

Supplementary Data for
Crowned Spiropyran Fluoroionophores with a Carboxyl Moiety for
the Selective Detection of Lithium ions

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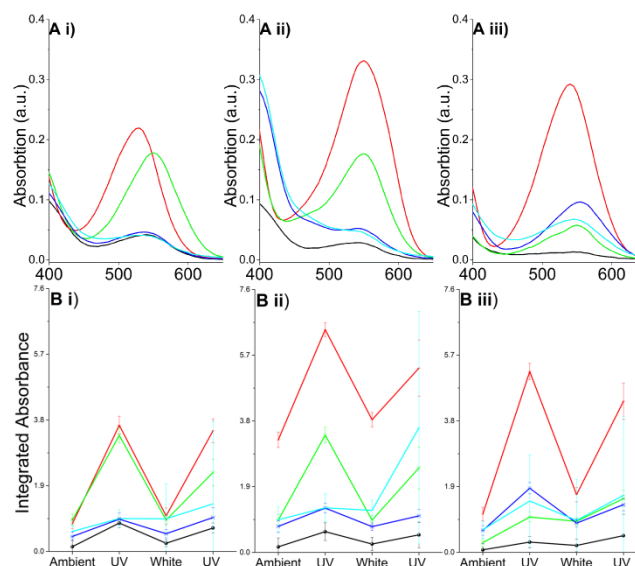


Figure S1. A) the absorbance spectra of crowned spiropyrans i) **1**, ii) **2**, iii) **3** after 10 min of UV black light irradiation in the presence of no ions (black), and 100x excess of lithium perchlorate (red), sodium perchlorate (green), potassium perchlorate (navy), and caesium sulphate (cyan). B) Integrated absorbance intensities (between 470 and 650 nm) of crowned spiropyran in the presence of metal salts during photocycling with UV black light and white light 10 min each.

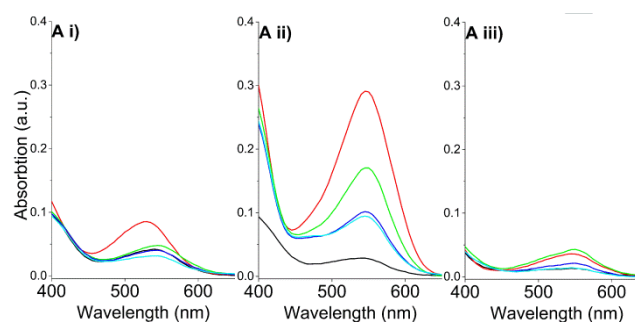


Figure S2. A) the absorbance spectra of crowned spiropyran i) **1**, ii) **2**, iii) **3** after 10 min of UV black light irradiation in the presence of no ions (black), and equimolar quantities of lithium perchlorate (red), sodium perchlorate (green), potassium perchlorate (navy), and caesium sulphate (cyan).

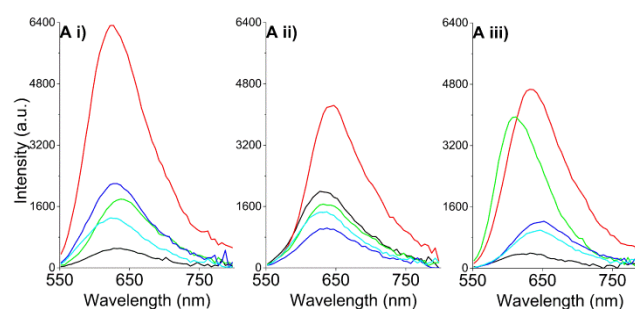


Figure S3. A) the fluorescence spectra of crowned spiropyran i) **1**, ii) **2**, iii) **3** after 10 min of UV black light irradiation in the presence of no ions (black), and 100x excess of lithium perchlorate (red), sodium perchlorate (green), potassium perchlorate (navy), and caesium sulphate (cyan).

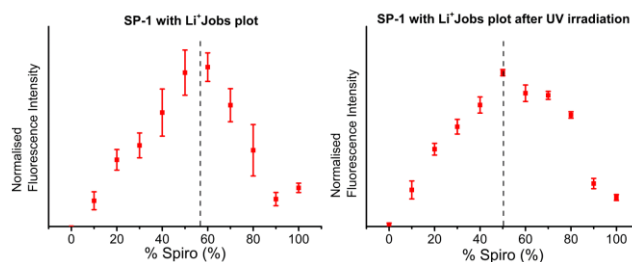


Figure S4. Jobs plot of the fluorescence of **SP-1** with LiClO_4 in the dark (left) and after UV_{352} irradiation for 10 min (right).

Jobs plot experimental

Stock solutions of spiropyran **SP-1** (100 μM) and LiClO_4 (100 μM) were prepared in HPLC grade acetonitrile. On the same microplate tray in triplicate the SP-1 and LiClO_4 solutions (combined total 100 μL) and acetonitrile (100 μL) were combined such that the total concentration was constant ($[\text{M}] + [\text{SP}] = 50 \mu\text{M}$) $[\text{SP}] = 0, 5, 10, 15, 20, 25, 30, 35, 40, 45,$ and $50 \mu\text{M}$. The absorbance and fluorescence spectra were recorded between 300 and 700 nm, and 552 and 697 nm, respectively, at 25 $^\circ\text{C}$ using a BioTek Synergy H4 Hybrid Multi-Mode Microplate Reader scanning with a resolution of 5 nm. Fluorescence excitation was at 532 nm with bandgap of 9 nm.

