

Supporting Information

Synthesis and Ring-Opening Metathesis Polymerisation of *o*-Alkoxy Benzothiadiazole Paracyclophane-1,9-dienes

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S1 General experimental details for synthesis

Unless otherwise stated, all reagents were purchased from commercial suppliers. All other chemicals were used without further purification. Analytical TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F254, Merk, Germany). Flash column chromatography was performed with silica gel (60 Å, 230-400 mesh). All reactions were carried out using standard Schlenk techniques under argon unless otherwise stated. Deoxygenated solvents were prepared either by purging with argon or by freeze-pump-thaw cycles (minimum of three times).

Nuclear magnetic resonance (NMR) spectra were obtained on Bruker spectrometers operating at either 400 MHz or 500 MHz for ^1H NMR spectroscopy. Chemical shifts are reported in part per million (ppm) relative to the indicated residual solvent (^1H NMR spectroscopy; 7.23 ppm for chloroform-*d* and 5.23 ppm for dichloromethane-*d*₂). The following abbreviations are used to indicate the multiplicity of the signals: s = singlet, d = doublet, m = multiplet, brm = broad multiplet. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) were carried out using a Shimadzu Biotech AXIMA Confidence MALDI mass spectrometer in linear (positive) mode. Calibration was conducted against poly(propylene glycol) ($M_n = 4.0 \text{ kg mol}^{-1}$) or Polymer Factory SpheriCal[®] MALDI-TOF-MS calibration standards (series of four monodisperse dendrimers in mass range 1716.82-3424.63 Da) where indicated. The polymer solution 50 μL (1 mg mL⁻¹ in THF) was mixed with 50 μL of a 10 mg mL⁻¹ solution of the matrix (dithranol) in THF. A drop of this solution was spotted onto a MALDI plate which had been pre-spotted with sodium iodide in THF (10 mg mL⁻¹). Atmospheric pressure chemical ionization (APCI) and high-resolution electrospray mass spectrometry (HRMS) measurements for all the synthetic intermediates were carried out using Agilent 6120 Quadrupole LC/MS and Thermo Scientific Exactive Plus EMR (extended mass range) Orbit respectively. Gel permeation chromatography (GPC) analyses were performed in THF solution ($\sim 1 \text{ mg mL}^{-1}$) at 40 °C using a GPC Agilent 1260 Infinity II with 2 \times PL gel 10 μm mixed-B and a PL gel 500 Å column, and equipped with a differential refractive index (DRI) detector employing narrow polydispersity polystyrene standards (Agilent Technologies) as a calibration reference. Samples were filtered through a Whatman Puradisc 4 mm syringe filter with 0.45 μm PTFE membrane before injection to equipment, and experiments were carried out with injection volume of 50 μL , flow rate of 1 mL min⁻¹. Results were analyzed using Agilent GPC/SEC Software Version 2.2. UV-Vis absorption spectra and optical densities were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer and Fluorescence emission spectra were obtained on a Varian Cary Eclipse fluorescence spectrophotometer. : The electrochemical CV were performed on a computer controlled CompactStat.h (Ivium Technologies ©) in a three-electrode configuration with a glassy carbon disk, Pt wire and Ag/Ag⁺ electrode as the working electrode, counter electrode, and reference electrode, respectively in a 0.1 M tetrabutylammonium hexafluorophosphate (NBu₄PF₆) acetonitrile solution as supporting electrolyte, at a scan rate of 50mV s⁻¹. The polymers solutions were drop casted on the glassy carbon disk and left to dry at room temperature before conducting the measurements. The potential of Ag/Ag⁺

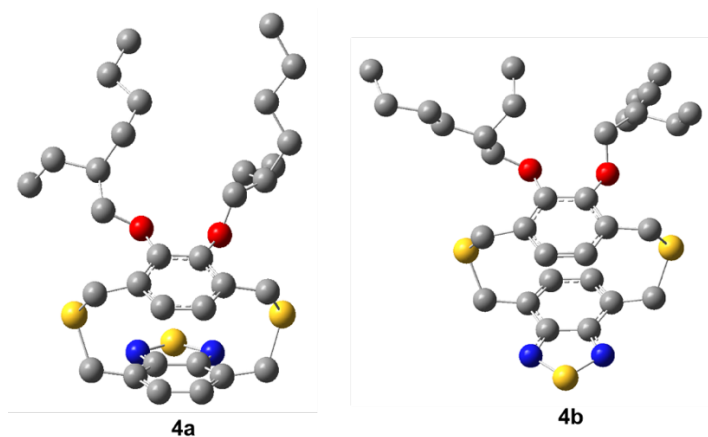
reference electrode was internally calibrated by using Ferrocene/Ferrocenium (Fc/Fc⁺) redox couple.

S2 Computational details

DFT calculations for monomers and polymers were conducted using Gaussian 09W package software. The molecular structures were visualized with the gaussview software. In the first step of the computational studies, full geometry optimizations were carried out using single point calculations with the B3LYP (Becke three-parameter hybrid correlation functional combined with Lee–Yang–Parr correlation functional)¹ with B3LYP/6-311G(d,p) basis set. The HOMO–LUMO energy calculations were carried out to evaluate the energetic behavior of polymers using B3LYP/6-311G(d,p) level to obtain the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital energies. Ring strain is calculated as an energy difference between optimized ring-closed **8a** and **8b** with an H₂ molecule (for atom balance) and the relevant ring-open *cis/trans* monomeric form with H-atoms inserted at the position of ring-opening.

Energies of compound 4-8

Compound	Energy (Hartree)	Energy (kcal/mol)
4a	-2702.06	-1695540
4b	-2702.06	-1695544
6a	-3164.22	-1985546
6b	-3164.23	-1985556
7a	-3314.61	-2079919
7b	-3314.63	-2079929
8a	-1903.123	-1194210
8b	-1903.127	-1194212



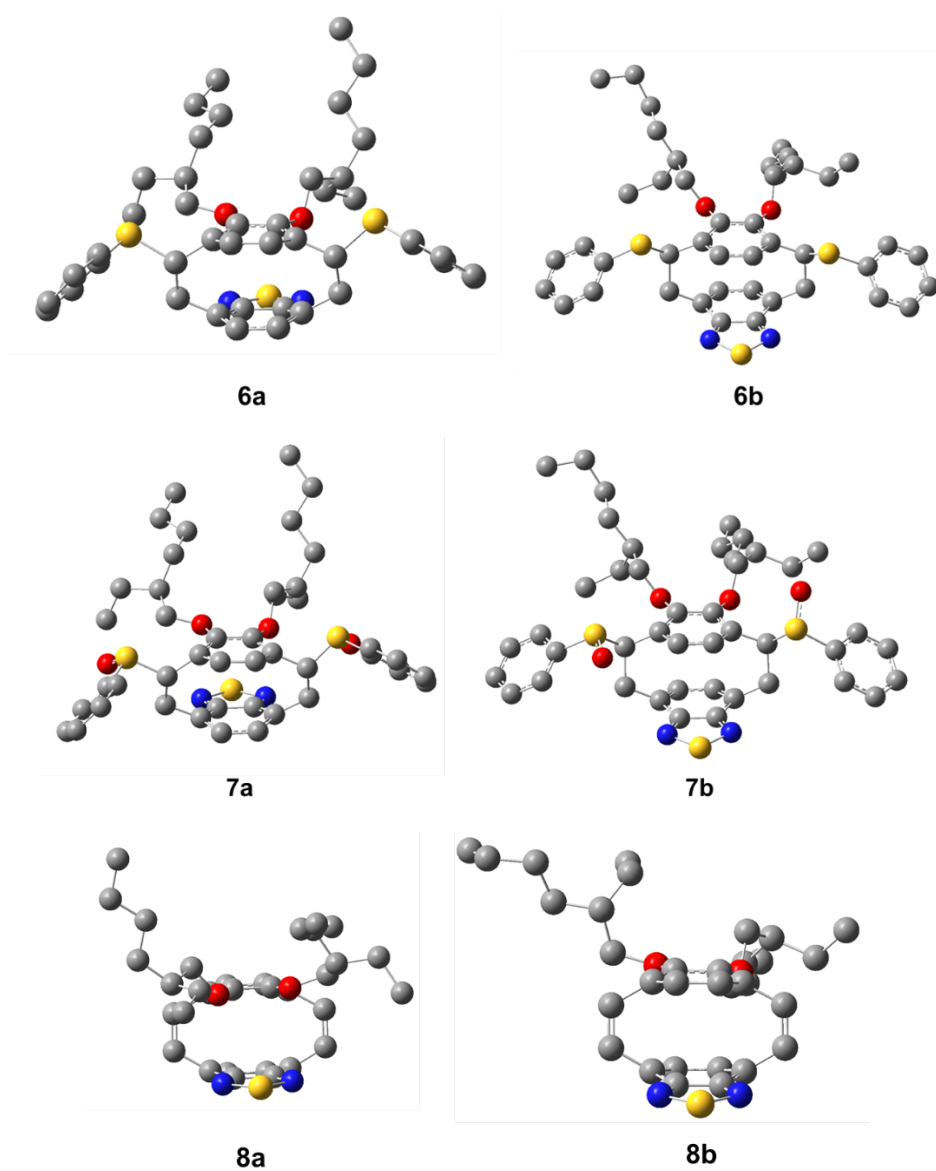
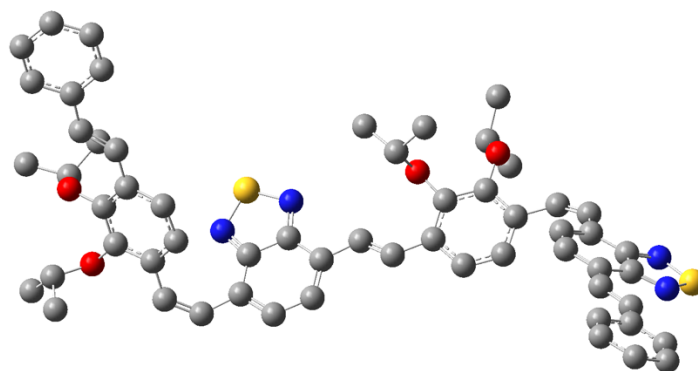
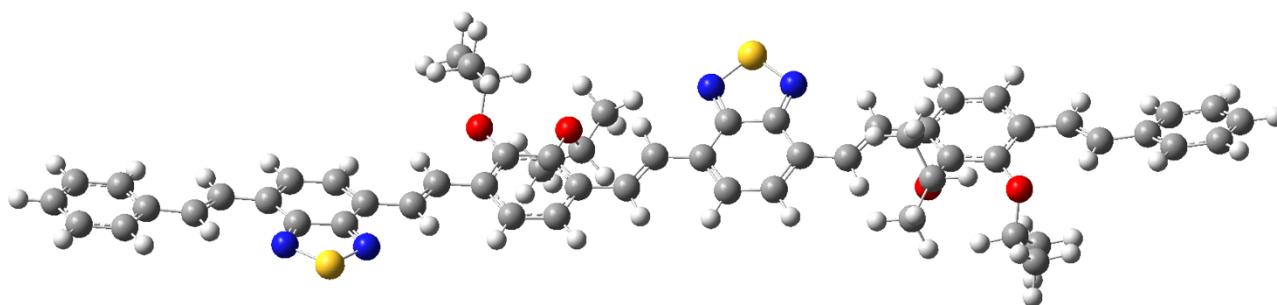


Figure S1 Optimised geometry of compounds 4-8



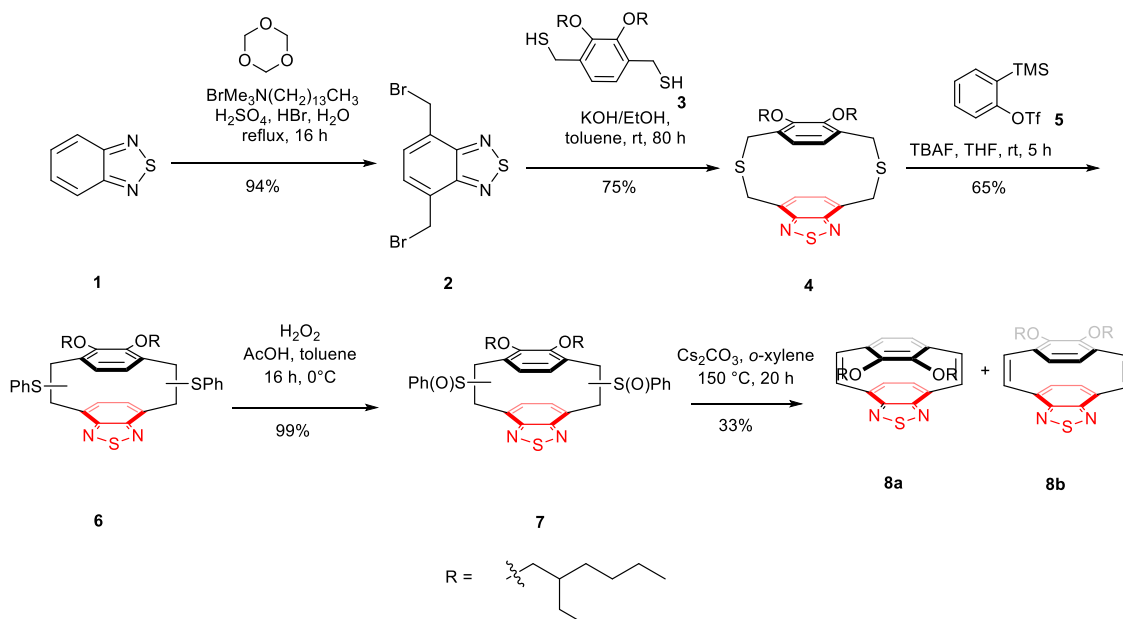
The computed electronic energy of optimised dimer *cis/trans* **9** = -3560.81242 Hartree (-2234409.794 kcal/mol)



The computed electronic energy of optimised dimer *trans* **9** = -3560.834393 Hartree (-2234423.582 kcal/mol)

Figure S2 Optimised geometry of dimers *cis/trans* **9** and *trans-9*

S3 Synthesis of paracyclophanediene monomers **8a** and **8b**



Synthesis of (1^{4E},1^{6E})-5²,5³-bis((2-ethylhexyl)oxy)-3,7-dithia-1(4,7)-benzo[*c*][1,2,5]thiadiazola-5(1,4)-benzenacyclooctaphane **4**

4,7-Bis(bromomethyl)benzo[*c*][1,2,5]thiadiazole **2** (9.43 g, 29.29 mmol) and (2,3-bis((2-ethylhexyl)oxy)-1,4-phenylene)dimethanethiol **3** (12.50 g, 29.29 mmol) were dissolved in deoxygenated toluene (1000 mL). This solution was added dropwise to KOH (6.57 g, 117.17 mmol) in deoxygenated ethanol (2200 mL), over 72 hours at room temperature. The solvent was removed *in vacuo* and the residue was dissolved in ethyl acetate (500 mL) after additional 2 hours. The organic layer was washed with water (2x500 mL), brine (200 mL) followed by drying with anhydrous MgSO₄.

