

**Novel spiropyrans with tunable characteristics incorporated
in highly cross-linked polymer matrix**

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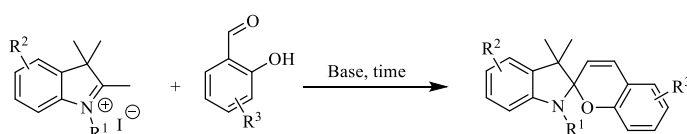
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Materials and methods

All used reagent-grade chemicals were purchased from commercial suppliers, unless otherwise stated. The solvents have been purified according to conventional methods. UV-vis spectra were recorded using an Evolution 200 spectrophotometer (Thermo Scientific, MA USA) in rectangular quartz cells with a 10 mm optical path. NMR spectra were recorded using an Avance III (Bruker, Fällanden, Switzerland) spectrometer with 600.13 MHz proton frequency in CDCl₃ and DMSO-d₆ at ambient temperature with the use of the residual solvent signal as an internal reference. High-resolution mass spectra were recorded in the positive ion mode using a Shimadzu LCMS8050 mass spectrometer. IR spectra were measured using a Bruker Alpha ATR-IR spectrometer.

Additional remarks



Scheme S1. General approach to spiropyrans.

Typical NMR spectrum and the assignment of the signals are shown at Figure S1 for **5b** as example. The overlapping of two resonances at 106 ppm in ¹³C NMR spectrum of **5b** in CDCl₃, while in DMSO-d₆ they appear as two separate peaks (see Online Supporting Information figure S11).

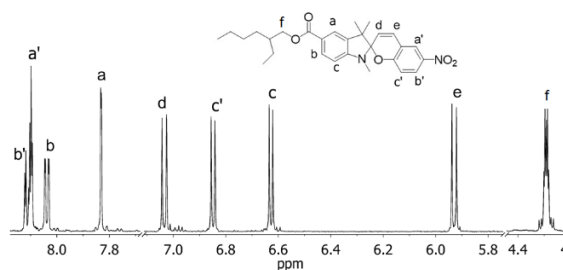
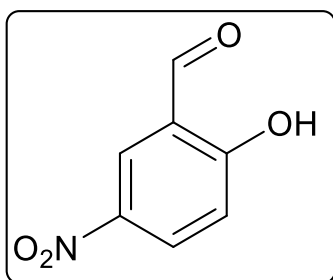


Figure S1. Fragment of ¹H NMR spectrum of **5b**.

Experimental Procedures

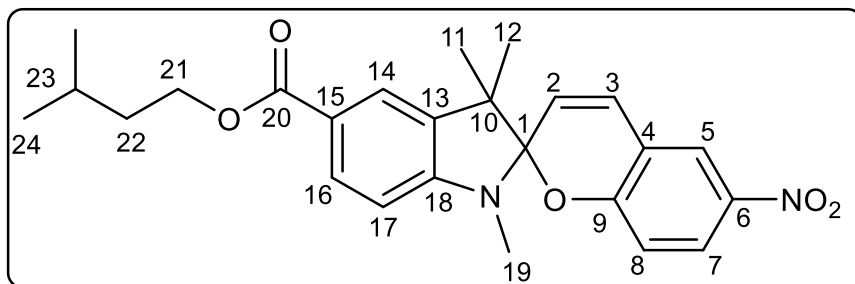
Preparation of 4-nitrosalicylic aldehyde **4**



Salicylaldehyde (2.55 mL, 24.00 mmol, 1.00 eq.) was dissolved in acetic acid (13.50 mL). Then, nitric acid (9.00 mL, 120.00 mmol, 5.00 eq.) was added dropwise. The reaction mixture was allowed to stir at room temperature overnight. A pale-yellow precipitate was collected by filtration, washed with water and used further without any further purification. Yield 3.3 g, (83%).

^1H NMR (600 MHz, CDCl_3) δ 11.60 (s, 1H), 10.00 (s, 1H), 8.56 (d, $^4J = 2.8$ Hz, 1H), 8.41 (dd, $^3J = 9.2$, $^4J = 2.8$ Hz, 1H), 7.13 (d, $^3J = 9.2$ Hz, 1H). The NMR data are in consistency with reported ones [S1].

Preparation of isopentyl 1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline]-5'-carboxylate 5a



A solution of 4-hydrazinobenzoic acid hydrochloride (1.50 g, 7.95 mmol), 3-methyl-2-butanone (1.36 g, 15.90 mmol, 1.71 mL) in dry glacial AcOH (50 mL) was heated to 130 °C under an argon atmosphere for 24 h. The reaction mixture was cooled down to ambient temperature and the solvent removed under reduced pressure. The residue was dissolved in MeCN (50 mL) and potassium carbonate (1.65 g, 11.93 mmol) was added at room temperature. Next, isoamyl bromide (1.80 g, 15.90 mmol, 1.42 mL) was added slowly and the reaction was stirred 24 h at 78 °C. The reaction mixture was diluted with Et₂O (25 mL) and H₂O (25 mL) and extracted with Et₂O (2x25 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed at reduced pressure. The residue was dissolved in 30 mL of MeCN, and iodomethane (3.39 g, 23.85 mmol, 1.42 mL) was added. The mixture was stirred for 24 h under reflux. After cooling, the solvent was removed under reduced pressure. The crude product was diluted with Et₂O (20 mL), filtered and washed with Et₂O. The obtained substance, 4-nitrosalicylic aldehyde (1.32 g, 7.95 mmol) and dry Et₃N (1.20 g, 11.93 mmol, 1.65 mL) were dissolved in EtOH, and this was refluxed under argon for 24 h. The reaction mixture was cooled down to -25 °C to cause precipitation of the condensation product. The crude product was filtered and washed cold EtOH (2x10 mL) to give 1.56 g (45%) of **5a**.

^1H NMR (600 MHz, DMSO- d_6) δ 8.25 (d, $^4J = 2.8$ Hz, 1H, H-5), 8.03 (dd, $^3J = 9.0$, $^4J = 2.8$ Hz, 1H, H-7), 7.84 (dd, $^3J = 8.3$, $^4J = 1.7$ Hz, 1H, H-16), 7.68 (d, $^4J = 1.8$ Hz, 1H, H-14), 7.27 (d, $^3J = 10.4$ Hz, 1H, H-2), 6.92 (d, $^3J = 9.0$ Hz, 1H, H-8), 6.73 (d, $^3J = 8.2$ Hz, 1H, H-17), 6.03 (d, $^3J = 10.4$ Hz, 1H, H-3), 4.27 (t, $^3J = 6.7$ Hz, 2H, H-21), 2.78 (s, 3H, H-19), 1.74 (non, 6.7 Hz, 1H, H-23), 1.61 (q, $J = 6.8$ Hz, 2H, H-22), 1.26, 1.15 (2s, 2x3H, H-11, H-12), 1.15 (s, 3H, H-12), 0.95 (d, $J = 6.6$ Hz, 6H, H-24).

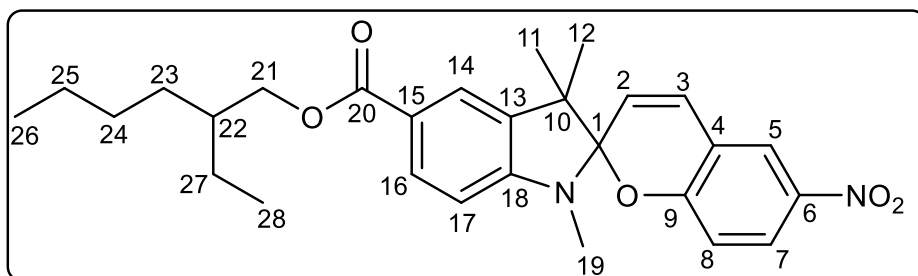
^{13}C NMR (151 MHz, DMSO- d_6) δ 166.27 (C-20), 159.38 (C-6), 151.92 (C-9), 141.26 (C-18), 136.56 (C-15), 131.19 (C-16), 129.02 (C-2), 126.29 (C-7), 123.35 (C-14), 123.12 (C-5), 121.27 (C-4a), 121.22 (C-3), 119.26 (C-13), 115.95 (C-8), 106.86 (C-17), 106.32 (C-13), 63.00 (C-21),

52.04 (C-1), 37.60 (C-22), 28.87 (C-19), 25.93 (C-11 or C-12), 25.27 (C-12 or C-11), 22.86 (C-23), 19.99 (C-24).

IR (ATR): ν (cm⁻¹) = 2958 (w), 2922 (w), 2870 (w), 1701 (m), 1651 (w), 1612(m), 1577 (w), 1519 (m, NO₂), 1468 (m), 1365 (w), 1335 (s), 1287 (m), 1269 (m), 1231 (s, C=O), 1181 (w), 1145 (w), 1088 (s), 1016 (m), 953 (s), 930 (s), 816 (m), 772 (m), 746 (m), 686 (w), 650 (w), 629 (w).

HRMS (ESI-TOF): m/z calcd. for [C₂₅H₂₈N₂O₅]⁺ 437.19982 [M+H]⁺, found 437.20803.

Preparation of 2-ethylhexyl 1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline]-5'-carboxylate 5b



A solution of 4-hydrazinobenzoic acid hydrochloride (1.50 g, 7.95 mmol), 3-methyl-2-butanone (1.36 g, 15.90 mmol, 1.71 ml) in dry glacial AcOH (50 ml) was heated to 130 °C under an argon atmosphere for 24 h. The reaction mixture was cooled down to ambient temperature and the solvent removed under reduced pressure. The residue was dissolved in MeCN (50 ml) and potassium carbonate (1.65 g, 11.93 mmol) was added at room temperature. Next, 2-ethylhexyl bromide (3.07 g, 15.90 mmol, 2.77 ml) was added slowly and the reaction was stirred 24 h at 78 °C. The reaction mixture was diluted with Et₂O (25 ml) and H₂O (25 ml) and extracted with Et₂O (2x25 ml). The combined organic layers were dried over Na₂SO₄ and the solvent was removed at reduced pressure. The residue was dissolved in 30 ml of MeCN and iodomethane (3.39 g, 23.85 mmol, 1.42 ml) was added. The mixture was stirred for 24 h under reflux. After cooling, the solvent was removed under reduced pressure. The crude product was diluted with Et₂O (20 ml), filtered and washed with Et₂O. The obtained compound, 4-nitrosalicylic aldehyde (1.32 g, 7.95 mmol) and dry Et₃N (1.20 g, 11.93 mmol, 1.65 ml) were dissolved in EtOH and refluxed under argon for 24h. The reaction mixture was cooled down to -25 °C to precipitate the condensation product. The crude product was filtered and washed cold EtOH (2x10ml) to give 1.52g (40%).

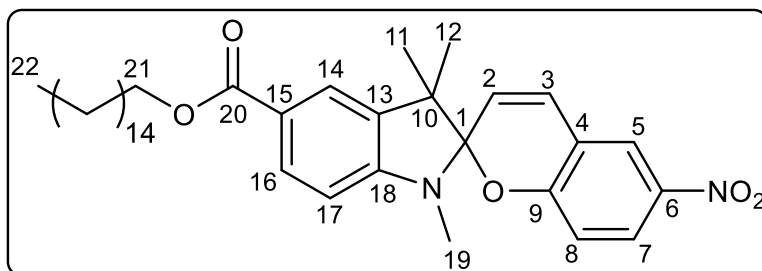
¹H NMR (600 MHz, CDCl₃) δ 8.07 – 8.03 (m, 2H, H-5, H-7), 7.98 (dd, ³J = 8.2, ⁴J = 1.7 Hz, 1H, H-16), 7.78 (d, ⁴J = 1.7 Hz, 1H, H-14), 6.98 (d, ³J = 10.3 Hz, 1H, H-2), 6.79 (d, ³J = 8.8 Hz, 1H, H-8) 6.57 (d, ³J = 8.2 Hz, 1H, H-17), 5.88 (d, ³J = 10.3 Hz, 1H, H-3), 4.28-4.20 (m, H), 2.83 (s, 3H, H-19), 1.75 (hept, ²J = 6.1 Hz, 1H, H-22), 1.53 – 1.32 (m, 5xCH₂+CH₃ (H-11 or H-12), 1.23 (s, 3H, H-12 or H-11), 0.98 (t, ²J = 7.5 Hz, 3H, H-28), 0.94 (t, ²J = 7.0 Hz, 3H, H-26).

¹³C NMR (151 MHz, CDCl₃) δ 166.94 (C-20), 159.31 (C-6), 151.50 (C-9), 141.26 (C-18), 136.10 (C-15), 131.09 (C-16), 128.60 (C-8), 126.00 (C-7), 123.23(C-14), 122.76 (C-5), 122.01 (C-4), 120.96 (C-2), 118.49 (C-13), 115.51 (C-3), 106.13 (C-17, C-13), 66.96 (C-21), 51.98 (C-1), 39.05 (C-22), 30.70 (C-23), 29.05 (C-24), 28.77 (C-23), 25.79 (C-11 or C-12), 24.10 (C-24), 23.01 (C-25), 19.88 (C-12 or C-11), 14.06 (C-28), 11.13 (C-26).

IR(ATR) ν (cm⁻¹) = 2960 (w), 2929 (w), 2872 (w), 1700 (m), 1650 (w), 1611 (m), 1519 (m, NO₂), 1468 (m), 1335 (m), 1266 (m), 1269 (m), 1228 (s, C=O), 1180 (w), 1145 (w), 1088 (s), 1016 (m), 950 (s), 920 (m), 810 (w), 771 (w), 732 (s), 684 (w), 649 (w), 629 (w).

HRMS (ESI-TOF): m/z calcd. for [C₂₈H₃₄N₂O₅]⁺ 479.24677 [M+H]⁺, found 479.25554.

Preparation of hexadecyl 1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline]-5'-carboxylate 5c



A solution of 4-hydrazinobenzoic acid hydrochloride (1.50 g, 7.95 mmol), 3-methyl-2-butanone (1.36 g, 15.90 mmol, 1.71 ml) in dry glacial AcOH (50 ml) was heated to 130 °C under an argon atmosphere for 24 h. The reaction mixture was cooled down to ambient temperature and the solvent removed under reduced pressure. The residue was dissolved in MeCN (50 ml) and potassium carbonate (1.65 g, 11.93 mmol) was added at room temperature. Next, hexadecyl bromide (4.85 g, 15.90 mmol, 4.86 ml) was added slowly and the reaction was stirred 24 h at 78 °C. The reaction mixture was diluted with Et₂O (25 ml) and H₂O (25 ml) and extracted with Et₂O (2x25 ml). The combined organic layers were dried over Na₂SO₄ and the solvent was removed at reduced pressure. The residue was dissolved in 30 ml of MeCN and iodomethane (3.39 g, 23.85 mmol, 1.42 ml) was added. The mixture was stirred for 24h under reflux. After cooling, the solvent was removed under reduced pressure. The crude product was diluted with Et₂O (20 ml), filtered and washed with Et₂O. The obtained compound, 4-nitrosalicylic aldehyde (1.32 g, 7.95 mmol) and dry Et₃N (1.20 g, 11.93 mmol, 1.65 ml) were dissolved in EtOH and refluxed under argon for 24h. The reaction mixture was cooled down to -25 °C to precipitate the condensation product. The crude product was filtered and washed cold EtOH (2x10ml) to give 2.02 g (43%).

