## Acid-Induced Rearrangement of Epoxygermacranolides: Synthesis of Furanoheliangolides

## and Cadinanes from Nobilin

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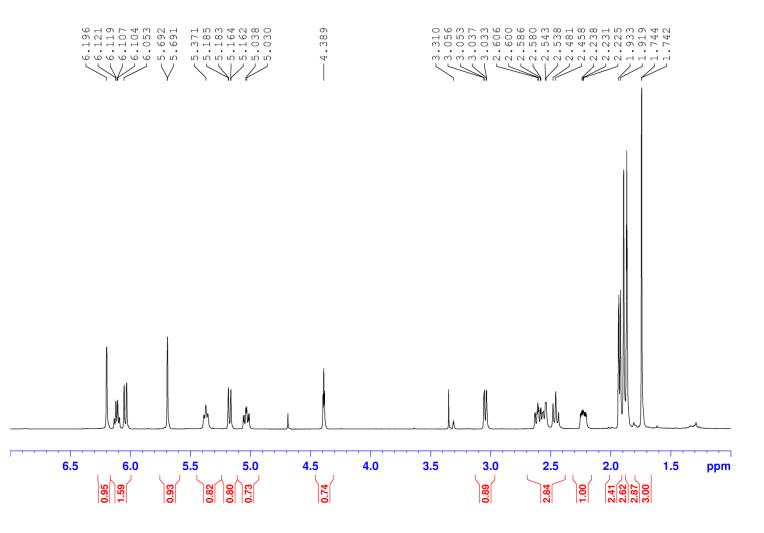
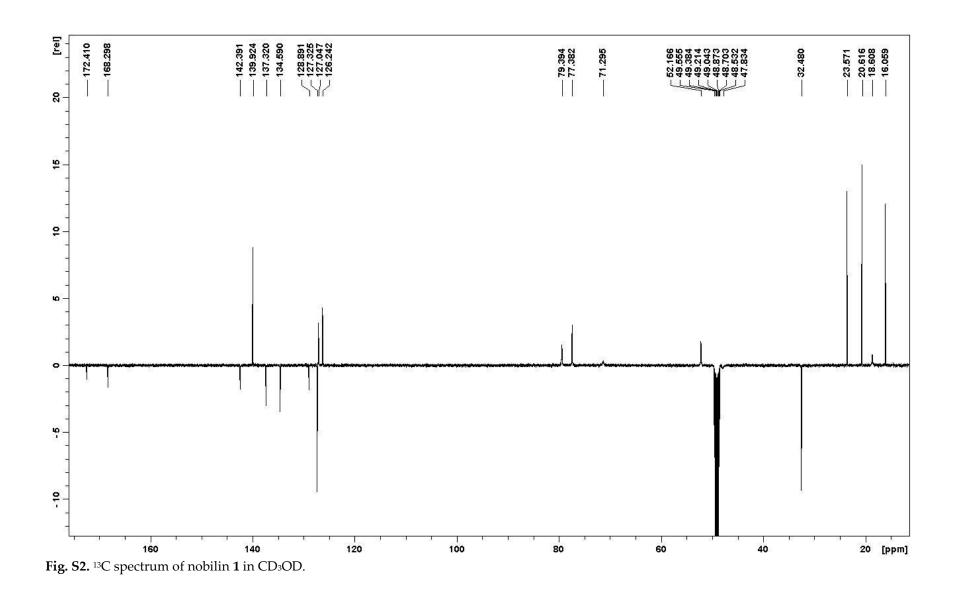


Fig. S1. <sup>1</sup>H NMR spectrum of nobilin 1 in CD<sub>3</sub>OD.



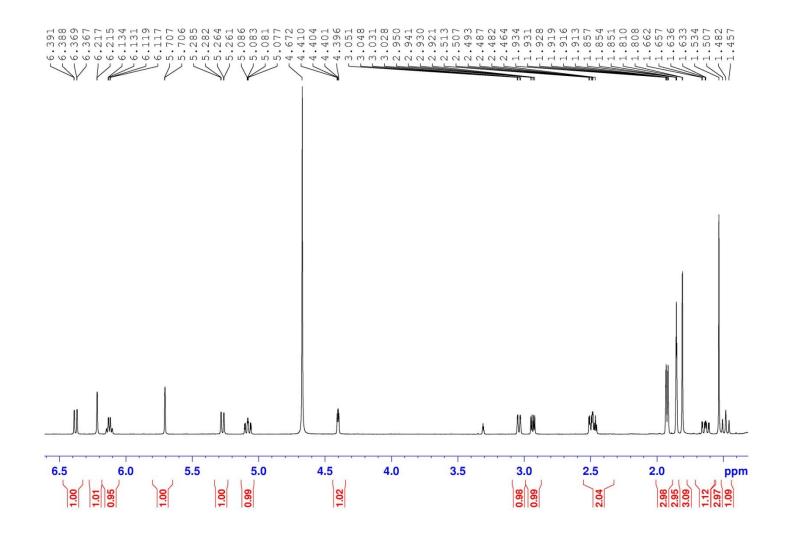
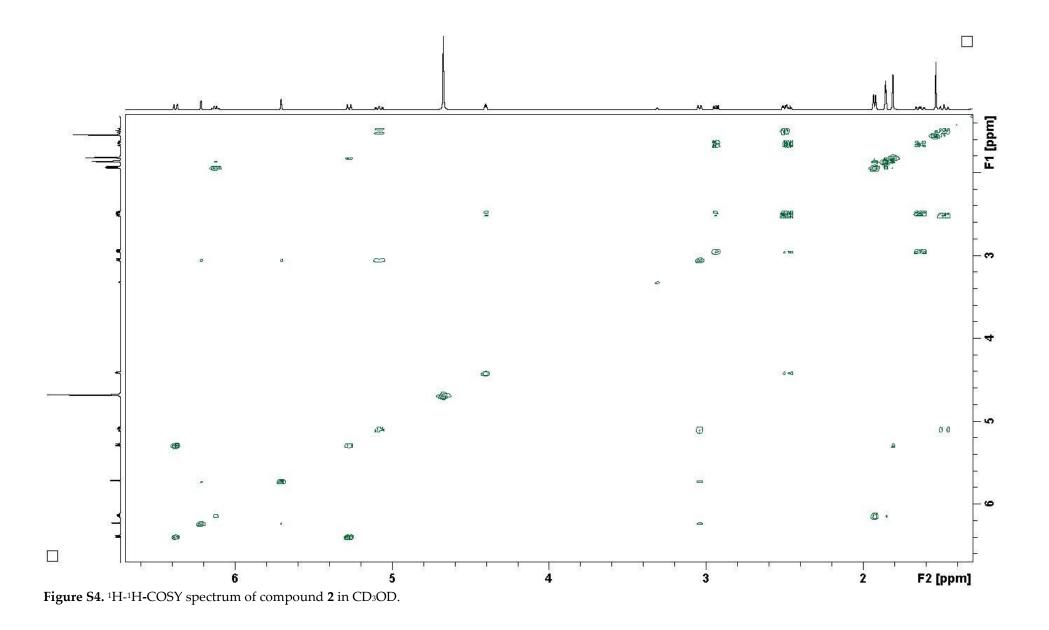
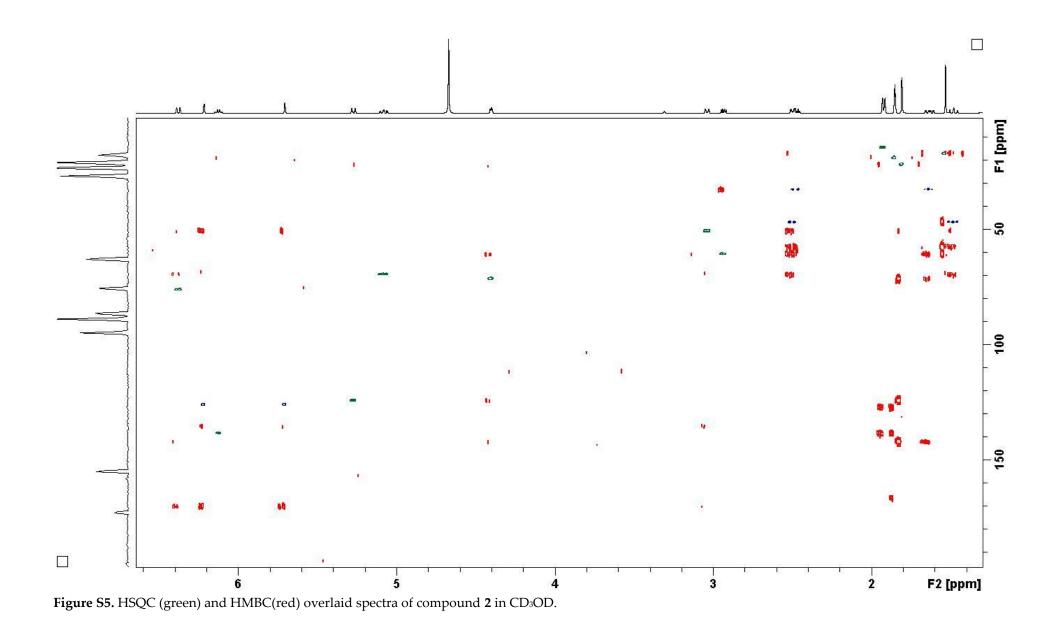
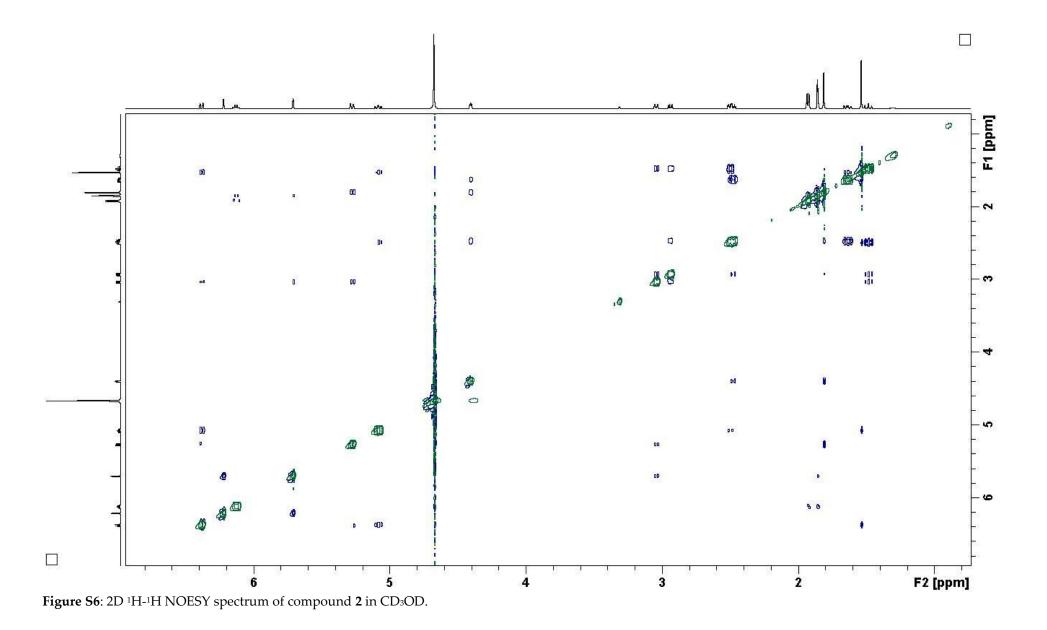
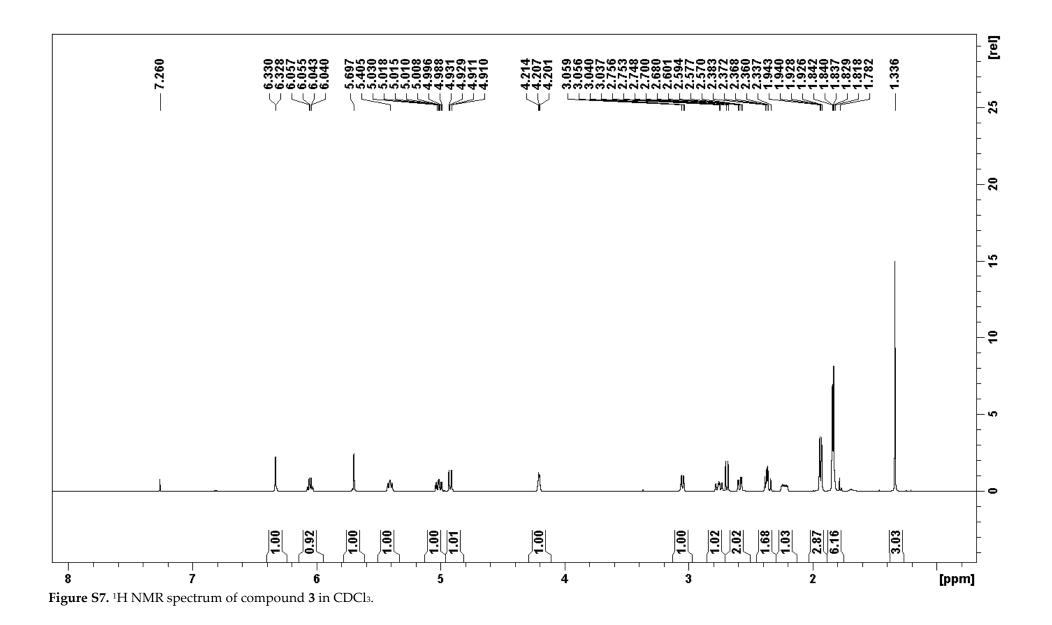


