Supporting Information

A Continuous Flow Based Irreversible Polycondensation Enables Synthesis of Polycarbonate Diols Beyond Batch Limitations

Jiawen Dai[1], Shuyuan Luo[1], Zhenjiang Li[1], Jie Sun[2], Haritz Sardon[3], Ning Zhu[1,*], Jin Huang[1,*] and Kai Guo[1]

1. State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, 30 Puzhu Road South, Nanjing 211816, China.
2. College of Food Science and Light Industry, NanjingTech University, Nanjing 211816, China

3. POLYMAT University of the Basque Country UPV/EHU, Avenida de Tolosa, 72, Donostia-San Sebastián 20018, Spain

Table of Contents

Materials

Hexane-1,6-diol (99%), heptane-1,7-diol (99%), octane-1,8-diol (99%), nonane-1,9-diol (99%), decane-1,10-diol (99%), NaOH (99%), 1,5,7-Triazabicyclo (4.4.0) dec-5-ene (97%), titanium oxysulfate-sulfuric acid hydrate (99.95%), hydroxyapatite particle (Size: 60 μm), chloroform-d (99.8%), trimethylolpropane were purchased from Shanghai Macklin Biochemical Co.,Ltd. 1,8-Diazabicycloundec-7-ene (99%), sulfamic acid (99.5%), acetylacetone (95%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 12-Molybdenum heteropoly acid hydrate (95%) were purchased from Beijing OKA Biotech Co., Ltd. Methanesulfonic acid (98%) were purchased from Meryer (Shanghai) Biochemical Technology Co., Ltd. Ethyl acetate (99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Toluene-2,4-diisocyanate (98%) were purchased from Energy Chemical Reagent Co., Ltd.Phenol were purchased from Shanghai J&K Chemical Technology Co., Ltd. Diphenyl carbonate were purchased from Shanghai Dibai Biotechnology Co., 4,4′-methylene-bis (cyclohexyl isocyanate) (HMDI) were purchased from Xuzhou Yihuiyang New Material Co., Ltd.

Instrumentation

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured using deuterated chloroform ($CDCl_3$) as solvent on a Bruker AVANCE Ultrashield Plus spectrometer at 298K.

Size Exclusion Chromatography (SEC) was performed in tetrahydrofuran (THF) at room temperature at a flow rate of 0.7 mL min^{-1} using an SSI 1500 pump equipped with a Waters column (5 μm, 300 mm × 7.8 mm), and a Wyatt Optilab rEX differential refractive index (DRI) detector with a 658 nm light source. All SEC data were analyzed using Wyatt Astra V 6.1.1 software. The molecular weight distribution (Đ) was determined by a calibration with standard polystyrene samples.

Differential scanning calorimetry (DSC) was performed on a Wyatt 250 analyser under the following steps. The obtained copolymer was heated from -80 °C to 200 °C at a rate of 10 °C min^{-1}, staying at 200 °C for 3 min to erase thermal history. Then the sample

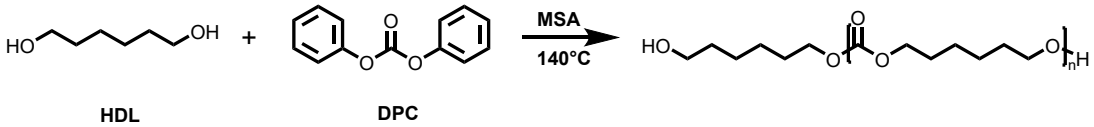
was cooled to -80 °C at a rate of 10 °C min^{-1}, keeping at -80 °C for 3 minutes. Finally, the sample was heated to 200 °C at a rate of 10 °C min^{-1}.

Thermogravimetric analysis (TGA) was performed on a Wyatt TGA 550 analyser under the following steps. The sample (5-10 mg) was heated from 30 °C to 200 °C with a heating rate of 10 °C min^{-1}.

Attenuated total reflection infrared spectrometry (ATR-FTIR) was performed using a Bruker，TENSOR 27 Spectrometer at a resolution of 2 cm^{-1} with a total of 2 to 24 scans.

Experimental Procedures

Polyaddition in batch reactor



HDL DPC

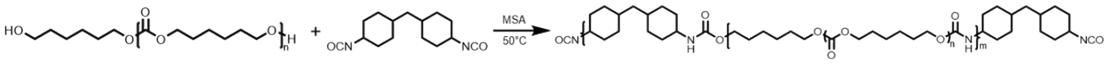
1, 6-Hexanediol (20 g, 0.17 mol, 1.0 equiv) and diphenyl carbonate (36.4 g, 0.17 mol, 1 equiv), MSA(0.49 g, 0.005 mol, 0.03 equiv) are added to the reaction flask. Placed in a heating tank at 140 °C temperature to react for 4 hours, the obtained product is polycarbonate polyol, and the product is purified by reduced pressure distillation.

Polyaddition of diol and diphenyl carbonate in continuous flow reactor

Polyaddition of diol and diphenyl carbonate was performed in continuous flow reactor, taking polyaddition of 1, 6-hexanediol and diphenyl carbonate as an example, 1, 6-hexanediol (2 g, 1 mmol, 1.0 equiv) melted in an oven at 100 °C was mixed with MSA (0.049 g, 0.5 mmol, 0.03 equiv) into a 20 mL sample vial A, diphenyl carbonate (3.26 g，0.015 mol, 0.9 equiv) melted in an oven at 100 °C into a 20 mL sample vial, transfer the two solutions into two syringes and secure them to the syringe pump. Set the total flow rate of the syringe pump to 0.026 mL/min. The reaction pipe with a tube length of 10 m and a retention volume of 7.85 mL (corresponding to a retention time of 5 h) is connected to two syringes through a T-type mixer, the reaction pipe is placed in a 160 °C blast drying oven, the syringe pump is turned on, the reaction solution is collected,

and the yield is calculated by ^{1}H NMR.

Polyaddition of polyol and 4,4′ -methylene-bis(cyclohexyl isocyanate) (HMDI) in continuous flow reactor



Polyaddition of polyol and 4,4′-methylene-bis(cyclohexyl isocyanate) (HMDI) was performed in continuous flow reactor, taking polyaddition of poly(hexamethylene carbonate) diol and HMDI as an example, poly(hexamethylene carbonate) diol (9.1 g, 4.6 mmol, 1.0 equiv), MSA (0.0062 g, 0.66 mmol, 0.14 equiv), phenol (10.9 g, 0.11 mol), ethyl acetate (2 mL) into a 50 mL sample vial A, HMDI (1.31 g, 0.005 mmol, 1.1 equiv), ethyl acetate (7.4 mL) into a 50 mL sample vial B. Transfer the two solutions into two syringes and secure them to the syringe pump. Set the total flow rate of the syringe pump to 0.785 mL/min. The reaction pipe with a tube length of 1 m and a retention volume of 0.785 mL (corresponding to a retention time of 1min) is connected to two syringes through a T-type mixer, the reaction pipe is placed at 25 °C, the syringe pump is turned on, the reaction solution is collected, and products characterized by FTIR.

Preparation of polyurethane adhesive

The crude polyurethane derived from poly (hexamethylene carbonate) and HMDI for 4 hours at 50 °C, containing phenol (26.1 g, 0.28 mol), MSA (0.43 g, 4.5 mmol, 0.45 equiv), poly(hexamethylene carbonate) diol (20 g, 10 mmol, 1.0 equiv), HMDI (3.9 g, 14.9 mmol, 1.5 equiv). Adding crude polyurethane (8 g) to each of five sample bottles, adding 0.11, 0.16, 0.22, 0.27 and 0.33 molar ratios of trimethylolpropane (22.4 mg, 33.5 mg, 44.5 mg, 56 mg, 67.5 mg) crosslinking agent and acetylacetone (0.08g, 0.8 mmol, 0.08 equiv) blocking agent, react in sample bottles for 1 hours at 50 °C. Adding ethyl acetate (3 mL) to each of five sample bottles and stir well.

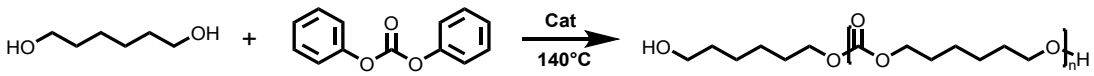
A sheet of PET film (30 μm) was placed on the coating panel, and the vacuum pump was turned on to ensure firm adhesion of the film to the panel. The coating blade height was adjusted to 30 μm. A sample of polyurethane adhesive was evenly dispensed 1–2 cm in front of the scraper. The coating blade was then activated to perform uniform coating at a speed of 100 mm/min, forming a polyurethane adhesive film with a uniform thickness of 30 μm on the PET surface. The coated PET film was subsequently placed in a constant-temperature oven and cured at 80 °C for 24 hours to obtain a complete polyurethane adhesive coating film, which was reserved for subsequent peel strength testing.

180° peel strength test

The characterization of PU-PSA samples was performed according to the international standard ISO 29862:2024. Briefly, the steel plate was first wiped with a clean non-woven fabric dipped in absolute ethanol and then dried using a clean piece of degreasing gauze. This cleaning procedure was repeated at least three times to ensure that the working surface of the steel plate was free from dust, contaminants, and scratches. After cleaning, the working surface of the plate was not touched by hands or any other objects. The width of the adhesive tape was measured using a measuring tool with an accuracy of no less than 0.05 mm. A piece of adhesive tape longer than 200 mm was then affixed to the cleaned test plate. A strip of polyester film (or other suitable material), approximately 200 mm in length and 40 mm in width, was placed under the opposite end of the test plate. To eliminate air bubbles between the tape and the steel surface, the sample was rolled back and forth three times using a pressure roller under its own weight. After this, the sample was allowed to stand in the testing environment for 20 minutes prior to testing. The free end of the adhesive tape was folded back 180° and peeled from the test plate to a length of 25 mm. The free end of the tape and the test plate were then clamped into the upper and lower grips of a peel strength testing machine, respectively, ensuring that the peeling interface was aligned with the force axis of the machine. The test was conducted at a peeling speed of 200 mm/min using a computerized peel strength tester. The instrument recorded the peel force curve in real time, and the resulting data were subsequently processed.

Supporting Tables

Table S1. Polyaddition of 1,6-hexanediol (HDL) and DPC catalyzed by Acidic catalysts.



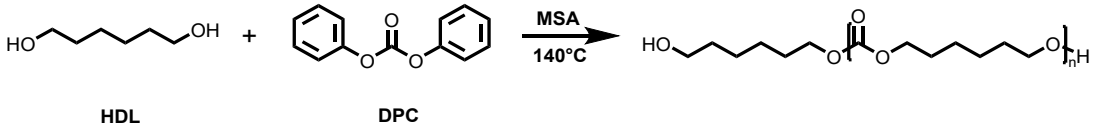
HDL DPC

Entry	catalyst	NMR yield/ mol%[b]	DP[c]	$M_{n,\ NMR}$ [d] / g·mol^{-1}
1	ASA	16	<1	N.A.[e]
2	Titanium oxysulfate-sulfuric acid hydrate	74	3	403
3	Hydroxyapatite	14	<1	N.A.
4	Bimetallic catalyst	32	<1	N.A.

