

## Molecular solar thermal systems – control of light harvesting and energy storage by protonation/deprotonation

Martin Drøhse Kilde,<sup>†</sup> Paloma Garcia Arroyo,<sup>†</sup> Anders S. Gertsen,<sup>†,‡</sup> Kurt V. Mikkelsen and Mogens Brøndsted Nielsen<sup>\*</sup>

*Department of Chemistry, University of Copenhagen, Universitetsparken 5,  
DK-2100 Copenhagen Ø, Denmark. E-mail: mbn@chem.ku.dk*

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<sup>†</sup> These authors contributed equally to the article.

<sup>‡</sup> Present address: Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

## SUPPORTING INFORMATION

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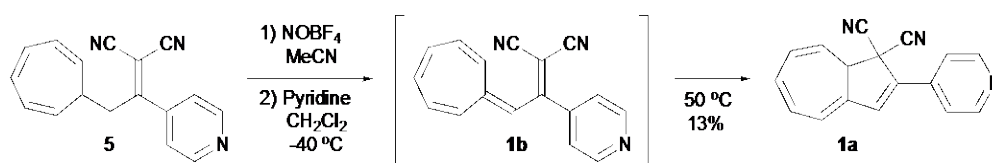
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## General methods – Synthesis and characterization

All air and moisture sensitive reactions were carried out under an inert atmosphere (either nitrogen or argon gas). All handling of photochromic compounds was done in the dark. Purification by column chromatography was carried out on silica gel (flash column, SiO<sub>2</sub> 40-63 μm; dry column, SiO<sub>2</sub> 15-40 μm). For purification of DHA compounds, all glassware was wrapped in tin foil to exclude compounds from light. Thin-layer chromatography (TLC) was carried out on commercially available precoated plates (silica 60) with fluorescence indicator; color change from yellow to red upon irradiation with UV light (365 nm, not 254 nm) indicated the presence of a DHA. All TLC analyses of DHA compounds were run in the dark by covering the TLC jar. NMR spectra were recorded either on a 500 or 300 MHz instrument. The residual solvent peak (CHCl<sub>3</sub> δ<sub>H</sub> = 7.26 ppm, δ<sub>C</sub> = 77.16 ppm) was used for calibration. Chemical shift values are referenced to the ppm scale and coupling constants are expressed in Hertz. High resolution mass spectrometry (HRMS) were recorded on a MALDI-FT-ICR instrument equipped with a 7 T magnet, using dithranol as the matrix. All melting points are uncorrected. UV-Vis absorption measurements were performed in a 1 cm path-length cuvette. Absorption data for the VHF compounds were obtained after light-induced ring opening of the corresponding DHAs using a UV lamp (365 nm). For some spectroscopic measurements a cryostat was placed inside the UV-Vis spectrophotometer, which kept the cuvette at low temperatures using liquid nitrogen. The neat solvent was used as baseline. Fluorescence spectroscopy measurements were performed with a Fluotime 300 (PicoQuant) instrument.

## Synthesis protocols

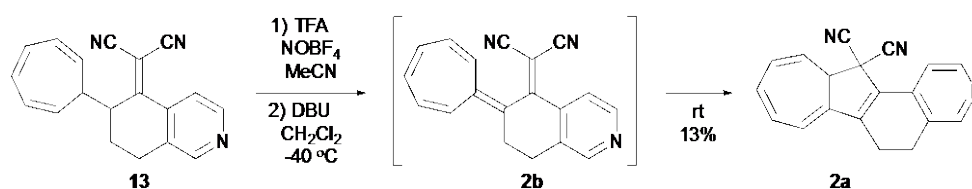
### 2-(Pyridin-4-yl)azulene-1,1(8aH)-dicarbonitrile (**1a**)



To a solution of **5** (300 mg, 1.15 mmol) in dry MeCN (20 mL) at -40 °C under an Ar atmosphere, NOBF<sub>4</sub> (287 mg, 2.45 mmol) was added. The solution turned reddish, and it was stirred for 45 min. The reaction mixture was diluted with dry CH<sub>2</sub>Cl<sub>2</sub> (45 mL), and then a 0 °C solution of pyridine (0.2 mL, 2.3 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise. The reaction mixture was stirred for an additional 3 h, whereupon it turned brownish. The solution was then excluded from light and heated to 50 °C until full conversion to DHA was observed by TLC. The reaction mixture was quenched with H<sub>2</sub>O (50 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL), dried with MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. Purification by flash column

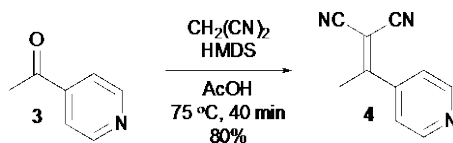
chromatography 1) (SiO<sub>2</sub> 40 – 63 μm, 40% EtOAc/heptane, loading: CH<sub>2</sub>Cl<sub>2</sub>), 2) (SiO<sub>2</sub> 40 – 63 μm, 40% EtOAc/toluene, loading: CH<sub>2</sub>Cl<sub>2</sub>), afforded **1a** as an orange solid (45 mg, 13%). TLC: *R<sub>f</sub>* = 0.32 (40% EtOAc/toluene). M.p.: 112.4 – 114 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.75 (d, *J* = 5.5 Hz, 2H), 7.59 – 7.57 (m, 2H), 7.09 (s, 1H), 6.63 – 6.59 (m, 1H), 6.56 (dd, *J* = 11.1, 6.0 Hz, 1H), 6.46 (d, *J* = 6.0 Hz, 1H), 6.34 (ddd, *J* = 10.2, 6.0, 2.1 Hz, 1H), 5.83 (dd, *J* = 10.2, 3.8 Hz, 1H), 3.81 (ddd, *J* = 6.0, 3.8, 2.1 Hz, 1H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 150.99, 137.76, 137.62, 137.48, 136.18, 132.41, 130.86, 128.02, 123.46, 120.01, 119.75, 114.67, 112.31, 51.01, 44.83 ppm. HR-MS (MALDI<sup>+</sup> FT-ICR, dithranol): *m/z* 258.10350 [M+H<sup>+</sup>], calcd. for [C<sub>17</sub>H<sub>12</sub>N<sub>3</sub><sup>+</sup>]: 258.10257.

### 5,11a-Dihydroazuleno[2,1-f]isoquinoline-12,12(6H)-dicarbonitrile (**2a**)



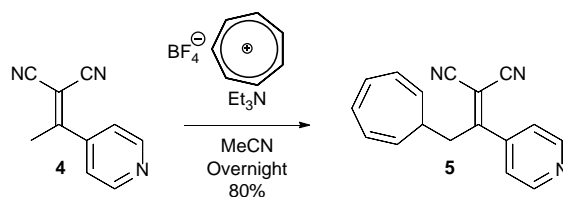
To a solution of **13** (100 mg, 0.35 mmol) in dry MeCN (10 mL) at -40 °C under an Ar atmosphere, TFA (0.05 mL, 0.70 mmol) was added. The solution was stirred for 10 min, and then NOBF<sub>4</sub> (128 mg, 1.10 mmol) was added. The starting pale yellow solution was stirred for 30 min, whereupon it turned darker, and it was allowed to reach rt. After additional 30 min, the reaction mixture was diluted with dry and cold CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and then a 0 °C solution of DBU (0.21 mL, 1.40 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added dropwise at -40 °C. After 30 min, the cold bath was removed, and the reaction mixture was stirred at rt for 1 h while the reaction vessel was excluded from light. The reaction mixture was quenched with H<sub>2</sub>O (30 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 30 mL), dried with MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (SiO<sub>2</sub> 40 – 63 μm, 60% EtOAc/toluene, loading: CH<sub>2</sub>Cl<sub>2</sub>) afforded **2a** as a yellow solid (13 mg, 13%). TLC: *R<sub>f</sub>* = 0.32 (60% EtOAc/toluene). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.64 (d, *J* = 5.0 Hz, 1H), 8.53 (s, 1H), 7.38 (d, *J* = 5.0 Hz, 1H), 6.66 (dd, *J* = 11.2, 6.3 Hz, 1H), 6.60 (dd, *J* = 11.2, 6.0 Hz, 1H), 6.40 (d, *J* = 6.3 Hz, 1H), 6.38 – 6.35 (m, 1H), 5.86 (dd, *J* = 10.2, 3.9 Hz, 1H), 3.81 – 3.78 (ddd, *J* = 6.0, 3.9, 1.9 Hz, 1H), 3.03 (t, *J* = 8.2 Hz, 2H), 2.74 (dt, *J* = 17.1, 8.2 Hz, 1H), 2.66 (dt, *J* = 17.1, 8.2 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 149.56, 148.94, 147.58, 137.54, 135.21, 132.40, 131.85, 130.75, 129.92, 127.86, 120.41, 120.03, 116.53, 114.58, 112.38, 50.98, 42.35, 23.90, 21.24 ppm. HR-MS (MALDI<sup>+</sup> FT-ICR, dithranol): *m/z* 284.11960 [M+H<sup>+</sup>], calcd. for [C<sub>19</sub>H<sub>14</sub>N<sub>3</sub><sup>+</sup>]: 284.11822.

### 2-(1-(Pyridin-4-yl)ethylidene)malononitrile (4)



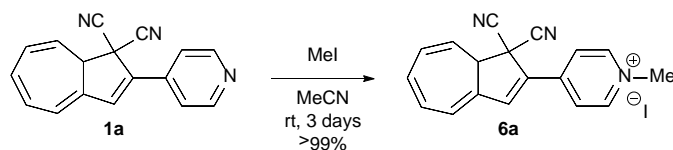
To a solution of 4-acetylpyridine **3** (5.00 g, 41.3 mmol) in AcOH (50 mL), HMDS (10.7 mL, 49.5 mmol) and malononitrile (5.50 g, 83.3 mmol) were added. The solution was then stirred at 75 °C for 40 min. The reaction mixture was quenched with a sat. aq. solution of NaHCO<sub>3</sub> (20 mL) and H<sub>2</sub>O (20 mL), and the aq. phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL). The combined organic extracts were washed with H<sub>2</sub>O (3 x 50 mL), dried with MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to afford **4** (5.58 g, 80%, with minor impurities) without further purification (purification by chromatography was not possible due to instability of **4**). TLC: *R<sub>f</sub>* = 0.13 (50% EtOAc/heptane). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.81 (dd, *J* = 4.5, 1.7 Hz, 2H), 7.40 (dd, *J* = 4.5, 1.7 Hz, 2H), 2.62 (s, 3H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 176.58, 150.47, 143.85, 121.24, 111.70, 111.62, 87.90, 24.08 ppm. HR-MS (MALDI<sup>+</sup> FT-ICR, dithranol): *m/z* 170.07159 [M+H<sup>+</sup>], calcd. for [C<sub>10</sub>H<sub>8</sub>N<sub>3</sub><sup>+</sup>]: 170.07127.

### 2-(2-(Cyclohepta-2,4,6-trien-1-yl)-1-(pyridin-4-yl)ethylidene)malononitrile (5)



To a solution of **4** (6.00 g, 35.5 mmol) in MeCN (50 mL), a suspension of finely divided tropylium tetrafluoroborate (6.31 g, 35.5 mmol) and Et<sub>3</sub>N (4.93 mL, 35.5 mmol) was added. The reaction mixture was stirred overnight at rt under Ar atmosphere. Then a sat. aq. solution of NH<sub>4</sub>Cl (60 mL) was added, and the mixture was filtered through a sintered glass funnel. The aq. phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL), and the combined organic extracts were washed with H<sub>2</sub>O (3 x 50 mL) and brine (3 x 50 mL), dried with MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. Purification by dry column vacuum chromatography (SiO<sub>2</sub> 15 – 40 μm, EtOAc/heptane, 0 – 100% 10% steps, 50 mL fractions) afforded **5** (7.36 g, 80%) as a brown oil. TLC: *R<sub>f</sub>* = 0.44 (40% EtOAc/toluene). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.77 (dd, *J* = 4.4, 1.7 Hz, 2H), 7.24 (dd, *J* = 4.4 1.7 Hz, 2H), 6.63 – 6.62 (m, 2H), 6.24 – 6.23 (m, 1H), 6.22 – 6.21 (m, 1H), 5.14 (dd, *J* = 9.2, 6.5 Hz, 2H), 3.14 (d, *J* = 8.0 Hz, 2H), 2.01 – 1.95 (m, 1H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 175.23, 150.99, 142.42, 131.37, 126.90, 122.36, 121.06, 111.60, 111.54, 89.04, 38.60, 37.40 ppm. HR-MS (MALDI<sup>+</sup> FT-ICR, dithranol): *m/z* 260.11876 [M+H<sup>+</sup>], calcd. for [C<sub>17</sub>H<sub>14</sub>N<sub>3</sub><sup>+</sup>]: 260.11822.

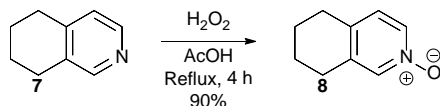
#### 4-(1,1-Dicyano-1,8a-dihydroazulen-2-yl)-1-methylpyridin-1-ium iodide (**6a**)



To a solution of **1a** (50 mg, 0.2 mmol) in MeCN (5 mL), iodomethane (0.1 mL, 1.6 mmol) was added. The solution was stirred at rt for 3 days under an Ar atmosphere, until no starting material could be detected (according to TLC). The solution was concentrated *in vacuo* to afford **6a** in quantitative yield (53 mg, >99%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN): δ 8.66 (d, *J* = 6.9, 2H), 8.23 (d, *J* = 6.9, 2H), 7.80 (s, 1H), 6.80 – 6.79 (m, 1H), 6.71 – 6.69 (m, 2H), 6.43 – 6.41 (m, 1H), 5.85 (dd, *J* = 10.2, 3.3 Hz, 1H), 4.28 (s, 3H), 4.00 – 3.99 (m, 1H) ppm. <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN): δ 146.77, 146.64, 145.94, 138.19, 135.11, 133.71, 131.59, 129.09, 128.79, 124.42, 121.55, 114.84, 112.86, 51.59, 48.84, 45.46. HR-MS (MALDI<sup>+</sup> FT-ICR, dithranol): *m/z* 136.06005 [M-I]<sup>2+</sup>, calcd. for [C<sub>16</sub>H<sub>14</sub>N<sub>3</sub><sup>2+</sup>]: 136.05884.

#### 5,6,7,8-Tetrahydroisoquinoline-*N*-oxide (**8**)

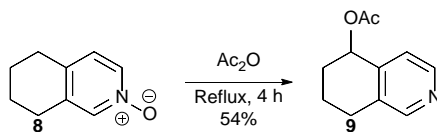
– prepared according to literature protocol (C.-Y. Cheng, L.-W. Hsin and J.-P. Liou, *Tetrahedron*, 1996, **52**, 10935).



To a solution of **7** (25 mL, 0.19 mol) in AcOH (20 mL), H<sub>2</sub>O<sub>2</sub> (63 mL, 0.88 mol) was added. The yellow reaction mixture was stirred under reflux for 4 h, whereupon it turned colorless. The reaction mixture was cooled to rt and concentrated *in vacuo* to ca. half of the starting volume. H<sub>2</sub>O (50 mL) was added, and the solution was concentrated again *in vacuo* until ca. half volume. After that, CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added, and the solution was neutralized with K<sub>2</sub>CO<sub>3</sub>, filtered, and concentrated *in vacuo* to afford **8** (26 g, 90%) as a white solid that was sufficiently pure for further reactions. TLC: *R<sub>f</sub>* = 0.33 (70% EtOAc/Heptane). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.02 (s, 1H), 7.98 (d, *J* = 6.6 Hz, 1H), 6.93 (d, *J* = 6.6 Hz, 1H), 2.65 – 2.61 (m, 4H), 1.73 – 1.72 (m, 4H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 139.28, 138.54, 136.19, 136.13, 126.06, 27.91, 26.22, 21.93, 21.6 ppm. HR-MS (MALDI<sup>+</sup> FT-ICR, dithranol): *m/z* 150.09238 [M+H<sup>+</sup>], calcd. for [C<sub>17</sub>H<sub>12</sub>N<sub>3</sub><sup>+</sup>]: 150.09134.

### 5-Acetoxy-5,6,7,8-tetrahydroisoquinoline (9)

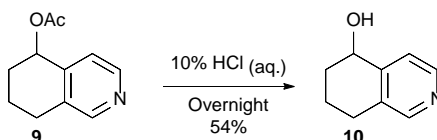
– prepared according to literature protocol (C.-Y. Cheng, L.-W. Hsin and J.-P. Liou, *Tetrahedron*, 1996, **52**, 10935).



A solution of **8** (24.0 g, 0.161 mol) in Ac<sub>2</sub>O (39 mL) was added dropwise to boiling Ac<sub>2</sub>O (150 mL). After complete addition of **8**, the reaction mixture was stirred under reflux for 4 h. Then the solution was concentrated *in vacuo*, and the resulting dark residue was distilled (122 °C, 0.5 mbar) to afford a racemic mixture of **9** (16.5 g, 54%) sufficiently pure for further reactions. TLC: *R*<sub>f</sub> = 0.37 (80% EtOAc/heptane). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.41 (s, 1 H), 8.37 (d, *J* = 5.1 Hz, 1H), 7.20 (d, *J* = 5.1 Hz, 1H), 5.92 (t, *J* = 5.1 Hz, 1H), 2.82 – 2.73 (m, 2 H), 2.11 (s, 3 H), 1.85 – 1.99 (m, 4H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.59, 150.47, 147.06, 143.39, 133.10, 122.79, 68.67, 28.54, 25.78, 21.28, 18.86 ppm. HR-MS (MALDI<sup>+</sup> FT-ICR, dithranol): *m/z* 192.10193 [M+H<sup>+</sup>], calcd. for [C<sub>11</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup>]: 192.10191.

### 5,6,7,8-Tetrahydroisoquinolin-5-ol (10)

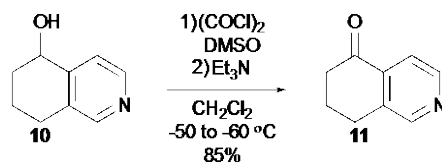
– prepared according to literature protocol (J. Epszajn and B. Bienik, *J. Chem. Soc., Perkin Trans 1*, 1985, 213).



A mixture of **9** (12.5 g, 65.4 mmol) in 10% aq. HCl (10.9 mL) was refluxed overnight, whereupon the reaction mixture turned orange. Then, the solution was basified with a sat. aq. solution of Na<sub>2</sub>CO<sub>3</sub>, and the aq. phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 50 mL). The combined organic extracts were dried with MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (SiO<sub>2</sub> 40 – 63 μm, 80% EtOAc/heptane, loading: CH<sub>2</sub>Cl<sub>2</sub>), afforded a racemic mixture of **10** (5.29 g, 54%) as a white solid. TLC: *R*<sub>f</sub> = 0.18 (80% EtOAc/heptane). M.p.: 82.5 – 84.5 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.41 (d, *J* = 5.1 Hz, 1H), 8.37 (s, 1H), 7.37 (d, *J* = 5.1 Hz, 1H), 4.75 – 4.73 (m, 1H), 2.84 – 2.70 (m, 3H), 2.13 – 2.09 (m, 1H), 2.03 – 1.98 (m, 1H), 1.85 – 1.81 (m, 2H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 150.53, 147.53, 147.36, 122.32, 67.66, 32.28, 26.14, 19.27 ppm; one signal is missing, presumably due to overlap. HR-MS (MALDI<sup>+</sup> FT-ICR, dithranol): *m/z* 150.09165 [M+H<sup>+</sup>], calcd. for [C<sub>9</sub>H<sub>12</sub>NO<sup>+</sup>]: 150.09134.

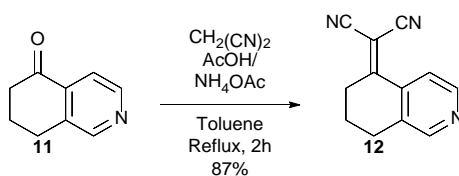
### 7,8-Dihydroisoquinolin-5(6H)-one (**11**)

– prepared according to literature protocol (D. R. Boyd, R. J. H. Davies, L. Hamilton and J. J. McCullough, *J. Chem. Soc.*, 1992, 31).



To a solution of oxalyl dichloride (2.90 mL, 33.8 mmol) in  $\text{CH}_2\text{Cl}_2$  (145 mL) under an Ar atmosphere at  $-50/-60$  °C, a solution of DMSO (5.00 mL, 70.4 mmol) in  $\text{CH}_2\text{Cl}_2$  (18 mL) was added, and the mixture was stirred for 15 min. Then, a solution of **10** (5.01 g, 33.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (36 mL) was added. The reaction mixture was stirred for 20 min at  $-50/-60$  °C, whereupon it turned yellow.  $\text{Et}_3\text{N}$  (23.4 mL, 168 mmol) was added, and the resulting thick mixture was stirred for additional 1.5 h and voluntarily allowed to warm to rt.  $\text{H}_2\text{O}$  (200 mL) was added, and the aq. phase was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 100 mL). The combined organic extracts were dried with  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. Purification by flash column chromatography ( $\text{SiO}_2$  40 – 63  $\mu\text{m}$ , 60% EtOAc/heptane, loading:  $\text{CH}_2\text{Cl}_2$ ) afforded **11** (4.18 g, 85%) as an orange solid. TLC:  $R_f = 0.19$  (50% EtOAc/heptane). M.p.: 42.5 – 44 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.67 (s, 1H), 8.62 (d,  $J = 5.0$  Hz, 1H), 7.75 (d,  $J = 5.0$  Hz, 1H), 2.98 (t,  $J = 6.2$  Hz, 2H), 2.72 – 2.70 (m, 2H), 2.20 (p,  $J = 6.2$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.80, 151.49, 148.71, 137.75, 137.61, 119.19, 39.24, 26.42, 23.05 ppm. HR-MS (MALDI<sup>+</sup> FT-ICR, dithranol):  $m/z$  148.07671 [ $\text{M}+\text{H}^+$ ], calcd. for [ $\text{C}_9\text{H}_{10}\text{NO}^+$ ]: 148.07569.

