Electronic Supplementary Information (ESI) for

Lewis acid enhanced switching of the 1,1-dicyanodihydroazulene / vinylheptafulvene photo/thermoswitch

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General Information

NMR Spectra were measured on a 500 MHz instruments (^{1}H = 500.132 MHz, ^{13}C = 125.770 MHz) with an observe cryoprobe. All chemical shift values are referenced to the solvent. Chloroform ($CDCl_3$) δ_H = 7.26 and δ_C = 77.16 ppm. Benzene (C_6D_6) δ_H = 7.16 and δ_C = 128.06 ppm. Dichloromethane (CD_2Cl_2) δ_H = 5.32 and δ_C = 54.00 ppm. Acetonitrile (CD_3CN) δ_H = 1.94 and δ_C = 1.32 ppm. All NMR spectra were obtained at 25.0°C. Chemical reactions were carried out under Schlenk conditions under an inert atmosphere (N_2), although no special precautions to exclude air were taken during subsequent work-up. NMR and UV Vis experiments were conducted in air. Flash and dry column vacuum chromatographic (DCVC)[S1] techniques were used. For column chromatographic purification of DHAs, the column was covered by an alumina foil to exclude light. All isolated fractions were kept in the dark. Melting points were uncorrected and determined using a Stuart SMP 40 automatic melting point machine. All spectroscopic measurements (including photolysis) were performed in a 1-cm path length quartz cuvette. UV Vis absorption spectra were obtained by scanning the wavelength from 800 to 200 nm. Photoswitching experiments were performed using a 150 W xenon arc lamp equipped with a monochromator; the DHA absorption maximum for each individual species was chosen as the wavelength of irradiation (line width 2.5 nm or 2 nm for ring opening experiment) or by using a UVP 6W UVGL-58 hand held UV lamp on long wavelength (365 nm) setting. The thermal ring-closure was performed by heating the sample (cuvette) by a Peltier unit in the UV Vis spectrophotometer. Analytical grade 1,2 dichloroethane (DCE) was dried over molecular sieves 4 Å (3-5 ppm H_2O measured by 831 Karl Fischer Coulometer, Metrohm) for the $ZnCl_2{\cdot}(Et_2O)_2$ experiments or passed through basic Al_2O_3 for the AgOTf experiments. CH_2Cl_2 was dried over molecular sieves 4 Å.

Reagents: $AlCl_3$, BBr_3 (1 M in either CH_2Cl_2 or hexanes), $BF_3{\cdot}Et_2O$, AgOTf, $ZnCl_2$, $ZnCl_2{\cdot}(Et_2O)_2$ (1.0 M solution in diethyl ether) and all other solvents were obtained from Sigma-Aldrich and used as received. 2-Phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (DHA - **1**) and 2-(Cyclohepta-2,4,6-trienyl-1-phenylethylidene)malononitrile were prepared by literature procedures[2e] and 2-(2-(2,4,6-Cycloheptatriene-1-ylidene)-1-phenylethylidene)malononitrile (VHF - **2**) formed via irradiation of **1** matched spectroscopic data.[2e] Presumably $[Ag(Et_2O)_3]OTf$[6] was prepared by weighing an amount of AgOTf and placing it in a volumetric flask and adding enough Et_2O (ca 5 ml) to dissolve the AgOTf and the solvent was removed under a stream of N_2 to give a white-grey coloured solid.

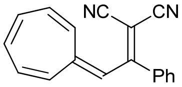
Abbreviations: DHA - 2-Phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile; VHF - 2-(2-(2,4,6-Cycloheptatriene-1-ylidene)-1-phenylethylidene)malononitrile; LA - Lewis Acids; TBR - thermal back reaction; DCE - 1,2 dichloroethane.

Reference:

S1	For the technique of dry column vacuum chromatography (DCVC), see: C. Rosenbohm and D. S. Pedersen *Synthesis* 2001, 2431.
2e	S. L. Broman, S. L. Brand, C. R. Parker, M. Å. Petersen, A. Kadziola and M. B. Nielsen, *Arkivoc*, In press.
6	M. Kuprat, M. Lehmann, A, Schulz and A. Villinger *Organometallics*, 2010, **29**, 1421.

Experimental

2-(2-(2,4,6-Cycloheptatriene-1-ylidene)-1-phenylethylidene)malononitrile (VHF - **2**)



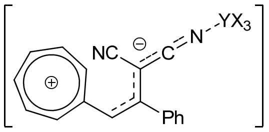
$AlCl_3$: To a mixture of DHA (64 mg, 0.25 mmol) and $AlCl_3$ (100 mg, 0.75 mmol) was added CH_2Cl_2 (8 ml).

BBr_3: To a solution of DHA (64 mg, 0.25 mmol) in CH_2Cl_2 (5 ml) was added BBr_3 (1 M in hexanes, 0.75 ml, 0.75 mmol).

The solutions both initially turned purple and were stirred for 15 min before being quenched with water (**caution**: can react violently when too much water is added initially) to give a dark red solution. A liquid-liquid exaction was performed (H_2O; 2 x 15 ml) and the red CH_2Cl_2 solution was evaporated to dryness. The residue was purified by column chromatography (CH_2Cl_2, flash silica). The first yellow fraction gave reconverted DHA **1** and second red band gave VHF **2** as a dark red solid ($AlCl_3$ reaction: 59 mg, 92%. BBr_3 reaction: 34 mg, 53%). For **2** to remain in the VHF form it would have to be crystallised. For example, it can be crystallised from C_6H_6, Et_2O / heptanes or CH_2Cl_2 / heptanes at 5°C via slow evaporation to give dark red crystals which may have a green sheen (Fig. S9). The compound degrades back to DHA in crystalline form with time; about 40% in a month at rt, they hold their darker colour for longer when stored at lower temperatures.

Mp. 77-84 °C (decolourise: red to yellow, see Fig. 3) (Et_2O / heptanes). Anal. Calc. ($C_{18}H_{12}N_2$): C, 84.35; H, 4.72; N, 10.93; *M*, 256.3. Found: C, 84.27; H, 4.43; N, 10.88. IR (KBr, cm^{-1}): 3057w, 3049w, 3020w, 2206m (CN), 1624m, 1572m, 1541m, 1503s, 1465s, 1431s, 1409s, 1369s, 1337s, 1252s, 1208s, 1117s, 827m, 734m, 555m. NMR: DHA was observed in the spectra; ^1H and ^{13}C NMR assignment of **1** and **2** in Table S5-S6 and Fig. S11; Compound **2** shows slight shift in δ_C and δ_H with concentration see Fig. S12 as an example in ^{13}C NMR. ^1H NMR (C_6D_6): δ 7.02- 6.92 (m, 5H, Ph), 6.08 (s, 1H, =CH), 5.79 (d, J = 11.0 Hz, 1H, C_7H_6), 5.60-5.52, 5.49-5.44 (2 x m, 2 x 2H, C_7H_6), 5.11 (dd, J = 12.0, 7.9 Hz, 1H, C_7H_6). ^{13}C NMR (C_6D_6): δ 168.11 {*C*=C(CN)$_2$}, 153.09, 142.33, 134.98, 134.97, 134.35, 133.59, 132.90 (7 x C_7H_6), 135.40, 130.75, 129.55, 128.40 (4 x Ph), 119.56 (=CH), 115.15, 115.02 (2 x CN), 78.40 {C=*C*(CN)$_2$}. ES-MS (MeOH, *m/z*): 279 $[M + Na]^+$; 535 $[2M + Na]^+$. ES-MS (MeOH + $[Ag(Et_2O)_3]OTf$, *m/z*): 181 $[Ag(Et_2O)]^+$; 363 $[M + Ag]^+$; 619 $[2M + Ag]^+$.

Suspected charge separated complex (**3**)



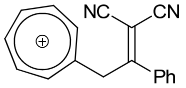
YX_3 = $AlCl_3$ or BBr_3

$AlCl_3$: To a mixture of **1** (10 mg, 0.039 mmol) and $AlCl_3$ (16 mg, 0.117 mmol) in a NMR tube was added CD_2Cl_2 (0.8 ml). The solutions turned from yellow to pink-purple colour rapidly and gave a purple precipitate and a yellow solution so only the CH tropylium and some phenyl were distinguishable. ^{1}H NMR (CD_2Cl_2): δ 9.11-9.15 (m, C_7H_6), 8.94 (d, J = 9.4 Hz, C_7H_6). ^{13}C NMR (CD_2Cl_2): δ 155.87, 155.59, 154.81 (3 x s, C_7H_6).

BBr_3: To a mixture of **1** (10 mg, 0.039 mmol) and BBr_3 (1 M in CH_2Cl_2, 0.2 ml) in a NMR tube was added CD_2Cl_2 (0.5 ml). The solutions turned from yellow to pink-purple colour rapidly, then the solution colour darkened and formed an oily precipitate.

^{1}H NMR (CD_2Cl_2): δ 9.1-9.3 (Br m), 7.5-6.7 (Br m). ^{13}C NMR (CD_2Cl_2): δ 157.39, 154.39, 153.16 (3 x C_7H_6) 132.16, 131.01, 130.46 (3 x Ph). The solvent was decanted off and the oily residue was dissolved in CD_3CN. ^{1}H NMR (CD_3CN): δ 8.95-8.93, 8.87-8.79 (2 x m, C_7H_6), 7.35-7.29, 7.19-7.16 (2 x m, Ph). ^{13}C NMR (CD_3CN): δ 157.30, 154.48, 153.18 (3 x C_7H_6) 131.01, 130.50, 129.67 (3 x Ph).

Tropylium species (**4**)



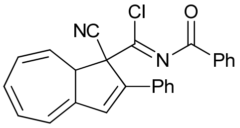
(a) A solution of DHA (9 mg, 0.035 mmol) in either CD_2Cl_2 or CD_3CN (0.6 ml) in a NMR tube was treated with $BF_3 \cdot Et_2O$ (43 μl, 1.0 M in Et_2O) and irradiated at 355 nm until the solution was clear (about 3 h).

^{1}H NMR (CD_2Cl_2): δ 9.09-9.01 (m, 4 x CH, C_7H_6), 8.95 (d, J = 9.6 Hz, 2H, CHCCH, C_7H_6), 7.58-7.46 (m, 5H, Ph), 5.04 (s, 2H, CH_2). ^{13}C NMR (CD_2Cl_2): δ 171.91 {*C*=C(CN)$_2$}, 167.08 (C, C_7H_6), 156.09, 155.39, 154.59 (3 x 2CH, C_7H_6), 133.67, 130.43, 128.96 (3 x Ph), 133.34 (Ph, C*i*), 112.93, 112.58 (2 x CN), 89.64 {C=*C(*CN)$_2$}, 47.51(CH_2).

^{1}H NMR (CD_3CN): δ 9.06, 9.00 (2 x m, 4 x CH, C_7H_6), 8.93 (d, J = 10.1 Hz, CHCCH, C_7H_6), 7.57-7.47 (m, 5H, Ph), 5.01 (s, 2H, CH_2). ^{13}C NMR (CD_3CN): δ 172.97{*C*=C(CN)$_2$}, 167.25 (C, C_7H_6), 156.77, 156.06, 154.94 (3 x 2CH, C_7H_6), 134.38 (Ph, C*i*), 133.68, 130.56, 129.42 (3 x Ph), 113.55, 113.52 (2 x CN), 90.34 {C=*C(*CN)$_2$}, 48.02 (CH_2).

(b) To a mixture of 2-(cyclohepta-2,4,6-trienyl-1-phenylethylidene)malononitrile (10 mg, 0.039 mmol) and $[Ph_3C]BF_4$ (13 mg, 0.039 mmol) was added either CD_2Cl_2 or CD_3CN (0.6 ml) in a NMR tube for 3 d (usual reaction performed at 80°C 2 h in DCE[2e]). The NMR confirmed the same compound was formed. See overlay of NMR spectra in Fig. S13.