¹H NMR (600 MHz, CDCl₃) δ 8.07 – 8.03 (m, 2H, H-5, H-7), 8.04 (d, ⁴J = 3.3 Hz, 1H, H-5), 7.99 (dd, ³J = 8.2, ⁴J = 1.6 Hz, 1H, H-16), 7.77 (d, ⁴J = 1.7 Hz, 1H, H-14), 6.98 (d, ³J = 10.3 Hz, 1H, H-3), 6.79 (d, ³J = 8.8 Hz, 1H, H-8), 6.57 (d, ³J = 8.2 Hz, 1H, H-17), 5.87 (d, ³J = 10.3 Hz, 1H, H-2), 4.31 (t, ³J = 6.7 Hz, 2H, H-20), 2.83 (s, 3H, H-19), 1.78 (quint, ³J = 6.9 Hz, 2H), 1.51 – 1.24 (m, 31H (14xCH₂+CH₃ (H-11 or H-12))), 1.35 (s, 3H, H-12 or H-11), 0.90 (t, ³J = 6.9 Hz, 6H, H-22).

¹³C NMR (151 MHz, CDCl₃) δ 166.87 (C-20), 159.31 (C-6), 151.49 (C-9), 141.26 (C-18), 136.06 (C-15), 131.15 (C-16), 128.59 (C-8), 125.99 (C-7), 123.22 (C-14), 122.75 (C-5), 121.97 (C-4), 120.97 (C-2), 118.49 (C-13), 115.50 (C-3), 106.12 (C-17, C-13), 64.71 (C-21), 51.99 (C-1), 31.92 (-CH₂-), 29.69 (-CH₂-), 29.65 (-CH₂-), 29.60 (-CH₂-), 29.56 (-CH₂-), 29.35 (-CH₂-), 29.33 (-CH₂-), 28.89 (-CH₂-), 28.76 (C-23), 26.10 (-CH₂-), 25.78 (C-11 or C-12), 22.68 (-CH₂-), 19.90 (C-12 or C-11), 14.10 (C-22).

IR (ATR) ν (cm^{-1}) = 2922 (m), 2852 (m), 1705 (w), 1612 (m), 1577 (w), 1520 (m, NO_2), 1468 (w), 1364 (w), 1337 (s), 1287 (m), 1269 (m), 1232 (s, C=O), 1180 (w), 1145 (w), 1088 (w), 1016 (m), 954 (m), 930 (m), 816 (w), 772 (w), 746 (w), 686 (w), 650 (w) cm^{-1} .

HRMS (ESI-TOF): m/z calcd. for $[\text{C}_{36}\text{H}_{50}\text{N}_2\text{O}_5]^+$ 591.37197 $[\text{M}+\text{H}]^+$, found 591.38118.

The general procedure for obtaining **5b** containing films

DGEBA-based epoxy resin ED-20 ($M_n=380$, functionality for epoxy groups $f_{\text{EP}}=1.99$, the average number of repeating units in the molecule $m = 0.12$) was kept at 60 °C for several hours to remove any crystallites, then thermostated at $23\pm 2^\circ\text{C}$. Compound **5b** (5.4 mg) was dissolved in freshly distilled chloroform (0.2 ml), and the solution was added to oligooxypropylenediamine Jeffamine D230 ($M_n=230$, NH group functionality $f_{\text{NH}}=3.99$, the average number of repeating units in the molecule $n = 2.5$) and mixed thoroughly until a homogeneous mixture was obtained. The resulting composition was then mixed with a stoichiometric amount of epoxy resin to get 0.14 wt. % of spiropyran content in the final polymer. All samples were obtained through film casting. Time-Temperature-Transformation (TTT) diagrams [S2, S3] were employed to determine the optimal curing mode. A two-step scenario was used to obtain a fully cured spiropyran-modified epoxy-amine system: 1) pre-curing for 109 min at 60°C, and 2) post-curing for 133 min at 90°C. The average thickness of the films was ca. 0.8 mm.

FTIR data of polymeric film without **5b**:

IR(ATR) ν (cm^{-1}) = 2964 (w), 2928 (w), 2869 (w), 1607 (m), 1581 (w), 1506 (w), 1455 (w), 1373 (w), 1362 (w), 1294 (w), 1233 (m), 1179 (w), 1102 (w), 1084 (w), 1031 (w), 1010 (m), 918 (w), 824 (m), 766 (w), 735 (w), 727 (w).

FTIR data of polymeric film without **5b**:

IR(ATR) ν (cm^{-1}) = 2964 (w), 2928 (w), 2869 (w), 1607 (m), 1581 (w), 1506 (w), 1455 (w), 1373 (w), 1362 (w), 1294 (w), 1233 (m), 1179 (w), 1102 (w), 1084 (w), 1031 (w), 1010 (m), 918 (w), 824 (m), 766 (w), 735 (w), 727 (w).

^1H NMR and ^{13}C NMR of synthesized compounds

Compound 4

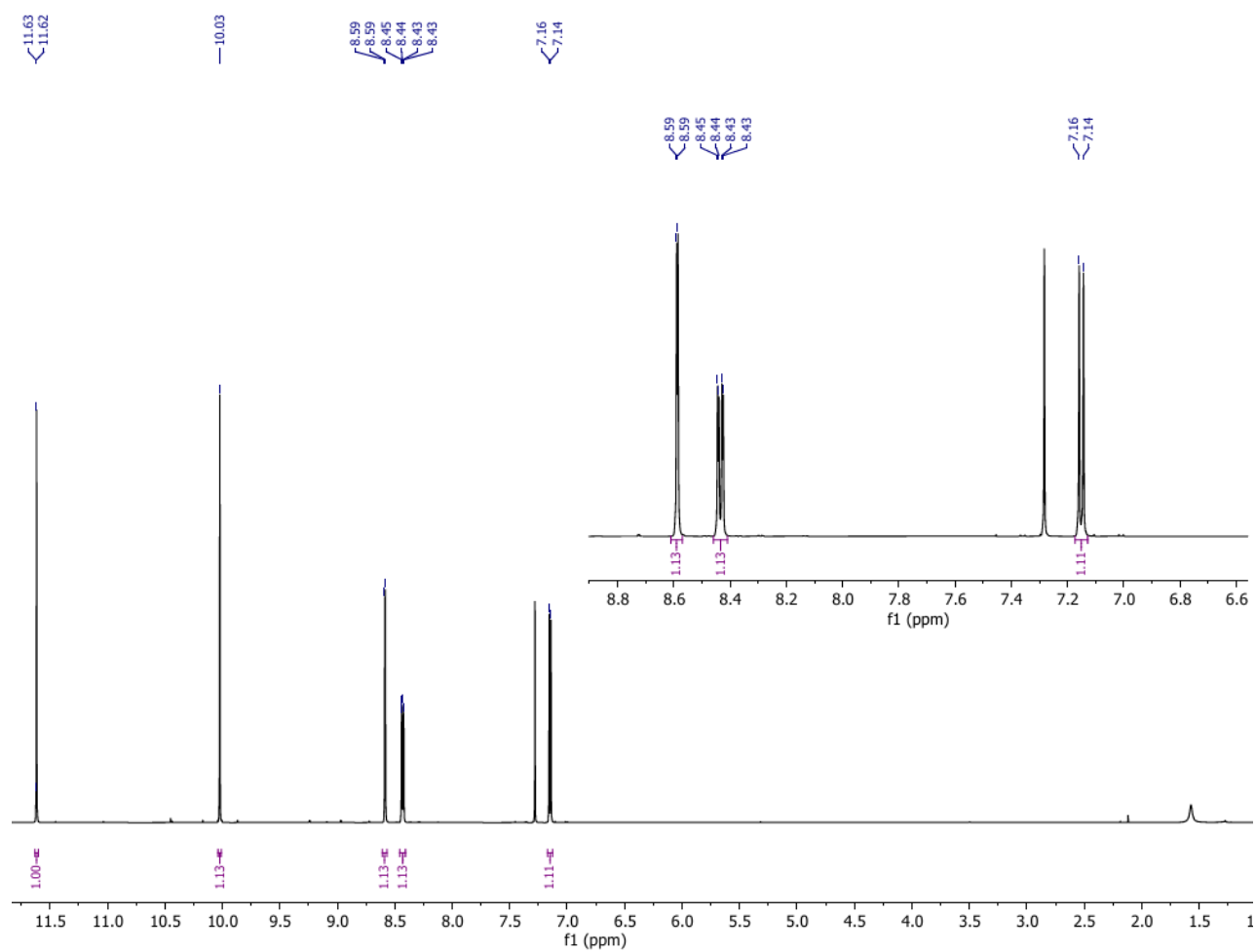


Figure S2. ^1H NMR of 4 (CDCl_3).

Compound 5a

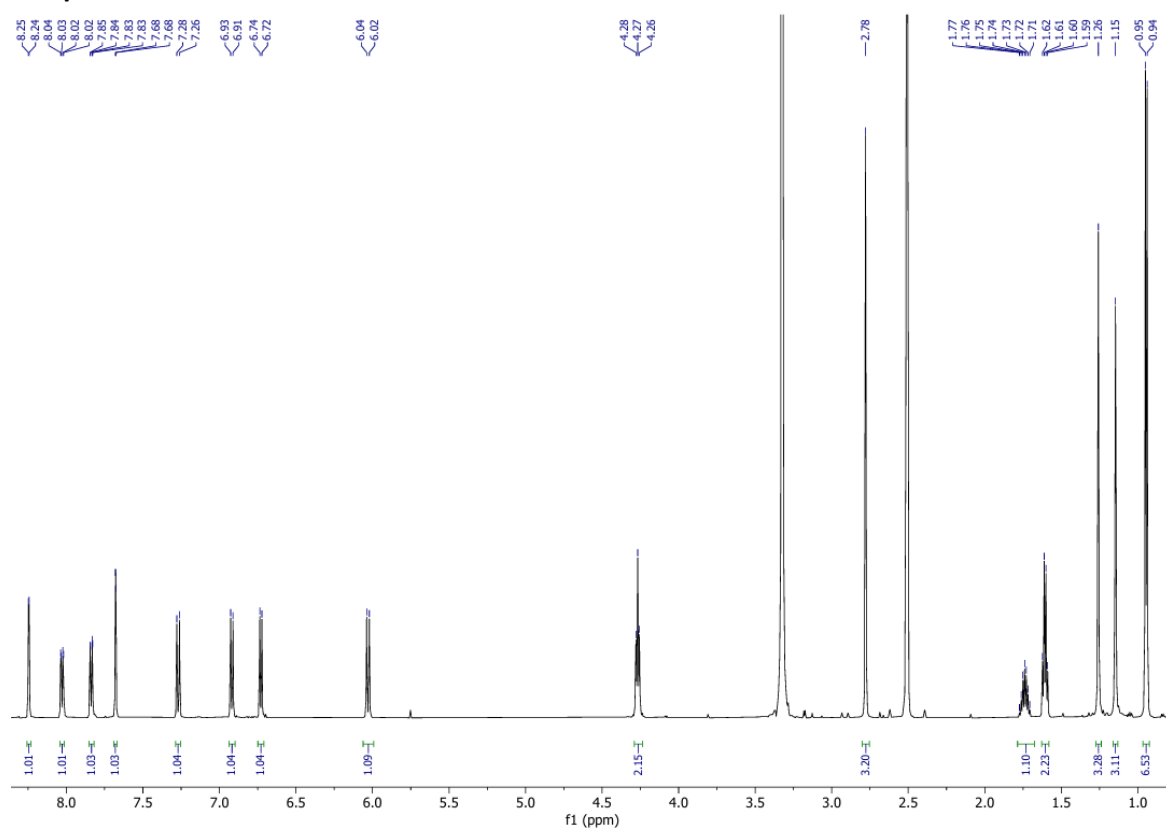


Figure S3. ¹H NMR of 5a (DMSO-d₆).

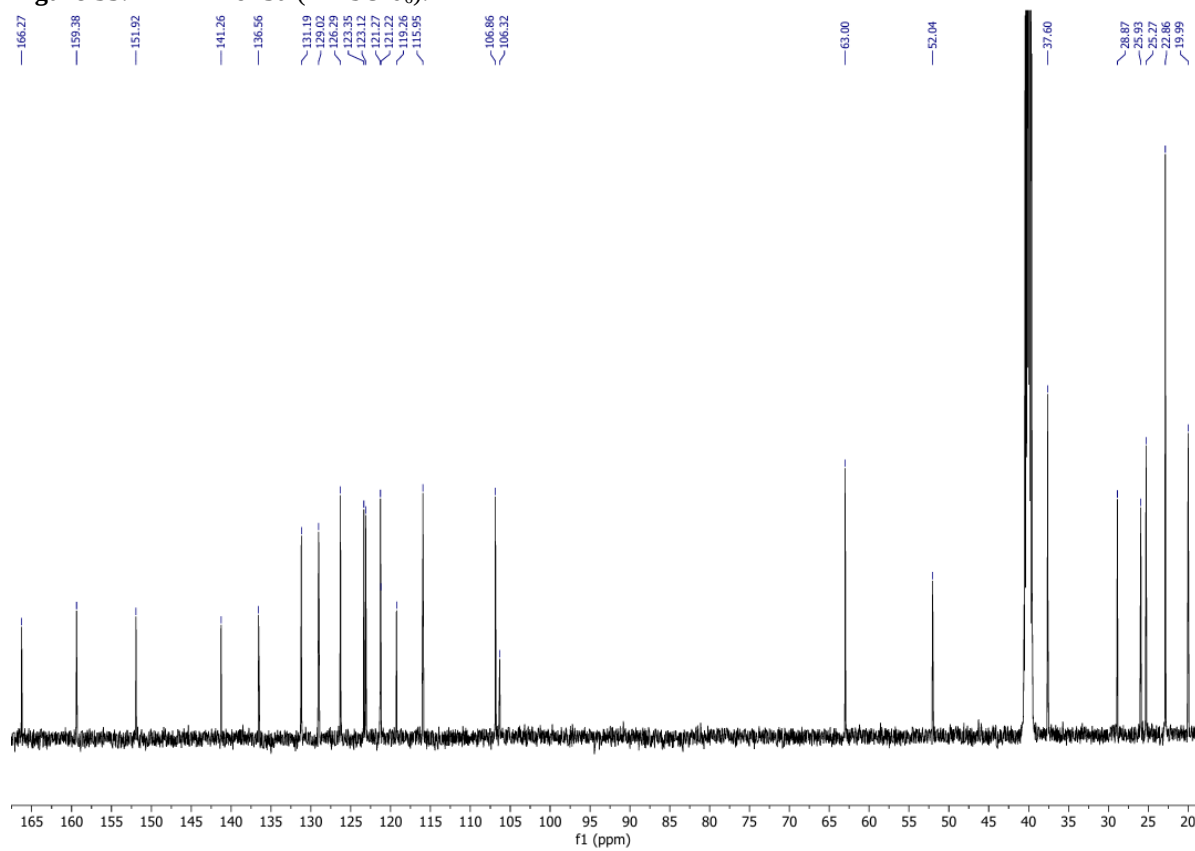


Figure S4. ¹³C NMR of 5a (DMSO-d₆).

