Electronic Supplementary Material (ESI) for Polymer Chemistry.

Chiroptical and emissive properties of a calix[4]arene-containing chiral poly(*p*-phenyleneethynylene) with enantioselective recognition ability

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Electronic Supplementary Information

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Experimental section

Instruments and methods. Melting points were measured in sealed capillaries on a Büchi 530 apparatus and are reported uncorrected. Infrared spectra (FT-IR) were measured on a Bruker Vertex 70 as KBr pellets (transmission mode). ^{1}H NMR spectra were collected on Bruker AVANCE II$^+$ spectrometers (300 and 400 MHz) at 25ºC and reported chemical shifts (δ/ppm) are internally referenced to TMS. The splitting parameters for ^{1}H NMR are denoted as follows: s (singlet), d (doublet), t (triplet), dd (double doublet), m (multiplet), and b (broad). Elemental analysis was performed at the Laboratorio Análisis Instrumental (C.A.C.T.I.) of Universidad de Vigo. Analytical thin-layer chromatography (TLC) was performed on E. Merck kieselgel 60, F-254 silica-gel 0.2 mm thick plates and column chromatography was performed on E. Merck kieselgel 60 (230–400-µm) silica gel.

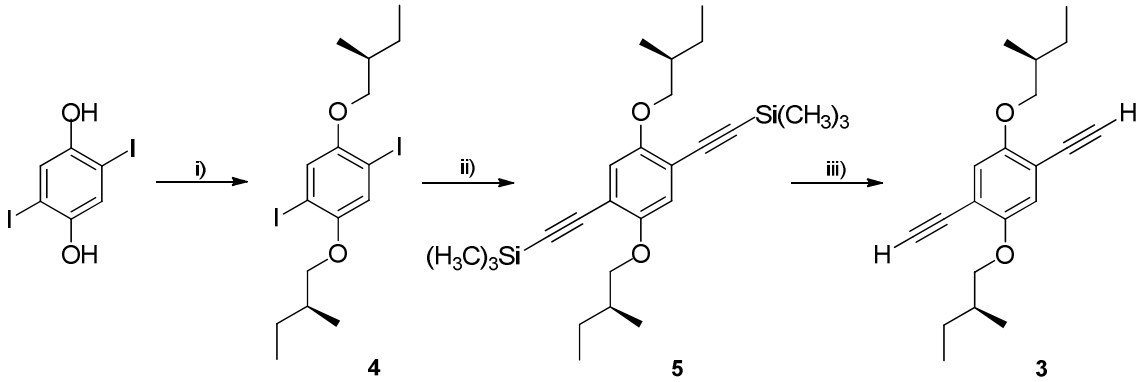
Materials. 2,5-Diiodo-1,4-hydroquinone was prepared by a literature procedure.[1] Dichlorobis(triphenylphosphine)palladium (II) (98%, Aldrich), copper(I) iodide (98%, Aldrich), ethynyltrimethylsilane (98%, Fluka), (*S*)-1-bromo-2-methylbutane (99%, Aldrich) were used as received. Triphenylphosphine (98%, Merck) was recrystallized from hexane; diethylamine (99%, Acros Organics) was previous dried from CaH_2 and distilled under N_2 prior to use; THF was pre-dried from Na and distilled from sodium/benzophenone; DMF was dried from BaO. Other reagents and solvents were reagent grade and were purified and dried by standard methods. Organic extracts were dried over anhydrous magnesium sulphate.

Synthesis. 1,4-Diiodo-2,5-bis(2-(*S*)-methylbutoxy)benzene (**4**). To a brown solution of 1,4-diiodo-2,5-hydroquinone (1.10 g, 3.04 mmol) in dry DMF (8.5 mL) was added K_2CO_3 (1.67 g, 12.08 mmol). The mixture was degassed and heated to 70ºC, followed by the addition of (*S*)-1-bromo-2-methylbutane (0.93 mL, 7.53 mmol) in dry DMF (0.95 mL). The resulting solution was stirred at this temperature under argon for 20h, after which the TLC ($CHCl_3$:hexane; 4:1) showed the completion of the reaction. DMF was removed by vacuum distillation, and the resulting residue dissolved in diethyl ether. The organic extract was washed with saturated aq. Na_2CO_3 and water and dried. Recrystalization from ethanol furnished a light brown solid in 32.0% (489 mg); mp 45º-46ºC; FTIR (ν/cm^{-1} (KBr)): 2959, 2931, 2916, 2874, 1487, 1463, 1353, 1215, 1057, 1014, 847, 795; ^{1}H NMR (δ/ppm; CD_2Cl_2, 300 MHz): 0.95 (t, *J*=7.5 Hz, 6H, -$OCH_2CH(CH_3)CH_2CH_3$), 1.06 (d, *J*=6.7 Hz, 6H, -$OCH_2CH(CH_3)CH_2CH_3$), 1.23-1.41 (m, 2H, -$OCH_2CH(CH_3)CHHCH_3$), 1.51-1.68 (m, 2H, -$OCH_2CH(CH_3)CHHCH_3$), 1.78-1.96 (m, 2H, -$OCH_2CH(CH_3)CH_2CH_3$), 3.72 (dd, *J*=8.8, *J*=6.4 Hz, 2H, -$OCHHCH(CH_3)CH_2CH_3$), 3.80 (dd,

J=8.8, *J*=5.7 Hz, 2H, -OCH*H*CH(CH_3)CH_2CH_3), 7.19 (s, 2H, Ar*H*). Anal. calcd. for $C_{16}H_{24}I_2O_2$: C, 38.27; H, 4.82%; found: C, 38.38; H, 4.85%.

((2,5-Bis((*S*)-2-methylbutoxy)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (**5**).[2] To a solution of **4** (450 mg, 0.90 mmol) in THF/$NHEt_2$ (3.8 mL/11.6 mL) were added $PdCl_2(PPh_3)_2$ (30 mg, 0.043 mmol), CuI (16 mg, 0.084 mmol), PPh_3 (22 mg, 0.084 mmol), and ethynyltrimethylsilane (0.30 mL, 2.1 mmol). The greenish solution was heated at 50ºC for 24h under argon. TLC control ($CHCl_3$:hexane; 1:2) revealed the reaction's completion. Solvents were removed and the residue taken in CH_2Cl_2. After successive washings with saturated aq. NH_4Cl, aq. $NaHSO_3$ (0.1M), aq. NH_4SCN (10%), and water, the organic phase was dried and evaporated to dryness. The residue was passed through a short silica column ($CHCl_3$:hexane; 1:2) and further recrystallized from $CHCl_3$:MeOH, yielding a slight yellowish solid in 40.2% (160 mg); mp 102-104ºC (mp lit.[3] 109 ºC); FTIR (ν/cm^{-1} (KBr)): 2962, 2931, 2922, 2878, 2154, 1500, 1464, 1408, 1390, 1250, 1226, 1207, 1041, 894, 844, 760; ^{1}H NMR (δ /ppm; $CDCl_3$, 400 MHz): 0.25 (s, 18H, -Si(C*H*$_3$)$_3$), 0.95 (t, *J*=7.5 Hz, 6H, -$OCH_2CH(CH_3)CH_2CH_3$), 1.04 (d, *J*=6.8 Hz, 6H, -$OCH_2CH(CH_3)CH_2CH_3$), 1.22-1.36 (m, 2H, -$OCH_2CH(CH_3)CHHCH_3$), 1.51-1.68 (m, 2H, -$OCH_2CH(CH_3)CHHCH_3$), 1.80-1.94 (m, 2H, -$OCH_2CH(CH_3)CH_2CH_3$), 3.74 (dd, *J*=8.7, *J*=6.3 Hz, 2H, -OC*H*HCH(CH_3)CH_2CH_3), 3.80 (dd, *J*=8.7, *J*=6.1 Hz, 2H, -OCH*H*CH(CH_3)CH_2CH_3), 6.88 (s, 2H, Ar*H*).

1,4-diethynyl-2,5-bis((*S*)-2-methylbutoxy)benzene (**3**).[3] To a solution of **5** (146 mg, 0.33 mmol) in THF (5.8 mL) was added aq. KOH (0.06 mL, at 20%) in MeOH (2.9 mL). The mixture was stirred under argon at rt for 5h, after which TLC ($CHCl_3$:hexane; 1:1) indicated the reaction's completion. MeOH (3 mL) was then added, the mixture filtered, and the filtrate evaporated. The title compound was obtained in 59.3% (58.4 mg), after passing through a short silica column ($CHCl_3$:MeOH; 1:3); mp 64º-65ºC; FTIR (ν/cm^{-1} (KBr)): 3270, 3254, 2958, 2930, 2875, 2106, 1495, 1465, 1408, 1383, 1271, 1220, 1199, 1035, 865, 837; ^{1}H NMR (δ/ppm; $CDCl_3$, 400 MHz): 0.95 (t, *J*=7.5 Hz, 6H, -$OCH_2CH(CH_3)CH_2CH_3$), 1.03 (d, *J*=6.7 Hz, 6H, -$OCH_2CH(CH_3)CH_2CH_3$), 1.21-1.35 (m, 2H, -$OCH_2CH(CH_3)CHHCH_3$), 1.50-1.66 (m, 2H, -$OCH_2CH(CH_3)CHHCH_3$), 1.82-1.97 (m, 2H, -$OCH_2CH(CH_3)CH_2CH_3$), 3.32 (s, 2H, -C≡C-*H*), 3.74 (dd, *J*=9.0, *J*=6.7 Hz, 2H, -OC*H*HCH(CH_3)CH_2CH_3), 3.83 (dd, *J*=9.0, *J*=6.0 Hz, 2H, -OCH*H*CH(CH_3)CH_2CH_3), 6.94 (s, 2H, Ar*H*).



Scheme S1. Synthesis of 1,4-diethynyl-2,5-bis((*S*)-2-methylbutoxy)benzene (**3**): i) (*S*)-1-bromo-2-methylbutane, K_2CO_3, DMF, 70ºC, 20h, 32%; ii) $PdCl_2(PPh_3)_2$, CuI, PPh_3, ethynyltrimethylsilane, diethylamine/THF, 50ºC, 24h, 40%; iii) KOH (20% aq.), THF/MeOH, rt, 5h, 59%.

