

Supplementary Information

Alkyl Substituted Poly(*p*-phenylene vinylene)s by Ring Opening Metathesis Polymerisation

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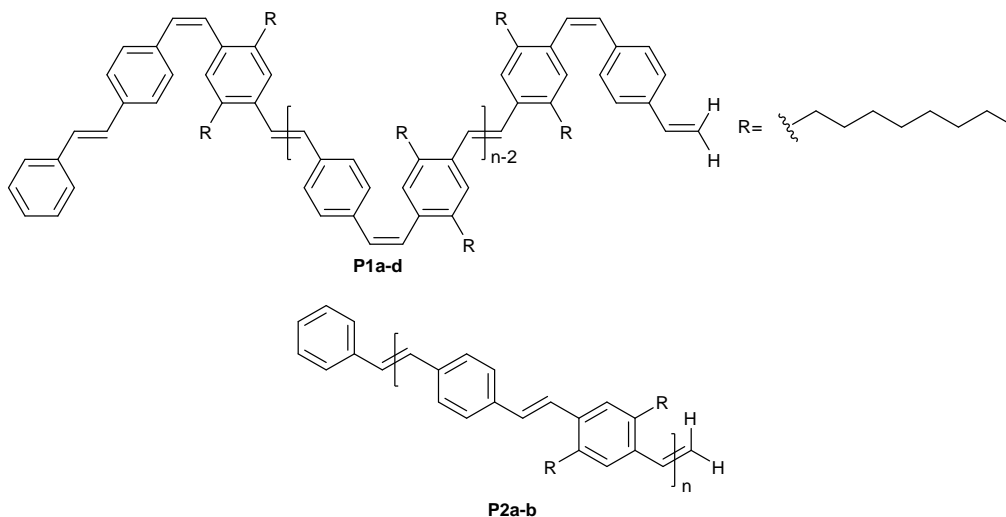
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1. General Procedures

Nuclear magnetic resonance (NMR) spectra were obtained on Bruker spectrometers operating at either 400 or 500 MHz, for ^1H nuclei. Chemical shifts are reported in ppm relative to the indicated residual solvent (^1H NMR spectroscopy: 7.26 ppm for D-chloroform, 7.16 ppm for D_6 -benzene). MALDI-TOF-MS was carried out using a Shimadzu Biotech AXIMA Confidence MALDI mass spectrometer in linear (positive) mode. Calibration was conducted against poly(propylene glycol) ($M_n = 4.0 \text{ kg mol}^{-1}$) (**P1a** and **P3a**) or Polymer Factory SpheriCal[®] MALDI-TOF-MS calibration standards (series of four monodisperse dendrimers in mass range 1716.82-3424.63 Da) (**P4**). 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}). Fourier transform-infrared (FT-IR) spectroscopy was conducted using a Nicolet iS5 (Thermo Scientific) with iD5 attenuated total reflection accessory. Gel permeation chromatography (GPC) was carried out in THF using a Viscotek GPCmax VE2001 solvent/sample module with 2 \times PL gel 10 μm MIXED-B + 1 \times PL gel 500A columns, a Viscotek VE3580 RI detector. The system was calibrated with narrow D_m PS standards with M_n between 0.2-1.8 $\times 10^3 \text{ kg mol}^{-1}$ (Polymer Laboratories). The eluent was THF at 40 $^\circ\text{C}$, with a flow rate of 1 mL min^{-1} . The analysed samples contained *n*-dodecane as flow marker. UV-Vis absorption spectra and photoluminescence spectra were recorded in chloroform on Varian Cary 5000 UV-Vis-NIR and Cary Eclipse Fluorescence Spectrophotometers. THF was freshly distilled over sodium/benzophenone and deoxygenated by freeze-pump-thaw (minimum of three cycles). 2nd Generation Grubbs Catalyst (**G2**) was obtained from Sigma-Aldrich and used as received. 3rd Generation Grubbs Catalyst (**G3**) was prepared by the procedure of Grubbs *et al.*, by the reaction of **G2** with an excess of 3-bromopyridine.¹ Ethyl vinyl ether was obtained from Sigma-Aldrich and deoxygenated by purging with argon for 2 hours.

2. Synthesis of *cis/trans*-vinylene Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (**P1a-d**) and *trans*-vinylene Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (**P2a-b**)



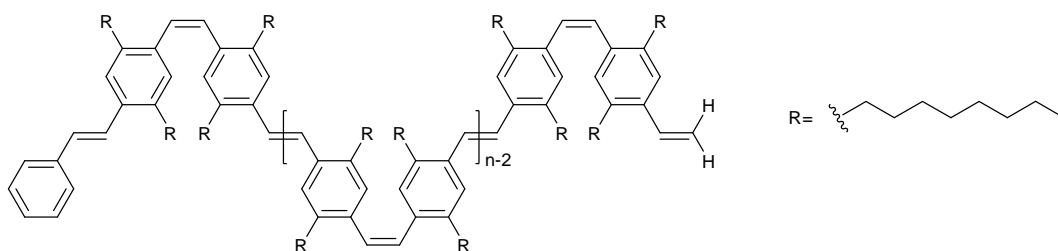
General procedure for synthesis of polymers P1a-d: In an argon filled glovebox cyclophanediene **M1** and **G3** were added to a vial with a stirrer bar, followed by deoxygenated, anhydrous THF ($[\mathbf{M1}]_{\text{I}} = [0.1]_{\text{I}}$). The vial was sealed, removed from the glovebox, wrapped in foil and mixed at room temperature for 10 minutes. The reaction was placed in a preheated oil bath at 40 °C and stirred until complete monomer conversion. The reaction was cooled to room temperature and deoxygenated ethyl vinyl ether was added and stirred at room temperature for 2 hours. The reaction was precipitated into a short methanol/Celite column, washed with methanol and the polymer extracted with chloroform. After evaporation of the solvent polymers **P1a-d** were isolated as green films.

General procedure for photoisomerisation of polymers P1a-b: Polymers **P1a-b** (**P1a**; 21 mg and **P1b**; 18 mg) were dissolved in deoxygenated THF (**P1a**; 14 mL and **P1b**; 14 mL) in an argon filled glovebox. The vial was sealed, removed from the glovebox and irradiated with $\lambda = 365$ nm for 24 hours. After evaporation of the solvent polymers **P2a-b** were isolated as green films (**P2a**; 19 mg, 91% and **P2b**; 15 mg, 83%).

