

## MHz unidirectional rotation of molecular rotary motors

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### Supplementary Online Information

#### Experimental section

All compounds were prepared following previously reported procedures.<sup>1</sup> Cryo-UV/Vis and CD kinetic experiments were performed using an Oxford Instruments OptistatDN variable temperature liquid nitrogen cryostat inserted in a Hewlett-Packard HP 8543 diode array spectrophotometer or a JASCO J-715 spectropolarimeter. NMR-data were obtained using a Varian Unity Plus Varian-500, operating for 499.86MHz for the <sup>1</sup>H nucleus and 125.69MHz for the <sup>13</sup>C nucleus. Transient absorption experiments were performed using Spectron Laser Systems SL801 Nd YAG laser, and for this work the 355 nm line of the pulsed Nd:YAG laser was used (energy approximately 35 mJ per pulse; system response 20 ns). Uvasol-grade solvents were used, except in the case of propane, which was received as a pressurized gas. To prepare spectroscopically clear propane samples, propane was liquefied at 200 K in a flame-dried nitrogen atmosphere and dried over MgSO<sub>4</sub>. A sample solution in isopentane was evaporated to near-dryness and diluted to the original volume with dried liquid propane by pouring it into the cuvet through a glass funnel with paper filter. This was performed in the outlet of a nitrogen-flushed cryostat, where a strong nitrogen stream prevented condensation of water on the outside of the cuvet. The cuvet was inserted into the cryostat as fast as possible after sample preparation, and then cooled to T < 120 K. Irradiations were performed using a 200W Oriel Xe(Hg) lamp or a 200W Oriel Hg-lamp fitted with suitable bandpass filters (typical bandwidth 10 nm).

#### UV/Vis spectroscopy

Sample solutions of 0.01 – 0.03 mM in a quartz cuvet were cooled and stabilized for 15 min. This solution was taken as the blanc before the start of irradiation. Irradiation was continued until no more change was observed in the spectrum (usually 10 – 15 min) resulting in the UV-difference spectrum of the sample at the photostationary state and the sample before irradiation. A suitable bandpass filter was mounted on the UV-beam exit to prevent photochemical conversion during the course of measurement of the thermal reaction, and thermal helix inversion was followed in time at a suitable wavelength. An exponential decay was fitted to the results to obtain the rate constant at that temperature.

#### CD-spectroscopy

After stabilization of a sample solution (0.01 – 0.03 mM) at the specified temperature the CD-spectrum was recorded. Irradiation was performed until no further change in the spectrum was observed. A spectrum of the sample at the photostationary state was recorded. The rate constant of the thermal reaction of the isomer resulting from irradiation to the original isomer was obtained by fitting an exponential decay to the curve obtained by following the reaction at the wavelength of largest change in the spectrum.

#### NMR-spectroscopy

Spectra of sample solutions enriched in one of the isomers were recorded at a specific temperature, and the conversion to the new isomer was followed by recording spectra at known time intervals. Isomer ratios were determined at each time interval by integration, and the rate constant of the thermal reaction was obtained by fitting an exponential decay to the data points.

#### Transient differential absorption spectroscopy

Solutions for analysis were prepared at OD 0.75 – 1 A.U. at the excitation wavelength, placed in a fluorescence cuvette and degassed with nitrogen gas. The UV/Vis spectrum of the sample solution was monitored throughout the experiments to verify sample stability. Activation parameters were obtained from Eyring plots over the temperature range 273 - 298 K. For compounds **2** and **6** single-shot experiments on fresh sample were averaged, to ensure the presence of a single isomer in the sample solution before each shot.

<sup>1</sup> Ter Wiel, M. K. J.; Vicario, J.; Davey, S. G.; Meetsma, A.; Feringa, B. L. *Org. Biomol. Chem.* **2005**, *3*, 28.

## Analytical data

Analytical data for compounds **3**, **4** and **5** are reported in ref 10. Analytical data of **1**, **2** and **6** are reported below. *Cis* – and *trans* isomers of **2** and **6** were assigned by X-ray crystallographic analysis of *trans*-**2** and *cis*-**6**. Pure *trans*-**6** could not be obtained in sufficient quantities for  $^{13}\text{C}$  or APT determination:

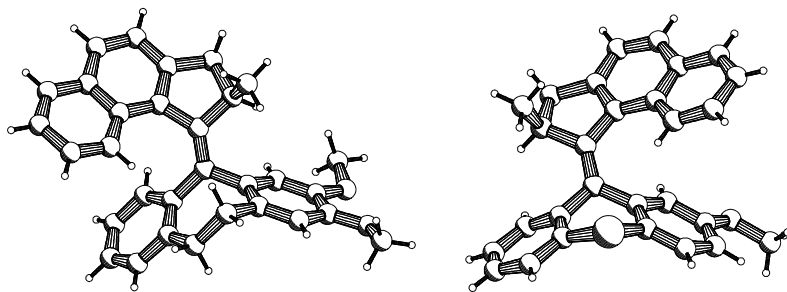
**1**:  $^1\text{H}$  NMR:  $\delta$ 7.55 (m, 3H), 7.26 (d,  $J$  = 8.1 Hz, 2H), 7.15 – 7.00 (m, 4H), 6.94 – 6.89 (m, 2H), 6.80 t,  $J$  = 7.5 Hz, 1H), 6.73 (d,  $J$  = 7.7 Hz, 1H), 6.36 (t,  $J$  = 7.5 Hz, 1H), 3.86 (dt,  $J$  = 13.7, 4.4 Hz, 1H), 3.70 (m, 1H), 3.38 (m, 2H), 2.89 (m, 1H), 2.61 (dt,  $J$  = 9.9, 3.7 Hz, 1H), 2.36 (d,  $J$  = 15.4 Hz, 1H), 0.75 ppm (d,  $J$  = 6.6 Hz, 3H).  $^{13}\text{C}$  NMR:  $\delta$ 145.6 (C), 145.0 (C), 144.9 (C), 141.0 (C), 139.3 (C), 136.4 (C), 135.4 (C), 134.9 (C), 133.9 (C), 131.4 (CH), 130.3 (CH), 130.0 (CH), 129.7 (C), 129.2 (CH), 128.4 (CH), 128.2 (CH), 127.3 (CH), 127.2 (CH), 127.0 (CH), 126.5 (CH), 125.8 (CH), 125.4 (CH), 124.4 (CH), 124.1 (CH), 39.8 (CH), 39.7 (CH<sub>2</sub>), 34.4 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 18.8 ppm (CH<sub>3</sub>).  $m/z$  (EI, %) HRMS calcd for 372.1878, found 372.1866.

*cis*-**2**:  $^1\text{H}$  NMR:  $\delta$ 7.72 (dt,  $J$  = 8.2, 3.7 Hz, 2H), 7.44 (d,  $J$  = 8.2 Hz, 1H), 7.31 (d,  $J$  = 8.6 Hz, 1H), 7.16 (m, 2H), 7.0 (t,  $J$  = 7.0 Hz, 1H), 6.8 (m, 3H), 6.54 (m, 2H), 3.75 (m, 7H), 3.55 (m, 3H), 3.08 (dt,  $J$  = 8.8, 4.4 Hz, 1H), 2.80 (m, 1H), 2.54 (d,  $J$  = 15.6 Hz, 1H), 0.77 ppm (d,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR:  $\delta$ 148.5 (C), 147.7 (C), 146.0 (C), 145.2 (C), 141.8 (C), 137.1 (C), 137.0 (C), 135.3 (C), 134.3 (C), 133.5 (C), 131.6 (C), 131.4 (CH), 129.8 (CH), 129.5 (CH), 129.3 (C), 128.2 (CH), 127.1 (CH), 126.8 (CH), 125.4 (CH), 124.7 (CH), 124.4 (CH), 124.3 (CH), 111.9 (2x C-H), 56.4 (CH<sub>3</sub>), 56.3 (CH<sub>3</sub>), 39.8 (CH), 39.7 (CH<sub>2</sub>), 34.2 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 19.0 ppm (CH<sub>3</sub>).  $m/z$  (EI, %): 433 (100), 401 (25), 291 (54), 251 (18). HRMS calcd for C<sub>31</sub>H<sub>28</sub>O<sub>2</sub> 432.2089, found 432.2068.