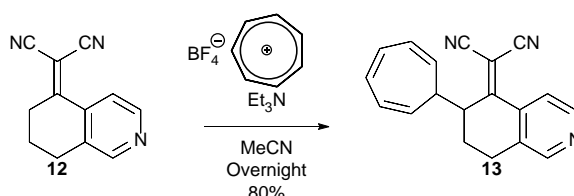
### 2-(7,8-Dihydroisoquinolin-5(6H)-ylidene)malononitrile (**12**)



To a solution of **11** (450 mg, 3.06 mmol) and malononitrile (404 mg, 6.12 mmol) in toluene (35 mL),  $\text{NH}_4\text{OAc}$  (471 mg, 6.12 mmol) and AcOH (0.52 mL, 9.17 mmol) were added, and the reaction mixture was stirred under reflux for 2 h, whereupon it turned reddish. Then, the aq. phase was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 50 mL), washed with  $\text{H}_2\text{O}$  (3 x 50 mL) and brine (3 x 50 mL), dried with  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. Purification by flash column chromatography ( $\text{SiO}_2$  40 – 63  $\mu\text{m}$ , 60% EtOAc/heptane, loading:  $\text{CH}_2\text{Cl}_2$ ) afforded **12** (522 mg, 87%) as a dark orange solid. Compound **12** can be recrystallized from boiling 96% EtOH. TLC:  $R_f = 0.16$  (60% EtOAc/heptane). M.p.: 71.6 – 73 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.66 (s, 1H), 8.66 (d,  $J = 5.4$  Hz, 1H), 8.02 (d,  $J = 5.4$  Hz, 1H), 3.08 – 3.05 (m, 2H), 2.92 (t,  $J = 6.4$  Hz, 2H), 2.08

(p,  $J = 6.4$  Hz, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.73, 148.67, 119.95, 112.88, 112.46, 32.73, 26.57, 22.13 ppm; four signals missing presumably due to overlap. HR-MS (MALDI<sup>+</sup> FT-ICR, dithranol):  $m/z$  196.08694 [ $\text{M}+\text{H}^+$ ], calcd. for  $[\text{C}_{12}\text{H}_{10}\text{N}_3^+]$ : 196.08692.

### 2-(6-(Cyclohepta-2,4,6-trien-1-yl)-7,8-dihydroisoquinolin-5(6H)-ylidene)malononitrile (**13**)



To a solution of **12** (460 mg, 2.36 mmol) in MeCN (40 mL) under an Ar atmosphere, tropylium tetrafluoroborate (422 mg, 2.36 mmol) and  $\text{Et}_3\text{N}$  (0.33 mL, 2.36 mmol) were added. The reaction mixture was stirred overnight at rt, whereupon a sat. aq. solution of  $\text{NH}_4\text{Cl}$  (70 mL) was added to the resulting brownish reaction mixture. Then, the aq. phase was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 50 mL), and the combined organic extracts were washed with  $\text{H}_2\text{O}$  (3 x 50 mL) and brine (3 x 50 mL), dried with  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. Purification by flash column chromatography ( $\text{SiO}_2$  40 – 63  $\mu\text{m}$ , 50% EtOAc/heptane, loading:  $\text{CH}_2\text{Cl}_2$ ) afforded **13** (536 mg, 80%) as an orange solid. TLC:  $R_f = 0.35$  (50% EtOAc/heptane). M.p.: 132.1 – 134 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.59 (d,  $J = 5.4$  Hz, 1H), 8.58 (s, 1H), 7.83 (d,  $J = 5.4$  Hz, 1H), 6.68 – 6.65 (m, 1H), 6.64 – 6.61 (m, 1H), 6.35 (dd,  $J = 5.3$  Hz, 1H), 6.26 (dd,  $J = 5.3$  Hz, 1H), 5.34 – 5.30 (m, 1H), 5.12 (dd,  $J = 9.5, 6.9$  Hz, 1H), 3.49 (dt,  $J = 11.4, 3.7$  Hz, 1H), 2.92 – 2.88 (m, 2H), 2.47 – 2.42 (m, 1H), 2.09 – 2.01 (m, 2H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  174.01, 151.79, 148.42, 135.62, 133.40, 131.60, 130.87, 127.52, 127.31, 121.45, 121.19, 120.72, 112.73, 112.36, 84.52, 41.60, 39.49, 24.69, 21.61 ppm. HR-MS (MALDI<sup>+</sup> FT-ICR, dithranol):  $m/z$  286.13381 [ $\text{M}+\text{H}^+$ ], calcd. for  $[\text{C}_{19}\text{H}_{16}\text{N}_3^+]$ : 286.13387. Elem. anal. calcd. for  $\text{C}_{19}\text{H}_{15}\text{N}_3$ : C: 79.98%, H: 5.30%, N: 14.73%; found: C: 79.40%, H: 5.32%, N: 14.31%.



## NMR spectra

### 2-(Pyridin-4-yl)azulene-1,1-dicarbonitrile (**1a**)

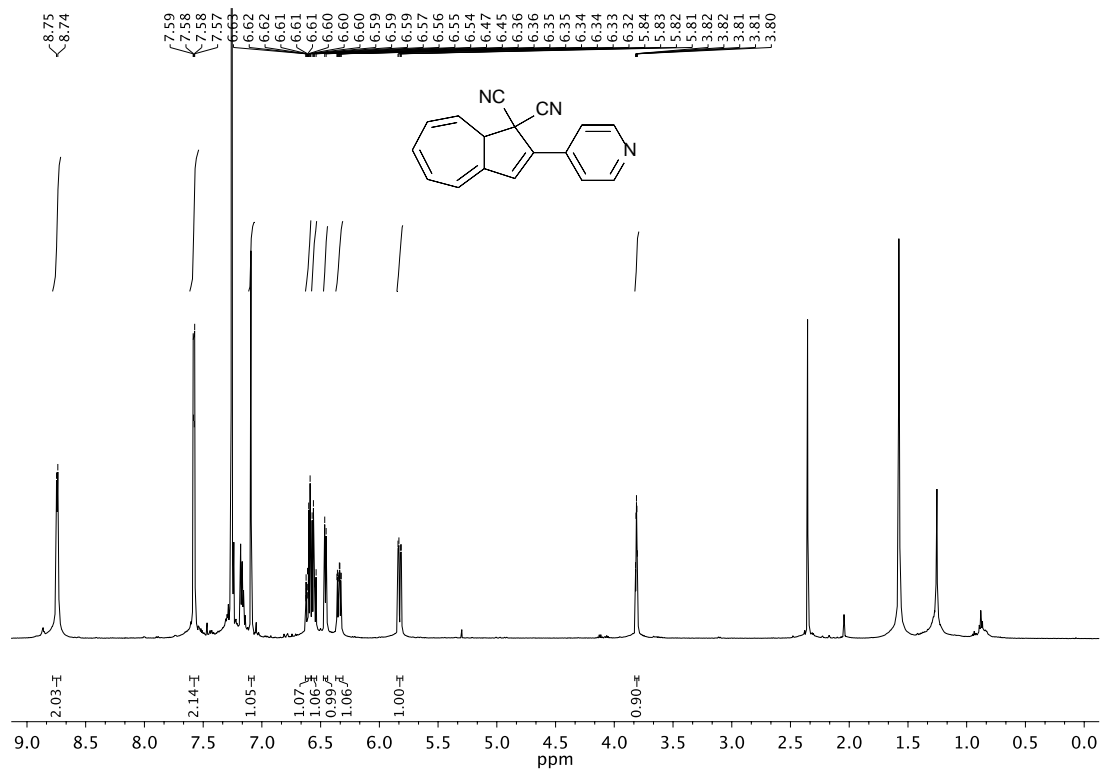


Figure S1:  $^1\text{H-NMR}$  spectrum of **1a** in  $\text{CDCl}_3$  (500 MHz).

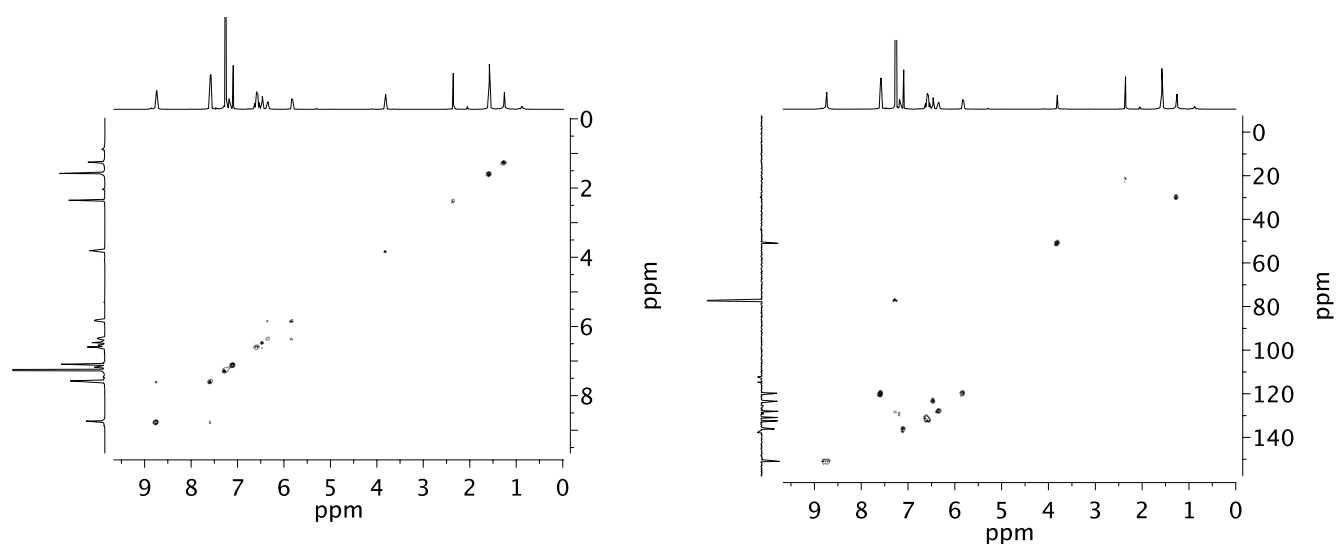


Figure S2: COSY (left) and  $^1\text{H} / ^{13}\text{C}$ -APT HSQC (right) spectra of **1a** in  $\text{CDCl}_3$  (500 / 126 MHz).

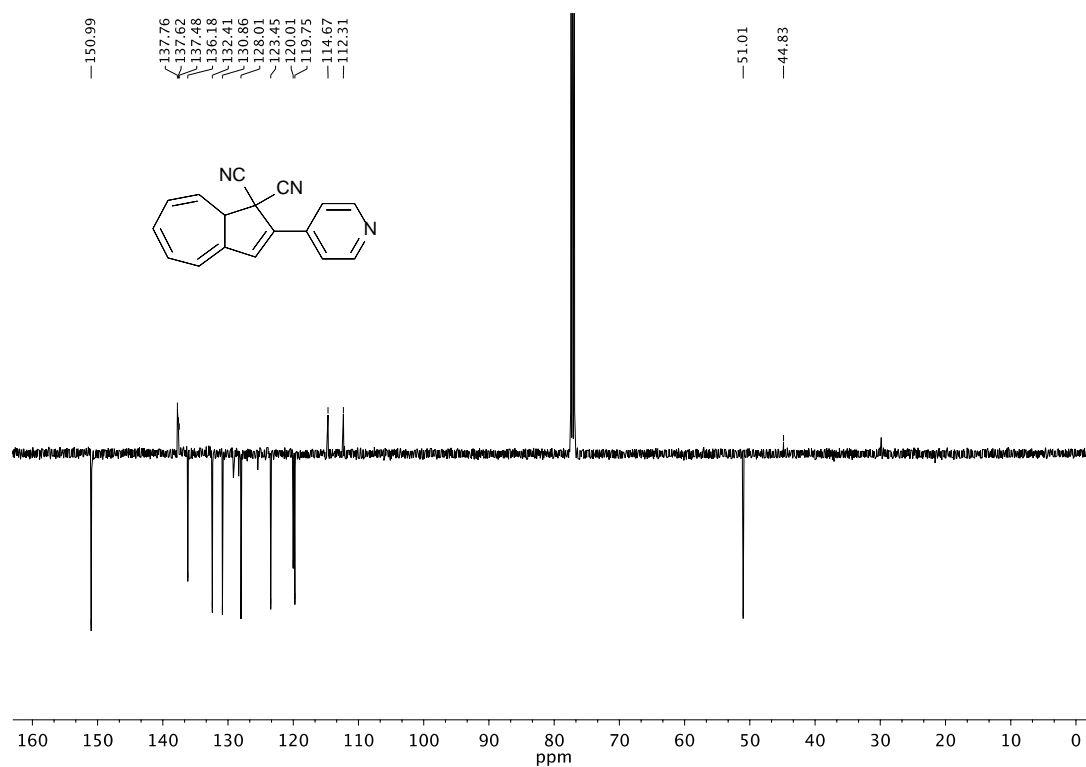


Figure S3: <sup>13</sup>C-APT spectrum of **1a** in CDCl<sub>3</sub> (126 MHz).

**5,11a-Dihydroazuleno[2,1-f]isoquinoline-12,12(6H)-dicarbonitrile (2a)**

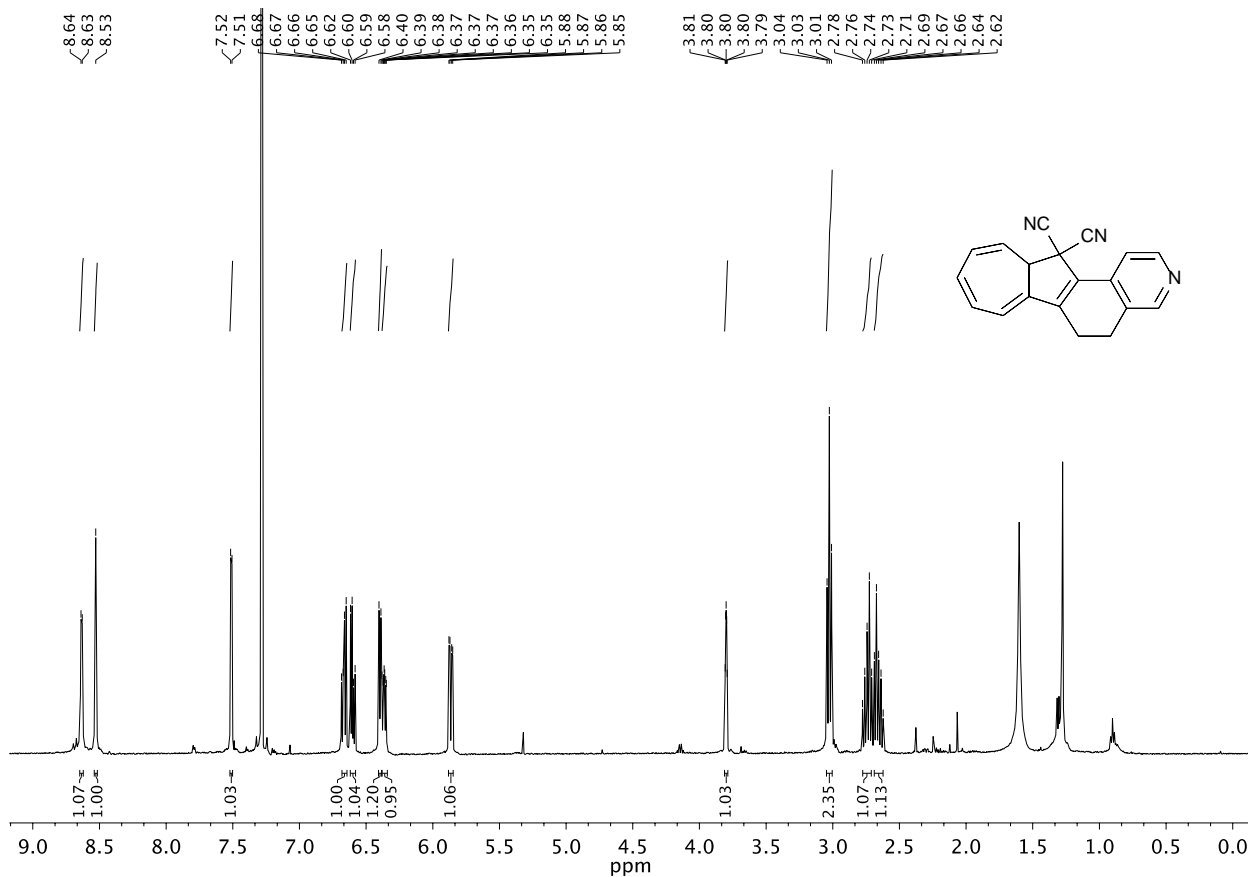


Figure S4: <sup>1</sup>H-NMR spectrum of **2a** in CDCl<sub>3</sub> (500 MHz).

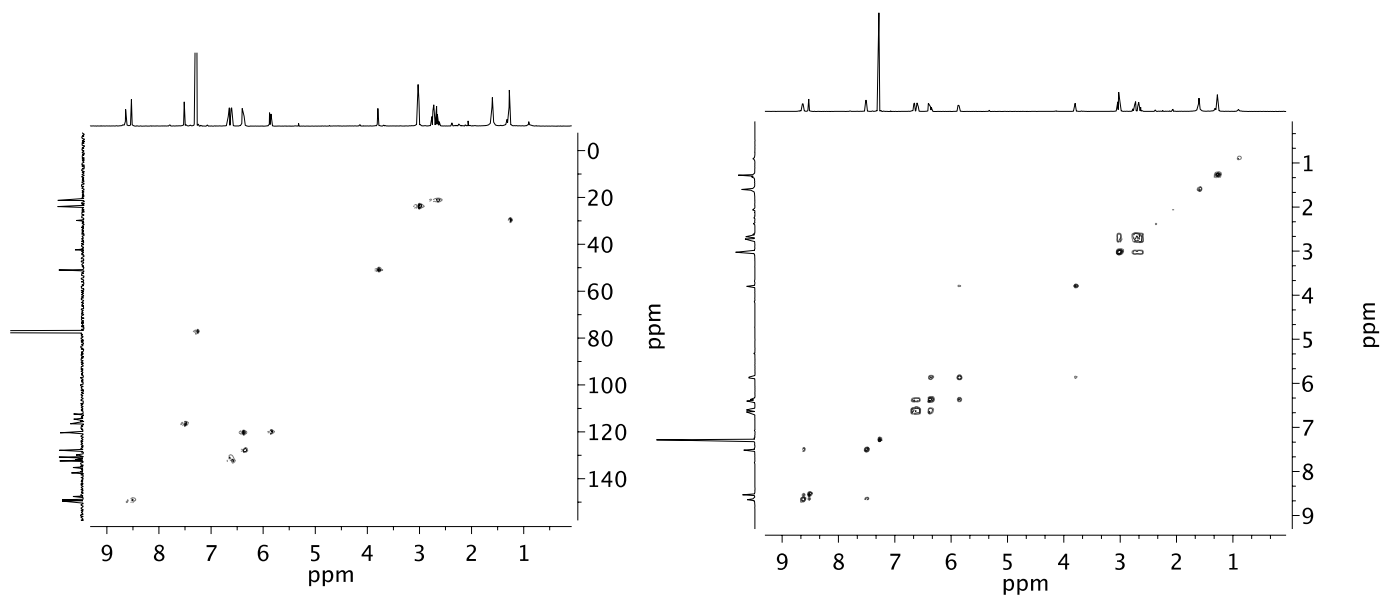


Figure S5: <sup>1</sup>H / <sup>13</sup>C-APT HSQC (left) and COSY (right) spectra of **2a** in CDCl<sub>3</sub> (500 / 126 MHz).

