Electronic Supporting Information

Tuning the Photochemical Properties of the Fulvalene-Tetracarbonyl-Diruthenium System

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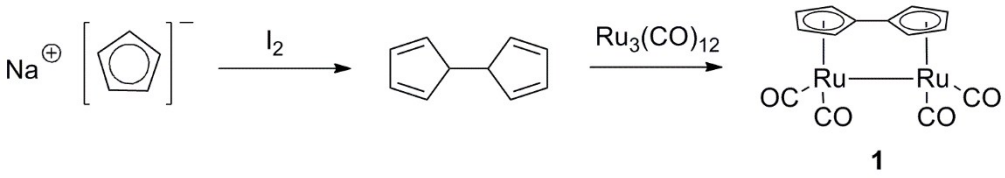
Synthesis

Triruthenium dodecacarbonyl, *p*-toluensulphonyl hydrazid, and sodium cyclopentadienide solution were purchased from Sigma-Aldrich and used as received. *n*-Butyllithium and methyllithium were purchased from Acros Organics and used as received. THF and diethyl ether were dried using an MB SPS-800 solvent purification system from M Braun. Trimethylcyclopetenone[1] and tetramethylcyclopentenone[2] were prepared according to published procedures. All glassware were dried at 130 °C over night. Experiments were performed using standard Schlenk techniques. NMR-spectra were recorded on a Varian 400-MR , and IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer.

*fulvalene-tetracarbonyl-diruthenium (**1**).*



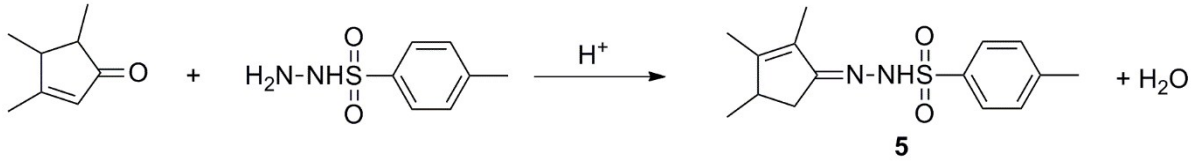
1

A solution of iodine (1.9 g, 7.5 mmol) in THF (13 ml) was added drop wise to a solution of sodium cyclopentadienide (2.0 M in THF, 7.5 ml, 15 mmol) in THF (50 ml) at -78°C.

The cooling bath was removed and after 25 min, the solution was transferred to a separatory funnel containing a chilled, nitrogen flushed mixture of 1 % aqueous sodium thiosulphate (50 ml) and heptane (75 ml). The mixture was shaken gently for 1 min, the layers separated, the organic phase washed with aqueous sodium thiosulphate (25 ml) and transferred to a flask

containing sodium sulphate under nitrogen atmosphere. The mixture was swirled for 1 min and cooled to -78°C. This solution was added in small portions to a refluxing solution of triruthenium dodecacarbonyl (2.13 g, 3.33 mmol) in xylenes (200 ml) under nitrogen atmosphere. Addition was complete after 1 h, 45 min. The solution was refluxed for another 15 min and then allowed to cool to ambient temperature. The solution was filtered through a pad of neutral aluminium oxide, the solvent was removed *in vacuo* and the last traces of xylenes were removed with a rotary vane pump to give a red semisolid. The product was washed with small portions (5 ml) of hexane/dichloromethane 2:1 until the residue formed a yellow powder, and the extracts were yellow rather than red. The solid product was dried *in vacuo* to give **1** as a yellow solid. Yield: 1.3 g (59%). Analytical data was identical to that previously published.

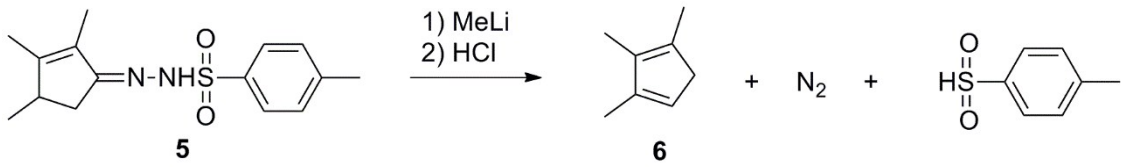
N*'-(2,3,4-trimethylcyclopent-2-ene-ylidene)tosylhydrazide (**5**).*



5

Trimethylcyclopentenone (18.1 g, 0.15mol), tosylhydrazine (27.3 g, 0.15 mol) and 35% hydrochloric acid (0.5 ml) were added to 180 ml of 96% ethanol. The mixture was refluxed under nitrogen atmosphere for 2 h. The volume of the solution was reduced to *c*. 70 ml, whereupon the product precipitated. The mixture was filtered, the solids washed with small portions of ethanol and dried by suction. The mother liquor was evaporated to a syrup, and left over night. The crystals where washed with small portions of ethanol. The combined solids where dried *in vacuo* to give **5** as a white solid. Yield: 26.6 g (61%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.88 (m, 2H, aryl), 7.29 (m, 2H, aryl), 2.63 (m, 2H, CH_2), 2.41 (s, 3H, Me), 1.78 (s, 3H, Me), 1.67 (s, 3H, Me), 1.03 (m, 3H, Me). ^{13}C-NMR ($CDCl_3$, 100.57 MHz) δ: 167.5, 156.8, 143.7, 135.5, 131.5, 129.3, 128.1, 40.04, 33.93, 21.58, 19.34, 13.40, 9.16. Anal. calcd. for $C_{15}H_{20}N_2O_2S$: C, 61.62; H, 6.89, N 9.58. Found: C, 61.77; H, 6.75; N 9.54.

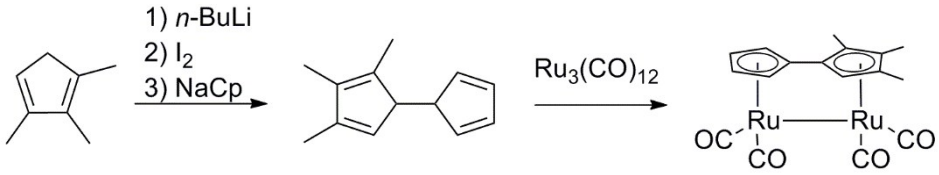
*Trimethylcyclopentadiene (**6**).*



5 6

N'-(2,3,4-trimethylcyclopent-2-ene-ylidene)tosylhydrazide (**5**, 14.0 g, 0.048 mol) was suspended in diethyl ether (200 ml). The mixture was stirred in a water bath. Methyllithium (1.6 M in diethyl ether, 65 ml, 0.10 mol) was added slowly. The mixture was stirred over night and quenched with 10% HCl (100 ml). The phases were separated, and the water phase was extracted with diethyl ether (50 ml). The combined organic phases were dried over sodium sulphate, evaporated *in vacuo* and the residue extracted with pentane (50 ml). The solution was filtered through a pad of silica and evaporated to give **6** as a slightly yellowish liquid. Yield: 2.59 g (50 %). The product was stored at -80°C, where it freezes to a solid. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.83 (m, 1H, CH), 2.77 (s, 2H, CH_2), 1.93 (m, 6H, 2×Me), 1.82 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$, 100.57 MHz) δ: 144.1, 136.5, 135.7, 123.0, 43.73, 14.23, 13.66, 10.72.

*(2,3,4-trimethylfulvalene)-tetracarbonyl-diruthenium (**2**).*

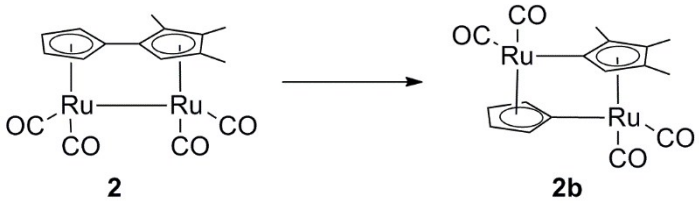


6 2

Trimethylcyclopentadiene (**6**, 0.81 g, 7.5 mmol) was dissolved in THF (25 ml). The solution was cooled to -78°C, and *n*-butyllithium (2.5 M in hexanes, 3.0 ml, 7.5 mmol) was added slowly. After 30 min, the solution was warmed up to ambient temperature and stirred for 30 min. The solution was cooled to -78°C, and a solution of iodine (1.90 g, 7.5 mmol) in THF (13 ml) was added drop wise. A solution of sodium cyclopentadienide (2.0 M in THF, 3.8 ml, 7.5 mmol) was added, and the cooling bath was removed. After 25 min, the solution was transferred to a separatory funnel containing a chilled, nitrogen flushed mixture of 1 % aqueous sodium thiosulphate (50 ml) and heptane (75 ml). The mixture was shaken gently for 1 min, the layers separated, the organic phase washed with aqueous sodium thiosulphate (25 ml) and transferred to a flask containing sodium sulphate under nitrogen atmosphere. The mixture was swirled for

1 min and cooled to -78°C. This solution was added in small portions to a refluxing solution of triruthenium dodecacarbonyl (2.13 g, 3.33 mmol) in xylenes (200 ml) under nitrogen atmosphere. Addition was complete after 1 h 15 min. The solution was refluxed for another 15 min, allowed to cool to ambient temperature and filtered through a pad of neural aluminium oxide. The solvent was removed *in vacuo* and the last traces of xylenes were removed with a rotary vane pump to give a red semisolid. The product was washed with small portions (5 ml) of hexane/dichloromethane 2:1 until the residue formed a brown powder, and the extracts were yellow rather than red. The remaining powder was extracted dichloromethane (approx. 100 ml in total) until the extracts were colourless. The solution was filtered through neutral aluminium oxide and evaporated *in vacuo* to give **2** as a yellow solid. Yield: 0.46 g (19%). ^{1}H-NMR (toluene-d_8, 400 MHz) δ: 5.15 (m, 1H, CH), 5.04 (m, 1H, CH), 3.64 (m, 1H, CH), 3.09 (m, 1H, CH), 2.92 (s, 1H, CH), 1.77 (s, 3H, Me), 1.72 (s, 1H, Me), 1.04 (s, 1H, Me). ^{13}C-NMR (toluene-d_8, 100.57 MHz) δ: 206.57, 205.54, 205.21, 105.2, 104.5, 94.50, 93.50, 87.98, 87.75, 87.54, 78.52, 78.20, 75.99, 13.09, 11.50, 11.48. IR (KBr): 3125 (s), 2918 (m), 1996 (s), 1943 (s), 1475 (w), 1450 (w), 1393 (m), 1383 (m), 1223 (w), 1147 (w), 1064 (w), 1040 (m), 1026 (m), 868 (m), 826 (s), 815 (s), 735 (m), 698 (m), 645 (m) cm^{-1}. Anal. calcd. for $C_{17}H_{14}O_4Ru_2$: C, 42.15; H, 2.29. Found: C, 42.15; H, 2.92.

