

Synthesis, Structure, Thermal Behavior and *cis/trans* Isomerization of 2,2'-(EMe₃)₂ (E = C, Si, Ge, Sn) Substituted Azobenzenes

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1. Reagents and Solvents

All reagents were used without purification unless stated otherwise.

Chemical	Supplier	Purity	Comments
1,3,5-Triisopropylbenzene	Sigma Aldrich	95%	stored in a glovebox
2-Iodoaniline	TCI	>98%	-
2,2'-Bipyridine	Sigma Aldrich	99%	stored in a glovebox
Bromotrimethyllead(IV)	Sigma Aldrich	97%	stored in a glovebox
<i>n</i> -Butyllithium	ACROS Organics		1.6 M in hexanes
CuCl	Alfa Aesar	>97%	stored in a glovebox
CuCN	Sigma Aldrich	98%	stored in a glovebox
Hexamethyldigermanium	Merck	techn.	stored in a glovebox
Hexamethyldisilane	ABCR	97%	stored in a glovebox
Hexamethylditin	ABCR	99%	stored in a glovebox
LiCl	Sigma Aldrich	99%	stored in a glovebox
MeI	Sigma Aldrich	99%	stored in a glovebox
MeLi	ACROS Organics		1.88 M in diethyl ether
Menthol	MERCK	99%	-
MnO ₂	MERCK	>80 %	activated
[Pd(PPh ₃) ₄]	TCI	>97%	stored in a glovebox
Trimethylsilyl chloride	Sigma Aldrich	99%	stored in a glovebox
Trimethylgermanium chloride	TCI	>98	stored in a glovebox
2- <i>tert</i> -Butylaniline	ACROS Organics	98%	-

All solvents for purification and extraction were used as received. In the case of *n*-pentane, the solvent was distilled prior use.

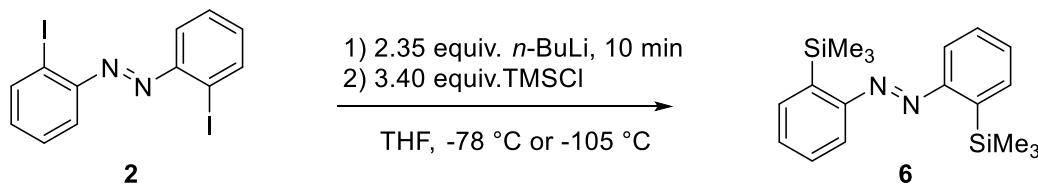
All solvents which were used for synthesis under inert conditions were dried by a solvent purification system from Inert Technologies.

Solvent	Supplier/ Drying Agent
Acetonitrile	Fisher Scientific, analytical grad / -
Chloroform- <i>d</i> ₁	Eurisotop, 99.8% / -
Dichlormethane	VWR, HPLC grade / SPS
Dimethylformamide	Acros / stored over molecular sieves
<i>n</i> -Pentane	VWR, techn. grade / SPS
Toluene	Fisher Scientific, HPLC grade / SPS
Tetrahydrofuran	VWR, HPLC grade / SPS

2. Syntheses

- a. Direct lithiation of 2,2'-diiodoazobenzene (**2**) with *n*-butyllithium and quenching with trimethylsilyl chloride (**9**)

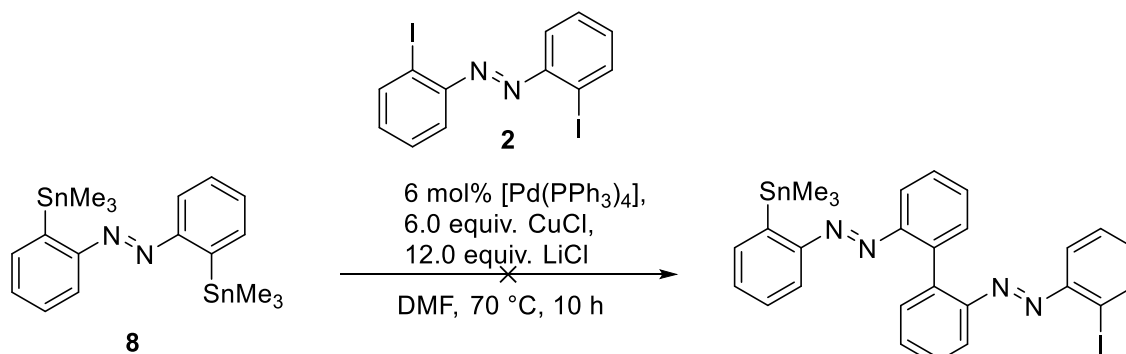
The method was adapted from Kano et al.[1] and used for 2,2'-Diiodo-4,4'-dimethylazobenzene.



Scheme SI1. Direct lithiation of the iodo-azobenzene **2** with *n*-butyllithium and further reaction with trimethylsilyl chloride (**9**).

In a 100 mL Schlenk flask, 2,2'-diiodoazobenzene (**2**) (1.02 g, 2.35 mmol) was dissolved in THF (30 mL) and the NMR standard 1,3,5-triisopropylbenzene (480 mg, 2.35 mmol) was added. After cooling the reaction mixture to the given temperature *n*-BuLi (3.1 mL, 5.00 mmol, 1.6 M in hexane) was added in one portion resulting in a dark color. Then, trimethylsilyl chloride (**9**) (1.02 mL, 8.00 mmol) was added rapidly. The reaction mixture was warmed to 25 °C over a period of 12 h. After evaporation of all volatiles the yield was found to be 95% for the reaction at -78 °C and 99% for the reaction performed at -105 °C by ¹H NMR spectroscopy.

- b. Reaction of the nucleophilic azobenzene **8** with the electrophilic azobenzene **2** under cross coupling conditions

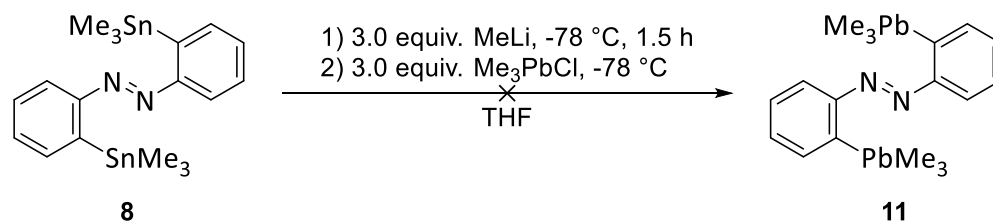


Scheme SI2. The reaction of the stannylated azobenzene **8** with azobenzene **2** under the previously used coupling conditions did not lead to any conversion.

In a glovebox, a pressure tube (total volume = 15.0 mL) was filled with **8** (75 mg, 0.15 mmol), **2** (65.1 mg, 150 μmol) [Pd(PPh₃)₄] (6.80 mg, 59.0 μmol), LiCl (75.0 mg, 1.77 mmol), CuCl (88.1 mg, 890 μmol) and DMF (6.00 mL). The vial was capped and heated for 10 h at 70 °C. The solution was cooled to 25 °C, chloroform (30 mL) was added and the mixture was extracted with hydrochloric acid (2 M, 2 x 55 mL), a saturated sodium carbonate solution (55 mL) and water (55 mL). The combined organic phases were dried over sodium sulfate, filtered, and the solvent was evaporated. A ¹H NMR experiment revealed that no reaction had occurred.

[1] Yamamura, M.; Kano, N.; Kawashima, T.; Matsumoto, T.; Harada, J.; Ogawa, K., Crucial Role of N...Si Interactions in the Solid-State Coloration of Disilylazobenzenes. *J. Org. Chem.* **2008**, 73, (21), 8244-8249, doi:10.1021/jo801334a.

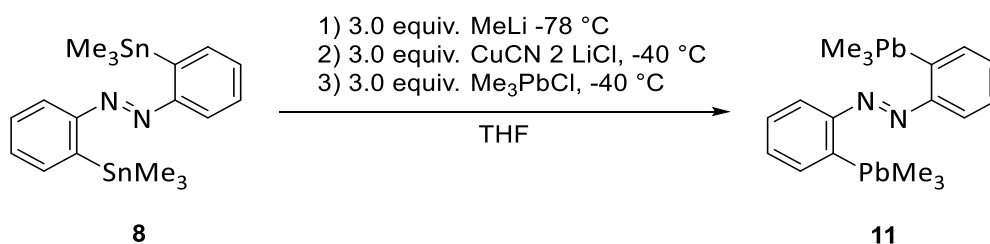
c. Attempted synthesis of 2,2'-bis(trimethyllead)azobenzene (**11**)



Scheme SI3. Attempt to synthesize plumbinated azobenzene **11** via a tin-lithium exchange followed by quenching with a lead electrophile.

Via tin-lithium-exchange

In a J. Young's tube, **8** (100 mg, 200 μmol) was dissolved in THF (10 mL) and cooled to -78 °C. Then MeLi (0.36 mL, 0.60 mmol, 1.66 M in Et₂O) was added over the course of 5 min. The reaction mixture turned black. After 60 min at this temperature, Me₃PbBr (200 mg, 1.26 mmol, dissolved in 2 mL of THF) was added in one portion. After 10 min at this temperature, the color changed to brown. The reaction mixture was warmed to 23 °C for 14 h, stirred for 2 d, to result in an orange color with a dark precipitate in the flask. Afterwards the solvent was removed; ¹H NMR analysis revealed an undefined mixture of products. The crude product was subjected to column chromatography (silica, pentane) but this purification attempt did not give any product.



Scheme SI4. Attempt to synthesize plumbinated azobenzene **11** via a tin-lithium exchange reaction followed by transmetalation to copper, followed by quenching with a lead electrophile.

Via tin-lithium-copper transmetalation

In a glovebox, CuCN (215 mg, 2.40 mmol) and LiCl (203 mg, 4.80 mmol) were dissolved in THF (5.0 mL) to obtain a CuCN 2 LiCl solution.

In a J. Young's tube, **8** (406 mg, 800 μmol) was dissolved in THF (20 mL) and cooled to -78 °C. Then MeLi (1.45 mL, 2.40 mmol, 1.66 M in Et₂O) was added over the course of 5 min. The reaction mixture turned black. After 90 min at this temperature the CuCN 2 LiCl –solution (see above) was added at -40 °C. After 1 h, Me₃PbBr (800 mg, 2.40 mmol, dissolved in 5 mL of THF) was added in one portion. The reaction mixture was warmed to 23 °C overnight (9 h). To the black mixture, an aqueous saturated NH₄Cl solution (0.2 mL) was added and the mixture turned orange. The reaction vessel was internally coated with a black precipitate, which was insoluble in organic solvents. The reaction mixture was dried over MgSO₄, filtered, and all volatiles were removed i. vac.. ¹H NMR analysis of the crude mixture revealed a complex mixture of products, which could not be identified. After filtration over a short plug

of silica with pentane as eluent a yellow oil (25 mg) could be obtained. Further analysis revealed that no aliphatic proton signals remained.

3. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR Spectra
2,2'-Diiodoazobenzene (2**)**

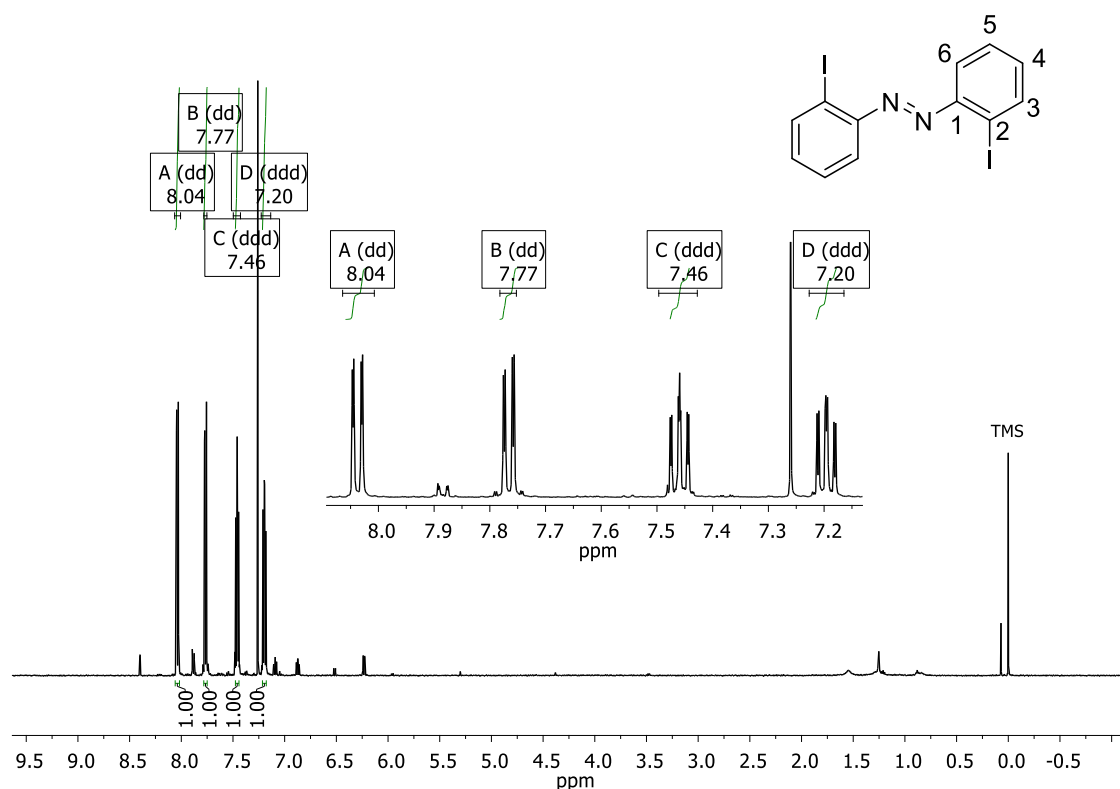


Figure SI1: ^1H NMR spectrum of compound **2**. The less intense signals in the aromatic region can be assigned to the *cis*-isomer.

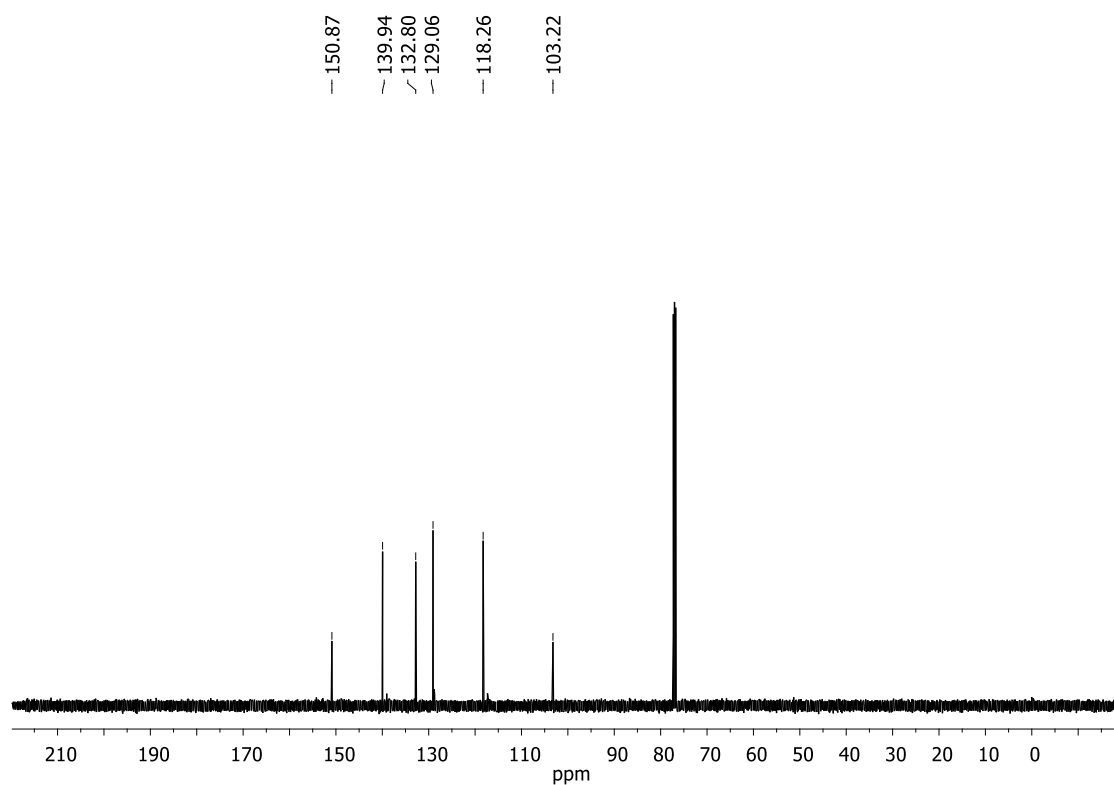


Figure SI2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **2**.

2,2'-Di(*tert*-butyl)azobenzene (**10**)

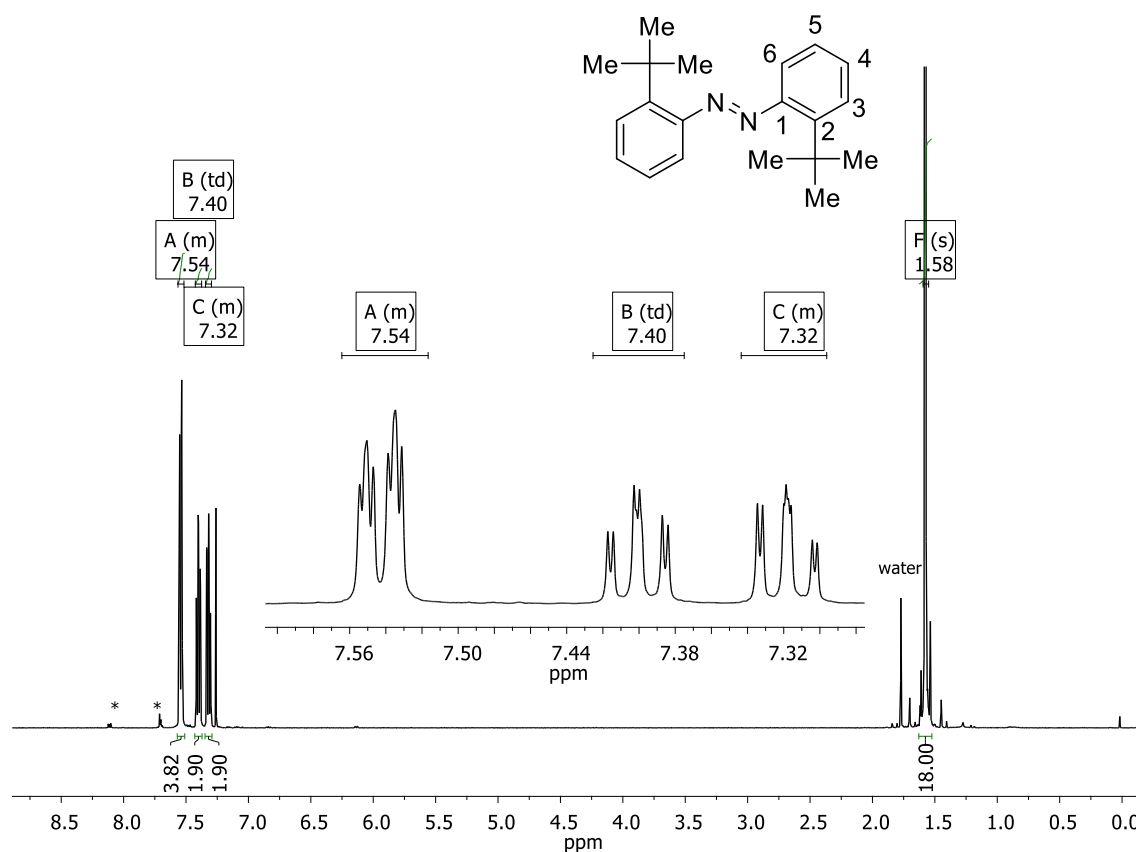


Figure S13: ¹H NMR spectrum of compound **10**. The less intense signals in the aromatic region can be assigned to the *cis*-isomer and traces of compound **16** (indicated with a star).