(*Z*)-*N*-[Chloro-(1-cyano-2-phenyl-1,8a-dihydroazulen-1-yl)methylene]benzamide (**5**)



To a Schlenk flask containing a stirring suspension of $AlCl_3$ (166 mg, 1.25 mmol) and Benzoylchloride (PhCOCl: 87 µl, 0.75 mmol) in CH_2Cl_2 (7 ml) was added DHA **1** (64 mg, 0.25 mmol). The colour of the solution rapidly turned from yellow to purple which became red within 1 h. The solution was allowed to stir for 8 h before the reaction was quench with water (**caution**: can react violently when too much water added initially) followed by NEt_3 (2 ml). A liquid-liquid exaction was performed (H_2O; 2 x 15 ml) and the red CH_2Cl_2 solution was evaporated to dryness. The residue was purified using dry column chromatography {neutralised silica, passing 10% NEt_3 in heptanes followed by heptanes, gradient elution CH_2Cl_2 – heptanes 4% increments}: The first yellow fraction gave unreacted **1**; the second yellow fraction gave **5** (36 mg, 36%); the dark red fraction contained **2**. Compound **5** was a yellow coloured oily solid which was not stable if workup was not under basic conditions (turns brown after a few days at rt in air). Recrystallisation from Et_2O / heptanes gave stable yellow crystals which were also suitable for X-ray diffraction.

Mp. 120.5-123.5 °C (Et_2O / heptanes). Anal. Calc. ($C_{25}H_{17}ClN_2O$): C, 75.66; H, 4.32; N, 7.06; *M*, 396.9. Found: C, 75.64; H, 4.23; N, 6.96. IR (KBr, cm^{-1}): 3068w, 3024w, 2920w, 2849w, 2243w (CN), 1709s (CO-N), 1661s (N=C), 1595m, 1409m, 1446m, 1313m, 1250s, 1173m, 1031m, 1009s, 931m, 907m, 875m, 854m, 793m, 770m, 743m, 714m, 691s, 503w. ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 – 7.71 (m, 2H), 7.61 – 7.54 (m, 3H), 7.50 – 7.40 (m, 3H), 7.35 (dd, *J* = 11.1, 4.7 Hz, 2H), 7.00 (s, 1H), 6.53 (dd, *J* = 11.3, 6.4 Hz, 1H), 6.42 (dd, *J* = 11.2, 6.2 Hz, 1H), 6.34 (dd, *J* = 6.3, 1.5 Hz, 1H), 6.24 (ddd, *J* = 10.3, 6.2, 2.2 Hz, 1H), 5.59 (dd, *J* = 10.3, 3.8 Hz, 1H), 4.11 (dt, *J* = 3.7, 1.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 174.80 (CO), 145.29 (ClC=N), 144.17, 141.03 (2 x C*i*), 134.47, 134.39, 132.66, 130.90, 130.88, 130.60, 129.80, 129.49, 129.35, 128.88, 127.65, 126.71, 120.56, 118.71 (CN), 118.57 (C8), 62.64 (C1), 53.73(C8a). ES-MS (MeOH, *m/z*): 305 $[M + H - PhCO]^+$, 419 $[M + Na]^+$, 815 $[2M + Na]^+$.

UV Vis Experiments

The concentration of DHA **1** in cuvette for Fig. 1 and Table 1-2 was 2.63 x 10^{-5} M except in Table 2 for entry 250 eq $[Ag(Et_2O)_3]OTf$ (where DHA: 1.97 x 10^{-5} M); Figure 2, S1-S3 (DHA: 3.28 x 10^{-5} M) unless EtOH was added to regenerate the VHF species. $ZnCl_2{\cdot}(Et_2O)_2$ for the solvent screening analysis was from a stock solution (0.0405 M) and stored in a Schlenk flask under Ar; while in the Lewis acid screening experiments $ZnCl_2{\cdot}(Et_2O)_2$ (1.0 M solution in diethyl ether) was used and the sample was used straight away to avoid degradation. The $ZnCl_2{\cdot}(Et_2O)_2$ solution in the solvent screening (Table S1) was 0.0405 M in ether and 7.9 x 10^{-4} M for solutions in Table 1 with varying ratios of DCE : Et_2O (9:1, 49:1, 199:1). $[Ag(Et_2O)_3]OTf$ samples were prepared by weighing an amount of AgOTf and placing it in a volumetric flask and adding enough Et_2O (ca 5 ml) to dissolve the AgOTf and the solvent was removed under a stream of N_2 to give a white-grey coloured solid. The concentration of $[Ag(Et_2O)_3]OTf$ in DCE was 5.14 x 10^{-4} M for samples 0.1-1 eq and 5.23 x 10^{-3} M for samples 10-250 eq.

Photoswitching experiment – general procedure

A sample of a pure photochromic DHA was dissolved in a given solvent. This stock solution was kept in the dark at all times. A sample of the stock solution was diluted further until the absorption of the DHA was well within the instruments limits. An absorption spectrum was measured of both the DHA and the corresponding VHF, Fig S1 (left), and the absorption spectra were baseline corrected. The molar absorption coefficient was worked out. The solution was then heated at a given temperature and an absorption spectrum was measured at a fixed interval of time, Fig S1 (right).

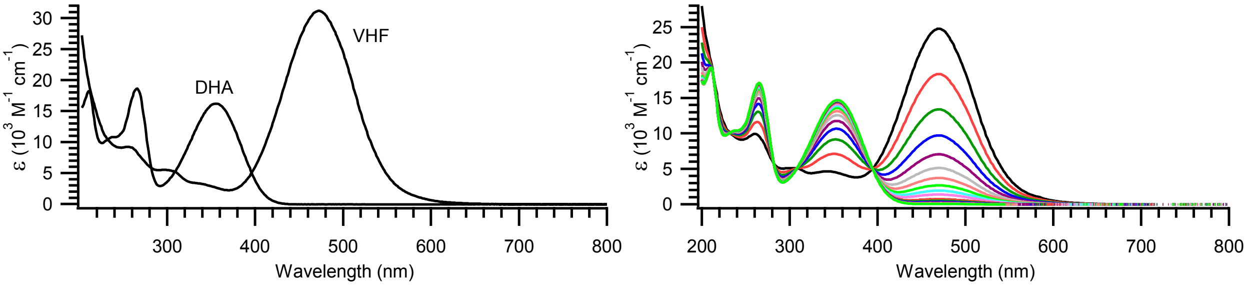


Fig. S1 Absorption spectra of DHA **1** and its corresponding VHF **2** in MeCN (left). Absorption spectra for the thermal ring-closure (VHF→DHA) measured every minute at 60 °C in MeCN (right).

The absorption maximum (λ_{max}) for both the DHA- and VHF-species were determined and at their respective λ_{max} the increase and decay were plotted against time (Fig. 2).

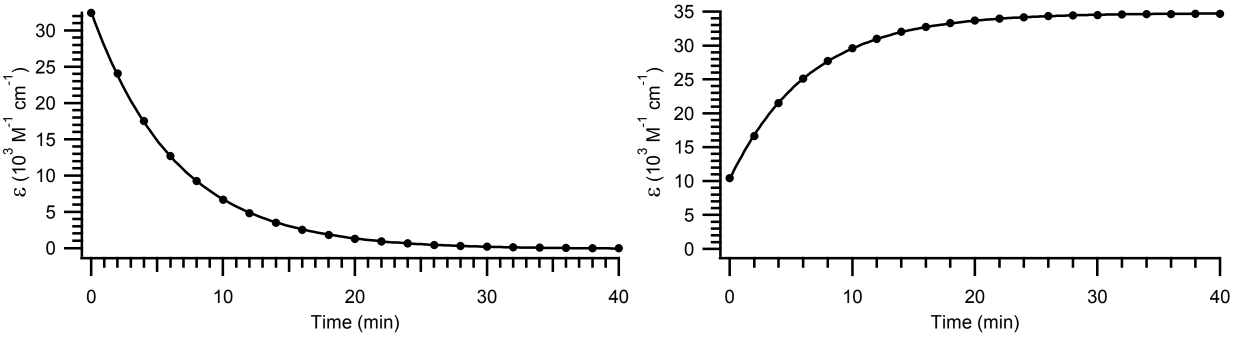


Fig. S2 Decay of absorption at λ_{VHF} (475 nm) with time (left) and increase of absorption at λ_{DHA} (355 nm) (right).

The rate of reaction was verified to follow first order kinetics by plotting ln(ε) against time, and a straight line was observed, Fig. 3 (left). The slope was calculated as the rate constant (min^{-1}), in the report the rate constants were given in s^{-1}. When fitting the graph, special care was taken to make sure the graph goes towards the absorption of the DHA-species.

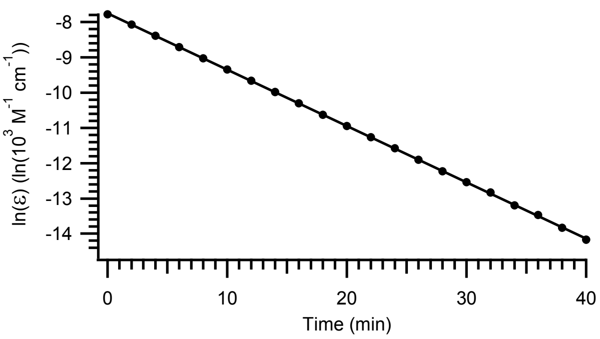


Fig. S3 Decay of absorption at λ_{VHF}; plot showing ln(λ_{VHF}) against time.

Table S1 Half-life of thermal back-reaction (min) of VHF **2** to DHA **1** in various solvents and compared with 10 eq of $ZnCl_2 \cdot (Et_2O)_2$ (0.0405 M in ether) at 35°C. Half-life calculated from ½ intensity of the λ_{max} of VHF band from the initial VHF absorption. * Signs of precipitation, probably $ZnCl_2$. (reaction) = VHF absorption was not identical after the second irradiation cycle. DHA **1** concentration 3.28 x 10^{-5} M.

Solvent	DHA/VHF λ_{max} (nm)	Half-life in neat solvent (min)	Half-life with 10 eq $ZnCl_2 \cdot (Et_2O)_2$ (min)
CH_2Cl_2	357/474	167	76
CH_2ClCH_2Cl (DCE)	357/475	161	92
$CHCl_3$	356/473	166	92
PhMe	359/465	525	527*
THF	356/465	358	351
MeCN	354/472	60	61
Acetone	356/469	121	120
EtOAc	354/462	290	286
EtOH (96%)	354/476	38	38
AcOH	354/470	40	40
$MeNO_2$	na/476	48	(reaction)
DMF	360/480	42 (reaction)	
NEt_3	353/450	882 (reaction)	

Table S2. Half-live of the thermal back-reaction of VHF **2** to DHA **1** with various Lewis acids and concentrations in 1,2-dichloroethane (DCE) at 25°C. Half-lives less than 500 min were calculated using Igor 5.0 form Wavemetrics (OR, USA). DHA **1** concentration 3.28 x 10^{-5} M.

