Electronic Supplementary Information

A New Type of Spirocyclic Photochromes Reacting with Light of both UV and Visible Ranges

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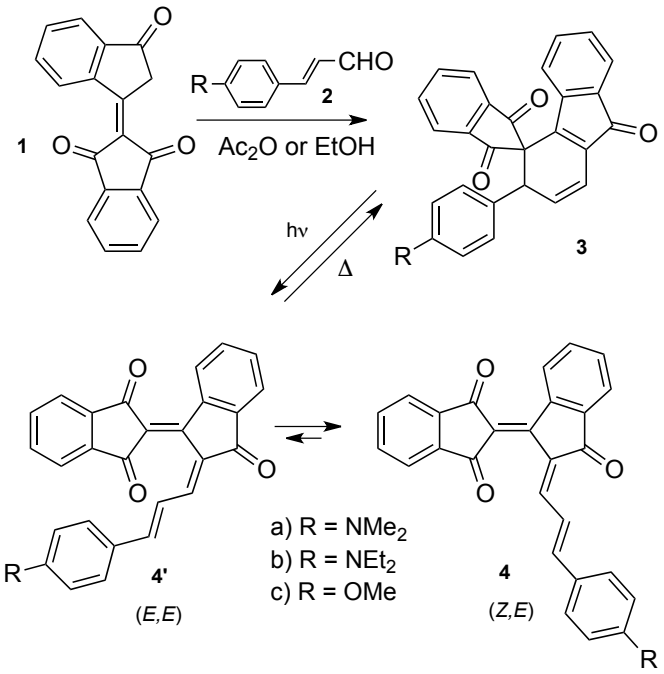

1. General

Bindone, cinnamic aldehyde derivatives and solvents were obtained from Sigma-Aldrich and Alfa-Aeser. Acetic anhydride was freshly distilled.

^{1}H spectra were recorded on Bruker AMX spectrometer at 500.13 and 125.77 MHz, respectively; and JEOL ECS400 at 399.78. Proton chemical shifts are given in ppm downfield from tetramethylsilane and coupling constants (*J*) in Hertz. Melting points were determined on a Büchi-510 apparatus and were not corrected.

X-ray crystallography data were collected on a Bruker-Nonius KappaCCD diffractometer with CCD detector using MoK_α radiation, λ = 0.71073 Å. The CIF files have been deposited at the Cambridge Crystallographic Data Centre: **3a**: CCDC 1436240, **3b**: CCDC 1436241 and **3c**: CCDC 1436242.

The UV–Vis absorption were recorded with Ocean Optics USB 4000 and JASCO V-660 in 4, 10 and 100 mm quartz cells.

Irradiation of solutions was done using a UVP LLC 95000505 lamp (254 nm), LED sources LUMOS 43 (Atlas Photonics) at 300, 315, 330, 350, 405, 450, 505 and 525 nm and lasers: Module Oxxius LBX-405-500-HPE-PP 405 nm, LBX-642-130-CIR-PP 642 nm, CryLas FQSS 266-200 (266 and 532 nm) and FQSS 355-300 (355 nm).

2. Synthesis

a) A mixture of bindone **1** (1 mmol) and the corresponding cinnamaldehyde (1.2 mmol) was dissolved in freshly distilled acetic anhydride (2 ml) and heated under reflux for 0.5 – 1.5 h. The formed products **3** were filtered off, washed with MeCN and dried on air and crystallized from MeCN or toluene. Derivatives **3a-c** do not exhibit characteristic melting points and slowly darken owing to the formation of **4** and finally melt leaving deeply colored spots. The initial reddish crystals of **3a-c** are formed upon cooling.
b) A mixture of bindone **1** (1 mmol) and the corresponding cinnamaldehyde (1.2 mmol) was refluxed in absolute ethanol for 2 -3 hours. The precipitated product was washed with ethanol, dried on air and crystallized.