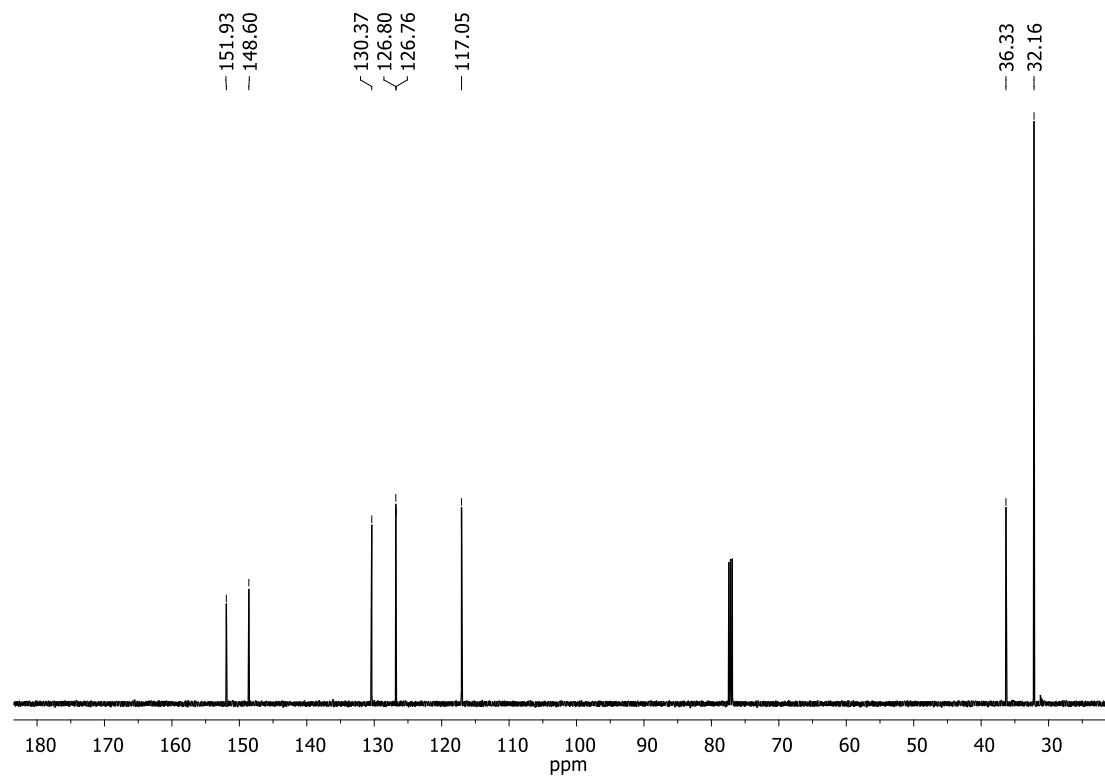


Figure S14: ¹³C{¹H} NMR spectrum of compound **10**.

1,6-Di(*tert*-butyl)phenazine (**16**)

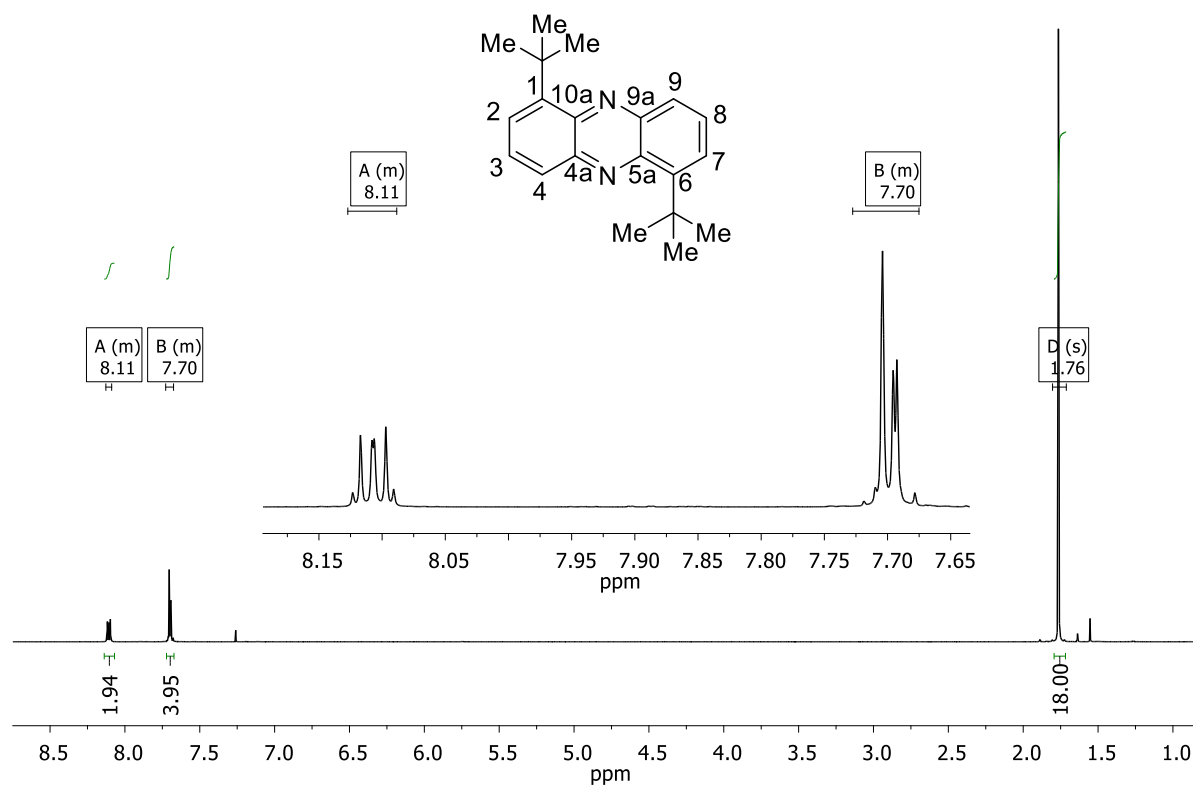


Figure S15: ^1H NMR spectrum of compound **16**.

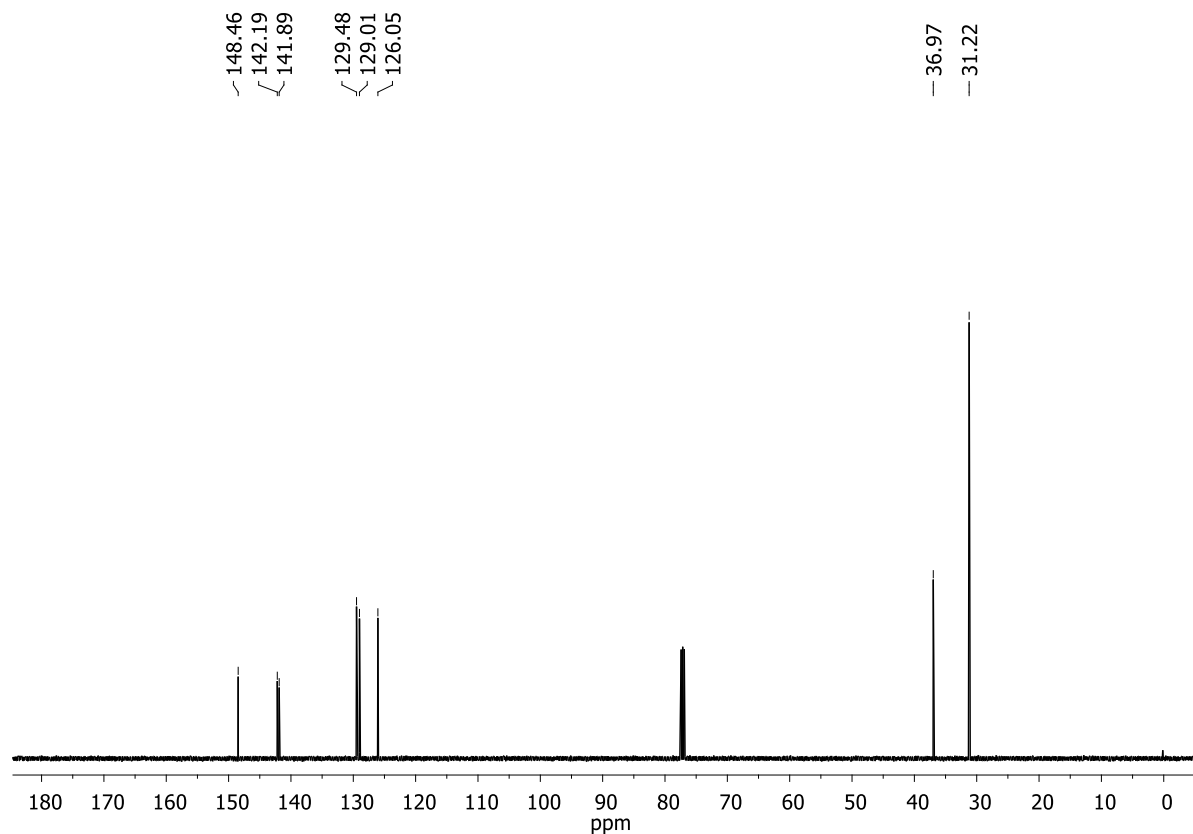


Figure S16: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **16**.

2,2'-bis(Trimethylsilyl)azobenzene (**6**)

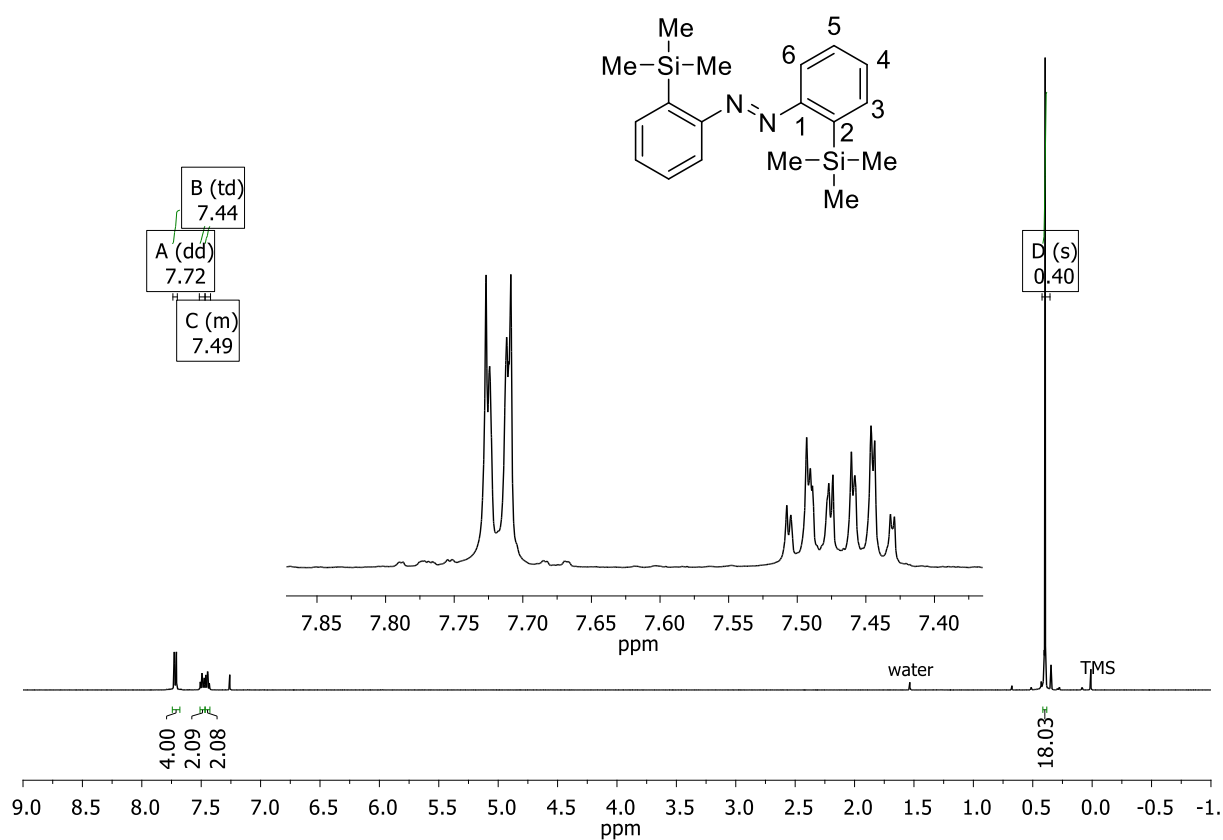


Figure S17: ^1H NMR spectrum of compound **6**.

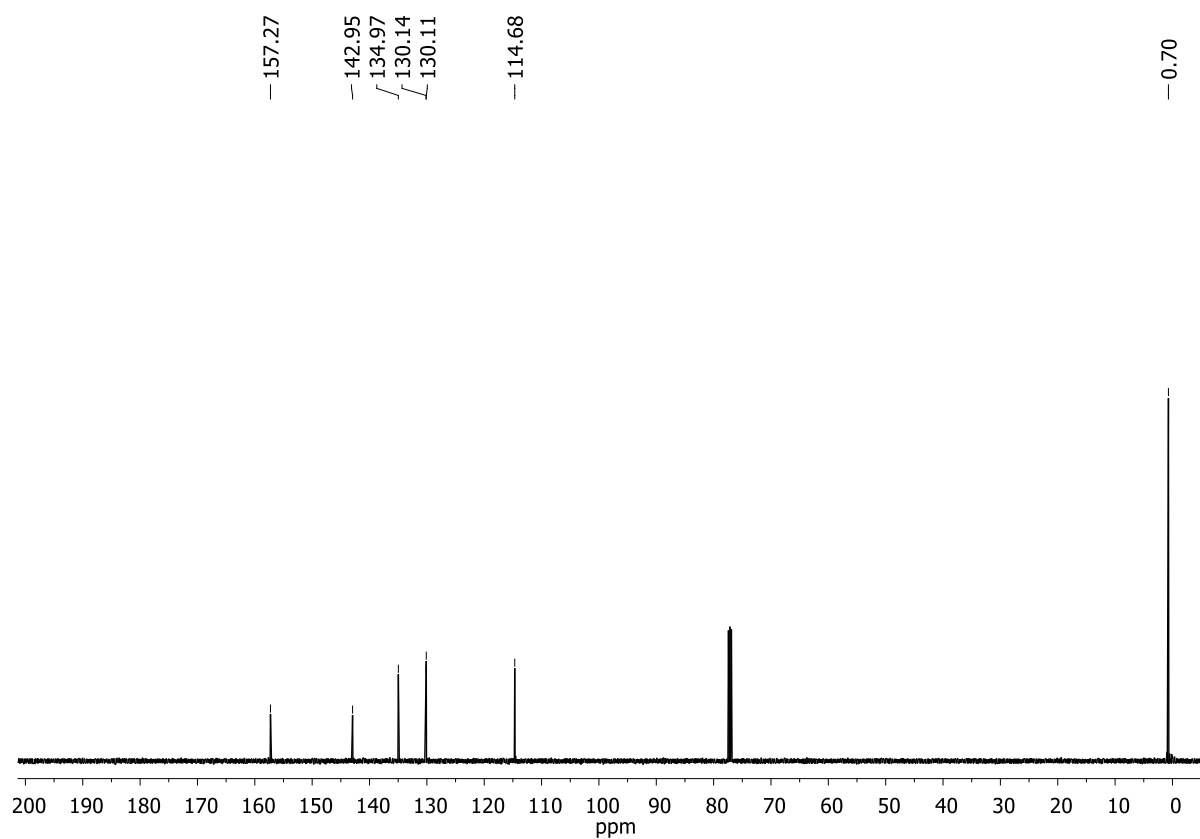


Figure S18: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **6**.

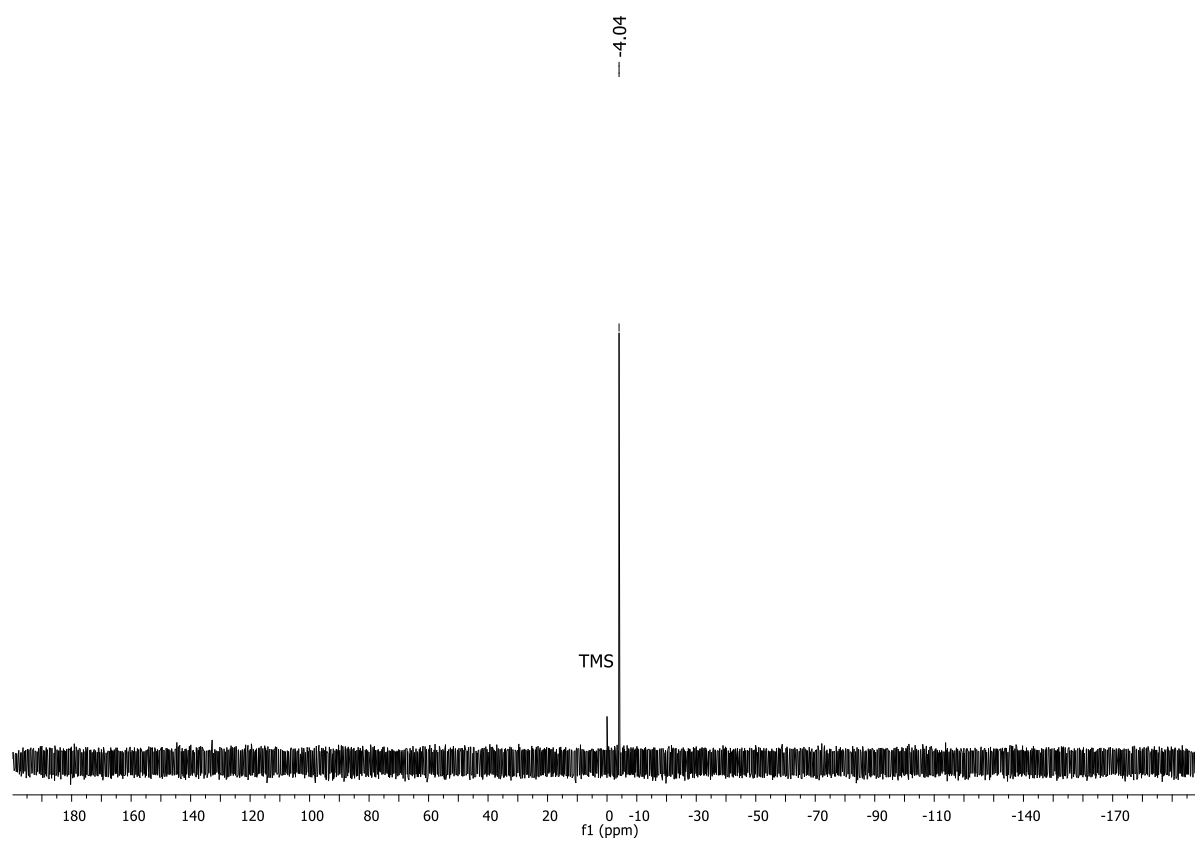


Figure S19: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound **6**.

2,2'-bis(Trimethylgermyl)azobenzene (**7**)

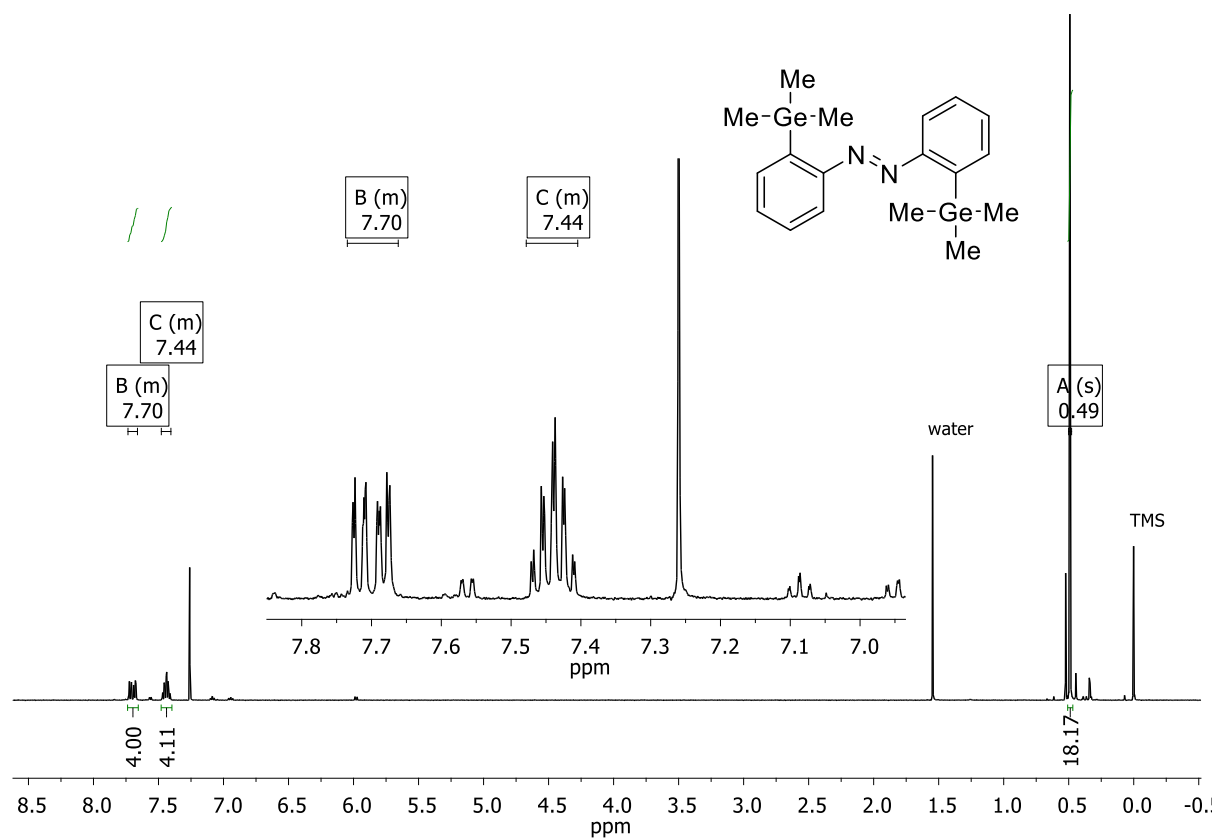


Figure S110: ¹H NMR spectrum of compound **7**. The less intense signals in the aromatic region can be assigned to the *cis*-isomer.

