Electronic Supplementary Material (ESI) for Polymer Chemistry.

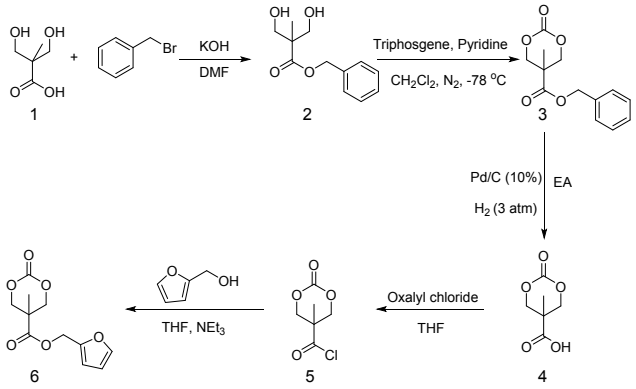
Squaramide and amine binary H-bond organocatalysis in polymerizations of cyclic carbonates, lactones, and lactide

Jingjing Liu, Jiaxi Xu, Zhenjiang Li, * Songquan Xu, Xin Wang, Haixin Wang, Tianfo Guo, Yu Gao, Lei Zhang and Kai Guo*

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, 30 Puzhu Road South, Nanjing 211816, China. Tel +86 25 5813 9926; Fax +86 25 5813 9935. E-mail: guok@njtech.edu.cn, zjli@njtech.edu.cn.

Content

Procedures for the Synthesis of functionality carbonates monomer



According to the references,[1] the followings are the synthesis methods of compound 2 : To a mixture of bis-MPA (compund 1, 19.16 g, 0.143 mol), potassium hydroxide (10.97 g, 0.166 mol), and DMF (115 mL) was added in a 250 mL flask and heated to 100 °C for 1 h. After the turbid solution turned out clarifying and homogenous, benzyl bromide (29.3 g, 0.172 mol) was added to the reaction system by constant funnel, and the reaction was continued at 100 °C for 16 h. The solution was cooled to room temperature and the solvent was removed under vacuum. Ethyl acetate (150 mL), n-hexanes (150 mL) and water (150 mL) were added to the residue. The organic layer was washed with water (100 mL), dried ($MgSO_4$), preserved overnight, filtrated and evaporated to give crude products which were recrystallized from toluene to give compound 2. ^{1}H NMR ($CDCl_3$) δ ppm 1.08 (s, 3H, -CH_3), 3.72 (d, 2H, -CH_2OH), 3.92 (d, 2H, -CH_2OH), 5.22 (s, 2H, -CH_2Ar), 7.36 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ ppm 17.14, 49.10, 66.642, 67.70, 127.93, 128.37, 128.71, 135.78, 175.69.

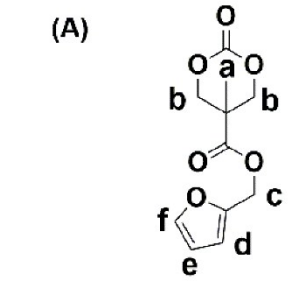
Synthesis of compound 3: compound 2 (22.4 g, 0.1 mol), pyridine (50 mL, 0.6 mol) and CH_2Cl_2 (300 mL) were added to the 500 mL flask which was chilled to - 78 °C with nitrogen blanketing. A solution of triphosgene (15.0 g, 0.05 mol) in CH_2Cl_2 was added dropwise to reaction system with stirred which was allowed to warm to room temperature for 2 h. Added saturated aqueous NH_4Cl (150 mL) when the reaction ended. The organic layer was washed with 1 M

aqueous HCl (3 x 200 mL), saturated aqueous $NaHCO_3$ (1 x 200 mL), dried ($MgSO_4$), filtered and evaporated to give compound 3. mp 72-74 °C. 1H NMR ($CDCl_3$) δ ppm1.30 (s, 3H, -CH_3), 4.18 (d, 2H, -CH_2O-), 4.67 (d, 2H, -CH_2O-), 5.20 (s, 2H, -CH_2Ar), and 7.33 (m, 5H, Ar). 13C NMR ($CDCl_3$) δ ppm 17.49, 40.27, 67.88, 72.98, 128.21, 128.79, 134.87, 147.53, 171.03.

Synthesis of compound 4: A mixture of crude compound 3 (24.3 g, 0.097 mol), ethyl acetate (250 mL), Pd/C (10% w/w, 1.6 g) was reacted under H_2 (3 atm) for 24 h. THF (250 mL) was added when the reaction ended. The mixture was filtered through celite and evaporated to give compound 4. ^{1}H NMR (DMSO-d_6) δ ppm 1.16 (s, 3H, CH_3),4.29 (d, 2H, OCH_2),4.52 (d, 2H, OCH_2),13.36 (br, 1H, COOH). ^{13}C NMR (DMSO-d_6) δ ppm 16.49(CH_3), 39.42 (CCH_3), 72.78 (OCH_2), 147.45 (OCH_2OO), 173.43 (COOH).

Synthesis of compound 6: Add THF (1.6 g, 0.01 mol) to compound 4 with 3 drops of DMF as catalyst. A solution of oxalyl chloride (1.3 g, 0.01 mol) dissolved in THF (20 mL) was added dropwise and stirred for 1 h under a flow of nitrogen. The solution was evaporated to give compound 5 (^{1}H NMR (DMSO-d_6) δ: 1.12 (s, 3H, OCH_3), 4.29 (d, 2H, OCH_2), 4.52 (d, 2H, OCH_2)) after reaction. Compound 6 was dissolved in THF (25 mL) and a solution of furfuryl-alcohol (0.98 g, 0.01 mol) and triethylamine (1.1 g, 0.011 mmol) in THF added to reaction system dropwise, causing a white precipitate to form, and stirring was continued for 3 h before it was filtered and evaporated to remove white solid. Purification by column chromatography (silica gel column, ethyl acetate/n-hexanes = 1:1) provided the white solid compound 6. ^{1}H NMR ($CDCl_3$) δ: 1.32 (s, 3H, CH_3), 4.17-4.20 (d, 2H, OCH_2), 4.67-4.70 (d, 2H, OCH_2), 5.17(s, 2H, $COOCH_2$), 6.36-6.44 (d, 2H, CH), 7.43 (d, H, OCH); ^{13}C NMR ($CDCl_3$) δ: 170.88, 148.35, 147.53, 143.72, 111.38, 110.74, 72.93, 59.55, 40.32, 17.50.

(A)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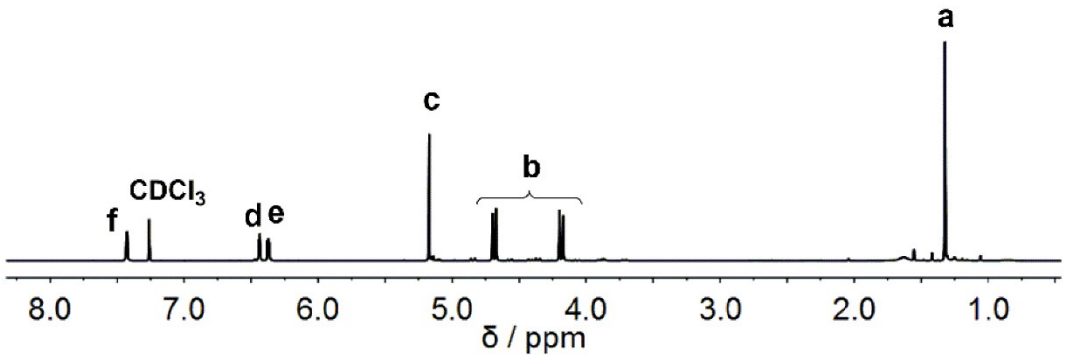
O a O
b b
O O
O c
f d
e


a
c
b
CDCl3
f
d e
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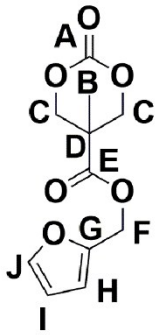
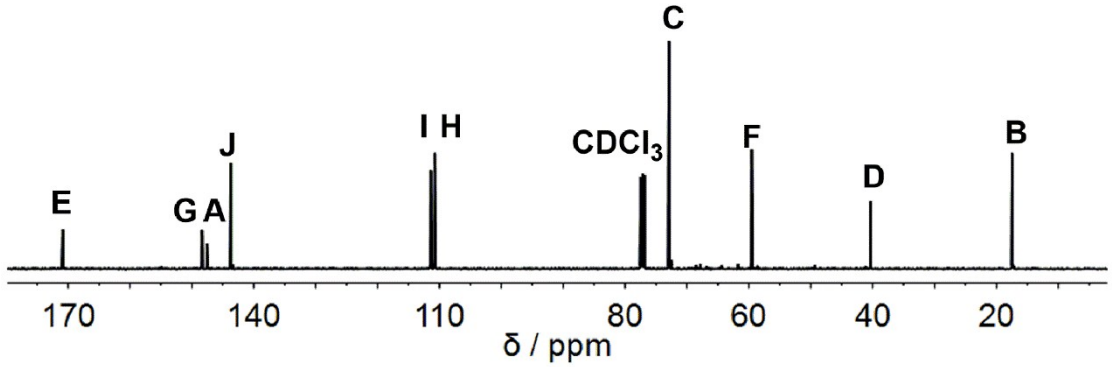
4.0
3.0
2.0
1.0
δ / ppm

