Supporting Information

for

Controlled Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides Through Bifunctional Thiourea-Quaternary Ammonium Salt Catalysts

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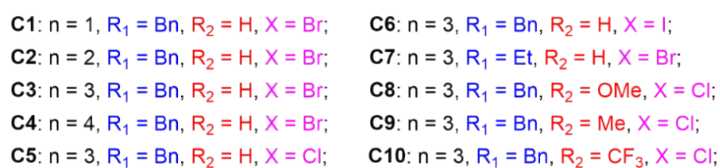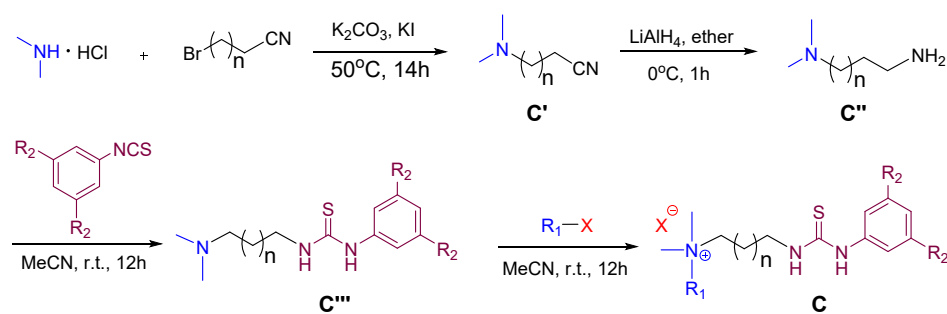## Content

1. General Information

Materials

All reagents were commercially available and used directly unless otherwise stated. Propylene oxide (PO), cyclohexene oxide (CHO) were purchased from Acros. Phthalate anhydride (PA), succinic anhydride (SA), diethylene glycol anhydride (DGA) and maleic anhydride (MA) were were purchased from TCI. All epoxides were dried were dried over CaH_2 for 48 h, distilled in N_2 or vacuum, and stored under nitrogen atmosphere. PA, MA, SA and DGA were purified by sublimation before use. All manipulations were performed using a standard Schlenk technique or in a nitrogen-filled Etelux Lab 2000 glovebox unless otherwise mentioned.

Instruments and measurements

NMR spectra were recorded on Bruker Avance 500 MHz pectrometers (^{1}H NMR 500 MHz, ^{13}C NMR 126 MHz). ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals. All in-situ IR spectroscopic reactions were carried out with a Mettler-Toledo ReactIR 15 Reaction Analysis System fitted with a Sentinel DiComp (diamond) High-Pressure Probe. Data were acquired and analyzed using ReactIR software version 7.0, the infrared spectrometer was set to collect one spectrum every 15s over the corresponding reaction time. MALDI-TOF-MS analysis were performed on a Bruker Daltonics UltrafleXtreme system. Crude polymer samples were dissolved in dichloromethane at 10 mg/mL. The matrix was chosen as α-cyano-4-hydroxycinnamic acid (HCCA). The resulting spectra were analyzed using the Bruker Daltonics flexAnalysis 3.4 software package. Gel permeation chromatography (GPC) was performed on a system equipped with a 1200 HPLC pump, an Optilab T-rEX RI detector, a ViscoStar-II viscometer and a DAWN HELEOS-II multiangle laser-light scattering (MALLS) detector at a wavelength of 690 nm (Wyatt Technology). One guard column and three 7.8 × 300 mm columns (Styragel® HT 2 DMF, Styragel® HT 3 DMF and Styragel® HT 4 DMF) were used. The mobile phase consisted of DMF containing 0.1 M LiBr at a flow rate of 1 mL min^{-1}. Samples were filtered through a 0.45 μm PTFE filter before analysis. Absolute molecular weights of polymers were determined using ASTRA software (Wyatt Technology).

2. General procedure for synthesis of the bifunctional thiourea catalysts C1-C10

C1: n = 1, R_1 = Bn, R_2 = H, X = Br; **C6**: n = 3, R_1 = Bn, R_2 = H, X = I;
C2: n = 2, R_1 = Bn, R_2 = H, X = Br; **C7**: n = 3, R_1 = Et, R_2 = H, X = Br;
C3: n = 3, R_1 = Bn, R_2 = H, X = Br; **C8**: n = 3, R_1 = Bn, R_2 = OMe, X = Cl;
C4: n = 4, R_1 = Bn, R_2 = H, X = Br; **C9**: n = 3, R_1 = Bn, R_2 = Me, X = Cl;
C5: n = 3, R_1 = Bn, R_2 = H, X = Cl; **C10**: n = 3, R_1 = Bn, R_2 = CF$_3$, X = Cl;

The bifunctional thiourea catalysts were synthesized by following the previous method.[1] Halogenated cyano compounds (3.3 mmol, 1.1 equiv) was diluted with 50 mL of acetonitrile and added to a suspension of dimethylamine hydrochloride (3.0 mmol, 1.0 equiv), K_2CO_3 (4.5 mmol, 1.5 equiv) and KI (0.3 mmol, 0.1 equiv) in 40 mL of acetonitrile at 50 °C. After stirring for 14 h, the reaction mixture was concentrated and further purified by extracting with 1.0 M brine and ether for three times. The ether phase was dried with Na_2SO_4, and the solvent was removed in vacuo to obtain tertiary aminated cyano **C'**. A suspension of LiAlH$_4$ (3.0 mmol, 1.5 equiv) in ether was slowly added to the ether solution (40 mL) of **C'** (2.0 mmol, 1.0 equiv) at 0 °C under nitrogen atmosphere. The mixture was stirred for 2 h at room temperature. LiAlH$_4$ was inactivated with deionized water and ether phase was discarded. Aqueous phase was extracted with CH_2Cl_2 for three times and dried with Na_2SO_4. Then the solvent was removed in vacuo to obtain primary amine compound **C''**.

To a solution of **C''** (1.5 mmol, 1.0 equiv) in acetonitrile was added phenylisothiocyanate (1.65 mmol, 1.1 equiv) at room temperature. After stirred for 12 h, the reaction mixture was concentrated in vacuo and purified by washing with a mixed solvent (acetonitrile/n-hexane = 1/1) for three times to give the thiourea/tertiary amine catalyst precursor **C'''**. To a solution of **C'''** (1.0 mmol, 1.0 equiv) in acetonitrile was added benzyl bromide (1.1 mmol, 1.1 equiv) at room temperature. After stirring for 12 h, the reaction mixture was concentrated in vacuo and further purified by washing with a mixed solvent (acetonitrile/n-hexane = 1/1) for three times to give the pre-designed thiourea/quaternary ammonium salt bifunctional catalyst **C**.

Bifunctional catalyst **C1.** 3-Bromopropionitrile, phenyl isothiocyanate, and benzyl bromide were used to obtain white solid catalyst **C1** (42% total yield). ^{1}H NMR (500 MHz, d_6-DMSO) δ 9.82 (s, 1H), 8.03 (t, J = 5.4 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.55 – 7.50 (m, 2H), 7.49 (s, 1H), 7.40 (d, J = 7.4 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.11 (dd, J = 10.4, 4.2 Hz, 1H), 4.57 (s, 2H), 3.63 – 3.50 (m, 2H), 3.32 – 3.26 (m, 2H), 2.99 (s, 6H), 2.17 – 2.08 (m, 2H). ^{13}C NMR (126 MHz, d_6-DMSO): δ 178.9, 137.4, 131.2, 128.5, 127.2, 126.8, 126.3, 122.4, 121.2, 64.1, 59.3, 47.6, 40.4, 20.5. HRMS (ESI) calcd for $C_{19}H_{26}N_3S^+$ [M−Br]$^+$ 328.1842, found 328.1848.

Bifunctional catalyst **C2.** 4-Bromobutyronitrile, phenyl isothiocyanate and benzyl bromide were used to obtain white solid catalyst **C2** (45% total yield). ^{1}H NMR (500 MHz, d_6-DMSO) δ 9.86 (s, 1H), 8.13 (t, J = 5.3 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.54 (dd, J = 13.1, 5.4 Hz, 3H), 7.49 (d, J = 8.1 Hz, 2H), 7.31 (t, J = 7.9 Hz, 2H), 7.09 (t, J = 7.3 Hz, 1H), 4.61 (d, J = 4.7 Hz, 2H), 3.54 (d, J = 5.7 Hz, 2H), 3.36 – 3.31 (m, 2H), 3.00 (s, 6H), 1.96 – 1.83 (m, 2H), 1.63 – 1.57 (m, 2H). ^{13}C NMR (126 MHz, d_6-DMSO): δ 181.0, 139.9, 133.4, 130.7, 129.4, 129.0, 128.6, 124.4, 122.9, 66.7, 63.5, 49.7, 43.5, 25.9, 20.1. HRMS (ESI) calcd for $C_{20}H_{28}N_3S^+$ [M−Br]$^+$ 342.1999, found 342.1991.

Bifunctional catalyst **C3.** 5-Bromovaleronitrile phenyl isothiocyanate and benzyl bromide were used to obtain white solid catalyst C3 (53% total yield). ^{1}H NMR (500 MHz, d_6-DMSO) δ 9.78 (s, 1H), 8.04 (t, J = 4.7 Hz, 1H), 7.57 (d, J = 6.0 Hz, 2H), 7.51 (d, J = 6.9 Hz, 3H), 7.47 (d, J = 7.9 Hz, 2H), 7.29 (t, J = 7.7 Hz, 2H), 7.07 (t, J = 7.2 Hz, 1H), 4.57 (s, 2H), 3.51 (s, 2H), 3.32 – 3.25 (m, 2H), 2.97 (s, 6H), 1.83 (s, 2H), 1.66 – 1.56 (m, 2H), 1.39 – 1.28 (m, 2H). ^{13}C NMR (126 MHz, d_6-DMSO): δ 178.7, 137.8, 131.2, 128.5, 127.2, 126.8, 126.4, 122.1, 120.9, 64.4, 61.7, 47.4, 41.5, 26.3, 21.6, 19.9. HRMS (ESI) calcd for $C_{21}H_{30}N_3S^+$ [M−Br]$^+$ 356.2155, found 356.2148.

Bifunctional catalyst **C4.** 6-Bromohexanonitrile, phenyl isothiocyanate and benzyl bromide were used to obtain white solid catalyst C4 (58% total yield). ^{1}H NMR (500 MHz, d_6-DMSO) δ 9.74 (s, 1H), 7.98 (t, J = 5.2 Hz, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.51 (t, J = 6.1 Hz, 3H), 7.47 (d, J = 7.9 Hz, 2H), 7.28 (t, J = 7.8 Hz, 2H), 7.06 (t, J = 7.3 Hz, 1H), 4.57 (s, 2H), 3.47 (s, 2H), 3.31 – 3.24 (m, 2H), 2.96 (s, 6H), 1.80 (dt, J = 15.3, 7.9 Hz, 2H), 1.56 (dt, J = 14.4, 7.2 Hz, 2H), 1.43 – 1.34 (m, 2H), 1.31 (dd, J = 14.1, 7.1 Hz, 2H). ^{13}C NMR (126 MHz, d_6-DMSO): δ 180.9, 140.0, 133.4, 130.7, 129.4, 128.9, 128.7, 124.3, 123.0, 66.5, 63.9, 49.6, 43.9, 28.6, 26.3, 26.0, 22.2. HRMS (ESI) calcd for $C_{22}H_{32}N_3S^+$ [M−Br]$^+$ 370.2312, found 370.2303.

Bifunctional catalyst **C5.** 5-Bromovaleronitrile, phenyl isothiocyanate and benzyl chloride were

used to obtain white solid catalyst C5 (55% total yield). ^{1}H NMR (500 MHz, d_6-DMSO) δ 10.39 (s, 1H), 8.63 (s, 1H), 7.57 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 6.4 Hz, 3H), 7.45 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 4.59 (s, 2H), 3.52 (s, 2H), 3.29 (m, 2H), 2.96 (s, 6H), 1.80 (dt, J = 15.2, 7.9 Hz, 2H), 1.61 (dt, J = 14.2, 7.2 Hz, 2H), 1.38 (m, 2H). ^{13}C NMR (126 MHz, d_6-DMSO) δ 181.07, 140.46, 133.44, 130.70, 129.38, 128.74, 128.65, 123.85, 122.54, 66.58, 63.89, 49.60, 43.44, 28.43, 23.85, 22.10. HRMS (ESI) calcd for $C_{21}H_{30}N_3S^+$ [M−Cl]$^+$ 356.2155, found 356.2142.