Quantities of reagents used:

Polymer	[M1]/[G3]	M1	G3	THF	Reaction Time	Yield
P1a	10	32 mg, 75 μmol	6.6 mg, 7.5 μmol	0.75 mL	1.5 hours	27 mg, 82%
P1b	20	46 mg, 107 μmol	4.8 mg, 5.4 μmol	1.10 mL	2 hours	42 mg, 89%
P1c	30	49 mg, 114 μmol	3.4 mg, 3.8 μmol	1.14 mL	4 hours	41 mg, 84%
P1d	40	54 mg, 126 μmol	2.8 mg, 2.6 μmol	1.26 mL	4 hours	47 mg, 87%

3. Synthesis of *cis/trans*-vinylene Poly(2,5-dioctyl-*p*-phenylenevinylene)s (P3a-c)

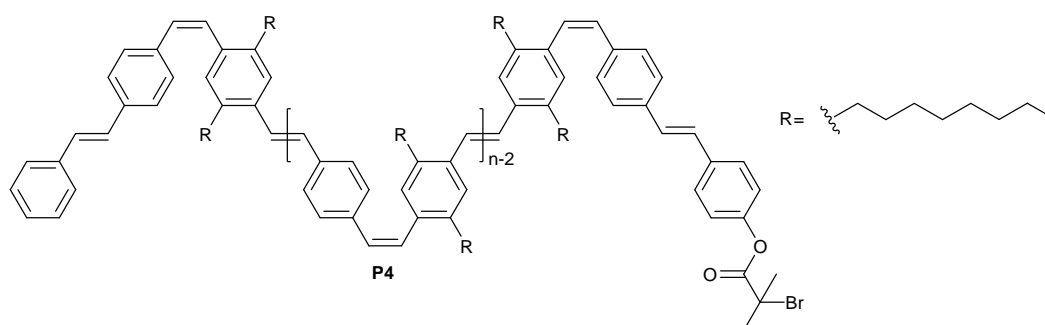


General procedure for the syntheses of polymers P3a-c: In an argon filled glovebox mixture of cyclophanedienes **M2** and **M3**, and **G3** were added to a vial with a stirrer bar, followed by deoxygenated anhydrous THF ($[\text{M2}]_{\text{I}} = [0.1]_{\text{I}}$). The vial was sealed, removed from the glovebox, wrapped in foil and mixed at room temperature for 10 minutes. The reaction was placed in a preheated oil bath at 40 °C and stirred until complete monomer conversion. After which the reaction was cooled to room temperature and deoxygenated ethyl vinyl ether was added and stirred at room temperature 2 hours. The reaction was precipitated by adding acetone, then poured onto a short Celite column, washed with acetone and the polymers extracted with hot chloroform. After evaporation of the solvent the polymers were isolated as green films.

Quantities of reagents used:

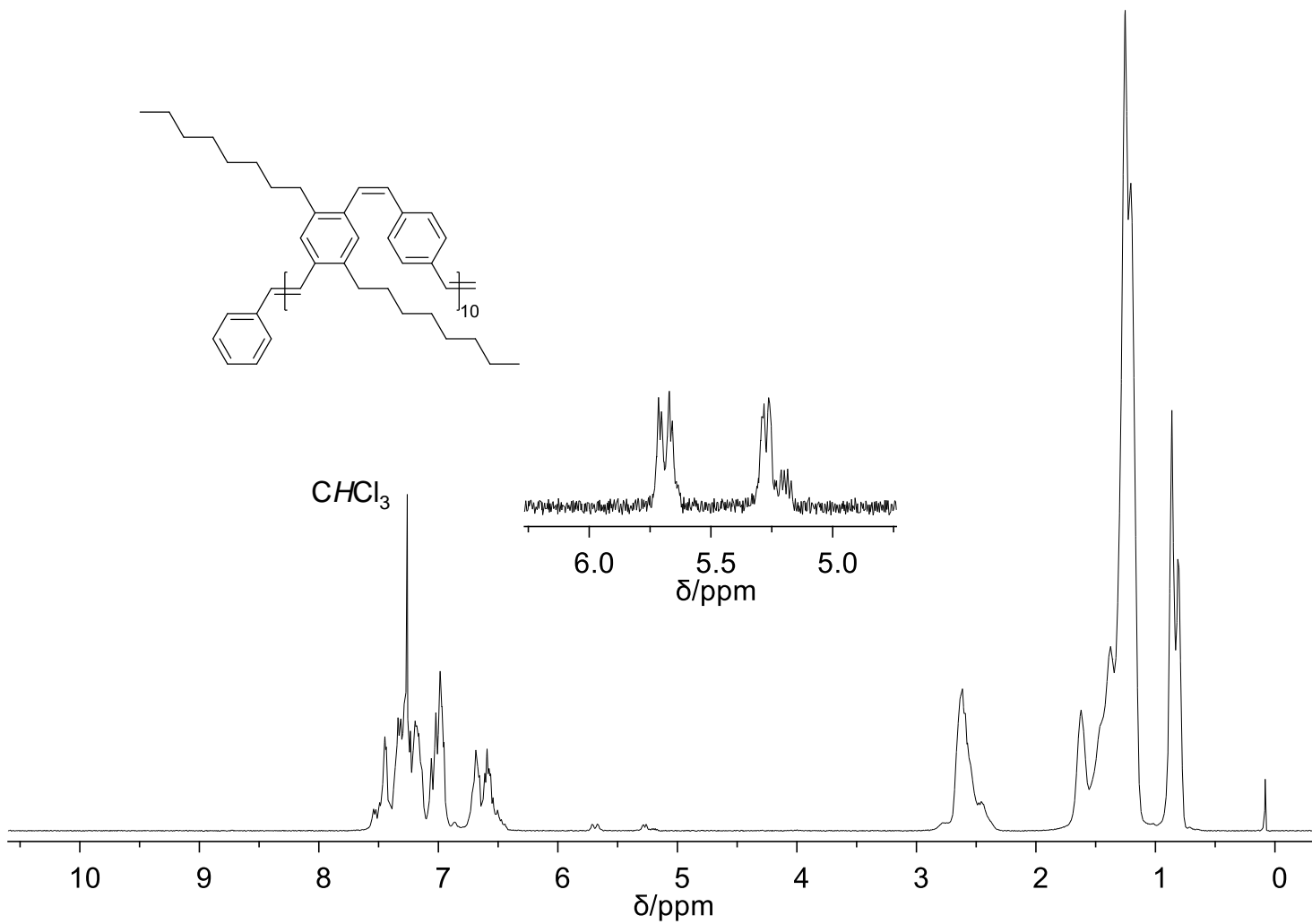
Polymer	[M2]/[G3]	Mixture of M2 and M3	G3	THF	Reaction time	Yield
P3a	10	101 mg (17.2 mg, 26.3 μ mol)	2.3 mg, 2.6 μ mol	0.26 mL	4 hours	11 mg, 63%
P3b	20	211 mg (35.9 mg, 54.9 μ mol)	2.4 mg, 2.8 μ mol	0.55 mL	6 hours	21 mg, 58%
P3c	30	212 mg, (36.0 mg, 55.2 μ mol)	1.6 mg, 1.8 μ mol	0.55 mL	8 hours	28 mg, 78%

