Electronic Supplementary Material (ESI) for Nanoscale.

STM induced manipulation of azulene-based molecules and nanostructures: The role of dipole moment

Supporting Information

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Table of Contents

Calculations of the dipole moment

	Structure	Dx	Dy	Dz	D
Gas phase	Single BCA molecule	-4.00	7.90	1.55	9.00
On Au(111) surface	Single BCA molecule	-4.45	7.70	1.20	8.95
	Dimer 1	0.20	-6.45	0.95	6.50
	Dimer 2	0.90	-1.75	1.20	2.30

Table S1. DFT calculations of dipole moment of the single BCA molecule and dimers (types 1 and 2) in Debye. The calculation in gas phase is done for the "surface" geometry to see in particular the effects of charge transfer to the surface. The numbers however are close to the true gas molecules calculated by DFTB and DFT methods. The dipole moments of dimers are smaller because the dipole moments of monomers are opposite and partially compensate one another. The columns show the three space components of the dipole moment and D is the absolute value.

Additional STM Data

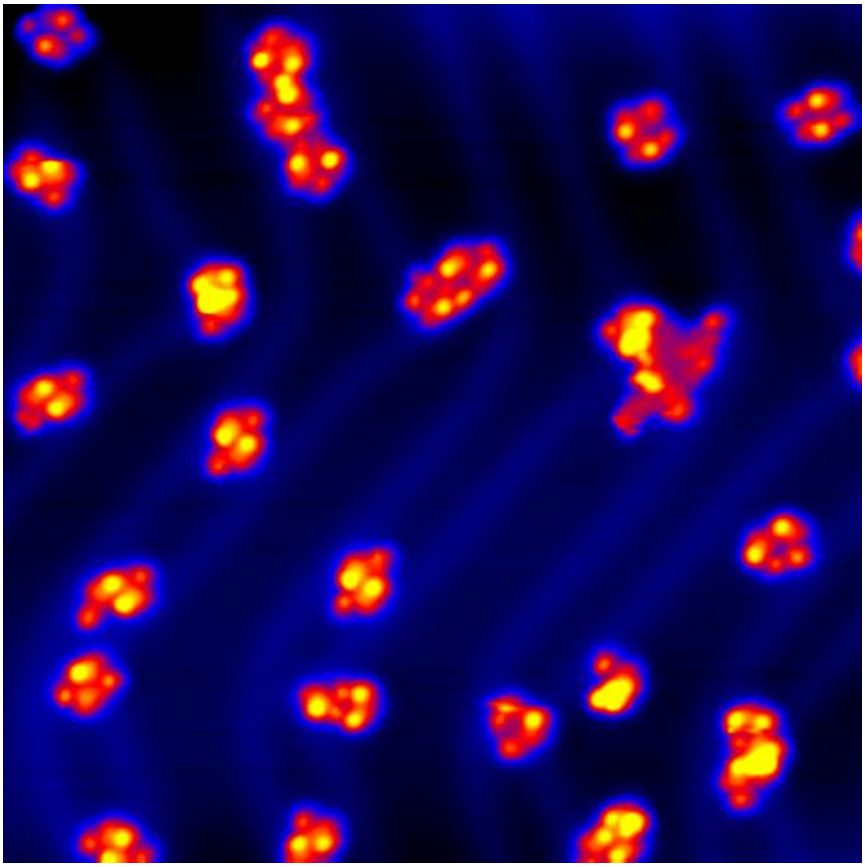


Figure S1. Overview STM image (30 x 30) nm^2 of the BCA molecules and nanostructures on Au (111) (I = 24 pA, V = 0.27 V).

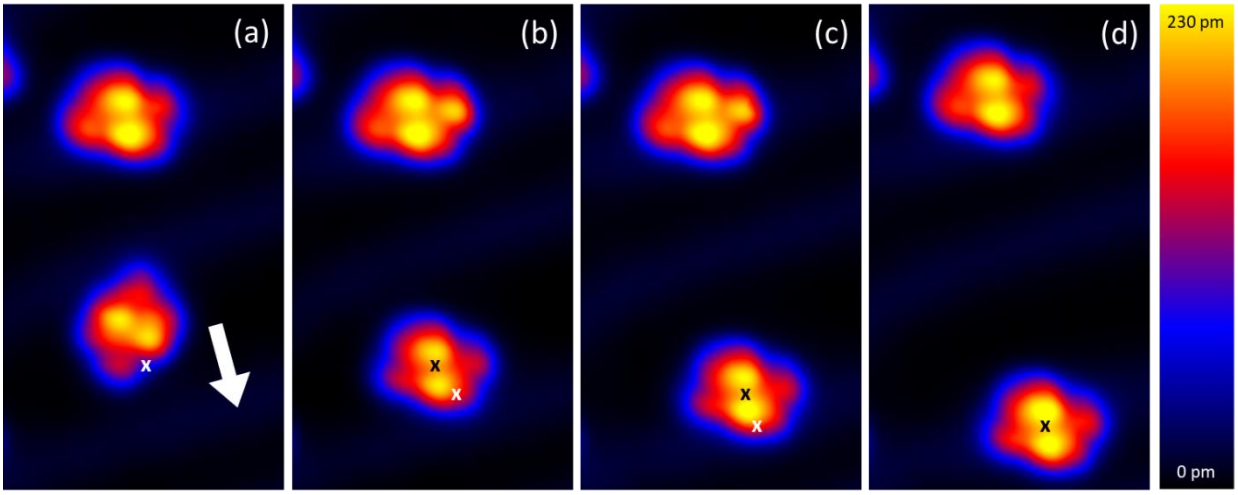


Figure S2. (a) – (d) Manipulation sequence of a BCA dimer 2 with high tip height relative to the Au(111) surface. STM images (7 x 12) nm², I = 20 pA, V = 0.25 V. The white and black marks indicate before and after the voltage pulse positions (V = 1.5 V, $I \approx$ 25 pA, t = 1 s), respectively. The dimer follows the directions of induced pulses at low applied current from center to center.

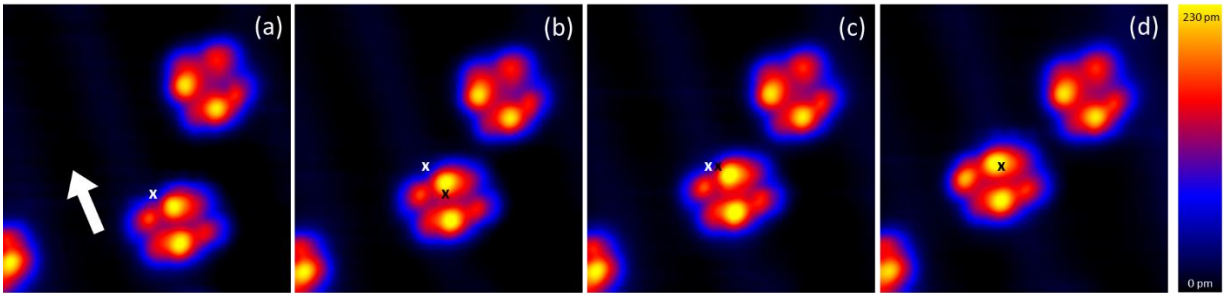


Figure S3. (a) – (d) Manipulation sequence of a BCA dimer 2 with low applied bias. STM images (8 x 8) nm², I = 20 pA, V = 0.25 V. The white and black marks indicate before and after the voltage pulse positions (V = 0.5 V, $I \approx$ 3 nA, t = 1 s), respectively. The dimer follows the directions of induced pulses at low applied bias.