The solution was filtered, concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (gradient: 0-3% ethyl acetate/petroleum ether) to obtain the desired product **4** (12.9 g, 75% yield) as a pale yellow semisolid. . **MS (HRMS):** 587.2592 [M+H]⁺ (calcd for C₃₂H₄₆O₂N₂S₃+H: 587.2794) **¹H NMR (500 MHz, CDCl₃) δ(ppm)** 7.10 (s, 2H), 5.67 (s, 2H), 4.54 (d, 2H, *J* = 15 Hz), 4.04 (d, 2H, *J* = 15 Hz), 3.98 (m, 2H), 3.94 (d, 2H, *J* = 15 Hz), 3.80 (m, 2H), 3.43 (d, 2H, *J* = 15 Hz), 1.83-1.74 (m, 2H), 1.27-1.69 (m, 18H), 0.87-1.00 (m, 12H). **¹³C NMR (500 MHz, CDCl₃) δ(ppm)** 154.76, 149.58, 130.71, 129.33, 128.93, 76.07, 40.53, 34.29, 32.86, 30.55, 30.15, 29.12, 23.81, 23.17, 14.12, 11.32, 11.10.

Synthesis of (1⁴E,1⁶E)-5²,5³-bis((2-ethylhexyl)oxy)-3,7-diphenyl-3λ⁴,7λ⁴-3λ⁴,7λ⁴-dithia-1(4,7)-benzo[c][1,2,5]thiadiazola-5(1,4)-benzenacyclooctaphane **6**

Compound **4** (8.00 g, 13.63 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **5** (9.76 g, 32.71 mmol) were dissolved in anhydrous THF (200 mL) and stirred at room temperature for 5 min. To this solution, TBAF·3H₂O (12.86 g, 40.76 mmol) dissolved in anhydrous THF (70 mL) was added dropwise using a syringe pump over a period of 5 hours. The resulting solution was stirred for one hour and the solvent removed *in vacuo* to obtain a brown oil. The crude was purified by silica gel flash column chromatography (gradient: 0-30% dichloromethane/petroleum ether) resulting in pale yellow oil (mixture of diastereomers **6**, 6.58 g, 65 % yield). **MS (HRMS):** 739.2341 [M+H]⁺ (calcd. for C₄₄H₅₄O₂N₂S₃+H: 739.3420).

Synthesis of monomer **8a and **8b****

A solution of bisphenylsulfide isomers **6** (1.60 g, 1.43 mmol) in benzene (60 ml) and acetic acid (20 ml) at 0 °C under an argon atmosphere. and hydrogen peroxide (0.41 ml, 4.02 mmol, 0.136 g, 30 wt % in acetic acid) was added. The mixture was stirred for an additional 12 hours. Upon consumption of the starting material (TLC), the reaction was warmed to room temperature and saturated NaHCO₃(aq) (20 mL) was added. The organic layer was washed with water (50 mL) and brine (50 mL). The organic layer was dried over magnesium sulfate, filtered and the solvent removed *in vacuo*. A clear viscous oil **7** (1.57 g, 99%) was obtained and used in the next step without any further purification. **MS (HRMS):** 771.2156 [M+H]⁺ (calcd. for C₄₄H₅₅O₄N₂S₃+H: 771.3318).

The crude intermediate **7** (1.57 g, 2.01 mmol) was dissolved in deoxygenated anhydrous *o*-xylene (50 mL) and cesium carbonate (2.64 g, 8.10 mmol) was added and the suspension was heated under reflux for 20 hours. Upon consumption of the starting material (TLC) the reaction was cooled to room temperature, filtered and the solvent removed by distillation under reduced pressure, to yield a brown oil. The crude product was purified by silica gel flash column chromatography (gradient: 15-20% dichloromethane/petroleum ether) to obtain a reddish oil (0.35 mg, 33% yield). (isolated as an inseparable mixture of **8a:8b** in ratio of 26:74, by integration of the aromatic protons). **MS (HRMS):** 519.3032 [M+H]⁺ (calcd. for C₃₂H₄₃O₂N₂S+H: 519.3040) **¹H NMR (500 MHz, CD₂Cl₂) δ(ppm)** 7.16

(d, 0.85H, $J = 10$ Hz), 7.09 (d, 2H, $J = 10$ Hz), 6.92 (s, 2H), 6.90 (d, 0.85H, $J = 10$ Hz), 6.85 (d, 2H, $J = 10$ Hz), 6.60 (s, 0.68H), 6.13 (s, 0.68H), 5.13 (s, 1.89H), 3.78-3.86 (m, 2H), 3.65-3.71 (m, 0.73H), 3.57-3.64 (m, 2H), 3.23-3.27 (m, 0.72H), 1.53-1.61 (m, 2H), 1.14-1.53 (m, 27H), 0.75-0.92 (m, 19H)
 ^{13}C NMR (500 MHz, CDCl_3) δ (ppm) 159.0, 156.0, 152.4, 152.3, 152.2, 151.5, 134.6, 134.5, 134.4, 134.3, 132.9, 132.6, 132.3, 132.0, 130.8, 130.4, 130.3, 130.0, 124.9, 122.2, 75.9, 75.0, 40.6, 40.5, 40.3, 30.5, 30.3, 30.2, 30.1, 29.4, 29.0, 23.8, 23.6, 23.5, 23.4, 23.1, 13.9, 11.2, 11.0, 10.8 ppm.

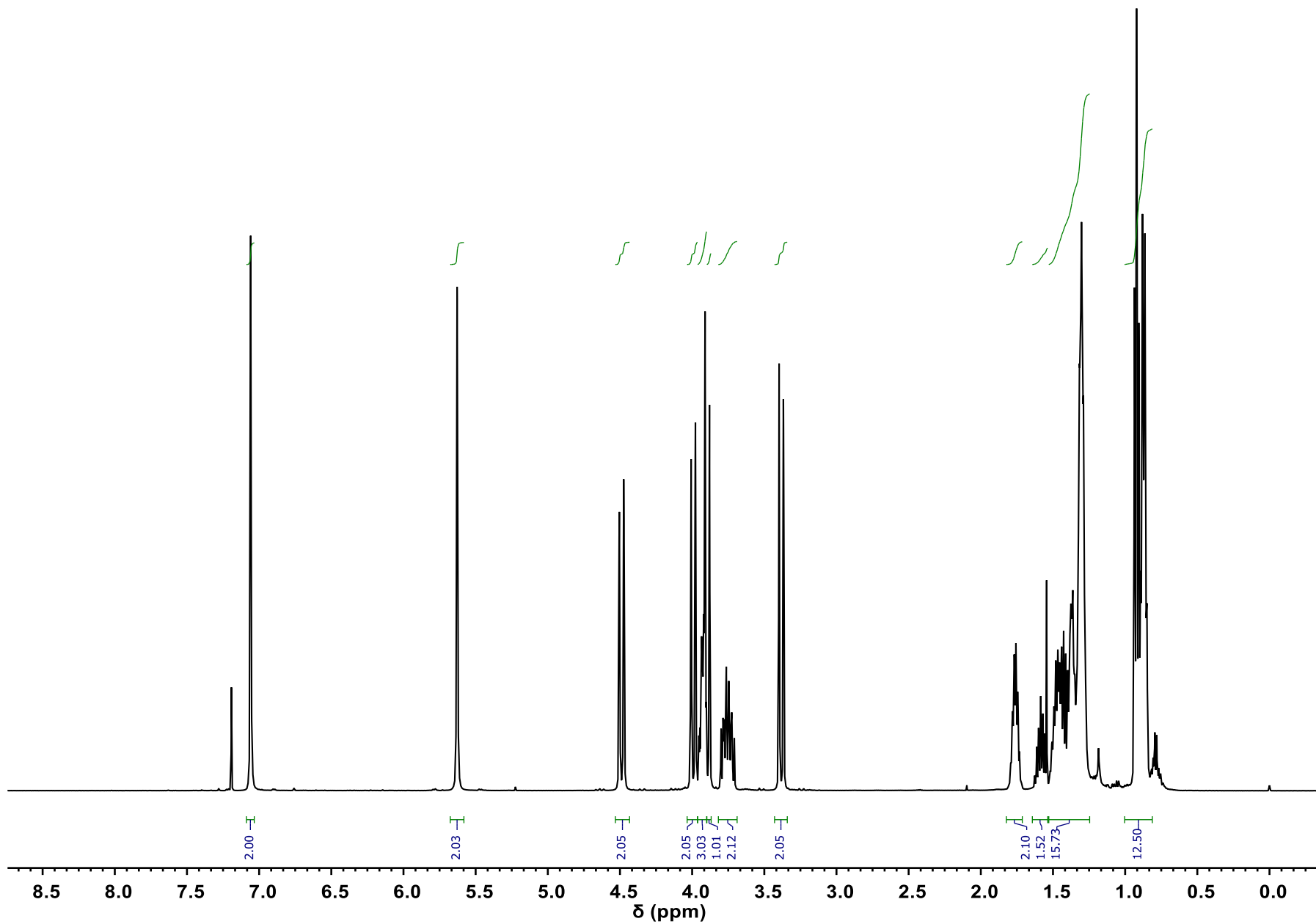


Figure S3 ¹H NMR spectrum of intermediate 4 in CDCl₃.

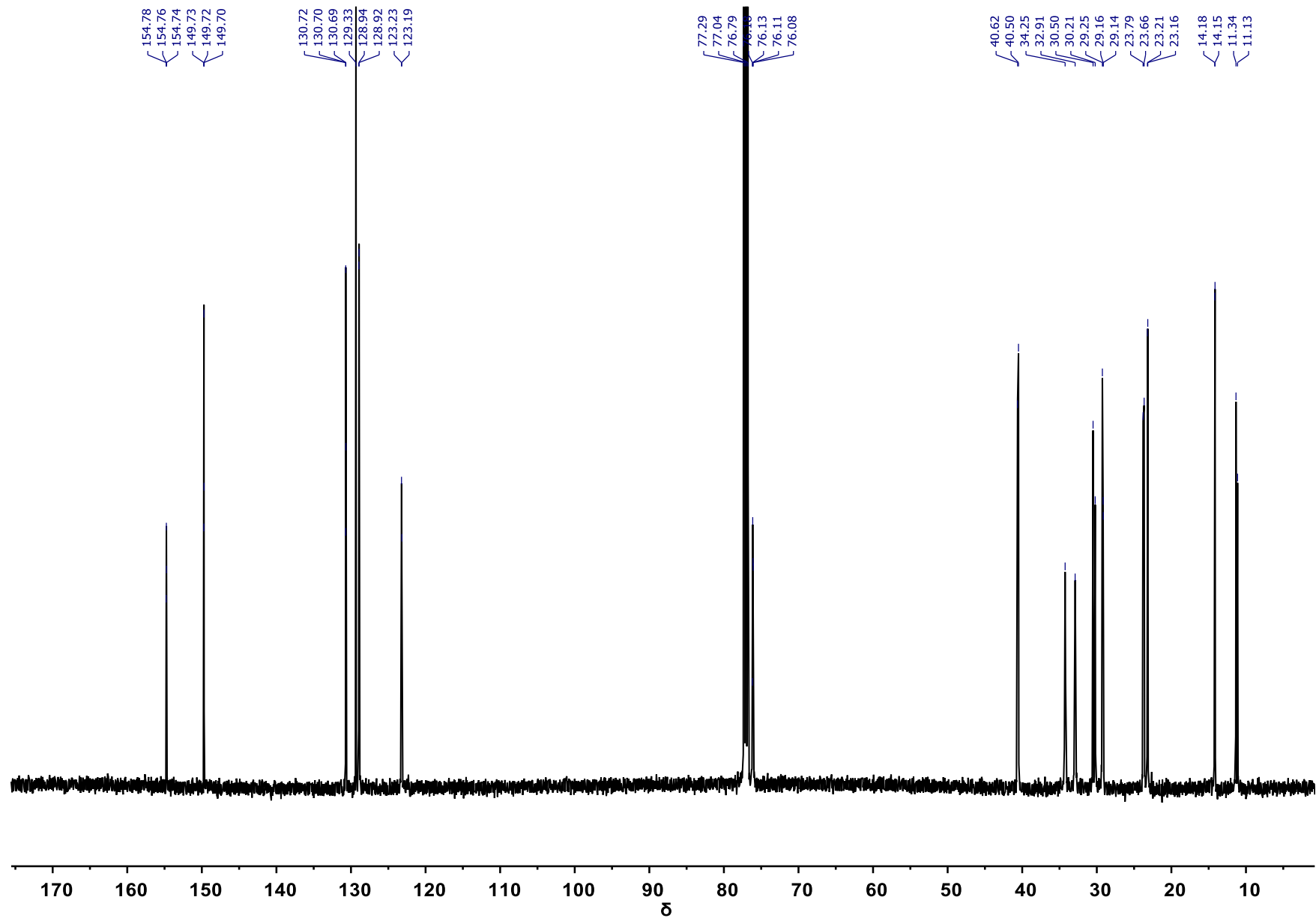


Figure S4 ^{13}C NMR spectrum of intermediate 4 in CDCl_3 .

