

## Supplementary Information

Photo Enhancement Reveals (*E,Z*) and (*Z,Z*) Configurations as Additional Intermediates in Iminium Ion Catalysis

Willibald J. Stockerl<sup>1</sup>, Ruth M. Gschwind\*<sup>1</sup>

<sup>1</sup>Institute of Organic Chemistry, University of Regensburg, 93040 Regensburg, Germany

E-mail: [ruth.gschwind@chemie.uni-regensburg.de](mailto:ruth.gschwind@chemie.uni-regensburg.de)

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## 1. General

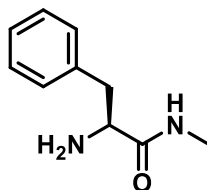
Commercially available chemicals were, unless otherwise stated, used without further purification. *Trans*-cinnamaldehyde was distilled under reduced pressure ( $2 \cdot 10^{-1}$  mbar) at 100 °C, degassed using the freeze-pump-thaw method and stored inside the glove box. Acetone was dried dynamically using 3Å molecular sieve, degassed by the freeze-pump-thaw method and stored under argon atmosphere in a Schlenk flask. EtOH and Et<sub>2</sub>O were distilled over sodium and benzophenone and stored under argon atmosphere in a Schlenk flask with 3Å molecular sieve. CD<sub>3</sub>CN and CD<sub>2</sub>Cl<sub>2</sub> were distilled over CaH<sub>2</sub>, degassed using the freeze-pump-thaw method and stored under argon atmosphere in a Schlenk flask with 3Å molecular sieve.

UV/Vis-spectra were recorded using an AvaLight-DH-S-BAL as light source and an AvaSpec-2048 for detection.

NMR experiments for routine measurements were recorded on a Bruker Avance 400 MHz at 25 °C. Detailed NMR spectroscopic investigations were performed on a Bruker Avance III HD 600 (600.03 MHz) with a 5 mm fluorine selective TBIF probe, on a Bruker Avance NEO 600 (600.03 MHz) with a 5 mm CryoProbe Prodigy BBO or on a Bruker Avance III HD 600 (600.25 MHz) with a 5 mm TCI CryoProbe using the reported *in situ* illumination setup with 5 mm amberized thin wall NMR tubes and for illumination at 365 nm a LG Innotek LEUVA66X00RV00 LED or an OSRAM LZ4-04UV0R-00000 was used.<sup>1</sup> For combined *in situ* illumination-NMR-UV/Vis spectroscopy the reported setup was used analogously.<sup>2</sup> NMR data were processed, evaluated and plotted with TopSpin 3.2 and 4.0 software and reported as follows: ppm, multiplicity, coupling constant, integral. All spectra are referenced to the solvent residual signal: Acetone-*d*<sub>6</sub>:  $\delta(^1\text{H}) = 2.05$  ppm,  $\delta(^{13}\text{C}) = 29.84$  ppm; CD<sub>2</sub>Cl<sub>2</sub>:  $\delta(^1\text{H}) = 5.32$  ppm,  $\delta(^{13}\text{C}) = 53.84$  ppm; CD<sub>3</sub>Cl:  $\delta(^1\text{H}) = 7.26$  ppm,  $\delta(^{13}\text{C}) = 77.16$  ppm; CD<sub>3</sub>CN:  $\delta(^1\text{H}) = 1.94$  ppm,  $\delta(^{13}\text{C}) = 118.26$  ppm. Further plotting of the spectra was performed with Origin 2019 and Corel Draw 2020 software.

## 2. Synthesis of model iminium ion 1

### 2.1 (S)-2-Amino-N-methyl-3-phenylpropanamide (2)



2

**2** was synthesized following a literature procedure.<sup>3</sup>

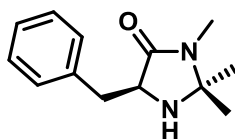
(S)-Phenylalanine (6.99 g, 42.30 mmol, 1.0 eq.) was suspended in MeOH (17.1 mL). The suspension was cooled down to 0 °C followed by a slow addition of thionyl chloride (6.04 g, 3.68 mL, 50.76 mmol, 1.2 eq.) under vigorous stirring. The newly formed white suspension was first heated to r.t. and then stirred under reflux for 23 h, which resulted in a light brown solution. Volatile components were removed under reduced pressure and subsequent a MeNH<sub>2</sub>-EtOH-solution (8.0 M, 21.15 mL, 169.20 mmol, 4.0 eq.) was slowly added. The solution was stirred for 23 h at r.t. under generation of a white precipitate. After another remove of volatile components *in vacuo* the precipitate was dissolved in an aq. sat. NaHCO<sub>3</sub>-solution (60 mL) followed by an extraction with CH<sub>2</sub>Cl<sub>2</sub> (3 · 55 mL) and drying over MgSO<sub>4</sub>. Purification by recrystallization (*n*-hexane/ EA 2:1) and drying under reduced pressure yielded **2** as a white solid (5.43 g, 30.5 mmol, 72 %).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C):** 7.20 – 7.35 (m, 6H, H-Ar & NH), 3.68 (dd, *J* = 9.1, 4.1 Hz, 1H, COCH), 3.29 (dd, *J* = 13.8, 4.3 Hz, 1H, CH<sub>2</sub>), 2.80 (d, *J* = 5.0 Hz, 3H, CH<sub>3</sub>), 2.73 (dd, *J* = 13.7, 9.1 Hz, 1H, CH<sub>2</sub>), 2.06 (s, 2H, NH<sub>2</sub>).

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 101 MHz, 25 °C):** 174.9, 138.2, 129.4, 128.8, 126.9, 56.6, 41.2, 26.0.

Analytical data are in agreement with the literature.<sup>3</sup>

### 2.2 (S)-5-Benzyl-2,2,3-trimethylimidazolidin-4-one (3)



3

**3** was synthesized following a literature procedure.<sup>4</sup>

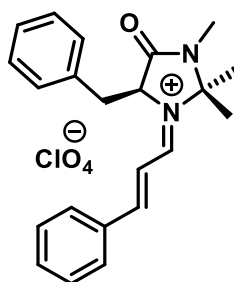
The synthesis was carried out in oven-dried glassware under argon atmosphere. Amid **2** (2.20 g, 12.35 mmol, 1.0 eq.) was dissolved in anhydrous (anh.) and degassed (deg.) EtOH (30 mL). Anh. and deg. acetone (2.38 g, 3.01 mL, 40.0 mmol, 3.3 eq.) and 3 Å molecular sieve (5 g) were added followed by stirring for 18 h under reflux. Afterwards the reaction mixture was allowed to cool down to r.t. and the solution was purified by filtration. Removing volatile components using reduced pressure yielded **3** as a beige oil (2.58 g, 11.8 mmol, 96 %).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C):** 7.19 – 7.32 (m, 5H, *H*-Ar), 3.79 (dd, *J* = 6.6, 4.6 Hz, 1H, *CH*), 3.14 (dd, *J* = 14.2, 4.5 Hz, 1H, *CH*<sub>2</sub>), 3.00 (dd, *J* = 14.2, 6.8 Hz, 1H, *CH*<sub>2</sub>), 2.75 (s, 3H, *NCH*<sub>3</sub>), 1.66 (bs, 1H, *NH*), 1.26 (s, 3H, *CH*<sub>3</sub>), 1.15 (s, 3H, *CH*<sub>3</sub>).

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 101 MHz, 25 °C):** 173.5, 137.3, 129.6, 128.7, 126.9, 75.7, 59.4, 37.4, 27.4, 25.5, 25.3.

Analytical data are in agreement with the literature.<sup>4</sup>

### 2.3 (S,E)-5-Benzyl-2,2,3-trimethyl-4-oxo-1-((E)-3-phenylallylidene)imidazolidin-1-ium perchlorate (**1**)



**1**

**1** was synthesized following a literature procedure.<sup>5</sup>

Imidazolidinone **3** (559 mg, 2.56 mmol, 1.0 eq.) was dissolved in Et<sub>2</sub>O (3.2 mL) and an aqueous HClO<sub>4</sub>-solution (70 %, 136 μL, 1.69 mmol, 1.32 eq.) in EtOH/Et<sub>2</sub>O 1:1 (6.4 mL) was added. After stirring for 15 min at r.t. the solvent was removed *in vacuo* giving the imidazolidinone salt as a yellow precipitant. The precipitant was redissolved in MeOH (6.4 mL), heated to 35 °C and *trans*-cinnamaldehyde (338 mg, 332 μL, 2.56 mmol, 2.0 eq.) was added. The reaction mixture was stirred for 1 h at 35 °C generating a red solution with a beige solid. Removing the supernatant solution, washing with anh. and deg. Et<sub>2</sub>O (10 · 2.0 mL) and drying the residue under reduced pressure yielded **1** as a light beige solid (906 mg, 2.09 mmol, 82 %), which was stored inside glove box freezer.

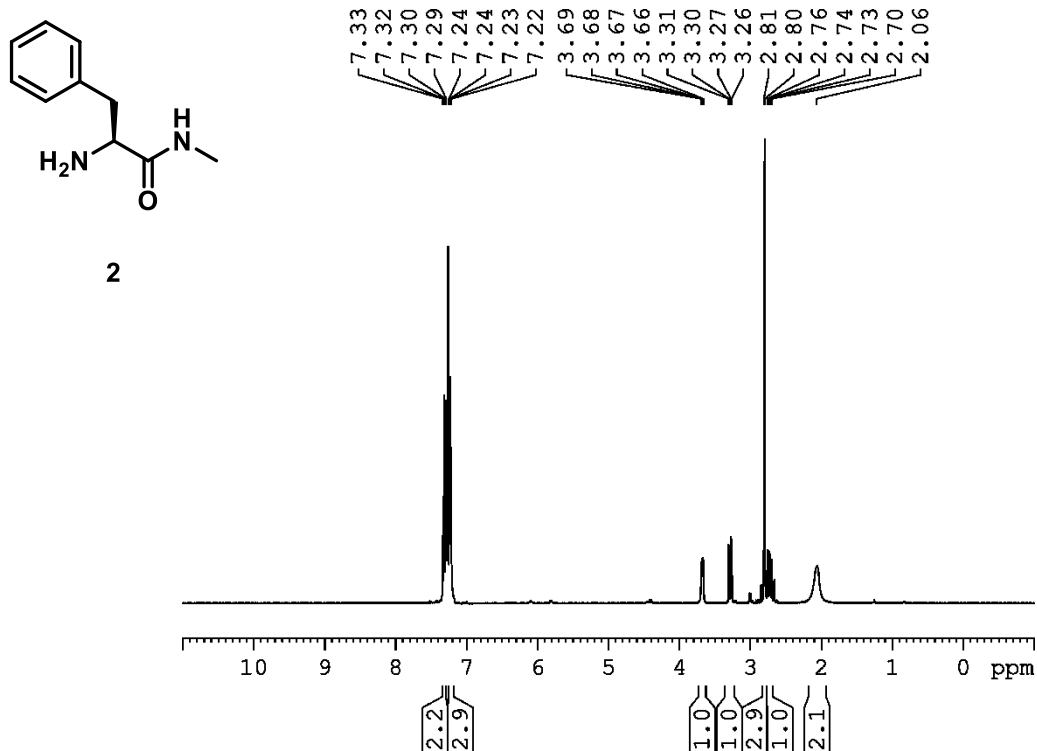
**<sup>1</sup>H-NMR (CD<sub>3</sub>CN, 400 MHz, 25 °C):** 8.74 (dd, *J* = 10.7, 1.9 Hz, 1H, C(1) - *H*), 8.20 (d, *J* = 15.1 Hz, 1H, C(3) - *H*), 7.90 – 7.95 (m, 2H, arom. *H*), 7.69 – 7.75 (m, 1H, arom. *H*), 7.58 – 7.65

(m, 2H, arom. *H*), 7.24 – 7.35 (m, 4H, arom. *H* + C(2) - *H*), 7.06 – 7.12 (m, 2H, arom. *H*), 5.18 – 5.23 (m, 1H, *CH*), 3.58 (dd, *J* = 14.7, 5.7 Hz, 1H, *CH*<sub>2</sub>), 3.47 (dd, *J* = 14.7, 3.7 Hz, 1H, *CH*<sub>2</sub>), 2.79 (s, 3H, *NCH*<sub>3</sub>), 1.70 (s, 3H, *CH*<sub>3</sub>), 0.80 (s, 3H, *CH*<sub>3</sub>).

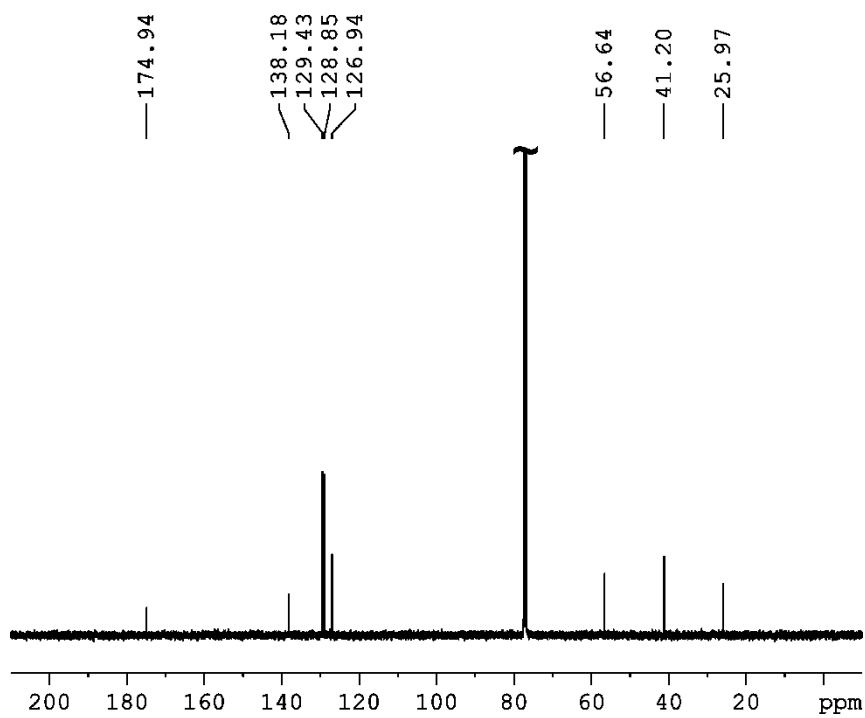
**<sup>13</sup>C-NMR (CD<sub>3</sub>CN, 101 MHz, 25 °C):** 168.2, 166.7, 165.2, 136.0, 134.7, 134.4, 132.4, 131.1, 130.6, 130.0, 129.1, 118.4, 86.5, 65.1, 37.2, 27.5, 26.0, 24.7.

Analytical data are in agreement with the literature.<sup>5</sup>

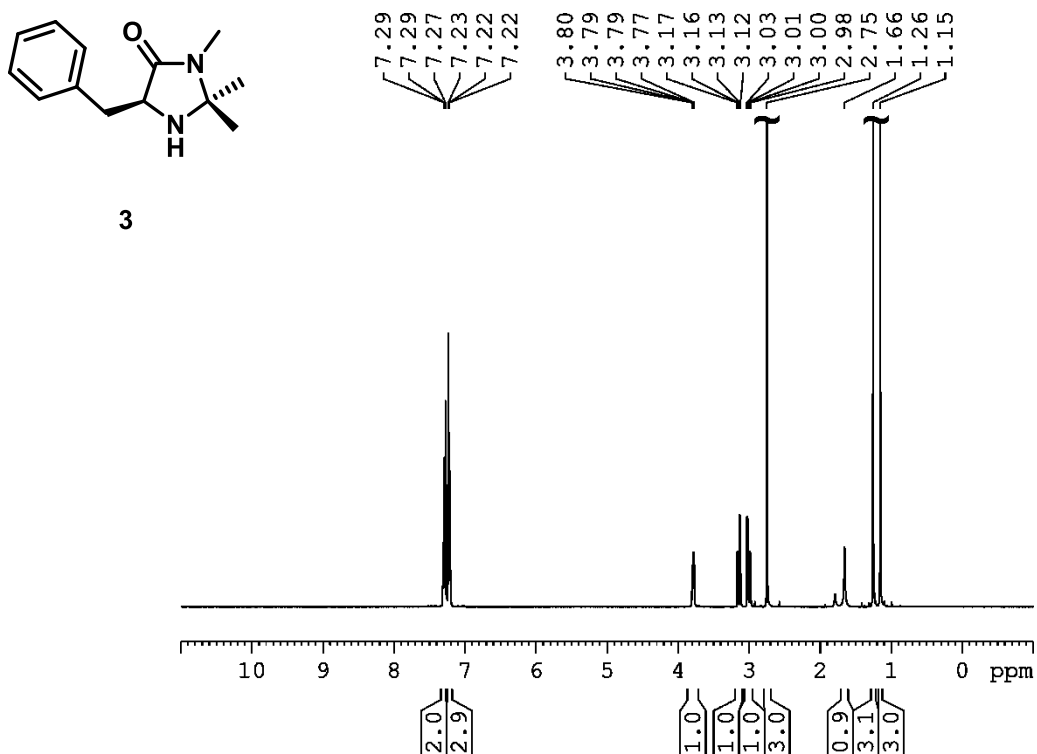
## 2.4 NMR-data



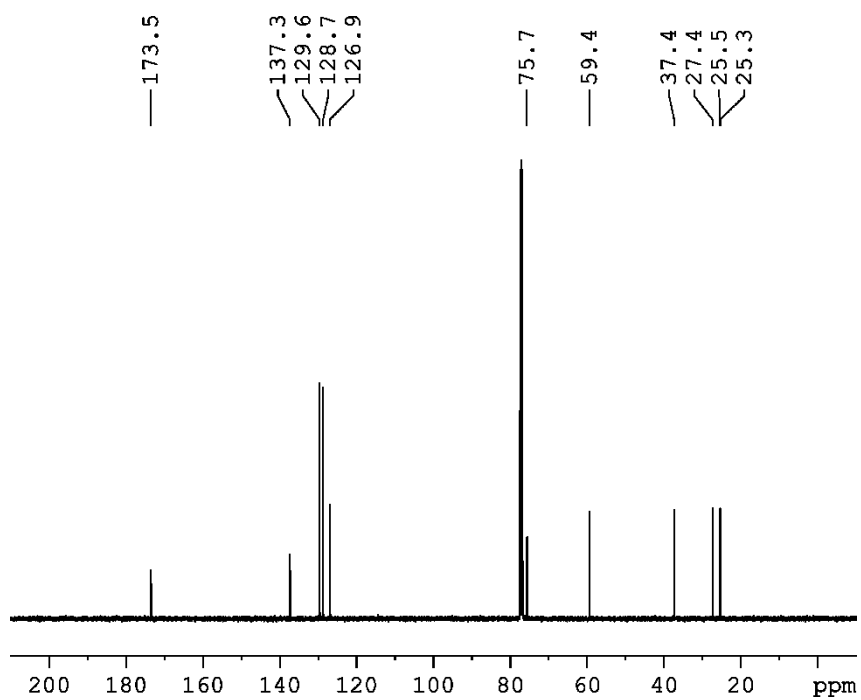
**Figure S1:** 1D-<sup>1</sup>H spectrum (ns = 16) of **2** measured in CDCl<sub>3</sub> at 25 °C.



**Figure S2:** 1D-<sup>13</sup>C NMR spectrum (ns = 1024) of **2** measured in CDCl<sub>3</sub> at 25 °C.

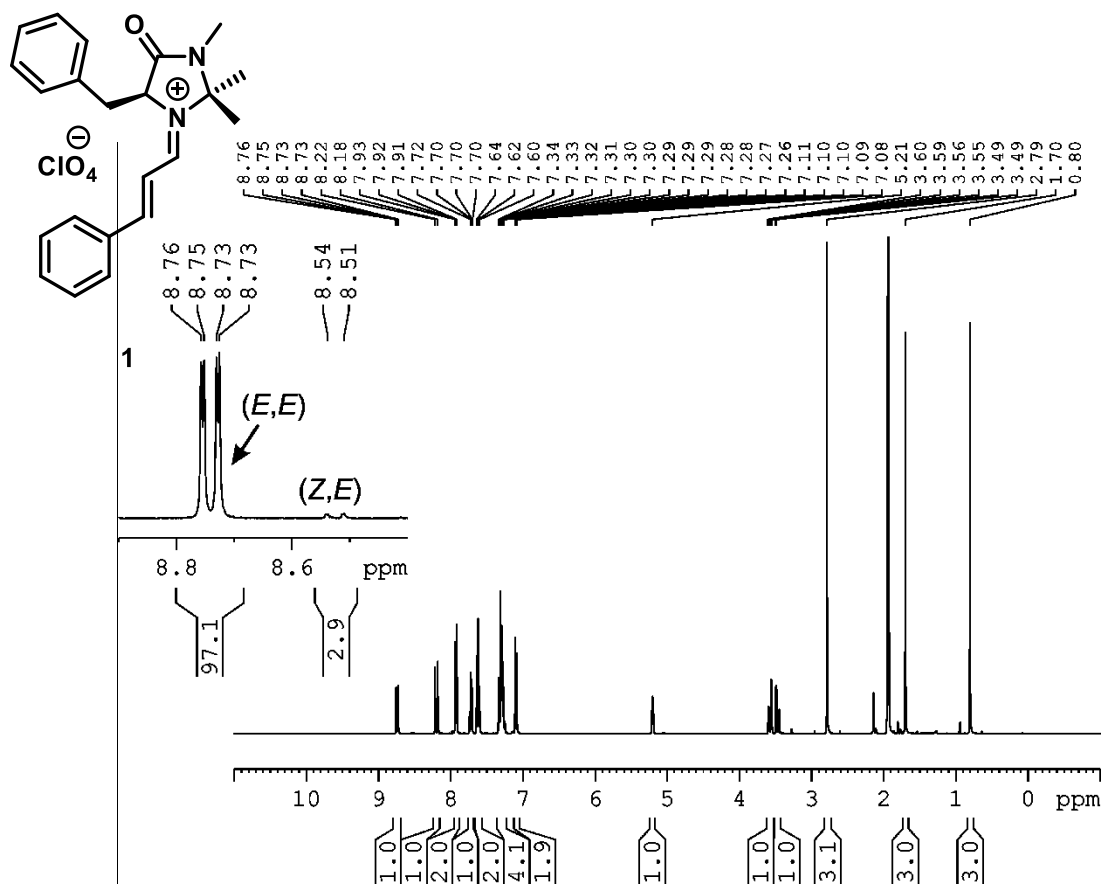


**Figure S3:** 1D-<sup>1</sup>H spectrum (ns = 16) of **3** measured in CDCl<sub>3</sub> at 25 °C.

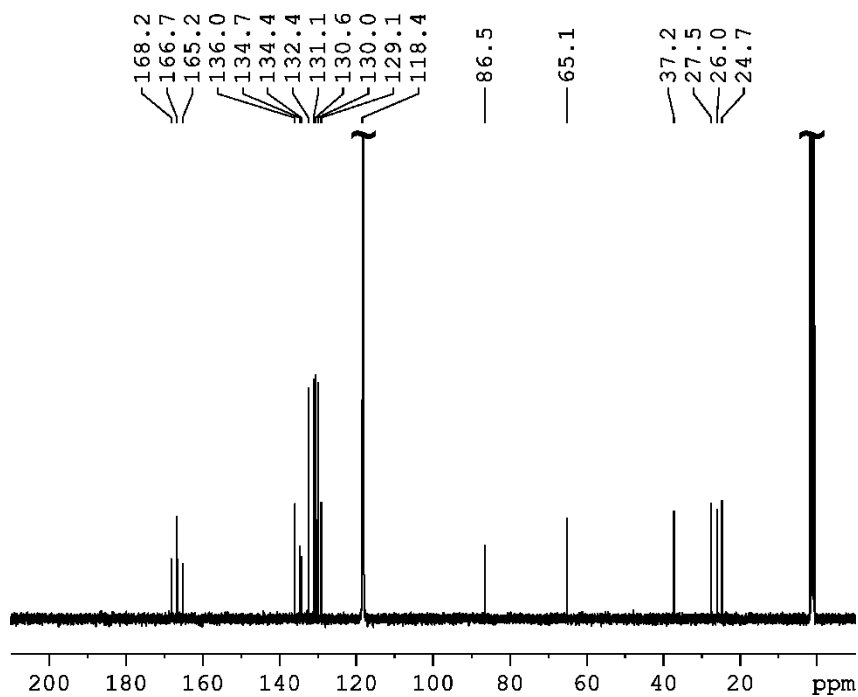


**Figure S4:** 1D-<sup>13</sup>C{<sup>1</sup>H} spectrum (ns = 1024) of **3** measured in CDCl<sub>3</sub> at 25 °C.





**Figure S5:** 1D- $^1\text{H}$  spectrum (ns = 16) of **1** measured in  $\text{CD}_3\text{CN}$  at 25 °C. The upper left section shows a (E,E)/(Z,E) ratio of ca. 97:3.



**Figure S6:** 1D- $^{13}\text{C}\{^1\text{H}\}$  spectrum (ns = 1024) of **1** measured in  $\text{CD}_3\text{CN}$  at 25 °C.

