Supplementary Material

Synthesis and properties of photoswitchable bis(hemi-indigo) derivatives bearing elongated alkyloxy substitutents

Sören Steup and Daria V. Berdnikova*

Organic Chemistry II, University of Siegen, and Center of Micro- and Nanochemistry and Engineering (Cµ); Adolf-Reichwein-Str. 2, 57076 Siegen, Germany
Email: berdnikova@chemie-bio.uni-siegen.de

Table of Contents

1. Materials and equipment

Reagents and solvents were obtained from commercial sources (Acros, Merck, Fischer) and used as received. Reactions were monitored on POLYGRAM® SIL G/UV$_{254}$ (Macherey-Nagel) TLC plates with detection by UV light irradiation (254 nm or 366 nm).

The NMR spectra were recorded with a *JEOL ECZ 500* (^{1}H: 500 MHz, ^{13}C: 125 MHz) and a *Varian VNMR-S 600* (^{1}H: 600 MHz, ^{13}C: 150 MHz) at T = 25 °C. The chemical shifts were referenced to the solvents ($CDCl_3$: δ(^{1}H) = 7.26 ppm, δ(^{13}C) = 77.0 ppm; DMSO-d_6: δ(^{1}H) = 2.50 ppm, δ(^{13}C) = 3.33 ppm) with the software MestReNova 12. The mass spectra (ESI) were recorded on a *Finnigan LCQ Deca* mass-spectrometer (driving voltage: 6 kV; Capillary temperature: 200 °C; injection rate: 5 µL/min). Elemental analyses were carried out with a HEKAtech EUROEA combustion analyzer by Mr Rochus Breuer (Organic Chemistry I, University of Siegen). The melting points were determined with a melting point determination apparatus *BÜCHI 545* (Büchi, Flawil, CH) and are uncorrected. The absorption spectra were recorded in Hellma quartz cells 114B-QS and 110-QS (layer thickness d = 10 mm) on a *Varian Cary 100 Bio-spectrophotometer*, equipped with a temperature-controlled sample holder and on an *Analytic Jena Specord S600* diode-array spectrophotometer equipped with a temperature controlled sample holder with six sample slots. Spectrofluorimetric measurements were performed in Hellma quartz cuvettes 114F-QS and 115F-QS (layer thickness d = 10 mm) on a *Varian Cary Eclipse fluorescence spectrometer* equipped with a temperature controller and a sample holder with four slots. Preparation and handling of the solutions were carried out under red light. Photochemical reactions were performed using commercial LED light sources of different wavelengths λ = 365–625 nm, manufactured by Roithner.

2. Photochemical studies

2.1. ^{1}H NMR spectroscopic monitoring of photoreactions

A solution of **5a** or **5b** in DMSO-*d*$_6$ (*c* = 3.00 mM) was irradiated in a 3-mm NMR tube with green light (*λ* = 520 nm, 2 x 50m A), from a home-made LED insert for NMR. ^{1}H NMR spectra were recorded every 1 min upon continuous irradiation of the sample inside the NMR spectrometer till no more changes occurred. For the monitoring of the backward isomerization, the solution obtained upon irradiation with green light was further irradiated with red light (*λ* = 625 nm, 2 x 200 mA), and ^{1}H NMR spectra were recorded every 1 min in each case. The irradiation was stopped when no further changes in the spectra occurred.

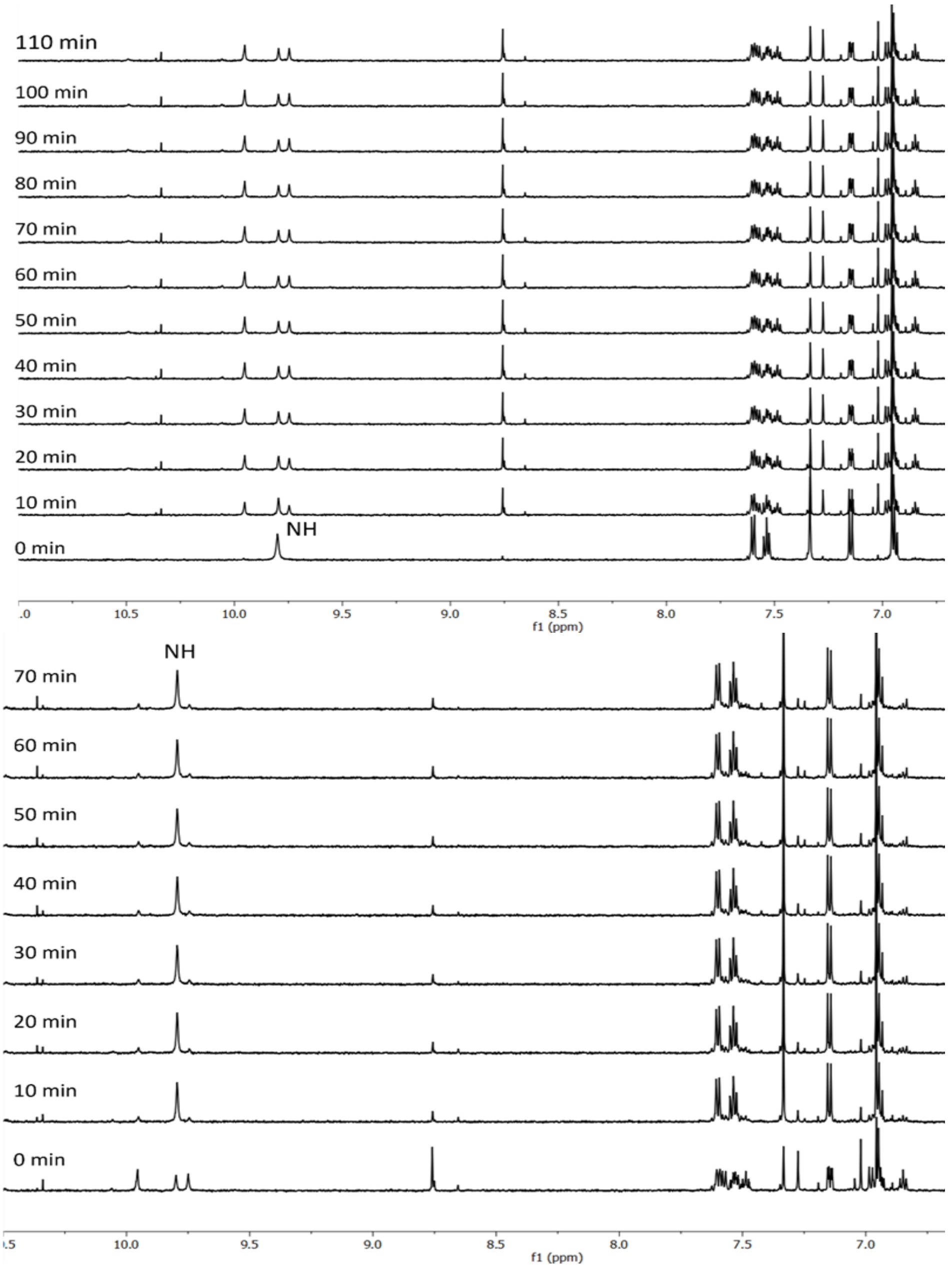

Figure S1. Real-time ^{1}H NMR spectroscopic monitoring with in situ irradiation of (A) the forward *Z,Z*–*E*,*Z* isomerization of **5b** upon irradiation at *λ* = 520 nm and (B) the follow-up backward *E,Z*–*Z*,*Z* isomerization of **5b** upon irradiation at *λ* = 625 nm (*c* = 3 mM) in DMSO-*d*$_6$.