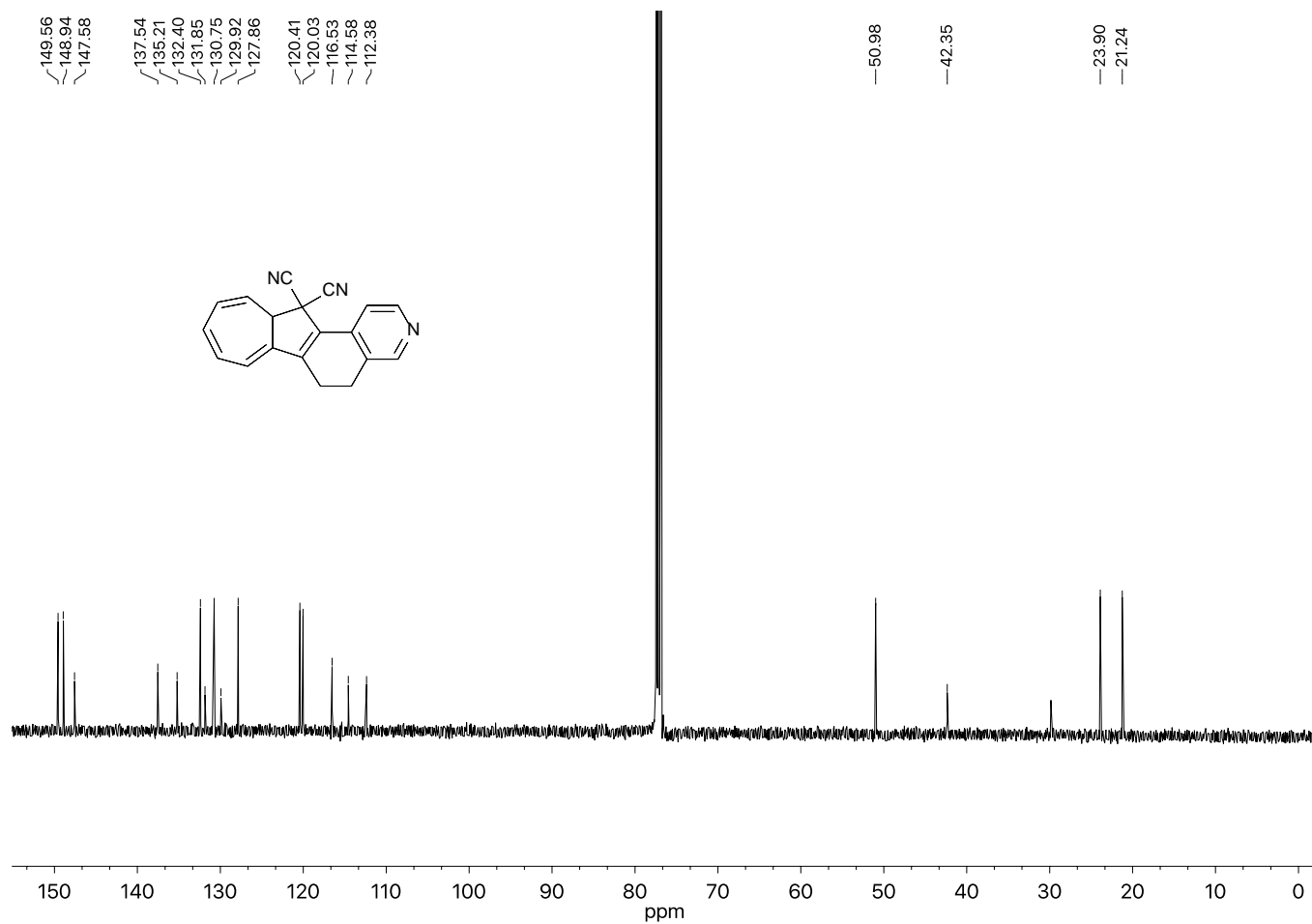


Figure S6:  $^{13}\text{C}$ -APT spectrum of **2a** in  $\text{CDCl}_3$  (126 MHz).

**2-(1-(Pyridin-4-yl)ethylidene)malononitrile (4)**

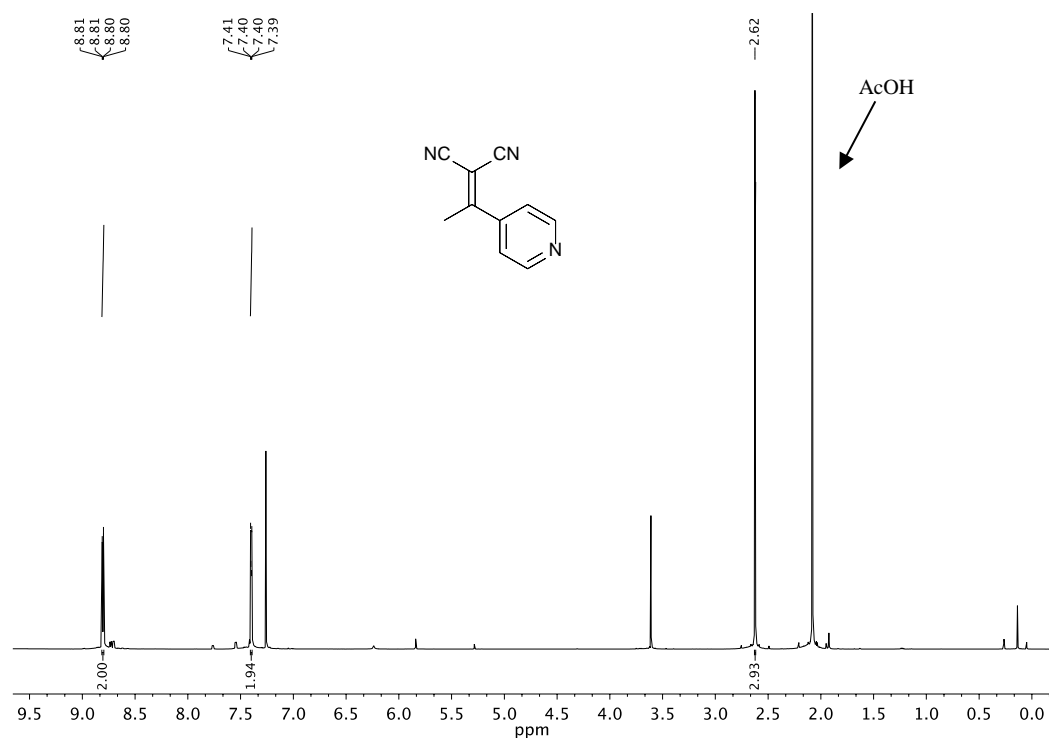


Figure S7: <sup>1</sup>H-NMR spectrum of **4** in CDCl<sub>3</sub> (500 MHz).

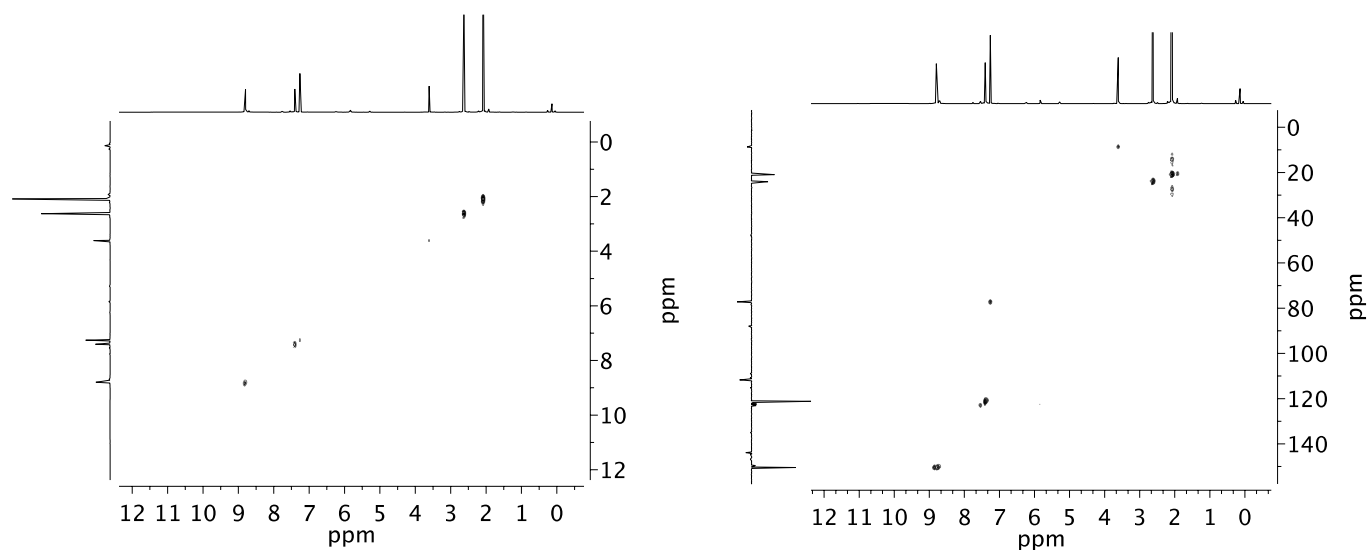


Figure S8: COSY (left) and <sup>1</sup>H / <sup>13</sup>C-APT HSQC (right) spectra of **4** in CDCl<sub>3</sub> (500 / 126 MHz).

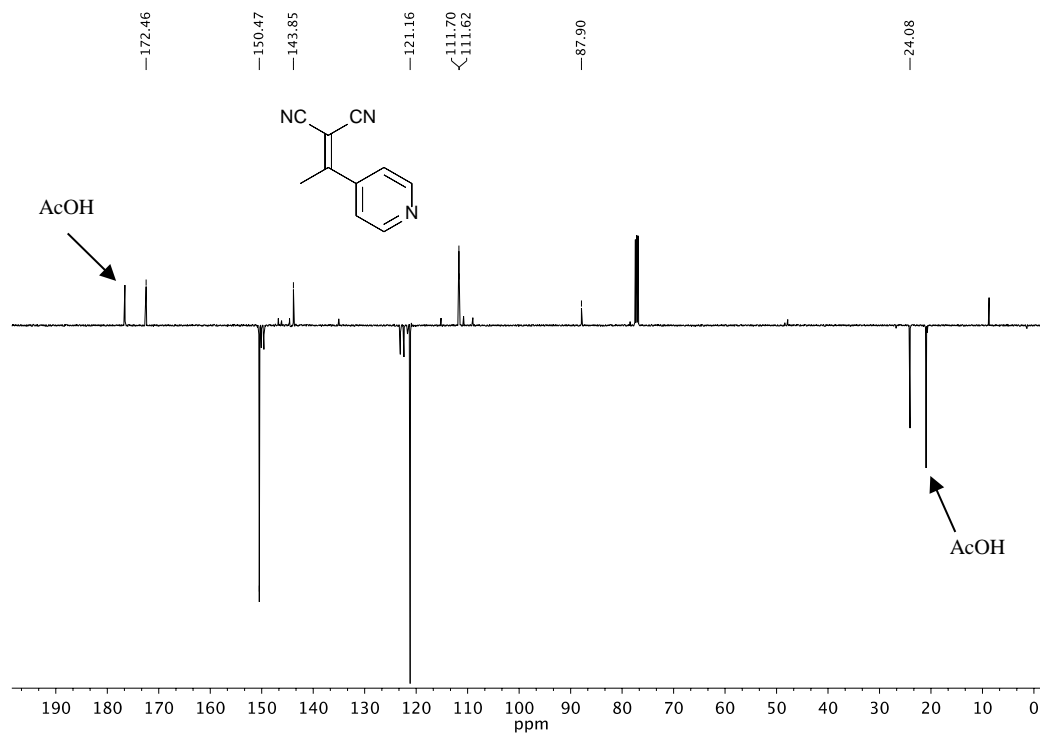


Figure S9: <sup>13</sup>C-APT spectrum of **4** in CDCl<sub>3</sub> (126 MHz).

**2-(2-(Cyclohepta-2,4,6-trien-1-yl)-1-(pyridin-4-yl)ethylidene)malononitrile (5)**

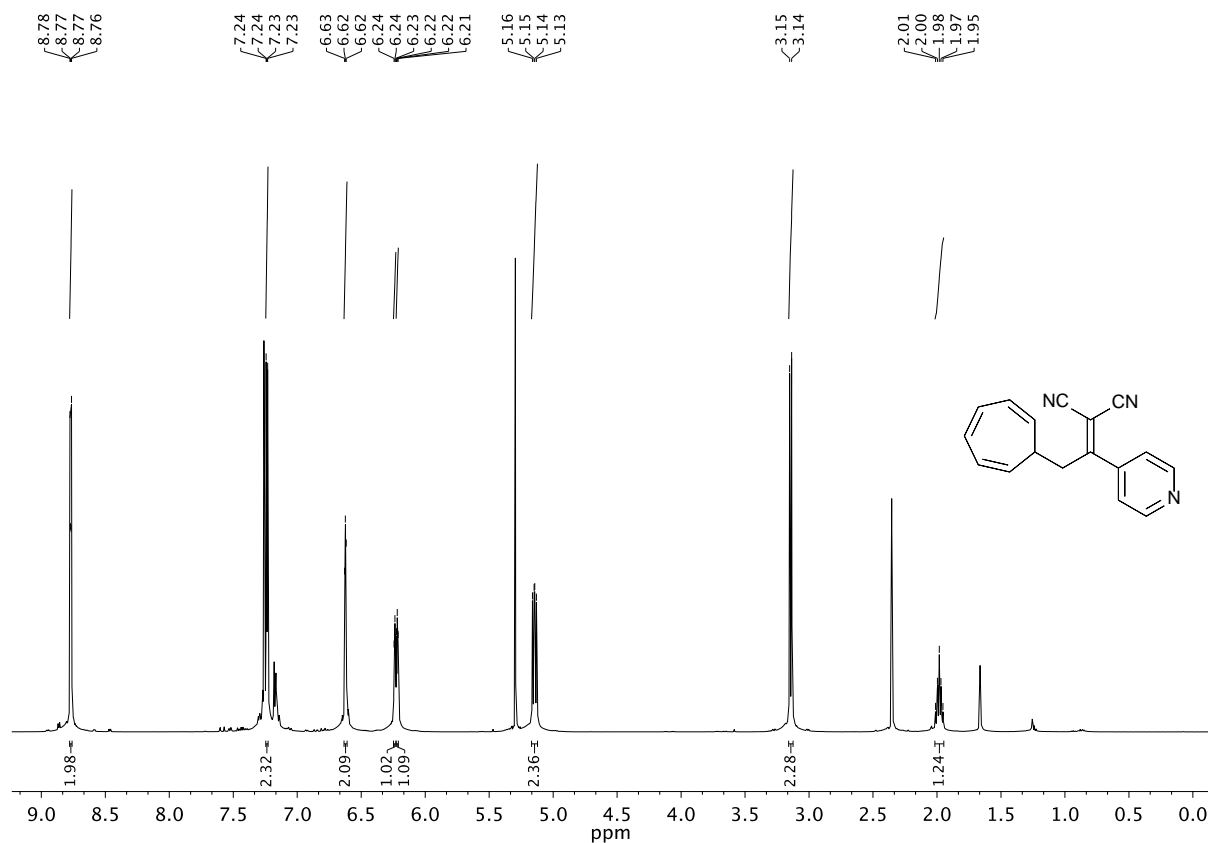


Figure S10:  $^1\text{H}$ -NMR spectrum of **5** in  $\text{CDCl}_3$  (500 MHz).

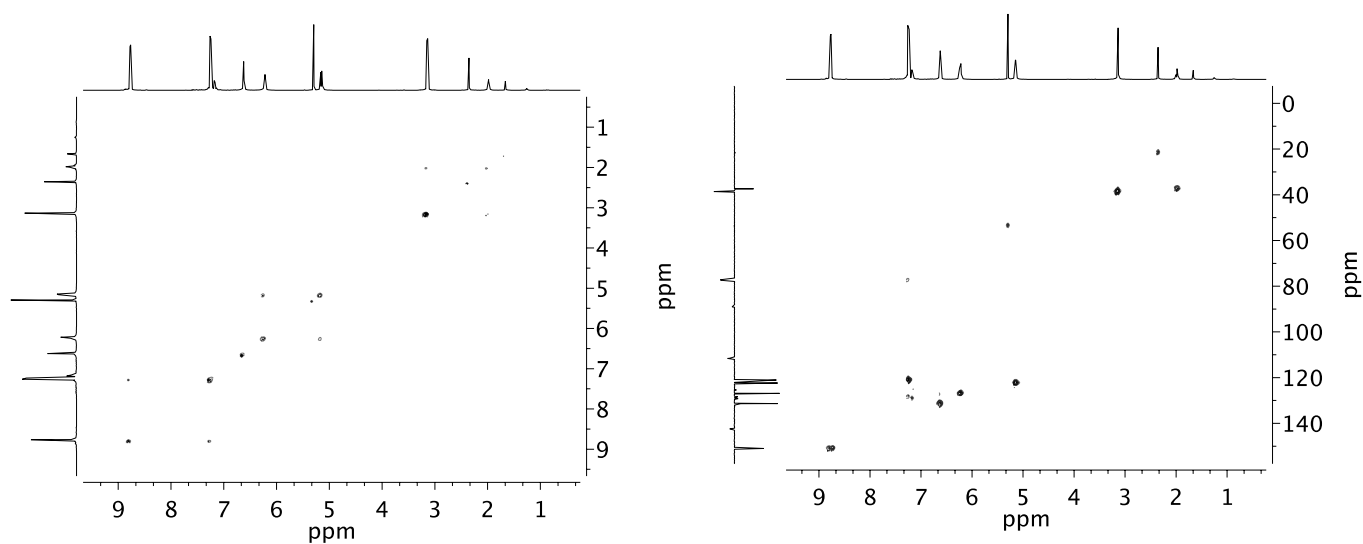


Figure S11: COSY (left) and  $^1\text{H}/^{13}\text{C}$ -APT HSQC (right) spectra of **5** in  $\text{CDCl}_3$  (500 / 126 MHz).

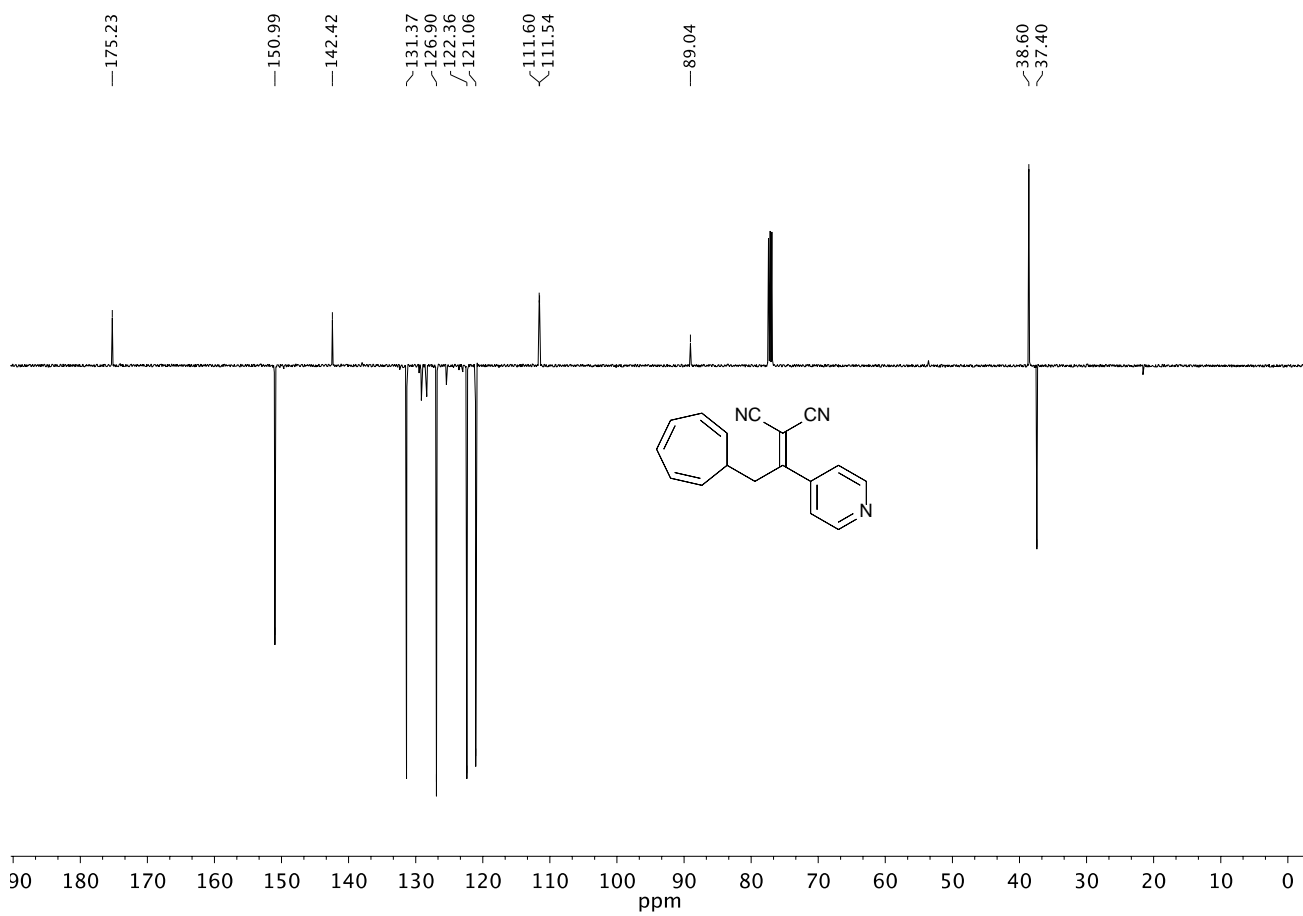


Figure S12:  $^{13}\text{C}$ -APT spectrum of **5** in  $\text{CDCl}_3$  (126 MHz).