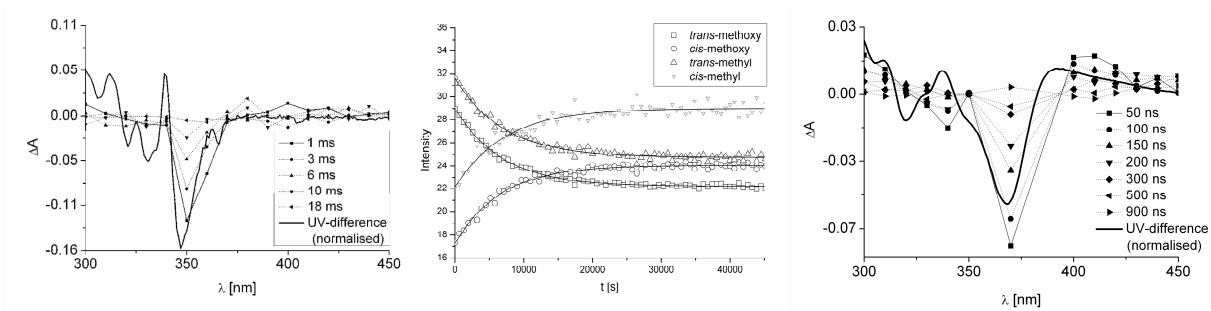
*trans*-**2**:  $^1\text{H}$  NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 7.69 (d,  $J$  = 8.1 Hz, 1H), 7.68 (d,  $J$  = 7.7 Hz, 1H), 7.34 –  $\delta$ 7.20 (m, 5H), 7.18 (t,  $J$  = 5.1 Hz, 1H), 6.90 (t,  $J$  = 7.3 Hz, 1H), 6.58 (s, 1H), 6.07 (s, 1H), 3.81 (m, 1H), 3.75 (s, 3H), 3.62 (m, 1H), 3.50 (m, 2H), 3.01 (m, 1H), 2.90 – 2.82 (m, 1H), 2.86 (s, 3H), 2.51 (d,  $J$  = 15.8 Hz, 1H), 0.75 ppm (d,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 148.6 (C), 146.9 (C), 145.7 (C), 145.1 (C), 144.8 (C), 139.7 (C), 135.5 (C), 133.8 (C), 133.4 (C), 132.9 (C), 129.8 (CH), 129.6 (C), 129.3 (C), 128.2 (CH), 127.7 (CH), 127.6 (CH), 127.3 (CH), 127.0 (CH), 126.4 (CH), 124.7 (CH), 124.4 (CH), 124.4 (CH), 114.7 (CH), 114.4 (CH), 56.1 (CH<sub>3</sub>), 55.8 (CH<sub>3</sub>), 39.7 (CH<sub>2</sub>), 39.5 (CH), 34.2 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 19.1 ppm (CH<sub>3</sub>).  $m/z$  (EI, %): 433 (100), 401 (24), 291 (51), 251 (16). HRMS calcd for C<sub>31</sub>H<sub>28</sub>O<sub>2</sub> 432.2089, found 432.2071.

*cis*-**6**:  $^1\text{H}$  NMR:  $\delta$ 7.70 (m, 3H), 7.58 (dd,  $J$  = 7.7, 1.1 Hz, 1H), 7.43 (d,  $J$  = 8.4 Hz, 1H), 7.40 (d,  $J$  = 8.4 Hz, 1H), 7.30 (dt,  $J$  = 7.7, 1.1 Hz, 1H), 7.18 (dq,  $J$  = 8.1, 1.1 Hz, 2H), 6.82 (m, 2H), 6.57 (dd,  $J$  = 8.4, 2.9 Hz, 1H), 6.23 (d,  $J$  = 2.6 Hz, 1H), 4.26 (m, 1H), 3.63 (dd,  $J$  = 15.8, 6.2 Hz, 1H), 2.93 (s, 3H), 2.62 (d,  $J$  = 15.8 Hz, 1H), 0.79 ppm (d,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR:  $\delta$ 158.6, 146.1, 145.7, 141.2, 137.8, 136.4, 135.1, 132.8, 130.0, 129.0, 128.6, 128.3, 12.8, 127.7, 127.6, 126.5, 126.1, 125.9, 124.7, 124.2, 123.7, 114.2, 113.4, 55.1, 39.6, 37.6, 19.6 ppm.  $m/z$  (EI, %): 406 (92.5), 391 (28.3), 375 (18.3), 265 (100). HRMS calcd for C<sub>28</sub>H<sub>22</sub>OS 406.1391, found 406.1384.