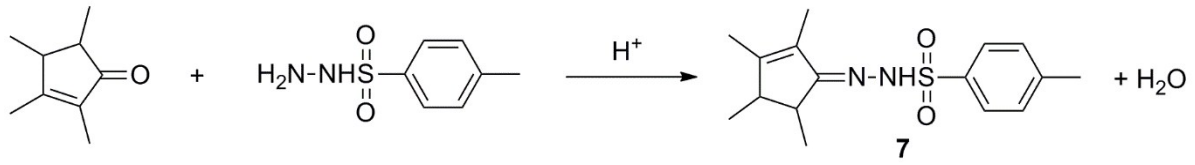
*(μ^2-σ^1-η^5-cyclopentadienyl)(μ^2-σ^1-η^5-2,3,4-trimethylcyclopentadienyl)-tetracarbonyl-diruthenium (**2b**).*



(2,3,4-trimethylfulvalene)-tetracarbonyl-diruthenium (**2**; 10 mg, 0.021 mmol) was dissolved in toluene (10 ml) under nitrogen atmosphere. The solution was placed in a water bath and irradiated with Osram Powerstar HQ-IR 150 W metal halide lamp for 100 min. The brown solution was evaporated to give **2b** as a brown powder in quantitative yield. ^{1}H-NMR (toluene-d_8, 400 MHz) δ:4.82 (m, 2H, 2×CH), 4.26 (m, 2H, 2×CH), 4.06 (m, 1H, CH), 1.76 (m, 3H, Me), 1.62 (m, 6H, 2×Me). ^{13}C-NMR (toluene-d_8, 100.57 MHz) δ: 203.0, 202.9,202.63, 201.95,

109.8, 106.3, 96.55, 96.35, 93.60, 91.40, 90.28, 89.32, 81.71, 15.04, 12.21, 10.93. IR (KBr): 3103 (w), 2957 (w), 2918 (w), 1999 (w), 1939 (w), 1773 (m), 1484 (w), 1441 (w), 1418 (w), 1396 (w), 1378 (w), 1360 (w), 1334 (w), 1314 (w), 1109 (w), 1025 (m), 1010 (m), 990 (m), 967 (m), 872 (m), 854 (s), 823 (s), 721 (w), 696 (w), 651 (s), 586 (s), 569 (s), 522 (s), 513 (s), 454 (m), 419 (w), 406 (w) cm^{-1}.

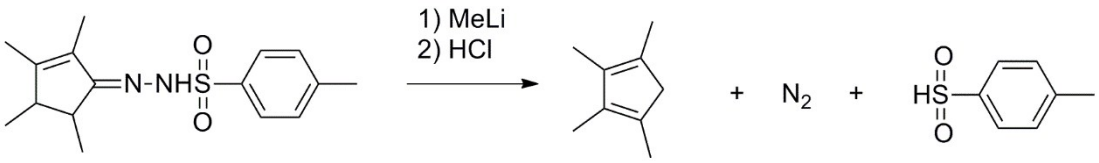
N*'-(2,3,4,5-tetramethylcyclopent-2-ene-ylidene)tosylhydrazide (**7**).*



7

2,3,4,5-Tetramethylcyclopentenone (10.2 g, 0.074 mol), tosylhydrazine (11.5 g, 0.062 mol) and 35% hydrochloric acid (0.45 ml) were added to 100 ml of 96% ethanol. The mixture was refluxed under nitrogen atmosphere for 2 h. The solution was allowed to cool to ambient temperature, whereupon white crystals formed, and then stored at -20°C over night. The mixture was filtered and the filtrate was concentrated *in vacuo* and 96% ethanol (5 ml) was added. The white precipitate was filtered off. The filtrate was once again concentrated *in vacuo,* 96% ethanol (5 ml) added, and the mixture filtered. The combined solids were washed with ethanol and dried *in vacuo* to give **7** as a white solid. Yield: 14 g (74 %). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.86 (m, 2H, aryl), 7.28 (m, 2H, aryl), 2.42 (s, 3H, Me), 1.76 (s, 3H, Me), 1.65 (s, 3H, Me), 1.08 (s, 3H, Me), 0.98 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$, 100.57 MHz) δ: 170.6, 155.0, 143.7, 135.3, 130.2, 129.66, 129.3, 128.11, 126.4, 50.46, 40.88, 21.59, 18.88, 16.88, 13.56, 9.17.

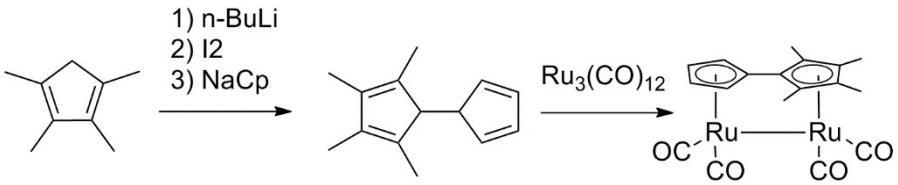
*Tetramethylcyclopentadiene (**8**).*



7 8

N'-(2,3,4,5-tetramethylcyclopent-2-ene-ylidene)tosylhydrazide (**7**, 7.0 g, 0.023 mol) was suspended in diethyl ether (100 ml). The mixture was stirred in a water bath. Methyl lithium (1.6 M in diethyl ether, 35 ml, 0.056 mol) was added slowly. The mixture was stirred over night and quenched with 10% HCl (50 ml). The phases were separated, and the water phase was extracted with diethyl ether (20 ml). The combined organic phases were dried over sodium sulphate, evaporated *in vacuo* and the residue extracted with pentane (50 ml). The solution was filtered through silica and evaporated *in vacuo* to give **8** as a slightly yellowish liquid. Yield: 1.9 g (68 %). The product was stored at -80°C, where it freezes to a solid. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.73 (s, 2H, CH_2), 1.92 (s, 6H, 2×Me), 1.81 (s, 6H, 2×Me). ^{13}C-NMR ($CDCl_3$, 100.57 MHz) δ: 136.1, 131.9, 48.39, 13.22, 11.13.

*(2,3,4,5-tetramethylfulvalene)-tetracarbonyl-diruthenium (**3**).*

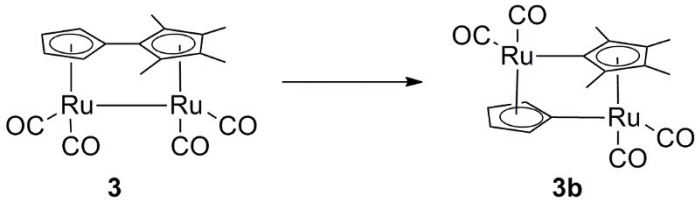


8 3

Tetramethylcyclopentadiene (**8**, 0.92 g, 7.5 mmol) was dissolved in THF (50 ml). The solution was cooled to -78°C, and *n*-butyllithium (2.5 M in hexanes, 3.0 ml, 7.5 mmol) was added slowly. After 30 min, the solution was warmed up to ambient temperature and stirred for 30 min. The solution was cooled to -78°C, and a solution of iodine (1.9 g, 7.5 mmol) in THF (12 ml) was added drop wise. A solution of sodium cyclopentadienide (2.0 M in THF, 3.8 ml, 7.5 mmol) was added, and the cooling bath was removed. After 25 min, the solution was transferred to a separatory funnel containing a chilled, nitrogen flushed mixture of 1 % aqueous sodium

thiosulphate (50 ml) and heptane (75 ml). The mixture was shaken gently for 1 min, the layers separated, the organic phase washed with aqueous sodium thiosulphate (25 ml) and transferred to a flask containing sodium sulphate under nitrogen atmosphere. The mixture was swirled for 1 min and cooled to -78°C. This solution was added in small portions to a refluxing solution of triruthenium dodecacarbonyl (2.13 g, 3.33 mmol) in xylenes (200 ml) under nitrogen atmosphere. Addition was complete after 1 h, 45 min. The solution was refluxed for another 15 min and then allowed to cool to ambient temperature. The solution was filtered through a pad of neutral aluminium oxide, the solvent was removed *in vacuo* and the last traces of xylenes were removed with a rotary vane pump to give a red semisolid. The product was washed with small portions (5 ml) of hexane/dichloromethane 2:1 until the residue formed a brown powder, and the extracts were yellow rather than red. The remaining powder was extracted hexane/dichloromethane 2:1 until the extracts were colourless (approx. 500 ml in total). The solution was filtered through a pad of neutral aluminium oxide and evaporated *in vacuo* to give **3** as a yellow solid. Yield: 1.03 g (41%). ^{1}H-NMR (toluene-d_8, 400 MHz) δ: 5.17 (m, 2H, CH), 3.67 (m, 2H, CH), 1.75 (s, 6H, 2×Me), 1.04 (s, 6H, 2×Me). ^{13}C-NMR (toluene-d_8, 100.57 MHz) δ: 206.2, 205.5, 103.4, 93.88, 92.0, 87.65, 86.70, 79.24, 77.20, 12.05, 11.78. IR (KBr): 2913 (w), 1990 (s), 1940 (s), 1475 (w), 1382 (w), 1065 (w), 1051 (w), 1025 (m), 878 (m), 817 (s), 702 (m), 602 (s), 548 (s), 525 (s), 499 (m), 472 (m) cm^{-1}. Anal. calcd. for $C_{18}H_{16}O_4Ru_2$: C, 43.37; H, 3.24. Found: C, 43.72; H, 3.41.