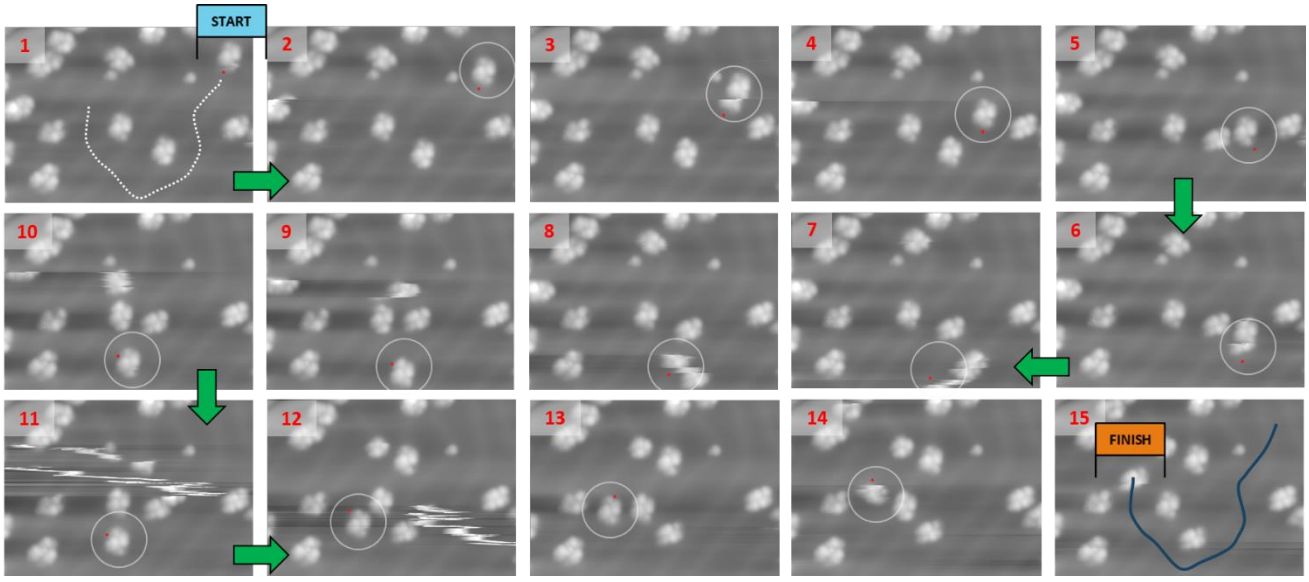


Figure S4. Manipulating a BCA dimer 2 through a “parcour”. STM images (28 x 20) nm² (I = 12 pA, V = 0.2 V) measured in the numbered order (#1 – 15; following the green arrows). The red dots mark voltage pulse positions (V = 1.2 V, $I \approx$ 2000 pA, t = 1 s) and the circle indicates the positions of the molecule. The molecule visible in the top right of image one follows the pulse position, passing the “parcours” that is visualized in the last image by the blue line.

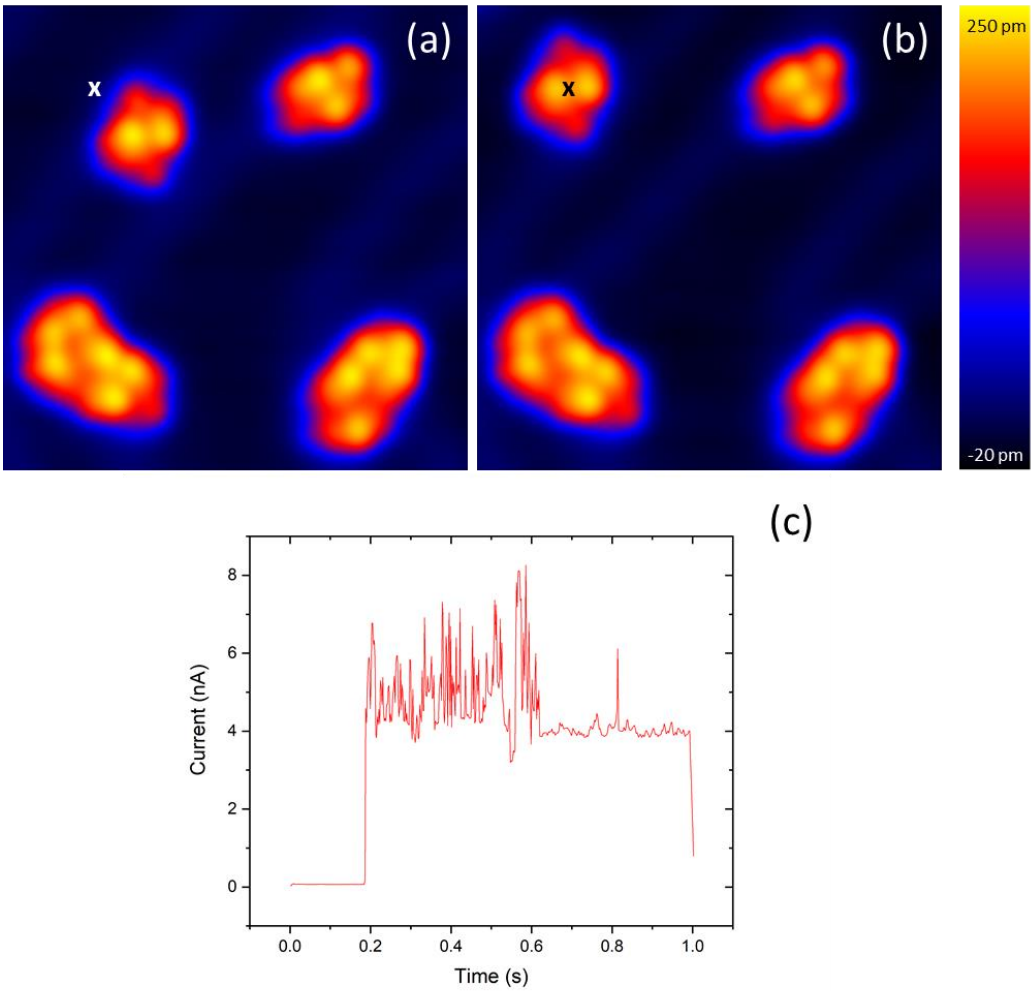


Figure S5. (a) – (b) Movement sequence of a BCA dimer induced by STM voltage pulses (V = 1200 mV, t = 1 s). STM images (13 x 13) nm², I = 12 pA, V = 200 mV. (c) The corresponding *I(t)* curve recorded during the pulse. The BCA dimer reacts with pulse within 0.2 s. The sudden increase of current (from $I \approx 70$ pA to 4 nA) shows the movement of the molecule towards the tip. The white and black marks indicate before and after the voltage pulse positions, respectively.