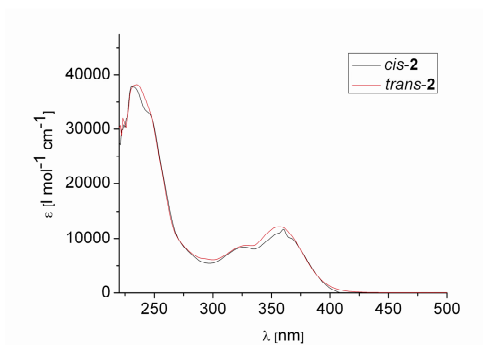
*trans*-**6** (<5% *cis*-**6**):  $^1\text{H}$  NMR:  $\delta$ 7.70 (d,  $J$  = 8.1 Hz, 1H), 7.66 (d,  $J$  = 8.4 Hz, 1H), 7.55 (d,  $J$  = 7.7 Hz, 1H), 7.49 (d,  $J$  = 8.4 Hz, 1H), 7.40 (d,  $J$  = 8.1 Hz, 1H), 7.34 (d,  $J$  = 2.2 Hz, 1H), 7.14 (t,  $J$  = 7.5 Hz, 1H), 6.97 (t,  $J$  = 7.7 Hz, 1H), 6.84 (d,  $J$  = 7.7 Hz, 1H), 6.77 (m, 2H), 6.69 (d,  $J$  = 7.0 Hz, 1H), 6.59 (t,  $J$  = 7.5 Hz, 1H), 4.30 (m, 1H), 3.85 (s, 3H), 3.61 (dd,  $J$  = 9.0, 6.2 Hz, 1H), 2.60 (d,  $J$  = 15.4 Hz, 1H), 0.79 ppm (d,  $J$  = 7.0 Hz, 3H).  $m/z$  (EI, %): 406 (92.5), 391 (28.3), 375 (18.3), 265 (100). HRMS calcd for C<sub>28</sub>H<sub>22</sub>OS 406.139, found 406.1387.



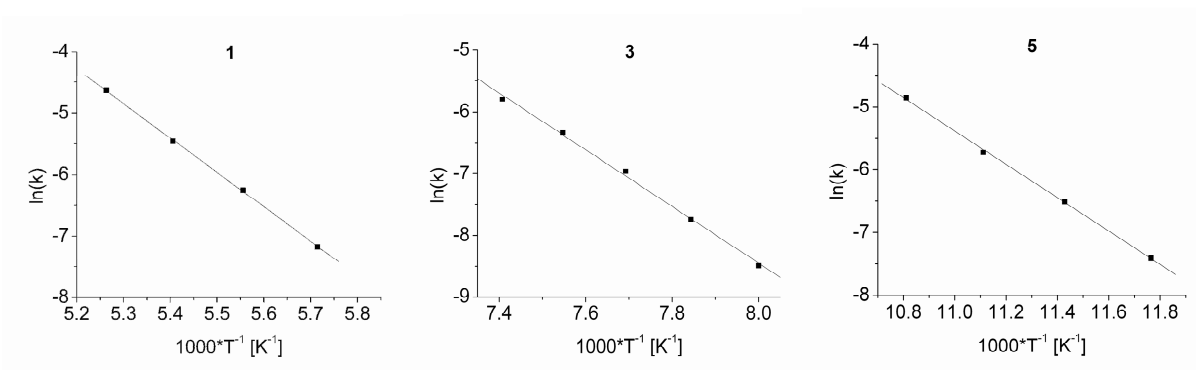
ORTEP plot of the X-ray structures of *trans*-**2** (left) and *cis*-**6** (right).