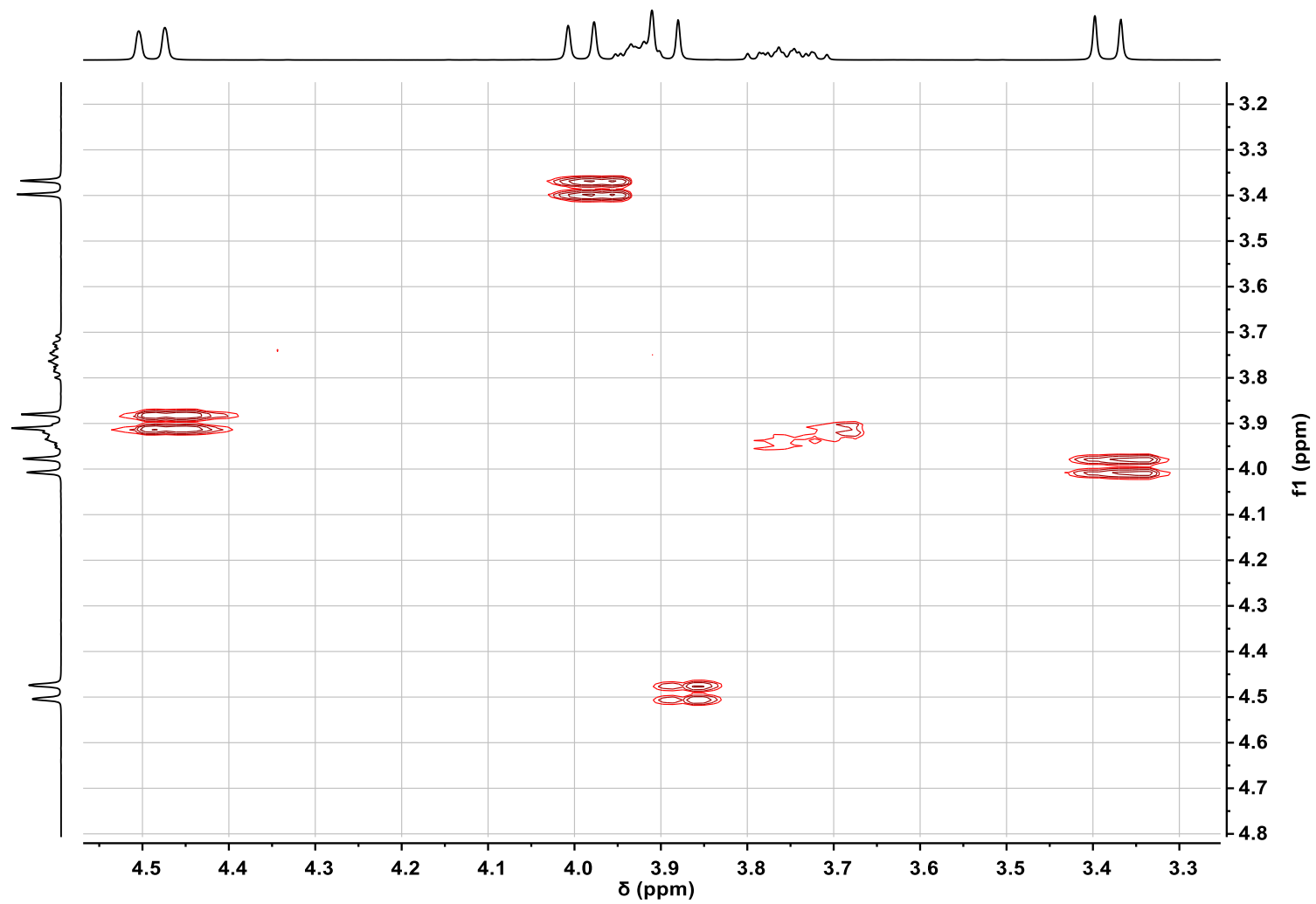


Figure S5 COSY spectrum of intermediate **4** in CDCl₃.

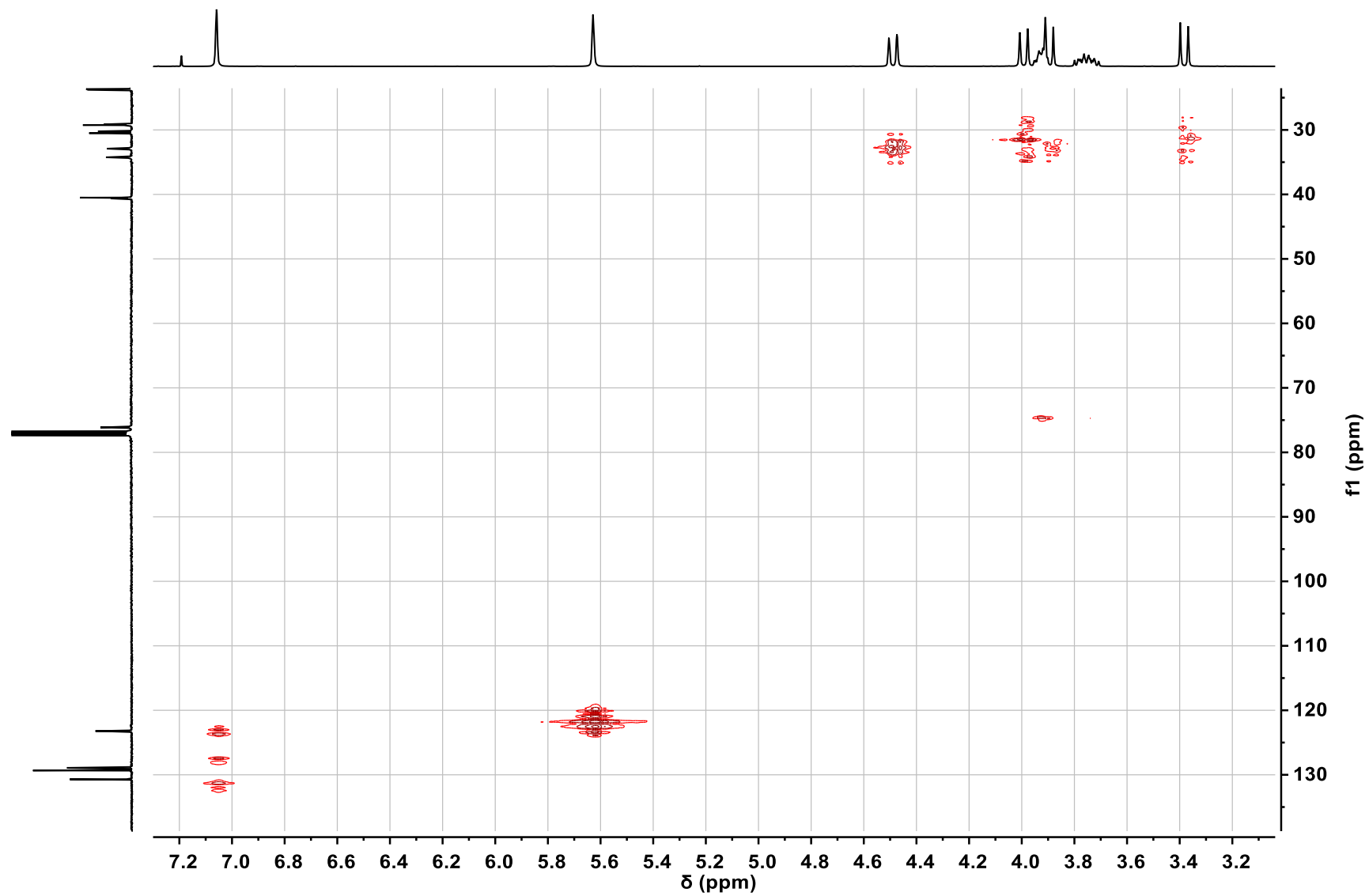


Figure S6 HSQC spectrum of intermediate 4 in CDCl_3 .

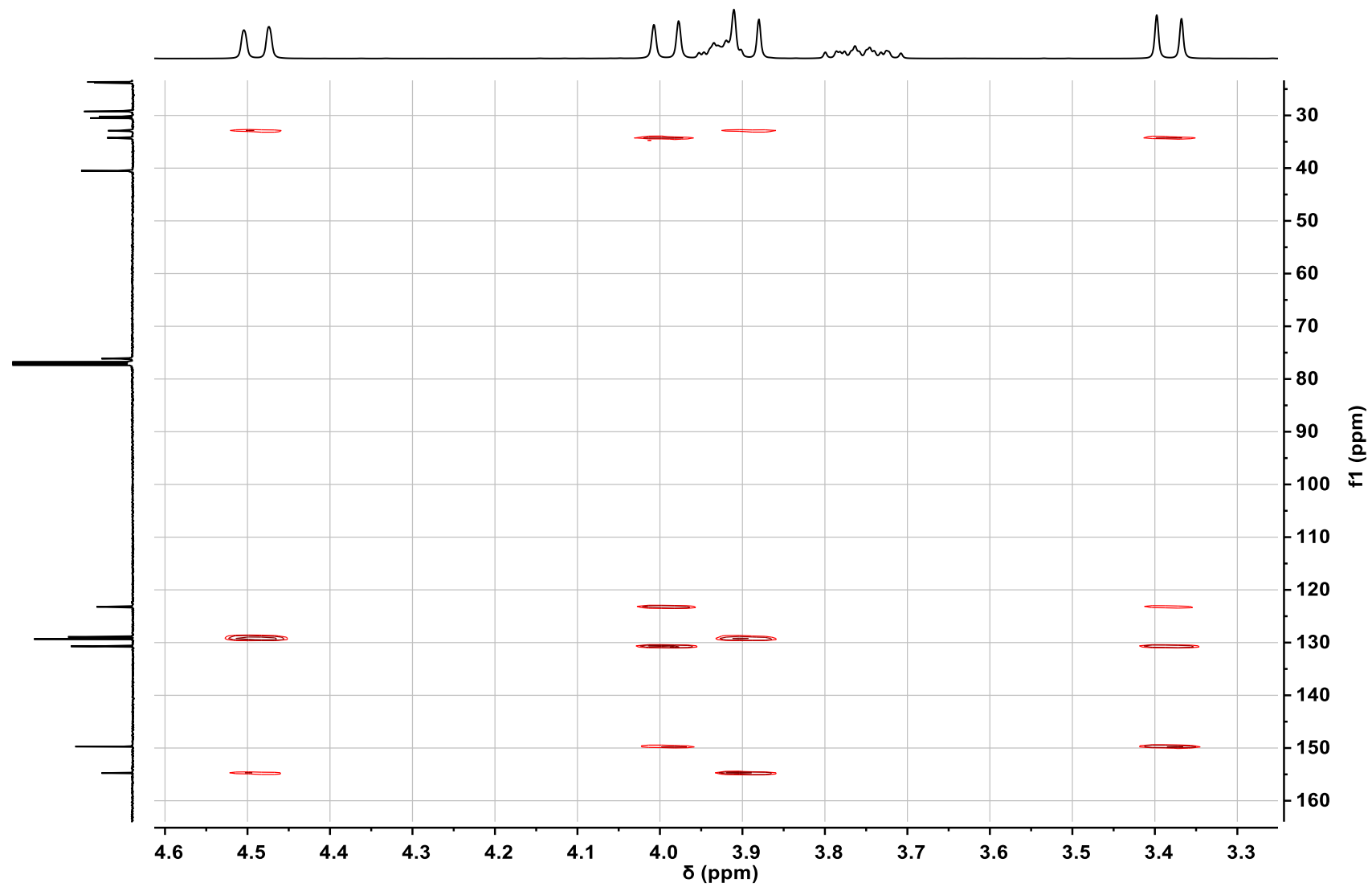


Figure S7 HMBC spectrum of intermediate **4** in CDCl₃.