Fitting procedure for the titration experiments. In the titration, polymer at fixed concentration $[P]_0$ is added with increasing amounts of amine, whose total concentration is $[A]_0$. In all steps, the concentrations of free polymer and amine are $[P]$ and $[A]$ respectively, and that of their 1:1 complex is $[AP]$. They are related through the dissociation constant by:

$$K_d = \frac{[A][P]}{[AP]}$$

Rearranging the expression of the dissociation constant, and using the mass equations, the fractional saturation Y, that is, the moles of amine bound per mole of the polymer, is equal to:

$$Y = \frac{[AP]}{[P]_0} = \frac{[A]}{K_d + [A]}$$

If at each point the amine is in excess with respect to the polymer, and/or the binding constant is sufficiently small, in the previous expression the free amine concentration $[A]$ may be replaced with the total amount of the amine $[A]_0$:

$$Y \approx \frac{[A]_0}{K_d + [A]_0}$$

At a fixed wavelength, the absorption spectrum of a mixture of P and AP (polymer and polymer/amine complex) is:

$$Abs = \varepsilon_P[P] + \varepsilon_{AP}[AP]$$

At the initial step (only polymer present):

$$Abs_0 = \varepsilon_P[P]_0$$

And at the hypothetical saturation (where all polymer is bound):

$$Abs_\infty = \varepsilon_{AP}[P]_0$$

The quantity ΔAbs, representing the fractional differential absorbance for each titration step, is thus equal to the fractional saturation Y:

$$\Delta Abs = \frac{Abs_0 - Abs}{Abs_0 - Abs_\infty} = \frac{[AP]}{[P]_0} = Y$$

Thus, a plot of $Abs_0 - Abs$ vs $[P]_0$ is a right-angle hyperbola with asymptote $Abs_0 - Abs_\infty$, whose non-linear fit easily yields the unknown parameters Abs_∞ and K_d. The fitting for the titrations of **P1** and **P2** with (*R*)- and (*S*)-MBA are respectively reported in Figures S8 and S9. The association constant K_a is then the reciprocal of K_d.

Stoichiometry evaluation (Job's method). The concentration of **P1**-(*R*)-MBA complex ([**P1**-(*R*)-MBA]) was plotted against the mole fraction (*f*) of (*R*)-MBA, being the stoichiometry of the complex found for *f* corresponding to the maximum of [**P1**-(*R*)-MBA]. The complex's concentration [**P1**-(*R*)-MBA] was calculated from [**P1**-(*R*)-MBA] = $(A_0 - A) / A_0$ x [**P1**], where $(A_0 - A) / A_0$ is the relative absorption intensities at 430 nm and [**P1**] the concentration of pure **P1**. The Job plot is depicted in Figure S10.

Spectroscopic and GPC data

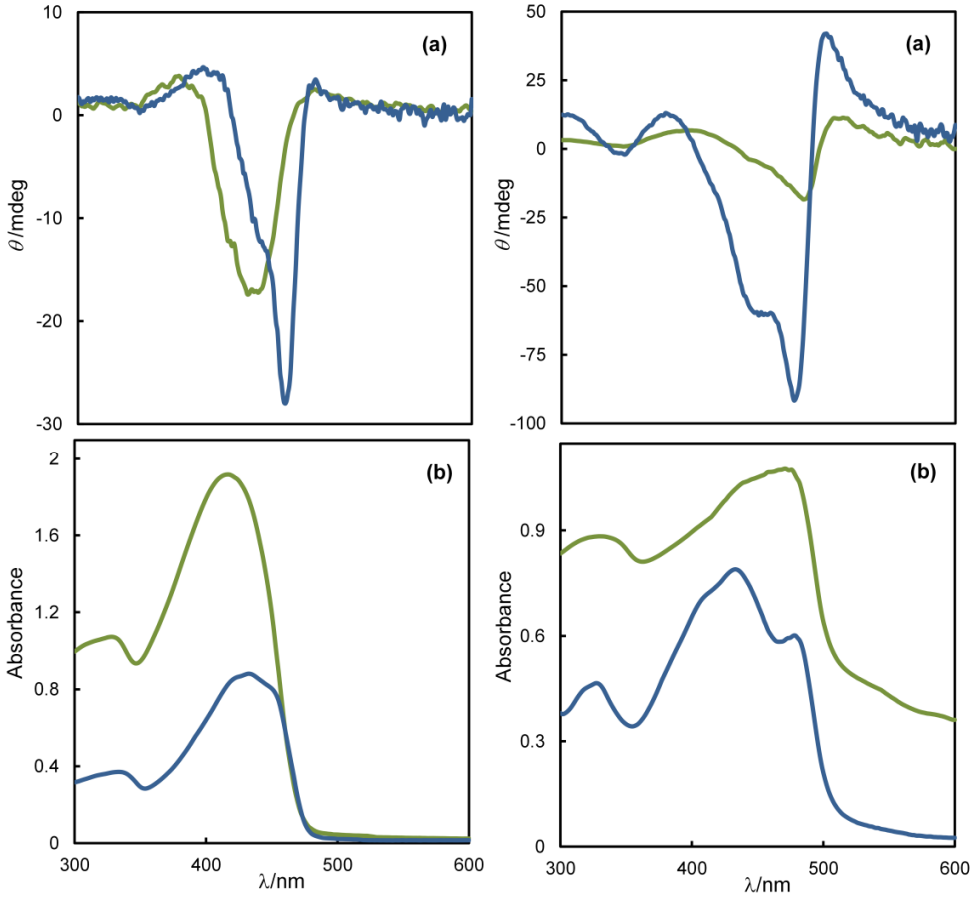


Figure S1. CD (top) and UV-Vis (bottom) spectra of **P1** (left) and **P2** (right) as films (green) and $CHCl_3$:MeOH solutions (blue) at 20ºC. Films obtained by drop-coating from 2.5 x 10^{-3} M solutions in $CHCl_3$.

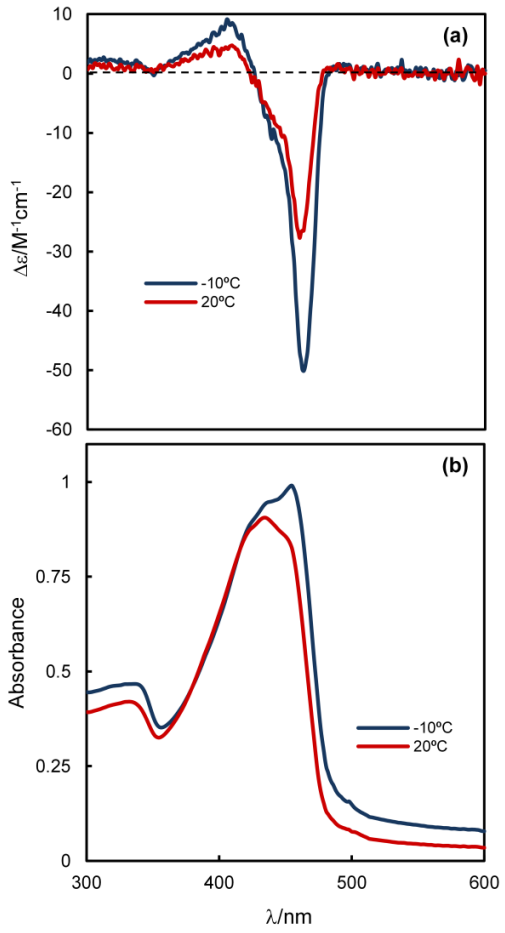


Figure S2. CD (a) and UV-Vis (b) spectra of **P1** solution at 20ºC (red) and upon cooling to -10ºC (blue).

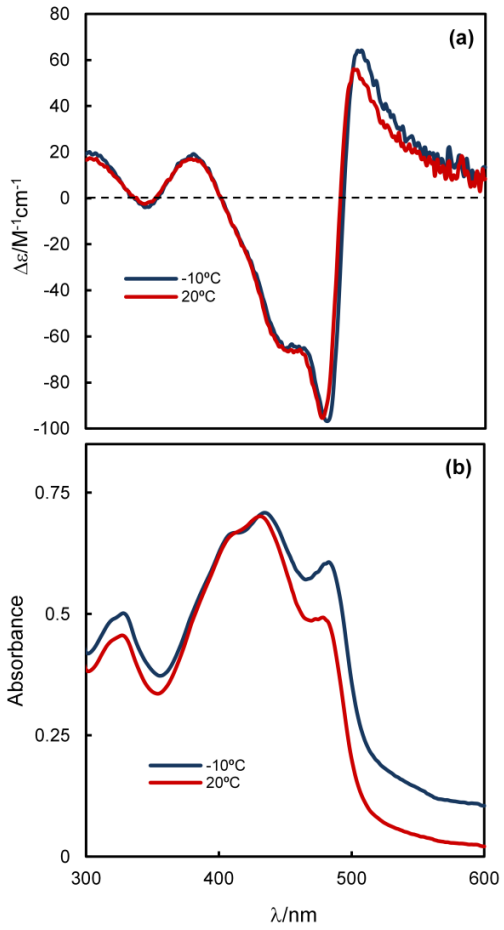


Figure S3. CD (a) and UV-Vis (b) spectra of **P2** solution at 20ºC (red) and upon cooling to -10ºC (blue).