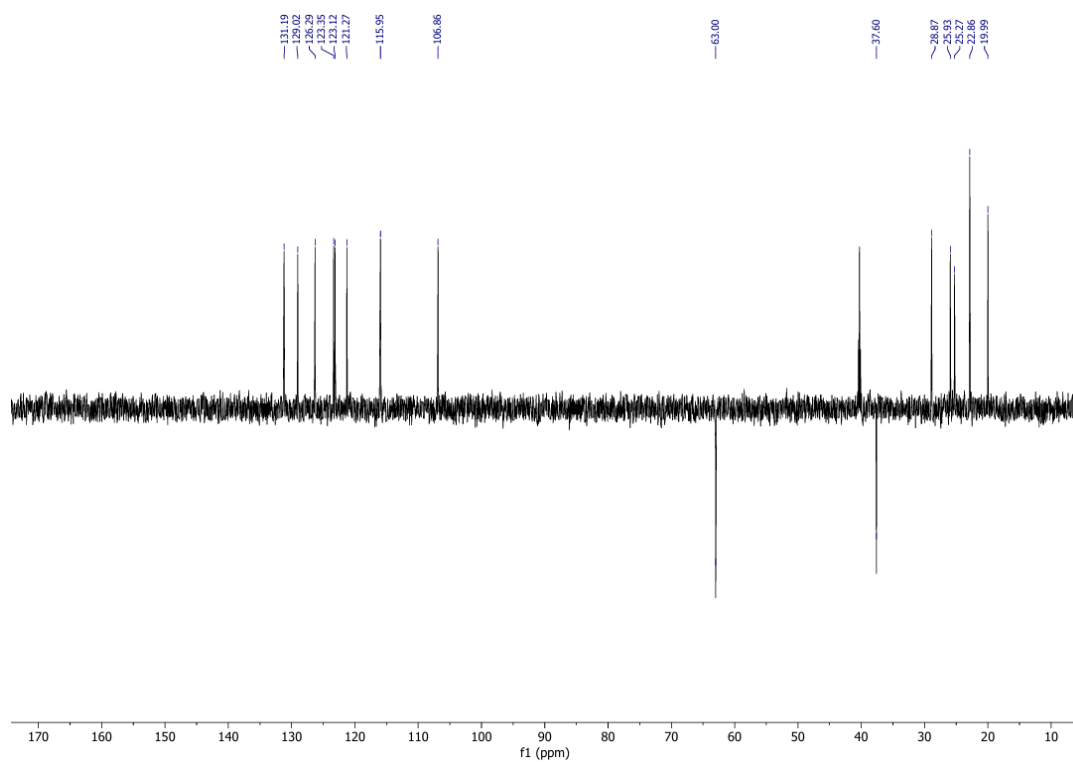


Figure S5. ^{13}C NMR (DEPT) of **5a** (DMSO-d_6).

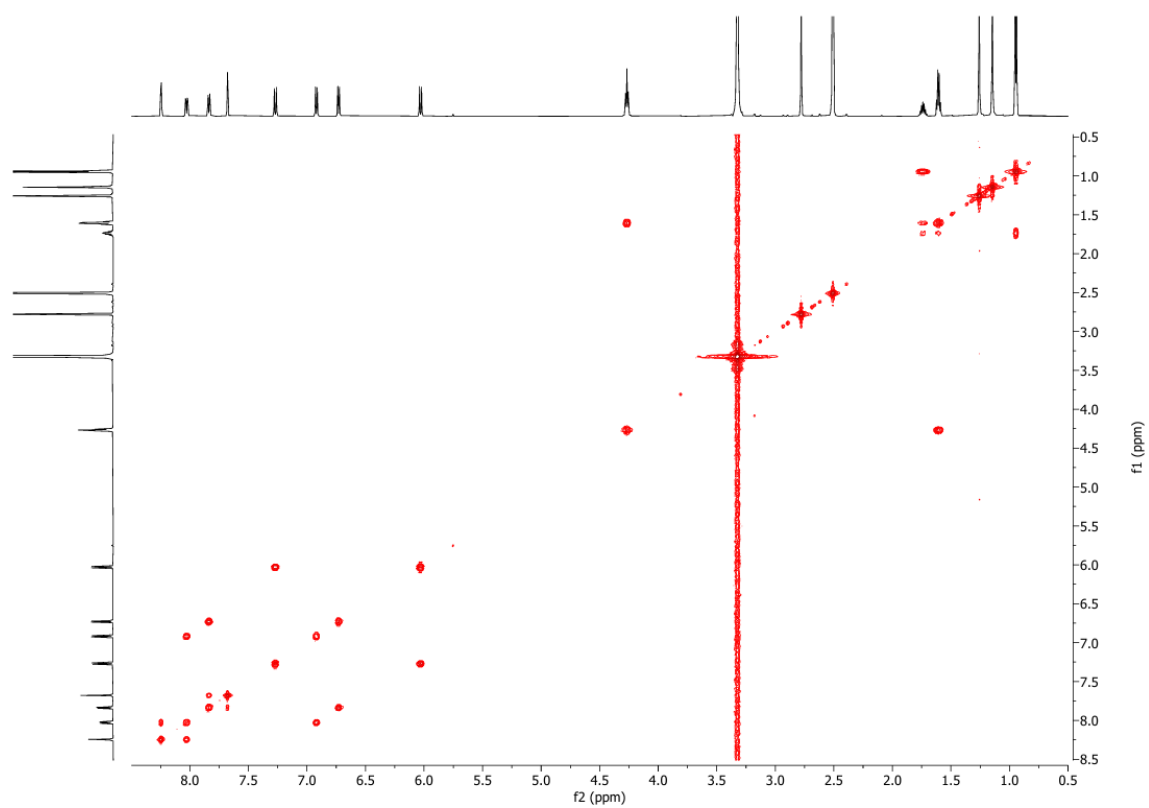


Figure S6. COSY of **5a** (DMSO-d_6).

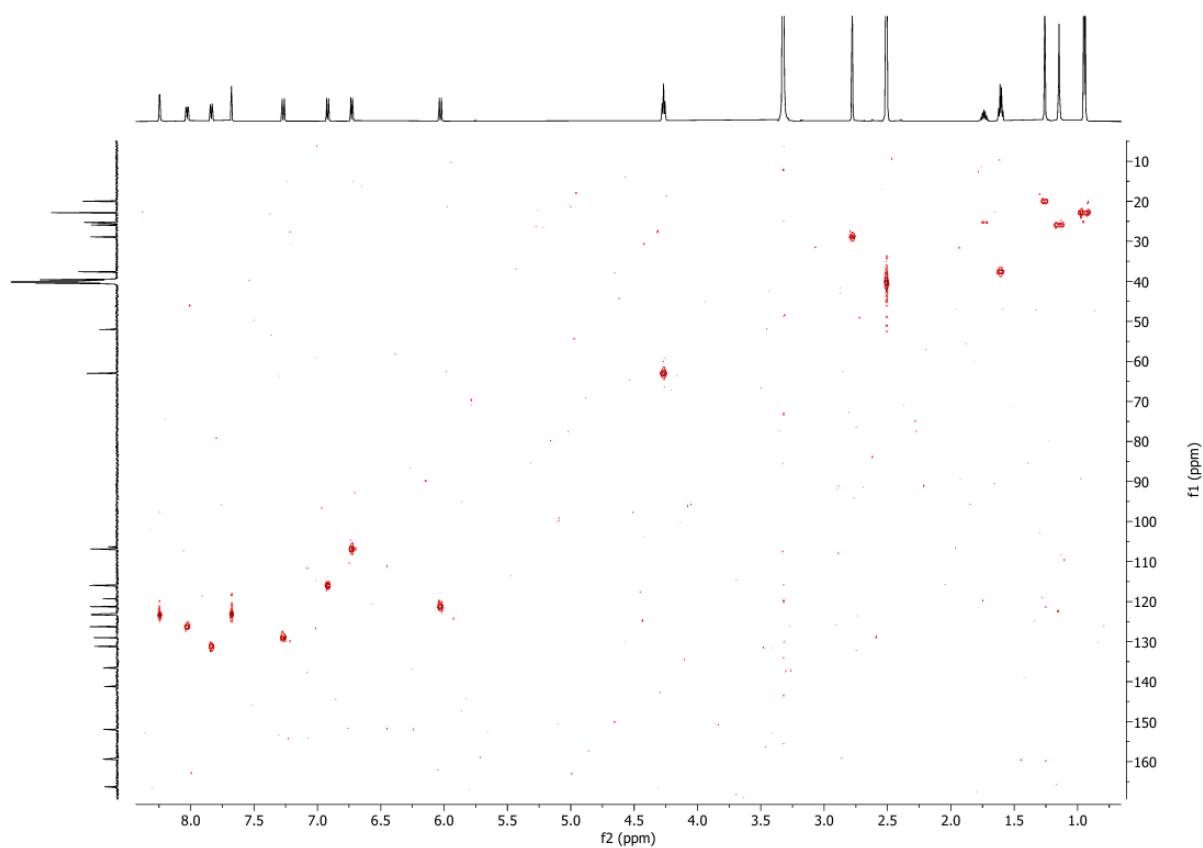


Figure S7. HSQC of **5a** (DMSO- d_6).

Compound 5b

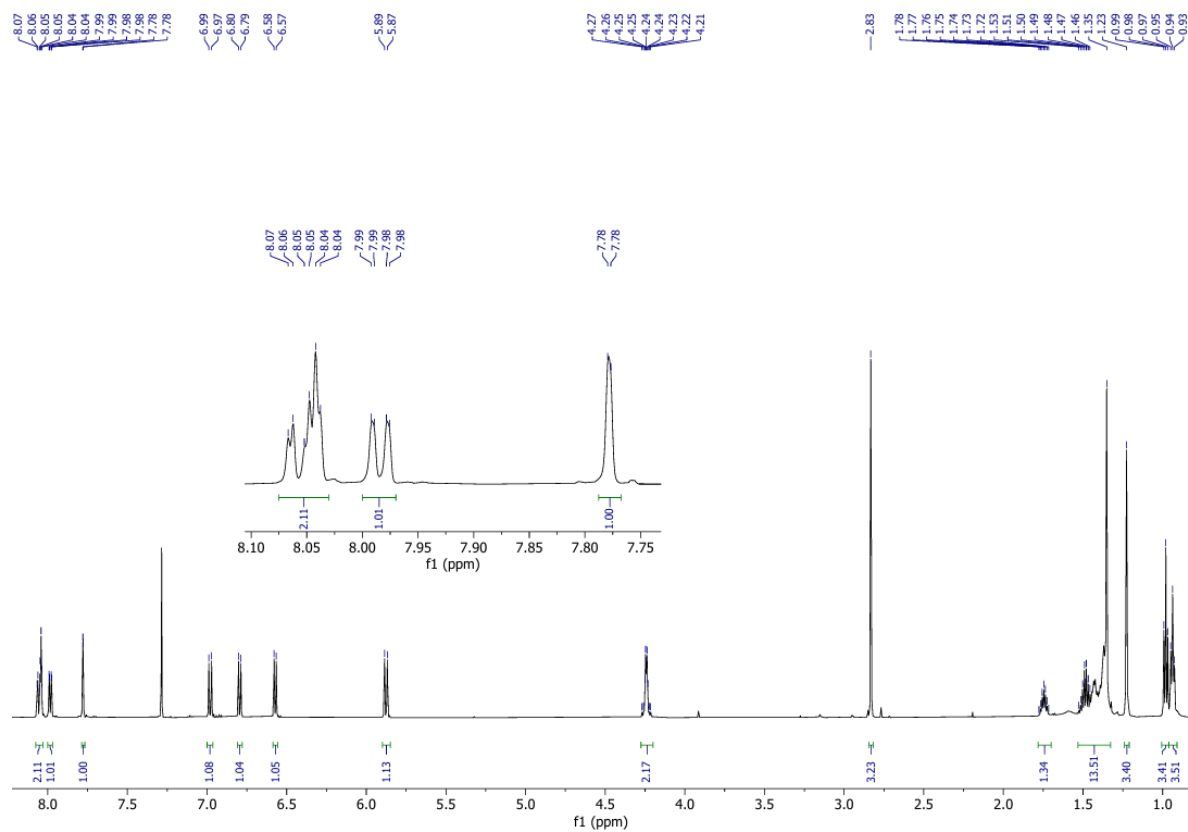


Figure S8. ^1H NMR of **5b** (CDCl_3).