NMR Spectra of Spiroprans and Intermediates

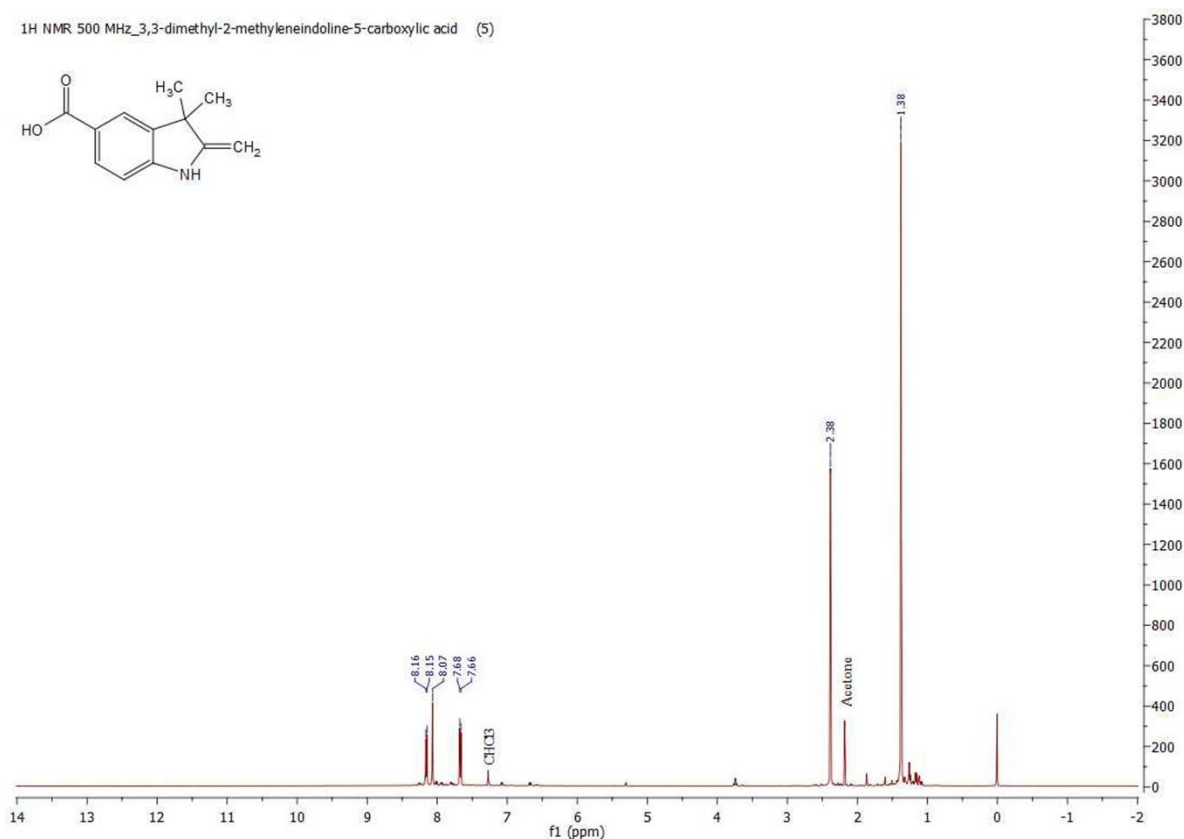


Figure S5. ^1H NMR spectrum of **5** recorded in CDCl_3 at 500 MHz

¹³C NMR 500 MHz_3,3-dimethyl-2-methyleneindoline-5-carboxylic acid (5)

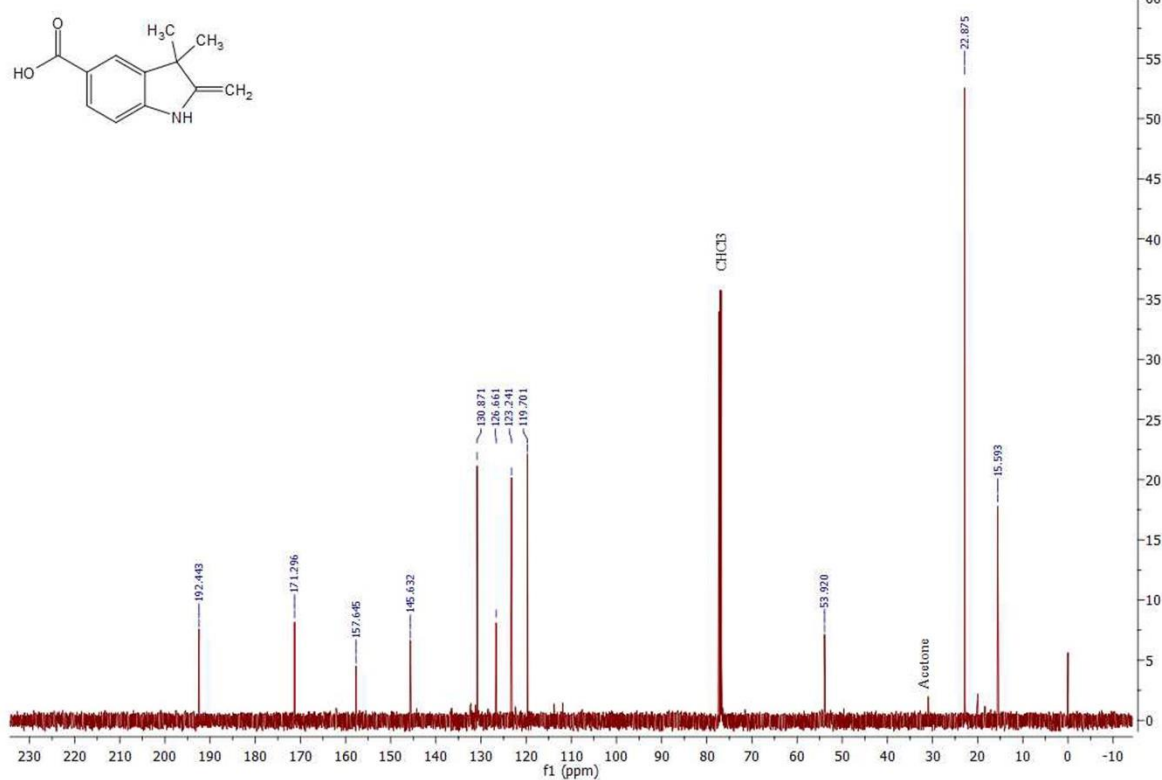


Figure S6. ¹³C NMR spectrum of **5** recorded in CDCl₃ at 126 MHz

¹H NMR 500 MHz_1,3,3-Trimethyl-2-methyleneindoline-5-carboxylic acid (6)

