

**Supporting Information**

**Tuning the hybridization properties of modified oligonucleotides: from flexible to conformationally constrained phosphonate internucleotide linkages.**

Ondřej Páv<sup>a</sup>, Ivan Barvík,<sup>b</sup> Radek Liboska,<sup>a</sup> Magdalena Petrová,<sup>a</sup> Ondřej Šimák,<sup>a,c</sup> Šárka Rosenbergová,<sup>a</sup> Pavel Novák,<sup>a</sup> Miloš Buděšínský,<sup>a</sup> and Ivan Rosenberg<sup>a</sup>

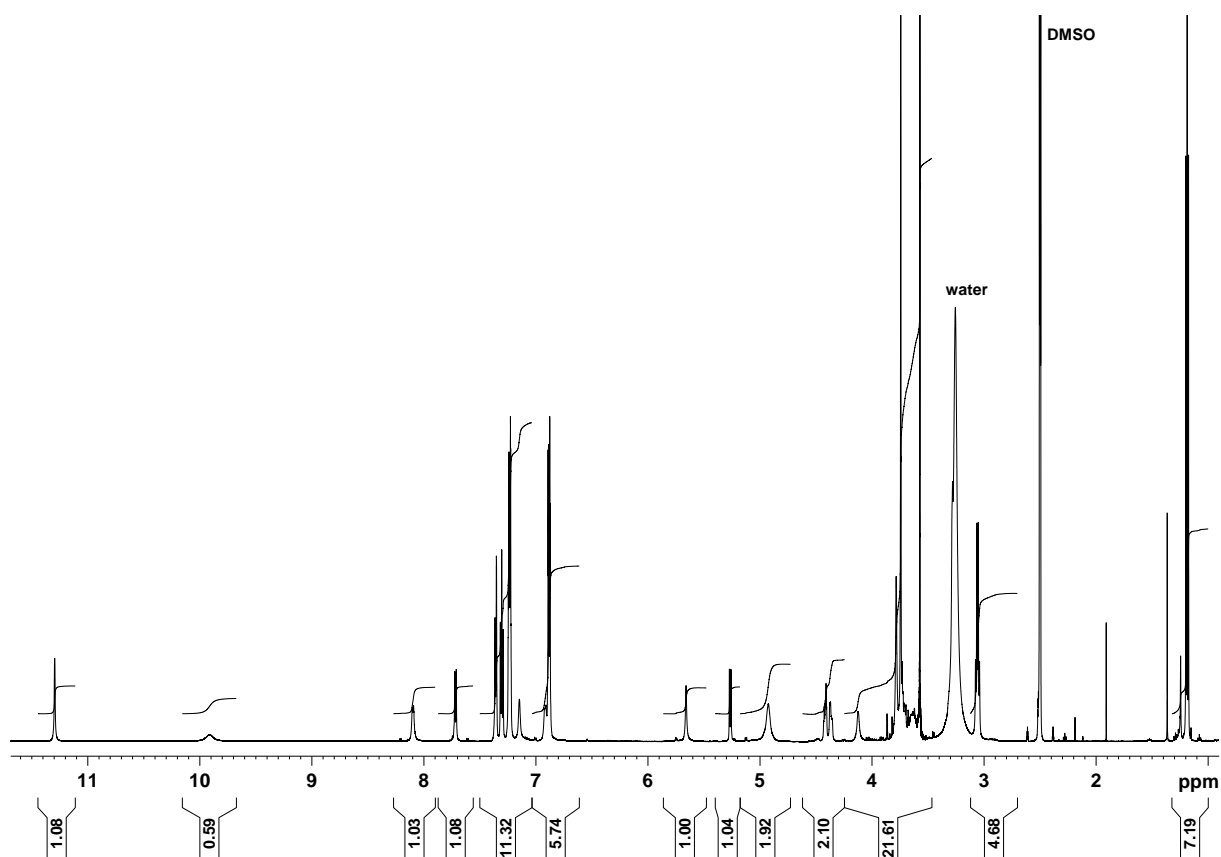
<sup>a</sup> Institute of Organic Chemistry and Biochemistry of the CAS, Flemingovo náměstí 2, 16610 Prague, Czech Republic.

<sup>b</sup> Faculty of Mathematics and Physics, Institute of Physics, Charles University, Ke Karlovu 5, 12116 Prague, Czech Republic.

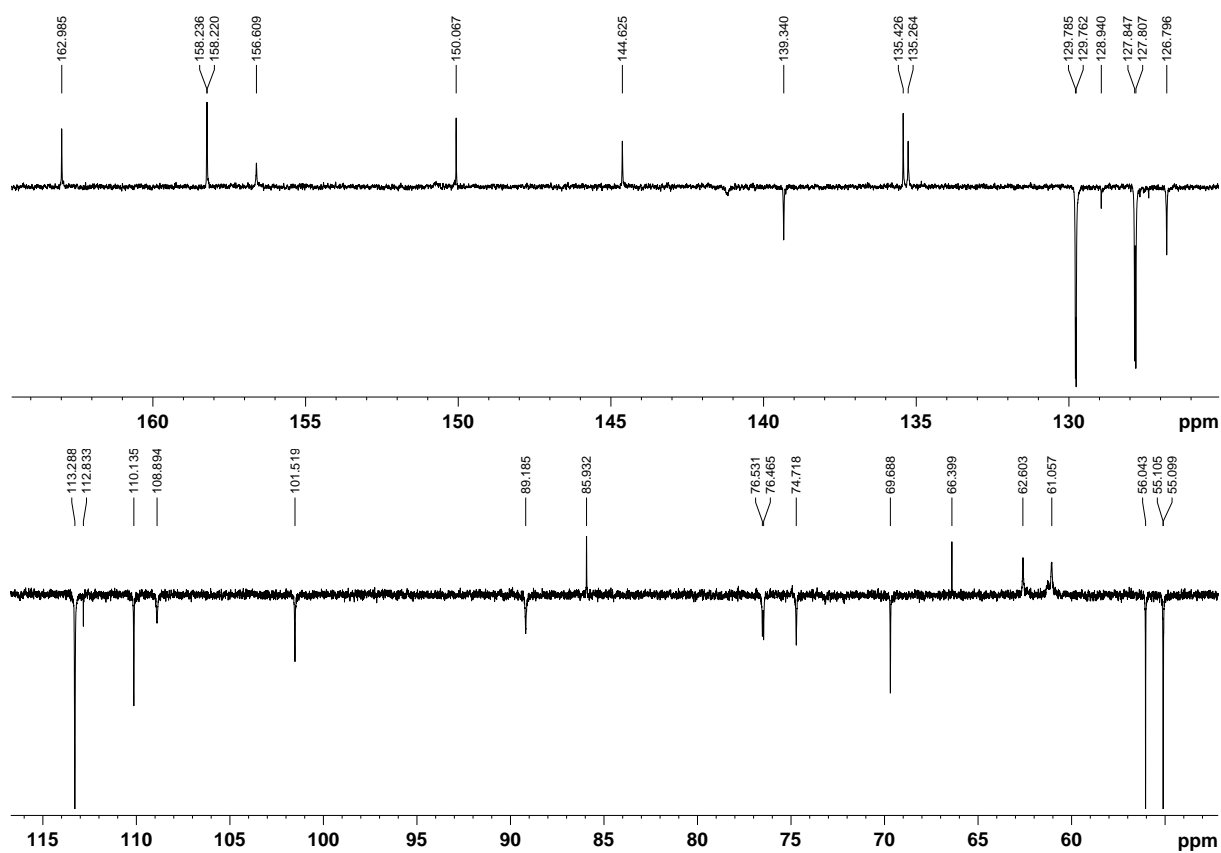
<sup>c</sup> Department of Chemistry of Natural Compounds, University of Chemistry and Technology, Technická 5, 16628 Prague, Czech Republic.

