Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis and Characterization of BPA-free Polyesters by Incorporating a Semi-rigid Cyclobutanediol Monomer

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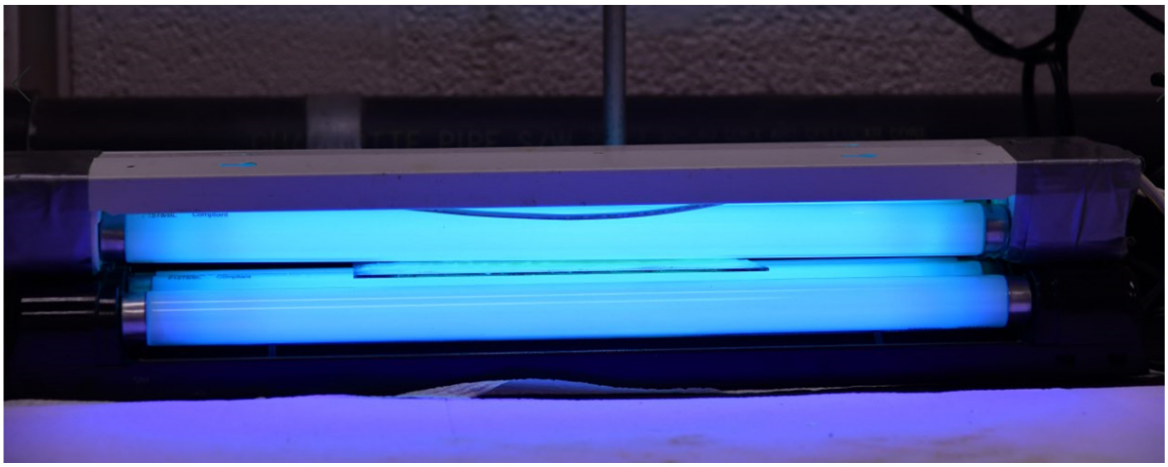

Figure S1. Setup for synthesis of CBDA-1 in the solid state

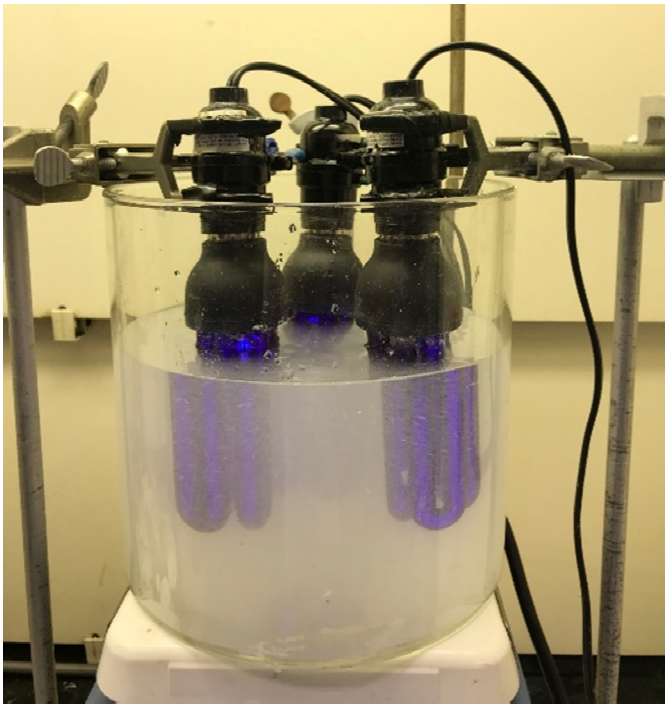

Figure S2. Setup for synthesis of CBDA-1 in brine slurry*

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* To ensure that the brine was as transparent as possible, 25 mL water was added into the brine before the reaction and each day during the slurry photoreaction.

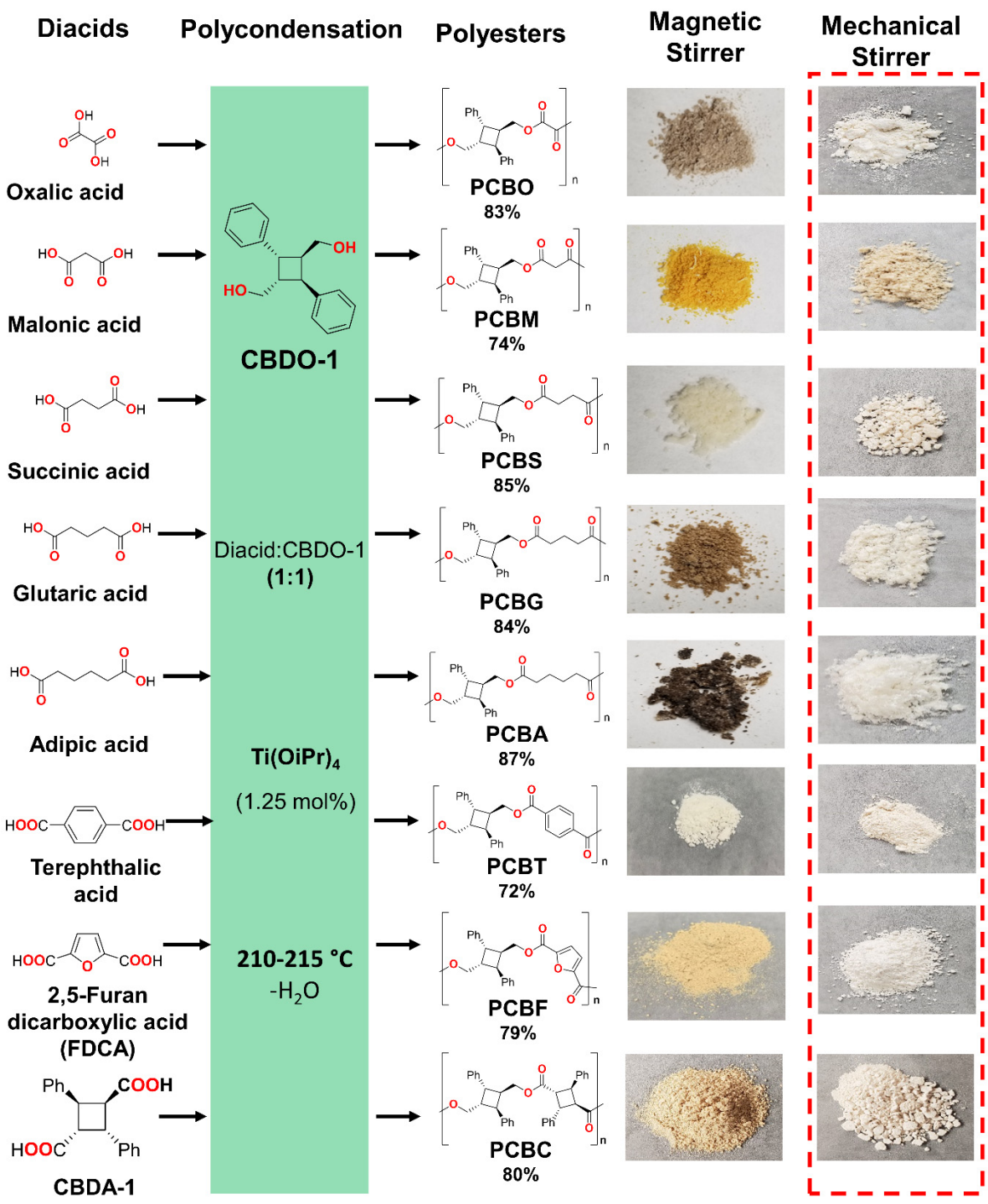
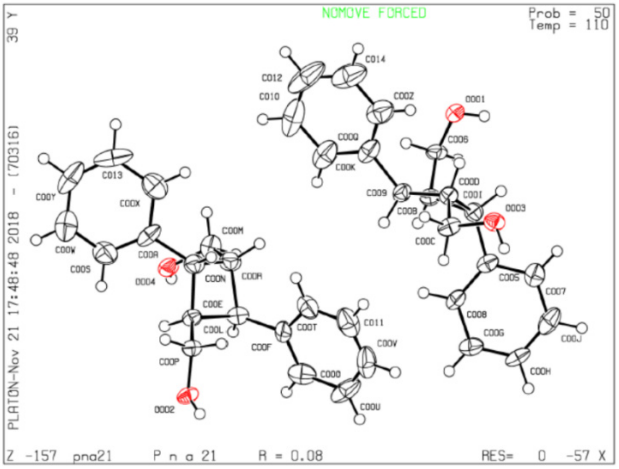
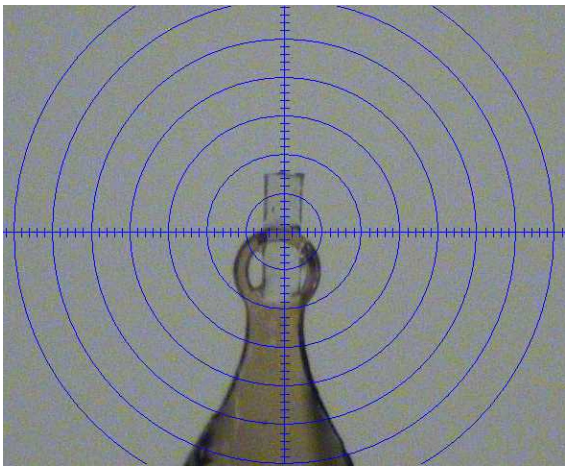


Figure S3. Synthesis of CBDO-1 based polyesters. Showing the color difference by using magnetic stirrer and external mechanical stirrer.

X-ray crystal structure and data of CBDO-1





CBDO-1	**Data**
CCDC #	1949075
Formula	C36 H40 O4
FW	536.68
Crystal Size [mm]	0.06 x 0.121 x 0.375
Crystal_system	orthorhombic
Space Group, Z	$Pna2_1$
a (Å)	17.9616 (7)
b (Å)	7.6761 (3)
c (Å)	21.5205(9)
α (°)	90
β (°)	90
γ (°)	90
V (Å3)	2967.1(2)
Temp. (K)	110(2)
ρcalc [g/cm^3]	1.201
μ [mm^{-1}]	0.604
Radiation Type	CuK\a
F(000)	1152
No of measured refl.	73145
of independent refl.	5263
No of refl. ($I \geq 2\sigma$)	4930
R1/wR2 ($I \geq 2\sigma$) [%]	7.82 /20.40
R1/wR2 (all data) [%]	8.25 /20.71

Conformation of cyclobutane ring and crystal packing of CBDO-1

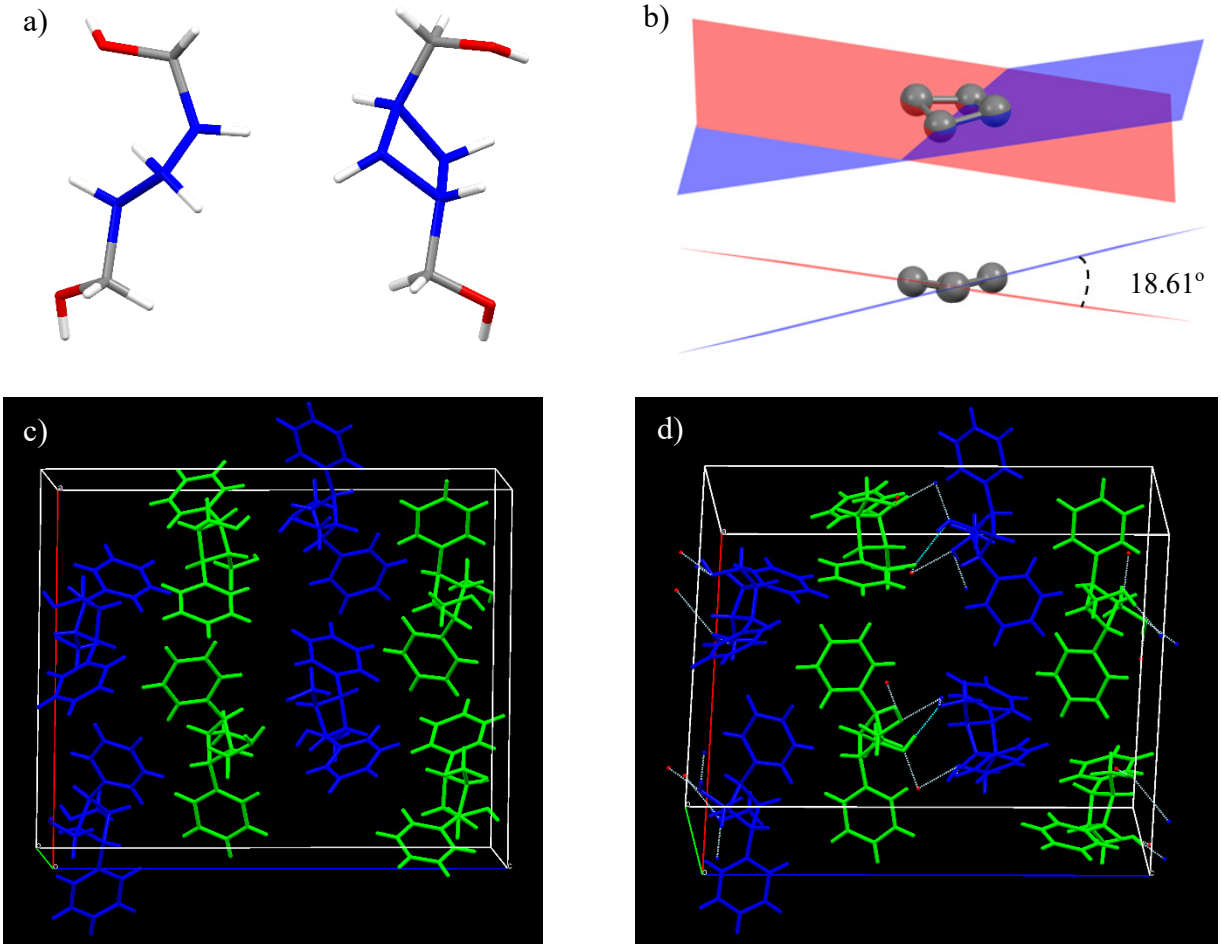


Figure S4. a) Two CBDO-1 molecules in the asymmetric unit cell (cyclobutane moiety highlighted in blue and the phenyl groups are omitted for clarity); b) Conformation of a cyclobutane ring in the crystal: The puckered cyclobutane ring of CBDO-1 with an angle of 18.61°, and the other one is 22.02° as shown in Figure 2 of the manuscript; c) The packing of CBDO-1 in crystal (In the unit cell, the molecules with the same symmetry equivalence are shown in the same color.); d) The packing of CBDO-1 in crystal with the hydrogen bonds shown in dash blue lines.

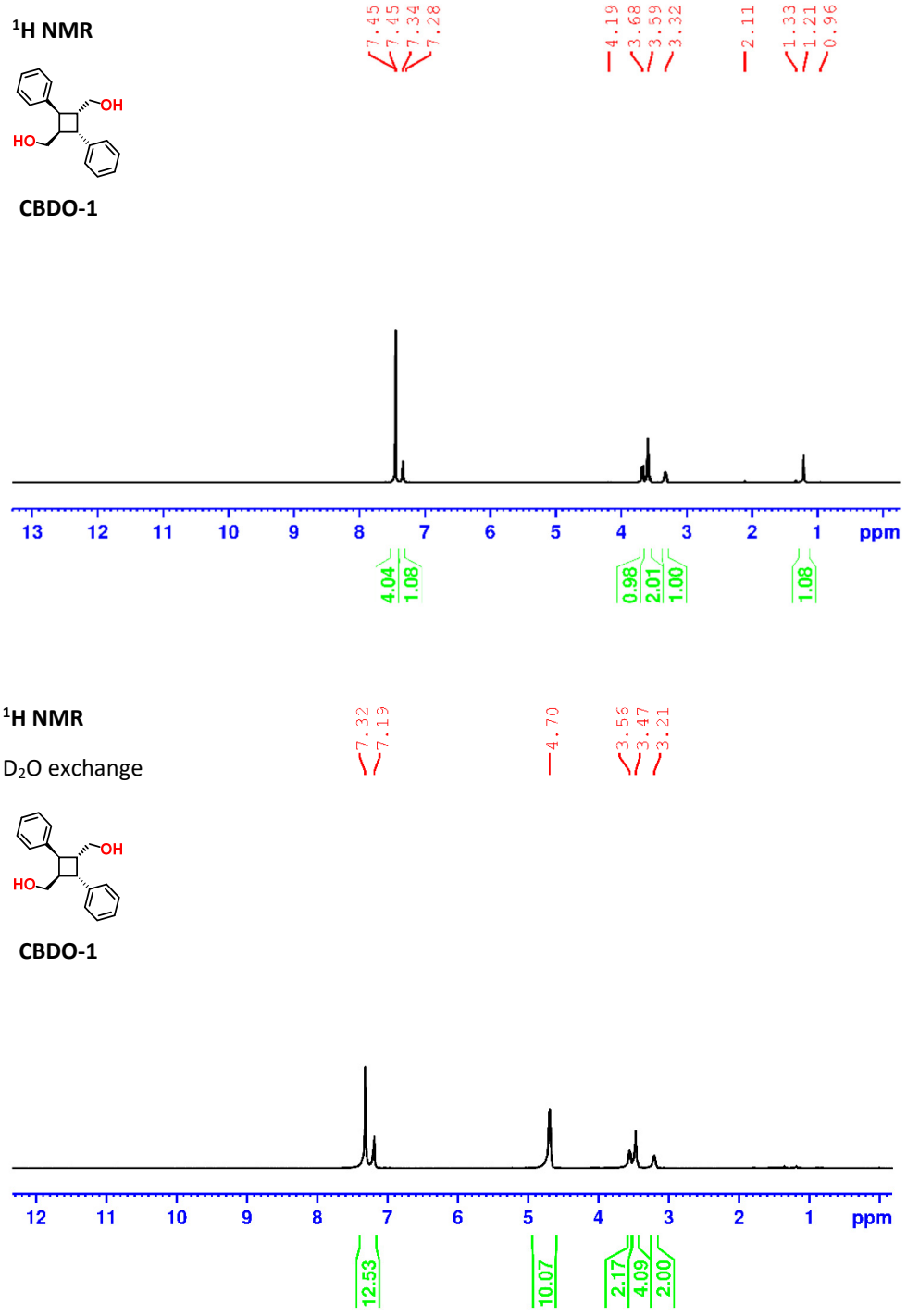


Figure S5. ^{1}H and D_2O exchange NMR spectra of **CBDO-1** in $CDCl_3$ at room temperature.