*(μ^2-σ^1-η^5-cyclopentadienyl)(μ^2-σ^1-η^5-2,3,4,5-tetramethylcyclopentadienyl)-tetracarbonyl-diruthenium (**3b**).*



(2,3,4,5-tetramethylfulvalene)-tetracarbonyl-diruthenium (**3**; 10 mg, 0.020 mmol) was dissolved in toluene (10 ml) under nitrogen atmosphere. The solution was placed in a water bath and irradiated with Osram Powerstar HQ-IR 150 W metal halide lamp for 35 min. The brown solution was evaporated to give **3b** as a brown powder in quantitative yield. ^{1}H-NMR

(toluene-d_8, 400 MHz) δ: 4.85 (m, 2H, 2×CH),4.26 (m, 2H, 2×CH), 2.07 (s, 6H, 2×Me), 1.78 (s, 6H, 2×Me). ^{13}C-NMR (toluene-d_8, 100.57 MHz) δ: 203.4, 202.51, 106.8, 105.8, 96.92, 91.10, 90.74, 83.56, 15.34, 11.37. IR (KBr): 3113 (w), 2960 (w), 2922 (w), 2865 (w), 1992 (s), 1942 (s), 1758 (s), 1457 (w), 1418 (w), 1396 (w), 1375 (m), 1364 (m), 1335 (m), 1292 (m), 1110 (m), 1026 (m), 988 (m), 874 (s), 855 (s), 823 (s), 730 (w), 714 (m), 695 (w), 650 (s), 575 (s), 561 (s), 521 (s), 510 (s), 493 (m), 464 (w), 455 (m), 435 (w), 411 (w) cm^{-1}.

Calculations

Quantum mechanical calculations where performed using Gaussian 09, rev B0.1.[3] Geometry optimizations where done in vacuum using the 6-311+G(d,p)[4] basis set for all elements except for Ru where effective core Potential LANL2DZ[5, 6] were used in combination with hybrid B3LYP[7, 8] functional. All structures were confirmed as local minima with calculated second derivatives of the Hessian matrix except for the transition state which had one negative eigenvalue. All triplet calculations were done unrestricted and the singlets were checked for instability.

Table ESI1 Optimized geometrical parameters of parent compounds (**P**) S_0, *syn*-biradicals (**A**) T_1, intermediate (**B**) T_1 and intermediate (**B**) S_0 at B3LYP/6-311+G(d,p)/LANL2DZ. All bond lengths in Å, angles in °.* Average bond length with a minima of 1.398 Å.

1	**P** S_0	2.895	1.446	0.0	1.437	1.424
	A T_1	4.529	1.465	38.8	1.429	1.436
	B T_1	5.713	1.460	172.4	1.429	1.435
	B S_0	5.539	1.416	180.0	1.448	1.417
2	**P** S_0	2.907	1.448	1.2	1.446	1.438
	A T_1	4.675	1.472	60.2	1.434	1.449
	BT_1	5.632	1.465	149.2	1.437	1.451
	B S_0	5.526	1.418	176.2	1.459	1.431
3	**P** S_0	2.911	1.452	0.7	1.451	1.432
	A T_1	4.778	1.473	60.8	1.434	1.446
	B T_1	5.521	1.471	131.8	1.438	1.446
	B S_0	5.558	1.422	177.4	1.465	1.426
1	**Exp.**[9]	2.821	1.457	-	1.416*	1.416*

Table ESI2 xyz coordinates from DFT calculations.

Compound 1 **Parent compound (P)** **S_0**

C	-2.879621	-1.579476	0.709604
C	-0.722759	-2.048017	-0.000011
C	-1.555398	-1.852879	1.154798
C	-1.555374	-1.852879	-1.154838
C	-2.879607	-1.579477	-0.709671
H	-3.738559	-1.417105	1.342343
H	-1.241602	-1.933987	2.183539
H	-1.241557	-1.933988	-2.183572
H	-3.738531	-1.417106	-1.342429
C	2.879608	-1.579477	0.709665
C	0.722761	-2.048017	0.000004
C	1.555375	-1.852882	1.154831
C	1.555399	-1.852875	-1.154805
C	2.879623	-1.579473	-0.709609
H	3.738532	-1.417107	1.342423
H	1.241558	-1.933994	2.183565
H	1.241604	-1.933981	-2.183546
H	3.738560	-1.417099	-1.342349
Ru	-1.447289	0.147049	-0.000018
Ru	1.447289	0.147049	0.000018
C	-1.611632	1.473969	1.332720
O	-1.766516	2.251290	2.164647
C	-1.611598	1.473971	-1.332759
O	-1.766402	2.251299	-2.164694
C	1.611596	1.473965	1.332765
O	1.766423	2.251288	2.164702
C	1.611630	1.473976	-1.332713
O	1.766492	2.251304	-2.164639

Compound 1 ***syn*-Biradical (A)** **T_1**

C	2.979434	-1.989909	-0.289809
C	-0.697681	-1.565225	-0.223638
C	-1.818900	-1.983774	0.556381
C	-1.188302	-1.220095	-1.517591
C	-2.592399	-1.520309	-1.563867
H	-3.970338	-2.304289	-0.000579
H	-1.773304	-2.349345	1.570839
H	-0.587530	-0.867866	-2.342404
H	-3.235726	-1.403791	-2.422290
C	2.592405	-1.520317	1.563861
C	0.697684	-1.565228	0.223635
C	1.188308	-1.220105	1.517588
C	1.818903	-1.983772	-0.556389
C	2.979438	-1.989909	0.289799
H	3.235732	-1.403804	2.422284
H	0.587537	-0.867881	2.342405
H	1.773303	-2.349338	-1.570849
H	3.970342	-2.304287	0.000565
Ru	-2.264468	0.222796	-0.028438
Ru	2.264469	0.222795	0.028438
C	-3.367967	0.855980	1.380839
O	-4.072767	1.188874	2.224522
C	-2.600405	1.779991	-1.065636
O	-2.832819	2.683908	-1.734253
C	2.600387	1.779994	1.065637

O	2.832791	2.683914	1.734255
C	3.367974	0.855991	-1.380829
O	4.072778	1.188896	-2.224505

Compound 1 Intermediate (B) **S_0**

Ru	2.769372	0.000000	0.035435
C	1.112442	-1.155503	1.115411
C	0.452301	-0.000007	0.544664
C	1.112435	1.155502	1.115396
C	2.041875	0.714695	2.089200
C	2.041880	-0.714677	2.089209
H	0.869935	2.184964	0.902635
H	2.635456	1.345033	2.733123
H	2.635466	-1.345002	2.733141
H	0.869951	-2.184969	0.902663
O	4.708127	2.191858	-0.823936
C	3.976469	1.352070	-0.540359
O	4.708130	-2.191844	-0.823972
C	3.976471	-1.352064	-0.540376
Ru	-2.769373	-0.000001	-0.035433
C	-0.452299	-0.000016	-0.544654
C	-1.112432	1.155482	-1.115408
C	-2.041870	0.714657	-2.089206
C	-2.041874	-0.714714	-2.089190
C	-1.112438	-1.155523	-1.115382
H	-2.635449	1.344984	-2.733142
H	-2.635458	-1.345051	-2.733112

H	-0.869947	-2.184985	-0.902615
O	-4.708147	-2.191827	0.823984
C	-3.976481	-1.352053	0.540386
O	-4.708120	2.191882	0.823892
C	-3.976466	1.352085	0.540333
H	-0.869932	2.184948	-0.902666

Compound 1 Intermediate (B) T_1

Ru	-2.856264	0.015863	0.020901
C	-1.209083	-1.261060	-1.017516
C	-0.526423	-0.115415	-0.505590
C	-1.106694	1.030807	-1.131179
C	-2.056178	0.581141	-2.109150
C	-2.119956	-0.827363	-2.039005
H	-0.796982	2.054127	-0.985766
H	-2.616712	1.212279	-2.781266
H	-2.740691	-1.468602	-2.645370
H	-1.002458	-2.288212	-0.759631
O	-4.729876	2.339701	0.632040
C	-4.024127	1.454516	0.438271
O	-4.926792	-2.062920	0.843273
C	-4.146215	-1.266300	0.569175
Ru	2.856264	0.015863	-0.020902
C	0.526423	-0.115405	0.505588
C	1.106692	1.030830	1.131155
C	2.056174	0.581184	2.109136
C	2.119953	-0.827322	2.039020

C	1.209082	-1.261040	1.017538
H	2.616708	1.212335	2.781241
H	2.740688	-1.468549	2.645399
H	1.002458	-2.288196	0.759674
O	4.926779	-2.062945	-0.843242
C	4.146207	-1.266316	-0.569157
O	4.729893	2.339682	-0.632068
C	4.024138	1.454503	-0.438288
H	0.796979	2.054146	0.985721

Compound 1 Transition State (C) S_0

C	-1.421928	2.477297	-0.709542
C	0.144964	0.874194	0.000000
C	-0.498185	1.496666	-1.153393
C	-0.498185	1.496666	1.153393
C	-1.421928	2.477297	0.709541
C	-3.072782	-0.585363	-1.330096
C	-3.072780	-0.585363	1.330097
C	1.421927	-2.477297	0.709542
C	-0.144964	-0.874194	0.000000
C	0.498185	-1.496666	1.153393
C	0.498185	-1.496666	-1.153393
C	1.421927	-2.477297	-0.709541
C	3.072781	0.585363	1.330097
C	3.072782	0.585363	-1.330096
H	-2.017923	3.117258	-1.342902
H	-0.265540	1.276528	-2.183741