2.2. Calculation of the absorption spectra of the photoproducts

The absorption spectra of the photoisomerization products *E,Z*-**5a** and *E,Z*-**5b** were obtained by using the absorption spectra of the starting isomers and the absorption spectra of PSS^{520} mixtures of same concentration. The N-H ^{1}H NMR signals after irradiation with λ = 520 nm were integrated to obtain the percentage of the starting photoinduced isomers in the corresponding PSS mixtures. The absorption spectra of the corresponding starting isomers were multiplied by their percentage in the PSS mixture and subtracted from the absorption spectra of the PSS mixtures, providing the absorption spectra of the photoproducts. To obtain the absorption spectra of the pure photoisomerization products, the residuals were divided by the photoproduct percentages. The obtained values were used to calculate the extinction coefficient of pure photoisomerization products.

2.3. Calculation of the composition of PSS at different wavelengths

For the wavelengths other than λ = 520 nm, the percentages of conversion in PSS were calculated from the absorption spectra of the corresponding PSS using Equation 1.

$$a = \frac{(A/c - \varepsilon_Z)}{(\varepsilon_E - \varepsilon_Z)} \times 100\% \qquad \text{(Eq. 1)}$$

a is the conversion (%) of the starting isomer in the PSS mixture, A is the absorbance of the PSS mixture, c is the concentration of all isomers in the mixture, ε_E is the molar extinction coefficient of the initial isomer and ε_Z is the molar extinction coefficient of the photoinduced isomer.

Table S1. Composition of photostationary states (conversion (%) of starting isomer) of **5a** and **5b** obtained upon irradiation at different wavelengths (c = 30 μM in DMSO)

	5a	**5b**
PSS^{365}	72%	63%
PSS^{375}	48%	54%
PSS^{405}	58%	68%
PSS^{470}	80%	58%
PSS^{505}	86%	78%
PSS^{520}	76%[a]	73%[a]
PSS^{570}	28%	62%

[a] The relative fractions were obtained from the NMR data.

2.4. Calculation of the Gibbs free activation energies and half-lives of photoisomers

Performed using the method described by Dube *et al*. (ref. [8] in main text). For the calculation of the Gibbs free activation energies Δ*G** for the thermal *E*,*Z*–*Z*,*Z* isomerization and corresponding lifetimes at 25 °C, the pre-irradiated solutions (λ_{irr} = 505 nm) of bis(hemi-indigo) derivatives **5a** and **5b** were heated at 70 °C in DMSO (*c* = 30 μM), and absorption spectra were recorded every 10 min overnight. Considering that the thermal *E*,*Z*–*Z*,*Z* isomerization of bis(hemi-indigos) **5a** and **5b** is a unimolecular first order reaction, which proceeds completely to the pure *E*,*Z*-isomer, Equation 2 can be applied.

$$-\frac{d[Z,E]}{dt}=\frac{d[Z,Z]}{dt}=k[Z,E] \qquad \text{(Eq. 2)}$$

where *k* is the rate constant of the thermal *E*,*Z*–*Z*,*Z* relaxation at a certain temperature.

From the exponential fitting of the thermal dark *E*,*Z*–*Z*,*Z* relaxation, after pre-irradiation by 520 nm light monitored at 70 °C, the rate constants *k* were obtained at a wavelength where only one out of two isomers absorbs (Figure S2).

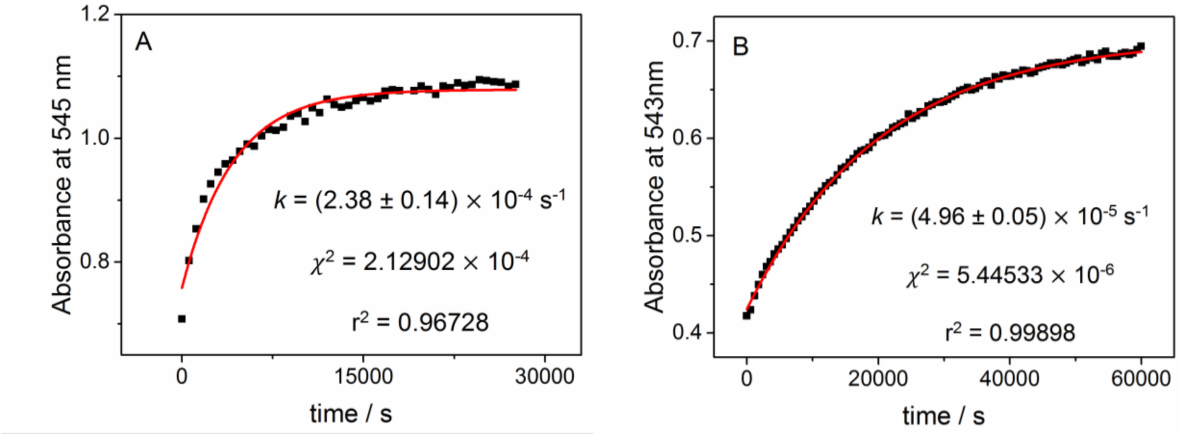

Figure S2. Evolution of the absorbance (black squares) for the thermal *E*,*Z*–*Z*,*Z* isomerization in DMSO, at 70 °C of **5a** (A), λ_{det} = 545 nm and **5b** (B), λ_{det} = 543 nm; solid red line indicates the fit of the experimental data to the monoexponential model.

For the calculation of the free activation energy Δ*G**, the *Eyring* equation was used:

$$k=\frac{k_BT}{h}e^{-\frac{\Delta G^*}{RT}} \qquad \text{(Eq. 3)}$$

where k_B is the Boltzmann constant, *h* is the Plank constant, *R* is the universal gas constant and *T* is the temperature in K. Equation 3 can be rearranged as following:

$$\Delta G^* = 8.314T\,(23.760 + \ln{(T/k)}) \qquad \text{(Eq. 4)}$$

Utilizing the obtained Δ*G** values, the half-lives of the *E*,*Z*-isomers of **5a** and **5b** at 25 °C were calculated (Table S2).

