Electronic Supplementary Information

Surface Activated Zinc-Glutarate for the Copolymerization of CO_2 and Epoxides

Yongmoon Yang,[a,†] Jong Doo Lee,[b,†] Yeong Hyun Seo,[c] Ju-Hyung Chae,[a] Sohee Bang,[b] Yeon-Joo Cheong,[a] Bun Yeoul Lee,[c] In-Hwan Lee,[d] Seung Uk Son,[b,*] and Hye-Young Jang[a,*]

[a] Department of Energy Systems Research, Ajou University, Suwon 16499, Korea

[b] Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea

[c] Department of Molecular Science and Technology, Ajou University, Suwon 16499, Korea

[d] Department of Chemistry, Ajou University, Suwon 16499, Korea

E-mail address of corresponding authors: hyjang2@ajou.ac.kr, sson@skku.edu

[†]Both authors have equally contributed to this work.

Table of Contents

I. Experimental section

Anhydrous solvents were transferred by an oven dried syringe. Solvents were distilled prior to use. Propylene oxide was dried by stirring over CaH_2 and then vacuum-transferred to a reservoir. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Jeol Resonance ECZ600R (600 MHz) spectrometer. Number average molecular weights (M_n) and weight average molecular weights (M_w) were calculated relative to linear polystyrene standards. Dispersity (*Đ*) values are reported as the quotient of M_w/M_n. Differential scanning calorimetry (DSC) was carried out under N_2 gas at a scan rate of 10 °C/min with DSC 200 F3 Maia from NETZSCH. SEM images were obtained using a JSM6700. N_2 adsorption- desorption isotherm curves were obtained using a Micromeritics ASAP2460. The surface areas and porosity of materials were characterized based on the Brunauer-Emmett-Teller (BET) theory. Pore size distribution diagrams were obtained by the DFT method. IR spectra were obtained using a Bruker VERTEX 70 FT-IR spectrometer. XPS spectra were obtained using a Thermo VG spectrometer. Solid state ^{13}C nuclear magnetic resonance (NMR) spectra were obtained at a cross-polarization/total side band suppression (CP/TOSS) mode using a 500 MHz Bruker ADVANCE II NMR spectrometer at the National Center for Inter-University Research Faciliteis (NCIRF) of Seoul National University. PXRD patterns were obtained using a Rigaku MAX-2200. TGA curves were obtained using a Seiko Exstar 7300. ICP-AES analysis was conducted using an OPTIMA8300.

General procedure for the synthesis of 2D ZnGA:

For the preparation of 2D ZnGA, zinc oxide (250 mg, 3.07 mmol) was suspended in acetic acid (17.6 mL) through vigorous stirring (1150 rpm) in a flame-dried 100 mL Schlenk flask. After glutaric acid (406 mg, 3.07 mmol), and distilled toluene (18 mL) were added, the reaction mixture was stirred at 50°C for 24 h. After the reaction mixture was cooled to room temperature, the solid (2D ZnGA) was separated by centrifugation, washed with acetone (40 mL) five times, and dried under vacuum at 80 °C for overnight.

General procedure for the synthesis of Co-ZnGA 2:

For the preparation of Co-ZnGA **2**, 2D ZnGA (213 mg, 1.08 mmol) was suspended in distilled methanol (3.8 mL) in a vacuum dried 5 mL round-bottom flask through sonication for 1 h. After $H_3Co(CN)_6$ (121 mg, 0.360 mmol) in distilled methanol (2.5 mL) was added quickly, the reaction mixture was stirred vigorously at room temperature for 24 h. The white solid (Co-ZnGA **2**) was separated by centrifugation, washed with anhydrous methanol (1.0 mL) three times, and dried under vacuum at room temperature. (150 mg)

Procedure for the synthesis of Co-ZnGA 5:

For the preparation of Co-ZnGA **5**, $Zn(OAc)_2$ (198 mg, 1.08 mmol) and glutaric acid (143 mg, 1.08 mmol) were suspended in distilled methanol (3.8 mL) in a vacuum dried 25 mL round-bottom flask through sonication for 1

h. Then, $H_3Co(CN)_6$ (121 mg, 0.360 mmol) in distilled methanol (2.5 mL) was added quickly to the reaction mixture. The resulting mixture was stirred vigorously at room temperature for 24 h. The white solid (Co-ZnGA **5**) was separated by centrifugation, washed with anhydrous methanol (1.0 mL) three times, and dried under vacuum at room temperature. (130 mg)

Representative procedure for the copolymerization of propylene oxide/CO_2:

An autoclave (50 mL) was assembled after charging with a magnetic stirring bar, Co-ZnGA **2** (8.7 mg) and propylene oxide (PO) (4.36 g, 75 mmol). The autoclave was pressurized with CO_2 gas to 40 bar at room temperature. And then immersed in an oil bath at room temperature. The reaction mixture was stirred (250 rpm) and heated at 80 °C for 20 hours. After being cooled to room temperature and vented unreacted CO_2 gas, the polymerization solution was transferred to 100 mL round-bottom flask by dissolving with dichloromethane, and all volatiles were removed using a rotary evaporator, leaving a waxy solid. The solid was recrystallized in dichloromethane and methanol mixture.

Representative procedure for the copolymerization of 1-hexene oxide/CO_2:

An autoclave (50 mL) was assembled after charging with a magnetic stirring bar, Co-ZnGA **2** (4.4 mg) and 1-hexene oxide (HO) (7.51 g, 75 mmol). The autoclave was pressurized with CO_2 gas to 40 bar at room temperature. And then immersed in an oil bath at room temperature. The reaction mixture was stirred (250 rpm) and heated at 90 °C for 20 hours. After being cooled to room temperature and vented unreacted CO_2 gas, and the polymerization solution was transferred to 100 mL round-bottom flask by dissolving with dichloromethane, and all volatiles were removed using a rotary evaporator, leaving a waxy solid. The solid was recrystallized in dichloromethane and methanol mixture.

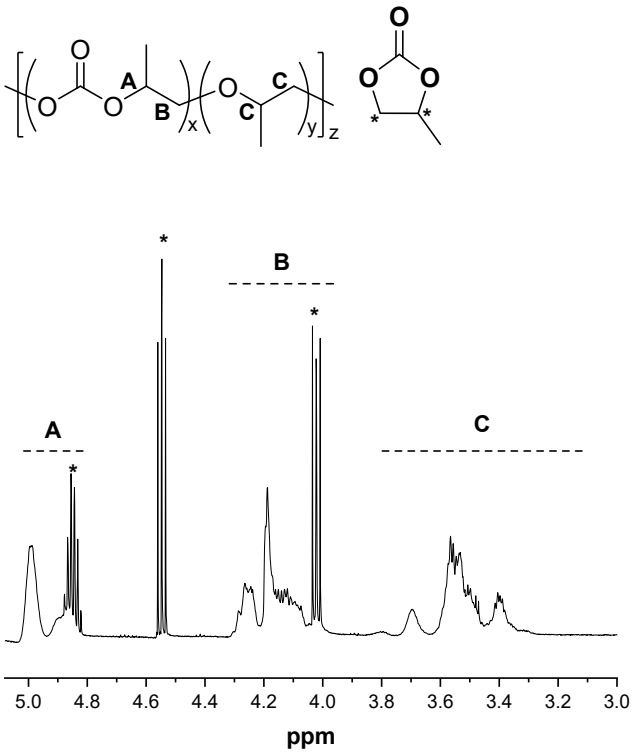
Representative procedure for the copolymerization of 1,2-butylene oxide/CO_2:

An autoclave (50 mL) was assembled after charging with a magnetic stirring bar, Co-ZnGA **2** (4.4 mg) and 1,2-butylene oxide (BO) (5.41 g, 75 mmol). The autoclave was pressurized with CO_2 gas to 40 bar at room temperature. And then immersed in an oil bath at room temperature. The reaction mixture was stirred (250 rpm) and heated at 90 °C for 20 hours. After being cooled to room temperature and vented unreacted CO_2 gas, and the polymerization solution was transferred to 100 mL round-bottom flask by dissolving with dichloromethane, and all volatiles were removed using a rotary evaporator, leaving a waxy solid. The solid was recrystallized in dichloromethane and methanol mixture.

Representative procedure for the copolymerization of styrene oxide/CO_2:

An autoclave (50 mL) was assembled after charging with a magnetic stirring bar, Co-ZnGA **2** (4.4 mg) and styrene oxide (SO) (9.01 g, 75 mmol). The autoclave was pressurized with CO_2 gas to 40 bar at room temperature. And then immersed in an oil bath at room temperature. The reaction mixture was stirred (250 rpm) and heated at 90 °C for 20 hours. After being cooled to room temperature and vented unreacted CO_2 gas, and the polymerization solution was transferred to 100 mL round-bottom flask by dissolving with dichloromethane, and all volatiles were removed using a rotary evaporator, leaving a solid. The solid was recrystallized in dichloromethane and methanol mixture.

Calculation of f_{CO2} and selectivity of polyme (entry 11, Table 1)



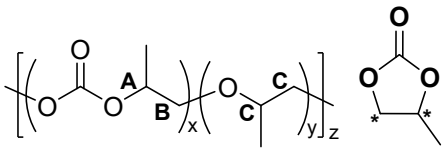
f_{CO2} = carbonate fraction = [polycarbonate]/[polymer]

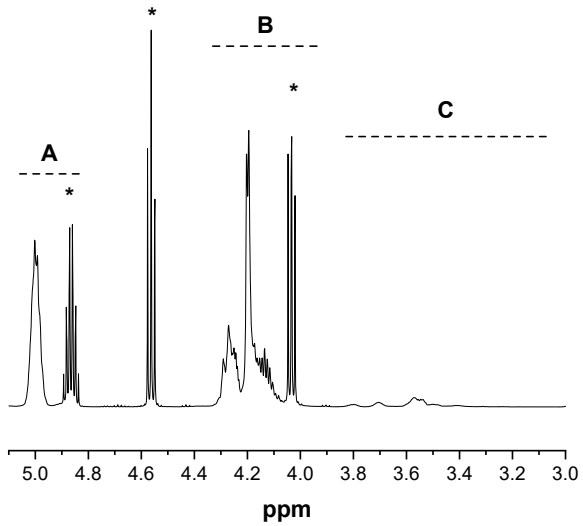
$$f_{CO2} = \frac{(I_A + I_B - 2 * I_{4.55})}{(I_A + I_B + I_C - 2 * I_{4.55})}$$

selectivity = [epoxide incorporated into polymer]/{[monomer carbonate]+[epoxide incorporated into polymer]}

$$selectivity\ (\%) = \frac{(I_A + I_B + I_C - 2 * I_{4.55})}{(I_A + I_B + I_C + I_{4.55})} \times 100$$

Calculation of f_{CO2} and selectivity (entry 2, Table 1)





$I_A = 3.32$, $I_B = 5.87$, $I_C = 0.35$, $I_{4.55} = 1.00$

$$f_{CO2} = \frac{(I_A + I_B - 2 * I_{4.55})}{(I_A + I_B + I_C - 2 * I_{4.55})} = \frac{(3.32 + 5.87 - 2 * 1.00)}{(3.32 + 5.87 + 0.35 - 2 * 1.00)} = 0.95$$

$$selectivity\ (\%) = \frac{(I_A + I_B + I_C - 2 * I_{4.55})}{(I_A + I_B + I_C + I_{4.55})} \times 100$$

$$= \frac{(3.32 + 5.87 + 0.35 - 2 * 1.00)}{(3.32 + 5.87 + 0.35 + 1.00)} \times 100 = 72\ \%$$

II. Additional data of catalysts

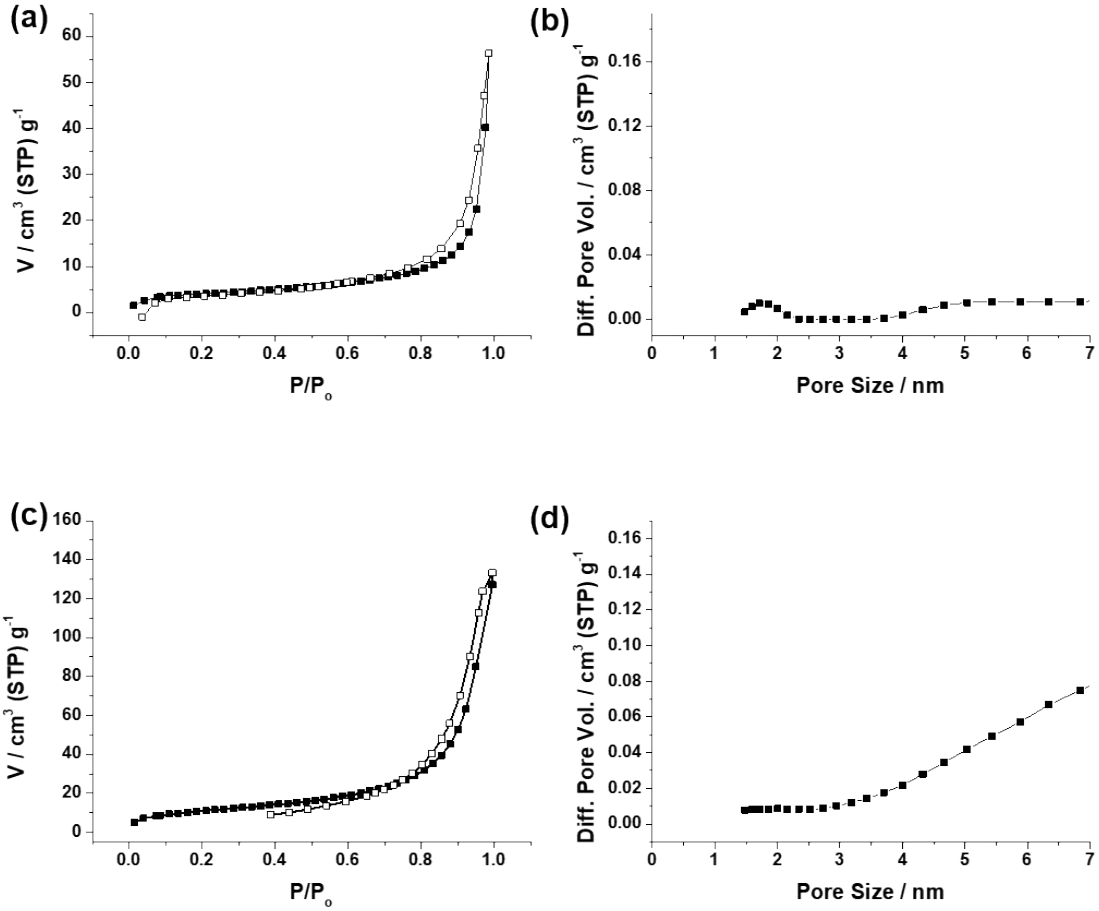


Figure S1. (a) N_2 adsorption-desorption isotherm curves of standard ZnGA obtained at 77K (BET surface area = 15 m^2/g). (b) Pore size distribution diagrams based on the DFT method of standard ZnGA (pore volume 0.03 cm^3/g). (c) N_2 adsorption-desorption isotherm curves of Co-ZnGA **1** obtained at 77K (BET surface area = 39 m^2/g). (b) Pore size distribution diagrams based on the DFT method of Co-ZnGA **1** (pore volume 0.13 cm^3/g).