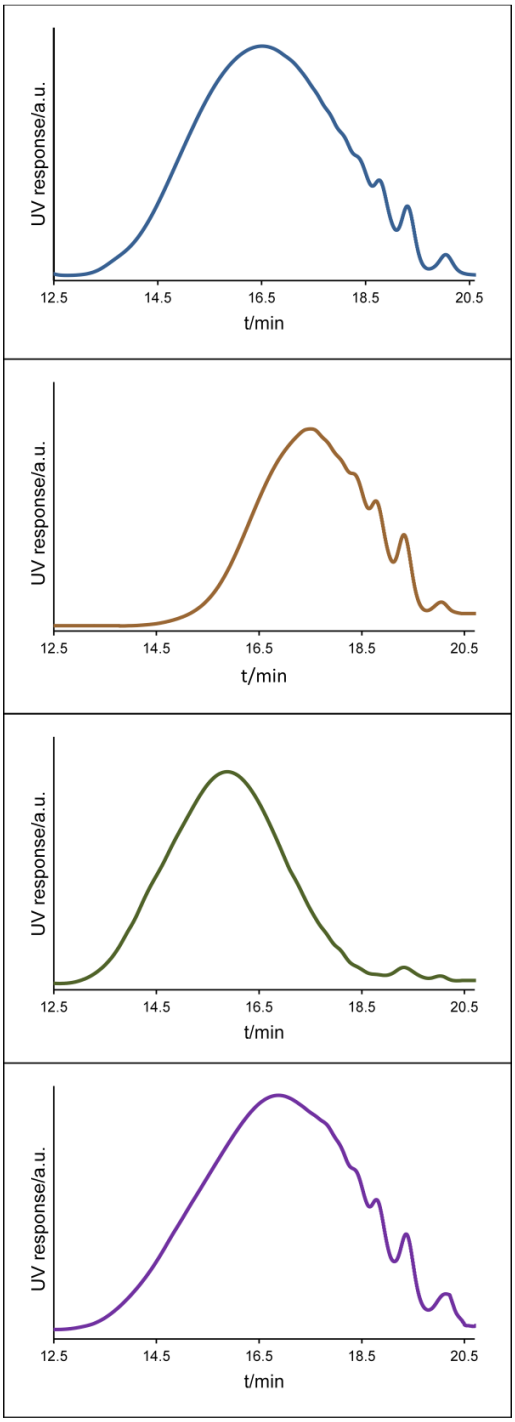


Figure S4. GPC traces of **P1**, **P1**-**SF**, **P1**-**IF**, and **P1**-**M** (from top to bottom).

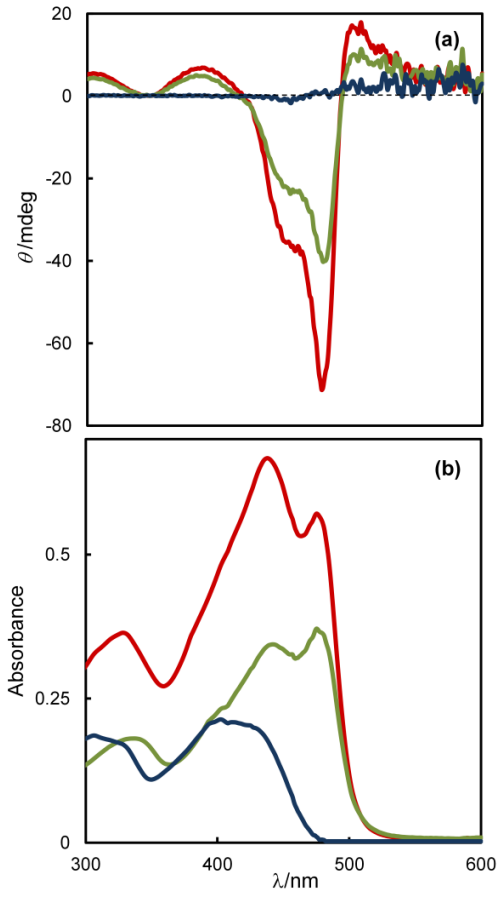


Figure S5. CD and UV-Vis spectra at 20ºC of the original **P2** solution (60% MeOH) (red), **P2-IF** (green), and **P2-SF** (blue), processed (see text) after thermal treatment.

Titration experiments

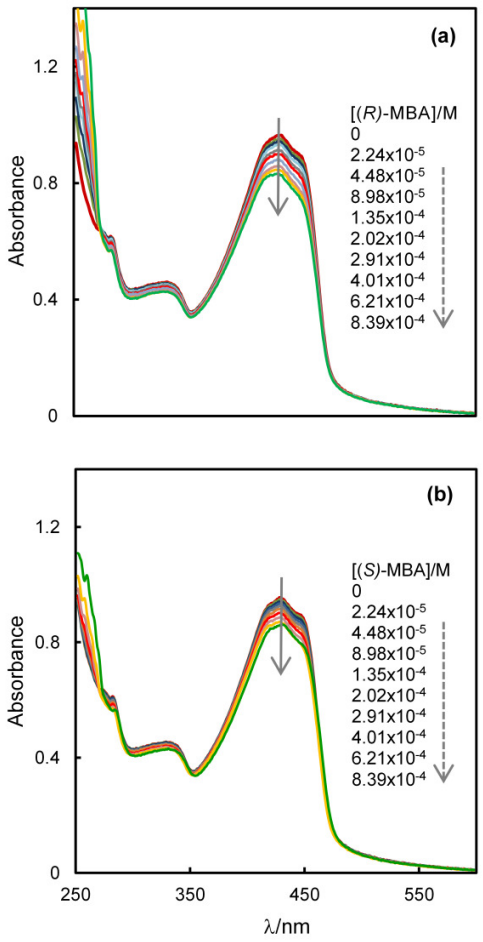


Figure S6. UV-Vis spectra of **P1** (2.0 x 10^{-5} M) in the presence of (*R*)-MBA (a) and (*S*)-MBA (b) in $CHCl_3$:MeOH (60:40) at 25ºC.

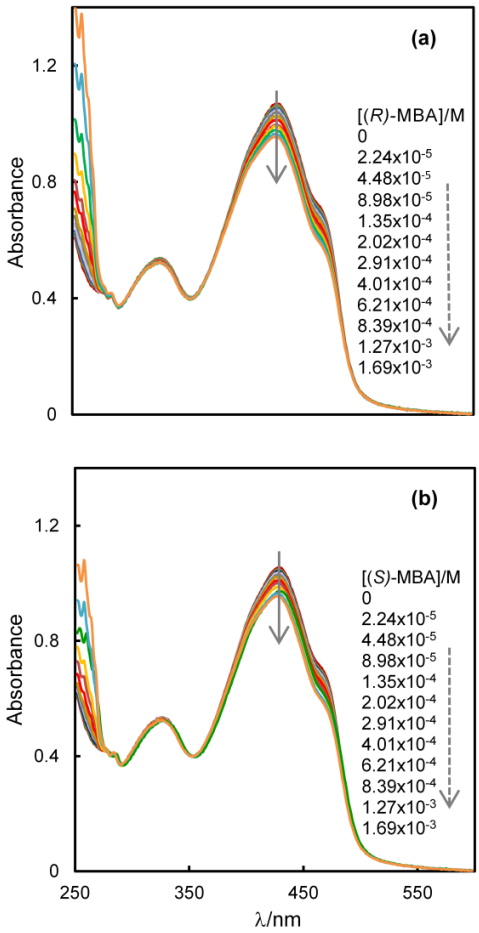
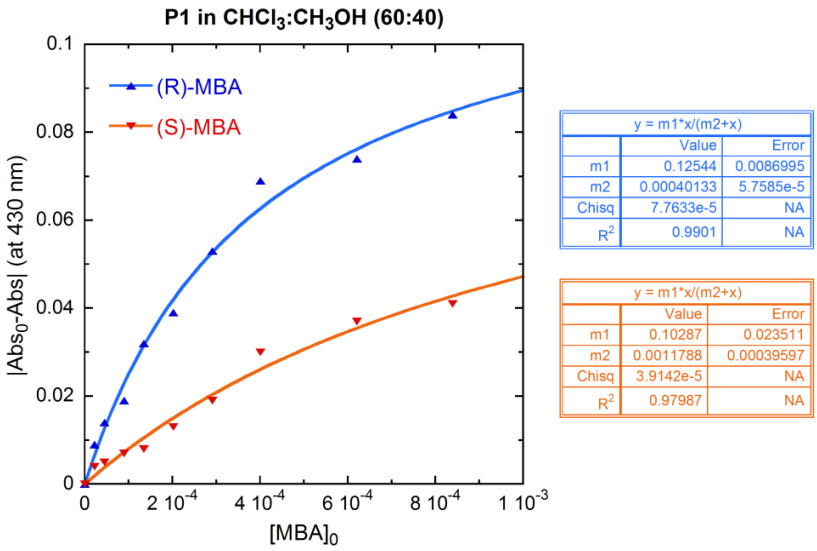


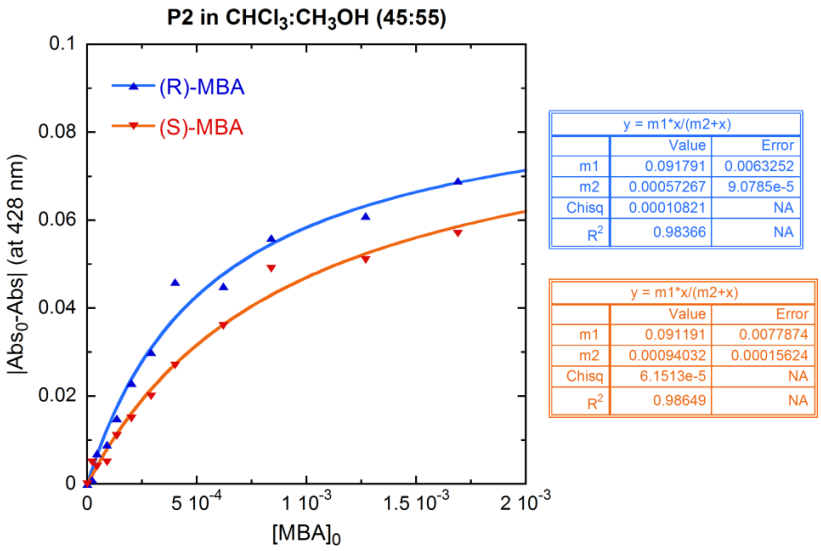
Figure S7. UV-Vis spectra of **P2** (2.0 x 10^{-5} M) in the presence of (*R*)-MBA (a) and (*S*)-MBA (b) in $CHCl_3$:MeOH (45:55) at 25ºC.



y = m1*x/(m2+x)		
	Value	Error
m1	0.12544	0.0086995
m2	0.00040133	5.7585e-5
Chisq	7.7633e-5	NA
R^2	0.9901	NA

y = m1*x/(m2+x)		
	Value	Error
m1	0.10287	0.023511
m2	0.0011788	0.00039597
Chisq	3.9142e-5	NA
R^2	0.97987	NA

Figure S8. Least-square non-linear fitting of titration data obtained for (*R*)- and (*S*)-MBA and **P1** (2.0 x 10^{-5} M) in $CHCl_3$:MeOH (60:40), monitored by the absorption at 430 nm. Fitting parameters m1 and m2 correspond to $Abs_0 - Abs_\infty$ and K_d, respectively.



y = m1*x/(m2+x)		
	Value	Error
m1	0.091791	0.0063252
m2	0.00057267	9.0785e-5
Chisq	0.00010821	NA
R^2	0.98366	NA

y = m1*x/(m2+x)		
	Value	Error
m1	0.091191	0.0077874
m2	0.00094032	0.00015624
Chisq	6.1513e-5	NA
R^2	0.98649	NA

Figure S9. Least-square non-linear fitting of titration data obtained for (*R*)- and (*S*)-MBA and **P2** (2.0 x 10^{-5} M) in $CHCl_3$:MeOH (45:55), monitored by the absorption at 428 nm. Fitting parameters m1 and m2 correspond to $Abs_0 - Abs_\infty$ and K_d, respectively.