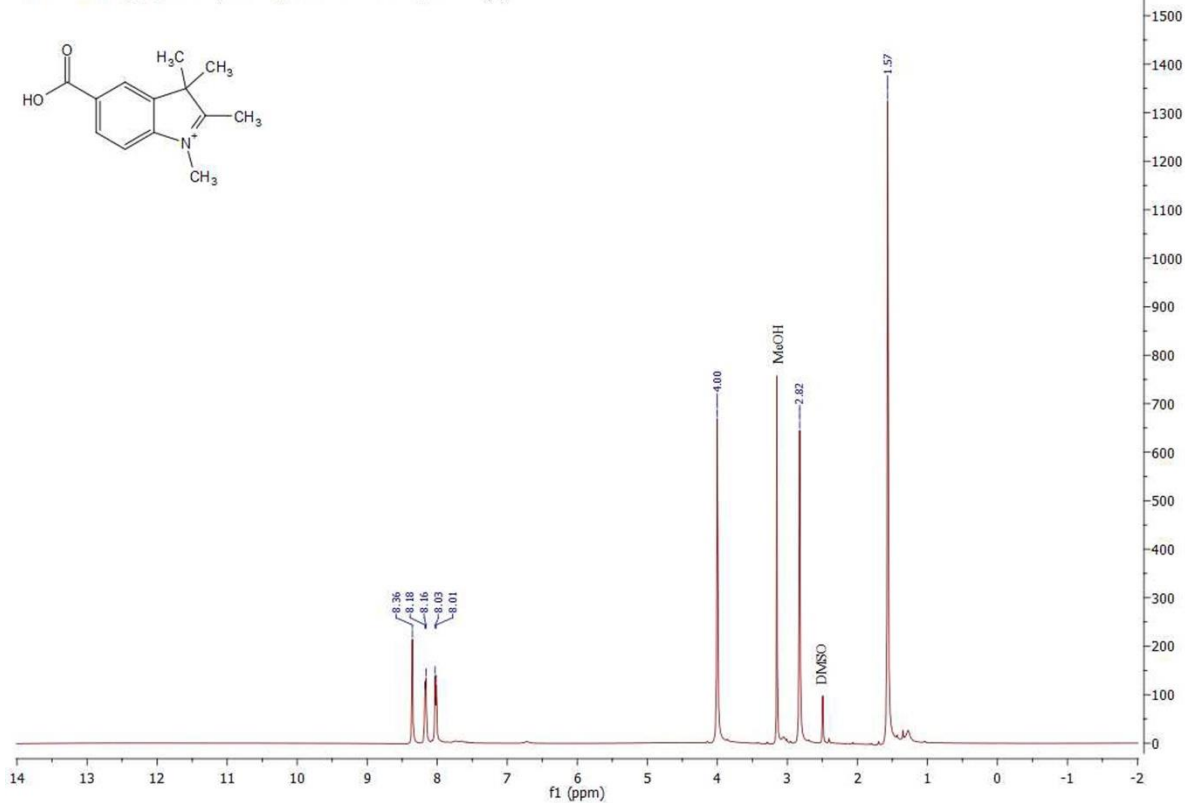


Figure S7. ¹H NMR spectrum of **6** recorded in d₆-DMSO at 500 MHz

¹³C NMR 500 MHz_1,3,3-Trimethyl-2-methyleneindoline-5-carboxylic add (6)