Additive	Solvent	Equivalents	Half-life (min)
	DCE	-	597
	DCE : Et_2O (49:1)	-	598
$[NBu_4]PF_6$	DCE	10	600
Acetic acid	DCE	250	600
Acetic acid	DCE	10	600
$HBF_4{\cdot}Et_2O$	DCE	50	574
$ZnCl_2{\cdot}(Et_2O)_2$ Table 1	DCE	0.1-25	
$[Ag(Et_2O)_3]OTf$ Table 2	DCE	0.1-250	
$AlCl_3{\cdot}THF$	DCE	10	600
$BF_3{\cdot}Et_2O$	DCE	50	Reaction with VHF
BBr_3	DCE	50	Reaction with DHA
$AlCl_3$	DCE	50	Reaction with DHA

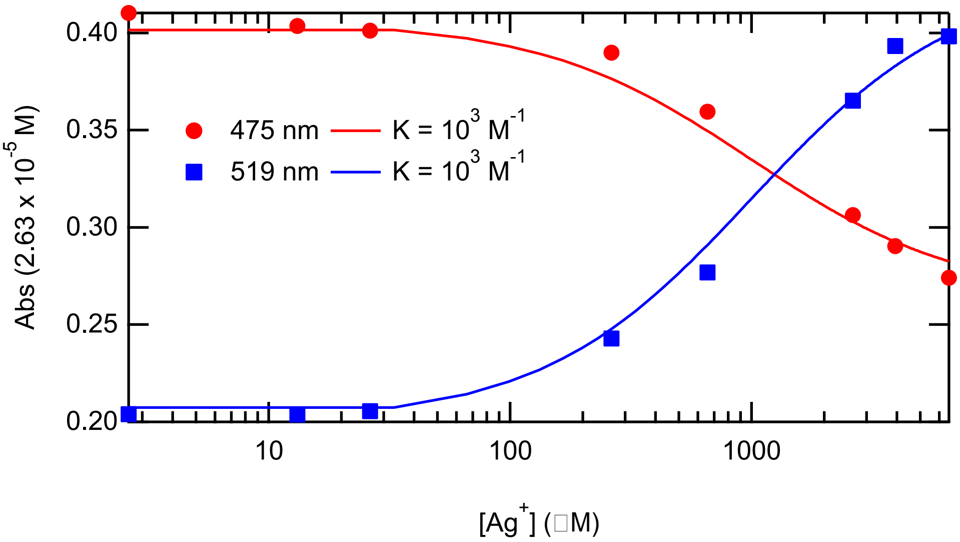


Fig. S4 The spectra of the VHF·Ag^+ recorded immediately after the photoinduced conversion of DHA to VHF was used to extract the equilibrium constant of VHF + Ag^+ = VHF·Ag^+. This was done either by resolving the spectra into a sum of VHF and VHF·Ag^+, and for each Ag^+ concentration calculate K, or by fitting the absorption changes as a function of $[Ag^+]_0$ to $A = (A_{start} + A_{end}*K*[Ag^+]_0)/(1+K*[Ag^+]_0)$ where it is assumed that $[Ag^+] \approx [Ag^+]_0$. Fits to other stochiometric ratios than 1:1 did not improve the fit.

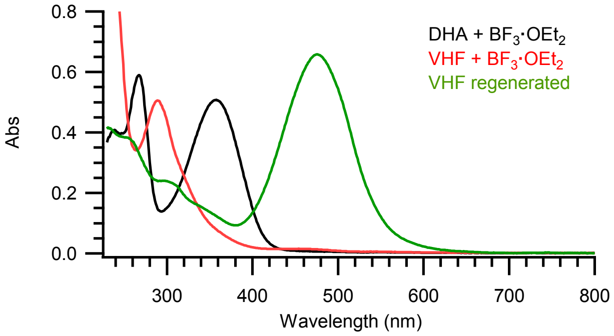


Fig. S5 UV Vis absorption spectra of the reaction $BF_3·Et_2O$ in DCE: No reaction with DHA (**1** – black trace) after 18 h (initial trace of **1** identical to the black trace so omitted for clarity). Irradiation of **1** at (357 nm) formed VHF (**2**) which reacted instantly with $BF_3·Et_2O$ to give tropylium species (**4** - red trace) presumably in the presence of some H_2O, followed by treatment EtOH to regenerate **2** (green trace) which underwent the TBR to **1** (not shown). DHA **1** concentration 3.28 x 10^{-5} M.

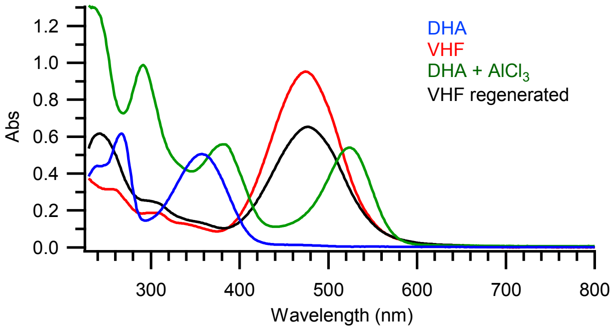


Fig. S6 UV Vis absorption spectra of the reaction of $AlCl_3$ in DCE: DHA (**1** – blue trace) in the absence of $AlCl_3$. $AlCl_3$ with **1** to give proposed intermediate (**3** – green trace) which could be converted back to VHF (**2** – black trace) upon addition of EtOH to the cuvette. VHF (**2** – red trace) in the absence of $AlCl_3$ given as a reference. DHA **1** concentration 3.28 x 10^{-5} M.

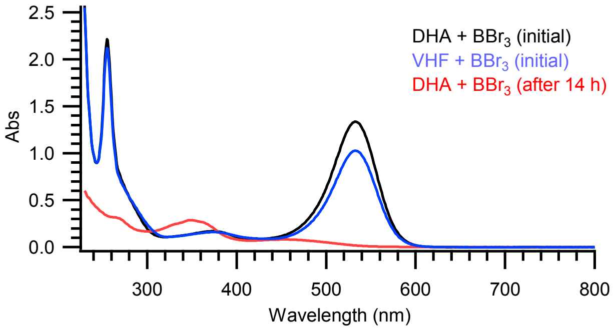


Fig. S7 UV Vis absorption spectra of the reaction of BBr_3 (1.0 M in CH_2Cl_2) in DCE: DHA (**1** - black) and VHF (**2** - blue) with BBr_3 to give proposed intermediate (**3**) which has the same peak at 533 nm which decays to the red trace after 14 h, after this period VHF was not regenerated upon addition of EtOH, VHF was regenerated within 1 h (Fig. 2). DHA **1** concentration 3.28 x 10^{-5} M.

Photo induced ring opening experiment

A 150 W xenon arc lamp equipped with a monochromator; the DHA **1** absorption maximum 358 nm as the wavelength of irradiation (line width 2 nm) in DCE. An initial UV Vis scan (800-200 nm) of the sample was run to check the DHA absorption was the same and that no VHF species was detectable. The sample in the cuvette (1 cm path length) was repeatedly irradiated for 5 second then quickly shaken manually to obtain a homogeneous solution. The UV Vis absorption was measured (520-450 nm at a scan rate of 600 nm/min e.g. around the VHF λ_{max}) every 10 second as the ring opening approached completion. Competition of the ring opening experiment was when three consecutive scans 10 seconds apart had an absorbance differing by 0.005.

Table S3 The time taken for the photo induced ring opening for full conversion of DHA **1** to VHF **2** in seconds, λ_{max} (nm) and absorbance at 25°C in DCE. The DHA concentration was kept constant (2.63×10^{-5} M giving absorption of 0.40) but the VHF absorption was significantly differed as well as a minor shift in λ_{max}. It must be noted that the rate of the thermal back reaction (TBR) of DHA **1** (597 min) was significantly faster with the addition of 10 eq of $ZnCl_2·(Et_2O)_2$ (49 : 1) [a] (98 min) and AgOTf $·(Et_2O)_3$ (71 min) which means the VHF was converting back to DHA faster during the experiment potentially requiring more irradiation time, conversely a fast TBR means the '100% conversion' to VHF would be harder to reach and a 'lower maximum conversion' level would be obtained in less time.

Additive	DHA λ_{max}	DHA Abs	VHF λ_{max}	VHF Abs	Ring opening (s)
	358	0.404	475	0.763	220
	358	0.406	475	0.767	220
10 eq $ZnCl_2·(Et_2O)_2$ (49 : 1) [a]	358	0.403	475	0.712	200
10 eq $ZnCl_2·(Et_2O)_2$ (49 : 1) [a]	358	0.405	476	0.719	190
10 eq AgOTf $·(Et_2O)_3$	358	0.400	478	0.638	180
10 eq AgOTf $·(Et_2O)_3$	358	0.406	479	0.639	180

[a] Ratio of CH_2ClCH_2Cl (DCE) : Et_2O in the $ZnCl_2·(Et_2O)_2$ solution; 147:1 Solvent ratio in cuvette.

Table S4 Photo induced ring opening speed (s) and ring closing (thermal back reaction in min) and absorbance of DHA and VHF with different additives. DHA **1** concentration 2.63×10^{-5} M in DCE.

Additive	Ring opening (s) **1** to **2**	Ring closing (min) TBR **2** to **1**	DHA **1** Abs	VHF **2** Abs
	220	597	0.405	0.765
10 eq $ZnCl_2·(Et_2O)_2$ (49 : 1) [a]	195	98	0.404	0.716
10 eq AgOTf $·(Et_2O)_3$	180	71	0.403	0.639

[a] Ratio of CH_2ClCH_2Cl (DCE) : Et_2O in the $ZnCl_2·(Et_2O)_2$ solution; 147:1 Solvent ratio in cuvette.

Photographs of Crystals and Solutions

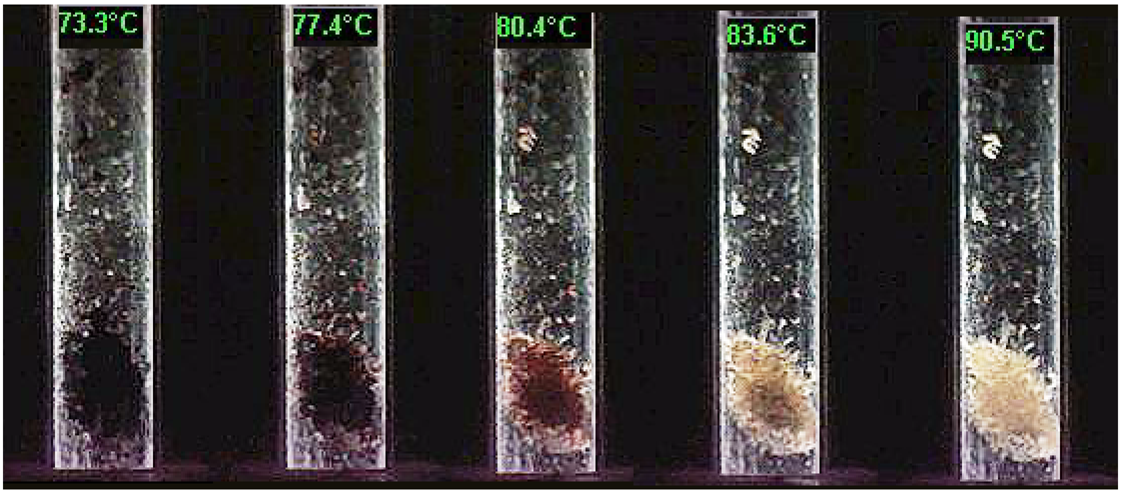


Fig. S8 The switching of the dark red VHF **2** crystals to the yellow DHA 1 crystals. This was observed between 77-84°C, starting temperature 65°C at a ramp rate of 1°C per min.

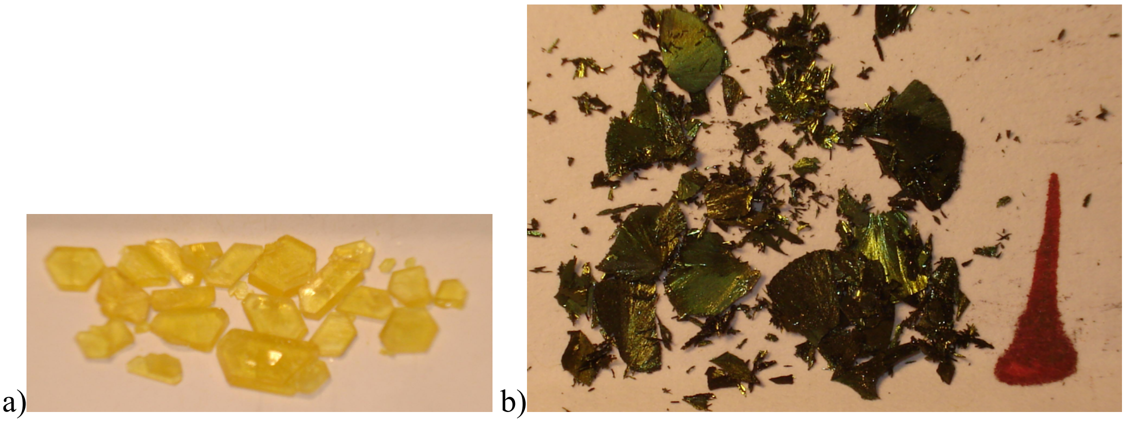


Fig. S9 a) DHA crystals; b) crystalline form of VHF showing metallic green sheen left (from C_6D_6 solution, slow evaporation), a drop of the red coloured mother liquor on right.

