Acid-catalysed thermal cycloreversion of a diarylethene: A potential way for triggered release of stored light energy?

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1. Materials and methods

Chemicals and solvents were purchased from ABCR, Alfa-Aesar, Sigma-Aldrich, Fisher Scientific and used as received. Solvents were dried using a Pure Solv Micro Solvent Purification System from Innovative Technologies. The water was deionized by a SG – LaboStar^{TM} 1-UV Reinstwassersystem. TLC plates are coated with SiO_2-60 UV_{254} and were purchased from Merck.

NMR spectra were recorded on a Bruker Avance II 300 (300.13 MHz for ^1H and 75.47 MHz for ^{13}C) and a Bruker Avance II 500 (500.13 MHz for ^1H and 125.76 MHz for ^{13}C) at room temperature. Spectra were referenced to the residual solvent signal. Deuterated solvents were purchased from EurisoTOP and used without further purification. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), quintet (q) and multiplet (m). Coupling constants (J) are given in Hz. Chemical shifts (δ) are given in ppm.

Ultra performance liquid chromatography coupled to mass spectrometry detection (UPLC-MS) was performed with a Waters Alliance system (gradient mixture of acetonitrile/water) equipped with Acquity UPLC column chromatographys. The Waters system consisted of a Waters Separations Module 2695, a Waters Diode Array Detector 996, a LCT Premier XE mass spectrometer, and a Waters Mass Detector ZQ 2000.

UV-vis spectroscopy was performed in quartz cuvettes (1.00 cm) on Agilent Cary 50 and Cary 60 instruments equipped with Peltier-thermostated cell holder (temperature accuracy ± 0.1 K). The Cary 60 instrument was equipped with a waveguide (orthogonal attachment with respect to the measuring beam) connected to a LOT Monochromator MSH-300 with variable slit (set to 5 mm). A LOT 500 W Hg high-pressure arc light source was used. The PSS and extinction coefficient of the closed isomer were determined by UPLC under neutral conditions. The extinction coefficient of the closed isomer at different temperatures was determined. The quantum yield has been determined by the initial slop method at 546 nm.

The molecular structures were generated and pre-optimized by MM2 with PerkinElmer CambridgeSoft Chem3D Ultra 10.0. Complete geometry optimizations and harmonic frequency calculations of the reactants, products, and transition states were performed using Gaussian 09 Rev. C.01 program package.[S1] The transition-state search was performed by using Opt=TS keyword using Berny algorithm to optimize to a transition state rather than a local minimum.[2] Each stationary point was characterized by the number of imaginary frequencies (NImag = 1 for transition state and NImag = 0 for the local minimum) and by total electronic energies and thermal correction to the Gibbs free energy. To follow unrestricted Kohn-Sham solution, the broken-symmetry guess was generated and followed using keyword Guess (mix, always). The B3LYP level of density functional theory (DFT) was used in combination with a 6-31G* basis set. Due to C1 symmetry the nosymm keyword is used. The stability of the Kohn-Sham orbitals were tested before and after geometry optimization using the keyword Stable=Opt. In cases where instability was found, the geometry optimization was repeated with the stable set of orbitals used as the initial guess.

Solvation by acetonitrile/water was calculated by using the scrf=(smd,solvent=acetonitrile) keyword. The static dielectric constant and dynamic dielectric constant was modified to simulate an acetonitrile:water (90:10) mixture. The static dielectric constant for this mixture is literature known.[S3] The dynamic dielectric constant was calculated by the Lorentz-Lorenz equation and the Maxwell equation.

In analogy to the proton exchange method for calculation of the pK_a of organic compounds a reference was used to compute the Gibbs free energy of the dehydration, to avoid the calculation of water, a proton or a hydroxide anion.[S4] The equilibrium constant of the dehydration of triphenylmethanol in acetonitrile:water (90:10) is literature known.[S5]

[S1] Gaussian 09, Revision C.01, 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[S2] P. D. Patel, I. A. Mikhailov, K. D. Belfield and A. E. Masunov, *Int. J. Quantum Chem*., 2009, **109**, 3711.

[S3] L. G. Gagliardi *et al., J. Chem. Eng. Data*, 2007, **52**, 1103.

[S4] J. Ho, M.L. Coote, *Theor. Chem. Acc.,* 2010**, 125**: 3.

[S5] N. Mathivanan, Robert A. McClelland, Steen Steenken, *J. Am. Chem. Soc.*, 1990, **112**, 8454.

2. Synthesis

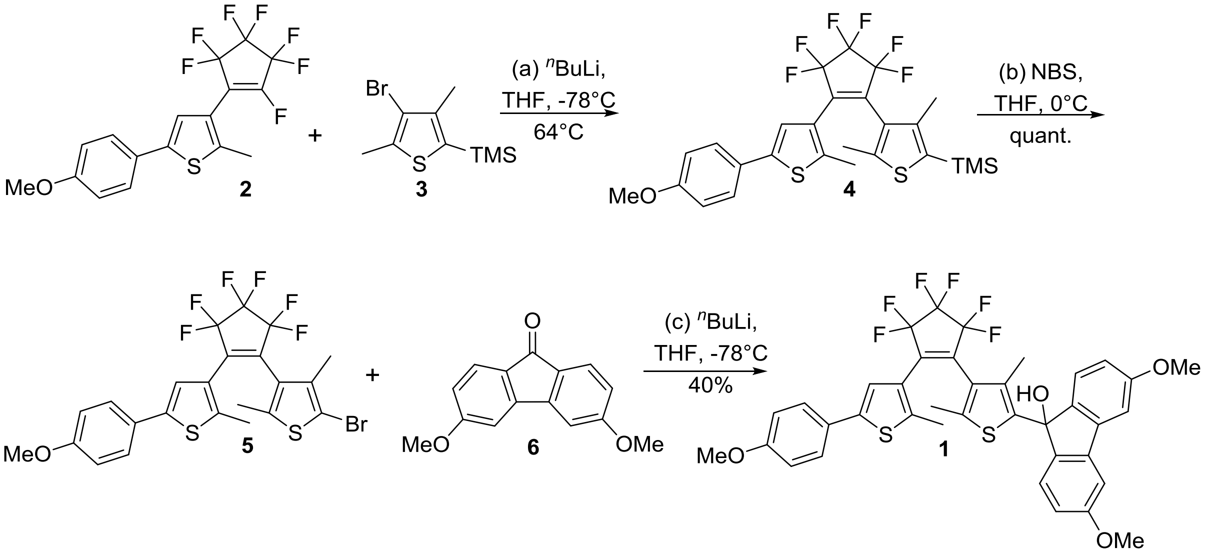

Figure S1 Synthesis of target compound 1.

Compound **1** was synthesized as shown in Scheme S1. The compounds **2**[S6], **3**[S7], and **6**[S8] were synthesized according to literature procedures.

(a) Synthesis of compound 4

In a dried 60 mL Schlenk tube **3** (0.84 g, 4 mmol, 1 eq.) was dissolved in 20 mL of dry tetrahydrofuran (THF) under argon and cooled to -78 °C. 2 mL of n-butyl lithium (2.3 M solution in cyclohexan, 4.4 mmol, 1.1 eq.) was added slowly and the reaction mixture was stirred for 1 h at -78 °C. Then, compound **2** (1.11 g, 2.8 mmol, 0.7 eq.) was dissolved in 5 mL of dry THF and added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with a saturated aqueous ammonium chloride solution, extracted three times with ethyl acetate and washed with water and brine. The organic phase was dried over magnesium sulphate and filtrated. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2:petroleum ether 1:9). Compound **4** (1.00 g, 1.79 mmol, 64 % yield) was isolated as a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.40 – 7.36 (m, 2H), 6.95 (s, 1H), 6.91 – 6.87 (m, 2H), 3.81 (s, 3H), 2.23 (d, *J* = 1.1 Hz, 3H), 2.11 (s, 3H), 2.10 (d, *J* = 1.8 Hz, 3H), 0.30 (s, 9H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 160.1, 145.2, 143.7, 142.0, 141.4, 132.9, 128.9, 128.8, 127.3, 126.6, 125.6, 122.3, 114.9, 55.9, 16.5, 16.4, 14.8, 0.0. ^{19}F NMR (471 MHz, CD_2Cl_2) δ -109.81 (dd, J = 263.40, 10.52 Hz, 1F),-109.89 (dd, J = 262.44, 8.36 Hz, 1F), -111.94 (dd, J = 262.56, 8.46 Hz, 1F), -112.17 (dd, J = 263.22, 10.09 Hz, 1F) -133.12 (dt, *J* = 240.01, 10.05 Hz, 1F), -134.32 (dt, *J* = 239.89, 9.91 Hz, 1F).
UPLC-TOF-ES+: m/z = 561.114 [M+H] (calc.: 561.117 for $[C_{26}H_{27}F_6OS_2Si]^+$)

[S6] S. H. Kawai, S. L. Gilat, J.-M. Lehn, *Eur. J. Org. Chem.*, 1999, 2359.

[S7] T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai, M. Irie, *J. Am. Chem. Soc.*, 2004, **126**, 14843.

[S8] P. Gandeepan, C.-H. Hung, C.-H. Cheng, *Chem. Com.*, 2012, **48**, 9379.

