Supplementary Information –

Photoswitchable fluorescent diheteroarylethenes. Substituent effects on photochromic and solvatochromic properties

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1. Synthetic Procedures

1,2-Bis(2-methyl-6-(4-cyanophenyl)-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**3**): A solution of **2** (50 mg, 0.064 mmol) and 4-cyanophenylboronic acid (28 mg, 0.19 mmol) were stirred in a mixture of THF (1.25 mL) and ethanol (0.75 mL) until dissolution. Palladium(II)acetate (0.1 mg, 0.0005 mmol), K_2CO_3 (18 mg, 0.13 mmol) and finally distilled water (1 mL) were then added and the mixture was stirred at room temperature for 90 min. Reaction was followed by thin layer chromatography (TLC). The reaction was quenched with NaCl (ss) and extracted with CH_2Cl_2. The organic layer was purified by silica gel column chromatography (cyclohexane:ethyl acetate 95:5 to 8:2) to give **3** (40.9 mg, 0.056 mmol, 87% yield) as a yellow solid. **3**: ^{1}H NMR (400 MHz, chloroform-*d*) δ 2.13 (s, 3.4H, p), 2.26 (s, 2.6H, ap) (57:43 p:ap), 7.26 (s, 1H), 7.28 (s, 1H), 7.56 - 7.72 (m, 5H), 7.73 - 7.85 (m, 6H), 7.94 (s, 1H), 7.97 (s, 1H). ^{13}C NMR: (ppm) 9.0, 9.1, 14.1, 22.7, 29.2, 29.3, 29.7, 31.7, 31.9, 53.8, 69.6, 112.9, 118.2, 121.5, 121.6, 123.0, 127.7, 127.7, 127.8, 127.8, 129.1, 132.2, 132.5, 133.0, 133.0, 136.3, 142.3, 142.3. HRMS (ESI) calculated for $C_{37}H_{20}F_6N_2O_4S_2$ [M-H] 733.0696, found: 733.0698 [M+Na]: 757.0661, found: 757.0659.

1,2-Bis(2-methyl-6-(4-formylphenyl)-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**4**): A solution of **2** (50 mg, 0.064 mmol) and 4-formylphenylboronic acid (29 mg, 0.19 mmol) were stirred in a mixture of THF (1.5 mL) and ethanol (0.75 mL) until dissolution. Palladium(II)acetate (0.1 mg, 0.5 µmol), K_2CO_3 (18 mg, 0.13 mmol) and finally distilled water (1 mL) were added and the mixture was stirred at room temperature for 60 min. The reaction was followed by TLC and quenched with NaCl (ss) and extracted with CH_2Cl_2. The organic layer was purified by silica gel column chromatography (cyclohexane:ethyl acetate 1:0 to 7:3) to yield **4** (30.1 mg, 41 µmol, 64% yield) as a yellow solid. **4**: ^{1}H NMR (400 MHz, chloroform-*d*) δ ppm 2.14 (s, 3,3H, p), 2.26 (s, 2.7H, ap) (55:45 p:ap), 7.28 (d, *J*=8.2 Hz, 2H), 7.64 - 7.73 (m, 2.8H), 7.76 (d, *J*=7.8 Hz, 2.2H), 7.86 (d, *J*=7.0 Hz, 1.2H), 7.94 - 7.99 (m, 2.8H), 8.01 (d, *J*=6.3 Hz, 3.4H), 10.06 (s, 1.1H), 10.09 (s, 0.8H). ^{13}C NMR: (ppm) 9.0, 9.0, 9.1, 19.4, 26.9, 60.3, 76.7, 77.0, 77.3, 89.0, 115.9, 121.6, 121.7, 122.7, 122.9, 127.7, 127.8, 128.0, 128.9, 129.2, 130.6, 130.7, 132.3, 132.4, 132.6, 136.2, 136.4, 143.0, 143.6, 143.9, 144.7, 190.7, 191.4, 191.5. HRMS (ESI) calculated for $C_{37}H_{22}F_6O_6S_2$ [M+Na]: 763.0654, found: 763.0650 [M+NH4]: 758.1100, found: 758.1103 [M-H] 739.0689, found: 739.0689.

1,2-Bis(2-methyl-6-(4-N-methylaminocarbonylphenyl)-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**5**): A solution of **2** (40 mg, 0.051 mmol) and 4-(N-methylaminocarbonyl)phenylboronic acid (37 mg, 0.204 mmol) in THF (2.8 mL) was stirred until dissolution. Tris(dibenzylideneacetone)dipalladium(0) (9.3 mg, 10 µmol), 97% tricyclohexylphosphine toluene solution (8 µL, 26 µmol) and saturated aqueous K_2CO_3 (2.8 mL) were added and the mixture was stirred at room temperature for 7 h. The reaction was followed by TLC. The reaction mixture was neutralized with dilute HCl, filtered to remove solids and the filtrate extracted with CH_2Cl_2. The organic layer was purified by silica gel column chromatography (cyclohexane:ethyl acetate 7:3 to 0:1) to yield **5** (17.9 mg, 22 µmol, 44% yield) as a yellow/orange solid. **5**: ^{1}H NMR (400 MHz, chloroform-*d*) δ ppm 2.12 (s, 3.1H, p), 2.25 (s, 2.9H, ap) (52:48 p:ap), 3.01 - 3.09 (m, 6H), 6.20 - 6.32 (m, 2H), 7.24 (s, 1H), 7.26 (s, 1H), 7.54 (d, *J*=8.2 Hz, 2H), 7.64 (d, *J*=7.8 Hz, 3H), 7.83 (d, *J*=8.2 Hz, 31H), 7.89 (d, *J*=8.2 Hz, 22H), 7.92 (s, 1H), 7.98 (s, 1H). ^{13}C NMR: (ppm) 8.9, 9.1, 26.9, 121.2, 121.4, 122.9, 123.7, 127.1, 127.3, 127.4, 127.8, 128.0, 128.5, 128.7, 132.1, 132.4, 135.0, 135.6, 136.1, 140.1, 140.5, 140.7, 143.0, 143.3,

143.6, 144.2, 167.2, 167.3. HRMS (ESI) calculated for $C_{39}H_{28}F_6N_2O_6S_2$ [M+H]: 799.1362, found: 799.1366 [M+Na]: 821.1186, found: 821.1185.

1,2-Bis(2-methyl-6-(4-methanesulphonylaminomethylphenyl)-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**6**): A solution of **2** (40 mg, 51 µmol) and 4-(methanesulphonylaminomethyl)phenylboronic acid (47 mg, 0.204 mmol) in THF (2.8 mL) was stirred until dissolution. Tris(dibenzylideneacetone)dipalladium(0) (9.3 mg, 10 µmol), 97% tricyclohexylphosphine toluene solution (8 µL, 26 µmol) and saturated aqueous K_2CO_3 (2.8 mL) were then added and the mixture was stirred at 40 °C for 24 h. The reaction was followed by TLC. The reaction mixture was neutralized with dilute HCl, filtered to remove solids and the filtrate extracted with CH_2Cl_2. The organic layer was purified by silica gel column chromatography (cyclohexane:ethyl acetate 7:3 to 1:3) to yield **6** (13 mg, 14 µmol, 28% yield) as a yellow solid. **6**: ^{1}H NMR (400 MHz, chloroform-*d*) δ 2.10 (s, 2.8H, p), 2.23 (s, 3.2H, ap) (47:53 p:ap), 2.88 (d, *J*=6.3 Hz, 6H), 4.30 (d, *J*=6.3 Hz, 2H, p), 4.35 (d, *J*=6.3 Hz, 2H, ap), 5.08 (t, *J*=6.1 Hz, 1H, p), 5.20 (t, *J*=6.1 Hz, 1H, ap), 7.24 (d, *J*=7.8 Hz, 2H), 7.33 - 7.48 (m, 6H), 7.55 (d, *J*=8.2 Hz, 2H), 7.59 (d, *J*=7.8 Hz, 1H), 7.79 (d, *J*=7.8 Hz, 1H), 7.83 (s, 1H), 7.91 (s, 1H). ^{13}C NMR: (ppm) 8.8, 9.0, 29.3, 41.0, 41.1, 46.5, 46.6, 121.0, 121.3, 122.9, 123.0, 123.8, 127.3, 127.5, 127.7, 128.0, 128.2, 128.6, 128.7, 128.9, 131.9, 132.2, 135.9, 137.4, 137.6, 138.0, 138.1, 143.3, 143.4, 143.7, 143.8. HRMS (ESI) calculated for $C_{39}H_{32}F_6N_2O_8S_4$ [M+Na]: 921.0835, found: 921.0838.