Bifunctional catalyst **C6**. 5-Bromovaleronitrile, phenyl isothiocyanate and benzyl iodide were used to obtain white solid catalyst C6 (48% total yield). ^{1}H NMR (500 MHz, d_6-DMSO) $δ$ 9.55 (s, 1H), 7.82 (s, 1H), 7.58 – 7.53 (m, 5H), 7.41 (d, J = 7.7 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.10 (t, J = 7.3 Hz, 1H), 4.54 (s, 2H), 3.51 (s, 2H), 3.27 (m, 2H), 2.97 (s, 6H), 1.90 – 1.78 (m, 2H), 1.61 (m, 2H), 1.39 – 1.29 (m, 2H). ^{13}C NMR (126 MHz, d_6-DMSO) $δ$ 180.83, 133.41, 130.76, 129.42, 129.09, 128.57, 124.56, 123.43, 66.74, 63.90, 49.66, 42.71, 28.53, 23.77, 22.11. HRMS (ESI) calcd for $C_{21}H_{30}N_3S^+$ [M−I]$^+$ 356.2155, found 356.2148.

Bifunctional catalyst **C7**. 5-Bromovaleronitrile, phenyl isothiocyanate and ethyl bromide were used to obtain white solid catalyst C7 (65% total yield). ^{1}H NMR (500 MHz, d_6-DMSO) δ 9.92 (s, 1H), 8.16 (s, 1H), 7.53 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.08 (t, J = 7.1 Hz, 1H), 3.51 (d, J = 4.1 Hz, 3H), 3.35 (s, 2H), 3.31 – 3.23 (m, 2H), 3.01 (s, 6H), 1.69 (s, 2H), 1.64 – 1.55 (m, 2H), 1.39 – 1.26 (m, 2H), 1.26 – 1.20 (m, 2H). ^{13}C NMR (126 MHz, d_6-DMSO) δ 178.64, 137.80, 126.61, 121.93, 120.63, 60.49, 56.69, 47.64, 42.75, 41.30, 26.12, 21.43, 19.65. HRMS (ESI) calcd for $C_{16}H_{28}N_3S^+$ [M−Br]$^+$ 294.1999, found 294.1990.

Bifunctional catalyst **C8**. 5-Bromovaleronitrile, 3,5-dimethoxy-phenyl isothiocyanate and benzyl chloride were used to obtain white solid catalyst C8 (42% total yield). ^{1}H NMR (500 MHz, d_6-DMSO) δ 10.43 (s, 1H), 8.61 (s, 1H), 7.69 – 7.25 (m, 5H), 6.90 (d, J = 7.9 Hz, 2H), 6.21 (s, 1H), 4.61 (s, 2H), 3.72 (m, 6H), 3.57 – 3.46 (m, 2H), 3.36 – 3.27 (m, 2H), 2.99 (s, 6H), 1.85 (s, 2H), 1.66 – 1.55 (m, 2H), 1.44 – 1.31 (m, 2H). ^{13}C NMR (126 MHz, d_6-DMSO) δ 178.52, 158.42, 139.97, 131.26, 128.51, 127.20, 127.13, 126.94, 126.49, 102.47, 98.11, 93.47, 64.37, 61.69, 53.40, 47.41, 40.12, 26.19, 21.70, 21.54. HRMS (ESI) calcd for $C_{23}H_{34}N_3O_2S^+$ [M−Cl]$^+$ 416.2367, found 416.2353.

Bifunctional catalyst **C9**. 5-Bromovaleronitrile, 3,5-dimethy-phenyl isothiocyanate and benzyl

chloride were used to obtain white solid catalyst C9 (56% total yield).^{1}H NMR (500 MHz, d_6-DMSO) δ 10.07 (s, 1H), 8.29 (d, J = 85.8 Hz, 1H), 7.67 − 7.45 (m, 5H), 7.11 (d, J = 7.8 Hz, 2H), 6.71 (s, 1H), 4.55 (s, 2H), 3.50 (d, J = 5.6 Hz, 2H), 3.28 (m, 2H), 2.97 (s, 6H), 2.24 (d, J = 2.1 Hz, 6H), 1.84 (m, 2H), 1.60 (m, 2H), 1.35 (m, 2H). ^{13}C NMR (126 MHz, d_6-DMSO) δ 180.89, 140.00, 137.82, 133.42, 130.71, 129.40, 128.63, 126.90, 120.61, 66.65, 63.92, 49.62, 43.54, 28.46, 23.84, 22.08, 21.49. HRMS (ESI) calcd for $C_{23}H_{34}N_3S^+$ [M−Cl]$^+$ 384.2468, found 384.2462.

Bifunctional catalyst **C10**. 5-Bromovaleronitrile, 3,5-ditrifluoromethyl-phenyl isothiocyanate and benzyl chloride were used to obtain white solid catalyst 10 (48% total yield).^{1}H NMR (500 MHz, d_6-DMSO) δ 11.23 (s, 1H), 8.86 (s, 1H), 8.41 (s, 2H), 7.69 (s, 1H), 7.54 (dd, J = 9.2, 6.5 Hz, 5H), 4.53 (s, 2H), 3.53 (d, J = 5.6 Hz, 2H), 3.31 − 3.22 (m, 2H), 2.95 (s, 6H), 1.92 − 1.77 (m, 2H), 1.69 − 1.56 (m, 2H), 1.44 − 1.31 (m, 2H).^{13}C NMR (126 MHz, DMSO) $δ$ 182.89 − 179.06, 142.81, 133.41, 130.69, 129.38, 128.60, 124.83, 122.4, 120.95, 115.98, 66.66, 63.88, 49.63, 43.46, 28.10, 23.81, 22.06. HRMS (ESI) calcd for $C_{23}H_{28}F_6N_3S^+$ [M−Cl]$^+$ 492.1903, found 492.1892.

3. General procedure for synthesis of poly(CHO-alt-PA)

In a glovebox, PA (0.3 g, 4.08 mmol), catalyst **C1** (7.0 mg, 20.38 μmol), and CHO (0.8 g, 8.15 mmol) were added into a 10-mL vial equipped with magnetic stirrer (The excess CHO was added as an alternative for a solvent to dissolve the catalyst and PA and to ensure the smooth enchainment during the ROPCOP process). The reaction mixture was heated to the target temperature and maintain it for the corresponding time. After the reaction was completed, it was cooled down to the room temperature, and added a small amount of CH_2Cl_2 to dissolve all unreacted PA into a clear solution. A small portion of the solution was taken out, and analyzed the conversion rate of PA and the selectivity of polyester using ^{1}H NMR. The other part of the solution was dropped into the stirred n-hexane to precipitate the polymer. Then the solid was filtered and dried to obtain the poly(CHO-alt-PA). In all catalytic results, the selectivity of polyester is > 99%.

4. Comparison of the catalyst activity of the bifunctional catalyst C3 and the two-

component catalyst system

Table S1 Comparison of the catalyst activity of the bifunctional catalyst **C3** and the two-component catalyst system with the same structure.[a]

Entry	CHO:PA:Cat.	t	Conv. (%)[b]		TOF (h^{-1})[c]		Ester (%)[b]
		(min)	TU/TBAB	C3	TU/TBAB	C3	
1	200:100:1	20	26	24	76	72	>99
2	500:250:1	40	28	24	105	90	>99
3	1000:500:1	60	21	19	103	95	>99
4	2000:1000:1	100	15	17	90	102	>99
5	4000:2000:1	180	11	20	73	133	>99
6	8000:4000:1	270	5	18	44	160	>99
7	12000:6000:1	720	7	30	35	150	>99
8	16000:8000:1	1440	7	38	23	126	>99
9	20000:10000:1	1440	3	28	12	116	>99
10	24000:12000:1	1440	<1	19	-	95	>99

[a]All polymerizations were carried out under conditions of strict removal of water and oxygen at 100 °C. [b]Conv. is the conversion of PA, and ester means the content of polyester in the polymer, which were determined by ^{1}H NMR spectroscopy. [c]TOF is the turnover frequency, calculated by (PA conversion)/(catalyst loading)/h.

5. Copolymerization of Versatile Epoxides with Anhydrides by bifunctional

thiourea catalyst

Table S2 Copolymerization of Versatile Epoxides with Anhydrides.[a]

Entry	Epoxide	Anhydride	Time (h)	Conv.[b] (%)	Ester[b] (%)	Mn^c (kDa)	$Đ^c$
1	PO	PA	24	>99	>99	5.7	1.11
2	PO	SA	24	>99	>99	6.3	1.12
3	PO	DGA	24	>99	>99	7.5	1.09
4[d]	PO	MA	24	-	-	-	-
5	CHO	PA	12	>99	>99	13.6	1.13
6	CHO	SA	12	>99	>75	5.8	1.12
7	CHO	DGA	12	>99	>99	4.3	1.14
8[d]	CHO	MA	12	-	-	-	-

[a]All polymerizations were carried out under conditions of strict removal of water and oxygen at 100 °C with an epoxide/anhydride/**C5** feeding ratio of 200:100:1. [b] Conv.(%) is the conversion of the anhydrides, and ester(%) is the percentage of ester linkage in the polymer, which were both determined by ^{1}H NMR spectroscopy. [c]Determined by GPC in THF, calibrated with polystyrene standards. [d] The reaction product was crosslinked and insoluble.
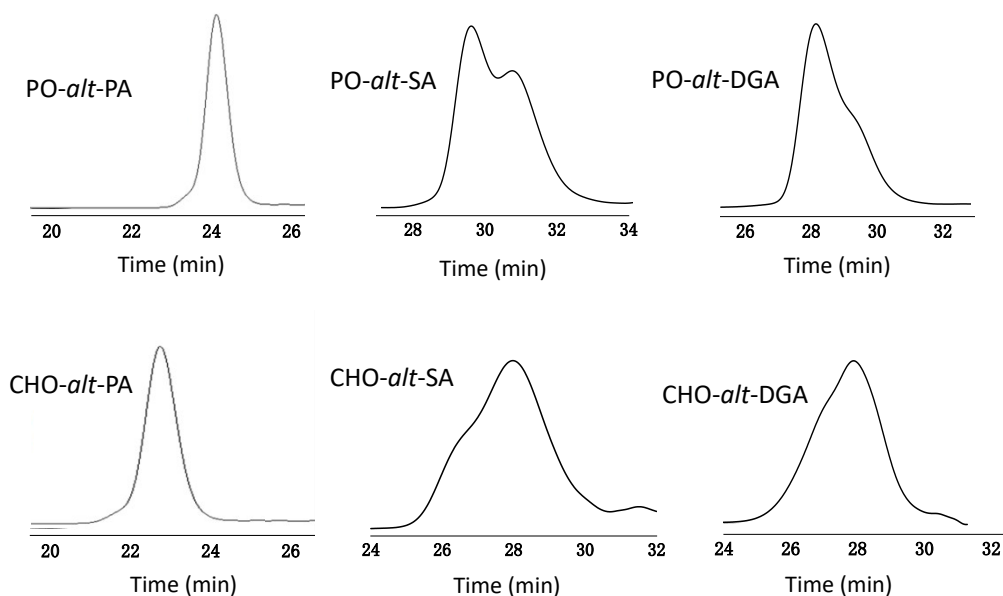
Figure S1 GPC of the resulted poly(epoxide-*alt*-anhydride)