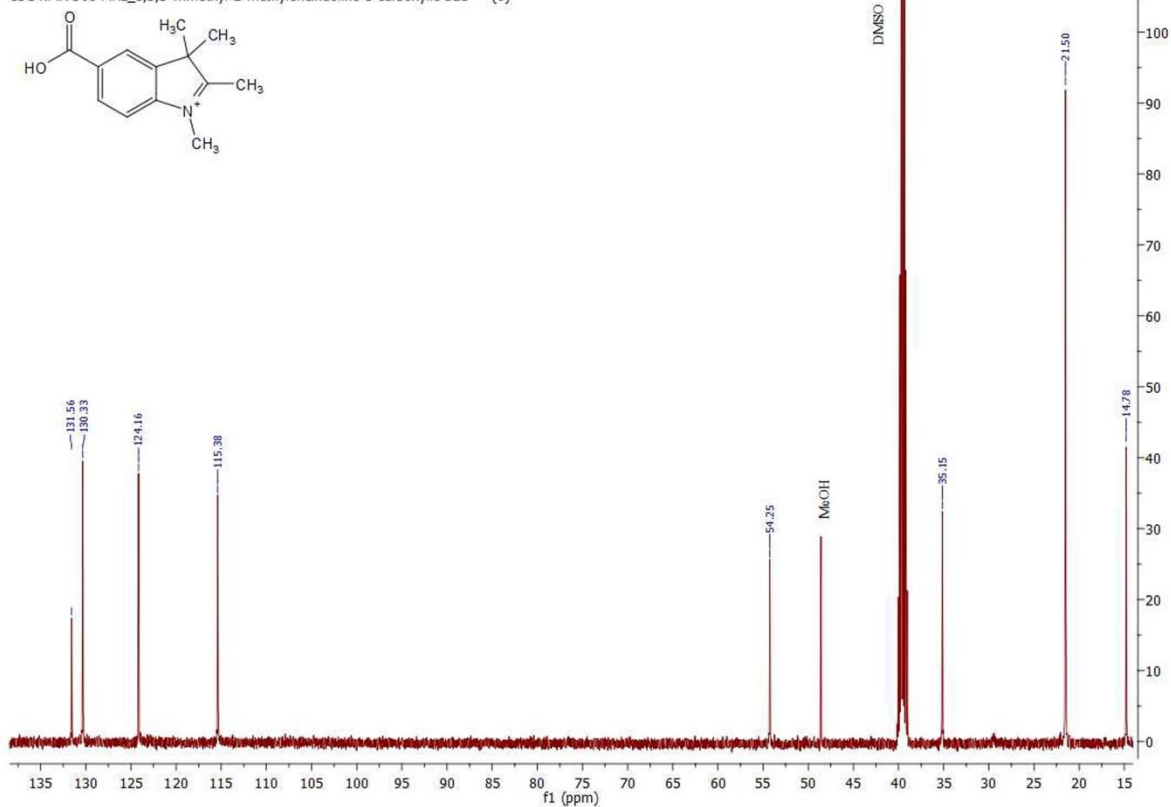


Figure S8. ¹³C NMR spectrum of **6** recorded in d₆-DMSO at 126 MHz

¹H NMR 500 MHz_3-(methyl-1-aza-12-crown-4-ether)-2-hydroxy-5-nitrobenzaldehyde (11)

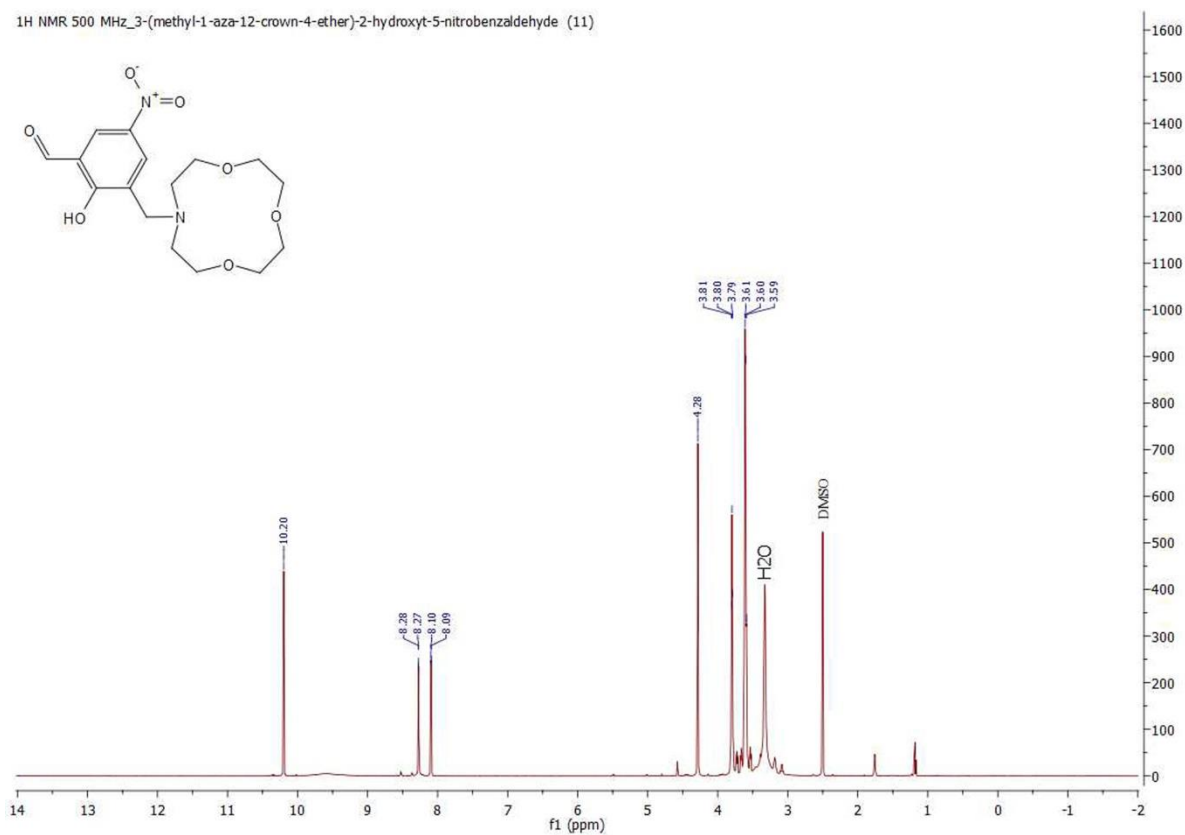


Figure S9. ¹H NMR spectrum of **11** recorded in d₆-DMSO at 500 MHz

¹³C NMR 500 MHz_3-(methyl-1-aza-12-crown-4-ether)-2-hydroxy-5-nitrobenzaldehyde (11)