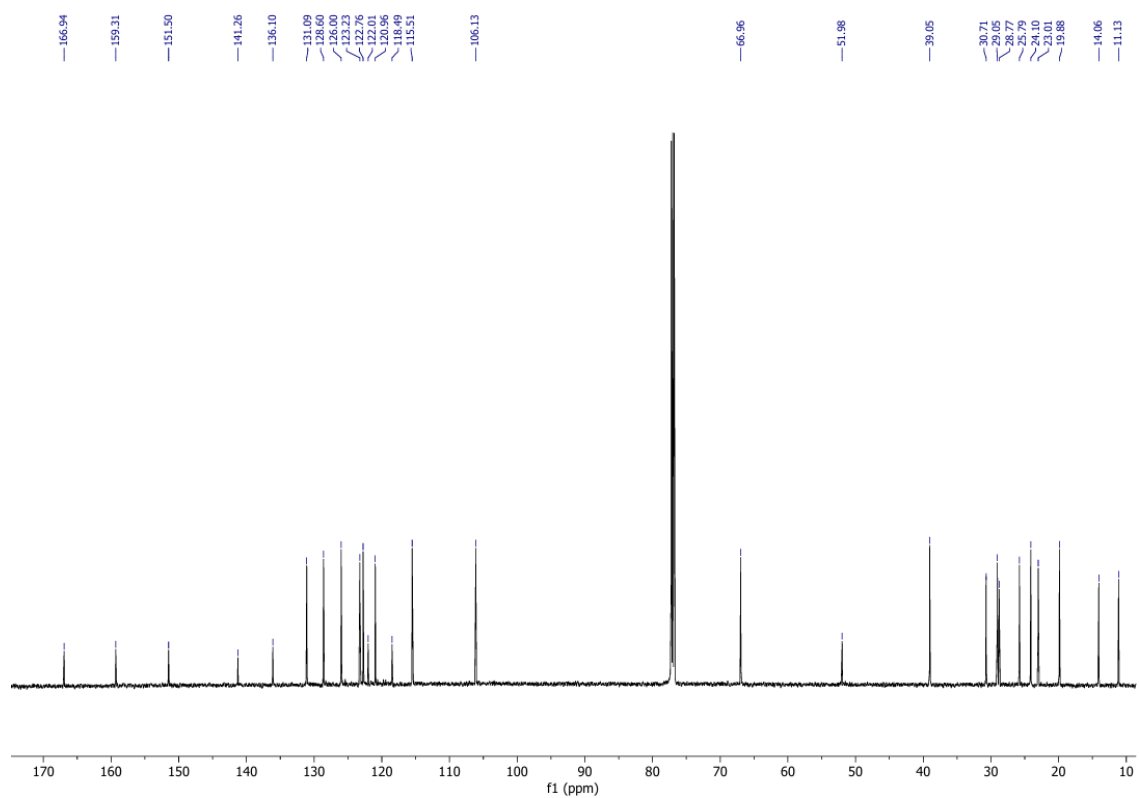


Figure S9 ^{13}C NMR of **5b** (CDCl_3).

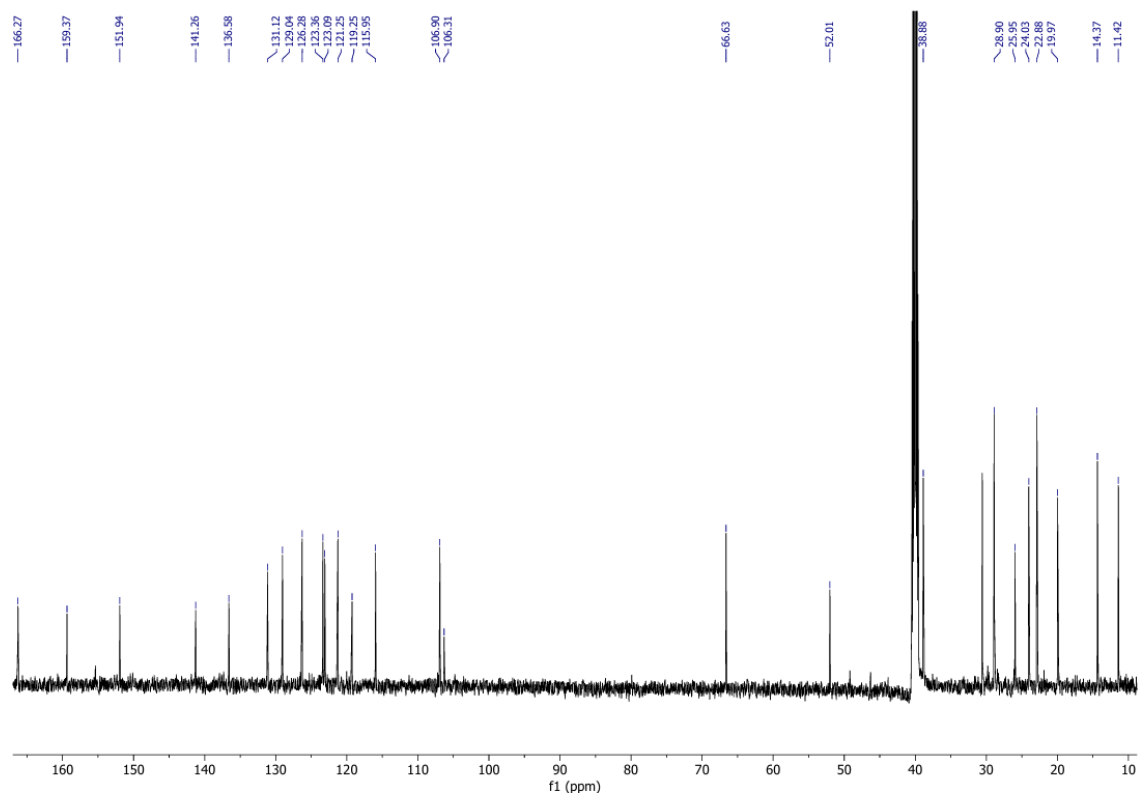


Figure S10. ^{13}C NMR of **5b** (DMSO-d_6).

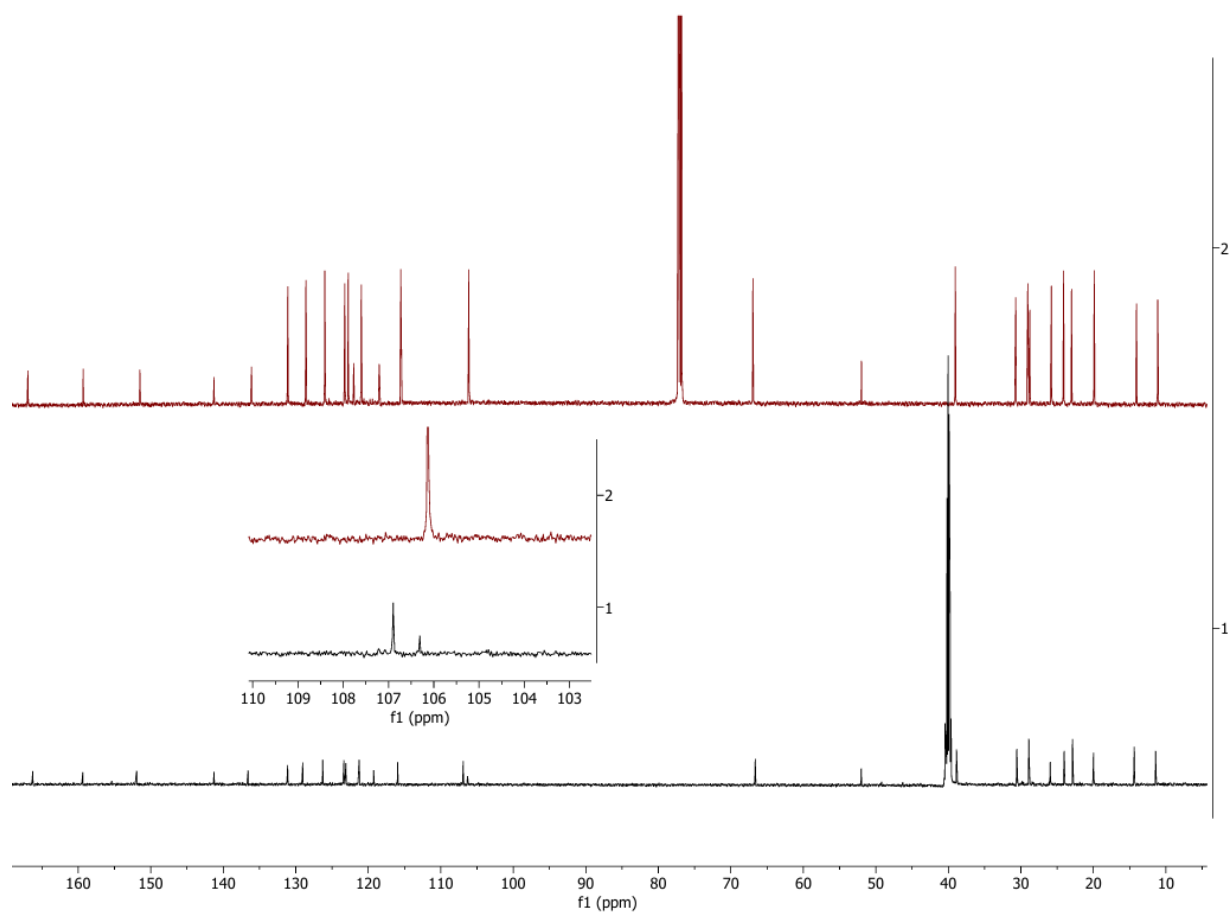


Figure S11. Comparative ^{13}C NMR of **5b** in CDCl_3 (top) and DMSO-d_6 (bottom).

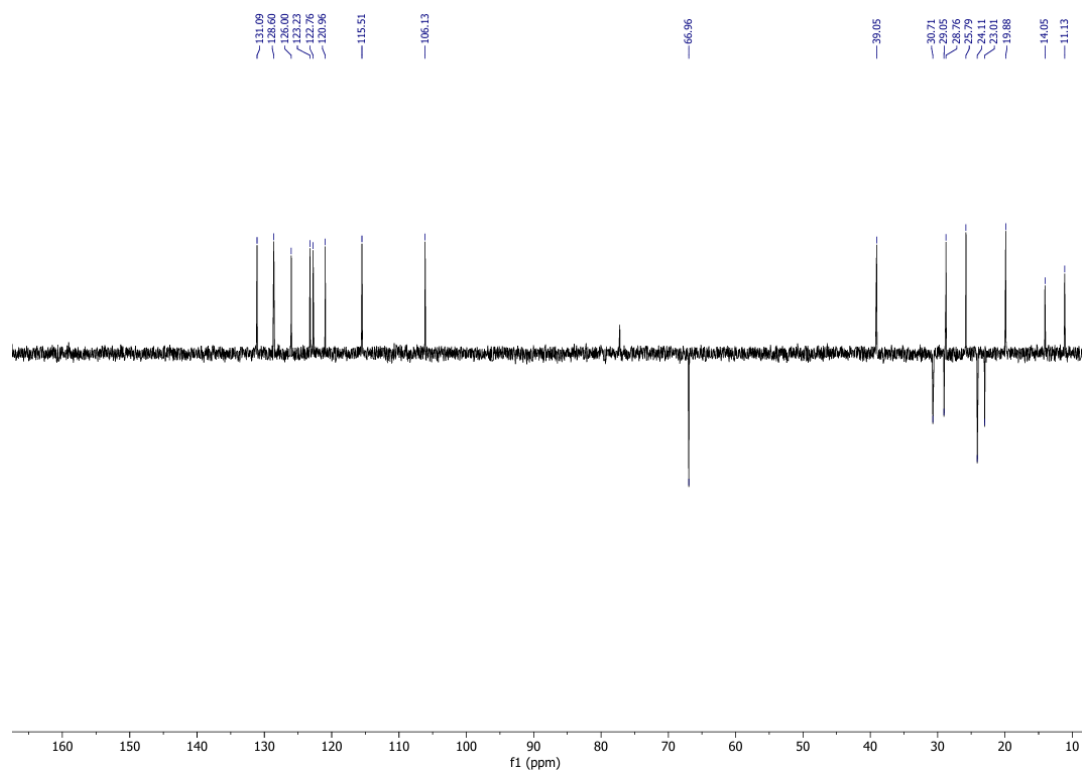


Figure S12. ^{13}C NMR (DEPT) of compound **5b** (CDCl_3).

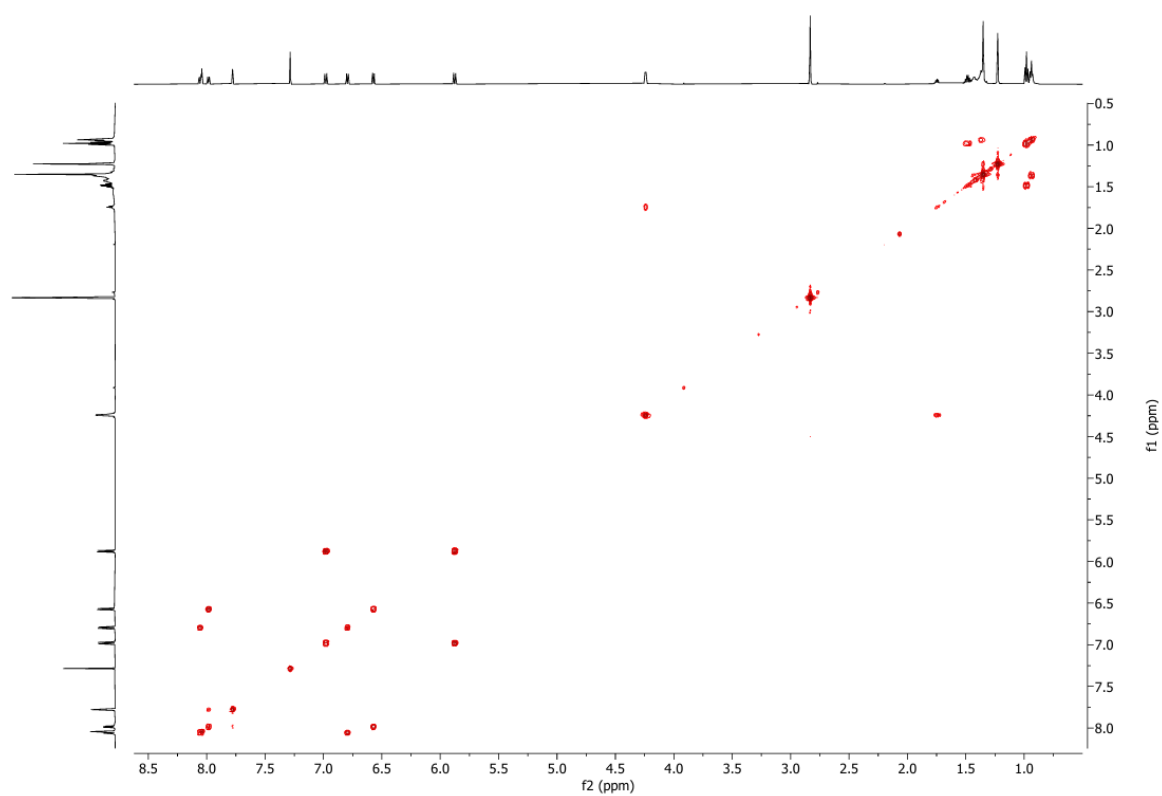


Figure S13. COSY of **5b** (CDCl₃).