5	MSA	90	9	1200
6	12-molybdenum heteropoly acid hydrate	82	5	662

[a]Unless other stated, the polyaddition were carried out at 140 °C or 4 h with an equimolar feed ratio of $[HDL]_0/[DPC]_0$ = 1:1 and a catalyst loading of 3 mol%; [b] polycarbonate NMR yield were determined by ^{1}H NMR spectroscopy in $CDCl_3$; [c] Determined from ^{1}H NMR, DP = $I_{4.12}/I_{3.63}$; [d] determined from ^{1}H NMR, $M_{n,NMR}$ = M(144 g·mol^{-1}) × DP; [e] N.A. = not available.

Table S2. Polyaddition of 1,6-hexanediol (HDL) and DPC catalyzed by MSA catalyst at different molar ratios.



HDL DPC

Entry	$[HDL]_0/[DPC]_0/[MSA]_0$	NMR yield/ mol%[b]	DP[c]	$M_{n,NMR}$ [d] / g·mol^{-1}
1	1/0.9/0.003	54	<1	N.A.
2	1/0.9/0.03	94	4	576
3	1/0.9/0.1	22	N.A.	N.A.

[a]Unless other stated, the polyaddition were carried out at 140 °C for 4 h with MSA catalyst. [b] polycarbonate NMR yield were determined by ^{1}H NMR spectroscopy in $CDCl_3$; [c] determined from ^{1}H NMR, DP = $I_{4.12}/I_{3.63}$; [d] determined from ^{1}H NMR, $M_{n,NMR}$ = M(144 g·mol^{-1}) × DP, N.A. = not available.

Supporting Figures

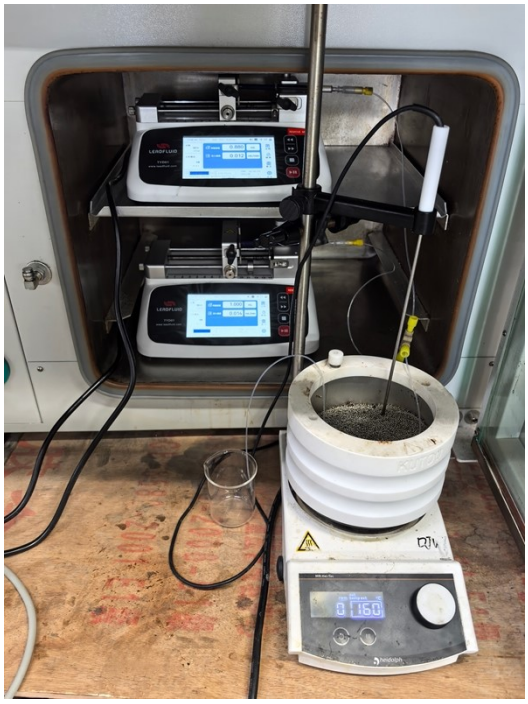


Figure S1. The continuous flow set-up for irreversible polyaddition.

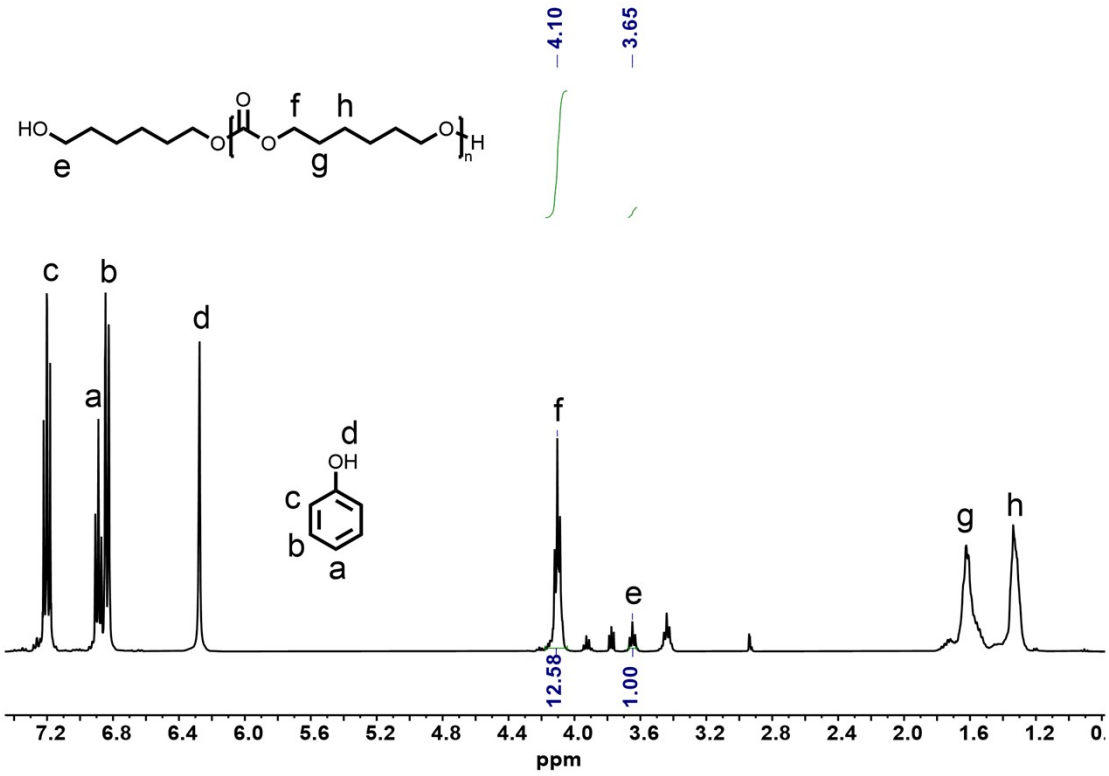


Figure S2. ^{1}H NMR spectrum ($CDCl_3$,400 MHz) of polymer. Experimental conditions: the polyaddition were carried out at 140 °C for 7 h with an equimolar feed ratio of $[HDL]_0/[DPC]_0$ = 1:1 and a catalyst loading of 3 mol%.

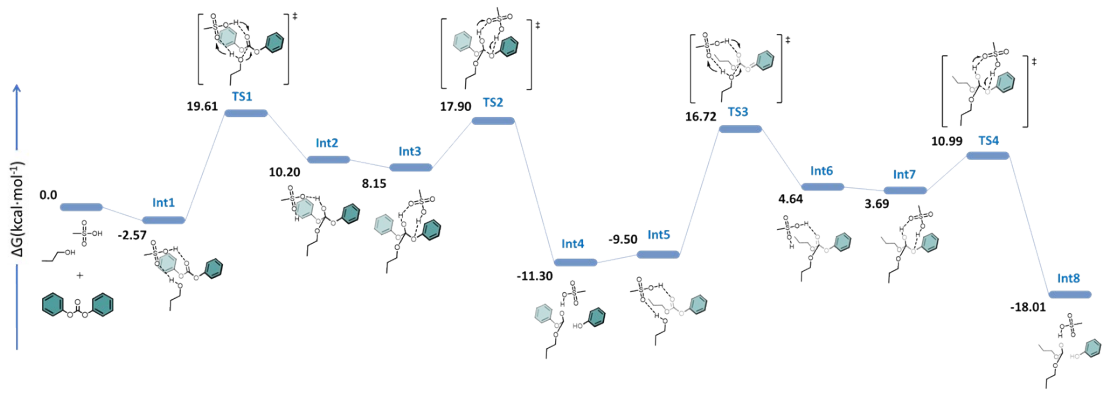


Figure S3. Energetic profiles for the MSA-catalyzed coupling reaction between aliphatic diols and diphenyl carbonate (DPC).

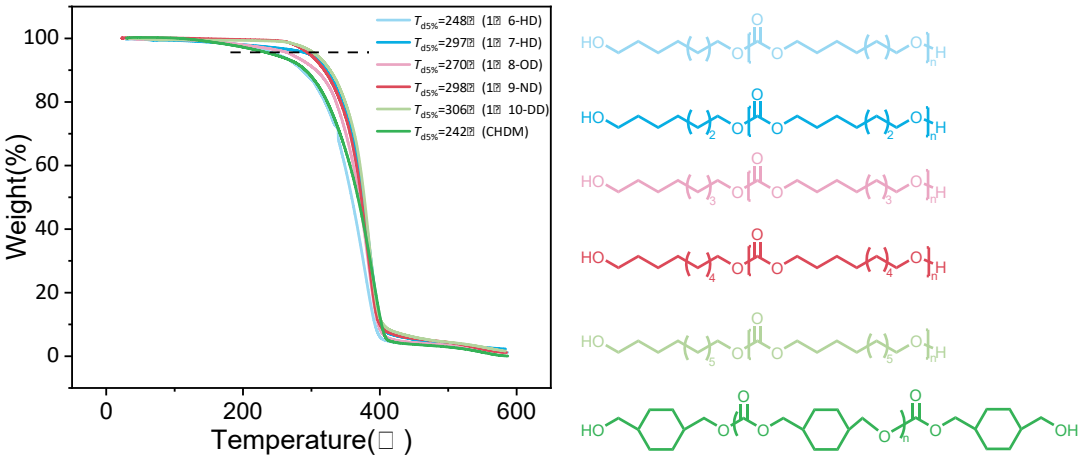


Figure S4. The TGA curves of obtained polycarbonate diols.

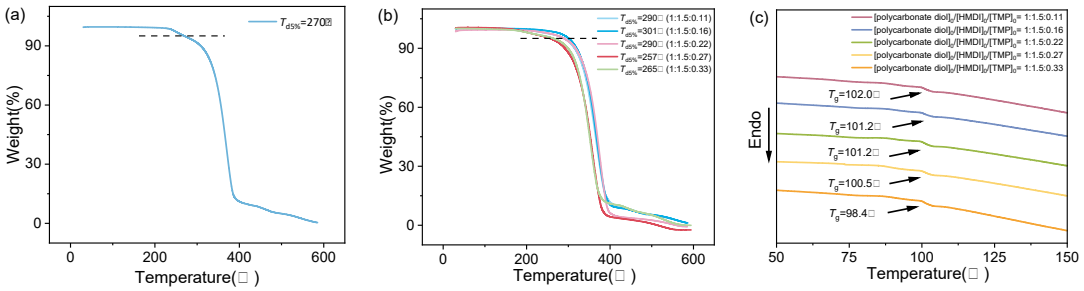
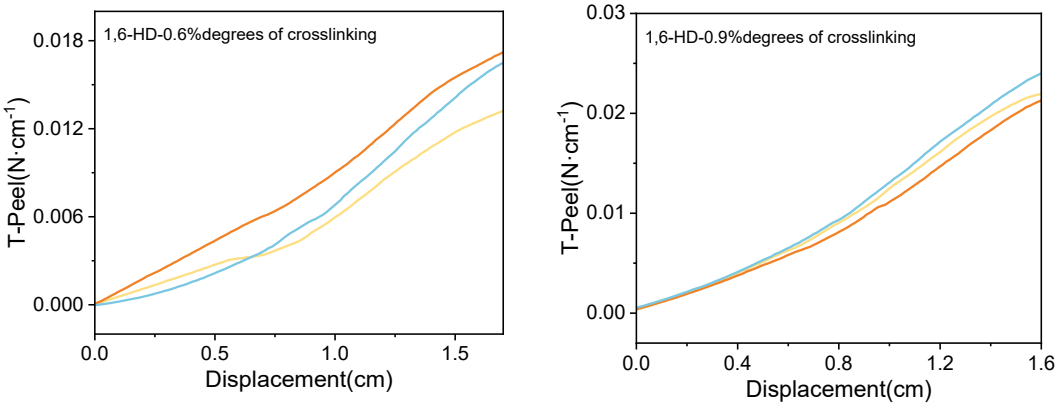


Figure S5. (a) the TGA curve of obtained polycarbonate-based polyurethane; (b) the TGA curve of obtained polyurethane with different ratios TMP; (c) the 2nd heating (10 °C/min under Ar) DSC curve of obtained polyurethane with different ratios TMP.