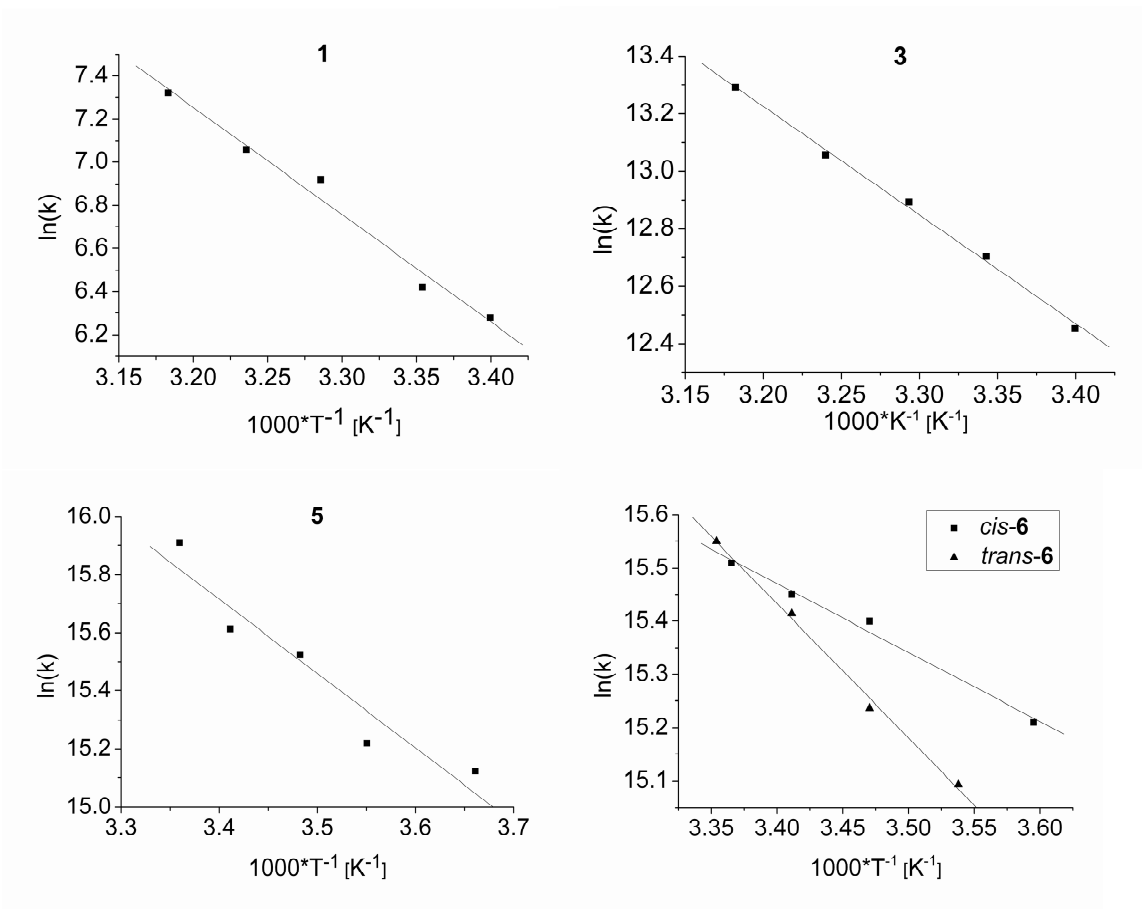
a) TA and UV/Vis-difference spectrum of **1**. b) Thermal isomerisation of motors **4** (20°C) c) TA and UV/Vis-difference spectrum of **5**.



UV/Vis-spectra of *cis*-**2** and *trans*-**2** in DCM at 20°C. Note that *trans*-**2** has higher absorption at 360 nm than *cis*-**2**, which is in agreement with the transient absorption kinetic analysis.

