Electronic Supporting Information

A natural light induced regioselective 6π-electrocyclisation / oxidative aromatisation reaction: Experimental and theoretical insights

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1. COMPUTATIONAL DETAILS THEORETICAL STUDIES BY DFT

Density functional theory calculations at the B3LYP level[1] were performed to calculate the structures of the isomers and the transition states. Frequency calculations were also performed to confirm the characteristics of the calculated structures as minima or transition states. Calculations of intrinsic reaction coordinates (IRC)[2] were also performed on transition states to confirm that such structures are indeed connecting two minima. Time-dependent density functional theory was used to calculate the energy of the first excited state. The standard 6-31G basis set was used.[3] All calculations were carried out with the Gaussian 03 software package.[4]

Cartesian coordinates of the optimized geometries:

I

E = -1075.7594987 a.u. ZPE = 0.371313 a.u.
G = -1075.438183 a.u.

C	2.61259300	-1.83454600	1.27304000
C	1.56431500	-0.89491300	0.96529500
C	0.72011100	-1.05732300	-0.10748800
C	0.87210800	-2.21237900	-0.95990100
C	1.85512200	-3.11955300	-0.71040600
C	2.15845300	-4.35122500	-1.49759000
C	-0.38557600	-0.11016600	-0.36645300
C	-0.33633500	1.25630200	-0.36470500
C	-1.79134200	-0.65207600	-0.60995100
C	-2.42477100	-1.41706700	0.60079100
C	-3.79727100	-1.97596500	0.12533000
C	-4.69369400	-0.68886900	0.01989000
C	-3.72074600	0.45214700	0.42892400
C	-2.68433700	0.62228100	-0.72522000
C	-1.72457900	1.78826300	-0.52129700
C	-2.86805300	-0.24861400	1.52183800
O	2.70361600	-2.95893100	0.36141400
O	3.42056700	-1.80258600	2.19814800
O	-2.06438200	2.98229900	-0.46306500
C	0.83689500	2.14825100	-0.27523600
C	2.02680600	1.85156000	-0.97192300
C	0.77512500	3.33961300	0.47637600
C	3.12810600	2.70583700	-0.90077400
C	1.88227400	4.19020400	0.54879000
C	3.06169000	3.87682800	-0.13496100
H	1.47698200	-0.04697000	1.63076400
H	0.22054500	-2.35649800	-1.81085900
H	1.47236400	-4.45517800	-2.34148000
H	2.07802500	-5.24047900	-0.86200700
H	3.18621700	-4.31904700	-1.87687200
H	-1.81371700	-1.28002200	-1.50968900
H	-1.76504400	-2.16614100	1.04500200
H	-4.20011000	-2.68044700	0.86119600
H	-3.71451700	-2.51053600	-0.82790300
H	-5.10434300	-0.54049200	-0.98477100
H	-5.53841100	-0.73887200	0.71602500
H	-4.20407300	1.39096100	0.70654000
H	-3.18380300	0.73301100	-1.69402600
H	-2.03772100	0.35982600	1.89293900
H	-3.46373400	-0.58500900	2.37682500
H	2.08083400	0.95486500	-1.58006200
H	-0.14267300	3.60076800	0.98716600
H	4.03475300	2.46182200	-1.44520500
H	1.81997400	5.10024000	1.13682400
H	3.91867200	4.54039000	-0.07860100

II

E = -1075.7515742 a.u. ZPE = 0.371474 a.u.
G = -1075.439632 a.u.