**4-(1,1-Dicyano-1,8a-dihydroazulen-2-yl)-1-methylpyridin-1-ium iodide (6a)**

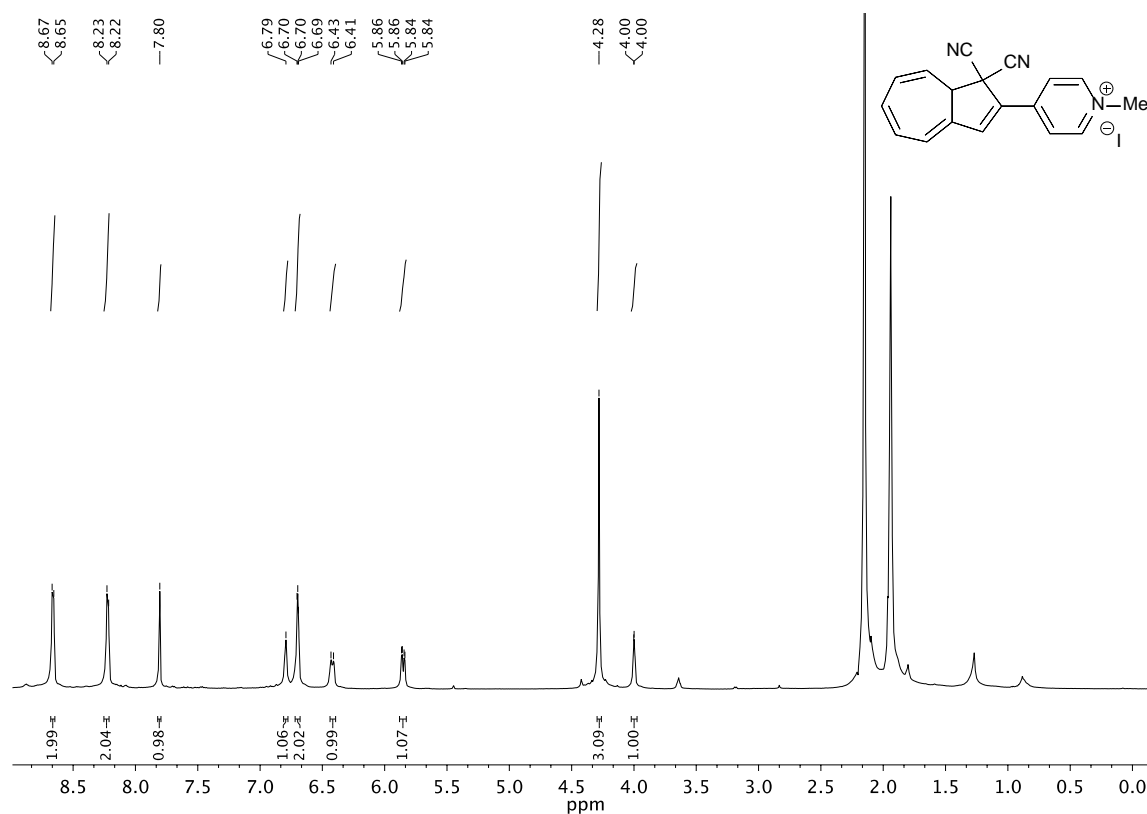


Figure S13: <sup>1</sup>H-NMR spectrum of **6a** in CD<sub>3</sub>CN (500 MHz).

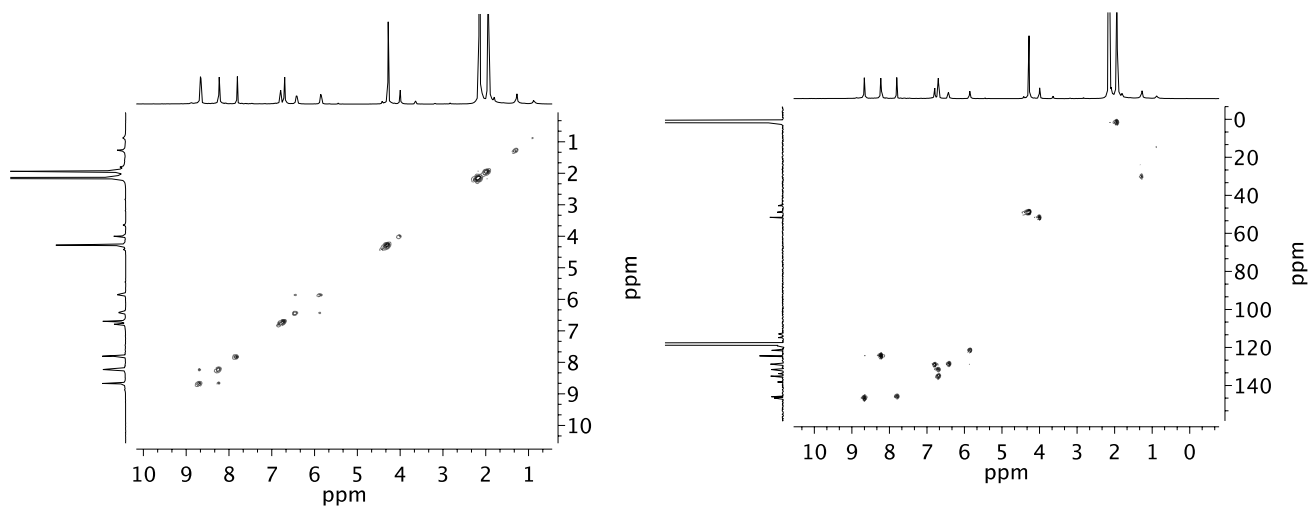


Figure S14: COSY (left) and <sup>1</sup>H / <sup>13</sup>C-APT HSQC (right) spectra of **6a** in CD<sub>3</sub>CN (500 / 126 MHz).

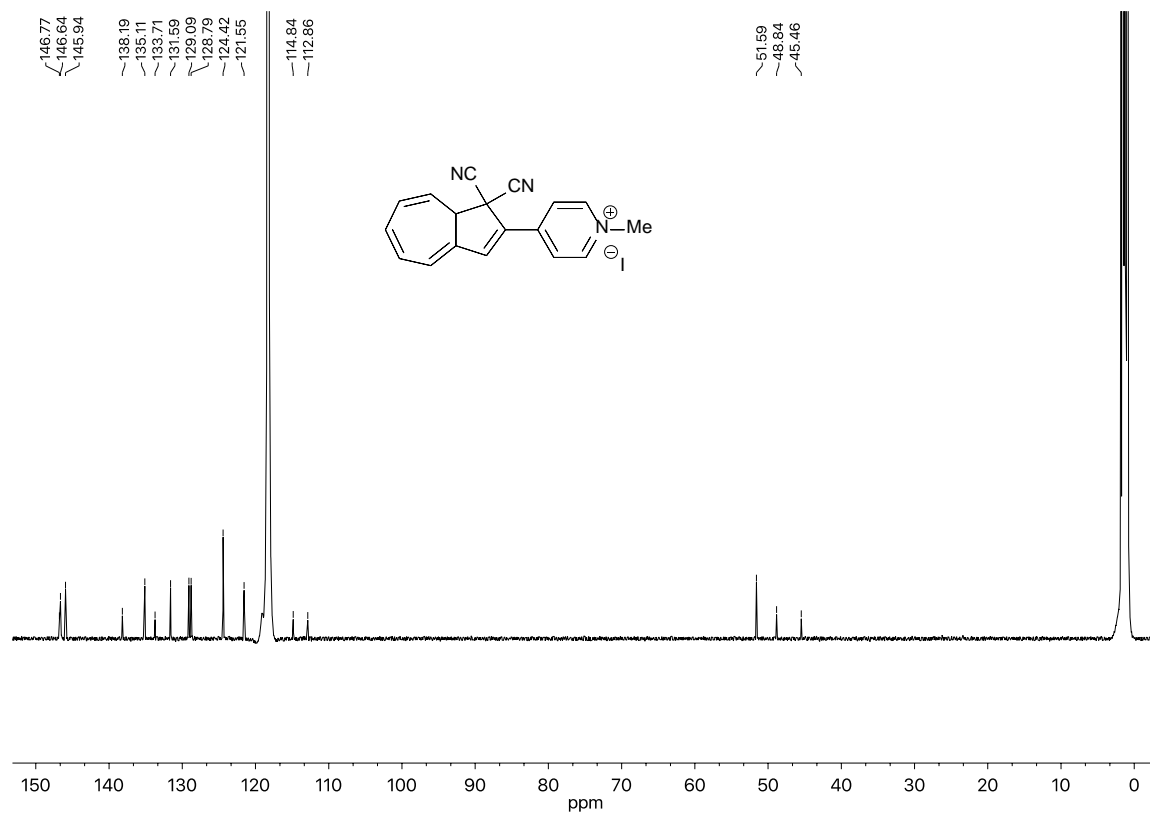


Figure S15:  $^{13}C$ -APT spectrum of **6a** in  $CD_3CN$  (126 MHz).

**5,6,7,8-Tetrahydroisoquinoline-*N*-oxide (8)**

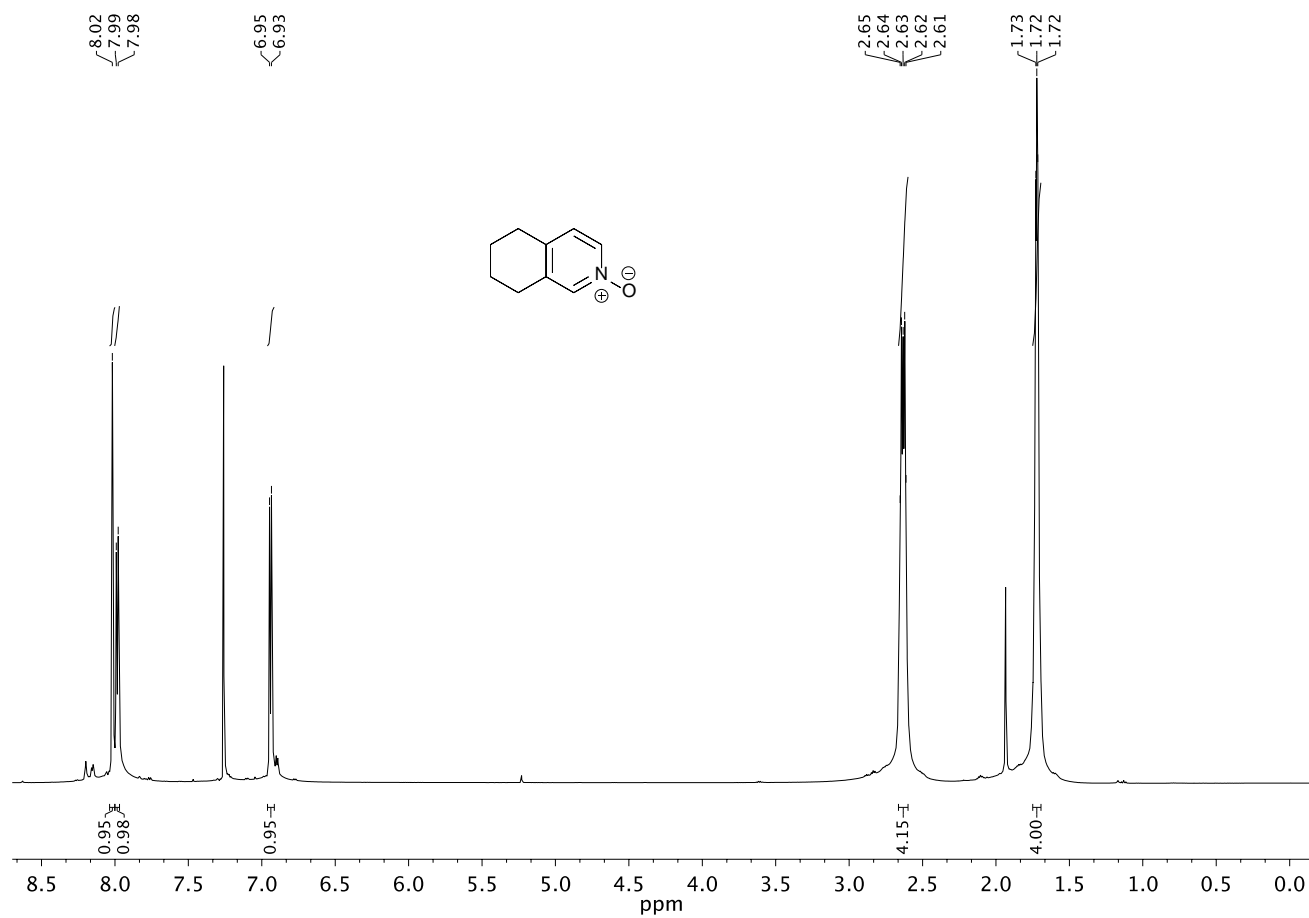


Figure S16: <sup>1</sup>H-NMR spectrum of **8** in CDCl<sub>3</sub> (500 MHz).

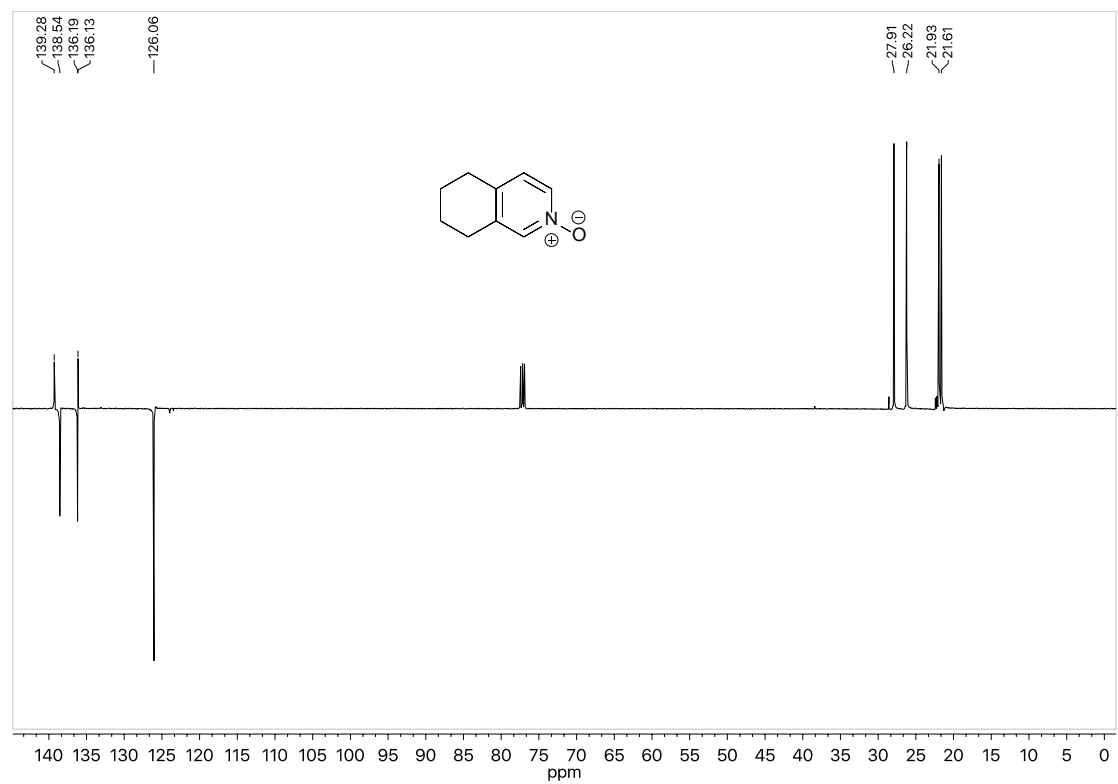


Figure S17:  $^{13}\text{C}$ -APT spectrum of **8** in  $\text{CDCl}_3$  (126 MHz).

### 5-Acetoxy-5,6,7,8-tetrahydroisoquinoline (**9**)

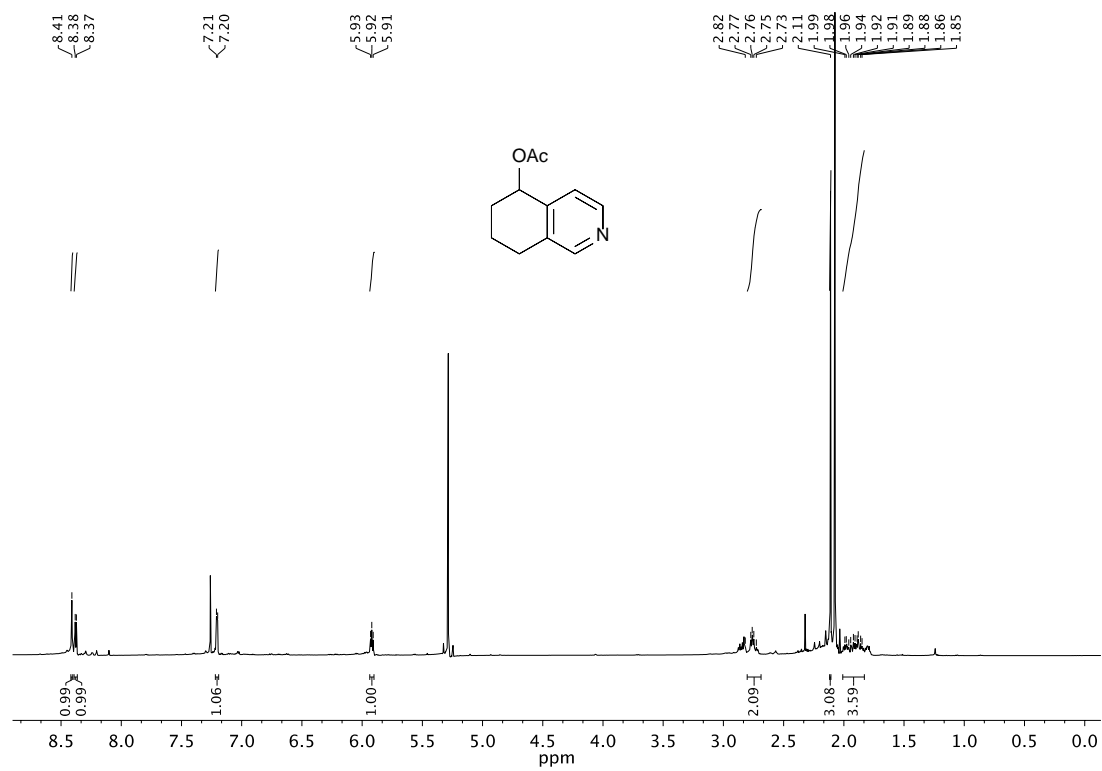


Figure S18: <sup>1</sup>H-NMR spectrum of **9** in CDCl<sub>3</sub> (500 MHz).

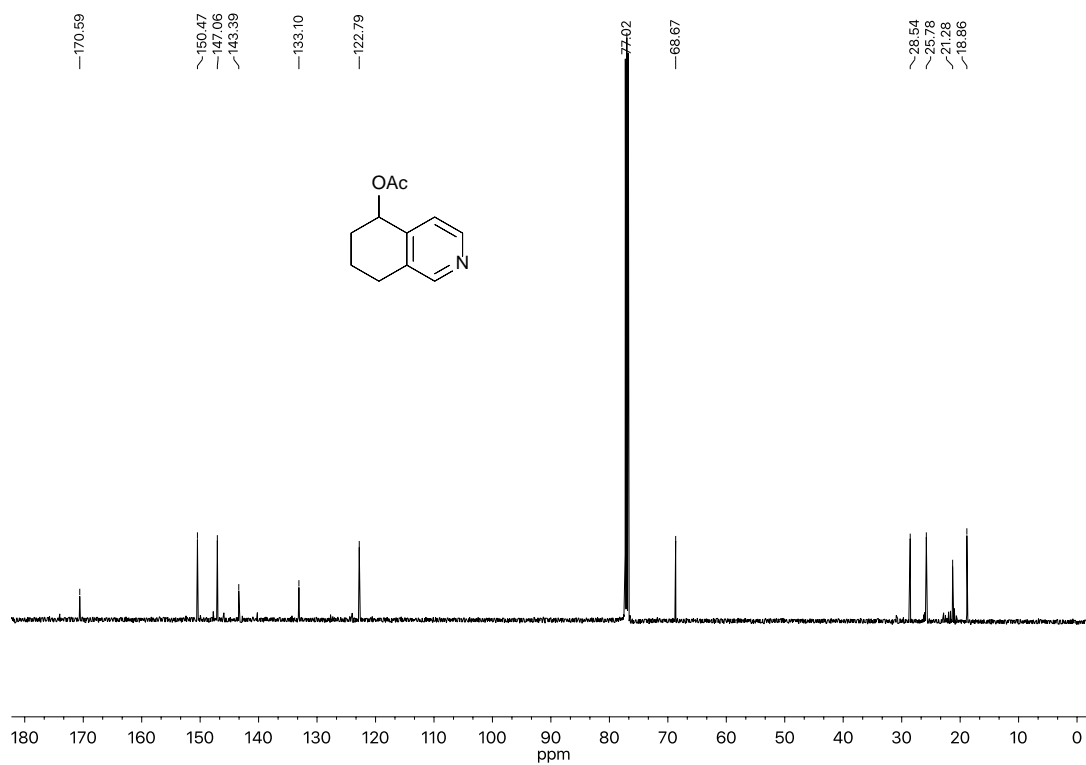


Figure S19:  $^{13}\text{C}$ -APT spectrum of **9** in  $\text{CDCl}_3$  (126 MHz).