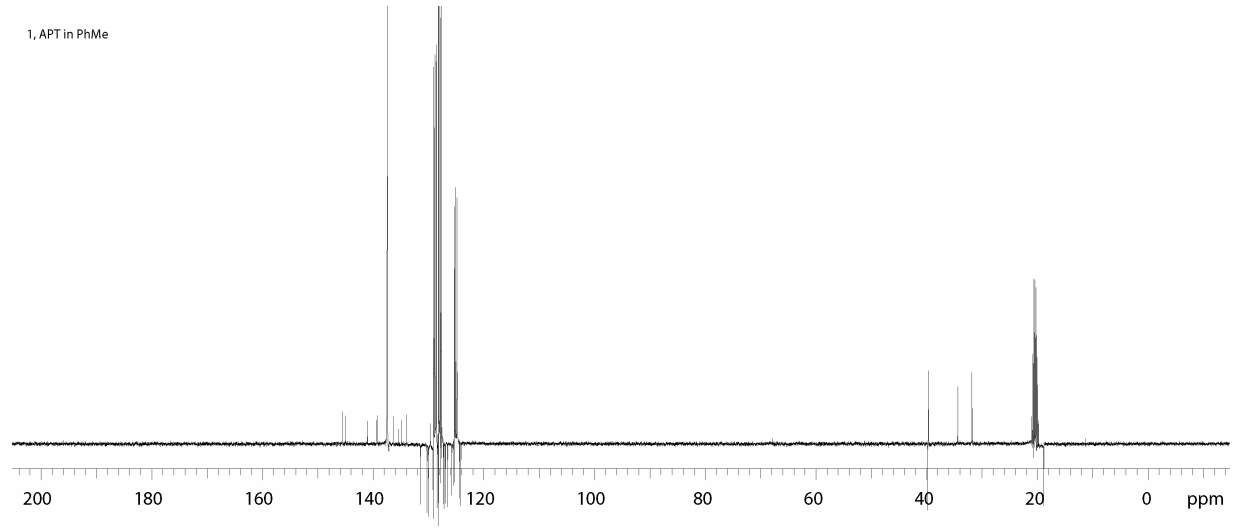
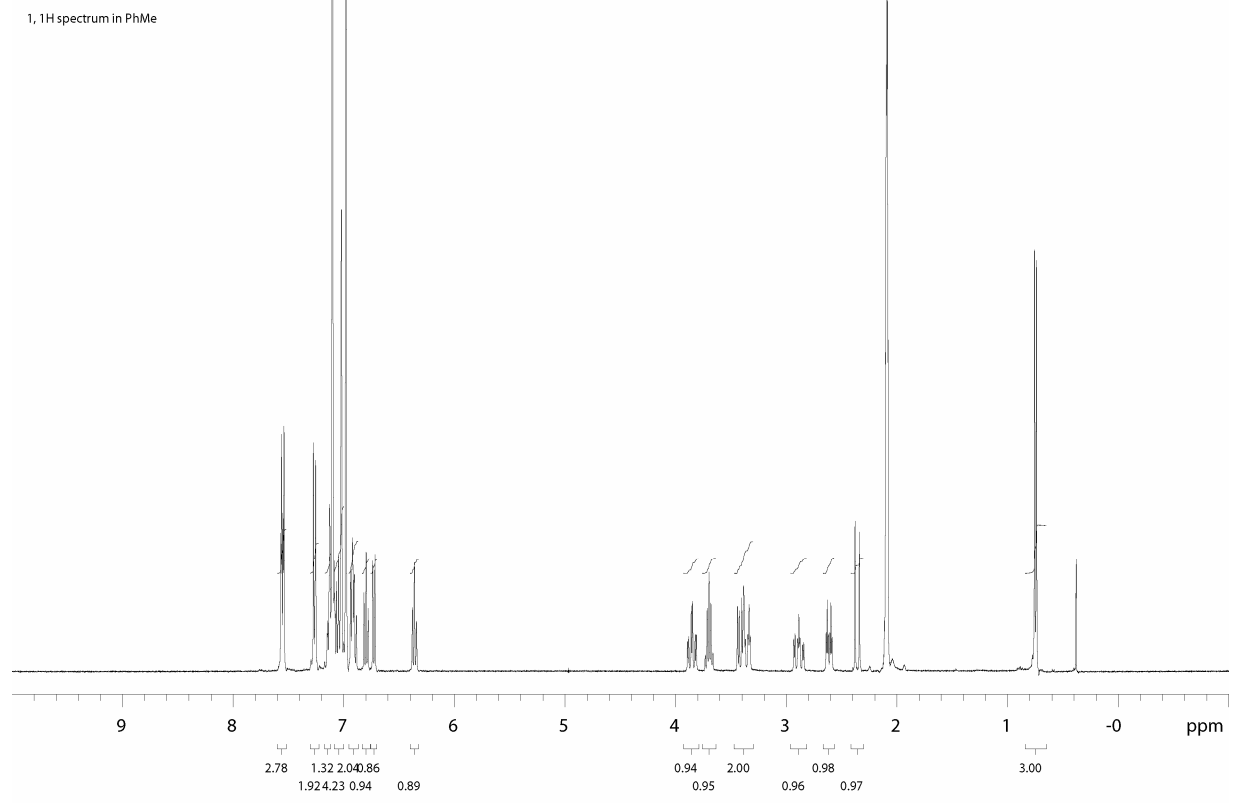