C	1.49692700	-3.38450700	-0.77325600
C	0.53197400	-2.32611300	-0.93537900
C	0.59108800	-1.15144300	-0.21997900
C	1.64025800	-0.97842500	0.75729300
C	2.55833900	-1.96128700	0.95351200
C	3.68908500	-1.94913900	1.92735200
C	-0.44077600	-0.11012000	-0.40048000
C	-0.27365200	1.24792800	-0.34317100
C	-1.89581700	-0.51211800	-0.62399100
C	-2.56770800	-1.27899600	0.56448000
C	-3.99420900	-1.69200100	0.09885000
C	-4.77601600	-0.32879600	0.07760900
C	-3.69890000	0.70144100	0.51771700
C	-2.67597600	0.83957000	-0.65285200
C	-1.61335500	1.90515600	-0.41979900
C	-2.88708200	-0.12492100	1.55271100
O	2.51297700	-3.12931100	0.21865200
O	1.54981700	-4.45959800	-1.36883600
O	-1.84192500	3.11949900	-0.28401100
C	0.97327400	2.03357500	-0.27999500
C	2.09277100	1.67305700	-1.05979200
C	1.05577100	3.18968200	0.52432900
C	3.26604400	2.42873100	-1.01775500
C	2.23451000	3.93972100	0.56758600
C	3.34307900	3.56234500	-0.19890900
H	-0.23807000	-2.51067300	-1.67217500
H	1.69399600	-0.07246800	1.34280500
H	3.70677600	-1.01421000	2.49203600
H	4.64490800	-2.06563600	1.40379100
H	3.60143800	-2.78750800	2.62800400
H	-1.99638100	-1.08651100	-1.55339100
H	-1.96756700	-2.10499500	0.95225300
H	-4.44072900	-2.39392900	0.81154100
H	-3.97960300	-2.18518800	-0.87952400
H	-5.19062400	-0.09468500	-0.90890200
H	-5.60900000	-0.33986200	0.78944100
H	-4.09201600	1.66349400	0.85258200
H	-3.18431800	1.04316100	-1.60184100
H	-1.99929900	0.39118700	1.93120200
H	-3.49152300	-0.45190600	2.40528200
H	2.03207600	0.80853000	-1.71227200
H	0.19268800	3.50238400	1.09774800
H	4.11466900	2.13918800	-1.62935000
H	2.28347400	4.82376100	1.19527800
H	4.25439000	4.15108200	-0.16745100

3a

E = -1075.7260816 a.u. ZPE = 0.372169 a.u.
G = -1075.400855 a.u.

C	-2.96859300	1.22880200	0.47635000
C	-1.99467800	0.32099000	-0.26967900
C	-0.61367500	0.98157400	-0.35421400
C	-0.62115100	2.40596500	-0.60077900
H	0.28060500	2.89541200	-0.94997200
C	-1.72955600	3.15480800	-0.41755000
C	-1.92071800	4.60971000	-0.67327800
H	-1.00626000	5.05507300	-1.07318600
H	-2.19588700	5.13264300	0.25060100
H	-2.73415100	4.77662100	-1.39030000
C	0.50204600	0.19825600	-0.36595700
C	0.43201100	-1.24880100	-0.31181600
C	-0.75025300	-1.92462100	-0.08719400
C	-0.87427300	-3.35285000	-0.16532900
H	0.03120500	-3.92584500	-0.32352200
C	-2.10246400	-3.95412200	-0.12003400
H	-2.17669700	-5.03307600	-0.21492500
C	-3.32179900	-3.18060400	-0.00334100
H	-4.27511300	-3.69600000	-0.06622600
C	-3.28110100	-1.84171900	0.18140000
H	-4.18703000	-1.26225900	0.30998700
C	-1.97005200	-1.10444900	0.34474000
C	1.93933200	0.65946300	-0.55980500
H	2.02491800	1.31305600	-1.43665100
C	2.60123900	1.33959800	0.68722500
H	1.96938700	2.09766100	1.15634000
C	4.00359300	1.85268600	0.25064700
H	4.43410000	2.49951900	1.02335100
H	3.95718600	2.43591900	-0.67627000
C	4.83654600	0.52914700	0.09015000
H	5.23830000	0.40279000	-0.92112300
H	5.68409100	0.50930500	0.78472900
C	3.80990800	-0.58014500	0.45253100
H	4.25036000	-1.54857200	0.69871500
C	2.77211500	-0.66545900	-0.70908000
H	3.27314100	-0.77003700	-1.67798300
C	1.77308800	-1.81226400	-0.54100400
C	2.98028100	0.11681500	1.56497300
H	2.11822000	-0.46617300	1.90380100
H	3.58330300	0.39123500	2.43736800
O	-2.89810000	2.58621500	0.15625800
O	-3.82819900	0.87028800	1.27495100
O	2.09551400	-3.01954300	-0.57917900
H	-1.84106800	-0.95638300	1.43930500
H	-2.39340900	0.25675300	-1.30402800