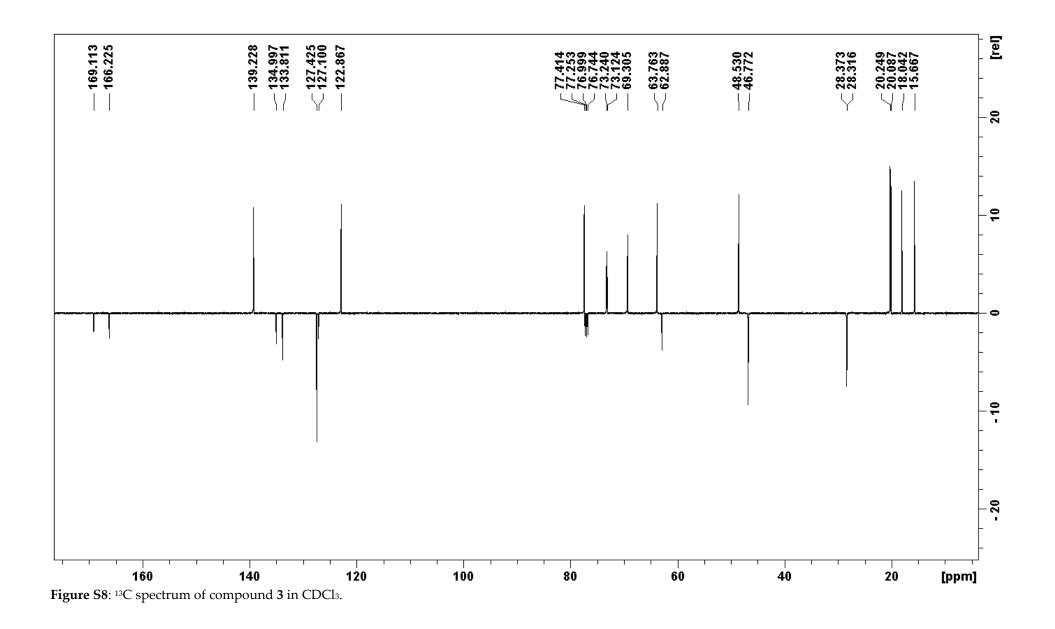
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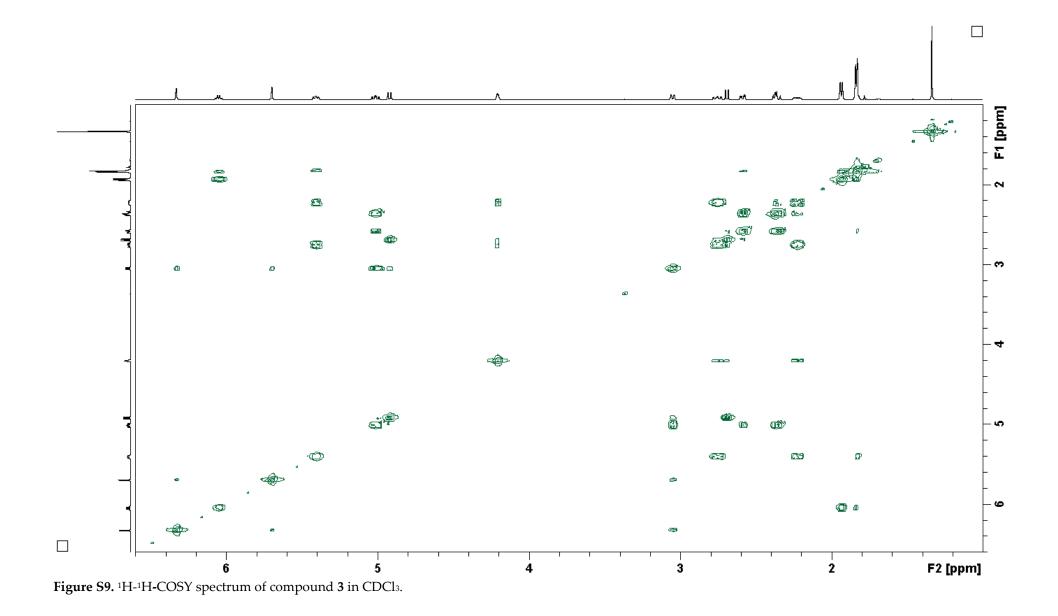


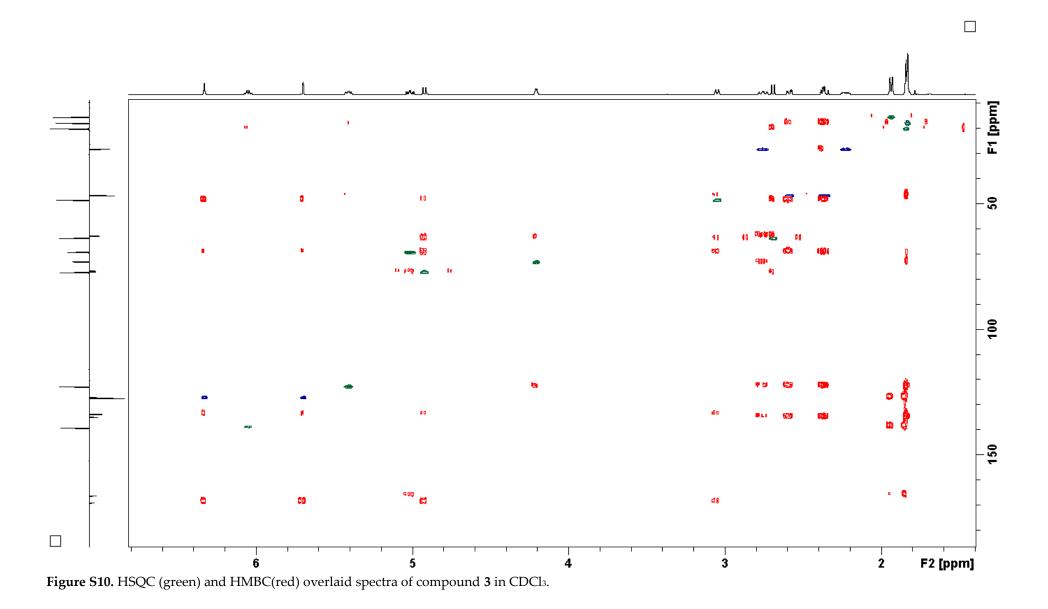


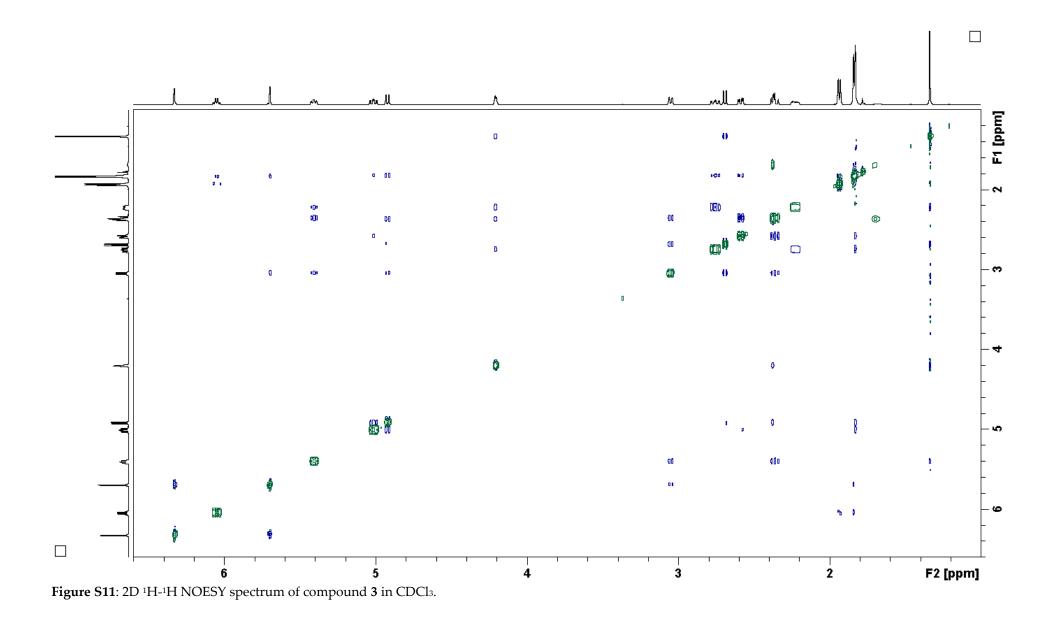












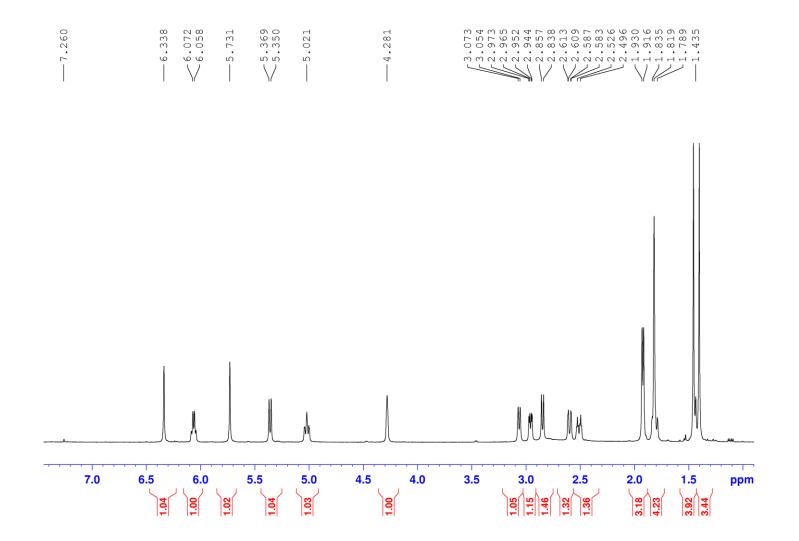


Figure S12. <sup>1</sup>H NMR spectrum of compound 4 in CDCl<sub>3</sub>.

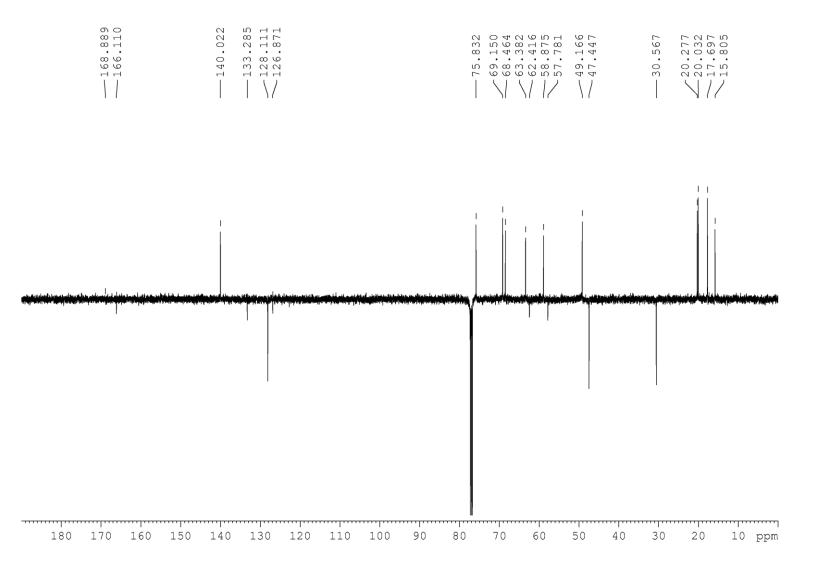
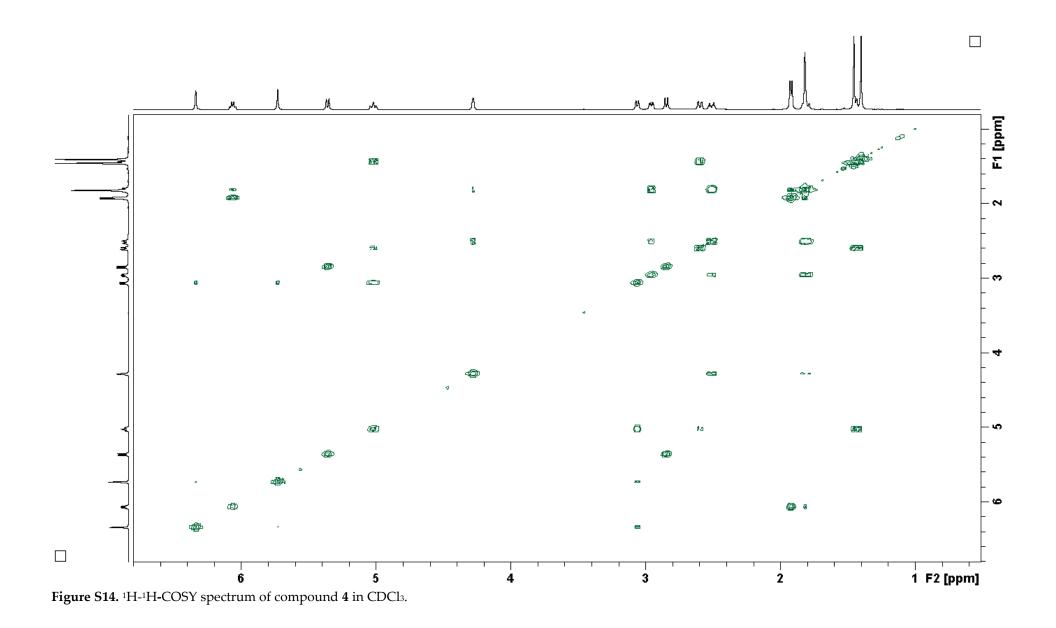
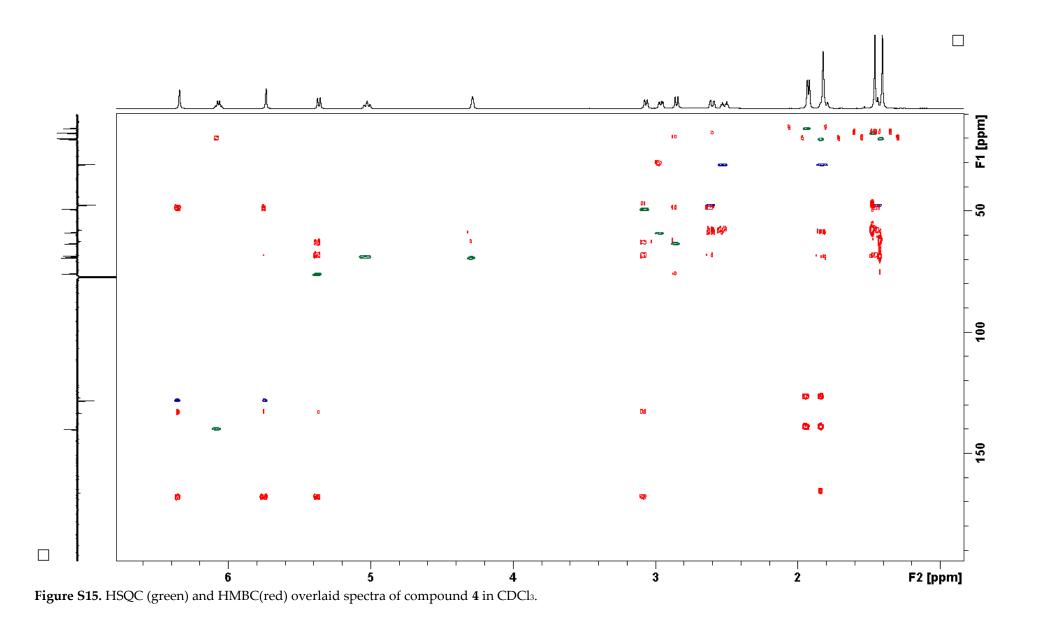


Figure S13: <sup>13</sup>C spectrum of compound 4 in CDCl<sub>3</sub>.