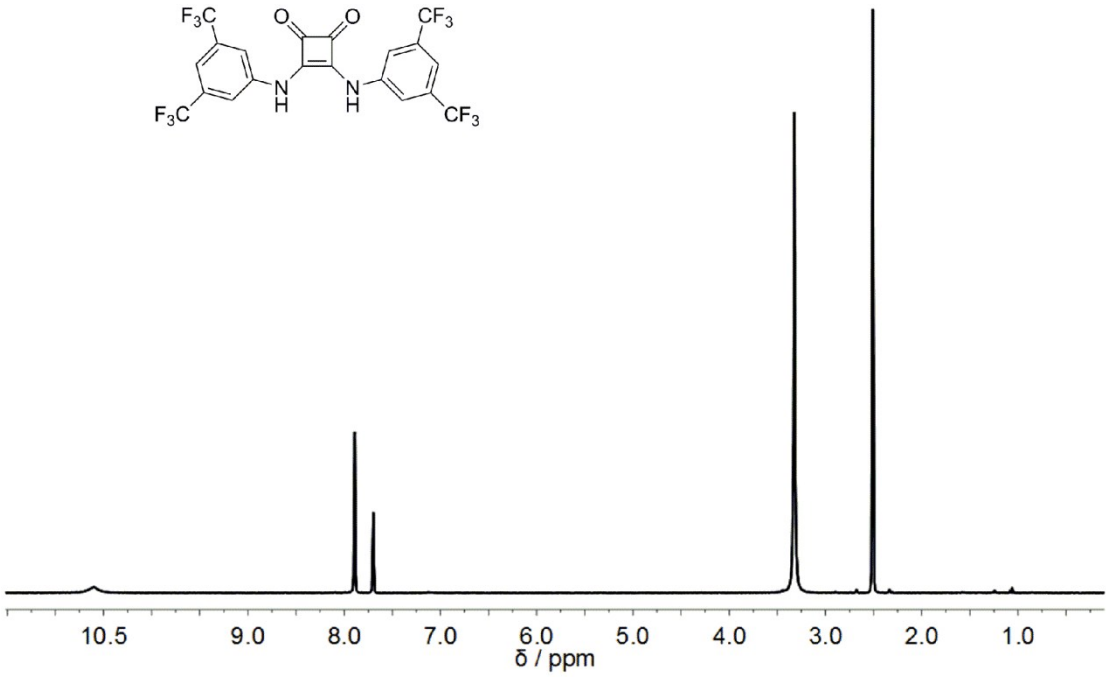
(B)


A O
O B O
C C
D E
O O
O G F
J H
I

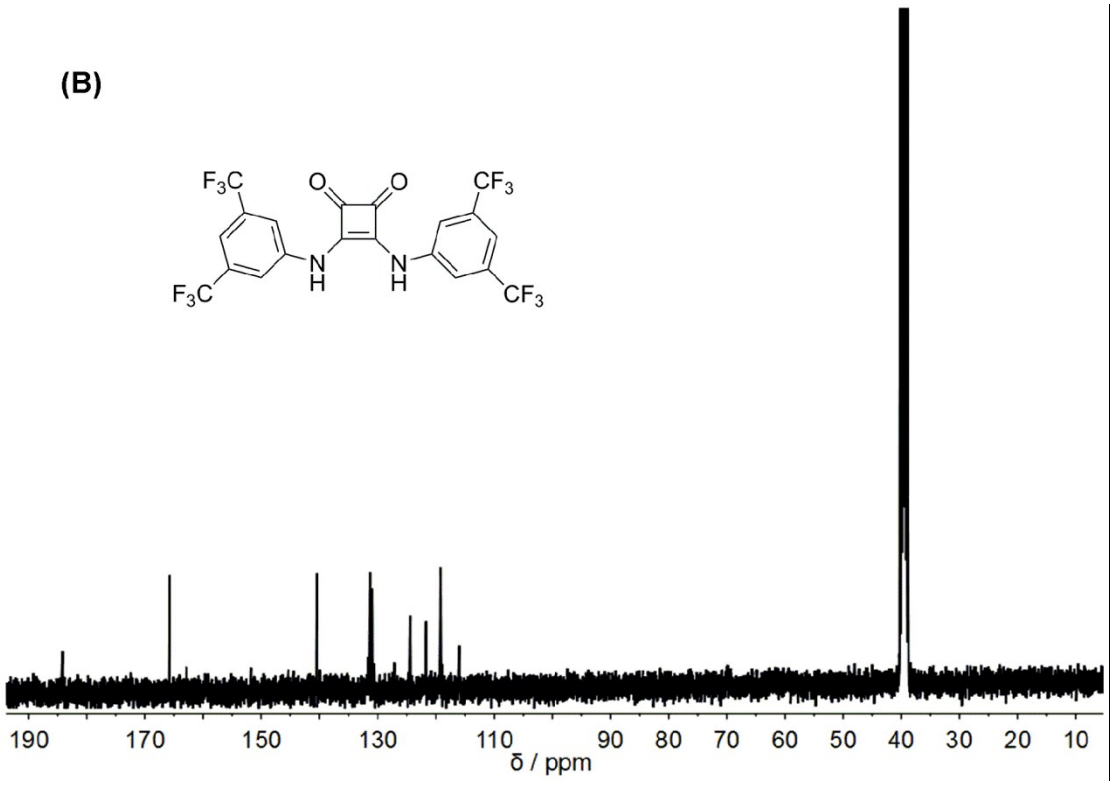

C
I H
J
CDCl3
F
B
D
E
G A
170
140
110
80
60
40
20
δ / ppm

^{1}H and ^{13}C NMR of squaramide catalysts

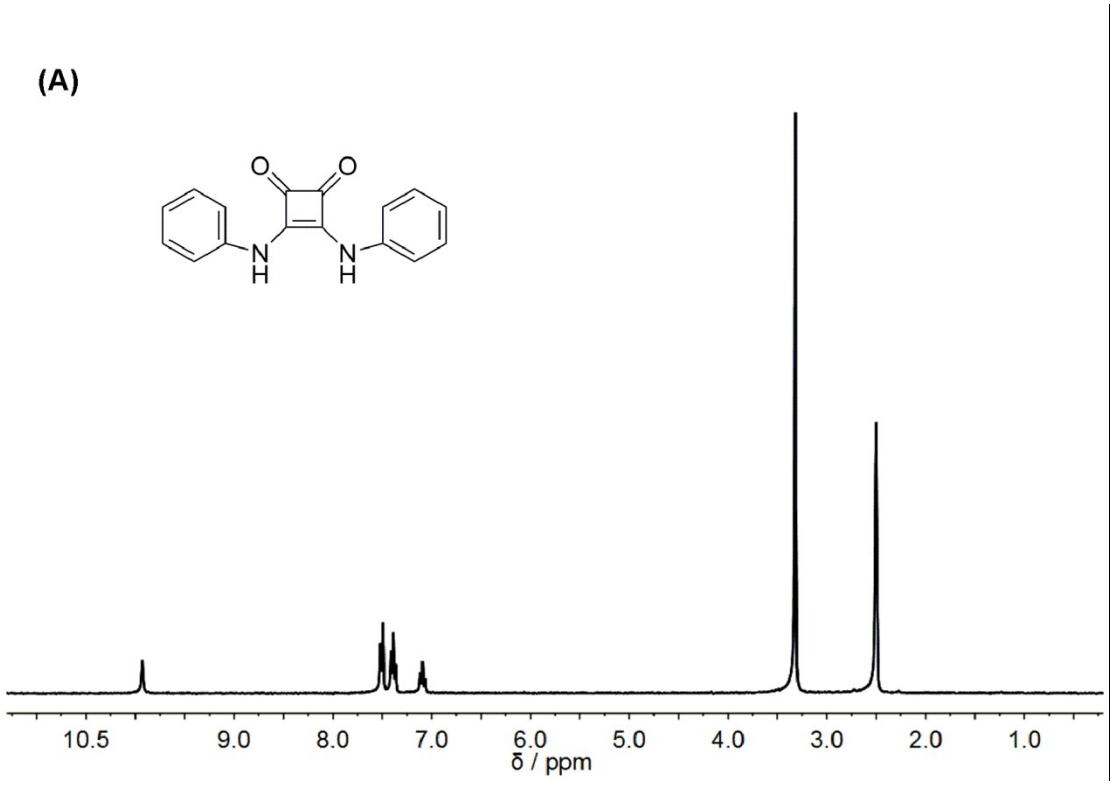
(A)



(B)



(A)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H
N
H
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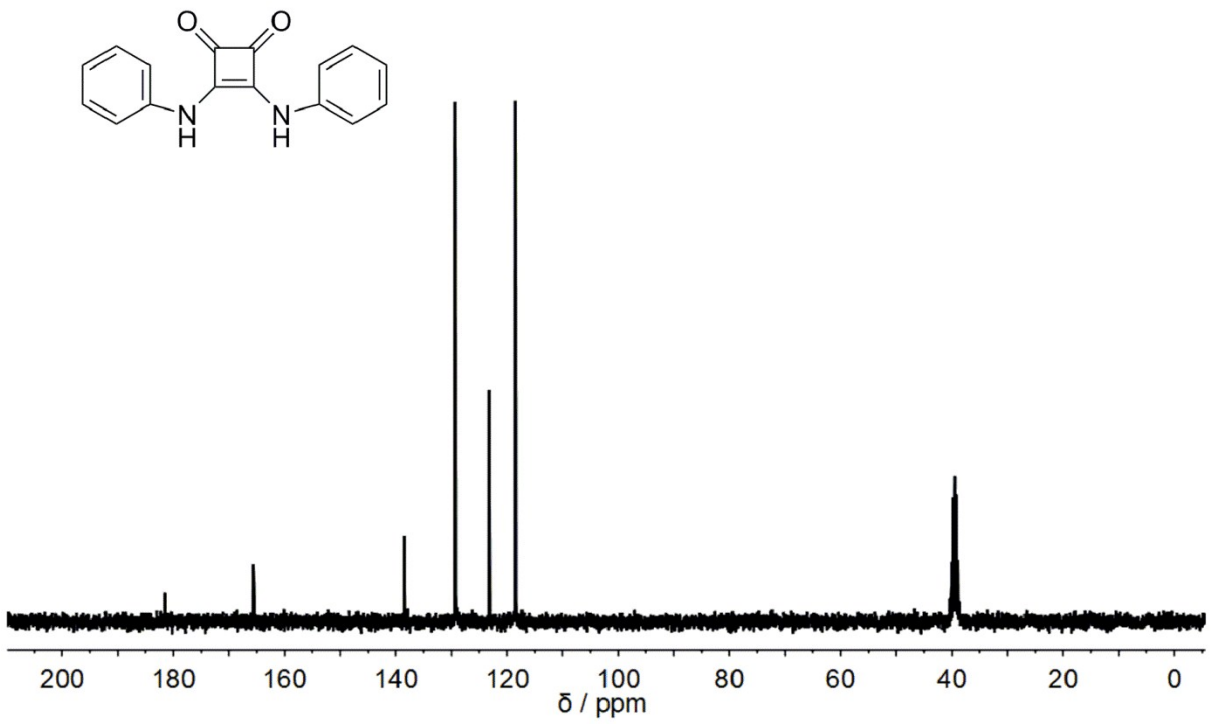
3.0
2.0
1.0
δ / ppm