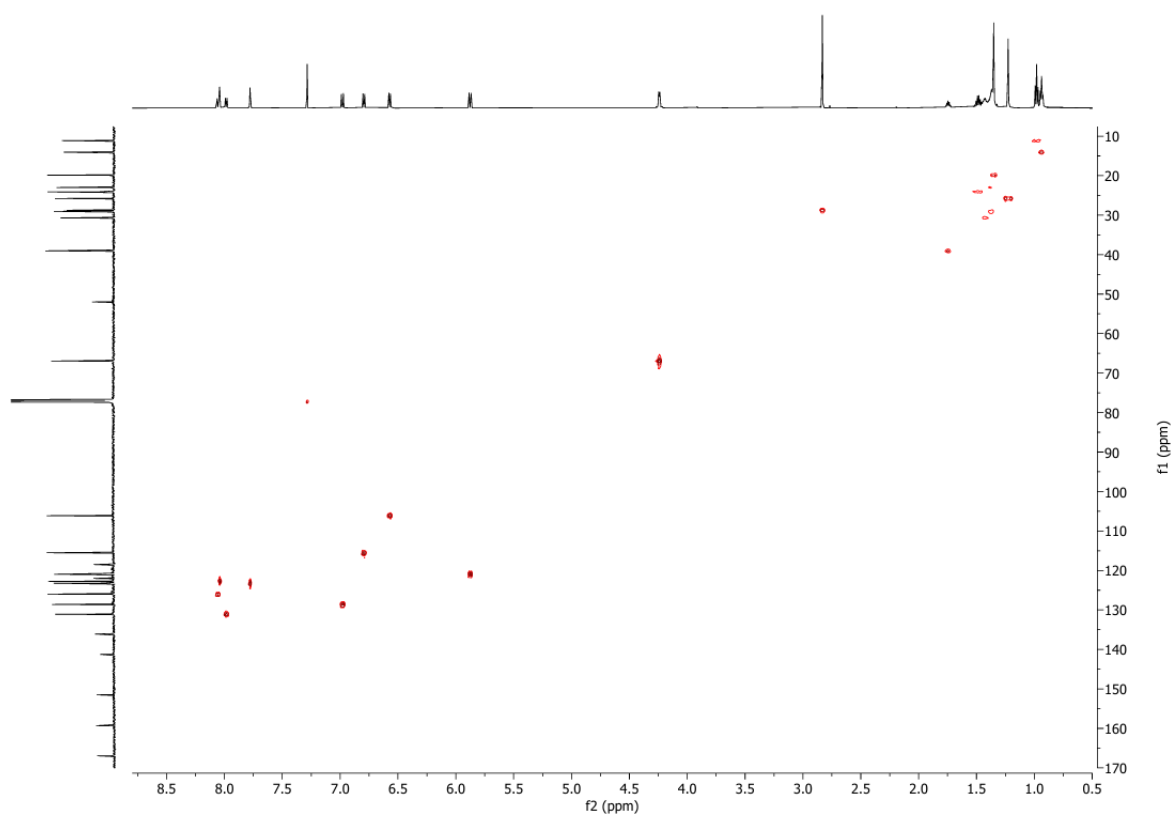


Figure S14. HSQC of **5b** (CDCl₃).

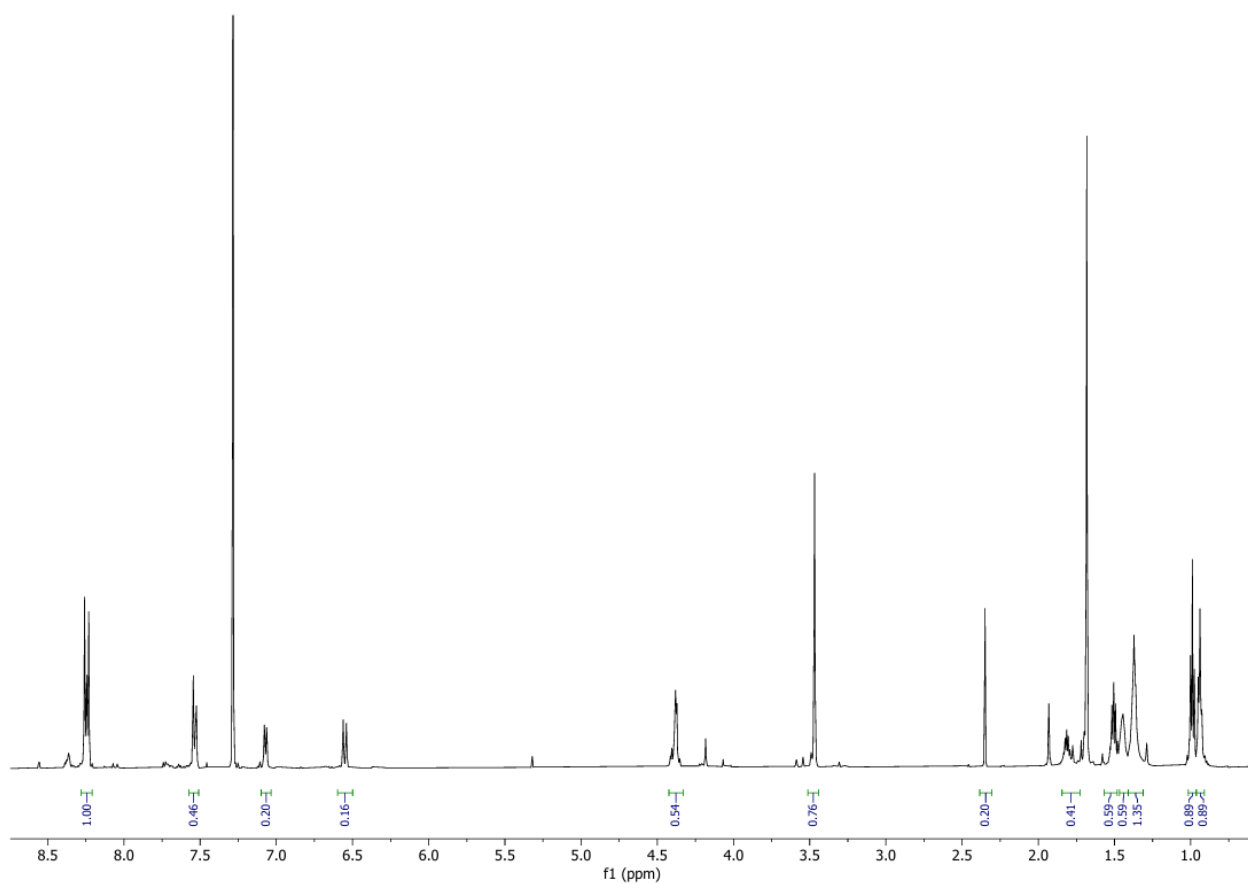


Figure S15. ^1H NMR of MC form of **5b** in the presence of HCl (CDCl_3).

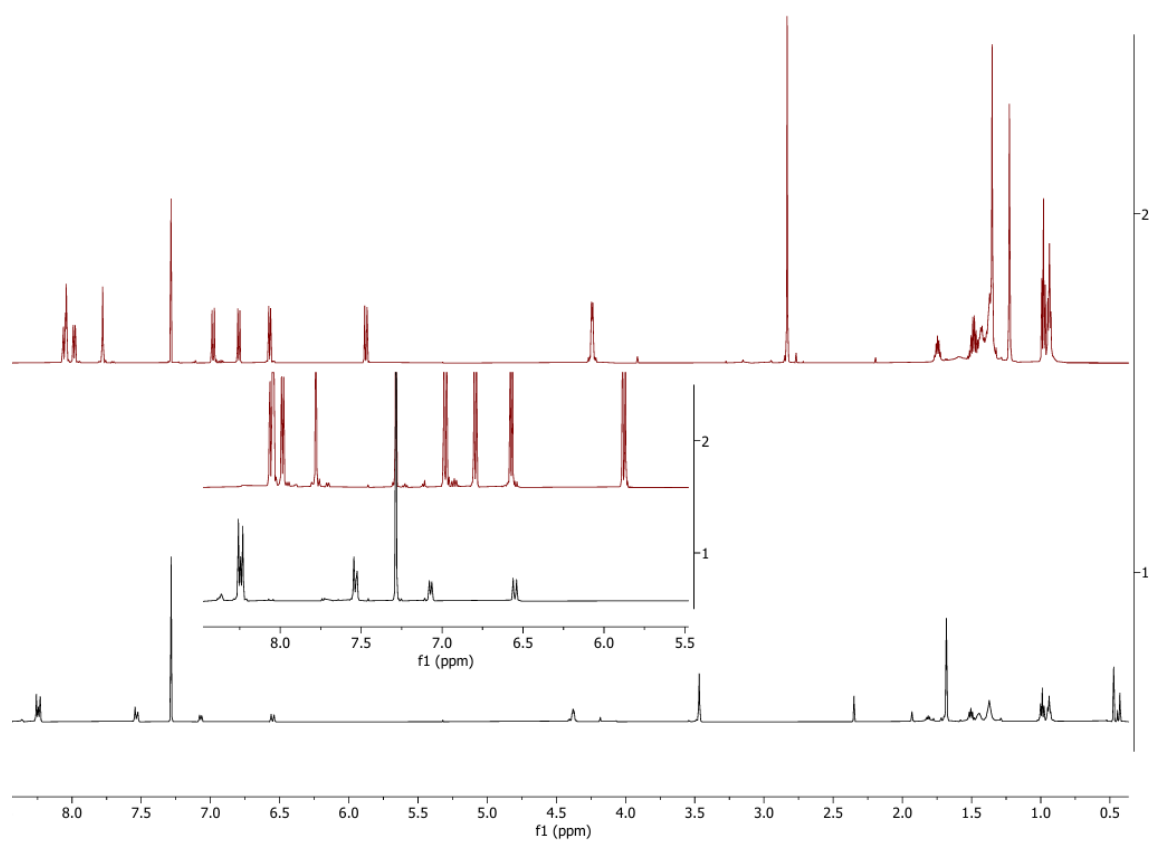


Figure S16. Comparative ^1H NMR of SP form(top) and MC form (bottom) of **5b** (CDCl_3).

Compound 5c

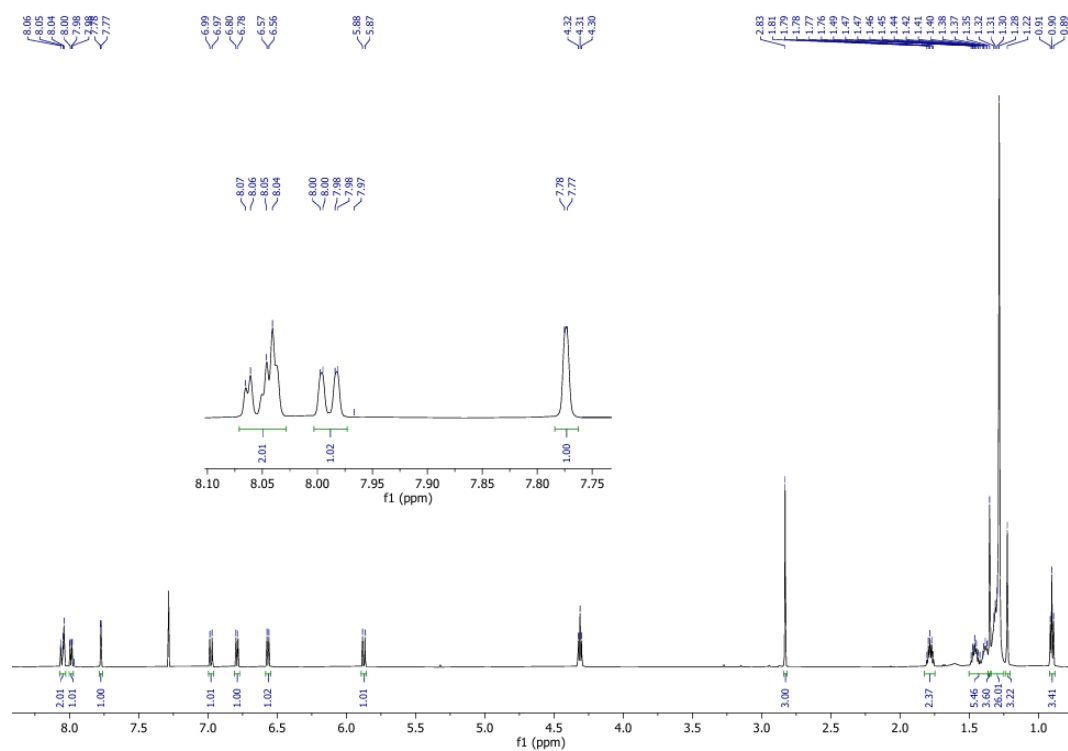


Figure S17. ¹H NMR of 5c (CDCl₃).

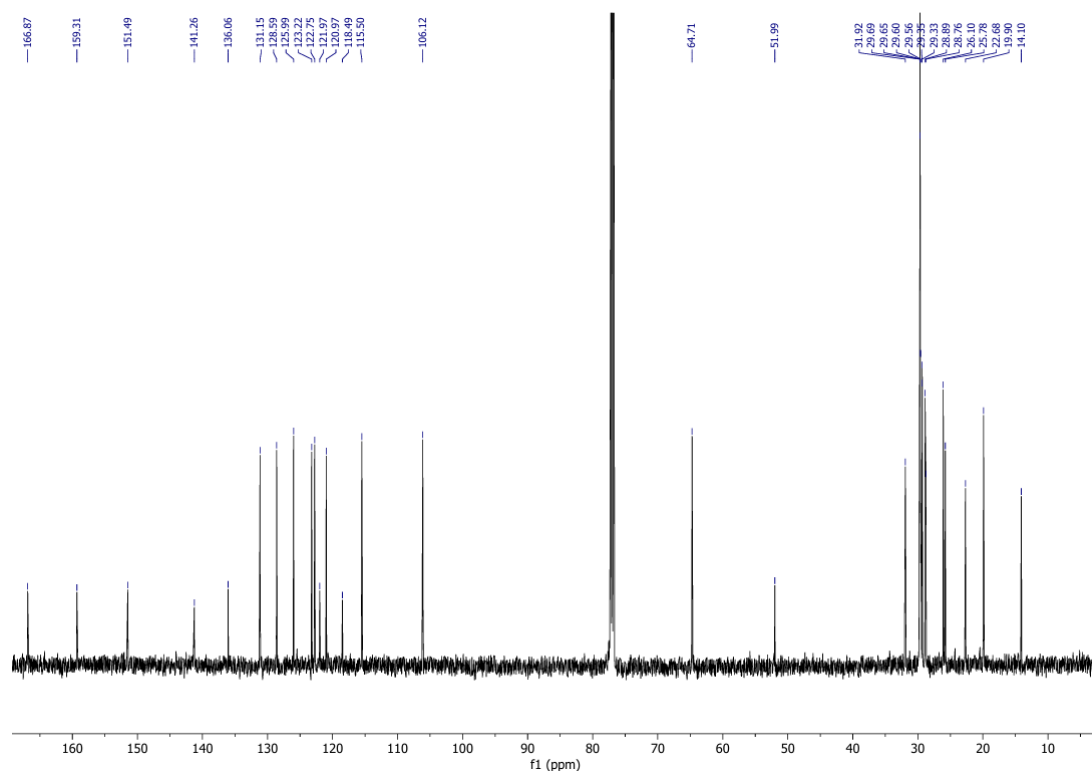


Figure S18. ¹³C NMR of 5c (CDCl₃).