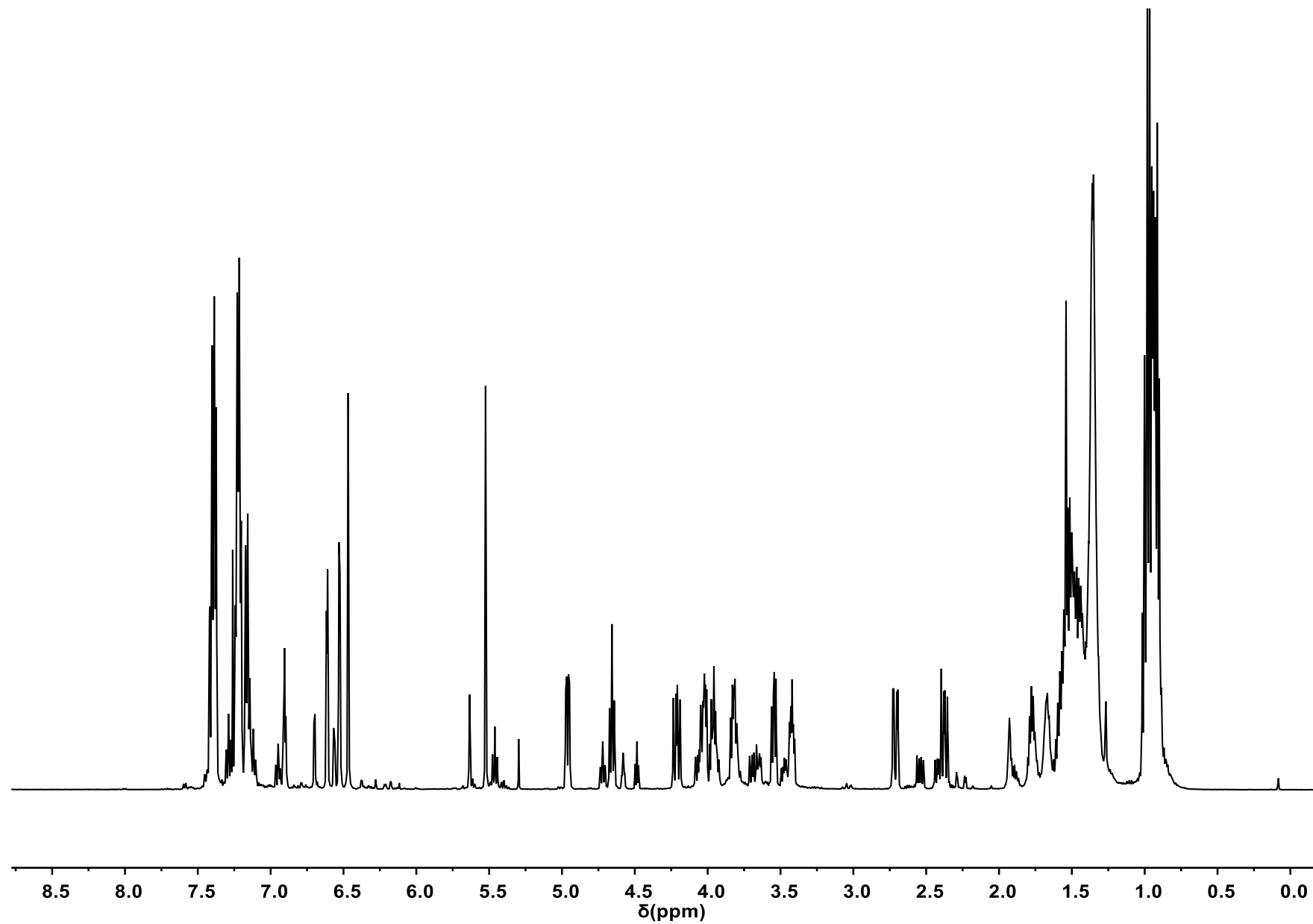


Figure S8 ^1H NMR spectrum of intermediate **6** in CDCl_3 .

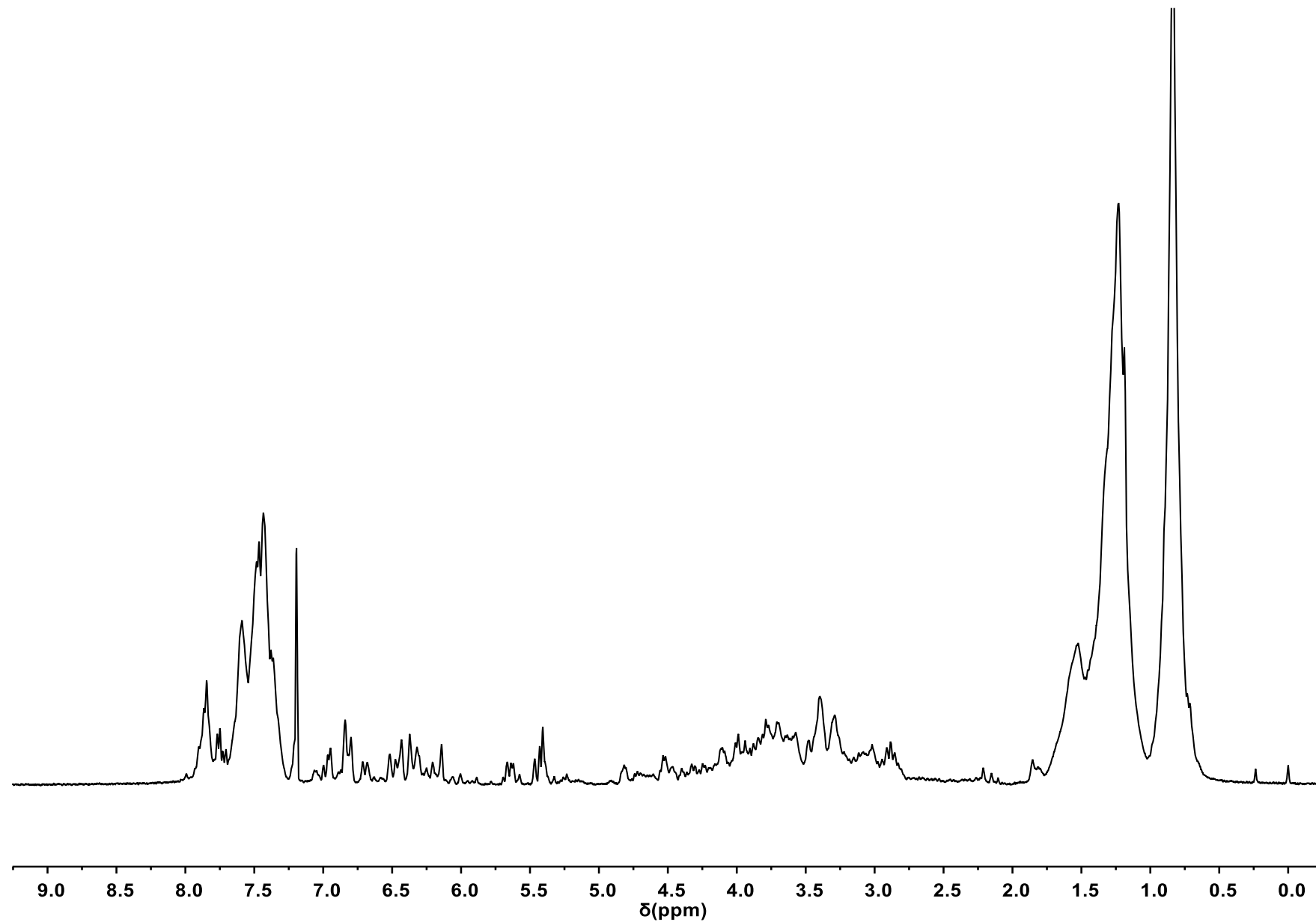


Figure S9 ^1H NMR spectrum of intermediate 7 in CDCl_3 .

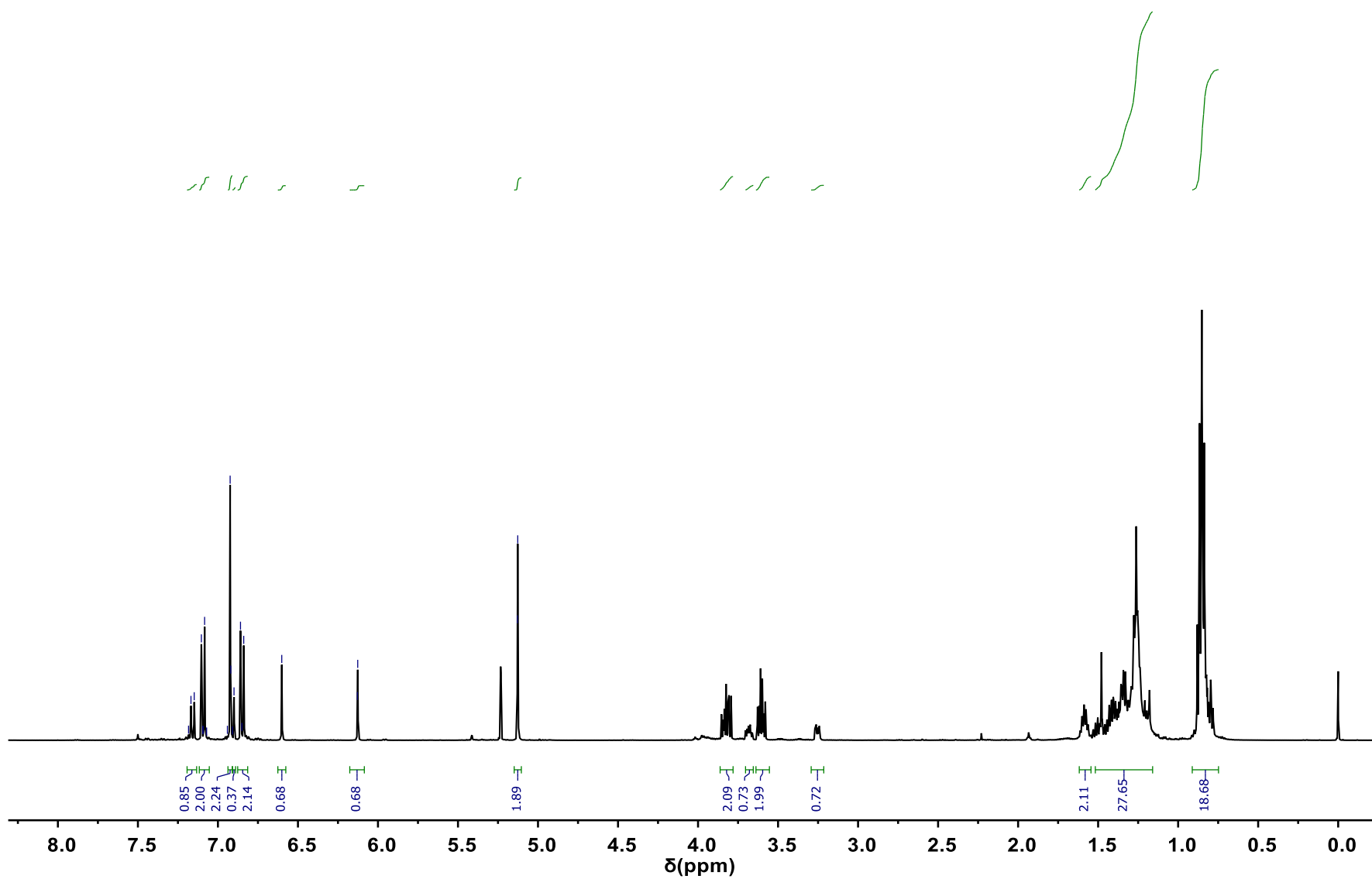


Figure S10 ¹H NMR spectrum of monomer **8a** and **8b** in CD₂Cl₂.

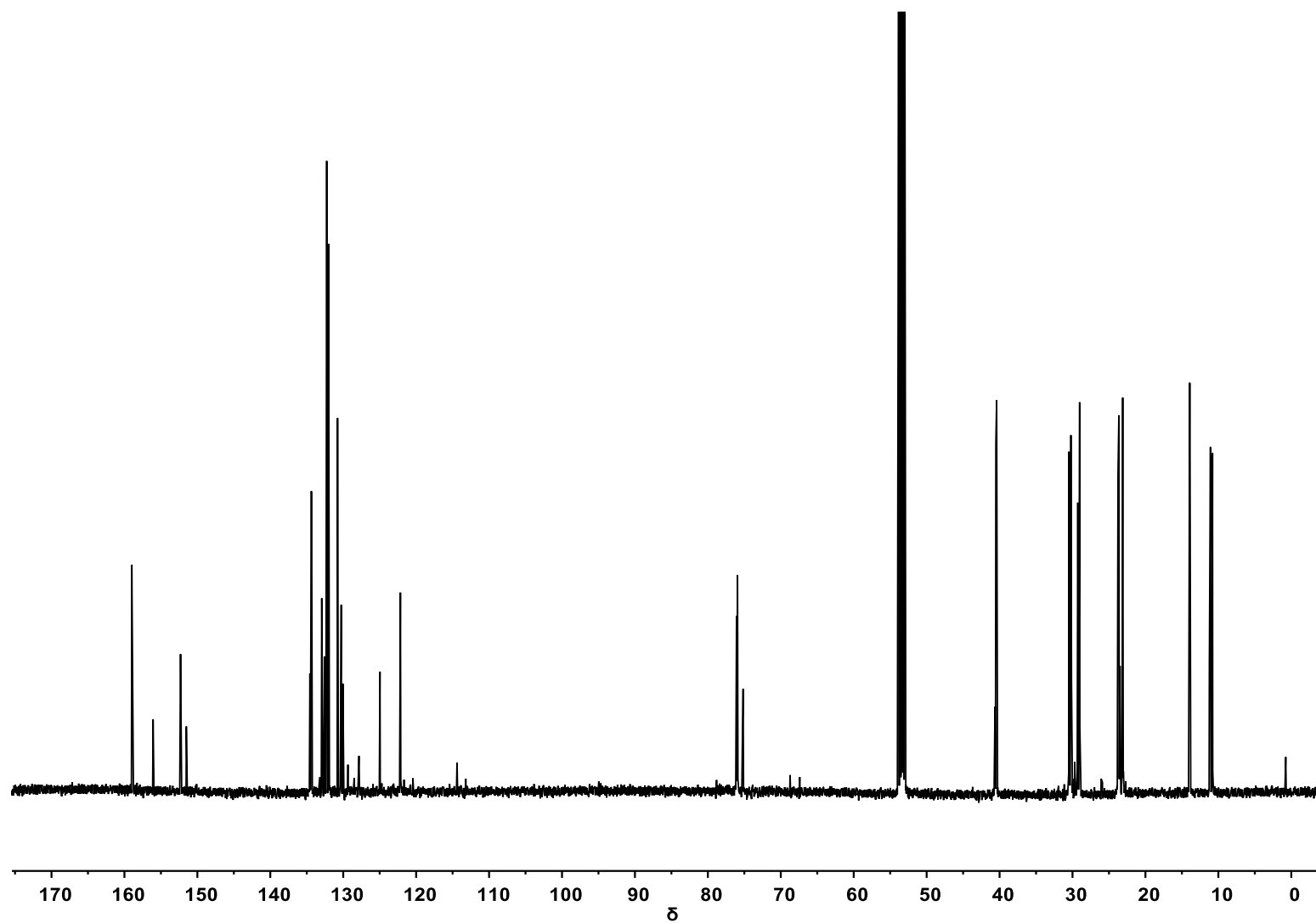


Figure S11 ^{13}C NMR spectrum of monomer **8a** and **8b** in CDCl_3 .