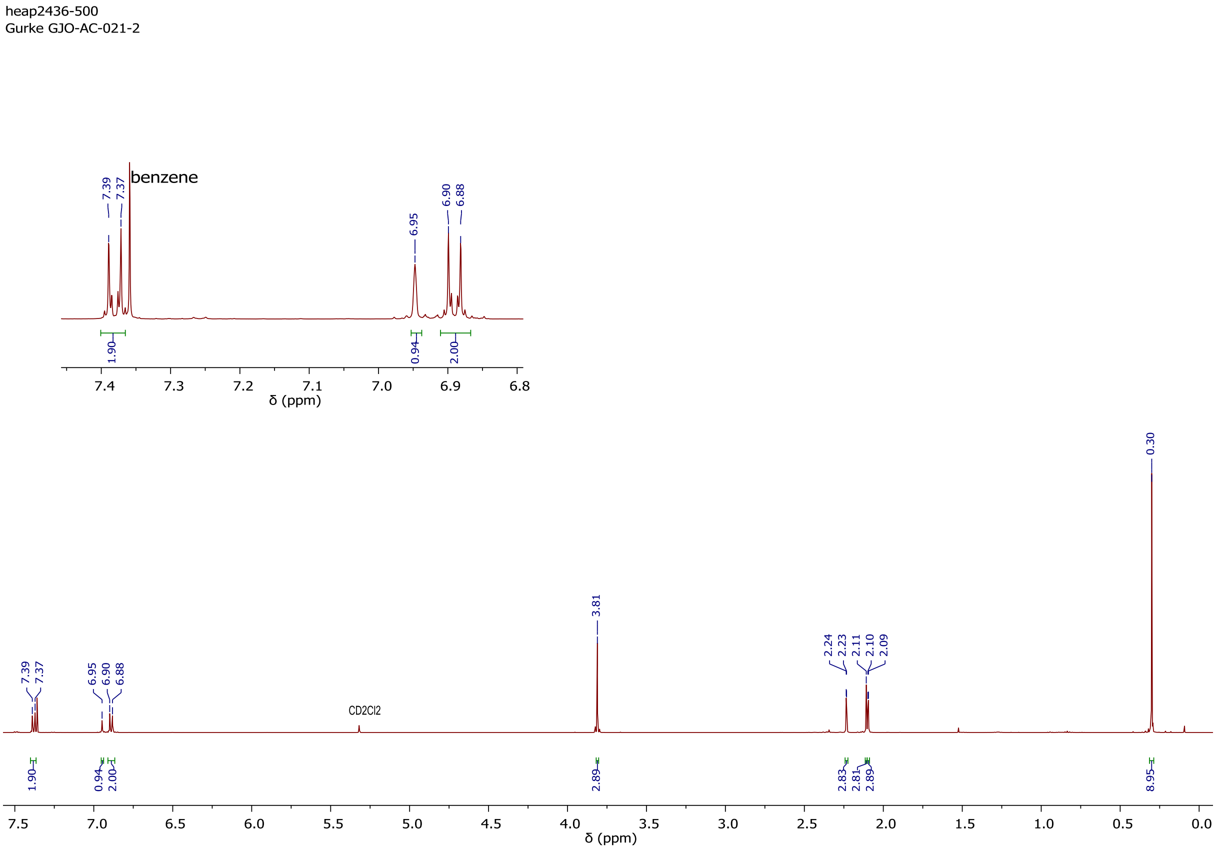

Figure S2 ^{1}H-NMR of Compound 4

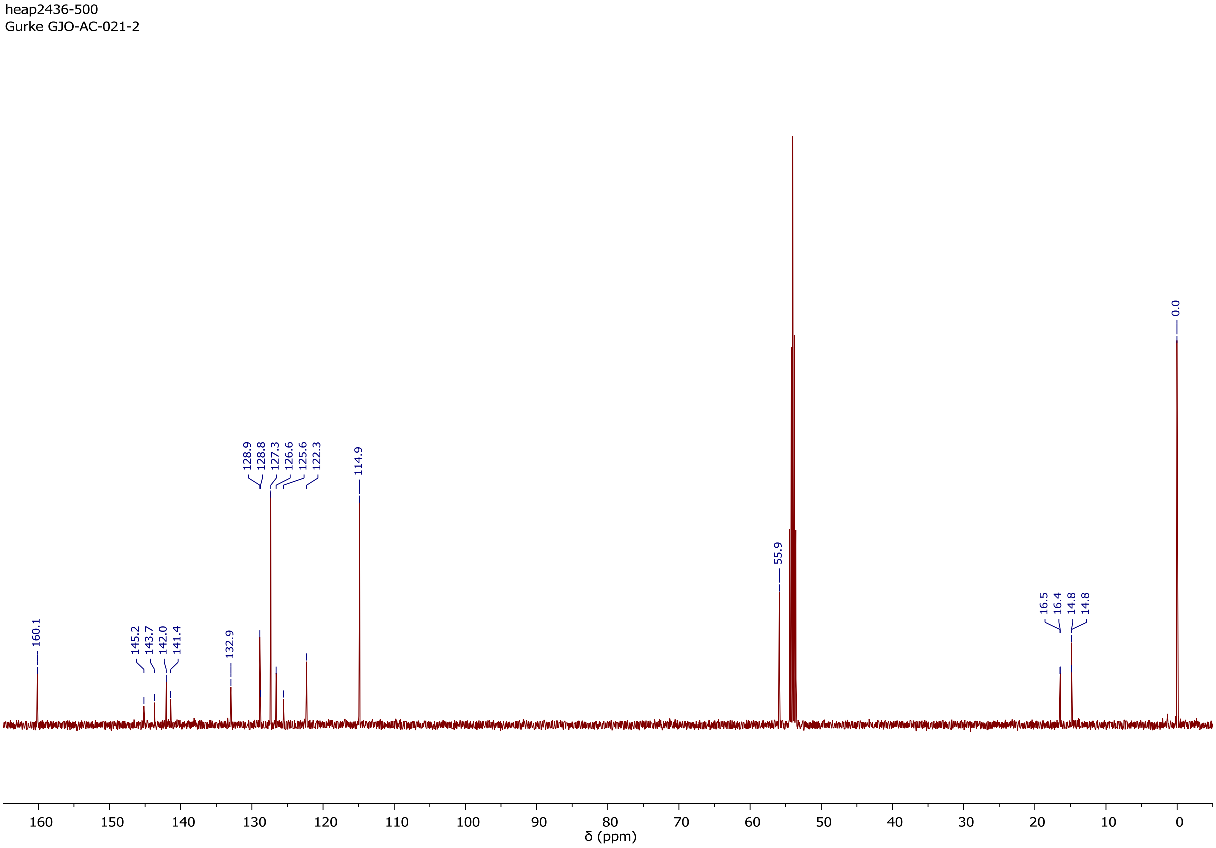

Figure S3 ^{13}C-NMR of Compound 4

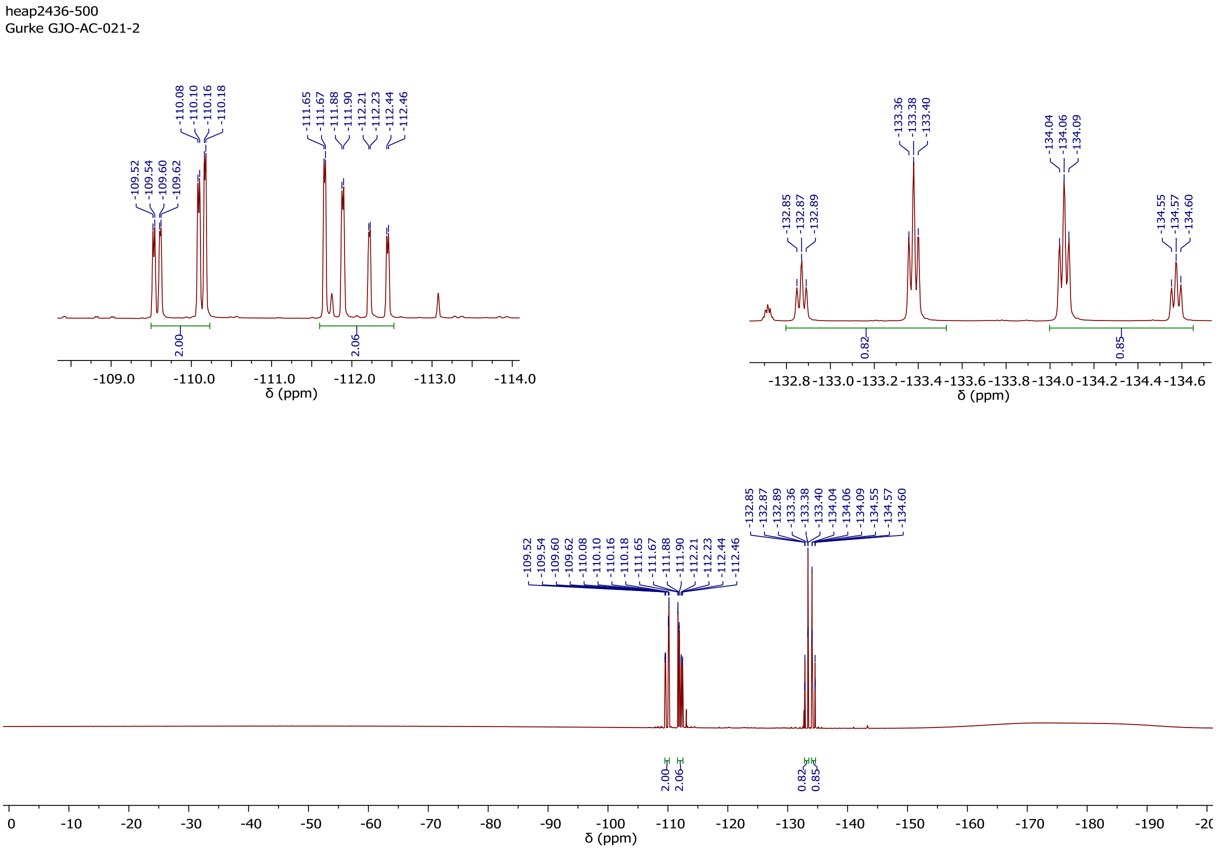

Figure S4 ^{19}F-NMR of Compound 4

(b) Synthesis of compound 5

Compound **4** (1.00 g, 1.79 mmol, 1 eq.) was dissolved in 15 mL of THF and cooled to 0 °C, after which *N*-bromosuccinimide (0.38 g, 2.15 mmol, 1.2 eq.) was added. The reaction mixture was stirred for 3 h at 0 °C and quenched afterwards with water, extracted with diethyl ether and washed with water and brine. The organic phase was dried over magnesium sulphate and filtrated. The solvent was removed under reduced pressure and the crude product was purified by recrystallization from ethanol to give compound **5** (1.01 g, 1.78 mmol, 99 % yield) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 – 7.38 (m, 2H), 6.99 (s, 1H), 6.93 – 6.89 (m, 2H), 3.83 (s, 3H), 2.21 (d, *J* = 1.2 Hz, 3H), 2.11 (s, 3H), 1.95 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 159.7, 142.1, 140.7, 140.4, 136.2, 127.1, 126.2, 125.8, 124.9, 121.5, 114.5, 107.4, 55.5, 14.9, 14.7, 14.6. ^{19}F NMR (471 MHz, CDCl$_3$) δ -110.04 (d, *J* = 263.8 Hz, 1F), -110.96 (s, 2F), -111.00 (d, *J* = 263.7 Hz, 1F), -133.27 (p, *J* = 5.5 Hz, 2F).
UPLC-TOF-ES+: m/z = 566,985 [M+H] (calc.: 566.988 $[C_{23}H_{18}BrF_6OS_2]^+$)