4. Synthesis of α -Bromoester Functionalised Monotelechelic Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (**P4**)

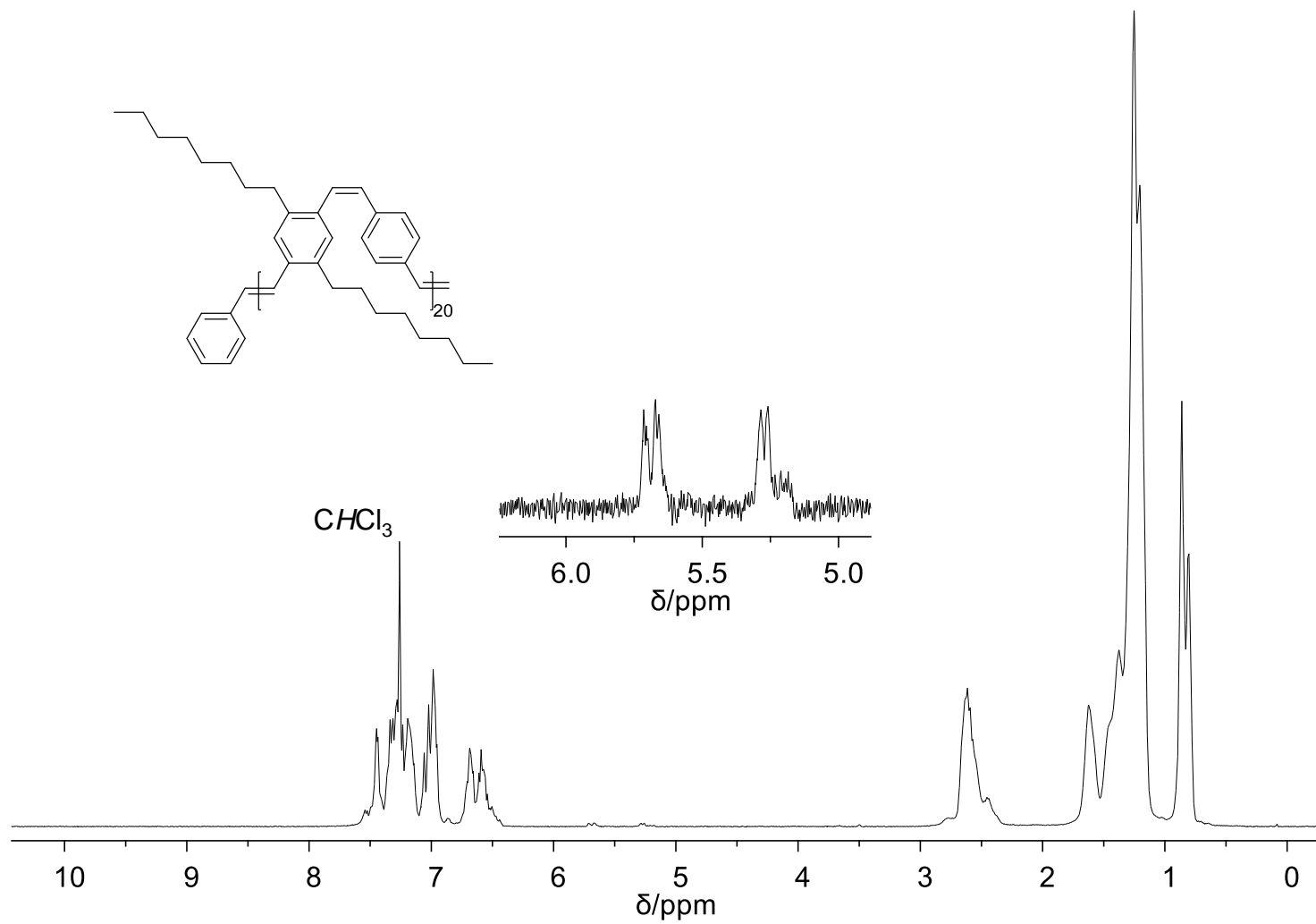


In an argon filled glovebox **M1** (30 mg, 70 μ mol) and **G3** (6.2 mg, 7.0 μ mol) were added to a vial and dissolved in deoxygenated anhydrous THF ($[\mathbf{M1}] = [0.1]$, 0.70 mL). The vial was sealed, removed from the glovebox, wrapped in foil and mixed at room temperature for 10 minutes. The solution was placed in a preheated oil bath at 40 °C and stirred for 3 hours. The reaction was cooled to room temperature, transferred back to the glovebox and quenched with 4-[(*E/Z*)-2-methoxyvinyl]phenyl-2-bromoisobutyrate (41.9 mg, 140 μ mol). The vial was sealed, removed from the glovebox, wrapped in foil and stirred for an additional 24 hours at 40 °C. The reaction was cooled to room temperature, precipitated into a short methanol/Celite column, washed with methanol and the polymer extracted with hot chloroform. The procedure was repeated once further and after evaporation of the solvent polymer **P4** was isolated as a green film (31 mg, 95%).

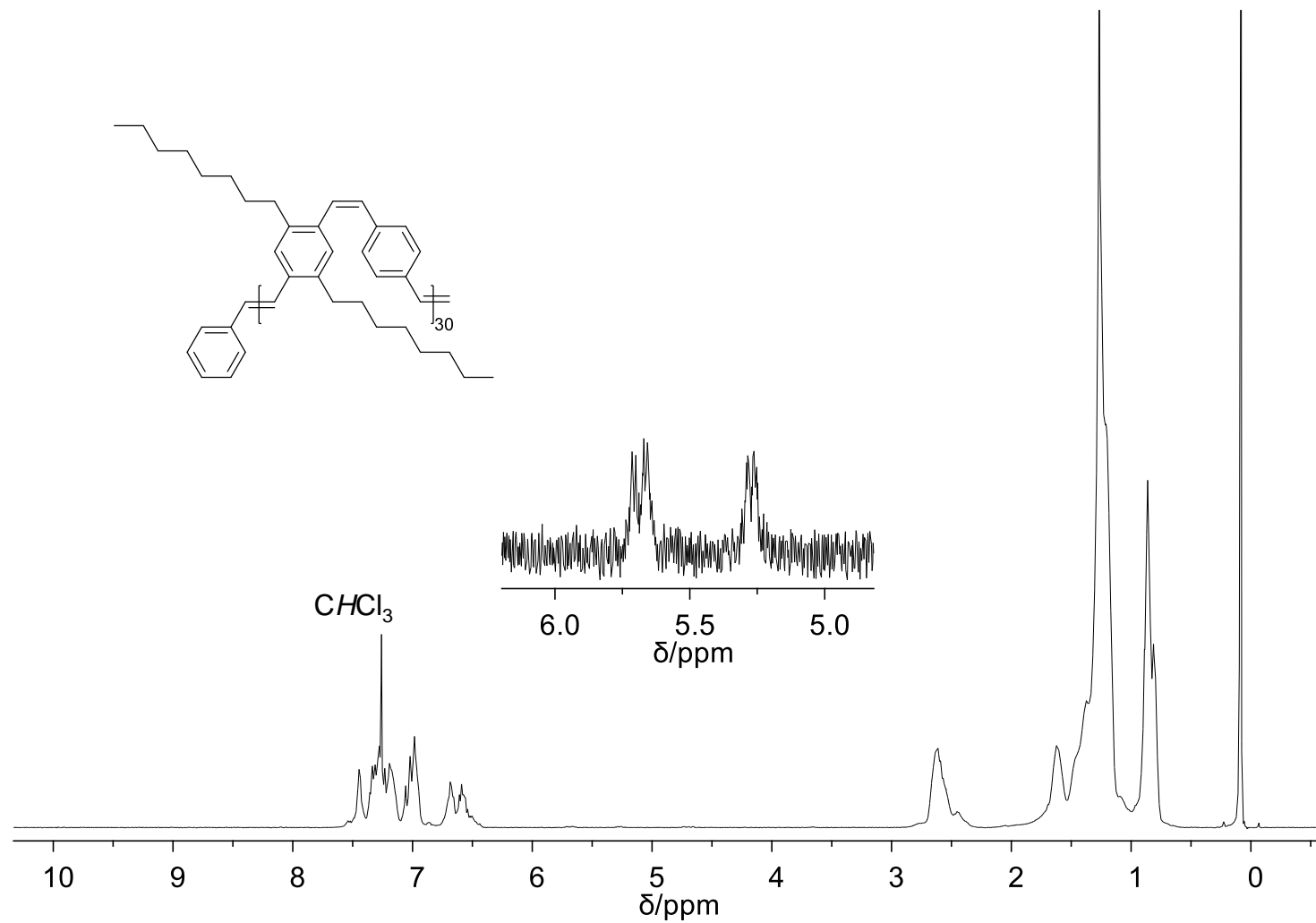
5. ^1H NMR (CDCl_3 , 400 MHz) of *cis/trans*-vinylene Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (P1a)