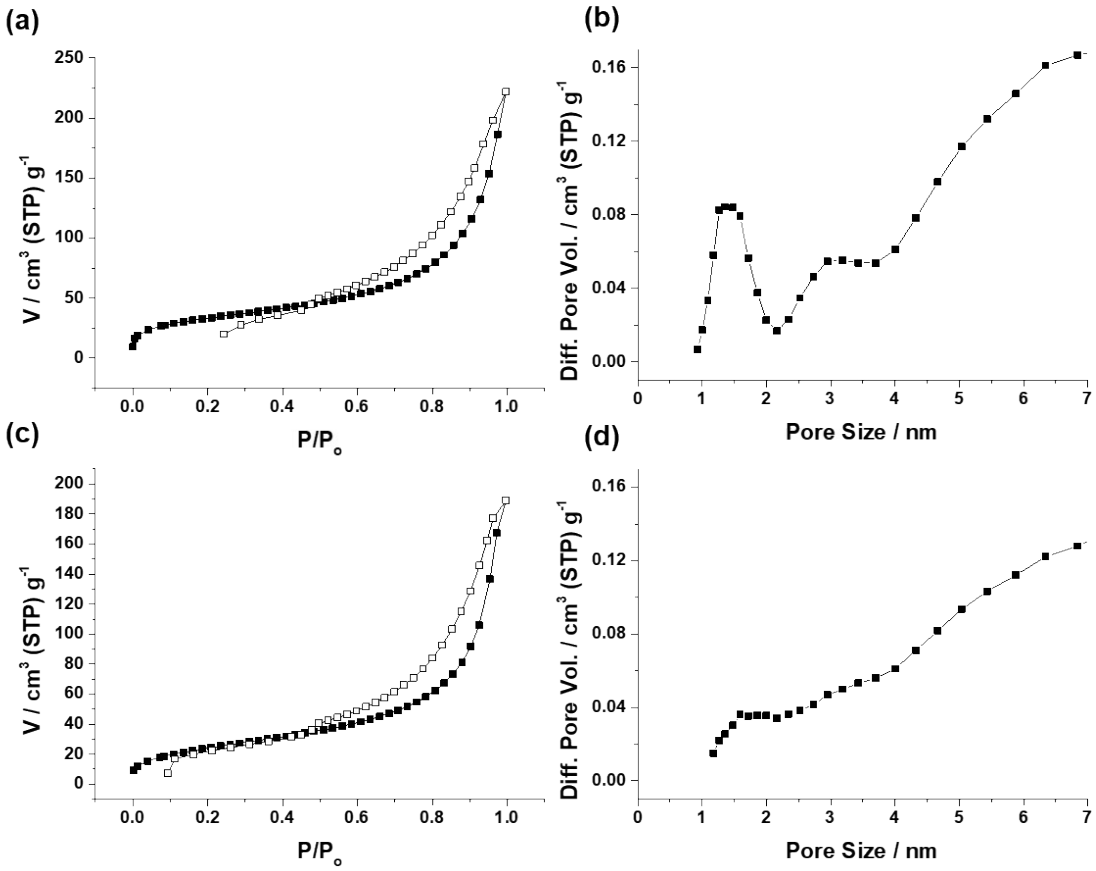


Figure S2. (a) N_2 adsorption-desorption isotherm curves of Co-ZnGA **3** obtained at 77K (BET surface area = 119 m^2/g). (b) Pore size distribution diagrams based on the DFT method of Co-ZnGA **3** (pore volume 0.24 cm^3/g). (c) N_2 adsorption-desorption isotherm curves of Co-ZnGA **4** obtained at 77K (BET surface area = 88 m^2/g). (b) Pore size distribution diagrams based on the DFT method of Co-ZnGA **4** (pore volume 0.20 cm^3/g).

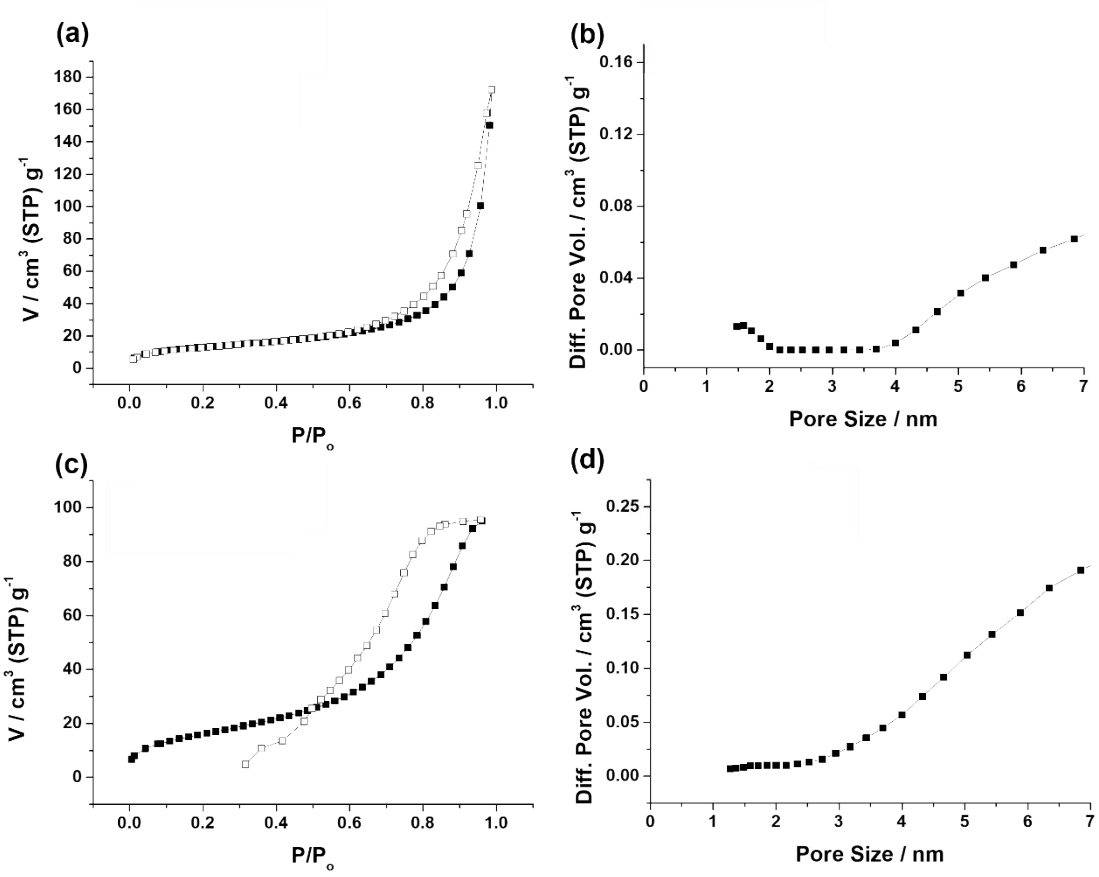


Figure S3. (a) N_2 adsorption-desorption isotherm curves of Co-ZnGA **5** obtained at 77K (BET surface area = 46 m^2/g). (b) Pore size distribution diagrams based on the DFT method of Co-ZnGA **5** (pore volume 0.14 cm^3/g). (c) N_2 adsorption-desorption isotherm curves of Co-ZnAc obtained at 77K (BET surface area = 59 m^2/g). (b) Pore size distribution diagrams based on the DFT method of Co-ZnAc (pore volume 0.14 cm^3/g).

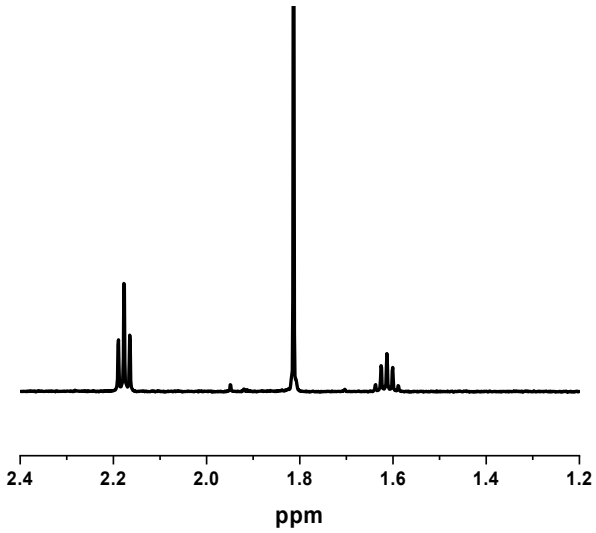


Figure S4. ^{1}H NMR of the mixture of 2D ZnGA and HCl. Glutarate: 2.18 and 1.61 ppm. Acetate: 1.81 ppm.

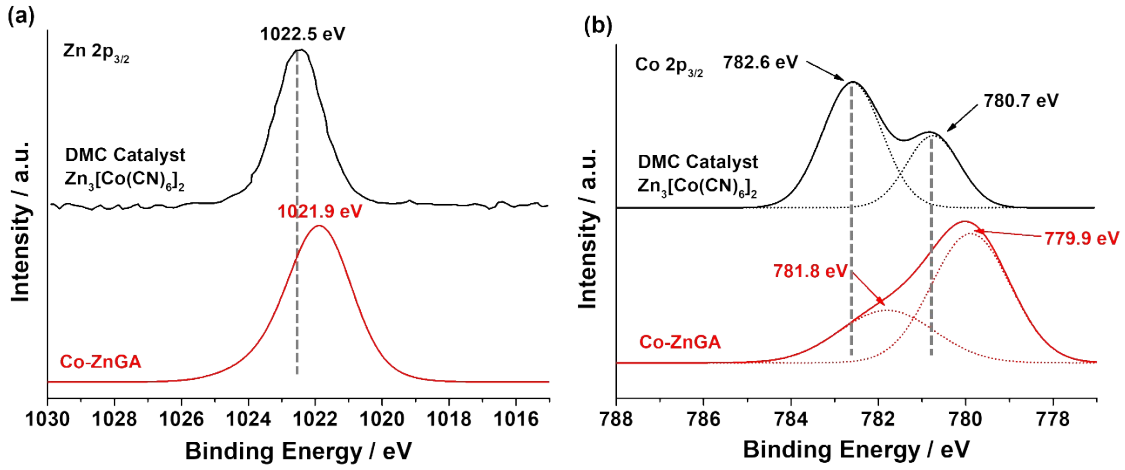
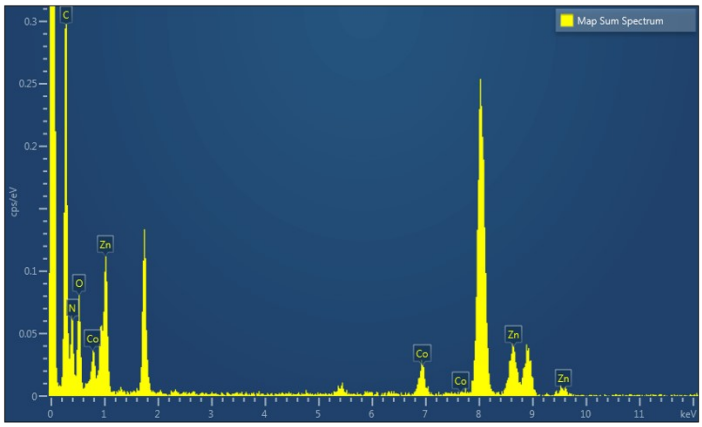


Figure S5. (a) XPS Zn 2p orbital spectra of DMC catalyst ($Zn_3[Co(CN)_6]_2$)[1] and Co-ZnGA **2** and (a) XPS Co 2p orbital spectra of DMC catalyst ($Zn_3[Co(CN)_6]_2$)[1] and Co-ZnGA **2**.

[1] K. Lawniczak-Jablonska, E. Dynowska, W. Lisowski, J. W. Sobczak, A. Chruściel, W. Hreczuch, J. Libera and A. Reszak, *X-Ray Spectrom.* 2015, **44**, 330-338.



