

Electronic Supplementary Information

A photoswitchable bis-azo derivative with a high temporal resolution

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Materials and general instrumentation. All reagents for synthesis were used as received without further purification. Flash chromatography was carried out over silica gel (SDS, 230-240 mesh). MeCN was distilled from calcium hydride under inert atmosphere. THF was distilled from sodium and benzophenone. Anhydrous DMF was stored over 4Å molecular sieves under nitrogen atmosphere. Melting points were determined by polarized optical microscopy (POM) using a Nikon Eclipse polarizing microscope equipped with a Linkam THMS 600 hot stage and a Linkam CI 93 programmable temperature controller at a scan rate of 5 °C min⁻¹. Electronic spectra were recorded in a Varian Cary 500E UV-Vis-NIR spectrophotometer. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were collected on a Varian Mercury spectrophotometer. HRMS was performed in a LC/MSD-TOF Agilent Technologies apparatus by means of the electrospray (ESI-MS) technique.

Synthesis of the azocompounds

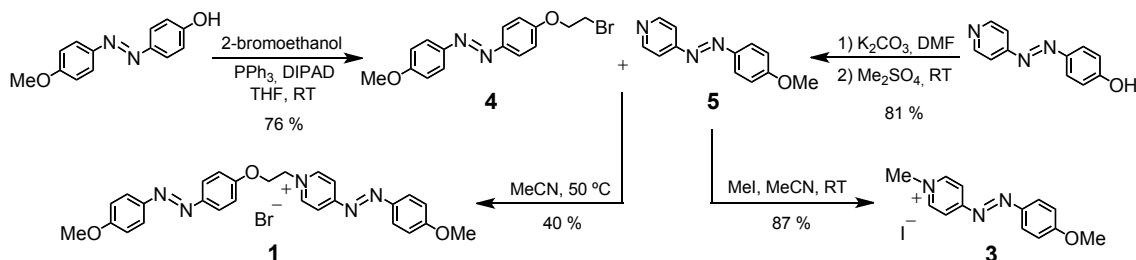


Figure S1. Synthetic concept for azo derivatives **1**, **3**, **4** and **5**.

4-hydroxy-4'-methoxyazobenzene and 4-(4'-hydroxyphenylazo)pyridine were prepared according to the literature procedures.^{1,2}

1. A solution of **4** (78 mg) and **5** (50 mg) in dry acetonitrile (25 cm³) was stirred at 50 °C under inert atmosphere for 48 hours thereby observing the formation of an orange precipitate. After the reaction was cooled down to room temperature, the product was isolated by vacuum filtration, washed thoroughly with hexane and dried. **1** was obtained as an orange solid. (Yield: 50 mg, 40 %). **m.p.** (POM, 5 °C min⁻¹): 220–222 °C. ¹H NMR (*d*₆-DMSO, 400 MHz): δ 3.85 (3H, s, O-CH₃); 3.94 (3H, s, O-CH₃); 4.66 (2H, t, O-CH₂, *J* = 4.6 Hz); 5.13 (2H, t, ⁺N-CH₂, *J* = 4.6 Hz); 7.11 (2H, d, ^{ar}H, *J* = 9.1 Hz); 7.13 (2H, d, ^{ar}H, *J* = 9.1 Hz); 7.25 (2H, d, ^{ar}H, *J* = 9.1 Hz); 7.83 (2H, d, ^{ar}H, *J* = 9.1 Hz); 7.84 (2H, d, ^{ar}H, *J* = 9.1 Hz); 8.08 (2H, d, ^{ar}H, *J* = 9.1 Hz); 8.40 (2H, d, ^{ar}H, *J* = 7.0 Hz); 9.30 (2H, d, ^{ar}H, *J* = 7.0 Hz) ppm. ¹³C NMR (*d*₆-DMSO, 125 MHz): δ 55.6, 56.2, 59.5, 66.4, 114.5, 115.2, 115.4, 119.7, 124.1, 124.2, 127.0, 146.1, 146.6,

146.7, 147.7, 159.5, 160.8, 161.6, 165.2 ppm. **HRMS** (ESI- MS): m/z calc for $C_{27}H_{26}N_5O_3$ [M^+] 468.2036; found 468.2031.

