Supporting Information

New synthetic route to substituted dihydroazulene photoswitches

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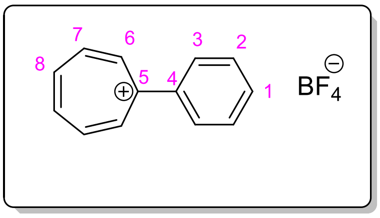
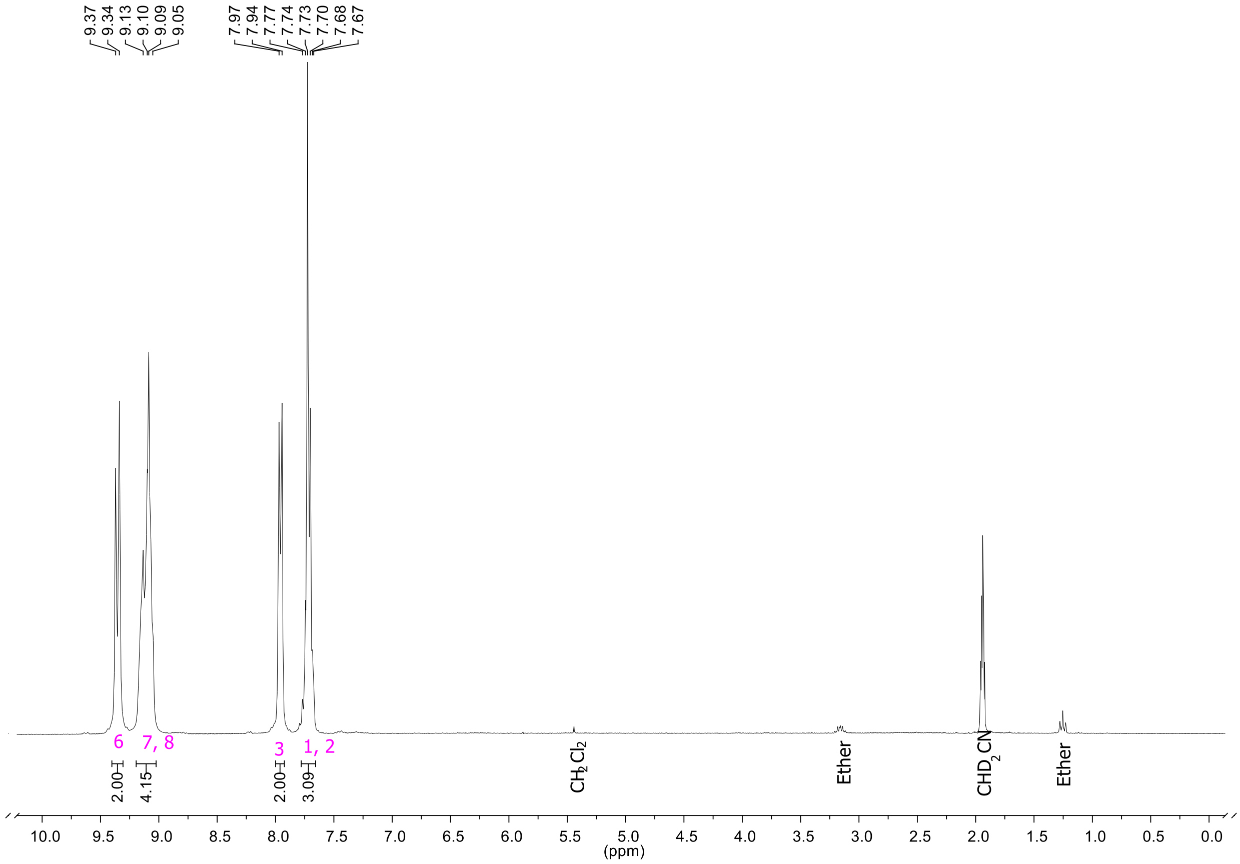
Phenyltropylium tetrafluoroborate (5)

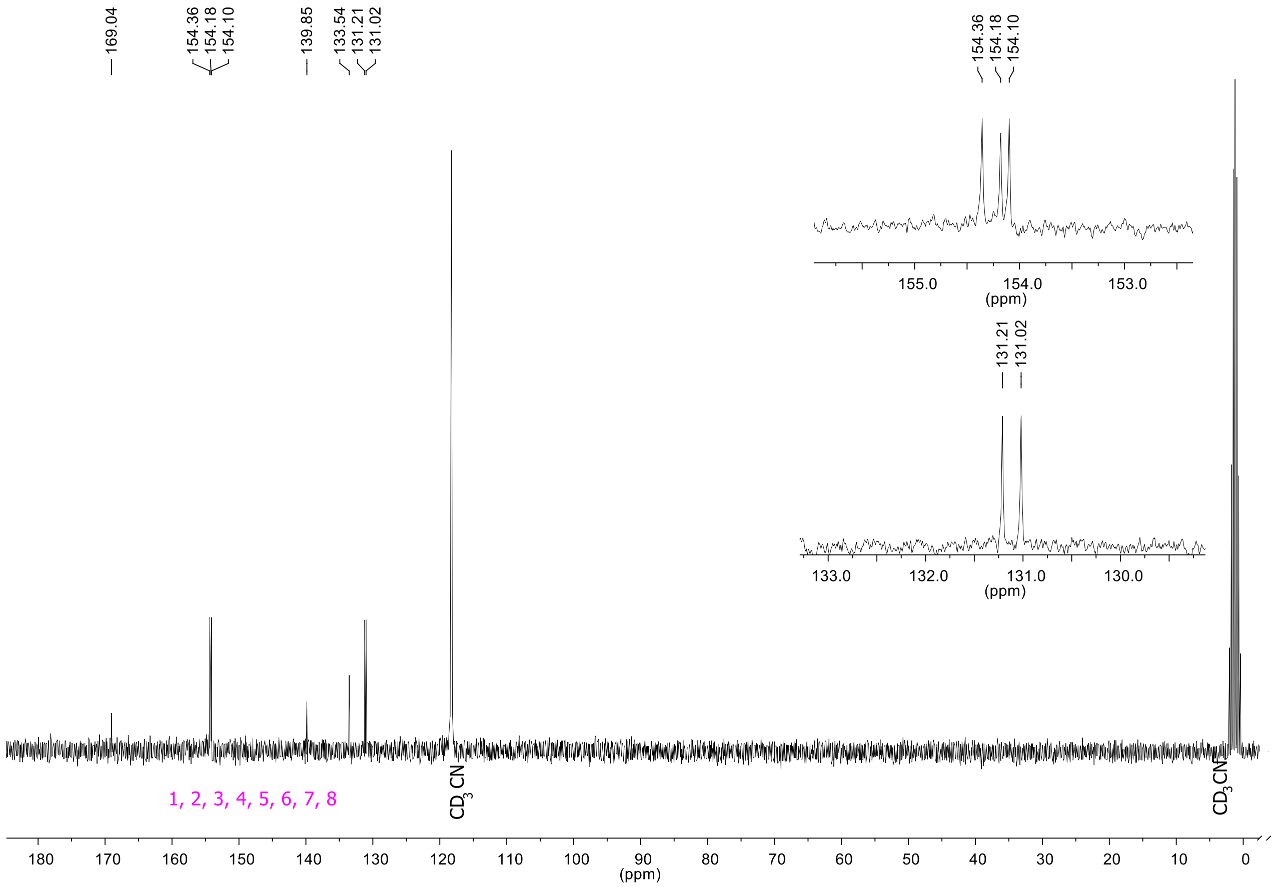


7-Phenylcyclohepta-1,3,5-triene **4** (1.56 g, 9.28 mmol) was dissolved in dry CH_2Cl_2 (25 mL) under an argon atmosphere. 1.5 molar equivalents of tritylium tetrafluoroborate (4.33 g, 13.1 mmol) were added, whereupon the solution turned dark yellow. Additional dry CH_2Cl_2 (25 mL) was added to dissolve the tritylium species. The reaction mixture was stirred for 5 h at rt. Then the reaction mixture was poured into dry ice-cold diethylether (800 mL), resulting in precipitation of the product as a strongly colored yellow powder, which was isolated and washed with dry diethylether. The phenyltropylium tetrafluoroborate **5** was dried on a vacuum pump and collected as a yellow powder (2.26 g, 96%). M.p. 147-154°C (decomp.). ^{1}H-NMR (300 MHz, CD_3CN): δ 9.35 (d, J = 10.0 Hz, $2H_6$), 9.09 (m, $4H_{7,8}$), 7.96 (d, J = 7.8 Hz, $2H_3$), 7.78 – 7.66 (m, $3H_{1,2}$). ^{13}C NMR (75 MHz, CD_3CN): δ 169.0, 154.4, 154.2, 154.1, 139.9, 133.5, 131.2, 131.0 ($C_{1\text{-}8}$). Calcd for $C_{13}H_{11}BF_4$: C 61.46, H 4.36; Found C 61.77, H 4.28.