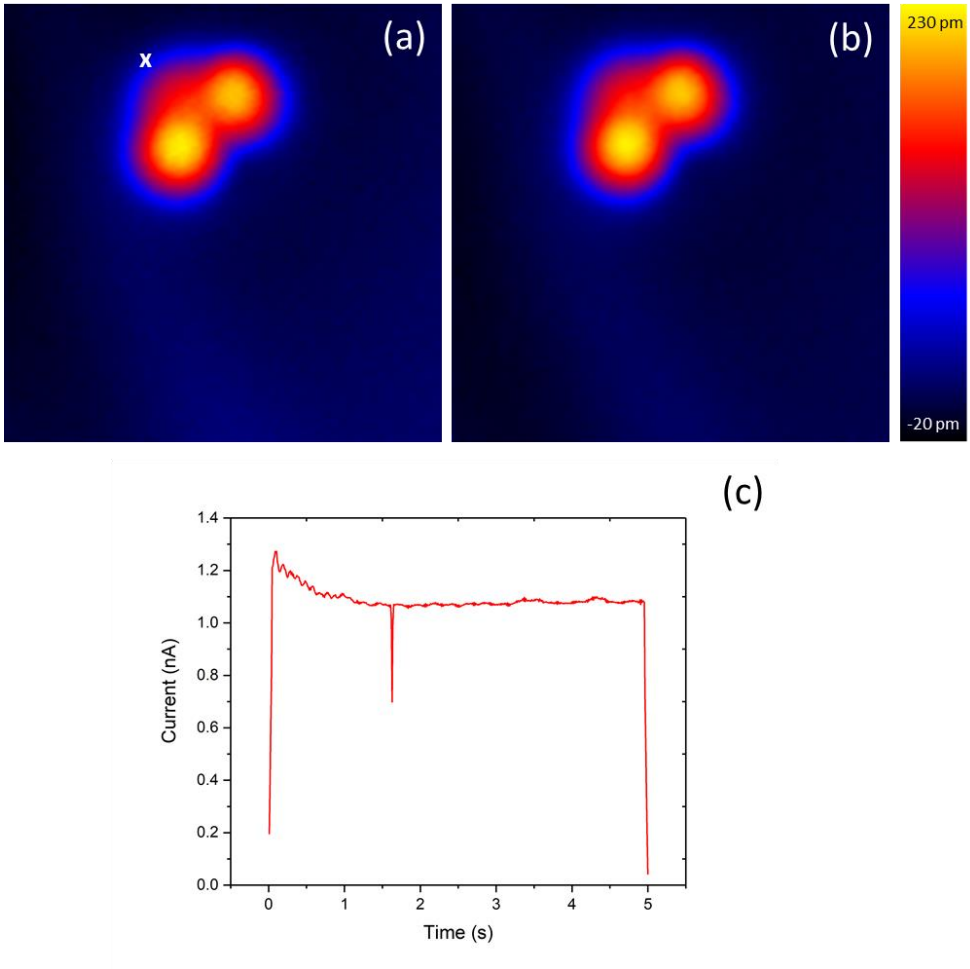


Figure S6. (a) – (b) Manipulation sequence of a single BCA molecule. STM images (5 x 5) nm², I = 2 pA, V = 1.0 V. The white mark indicates the voltage pulse positions (V = 1.8 V, $I \approx$ 1.2 nA, t = 5 s), respectively. (c) Representative I(t) curve for demonstrating signal from voltage pulse. The single molecule does not move after the pulse under similar parameters on moving the BCA dimers (i.e. Fig. S4).

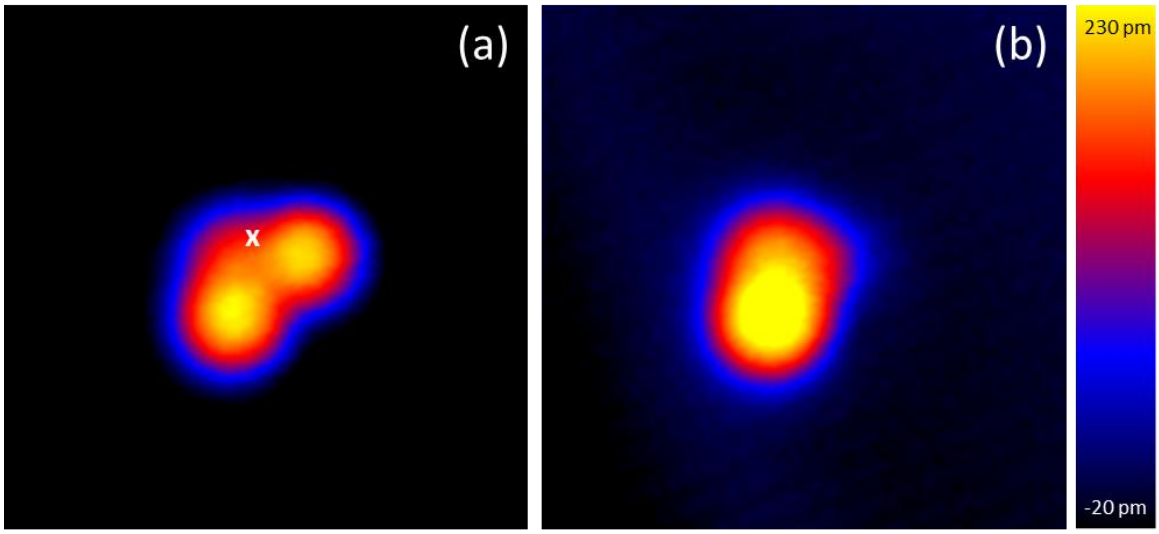


Figure S7. Dissociation/Cleavage of a single BCA molecule. STM images (5 x 5) nm², I = 2 pA, V = 1.0 V. (a) A voltage pulse at the marked position was applied (V = 2.5 V, $I \approx$ 2 nA, t = 5 s). The white mark indicates the voltage pulse positions. (b) A part of the monomer is cleaved after applying the voltage pulse. It has a very good agreement with one part (a *tert*-butyl group) of the monomer of dimer 2, compared to the experimental and simulated STM images (i.e. Fig. 3).