3. Methyl iodide (0.2 cm³) was added to a solution of **5** (20 mg) in anhydrous acetonitrile (10 cm³). The reaction mixture was stirred at room temperature for 4 hours. Then, the solvent was distilled off under reduced pressure and the crude was dissolved in the minimum amount of CH_2Cl_2 . **3** was precipitated as an orange solid by adding hexane, isolated by vacuum filtration, washed thoroughly with hexane and dried. (Yield: 29 mg, 87 %). **¹H NMR** (d_6 -acetone, 400 MHz): δ 4.00 (3H, s, O- CH_3); 4.71 (3H, s, $^+N-CH_3$); 7.25 (2H, d, aH , $J = 9.0$ Hz); 8.12 (2H, d, aH , $J = 9.0$ Hz); 8.43 (2H, d, aH , $J = 6.7$ Hz); 9.38 (2H, d, aH , $J = 6.7$ Hz) ppm. **¹³C NMR** ($CDCl_3$, 100 MHz): δ 49.0, 56.0, 115.0, 120.1, 127.7, 147.2, 147.3, 160.8, 165.8 ppm. **HRMS** (ESI-MS): m/z calc for $C_{13}H_{14}N_3O$ [M^+] 228.1137; found 228.1132.

4. 4-hydroxy-4-methoxyazobenzene (1.5 g), PPh_3 (1.9 g) and DIPAD (1.4 cm³) were dissolved in anhydrous THF (30 cm³) under inert atmosphere. The reaction was stirred at room temperature for 30 minutes. Then, 2-bromoethanol (0.5 cm³) was added to the reaction mixture and the resulting solution was stirred at room temperature for 72 hours. Afterwards, the solvent was distilled off under reduced pressure and the crude was purified by flash column chromatography using a mixture of hexanes and ethyl acetate (1:1 v/v) as eluent. **4** was obtained as a yellow solid. (Yield : 1.68 g, 76 %). **¹H NMR** ($CDCl_3$, 400 MHz): δ 3.68 (2H, t, Br- CH_2 , $J = 6.3$ Hz), 3.89 (3H, s, O- CH_3), 4.37 (2H, t, O- CH_2 , $J = 6.3$ Hz), 7.00 (2H, d, aH , $J = 8.9$ Hz); 7.01 (2H, d, aH , $J = 8.9$ Hz); 7.88 (2H, d, aH , $J = 8.9$ Hz); 7.89 (2H, d, aH , $J = 8.9$ Hz) ppm. **¹³C NMR** ($CDCl_3$, 100 MHz): δ 28.8, 55.5, 68.0, 114.1, 114.8, 124.3, 124.4, 147.0, 147.4, 159.9, 161.6 ppm. **HRMS** (ESI-MS): m/z calc for $C_{15}H_{16}BrN_2O_2$ [MH^+] 335.0395; found 335.0392.

5. A solution of 4-(4'-hydroxyphenylazo)pyridine (200 mg) and potassium carbonate (300 mg) in anhydrous DMF (30 cm³) was stirred for 30 minutes under inert atmosphere. Then, dimethyl sulfate (126 mg) was added. The solution was stirred at room temperature overnight. After, the reaction mixture was diluted with water and the product was extracted with ethyl acetate. The combined organic extract was dried over anhydrous sodium sulfate, filtered and the solvent was distilled off under reduced pressure. The crude was purified by flash column chromatography using a mixture of hexane and ethyl acetate (1:2 v/v) as eluent. **5** was obtained as a brown solid. (Yield: 174 mg, 81 %). **¹H NMR** ($CDCl_3$, 400 MHz): δ 3.92 (3H, s, O- CH_3); 7.05 (2H, d, aH , $J = 9.1$ Hz); 7.77 (2H, d, aH , $J = 6.2$ Hz); 7.99 (2H, d, aH , $J = 9.1$ Hz); 8.78 (2H, d, aH , $J = 6.2$ Hz) ppm. **¹³C NMR** (d_6 -acetone, 100 MHz): δ 57.1, 116.4, 117.6, 127.2, 148.5, 153.2, 159.0, 165.4 ppm. **HRMS** (ESI-MS): m/z calc for $C_{12}H_{12}N_3O$ [MH^+] 214.0980; found 214.0976.