Element	Line Type	Wt%	Wt% Sigma	Atomic %
C	K series	67.78	1.98	81.06
N	K series	8.58	1.42	8.80
O	K series	7.12	0.92	6.39
Co	K series	4.93	0.65	1.20
Zn	K series	11.60	1.22	2.55
Total:		100.00		100.00

Figure S6. TEM-EDS of Co-ZnGA **2**.

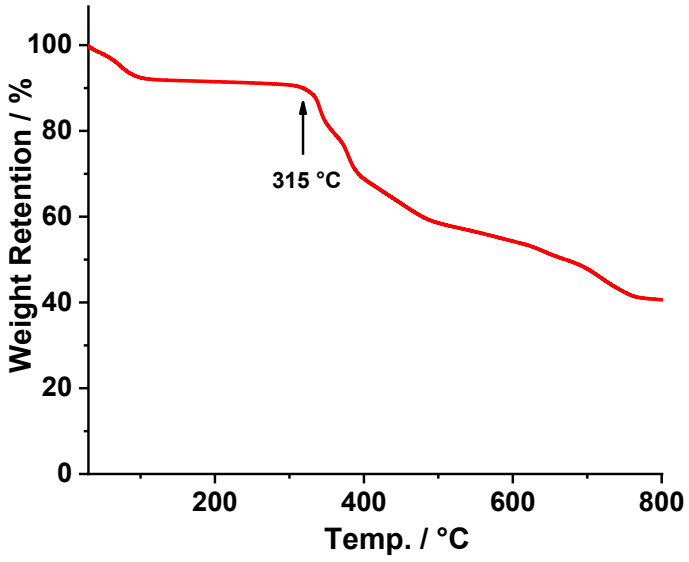


Figure S7. TGA curve of Co-ZnGA **2**

III. ^{1}H NMR spectra of polymers

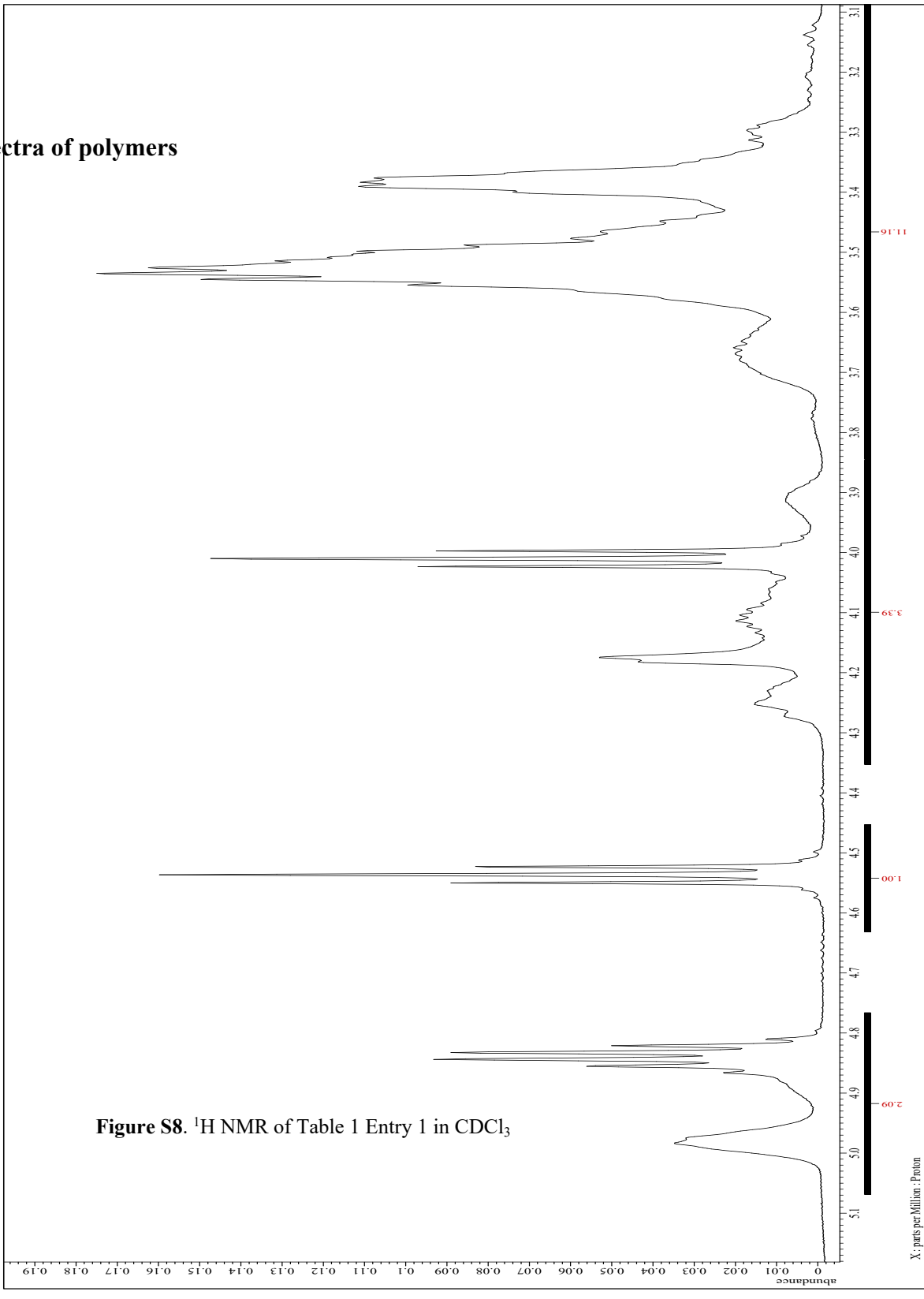


Figure S8. ^{1}H NMR of Table 1 Entry 1 in $CDCl_3$

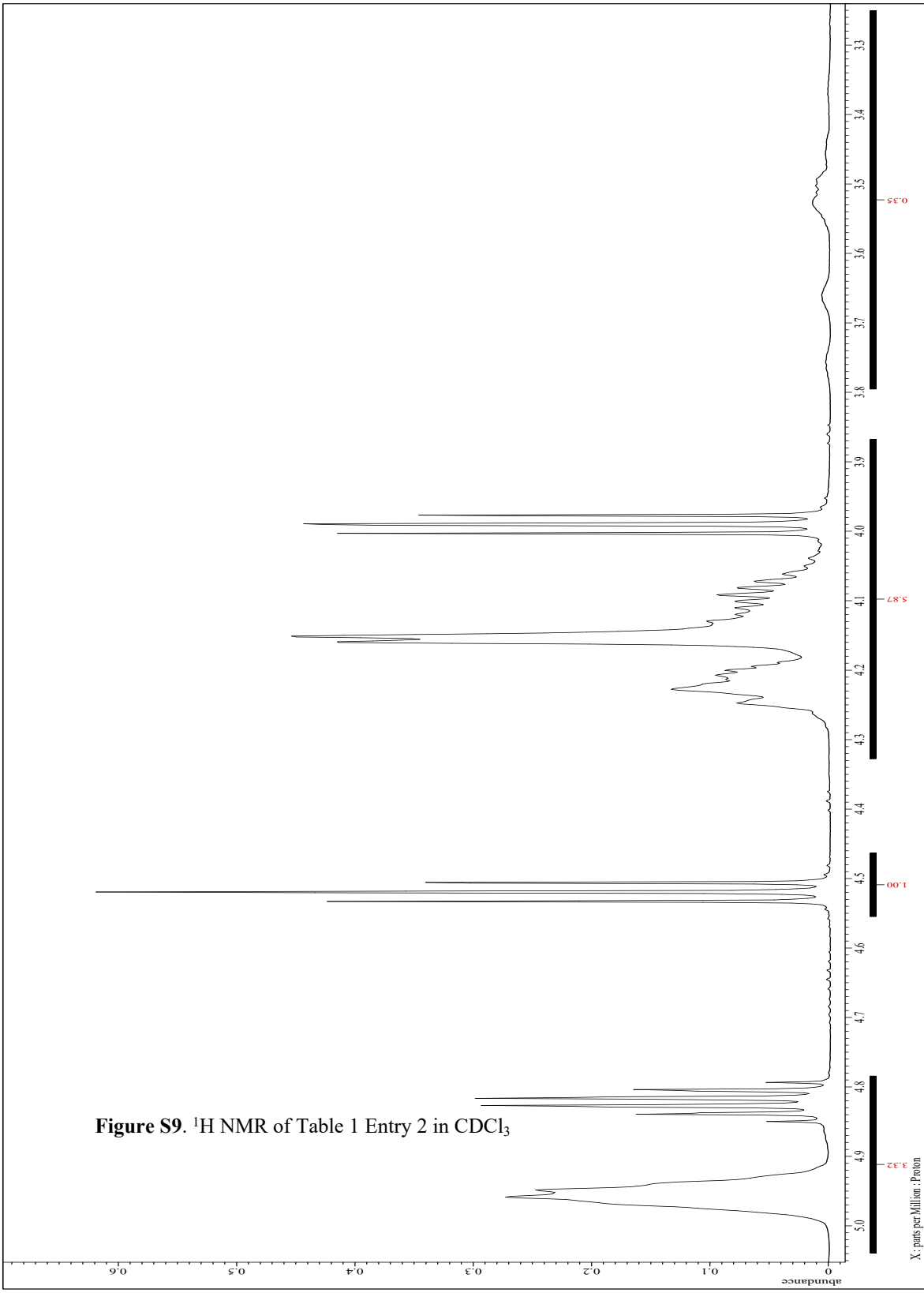