## 2.5 UV/Vis-data

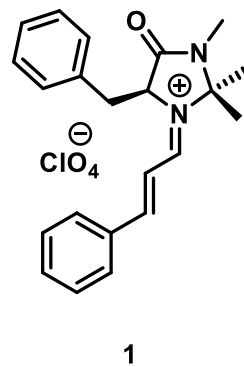
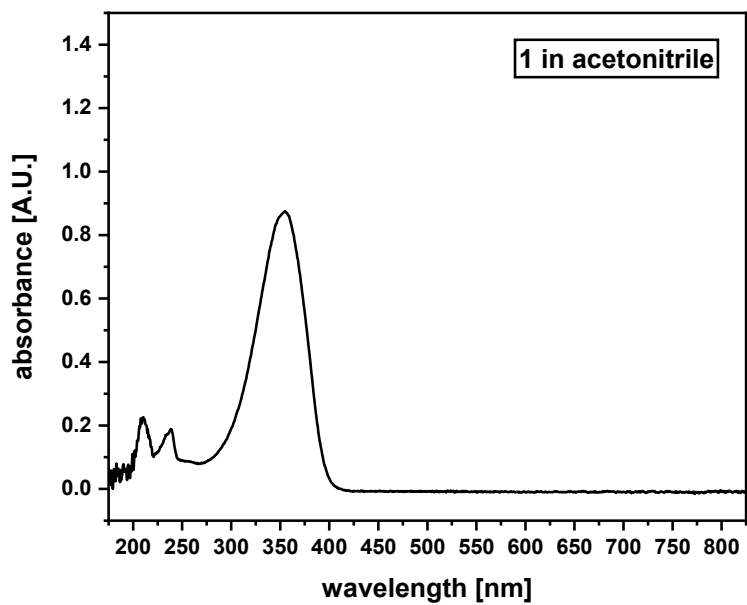


Figure S7: UV/Vis spectrum of **1** measured in CH<sub>3</sub>CN at r.t.

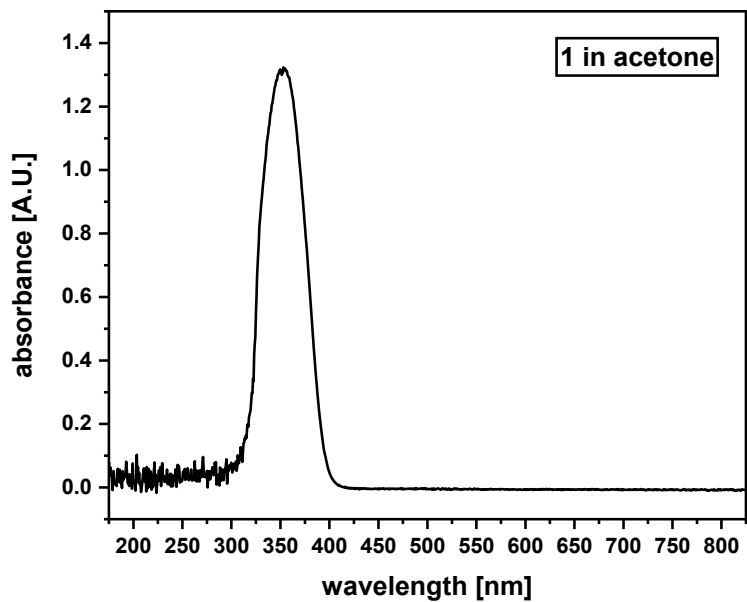
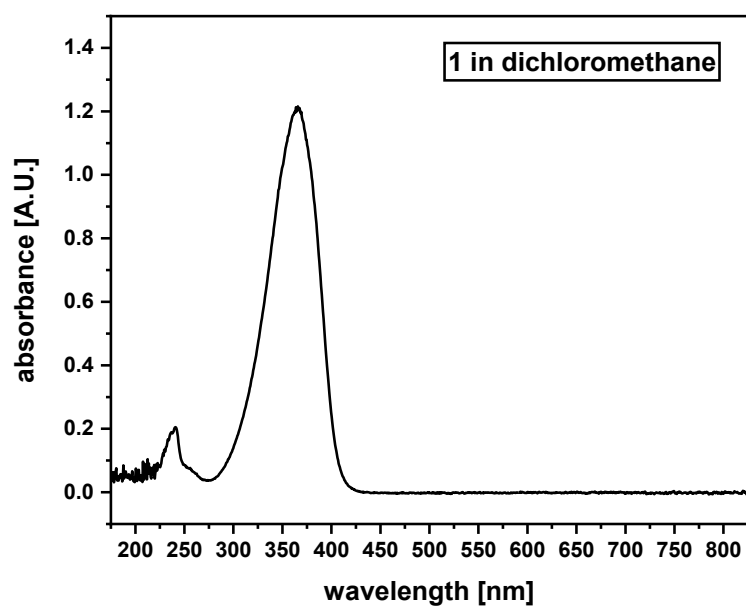


Figure S8: UV/Vis spectrum of **1** measured in acetone at r.t.



**Figure S9:** UV/Vis spectrum of **1** measured in CH<sub>2</sub>Cl<sub>2</sub> at r.t.

### **3. NMR sample preparation**

#### **3.1 Preparation of the NMR samples for *in situ* illumination NMR spectroscopy**

An oven dried 5 mm amberized thin wall NMR tube was charged inside the glove box with iminium ion **1** and connected to a Schlenk line. The respective solvent (0.3 mL) was added under argon atmosphere *via* a syringe. Afterwards an *in situ* illumination insert as described in literature (glass fiber: Thorlabs; fiber type: MM, FP1500URT, 0.50 NA, 300 - 1200 nm, 1500  $\mu\text{m}$  core) was inserted into the NMR tube using the Schlenk line technique and fastened with parafilm.<sup>1</sup>

#### **3.2 Preparation of the NMR samples for diffusion ordered spectroscopy (DOSY)**

An oven dried 5 mm NMR tube was charged inside the glove box with iminium ion **1** and connected to a Schlenk line. The respective solvent (0.5 mL) and anh. TMS were added under argon atmosphere *via* syringes and the NMR tube was sealed with additional parafilm.

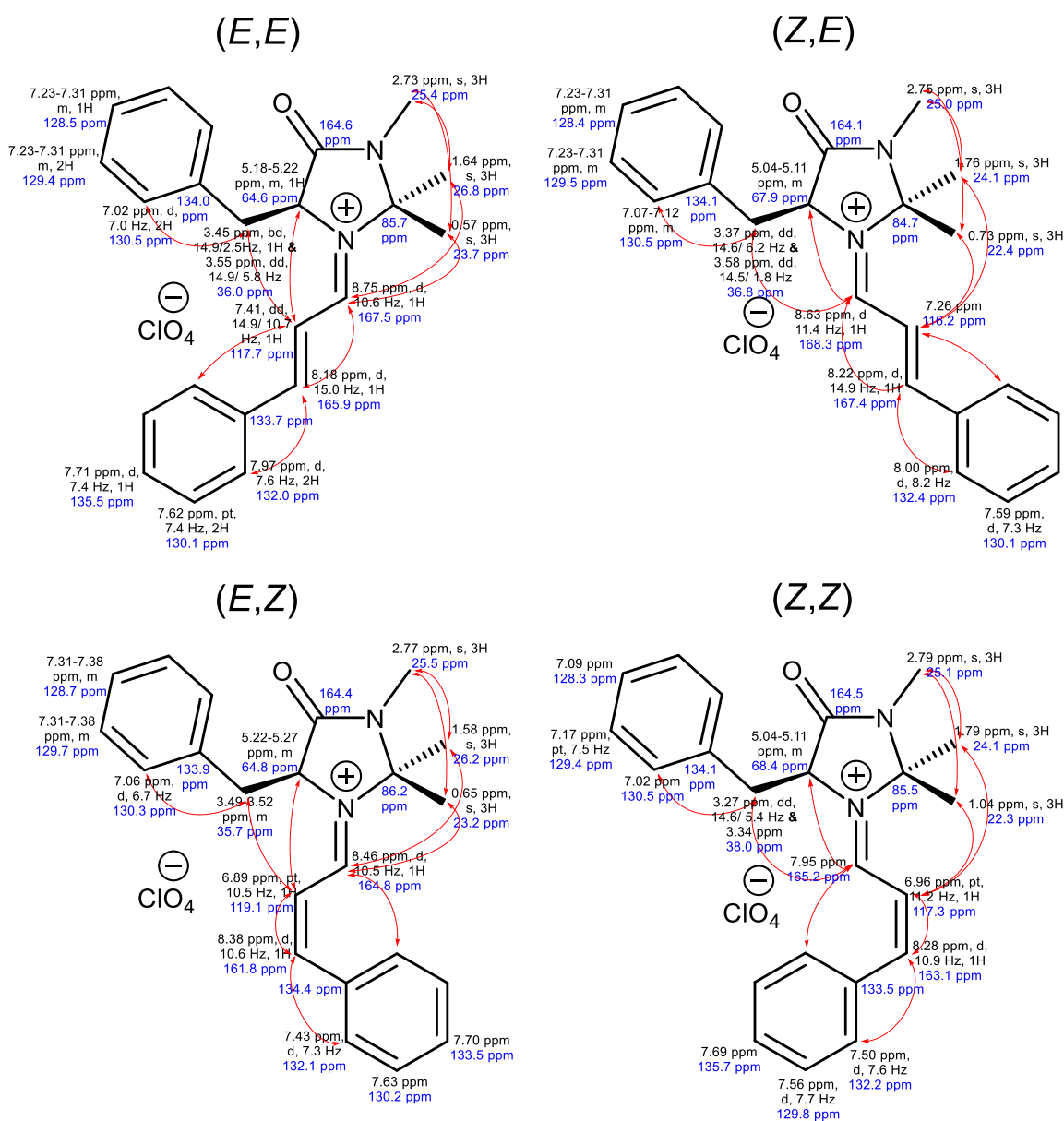
#### **3.3 Preparation of the NMR sample for combined *in situ* illumination-NMR-UV/Vis spectroscopy**

An oven dried 5 mm amberized thin wall NMR tube was charged inside the glove box with iminium ion **1**. The NMR tube was connected to a Schlenk line and anh. and deg.  $\text{CD}_3\text{CN}$  (0.3 mL) was added under argon atmosphere using a syringe. Following the literature,<sup>2</sup> the PTFE reflector was added under argon and the coaxial insert was positioned at a distance of ca. 1 mm from the reflector. Lastly, the insert was fastened with parafilm at the NMR tube.

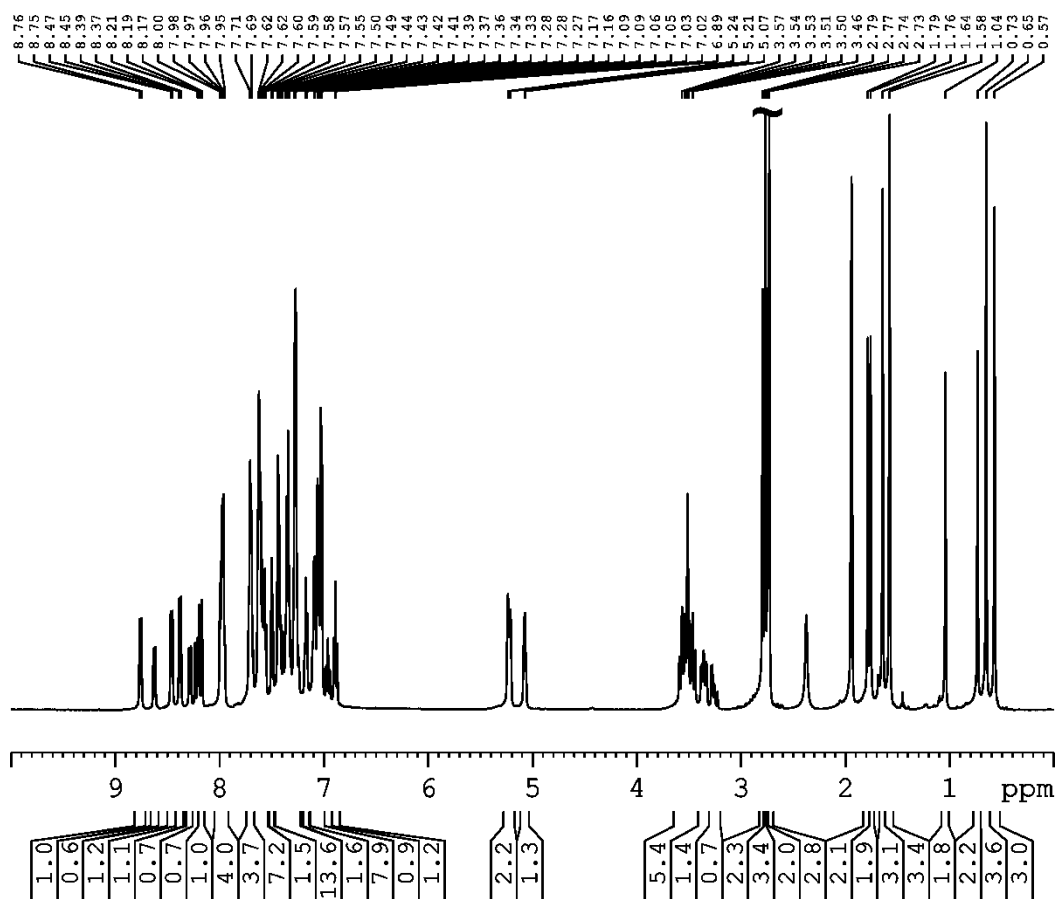
## 4. Structure elucidation of iminium ion 1 at -40 °C in different solvents

### 4.1 Structure elucidation of iminium ion 1 at -40 °C in CD<sub>3</sub>CN

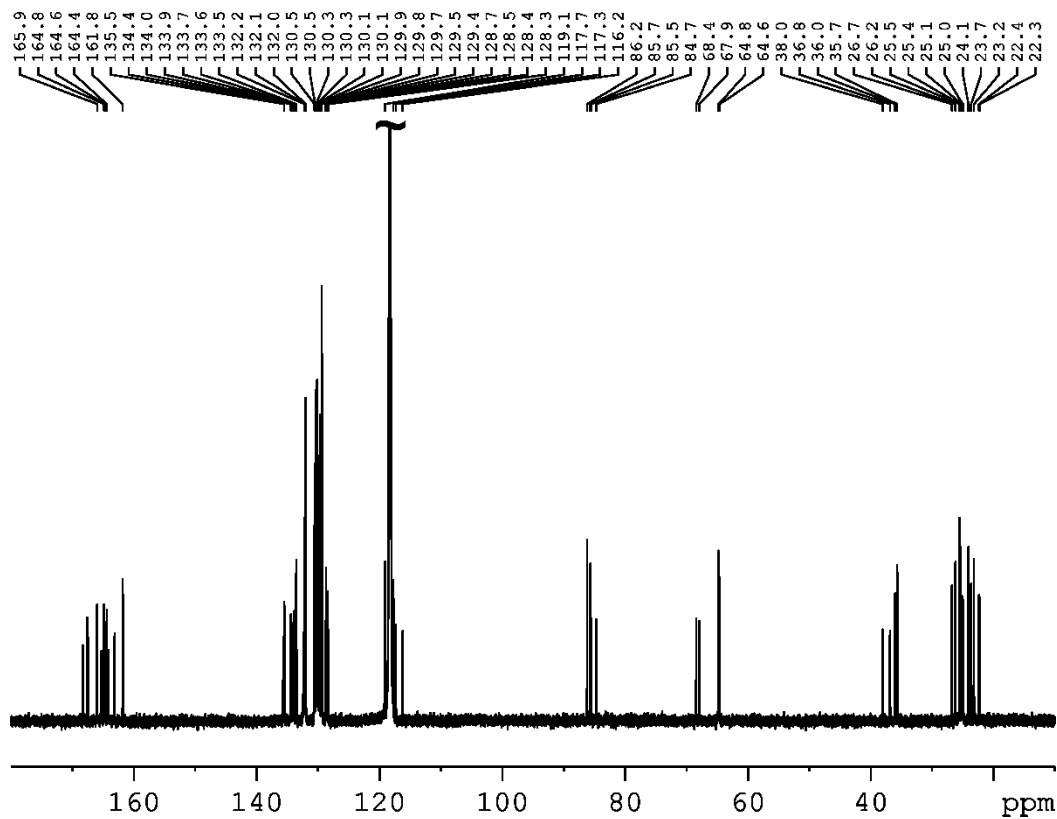
To assign the signals for (*E,E*), (*Z,E*), (*E,Z*) and (*Z,Z*) of iminium ion 1 in CD<sub>3</sub>CN at -40 °C (Figure S10) a standard set of NMR experiments (<sup>1</sup>D-<sup>1</sup>H; <sup>1</sup>D-<sup>13</sup>C{<sup>1</sup>H}; <sup>2</sup>D-<sup>1</sup>H, <sup>1</sup>H correlated spectroscopy (COSY); <sup>2</sup>D-<sup>1</sup>H, <sup>1</sup>H nuclear Overhauser enhancement spectroscopy (NOESY), <sup>2</sup>D-<sup>1</sup>H, <sup>13</sup>C heteronuclear multiple bond correlation (HMBC); <sup>2</sup>D-<sup>1</sup>H, <sup>13</sup>C heteronuclear single quantum coherence (HSQC)) was measured under continuous UV-illumination using the *in situ* illumination setup to populate simultaneously all four configuration isomers. The configuration of the C=N and C=C double bond can be clearly assigned *via* the associated coupling constants and explicit NOE patterns.



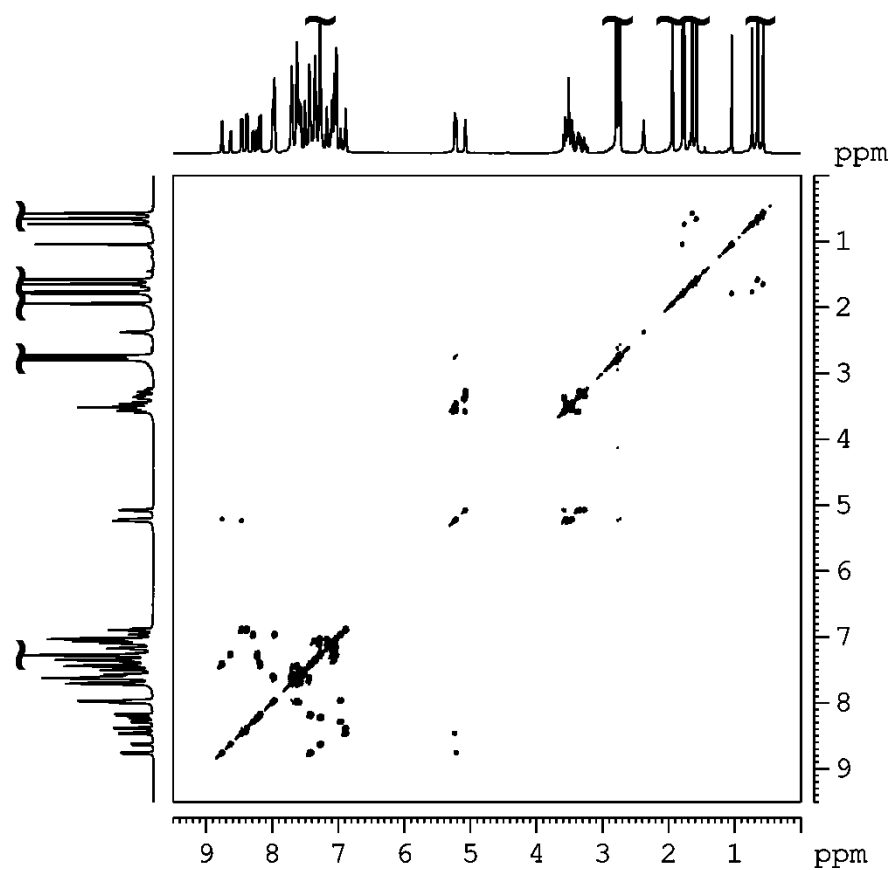
**Figure S10:** Structure determination of the four configuration isomers (*E,E*), (*Z,E*), (*E,Z*) and (*Z,Z*) in CD<sub>3</sub>CN at -40 °C. Therefore, a sample of iminium ion 1 in anh. and deg. CD<sub>3</sub>CN (50 mM) was continuously illuminated at -40 °C with an LED emitting at 365 nm. <sup>1</sup>H chemical shift, multiplicity, coupling constants and integral are highlighted black and <sup>13</sup>C blue. Distinct NOE interactions, which confirm the double bond configurations, are indicated *via* red arrows. An average ratio of (*E,E*)/(*Z,E*)/(*E,Z*)/(*Z,Z*) = 28:21:34:17 was present during illumination.



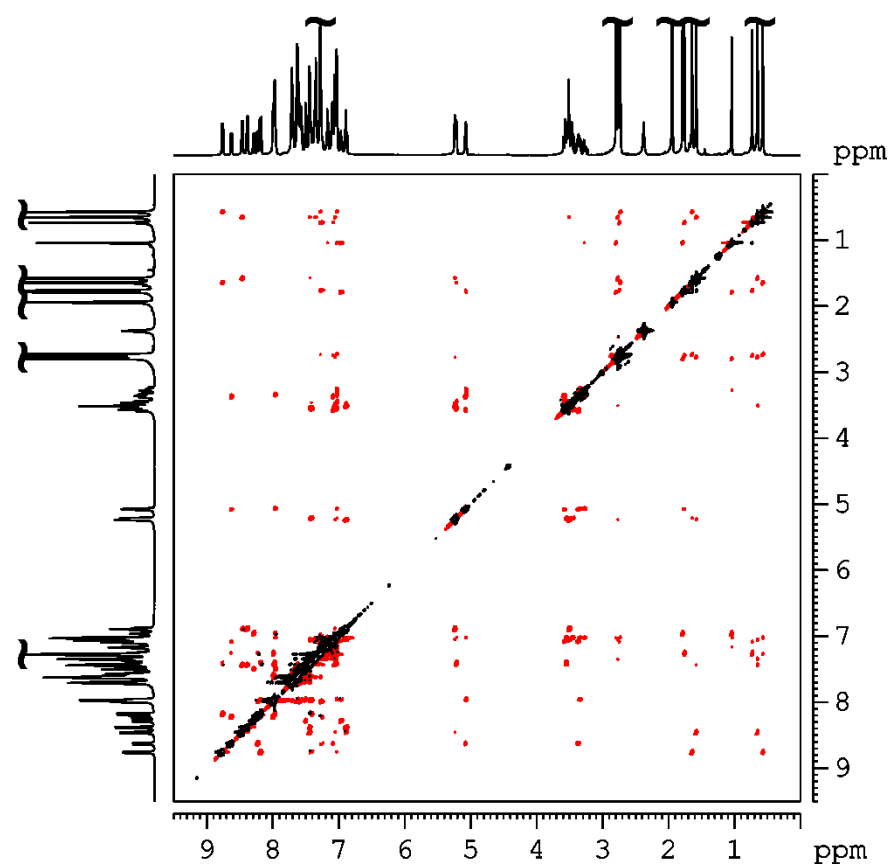
**Figure S11:** 1D- $^1\text{H}$  spectrum (ns = 16) of **1** in anh. and deg.  $\text{CD}_3\text{CN}$  (50 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination. The integrals are calibrated on the (*E,E*) isomer.



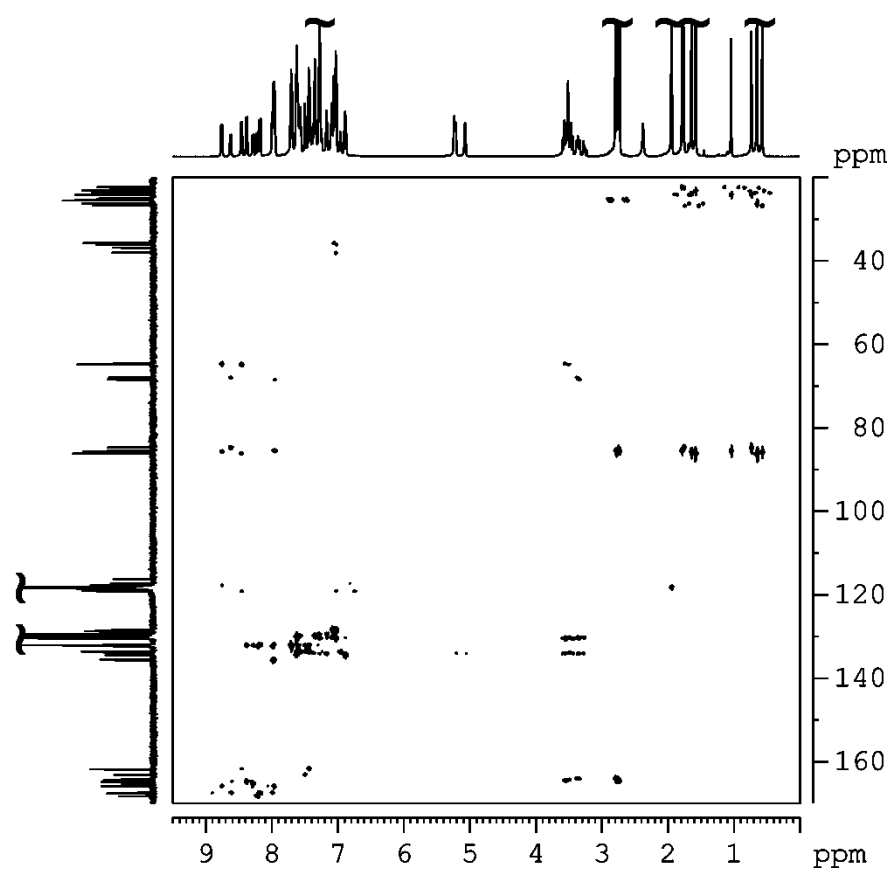
**Figure S12:** 1D- $^{13}\text{C}\{^1\text{H}\}$  spectrum (ns = 2048) of **1** in anh. and deg.  $\text{CD}_3\text{CN}$  (50 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination.