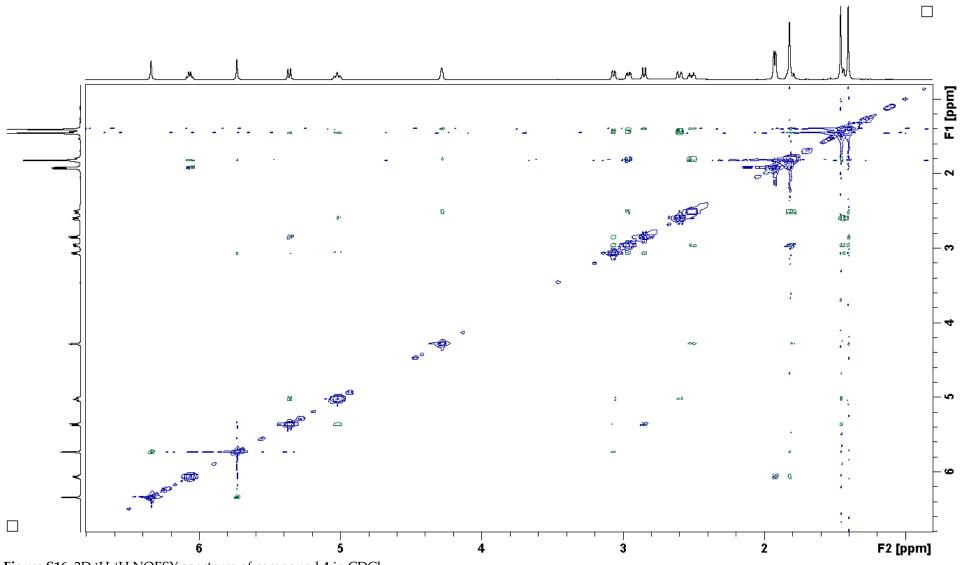
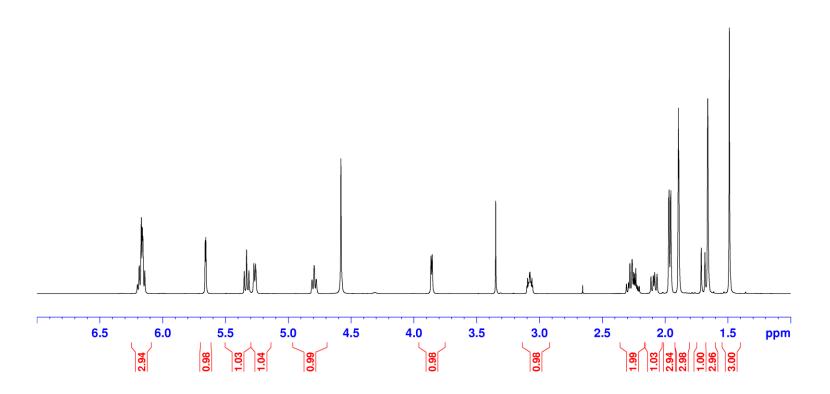


Figure S16: 2D <sup>1</sup>H-<sup>1</sup>H NOESY spectrum of compound 4 in CDCl<sub>3</sub>.





**Figure S17**: <sup>1</sup>H-NMR spectrum of compound **5** in CD<sub>3</sub>OD.

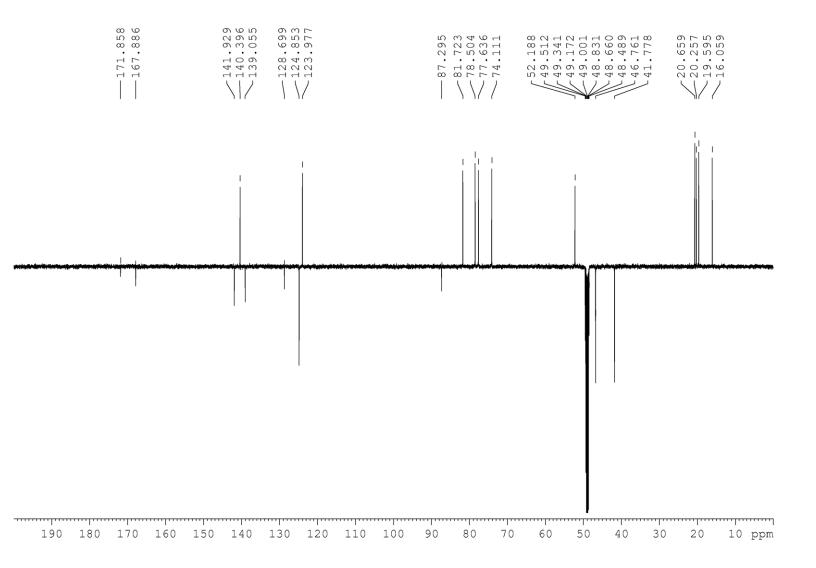
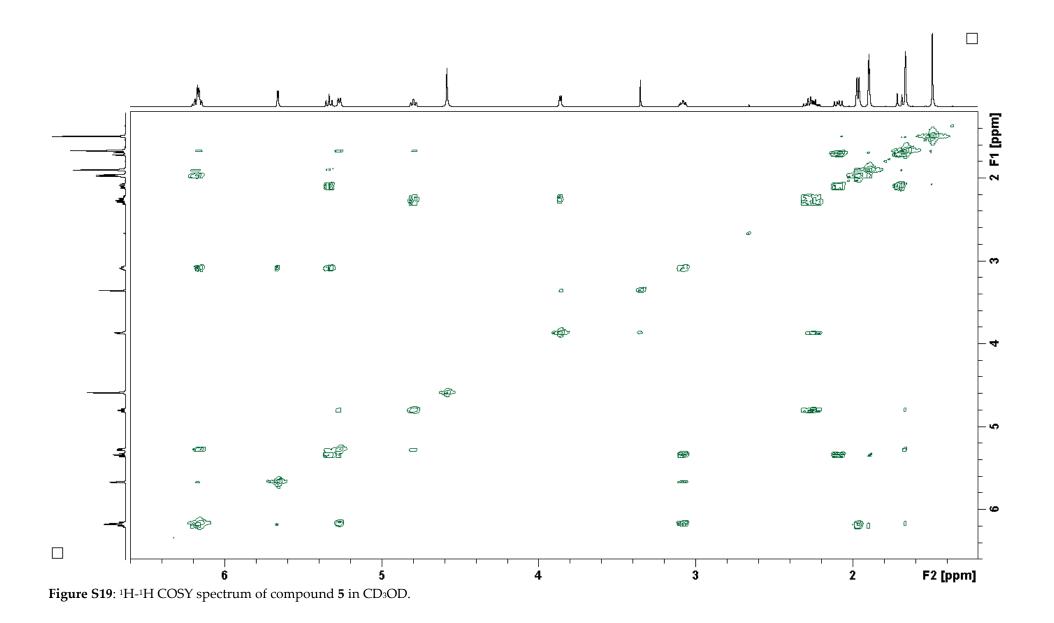
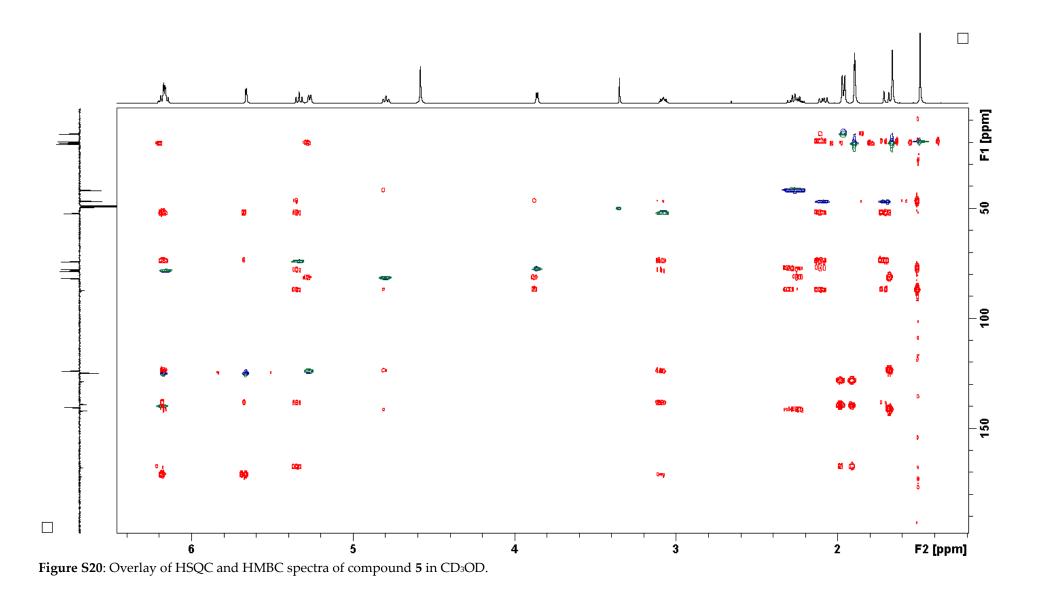
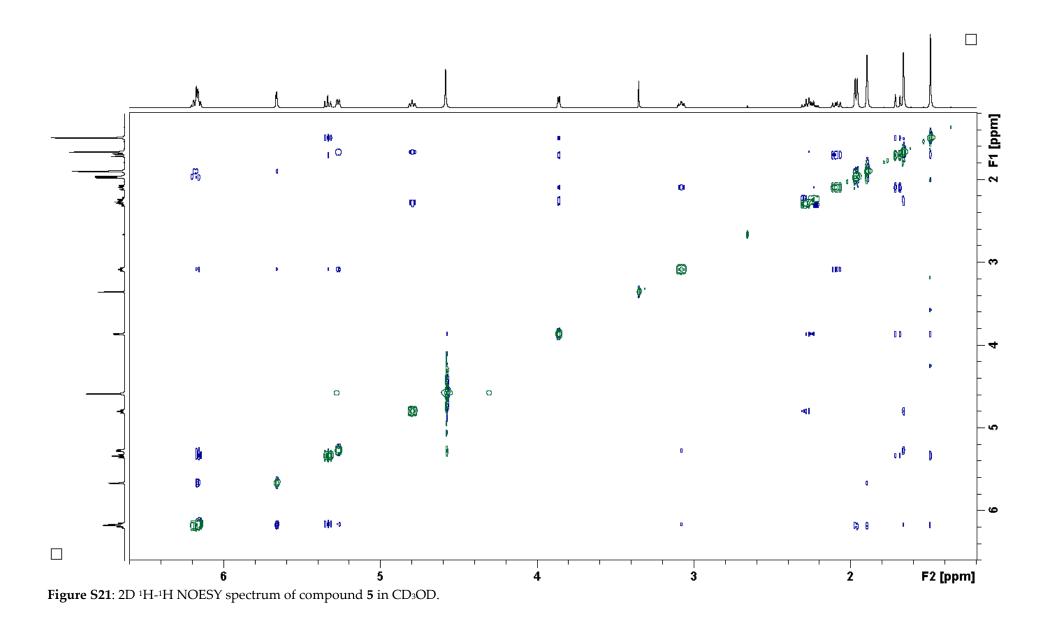
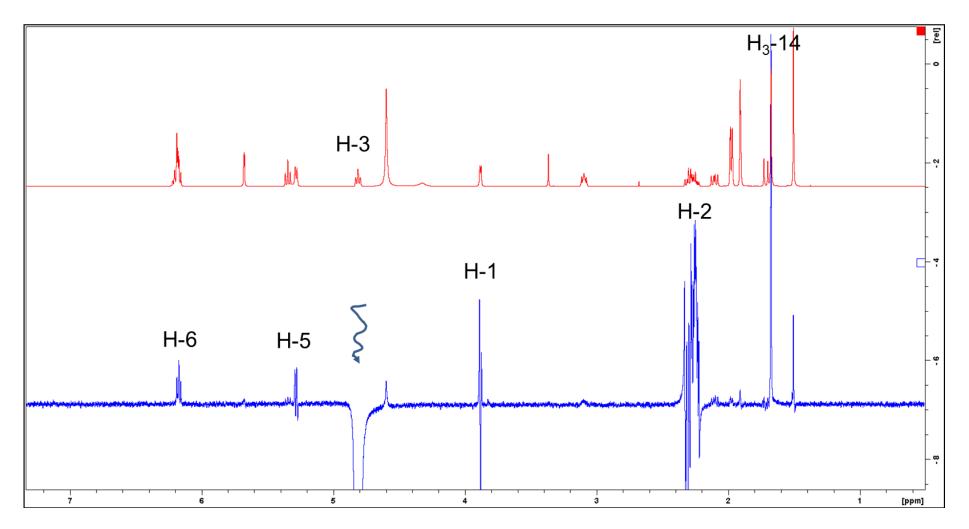


Figure S18: <sup>13</sup>C spectrum of compound 5 in CD<sub>3</sub>OD.

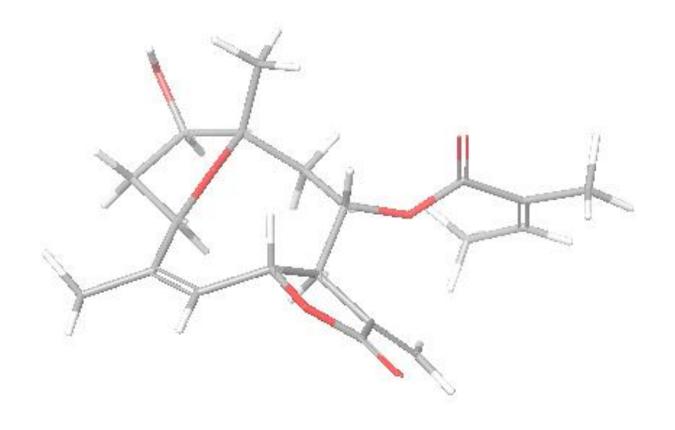








**Figure S22**: 1D Selective NOESY spectrum of compound **5** in CD<sub>3</sub>OD (D8 = 0.3 sec).



**Figure S23:** DFT 6-31+G(d,p) optimized structure of **5**.

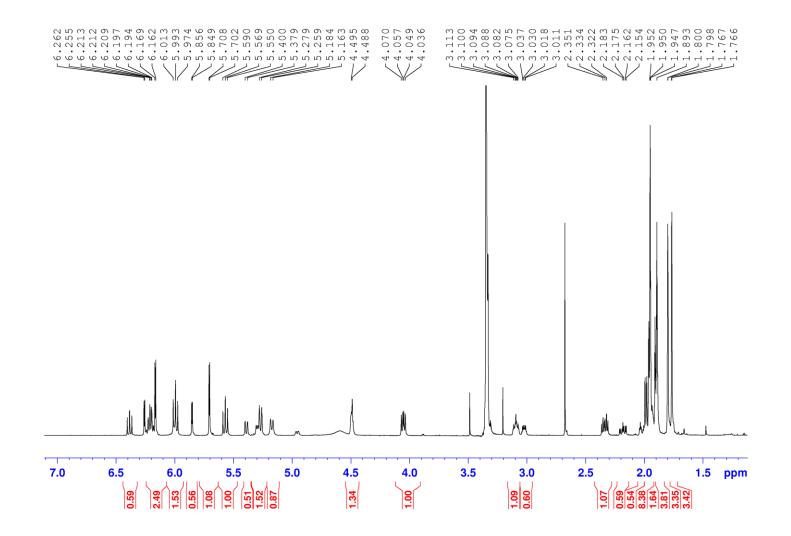


Figure S24: <sup>1</sup>H-NMR spectrum of compounds 6-7 in CD<sub>3</sub>OD.