NMR Spectra

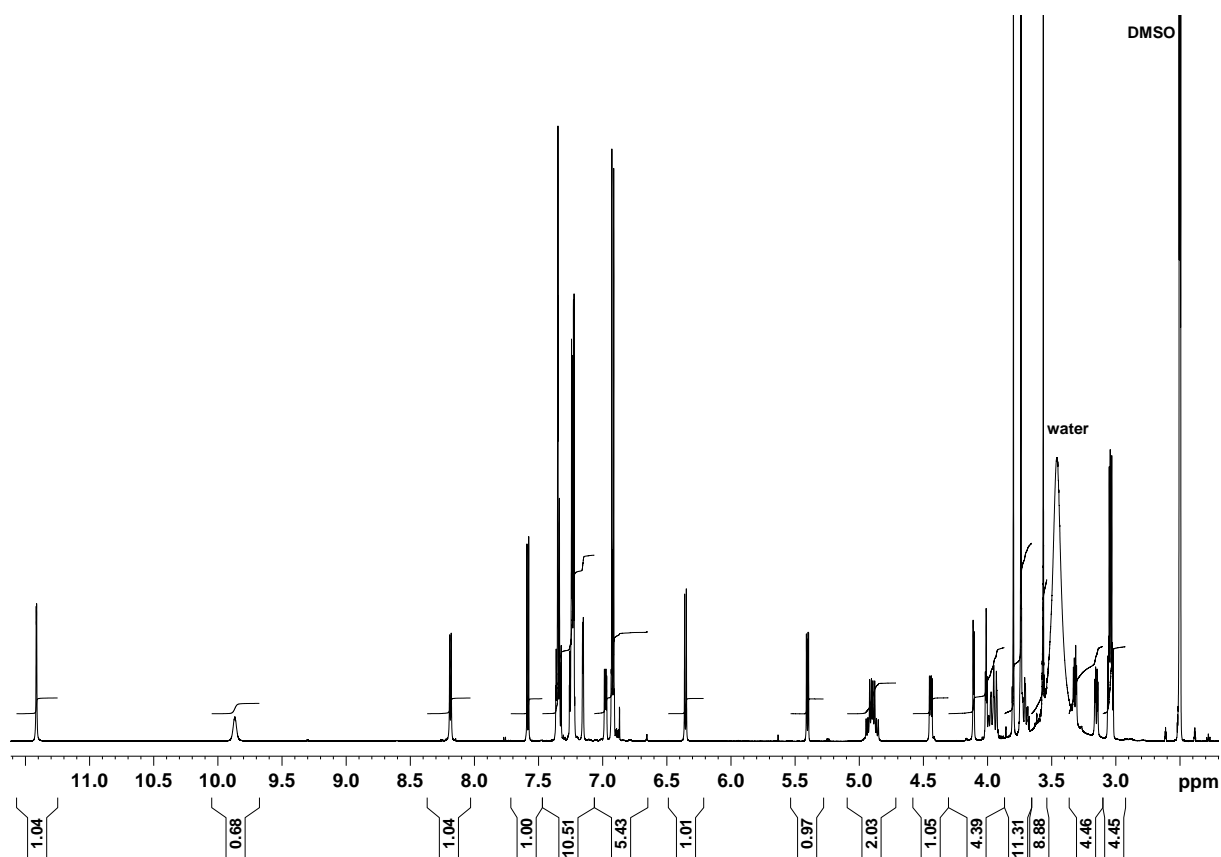
2



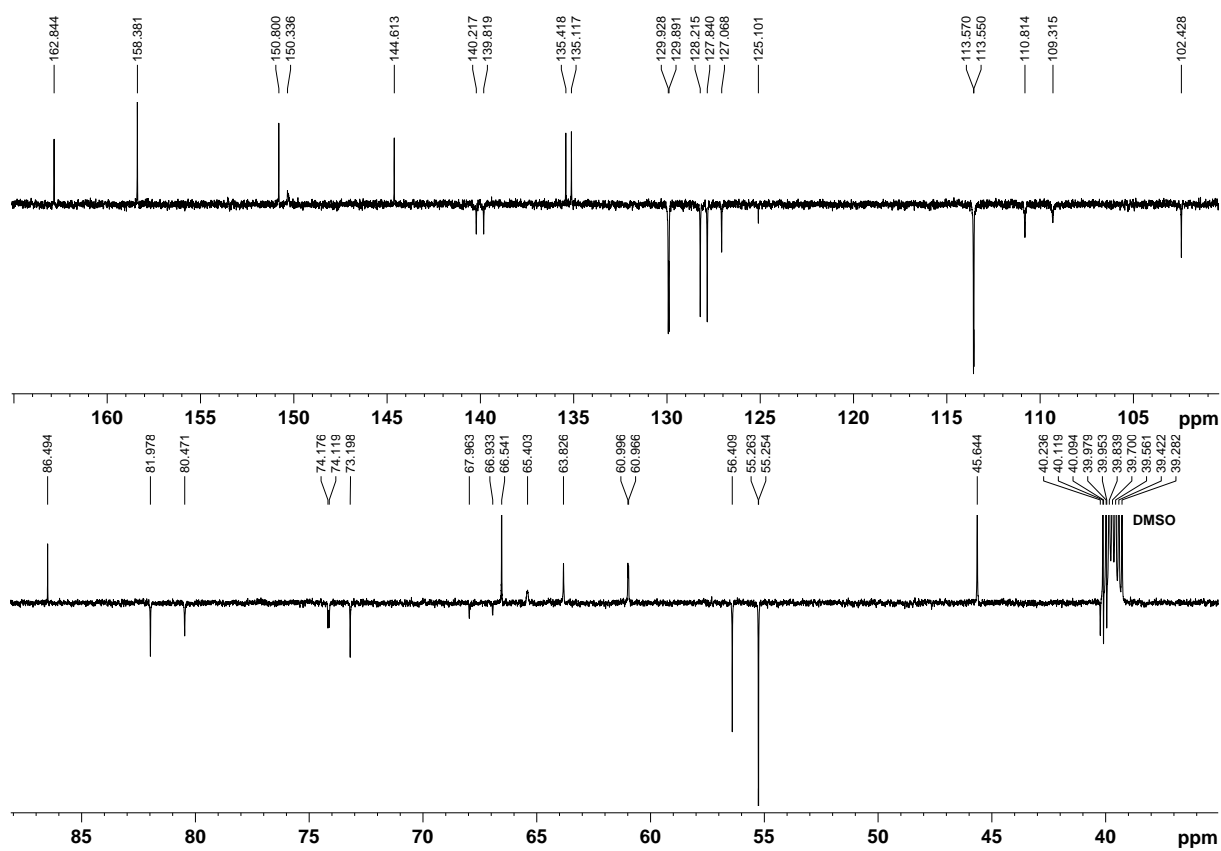
**Figure S1** <sup>1</sup>H NMR spectrum (600 MHz) of compound **23a** in d<sub>6</sub>DMSO at 47 °C.



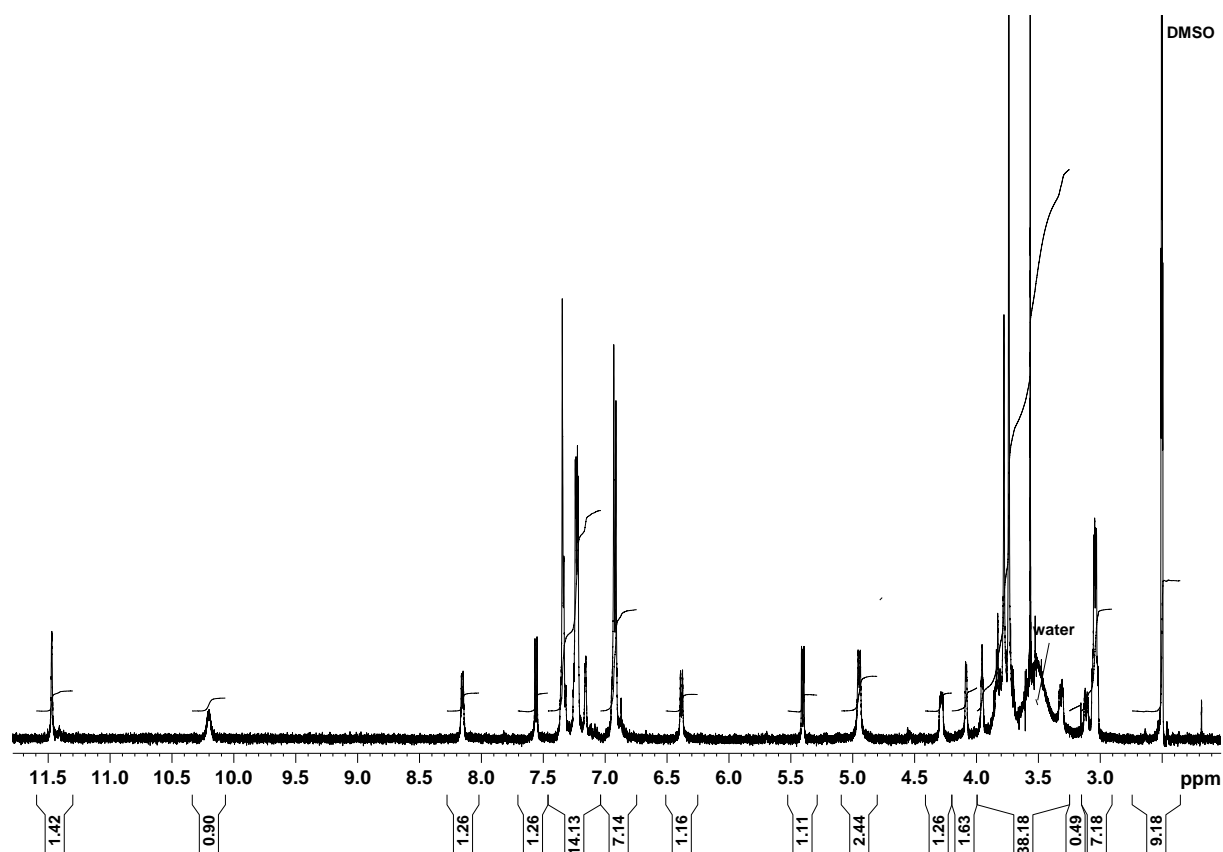
**Figure S2** <sup>13</sup>C NMR spectrum (150.9 MHz) of compound **23a** in d<sub>6</sub>DMSO at 47 °C.



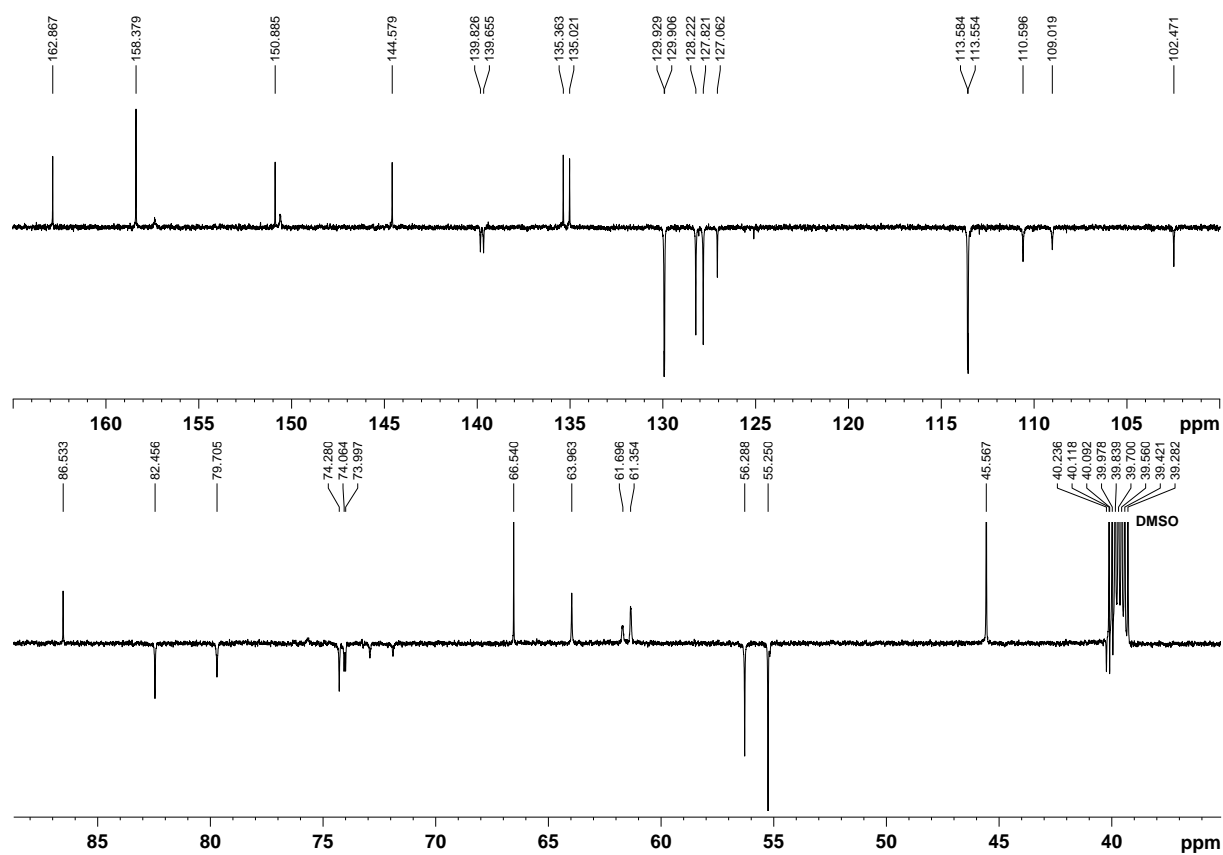
**Figure S3**  $^1\text{H}$  NMR spectrum (600 MHz) of compound **24a** in  $d_6\text{DMSO}$  at 47 °C.