### 5,6,7,8-Tetrahydroisoquinolin-5-ol (**10**)

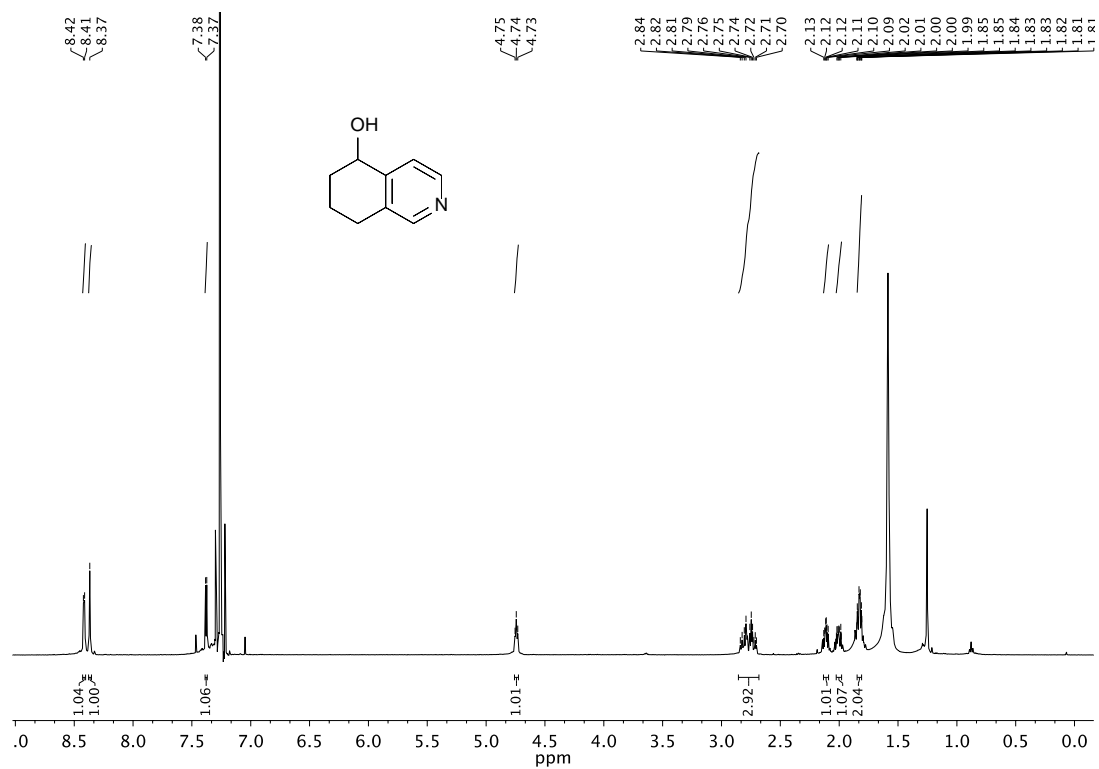


Figure S20: <sup>1</sup>H-NMR spectrum of **10** in CDCl<sub>3</sub> (500 MHz).

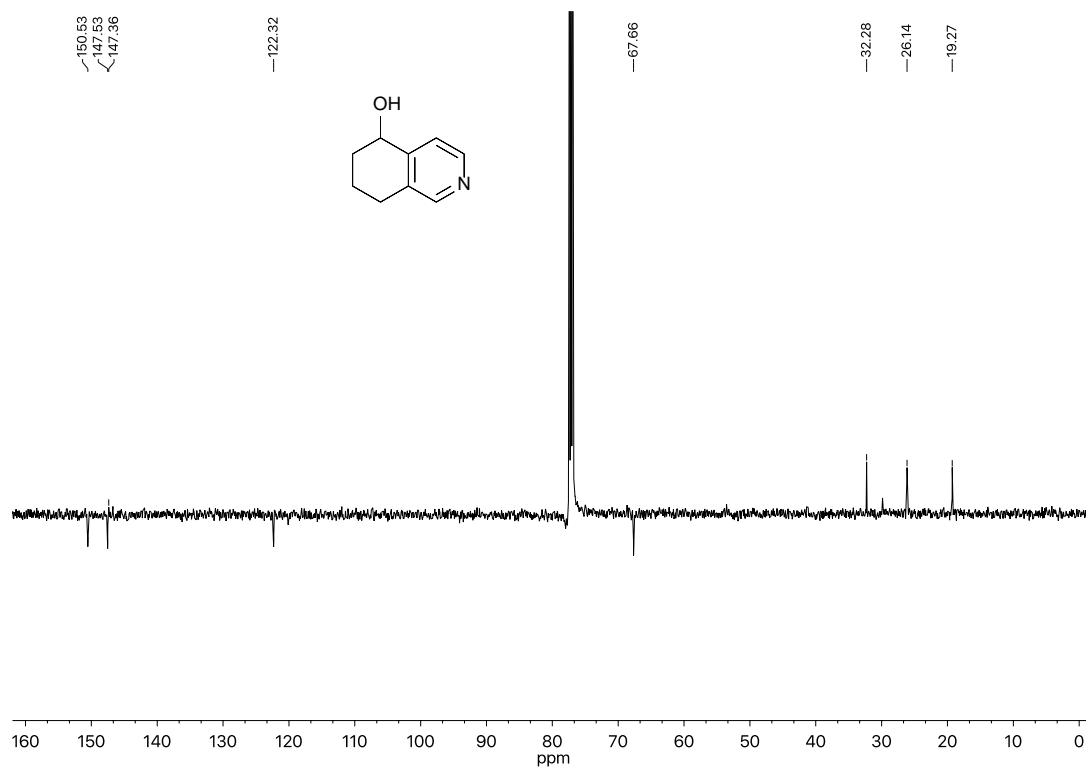


Figure S21:  $^{13}\text{C}$ -APT spectrum of **10** in  $\text{CDCl}_3$  (126 MHz).



7,8-Dihydroisoquinolin-5(6H)-one (**11**)

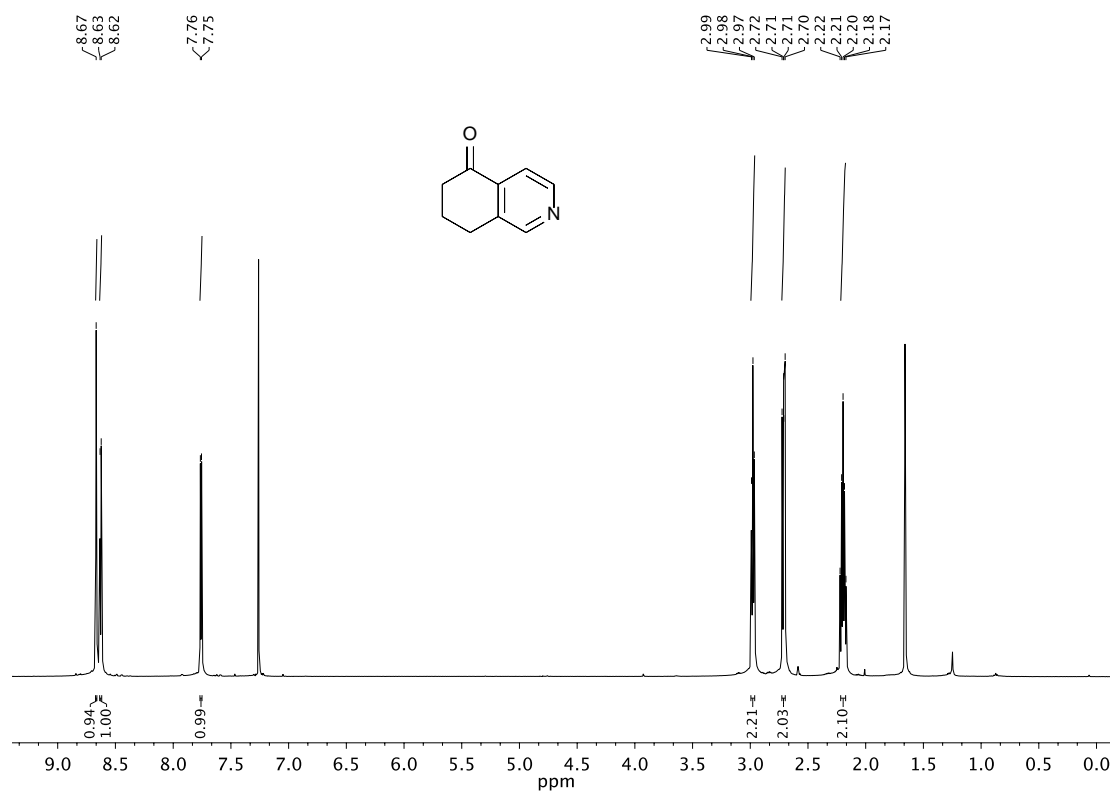


Figure S22: <sup>1</sup>H-NMR spectrum of **11** in CDCl<sub>3</sub> (500 MHz).

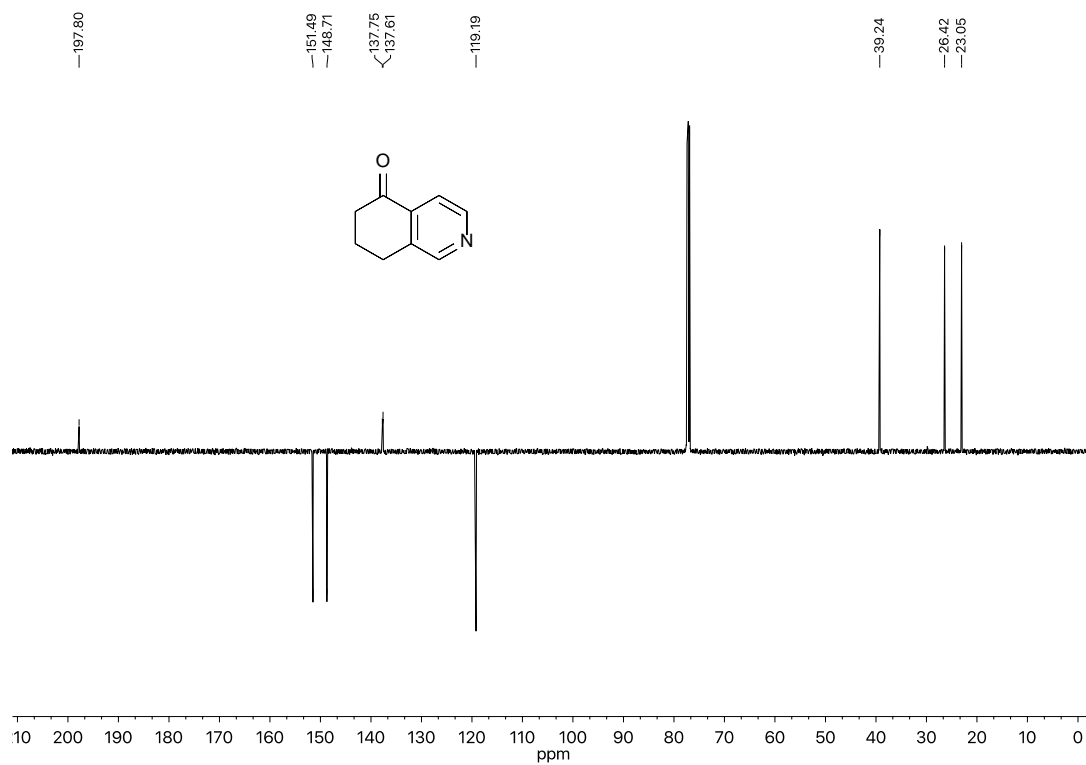


Figure S23: <sup>13</sup>C-APT spectrum of **11** in CDCl<sub>3</sub> (126 MHz).

**2-(7,8-Dihydroisoquinolin-5(6H)-ylidene)malononitrile (12)**

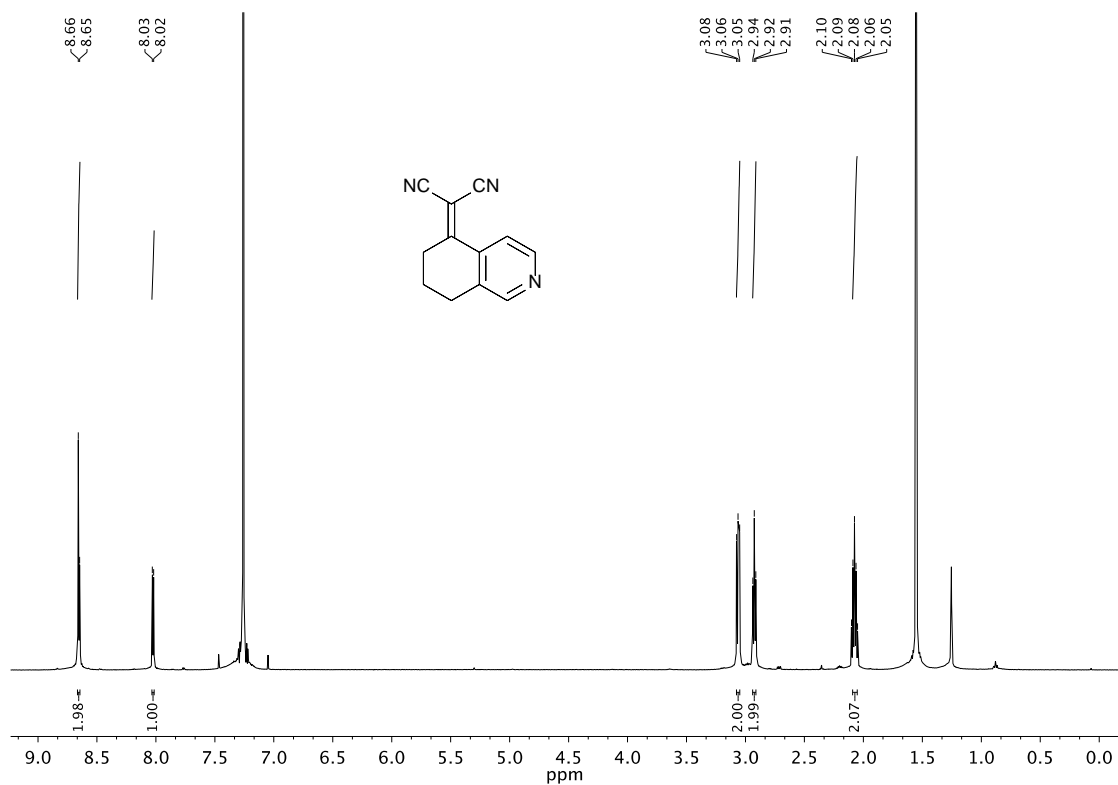


Figure S24:  $^1\text{H}$ -NMR spectrum of **12** in  $\text{CDCl}_3$  (500 MHz).

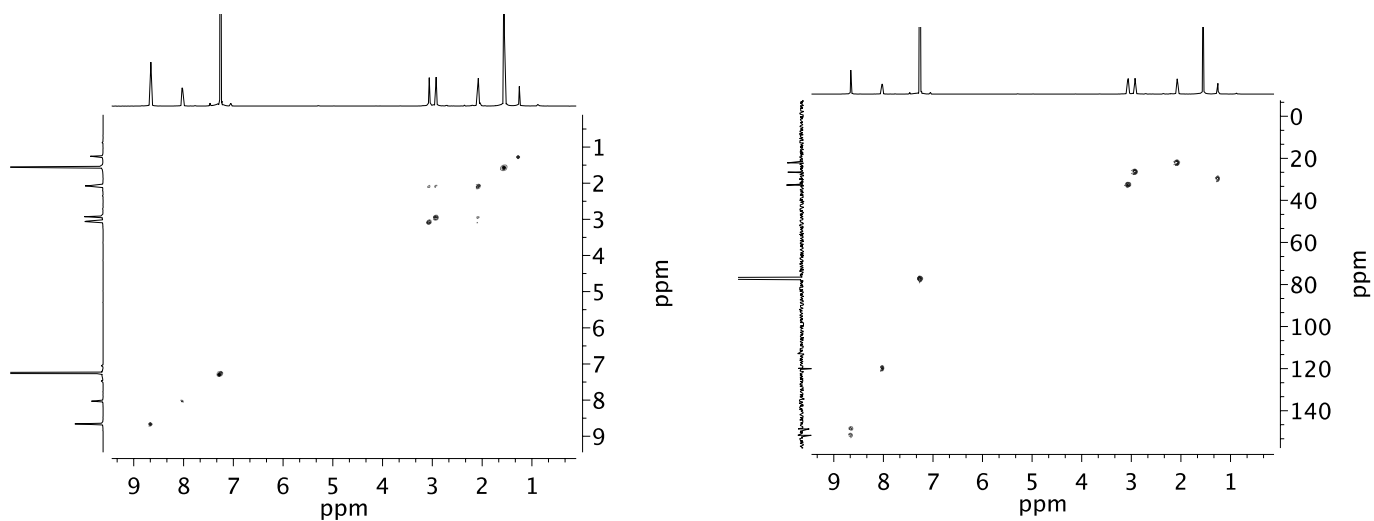


Figure S25: COSY (left) and  $^1\text{H}/^{13}\text{C}$ -APT HSQC (right) spectra of **12** in  $\text{CDCl}_3$  (500 / 126 MHz).

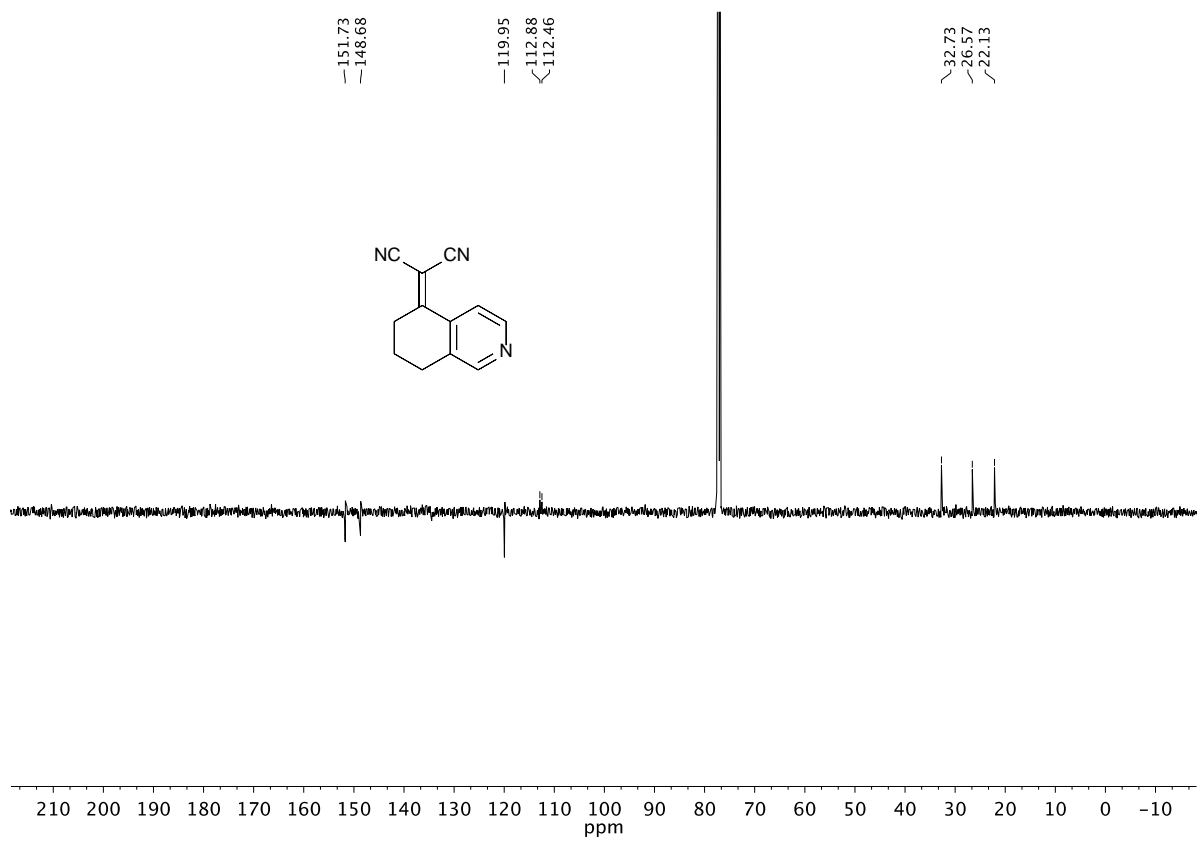


Figure S26:  $^{13}\text{C}$ -APT spectrum of **12** in  $\text{CDCl}_3$  (126 MHz).

2-(6-(Cyclohepta-2,4,6-trien-1-yl)-7,8-dihydroisoquinolin-5(6*H*)-ylidene)malononitrile (**13**)

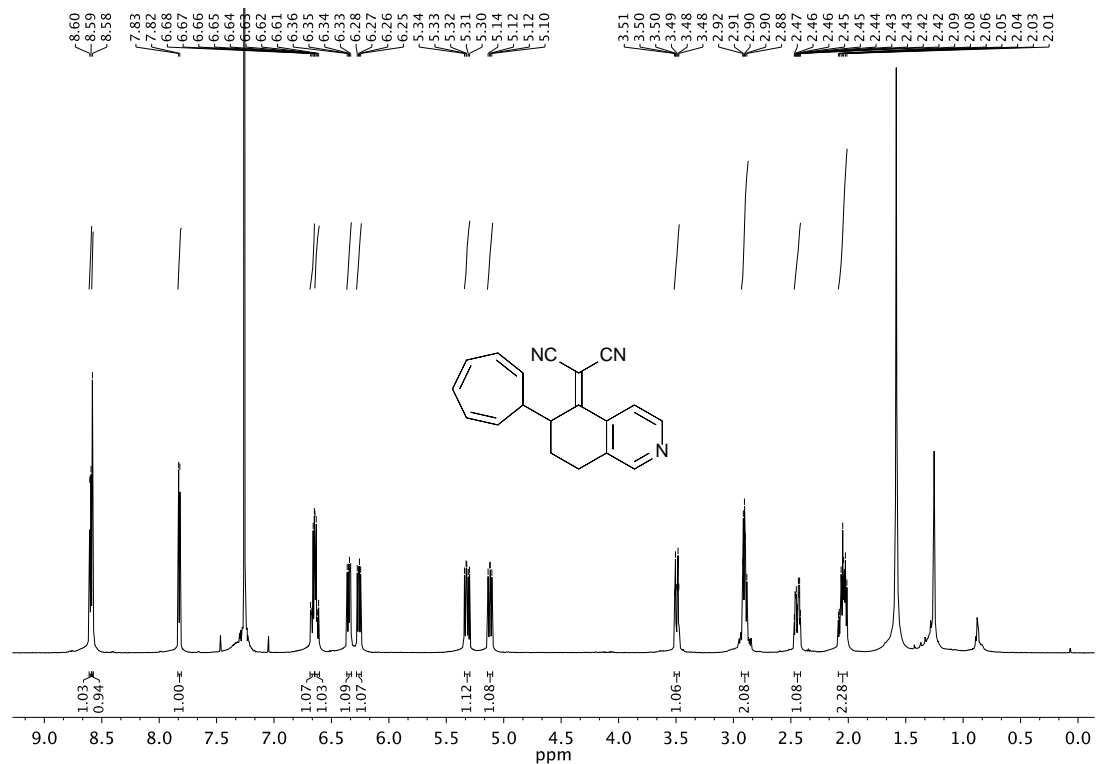


Figure S27:  $^1\text{H}$ -NMR spectrum of **13** in  $\text{CDCl}_3$  (500 MHz).