H	-0.265540	1.276528	2.183741
H	-2.017924	3.117259	1.342901
H	2.017923	-3.117258	1.342902
H	0.265540	-1.276527	2.183741
H	0.265540	-1.276529	-2.183741
H	2.017923	-3.117259	-1.342901
O	-3.698079	-1.083664	-2.156282
O	-3.698076	-1.083663	2.156284
O	3.698077	1.083664	2.156283
O	3.698080	1.083663	-2.156282
Ru	-2.010032	0.248613	0.000000
Ru	2.010032	-0.248613	0.000000

Compound 1 Transition State (C) T_1

C	1.845590	2.492159	0.707640
C	0.014036	1.215767	-0.000001
C	0.748136	1.687965	1.149698
C	0.748136	1.687964	-1.149699
C	1.845591	2.492158	-0.707641
C	2.947612	-0.760403	1.343945
C	2.947612	-0.760403	-1.343944
C	-1.417078	-2.429112	-0.712538
C	0.139681	-0.826266	0.000000
C	-0.508406	-1.423699	-1.146110
C	-0.508407	-1.423699	1.146110
C	-1.417078	-2.429113	0.712537
C	-3.003267	0.731854	-1.381089

C	-3.003266	0.731855	1.381090
H	2.546822	3.015911	1.341445
H	0.480762	1.513770	2.181800
H	0.480764	1.513769	-2.181801
H	2.546822	3.015910	-1.341446
H	-1.987150	-3.088170	-1.350565
H	-0.277462	-1.198666	-2.176253
H	-0.277463	-1.198667	2.176253
H	-1.987150	-3.088170	1.350564
O	3.495983	-1.330418	2.178385
O	3.495985	-1.330418	-2.178383
O	-3.416037	1.380308	-2.231450
O	-3.416036	1.380308	2.231451
Ru	2.009322	0.198684	0.000000
Ru	-2.261105	-0.362458	0.000000

Compound 1 **Photoisomer (PI)** **S_0**

C	1.664167	-2.408651	-0.705585
C	-0.285119	-1.314693	-0.000055
C	0.479650	-1.715537	-1.143954
C	0.479595	-1.715621	1.143852
C	1.664133	-2.408703	0.705489
C	2.776457	0.657969	-1.360045
C	2.776411	0.657896	1.360190
C	-1.664169	2.408643	0.705595
C	0.285118	1.314694	0.000056
C	-0.479652	1.715525	1.143959

C	-0.479593	1.715634	-1.143848
C	-1.664132	2.408710	-0.705480
C	-2.776461	-0.657947	1.360047
C	-2.776407	-0.657919	-1.360189
H	2.407822	-2.862960	-1.343414
H	0.191959	-1.572728	-2.174477
H	0.191854	-1.572890	2.174372
H	2.407757	-2.863059	1.343321
H	-2.407825	2.862945	1.343427
H	-0.191964	1.572704	2.174481
H	-0.191851	1.572913	-2.174369
H	-2.407754	2.863074	-1.343308
O	3.382397	1.148303	-2.201750
O	3.382326	1.148194	2.201934
O	-3.382405	-1.148262	2.201759
O	-3.382313	-1.148235	-2.201928
Ru	1.748993	-0.181204	0.000032
Ru	-1.748993	0.181204	-0.000040

Compound 1 Photoisomer (PI) T_1

C	1.829636	2.389388	0.705846
C	-0.174007	1.386766	-0.000008
C	0.610306	1.749659	1.141445
C	0.610214	1.749577	-1.141555
C	1.829576	2.389337	-0.706100
C	2.779449	-0.707813	1.369813
C	2.779461	-0.707843	-1.369883
C	-1.594135	-2.453310	-0.713240

C	0.298877	-1.274358	-0.000024
C	-0.470458	-1.687121	-1.138465
C	-0.470370	-1.687196	1.138452
C	-1.594071	-2.453365	0.713265
C	-2.736615	0.806306	-1.428207
C	-2.736446	0.806439	1.428374
H	2.600149	2.802882	1.341134
H	0.319152	1.626018	2.175044
H	0.318973	1.625866	-2.175121
H	2.600040	2.802780	-1.341482
H	-2.303467	-2.960750	-1.350686
H	-0.203518	-1.509558	-2.169958
H	-0.203346	-1.509704	2.169935
H	-2.303357	-2.960842	1.350734
O	3.364027	-1.213519	2.218028
O	3.364053	-1.213559	-2.218082
O	-3.097888	1.433901	-2.313487
O	-3.097627	1.434136	2.313618
Ru	1.787792	0.165741	-0.000049
Ru	-2.034466	-0.285813	0.000083

Compound 2 **Parent compound (P)** **S_0**

C	-2.845803	-2.187772	-0.022689
C	-0.629008	-1.944943	-0.673304
C	-1.496072	-2.317840	0.411760
C	-1.485417	-1.558201	-1.766393

C	-2.837941	-1.724244	-1.362782
C	2.838152	-0.919010	0.219043
C	0.783712	-1.634858	-0.606929
C	1.628857	-1.614928	0.566640
C	1.483815	-0.925373	-1.643891
C	2.746685	-0.499211	-1.145734
C	4.056677	-0.784213	1.083670
C	1.394633	-2.330464	1.869383
C	3.832649	0.140107	-1.958893
H	-3.721781	-2.426117	0.560808
H	-1.190237	-2.676197	1.378968
H	-1.158208	-1.226395	-2.738838
H	-3.707816	-1.539700	-1.974261
H	1.130806	-0.768389	-2.651428
H	4.685969	-1.678372	1.001893
H	3.800716	-0.654012	2.135838
H	4.661503	0.072566	0.783835
H	2.260781	-2.230535	2.524244
H	1.234261	-3.399993	1.700735
H	0.531774	-1.942612	2.412953
H	4.532189	-0.620628	-2.323637
H	4.405018	0.865922	-1.379129
H	3.420057	0.655104	-2.828245
Ru	-1.818755	-0.065669	-0.032162
C	-2.203779	0.690483	1.652072
O	-2.480974	1.105475	2.688132
C	-2.299586	1.559205	-0.858394
O	-2.641630	2.518871	-1.391349
Ru	1.019020	0.559757	0.037158

C	0.965651	1.422472	1.716397
O	1.000731	1.918312	2.753991
C	0.853782	2.230134	-0.831561
O	0.819530	3.235022	-1.390015

Compound 2 ***syn*-Biradical (A)** T_1

C	2.674272	-1.521769	-1.650766
C	0.842433	-1.356826	-0.232100
C	1.345487	-0.991271	-1.516146
C	3.012691	-2.161795	-0.438380
C	-2.794237	-1.321086	0.698277
C	-0.506298	-1.129997	0.310935
C	-1.726826	-1.664540	-0.220190
C	-0.832285	-0.399243	1.491368
C	-2.239286	-0.542986	1.752824
C	-4.203236	-1.829330	0.622234
C	-1.847683	-2.621913	-1.370962
C	-2.946074	-0.063117	2.985361
H	3.301039	-1.442540	-2.525641
H	0.789153	-0.467299	-2.278610
H	1.822459	-2.458932	1.445437
H	3.942869	-2.664140	-0.221414
H	-0.122109	0.114653	2.122819
H	-4.291479	-2.794567	1.135367
H	-4.525780	-1.977939	-0.409556
H	-4.904861	-1.139414	1.093887
H	-2.769730	-2.466485	-1.933898

H	-1.854403	-3.656244	-1.007916
H	-1.011035	-2.521929	-2.063017
H	-2.949729	-0.847868	3.750758
H	-3.984068	0.206551	2.783605
H	-2.448354	0.809941	3.411512
Ru	2.696375	0.107178	0.031179
C	3.275253	1.665232	-0.892460
O	3.646469	2.568721	-1.495823
C	3.923565	0.421445	1.445439
O	4.693411	0.556317	2.287671
Ru	-1.940135	0.644493	-0.238188
C	-3.060403	0.926830	-1.745596
O	-3.784898	1.042473	-2.632178
C	-2.161390	2.440036	0.356953
O	-2.328633	3.497494	0.775332

Compound 2 **Intermediate (B)** **S_0**

Ru	2.518272	-0.237545	-0.362822
O	4.511045	1.497088	-1.890919
C	3.755022	0.814146	-1.356107
O	4.287690	-2.716687	-0.585150
C	3.617851	-1.782498	-0.549366
C	0.888561	-0.899238	1.071611
C	0.246531	0.079902	0.217081
C	1.003659	1.315360	0.383877
C	1.975337	1.104681	1.412505
C	1.897479	-0.270733	1.840423

C	0.699955	2.643911	-0.248975
C	2.837954	2.150134	2.051172
C	-0.745068	-0.236674	-0.745733
C	-1.503454	0.660527	-1.596534
C	-2.503781	-0.081667	-2.271991
C	-2.446954	-1.430676	-1.809019
C	1.415279	-1.520710	-0.846001
C	2.640727	-0.886339	2.985500
H	0.578456	-1.926393	1.187442
H	1.472141	3.375086	-0.008648
H	-0.253498	3.039133	0.117327
H	0.643537	2.579437	-1.336672
H	3.756148	1.716751	2.449498
H	2.304566	2.625903	2.882758
H	3.119173	2.933791	1.347285
H	-1.300064	1.704819	-1.757194
H	-3.180517	0.301483	-3.020006
H	-3.074420	-2.241225	-2.146072
H	-1.118880	-2.423150	-0.335178
H	3.671394	-0.533013	3.039943
H	2.658966	-1.974102	2.900736
H	2.149417	-0.633288	3.932074
Ru	-2.995563	-0.077757	-0.024882
O	-4.762843	-1.846241	1.719070
C	-4.090974	-1.153774	1.092322
O	-4.865962	2.301162	0.331881
C	-4.155073	1.401232	0.237007