1,2-Bis(2-methyl-6-(4-ethynylphenyl)-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**7**): A solution of **2** (50 mg, 64 µmol) and 4-(dihydroxyborophenyl)acetylene (28 mg, 0.19 mmol) were stirred in a mixture of THF (0.75 mL) and ethanol (0.75 mL) until dissolution. Palladium(II)acetate (0.1 mg, 0.5 µmol), K_2CO_3 (18 mg, 0.13 mmol) and finally distilled water (1 mL) were then added and the mixture was stirred at room temperature for 140 min. Reaction was followed by TLC. The reaction was quenched with NaCl (ss) and extracted with CH_2Cl_2. The organic layer was purified by silica gel column chromatography (cyclohexane:ethyl acetate 1:0 to 7:3) to yield **4** (31.3 mg, 43 µmol, 67% yield) as a yellow solid.**7**: ^{1}H NMR (400 MHz, chloroform-*d*) δ ppm 2.11 (s, 3.1H, p), 2.24 (s, 2.9H, ap) (52:48 p:ap), 3.18 (s, 1H), 3.19 (s, 1H), 7.22 (s, 1H), 7.24 (s, 1H), 7.47 (d, J=7.8Hz, 2H), 7.51 - 7.64 (m, 7H), 7.80 (d, *J*=7.8 Hz, 1H), 7.92 (s, 1H), 7.97 (s, 1H). ^{13}C NMR: δ ppm 8.9, 9.0, 14.1, 18.0, 29.2, 29.7, 31.9, 77.2,

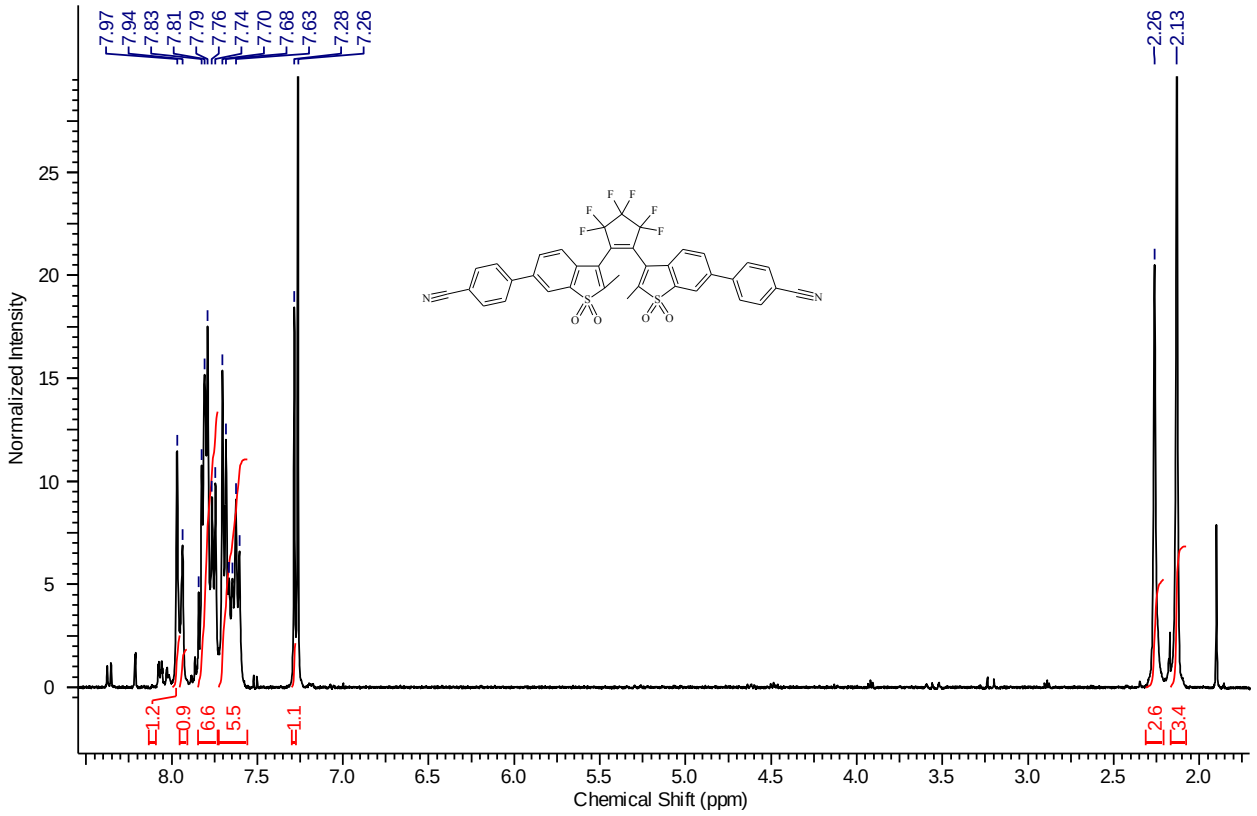
79.0, 79.5, 82.8, 82.8, 121.1, 121.2, 121.3, 123.0, 123.7, 123.7, 126.9, 127.0, 127.1, 128.2, 128.4, 131.9, 132.1, 132.9, 132.9, 133.1, 136.1, 137.6, 138.1, 138.1, 142.9, 143.2, 143.4, 143.5, 144.1, 146.5, 206.8. HRMS (ESI) calculated for $C_{39}H_{22}F_6O_4S_2$ [M-H] 731.0791, found: 731.0787 [M+Na]: 755.0756, found: 755.0751.

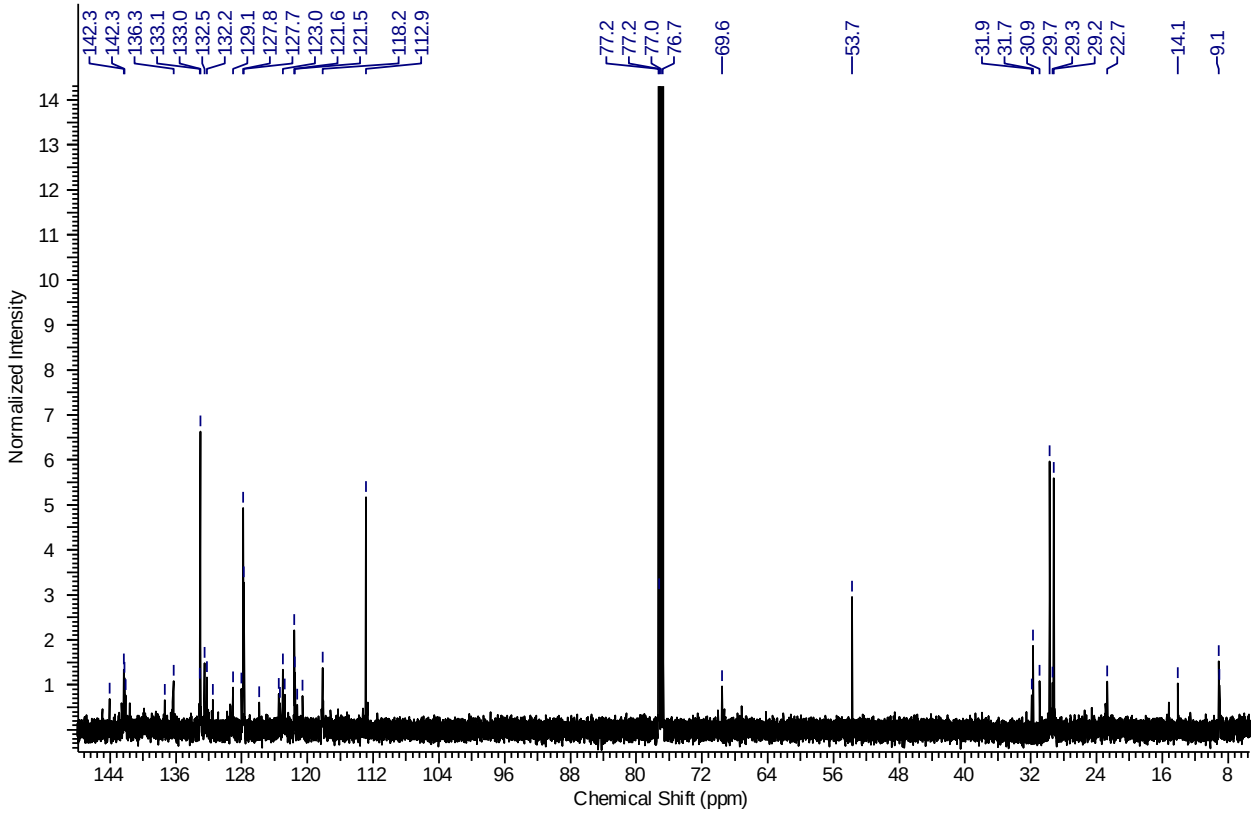
1,2-Bis(2-methyl-6-(4-(2-bromoethoxy)phenyl)-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**8**): A solution of **2** (40 mg, 51 µmol) and 4-(2-bromoethoxy)phenylboronic acid (50 mg, 0.204 mmol) in THF (2.8 mL) was stirred until dissolution. Tris(dibenzylideneacetone)dipalladium(0) (9.3 mg, 10 µmol), 97% tricyclohexylphosphine toluene solution (8 µL, 0.026 mmol) and saturated aqueous K_2CO_3 (2.8 mL) were then added and the mixture was stirred at 55 °C for 24 h. The reaction was followed by TLC. The reaction mixture was neutralized with dilute HCl, filtered to remove solids and the filtrate extracted with CH_2Cl_2. The organic layer was purified by silica gel column chromatography (cyclohexane:ethyl acetate 1:0 to 7:3) to yield **8** (12.2 mg, 13 µmol, 26% yield) as an orange/red solid. **8**: ^{1}H NMR (400 MHz, chloroform-*d*) δ ppm 2.10 (s, 3.2H, p), 2.23 (s, 2.8H, ap) (53:47 p:ap), 3.63 - 3.70 (m, 4H), 4.28 - 4.39 (m, 4H), 6.97 (d, *J*=8.6 Hz, 2H), 7.02 (d, *J*=8.2 Hz, 2H), 7.20 (s, 1H), 7.22 (s, 1H), 7.45 (d, *J*=8.6 Hz, 2H), 7.49 - 7.56 (m, 2H), 7.59 (d, *J*=7.8 Hz, 1H), 7.75 (d, *J*=8.2 Hz, 1H), 7.88 (s, 1H), 7.93 (s, 1H). ^{13}C NMR: (ppm) 8.9, 9.0, 28.8, 28.8, 68.0, 115.5, 115.6, 120.8, 120.9, 122.7, 122.8, 123.9, 127.3, 127.5, 128.4, 128.4, 128.7, 131.1, 131.1, 131.3, 131.6, 136.0, 142.8, 143.5, 143.7, 143.9, 158.9. HRMS (ESI) calculated for $C_{39}H_{28}Br_2F_6O_6S_2$ [M+Na]: 952.9469, found: 952.9473.