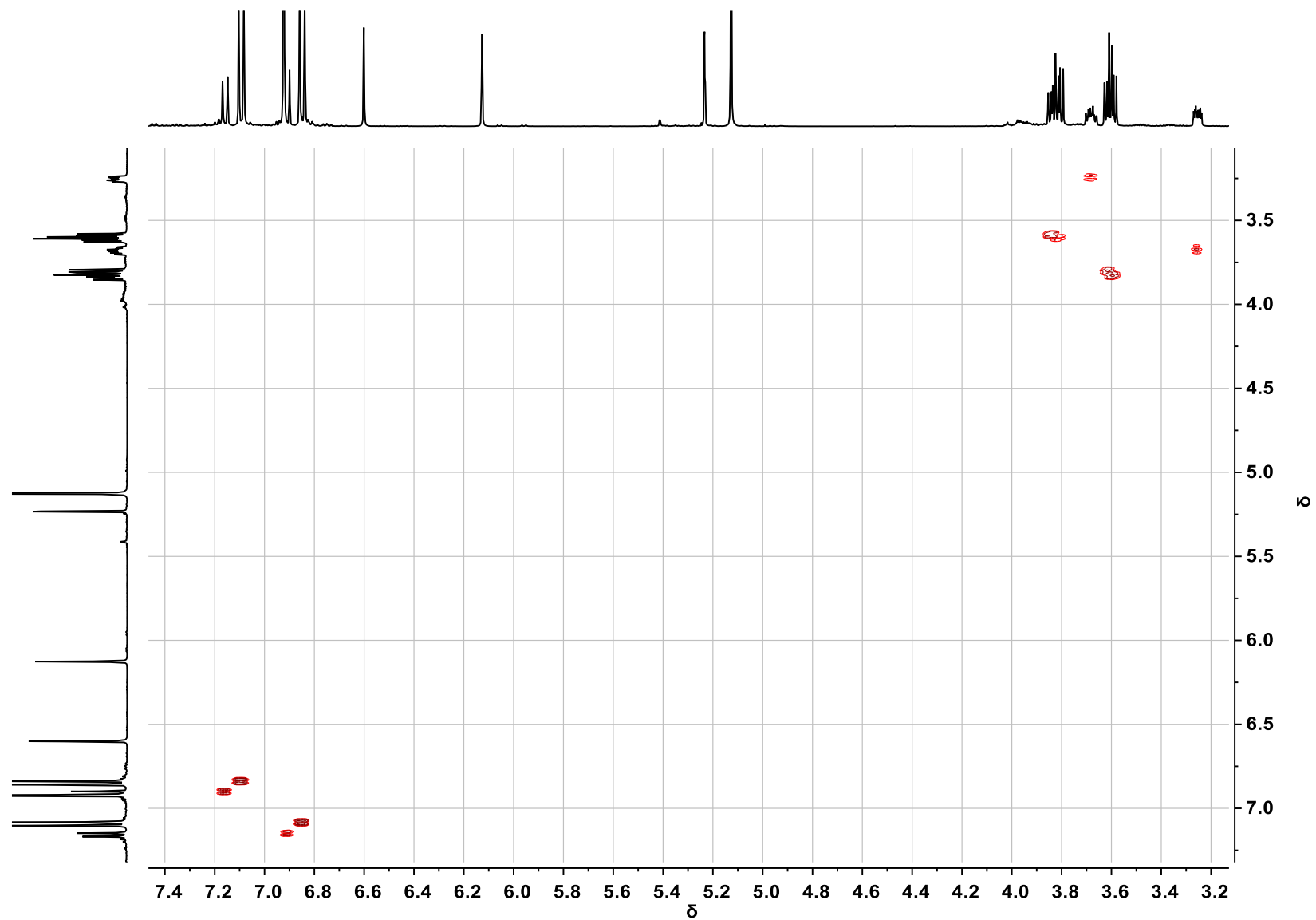


Figure S12 ¹H-¹H COSY NMR spectrum of monomer **8a** and **8b** in CDCl₃.

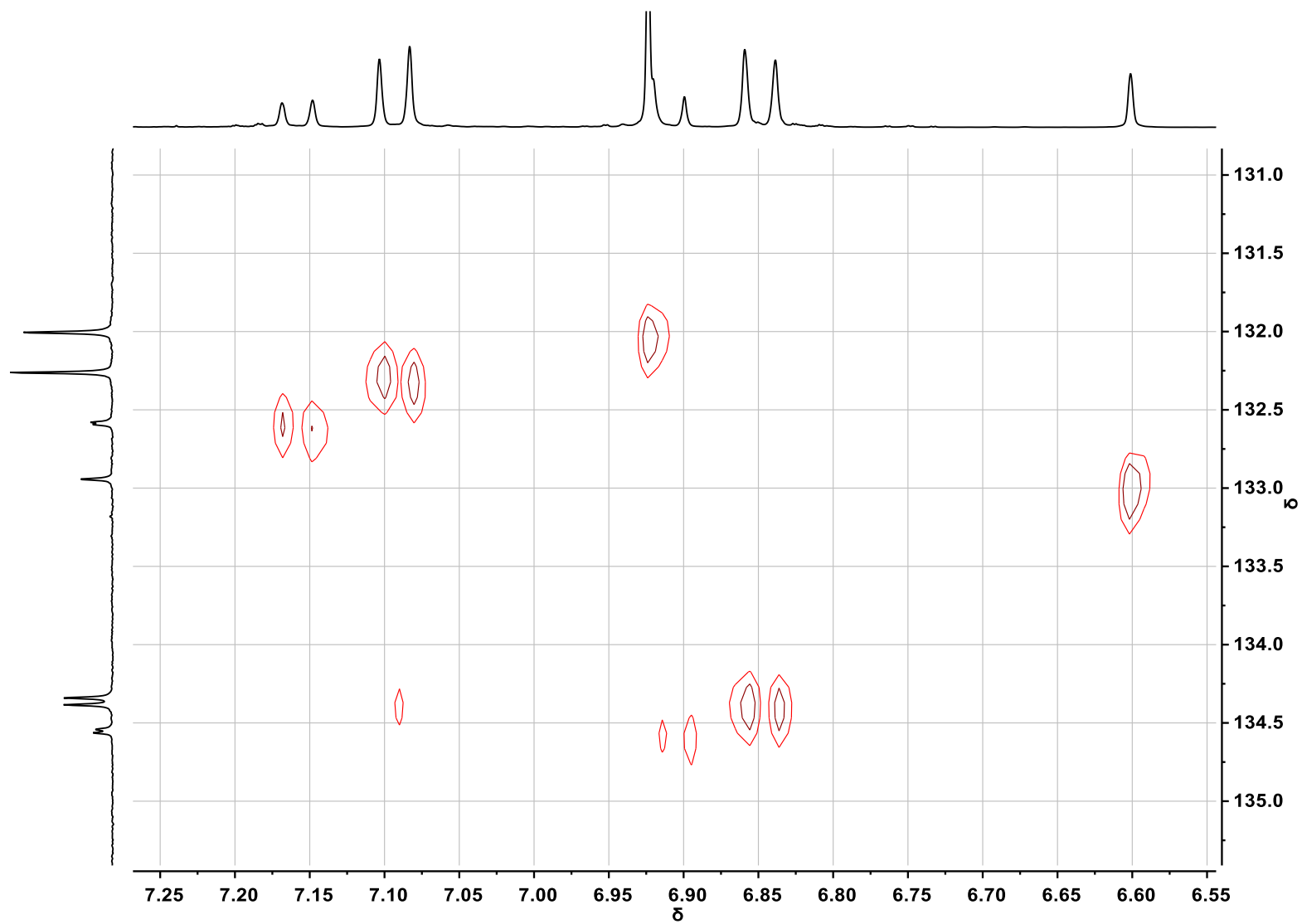


Figure S13 HSQC spectrum of monomer **8a** and **8b** in CDCl_3 .