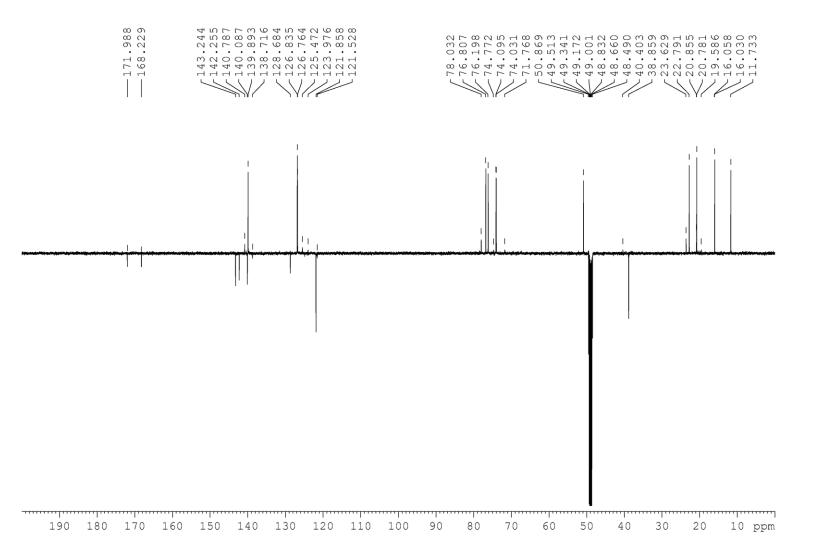
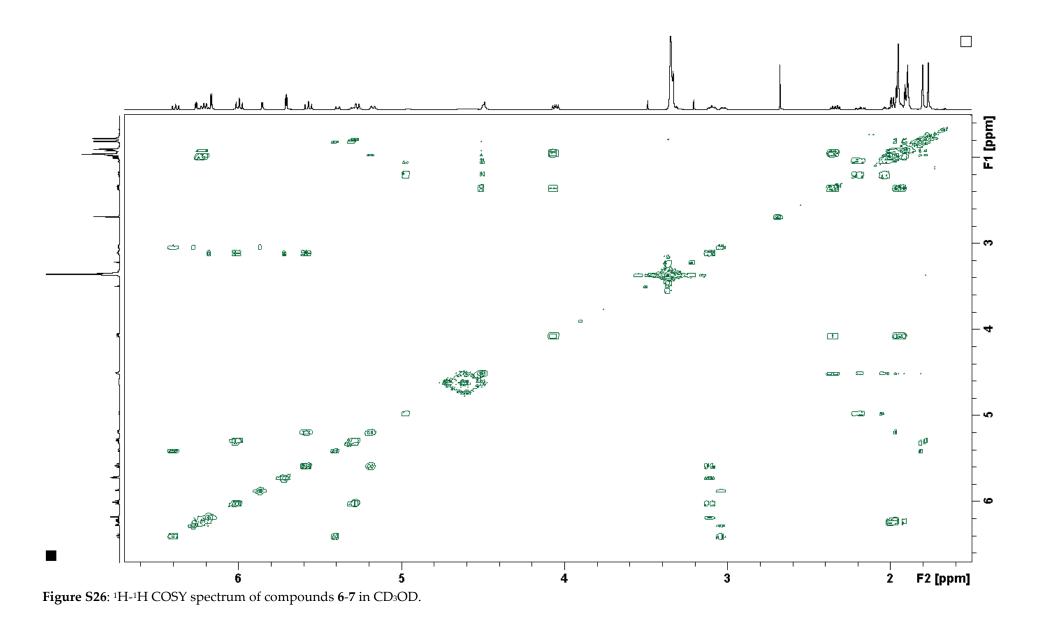
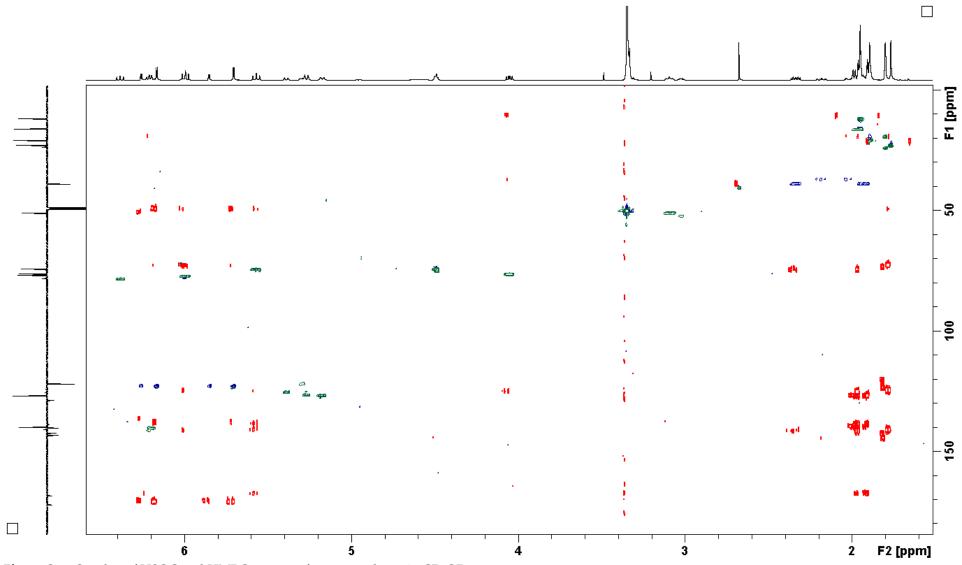
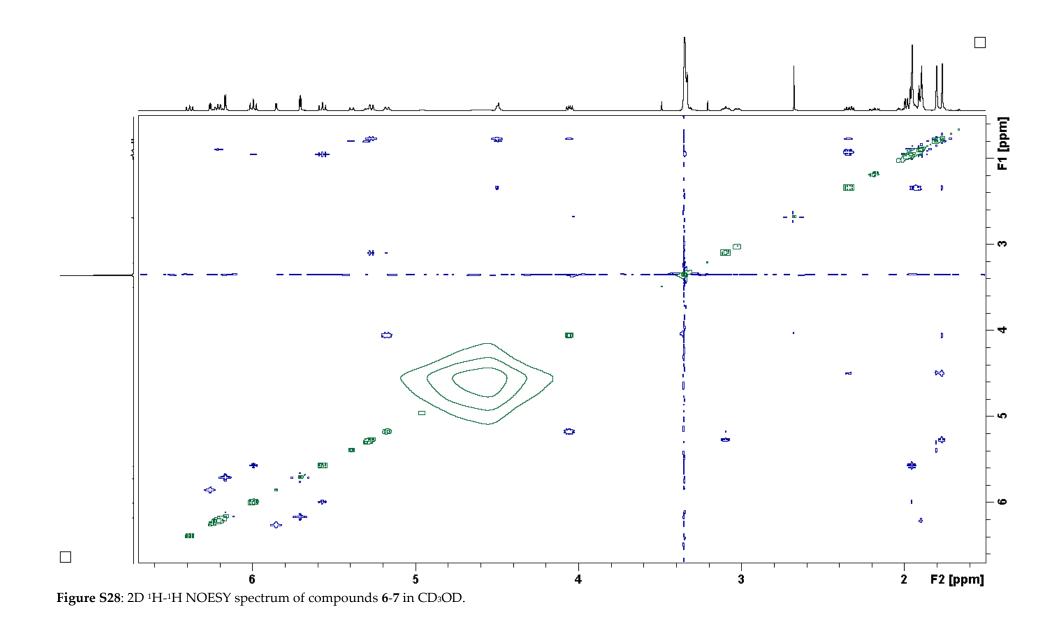


Figure S25: <sup>13</sup>C spectrum of compounds 6-7 in CD<sub>3</sub>OD.





**Figure S27**: Overlay of HSQC and HMBC spectra of compounds 6-7 in CD<sub>3</sub>OD.



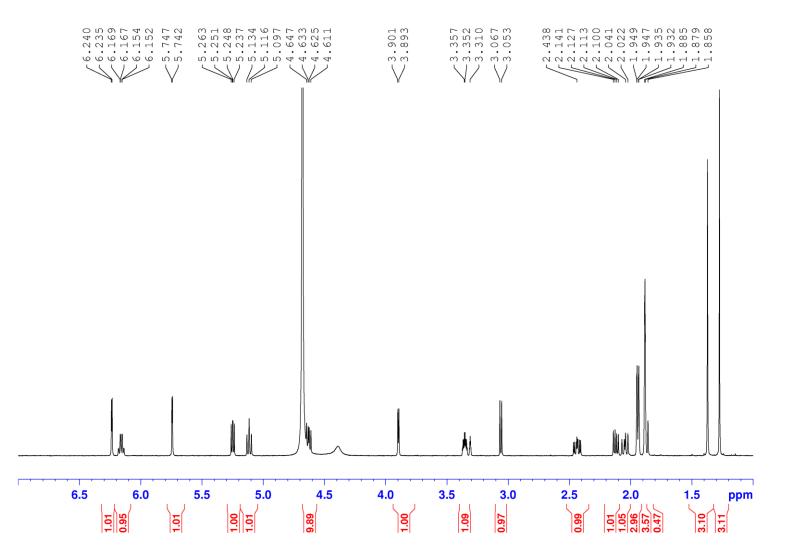


Figure S29: <sup>1</sup>H-NMR spectrum of compound 8 in CD<sub>3</sub>OD.

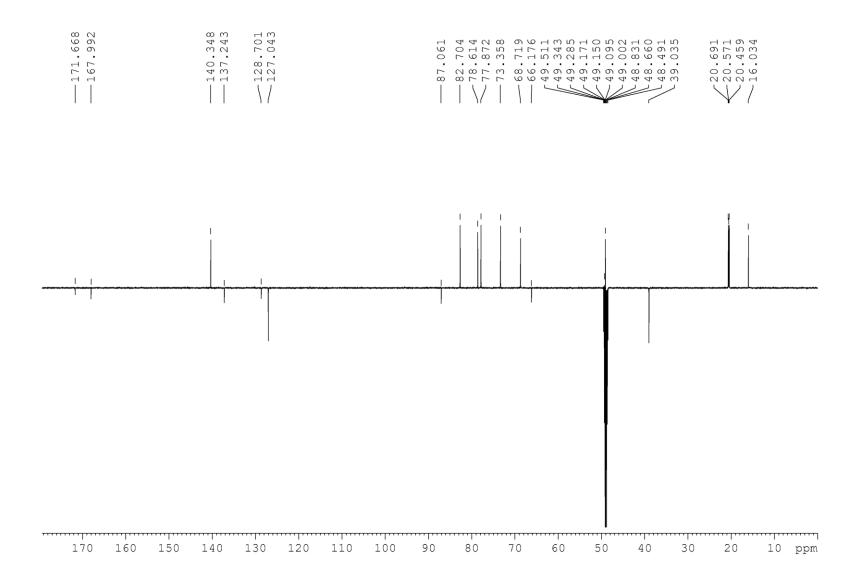
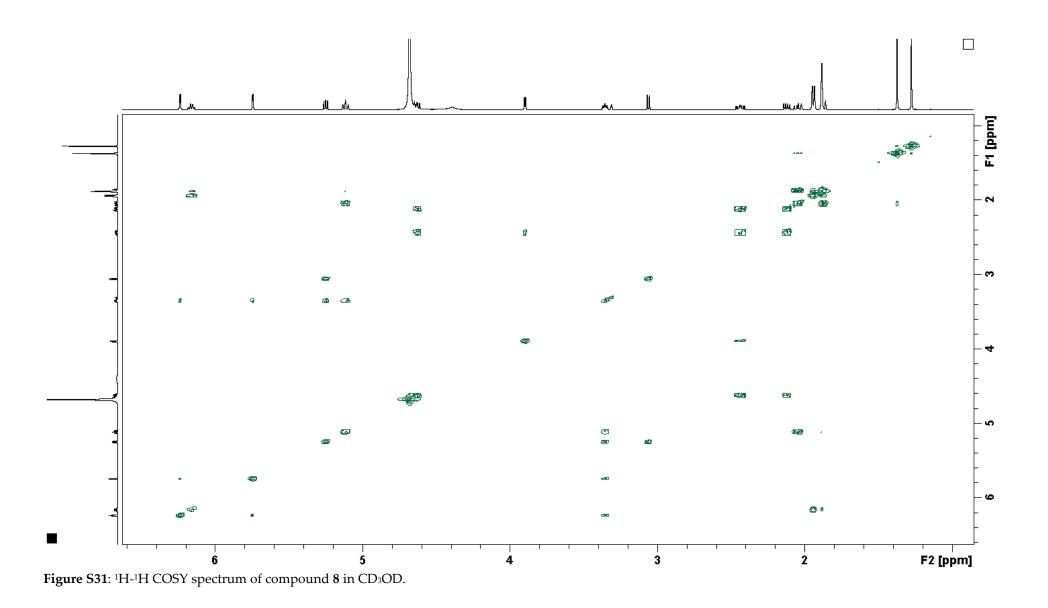


Figure S30: <sup>13</sup>C spectrum of compound 8 in CD<sub>3</sub>OD.