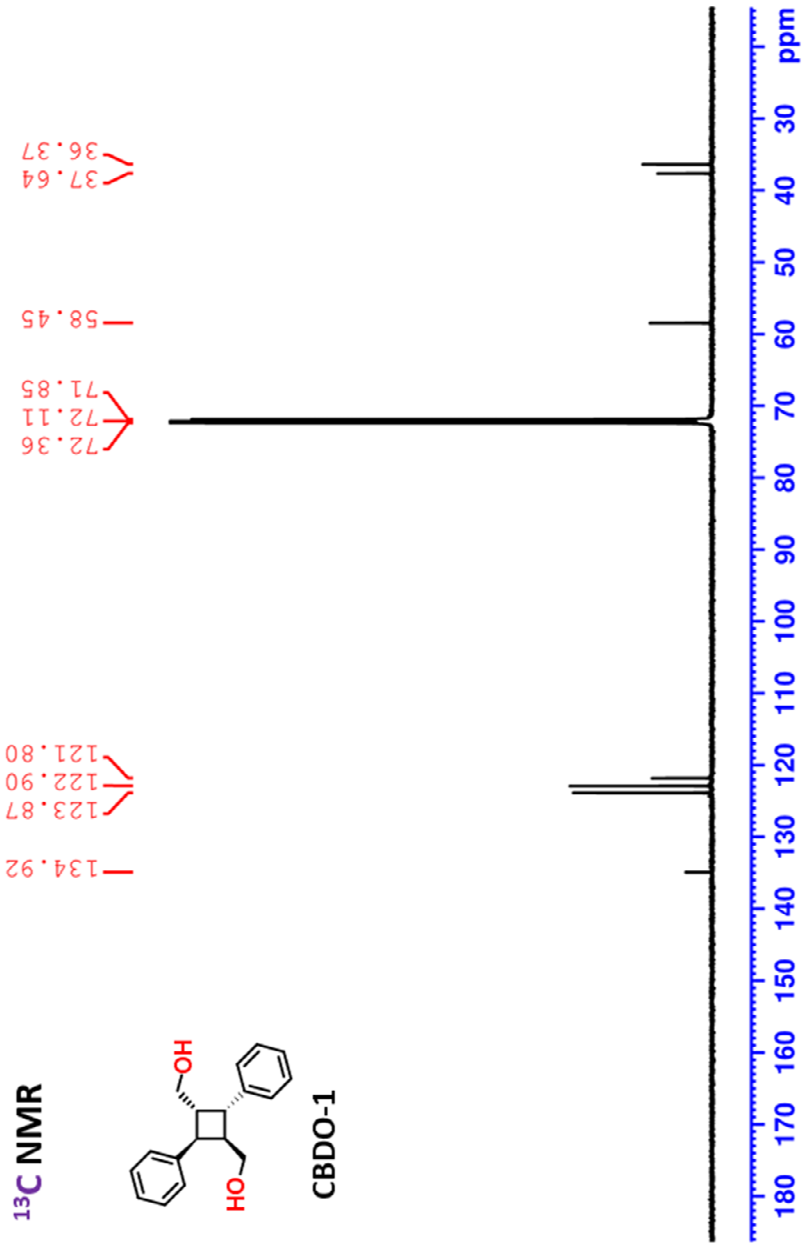


Figure S6. ^{13}C NMR spectrum of **CBDO-1** in $CDCl_3$ at room temperature.

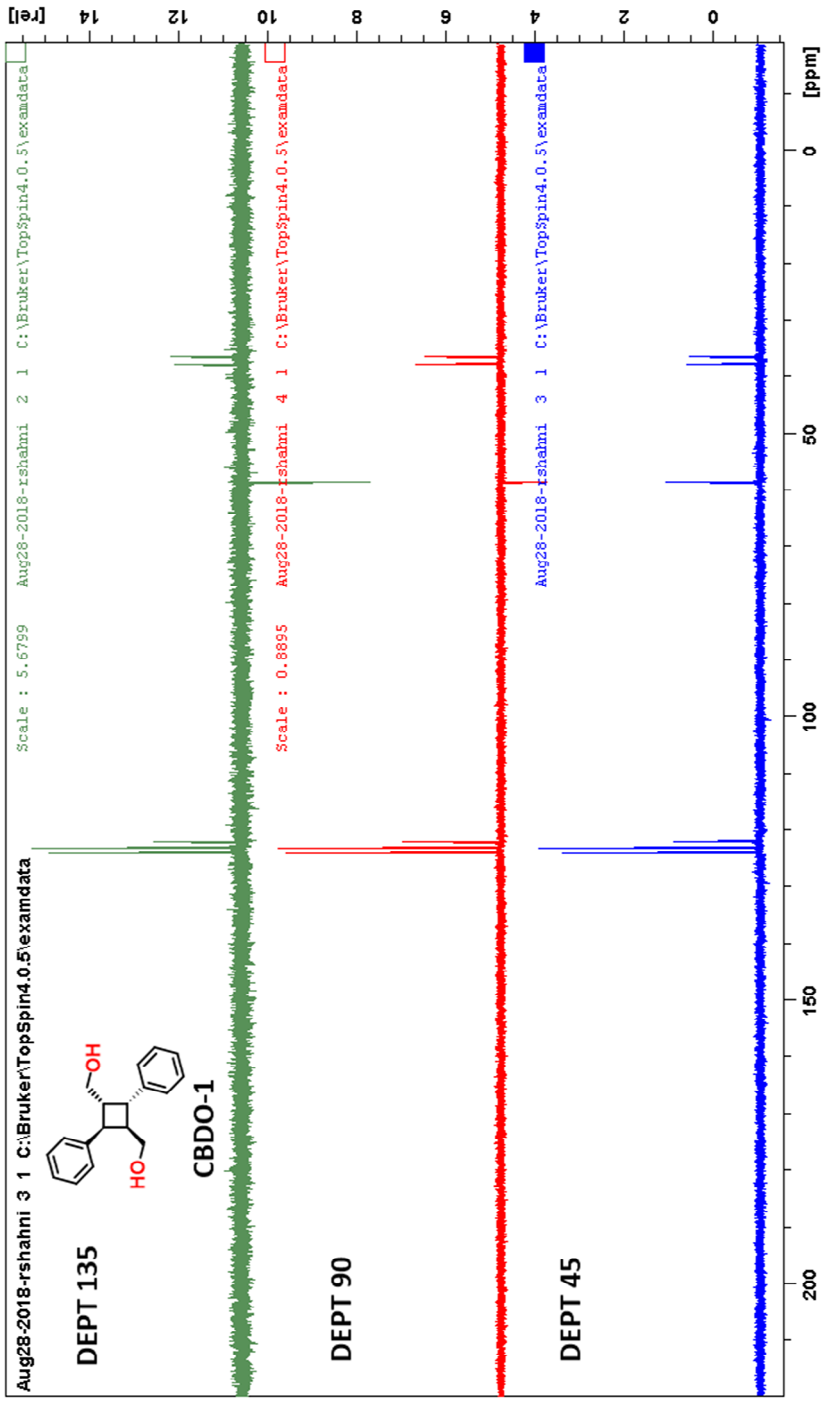


Figure S7. DEPT 45, 90 and 135 spectra of **CBDO-1** in $CDCl_3$ at room temperature.

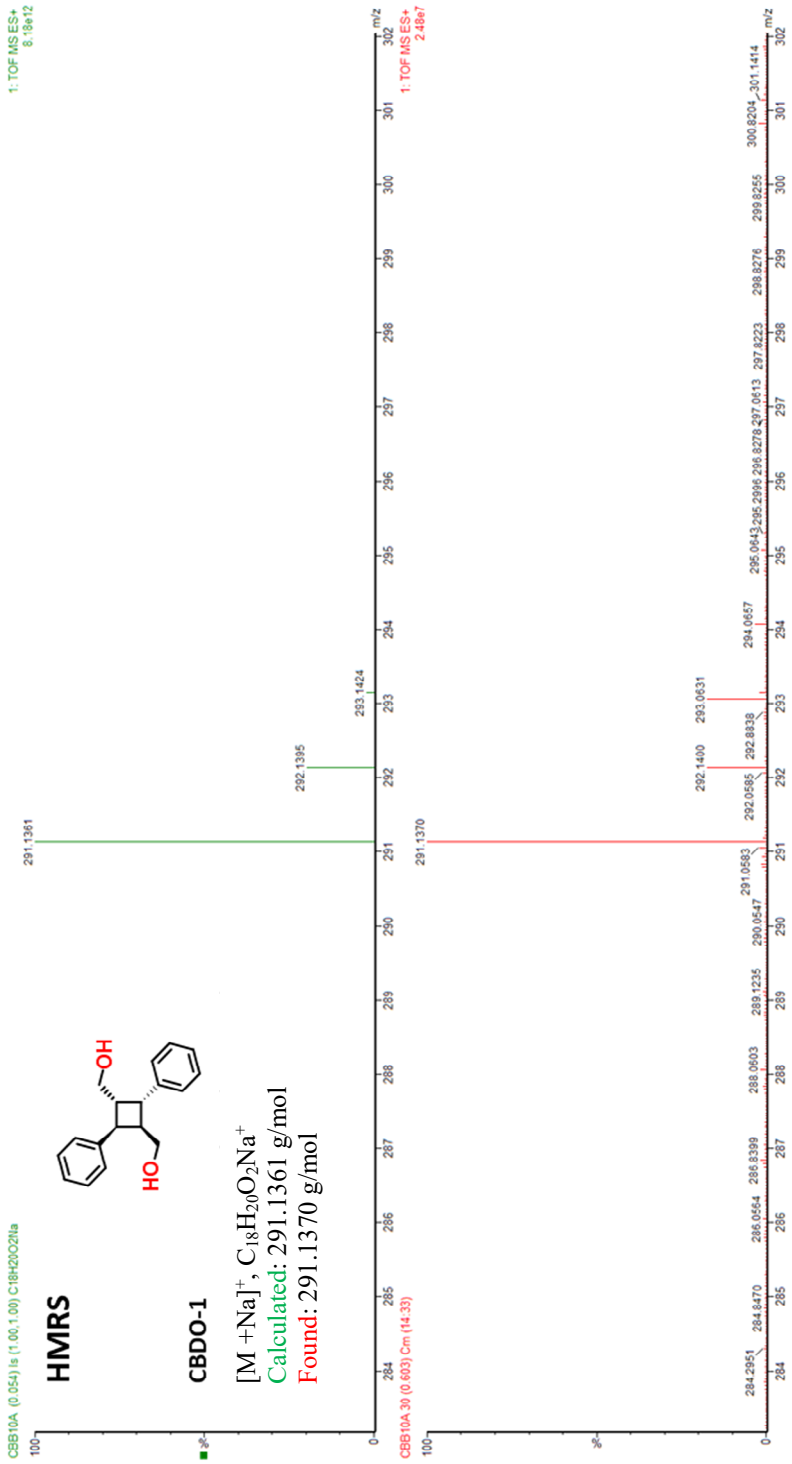


Figure S8. High resolution mass spectrometry of **CBDO-1**.

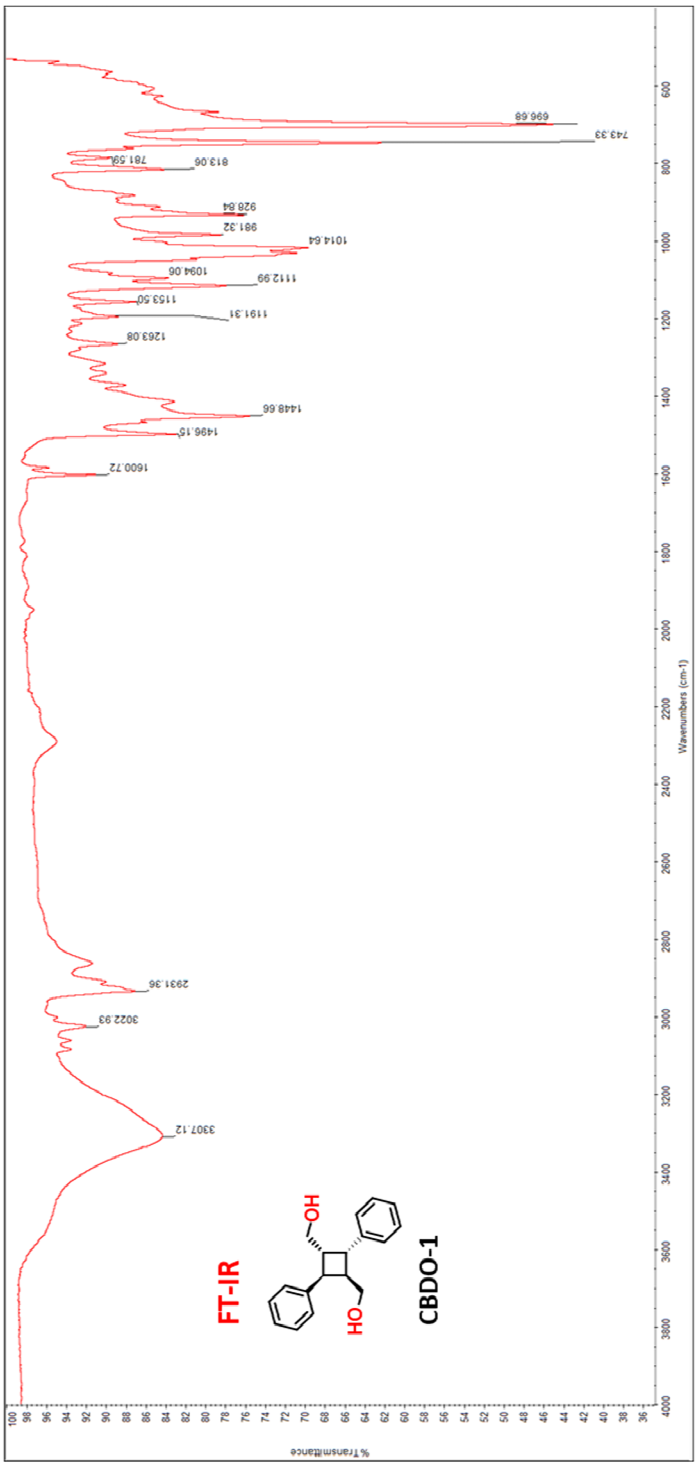


Figure S9. FT-IR spectrum of **CBDO-1** using ATR detector.

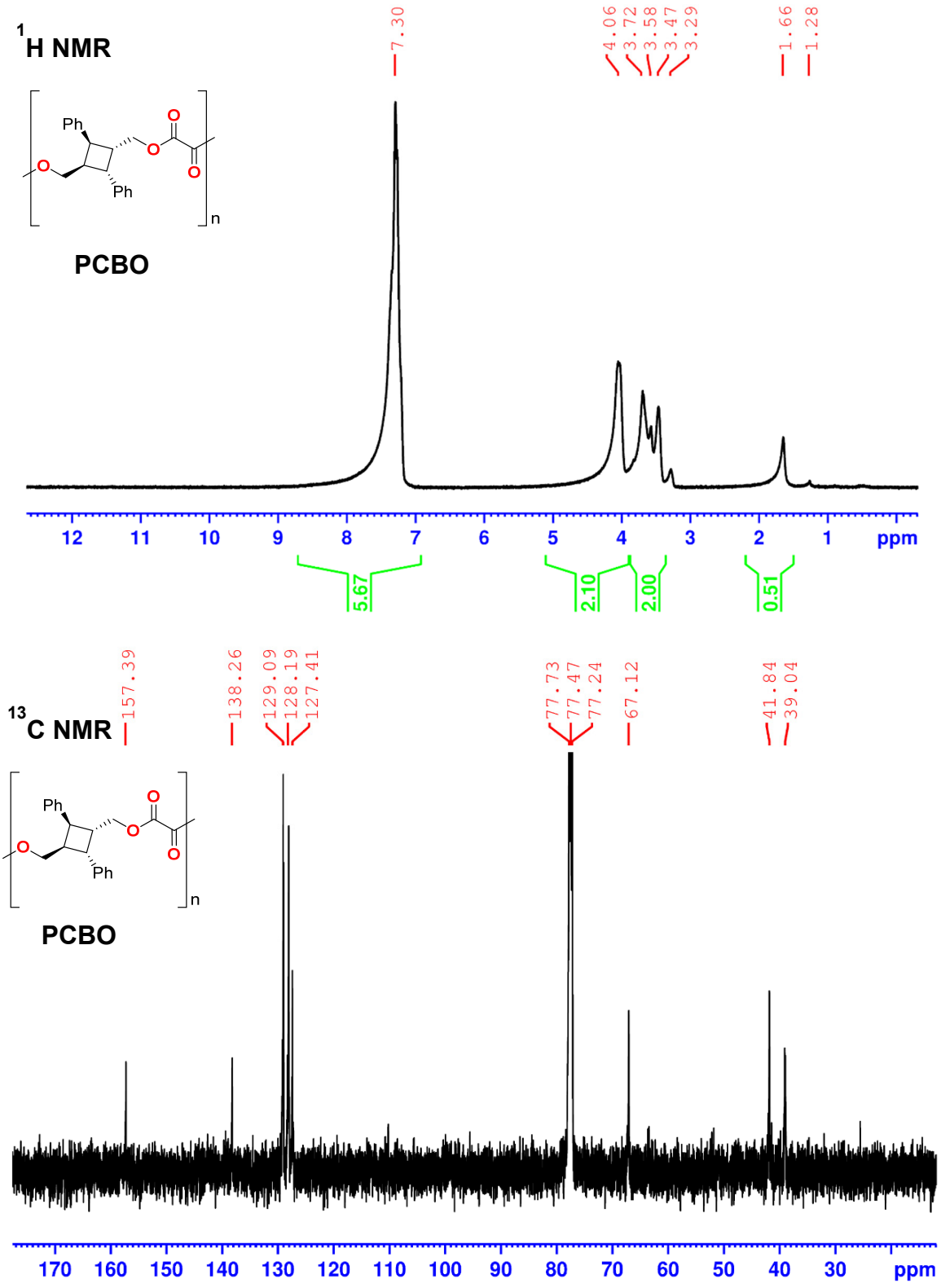


Figure S10. ^{1}H and ^{13}C NMR spectra of **PCBO** in $CDCl_3$ at room temperature

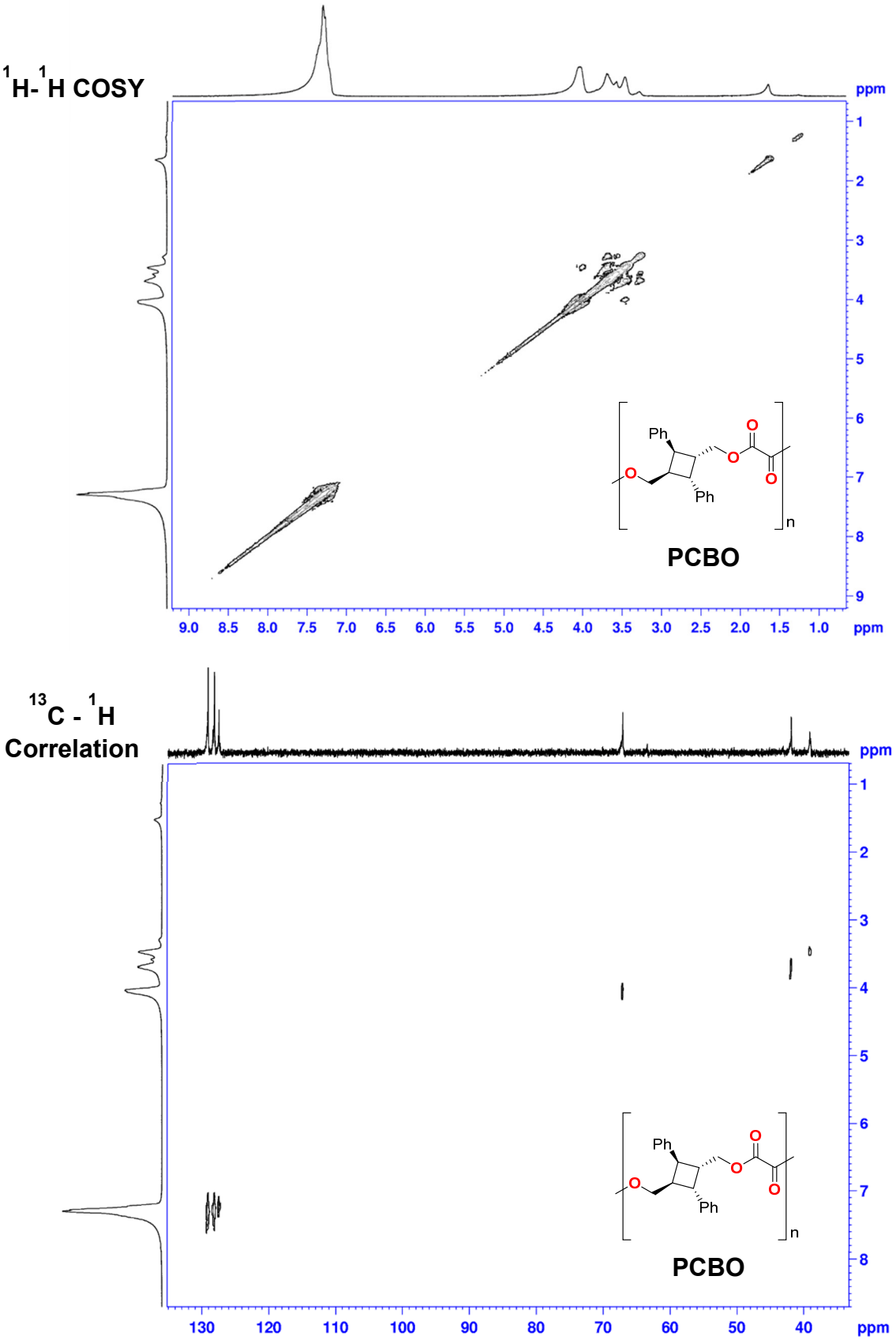


Figure S11. COSY and CH-correlation spectra of **PCBO** in $CDCl_3$ at room temperature.