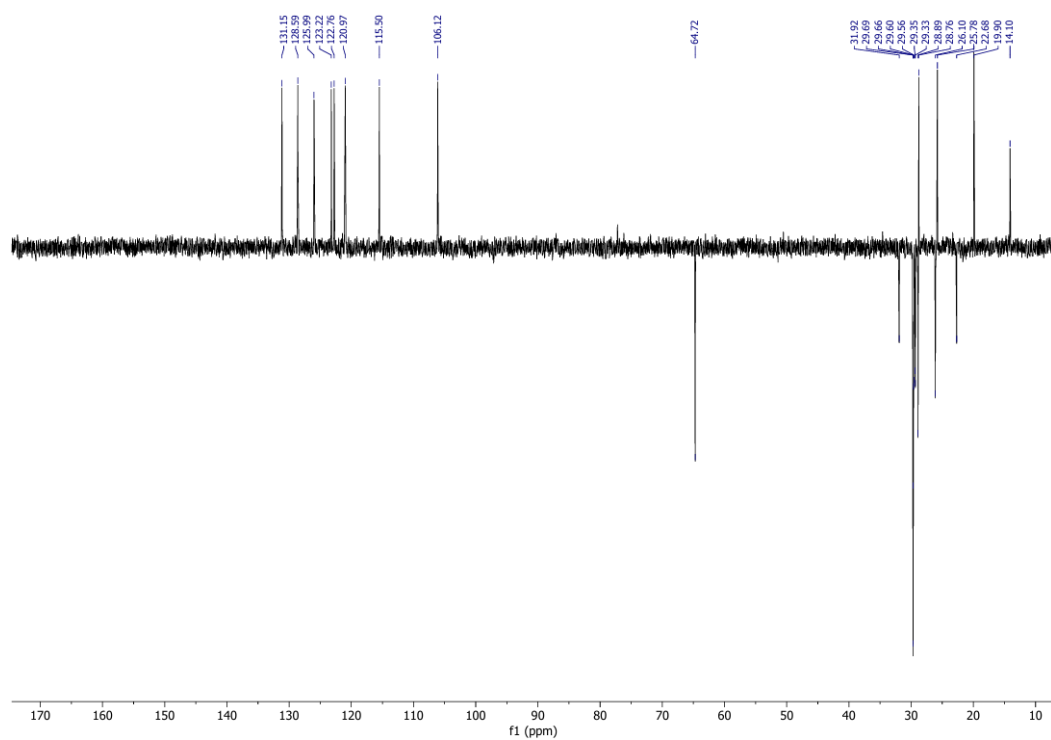


Figure S19. ^{13}C NMR (DEPT) of **5c** (CDCl_3).

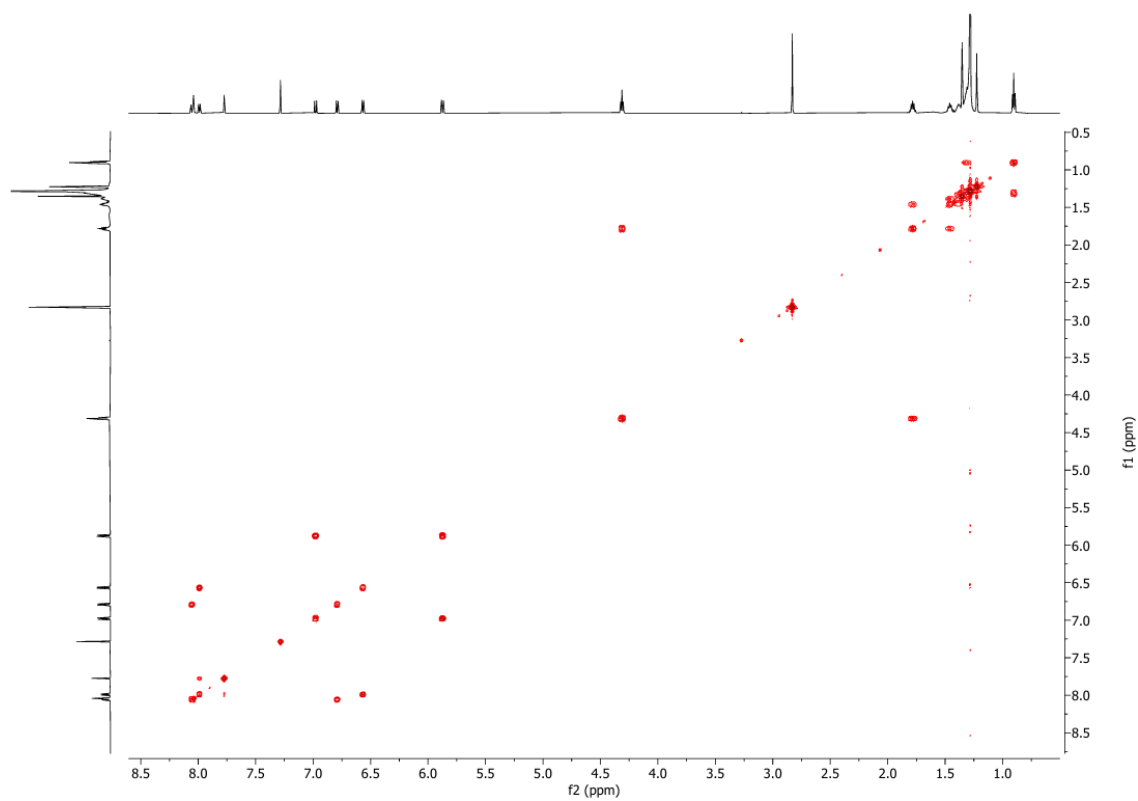


Figure S20. COSY of **5c** (CDCl_3).

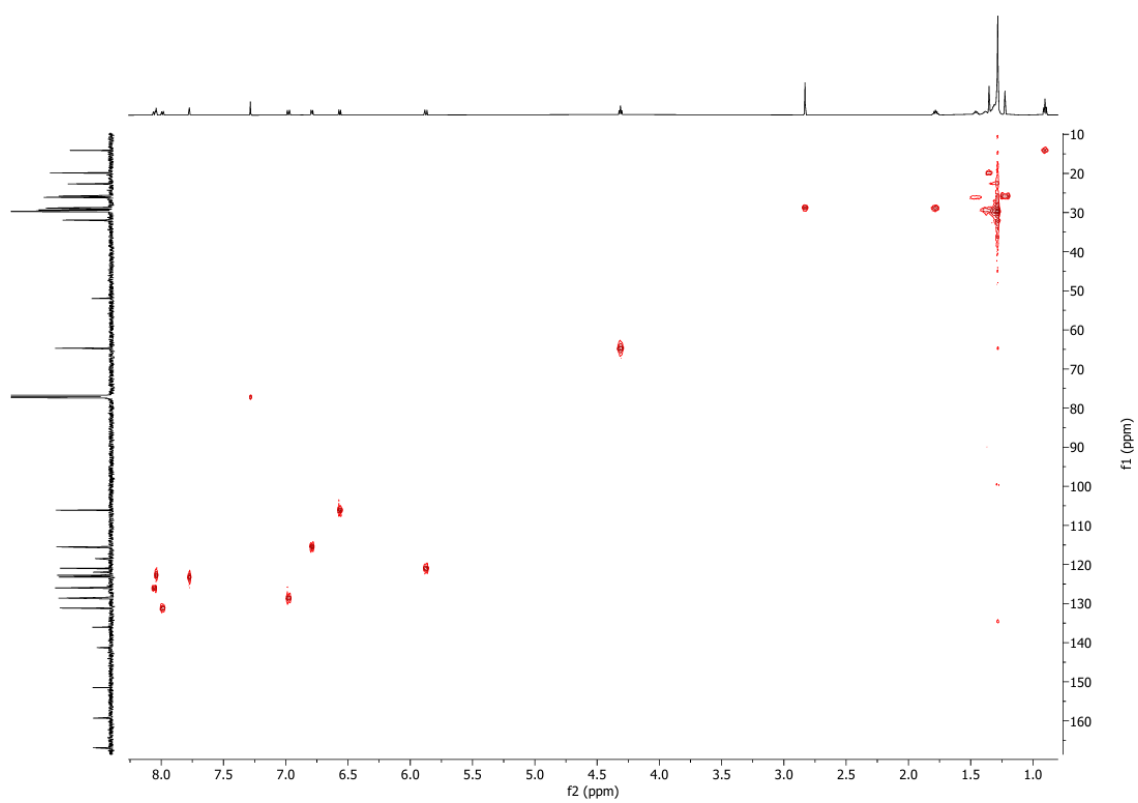


Figure S21. HSQC of **5c** (CDCl₃).

HRMS spectra of 5a-c

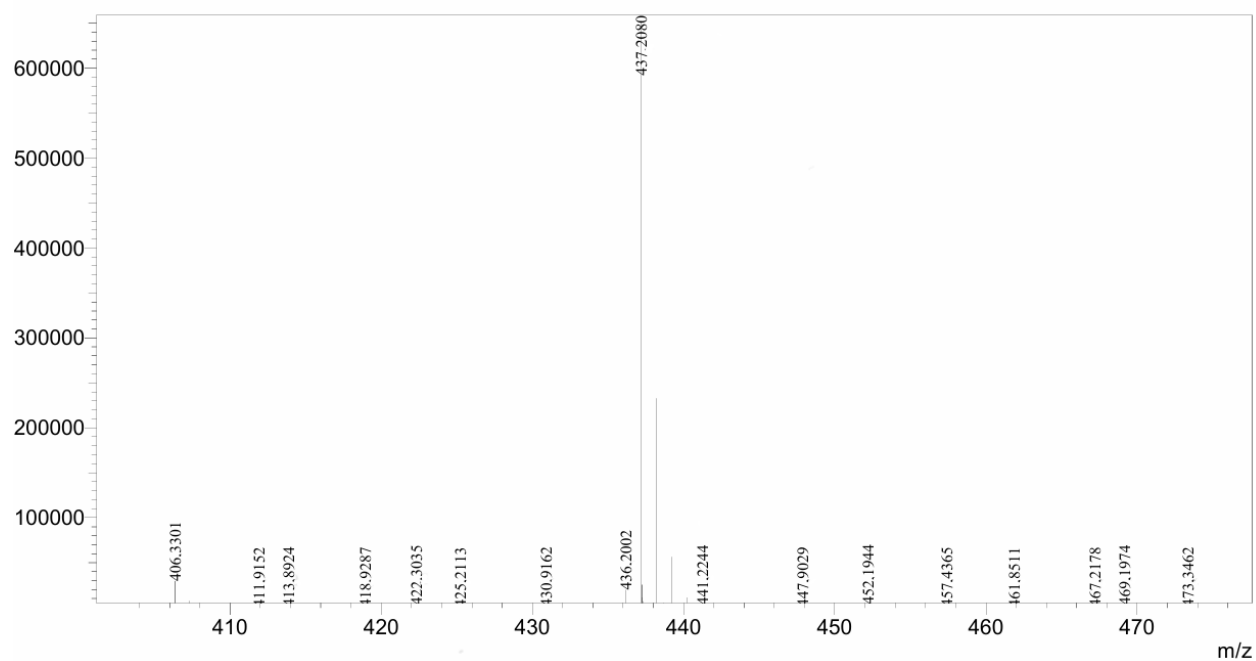


Figure S22. HRMS spectrum of 5a.

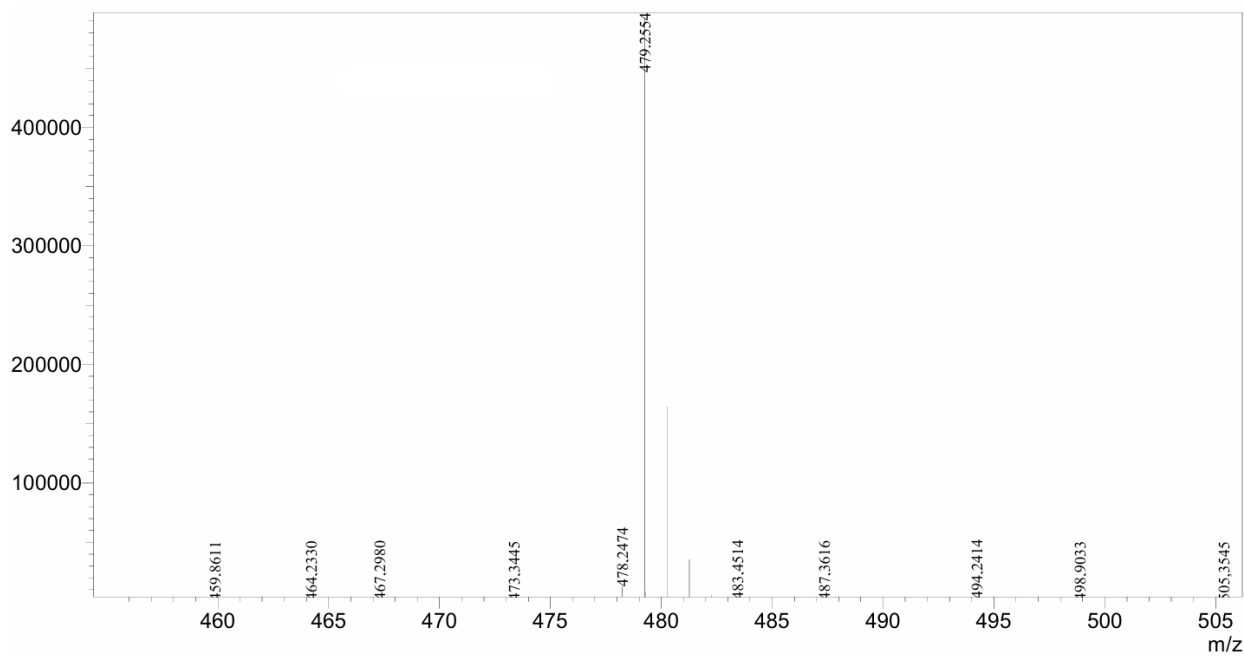


Figure S23. HRMS spectrum of 5b.