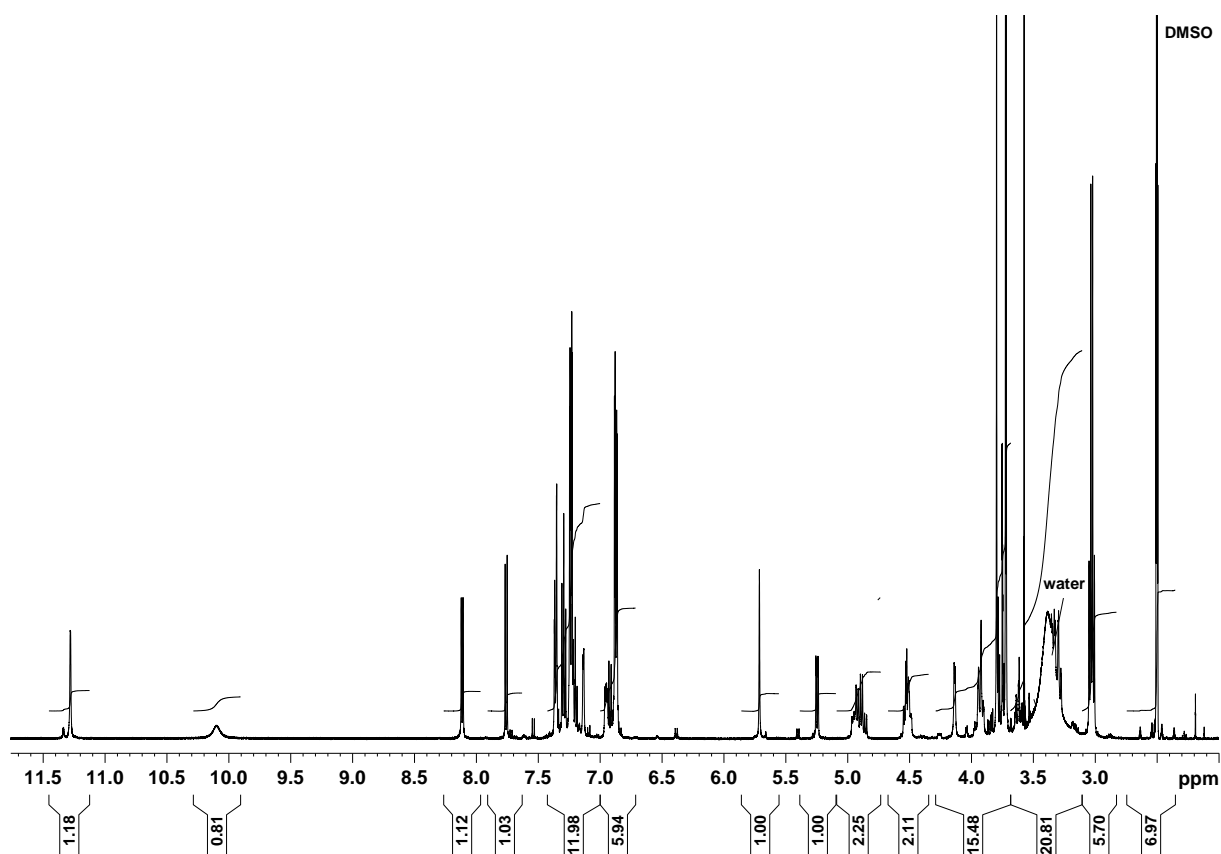
**Figure S4**  $^{13}\text{C}$  NMR spectrum (150.9 MHz) of compound **24a** in  $d_6\text{DMSO}$  at 47 °C.



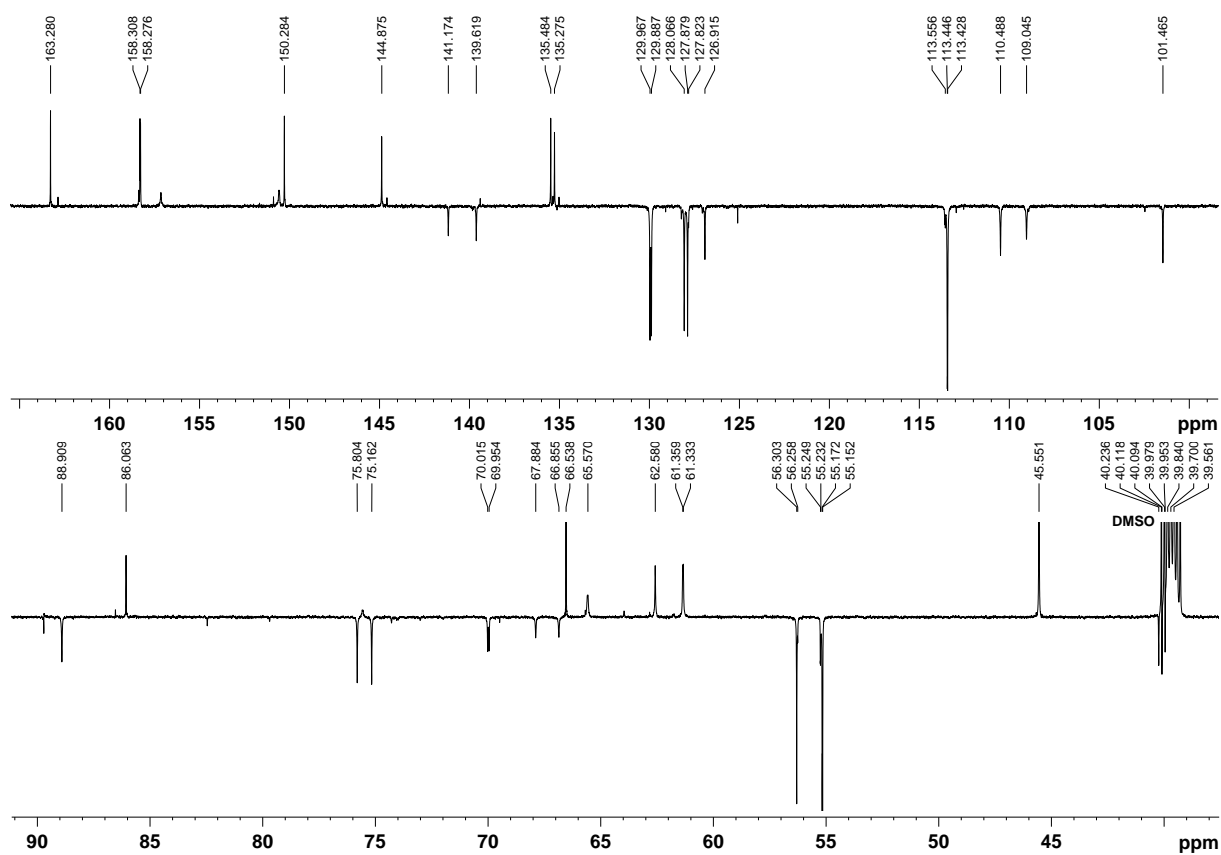
**Figure S5**  $^1\text{H}$  NMR spectrum (500 MHz) of compound **23b** in  $d_6\text{DMSO}$  at  $50\text{ }^\circ\text{C}$ .



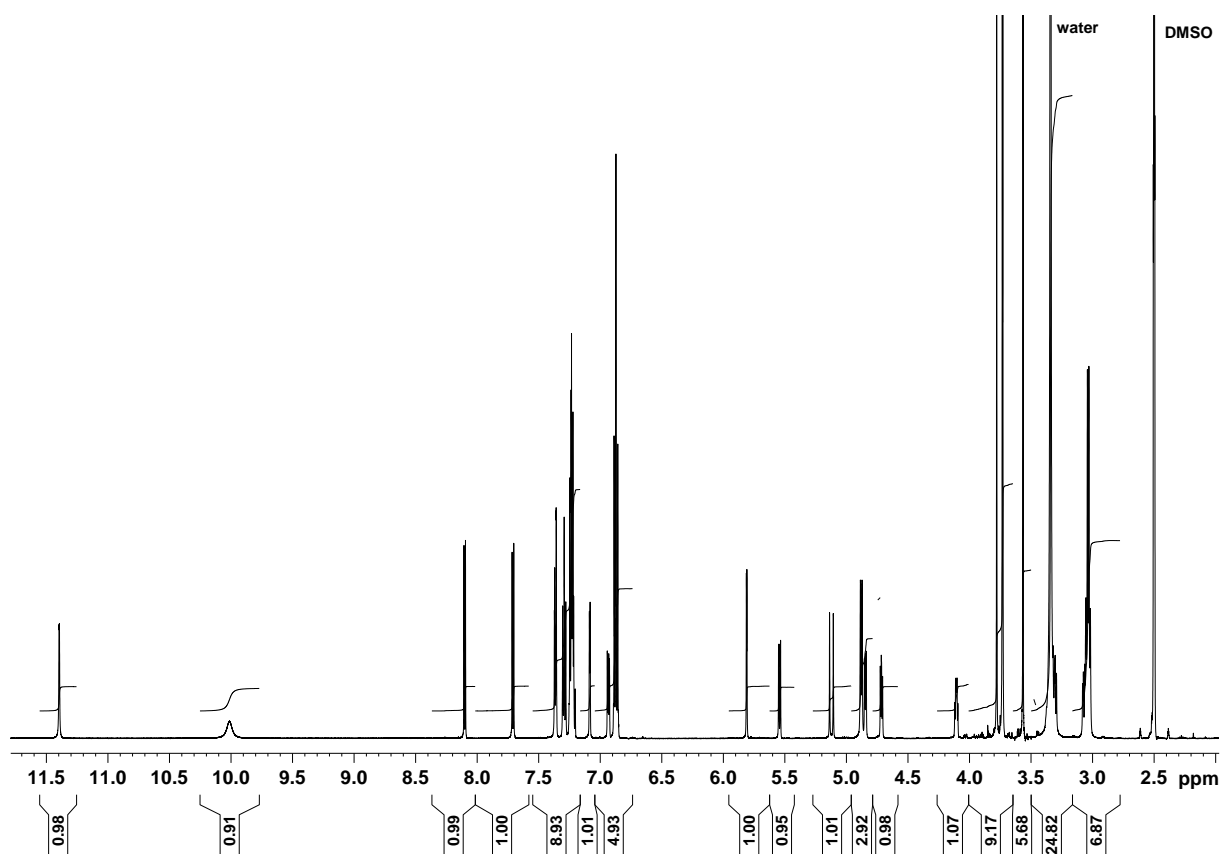
**Figure S6**  $^{13}\text{C}$  NMR spectrum (150.9 MHz) of compound **23b** in  $d_6\text{DMSO}$ .