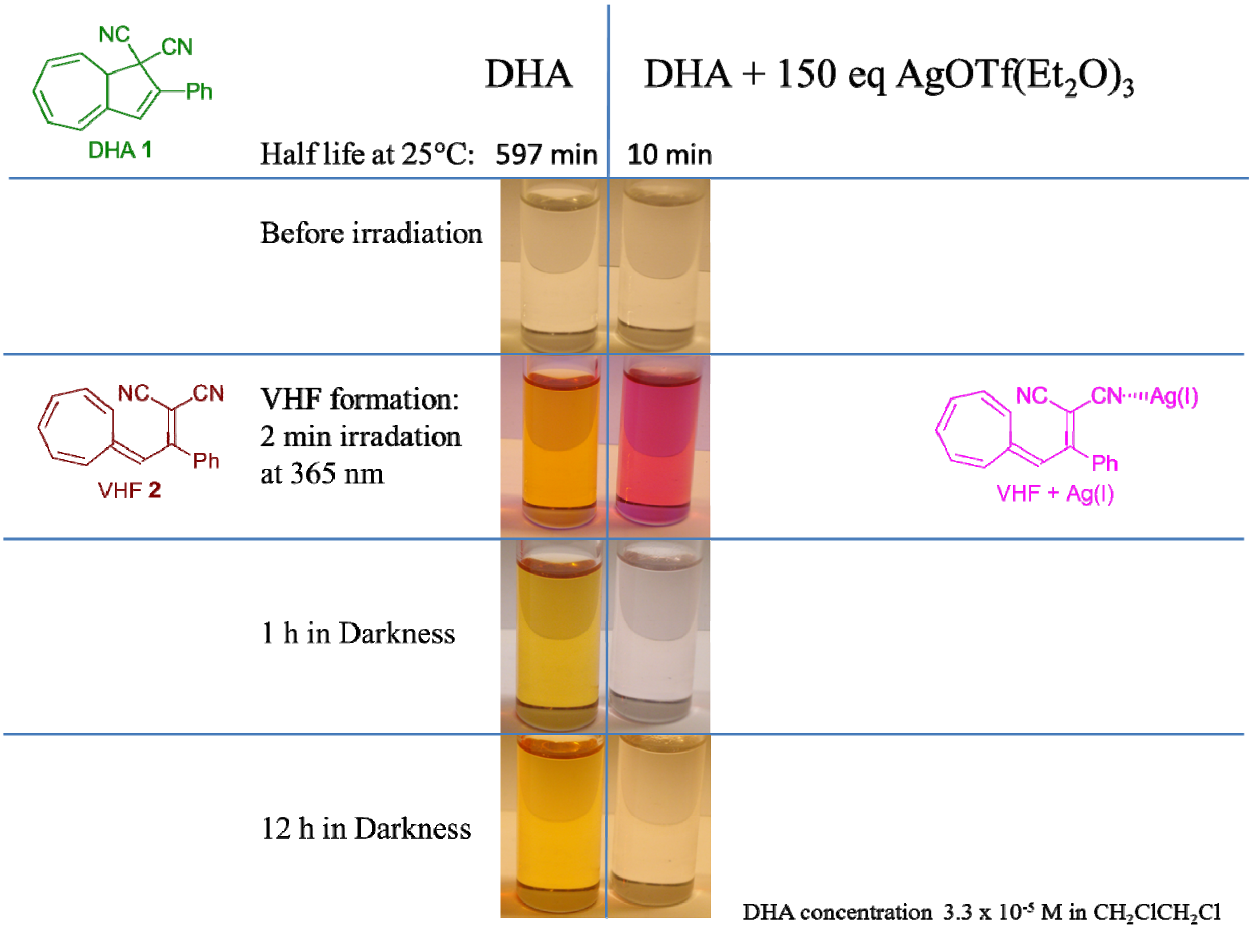


Fig. S10 Pictures of solutions of DHA (left) and DHA + 150 eq Ag(OTf)$(Et_2O)_3$ (right), followed by irradiation to form the VHF and then the thermal back reaction in the dark to DHA in DCE. DHA appears clear coloured (instead of pale yellow) and VHF appears yellow-orange colour (instead of red) solution because the solutions are dilute (3.3 x 10^{-5} M).

DHA and VHF ^{1}H and ^{13}C NMR assignment

Table S5 Assigned signals (chemical shift in ppm) of DHA **1** in $CDCl_3$. Atom numbering is shown in Fig. S11a. NMR data from reference 2e (S. L. Broman, S. L. Brand, C. R. Parker, M. Å. Petersen, A. Kadziola and M. B. Nielsen, *Arkivoc*, In press).

	1	2	3	3a	4	5	6	7
δ_C	45.4	140.3[a]	132.5	130.6	121.1	131.0	131.0	127.8
δ_H	-	-	6.89	-	6.34	6.48	6.58	6.31
	8	8a	*i*	*o*	*m*	*p*	CN	CN
δ_C	119.6	51.3	138.8[a]	126.4	129.4	130.2	115.3	112.9
δ_H	5.82	3.79	-	7.7	7.5	7.4	-	-

[a] Assigned by ^{1}H / ^{13}C HMBC.

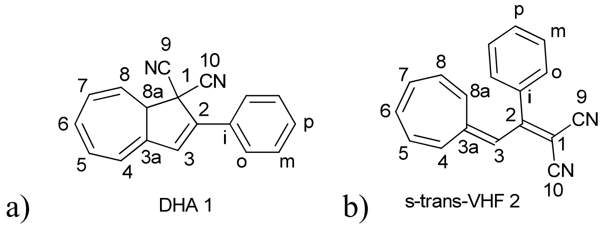


Fig. S11 Numbering of a) DHA **1** and b) VHF **2** for NMR labelling.

Table S6 Assigned signals (chemical shift in ppm) of VHF **2** in C_6D_6. Atom numbering is shown in Fig. S11b. ^{1}H / ^{13}C HMBC and selectively excited 1D INADEQUATE was used to assign the carbon skeleton which was complemented by the TOCSY and NOE studies previously reported.[2e]

	1	2	3	3a	4	5-8[a]	
δ_C	78.40	168.11	119.56	153.09	142.33	134.98, 134.97, 134.35, 133.59	
δ_H	-	-	6.08	-	5.79	5.60-5.52, 5.49-5.44	
	8a	*i*	*o*[b]	*m*[b]	*p*[b]	CN	CN
δ_C	132.90	135.40	128.40, 129.55		130.75	115.15	115.02
δ_H	5.11	-	7.02-6.92			-	-

a) The δ_C and δ_H on 5-8 were to close together to assign individually. b) Only the *ipso* and *para* C of the Ph were assigned.

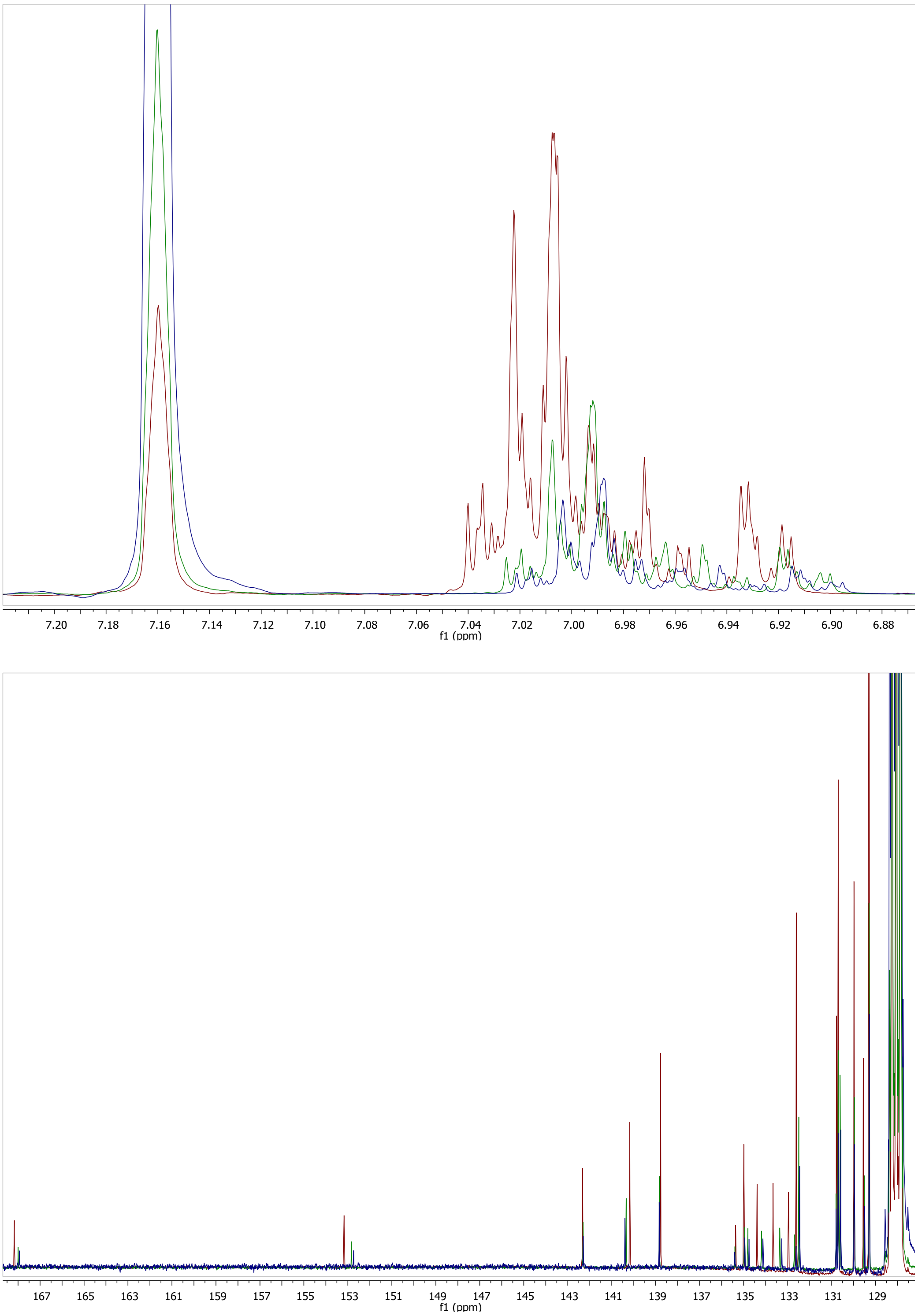


Fig. S12 Shift in δ_C and δ_H with concentration with VHF **2**. Solutions in C_6D_6: Red trace is concentrated, Green trace is diluted by 0.1 ml in 0.6 ml; Blue trace is most dilute it has had 0.1 ml of previous dilution diluted in 0.6 ml. The C_6D_6 can be seen referenced in each spectrum.

