot10^{-2}$	$1.92\cdot10^{-2}$	$3.49\cdot10^{-4}$	59.0%	4.69%	4.46%	0.81%	9.62%	15.3%
68	9.4	Included	6.7	5.3	7.4	282637	$1.13\cdot10^{-1}$	$2.84\cdot10^{-2}$	$2.20\cdot10^{-1}$	$3.89\cdot10^{-2}$	$1.85\cdot10^{-2}$	$4.21\cdot10^{-4}$	51.0%	4.51%	4.29%	0.98%	6.60%	24.5%
69	8.9	Included	6.3	4.9	6.9	266875	1.37	$2.38\cdot10^{-2}$	$2.09\cdot10^{-1}$	$3.90\cdot10^{-2}$	$1.85\cdot10^{-2}$	$6.31\cdot10^{-4}$	48.4%	4.53%	4.28%	1.47%	5.52%	29.7%
70	8.4	Included	5.9	4.5	6.4	233358	1.62	$1.88\cdot10^{-2}$	$1.95\cdot10^{-1}$	$3.88\cdot10^{-2}$	$1.84\cdot10^{-2}$	$6.84\cdot10^{-4}$	45.2%	4.51%	4.28%	1.59%	4.37%	35.2%
71	7.9	Included	5.6	4.1	5.8	319818	1.82	$1.57\cdot10^{-2}$	$1.85\cdot10^{-1}$	$4.00\cdot10^{-2}$	$1.90\cdot10^{-2}$	$5.35\cdot10^{-4}$	43.0%	4.64%	4.40%	1.24%	3.65%	39.5%
72	7.3	Included	5.2	3.8	5.3	224186	2.03	$1.18\cdot10^{-2}$	$1.71\cdot10^{-1}$	$3.84\cdot10^{-2}$	$1.82\cdot10^{-2}$	$9.07\cdot10^{-4}$	39.6%	4.45%	4.22%	2.11%	2.73%	44.0%
73	6.8	Included	4.8	3.4	4.8	280951	2.62	$6.34\cdot10^{-3}$	$1.38\cdot10^{-1}$	$3.70\cdot10^{-2}$	$1.76\cdot10^{-2}$	$6.10\cdot10^{-4}$	32.0%	4.30%	4.08%	1.42%	1.47%	56.9%
74	6.3	Included	4.4	3.0	4.2	299063	3.03	$2.93\cdot10^{-3}$	$1.12\cdot10^{-1}$	$3.59\cdot10^{-2}$	$1.71\cdot10^{-2}$	$6.69\cdot10^{-4}$	26.1%	4.17%	3.96%	1.55%	0.68%	65.6%
75	5.7	Included	4.1	2.6	3.7	277714	3.52	$1.26\cdot10^{-3}$	$8.36\cdot10^{-2}$	$3.16\cdot10^{-2}$	$1.52\cdot10^{-2}$	$7.01\cdot10^{-4}$	19.4%	3.67%	3.52%	1.63%	0.29%	76.2%
76	5.2	Included	3.7	2.3	3.2	246315	3.83	$4.30\cdot10^{-4}$	$6.13\cdot10^{-2}$	$2.80\cdot10^{-2}$	$1.35\cdot10^{-2}$	$6.07\cdot10^{-4}$	14.2%	3.25%	0.31%	1.41%	0.10%	83.0%

77	4.7	Included	3.3	1.9	2.7	257447	4.01	$1.98\cdot10^{-4}$	$4.93\cdot10^{-2}$	$2.58\cdot10^{-2}$	$1.25\cdot10^{-2}$	$4.42\cdot10^{-4}$	11.4%	3.00%	2.90%	1.03%	0.05%	86.9%
78	4.1	Included	2.9	1.5	2.1	235113	4.16	$6.81\cdot10^{-5}$	$3.84\cdot10^{-2}$	$2.32\cdot10^{-2}$	$1.13\cdot10^{-2}$	$4.22\cdot10^{-4}$	8.91%	2.69%	2.62%	0.98%	0.02%	90.2%
79	3.6	Included	2.6	1.1	1.6	267421	4.25	$4.49\cdot10^{-5}$	$2.92\cdot10^{-2}$	$1.98\cdot10^{-2}$	$9.71\cdot10^{-3}$	$3.19\cdot10^{-4}$	6.78%	2.30%	2.25%	0.74%	0.01%	92.1%
80	3.1	Included	2.2	0.8	1.1	270800	4.44	$6.28\cdot10^{-5}$	$2.29\cdot10^{-2}$	$1.78\cdot10^{-2}$	$8.76\cdot10^{-3}$	$2.65\cdot10^{-4}$	5.31%	2.07%	2.03%	0.62%	0.01%	96.3%
81	2.5	Included	1.8	0.4	0.5	247315	4.60	$2.02\cdot10^{-5}$	$1.65\cdot10^{-2}$	$1.49\cdot10^{-2}$	$7.33\cdot10^{-3}$	$2.41\cdot10^{-4}$	3.84%	1.73%	1.70%	0.56%	0.00%	99.7%
82	2.0	Included	1.4	0.0	0.0	366489	4.62	$3.00\cdot10^{-5}$	$1.09\cdot10^{-2}$	$1.15\cdot10^{-2}$	$5.70\cdot10^{-3}$	$1.13\cdot10^{-4}$	2.53%	1.33%	1.32%	0.26%	0.01%	99.9%
83	1.5	Excluded	1.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
84	1.0	Excluded	0.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
85	0.4	Excluded	0.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
86	0.0	Excluded	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

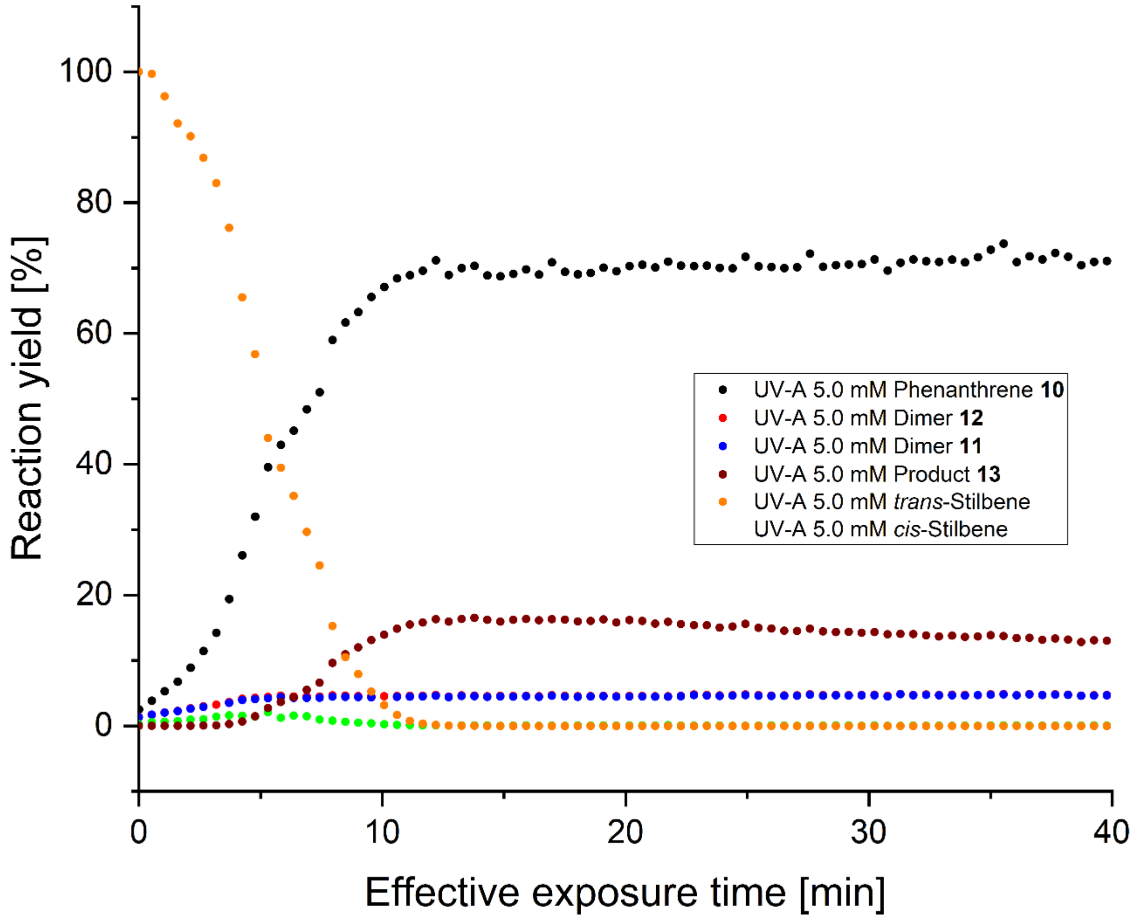


Figure S 18. Results of Switch-Off optimisation of Mallory photoreaction using UV-B light and 5.0 mM stilbene concentration. Top: Reaction components GC areas, conversion, and yield plotted against uncorrected residence time. Bottom: Reaction components GC areas, conversion, and yield plotted against exposure time, corrected for light inhomogeneity.

2. 4. 2. 4. Switch-Off experiment results using UV-B light and 50.0 mM stilbene concentration

Cis-stilbene (445.0 µL, 450.2 mg, 2.50 mmol, 1.0 eq., 50.0 mM solution), iodine (63.0 mg, 0.25 mmol, 0.1 eq., 5.0 mM solution), and dibutyl ether (1.5 mL, 1.17 g, 9.0 mmol, 3.6 eq., 180.0 mM solution) were dissolved in cyclohexane (48.0 mL, 106.6 vol.), obtained solution was saturated with oxygen by bubbling gaseous O_2 for 15 minutes, and then connected to flow reagents stream. Cyclohexane was connected to flow solvents stream. The UV-B lamp (Philips PL-L 36W/01/4P) and water cooling were then turned on and system was allowed to equilibrate for 30 minutes. Then reaction mixture was injected into the photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA). Effective exposure time was set to 180 minutes (which corresponds to 0.177 mL/min flow rate). Once the photoreactor was filled with reaction mixture, the UV lamp was switched off, the pump was switched to solvent stream, the reaction mixture was eluted from the photoreactor, and was collected into vials (0.375 mL of reaction mixture, diluted to 1.0 mL with acetone). Collected samples were then analysed using off-line GC.

Table S 14. Results of Switch-Off optimisation performed for Mallory reaction of cis-stilbene using UV-B light and 50.0 mM stilbene concentration.

#	Residence time [min]	Included/Excluded	Reactor volume [mL]	Effective Reactor Volume [mL]	Effective exposure time [min]	IS GC Area	Area Ratio *cis*-Stilbene/IS	Area Ratio *trans*-Stilbene/IS	Area Ratio Phenanthrene 10/IS	Area Ratio Dimer ABAB 12/IS	Area Ratio Dimer AABB 11/IS	Area Ratio Product 13/IS	Phenanthrene yield [%]	Dimer 12 yield [%]	Dimer 11 yield [%]	Product 13 yield [%]	*trans*-Stilbene yield [%]	Remaining *cis*-Stilbene [%]
1	174.0	Excluded	30.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	171.9	Excluded	30.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	169.8	Excluded	30.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	167.7	Excluded	29.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	165.5	Included	29.3	27.8	156.8	87536	0.00	$5.48\cdot10^{-2}$	$3.00\cdot10^{-1}$	$4.01\cdot10^{-2}$	$1.88\cdot10^{-2}$	$2.33\cdot10^{-2}$	69.6%	4.65%	2.18%	3.18%	12.7%	0.00%
6	163.4	Included	28.9	27.4	154.7	215570	$4.64\cdot10^{-6}$	$5.62\cdot10^{-2}$	$3.06\cdot10^{-1}$	$4.18\cdot10^{-2}$	$1.95\cdot10^{-2}$	$4.40\cdot10^{-3}$	71.0%	4.85%	2.27%	0.60%	13.0%	0.00%
7	161.3	Included	28.6	27.0	152.5	209302	$1.43\cdot10^{-5}$	$5.59\cdot10^{-2}$	$3.04\cdot10^{-1}$	$4.10\cdot10^{-2}$	$1.92\cdot10^{-2}$	$1.08\cdot10^{-2}$	70.7%	4.76%	2.23%	1.48%	13.0%	0.00%
8	159.2	Included	28.2	26.6	150.4	215947	$1.39\cdot10^{-5}$	$5.61\cdot10^{-2}$	$3.04\cdot10^{-1}$	$4.09\cdot10^{-2}$	$1.91\cdot10^{-2}$	$1.02\cdot10^{-2}$	70.6%	4.75%	2.22%	1.39%	13.0%	0.00%
9	157.1	Included	27.8	26.3	148.3	211077	$3.32\cdot10^{-5}$	$5.58\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.04\cdot10^{-2}$	$1.89\cdot10^{-2}$	$1.08\cdot10^{-2}$	70.1%	4.68%	2.19%	1.47%	13.0%	0.01%
10	154.9	Included	27.4	25.9	146.2	205224	$2.44\cdot10^{-5}$	$5.69\cdot10^{-2}$	$3.07\cdot10^{-1}$	$4.15\cdot10^{-2}$	$1.94\cdot10^{-2}$	$1.08\cdot10^{-2}$	71.3%	4.81%	2.25%	1.47%	13.2%	0.01%
11	152.8	Included	27.1	25.5	144.1	211052	$2.37\cdot10^{-5}$	$5.77\cdot10^{-2}$	$3.10\cdot10^{-1}$	$4.21\cdot10^{-2}$	$1.97\cdot10^{-2}$	$1.06\cdot10^{-2}$	71.9%	4.88%	2.28%	1.45%	13.4%	0.00%
12	150.7	Included	26.7	25.1	141.9	209613	$2.39\cdot10^{-5}$	$5.71\cdot10^{-2}$	$3.06\cdot10^{-1}$	$4.12\cdot10^{-2}$	$1.93\cdot10^{-2}$	$1.11\cdot10^{-2}$	70.9%	4.78%	2.24%	1.52%	13.3%	0.00%
13	148.6	Included	26.3	24.8	139.8	284324	$2.81\cdot10^{-5}$	$5.79\cdot10^{-2}$	$3.08\cdot10^{-1}$	$4.21\cdot10^{-2}$	$1.97\cdot10^{-2}$	$8.28\cdot10^{-2}$	71.5%	4.89%	2.29%	1.13%	13.4%	0.01%
14	146.5	Included	25.9	24.4	137.7	213074	$1.88\cdot10^{-5}$	$5.73\cdot10^{-2}$	$3.04\cdot10^{-1}$	$4.09\cdot10^{-2}$	$1.92\cdot10^{-2}$	$1.51\cdot10^{-2}$	70.5%	4.74%	2.22%	2.05%	13.3%	0.00%
15	144.4	Included	25.6	24.0	135.6	202303	$3.95\cdot10^{-5}$	$6.01\cdot10^{-2}$	$3.16\cdot10^{-1}$	$4.25\cdot10^{-2}$	$1.97\cdot10^{-2}$	$1.19\cdot10^{-2}$	73.3%	4.93%	2.28%	1.62%	14.0%	0.01%
16	142.2	Included	25.2	23.6	133.5	227340	$3.52\cdot10^{-5}$	$5.97\cdot10^{-2}$	$3.12\cdot10^{-1}$	$4.21\cdot10^{-2}$	$1.96\cdot10^{-2}$	$1.04\cdot10^{-2}$	72.5%	4.89%	2.28%	1.42%	13.9%	0.01%
17	140.1	Included	24.8	23.3	131.4	212058	$3.77\cdot10^{-5}$	$5.89\cdot10^{-2}$	$3.07\cdot10^{-1}$	$4.15\cdot10^{-2}$	$1.94\cdot10^{-2}$	$1.27\cdot10^{-2}$	71.3%	4.82%	2.25%	1.73%	13.7%	0.01%
18	138.0	Included	24.4	22.9	129.2	205409	$2.92\cdot10^{-5}$	$5.85\cdot10^{-2}$	$3.04\cdot10^{-1}$	$4.11\cdot10^{-2}$	$1.92\cdot10^{-2}$	$1.21\cdot10^{-2}$	70.5%	4.77%	2.23%	1.65%	13.6%	0.01%
19	135.9	Included	24.1	22.5	127.1	211439	$2.84\cdot10^{-5}$	$5.90\cdot10^{-2}$	$3.06\cdot10^{-1}$	$4.13\cdot10^{-2}$	$1.93\cdot10^{-2}$	$1.15\cdot10^{-2}$	70.9%	4.79%	2.24%	1.56%	13.7%	0.01%
20	133.8	Included	23.7	22.1	125.0	255518	$4.30\cdot10^{-5}$	$5.92\cdot10^{-2}$	$3.04\cdot10^{-1}$	$4.13\cdot10^{-2}$	$1.93\cdot10^{-2}$	$1.01\cdot10^{-2}$	70.6%	4.80%	2.24%	1.38%	13.7%	0.01%
21	131.6	Included	23.3	21.8	122.9	224739	$4.00\cdot10^{-5}$	$5.94\cdot10^{-2}$	$3.05\cdot10^{-1}$	$4.17\cdot10^{-2}$	$1.95\cdot10^{-2}$	$1.34\cdot10^{-2}$	70.7%	4.84%	2.26%	1.83%	13.8%	0.01%

22	129.5	Included	22.9	21.4	120.8	179956	$2.22\cdot10^{-5}$	$5.98\cdot10^{-2}$	$3.05\cdot10^{-1}$	$4.13\cdot10^{-2}$	$1.93\cdot10^{-2}$	$1.50\cdot10^{-2}$	70.9%	4.79%	2.24%	2.04%	13.9%	0.00%
23	127.4	Included	22.6	21.0	118.6	326953	$4.28\cdot10^{-5}$	$6.01\cdot10^{-2}$	$3.04\cdot10^{-1}$	$4.25\cdot10^{-2}$	$1.99\cdot10^{-2}$	$6.88\cdot10^{-3}$	70.4%	4.94%	2.31%	0.94%	14.0%	0.01%
24	125.3	Included	22.2	20.6	116.5	185934	$3.76\cdot10^{-5}$	$5.98\cdot10^{-2}$	$2.99\cdot10^{-1}$	$3.99\cdot10^{-2}$	$1.86\cdot10^{-2}$	$2.20\cdot10^{-2}$	69.3%	4.63%	2.16%	3.00%	13.9%	0.01%
25	123.2	Included	21.8	20.3	114.4	208392	$4.32\cdot10^{-5}$	$6.16\cdot10^{-2}$	$3.06\cdot10^{-1}$	$4.14\cdot10^{-2}$	$1.93\cdot10^{-2}$	$1.10\cdot10^{-2}$	71.0%	4.80%	2.24%	1.50%	14.3%	0.01%
26	121.0	Included	21.4	19.9	112.3	212004	$2.36\cdot10^{-5}$	$6.13\cdot10^{-2}$	$3.03\cdot10^{-1}$	$4.12\cdot10^{-2}$	$1.91\cdot10^{-2}$	$1.27\cdot10^{-2}$	70.3%	4.78%	2.22%	1.73%	14.2%	0.00%
27	118.9	Included	21.1	19.5	110.2	216437	$2.31\cdot10^{-5}$	$6.14\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.09\cdot10^{-2}$	$1.91\cdot10^{-2}$	$1.26\cdot10^{-2}$	70.2%	4.74%	2.21%	1.72%	14.3%	0.00%
28	116.8	Included	20.7	19.1	108.1	217317	$3.22\cdot10^{-5}$	$6.18\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.13\cdot10^{-2}$	$1.92\cdot10^{-2}$	$1.31\cdot10^{-2}$	70.1%	4.80%	2.23%	1.79%	14.3%	0.01%
29	114.7	Included	20.3	18.8	105.9	222326	$3.15\cdot10^{-5}$	$6.17\cdot10^{-2}$	$3.01\cdot10^{-1}$	$4.09\cdot10^{-2}$	$1.91\cdot10^{-2}$	$1.33\cdot10^{-2}$	69.8%	4.75%	2.22%	1.81%	14.3%	0.01%
30	112.6	Included	19.9	18.4	103.8	238276	$4.20\cdot10^{-5}$	$6.40\cdot10^{-2}$	$3.09\cdot10^{-1}$	$4.23\cdot10^{-2}$	$2.04\cdot10^{-2}$	$1.28\cdot10^{-2}$	71.8%	4.91%	2.37%	1.75%	14.9%	0.01%
31	110.5	Included	19.6	18.0	101.7	244990	$4.08\cdot10^{-5}$	$6.27\cdot10^{-2}$	$3.01\cdot10^{-1}$	$4.08\cdot10^{-2}$	$1.90\cdot10^{-2}$	$1.41\cdot10^{-2}$	69.8%	4.73%	2.20%	1.92%	14.5%	0.01%
32	108.3	Included	19.2	17.6	99.6	226005	$3.98\cdot10^{-5}$	$6.31\cdot10^{-2}$	$3.00\cdot10^{-1}$	$4.07\cdot10^{-2}$	$1.89\cdot10^{-2}$	$1.54\cdot10^{-2}$	69.7%	4.72%	2.20%	2.10%	14.6%	0.01%
33	106.2	Included	18.8	17.3	97.5	224658	$3.12\cdot10^{-5}$	$6.37\cdot10^{-2}$	$3.01\cdot10^{-1}$	$4.05\cdot10^{-2}$	$1.88\cdot10^{-2}$	$1.44\cdot10^{-2}$	69.8%	4.70%	2.18%	1.97%	14.8%	0.01%
34	104.1	Included	18.4	16.9	95.3	245450	$4.07\cdot10^{-5}$	$6.45\cdot10^{-2}$	$3.01\cdot10^{-1}$	$4.08\cdot10^{-2}$	$1.90\cdot10^{-2}$	$1.33\cdot10^{-2}$	69.9%	4.73%	2.20%	1.81%	15.0%	0.01%
35	102.0	Included	18.1	16.5	93.2	228351	$3.07\cdot10^{-5}$	$6.63\cdot10^{-2}$	$3.07\cdot10^{-1}$	$4.18\cdot10^{-2}$	$1.95\cdot10^{-2}$	$1.55\cdot10^{-2}$	71.3%	4.85%	2.26%	2.12%	15.4%	0.01%
36	99.9	Included	17.7	16.1	91.1	226575	$2.21\cdot10^{-5}$	$6.54\cdot10^{-2}$	$3.00\cdot10^{-1}$	$4.10\cdot10^{-2}$	$1.91\cdot10^{-2}$	$1.48\cdot10^{-2}$	69.6%	4.76%	2.22%	2.01%	15.2%	0.00%
37	97.7	Included	17.3	15.8	89.0	231280	$4.32\cdot10^{-5}$	$6.58\cdot10^{-2}$	$3.00\cdot10^{-1}$	$4.08\cdot10^{-2}$	$1.89\cdot10^{-2}$	$1.41\cdot10^{-2}$	69.7%	4.74%	2.20%	1.92%	15.3%	0.01%
38	95.6	Included	16.9	15.4	86.9	265778	$4.14\cdot10^{-5}$	$6.61\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.12\cdot10^{-2}$	$1.92\cdot10^{-2}$	$1.26\cdot10^{-2}$	70.1%	4.79%	2.23%	1.72%	15.3%	0.01%
39	93.5	Included	16.6	15.0	84.7	282347	$4.25\cdot10^{-5}$	$6.60\cdot10^{-2}$	$3.01\cdot10^{-1}$	$4.18\cdot10^{-2}$	$1.95\cdot10^{-2}$	$1.40\cdot10^{-2}$	70.0%	4.86%	2.26%	1.90%	15.3%	0.01%
40	91.4	Included	16.2	14.6	82.6	230054	$4.78\cdot10^{-5}$	$6.65\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.02\cdot10^{-2}$	$1.87\cdot10^{-2}$	$1.81\cdot10^{-2}$	70.0%	4.66%	2.16%	2.47%	15.4%	0.01%
41	89.3	Included	15.8	14.3	80.5	207830	$3.37\cdot10^{-5}$	$6.78\cdot10^{-2}$	$3.04\cdot10^{-1}$	$3.97\cdot10^{-2}$	$1.84\cdot10^{-2}$	$1.64\cdot10^{-2}$	70.6%	4.60%	2.14%	2.24%	15.7%	0.01%
42	87.1	Included	15.4	13.9	78.4	231287	$3.46\cdot10^{-5}$	$6.76\cdot10^{-2}$	$3.01\cdot10^{-1}$	$3.96\cdot10^{-2}$	$1.85\cdot10^{-2}$	$1.39\cdot10^{-2}$	69.8%	4.59%	2.14%	1.90%	15.7%	0.01%
43	85.0	Included	15.1	13.5	76.3	279235	$4.30\cdot10^{-5}$	$6.87\cdot10^{-2}$	$3.02\cdot10^{-1}$	$4.01\cdot10^{-2}$	$1.86\cdot10^{-2}$	$1.27\cdot10^{-2}$	70.2%	4.65%	2.16%	1.74%	15.9%	0.01%
44	82.9	Included	14.7	13.1	74.2	226204	$3.98\cdot10^{-5}$	$6.87\cdot10^{-2}$	$3.01\cdot10^{-1}$	$4.00\cdot10^{-2}$	$1.86\cdot10^{-2}$	$1.92\cdot10^{-2}$	69.9%	4.64%	2.16%	2.61%	15.9%	0.01%
45	80.8	Included	14.3	12.8	72.0	227278	$5.28\cdot10^{-5}$	$6.87\cdot10^{-2}$	$2.98\cdot10^{-1}$	$3.97\cdot10^{-2}$	$1.84\cdot10^{-2}$	$1.58\cdot10^{-2}$	69.2%	4.61%	2.14%	2.15%	15.9%	0.01%
46	78.7	Included	13.9	12.4	69.9	246016	$5.28\cdot10^{-5}$	$6.94\cdot10^{-2}$	$3.00\cdot10^{-1}$	$4.02\cdot10^{-2}$	$1.87\cdot10^{-2}$	$1.47\cdot10^{-2}$	69.7%	4.67%	2.17%	2.00%	16.1%	0.01%
47	76.6	Included	13.6	12.0	67.8	241549	$6.62\cdot10^{-5}$	$6.89\cdot10^{-2}$	$2.97\cdot10^{-1}$	$3.99\cdot10^{-2}$	$1.85\cdot10^{-2}$	$1.64\cdot10^{-2}$	68.9%	4.63%	2.15%	2.24%	16.0%	0.01%
48	74.4	Included	13.2	11.6	65.7	228163	$4.38\cdot10^{-5}$	$6.87\cdot10^{-2}$	$2.96\cdot10^{-1}$	$3.96\cdot10^{-2}$	$1.84\cdot10^{-2}$	$1.71\cdot10^{-2}$	68.7%	4.60%	2.13%	2.32%	16.0%	0.01%
49	72.3	Included	12.8	11.3	63.6	258473	$5.03\cdot10^{-5}$	$6.93\cdot10^{-2}$	$2.98\cdot10^{-1}$	$4.02\cdot10^{-2}$	$1.86\cdot10^{-2}$	$1.46\cdot10^{-2}$	69.1%	4.67%	2.16%	1.99%	16.1%	0.01%
50	70.2	Included	12.4	10.9	61.4	229954	$6.52\cdot10^{-5}$	$7.10\cdot10^{-2}$	$3.04\cdot10^{-1}$	$4.11\cdot10^{-2}$	$1.89\cdot10^{-2}$	$1.85\cdot10^{-2}$	70.5%	4.77%	2.20%	2.53%	16.5%	0.01%
51	68.1	Included	12.1	10.5	59.3	236963	$3.38\cdot10^{-5}$	$6.90\cdot10^{-2}$	$2.96\cdot10^{-1}$	$3.97\cdot10^{-2}$	$1.84\cdot10^{-2}$	$1.64\cdot10^{-2}$	68.7%	4.61%	2.14%	2.23%	16.0%	0.01%

52	66.0	Included	11.7	10.1	57.2	253319	$4.74\cdot10^{-5}$	$7.00\cdot10^{-2}$	$2.99\cdot10^{-1}$	$4.05\cdot10^{-2}$	$1.87\cdot10^{-2}$	$1.60\cdot10^{-2}$	69.4%	4.70%	2.17%	2.17%	16.2%	0.01%
53	63.8	Included	11.3	9.8	55.1	231719	$4.75\cdot10^{-5}$	$6.95\cdot10^{-2}$	$2.96\cdot10^{-1}$	$4.00\cdot10^{-2}$	$1.85\cdot10^{-2}$	$1.86\cdot10^{-2}$	68.8%	4.64%	2.15%	2.54%	16.1%	0.01%
54	61.7	Included	10.9	9.4	53.0	232313	$6.89\cdot10^{-5}$	$6.93\cdot10^{-2}$	$2.95\cdot10^{-1}$	$4.02\cdot10^{-2}$	$1.86\cdot10^{-2}$	$1.74\cdot10^{-2}$	68.4%	4.67%	2.16%	2.37%	16.1%	0.01%
55	59.6	Included	10.6	9.0	50.8	226058	$5.75\cdot10^{-5}$	$6.94\cdot10^{-2}$	$2.95\cdot10^{-1}$	$3.97\cdot10^{-2}$	$1.84\cdot10^{-2}$	$1.84\cdot10^{-2}$	68.6%	4.61%	2.13%	2.51%	16.1%	0.01%
56	57.5	Included	10.2	8.6	48.7	243604	$9.44\cdot10^{-5}$	$7.08\cdot10^{-2}$	$3.01\cdot10^{-1}$	$4.07\cdot10^{-2}$	$1.88\cdot10^{-2}$	$1.65\cdot10^{-2}$	70.0%	4.72%	2.18%	2.25%	16.4%	0.02%
57	55.4	Included	9.8	8.3	46.6	240998	$1.54\cdot10^{-4}$	$7.04\cdot10^{-2}$	$3.00\cdot10^{-1}$	$4.09\cdot10^{-2}$	$1.89\cdot10^{-2}$	$1.86\cdot10^{-2}$	69.6%	4.75%	2.19%	2.54%	16.3%	0.03%
58	53.2	Included	9.4	7.9	44.5	239311	$3.13\cdot10^{-4}$	$6.89\cdot10^{-2}$	$2.96\cdot10^{-1}$	$3.19\cdot10^{-2}$	$1.83\cdot10^{-2}$	$1.86\cdot10^{-2}$	68.6%	3.71%	2.12%	2.53%	16.0%	0.07%
59	51.1	Included	9.1	7.5	42.4	244122	$7.86\cdot10^{-4}$	$7.02\cdot10^{-2}$	$3.05\cdot10^{-1}$	$4.13\cdot10^{-2}$	$1.91\cdot10^{-2}$	$1.80\cdot10^{-2}$	70.8%	4.80%	2.22%	2.45%	16.3%	0.16%
60	49.0	Included	8.7	7.1	40.3	237214	$1.79\cdot10^{-3}$	$6.63\cdot10^{-2}$	$2.93\cdot10^{-1}$	$3.94\cdot10^{-2}$	$1.83\cdot10^{-2}$	$1.97\cdot10^{-2}$	67.9%	4.58%	2.12%	2.68%	15.4%	0.37%
61	46.9	Included	8.3	6.8	38.1	222033	$3.84\cdot10^{-3}$	$6.51\cdot10^{-2}$	$2.95\cdot10^{-1}$	$4.01\cdot10^{-2}$	$1.86\cdot10^{-2}$	$1.99\cdot10^{-2}$	68.6%	4.66%	2.15%	2.71%	15.1%	0.80%
62	44.8	Included	7.9	6.4	36.0	283267	$8.12\cdot10^{-3}$	$6.29\cdot10^{-2}$	$2.93\cdot10^{-1}$	$3.98\cdot10^{-2}$	$1.84\cdot10^{-2}$	$1.50\cdot10^{-2}$	68.1%	4.62%	2.14%	2.05%	14.6%	1.70%
63	42.7	Included	7.6	6.0	33.9	247047	$1.48\cdot10^{-2}$	$5.89\cdot10^{-2}$	$2.88\cdot10^{-1}$	$3.96\cdot10^{-2}$	$1.83\cdot10^{-2}$	$2.15\cdot10^{-2}$	66.8%	4.59%	2.13%	2.92%	13.7%	3.10%
64	40.5	Included	7.2	5.6	31.8	240042	$2.44\cdot10^{-2}$	$5.40\cdot10^{-2}$	$2.81\cdot10^{-1}$	$3.94\cdot10^{-2}$	$1.83\cdot10^{-2}$	$1.93\cdot10^{-2}$	65.2%	4.58%	2.12%	2.63%	12.5%	5.10%
65	38.4	Included	6.8	5.3	29.7	220839	$3.67\cdot10^{-2}$	$4.78\cdot10^{-2}$	$2.71\cdot10^{-1}$	$3.96\cdot10^{-2}$	$1.83\cdot10^{-2}$	$1.97\cdot10^{-2}$	62.9%	4.60%	2.12%	2.68%	11.1%	7.68%
66	36.3	Included	6.4	4.9	27.5	228822	$4.87\cdot10^{-2}$	$4.16\cdot10^{-2}$	$2.64\cdot10^{-1}$	$4.00\cdot10^{-2}$	$1.85\cdot10^{-2}$	$1.72\cdot10^{-2}$	61.3%	4.64%	2.15%	2.34%	9.66%	10.2%
67	34.2	Included	6.1	4.5	25.4	243644	$7.05\cdot10^{-2}$	$3.52\cdot10^{-2}$	$2.53\cdot10^{-1}$	$4.03\cdot10^{-2}$	$1.87\cdot10^{-2}$	$1.61\cdot10^{-2}$	58.7%	4.67%	2.16%	2.20%	8.16%	14.8%
68	32.1	Included	5.7	4.1	23.3	283566	$1.13\cdot10^{-1}$	$2.02\cdot10^{-2}$	$2.19\cdot10^{-1}$	$3.87\cdot10^{-2}$	$1.80\cdot10^{-2}$	$1.39\cdot10^{-2}$	50.8%	4.49%	2.09%	1.89%	4.69%	23.7%
69	29.9	Included	5.3	3.8	21.2	267764	$1.37\cdot10^{-1}$	$1.59\cdot10^{-2}$	$2.08\cdot10^{-1}$	$3.86\cdot10^{-2}$	$1.80\cdot10^{-2}$	$1.33\cdot10^{-2}$	48.2%	4.48%	2.09%	1.81%	3.68%	28.6%
70	27.8	Included	4.9	3.4	19.1	234160	$1.62\cdot10^{-1}$	$1.20\cdot10^{-2}$	$1.93\cdot10^{-1}$	$3.84\cdot10^{-2}$	$1.79\cdot10^{-2}$	$1.31\cdot10^{-2}$	44.9%	4.46%	2.08%	1.78%	2.79%	34.0%
71	25.7	Included	4.6	3.0	16.9	320922	$1.82\cdot10^{-1}$	$1.64\cdot10^{-2}$	$1.84\cdot10^{-1}$	$3.97\cdot10^{-2}$	$1.85\cdot10^{-2}$	$7.50\cdot10^{-3}$	42.7%	4.60%	2.14%	1.02%	3.80%	38.1%
72	23.6	Included	4.2	2.6	14.8	224904	$2.03\cdot10^{-1}$	$6.14\cdot10^{-3}$	$1.70\cdot10^{-1}$	$3.79\cdot10^{-2}$	$1.77\cdot10^{-2}$	$1.24\cdot10^{-2}$	39.4%	4.40%	2.06%	1.69%	1.42%	42.5%
73	21.5	Included	3.8	2.3	12.7	281904	$2.62\cdot10^{-1}$	$3.18\cdot10^{-3}$	$1.37\cdot10^{-1}$	$3.67\cdot10^{-2}$	$1.72\cdot10^{-2}$	$6.37\cdot10^{-3}$	31.8%	4.25%	2.00%	0.87%	0.74%	54.8%
74	19.4	Included	3.4	1.9	10.6	299973	$3.02\cdot10^{-1}$	$1.20\cdot10^{-3}$	$1.12\cdot10^{-1}$	$3.55\cdot10^{-2}$	$1.68\cdot10^{-2}$	$4.46\cdot10^{-3}$	25.9%	4.13%	1.95%	0.61%	0.28%	63.3%
75	17.2	Included	3.1	1.5	8.5	278622	$3.51\cdot10^{-1}$	$4.74\cdot10^{-4}$	$8.30\cdot10^{-2}$	$3.13\cdot10^{-2}$	$1.50\cdot10^{-2}$	$2.78\cdot10^{-3}$	19.3%	3.64%	1.74%	0.38%	0.11%	73.4%
76	15.1	Included	2.7	1.1	6.4	247173	$3.83\cdot10^{-1}$	$1.74\cdot10^{-4}$	$6.08\cdot10^{-2}$	$2.77\cdot10^{-2}$	$1.33\cdot10^{-2}$	$1.32\cdot10^{-3}$	14.1%	3.22%	1.55%	0.18%	0.04%	80.1%
77	13.0	Included	2.3	0.8	4.2	258338	$4.00\cdot10^{-1}$	0.00	$4.89\cdot10^{-2}$	$2.56\cdot10^{-2}$	$1.23\cdot10^{-2}$	$5.45\cdot10^{-4}$	11.4%	2.97%	1.43%	0.07%	0.00%	83.8%
78	10.9	Included	1.9	0.4	2.1	235992	$4.15\cdot10^{-1}$	$3.81\cdot10^{-5}$	$3.80\cdot10^{-2}$	$2.29\cdot10^{-2}$	$1.11\cdot10^{-2}$	$4.24\cdot10^{-4}$	8.83%	2.66%	1.29%	0.06%	0.01%	86.9%
79	8.8	Included	1.6	0.0	0.0	268291	$4.25\cdot10^{-1}$	$2.61\cdot10^{-5}$	$2.89\cdot10^{-2}$	$1.96\cdot10^{-2}$	$9.57\cdot10^{-3}$	$2.07\cdot10^{-4}$	6.70%	2.28%	1.11%	0.03%	0.01%	88.9%
80	6.6	Excluded	1.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
81	4.5	Excluded	0.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

82	2.4	Excluded	0.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
83	0.3	Excluded	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

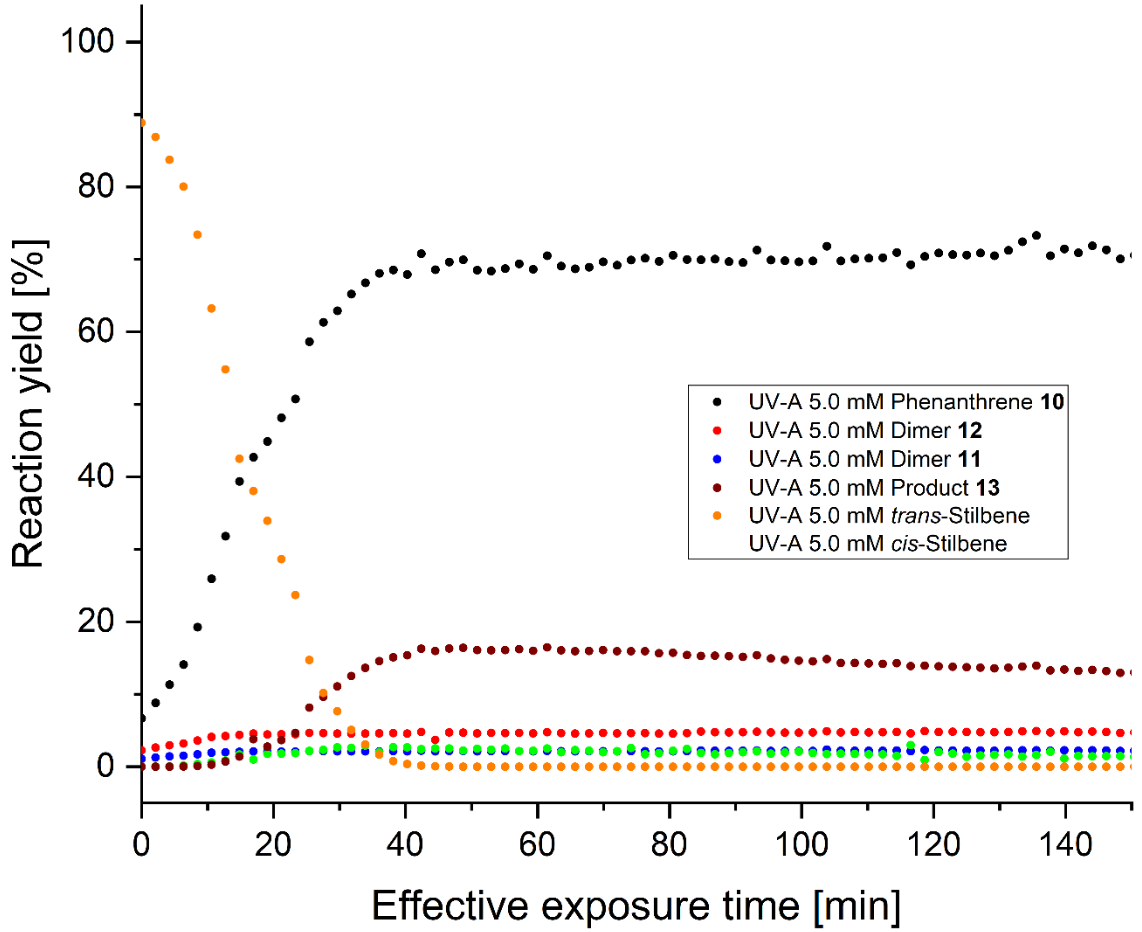


Figure S 19. Results of Switch-Off optimisation of Mallory photoreaction using UV-B light and 50.0 mM stilbene concentration. Top: Reaction components GC areas, conversion, and yield plotted against uncorrected residence time. Bottom: Reaction components GC areas, conversion, and yield plotted against exposure time, corrected for light inhomogeneity.