Table S2. Gibbs free activation energies Δ*G** for the thermal *E*,*Z*–*Z*,*Z* isomerization and corresponding half-lives at 25 °C of bis(hemi-indigos) **5a** and **5b**

	5a	**5b**
ΔG^*/ kJ mol^{-1}	108.2	112.7
τ / d	17	104

2.5. Calculation of the photoisomerization quantum yields

The quantum yields of the *E*,*Z*–*Z,Z* isomerization were determined upon irradiation with 520-nm (green) light. In the used setup, the irradiation was performed by placing a LED with known radiant power on the top of a photometric cell. Equation 5 was used for the calculation of the LED photon flux I_0 = 3.62E-08 mol L^{-1} s^{-1} of the LED.

$$I_0 = \frac{\lambda P_{\mathrm{LED}}}{hcN_A V} \times 0.001 \qquad \text{(Eq. 5)}$$

where λ is the peak wavelength of the LED, *h* is the Plank constant, *c* is the speed of light in vacuum, N_A is the Avogadro constant and *V* is the reaction volume.

The photoisomerization quantum yields were then calculated according to Equation 6.

$$\phi = \frac{\Delta A/\Delta T}{I_0\left(1 - 10^{-A'}\right) \cdot \varepsilon \cdot 1000} \qquad \text{(Eq. 6)}$$

where Δ*A*/Δ*t* is the change of absorbance at the detection wavelength within the time, I_0 is the intensity of the light source, A′ is the initial absorption of the sample at the irradiation wavelength and ε is the extinction coefficient at the detection wavelength. For the forward *E,Z*–*Z,Z* switching of **5a** and **5b** that starts from 100% of the *Z,Z*-isomer, Δ*A*/Δ*t* corresponds to the initial slope of the *A vs t* kinetics recorded at the wavelength, where the absorbance of the *Z,Z*-isomer is close to zero.

Table S3. Quantum yields of the photochemical *E*,*Z*–*Z,Z* isomerization of compounds **5a** and **5b** at 505 nm in different solvents (*c* = 30 μM)

Solvent	5a	5b
Dioxane	n.d.	79%
Toluene	65%	40%
$CHCl_3$	12%	5%
EtOAc	n.d.	30%
EtOH	16%	30%
MeOH	35%	7%
MeCN	57%	22%
DMSO	42%	20%

3. NMR data

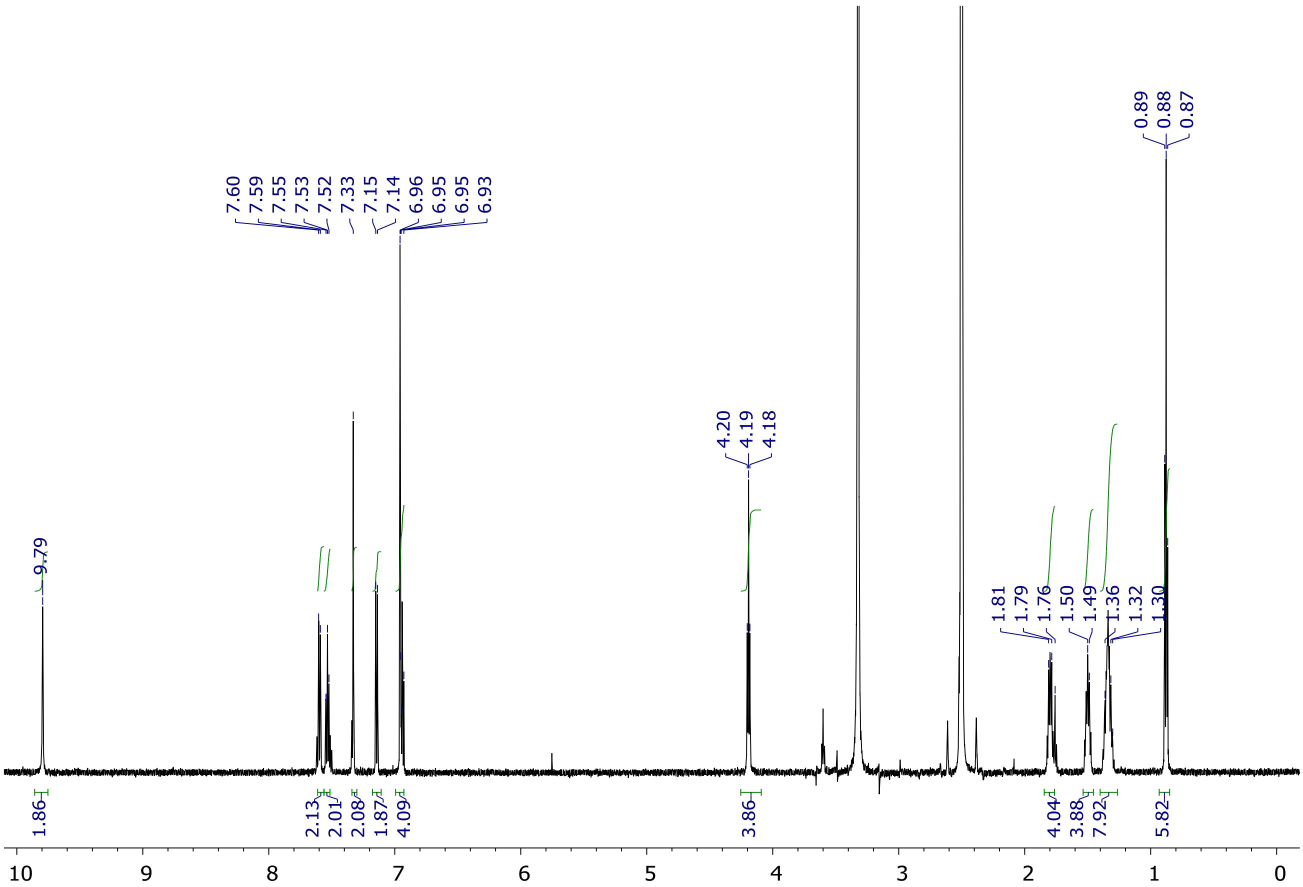

Figure S3. ^{1}H NMR spectrum of **5a** in DMSO-d_6.