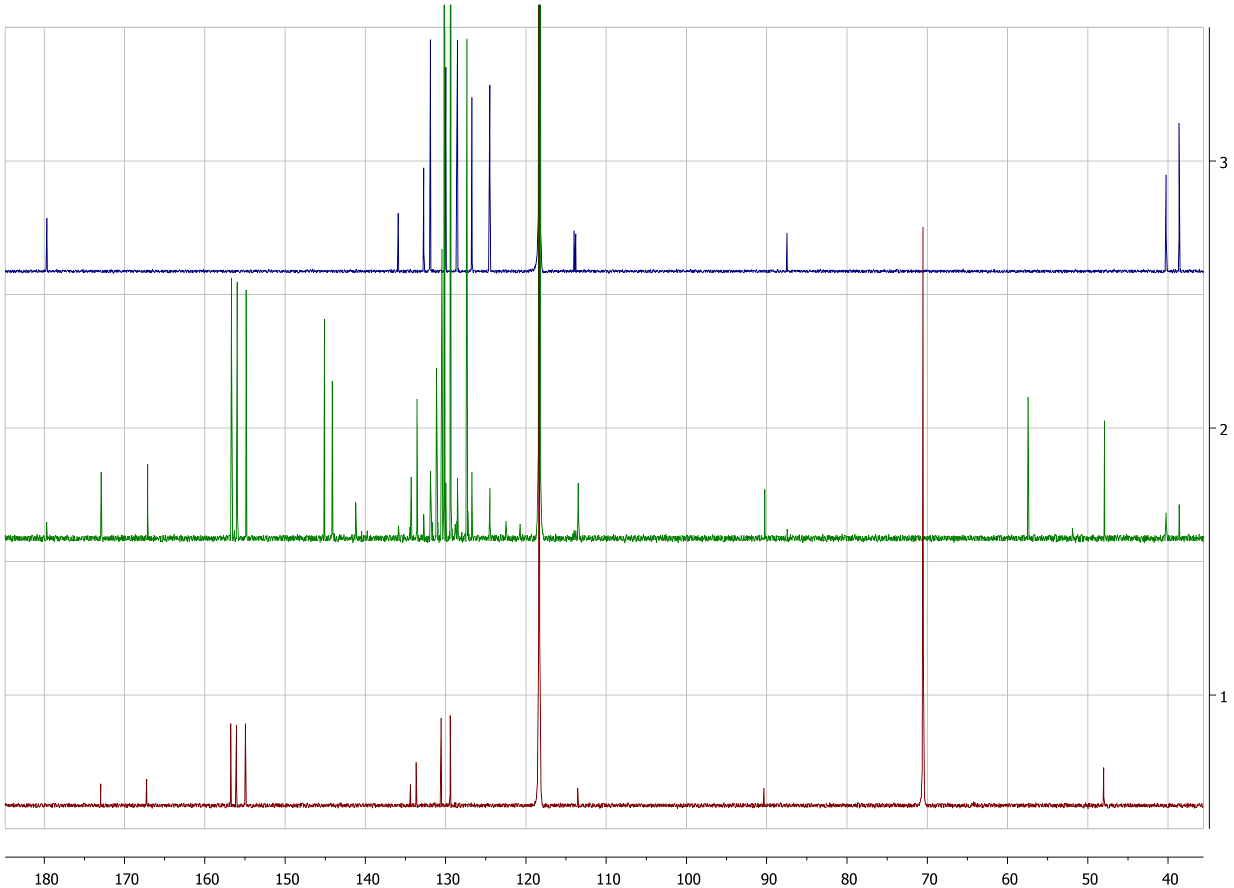
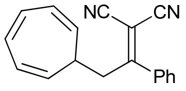
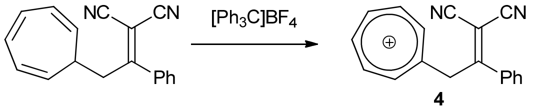


Fig. S13 Comparison of ^{13}C NMR of the reactions (CD_3CN) for the formation of tropylium species **4** shown below.

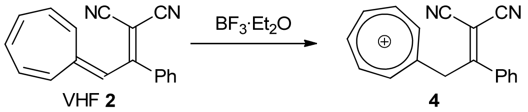
^{13}C NMR of compound 2-(Cyclohepta-2,4,6-trienyl-1-phenylethylidene)malononitrile in blue trace (top)



^{13}C NMR of reaction of 2-(Cyclohepta-2,4,6-trienyl-1-phenylethylidene)malononitrile and $[Ph_3C]BF_4$ in green trace (middle)



^{13}C NMR from reaction of VHF **2** and $BF_3{\cdot}Et_2O$ in red trace (bottom)



Crystallographic Data

Single-crystal X-ray diffraction data were collected at 122 K using a Nonius Kappa CCD area-detector diffractometer with MoKα radiation (λ = 0.71073 Å) equipped with an Oxford Cryostreams low-temperature device. The structure was solved using direct methods (SHELXS97) and refined using the SHELXL97 software package.[S2] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the difference Fourier map but refiened at calculated positions.

CCDC-804840 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reference:

S2 Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

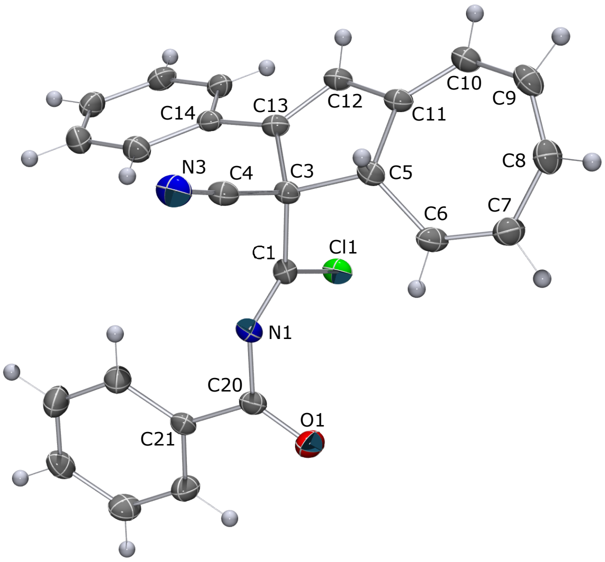


Fig. S14 Ortep diagram of carbimidoyl chloride compound **5**. Selected bond lengths shown in Table S7.

Table S7 Selected bond lengths (Å) of compound **5**.

N1—C1	1.250 (2)	C6—C7	1.339 (2)	C16—C17	1.383 (3)
N1—C20	1.425 (2)	C7—C8	1.451 (2)	C17—C18	1.392 (3)
N3—C4	1.142 (2)	C8—C9	1.348 (3)	C18—C19	1.386 (2)
O1—C20	1.209 (2)	C9—C10	1.442 (2)	C20—C21	1.483 (2)
Cl1—C1	1.7567 (16)	C10—C11	1.347 (2)	C21—C26	1.385 (2)
C1—C3	1.532 (2)	C11—C12	1.441 (2)	C21—C22	1.389 (2)
C3—C4	1.481 (2)	C12—C13	1.344 (2)	C22—C23	1.383 (2)
C3—C13	1.541 (2)	C13—C14	1.467 (2)	C23—C24	1.384 (3)
C3—C5	1.591 (2)	C14—C19	1.403 (2)	C24—C25	1.376 (3)
C5—C6	1.503 (2)	C14—C15	1.405 (2)	C25—C26	1.390 (3)
C5—C11	1.517 (2)	C15—C16	1.388 (2)		

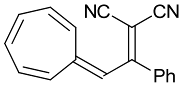
Table 8 Crystallographic data for **5**

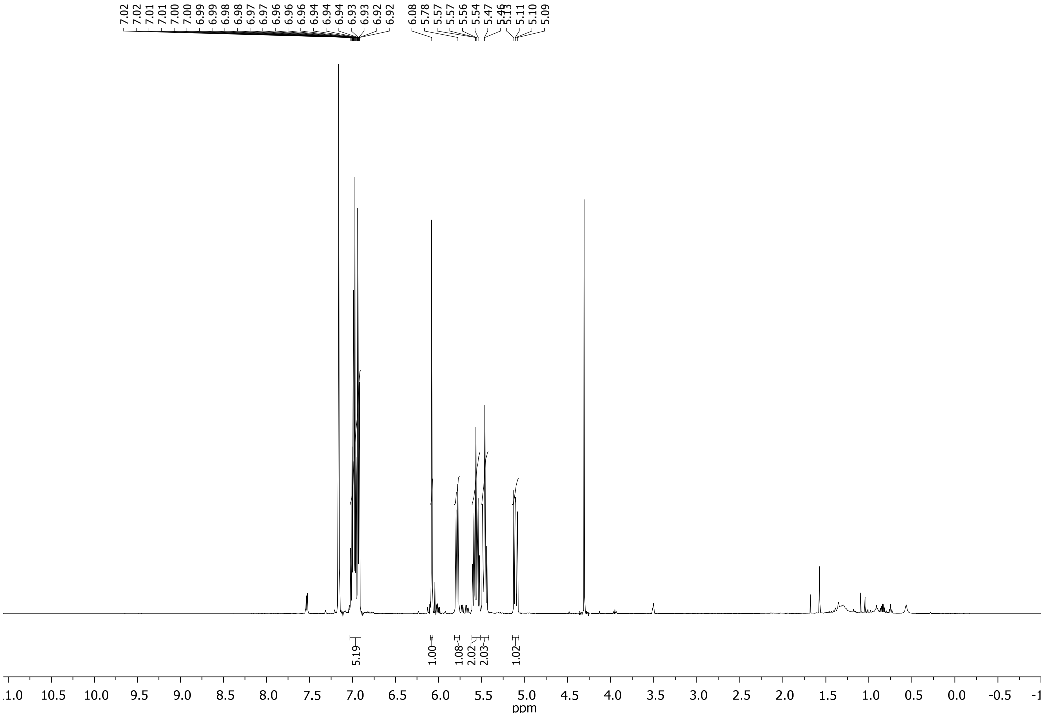
Compound reference	CCDC-804840 (**5**)
Chemical formula	$C_{25}H_{17}ClN_2O$
Formula Mass	396.86
Crystal system	Triclinic
a/Å	8.3826(11)
b/Å	13.9767(17)
c/Å	16.7662(20)
α/°	91.452(12)
β/°	96.337(10)
γ/°	96.790(10)
Unit cell volume/Å^3	1937.2(3)
Temperature/K	122(1)
Space group	P-1
No. of formula units per unit cell, Z	4
Radiation type	MoKα
Absorption coefficient, μ/mm^{-1}	0.216
No. of reflections measured	70576
No. of independent reflections	8895
R_{int}	0.1168
Final R_1 values ($I > 2\sigma(I)$) [a]	0.0417
Final $wR(F^2)$ values ($I > 2\sigma(I)$) [b]	0.0966
Final R_1 values (all data) [a]	0.0549
Final $wR(F^2)$ values (all data) [b]	0.1075
Goodness of fit on F^2	1.059

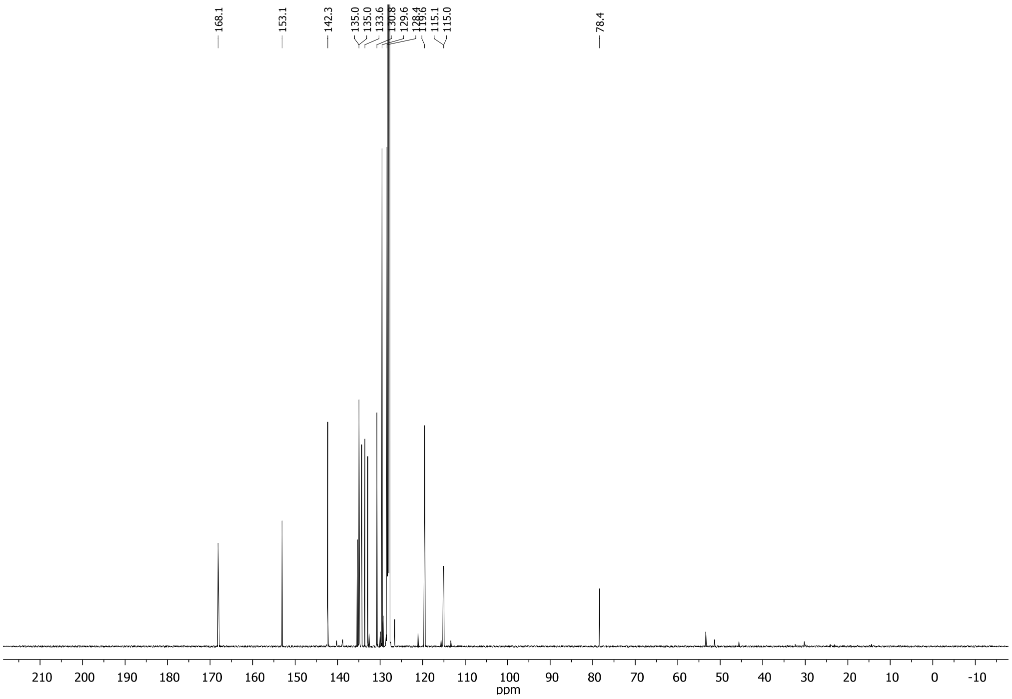
[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

NMR Spectra:

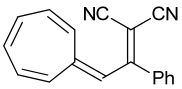
2-(2-(2,4,6-Cycloheptatriene-1-ylidene)-1-phenylethylidene)malononitrile (VHF - **2**) – ^{1}H and ^{13}C NMR. Spectra also shows DHA from conversion of VHF.