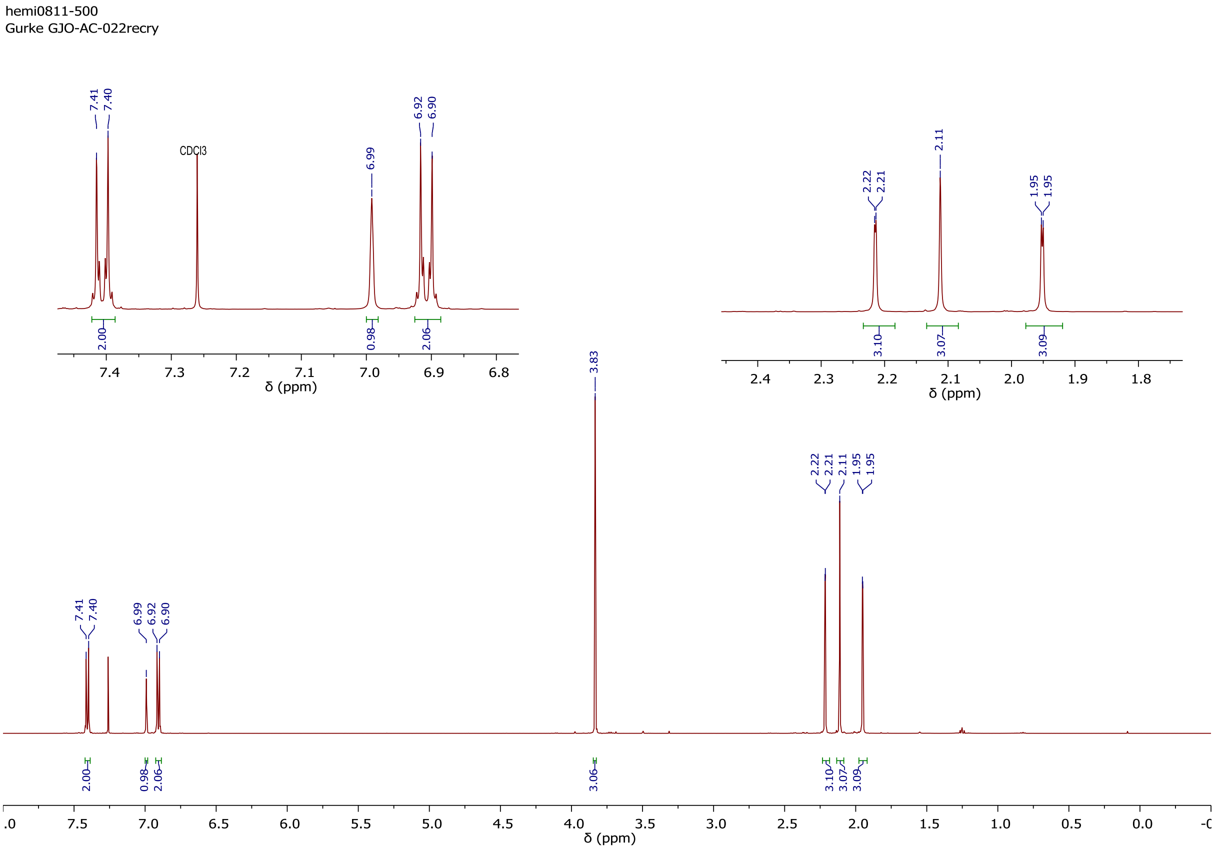

Figure S5 ^{1}**H-NMR of Compound 5**

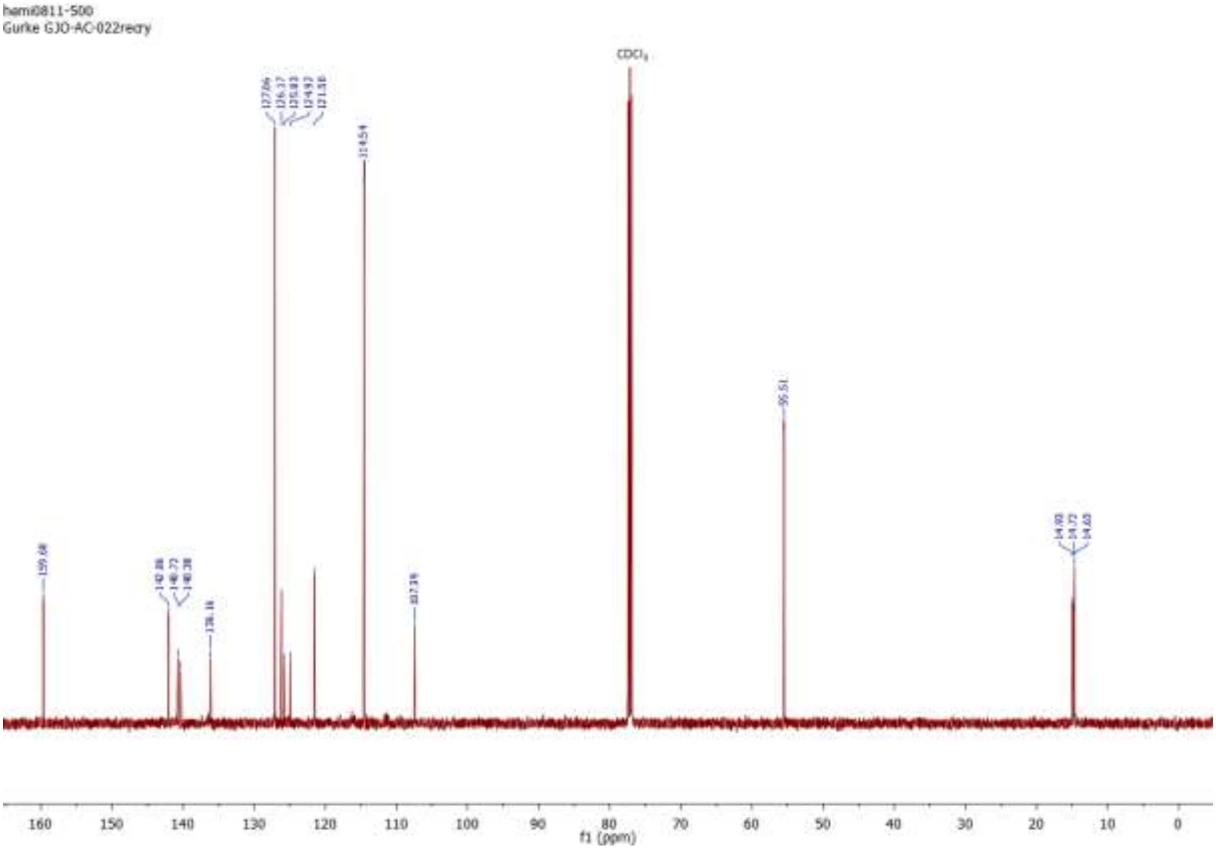

Figure S6 ^{13}**C-NMR of Compound 5**

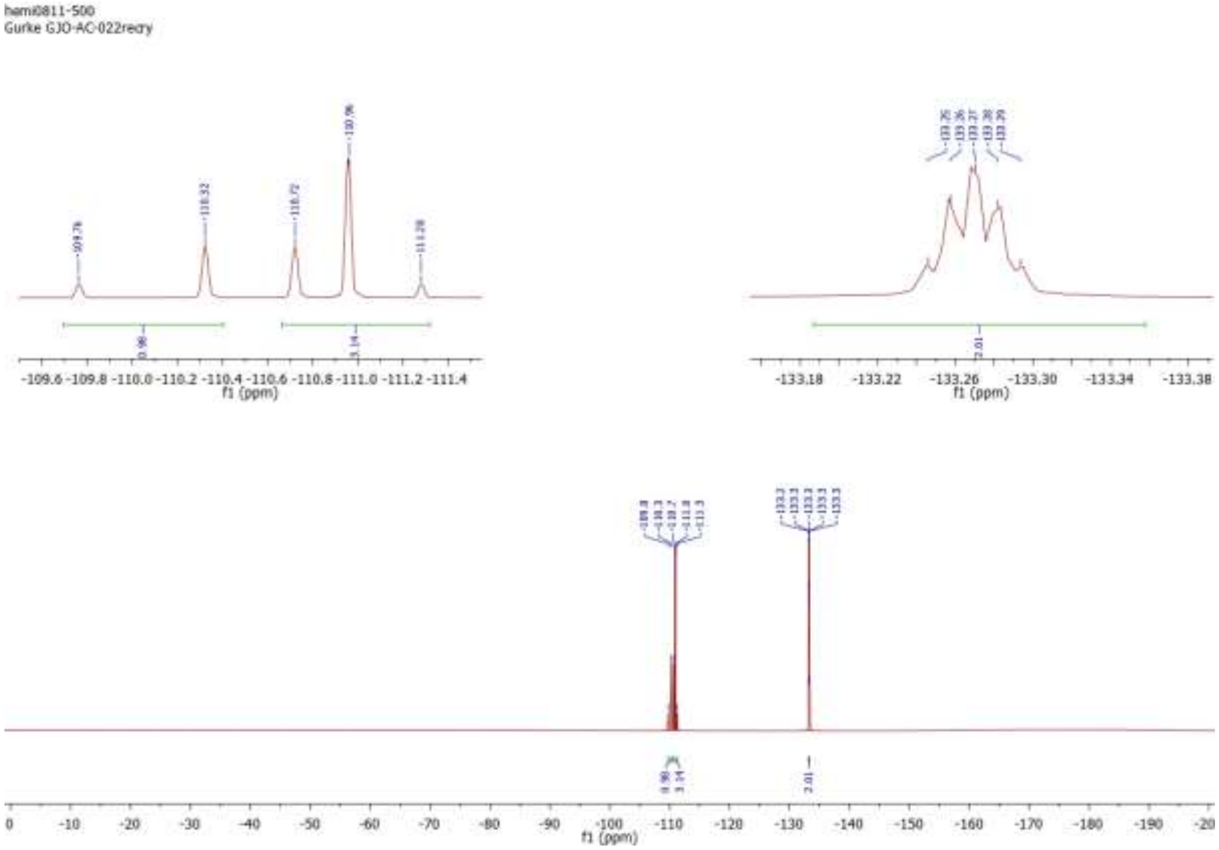

Figure S7 ^{19}F-NMR of Compound 5

(c) Synthesis of compound 1

In a dried 10 mL Schlenk tube **5** (85 mg, 0.15 mmol, 1 eq.) was dissolved in 1.5 mL of dry THF under argon and cooled to -78 °C. First 0.09 mL of n-butyl lithium (2.3 M solution in cyclohexane, 0.2 mmol, 1.3 eq.) was added an the reaction mixture stirred for 2 h at -78 °C. Compound **2** (60 mg, 0.15 mmol, 1 eq.) was added slowly at -78 °C to the previously prepared reaction mixture and allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with a 1 M sodium hydroxide solution, extracted three times with diethyl ether and washed with water and brine. The organic phase was dried over magnesium sulphate and filtrated. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2:petroleum ether 1:9) , followed by a recycling gel permeation chromatography. Compound **1** (44 mg, 0.060 mmol, 40 % yield) was isolated as a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.39 – 7.35 (m, 2H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.11 (d, ^{2}J = 2.4 Hz, 1H), 7.08 (d, *J* = 2.3 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.93 – 6.89 (m, 2H), 6.86 (s, 1H), 6.79 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.62 (dd, *J* = 8.3, 2.3 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.76 (s, 3H), 2.65 (s, 1H), 2.27 (d, *J* = 1.5 Hz, 3H), 1.96 (s, 3H), 0.98 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 161.7, 161.5, 160.1, 141.9, 141.3, 140.1, 137.3, 131.0, 128.9, 127.6, 127.4, 126.6, 125.8, 125.5, 122.1, 114.8, 114.6, 106.2, 106.1, 81.4, 56.1, 56.0, 55.9, 14.7, 13.0, 12.9. ^{19}F NMR (471 MHz, CD_2Cl_2) δ -109.89 (d, *J* = 262.4 Hz, 1F), -110.85 (d, *J* = 265.2 Hz, 2F), -111.50 (d, *J* = 262.2 Hz, 1F), -112.00 (d, *J* = 263.4 Hz, 2F), -133.76 (s, 2F).
UPLC-TOF-ES+: m/z = 711.145 [M-H_2O] (calc.: 711.146 for $[C_{38}H_{29}F_6O_3S_2]^+$)

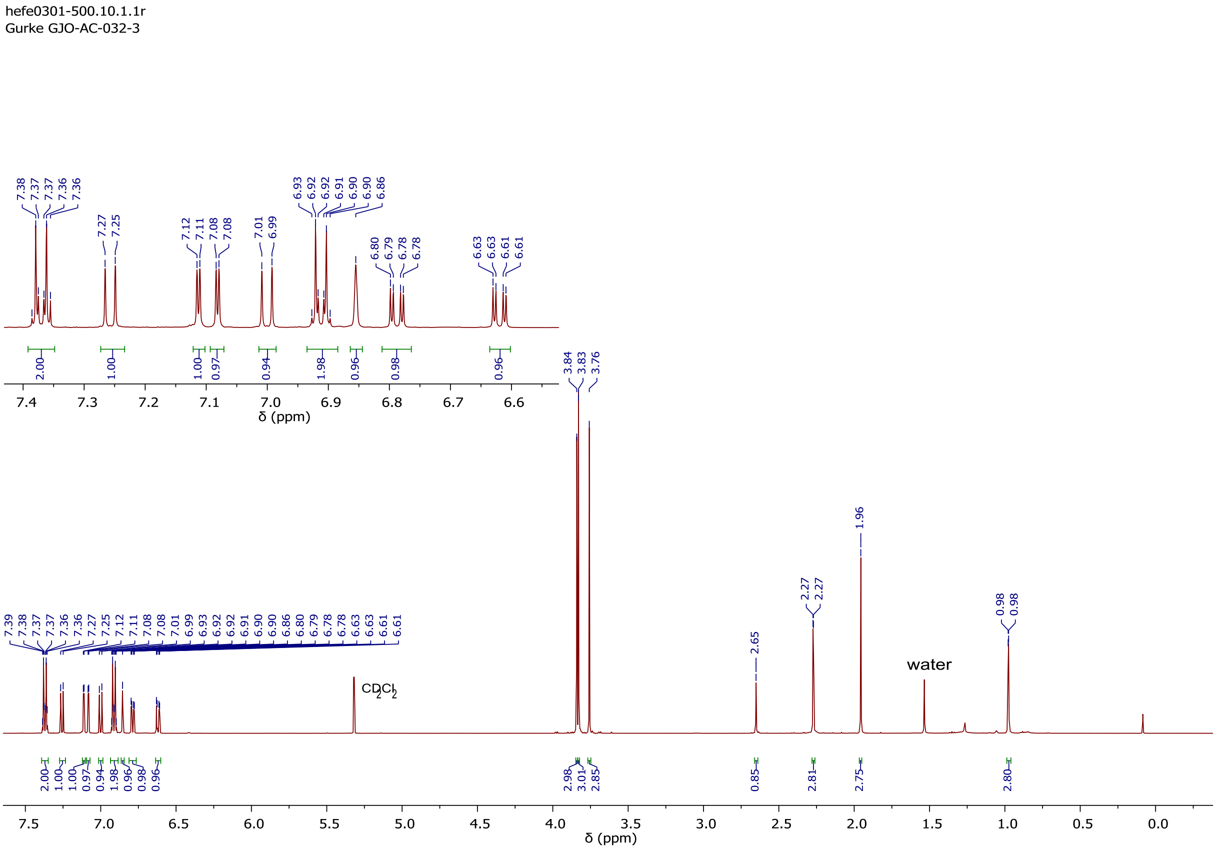

Figure S8 ^{1}H-NMR of Compound 1

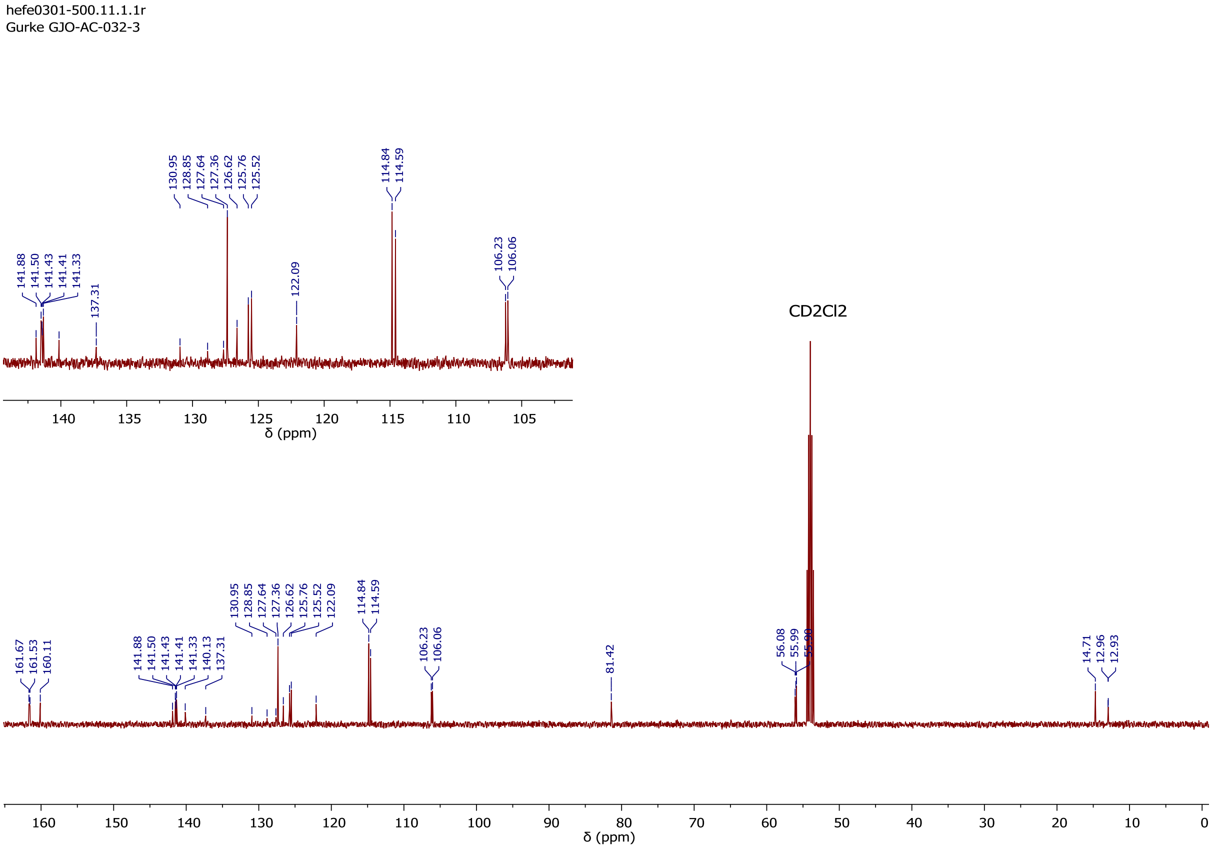

Figure S9 ^{13}C-NMR of Compound 1

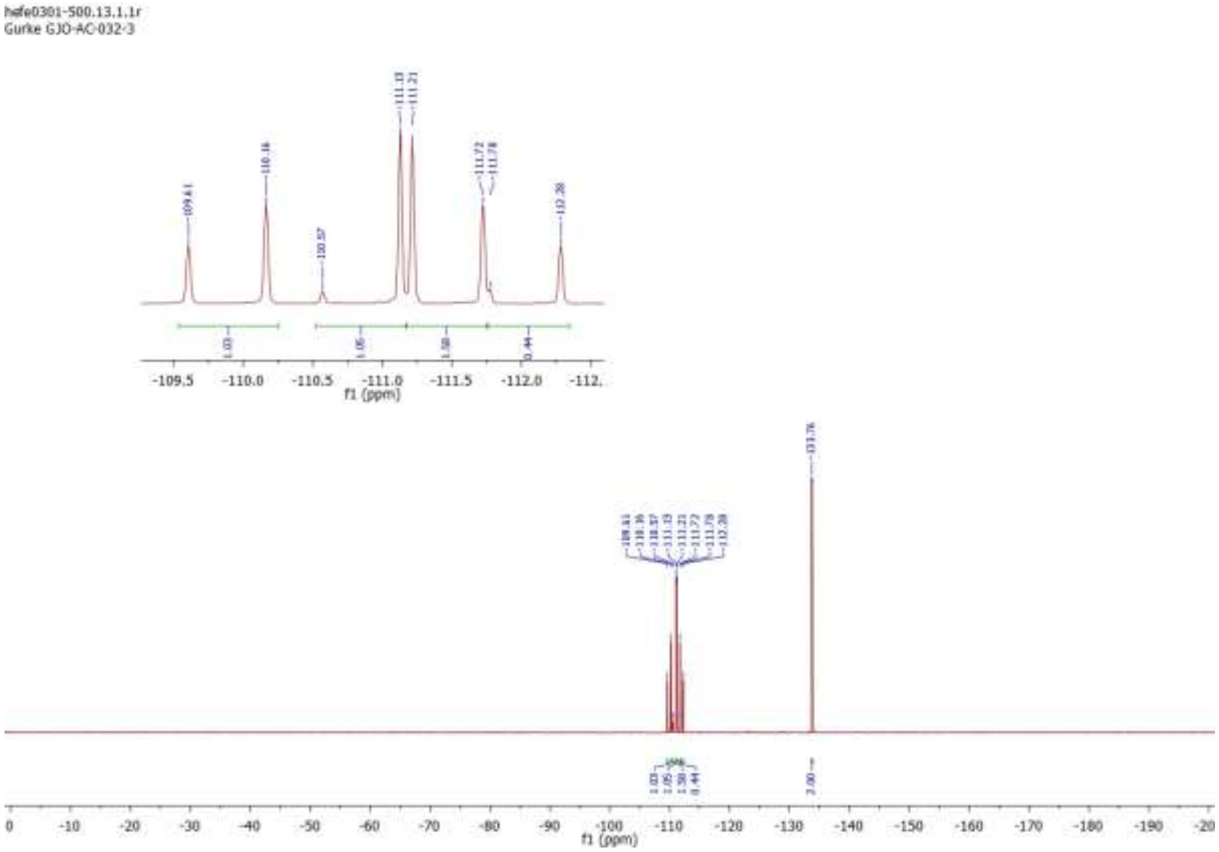

Figure S10 ^{19}F-NMR of Compound 1

3. UV/VIS Measurements

(a) Determination of the extinction coefficient

The extinction coefficient of the uncharged closed form **1c** and the PSS have been calculated by correlating the absorbance with the amount of closed isomer determined by UPLC. The UV/vis detector was set to 310 nm (isosbestic point) and the UPLC peaks were integrated to calculate the ratio of **1o** to **1c**.