^{1}H and ^{13}C NMR spectra for the resulted poly(epoxide-*alt*-anhydride)
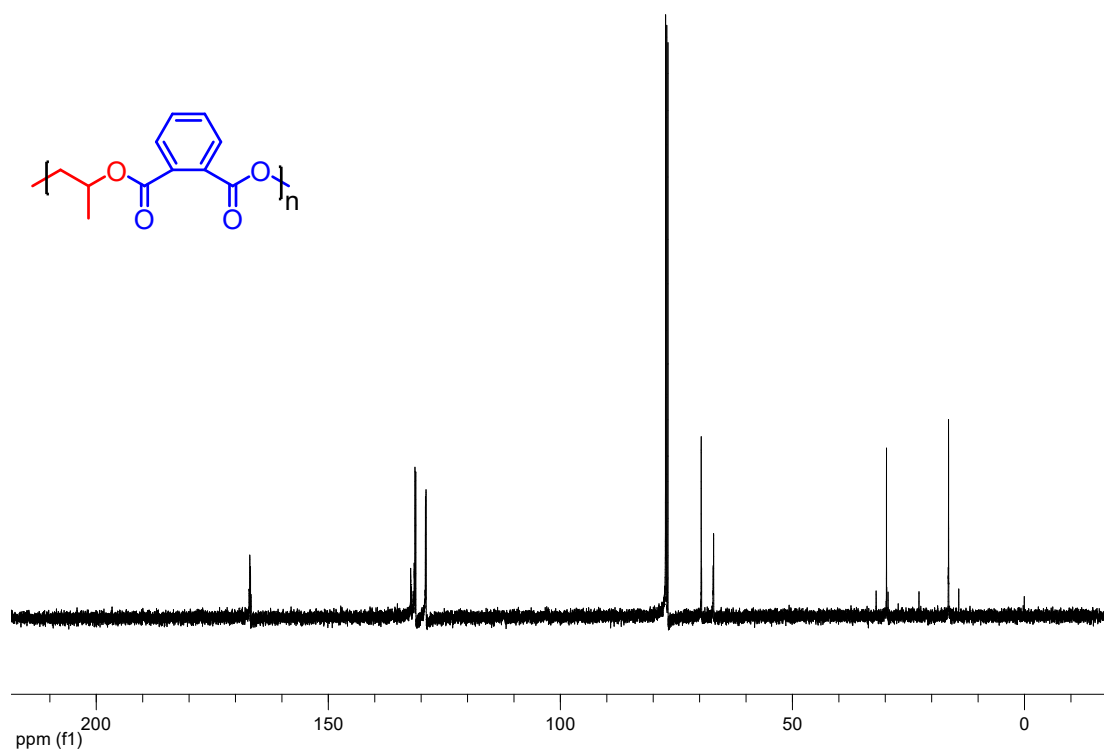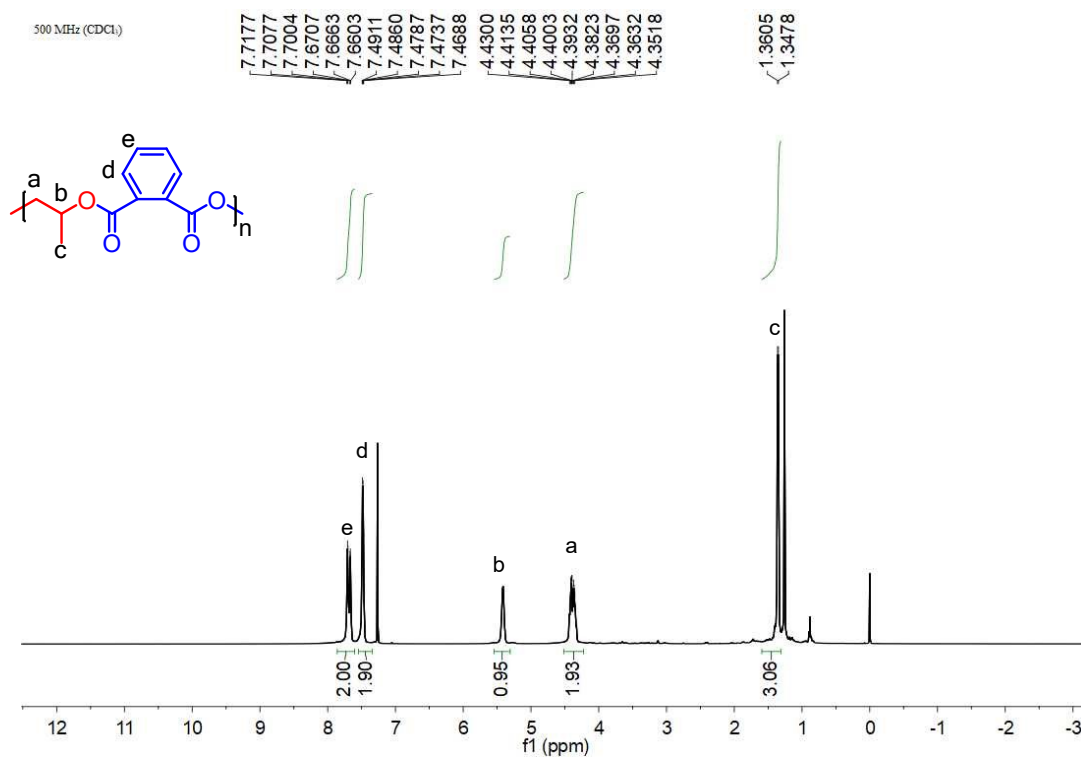
Figure S2 ^{1}H (500 M) and ^{13}C (126 M) NMR spectra for the resulted poly(PO-*alt*-PA) in CDCl$_3$
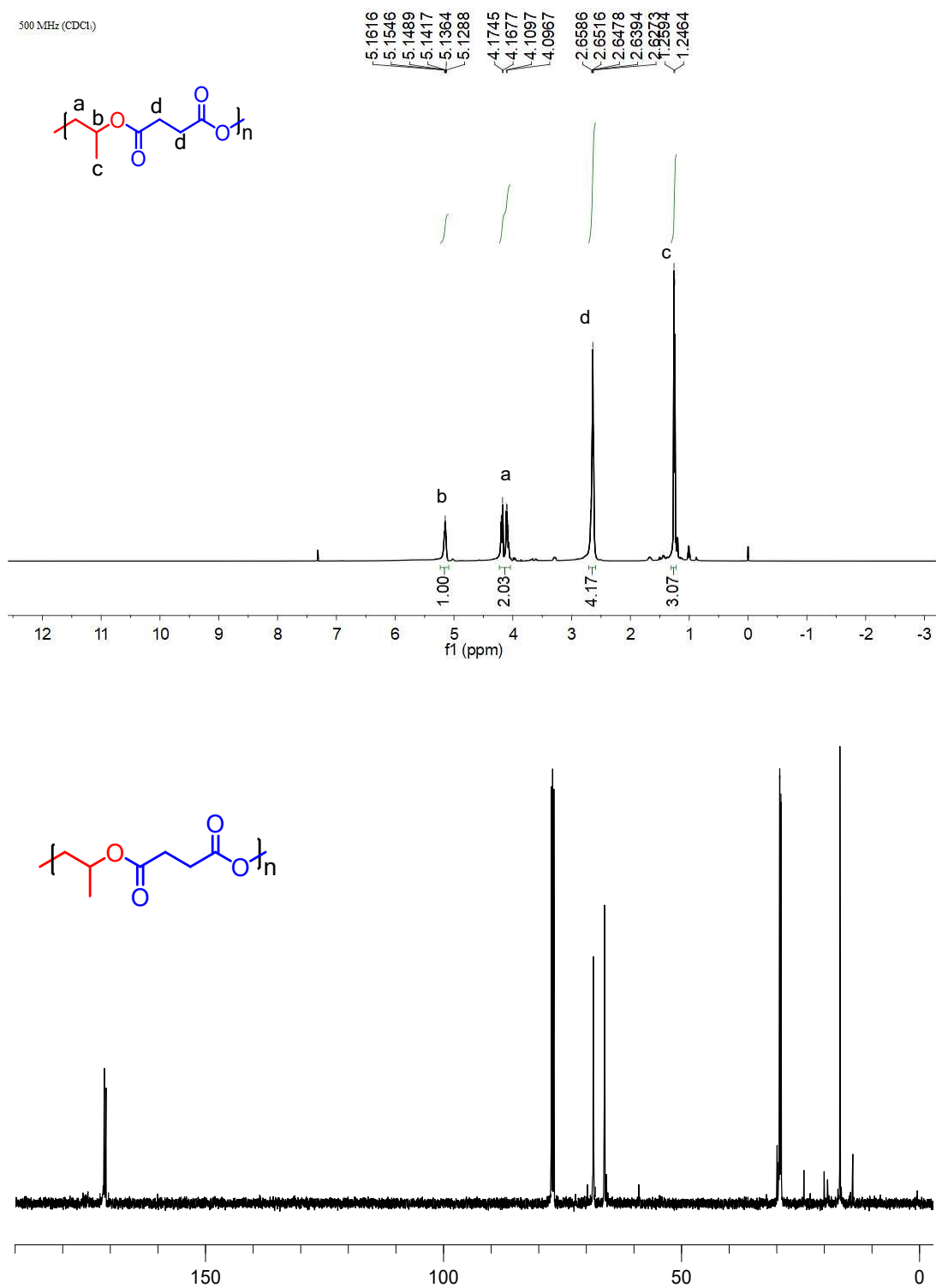
Figure S3 ^{1}H (500 M) and ^{13}C (126 M) NMR spectra for the resulted poly(PO-*alt*-SA) in CDCl$_3$
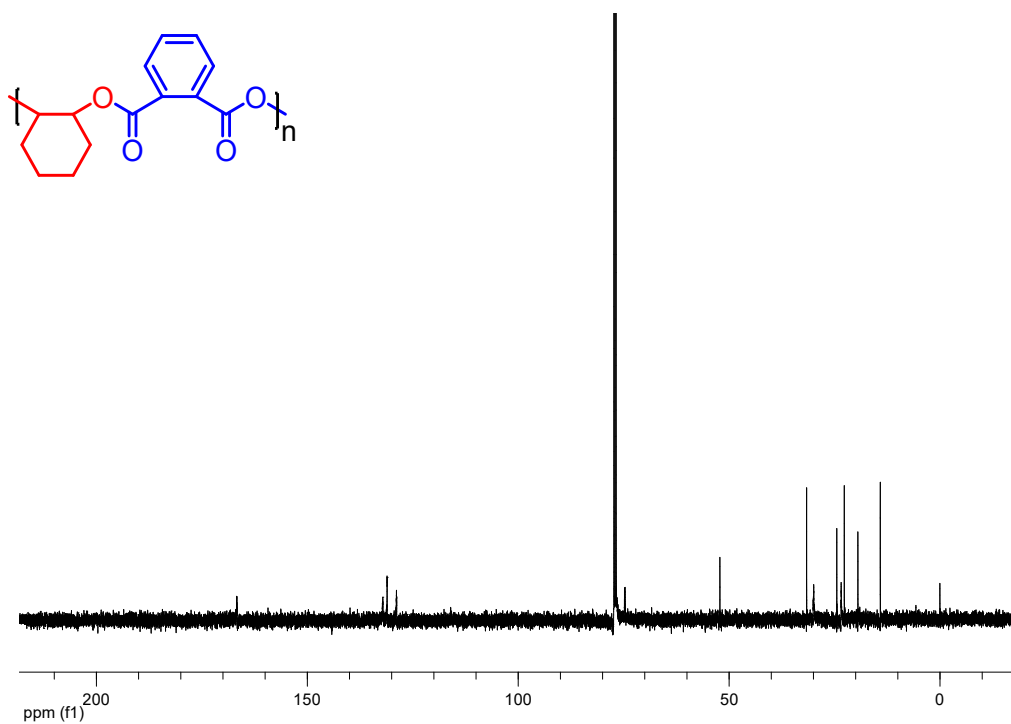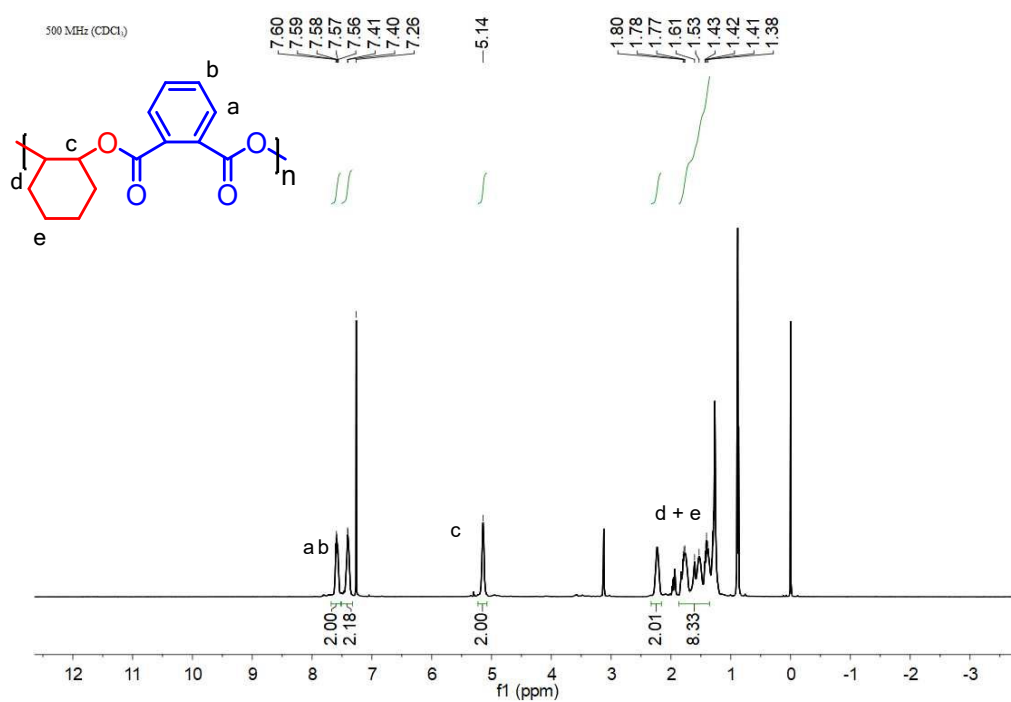