Compound 2 **Intermediate (B)** **T_1**

Ru	2.565695	0.050910	-0.488628
O	3.994097	2.686582	-1.042283
C	3.453951	1.683817	-0.879336
O	4.821900	-1.635931	-1.660890
C	3.963938	-0.983155	-1.260925
C	1.213136	-1.504651	0.540533
C	0.366647	-0.393844	0.240531
C	0.881538	0.741721	0.954161
C	1.989005	0.282228	1.770467
C	2.189702	-1.102326	1.513844
C	0.242626	2.095362	1.084918
C	2.705454	1.095237	2.807211
C	-0.790818	-0.481096	-0.652830
C	-1.351359	0.523597	-1.501562
C	-2.420176	-0.064237	-2.259097
C	-2.570817	-1.402341	-1.836317
C	-1.594390	-1.653014	-0.814393
C	3.149649	-2.020413	2.209780
H	1.091022	-2.506926	0.157166
H	0.957013	2.833115	1.453113
H	-0.589488	2.055964	1.797322
H	-0.154980	2.467390	0.142443
H	3.695180	0.687030	3.016713
H	2.142757	1.102300	3.748285
H	2.835453	2.132832	2.495572
H	-0.957913	1.515477	-1.653673

H	-2.998670	0.432790	-3.022411
H	-3.290631	-2.112920	-2.212165
H	-1.434207	-2.596102	-0.314885
H	4.090953	-1.523645	2.450483
H	3.378269	-2.892132	1.593710
H	2.715552	-2.383508	3.148487
Ru	-3.045153	-0.024384	-0.005764
O	-5.171226	-1.659065	1.441796
C	-4.365451	-1.021155	0.928569
O	-4.689574	2.536202	0.149332
C	-4.066918	1.570755	0.129352

Compound 2 **Transition State (C)** **S_0**

C	-1.638259	1.724432	-1.179370
C	0.182590	0.600767	-0.176097
C	-0.548687	0.848041	-1.416805
C	-0.567525	1.340476	0.847738
C	-1.655958	2.024974	0.218440
C	-0.161700	1.565973	2.274948
C	-2.565320	3.012536	0.887168
C	-2.523778	2.318897	-2.233515
H	-0.270916	0.458475	-2.384595
H	0.362867	2.524187	2.365804
H	0.522380	0.800370	2.632973
H	-1.023767	1.598210	2.944141
H	-2.797800	2.721279	1.912354
H	-3.507167	3.120826	0.347708

H	-2.090435	4.000294	0.926092
H	-2.527635	1.703466	-3.134654
H	-2.162670	3.315274	-2.512724
H	-3.554430	2.423925	-1.891404
C	-2.752647	-1.599624	-1.111786
C	-2.706216	-1.096681	1.506065
C	-3.307966	-2.329882	-1.807196
C	-3.229362	-1.515360	2.442631
Ru	-1.817079	-0.376512	-0.004133
C	2.057342	-2.365499	0.928947
C	0.219672	-1.149435	0.098436
C	0.981067	-1.515548	1.289737
C	0.948670	-1.788876	-0.997575
C	2.038503	-2.532372	-0.479540
H	2.763738	-2.814838	1.610997
H	0.722409	-1.242141	2.299344
H	0.667820	-1.738090	-2.037917
H	2.728829	-3.129415	-1.056534
C	3.156937	0.998958	1.112497
C	3.115445	0.655067	-1.517659
O	3.705642	1.700353	1.841370
O	3.633047	1.142677	-2.421894
Ru	2.232421	-0.168411	-0.058836

Compound 2 **Transition State (C)** **T_1**

C	-1.603413	1.715367	-1.141199

C	0.183941	0.563026	-0.130473
C	-0.533681	0.805180	-1.363375
C	-0.576611	1.256227	0.893845
C	-1.647657	1.981392	0.268401
C	-0.206670	1.397288	2.339563
C	-2.545071	2.982119	0.934509
C	-2.452459	2.352463	-2.199610
H	-0.240393	0.433879	-2.334286
H	0.472918	2.246934	2.472831
H	0.305866	0.515657	2.718714
H	-1.082715	1.576734	2.965290
H	-2.765162	2.710281	1.967969
H	-3.495223	3.084916	0.406785
H	-2.070789	3.971011	0.950444
C	-2.575065	-1.765621	-1.185505
C	-2.717188	-1.201625	1.518152
O	-2.853392	-2.627918	-1.889747
O	-3.060930	-1.724118	2.480730
Ru	-2.081607	-0.308615	-0.048385
C	2.486107	-2.317196	0.872336
C	0.427790	-1.441602	0.160797
C	1.285764	-1.670511	1.301571
C	1.188965	-1.900166	-0.980133
C	2.427084	-2.456549	-0.534488
H	3.292625	-2.649700	1.510176
H	1.036134	-1.464250	2.330842
H	0.854638	-1.876475	-2.007149
H	3.181122	-2.913642	-1.159133
C	3.026656	1.138377	1.126193

C	2.944298	0.839659	-1.529677
O	3.509108	1.884360	1.858169
O	3.363447	1.399611	-2.443137
Ru	2.221957	-0.108178	-0.054623
H	-2.429472	1.770884	-3.123084
H	-2.082672	3.358102	-2.432086
H	-3.494888	2.452106	-1.888528

Compound 2 **Photoisomer (PI)** **S_0**

C	-2.433915	-2.311713	0.220547
C	-0.280720	-1.549771	-0.317005
C	-1.116945	-2.038445	0.738295
C	-1.123460	-1.471637	-1.476255
C	-2.435900	-1.962983	-1.147051
C	2.301385	-1.115367	-1.626769
C	2.316679	-1.822979	1.010413
O	2.784291	-1.475848	-2.605043
O	2.806313	-2.625827	1.669832
Ru	1.493888	-0.462936	-0.035498
H	-3.262879	-2.727352	0.774000
H	-0.802059	-2.222527	1.754225
H	-0.812165	-1.154607	-2.459963
H	-3.268197	-2.061031	-1.828317
C	-2.746415	0.658700	1.681183
C	-2.869012	1.324132	-0.936815
C	1.967480	1.832853	-0.121082

C	-0.206435	1.062095	0.329166
C	0.656977	1.575786	-0.700668
C	0.599848	0.950254	1.508357
C	1.926791	1.448690	1.245614
C	3.098320	2.545316	-0.803686
C	0.262367	1.985535	-2.090504
O	-3.191037	1.044361	2.666482
O	-3.411384	2.118077	-1.564366
Ru	-1.992188	-0.020417	0.077032
C	2.993141	1.661189	2.279444
H	0.259155	0.602971	2.472831
H	4.055660	2.330843	-0.326194
H	2.942871	3.629878	-0.761227
H	3.181385	2.269454	-1.856165
H	1.094996	1.903173	-2.791939
H	-0.073617	3.028809	-2.100485
H	-0.557911	1.375975	-2.466998
H	3.996694	1.551472	1.865264
H	2.889621	0.953598	3.104244
H	2.915031	2.670824	2.698888

Compound 2 Photoisomer (PI) T_1

C	2.657715	2.253542	-0.035376
C	0.467005	1.543350	-0.481315
C	1.335244	2.097849	0.512723
C	1.292714	1.320269	-1.638488
C	2.627962	1.780449	-1.364918

C	-3.351130	0.402171	-0.869906
C	-1.999931	2.381297	0.467937
O	-4.380635	0.380542	-1.373424
O	-2.277800	3.379163	0.965261
Ru	-1.491016	0.724546	-0.254434
H	3.513353	2.673659	0.472421
H	1.042251	2.390694	1.509882
H	0.957011	0.926338	-2.585830
H	3.458262	1.770134	-2.055860
C	2.742528	-0.606825	1.714959
C	2.844921	-1.519700	-0.823376
C	-1.844109	-2.001336	0.111256
C	0.196623	-0.909542	0.348002
C	-0.636890	-1.614263	-0.579992
C	-0.605690	-0.694323	1.525659
C	-1.839736	-1.382200	1.394816
C	-2.914070	-2.891895	-0.432948
C	-0.244228	-2.147102	-1.928770
O	3.141387	-0.932894	2.740532
O	3.332243	-2.410460	-1.359819
Ru	2.065084	-0.018782	0.040459
C	-2.892333	-1.511102	2.453476
H	-0.274543	-0.190244	2.422271
H	-3.853321	-2.777498	0.111747
H	-2.618123	-3.945637	-0.355384
H	-3.110641	-2.696959	-1.490697
H	-1.100910	-2.209507	-2.604178
H	0.177585	-3.156061	-1.844897
H	0.511834	-1.520215	-2.400590

H	-3.900195	-1.372313	2.053223
H	-2.741324	-0.775437	3.245567
H	-2.861348	-2.505229	2.914380

Compound 3 **Parent compound (P)** **S_0**

C	2.837763	-2.085682	-0.707983
C	0.618293	-2.017651	0.000033
C	1.488019	-2.033934	-1.151746
C	1.488049	-2.033924	1.151788
C	2.837782	-2.085675	0.707989
C	-2.773570	-0.677326	-0.715107
C	-0.790041	-1.665110	0.000047
C	-1.558096	-1.283145	-1.170322
C	-1.558059	-1.283064	1.170415
C	-2.773547	-0.677277	0.715196
C	-3.924898	-0.254827	-1.580278
C	-1.267736	-1.614068	-2.611471
C	-1.267658	-1.613882	2.611578
C	-3.924845	-0.254705	1.580380
H	3.708192	-2.135886	-1.343990
H	1.183352	-2.042062	-2.182012
H	1.183411	-2.042052	2.182062
H	3.708227	-2.135877	1.343974
H	-4.604279	-1.097570	-1.755385
H	-3.593145	0.111389	-2.552253
H	-4.502371	0.542306	-1.110936