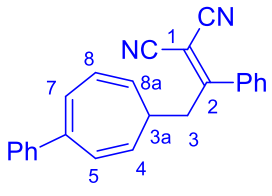
Phenyltropylium tetrafluoroborate (**5**) – ^{1}H-NMR (300 MHz, CD_3CN):



Phenyltropylium tetrafluoroborate (**5**) – ^{13}C-NMR (75 MHz, CD_3CN):



Compounds 7, 8, and 9 (mixture)



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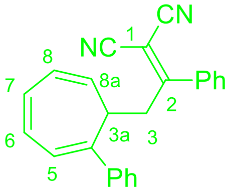

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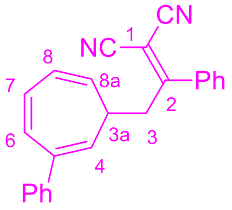

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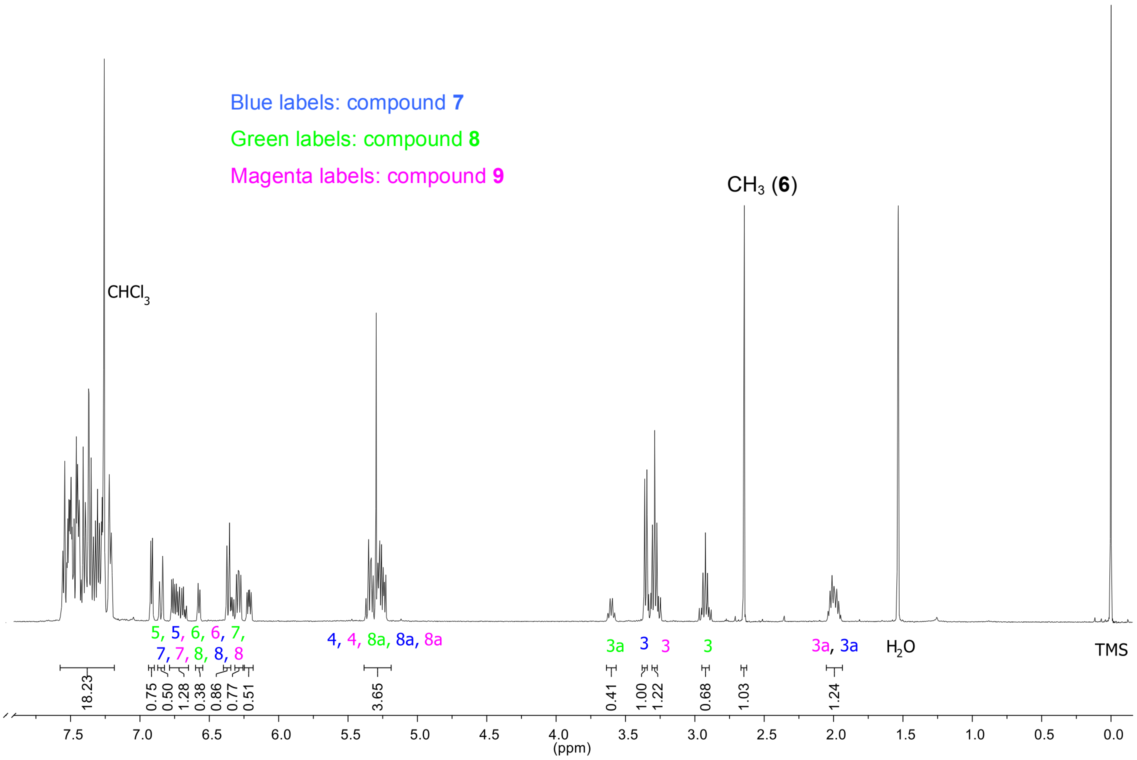
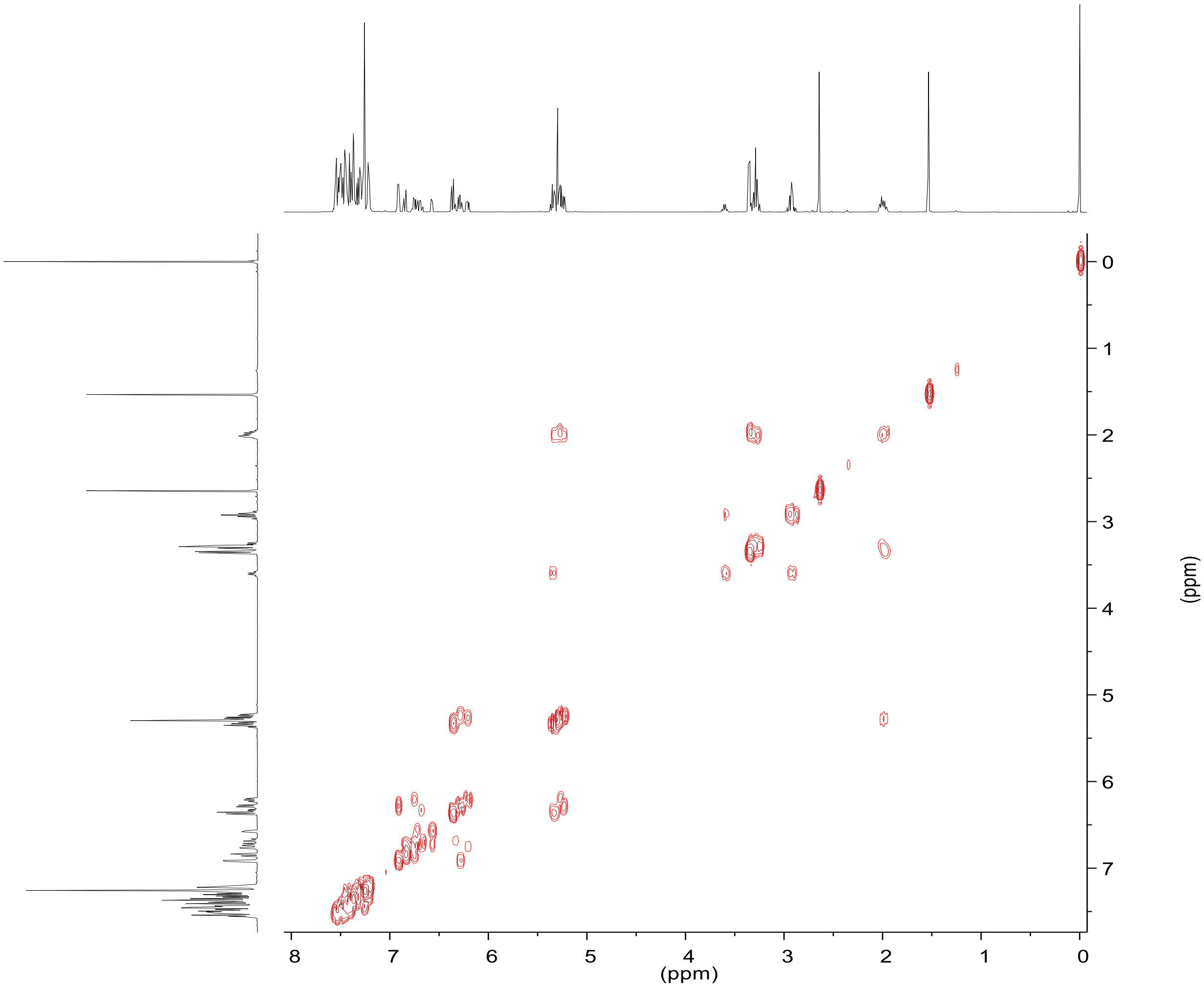
Phenyltropylium tetrafluoroborate **5** (1.59 g, 6.24 mmol) and α-cyano-β-phenylcrotononitrile **6** (1.07 g, 6.37 mmol) were dissolved under an argon atmosphere in dry CH_2Cl_2 (70 mL). The greenish solution was cooled to -78°C. Et_3N (0.70 g, 6.90 mmol) was added and the solution was allowed to reach rt. The yellow solution was stirred for 3 h, then aqueous HCl (1 M, 100 mL) was added. The organic phase was washed with H_2O (2 x 250 mL), dried ($MgSO_4$), and concentrated *in vacuo* to provide a mixture of three regioisomers as a sticky brown solid (1.77 g), also containing remains of α-cyano-β-phenylcrotononitrile (content of 5.6% in mixture). According to TLC, no separation was possible. The mixture was used for the next step without further purification. According to ^{1}H-NMR, the following ratio between isomers was estimated: **7** ("6-Ph"): 34.5% / **8** ("4-Ph"): 23.4% / **9** ("5-Ph"): 42.1%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.58 – 7.18 (m, H_{Ph}), 6.92 (d, *J* = 6.2 Hz, 6H), 6.85 (d, *J* = 11.3 Hz, 4H), 6.79 – 6.65 (m, 10H), 6.57 (d, *J* = 6.0 Hz, 3H), 6.36 (d, *J* = 9.5 Hz, 7H), 6.29 (dd, *J* = 9.4 Hz, 6.3 Hz, 6H), 6.21 (dd, *J* = 9.4 Hz, 5.6 Hz, 4H), 5.38 – 5.19 (m, 29$H_{4,\ 4,\ 8a,\ 8a,\ 8a}$), 3.60 (q, *J* = 8.1 Hz, 3H_{3a}), 3.35 (d, *J* = 7.9 Hz, 8H_3), 3.29 (t, *J* = 8.0 Hz, 10H_3), 2.92 (t, *J* = 8.1 Hz, 5H_3), 1.99 (m, 10$H_{3a,\ 3a}$).