3a´

E = -1075.7081695 a.u. ZPE = 0.372141 a.u.
G = -1075.383162 a.u.

C	3.32521200	-0.69556400	-0.24321800
C	2.01390200	-0.07458000	-0.70682500
C	0.77152500	-0.91828100	-0.42545000
C	0.96550900	-2.32899300	-0.19306500
H	0.10216900	-2.98230500	-0.15868800
C	2.18536500	-2.87534000	-0.01173100
C	2.53463500	-4.30442800	0.22333600
H	1.63640600	-4.92712600	0.21972800
H	3.04518400	-4.42732500	1.18638000
H	3.22004100	-4.67024400	-0.55115300
C	-0.44082000	-0.31530900	-0.56304200
C	-0.57034500	1.12843600	-0.69520100
C	0.47214700	1.99040800	-0.44159200
C	0.29748000	3.38790200	-0.11121700
H	-0.61385900	3.88040800	-0.42689600
C	1.18076600	3.98808500	0.74228000
H	1.01302800	5.01303900	1.05856800
C	2.28219600	3.24545200	1.33304400
H	2.84285400	3.70110700	2.14316300
C	2.61212100	2.01360900	0.88112600
H	3.46903000	1.47822800	1.26800300
C	1.90131800	1.46288300	-0.34489900
C	-1.81434900	-0.97473600	-0.56083800
H	-1.85418000	-1.77035100	-1.31505900
C	-2.32858500	-1.51985600	0.81700200
H	-1.58177800	-2.09431900	1.37006100
C	-3.65450900	-2.28787500	0.54577300
H	-3.96474200	-2.84494000	1.43706600
H	-3.55301700	-3.00936800	-0.27302500
C	-4.67346100	-1.13761700	0.21352500
H	-5.11012400	-1.23664500	-0.78628700
H	-5.50037100	-1.12219600	0.93252600
C	-3.81068600	0.14806900	0.34739200
H	-4.38006500	1.07273900	0.46154100
C	-2.82528400	0.19202500	-0.86040100
H	-3.35712300	0.08632600	-1.81268200
C	-1.99198300	1.47467700	-0.88595800
C	-2.85570200	-0.23569800	1.51032000
H	-2.07879700	0.50918300	1.70890500
H	-3.38612400	-0.44731000	2.44518100
O	3.35132500	-2.06664800	0.00358500
O	4.38475000	-0.08212500	-0.14547200
O	-2.48035900	2.61526000	-1.02624400
H	2.43230900	1.96381400	-1.17679300
H	2.11470700	-0.08421400	-1.80765300

V

E = -1075.6871596 a.u. ZPE = 0.369024 a.u.
G = -1075.367564 a.u.