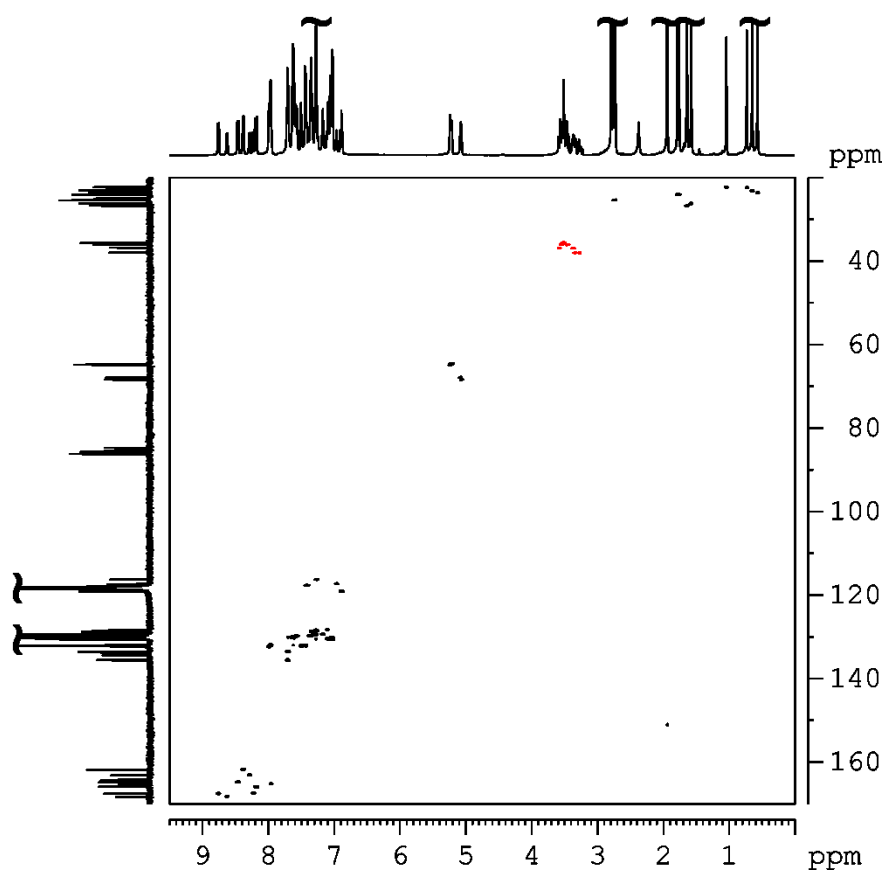
**Figure S13:** 2D- $^1\text{H}$ ,  $^1\text{H}$  COSY spectrum of **1** in anh. and deg.  $\text{CD}_3\text{CN}$  (50 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination.



**Figure S 14:** 2D- $^1\text{H}$ ,  $^1\text{H}$  NOESY spectrum (mixing time = 0.5 s) of **1** in anh. and deg.  $\text{CD}_3\text{CN}$  (50 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination.



**Figure S15:** 2D- $^1\text{H}$ ,  $^{13}\text{C}$  HMBC spectrum of **1** in anh. and deg.  $\text{CD}_3\text{CN}$  (50 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination.

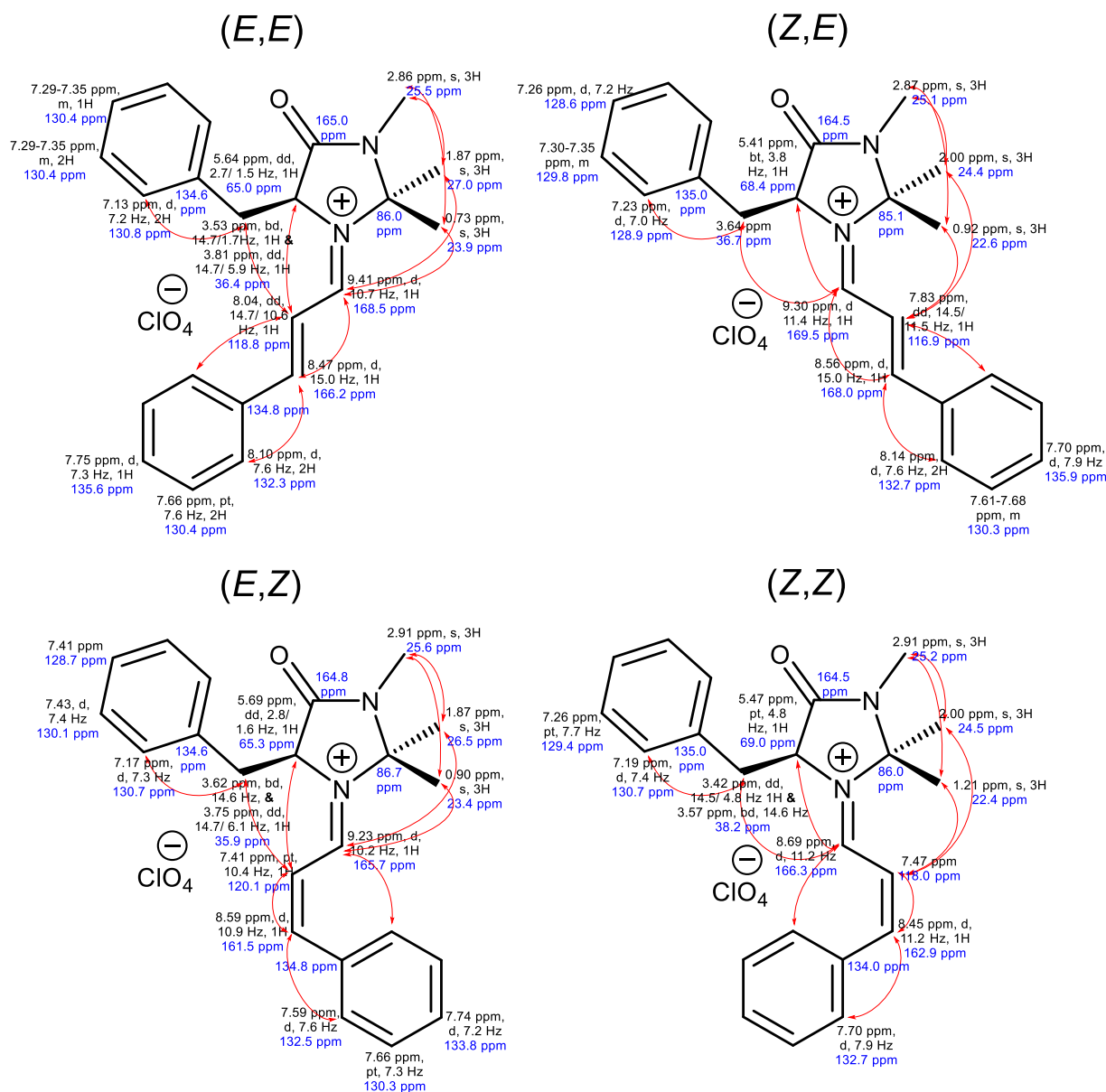


**Figure S16:** 2D- $^1\text{H}$ ,  $^{13}\text{C}$  HSQC spectrum of **1** in anh. and deg.  $\text{CD}_3\text{CN}$  (50 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination.

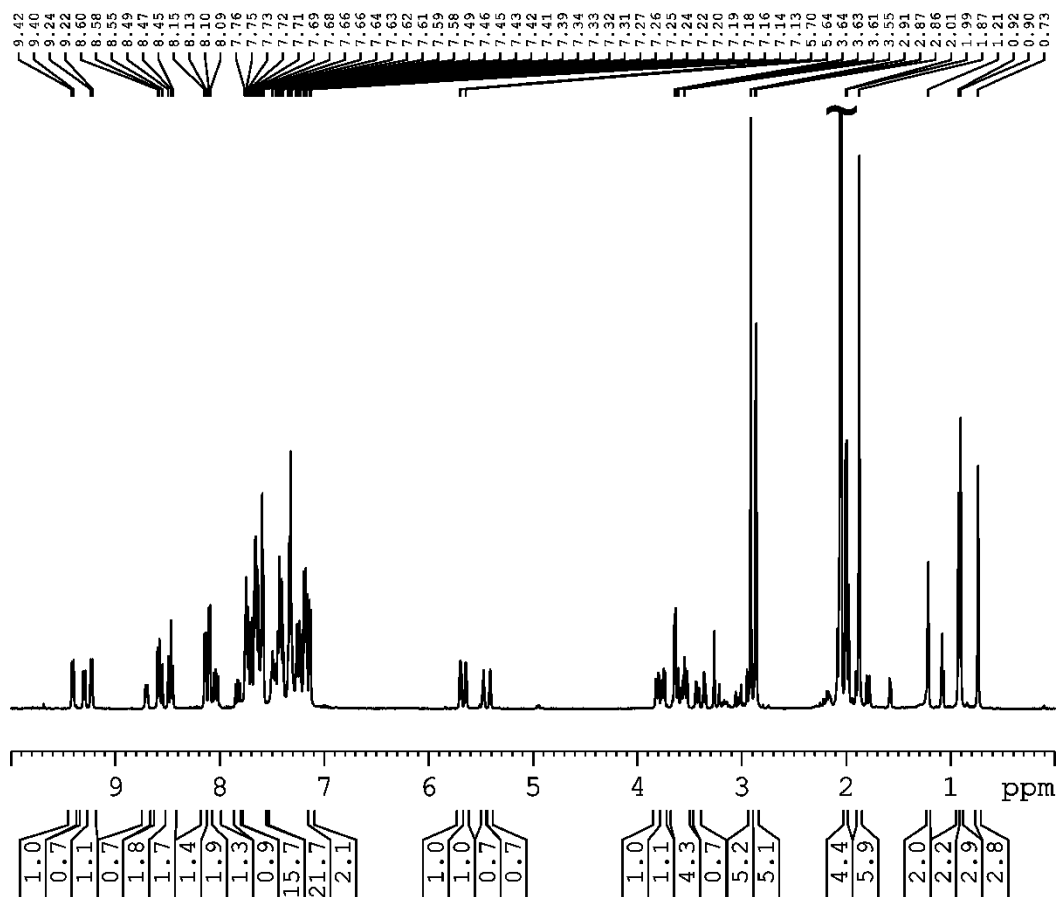


## 4.2 Structure elucidation of iminium ion **1** at -40 °C in acetone-*d*<sub>6</sub>

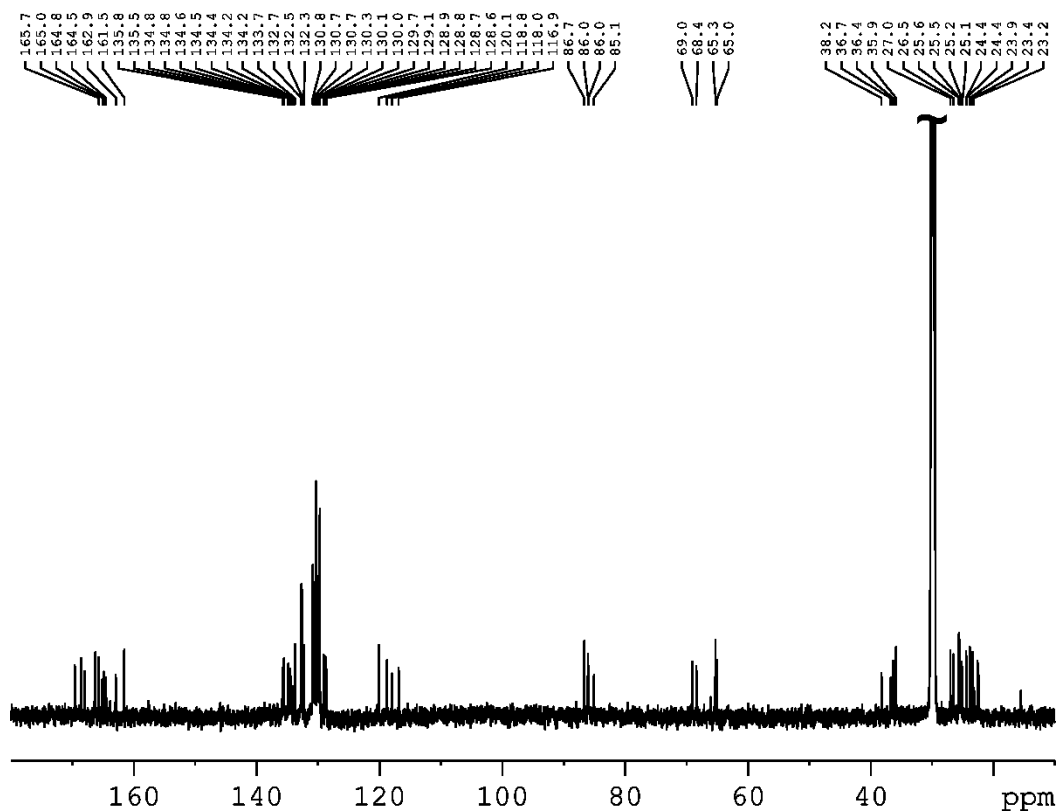
To assign the signals for (*E,E*), (*Z,E*), (*E,Z*) and (*Z,Z*) of iminium ion **1** in acetone-*d*<sub>6</sub> at -40 °C (Figure S17) a standard set of NMR experiments (<sup>1</sup>D-<sup>1</sup>H; 1D-<sup>13</sup>C{<sup>1</sup>H}; 2D-<sup>1</sup>H, <sup>1</sup>H COSY; 2D-<sup>1</sup>H, <sup>1</sup>H NOESY, 2D-<sup>1</sup>H, <sup>13</sup>C HMBC; 2D-<sup>1</sup>H, <sup>13</sup>C HMQC) was measured under continuous UV-illumination using the *in situ* illumination setup to populate simultaneously all four configuration isomers. The configuration of the C=N and C=C double bond can be clearly assigned *via* the associated coupling constants and explicit NOE patterns.



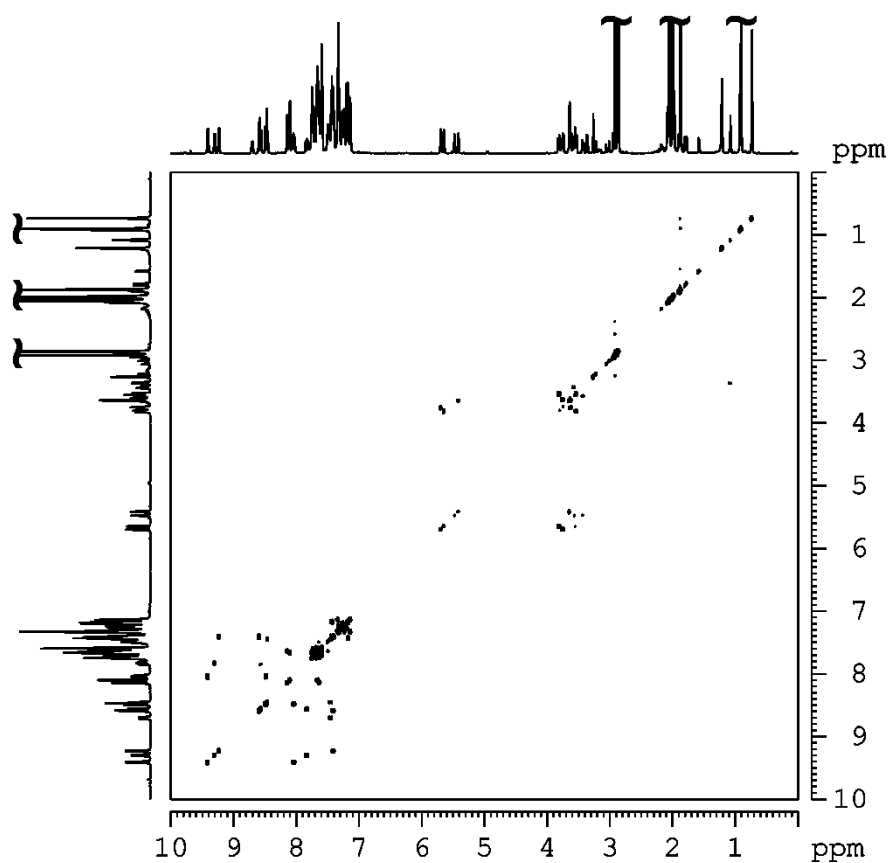
**Figure S17:** Structure determination of the four configuration isomers (*E,E*), (*Z,E*), (*E,Z*) and (*Z,Z*) in acetone-*d*<sub>6</sub> at -40 °C. Therefore, a sample of iminium ion **1** in acetone-*d*<sub>6</sub> (50 mM) was continuously illuminated at -40 °C with an LED emitting at 365 nm. <sup>1</sup>H chemical shift, multiplicity, coupling constants and integral are highlighted black and <sup>13</sup>C blue. Distinct NOE interactions, which confirm the double bond configurations, are indicated *via* red arrows. An average ratio of (*E,E*)/(*Z,E*)/(*E,Z*)/(*Z,Z*) = 29:21:30:20 was present during illumination.



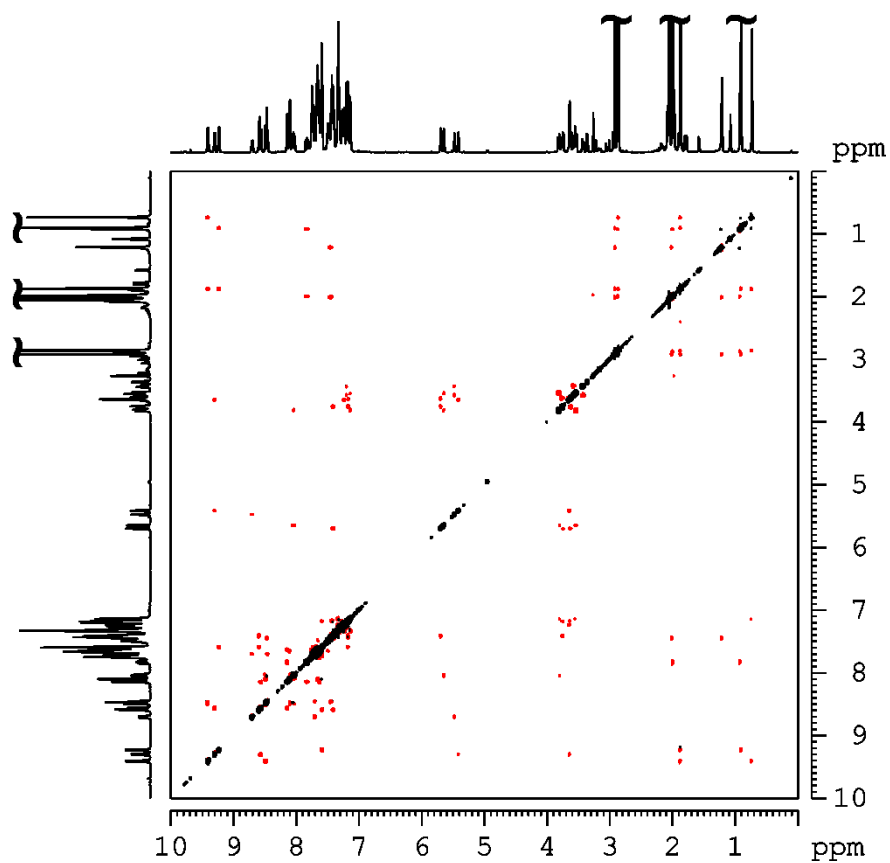
**Figure S18:** 1D- $^1\text{H}$  spectrum (ns = 16) of **1** in acetone- $d_6$  (50 mM) measured at  $-40\text{ }^\circ\text{C}$  under continuous UV-illumination. The integrals are calibrated on the (*E,E*) isomer.



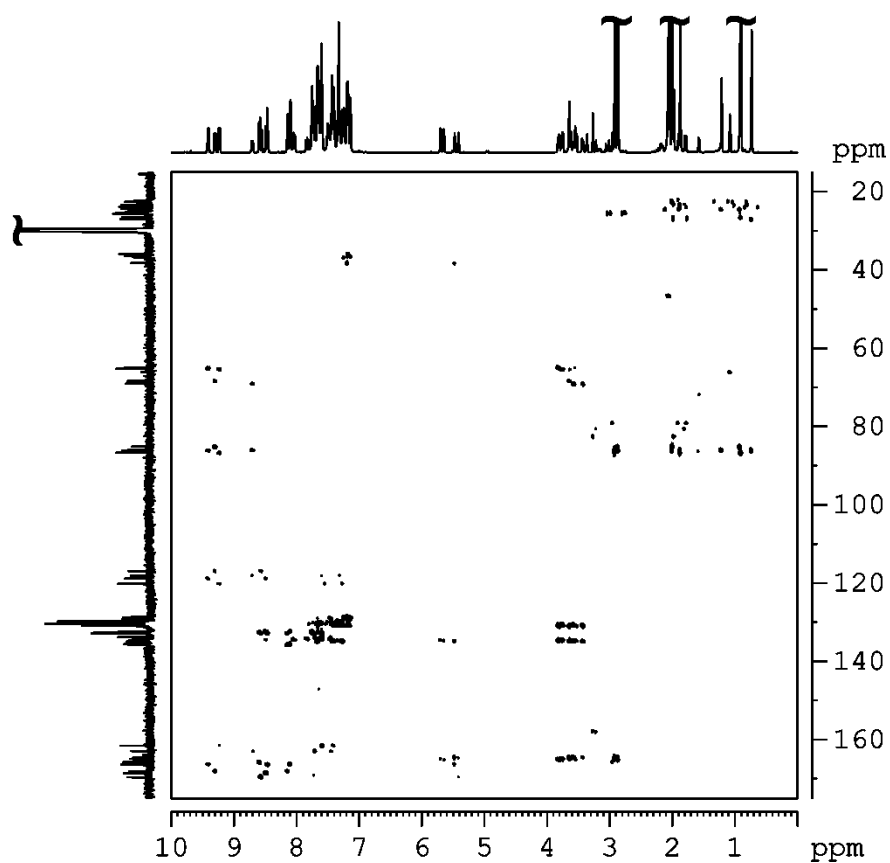
**Figure S19:** 1D- $^{13}\text{C}\{^1\text{H}\}$  spectrum (ns = 6144) of **1** in acetone- $d_6$  (50 mM) measured at  $-40\text{ }^\circ\text{C}$  under continuous UV-illumination.



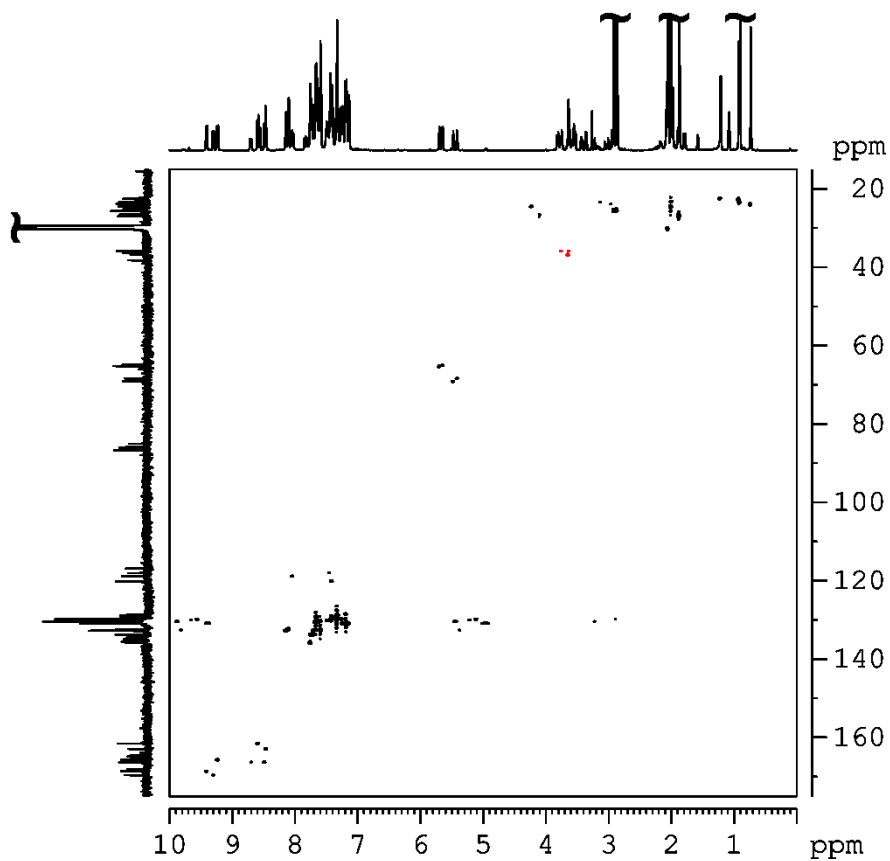
**Figure S20:** 2D-<sup>1</sup>H, <sup>1</sup>H COSY spectrum of **1** in acetone-*d*<sub>6</sub> (50 mM) measured at -40 °C under continuous UV-illumination.



**Figure S21:** 2D-<sup>1</sup>H, <sup>1</sup>H NOESY spectrum (mixing time = 0.5 s) of **1** in acetone-*d*<sub>6</sub> (50 mM) measured at -40 °C under continuous UV-illumination.