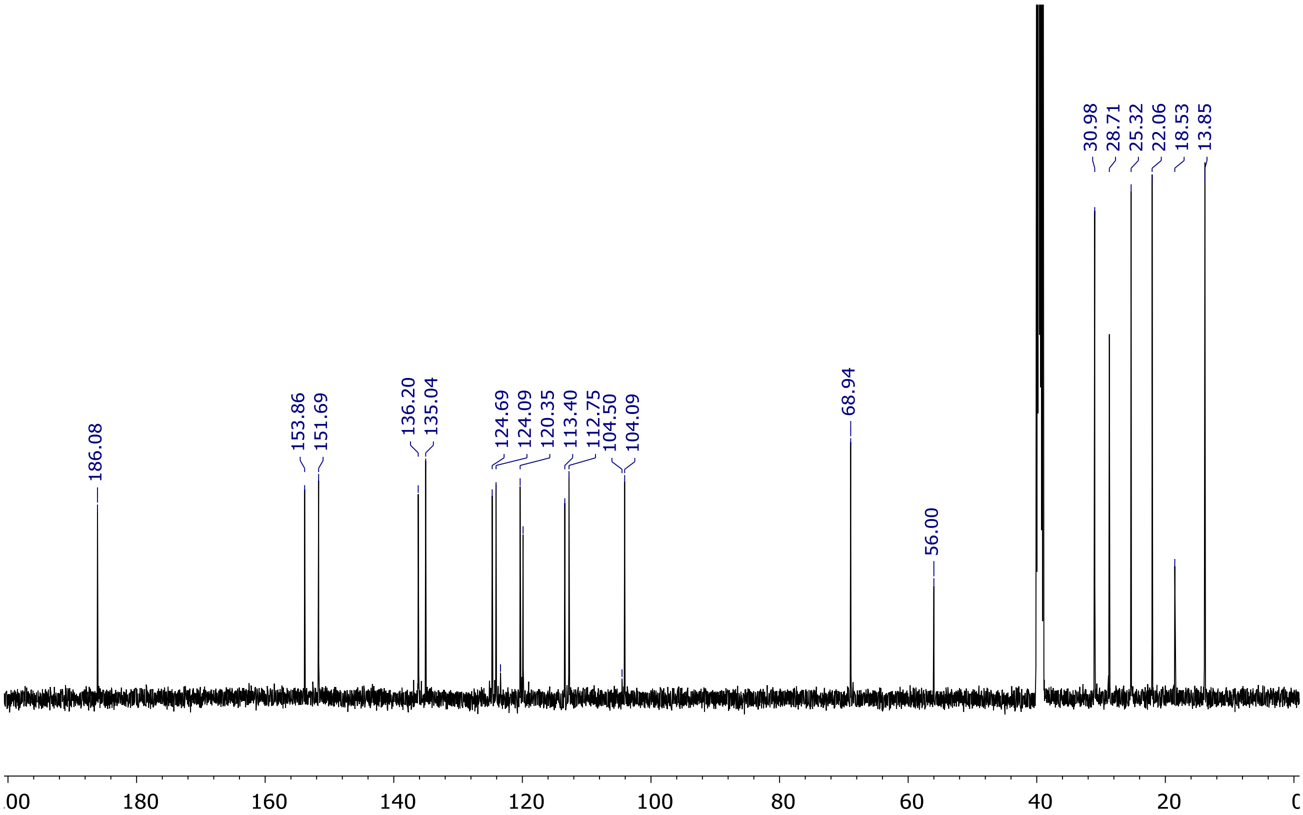

Figure S4. ^{13}C NMR spectrum of **5a** in DMSO-d_6.

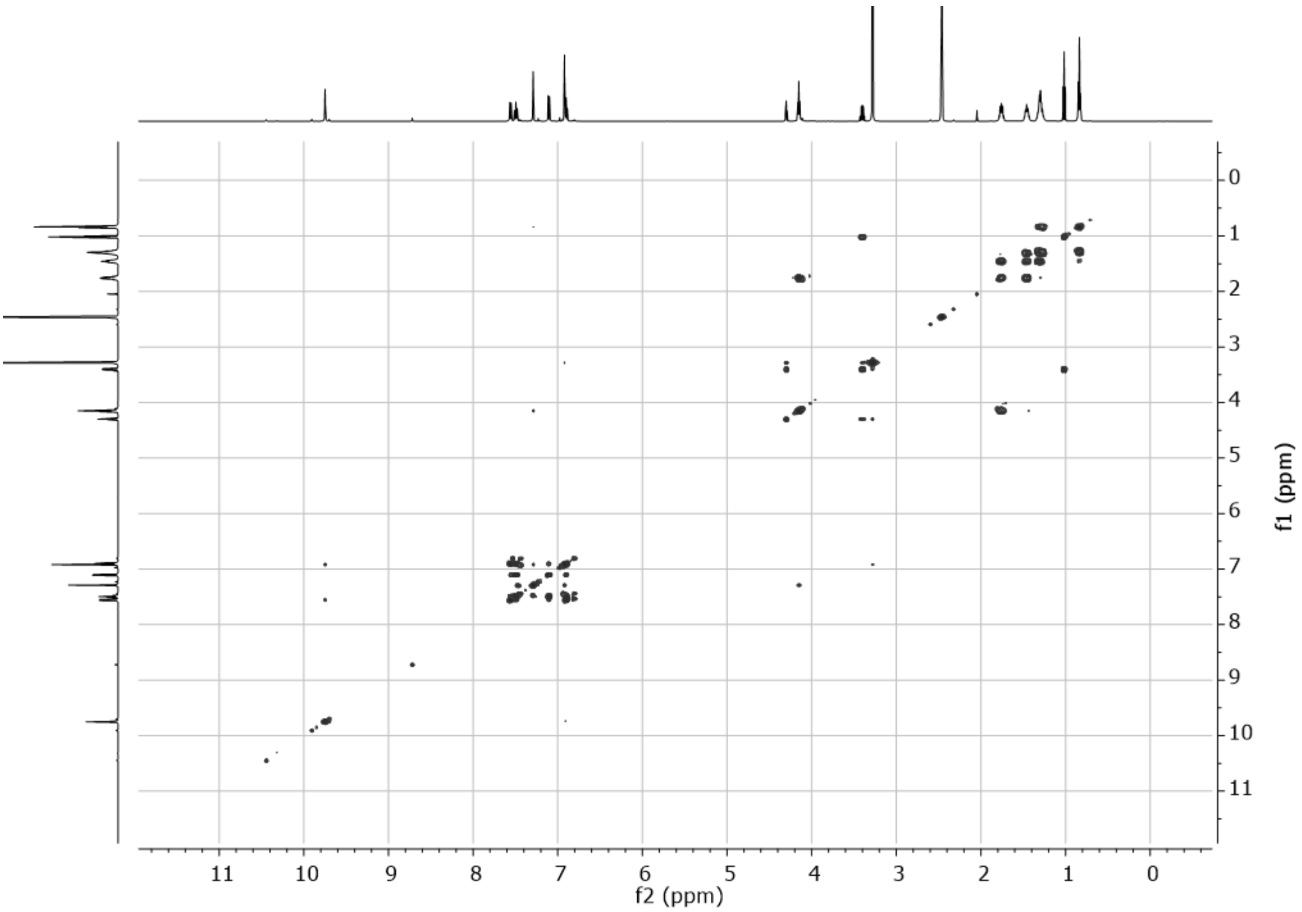

Figure S5. COSY NMR spectrum of **5a** in DMSO-d_6.