2. 4. 2. 5. Switch-Off experiment results using UV-C light and 5.0 mM stilbene concentration

Cis-stilbene (44.5 µL, 45.0 mg, 0.25 mmol, 1.0 eq., 5.0 mM solution), iodine (6.3 mg, 0.025 mmol, 0.1 eq., 0.5 mM solution), and dibutyl ether (0.15 mL, 117.1 mg, 0.90 mmol, 3.6 eq., 18.0 mM solution) were dissolved in cyclohexane (50.0 mL, 1111.1 vol.), obtained solution was saturated with oxygen by bubbling gaseous O_2 for 15 minutes, and then connected to flow reagents stream. Cyclohexane was connected to flow solvents stream. The UV-A lamp (PISCES PLL 36W) and water cooling were then turned on and system was allowed to equilibrate for 30 minutes. Then reaction mixture was injected into the photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA). Effective exposure time was set to 45 minutes (which corresponds to 0.707 mL/min flow rate). Once the photoreactor was filled with reaction mixture, the UV lamp was switched off, the pump was switched to solvent stream, the reaction mixture was eluted from the photoreactor, and was collected into vials (0.375 mL of reaction mixture, diluted to 1.0 mL with acetone). Collected samples were then analysed using off-line GC.

Table S 15. Results of Switch-Off optimisation performed for Mallory reaction of cis-stilbene using UV-C light and 5.0 mM stilbene concentration.

#	Residence time [min]	Included/Excluded	Reactor volume [mL]	Effective Reactor Volume [mL]	Effective exposure time [min]	IS GC Area	Area Ratio *cis*-Stilbene/IS	Area Ratio *trans*-Stilbene/IS	Area Ratio Phenanthrene 10/IS	Area Ratio Dimer ABAB 12/IS	Area Ratio Dimer AABB 11/IS	Area Ratio Product 13/IS	Phenanthrene yield [%]	Dimer 12 yield [%]	Dimer 11 yield [%]	Product 13 yield [%]	*trans*-Stilbene yield [%]	Remaining *cis*-Stilbene [%]
1	45.0	Excluded	31.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	44.4	Excluded	31.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	43.9	Excluded	31.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	43.4	Excluded	30.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	42.9	Excluded	30.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	42.3	Included	29.9	28.5	40.3	51039	$3.53\cdot10^{-4}$	$1.53\cdot10^{-3}$	$2.93\cdot10^{-1}$	0.00	0.00	0.00	67.9%	0.00%	0.00%	0.00%	0.35%	0.08%
7	41.8	Included	29.6	28.1	39.8	53524	$3.36\cdot10^{-4}$	$1.21\cdot10^{-3}$	$2.98\cdot10^{-1}$	0.00	0.00	0.00	69.3%	0.00%	0.00%	0.00%	0.28%	0.08%
8	41.3	Included	29.2	27.8	39.3	50467	$3.57\cdot10^{-4}$	$1.41\cdot10^{-3}$	$2.97\cdot10^{-1}$	0.00	0.00	0.00	68.9%	0.00%	0.00%	0.00%	0.33%	0.08%
9	40.7	Included	28.8	27.4	38.7	51280	$3.51\cdot10^{-4}$	$1.52\cdot10^{-3}$	$2.97\cdot10^{-1}$	0.00	0.00	0.00	69.0%	0.00%	0.00%	0.00%	0.35%	0.08%
10	40.2	Included	28.4	27.0	38.2	53008	$3.40\cdot10^{-4}$	$1.34\cdot10^{-3}$	$2.96\cdot10^{-1}$	0.00	0.00	0.00	68.6%	0.00%	0.00%	0.00%	0.31%	0.08%
11	39.7	Included	28.1	26.6	37.7	54139	$3.88\cdot10^{-4}$	$1.33\cdot10^{-3}$	$2.98\cdot10^{-1}$	0.00	0.00	0.00	69.1%	0.00%	0.00%	0.00%	0.31%	0.09%
12	39.1	Included	27.7	26.3	37.1	54960	$3.82\cdot10^{-4}$	$1.22\cdot10^{-3}$	$3.01\cdot10^{-1}$	0.00	0.00	0.00	70.0%	0.00%	0.00%	0.00%	0.28%	0.09%
13	38.6	Included	27.3	25.9	36.6	52551	$4.00\cdot10^{-4}$	$1.29\cdot10^{-3}$	$3.07\cdot10^{-1}$	0.00	0.00	0.00	71.1%	0.00%	0.00%	0.00%	0.30%	0.09%
14	38.1	Included	26.9	25.5	36.1	55072	$3.99\cdot10^{-4}$	$1.33\cdot10^{-3}$	$3.00\cdot10^{-1}$	0.00	0.00	0.00	69.6%	0.00%	0.00%	0.00%	0.31%	0.09%
15	37.6	Included	26.6	25.1	35.5	56342	$4.44\cdot10^{-4}$	$1.26\cdot10^{-3}$	$3.10\cdot10^{-1}$	0.00	0.00	0.00	72.0%	0.00%	0.00%	0.00%	0.29%	0.11%
16	37.0	Included	26.2	24.8	35.0	55679	$3.95\cdot10^{-4}$	$1.33\cdot10^{-3}$	$3.11\cdot10^{-1}$	0.00	0.00	0.00	72.1%	0.00%	0.00%	0.00%	0.31%	0.09%

17	36.5	Included	25.8	24.4	34.5	55675	$3.77\cdot10^{-4}$	$1.37\cdot10^{-3}$	$3.06\cdot10^{-1}$	0.00	0.00	0.00	71.1%	0.00%	0.00%	0.00%	0.32%	0.09%
18	36.0	Included	25.4	24.0	33.9	56093	$3.74\cdot10^{-4}$	$1.41\cdot10^{-3}$	$3.03\cdot10^{-1}$	0.00	0.00	0.00	70.3%	0.00%	0.00%	0.00%	0.33%	0.09%
19	35.4	Included	25.1	23.6	33.4	62719	$3.51\cdot10^{-4}$	$1.40\cdot10^{-3}$	$3.01\cdot10^{-1}$	0.00	0.00	0.00	69.8%	0.00%	0.00%	0.00%	0.33%	0.08%
20	34.9	Included	24.7	23.3	32.9	57953	$3.80\cdot10^{-4}$	$1.48\cdot10^{-3}$	$3.04\cdot10^{-1}$	0.00	0.00	0.00	70.7%	0.00%	0.00%	0.00%	0.34%	0.09%
21	34.4	Included	24.3	22.9	32.4	53154	$3.57\cdot10^{-4}$	$1.30\cdot10^{-3}$	$3.00\cdot10^{-1}$	0.00	0.00	0.00	69.5%	0.00%	0.00%	0.00%	0.30%	0.08%
22	33.8	Included	23.9	22.5	31.8	57533	$3.82\cdot10^{-4}$	$1.29\cdot10^{-3}$	$3.04\cdot10^{-1}$	0.00	0.00	0.00	70.5%	0.00%	0.00%	0.00%	0.30%	0.09%
23	33.3	Included	23.6	22.1	31.3	53046	$3.96\cdot10^{-4}$	$1.43\cdot10^{-3}$	$3.03\cdot10^{-1}$	0.00	0.00	0.00	70.4%	0.00%	0.00%	0.00%	0.33%	0.09%
24	32.8	Included	23.2	21.8	30.8	59145	$3.55\cdot10^{-4}$	$1.45\cdot10^{-3}$	$3.08\cdot10^{-1}$	0.00	0.00	0.00	71.4%	0.00%	0.00%	0.00%	0.34%	0.08%
25	32.2	Included	22.8	21.4	30.2	55757	$3.95\cdot10^{-4}$	$1.60\cdot10^{-3}$	$3.07\cdot10^{-1}$	0.00	0.00	0.00	71.2%	0.00%	0.00%	0.00%	0.37%	0.09%
26	31.7	Included	22.4	21.0	29.7	55204	$3.99\cdot10^{-4}$	$1.52\cdot10^{-3}$	$3.06\cdot10^{-1}$	0.00	0.00	0.00	70.9%	0.00%	0.00%	0.00%	0.35%	0.09%
27	31.2	Included	22.1	20.6	29.2	56854	$3.52\cdot10^{-4}$	$1.53\cdot10^{-3}$	$3.05\cdot10^{-1}$	0.00	0.00	0.00	70.8%	0.00%	0.00%	0.00%	0.36%	0.08%
28	30.7	Included	21.7	20.3	28.6	55798	$3.76\cdot10^{-4}$	$1.54\cdot10^{-3}$	$3.07\cdot10^{-1}$	0.00	0.00	0.00	71.2%	0.00%	0.00%	0.00%	0.36%	0.09%
29	30.1	Included	21.3	19.9	28.1	58280	$3.09\cdot10^{-4}$	$1.53\cdot10^{-3}$	$3.05\cdot10^{-1}$	0.00	0.00	0.00	70.7%	0.00%	0.00%	0.00%	0.35%	0.07%
30	29.6	Included	20.9	19.5	27.6	68723	$2.91\cdot10^{-4}$	$1.51\cdot10^{-3}$	$3.10\cdot10^{-1}$	0.00	0.00	0.00	71.9%	0.00%	0.00%	0.00%	0.35%	0.07%
31	29.1	Included	20.6	19.1	27.1	58577	$3.93\cdot10^{-4}$	$1.50\cdot10^{-3}$	$3.06\cdot10^{-1}$	0.00	0.00	0.00	71.0%	0.00%	0.00%	0.00%	0.35%	0.09%
32	28.5	Included	20.2	18.8	26.5	56247	$3.20\cdot10^{-4}$	$1.67\cdot10^{-3}$	$3.17\cdot10^{-1}$	0.00	0.00	0.00	73.7%	0.00%	0.00%	0.00%	0.39%	0.07%
33	28.0	Included	19.8	18.4	26.0	57484	$3.48\cdot10^{-4}$	$1.57\cdot10^{-3}$	$3.12\cdot10^{-1}$	$1.74\cdot10^{-4}$	0.00	0.00	72.5%	0.02%	0.00%	0.00%	0.36%	0.08%
34	27.5	Included	19.4	18.0	25.5	60465	$3.47\cdot10^{-4}$	$1.54\cdot10^{-3}$	$3.10\cdot10^{-1}$	0.00	0.00	0.00	71.9%	0.00%	0.00%	0.00%	0.36%	0.08%
35	26.9	Included	19.1	17.6	24.9	54922	$2.91\cdot10^{-4}$	$1.68\cdot10^{-3}$	$3.08\cdot10^{-1}$	0.00	0.00	0.00	71.4%	0.00%	0.00%	0.00%	0.39%	0.07%
36	26.4	Included	18.7	17.3	24.4	70297	$3.13\cdot10^{-4}$	$1.58\cdot10^{-3}$	$3.20\cdot10^{-1}$	0.00	0.00	$7.38\cdot10^{-4}$	74.3%	0.00%	0.00%	0.09%	0.37%	0.07%
37	25.9	Included	18.3	16.9	23.9	64892	$2.93\cdot10^{-4}$	$1.57\cdot10^{-3}$	$3.12\cdot10^{-1}$	$2.00\cdot10^{-4}$	0.00	0.00	72.3%	0.02%	0.00%	0.00%	0.36%	0.07%
38	25.4	Included	17.9	16.5	23.3	60772	$2.96\cdot10^{-4}$	$1.68\cdot10^{-3}$	$3.18\cdot10^{-1}$	0.00	0.00	0.00	73.8%	0.00%	0.00%	0.00%	0.39%	0.07%
39	24.8	Included	17.6	16.1	22.8	58752	$3.06\cdot10^{-4}$	$1.65\cdot10^{-3}$	$3.17\cdot10^{-1}$	$2.55\cdot10^{-4}$	0.00	0.00	73.5%	0.03%	0.00%	0.00%	0.38%	0.07%
40	24.3	Included	17.2	15.8	22.3	63471	$2.99\cdot10^{-4}$	$1.64\cdot10^{-3}$	$3.10\cdot10^{-1}$	$1.58\cdot10^{-4}$	0.00	$7.59\cdot10^{-4}$	71.9%	0.02%	0.00%	0.09%	0.38%	0.07%
41	23.8	Included	16.8	15.4	21.7	57906	$3.63\cdot10^{-4}$	$1.55\cdot10^{-3}$	$3.10\cdot10^{-1}$	$3.11\cdot10^{-4}$	0.00	0.00	71.9%	0.04%	0.00%	0.00%	0.36%	0.09%
42	23.2	Included	16.4	15.0	21.2	77791	$3.09\cdot10^{-4}$	$1.68\cdot10^{-3}$	$3.06\cdot10^{-1}$	$2.06\cdot10^{-4}$	0.00	0.00	71.0%	0.02%	0.00%	0.00%	0.39%	0.07%
43	22.7	Included	16.1	14.6	20.7	57147	$2.97\cdot10^{-4}$	$1.64\cdot10^{-3}$	$3.07\cdot10^{-1}$	$2.97\cdot10^{-4}$	0.00	$8.43\cdot10^{-4}$	71.2%	0.03%	0.00%	0.10%	0.38%	0.07%
44	22.2	Included	15.7	14.3	20.2	56193	$3.38\cdot10^{-4}$	$1.71\cdot10^{-3}$	$3.05\cdot10^{-1}$	$3.20\cdot10^{-4}$	0.00	$1.05\cdot10^{-3}$	70.8%	0.04%	0.00%	0.12%	0.40%	0.08%
45	21.6	Included	15.3	13.9	19.6	64967	$3.69\cdot10^{-4}$	$1.62\cdot10^{-3}$	$3.06\cdot10^{-1}$	$3.54\cdot10^{-4}$	0.00	$7.98\cdot10^{-4}$	71.1%	0.04%	0.00%	0.09%	0.38%	0.09%
46	21.1	Included	14.9	13.5	19.1	67465	$3.41\cdot10^{-4}$	$1.67\cdot10^{-3}$	$3.09\cdot10^{-1}$	$3.41\cdot10^{-4}$	0.00	$9.33\cdot10^{-4}$	71.8%	0.04%	0.00%	0.11%	0.39%	0.08%

47	20.6	Included	14.6	13.1	18.6	81310	$3.94\cdot10^{-4}$	$1.56\cdot10^{-3}$	$3.09\cdot10^{-1}$	$3.20\cdot10^{-4}$	0.00	$1.00\cdot10^{-3}$	71.7%	0.04%	0.00%	0.12%	0.36%	0.09%
48	20.0	Included	14.2	12.8	18.0	59129	$4.23\cdot10^{-4}$	$1.56\cdot10^{-3}$	$3.14\cdot10^{-1}$	$4.23\cdot10^{-4}$	0.00	$1.19\cdot10^{-3}$	72.8%	0.05%	0.00%	0.14%	0.36%	0.10%
49	19.5	Included	13.8	12.4	17.5	58453	$4.79\cdot10^{-4}$	$1.63\cdot10^{-3}$	$3.07\cdot10^{-1}$	$3.76\cdot10^{-4}$	0.00	$1.65\cdot10^{-3}$	71.2%	0.04%	0.00%	0.19%	0.38%	0.11%
50	19.0	Included	13.4	12.0	17.0	62446	$6.09\cdot10^{-4}$	$1.52\cdot10^{-3}$	$3.04\cdot10^{-1}$	$4.16\cdot10^{-4}$	0.00	$1.84\cdot10^{-3}$	70.5%	0.05%	0.00%	0.21%	0.35%	0.15%
51	18.5	Included	13.1	11.6	16.4	80672	$7.69\cdot10^{-4}$	$1.36\cdot10^{-3}$	$3.08\cdot10^{-1}$	$4.83\cdot10^{-4}$	0.00	$1.97\cdot10^{-3}$	71.5%	0.06%	0.00%	0.23%	0.32%	0.19%
52	17.9	Included	12.7	11.3	15.9	60667	$9.23\cdot10^{-4}$	$1.48\cdot10^{-3}$	$3.04\cdot10^{-1}$	$3.96\cdot10^{-4}$	0.00	$2.81\cdot10^{-3}$	70.5%	0.05%	0.00%	0.33%	0.34%	0.23%
53	17.4	Included	12.3	10.9	15.4	57246	$1.10\cdot10^{-3}$	$1.43\cdot10^{-3}$	$3.10\cdot10^{-1}$	$4.89\cdot10^{-4}$	0.00	$2.85\cdot10^{-3}$	71.9%	0.06%	0.00%	0.33%	0.33%	0.27%
54	16.9	Included	11.9	10.5	14.9	62404	$1.31\cdot10^{-3}$	$1.35\cdot10^{-3}$	$3.09\cdot10^{-1}$	$4.81\cdot10^{-4}$	0.00	$3.38\cdot10^{-3}$	71.7%	0.06%	0.00%	0.39%	0.31%	0.32%
55	16.3	Included	11.6	10.1	14.3	60555	$1.50\cdot10^{-3}$	$1.26\cdot10^{-3}$	$3.00\cdot10^{-1}$	$5.12\cdot10^{-4}$	0.00	$5.44\cdot10^{-3}$	69.6%	0.06%	0.00%	0.63%	0.29%	0.37%
56	15.8	Included	11.2	9.8	13.8	64184	$1.95\cdot10^{-3}$	$1.29\cdot10^{-3}$	$3.00\cdot10^{-1}$	$5.76\cdot10^{-4}$	0.00	$5.77\cdot10^{-3}$	69.6%	0.07%	0.00%	0.67%	0.30%	0.48%
57	15.3	Included	10.8	9.4	13.3	71704	$2.51\cdot10^{-3}$	$1.37\cdot10^{-3}$	$3.16\cdot10^{-1}$	$6.55\cdot10^{-4}$	0.00	$6.82\cdot10^{-3}$	73.3%	0.08%	0.00%	0.79%	0.32%	0.62%
58	14.7	Included	10.4	9.0	12.7	57831	$2.89\cdot10^{-3}$	$9.68\cdot10^{-3}$	$3.01\cdot10^{-1}$	$5.53\cdot10^{-4}$	$1.73\cdot10^{-4}$	$1.04\cdot10^{-2}$	69.9%	0.06%	0.02%	1.20%	0.22%	0.72%
59	14.2	Included	10.1	8.6	12.2	70903	$3.88\cdot10^{-3}$	$1.09\cdot10^{-3}$	$3.10\cdot10^{-1}$	$6.21\cdot10^{-4}$	$1.69\cdot10^{-4}$	$8.93\cdot10^{-3}$	71.9%	0.07%	0.02%	1.04%	0.25%	0.97%
60	13.7	Included	9.7	8.3	11.7	59325	$4.48\cdot10^{-3}$	$1.18\cdot10^{-3}$	$2.92\cdot10^{-1}$	$6.24\cdot10^{-4}$	$2.02\cdot10^{-4}$	$1.10\cdot10^{-2}$	67.9%	0.07%	0.02%	1.28%	0.27%	1.12%
61	13.2	Included	9.3	7.9	11.1	59735	$5.68\cdot10^{-3}$	$1.12\cdot10^{-3}$	$2.98\cdot10^{-1}$	$7.20\cdot10^{-4}$	$2.01\cdot10^{-4}$	$1.20\cdot10^{-2}$	69.2%	0.08%	0.02%	1.39%	0.26%	1.41%
62	12.6	Included	8.9	7.5	10.6	65230	$7.42\cdot10^{-3}$	$9.81\cdot10^{-4}$	$2.98\cdot10^{-1}$	$7.51\cdot10^{-4}$	$2.30\cdot10^{-4}$	$1.30\cdot10^{-2}$	69.2%	0.09%	0.03%	1.51%	0.23%	1.85%
63	12.1	Included	8.6	7.1	10.1	62585	$9.08\cdot10^{-3}$	$8.79\cdot10^{-4}$	$2.88\cdot10^{-1}$	$6.39\cdot10^{-4}$	$2.08\cdot10^{-4}$	$1.56\cdot10^{-2}$	66.8%	0.07%	0.02%	1.81%	0.20%	2.27%
64	11.6	Included	8.2	6.8	9.5	61799	$1.22\cdot10^{-2}$	$7.77\cdot10^{-4}$	$2.90\cdot10^{-1}$	$8.41\cdot10^{-4}$	$2.91\cdot10^{-4}$	$1.64\cdot10^{-2}$	67.3%	0.10%	0.03%	1.91%	0.18%	3.05%
65	11.0	Included	7.8	6.4	9.0	51540	$1.40\cdot10^{-2}$	$5.82\cdot10^{-4}$	$2.78\cdot10^{-1}$	$9.31\cdot10^{-4}$	$3.30\cdot10^{-4}$	$2.03\cdot10^{-2}$	64.5%	0.11%	0.04%	2.36%	0.14%	3.50%
66	10.5	Included	7.4	6.0	8.5	86737	$2.04\cdot10^{-2}$	$4.96\cdot10^{-4}$	$2.84\cdot10^{-1}$	$1.03\cdot10^{-3}$	$4.04\cdot10^{-4}$	$1.40\cdot10^{-2}$	66.0%	0.12%	0.05%	1.62%	0.12%	5.11%
67	10.0	Included	7.1	5.6	8.0	70852	$2.16\cdot10^{-2}$	$4.52\cdot10^{-4}$	$2.71\cdot10^{-1}$	$1.07\cdot10^{-3}$	$4.80\cdot10^{-4}$	$2.43\cdot10^{-2}$	63.0%	0.12%	0.06%	2.81%	0.10%	5.40%
68	9.4	Included	6.7	5.3	7.4	57139	$3.39\cdot10^{-2}$	$3.15\cdot10^{-4}$	$2.60\cdot10^{-1}$	$1.16\cdot10^{-3}$	$6.65\cdot10^{-4}$	$1.29\cdot10^{-2}$	60.4%	0.13%	0.08%	1.50%	0.07%	8.48%
69	8.9	Included	6.3	4.9	6.9	58569	$5.34\cdot10^{-2}$	$1.71\cdot10^{-4}$	$2.54\cdot10^{-1}$	$1.18\cdot10^{-3}$	$5.12\cdot10^{-4}$	$2.24\cdot10^{-2}$	58.9%	0.14%	0.06%	2.61%	0.04%	13.4%
70	8.4	Included	5.9	4.5	6.4	68803	$7.30\cdot10^{-2}$	0.00	$2.42\cdot10^{-1}$	$1.24\cdot10^{-3}$	$5.52\cdot10^{-4}$	$1.99\cdot10^{-2}$	56.2%	0.14%	0.06%	2.31%	0.00%	18.3%
71	7.9	Included	5.6	4.1	5.8	69290	$9.28\cdot10^{-2}$	0.00	$2.37\cdot10^{-1}$	$1.34\cdot10^{-3}$	$6.78\cdot10^{-4}$	$2.16\cdot10^{-2}$	55.0%	0.16%	0.08%	2.51%	0.00%	23.2%
72	7.3	Included	5.2	3.8	5.3	63072	$1.05\cdot10^{-1}$	0.00	$2.31\cdot10^{-1}$	$1.28\cdot10^{-3}$	$6.02\cdot10^{-4}$	$2.38\cdot10^{-2}$	53.7%	0.15%	0.07%	2.77%	0.00%	26.3%
73	6.8	Included	4.8	3.4	4.8	59122	$1.27\cdot10^{-1}$	0.00	$2.20\cdot10^{-1}$	$1.54\cdot10^{-3}$	$6.09\cdot10^{-4}$	$2.26\cdot10^{-2}$	51.0%	0.18%	0.07%	2.62%	0.00%	31.7%
74	6.3	Included	4.4	3.0	4.2	61874	$1.51\cdot10^{-1}$	0.00	$2.08\cdot10^{-1}$	$1.37\cdot10^{-3}$	$7.11\cdot10^{-4}$	$1.98\cdot10^{-2}$	48.3%	0.16%	0.08%	2.30%	0.00%	37.7%
75	5.7	Included	4.1	2.6	3.7	62742	$1.75\cdot10^{-1}$	0.00	$1.93\cdot10^{-1}$	$1.59\cdot10^{-3}$	$9.24\cdot10^{-4}$	$1.91\cdot10^{-2}$	44.7%	0.18%	0.11%	2.21%	0.00%	43.8%
76	5.2	Included	3.7	2.3	3.2	63366	$2.03\cdot10^{-1}$	0.00	$1.76\cdot10^{-1}$	$1.37\cdot10^{-3}$	$6.94\cdot10^{-4}$	$1.84\cdot10^{-2}$	40.9%	0.16%	0.08%	2.13%	0.00%	50.9%

77	4.7	Included	3.3	1.9	2.7	64692	$2.38\cdot10^{-1}$	0.00	$1.59\cdot10^{-1}$	$1.33\cdot10^{-3}$	$7.73\cdot10^{-4}$	$1.70\cdot10^{-2}$	36.9%	0.15%	0.09%	1.97%	0.00%	59.4%
78	4.1	Included	2.9	1.5	2.1	71239	$2.71\cdot10^{-1}$	0.00	$1.37\cdot10^{-1}$	$1.21\cdot10^{-3}$	$6.60\cdot10^{-4}$	$1.33\cdot10^{-2}$	31.8%	0.14%	0.08%	1.54%	0.00%	67.9%
79	3.6	Included	2.6	1.1	1.6	72199	$3.14\cdot10^{-1}$	0.00	$1.17\cdot10^{-1}$	$1.14\cdot10^{-3}$	$7.20\cdot10^{-4}$	$1.34\cdot10^{-2}$	27.3%	0.13%	0.08%	1.56%	0.00%	78.5%
80	3.1	Included	2.2	0.8	1.1	65174	$3.33\cdot10^{-1}$	0.00	$9.05\cdot10^{-2}$	$9.36\cdot10^{-4}$	$4.45\cdot10^{-4}$	$1.20\cdot10^{-2}$	21.0%	0.11%	0.05%	1.40%	0.00%	83.2%
81	2.5	Included	1.8	0.4	0.5	83434	$3.70\cdot10^{-1}$	0.00	$7.07\cdot10^{-2}$	$9.35\cdot10^{-4}$	$4.31\cdot10^{-4}$	$6.84\cdot10^{-3}$	16.4%	0.11%	0.05%	0.79%	0.00%	92.7%
82	2.0	Included	1.4	0.0	0.0	90107	$4.00\cdot10^{-1}$	0.00	$5.15\cdot10^{-2}$	$8.77\cdot10^{-4}$	$4.55\cdot10^{-4}$	$7.69\cdot10^{-3}$	12.0%	0.10%	0.05%	0.89%	0.00%	100.0%
83	1.5	Excluded	1.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
84	1.0	Excluded	0.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
85	0.4	Excluded	0.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
86	0.0	Excluded	0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

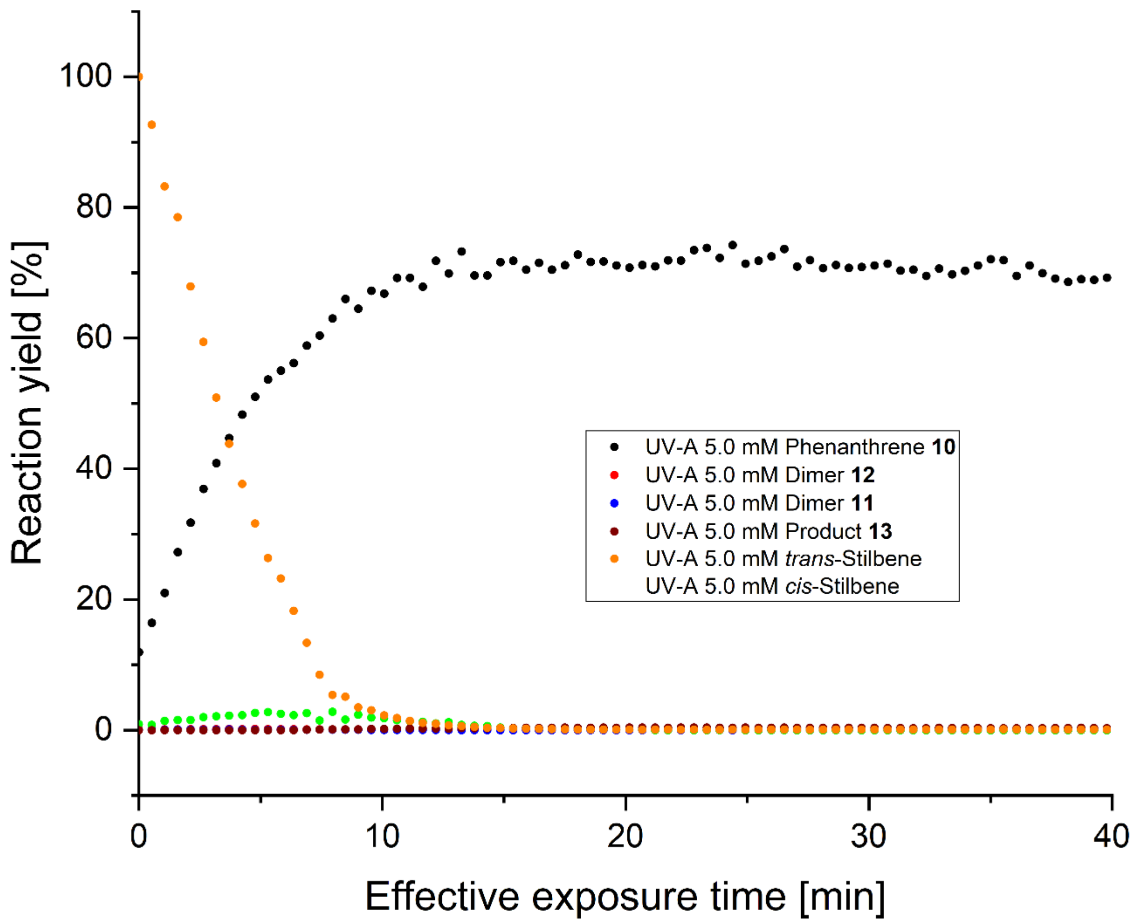


Figure S 20. Results of Switch-Off optimisation of Mallory photoreaction using UV-C light and 5.0 mM stilbene concentration. Top: Reaction components GC areas, conversion, and yield plotted against uncorrected residence time. Bottom: Reaction components GC areas, conversion, and yield plotted against exposure time, corrected for light inhomogeneity.

2. 4. 2. 6. Switch-Off experiment results using UV-C light and 50.0 mM stilbene concentration

Cis-stilbene (445.0 µL, 450.2 mg, 2.50 mmol, 1.0 eq., 50.0 mM solution), iodine (63.0 mg, 0.25 mmol, 0.1 eq., 5.0 mM solution), and dibutyl ether (1.5 mL, 1.17 g, 9.0 mmol, 3.6 eq., 180.0 mM solution) were dissolved in cyclohexane (48.0 mL, 106.6 vol.), obtained solution was saturated with oxygen by bubbling gaseous O_2 for 15 minutes, and then connected to flow reagents stream. Cyclohexane was connected to flow solvents stream. The UV-C lamp (PISCES PLL 36W) and water cooling were then turned on and system was allowed to equilibrate for 30 minutes. Then reaction mixture was injected into the photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA).

Effective exposure time was set to 180 minutes (which corresponds to 0.177 mL/min flow rate). Once the photoreactor was filled with reaction mixture, the UV lamp was switched off, the pump was switched to solvent stream, the reaction mixture was eluted from the photoreactor, and was collected into vials (0.375 mL of reaction mixture, diluted to 1.0 mL with acetone). Collected samples were then analysed using off-line GC.

Table S 16. Results of Switch-Off optimisation performed for Mallory reaction of cis-stilbene using UV-C light and 50.0 mM stilbene concentration.

#	Residence time [min]	Included/Excluded	Reactor volume [mL]	Effective Reactor Volume [mL]	Effective exposure time [min]	IS GC Area	Area Ratio *cis*-Stilbene/IS	Area Ratio *trans*-Stilbene/IS	Area Ratio Phenanthrene 10/IS	Area Ratio Dimer ABAB 12/IS	Area Ratio Dimer AABB 11/IS	Area Ratio Product 13/IS	Phenanthrene yield [%]	Dimer 12 yield [%]	Dimer 11 yield [%]	Product 13 yield [%]	*trans*-Stilbene yield [%]	Remaining *cis*-Stilbene [%]
1	174.0	Excluded	30.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	171.9	Excluded	30.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	169.8	Excluded	30.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	167.7	Excluded	29.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	165.5	Included	29.3	27.8	156.8	50933	0.00	0.00	$3.07\cdot10^{-1}$	0.00	0.00	0.00	71.1%	0.00%	0.00%	0.00%	0.00%	0.00%
6	163.4	Included	28.9	27.4	154.7	50906	0.00	0.00	$2.95\cdot10^{-1}$	0.00	0.00	0.00	68.5%	0.00%	0.00%	0.00%	0.00%	0.00%
7	161.3	Included	28.6	27.0	152.5	53446	0.00	0.00	$3.00\cdot10^{-1}$	0.00	0.00	0.00	69.7%	0.00%	0.00%	0.00%	0.00%	0.00%
8	159.2	Included	28.2	26.6	150.4	50325	0.00	0.00	$2.99\cdot10^{-1}$	0.00	0.00	0.00	69.5%	0.00%	0.00%	0.00%	0.00%	0.00%
9	157.1	Included	27.8	26.3	148.3	51194	0.00	0.00	$2.99\cdot10^{-1}$	0.00	0.00	0.00	69.4%	0.00%	0.00%	0.00%	0.00%	0.00%
10	154.9	Included	27.4	25.9	146.2	52919	0.00	0.00	$2.97\cdot10^{-1}$	0.00	0.00	0.00	69.0%	0.00%	0.00%	0.00%	0.00%	0.00%
11	152.8	Included	27.1	25.5	144.1	54042	0.00	0.00	$2.99\cdot10^{-1}$	0.00	0.00	0.00	69.5%	0.00%	0.00%	0.00%	0.00%	0.00%
12	150.7	Included	26.7	25.1	141.9	54875	0.00	0.00	$3.03\cdot10^{-1}$	0.00	0.00	0.00	70.3%	0.00%	0.00%	0.00%	0.00%	0.00%
13	148.6	Included	26.3	24.8	139.8	52435	0.00	0.00	$3.08\cdot10^{-1}$	0.00	0.00	0.00	71.6%	0.00%	0.00%	0.00%	0.00%	0.00%
14	146.5	Included	25.9	24.4	137.7	54972	0.00	0.00	$3.01\cdot10^{-1}$	0.00	0.00	0.00	69.9%	0.00%	0.00%	0.00%	0.00%	0.00%
15	144.4	Included	25.6	24.0	135.6	56191	0.00	0.00	$3.12\cdot10^{-1}$	0.00	0.00	0.00	72.4%	0.00%	0.00%	0.00%	0.00%	0.00%
16	142.2	Included	25.2	23.6	133.5	55545	0.00	0.00	$3.12\cdot10^{-1}$	0.00	0.00	0.00	72.4%	0.00%	0.00%	0.00%	0.00%	0.00%
17	140.1	Included	24.8	23.3	131.4	55517	0.00	0.00	$3.08\cdot10^{-1}$	0.00	0.00	0.00	71.6%	0.00%	0.00%	0.00%	0.00%	0.00%
18	138.0	Included	24.4	22.9	129.2	55964	0.00	0.00	$3.04\cdot10^{-1}$	0.00	0.00	0.00	70.6%	0.00%	0.00%	0.00%	0.00%	0.00%
19	135.9	Included	24.1	22.5	127.1	62613	0.00	0.00	$3.03\cdot10^{-1}$	0.00	0.00	0.00	70.3%	0.00%	0.00%	0.00%	0.00%	0.00%
20	133.8	Included	23.7	22.1	125.0	57839	0.00	0.00	$3.06\cdot10^{-1}$	0.00	0.00	0.00	71.0%	0.00%	0.00%	0.00%	0.00%	0.00%
21	131.6	Included	23.3	21.8	122.9	53018	0.00	0.00	$3.01\cdot10^{-1}$	0.00	0.00	0.00	70.0%	0.00%	0.00%	0.00%	0.00%	0.00%