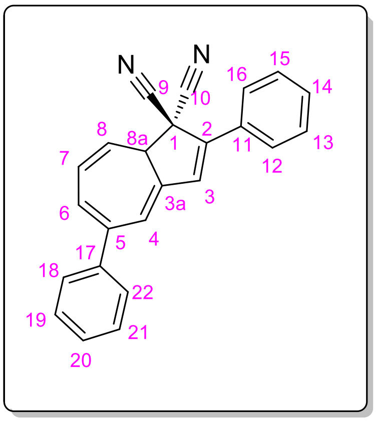
Mixture of **7**, **8**, and **9** (and unreacted **6**) – ^{1}H-NMR (500 MHz, $CDCl_3$):



Mixture of **7**, **8**, and **9** (and unreacted **6**) – ^{1}H-^{1}H COSY NMR (300 MHz, $CDCl_3$):

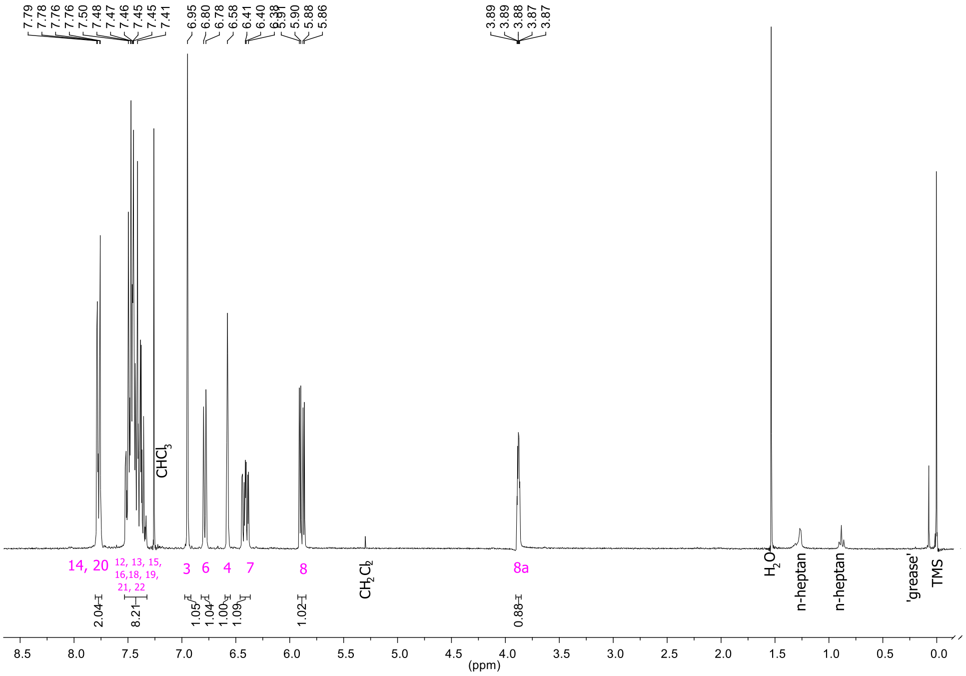


1,1-Dicyano-2,5-diphenyl-1,8a-dihydroazulene (3)