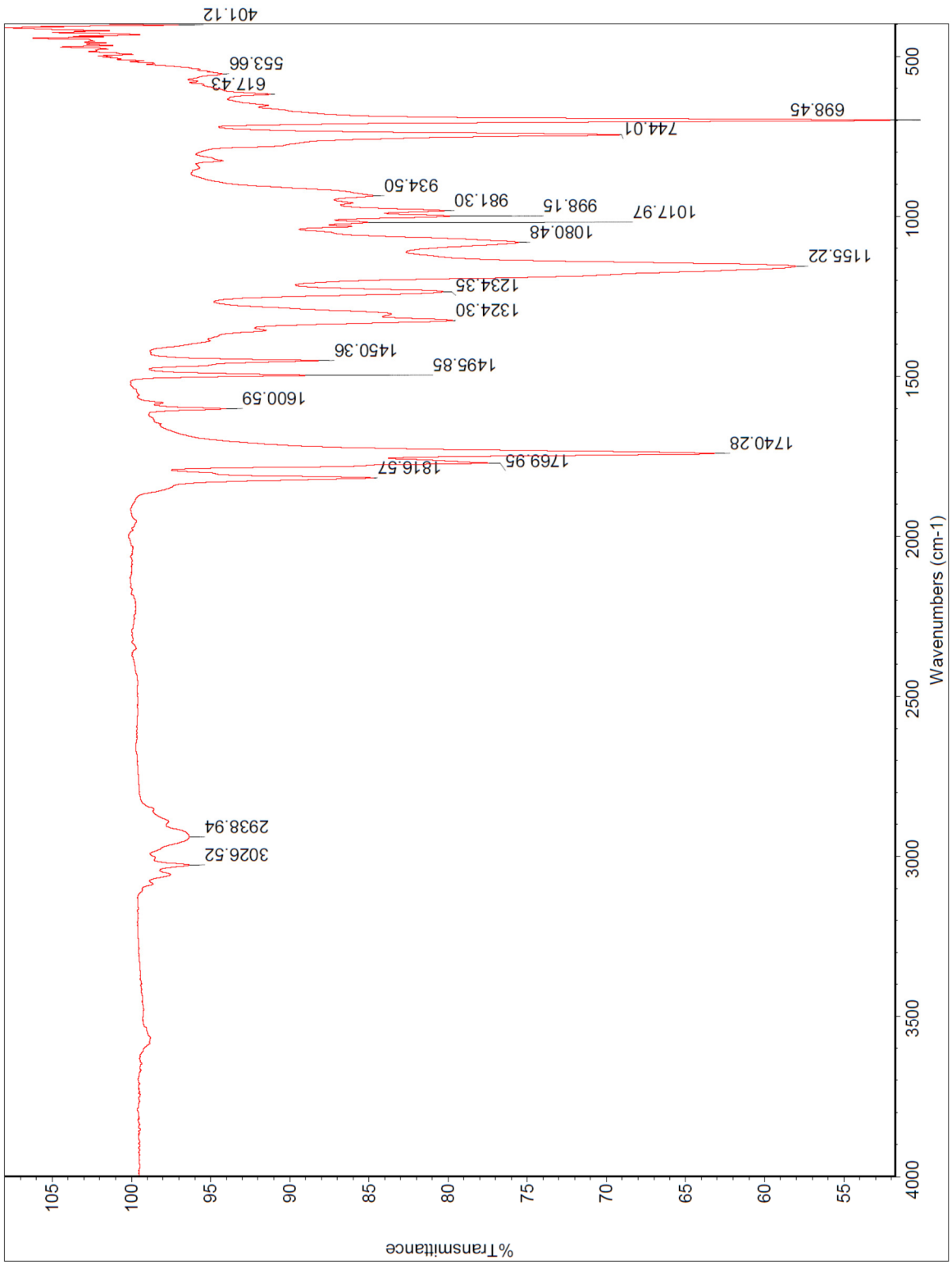


Figure S12. FT-IR spectrum of **PCBO** using ATR detector.

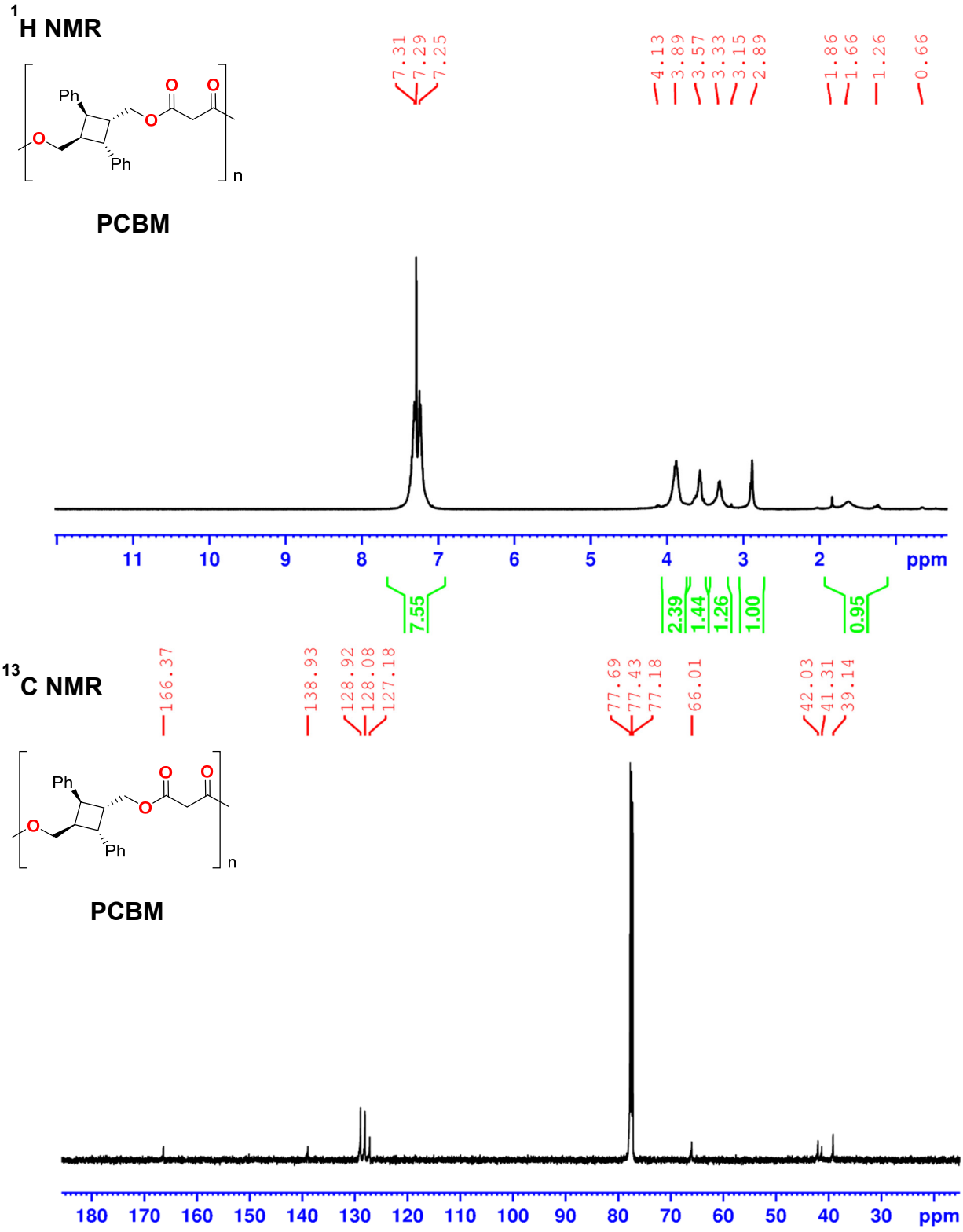


Figure S13. ^{1}H and ^{13}C NMR spectra of **PCBM** in $CDCl_3$ at room temperature.

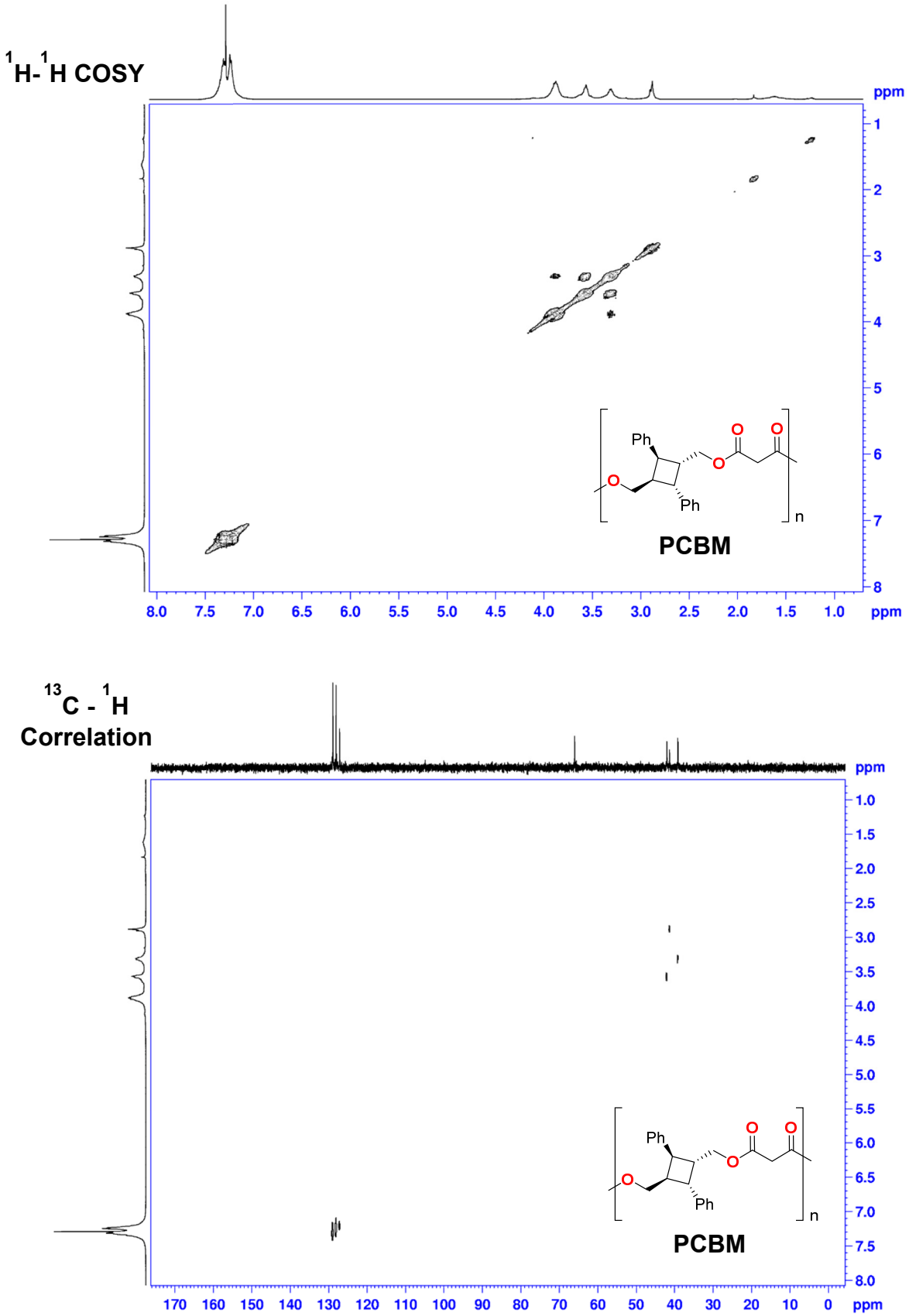


Figure S14.COSY and C-H correlation spectra of **PCBM** in $CDCl_3$ at room temperature.

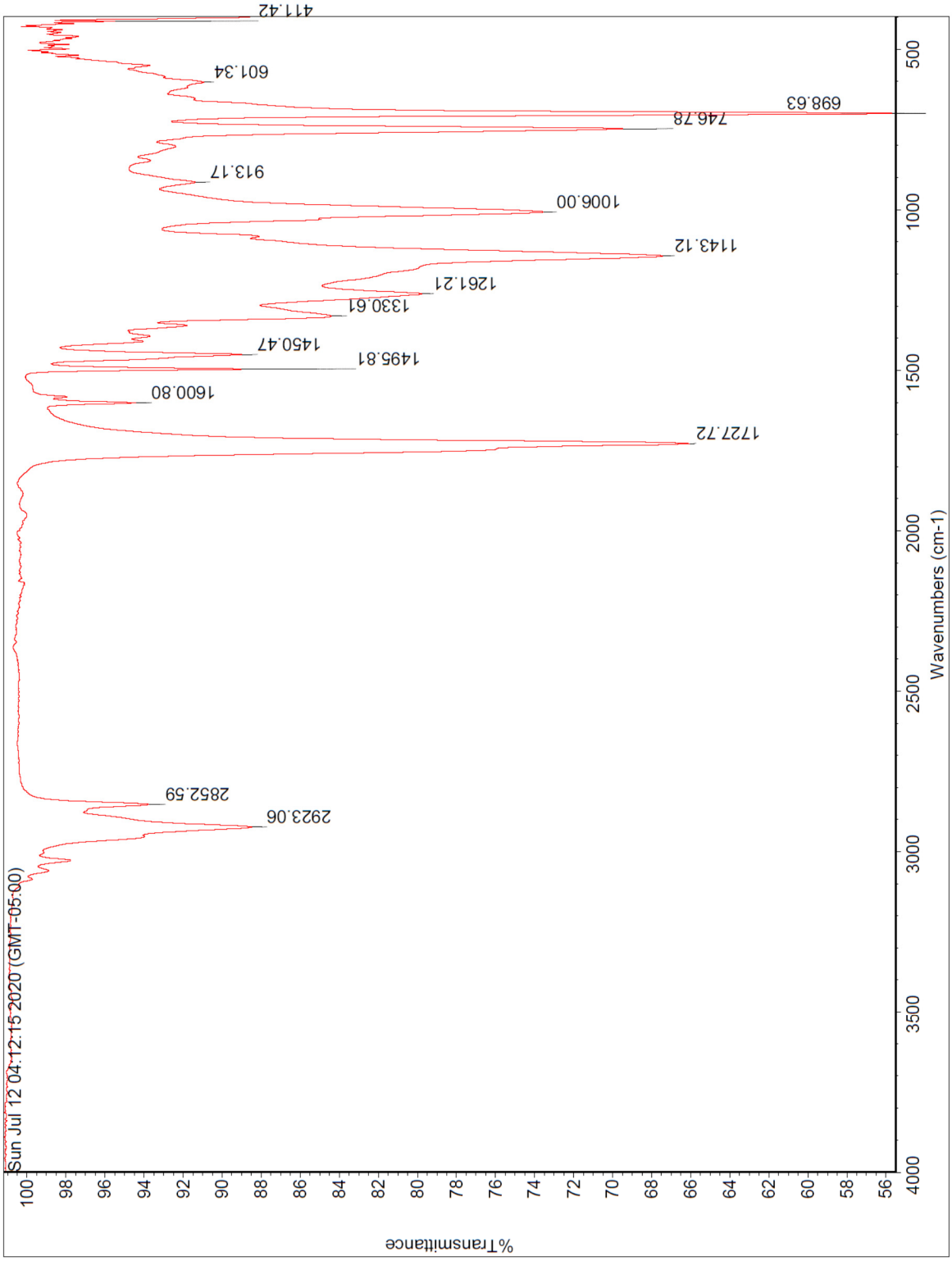


Figure S15. FT-IR spectrum of **PCBM** using ATR detector.