22	129.5	Included	22.9	21.4	120.8	57429	0.00	0.00	$3.05\cdot10^{-1}$	0.00	0.00	0.00	70.8%	0.00%	0.00%	0.00%	0.00%	0.00%
23	127.4	Included	22.6	21.0	118.6	52904	0.00	0.00	$3.05\cdot10^{-1}$	0.00	0.00	0.00	70.8%	0.00%	0.00%	0.00%	0.00%	0.00%
24	125.3	Included	22.2	20.6	116.5	59021	0.00	0.00	$3.10\cdot10^{-1}$	0.00	0.00	0.00	71.8%	0.00%	0.00%	0.00%	0.00%	0.00%
25	123.2	Included	21.8	20.3	114.4	55592	0.00	0.00	$3.09\cdot10^{-1}$	0.00	0.00	0.00	71.7%	0.00%	0.00%	0.00%	0.00%	0.00%
26	121.0	Included	21.4	19.9	112.3	55079	0.00	0.00	$3.08\cdot10^{-1}$	0.00	0.00	0.00	71.4%	0.00%	0.00%	0.00%	0.00%	0.00%
27	118.9	Included	21.1	19.5	110.2	56719	0.00	0.00	$3.07\cdot10^{-1}$	0.00	0.00	0.00	71.2%	0.00%	0.00%	0.00%	0.00%	0.00%
28	116.8	Included	20.7	19.1	108.1	55666	0.00	0.00	$3.09\cdot10^{-1}$	0.00	0.00	0.00	71.6%	0.00%	0.00%	0.00%	0.00%	0.00%
29	114.7	Included	20.3	18.8	105.9	58166	0.00	0.00	$3.06\cdot10^{-1}$	0.00	0.00	0.00	71.1%	0.00%	0.00%	0.00%	0.00%	0.00%
30	112.6	Included	19.9	18.4	103.8	68542	0.00	0.00	$3.12\cdot10^{-1}$	0.00	0.00	0.00	72.3%	0.00%	0.00%	0.00%	0.00%	0.00%
31	110.5	Included	19.6	18.0	101.7	58443	0.00	0.00	$3.08\cdot10^{-1}$	0.00	0.00	0.00	71.4%	0.00%	0.00%	0.00%	0.00%	0.00%
32	108.3	Included	19.2	17.6	99.6	56081	0.00	0.00	$3.19\cdot10^{-1}$	0.00	0.00	0.00	74.1%	0.00%	0.00%	0.00%	0.00%	0.00%
33	106.2	Included	18.8	17.3	97.5	57354	0.00	0.00	$3.14\cdot10^{-1}$	0.00	0.00	0.00	72.9%	0.00%	0.00%	0.00%	0.00%	0.00%
34	104.1	Included	18.4	16.9	95.3	60306	0.00	0.00	$3.11\cdot10^{-1}$	0.00	0.00	0.00	72.3%	0.00%	0.00%	0.00%	0.00%	0.00%
35	102.0	Included	18.1	16.5	93.2	54768	0.00	0.00	$3.09\cdot10^{-1}$	$2.74\cdot10^{-4}$	$9.1\cdot10^{-5}$	0.00	71.8%	0.03%	0.01%	0.00%	0.00%	0.00%
36	99.9	Included	17.7	16.1	91.1	70109	0.00	0.00	$3.22\cdot10^{-1}$	$3.14\cdot10^{-4}$	$2.00\cdot10^{-4}$	0.00	74.7%	0.04%	0.02%	0.00%	0.00%	0.00%
37	97.7	Included	17.3	15.8	89.0	64735	0.00	0.00	$3.13\cdot10^{-1}$	$4.79\cdot10^{-4}$	$1.85\cdot10^{-4}$	0.00	72.7%	0.06%	0.02%	0.00%	0.00%	0.00%
38	95.6	Included	16.9	15.4	86.9	60582	0.00	0.00	$3.20\cdot10^{-1}$	$4.29\cdot10^{-4}$	$1.98\cdot10^{-4}$	0.00	74.2%	0.05%	0.02%	0.00%	0.00%	0.00%
39	93.5	Included	16.6	15.0	84.7	58556	0.00	0.00	$3.19\cdot10^{-1}$	$5.64\cdot10^{-4}$	$2.56\cdot10^{-4}$	0.00	73.9%	0.07%	0.03%	0.00%	0.00%	0.00%
40	91.4	Included	16.2	14.6	82.6	63323	0.00	0.00	$3.11\cdot10^{-1}$	$4.11\cdot10^{-4}$	$1.74\cdot10^{-4}$	0.00	72.3%	0.05%	0.02%	0.00%	0.00%	0.00%
41	89.3	Included	15.8	14.3	80.5	57767	0.00	0.00	$3.11\cdot10^{-1}$	$6.06\cdot10^{-4}$	$2.42\cdot10^{-4}$	0.00	72.2%	0.07%	0.03%	0.00%	0.00%	0.00%
42	87.1	Included	15.4	13.9	78.4	77608	$3.61\cdot10^{-4}$	0.00	$3.07\cdot10^{-1}$	$5.80\cdot10^{-4}$	$2.71\cdot10^{-4}$	$7.64\cdot10^{-4}$	71.3%	0.07%	0.03%	0.10%	0.00%	0.09%
43	85.0	Included	15.1	13.5	76.3	56972	$1.76\cdot10^{-4}$	0.00	$3.09\cdot10^{-1}$	$5.44\cdot10^{-4}$	$1.93\cdot10^{-4}$	$1.24\cdot10^{-3}$	71.7%	0.06%	0.02%	0.17%	0.00%	0.04%
44	82.9	Included	14.7	13.1	74.2	56079	$1.96\cdot10^{-4}$	0.00	$3.07\cdot10^{-1}$	$6.06\cdot10^{-4}$	$2.32\cdot10^{-4}$	$7.93\cdot10^{-4}$	71.1%	0.07%	0.03%	0.11%	0.00%	0.05%
45	80.8	Included	14.3	12.8	72.0	64803	$2.78\cdot10^{-4}$	0.00	$3.08\cdot10^{-1}$	$6.94\cdot10^{-4}$	$1.70\cdot10^{-4}$	$6.29\cdot10^{-4}$	71.5%	0.08%	0.02%	0.09%	0.00%	0.07%
46	78.7	Included	13.9	12.4	69.9	67277	$2.97\cdot10^{-4}$	0.00	$3.11\cdot10^{-1}$	$6.54\cdot10^{-4}$	$2.82\cdot10^{-4}$	$1.27\cdot10^{-4}$	72.1%	0.08%	0.03%	0.17%	0.00%	0.07%
47	76.6	Included	13.6	12.0	67.8	81147	0.00	0.00	$3.10\cdot10^{-1}$	$6.28\cdot10^{-4}$	$2.46\cdot10^{-4}$	$8.67\cdot10^{-4}$	72.0%	0.07%	0.03%	0.12%	0.00%	0.00%
48	74.4	Included	13.2	11.6	65.7	58959	$4.41\cdot10^{-4}$	0.00	$3.15\cdot10^{-1}$	$6.95\cdot10^{-4}$	$1.70\cdot10^{-4}$	$1.32\cdot10^{-3}$	73.2%	0.08%	0.02%	0.18%	0.00%	0.10%
49	72.3	Included	12.8	11.3	63.6	58283	$3.26\cdot10^{-4}$	0.00	$3.08\cdot10^{-1}$	$6.18\cdot10^{-4}$	$2.57\cdot10^{-4}$	$1.14\cdot10^{-3}$	71.6%	0.07%	0.03%	0.16%	0.00%	0.08%
50	70.2	Included	12.4	10.9	61.4	62280	0.00	0.00	$3.05\cdot10^{-1}$	$7.23\cdot10^{-4}$	$2.41\cdot10^{-4}$	$1.67\cdot10^{-3}$	70.9%	0.08%	0.03%	0.23%	0.00%	0.00%
51	68.1	Included	12.1	10.5	59.3	80477	0.00	0.00	$3.10\cdot10^{-1}$	$8.08\cdot10^{-4}$	$1.99\cdot10^{-4}$	$1.61\cdot10^{-3}$	71.9%	0.09%	0.02%	0.22%	0.00%	0.00%

52	66.0	Included	11.7	10.1	57.2	60512	0.00	0.00	$3.05\cdot10^{-1}$	$7.60\cdot10^{-4}$	$2.31\cdot10^{-4}$	$2.02\cdot10^{-3}$	70.8%	0.09%	0.03%	0.28%	0.00%	0.00%
53	63.8	Included	11.3	9.8	55.1	57071	0.00	0.00	$3.11\cdot10^{-1}$	$8.94\cdot10^{-4}$	$2.98\cdot10^{-4}$	$2.01\cdot10^{-3}$	72.2%	0.10%	0.03%	0.27%	0.00%	0.00%
54	61.7	Included	10.9	9.4	53.0	62226	$1.30\cdot10^{-3}$	0.00	$3.10\cdot10^{-1}$	$9.64\cdot10^{-4}$	$2.57\cdot10^{-4}$	$2.32\cdot10^{-3}$	72.0%	0.11%	0.03%	0.32%	0.00%	0.31%
55	59.6	Included	10.6	9.0	50.8	60427	$1.62\cdot10^{-3}$	0.00	$3.01\cdot10^{-1}$	$8.27\cdot10^{-4}$	$3.48\cdot10^{-4}$	$3.43\cdot10^{-3}$	69.9%	0.10%	0.04%	0.47%	0.00%	0.38%
56	57.5	Included	10.2	8.6	48.7	64017	$1.95\cdot10^{-3}$	0.00	$3.01\cdot10^{-1}$	$8.44\cdot10^{-4}$	$3.44\cdot10^{-4}$	$4.11\cdot10^{-3}$	69.9%	0.10%	0.04%	0.56%	0.00%	0.46%
57	55.4	Included	9.8	8.3	46.6	71509	$2.62\cdot10^{-3}$	0.00	$3.17\cdot10^{-1}$	$9.37\cdot10^{-4}$	$3.22\cdot10^{-4}$	$4.51\cdot10^{-3}$	73.7%	0.11%	0.04%	0.61%	0.00%	0.62%
58	53.2	Included	9.4	7.9	44.5	57704	$2.93\cdot10^{-3}$	0.00	$3.03\cdot10^{-1}$	$1.02\cdot10^{-3}$	$3.29\cdot10^{-4}$	$6.48\cdot10^{-3}$	70.3%	0.12%	0.04%	0.88%	0.00%	0.69%
59	51.1	Included	9.1	7.5	42.4	70682	$4.06\cdot10^{-3}$	0.00	$3.11\cdot10^{-1}$	$9.76\cdot10^{-4}$	$3.96\cdot10^{-4}$	$5.14\cdot10^{-3}$	72.2%	0.11%	0.05%	0.70%	0.00%	0.96%
60	49.0	Included	8.7	7.1	40.3	59161	$4.60\cdot10^{-3}$	0.00	$2.94\cdot10^{-1}$	$1.01\cdot10^{-3}$	$4.39\cdot10^{-4}$	$8.39\cdot10^{-3}$	68.2%	0.12%	0.05%	1.14%	0.00%	1.08%
61	46.9	Included	8.3	6.8	38.1	59526	$5.86\cdot10^{-3}$	0.00	$3.00\cdot10^{-1}$	$9.91\cdot10^{-4}$	$4.20\cdot10^{-4}$	$8.15\cdot10^{-3}$	69.7%	0.12%	0.05%	1.11%	0.00%	1.38%
62	44.8	Included	7.9	6.4	36.0	65005	$7.60\cdot10^{-3}$	0.00	$3.00\cdot10^{-1}$	$1.06\cdot10^{-3}$	$5.08\cdot10^{-4}$	$9.00\cdot10^{-3}$	69.7%	0.12%	0.06%	1.23%	0.00%	1.79%
63	42.7	Included	7.6	6.0	33.9	62437	$9.21\cdot10^{-3}$	0.00	$2.89\cdot10^{-1}$	$1.11\cdot10^{-3}$	$4.48\cdot10^{-4}$	$1.10\cdot10^{-2}$	67.2%	0.13%	0.05%	1.50%	0.00%	2.17%
64	40.5	Included	7.2	5.6	31.8	61573	$1.25\cdot10^{-2}$	0.00	$2.92\cdot10^{-1}$	$1.38\cdot10^{-3}$	$6.17\cdot10^{-4}$	$1.19\cdot10^{-2}$	67.7%	0.16%	0.07%	1.62%	0.00%	2.94%
65	38.4	Included	6.8	5.3	29.7	51401	$1.44\cdot10^{-2}$	0.00	$2.79\cdot10^{-1}$	$1.23\cdot10^{-3}$	$4.47\cdot10^{-4}$	$1.55\cdot10^{-2}$	64.9%	0.14%	0.05%	2.11%	0.00%	3.39%
66	36.3	Included	6.4	4.9	27.5	86531	$2.08\cdot10^{-2}$	0.00	$2.86\cdot10^{-1}$	$1.20\cdot10^{-3}$	$5.08\cdot10^{-4}$	$9.50\cdot10^{-3}$	66.3%	0.14%	0.06%	1.29%	0.00%	4.89%
67	34.2	Included	6.1	4.5	25.4	70681	$2.20\cdot10^{-2}$	0.00	$2.73\cdot10^{-1}$	$1.22\cdot10^{-3}$	$5.09\cdot10^{-4}$	$1.99\cdot10^{-2}$	63.3%	0.14%	0.06%	2.71%	0.00%	5.18%
68	32.1	Included	5.7	4.1	23.3	56958	$3.46\cdot10^{-2}$	0.00	$2.62\cdot10^{-1}$	$1.32\cdot10^{-3}$	$6.14\cdot10^{-4}$	$2.23\cdot10^{-2}$	60.8%	0.15%	0.07%	3.04%	0.00%	8.15%
69	29.9	Included	5.3	3.8	21.2	58426	$5.43\cdot10^{-2}$	0.00	$2.55\cdot10^{-1}$	$1.39\cdot10^{-3}$	$5.82\cdot10^{-4}$	$1.81\cdot10^{-2}$	59.2%	0.16%	0.07%	2.46%	0.00%	12.8%
70	27.8	Included	4.9	3.4	19.1	68658	$7.39\cdot10^{-2}$	0.00	$2.44\cdot10^{-1}$	$1.46\cdot10^{-3}$	$7.87\cdot10^{-4}$	$1.65\cdot10^{-2}$	56.5%	0.17%	0.09%	2.24%	0.00%	17.4%
71	25.7	Included	4.6	3.0	16.9	69135	$9.40\cdot10^{-2}$	0.00	$2.39\cdot10^{-1}$	$1.35\cdot10^{-3}$	$7.38\cdot10^{-4}$	$1.96\cdot10^{-2}$	55.4%	0.16%	0.09%	2.66%	0.00%	22.2%
72	23.6	Included	4.2	2.6	14.8	62923	$1.07\cdot10^{-1}$	0.00	$2.33\cdot10^{-1}$	$1.35\cdot10^{-3}$	$7.63\cdot10^{-4}$	$2.21\cdot10^{-2}$	54.0%	0.16%	0.09%	3.01%	0.00%	25.2%
73	21.5	Included	3.8	2.3	12.7	58949	$1.28\cdot10^{-1}$	0.00	$2.21\cdot10^{-1}$	$1.46\cdot10^{-3}$	$7.29\cdot10^{-4}$	$2.06\cdot10^{-2}$	51.4%	0.17%	0.08%	2.81%	0.00%	30.2%
74	19.4	Included	3.4	1.9	10.6	61667	$1.52\cdot10^{-1}$	0.00	$2.10\cdot10^{-1}$	$1.49\cdot10^{-3}$	$7.30\cdot10^{-4}$	$1.84\cdot10^{-2}$	48.7%	0.17%	0.08%	2.51%	0.00%	35.9%
75	17.2	Included	3.1	1.5	8.5	62563	$1.77\cdot10^{-1}$	0.00	$1.94\cdot10^{-1}$	$1.41\cdot10^{-3}$	$6.23\cdot10^{-4}$	$1.76\cdot10^{-2}$	45.1%	0.16%	0.07%	2.40%	0.00%	41.8%
76	15.1	Included	2.7	1.1	6.4	63191	$2.06\cdot10^{-1}$	0.00	$1.77\cdot10^{-1}$	$1.41\cdot10^{-3}$	$7.44\cdot10^{-4}$	$1.71\cdot10^{-2}$	41.2%	0.16%	0.09%	2.33%	0.00%	48.6%
77	13.0	Included	2.3	0.8	4.2	64532	$2.40\cdot10^{-1}$	0.00	$1.60\cdot10^{-1}$	$1.32\cdot10^{-3}$	$7.59\cdot10^{-4}$	$1.58\cdot10^{-2}$	37.2%	0.15%	0.09%	2.15%	0.00%	56.6%
78	10.9	Included	1.9	0.4	2.1	71089	$2.74\cdot10^{-1}$	0.00	$1.38\cdot10^{-1}$	$1.27\cdot10^{-3}$	$6.75\cdot10^{-4}$	$1.32\cdot10^{-2}$	32.0%	0.15%	0.08%	1.80%	0.00%	64.6%
79	8.8	Included	1.6	0.0	0.0	71984	$3.16\cdot10^{-1}$	0.00	$1.18\cdot10^{-1}$	$1.19\cdot10^{-3}$	$5.83\cdot10^{-4}$	$1.28\cdot10^{-2}$	27.5%	0.14%	0.07%	1.75%	0.00%	74.6%
80	6.6	Excluded	1.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
81	4.5	Excluded	0.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

82	2.4	Excluded	0.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
83	0.3	Excluded	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

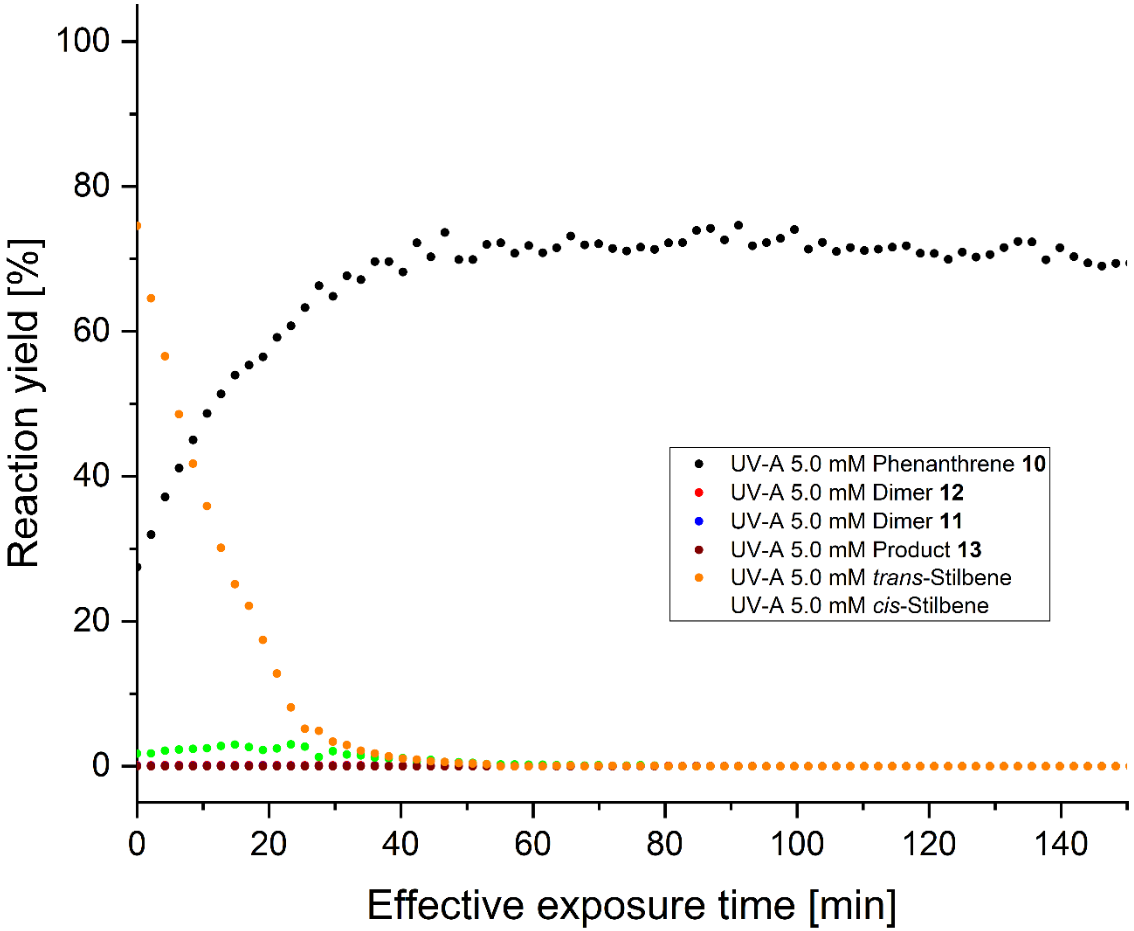


Figure S 21. Results of Switch-Off optimisation of Mallory photoreaction using UV-C light and 50.0 mM stilbene concentration. Top: Reaction components GC areas, conversion, and yield plotted against uncorrected residence time. Bottom: Reaction components GC areas, conversion, and yield plotted against exposure time, corrected for light inhomogeneity.

2. 4. 3. Validation of Switch-Off results obtained in Mallory photocyclisation of *cis*-stilbene

Two validation experiments were performed, first utilizing UV-A light source and 5.0 mM concentration of *cis*-stilbene and second utilizing UV-A light source and 50.0 mM *cis*-stilbene concentration with optimum effective exposure times of 24 minutes and 50 minutes, respectively, obtained from the switch-off optimisation experiments. Additionally to validation, second experiment utilising 50.0 mM *cis*-stilbene concentration was performed in order to isolate and fully characterise the reaction products **10**, **11**, **12**, and **13**.

2. 4. 3. 1. Irradiation over 24 minutes of effective exposure time under UV-A light and 5.0 mM *cis*-stilbene concentration

Cis-stilbene (50.6 mg, 50.0 µL, 0.28 mmol, 1.00 eq.) and iodine (7.1 mg, 0.03 mmol, 0.10 eq.) were dissolved in cyclohexane (50.0 mL, 988.1 vol.) and the solution was saturated with oxygen. The mixture was then injected into photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA) equipped with UV-A lamp (Philips PLL 36W). Irradiation over 24 minutes of effective exposure time was set (corresponding to 1.06 mL/min). After injection of 50.0 mL, reaction mixture was eluted from photoreactor using pure cyclohexane, obtained crude mixture was then washed with a saturated solution of sodium thiosulfate (20 mL), water (20 mL) and brine (2x20 mL). The organic layer was then dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure to afford the desired phenanthrene (48.0 mg, 0.27 mmol, 96.4% yield) as a white solid. NMR data was consistent with literature.[2]

2. 4. 3. 2. Irradiation over 50 minutes of effective exposure time under UV-A light and 50.0 mM *cis*-stilbene concentration

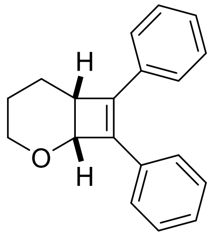
Cis-stilbene (721.0 mg, 4.00 mmol, 1.00 eq., 50.0 mM solution) and iodine (101.6 mg, 0.40 mmol, 0.10 eq., 5.0 mM solution) were dissolved in cyclohexane (80.0 mL, 111.0 vol.) and then the mixture was injected into photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA) equipped with UV-A lamp (Philips PLL 36W). Irradiation over 50 minutes of effective exposure time was set (corresponding to 0.606 mL/min flow rate). After injection of 80.0 mL, reaction mixture was eluted from photoreactor using pure cyclohexane, reaction mixture was then collected, solvent was removed, and obtained residue was initially purified using column chromatography (SiO_2; *n*-hexane:AcOEt 9:1) affording fractions containing recovered *cis*-stilbene (371.9 mg, 2.06 mmol, recovery of 51.6% of starting material), phenanthrene **10** (71.2 mg, 0.40 mmol, 10.0% yield, NMR data was consistent with literature[2]) and combined fraction containing 1,2,3,4-tetraphenylcyclobutane isomers **11** and **12** and 1,2-diphenyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene **13** (total mass of 263.6 mg). The latter was then repurified using preparative HPLC system (Cosmosil Buckyprep column, *n*-hexane:AcOEt 9:1) and afforded fractions containing (1α,2α,3β,4β)-1,2,3,4-tetraphenylcyclobutane **11** and (1α,2β,3α,4β)-1,2,3,4-tetraphenylcyclobutane **12** as white solids (total mass of 121.9 mg, 0.34 mmol, 8.5% yield), and fraction containing pure 1,2-diphenyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene **13** as yellow solid (124.7 mg, 0.35 mmol, 8.7% yield).

Full characterisation data of the compounds **10**, **11**, **12**, and **13** can be found in section 3. 3. Procedure for synthesis of compounds 10, 11, 12, and 13: of this document.

3. Syntheses and characterization data

3. 1. Procedures for synthesis of compounds 1, 2, 3, and 4:

3. 1. 1. *cis*-7,8-Diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (1):

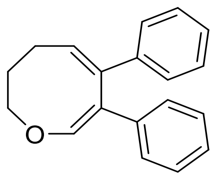


$C_{19}H_{18}O$
MW: 262.352
CAS 15895-76-8

Diphenylacetylene (1.51 g, 8.47 mmol, 0.056 M solution) was dissolved in 3,4-dihydro-2*H*-pyran (150.0 mL, 100.0 vol.) and the mixture was injected into photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA) equipped with UV-C lamp (DuraBulb 36W UV-C 253.7 nm). Irradiation over 43 minutes of effective exposure time was set (corresponding to 0.670 mL/min). After injection of 145.0 mL, reaction mixture was eluted from photoreactor using pure 3,4-dihydro-2*H*-pyran, reaction mixture was then collected, solvent was removed, and obtained material was initially purified by flash chromatography (SiO_2; *n*-hexane:AcOEt 9:1), and then by automated column chromatography system (Biotage Selekt, Biotage HP-Sphere 25 micron). Fractions containing product were combined, solvent was removed, remaining residue was dried *in vacuo,* and 7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene was obtained as slightly yellow, dense oil, which was further purified by vacuum distillation (230 °C at 4.0 mbar) (1.521 g, 5.80 mmol, 70.8% yield). Upon prolonged time the product crystallised to give slightly yellow solid. NMR data was consistent with literature.[1]

R_f = 0.49 (*n*-hexane:AcOEt 9:1). **GC R_t =** 7.80 min. **Mp.** 60.5 – 61.8 °C. Lit. 56 – 58 °C.[3] **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 7.65 (m, 2H), 7.56 (m, 2H), 7.39 – 7.27 (m, 6H), 4.85 (d, J=4.5 Hz, 1H), 3.93 (ddd, J=11.2, 7.8, 5.9 Hz, 1H), 3.77 (ddd, J=11.2, 8.3, 6.2 Hz, 1H), 3.33 (ddd, J=6.1, 5.2, 4.5 Hz, 1H), 2.19 (dddd, J=13.5, 9.0, 6.1, 5.3 Hz, 1H), 2.00 (dddd, J=13.6, 7.3, 5.2, 5.2 Hz, 1H), 1.78 (m, 1H), 1.66 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =** 143.8 (C), 140.7 (C), 135.0 (C), 134.7 (C), 128.6 (2xCH), 128.5 (CH), 128.0 (CH), 127.0 (CH), 126.7 (CH), 70.7 (CH), 62.0 (CH_2), 40.5 (CH), 23.1 (CH_2), 20.4 (CH_2). **UV-Vis (MeCN) λ_{max} (ε):** 229 nm (16110 ± 80 $M^{-1}cm^{-1}$), 298 nm (12367 ± 13 $M^{-1}cm^{-1}$). **LRMS (EI) m/z =** 262.3 ($M^{\cdot+}$), 247.2, 233.2, 215.2, 203.2, 191.2, 178.2, 152.2, 128.2, 102.1, 91.1, 77.1, 55.2. **LRMS (ESI+) m/z =** 263.3 (M + H^+).

3. 1. 2. 3,4-Dihydro-6,7-diphenyl-2*H*-oxocin (2):

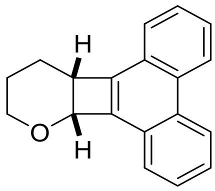


$C_{19}H_{18}O$
MW: 262.352
CAS 69321-82-0

7,8-Diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (208.1 mg, 0.79 mmol, 3.81 mM solution) was dissolved in anhydrous acetonitrile (208.0 mL, 1000.0 vol.) and sonicated under high nitrogen flow for 15 minutes. The solution was then transferred to the jacketed photoreactor equipped with UV-B lamp (36 W, Philips PL-L 36W/09/4P) and set to 25 °C. Reaction mixture was then vigorously stirred for 30 minutes while passing high flow of nitrogen through the solution. After 30 minutes, the UV-B lamp was turned on and reaction mixture was irradiated for 20 hours. Solvent was then removed, obtained residue was preadsorbed onto silica and purified using automated chromatography system (Biotage Selekt, Biotage HP-Sphere 25 micron). Fractions containing product were combined, solvent was removed, remaining residue was dried *in vacuo,* and 3,4-dihydro-6,7-diphenyl-2*H*-oxocin was obtained as a white solid (8.6 mg, 0.03 mmol, 3.8% yield). NMR data was consistent with literature.[1]

R_f = 0.52 (*n*-hexane:AcOEt 9:1). **GC R_t =** 7.59 min. **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 7.31 (m, 2H), 7.19 – 6.99 (m, 8H), 6.80 (s, 1H), 6.12 (t, J= 8.2 Hz, 1H), 4.62 (br s, 1H), 3.84 (br s, 1H), 2.70 (br s, 1H), 2.57 (br s, 1H), 1.93 (br s, 1H), 1.44 (br s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =** 147.7 (CH), 141.2 (C), 140.4 (C), 139.9 (C), 129.4 (CH), 128.2 (C), 128.2 (CH), 128.2 (CH), 127.5 (CH), 127.3 (CH), 126.7 (CH), 126.1 (CH), 66.6 (CH_2), 26.1 (CH_2), 23.8 (CH_2). **LRMS (EI) m/z =** 262.3 ($M^{\cdot+}$), 247.2, 133.2, 215.2, 203.2, 191.2, 178.1, 165.1, 152.1, 141.1, 128.1, 115.1, 105.1, 91.1, 77.1, 63.1, 51.1. **HRMS (EI) m/z =** 262.1351 ($M^{\cdot+}$), 247.1120, 233.0961, 215.0855, 203.0853, 191.0853, 178.0777, 165.0699, 152.0619, 128.0620, 115.0543, 101.0386, 91.0542, 77.0386; calculated for: $C_{19}H_{18}O$ 262.1358, $C_{18}H_{15}O$ 247.1123, $C_{17}H_{13}O$ 233.0966, $C_{17}H_{11}$ 215.0861, $C_{16}H_{11}$ 203.0861, $C_{15}H_{11}$ 191.0861, $C_{14}H_{10}$ 178.0783, $C_{13}H_9$ 165.0704, $C_{12}H_8$ 152.0626, $C_{10}H_8$ 128.0626, C_9H_7 115.0548, C_8H_5 101.0391, C_7H_7 91.0548, C_6H_5 77.0391.

3. 1. 3. *cis*-8*c*,11,12,12*a*-Tetrahydro-10*H*-phenanthro[9',10':3,4]cyclobuta[1,2-*b*]pyran (3):

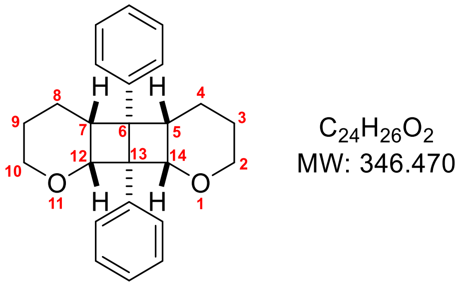


$C_{19}H_{16}O$
MW: 260.336
CAS 69321-81-9

7,8-Diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (101.1 mg, 0.39 mmol, 1.90 mM solution) was dissolved in cyclohexane (202.0 mL, 2000.0 vol.) through which air was constantly bubbled. Mixture was poured into jacketed photoreactor set at 30 °C, equipped with UV-B light source (36W, Philips PL-L 36W/09/4P lamp) and was vigorously stirred for 16 hours while irradiated. Solvent was then removed from reaction mixture, and obtained residue was preadsorbed onto silica, and purified using automated chromatography system (Biotage Selekt, Biotage HP-Sphere 25 micron). 8c,11,12,12a-Tetrahydro-10*H*-phenanthro[9',10':3,4]cyclobuta[1,2-*b*]pyran was obtained as a white solid (26.2 mg, 0.10 mmol, 25.6% yield). NMR data was consisted with literature.[1]

R_f = 0.47 (*n*-hexane:AcOEt 9:1). **GC R_t =** 8.76 min. **Mp.** = 153.7 – 154.0 °C. Lit. 161 °C.[1] **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 8.80 – 8.71 (m, 2H), 7.97 (m, 1H), 7.81 (ddd, J=7.5, 1.7, 0.6 Hz, 1H) 7.70 – 7.59 (m, 4H), 5.45 (d, J=4.3 Hz, 1H), 4.04 (dt, J=6.0, 4.5 Hz, 1H), 3.91 – 3.78 (m, 2H), 2.37 (dddd, J=13.7, 10.2, 6.0, 5.3 Hz, 1H), 2.22 (dddd, J=13.7, 6.2, 5.3, 4.6 Hz, 1H), 1.64 (m, 1H), 1.40 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =** 143.3 (C), 141.1 (C), 132.1 (C), 130.8 (C), 129.0 (C), 128.6 (C), 127.3 (CH), 126.9 (CH), 126.8 (CH), 126.2 (CH), 124.1 (CH), 123.9 (CH), 123.7 (CH), 123.6 (CH), 72.9 (CH), 62.1 (CH_2), 42.4 (CH), 23.2 (CH_2), 20.0 (CH_2). **LRMS (EI) m/z =** 260.2 ($M^{\cdot+}$), 231.2, 215.2, 203.2, 189.2, 176.1, 165.1, 115.6, 101.3, 94.7, 75.1. **HRMS (EI) m/z =** 260.1194 ($M^{\cdot+}$), 231.0806, 215.0857, 203.0852, 189.0700, 165.0699, 150.0463, 115.5398, 101.0389; calculated for $C_{19}H_{16}O$ 260.1201, $C_{17}H_{11}O$ 231.0810, $C_{17}H_{11}$ 215.0816, $C_{16}H_{11}$ 203.0861, $C_{15}H_9$ 189.0704, $C_{13}H_9$ 165.0704, $C_{12}H_6$ 150.0470, C_8H_5 101.0391.

3. 1. 4. (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^5,14^,0^7,12^]tetradecane (4):



7,8-Diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (0.131 g, 0.50 mmol, 55.5 mM solution) was dissolved in 3,4-dihydro-2*H*-pyran (9.0 mL, 68.7 vol.) and the mixture was injected into photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA) equipped with UV-B lamp (Philips PL-L 36W/01/4P). Effective exposure time of 288 minutes was set (corresponding to 0.100 mL/min total flow rate). After injection, reaction mixture was eluted from photoreactor using pure 3,4-dihydro-2*H*-pyran, reaction mixture was then collected, solvent was removed, and crude was purified by flash chromatography (SiO_2; toluene:AcOEt 9:1). Fractions containing product were combined, solvent was removed, remaining residue was dried *in vacuo,* and desired product was obtained as colourless oil (0.037 g, 0.11 mmol, 21.4% yield).

R_f = 0.43 (*n*-hexane:AcOEt 9:1). **GC R_t =** 10.49 min. **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 7.31 – 7.15 (m, 10H), 4.55 (d, J=5.4 Hz, 2H), 3.48 (ddd, J=11.1 , 5.7, 5.7 Hz, 2H), 3.26 (ddd, J=11.1, 7.6, 4.8 Hz, 2H), 2.75 (ddd, J=7.5, 7.5, 5.3 Hz, 2H), 1.69 (m, 2H), 1.43 – 1.15 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =** 138.8 (C), 136.6 (C), 129.7 (CH), 127.4 (CH), 127.2 (CH), 126.0 (CH), 125.9 (CH), 75.1 (CH), 64.1 (C), 63.3 (CH_2), 59.4 (C), 42.8 (CH), 21.5 (CH_2), 20.5 (CH_2). **^{1}H NMR (500 MHz, 373 K, DMSO-d_6) δ (ppm) =** 7.28 (m, 2H), 7.22 – 7.17 (m, 5H), 7.16 – 7.10 (m, 3H), 4.50 (d, J=5.4 Hz, 2H), 3.40 (ddd, J=11.2, 6.6, 5.8 Hz, 2H), 3.24 (ddd J=11.1, 7.4, 5.0 Hz, 2H), 2.80 (ddd, J=7.9, 7.8, 5.5 Hz, 2H), 1.66 (m, 2H), 1.39 – 1.30 (m, 2H), 1.26 – 1.16 (m, 4H). **^{13}C NMR (126 MHz, 353 K, DMSO-d_6) δ (ppm) =** 138.2, 136.3, 129.2, 126.5, 126.2, 125.2, 124.7, 74.0, 63.1, 61.7, 58.6, 41.8, 20.4, 19.3. **FT-ATR-IR IR ν (cm^{-1}) =** 3059, 3025, 2949, 2920, 2845, 1602, 1495, 1445, 1178, 1129, 1088, 1062, 1033, 951, 911, 761, 734, 702, 648, 577. **HRMS (ESI+) m/z:** 369.1821 [M + Na^+], 715.3730 [2M + Na^+], calculated for $C_{24}H_{26}O_2Na^+$ 369.1825, for $C_{48}H_{52}O_4Na^+$ 715.3758. **HRMS (EI) m/z =** 346.1933 ($M^{\cdot+}$), 301.1584, 287.1437, 262.1347, 211.1114, 186.1041, 169.1012, 141.0703, 128.0623, 115.0546, 103.0547, 91.0544, 77.0388, 41.0388; calculated for $C_{24}H_{26}O_2$ 346.1933, $C_{22}H_{21}O$ 301.1592, $C_{21}H_{19}O$ 287.1436, $C_{19}H_{18}O$ 262.1358, $C_{15}H_{15}O$ 211.1123, $C_{13}H_{14}O$ 186.1045, $C_{13}H_{13}$ 169.1017, $C_{11}H_9$ 141.0704, $C_{10}H_8$ 128.0626, C_9H_7 115.0548, C_8H_7 103.0548, C_7H_7 91.0548, C_6H_5 77.0388, C_3H_5 41.0391.

7,8-Diphenyl-2-oxabicyclo[4.2.0]oct-7-ene **1** has two distinctive sites from which the reaction can occur, namely *endo* and *exo* faces*,* which are marked in the 3D model of molecule when looking at the plane of the cyclobutene ring (Figure S 22. 3D model of the 7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene **1** showing endo and exo faces of the molecule.).

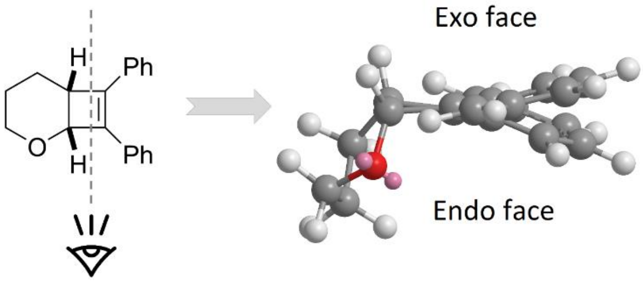


*Figure S 22. 3D model of the 7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene **1** showing endo and exo faces of the molecule.*

The 3,4-dihydro-2*H*-pyran can react with the **1** by *endo* or *exo* addition and depending on the geometry of pyran addition, it can afford head-to-head (HH) or head-to-tail (HT) products.

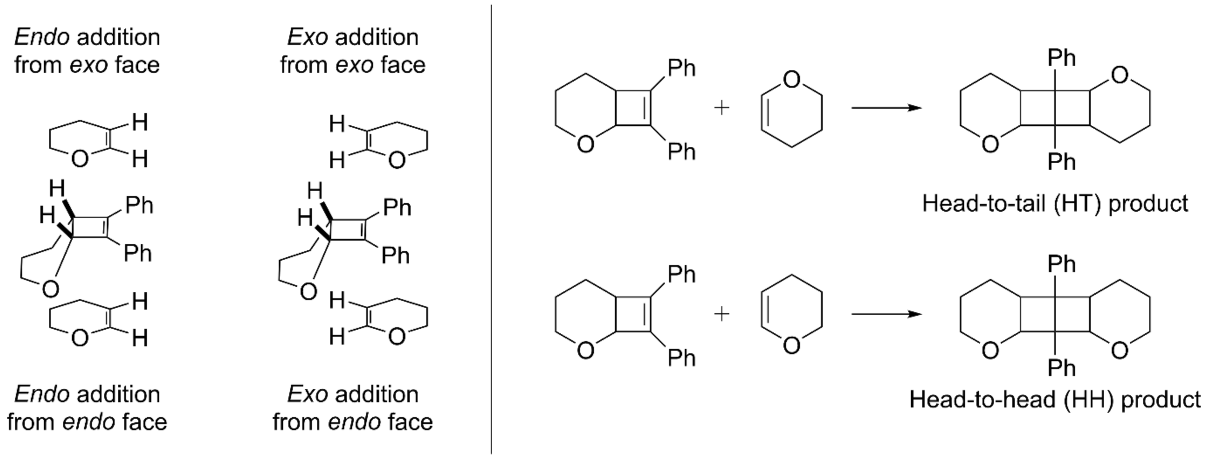
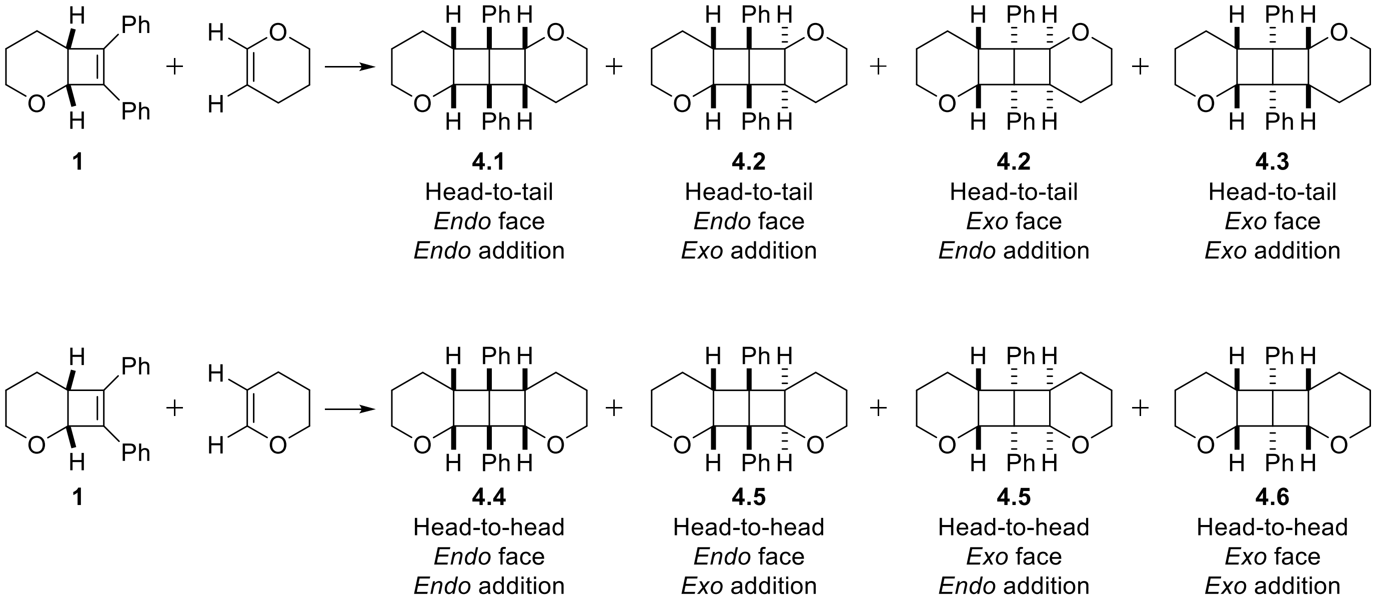


*Figure S 23. Left. Examples of endo and exo additions of 3,4-dihydro-2H-pyran, form both endo and exo faces of **1**. Right: Reactions affording head-to-head and head-to-tail products.*

Theoretically 8 different products can be obtained in the above-mentioned [2+2] photoreaction, however *exo* addition of 3,4-dihydro-2*H*-pyran at *endo* face of **1** and respective *endo* addition at *exo* face afford the same isomers, marked as **4.2** for head-to-tail and **4.5** for head-to-head additions, thus leaving only 6 possible isomers of **4** that can be formed in this particular [2+2] photocycloaddition.