C	1.06483400	3.70082300	-0.34986000
C	0.20433700	2.71791400	-0.09786200
C	0.47010200	1.29019700	-0.15841200
C	1.91564700	0.82117300	-0.38601000
C	2.72321200	1.06857700	0.90863100
C	2.67965800	0.05755200	2.02856700
C	-0.49641400	0.35546300	0.09400000
C	-0.20623500	-1.06808800	0.16031400
C	-1.95132200	0.61863900	0.45719000
C	-2.89000000	1.02571100	-0.73054500
C	-4.27808800	1.38583700	-0.12676700
C	-4.84992800	-0.01030700	0.31445800
C	-3.72326800	-0.99969300	-0.09509600
C	-2.52457700	-0.78493800	0.87926500
C	-1.38841600	-1.78664200	0.66254900
C	-3.19036400	-0.34323700	-1.39755600
O	3.34735900	2.13818600	1.02235200
O	1.77499600	4.62318800	-0.58602600
O	-1.49725800	-3.01522600	0.86657800
C	1.00211500	-1.59377100	-0.24526900
C	1.95144400	-0.62290500	-0.94832000
C	1.37698400	-2.97491700	-0.13706800
C	3.35352600	-1.14788100	-1.13044400
C	2.63532700	-3.38916800	-0.48239400
C	3.64658000	-2.45551200	-0.94534400
H	-0.79386400	3.05276800	0.17166600
H	3.17993300	0.47326600	2.90543800
H	3.18359600	-0.86953500	1.73154300
H	1.64608700	-0.20495500	2.27849600
H	-2.02192800	1.35864100	1.26476700
H	-2.46759800	1.79709600	-1.37946600
H	-4.91747100	1.85396000	-0.88361400
H	-4.19260600	2.08868000	0.70997200
H	-5.06690700	-0.05721900	1.38714900
H	-5.77876900	-0.24317300	-0.21851800
H	-4.03371000	-2.04461900	-0.16060600
H	-2.85153600	-0.83552800	1.92395500
H	-2.30442100	-0.83604200	-1.81013600
H	-3.95175000	-0.27424200	-2.18214400
H	0.64354900	-3.66469300	0.26326100
H	4.10998400	-0.44397700	-1.46808400
H	2.90701000	-4.43429000	-0.37300400
H	4.65146200	-2.82517700	-1.12531300

H 2.38921500 1.46937800 -1.13404700
H 1.51802300 -0.51848000 -1.96870900

4a

E = -1074.6000848 a.u. ZPE = 0.351060 a.u.
G = -1074.295180 a.u.

C -3.09608600 1.21768800 0.13987600
C -1.91745200 0.35332500 -0.01375500
C -0.66026500 0.96660900 -0.22723300
C -0.54359300 2.40140100 -0.31876000
H 0.42145700 2.85240000 -0.50103700
C -1.63179300 3.19356300 -0.19031700
C -1.69740700 4.68181900 -0.26269300
H -0.70772400 5.10574300 -0.44929500
H -2.08928000 5.09566200 0.67370300
H -2.37559400 4.99832300 -1.06352400
C 0.49441800 0.13998900 -0.37043200
C 0.38735000 -1.23827800 -0.33300400
C -0.86190400 -1.90144000 -0.12141500
C -0.95715500 -3.31650300 -0.07433700
H -0.05213100 -3.89569600 -0.20517200
C -2.17873200 -3.92920800 0.13689700
H -2.24432100 -5.01183400 0.17233100
C -3.33991900 -3.14524200 0.30711600
H -4.29701500 -3.62950700 0.47304200
C -3.27941300 -1.76259400 0.26561900
H -4.17559400 -1.17591700 0.39673800
C -2.04213300 -1.09130700 0.04950400
C 1.92065400 0.61311600 -0.58499000
H 1.99050000 1.26735000 -1.46272700
C 2.61231200 1.28752100 0.65391100
H 2.00063700 2.04684200 1.14666400
C 4.00476500 1.79626500 0.18086500
H 4.45719600 2.43932000 0.94389100
H 3.93678400 2.38201900 -0.74304000
C 4.82759300 0.47008200 -0.00407100
H 5.20116900 0.34405100 -1.02609500
H 5.69338200 0.44583600 0.66711700
C 3.80742700 -0.63594900 0.38495100
H 4.25027900 -1.60609300 0.61915500
C 2.73938200 -0.71568500 -0.74782900
H 3.20826100 -0.82937700 -1.73148000
C 1.72760200 -1.84253200 -0.54228900
C 3.00873300 0.06195300 1.51892500
H 2.15463500 -0.51878600 1.88031600
H 3.63370900 0.33407300 2.37612300
O -2.87092900 2.62333000 0.03904800
O -4.26774100 0.89551800 0.34762400
O 2.01959000 -3.05284400 -0.54241400

$TS_{I\text{-}3a'}$

E = -1075.6898556 a.u. ZPE = 0.370914 a.u.
G = -1075.366065 a.u.