Figure S4 ¹H (500 M) and ¹³C (126 M) NMR spectra for the resulted poly(CHO-*alt*-PA) in CDCl₃
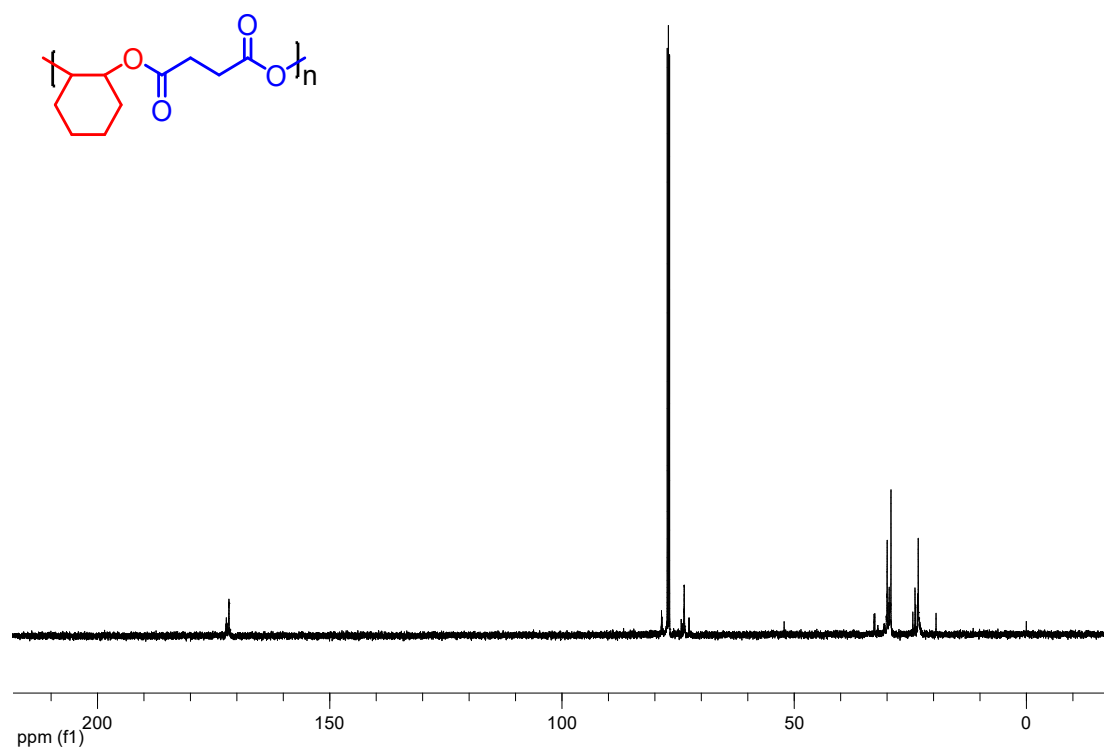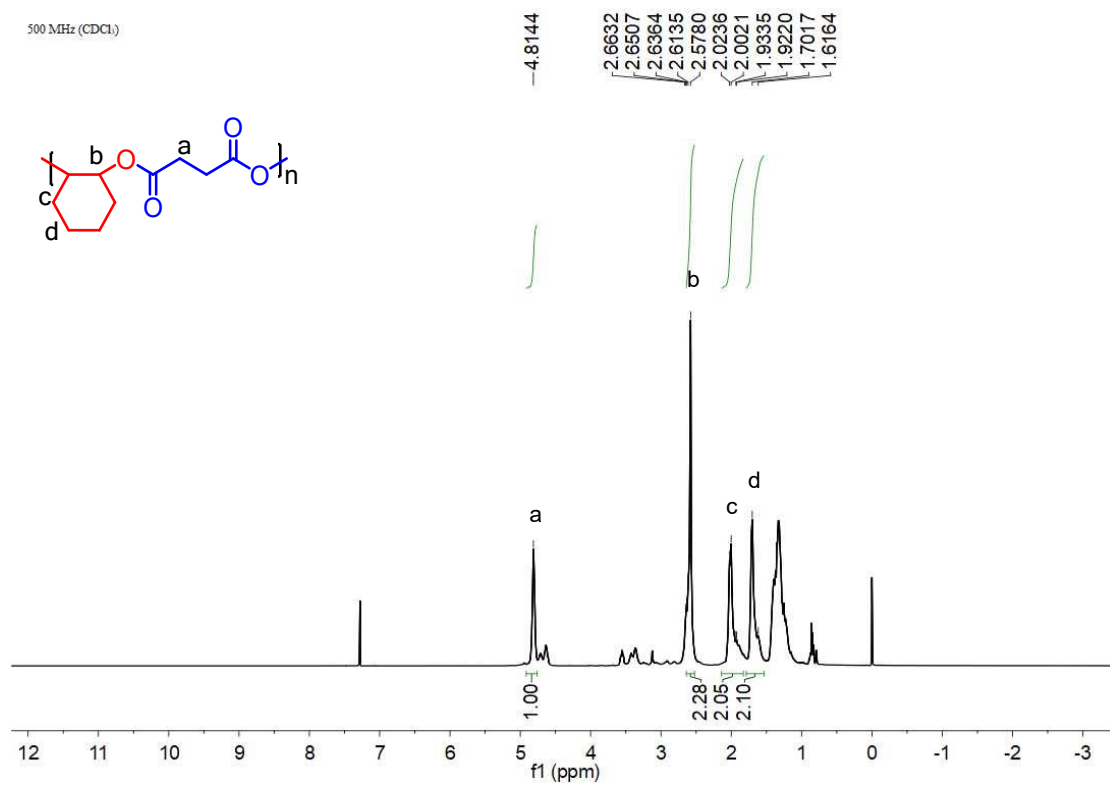
Figure S5 ^{1}H (500 M) and ^{13}C (126 M) NMR spectra for the resulted poly(CHO-*alt*-SA) in CDCl$_3$
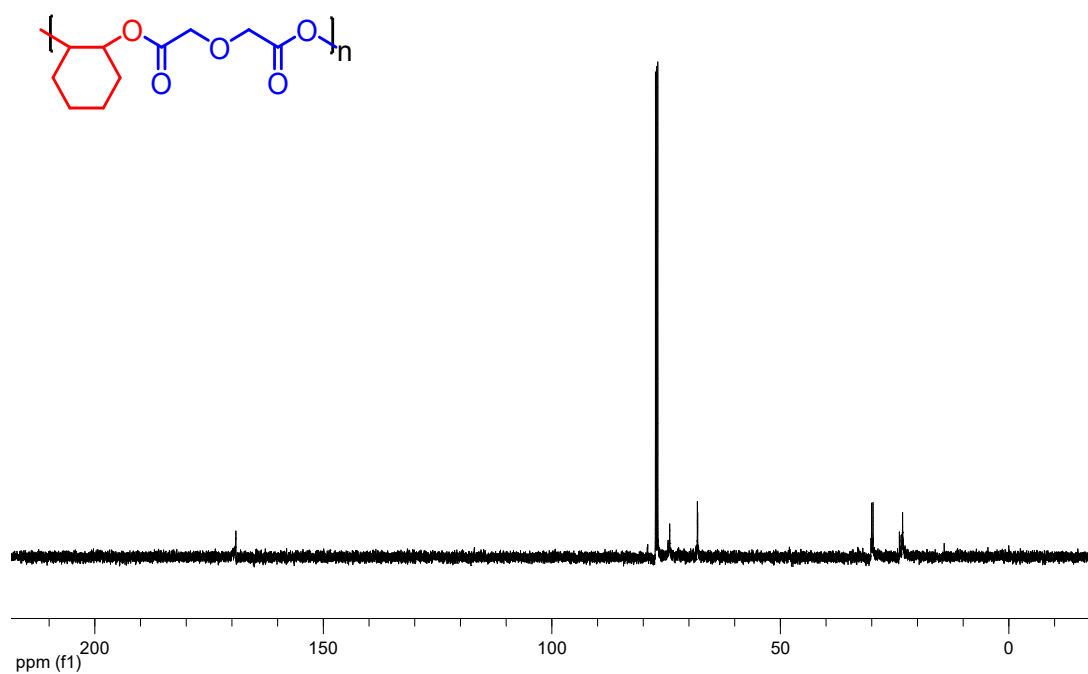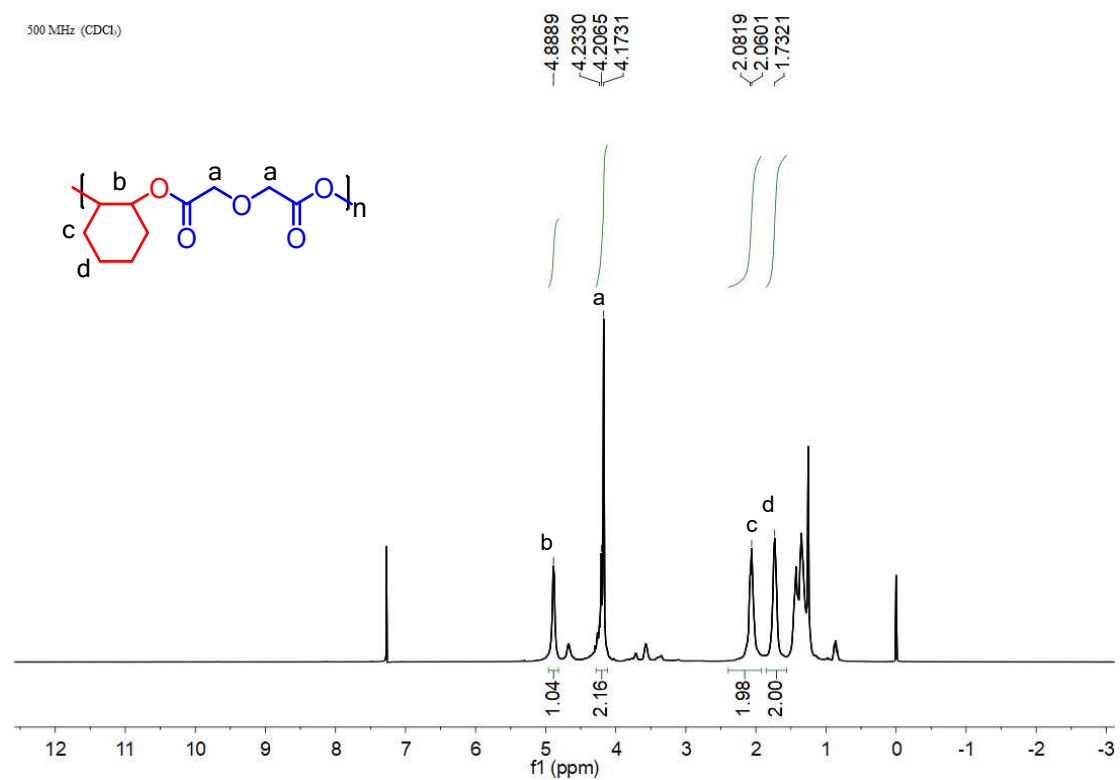
Figure S6 ¹H (500 M) and ¹³C (126 M) NMR spectra for the resulted poly(CHO-*alt*-DGA) in CDCl₃