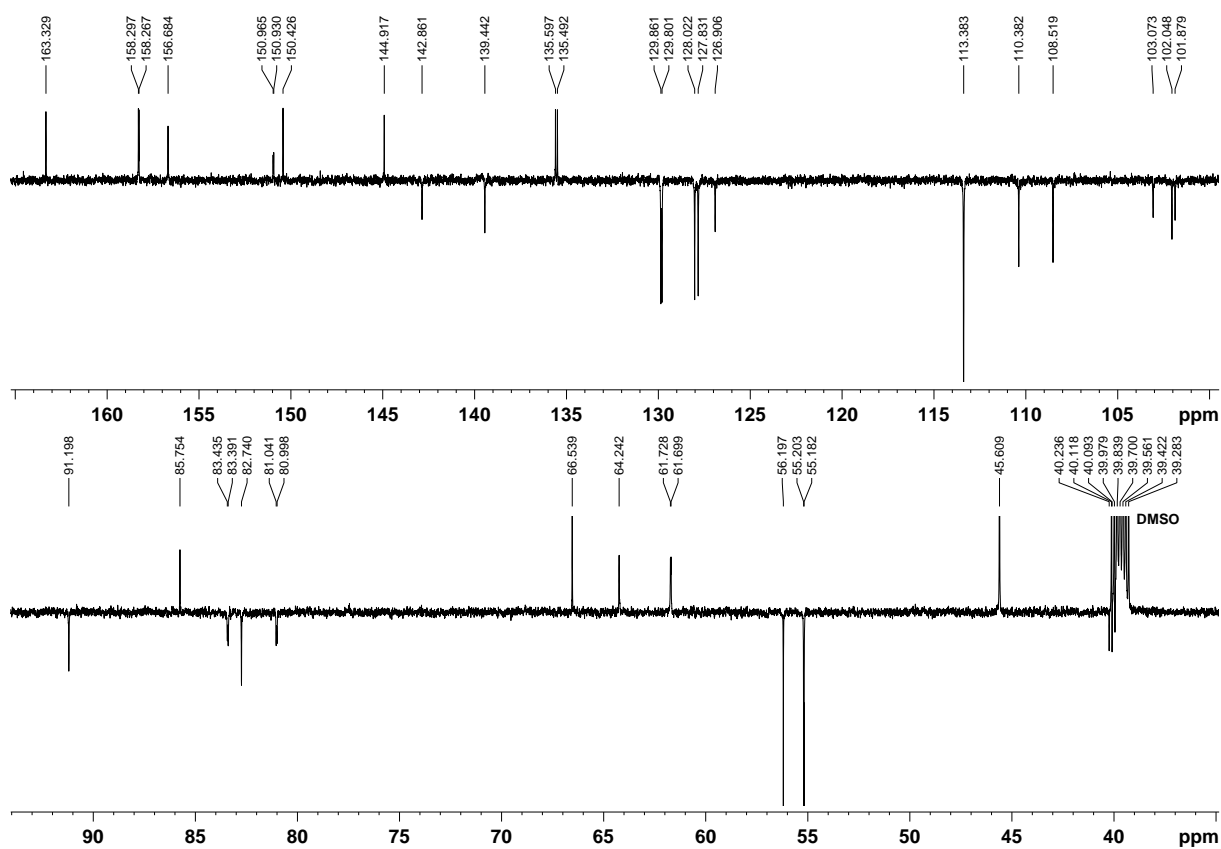
**Figure S7**  $^1\text{H}$  NMR spectrum (500 MHz) of compound **24b** in  $d_6\text{DMSO}$  at 50 °C.



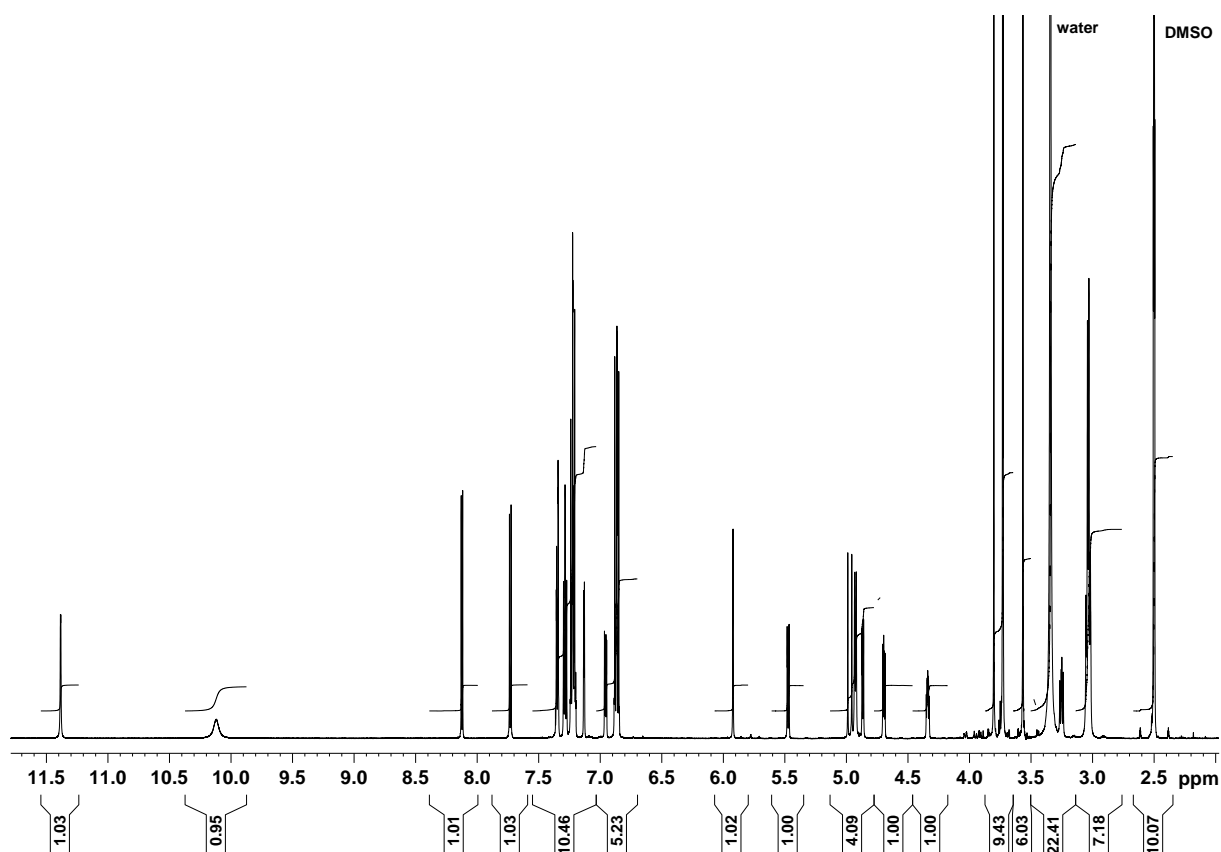
**Figure S8**  $^{13}\text{C}$  NMR spectrum (150.9 MHz) of compound **24b** in  $d_6\text{DMSO}$ .



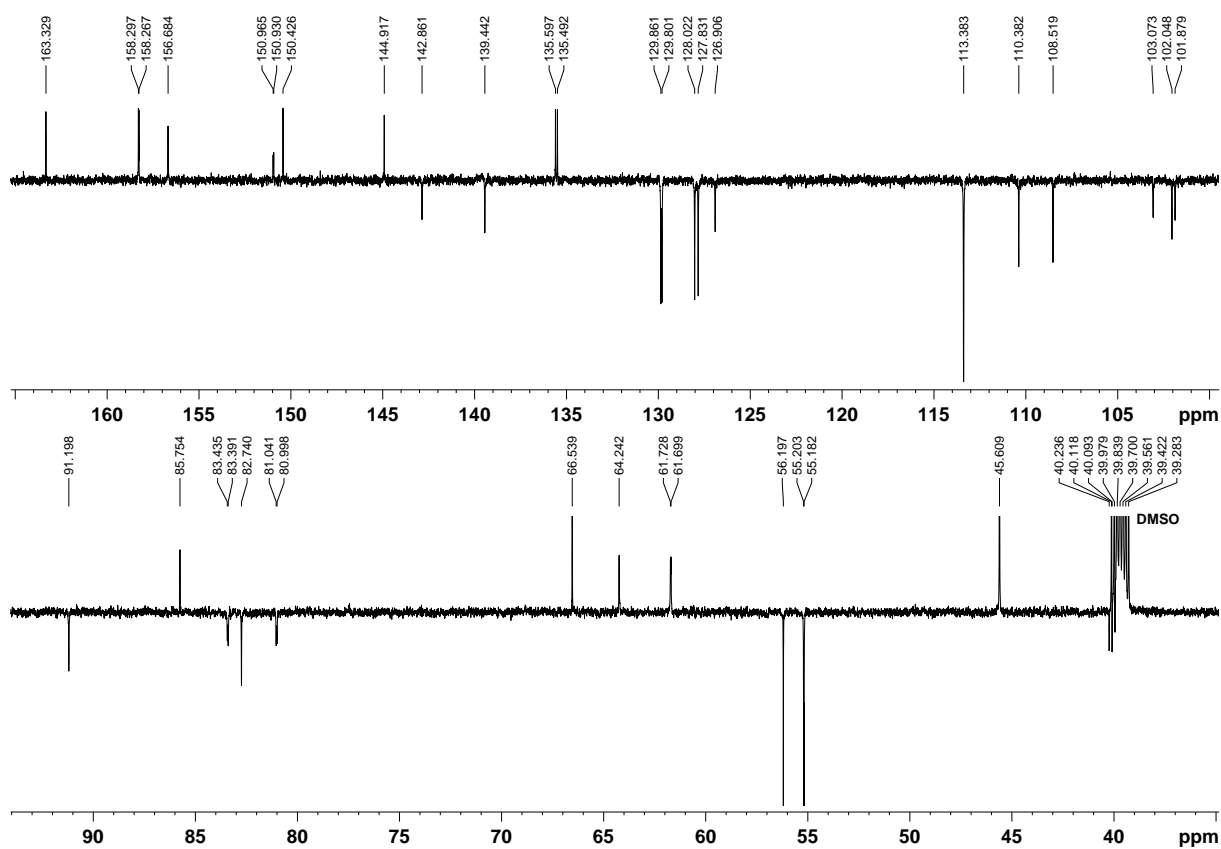
**Figure S9** <sup>1</sup>H NMR spectrum (600 MHz) of compound **27a** in d<sub>6</sub>DMSO.