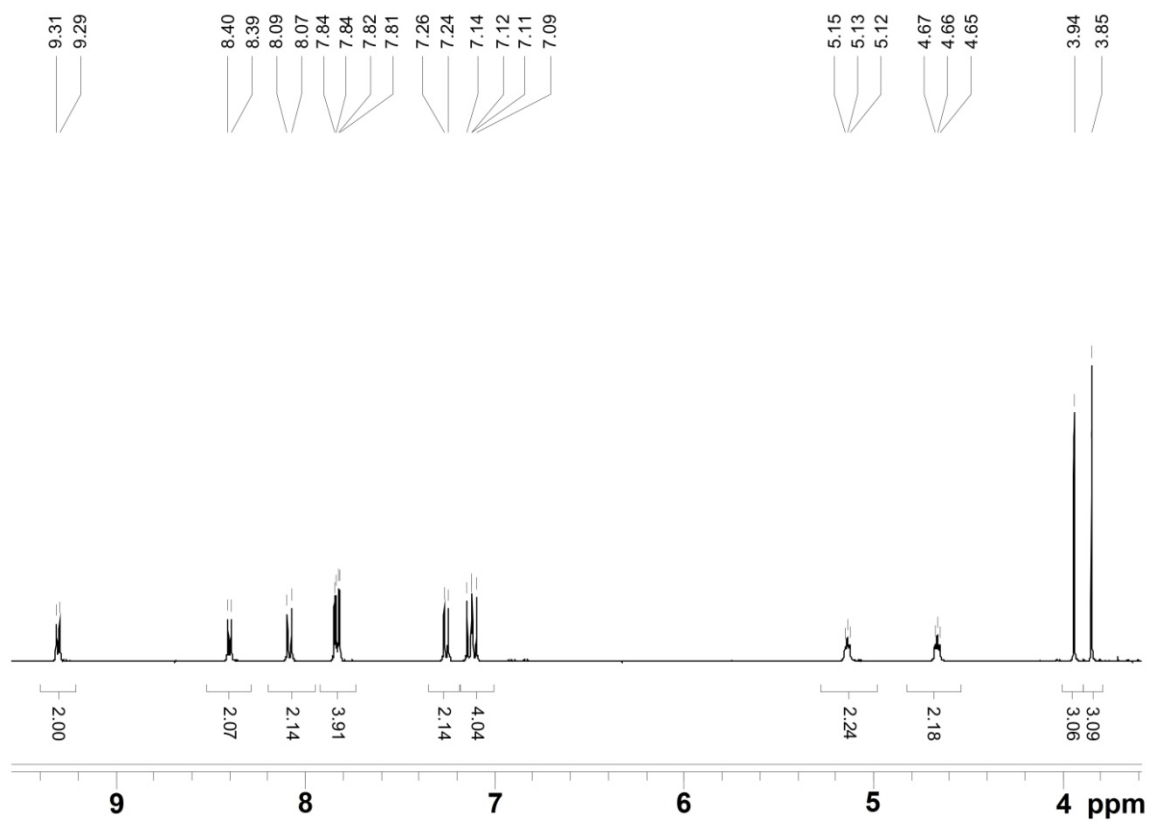


Figure S2. ^1H NMR spectrum of **1** in d_6 -DMSO.

