Electronical Supporting Information

for

Efficient reversible photoisomerisation with large hydrodynamic size-switching of a main-chain poly(azobenzene-trisiloxane)

Mathias Dowds,[‡a,b,c] Dennis Bank,[‡d] Jan Strueben,[a] David Presa Soto,[e] Frank D. Sönnichsen,[a] Falk Renth,[*d] Friedrich Temps[*d] and Anne Staubitz[*a,b,c]

[a.] *Otto-Diels-Institute for Organic Chemistry, University of Kiel, Otto-Hahn-Platz 4, D-24098 Kiel, Germany.*
[b.] *University of Bremen, Institute for Analytical and Organic Chemistry, Leobener Straße 7, D-28359 Bremen, Germany. E-mail: staubitz@uni-bremen.de*
[c.] *University of Bremen, MAPEX Center for Materials and Processes, Bibliothekstraße 1, D-28359 Bremen, Germany*
[d.] *Institute for Physical Chemistry, University of Kiel, Max-Eyth-Str. 1, D-24098 Kiel, Germany. E-mail: temps@phc.uni-kiel.de*
[e.] *Universidad de Oviedo, Facultad de Química, Departamento de Química Orgánica e Inorgánica, Julián Clavería s/n, 33006, Oviedo, Spain.*
** corresponding authors*
‡ These authors contributed equally.

Table of Contents

Abbreviations

The use of abbreviations follows the conventions from the ACS Style guide.[1] In addition, the following abbreviations are used.

Abbreviation	**Long form**
at (NMR)	Apparent triplet
DCM	Dichloromethane
dd (NMR)	Doublet of doublets
HMBC	Heteronuclear multiple bond correlation
HSQC	Heteronuclear single quantum coherence
MeTHF	2-Methyltetrahydrofuran
PSS	Photostationary state

Analytical Equipment and Equipment for Syntheses

NMR spectra were either recorded on a Bruker Avance Neo 500 (^{1}H NMR: 500 MHz) or on a Bruker Avance II HD 600 (^{1}H NMR: 600 MHz) FT-NMR spectrometer at 298 K. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were referenced using tetramethyl silane (TMS).

The exact assignment of the peaks was performed by two-dimensional NMR spectroscopy such as ^{1}H COSY, ^{1}H NOESY, ^{1}H/^{13}C{^{1}H} HSQC, ^{1}H/^{13}C{^{1}H} HMBC and ^{1}H/^{29}Si{^{1}H} HMBC if possible. ^{1}H DOSY experiments were analysed with the Bruker Topspin 4.03 software to determine the T1/T2 dynamics.

Mass spectrometric measurements were performed in the positive ion collection mode using a JEOL-Accu TOF 4GGCV EI mass spectrometer, or a Thermo Fisher Q Exactive Plus with a quadruple Orbitrap ESI mass spectrometer. Electron ionisation (EI) was performed using an ionization potential of 70 eV.

IR spectra were measured using a Perkin Elmer Paragon 1000 FT-IR spectrometer equipped with an A531-G Golden-Gate-ATR-unit.

UV spectra of the compounds 4,4'-bis(iodo)azobenzene, 4,4'-bis(trimethylstannyl)azobenzene and 4,4'-bis(hydroxydimethylsilane)azobenzene were recorded at 25 °C using a Perkin Elmer Lambda 14 UV spectrometer in acetonitrile. Quartz cuvettes with a light path length of 10 mm from Hellma Analytics were used.

Melting points were measured on an electrothermal IA6304 capillary melting point apparatus and are uncorrected.

Elemental analysis was performed on a EURO EA elemental analyzer by EURO VECTOR Intruments.

Conventional gel permeation chromatography was performed on a Viscotek GPC max VE2001 equipped with a Viscotek VE3580 RI detector and a column set of LT5000 and LT4000 in THF (VWR,

HPLC-grade) with a flow rate of 1 mL/min. Calibration and analysis was done with OmniSEC 4.6.2 software using polystyrene standards. Origin 2016 was used for plotting the chromatograms.
The irradiation experiments were carried out using a square array (diameter = 50 mm) of 12 LEDs (365 nm) with an individual optical power of 300 mW or one Luxeon LXML-PR01 LED (450 nm) with an optical power of 900 mW. The irradiation equipment was assembled by Sahlmann Photochemical Solutions. NMR and GPC samples were irradiated for 90 minutes.
Reactions that required inert workup were conducted in a labmaster 130 glove box by MBraun, flushed with nitrogen.
Microwave assisted syntheses were performed on a Biotage Initiator+ SP Wave peptide synthesiser in the organic synthesis mode. The times given in the experimental procedures include the heating time to reach the given temperature.
The cooling of inert syntheses was achieved by using a cooling block connected to a Julabo FP88 cryostate inside the glove box.
Viscosities were determined at 298 K using a capillary viscometer ("Ostwald viscometer") with a capillary diameter of d = 0.3 mm and capillary constant of approx. K= 6.25 10^{-9} m^2/s^2 by SI Analytics. The capillary constant was determined by reference measurements with water at 20 °C.

Reagents

If not noted otherwise, all reagents were used as received. Hydrochloric acid solutions were prepared by diluting the concentrated acid.

Reagent	Supplier	Purity or concentration	Notes
[$Pd(PPh_3)_4$]	Aldrich	99%	
4-Iodoaniline	Acros	98%	
Copper (I) bromide	Sigma-Aldrich	98%	
Dichlorodimethylsilane	Acros	99%	Distilled from CaH_2 and degassed before use
Hexamethyldistannane	Acros	99%	
Hydrochloric acid	Grüssing	37.5%	
Magnesium sulphate	Grüssing		
Methyl lithium	Acros	3% in MeTHF / Cumol	Exact concentration was determined by titration against menthol and 1,10-phenanthroline as indicator.[2]
Monopotassium phosphate	Merck	Extra pure	
Phenyl isocyanate	Alfa Aesar	>98%	Degassed before use
Pyridine	Grüssing	99.5%	
Pyrrolidine	Alfa Aesar	99%	Degassed before use
Sodium hydroxide	Grüssing	99%	

Solvents

All solvents that were purchased in technical grade were purified by distillation prior to use. Solvents of purities higher than 99% were not purified further. Some solvents were degassed by three freeze-pump-thaw cycles, then the flask was again filled with nitrogen and the solvent stored over molecular sieves with the pore size 3 Å.

The following solvents were dried in a solvent purification system PS-MD-5 by Innovative Technology: dichloromethane, tetrahydrofuran.

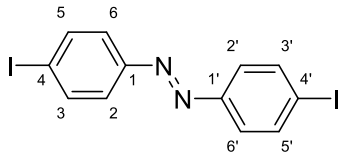
Solvent	Supplier	Purity	Drying procedure	Degassed
Acetonitrile	Sigma-Aldrich	>99.9%, HPLC grade	none	No
Benzene-d_6	Deutero	99.5% D	Distilled from CaH_2, stored over molecular sieve 3 Å	Yes
Chlorobenzene	Acros	99.9%, HPLC grade	Distilled from CaH_2, stored over molecular sieve 3 Å	Yes
Chloroform	VWR	Techn. grade	none	No
Chloroform-*d*	Euriso-top	99.8% D	none	No
Dichloromethane	VWR	HPLC grade	PS-MD-5	Yes
Dichloromethane	BCD	Techn. grade	none	No
Dichloromethane-d_2	Deutero	99.6% D	none	No
Diethyl ether	Alfa-Aesar	Spectrophotometric grade, >99%, inhibitor free	Molecular sieve 3 Å	Yes
Diethyl ether	BCD	Techn. grade	none	No
Ethanol	CMP Walther	Techn. grade, denatured with benzine	none	No
***n*-Hexane**	CMP Walther	Techn. grade	none	No
***n*-Hexane**	CMP Walther	Techn. grade	Distilled from CaH_2, stored over molecular sieve 3 Å	Yes
Methanol	Acros	99.8%, anhydrous, stored over molecular sieve 3 Å		No
***n*-Pentane**	CMP Walther	Techn. grade	none	No
Tetrahydrofuran	VWR	HPLC grade	PS-MD-5, followed by distillation from Na	Yes
Toluene	Acros	99.85%, Extra dry, stored over molecular sieves	none	Yes
Water (for viscosity measurements)	Honeywell	Chromasolv™ Plus, HPLC grade	none	No

References

1 A. M. Coghill and L. R. Garson, Eds., *The ACS Style Guide: Effective Communication of Scientific Information*, American Chemical Society, Washington, DC, 3rd edn., 2006.
2 H.-S. Lin and L. A. Paquette, *Synth. Commun.*, 1994, **24**, 2503–2506.
3 J. Strueben, P. J. Gates and A. Staubitz, *J. Org. Chem.*, 2014, **79**, 1719–1728.
4 G. M. K. Hughes and B. C. Saunders, *J. Chem. Soc. Resumed*, 1954, **0**, 4630–4634.
5 J. Strüben, J. Hoffmann, D. Presa-Soto, C. Näther and A. Staubitz, *Acta Crystallogr. Sect. E Crystallogr. Commun.*, 2016, **72**, 1590–1594.
6 V. Passarelli, F. Benetollo, P. Zanella, G. Carta and G. Rossetto, *Dalton Trans.*, 2003, 1411–1418.
7 P. R. Dvornic and R. W. Lenz, *J. Appl. Polym. Sci.*, 1980, **25**, 641–652.
8 K. Röttger, S. Wang, F. Renth, J. Bahrenburg and F. Temps, *Appl. Phys- B Lasers Opt.*, 2015, **118**, 185–193.
9 S. Wang, S. Schatz, M. C. Stuhldreier, H. Böhnke, J. Wiese, C. Schröder, T. Raeker, B. Hartke, J. K. Keppler, K. Schwarz, F. Renth and F. Temps, *Phys. Chem. Chem. Phys.*, 2017, **19**, 30683–30694.
10 F. Renth, M. Foca, A. Petter and F. Temps, *Chem. Phys. Lett.*, 2006, **428**, 62–67.
11 F. Renth, R. Siewertsen, F. Strübe, J. Mattay and F. Temps, *Phys. Chem. Chem. Phys.*, 2014, **16**, 19556–19563.
12 I. H. M. Van Stokkum, D. S. Larsen and R. Van Grondelle, *Biochim. Biophys. Acta*, 2004, **1657**, 82–104.
13 E. R. Henry and J. Hofrichter, in *Essential Numerical Computer Methods,* ed. M. Johnson, 1st edn., 2010, pp. 81–139.

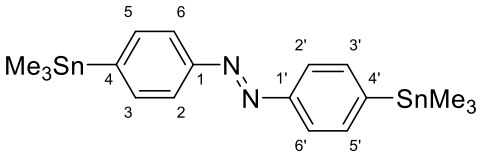
Synthetic Procedures

4,4'-Bis(iodo)azobenzene (S1)



This compound has been synthesised before,[3] the procedure was optimised as follows:
CuBr (7.24 g, 45.7 mmol) was dissolved in pyridine (90 mL), and stirred for 30 min, before the precipitate was removed by filtration. The filtrate was diluted with pyridine (20 mL). 4-Iodoaniline (14.3 g, 65.3 mmol) was added in one portion and the mixture was stirred for 20 h at 24 °C while bubbling air through the solution via a syringe (0.2 bar, 250 L/h, diameter: 1 mm). Hydrochloric acid (2 N, 200 mL) was added to the solution and the aqueous phase was extracted with diethyl ether (1 x 300 mL) and dichloromethane (2 x 200 mL). The combined organic phases were washed with hydrochloric acid (2 N, 2 x 200 mL) and the solvents were removed in vacuo. The crude solid product was purified by washing it with boiling ethanol (300 mL). After drying the product in vacuo, an orange solid was obtained without further purification (9.24 g, 21.3 mmol, 65%, Lit.:[3] 61%).
Mp: 237 °C (Lit.:[3] 210 °C, Lit.:[4] 237-238 °C).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, ^{3}J = 8.7 Hz, 4H, H-3,3',5,5'), 7.64 (d, ^{3}J = 8.7 Hz, 4H, H-2,2',6,6') ppm.
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 151.9 (C-1,1'), 138.6 (C-3,3',5,5'), 124.7 (C-2,2',6,6'), 98.3 (C-4,4') ppm.
IR (ATR): $\tilde{\nu}$ = 3079 (w), 1575 (m), 1561 (m), 1470 (m), 1393 (s), 1297 (s), 1280 (s), 1156 (m), 1097 (s), 1051 (s), 1002 (s), 833 (vs), 811 (vs), 714 (vs), 539 (vs), 525 (vs) cm^{-1}.
HRMS (EI-TOF) *m/z* (%): $[M]^+$ calcd. for $[C_{12}H_8N_2I_2]^+$ 433.8777, found 433.8767 (60), 230.94 (100) $[M-C_6H_4I]^+$, 202.93 (100) $[M-C_6H_4IN_2]^+$.
UV-VIS (acetonitrile, 25 °C): *E* isomer: $\lambda_{\pi-\pi^*}$ = 350 nm, $\lambda_{n-\pi^*}$ = 443 nm; PSS (365 nm): $\lambda_{\pi-\pi^*}$ = 301 nm, $\lambda_{n-\pi^*}$ = 442 nm; thermal half-life time *Z*→*E*: 65.5 ± 0.5 h.

4,4'-Bis(trimethylstannyl)azobenzene (1)



This compound has been before,[3] the procedure was optimised as follows:
Under a nitrogen atmosphere, 4,4''-bis(iodo-)azobenzene (**S1**, 1.30 g, 3.00 mmol), hexamethyldistannane (2.29 g, 7.00 mmol) and $[Pd(PPh_3)_4]$ (139 mg, 120 µmol, 4 mol%) were dissolved in toluene (18 mL) and THF (2 mL) in a microwave reaction vessel. The reaction mixture was heated for 30 min to 170 °C. Five such reaction batches were combined for the work-up. Then, the solvent was removed under reduced pressure followed by purification by column chromatography (eluent: *n*-pentane, R_f = 0.65). The product was obtained as orange solid (7.23 g, 14.3 mmol, 95%, Lit.:[3] 81%).
Mp: 54 °C (Lit.:[3] 54 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, ^{3}J = 8.2 Hz, 4 H, H-3,3',5,5'), 7.65 (d, ^{3}J = 8.2 Hz, 4 H, H-2,2',6,6'), 0.34 (s, 18 H, Sn(CH_3)$_3$) ppm.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 152.9 (C-4,4'), 147.2 (C-1, 1'), 136.6 (C-2,2',6, 6'), 122.1 (C-3,3',5,5'), −9.3 (Sn(CH_3)$_3$) ppm.

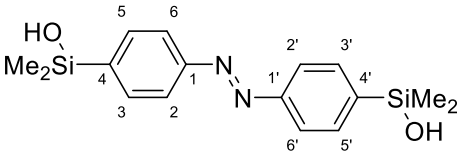
^{119}Sn{^{1}H} NMR (187 MHz, $CDCl_3$): δ = −25.03 ppm.

IR (ATR): $\tilde{\nu}$ = 3067 (w), 3024 (w), 2987 (w), 2917 (w), 1925 (w), 1437 (m), 1383 (m), 1306 (m), 1067 (m), 1011 (m), 831 (s), 761 (s), 583 (s), 508 (s) cm^{-1}.

HRMS (ESI-FTMS) *m/z*: $[M+H]^+$ calcd. for $[C_{18}H_{26}N_2Sn_2+H]^+$ 511.0213, found 511.0227.

UV-VIS (acetonitrile, 25 °C): *E* isomer: $\lambda_{\pi-\pi*}$ = 334 nm, $\lambda_{n-\pi*}$ = 443 nm; PSS (365 nm): $\lambda_{\pi-\pi*}$ = 289 nm, $\lambda_{n-\pi*}$ = 447 nm; thermal half-life time *Z*→*E*: 48.7 ± 1.2 h.

4,4'-Bis(hydroxydimethylsilane)azobenzene (2)



This compound has been synthesised before,[5] the procedure was optimised as follows:

Under argon atmosphere, 4,4'-bis(trimethylstannyl-)azobenzene (**1**, 3.00 g, 5.91 mmol) was dissolved in dry THF (70 mL). Methyl lithium (20 mL) was added at -78 °C. The orange solution turned dark and was stirred 15 min. Then, dichlorodimethylsilane (24 mL, 25.7 g, 199 mmol) was added. The reaction was allowed to warm to 25 °C by removing the cooling bath. The solvent and the excess of dichlorodi-methylsilane were removed *in vacuo*. The residual orange solid was dissolved in THF (40 mL) and added (rate: 1 mL/min) to a solution of sodium methoxide in methanol (13.5 mL of 4.5 N solution, diluted with 20 mL MeOH). Inert conditions were maintained until this point. The mixture was opened to air and a solution of sodium hydroxide in methanol and water (24 mL, 5 mol/L, MeOH:H_2O 10:1) was added. The resulting mixture was stirred 15 minutes, before a solution of sodium hydroxide in water (24 mL, 5 mol/L) was added. The reaction mixture was stirred 5 h, for all these steps, the temperature was held at 25 °C. This mixture was poured into a vigorously stirred solution of mono potassium phosphate in water (150 mL, 1 mol/L). The resulting solution was extracted with chloroform (4 x 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by solvent diffusion crystallisation: A saturated solution in chloroform was overlaid with *n*-hexane and cooled to -30 °C for 48 h. After three crystallisation cycles, the product was obtained as orange solid (845 mg, 2.56 mmol, 43%, Lit.:[5] 35%).