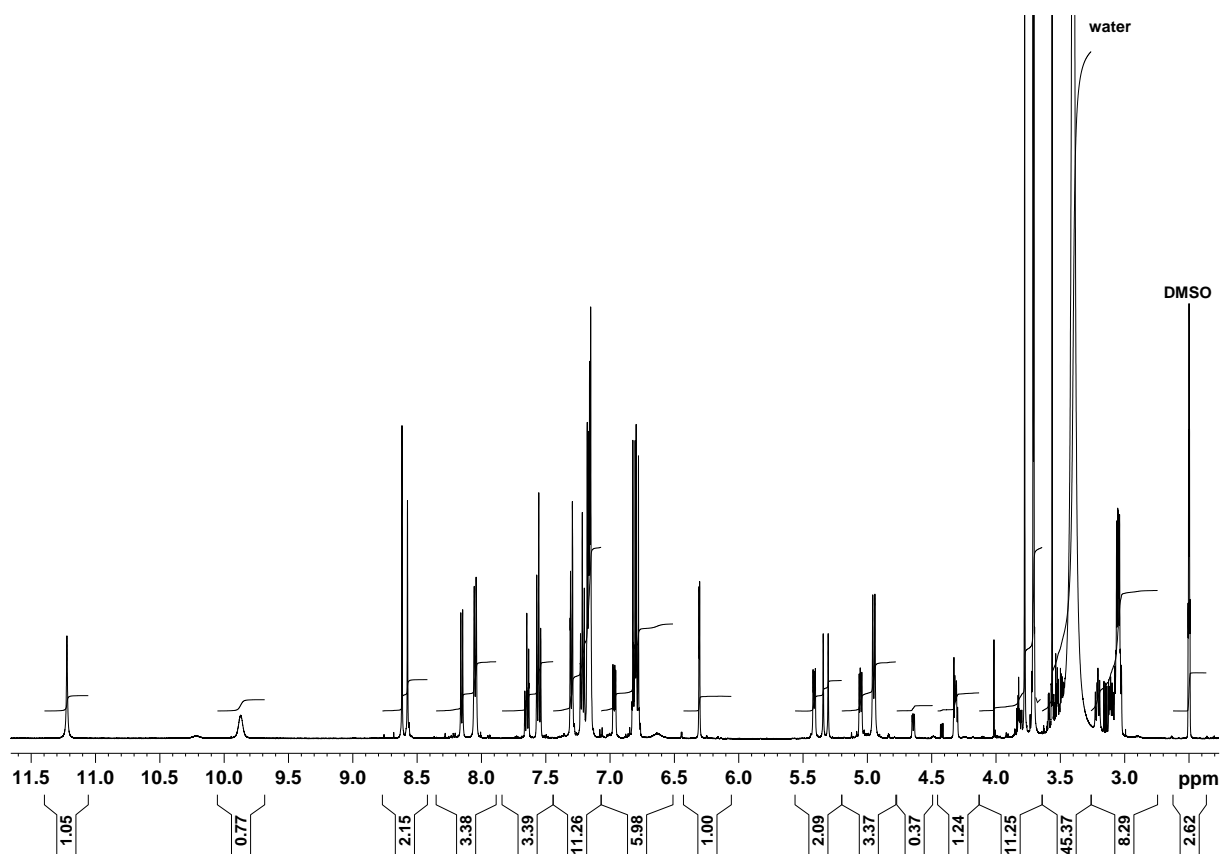
**Figure S10** <sup>13</sup>C NMR spectrum (150.9 MHz) of compound **27a** in d<sub>6</sub>DMSO.



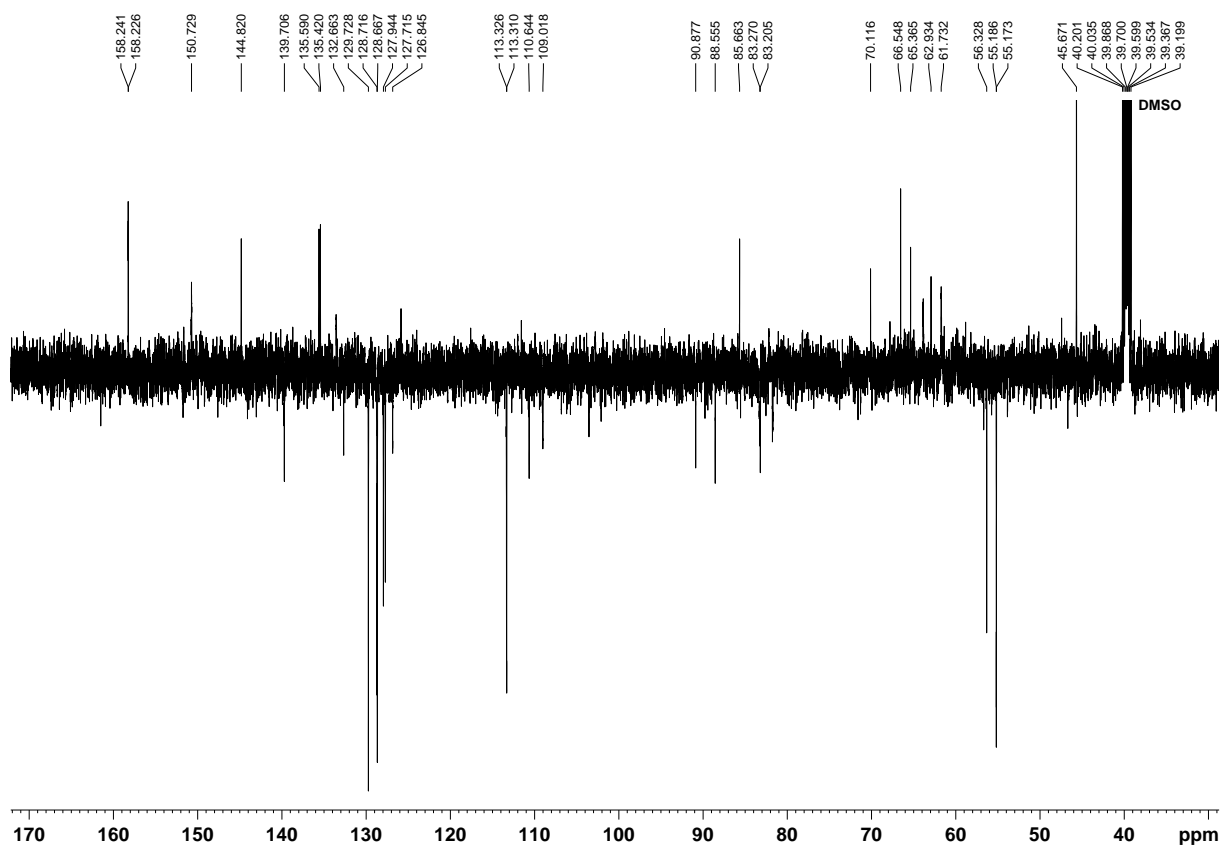
**Figure S11**  $^1\text{H}$  NMR spectrum (600 MHz) of compound **27b** in  $d_6\text{DMSO}$ .