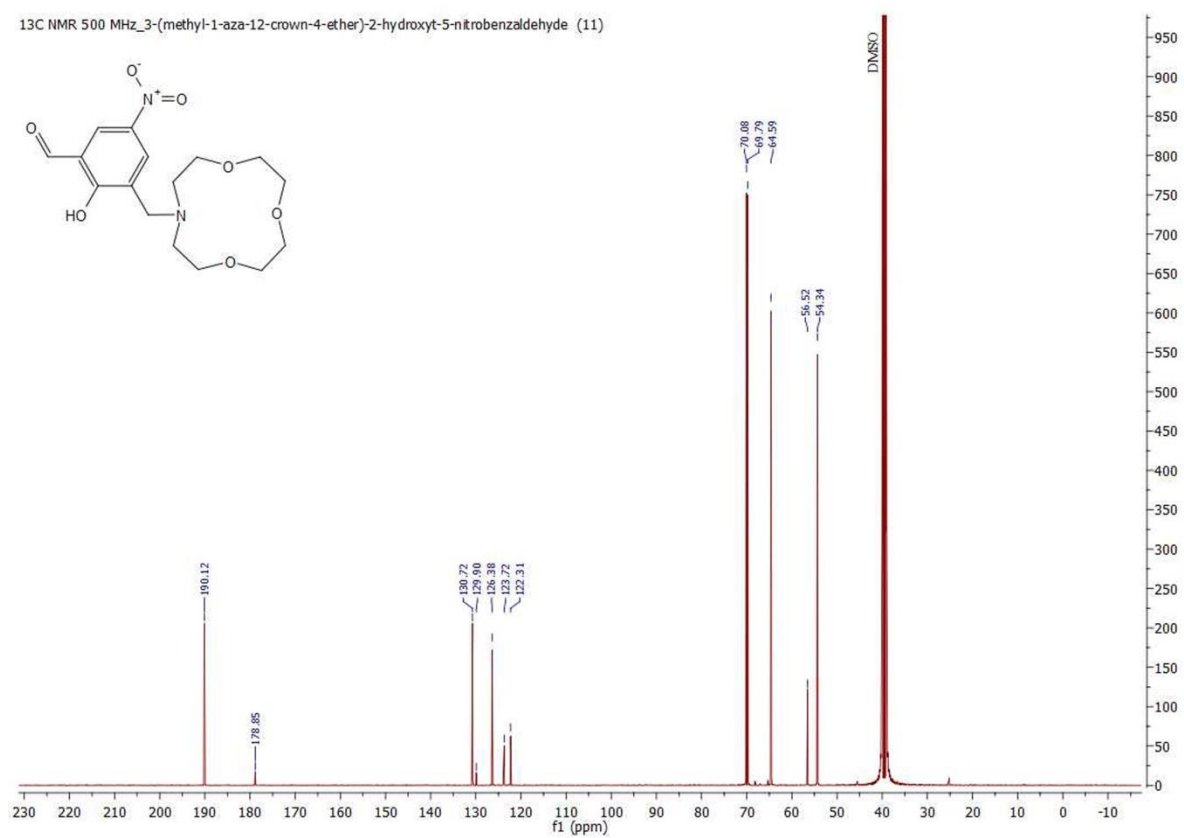


Figure S10. ¹³C NMR spectrum of **11** recorded in d₆-DMSO at 126 MHz

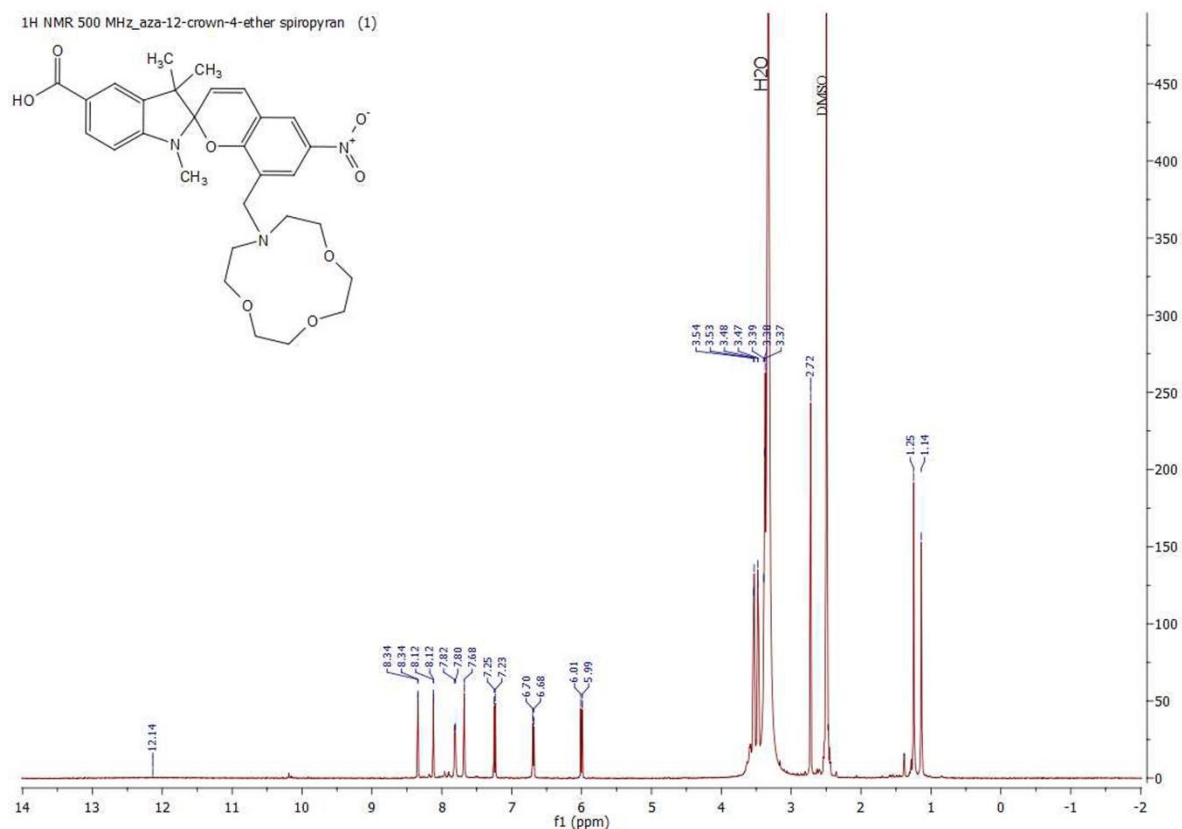


Figure S11. 1H NMR spectrum of **1** recorded in d6-DMSO at 500 MHz