2. ^{1}H and ^{13}C NMR Spectra

^{1}H and ^{13}C NMR spectra are shown for all compounds almost completely in the open form (< 5-10% closed form). Unassigned peaks in ^{1}H spectra correspond to closed isomer protons. Closed isomer carbon atoms are assumed non-observable in ^{13}C spectra.

Compound 3:





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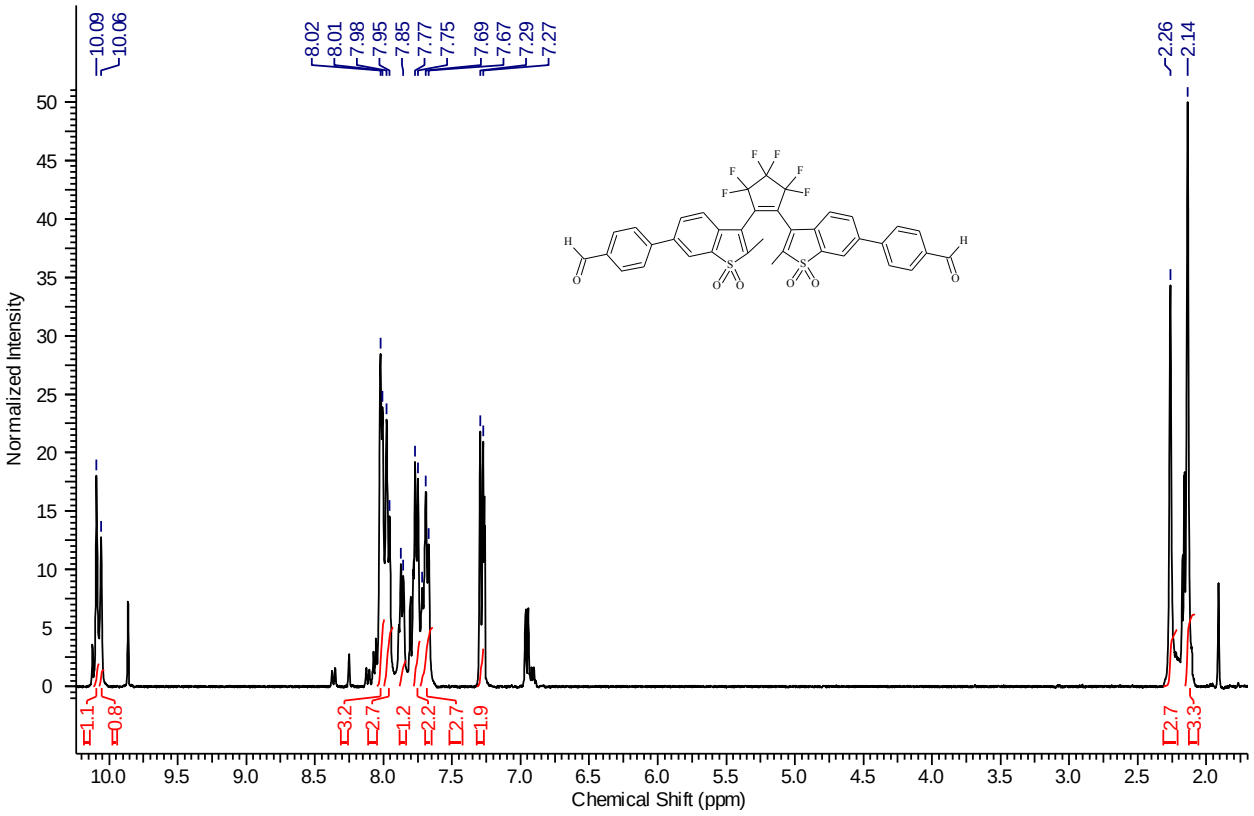
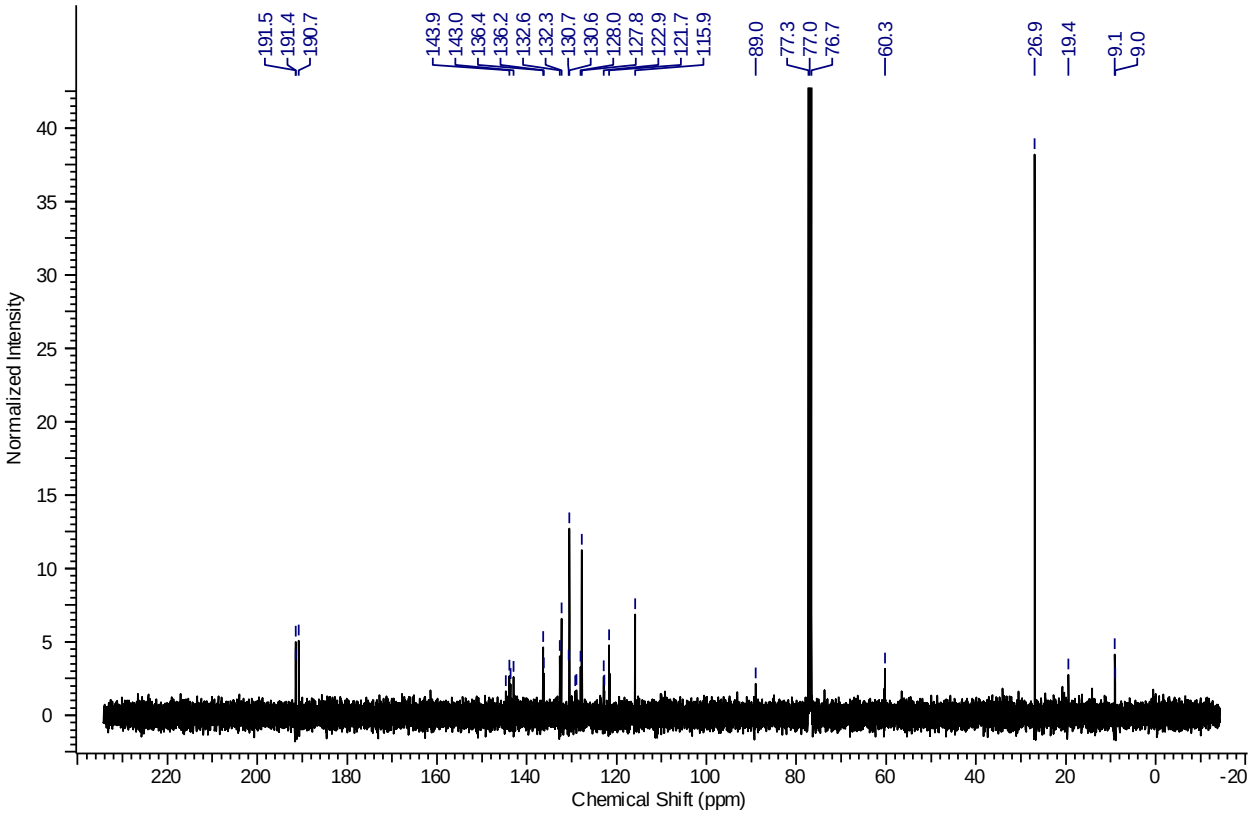
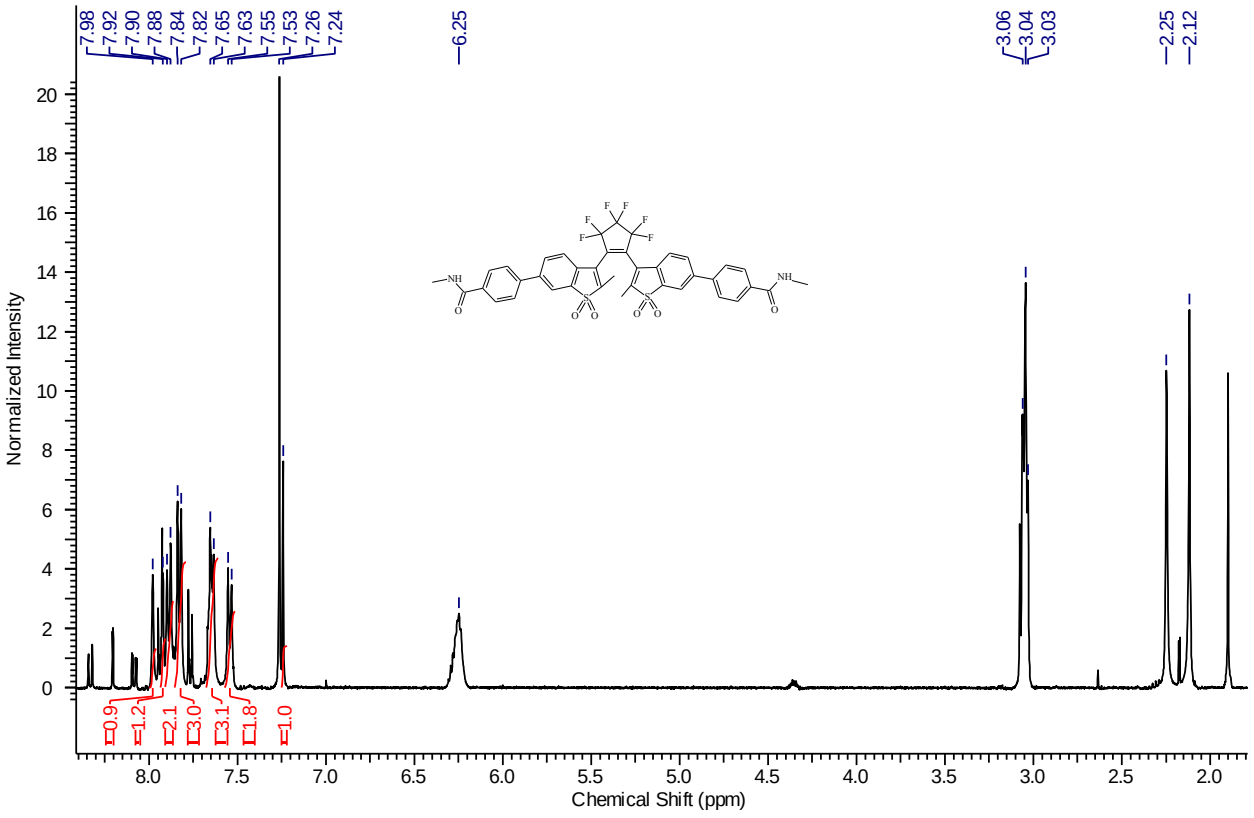
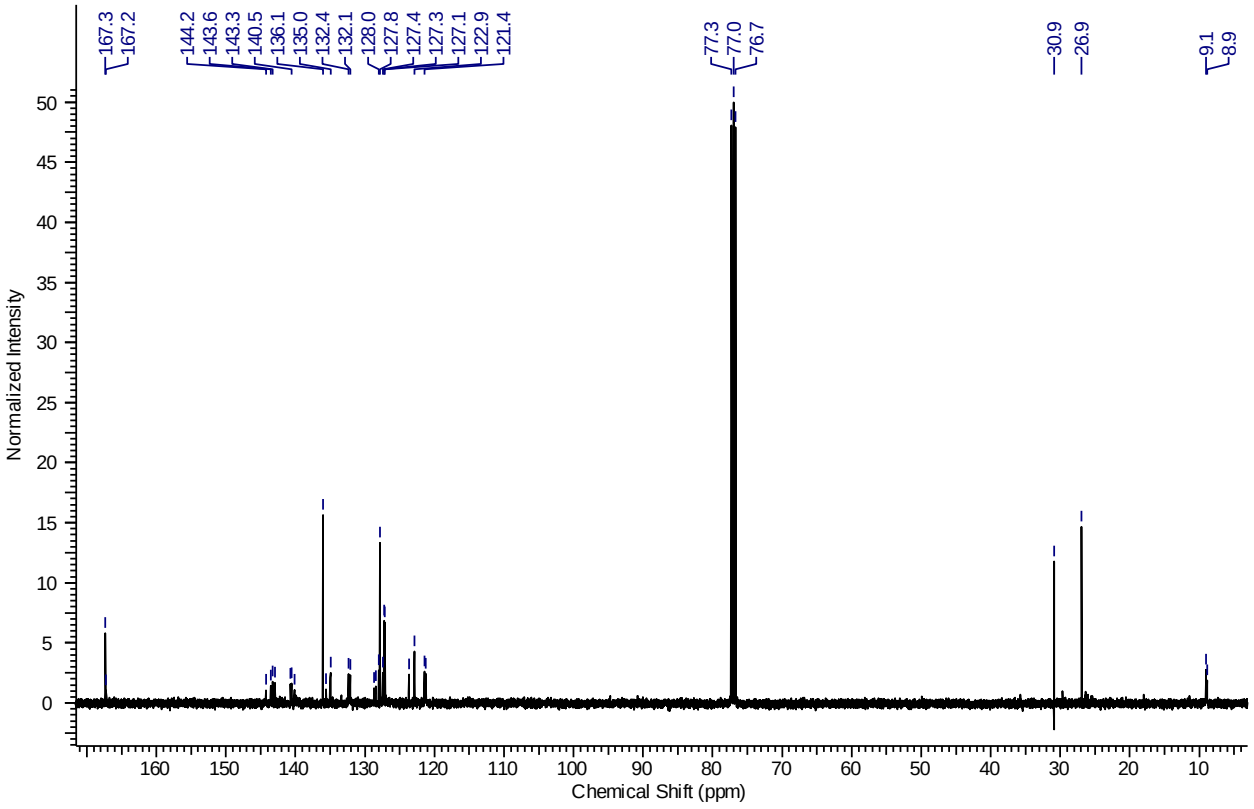