**Figure S12**  $^{13}\text{C}$  NMR spectrum (150.9 MHz) of compound **27b** in  $d_6\text{DMSO}$ .

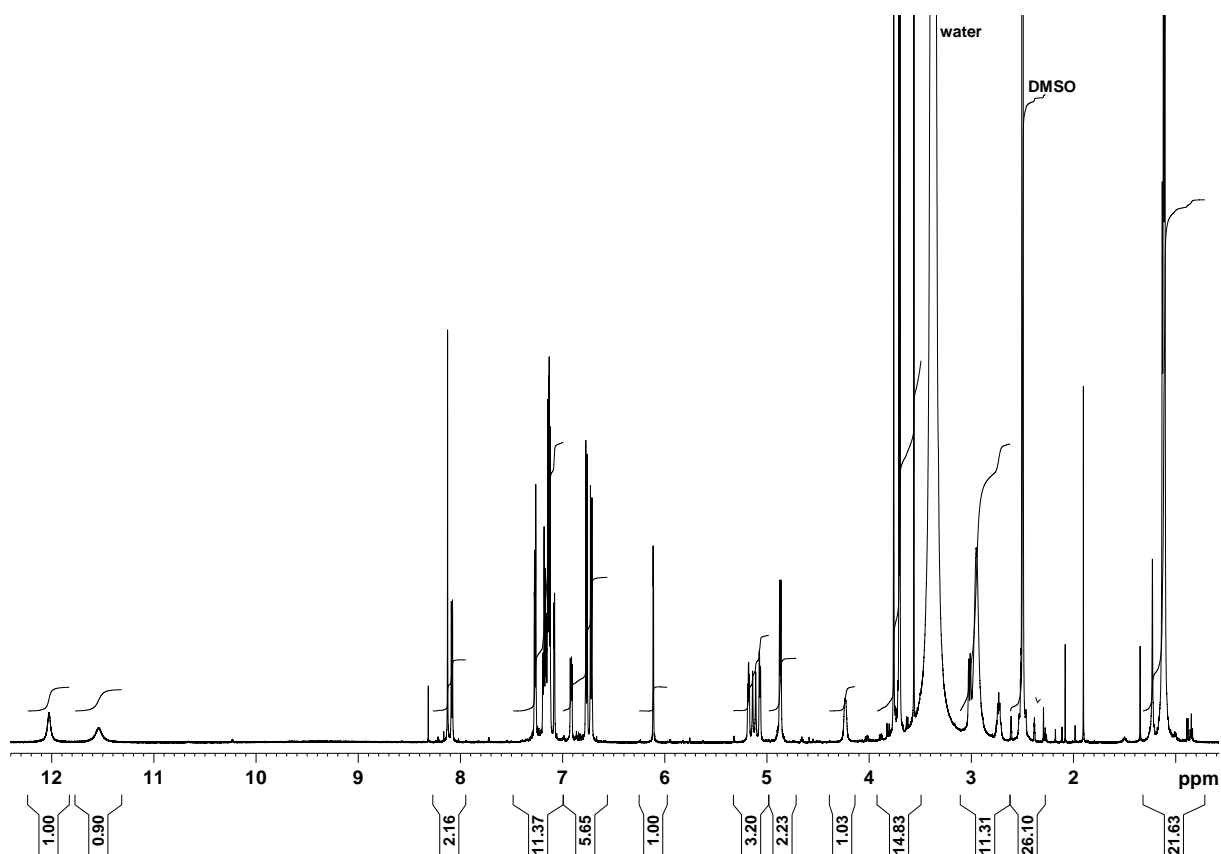


**Figure S13**  $^1\text{H}$  NMR spectrum (500 MHz) of compound **33a** in  $d_6\text{DMSO}$ .

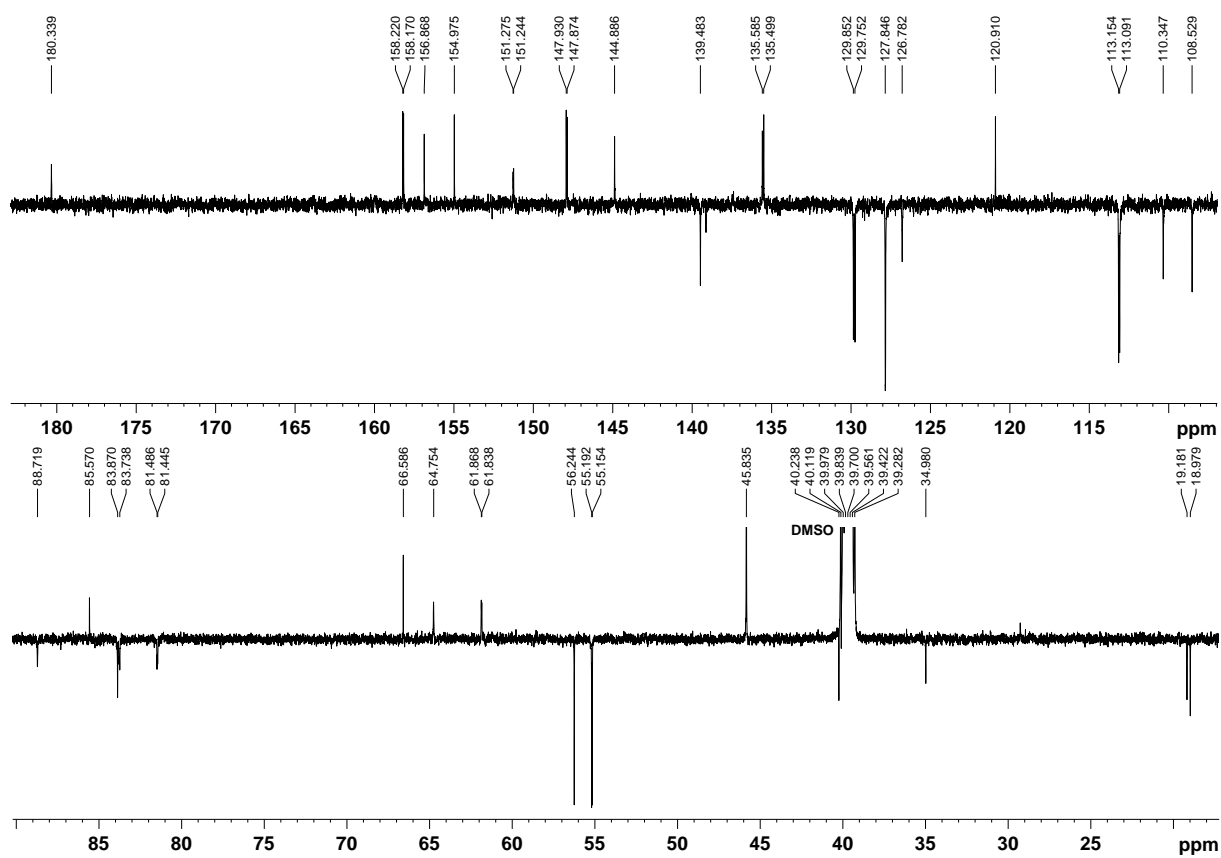


**Figure S14**  $^{13}\text{C}$  NMR spectrum (125.7 MHz) of compound **33a** in  $d_6\text{DMSO}$ .

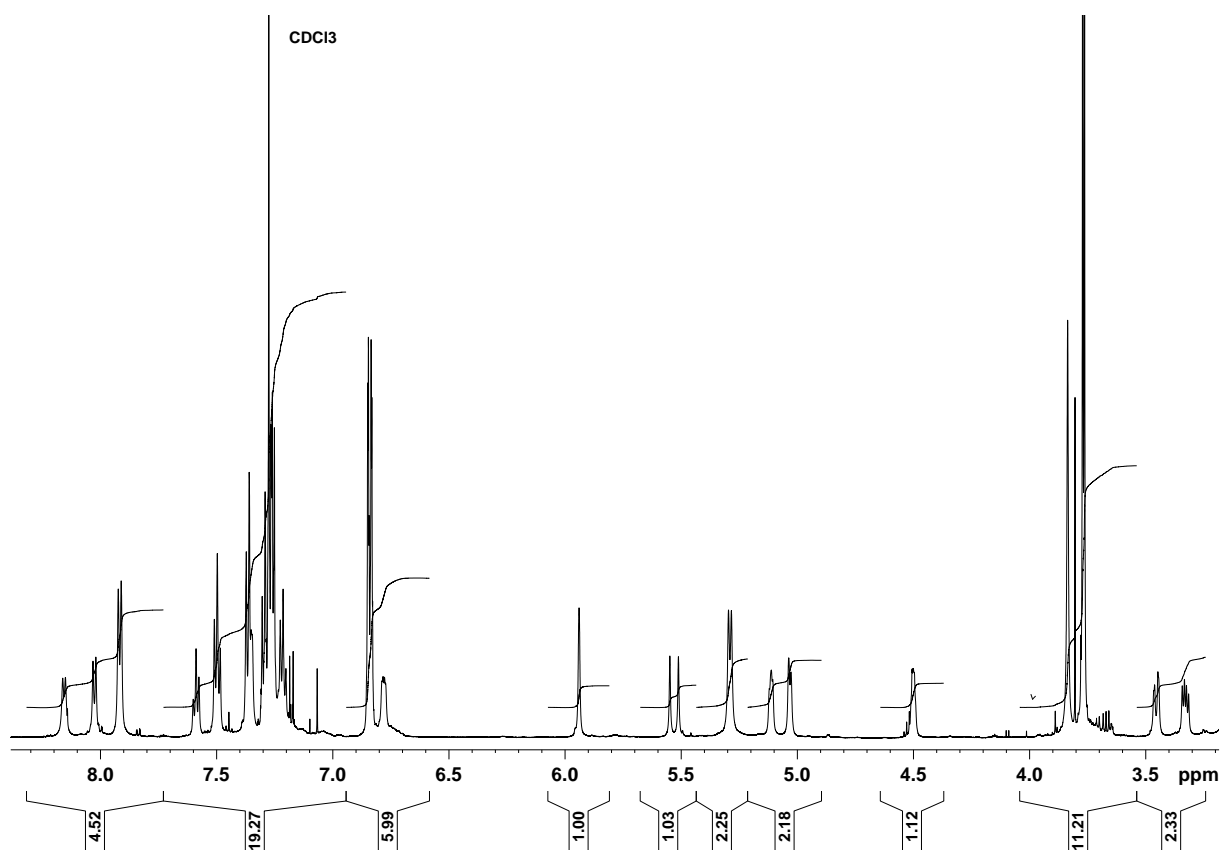




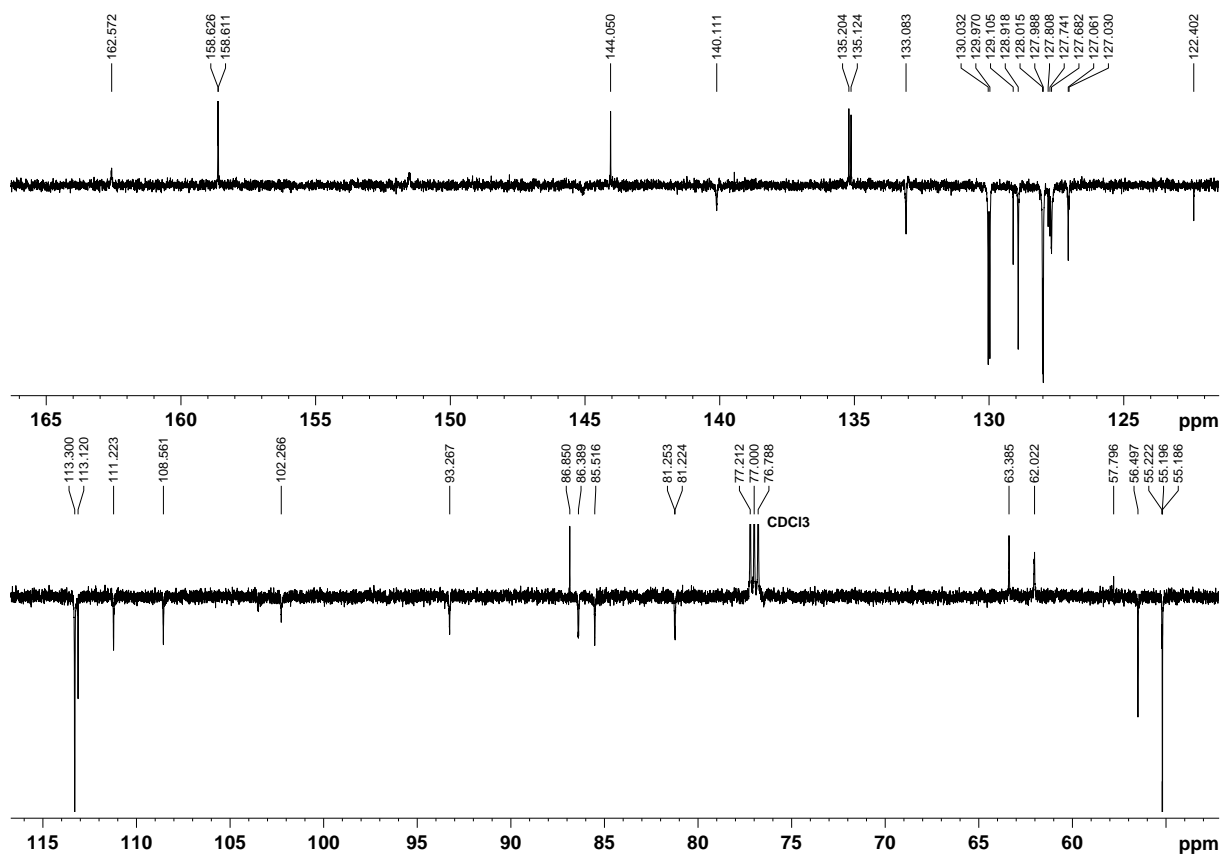
**Figure S15**  $^1\text{H}$  NMR spectrum (600 MHz) of compound **33b** in  $d_6\text{DMSO}$ .