Mp.: T = 141 °C, Lit.:[5] 141 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, ^{3}J = 8.3 Hz, 4 H, H-3,3',5,5'), 7.75 (d, ^{3}J = 8.3 Hz, 4 H, H-2,2',6,6'), 1.99 (s, 1H, OH), 0.46 (s, 12 H, Si(CH_3)$_2$) ppm.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 153.6 (C-1,1'), 143.0 (C-4,4'), 134.0 (C-3,3'), 122.3 (C-2,2'), 0.2 (Si(CH_3)$_2$) ppm.

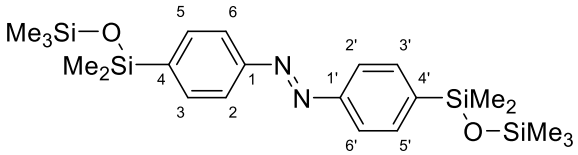
^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = 7.77 ppm.

IR (ATR): $\tilde{\nu}$ = 141 (m), 2956 (w), 1385 (m), 1251 (m), 1106 (w), 859 (s), 833 (s), 815 (s), 776 (s), 667 (s), 553 (s), 529 (m), 491 (m) cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]+ calcd. for $[C_{16}H_{22}N_2O_2Si_2]^+$ 330.12198, found 330.12163 (35), 151.06 (100) $[M\text{-}HOSi(CH_3)_2C_6H_4N_2]^+$.

UV-VIS (acetonitrile, 25 °C): *E* isomer: $\lambda_{\pi-\pi*}$ = 331 nm, $\lambda_{n-\pi*}$ = 444 nm; PSS (365 nm): $\lambda_{\pi-\pi*}$ = 291 nm, $\lambda_{n-\pi*}$ = 444 nm; thermal half-life time *Z*→*E*: 34.7 ± 0.3 h.

4,4'-Bis(1,1,3,3,3-pentamethyldisiloxanyl)azobenzene (5)



Compound **2** (100 mg, 303 µmol) was dissolved in dry DCM (2 mL), deprotonated with triethyl amine (90 µL, 67 mg, 670 µmol) and stirred at 0 °C for 1 h, before trimethylsilyl chloride (90 µL, 75 mg, 670 µmol) was added and the mixture was stirred at 0 °C for another 2 h. The reaction mixture was diluted with dry *n*-hexane and filtered through celite. After column chromatography (DCM:*n*-hexane 10:90), the product was obtained as orange liquid (102 mg, 216 µmol, 71%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (d, ^{3}J = 8.2 Hz, 4 H, H-2,2',6,6'), 7.70 (d, ^{3}J = 8.2 Hz, 4 H, H-3,3',5,5'), 0.36 (s, Si-(CH_3)$_2$, 12 H), 0.11 (s, 18H) ppm.

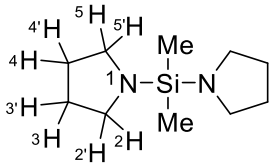
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 153.4 (C-1,1'), 144.1 (C-4,4'), 133.9 (C-3,3',5,5'), 122.1 (C-2,2',6,6'), 2.1 (Si-(CH_3)$_3$), 1.0 (Si-(CH_3)$_2$) ppm.

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = 9.2 (*Si*-(CH_3)$_3$), -2.6 (*Si*-(CH_3)$_2$) ppm.

IR (ATR): $\tilde{\nu}$ = 3025 (w), 2957 (m), 2898 (w), 1591 (w), 1387 (w), 1252 (s), 1110 (s), 1043 (vs), 1014 (s), 835 (vs), 798 (vs), 780 (vs), 751 (s), 686 (s), 611 (m), 556 (m), 529 (m) cm^{-1}.

HRMS (EI-TOF) *m/z*: $[M]^+$ (%) calcd. for $[C_{22}H_{38}N_2O_2Si_4]^+$ 474.20103, found 474.20058 (40), 147.06 (100) $[Si(CH_3)_3\text{-}O\text{-}Si(CH_3)_2]^+$.

Bis(pyrrolidin-1-yl)dimethylsilane (S2)



This reaction was performed entirely under nitrogen atmosphere. To a solution of dichlorodimethylsilane (80.0 mL, 85.6 g, 663 mmol) in *n*-hexane (150 mL), pyrrolidine (230 mL, 196 g, 2.76 mol) was added dropwise over the course of 1 h at 0 °C. After completion of the addition, the ice bath was removed and the reaction was stirred for 15 h. A precipitate of the amino hydrochloride, which had formed, was removed by filtration under inert conditions. The liquid was placed in a J. Young's flask and the remaining solvent was removed *in vacuo*. A colourless liquid (116 g, 585 mmol, 88%, Lit.:[6] 95%) was obtained.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.93 – 2.88 (m, 8 H, H-2,2',5,5'), 1.67 – 1.62 (m, 8 H, H-3,3',4,4'), 0.04 (s, 6 H, Si-CH_3) ppm.

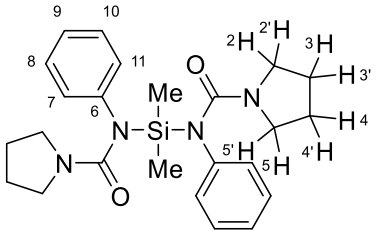
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 46.8 (C-2,5), 26.9 (C-3,4), -3.3 (Si-CH_3) ppm

^{29}Si{^{1}H} NMR (187 MHz, $CDCl_3$): δ = -8.11 ppm.

HRMS (ESI-FTMS): *m/z*: $[M+H]^+$ calcd. for $[C_{10}H_{23}N_2{}^{28}Si]^+$ 199.16250; found 199.16255.

Elem. Anal. Calcd. for $C_{10}H_{22}N_2Si$: C 60.54, H 11.18, N 14.12; found: C 60.61, H 11.27, N 14.27.

Bis(*N*-phenyl-*N*-pyrrolidinecarbonylamino)dimethylsilane (4)



The reaction was performed entirely under inert conditions. Bis(pyrrolidinyl)dimethyl silane (**S2**, 40.0 g, 201 mmol) was dissolved in dry diethyl ether (250 mL) and cooled in an ice bath to 0 °C. Then phenyl isocyanate (45.0 mL, 49.3 g, 410 mmol) was added dropwise at 0 °C over the course of 3 h and the reaction mixture was allowed to warm to 25 °C over the course of 15 h. The white precipitate of bis(*N*-phenyl-*N*'-pyrrolidinyl)dimethylsilane was collected by filtration under inert conditions. The product was washed with dry diethyl ether (20 mL) and dried at 0.05 mbar for 12 h to receive the product as colourless solid (79.6 g, 182 mmol, 91%, Lit.:[7] 85%).

Mp.: T = 72 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 – 7.15 (m, H-8,10), 7.07 (t, ^{3}J = 7.5 Hz, 2 H, H-9,9'), 6.95 – 6.91 (m, 4 H, H-7,11), 2.88 (m, 8 H, H-2,5), 1.58 (m, 8 H, H-3,4), 0.37 (s, 6 H, Si-CH_3) ppm.

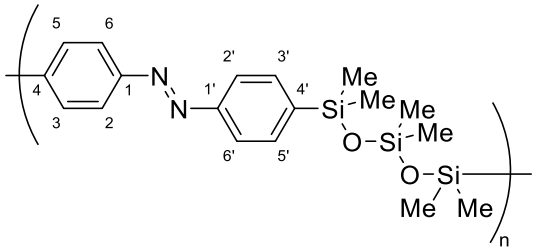
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 159.7 (*C*=O), 143.0 (C-6), 128.9 (C-7,11), 128.5 (C-8,10), 125.1 (C-9), 47.7 (C-2,5), 25.4 (C-3,4), -1.5 (Si-*C*H_3) ppm.

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = -3.57 ppm.

HRMS (ESI): Despite inert sample preparation, no traces of the $[M+H]^+$ peak could be detected. Instead, the free urea ligand was found: *m/z (%)*: $[M+H]^+$ calcd. for $[C_{11}H_{14}N_2O+H]^+$ 191.11789; found 191.11789 (90); $[M+K]^+$ calcd. for $[C_{11}H_{14}N_2O+K]^+$ 229.07377; found 229.07381 (100).

Elem. Anal. Calcd. for $C_{25}H_{35}N_4O_2Si$: C 66.48, H 7.81, N 12.40, O 7.08; found: C 66.60, H 7.90, N 12.56, O 7.13.

Poly(4,4'-azobenzene-*alt*-hexamethyl-trisiloxane) (6)



This reaction was performed in a nitrogen filled glove box. 4,4'-bis(Hydroxydimethylsilane)-azobenzene (**2**, 317 mg, 960 µmol), was dissolved in chlorobenzene (2 mL). A solution of bis(*N*-phenyl-*N*-pyrrolidinecarbonylamino)dimethyl silane (419 mg, 960 µmol) in chlorobenzene (8 mL) was added with a rate of 0.015 mL/min at -45 °C. The solution was stirred for 5 d at 25 °C, while the reaction progress was monitored by GPC. Once the retention volume measured by GPC remained unchanged, the solvent was evaporated and the polymer was purified by dissolving it in THF and precipitation into methanol (10 fold excess) for three times. The product was obtained as orange solid (227 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, ^{3}J = 8.2 Hz, 4 H, H-2,2'), 7.69 (d, ^{3}J = 8.2 Hz, 4 H, H-3,3'), 0.40 – 0.35 (m, 12 H, C-Si(CH_3)$_2$-O), 0.11 – 0.07 (m, 6H, O-Si(CH_3)$_2$-O) ppm.
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 153.4 (C-1,1'), 143.6 (C-4,4'), 134.0 (C-3,3'), 122.1 (C-2,2'), 1.5 (C-Si(CH$_3$)$_2$-O), 0.9 (O-Si(CH$_3$)$_2$-O) ppm.
^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = -2.33 (C-Si(CH$_3$)$_2$-O), -18.93 (O-Si(CH$_3$)$_2$-O) ppm.
IR (ATR): $\tilde{\nu}$ = 3026 (w), 2958 (m), 1591 (w), 1386 (w), 1257 (s), 1161 (w), 1109 (s), 1030 (vs), 1012 (s), 958 (w), 835 (s), 817 (s), 781 (vs), 720 (m), 702 (m), 686 (m), 665 (m), 623 (m), 555 (s), 528 (m) cm^{-1}.
GPC (THF, 1 mL/min, conv. calibration (PS), ambient light): M_n = 25.9 kDa; M_w = 50.6 kDa; PDI = 1.95.

Investigation of the Switching Behaviour of the Monomers and the Polymer

^{1}H NMR measurements: PSS and DOSY

Similar to the GPC analysis, the sample solutions were measured directly after dissolving and after irradiation with UV light for 90 minutes (PSS-365). To compare the data with the results from GPC and ultrafast measurements, three different solvents were used: chloroform-*d*, THF-d_8 and *n*-hexane-d_{14}. In chloroform and THF, the sample concentration was approx. 3 mg/mL., As the polymer tends to form aggregates in *n*-hexane, the sample concentration was reduced to 0.3 mg/mL.

For the analysis of the composition and the diffusion constants, the signals corresponding to the aromatic azobenzene units were used. In all three solvents, the polymer's azo groups were found to be almost quantitatively (min. 98%) in the *E*-form at ambient conditions. In the PSS, the *Z*-isomer was enriched to 50% (*n*-hexane), 58% (THF) and 67% (chloroform). In the "all-*E*-state", the polymer's signals showed negligible line broadening due to the geometric regularity of the adjacent monomers. Upon switching, the local environment of each azobenzene unit varied, leading to significant line broadening. The diffusion constants were obtained using the T1/T2 fitting with the "Topspin 4" software. In the PSS, the diffusion constant and thus the hydrodynamic radii differ significantly from the values before UV irradiation. However, the signals of *E*- and *Z*-azobenzene units show the same diffusion behaviour, indicating an incomplete switching of the azobenzene units in each chain. For plotting, the data were treated with the dosy2d command.

The hydrodynamic radii *r* were calculated using the Stokes-Einstein equation with the diffusion constant *D*, Boltzmann constant k_B, Temperature $T = 298\ K$ and the dynamic viscosity η:

$$r = \frac{k_B T}{6\pi\eta D}$$

To determine the dynamic viscosities η of the deuterated solvents, a capillary viscometer with a capillary constant $K = 6.25\ 10^{-9}\ m^2/s^2$[a] was used. The solvents' flow time *t* was measured and the viscosities could be calculated by multiplication of the flow time with the capillary constant *K* and the solvents density ρ[b]:

$$\eta = \rho \times K \times t$$

The calculated radii *r* were used to calculate the corresponding hydrodynamic volumes:

$$V = \frac{4}{3}\pi r^3$$

Table S1 Measured viscosities of the deuterated solvents that were used in ^{1}H DOSY NMR measurements. Capillary constant $K = 6.25\ 10^{-9}\ m^2/s^2$. The temperature was 298 K. Flow times are averages of five measurements; the standard deviation for the last counting digit is given in brackets.

Solvent	**Density[c]** ρ **/ kg m^{-3}**	**Flow time** t **/ s**	**Viscosity** η **/ 10^{-4} Pa s**
Chloroform-*d*	1500	56.5 (6)	5.30 (5)
THF-d_8	985	78.6 (7)	4.84 (4)
***n*-Hexane-d_{14}**	767	62.8 (3)	3.01 (1)

Table S2 Overview of ^{1}H DOSY NMR results of the disiloxane functionalised azobenzene **5**. Under the given irradiation conditions, the diffusion constants were determined for aromatic signals assigned to *E* and *Z* iso-

[a] Determined by calibration measurements with water. (20 °C, kinematic viscosity ν = 10^{-6} m^2/s).

[b] As provided by the supplier.

[c] As provided by the supplier.

mers and used to calculate the corresponding hydrodynamic volume via the hydrodynamic radius. The ratio between *E*- and *Z*-azobenzene was determined by integration of the aromatic signals.

No.	Solvent	Irradiation	Diffusion constant / 10^{-10} m^2/s		Hydrodynamic radius / nm		Hydrodynamic volume / nm^3		*E*:*Z* Ratio
			***E*-Azo**	***Z*-Azo**	***E*-Azo**	***Z*-Azo**	***E*-Azo**	***Z*-Azo**	
1	$CDCl_3$	None	7.77	-	0.530	-	0.625	-	98:2
2	$CDCl_3$	PSS-365	7.46	8.67	0.552	0.475	0.705	0.450	33:67
3	THF	None	8.52		0.529	-	0.620	-	96:4
4	THF	PSS-365	8.65	9.11	0.521	0.495	0.593	0.508	36:64
5	Hexane	None	13.4	-	0.543	-	0.669	-	95:5
6	Hexane	PSS-365	13.6	14.9	0.532	0.486	0.630	0.479	54:46

Table S3 Overview of ^{1}H DOSY NMR results of the azobenzene-trisiloxane copolymer **6**. Under the given irradiation conditions, the diffusion constants were determined for aromatic signals assigned to *E* and *Z* isomers and used to calculate the corresponding hydrodynamic volume via the hydrodynamic radius. The ratio between *E*- and *Z*-azobenzene was determined by integration of the aromatic signals.

No.	Solvent	Irradiation	Diffusion constant / 10^{-10} m^2/s		Hydrodynamic radius / nm		Hydrodynamic volume / nm^3		*E*:*Z* Ratio
			***E*-Azo**	***Z*-Azo**	***E*-Azo**	***Z*-Azo**	***E*-Azo**	***Z*-Azo**	
1	$CDCl_3$	None	0.928	-	4.44		366		98:2
2	$CDCl_3$	5 min UV	1.02	1.10	4.05	3.75	278	221	60:40
3	$CDCl_3$	7 min UV	1.03	1.09	4.01	3.78	270	227	47:53
4	$CDCl_3$	11 min UV	1.03	1.07	4.00	3.86	267	242	36:63
5[a]	$CDCl_3$	90 min UV	1.05	1.07		3.89		246	33:67
6[a]	$CDCl_3$	20 min blue	0.979	0.995		4.20		310	86:14
7	THF	None	1.02	-	4.42	-	363	-	100:0
8[a]	THF	90 min UV	1.09	1.13		4.05		279	42:58
9	Hexane	None	2.32	-	3.13	-	128	-	100:0
10[a]	Hexane	90 min UV	3.64	3.26		2.10		39	50:50

a) The diffusion rates corresponding to the *E* and *Z* signals in the ^{1}H NMR spectrum were averaged to calculate the hydrodynamic radius and volume.