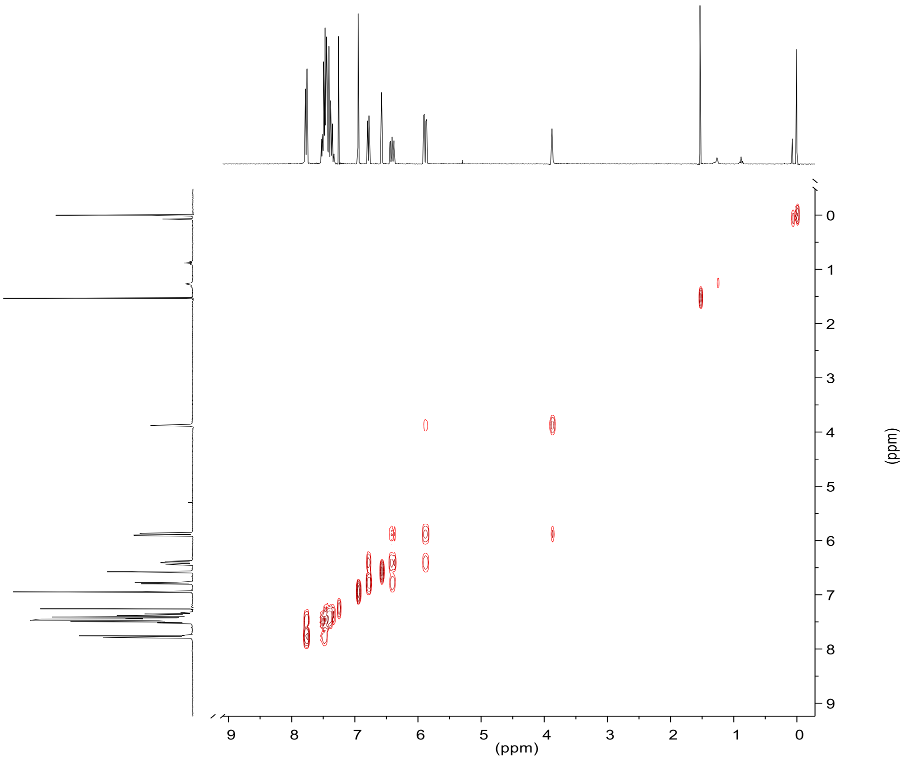


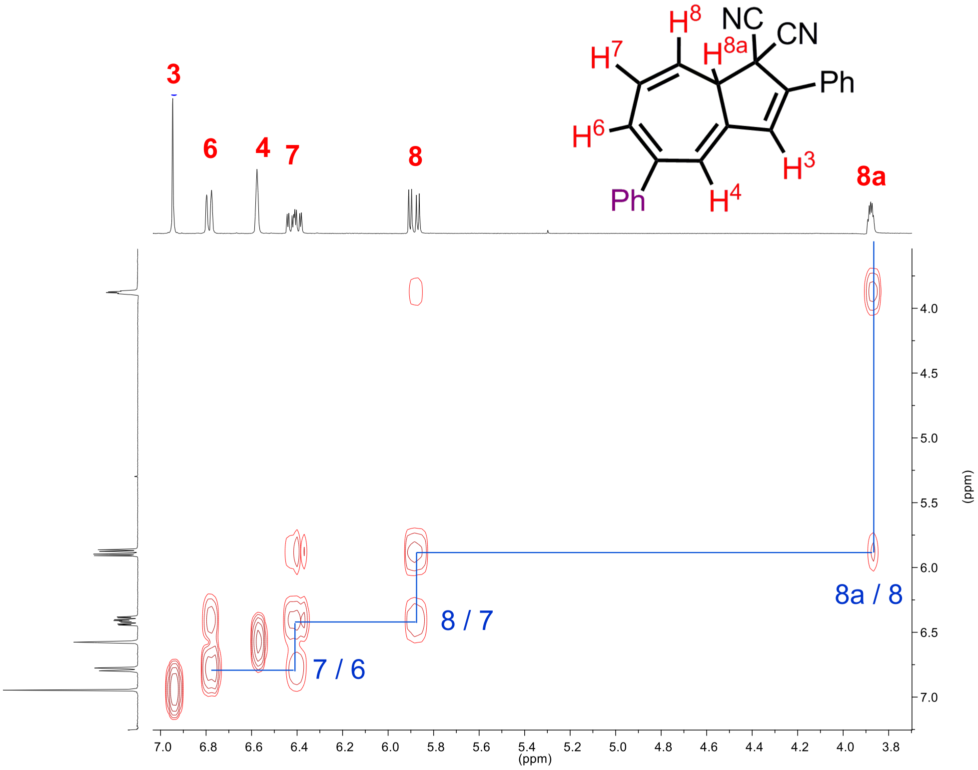
A crude mixture (1.63 g) of the three regioisomers **7**, **8**, and **9** (4.59 mmol, after correction for the impurity **6**, see above) was dissolved in CH_2ClCH_2Cl (10 mL). Then tritylium tetrafluoroborate (1.63 g, 4.95 mmol) dissolved in CH_2ClCH_2Cl (50 mL) was added under an argon atmosphere. The mixture was heated to 80°C, by which it turned dark red in color. Toluene (110 mL) was added, and the solution was cooled on an ice bath for 1.5 h. Then Et_3N (0.52 g, 5.15 mmol) was added, and the solution was cooled for 10 min. Stirring at 80°C for 1 h followed by concentration *in vacuo* yielded a mixture of DHAs (together with triphenylmethane and triphenylmethanol). By repeated column chromatography (SiO_2, 1. column: EtOAc/heptane 1:9; 2. column: CH_2Cl_2/heptane 2:1), it was possible to isolate **3** (195 mg, ca. 12%) as a fine, yellow powder. M.p. 128-129°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (dd, J = 8.2, 1.5 Hz, $2H_{14, 20}$), 7.53 – 7.32 (m, $8H_{12, 13, 15, 16, 18, 19, 21, 22}$), 6.95 (s, $1H_3$), 6.79 (d, J = 6.5 Hz, $1H_6$), 6.58 (s, $1H_4$), 6.41 (ddd, J = 10.1, 6.5, 2.0 Hz, $1H_7$), 5.89 (dd, J = 10.1, 3.6 Hz, $1H_8$), 3.88 (dt, J = 3.6, 2.0 Hz, $1H_{8a}$). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.5, 142.1, 141.5, 140.8, 132.4, 130.6, 130.3, 129.4, 128.8, 128.3, 128.3, 127.8, 127.1, 126.5, 122.2, 119.9, 115.3, 112.9, 50.9, 45.3. R_f (TLC, EtOAc/heptane 1:9) = 0.35, R_f (TLC, CH_2Cl_2/heptane 2:1) = 0.60.

DHA **3** – ^{1}H-NMR (300 MHz, $CDCl_3$):

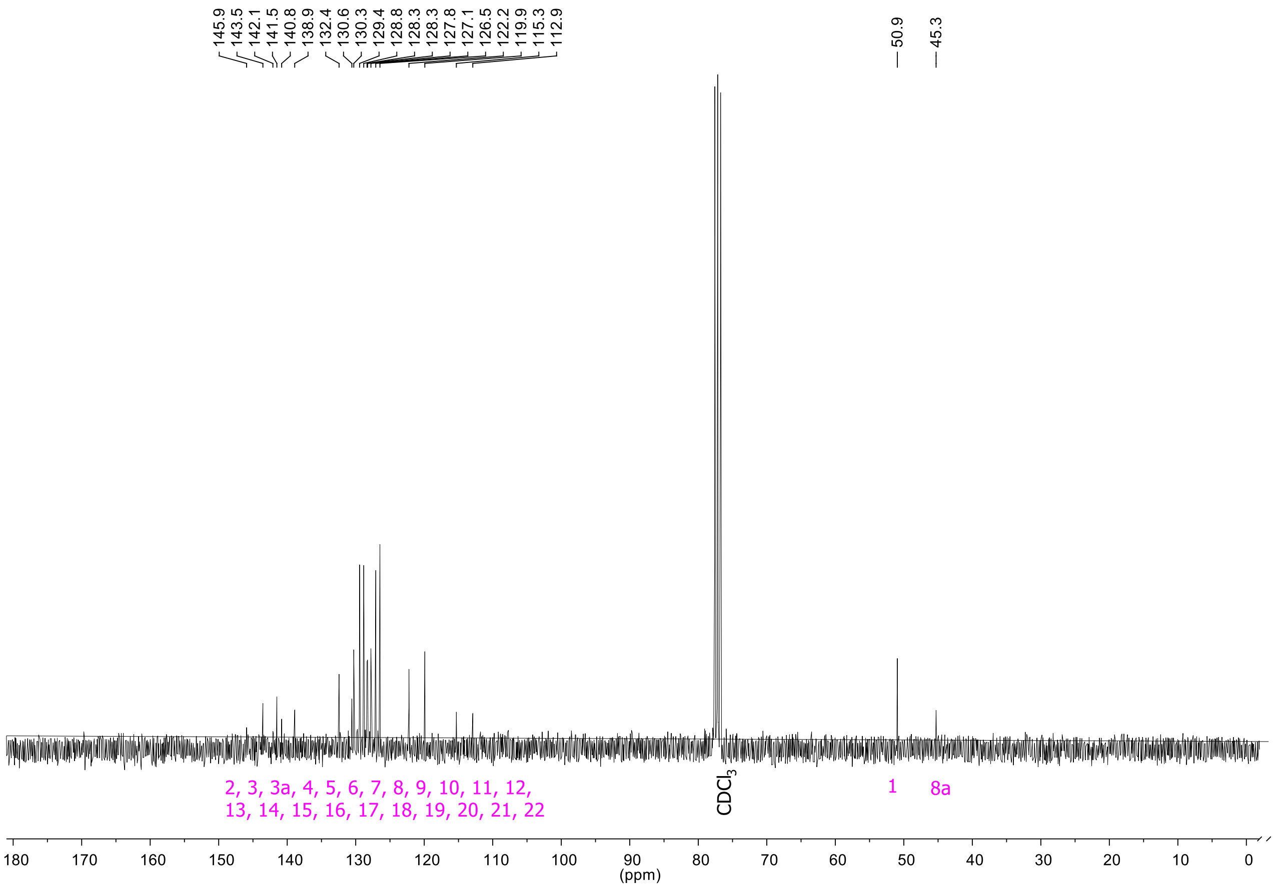


DHA **3** – ^{1}H-^{1}H COSY NMR (300 MHz, $CDCl_3$):



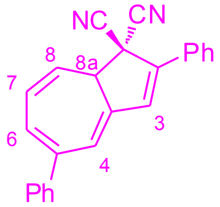


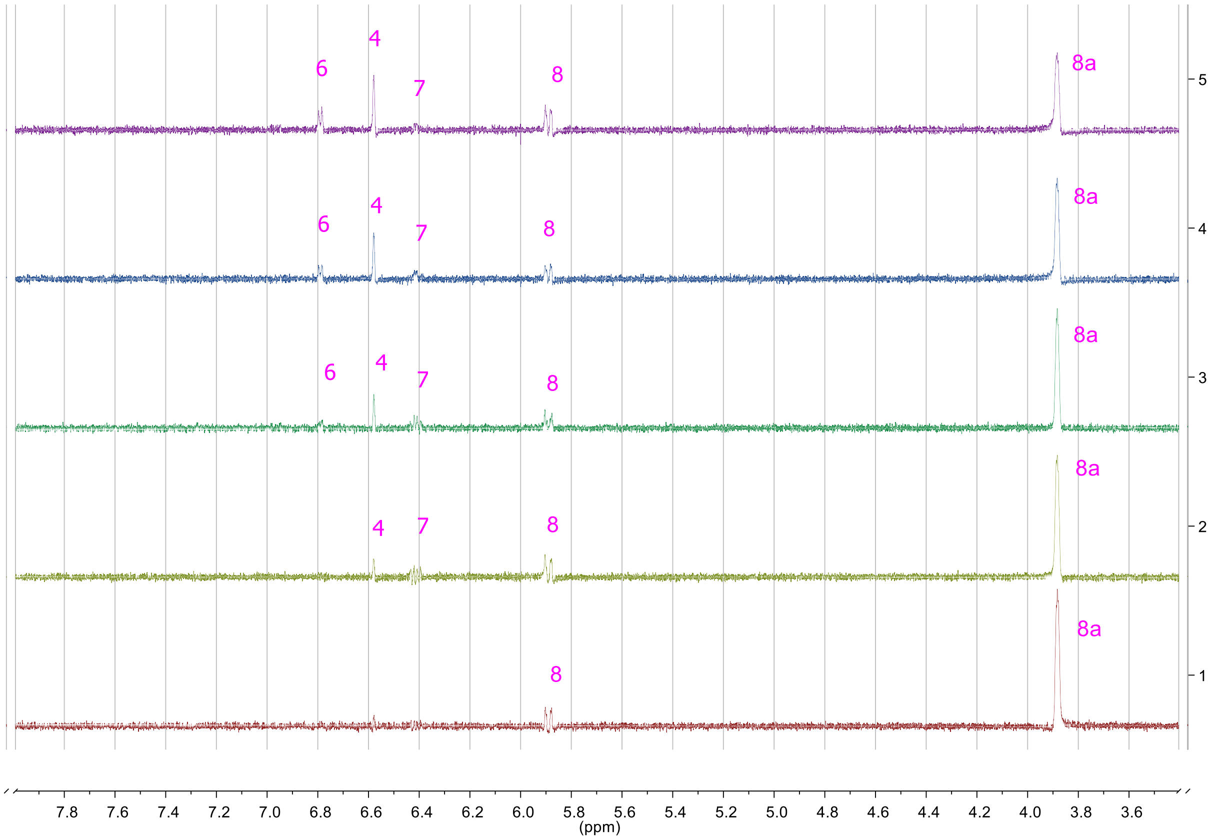
DHA **3** – ^{13}C-NMR (75 MHz, $CDCl_3$):