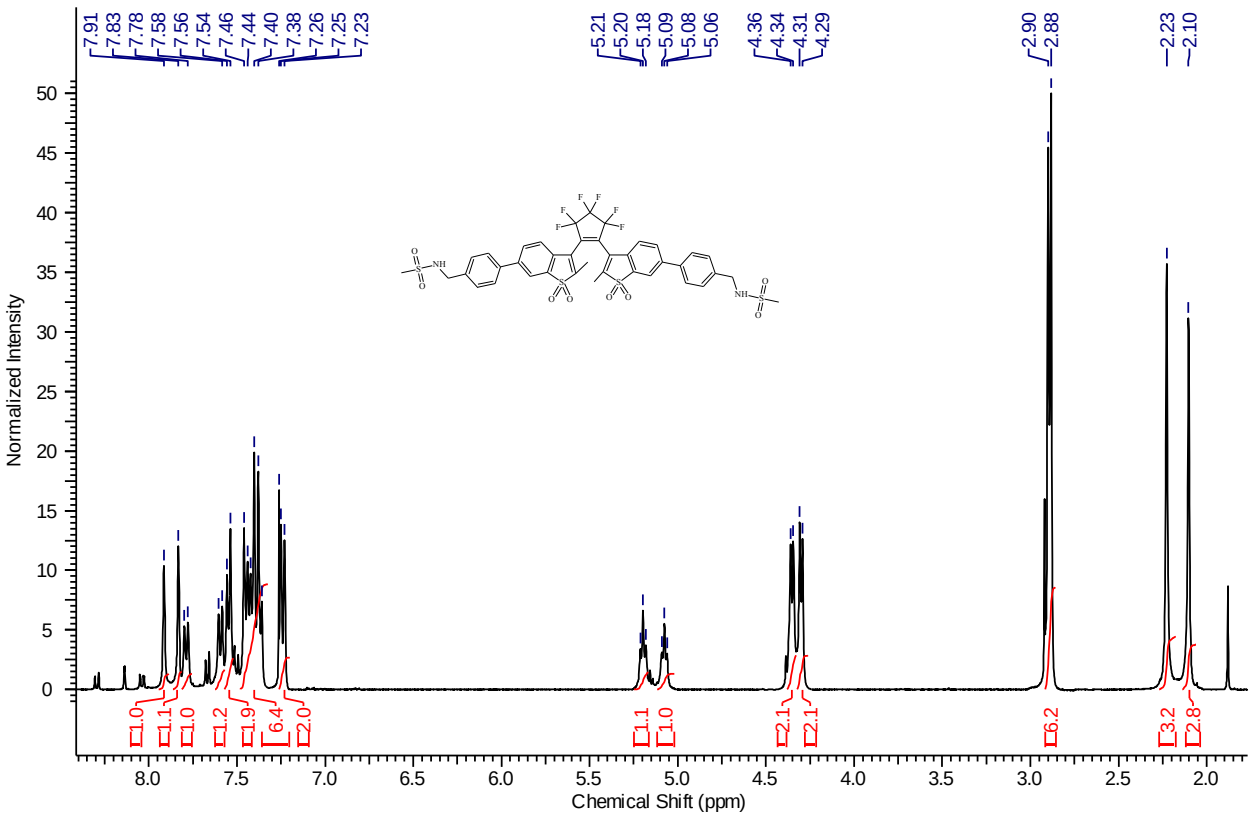


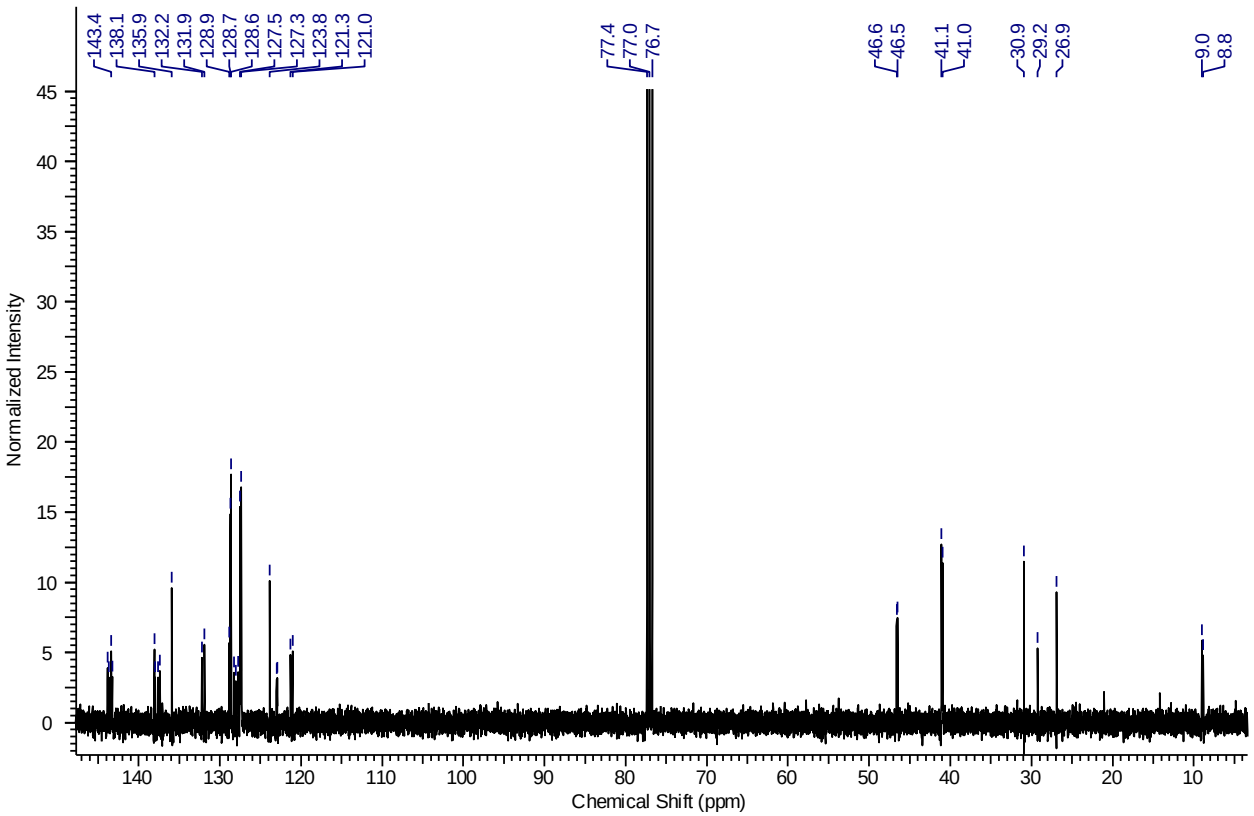
Compound 5:





Compound 6:





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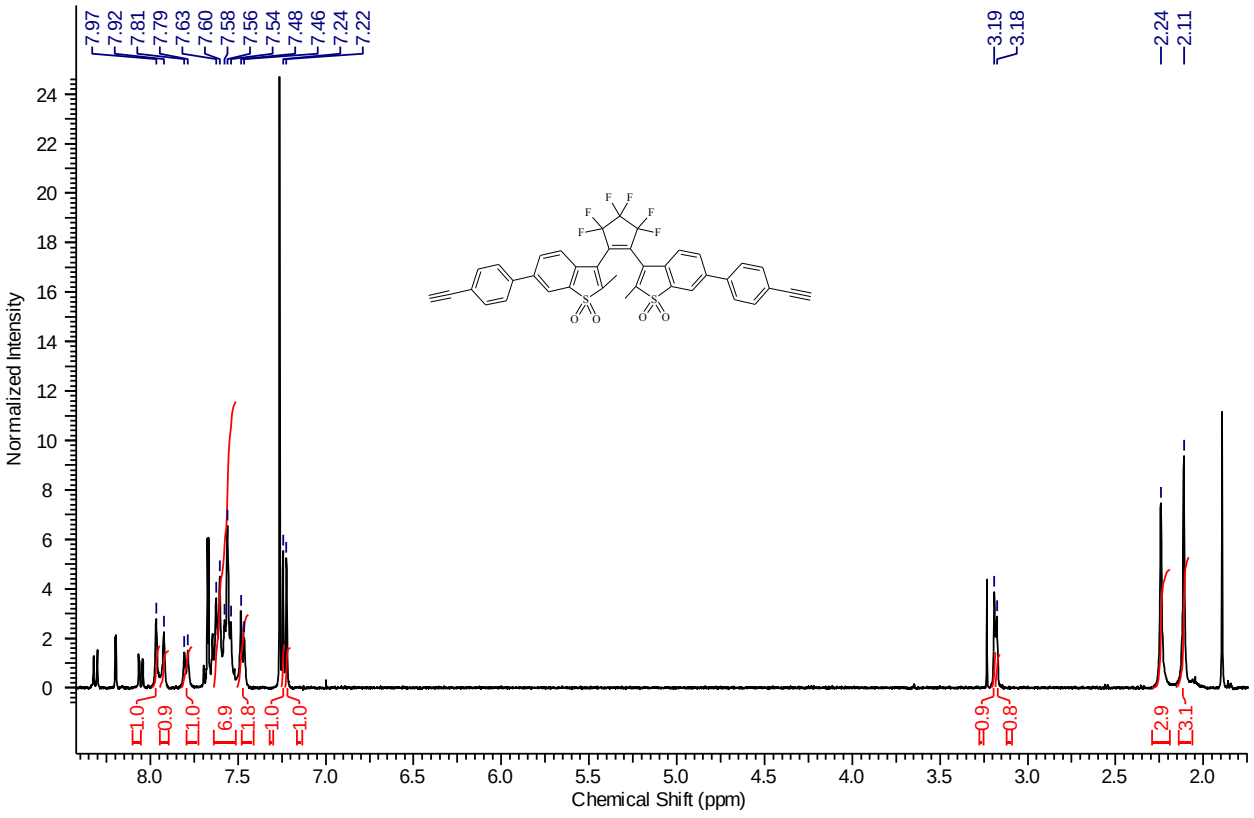