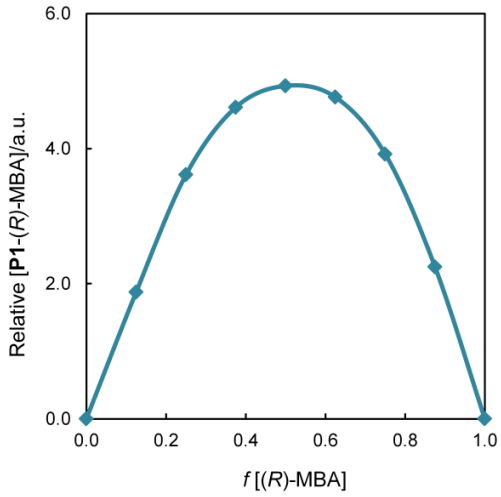


Figure S10. Job plot of the binding of **P1** with (*R*)-MBA in CHCl3:MeOH (60:40) solution at a constant total concentration of 2.0 x 10^{-5} M; data obtained from absorbance changes at 430 nm at 25ºC.

NMR spectra

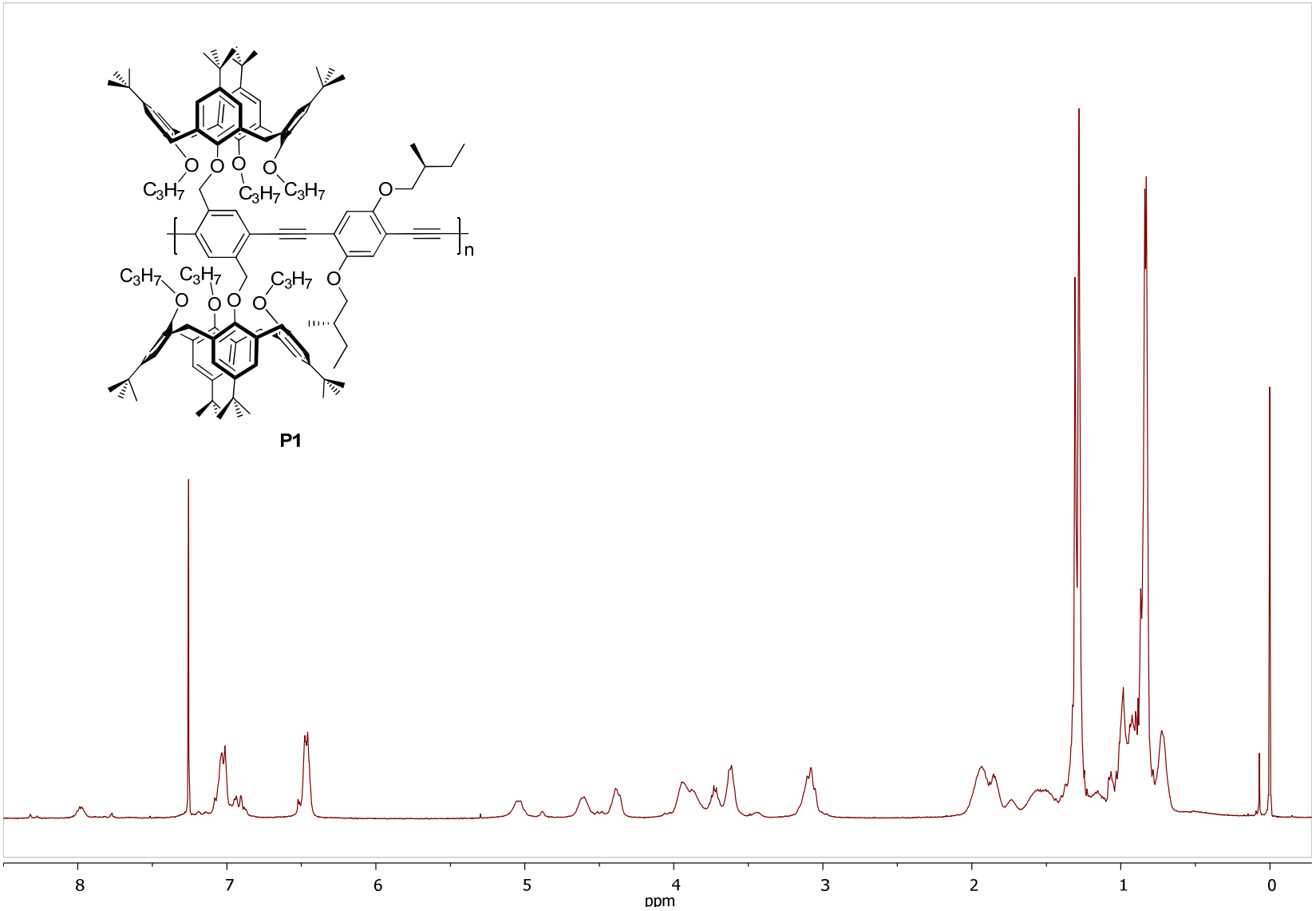


Figure S11. ^{1}H NMR spectrum of **P1** ($CDCl_3$, 400MHz, 25ºC).[4]

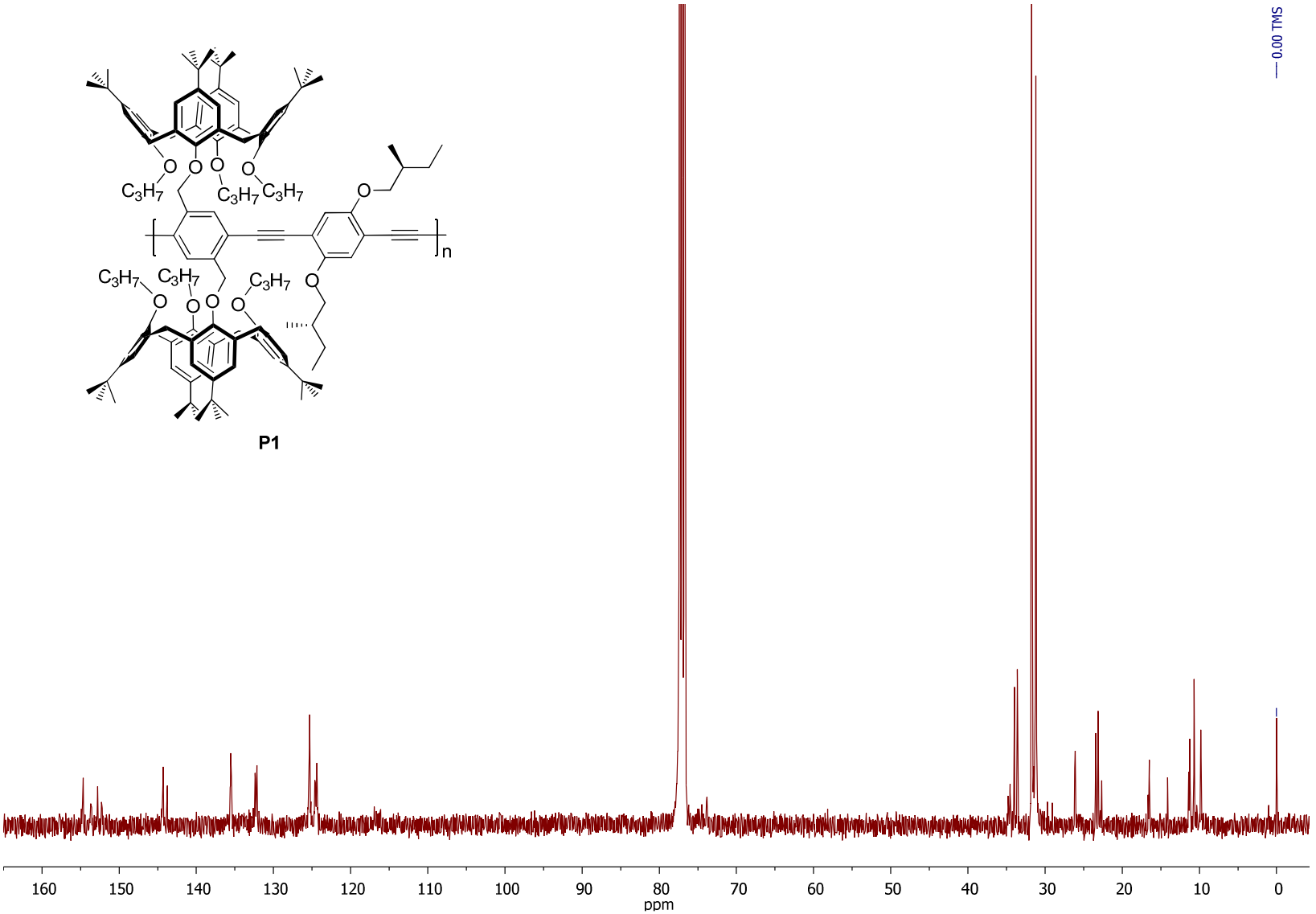


Figure S12. ^{13}C NMR spectrum of **P1** ($CDCl_3$, 100MHz, 25ºC).[4]