C -3.23666200 0.95833800 -0.66555600
C -1.93332100 0.34650900 -1.02331800
C -0.70867300 0.97323500 -0.55090100
C -0.81252300 2.25717600 0.09899000
H 0.08249100 2.79429200 0.37766900
C -2.01121700 2.81264100 0.39761600
C -2.27422000 4.11935000 1.06579800
H -1.33706900 4.63875700 1.28193100
H -2.82053800 3.97580300 2.00593900
H -2.89493600 4.76119800 0.42888400
C 0.48454400 0.24912900 -0.69262600
C 0.50269100 -1.17403300 -0.66000700
C -0.60355600 -1.97342600 -0.25531300
C -0.42499600 -3.00951500 0.70722800
H 0.58004400 -3.36065300 0.90366100
C -1.49444800 -3.48334400 1.44282300
H -1.32600800 -4.22783500 2.21427800
C -2.81307000 -2.97865100 1.23273400
H -3.62876400 -3.34808300 1.84639800
C -3.06112900 -2.09045300 0.21852700
H -4.06933500 -1.77395500 -0.02476400
C -1.97878400 -1.59592000 -0.61973700
C 1.90581500 0.81469300 -0.71522300
H 1.99617100 1.53948700 -1.53302900
C 2.49179700 1.44234700 0.60516800
H 1.81253600 2.10818900 1.13840600
C 3.84804400 2.10570600 0.22351400
H 4.21894900 2.71943600 1.05217800
H 3.75544500 2.75785500 -0.65210500
C 4.78937200 0.87453300 -0.03515300
H 5.18809800 0.85641100 -1.05536100
H 5.64398500 0.87840500 0.65079900
C 3.86444500 -0.34037500 0.24872600
H 4.38344000 -1.28335400 0.43054400
C 2.82814300 -0.44068400 -0.90760700
H 3.31428600 -0.48470900 -1.88879500
C 1.90434200 -1.64286300 -0.72895000
C 2.97274200 0.20037900 1.39853000
H 2.16521900 -0.47965500 1.68743600
H 3.54273600 0.46786000 2.29485600
O -3.20748300 2.14412300 0.09049200
O -4.33780700 0.49426100 -0.96347300
O 2.30332200 -2.82139300 -0.64109800
H -2.19495200 -1.74117300 -1.67493200
H -1.91208700 0.11717500 -2.08293700

$2a\_H^+$

E = -1076.1207802 a.u. ZPE = 0.383770 a.u.
G = -1076.786441 a.u.

C -2.42262800 2.18284500 0.84496500
C -1.66259600 1.05575800 0.63495000
C -0.49822600 1.14235500 -0.16161900
C -0.16781700 2.43130400 -0.70533500
C -0.95450700 3.52731200 -0.49732000
C -0.78010500 4.91167900 -1.00454100
C 0.39977000 0.01882300 -0.37233400
C 0.08868200 -1.32336400 -0.28978900
C 1.88975600 0.25908500 -0.64338400
C 2.67615700 0.99043200 0.49915500
C 4.12373500 1.23286200 -0.02074500
C 4.75682000 -0.20495300 -0.00557000
C 3.59184500 -1.09763100 0.50332500
C 2.52606900 -1.16915500 -0.63740700
C 1.37564700 -2.11218400 -0.34641600
C 2.89884300 -0.15507500 1.52298800
O -2.09914500 3.38735000 0.29176800
O -3.52061200 2.18941500 1.60179000
O 1.46555400 -3.33113100 -0.15316400
C -1.20871000 -1.99703500 -0.24600000
C -2.27458700 -1.56624700 -1.07372600
C -1.39814500 -3.13854200 0.56864200
C -3.49431200 -2.23863600 -1.06697700
C -2.63083600 -3.79476900 0.58347100
C -3.67951700 -3.35003900 -0.23013000
H -1.97499000 0.13411700 1.10111100
H 0.71641700 2.55032200 -1.31458400
H 0.12120600 4.98465500 -1.61547800
H -0.70032900 5.62261600 -0.17398300
H -1.64119200 5.21426200 -1.61177500
H 2.02959600 0.77100700 -1.60433500
H 2.18462600 1.88995100 0.88017400
H 4.66092100 1.90958400 0.65134400
H 4.13456400 1.68674200 -1.01824000
H 5.11906000 -0.51871900 -0.98969000
H 5.60390300 -0.25526600 0.68598100
H 3.89085900 -2.08301900 0.86428700
H 2.98596700 -1.45328900 -1.59022100
H 1.97410700 -0.56097900 1.94710200
H 3.55732600 0.13738800 2.34625900