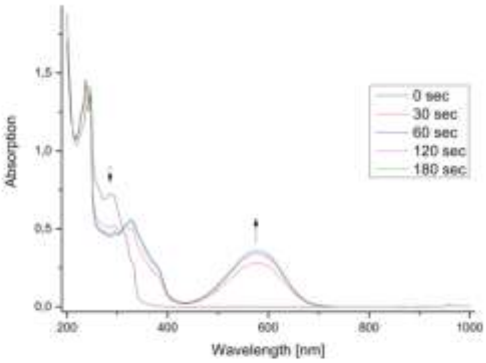

Figure S11 UV/vis trace shows the evolution of the closed isomer upon light irradiation of a $1.88 \cdot 10^{-5}$M solution (acetonitrile 1 vol% water) 1o with 302 nm light in a 1 cm cuvette after 0 sec, 30 sec, 60 sec, 120 sec and 180 sec.

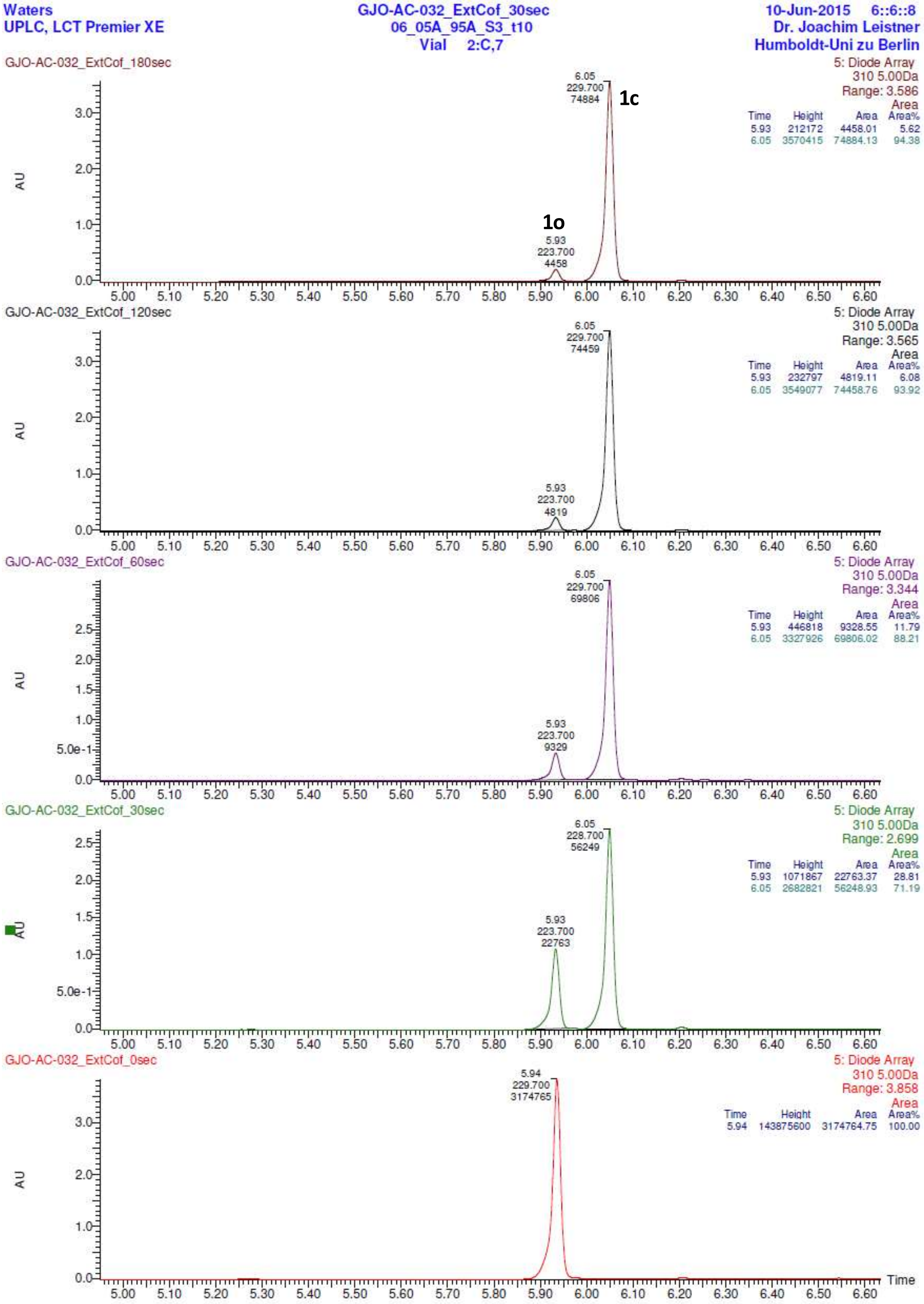

Figure S12 UPLC separation of the irradiated solutions shown in Figure S11 detected at 310 nm and integrated to determine the ratio of the open to the closed isomer; from 0 sec (bottom) to 180 sec (top) irradiation time.

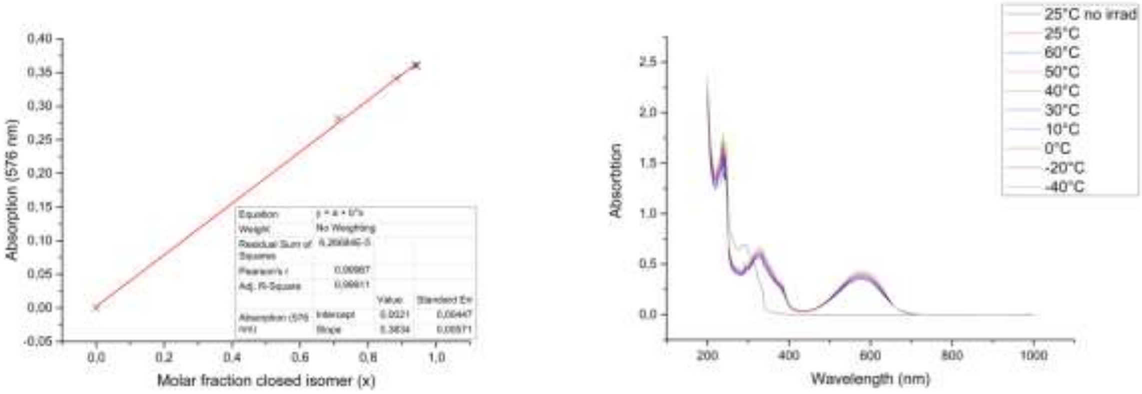

Figure S13 Left: Plot of the conversion measured in Figure S12 vs. absorption at 576 nm from Figure S11; Right: Temperature dependence absorption spectrum of the closed isomer.

The extinction coefficient has been studied at different temperatures for the experiments at 60 °C.

Temperature [°C]	*Absorption (576 nm)*	ε *[L M^{-1}]*
25	0.375 ± 0.004	20565 ± 350
60	0.349 ± 0.003	19124 ± 710
50	0.357 ± 0.004	19600 ± 720
40	0.366 ± 0.004	20075 ± 740
30	0.373 ± 0.004	20467 ± 760
10	0.389 ± 0.004	21350 ± 790
0	0.397 ± 0.004	21770 ± 800
-20	0.413 ± 0.004	22654 ± 840
-40	0.431 ± 0.004	23648 ± 870

(b) Determination of quantum yields and actinometry

The extinction coefficients of the open diarylethene isomers were determined upon precise preparation of stock solutions with defined concentrations and subsequent measurement of the absorption spectra. The molar absorptivity of the closed form was determined equally with respect to the ratio of isomers in the photostationary state via UPLC-UV/vis-detector. The light intensity at 313 nm and 576 nm was determined by using ferrioxalate actinometry.[S6] Therefore 3 mL of a 0.006 M solution of ferrioxalate in 0.05 M H_2SO_4 was irradiated and 0.5 mL of phenanthroline (0.1 wt% in 0.5 M H_2SO_4/1.6 M NaOAc) were added subsequently. The resulting absorbance at 510 nm was used to calculate the light intensity via formula S 1.

$$I_0 = \frac{\Delta A_{510nm}}{\Delta t * \varepsilon_{510nm} * \Phi_{\text{irr}} * 1000} * \frac{3.5ml}{3ml} \qquad \textbf{(S1)}$$

Thereby ΔA_{510nm} is the difference of the absorption at 510 nm for an irradiated versus a non-irradiated solution, Δt is the irradiation time, ε_{510nm} is 11100 M^{-1} cm^{-1} and Φ_{irr} is the quantum yield at the used irradiation wavelength (1.24 for 302 nm and 1.14 for 546 nm).

For the ring-opening a wavelength was needed that exceeds the range for ferrioxalate actinometry. Therefore, actinometry via 1,2-Bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene was performed.[S7] A solution of the switch in *n*-hexane was irradiated at 22 °C approximately for 5 min at 313 nm. The concentration of the closed form in the solution was then determined from the absorbance at 546 nm and with that the extinction coefficient at the irradiation wavelength can be calculated. The ring opening reaction was performed at the wavelength, which's quantum yield was to be determined in time intervals of 30 s or 60 s. The absorbance at the irradiation wavelength was plotted to the following equation:

[S6] a) C. G. Hatchard, C. A. Parker, *Proc. Roy. Soc. London, Ser. A* 1956, **235**, 518; b) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. in *Handbook of Photochemistry, Third Edition*; CRC Press: Boca Raton, 2006, 601.

[S7] T. Sumi, Y. Takagi, A. Yagi, M. Morimoto, M. Irie *Chem. Commun.,* 2014, **50**, 3928.

$$\log\left(10^{Abs'(t)}-1\right)-\log\left(10^{Abs'(t=0)}-1\right)=1000*\varepsilon*I_0*l*\Phi_{cl\to op}*t \qquad \textbf{(S2)}$$

Since the quantum yield for the ring opening is given for every wavelength, I_0 can be calculated from the slope. For the determination of the quantum yield formula SI 3 was used:

$$\Phi=\frac{\Delta A/_{\Delta t}}{(1-10^{-A'})*\varepsilon*I_0*1000} \qquad \textbf{(S3)}$$

for which $\Delta A/\Delta t$ is the change of absorbance at a wavelength, which changes upon irradiation within the time. $1-10^{-A'}$ is the percentage of the absorbed photons by the solution at irradiation wavelength, ε is the extinction coefficient at observed wavelength and I_0 is the light intensity. This method of calculating the quantum yield was applied for maximum 5% of photochemical conversion.

(c) Study of the acid dependence

For analysing the dependence of the thermal cycloreversion on the acid concentration, the evolution of the band at 576 nm upon irradiation of **1o** has been observed (see Figure 3b). By measuring the photo kinetics of the cyclisation in the absence and the presence of acid, molar fraction of **1c** at the PSS ($x_{PSS}(H^+)$), the rate constant of the photocyclisation (k_{UV}) and photocycloreversion (k_{-UV}) as well as the overall rate constant of the thermal back reaction (k_t) can be determined, which are defined by the reaction below and in the equations **(S4)** and **(S5)**:

$$\boldsymbol{O} \underset{k_{-UV}+k_t}{\overset{k_{UV}}{\rightleftharpoons}} \boldsymbol{C}$$

$$[\dot{C}]=k_{UV}[O]-(k_{-UV}+k_t)[C] \qquad \textbf{(S4)}$$

$$x_{PSS}=\frac{[C]}{[O]+[C]}=\frac{[C]}{[O]_0}=\frac{k_{-UV}+k_{UV}+k_t}{k_{UV}} \qquad \textbf{(S5)}$$

Integration of the photokinetic rate equations has been achieved using numerical methods. The Runge-Kutta-algorithm has been applied to calculate concentration-time profiles from given starting conditions (***O**(0)* = ***O**₀* and ***C**(0)* = 0). In the absence of acid k_t has been neglected. From this k_{UV} and k_{-UV} could be determined. From the data in the presence of acid k_{UV} and the total rate constant of the back reaction ($k_{-UV}+k_t$) has been determined. Because k_{UV} *is* constant with increasing TfOH concentration it has been assumed that the k_{-UV} is independent, too. Using this assumption, k_t has been calculated from $k_{-UV}+k_t$. This data were reproduced twice. The experiments show a deviation from the linear behaviour for high proton concentrations.

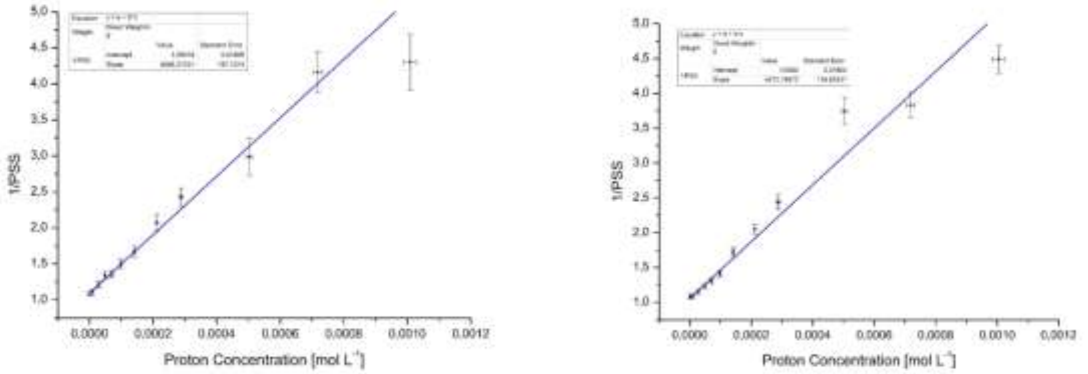

Figure S14 Linear Plot of the inverse PSS composition of 1o vs. the proton concentration at 60°C in acetonitrile containing 1 vol% water.