6. ¹H and ¹³C NMR spectra for the bifunctional thioure catalysts
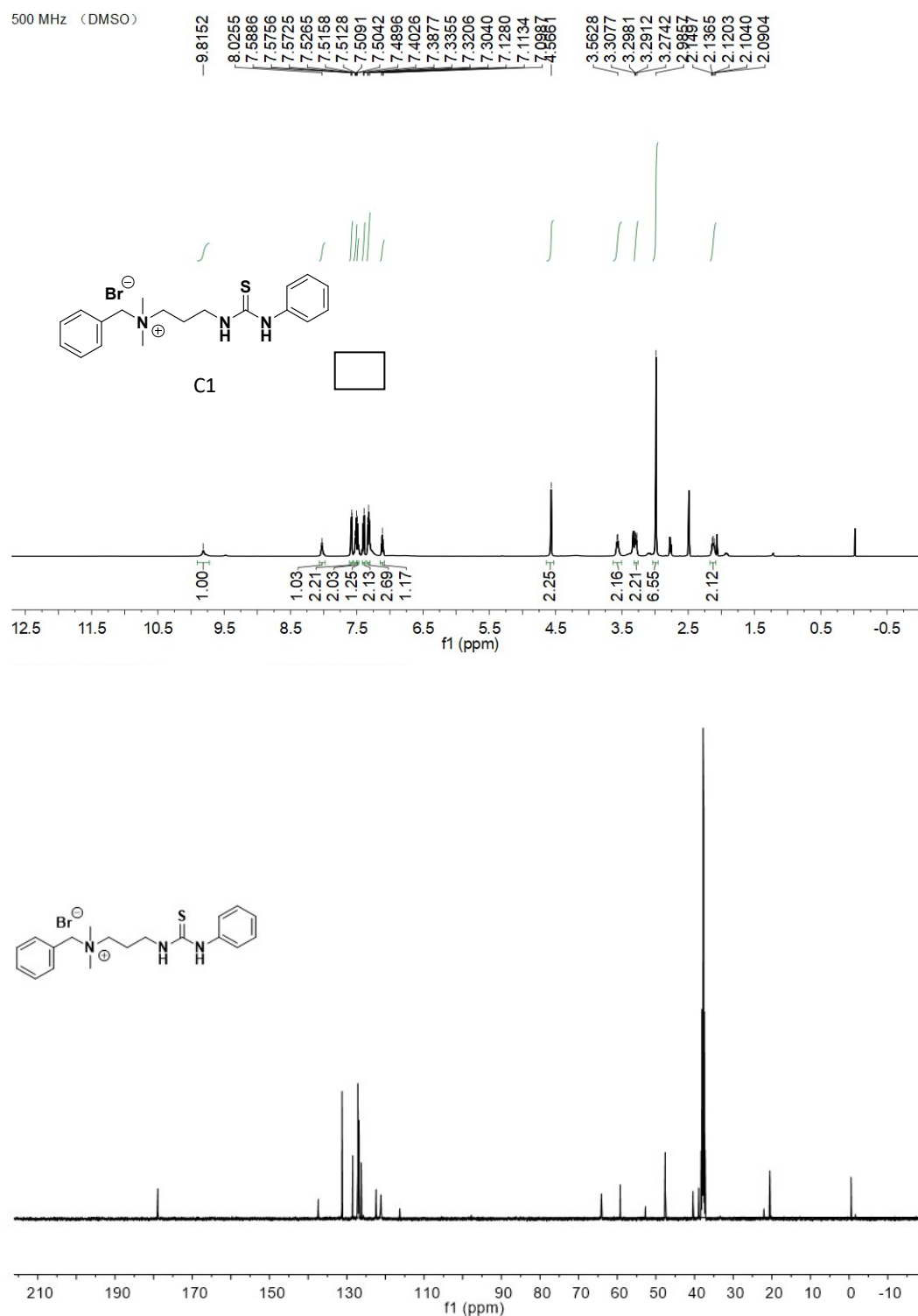
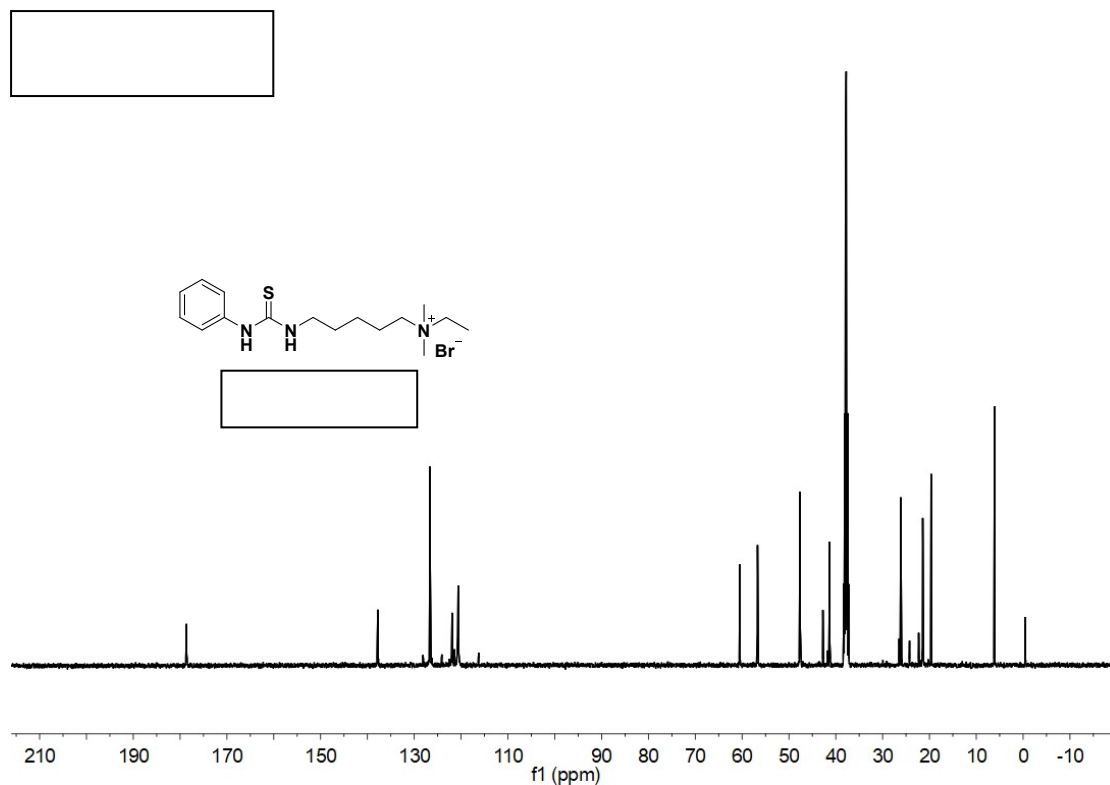**Figure S7** ¹H (500 M) and ¹³C (126 M) NMR spectra for the bifunctional catalyst **C1** in DMSO
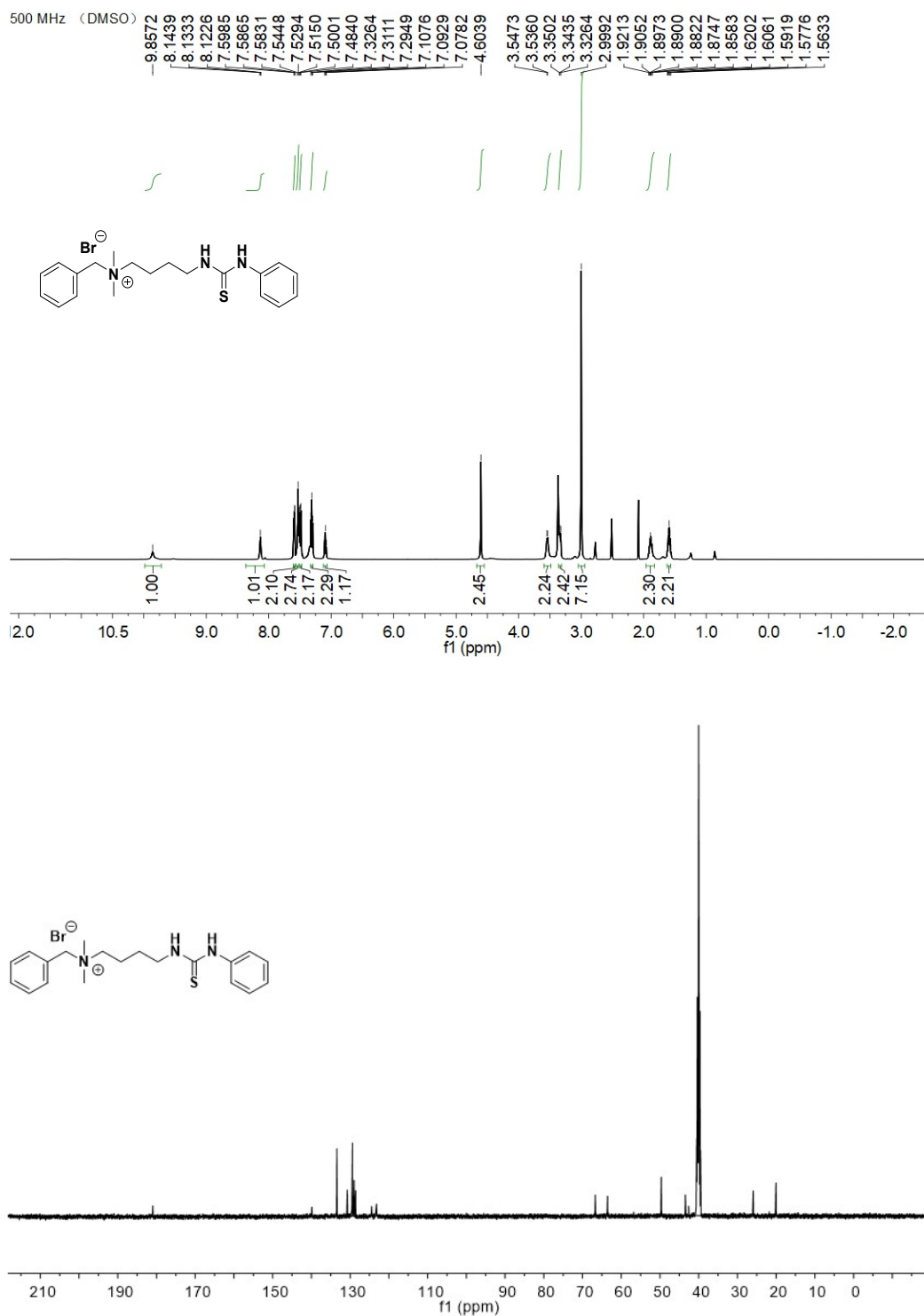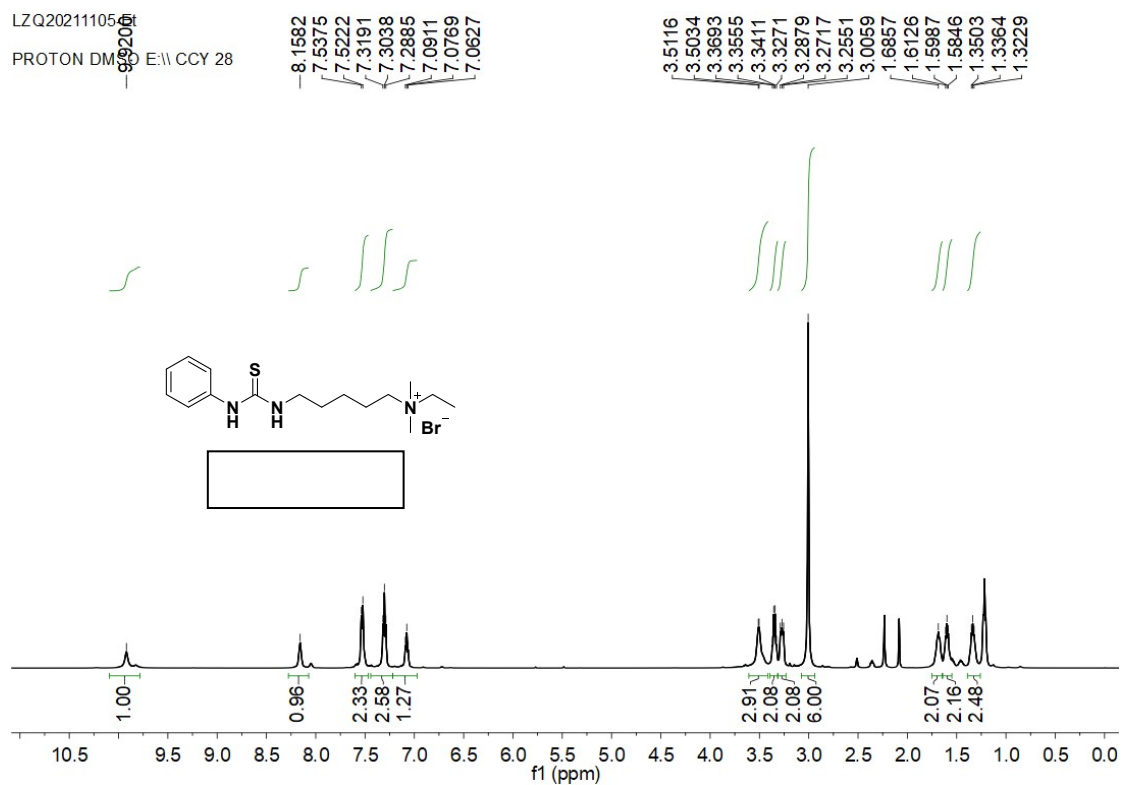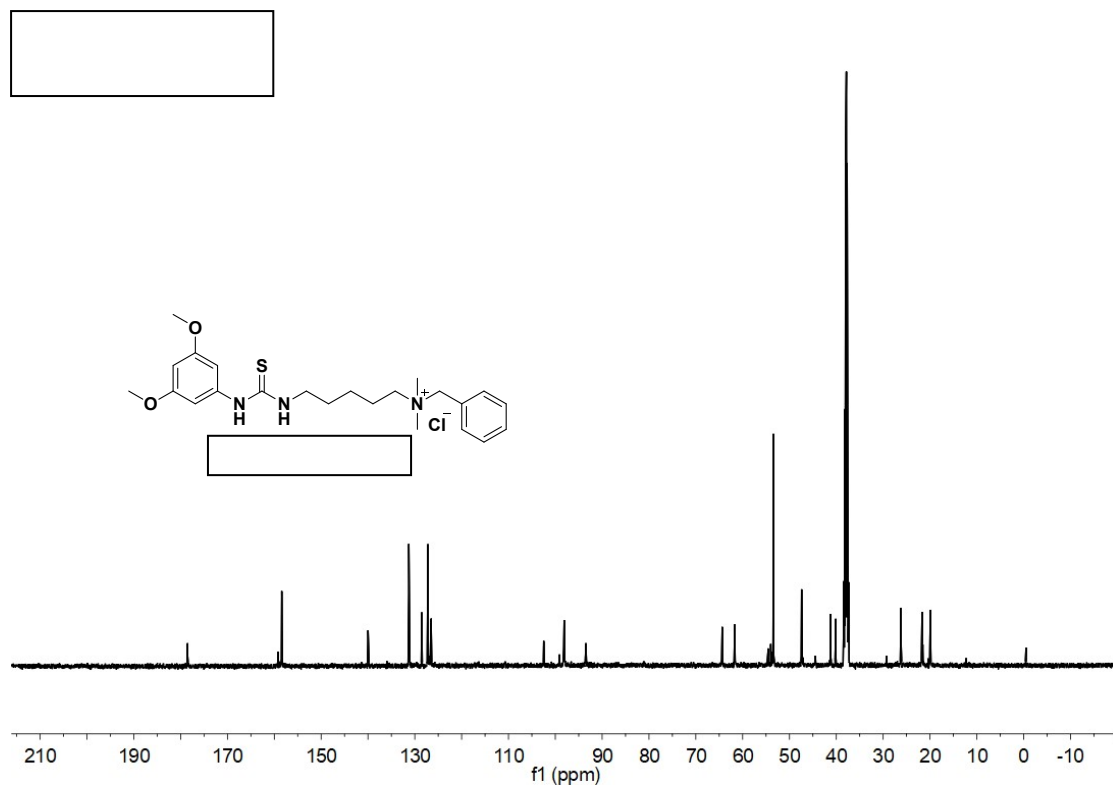
Figure S8 ^{1}H (500 M) and ^{13}C (126 M) NMR spectra for the bifunctional catalyst **C2** in DMSO
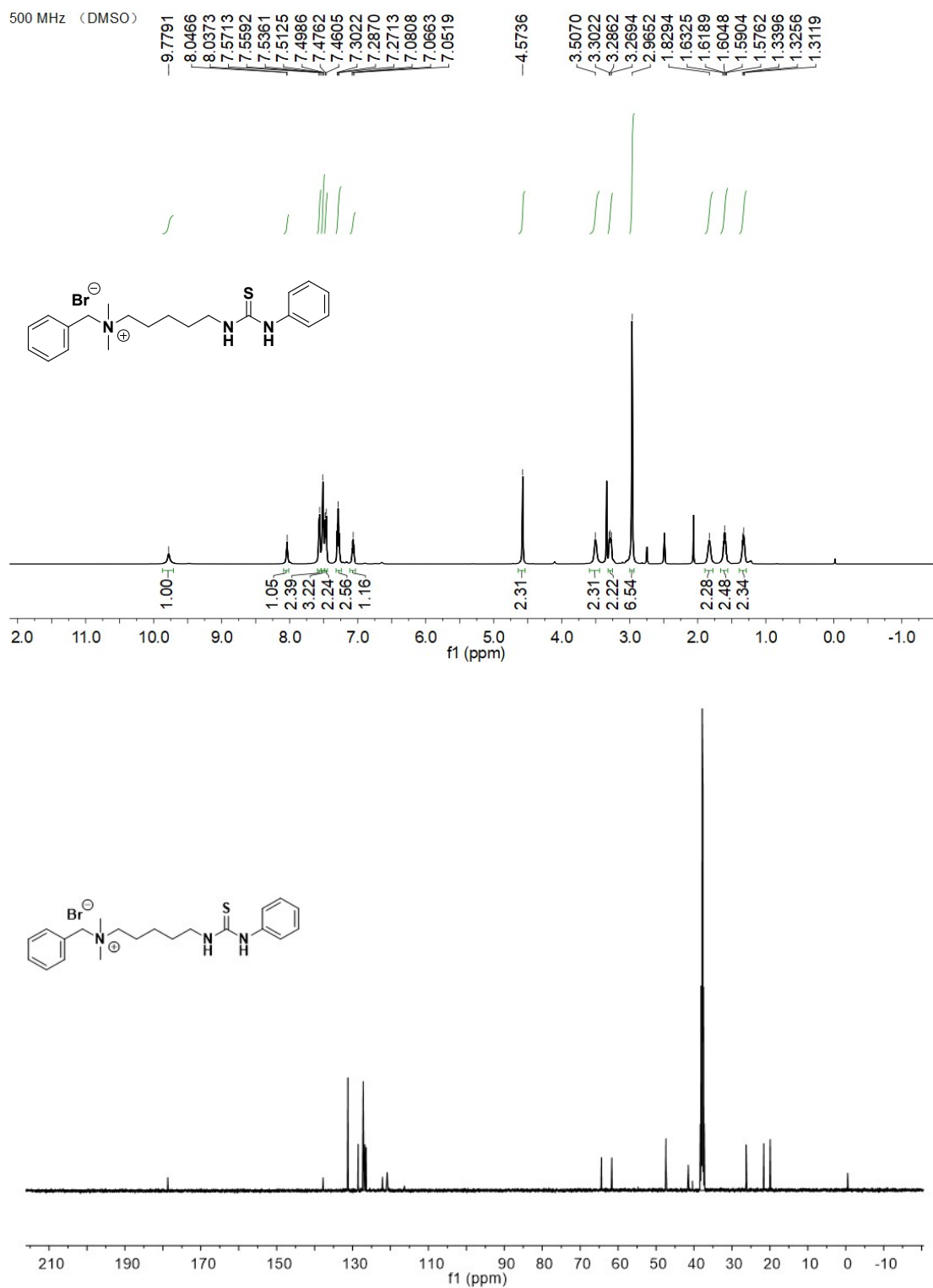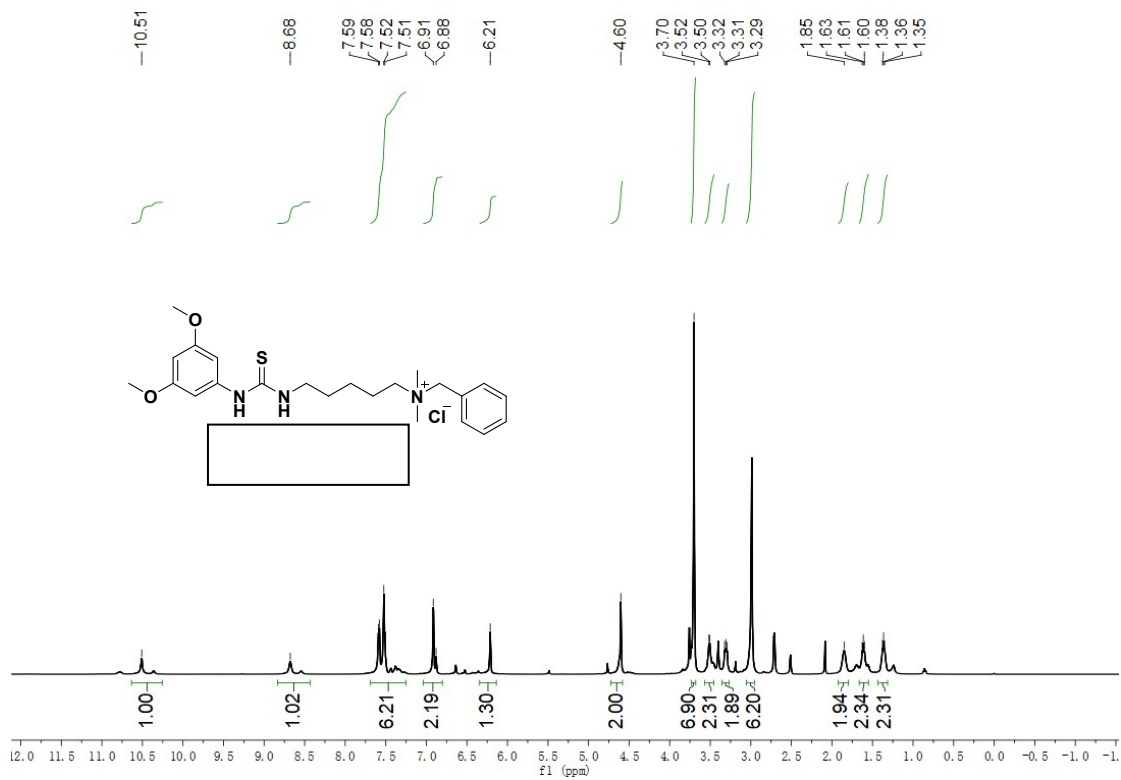
Figure S9 [1]H (500 M) and ^{13}C (126 M) NMR spectra for the bifunctional catalyst **C3** in DMSO