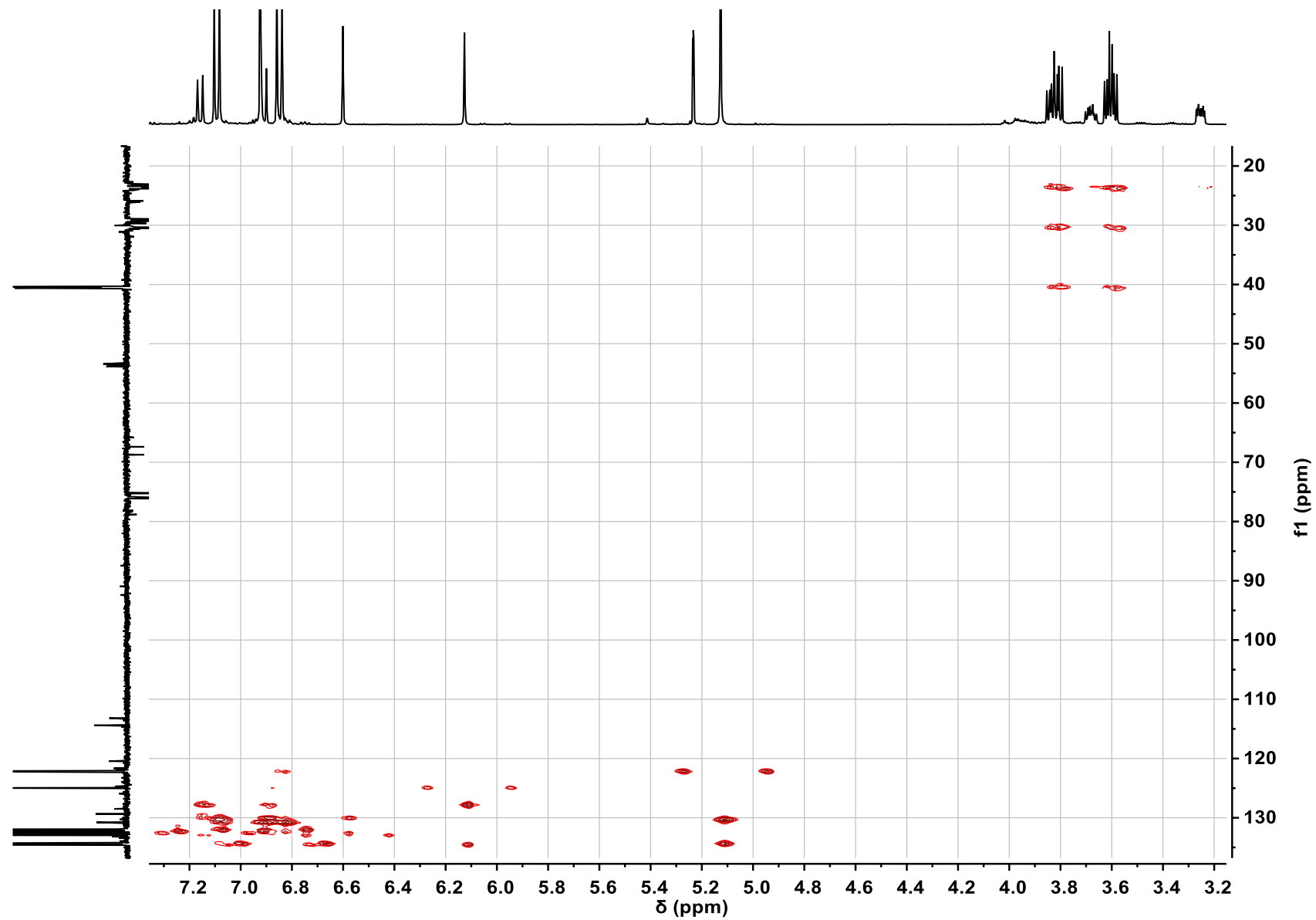


Figure S14 HMBC spectrum of monomer **8a** and **8b** in CDCl₃

S4 The temperature dependence of **8a** and **8b**

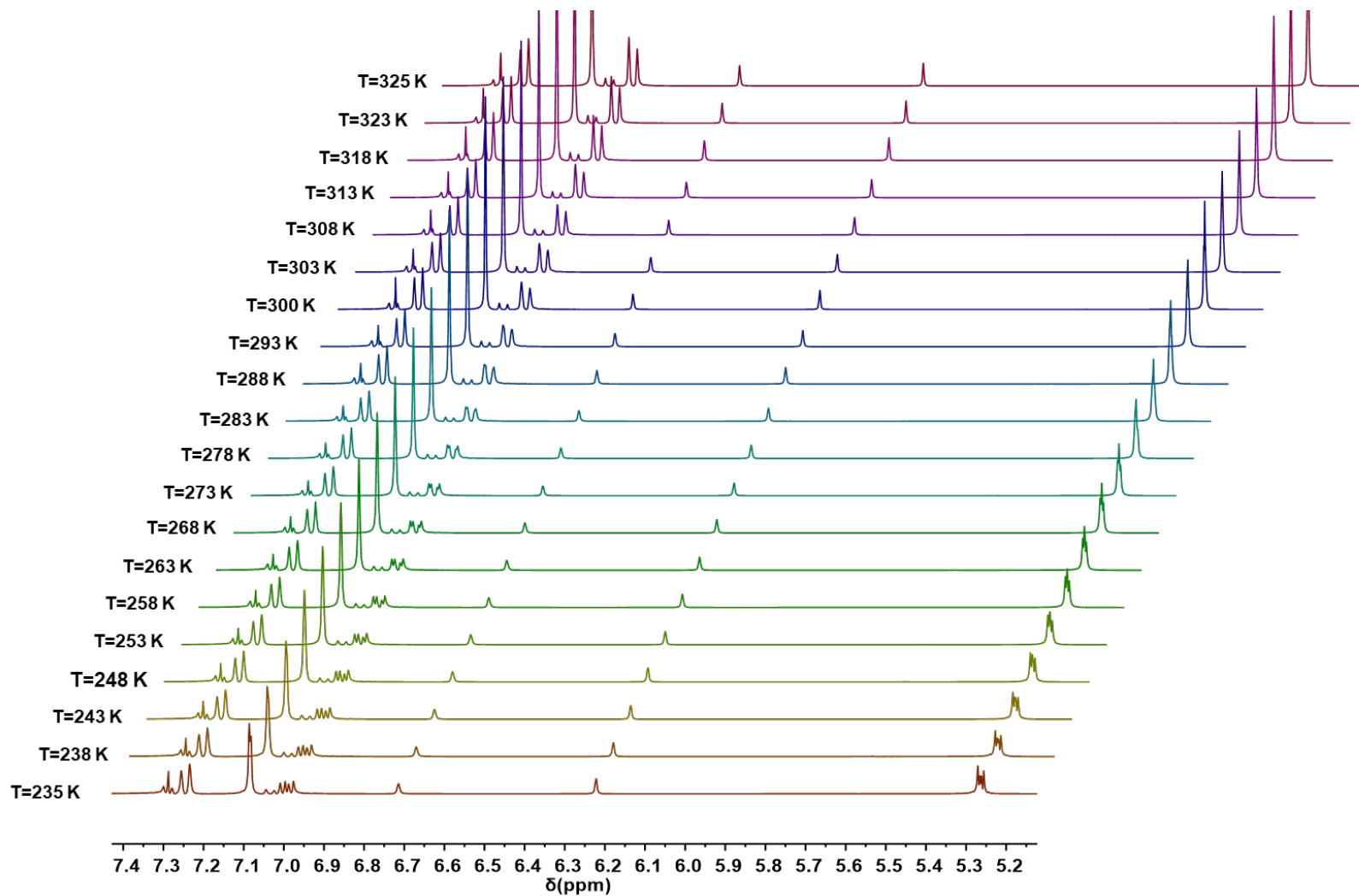


Figure S15 Variable temperature ¹H NMR spectra of monomer **8a** and **8b** in CDCl₃ (δ 5.2-7.4 ppm).

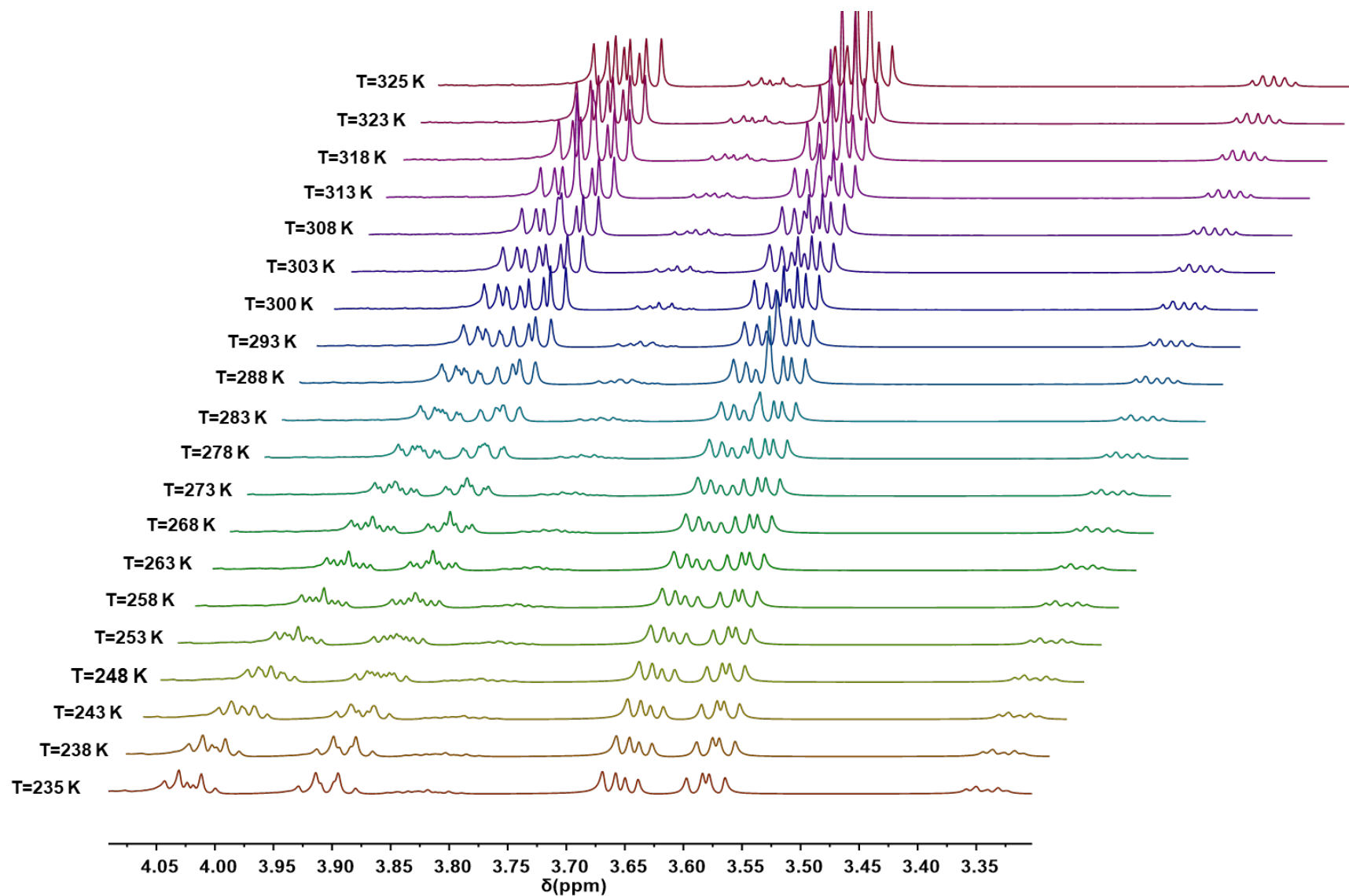


Figure S16 Variable temperature ¹H NMR spectra of monomer **8a** and **8b** in CDCl₃ (δ 3.4-4.0 ppm).

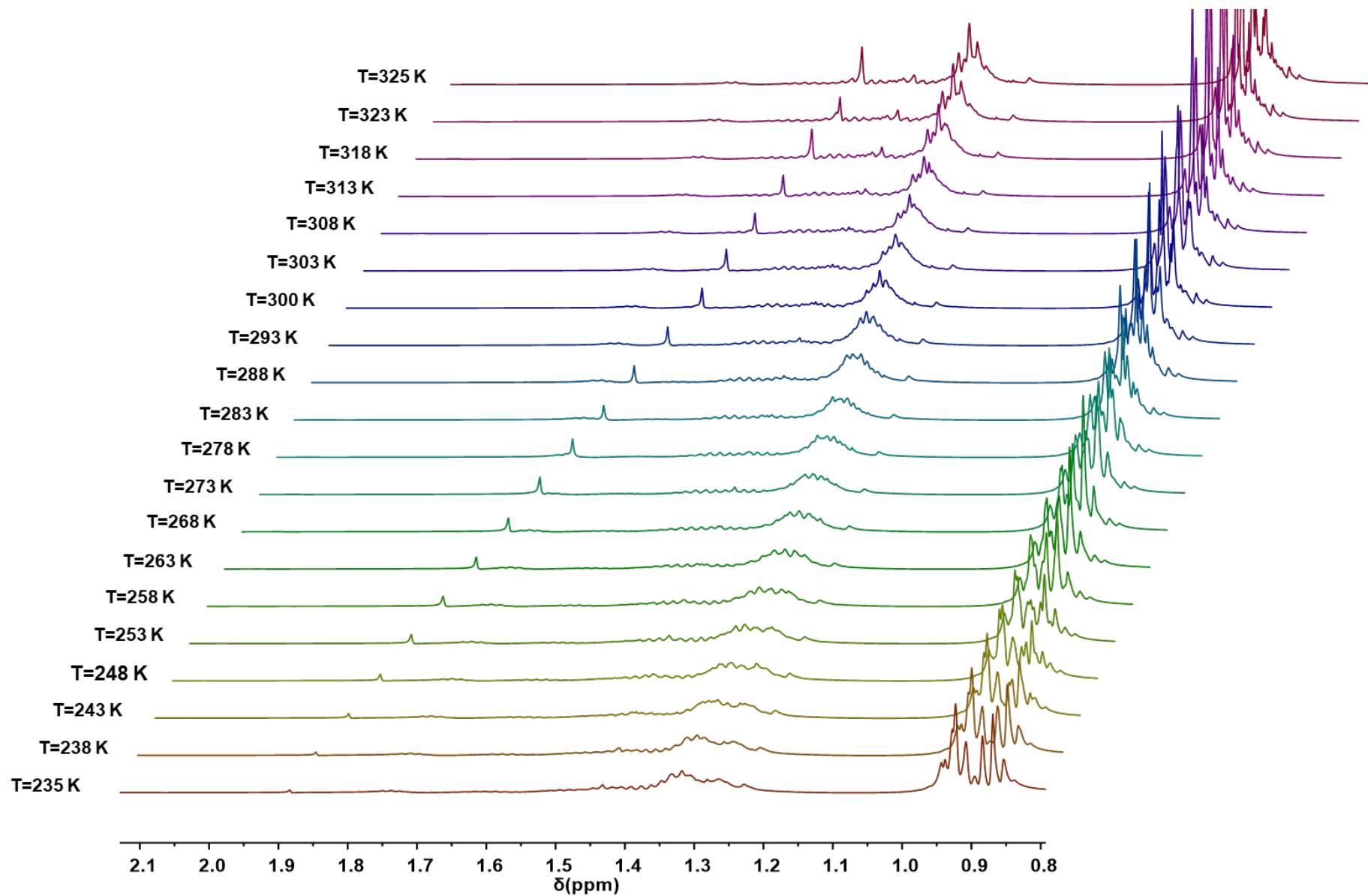


Figure S17 Variable temperature ¹H NMR spectra of monomer **8a** and **8b** in CDCl₃ (δ 0.8-2 ppm).

S5 ROMP of monomers **8** with **G2** catalyst; *in-situ* ^1H NMR experiments

General experimental procedure: Monomer **8** and **G2** (5.53mg, 6.51 μmol) catalyst were separately dissolved in THF- d_8 ($[\text{M}] = 100 \text{ mM}$) which was degassed for 10 min prior to use. Then the catalyst's solution was added to the monomer **8** (30 mg, 65.12 μmol) solution. The solution was transferred into a Young's NMR tube, sealed, removed from the glovebox and kept in an ice bath. The first ^1H NMR spectrum for $t=0$ was recorded at 25 $^\circ\text{C}$. Then the spectrometer probe was set at 55 $^\circ\text{C}$ and the NMR spectra were recorded at 5 min intervals throughout the ROMP. At the end of the reaction, deoxygenated ethyl vinyl ether was added and stirred at room temperature for 5 hours. The reaction was precipitated into a short methanol/Celite column, washed the catalyst with methanol followed by extraction of the polymer with chloroform. After evaporation of chloroform, polymer was isolated as maroon amorphous film.