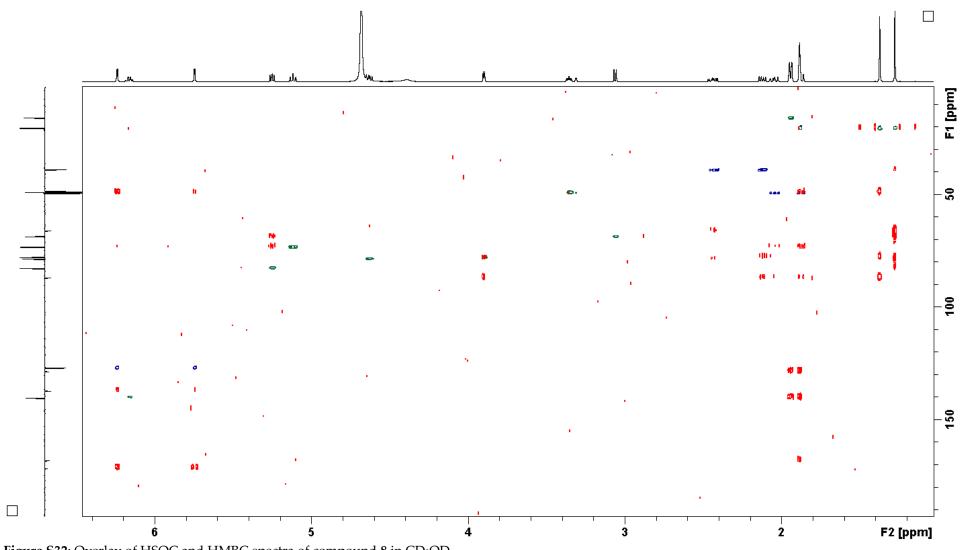
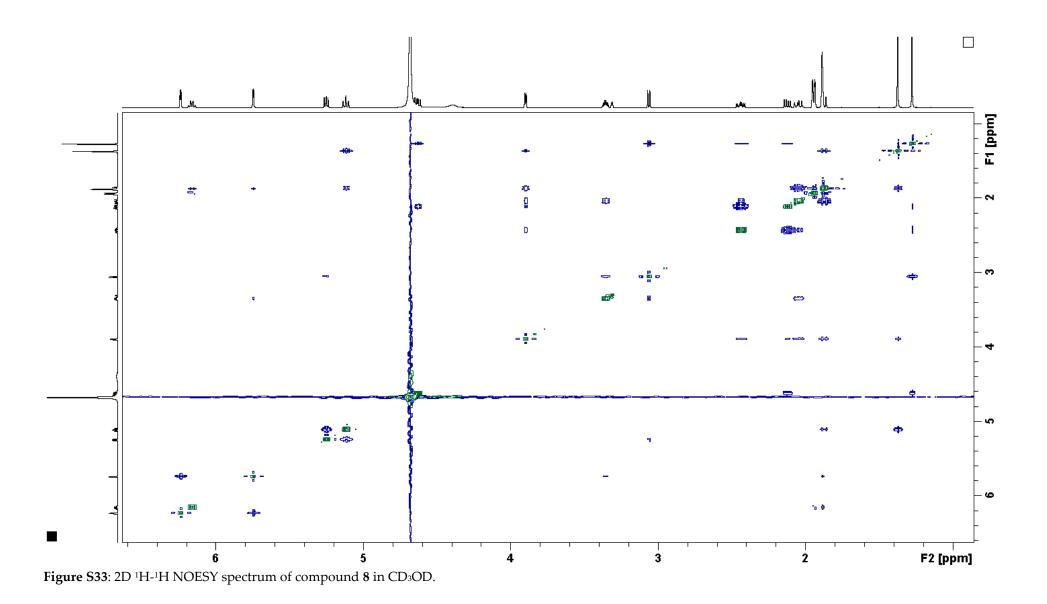


Figure S32: Overlay of HSQC and HMBC spectra of compound 8 in CD<sub>3</sub>OD.



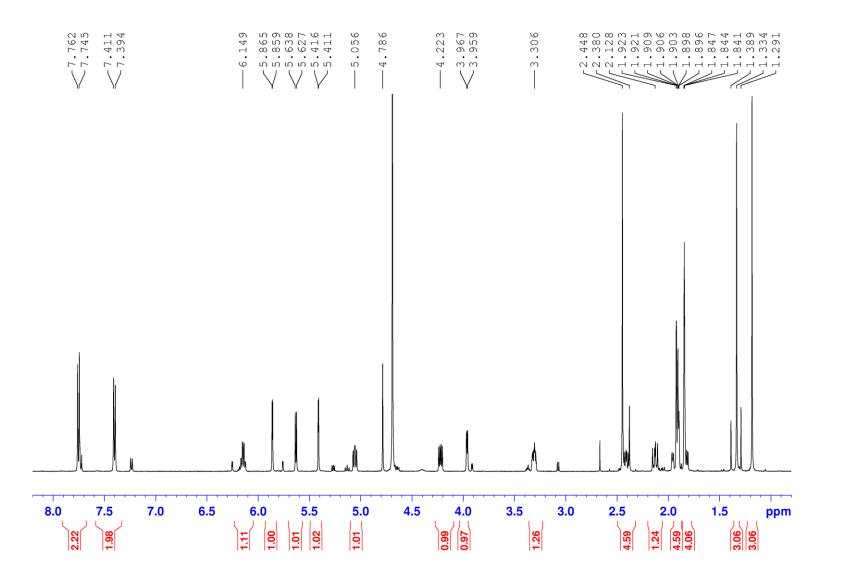


Figure S34: <sup>1</sup>H-NMR spectrum of compound 9 in CD<sub>3</sub>OD.

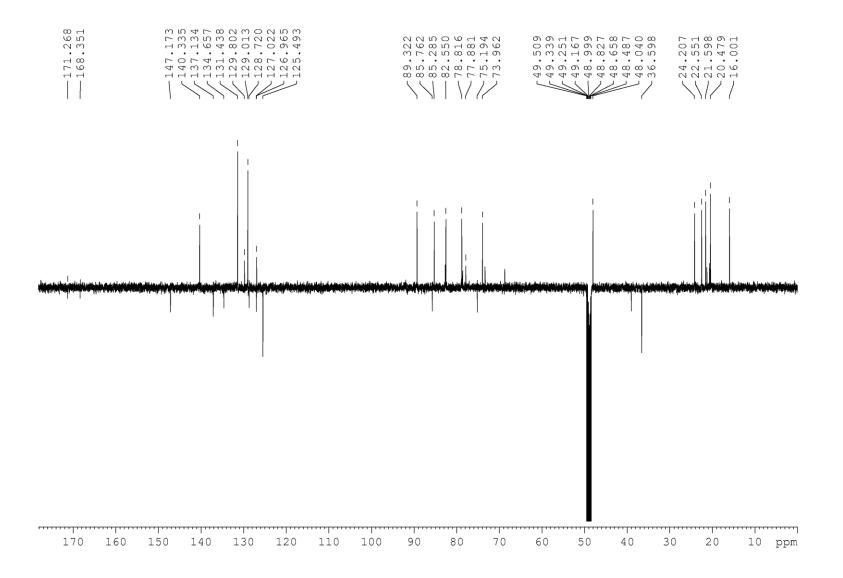
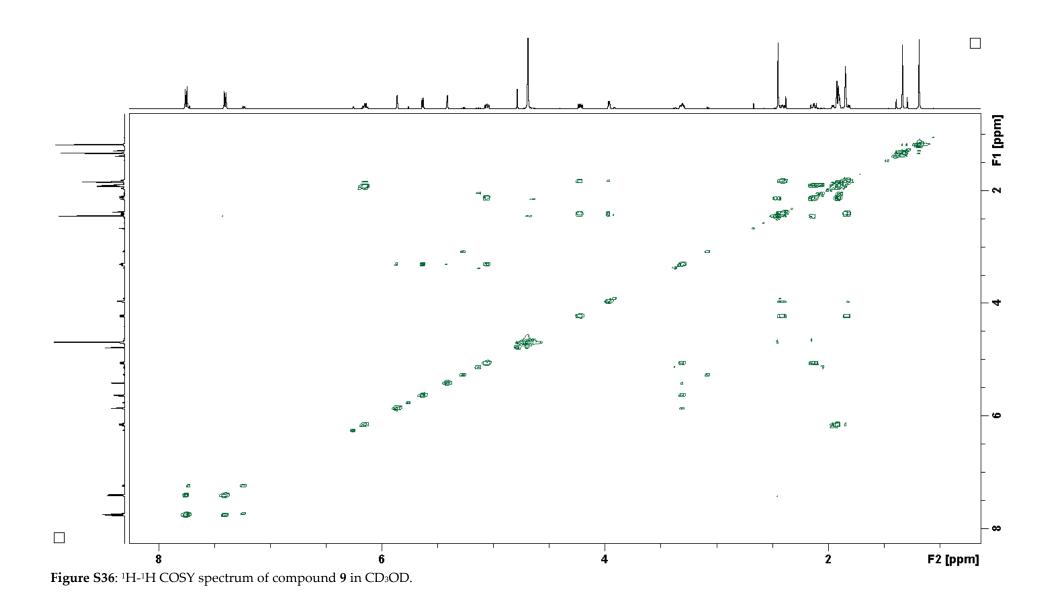
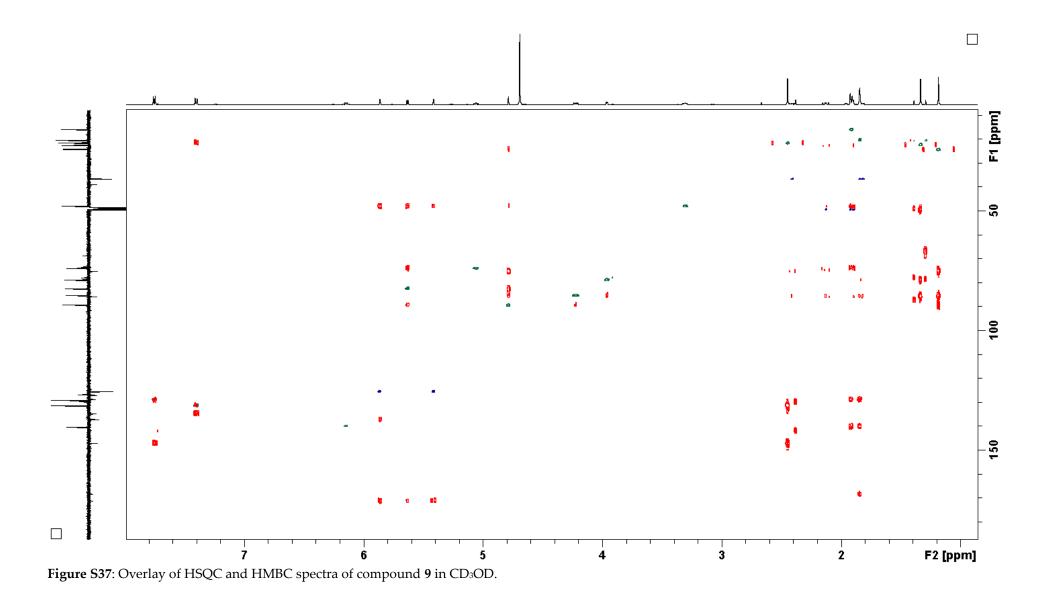
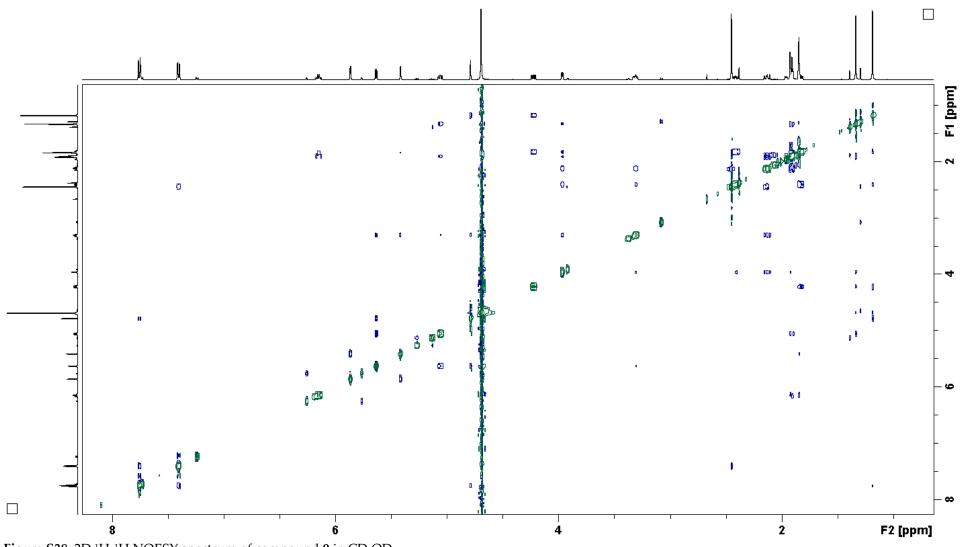


Figure S35: <sup>13</sup>C spectrum of compound 9 in CD<sub>3</sub>OD.