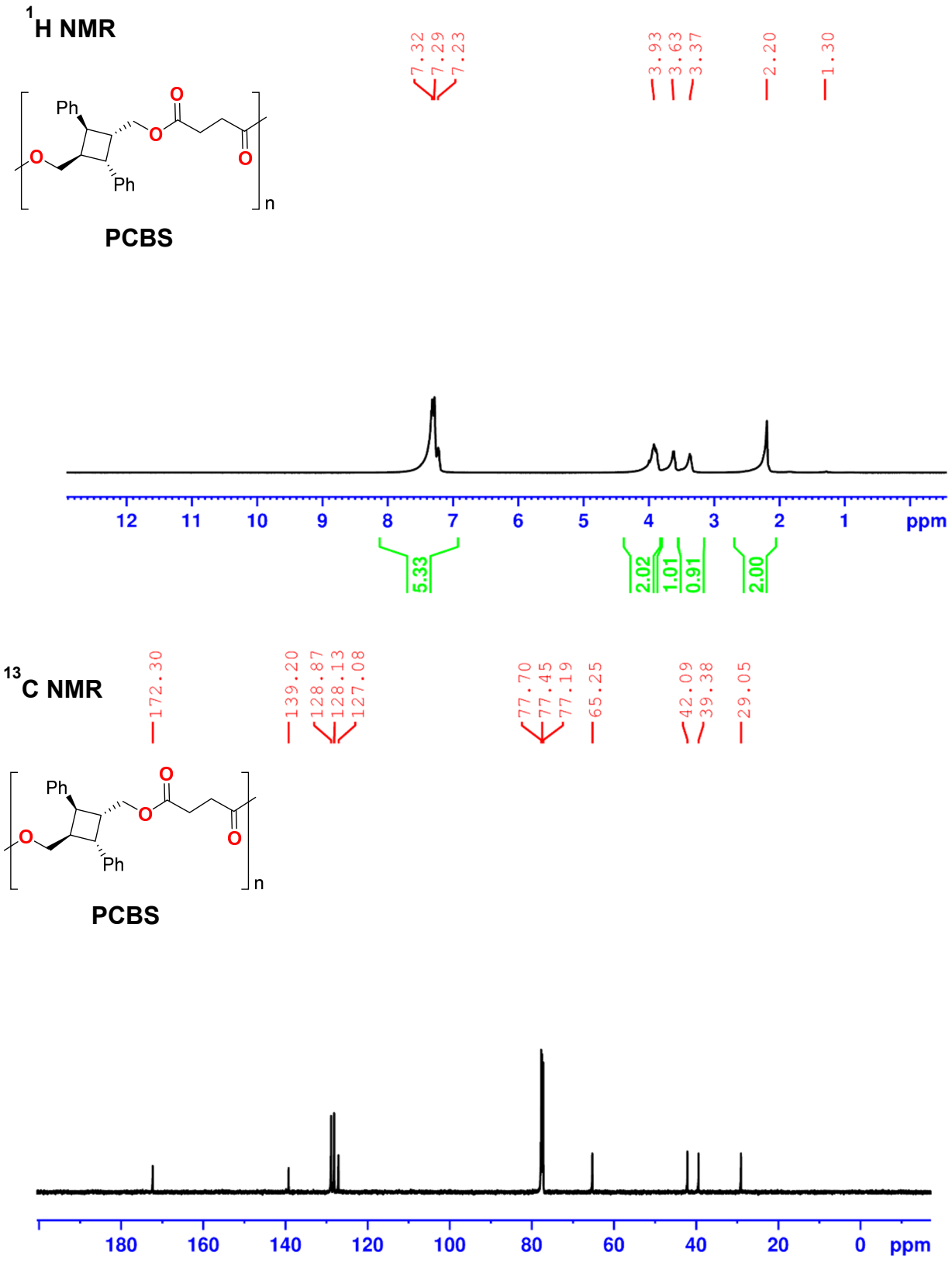


Figure S16. ^{1}H and ^{13}C NMR spectra of **PCBS** in $CDCl_3$ at room temperature.

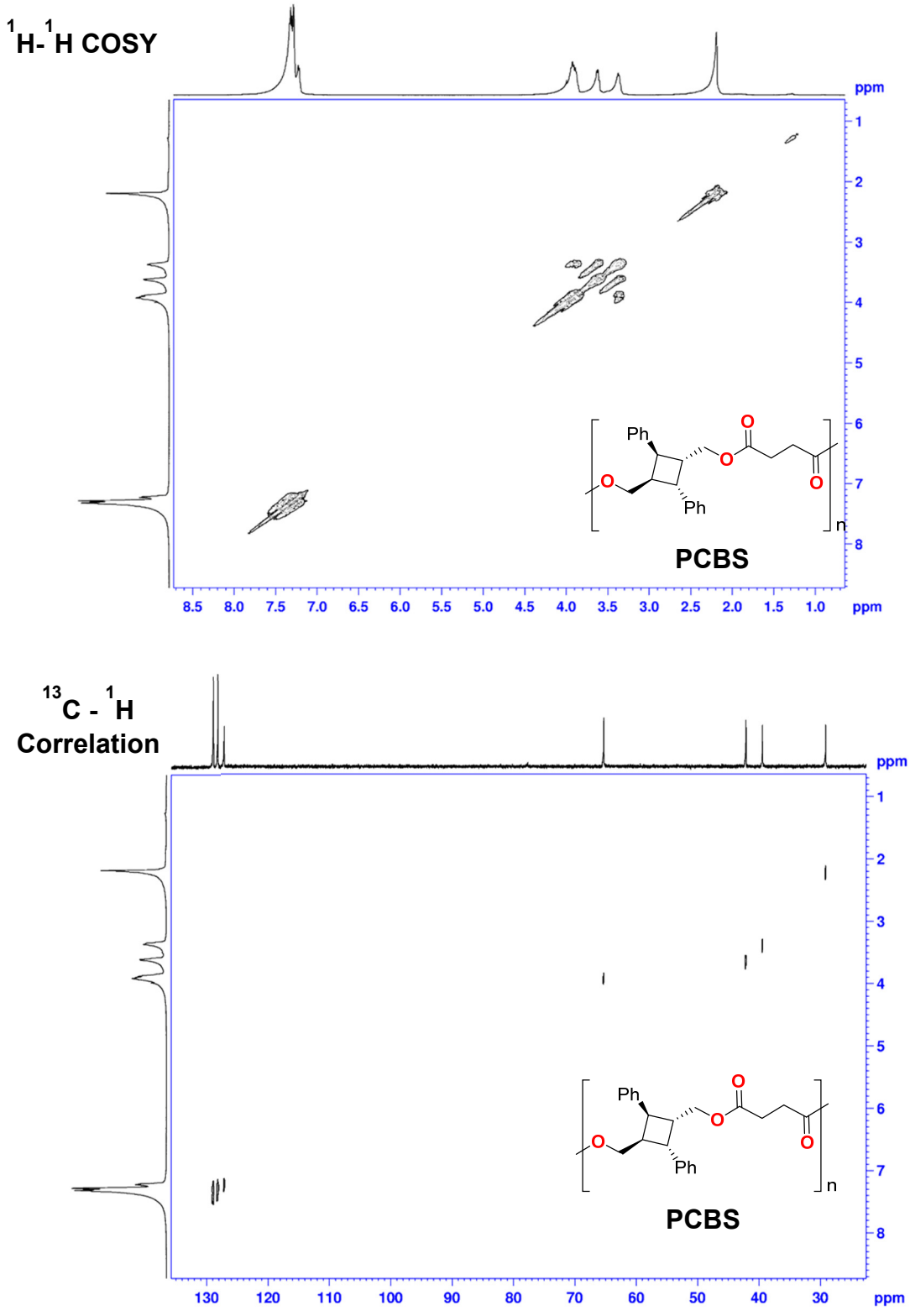


Figure S17.COSY and C-H correlation spectra of **PCBS** in $CDCl_3$ at room temperature.

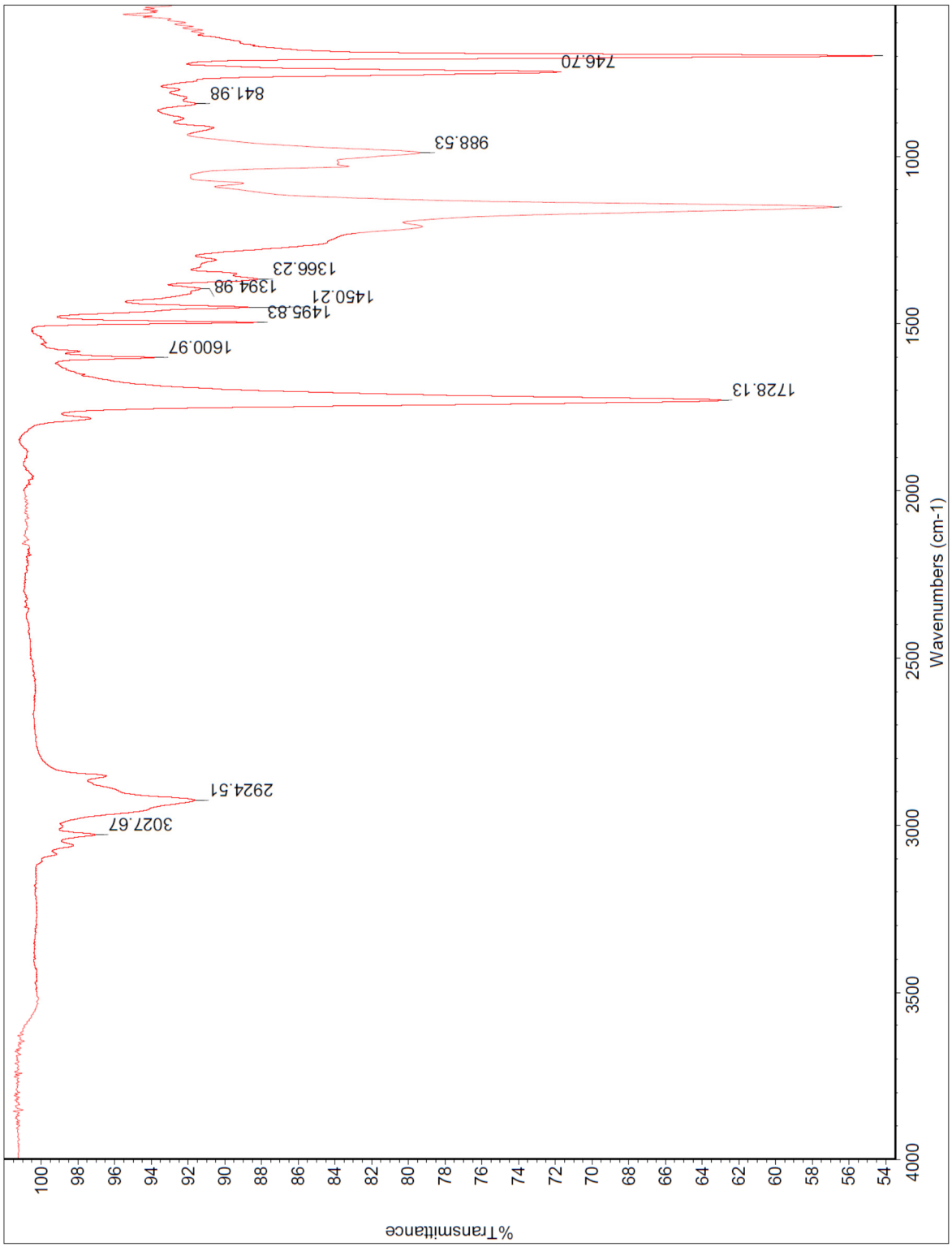


Figure S18. FT-IR spectrum of **PCBS** using ATR detector.

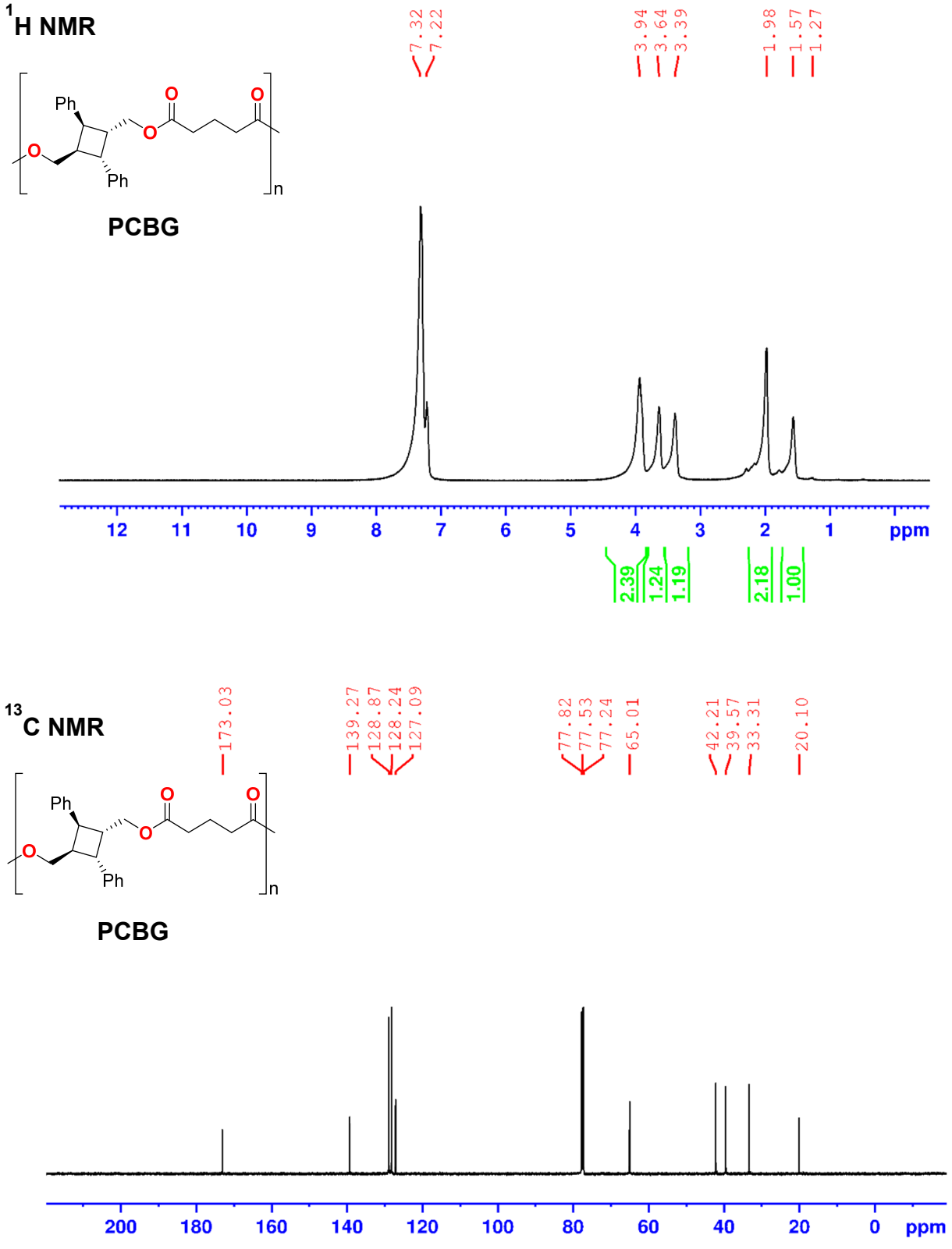


Figure S19. ^{1}H and ^{13}C NMR spectra of **PCBG** in $CDCl_3$ at room temperature.

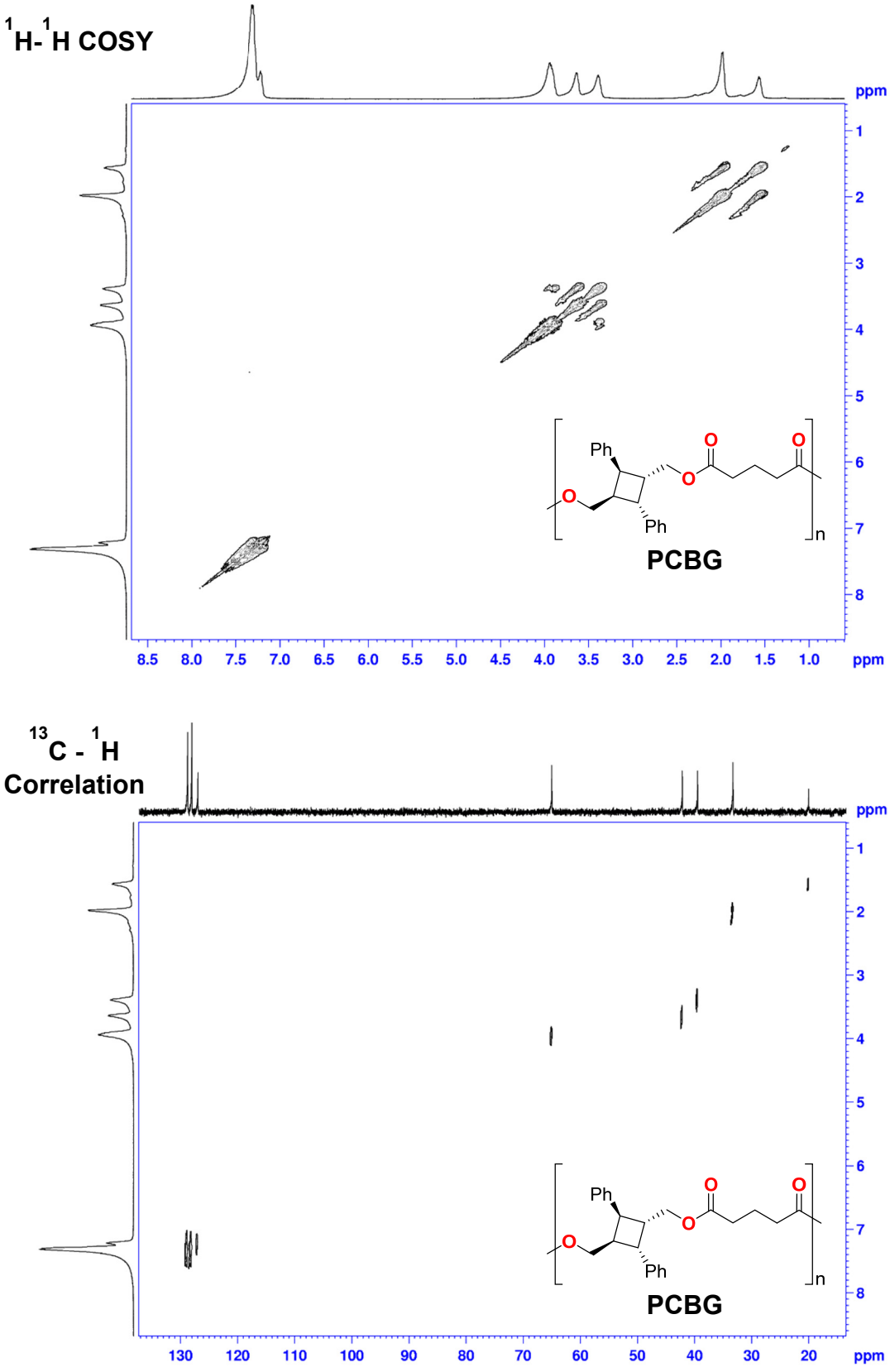


Figure S20.COSY and C-H correlation spectra of **PCBG** in $CDCl_3$ at room temperature.