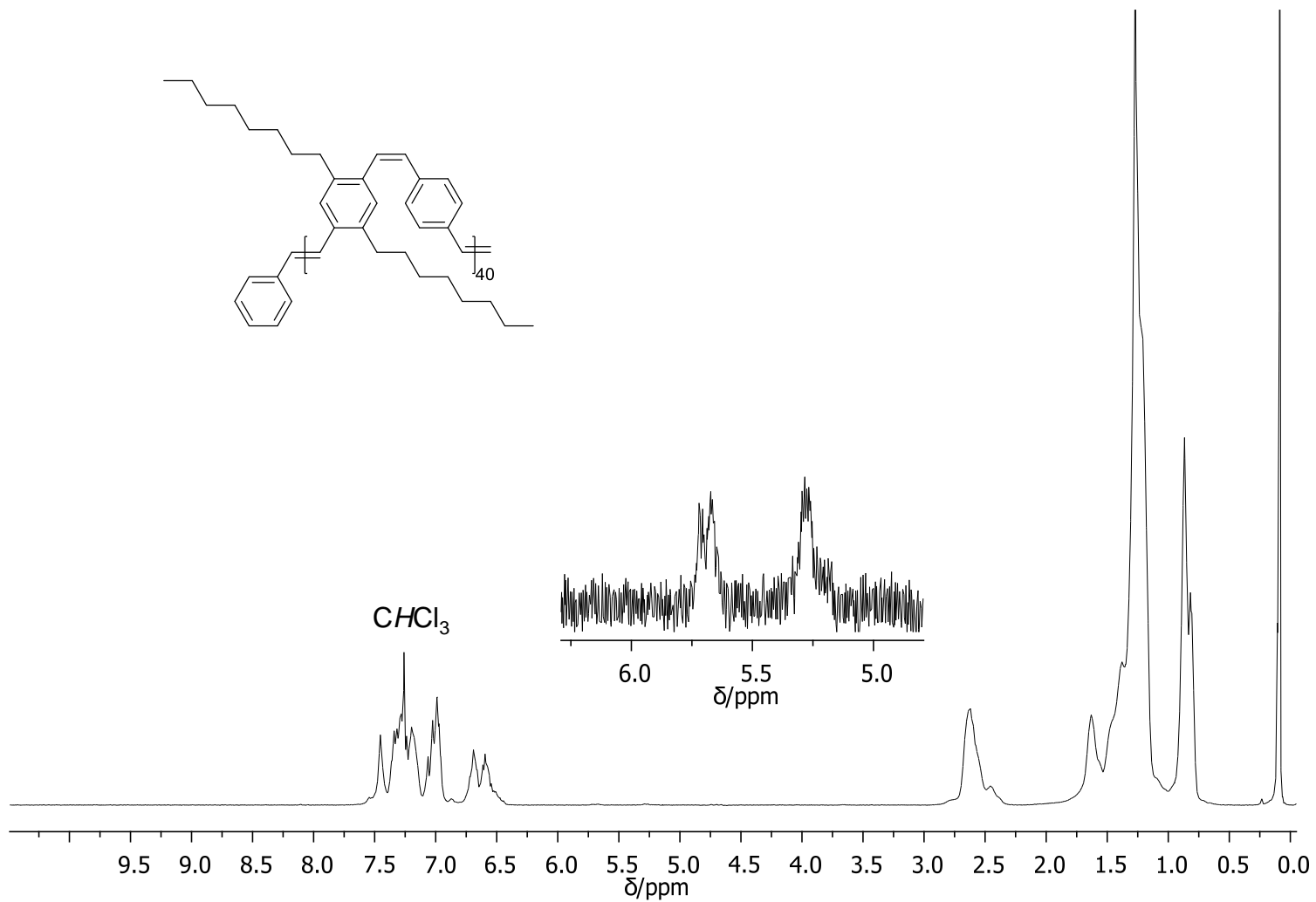
6. ^1H NMR (CDCl_3 , 400 MHz) of *cis/trans*-vinylene Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (P1b)



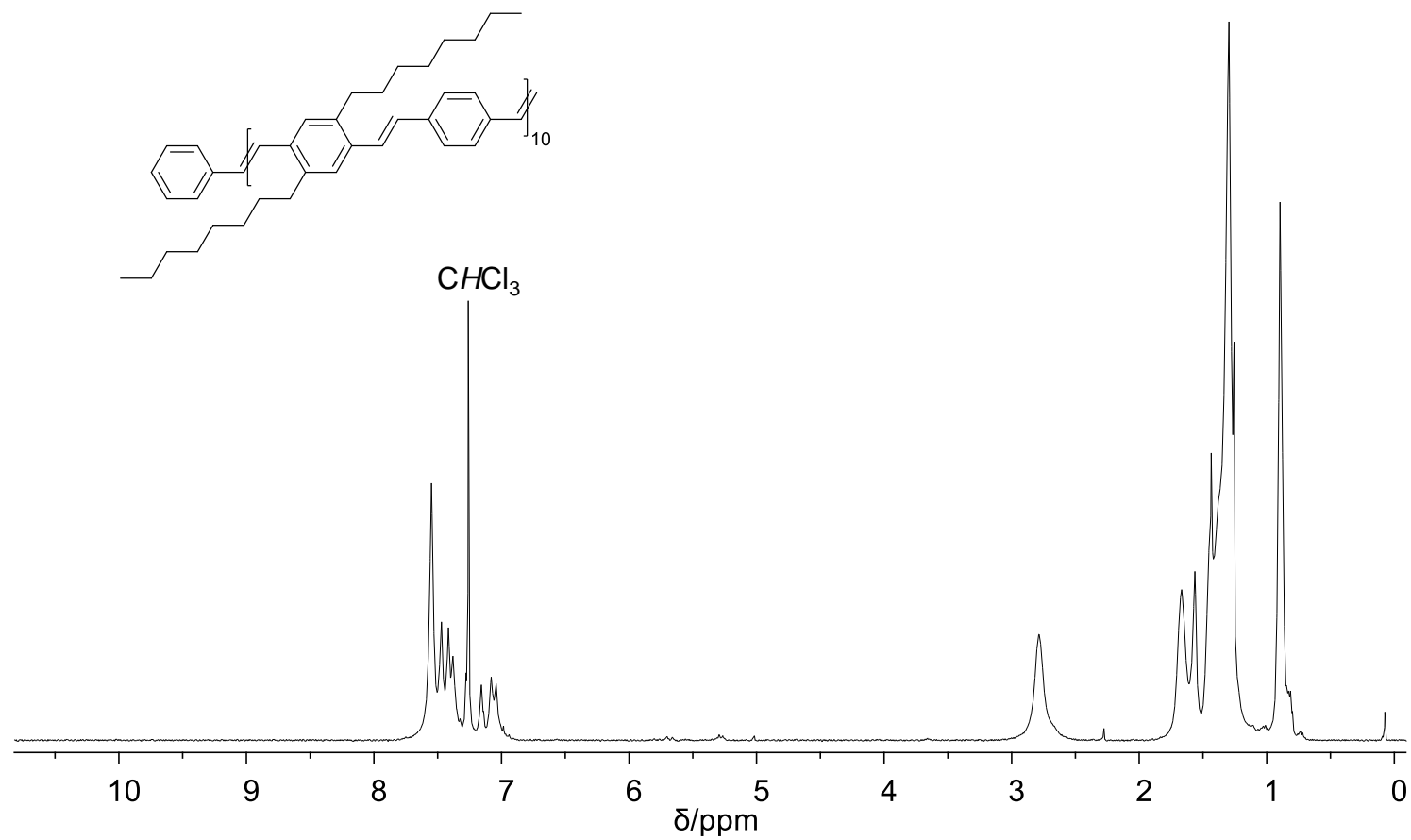
7. ^1H NMR (CDCl_3 , 400 MHz) of *cis/trans*-vinylene Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (P1c)