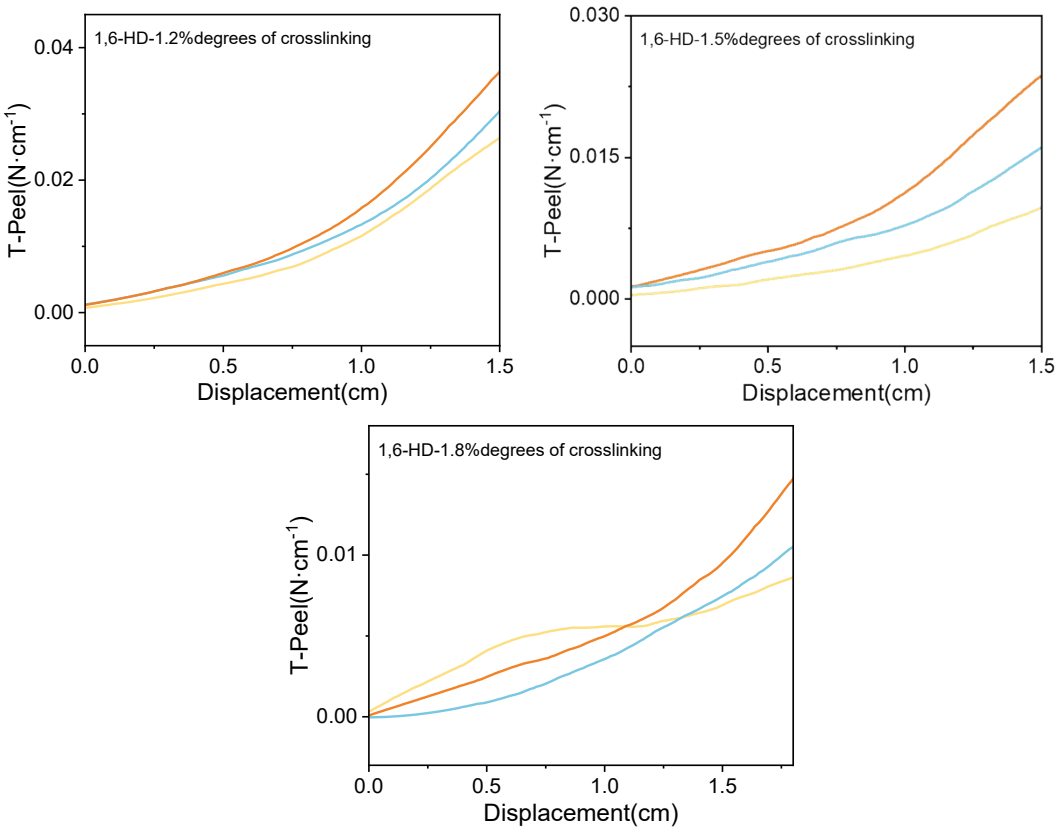


Figure S6. The peel force curves of obtained polyurethane pressure-sensitive adhesives (PU-PSAs) prepared from poly(hexamethylene carbonate) diol.

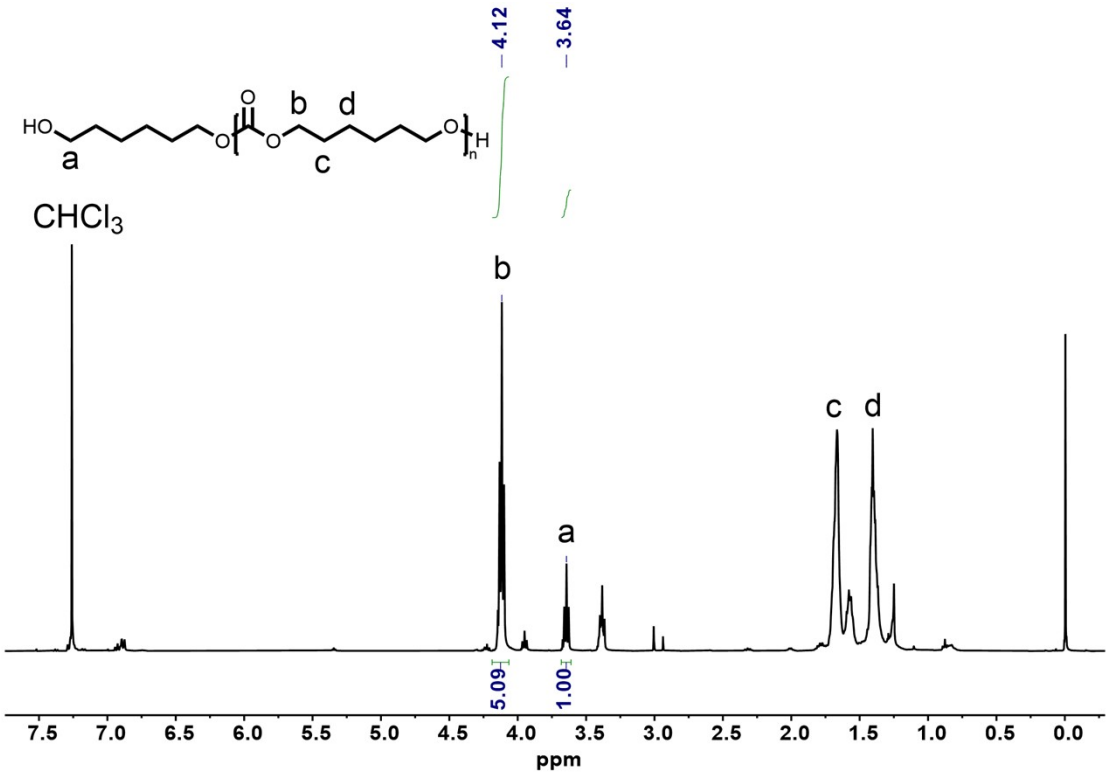


Figure S7. ^{1}H NMR spectrum ($CDCl_3$,400 MHz) of poly(hexamethylene carbonate) diol.

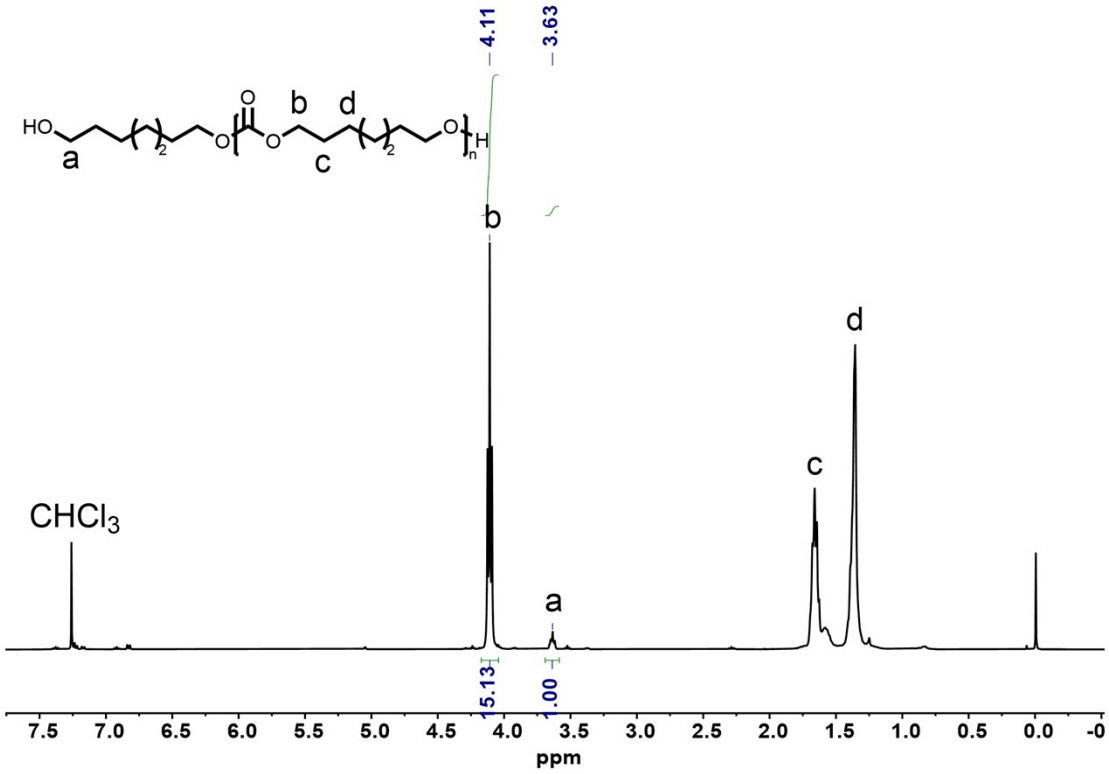


Figure S8. ^{1}H NMR spectrum ($CDCl_3$,400 MHz) of poly(heptamethylene carbonate) diol.

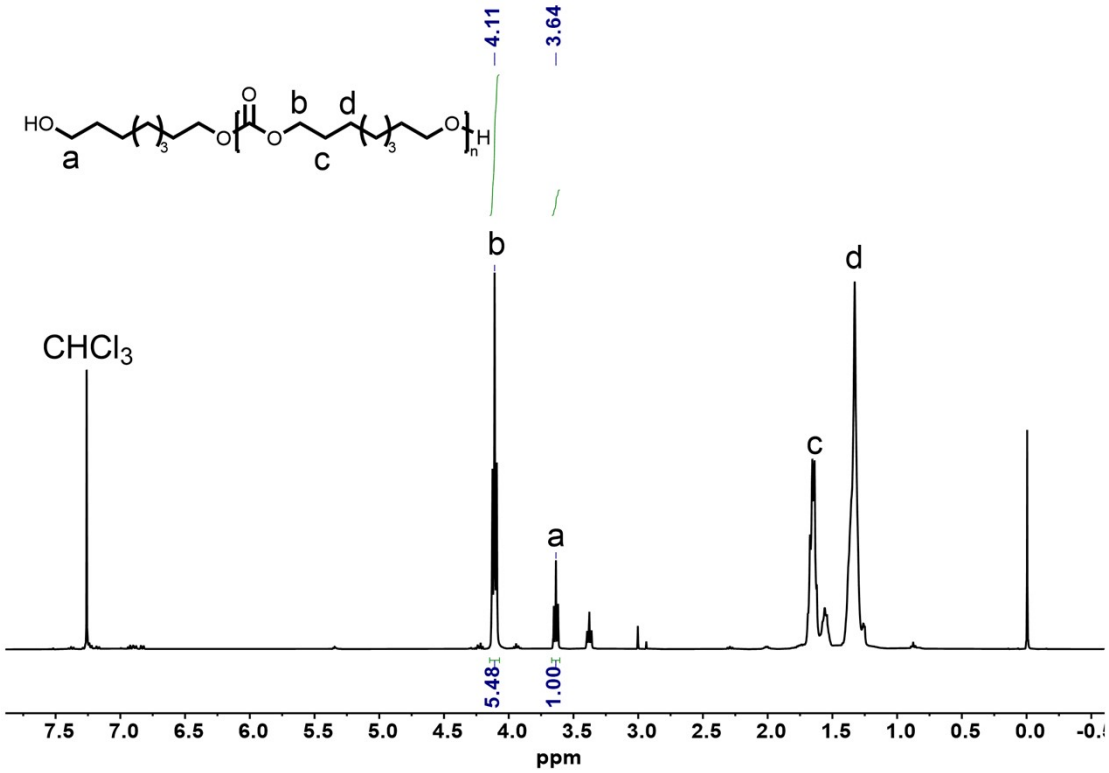


Figure S9. ^{1}H NMR spectrum ($CDCl_3$,400 MHz) of poly(octamethylene carbonate) diol.