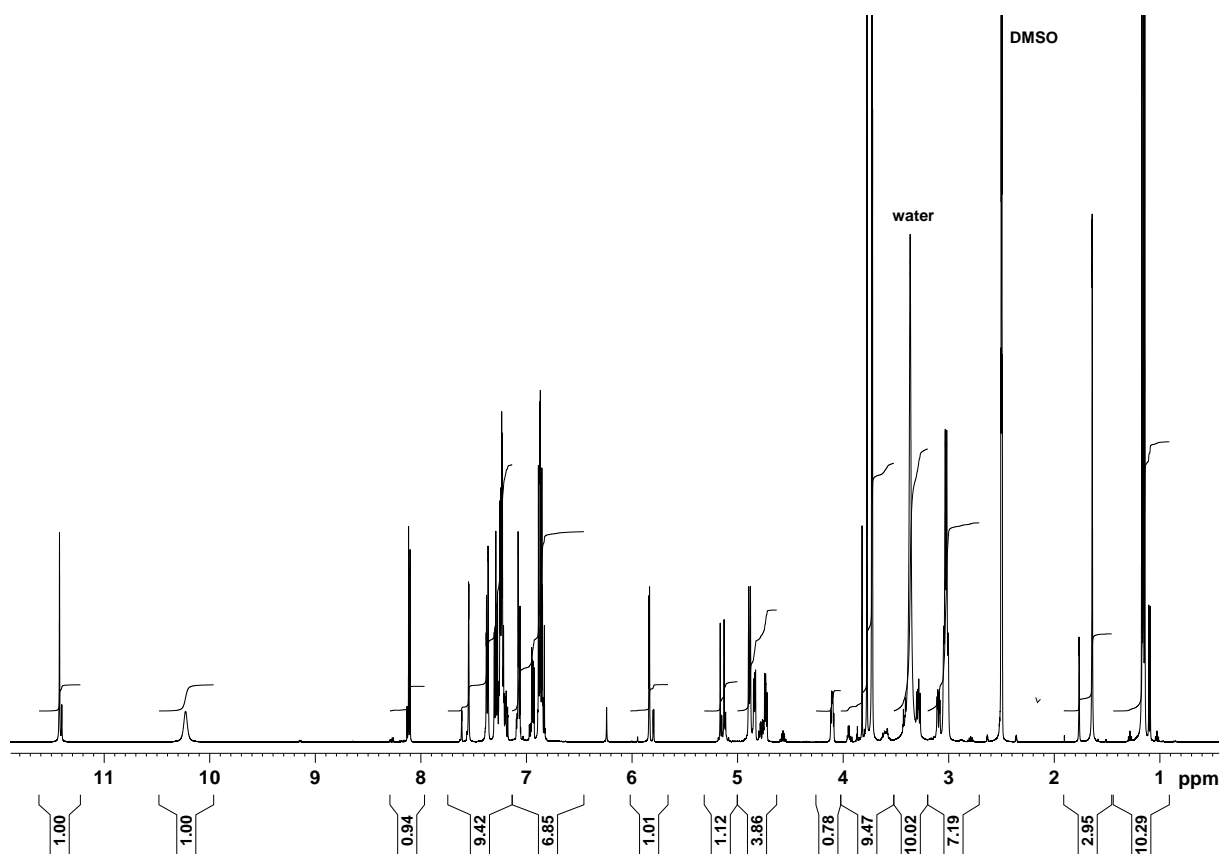
**Figure S16**  $^{13}\text{C}$  NMR spectrum (150.9 MHz) of compound **33b** in  $d_6\text{DMSO}$ .



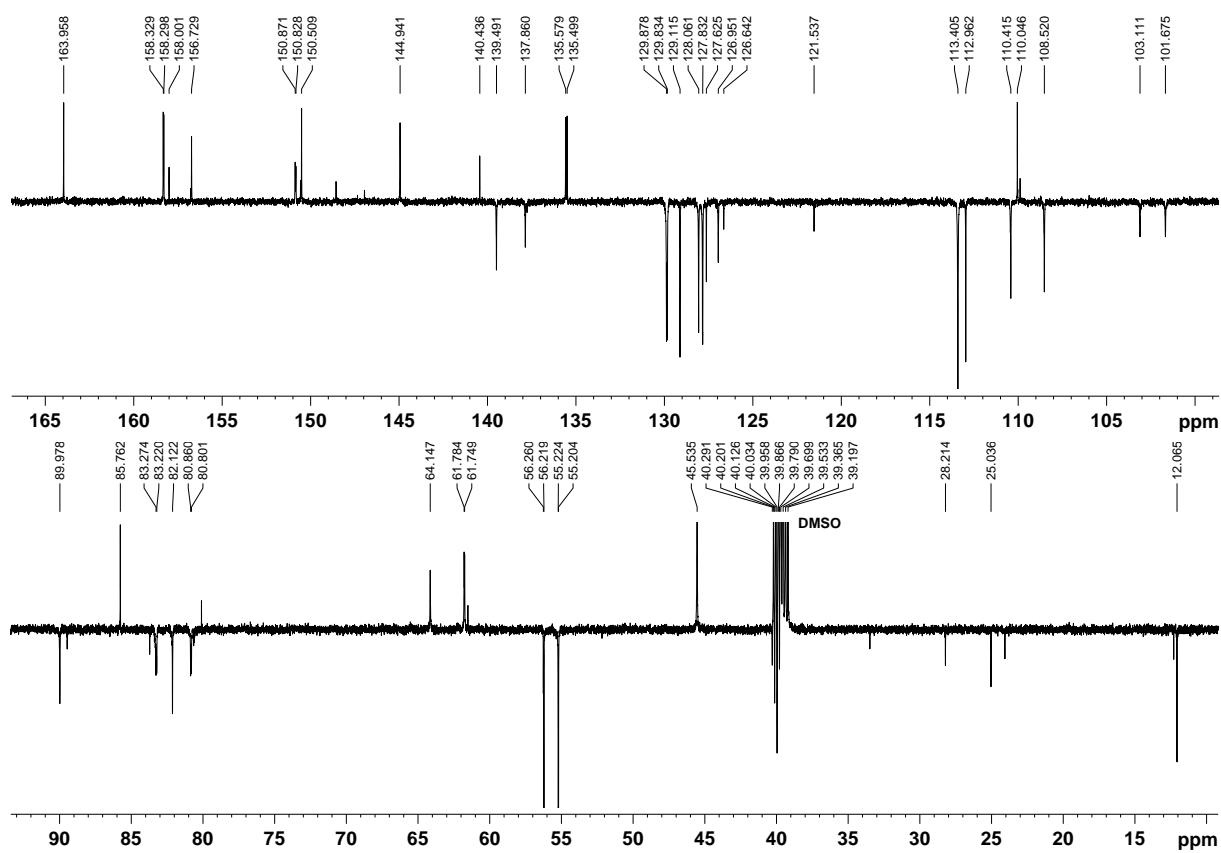
**Figure S17**  $^1\text{H}$  NMR spectrum (600 MHz) of compound **33c** in  $\text{CDCl}_3$ .



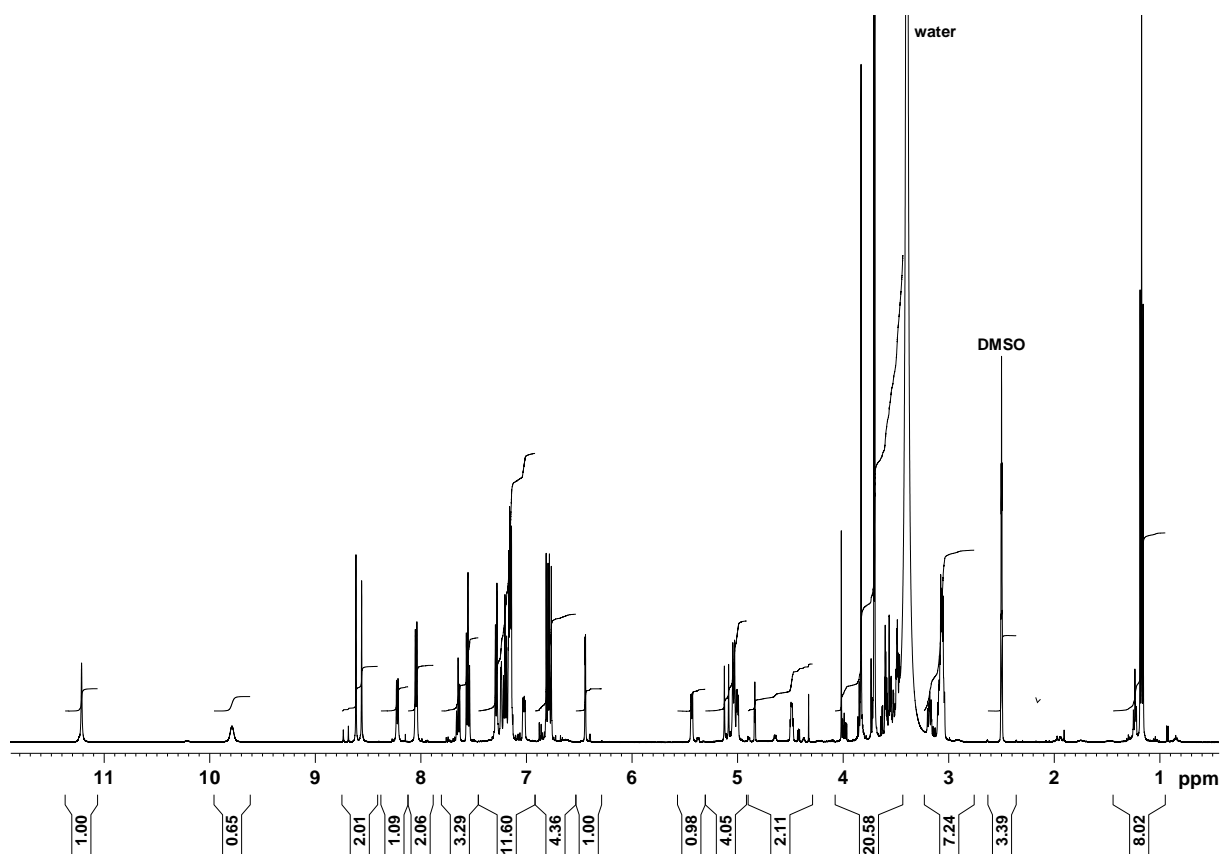
**Figure S18**  $^{13}\text{C}$  NMR spectrum (150.9 MHz) of compound **33c** in  $\text{CDCl}_3$ .