(d) Derivation of the equations

$$\begin{tikzcd}
\boldsymbol{O}+H^+ \arrow[r, shift left, "k_{UV}"] \arrow[d, shift left, "k_{-III}"] & \boldsymbol{C}+H^+ \arrow[l, shift left, "k_{-UV}"] \arrow[d, shift left, "k_I"] \\
\boldsymbol{O}^+ + H_2O \arrow[u, shift left, "k_{III}"] \arrow[r, shift left, "k_{-II}"] & \boldsymbol{C}^+ + H_2O \arrow[l, shift left, "k_{II}"] \arrow[u, shift left, "k_{-I}"]
\end{tikzcd}$$

As shown above the experimental data suggest a linear dependence of 1/PSS and k_t on the acid concentration. To describe the observations we expect the left shown reaction cycle.

$$x_{PSS}=f([H^+]) \qquad \textbf{(S6)}$$

$$k_t=f([H^+]) \qquad \textbf{(S7)}$$

Due to the fact that no charged form neither in the open form nor in the closed form are observable in the UV/vis absorption spectrometry experiment and from the data of the titration experiments (see Figure 2b) it is reasonable to assume that the dehydration is much faster than the hydration in the open state at the used acid concentration **(S8)**. The outcome of this is that the concentration of the charged species negligible **(S9).** In the PSS under constant irradiation we assume that the concentrations of all species are constant and the change of the concentrations over time is zero **(S10)**. According to the observation that there is no uncharged closed form generated in the titration experiment, we assume that the charged ring opening is not reversible, neither thermally nor photochemically **(S11)**.

$$k_{-III}[H^+][O] \gg k_{III}[H_2O][O^+] \tag{S8}$$

$$[O] + [C] \gg [O^+] + [C^+] \tag{S9}$$

$$[\dot{C}] = [\dot{O}] = [\dot{O^+}] = [\dot{C^+}] = 0 \tag{S10}$$

$$k_{-II}[O^+] = 0 \tag{S11}$$

Furthermore, we define k_{aq}^{-I} as following:

$$k_{aq}^{-I} = k_{-I}[H_2O] \tag{S12}$$

Taking the assumptions into account, the rate equation for $[\dot{C}]$ and $[\dot{C^+}]$ can be expressed as in the equations **(S13)** and **(S14)**:

$$[\dot{C}] = k_{UV}[O] - k_{-UV}[C] + k_{aq}^{-I}[C^+] - k_I[C][H^+] = 0 \tag{S13}$$

$$[\dot{C^+}] = -k_{aq}^{-I}[C^+] + k_I[C][H^+] - \ k_{II}[C^+] = 0 \tag{S14}$$

From equation **(S14)** the concentration of the charged closed form can be expressed as following:

$$[C^+] = \frac{k_I[H^+]}{k_{aq}^{-I} + k_{II}}[C] \tag{S15}$$

The combination of **(S13)** and **(S15)** leads to **(S16),** which can be rearranged to **(S17)**

$$k_{UV}[O] + \{(\frac{k_{aq}^{-I}}{k_{aq}^{-I} + k_{II}} - 1)k_I[H^+] - k_{-UV}\}[C] = 0 \tag{S16}$$

$$\frac{[O]_0}{[C]} = \left(\frac{k^I}{k^{UV}} - \frac{k^I k_{aq}^{-I}}{(k_{aq}^{-I} + k^{II})k^{UV}}\right)[H^+] + \frac{k_{-UV} + k_{UV}}{k_{UV}} \tag{S17}$$

The combination of **(S17)** with the definition of the PSS **(S5)** leads to the linear equation **(1)**, which expresses the dependence of the PSS on the acid concentration [H$^+$]. Furthermore the equation **(S18)** can be formed and rearranged to **(S19)**, which leads to equation **(2).** This one expresses the dependence of k_t on the acid concentration [H$^+$].

$$\boldsymbol{\frac{1}{x_{PSS}\,(H^+)} = \alpha[H^+] + \frac{1}{x_{PSS}^0}} \tag{1}$$

$$\frac{k_{-UV} + k_{UV} + k_t}{k_{UV}} = \left(\frac{k^I}{k_{UV}} - \frac{k^I k_{aq}^{-I}}{(k_{aq}^{-I} + k^{II})k_{UV}}\right)[H^+] + \frac{k_{-UV} + k_{UV}}{k_{UV}} \tag{S18}$$

$$k_t = \left(k^I - \frac{k^I k_{aq}^{-I}}{(k_{aq}^{-I} + k^{II})}\right)[H^+] \tag{S19}$$

$$\boldsymbol{k_t = \beta[H^+]} \tag{2}$$

Bother α and β are linearity factors of the acid concentration [H$^+$]. In contrast to β, α is dependent on the light intensity.

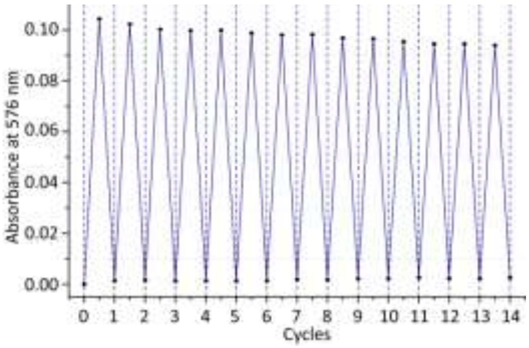

Figure S 15 Irradiation cycles alternating 302 nm and thermal back reaction.

4. Transient absorption measurements

(a) Transient absorption

The TA setup with applications has been described elsewhere [S9], [S10]. It provides spectral coverage 275 – 690 nm with a 0.1 ps instrumental response and timing precision of 0.02 ps over the full probe range. A solution of **1o** in TFA was flown through a sample cell of 0.4 mm internal thickness. Transient absorption spectra $\Delta A(\lambda, t)$ of **1o** were recorded upon 563 nm excitation. 10 – 20 pump-probe scans were averaged to improve the signal-to-noise ratio. All TA spectra were recorded at the magic angle between pump- and probe polarizations.

(b) Spectral corrections

The recorded absorption spectra contain both, the signal of the chromophore and the solvent. Transient absorption spectra of the solvent were recorded separately and subtracted to obtain the pure spectra of the chromophore.

To obtain a uniform time-zero for all frequencies (chirp-correction) the time-zero correction-function is determined independently from the transient absorption measurement of the solvent.

Spectral contributions that remain constant throughout a scan, before and after time-zero (fluorescence, scattering), are subtracted by an averaged spectrum that is calculated from the spectra of negative delay times.

(c) Kinetic evaluation

To obtain time constants and Decay-associated spectra (DAS) a global fit is performed with a sum of exponential time-functions $\sum_i A_i(\lambda) e^{-\frac{t}{\tau_i}}$. The integer i refers to the number of time-functions, τ_i is the time-constant and $A_i(\lambda)$ is the wavelength-dependent factor which is also known as DAS. It contains the spectral components that decay with τ_i.

(d) Species-associated spectra (SAS)

The spectral evolution can be described by migrating population that moves between virtual levels or energetic sinks on the potential-energy surface (PES). Each virtual level is characterized by a SAS. The technical implementation is done by solving a system of differential equations (rate equation). For the very example in the main text the kinetic scheme is chosen to be:

A → B → C → D → E

A, B and C refer to virtual levels on the excited-state. D and E refer to hot and vibrationally cool S_0. Within this scheme there is also implemented that there is direct access to D from B. The differential equations to solve are:

$$[\dot{A}] = -k_1[A] \quad \textbf{(S20)}$$

$$[\dot{B}] = +k_1[A] - k_2[B] - k_5[B] \quad \textbf{(S21)}$$

$$[\dot{C}] = +k_2[B] + k_3[C] \quad \textbf{(S22)}$$

$$[\dot{D}] = +k_5[B] + k_3[C] - k_4[D] \quad \textbf{(S23)}$$

$$[\dot{E}] = +k_4[D] \quad \textbf{(S24)}$$

$k_1 \ldots k_5$ refer to the rate-constants and are the inverted time-constants.

(e) Results

Transient absorption spectra of GJO in TFA are measured with 563 nm excitation. Spectra were detected in the range 275 – 690 nm and are shown in **Figure S15**. The spectrum develops within the convolution time of the pump- and probe-pulse. Negative bands at 310 nm and between 470 and 605 nm refer to bleach while positive bands correspond to Excited-state absorption (ESA). Stimulated emission is hardly detected at > 600 nm and short-living (< 100 fs). The initially populated Franck-Condon (FC) region is left within tens of femtoseconds, which is seen as development of vibrational structure on ESA in the region 320 – 470 nm (a). This evolution is outlined with the kinetic trace associated with the peak at 445 nm (**Fig. S16**, f). **Figure S15**, b and c, show that the subsequent radiationless relaxation to the vibrationally hot electronic ground-state proceeds in two tranches. The major fraction relaxes with a time-constant of 0.3 ps (b). The remaining (smaller) fraction still moves on the potential energy surface of S_1, but then follows a while later with $\tau = 2$ ps (c). This bi-exponential behavior is also drawn in the kinetic traces of **Figure S16**; a, d for bleach-decay and c, e for ESA-decay. Cooling in S_0 is indicated by the

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[S9] S. A. Kovalenko, A. L. Dobryakov, J. Ruthmann, N. P. Ernsting, *Phys. Rev. A*, 1999, **59**, 2369.

[S10] A. L. Dobryakov, S. A. Kovalenko, A. Weigel, J. L. Perez-Lustres, J. Lange, A. Müller, N. P. Ernsting, *Rev. Sci. Instrum.* 2010, **81**, 113106.

typical dispersive line-shape on the low-frequency region of the $S_1 \leftarrow S_0$ absorption band in **Figure S15**, d. Here, the final relaxation to cold S_0 proceeds with an 11 ps time-constant (see also **Figure S16**, b).

Species associated spectra (SAS) correspond to virtual levels (or base-spectra) that are populated by wave-packets throughout the relaxation process. They are considered as stable thermodynamic sinks between whose the migration of population leads the temporal changes which are seen in the measured absorption spectra. All the SAS that are obtained are shown in **Figure S17**. The FC-spectrum represents the situation in which population just reached S_1 without any further relaxation (a). After relaxation from the FC-region the population reaches two stable sites in S_1. A first site from where the major fraction relaxes radiationless to S_0. And a second site, which is populated by only the remaining excited fraction and from where S_0 is populated in a second tranche (b). Both sites have similar base-spectra whereby a big change in the molecule's conformation is therefore not expected. The vibrationally hot S_0-state is indicated by the dispersive line-shapes which are located on the red flank of bleach (c).

(f) Conclusion

The molecule **1o** quantitatively converts the initial photon-energy into heat. Within this process there is no big change in the molecules conformation registered.

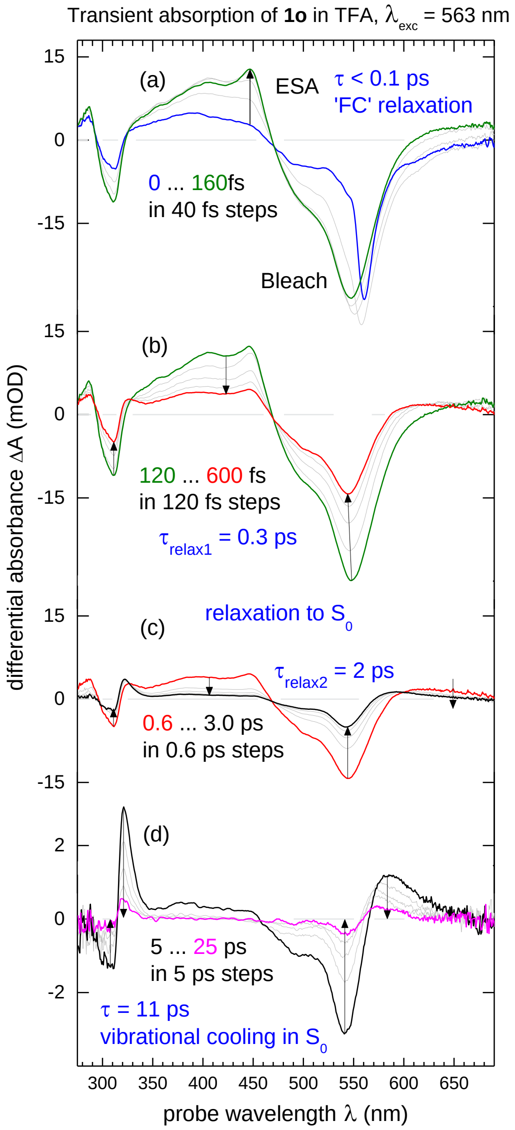

Figure S16 Transient absorption spectra of 1o **in TFA measured with 563 nm excitation. a – The spectrum develops within the convolution time of the pump- and probe-pulse. Bleach appears with a negative sign and is seen at 310 nm and in the region 470 – 605 nm. Positive bands are attributed to ESA that develops structure on an ultrafast time-scale when population leaves the Franck-Condon site of the excited state. b and c – Radiationless relaxation to S_0 follows immediately with two time-constants: 0.3 ps and 2 ps. d – Dispersive line-shapes around the Bleach regions indicate the molecule is in a vibrationally hot state in S_0. Cooling proceeds with τ = 11 ps.**