(B)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N
H
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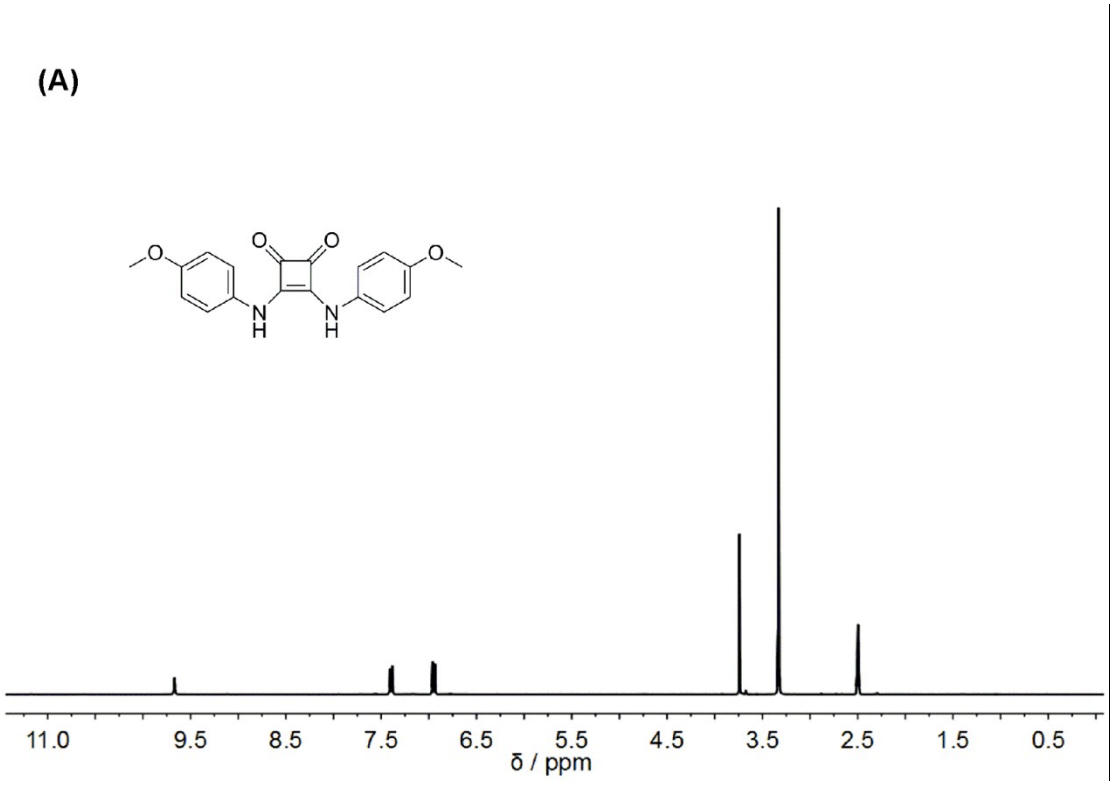
60
40
20
0
δ / ppm

(A)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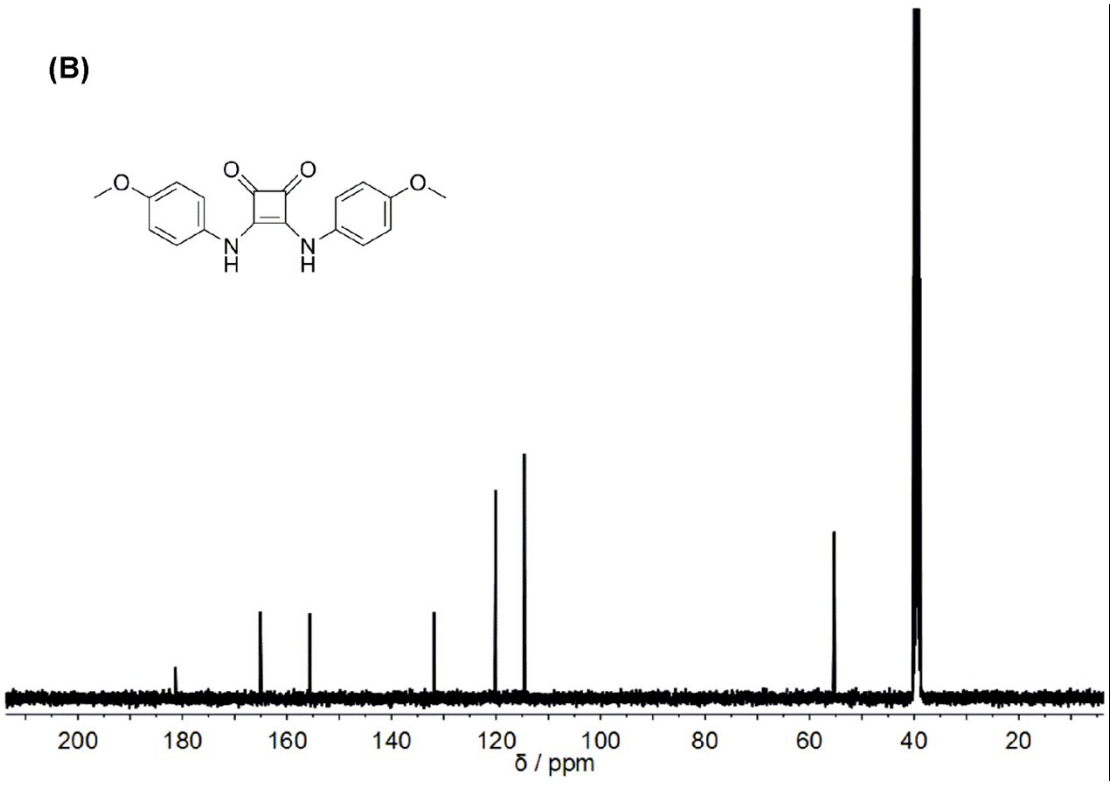
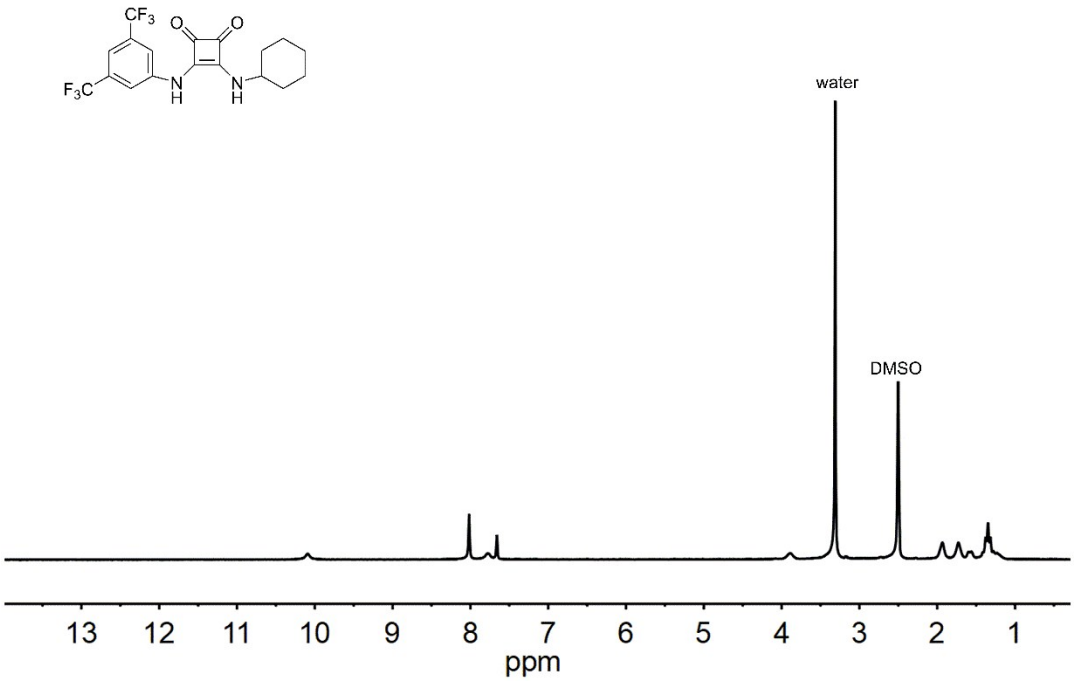
5.5
4.5
3.5
2.5
1.5
0.5
δ / ppm