*Scheme S 3. Theoretically plausible structures of the [2+2] photocycloaddition products between 7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene **1** and 3,4-dihydro-2H-pyran.*

In the ^{13}C NMR spectra of structures **4.1** and **4.3** only 4 aromatic signals should be visible, due to the C2 axis of symmetry, however experimental ^{13}C NMR spectrum shows 7 aromatic signals (Figure S 42. ^{13}C (top) and DEPT-135 (bottom) NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$.) thus **4.1** and **4.3** were dismissed as potential structures of the bis-addition product.

In the ^{13}C NMR spectra of structures **4.2** and **4.5** signals originating from cyclobutane rings should be distinguishable, due to no symmetry elements (apart from identity element), so 6 signals would be expected, however only 4 are observed (Figure S 42. ^{13}C (top) and DEPT-135 (bottom) NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$.), thus structures **4.2** and **4.5** were dismissed as potential structures of the bis-addition product.

Structure **4.4** can be formed in an *endo* addition of 3,4-dihydro-2*H*-pyran to the *endo* face of the **1** (Figure S 24. Endo [2+2] photocycloaddition of **1** and 3,4-dihydro-2H-pyran at the endo face of **1** affording **4.4**.), whereas structure **4.6** can be formed in an *exo* addition of the 3,4-dihydro-2*H*-pyran to the *exo* face of the **1** (Figure S 25. Exo [2+2] photocycloaddition of **1** and 3,4-dihydro-2H-pyran at the exo face of **1** affording **4.6**.), thus making the formation of **4.6** much more favourable.

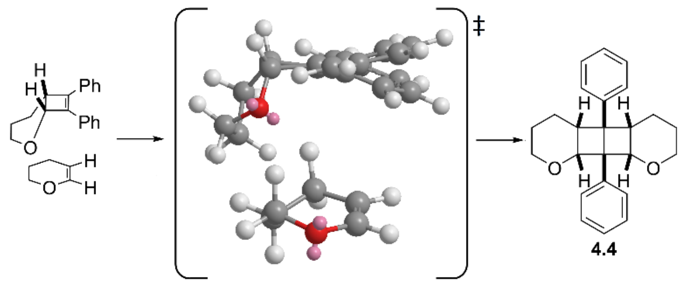


*Figure S 24. Endo [2+2] photocycloaddition of **1** and 3,4-dihydro-2H-pyran at the endo face of **1** affording **4.4**.*

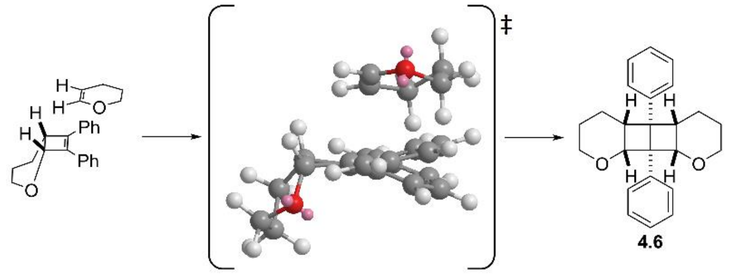


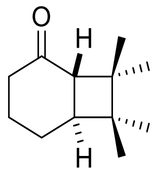
*Figure S 25. Exo [2+2] photocycloaddition of **1** and 3,4-dihydro-2H-pyran at the exo face of **1** affording **4.6**.*

Based on all evidence, the structure **4.6** was determined to be the most probable structure of the bis-addition product obtained in the [2+2] photocycloaddition of 7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene **1** with 3,4-dihydro-2*H*-pyran.

3. 2. Procedure for synthesis of compounds 5, 6, 7, 8, and 9:

To a 250.0 mL round-bottom flask flushed with nitrogen, cyclohex-2-enone (536.5 mg, 532.4 µL, 5.58 mmol, 1.0 eq., 25.4 mM solution), tetramethylethylene (9.2451 g, 13.0673 mL, 109.85 mmol, 19.7 eq., 499.3 mM solution), dibutyl ether (internal standard, 628.9 mg, 816.8 µL, 4.83 mmol, 0.87 eq., 22.0 mM solution) and anhydrous acetonitrile (205.6 mL, 383.2 vol.) were added and resulting mixture was sonicated under high nitrogen flow for 15 minutes in order to remove oxygen from solution. Effective exposure time of 50 minutes was set (corresponding to 0.569 mL/min total flow rate) and mixture was injected into the photoreactor (31.8 mL internal volume, 1.00 mm ID, 1.60 mm OD, PFA) equipped with UV-A lamp (Philips PLL 36W). Once the 195.0 mL of the mixture was entirely injected, it was eluted using acetonitrile (anhydrous and deoxygenated) out of the flow system. After collection of reaction mixture, solvent was removed, obtained residue was purified by column chromatography (SiO_2; toluene:Et_2O 100:0 to 75:25 then Et_2O, then pure Et_2O) and then by automated column chromatography system (Biotage Selekt, Biotage HP-Sphere 25 micron).

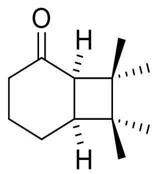
3. 2. 1. *trans*-7,7,8,8-Tetramethylbicyclo[4.2.0]octan-2-one (5):



$C_{12}H_{20}O$
MW: 180.291
CAS 100675-56-7

Obtained as colourless oil (404.1 mg, 2.24 mmol, 45.3% yield). Compound reported in the literature (see [4,5]), but no spectral data was given. **R_f =** 0.52 (toluene:diethyl ether 9:1). **GC R_t =** 3.59 min. **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 2.40 (d, J=13.4 Hz, 1H), 2.18 – 2.11 (m, 2H), 2.11 – 2.00 (m, 2H), 1.77 (m, 1H), 1.65 (dddd, J=12.2, 5.0, 3.6, 2.6 Hz, 1H), 1.46 (dddd, J=12.1, 11.7, 11.6, 4.8 Hz, 1H), 1.17 (s, 3H), 1.00 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =** 209.5 (C), 56.7 (CH), 51.5 (CH), 43.5 (C), 42.8 (C), 41.3 (CH_2), 28.2 (CH_2), 25.1 (CH_2), 23.7 (CH_3), 23.0 (CH_3), 19.4 (CH_3), 18.6 (CH_3). **LRMS (EI) m/z =** 180.2 ($M^{\cdot+}$), 165.2, 137.2, 124.2, 109.2, 98.2, 83.2, 67.1, 55.1, 41.1.

3. 2. 2. *cis*-7,7,8,8-Tetramethylbicyclo[4.2.0]octan-2-one (6):

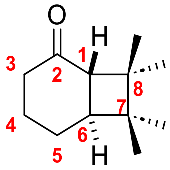


$C_{12}H_{20}O$
MW: 180.291
CAS 100675-57-8

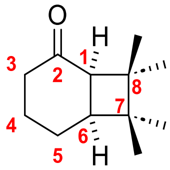
Obtained as colourless oil (153.1 mg, 0.85 mmol, 17.2% yield). Compound reported in the literature (see [4,5]), but no spectral data was given. **R_f =** 0.49 (toluene:diethyl ether 9:1). **GC R_t =** 3.71 min. **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 2.72 (d, J=9.3 Hz, 1H), 2.39 (dddt, J=18.6, 5.1, 3.6, 1.9, 1.9 Hz, 1H), 2.19 (ddd, J=10.9, 9.4, 7.9 Hz, 1H), 2.11 (ddd, J=18.2, 12.4, 5.6 Hz, 1H), 1.95 (m, 1H), 1.84 (m, 1H), 1.65 (m, 1H), 1.54 (m, 1H), 1.10 (s, 3H), 1.05 (s, 3H), 1.03 (s, 3H), 0.92 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)** = 214.4 (C), 50.7 (CH), 44.5 (C), 42.6 (CH), 41.4 (CH_2), 39.8 (C), 27.3 (CH_3), 26.4 (CH_3), 24.1 (CH_2), 23.1 (CH_3), 22.0 (CH_2), 19.2 (CH_3). **LRMS (EI) m/z =** 180.2 ($M^{\cdot+}$), 165.2, 137.2, 124.2, 111.2, 98.2, 83.2, 69.2, 55.2, 41.2.

3. 2. 3. Structural assignment of the *trans-* and *cis*-bicyclo[4.2.0]octan-2-ones 5 and 6:

Stereochemistry of the *trans*-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**5**) and *cis*-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**6**) have been assigned on the basis of the vicinal coupling constants in the ^{1}H NMR spectra between hydrogens **1** and **6** (Scheme S 4.).



trans-7,7,8,8-tetramethyl bicyclo[4.2.0]octan-2-one (**5**)



cis-7,7,8,8-tetramethyl bicyclo[4.2.0]octan-2-one (**6**)

*Scheme S 4. Structures and atom numbering of compounds **5** and **6**.*

Theoretical calculations of the same vicinal coupling constants for both molecules **5** and **6** have been performed using following procedure[6]:

1. Molecule geometry was optimised with B3LYP/6-31G(d) method.[7]
2. NMR single-point calculation was run with B3LYP/6-31G(d,p) basis.
3. Calculated Fermi contact J values was scaled by a factor of 0.9155.[6]

Comparison of the theoretical and experimental values of the H**1**-H**6** coupling constant are in good agreement (Table S 17.).

*Table S 17. Theoretical and experimental values of the coupling constant between hydrogens 1 and 6 in molecules **5** and **6**.*

	trans-7,7,8,8-Tetramethyl bicyclo[4.2.0]octan-2-one (**5**)	*cis*-7,7,8,8-Tetramethyl bicyclo[4.2.0]octan-2-one (**6**)
Theoretical $^3J_{H-H}$ value [Hz]	13.07	9.02
Experimental $^3J_{H-H}$ value [Hz]	13.35	9.32

Additionally, optimised geometries of the molecules **5** and **6** (Table S 18.) were used for determination of the dihedral angle between cyclobutane hydrogens and subsequent calculation of the coupling constant using Karplus-type relationships. A reverse calculation was also performed, in which cyclobutane hydrogens dihedral angles were calculated from experimental value of the coupling constants. All obtained values are in agreement with the structural assignment of molecules **5** and **6** made in this report.

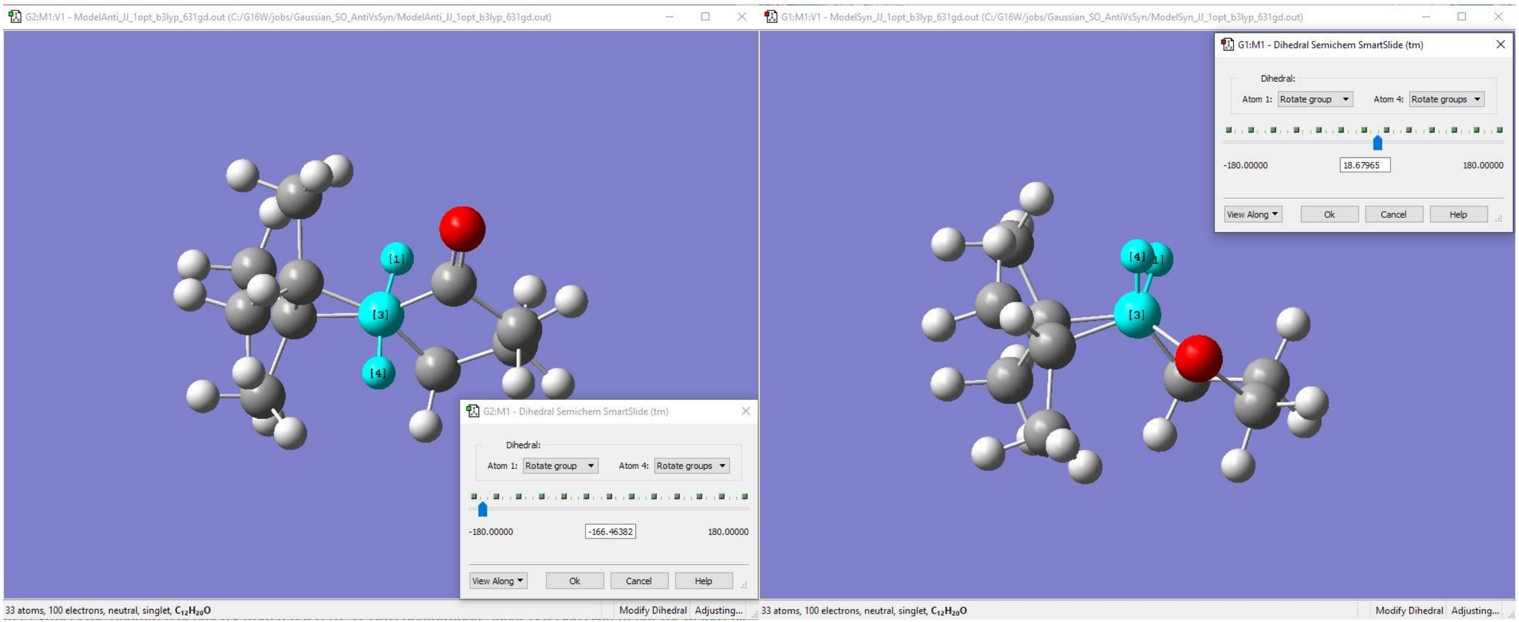


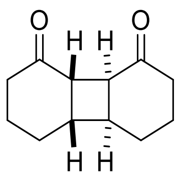
*Figure S 26. Graphical presentation of the optimised (B3LYP/6-31G(d)) molecules **5** (left) and **6** (right) geometries along the C1-C6 axis, with indicated values of the dihedral angle between H1-C1-C6-H6.*[8]

Table S 18. Calculated values of H1-C1-C6-H6 dihedral angles and H1-H6 vicinal coupling constants.

Molecule	Geometry optimisation method	Calculated dihedral angle (H1-C1-C6-H6) [°]	Calculated $^3J_{H-H}$ values[a] [Hz]			Experimental $^3J_{H-H}$ value obtained from ^{1}H NMR [Hz]	Calculated dihedral angle value from experimental $^3J_{H-H}$ coupling constant [°]		
			HLA with β-substituent correction[b,9,10]	HLA[c,9,10]	DAD (cross terms)[c,11,12]		HLA with β-substituent correction[b,9,10]	HLA[c,9,10]	DAD (cross terms)[d,11,12]
trans-7,7,8,8-Tetramethyl bicyclo[4.2.0] octan-2-one (**5**)	B3LYP/ 6-31G(d)	166.5	12.57	11.33	11.47	13.35	n/a[e]	n/a[e]	0.0/360.0 **159.1** 200.9
cis-7,7,8,8-Tetramethyl bicyclo[4.2.0] octan-2-one (**6**)	B3LYP/ 6-31G(d)	18.7	10.16	9.28	8.98	9.32	**24.1** 146.2 213.2 335.3	**17.0** 149.2 208.3 340.3	**15.2** 149.4 208.2 342.0

[a] – vicinal coupling constants and dihedral angles values were calculated using MestReJ software (MestReLab Research©)
[b] – χ[R₁=CHO2]=-0.094, χ[R₂=CC3]=0.172, χ[R₃=CC3]=0.172, χ[R₄=CH2C]=0.324
[c] – λ[R₁=C(O)R]=0.50, λ[R₂=CMe3]=0.48, λ[R₃=CMe3]=0.48, λ[R₄=CH2CH2R]=0.176
[d] – The dihedral angle values were obtained using substituent-uncorrected DAD (cross-terms) equation
[e] – Value of 13.35 Hz is above the upper limit of the predictive equation used

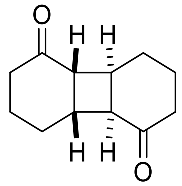
3. 2. 4. *cis-anti-cis*-Tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (7):



$C_{12}H_{16}O_2$
MW: 192.258
CAS 53092-46-9

Obtained as yellow solid (27.9 mg, 0.15 mmol, 2.9% yield). NMR data was consistent with literature.[13,14] **R_f =** 0.10 (toluene:Et_2O 9:1), 0.23 (*n*-hexane:AcOEt 8:2). **GC R_t =** 5.63 min. **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 3.12 (dd, J=6.4, 1.7 Hz, 2H), 2.82 (ddd, J =5.8, 4.4, 1.8 Hz, 2H), 2.42 (ddd, J=14.3, 4.9, 3.7, 1.2 Hz, 2H), 2.27 (dddd, J=14.3, 12.1, 5.2, 0.5 Hz, 2H), 1.98 (ddddd, J=13.5, 4.5, 4.5, 4.2, 4.2 Hz, 2H), 1.86 (ddddd, J=13.5, 12.0, 12.0, 3.7, 3.7 Hz, 2H), 1.70 (ddddd, J=13.7, 12.0, 4.4, 4.2, 0.5 Hz, 2H), 1.52 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =** 213.4 (C), 47.8 (CH), 41.2 (CH_2), 40.3 (CH), 25.2 (CH_2), 23.0 (CH_2). **LRMS (EI) m/z =** 192.2 ($M^{\cdot+}$), 175.2, 164.2, 149.2, 136.22, 121.1, 108.1, 96.1, 79.1, 68.1, 55.1, 41.2. **LRMS (ESI+) m/z =** 193.3 (M + H^+), 215.2 (M + Na^+), 308.4, 407.3 (2M + Na^+).

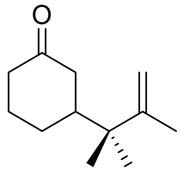
3. 2. 5. *cis-anti-cis*-Tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (8):



$C_{12}H_{16}O_2$
MW: 192.258
CAS 712-27-6

Obtained as slightly yellow solid (17.2 mg, 0.09 mmol, 1.8% yield). NMR data was consisted with literature.[13,14] **R_f =** 0.04 (toluene:Et_2O 9:1), 0.14 (*n*-hexane:AcOEt 8:2). **GC R_t =** 5.49 min. **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 3.05 (m, 2H), 2.66 (t, J=7.5 Hz, 2H), 2.44 (m, 2H), 2.27 (m, 2H), 2.04 -1.81 (m, 6H), 1.70 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =** 213.2 (C), 47.7 (CH), 40.2 (CH_2), 38.5 (CH), 27.1 (CH_2), 21.5 (CH_2). **LRMS (EI) m/z =** 192.2 ($M^{\cdot+}$), 163.2, 150.2, 136.2, 119.2, 108.2, 96.2, 79.2, 68.2, 55.1, 41.2. **LRMS (ESI+) m/z =** 193.3 (M + H^+), 215.2 (M + Na^+), 407.4 (2M + Na^+).

3. 2. 6. 3-(1,1,2-Trimethyl-2-propen-1-yl)cyclohexanone (9):



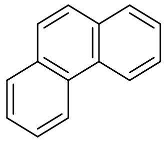
$C_{12}H_{20}O$
MW: 180.291
CAS 100675-58-9

Obtained as colourless oil (67.4 mg, 0.37 mmol, 7.5% yield). Compound reported in the literature (see [4]), but no spectral data was given. **R_f =** 0.49 (toluene:diethyl ether 9:1). **GC R_t =** 4.01 min. **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 4.79 (br s, 1H), 4.72 (br s, 1H), 2.36 (ddd, J=14.2, 4.4, 2.1 Hz, 1H), 2.30 (m, 1H), 2.22 (ddd, J=14.0, 13.8, 6.4 Hz), 2.09 (m, 1H), 2.03 (dd, J=13.6, 13.5 Hz, 1H), 1.85 – 1.74 (m, 2H), 1.68 (s, 3H), 1.56 (m, 1H), 1.32 (ddd, J=13.3, 12.8, 3.7 Hz, 1H), 1.04 (s, 3H), 1.00 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =** 213.0 (C), 151.5 (C), 110.7 (CH_2), 45.3 (CH), 43.8 (CH_2), 41.6 (CH_2), 41.3 (C), 26.4 (CH_2), 25.9 (CH_2), 23.6 (CH_3), 23.3 (CH_3), 19.5 (CH_3). **LRMS (EI) m/z =** 137.1, 107.2, 83.2, 69.1, 55.1, 41.1.

3. 3. Procedure for synthesis of compounds 10, 11, 12, and 13:

Cis-stilbene (721.0 mg, 4.00 mmol, 1.00 eq., 50.0 mM solution) and iodine (101.6 mg, 0.40 mmol, 0.10 eq., 5.0 mM solution) were dissolved in cyclohexane (80.0 mL, 111.0 vol.), obtained solution was saturated with oxygen by bubbling O_2 for 15 minutes, and then the mixture was injected into photoreactor (internal volume of 31.8 mL, 1.00 mm I.D., 1.60 mm O.D., PFA) equipped with UV-A lamp (Philips PLL 36W UVA). Irradiation over 50 minutes of effective exposure time was set (corresponding to 0.606 mL/min flow rate). After injection of 80.0 mL, reaction mixture was eluted from photoreactor using pure cyclohexane, reaction mixture was then collected, solvent was removed, and obtained residue was initially purified using column chromatography (SiO_2; *n*-hexane:AcOEt 9:1) affording fractions containing recovered stilbene (371.9 mg, 2.06 mmol, recovery of 51.6% of starting material), phenanthrene (71.2 mg, 0.40 mmol, 10.0% yield) and combined fraction containing 1,2,3,4-tetraphenylcyclobutane isomers and 1,2-diphenyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene (263.6 mg). The latter was then repurified using preparative HPLC system (Cosmosil Buckyprep column, *n*-hexane:AcOEt 9:1) and afforded fractions containing (1α,2α,3β,4β)-1,2,3,4-tetraphenylcyclobutane and (1α,2β,3α,4β)-1,2,3,4-tetraphenylcyclobutane as white solids (total mass of 121.9 mg, 0.34 mmol, 8.5% yield), and fraction containing pure 1,2-diphenyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene (124.7 mg, 0.35 mmol, 8.7% yield).

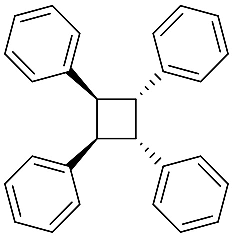
3. 3. 1. Phenanthrene (10):



$C_{14}H_{10}$
MW: 178.234
CAS 85-01-8

White solid. **R_f =** 0.70 in 10% AcOEt in *n*-hexane. **GC R_t =** 5.67 min. NMR data was consistent with literature.[2] **Mp.** 100.0 – 100.3 °C. Lit. 99.1 – 100.5 °C.[2] **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 8.70 (ddd, J=8.0, 1.3, 0.6 Hz, 2H), 7.90 (ddd, J=7.7, 1.6, 0.6 Hz, 2H), 7.75 (s, 2H), 7.67 (ddd, J=8.3, 7.0, 1.6 Hz, 2H), 7.61 (ddd, J=7.7, 7.0, 1.3 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =** 132.2, 130.4, 128.7, 127.1, 126.7, 122.8.

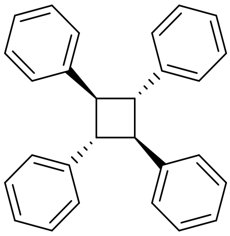
3. 3. 2. (1α,2α,3β,4β)-1,2,3,4-Tetraphenylcyclobutane (11):



$C_{28}H_{24}$
MW: 360.500
CAS 54515-63-8

White solid. **R_f =** 0.55 in 10% AcOEt in *n*-hexane. **GC R_t =** 10.11 min. Compound reported in the literature (see [15]), but no spectral data was given. Mp. = 158.0 – 158.7 °C. Lit. = 163 °C.[15] **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 7.21 – 7.01 (m, 20H), 4.48 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =** 140.9 (C), 128.3 (CH), 128.1 (CH), 126.0 (C), 47.7 (CH). **LRMS (EI) m/z =** 180.2 ($C_{14}H_{12}$).

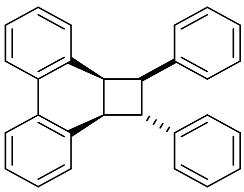
3. 3. 3. (1α,2β,3α,4β)-1,2,3,4-Tetraphenylcyclobutane (12):



$C_{28}H_{24}$
MW: 360.500
CAS 54515-64-9

White solid. **R_f =** 0.48 in 10% AcOEt in *n*-hexane. **GC R_t =** 10.33 min. Compound reported in the literature (see [15]), but no spectral data was given. **Mp. =** 147.7 – 148.5 °C. Lit. = 150 °C.[15] **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 7.33 – 7.28 (m, 16H), 7.22 (m, 4H), 3.70 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) =** 142.8 (C), 128.7 (CH), 127.2 (CH), 126.7 (CH), 51.8 (CH). **LRMS (EI) m/z =** 180.2 ($C_{14}H_{12}$).

3. 3. 4. (1α,2β,2aR,10bS)-1,2-Diphenyl-1,2,2a,10b-tetrahydrocyclobuta[*l*]phenanthrene (13):



$C_{28}H_{22}$
MW: 358.484
CAS 79646-57-4

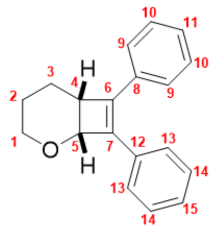
White solid. **R$_f$ =** 0.46 in 10% AcOEt in *n*-hexane. **GC R$_t$ =** 8.06 min. NMR data was consisted with literature.[16] **Mp. =** 181.7 – 182.3 °C, Lit. = 183.5 – 184.5 °C.[16] **^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) =** 7.98 (dd, J=8.1, 1.3 Hz, 1H), 7.94 (dd, J=8.0, 1.2 Hz, 1H), 7.32 (td, J=7.7, 1.5 Hz, 1H), 7.29 – 7.14 (m, 10H), 7.06 (dd, J=7.5, 1.5 Hz, 1H), 7.01 – 6.94 (m, 2H), 6.84 (td, J= 7.4, 1.3 Hz, 1H), 6.23 (dt, J =7.7, 1.2 Hz, 1H), 4.36 (dd, J=11.2, 8.6 Hz, 1H), 4.25 (dd, J=8.6, 8.5 Hz, 1H), 3.99 (dd, J=11.2, 9.4 Hz, 1H), 3.82 (dd, J=8.9, 8.9 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) =** 142.2, 138.7, 136.0, 133.1, 132.9, 132.3, 132.2, 129.2, 128.5, 128.4, 128.0, 127.8, 127.5, 127.0, 127.0, 126.8, 126.7, 126.6, 123.9, 122.9, 53.2, 51.8, 42.7, 40.5. **LRMS (EI) m/z =** 281.2, 267.2, 253.2, 207.2, 191.1, 178.2, 165.2, 152.2, 133.1, 96.1, 76.2, 44.2.

4. NMR, UV-Vis, IR, and MS spectra

Figure S 27. ^{1}H NMR spectrum of cis-7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (**1**). 81
Figure S 28. ^{13}C (top) and DEPT-135 (bottom) NMR spectra of cis-7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (**1**). 82
Figure S 29. UV-Vis absorbance of cis-7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene in acetonitrile....... 83
Figure S 30. Determination of molar extinction coefficient o cis-f7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene. 83
Figure S 31. Electrospray ionisation mass spectrum of cis-7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (**1**). 84
Figure S 32. Electron ionization mass spectrum of cis-7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (**1**). 84
Figure S 33. ^{1}H NMR spectrum of 3,4-dihydro-6,7-diphenyl-2H-oxocin (**2**). 85
Figure S 34. ^{13}C (top) and DEPT-135 (bottom) NMR spectra of 3,4-dihydro-6,7-diphenyl-2H-oxocin (**2**). 86
Figure S 35. Electron ionisation mass spectrum of 3,4-dihydro-6,7-diphenyl-2H-oxocin (**2**). 86
Figure S 36. High resolution electron ionisation mass spectrum of 3,4-dihydro-6,7-diphenyl-2H-oxocin (**2**). 87
Figure S 37. ^{1}H NMR spectrum of 8c,11,12,12a-tetrahydro-10H-phenanthro[9′,10′:3,4]cyclobuta[1,2-b]pyran (**3**). 88
Figure S 38. ^{13}C (top) and DEPT-135 (bottom) NMR of 8c,11,12,12a-tetrahydro-10H-phenanthro[9′,10′:3,4]cyclobuta[1,2-b]pyran (**3**). 89
Figure S 39. Electron ionisation mass spectrum of 8c,11,12,12a-tetrahydro-10H-phenanthro[9′,10′:3,4]cyclobuta[1,2-b]pyran (**3**). 89
Figure S 40. High resolution electron ionisation mass spectrum of 8c,11,12,12a-tetrahydro-10H-phenanthro[9′,10′:3,4]cyclobuta[1,2-b]pyran (**3**). 90
Figure S 41. ^{1}H NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in CDCl$_3$. 91
Figure S 42. ^{13}C (top) and DEPT-135 (bottom) NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in CDCl$_3$. 92
Figure S 43. HSQC NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-Diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in CDCl$_3$ 93
Figure S 44. HMBC NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-Diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in CDCl$_3$ 94

Figure S 45. COSY NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-Diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$ 95
Figure S 46. TOCSY NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-Diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$ 96
Figure S 47. NOESY NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-Diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$ 97
Figure S 48. ^{1}H NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in DMSO-d_6 at 100 °C. 98
Figure S 49. ^{13}C NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in DMSO-d_6 at 80 °C. 99
Figure S 50. FT-ATR-IR spectrum of neat of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**). 99
Figure S 51. High resolution electrospray ionisation mass spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**). 100
Figure S 52. High resolution electron ionisation mass spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**). 100
Figure S 53. ^{1}H NMR spectrum of trans-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**5**). 101
Figure S 54. ^{13}C (top) and DEPT-135 (bottom) NMR spectrum of trans-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**5**). 102
Figure S 55. Electron ionisation mass spectrum of trans-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**5**). 102
Figure S 56. ^{1}H NMR spectrum of cis-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**6**). 103
Figure S 57. ^{13}C NMR spectrum of cis-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**6**). 103
Figure S 58. Electron ionisation mass spectrum of cis-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**6**). 104
Figure S 59. ^{1}H NMR spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (**7**). 104
Figure S 60. ^{13}C (top) and DEPT-135 (bottom) NMR spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (**7**). 105
Figure S 61. Electrospray ionisation mass spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (**7**). 105
Figure S 62. Electron ionisation mass spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (7). 106
Figure S 63. ^{1}H NMR spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (**8**). 106
Figure S 64. ^{13}C (top) and DEPT-135 (bottom) NMR spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (**8**). 107
Figure S 65. Electrospray ionisation mass spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (**8**). 107
Figure S 66. Electron ionisation mass spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (**8**). 108
Figure S 67. ^{1}H NMR spectrum of 3-(2,3-dimethylbut-3-en-2-yl)cyclohexan-1-one (**9**). 108
Figure S 68. ^{13}C NMR spectrum of 3-(2,3-dimethylbut-3-en-2-yl)cyclohexan-1-one (**9**). 109
Figure S 69. Electron ionisation mass spectrum of 3-(2,3-dimethylbut-3-en-2-yl)cyclohexan-1-one (**9**). 109
Figure S 70. ^{1}H NMR spectrum of phenanthrene (**10**). 110
Figure S 71. ^{13}C NMR spectrum of phenanthrene (**10**). 110
Figure S 72. ^{1}H NMR spectrum of (1α,2α,3β,4β)-1,2,3,4-Tetraphenylcyclobutane (**11**). 111

Figure S 73. ^{13}C NMR spectrum of (1α,2α,3β,4β)-1,2,3,4-Tetraphenylcyclobutane (**11**). 111
Figure S 74. Electron ionisation mass spectrum of (1α,2α,3β,4β)-1,2,3,4-Tetraphenylcyclobutane (**11**). 112
Figure S 75. ^{1}H NMR spectrum of (1α,2β,3α,4β)-1,2,3,4-Tetraphenylcyclobutane (**12**). 112
Figure S 76. ^{13}C NRM spectrum of (1α,2β,3α,4β)-1,2,3,4-Tetraphenylcyclobutane (**12**). 112
Figure S 77. Electron ionisation mass spectrum of (1α,2β,3α,4β)-1,2,3,4-Tetraphenylcyclobutane (**12**). 113
Figure S 78. ^{1}H NMR spectrum of (1α,2β,2aR,10bS)-1,2-diphenyl-1,2,2a,10b-tetrahydrocyclobuta[l]phenanthrene (**13**). 113
Figure S 79. ^{13}C (top) and DEPT-135 (bottom) NMR spectrum of (1α,2β,2aR,10bS)-1,2-diphenyl-1,2,2a,10b-tetrahydrocyclobuta[l]phenanthrene (**13**). 114
Figure S 80. Electron ionisation mass spectrum of (1α,2β,2aR,10bS)-1,2-diphenyl-1,2,2a,10b-tetrahydrocyclobuta[l]phenanthrene (**13**). 115



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.65 (m, 2H, 13), 7.56 (m, 2H, 9), 7.39 – 7.27 (m, 6H, [10, 11, 14, 15]), 4.85 (d, J=4.5 Hz, 1H, 5), 3.93 (ddd, J=11.2, 7.8, 5.9 Hz, 1H, 1), 3.77 (ddd, J=11.2, 8.3, 6.2 Hz, 1H, 1), 3.33 (ddd, J=6.1, 5.2, 4.5 Hz, 1H, 4), 2.19 (dddd, J=13.5, 9.0, 6.1, 5.3 Hz, 1H, 3), 2.00 (dddd, 13.6, 7.3, 5.2, 5.2 Hz, 1H, 3), 1.78 (m, 1H, 2), 1.66 (m, 1H, 2).

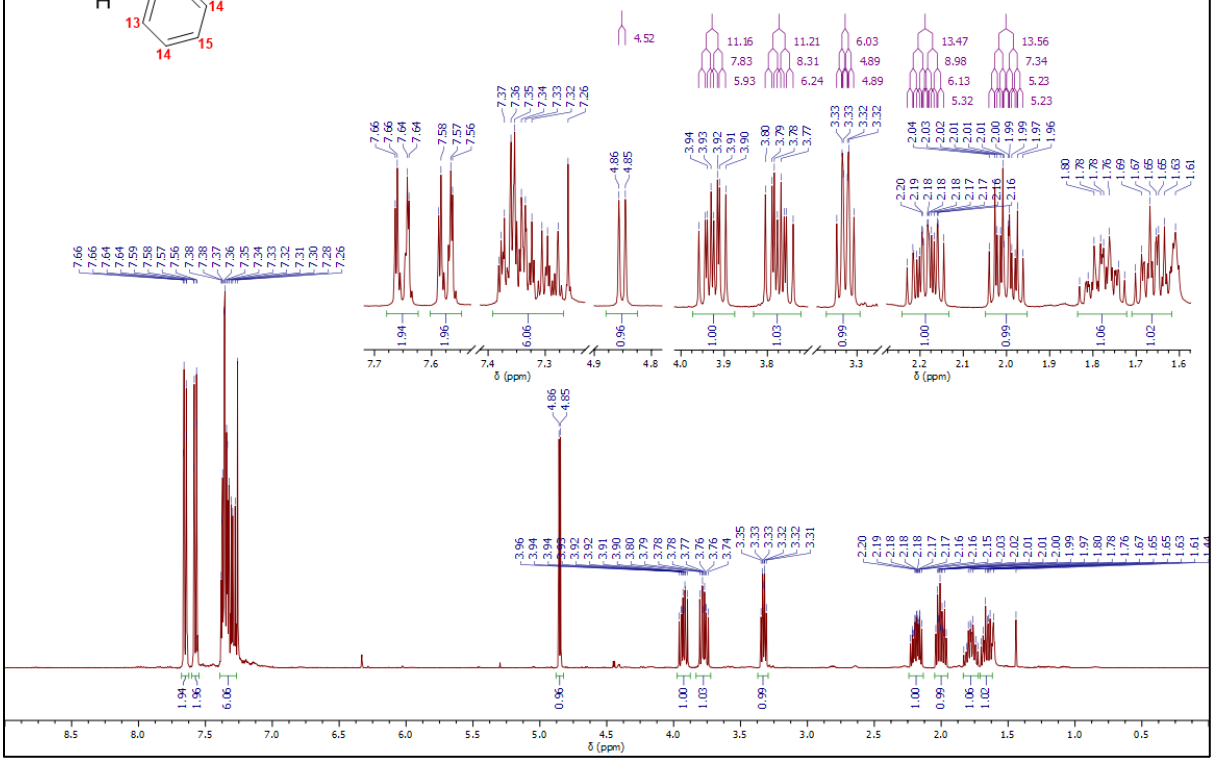


*Figure S 27. ^{1}H NMR spectrum of cis-7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (**1**).*

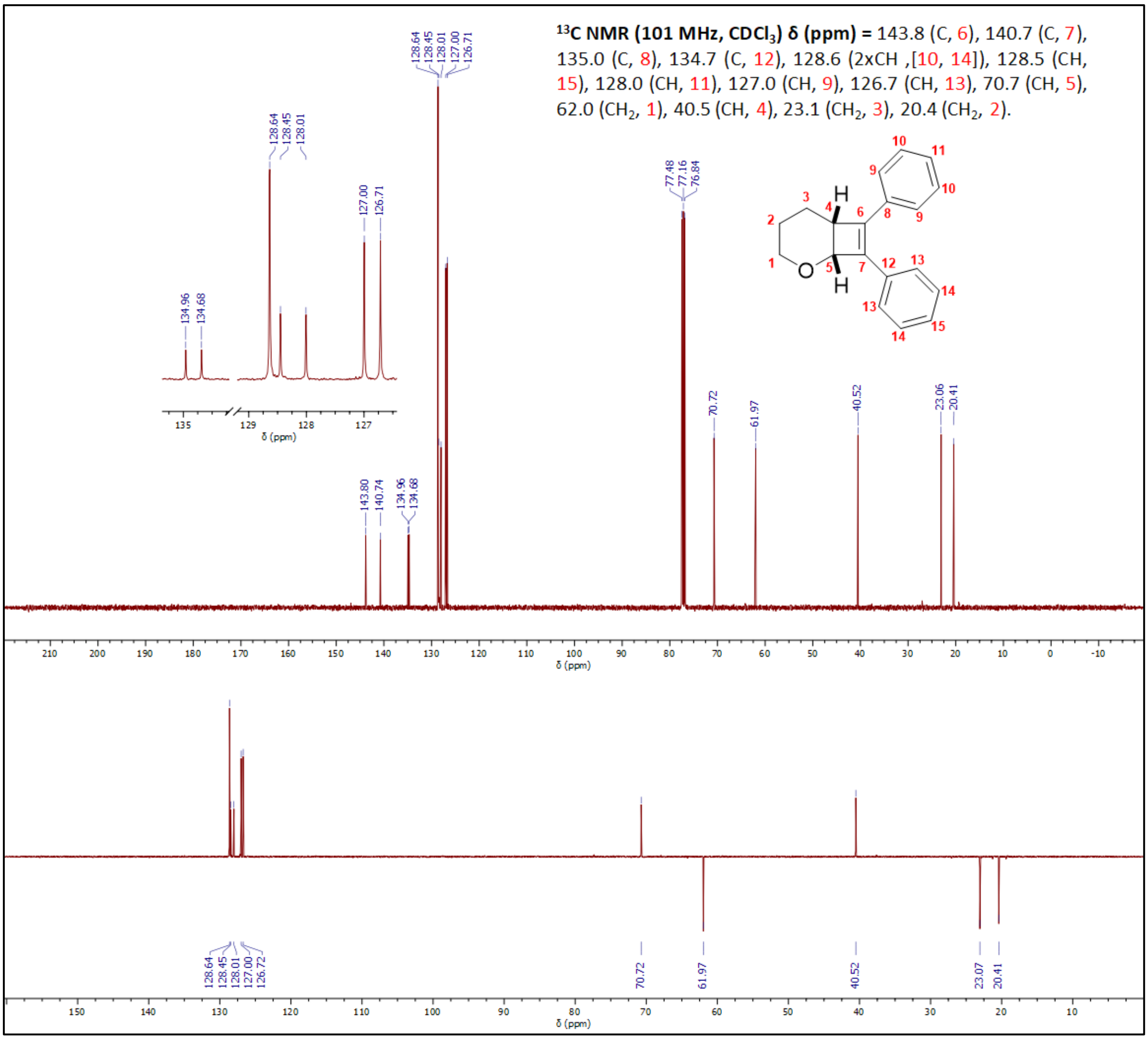


*Figure S 28. ^{13}C (top) and DEPT-135 (bottom) NMR spectra of cis-7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (**1**).*

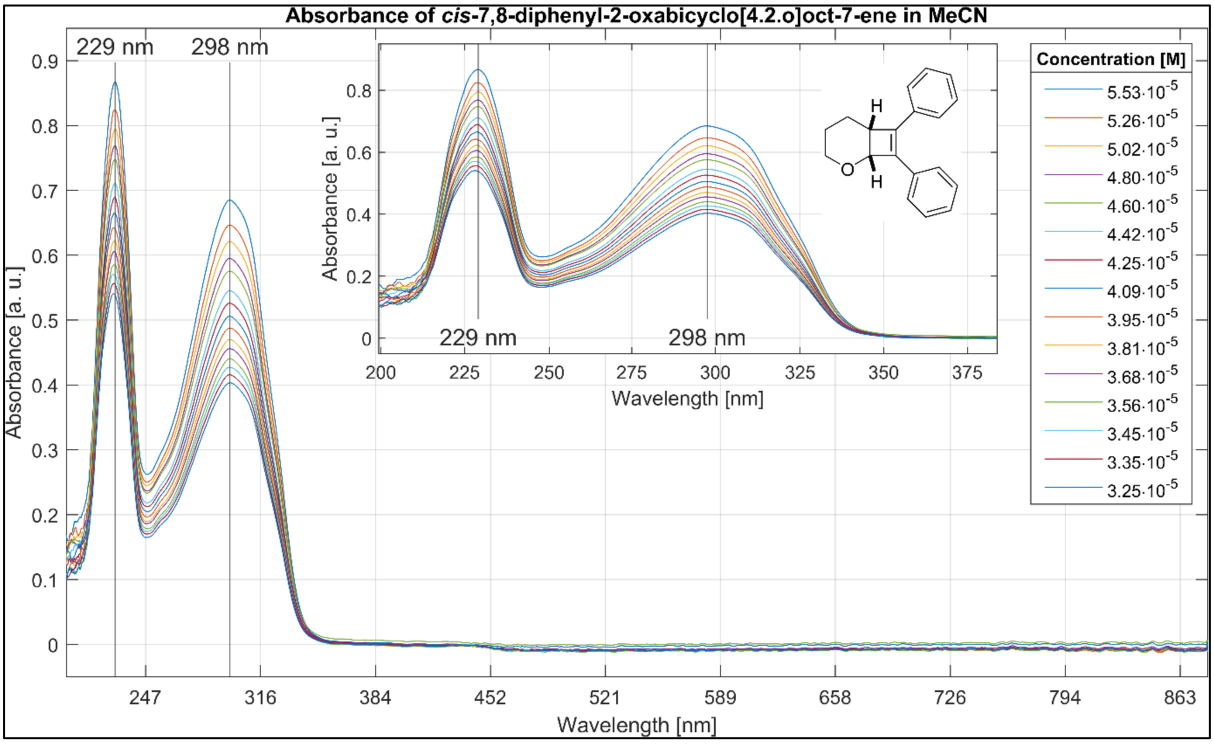


Figure S 29. UV-Vis absorbance of cis-7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene in acetonitrile.