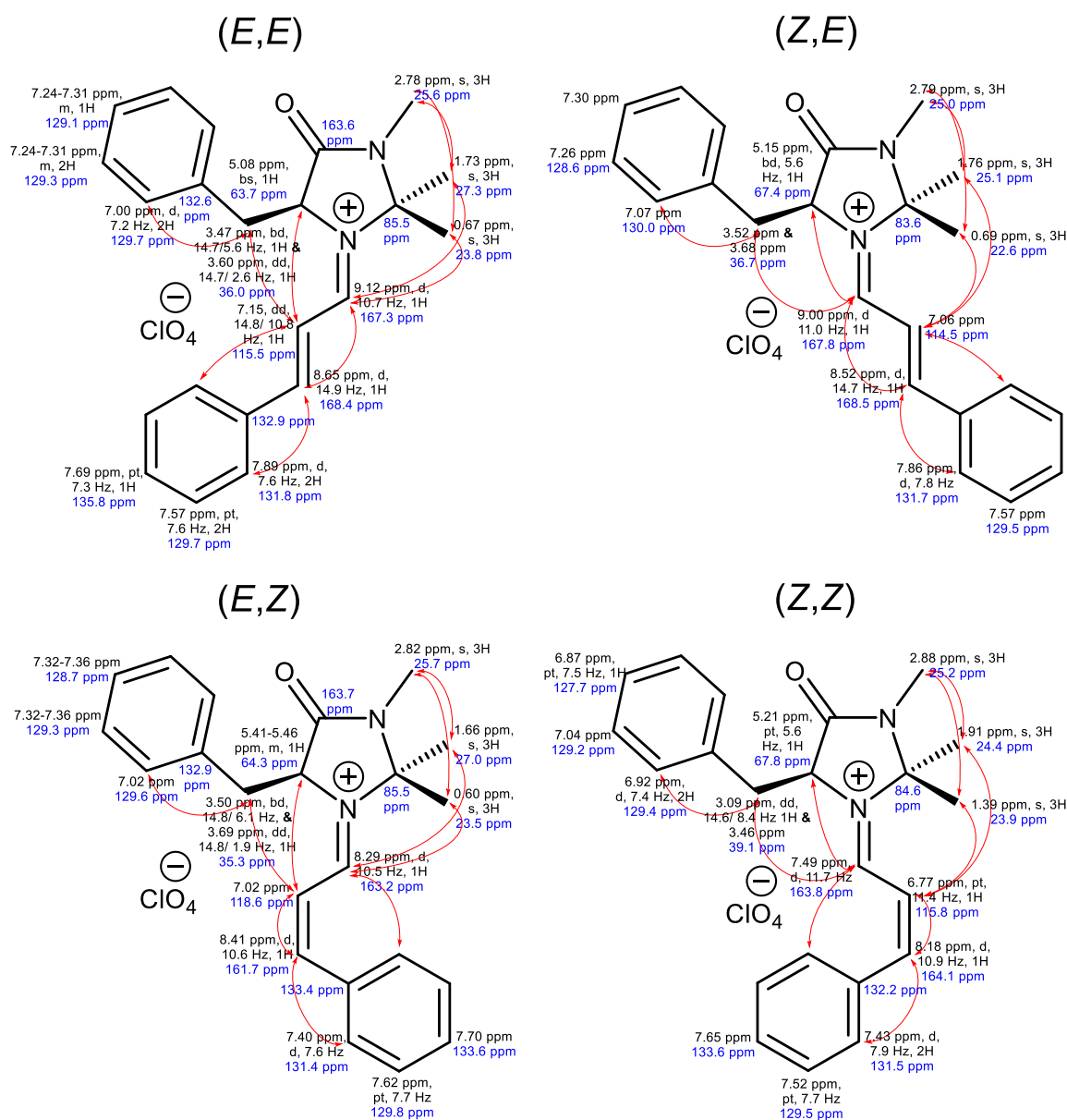
**Figure S22:** 2D- $^1\text{H}$ ,  $^{13}\text{C}$  HMBC spectrum of **1** in acetone- $d_6$  (50 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination.



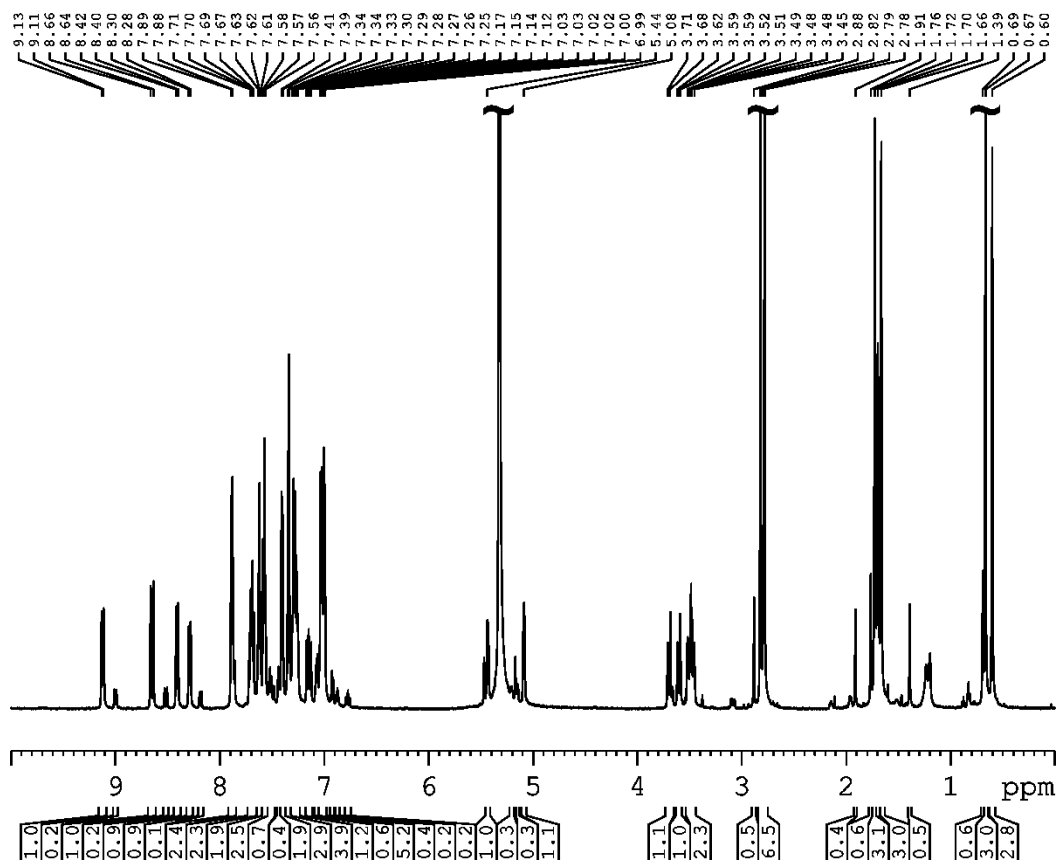
**Figure S23:** 2D- $^1\text{H}$ ,  $^{13}\text{C}$  HSQC spectrum of **1** in acetone- $d_6$  (50 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination.

### 4.3 Structure elucidation of iminium ion **1** at -40 °C in CD<sub>2</sub>Cl<sub>2</sub>

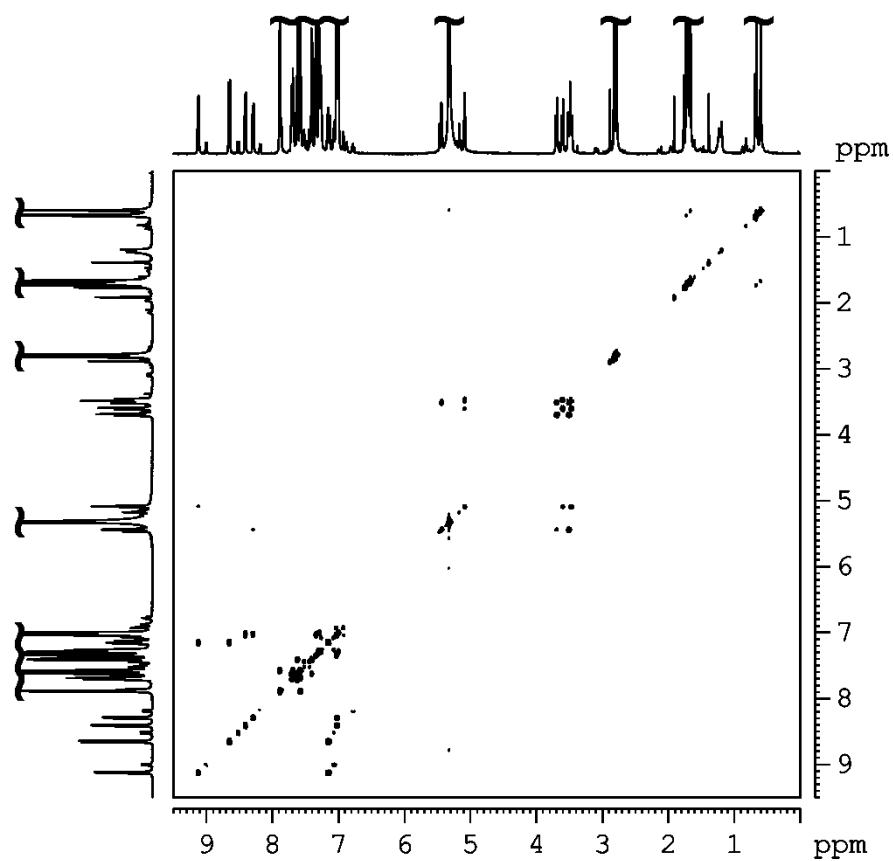
To assign the signals for (*E,E*), (*Z,E*), (*E,Z*) and (*Z,Z*) of iminium ion **1** in CD<sub>2</sub>Cl<sub>2</sub> at -40 °C (Figure S24) a standard set of NMR experiments (1D-<sup>1</sup>H; 2D-<sup>1</sup>H, <sup>1</sup>H COSY; 2D-<sup>1</sup>H, <sup>1</sup>H NOESY, 2D-<sup>1</sup>H, <sup>13</sup>C HMBC; 2D-<sup>1</sup>H, <sup>13</sup>C HSQC) was measured under continuous UV-illumination using the *in situ* illumination setup to populate simultaneously all four configuration isomers. The configuration of the C=N and C=C double bond can be clearly assigned *via* the associated coupling constants and explicit NOE patterns. **1** is only moderately soluble in CD<sub>2</sub>Cl<sub>2</sub> (< 50 mM). Thus, it was not possible to record a 1D-<sup>13</sup>C{<sup>1</sup>H} with sufficient signal to noise ratio. <sup>13</sup>C chemical shifts are assigned based on the 2D-<sup>1</sup>H, <sup>13</sup>C HMBC/HSQC spectra.



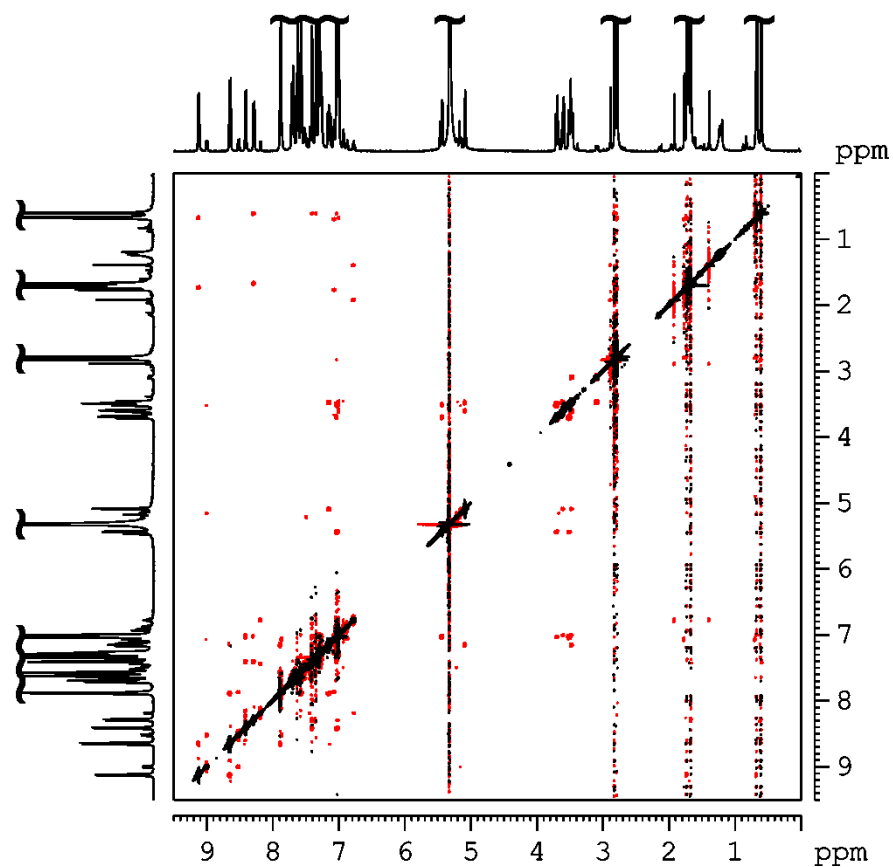
**Figure S24:** Structure determination of the four configuration isomers (*E,E*), (*Z,E*), (*E,Z*) and (*Z,Z*) in CD<sub>2</sub>Cl<sub>2</sub> at -40 °C. Therefore, a sample of iminium ion **1** in anh. and deg. CD<sub>2</sub>Cl<sub>2</sub> (10 mM) was continuously illuminated at -40 °C with an LED emitting at 365 nm. <sup>1</sup>H chemical shift, multiplicity, coupling constants and integral are highlighted black and <sup>13</sup>C blue. Distinct NOE interactions, which confirm the double bond configurations, are indicated *via* red arrows. An average ratio of (*E,E*)/(*Z,E*)/(*E,Z*)/(*Z,Z*) = 45:8:41:6 was present during illumination.



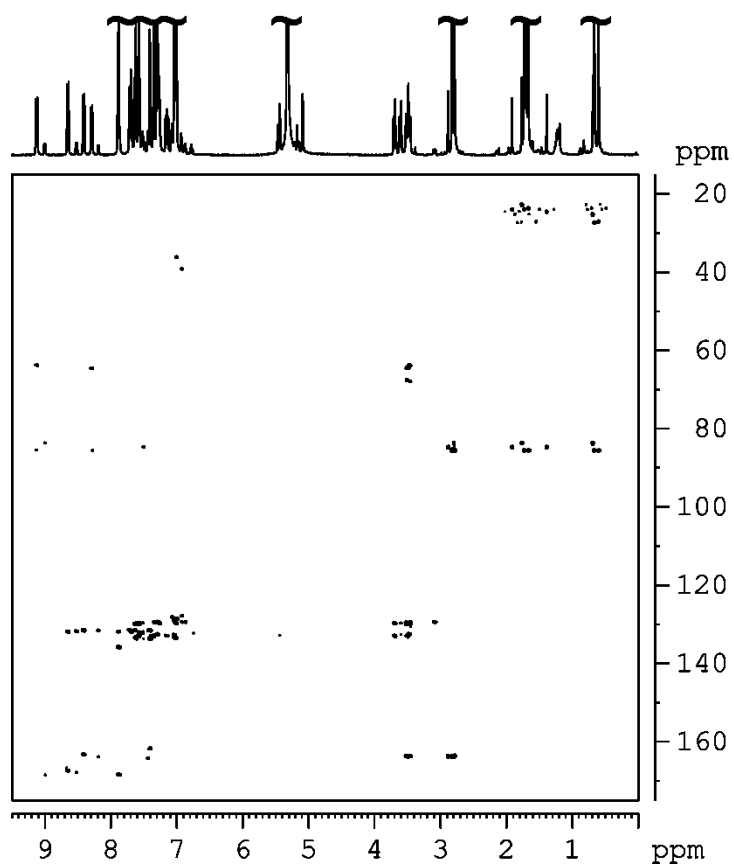
**Figure S25:** 1D-<sup>1</sup>H spectrum (ns = 16) of **1** in CD<sub>2</sub>Cl<sub>2</sub> (10 mM) measured at -40 °C under continuous UV-illumination. The integrals are calibrated on the (*E,E*) isomer.



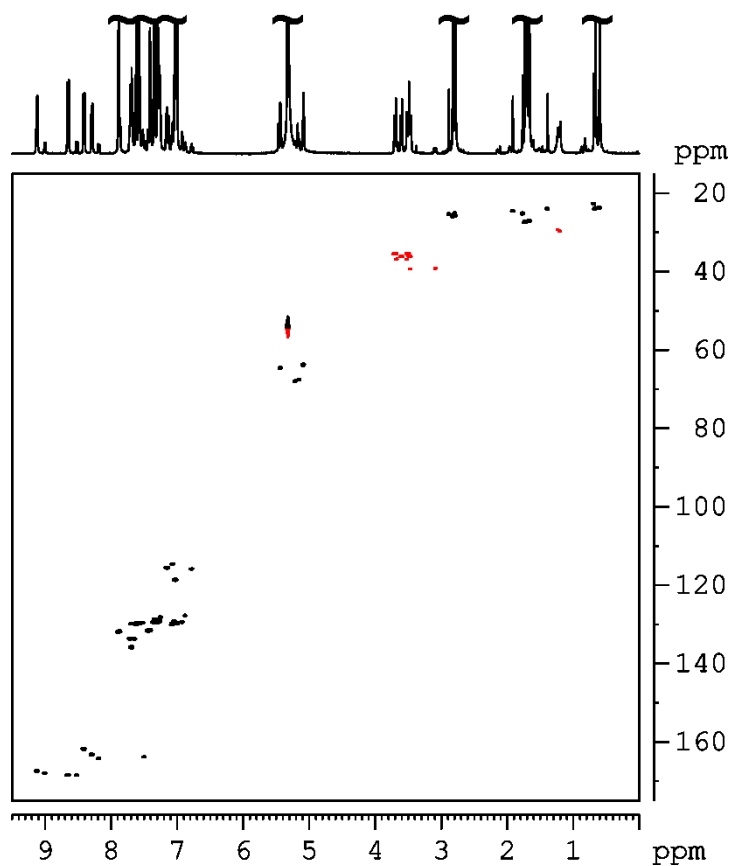
**Figure S26:** 2D- $^1\text{H}$ ,  $^1\text{H}$  COSY spectrum of **1** in  $\text{CD}_2\text{Cl}_2$  (10 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination.



**Figure S27:** 2D- $^1\text{H}$ ,  $^1\text{H}$  NOESY spectrum (mixing time = 0.5 s) of **1** in  $\text{CD}_2\text{Cl}_2$  (10 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination.



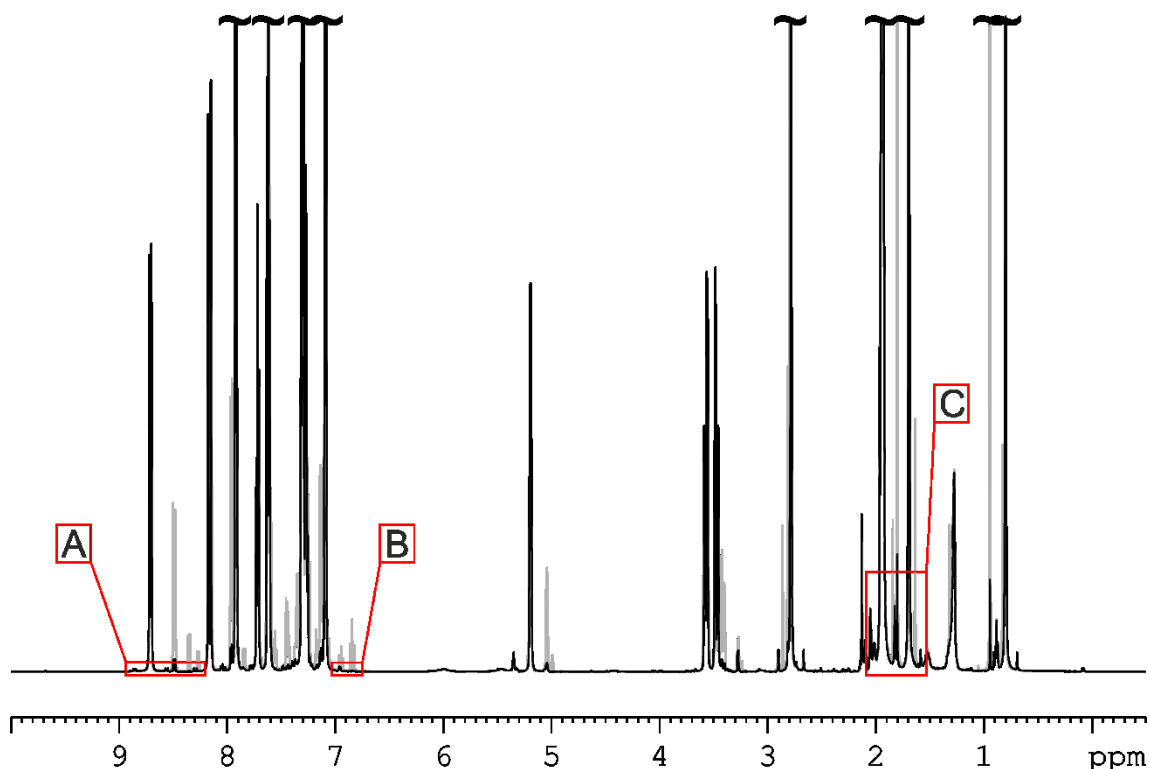
**Figure S28:** 2D- $^1\text{H}$ ,  $^{13}\text{C}$  HMBC spectrum of **1** in  $\text{CD}_2\text{Cl}_2$  (10 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination.



**Figure S29:** 2D- $^1\text{H}$ ,  $^{13}\text{C}$  HSQC spectrum of **1** in  $\text{CD}_2\text{Cl}_2$  (10 mM) measured at  $-40^\circ\text{C}$  under continuous UV-illumination.

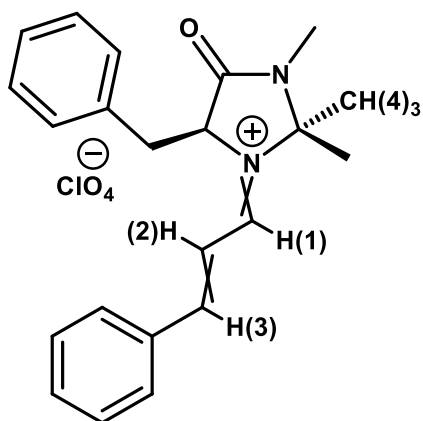


## 5. Detection of (*E,Z*) in thermal equilibrium at 25 °C, i.e. under general synthetic conditions

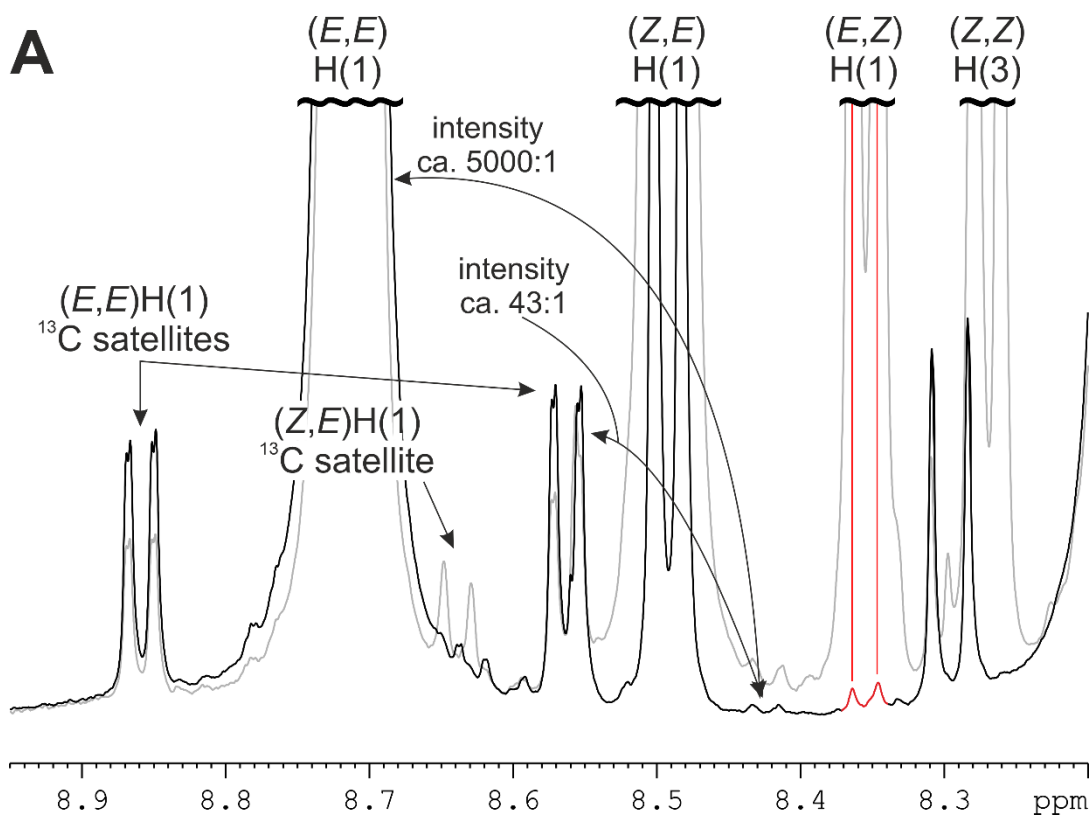


**Figure S30:** 1D- $^1\text{H}$  spectrum (ns = 1024 (grey spectrum), 2048 (black spectrum)) of **1** in anh. and deg.  $\text{CD}_3\text{CN}$  (10 mM) measured at 25 °C in the dark (black spectrum) and under continuous UV-illumination (grey spectrum). The three sections A, B and C, which contain the  $^1\text{H}$ -signals to confirm the presence of (*E,Z*) in thermal equilibrium (i.e. without illumination) are depicted in detail in Figure S32-S34. Because only half of the scans were measured under continuous illumination, the intensities of the two spectra were adjusted *via* the solvent residual signal.