Figure S9. ^{1}H NMR of Table 1 Entry 2 in $CDCl_3$

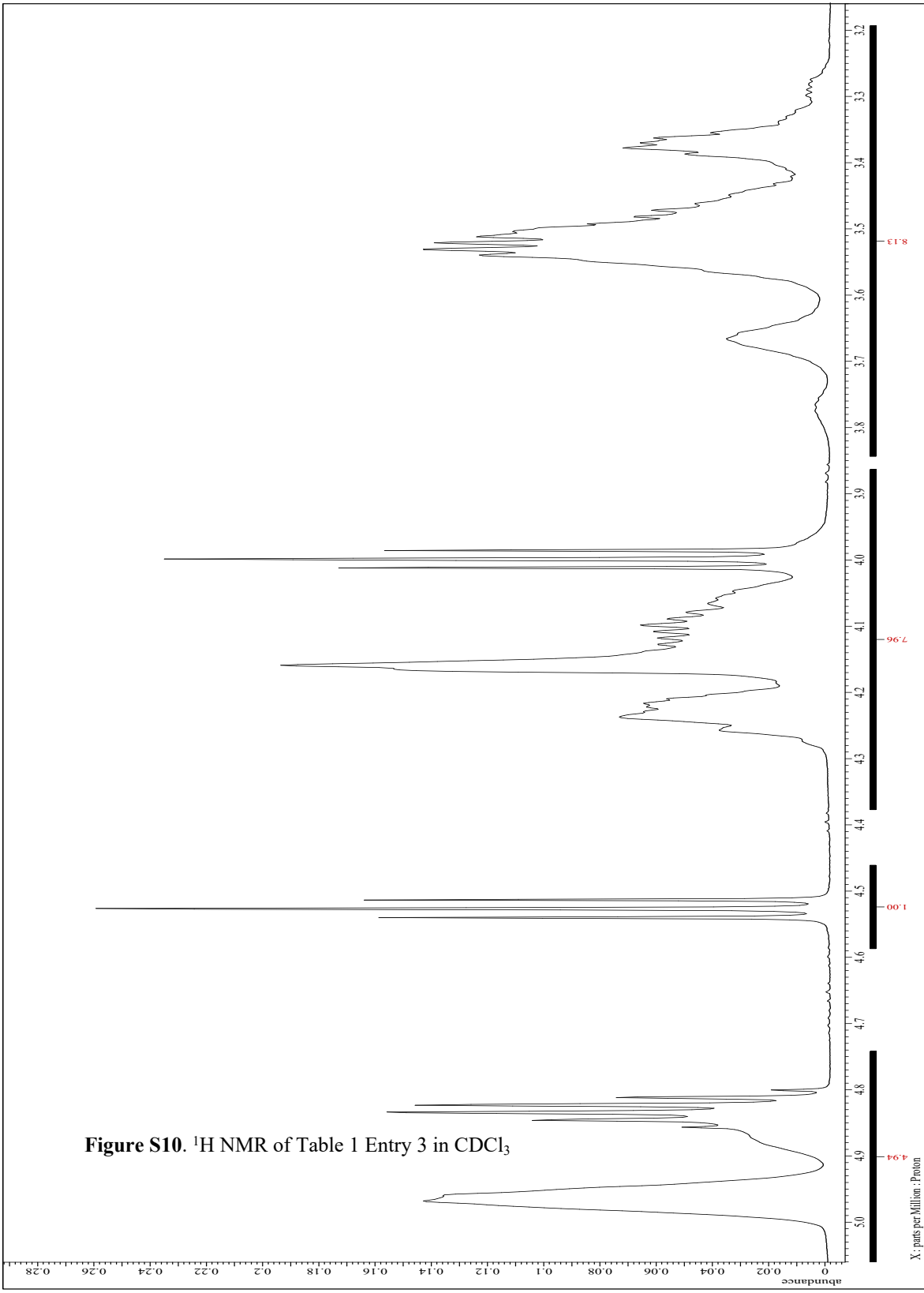


Figure S10. ^{1}H NMR of Table 1 Entry 3 in $CDCl_3$

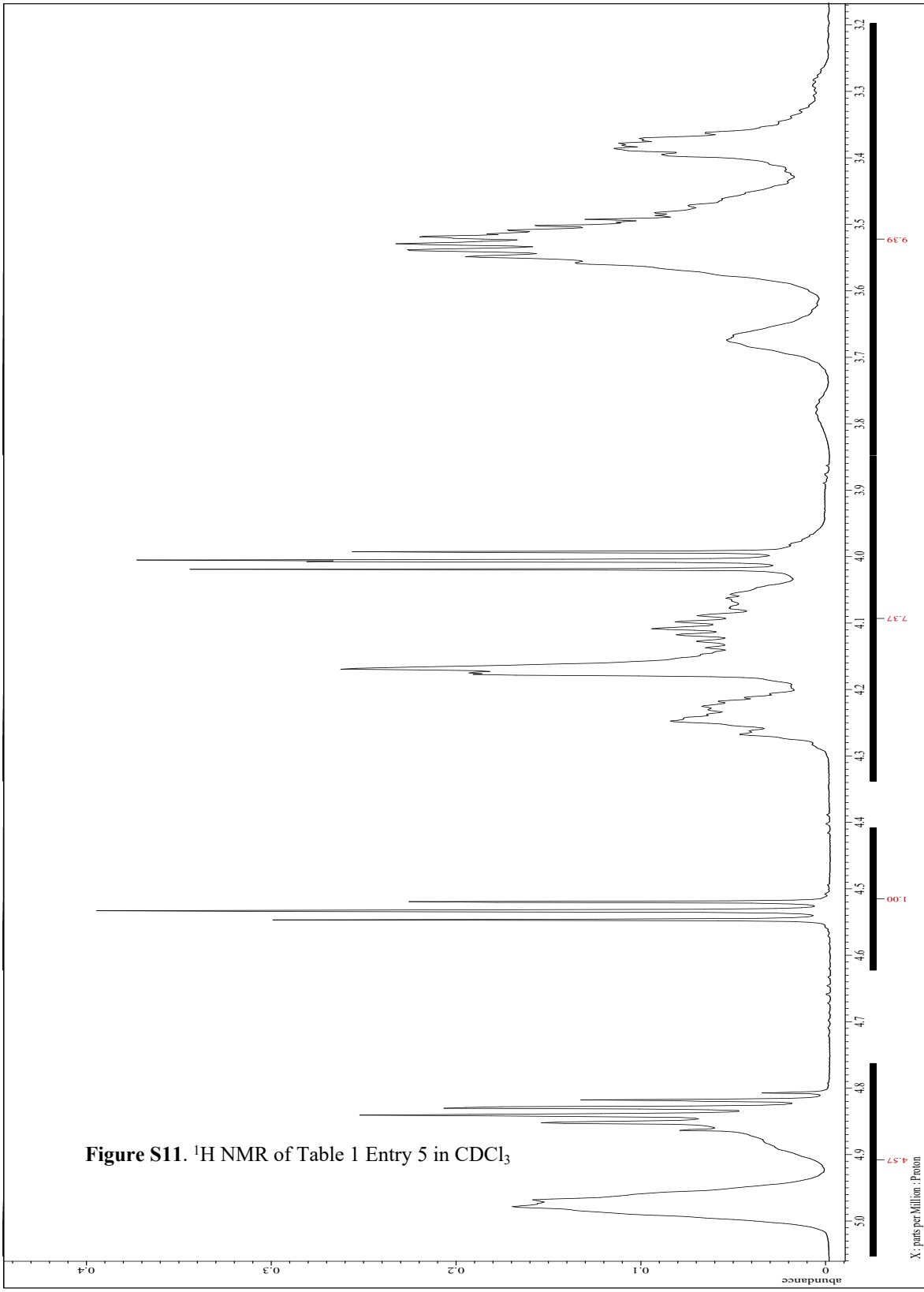


Figure S11. ^{1}H NMR of Table 1 Entry 5 in $CDCl_3$

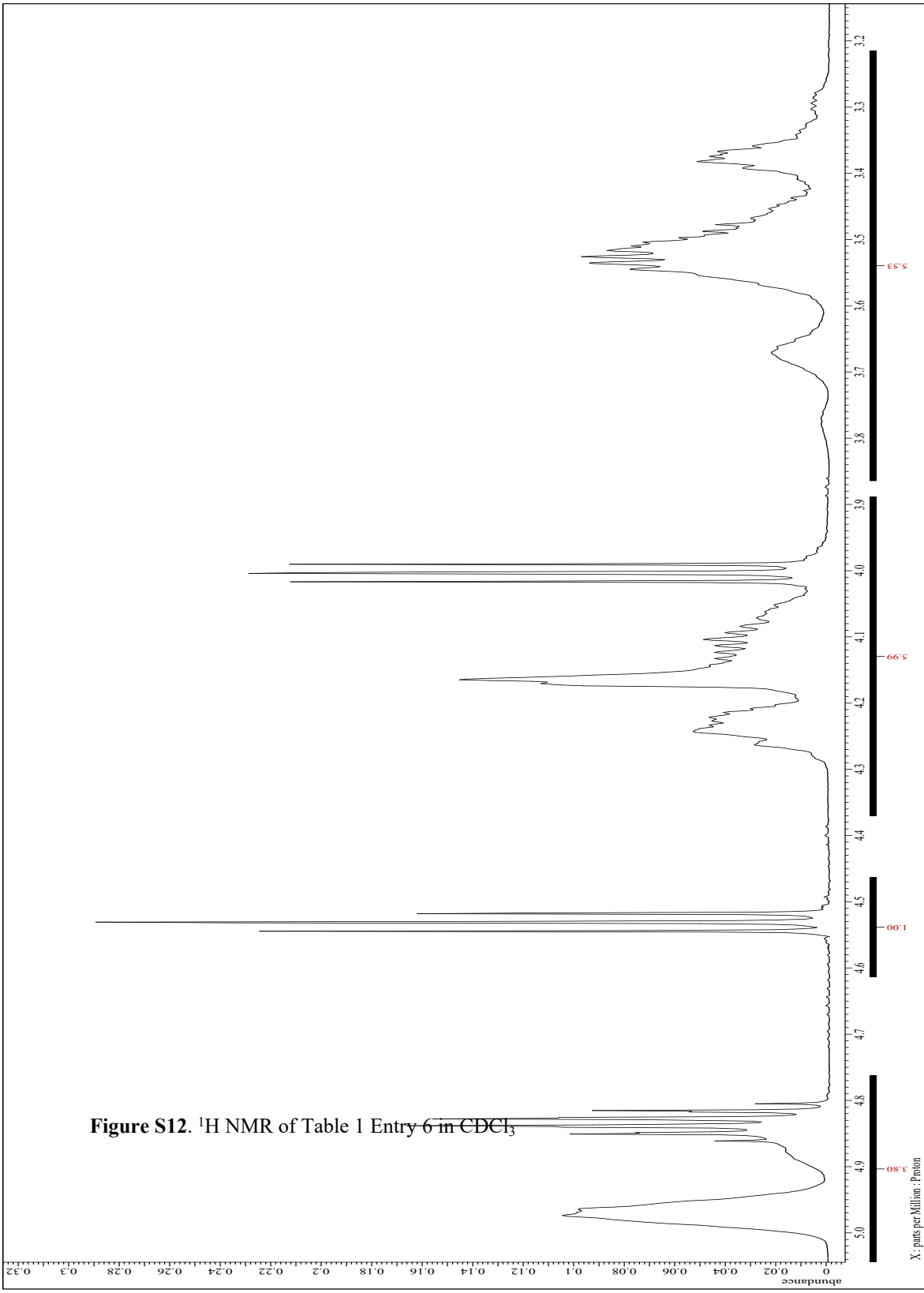


Figure S12. ^{1}H NMR of Table 1 Entry ~~6 in $CDCl_3$~~

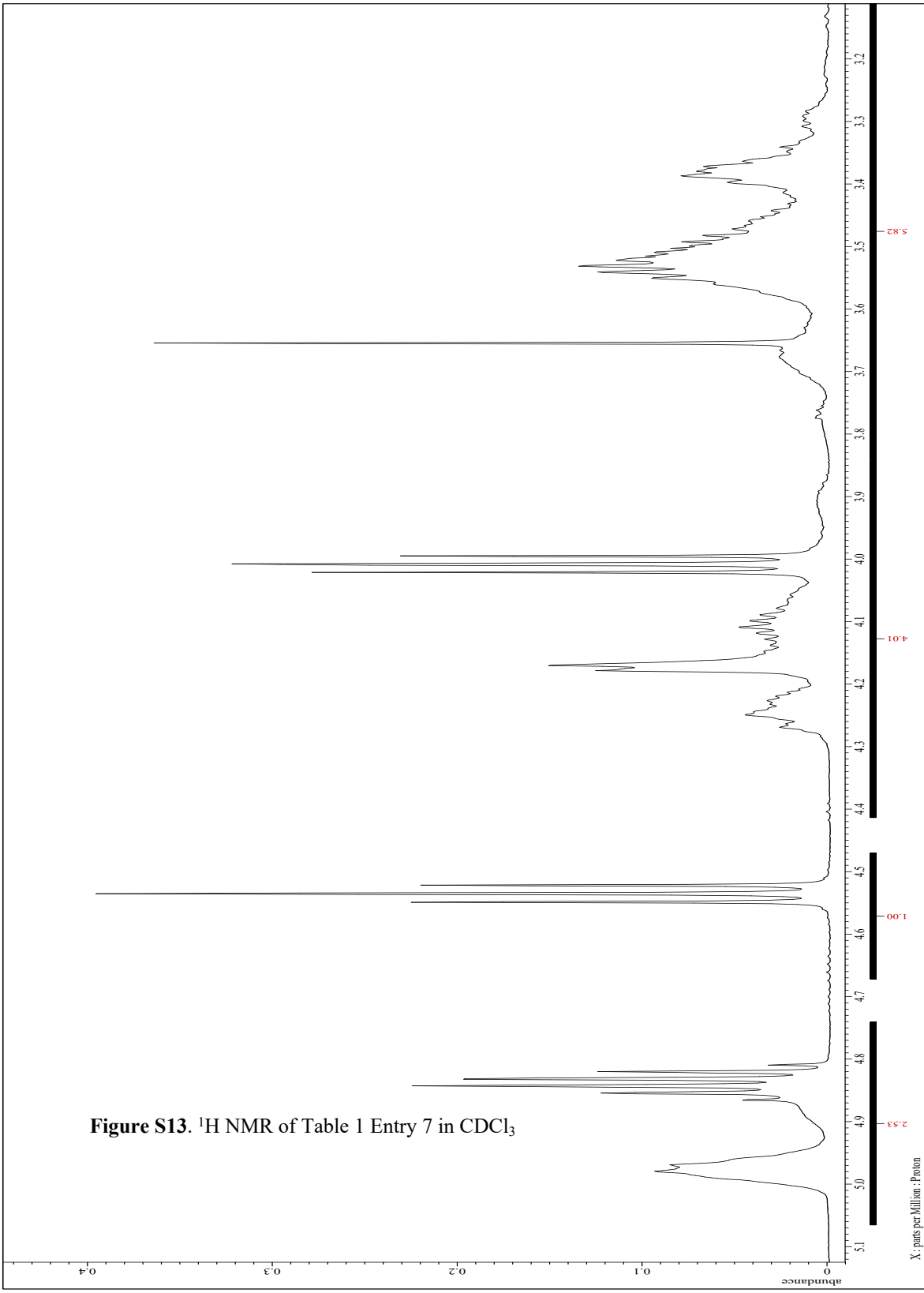


Figure S13. ^{1}H NMR of Table 1 Entry 7 in $CDCl_3$

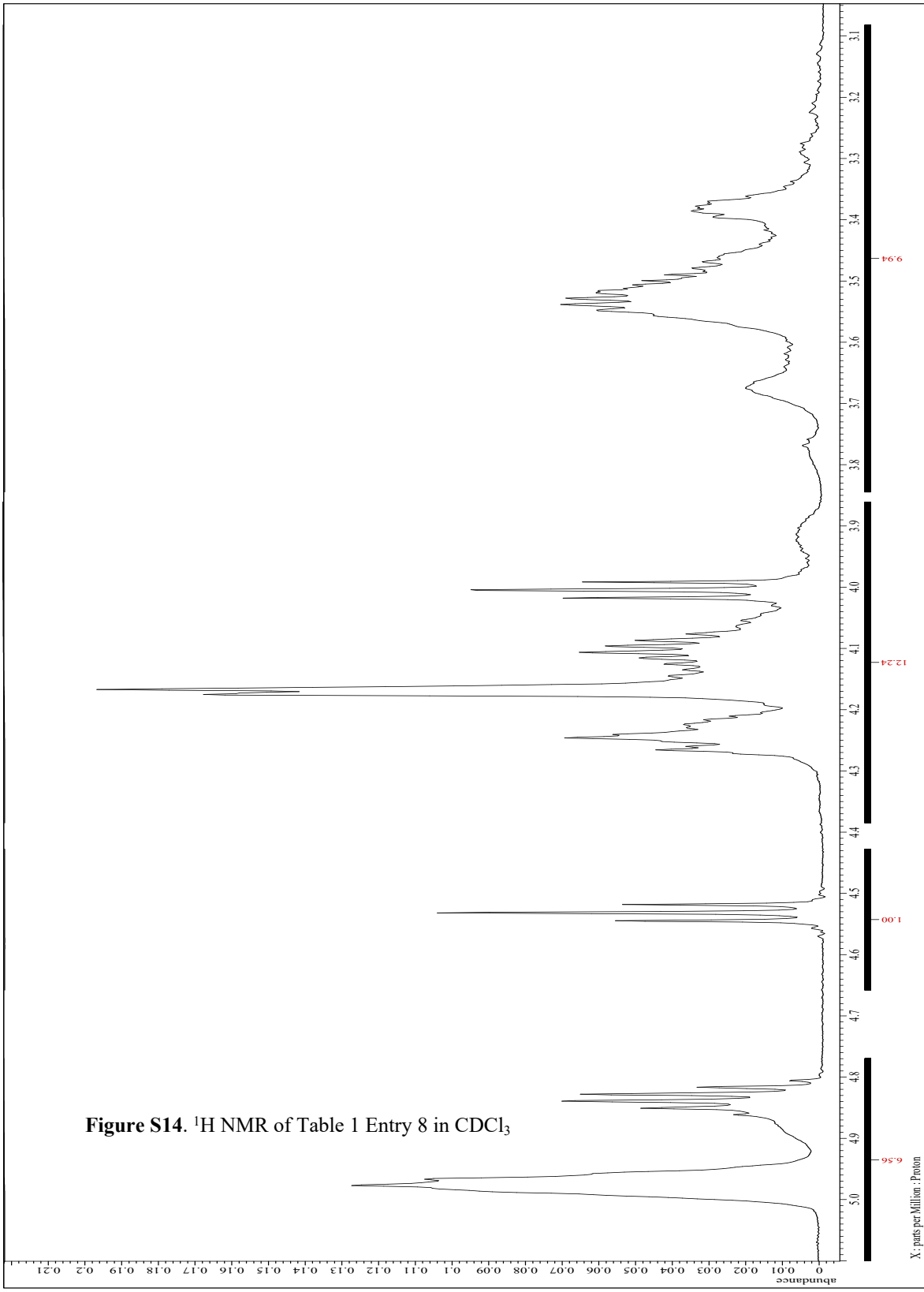


Figure S14. ^{1}H NMR of Table 1 Entry 8 in $CDCl_3$