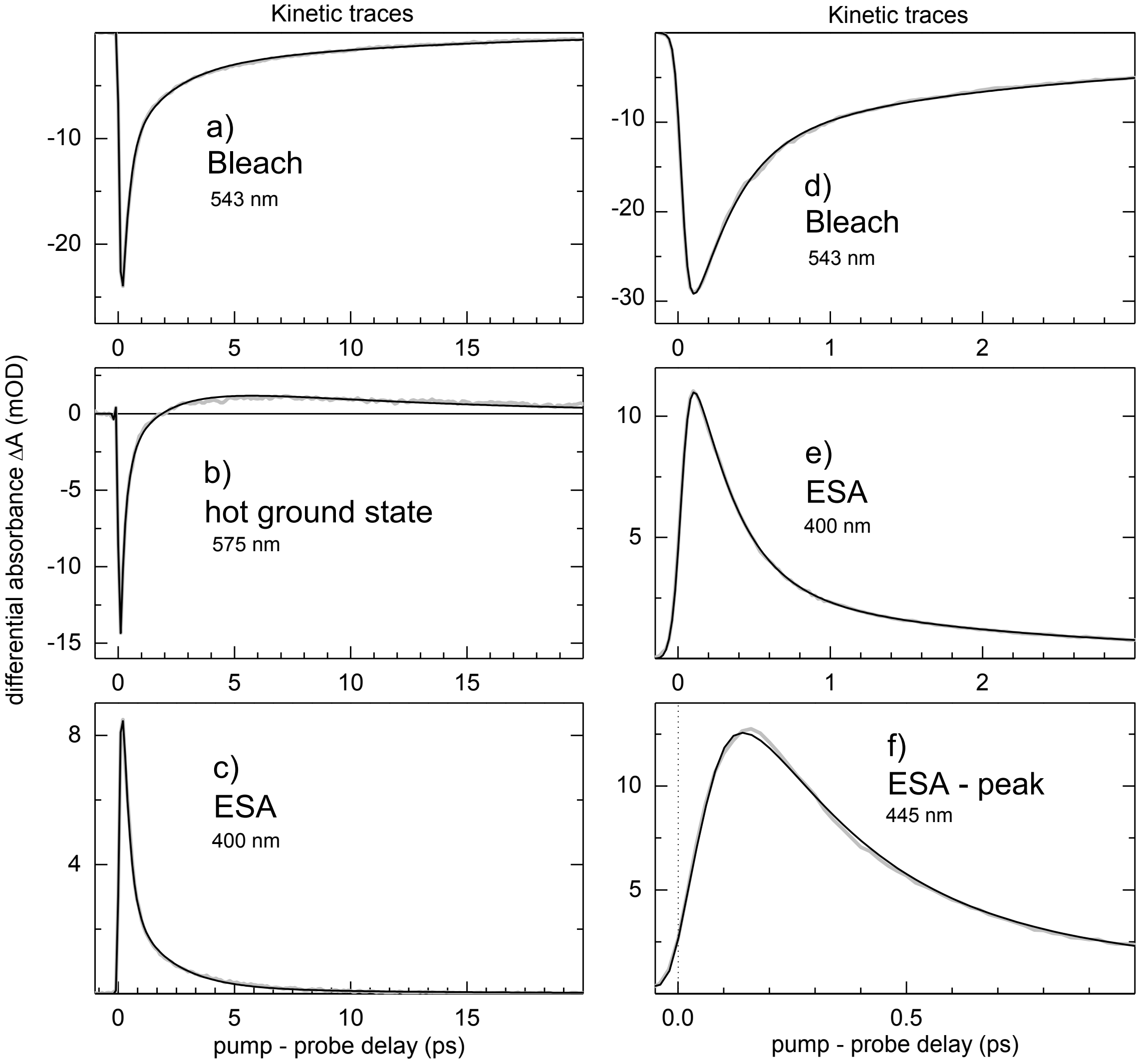

Figure S17 Kinetic traces (grey line) and the result of a global fit (black line) with 4 exponential time-functions. a and d – The relaxation into the electronic ground state proceeds in two tranches, with τ = 0.3 ps and τ = 2 ps. c and e – The bi-exponential decay of ESA with the same time-constants is represented with the kinetic trace at 400 nm. b – Vibrational cooling in S_0 proceeds with an 11 ps time-constant. f - The initial relaxation away from the FC-region is best seen in the development of structure in the ESA band between 320 and 470 nm, at 445 in particular.

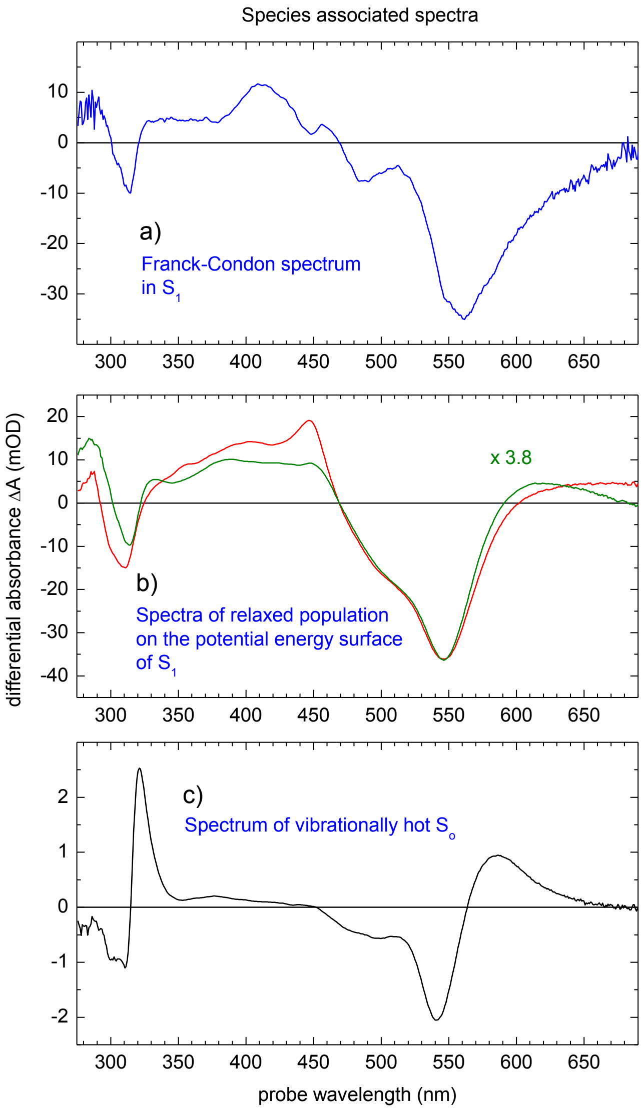

Figure S18 Species associated spectra (SAS) of 1o in TFA upon 563 nm excitation. a – FC spectrum in S_1. b – The second SAS corresponds to the relaxed state, away from the FC region (red). While the major part of the population already reaches the hot electronic ground-state within 1 ps the remaining fraction still moves in S_1, giving the third SAS (green). c – The hot S_0 is populated in two tranches. The corresponding SAS contains the typical dispersive line-shapes around the bleach-regions.

5. DFT Calculations

(a) Results

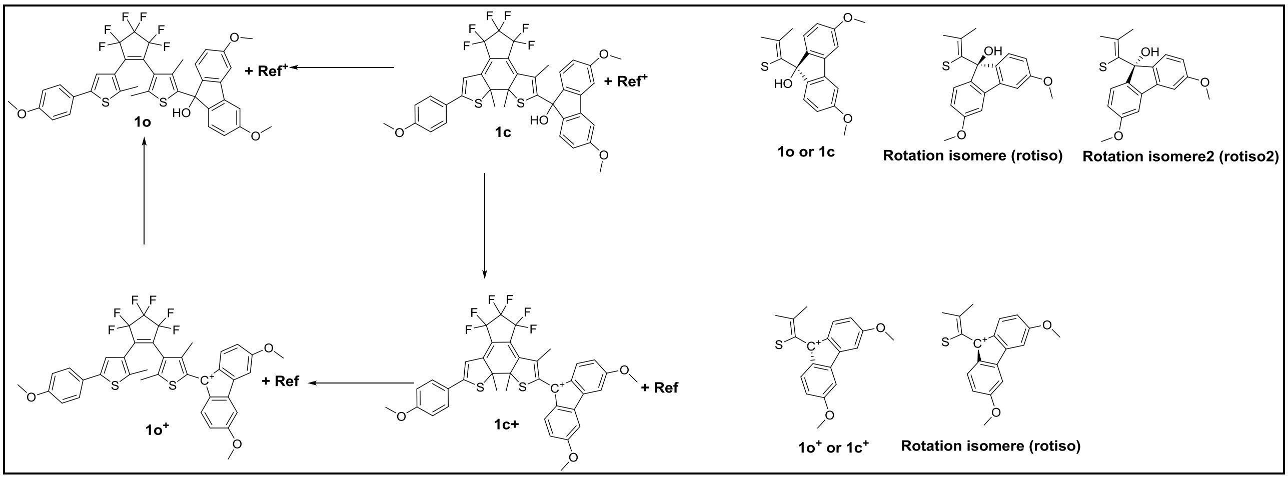

Figure S 19 All calculated structures for analyses of the reaction cycle, including the charged and uncharged form, ther rotation isomers and the charged and uncharged reference triphenylmethanol.

All imported values are listed in the table below. Only the energetic lowest rotation isomer has been use for the calculation.

in Hartree/Particle	Opt		Freq	MeCN/aq	
	ε_{gas}	G_{corr} [S11]	ΔG_{solv}	$E_{gas} + G_{corr} = G_{gas}$	$E_{gas} + G_{corr} + \Delta G_{solv} = G_{sol}$ [S12]
1o	-3162,4767	0,5118	-0,0432	-3161,9649	-3162,0082
1o_rotiso	-3162,4729				
1o_rotiso2	-3162,4735				
1o$^+$	-3086,4326	0,5024	-0,0939	-3085,9302	-3086,0241
1o$^+$_rotiso	-3086,4299				
1c	-3162,4545	0,5191	-0,0437	-3161,9354	-3161,9791
1c_rotiso	-3162,4518				
1c_rotiso2	-3162,4522				
1c$^+$	-3086,4200	0,5075	-0,0880	-3085,9125	-3086,0005
1c$^+$_rotiso	-3086,4185				
1c_ts	-3162,4011	0,5141	-0,0425	-3161,8870	-3161,9295
1c$^+$_ts	-3086,3872	0,5053	-0,0907	-3085,8819	-3085,9726
Ref	-808,8988	0,2497	-0,0230	-808,6490	-808,6721
Ref$^+$	-732,8420	0,2386	-0,0747	-732,6034	-732,6781

The table below shows all imported free Gibbs energies of the reactions within the reaction cycle.

[S11] http://www.gaussian.com/g_whitepap/thermo.htm 21.12.2016, 15:00.

[S12] J. Ho, A. Klamt and M. L. Coote J. Phys. Chem. A 2010, 114, 13442.

ΔG in kJ/mol		
	ΔG_{gas}	ΔG_{sol}
Closed dehydration (1c → 1c^{+})	-22	-2
Charged cycloreversion (1c^{+} → 1o^{+})	-46	-62
Open hydration (1o^{+} → 1o)	-9	-12
Open dehydration (1o → 1o^{+})	9	12
Unharged cycloreversion (1c → 1o)	-78	-76
Transition state charged cycloreversion (1c* → TS^{+})	80	73
Transition state uncharged cycloreversion (1c → TS)	127	130

(b) Transition states TS and TS^{+}

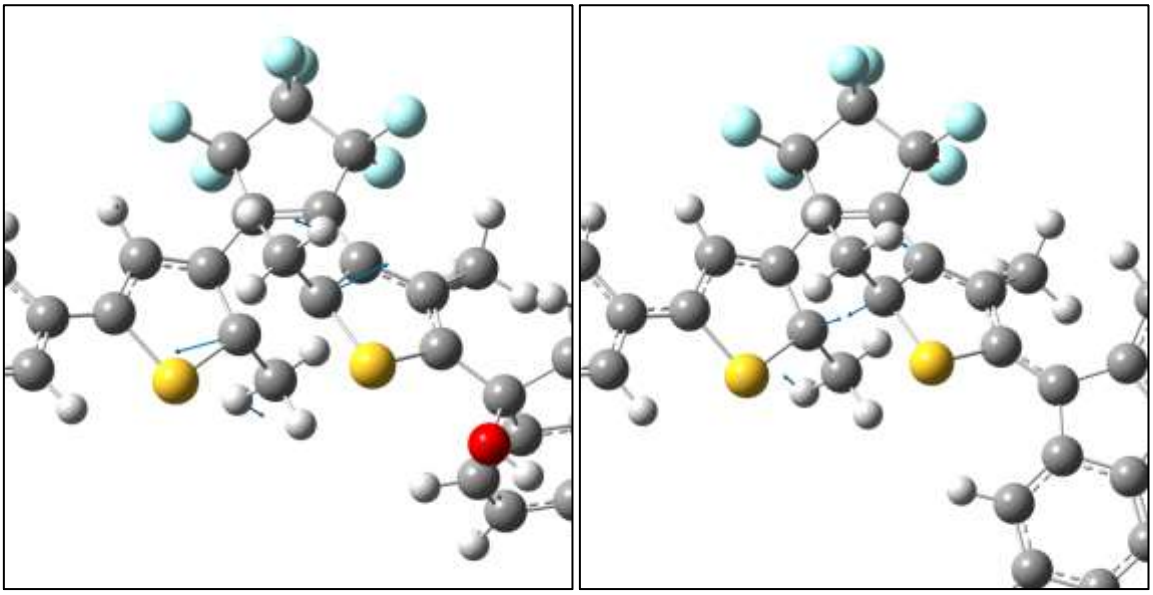

Figure S20 The displacement vector (blue arrows) of the imaginary frequency of the uncharged transition state TS (left) and of the charged one TS^{+} (right) from the gas phase calculation. The vector shows in both causes in the direction of bond cleavage, calculated from the gas phase optimised structure.

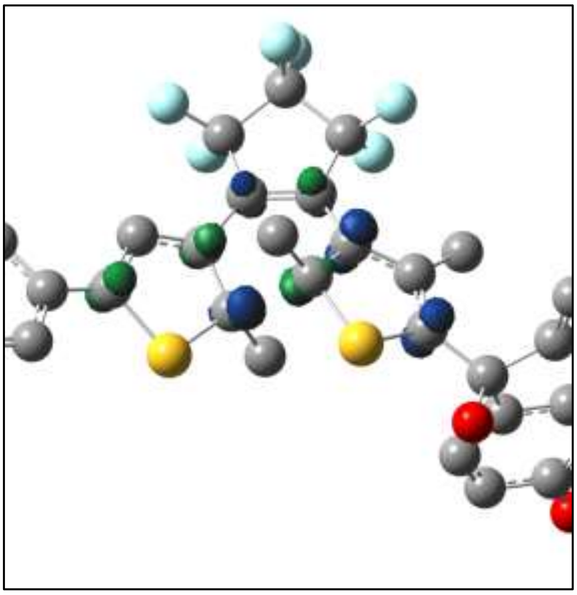

Figure S21 The spin density function of the uncharged transition state TS, shows a strong biradical character with a unsymmetrical p-orbital on central α-thiophene carbon atom and an alternating α- and β-spin density fraction within the π-conjugated framework of the DAE, calculated from the gas phase optimised structure.