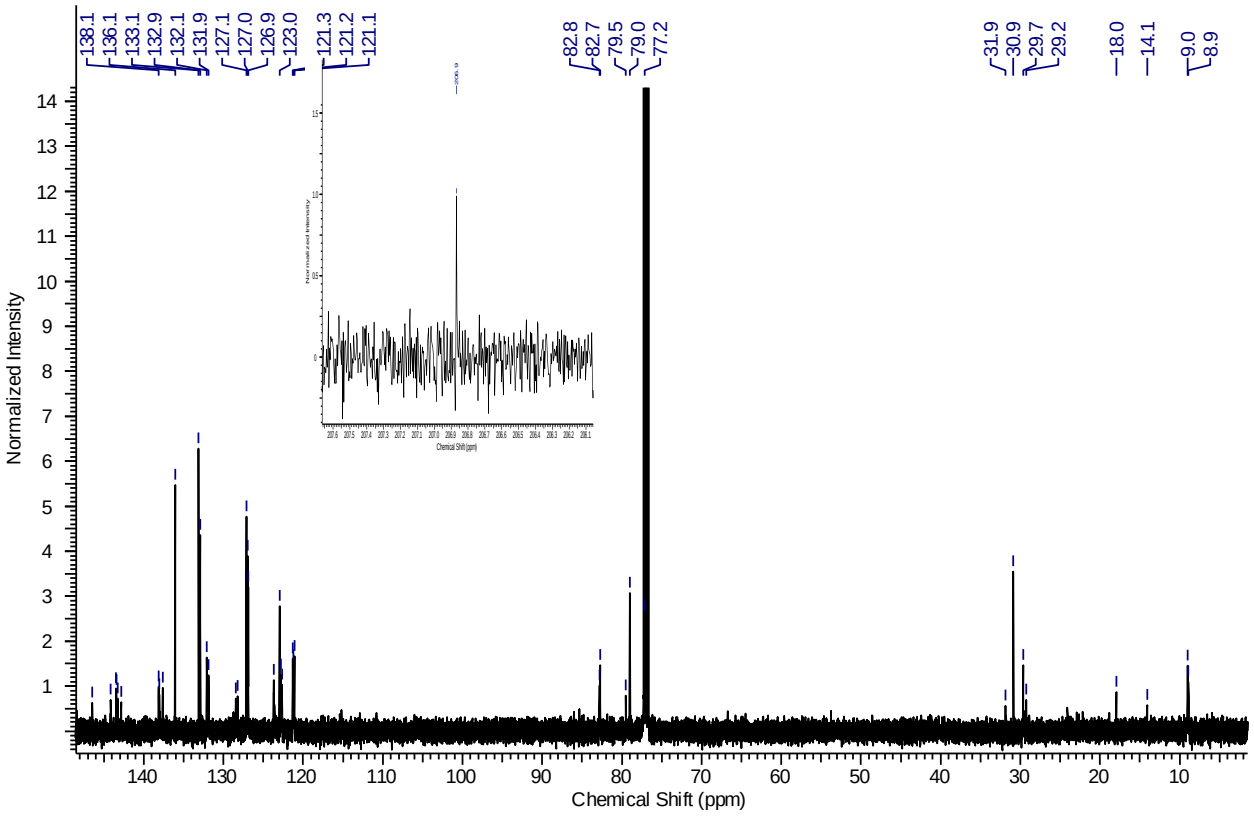

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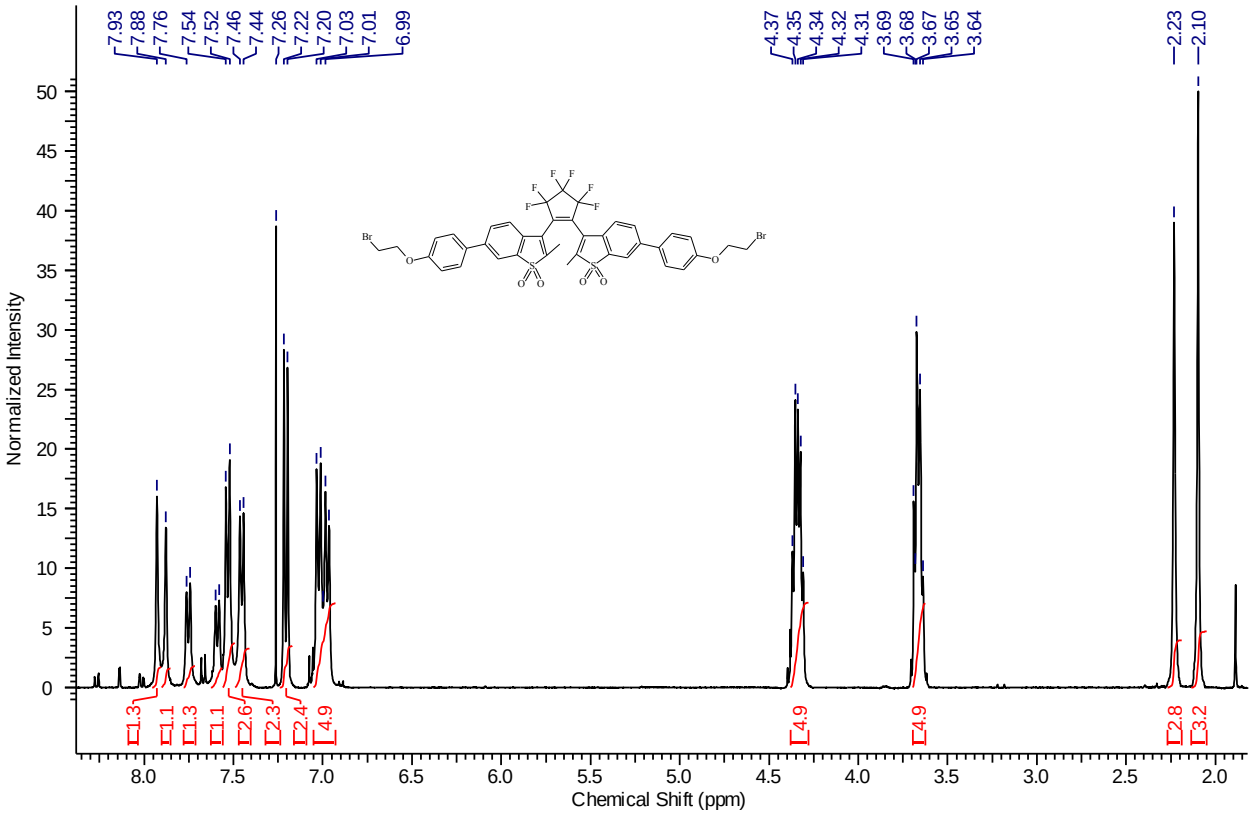
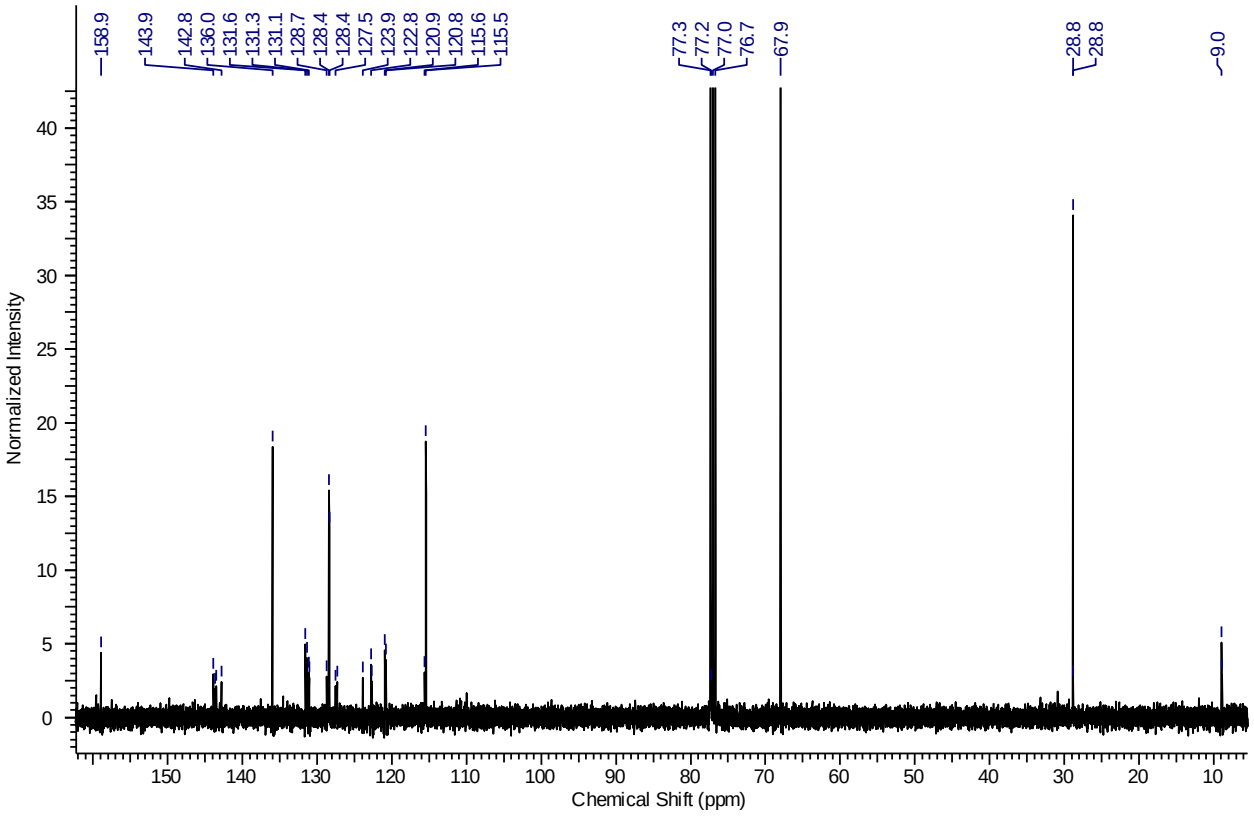
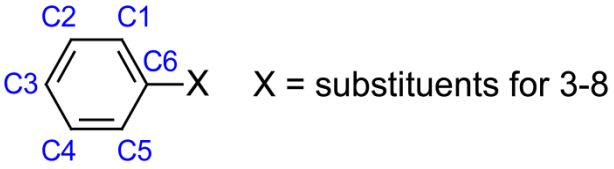




3. Hammett constant



Scheme S1: Structure of substituted benzene rings used for ^{13}C NMR Hammett correlations.

The chemical shift of the carbon in *para* to the substitution (C3) divided by that of a carbon atom in benzene was used as the Hammett parameter σ':[1]

$$\sigma' = \frac{^{13}C\ shift\ of\ C3}{^{13}C\ shift\ of\ C\ in\ benzene}$$

4. Linear fits for Figure 2

Linear Regressions [$y = (c \pm \Delta c) + (m \pm \Delta m)x$]:

(A) $\mathbf{y = (756 \pm 57) - (302 \pm 56)\sigma'}$ Adjusted R^2 = 0.848

(B) $\mathbf{y = (787 \pm 57) - (336 \pm 57)\sigma'}$ Adjusted R^2 = 0.871

5. Solvent dependence

Table S1: Solvent dependence of photophysical properties of **4c-7c**

Solvent	E_T^N	4c				5c			
		λ_{max} (nm), ε (mM^{-1} cm^{-1})	λ_{max}^{em} (nm)	φ_f	τ (ns)	λ_{max} (nm), ε (mM^{-1} cm^{-1})	λ_{max}^{em} (nm)	φ_f	τ (ns)
Heptane	0.012	433/4	505	0.46	2.44	-	-	-	-
Dioxane	0.164	443/41	518	0.48	2.07	448/33	520	0.73	2.10
THF	0.207	442/32	521	0.35	-	447/31	524	0.42	-
AcOEt	0.228	440/43	516	0.3	1.17	444/36	521	0.33	1.25
DCM	0.309	439/41	516	0.48	-	439/41	517	0.62	-
ACN	0.46	437/33	517	0.16	-	440/41	533	0.16	-
Methanol	0.762	441/56	527	0.15	0.54	446/29	521	0.22	0.78

Solvent	E_T^N	6c				7c			
		λ_{max} (nm), ε (mM^{-1} cm^{-1})	λ_{max}^{em} (nm)	φ_f	τ (ns)	λ_{max} (nm), ε (mM^{-1} cm^{-1})	λ_{max}^{em} (nm)	φ_f	τ (ns)
Heptane	0.012	-	-	-	-	444/29	513	0.64	2.24
Dioxane	0.164	448/25	526	0.42	2.05	454/37	532	0.74	2.11
THF	0.207	452/23	535	0.33	-	444/42	539	0.51	-
AcOEt	0.228	446/38	532	0.31	1.25	451/35	535	0.31	1.56
DCM	0.309	446/30	524	0.45	-	444/33	533	0.61	-
ACN	0.46	447/25	535	0.18	-	450/5	547	0.26	-
Methanol	0.762	445/56	539	0.21	0.87	444/44	545	0.32	1.21

E_T^N = normalized molar electronic transition energy[2]; λ_{max} = absorption maximum; ε = molar absorption coefficient; λ_{max}^{em} = fluorescence emission maximum; Φ_f = fluorescence quantum yield; τ = fluorescence lifetime

Table S2: Solvent dependence on the absorption maxima of **3o-8o**

Solvent	λ_{max} (nm)					
	3o	4o	5o	6o	7o	8o
Heptane	292, 336	294, 335	-	-	299, 334	305, 343
Dioxane	292, 336	298, 334	292, 338	292, 335	297, 336	307, 347
THF	295, 332	306, 336	292, 334	302, 333	296, 336	312, 351
AcOEt	294, 327	297, 331	299, 330	289, 333	300, 334	308, 351
DCM	296, 331	304, 332	295, 332	296, 333	297, 336	311, 350
ACN	294, 331	298, 333	294, 334	283, 340	297, 339	314, 360
Methanol	297, 336	297, 332	290, 330	292, 332	297, 334	305, 348

λ_{max} = absorption maximum

Table S3. Fluorescence decay parameters for compound **3** in different solvents

Solvent	τ_f (ns)	k_f (ns^{-1})	k_{nr} (ns^{-1})	$k_{c\rightarrow o}$ (μs^{-1})
Heptane	2.5	0.016	0.38	2.5
Dioxane	2.1	0.24	0.24	1.2
AcOEt	1.1	0.26	0.64	4.5
Methanol	0.7	0.17	1.3	4.4

τ_f = fluorescence lifetime; k_f = fluorescence rate constant; k_{nr} = non-radiative decay rate constant; $k_{c\rightarrow o}$ = cycloreversion rate constant.