GPC measurement

The polymer was dissolved in THF (ca. 1 mg/mL) in a brown-glass GC vial and immediately, the GPC run was performed. Determination of the molecular weights was performed using a refraction index detector by conventional calibration. Linear poly(styrene) with narrow PDI standards were used for calibration. For switching, a stock solution of the polymer was prepared (1 mg/mL) and split into four samples. These samples were measured without irradiation, before the sample solutions were transferred to UV cuvettes and subjected to UV light (365 nm) for 90 minutes, before each sample was measured again. The results were averaged and the standard deviation was derived. The number

average molecular weight (M_n) decreased from 25.9 ± 0.5 to 19.4 ± 0.8 kDa, the weight average molecular weight (M_W) decreases from 50.6 ± 0.8 to 37.2 ± 1.9 kDa (Figure S1).

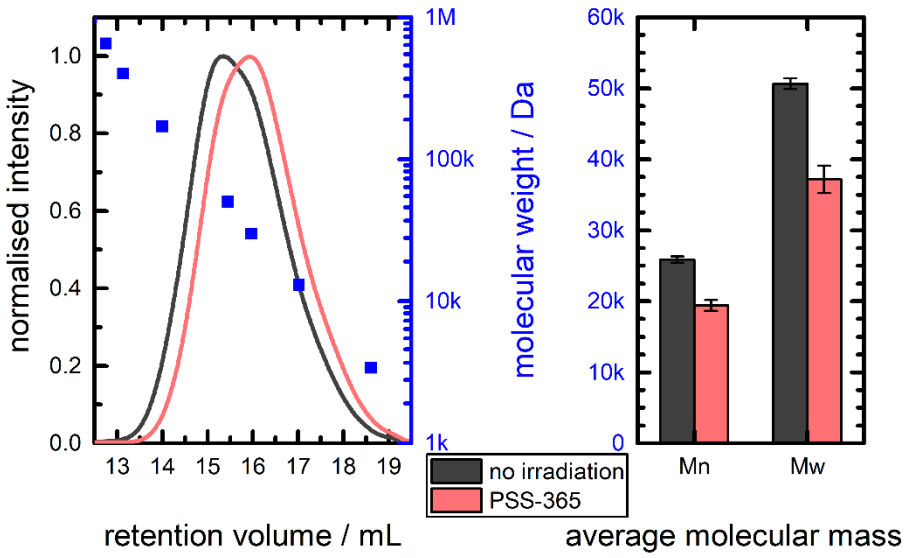


Figure S1 GPC results of switching the polymer **6**. Left: GPC traces (THF, 1 mL/min) of the polymer **6** before (grey) and after (light red) irradiation with UV light (365 nm) for 90 min. The curves are averaged over four measurements and normalised for better clarity. Black squares represent narrow polystyrene standards that were used for the calibration. For the corresponding molecular weight see the right Y-axis. Right: Comparison of the apparent molecular weights of the **6** sample before (grey) and after (light red) irradiation. The number average molecular weight (M_n) decreased from 25.9 ± 0.5 to 19.4 ± 0.8 kDa, the weight average molecular weight (M_W) decreases from 50.6 ± 0.8 to 37.2 ± 1.9 kDa. The error bars indicate the standard deviation

Femtosecond Transient Electronic Absorption Spectroscopy (TEAS)

The setup for transient electronic absorption spectroscopy was based on a regeneratively amplified Ti:Sa laser system (Clark MXR CPA 2001) and has been described before.[8–11] Pulses for the excitation of the azobenzene chromophores at λ_{exc} = 320 nm with < 100 fs pulse duration (FWHM) were generated by frequency doubling of compressed 640 nm pulses from a non-collinear optical parametric amplifier. For broadband detection in a range of λ_{probe} = 325 – 675 nm, spectrally broad pulses were obtained by supercontinuum generation (SCG) in a 1 mm CaF_2 plate using the 775 nm Ti:Sa laser fundamental, split into probe and reference beams and focused into the sample cell so that the probe and pump beams overlapped spatially. Spectrally resolved detection was done using a prism spectrograph equipped with two fast frame transfer CCD cameras (S7030-0906, Hamamatsu). The molecules were excited with pump energies of 250 nJ/pulse under magic angle conditions, i.e., rotating the relative angle between the polarization of the pump and probe beams to 54.7° using a Berek variable wave plate. All measurements were done at room temperature using solutions with an optical density of ~0.3 in *n*-hexane (UVASOL®, purity > 99 %) as solvent and pumped through a home-built flow cell with an optical path length of 1 mm to avoid accumulation of the photo product.

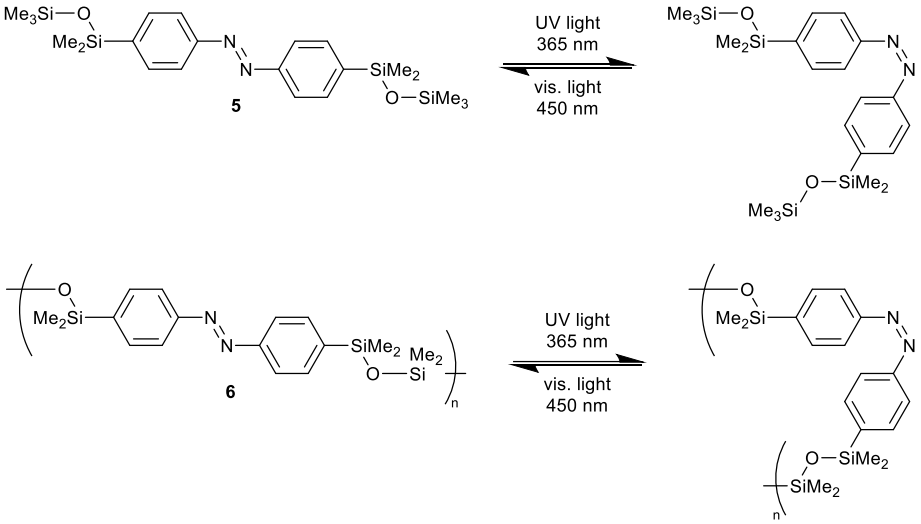
SVD-based global analysis of the transient electronic absorption data

The quantitative analysis of the transient electronic absorption data was based on the singular value decomposition (SVD) of the time-zero corrected data matrices,[12] where background and solvent contributions had been subtracted before. The SVD of the pre-processed data matrix D is given by

$$\boldsymbol{D} = \boldsymbol{USV^T},$$

where the columns of the matrices $\boldsymbol{U}$ and $\boldsymbol{V}$ correspond to orthonormal SVD time traces $\boldsymbol{U_i}(t)$ and SVD spectra $\boldsymbol{V_i}(\lambda)$, and $\boldsymbol{S}$ is a diagonal matrix containing the non-negative singular values $\boldsymbol{s_i}$ in decreasing order.[12,13] The number of relevant SVD components *n*, which identifies the number of recoverable spectroscopical species within the experimental errors, was determined using a scree plot of the singular values, by inspection of the SVD time traces and SVD spectra, and by checking the reconstructed reduced transient absorption matrices of rank *n* versus the input data matrices for remaining systematic deviations. The optimal global decay time constants and corresponding decay-associated difference spectra (DADS) describing the data were then extracted by simultaneous non-linear least-squares fitting to the SVD time profiles using a sum of exponential decay functions convoluted with the instrument response function (IRF) and a convoluted step function corresponding to a decay time of infinity to account for the permanent absorption changes.

Photostability tests of compound 5 and polymer 6



The concentration of **5** and **6** in the NMR measurements was approximately 0.5 mg/mL, the irradiation times for the alternating irradiation with 365 nm and 450 nm light were three minutes for each cycle.

Cyclic UV-Vis measurements of polymer 6

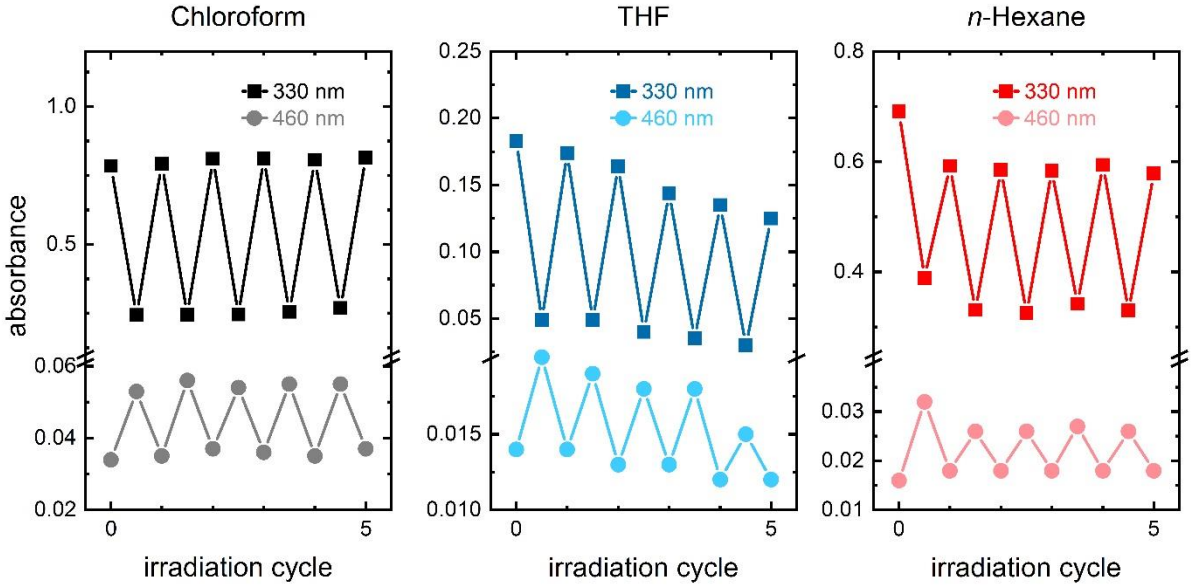


Figure S2. Photoswitching and photostability of polymer **6** as monitored by UV-VIS spectroscopy. The symbols show the normalised absorbances at 330 nm and 460 nm obtained after alternating irradiation of polymer **6** with 365 nm and 450 nm light into the respective photostationary states in chloroform (left panel, black), THF (center panel, blue) and *n*-hexane (right panel, red). The chosen wavelengths represent the absorption behaviour of the S_2 ($\pi\pi^*$) bands (dark squares) and S_1 ($n\pi^*$) bands (light circles). The first symbol corresponds to the thermal equilibrium, thereafter each cylce consists of two data points representing the PSS_{365} and PSS_{450}, respectively.

Repeated switching cycles of compound 5 by irradiation with 365 nm and 450 nm light monitored by ^{1}H NMR measurements

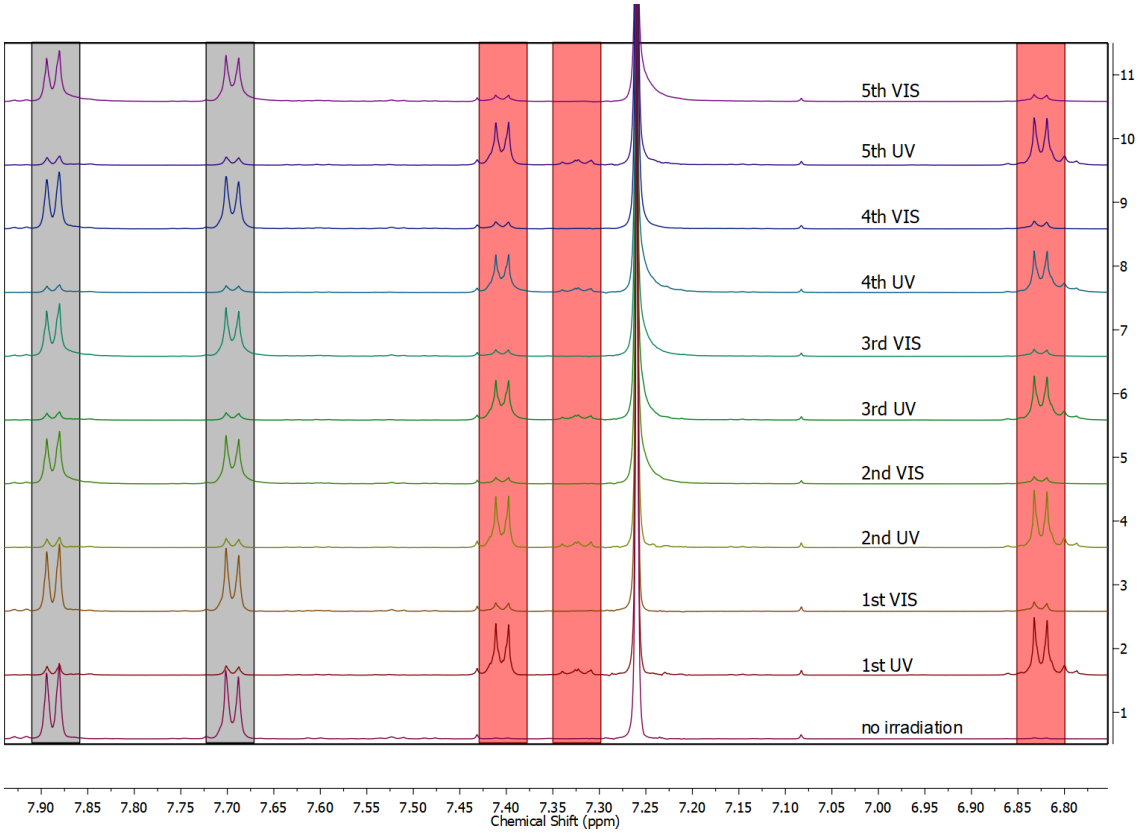


Figure S3. Aromatic region of the ^{1}H NMR spectra of **5** before and after alternating irradiation into the PSS with 365 nm and 450 nm light. Signals corresponding to *E*-isomers are highlighted in grey, signals of *Z*-isomers are highlighted in pink.

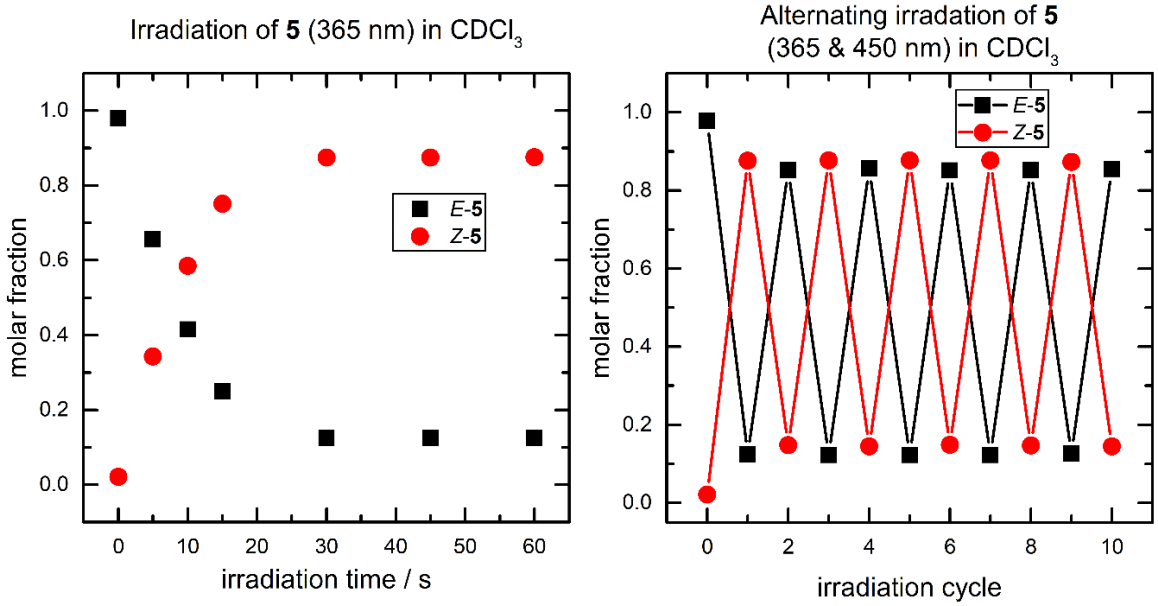


Figure S4. Left: molar fractions of *E*-isomers of **5** (black squares) and *Z*-isomers of **5** (red circles) for a series of consecutive irradiations with 365 nm light in $CDCl_3$. **Right**: molar fractions of *E*-isomers of **5** (black squares) and *Z*-azobenzene units of **5** (red circles) upon alternating irradiation with 365 nm light and 450 nm light.