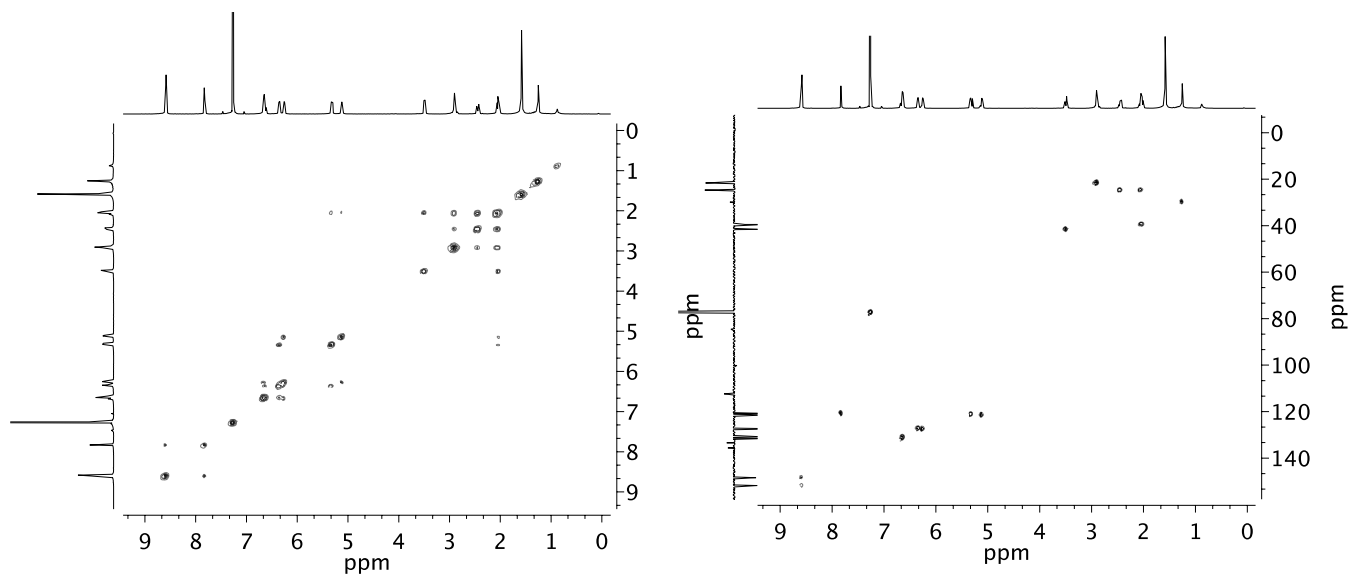


Figure S28: COSY (left) and  $^1\text{H} / ^{13}\text{C}$ -APT HSQC (right) spectra of **13** in  $\text{CDCl}_3$  (500 / 126 MHz).

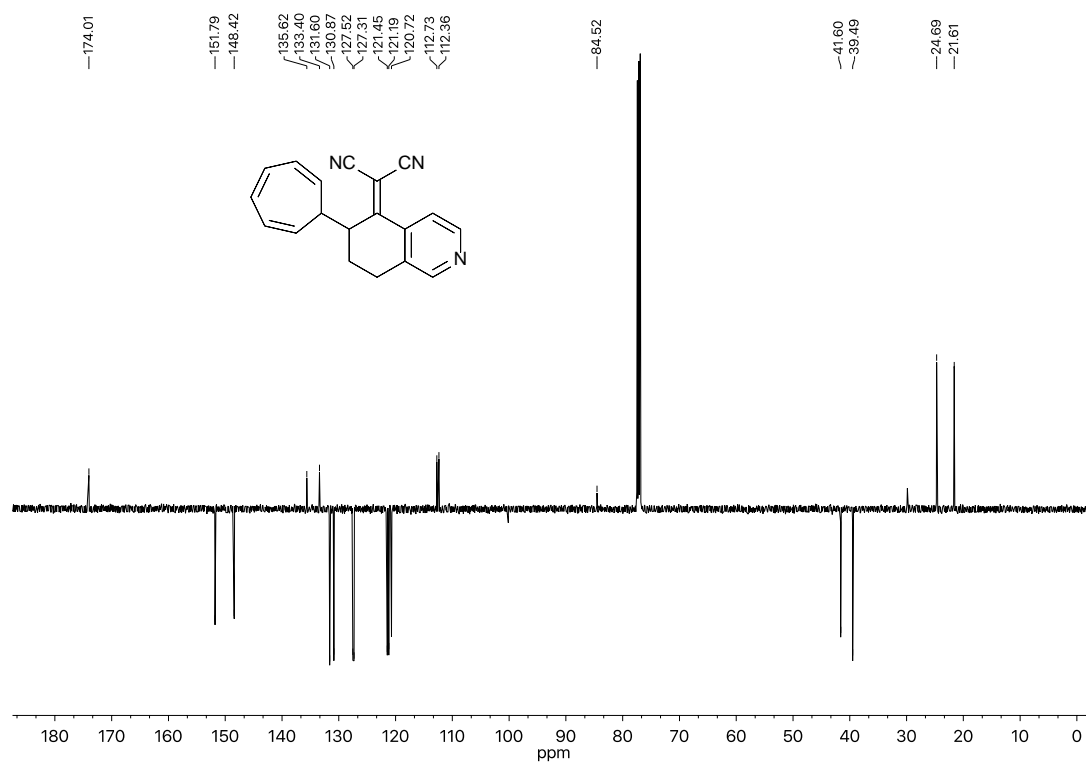


Figure S29:  $^{13}\text{C}$ -APT spectrum of **13** in  $\text{CDCl}_3$  (126 MHz).

## UV-Vis absorption studies

### Acid (TFA) / base (Et<sub>3</sub>N) treatment of **1a**

#### Protonation of **1a**

A sample of a pure photochromic DHA **1a** (9.2 mg,  $M_w = 257.296$  g/mol,  $3.58 \times 10^{-5}$  mol) was dissolved in MeCN (100.0 mL). This stock solution (conc. =  $3.58 \times 10^{-4}$  mol/L) was kept in the dark at all times. A sample of the stock solution (500  $\mu$ L,  $1.8 \times 10^{-7}$  mol) was diluted with MeCN (2050  $\mu$ L), which gave a total volume of 2550  $\mu$ L (DHA conc. =  $7.0 \times 10^{-5}$  mol/L) and a spectrum was acquired (25 °C).

A stock solution of TFA ( $\delta = 1.49$  g/mL,  $M_w = 114.02$  g/mol) was prepared:

TFA<sub>stock\_solution1</sub>: 0.27 mL ( $n = 0.0035$  mol) in 100 mL MeCN (conc. =  $0.035 \times$  mol/L)

From this TFA stock solution, **two** new stock solutions were prepared by taking 1 mL of TFA<sub>stock\_solution1</sub> and diluting with MeCN (100.0 mL and 20.0 mL, respectively):

TFA<sub>stock\_solution2</sub> = 1 mL of TFA<sub>stock\_solution1</sub> / 100.0 mL MeCN = 0.00035 mol/L.

TFA<sub>stock\_solution3</sub> = 1 mL of TFA<sub>stock\_solution1</sub> / 20.0 mL MeCN = 0.00175 mol/L.

Spectra following the protonation of **1a** were recorded with the following solutions, all keeping the total volume and amount of **1a** constant (Fig. S30):

**DHA\_1** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 2050  $\mu$ L MeCN

**DHA\_2** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 2000  $\mu$ L MeCN and 50  $\mu$ L TFA<sub>stock\_solution2</sub> (= **0.1 equiv. TFA**)

**DHA\_3** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1550  $\mu$ L MeCN and 500  $\mu$ L TFA<sub>stock\_solution2</sub> (= **1 equiv. TFA**)

**DHA\_4** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 800  $\mu$ L MeCN and 1250  $\mu$ L TFA<sub>stock\_solution2</sub> (= **2.5 equiv TFA**)

**DHA\_5** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 50  $\mu$ L MeCN and 2000  $\mu$ L TFA<sub>stock\_solution2</sub> (= **4 equiv. TFA**)

**DHA\_6** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1500  $\mu$ L MeCN and 500  $\mu$ L TFA<sub>stock\_solution3</sub> (= **5 equiv. TFA**)

**DHA\_7** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1450  $\mu$ L MeCN and 600  $\mu$ L TFA<sub>stock\_solution3</sub> (= **6 equiv. TFA**)

**DHA\_8** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1300  $\mu$ L MeCN and 750  $\mu$ L TFA<sub>stock\_solution3</sub> (= **7.5 equiv. TFA**)

**DHA\_9** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1050  $\mu$ L MeCN and 1000  $\mu$ L TFA<sub>stock\_solution3</sub> (= **10 equiv. TFA**)

**DHA\_10** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 550  $\mu$ L MeCN and 1500  $\mu$ L TFA<sub>stock\_solution3</sub> (= **15 equiv. TFA**)

**DHA\_11** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 50  $\mu$ L MeCN and 2000  $\mu$ L TFA<sub>stock\_solution3</sub> (= **20 equiv. TFA**)

**DHA\_12** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1900  $\mu$ L MeCN and 150  $\mu$ L TFA<sub>stock\_solution</sub> (= **30 equiv. TFA**)

**DHA\_13** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1800  $\mu$ L MeCN and 250  $\mu$ L TFA<sub>stock\_solution</sub> (= **50 equiv. TFA**)

**DHA\_14** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1550  $\mu$ L MeCN and 500  $\mu$ L TFA<sub>stock\_solution</sub> (= **100 equiv. TFA**)

**DHA\_15** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1050  $\mu$ L MeCN and 1000  $\mu$ L TFA<sub>stock\_solution</sub> (= **200 equiv. TFA**)

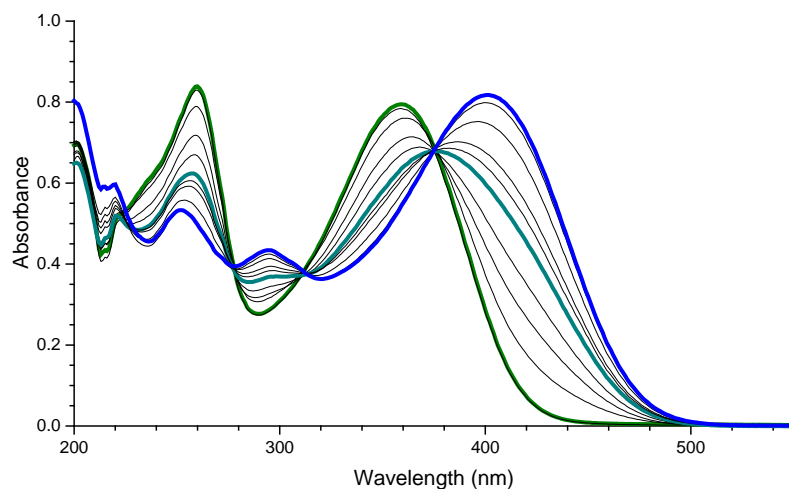


Figure S30: Spectra resulting from gradual protonation of **1a** (conc.  $7.0 \times 10^{-5}$  mol/L.). Green = **1a**, Cyan = **1a** + 5 equiv. TFA, Blue = **1a** + 200 equiv. TFA.

#### Deprotonation of **1aH<sup>+</sup>** (with 20 equiv. **Et<sub>3</sub>N**)

A stock solution of **Et<sub>3</sub>N** ( $\delta = 0.726$  g/mL,  $M_w = 101.19$  g/mol) was prepared.

**Et<sub>3</sub>N<sub>stock\_solution1</sub>**: 0.16 mL ( $n = 0.0011$  mol) in 10.0 mL MeCN (conc. = 0.11 mol/L)

From this **Et<sub>3</sub>N** stock solution, another stock solution was prepared by taking 1.0 mL of **Et<sub>3</sub>N<sub>stock\_solution1</sub>** and diluting with MeCN (10.0 mL):

**Et<sub>3</sub>N<sub>stock\_solution2</sub>** = 1.0 mL of **TFA<sub>stock\_solution1</sub>** / 10.0 mL MeCN = 0.011 mol/L.

To the cuvette containing DHA **1a** and 20 equiv. of TFA (entry: **DHA\_11**) was added 500  $\mu$ L of **Et<sub>3</sub>N<sub>stock\_solution2</sub>** (= 20 equiv.), and a spectrum was acquired (red curve) (Fig. S31). This resulted in a change in the absorption going from a  $\lambda_{max} = 401$  nm (blue curve) back to the original starting absorption maximum of DHA **1a** ( $\lambda_{max} = 359$ ) (green curve) (Fig. S31). Since the cuvette has been diluted with 300  $\mu$ L of solvent, the absorbance has decreased a bit compared to the starting spectrum.



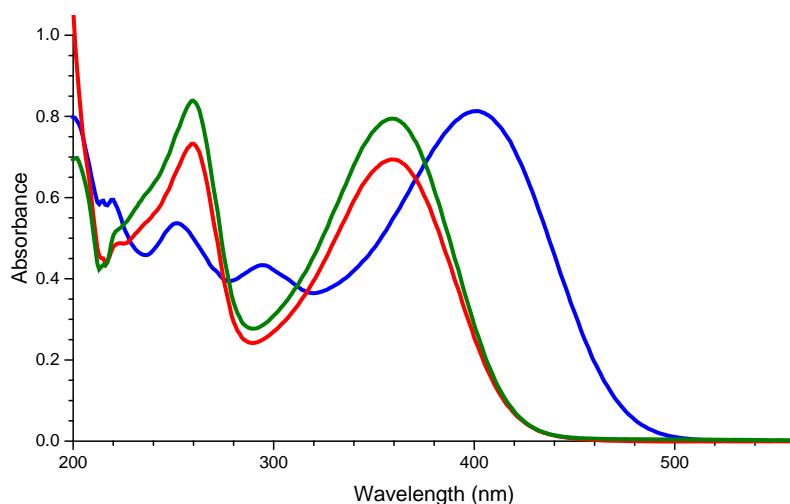


Figure S31: UV-Vis absorption spectra resulting from protonation of **1a** (conc.  $7.0 \times 10^{-5}$  mol/L) to **1aH<sup>+</sup>** and subsequently deprotonation with Et<sub>3</sub>N to yield **1a** once again (red curve; lower intensity relative to the initial green curve due to the small dilution of the sample). Green = **1a**, Blue = **1a** + 20 equiv. TFA. Red = **1a** in a 20 equivalent mixture of TFA and Et<sub>3</sub>N.

### Switching of **1a/1b** at 25 °C

An UV-Vis absorption spectrum of the pure DHA **1a** was acquired at 25 °C. The sample was then irradiated in front of a UV-lamp with UV-light (365 nm) for a short while (seconds), then a UV-Vis absorption spectrum was acquired. This procedure was repeated until no change in the absorption spectrum could be seen, going from DHA to VHF. When fully converted, the VHF to DHA back-reaction was monitored at 25 °C by acquiring a UV-Vis absorption spectrum over five half-lives. The conversion of DHA **1a** → VHF **1b** occurred with isosbestic points in the absorption spectra and also from VHF → DHA (see Fig. 1 in article). The absorption maximum ( $\lambda_{\text{max}}$ ) for the VHF-species **1b** was found and a plot of the decay of VHF absorbance against time (first-order kinetics) was performed. The exponential decay of the VHF absorbance was subjected to curve fitting, from which the rate constant  $k_{25^\circ\text{C}}$  (VHF → DHA) was determined (Fig. 1, inset, and Table 1 in the article).

### Switching of **1a/1b** with TFA (20 equiv.) at 25 °C

An UV-Vis absorption spectrum of **DHA\_11** = 500  $\mu\text{L}$  of DHA<sub>stock\_solution</sub> diluted with 50  $\mu\text{L}$  MeCN and 2000  $\mu\text{L}$  TFA<sub>stock\_solution3</sub> (= 20 equiv. TFA) was acquired at 25 °C. The sample was then irradiated in front of a UV-lamp with UV-light (365 nm) for a short while (seconds), then a UV-Vis absorption spectrum was acquired. This procedure was repeated until no change in the absorption spectrum could be seen, going from DHA to VHF. When fully converted, the VHF **1bH<sup>+</sup>** to DHA back-reaction was monitored at 25 °C by acquiring a UV-Vis absorption spectrum over five half-lives. The conversion of DHA **1aH<sup>+</sup>** → VHF **1bH<sup>+</sup>** occurred with isosbestic points in the absorption spectra and also from VHF → DHA. The absorption maximum ( $\lambda_{\text{max}}$ ) for the VHF-species **1bH<sup>+</sup>** was found and a plot of the decay of VHF absorbance against time (first-order kinetics) was performed. The exponential decay of the VHF absorbance was subjected to curve fitting, from which the rate constant  $k_{25^\circ\text{C}}$  (VHF → DHA) was determined (Table 1 in the article).

### Switching of 1a/1b after acid/base addition

The cuvette containing DHA **1a**, TFA (20 equiv.) and Et<sub>3</sub>N (20 equiv.) was subjected to light irradiation (365 nm), until no change in the absorption spectrum could be seen, going from DHA ( $\lambda_{\max} = 359$  nm) to VHF. When fully converted, the VHF to DHA back-reaction was monitored at 25 °C by acquiring a UV-Vis absorption spectrum every two minutes. Half-life of the back-reaction was determined to  $t_{1/2} = 69$  min.

### Back-reaction of 1b (+ addition of TFA and afterwards Et<sub>3</sub>N)

A sample of a pure photochromic DHA, **1a** (conc. =  $3.58 \times 10^{-4}$  mol/L in MeCN) was diluted with MeCN (2000  $\mu$ L), which was light irradiated (365 nm) until no further change in the absorption spectrum.

The back-reaction (Py-VHF **1b**  $\rightarrow$  Py-DHA **1a**) was followed over 75 min. (above one half-life). Then, 20 equiv. of TFA (100  $\mu$ L of TFA<sub>stock\_solution1</sub>) was added, and the decay was once again followed with 60 s in between the last scan of **1b/1a** mixture and **1bH<sup>+</sup>/1aH<sup>+</sup>** mixture. The back-reaction of this acidified mixture was followed over 16 min (above one half-life). Then, 20 equiv. of Et<sub>3</sub>N (300  $\mu$ L of Et<sub>3</sub>N<sub>stock\_solution1</sub>) was added, and the decay was followed with 30 s in between the last scan of **1bH<sup>+</sup>/1aH<sup>+</sup>** mixture and the **1b-TFA-Et<sub>3</sub>N/1a-TFA-Et<sub>3</sub>N** mixture (Fig. S32).

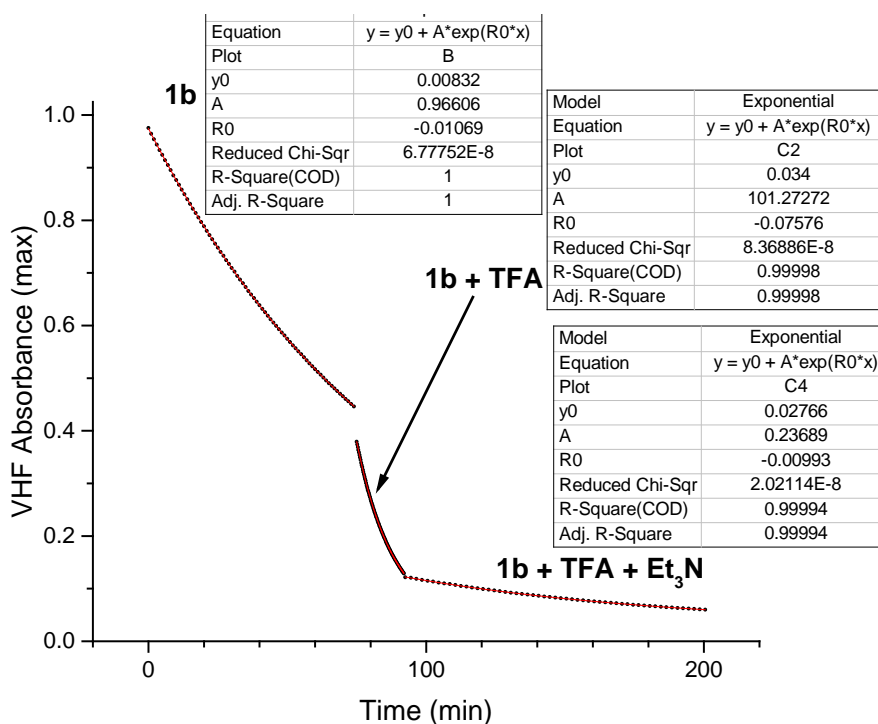


Figure S32: Decay of VHF (**1b**, **1b + TFA** and **1b + TFA + Et<sub>3</sub>N**) absorbance (maximum of the specific VHF) against time (min) (first-order kinetics).

From all the data, exponential plots were obtained with excellent fits. A logarithmic plot of the absorbance against time before and after addition of TFA as well as after subsequent addition of Et<sub>3</sub>N gave linear correlations in each of the three regimes (Fig. S33). By the addition of TFA, the slope was greatly increased

and after the addition of Et<sub>3</sub>N the slope was significantly lowered, approaching that observed before addition of TFA.