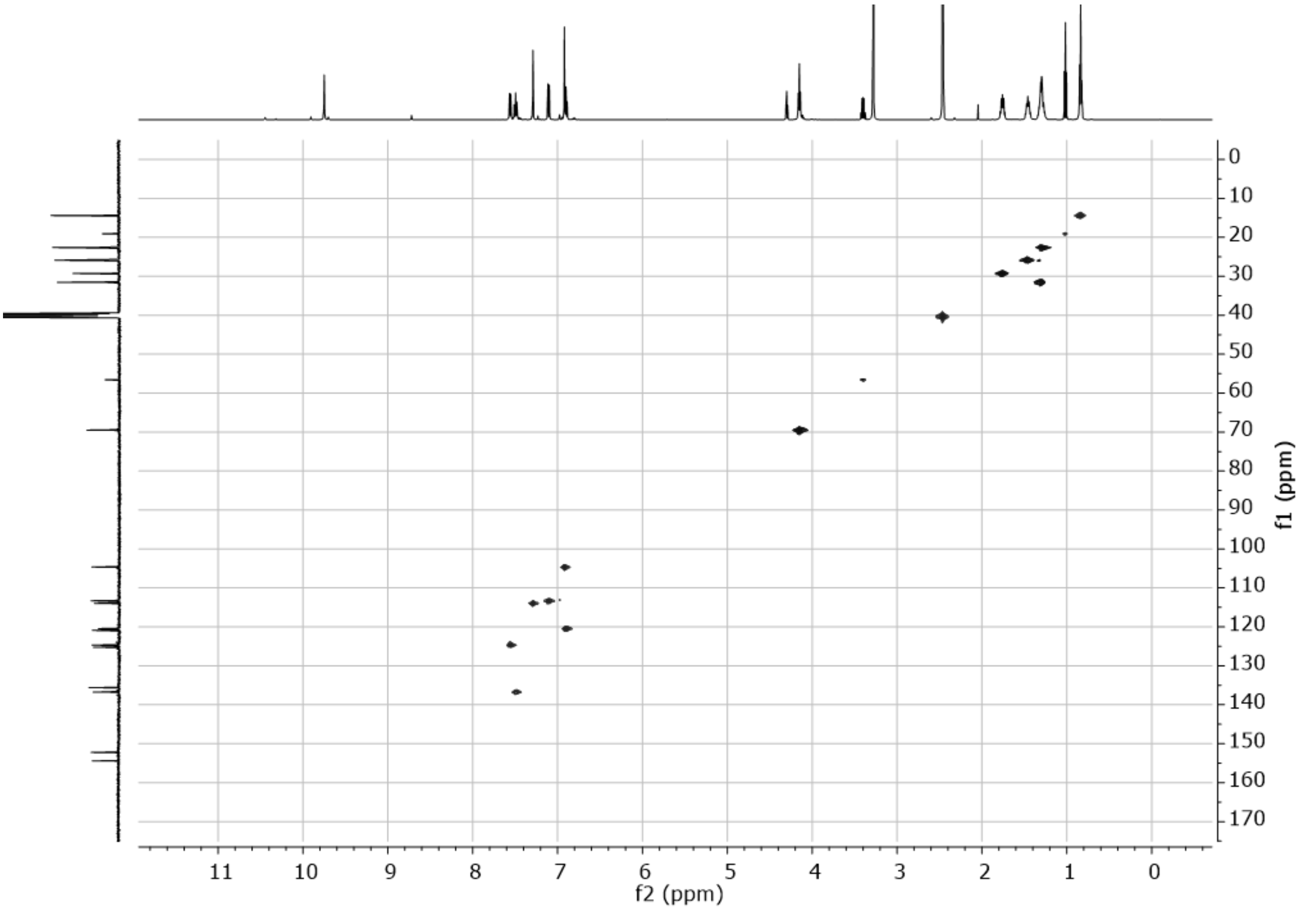

Figure S6. HSQC NMR spectrum of **5a** in DMSO-d_6.

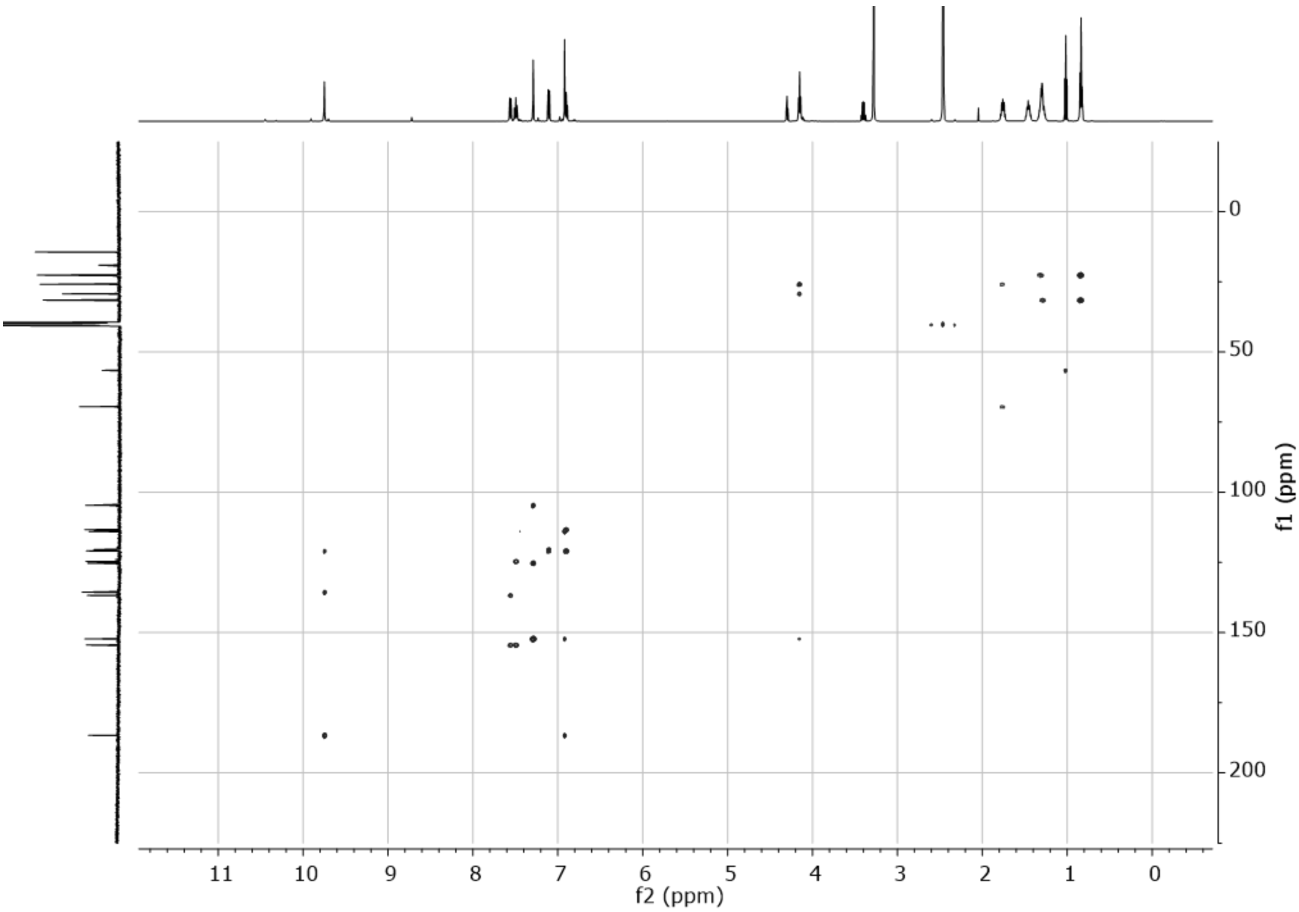

Figure S7. HMBC NMR spectrum of **5a** in DMSO-d_6.