Repeated switching cycles of polymer 6 by irradiation with 365 nm and 450 nm light monitored by ^{1}H NMR measurements

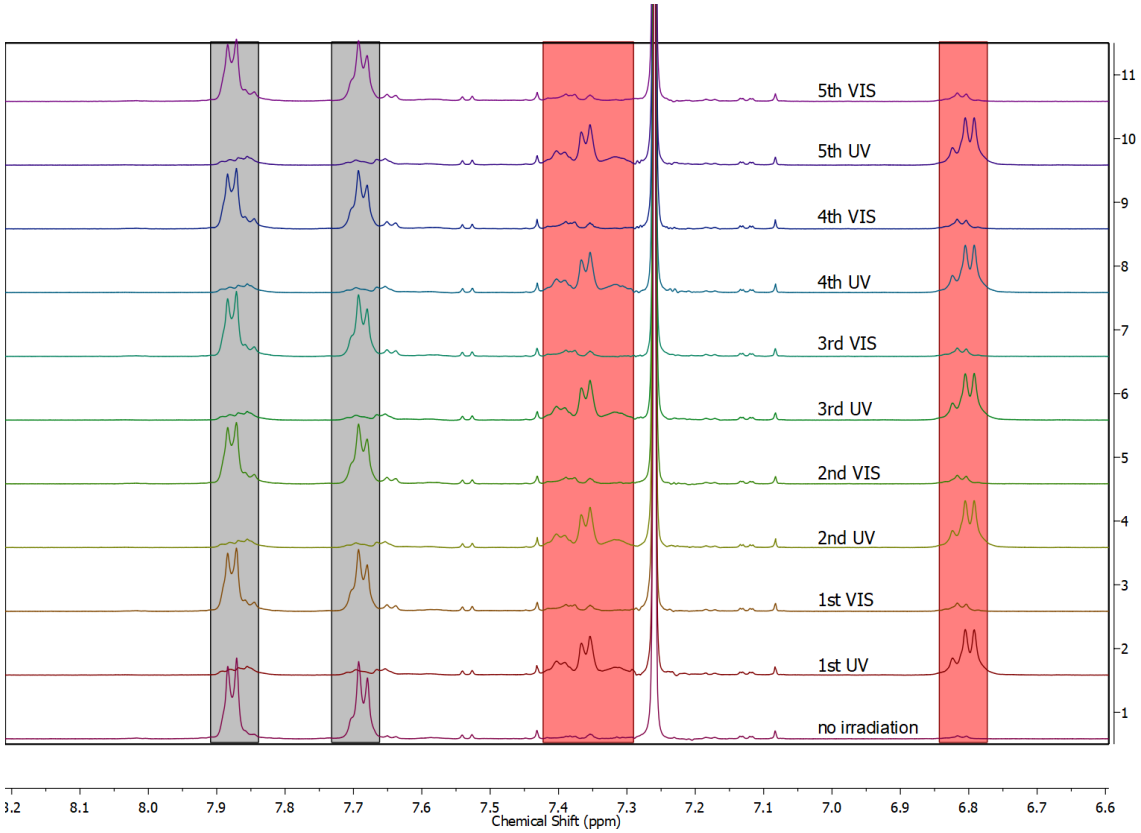


Figure S5. Aromatic region of the ^{1}H NMR spectra of **6** before and after alternating irradiation into the PSS_{365} and PSS_{450}. Signals corresponding to *E*-isomers are highlighted in grey, signals of *Z*-isomers are in pink.

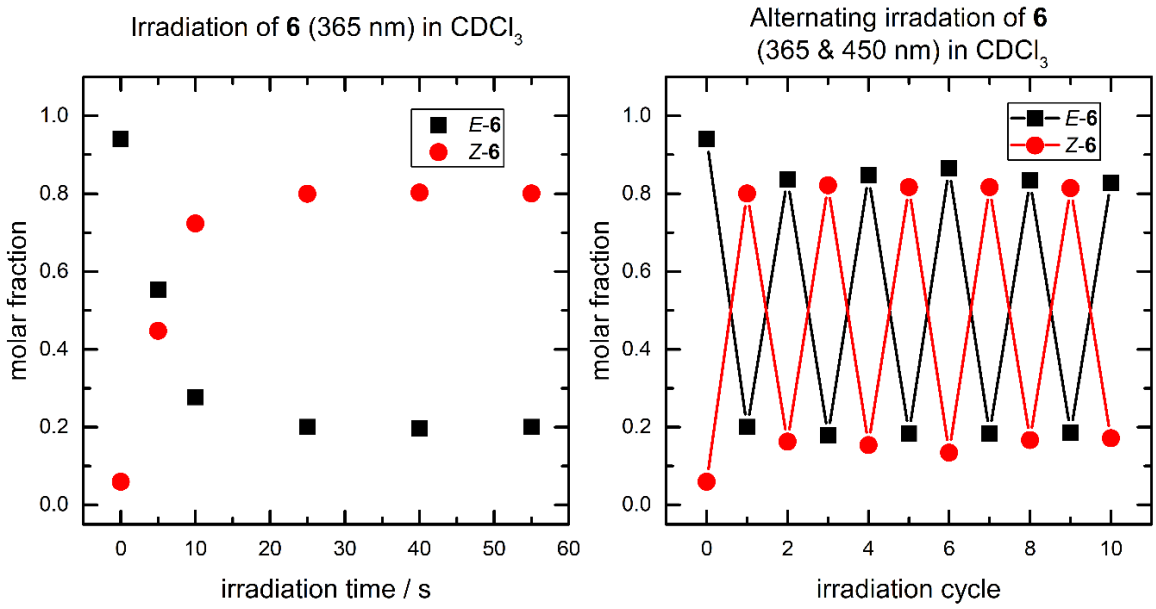


Figure S6. Left: molar fractions of *E*-azobenzene units of **6** (black squares) and *Z*-azobenzene units of **6** (red circles) for a series of consecutive irradiations with 365 nm light in $CDCl_3$. **Right**: molar fractions of *E*-azobenzene units of **6** (black squares) and *Z*-isomer units of **6** (red circles) upon alternating irradiation (365 nm and 450 nm light).

Supplementary Plots of UV-VIS Spectra of all Azobenzene Derivatives

4,4'-Bis(iodo)azobenzene in acetonitrile

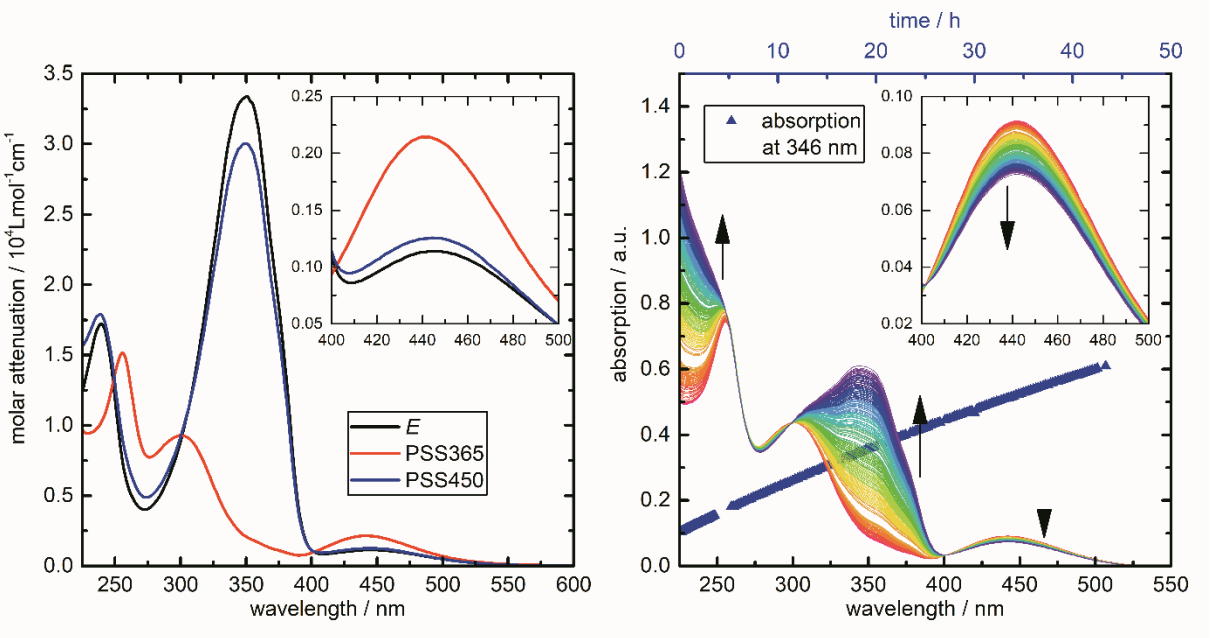


Figure S7. UV-VIS analysis of 4,4'bis(iodo)azobenzene. Left: absorption spectra of the molecule without irradiation (black), of the PSS after irradiation with UV light (365 nm) (red) and of the PSS after irradiation with blue light (450 nm) (blue). Right: thermal relaxation after irradiation with UV light. Red represents the starting point, violet represents the end point. The spectra were recorded with a delay of 15 min over the course of 44 h. The time profile of the thermal relaxation of the ππ band is shown as blue triangles and was used to determine the half-life time via an exponential fit to be 65.5 ± 0.5 h. Arrows indicate the change in absorption of the nn* (<250 nm), ππ* (ca. 350 nm) and nπ* (ca.450 nm) bands.

4,4'-Bis(trimethylstannyl)azobenzene (1) in acetonitrile

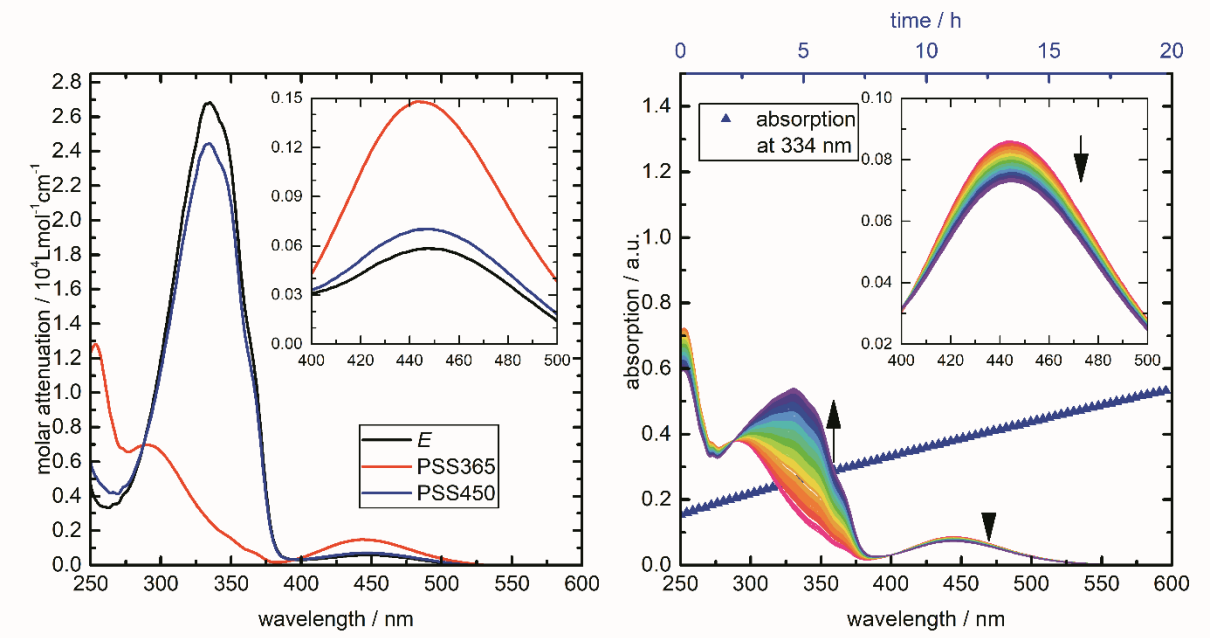


Figure S8. UV-VIS analysis of 4,4'bis(trimethylstannyl)azobenzene (**1**). Left: absorption spectra of the molecule without irradiation (black), of the PSS after irradiation with UV light (365 nm) (red) and of the PSS after irradiation with blue light (450 nm) (blue). Right: thermal relaxation after irradiation with UV light. Red represents the starting point, violet represents the end point. The spectra were recorded with a delay of 15 min over the course of 20 h. The time profile of the thermal relaxation of the ππ band is shown as blue triangles and was used to determine the half-life time via an exponential fit to be 48.7 ± 1.2 h. Arrows indicate the change in absorption of the ππ* (ca. 330 nm) and nπ* (ca.450 nm) bands.

4,4'-Bis(hydroxydimethylsilane)azobenzene (2) in acetonitrile

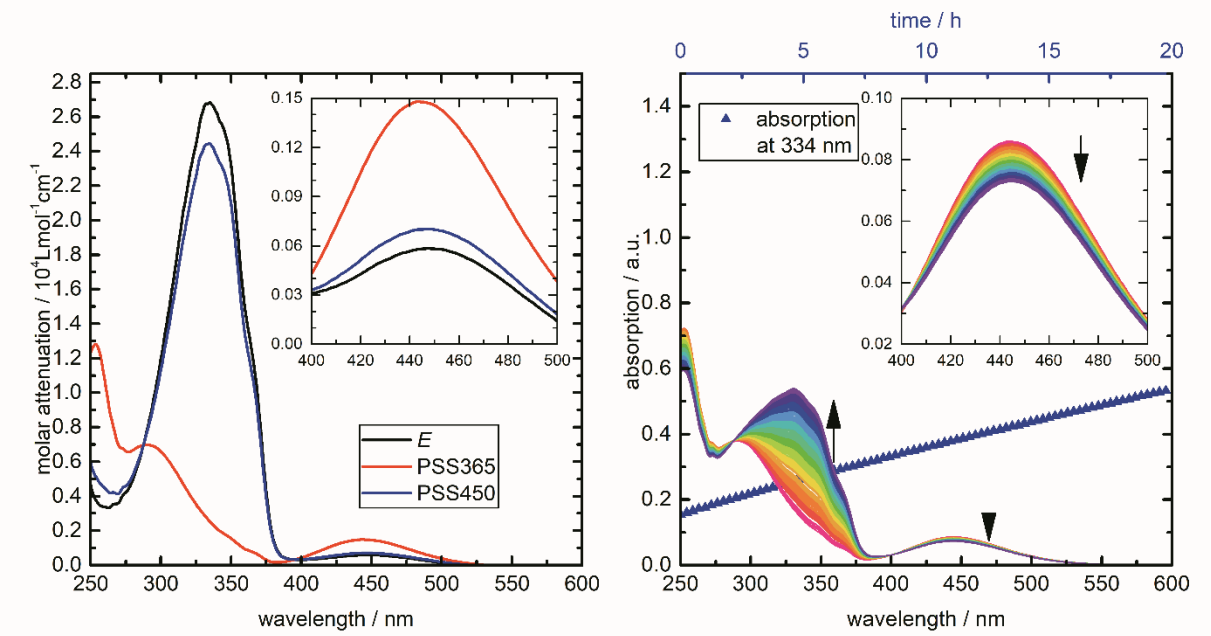


Figure S9. UV-VIS analysis of 4,4'bis(hydroxydimethylsilane)azobenzene (**2**). Left: absorption spectra of the molecule without irradiation (black), of the PSS after irradiation with UV light (365 nm) (red) and of the PSS after irradiation with blue light (450 nm) (blue). Right: thermal relaxation after irradiation with UV light. Red represents the starting point, violet represents the end point. The spectra were recorded with a delay of 15 min over the course of 11.5 h. The time profile of the thermal relaxation of the ππ band is shown as blue triangles and was used to determine the half-life time via an exponential fit to be 34.7 ± 0.3 h. Arrows indicate the change in absorption of the ππ* (ca. 330 nm) and nπ* (ca.450 nm) bands.

4,4'-Bis(1,1,3,3,3-pentamethyldisiloxanyl)azobenzene (5) in *n*-hexane

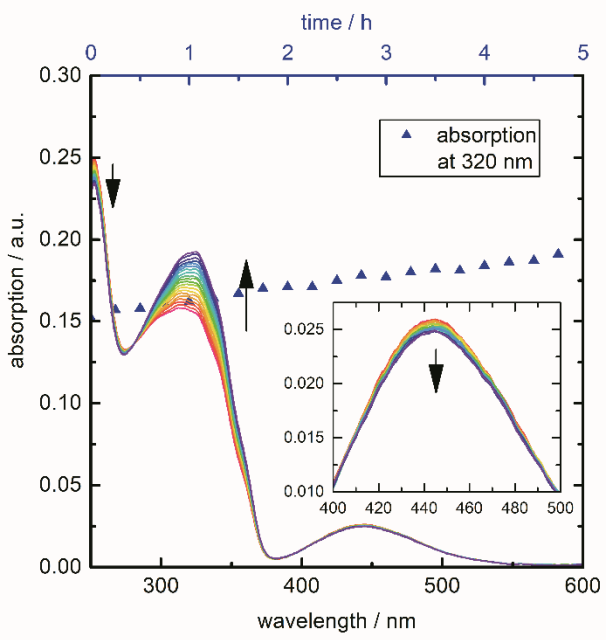


Figure S10. UV-VIS analysis of 4,4'-Bis(1,1,3,3,3-pentamethyldisiloxanyl)azobenzene (**5**) in *n*-hexane. Thermal relaxation after irradiation with UV light. Red represents the starting point, violet represents the end point. The spectra were recorded with a delay of 15 min over the course of 5 h. The time profile of the thermal relaxation of the $\pi\pi$ band is shown as blue triangles and was used to determine the half-life time via an exponential fit to be 15 ± 2 h. Arrows indicate the change in absorption of the $\pi\pi^*$ (ca. 330 nm) and $n\pi^*$ (ca.450 nm) bands.