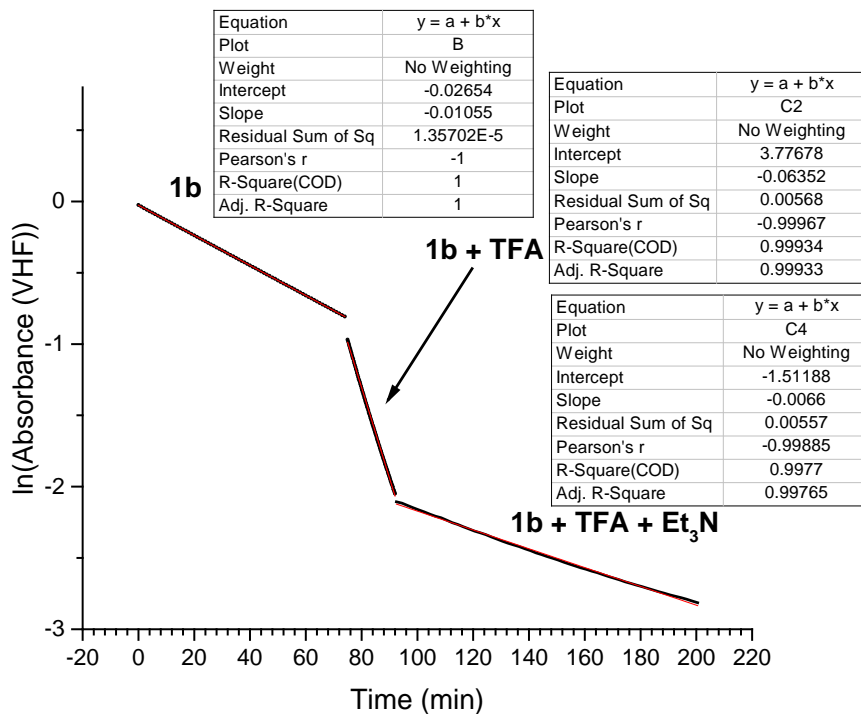


Figure S33: Natural logarithm ( $\ln$ ) of the VHF absorbance (480 nm for **1b** and **1b + TFA + Et<sub>3</sub>N** mixture and 483 nm for **1b + TFA** mixture is used) against time. The thermal heat release is activated by addition of TFA (steep slope) and the heat release is retarded again upon addition of Et<sub>3</sub>N.

## Acid (TFA) / base (Et<sub>3</sub>N) treatment of **2a**

### Protonation of **2a**

A sample of a pure photochromic DHA **2a** (2.8 mg,  $M_w = 283.334$  g/mol,  $9.9 \times 10^{-6}$  mol) was dissolved in abs. EtOH (25.0 mL). This stock solution (conc. =  $4.0 \times 10^{-4}$  mol/L) was kept in the dark at all times. A sample of the stock solution (500  $\mu$ L,  $2.0 \times 10^{-7}$  mol) was diluted with abs. EtOH (2550  $\mu$ L), which gave a total volume of 3050  $\mu$ L (DHA conc. =  $6.6 \times 10^{-5}$  mol/L), and a spectrum was acquired (25 °C).

A stock solution of TFA ( $\delta = 1.49$  g/mL,  $M_w = 114.02$  g/mol) was prepared:

TFA<sub>stock\_solution1</sub>: 0.25 mL ( $n = 0.0033$  mol) in 100.0 mL abs. EtOH (conc. = 0.033 mol/L)

From this TFA stock solution, **two** new stock solutions were prepared by taking 1.0 mL of TFA<sub>stock\_solution1</sub> and diluting with abs. EtOH (100.0 mL and 20.0 mL, respectively):

TFA<sub>stock\_solution2</sub> = 1.0 mL of TFA<sub>stock\_solution1</sub> / 100.0 mL abs. EtOH = 0.00033 mol/L.

TFA<sub>stock\_solution3</sub> = 1.0 mL of TFA<sub>stock\_solution1</sub> / 20.0 mL abs. EtOH = 0.00165 mol/L.

Spectra following the protonation of **2a** were recorded with the following solutions, all keeping the total volume and amount of **2a** constant:

**DHA\_1** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 2550  $\mu$ L abs. EtOH

**DHA\_2** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 2050  $\mu$ L abs. EtOH and 500  $\mu$ L TFA<sub>stock\_solution2</sub> (= **1 equiv TFA**)

**DHA\_3** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1300  $\mu$ L abs. EtOH and 1250  $\mu$ L TFA<sub>stock\_solution2</sub> (= **2.5 equiv TFA**)

**DHA\_4** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 50  $\mu$ L abs. EtOH and 2500  $\mu$ L TFA<sub>stock\_solution2</sub> (= **5 equiv TFA**)

**DHA\_5** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1550  $\mu$ L abs. EtOH and 1000  $\mu$ L TFA<sub>stock\_solution3</sub> (= **10 equiv TFA**)

**DHA\_6** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 550  $\mu$ L abs. EtOH and 2000  $\mu$ L TFA<sub>stock\_solution3</sub> (= **20 equiv TFA**)

**DHA\_7** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 2300  $\mu$ L abs. EtOH and 250  $\mu$ L TFA<sub>stock\_solution</sub> (= **50 equiv TFA**)

**DHA\_8** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 2050  $\mu$ L abs. EtOH and 500  $\mu$ L TFA<sub>stock\_solution</sub> (= **100 equiv TFA**)

**DHA\_9** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 1550  $\mu$ L abs. EtOH and 1000  $\mu$ L TFA<sub>stock\_solution</sub> (= **200 equiv TFA**)

**DHA\_10** = 500  $\mu$ L of DHA<sub>stock\_solution</sub> diluted with 550  $\mu$ L abs. EtOH and 2000  $\mu$ L TFA<sub>stock\_solution</sub> (= **400 equiv TFA**)

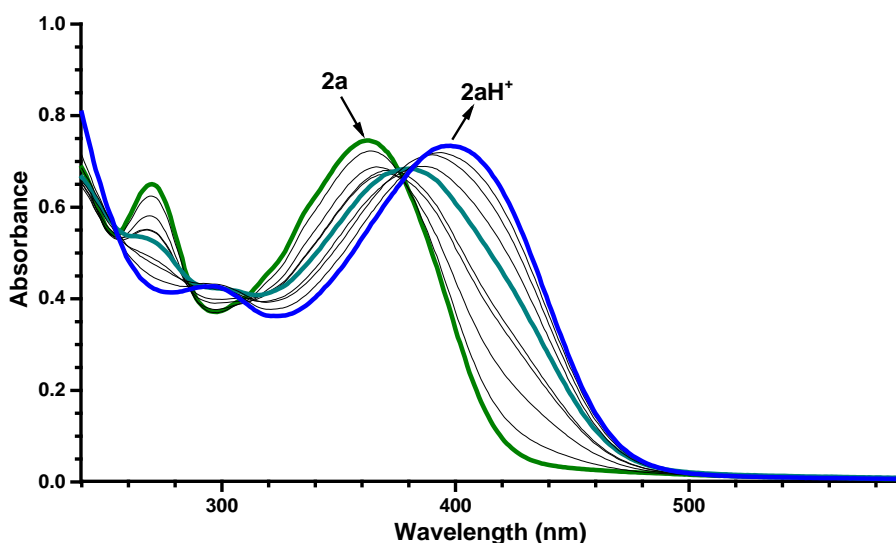


Figure S34: UV-Vis absorption spectra resulting from gradual protonation of **2a** in EtOH (conc.  $6.6 \times 10^{-5}$  mol/L). Green = **2a**, Cyan = **2a** + 20 equiv. TFA, Blue = **2a** + 400 equiv. TFA.

#### Switching of **2a/2b** at $-50$ °C

A sample of the DHA **2a** stock solution ( $500 \mu\text{L}$ ,  $2.0 \times 10^{-7}$  mol) was diluted with abs. EtOH ( $2000 \mu\text{L}$ ) in a quartz cuvette, which gave a total volume of  $2500 \mu\text{L}$  (DHA conc. = mol/L). The cuvette was placed in a cryostat, and a spectrum was acquired ( $25$  °C). The cuvette was then cooled to  $-50$  °C by using a cryostat together with liquid nitrogen. A UV-Vis absorption spectrum of the pure DHA **2a** was acquired. The sample (inside the cryostat) was irradiated with UV-light ( $365$  nm) for a short while (seconds), then a UV-Vis absorption spectrum was acquired. This procedure was repeated until no change in the absorption spectrum could be seen, going from DHA to VHF. When fully converted, the VHF to DHA back-reaction was monitored at  $-50$  °C by acquiring a UV-Vis absorption spectrum over five half-lives. The conversion of DHA **2a**  $\rightarrow$  VHF **2b** occurred with isosbestic points in the absorption spectra and also from VHF  $\rightarrow$  DHA (see Fig. 5 in article). The absorption maximum ( $\lambda_{\text{max}}$ ) for the VHF-species **2b** was found and a plot of the decay of VHF absorbance against time (first-order kinetics) was performed. The exponential decay of the VHF absorption was subjected to curve fitting, from which the rate constant  $k_{-50^\circ\text{C}}$  (VHF  $\rightarrow$  DHA) was determined ((Fig. 5, inset and Table 1, in the article)

## Emission studies

### Fluorescence of **2a** and **2aH<sup>+</sup>** at 25 °C

A sample of the **2a** stock solution (50  $\mu\text{L}$ ,  $2.0 \times 10^{-7}$  mol) was diluted with abs. EtOH (2500  $\mu\text{L}$ ), which gave a total volume of 2550  $\mu\text{L}$  and a UV/Vis absorbance spectrum was acquired (note: absorbance below 0.1) (25 °C) followed by an emission spectrum starting at 360 nm and with excitation at 350 nm.

**2a\_flores** = 50  $\mu\text{L}$  of  $\text{DHA}_{\text{stock\_solution}}$  diluted with 2500  $\mu\text{L}$  abs. EtOH

**2aH<sup>+</sup>\_flores** = 50  $\mu\text{L}$  of  $\text{DHA}_{\text{stock\_solution}}$  diluted with 2300  $\mu\text{L}$  abs. EtOH and 200  $\mu\text{L}$   $\text{TFA}_{\text{stock\_solution}}$ <sup>3</sup> (= **20 equiv TFA**)

## Calculations

### Thermochemical data at 298.15 K

A summary of computed data at 298.15 K is shown in Table S1 (while data at 203.15 K are listed in the manuscript). Optimized structures are shown below.

**Table S1.** Relative transition state stability ( $\Delta\Delta G_{TS}$ ; if negative (positive),  $TS_P$  ( $TS_T$ ) is lower in energy), thermal back-reaction barrier ( $\Delta G_{TBR}$ ), and energy storage capacity ( $\Delta H_{storage}$ ) in  $\text{kJ mol}^{-1}$ , energy density (En. dens.) in  $\text{MJ kg}^{-1}$ , and equilibrium constant (K) for the *s-cis/s-trans* VHF conformational change of **1b** for both the neutral and protonated species in different environments at 298.15 K. An asterisk marks that no  $TS_T$  type transition state was located for the given solvation.

		Vacuum	PhMe	$\text{CH}_2\text{Cl}_2$	EtOH	MeCN	Vacuum molecule + EtOH	EtOH molecule + EtOH
<b>1a/1b</b>	$\Delta\Delta G_{TS}$	-8.058	-9.071	-7.422	*	*	-7.979	*
	$\Delta\Delta G_{VHF}$	7.110	7.753	7.989	8.031	8.060	6.847	10.19
	K	0.057	0.044	0.040	0.039	0.039	0.063	0.016
	$\Delta G_{TBR}$	104.9	95.73	88.61	86.55	86.19	105.8	86.99
	$\Delta G'_{TBR}$	112.2	103.6	96.70	94.68	94.34	112.80	97.22
	$\Delta H_{storage}$	37.11	32.16	27.64	26.14	25.85	36.35	26.10
	En. dens.	0.144	0.125	0.107	0.102	0.100	0.141	0.101
<b>1aH<sup>+</sup>/1bH<sup>+</sup></b>	$\Delta\Delta G_{TS}$	-9.851	-7.404	*	*	*	-11.46	*
	$\Delta\Delta G_{VHF}$	-5.619	-3.088	3.946	5.264	5.540	-2.641	6.863
	K	9.645	3.475	0.204	0.120	0.107	2.902	0.063
	$\Delta G_{TBR}$	88.80	86.49	79.06	79.01	78.99	89.71	N/A
	$\Delta G'_{TBR}$	89.05	87.11	83.47	84.55	84.78	90.44	N/A
	$\Delta H_{storage}$	60.36	49.37	38.34	34.74	34.05	56.04	29.71
	En. dens.	0.234	0.191	0.148	0.134	0.132	0.217	0.115
<b>2a/2b</b>	$\Delta\Delta G_{TS}$	-7.315	-9.179	*	*	*	-9.318	*
	$\Delta G_{TBR}$	93.68	80.09	69.98	67.20	66.65	91.42	66.50
	$\Delta H_{storage}$	67.13	64.94	62.25	61.19	60.97	69.83	62.17
	En. dens.	0.237	0.229	0.220	0.216	0.215	0.246	0.219
<b>2aH<sup>+</sup>/2bH<sup>+</sup></b>	$\Delta\Delta G_{TS}$	-13.20	-10.39	*	*	*	-14.81	*
	$\Delta G_{TBR}$	68.24	60.99	56.79	56.09	55.96	71.05	60.11
	$\Delta H_{storage}$	84.12	79.68	73.10	70.81	70.38	80.01	69.17
	En. dens.	0.297	0.281	0.258	0.250	0.248	0.282	0.244

## TD-DFT excitation energies

The calculated excitation energies for systems **1** and **2** are shown in Table S2.

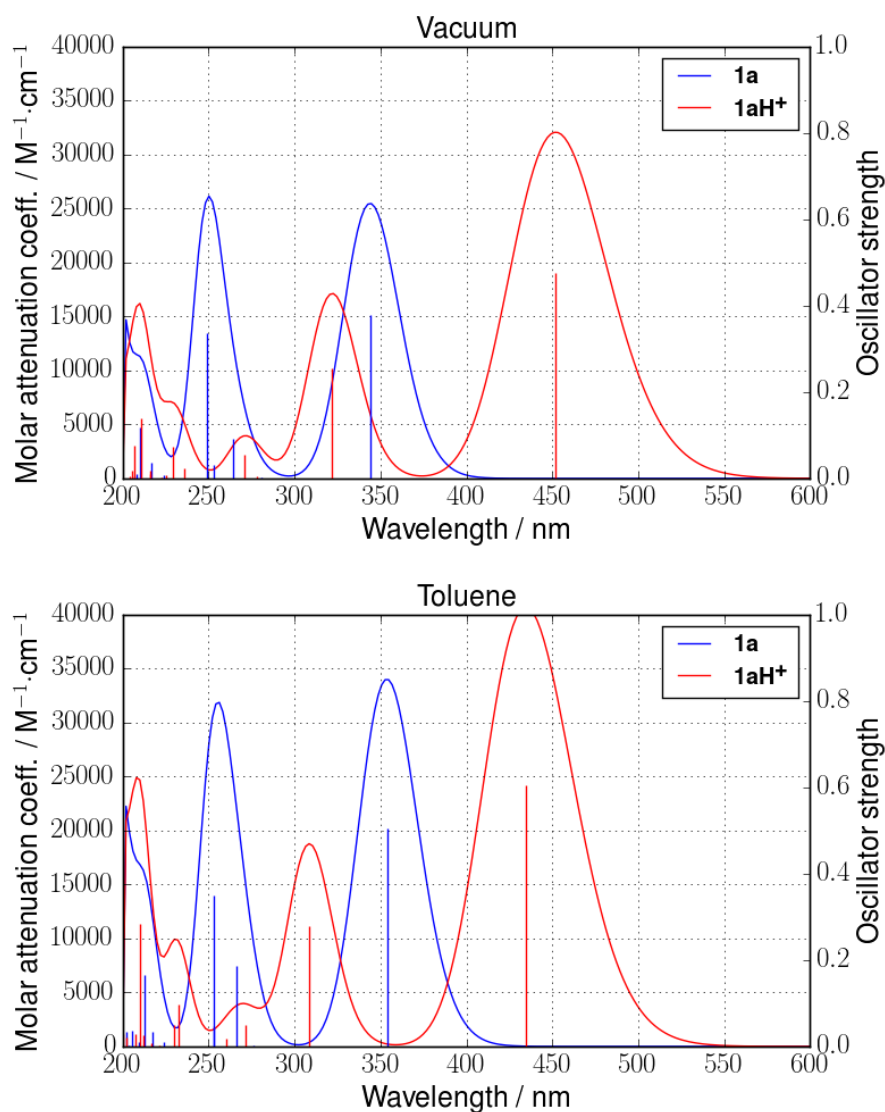
**Table S2.** Vertical excitation energies in eV for both the neutral and protonated DHAs and VHF<sub>s</sub> of systems **1** and **2** in different environments based on the geometries calculated at 298.15 K. Calculated using linear response TD-DFT at the M06-2X/6-311++G(d,p) level of theory.

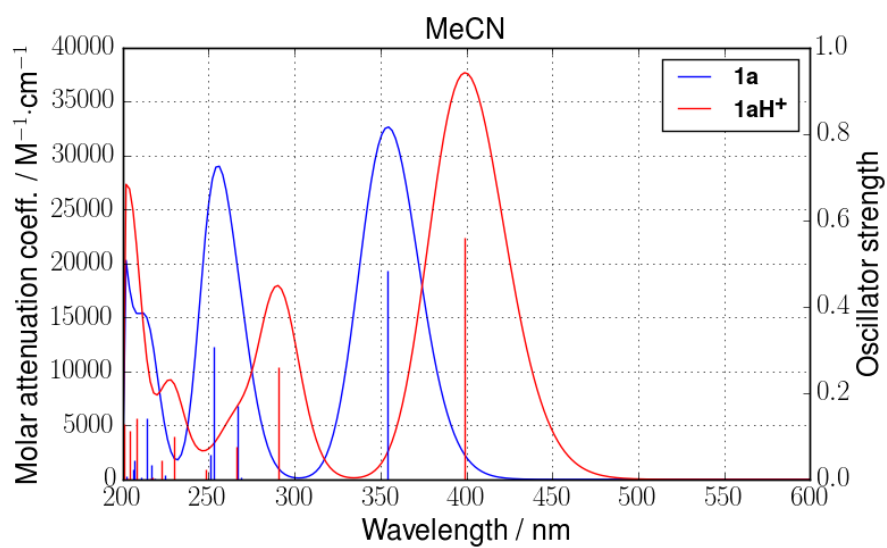
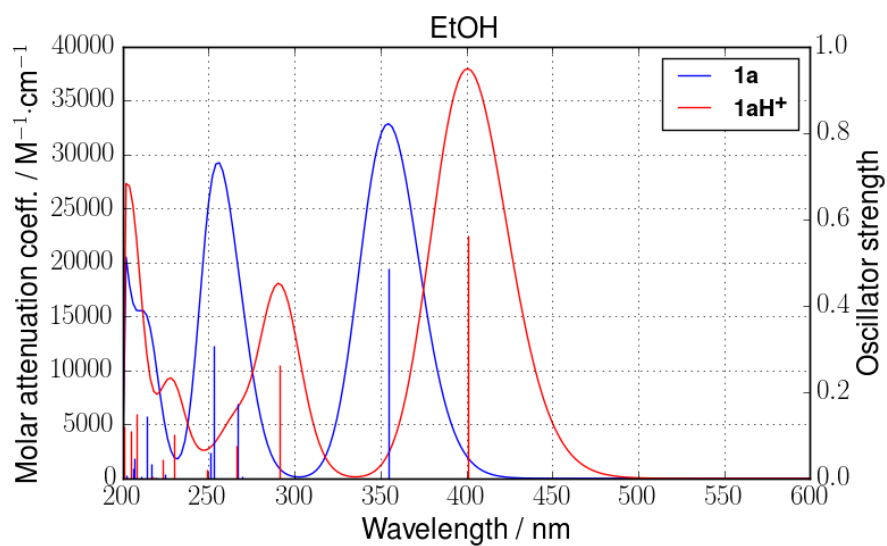
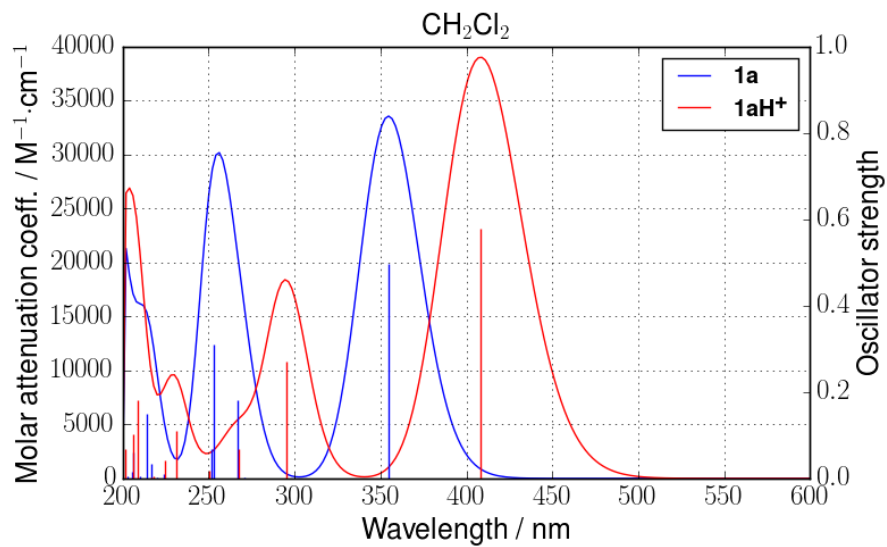
	Vacuum	Toluene	CH <sub>2</sub> Cl <sub>2</sub>	EtOH	MeCN
<b>1a</b>	3.60	3.50	3.50	3.50	3.50
<b>1aH<sup>+</sup></b>	2.74	2.85	3.04	3.09	3.11
<i>s-cis-1b</i>	2.96	2.75	2.69	2.68	2.68
<i>s-cis-1bH<sup>+</sup></i>	2.05	2.28	2.41	2.45	2.45
<i>s-trans-1b</i>	3.09	2.84	2.78	2.77	2.77
<i>s-trans-1bH<sup>+</sup></i>	2.08	2.34	2.50	2.54	2.55
<b>2a</b>	3.57	3.48	3.47	3.48	3.48
<b>2aH<sup>+</sup></b>	2.83	2.92	3.08	3.13	3.14
<b>2b</b>	2.92	2.73	2.67	2.65	2.65
<b>2bH<sup>+</sup></b>	2.14	2.23	2.33	2.37	2.37