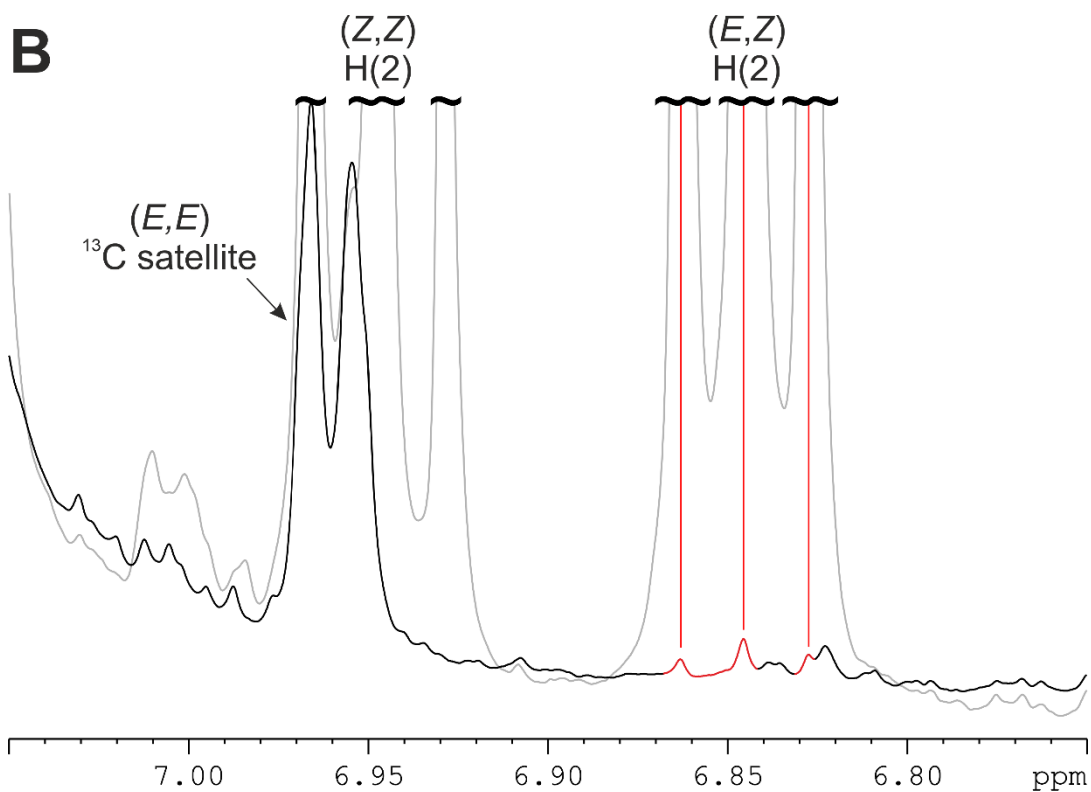
Routine NMR spectroscopy often suffers from its low sensitivity. To check whether next to the already reported (*E,E*) and (*Z,E*) isomers also traces of (*E,Z*) and (*Z,Z*) are present without additional illumination at room temperature (25 °C), we measured a quantitative 1D- $^1\text{H}$  NMR spectrum of **1** with highest possible signal to noise ratio (Figure S30, black spectrum). Therefore a proton optimized TCI CryoProbe was selected. Such a probe gives a signal to noise enhancement of up to a factor of 5 compared to an equivalent room temperature probe. Thus, accumulating 2048 scans gave already an impressive signal to noise ratio. Signals around 5000-times smaller than (*E,E*)H(1) or ca. 43-times less intense as the associated (*E,E*)H(1)  $^{13}\text{C}$  satellites could be obtained (see Figure S32). Based on their chemical shift and multiplicity several signals were selected as potential candidates for (*E,Z*) and (*Z,Z*). However, their intensity is too low for a classic structure elucidation. This is only possible *via* selective photo enhancement (Figure S30, grey spectrum). Therefore, we illuminated the NMR sample *in situ* using a UV-LED (OSRAM LZ4-04UV0R-00000, 365 nm peak wavelength, operated at 0.1 A). Three signals could be identified, which are already present in the dark and can be assigned to the (*E,Z*) isomer due to their explicit response to UV-illumination (Figure S32-S34). For (*Z,Z*) no such signals could be identified in the dark spectrum.



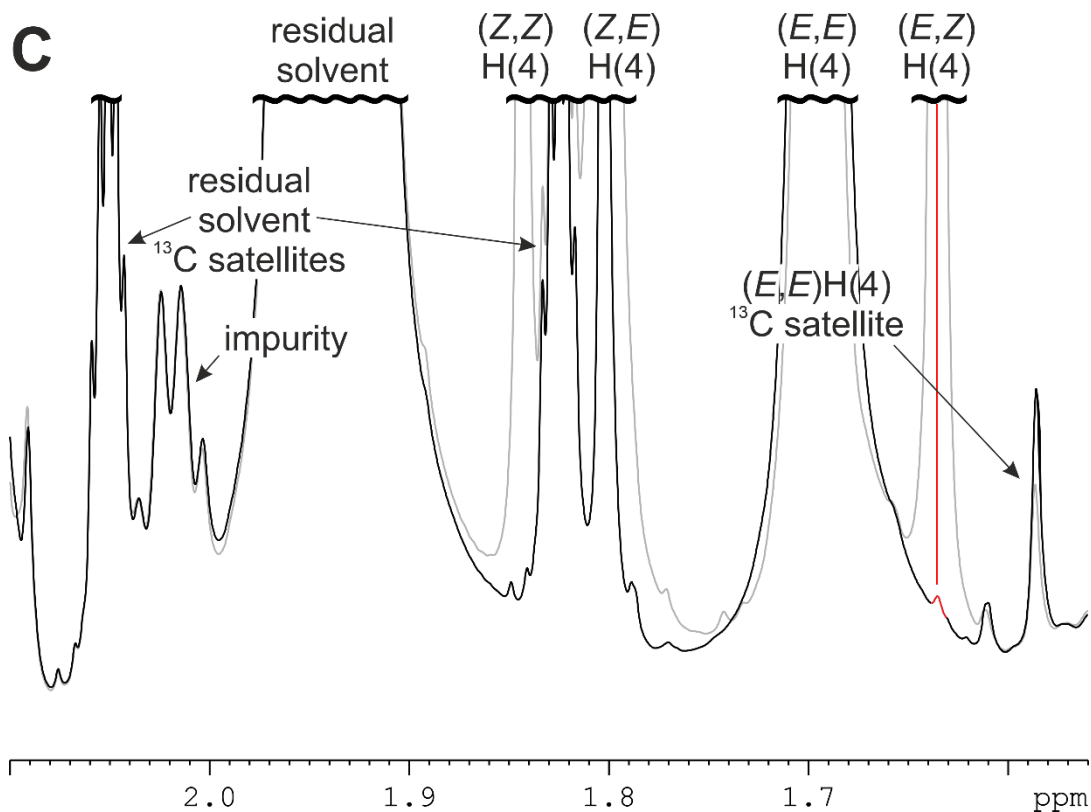
**Figure S31:** General depiction of iminium ion **1**. The four highlighted protons H(1), H(2), H(3) and H(4) were used to determine whether next to (*E,E*) (*Z,E*) also traces of (*E,Z*) and (*Z,Z*) can be detected under general synthetic conditions, i.e. in thermal equilibrium without additional UV-illumination.



**Figure S32:** Detailed depiction of Figure S30, section A (128-fold expansion). Without illumination (black spectrum) a signal (highlighted red) could be identified, which may be assigned to (*E,Z*) due to similar chemical shift and multiplicity. As this signal responds to UV-illumination with a significant increase in intensity, this signal can be unambiguously assigned to (*E,Z*)H(1) (see Figure S31).



**Figure S33:** Detailed depiction of Figure S30, section B (128-fold expansion). Without illumination (black spectrum) a signal (highlighted red) could be identified, which may be assigned to (E,Z) due to similar chemical shift and multiplicity. As this signal responds to UV-illumination with a significant increase in intensity, this signal can be unambiguously assigned to (E,Z)H(2) (see Figure S31).



**Figure S34:** Detailed depiction of Figure S30, section C (16-fold expansion). Without illumination (black spectrum) a signal (highlighted red) could be identified, which may be assigned to (E,Z) due to similar chemical shift and multiplicity. As this signal responds to UV-illumination with a significant increase in intensity, this signal can be unambiguously assigned to (E,Z)H(4) (see Figure S31).

## 6. Determination of thermal (Z) → (E) isomerization rate constants for iminium ion 1 at various conditions

### 6.1 Method

The NMR samples were illuminated continuously with an UV-LED (LG Innotek LEUVA66X00RV00) operated with 0.5 A and emitting at a peak wavelength of 365 nm until at least the photostationary state of (Z,E) was achieved. Afterwards the illumination was stopped (t = 0 s) followed by recording the thermal (Z) → (E) isomerization processes *via* a quantitative 1D-<sup>1</sup>H NMR kinetic. For a quantitative evaluation we measured the 1D-<sup>1</sup>H NMR spectra as following: For a sufficient signal to noise ratio 16 scans were accumulated per spectrum. A relaxation delay of d1 = 4 s in combination with a 30 ° pulse ensured full relaxation before each scan and pulse lengths for <sup>1</sup>H-experiments were calibrated. Based on these curves, we obtained the different isomerization rates  $k_{(Z) \rightarrow (E)}$  by mathematical fitting as first order reaction process (Equation 1).

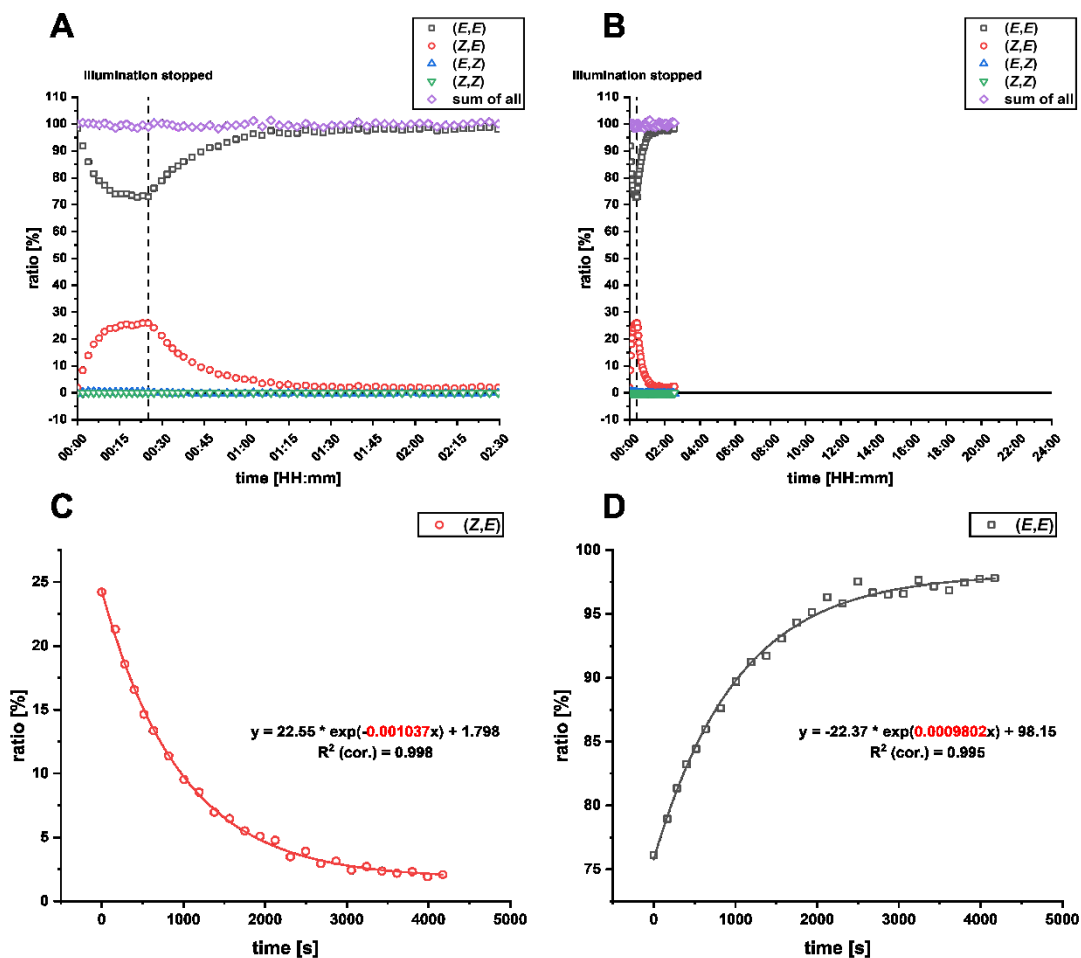
$$y = A_1 * e^{-k_{(Z) \rightarrow (E)}x} + y_0$$

**Equation 1:** Mathematical fitting for thermal (Z) → (E) isomerization process as first order reaction process.

We investigated different temperatures, solvents and concentrations to analyze the stabilities of the different (Z)-configured double bond isomers.

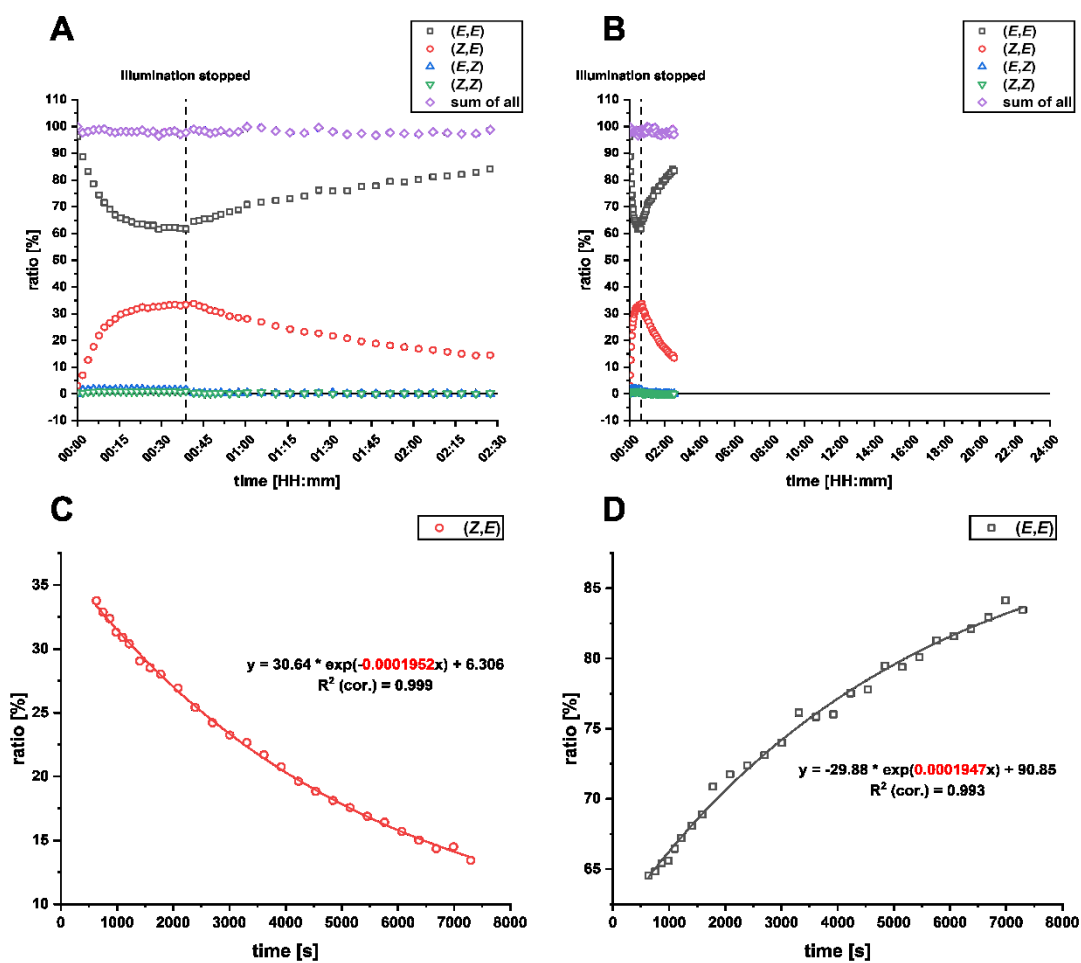
## 6.2 Influence of Temperature

10 mM, CD<sub>3</sub>CN, 20 °C



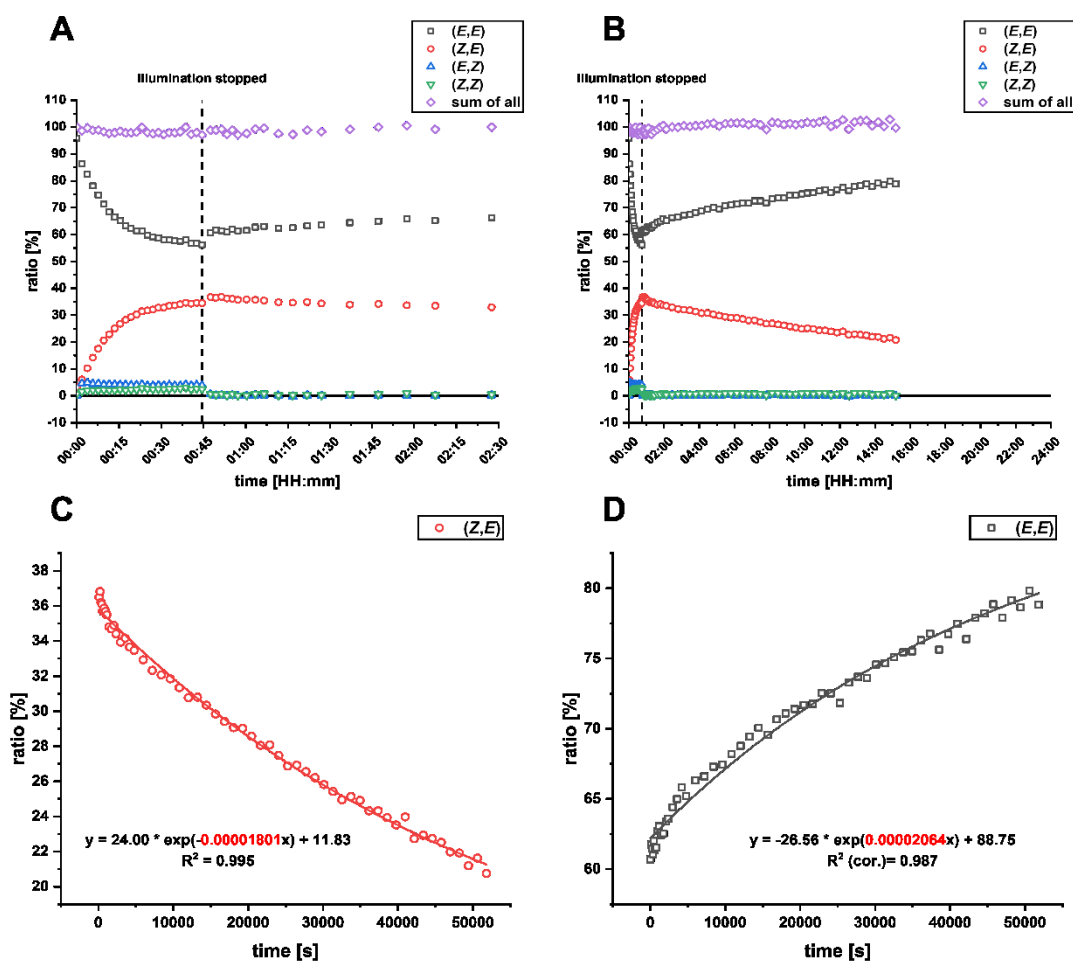
**Figure S35:** 1D-<sup>1</sup>H kinetic of photoinduced and thermal isomerization of iminium ion **1** measured at 20 °C in acetonitrile-*d*<sub>3</sub> (10 mM). **A:** First 2.5 h of the recorded 1D-<sup>1</sup>H-kinetic show in detail how UV-illumination (365 nm) triggers (E) → (Z) isomerization and after stopping illumination the associated thermal (Z) → (E) isomerization processes. The dashed vertical line indicates the end of illumination. **B:** To facilitate comparison with other 1D-<sup>1</sup>H kinetics, the x-axes is set to 24 h. **C** and **D:** Decay and grow curves for thermal (Z) → (E) isomerization of the C=N double bond including mathematical fitting. The obtained values for  $k_{(Z) \rightarrow (E)}$  are given in Table S1.

10 mM, CD<sub>3</sub>CN, 0 °C



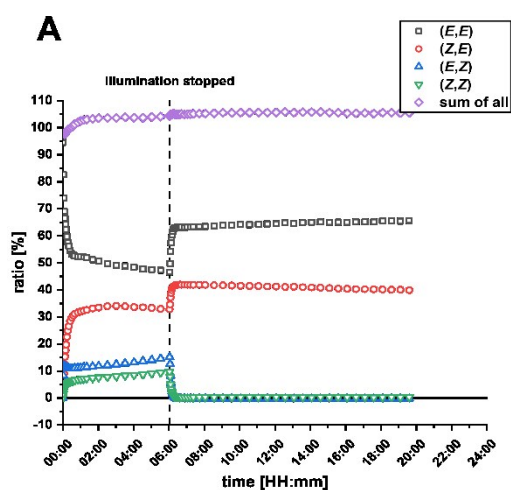
**Figure S36:** 1D-<sup>1</sup>H kinetic of photoinduced and thermal isomerization of iminium ion **1** measured at 0 °C in acetonitrile-*d*<sub>3</sub> (10 mM). **A:** First 2.5 h of the recorded 1D-<sup>1</sup>H kinetic show in detail how UV-illumination (365 nm) triggers (*E*) → (*Z*) isomerization and after stopping illumination the associated thermal (*Z*) → (*E*) isomerization processes. The dashed vertical line indicates the end of illumination. **B:** To facilitate comparison with other 1D-<sup>1</sup>H kinetics, the x-axis is set to 24 h. **C** and **D:** Decay and grow curves for thermal (*Z*) → (*E*) isomerization of the C=N double bond including mathematical fitting. The obtained values for  $k_{(Z) \rightarrow (E)}$  are given in Table S1.

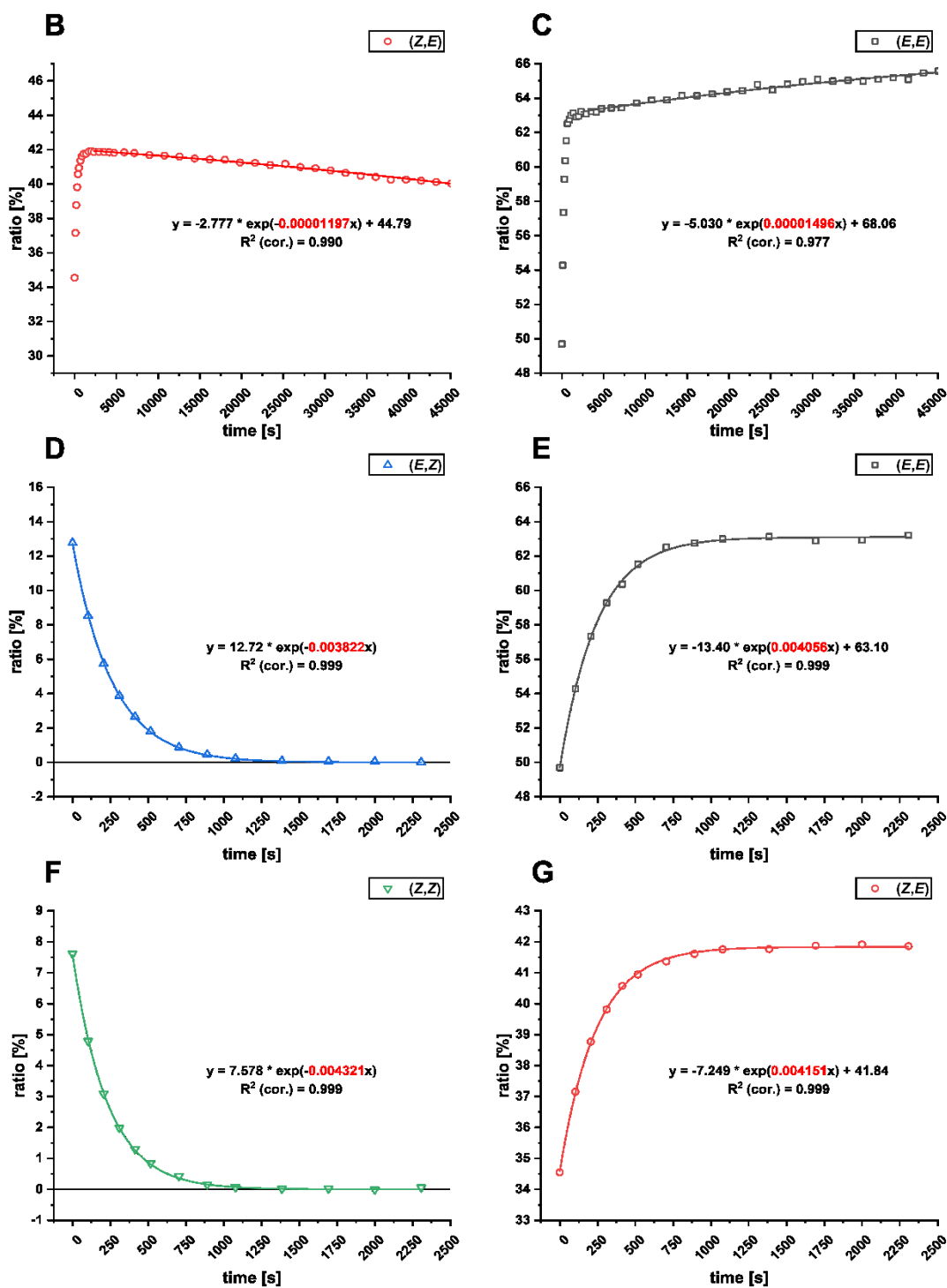
10 mM, CD<sub>3</sub>CN, -20 °C



**Figure S37:** 1D-<sup>1</sup>H kinetic of photoinduced and thermal isomerization of iminium ion **1** measured at -20 °C in acetonitrile-*d*<sub>3</sub> (10 mM). **A:** First 2.5 h of the recorded 1D-<sup>1</sup>H kinetic show in detail how UV-illumination (365 nm) triggers (*E*) → (*Z*) isomerization and after stopping illumination the associated thermal (*Z*) → (*E*) isomerization processes. The dashed vertical line indicates the end of illumination. **B:** To facilitate comparison with other 1D-<sup>1</sup>H kinetics, the x-axis is set to 24 h. **C** and **D:** Decay and growth curves for thermal (*Z*) → (*E*) isomerization of the C=N double bond including mathematical fitting. The obtained values for *k*<sub>(*Z*) → (*E*)</sub> are given in Table S1.