H	-2.12181200	-0.73314700	-1.75242400
H	-0.58306400	-3.50299300	1.17934100
H	-4.29434100	-1.91415800	-1.72357300
H	-2.76786800	-4.66064600	1.22147000
H	-4.62954000	-3.87330500	-0.22673800
H	-3.96380700	3.06086000	1.68359900

3a´_H$^+$

E = -1076.0464482 a.u. ZPE = 0.383716 a.u.
G = -1076.710037 a.u.

C	3.32521200	-0.69556400	-0.24321800
C	2.01390200	-0.07458000	-0.70682500
C	0.77152500	-0.91828100	-0.42545000
C	0.96550900	-2.32899300	-0.19306500
H	0.10216900	-2.98230500	-0.15868800
C	2.18536500	-2.87534000	-0.01173100
C	2.53463500	-4.30442800	0.22333600
H	1.63640600	-4.92712600	0.21972800
H	3.04518400	-4.42732500	1.18638000
H	3.22004100	-4.67024400	-0.55115300
C	-0.44082000	-0.31530900	-0.56304200
C	-0.57034500	1.12843600	-0.69520100
C	0.47214700	1.99040800	-0.44159200
C	0.29748000	3.38790200	-0.11121700
H	-0.61385900	3.88040800	-0.42689600
C	1.18076600	3.98808500	0.74228000
H	1.01302800	5.01303900	1.05856800
C	2.28219600	3.24545200	1.33304400
H	2.84285400	3.70110700	2.14316300
C	2.61212100	2.01360900	0.88112600
H	3.46903000	1.47822800	1.26800300
C	1.90131800	1.46288300	-0.34489900
C	-1.81434900	-0.97473600	-0.56083800
H	-1.85418000	-1.77035100	-1.31505900
C	-2.32858500	-1.51985600	0.81700200
H	-1.58177800	-2.09431900	1.37006100
C	-3.65450900	-2.28787500	0.54577300
H	-3.96474200	-2.84494000	1.43706600
H	-3.55301700	-3.00936800	-0.27302500
C	-4.67346100	-1.13761700	0.21352500
H	-5.11012400	-1.23664500	-0.78628700
H	-5.50037100	-1.12219600	0.93252600
C	-3.81068600	0.14806900	0.34739200
H	-4.38006500	1.07273900	0.46154100
C	-2.82528400	0.19202500	-0.86040100
H	-3.35712300	0.08632600	-1.81268200
C	-1.99198300	1.47467700	-0.88595800
C	-2.85570200	-0.23569800	1.51032000
H	-2.07879700	0.50918300	1.70890500
H	-3.38612400	-0.44731000	2.44518100
O	3.35132500	-2.06664800	0.00358500
O	4.43806068	-0.05125980	-0.14055391
O	-2.48035900	2.61526000	-1.02624400
H	2.43230900	1.96381400	-1.17679300
H	2.11470700	-0.08421400	-1.80765300
H	5.17187915	-0.66250795	-0.23795082

3a_H$^+$

E = -1076.0641901 a.u. ZPE = 0.383885 a.u.
G = -1076.727395 a.u.