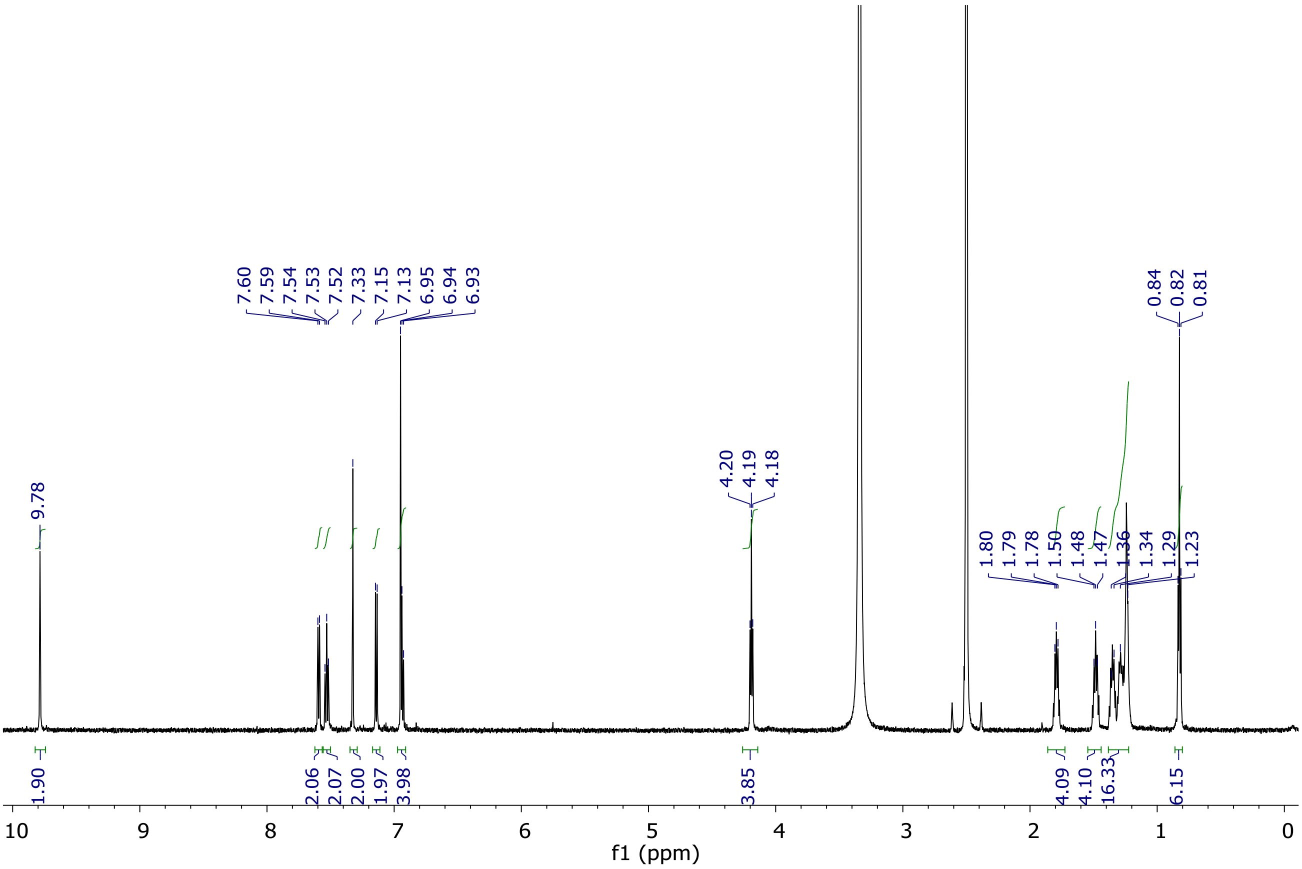

Figure S8. ^{1}H NMR spectrum of **5b** in DMSO-d_6.