3-(4-(Dimethylamino)phenyl)spiro[fluorene-4,2'-[2*H*]indene]-1',3',9(*3H*)-trione 3a

Yield: 63 % (method a), 71 % (method b) of reddish crystals, turn deep green above 200°C and revert to red upon cooling. Decomposes upon heating above 220°C.
^{1}H NMR (CD_2Cl_2): 2.77 (6H, t, J=7.0 Hz, CH_3); 4.63 (1H, dd, J_1=3.4, J_2=3.0, CH); 6.06 (1H, dd, J_1=9.7, J_2=3.0, CH); 6.19 (1H, td, J_1=7.3, J_2=0.71, CH); 6.38 (2H, d, J=8.9, CH); 6.53 (1H, dd, J_1=9.7, J_2=3.4, CH); 6.84 (2H, d, J=8.9, CH); 7.03 (1H, ddd, J_1=7.55, J_2=1.2, CH); 7.11 (1H, ddd, J_1=7.4, J_2=0.8, CH); 7.39 (1H, ddd, J_1=7.1, J_2=1.0, CH); 7.74 (1H, ddd, J_1=7.6, J_2=1.0, CH); 7.80 (1H, ddd, J_1=7.4, J_2=1.2, J_3=0.8, CH); 7.97 (1H, ddd, J_1=7.6, J_2=1.0, J_3=0.8, CH).
Calculated: C 80.72, H 4.91, N 3.25; $C_{29}H_{21}NO_3$; found: C 80.81, H 4.95, N 3.18.

trans-3-(4-(Dimethylamino)phenyl)allylidene)-[1,2'-biindenylidene]-1',3,3'(2*H*)-trione 4a

^{1}H NMR (CD_2Cl_2): 3.11 (6H, s, CH_3); 6.69 (2H, d, *J*=8.7, CH); 7.33 (1H, d, *J*=14.9, CH); 7.51 (1H, m, CH); 7.56 (1H, m, CH); 7.59 (2H, ddd, J_1=7.3, J_2=1.0, CH); 7.62 (2H, d, *J*=8.5, CH); 7.81 (1H, d, *J*=7.8, CH); 7.91 (2H, m, CH); 8.18 (1H, d, *J*=12.1, CH); 8.67 (1H, dd, J_1=14.9, J_2=12.1, CH); 8.88 (1H, d, *J*=8.0, CH).

3-(4-(Diethylamino)phenyl)spiro[fluorene-4,2'-[2*H*]indene]-1',3',9(*3H*)-trione 3b

Yield: 42 % (a), 68% (b) of reddish crystals, turn deep green above 120°C.

^{1}H NMR (CD_2Cl_2): 0.96 (6H, t, *J*=7.0, CH_3); 3.16 (4H, q, *J*=7.0, CH_2); 4.60 (1H, dd, J_1=3.4, J_2=3.0, CH); 6.07 (1H, dd, J_1=9.7, J_2=3.0, CH); 6.21 (1H, d, J_1=7.3, CH); 6.31 (2H, d, *J*=8.8, CH); 6.53 (1H, dd, J_1=9.7, J_2=3.4, CH); 6.79 (2H, d, *J*=8.8, CH); 7.04 (1H, ddd, J_1=7.6, J_2=1.2, CH); 7.11 (1H, ddd, J_1=7.10, J_2=0.7, CH); 7.39 (1H, ddd, J_1=7.1, J_2=0.6, CH); 7.66 (1H, m, CH); 7.71 (1H, ddd, J_1=7.6, J_2=7.2 and J_3=1.2, CH); 7.77 (1H, ddd, J_1=7.4, J_2=1.3, CH); 7.95 (1H, td, J_1=7.6, J_2=1.3, CH).

Calculated: C 81.02, H 5.48, N 3.05; $C_{31}H_{25}NO_3$; found: C 81.12, H 5.55, N 3.11.

3-(4-Methoxyphenyl)spiro[fluorene-4,2'-[2*H*]indene]-1',3',9(*3H*)-trione 3c

Yield: 75 % (a) of yellow-orange crystals, turn deep violet above 140°C.