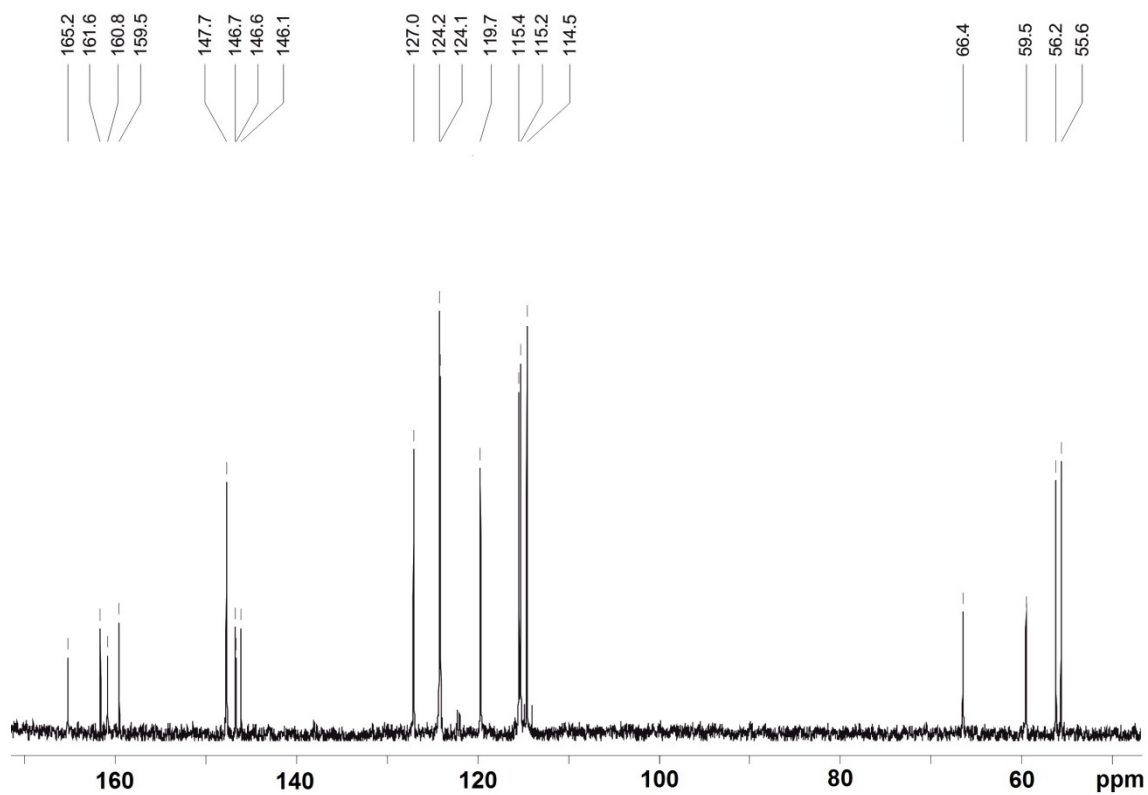


Figure S3. ^{13}C NMR spectrum of **1** in d_6 -DMSO.

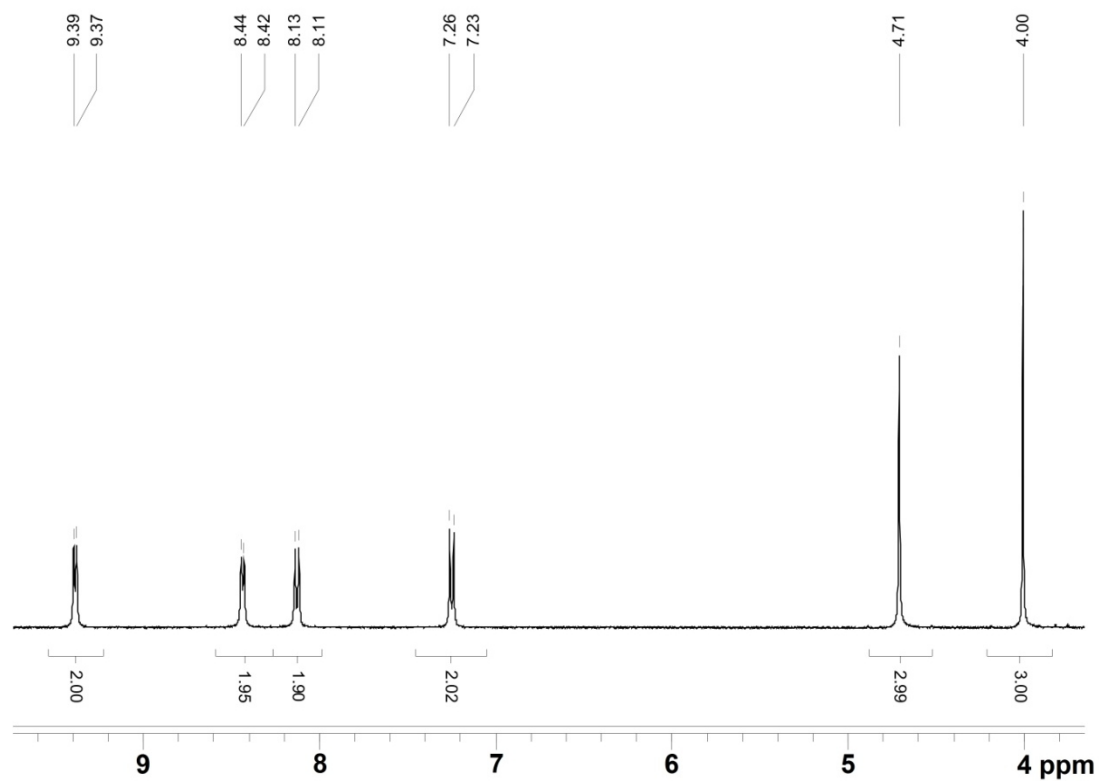


Figure S4. ^1H NMR spectrum of **3** in d_6 -acetone.