Poly(4,4'-azobenzene-*alt*-hexamethyl-trisiloxane) (6) in *n*-hexane

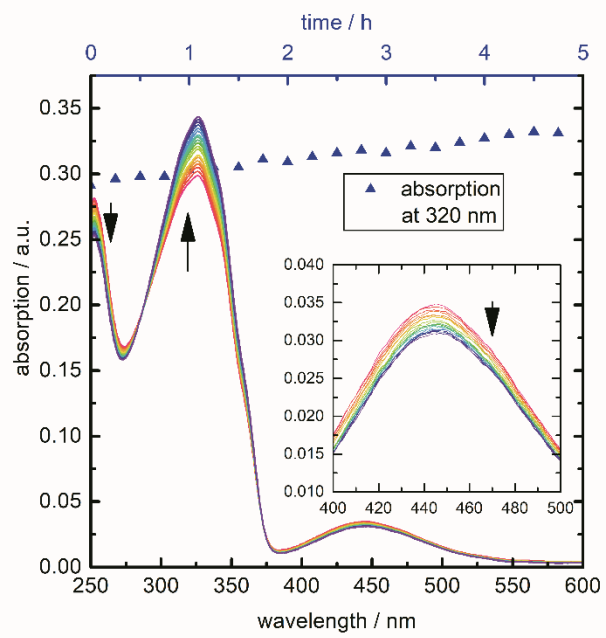
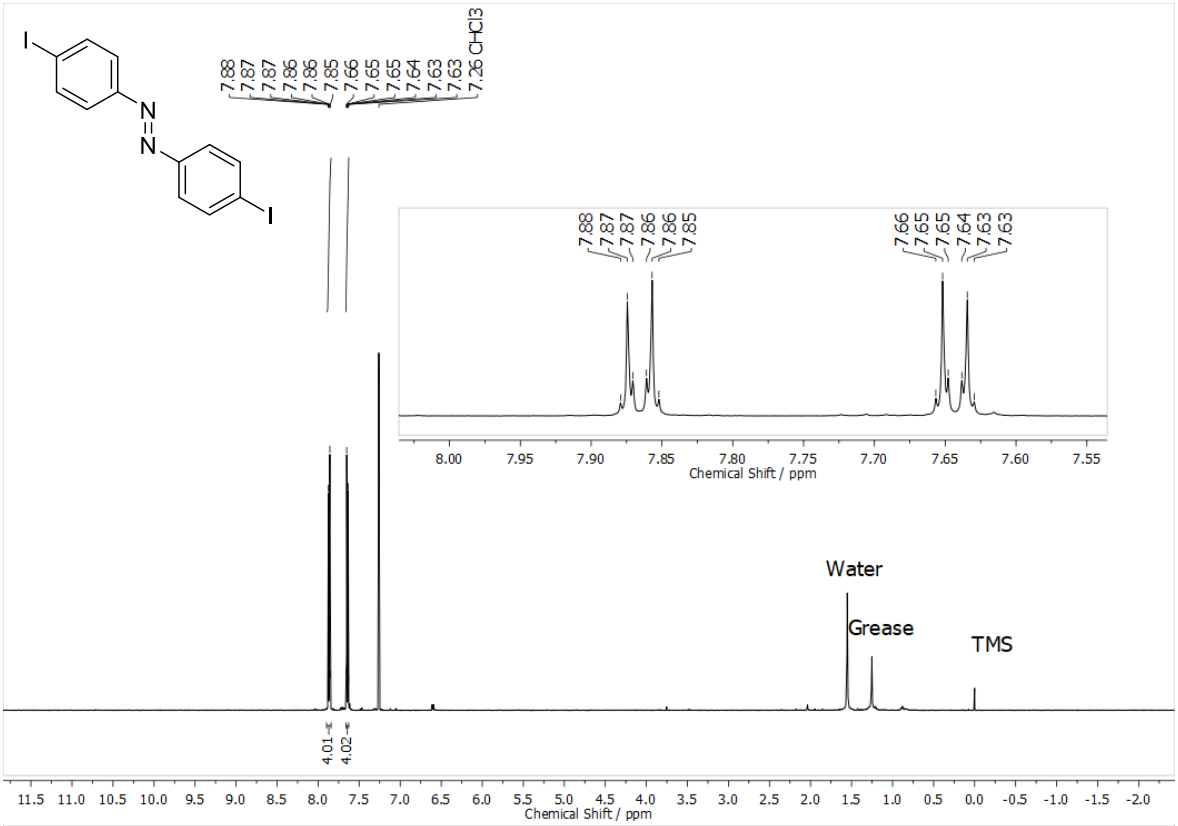
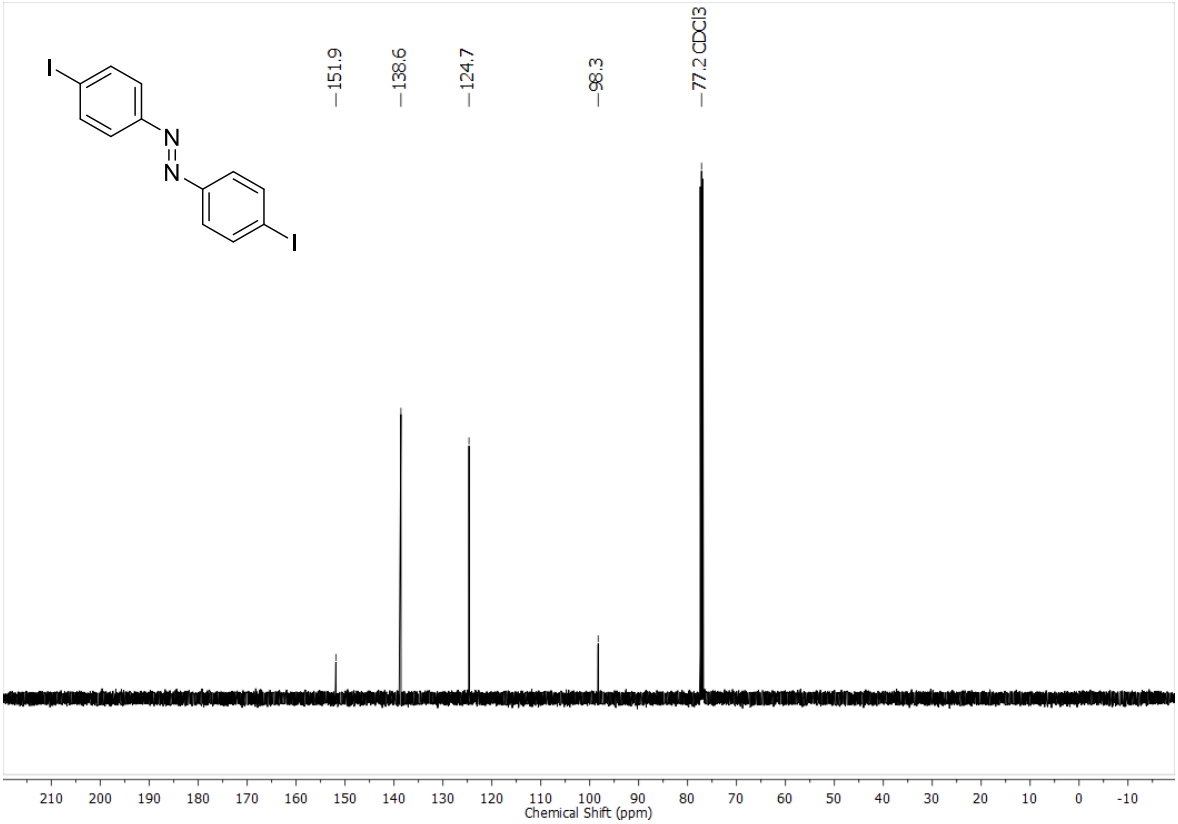


Figure S11. UV-VIS analysis of Poly(4,4'-azobenzene-*alt*-hexamethyl-trisiloxane) (**6**) in *n*-hexane. Thermal relaxation after irradiation with UV light. Red represents the starting point, violet represents the end point. The spectra were recorded with a delay of 15 min over the course of 5 h. The time profile of the thermal relaxation of the $\pi\pi$ band is shown as blue triangles and was used to determine the half-life time via an exponential fit to be 25 ± 2 h. Arrows indicate the change in absorption of the $\pi\pi^*$ (ca. 330 nm) and $n\pi^*$ (ca.450 nm) bands.

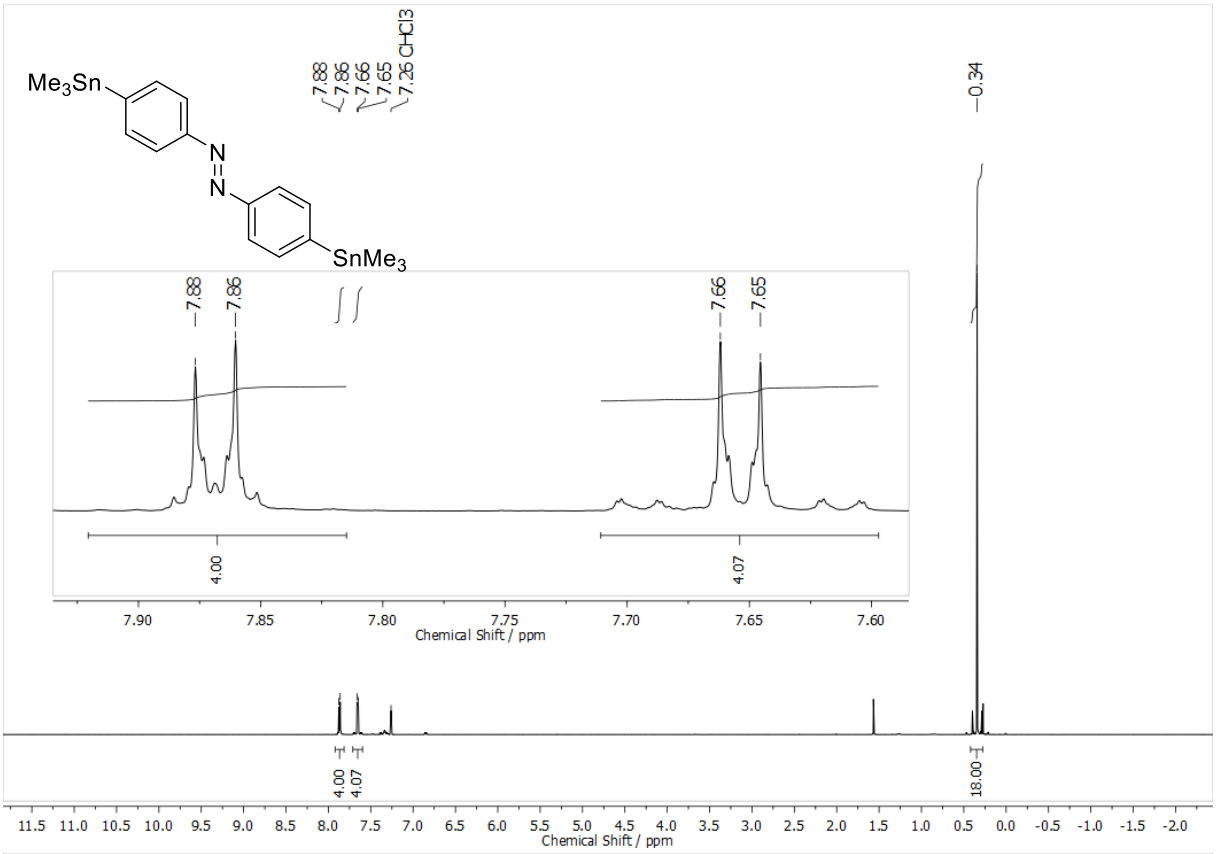
Plotted ^{1}H, $^{13}C\{^{1}H\}$ NMR and $^{29}Si\{^{1}H\}$ or $^{119}Sn\{^{1}H\}$ NMR spectra for all compounds

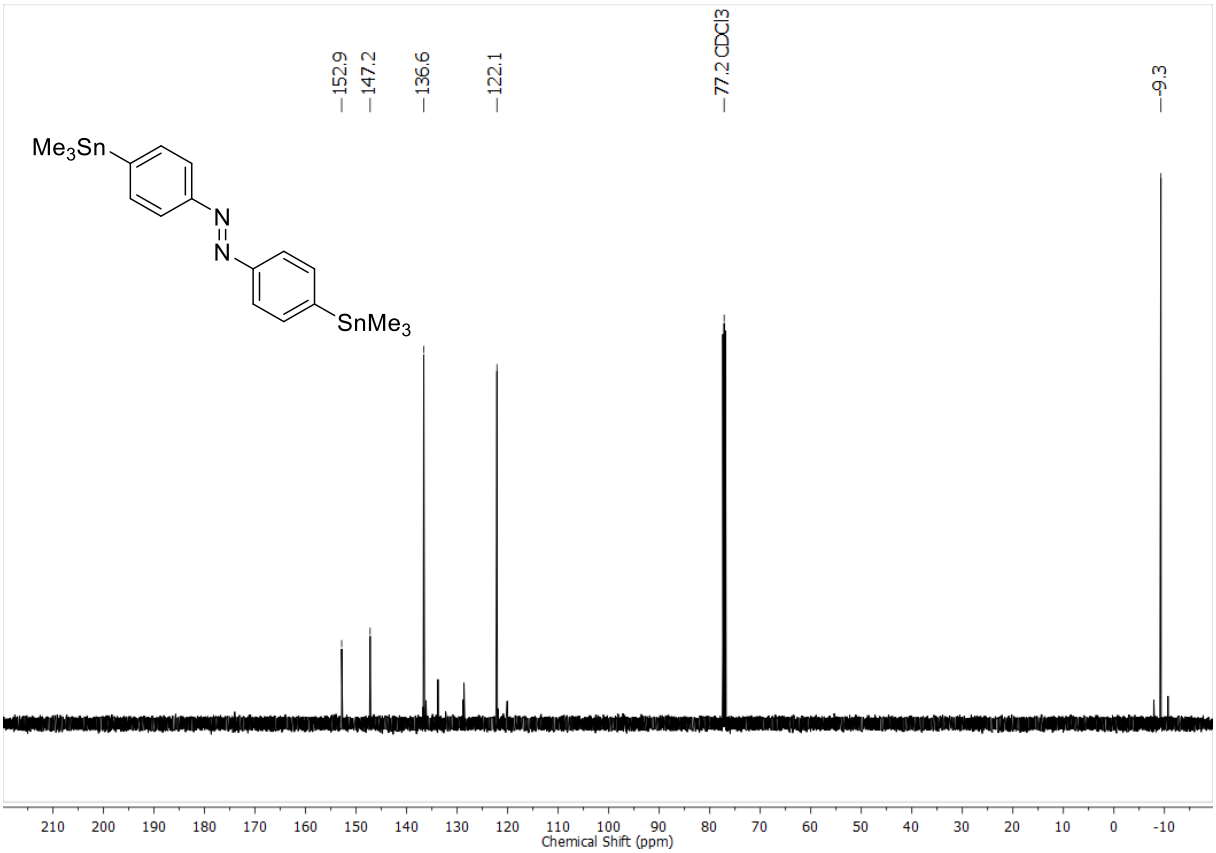
4,4'-Bis(iodo)azobenzene (S1) in chloroform-*d*