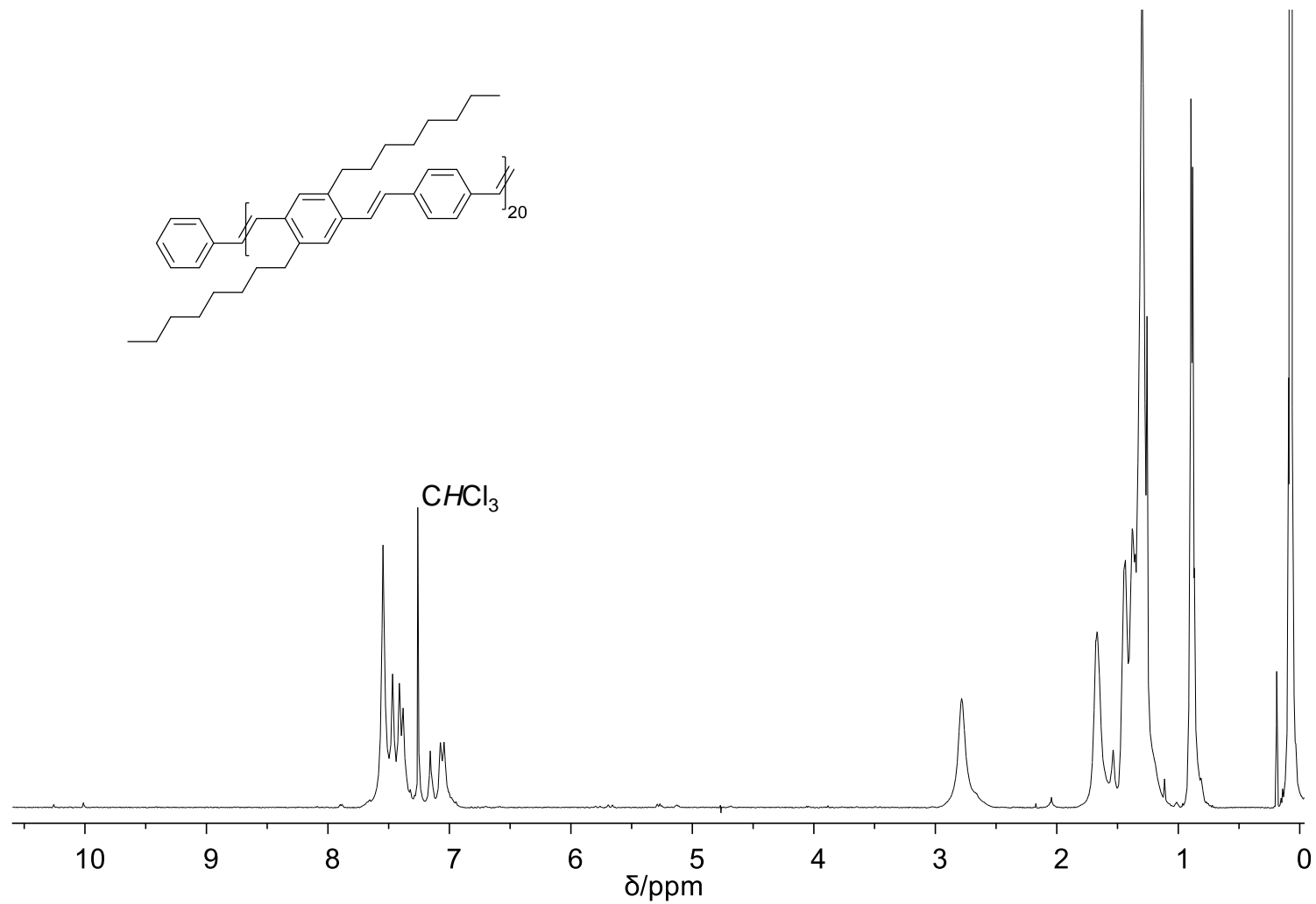
8. ^1H NMR (CDCl_3 , 400 MHz) of *cis/trans*-vinylene Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (P1d)