6. Lippert-Mataga fitting

Table S4: Solvent dielectric constants (ε) and refractive indexes (η)[3,4] and calculated values of orientation polarizability (Δf) and Stokes shift (Δν) for all compounds.

Solvent	ε	η	Δf	Δν					
				3c	**4c**	**5c**	**6c**	**7c**	**8c**
Heptane	1.92	1.3855	5.E-05	2923	3293			3029	2967
Dioxane	2.209	1.4175	0.022	3671	3268	3091	3310	3229	3424
THF	7.58	1.405	0.210	3428	3431	3287	3432	3970	3783
AcOEt	6.02	1.3719	0.200	3366	3347	3329	3625	3481	4209
DCM	9.08	1.4242	0.218	3303	3399	3437	3338	3761	3734
ACN	38.8	1.3442	0.306	3677	3541	3966	3680	3941	4247
Methanol	33.62	1.3288	0.309	3947	3700	3228	3919	4174	4558

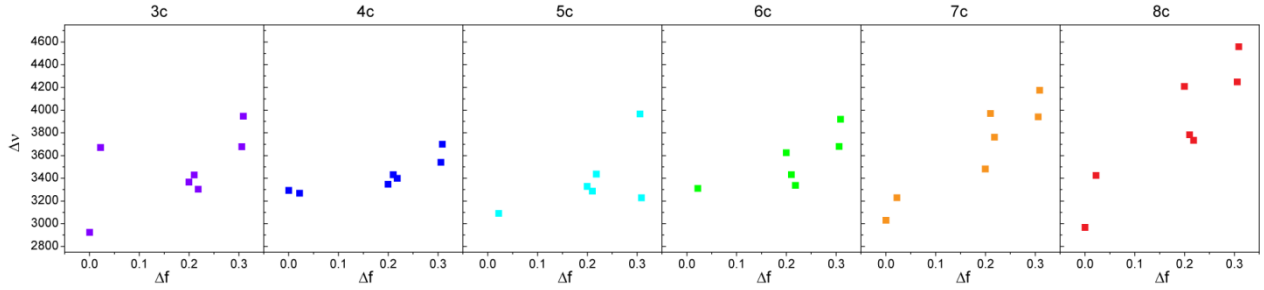


Figure S1: Lippert-Mataga plots for closed isomers of all compounds. $\Delta\nu = \nu_A - \nu_F$ (cm^{-1}) is plotted against solvent orientation polarizability $\Delta f = \frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}$.

Each Lippert-Mataga plot was fitted with a linear fit and the slopes are plotted against the Hammett constant σ'.

Table S5: Parameters for Linear fits of Lippert-Mataga plots.

Compound	σ'	Slope	Intercept
3c	1.03	1561	3191
4c	1.05	1040	3238
5c	1.02	1769	3016
6c	1.00	1679	3196
7c	1.00	3162	3083
8c	0.95	3975	3127

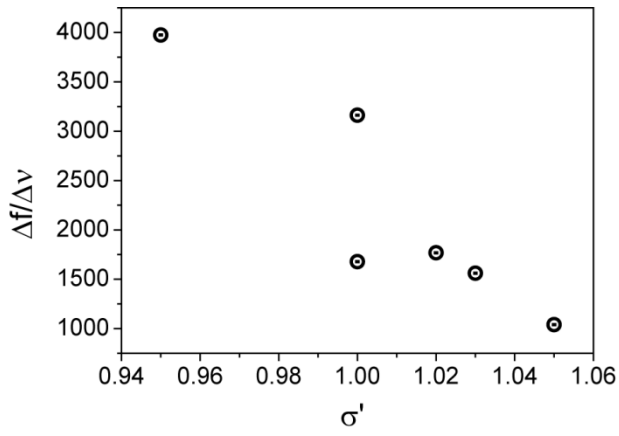


Figure S2: Slope of Lippert-Mataga plot vs. Hammett constant σ'. Electron-donating substituents are more sensitive to solvent polarity.

7. Catalán Fits

All fits were made with *Mathematica* software. The absorbance maxima (ν_{abs}), fluorescence maxima (ν_{fl}), Stokes shifts ($\Delta\nu$), quantum yields and fluorescence lifetimes are fitted with all parameters of the Catalán equation[5,6] (Equation 1), and then those with values of $p < 0.25$ were chosen and the fit repeated with just those parameters. Fits with $R^2 < 0.8$ are excluded from the data presented below. Absorbance data did not fit well with the equation ($R^2 < 0.8$). Fluorescence lifetime fits were conducted with one parameter at a time as multi-parameter regressions were not possible.

Table S6: Dependence of ν_{abs}, ν_{fl}, and $\Delta\nu$ of **3c-8c** on Catalán solvent parameters

Fluorescence maxima fits:

Compound	R^2	y_0	Δy_0	a_{SP}	Δa_{SP}	b_{SdP}	Δb_{SdP}	c_{SA}	Δc_{SA}	d_{SB}	Δd_{SB}
3c	0.83	19.95	0.08	-	-	-0.37	0.10	-	-	-0.44	0.17
4c	0.96	20.76	0.50	-1.24	0.73	-0.30	0.12	-1.26	0.21	-0.91	0.19
5c	0.95	20.29	0.26	-0.92	0.28	-0.17	0.07	-	-	-0.73	0.09
7c	0.83	19.36	0.14	-	-	-1.12	0.20	-	-	-	-
8c	0.91	19.13	0.26	-	-	-2.16	0.34	-	-	-1.36	0.58

Stokes Shift fits:

Compound	R^2	y_0	Δy_0	a_{SP}	Δa_{SP}	b_{SdP}	Δb_{SdP}	c_{SA}	Δc_{SA}	d_{SB}	Δd_{SB}
4c	0.97	2.99	0.07	-	-	0.48	0.12	1.79	0.19	-	-
5c	0.87	-5.71	2.24	8.93	3.18	2.54	0.57	-	-	2.55	0.98
8c	0.93	4.90	0.72	-3.09	1.02	1.16	0.18	-	-	0.89	0.31

Quantum Yield fits:

Compound	R^2	y_0	Δy_0	a_{SP}	Δa_{SP}	b_{SdP}	Δb_{SdP}	c_{SA}	Δc_{SA}	d_{SB}	Δd_{SB}
3c	0.99	-1.92	0.09	3.03	0.14	-	-	-0.07	0.04	0.44	0.03
4c	0.88	-0.99	0.32	2.39	0.46	-0.20	0.08	-	-	-0.32	0.14
7c	0.99	-1.53	0.16	3.39	0.23	-0.63	0.04	0.59	0.07	-	-

Fluorescence Lifetime fits:

Compound	R^2	y_0	Δy_0	a_{SP}	Δa_{SP}	b_{SdP}	Δb_{SdP}	c_{SA}	Δc_{SA}	d_{SB}	Δd_{SB}
3c	0.94	2.54	0.17	-	-	-2.14	0.30	-	-	-	-
4c	0.96	2.55	0.14	-	-	-2.19	0.25	-	-	-	-
5c	0.94	2.73	0.26	-	-	-2.23	0.39	-	-	-	-
6c	0.91	2.60	0.28	-	-	-1.99	0.43	-	-	-	-
7c	0.92	2.33	0.11	-	-	-1.21	0.20	-	-	-	-
5c	1.00	-5.47	0.12	10.26	0.19	-	-	-	-	-	-
6c	0.99	-4.76	0.35	9.22	0.52	-	-	-	-	-	-

Cyclization Quantum Yield fit:

Compound	R^2	y_0	Δy_0	a_{SP}	Δa_{SP}	b_{SdP}	Δb_{SdP}	c_{SA}	Δc_{SA}	d_{SB}	Δd_{SB}
8c	0.98	0.327	0.015			-0.25	0.02	0.10	0.03	-0.30	0.03

Coefficients (y_0, a_{SP}, b_{SdP}, c_{SA}, d_{SB}; cm^{-1}), respective standard errors (Δi) and correlation coefficients (R^2). The calculations were performed with *Mathematica* software. Only regressions with $R^2 > 0.8$ are included. Parameters were excluded from the fits if $p>0.25$.

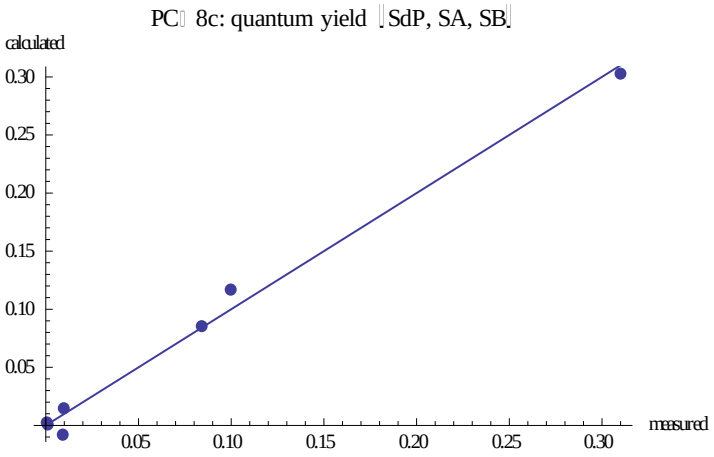


Figure S3: Calculated cyclization quantum yield values of compound **8** from Catalán regression of solvent dipolarity, solvent acidity and solvent basicity, plotted against the measured values. The straight line indicated equivalence between measured and calculated values of the regression, and not a fit. As can be seen, a very good approximation of the measured values was obtained with the regression.