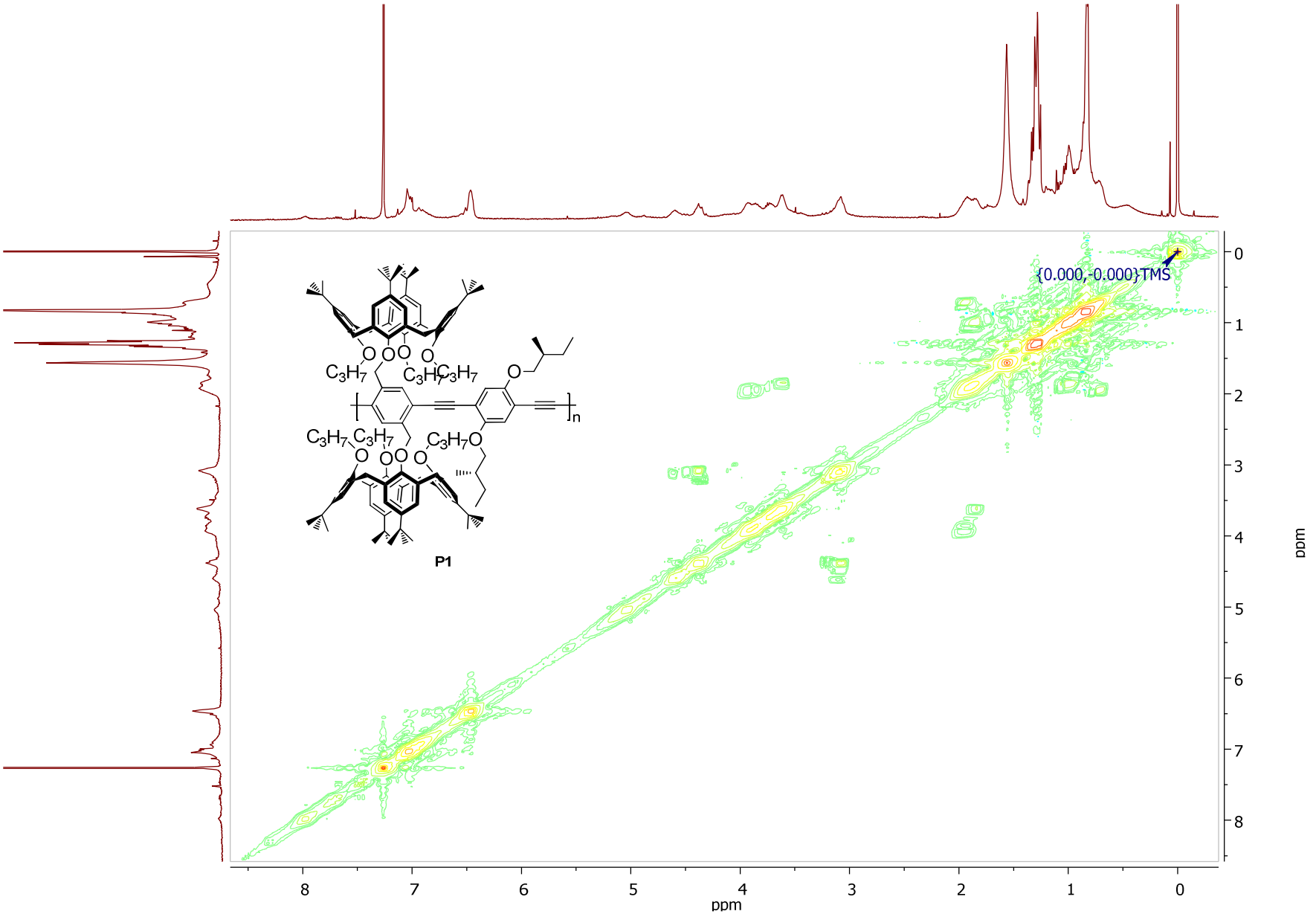


Figure S13. ^{1}H-^{1}H COSY spectrum of **P1** ($CDCl_3$, 400MHz, 25ºC).[4]

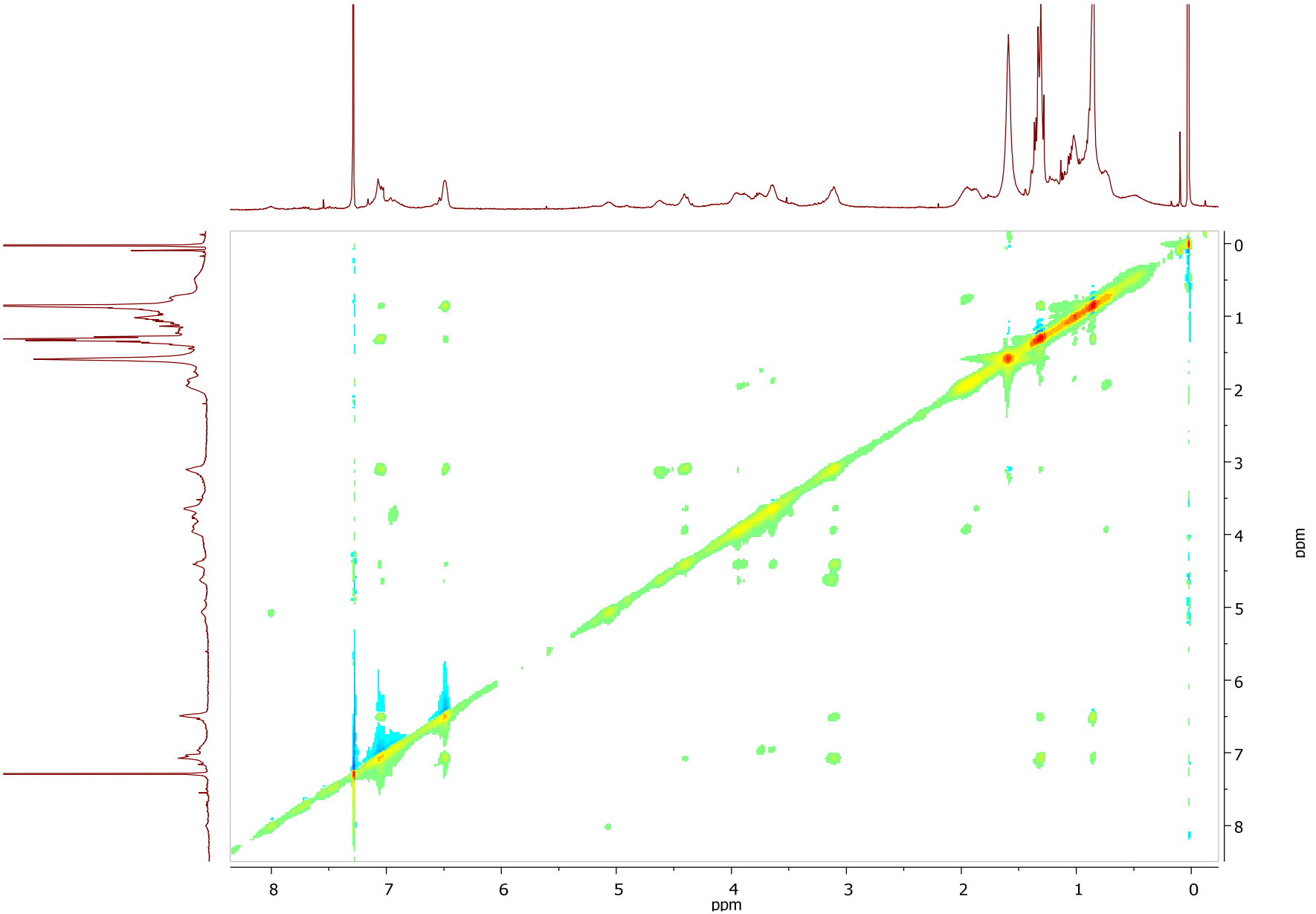


Figure S14. NOESY spectrum of **P1** ($CDCl_3$, 400MHz, 25ºC).[4]