Additional DFT calculations

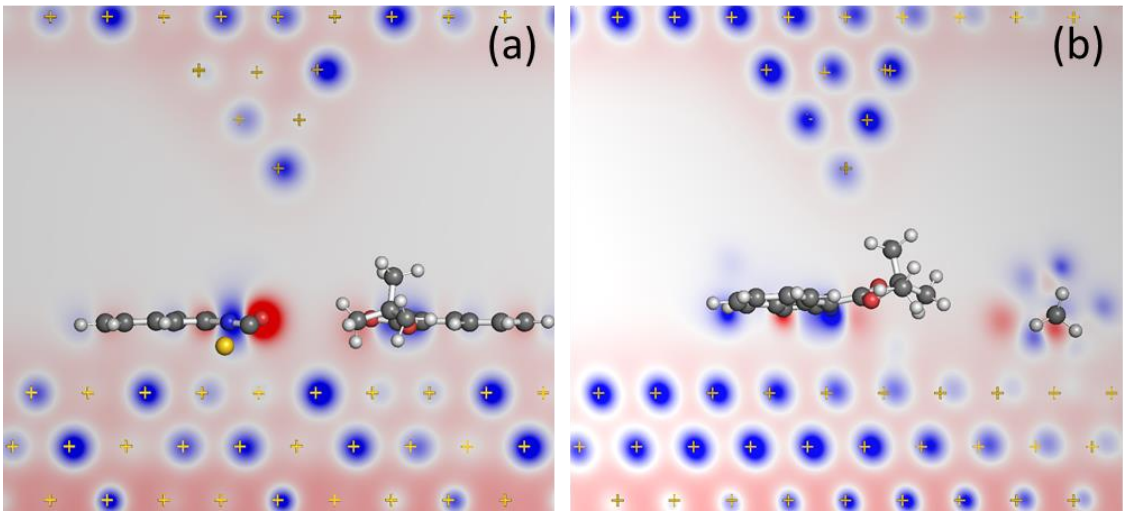


Figure S8. DFT calculated charge distribution (side view) for dimers (a) 1 and (b) 2, respectively on a Au(111) surface. The STM tip is also shown in upper part of the images.

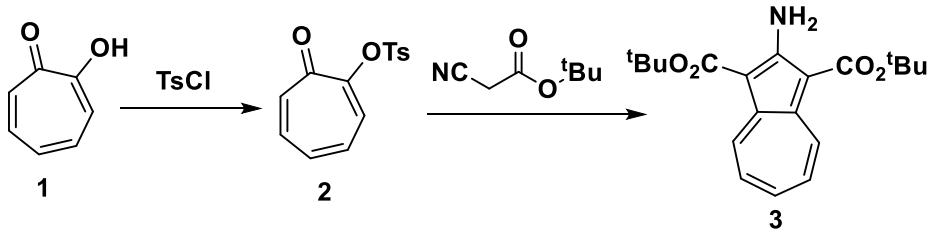
Chemical Synthesis

General information

All the starting materials were purchased from commercial suppliers such as abcr GmbH, Acros Organics, Alfa Aeser and Sigma Aldrich and were used without any prior purification. All reactions were performed with the standard vacuum-line and Schleck techniques under nitrogen.

NMR-spectra of ^{1}H and ^{13}C nucleus were recorded on a Bruker Avence III 500MHz (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometer at room temperature. The spectra were referenced to the residual solvent signals. The NMR signal of $CDCl_3$ was assigned to $\delta = 7.26$ ppm (^{1}H) and $\delta = 77.16$ ppm (^{13}C). The following abbreviations were used for ^{1}H NMR spectra data as listed: s - singlet, d - doublet, t – triplet and m -multiplet. The UV/Vis measurements were carried out on a Perkin Elmer "Lamda800" instrument. The samples were prepared from 10 mg/ml solution in chloroform. The IR spectra were obtained using a Bruker Vertex 80v FTIR spectrometer, working at a resolution of 4 cm^{-1} for 100 scans in the wavelength range of 4000-600 cm^{-1}. Elemental analysis was performed on a Vario EL cube CHNS-analyzer.

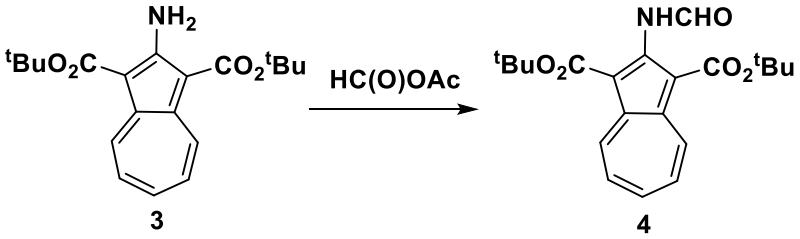
Synthesis of di-*tert*-butyl 2-hydroxyazulene-1,3-dicarboxylate (3):



7-Oxocyclohepta-1,3,5-trienyl 4-methylbenzenesulfonate **2** (1.18 g, 4.3 mmol) was introduced in a 100 mL oven-dried flask equipped with a magnetic stirrer. *Tert*-butyl cyanoacetate (1.21 g, 1.22 mL, 8.6 mmol) was added and the reaction flask was put into an ice bath. Sodium ethoxide (0.58 g, 8.6 mmol) was partially dissolved in dry THF (50 mL) and added dropwise over 15 min to the mixture. After completion of the addition, the yellow reaction mixture was stirred for 6 h at 0°C and then allowed to warm up to room temperature overnight. The reaction was quenched by addition of 100 mL water and extracted with $CHCl_3$ (3 x 100mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated via reduced pressure. The crude product was purified by column chromatography to afford the title compound (0.253 g, 0.74 mmol) as a yellow solid in 17% yield.

IR (FTIR, cm^{-1}): 3506, 3378 (ν_{NH_2}), 1671, 1588 ($\nu_{C=O}$). **^{1}H NMR** (500 MHz, $CDCl_3$): δ1.69 (s, 18H, C*H*$_3$), 7.38 (t, 1H, H^6), 7.48 (t, 2H, H^{5,7}), 7.76 (s, 2H, N*H*$_2$), 9.14 (d, 2H, H^{4,8}) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): 28.76 (*C*H$_3$), 80.82 (*C*^{t}Bu), 100.83, 131.07, 132.11, 132.48, 145.86 (aromatic *C*), 162.30, 166.15 (*C*O$_2$tBu) ppm. Anal. Calcd for $C_{20}H_{25}NO_4$, %: C, 69.95; H, 7.34; N, 4.08; O, 18.63. Found: C, 70.05; H, 6.64; N, 4.19; O, 19.12.

Synthesis of 2-formamido-1,3-di-*tert*-butyloxycarbonyl azulene (4):

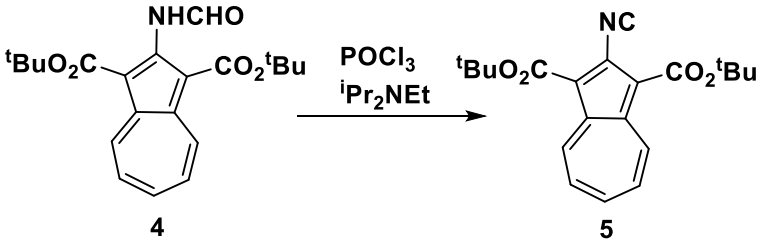


3 4

To the deep yellow di-*tert*-butyl 2-hydroxyazulene-1,3-dicarboxylate (**3**) (0.2 g, 0.58 mmol) was added acetic formic anhydride (2.0 mL). The reaction mixture was stirred for 3h at room temperature, then the volatiles were removed under reduced pressure and the residue was purified by means of column chromatography on a short silica gel column using 4:1 $CHCl_3/Et_2O$ as eluent. The product **4** was obtained as an orange solid (0.208 g, 0.56 mmol) in 96% yield.