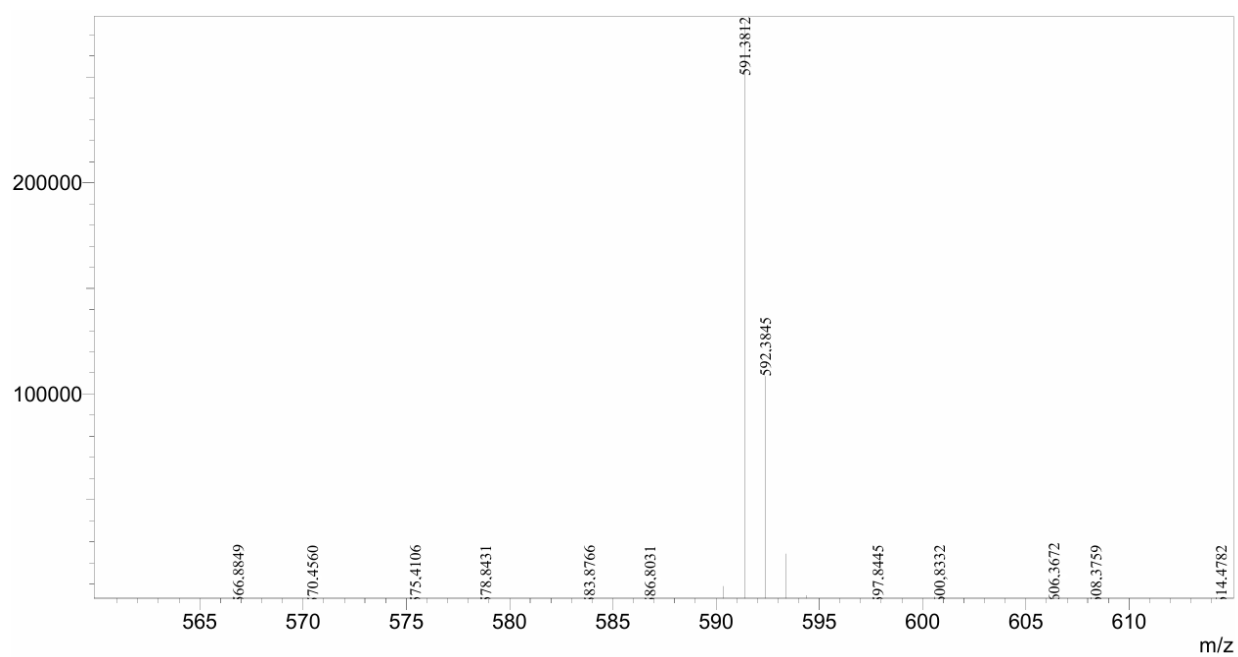


Figure S24. HRMS spectrum of **5c**.

UV-vis spectra of 5a-c

Sample preparation

Of each new spiropyrans, a stock solution was prepared in CHCl_3 (dry, 10 ml, $3.00 \text{ mmol dm}^{-3}$). A specified volume (100 μl) was then out of this solution and diluted to give a final volume of 3.00 ml to obtain desired concentration ($1 \times 10^{-4} \text{ mol dm}^{-3}$).

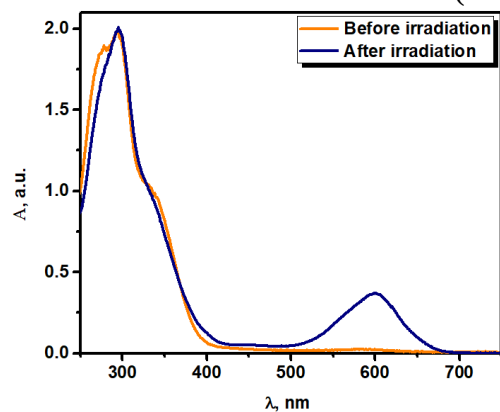


Figure S25. UV-vis spectra of 5a.

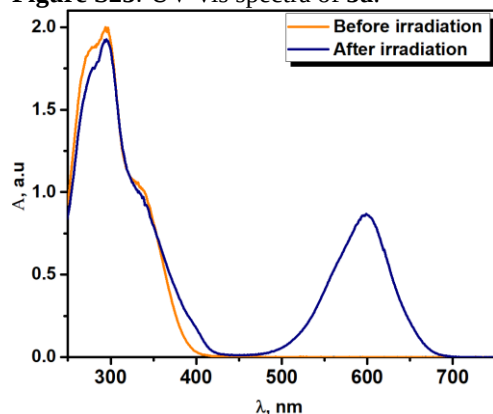


Figure S26. UV-vis spectra of 5b.

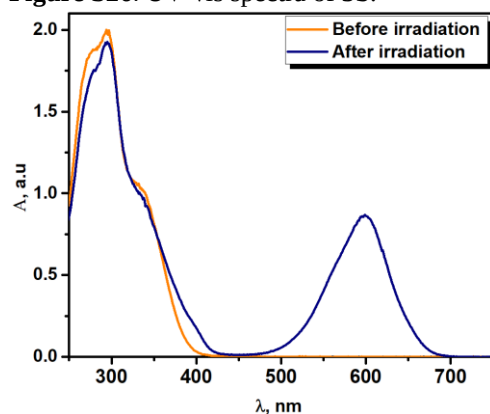


Figure S27. UV-vis spectra of 5c.

UV-vis spectra of **5b** upon cyclic irradiation

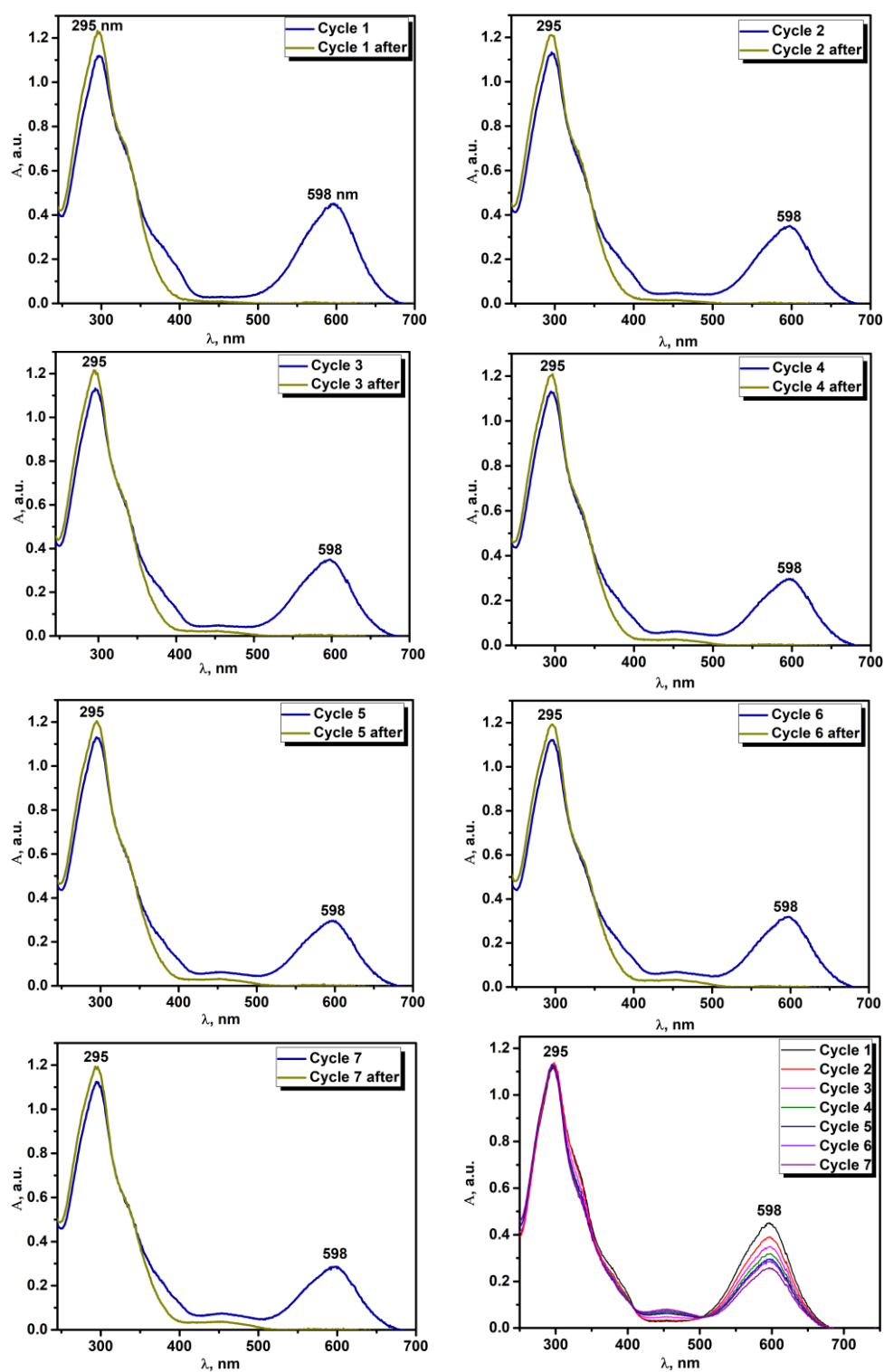


Figure S28. Set of UV-vis spectra of **5b** after cycled switching.

UV-vis spectra of film, containing 5b, upon cyclic irradiation

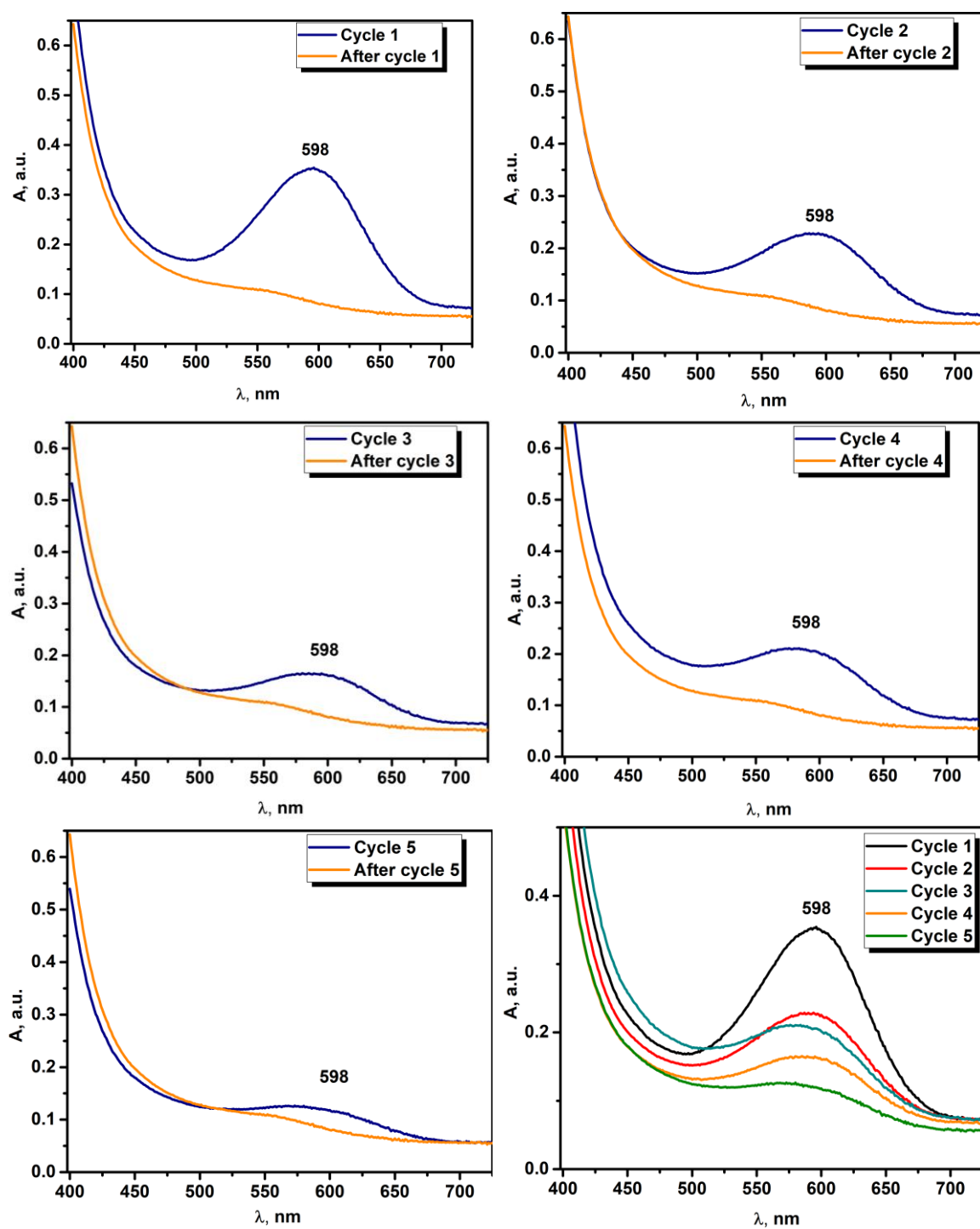


Figure S29 Set of UV-vis spectra of **5b** film after cycled switching.

FTIR spectra of 5a-c and functional material

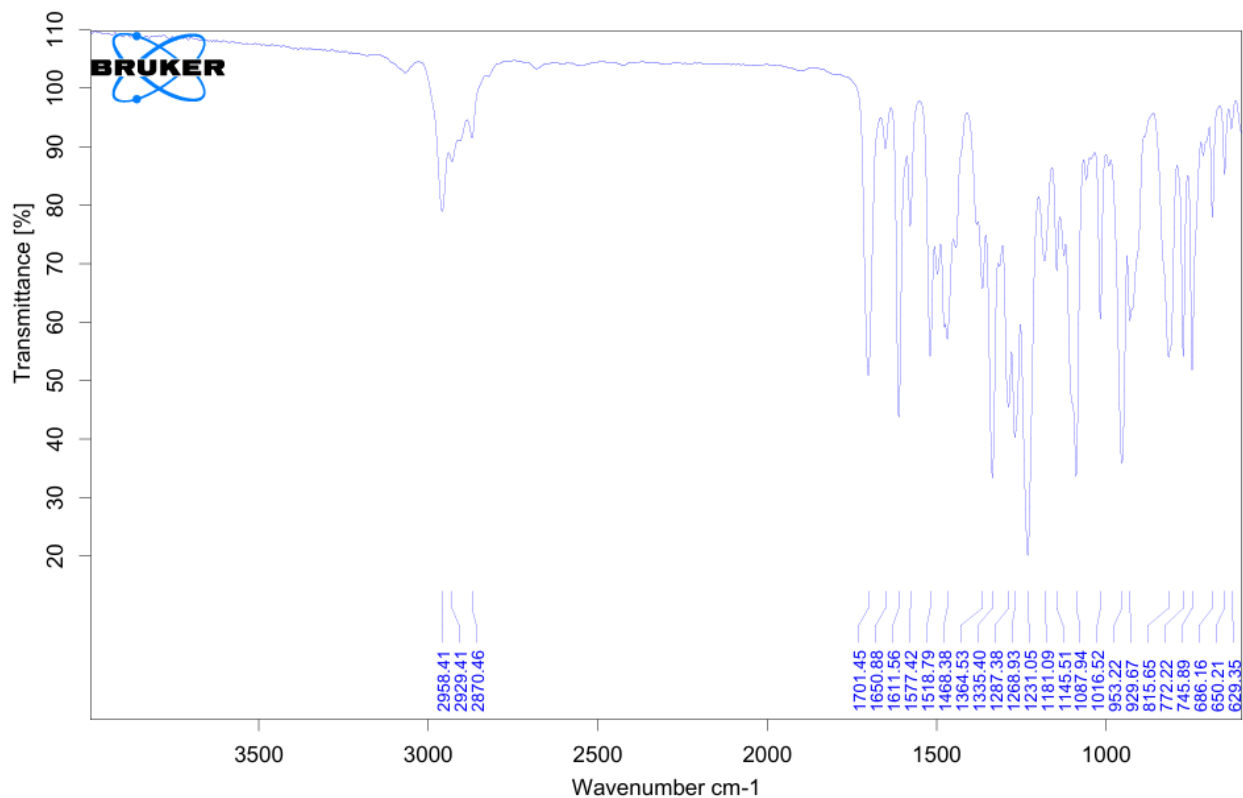


Figure S30. FTIR spectra of 5a.