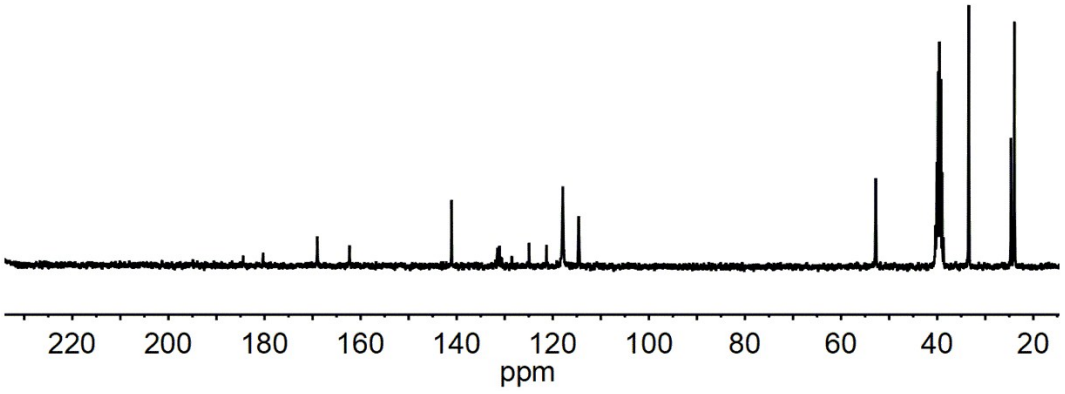
(B)


200
180
160
140
120
100
80
60
40
20
δ / ppm

(A)


water
DMSO
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

(B)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160
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120
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80
60
40
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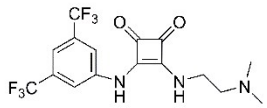
ppm

(A)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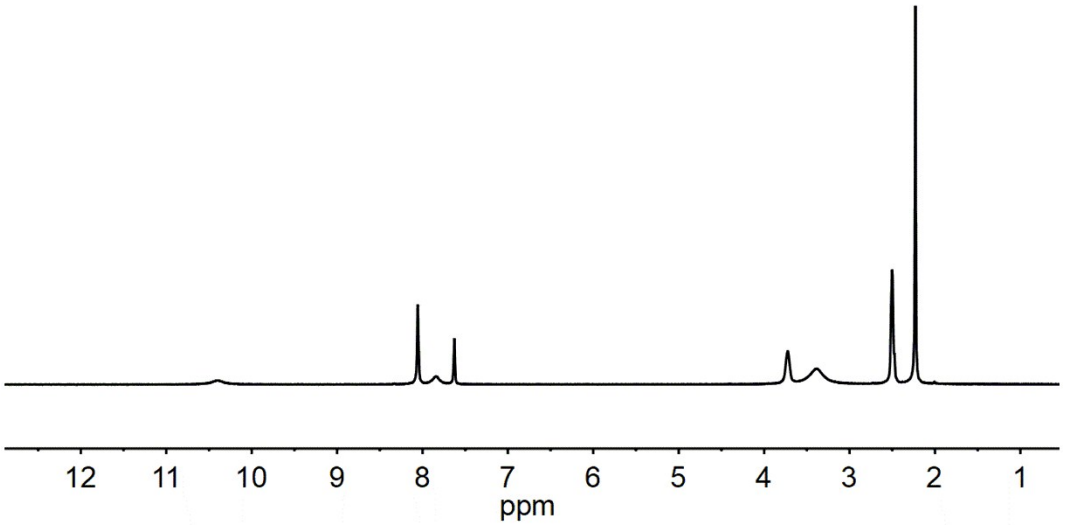
O
F3C
N
H
N
H
N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8
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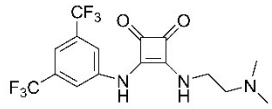
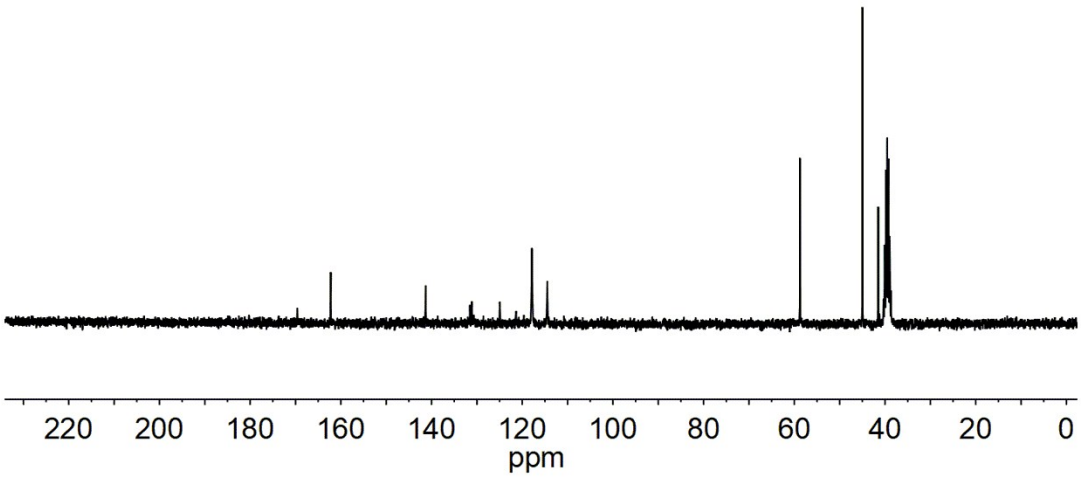
6
5
4
3
2
1
ppm

(B)


CF3
O
O
F3C
N
H
N
H
N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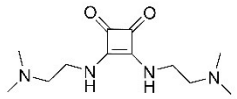
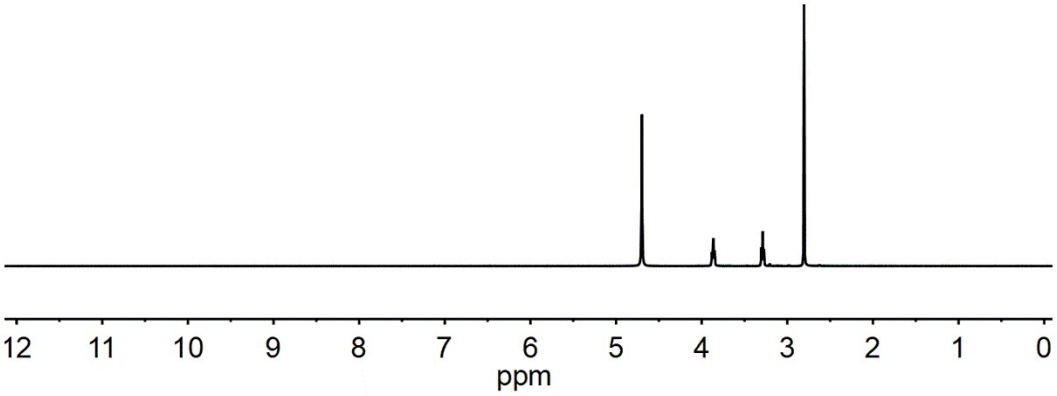
ppm

(A)



D_2O
^1H NMR



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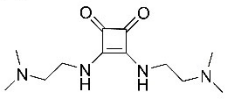
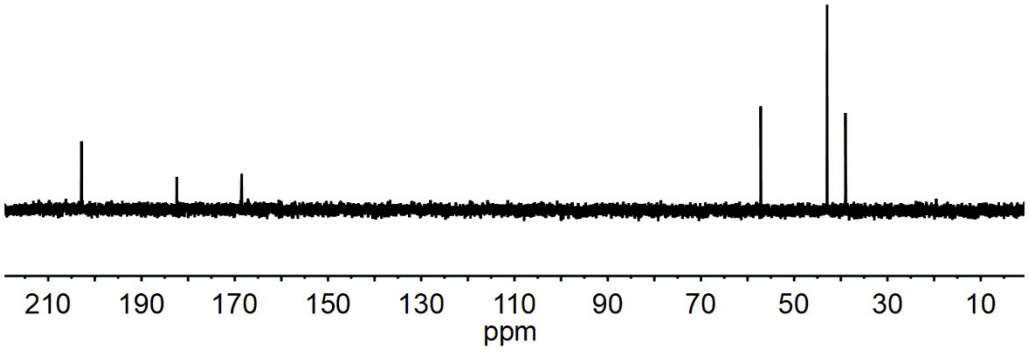