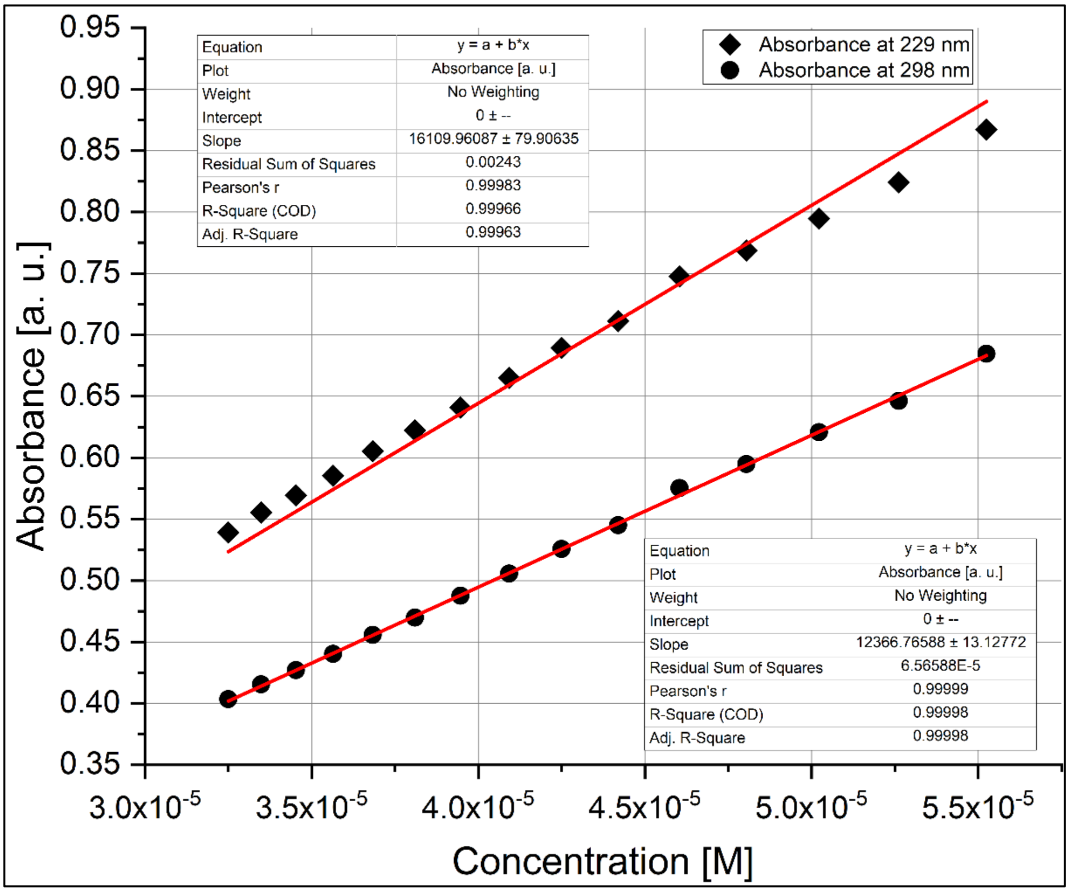


Figure S 30. Determination of molar extinction coefficient o cis-f7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene.

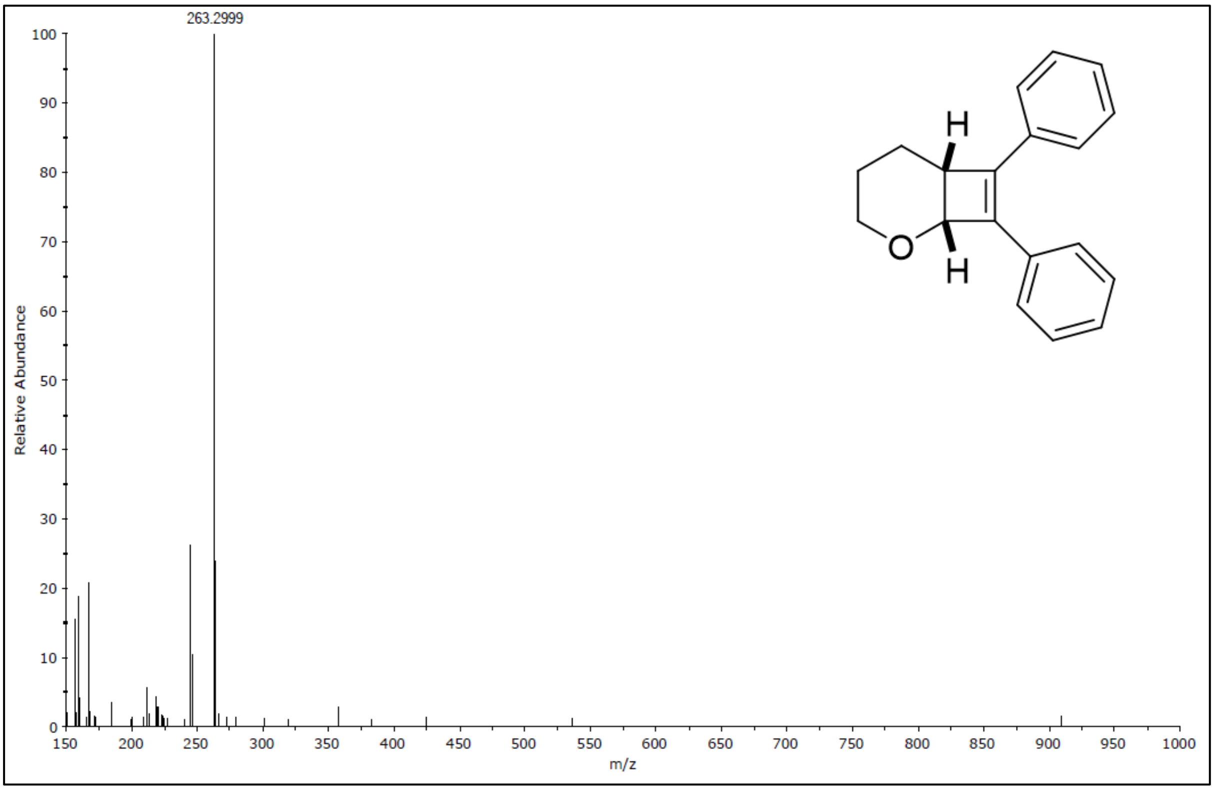


*Figure S 31. Electrospray ionisation mass spectrum of cis-7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (**1**).*

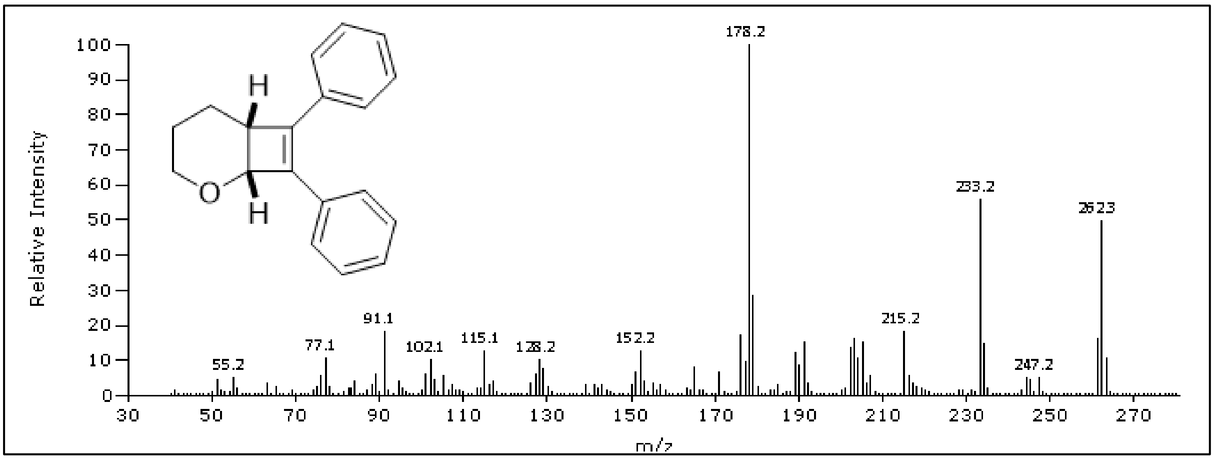
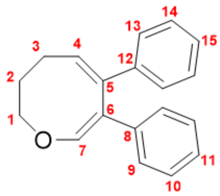


*Figure S 32. Electron ionization mass spectrum of cis-7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (**1**).*



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.31(m, 2H, 13), 7.19 – 6.99 (m, 8H, [9, 10, 11, 14, 15]), 6.80 (s, 1H, 7), 6.12 (t, J= 8.2 Hz, 1H, 4), 4.62 (br s, 1H, 1), 3.84 (br s, 1H, 1), 2.70 (br s, 1H, 3), 2.57 (br s, 1H, 3), 1.93 (br s, 1H, 2), 1.44 (br s, 1H, 2).

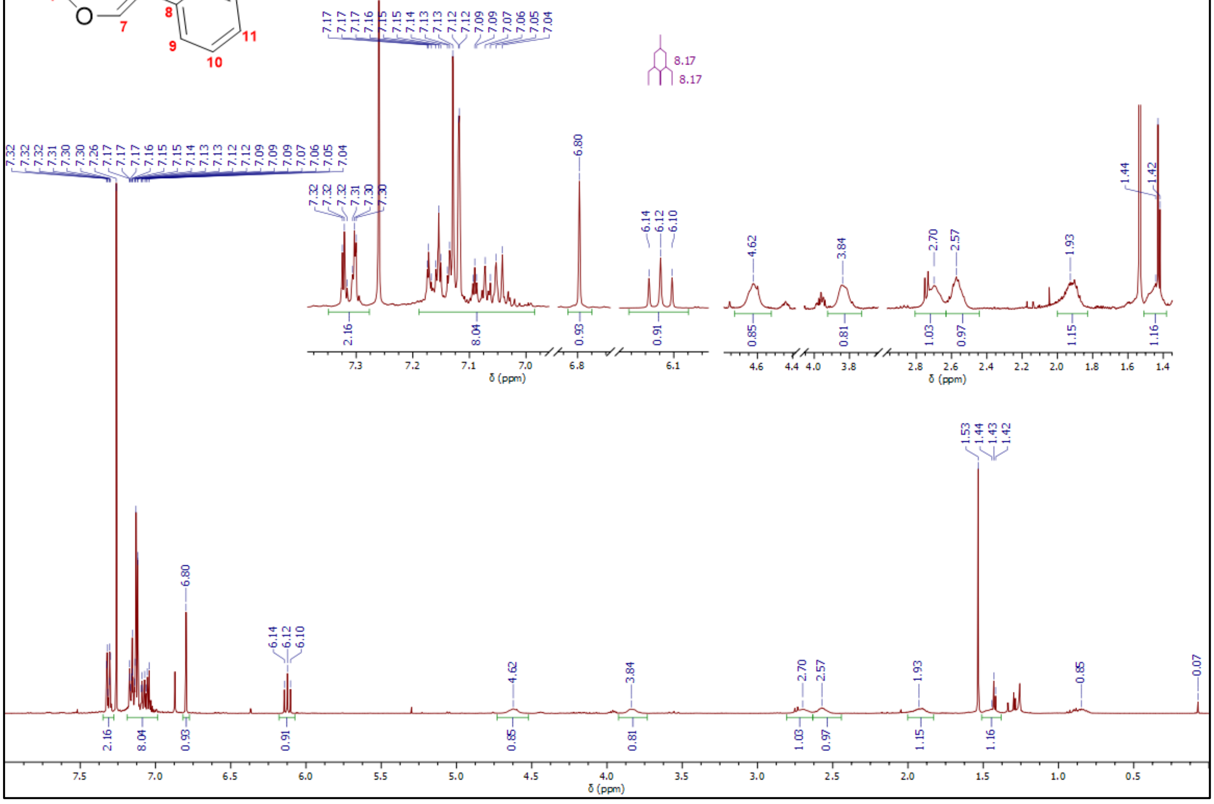


*Figure S 33. ^{1}H NMR spectrum of 3,4-dihydro-6,7-diphenyl-2H-oxocin (**2**).*

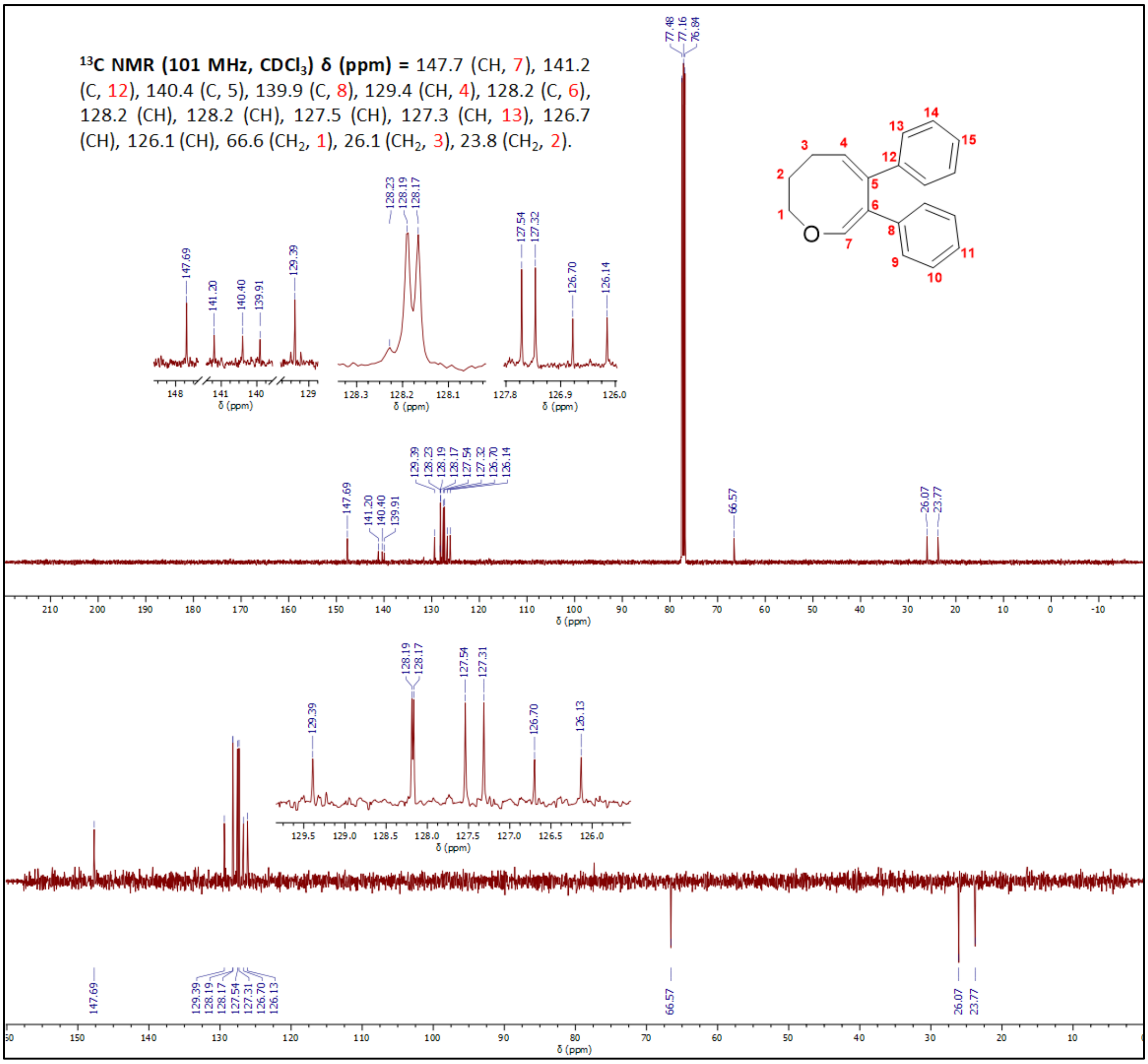


*Figure S 34. ^{13}C (top) and DEPT-135 (bottom) NMR spectra of 3,4-dihydro-6,7-diphenyl-2H-oxocin (**2**).*

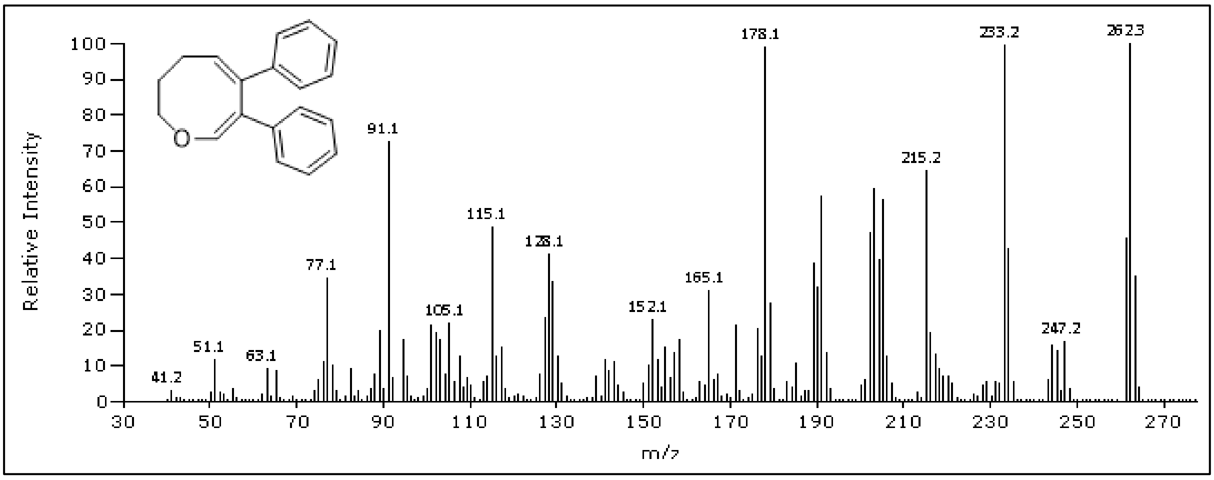


*Figure S 35. Electron ionisation mass spectrum of 3,4-dihydro-6,7-diphenyl-2H-oxocin (**2**).*

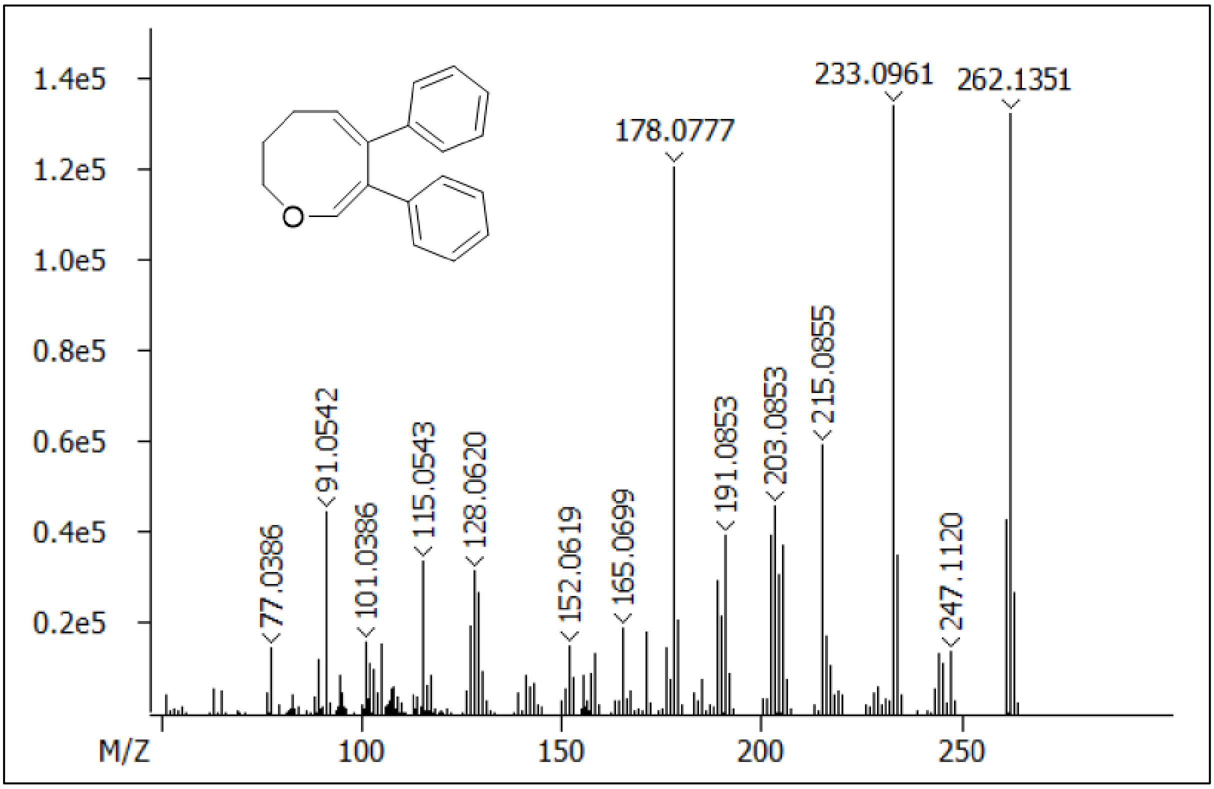


*Figure S 36. High resolution electron ionisation mass spectrum of 3,4-dihydro-6,7-diphenyl-2H-oxocin (**2**).*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.80 – 8.71 (m, 2H, [10, 13]), 7.97 (m, 1H, 16), 7.81 (ddd, J=7.5, 1.7, 0.6 Hz, 1H, 7) 7.70 – 7.59 (m, 4H, [8, 9, 14, 15]), 5.45 (d, J=4.3 Hz, 1H, 19), 4.04 (dt, J=6.0, 4.5 Hz, 1H, 4), 3.91 – 3.78 (m, 2H, 1), 2.37 (dddd, J=13.7, 10.2, 6.0, 5.3 Hz, 1H, 3a), 2.22 (dddd, J=13.7, 6.2, 5.3, 4.6 Hz, 1H, 3b), 1.64 (m, 1H, 2), 1.40 (m, 1H, 2).

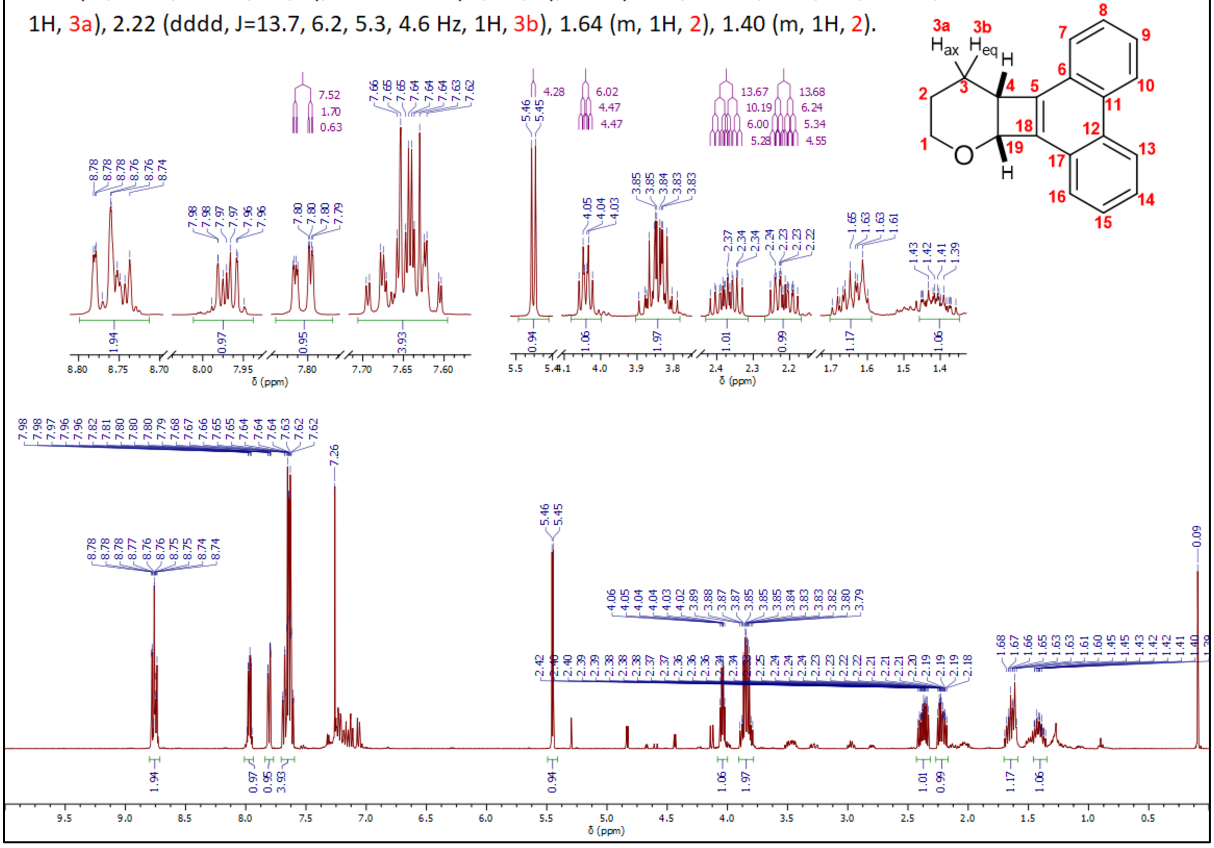


*Figure S 37. ^{1}H NMR spectrum of 8c,11,12,12a-tetrahydro-10H-phenanthro[9',10':3,4]cyclobuta[1,2-b]pyran (**3**).*

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 143.3 (C, 5), 141.1 (C, 18), 132.1 (C, 11), 130.8 (C, 12), 129.0 (C, 17), 128.6 (C, 6), 127.3 (CH), 126.9 (CH), 126.8 (CH), 126.2 (CH), 124.1 (CH, [10/13]), 123.9 (CH, [13/10]), 123.7 (CH, 7), 123.6 (CH, 16), 72.9 (CH, 19), 62.1 (CH_2, 1), 42.4 (CH, 4), 23.2 (CH_2, 3), 20.0 (CH_2, 2).

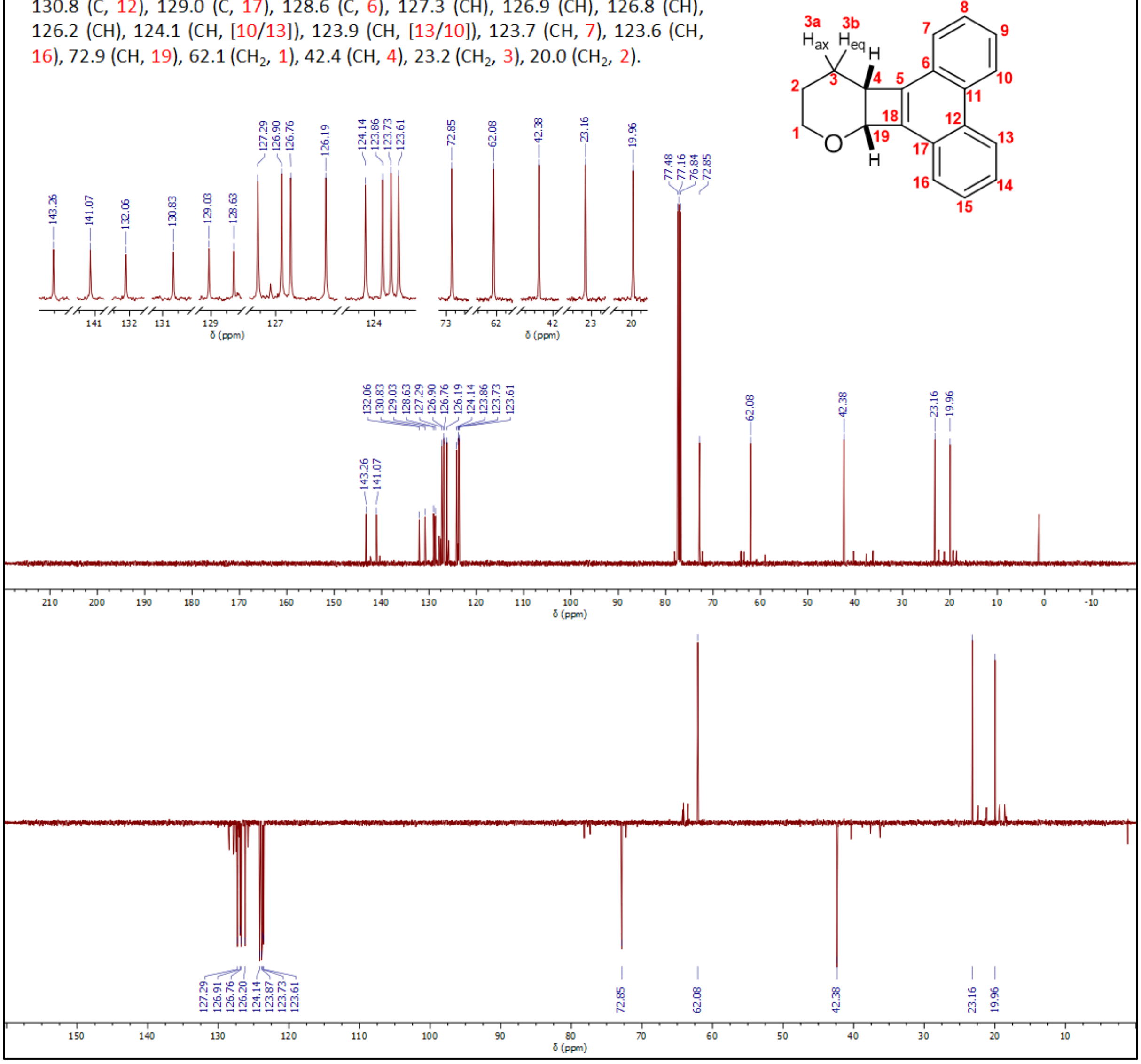


*Figure S 38. ^{13}C (top) and DEPT-135 (bottom) NMR of 8c,11,12,12a-tetrahydro-10H-phenanthro[9',10':3,4]cyclobuta[1,2-b]pyran (**3**).*

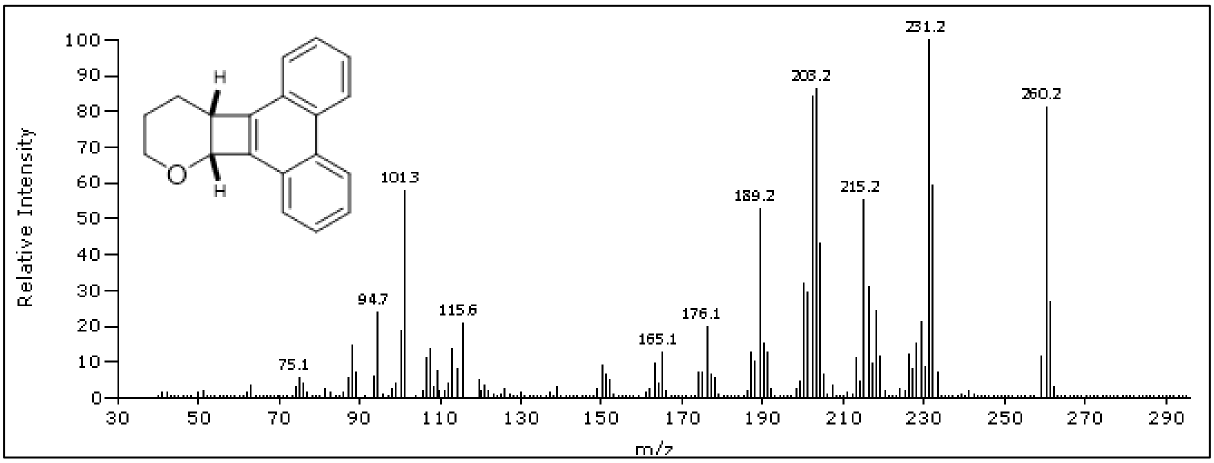


*Figure S 39. Electron ionisation mass spectrum of 8c,11,12,12a-tetrahydro-10H-phenanthro[9',10':3,4]cyclobuta[1,2-b]pyran (**3**).*

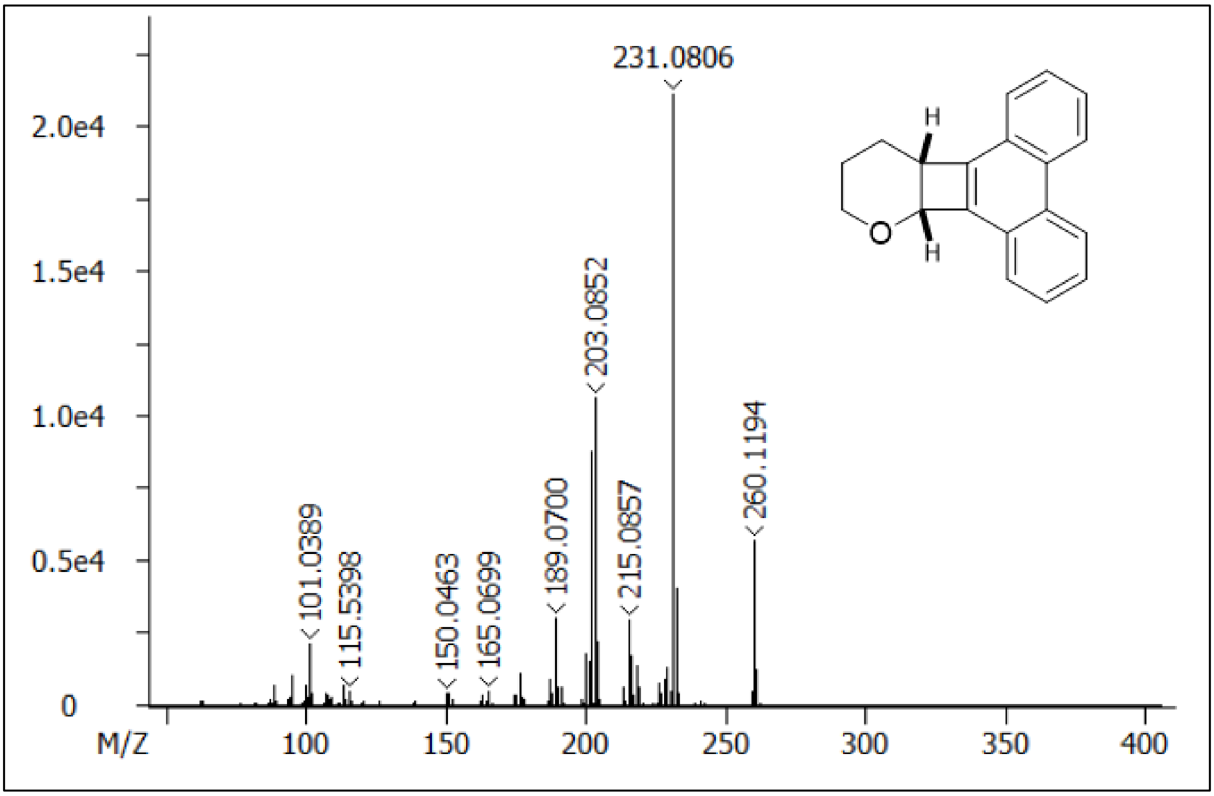


*Figure S 40. High resolution electron ionisation mass spectrum of 8c,11,12,12a-tetrahydro-10H-phenanthro[9',10':3,4]cyclobuta[1,2-b]pyran (**3**).*