S17
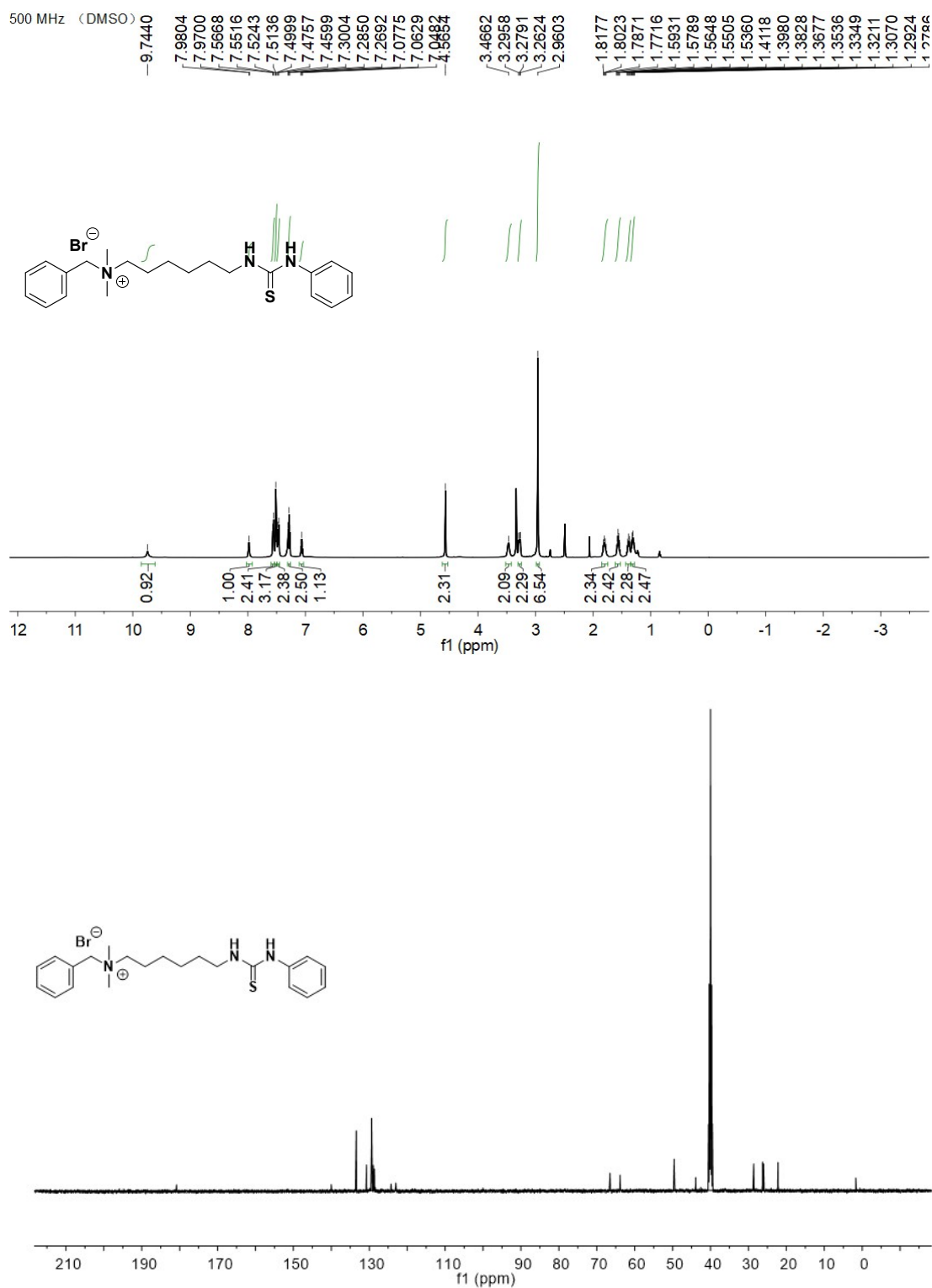
Figure S10 ^{1}H (500 M) and ^{13}C (126 M) NMR spectra for the bifunctional catalyst **C4** in DMSO
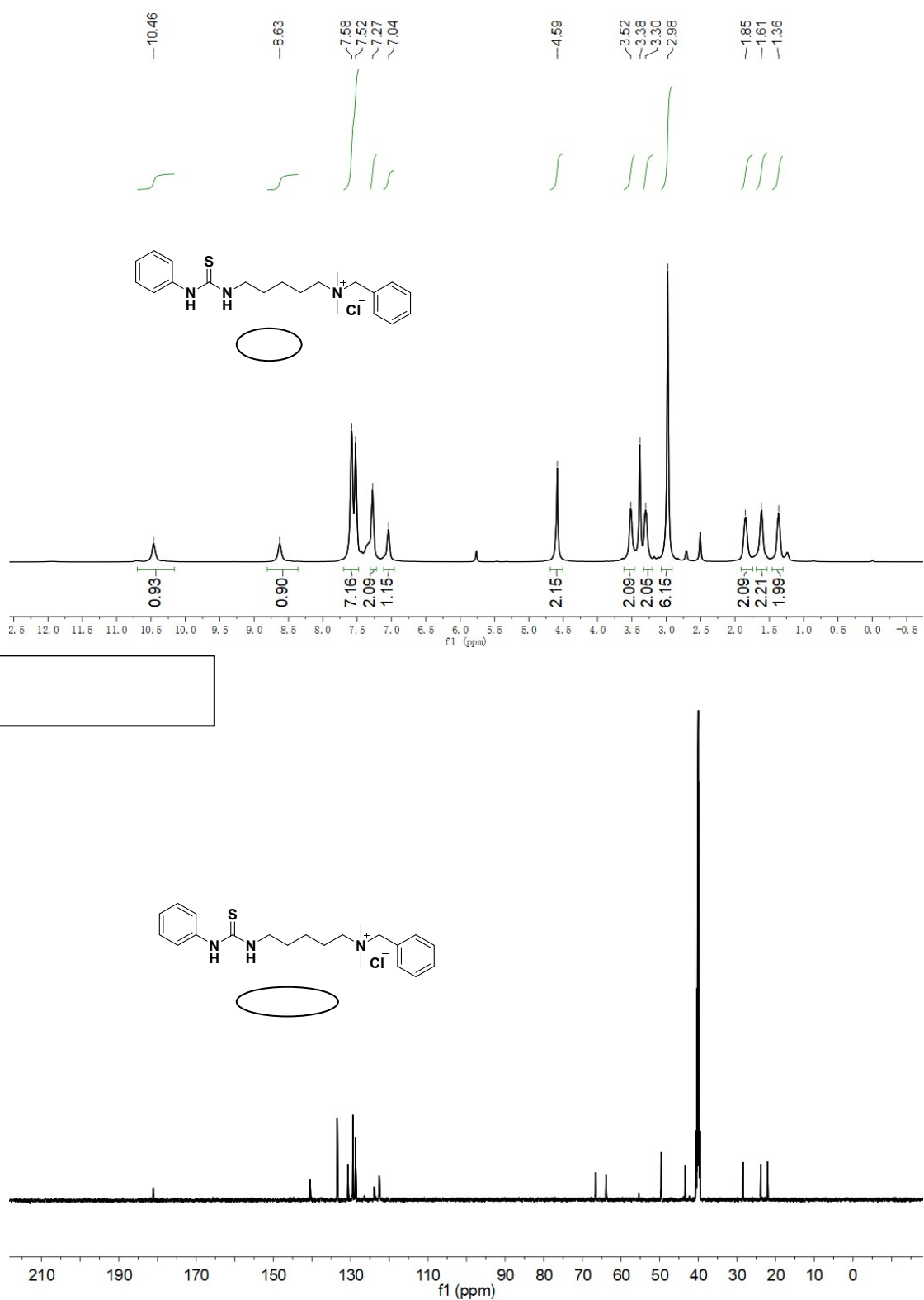
Figure S11 ^{1}H (500 M) and ^{13}C (126 M) NMR spectra for the bifunctional catalyst **C5** in DMSO
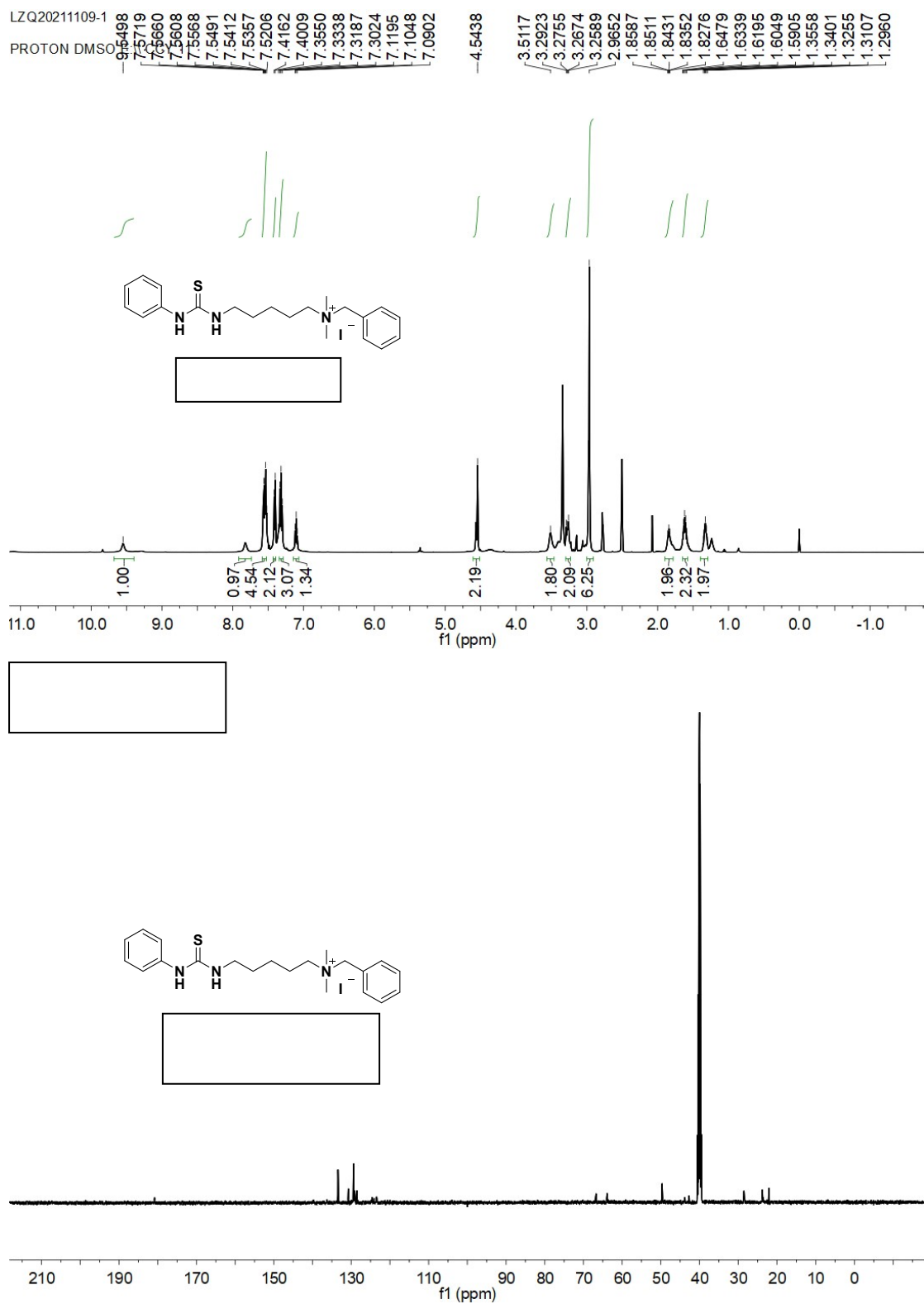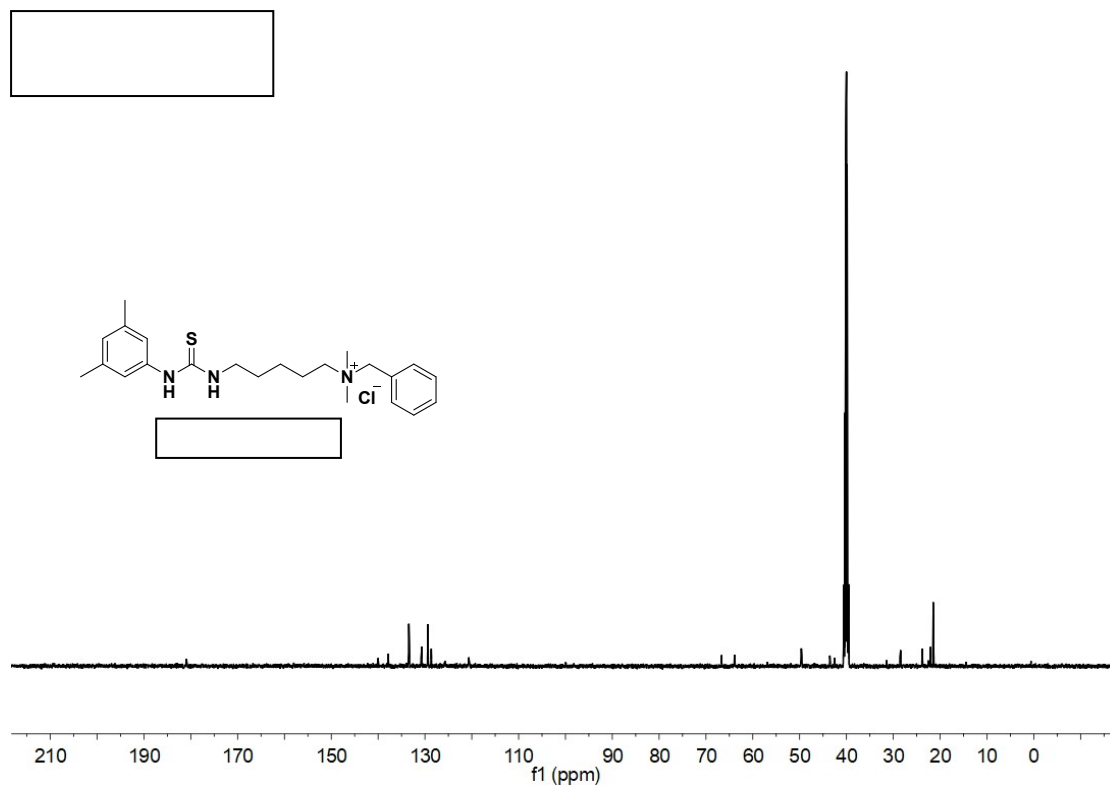
Figure S12 ^{1}H (500 M) and ^{13}C (126 M) NMR spectra for the bifunctional catalyst **C6** in DMSO