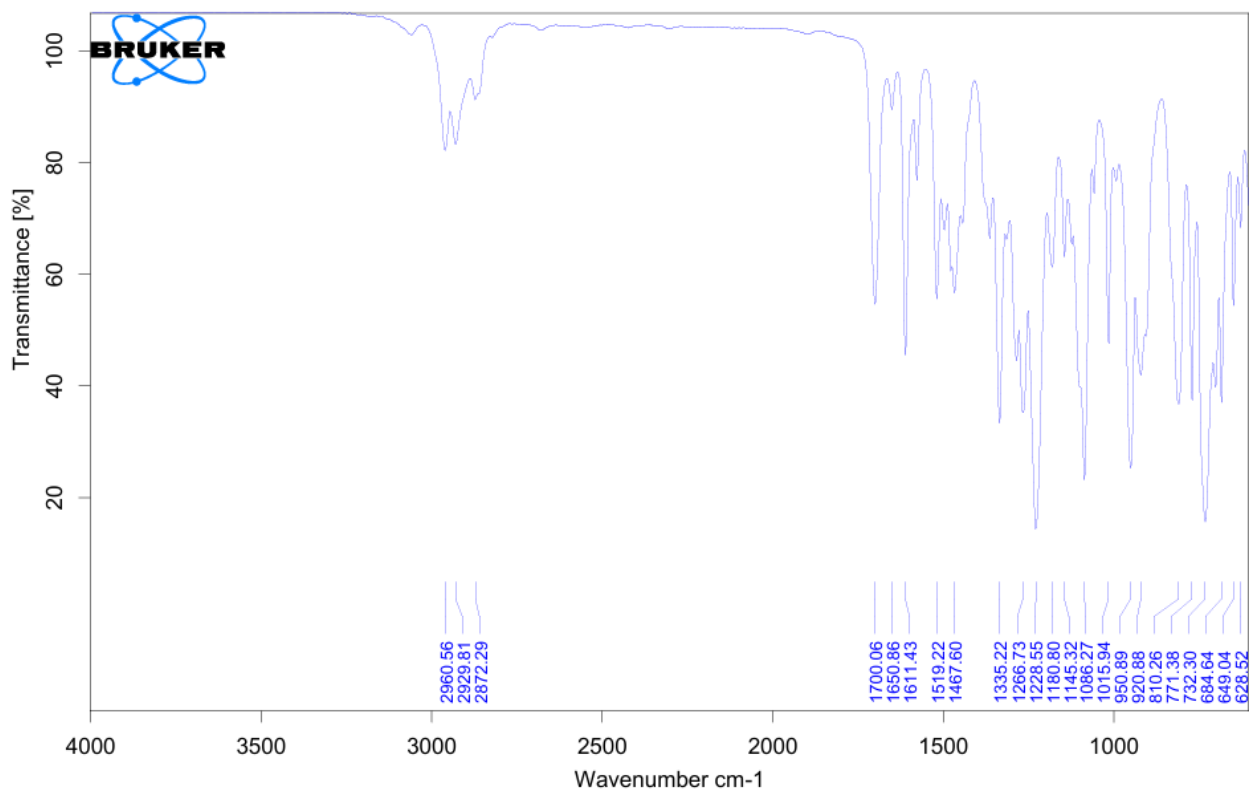


Figure S31. FTIR spectra of compound 5b.

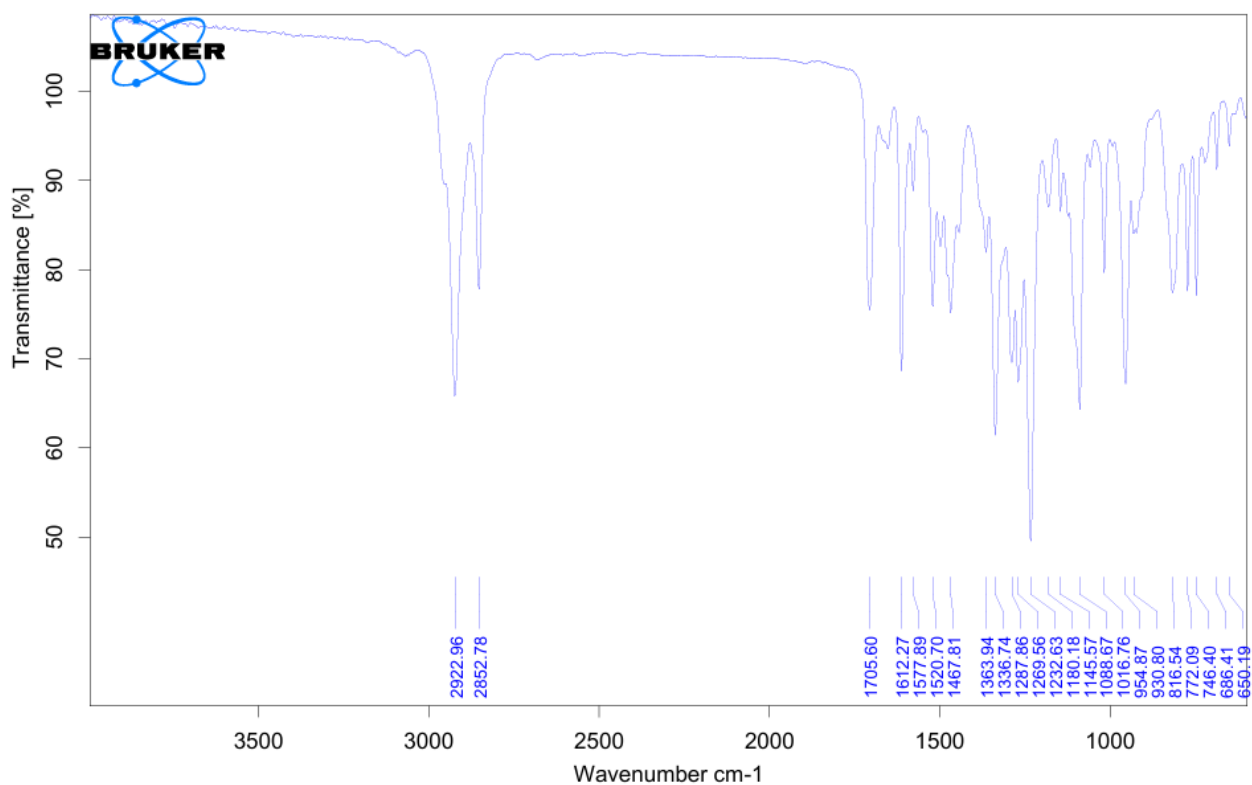


Figure S32. FTIR spectra of **5c**.

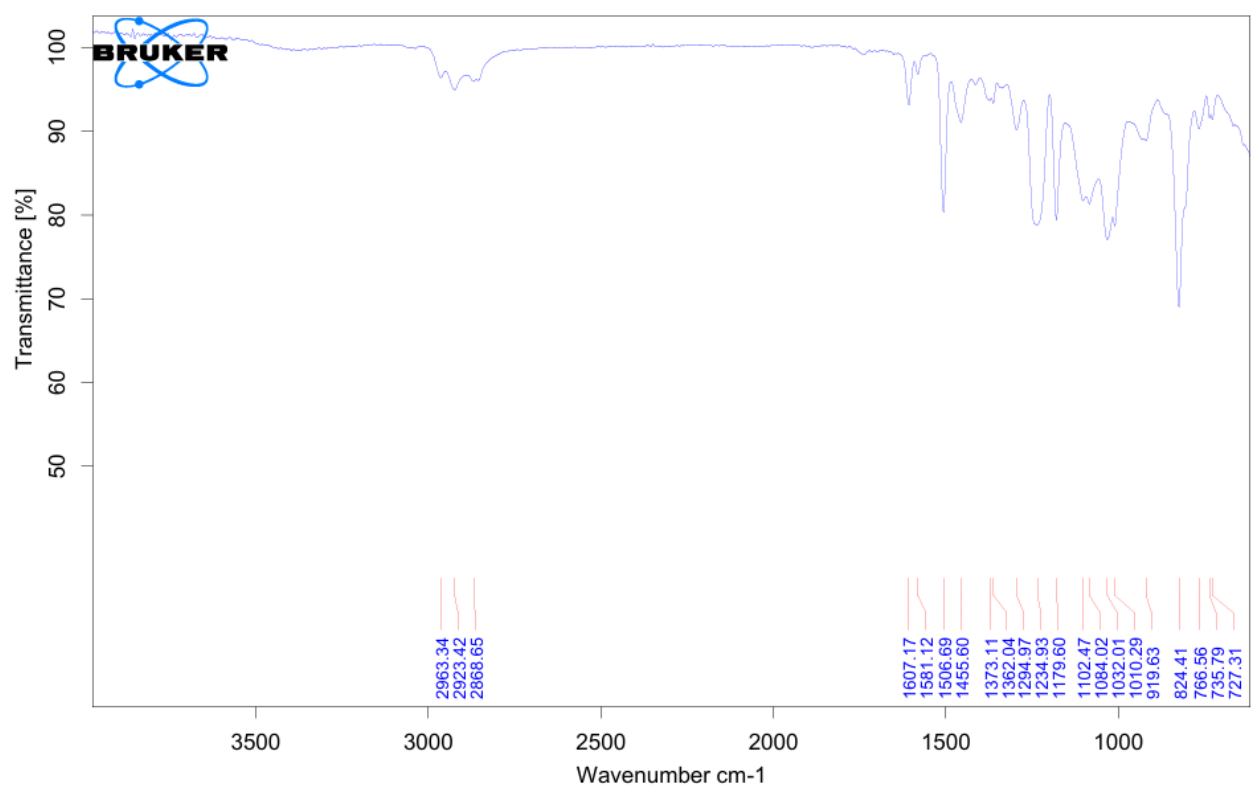


Figure S33. FTIR spectra of polymer film without **5b**.

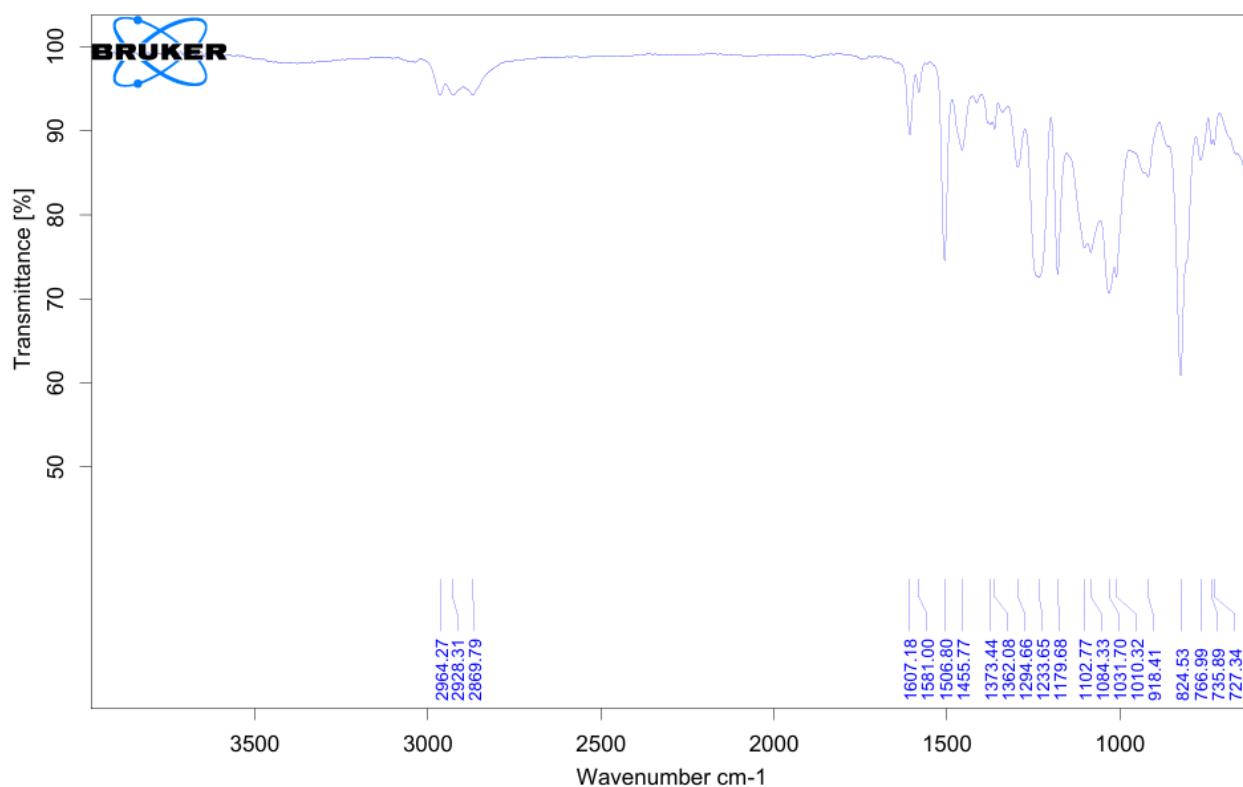


Figure S34. IR spectra of polymer film with **5b**.

References

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