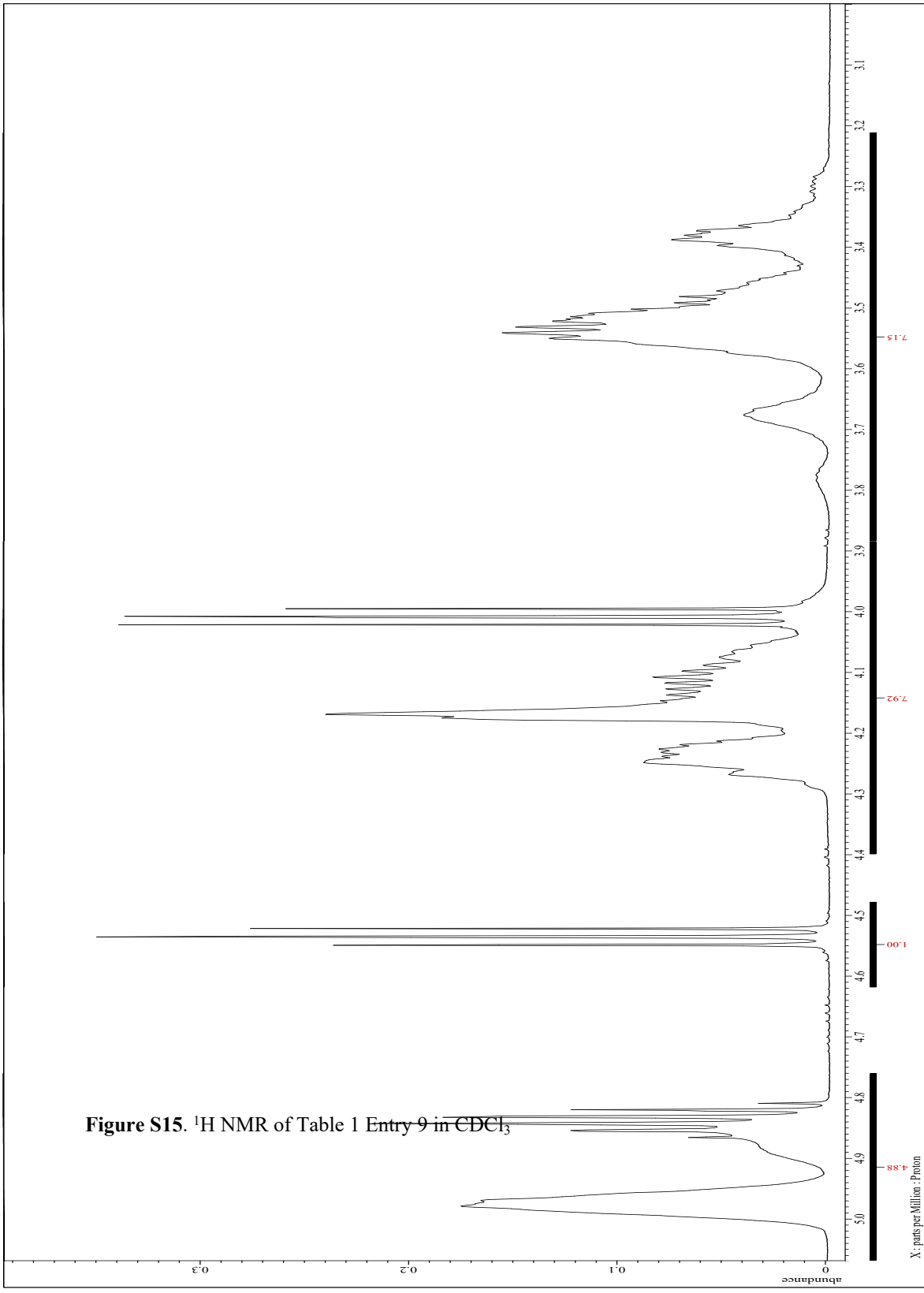


Figure S15. ^{1}H NMR of Table 1 ~~Entry 9 in $CDCl_3$~~

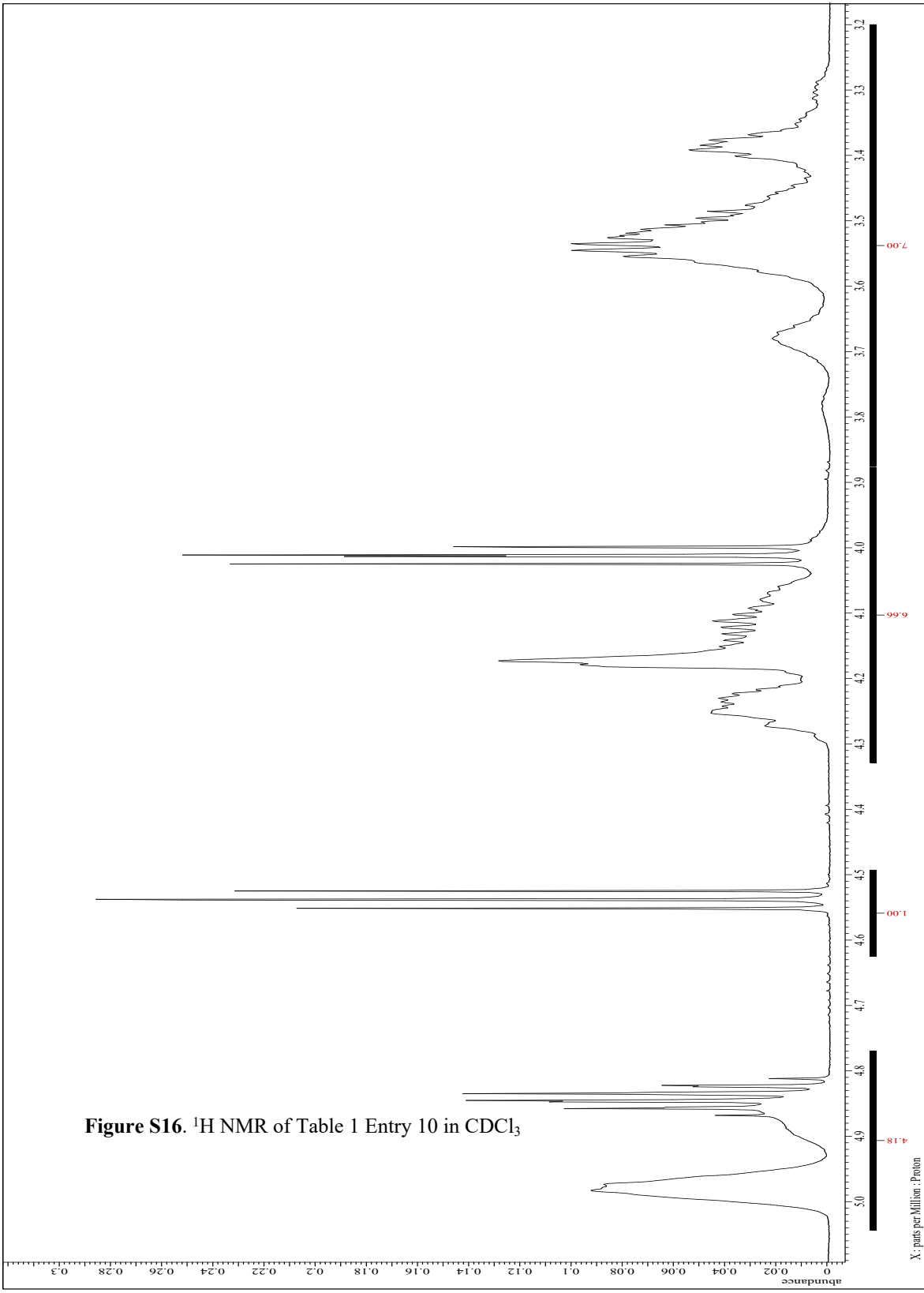


Figure S16. ^{1}H NMR of Table 1 Entry 10 in $CDCl_3$

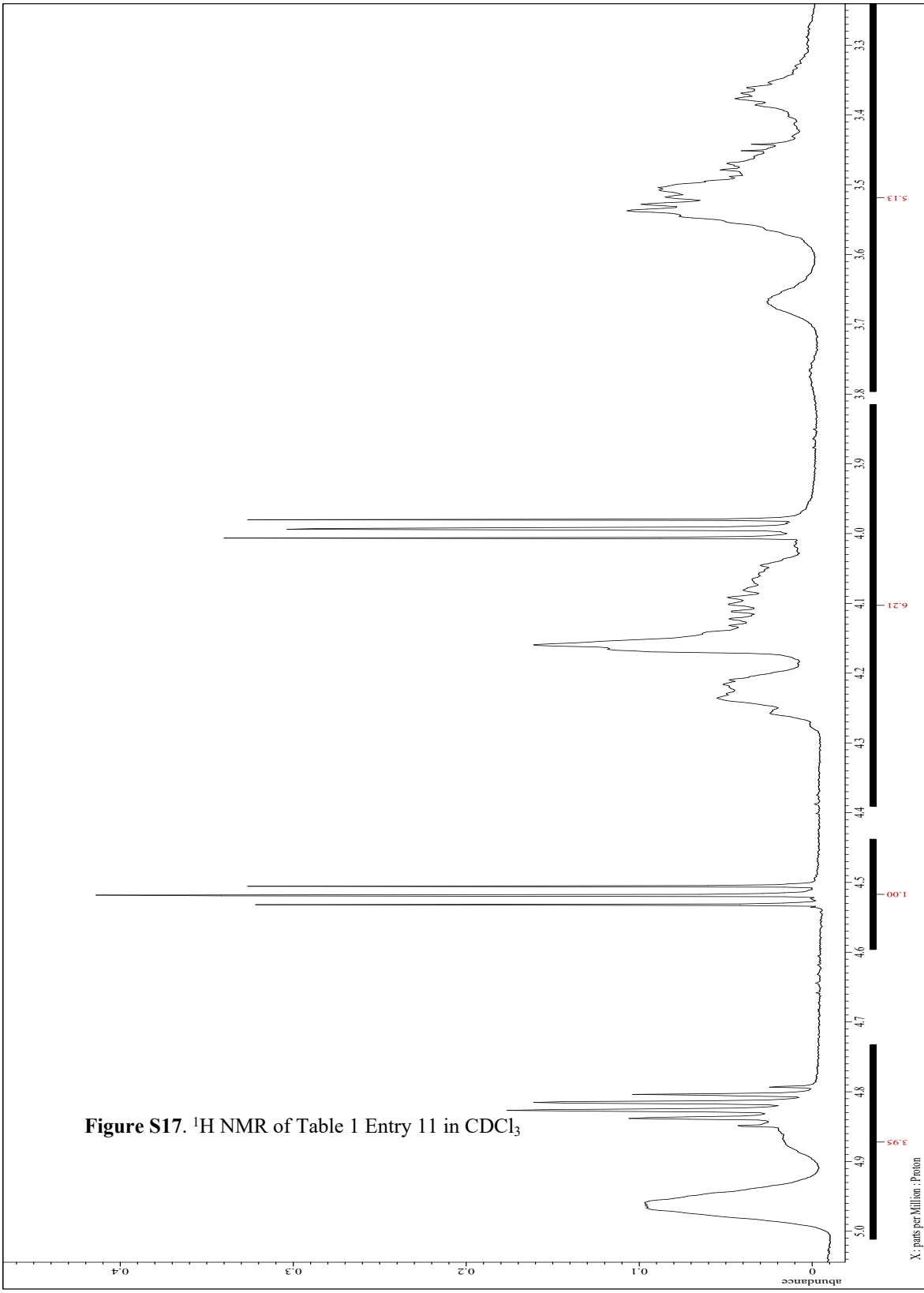


Figure S17. ^{1}H NMR of Table 1 Entry 11 in $CDCl_3$

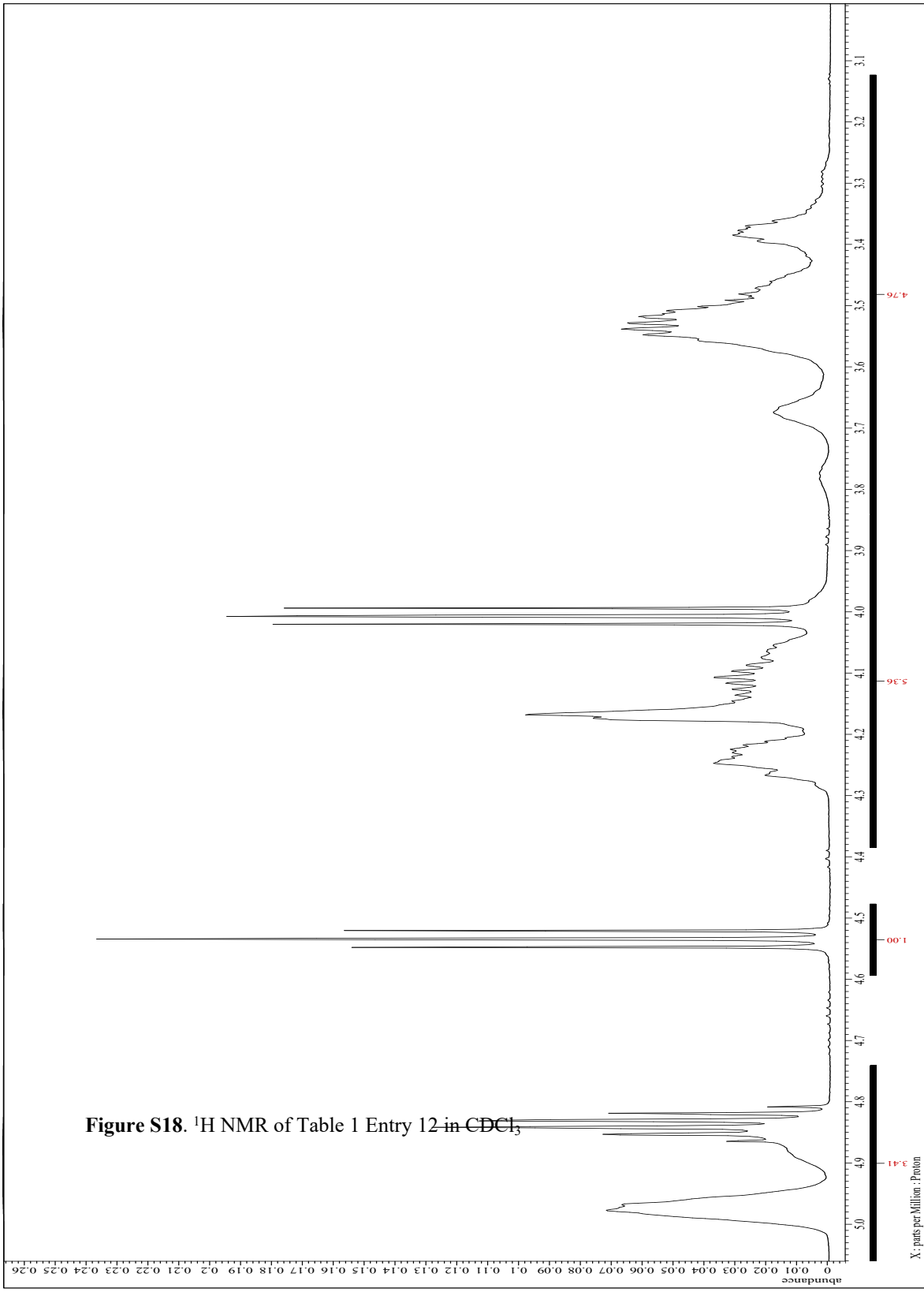


Figure S18. ^{1}H NMR of Table 1 Entry 12 ~~in $CDCl_3$~~

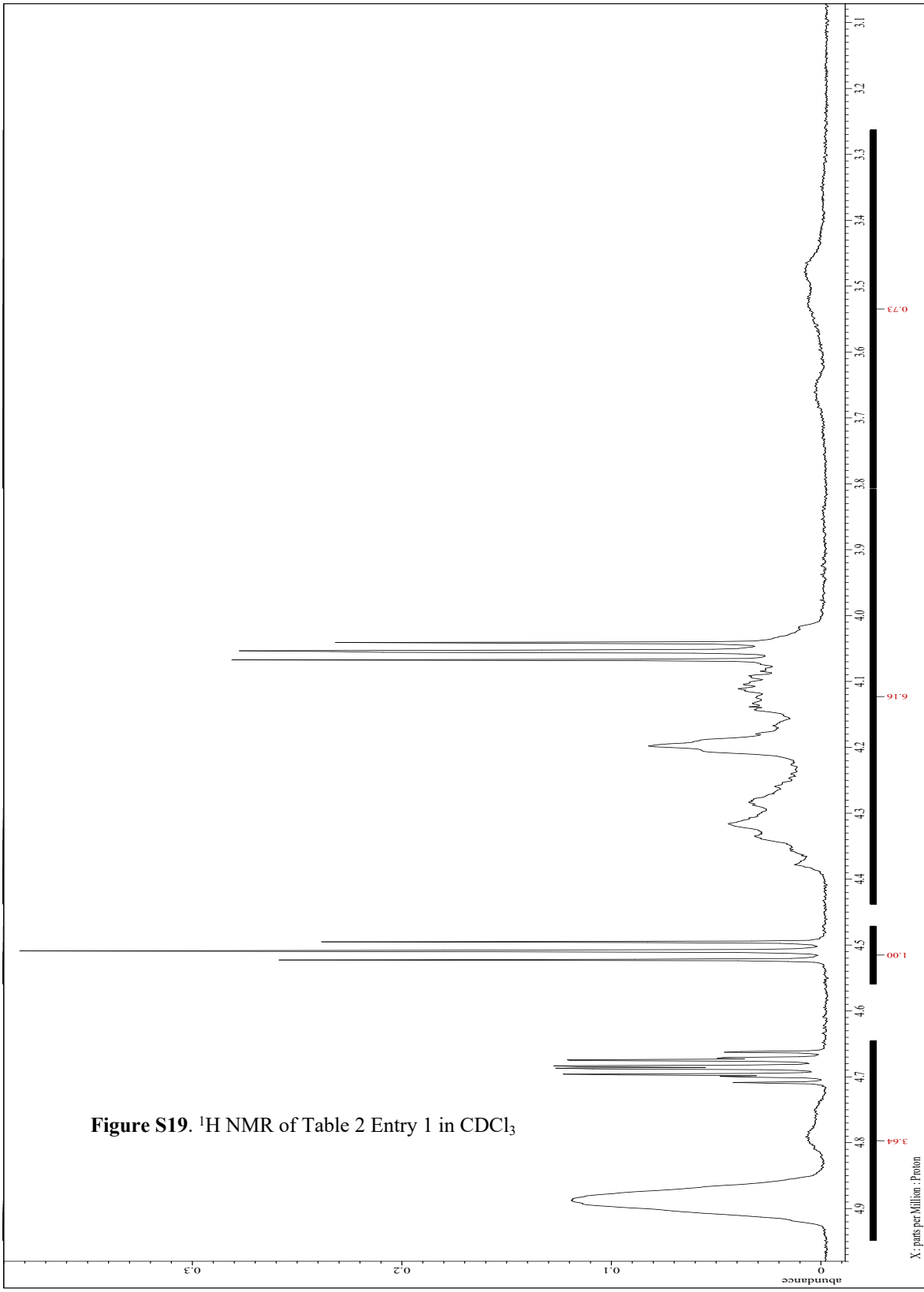


Figure S19. ^{1}H NMR of Table 2 Entry 1 in $CDCl_3$

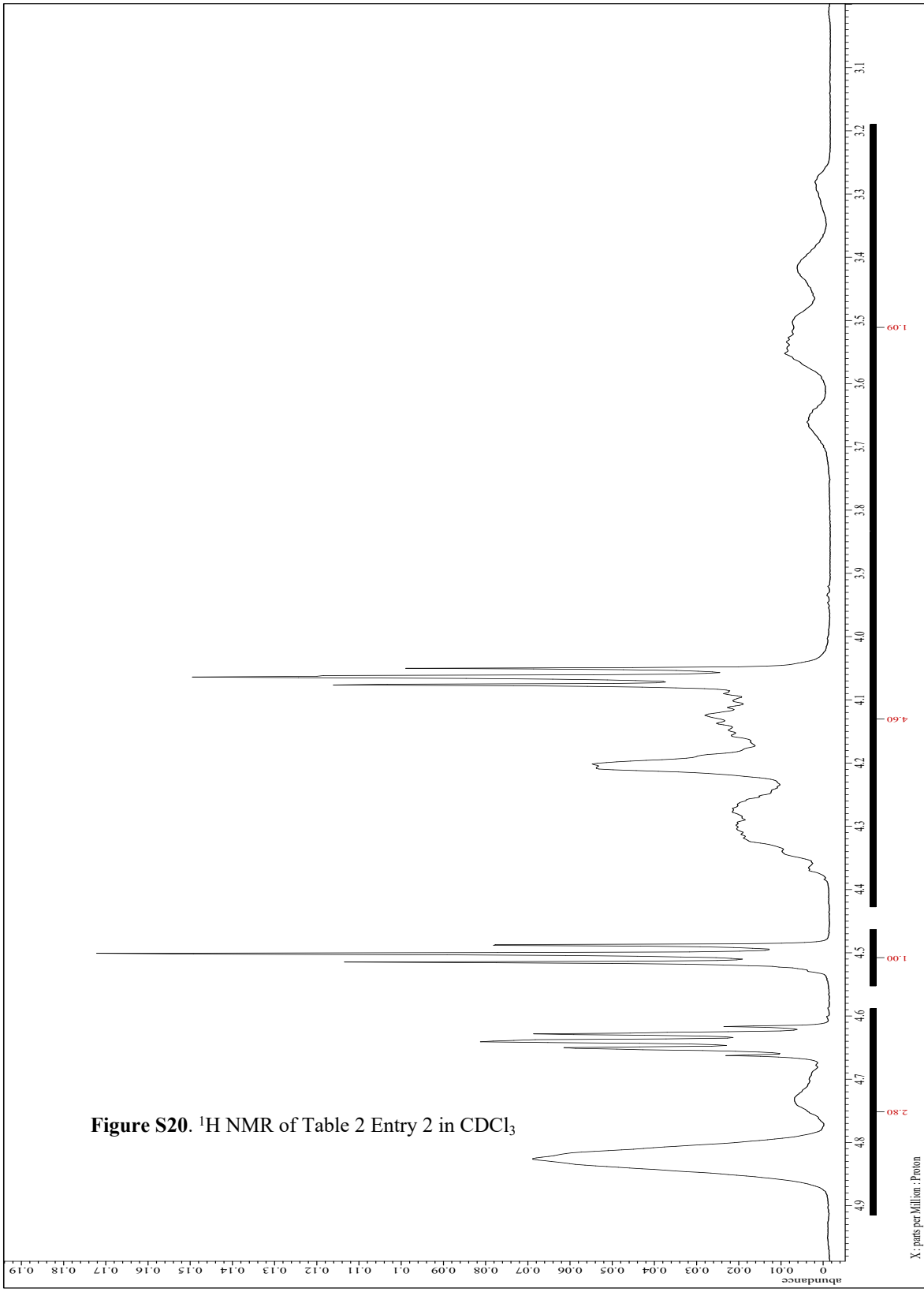