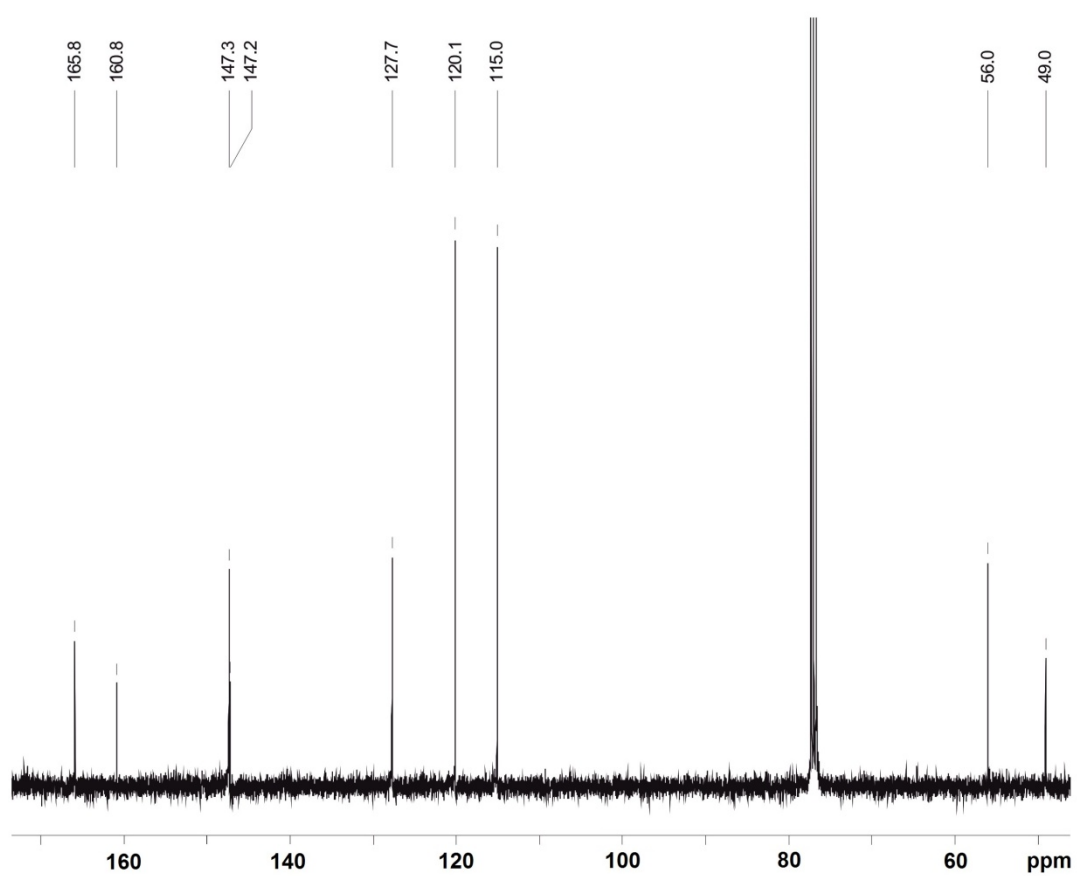


Figure S5. ^{13}C NMR spectrum of **3** in CDCl_3 .