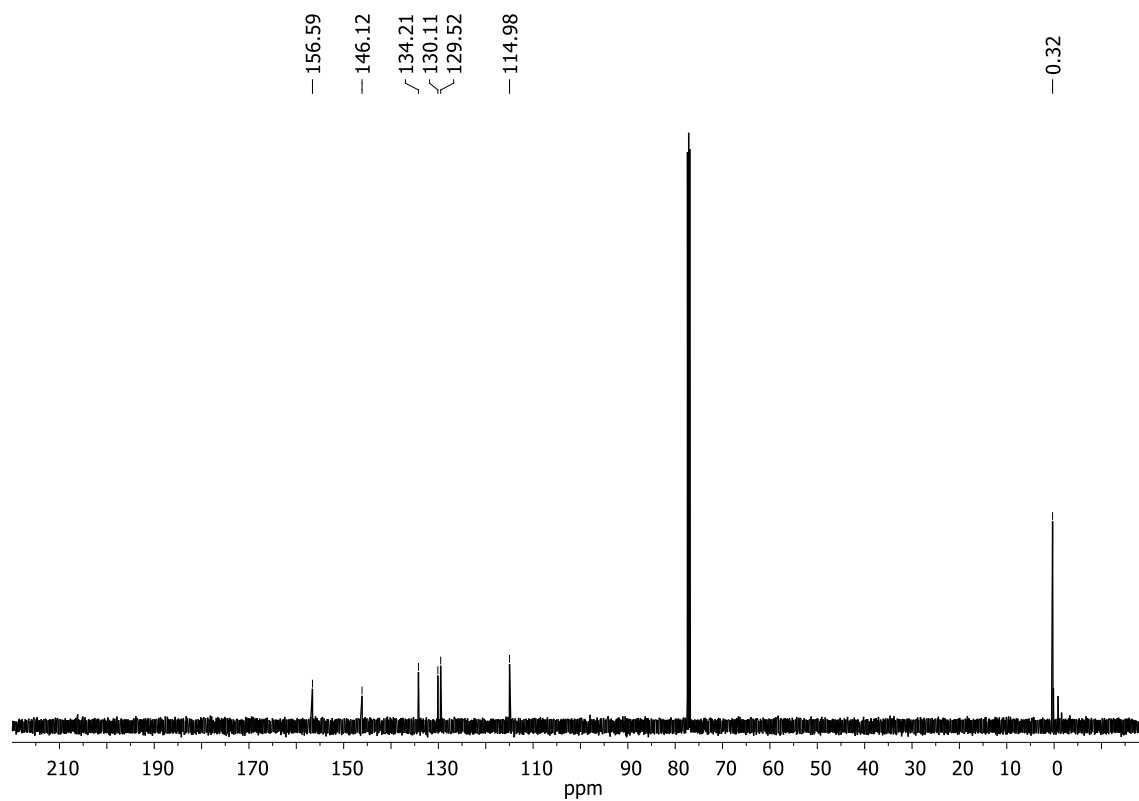


Figure S111: ¹³C{¹H} NMR spectrum of compound **7**.

2,2'-bis(Trimethylstanny)azobenzene (**8**)

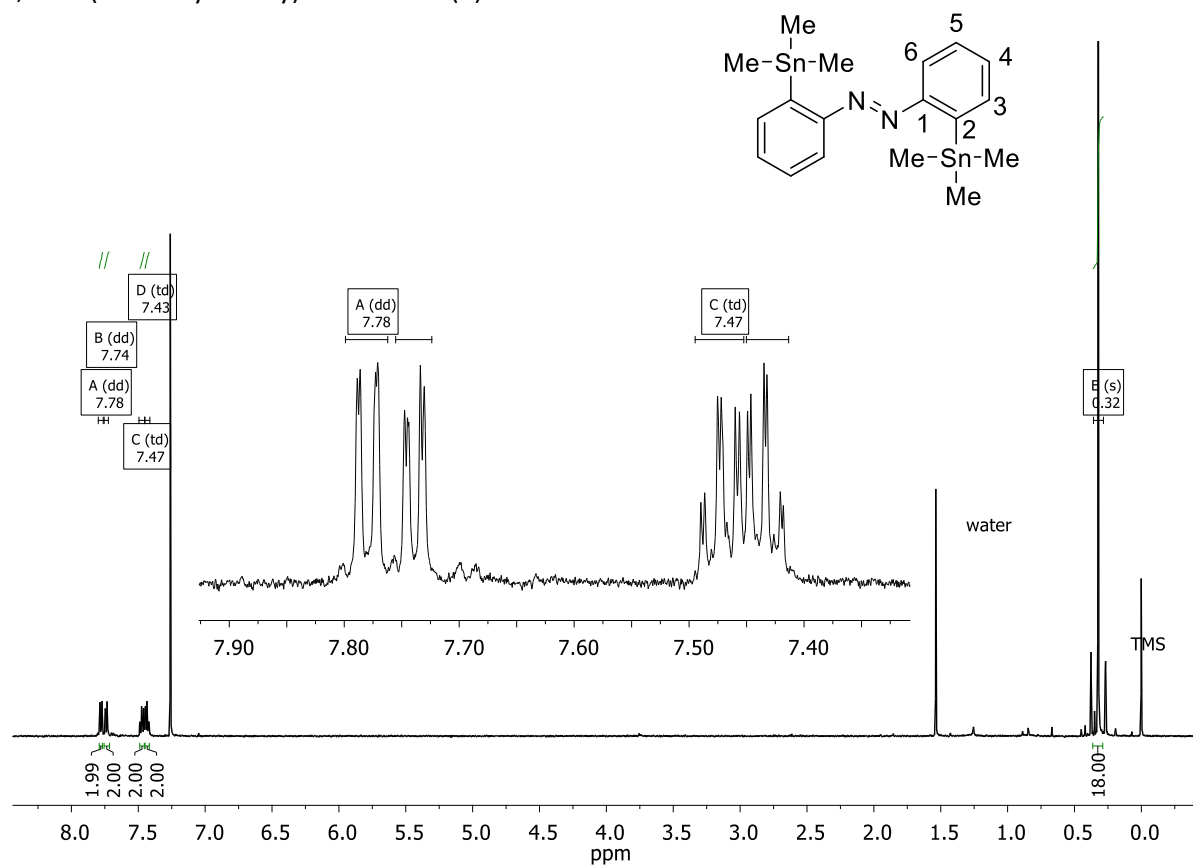


Figure SI12: ^1H NMR spectrum of compound **8**.

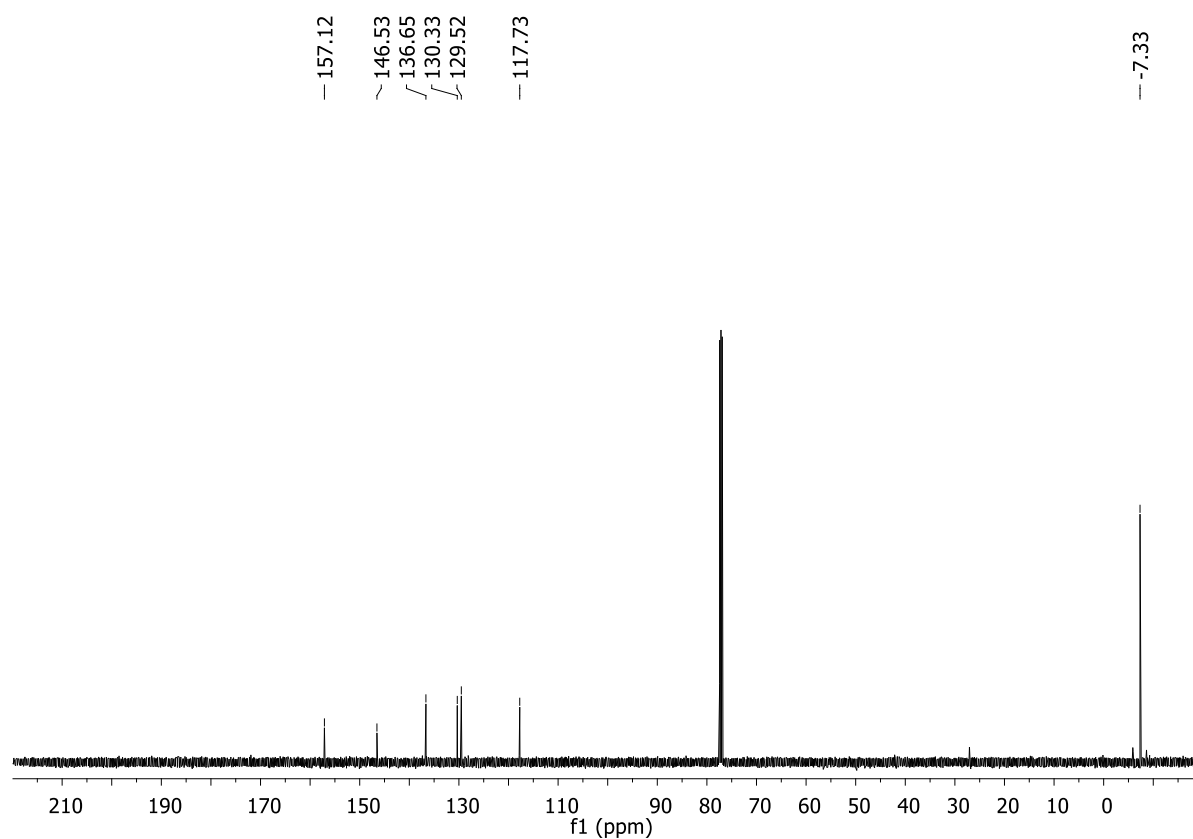


Figure SI13: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **8**.

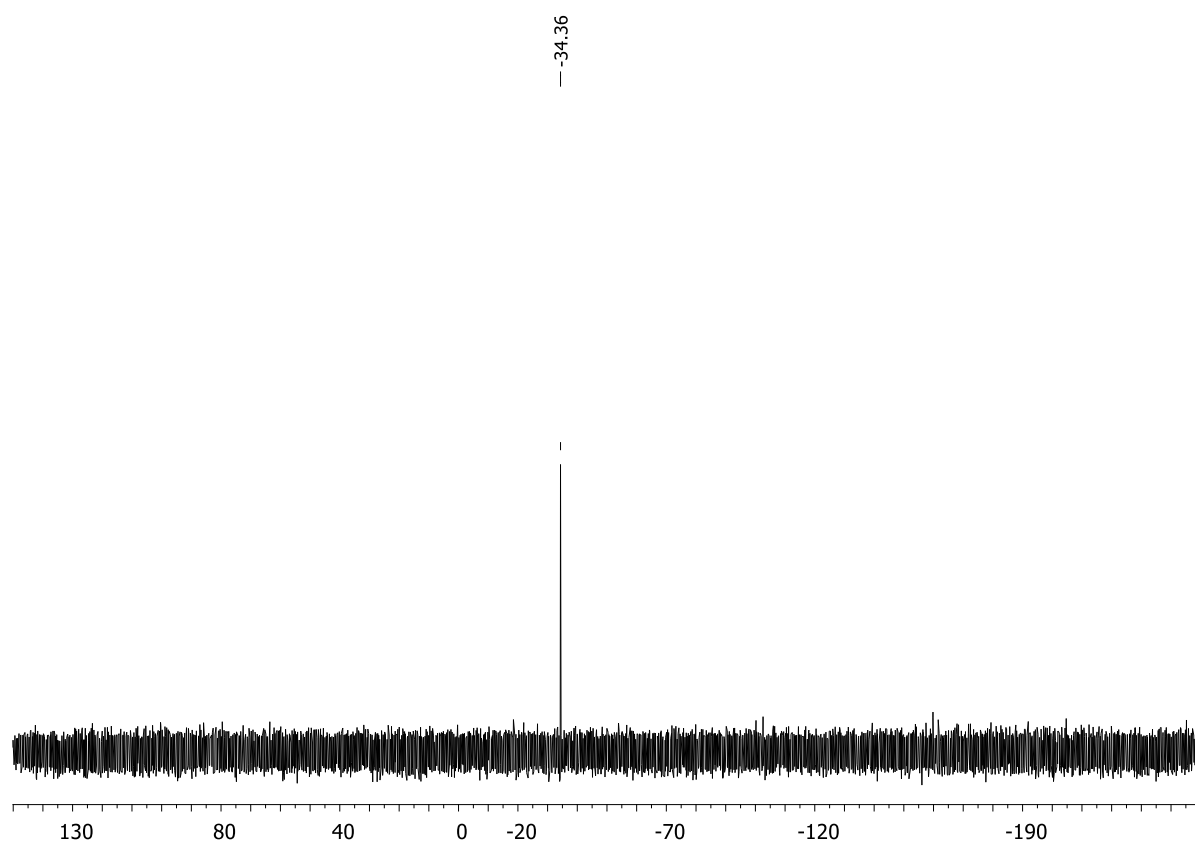


Figure S114: $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of compound **8**.

4. UV/Vis Spectra and ^1H NMR Spectra of the Switching Experiments

The solutions for the UV-vis spectra were prepared using a stock solution with the appropriate amount of compound in cyclohexane and diluting it to obtain different concentrations.

For the switching experiments we used the maximum of the $\pi\pi^*$ -band and not a absorption value at a fixed wavelength, since the position of the absorption maximum shifted slightly during the switching process.

2,2'-Di(*tert*-butyl)azobenzene (**10**)

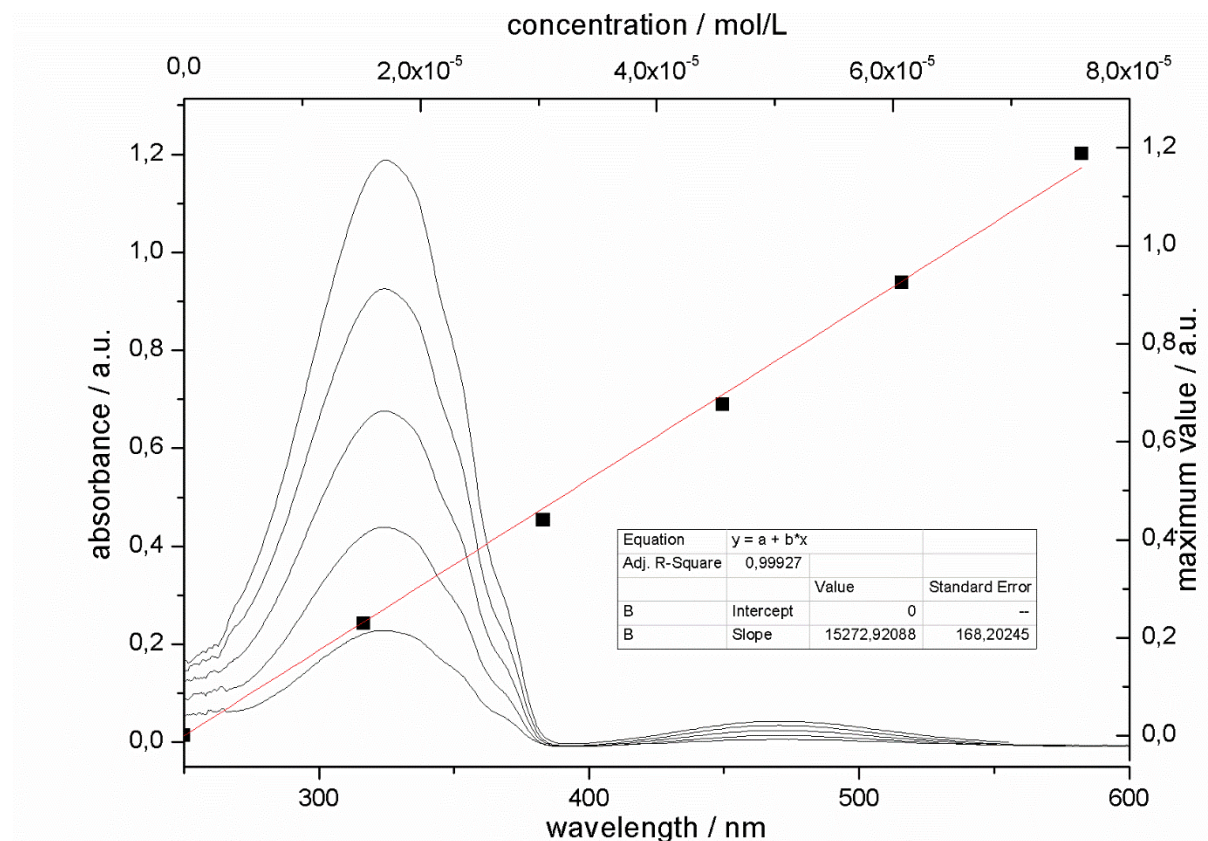


Figure S115: Absorption spectra of compound **10** and linear fitting to according to Lambert-Beer's-law.

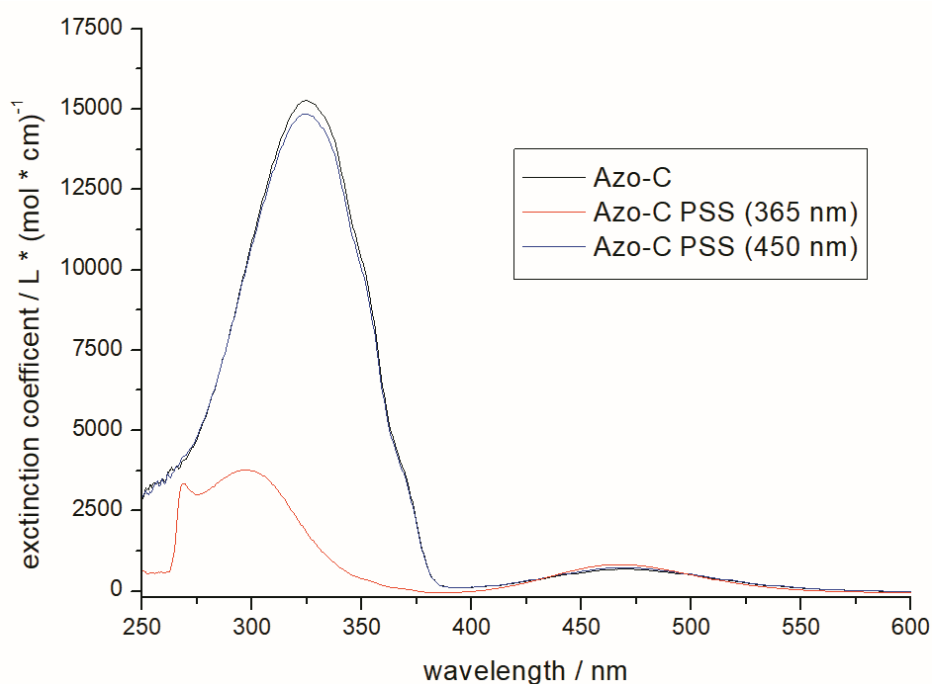


Figure SI16: Comparison of the absorption spectra of compound **10** dissolved as synthesized (black), after 3 min of irradiation with 365 nm light (red) and after 15 min of irradiation with 450 nm light (blue). The concentration was 4.56×10^{-5} M in cyclohexane.

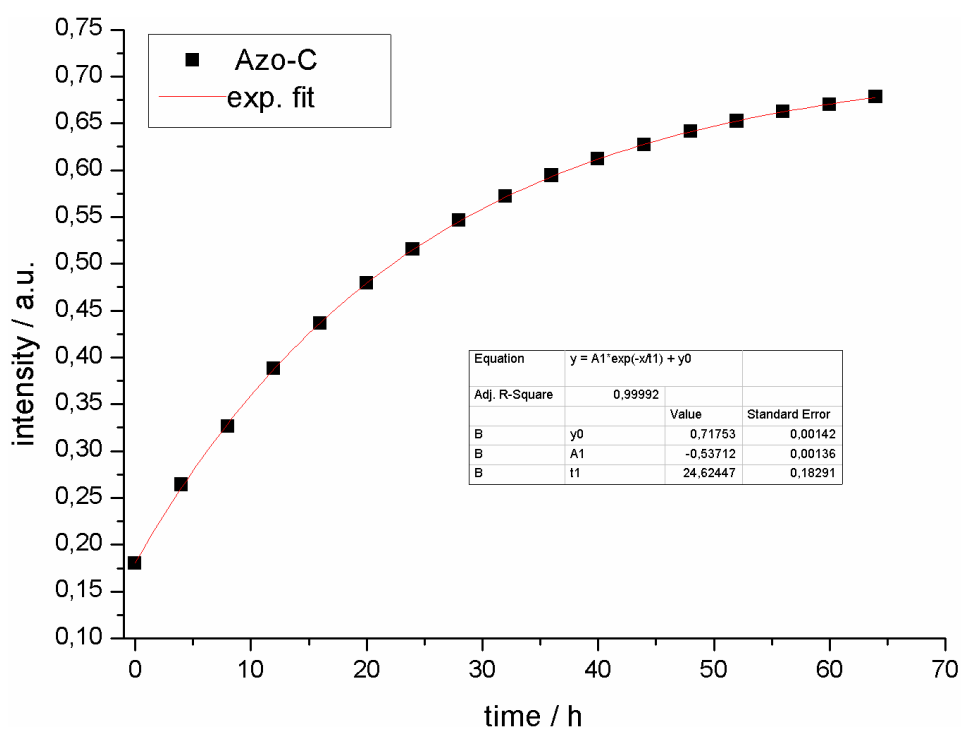


Figure SI17: Absorption value of the $\pi\pi^*$ band from compound **10** plotted against the time after irradiation at 365 nm for 3 mins. The concentration was 4.56×10^{-5} M in cyclohexane.