IR (FTIR, cm^{-1}): 2349 (ν_{NH}), 1663 ($\nu_{C=O}$). **^{1}H NMR** (500 MHz, $CDCl_3$): δ1.67 (s, 18H, C*H*$_3$), 7.66 (t, 2H, H^{5,7}), 7.78 (t, 1H, H^6), 8.72 (s, 1H, C*H*O), 9.43 (d, 2H, H^{4,8}), 10.23 (s, br, 1H, N*H*) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): 28.50 (*C*H$_3$), 82.28 (*C*^{t}Bu) 131.20, 136.38, 137.94 (aromatic *C*), 164.85 (*C*O$_2$tBu), 176.65 (N*C*) ppm. Anal. Calcd for $C_{21}H_{25}NO_5$, %: C, 67.91; H, 6.78; N, 3.77; O, 21.54. Found: C, 67.69; H, 6.37; N, 3.83; O, 22.11.

Synthesis of di-*tert*-butyl 2-hydroxyazulene-1,3-dicarboxylate (5):



4 5

To a stirring solution of 2-formamido-1,3-di-*tert*-butyloxycarbonyl azulene (**4**) (0.152 g, 0.41 mmol) and ^{i}Pr$_2$Net (0.5 mL, 3.0 mmol), phosphorus oxychloride (0.18 mL, 2.0 mmol) was added dropwise over a 3 min period. After 2 h stirring at room temperature, the reaction mixture was quenched with 100 mL of 10 % aqueous K_2CO_3. The phases were separated and the

extraction was completed with additional portions of CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and evaporated in vacuo. The crude product was subjected to column chromatography on a short silica gel column (4:1 CHCl3/Et_2O). A raspberry colored band was collected, which upon solvent removal, gave the title compound **5** (0.124 g, 0.34 mmol) in 84 % yield.

IR (FTIR, cm^{-1}): 2128 ($\nu_{N\equiv C}$), 1673 ($\nu_{C=O}$). **^{1}H NMR** (500 MHz, $CDCl_3$): δ1.71 (s, 18H, CH_3), 7.77 (t, 2H, $H^{5,7}$), 7.99 (t, 1H, H^6), 9.80 (d, 2H, $H^{4,8}$) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): 28.63 (*C*H_3), 82.57 (*C*^{t}Bu), 113.88, 131.50, 141.05, 141.36, 142.20 (aromatic *C*), 162.99 (*C*O_2tBu), 176.65 (N*C*) ppm. Anal. Calcd for $C_{21}H_{23}NO_4$, %: C, 71.37; H, 6.56; N, 3.96; O, 18.11. Found: C, 71.36; H, 6.60; N, 3.85; O, 18.19.