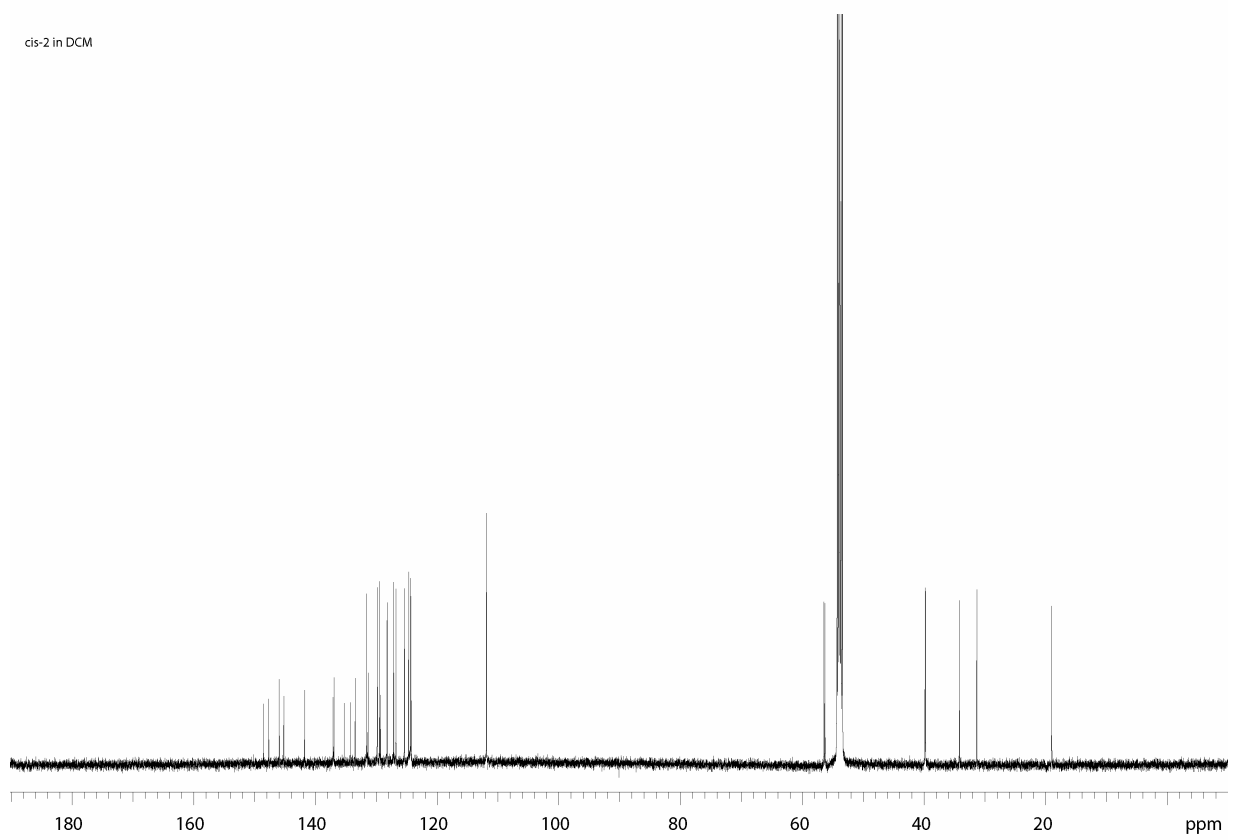
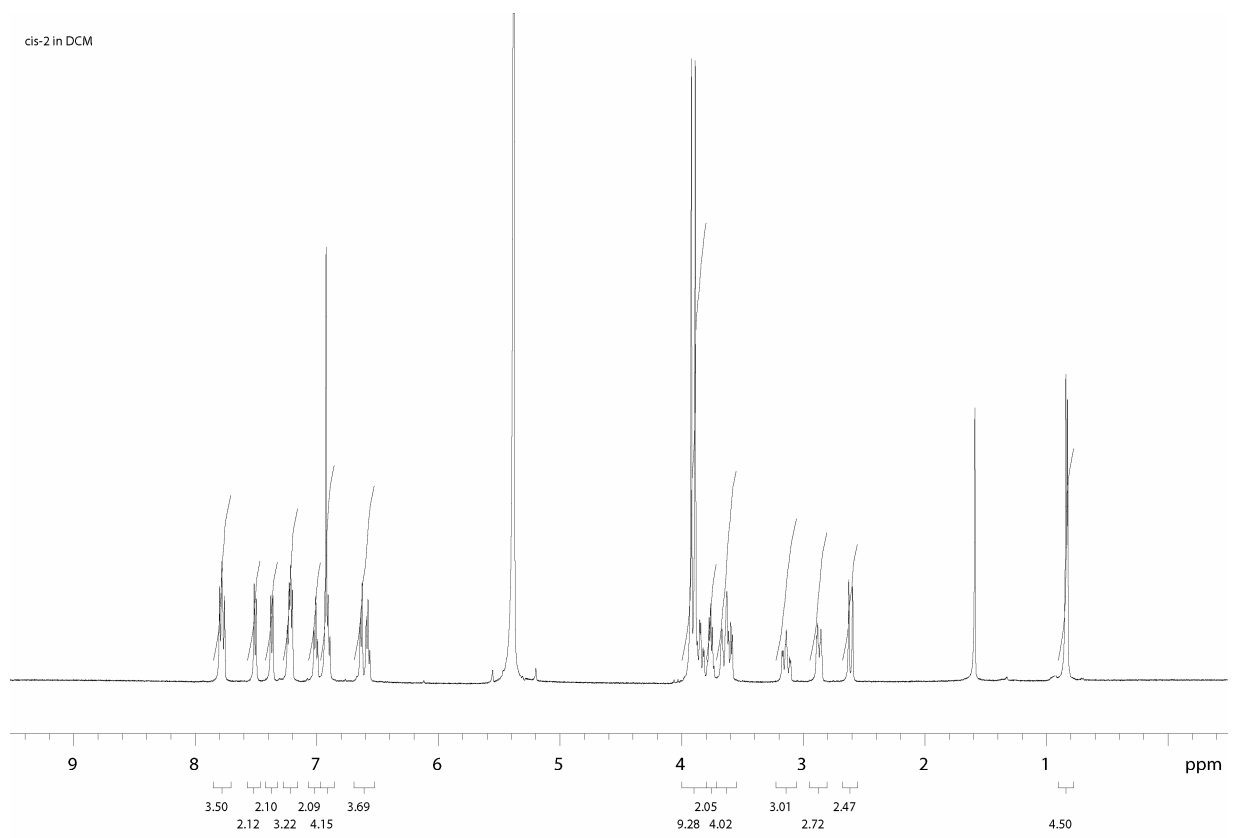
Arrhenius plots of compounds **1** (iso-pentane, UV-spectroscopy), **3** (iso-pentane, CD-spectroscopy), **5** (propane, CD-spectroscopy) by cryogenic techniques.