D_2O
^{13}C NMR



Syntheses of *α, ω*-Dihydroxy Telechelic, and End-Functionalized PTMCs

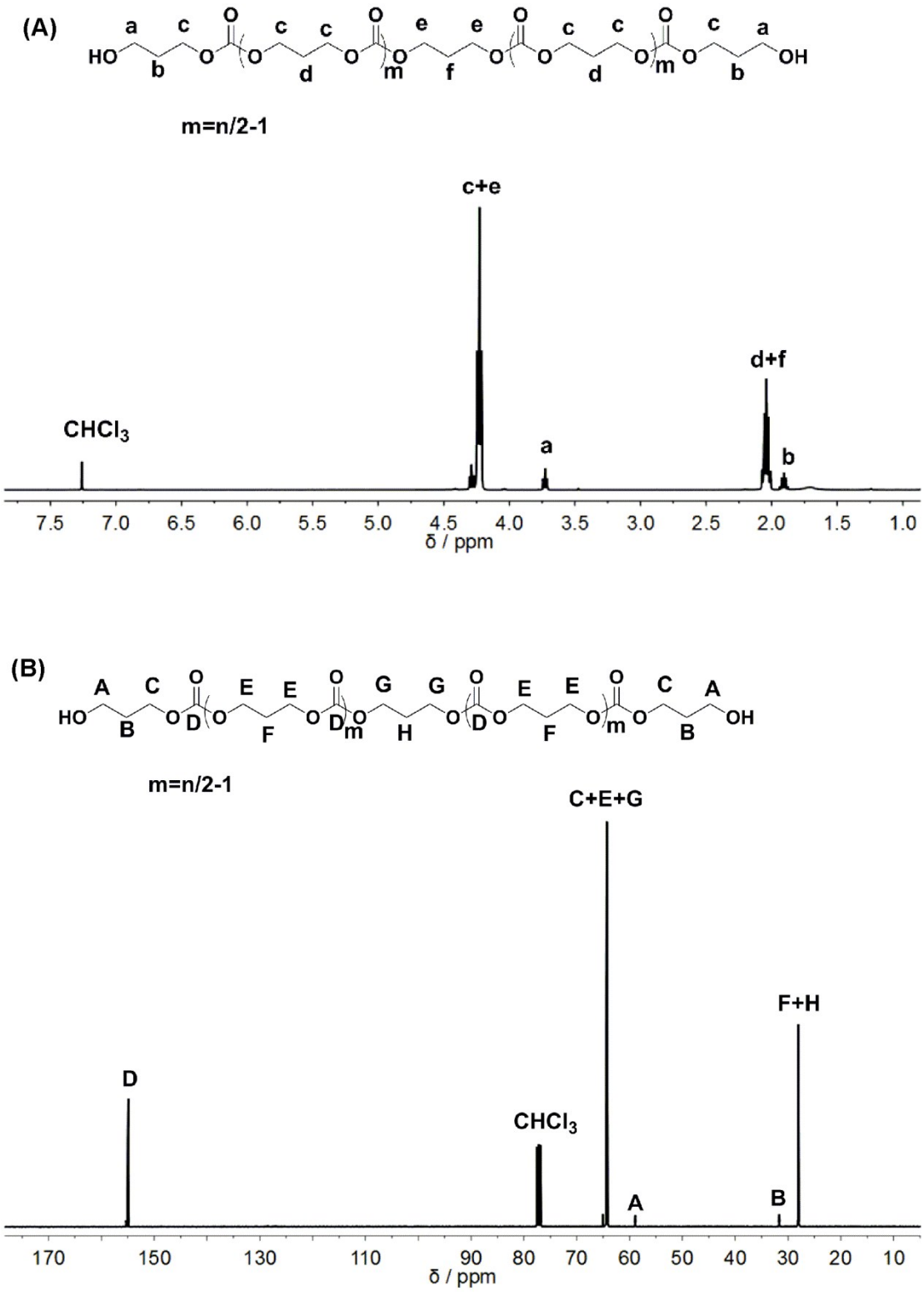


Figure S1 (A) ^{1}H NMR and (B) ^{13}C NMR spectrum of *α, ω*-Dihydroxy Telechelic PTMC initiated from 1, 3-propanediol in $CDCl_3$.

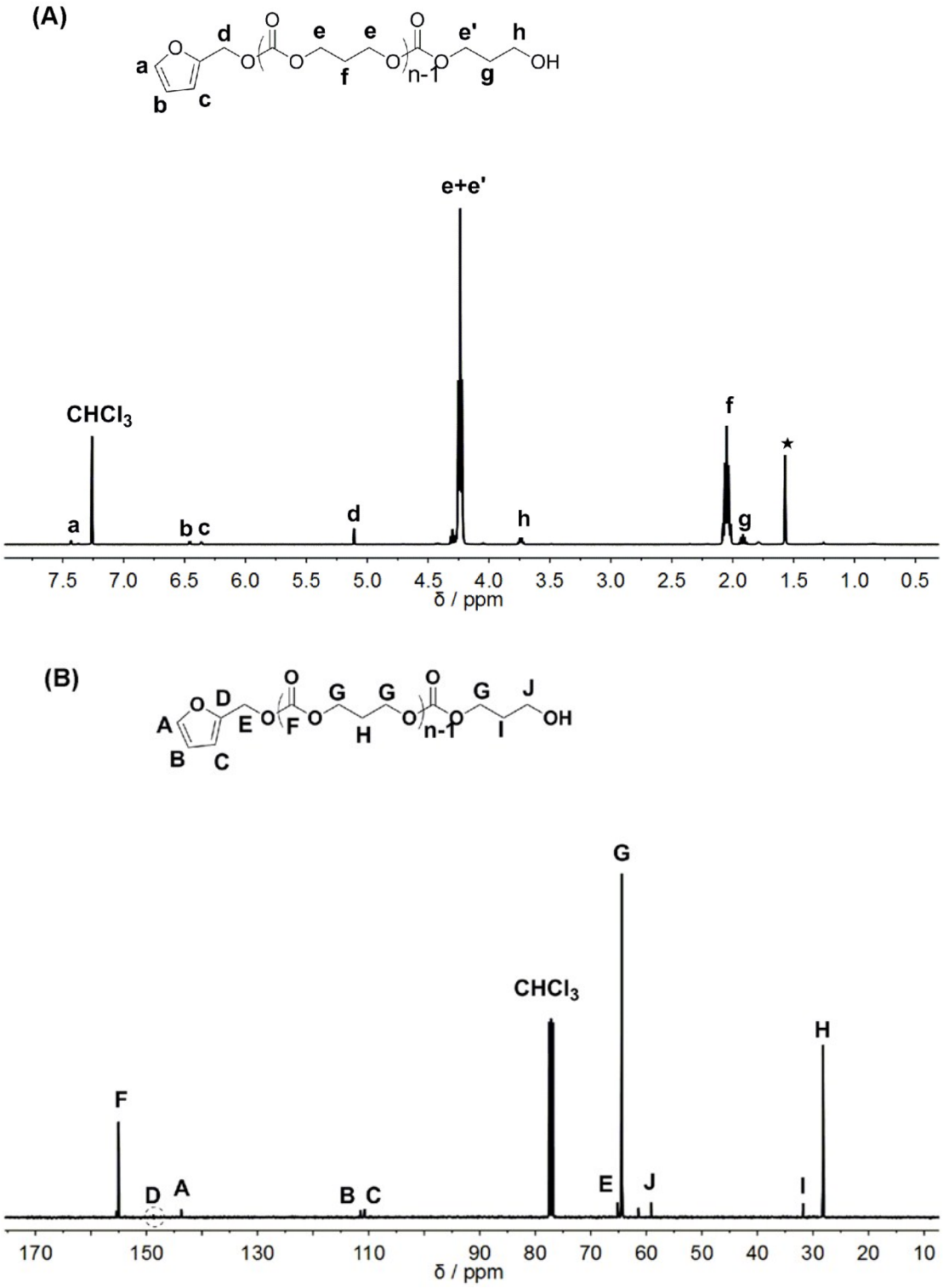


Figure S2 (A) ^{1}H NMR and (B) ^{13}C NMR spectrum of End-functionalized PTMC initiated from Furfuryl alcohol in $CDCl_3$.

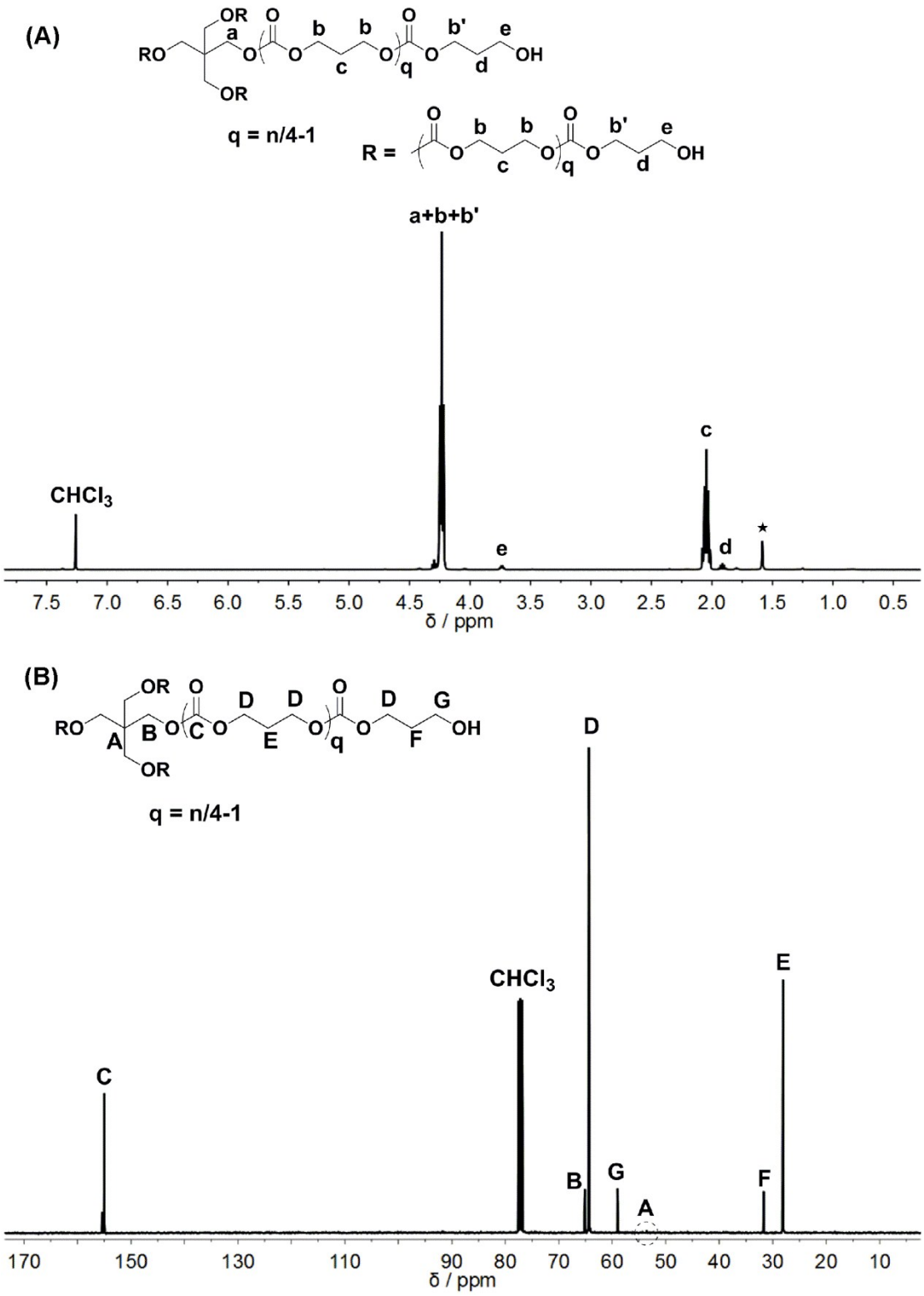


Figure S3 (A) ^{1}H NMR and (B) ^{13}C NMR spectrum of PTMC initiated from Pentaerythritol in $CDCl_3$.