NMR Data

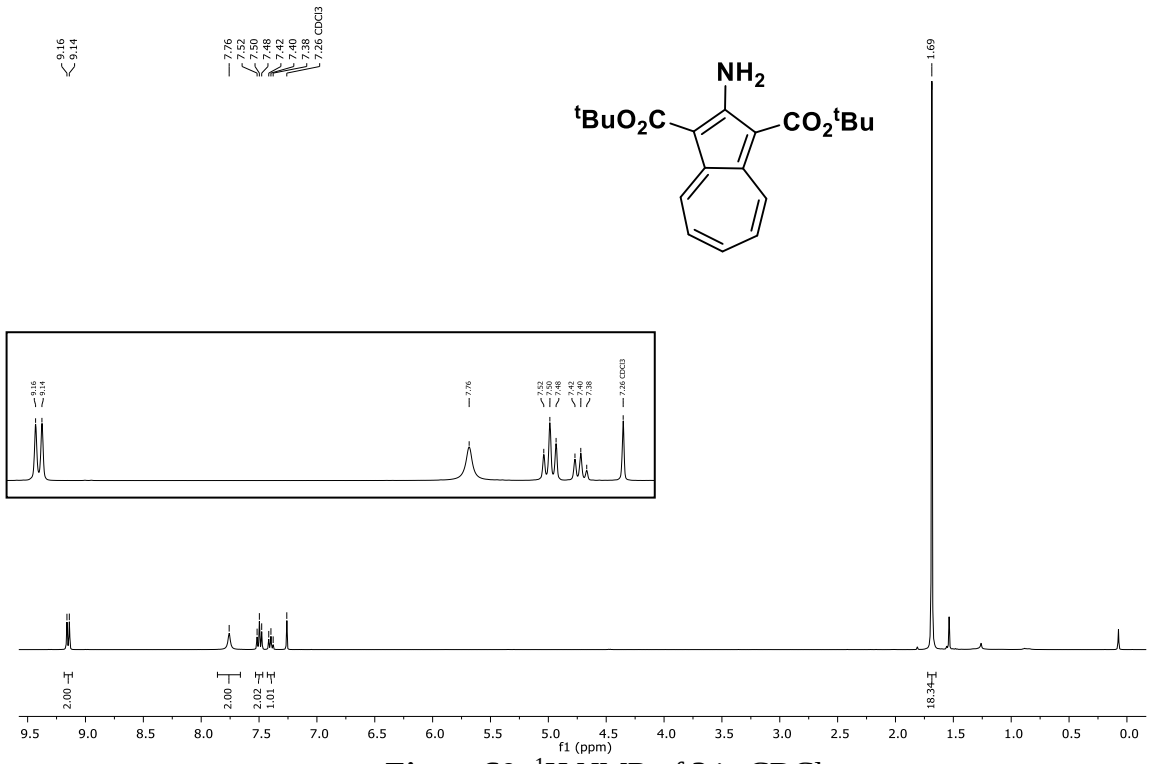


Figure S9: ^{1}H NMR of **3** in $CDCl_3$

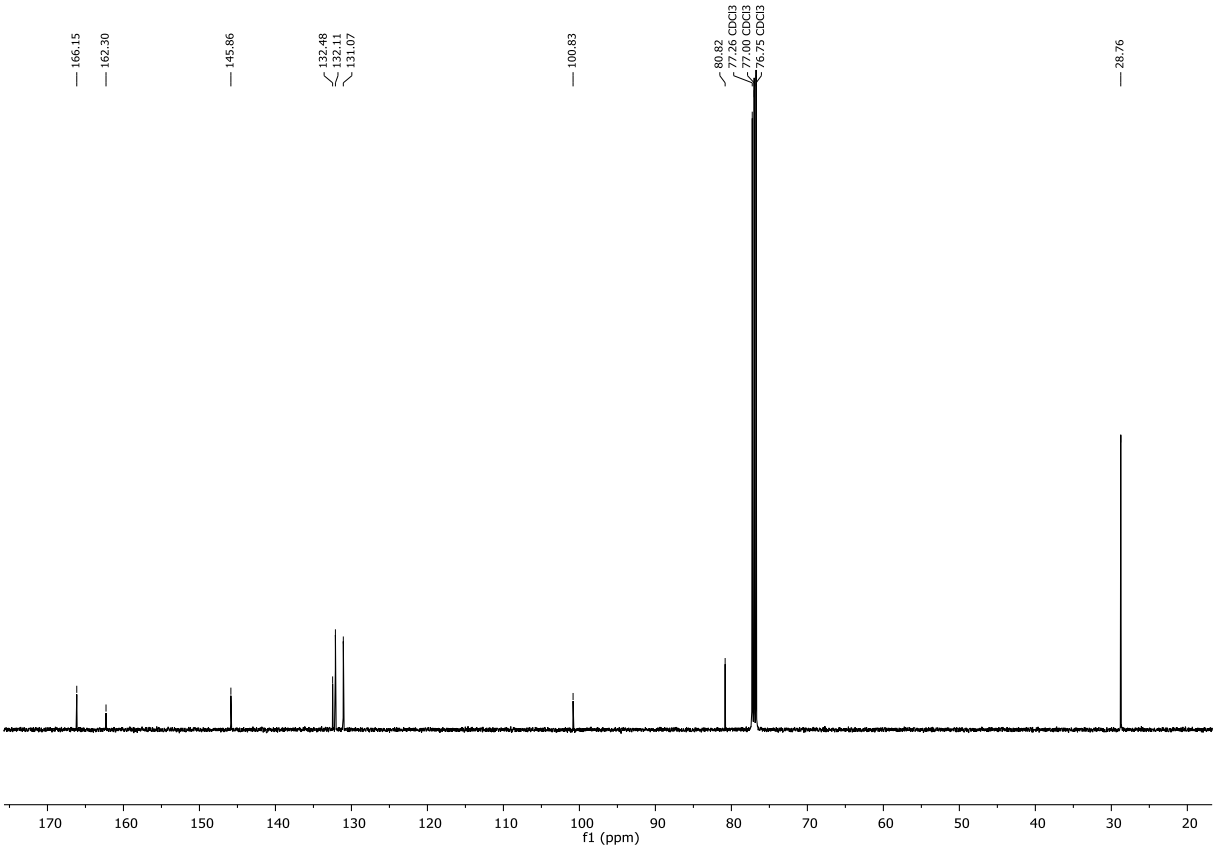


Figure S10: ^{13}C NMR of **3** in $CDCl_3$

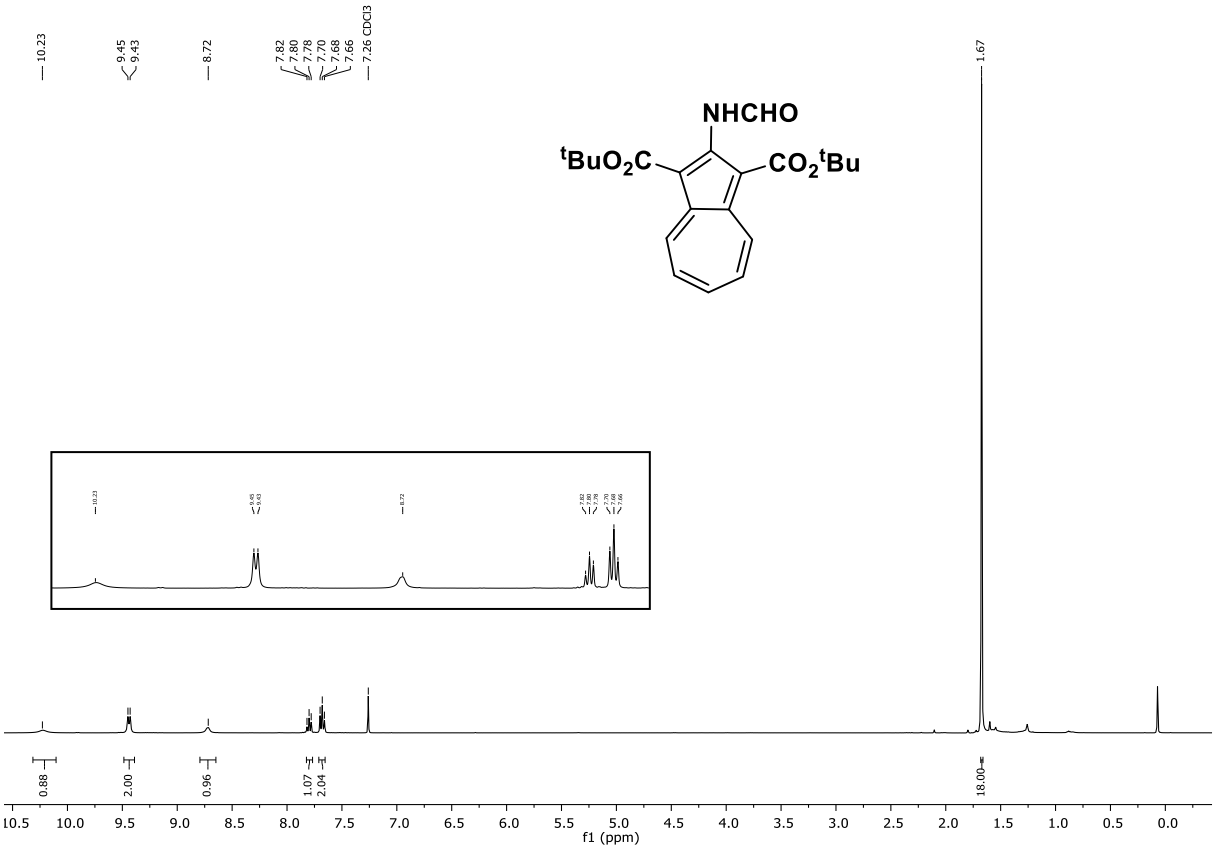


Figure S11: ^{1}H NMR of **4** in $CDCl_3$