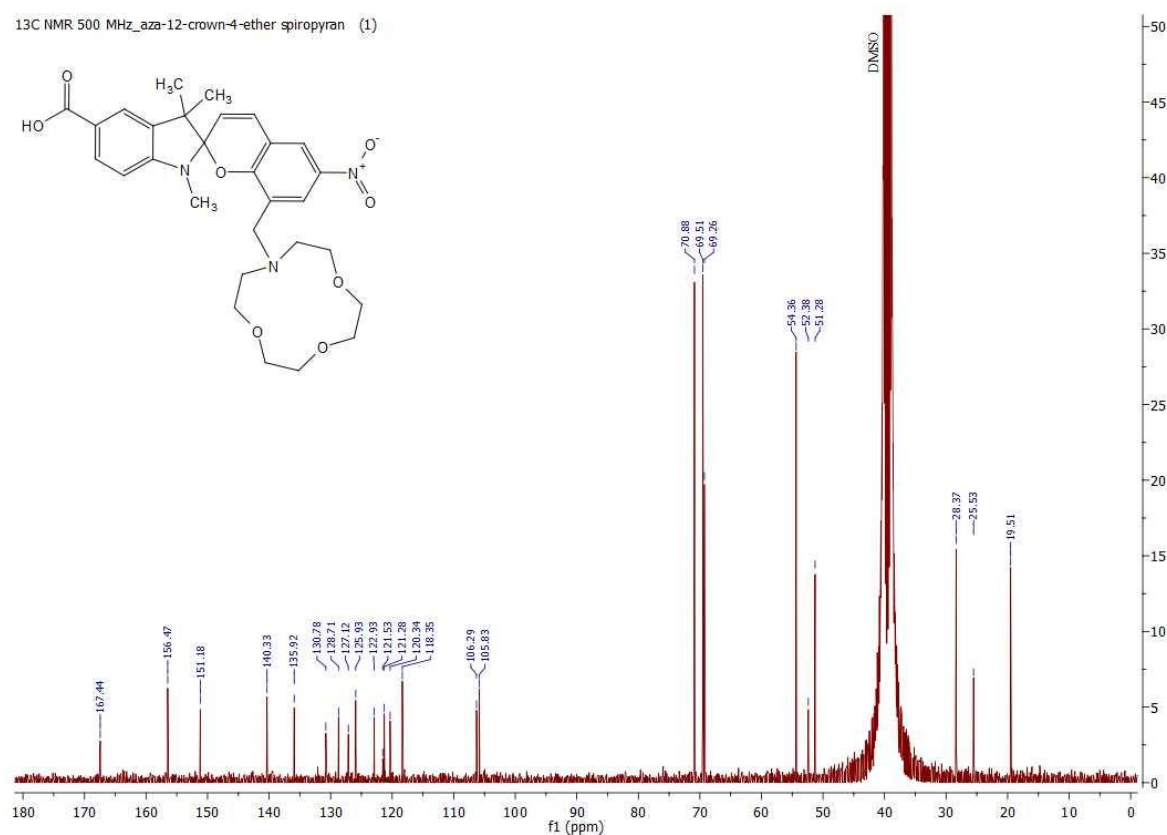


Figure S12. 13C NMR spectrum of **1** recorded in d6-DMSO at 126 MHz

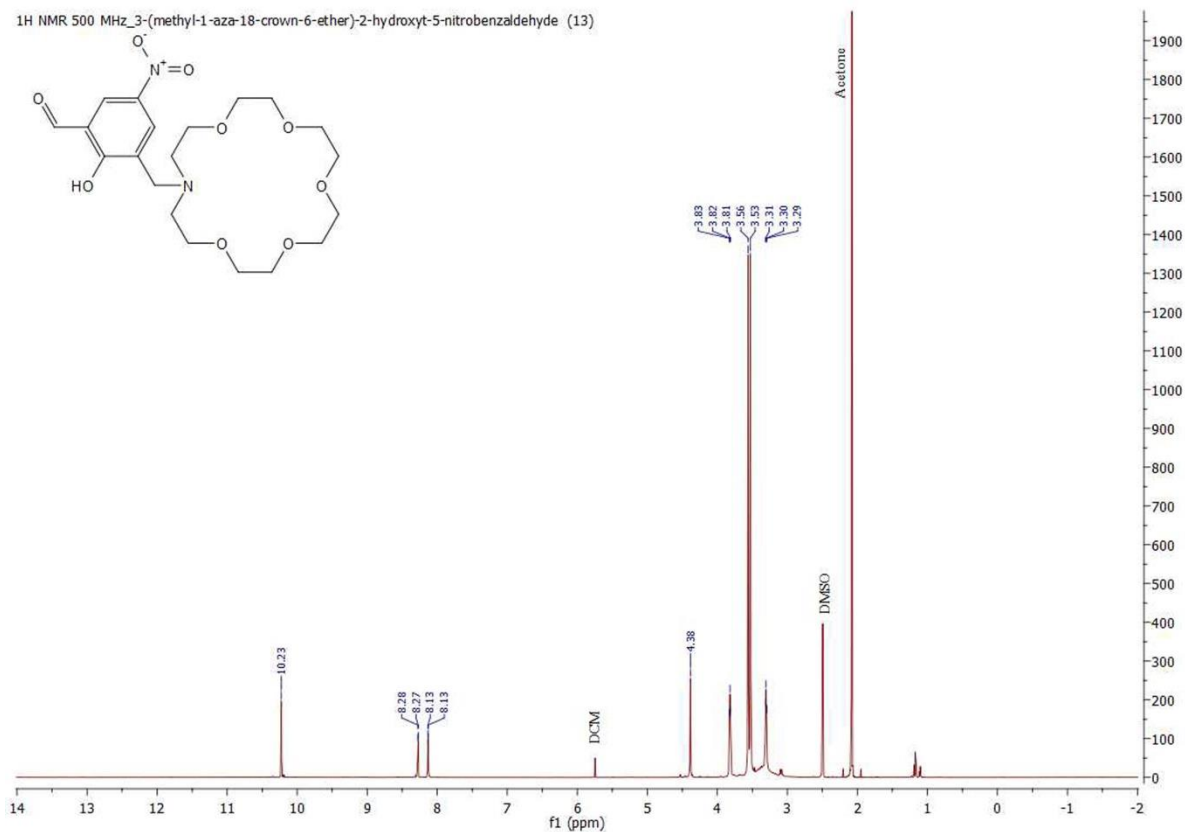