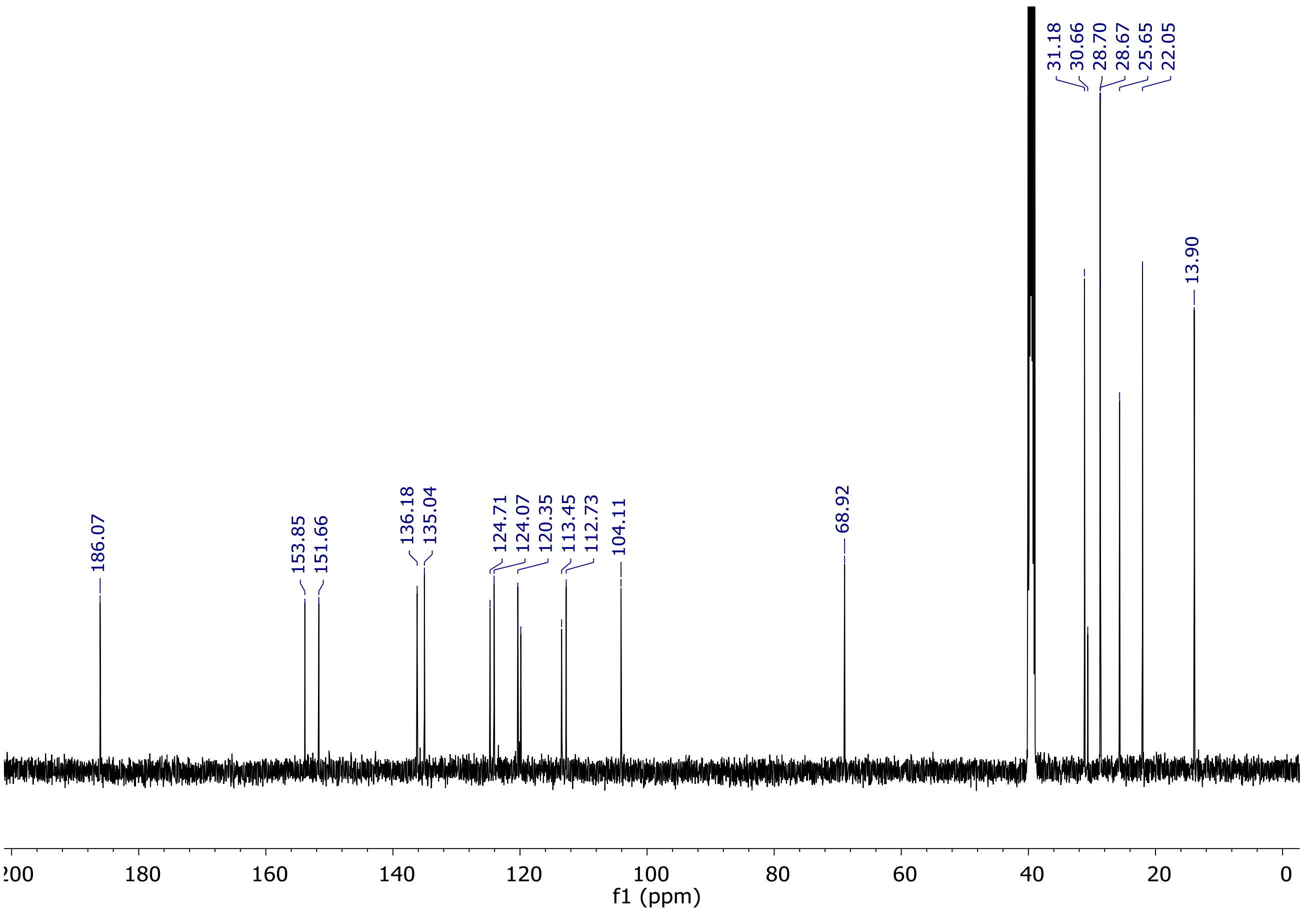

Figure S9. ^{13}C NMR spectrum of **5b** in DMSO-*d*$_6$.

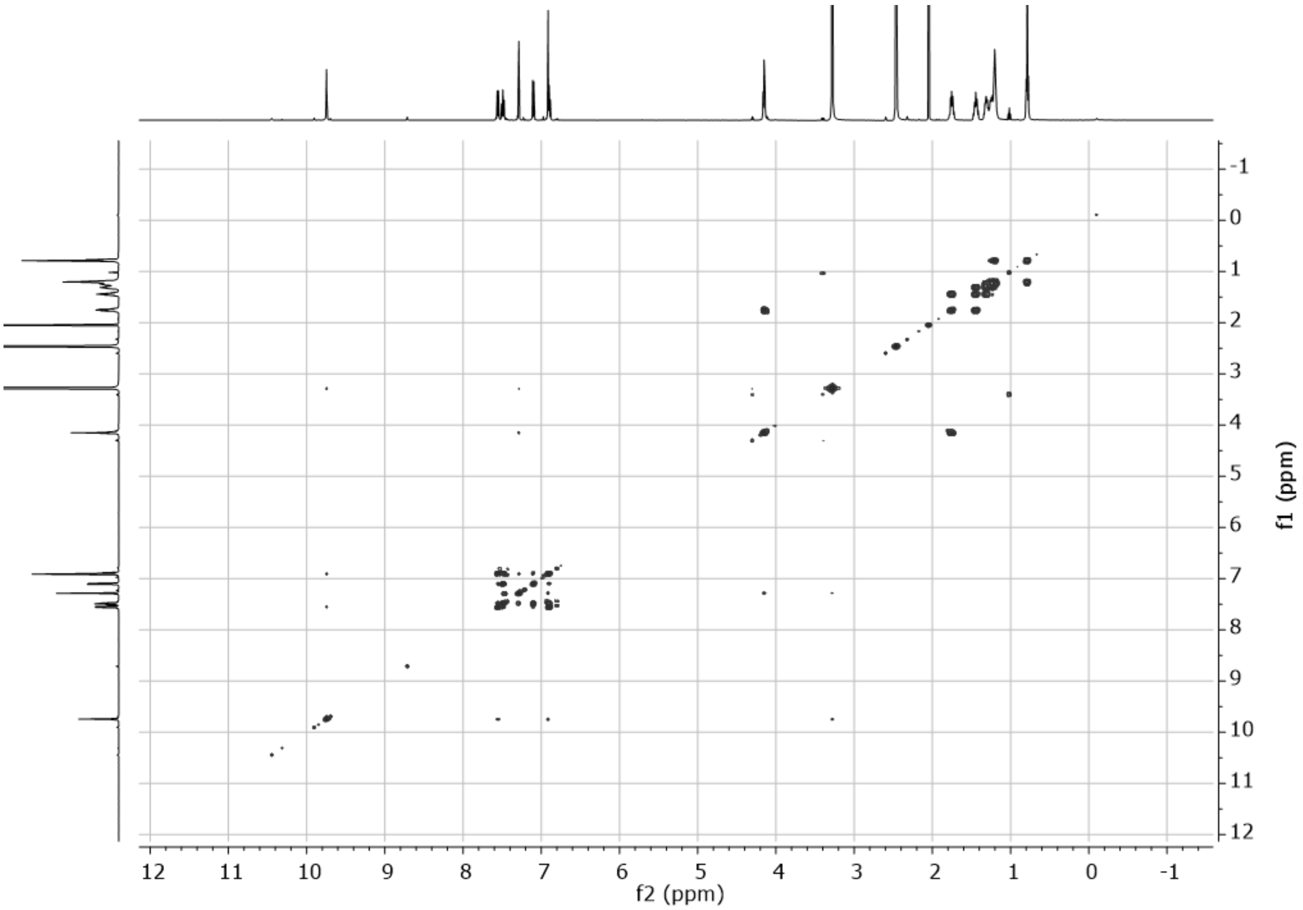

Figure S10. COSY NMR spectrum of **5a** in DMSO-*d*$_6$.