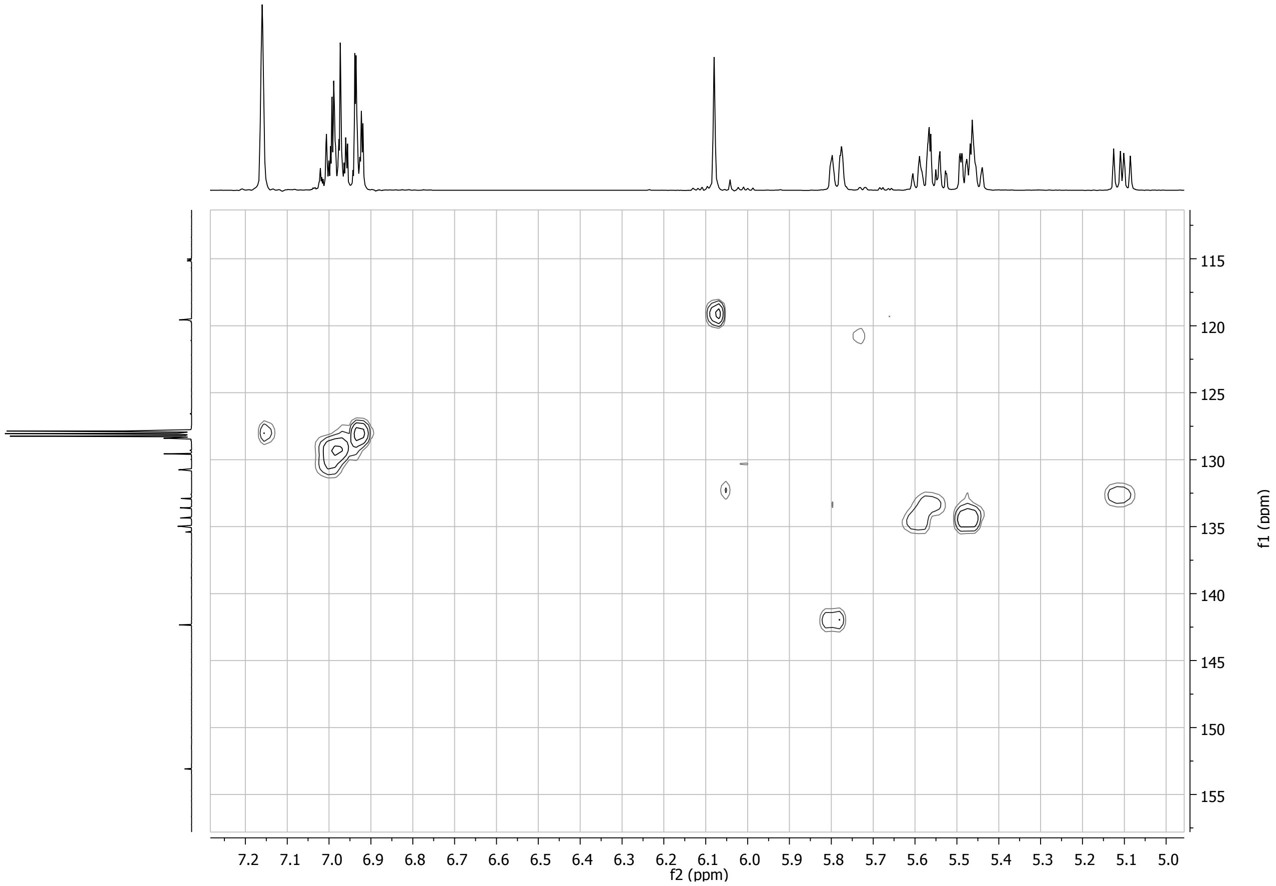




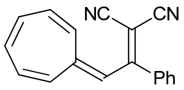


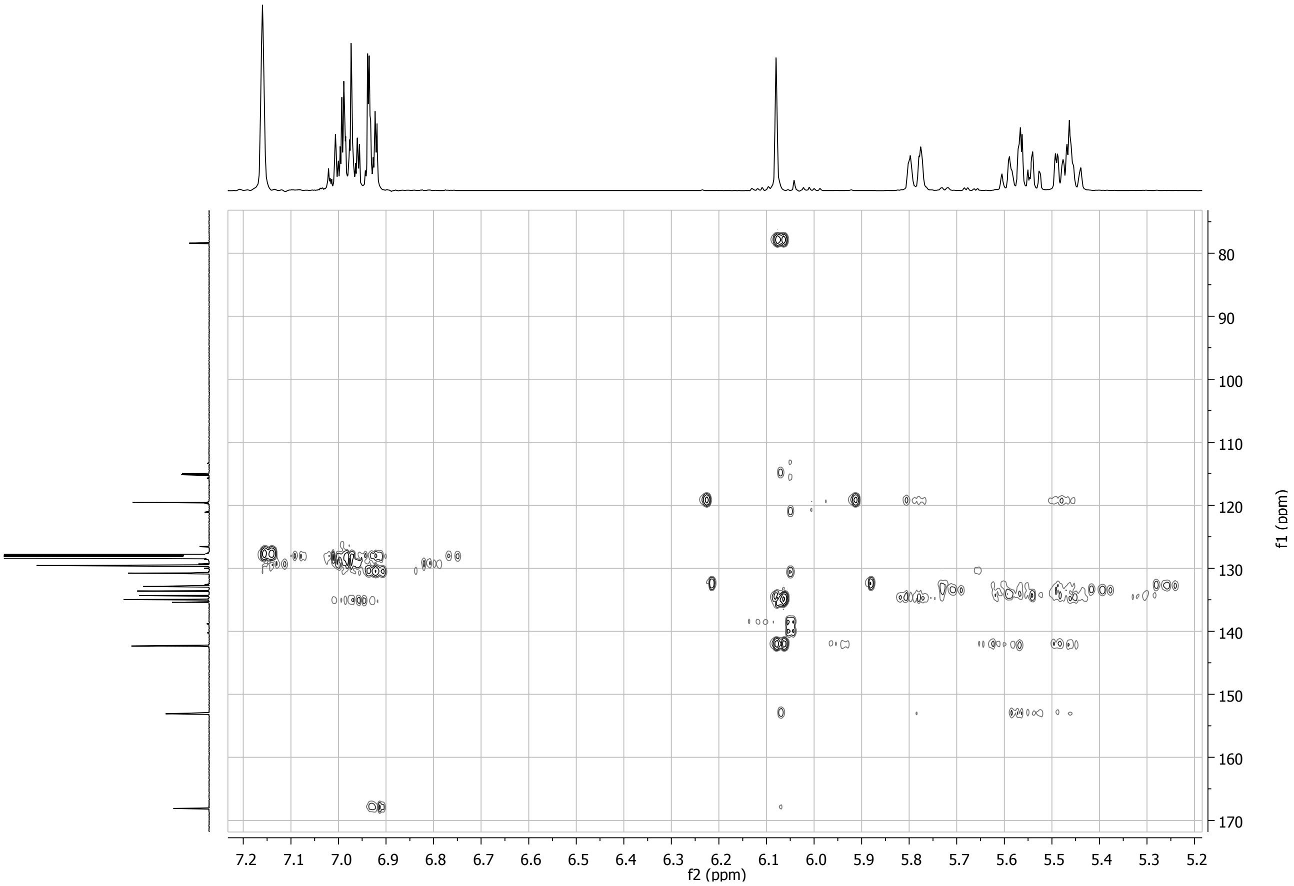
2-(2-(2,4,6-Cycloheptatriene-1-ylidene)-1-phenylethylidene)malononitrile (VHF - **2**) - ^{1}H / ^{13}C HSQC



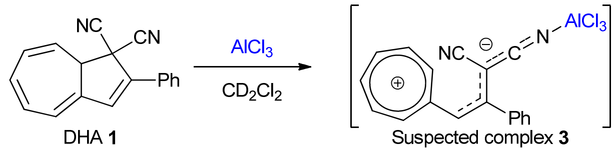


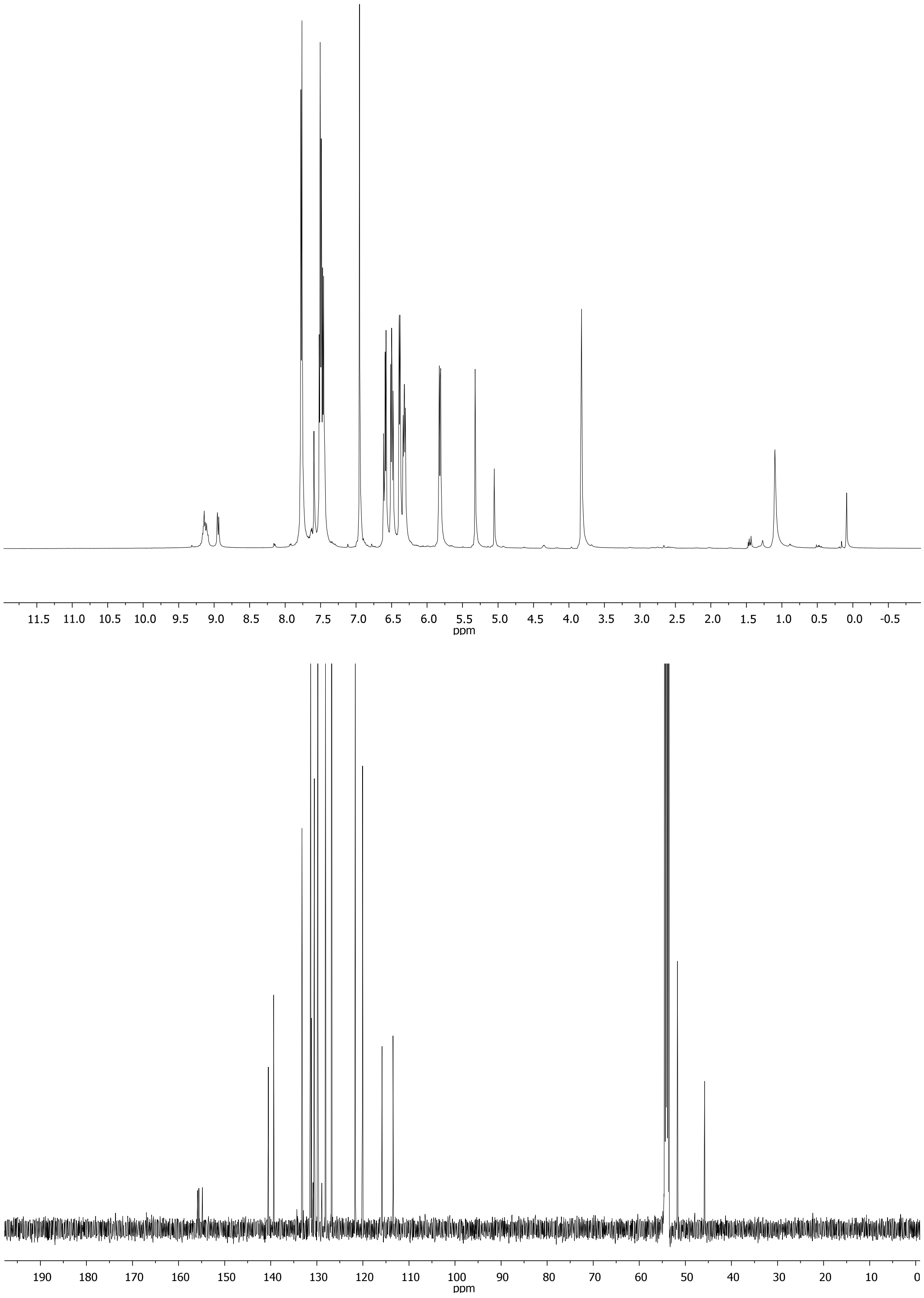
2-(2-(2,4,6-Cycloheptatriene-1-ylidene)-1-phenylethylidene)malononitrile (VHF - **2**) - ^{1}H / ^{13}C HMBC