Figure S13 ^{1}H (500 M) and ^{13}C (126 M) NMR spectra for the bifunctional catalyst **C7** in DMSO
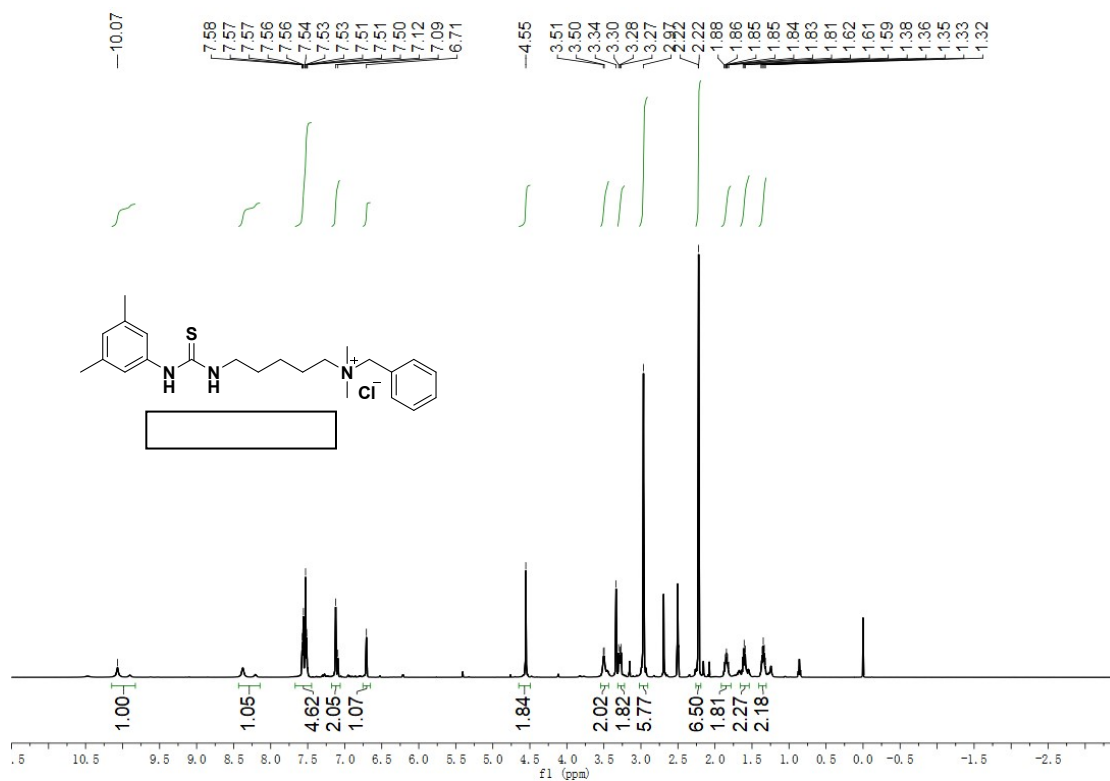
Figure S14 ^{1}H (500 M) and ^{13}C (126 M) NMR spectra for the bifunctional catalyst **C8** in DMSO