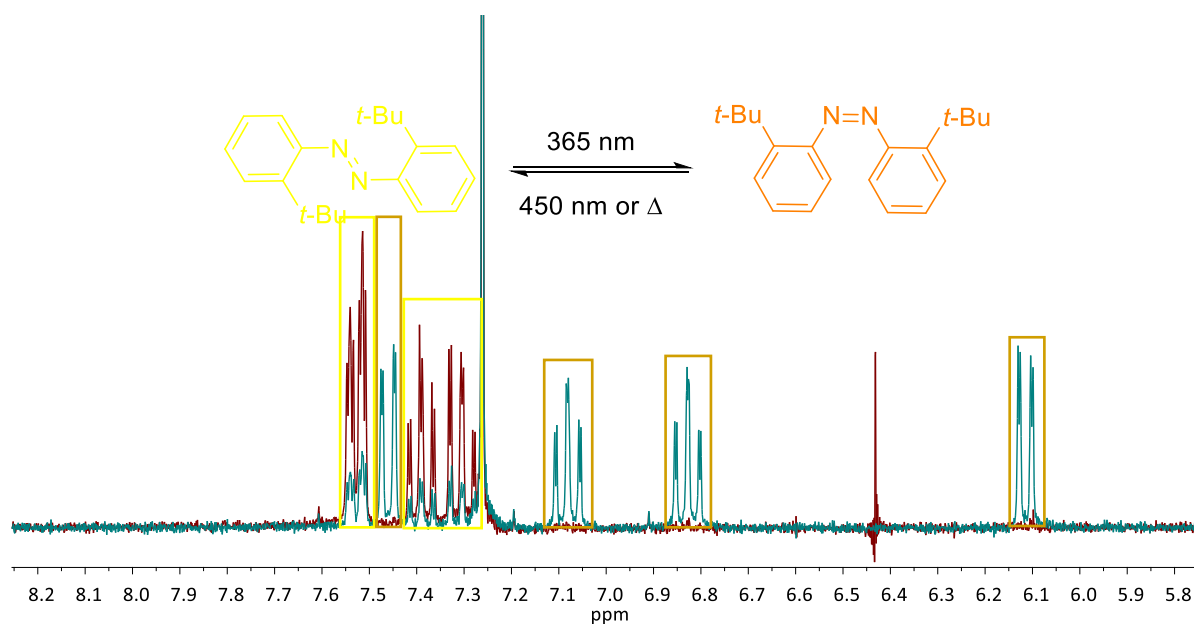


Figure SI18: ^1H NMR (300 MHz) spectra of compound **10** before (red) and after irradiation (blue) with 365 nm (15 min) in CDCl_3 . The concentration was 4.84×10^{-3} M.

^1H NMR spectroscopic monitoring of the switching of compound **10**:

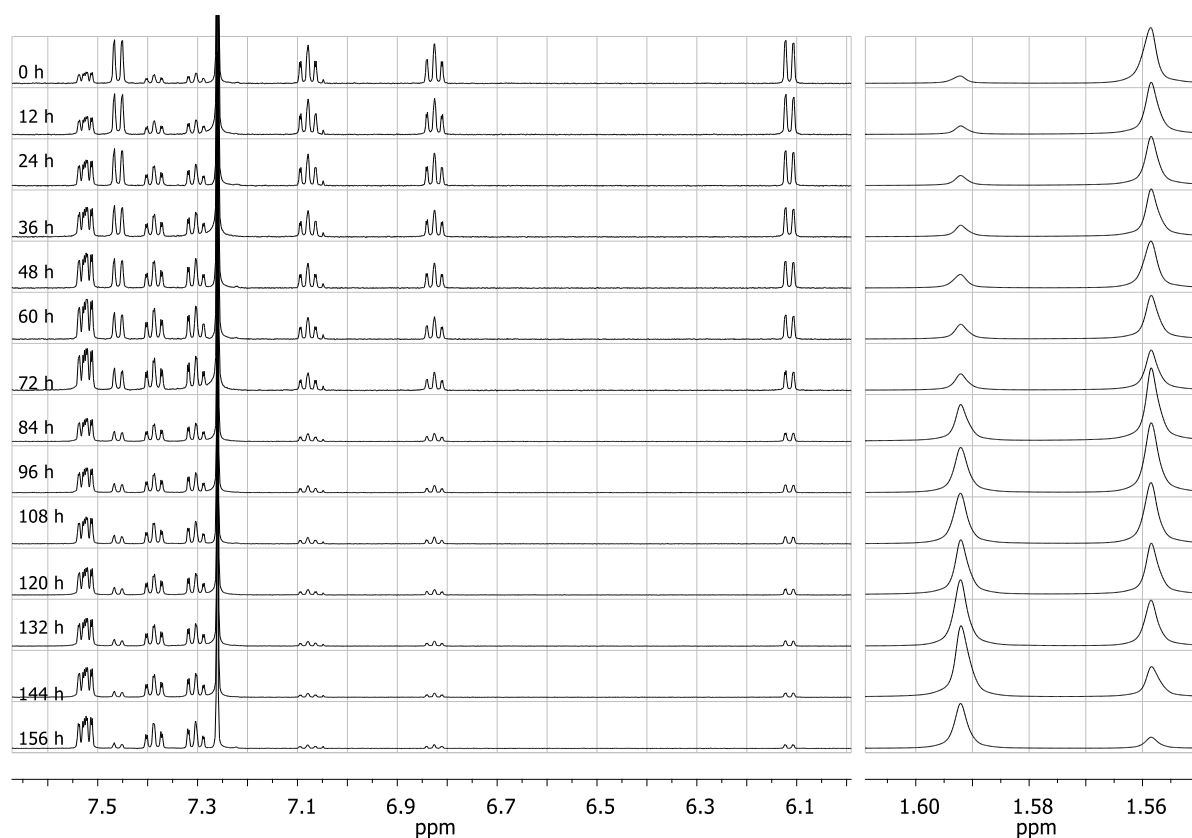


Figure SI19: ^1H NMR (500 MHz) spectra of **10** in CDCl_3 measured every 12 h after irradiation at 365 nm for 15 mins.

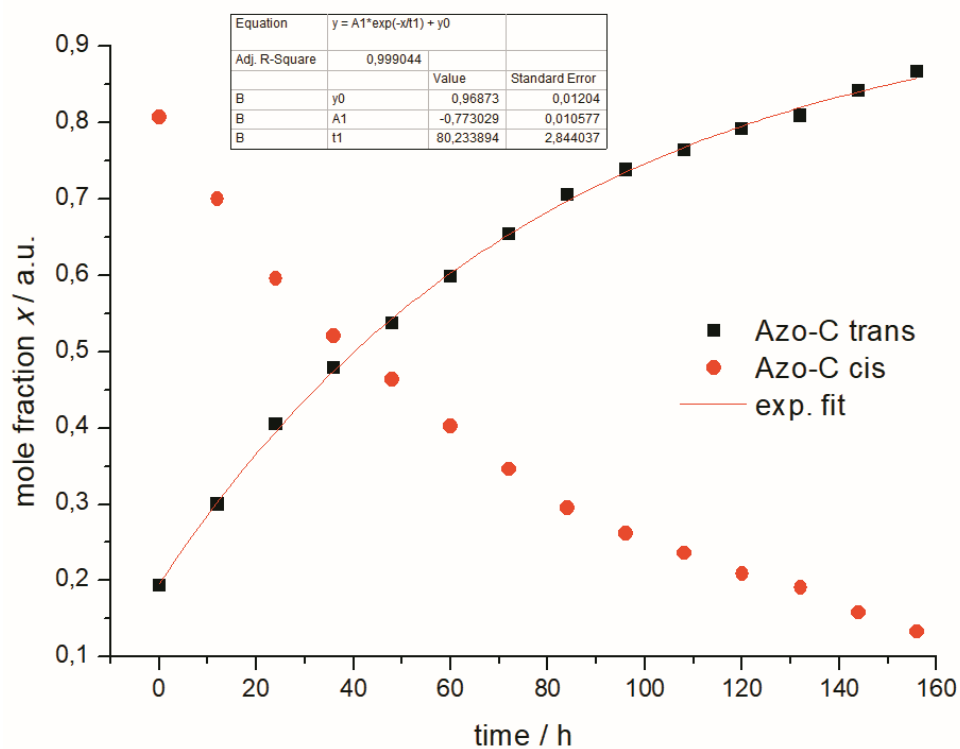


Figure S120: Mole fraction of *cis* and *trans*-azobenzene **10** vs. time gives the thermal relaxation at 300 K.

2,2'-bis(Trimethylsilyl)azobenzene (**6**)

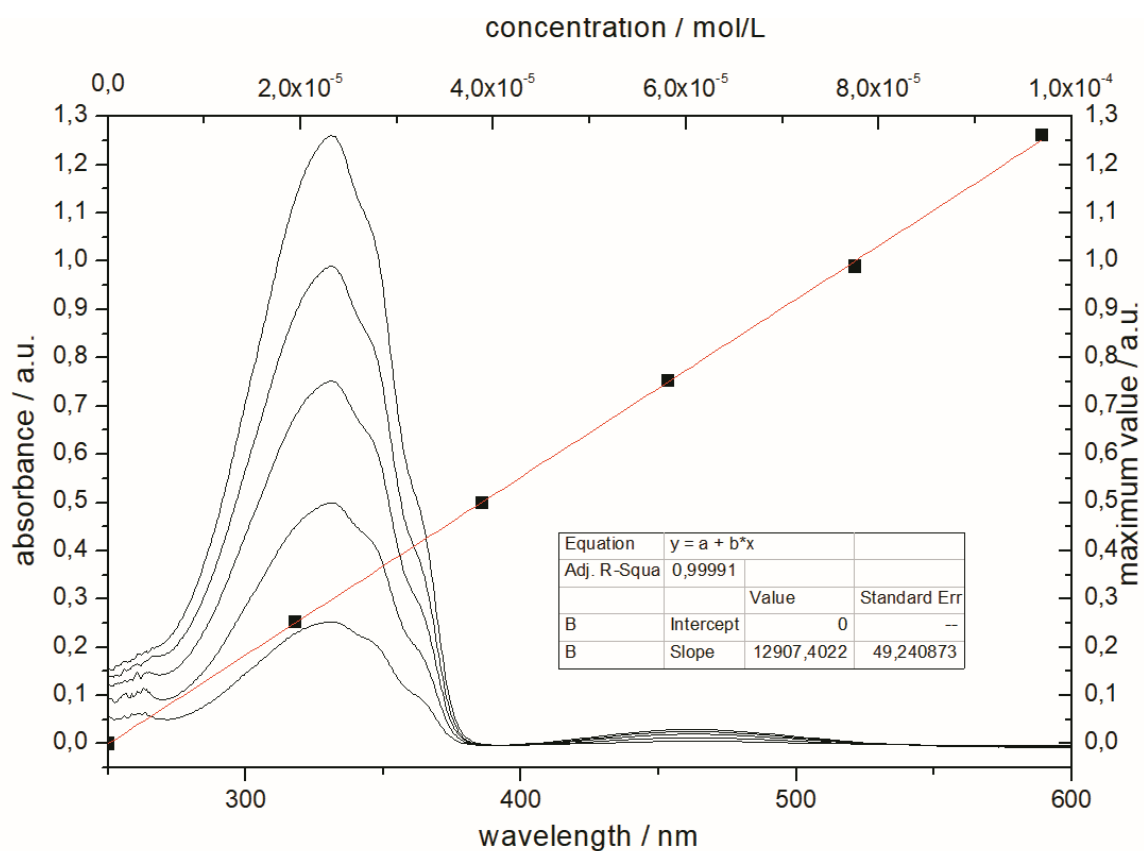


Figure S121: Absorption spectra of compound **6** and linear fitting to according to Lambert-Beer's-law.

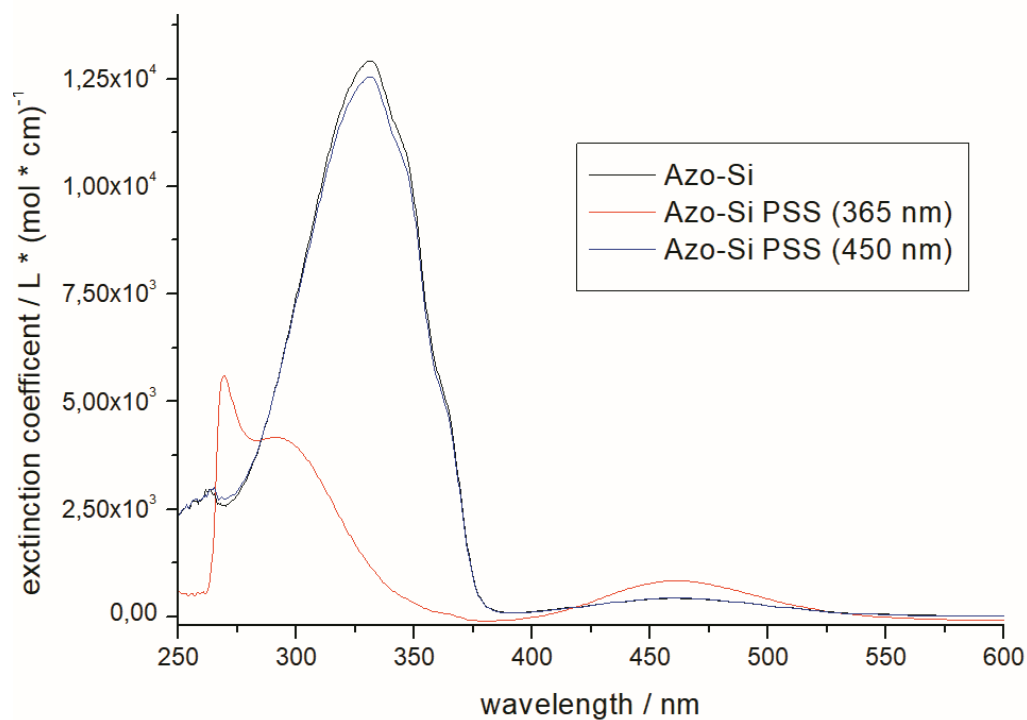


Figure SI 22: Comparison of the absorption spectra of compound **6** as dissolved (black), after 3 min irradiation with 365 nm light (red) and after 15 min irradiation with 450 nm light (blue). The concentration was 9.70×10^{-5} M in cyclohexane.

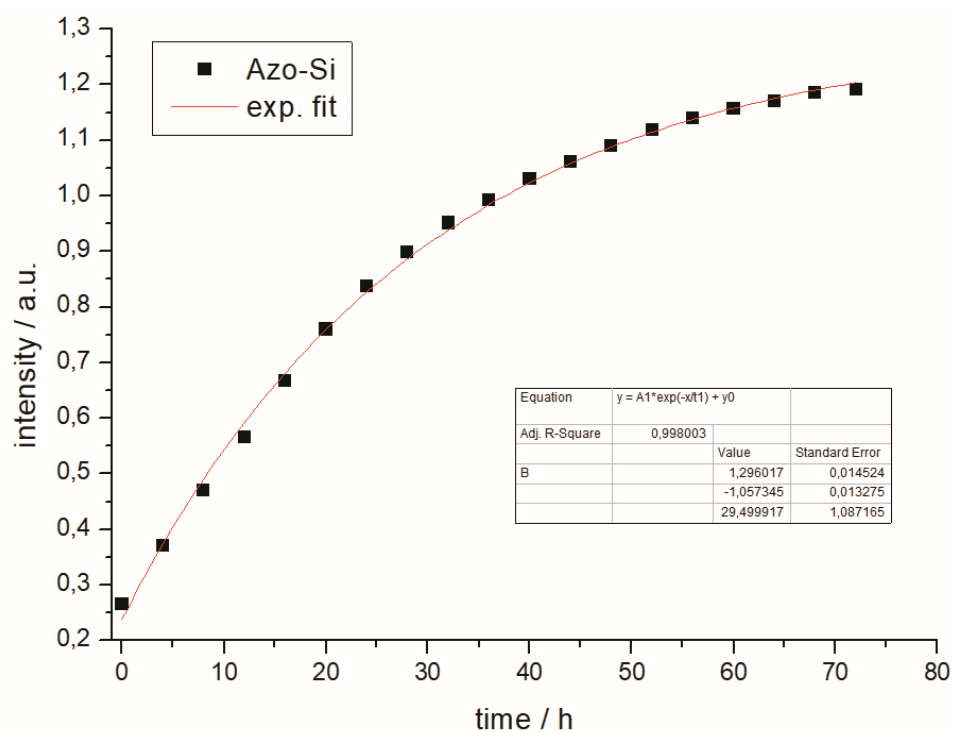


Figure SI23: Absorption value of the $\pi\pi^*$ band from compound **6** plotted against the time after irradiation at 365 nm for 3 mins. The concentration was 9.70×10^{-5} M in cyclohexane.

^1H NMR spectroscopic monitoring of the switching of **6**:

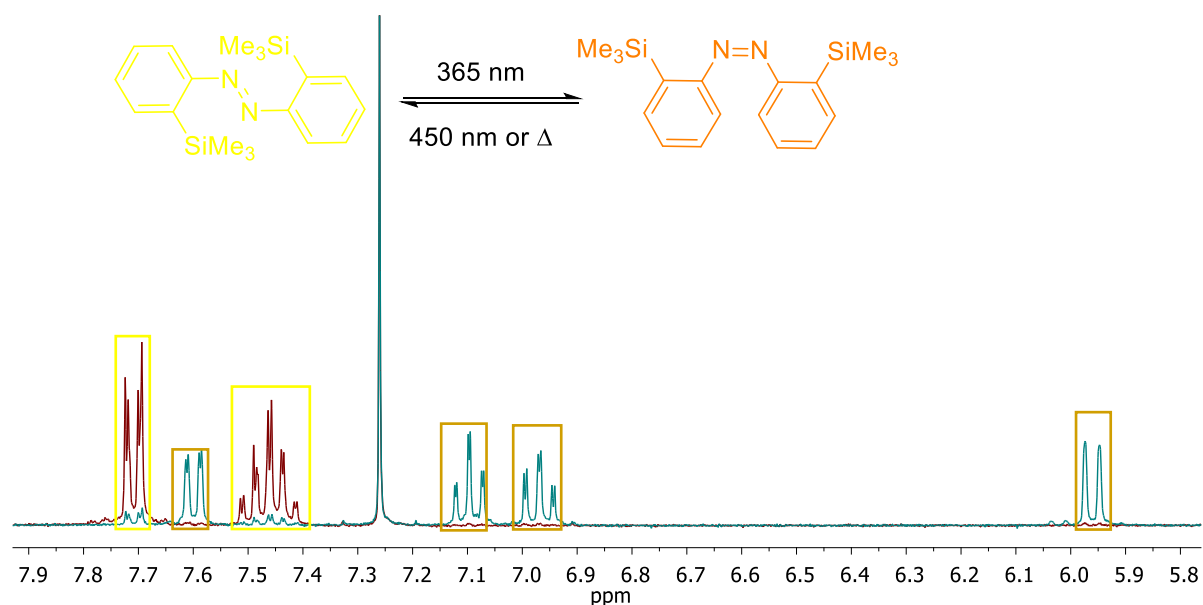


Figure S124: ^1H NMR (300 MHz) spectra of compound **6** before (red) and after (blue) irradiation with 365 nm (15 min) in CDCl_3 . The concentration was 1.07×10^{-2} M.