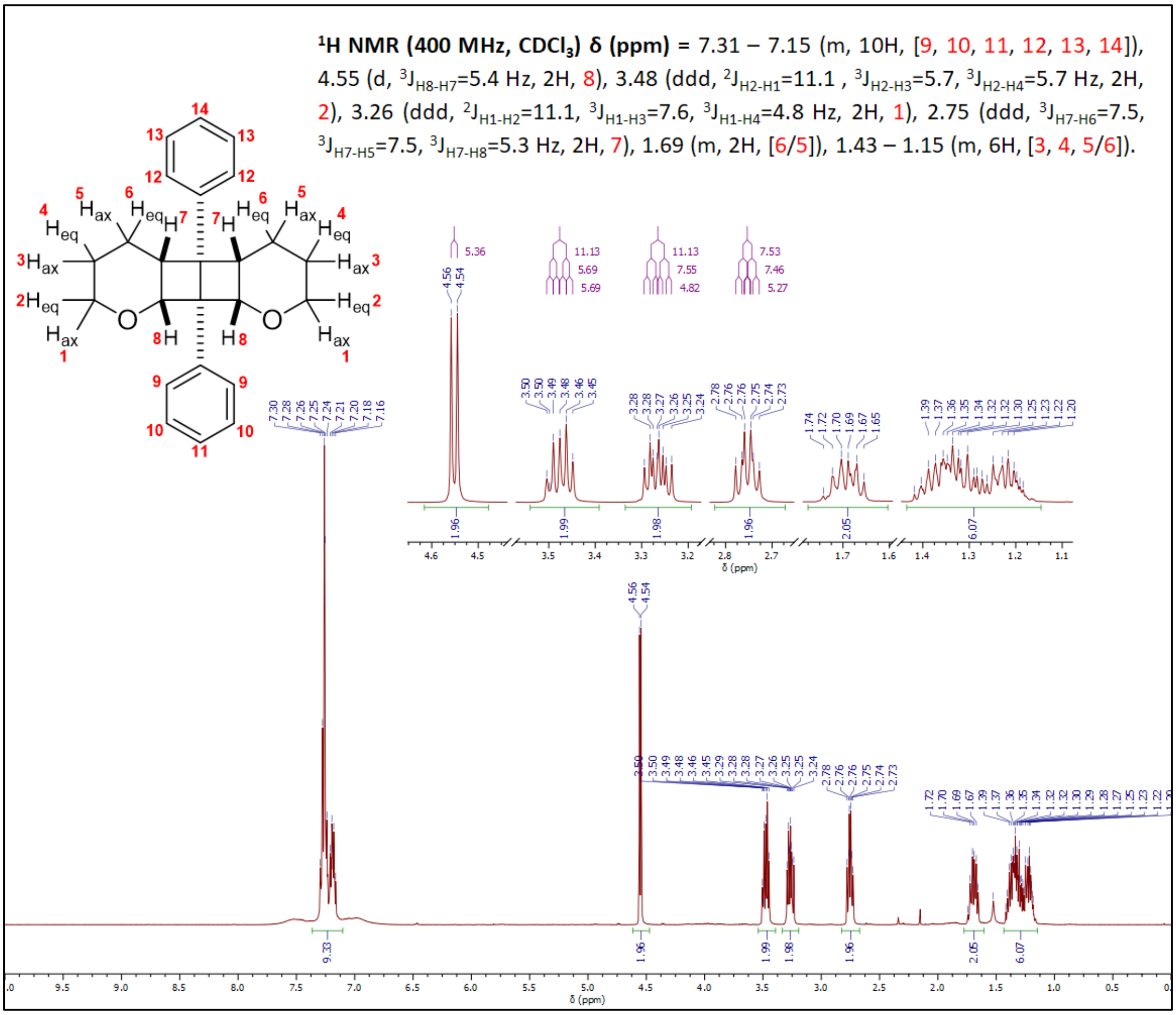


*Figure S 41. ^{1}H NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$.*

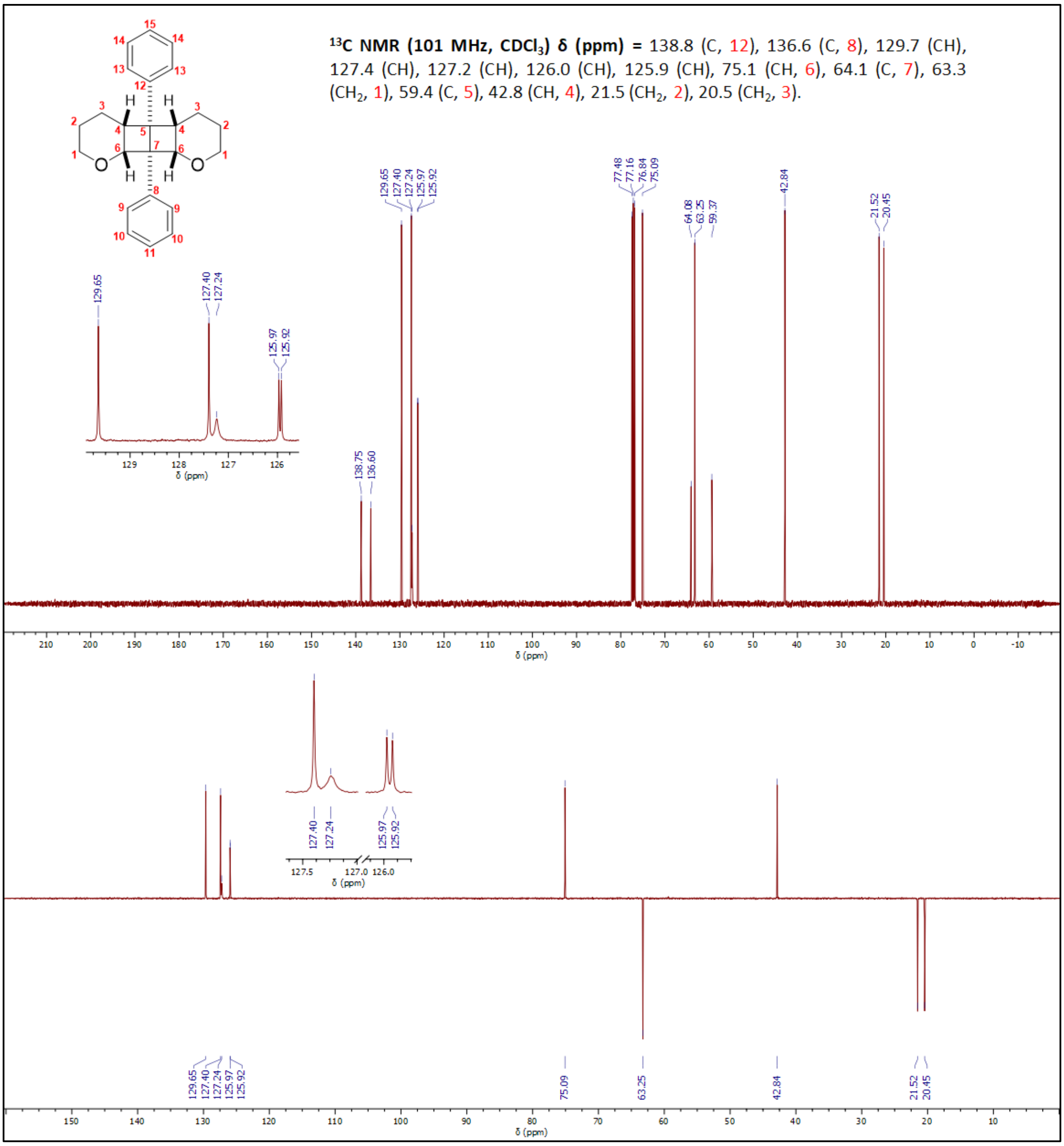


*Figure S 42. ^{13}C (top) and DEPT-135 (bottom) NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$.*

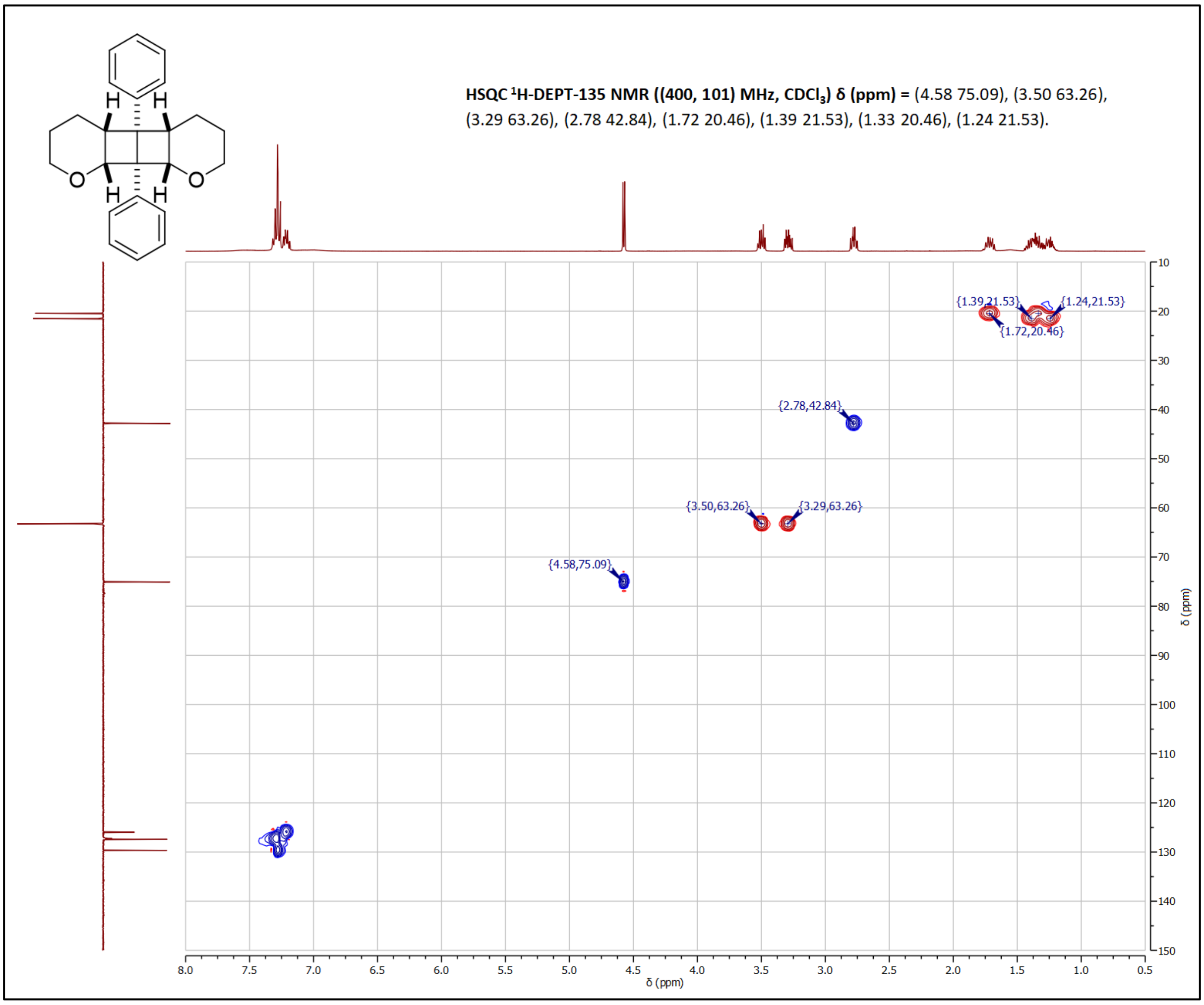
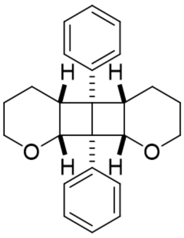


*Figure S 43. HSQC NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-Diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$*



HMBC ^1H-^{13}C NMR ((400, 101) MHz, $CDCl_3$) δ (ppm) = (7.29 64.09), (4.58 20.46), (4.58 59.38), (4.58 63.26), (4.58 138.76), (3.50 20.46), (3.50 75.09), (3.29 20.46), (3.29 75.09), (2.78 20.46), (2.78 59.38), (2.78 64.09), (2.78 75.09), (2.78 138.76), (1.72 21.53), (1.72 42.84), (1.72 59.38), (1.72 63.26), (1.72 75.09), (1.39 20.46), (1.39 42.84), (1.39 63.26), (1.33 21.53), (1.33 42.84), (1.33 59.38), (1.33 63.26), (1.33 75.09), (1.24 20.46), (1.24 42.84), (1.24 63.26).

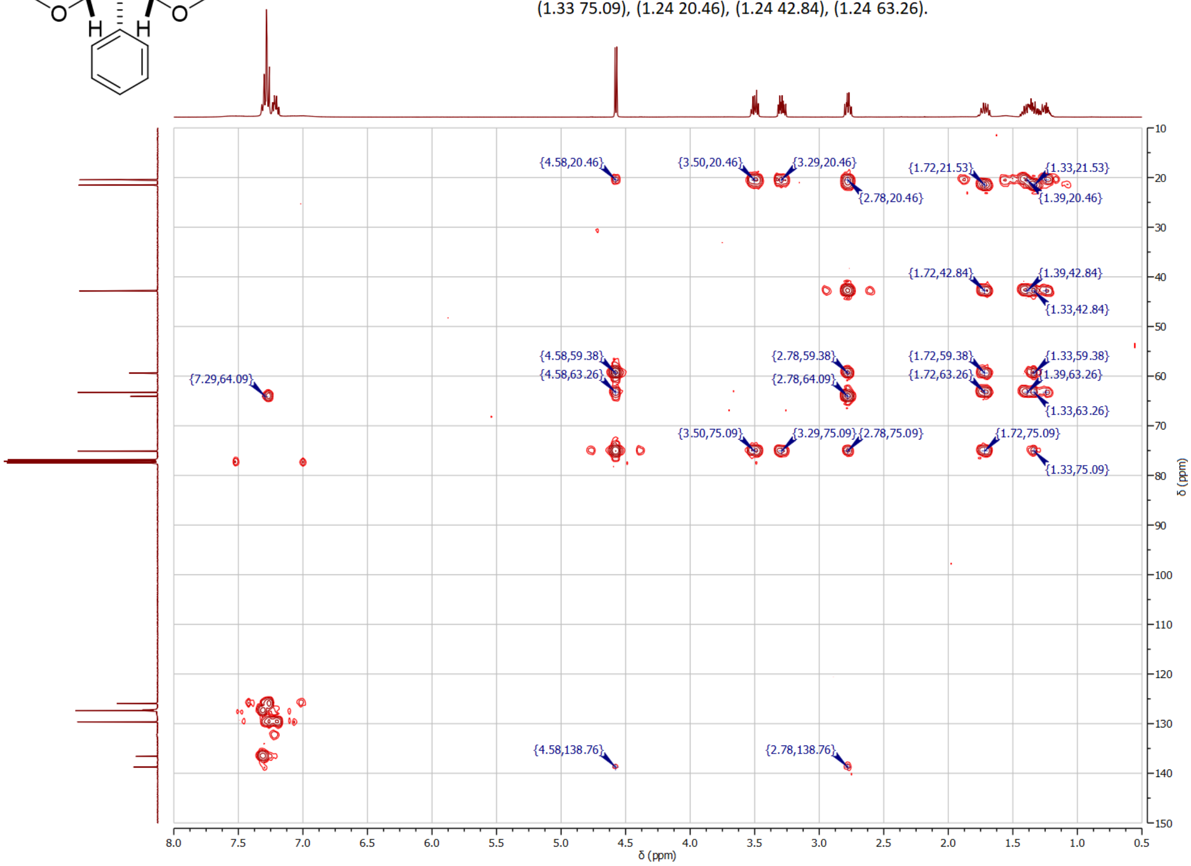
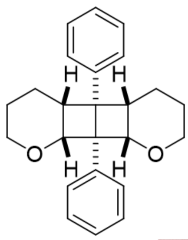


*Figure S 44. HMBC NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-Diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$*



COSY ^1H-^1H NMR ((400, 400) MHz, $CDCl_3$) δ (ppm) = (4.57 2.78), (3.50 1.24), (3.50 1.39), (3.50 3.29), (3.29 1.24), (3.29 1.39), (3.29 3.50), (2.77 1.39), (2.77 1.75), (2.77 4.58), (1.71 1.24), (1.71 1.39), (1.71 2.78), (1.38 1.26), (1.38 3.29), (1.38 3.50), (1.33 1.72), (1.33 2.78), (1.25 3.29), (1.25 3.50), (1.24 1.39), (1.24 1.72).

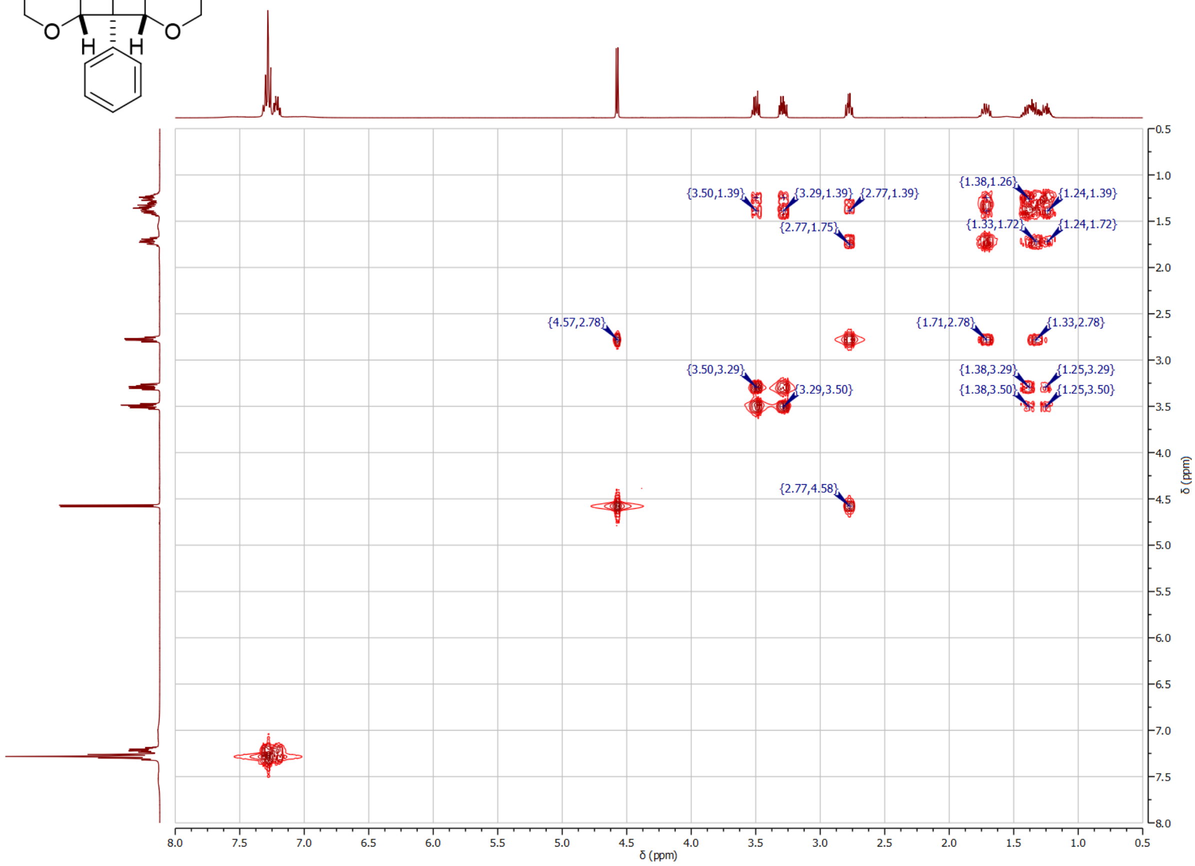
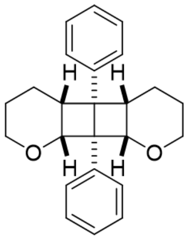


*Figure S 45. COSY NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-Diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$*



TOCSY ^1H-^1H NMR ((400, 400) MHz, $CDCl_3$) δ (ppm) = (4.58 1.24), (4.58 1.33), (4.58 1.39), (4.58 1.72), (4.58 2.78), (4.58 3.29), (4.58 3.50), (3.51 1.26), (3.51 1.33), (3.51 1.39), (3.51 1.72), (3.51 2.78), (3.51 3.29), (3.51 4.58), (3.29 1.24), (3.29 1.33), (3.29 1.39), (3.29 1.75), (3.29 2.78), (3.29 3.50), (3.29 4.58), (2.78 1.26), (2.78 1.39), (2.78 1.72), (2.78 3.29), (2.78 3.50), (2.78 4.58), (1.72 1.24), (1.72 1.33), (1.72 1.39), (1.72 2.78), (1.72 3.29), (1.72 3.50), (1.72 4.58), (1.39 1.24), (1.39 1.33), (1.39 1.72), (1.39 2.78), (1.39 3.29), (1.39 3.50), (1.39 4.58), (1.34 1.24), (1.34 1.39), (1.34 1.72), (1.34 2.78), (1.34 3.29), (1.34 3.50), (1.34 4.58), (1.26 1.33), (1.26 3.29), (1.26 4.58), (1.25 1.39), (1.25 1.72), (1.25 2.78), (1.25 3.50).

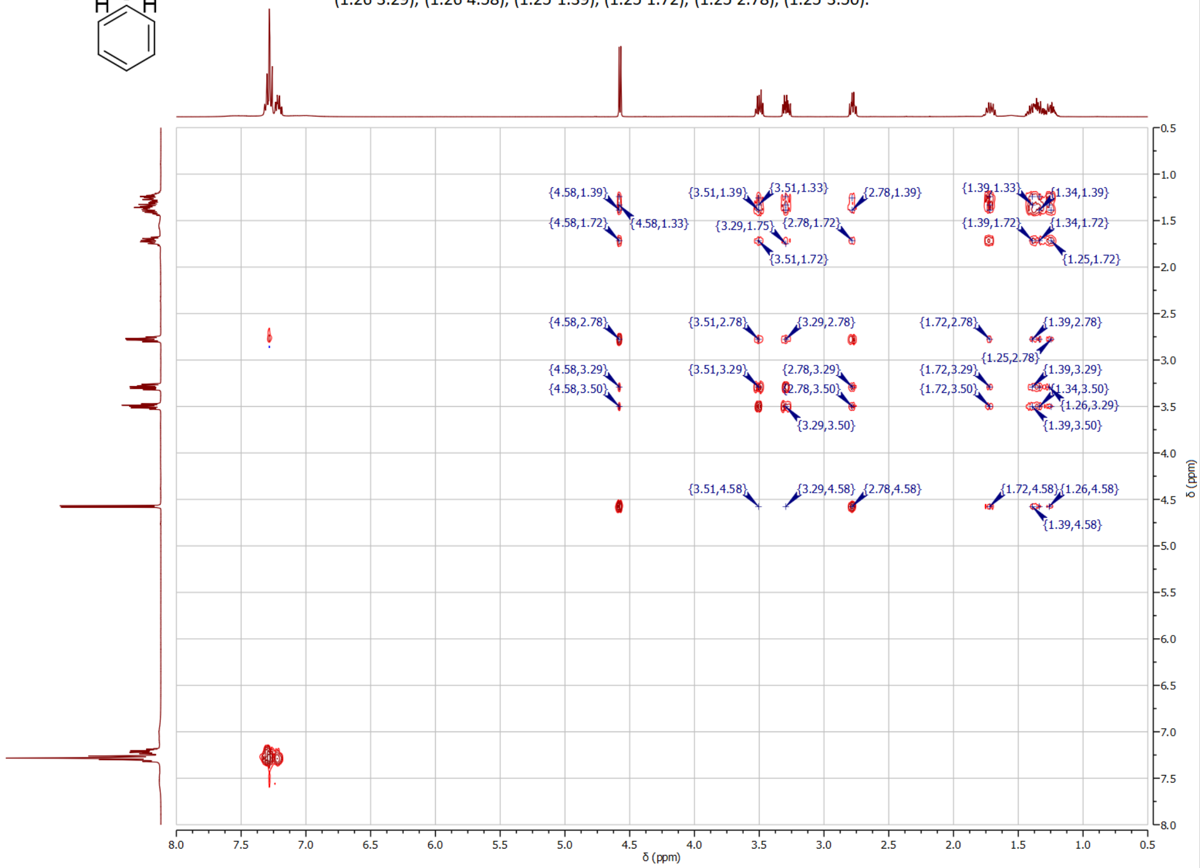


*Figure S 46. TOCSY NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-Diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$*

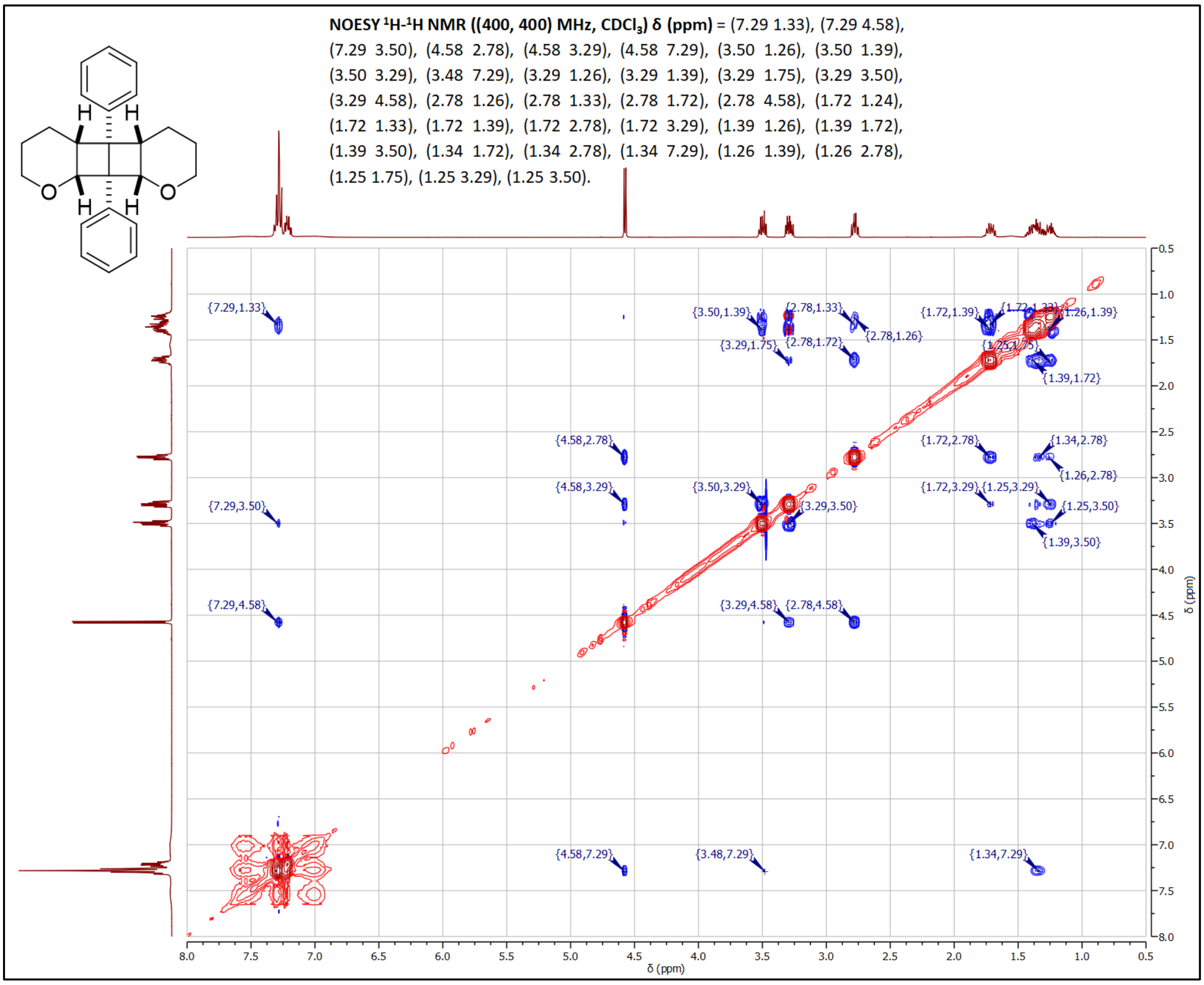
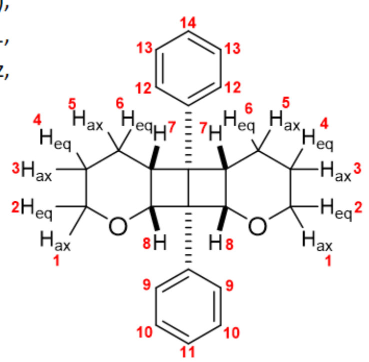


*Figure S 47. NOESY NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-Diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in $CDCl_3$*

^{1}H NMR (500 MHz, 373 K, DMSO-d$_6$) δ (ppm) = 7.28 (m, 2H, 9), 7.22 – 7.17 (m, 5H, [10, 11, 12]), 7.16 – 7.10 (m, 3H, [13, 14]), 4.50 (d, $^{3}J_{H8\text{-}H7}$=5.4 Hz, 2H, 8), 3.40 (ddd, $^{2}J_{H2\text{-}H1}$=11.2, $^{3}J_{H2\text{-}H3}$=6.6, $^{3}J_{H2\text{-}H4}$=5.8 Hz, 2H, 2), 3.24 (ddd, $^{2}J_{H1\text{-}H2}$=11.1, $^{3}J_{H1\text{-}H3}$=7.4, $^{3}J_{H1\text{-}H4}$=5.0 Hz, 2H, 1), 2.80 (ddd, $^{3}J_{H7\text{-}H6}$=7.9, $^{3}J_{H7\text{-}H5}$=7.8, $^{3}J_{H7\text{-}H8}$=5.5 Hz, 2H, 7), 1.66 (m, 2H, [6/5]), 1.39 – 1.30 (m, 2H, [5/6]), 1.26 – 1.16 (m, 4H, [3, 4]).



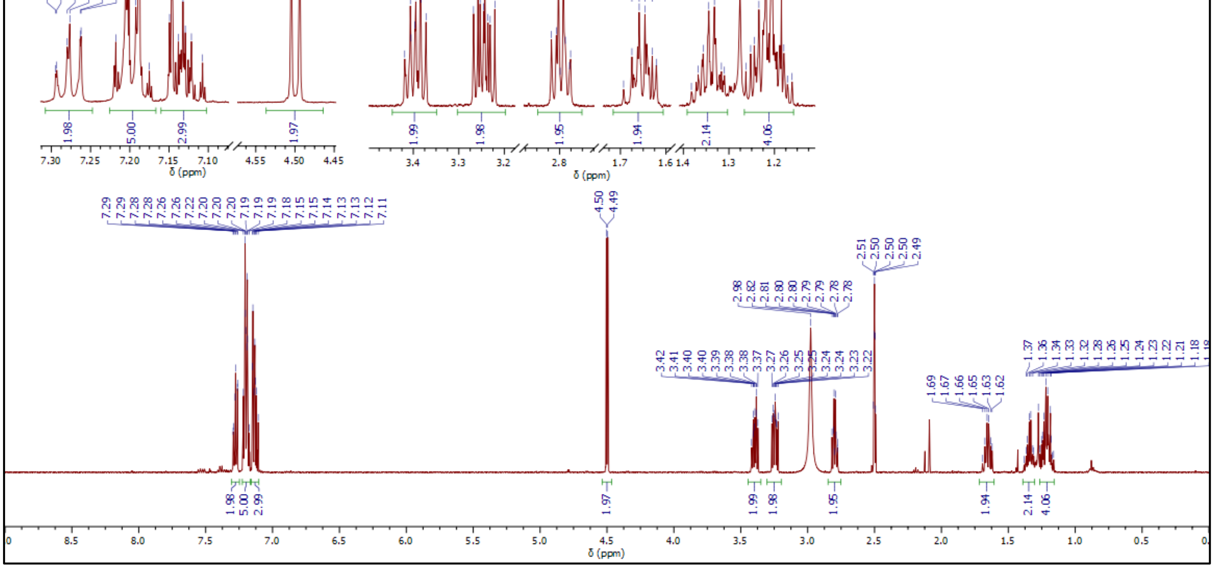


*Figure S 48. ^{1}H NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in DMSO-d$_6$ at 100 °C.*

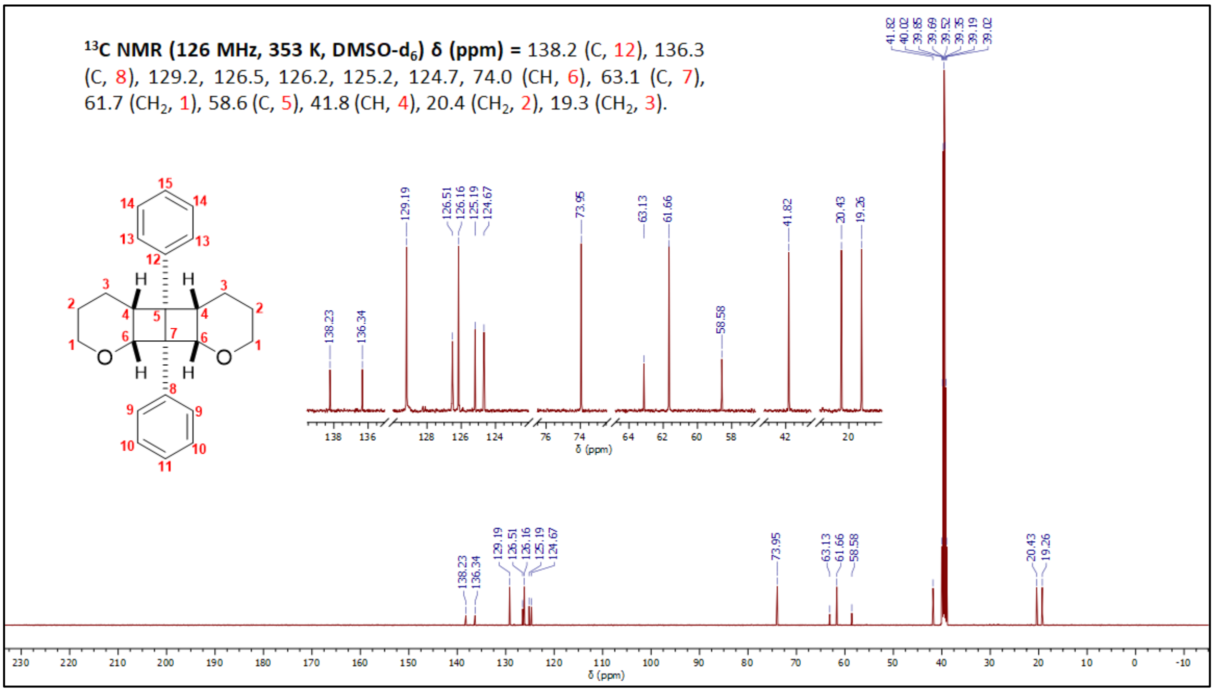


*Figure S 49. ^{13}C NMR spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**) in DMSO-d_6 at 80 °C.*

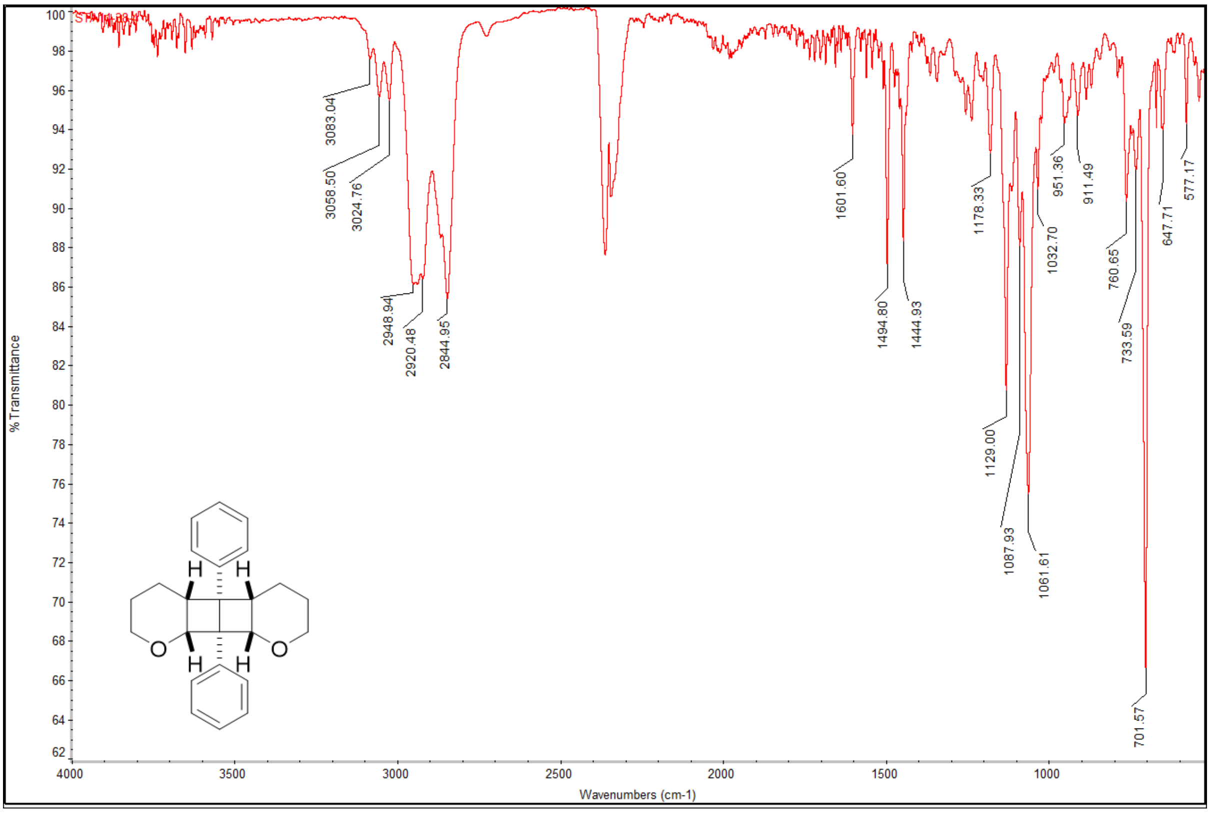


*Figure S 50. FT-ATR-IR spectrum of neat of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**).*

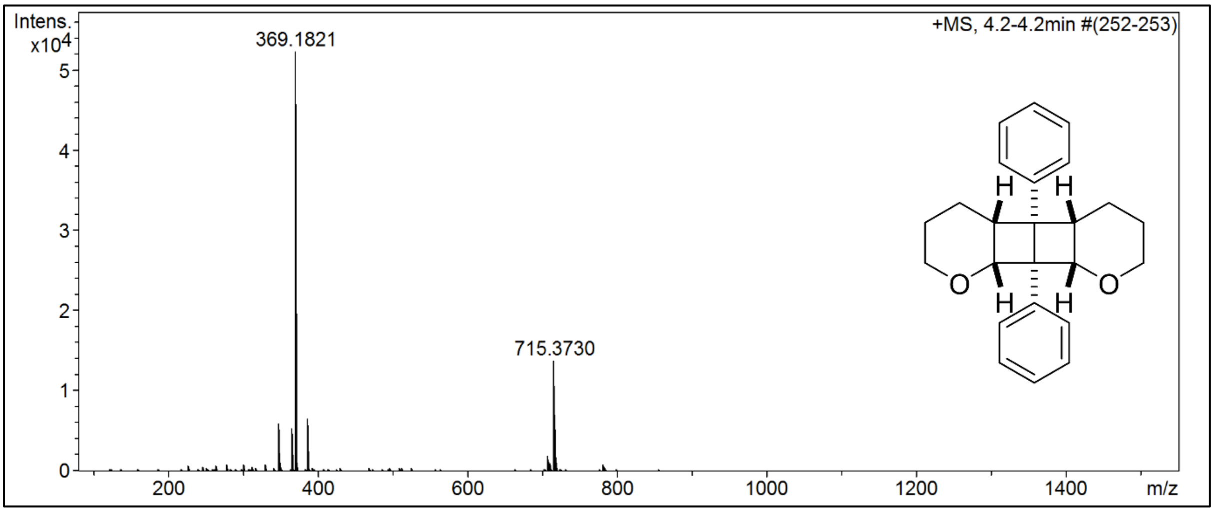


*Figure S 51. High resolution electrospray ionisation mass spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**).*

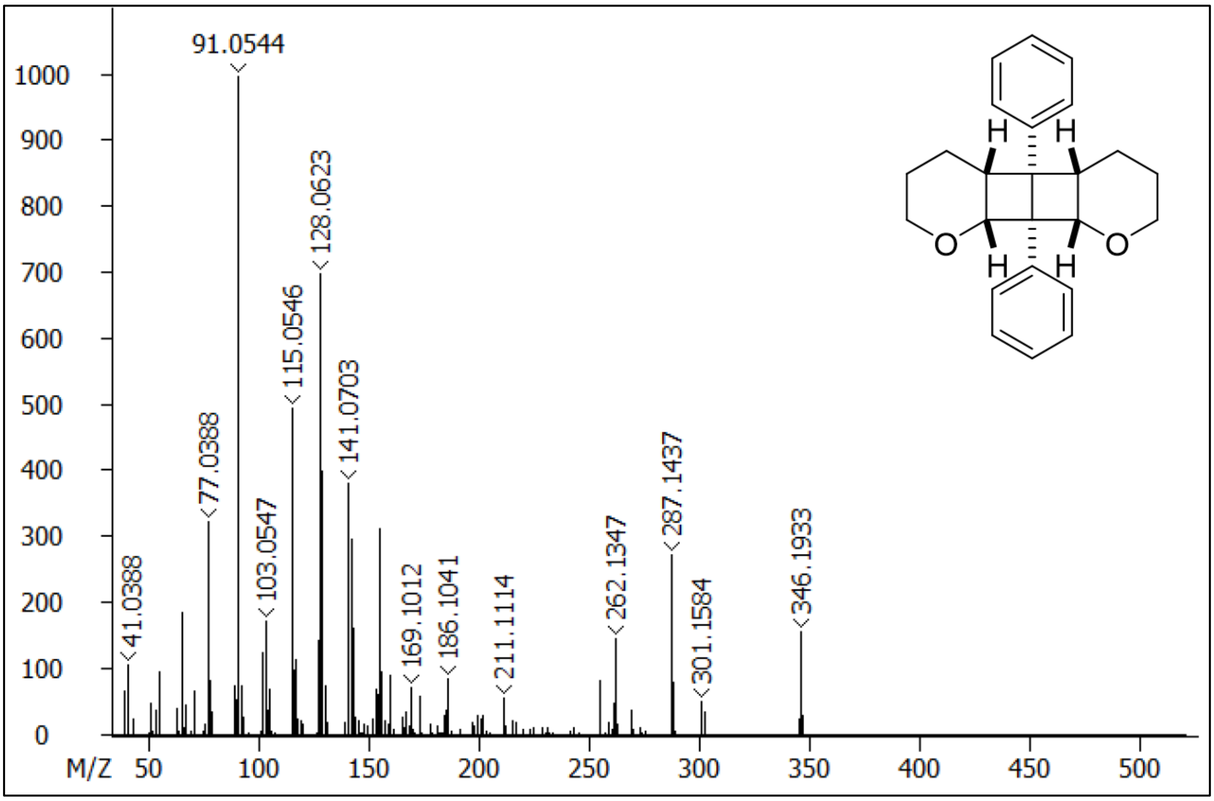
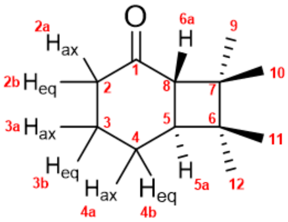


*Figure S 52. High resolution electron ionisation mass spectrum of (5α,6β,7α,12α,13β,14α)-1,11-Dioxa-6,13-diphenyltetracyclo[6.6.0.0^{5,14},0^{7,12}]tetradecane (**4**).*



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.40 (d, $^{3}J_{H6a\text{-}H5a}$=13.4 Hz, 1H, 6a), 2.18 – 2.11 (m, 2H, [2a, 2b]), 2.11 – 2.00 (m, 2H, [3a/3b, 5a]), 1.77 (m, 1H, [3b/3a]), 1.65 (dddd, J=12.2, 5.0, 3.6, 2.6 Hz, 1H, 4b), 1.46 (dddd, J=12.1, 11.7, 11.6, 4.8 Hz, 1H, 4a), 1.17 (s, 3H, 9), 1.00 (s, 3H, 11), 0.90 (s, 3H, 10), 0.88 (s, 3H, 12).