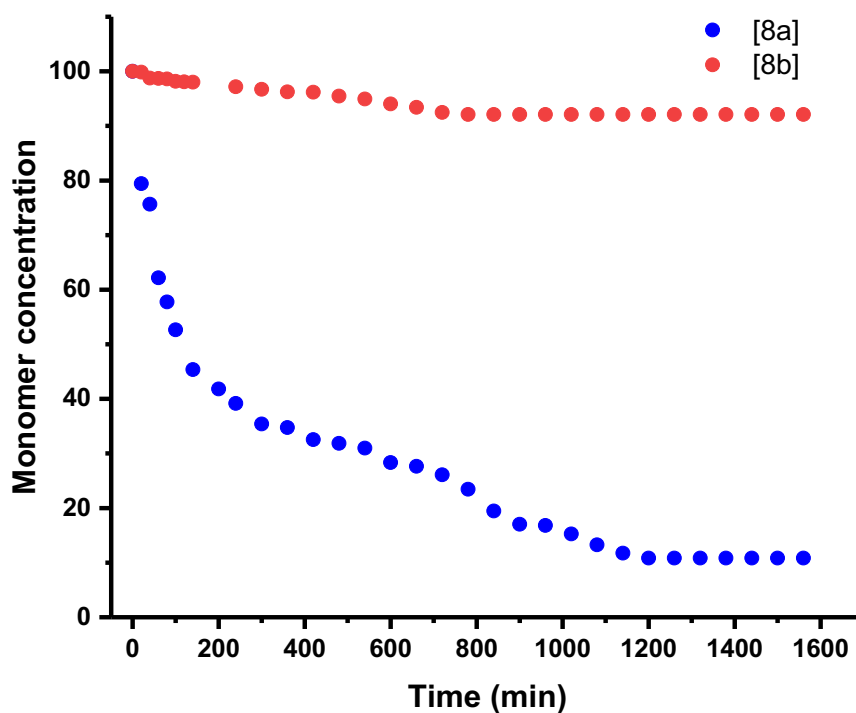


Figure S18 Conversion of **[8a]** and **[8b]** during ROMP with **G2** at 55 $^\circ\text{C}$,

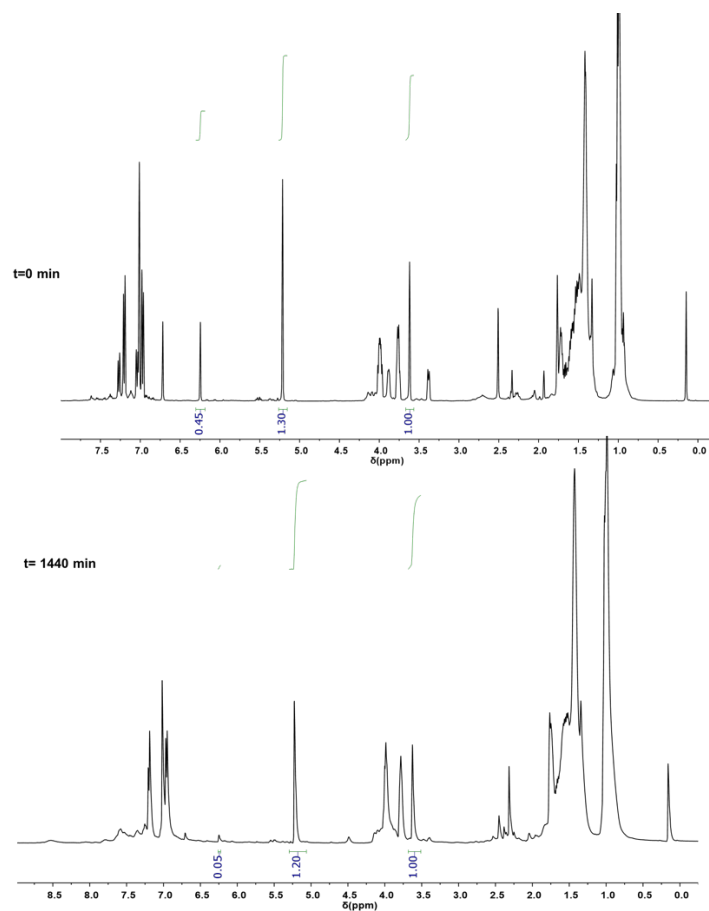
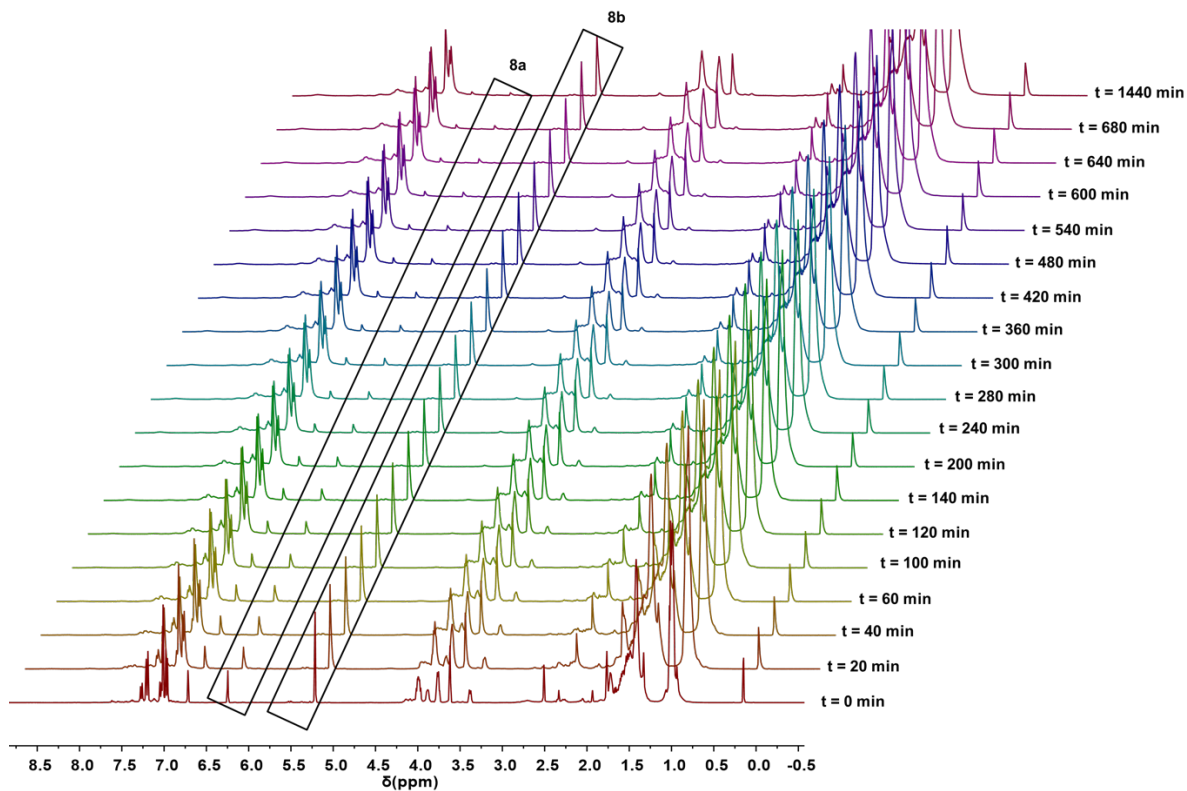


Figure S19 ROMP of monomers **8a** and **8b** with **G2** catalyst; *in-situ* ^1H NMR experiment in $\text{THF-}d_8$ at 55°C ^1H NMR stack of monomer consumption

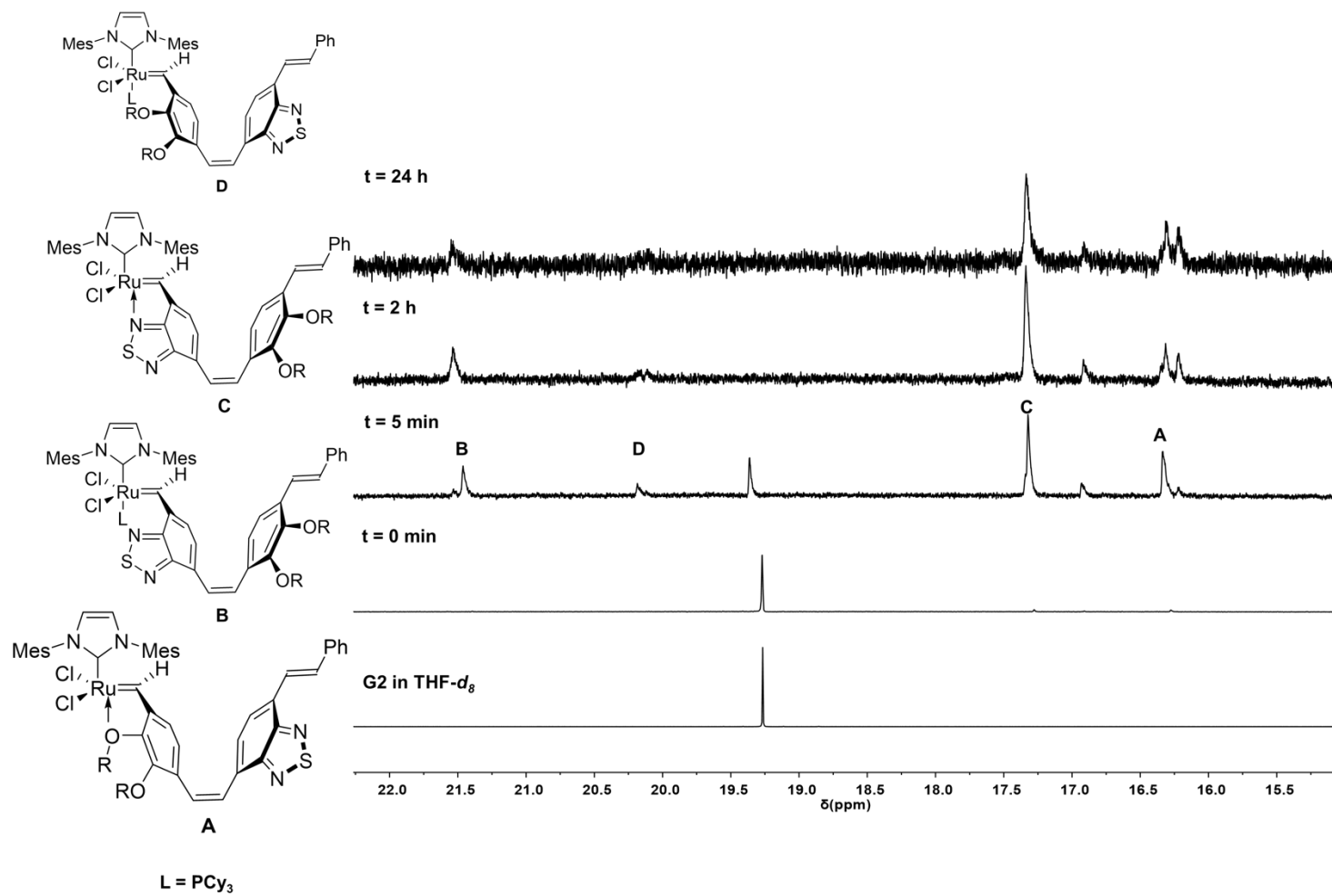


Figure S20 ROMP of monomer **8a** and **8b** with **G2** catalyst; *In-situ* ^1H NMR experiment – carbene region.

S6 ROMP of monomer of 8 with G2 catalyst (bulk experiments)

In an argon filled glovebox a solution of **G2** (2.62 mg, 3.08 μmol) in anhydrous, degassed THF ($[\text{M}] = 100 \text{ mM}$) was added into a vial containing cyclophanediene monomer **8** (60 mg, 65.12 μmol). The vial was sealed, wrapped in foil and mixed at room temperature for 10 minutes. The reaction was placed in a preheated oil bath at 60 °C and stirred until complete monomer conversion observed by SEC and TLC. The reaction was cooled to room temperature and deoxygenated ethyl vinyl ether was added and stirred at room temperature for 4 h. The reaction was precipitated on to a short methanol/Celite column, washed with methanol and the polymer extracted with chloroform. The chloroform layer was evaporated by reduced pressure to give poly(*p*-phenylenevinylenes) as maroon films.

S7 *Cis-trans* isomerisation of 9

Polymers **9** was dissolved in degassed dichloromethane (1 mg/mL) in an argon filled glovebox. The vial was sealed, removed from the glovebox and subjected to photoisomerisation by irradiating with $\lambda = 365 \text{ nm}$ for 24 hours. After evaporation of the solvent polymer were isolated as purple solid in quantitative yields.