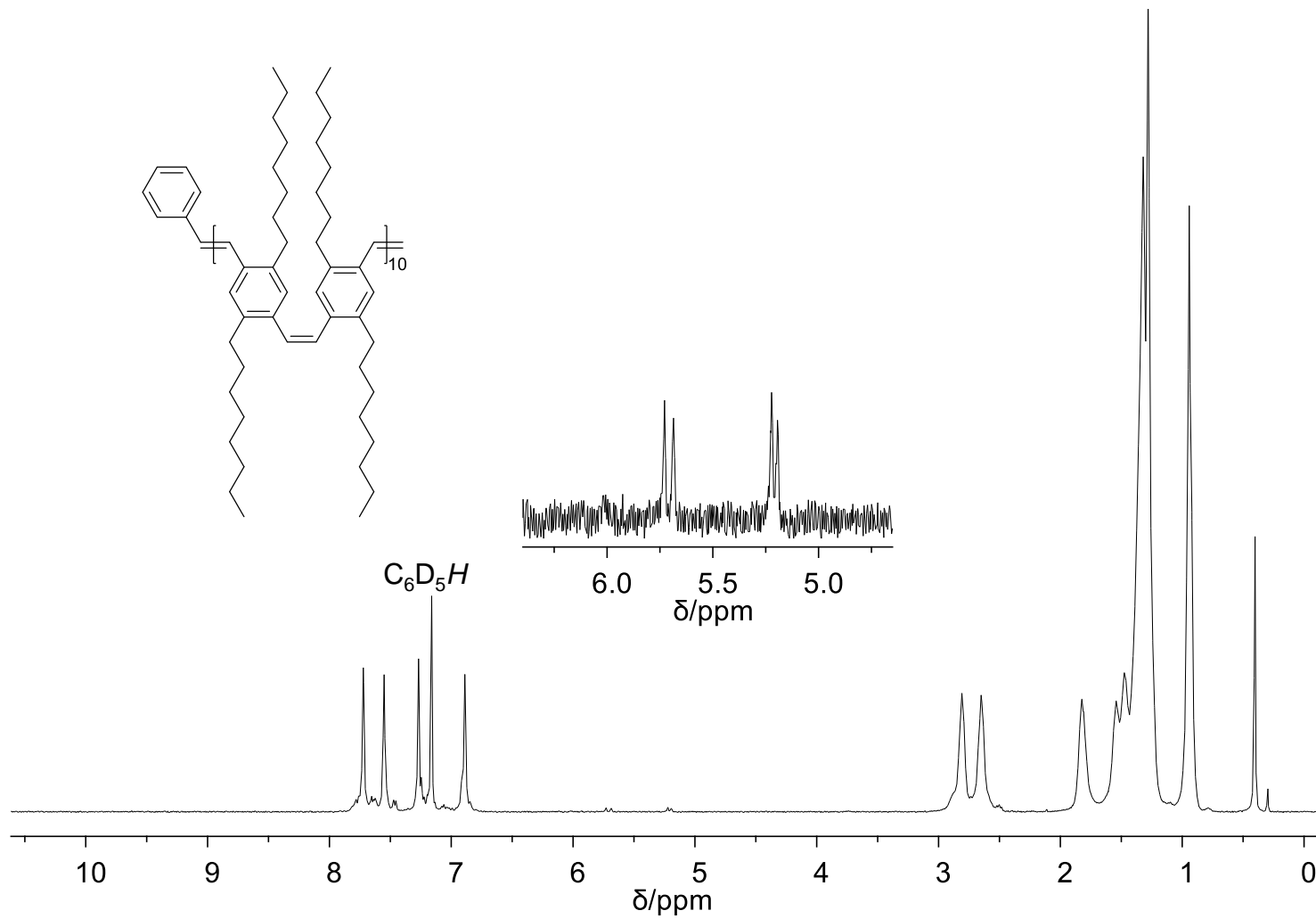
9. ^1H NMR (CDCl_3 , 400 MHz) of *trans*-vinylene Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (P2a)



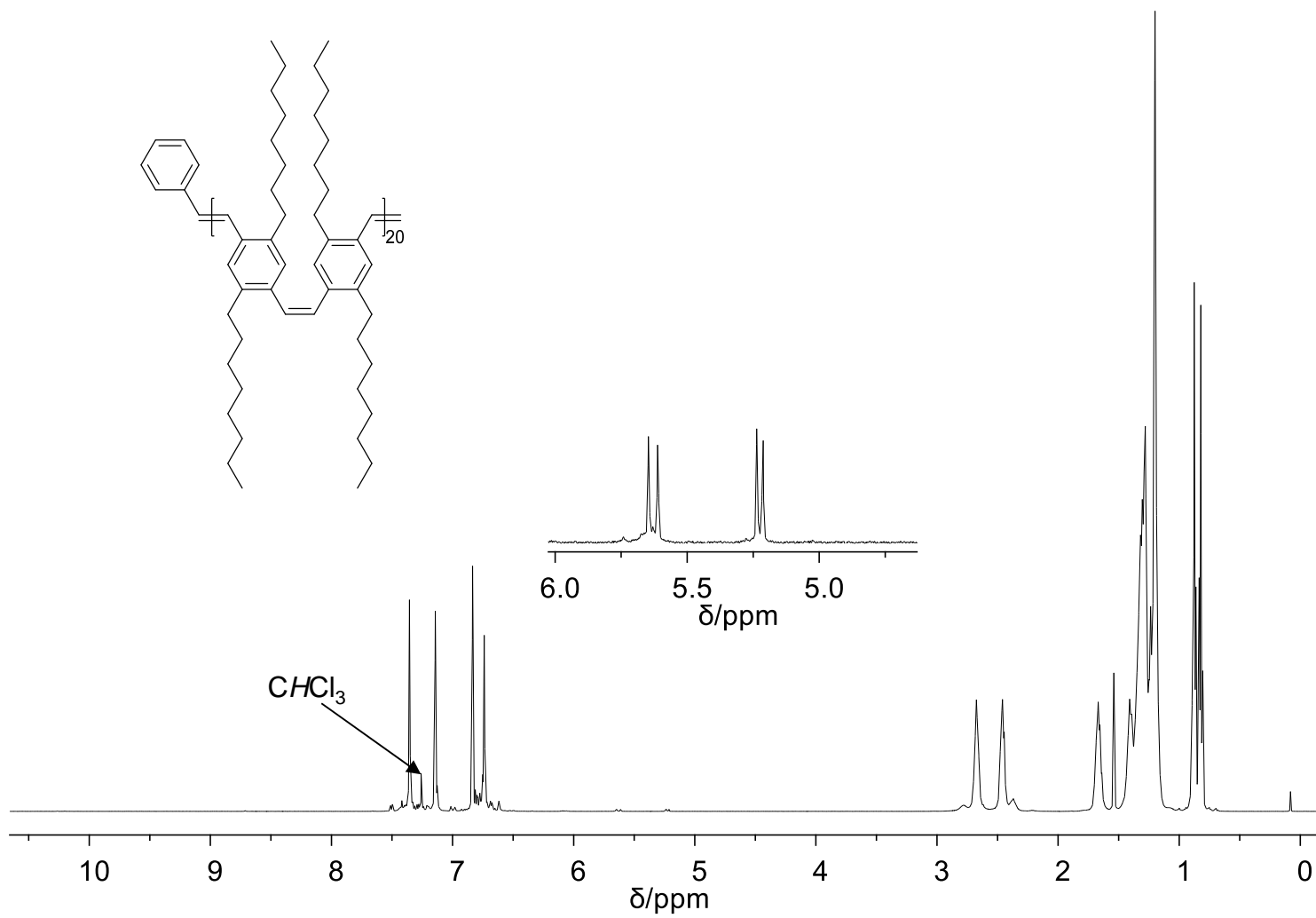
10. ^1H NMR (CDCl_3 , 500 MHz) of *trans*-vinylene Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (P2b)