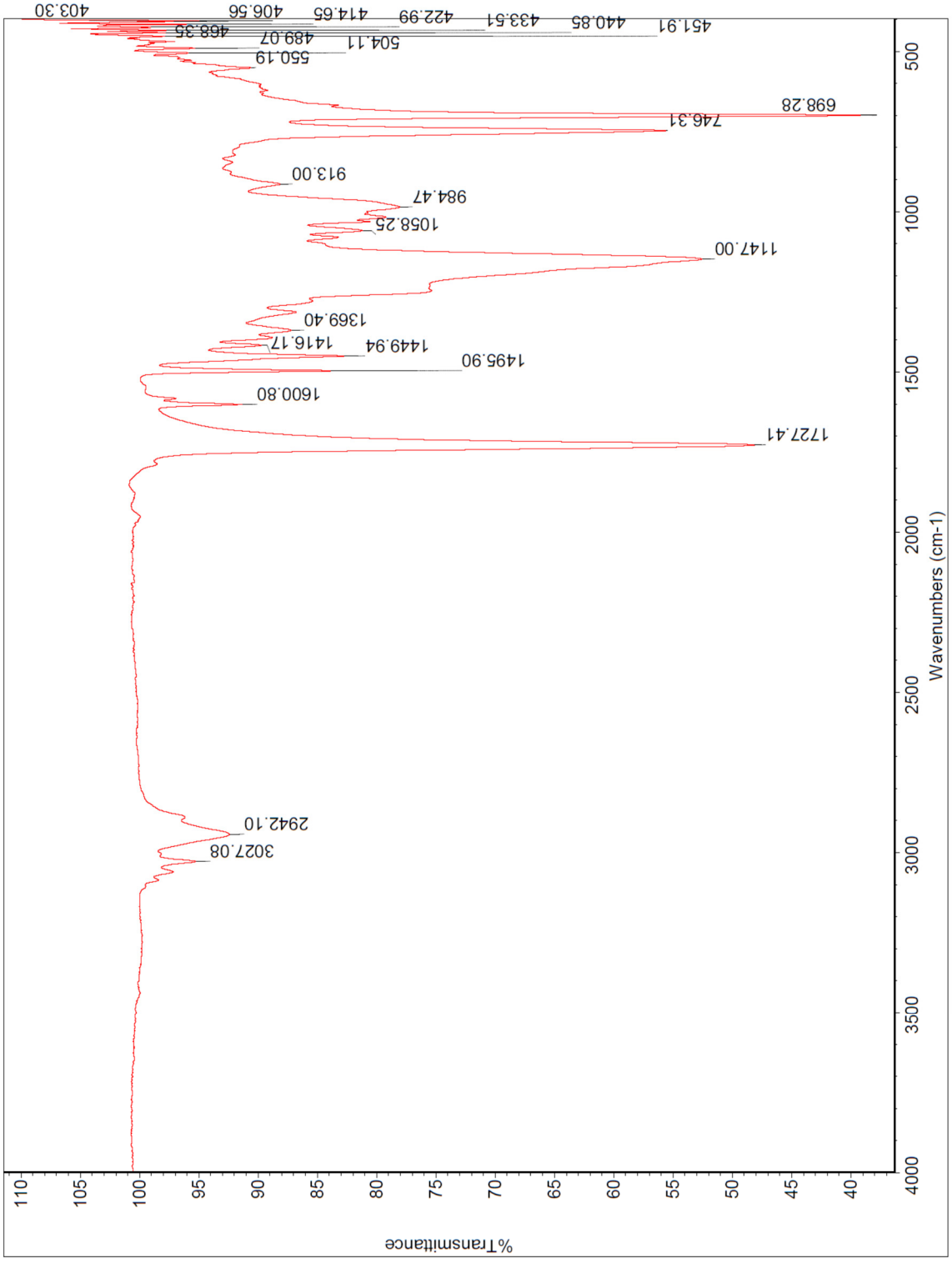


Figure S21. FT-IR spectrum of **PCBG** using ATR detector

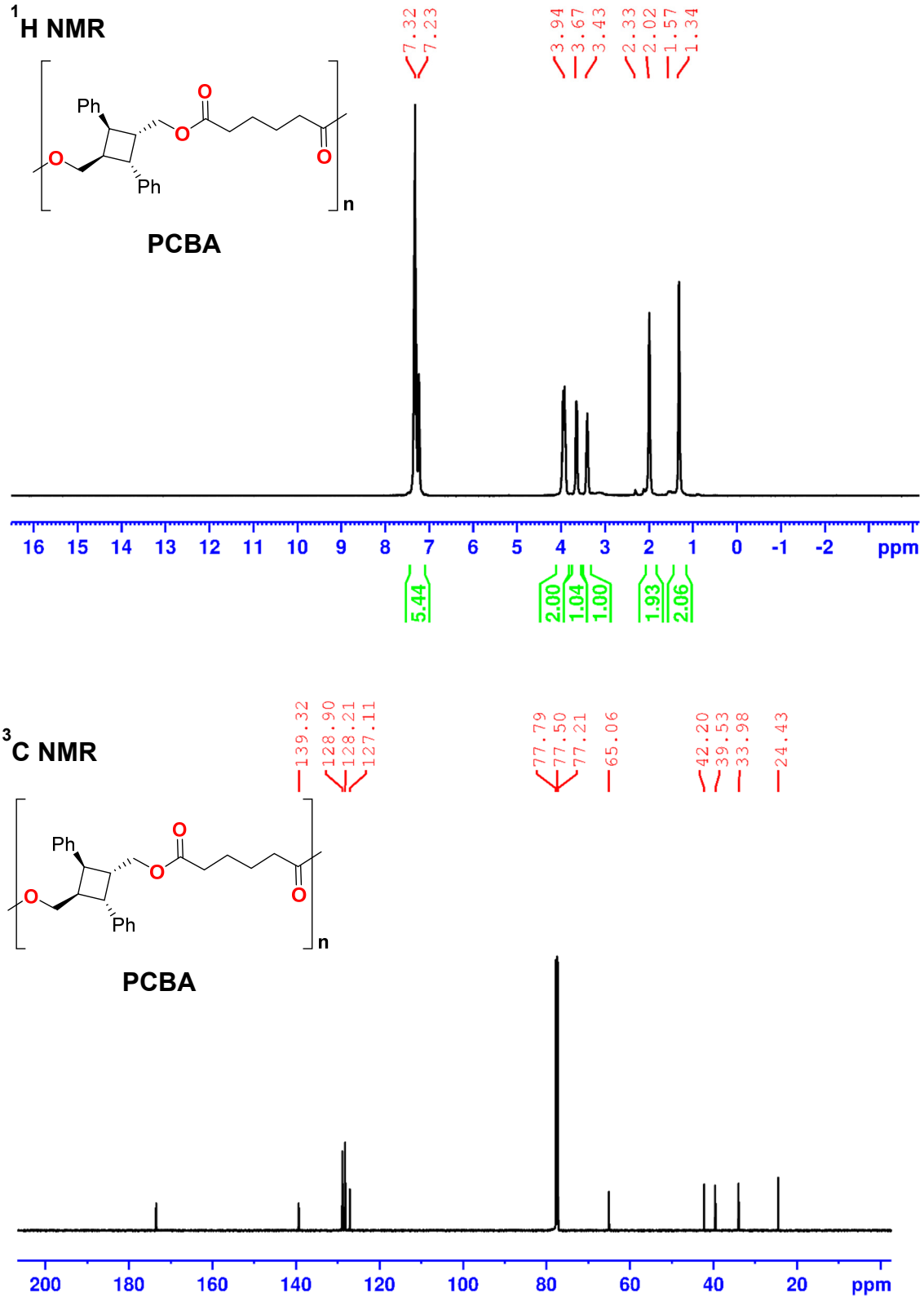


Figure S22. ^{1}H and ^{13}C NMR spectra of **PCBA** in $CDCl_3$ at room temperature.

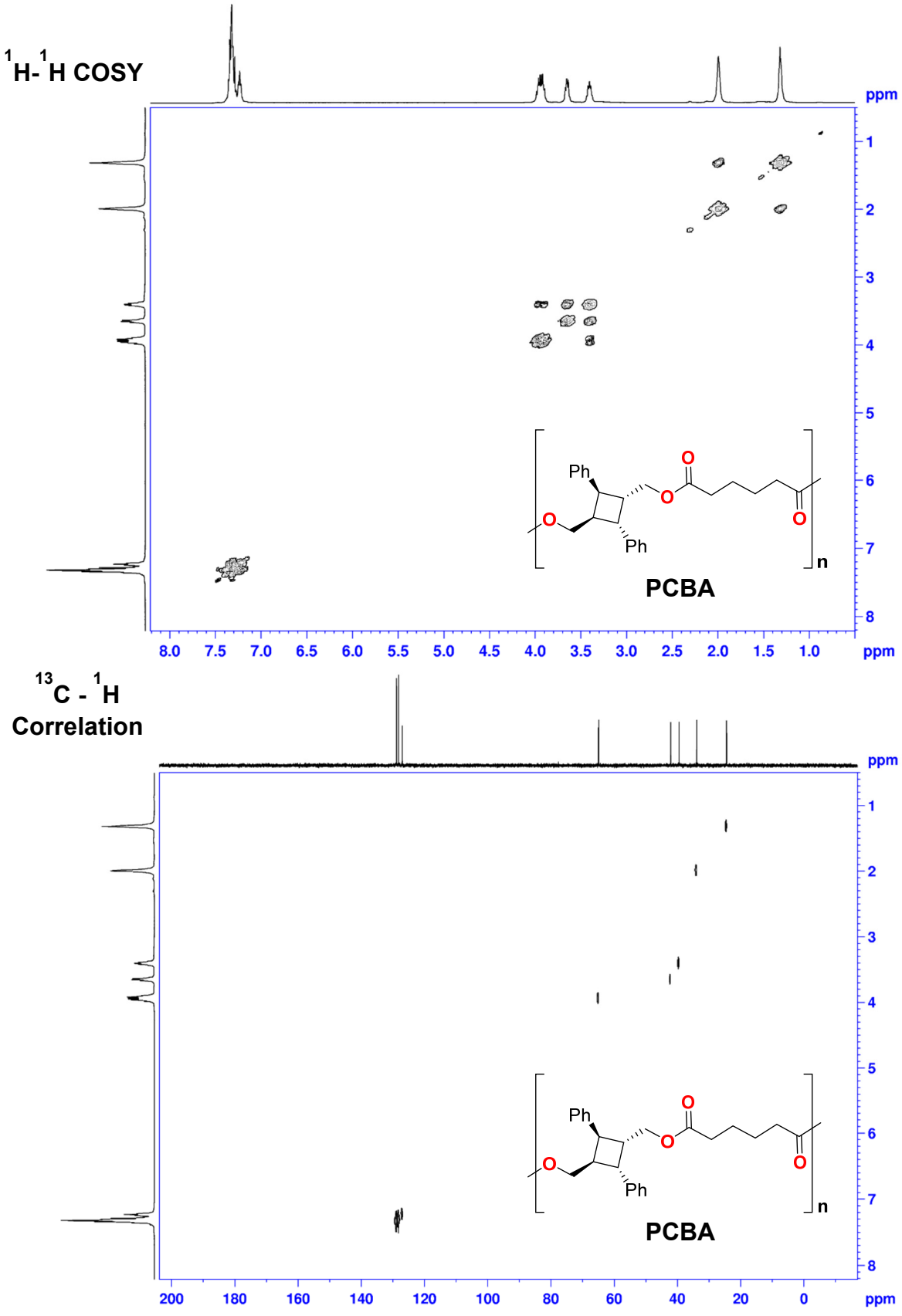


Figure S23.COSY and C-H correlation spectra of **PCBA** in $CDCl_3$ at room temperature.

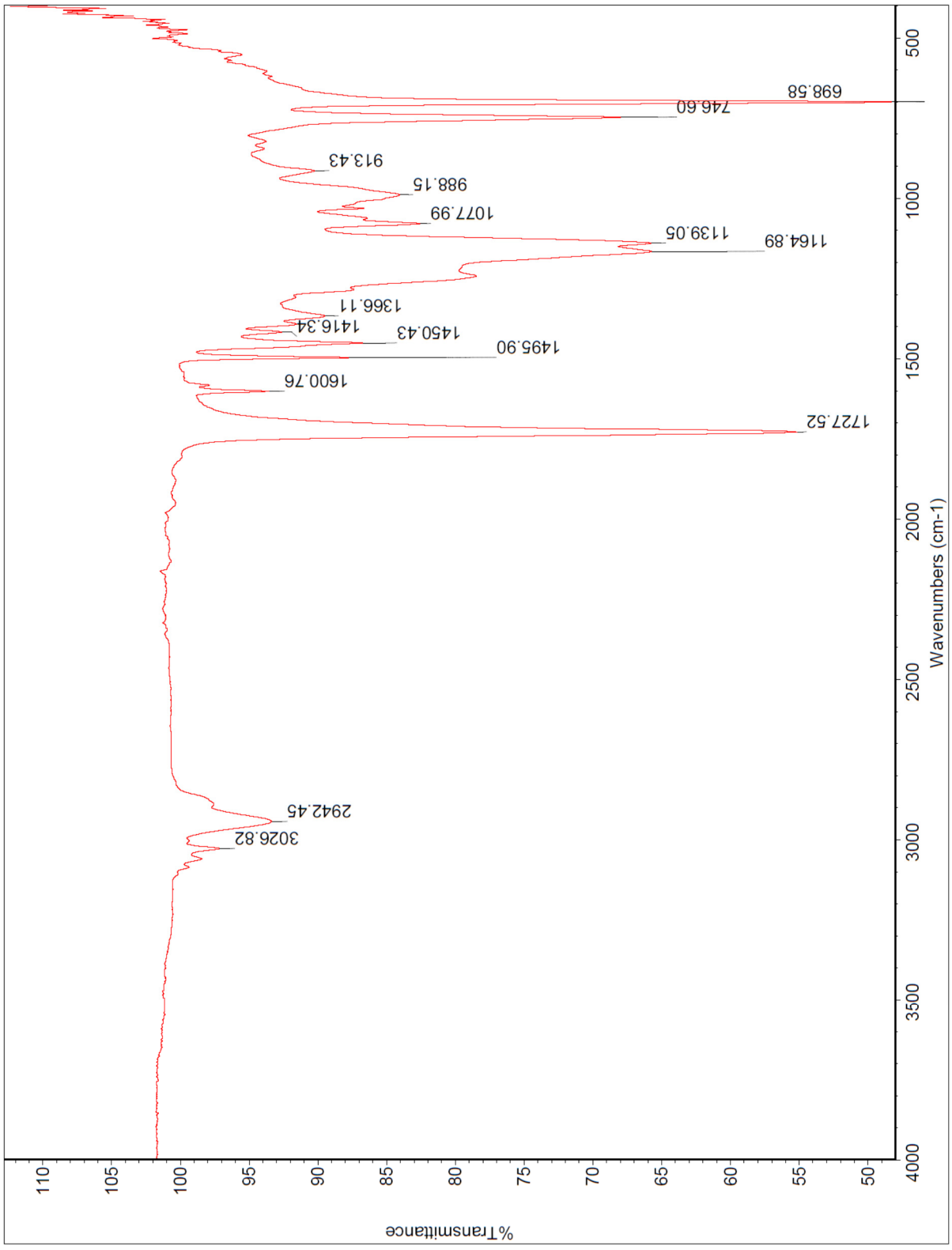


Figure S24. FT-IR spectrum of **PCBA** using ATR detector.

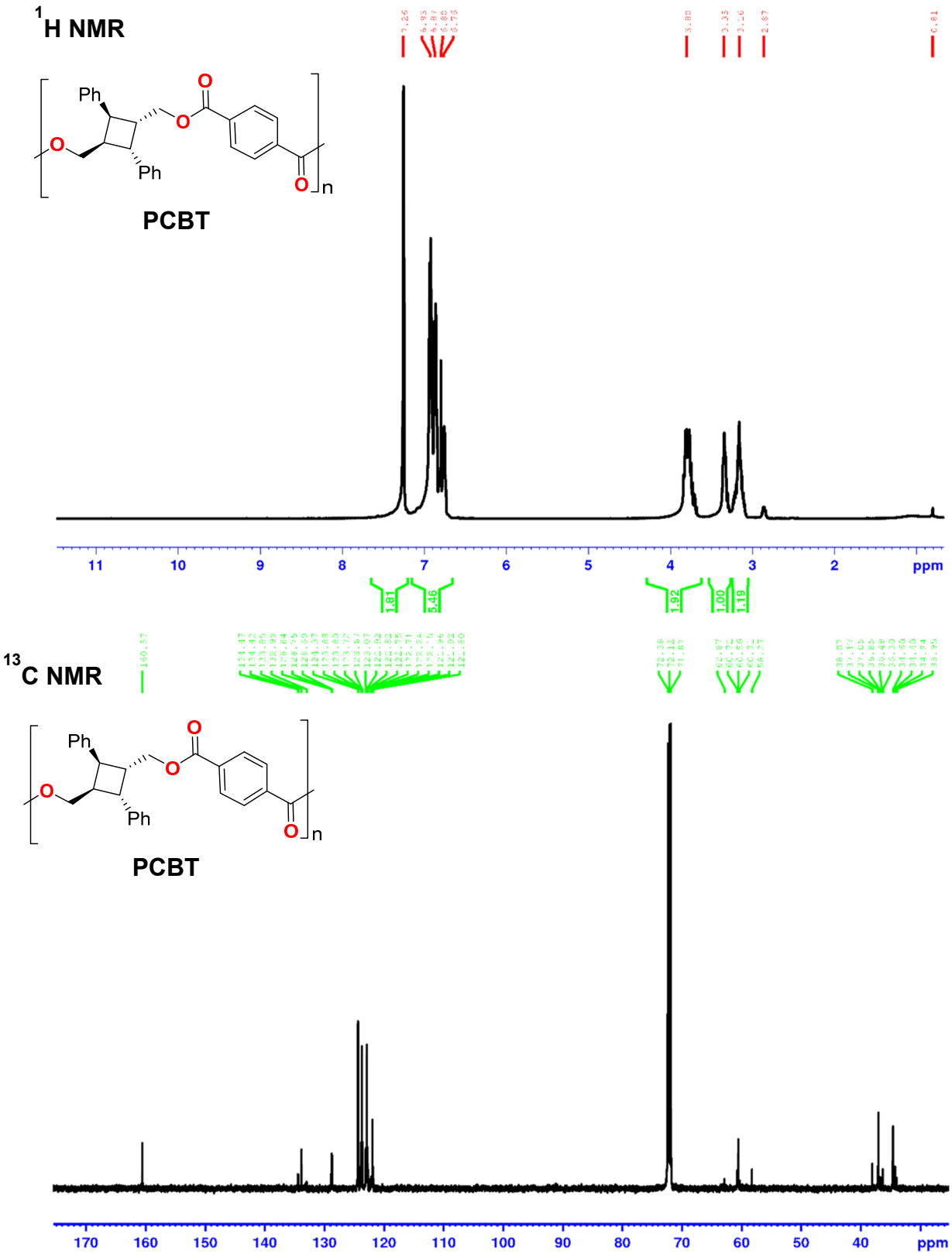


Figure S25. ^{1}H and ^{13}C NMR spectra of **PCBT** in $CDCl_3$ at room temperature.