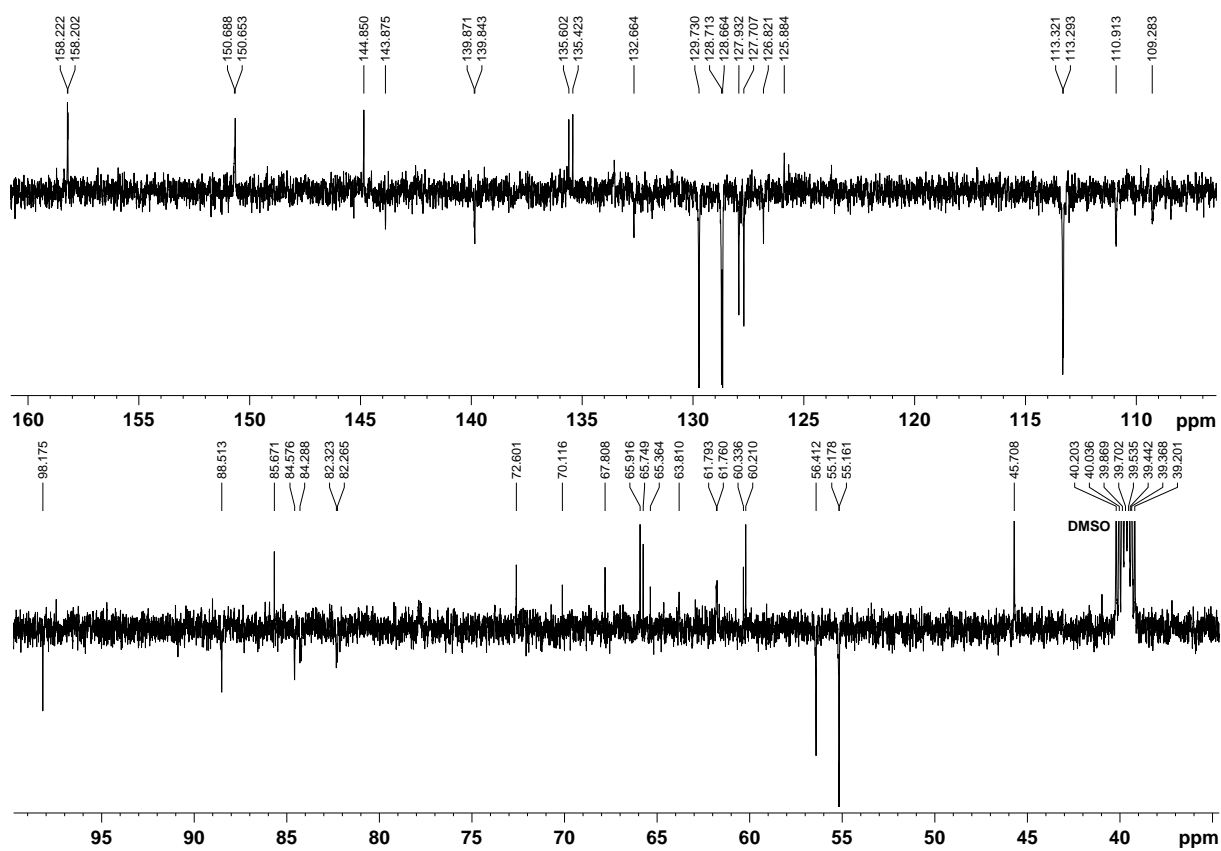
**Figure S19**  $^1\text{H}$  NMR spectrum (500 MHz) of compound **33d** in  $d_6\text{DMSO}$ .



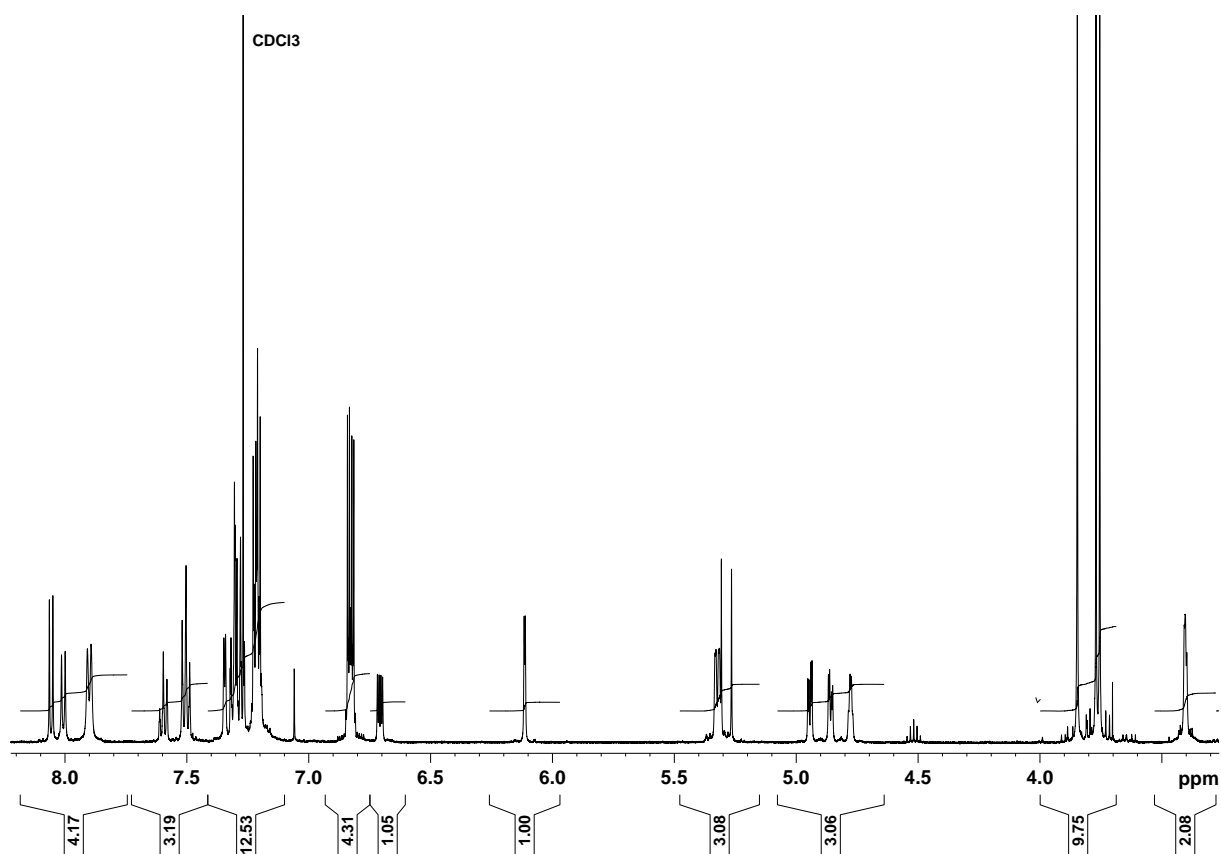
**Figure S20**  $^{13}\text{C}$  NMR spectrum (125.7 MHz) of compound **33d** in  $d_6\text{DMSO}$ .



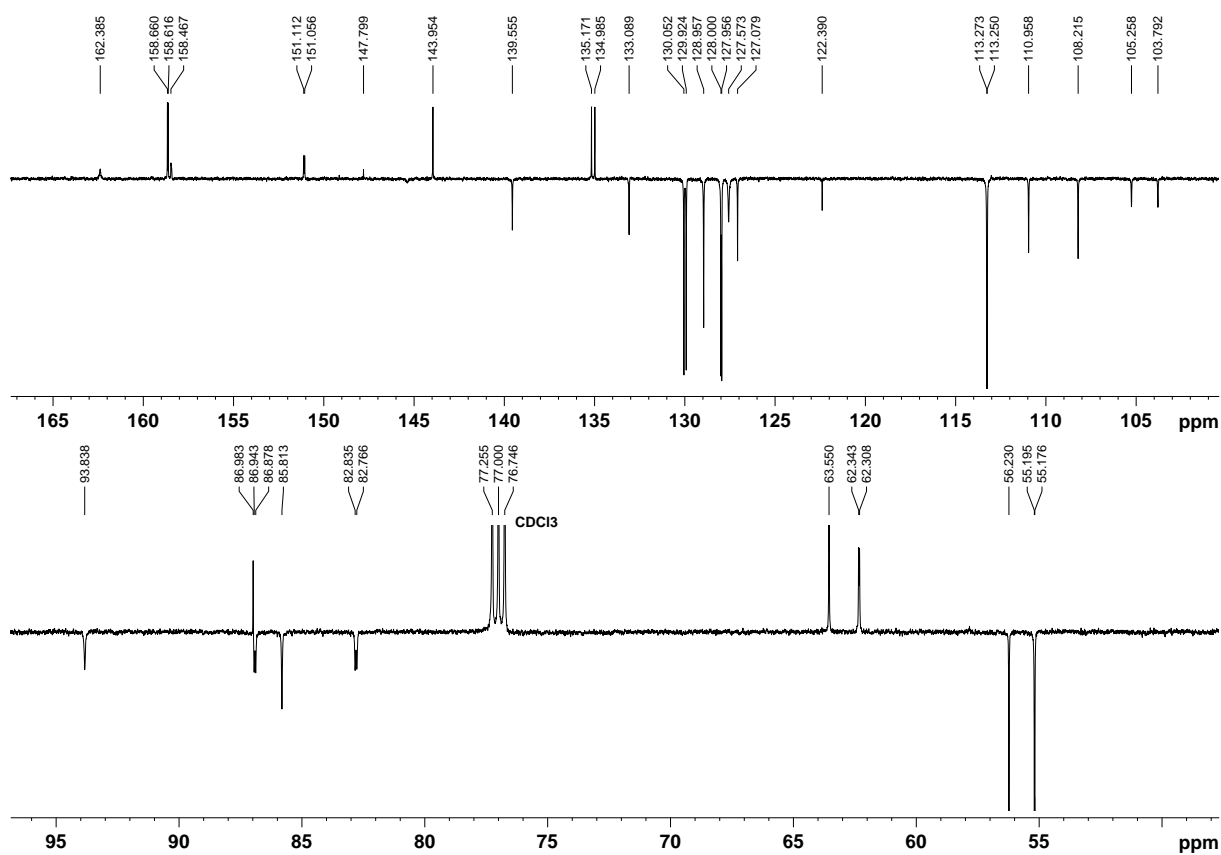
**Figure S21**  $^1\text{H}$  NMR spectrum (500 MHz) of compound **34a** in  $d_6\text{DMSO}$ .



**Figure S22**  $^{13}\text{C}$  NMR spectrum (125.7 MHz) of compound **34a** in  $d_6\text{DMSO}$ .



**Figure S23** <sup>1</sup>H NMR spectrum (500 MHz) of compound **34c** in CDCl<sub>3</sub>.



**Figure S24** <sup>13</sup>C NMR spectrum (125.7 MHz) of compound **34c** in CDCl<sub>3</sub>.