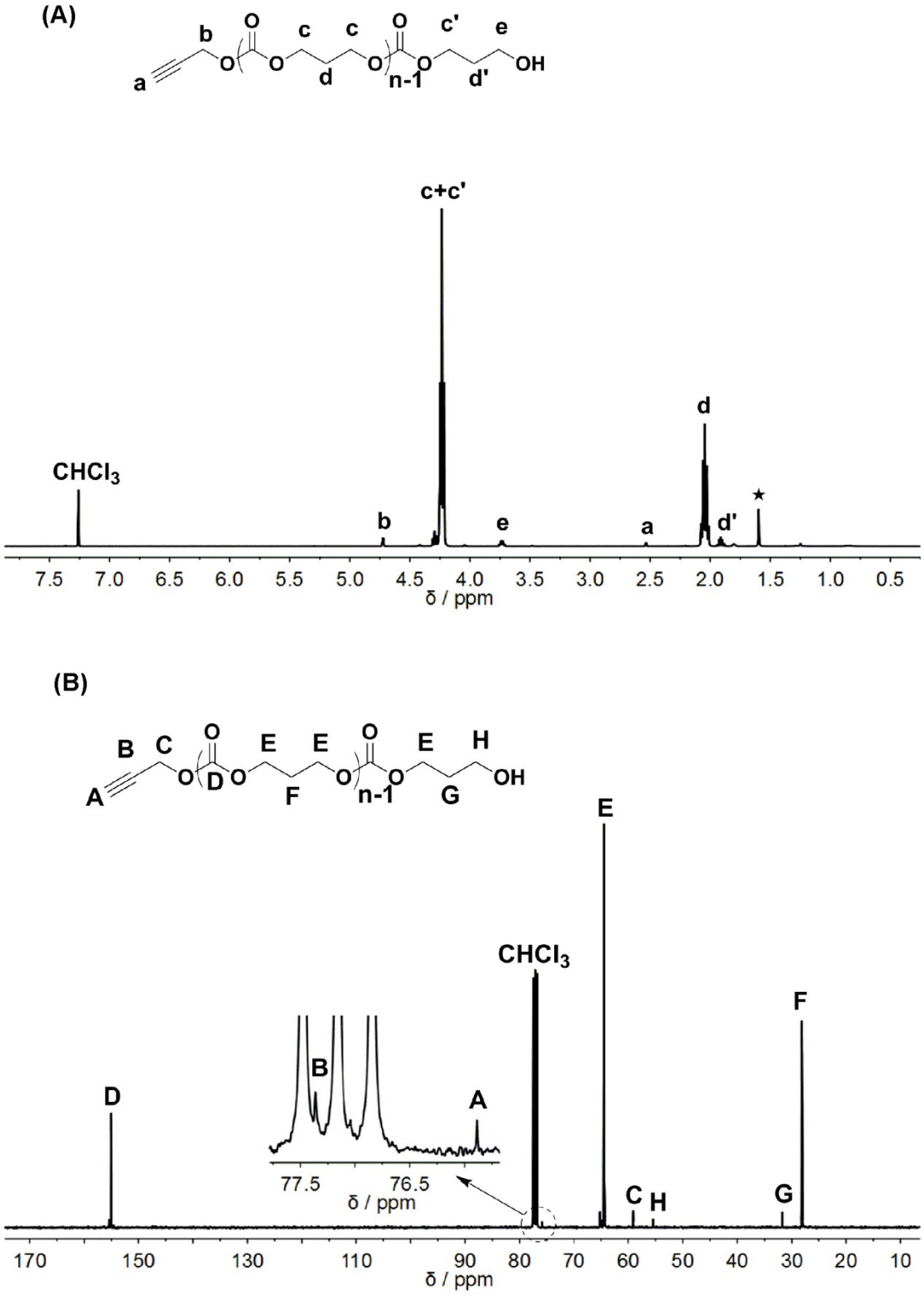


Figure S4 (A) ^{1}H NMR and (B) ^{13}C NMR spectrum of End-functionalized PTMC initiated from Propargyl alcohol in $CDCl_3$.

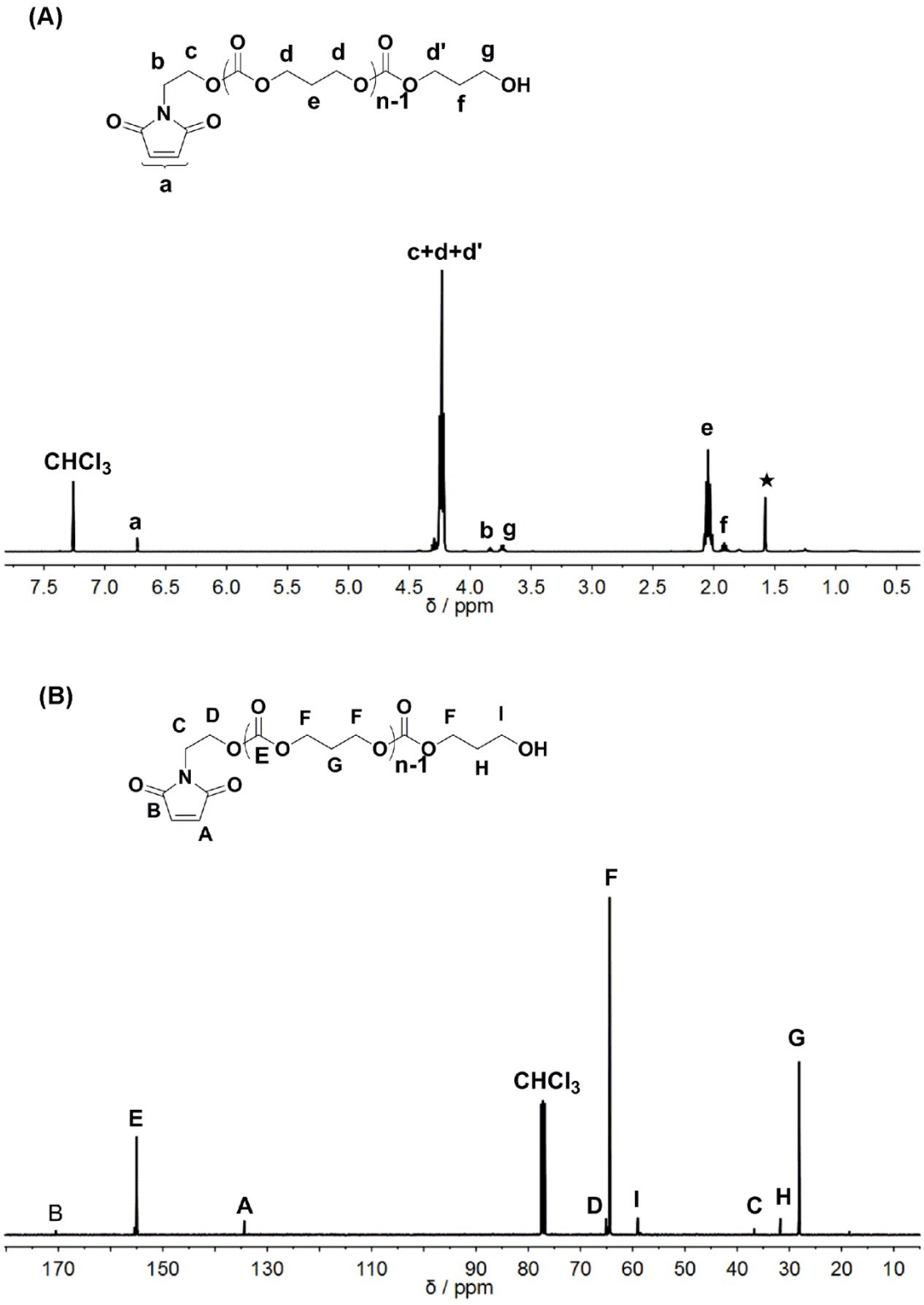


Figure S5 (A) ^{1}H NMR and (B) ^{13}C NMR spectrum of End-functionalized PTMC initiated from *N*-(2-hydroxyethyl)maleimide in $CDCl_3$.