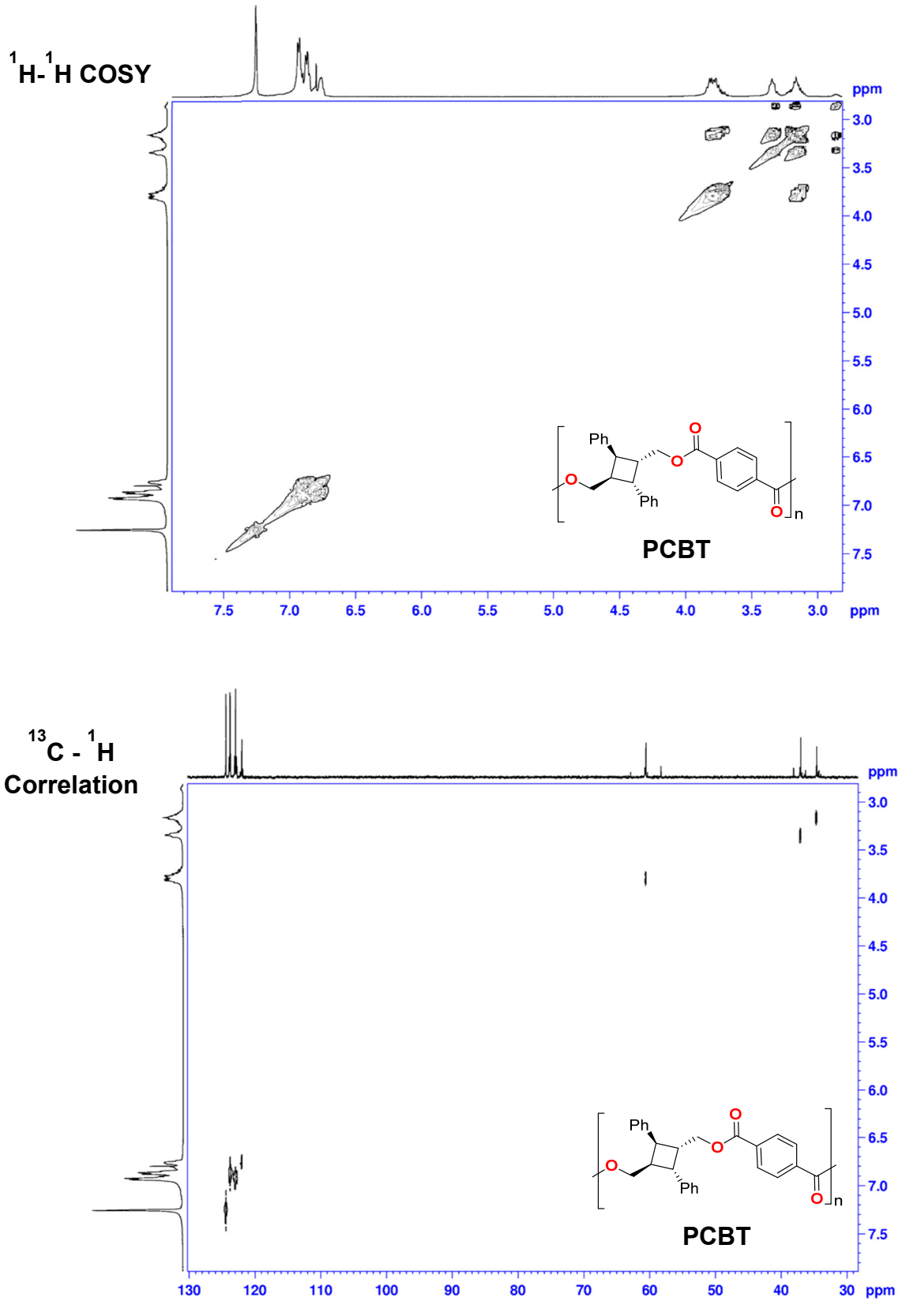


Figure S26.COSY and C-H correlation spectra of **PCBT** in $CDCl_3$ at room temperature.

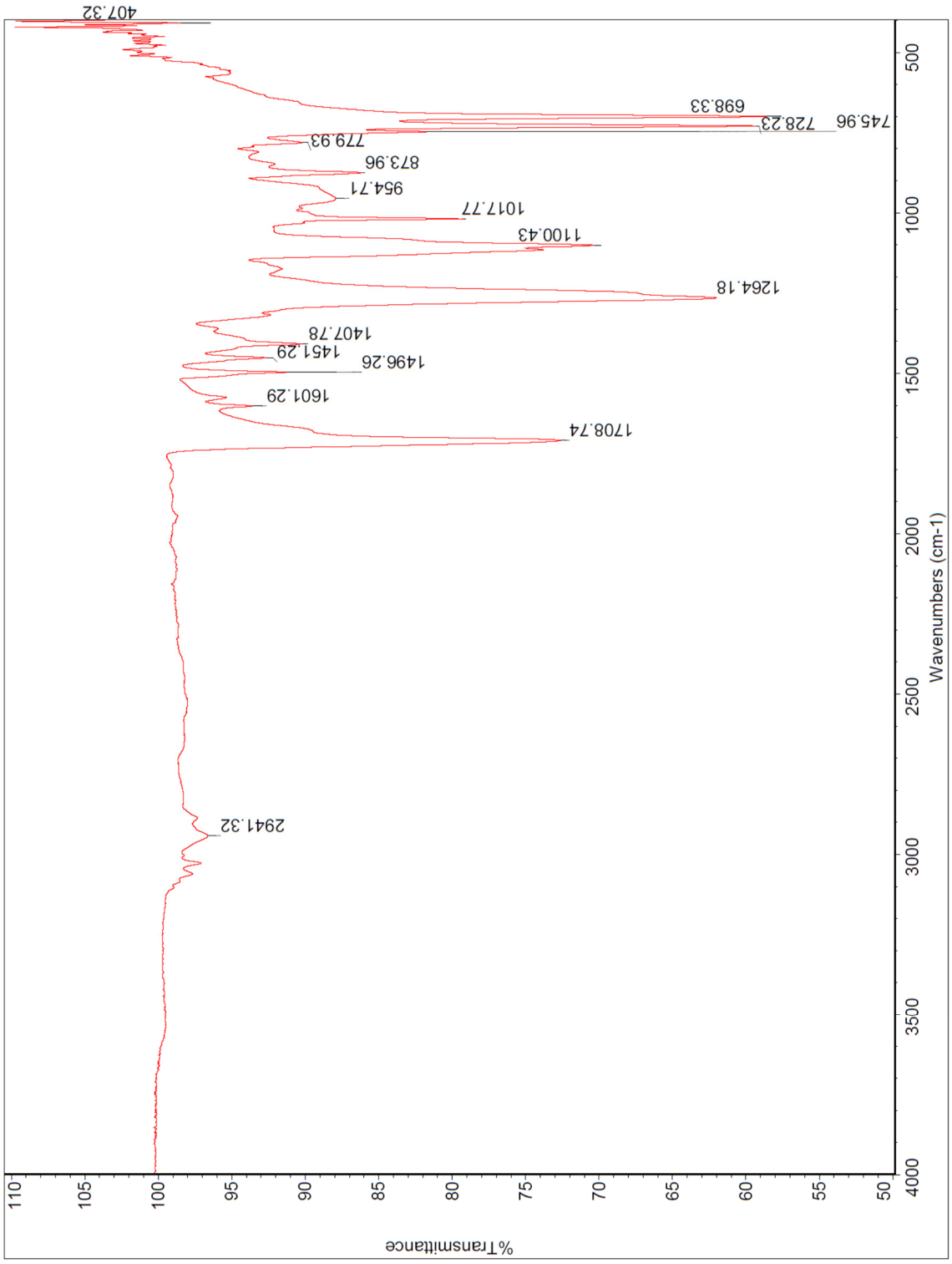


Figure S27. FT-IR of spectrum **PCBT** using ATR detector.

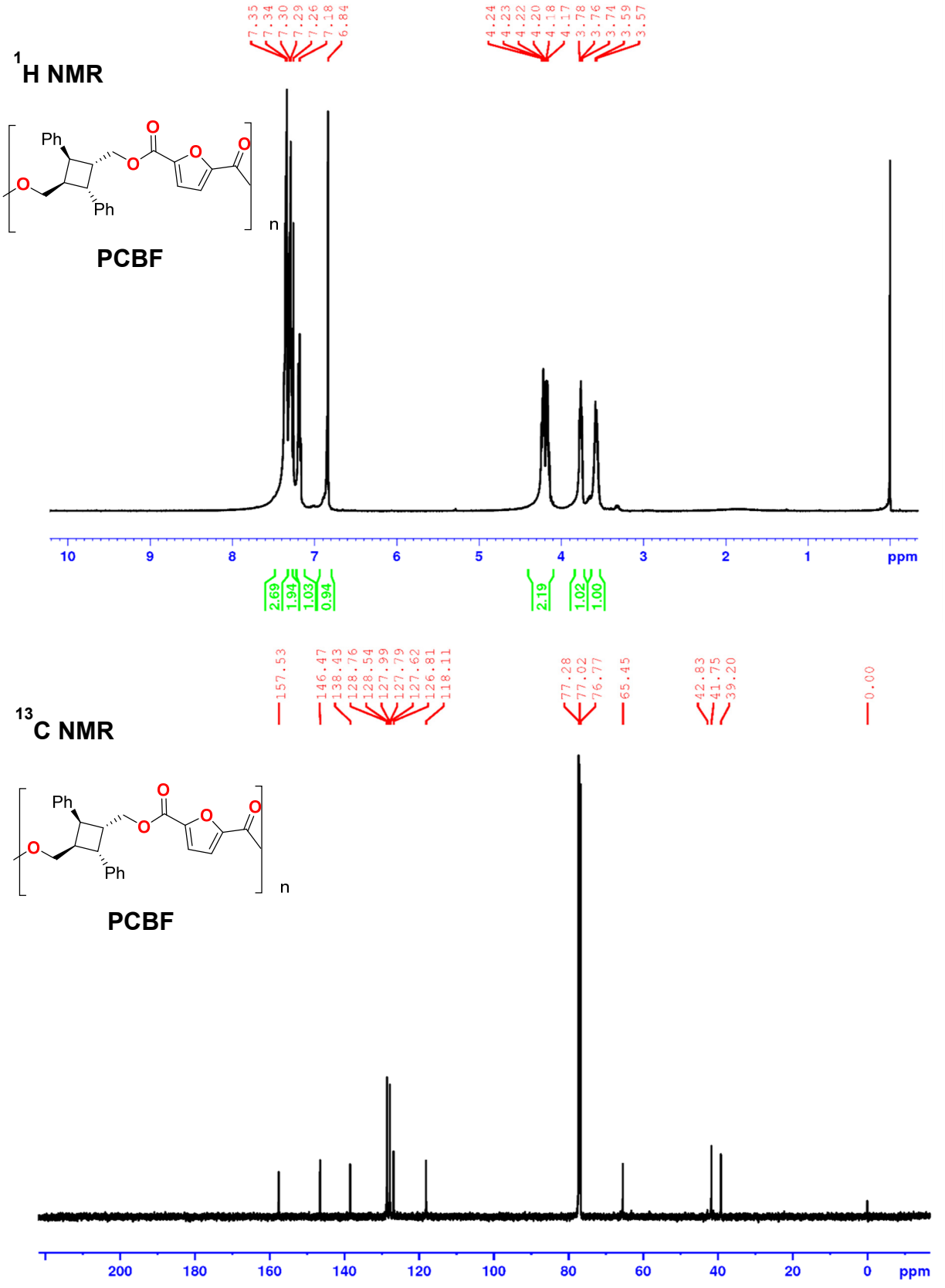


Figure S28. ^{1}H and ^{13}C NMR spectra of **PCBF** in $CDCl_3$ at room temperature.

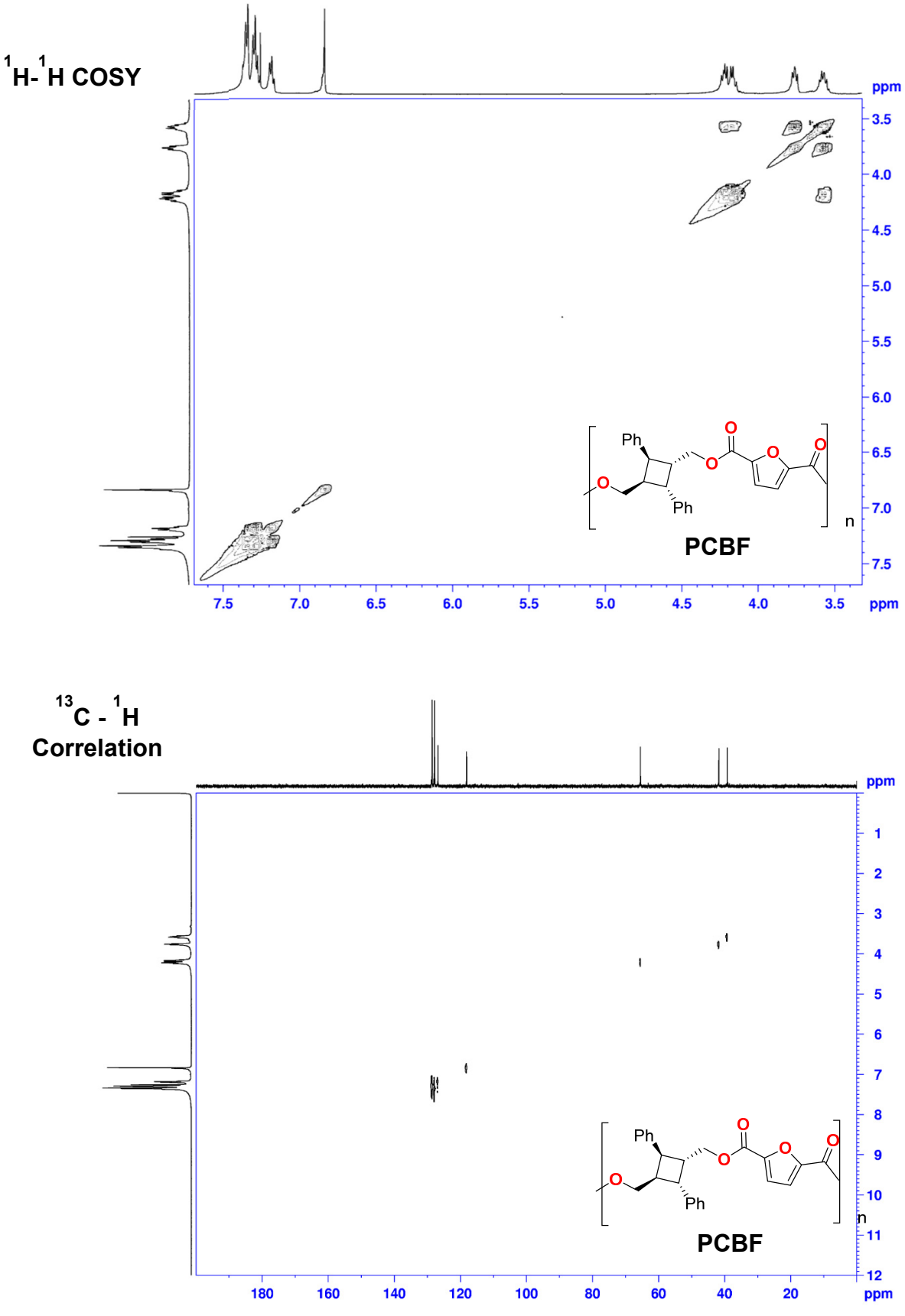


Figure S29.COSY and C-H correlation spectra of **PCBF** in $CDCl_3$ at room temperature.

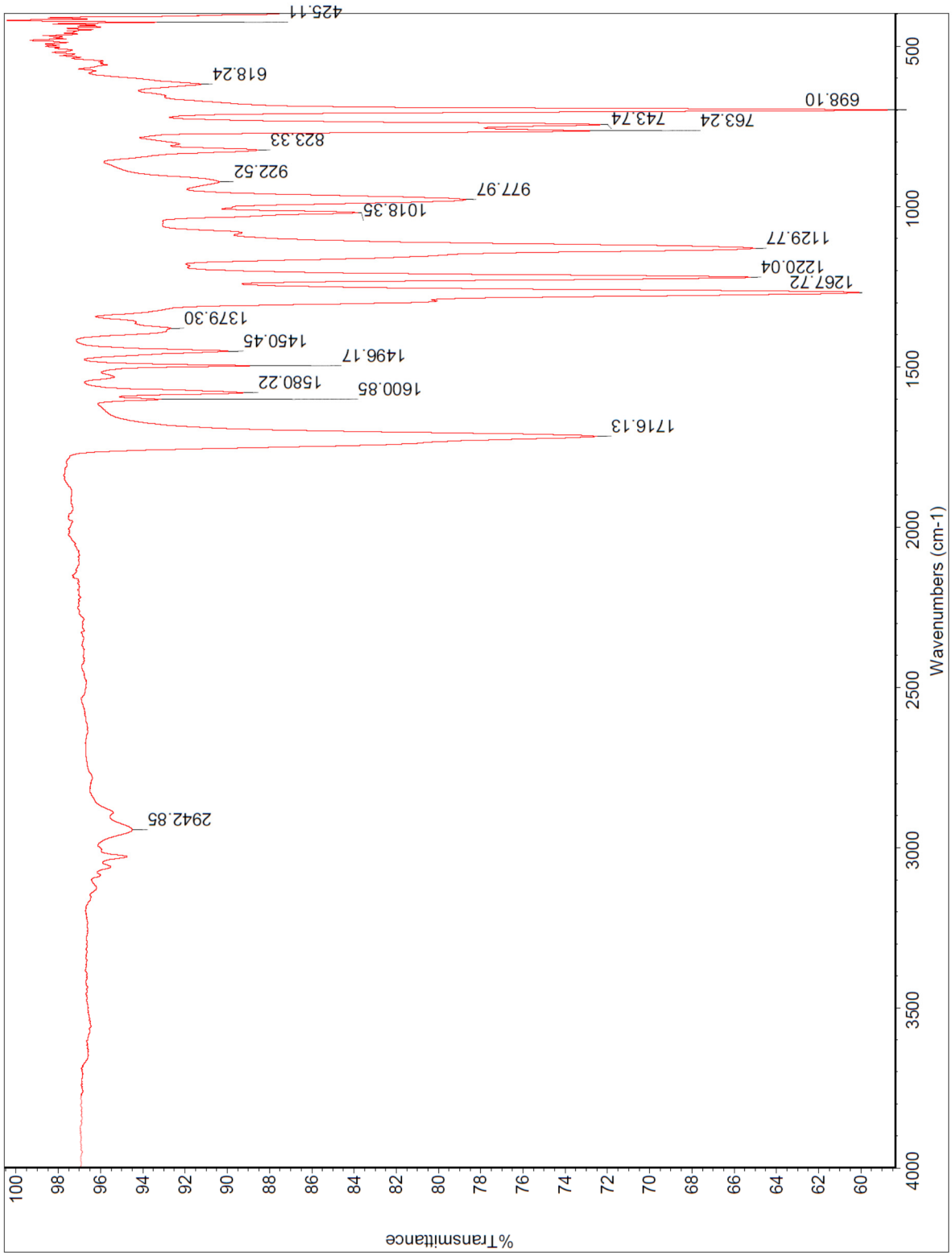


Figure S30. FT-IR spectrum of **PCBF** using ATR detector.