H	-2.149502	-1.431471	-3.226482
H	-1.010948	-2.671533	-2.722081
H	-0.452760	-1.022899	-3.032732
H	-2.149381	-1.431159	3.226613
H	-0.452616	-1.022740	3.032748
H	-1.010950	-2.671358	2.722271
H	-4.604200	-1.097444	1.755613
H	-4.502357	0.542363	1.110976
H	-3.593050	0.111627	2.552296
Ru	1.858642	-0.060561	0.000003
C	2.320854	1.193363	-1.329459
O	2.649055	1.916791	-2.161147
C	2.320841	1.193376	1.329458
O	2.649032	1.916808	2.161147
Ru	-0.970681	0.625683	-0.000026
C	-0.831626	1.949783	-1.340570
O	-0.817004	2.732618	-2.183821
C	-0.831621	1.949893	1.340409
O	-0.816997	2.732799	2.183594

Compound 3 ***syn*-Biradical (A)** **T_1**

C	-2.981824	-2.181601	-0.441711
C	-0.836474	-1.317917	-0.206298
C	-1.894314	-1.994851	0.477636
C	-1.319470	-1.003982	-1.512534
C	-2.628390	-1.575083	-1.667725
C	2.313830	-0.506972	1.681948

C	0.518528	-1.085868	0.323483
C	0.893472	-0.324149	1.479465
C	1.707111	-1.671109	-0.233680
C	2.811920	-1.332528	0.634953
C	3.090954	-0.023806	2.870523
C	-0.034262	0.375131	2.430225
C	1.764111	-2.669558	-1.354837
C	4.203118	-1.883175	0.527171
H	-3.904633	-2.700154	-0.230686
H	-1.838990	-2.391585	1.479952
H	-0.754929	-0.492705	-2.277741
H	-3.231683	-1.543497	-2.561715
H	3.027358	-0.750884	3.689125
H	2.708450	0.925767	3.247884
H	4.146840	0.114332	2.633618
H	0.446669	1.230650	2.907177
H	-0.365553	-0.302276	3.225833
H	-0.929202	0.738120	1.916730
H	1.734784	-3.691131	-0.957839
H	2.681238	-2.571443	-1.938225
H	0.920590	-2.558192	-2.036126
H	4.287083	-2.826016	1.081081
H	4.942893	-1.192924	0.935395
H	4.477739	-2.087795	-0.508738
Ru	-2.751043	0.103176	-0.046778
C	-4.122298	0.409814	1.230712
O	-4.979772	0.538367	1.984742
C	-3.249787	1.649362	-1.034778
O	-3.568871	2.544477	-1.679025

Ru	1.990470	0.617238	-0.333058
C	2.258066	2.426212	0.199115
O	2.454998	3.491146	0.586740
C	3.087015	0.822734	-1.873581
O	3.797235	0.891711	-2.776642

Compound 3 **Intermediate (B)** **S_0**

Ru	-2.532799	0.000002	-0.433772
O	-4.445691	-2.218581	-1.301122
C	-3.722804	-1.367128	-1.025242
O	-4.445691	2.218582	-1.301128
C	-3.722803	1.367131	-1.025246
C	-0.918631	1.171187	0.684995
C	-0.221881	-0.000006	0.147114
C	-0.918639	-1.171190	0.685002
C	-1.888088	-0.720440	1.628208
C	-1.888082	0.720449	1.628204
C	-0.561835	-2.617921	0.480034
C	-2.676724	-1.575260	2.573707
C	0.785527	-0.000012	-0.857086
C	1.519734	-1.152161	-1.359056
C	2.560274	-0.712384	-2.210444
C	2.560271	0.712347	-2.210456
C	1.519729	1.152133	-1.359075
C	-0.561816	2.617914	0.480030
C	-2.676715	1.575277	2.573694
H	-1.273407	-3.264994	0.992671

H	0.430938	-2.836651	0.886399
H	-0.569817	-2.903149	-0.572704
H	-3.626345	-1.108098	2.835651
H	-2.113321	-1.731122	3.501453
H	-2.897613	-2.556034	2.152660
H	1.278494	-2.184148	-1.183405
H	3.228631	-1.346472	-2.772124
H	3.228624	1.346430	-2.772145
H	1.278482	2.184122	-1.183442
H	-1.273382	3.264990	0.992674
H	-0.569802	2.903148	-0.572707
H	0.430960	2.836636	0.886391
H	-3.626337	1.108120	2.835641
H	-2.897603	2.556049	2.152639
H	-2.113314	1.731147	3.501440
Ru	3.012704	0.000000	-0.063255
O	4.789015	2.185206	1.101694
C	4.112554	1.346129	0.697688
O	4.789021	-2.185181	1.101731
C	4.112558	-1.346113	0.697711

Compound 3 **Intermediate (B)** **T_1**

Ru	2.456238	0.298768	-0.473364
O	3.591001	3.118378	-0.740764
C	3.159572	2.052754	-0.688412
O	4.782472	-0.997341	-1.965432
C	3.894324	-0.484952	-1.443296

C	1.364161	-1.538830	0.420233
C	0.371176	-0.511637	0.269041
C	0.768325	0.613125	1.071988
C	1.958638	0.232494	1.799342
C	2.324789	-1.082770	1.399871
C	-0.029175	1.856117	1.348578
C	2.604477	1.038169	2.887308
C	-0.814321	-0.623093	-0.595061
C	-1.302461	0.327285	-1.545356
C	-2.414758	-0.254901	-2.241336
C	-2.660343	-1.530862	-1.687631
C	-1.699716	-1.744331	-0.641374
C	1.330247	-2.919962	-0.172702
C	3.425252	-1.911188	1.993477
H	0.618486	2.713761	1.539144
H	-0.657396	1.714881	2.236015
H	-0.688860	2.114010	0.521811
H	3.667432	0.810808	2.979021
H	2.134083	0.824998	3.854731
H	2.509586	2.110087	2.707679
H	-0.833191	1.268484	-1.786409
H	-2.958456	0.202383	-3.053726
H	-3.426401	-2.225039	-1.996308
H	-1.609332	-2.639136	-0.045735
H	2.337638	-3.310353	-0.325724
H	0.819529	-2.931772	-1.136135
H	0.808924	-3.619372	0.491617
H	4.247477	-1.291262	2.353567
H	3.835865	-2.620972	1.273778

H	3.049732	-2.490043	2.845927
Ru	-3.040023	0.051192	-0.016805
O	-5.154815	-1.310016	1.703238
C	-4.352472	-0.770244	1.082924
O	-4.654954	2.627342	-0.222379
C	-4.040752	1.663385	-0.105776

Compound 3 **Transition State (C)** **S_0**

C	-1.681311	1.875185	-0.714248
C	0.167103	0.590511	-0.000006
C	-0.573733	1.102611	-1.170501
C	-0.573668	1.102534	1.170551
C	-1.681272	1.875173	0.714423
C	-0.150789	1.068349	2.613920
C	-2.589858	2.686083	1.590099
C	-2.590058	2.686073	-1.589985
C	-0.150994	1.068427	-2.613799
H	0.701694	0.415934	2.778858
H	-0.960817	0.757091	3.277252
H	0.160362	2.071940	2.925402
H	-2.735843	2.218638	2.564576
H	-3.571522	2.824437	1.135353
H	-2.161694	3.680884	1.763569
H	-2.735292	2.218964	-2.564732
H	-2.162392	3.681203	-1.762763
H	-3.572012	2.823601	-1.135613

H	0.703050	0.417930	-2.778266
H	0.157764	2.072515	-2.926044
H	-0.960261	0.754768	-3.276947
C	-2.731997	-1.403123	-1.335393
C	-2.731656	-1.403334	1.335575
O	-3.265559	-1.990299	-2.170562
O	-3.264993	-1.990670	2.170774
Ru	-1.828580	-0.406053	0.000058
C	2.042662	-2.483831	0.708781
C	0.233308	-1.147498	-0.000200
C	0.970495	-1.672917	1.150981
C	0.970447	-1.672520	-1.151602
C	2.042629	-2.483585	-0.709730
H	2.732655	-3.020271	1.343000
H	0.697143	-1.523064	2.181376
H	0.697081	-1.522236	-2.181935
H	2.732613	-3.019791	-1.344158
C	3.181281	0.809471	1.318752
C	3.181298	0.809954	-1.318473
O	3.734460	1.402060	2.135801
O	3.734480	1.402850	-2.135298
Ru	2.255103	-0.182343	-0.000048

Compound 3 **Transition State (C)** **T_1**

C	1.651650	1.852317	0.716709
C	-0.167034	0.540742	0.000003

C	0.569442	1.028023	1.161540
C	0.569314	1.028601	-1.161328
C	1.651567	1.852646	-0.716190
C	0.154190	0.952862	-2.601542
C	2.532768	2.699192	-1.586849
C	2.533017	2.698534	1.587533
C	0.154406	0.951282	2.601709
H	1.015969	0.926671	-3.270691
H	-0.435720	1.839852	-2.860967
H	-0.466435	0.087820	-2.812934
H	2.677410	2.256033	-2.572908
H	3.518095	2.849112	-1.141529
H	2.087142	3.690571	-1.735579
C	2.650312	-1.528590	1.383467
C	2.650112	-1.528607	-1.383848
O	2.955797	-2.236081	2.234712
O	2.955446	-2.236176	-2.235080
Ru	2.095653	-0.328629	-0.000137
C	-2.465780	-2.426550	-0.707333
C	-0.441204	-1.465019	-0.000323
C	-1.250530	-1.821585	-1.146726
C	-1.250465	-1.822116	1.145963
C	-2.465741	-2.426872	0.706359
H	-3.242504	-2.826517	-1.343371
H	-0.957193	-1.727877	-2.179742
H	-0.957110	-1.728901	2.179011
H	-3.242414	-2.827145	1.342269
C	-3.016236	0.980181	-1.327812
C	-3.016158	0.979611	1.328430

O	-3.487550	1.636850	-2.147482
O	-3.487475	1.635940	2.148376
Ru	-2.235354	-0.122596	0.000054
H	2.678287	2.254803	2.573240
H	2.087213	3.689705	1.737096
H	3.518087	2.848972	1.141825
H	1.016255	0.929087	3.270887
H	-0.439287	1.835879	2.860645
H	-0.462480	0.083680	2.813608