#	ESP (CHelpG)		
1	0,059	7	-0,024
2	- 0,066	8	-0,075
3	0,125	9	0,107
4	-0,199	10	-0,174
5	**0,320**	11	0,005
6	- 0,170	12	-0,073
		13	0,247

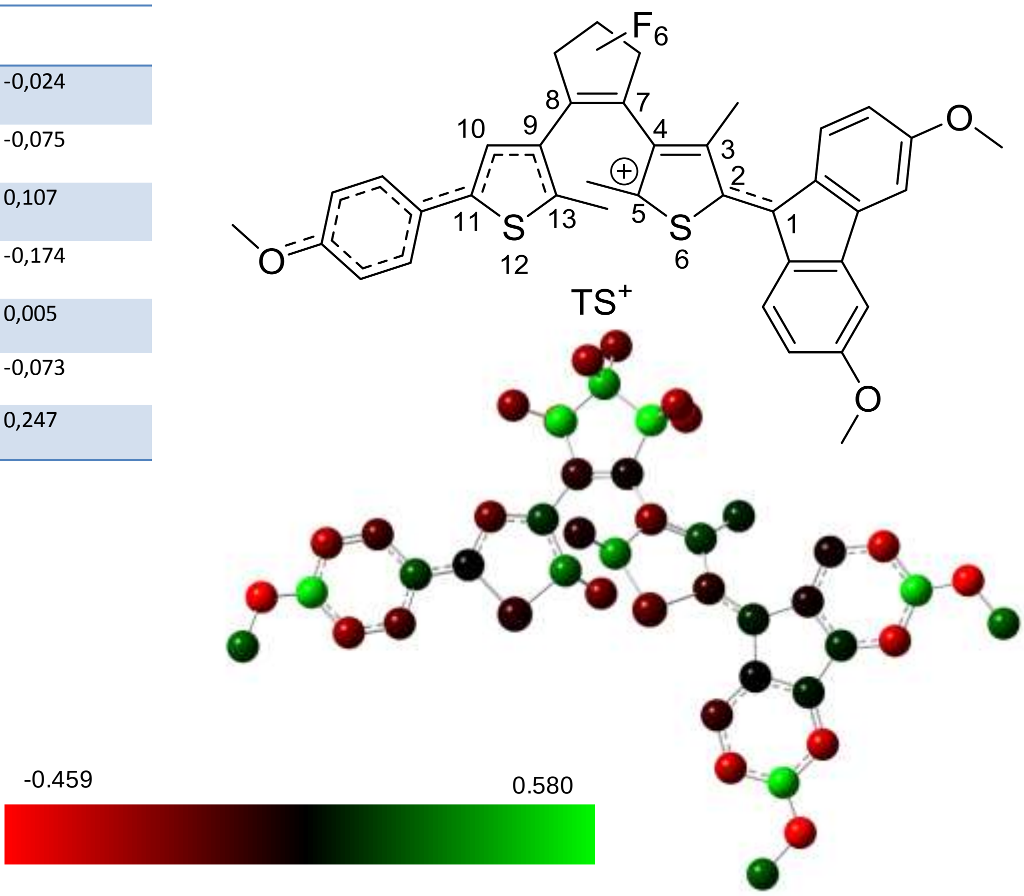

Figure S20: Charge distribution of the charged transition state TS^+ from CHalpG keyword, calculated from the SMD optimised structure. [S13]

[S13] C. M. Breneman and K. B. Wiberg, *J. Comp. Chem.*, 1990, **11**, 361.

(c) Calculated Structures

Uncharged open 1o

```
Charge =  0 Multiplicity = 1
 Symbolic Z-Matrix:
 C                      -1.66456   2.09451   1.35302
 C                      -0.49658   1.52613   1.75871
 C                      -2.59906   1.64375   0.30982
 C                       0.02907   0.18863   1.42209
 C                      -0.70536  -0.95457   1.68621
 S                       0.19826  -2.37558   1.2849
 C                       1.57321  -1.4383    0.75323
 C                       1.34657  -0.08786   0.88346
 C                      -4.01581   1.51706   0.5225
 C                      -4.71322   1.08413  -0.57688
 S                      -3.61082   0.85647  -1.92228
 C                      -2.22206   1.31907  -0.98224
 C                       2.79057  -2.17233   0.21693
 C                      -2.08112  -1.09393   2.27376
 C                      -0.86673   1.35545  -1.62299
 C                      -6.15511   0.83538  -0.70708
 C                      -0.92548   3.36348   3.28186
 C                      -6.66658  -0.14313  -1.58444
 C                      -8.03096  -0.37947  -1.68699
 C                       0.19146   2.40719   2.78478
 C                      -8.93654   0.35513  -0.9058
 C                      -8.45131   1.33443  -0.02914
 C                      -1.9203    3.39103   2.09324
 C                      -7.07692   1.56906   0.0562
 C                       4.12401  -1.72865   0.82712
 C                       5.04331  -1.37662  -0.18215
 C                       4.37562  -1.51728  -1.49081
 C                       3.05968  -1.95424  -1.27676
 C                       4.86246  -1.2863   -2.78128
 C                       4.00028  -1.5102   -3.86517
 C                       2.68211  -1.95626  -3.65181
 C                       2.21026  -2.17689  -2.35843
 C                       4.49957  -1.68207   2.15914
 C                       5.80144  -1.27976   2.49952
 C                       6.712    -0.92674   1.49163
 C                       6.33369  -0.97429   0.13725
 O                       2.52811  -3.56591   0.49602
 O                       4.34801  -1.3239   -5.17291
 O                       7.99579  -0.52011   1.72365
 O                     -10.25619   0.04632  -1.07267
 C                     -11.2229    0.74549  -0.29851
 C                       5.66179  -0.87062  -5.4743
 C                       8.45439  -0.43286   3.0674
 F                       0.74093   1.70268   3.8118
 F                       1.20422   3.16535   2.24525
 F                      -0.47203   4.58629   3.63098
 F                      -1.53588   2.81203   4.36684
 F                      -3.20553   3.52848   2.53838
 F                      -1.67001   4.48052   1.29882
 H                      -4.48638   1.70043   1.48063
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 H                      -2.18809  -2.04645   2.80341
 H                      -0.24684   2.13077  -1.16227
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 H                      -5.98321  -0.74163  -2.18161
 H                      -8.4183   -1.13843  -2.36019
 H                      -9.12566   1.92854   0.57751
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 H                       1.19183  -2.52377  -2.20186
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 H                       6.08723  -1.24228   3.54442
 H                       7.06175  -0.69258  -0.61817
 H                       3.2473   -4.08943   0.10651
 H                     -12.18992   0.33212  -0.5897
 H                     -11.06489   0.58433   0.77591
 H                     -11.20564   1.8215   -0.51558
 H                       5.70565  -0.79472  -6.56201
 H                       6.41971  -1.58507  -5.12728
 H                       5.8549    0.11508  -5.0312
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 H                       9.48814  -0.08897   3.00447
 H                       7.86295   0.28999   3.64405
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 H                       1.82503   1.89797   0.17998
 H                       3.00367   1.2429    1.31365
 H                       2.95789   0.65415  -0.35082
```

Charged open 1o⁺

Input

```
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 C                      -0.17514   1.59657   0.28348
 C                       0.48083   0.81115   1.23643
 S                       1.80983  -0.03692   0.5505
 C                       1.56785   0.71426  -1.02907
 C                       0.44604   1.56292  -1.00342
 C                      -3.42968   0.22788   2.83198
 C                      -3.81422  -1.09033   2.87814
 S                      -3.62883  -1.81492   1.28917
 C                      -2.99991  -0.35429   0.59178
 C                       2.47217   0.41133  -2.08825
 C                       0.20171   0.6814    2.70184
 C                      -2.68059  -0.30782  -0.87303
 C                      -4.33311  -1.85593   4.01551
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 C                       3.89162   0.64788  -3.93361
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 C                       4.44389   2.71571  -5.03244
 C                       3.6171    3.42621  -4.14269
 C                       2.91433   2.74226  -3.1495
 C                       2.85035  -2.15478  -1.79752
 C                       3.5058   -3.2574   -2.32161
 C                       4.36013  -3.12409  -3.43837
 C                       4.55145  -1.85902  -4.05331
 F                      -3.84807   3.14513   2.91716
 O                       5.15806   3.27184  -6.01898
 O                       4.93801  -4.25598  -3.86055
 O                      -5.76321  -4.08008   7.25519
 C                      -6.49327  -3.48143   8.32468
 C                       5.10097   4.69028  -6.23864
 C                       5.82409  -4.24345  -4.98982
 C                      -1.31585   3.92981   0.50371
 F                      -4.3823    3.36877   0.80183
 F                      -2.97742   5.56963   1.15753
 C                      -2.36618   4.43187   1.53072
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 F                      -0.08084   4.4582    0.73206
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 H                       6.68632  -3.59596  -4.79791
 C                      -0.14526   2.2312   -2.21652
 H                      -1.22925   2.08317  -2.23789
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 H                       0.27106   1.83179  -3.14277
```

Uncharged closed 1c

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```

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 C                  -2.01928   -0.4183    -0.7616
 C                  -0.75668   -0.75203    0.06582
 C                  -0.23535    0.53368    0.74232
 C                  -1.19497    1.3128     1.34561
 S                   0.64774   -1.38034   -0.9724
 C                   1.76631   -0.25577   -0.20221
 C                   1.20112    0.66959    0.64202
 C                  -4.39288   -0.2297    -0.1382
 C                  -4.47173   -1.30235   -0.98933
 S                  -2.87745   -1.9071    -1.50297
 C                   3.23395   -0.39664   -0.59747
 C                  -5.68739   -1.96115   -1.46495
 C                  -1.7559     0.5823    -1.91937
 C                  -1.00395   -1.80536    1.1802
 C                  -1.05986    2.44862    2.32051
 C                  -5.65309   -3.2469    -2.04913
 C                  -6.81018   -3.8755    -2.48367
 C                  -2.45989    2.54647    3.00872
 C                  -8.05334   -3.23556   -2.35434
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 C                  -3.45606    1.96306    1.96892
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 O                  -9.13127   -3.93089   -2.81
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 C                   4.98574    1.26144   -0.76432
 C                   3.79754    0.80859   -1.35813
 C                   5.70926    2.3244    -1.31298
 C                   5.21843    2.92795   -2.48087
 C                   4.02908    2.46981   -3.07916
 C                   3.31688    1.41057   -2.51898
 C                   4.22977   -1.40095    1.62515
 C                   5.27347   -1.35572    2.56393
 C                   6.29575   -0.40364    2.4306
 C                   6.28874    0.50782    1.3587
 O                   7.34862   -0.2803     3.29167
 O                   5.82539    3.97162   -3.11715
 C                   7.42925   -1.15931    4.40738
 C                   7.02703    4.50243   -2.57165
 O                   3.28404   -1.58517   -1.41528
 F                  -2.76732    3.80113    3.40165
 F                  -2.45854    1.74601    4.11113
 F                  -4.50454    1.33428    2.5884
 F                  -4.0156     3.00118    1.25276
 F                  -0.09828    2.28111    3.27712
 F                  -0.78864    3.65757    1.70961
 H                  -5.26451    0.21172    0.33062
 H                  -2.70318    0.82787   -2.40686
 H                  -1.31662    1.50774   -1.53314
 H                  -1.07979    0.15563   -2.66332
 H                  -1.78372   -1.46721    1.86922
 H                  -1.30496   -2.76558    0.75453
 H                  -0.08094   -1.94923    1.74869
 H                  -4.70578   -3.76885   -2.15226
 H                  -6.77689   -4.8666    -2.92576
 H                  -9.05654   -1.42887   -1.68538
 H                  -7.01173   -0.33389   -0.93738
 H                 -11.1165    -4.07773   -3.11571
 H                 -10.68307   -3.14463   -1.65426
 H                 -10.48732   -2.41352   -3.28151
 H                   6.62301    2.66788   -0.84064
 H                   3.68385    2.96495   -3.98159
 H                   2.39968    1.06275   -2.98719
 H                   3.44267   -2.14322    1.73166
 H                   5.27524   -2.06149    3.38665
 H                   7.09491    1.23193    1.28394
 H                   8.3355    -0.87271    4.9434
 H                   6.56127   -1.04394    5.06925
 H                   7.5107    -2.20551    4.08522
 H                   6.86498    4.89694   -1.56021
 H                   7.82258    3.74627   -2.54979
 H                   7.31841    5.31681   -3.23684
 H                   4.17403   -1.64482   -1.79951
 C                   1.97553    1.7709     1.3213
 H                   1.45185    2.72651    1.22697
 H                   2.10245    1.57268    2.39087
 H                   2.96381    1.89795    0.88263
```

Charged closed 1c$^+$