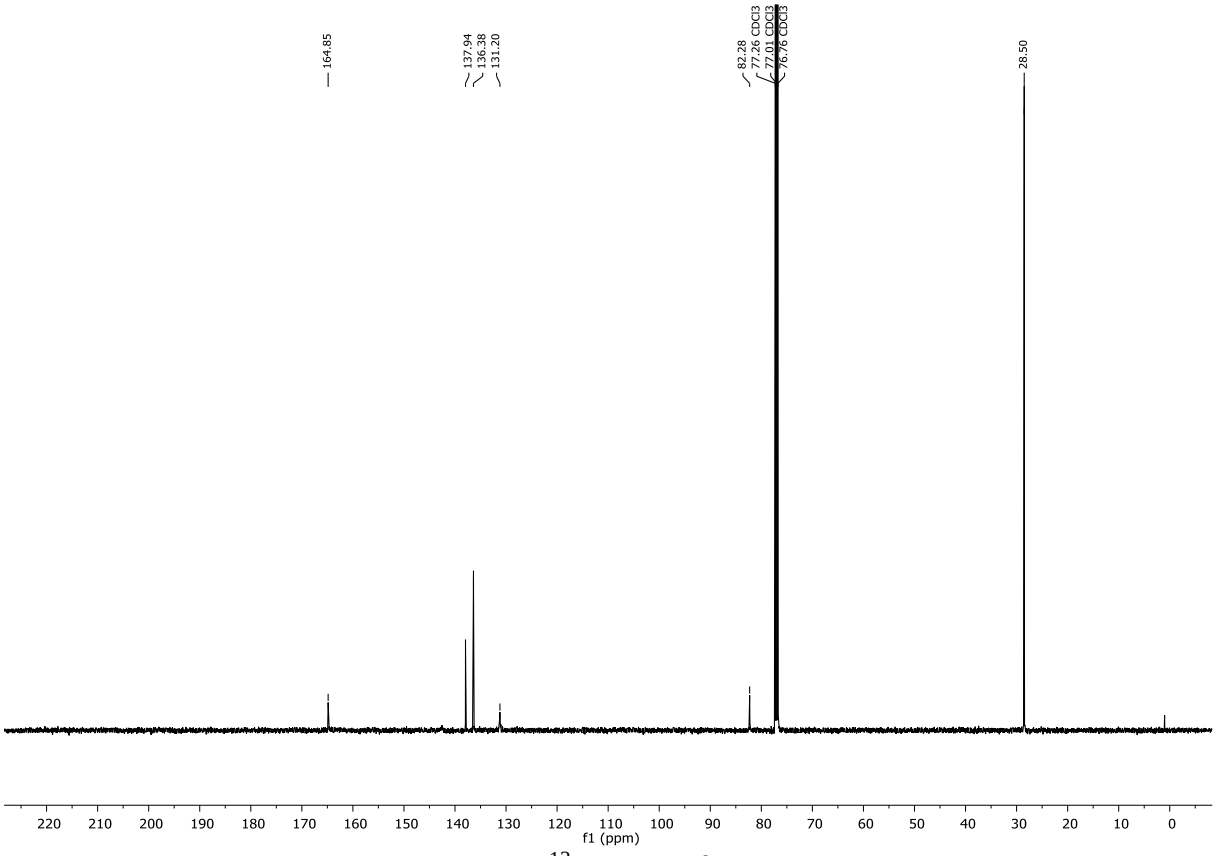


Figure S12: ^{13}C NMR of **4** in $CDCl_3$

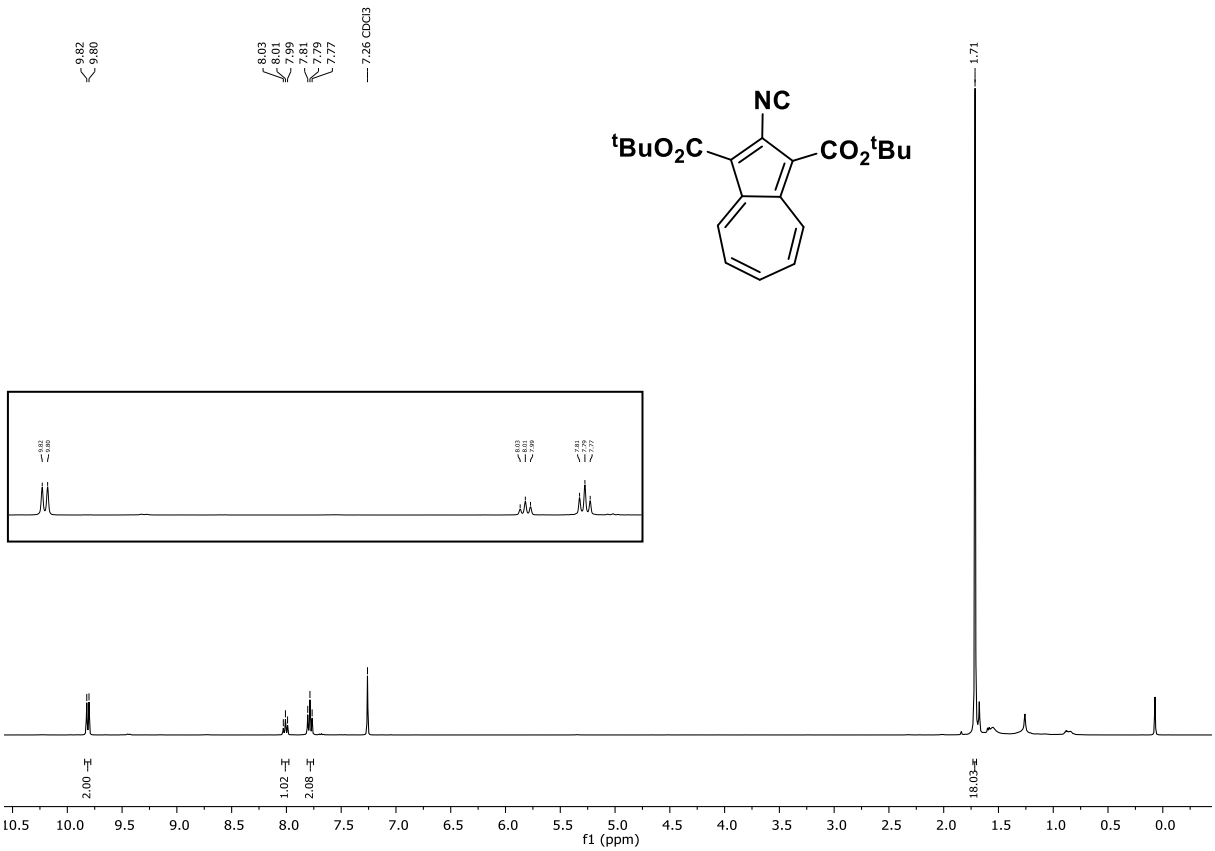


Figure S13: ^{1}H NMR of **5** in $CDCl_3$

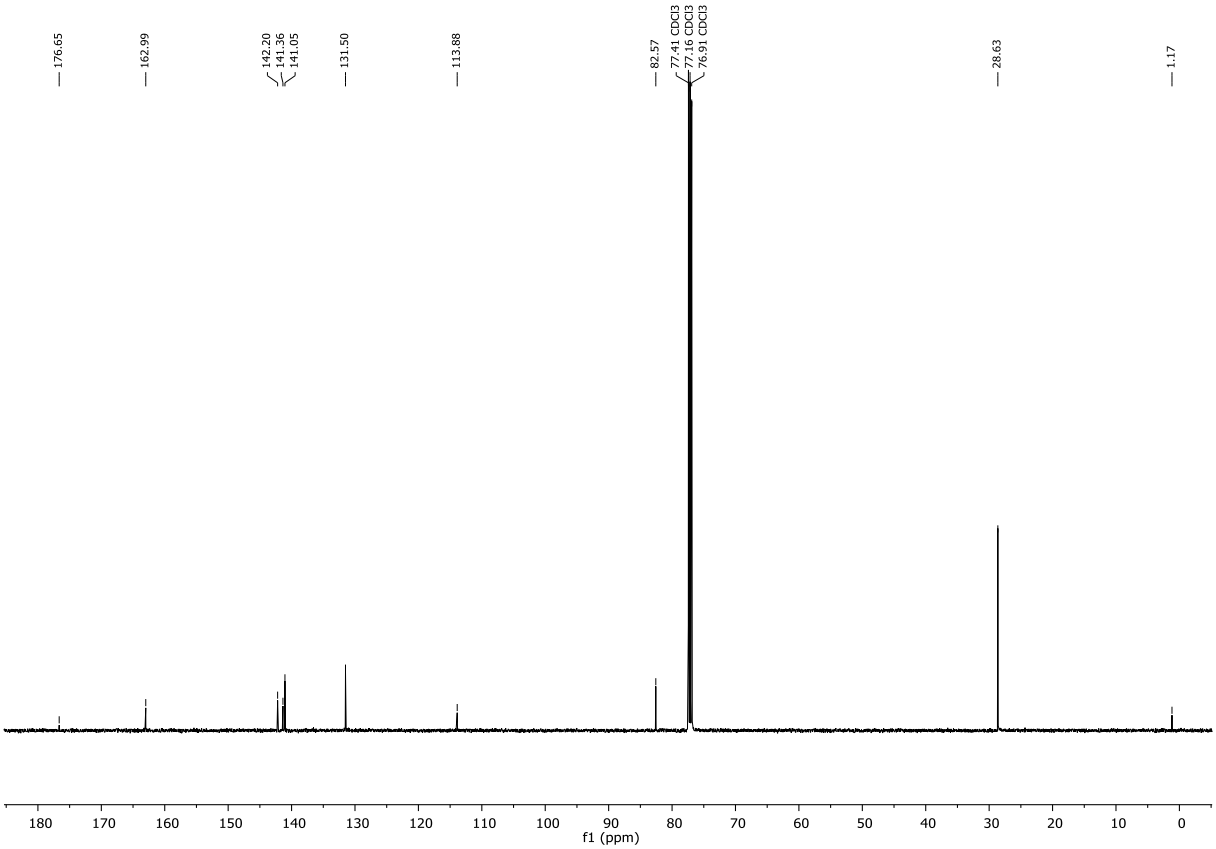


Figure S14: ^{13}C NMR of **5** in $CDCl_3$