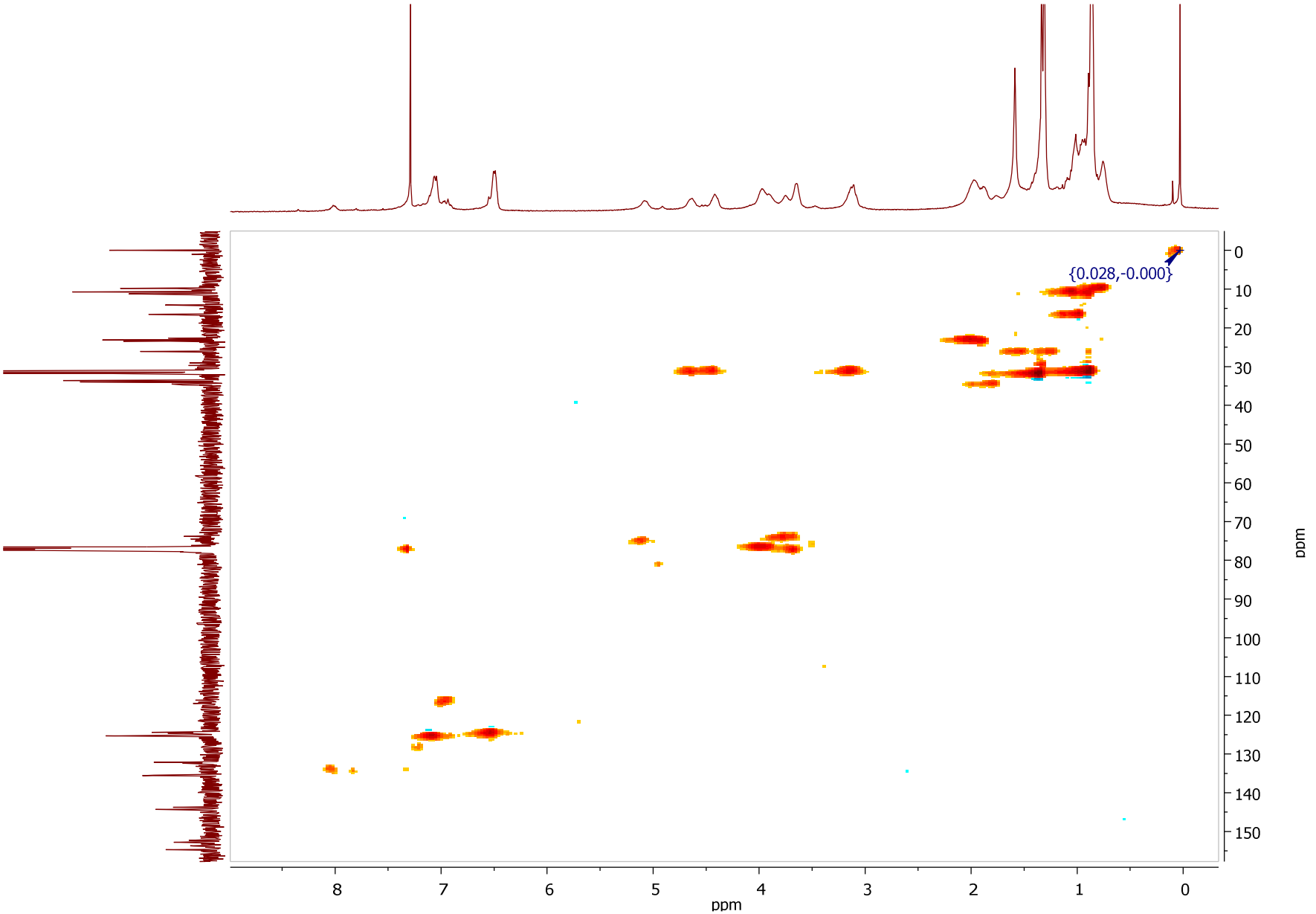


Figure S15. ^{13}C-^{1}H HSQC spectrum of **P1** ($CDCl_3$, 25ºC).[4]

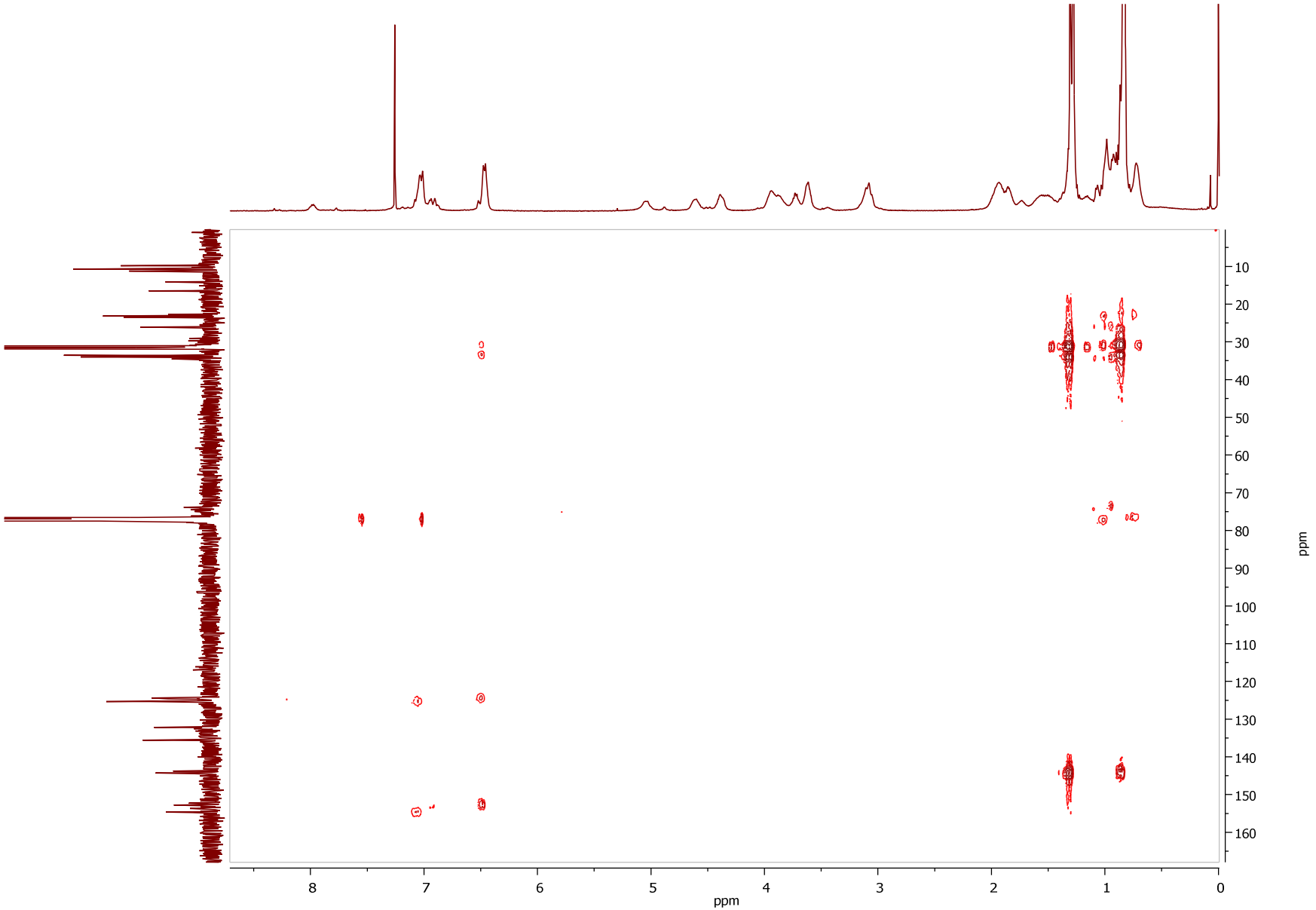


Figure S16. ^{13}C-^{1}H HMBC spectrum of **P1** ($CDCl_3$, 25ºC).[4]

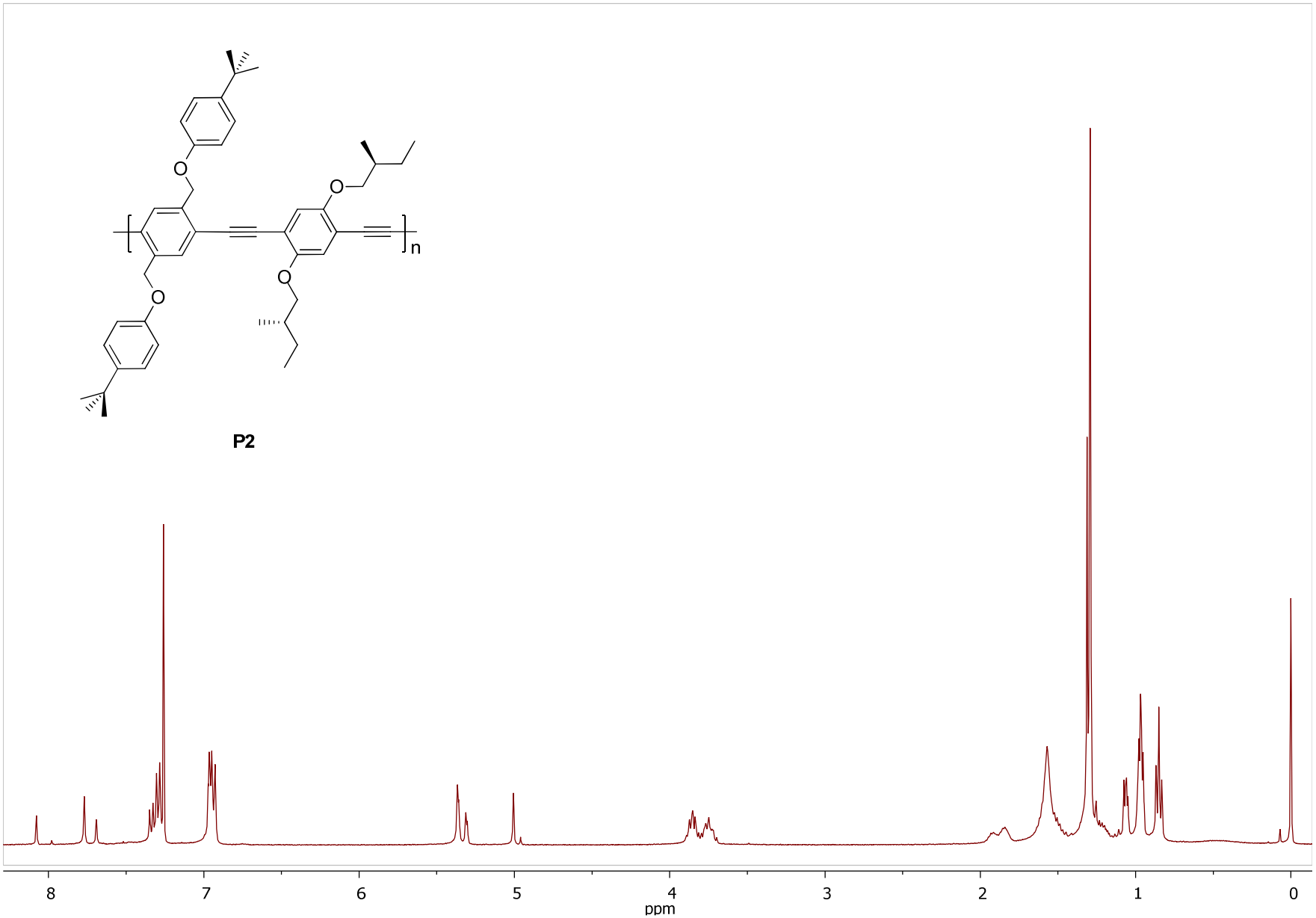


Figure S17. ^{1}H NMR spectrum of **P2** ($CDCl_3$, 400MHz, 25ºC).[4]