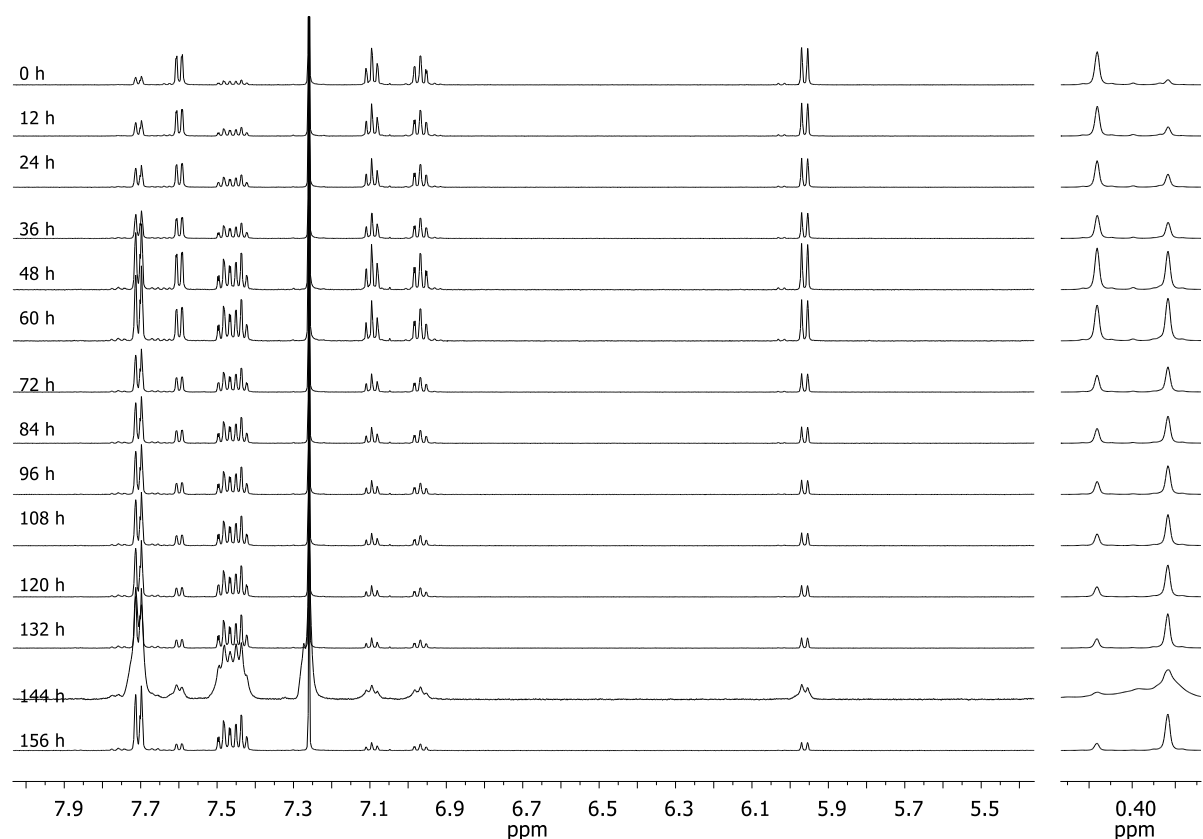


Figure S125: ^1H NMR (500 MHz) spectra of **6** in CDCl_3 measured every 12 h after irradiation at 365 nm for 15 min. The second to last NMR spectrum failed to shim but integrals could be determined.

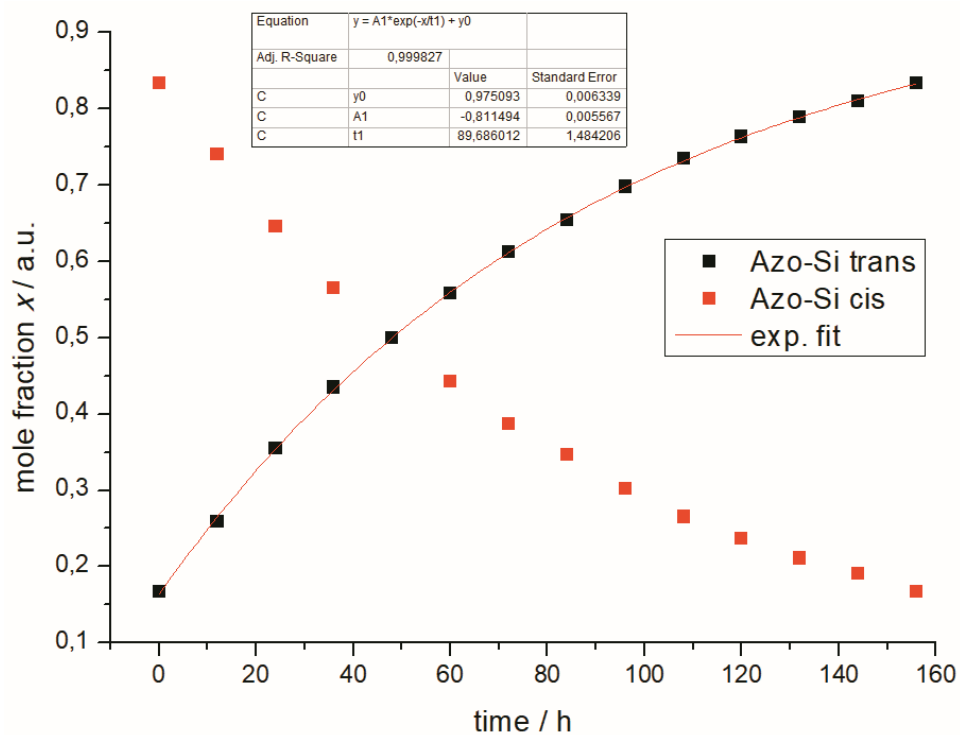


Figure S126: Mole fraction of cis and trans-azobenzene **6** vs. time gives the thermal relaxation at 300 K.

2,2'-bis(Trimethylgermyl)azobenzene (**7**)

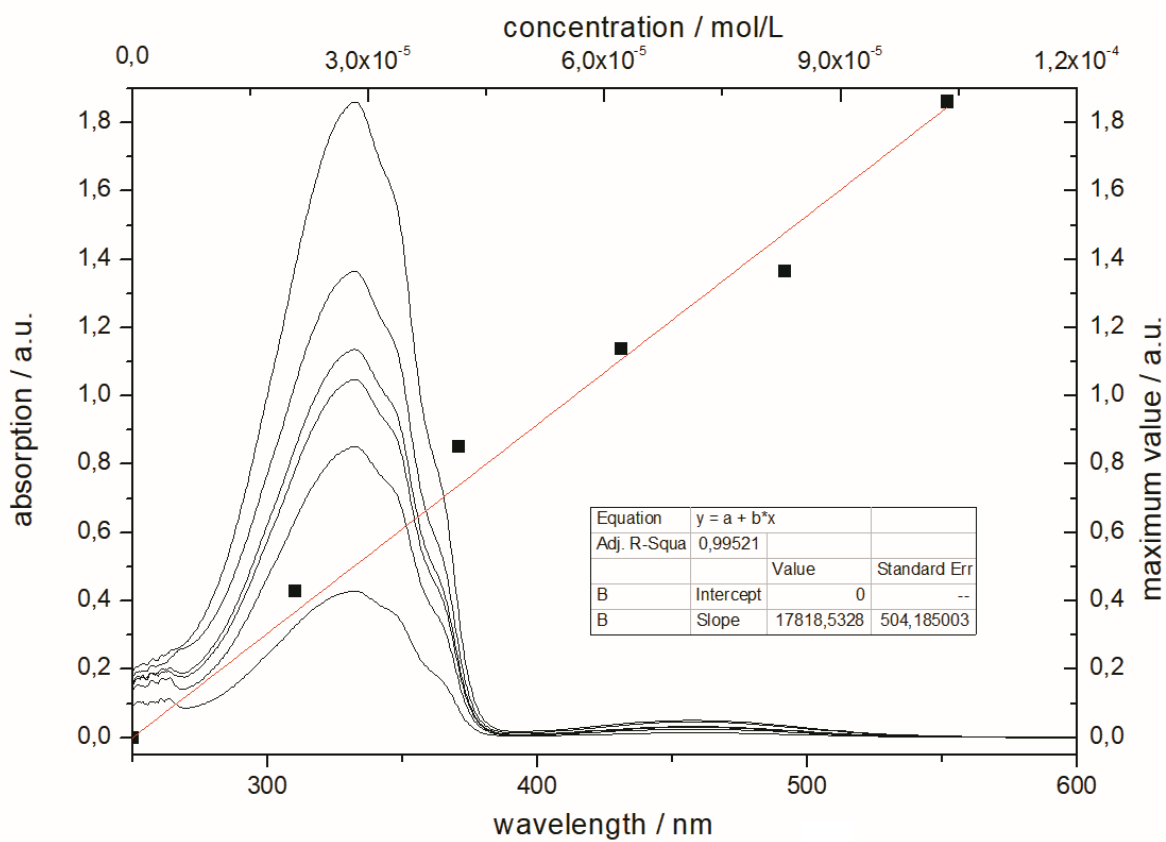


Figure S127: Absorption spectra of compound **7** and linear fitting to according to Lambert-Beer's-law.

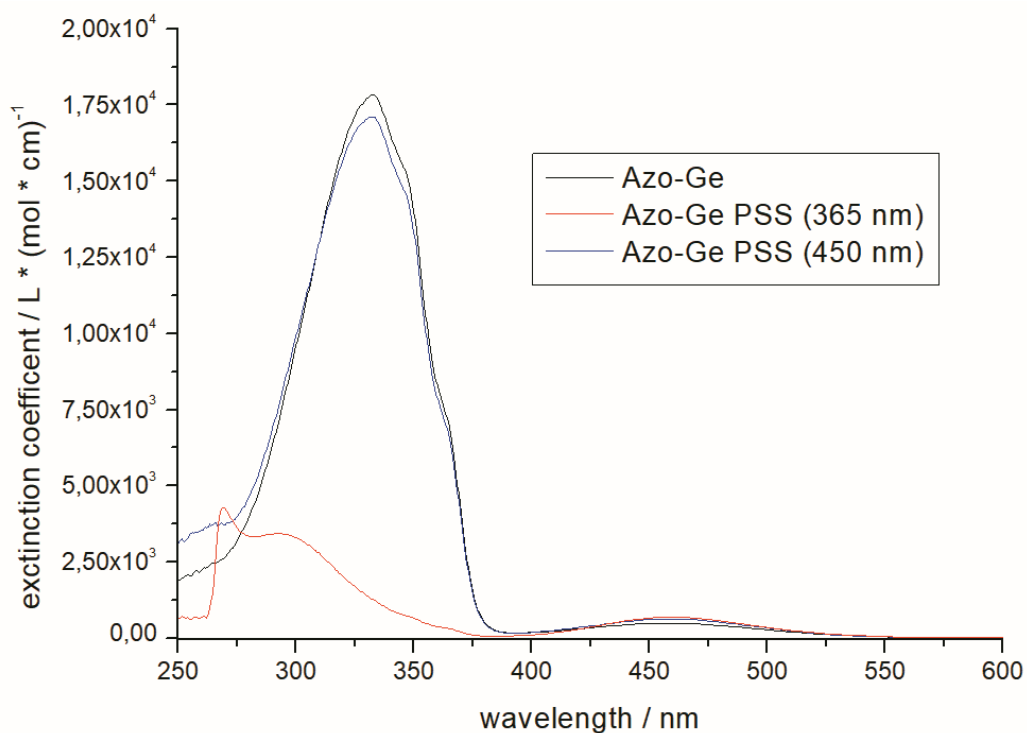


Figure S128: Comparison of the absorption spectra of compound **7** as dissolved (black), after 3 min irradiation with 365 nm light (red) and after 15 min irradiation with 450 nm light (blue). The concentration was 6.22×10^{-5} M in cyclohexane.

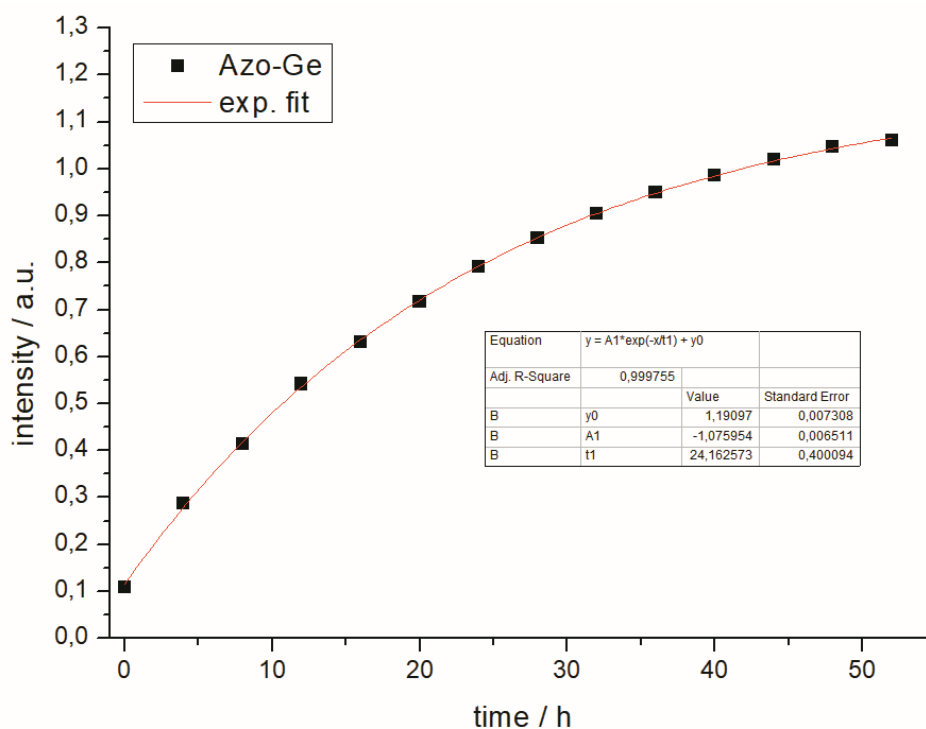


Figure S129: Absorption value of the $\pi\pi^*$ band from compound **7** plotted against time after irradiation at 365 nm for 3 mins. The concentration was 6.22×10^{-5} M in cyclohexane.

^1H NMR spectroscopic monitoring of the switching of **7**:

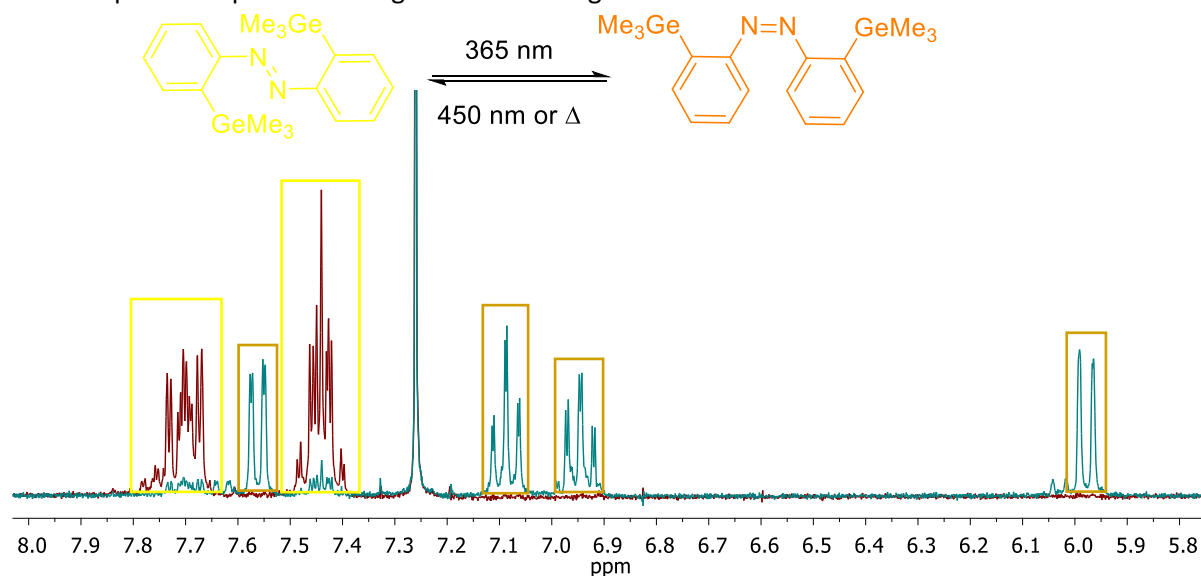


Figure SI 30: ^1H NMR (300 MHz) spectra of compound **7** in CDCl_3 before (red) and after (blue) irradiation with 365 nm (15 min) in CDCl_3 . The concentration was 7.53×10^{-3} M.

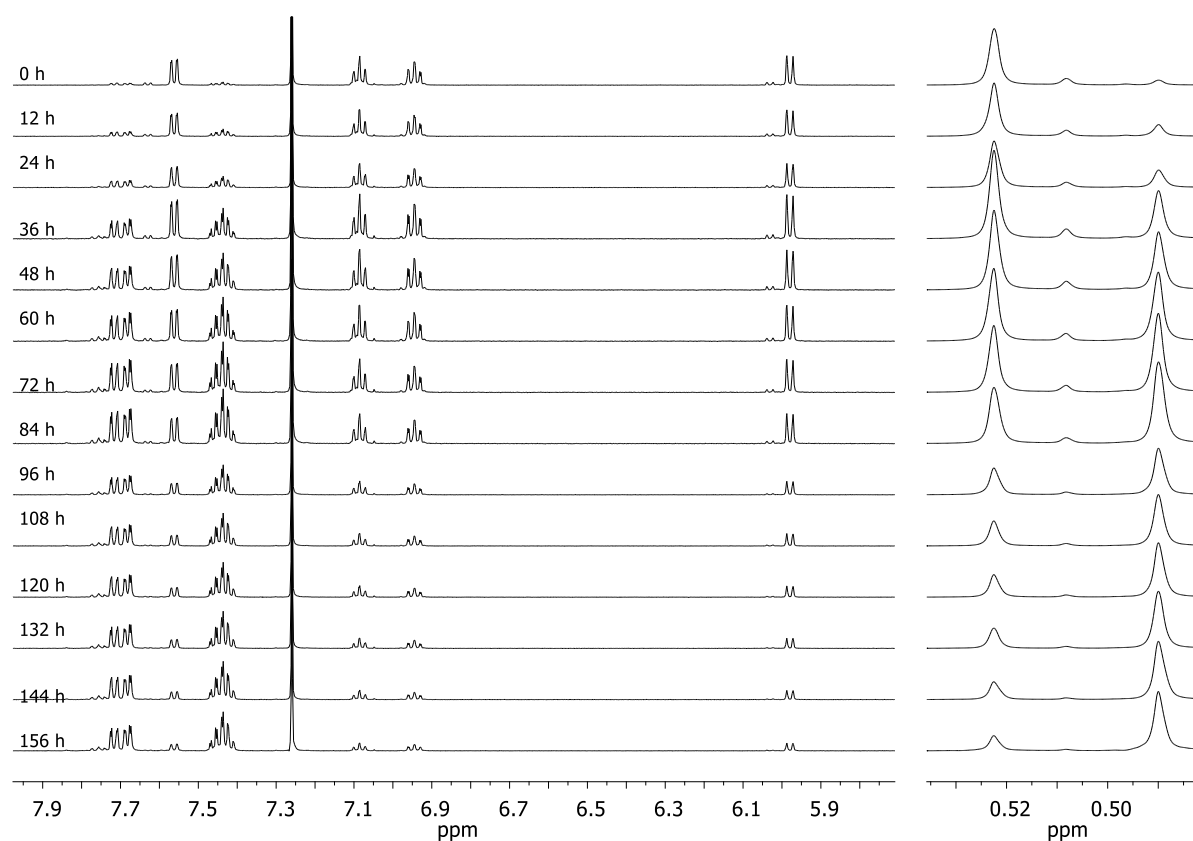


Figure SI31: ^1H NMR (500 MHz) spectra of **7** measured every 12 h after irradiation at 365 nm for 15 mins.