^{1}H NMR (CD_2Cl_2): 3.61 (3H, s, OCH_3); 4.69 (1H, dd, J_1=3.4, J_2=2.9, CH); 6.06 (1H, dd, J_1=9.7, J_2=2.9, CH); 6.19 (1H, d, *J*=7.2, CH); 6.56 (1H, dd, J_1=9.7, J_2=3.4, CH); 6.57 (2H, d, *J*=8.82, CH); 6.93 (2H, d, *J*=8.6, CH); 7.04 (1H, dd, J_1=7.5, J_2=1.2, CH); 7.12 (1H, dd, J_1=7.4, J_2=0.9, CH); 7.40 (1H, ddd, J_1=7.1, J_2=1.2, J_3=0.9, CH); 7.68 (2H, m, CH); 7.74 (1H, dd, J_1=7.2, J_2=1.3, CH); 7.78 (1H, dd, J_1=7.3, J_2=1.3, CH).

Calculated: C 80.37, H 4.34; $C_{28}H_{18}O_4$; found: C 80.44, H 4.30

trans-3-(4-Methoxyphenyl)allylidene)-[1,2'-biindenylidene]-1',3,3'(2*H*)-trione 4c (generated by irradiation of the solution in CD_2Cl_2 at 532 nm).

^{1}H NMR (CD_2Cl_2): 3.88 (3H, s, OCH_3); 6.97 (2H, d, *J*=8.8, CH); 7.30 (1H, d, *J*=15.1, CH); 7.68 (4H, m, CH); 7.81 (2H, m, CH); 7.86 (1H, td, J_1=7.3, J_2=0.8, CH); 7.96 (1H, td, J_1=7.7, J_2=1.3, J_3=0.8, CH); 8.13 (1H, d, *J*=11.9, CH); 8.69 (1H, dd, J_1=15.1, J_2=11.9, CH); 9.05 (1H, d, *J*=7.7, CH).