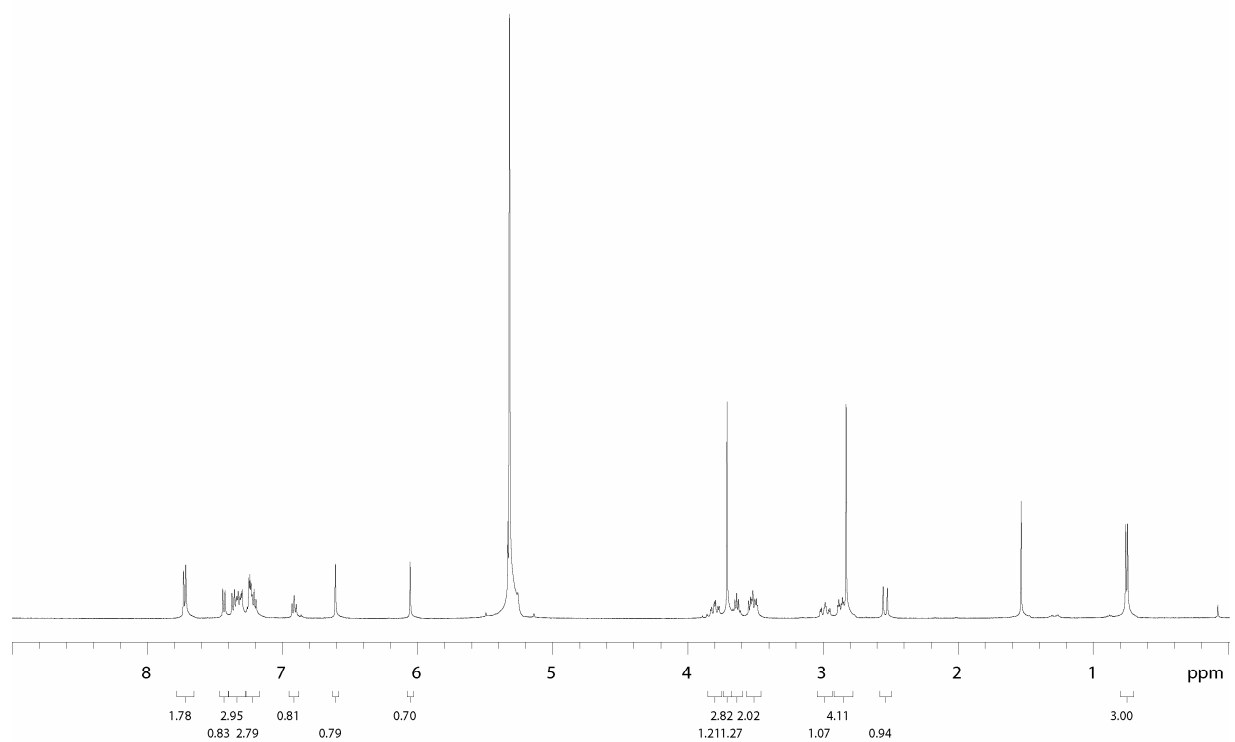
Arrhenius plots of compounds **1** (toluene), **3** (hexane), **5** (dichloromethane), and *cis*- and *trans*-**6** (dichloromethane) obtained by TA spectroscopy at ambient temperatures.

Next pages: full spectra of all compounds not previously reported.





trans-2, proton spectrum in DCM



trans-2, APT in DCM