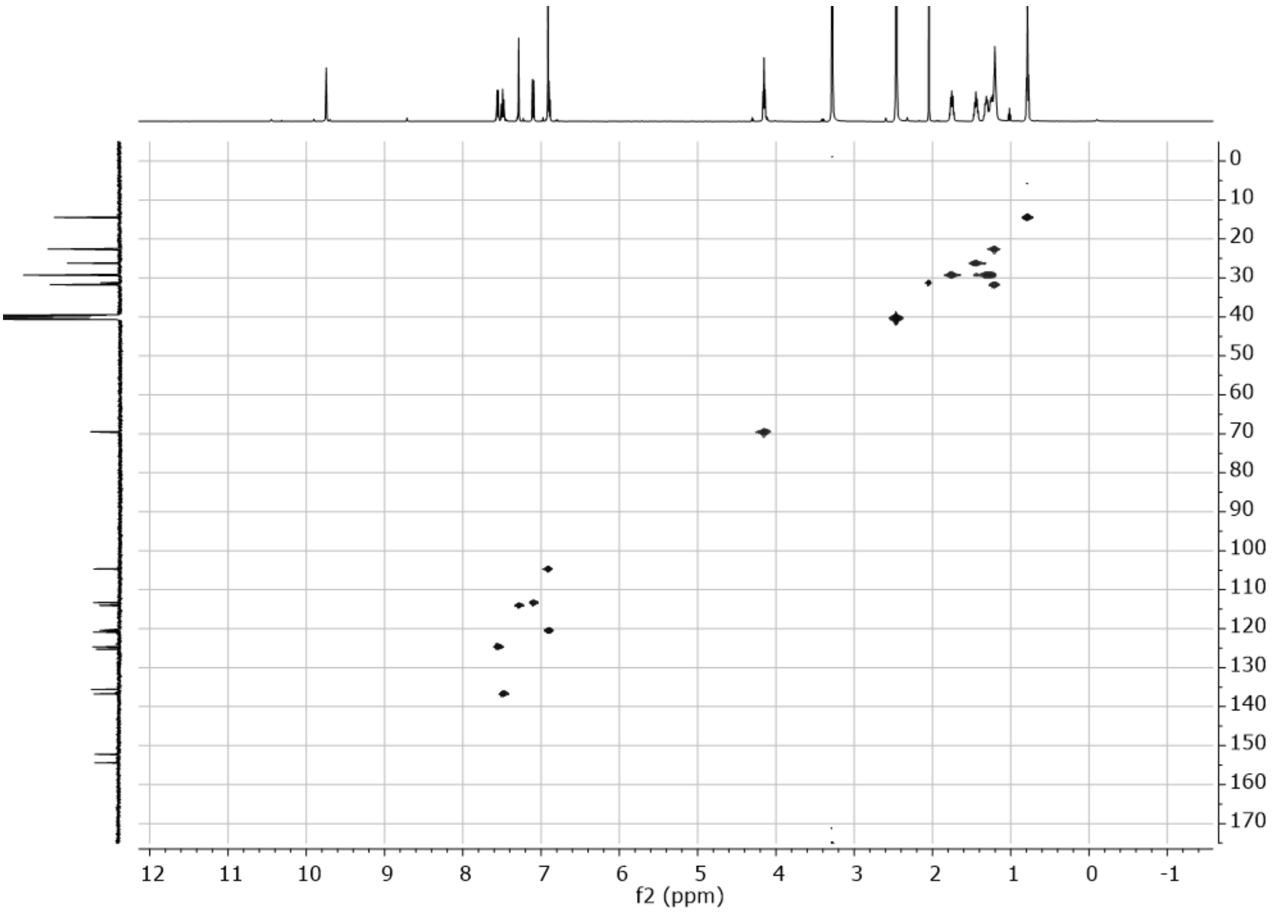

Figure S11. HSQC NMR spectrum of **5a** in DMSO-d_6.

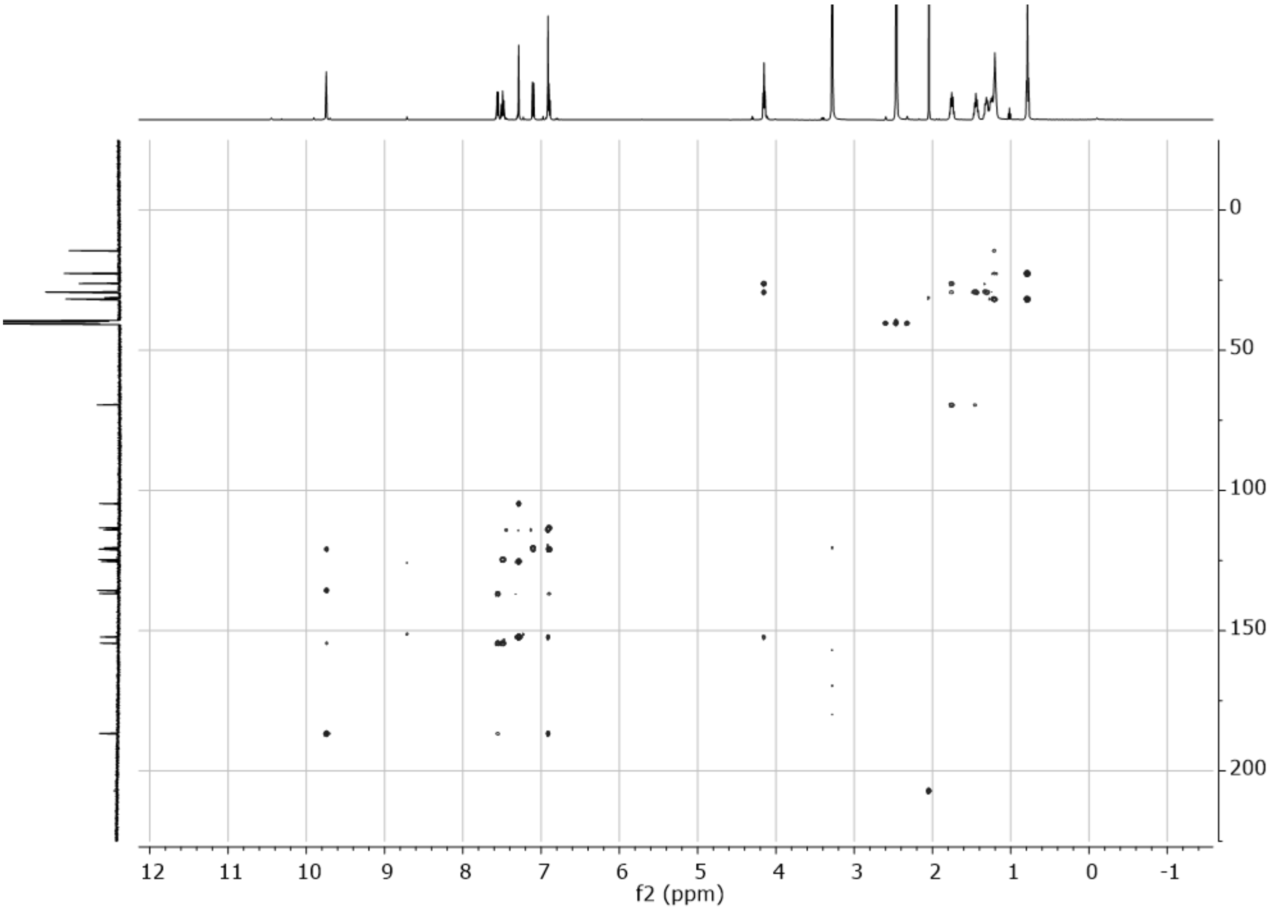

Figure S12. HMBC NMR spectrum of **5a** in DMSO-d_6.