Identification of 5-Ph-DHA (**3**) using TOCSY ($CDCl_3$):

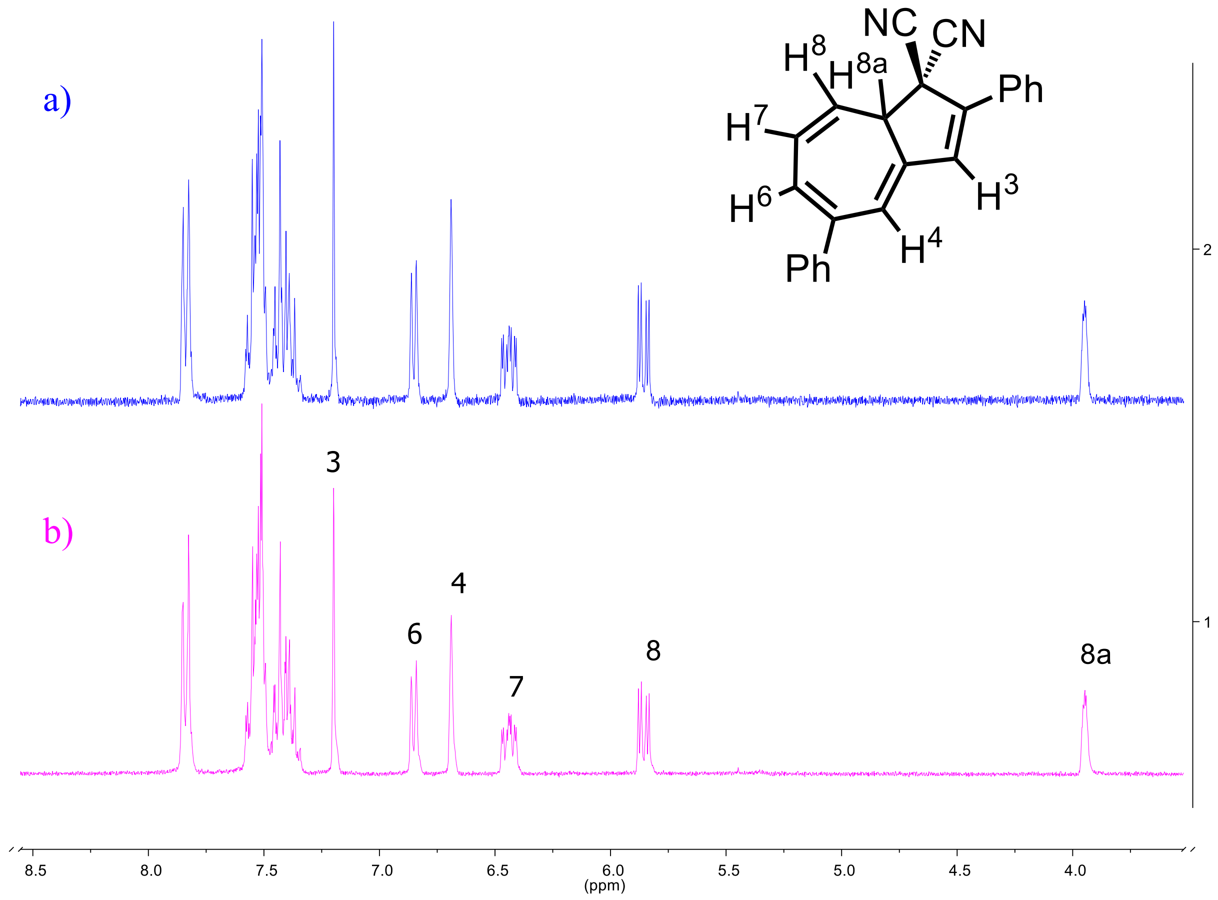
Irradiation of signal at 3.88 ppm (H-8a)





TOCSY spectroscopy allowed assignment of the protons H-8, H-7 and H-4 as these coupled through-space with H-8a as did H-6.

Light – heat (ring-opening/closure) cycle of DHA **3** recorded by ^{1}H-NMR (CD_3CN):

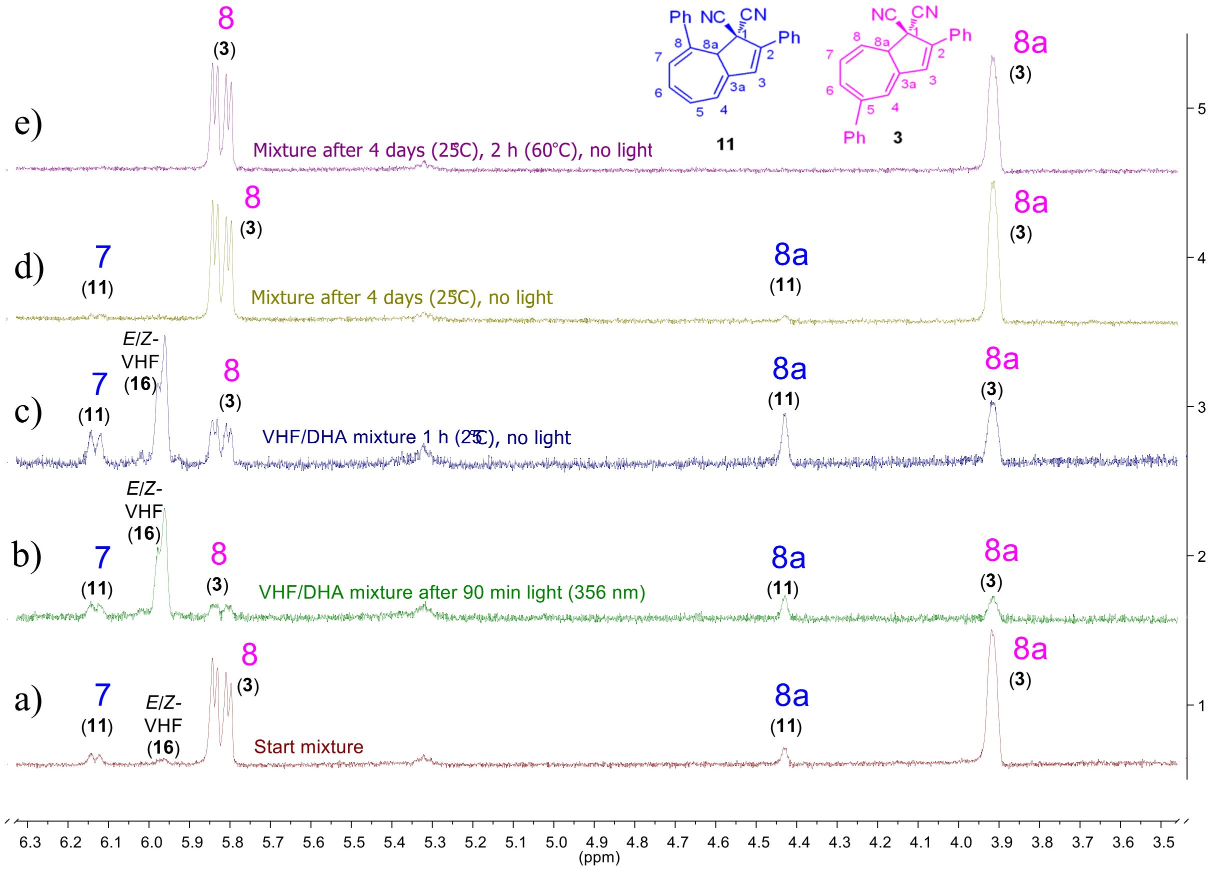


a) Blue spectrum: ^{1}H-NMR of 5-phenyl-DHA **3** in CD_3CN.

b) Magenta spectrum: Resulting ^{1}H-NMR of 5-phenyl DHA after excitation at 356 nm for 2 h in CD_3CN (ring-opening) and subsequent heating at 60°C for 2 h (ring-closure). No isomerization to 8-phenyl-DHA was observed in this experiment.