3. ^{1}H NMR Spectra

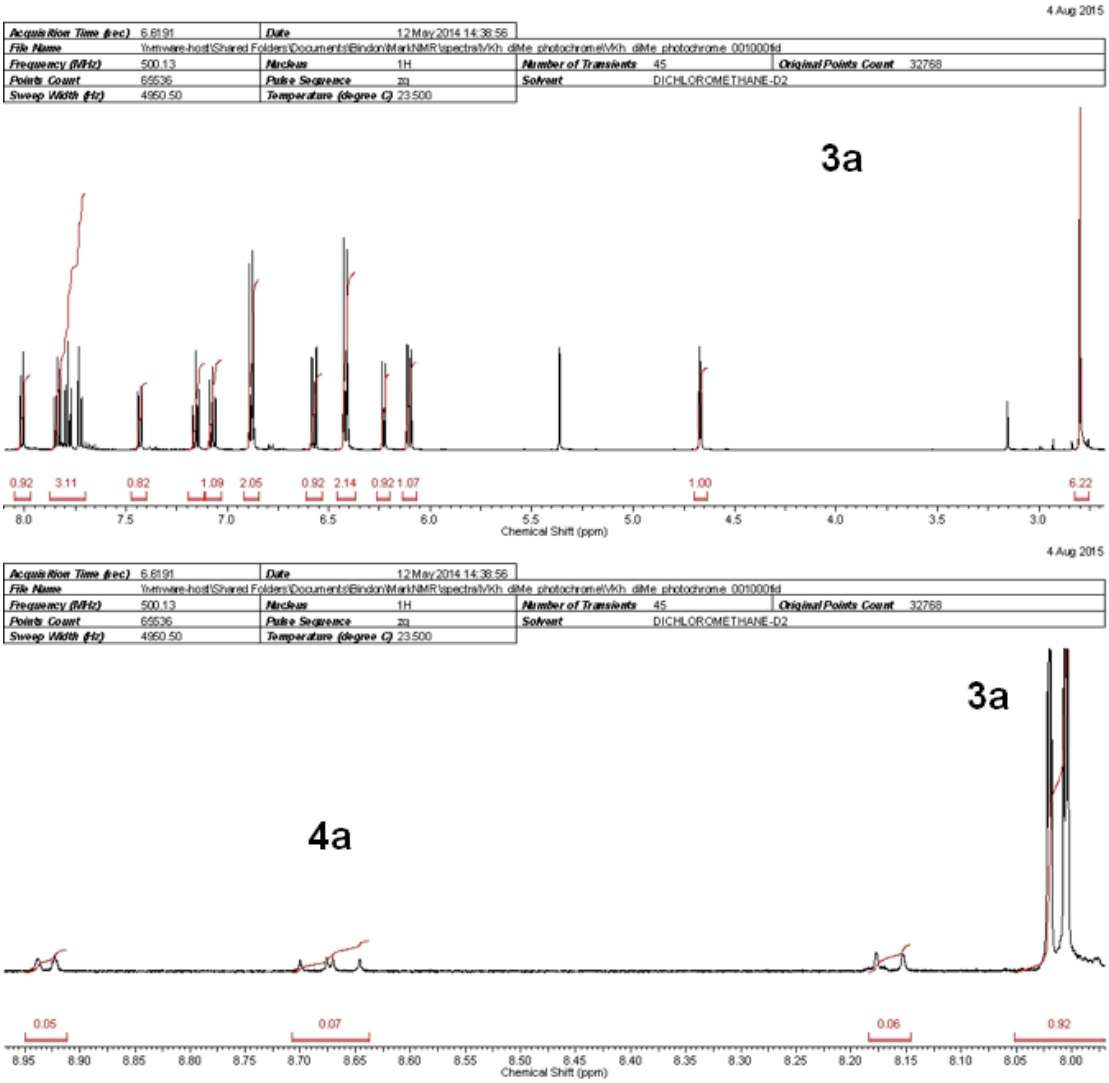

Figure 1S. ^{1}H-NMR spectra (low field region) of **3a** and **4a** in CD_2Cl_2.

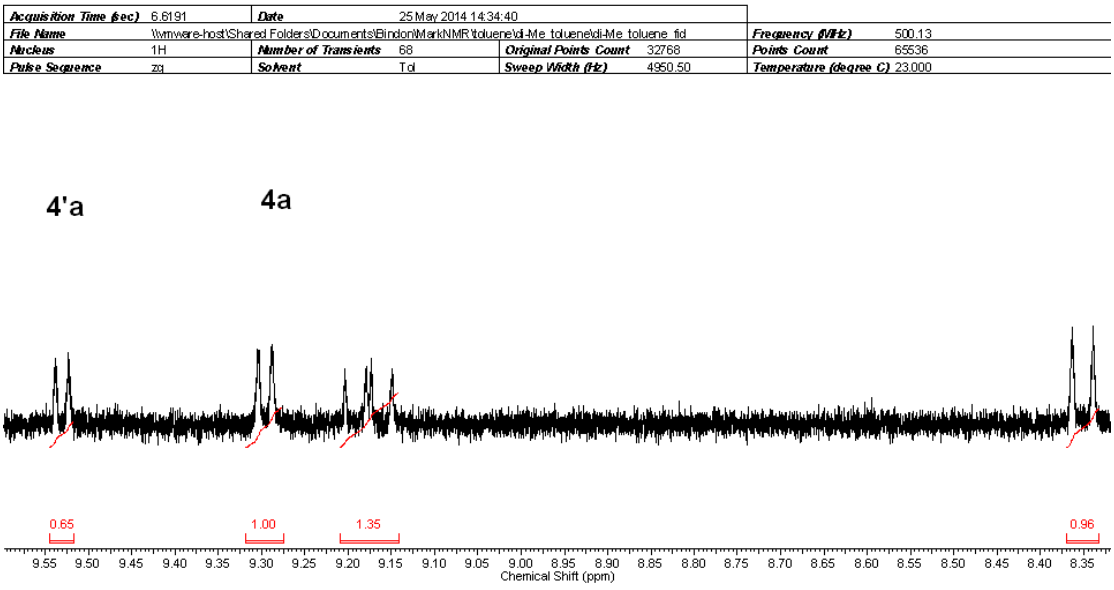

Figure 2S. ^{1}H-NMR spectra (low field region) of **4a** and **4'a** in toluene$_{d8}$