Diblock Copolymerization of TMC and LA

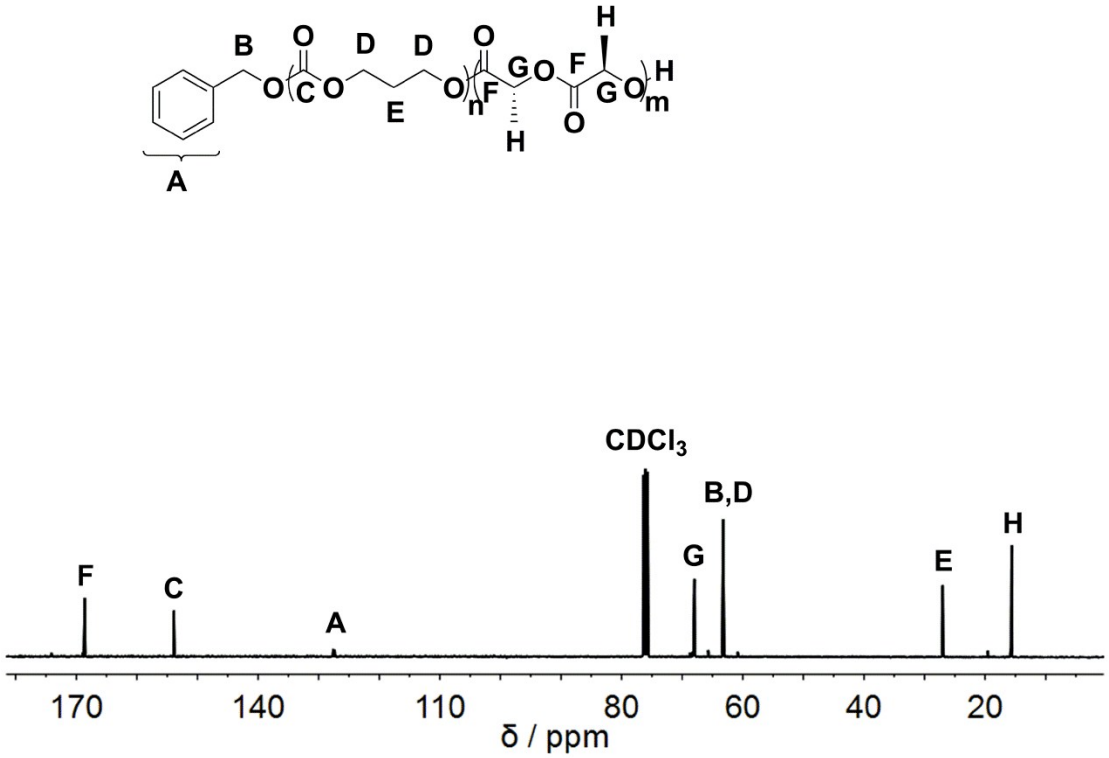


Figure S6 ^{13}C NMR spectrum of PTMC-*b*-PLA initiated from BnOH in $CDCl_3$.

^{1}H and ^{13}C NMR of block-polymers with TMC and VL

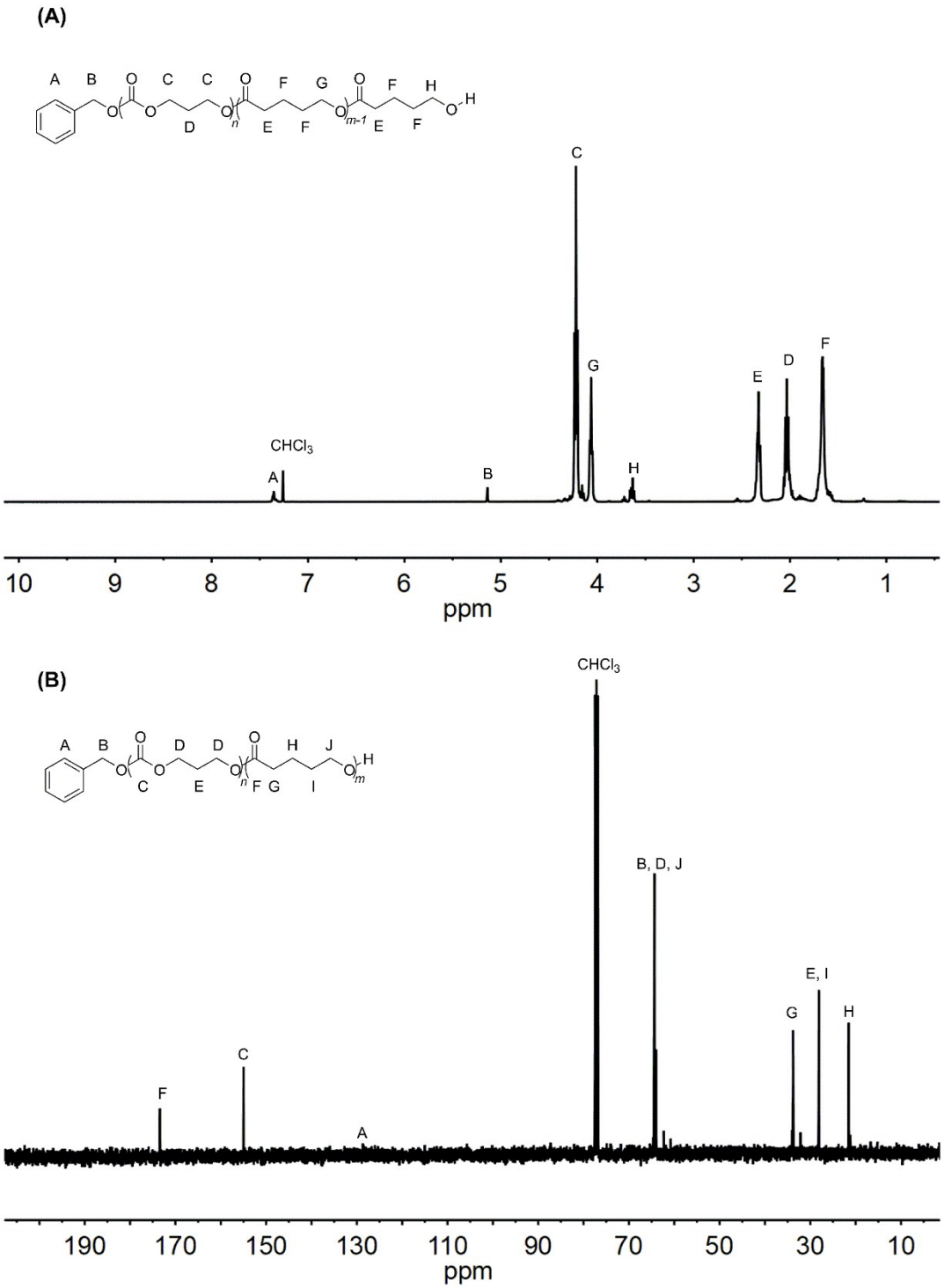


Figure S7 (A) ^{1}H NMR and (B) ^{13}C NMR spectrum of poly(trimethylene carbonate) (PTMC)-block-poly(δ-valerolactone) (PVL).

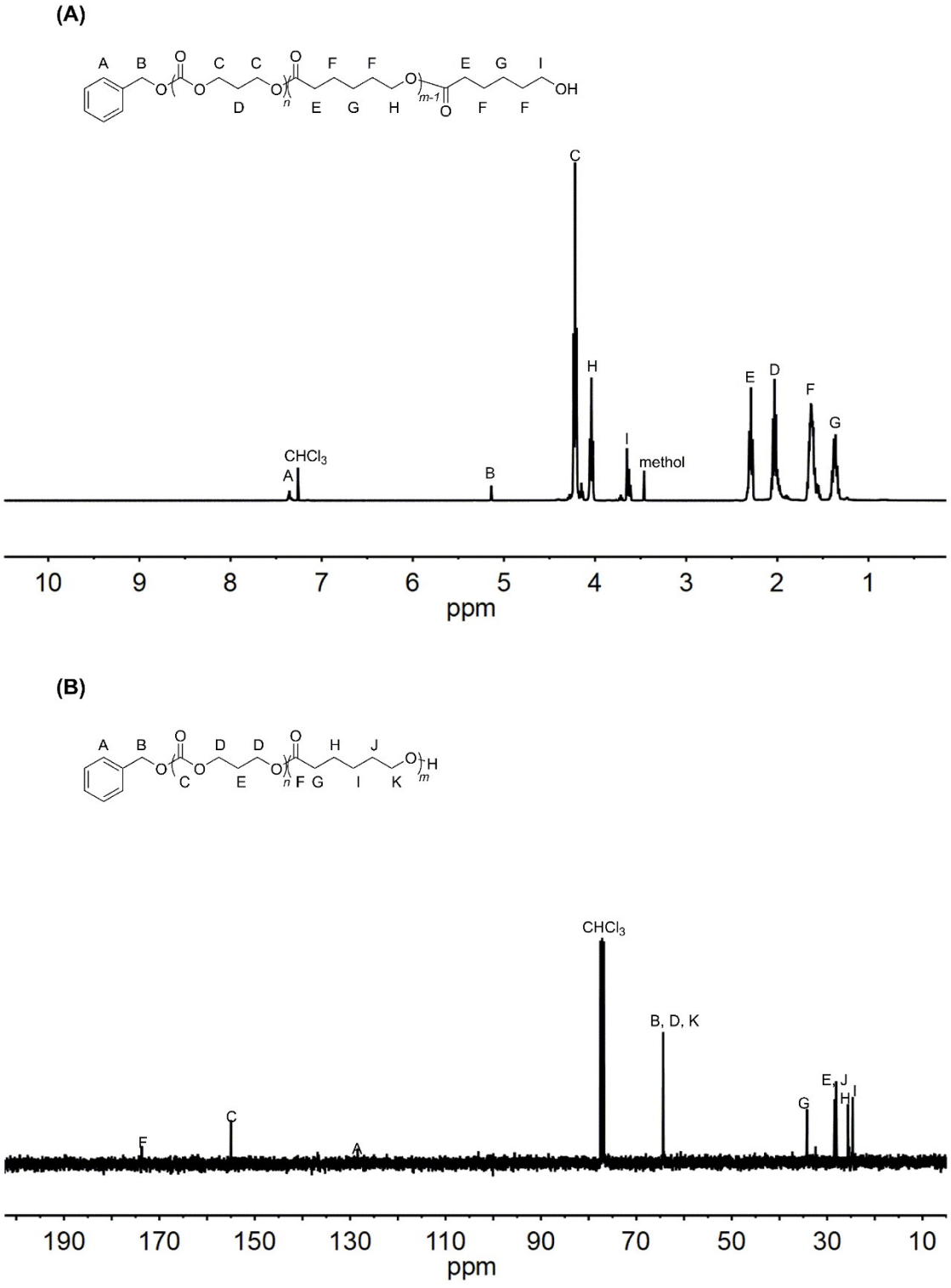


Figure S8 (A) ^{1}H NMR and (B) ^{13}C NMR spectrum of poly(trimethylene carbonate) (PTMC)-block-poly(ε-caprolactone) (PCL).