Isomerization at 25°C

Light – heat cycle of DHAs **3** and **11** recorded by ^{1}H-NMR (CD_3CN):



a) Start: mixture of DHAs **3** and **11** and a small content of *E*/*Z*-VHFs **16**.

b) Mixture after irradiation at 356 nm.

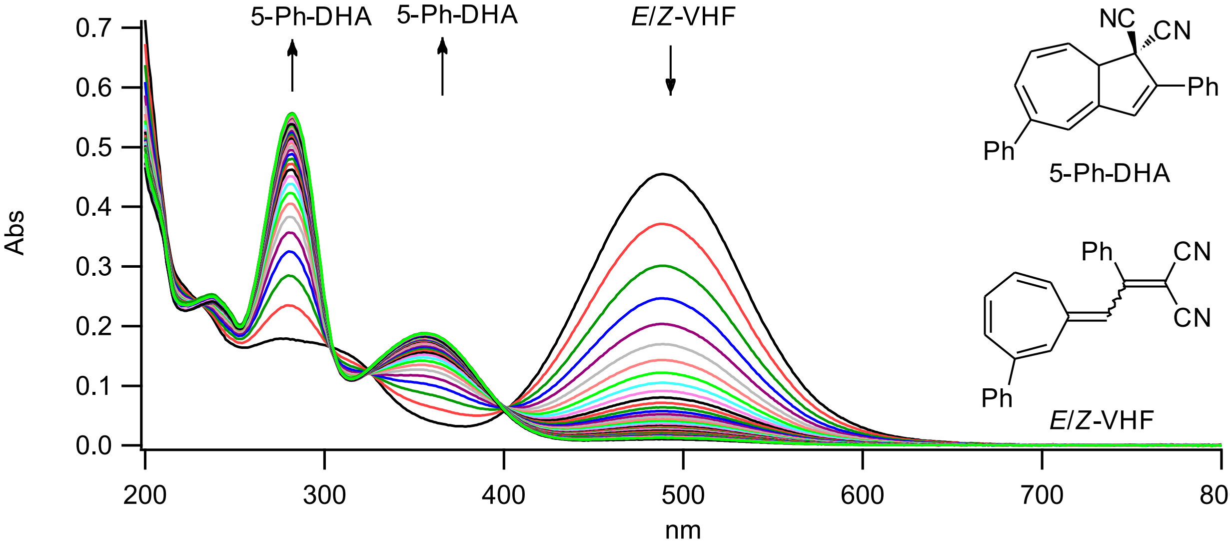
c) Mixture after 1 h in the dark at 25 °C.

d) Mixture after 4 days in the dark at 25 °C.

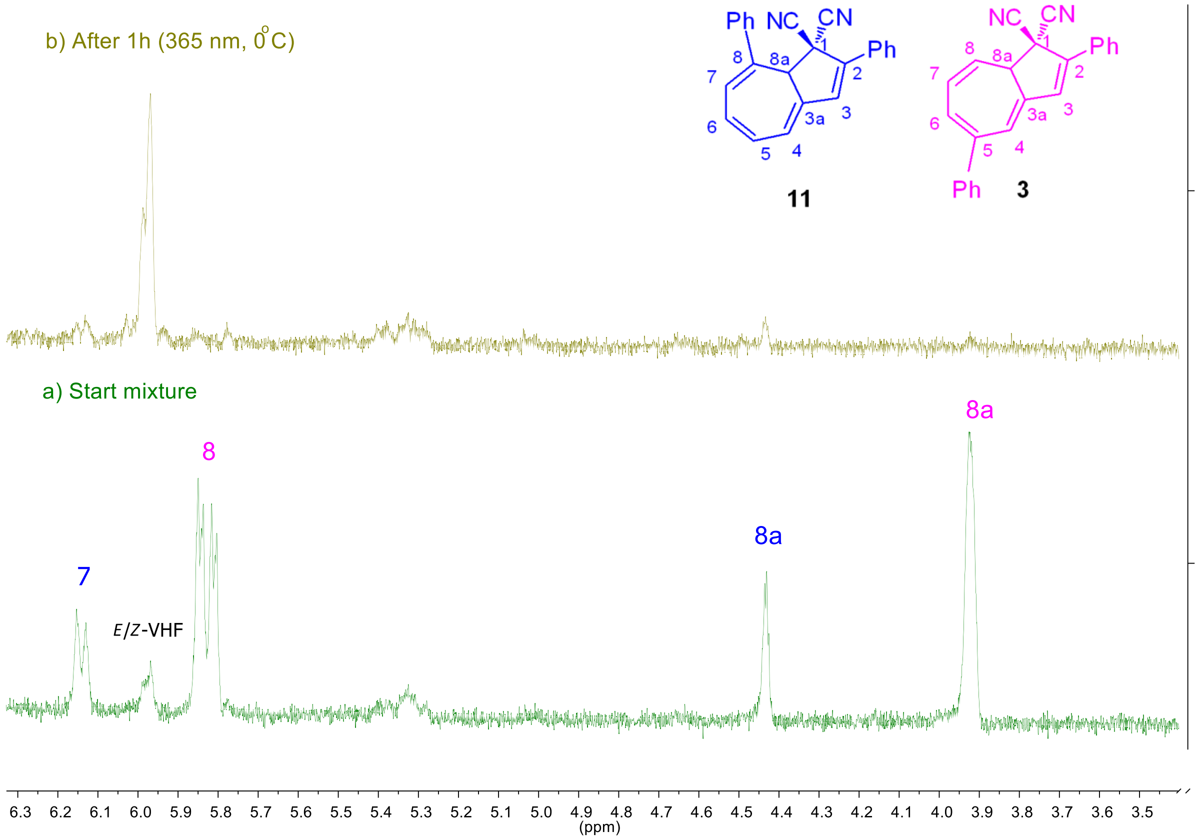
e) Mixture after 4 days in the dark at 25 °C followed by 2 h at 60 °C.

Assignment of the H-7 of DHA **11** was tentatively done based on coupling constants.

Thermal ring-closure of *E*/Z-VHFs to DHA **3** in MeCN recorded by UV-Vis spectroscopy (at 60 ^{o}C):



Ring-opening of 8-phenyl-DHA (**11**) and 5-phenyl-DHA (**3**) at 0°C (CD_3CN):

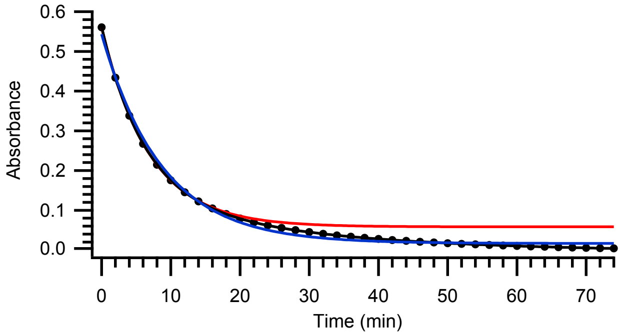


b) Mixture (in CD_3CN) after 1h on ice (0°C) at 365 nm. This experiment shows that 8-phenyl-DHA (**11**) can be ring-opened by light, although the process seems to be slower than light-induced opening of 5-phenyl-DHA (**3**) (by comparison of residual DHA H-8a signals).

a) Start mixture of 8-phenyl-DHA (**11**) and 5-phenyl-DHA (**3**) and some *E*/*Z*-VHF.