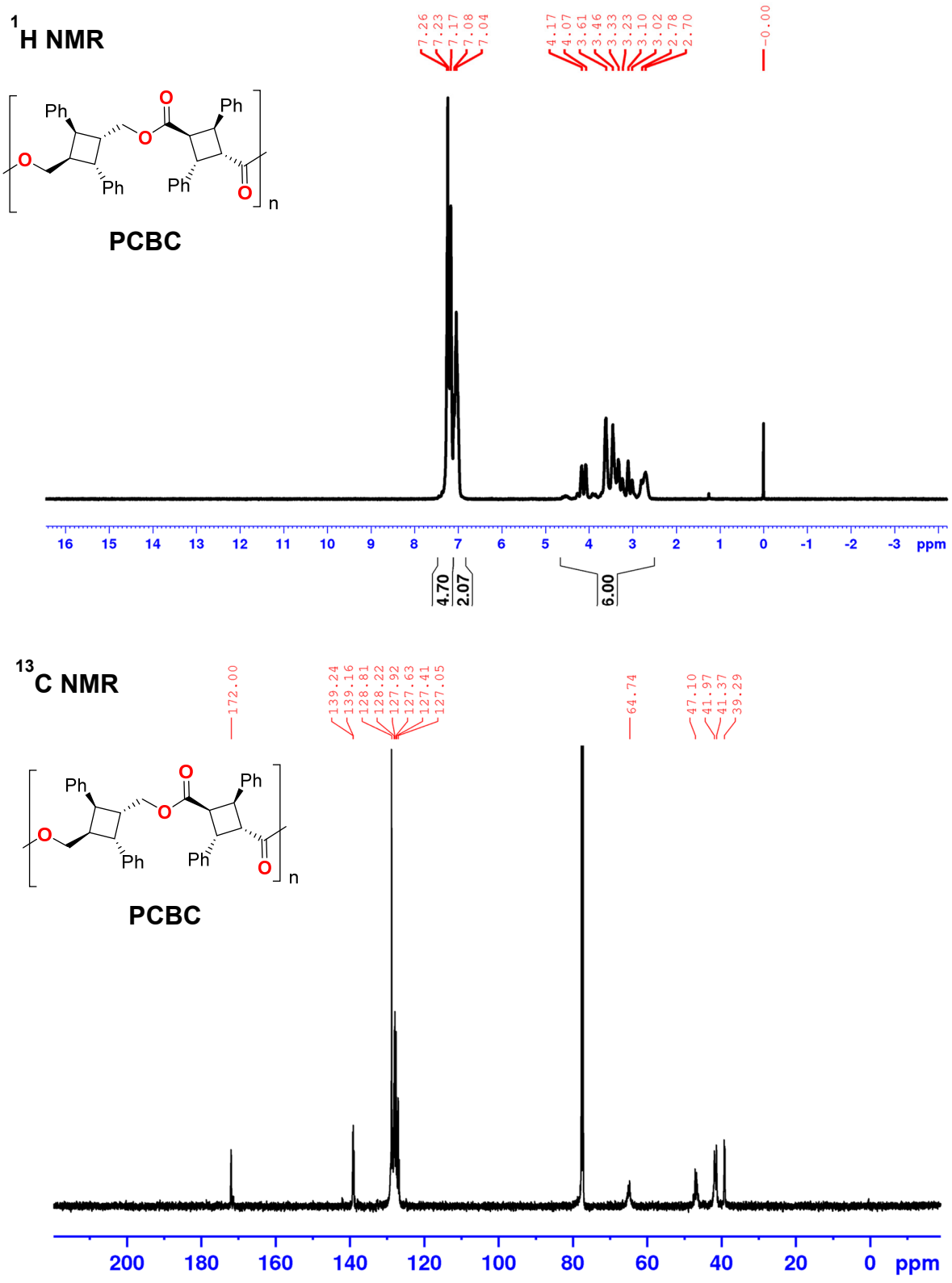


Figure S31. ^{1}H and ^{13}C NMR spectra of **PCBC** in $CDCl_3$ at room temperature.

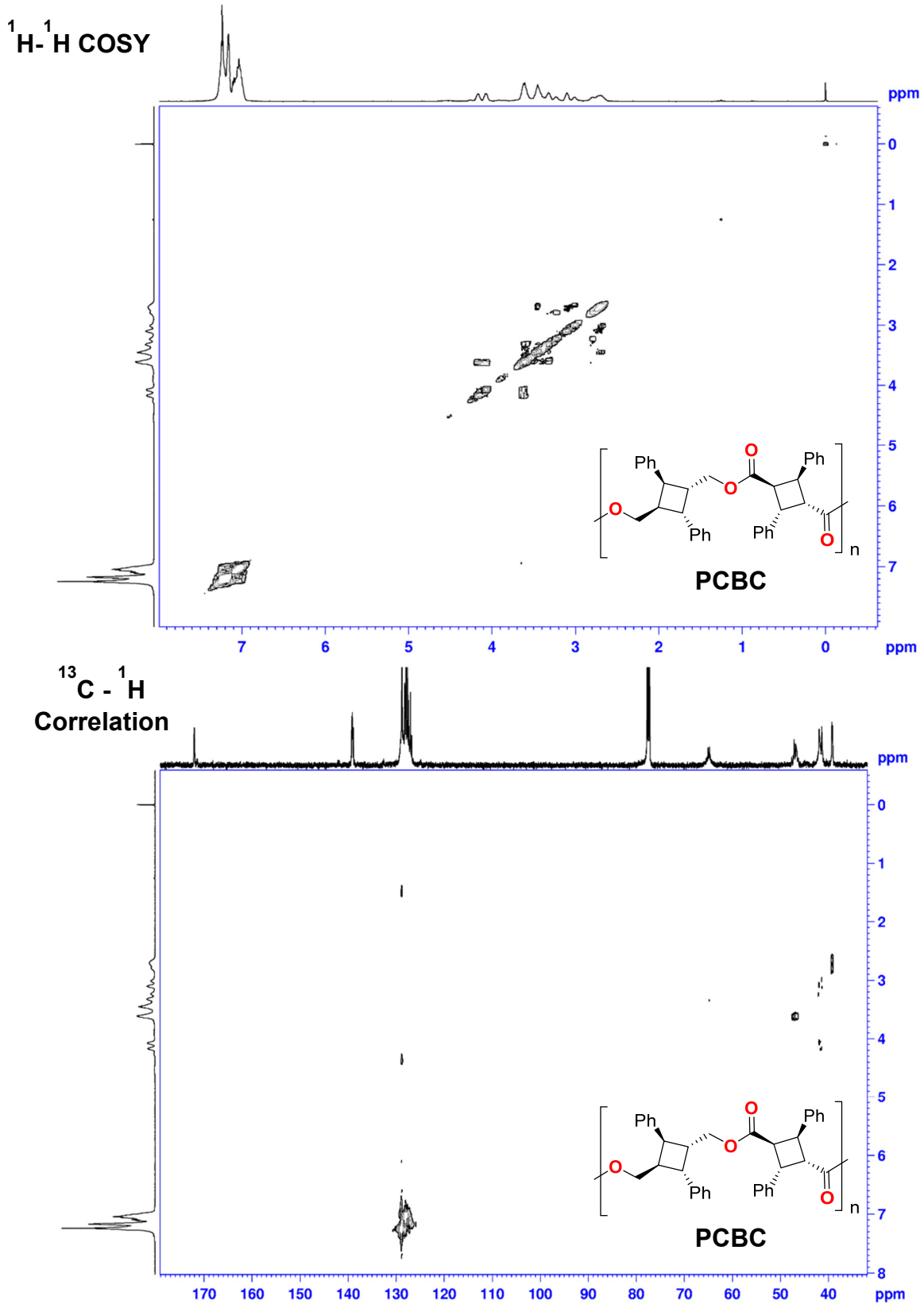


Figure S32.COSY and C-H correlation spectra of **PCBC** in $CDCl_3$ at room temperature.

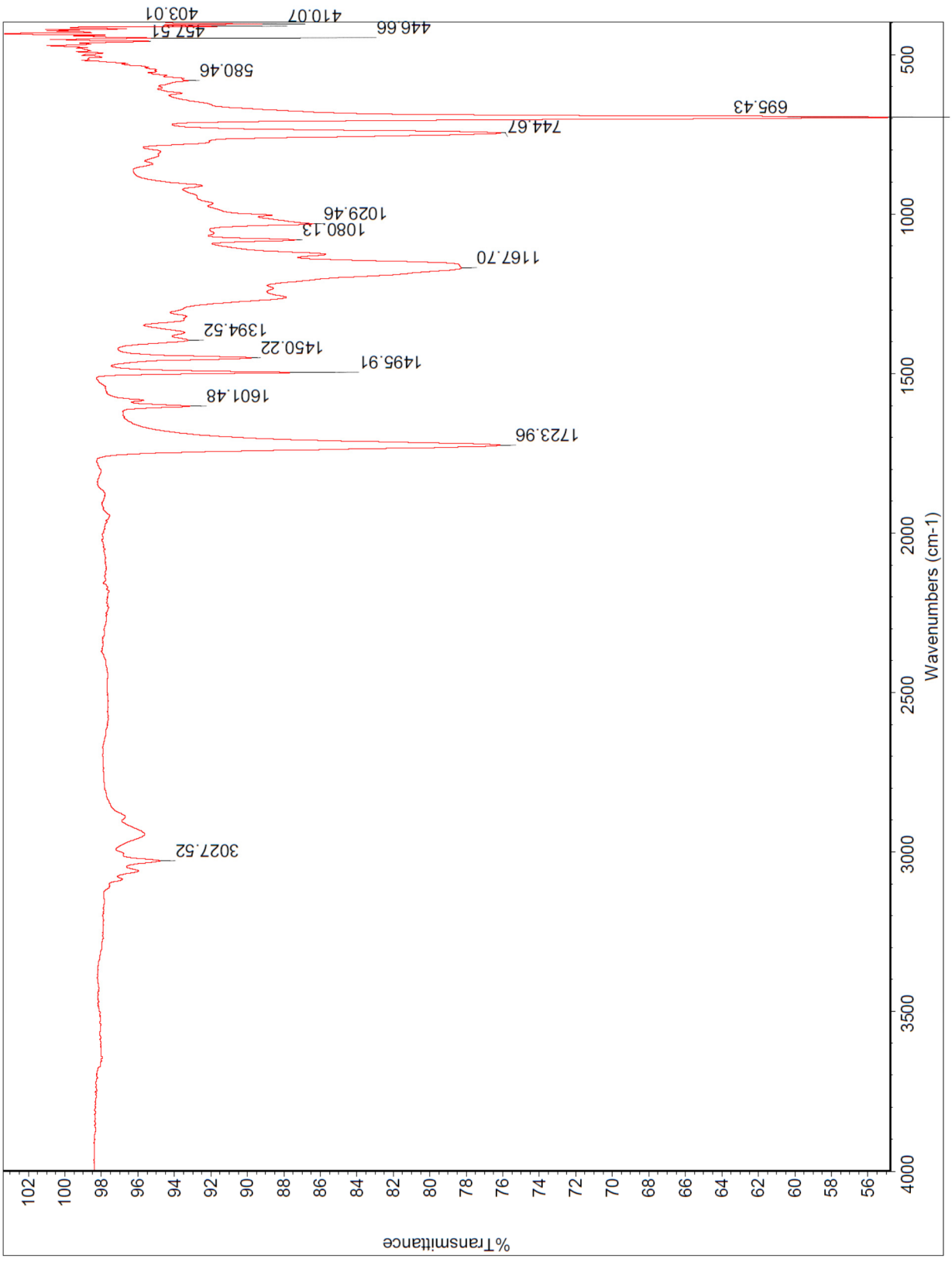


Figure S33. FT-IR spectrum of **PCBC** using ATR detector.