Compound 3 **Photoisomer (PI)** **S_0**

C	2.427551	2.229584	0.705906
C	0.275542	1.616934	-0.000030
C	1.114478	1.833104	1.142616
C	1.114481	1.833065	-1.142680
C	2.427553	2.229559	-0.705980
C	-2.317010	1.537489	-1.366940
C	-2.317002	1.537532	1.366892
O	-2.804900	2.138541	-2.216243
O	-2.804886	2.138612	2.216179
Ru	-1.500752	0.495835	-0.000009
H	3.257609	2.497351	1.342916
H	0.800063	1.766455	2.172977
H	0.800070	1.766381	-2.173040
H	3.257613	2.497305	-1.342997
C	2.848644	-0.999053	1.336918
C	2.848645	-0.999098	-1.336883

C	-1.955727	-1.682923	-0.709795
C	0.198744	-1.072935	0.000018
C	-0.633957	-1.284349	-1.157606
C	-0.633957	-1.284306	1.157649
C	-1.955726	-1.682898	0.709854
C	-3.064813	-2.172633	-1.595198
C	-0.202768	-1.310913	-2.596673
O	3.385014	-1.604918	2.151604
O	3.385014	-1.604991	-2.151549
Ru	1.996361	0.042936	-0.000001
C	-0.202769	-1.310812	2.596719
C	-3.064825	-2.172563	1.595267
H	-4.038872	-2.077641	-1.113552
H	-2.916840	-3.231834	-1.837240
H	-3.106827	-1.625955	-2.538426
H	-1.033517	-1.096896	-3.271613
H	0.187034	-2.300770	-2.860531
H	0.585761	-0.587255	-2.795774
H	-1.033523	-1.096781	3.271648
H	0.585750	-0.587136	2.795795
H	0.187046	-2.300654	2.860613
H	-4.038873	-2.077589	1.113594
H	-3.106856	-1.625835	2.538465
H	-2.916862	-3.231752	1.837365

Compound 3 **Photoisomer (PI)** **T_1**

C	-2.580316	1.760279	-1.525927
C	-0.440236	1.531130	-0.588835
C	-1.244734	1.279370	-1.755171
C	-1.323486	2.131830	0.365249
C	-2.631922	2.279507	-0.214220
C	2.021823	2.328667	0.445621
C	3.344194	0.428083	-1.019432
O	2.307615	3.311201	0.969468
O	4.338738	0.469080	-1.590024
Ru	1.502375	0.694241	-0.319064
H	-3.395932	1.735455	-2.233772
H	-0.893430	0.850082	-2.681027
H	-1.046978	2.467739	1.352924
H	-3.493631	2.724552	0.261183
C	-2.840284	-1.509472	-0.903743
C	-2.853295	-0.543144	1.589372
C	1.863500	-1.397692	1.277600
C	-0.207896	-0.914727	0.307006
C	0.615635	-0.723062	1.483381
C	0.609087	-1.591267	-0.660060
C	1.836432	-1.986596	-0.012336
C	2.947323	-1.557493	2.301493
C	0.186057	-0.161862	2.806680
O	-3.327884	-2.404119	-1.433324
O	-3.344858	-0.847753	2.581322
Ru	-2.068934	0.000481	-0.052092
C	0.190417	-2.108108	-2.007743
C	2.894179	-2.852363	-0.618904
H	3.924008	-1.714419	1.839643

H	2.749439	-2.420598	2.948904
H	3.023891	-0.680693	2.946930
H	1.023825	0.281265	3.349113
H	-0.230124	-0.953021	3.442429
H	-0.584446	0.599001	2.695857
H	1.037333	-2.174179	-2.694628
H	-0.565439	-1.472815	-2.466561
H	-0.239555	-3.113773	-1.924633
H	3.849600	-2.754515	-0.100707
H	3.058716	-2.618582	-1.674125
H	2.603527	-3.909032	-0.570393

Determination of isomerization quantum yields

Isomerization quantum yields were determined in degassed deuterated toluene (except for the viscosity-dependent measurements, which were performed in the corresponding hydrocarbons); light of 400±5.4 nm from a Spex Fluorolog τ2 spectrofluorimeter (JY Horiba) was used to afford conversions between 8 and 19%. The photonflux of the lamp was measured with potassium ferrioxalate actinometry,[10] and isomerization yields were determined by ^{1}H-NMR spectroscopy.

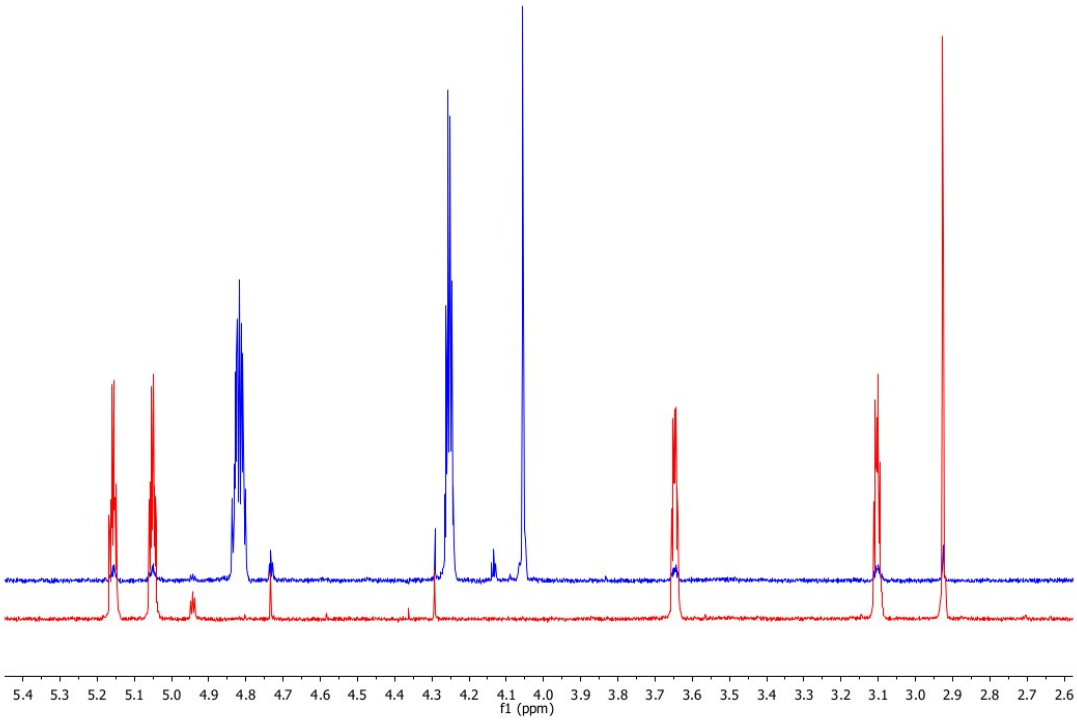


Figure ESI1. Section of the ^{1}H-NMR spectrum of **2** (red) and **2b** (blue) in toluene-d_8, showing the shifts of the Cp protons. Integration of these peaks was used to determine the extent of reaction after illumination.

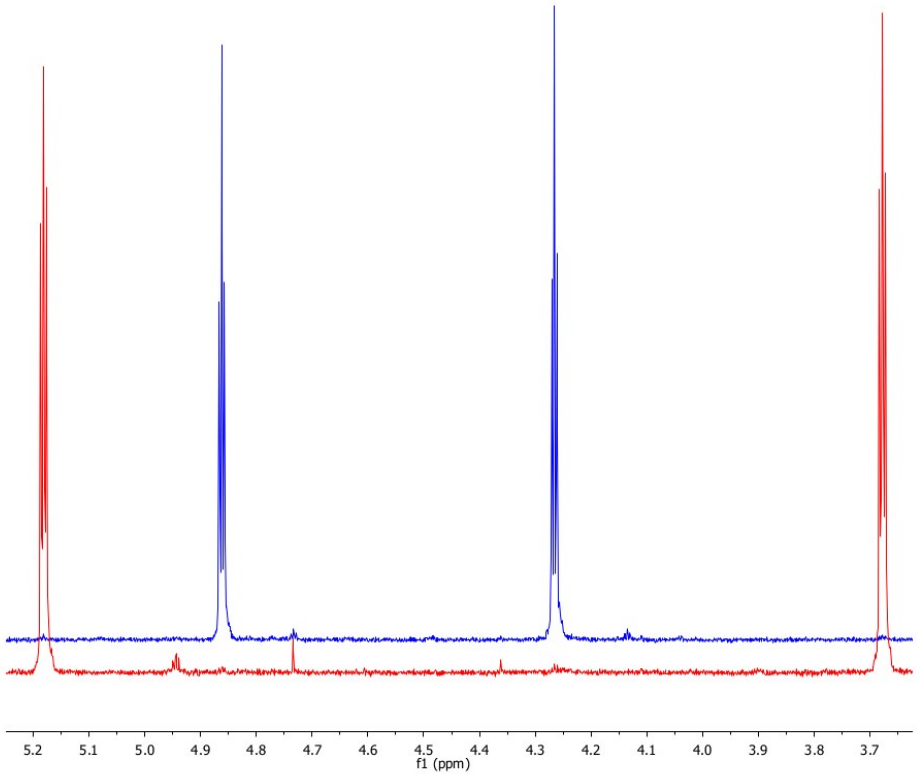


Figure ESI2. Section of the ^{1}H-NMR spectrum of **3** (red) and **3b** (blue) in toluene-d_8, showing the shifts of the Cp protons. Integration of these peaks was used to determine the extent of reaction after illumination.