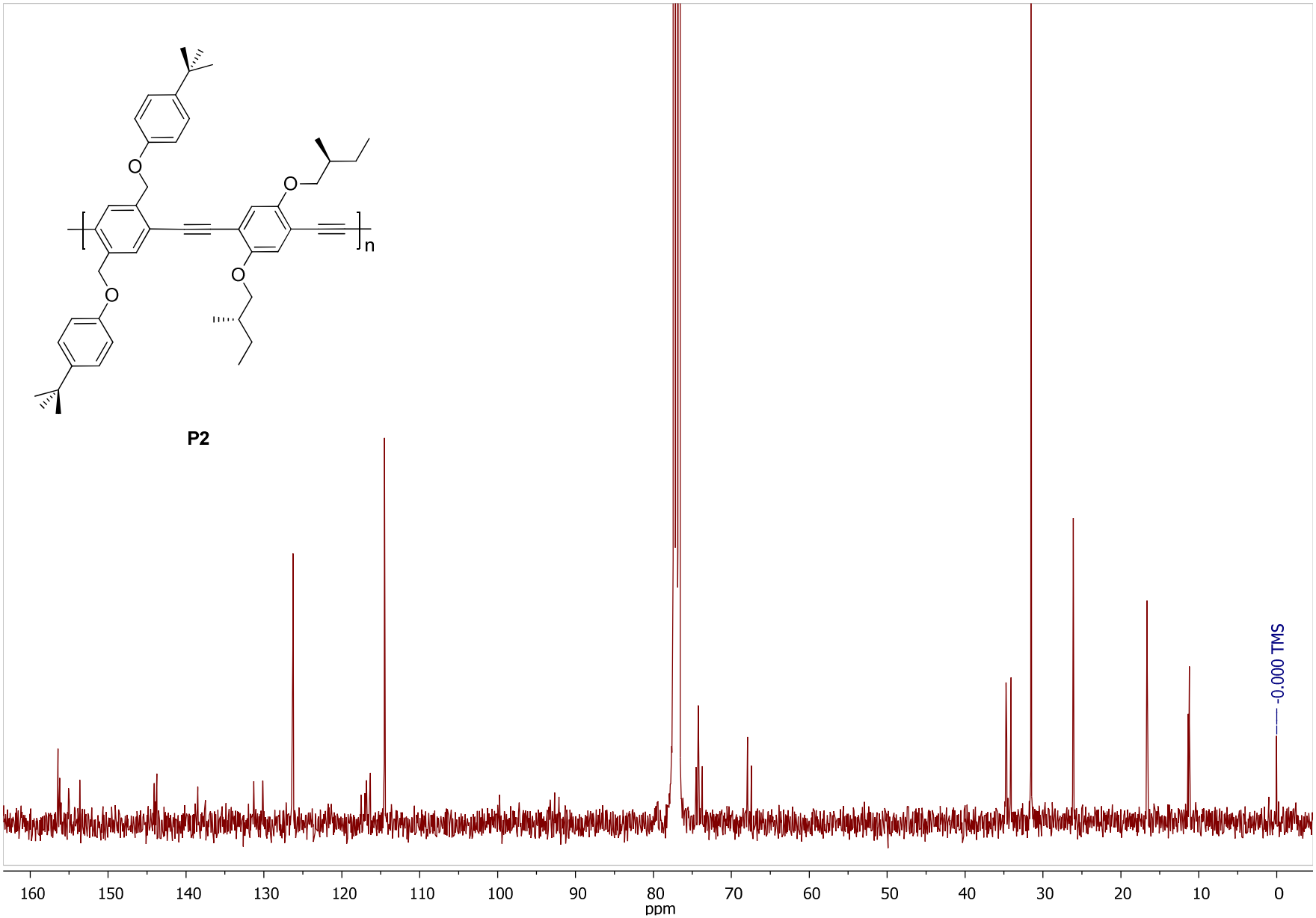


Figure S18. ^{13}C NMR spectrum of **P2** ($CDCl_3$, 100MHz, 25ºC).[4]

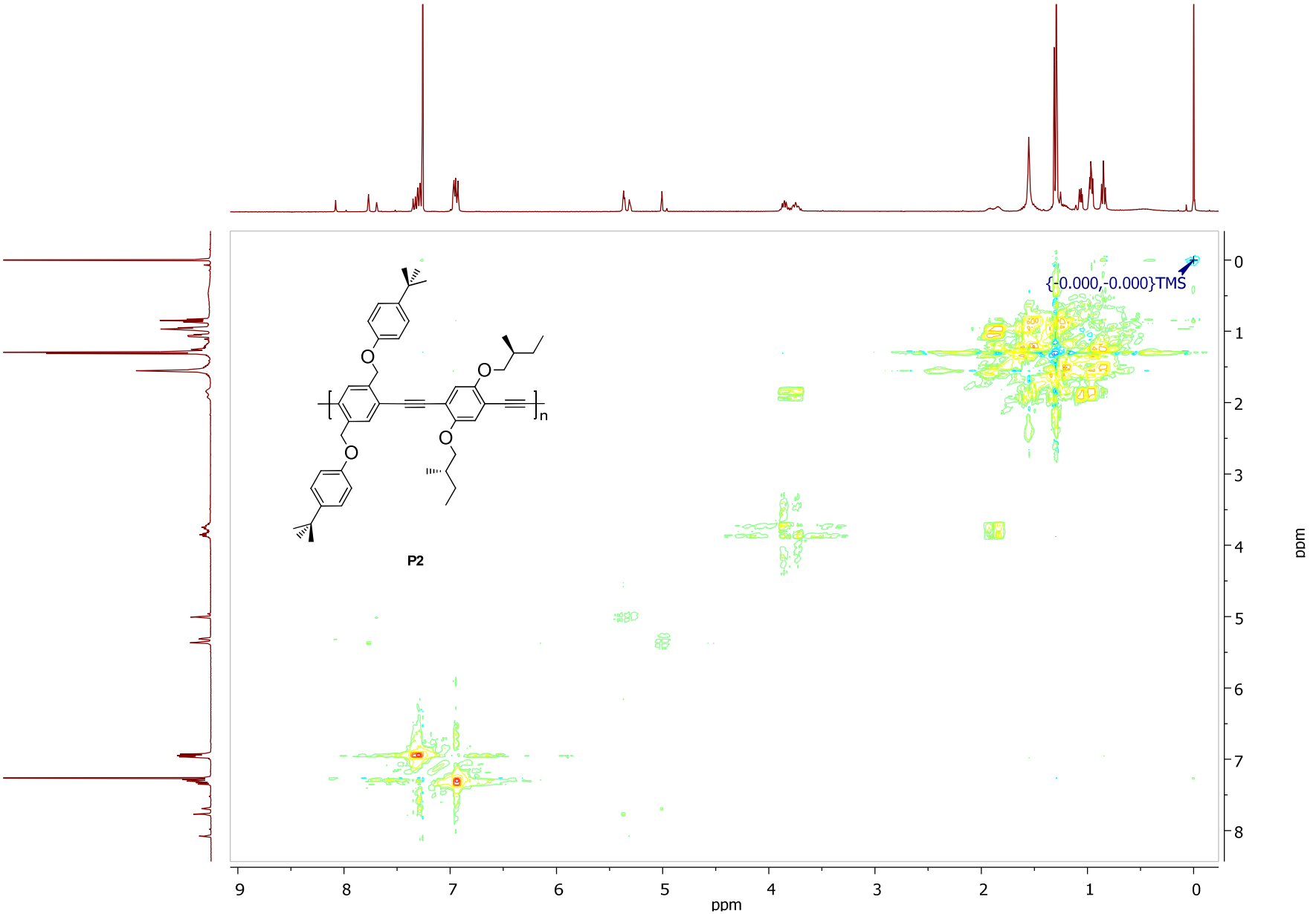


Figure S19. ^{1}H-^{1}H COSY spectrum of **P2** ($CDCl_3$, 400MHz, 25ºC).[4]