Figure S20. ^{1}H NMR of Table 2 Entry 2 in $CDCl_3$

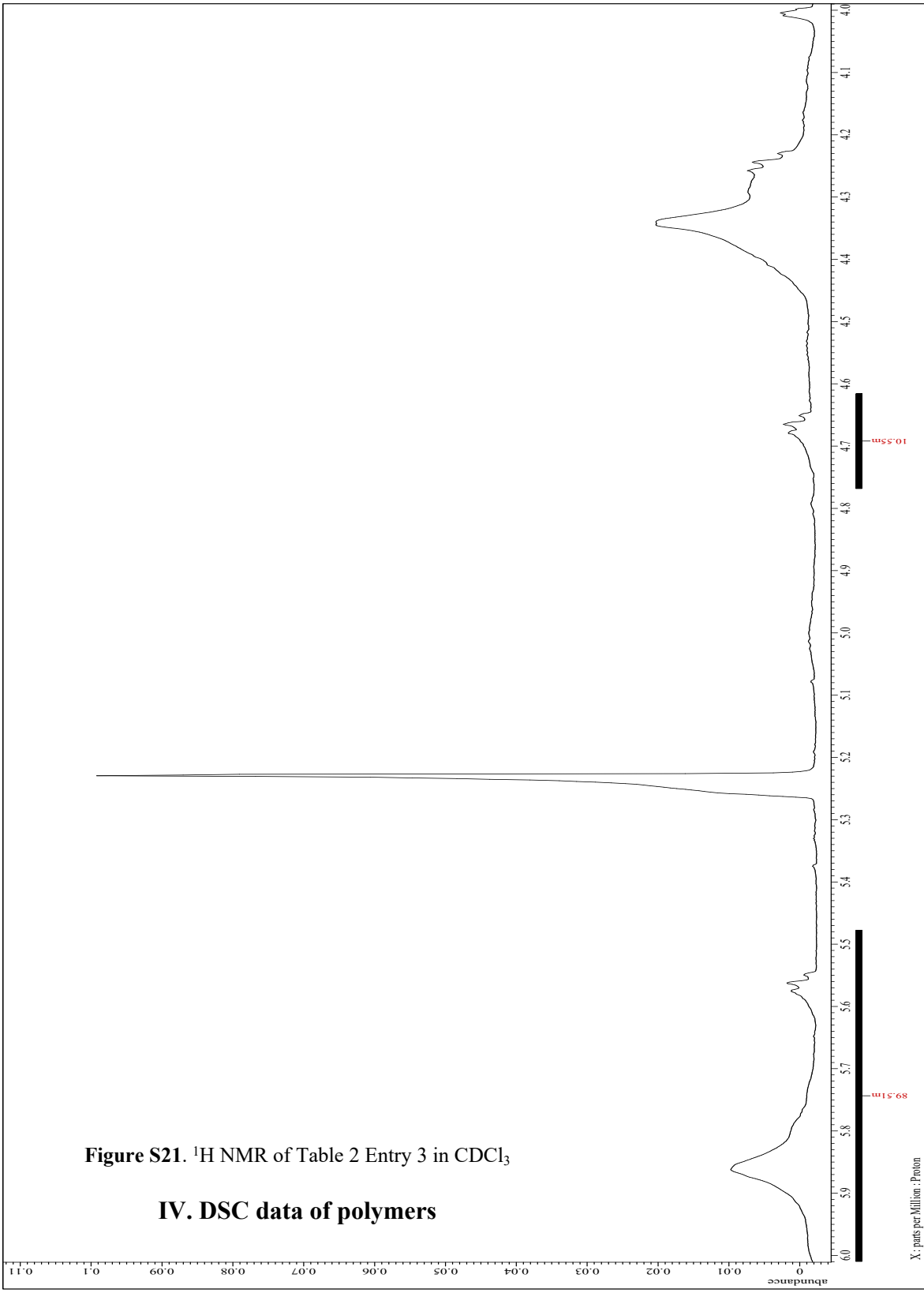


Figure S21. ^{1}H NMR of Table 2 Entry 3 in $CDCl_3$

IV. DSC data of polymers

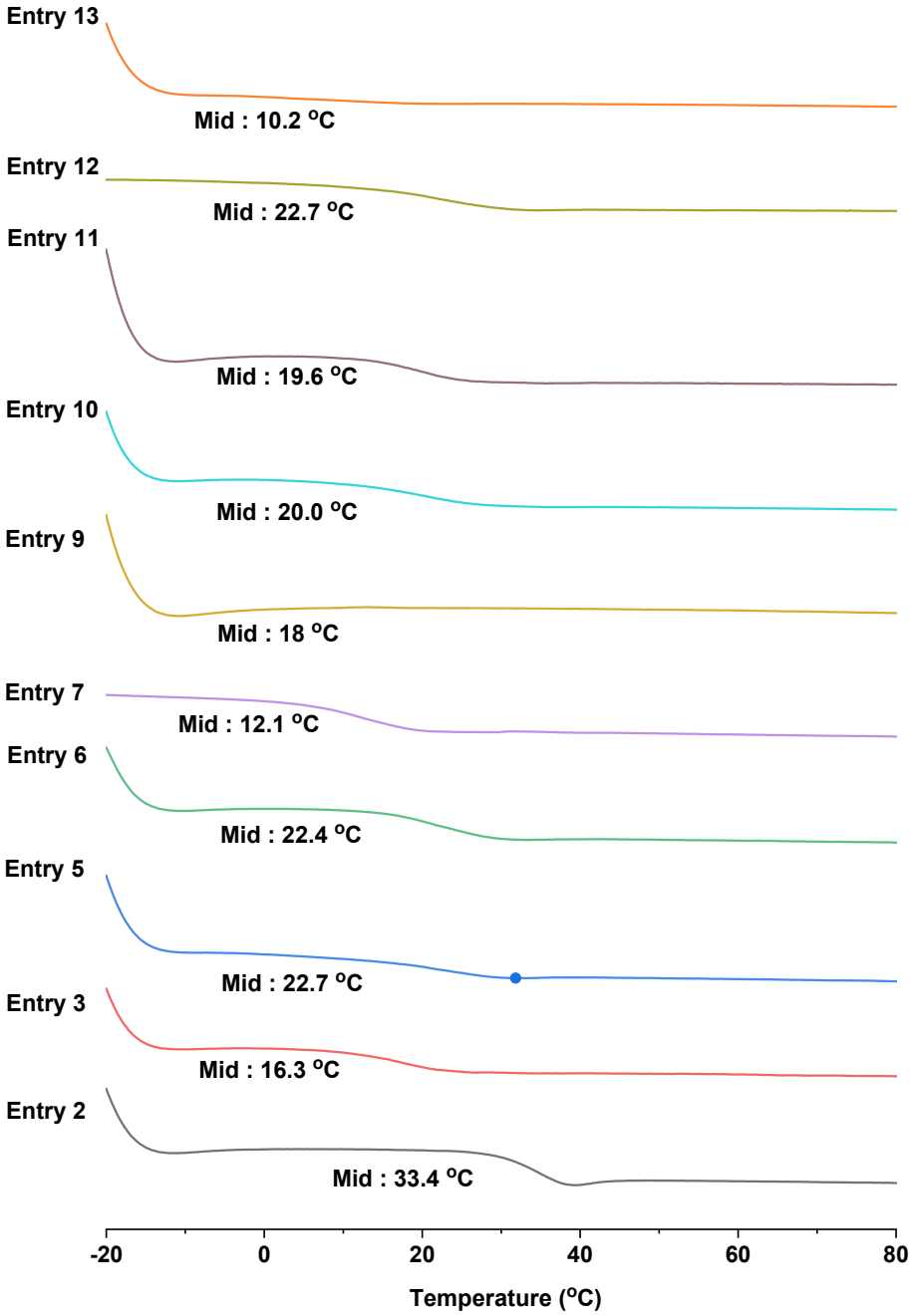


Figure S22. DSC thermograms of polycarbonates in Table 1.

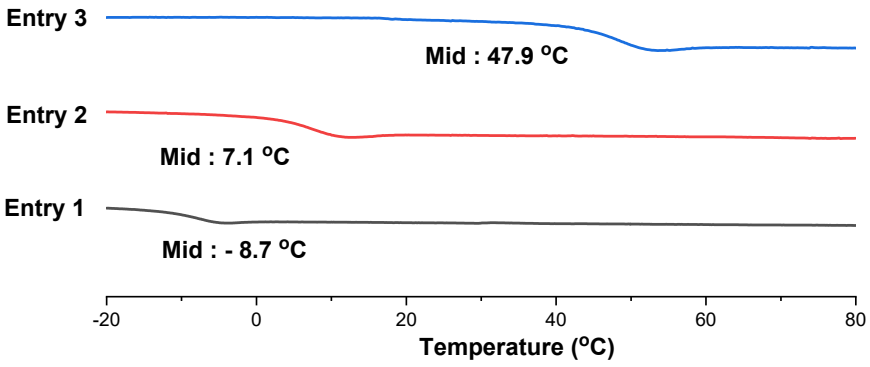


Figure S23. DSC thermograms of polycarbonates in Table 2, entries 1-3.

V. TGA data of polymers

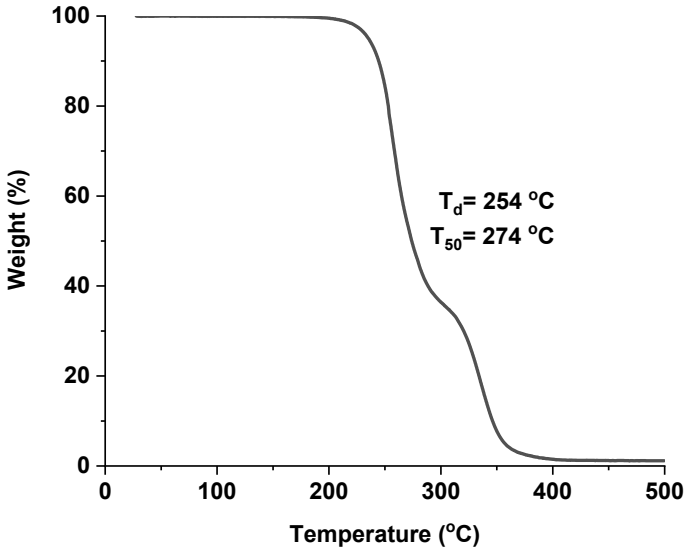


Figure S24. TGA curve of the polymer (Table 1, entries 11)