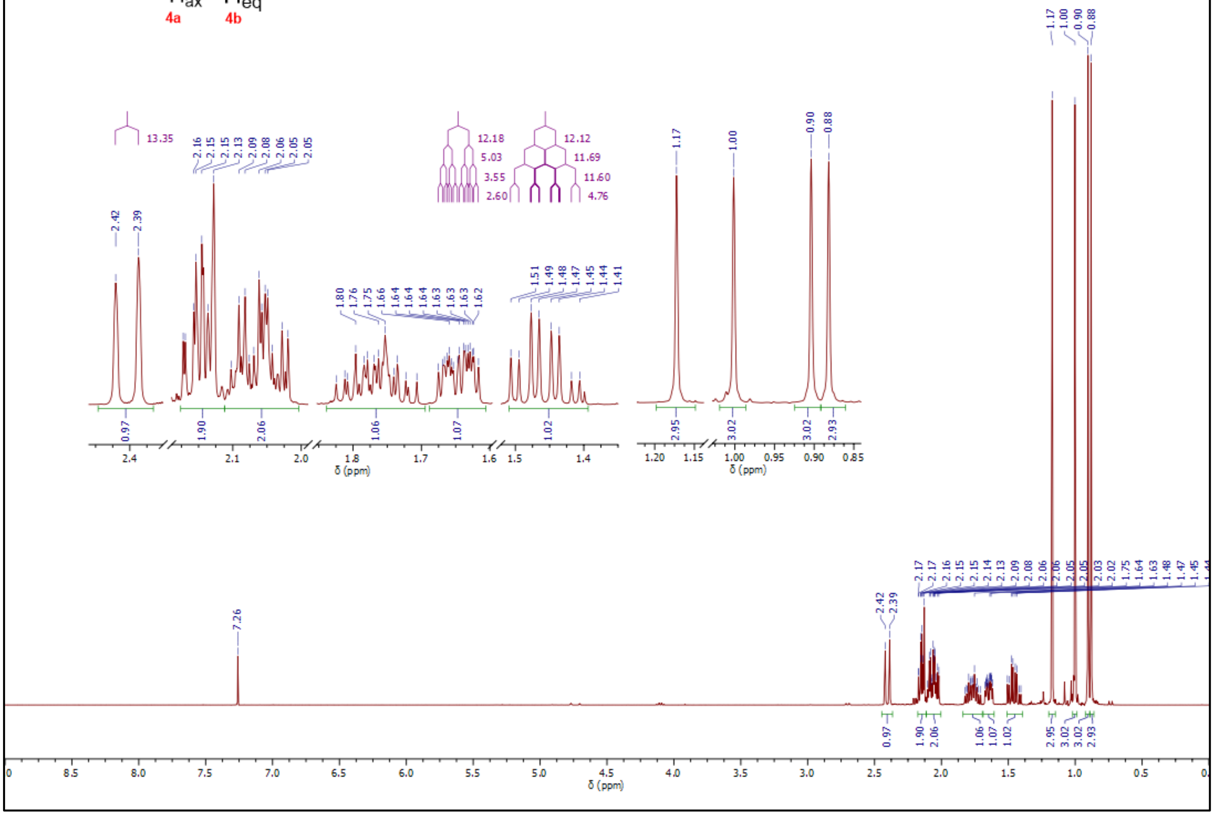


*Figure S 53. ^{1}H NMR spectrum of trans-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**5**).*

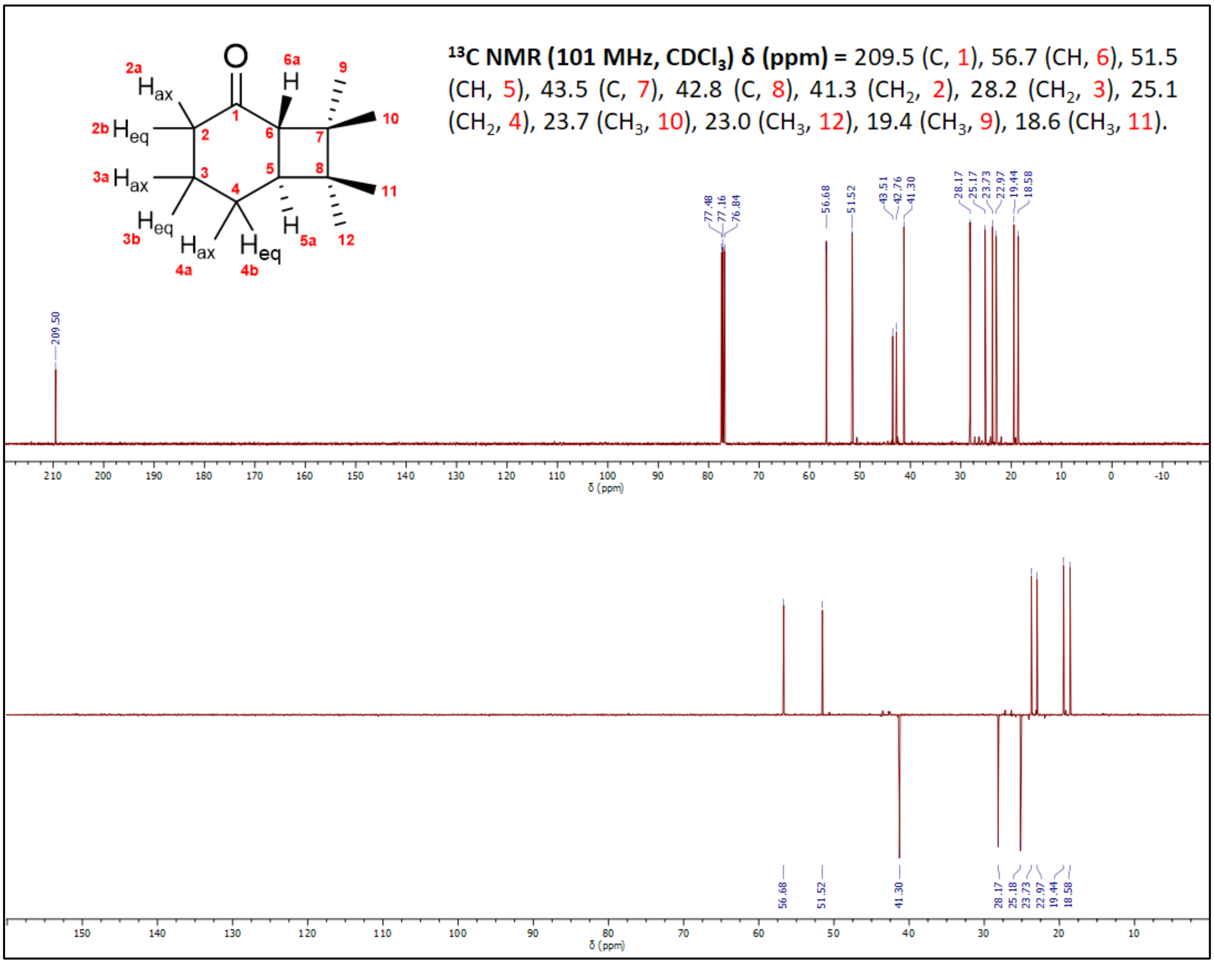


*Figure S 54. ^{13}C (top) and DEPT-135 (bottom) NMR spectrum of trans-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**5**).*

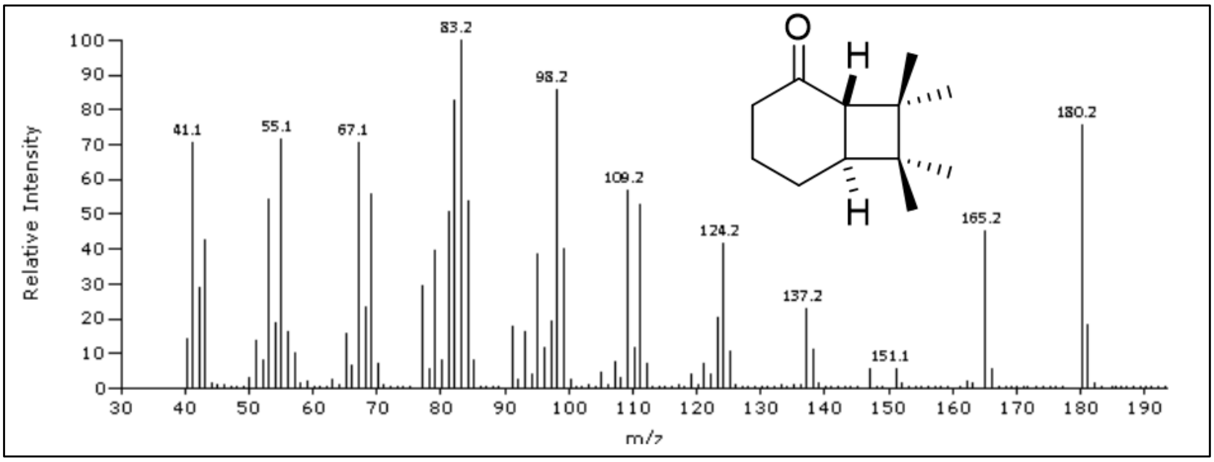


*Figure S 55. Electron ionisation mass spectrum of trans-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**5**).*

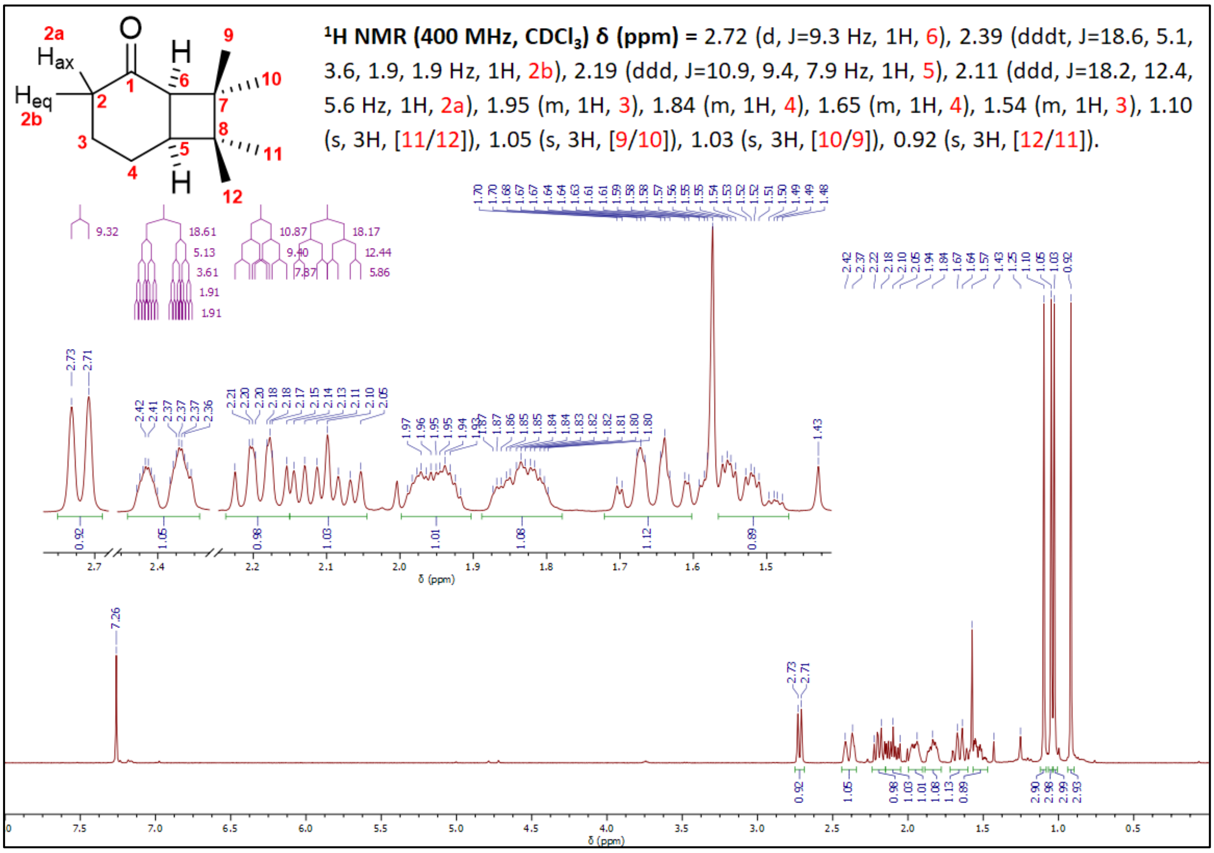


*Figure S 56. ¹H NMR spectrum of cis-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**6**).*

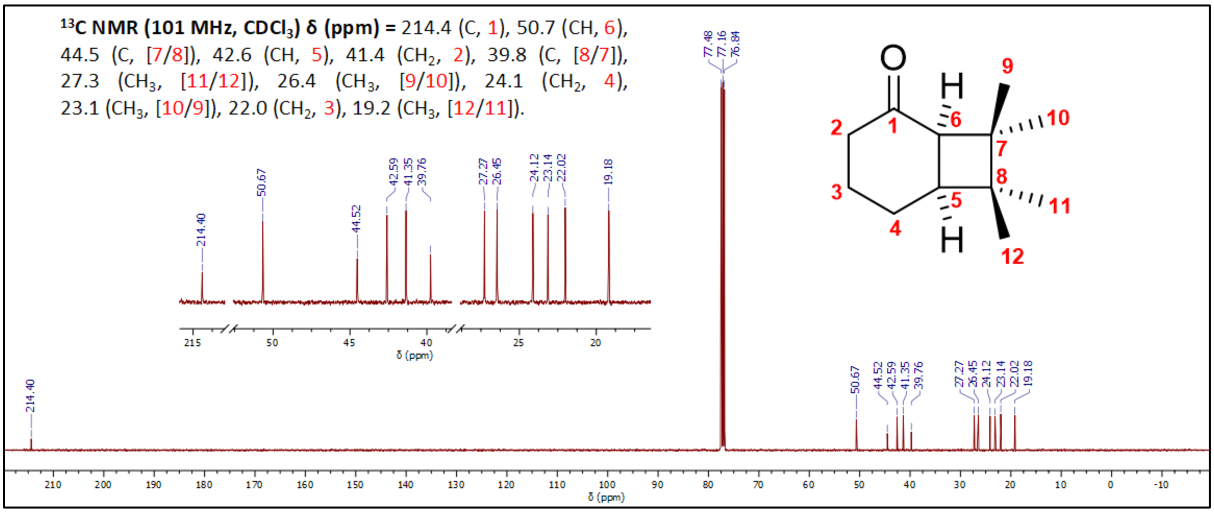


*Figure S 57. ¹³C NMR spectrum of cis-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**6**).*

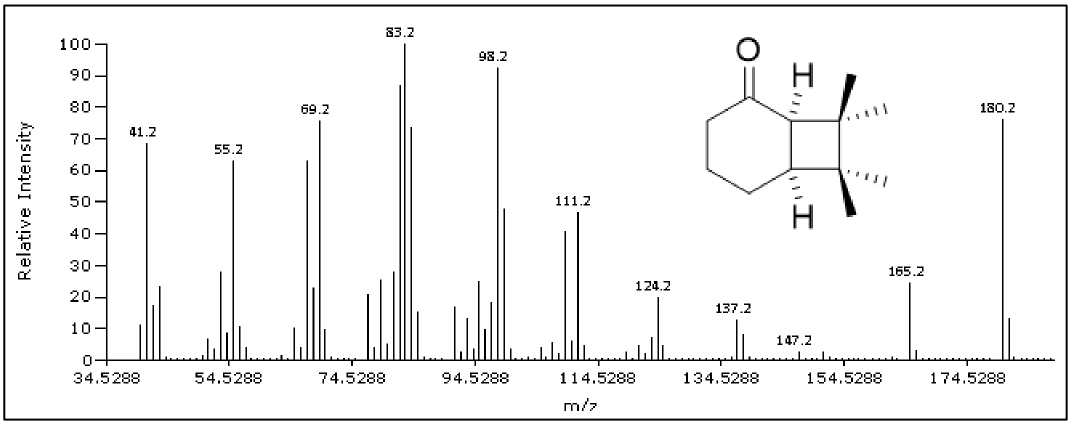
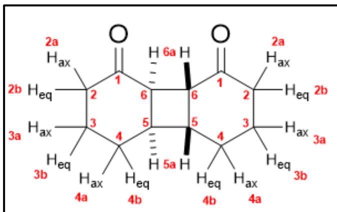


*Figure S 58. Electron ionisation mass spectrum of cis-7,7,8,8-tetramethylbicyclo[4.2.0]octan-2-one (**6**).*



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.12 (dd, $^3J_{H6a-H6a}$=6.4, $^3J_{H6a-H5a}$=1.7 Hz, 2H, **6a**), 2.82 (ddd, $^3J_{H5a-H5a}$ =5.8, $^3J_{H5a-H4a}$=4.4, $^3J_{H5a-H6a}$=1.8 Hz, 2H, **5a**), 2.42 (ddd, $^2J_{H2b-H2a}$=14.3, $^3J_{H2b-H3b}$=4.9, $^3J_{H2b-H3a}$=3.7, $^4J_{H2b-H4b}$=1.2 Hz, 2H, **2b**), 2.27 (dddd, $^2J_{H2a-H2b}$=14.3, $^3J_{H2a-H3a}$=12.1, $^3J_{H2a-H3b}$=5.2, $^4J_{H2a-H4a}$=0.5 Hz, 2H, **2a**), 1.98 (ddddd, $^2J_{H3b-H3a}$=13.5, $^3J_{H3b-H2b}$= 4.5, $^3J_{H3b-H4a}$= 4.5, $^3J_{H3b-H2a}$= 4.2, $^3J_{H3b-H4b}$= 4.2 Hz, 2H, **3b**), 1.86 (ddddd, $^2J_{H3a-H3b}$=13.5, $^3J_{H3a-H2a}$=12.0, $^3J_{H3a-H4a}$=12.0, $^3J_{H3a-H2b}$=3.7, $^3J_{H3a-H4b}$=3.7 Hz, 2H, **3a**), 1.70 (ddddd, $^2J_{H4a-H4b}$=13.7, $^3J_{H4a-H3a}$=12.0, $^3J_{H4a-H3b}$=4.4, $^3J_{H4a-H5a}$=4.2, $^4J_{H4a-H2a}$=0.5 Hz, 2H, **4a**), 1.52 (m, 2H, **4b**).

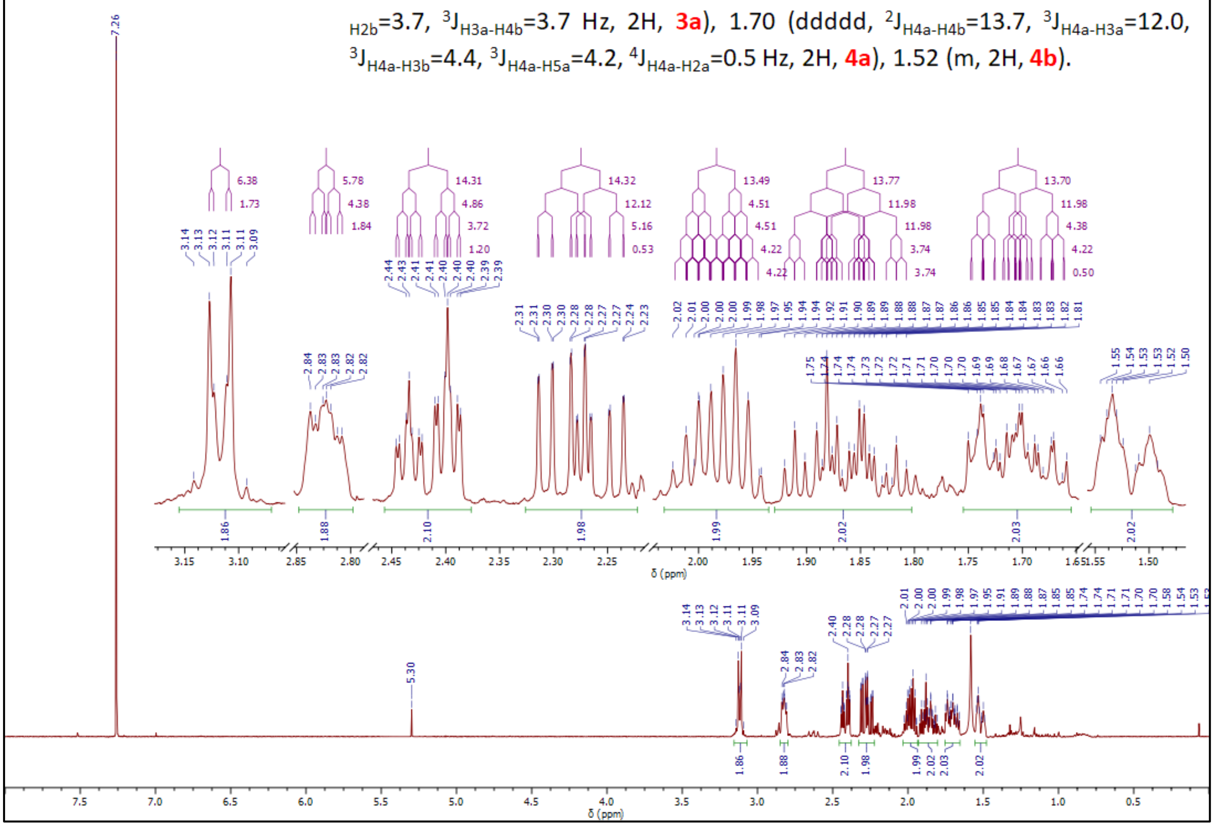


*Figure S 59. ^{1}H NMR spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (**7**).*

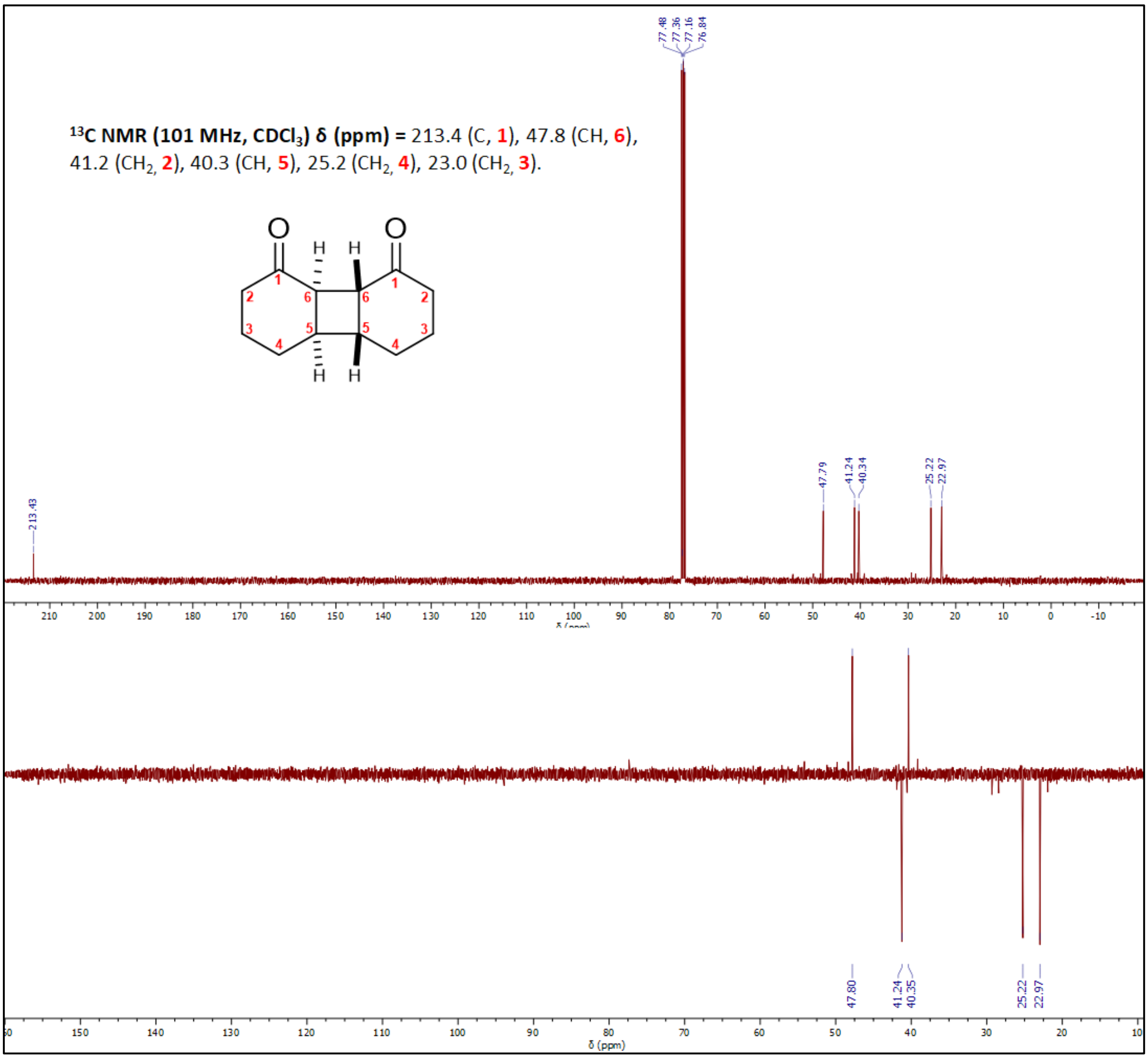


*Figure S 60. [13]C (top) and DEPT-135 (bottom) NMR spectrum of cis-anti-cis-tricyclo[6.4.0.0[2,7]]dodecane-3,12-dione (**7**).*

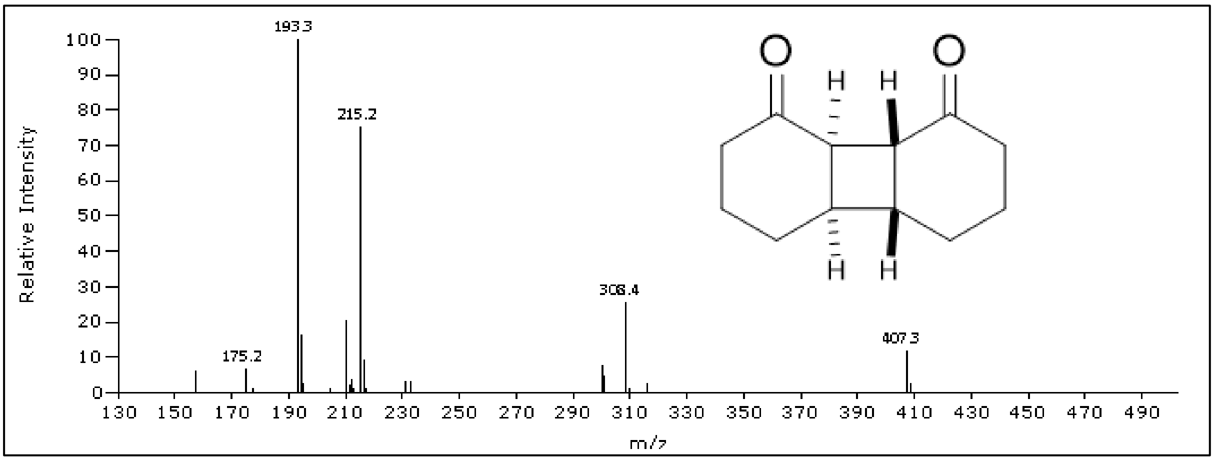


*Figure S 61. Electrospray ionisation mass spectrum of cis-anti-cis-tricyclo[6.4.0.0[2,7]]dodecane-3,12-dione (**7**).*

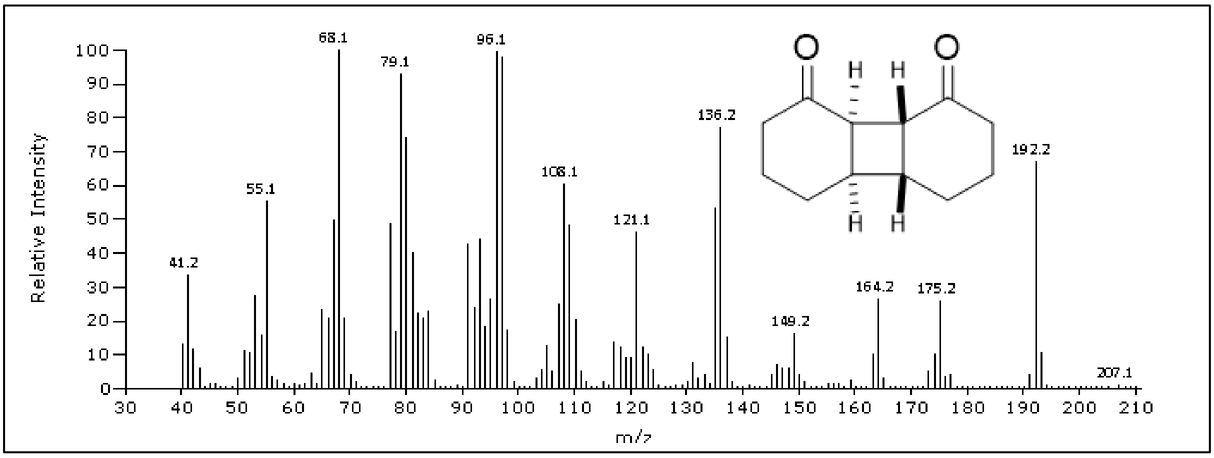


Figure S 62. Electron ionisation mass spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (7).

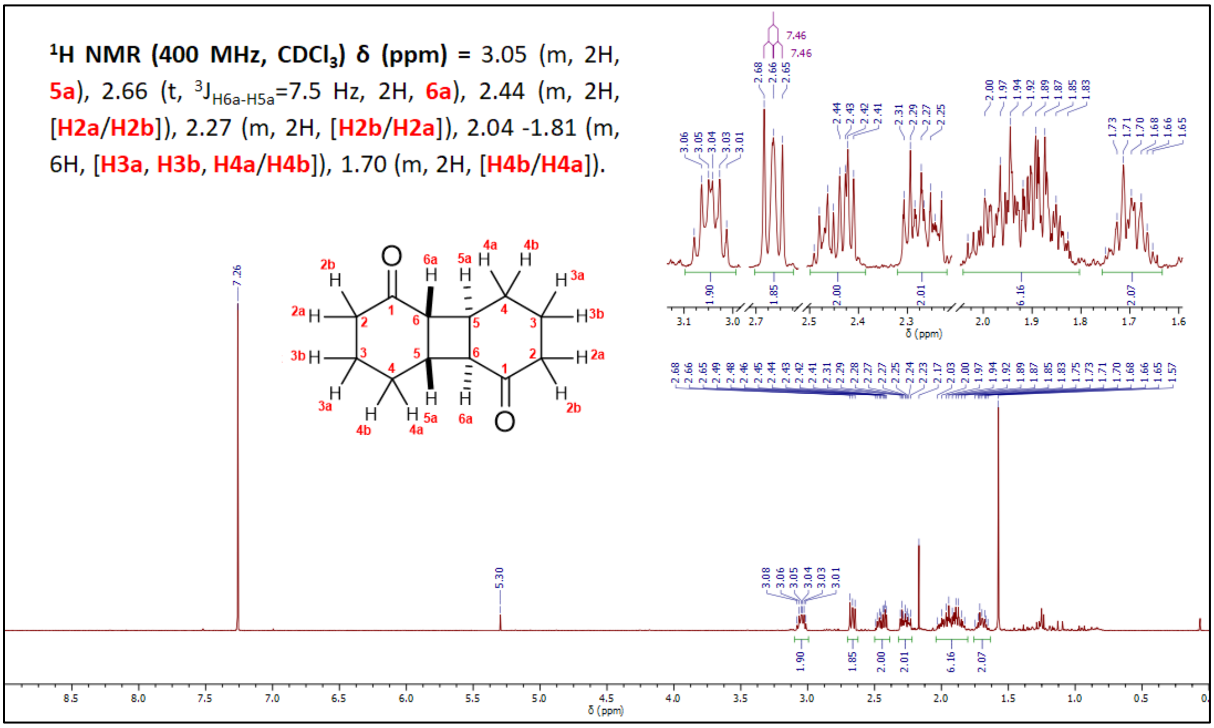


*Figure S 63. ^{1}H NMR spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (**8**).*

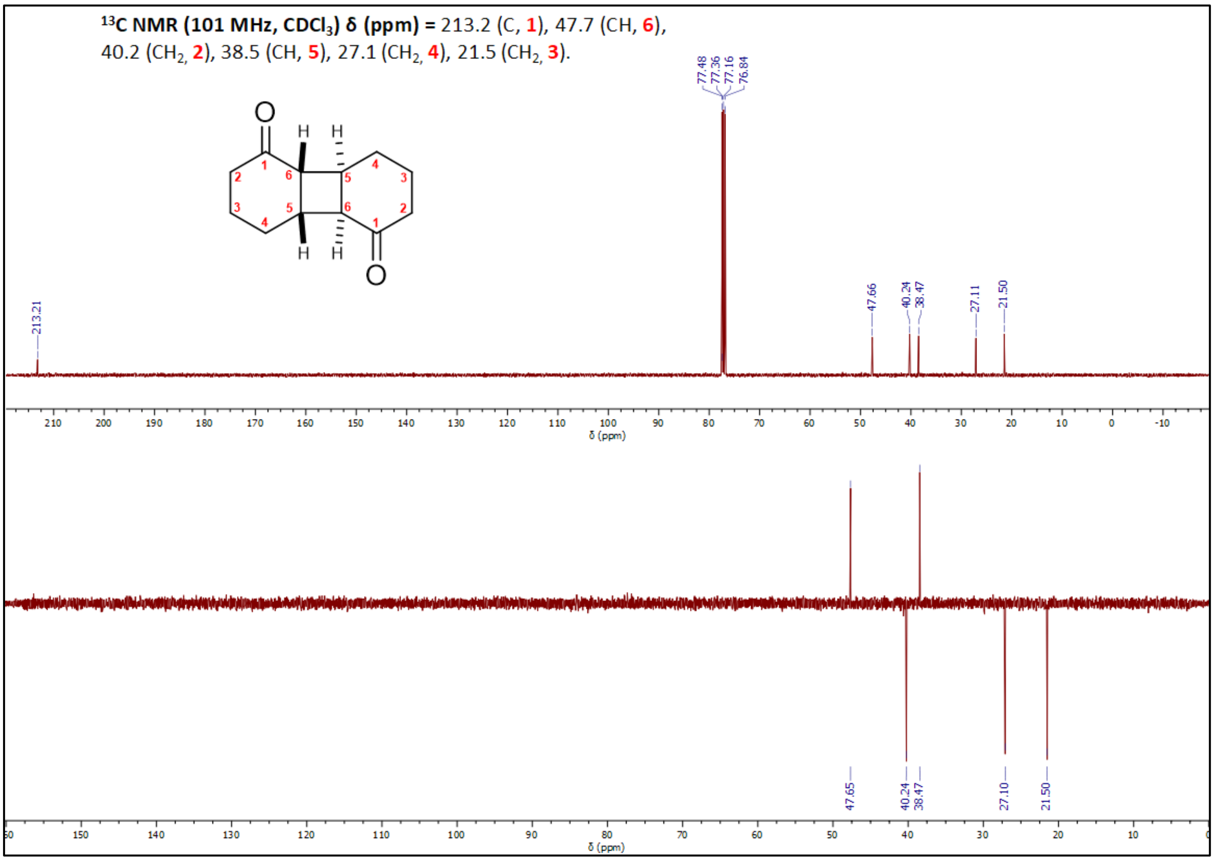


*Figure S 64. ^{13}C (top) and DEPT-135 (bottom) NMR spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (**8**).*

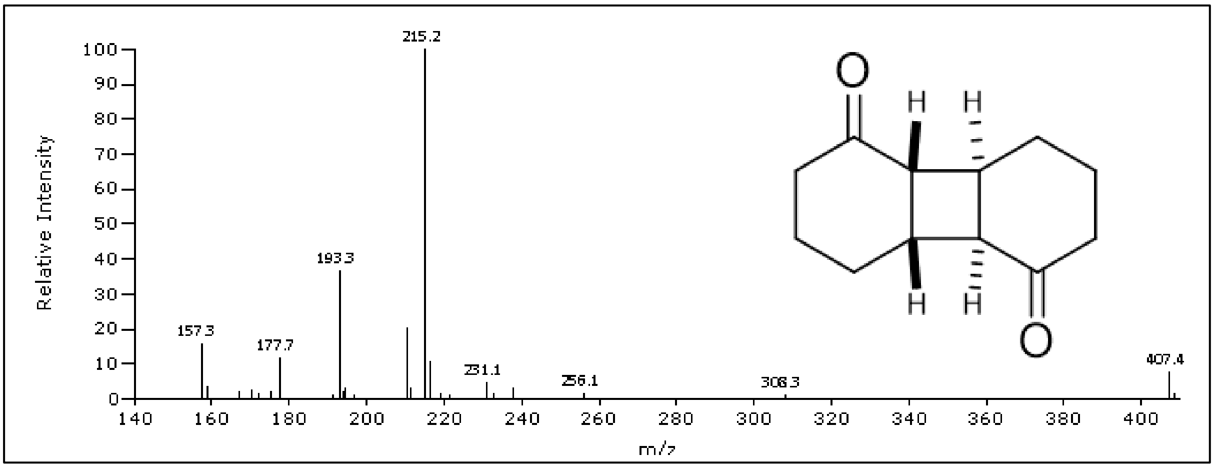


*Figure S 65. Electrospray ionisation mass spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (**8**).*

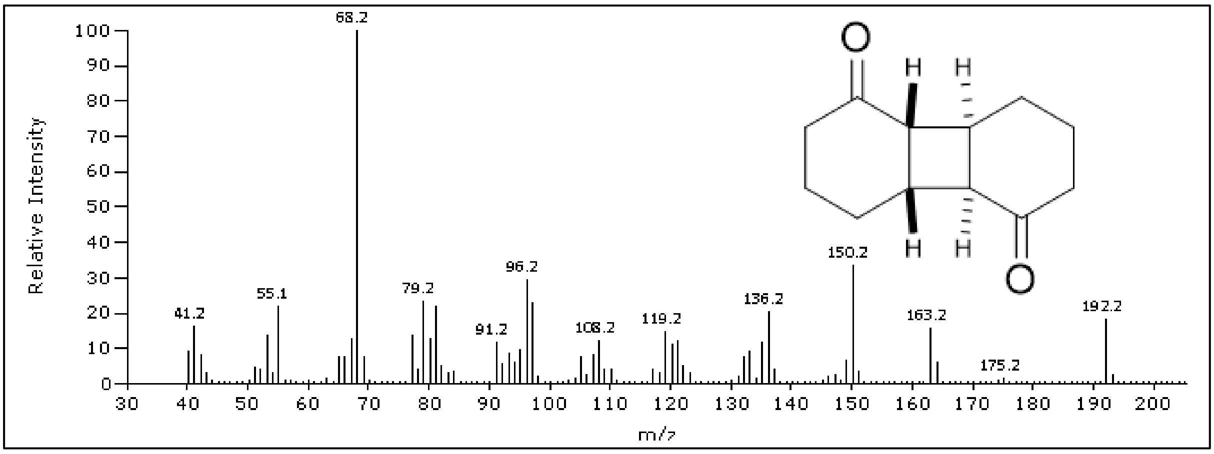
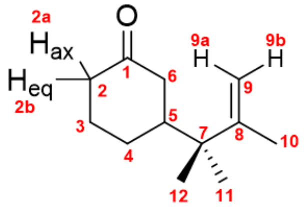


*Figure S 66. Electron ionisation mass spectrum of cis-anti-cis-tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (**8**).*



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.79 (br s, 1H, 9b), 4.72 (br s, 1H, 9a), 2.36 (ddd, J=14.2, 4.4, 2.1 Hz, 1H, 2b), 2.30 (m, 1H, 6), 2.22 (ddd, J=14.0, 13.8, 6.4 Hz, 2a), 2.09 (m, 1H, 3), 2.03 (dd, J=13.6, 13.5 Hz, 1H, 6), 1.85 – 1.74 (m, 2H, [4, 5]), 1.68 (s, 3H, 10), 1.56 (m, 1H, 3), 1.32 (ddd, J=13.3, 12.8, 3.7 Hz, 1H, 4), 1.04 (s, 3H, [11/12]), 1.00 (s, 3H, [12/11]).