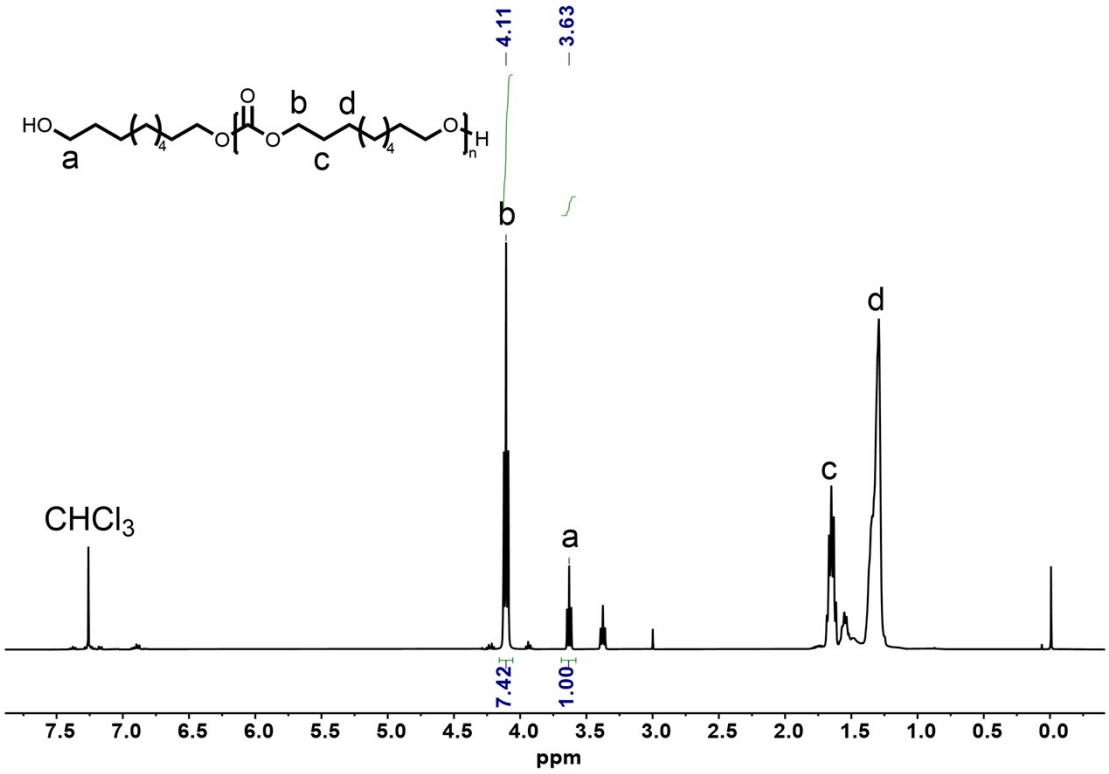


Figure S10. ^{1}H NMR spectrum ($CDCl_3$,400 MHz) of poly(nonamethylene carbonate) diol.

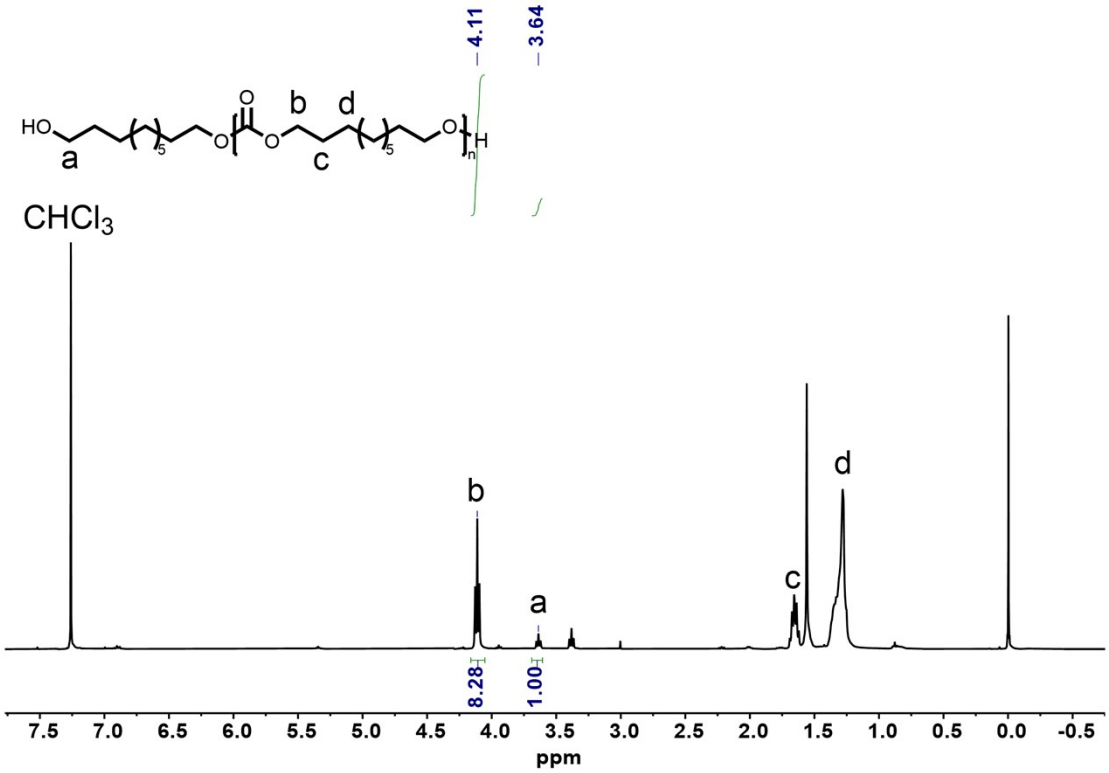


Figure S11. ^{1}H NMR spectrum ($CDCl_3$,400 MHz) of poly(decamethylene carbonate) diol.

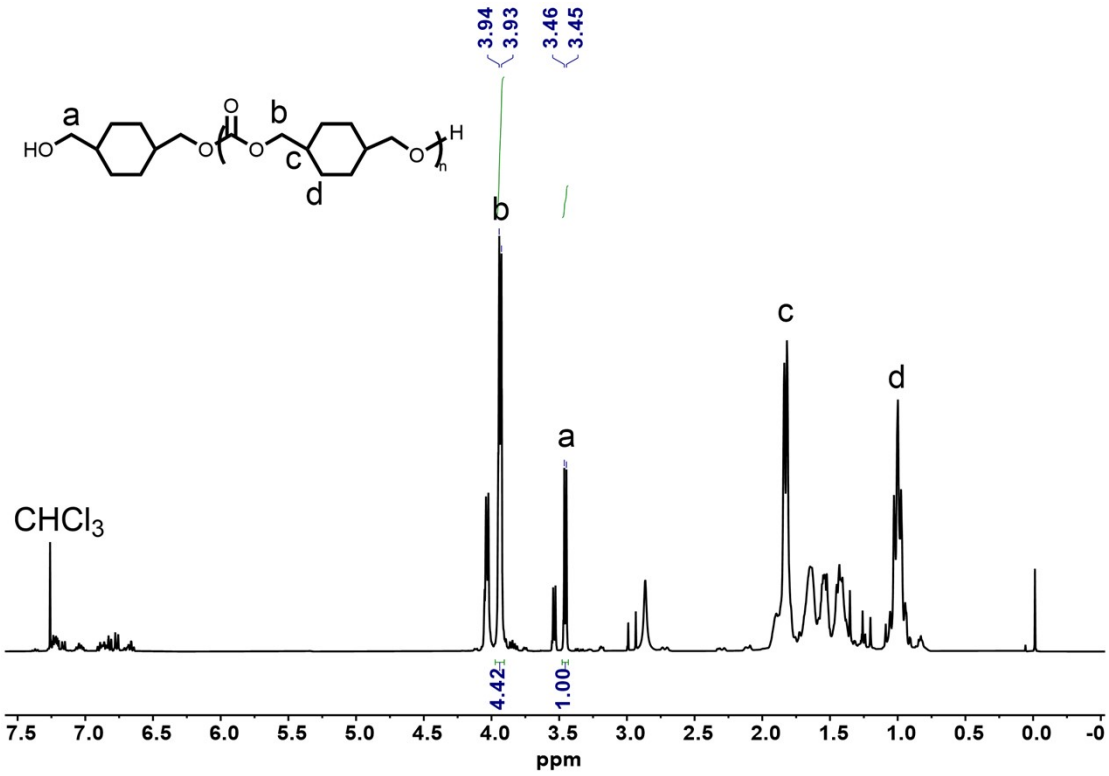


Figure S12. ^{1}H NMR spectrum ($CDCl_3$,400 MHz) of poly(cyclohexanedimethyl carbonate) diol.

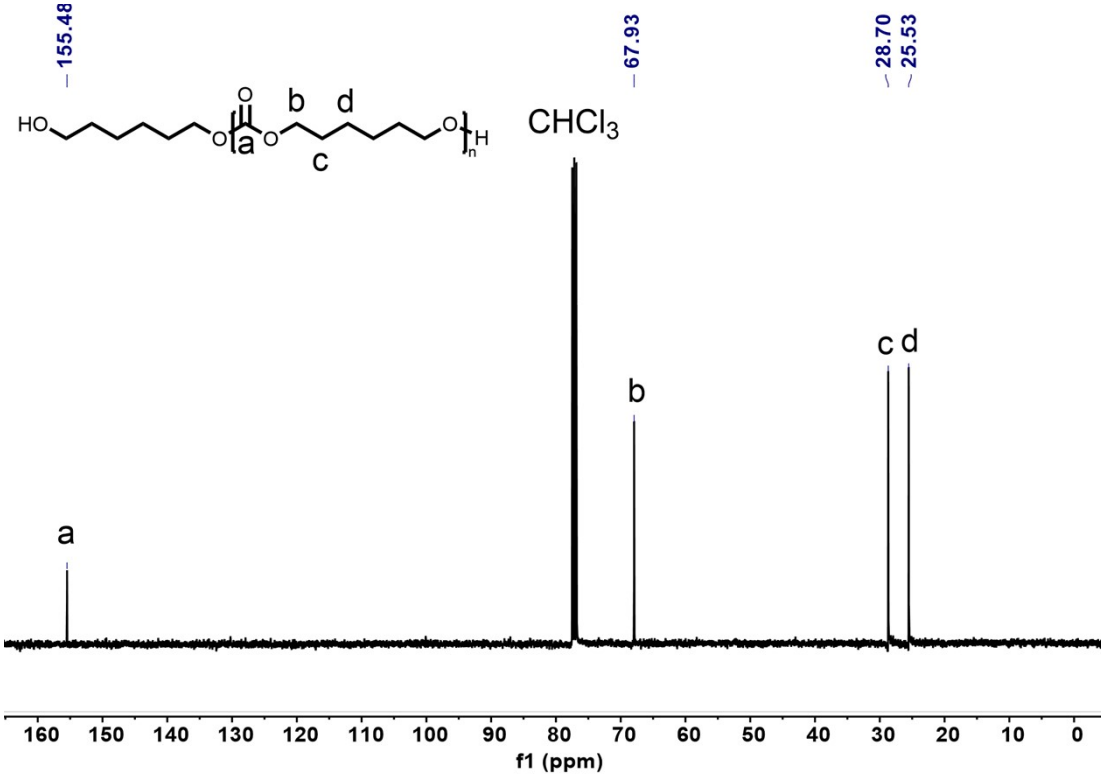


Figure S13. ^{13}C NMR spectrum ($CDCl_3$,400 MHz) of poly(hexamethylene carbonate) diol.