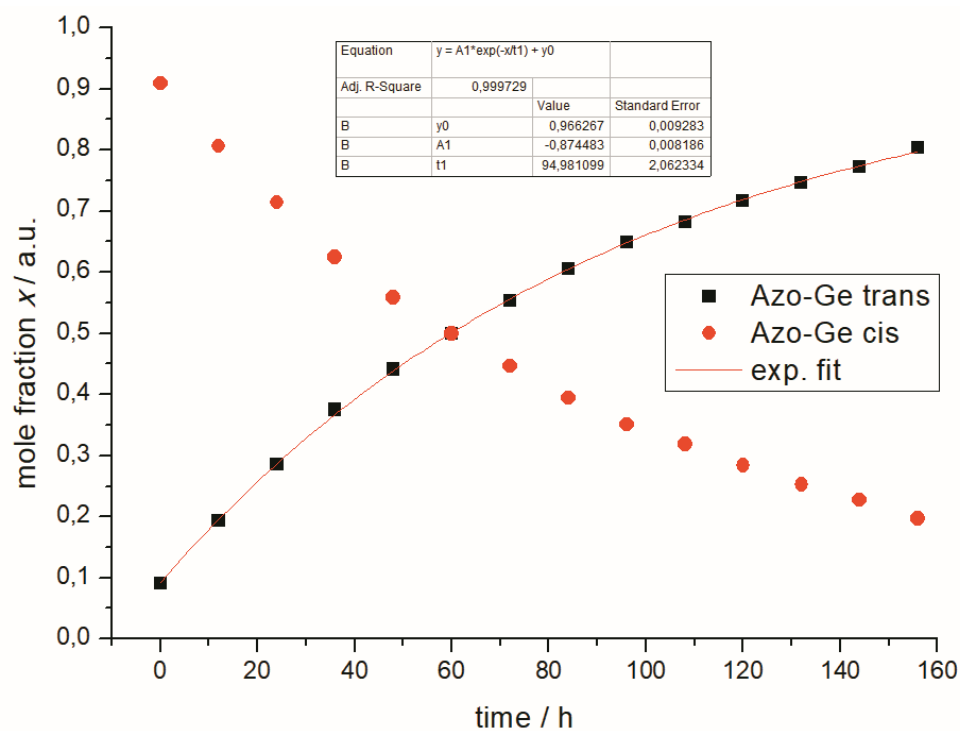


Figure S132: Mole fraction of cis and trans-azobenzene **7** vs time gives the thermal relaxation at 300 K.
2,2'-bis(Trimethyltin)azobenzene (**8**)

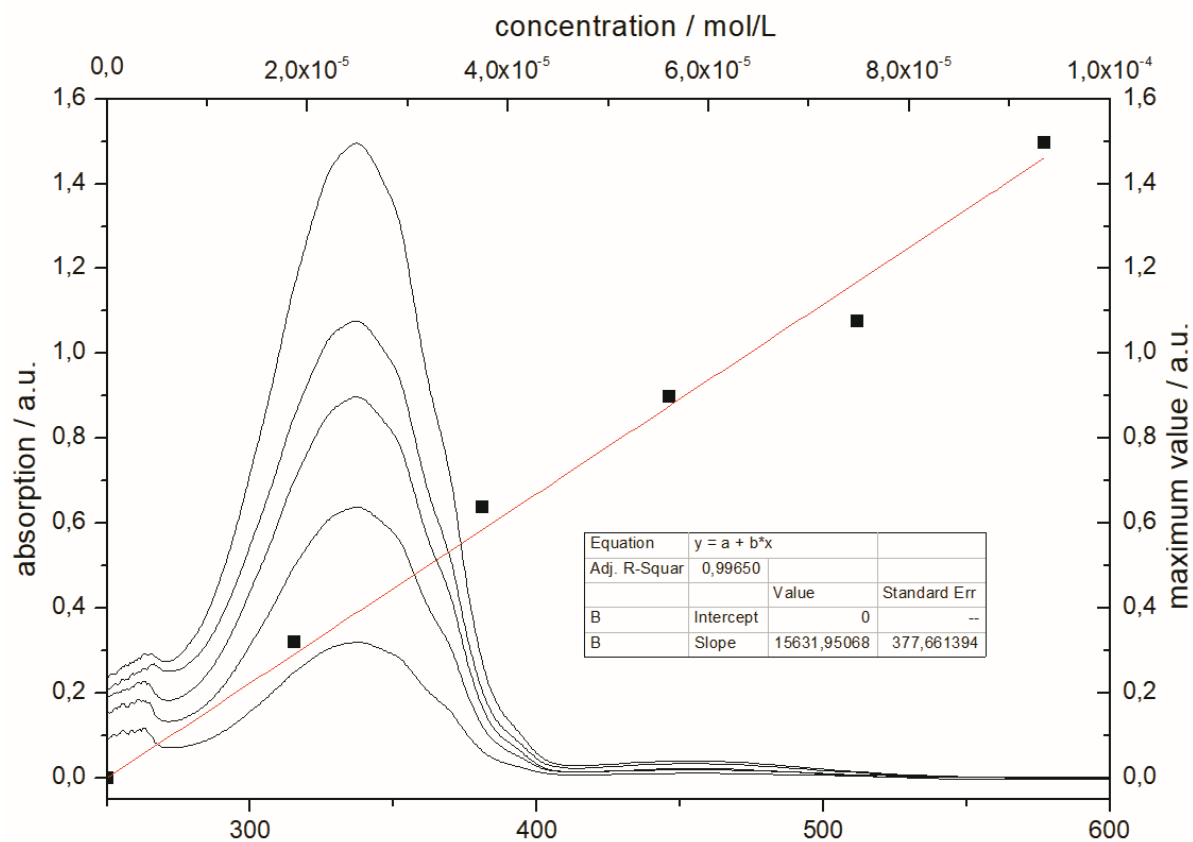


Figure S133: Absorption spectra of compound **8** and linear fitting to according to Lambert-Beer's-law.

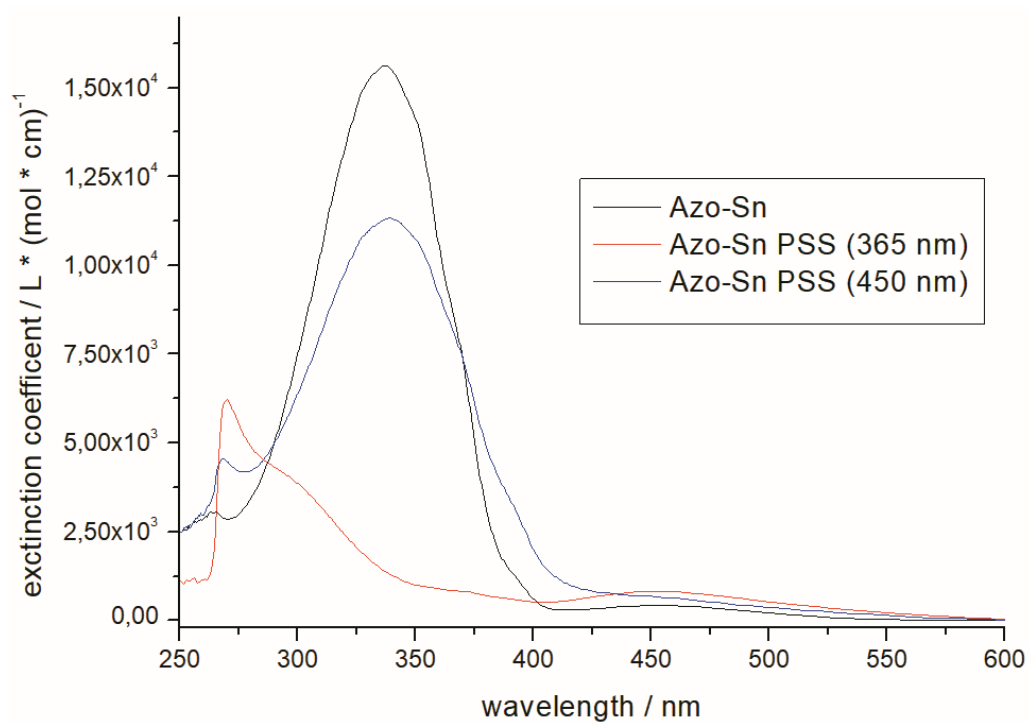


Figure S134: Comparison of the absorption spectra of compound **8** as dissolved (black), after 3 min irradiation with 365 nm light (red) and after 15 min irradiation with 450 nm light (blue). The concentration was 5.60×10^{-5} M in cyclohexane.

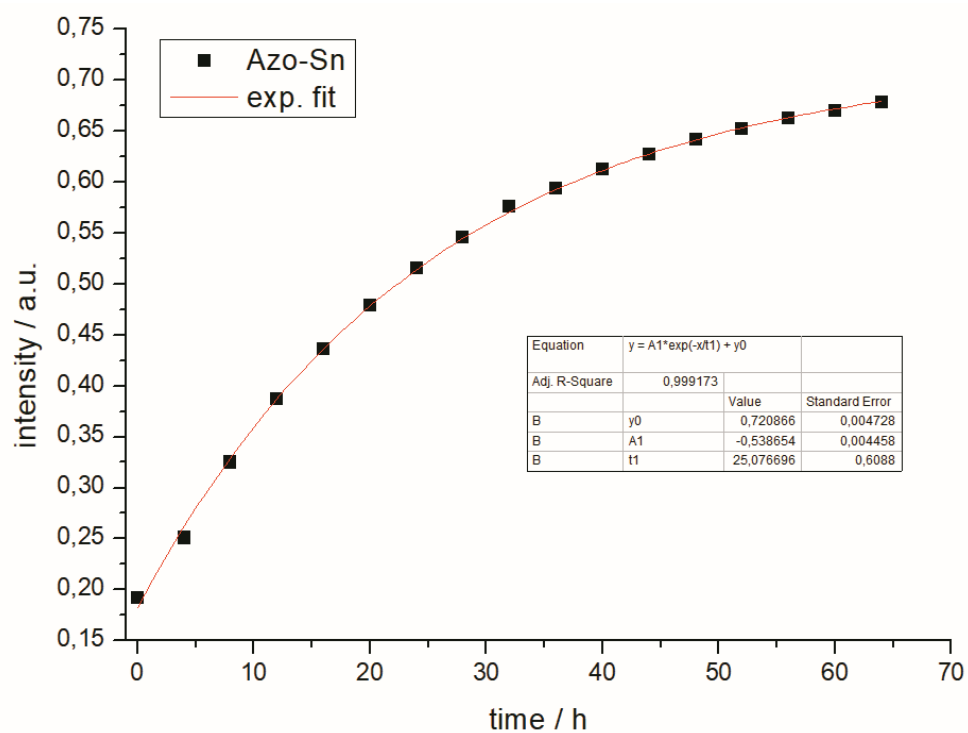


Figure S135: Absorption value of the $\pi\pi^*$ band from compound **8** plotted against the time after irradiation at 365 nm for 3 min. The concentration was 5.60×10^{-5} M in cyclohexane.

^1H NMR spectroscopic monitoring of the switching of **8**:

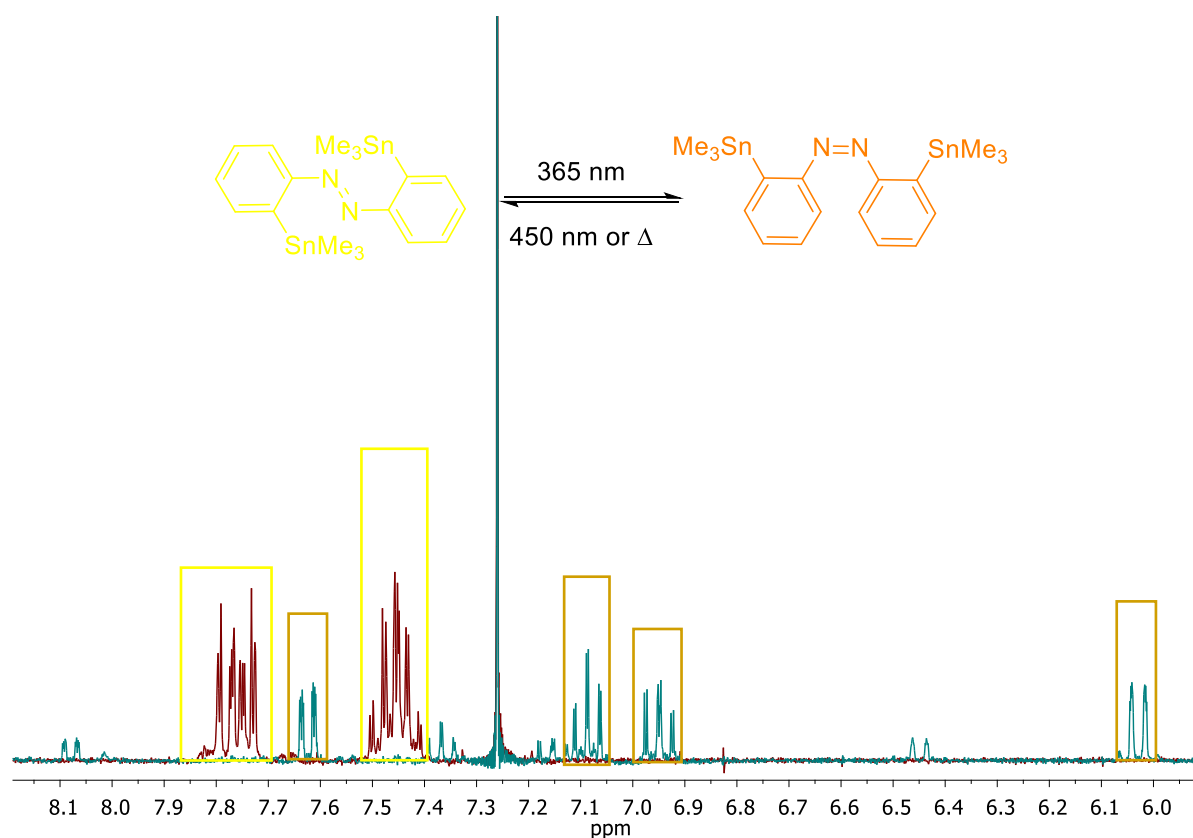


Figure SI36: ^1H NMR (300 MHz) spectra of compound **8** in CDCl_3 before (red) and after (blue) irradiation with 365 nm (15 min). The concentration was 6.56×10^{-3} M.

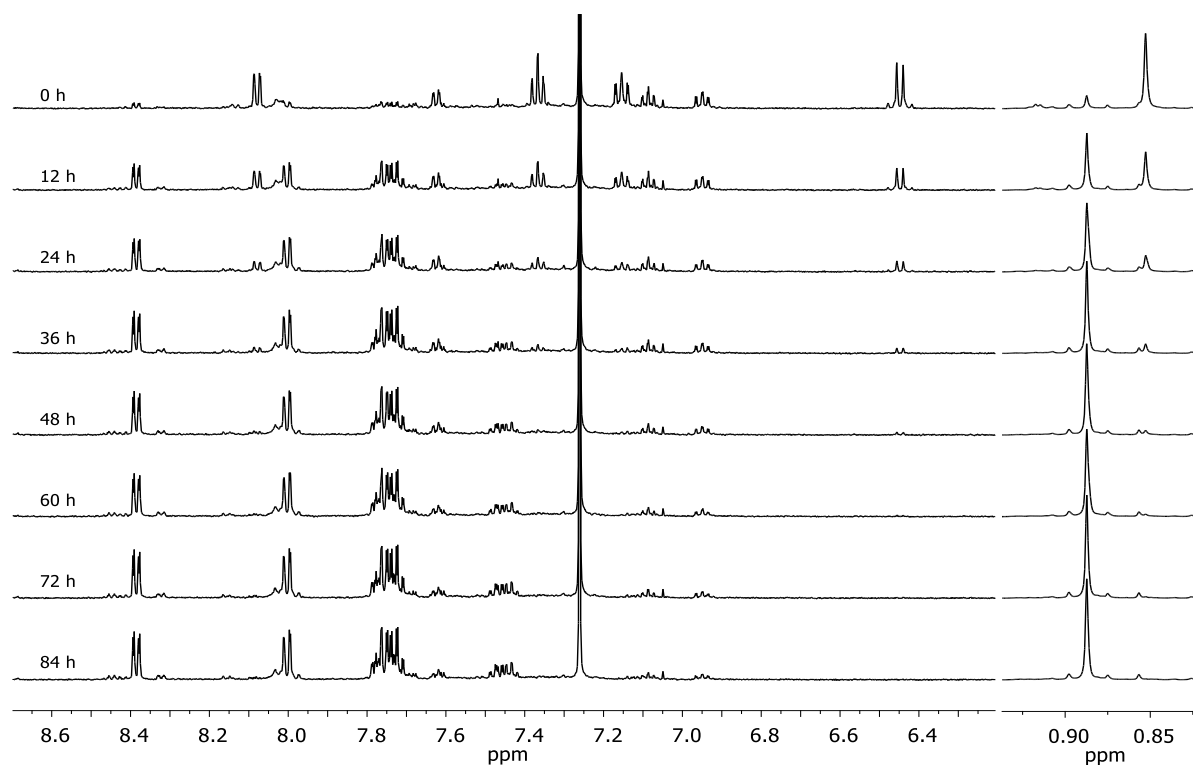


Figure SI37: ^1H NMR (500 MHz) spectra of **8** measured every 12 h after irradiation at 365 nm for 15 min.

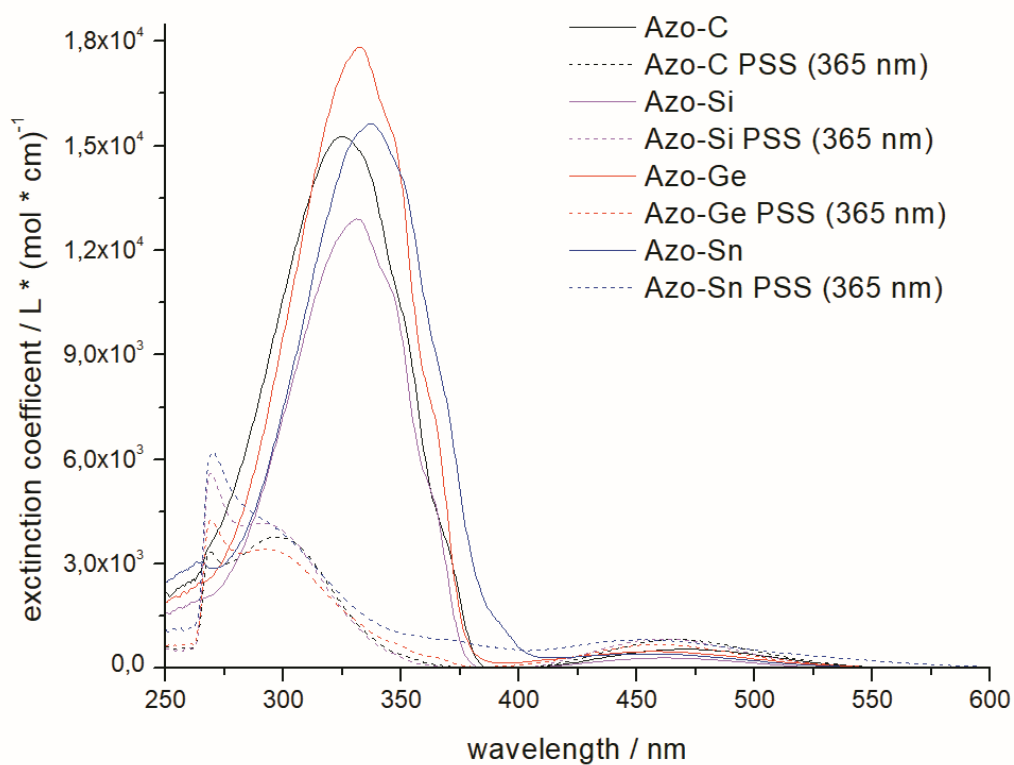


Figure S138: Comparison of the switching behavior of all target molecules with their respective absorption spectra after irradiation at 365 nm for 3 min.

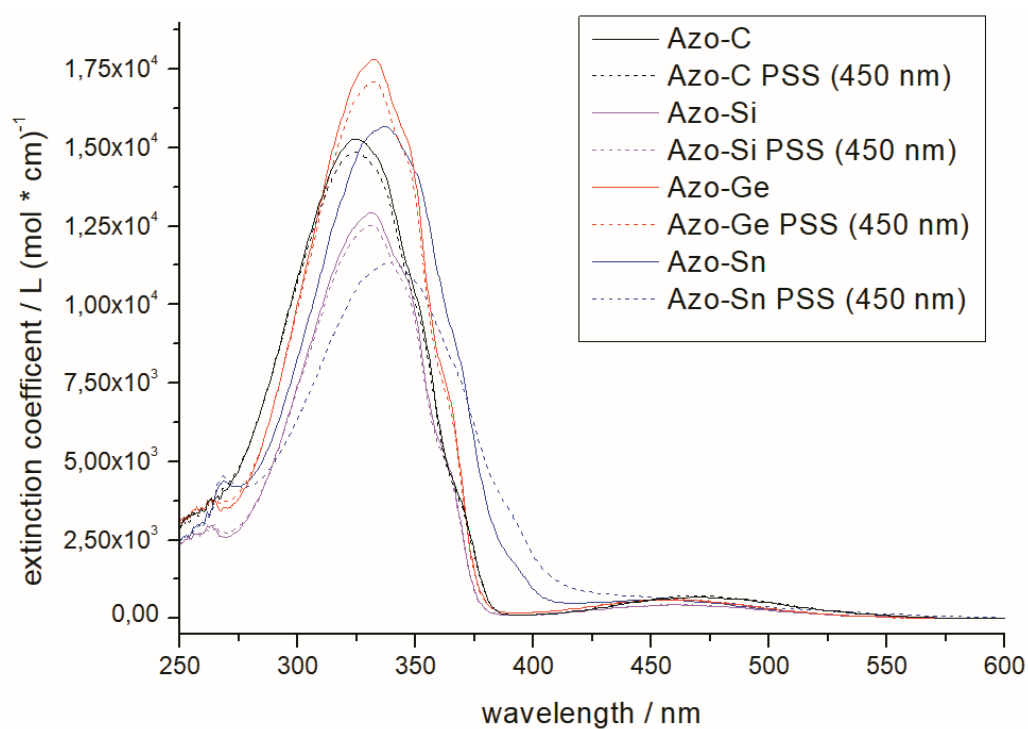


Figure S139: Comparison of the switching behavior of all target molecules with their respective absorption spectra after irradiation at 450 nm for 15 min.