**Figure S38**: 2D <sup>1</sup>H-<sup>1</sup>H NOESY spectrum of compound **9** in CD<sub>3</sub>OD.

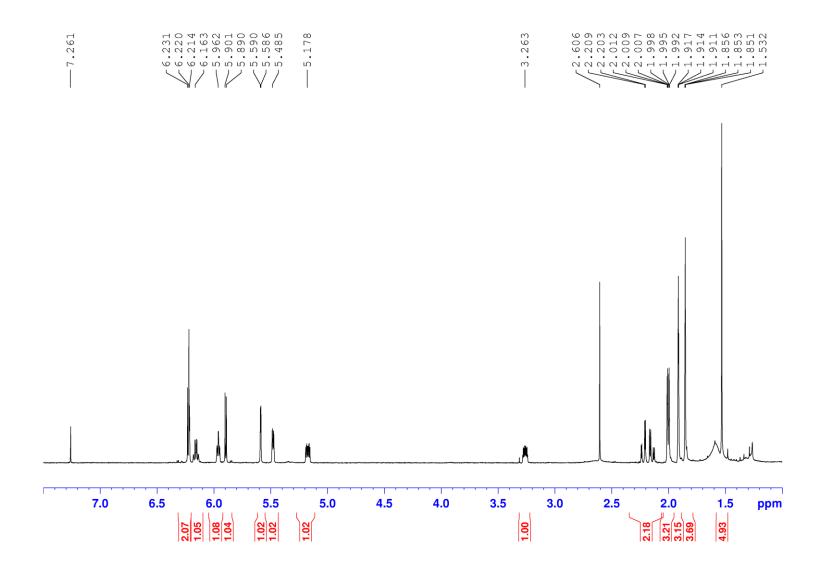
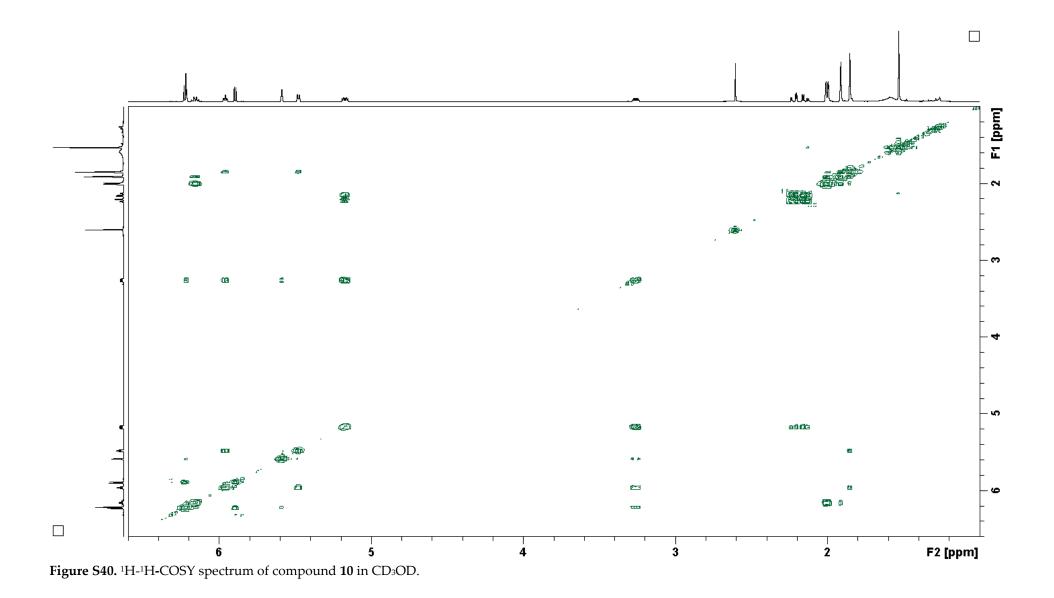
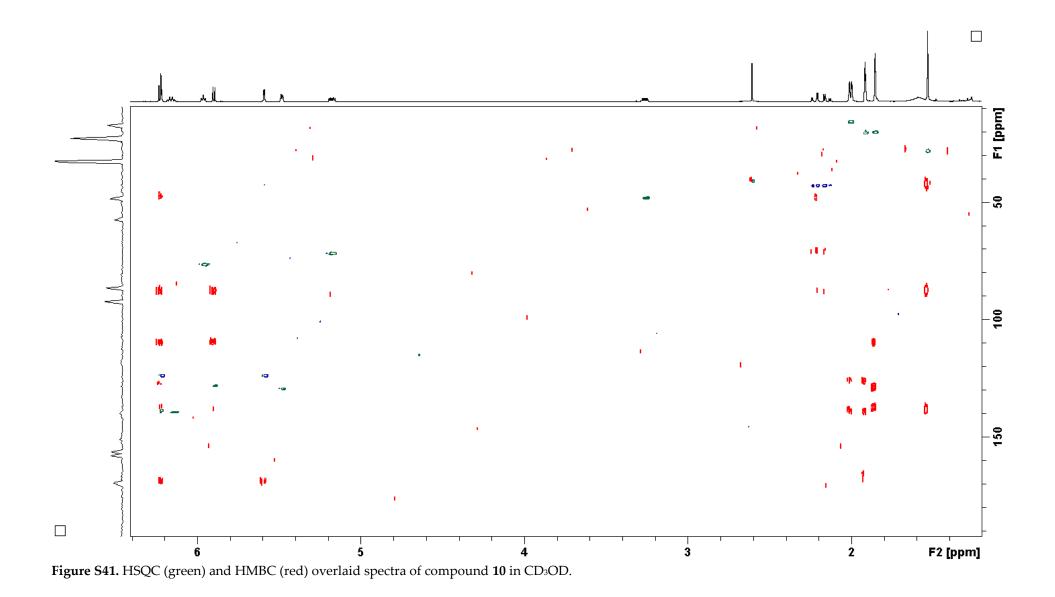
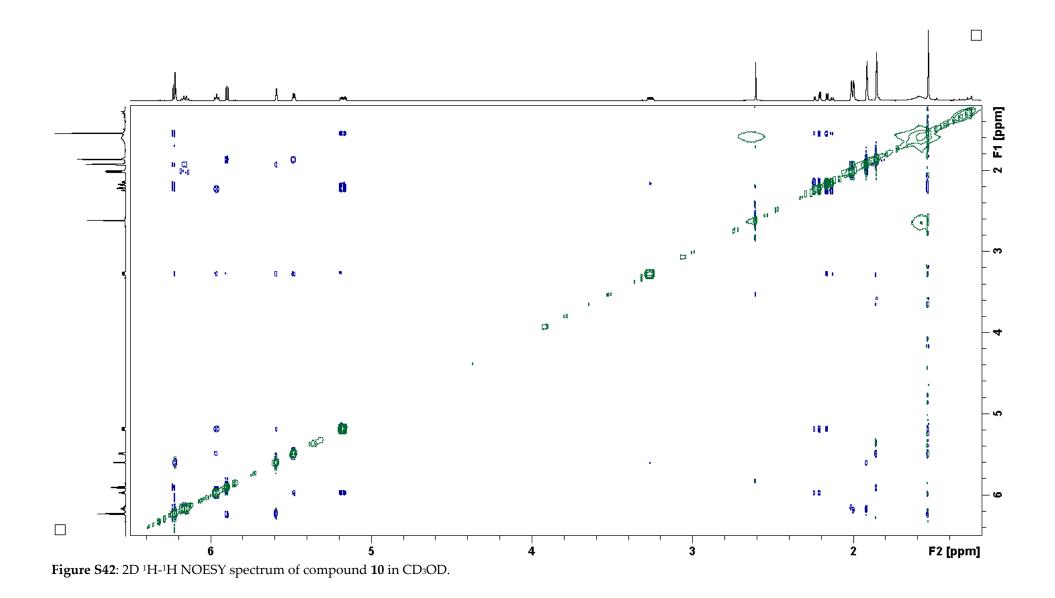


Figure S39. <sup>1</sup>H NMR spectrum of compound 10 in CD<sub>3</sub>OD.







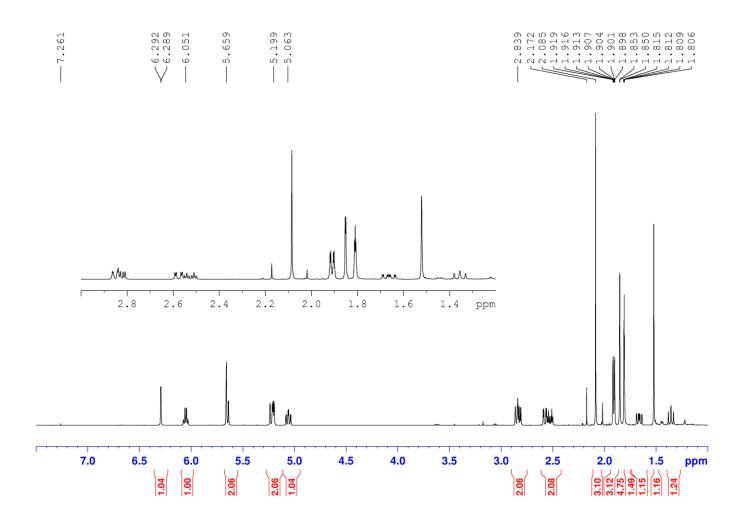
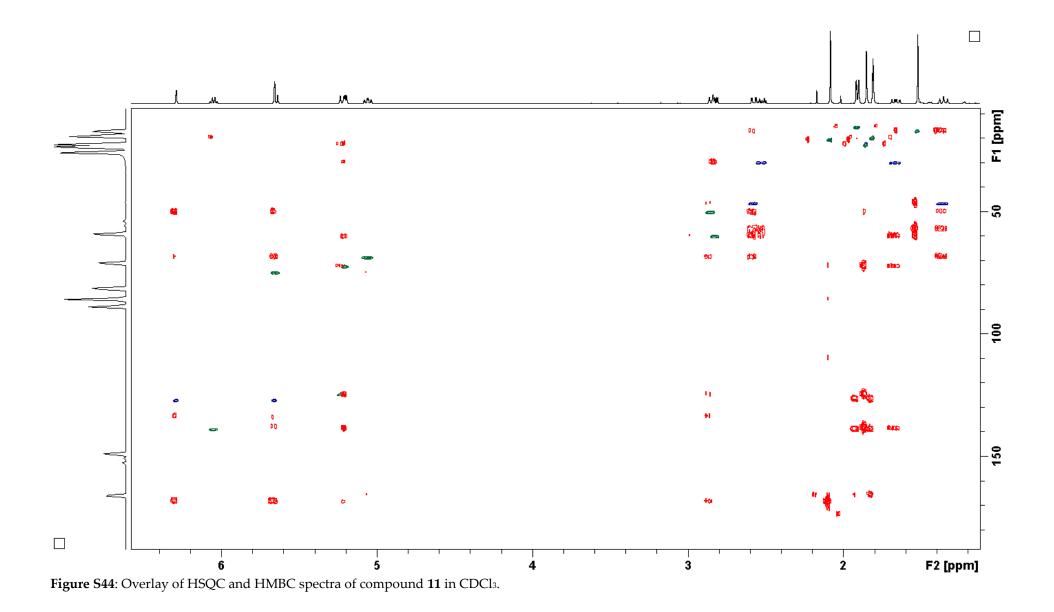


Figure S43: <sup>1</sup>H-NMR spectrum of compound 11 in CDCl<sub>3</sub>.



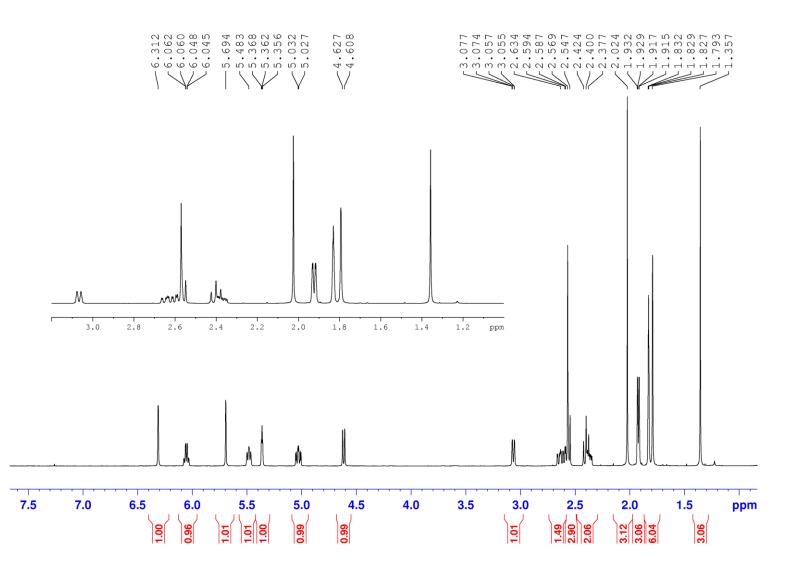
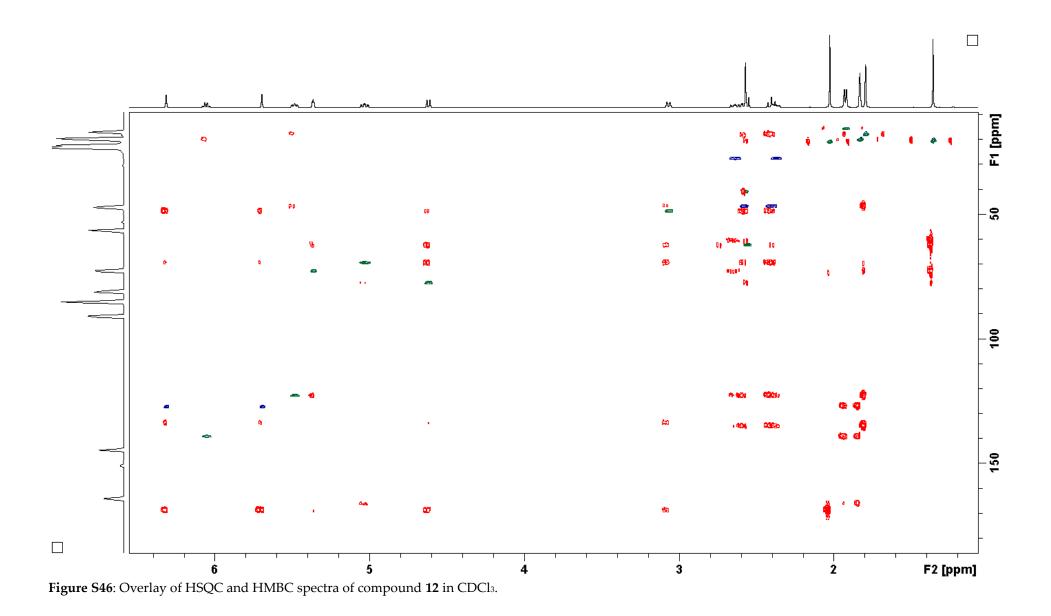


Figure S45: <sup>1</sup>H-NMR spectrum of compound 12 in CDCl<sub>3</sub>.