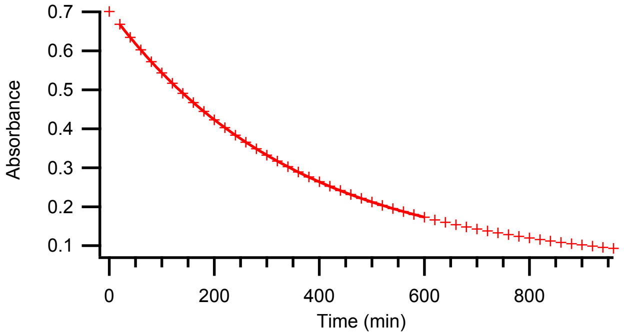
UV-Vis Absorption Studies on *E*/*Z*-VHFs **16** in MeCN:

Decay in absorbance (488 nm) at 60 °C:



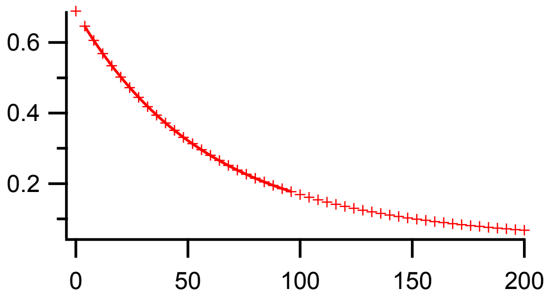
Decay in the absorption of *E*/*Z*-VHFs **16** in MeCN at 60 °C. The data were fitted by a single exponential (blue curve), a sum of two exponentials (black curve), and a single exponential using only data points of the first 12 min (red curve). All three exponential fits allowed the absorbance to converge to a constant value at t = ∞.

Decay in absorbance (488 nm) at 25 °C:



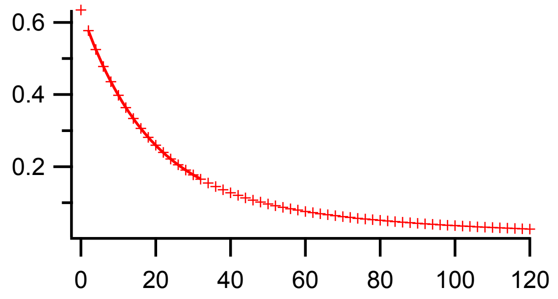
Fitting “first data points” by single exponential: rate constant k = 4.71 x 10^{-5} s^{-1}

Decay in absorbance (488 nm) at 40 °C:



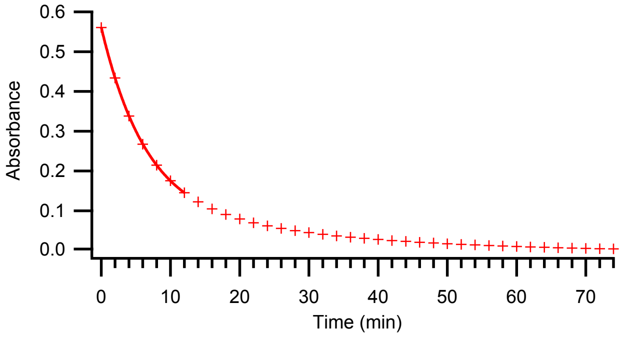
Fitting “first data points” by single exponential: rate constant k = 2.93 x 10^{-4} s^{-1}

Decay in absorbance (488 nm) at 50 °C:



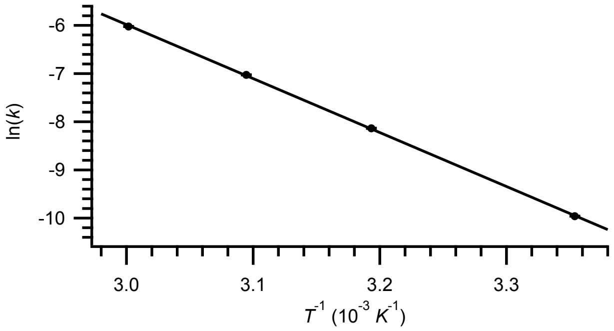
Fitting "first data points" by single exponential: rate constant k = 8.89 x 10^{-4} s^{-1}

Decay in absorbance (488 nm) at 60 °C:



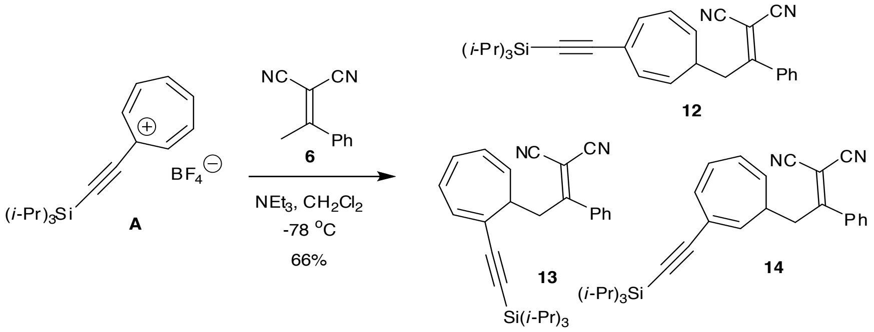
Fitting "first data points" by single exponential: rate constant k = 2.42 x 10^{-3} s^{-1}

Arrhenius Plot:



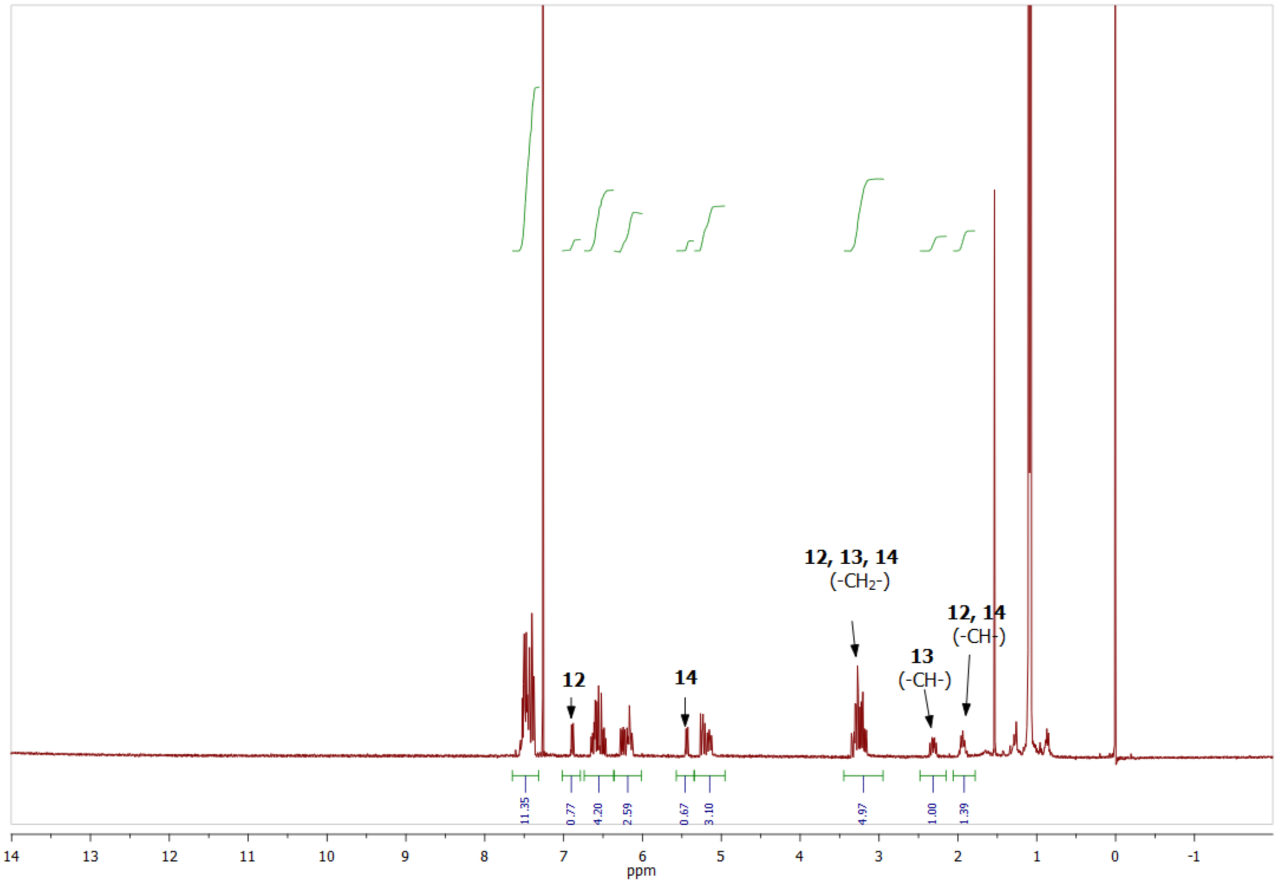
Arrhenius plot for the thermal conversion of VHFs **16** to DHAs. ([k] = s^{-1})

Compounds 12, 13, and 14 (mixture)