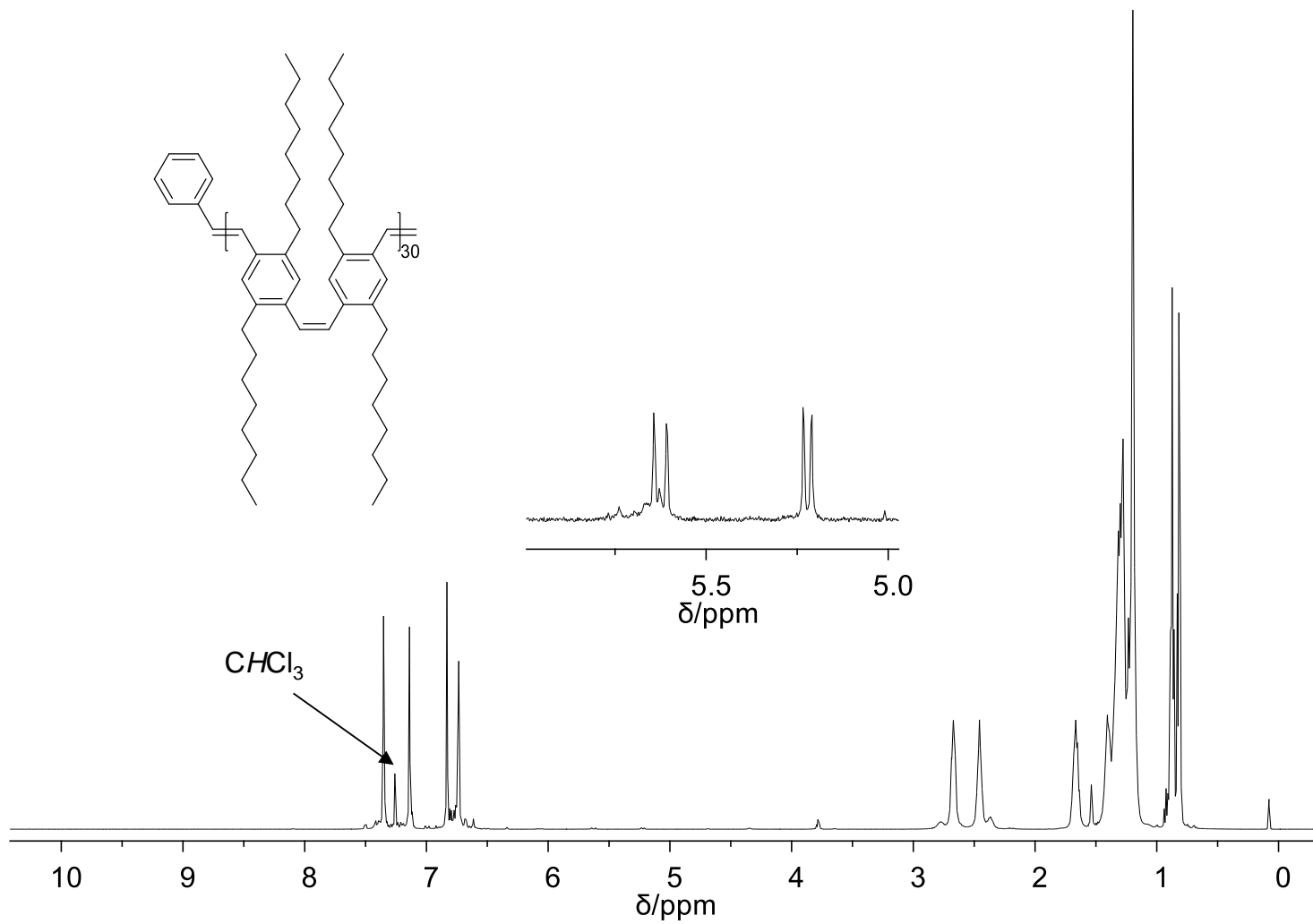
11. ^1H NMR (C_6D_6 , 400 MHz) of *cis/trans*-vinylene Poly(2,5-dioctyl-*p*-phenylenevinylene)s (P3a)



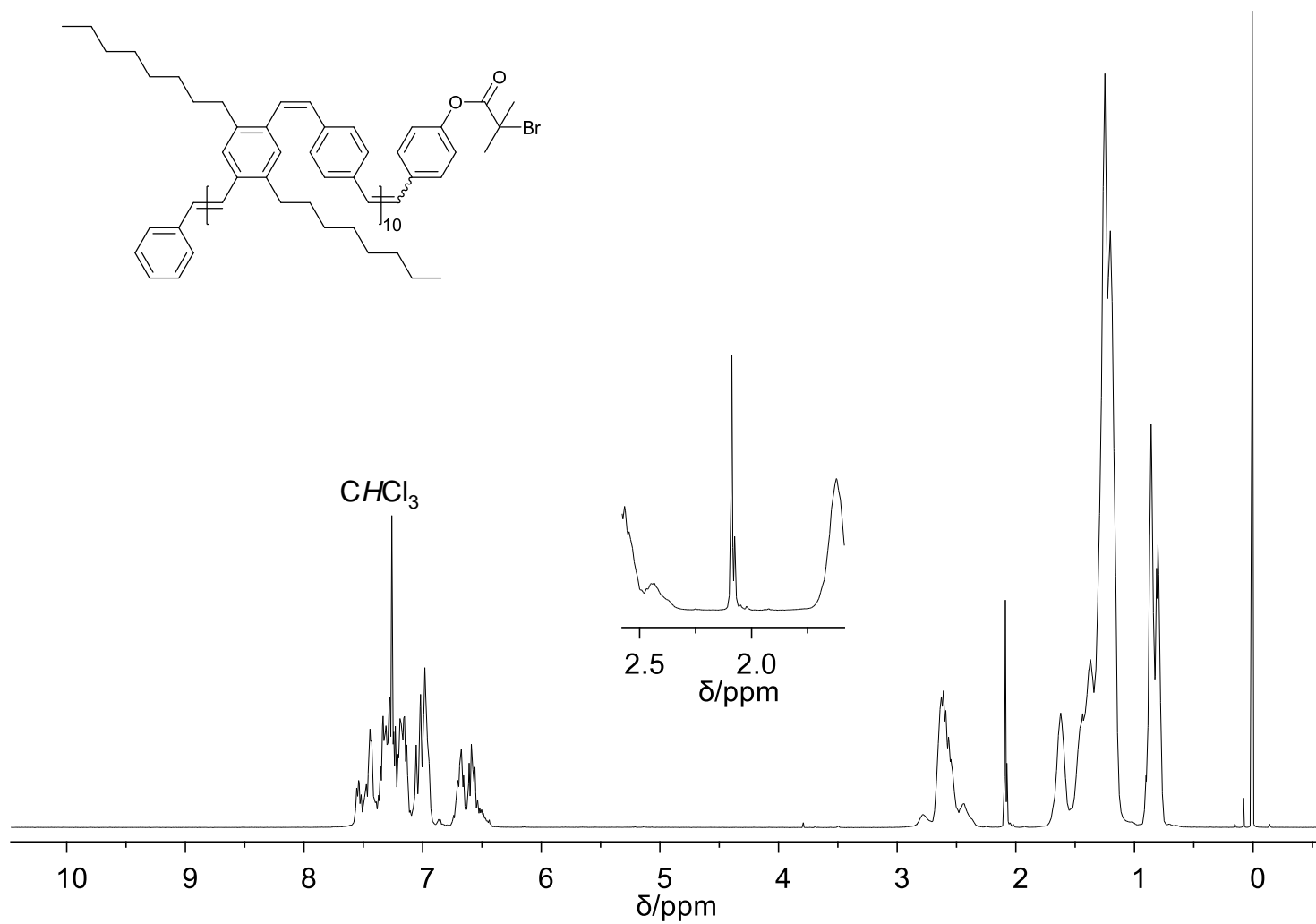
12. ^1H NMR (CDCl_3 , 500 MHz) of *cis/trans*-vinylene Poly(2,5-dioctyl-*p*-phenylenevinylene)s (P3b)