5. Thermoanalysis (DSC and TGA) and ^1H / $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of the Respective Compounds After Thermoanalysis

2,2'-Di(*tert*-butyl)azobenzene (**10**)

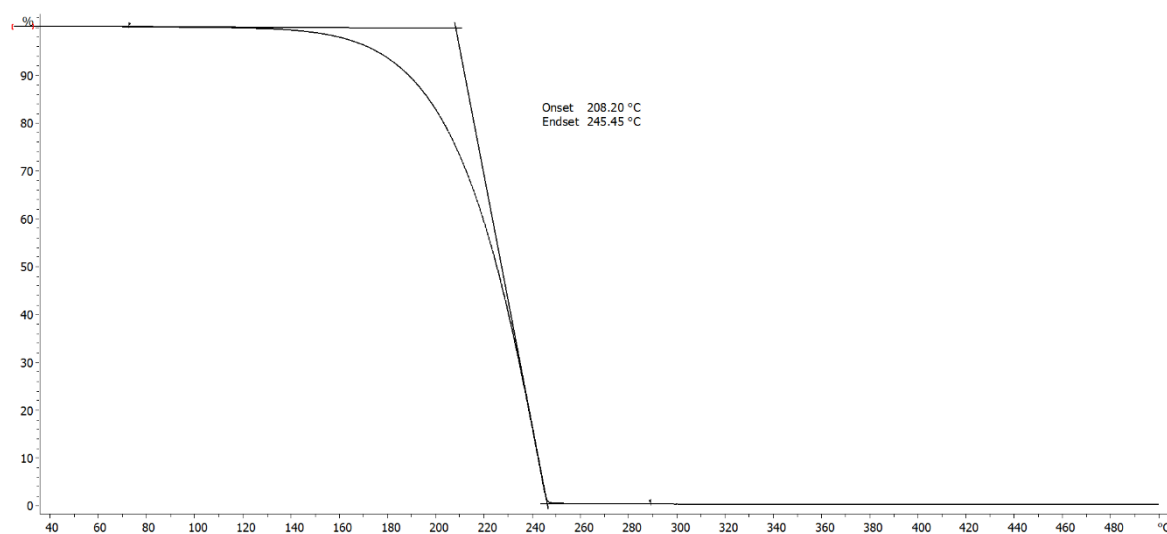


Figure SI40: Thermogravimetric analysis of compound **10** with a heating rate of 10 K / min under a nitrogen flow of 20 mL/min in a open aluminium crucible (40 μL).

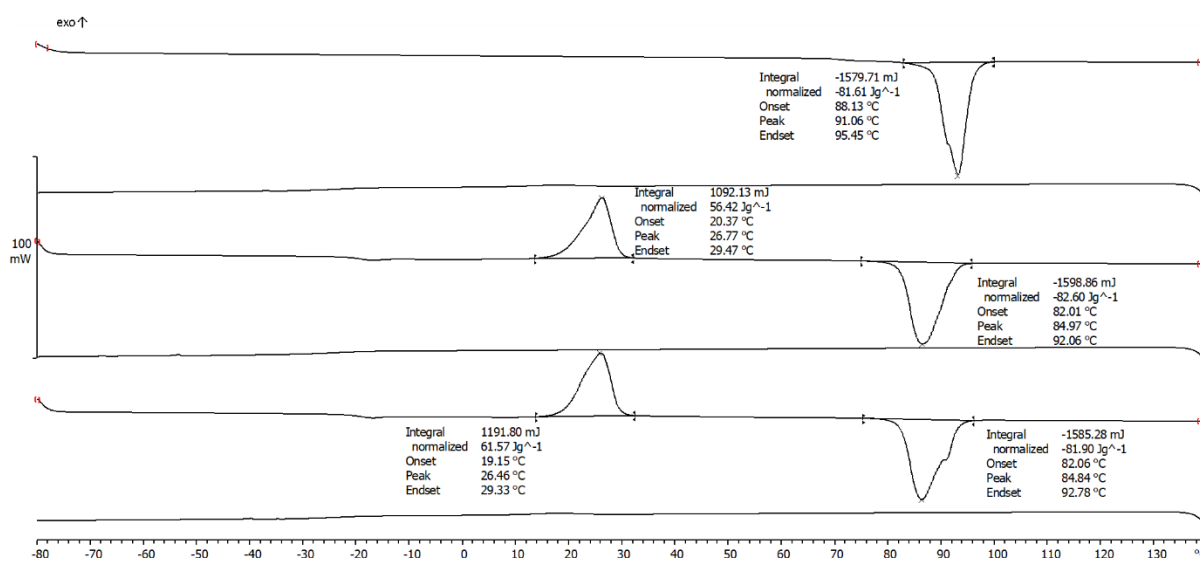


Figure SI41: Dynamic scanning calorimetry of compound **10** with a heating rate of 10 K / min under a flow of nitrogen (20 mL / min) in an aluminium crucible (40 μL) with a pierced lid.

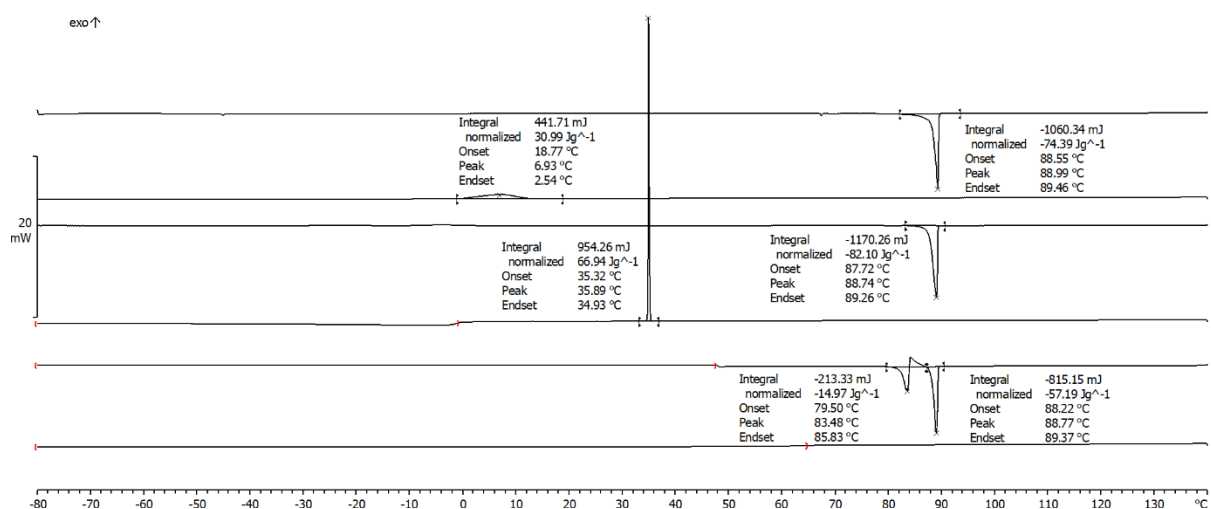


Figure SI42: Dynamic scanning calorimetry of compound **10** with a heating rate of 0.5 K / min under nitrogen flow (20 mL / min) in an aluminium crucible with a pierced lid (40 μ L).

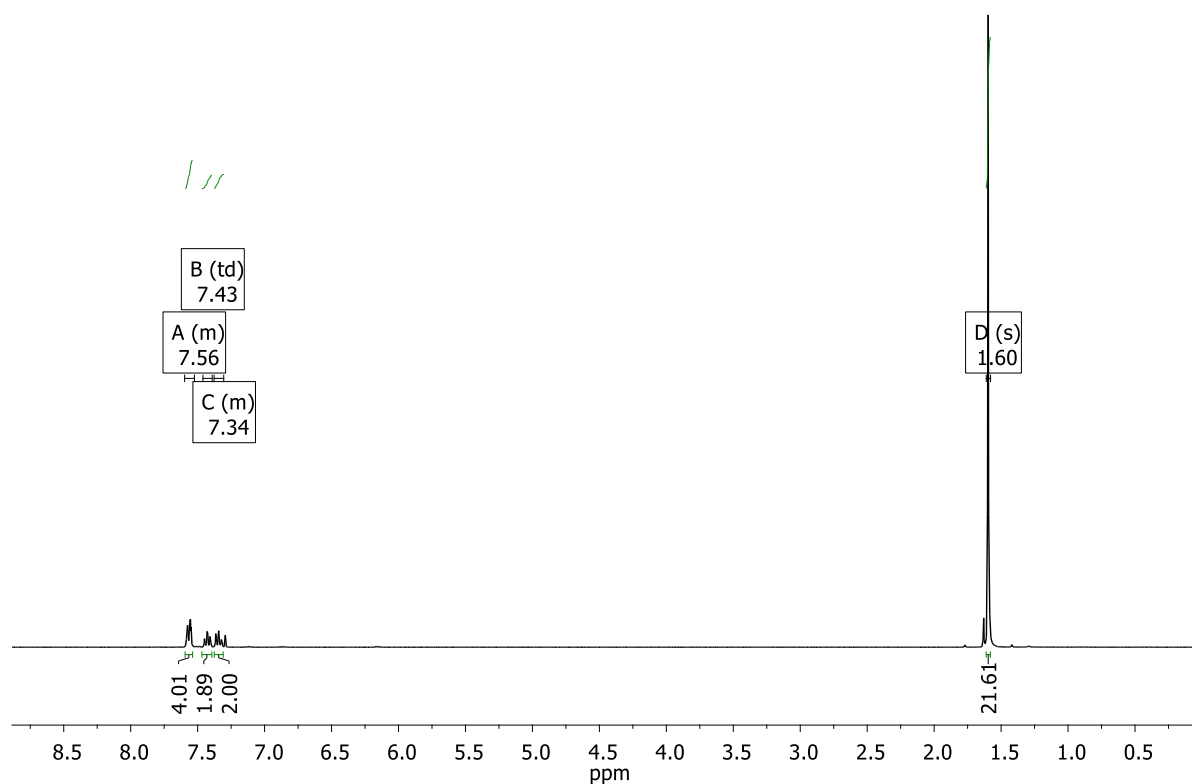


Figure SI43: ¹H NMR (380 MHz) spectrum of compound **10** after DSC.

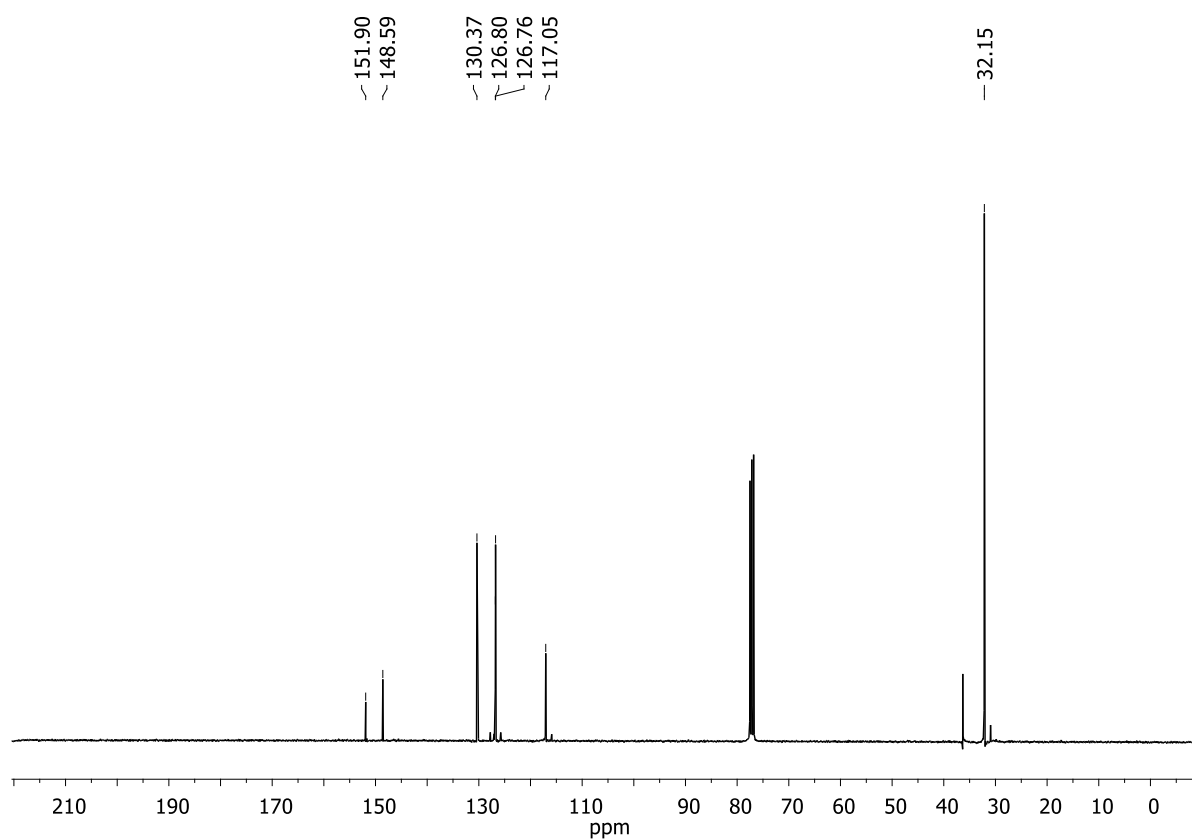


Figure SI44: $^{13}\text{C}\{^1\text{H}\}$ NMR (76 MHz) spectrum of compound **10** after DSC.

Due to the fact that the TG analyses showed a constant loss of mass at higher temperature we were interested in the nature of this process. Therefore we interrupted the measurement at 220 °C at measured ^1H and ^{13}C NMR spectra.

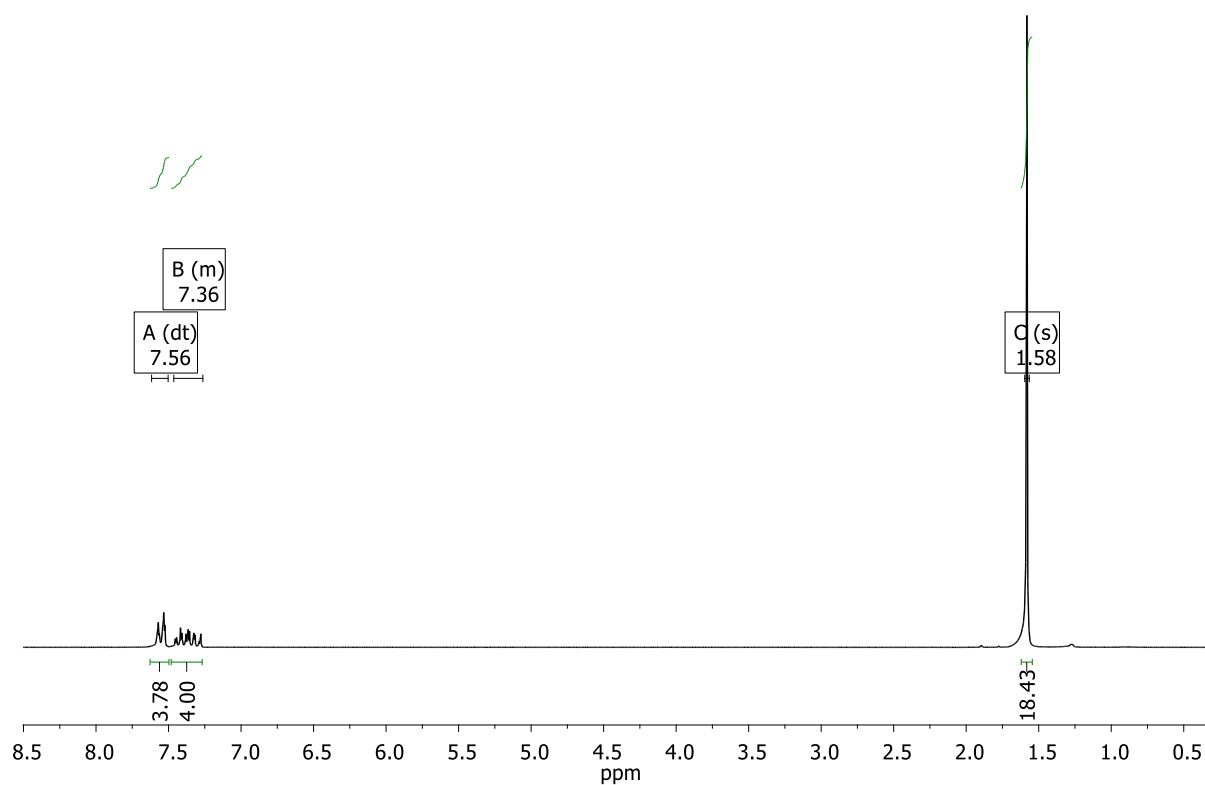


Figure SI45: ^1H NMR (380 MHz) spectrum of compound **10** after interrupting the TG analyses at 220°C.

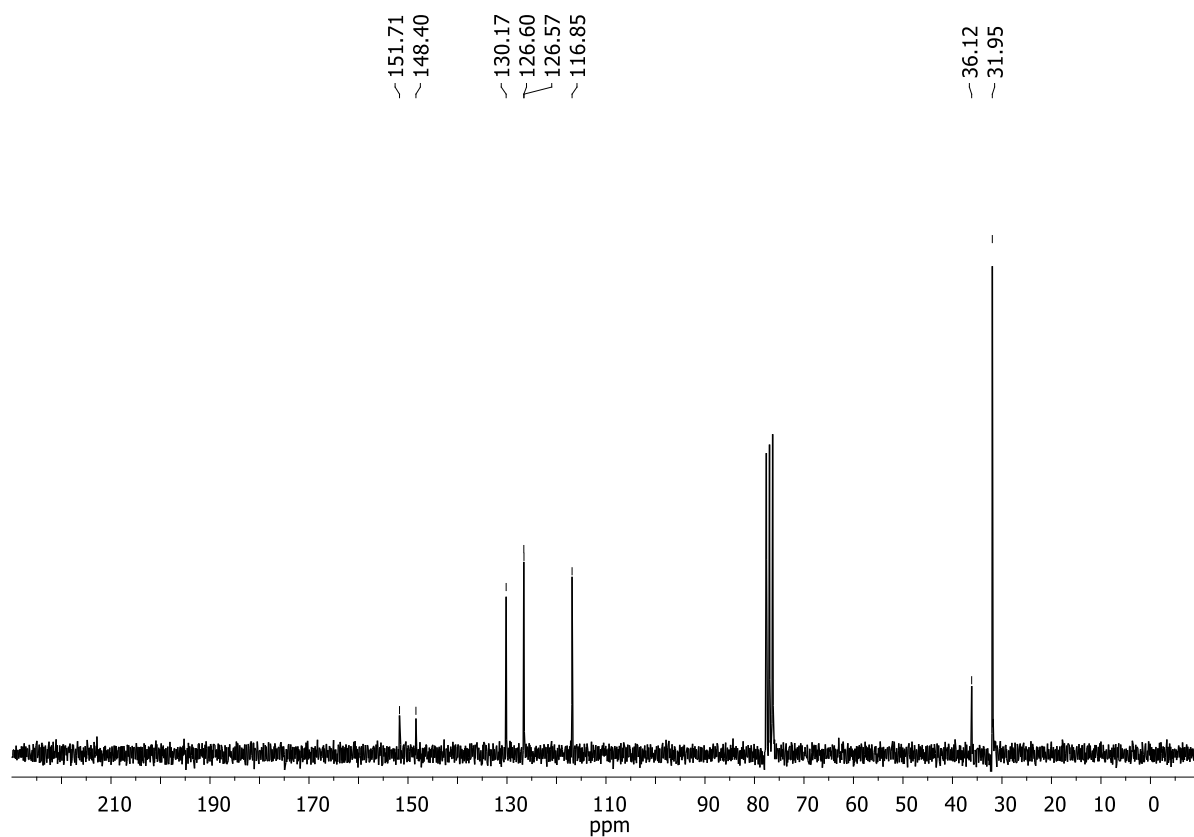


Figure SI46: $^{13}\text{C}\{^1\text{H}\}$ NMR (76 MHz) spectrum of compound **10** after interrupting the TG analyses at 220°C.

The obtained spectra are in agreement with the spectra of the purified materials indicating no decomposition but evaporation of the molten azobenzene.

2,2'-bis(Trimethylsilyl)azobenzene (**6**)

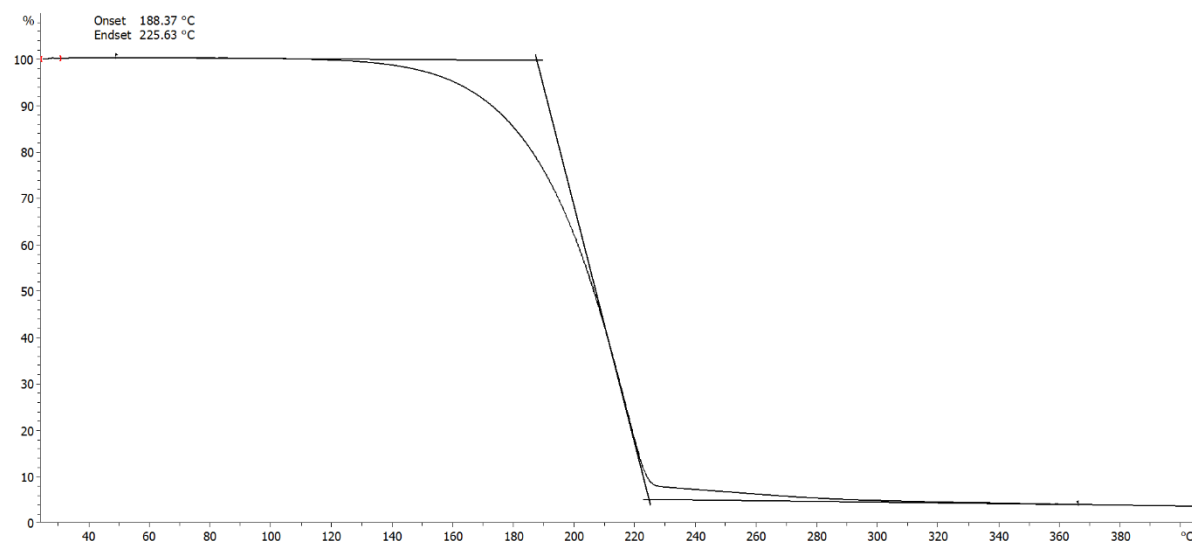


Figure SI47: Thermogravimetric analysis of compound **6** with a heating rate of 10 K / min under a nitrogen flow of 20 mL/min in a open aluminium crucible (40 μ L).