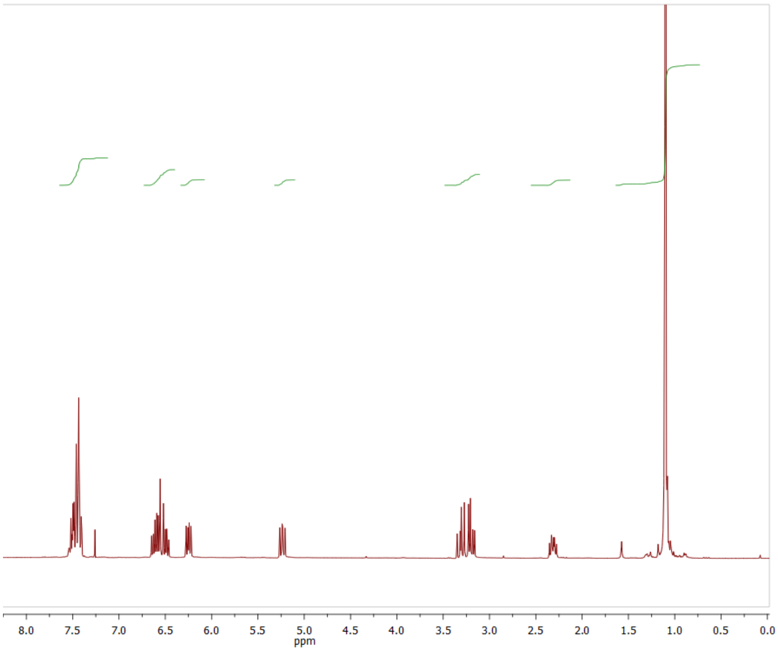
Triisopropylsilylethynyltropylium tetrafluoroborate **A** (373 mg, 1.0 mmol) and α-cyano-β-phenylcrotononitrile (176 mg, 1.0 mmol) were dissolved in dry CH_2Cl_2 (5 mL) under N_2 atmosphere. The mixture was cooled to -78°C and then triethylamine (106 mg, 1.0 mmol) was added. After stirring for 4 h, 4 M HCl (aq) was added, and the organic phase was washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, EtOAc/heptane 15:85) gave a mixture of isomers **12**, **13**, and **14** (302 mg, 66%) in an estimated ratio of 0.77 / 1 / 0.67 according to ^{1}H-NMR (see below); slightly yellowish oil.

Mixture of **12**, **13**, and **14** - ^{1}H-NMR (300 MHz, $CDCl_3$):

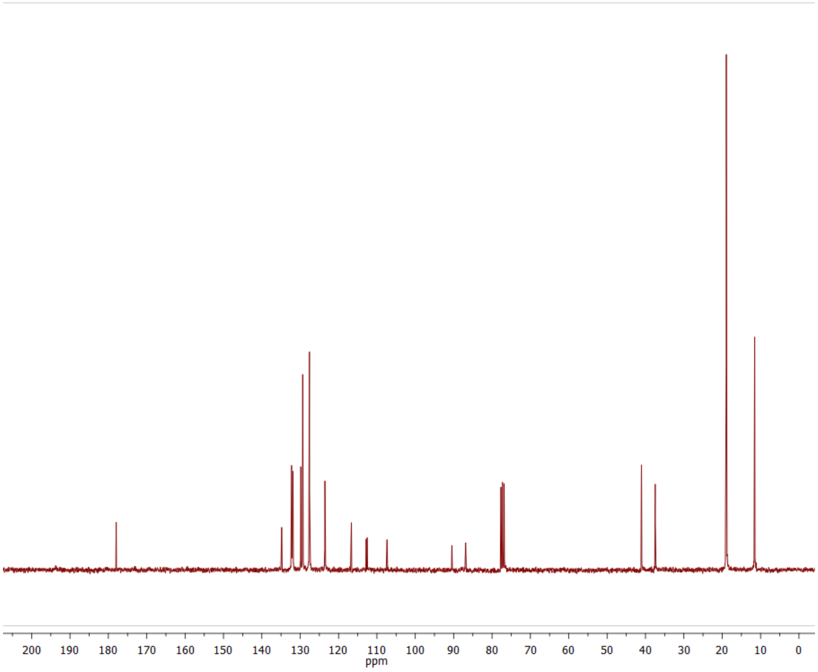


In a parallel synthesis, it was possible by two flash column chromatographic purifications (1: EtOAc/heptane, 18:82; 2: EtOAc/heptane 15:85) to obtain compound **13** pure as a slightly yellowish oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.55-7.40 (m, 5H), 6.63-6.43 (m, 3H), 6.23 (dd, *J* = 9.7, 5.9 Hz, 1H), 5.24 (dd, *J* = 9.7, 7.3 Hz, 1 H), 3.24 (m, 2H), 2.32 (m, 1H), 1.10 (m, 21H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 177.7, 134.6, 132.0, 131.8, 131.6, 129.6, 129.1, 127.3, 123.3, 116.4, 112.5, 112.3, 107.1, 90.2, 86.6, 40.8, 37.2, 18.7, 11.2; two overlapping signals in the aromatic region. MS (FAB): *m/z* 439 (MH^+). Found: C 79.70, H 7.37, N 6.08; Calcd for $C_{29}H_{34}N_2Si$: C 79.40, H 7.81, N 6.39.

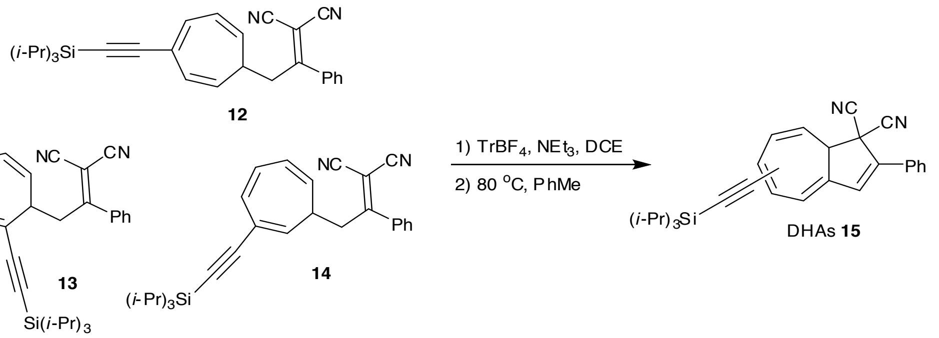
Compound **13** – ^{1}H-NMR (300 MHz, $CDCl_3$):



Compound **13** – ^{13}C-NMR (75 MHz, $CDCl_3$):

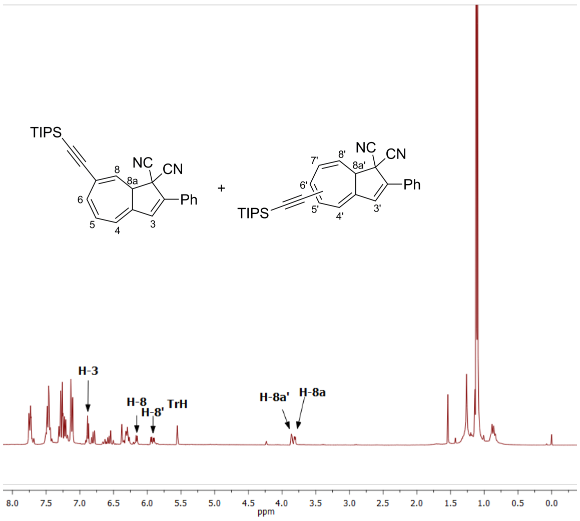


DHAs 15 (mixture)



A mixture of **12**, **13**, and **14** (302 mg, 0.69 mmol) was dissolved in dry CH_2ClCH_2Cl (10 mL) and then $TrBF_4$ (228 mg 0.69 mmol) was added under an argon atm. The reaction mixture was stirred at 0˚C for 1.5 h and then cooled to 0˚C. Toluene (10 mL) was added, and then Et_3N (0.1 mL, 0.69 mmol) was added dropwise. After stirring for 1 h at this temperature, the reaction mixture was heated to 80˚C and stirred for 1 h. Then the solution was concentrated *in vacuo*. Purification of the residue by flash column chromatography (SiO_2, CH_2Cl_2/hexane 6:4) afforded two fractions that according to NMR contained DHAs (in addition to other compounds). TLC spots of the fractions showed the expected DHA to VHF conversion (color change from yellow to red) upon UV irradiation. It was not possible to isolate pure DHAs.

Fraction 1 – ^{1}H-NMR (300 MHz, $CDCl_3$):



Fraction 2 – ^{1}H-NMR (300 MHz, $CDCl_3$):