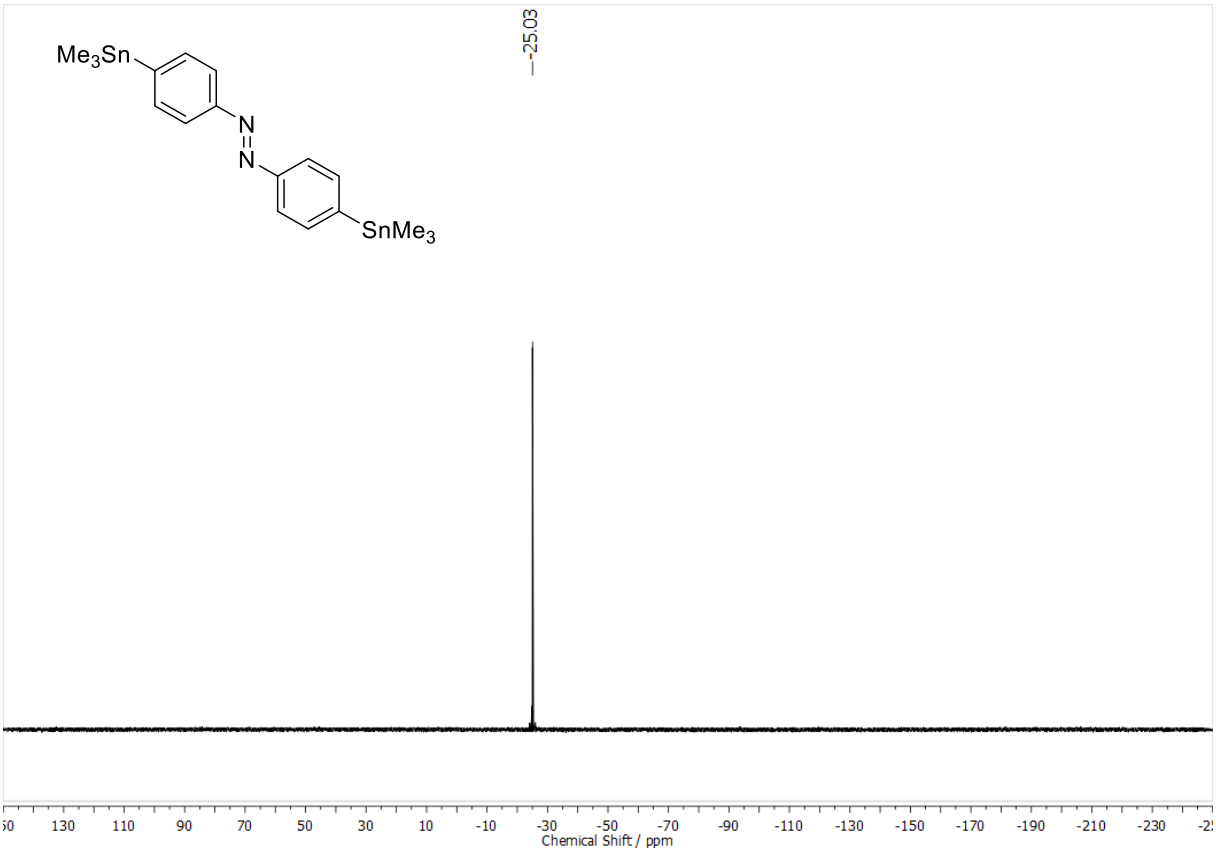




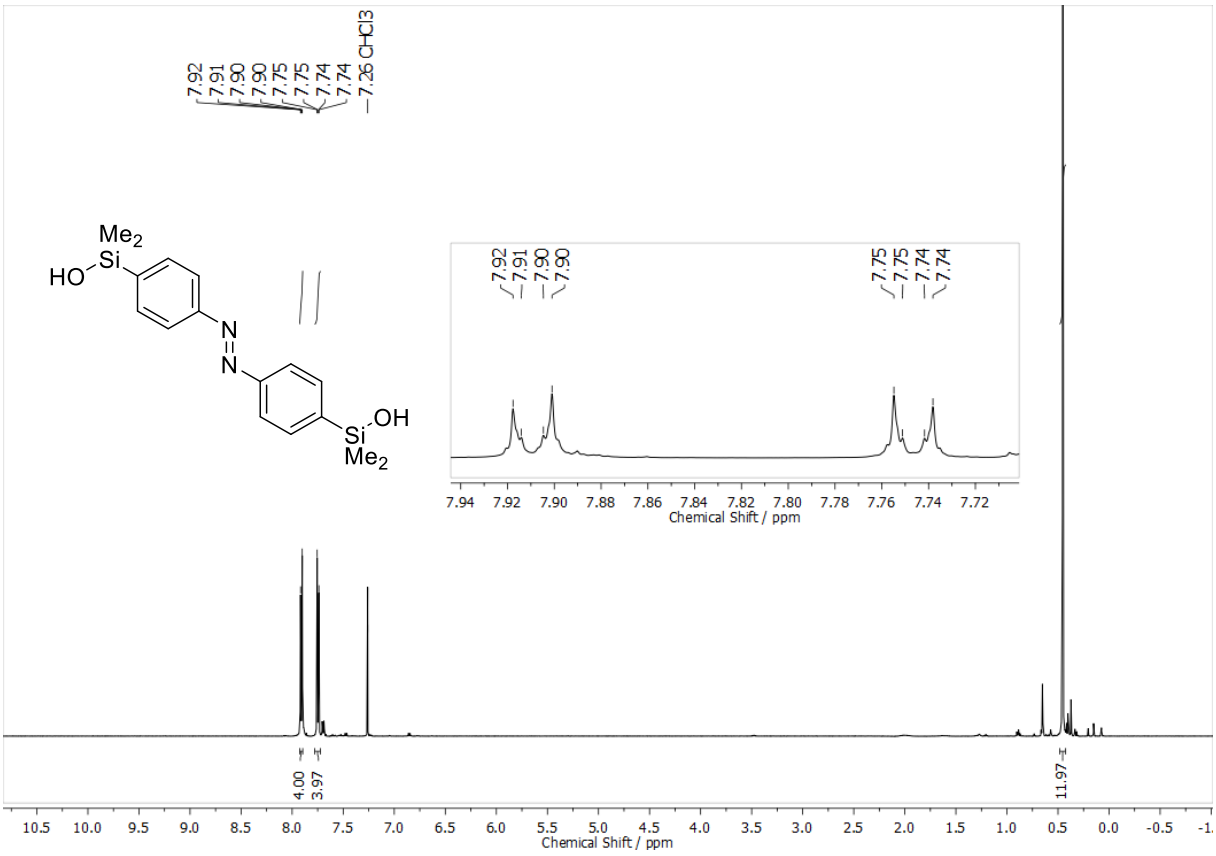
4,4'-Bis(trimethylstannyl)azobenzene (1) in chloroform-*d*

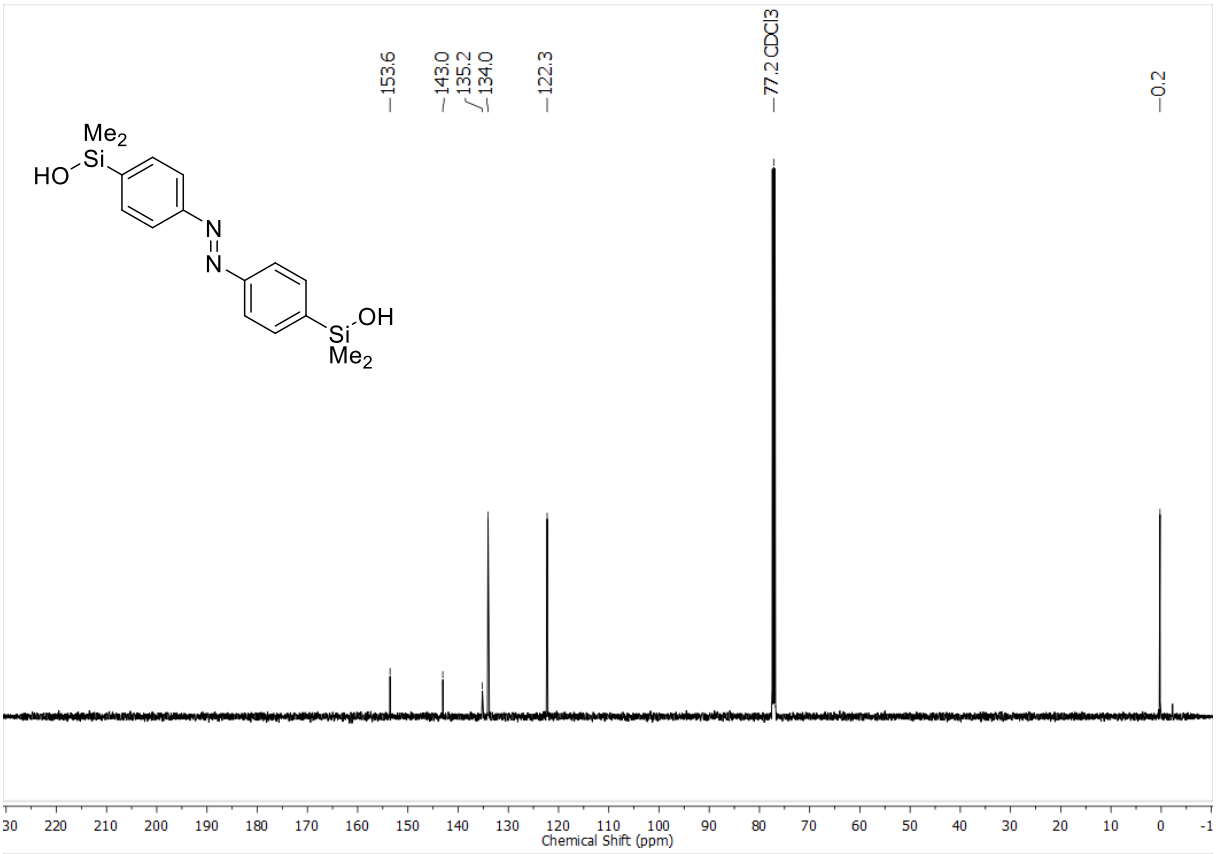

Me3Sn
SnMe3
7.88
7.86
7.66
7.65
7.26 CHCl3
0.34
4.00
4.07
18.00
Chemical Shift / ppm

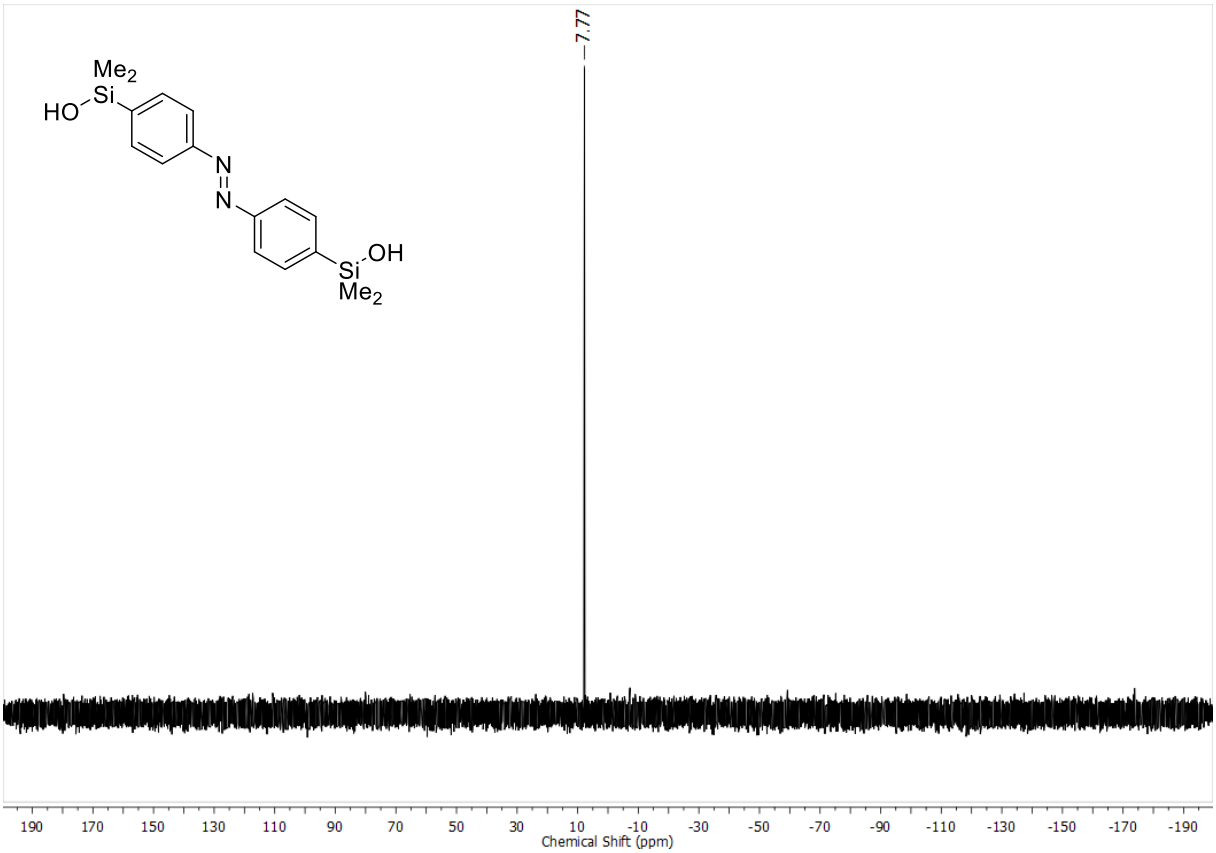

Me3Sn
SnMe3
152.9
147.2
136.6
122.1
77.2 CDCl3
9.3
Chemical Shift (ppm)



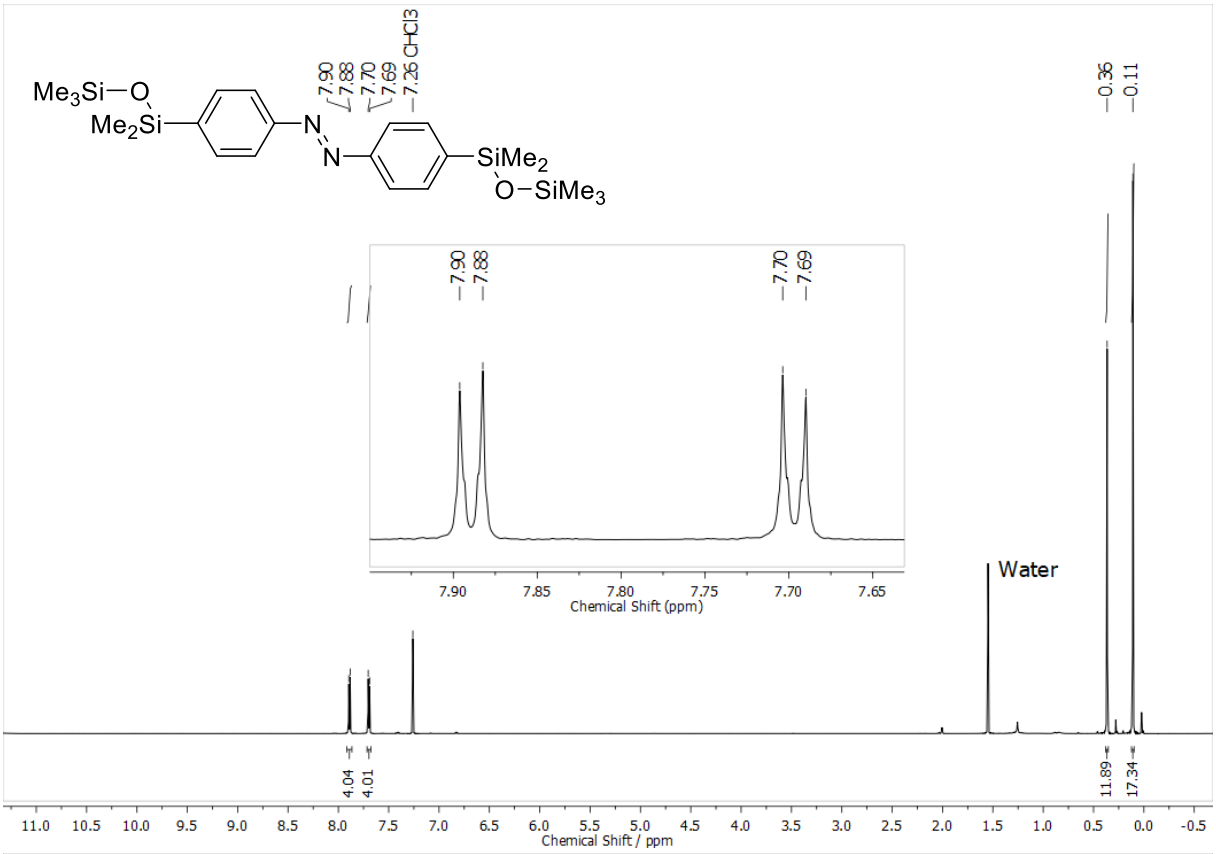
4,4’-Bis(hydroxydimethylsilane)azobenzene (2) in chloroform-*d*