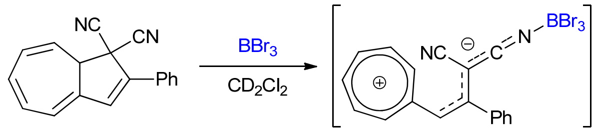


Suspected charge separated complex (**3**) – ^{1}H and ^{13}C NMR



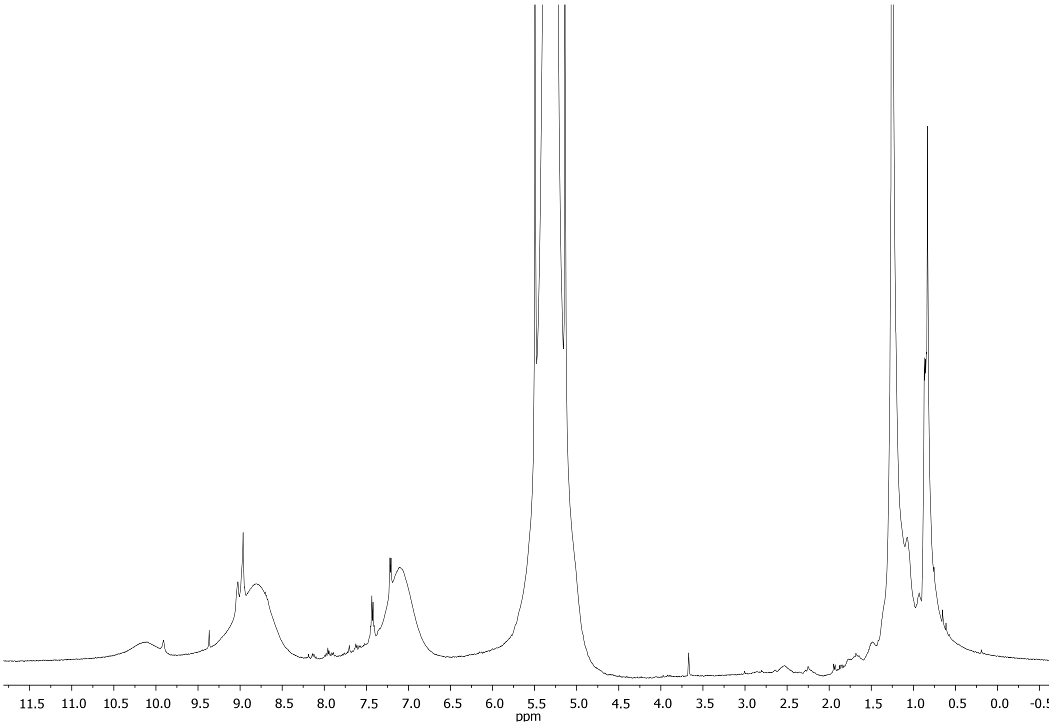


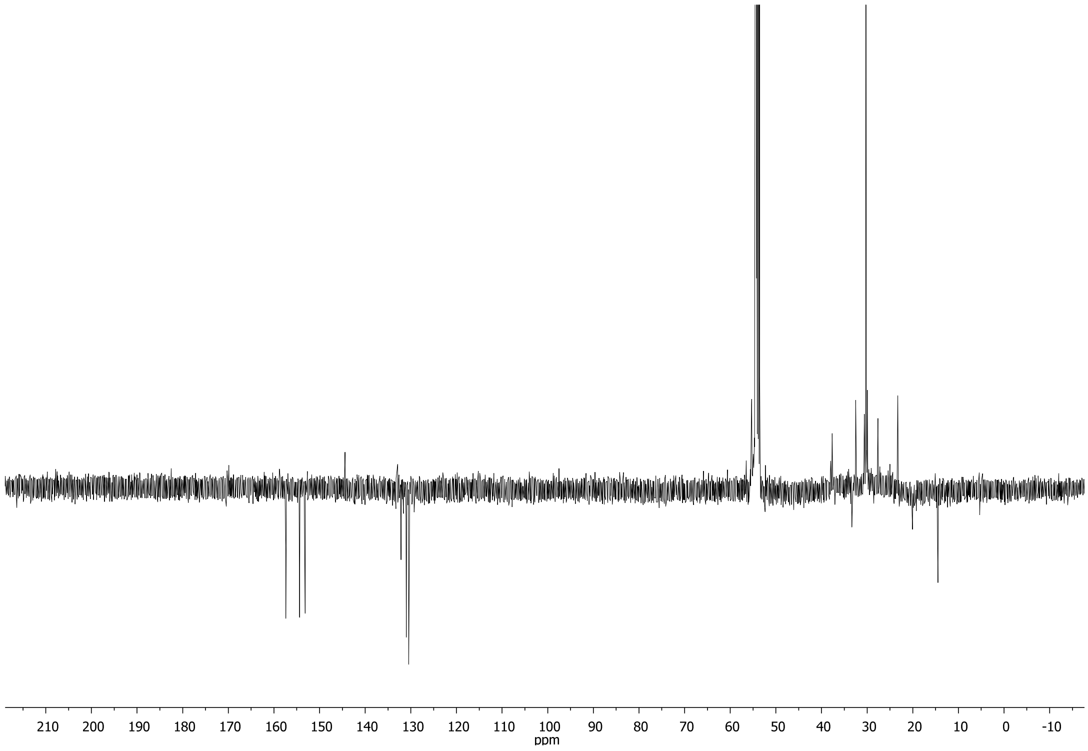
Suspected charge separated complex (**3**) – ^{1}H and ^{13}C APT NMR CH and CH_3 down



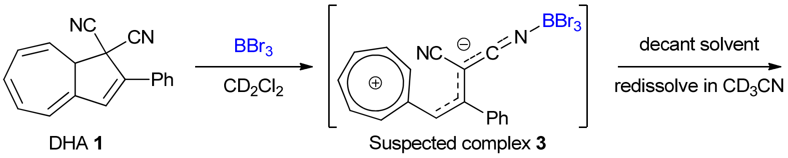
DHA **1**

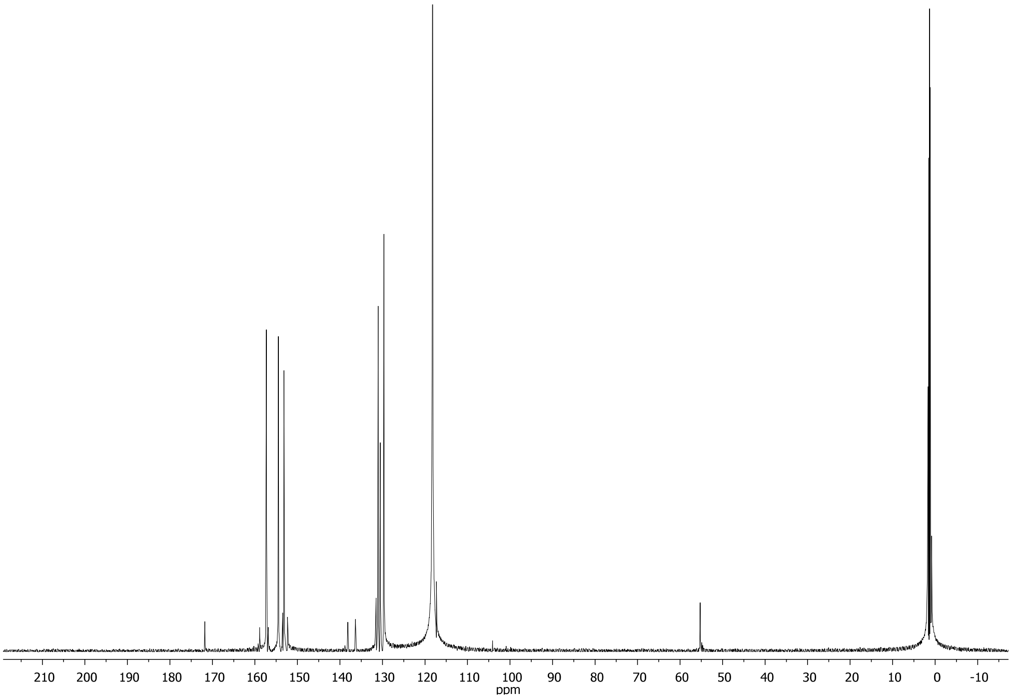
Suspected complex **3**

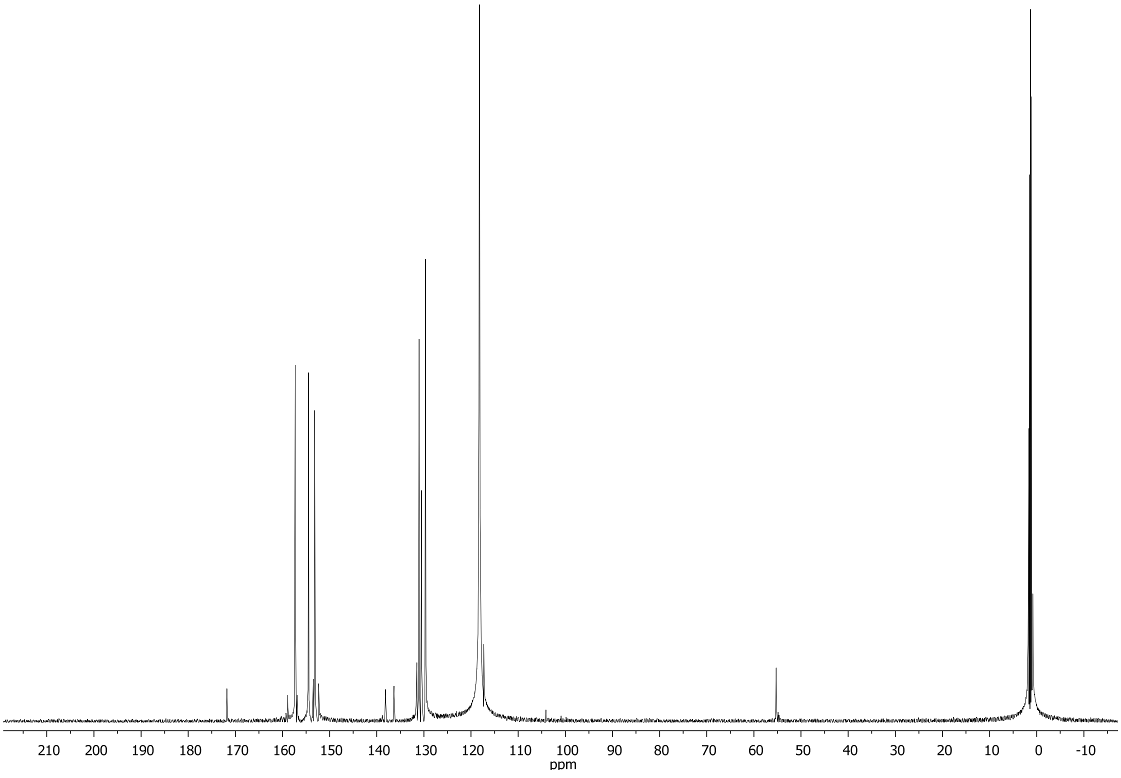




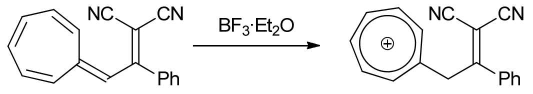
Suspected charge separated complex (**3**) – ^{1}H and ^{13}C NMR