Figure S15 ^{1}H (500 M) and ^{13}C (126 M) NMR spectra for the bifunctional catalyst **C9** in DMSO
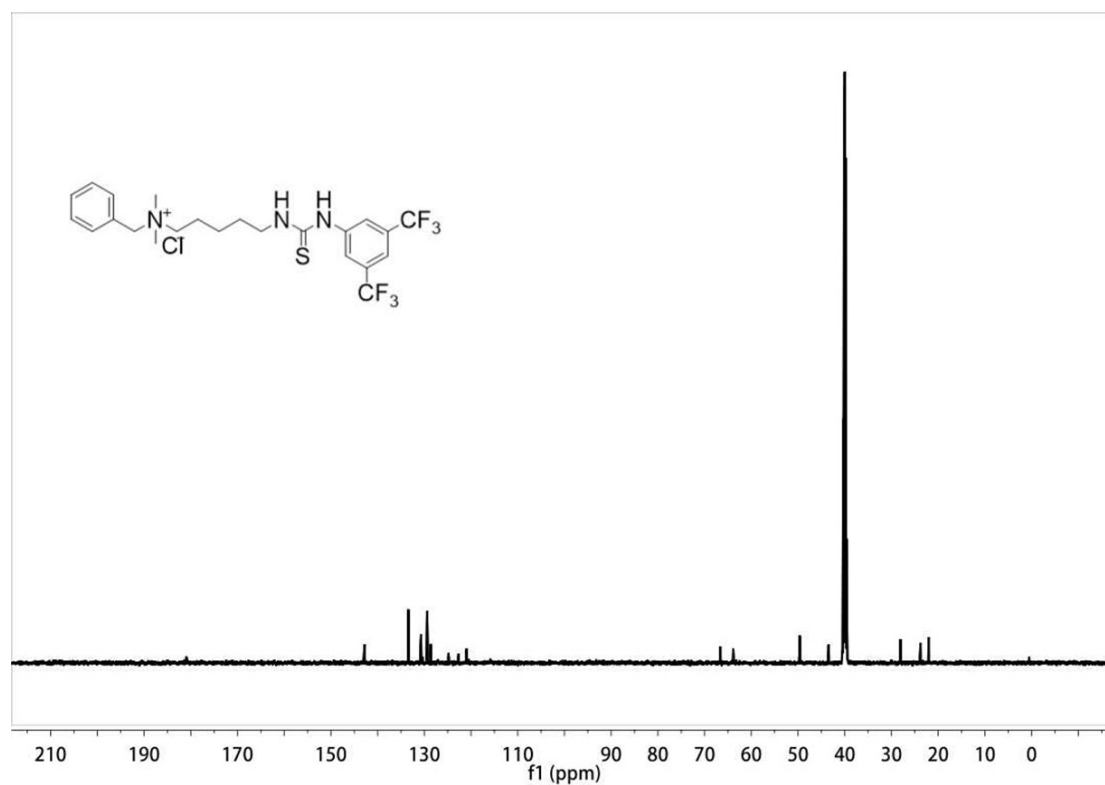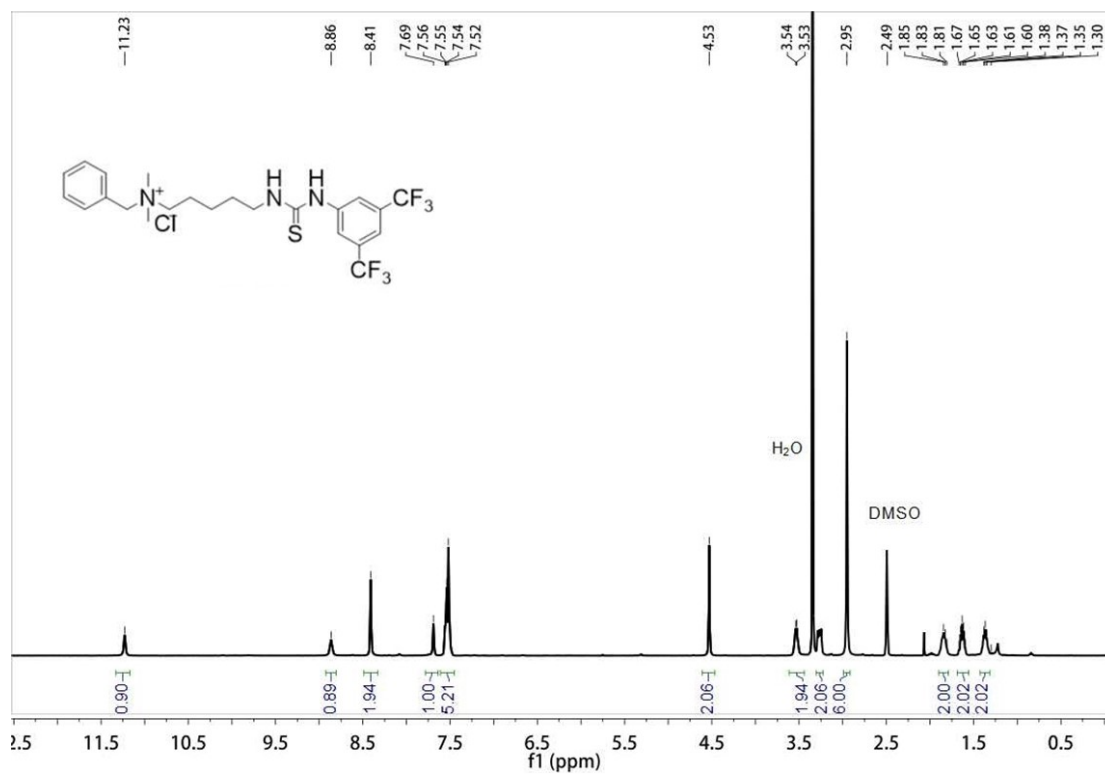
Figure S16 [1]H (500 M) and ^{13}C (126 M) NMR spectra for the bifunctional catalyst **C10** in DMSO

7.References

1.   (a) Z. Q. Li, Y. Y. Zhang, Y. J. Zheng, B. Li and G. P. Wu, *J. Org. Chem.*, 2022, **87**, 3145-3155;

     (b) K. Y. Wang, Z. Q. Li, M. N. Xu, B. Li, *Macromolecules*, 2023, **56**, 5599-5609.