Infrared Spectra

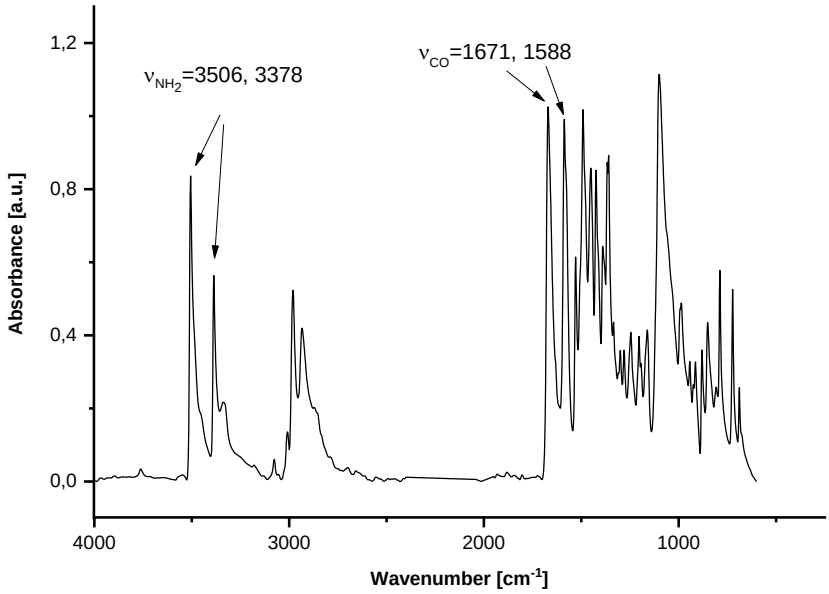


Figure S15*:* IR Spectrum of **3**

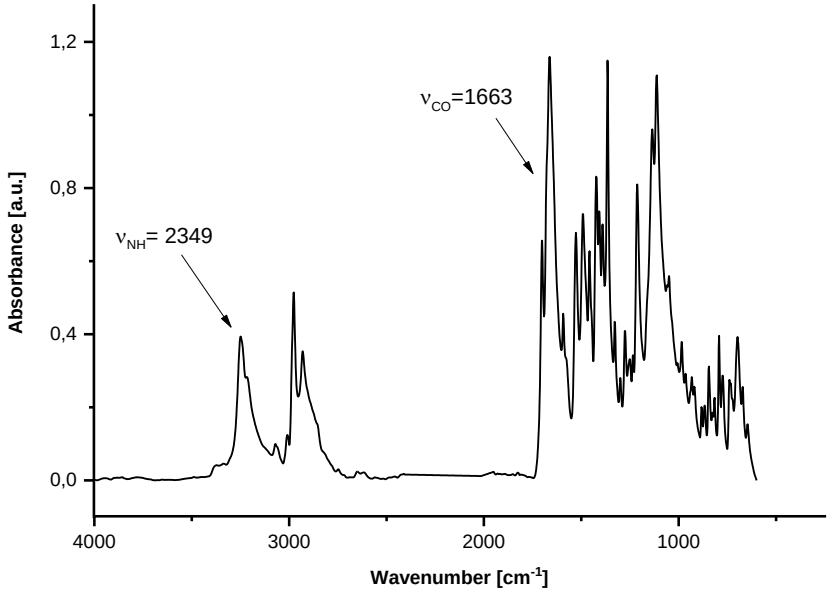


Figure S16: IR Spectrum of **4**

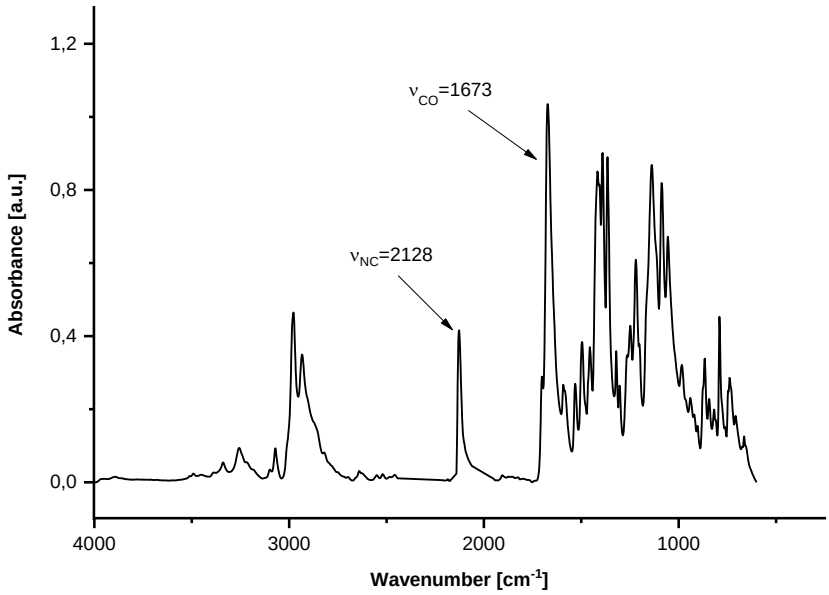


Figure S17: IR Spectrum of **5**