10 mM, CD<sub>3</sub>CN, -40 °C





**Figure S38:**  $1D-1H$  kinetic of photoinduced and thermal isomerization of iminium ion **1** measured at  $-40\text{ }^\circ\text{C}$  in acetonitrile- $d_3$  (10 mM). **A:** Complete  $1D-1H$  kinetic show how UV-illumination (365 nm) triggers  $(E) \rightarrow (Z)$  isomerization and after stopping illumination the associated thermal  $(Z) \rightarrow (E)$  isomerization processes. The dashed vertical line indicates the end of illumination. **B - G:** Decay and grow curves for thermal  $(Z) \rightarrow (E)$  isomerization of the C=N and C=C double bond including mathematical fitting. The obtained values for  $k_{(Z) \rightarrow (E)}$  are given in Table S1, S2 and S3.

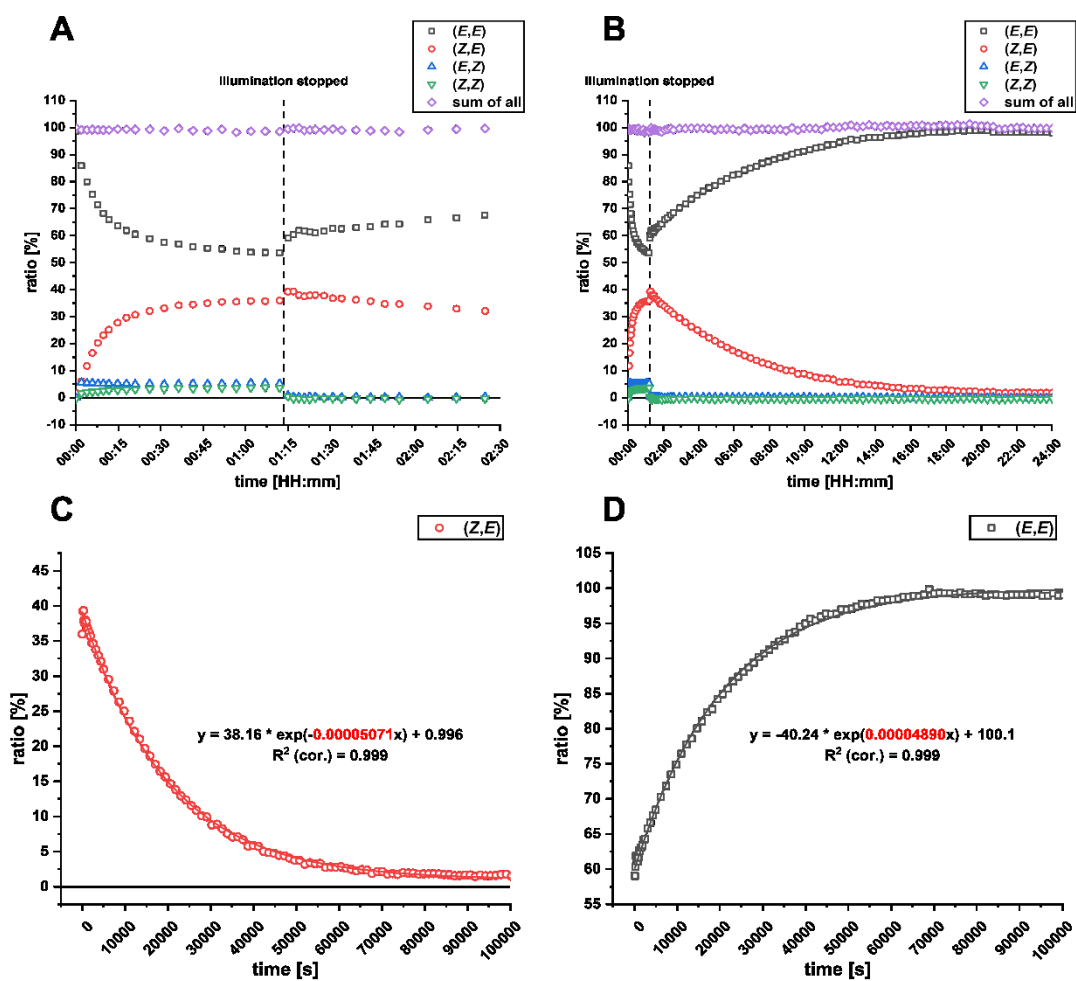


**Table S1:** Temperature dependence (20, 0, -20, -40 °C) of thermal (Z) → (E) isomerization processes of iminium ion **1** in acetonitrile-*d*<sub>3</sub> (10 mM) after UV-triggered (E) → (Z) isomerization (λ = 365 nm). To obtain  $k_{(Z) \rightarrow (E)}$  the associated isomerization curves (see Figure S35-S38) were mathematically fitted and Equation 1 was applied.

Entry	T [°C]		Process	$k_{Z \rightarrow E}$ [ $10^{-3} \text{ s}^{-1}$ ]
1	20	(Z,E) → (E,E)	(Z,E)-decay	1.037
2			(E,E)-grow	0.9802
3		(E,Z) → (E,E)	(E,Z)-decay	-
4			(E,E)-grow	-
5		(Z,Z) → (Z,E)	(Z,Z)-decay	-
6			(Z,E)-grow	-
<hr/>				
7	0	(Z,E) → (E,E)	(Z,E)-decay	0.1952
8			(E,E)-grow	0.1947
9		(E,Z) → (E,E)	(E,Z)-decay	-
10			(E,E)-grow	-
11		(Z,Z) → (Z,E)	(Z,Z)-decay	-
12			(Z,E)-grow	-
<hr/>				
13	-20	(Z,E) → (E,E)	(Z,E)-decay	0.01801
14			(E,E)-grow	0.02064
15		(E,Z) → (E,E)	(E,Z)-decay	-
16			(E,E)-grow	-
17		(Z,Z) → (Z,E)	(Z,Z)-decay	-
18			(Z,E)-grow	-
<hr/>				
19	-40	(Z,E) → (E,E)	(Z,E)-decay	0.01197
20			(E,E)-grow	0.01496
21		(E,Z) → (E,E)	(E,Z)-decay	3.822
22			(E,E)-grow	4.056
23		(Z,Z) → (Z,E)	(Z,Z)-decay	4.321
24			(Z,E)-grow	4.151

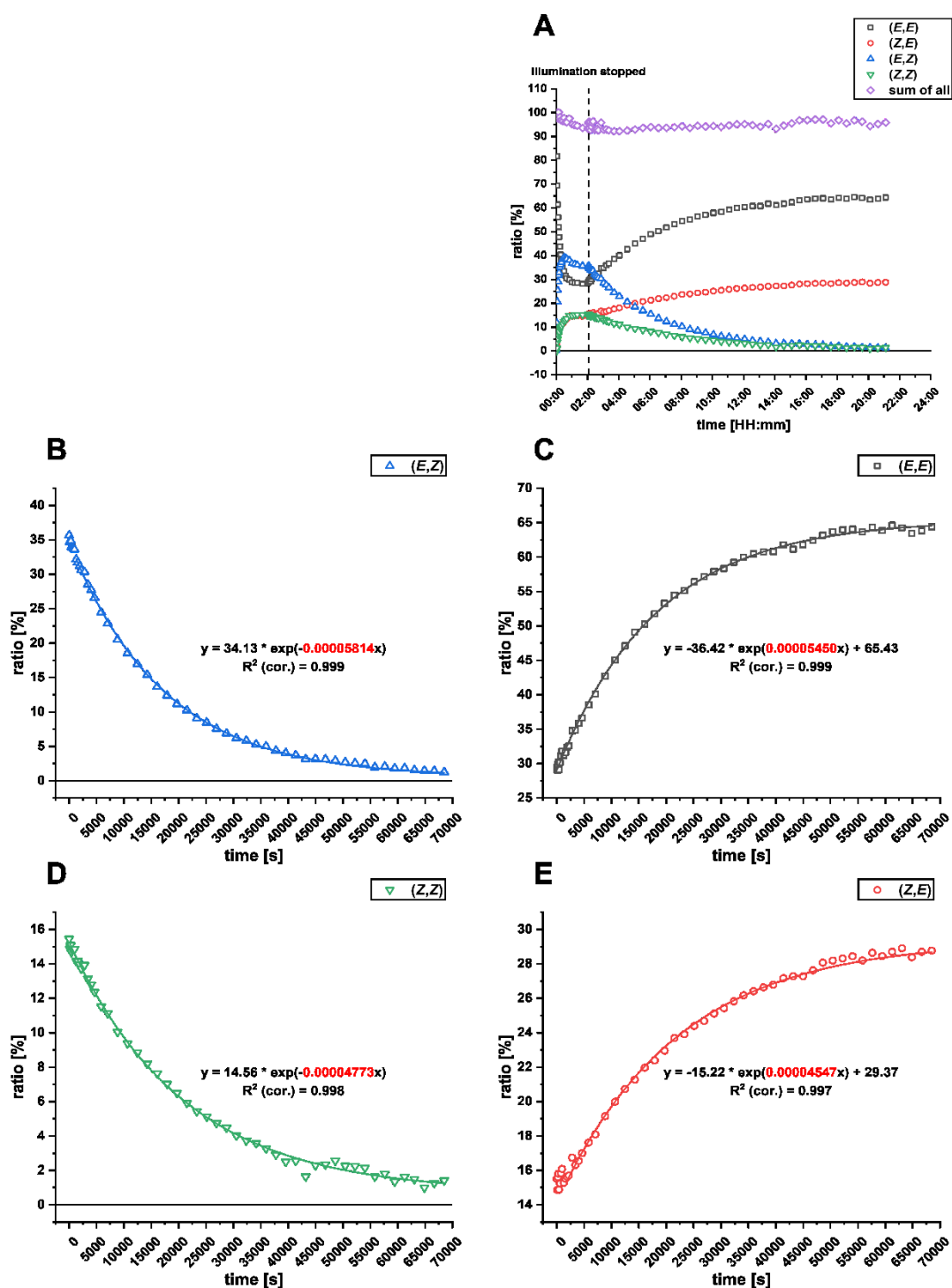
### 6.3 Influence of Solvent

10 mM, acetone- $d_6$ , -40 °C



**Figure S39:** 1D-<sup>1</sup>H kinetic of photoinduced and thermal isomerization of iminium ion **1** measured at -40 °C in acetone- $d_6$  (10 mM). **A:** First 2.5 h of the recorded 1D-<sup>1</sup>H kinetic show in detail how UV-illumination (365 nm) triggers (E) → (Z) isomerization and after stopping illumination the associated thermal (Z) → (E) isomerization processes. The dashed vertical line indicates the end of illumination. **B:** To facilitate comparison with other 1D-<sup>1</sup>H kinetics, the x-axis is set to 24 h. **C - H:** Decay and growth curves for thermal (Z) → (E) isomerization of the C=N and C=C double bond including mathematical fitting. The obtained values for  $k_{(Z) \rightarrow (E)}$  are given in Table S2.

10 mM, CD<sub>2</sub>Cl<sub>2</sub>, -40 °C



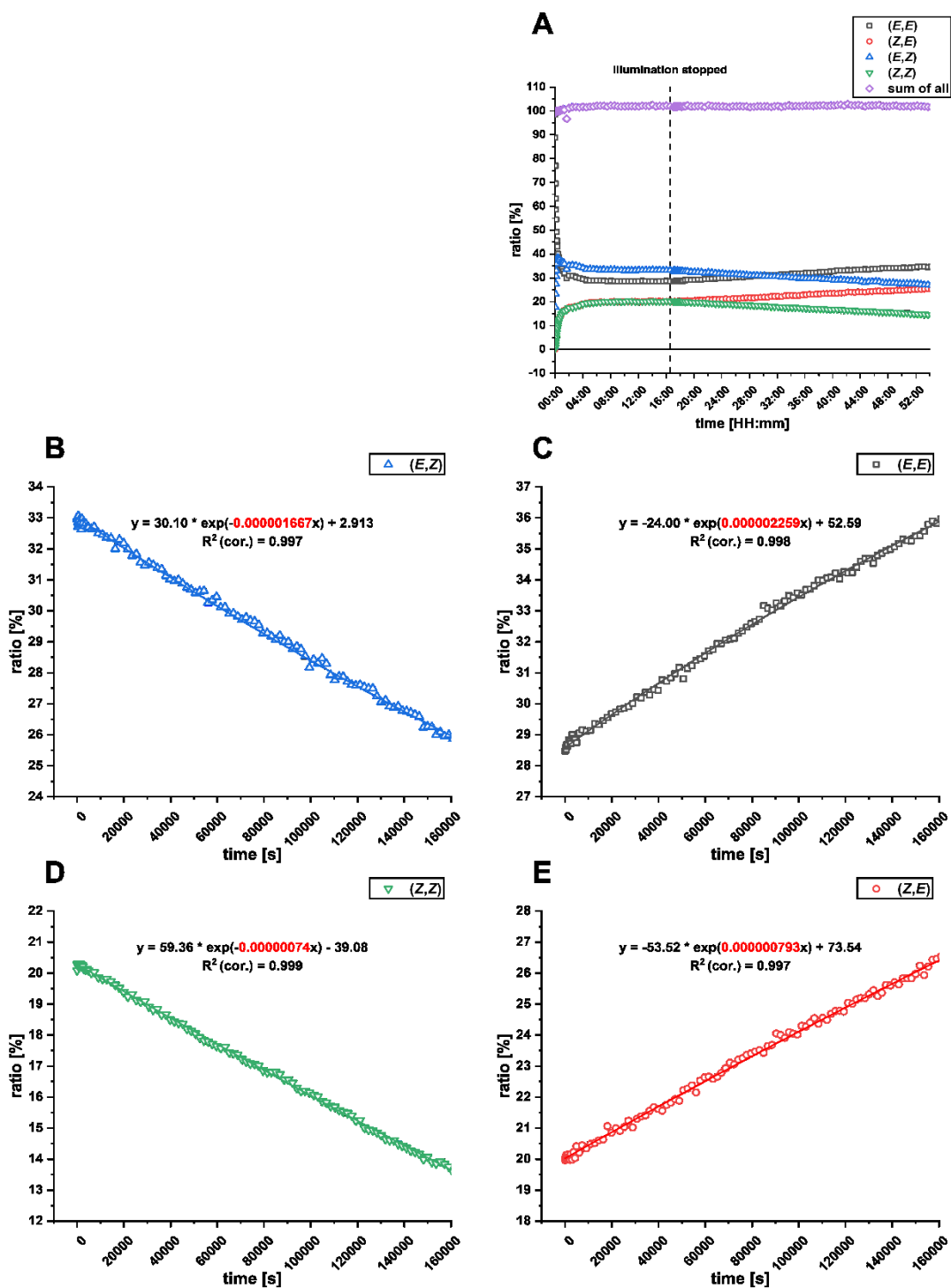
**Figure S40:** 1D-<sup>1</sup>H kinetic of photoinduced and thermal isomerization of iminium ion **1** measured at -40 °C in dichloromethane-*d*<sub>2</sub> (10 mM). **A:** Complete 1D-<sup>1</sup>H kinetic shows how UV-illumination (365 nm) triggers (E) → (Z) isomerization and after stopping illumination the associated thermal (Z) → (E) isomerization processes. The dashed vertical line indicates the end of illumination. **B - E:** Decay and grow curves for thermal (Z) → (E) isomerization of the C=N and C=C double bond isomerization including mathematical fitting. The obtained values for  $k_{(Z) \rightarrow (E)}$  are given in Table S2.

**Table S2:** Solvent dependence (acetone- $d_6$ , acetonitrile- $d_3$ , dichloromethane- $d_2$ ) (10 mM) of thermal ( $Z$ )  $\rightarrow$  ( $E$ ) isomerization processes of iminium ion **1** at -40 °C after UV-triggered ( $E$ )  $\rightarrow$  ( $Z$ ) isomerization ( $\lambda = 365$  nm). To obtain  $k_{(Z) \rightarrow (E)}$  the associated isomerization curves (see Figure S38-S40) were mathematically fitted and Equation 1 was applied.

Entry	Solvent	Process	$k_{Z \rightarrow E}$ [ $10^{-3} \text{ s}^{-1}$ ]	
1	Acetone- $d_6$	( $Z,E$ )-decay	0.05071	
2		( $Z,E$ ) $\rightarrow$ ( $E,E$ )	( $E,E$ )-grow	0.0489
3		(E,Z) $\rightarrow$ ( $E,E$ )	( $E,Z$ )-decay	-
4			( $E,E$ )-grow	-
5		(Z,Z) $\rightarrow$ ( $Z,E$ )	(Z,Z)-decay	-
6			(Z,E)-grow	-
7	CD <sub>3</sub> CN	( $Z,E$ )-decay	0.01197	
8		( $Z,E$ ) $\rightarrow$ ( $E,E$ )	( $E,E$ )-grow	0.01496
9		(E,Z) $\rightarrow$ ( $E,E$ )	( $E,Z$ )-decay	3.822
10			( $E,E$ )-grow	4.056
11		(Z,Z) $\rightarrow$ ( $Z,E$ )	(Z,Z)-decay	4.321
12			(Z,E)-grow	4.151
13	CD <sub>2</sub> Cl <sub>2</sub>	( $Z,E$ )-decay	-	
14		( $Z,E$ ) $\rightarrow$ ( $E,E$ )	( $E,E$ )-grow	-
15		(E,Z) $\rightarrow$ ( $E,E$ )	( $E,Z$ )-decay	0.05814
16			( $E,E$ )-grow	0.0545
17		(Z,Z) $\rightarrow$ ( $Z,E$ )	(Z,Z)-decay	0.04773
18			(Z,E)-grow	0.04547

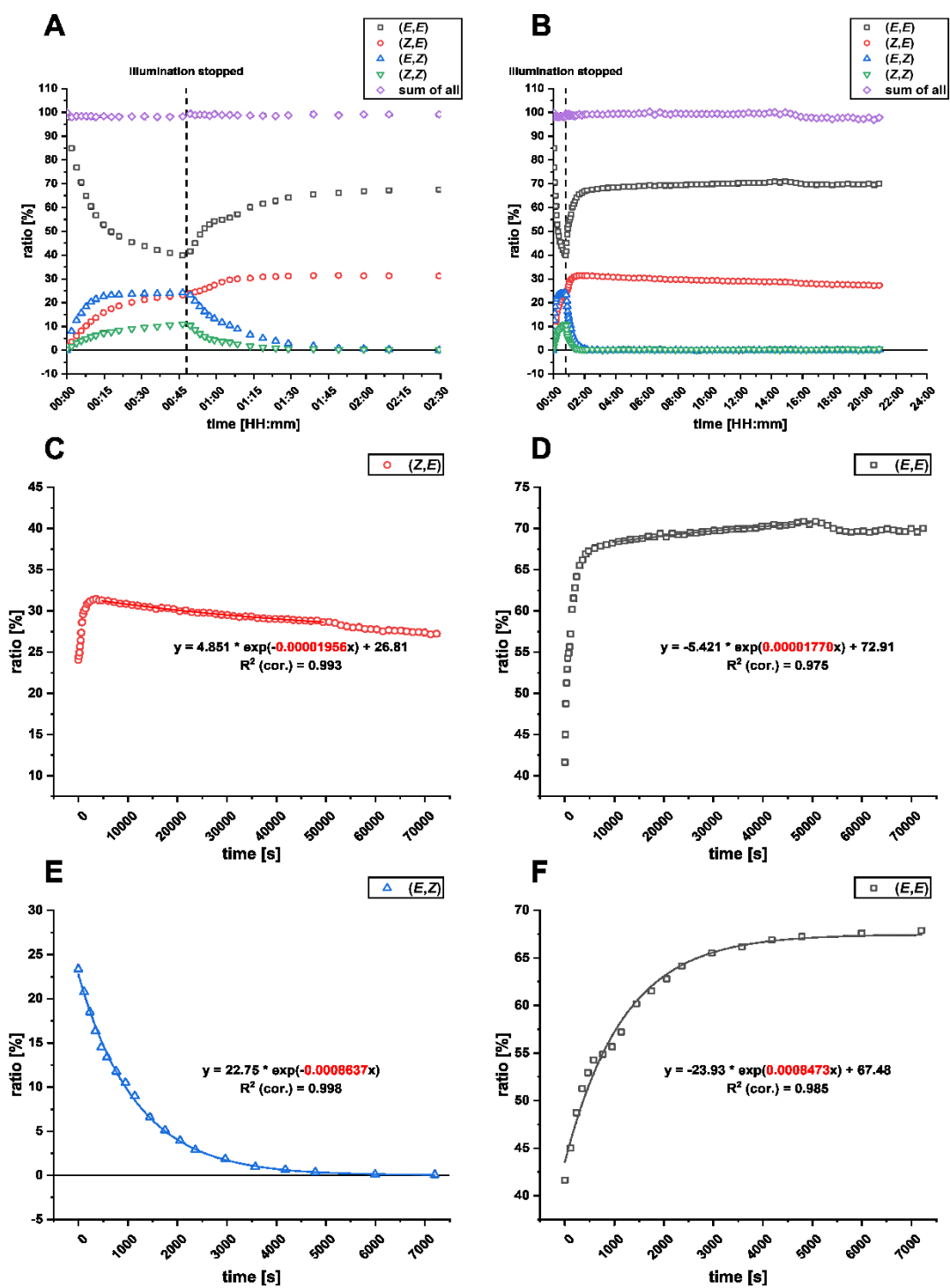
## 6.4 Influence of Concentration

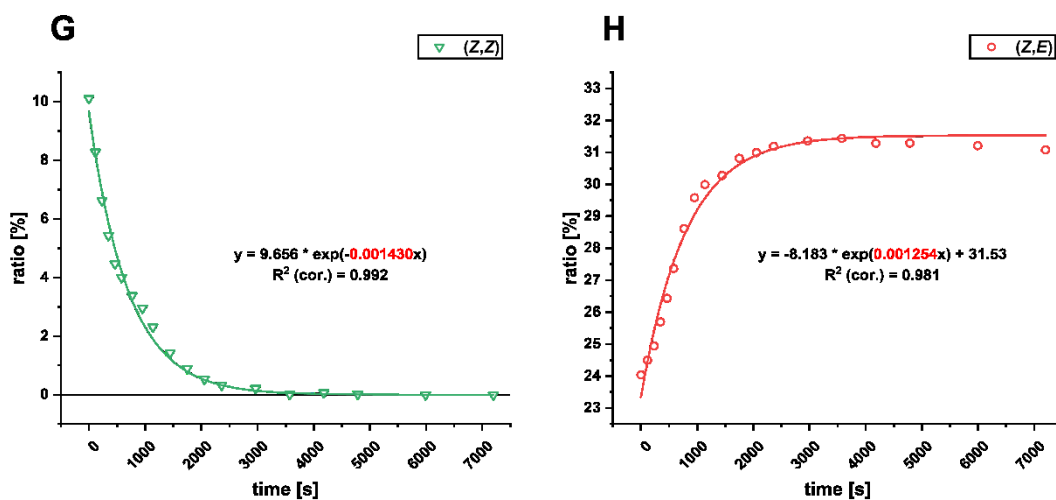
50 mM, CD<sub>3</sub>CN, -40 °C



**Figure S41:** 1D-<sup>1</sup>H kinetic of photoinduced and thermal isomerization of iminium ion **1** measured at -40 °C in acetonitrile-*d*<sub>3</sub> (50 mM). **A:** Complete 1D-<sup>1</sup>H kinetic shows how UV-illumination (365 nm) triggers (*E*) → (*Z*) isomerization and after stopping illumination the associated thermal (*Z*) → (*E*) isomerization processes. The dashed vertical line indicates the end of illumination. **B - E:** Decay and grow curves for thermal (*Z*) → (*E*) isomerization of the C=C double bond including mathematical fitting. The obtained values for  $k_{(Z) \rightarrow (E)}$  are given in Table S3.