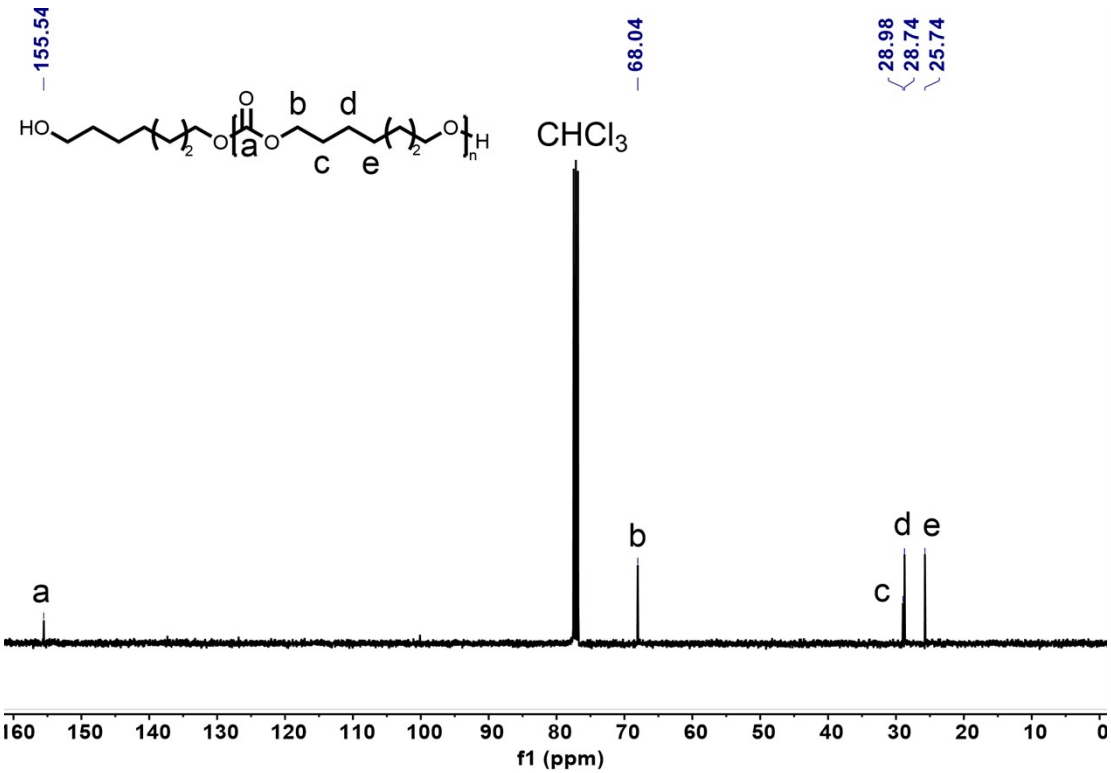


Figure S14. ^{13}C NMR spectrum ($CDCl_3$,400 MHz) of poly(heptamethylene carbonate) diol.

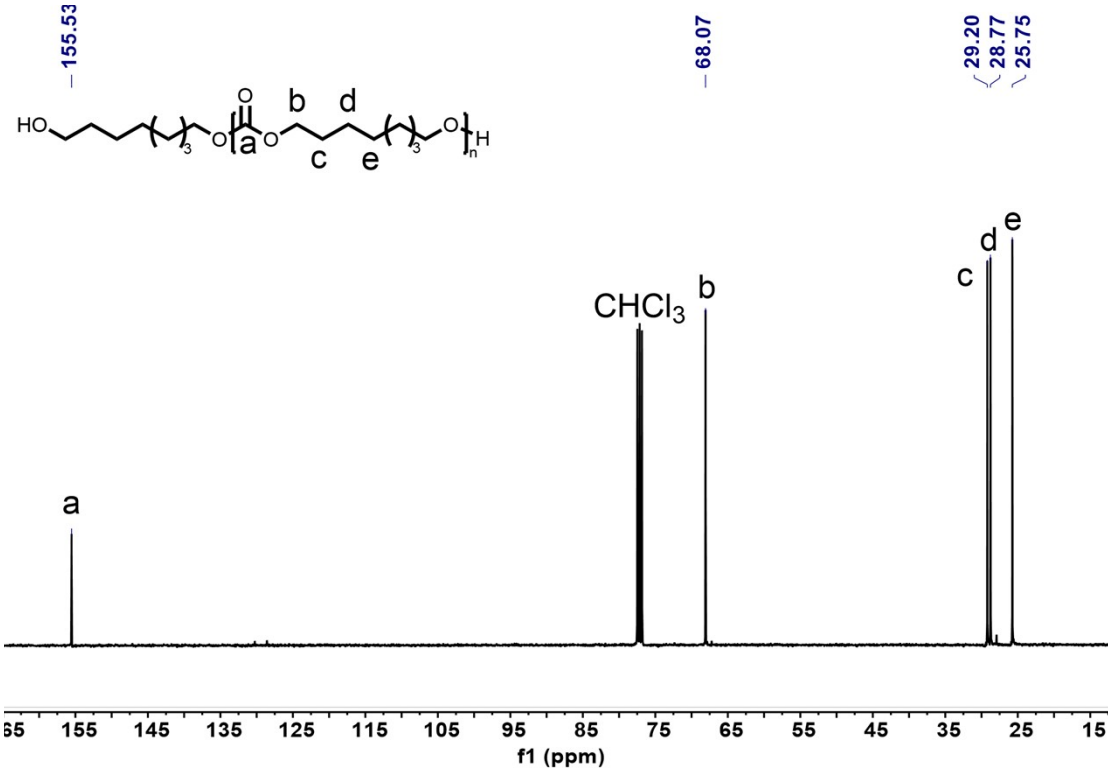


Figure S15. ^{13}C NMR spectrum ($CDCl_3$,400 MHz) of poly(octamethylene carbonate) diol.

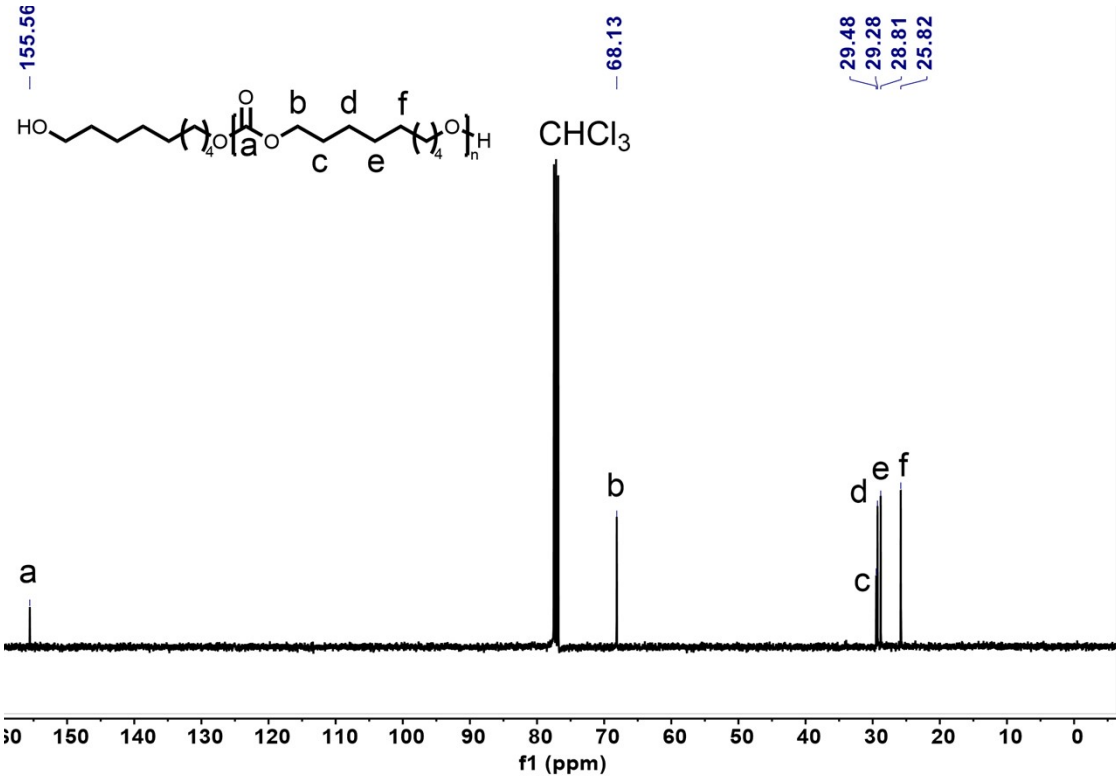


Figure S16. ^{13}C NMR spectrum ($CDCl_3$,400 MHz) of poly(nonamethylene carbonate) diol.

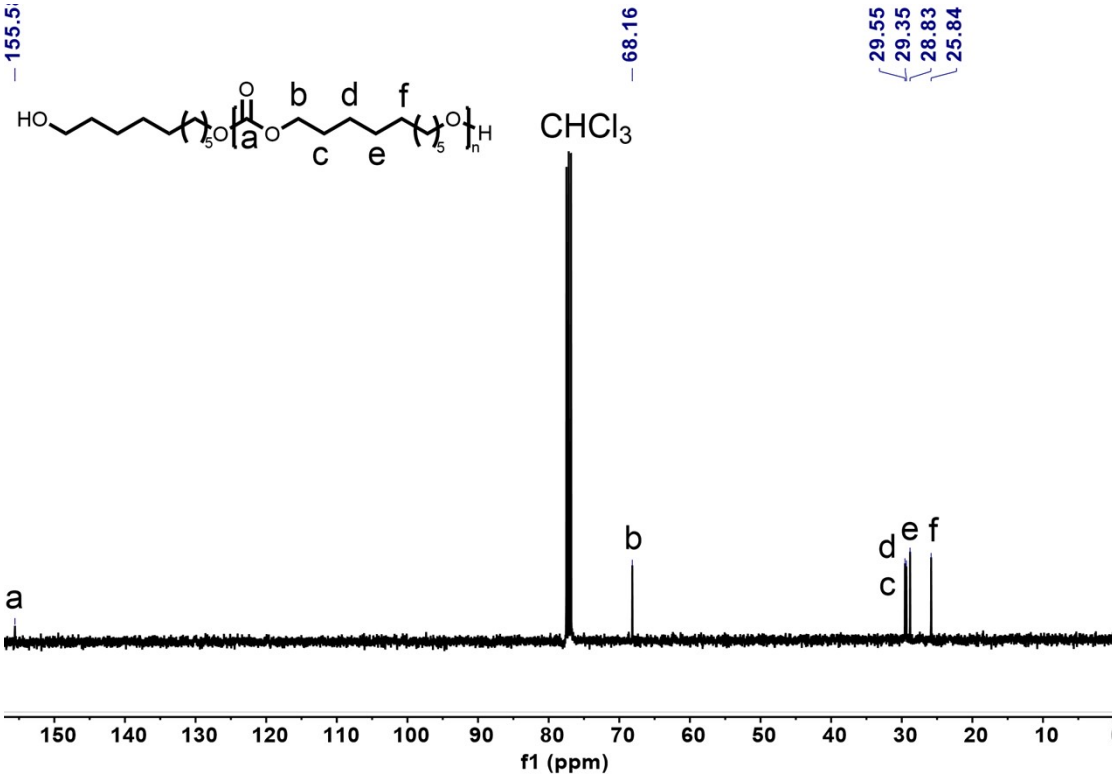


Figure S17. ^{13}C NMR spectrum ($CDCl_3$,400 MHz) of poly(decamethylene carbonate)

diol.