Determination of Eyring parameters

Samples of **1-3** were prepared directly in s cuvette at a typical absorption of 0.2 at 400 nm. The solvent used was toluene and a Teflon cap was needed to prevent evaporation of solvent during the experiment. After preparation the sample was degassed with nitrogen for 20 minutes. The cuvette was placed in a water bath for cooling and $NaNO_2$ was dissolved in the water working as a solvent filter with a cutoff wavelength of 410 nm (defined as the wavelength where there is less than 50% transmittance). Photoconversion to isomers **1b-3b** was performed by exposure to an Osram Powerstar HQI-R 150 W, metal halide lamp for 45 minutes.

The parent molecule absorbs at 400 nm whereas the photoisomer does not. Therefore the reaction rate can be observed by measuring the absorbance increase at 400 nm. Absorbance measurements were performed using a Cary 4000 spectrophotometer equipped with a temperature regulated sample changer. Temperature was continuously measured in a reference cuvette filled with water. The concentration increase of the parent compound (**1-3**) was fitted

to first order kinetics, according to equation 1, where C_{0b} is the concentration of the metastable isomer at the starting point, C_{Final} is the concentration of the parent molecule when the reaction is completed, k is the rate constant (s^{-1}) and t is the time (s). As the concentration is directly proportional to the absorbance the fitting could be done directly to the absorbance data. Before the fitting was done the absorbance was normalized.

$$y = \quad y = C_{Final} - C_{0b}\, e^{-kT} \quad (1)$$

Fitting was done using an in-house made Matlab script. The obtained rate constants were then used to calculate the enthalpy of activation by fitting them to the Eyring equation:

$$k = (k_B T/h)\, e^{(\Delta S^{\ddagger}/R)}\, e^{-(\Delta H^{\ddagger}/RT)} \quad (2)$$

Where k_B is Boltzmann's constant, T is the temperature in K, h is Planck's constant, R is the gas constant, $\Delta H^{\ddagger}$ is the enthalpy of activation and $\Delta S^{\ddagger}$ is the entropy of activation.

Eyring plots of the thermal isomerization of **1-3** are shown in Fig. ESI4-6. Red marks are the determined rate constants with error bars, blue line is the best fit to the Eyring equation, and blue marks are the residuals to the fit.

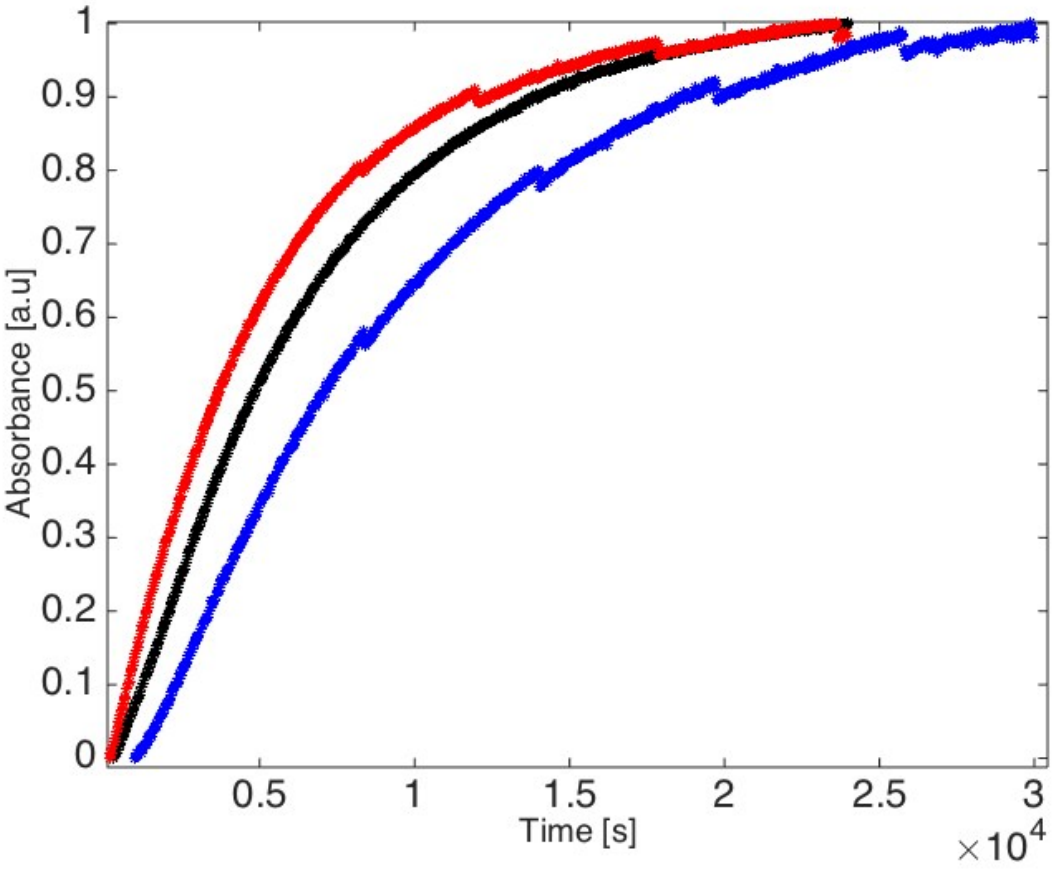


Figure ESI3. Back-reaction of 1 (blue), 2 (black) and 3 (red) followed by UV-.vis spectroscopy at 400 nm at 75°C.

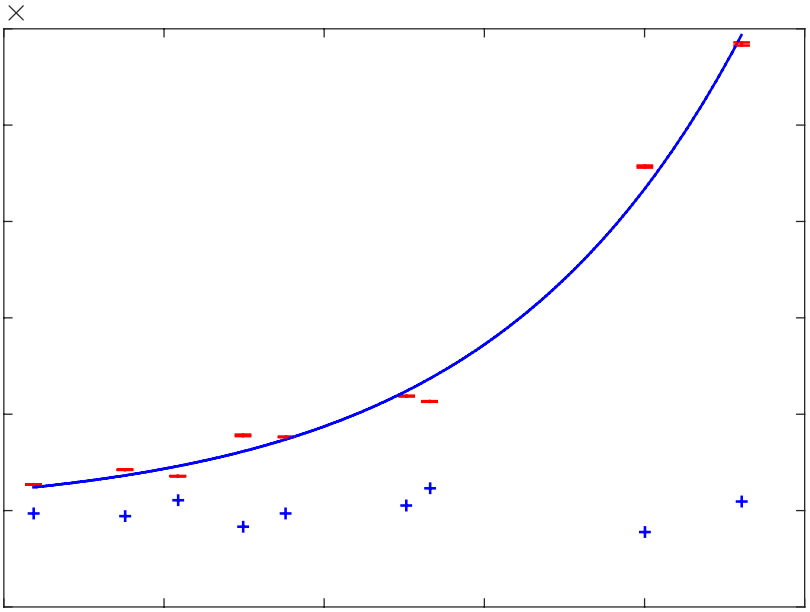


Figure ESI4. Eyring plot of **1**.

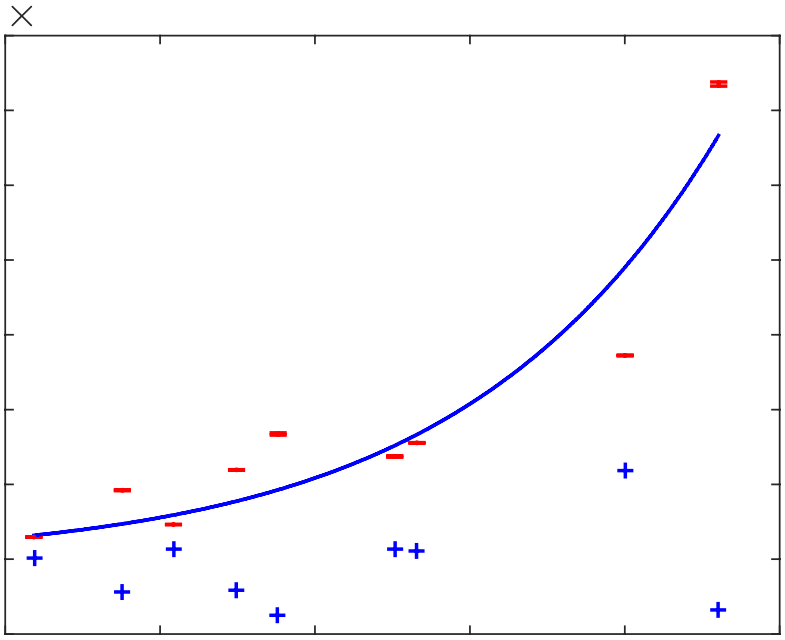


Figure ESI5. Eyring plog of **2**.

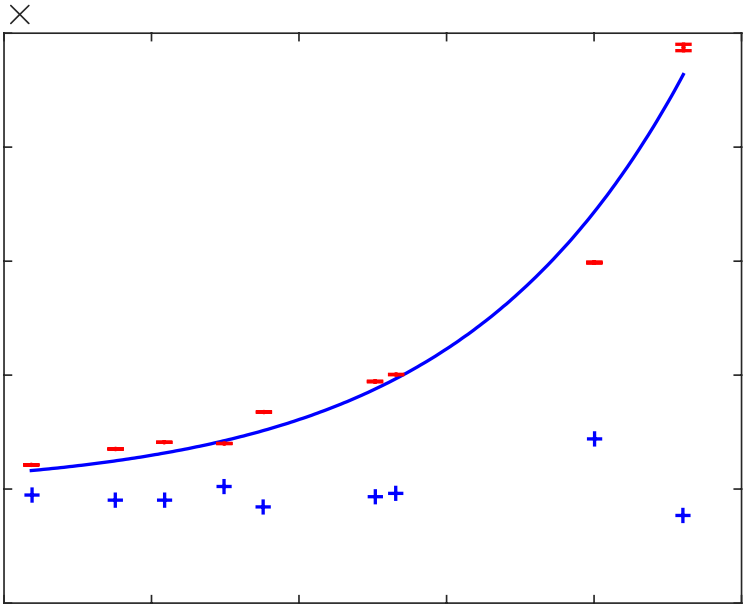


Figure S6. Eyring plot of **3**.

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