C	-2.83352300	1.26576800	0.45369600
C	-1.98765200	0.30664300	-0.31850800
C	-0.59545500	0.97305200	-0.38851600
C	-0.58449600	2.38233100	-0.66897100
H	0.32303000	2.84571000	-1.03922900
C	-1.65916800	3.18015700	-0.47828100
C	-1.92279800	4.61716900	-0.73169700
H	-1.03148600	5.07687600	-1.16651700
H	-2.17026500	5.15234300	0.19235700
H	-2.75208800	4.76174800	-1.43449600
C	0.52217300	0.17141000	-0.38754300
C	0.44218300	-1.25868000	-0.29589800
C	-0.75192900	-1.93297400	-0.09798500
C	-0.87007700	-3.35703500	-0.14445400
H	0.03938600	-3.93455400	-0.25547500
C	-2.10323800	-3.96006600	-0.13458600
H	-2.16953500	-5.04042300	-0.20775600
C	-3.32849700	-3.19231800	-0.09735800
H	-4.27449100	-3.71123200	-0.20587600
C	-3.29628400	-1.84860000	0.05732800
H	-4.21325900	-1.27183000	0.10361600
C	-1.99088600	-1.12022800	0.28560200
C	1.95944000	0.62282400	-0.58625400
H	2.04738100	1.24935300	-1.48162200
C	2.60738100	1.34459900	0.65118900
H	1.97119200	2.11673300	1.09175600
C	4.00989500	1.84781300	0.20238100
H	4.42954900	2.52000400	0.95793700
H	3.96876100	2.40265000	-0.74148600
C	4.84869000	0.52379000	0.09058000
H	5.25954400	0.36663200	-0.91182700
H	5.68978200	0.52938800	0.79132000
C	3.82523400	-0.57738900	0.48374100
H	4.26685200	-1.53565000	0.76237000
C	2.79412900	-0.70448100	-0.68309900
H	3.29982000	-0.84130000	-1.64465800
C	1.79500400	-1.83878700	-0.48190200
C	2.98525600	0.15034700	1.56778700
H	2.12695500	-0.42773900	1.92673300
H	3.58240800	0.45713000	2.43194700
O	-2.77869100	2.55403200	0.24346500
O	-3.69785800	0.85353000	1.36621900
O	2.08828600	-3.04755800	-0.46527600
H	-1.89483000	-1.00450500	1.38722700
H	-2.41409100	0.26650500	-1.34639600
H	-4.17079800	1.57005800	1.85129400