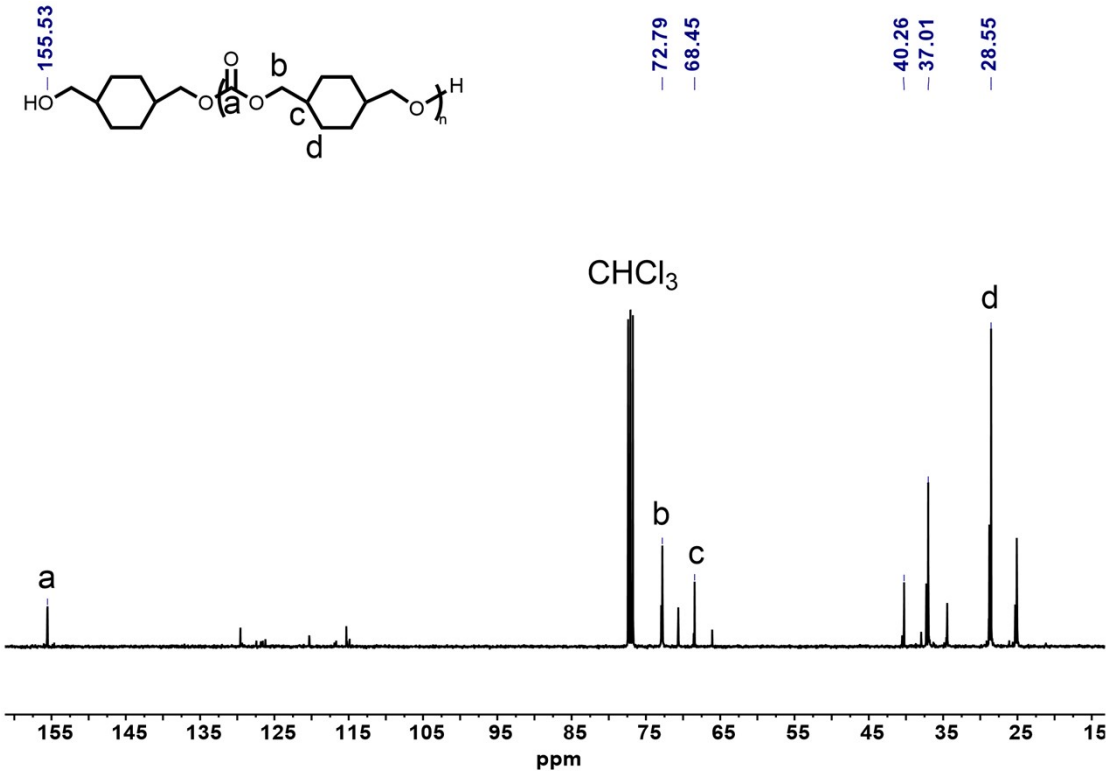


Figure S18. ^{13}C NMR spectrum ($CDCl_3$,400 MHz) of poly(cyclohexanedimethyl carbonate) diol.

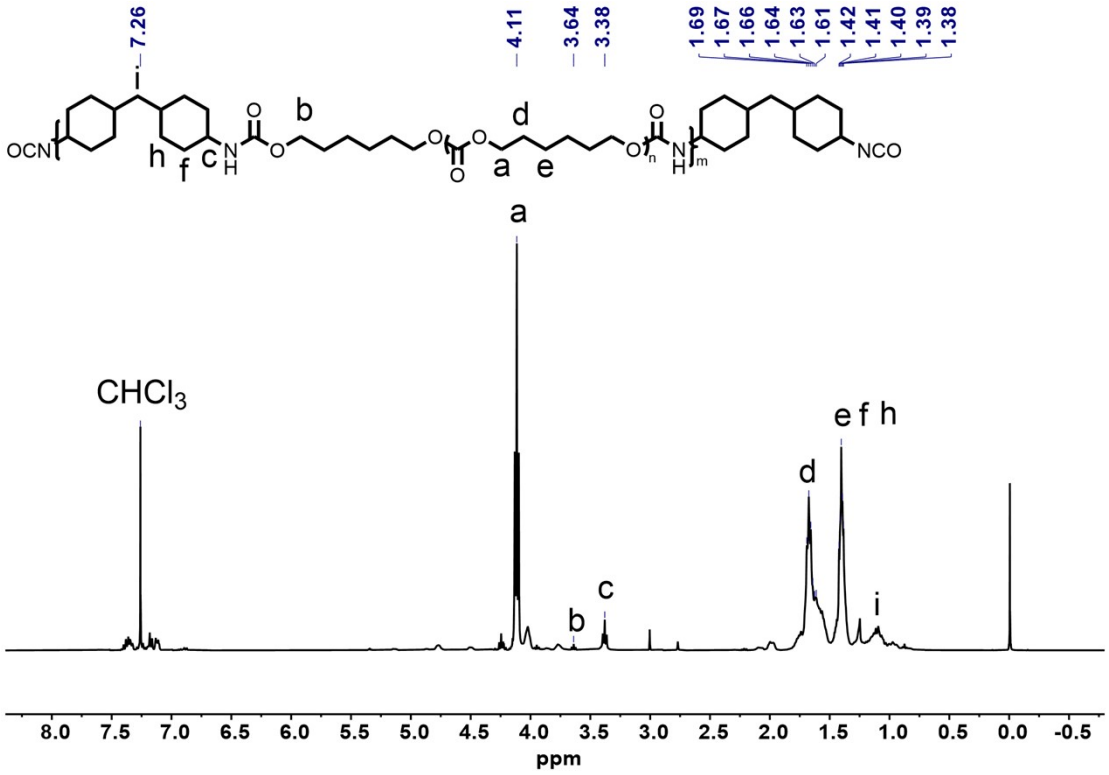


Figure S19. ^{1}H NMR spectrum ($CDCl_3$,400 MHz) of polyurethane prepolymer.

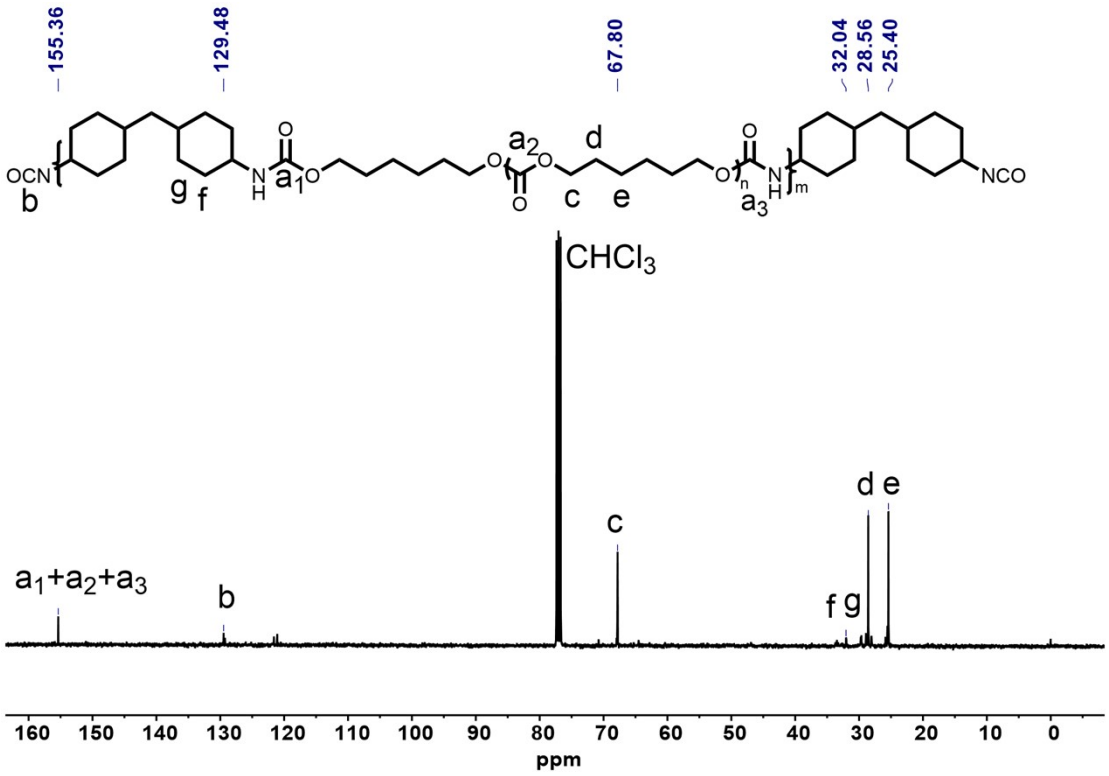
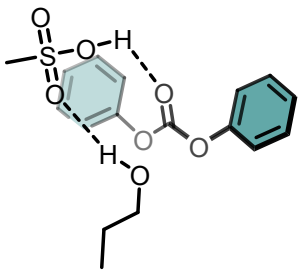


Figure S20. ^{13}C NMR spectrum ($CDCl_3$,400 MHz) of polyurethane prepolymer.

DFT Calculation

Geometry optimizations of structures, binding energy of complexes were performed using Gaussian 16 program[1], the structures were illustrated by CYLview[2]. the structures were optimized at ωB97XD/6-31+G(d) and single-point energy were obtained on optimized structures with ωB97XD/6-31+G(d',p').