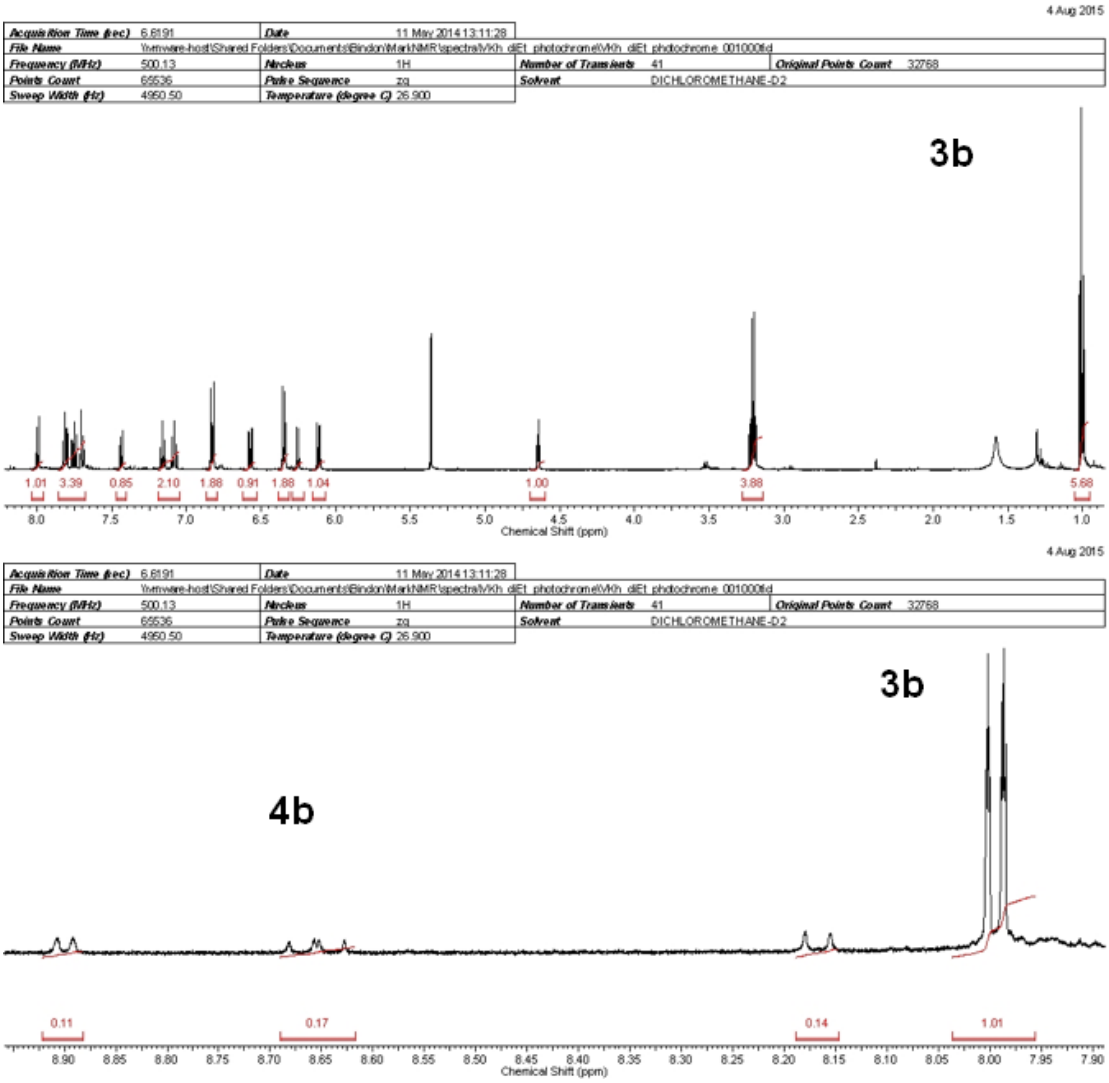

Figure 3S. ^{1}H-NMR spectra (low field region) of **3b** and **4b** in CD_2Cl_2.