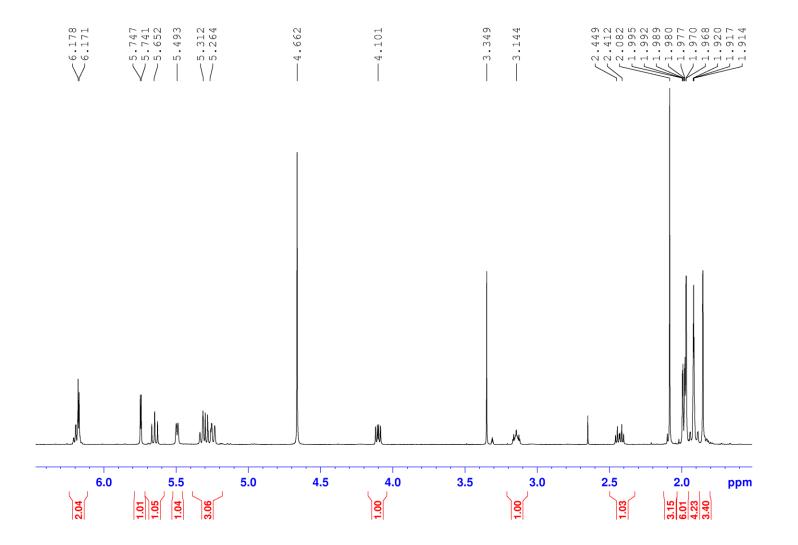
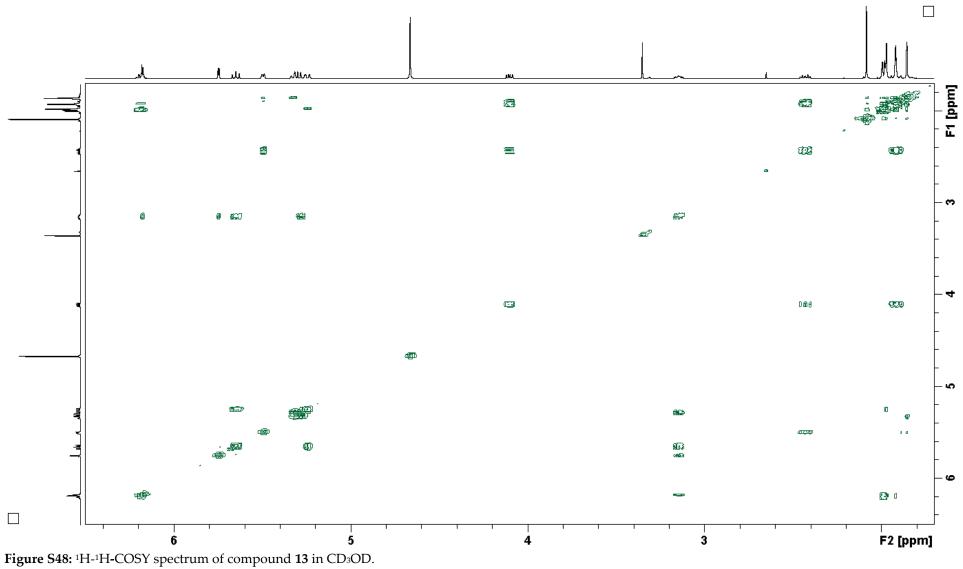
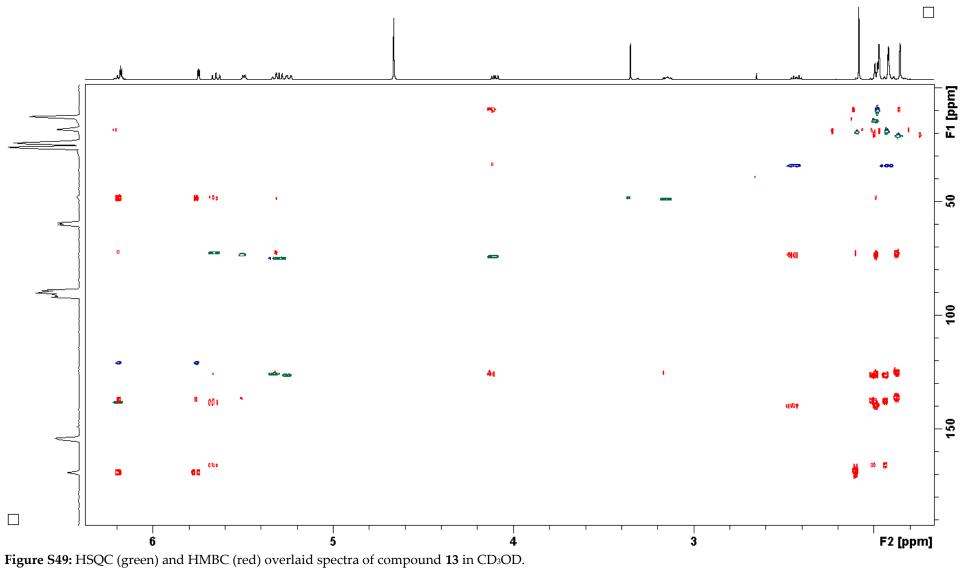
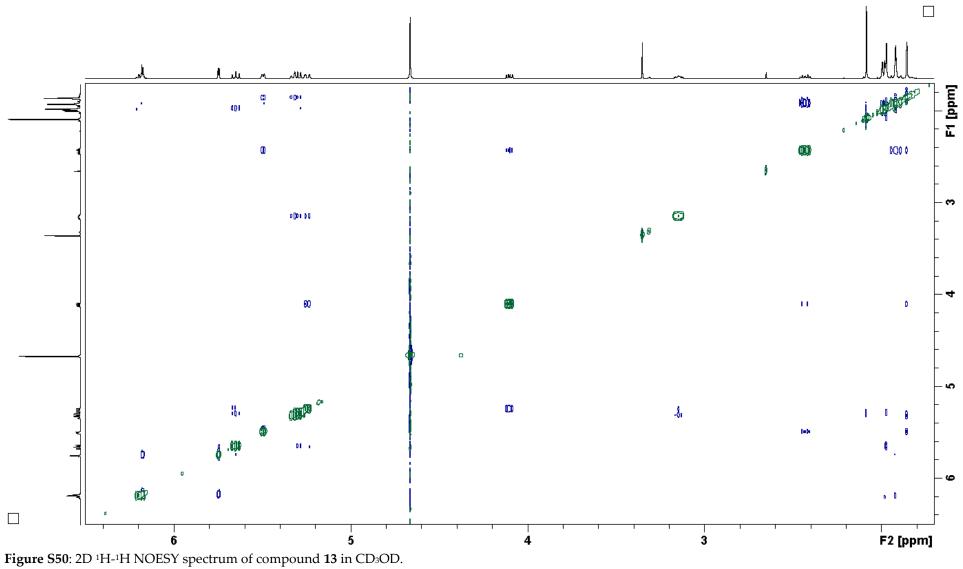


Figure S47: <sup>1</sup>H NMR spectrum of compound 13 in CD<sub>3</sub>OD.







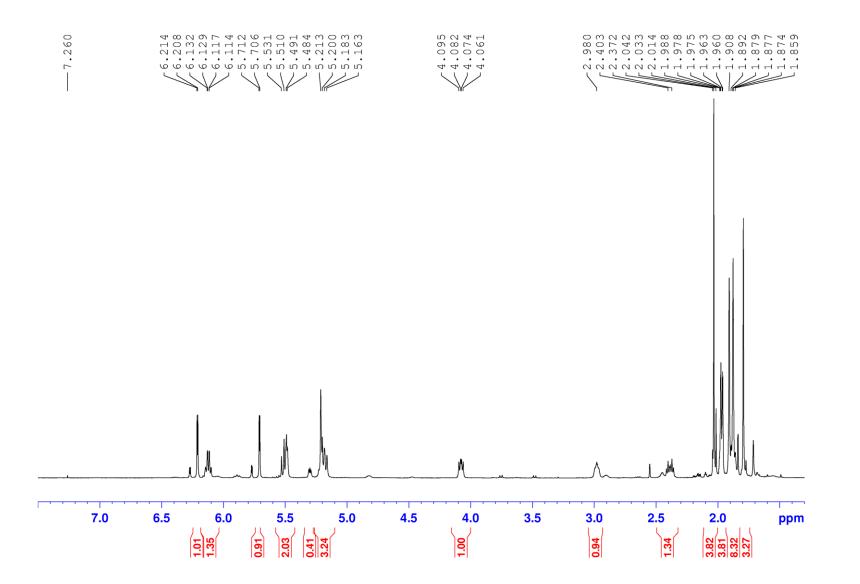
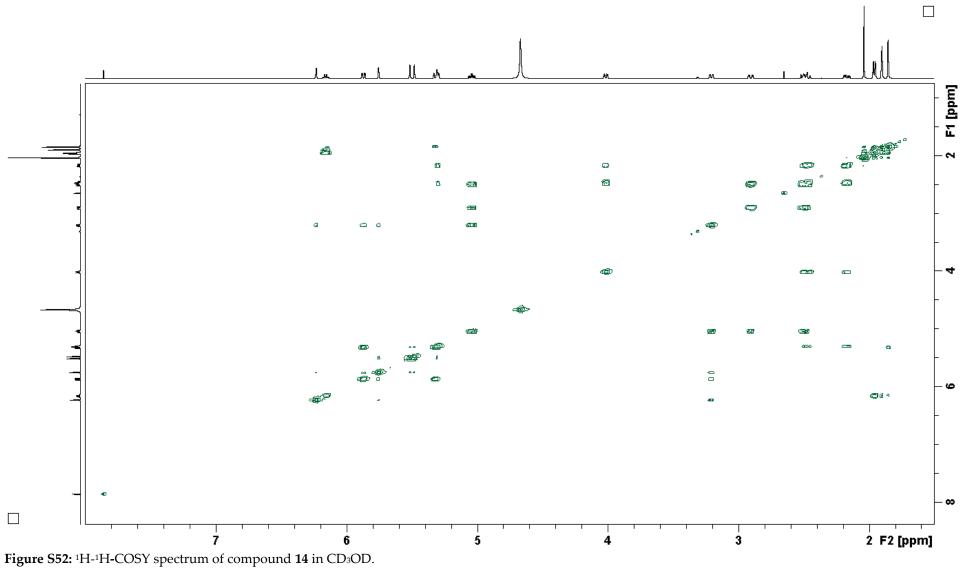
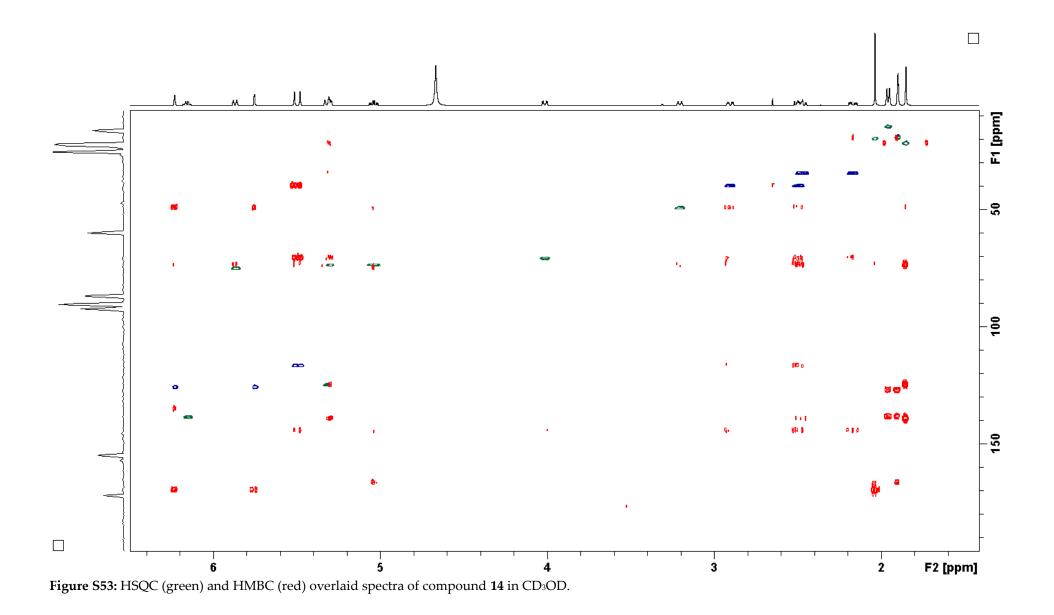
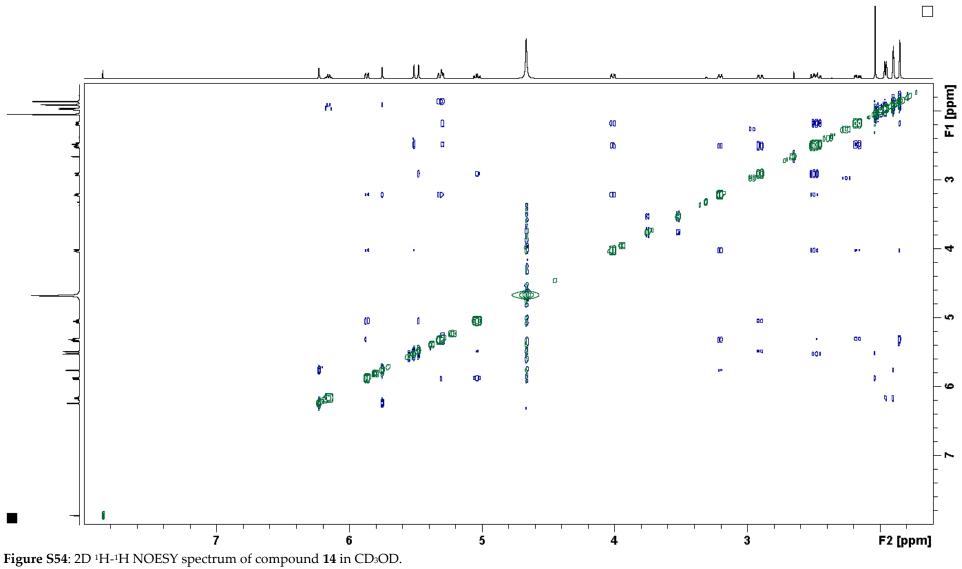


Figure S51: <sup>1</sup>H NMR spectrum of compound 14 in CD<sub>3</sub>OD.