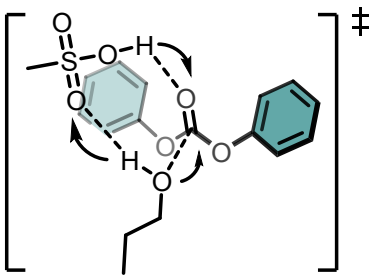
Int1



S	-1.59664900	2.60392500	0.57553300
O	-1.56542900	1.56542400	1.60611500
O	-1.93758200	3.95784900	0.94880700

C	-2.66713800	2.04150000	-0.73175300
H	-3.66733100	1.94010900	-0.30706700
H	-2.65519500	2.78986800	-1.52518500
H	-2.30520400	1.07556100	-1.08920900
O	-0.16880500	2.68401700	-0.13604000
H	0.11187100	1.78993600	-0.45385000
C	0.90844500	-0.84344400	2.99479700
H	0.13557000	-1.07669200	3.74326000
H	1.51037000	-0.00805400	3.38328100
C	1.79104500	-2.05913700	2.76082300
H	2.55883800	-1.79906500	2.02116800
H	2.31513400	-2.28312200	3.69901200
C	1.00960100	-3.28457500	2.28927200
H	0.52063700	-3.09185200	1.33038600
H	1.67299500	-4.14657600	2.16152300
H	0.23666200	-3.56065700	3.01780700
O	0.30265400	-0.48014700	1.76435900
H	-0.31098600	0.26520400	1.88863500
C	0.48401400	-0.91889100	-0.96667000
O	1.73609800	-1.33596200	-0.85067400
O	-0.31626900	-1.97847300	-0.90395100
O	0.11577200	0.22015000	-1.16843000
C	2.75938600	-0.38086700	-0.88553700
C	3.69772100	-0.50095700	-1.89897300
C	2.85547900	0.58761900	0.10418600
C	4.76786300	0.39124700	-1.92766500
H	3.58766500	-1.28117100	-2.64526500
C	3.92622300	1.47628500	0.05760700
H	2.10186700	0.63008900	0.88369600
C	4.88148500	1.38117300	-0.95363600
H	5.51145200	0.31070300	-2.71484500
H	4.01092700	2.24655300	0.81816400
H	5.71430200	2.07730100	-0.98132300
C	-1.69276000	-1.72205100	-0.91386600
C	-2.36237600	-1.68584400	-2.12848300
C	-2.34644300	-1.56681800	0.29896100
C	-3.74001500	-1.47632900	-2.12422500
H	-1.81157700	-1.81581600	-3.05459100
C	-3.72355100	-1.35747900	0.28854200
H	-1.77012900	-1.58695800	1.21740600
C	-4.42047100	-1.31175600	-0.91795300
H	-4.28052900	-1.44473700	-3.06552100
H	-4.24906900	-1.22406800	1.22921100
H	-5.49443400	-1.15026500	-0.91926900

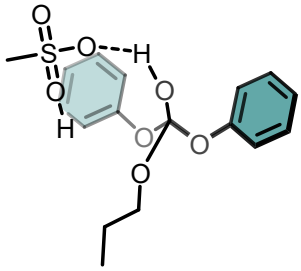
TS1



S	0.21543700	2.00071800	1.37144600
O	0.43632300	0.63294000	1.92322200
O	1.34579900	2.90595100	1.47557300
C	-1.14009200	2.69546100	2.29655600
H	-0.82255600	2.78625200	3.33667500
H	-1.36550400	3.67732400	1.87751600
H	-2.00081800	2.03079100	2.20913100
O	-0.32579400	1.89821900	-0.05374100
H	-0.54270500	0.79585000	-0.47981500
C	0.98099700	-2.60133900	1.23681300
H	1.94122700	-2.07675400	1.27434900
H	1.01407100	-3.35267000	0.44694800
C	0.61320000	-3.21629700	2.57525600
H	-0.34955100	-3.72984400	2.47160900
H	1.36580600	-3.98732400	2.78564500
C	0.56243600	-2.21204600	3.72644000
H	-0.22558600	-1.46739300	3.57780200
H	0.36374600	-2.72462100	4.67294800
H	1.51065900	-1.67152100	3.82395900
O	-0.03973000	-1.65961600	0.82739100
H	0.10358000	-0.76451800	1.27222100
C	-0.17727900	-1.31670400	-0.82241500
O	1.11950300	-1.29737600	-1.25144900
O	-0.75160000	-2.51294500	-1.17602400
O	-0.90872100	-0.27750100	-0.88095400
C	1.69500900	-0.08274000	-1.62730100
C	2.59630900	0.52490200	-0.76757600
C	1.38999900	0.44993900	-2.87290000
C	3.19466700	1.72021800	-1.15811400
H	2.79903800	0.08882400	0.20525800
C	1.99646100	1.64311800	-3.25321100
H	0.68212800	-0.06207400	-3.51790200
C	2.89599900	2.27891900	-2.39776400

H	3.87302200	2.22427800	-0.47786200
H	1.76145900	2.07918900	-4.21968200
H	3.35649800	3.21640200	-2.69446000
C	-0.84343400	-2.72185600	-2.55051100
C	-0.02545300	-3.68497100	-3.12729500
C	-1.76791200	-2.00610400	-3.30370500
C	-0.13455700	-3.93722500	-4.49269000
H	0.68928600	-4.21651700	-2.50758700
C	-1.86158900	-2.26101600	-4.67047800
H	-2.39122800	-1.26229200	-2.81983700
C	-1.04899400	-3.22425200	-5.26663100
H	0.50147300	-4.68799100	-4.95243500
H	-2.57845300	-1.70666300	-5.26928900
H	-1.12979000	-3.42055800	-6.33165600

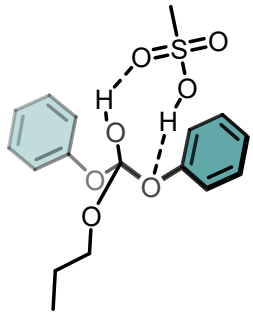
Int2



S	-1.68481200	2.45166300	-0.46085600
O	-1.41621700	1.81647000	0.97858200
O	-2.09837200	3.82044000	-0.26592900
C	-3.05331100	1.48707700	-1.06083300
H	-3.88464500	1.60195400	-0.36472700
H	-3.31458200	1.87780800	-2.04629200
H	-2.74474700	0.44155200	-1.12775100
O	-0.51696800	2.15649800	-1.30012700
H	-0.11483100	0.41765200	-1.35269700
C	1.03084300	-0.48025700	1.99559600
H	1.91143900	-1.10251500	1.81972900
H	0.29743200	-1.07098700	2.55465800
C	1.41214200	0.79375800	2.72834600
H	0.51394500	1.38917200	2.93512700
H	1.81230600	0.48819600	3.70334200
C	2.44121100	1.63454300	1.97351500
H	2.03199800	2.00456600	1.02904800
H	2.74521900	2.49869000	2.57254300
H	3.33638600	1.04690900	1.73730100

O	0.45937100	-0.11452300	0.72283900
H	-0.75107600	1.08084500	0.89590100
C	0.36925400	-1.12587000	-0.25403200
O	1.58998400	-1.76063300	-0.44165000
O	-0.43794000	-2.18038200	0.17108200
O	-0.13586500	-0.56195400	-1.38765100
C	2.74712900	-1.02796500	-0.61705200
C	3.89292000	-1.61847900	-0.08444700
C	2.82816300	0.19229800	-1.28390800
C	5.12298200	-0.98156000	-0.20642400
H	3.79917000	-2.57478800	0.42131200
C	4.06553400	0.82518400	-1.38942100
H	1.95475100	0.65830200	-1.71828400
C	5.21417600	0.24981800	-0.85410500
H	6.01061600	-1.44795400	0.21129500
H	4.12251500	1.78151200	-1.90111400
H	6.17205900	0.75295700	-0.94428300
C	-1.80455000	-1.96461500	0.14539100
C	-2.53314700	-2.39233400	-0.96178900
C	-2.44414600	-1.39184000	1.23997500
C	-3.91668600	-2.24000200	-0.96979500
H	-2.00470100	-2.83179000	-1.80081400
C	-3.83006700	-1.23996000	1.22333200
H	-1.86516700	-1.07316200	2.10002000
C	-4.56869100	-1.66261300	0.12109300
H	-4.48784800	-2.57487400	-1.83086000
H	-4.32898000	-0.79233300	2.07794100
H	-5.64874700	-1.54876000	0.11247800

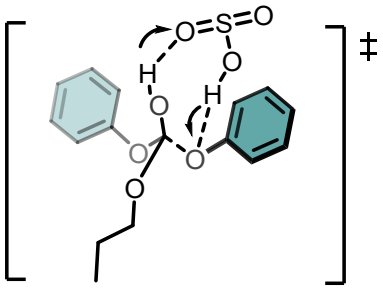
Int3



S	-1.72753500	2.79574800	-0.02487300
O	-0.49884500	2.62372000	-1.02504300
O	-2.96835800	2.45457300	-0.68958600
C	-1.66107200	4.55510100	0.21446200
H	-1.76933400	5.03708800	-0.75807500

H	-2.49514900	4.81886300	0.86717300
H	-0.70787600	4.80968000	0.67823100
O	-1.39705600	2.13863400	1.24197200
H	-0.63276700	0.50938000	1.61296500
C	1.15433300	-2.36032700	-0.95769400
H	1.48495700	-1.58165700	-1.65512100
H	0.23220600	-2.80828600	-1.34586300
C	2.23765800	-3.40540100	-0.76558700
H	1.87425200	-4.16975700	-0.06785000
H	2.38118200	-3.90318800	-1.73314600
C	3.56064400	-2.82356700	-0.26918400
H	3.44555900	-2.38292200	0.72476800
H	4.32948300	-3.60126900	-0.21201700
H	3.92344200	-2.03416800	-0.93856700
O	0.87899500	-1.77272600	0.32110800
H	-0.00078800	1.78497400	-0.81950800
C	0.16945300	-0.61080800	0.30947700
O	0.90937600	0.44722400	-0.32747500
O	-0.95291200	-0.61577800	-0.52394900
O	-0.11821500	-0.32419600	1.60515600
C	2.25767800	0.60690100	-0.04659300
C	3.05136800	0.98505800	-1.12512200
C	2.80041200	0.43864900	1.22383700
C	4.41377300	1.19623600	-0.93276500
H	2.59385300	1.10435800	-2.10292800
C	4.16778800	0.63914100	1.39750600
H	2.16839400	0.14037000	2.05120000
C	4.97804100	1.01718400	0.32862600
H	5.03414400	1.49210800	-1.77375400
H	4.60040100	0.49892900	2.38395200
H	6.04223000	1.17244600	0.47834600
C	-2.06453200	-1.37025300	-0.18877100
C	-3.25438200	-0.94832500	-0.77657400
C	-2.02705800	-2.49812900	0.62833300
C	-4.42040000	-1.67174600	-0.55256900
H	-3.25323600	-0.04832800	-1.38216400
C	-3.20749800	-3.20763700	0.84684100
H	-1.10218400	-2.81132400	1.09688200
C	-4.40358900	-2.80562300	0.25912100
H	-5.34835900	-1.33846800	-1.00816700
H	-3.18307800	-4.08455900	1.48767700
H	-5.31637500	-3.36657400	0.43641800