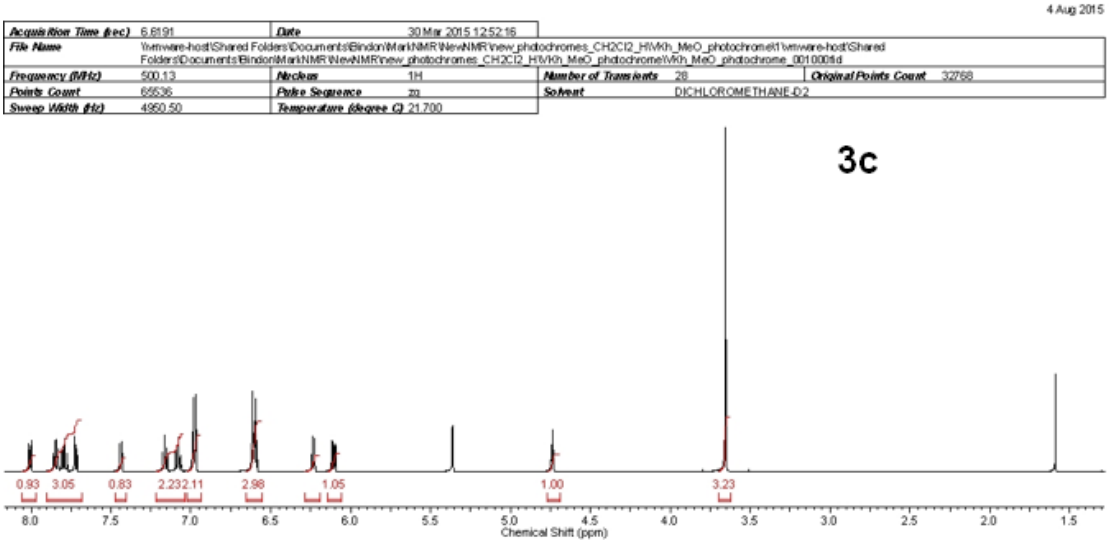

Figure 4S. ^{1}H-NMR spectra of **3c** in CD_2Cl_2.

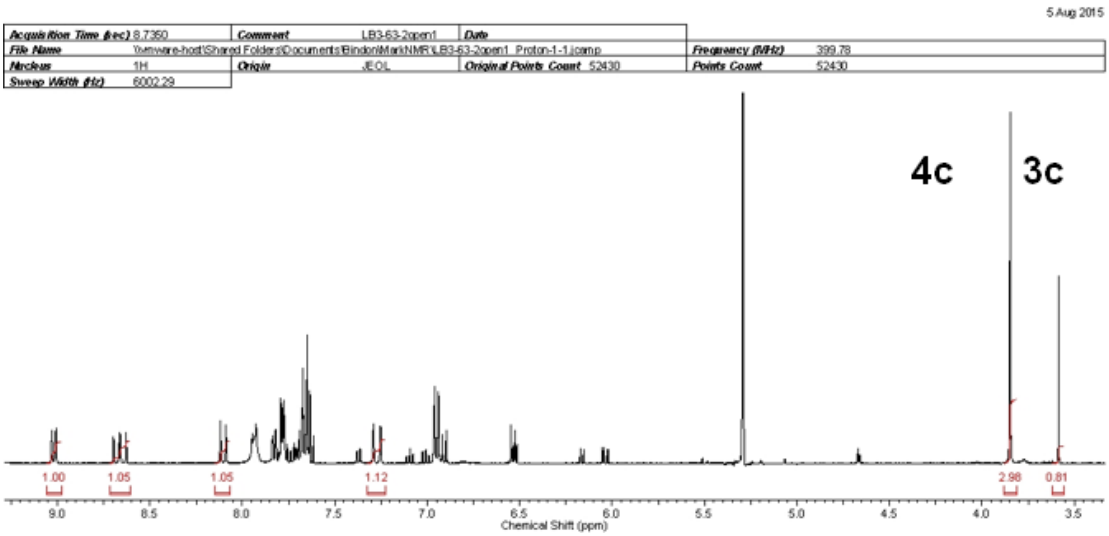

Figure 5S. ^{1}H-NMR spectra of **3c** in CD_2Cl_2 after irradiation at 505 nm. Major signals correspond to **4c**.