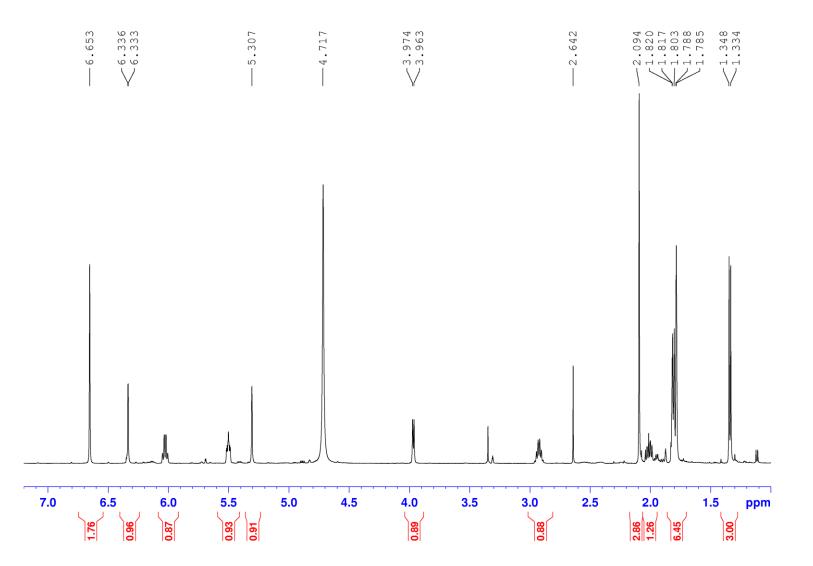
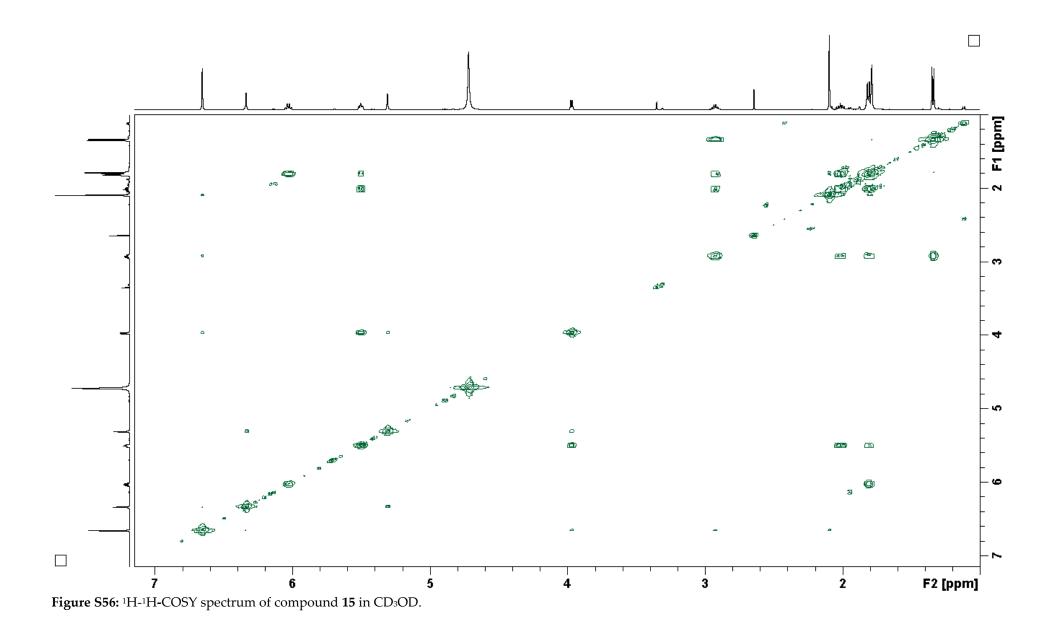
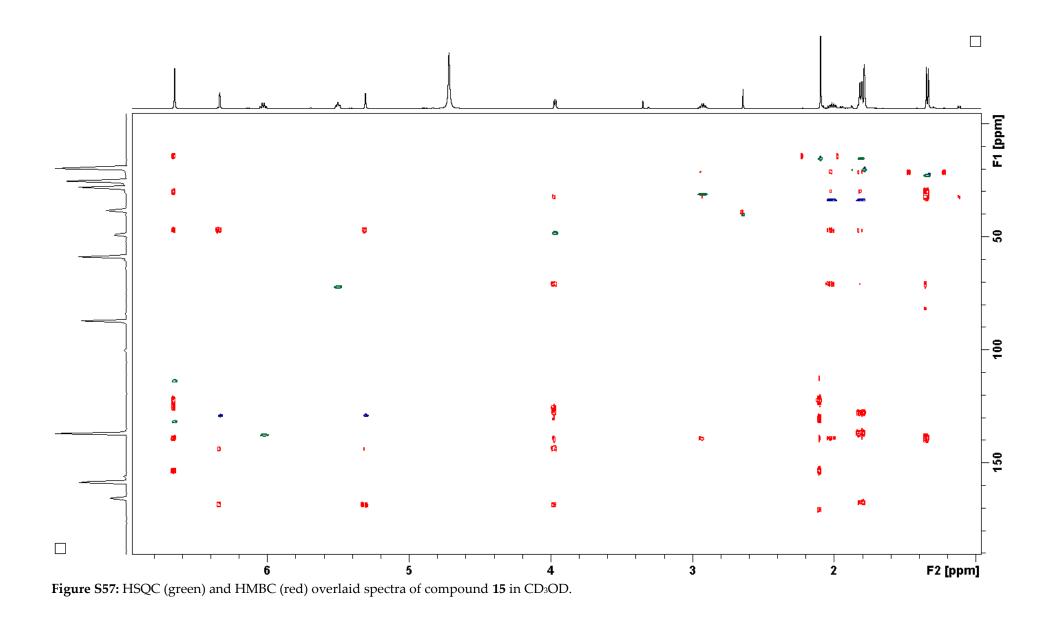


Figure S55: <sup>1</sup>H NMR spectrum of compound **15** in CD<sub>3</sub>OD.





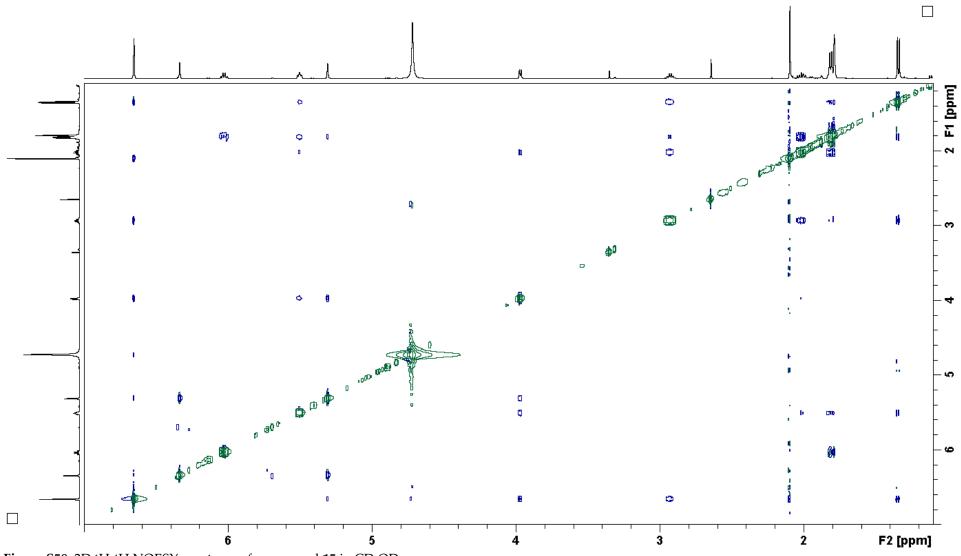


Figure S58: 2D <sup>1</sup>H-<sup>1</sup>H NOESY spectrum of compound 15 in CD<sub>3</sub>OD.

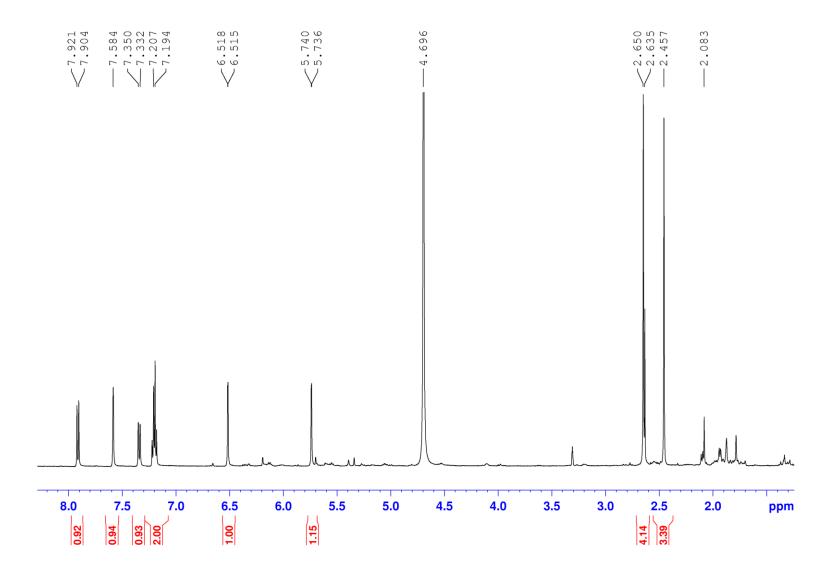
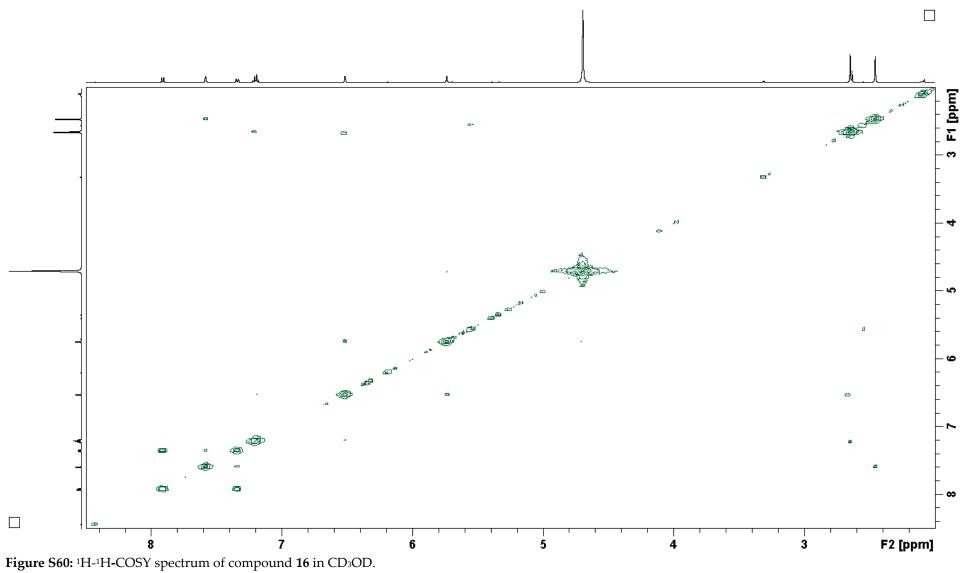
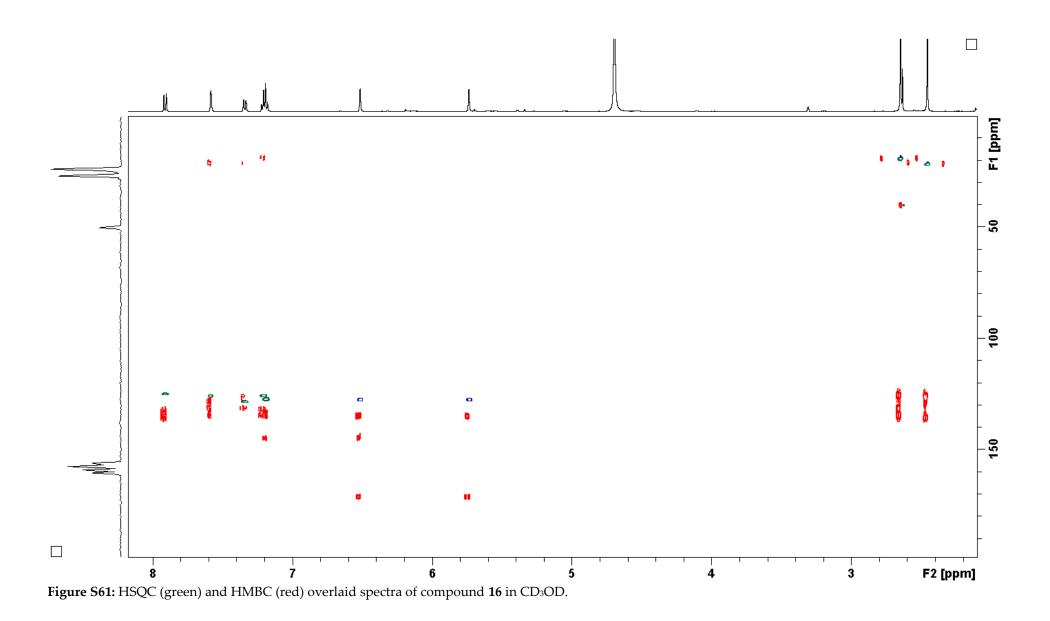


Figure S59: <sup>1</sup>H NMR spectrum of compound 16 in CD<sub>3</sub>OD.





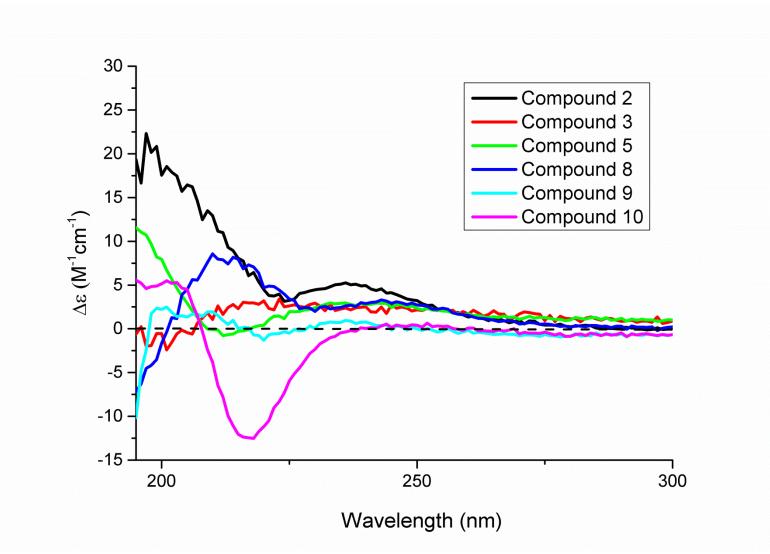
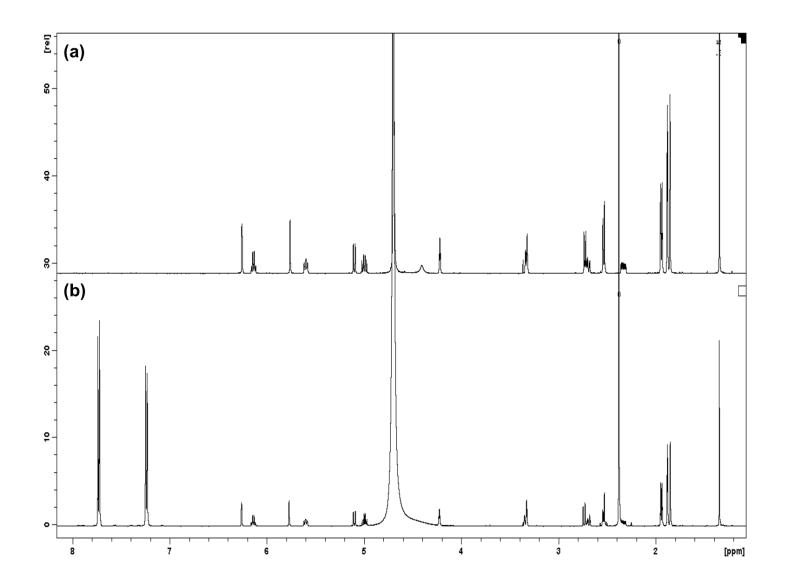


Figure S62: ECD spectra in MeOH of compounds 2, 3, 5, 8-10.



**Figure S63:** Overlay of <sup>1</sup>H NMR spectra of **3** (a) and of the reaction of **3** with *p*TSOH after 24 hours (b).