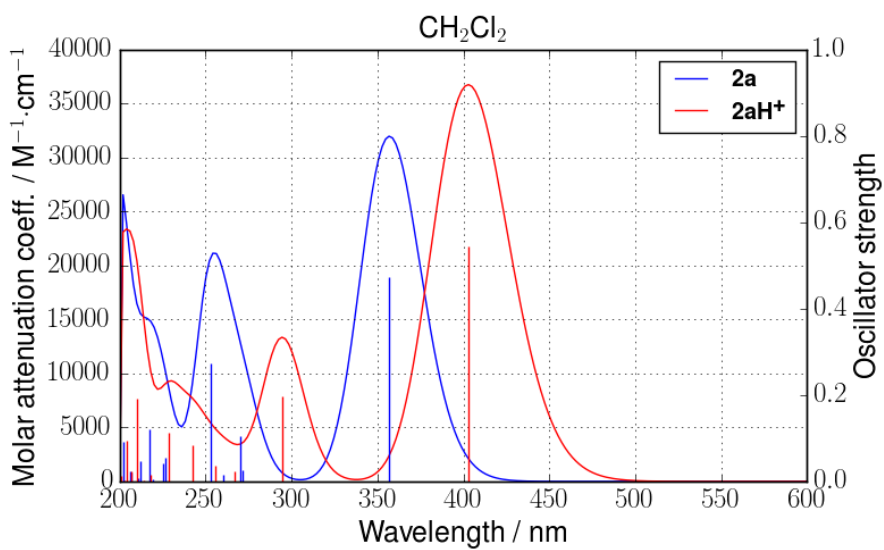
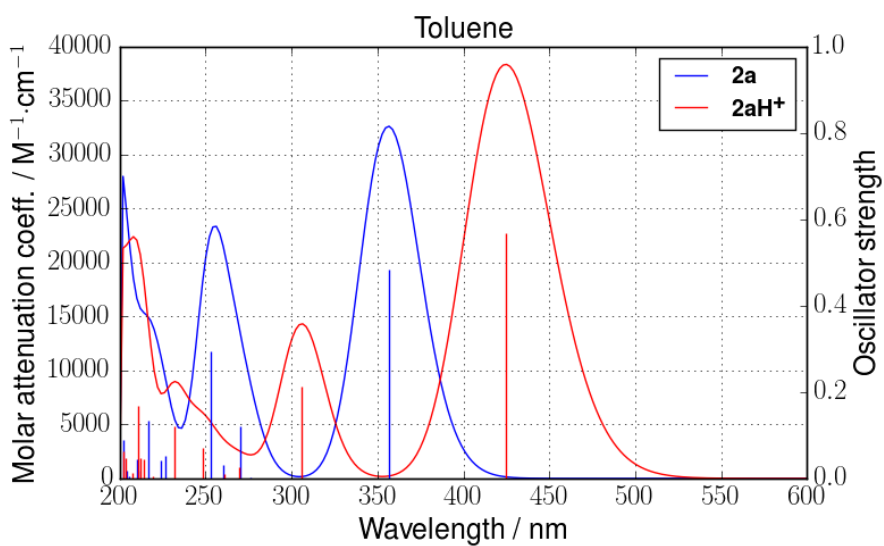
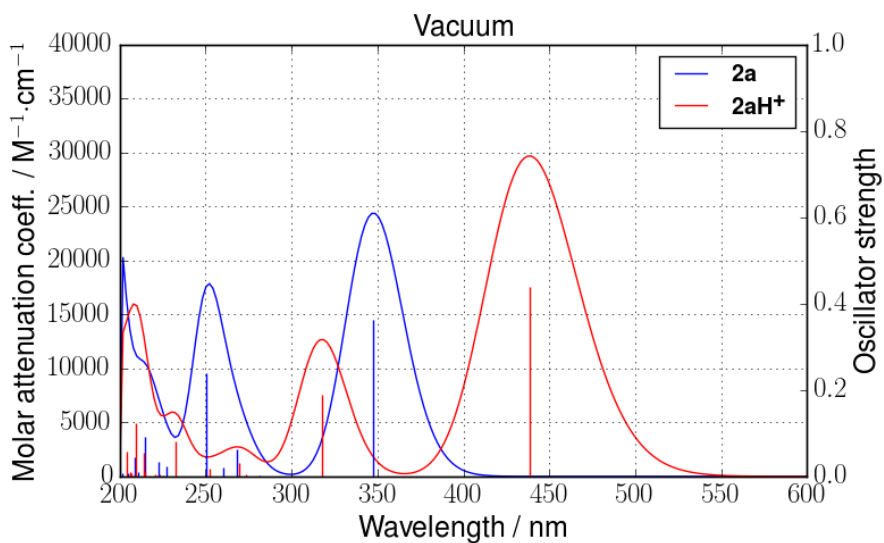


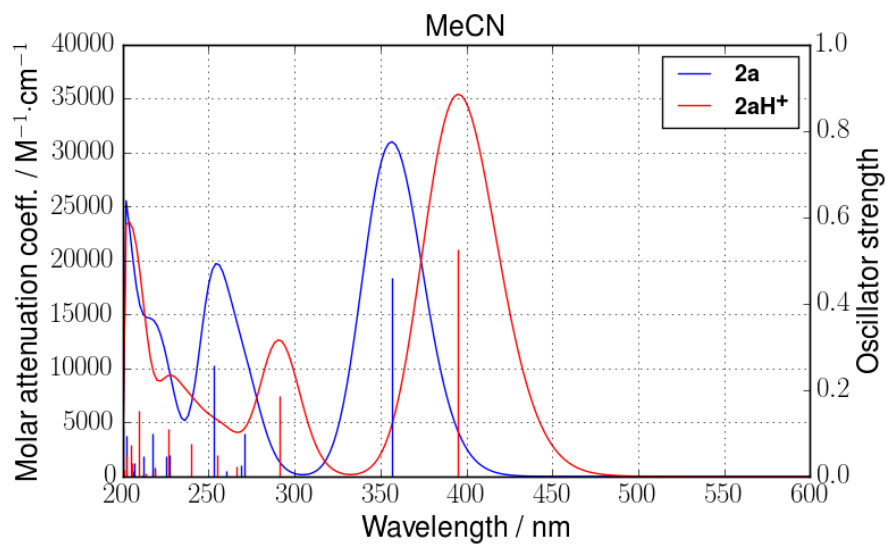
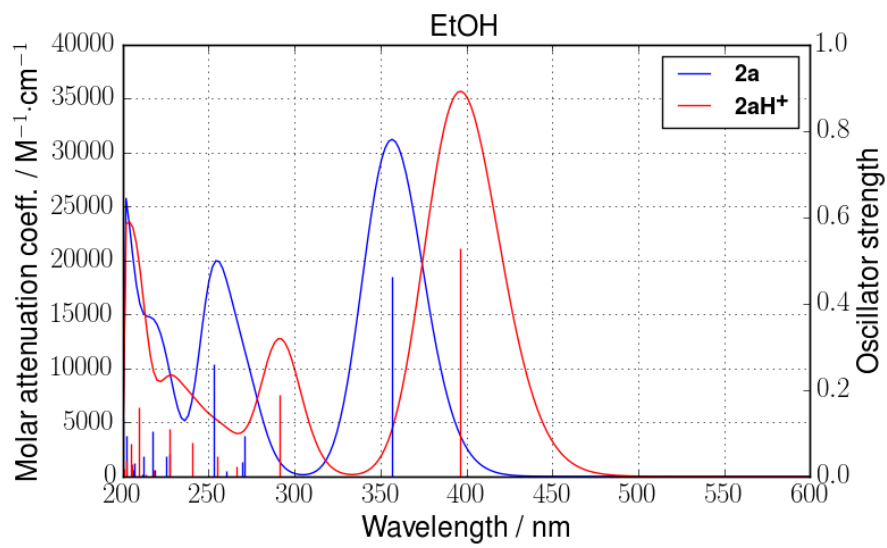
## UV-Vis spectra of both neutral and protonated DHAs

UV-Vis spectra of both protonated and non-protonated DHAs **1a** and **2a** in different environments were calculated using linear response TD-DFT at the M06-2X/6-311++G(d,p) level of theory based on the 298.15 K geometries. Gaussians with a standard deviation of 0.4 eV are fitted to the oscillator strengths in order to produce the absorption curves. The 30 lowest excited states are calculated for each compound, but only the ones between 200 nm and 600 nm are shown in the plots below.



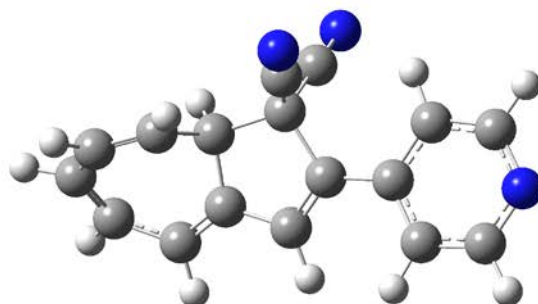




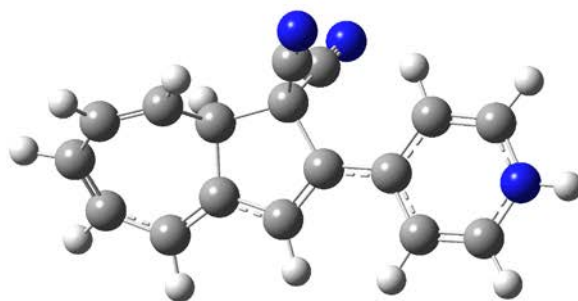


## Geometries of system 1

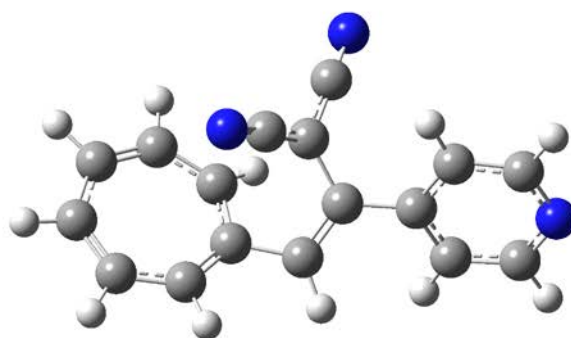
1a



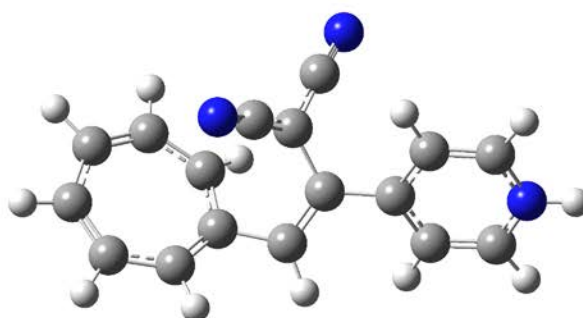
1aH<sup>+</sup>



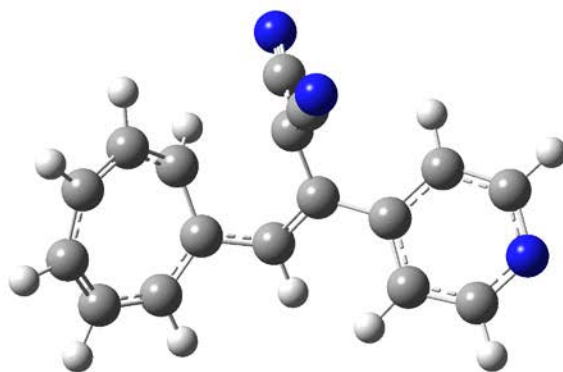
TSc of system 1



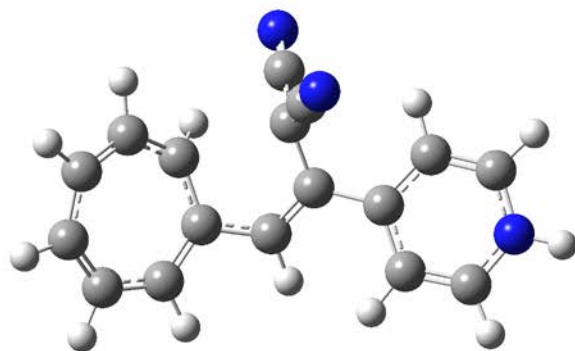
TScH<sup>+</sup> of system 1



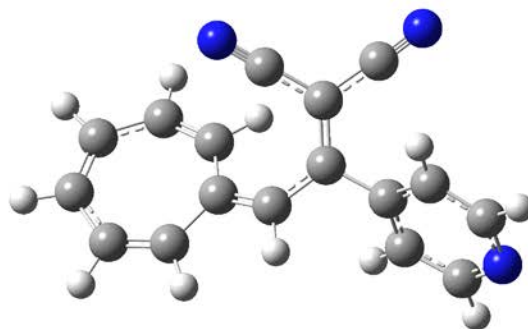
**TS<sub>T</sub> of system 1**



**TS<sub>T</sub>H<sup>+</sup> of system 1**

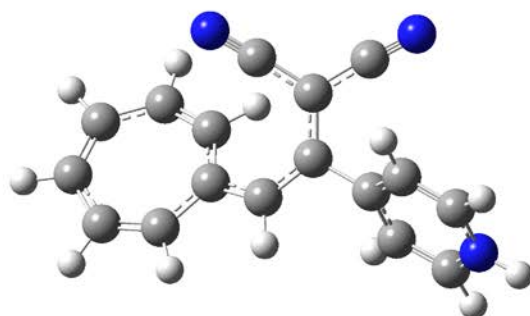


***cis*-1b**

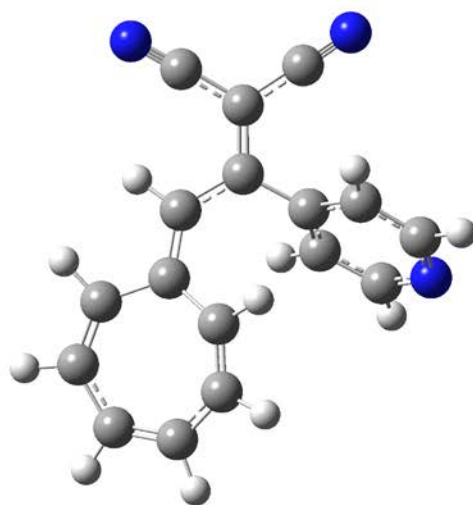


**S-**

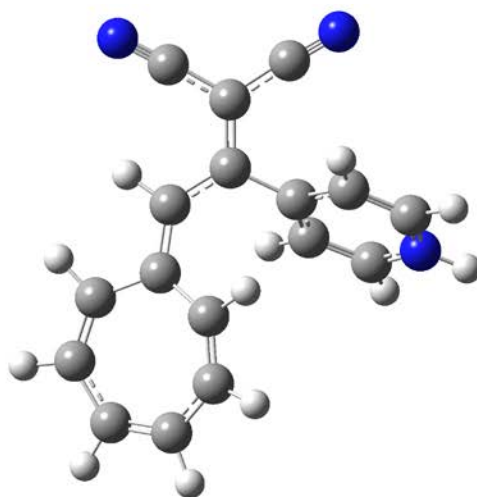
***s-cis*-1bH<sup>+</sup>**



*s-trans*-1b

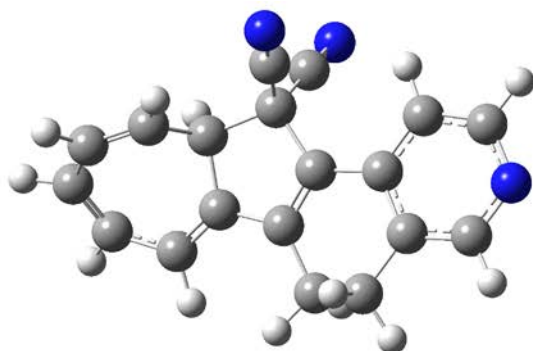


*s-trans*-1bH<sup>+</sup>

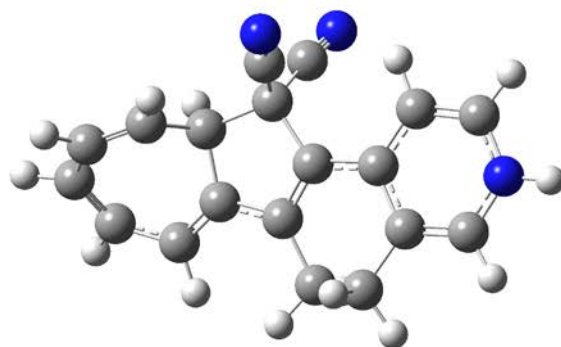


## Geometries of system 2

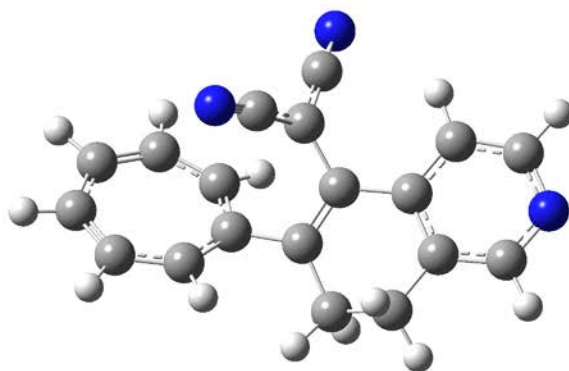
2a



2aH<sup>+</sup>

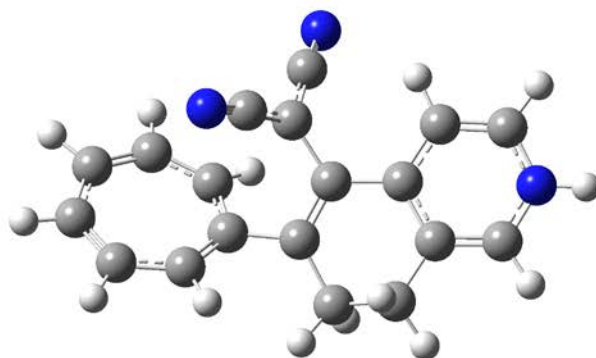


TSc of system 2

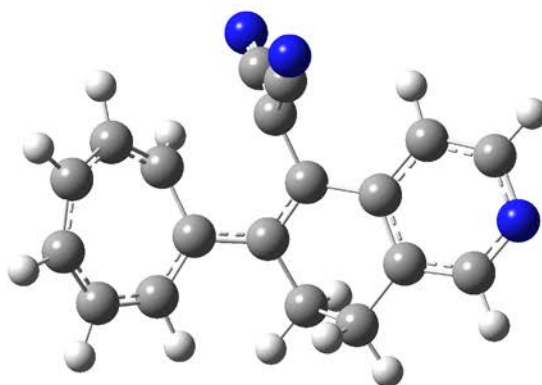




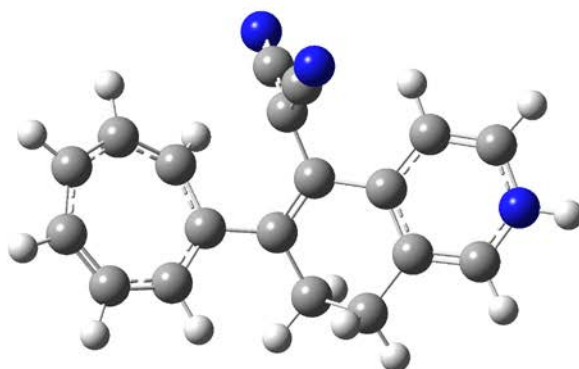
**TScH<sup>+</sup> of system 2**



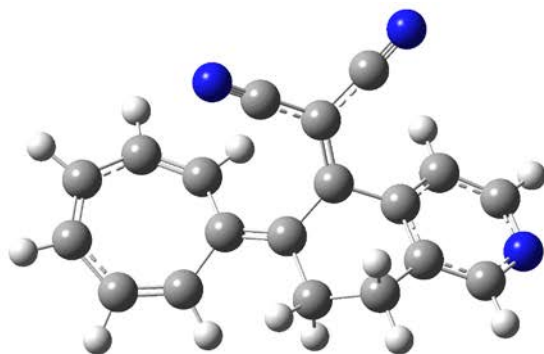
**TS<sub>T</sub> of system 2**



**TS<sub>T</sub>H<sup>+</sup> of system 2**



**2b**



**2bH<sup>+</sup>**