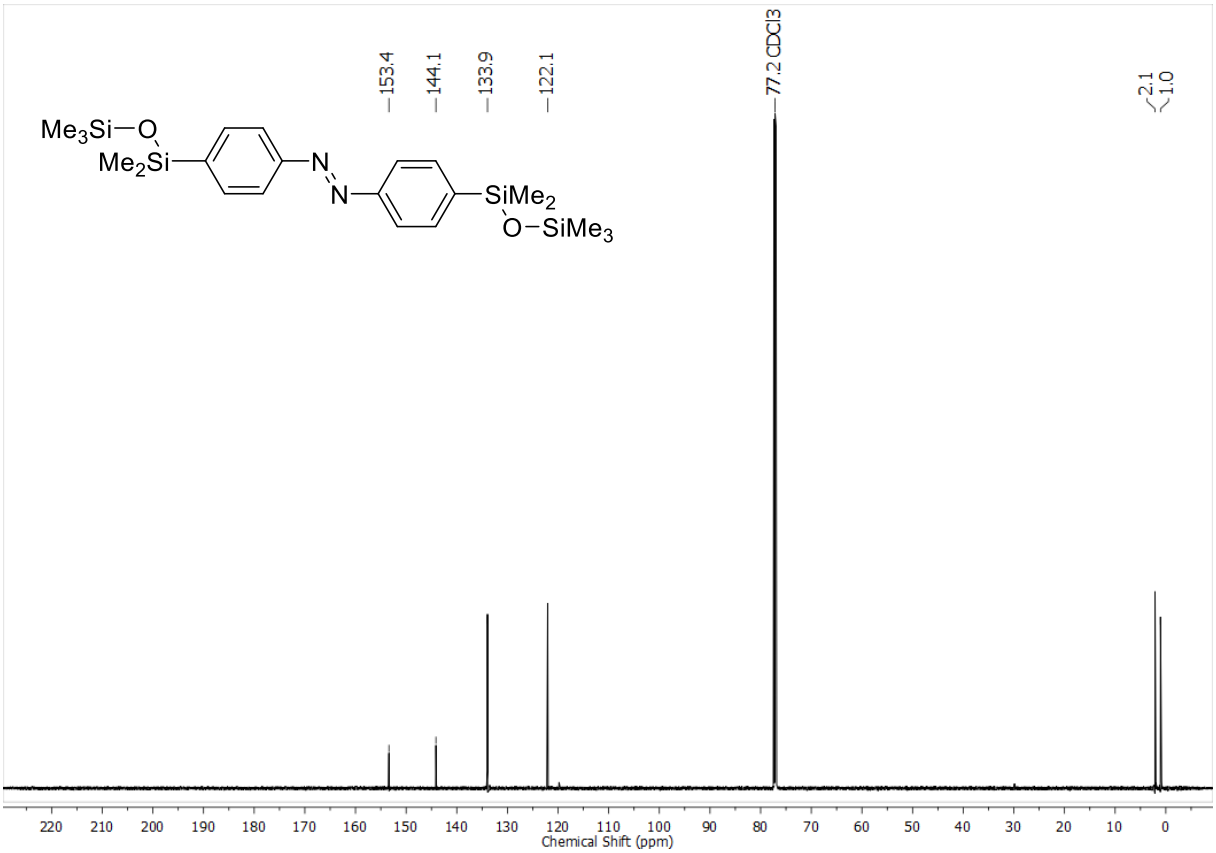


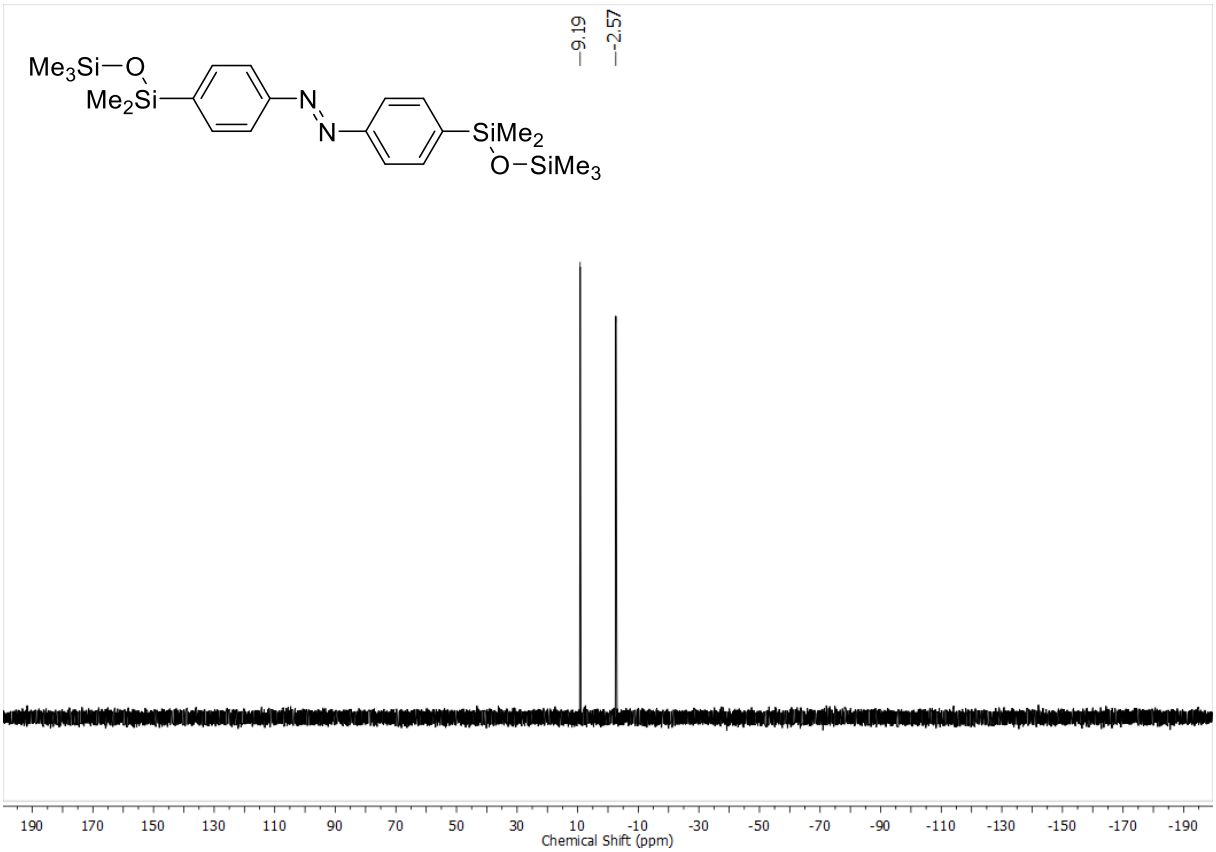




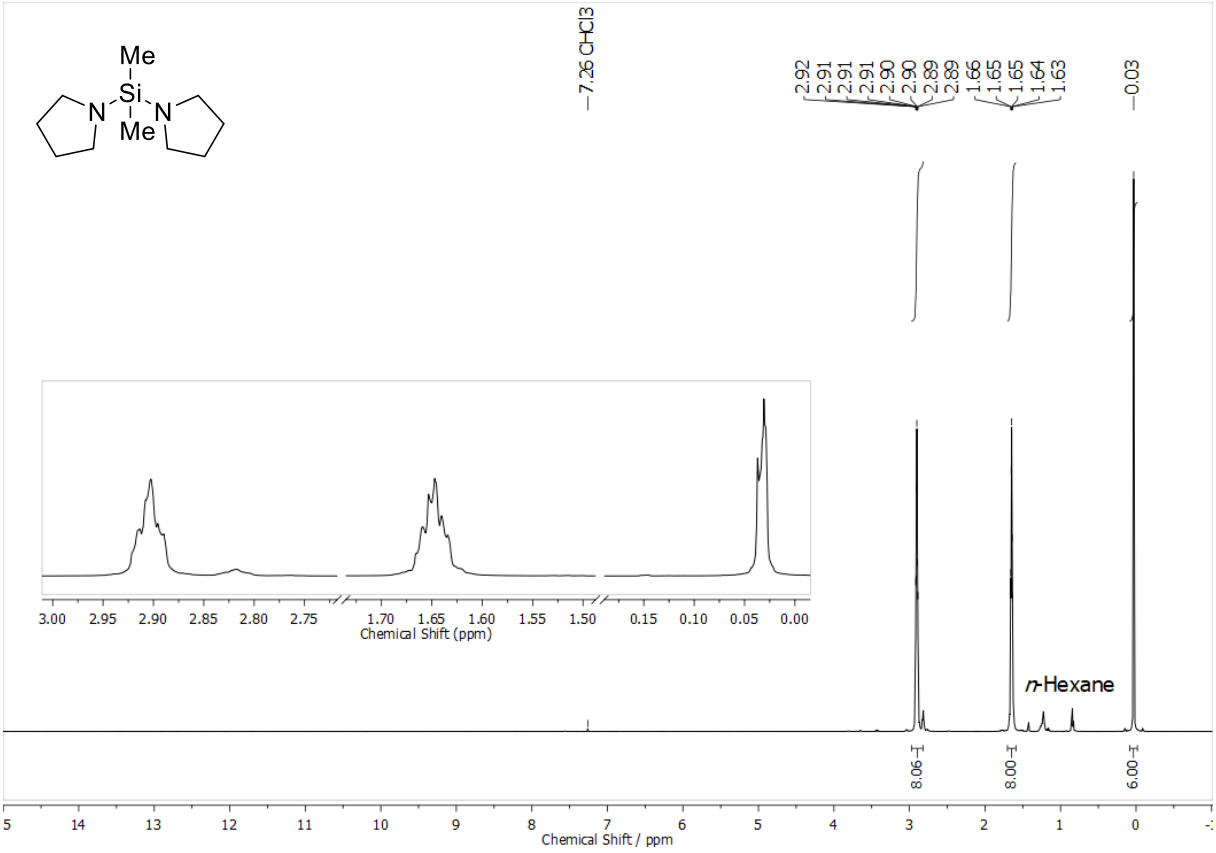
4,4'-Bis(1,1,3,3,3-pentamethyldisiloxanyl)azobenzene (5) chloroform-*d*

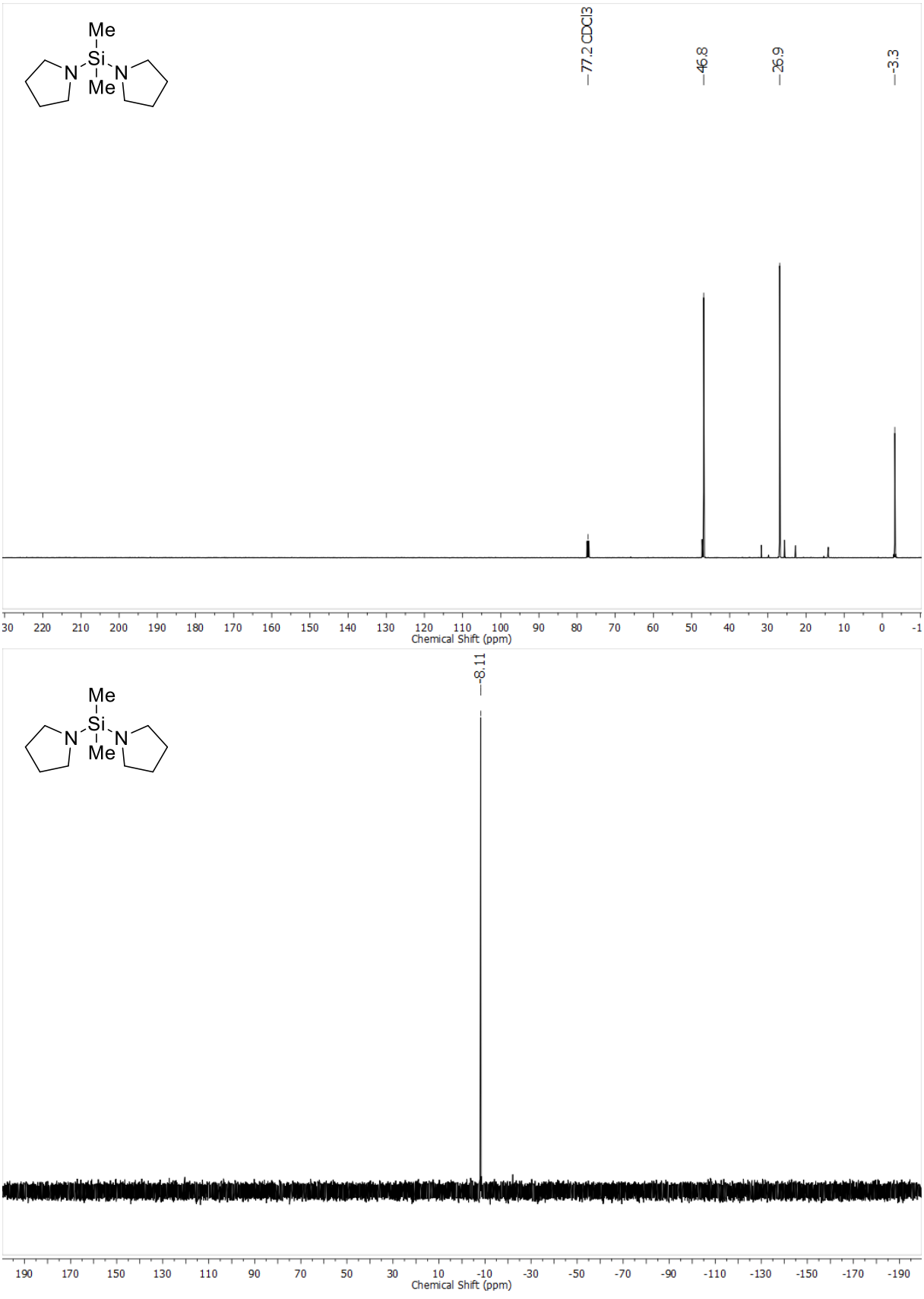

Me3Si—O
Me2Si
N
N
SiMe2
O—SiMe3
7.90
7.88
7.70
7.69
7.26 CHCl3
0.36
0.11
Water
Chemical Shift (ppm)
Chemical Shift / ppm
4.04
4.01
11.89
17.34


Me3Si—O
Me2Si
N
N
SiMe2
O—SiMe3
153.4
144.1
133.9
122.1
77.2 CDCl3
2.1
1.0
Chemical Shift (ppm)

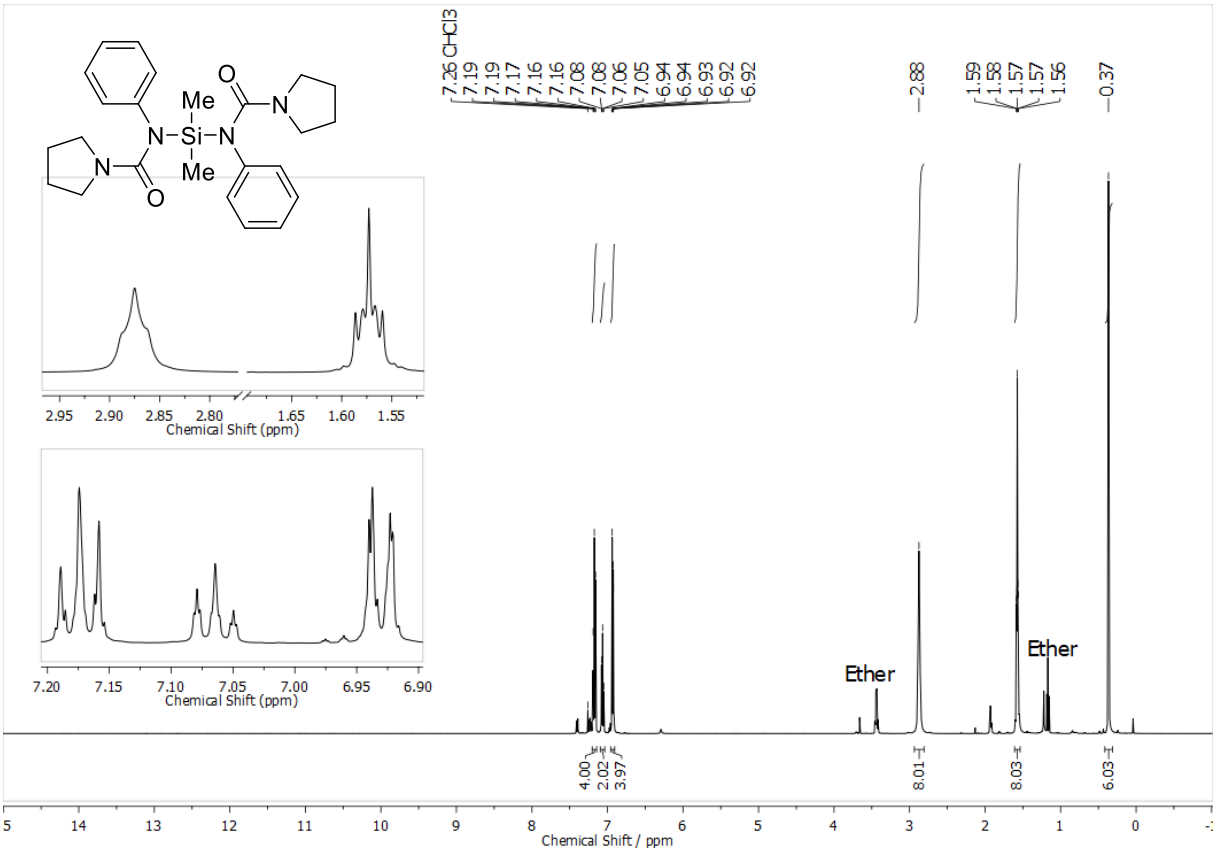


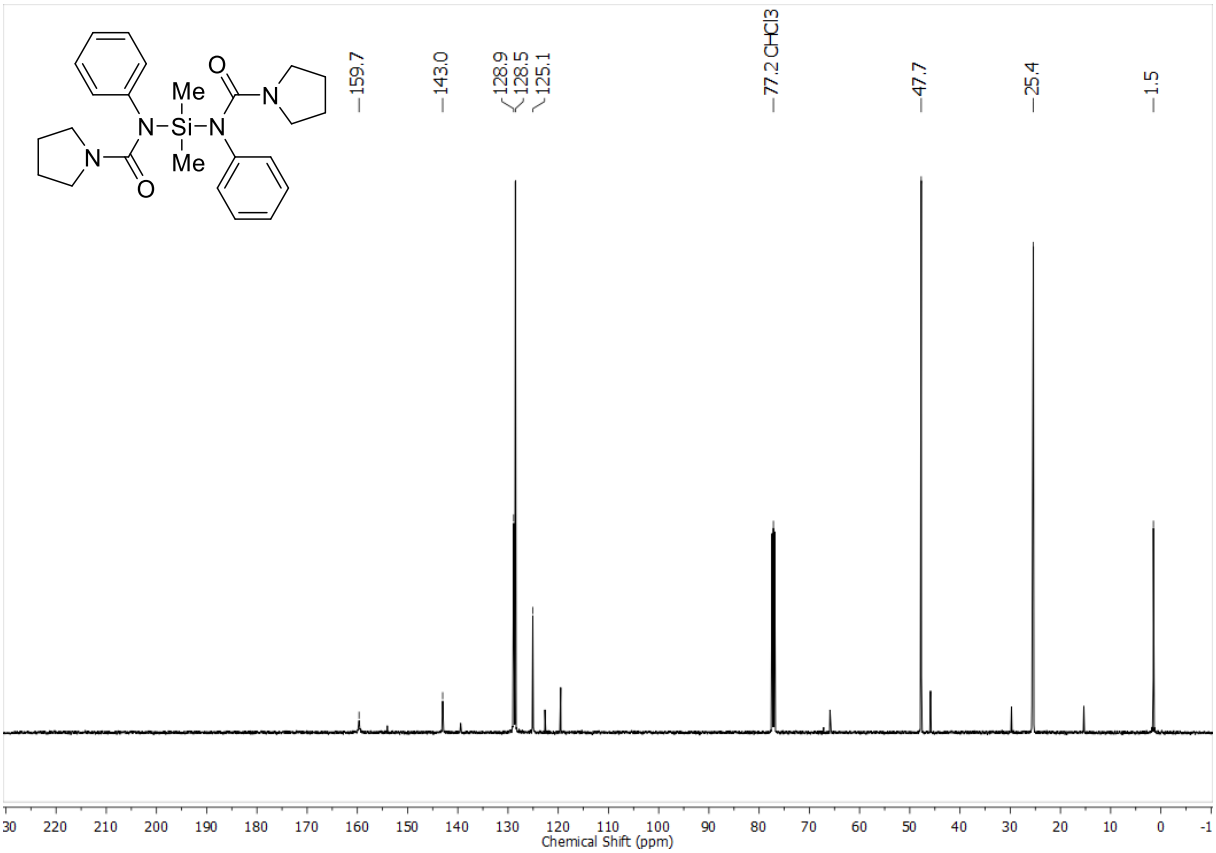
Bis(pyrrolidin-1-yl)dimethylsilane (S2) in chloroform-*d*