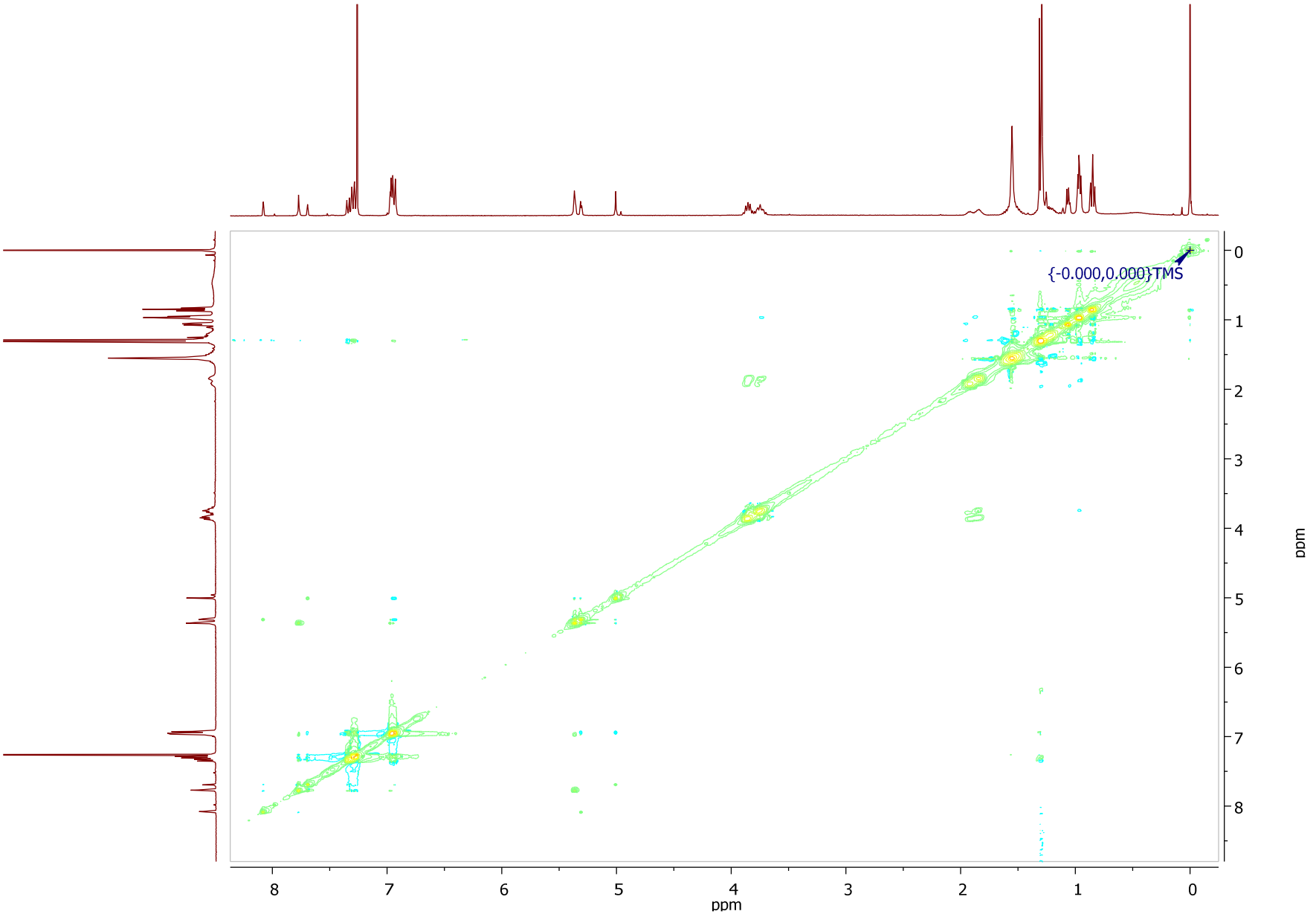


Figure S20. NOESY spectrum of **P2** ($CDCl_3$, 400MHz, 25ºC).[4]

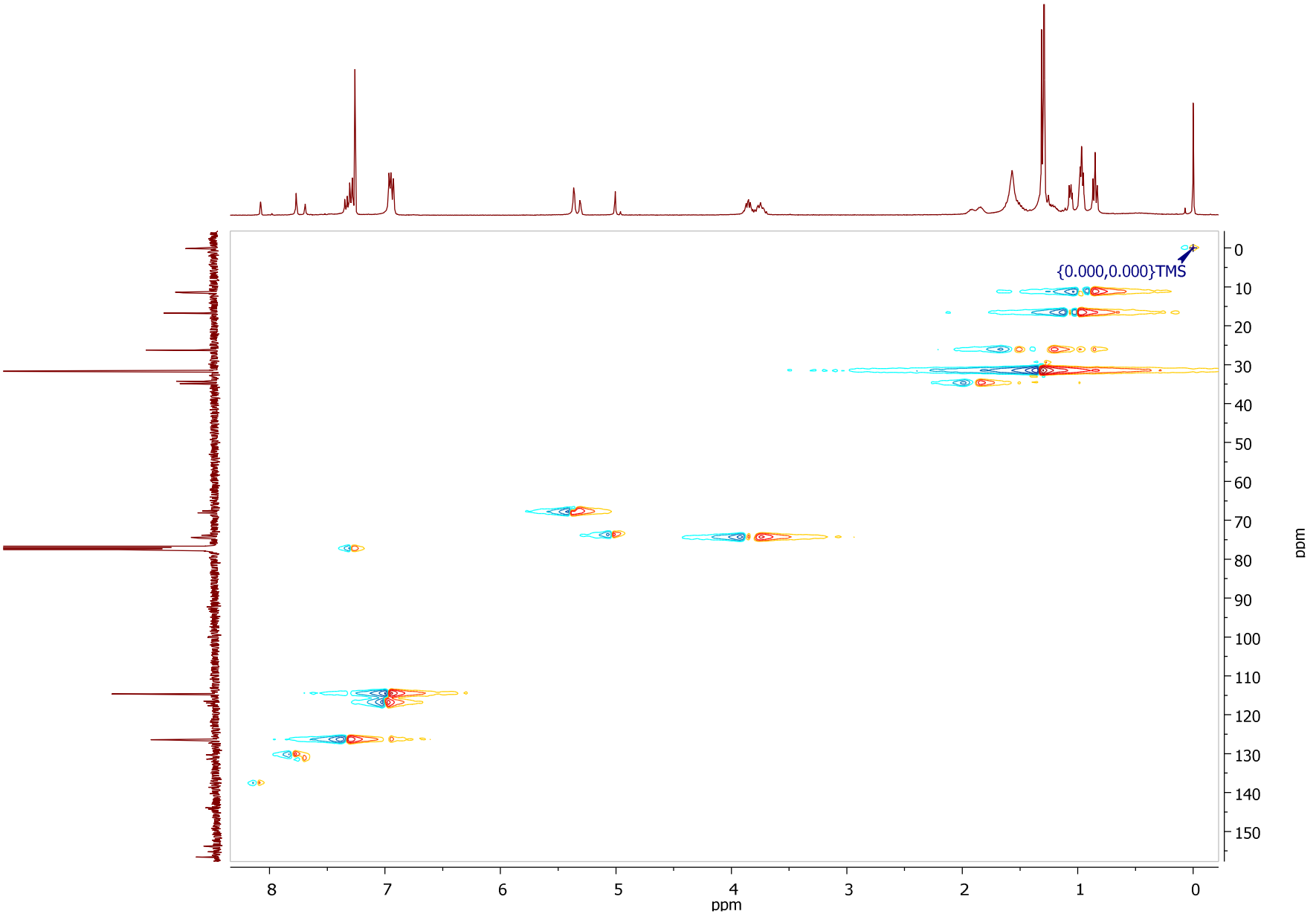


Figure S21. ^{13}C-^{1}H HSQC spectrum of **P2** ($CDCl_3$, 25ºC).[4]

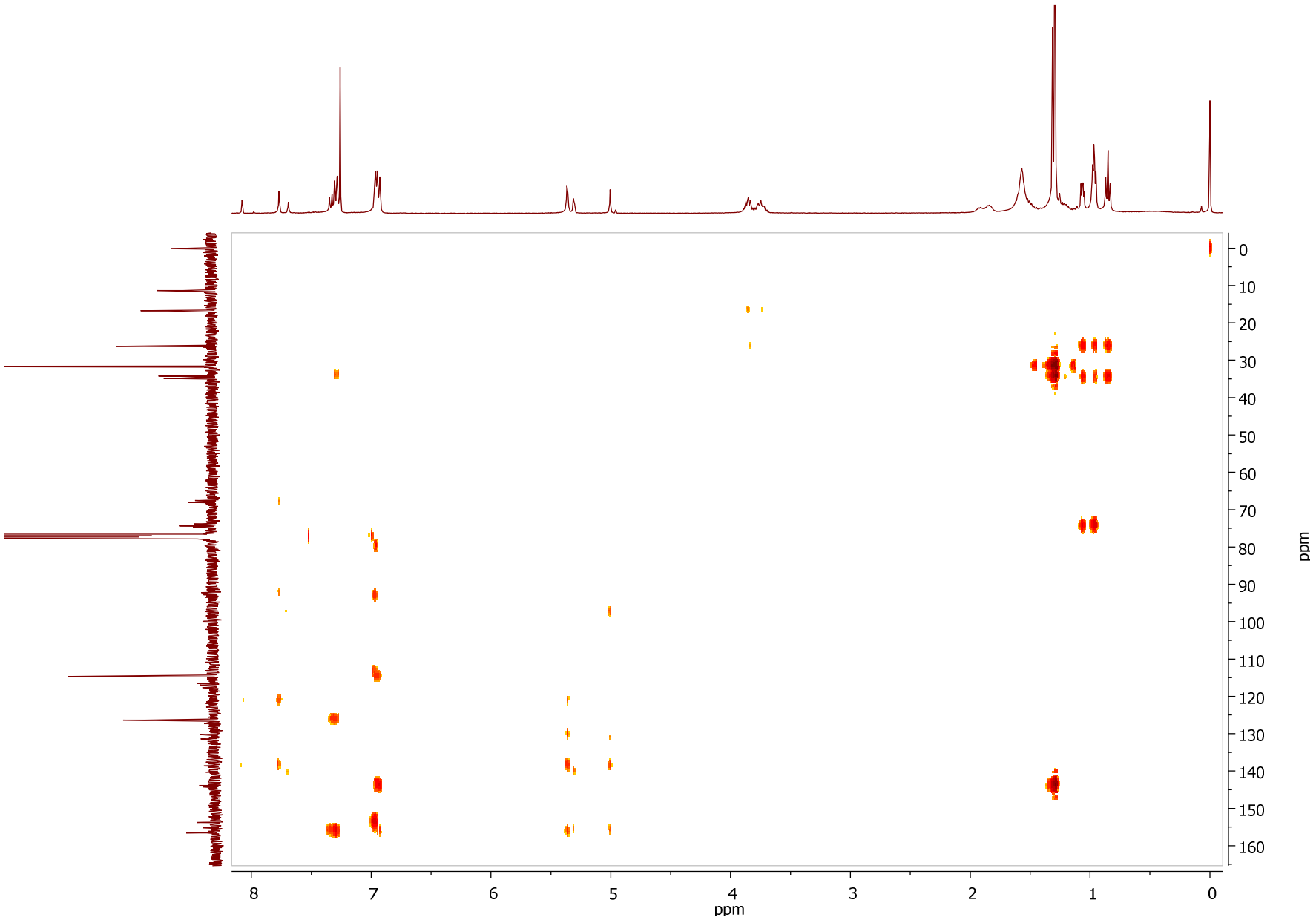


Figure S22. ^{13}C-^{1}H HMBC spectrum of **P2** ($CDCl_3$, 25ºC).[4]

Notes and references

1 Q. Zhou and T. M. Swager, *J. Am. Chem. Soc.*, 1995, **117**, 7017-7018.

2 The synthesis of **5** was reported before using 2,5-dibromo-1,4-hydroquinone as the starting material and a different experimental procedure.[3]

3 R. Fiesel and U. Scherf, *Macromol. Rapid Commun.*, 1998, **19**, 427-431.

4 NMR data processed with MNova (version 6.1.0) from Mestrelab Research SL.