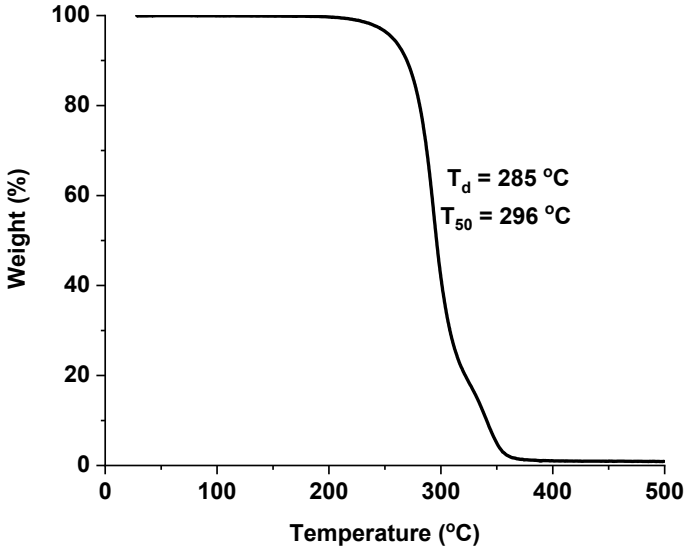


Figure S25. TGA curve of the polymer (Table 2, entries 1)

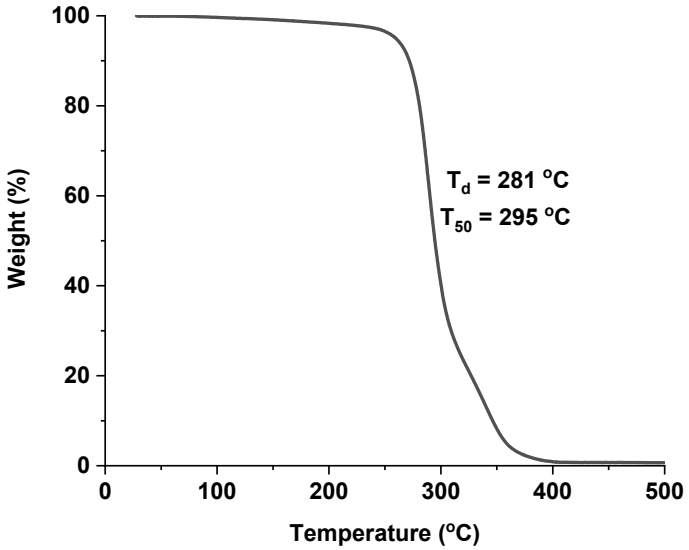


Figure S26. TGA curve of the polymer (Table 2, entries 2)

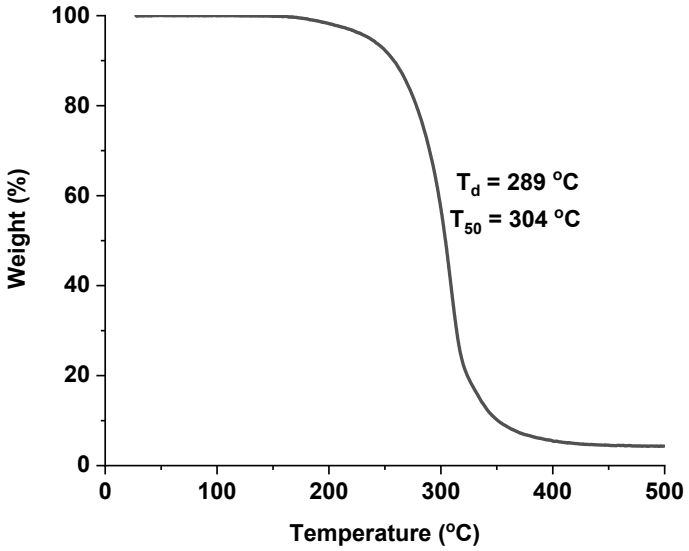


Figure S27. TGA curve of the polymer (Table 2, entries 3)

VI. GPC data of polymers

- THF was used as the solvent for GPC analysis

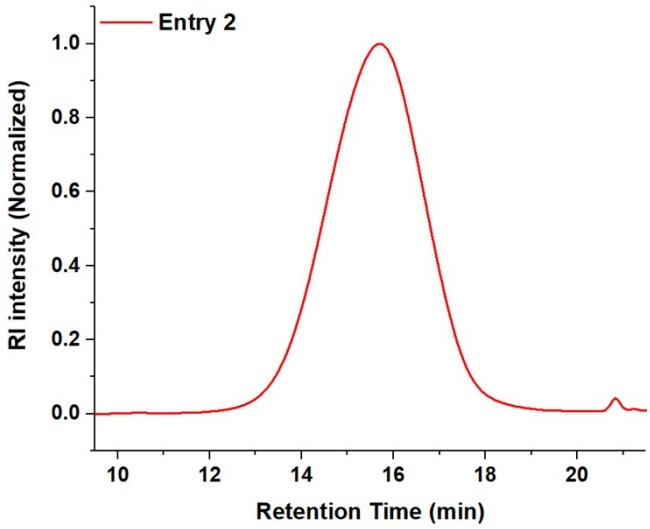


Figure S28. GPC elution curve of reduced polycarbonates (Table 1, entry 2) in THF