25 mM, CD<sub>3</sub>CN, -40 °C





**Figure S42:** 1D-<sup>1</sup>H kinetic of photoinduced and thermal isomerization of iminium ion **1** measured at -40 °C in acetonitrile-*d*<sub>3</sub> (25 mM). **A:** First 2.5 h of the recorded 1D-<sup>1</sup>H kinetic show in detail how UV-illumination (365 nm) triggers (*E*) → (*Z*) isomerization and after stopping illumination the associated thermal (*Z*) → (*E*) isomerization processes. The dashed vertical line indicates the end of illumination. **B:** To facilitate comparison with other 1D-<sup>1</sup>H kinetics, the x-axis is set to 24 h. **C - H:** Decay and grow curves for thermal (*Z*) → (*E*) isomerization of the C=N and C=C double bond including mathematical fitting. The obtained values for  $k_{(Z) \rightarrow (E)}$  are given in Table S3.

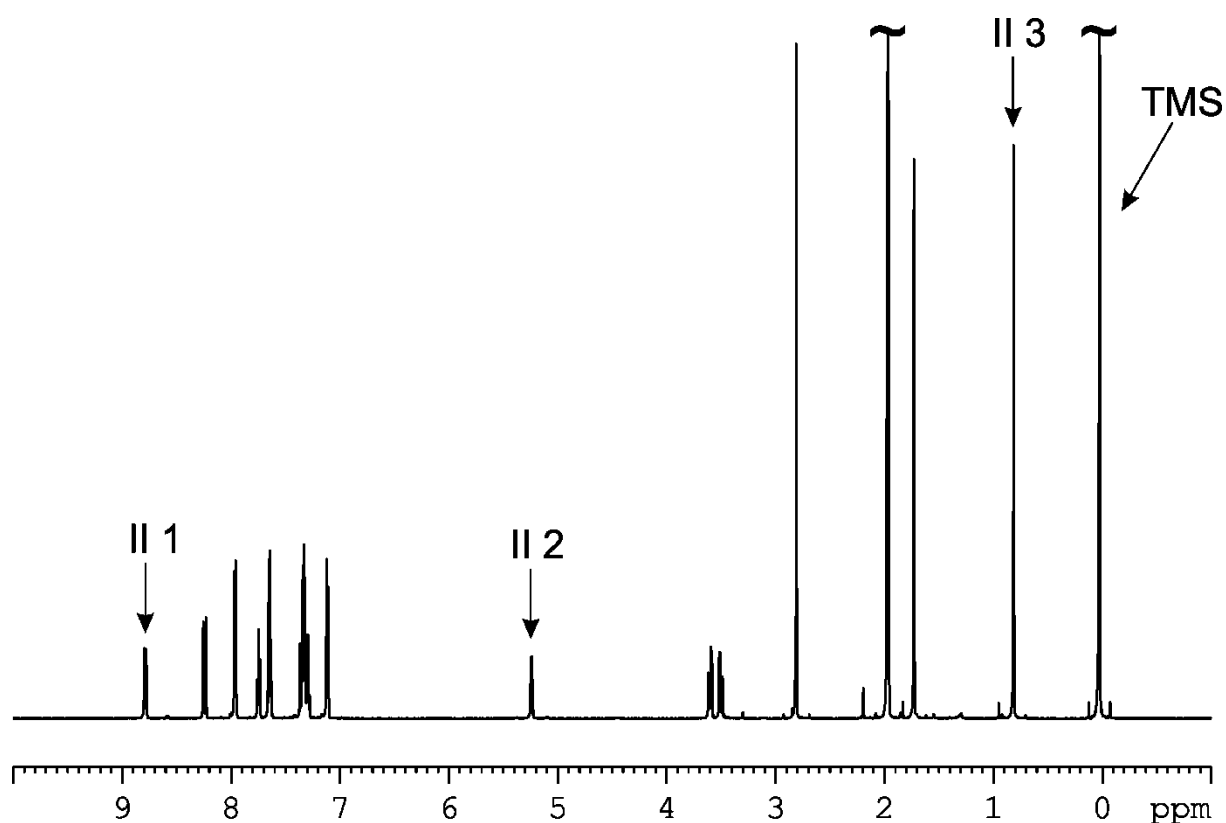
**Table S3:** Concentration dependence (50, 25, 10 mM) of thermal (*Z*) → (*E*) isomerization processes of iminium ion **1** in acetonitrile-*d*<sub>3</sub> at -40 °C after UV-triggered (*E*) → (*Z*) isomerization ( $\lambda = 365$  nm). To obtain  $k_{(Z) \rightarrow (E)}$  the associated isomerization curves (see Figure S38, S41, S42) were mathematically fitted and Equation 1 was applied.

Entry	c [mM]	Process	$k_{Z \rightarrow E}$ [ $10^{-3} \text{ s}^{-1}$ ]	
1	50	( <i>Z,E</i> ) → ( <i>E,E</i> )	( <i>Z,E</i> )-decay	-
2		( <i>E,E</i> )-grow	-	
3		( <i>E,Z</i> ) → ( <i>E,E</i> )	( <i>E,Z</i> )-decay	0.001667
4		( <i>E,E</i> )-grow	0.002259	
5		( <i>Z,Z</i> ) → ( <i>Z,E</i> )	( <i>Z,Z</i> )-decay	0.00074
6		( <i>Z,E</i> )-grow	0.000793	
7	25	( <i>Z,E</i> ) → ( <i>E,E</i> )	( <i>Z,E</i> )-decay	0.01956
8		( <i>E,E</i> )-grow	0.0177	
9		( <i>E,Z</i> ) → ( <i>E,E</i> )	( <i>E,Z</i> )-decay	0.8637
10		( <i>E,E</i> )-grow	0.8473	
11		( <i>Z,Z</i> ) → ( <i>Z,E</i> )	( <i>Z,Z</i> )-decay	1.43
12		( <i>Z,E</i> )-grow	1.254	
13	10	( <i>Z,E</i> ) → ( <i>E,E</i> )	( <i>Z,E</i> )-decay	0.01197
14		( <i>E,E</i> )-grow	0.01496	
15		( <i>E,Z</i> ) → ( <i>E,E</i> )	( <i>E,Z</i> )-decay	3.822
16		( <i>E,E</i> )-grow	4.056	
17		( <i>Z,Z</i> ) → ( <i>Z,E</i> )	( <i>Z,Z</i> )-decay	4.321
18		( <i>Z,E</i> )-grow	4.151	

## 7. Aggregate-investigations of (*E,E*) by diffusion ordered spectroscopy (DOSY) using different concentrations, temperatures and solvents

### 7.1 Method

For DOSY measurements the dstebpgp3s pulse program, a convection suppressing DSTE (double stimulated echo) pulse sequence developed by Jerschow and Müller was applied in a pseudo 2D mode.<sup>6</sup> The diffusion time delay was set to 100 ms and a gradient pulse of 1350 - 2300  $\mu$ s was applied. Sine.100 as gradient program and a linear gradient ramp with 20 increments between 10% and 95% of the maximum gradient strength were used. For z-only gradients 100 %, -13.17%, -17.13% and -15.17% were used. NMR data were processed and evaluated with TopSpin 3.2 (Topspin T1/T2 Module). Diffusion coefficients and average volumes were obtained according to Jerschow and Müller.<sup>6</sup>



**Figure S43:** Representative 1D-<sup>1</sup>H NMR spectrum of iminium ion **1** measured in anh. and deg. CD<sub>3</sub>CN at 20 °C. The volumes given in Tables S4 and S5 correspond to mean values with standard deviation (SD). These DOSY-values were obtained by evaluation of the intense and non-overlapping signals II 1, II 2 and II 3 of (*E,E*).



## 7.2 Influence of concentration, temperature and solvent

We aimed to experimentally determine the volumes of (*E,E*) at different conditions, i.e. the influence of temperature, concentration and solvents on the aggregate size was investigated. Assuming that model iminium ion **1** forms a contact ion pair in aprotic solvents, a monomer volume of 412 Å<sup>3</sup> was calculated for (*E,E*) based on the known intermolecular van der Waals radii of the corresponding functional groups and atoms.<sup>7, 8</sup> Given this monomer volume, we are able to assign the DOSY volumes to a certain aggregate size.

The influence of the concentration on the aggregation of iminium ion **1** was determined by investigating differentially concentrated samples at 20 and -40 °C (Table S4).

**Table S4:** Mean diffusion coefficients and average volumes of (*E,E*) at different temperatures (20 and -40 °C) and concentrations (50, 25, 10 mM) in anh. and deg. CD<sub>3</sub>CN.

Entry	T [°C]	c [mM]	mean diffusion	average volume [Å <sup>3</sup> ]
			coefficient [E-9 m <sup>2</sup> /s] with SD	with SD
1	20	50	5.58 ± 0.0731	844.5 ± 28.92
2		25	5.72 ± 0.0693	851.7 ± 27.0
3		10	5.87 ± 0.045	809.7 ± 16.16
4	-40	50	1.89 ± 0.00684	1152 ± 11.15
5		25	2.0 ± 0.0258	1036 ± 35.51
6		10	2.06 ± 0.0153	1063 ± 21.06

We similarly investigated the influence of different solvents, also at 20 and -40 °C (Table S5).

**Table S5:** Mean diffusion coefficients and average volumes of (*E,E*) at different temperatures (20 and -40 °C) and in different solvents (acetone-*d*<sub>6</sub>, CD<sub>3</sub>CN, CD<sub>2</sub>Cl<sub>2</sub>) (10 mM).

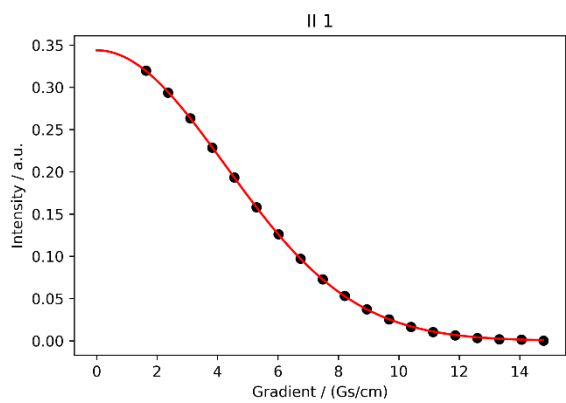
Entry	T [°C]	Solvent	mean diffusion	average volume [Å <sup>3</sup> ]
			coefficient [E-9 m <sup>2</sup> /s] with SD	with SD
1	20	acetone- <i>d</i> <sub>6</sub>	6.41 ± 0.107	1053 ± 44.7
2		CD <sub>3</sub> CN	5.87 ± 0.045	809.7 ± 16.16
3		CD <sub>2</sub> Cl <sub>2</sub>	4.54 ± 0.0167	753.9 ± 7.423
4	-40	acetone- <i>d</i> <sub>6</sub>	2.39 ± 0.0348	1276.8 ± 47.95
5		CD <sub>3</sub> CN	2.06 ± 0.0153	1063 ± 21.06
6		CD <sub>2</sub> Cl <sub>2</sub>	1.65 ± 0.00985	981.1 ± 15.03

Herein we found, that the biggest (*E,E*) volume was obtained in the most nucleophilic solvent. We believe this volume increase indicates an improving interaction of the iminium ion and the solvent molecule, similar to previous studies on enamine intermediates.<sup>9</sup>

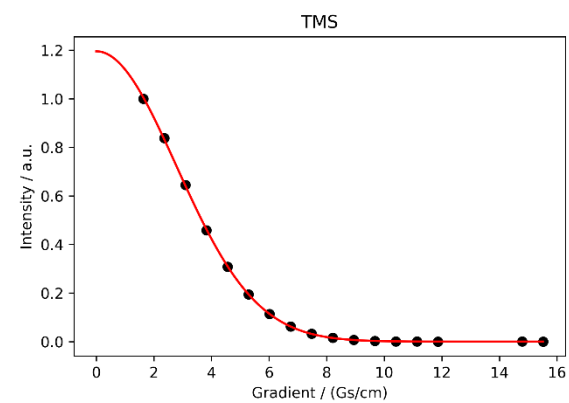
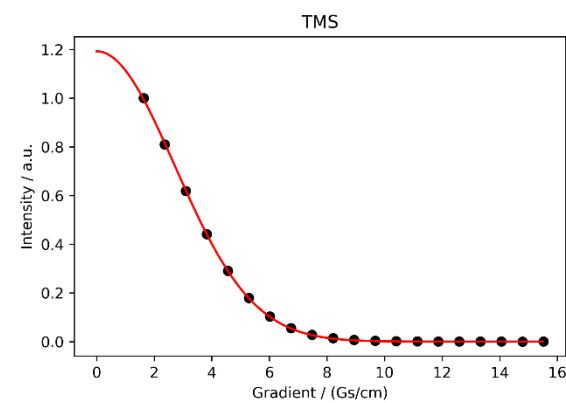
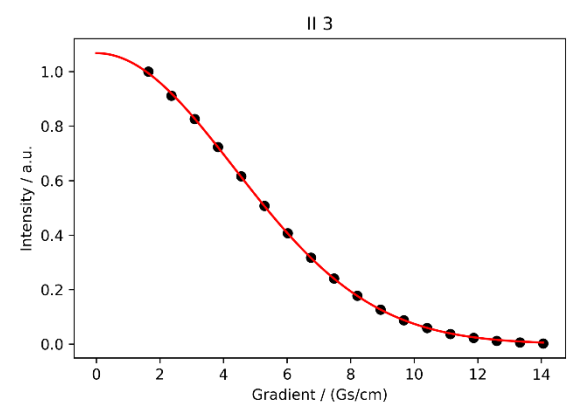
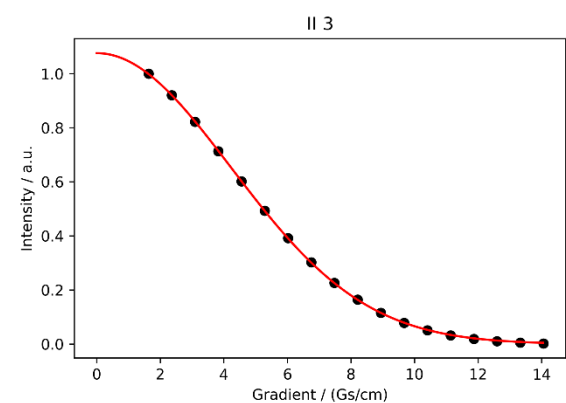
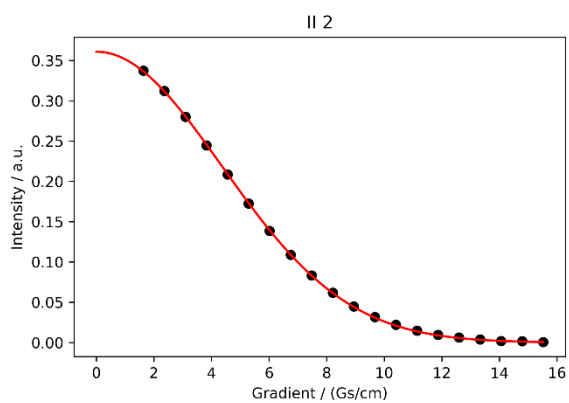
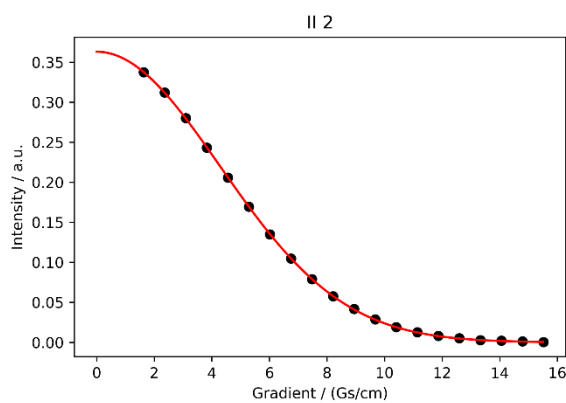
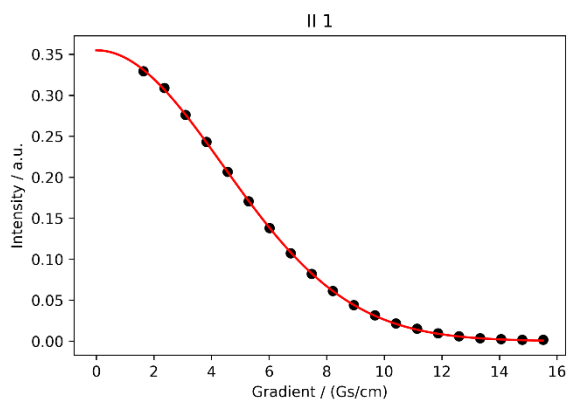
## 7.3 DOSY plots

Concentration dependence (see Table S4)

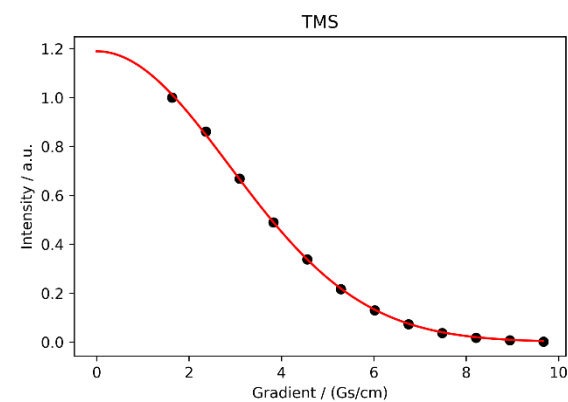
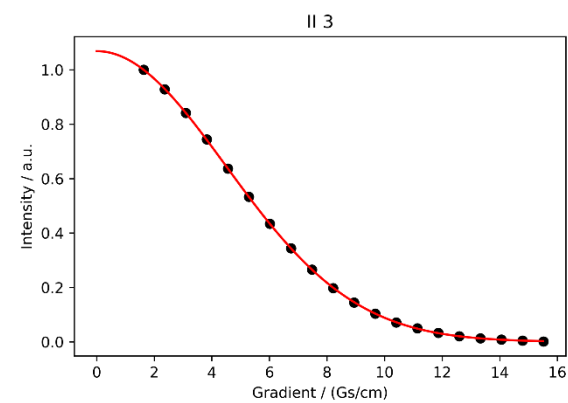
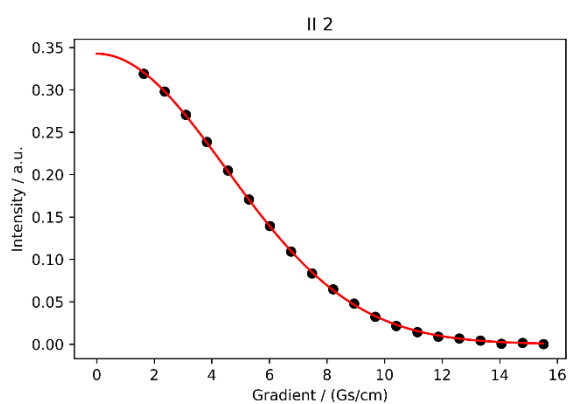
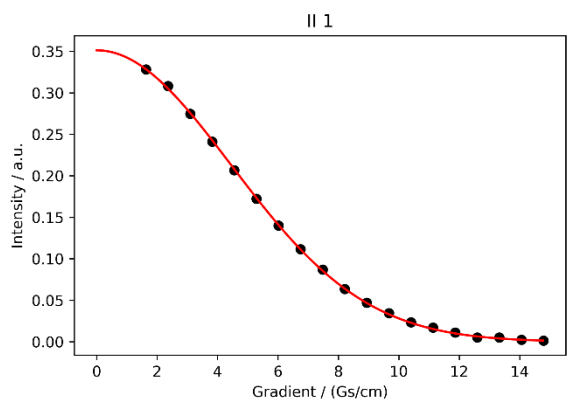
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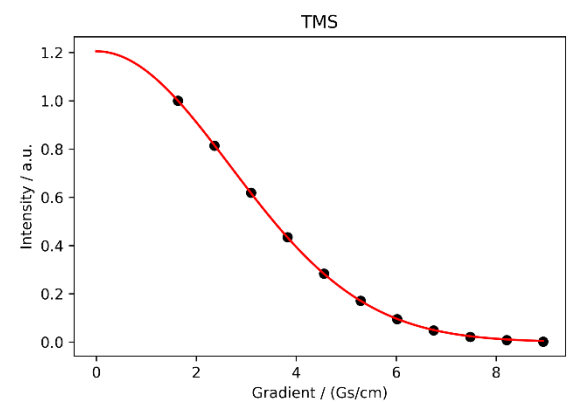
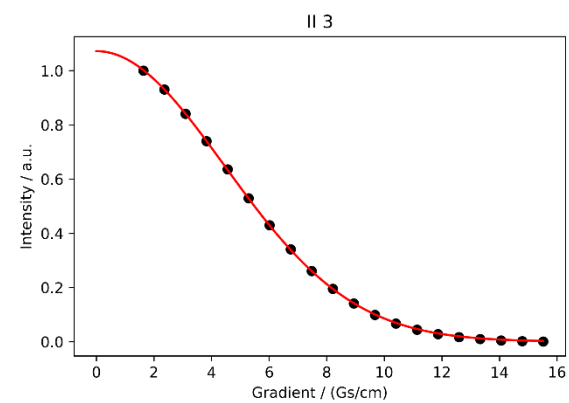
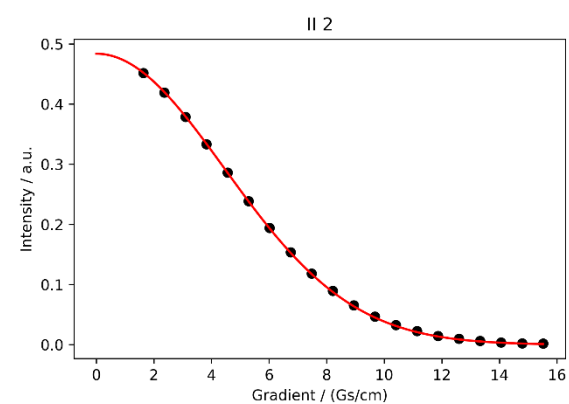
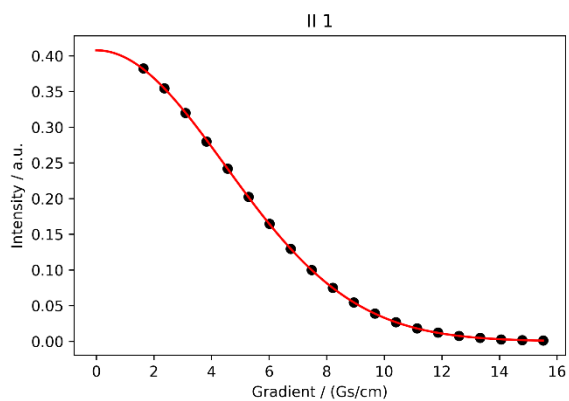
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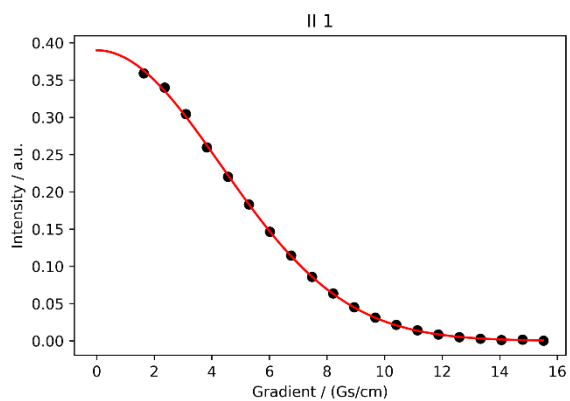
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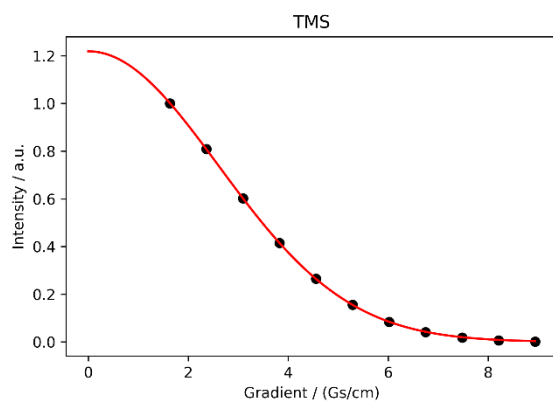
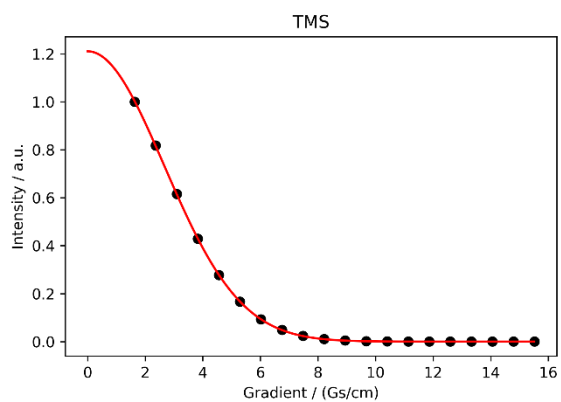
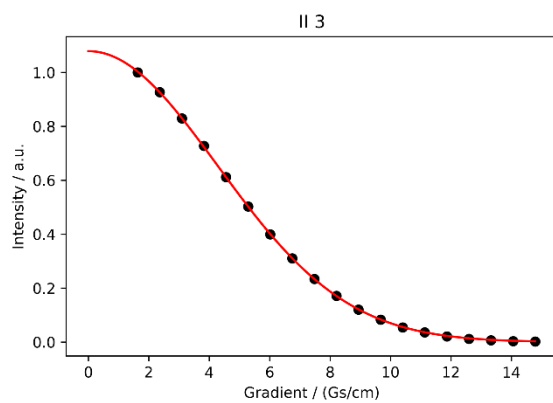
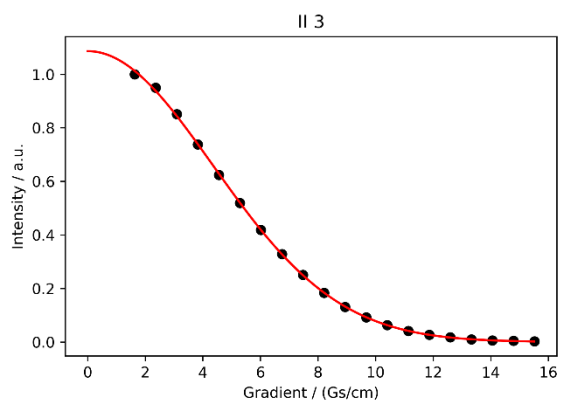
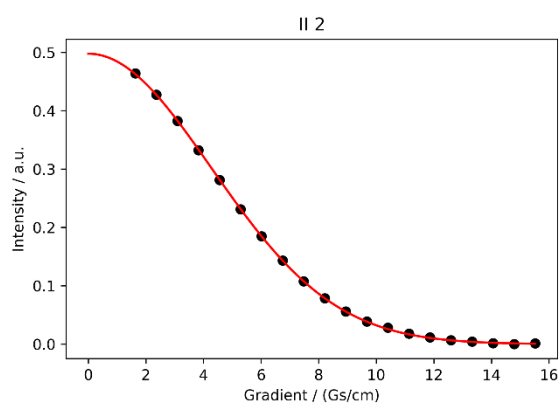
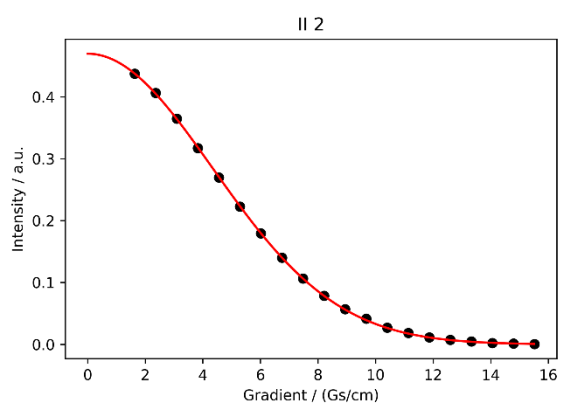
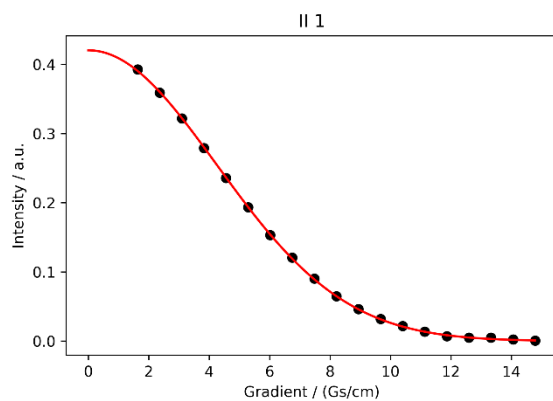
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entry 5