4. Short intermolecular distances H…O and C…O.

Table 1S. Short intermolecular distances H…O and C…O and angles C-H…O in **3a**, **3b** and **3c**.

	$d_{H...O}$(Å)	$d_{C...O}$(Å)	$<_{C-H...O}$(°)		
3a					
	2.68	3.231(11)	117.4	O2....C3	[0.5-x, y, z-0.5]
	2.65	3.216(11)	118.7	O2....C3	[0.5-x, y, z-0.5]
	2.66	3.592(10)	168.2	O1.....C9	[1-x, 1-y, 0.5+z]
	2.60	3.452(10)	149.1	O1....C16	[1-x, -y, 0.5+z]
	2.61	3.247(11)	124.9	O2.....C19	[1-x, -y, z-0.5]
	2.58	3.305(10)	133.7	O3..... C23	[x-0.5, 1-y, z]
	2.63	3.137(12)	112.1	O3.....C28	[1-x, 1-y, 0.5+z]
3b					
	2.81	3.693(4)	158.8	C7-H7...O3_$1	
	2.42	3.183(4)	138.9	C16-H16...O2_$2	
	2.76	3.568(4)	145.8	C26-H26...O1_$3	
	2.82	3.638(10)	143.1	C31A_a-H31B_a...O3_$5	
	3.07	3.690(15)	123.8	C31B_b-H31E_b...O2_$6	
3c					
	2.64	3.227(2)	120.4	C4-H4...O8_$1	
	2.73	3.282(2)	117.9	C5-H5...O8_$1	
	2.67	3.5098(19)	147.7	C7-H7...O1_$2	
	2.60	3.2715(16)	127.7	C11-H11...O6_$3	
	2.79	3.3755(16)	120.7	C12-H12...O6_$3	
	2.42	3.2107(18)	140.8	C17-H17...O3_$1	
	2.95	3.802(2)	150.4	C24-H24...O5	
	2.56	3.2263(19)	127.2	C32-H32...O4_$4	
	2.81	3.361(2)	117.5	C33-H33...O4_$4	

2.83	3.384(2)	118.4	C34-H34...O6_$5
2.75	3.3402(17)	120.9	C35-H35...O6_$5
2.54	3.2614(18)	133.1	C39-H39...O1_$6
2.46	3.1953(18)	133.6	C45-H45...O7_$4
2.87	3.6223(19)	136.5	C52-H52...O2_$6
2.86	3.519(3)	125.4	C56-H56B...O4_$7

6. Quantum Mechanical Calculations.

Reference:
Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

3a td=(nstates=12) b3lyp/6-31g(d,p)

Excited State 1: Singlet-A 2.1326 eV 581.37 nm f=0.0091 <S**2>=0.000
112 ->114 0.25156
113 ->114 0.64855
113 ->115 0.10470

3a td=(nstates=10) b3lyp/6-31g(d,p) scrf=(solvent=dichloromethane)

Excited State 1: Singlet-A 1.9386 eV 639.55 nm f=0.0037 <S**2>=0.000
112 ->114 0.12109
113 ->114 0.68803

4a td=(nstates=12) b3lyp/6-31g(d,p)

Excited State 1: Singlet-A 2.2573 eV 549.25 nm f=0.6800 <S**2>=0.000
112 ->114 -0.12021
113 ->114 0.66755
113 ->115 0.15565

Table 2S. Energy differences (ZPE corrected) between **3** and **4**, (in kcal/mol)[a]

	ΔE	ΔH°	ΔG°
a *(ZE)*	10.35	9.79	12.93
a *(EE)*	7.00	6.46	8.97
a *(ZZ)*	4.71	4.20	6.78
a *(EZ)*	3.34	2.89	5.08
a[b] *(ZE)*	11.30	10.79	13.11
a[c] *(ZE)*	10.17	-	-
c	8.60	8.03	10.35
c[b]	8.41	-	-

[a] B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p). [b] in CH_2Cl_2. [c] B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d,p).