2. NMR SPECTRA FOR COMPOUNDS 5 AND 6

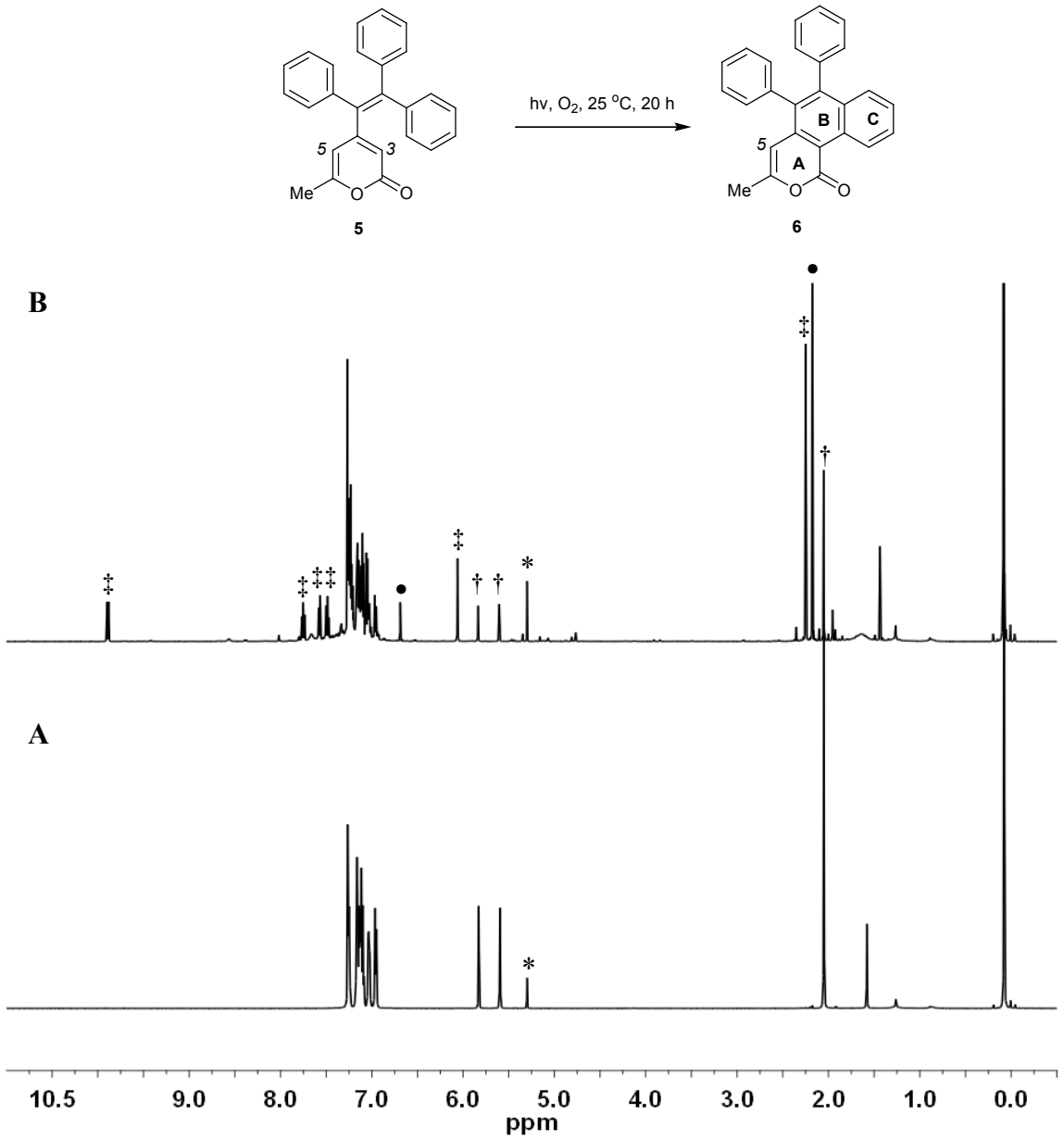

Figure S1. **A:** ^{1}H NMR spectrum of compound **5** in $CDCl_3$ at $t = 0$. **B:** ^{1}H NMR spectrum following 20 h of irradiation (400 nm). Key: ‡ = proton resonances from **6**; † = proton resonances from **5**; * = residual CH_2Cl_2; ● = Uncharacterised product(s).

Comment: A characteristic proton resonance (*H5*) for compound **6** is observed at δ = 6.06 (1H, q, *J* = 1 Hz), which is coupled (^4J) to the methyl group in ring **A** at δ = 2.25 (3H, d, *J* = 1 Hz). Both the *H3* and *H5* chemical shifts for compound **2a** and the *H5* chemical shift for **4a** can be compared with the similar proton environments in compounds **5** and **6**, respectively. Specifically, the *H5* resonance becomes deshielded on forming the electrocyclisation / aromatisation product **6**. Four separate deshielded aromatic proton resonances are also observed for **6** {δ = 9.89 (1H, d, *J* = 8.5 Hz); 7.75 (1H, ddd, *J* = 1.3, 6.8, 8.4 Hz); 7.57 (1H, dd, *J* = 0.9, 8.4 Hz); 7.48 (1H, ddd, *J* = 1.3, 6.8, 8.5 Hz)} are observed which are characteristic of ring **C**. Further characterisation of compound **6** has not been possible, as prolonged irradiation leads to degradation.

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