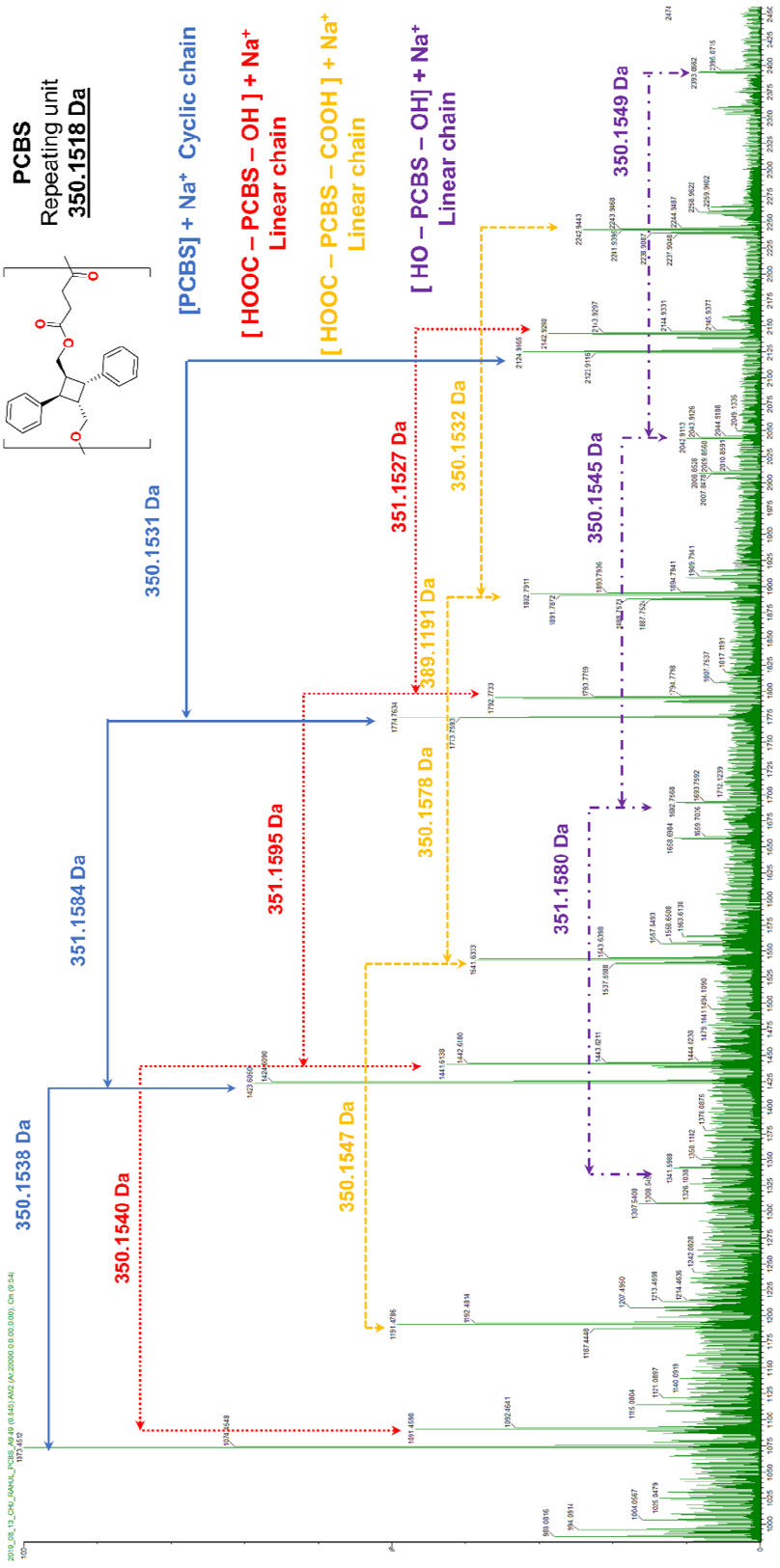


Figure S34. MALDI-TOF-MS spectrum of **PCBS.**

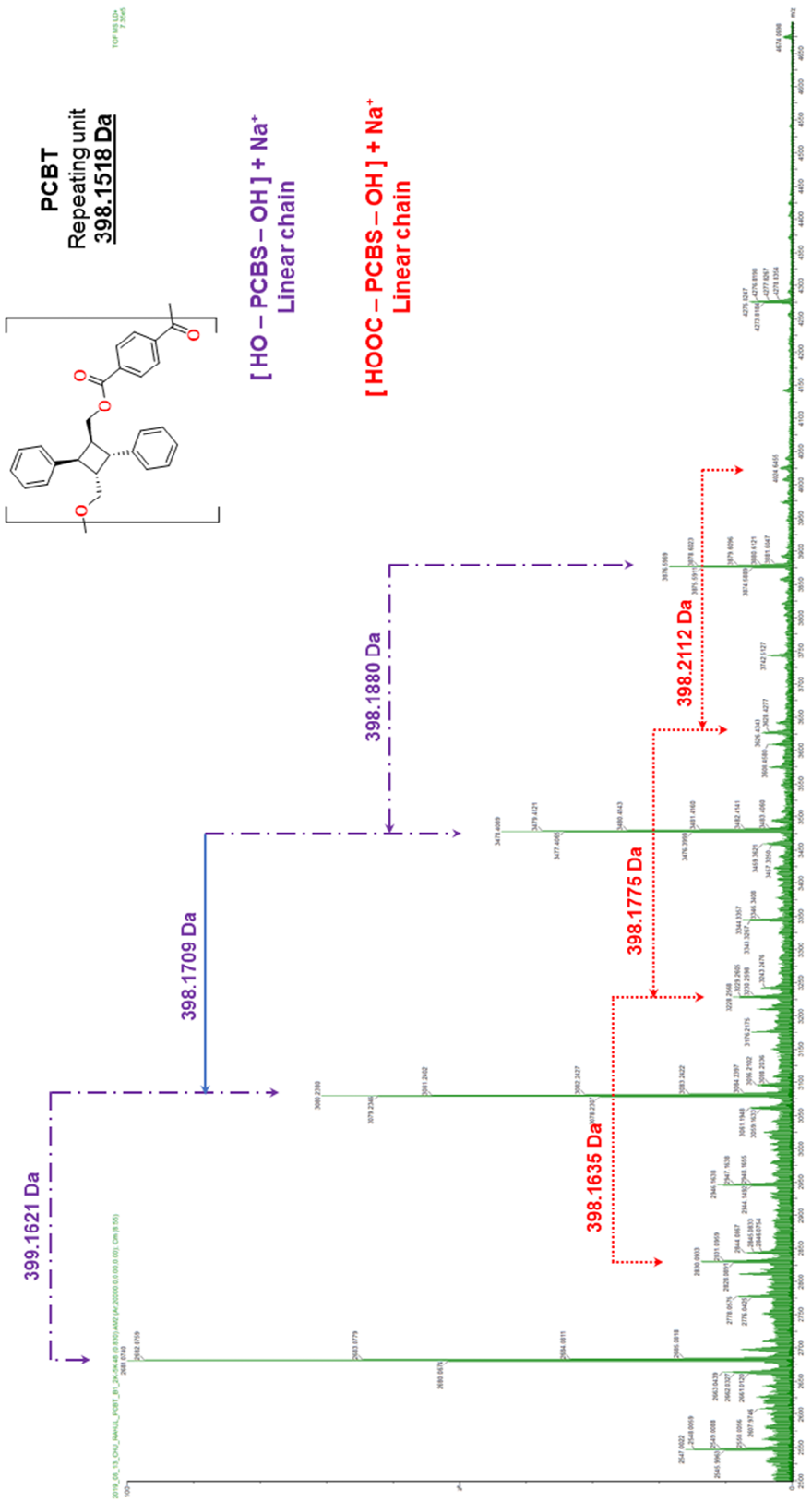


Figure S35. MALDI-TOF-MS spectrum of **PCBT.**

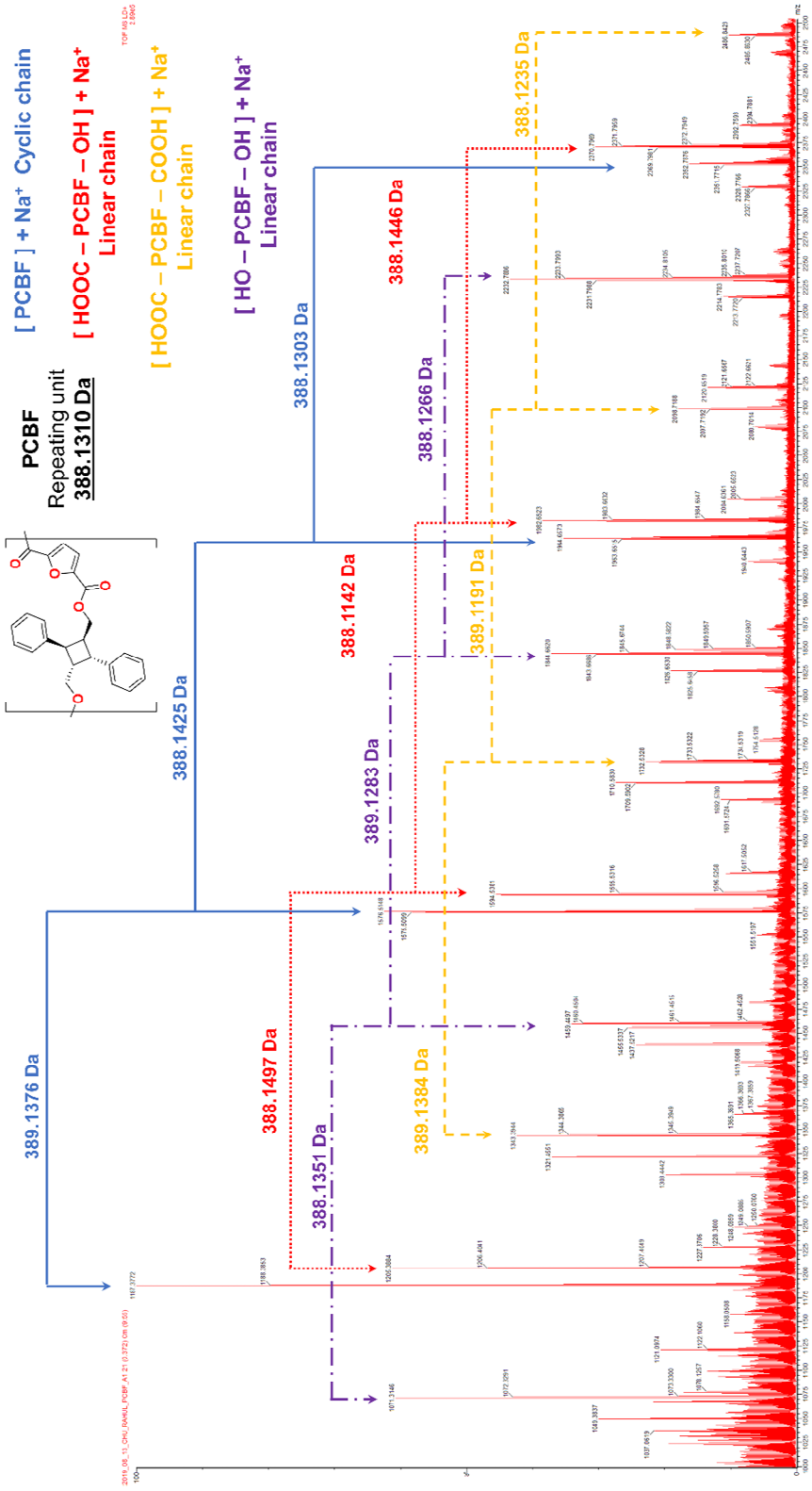


Figure S36. MALDI-TOF-MS spectrum of **PCBF.**

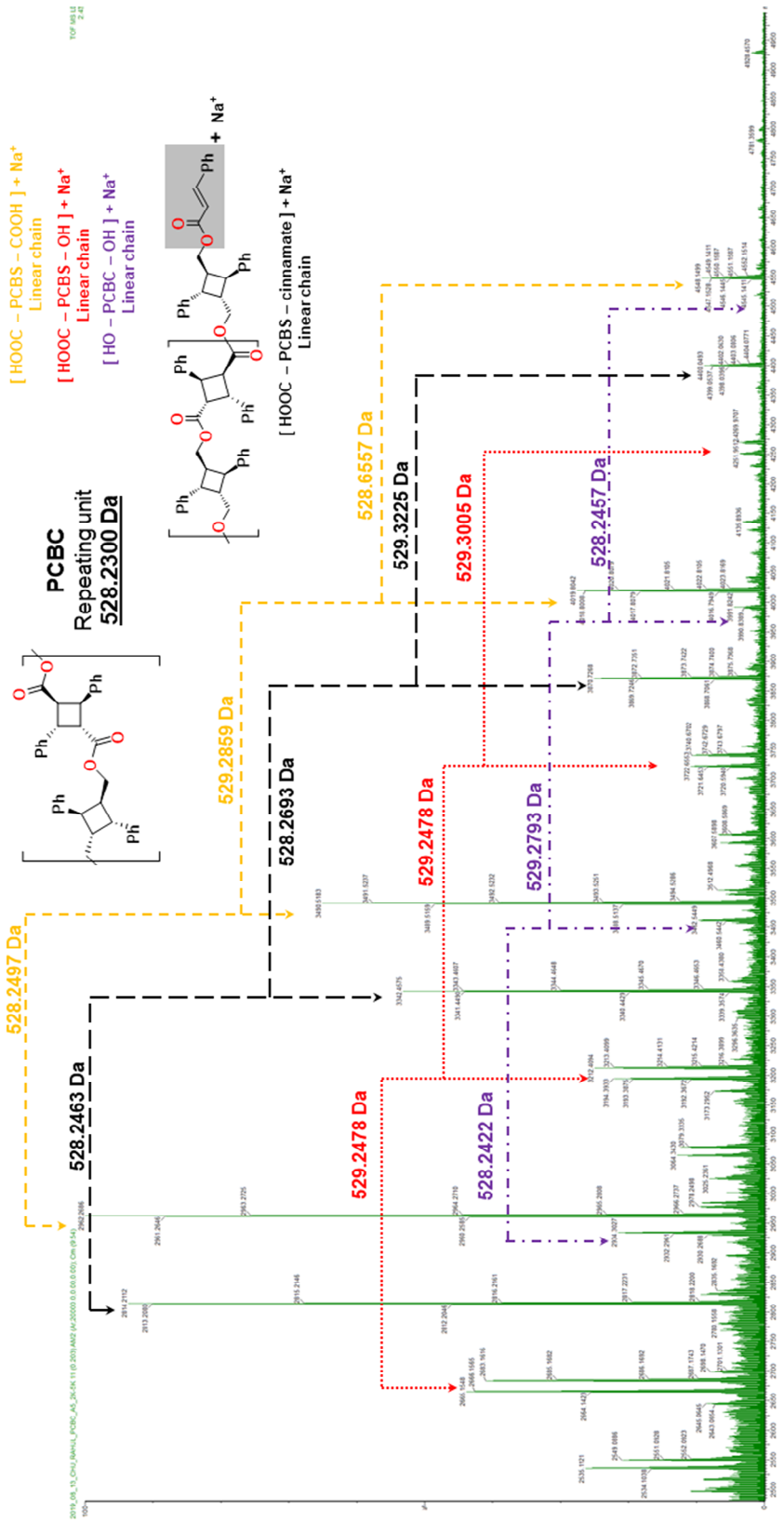


Figure S37. MALDI-TOF-MS spectrum of **PCBC.**

Table S1. Thermo-physical properties of some known polyesters compared with synthesized Polyesters.

Polyester	Glass Transition Temperature, T_g (°C)
Polyethylene Succinate	-11 to -1
PCBS	53
Polyethylene Adipate	-70 to -40
PCBA	35
Polyethylene Terephthalate	64 to 84
PCBT	114
Polyethylene Furan 2,5 dicarboxylate	80 to 87
PCBF	109

Table S2. Available commercial polystyrene and poly(methyl methacrylate) standards listed by peak molecular weight (Mp) and retention times obtained on PLgel Minimix-D column with THF as a mobile phase (3 μL injection volume and 0.3 mL/min flow rate).

PS Standards (Mp)	580	1480	2340	5030	8450	19760	38100	70950	132900	271800
Retention Time (min)	9.2	8.8	8.4	8.0	7.7	7.2	6.9	6.5	6.2	6.0
PMMA Standards (Mp)	550	960	1780	2880	4640	6850	10280	17810	26080	56600
Retention Time (min)	9.4	9.3	8.7	8.4	8.1	7.9	7.7	7.4	7.2	6.7

Table S3. Diffusion Coefficient – Molecular weight results of PS calibration curve using DOSY.

Samples	M (g/mol)	D (10^{-10}) (m^2/s)	logD	logM
PS	1480	6.50 ± 0.02	-9.18709	3.170262
PS	2340	4.98 ± 0.03	-9.30277	3.369216
PS	5030	3.29 ± 0.04	-9.4828	3.701568
PS	8450	2.44 ± 0.01	-9.61261	3.926857
PS	19760	1.53 ± 0.04	-9.81531	4.295787
PS	38100	1.03 ± 0.02	-9.98716	4.580925
PS	70950	0.87 ± 0.01	-10.059	4.850952
PS	132900	0.56 ± 0.01	-10.2472	5.123525

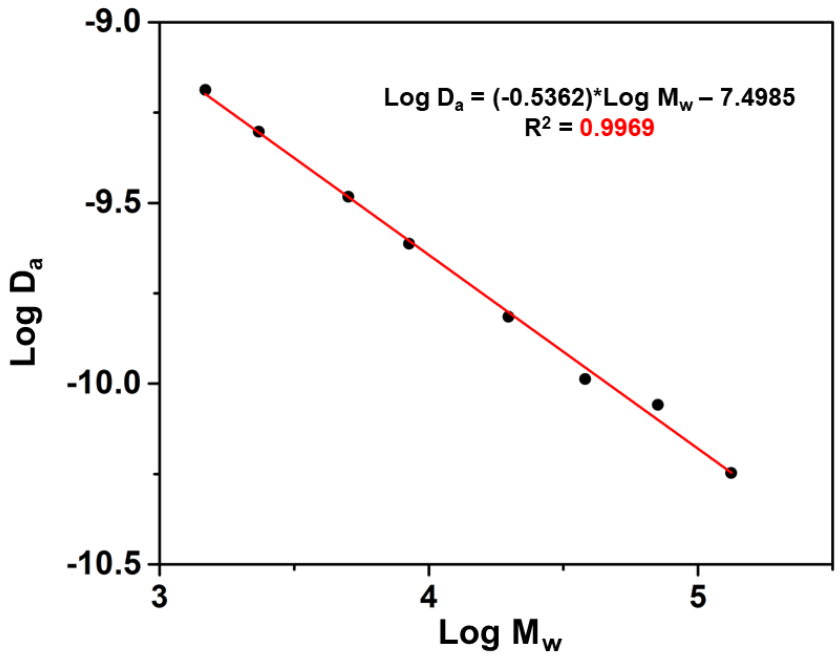


Figure S38. PS calibration curve in $CDCl_3$ for M_w prediction

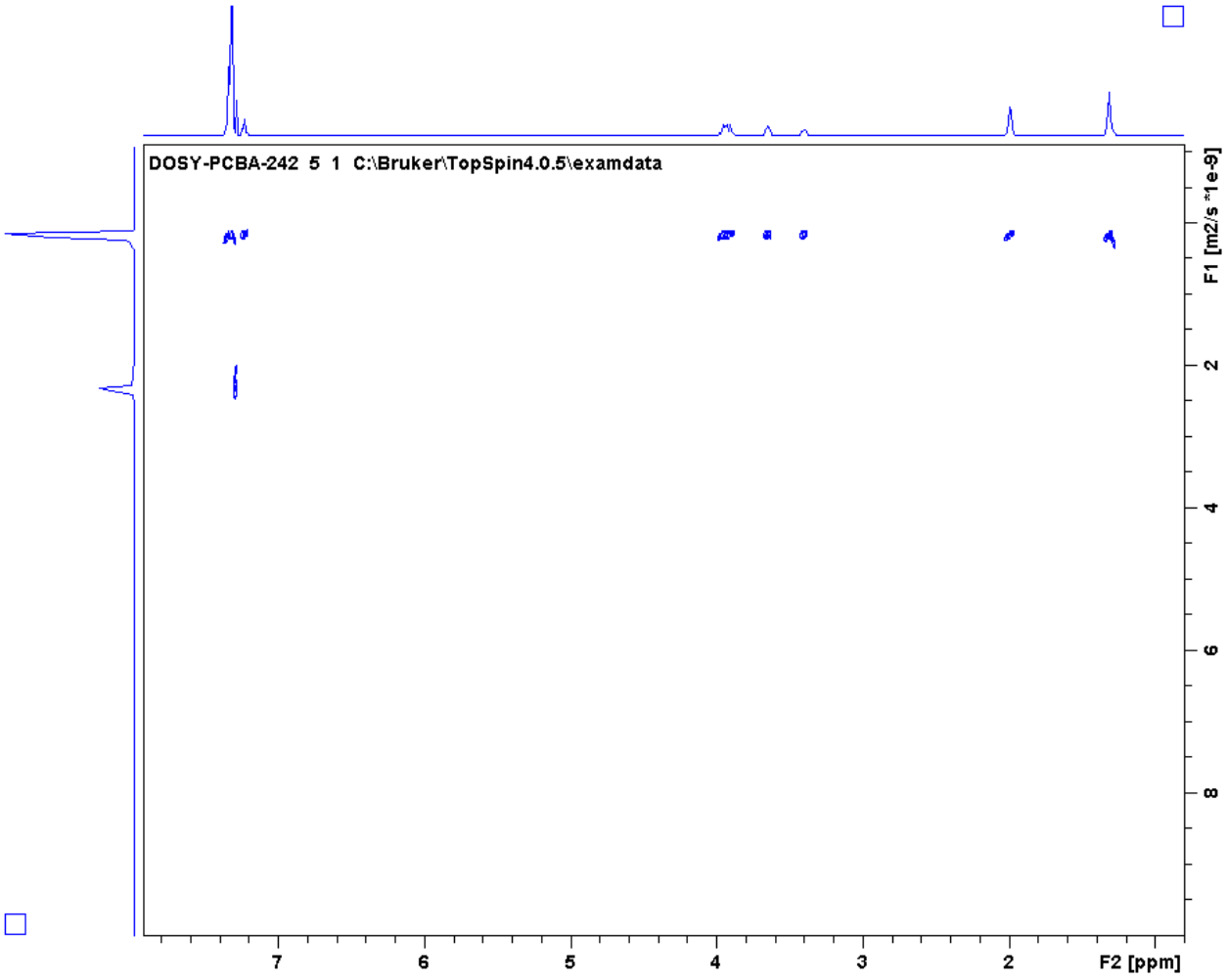


Figure S39. 2D DOSY spectra of **PCBA** in $CDCl_3$ for molecular weight calculation

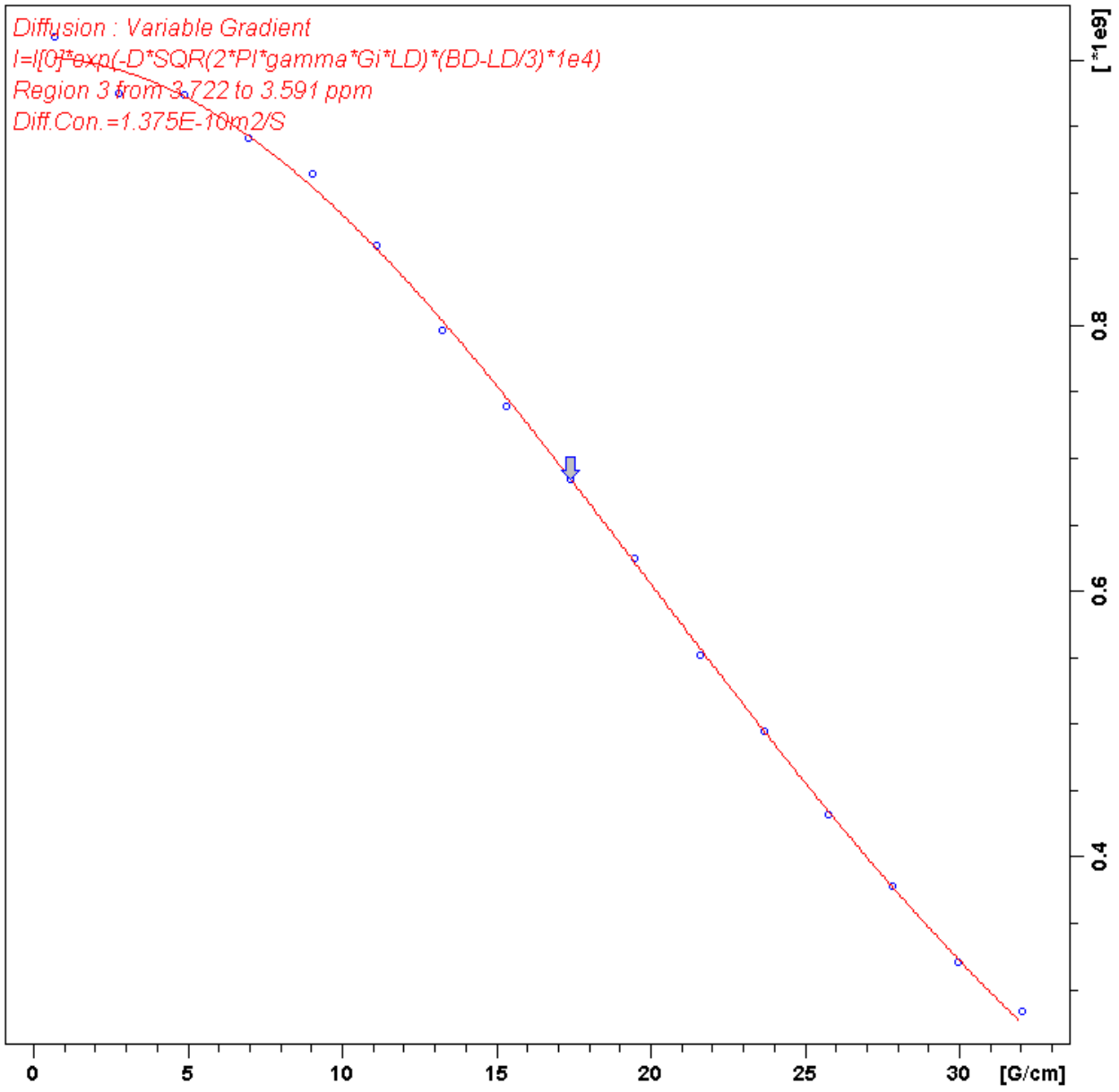


Figure S40. Exemplary signal intensity (Int) decay curve of cyclobutane ring protons (chemical shift = 3.67 ppm) derived from DOSY on a PCBA sample using diffusion time Δ = 100 ms. The data was fitted (—) with the Stejskal-Tanner equation ($I = I_o exp\text{-}(\gamma^2 g^2 \delta^2) D(\Delta\text{-}\delta/3)$) to derive a diffusion coefficient D = 1.375· 10^{-11}, which using the PS calibration (Figure S38) resulted in an M_w = 25,700 g/mol.