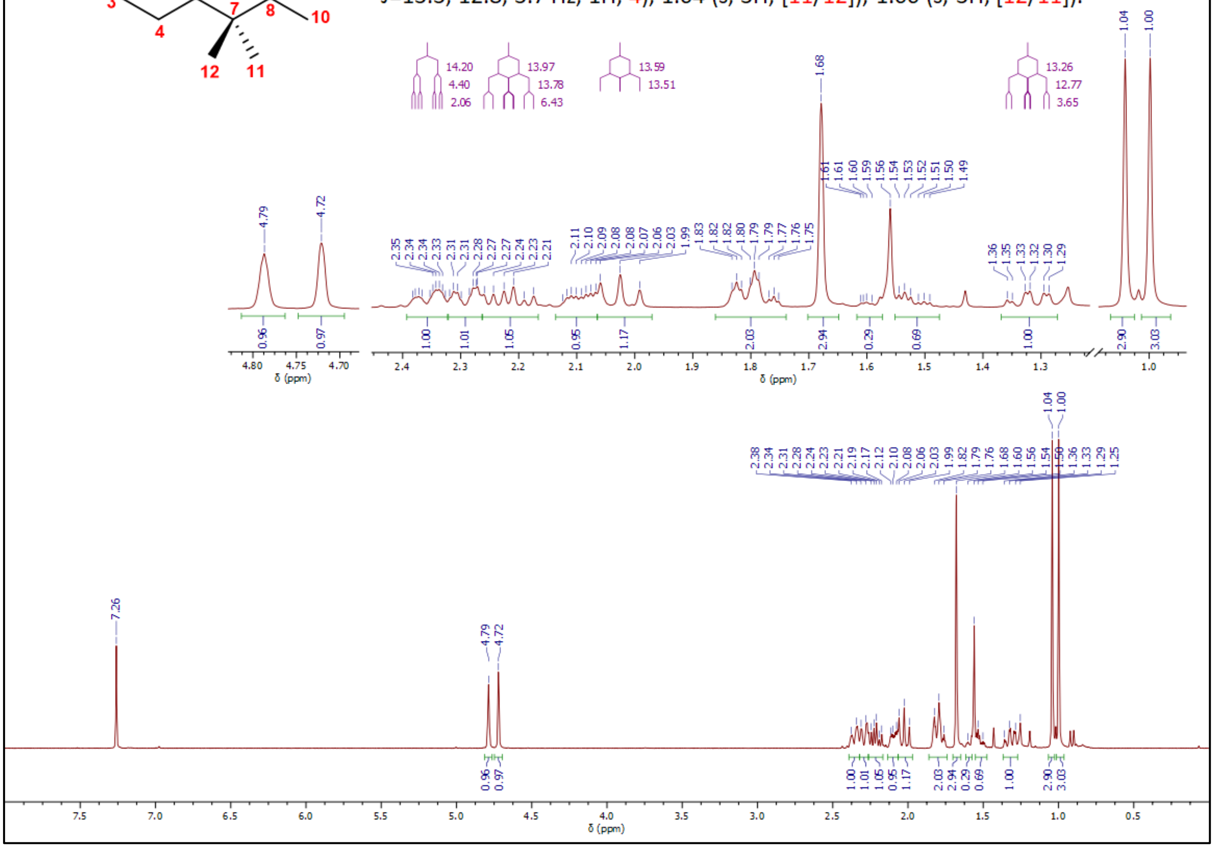


*Figure S 67. ^{1}H NMR spectrum of 3-(2,3-dimethylbut-3-en-2-yl)cyclohexan-1-one (**9**).*

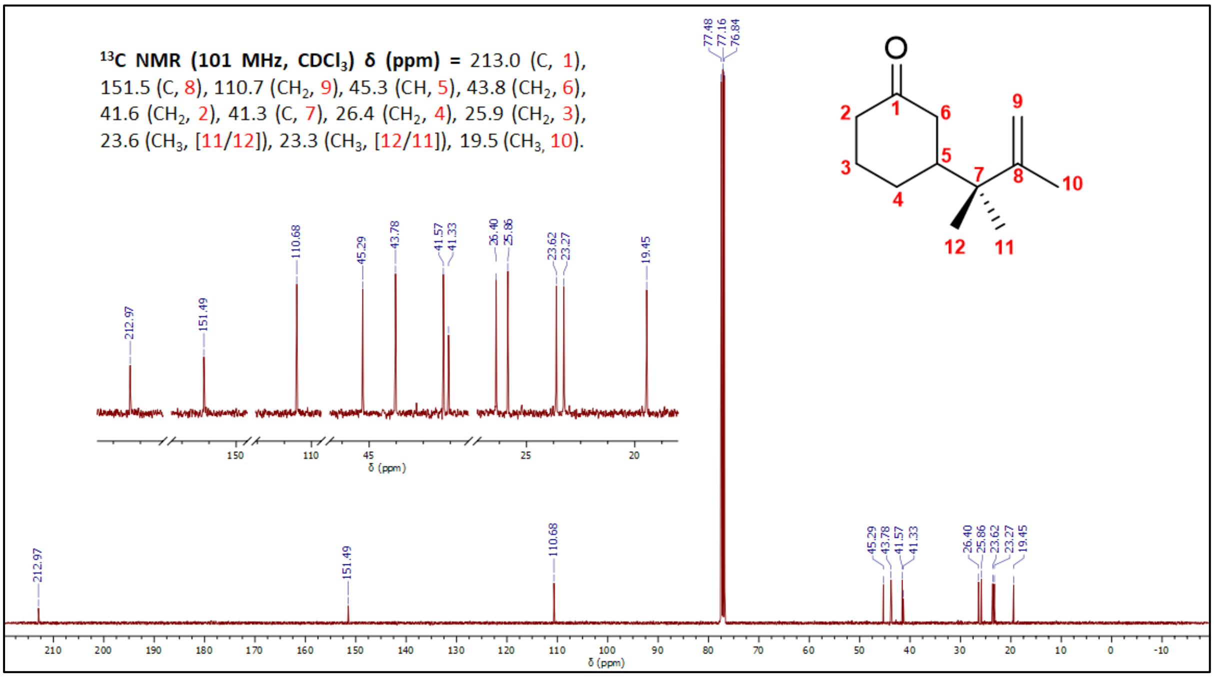


*Figure S 68. ¹³C NMR spectrum of 3-(2,3-dimethylbut-3-en-2-yl)cyclohexan-1-one (**9**).*

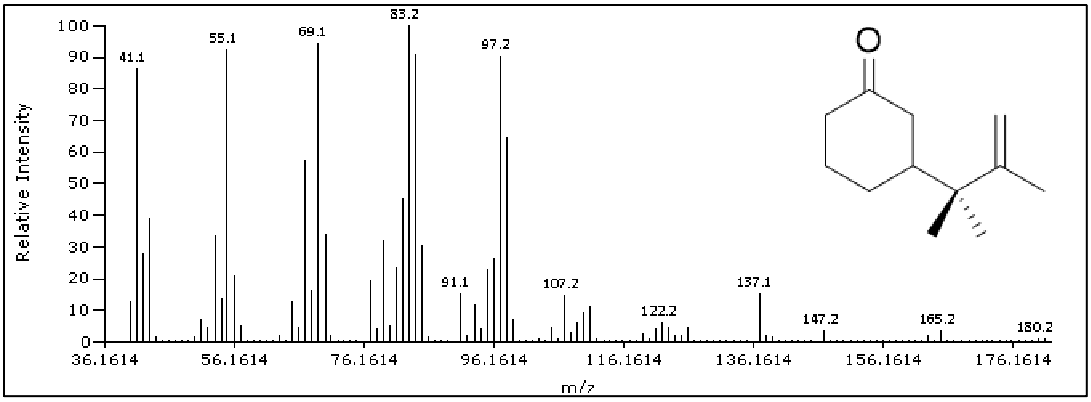


*Figure S 69. Electron ionisation mass spectrum of 3-(2,3-dimethylbut-3-en-2-yl)cyclohexan-1-one (**9**).*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.70 (ddd, $^3J_{H5-H4}$=8.0 Hz, $^4J_{H5-H3}$=1.3 Hz, $^5J_{H5-H2}$=0.6 Hz, 2H, 5), 7.90 (ddd, $^3J_{H2-H3}$=7.7 Hz, $^4J_{H2-H4}$=1.6 Hz, $^5J_{H2-H5}$=0.6 Hz, 2H, 2), 7.75 (s, 2H, 1), 7.67 (ddd, $^3J_{H4-H5}$=8.3 Hz, $^3J_{H4-H3}$=7.0 Hz, $^4J_{H4-H2}$=1.6 Hz, 2H, 4), 7.61 (ddd, $^3J_{H3-H2}$=7.7 Hz, $^3J_{H3-H4}$=7.0 Hz, $^4J_{H3-H5}$=1.3 Hz, 2H, 3).

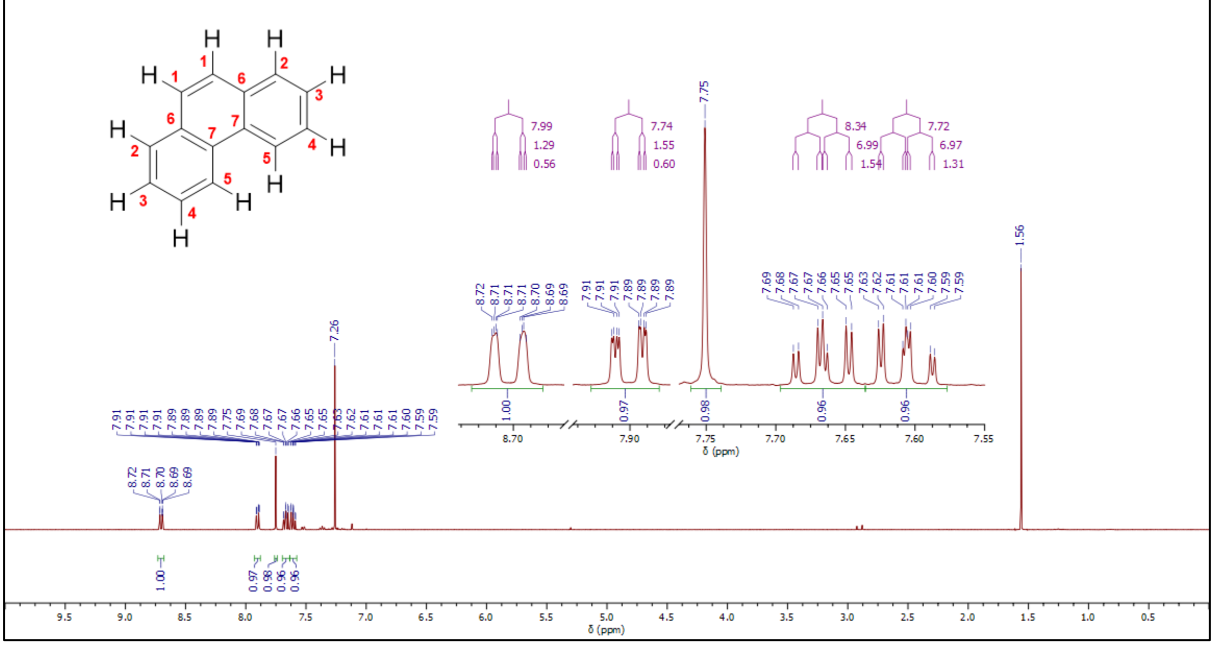


*Figure S 70. ^{1}H NMR spectrum of phenanthrene (**10**).*

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 132.2 (C, 6), 130.4 (C, 7), 128.7 (CH, 2), 127.1 (CH, 1), 126.7 (CH, [3, 4]), 122.8 (CH, 5).

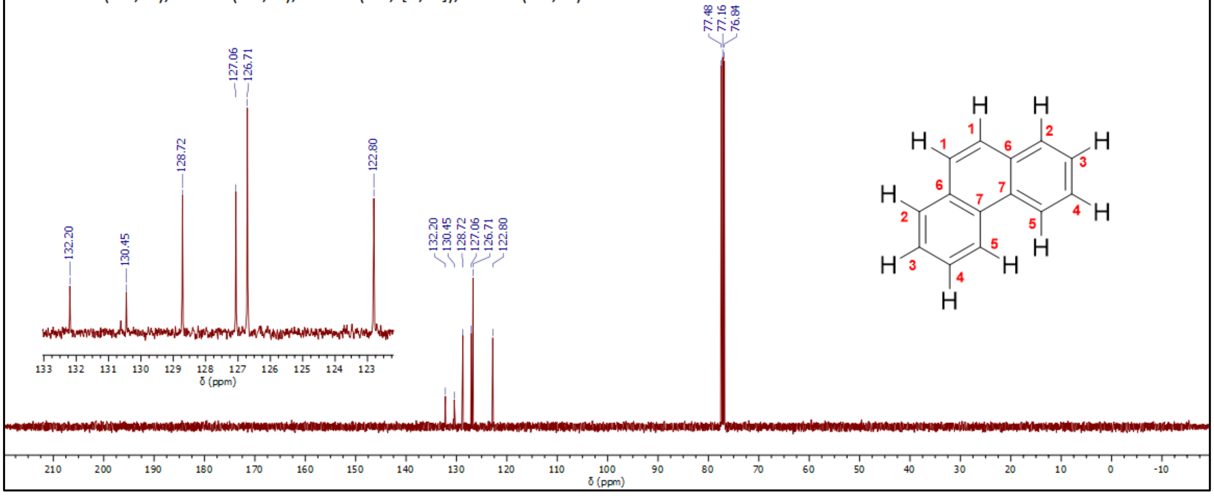


*Figure S 71. ^{13}C NMR spectrum of phenanthrene (**10**).*

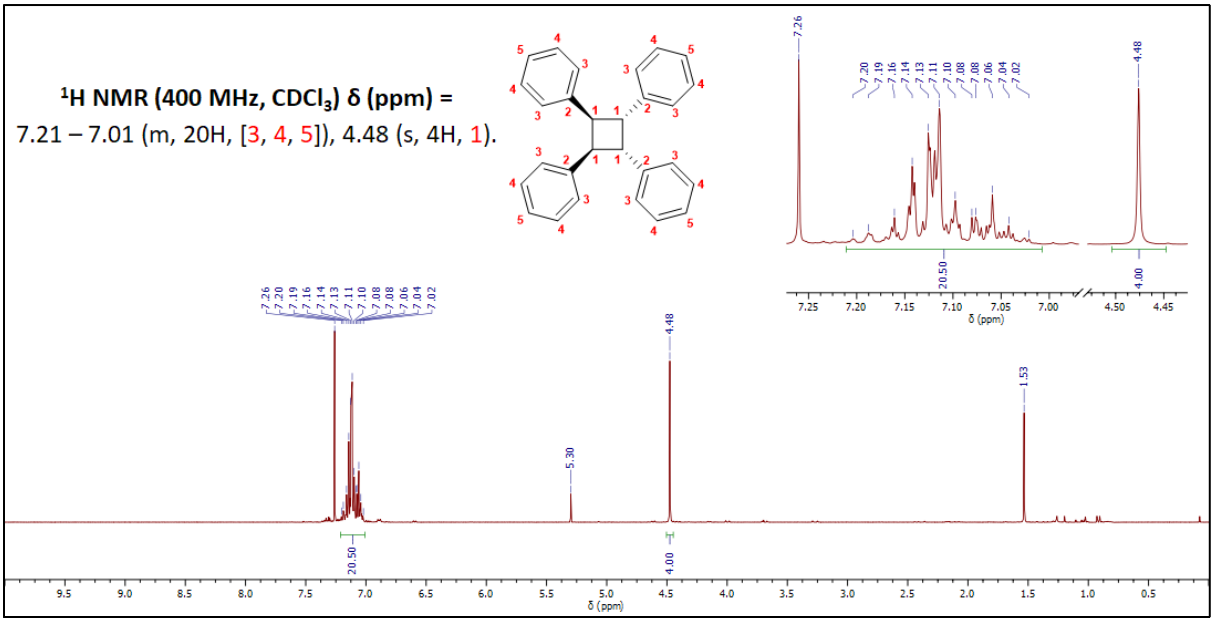


Figure S 72. ¹H NMR spectrum of (1α,2α,3β,4β)-1,2,3,4-Tetraphenylcyclobutane (**11**).

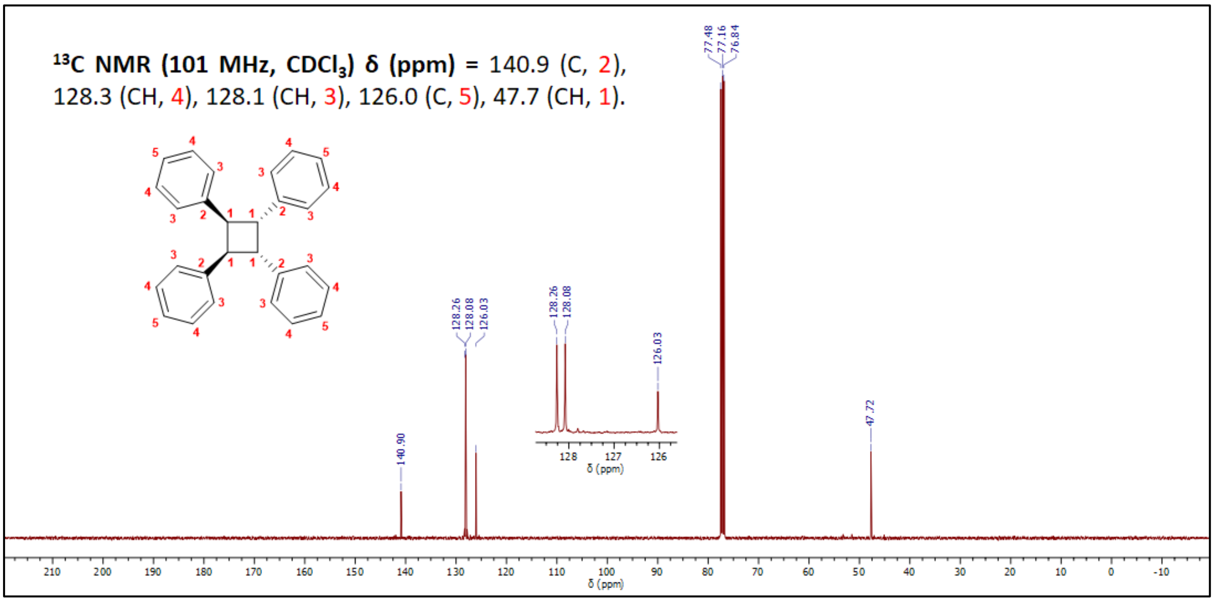


Figure S 73. ¹³C NMR spectrum of (1α,2α,3β,4β)-1,2,3,4-Tetraphenylcyclobutane (**11**).

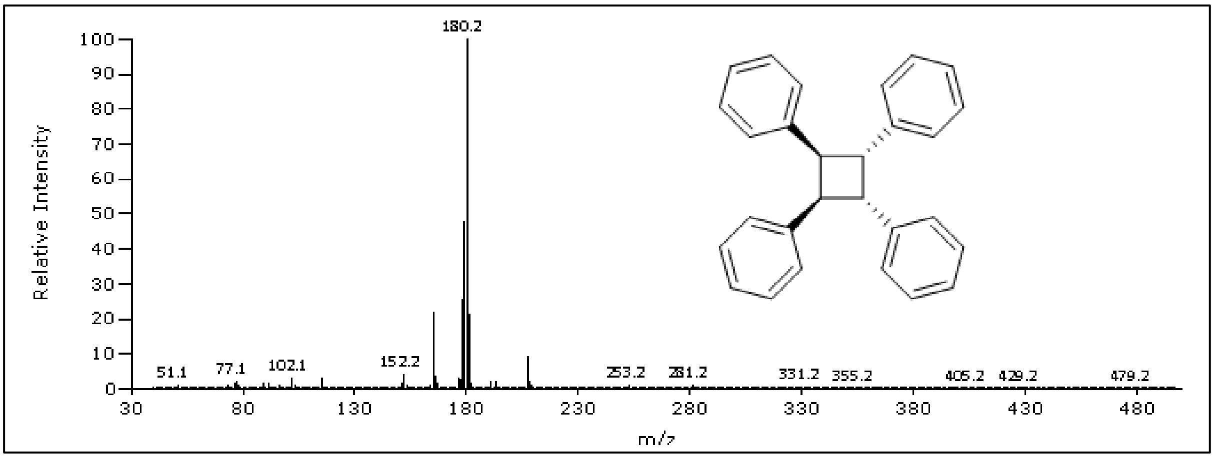


*Figure S 74. Electron ionisation mass spectrum of (1α,2α,3β,4β)-1,2,3,4-Tetraphenylcyclobutane (**11**).*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.33 – 7.28 (m, 16H, [3, 4]), 7.22 (m, 4H, 5), 3.70 (s, 4H, 1).

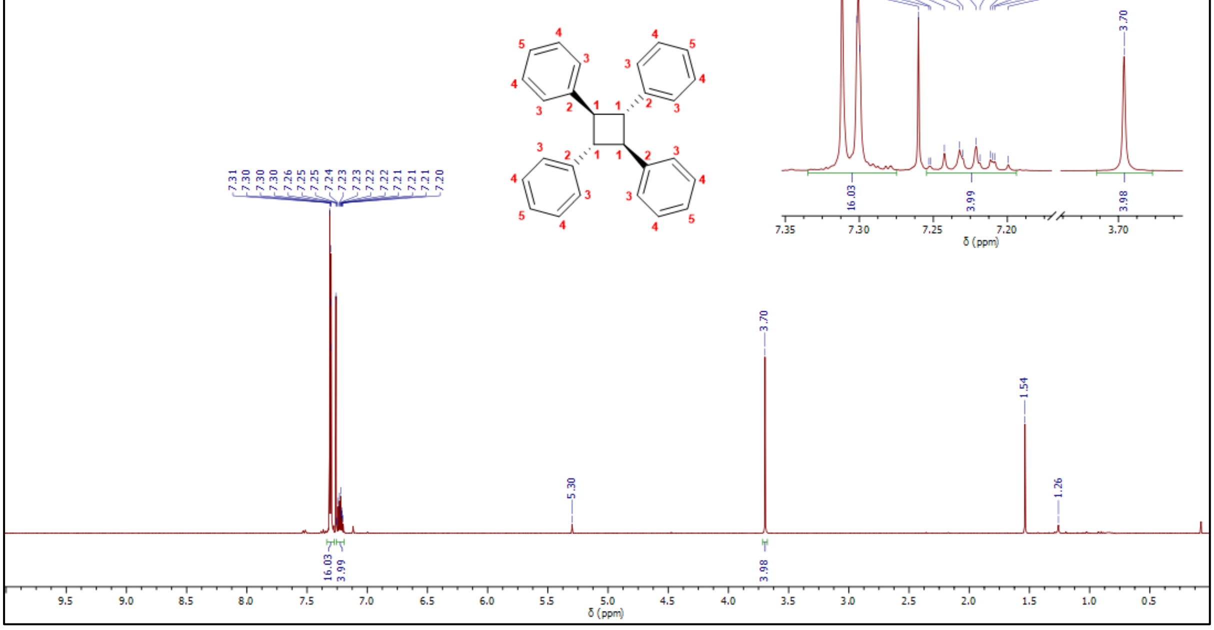


*Figure S 75. ^{1}H NMR spectrum of (1α,2β,3α,4β)-1,2,3,4-Tetraphenylcyclobutane (**12**).*

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 142.8 (C, 2), 128.7 (CH, 4), 127.2 (CH, 3), 126.7 (CH, 5), 51.8 (CH, 1).

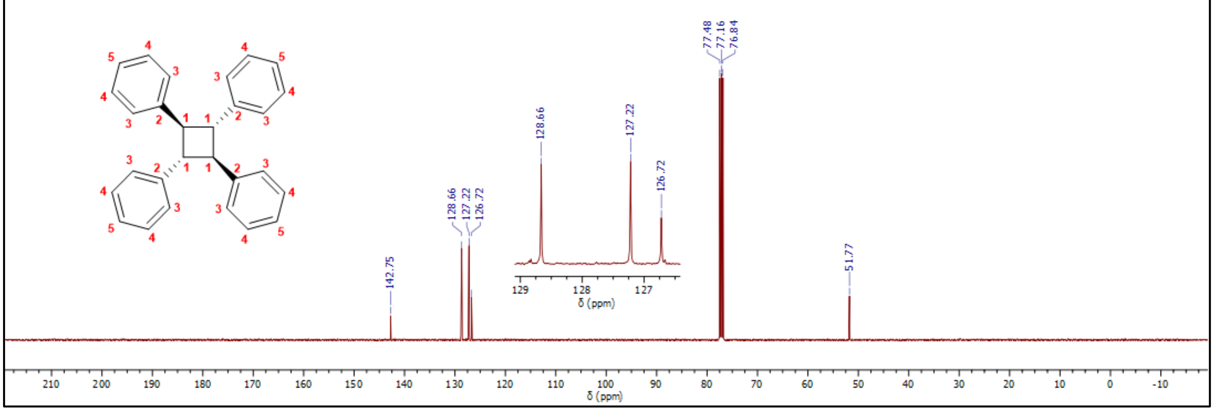


*Figure S 76. ^{13}C NRM spectrum of (1α,2β,3α,4β)-1,2,3,4-Tetraphenylcyclobutane (**12**).*

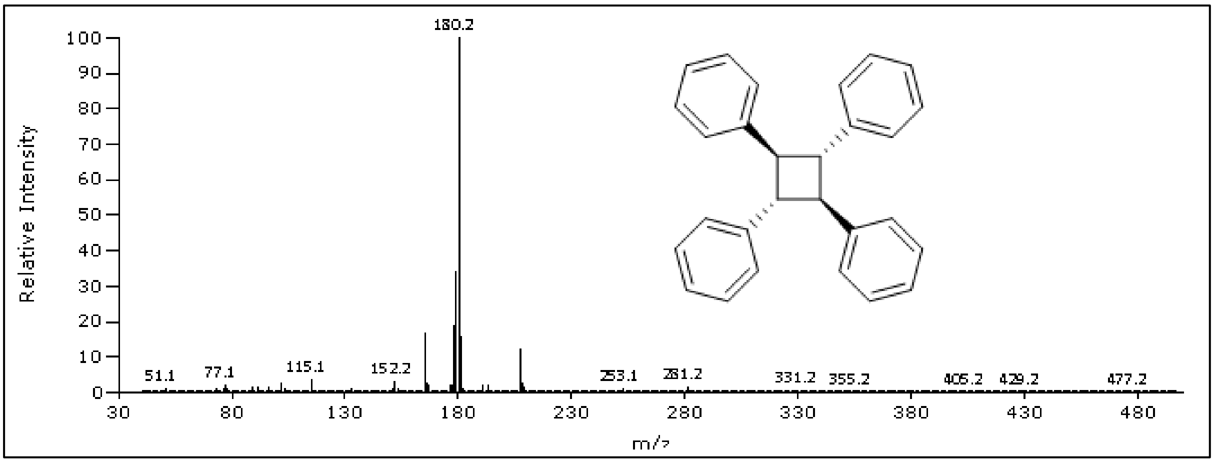


*Figure S 77. Electron ionisation mass spectrum of (1α,2β,3α,4β)-1,2,3,4-Tetraphenylcyclobutane (**12**).*

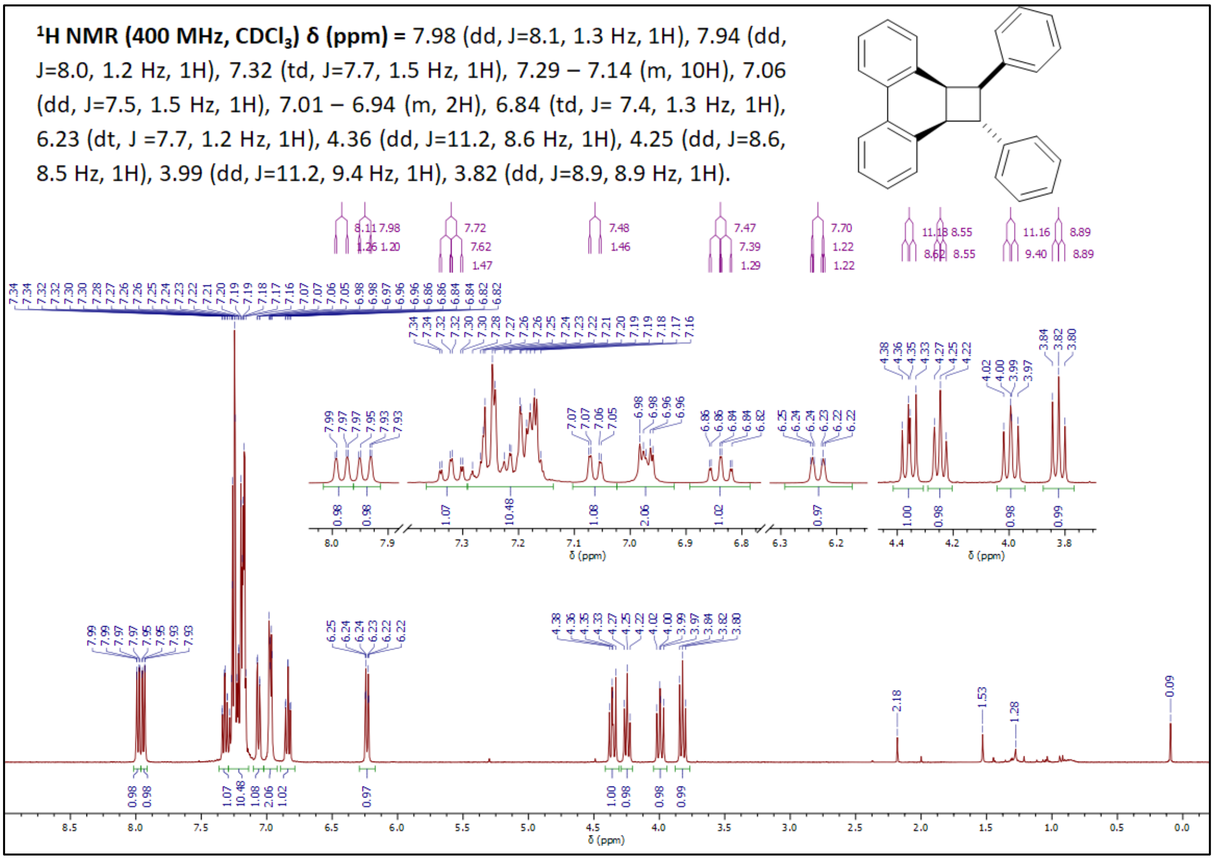
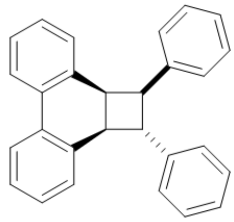


*Figure S 78. ^{1}H NMR spectrum of (1α,2β,2aR,10bS)-1,2-diphenyl-1,2,2a,10b-tetrahydrocyclobuta[l]phenanthrene (**13**).*

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 142.2, 138.7, 136.0, 133.1, 132.9, 132.3, 132.2, 129.2, 128.5, 128.4, 128.0, 127.8, 127.5, 127.0, 127.0, 126.8, 126.7, 126.6, 123.9, 122.9, 53.2, 51.8, 42.7, 40.5.



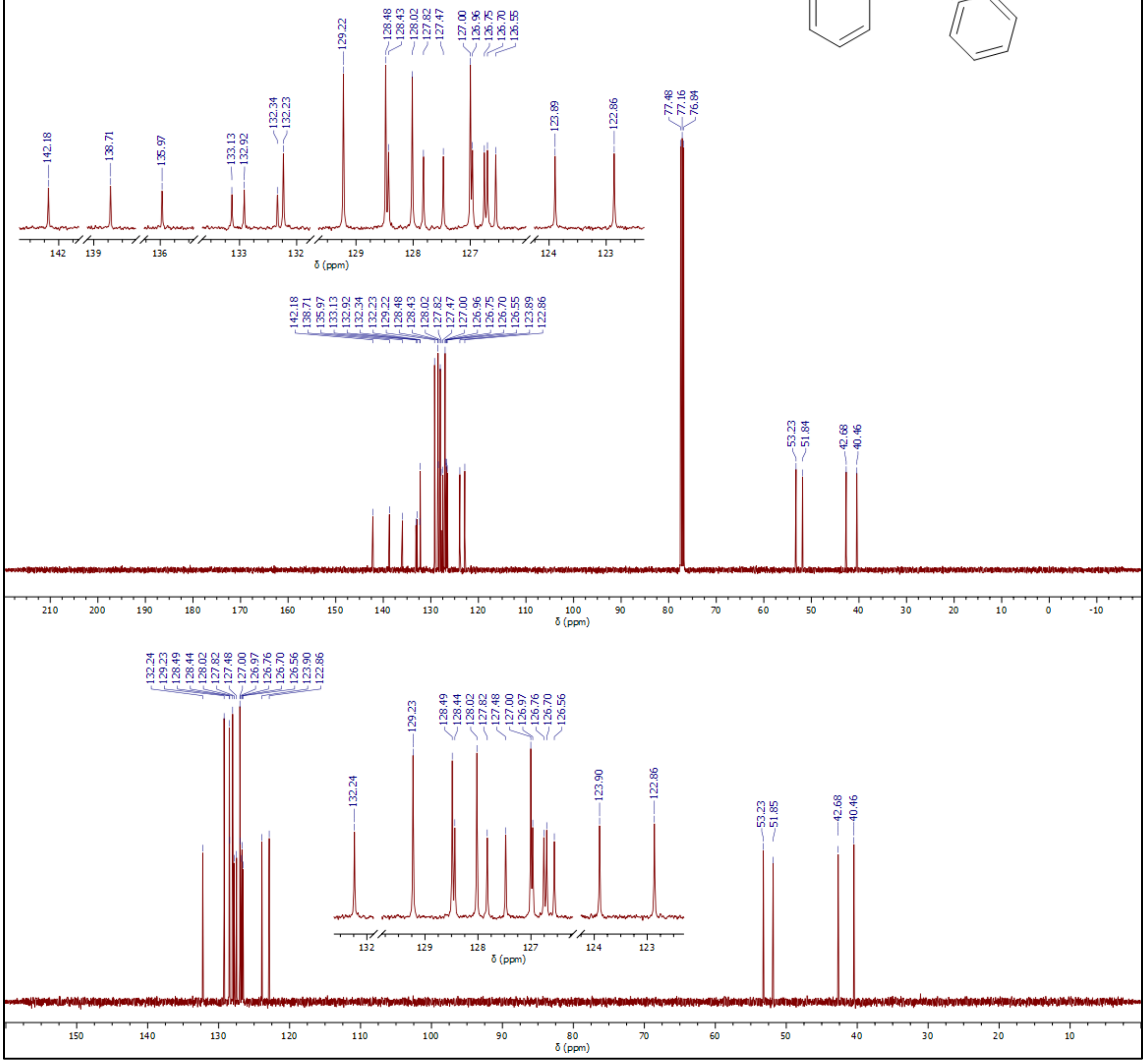


*Figure S 79. ^{13}C (top) and DEPT-135 (bottom) NMR spectrum of (1α,2β,2aR,10bS)-1,2-diphenyl-1,2,2a,10b-tetrahydrocyclobuta[l]phenanthrene (**13**).*

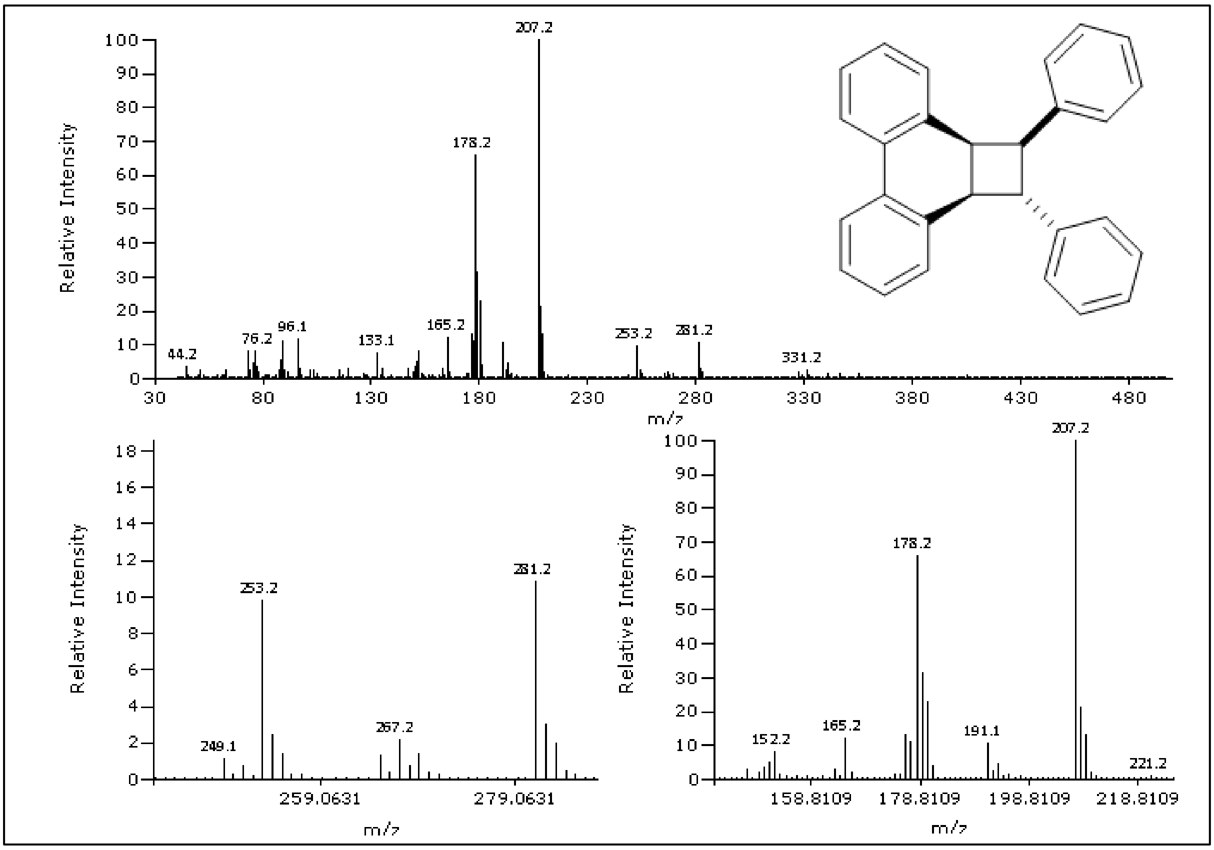


*Figure S 80. Electron ionisation mass spectrum of (1α,2β,2aR,10bS)-1,2-diphenyl-1,2,2a,10b-tetrahydrocyclobuta[l]phenanthrene (**13**).*

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