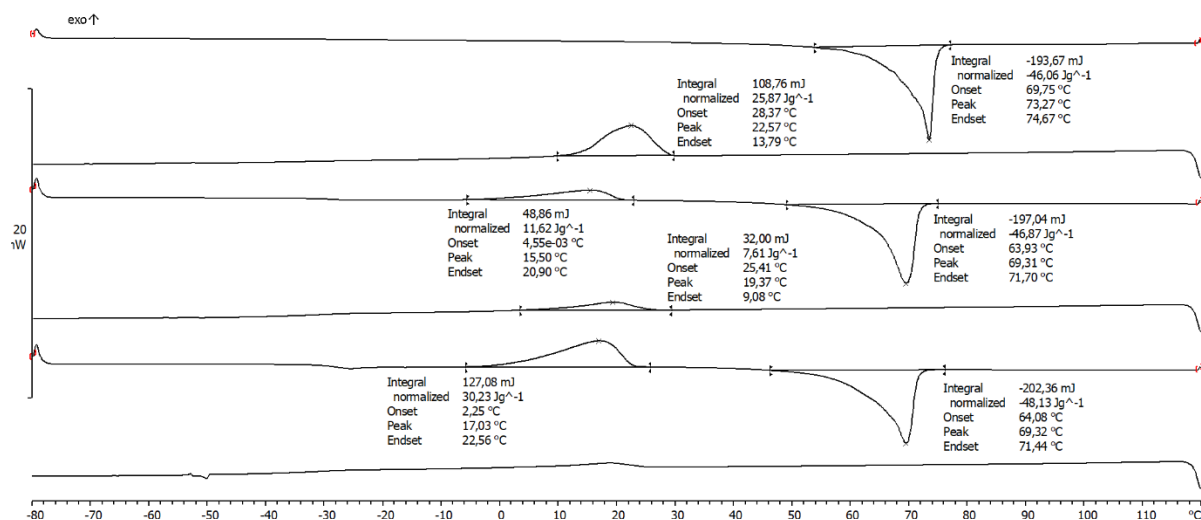


Figure SI48: Dynamic scanning calorimetry of compound **6** with a heating rate of 10 K / min under nitrogen flow (20 mL / min) in an aluminium crucible with a pierced lid (40 μ L).

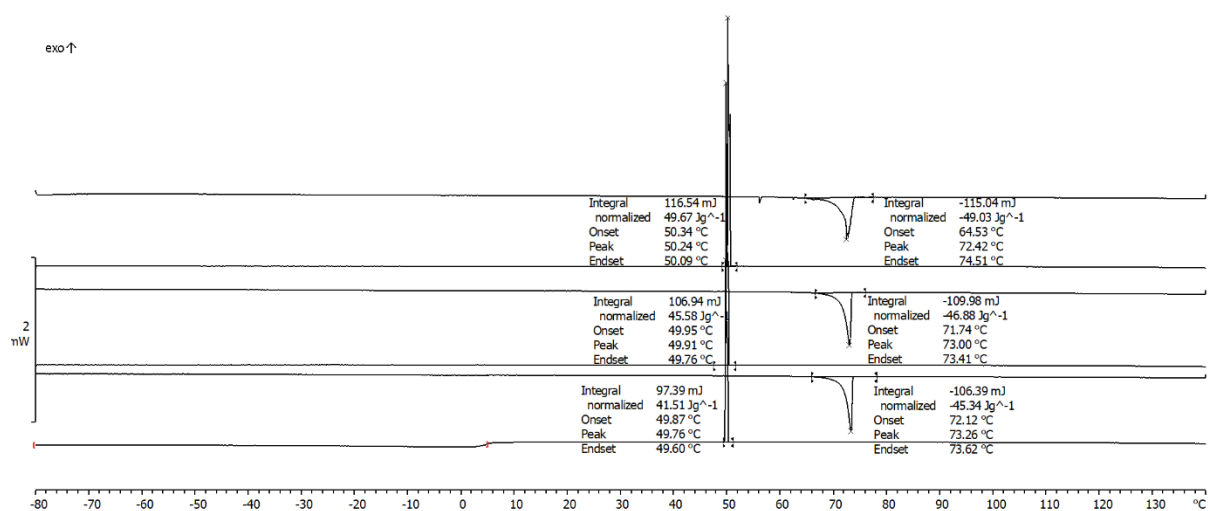


Figure SI49: Dynamic scanning calorimetry of compound **6** with a heating rate of 0.5 K / min under nitrogen flow (20 mL/min) in an aluminium crucible with a pierced lid (40 μ L).

2,2'-bis(Trimethylgermyl)azobenzene (**7**)

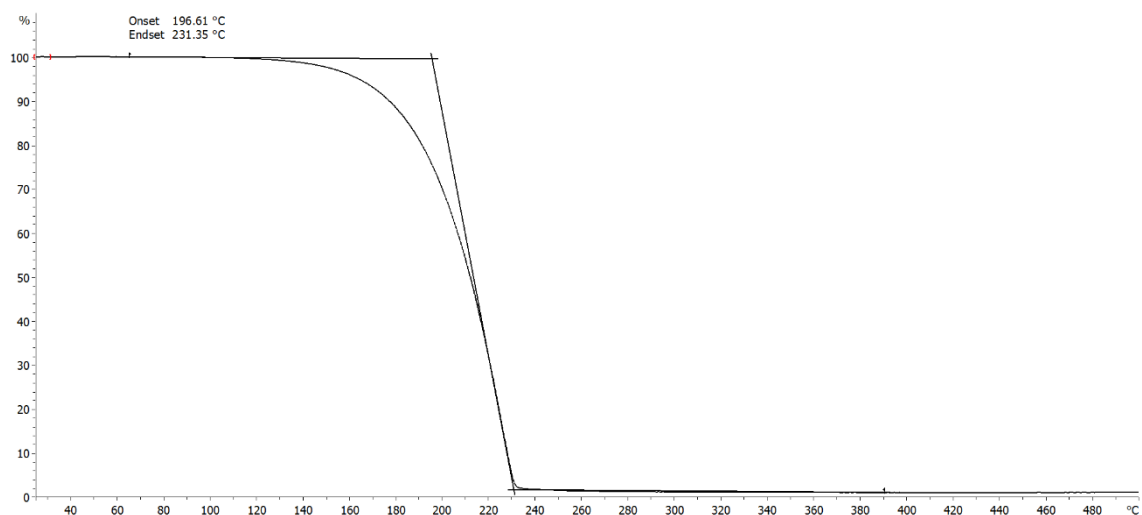


Figure SI50: Thermogravimetric analysis of compound **7** with 10 K / min under a nitrogen flow of 20 mL/min in a open aluminium crucible (40 μ L).

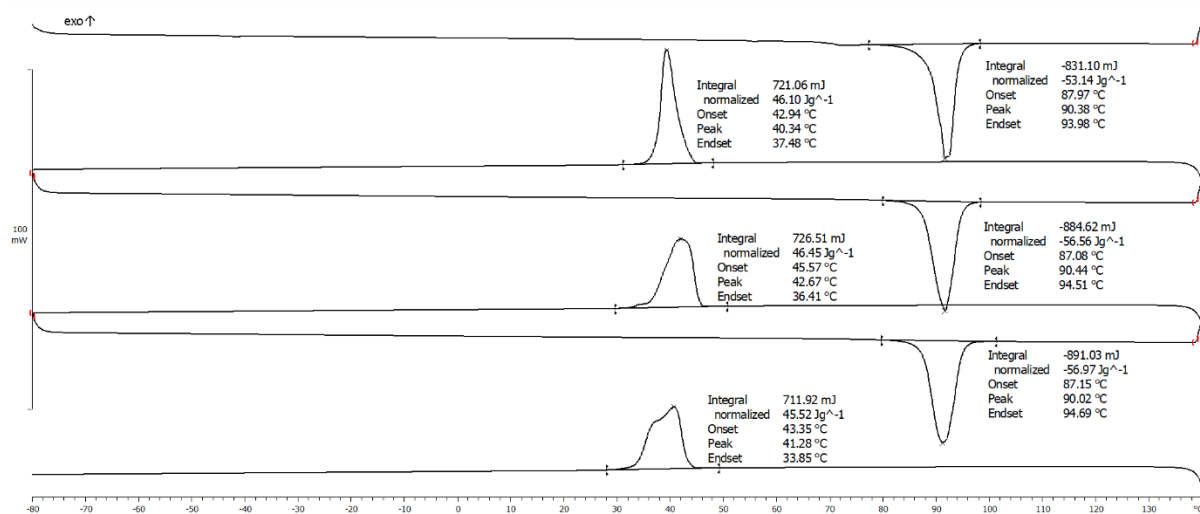


Figure S151: Dynamic scanning calorimetry of compound **7** with a heating rate of 10 K / min under nitrogen flow (20 mL/min) in an aluminium crucible with a pierced lid (40 µL).

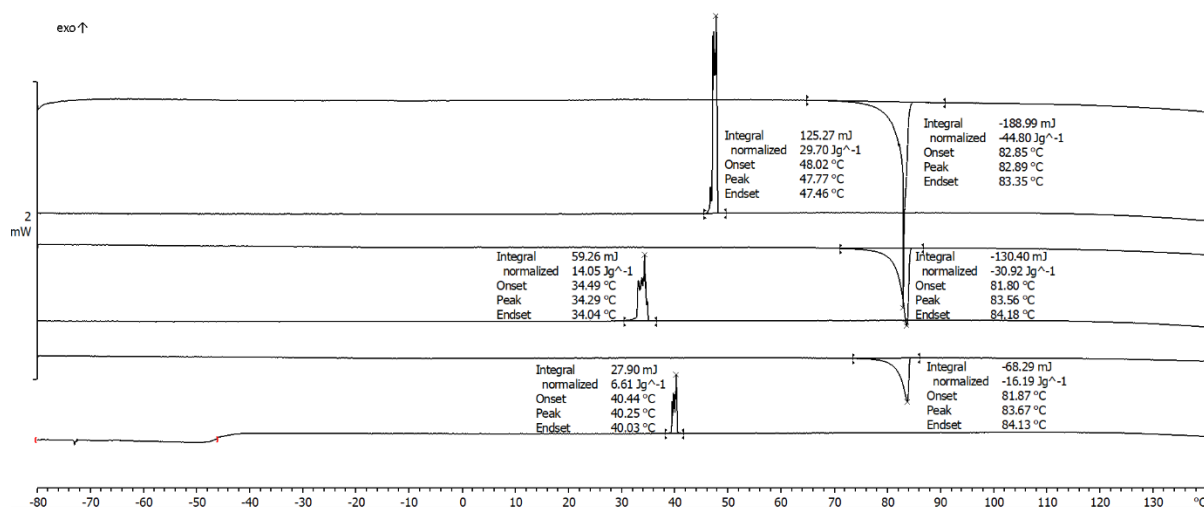


Figure S152: Dynamic scanning calorimetry of compound **7** with a heating rate of 0.5 K / min under nitrogen flow (20 mL/min) in a closed aluminium crucible (40 µL).

2,2'-bis(Trimethylstannyl)azobenzene (**8**)

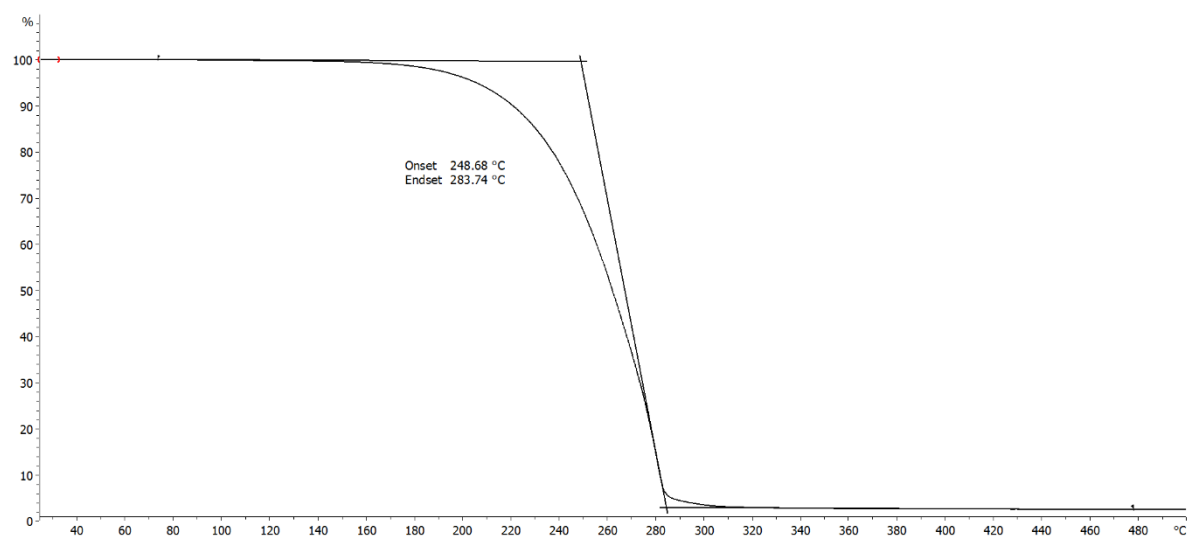


Figure SI53: Thermogravimetric analysis of compound **8** with a heating rate of 10 K / min under a nitrogen flow of 20 mL/min in a open aluminium crucible (40 µL).

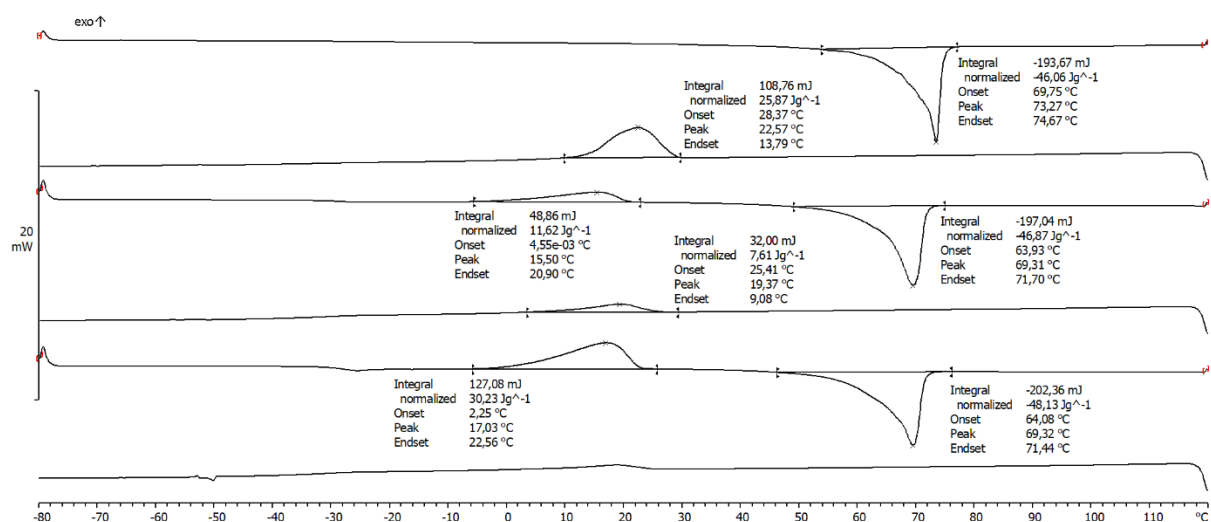


Figure SI54: Dynamic scanning calorimetry of compound **8** with a heating rate of 10 K / min under nitrogen flow (20 mL/min) in a closed aluminium crucible (40 µL).

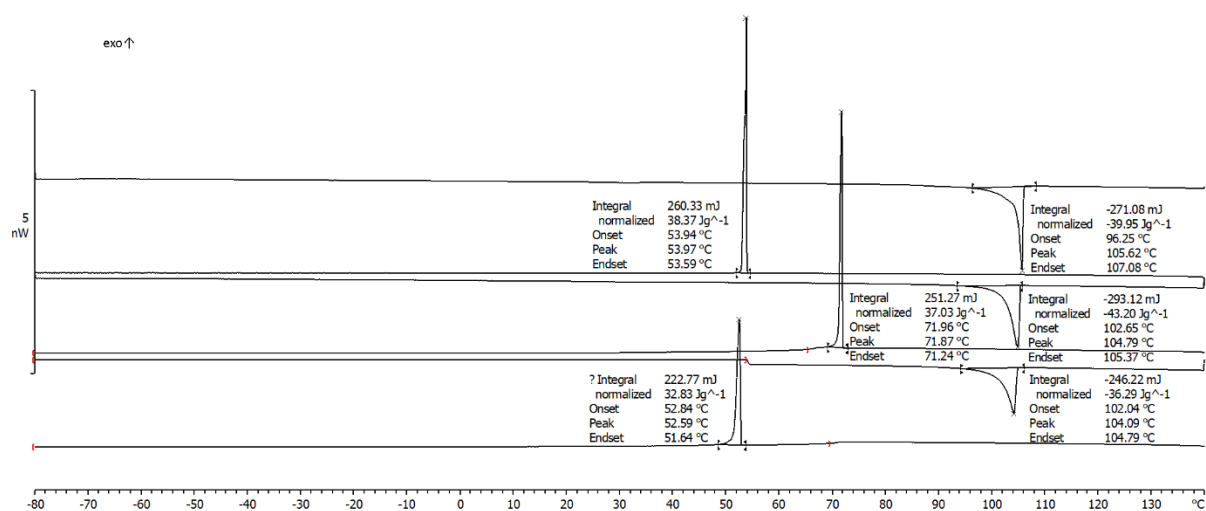


Figure SI55: Dynamic scanning calorimetry of compound **8** with a heating rate of 0.5 K / min under nitrogen flow (20 mL/min) in a closed aluminium crucible (40 µL).

1,6-Di(*tert*-butyl)phenanzine (**16**)

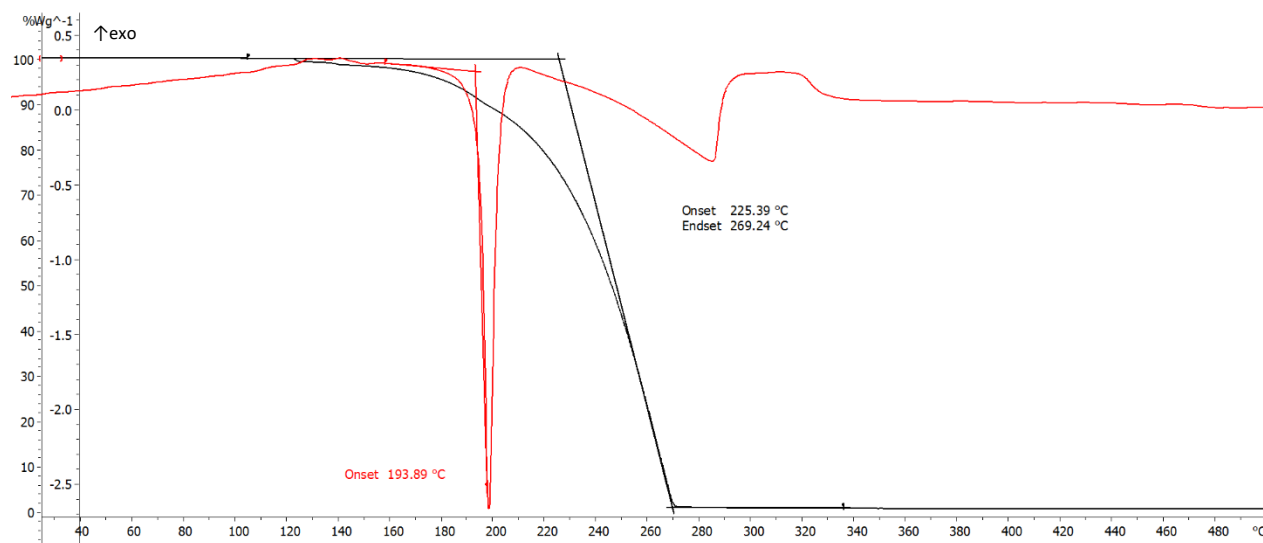


Figure SI56: Thermogravimetric analysis of compound **16** with a heating rate of 10 K / min under a nitrogen flow of 20 mL/min in a open aluminium crucible (40 µL). The red line indicates the DSC data.