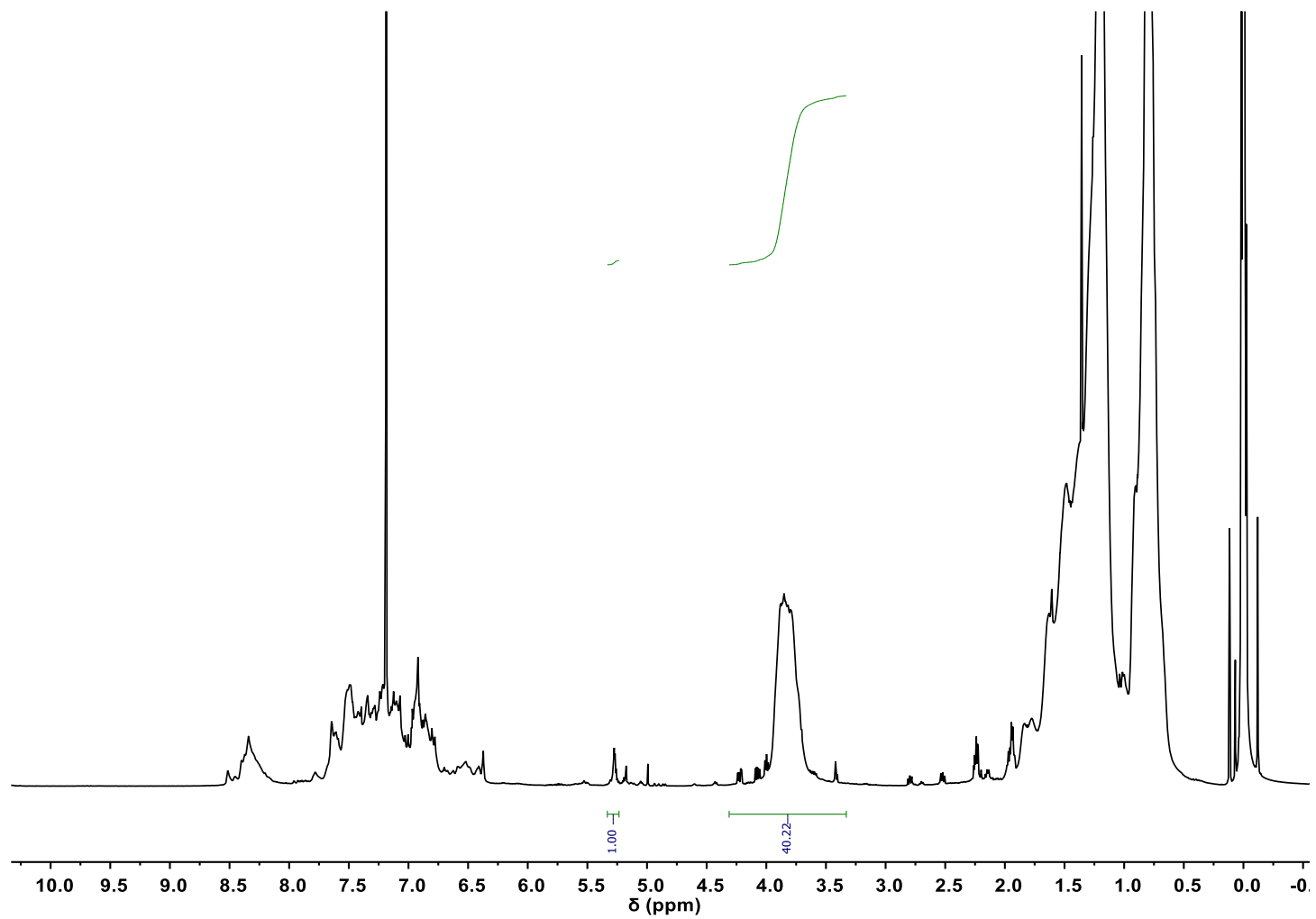


Figure S21 NMR spectrum of polymer **9** in CDCl₃.

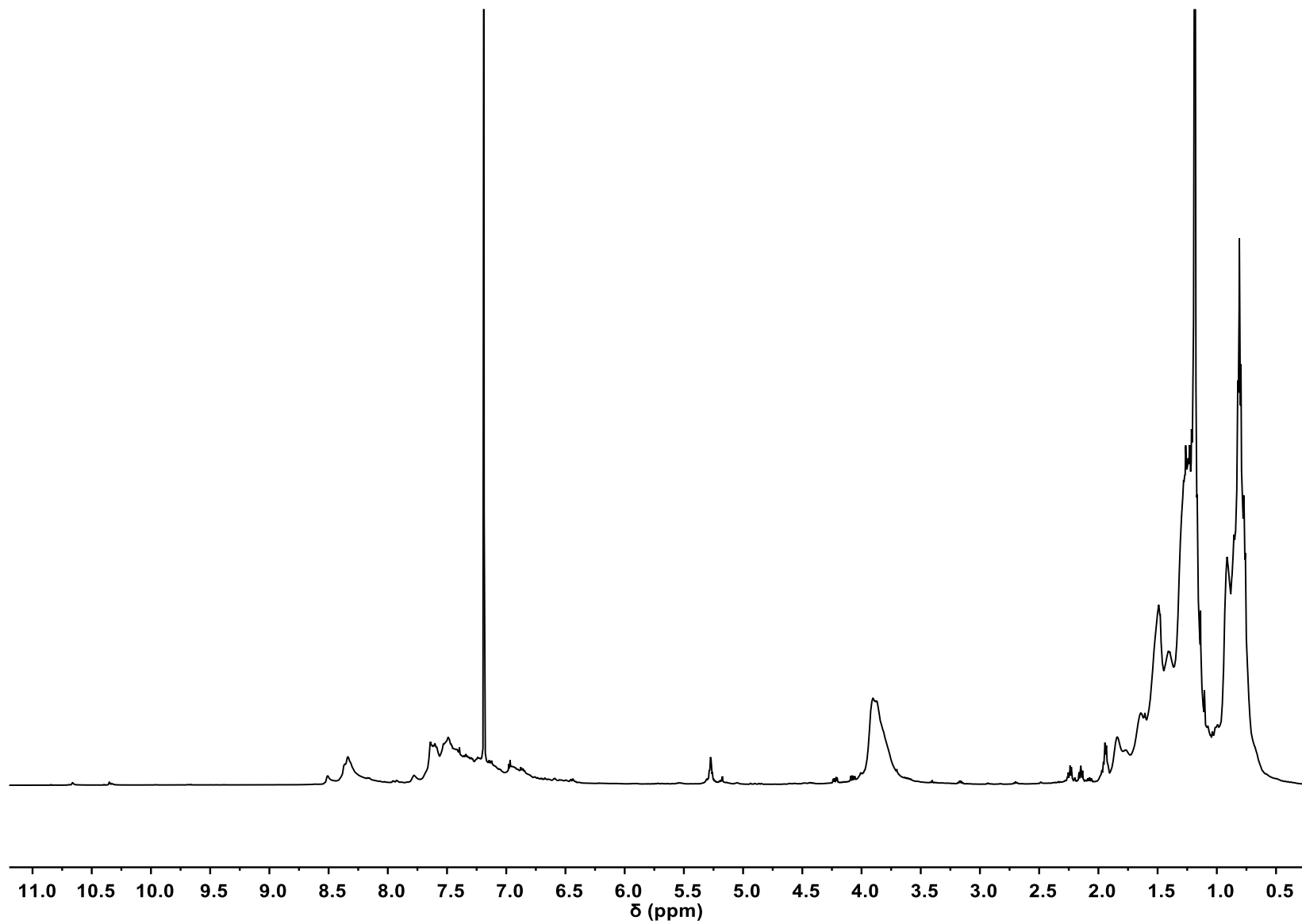
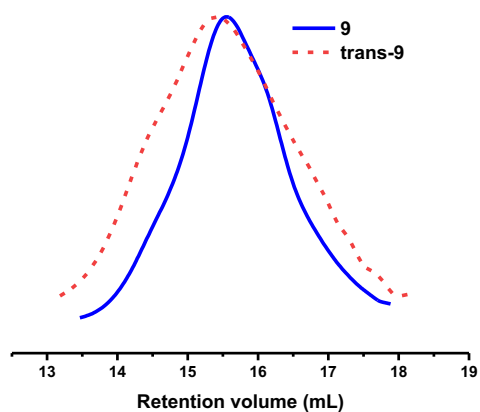


Figure S22 NMR spectrum of polymer *trans* 9 in CDCl₃.

S8 SEC traces



Polymers	$M_{n(cal)}$ (kD)	M_n (kD)	\mathcal{D}
9	5.2	5.8	1.56
<i>Trans-9</i>	5.2	8.4	1.89

Figure S23 SEC traces of **9** and *trans-9* in THF.

S9 Optical properties of polymers

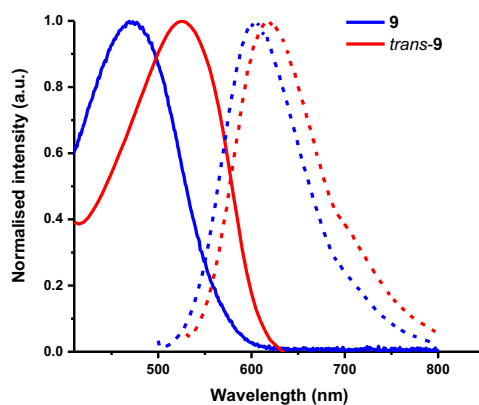


Figure S24 Absorption and emission profiles of copolymers **9** (Ex = 470 nm) and *trans-9* (Ex = 520 nm) in CHCl_3 solution.

Table S1: UV-vis and PL data of polymer **9** in chloroform solution.

Polymers	$\lambda_{\max(abs.)}$	$\lambda_{(excit.)}$	$\lambda_{\max(PL)}$	E_g (eV) ^a
9	479	470	605	2.15
<i>Trans-9</i>	530	520	621	2.03

a. $E_g = 1240 / \lambda_{onset}$

S10 Electrochemical properties of polymers

Table S2 Electrochemical properties of polymer **9** in solid state.

Polymers	[O] _{onset} (V)	[R] _{onset} (V)	HOMO (eV) ^a	LUMO (eV) ^a	E _g (eV) ^b
9	0.71	-1.22	5.42	3.49	1.93
<i>Trans-9</i>	0.35	-1.52	5.06	3.19	1.87

a. HOMO = (E_{ox}^{onset} - F_{Cox}) + 4.8, LUMO = (E_{red}^{onset} - F_{Cox}) + 4.8, b. E_g (elc.) = HOMO - LUMO

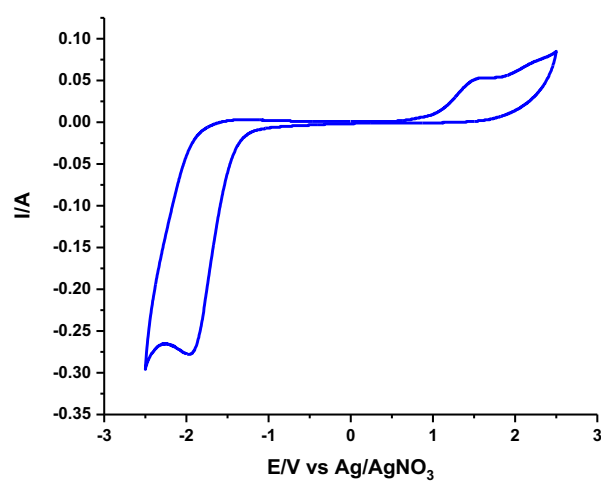


Figure S25 Cyclic voltammograms for **9** on a Pt electrode in an acetonitrile solution containing 0.1 M *n*-Bu₄NPF₆.

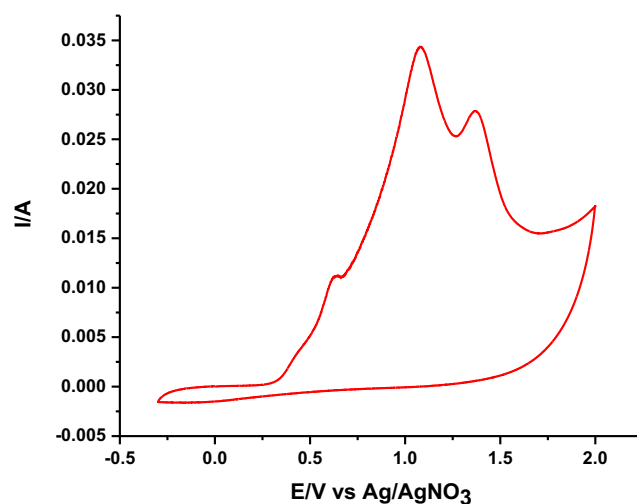


Figure S26 Cyclic voltammograms of irreversible oxidation *trans-9* on a Pt electrode in an acetonitrile solution containing 0.1 M *n*-Bu₄NPF₆

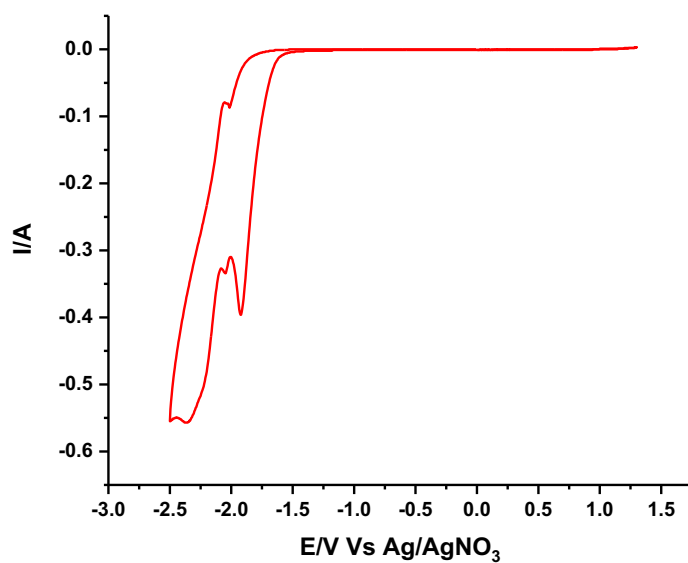


Figure S27 Cyclic voltammograms of irreversible reduction *trans*-**9** on a Pt electrode in an acetonitrile solution containing 0.1 M *n*-Bu₄NPF₆

S11 References

- 1 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.