Figure S13. 1H NMR spectrum of **13** recorded in d6-DMSO at 500 MHz

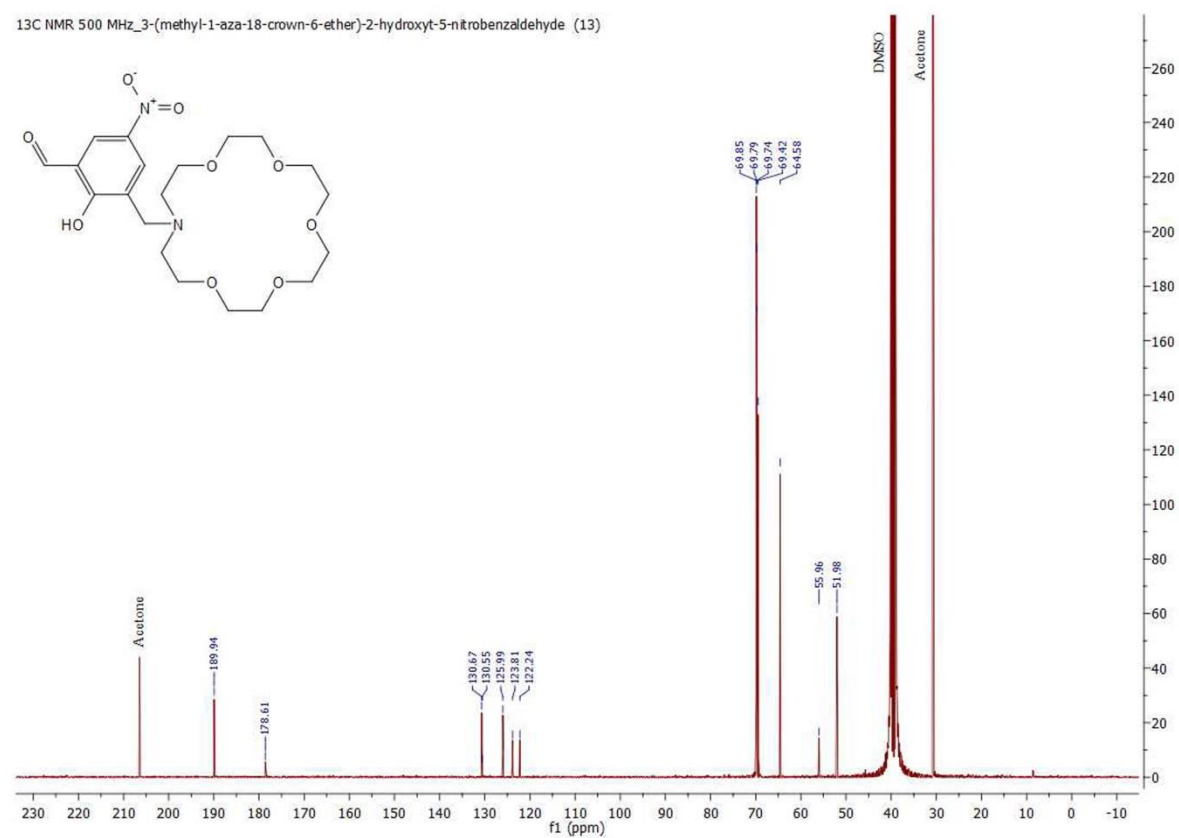


Figure S14. 13C NMR spectrum of **13** recorded in d6-DMSO at 126 MHz

1H NMR 500 MHz_aza-18-crown-6-ether spiropyran (3)