M_n: 49.3 K, M_w: 87.4 K, $Đ$: 1.76

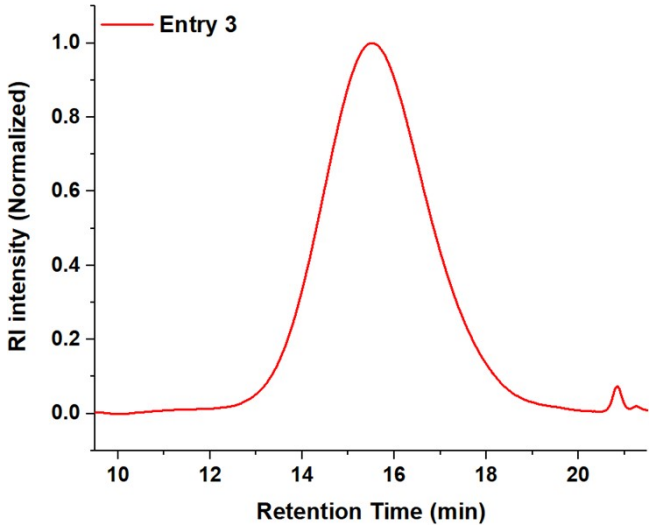


Figure S29. GPC elution curve of reduced polycarbonates (Table 1, entry 3) in THF

M_n: 42.3 K, M_w: 87.4 K, $Đ$: 2.06

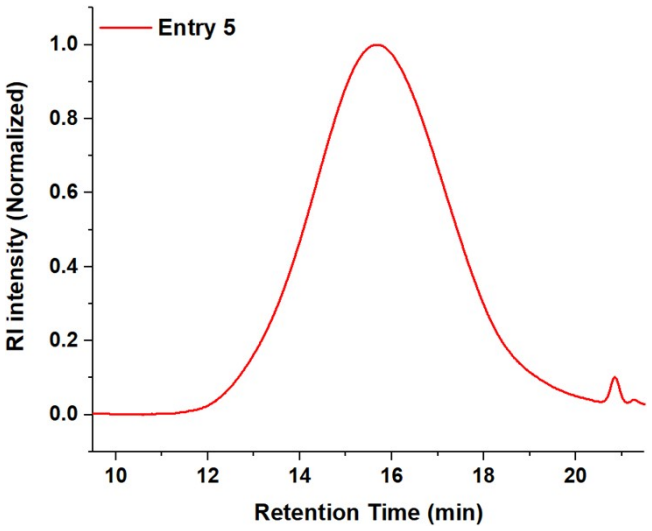


Figure S30. GPC elution curve of reduced polycarbonates (Table 1, entry 5) in THF

M_n: 30.1 K, M_w: 101.2 K, $Đ$: 3.42

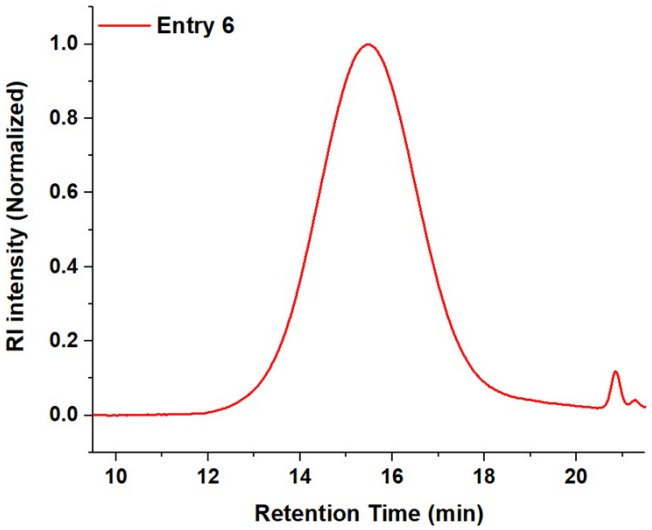


Figure S31. GPC elution curve of reduced polycarbonates (Table 1, entry 6) in THF

M_n: 51.7 K, M_w: 98.1 K, $Đ$: 1.92

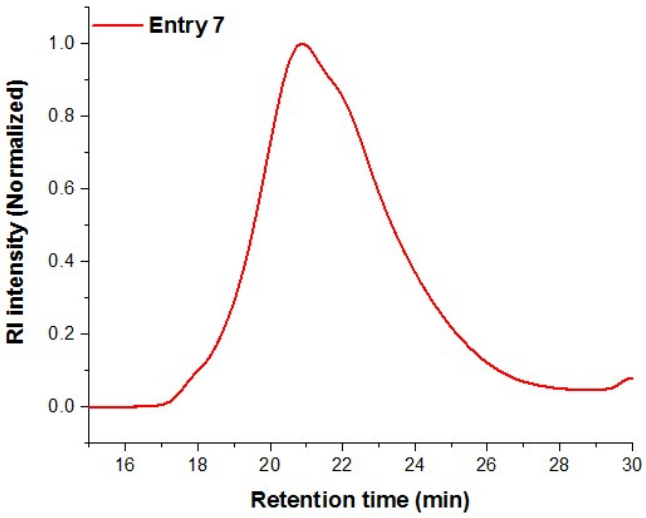


Figure S32. GPC elution curve of reduced polycarbonates (Table 1, entry 7) in THF

M_n: 50.0 K, M_w: 154.5 K, $Đ$: 3.09

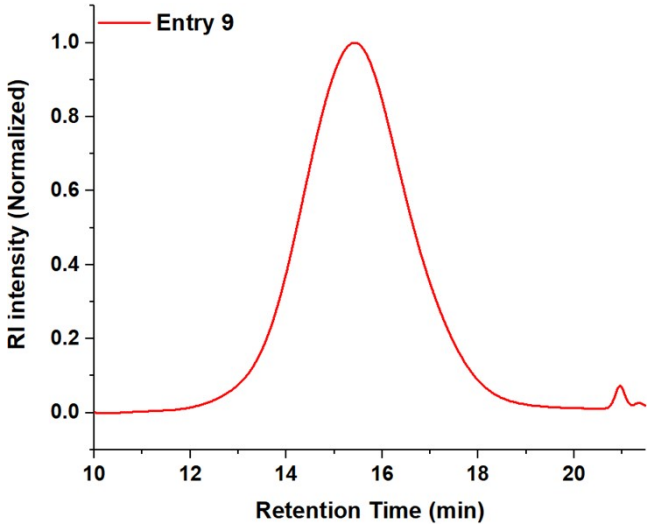


Figure S33. GPC elution curve of reduced polycarbonates (Table 1, entry 9) in THF

M_n: 48.6 K, M_w: 100.6 K, $Đ$: 2.07

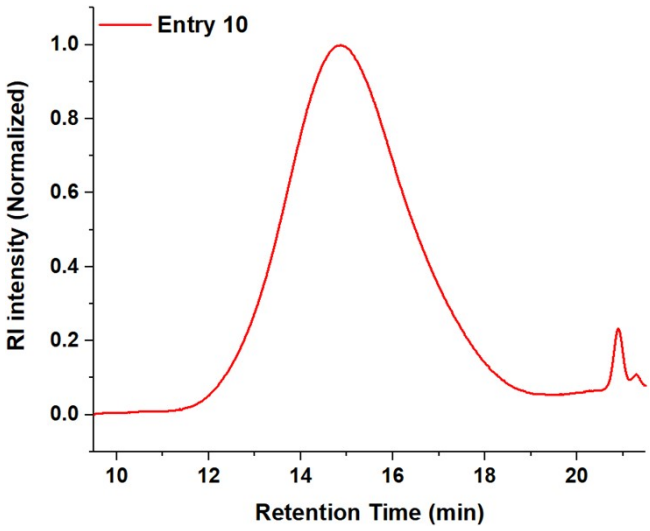


Figure S34. GPC elution curve of reduced polycarbonates (Table 1, entry 10) in THF

M_n: 59.6 K, M_w: 155.2 K, $Đ$: 2.61

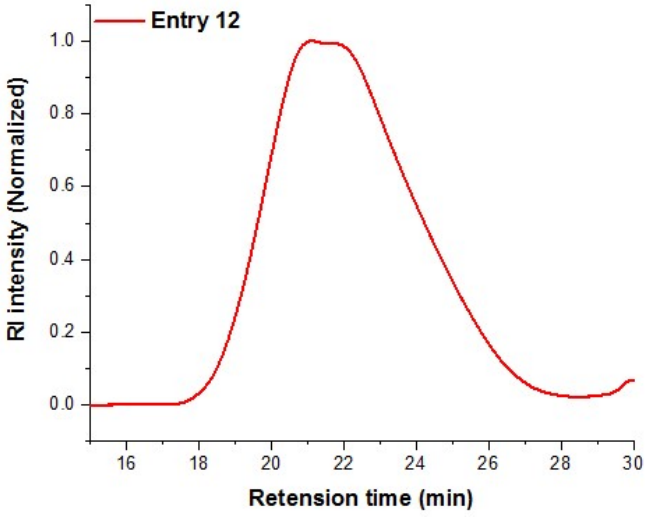


Figure S35. GPC elution curve of reduced polycarbonates (Table 1, entry 12) in THF

M_n: 39.6 K, M_w: 114.3 K, $Đ$: 2.89

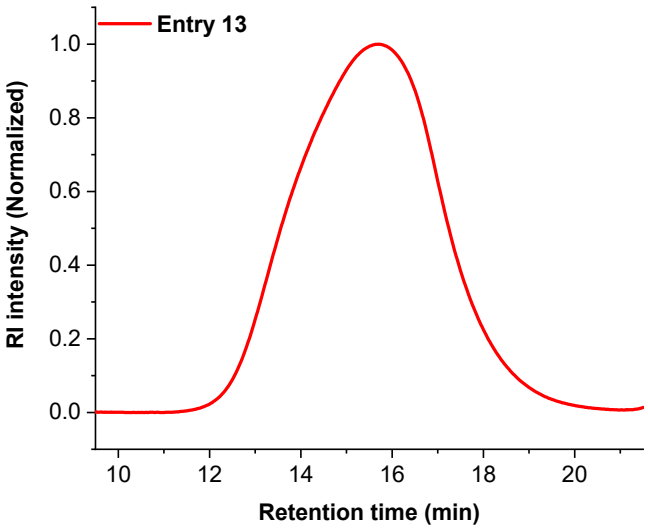


Figure S36. GPC elution curve of reduced polycarbonates (Table 1, entry 13) in THF

M_n: 87.8 K, M_w: 252.2 K, $Đ$: 2.87

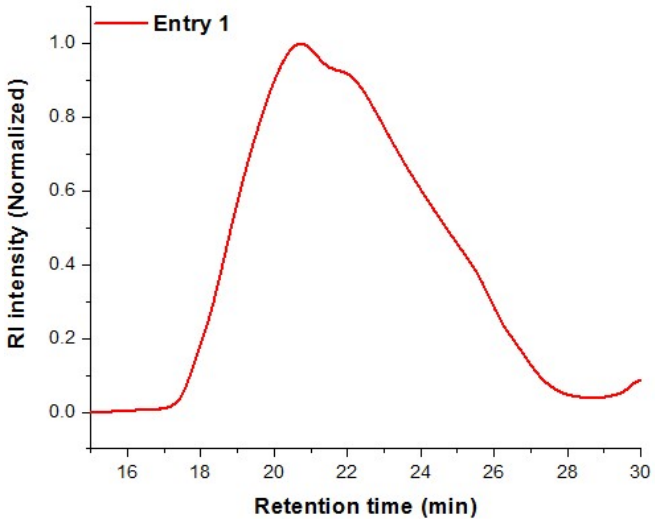


Figure S37. GPC elution curve of reduced polycarbonates (Table 2, entry 1) in THF

M_n: 50.0 K, M_w: 154.5 K, $Đ$: 3.09

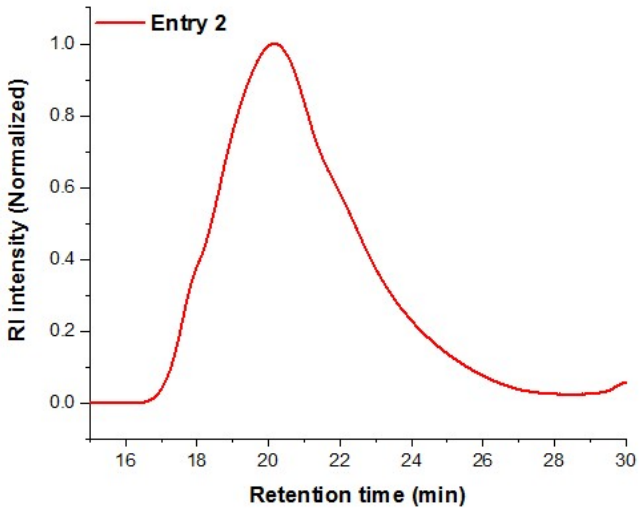


Figure S38. GPC elution curve of reduced polycarbonates (Table 2, entry 2) in THF

M_n: 36.5 K, M_w: 172.4 K, $Đ$: 4.72

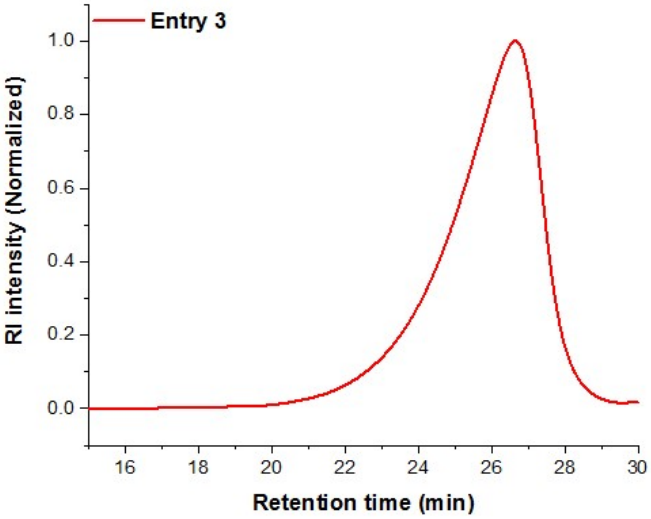


Figure S39. GPC elution curve of reduced polycarbonates (Table 2, entry 3) in THF

M_n: 8.2 K, M_w: 12.4 K, $Đ$: 1.52