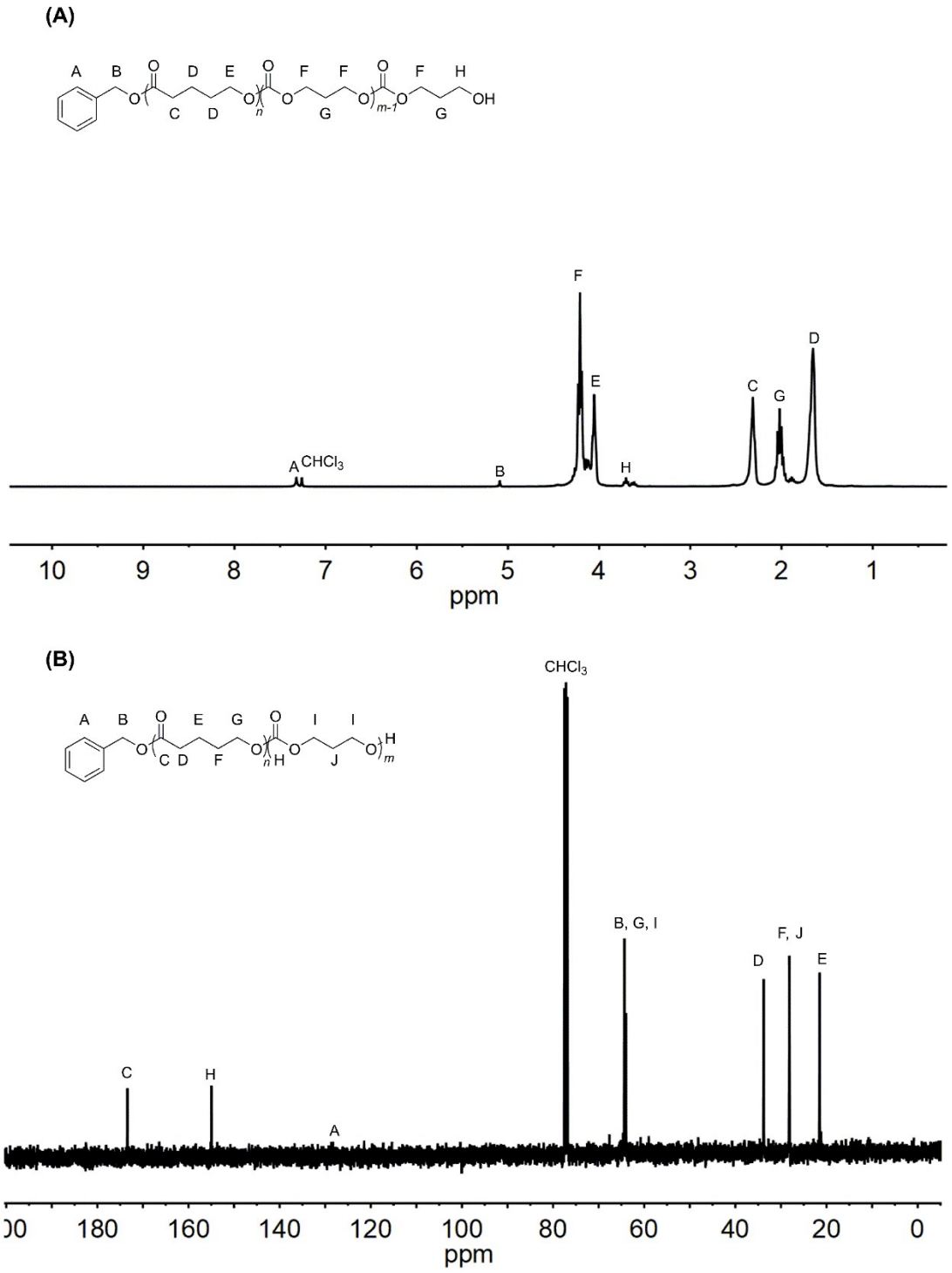


Figure S9 (A) ^{1}H NMR and (B) ^{13}C NMR spectrum of poly(δ-valerolactone) (PVL)-block-poly(trimethylene carbonate) (PTMC).

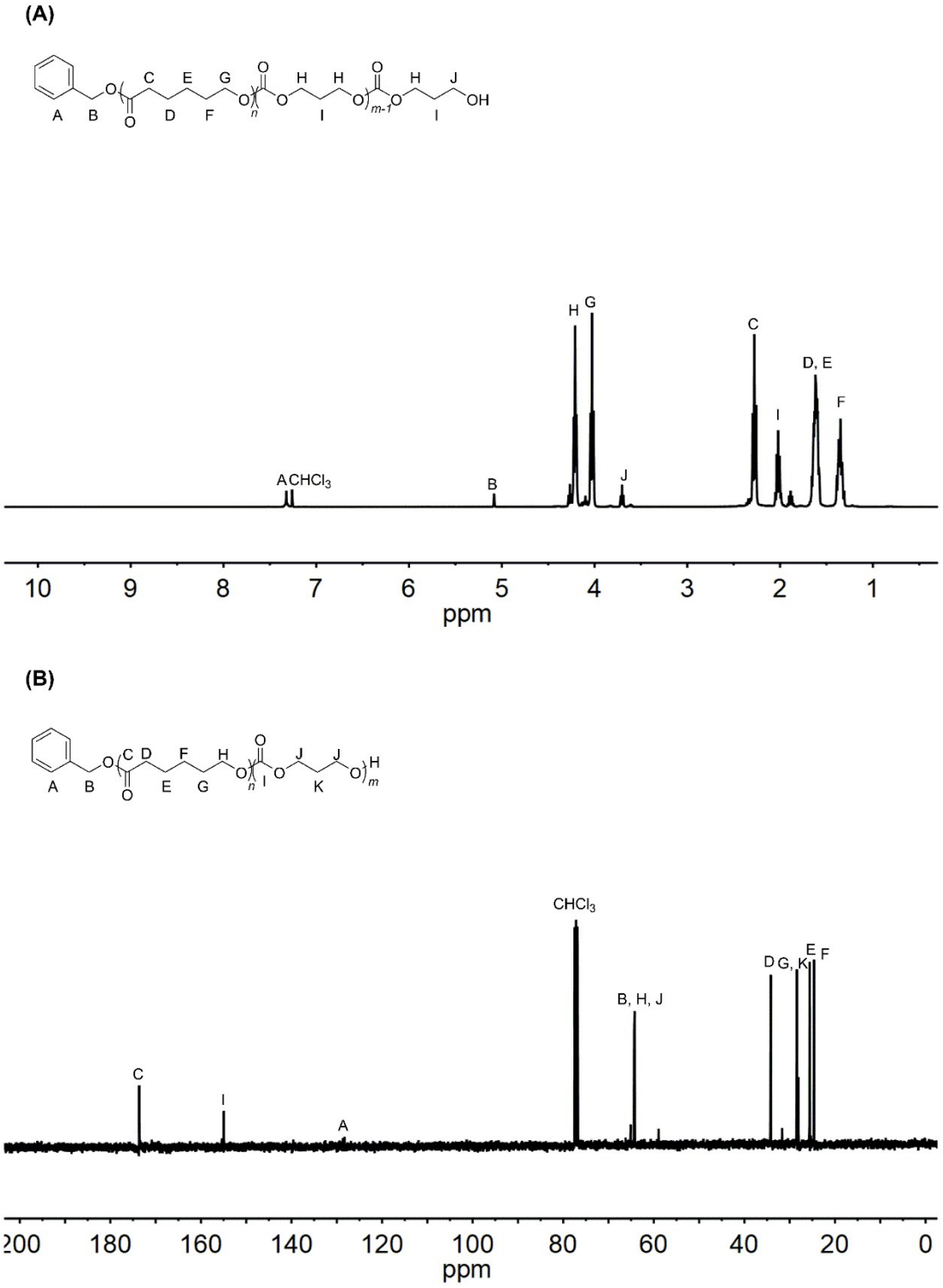


Figure S10 (A) ^{1}H NMR and (B) ^{13}C NMR spectrum of poly(ε-caprolactone) (PCL)-block-poly(trimethylene carbonate) (PTMC)

Reference

1. Pratt, R. C.; Nederberg, F.; Waymouth, R. M.; Hedrick, J. L., Tagging alcohols with cyclic carbonate: a versatile equivalent of (meth)acrylate for ring-opening polymerization. *Chem. Commun.* **2008,** (1), 114-116.