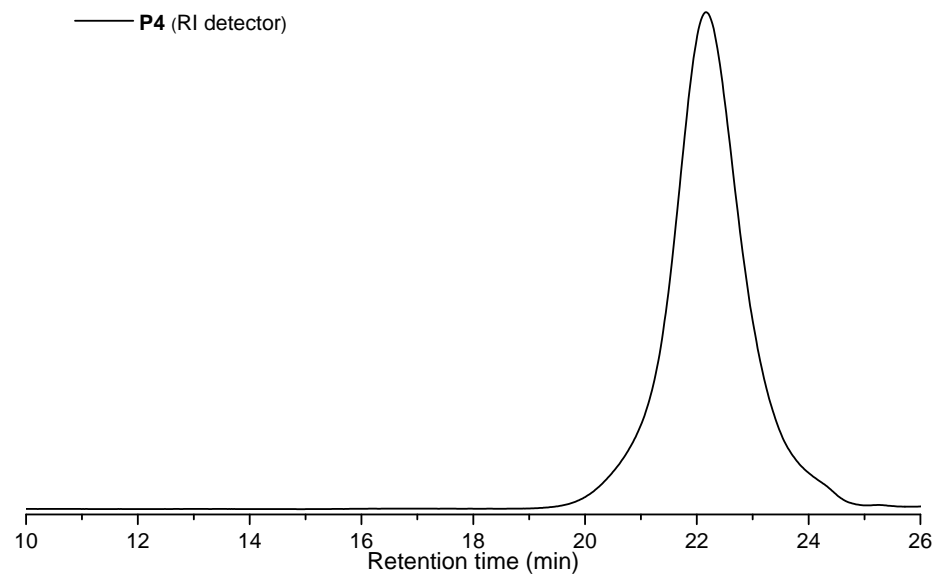
13. ^1H NMR (CDCl_3 , 500 MHz) of *cis/trans*-vinylene Poly(2,5-dioctyl-*p*-phenylenevinylene)s (P3c)



14. ^1H NMR (CDCl_3 , 400 MHz) of α -Bromoester Functionalised Monotelechelic Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (P4)



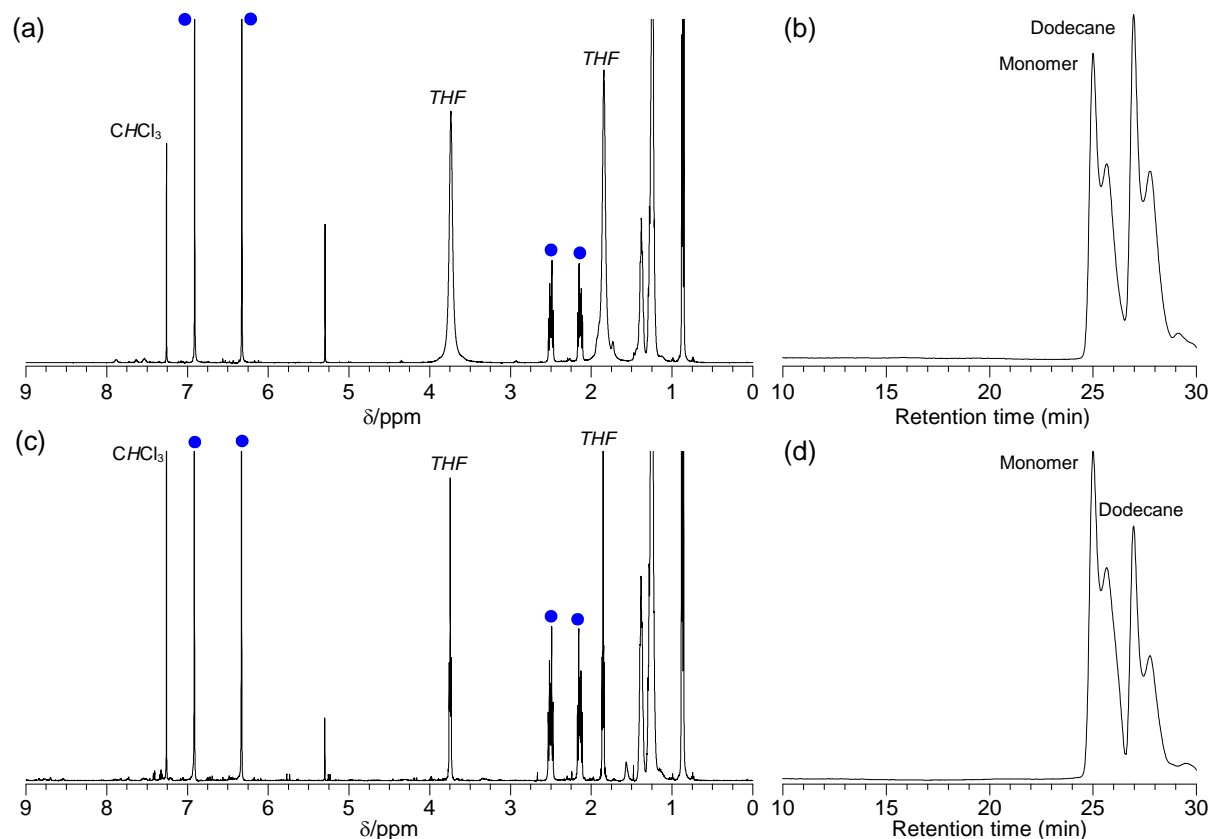
15. GPC Trace of α -Bromoester Functionalised Monotelechelic Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (P4)



$$M_n = 6.0 \text{ kg mol}^{-1}$$

$$D_m = 1.31$$

16. Reactivity of M3 with G3 and G2



Crude ¹H NMR spectra and GPC chromatograms; (a) & (b) attempted ROMP of **M3** (indicated with ●) with **G2** and (c) & (d) attempted ROMP of **M3** (indicated with ●) with **G3** complex.

17. Measurement of Photoluminescence Quantum Yields of *cis/trans*-vinylene Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (**P1a-d**), *trans*-vinylene Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (**P2a-b**), *cis/trans*-vinylene Poly(2,5-dioctyl-*p*-phenylenevinylene)s (**P3a-c**) and α -Bromoester Functionalised Monotelechelic Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s (**P4**)

Photoluminescence quantum yields (PLQYs) were measured in dilute solutions of the polymers (**P1a-d**, **P2a-b**, **P3a-c** and **P4**) in chloroform against quinine sulfate as a reference (in 0.1 M H₂SO₄ solution (PLQY = 0.52 at 25°C)).² Initially absorption spectra of each polymer sample were recorded in chloroform followed by fluorescence spectra, by exciting the polymers at 350 nm or 370 nm for polymers **P2a-b**. This process was repeated for five different concentrations for each sample, with the intensity of the absorption at 350 nm (370

nm for polymers **P2a-b**) kept under 0.1 to minimize the self-quenching and re-absorbance effect. PLQYs were calculated for each sample using Equation 1.

$$Q = Q_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2} \text{ (Equation 1)}$$

Q = quantum yield, I = integrated intensity, n = refractive index of the solvent, OD = optical density and the subscript R refers to the reference fluorophore (quinine sulfate).

Values for OD_R and I_R were obtained by measuring both the optical density at 350 nm (370 nm for polymers **P2a-b**) and the integrated fluorescence (360-685 nm, λ_{ex} = 350 nm and 380-685 nm, λ_{ex} = 370 nm for polymers **P2a-b**), with solutions of fluorescein at five different concentrations (optical densities between 0.01 and 0.1). Plotting of the optical density vs. the integrated fluorescence of the five solutions resulted in a linear gradient.

18. References

1. J. A. Love, J. P. Morgan, T. M. Trnka and R. H. Grubbs, *Angew. Chem.-Int. Edit.*, 2002, **41**, 4035-4037.
2. W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229-235.