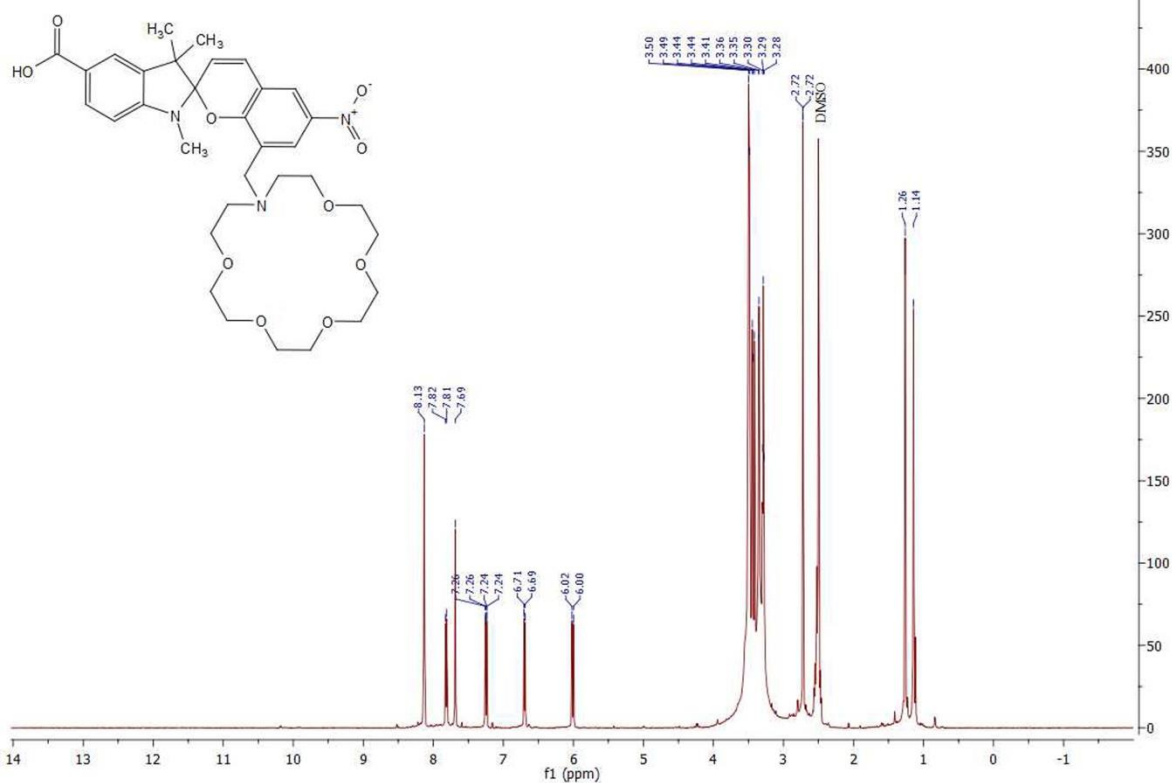


Figure S15. ¹H NMR spectrum of **3** recorded in d₆-DMSO at 500 MHz

¹³C NMR 500 MHz_aza-18-crown-6-ether spiropyran (3)

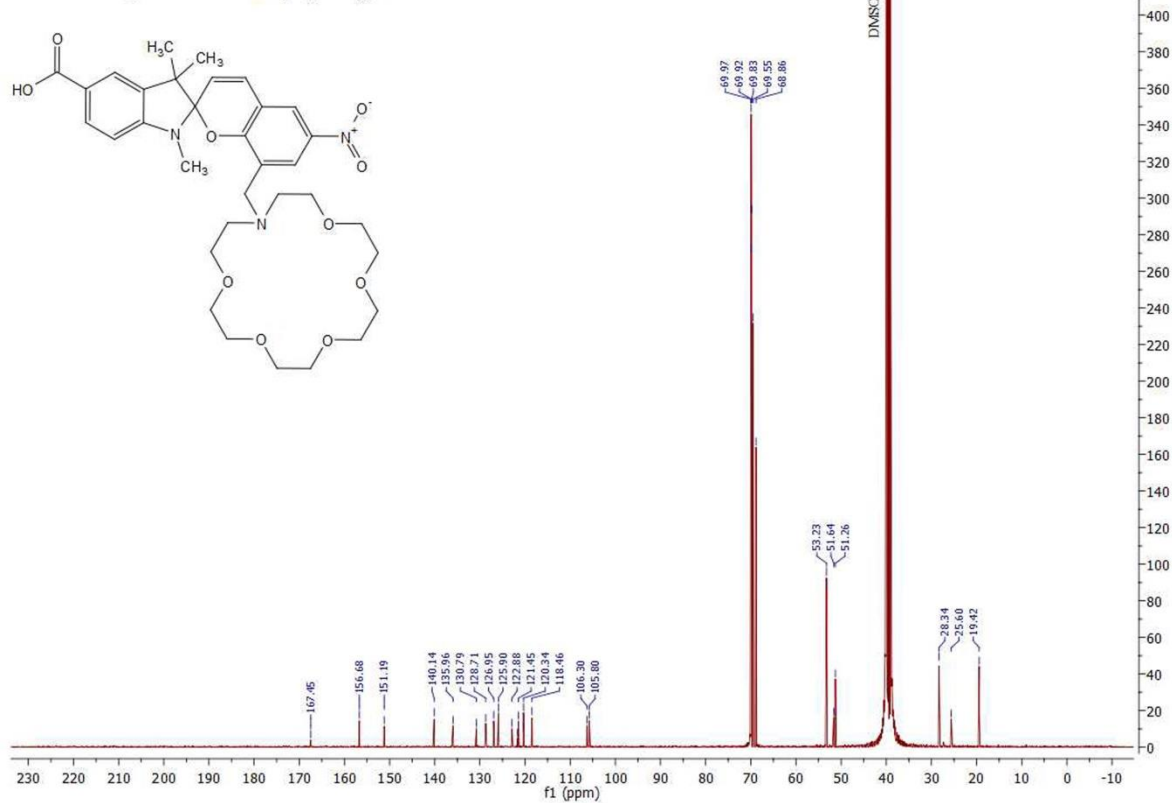


Figure S16. ¹³C NMR spectrum of **3** recorded in d₆-DMSO at 126 MHz