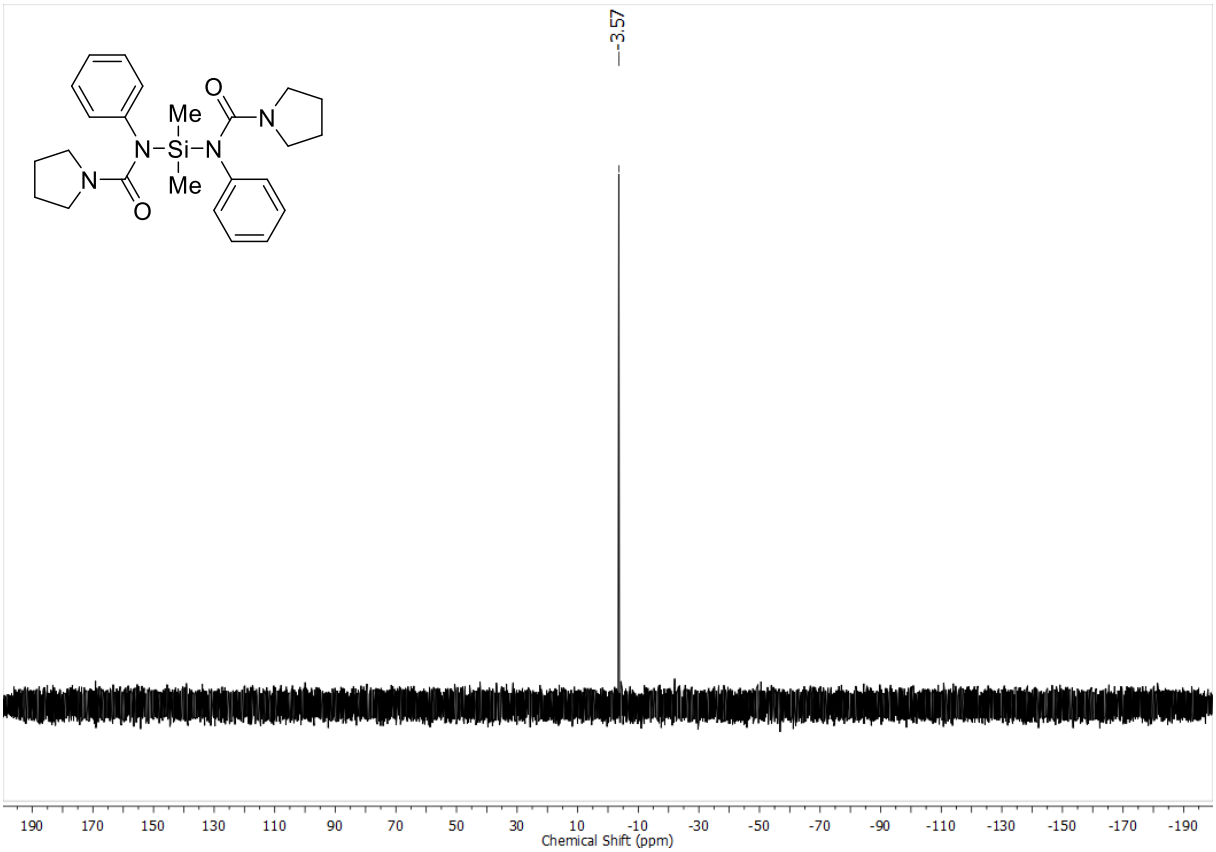




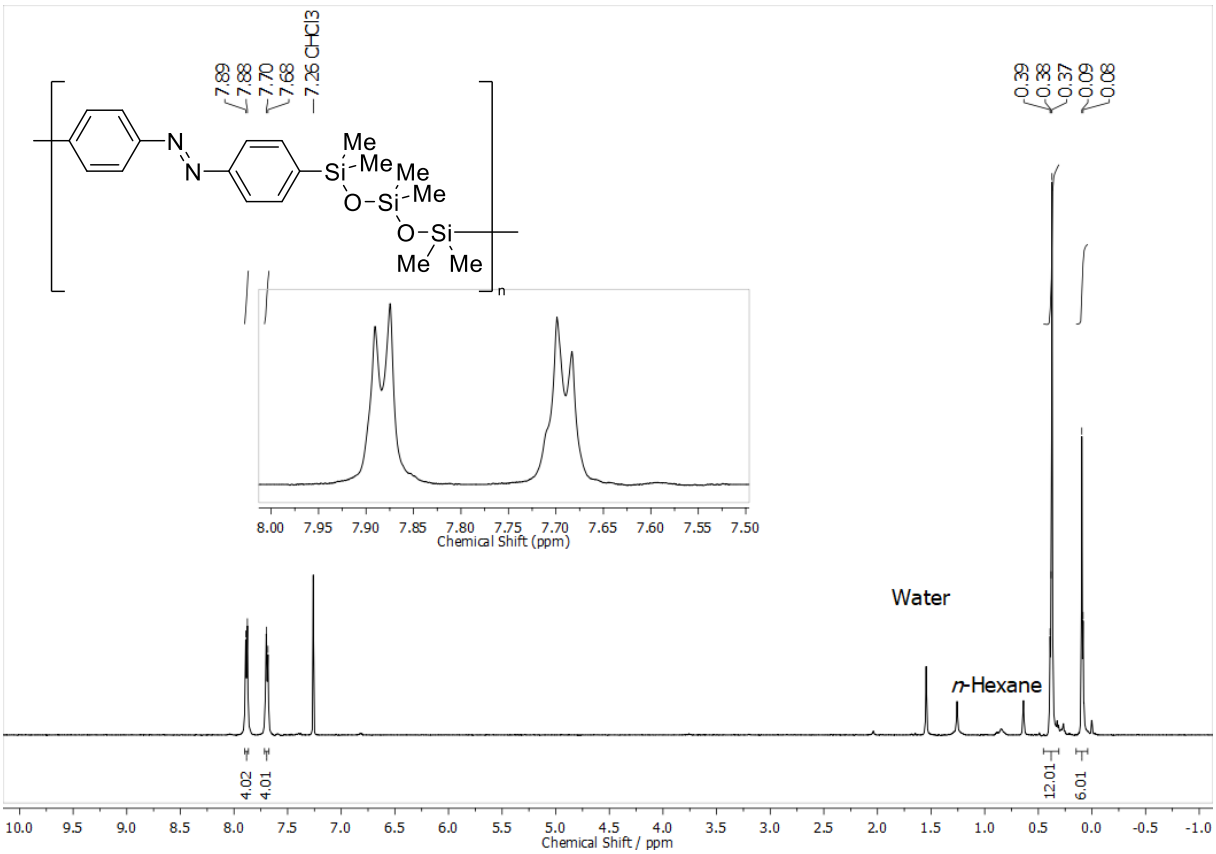
Bis(*N*-phenyl-*N*-pyrrolidinecarbonylamino)dimethylsilane (4) in chloroform-*d*

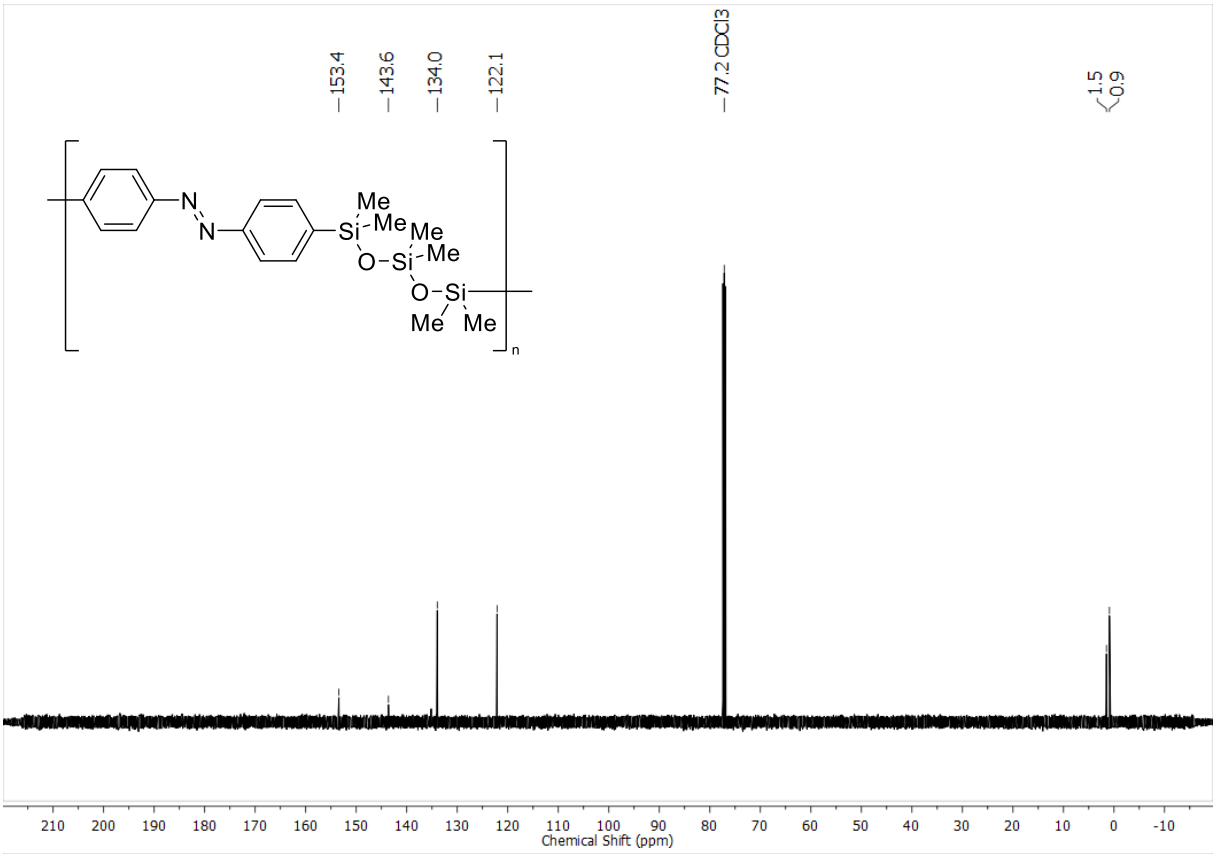

Me
N–Si–N
Me
O
N
O
7.26 CHCl3
7.19
7.19
7.17
7.16
7.16
7.08
7.08
7.06
7.05
6.94
6.94
6.93
6.92
6.92
2.88
1.59
1.58
1.57
1.57
1.56
0.37
Ether
Ether
4.00
2.02
3.97
8.01
8.03
6.03
Chemical Shift (ppm)
Chemical Shift / ppm

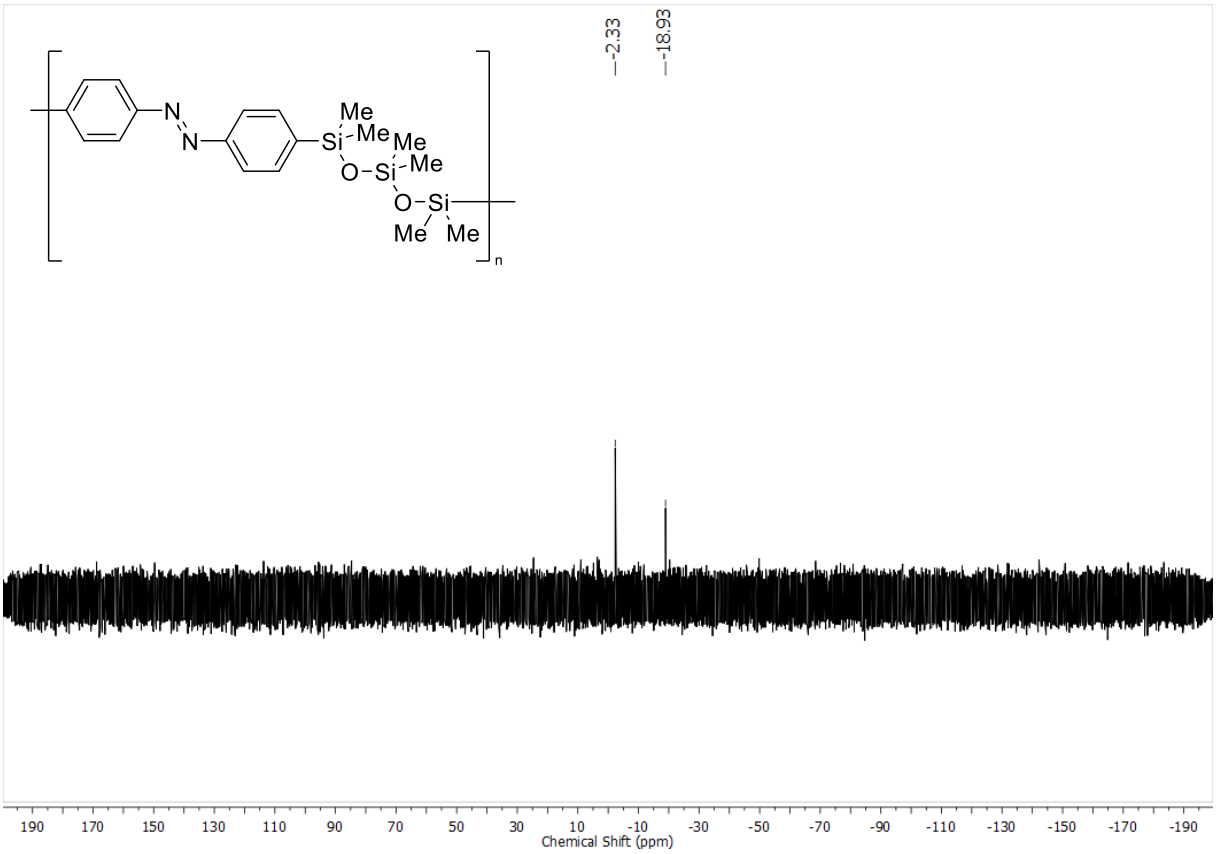

Me
N–Si–N
Me
O
N
O
159.7
143.0
128.9
128.5
125.1
77.2 CHCl3
47.7
25.4
1.5
Chemical Shift (ppm)



Poly(4,4'-azobenzene-*alt*-hexamethyl-trisiloxane) (6) in chloroform-*d*




153.4
143.6
134.0
122.1
77.2 CDCl3
1.5
0.9
Me
Me
Me
Me
Me
Me
Me
Me
N
N
Si
O
Si
O
Si
n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


2.33
-18.93
Me
Me
Me
Me
Me
Me
Me
Me
N
N
Si
O
Si
O
Si
n
190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
Chemical Shift (ppm)