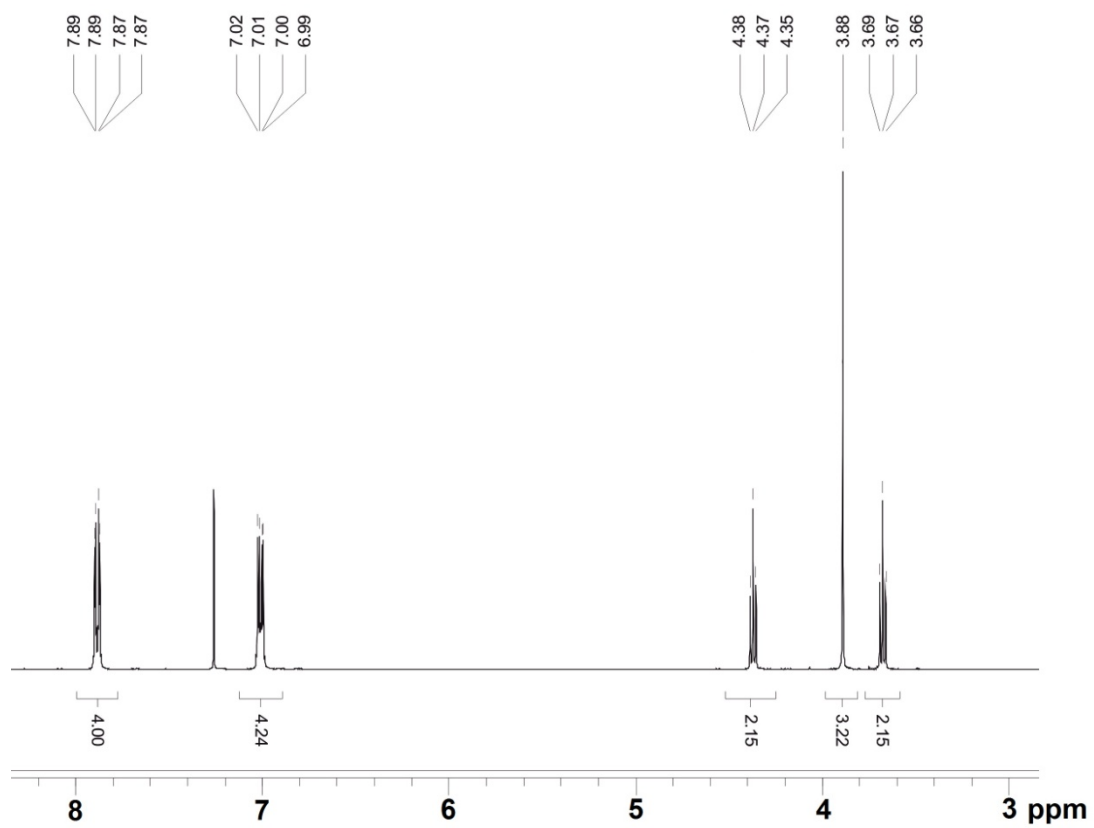


Figure S6. ^1H NMR spectrum of **4** in CDCl_3 .

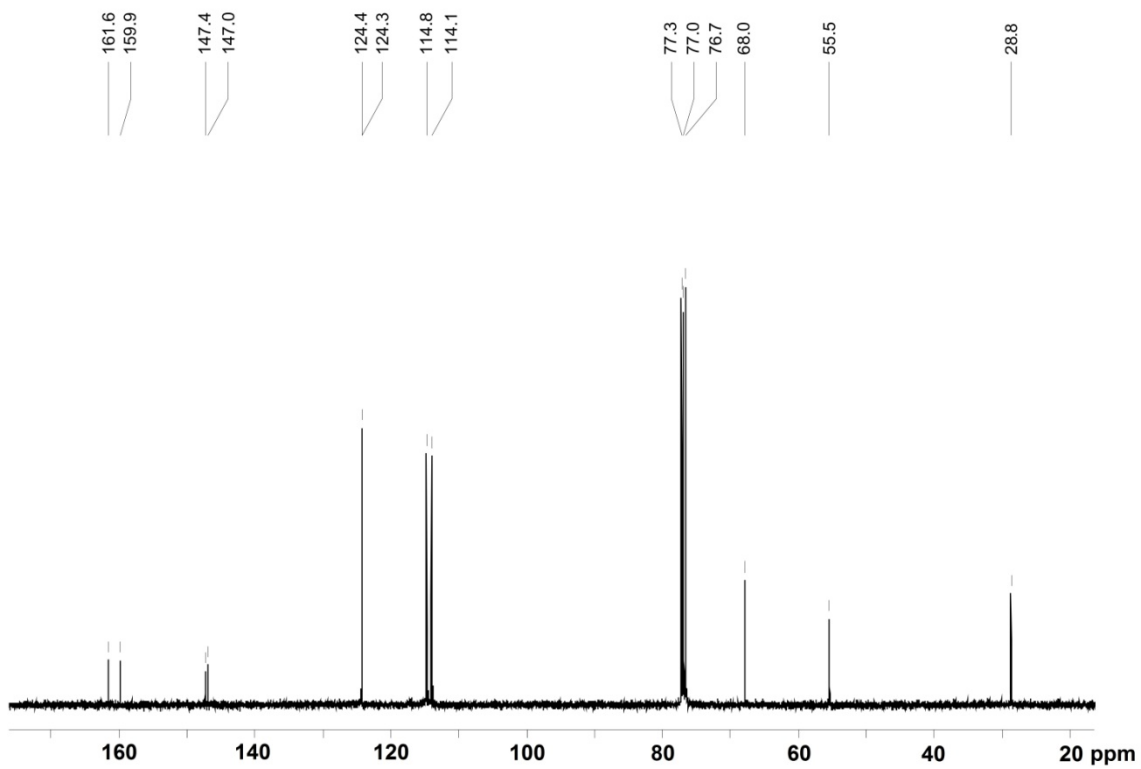


Figure S7. ^{13}C NMR spectrum of **4** in CDCl_3 .