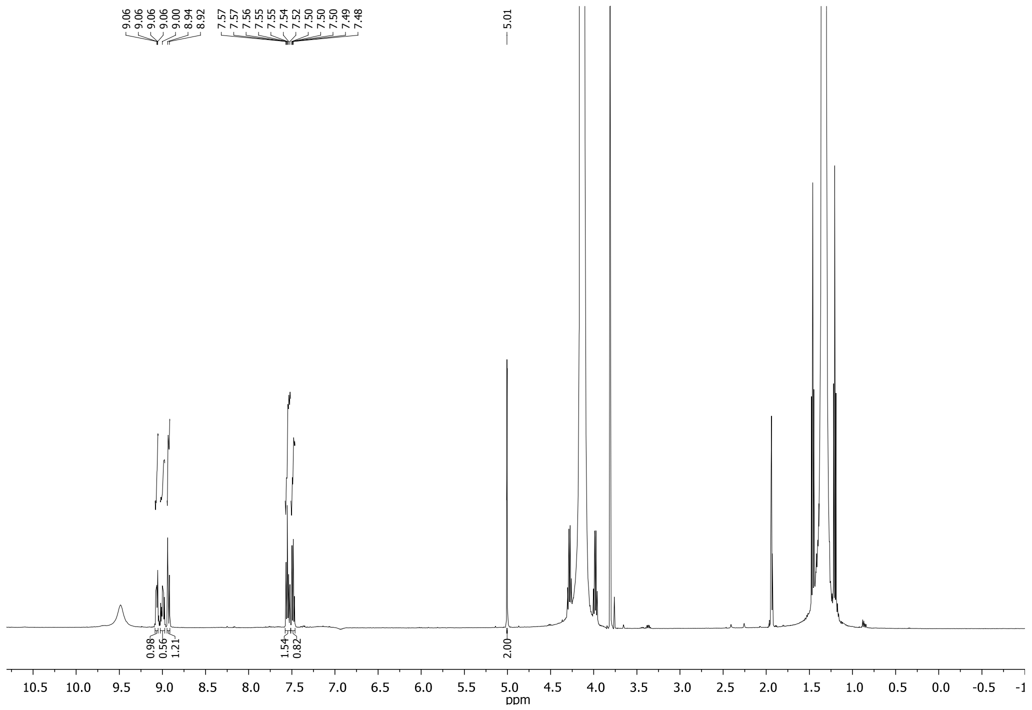


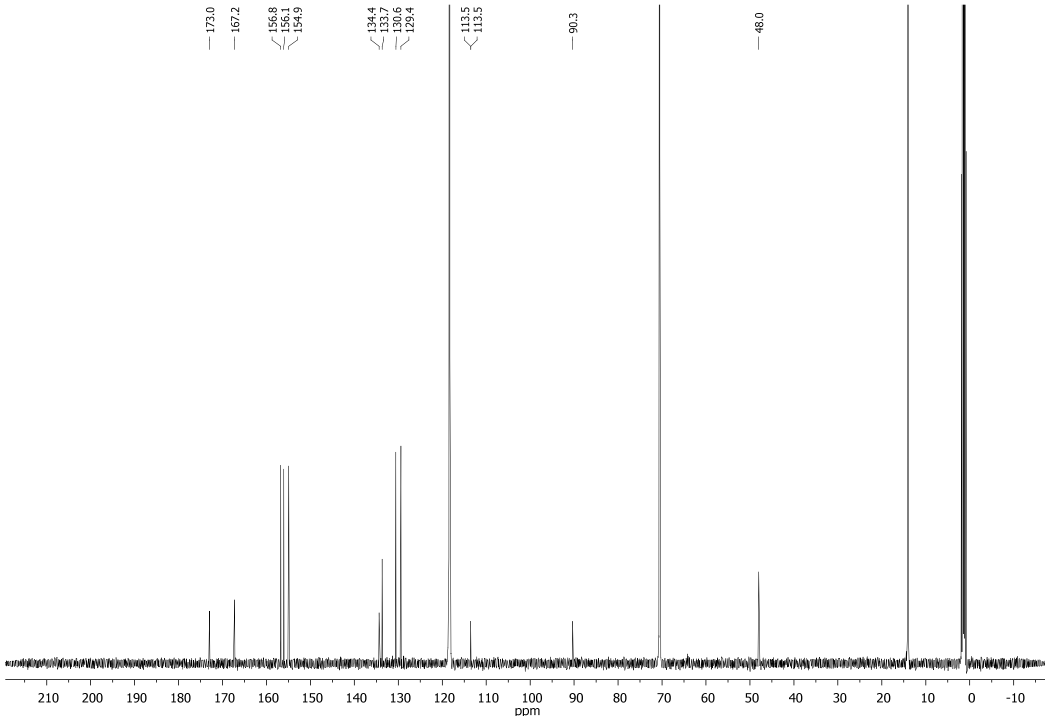


Tropylium species (**4**) – ^{1}H and ^{13}C NMR

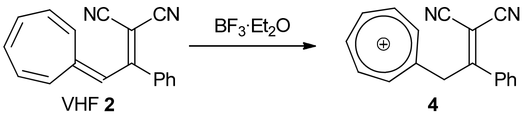


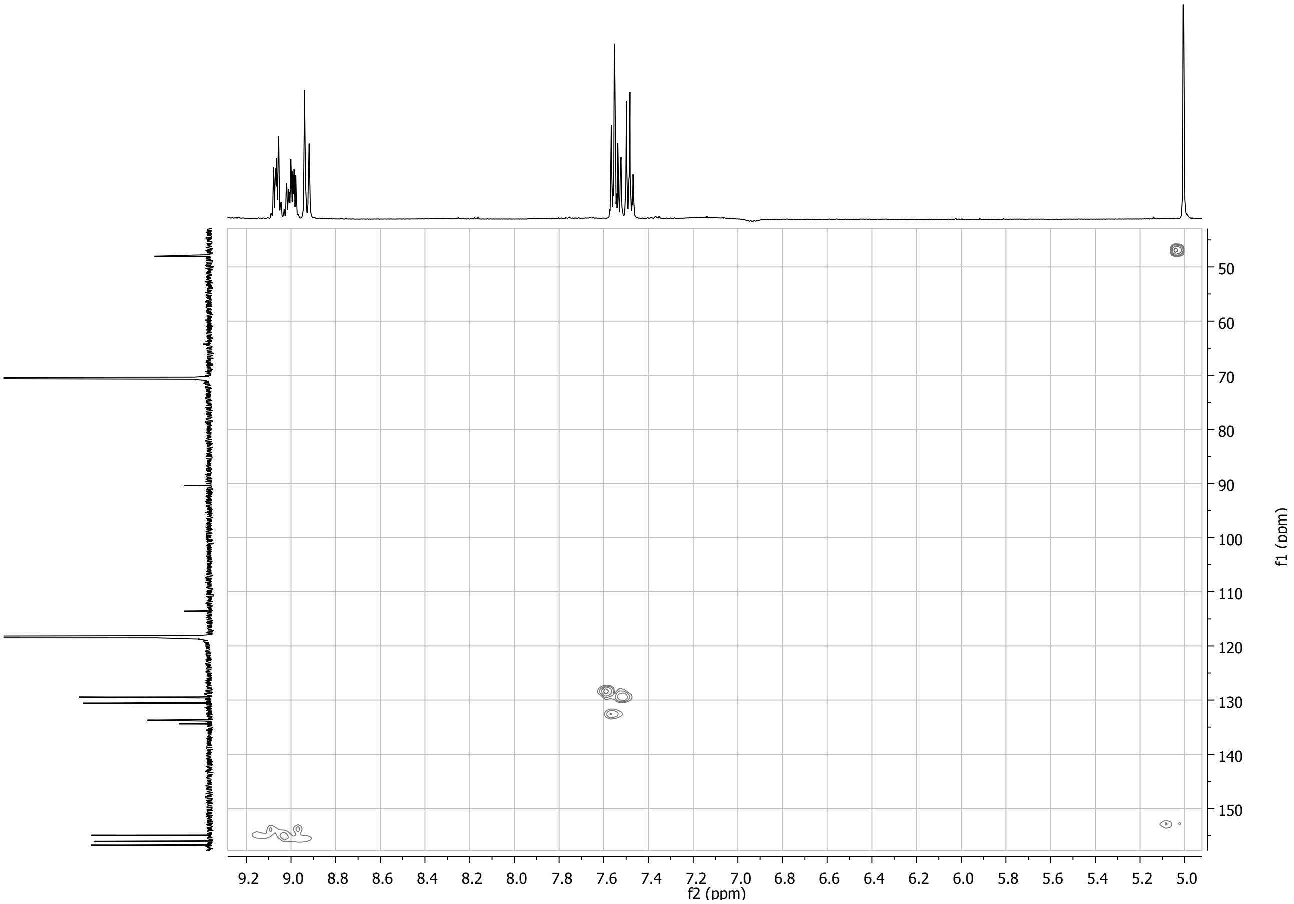
VHF **2** **4**



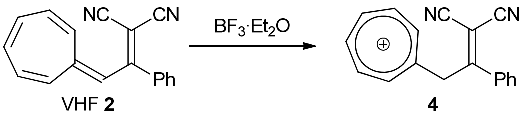


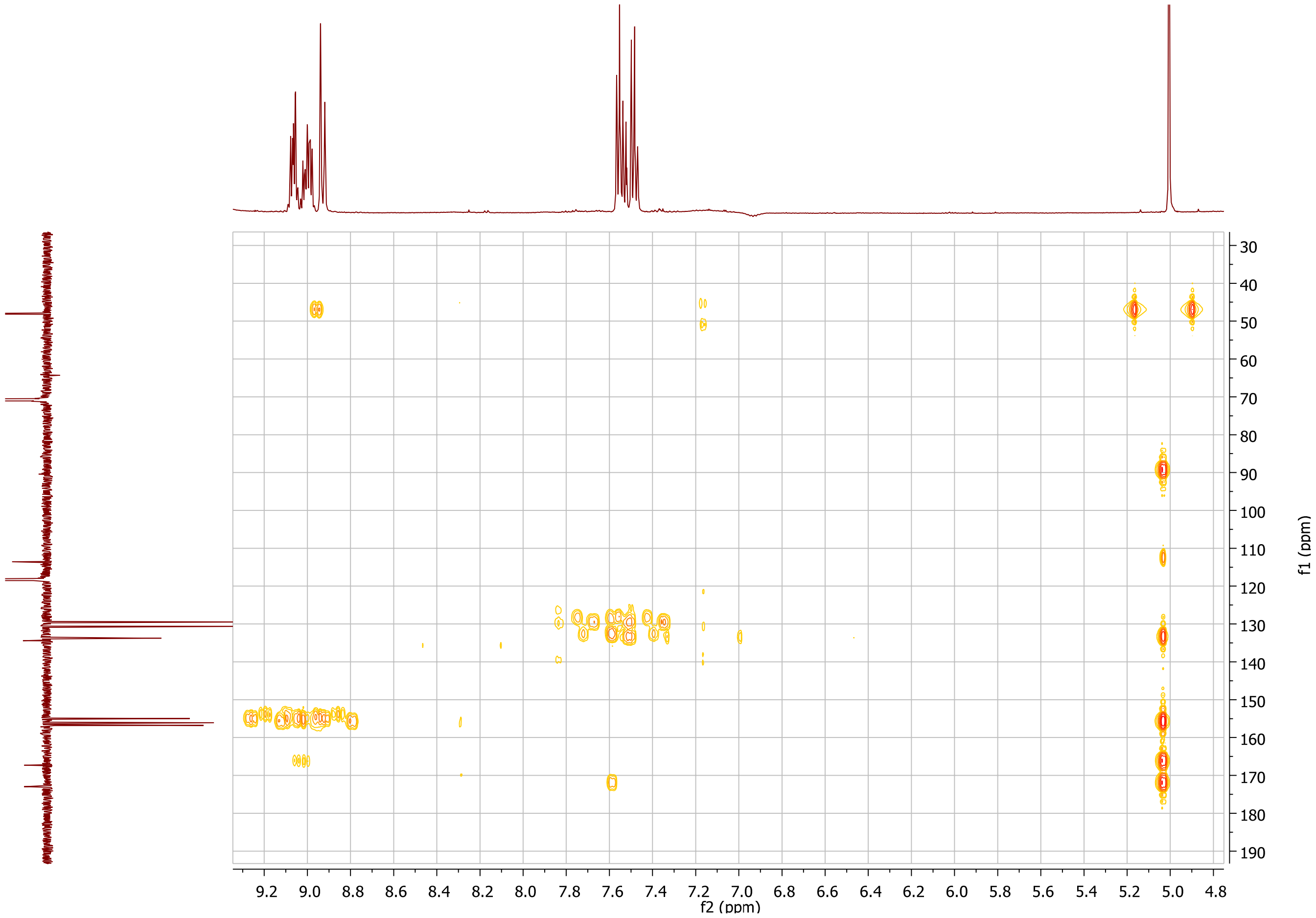
Tropylium species (**4**) - ^1H / ^{13}C HSQC





Tropylium species (**4**) - ^{1}H / ^{13}C HMBC





(*Z*)-*N*-[Chloro-(1-cyano-2-phenyl-1,8a-dihydroazulen-1-yl)methylene]benzamide (**5**) – ^{1}H and ^{13}C NMR