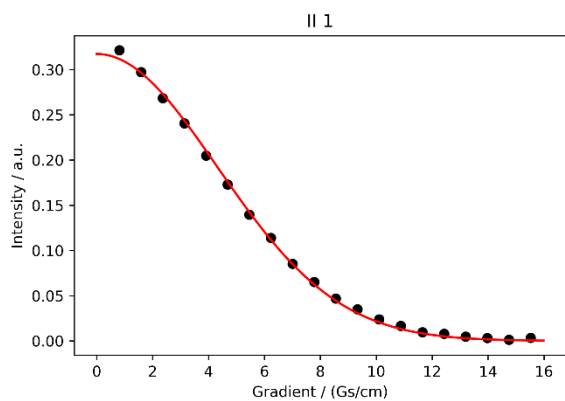


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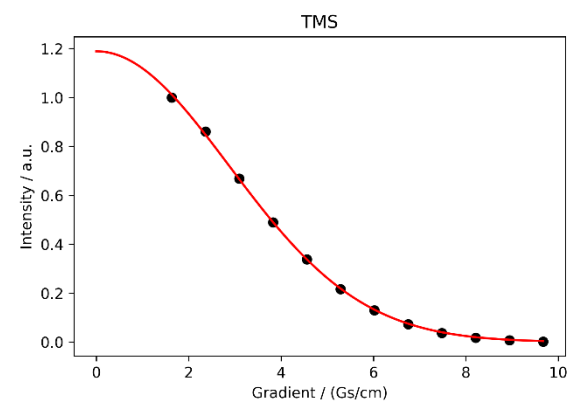
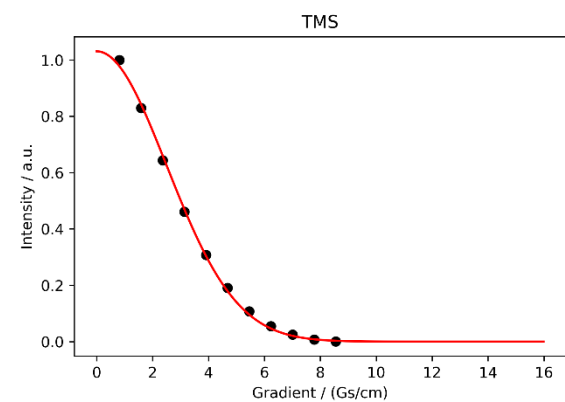
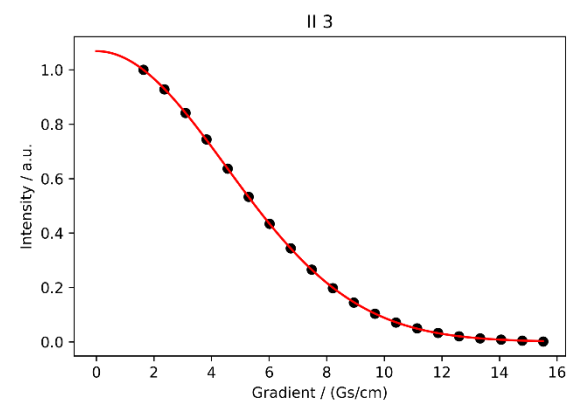
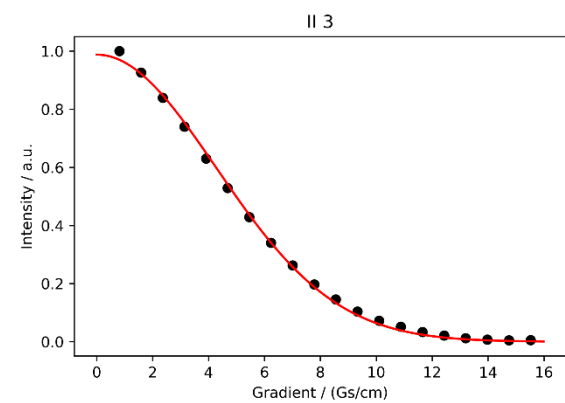
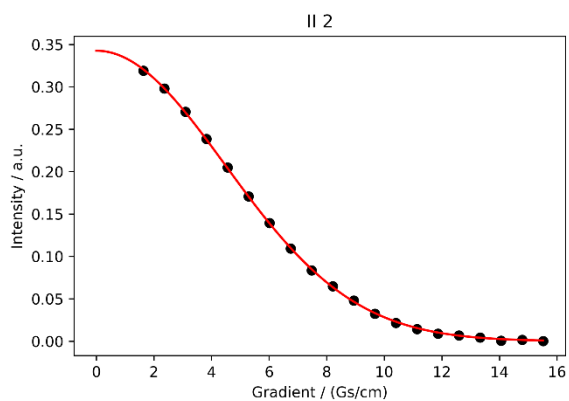
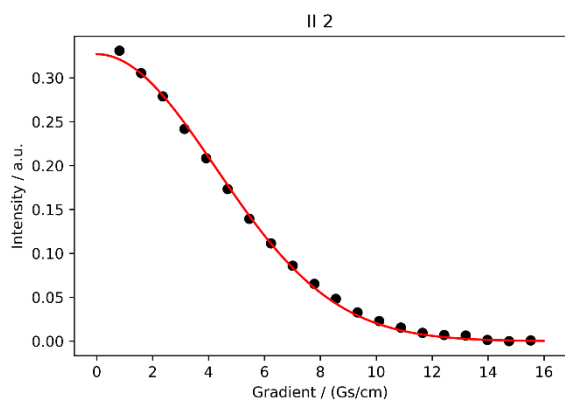
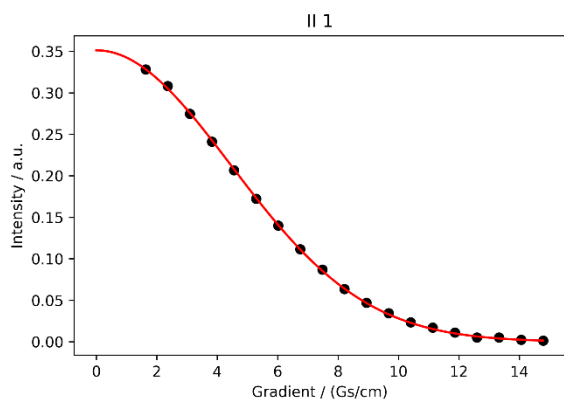


# Solvent-dependence (see Table S5)

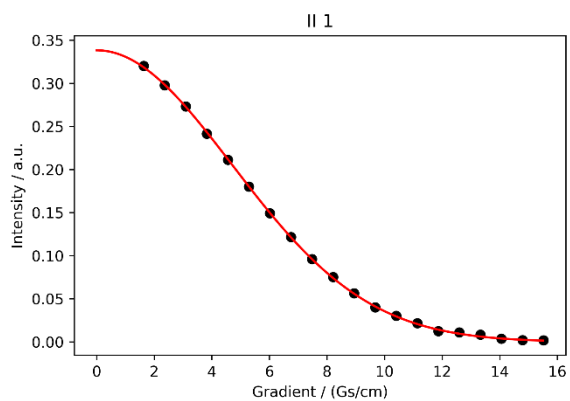
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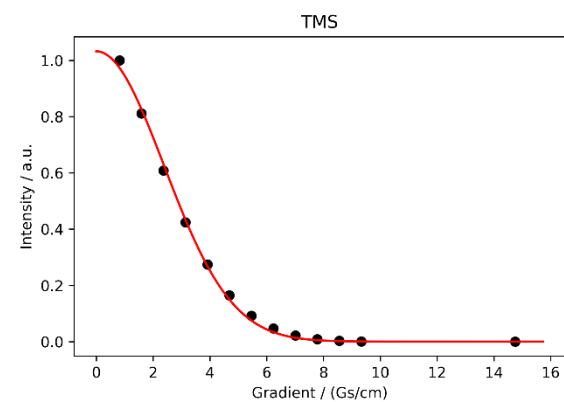
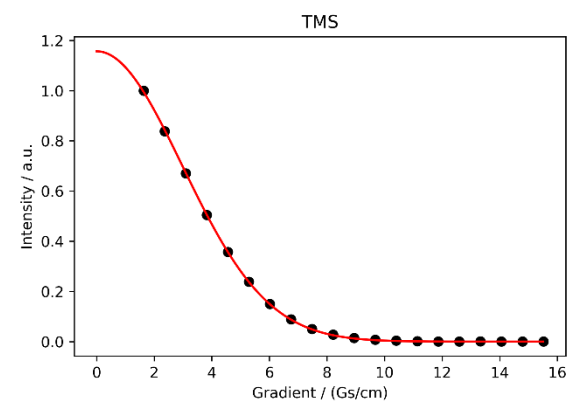
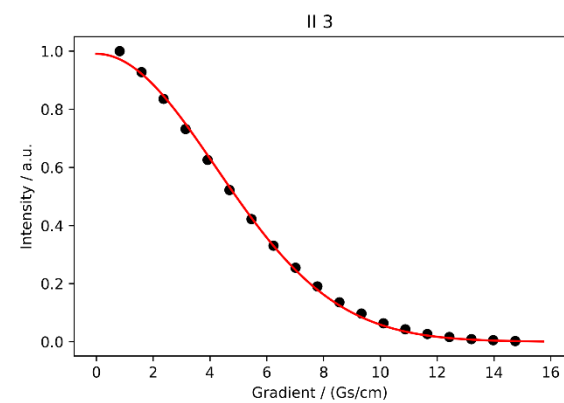
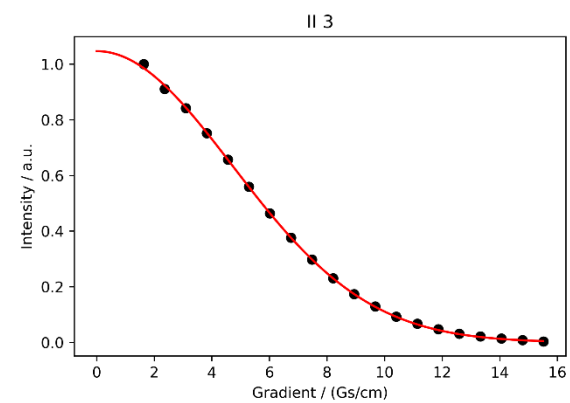
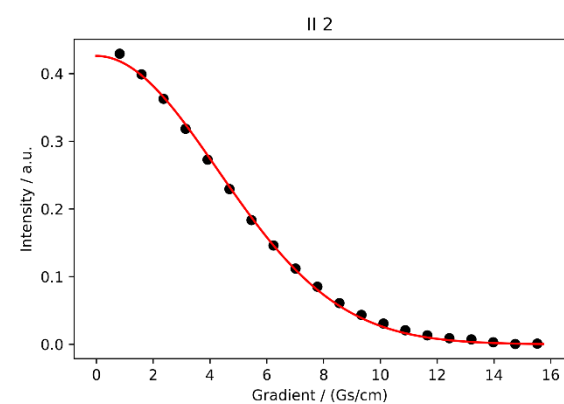
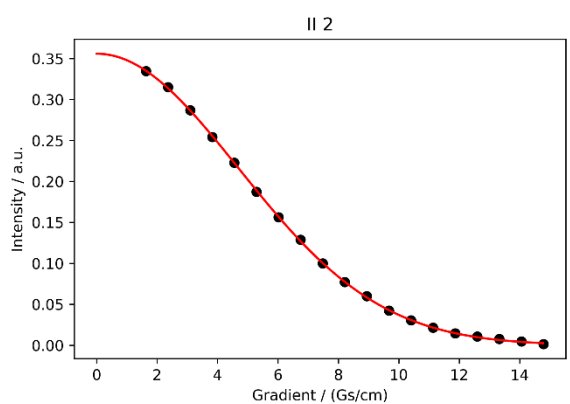
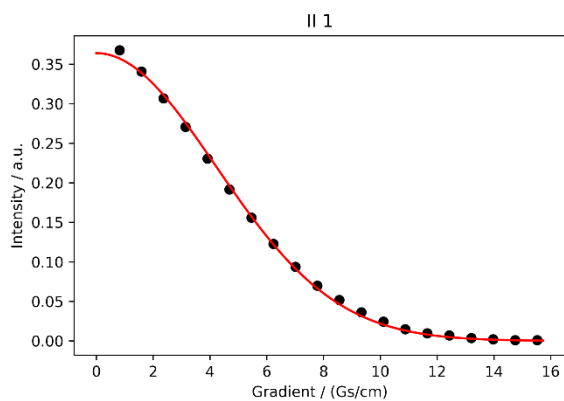
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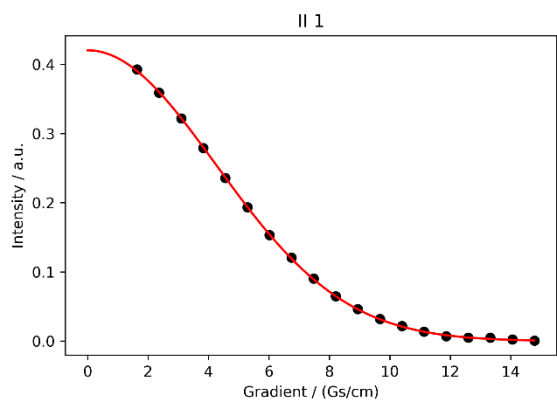
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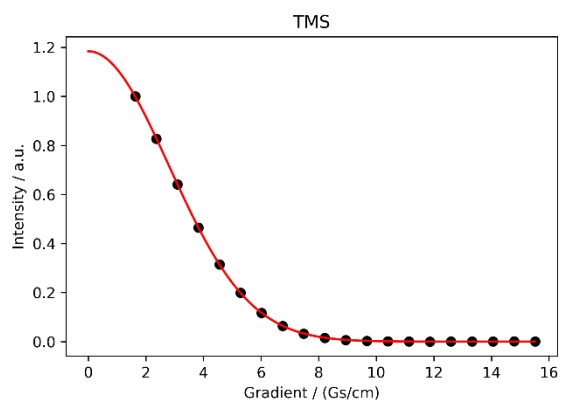
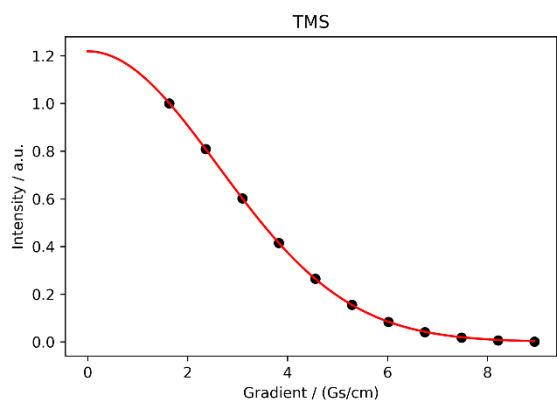
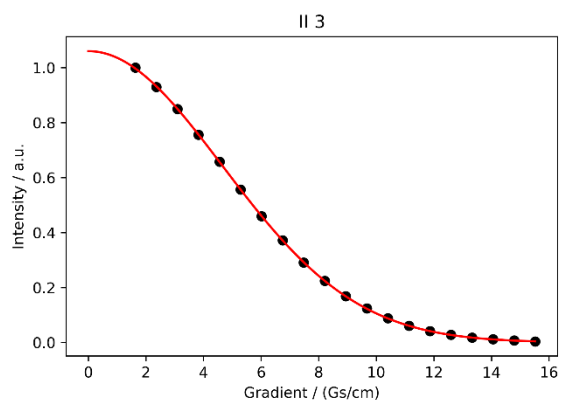
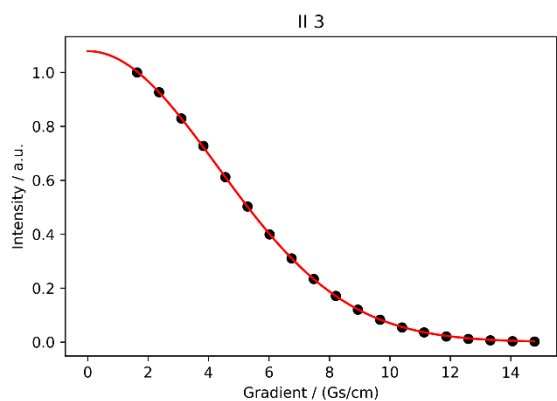
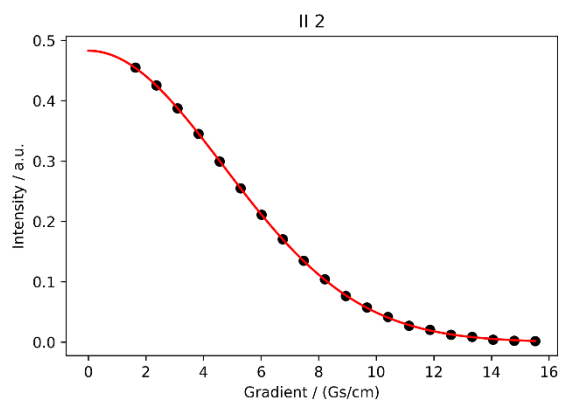
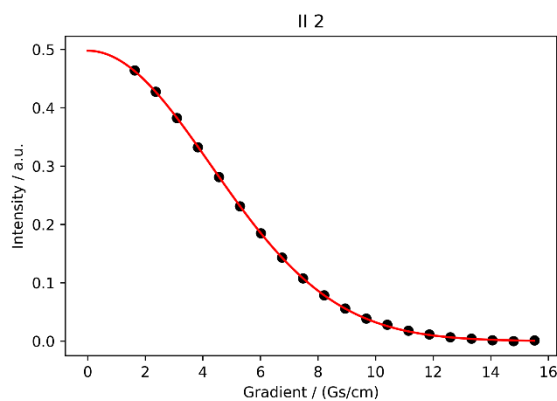
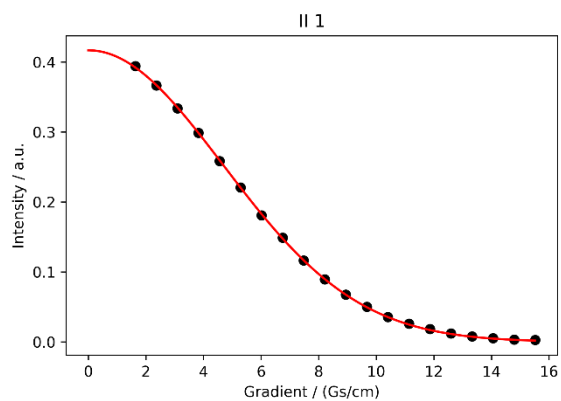
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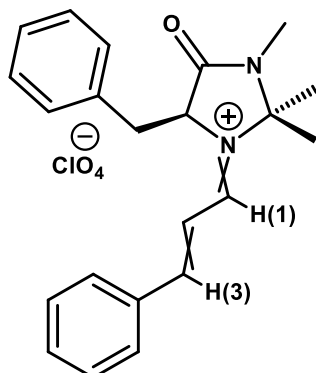


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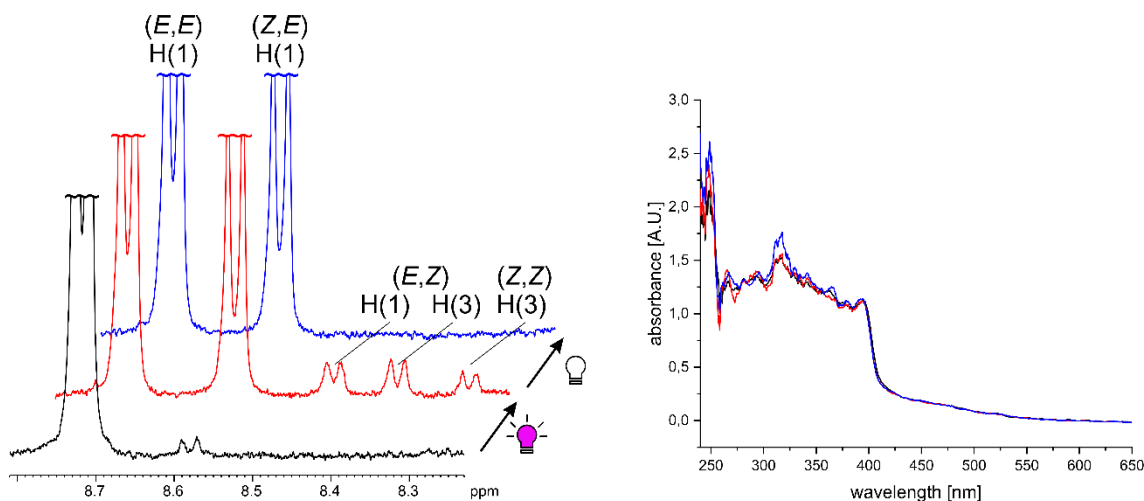


## 8. Combined *in situ* illumination-NMR-UV/Vis spectroscopy of **1** in CD<sub>3</sub>CN at -40 °C

We were wondering whether the amount of (*Z*)-configured isomers can be increased by a more selective photo illumination. However, for this adequately separated UV/Vis spectra of the different configuration isomers are essential, which we investigated using combined *in situ* illumination-NMR-UV/Vis spectroscopy. This method allows to simultaneously record UV/Vis and NMR spectra of photochemically generated species.<sup>2</sup> Thus, potential new UV/Vis bands can more easily be interpreted due to e.g. additional structural information obtained *via* NMR spectroscopy.



**Figure S44:** General depiction of iminium ion **1** with the two highlighted protons H(1), and H(3).



**Figure S45:** Photoinduced (*E*)  $\rightarrow$  (*Z*) and thermal (*Z*)  $\rightarrow$  (*E*) isomerization of iminium **1** in anh. and deg. CD<sub>3</sub>CN (7.5 mM) at -40 °C. Left: Stacked 1D-<sup>1</sup>H NMR spectra (section of the protons bound to the iminium ion carbon) in thermal equilibrium (black spectrum), during UV-illumination (red spectrum) and shortly after illumination is stopped (blue spectrum). Right: Associated UV/Vis-spectra.

In order to detect potential adequately separated UV/Vis signals of the low populated (*Z*)-configured isomers, a sample concentration was chosen which gives a saturated (*E,E*) absorption signal between ca. 275 and 425 nm. While a distinct population gain of (*Z,E*) and also adequate signals for (*E,Z*) and (*Z,Z*) can be observed in the NMR spectrum upon UV-illumination (Figure S45 left, red spectrum), no new absorption bands are detectable in the associated UV/Vis spectrum (Figure S45 right, red spectrum). This shows that all configuration isomers absorb within the same wavelength range. Therefore, a selective gain of one isomer by photo illumination seems not possible.



## 9. References

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