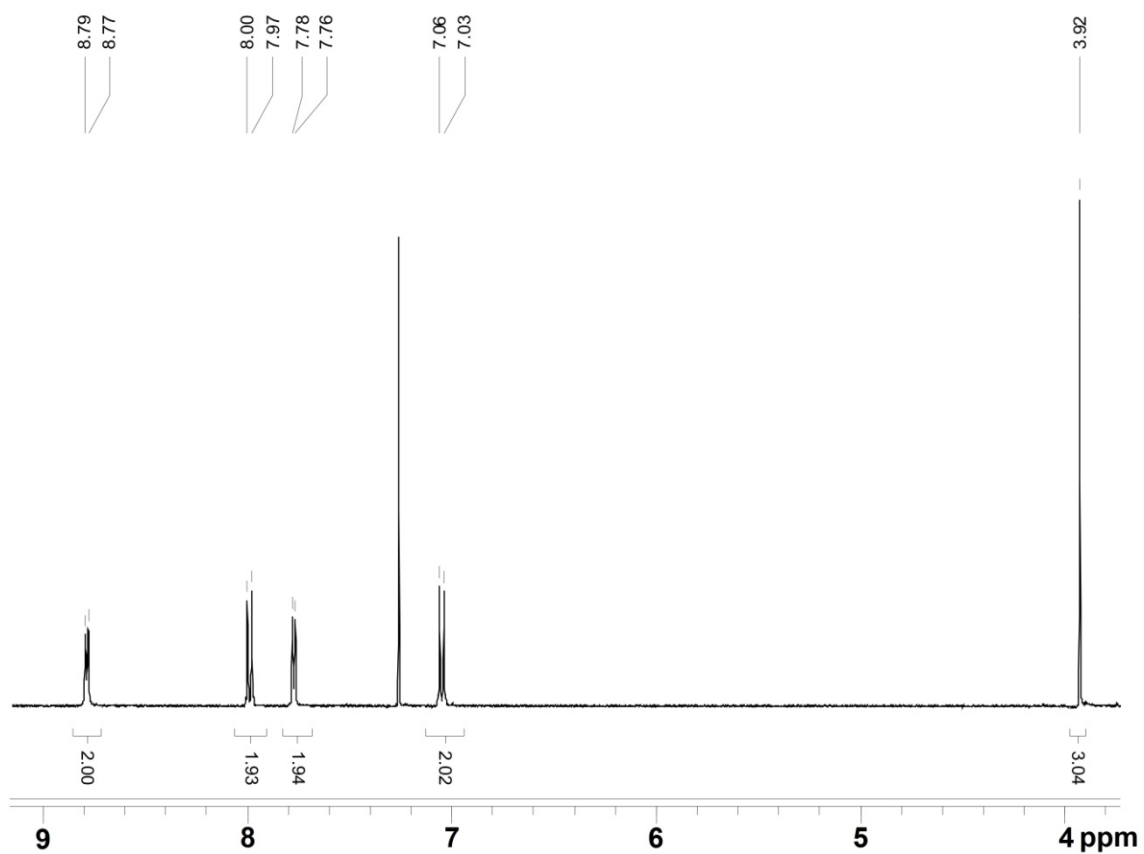


Figure S8. ^1H NMR spectrum of **5** in CDCl_3 .