8. Photoconversion Parameters Calculations

Photoconversion (cyclization and cycloreversion) experiments were conducted and the changes in absorbance over time were fitted with a monoexponential curve for each compound in each solvent. The monoexponential rate constant derived from this fit is equal to k_{eq}.[7] The following relationships were used to calculate the cyclization and cycloreversion rate constants and quantum yields for each irradiation wavelength:

$$k_{eq} = k_{o\to c} + k_{c\to o}$$

$$\alpha_{PS} = k_{o\to c}/k_{eq}$$

$$k_{o\to c} = k_{ex,o} \times \Phi_{o\to c}$$

$$k_{c\to o} = k_{ex,c} \times \Phi_{c\to o}$$

For the excitation rate constants (for species *i*): $k_{ex,i} = \sigma_{i,\lambda} \times \Psi_{\lambda}$, where $\sigma_{i,\lambda}$ is the absorption cross-section at wavelength λ ($\sigma_{i,\lambda} = \frac{10^3 ln10}{N} \times \varepsilon_i$, cm^{2}molecule^{-1}) and Ψ_{λ} is the photon flux ($\Psi_{\lambda} = 5 \times 10^{15} \times \lambda \times I$, photons s^{-1} cm^{-2}; I is the irradiance, W cm^{-2}).

For calculation of the fluorescence and non-radiative decay rate constants the following relationships were used:[8]

$$k_f = \frac{\Phi_f}{\tau_f} \qquad k_{c\to o} = \frac{\Phi_{c\to o}}{\tau_f} \qquad k_{nr} = \frac{1}{\tau_f} - (k_f + k_{c\to o})$$

9. Fatigue and photoconversion cycles

The fatigue of compounds **5, 6** and **7** was evaluated by repeatedly photoswitching the compounds in ethyl acetate (~1×10^{-5} M) using UV (340 nm) and visible (445 nm) light, and of compound **5** by constant irradiation with UV light in different solvents. Intensities used are described in the Experimental Section. The irradiation times necessary to fully convert samples were determined in previous kinetics experiments.

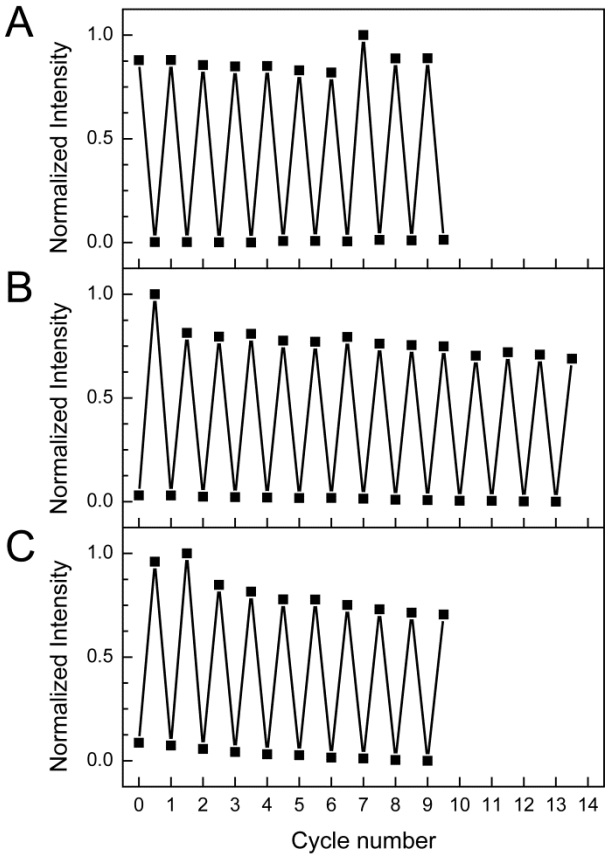


Figure S4: Normalized fluorescence intensity for compounds (A) **5**, (B) **6** and (C) **7** during photoswitching cycles. One complete cycle involves closing and opening the sample.

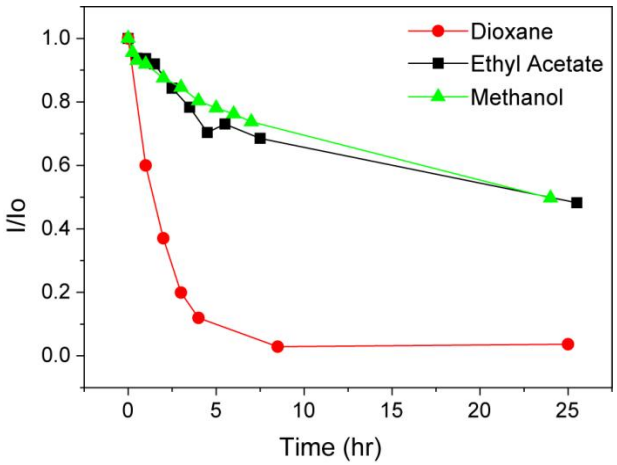
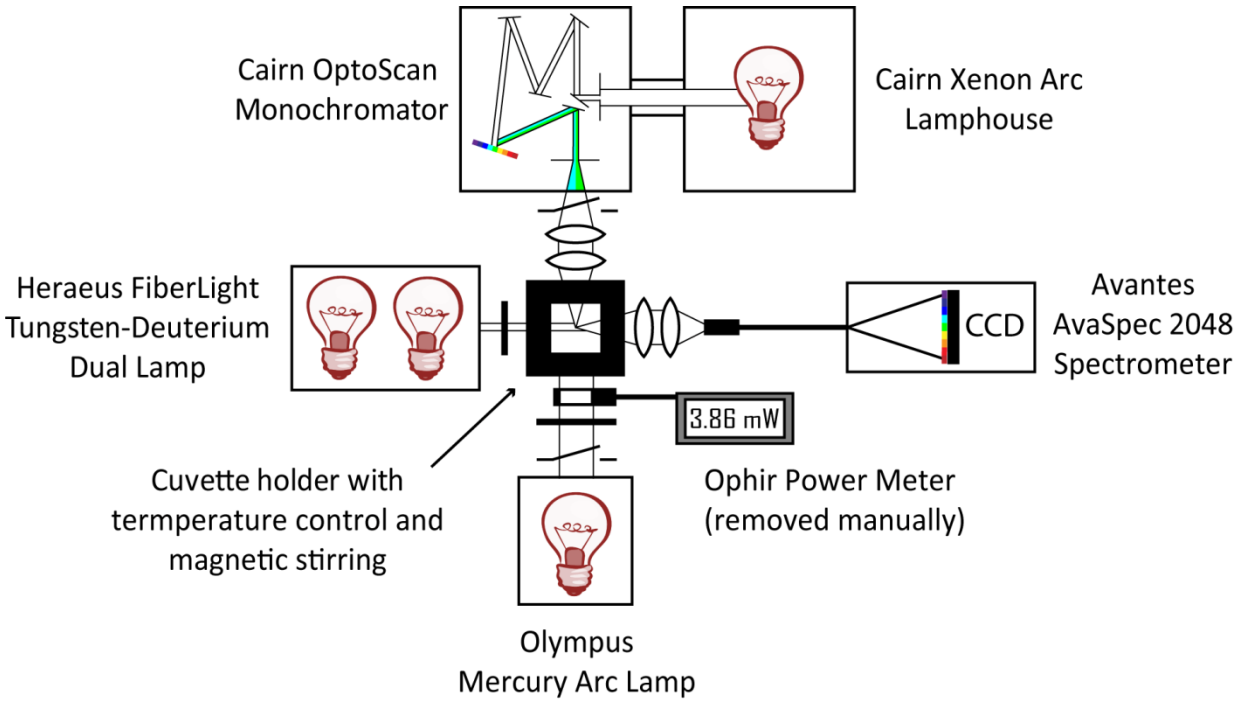


Figure S5. Photodegradation of compound **5** in 1,4-dioxane, ethyl acetate, and methanol under constant irradiation with UV light (340 nm, ~10 mW/cm^2).

10. Custom Built Spectrometer

A custom built dual absorbance-fluorescence spectrometer with photoconversion capabilities was used to determine spectra and photoconversion (cyclization, cycloreversion) kinetics and quantum yields. The following Scheme S2 describes the instrument. The components are: Avantes AvaSpec 2048 spectrometer; Cairn OptoScan monochromator with corresponding power supply (fluorescence excitation and photoconversion); Heraeus Deuterium-Tungsten FiberLight dual lamp with collimated light output (UV absorption); Olympus Mercury Arc Lamp (photoconversion); cuvette holder with water cooling and magnetic stirring; corresponding optics including UV lenses, neutral density and bandpass filters, shutters and fiber optic cable; necessary control boxes and power sources. All components are connected by USB to a computer, and controlled with customized LabView programs. Future plans include the addition of a custom-built electronic filter wheel for automated cycling. Capabilities of the equipment include recording of: dark noise, reference intensities, blank and absorbance spectra; excitation and emission spectra; automated kinetics; automated photocycling. The Hg arc lamp used for photoconversion has a maximal output of ~150 mW at 450 nm and ~60 mW at 340 nm.



Scheme S2: Illustration of the experimental setup of the custom built spectrometer.

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