```
Charge =  1 Multiplicity = 1
 Symbolic Z-Matrix:
 C                  -2.96063    1.35388    1.94387
 C                  -3.26585    0.28984    1.0838
 C                  -2.19851   -0.0755     0.06357
 C                  -0.82306   -0.07945    0.78225
 C                  -0.5687     1.33231    1.35075
 C                  -1.66477    1.90887    2.01809
 S                   0.59327   -0.38191   -0.37496
 C                   1.52868    0.98128    0.305
 C                   0.73253    1.82571    1.12952
 C                  -4.41368   -0.48874    1.01417
 C                  -4.31444   -1.60861    0.16978
 S                  -2.73909   -1.73639   -0.5919
 C                   2.88636    1.13998   -0.04694
 C                  -5.3445    -2.5869    -0.07149
 C                  -2.28932    0.92506   -1.1223
 C                  -0.73225   -1.12211    1.92758
 C                  -1.70562    3.10154    2.95727
 C                  -5.10528   -3.73026   -0.87019
 C                  -6.09035   -4.67534   -1.10884
 C                  -3.02907    2.91823    3.77058
 C                  -7.37123   -4.5019    -0.54554
 C                  -7.63388   -3.3681     0.25542
 C                  -3.93201    2.05521    2.84468
 C                  -6.64497   -2.43663    0.48592
 O                  -8.39765   -5.34794   -0.70996
 C                  -8.23498   -6.52778   -1.50982
 C                   3.94542    1.69068    0.78984
 C                   5.15921    1.70767    0.05108
 C                   4.88267    1.14381   -1.27997
 C                   3.51018    0.75143   -1.31092
 C                   5.70484    0.98171   -2.3719
 C                   5.17049    0.40318   -3.55115
 C                   3.82042    0.02021   -3.60426
 C                   2.99451    0.19995   -2.48967
 C                   3.98049    2.02255    2.15701
 C                   5.16663    2.44987    2.73274
 C                   6.35129    2.52712    1.96808
 C                   6.35403    2.12831    0.61258
 O                   7.43871    2.96502    2.63009
 O                   6.04673    0.2711    -4.56668
 C                   8.69586    3.06506    1.95262
 C                   5.61279   -0.29629   -5.80692
 F                  -3.58756    4.08925    4.12035
 F                  -2.74998    2.21084    4.89566
 F                  -4.72157    1.20561    3.56726
 F                  -4.78328    2.86765    2.13985
 F                  -0.64633    3.17689    3.80574
 F                  -1.76711    4.28419    2.26848
 H                  -5.29247   -0.28576    1.61224
 H                  -2.05321    1.93887   -0.78654
 H                  -1.59063    0.65067   -1.91499
 H                  -3.3037     0.92505   -1.52939
 H                  -1.50459   -0.95112    2.68416
 H                  -0.83927   -2.14033    1.54618
 H                   0.24326   -1.04114    2.41327
 H                  -4.1254    -3.8875    -1.31229
 H                  -5.86402   -5.53777   -1.72448
 H                  -8.62685   -3.25073    0.67717
 H                  -6.882     -1.57392    1.09871
 H                  -9.20271   -7.02765   -1.48385
 H                  -7.98124   -6.26367   -2.54217
 H                  -7.46771   -7.18264   -1.08269
 H                   6.74715    1.28606   -2.37242
 H                   3.40396   -0.41672   -4.50387
 H                   1.95398   -0.09518   -2.56784
 H                   3.09782    1.92874    2.77912
 H                   5.21732    2.71692    3.78325
 H                   7.2698     2.12553    0.03246
 H                   9.39336    3.45339    2.69455
 H                   9.0336     2.08068    1.6089
 H                   8.62979    3.76039    1.1081
 H                   5.26312   -1.32495   -5.66295
 H                   4.8214     0.31306   -6.25815
 H                   6.49235   -0.29292   -6.45052
 C                   1.15598    3.22953    1.49243
 H                   1.32405    3.35586    2.5642
 H                   2.06489    3.51825    0.96637
 H                   0.36851    3.93422    1.20968
```

Reference (Triphenylmethanol)

```
Charge =  0 Multiplicity = 1
 Symbolic Z-Matrix:
 C                   0.01877   -0.01125    0.66973
 C                  -0.23485    1.43636    0.20949
 C                  -1.14749   -0.91869    0.22303
 C                   1.39009   -0.54805    0.20378
 C                  -0.70528    1.71295   -1.08244
 C                  -0.89403    3.02944   -1.50876
 C                  -0.62368    4.09506   -0.64569
```

```
 C                      -0.16109   3.82871   0.64471
 C                       0.03537   2.51059   1.06853
 C                      -1.11115  -1.65923  -0.96723
 C                      -2.2094   -2.42792  -1.36592
 C                      -3.36216  -2.46985  -0.57875
 C                      -3.40882  -1.73296   0.60838
 C                      -2.31302  -0.96239   1.00281
 C                       1.72518  -1.88676   0.47651
 C                       2.98668  -2.39379   0.16276
 C                       3.94202  -1.57115  -0.44244
 C                       3.62     -0.24304  -0.72477
 C                       2.35659   0.26441  -0.40146
 O                       0.04426   0.04817   2.11462
 H                      -0.93382   0.89851  -1.76304
 H                      -1.26022   3.2199   -2.51467
 H                      -0.77635   5.11994  -0.97474
 H                       0.04957   4.64748   1.32864
 H                       0.39539   2.30891   2.07056
 H                      -0.21913  -1.64721  -1.58702
 H                      -2.15784  -2.9976   -2.29069
 H                      -4.21443  -3.07069  -0.8861
 H                      -4.30136  -1.75492   1.22907
 H                      -2.35341  -0.38752   1.92259
 H                       0.986    -2.5502    0.92128
 H                       3.21961  -3.43272   0.38303
 H                       4.9242   -1.96395  -0.69273
 H                       4.35235   0.40753  -1.19643
 H                       2.12848   1.30111  -0.62449
 H                       0.38439  -0.79867   2.44413
```

Reference^{+} (Triphenylmethyl cation)

```
Charge =  1 Multiplicity = 1
 Symbolic Z-Matrix:
 C                       0.00016   0.0004    0.00103
 C                      -0.73689   1.2488    0.00085
 C                      -0.71282  -1.26298  -0.00013
 C                       1.45058   0.01433   0.00083
 C                      -0.23537   2.38759  -0.68504
 C                      -0.95228   3.57725  -0.69667
 C                      -2.1653    3.67127  -0.00125
 C                      -2.67034   2.56505   0.69522
 C                      -1.97717   1.36125   0.68489
 C                      -1.95309  -1.3963   -0.68089
 C                      -2.62463  -2.61228  -0.69227
 C                      -2.0977   -3.71081   0.00006
 C                      -0.88421  -3.59698   0.69163
 C                      -0.18804  -2.39492   0.68055
 C                       2.16751   1.03142   0.68617
 C                       3.5566    1.02967   0.69721
 C                       4.26243   0.03975   0.00001
 C                       3.57481  -0.96271  -0.697
 C                       2.18603  -0.98954  -0.68529
 H                       0.68741   2.30827  -1.25049
 H                      -0.57383   4.43152  -1.24994
 H                      -2.71778   4.60678  -0.00255
 H                      -3.60122   2.64828   1.24812
 H                      -2.35369   0.51616   1.25153
 H                      -2.34786  -0.55646  -1.243
 H                      -3.55552  -2.71124  -1.24257
 H                      -2.63357  -4.65595   0.00098
 H                      -0.48967  -4.44542   1.24259
 H                       0.73485  -2.30121   1.24343
 H                       1.62452   1.78178   1.25193
 H                       4.09332   1.79371   1.25155
 H                       5.34884   0.04924   0.00068
 H                       4.12535  -1.7166   -1.25171
 H                       1.65714  -1.7504   -1.24992
```

Uncharged transition state TS

```
Charge =  0 Multiplicity = 1
 Symbolic Z-Matrix:
 C                      -2.55869   1.26761   1.01909
 C                      -3.02753   0.52849  -0.13616
 C                      -2.04447   0.01473  -1.08844
 C                      -0.75908  -0.89538   0.25546
 C                      -0.26636   0.28806   0.95566
 C                      -1.26897   1.18357   1.51729
 S                       0.62239  -1.66662  -0.5669
 C                       1.73846  -0.42776  -0.02711
 C                       1.12496   0.53258   0.77463
 C                      -4.31245  -0.01332  -0.29638
 C                      -4.43983  -0.9478   -1.32211
 S                      -2.90096  -1.1407   -2.1645
 C                       3.18353  -0.51882  -0.49082
 C                      -5.61134  -1.73453  -1.67531
 C                      -1.13722   0.95962  -1.85978
 C                      -1.65722  -1.90758   0.95236
 C                      -1.11416   2.10619   2.69469
 C                      -5.53361  -2.82994  -2.56823
 C                      -6.6519   -3.58045  -2.89645
 C                      -2.57298   2.40526   3.14155
 C                      -7.90447  -3.26542  -2.34519
 C                      -8.01196  -2.18121  -1.46189
 C                      -3.40461   2.18637   1.84907
 C                      -6.88058  -1.43343  -1.13982
 O                      -8.94292  -4.06218  -2.72801
 C                     -10.238    -3.79832  -2.2008
 C                       4.2101   -0.56916   0.64731
 C                       5.21071   0.40702   0.46025
 C                       4.88392   1.18345  -0.75131
 C                       3.69287   0.6818   -1.29797
 C                       5.56007   2.25404  -1.34369
 C                       5.01983   2.81647  -2.51002
 C                       3.82904   2.30912  -3.06357
 C                       3.16551   1.24226  -2.45919
 C                       4.275    -1.43853   1.72342
 C                       5.34288  -1.34085   2.63003
 C                       6.33434  -0.36526   2.44294
 C                       6.27151   0.51846   1.34972
 O                       7.40668  -0.19163   3.27077
 O                       5.57866   3.86252  -3.18631
 C                       7.54139  -1.03892   4.40571
 C                       6.78452   4.4318   -2.69159
 O                       3.23434  -1.72529  -1.2841
 F                      -2.72736   3.63682   3.67452
 F                      -2.94861   1.49237   4.07959
 F                      -4.64687   1.68758   2.15319
 F                      -3.6303    3.39119   1.22725
 F                      -0.38386   1.57719   3.72004
 F                      -0.5127    3.30495   2.36919
 H                      -5.12444   0.21329   0.38309
 H                      -0.61766   1.64542  -1.18729
 H                      -0.38862   0.40363  -2.43355
 H                      -1.73095   1.55707  -2.5612
 H                      -2.50949  -1.42491   1.43422
 H                      -2.03762  -2.65008   0.24302
 H                      -1.08803  -2.43654   1.72543
 H                      -4.57673  -3.10447  -3.00381
 H                      -6.57905  -4.42218  -3.57861
 H                      -8.9656   -1.90692  -1.02487
 H                      -6.9975   -0.59052  -0.46554
 H                     -10.89414  -4.55206  -2.63888
 H                     -10.24951  -3.89428  -1.10737
 H                     -10.58825  -2.79808  -2.48679
 H                       6.47675   2.63311  -0.90556
 H                       3.44489   2.77071  -3.96815
 H                       2.24935   0.85466  -2.89689
 H                       3.50823  -2.19447   1.87357
 H                       5.38614  -2.02278   3.47144
 H                       7.05402   1.2631    1.23506
 H                       8.45391  -0.71474   4.90867
 H                       6.68899  -0.92922   5.08846
 H                       7.64209  -2.09065   4.10795
 H                       6.64632   4.84487  -1.68396
 H                       7.5975    3.69411  -2.67928
 H                       7.03585   5.2376   -3.3831
 H                       4.14216  -1.82812  -1.61324
 C                       1.8464    1.73433   1.3328
 H                       1.43477   2.66506   0.92709
 H                       1.74856   1.78306   2.42132
 H                       2.90915   1.7124    1.09837
```

Charged transition state TS^{+}

```
Charge =  1 Multiplicity = 1
 Symbolic Z-Matrix:
 C                      -2.95344   1.48603   1.9736
 C                      -3.29066   0.54491   0.90148
 C                      -2.31114   0.29052  -0.13466
 C                      -0.74388  -0.20663   1.10193
 C                      -0.50813   1.11966   1.70227
 C                      -1.66789   1.75016   2.34356
 S                       0.68472  -0.63542   0.16015
 C                       1.55434   0.86757   0.56729
 C                       0.71192   1.70162   1.39154
 C                      -4.35936  -0.33919   0.92023
 C                      -4.31652  -1.327    -0.09082
 S                      -2.90177  -1.1076   -1.08218
 C                       2.85261   1.06687   0.10538
 C                      -5.25483  -2.40137  -0.29342
 C                      -1.76182   1.40681  -1.00964
 C                      -1.26483  -1.3679    1.93673
 C                      -1.6525    2.70698   3.52068
 C                      -5.04953  -3.3929   -1.2816
 C                      -5.95738  -4.42006  -1.48697
```

C	-3.10068	2.62649	4.08972
C	-7.12341	-4.48747	-0.69698
C	-7.34987	-3.50806	0.29477
C	-3.94847	2.19347	2.85729
C	-6.43741	-2.49336	0.49126
O	-8.06805	-5.43285	-0.80918
C	-7.93345	-6.46756	-1.79327
C	3.92782	1.79686	0.7862
C	5.08258	1.7931	-0.03636
C	4.7684	1.04253	-1.25999
C	3.43329	0.55759	-1.14945
C	5.53987	0.79375	-2.37685
C	4.98968	0.03375	-3.43307
C	3.67105	-0.44153	-3.34859
C	2.8966	-0.17173	-2.21378
C	4.03555	2.29925	2.09493
C	5.2277	2.86618	2.52223
C	6.34792	2.92037	1.66605
C	6.28327	2.35569	0.37694
O	7.44778	3.50587	2.18622
O	5.81568	-0.17219	-4.48376
C	8.63903	3.59549	1.40066
C	5.35161	-0.92355	-5.60681
F	-3.51758	3.77625	4.64346
F	-3.15162	1.6436	5.02554
F	-4.99592	1.40389	3.23827
F	-4.48547	3.28551	2.23834
F	-0.72047	2.38474	4.45245
F	-1.4158	3.99903	3.1331
H	-5.12455	-0.32108	1.68393
H	-1.43943	2.25697	-0.40601
H	-0.90832	1.05693	-1.5997
H	-2.53468	1.75966	-1.70055
H	-2.14107	-1.09028	2.52423
H	-1.51662	-2.23098	1.31371
H	-0.47887	-1.67663	2.6341
H	-4.15787	-3.36438	-1.90221
H	-5.7594	-5.16012	-2.25332
H	-8.25405	-3.57415	0.89123
H	-6.6461	-1.75339	1.25625
H	-8.81878	-7.0918	-1.67661
H	-7.91035	-6.0418	-2.80235
H	-7.03283	-7.06335	-1.60876
H	6.55444	1.16648	-2.48038
H	3.23765	-1.01889	-4.1566
H	1.87783	-0.5432	-2.19185
H	3.21088	2.22977	2.79489
H	5.33062	3.26339	3.5269
H	7.15357	2.33231	-0.26893
H	9.36186	4.11689	2.0283
H	9.0204	2.59831	1.15127
H	8.462	4.17195	0.48509
H	5.08798	-1.94643	-5.31271
H	4.49111	-0.43369	-6.07795
H	6.18746	-0.94757	-6.30628
C	1.03012	3.15251	1.66358
H	1.19197	3.35064	2.72757
H	1.91687	3.47519	1.12008
H	0.19461	3.78395	1.34708