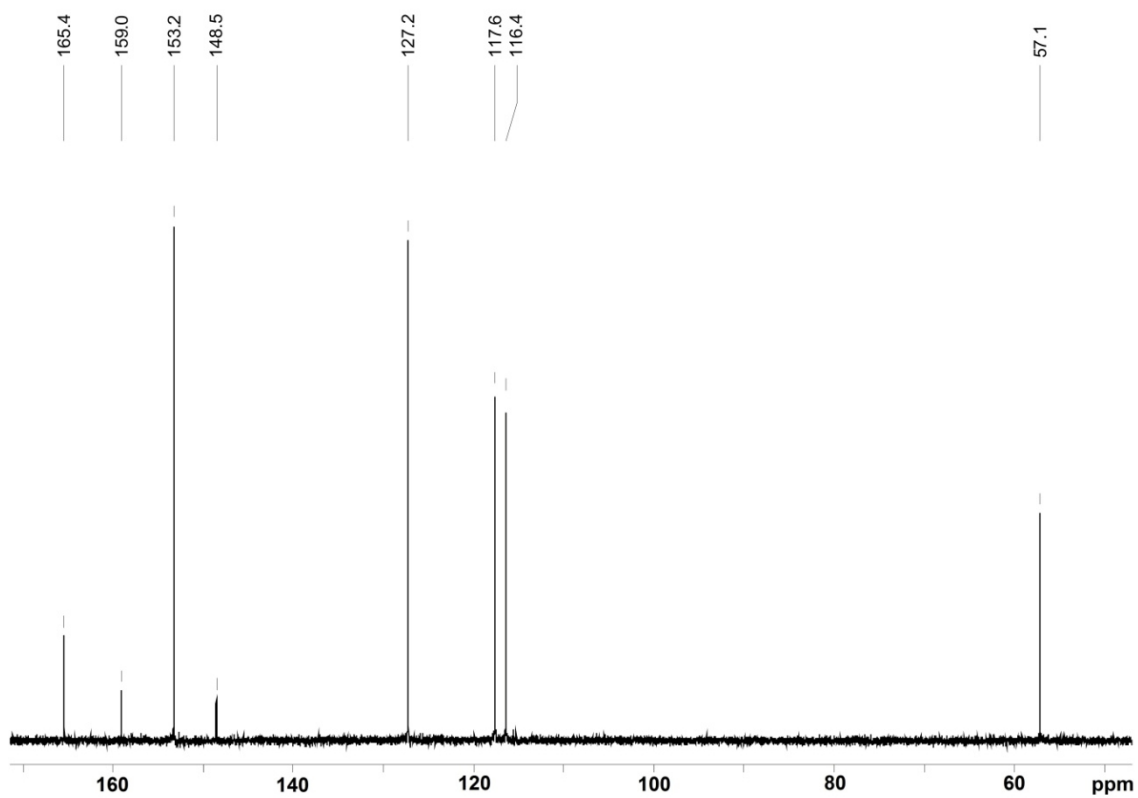


Figure S9. ^{13}C NMR spectrum of **5** in d_6 -acetone.

Kinetic experiments. A population of *cis*-azobenzenes was generated by UV photolysis and its relaxation was followed by time-resolved UV-Vis spectroscopy. For long-lived *cis*-azobenzenes, the samples were irradiated with a Philips high-pressure mercury lamp (total nominal power 500 W) whose light was filtered through a 0.5 M solution of Co(NO₃)₂ in water. Irradiation ($\lambda_{\text{irrad}} = 320\text{-}390$ nm) was pursued until no further changes could be observed in the electronic spectrum of the sample; the usual irradiation time was 10 minutes. Afterwards, the solutions were thermostated in the dark at the desired temperature (± 0.1 K) and the thermal *cis*-to-*trans* isomerisation was monitored by absorption spectroscopy using a Varian Cary 500E UV-Vis-NIR spectrophotometer. For short-lived samples, the thermal *cis*-to-*trans* isomerisation process was studied by means of the nanosecond laser flash photolysis technique. In this case, the *cis* isomer of the corresponding azoderivative was generated by a Q-switched Nd-YAG laser (355 nm or 532 nm, 5 ns pulse width, 1-10 mJ per pulse). The concomitant absorbance changes were monitored at 90° by a white-light analysing beam produced by a Xe lamp (PTI, 75 W) in combination with a dual-grating monochromator (PTI 101) coupled to a Hamamatsu R928 photomultiplier for detection.³ No photo-isomerisation of the azocompounds was promoted by observation wavelength of the spectrophotometer. In all instances, the experiments were realized in 1 cm optical path quartz cells (Hellma). No photo-degradation of the compounds was observed.

¹ X. Song, J. Li and S. Zhang, *Liq. Cryst.*, 2003, **30**, 331.

² M. Amaike, H. Kobayashi, K. Sakurai and S. Shinkai, *Supramol. Chem.*, 2002, **14**, 245.

³ N. Rubio, A. Jiménez-Banzo, T. Torres and S. Nonell, *J. Photochem. Photobiol. A*, 2007, **185**, 214.