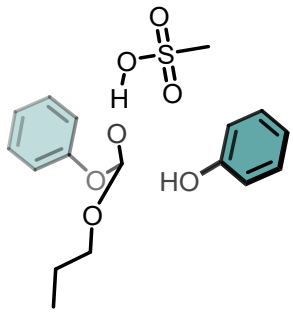
TS2



S	-1.53613800	2.76336900	0.03738800
O	-0.43237600	2.50919300	-0.95408000
O	-2.87875200	2.54859300	-0.49611600
C	-1.38197500	4.48946200	0.45143800
H	-1.54393100	5.06804800	-0.45930700
H	-2.14347300	4.72586800	1.19621800
H	-0.38197300	4.66760800	0.84902700
O	-1.25354900	2.02485300	1.31191600
H	-0.75304000	0.56005700	1.32721500
C	1.44166100	-2.29853500	1.20984900
H	0.74087700	-2.60741200	1.99210400
H	2.02356300	-1.44618900	1.56700200
C	2.33404800	-3.44058300	0.76995100
H	3.02260200	-3.07543000	-0.00128200
H	2.94770400	-3.71573400	1.63680100
C	1.56293500	-4.65878500	0.26372400
H	0.99620900	-4.41757000	-0.64086300
H	2.24687700	-5.47841800	0.02204700
H	0.85772400	-5.02114500	1.02132700
O	0.66164200	-1.89678500	0.05527200
H	0.27949900	1.26238400	-0.85996100
C	-0.08505800	-0.81009600	0.13610000
O	0.84855400	0.37767800	-0.76107000
O	-1.11702800	-0.77998600	-0.73656200
O	-0.24288400	-0.32340400	1.33676500
C	2.11030300	0.62543700	-0.23537500
C	3.17850600	-0.07537800	-0.78199400
C	2.27500100	1.50366900	0.83065700
C	4.44850000	0.10315600	-0.24001400
H	2.99933600	-0.74665700	-1.61542200
C	3.55273300	1.68074400	1.35572600
H	1.41504400	2.02413900	1.24032200
C	4.63649800	0.97882500	0.82900200
H	5.29259600	-0.43811000	-0.65718400
H	3.69860000	2.36433200	2.18676000
H	5.62852000	1.11869700	1.24797900

C	-2.27471200	-1.46391100	-0.32604900
C	-3.42040200	-0.71282900	-0.10904400
C	-2.26136200	-2.84937800	-0.21174500
C	-4.59014000	-1.38039700	0.24929900
H	-3.39135500	0.36706300	-0.22628800
C	-3.43742400	-3.49856400	0.15704600
H	-1.35142900	-3.40384300	-0.41379500
C	-4.60146600	-2.76711600	0.38796100
H	-5.49572000	-0.80650500	0.42163700
H	-3.44356500	-4.58051700	0.25260000
H	-5.51710200	-3.27856900	0.66987600

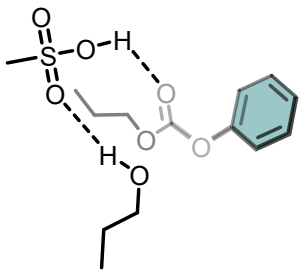
Int4



S	3.65730200	-0.67804600	-0.10844500
O	3.13149500	0.43267900	0.69547600
O	3.44575300	-2.02772000	0.37455900
C	5.39230600	-0.40550300	-0.37576700
H	5.88212700	-0.51470700	0.59341500
H	5.75352900	-1.16119900	-1.07450300
H	5.53378400	0.59992800	-0.77252900
O	3.15354600	-0.51250200	-1.60238300
H	2.17635200	-0.26472400	-1.63325800
C	-1.84649800	1.30689900	-1.64150300
H	-1.62478900	1.24460800	-2.71191700
H	-1.22058000	2.07835400	-1.18919900
C	-3.31916300	1.53855400	-1.37707400
H	-3.47659500	1.57305200	-0.29335000
H	-3.55795000	2.53810000	-1.76119100
C	-4.22674500	0.48917500	-2.01747600
H	-4.01786200	-0.50765000	-1.61611700
H	-5.27993200	0.71653900	-1.82379300
H	-4.08526600	0.45462100	-3.10459000
O	-1.50508100	0.03192600	-1.04222600
H	1.48435100	0.62268500	1.40666000
C	-0.25888300	-0.36288900	-1.13237600

O	0.56563300	0.73503900	1.72335700
O	-0.01497600	-1.54103600	-0.56902900
O	0.63518500	0.25042700	-1.69603600
C	0.05931300	1.93377500	1.34496800
C	0.78088600	2.84514500	0.56779400
C	-1.24585200	2.23597600	1.74288900
C	0.19196900	4.05279900	0.20054600
H	1.78905000	2.59724400	0.24917800
C	-1.82207800	3.44480500	1.36648400
H	-1.79269800	1.51359000	2.34168200
C	-1.11051600	4.36127600	0.59151700
H	0.75938800	4.75576900	-0.40337100
H	-2.83734700	3.67165900	1.68122600
H	-1.56290100	5.30493000	0.30178500
C	-1.03590500	-2.22637600	0.10628200
C	-1.71275200	-3.22870000	-0.57109100
C	-1.28333600	-1.92762800	1.43733600
C	-2.68863900	-3.95237800	0.11124100
H	-1.47363800	-3.43667100	-1.60923600
C	-2.26148800	-2.65968000	2.10597100
H	-0.71823000	-1.13598600	1.91926800
C	-2.96540800	-3.66733700	1.44720700
H	-3.22870200	-4.74192200	-0.40280700
H	-2.46997800	-2.44238600	3.14944700
H	-3.72464700	-4.23508200	1.97688000

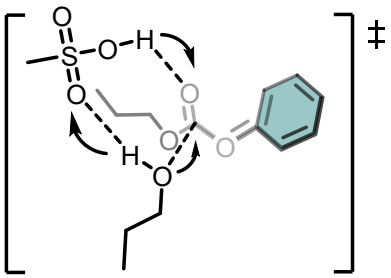
Int5



S	2.32642300	-2.13236600	-0.13687900
O	1.76499100	-1.61762500	1.11288700
O	3.18862300	-3.29171600	-0.10295700
C	3.14758400	-0.78491100	-0.96195300
H	3.97005300	-0.46534900	-0.31986000
H	3.52120000	-1.15135500	-1.91894500
H	2.43245900	0.02891300	-1.09762200
O	1.13211200	-2.48646200	-1.13579900
H	0.50469800	-1.72205400	-1.19552600

C	-1.47371000	-0.99004500	2.69185300
H	-0.80724500	-0.61429400	3.48445700
H	-1.62837800	-2.06480300	2.86573200
C	-2.80302000	-0.25456900	2.74598800
H	-3.44377700	-0.63537000	1.93990600
H	-3.29714200	-0.51263600	3.69168700
C	-2.65910900	1.26169000	2.62527200
H	-2.20120900	1.53890800	1.67216500
H	-3.63517300	1.75512100	2.68715500
H	-2.03206000	1.65900300	3.43352600
O	-0.88639900	-0.78075900	1.41870500
H	0.00549600	-1.17026000	1.39971700
C	-0.99377800	0.61720500	-0.92869100
O	-2.29317200	0.45185200	-0.90941700
O	-0.70050100	1.83023300	-0.45596500
O	-0.16914400	-0.16738600	-1.36471100
C	0.65204900	2.11099200	-0.24557500
C	1.36284300	2.78561900	-1.22753900
C	1.22213500	1.75588800	0.96838300
C	2.69665800	3.10868700	-0.98363900
H	0.87691500	3.04809800	-2.16180600
C	2.55580200	2.08319100	1.19900600
H	0.62628900	1.21626800	1.69654400
C	3.29313500	2.75874200	0.22735300
H	3.26747400	3.63731400	-1.74125400
H	3.01838300	1.80230000	2.14026800
H	4.33209800	3.01434900	0.41378700
C	-2.77421200	-0.86623200	-1.25174800
H	-2.40877500	-1.12214500	-2.25194600
H	-2.35648200	-1.56375900	-0.52058600
C	-4.28827200	-0.82502900	-1.20208400
H	-4.64216800	-1.85077000	-1.36438100
H	-4.60217200	-0.53791400	-0.19153600
C	-4.90712700	0.11517300	-2.23532700
H	-5.99994700	0.09007600	-2.17800800
H	-4.58402700	1.14762000	-2.07024400
H	-4.61722100	-0.17289900	-3.25290600

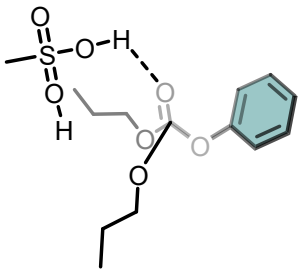
TS3



S	-0.16323500	2.01344200	1.70069800
O	0.14958100	0.63391400	2.17558300
O	0.94636100	2.95315000	1.78235600
C	-1.47942300	2.61322600	2.74267200
H	-1.10071800	2.66355900	3.76487900
H	-1.76345300	3.60595000	2.39004700
H	-2.32182200	1.92335200	2.67461300
O	-0.77371900	1.95012200	0.31288400
H	-0.94106400	0.77577200	-0.28359900
C	0.92663100	-2.46471800	1.20639700
H	1.83095600	-1.84692200	1.27639800
H	1.03086100	-3.14430000	0.35682300
C	0.68238800	-3.23514900	2.49454500
H	-0.21642100	-3.85033300	2.36825000
H	1.52718800	-3.92469600	2.62373200
C	0.54660800	-2.34242100	3.72764800
H	-0.33401400	-1.69616000	3.66044000
H	0.44857100	-2.94953100	4.63341000
H	1.42096400	-1.69237500	3.84503000
O	-0.19190000	-1.62249500	0.89222300
H	-0.13700700	-0.77685100	1.42301900
C	-0.34055500	-1.10471400	-0.89922000
O	0.92233900	-0.93439300	-1.24574300
O	-0.81502300	-2.29602900	-1.31746800
O	-1.19350100	-0.15845700	-0.80252700
C	-0.67701900	-2.62944100	-2.66012100
C	-0.47656600	-3.97500400	-2.93869200
C	-0.79692500	-1.68599100	-3.67481700
C	-0.38644900	-4.38490900	-4.26621900
H	-0.39681000	-4.68170000	-2.11897500
C	-0.69242400	-2.10953700	-4.99752300
H	-0.97982100	-0.64247300	-3.43942900
C	-0.48814600	-3.45460100	-5.29896700
H	-0.23114300	-5.43593700	-4.49114100
H	-0.78219700	-1.37929800	-5.79634500
H	-0.41327800	-3.77632500	-6.33310300
C	1.57048000	0.33928400	-1.03412400

H	0.96233000	1.12894800	-1.48475200
H	1.63915100	0.51645500	0.04356100
C	2.94416300	0.26089500	-1.66681000
H	3.50203000	-0.56445300	-1.20918500
H	2.83585400	0.02623500	-2.73206500
C	3.69783100	1.57857000	-1.48156000
H	3.81418600	1.82501600	-0.42071000
H	4.69498600	1.51708400	-1.92754300
H	3.16658300	2.41023600	-1.95729200

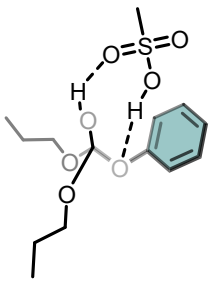
Int6



S	-1.92256500	1.93365900	-1.02870000
O	-1.59125000	1.70716000	0.51625600
O	-2.78815800	3.08561500	-1.12092500
C	-2.83023800	0.46188500	-1.44631600
H	-3.71216200	0.41190700	-0.80704600
H	-3.11531700	0.54524900	-2.49695800
H	-2.18455300	-0.40443400	-1.28715300
O	-0.65381500	1.91638200	-1.76518800
H	0.31308500	0.39198500	-1.48165300
C	1.45670400	0.57101500	1.95924000
H	2.53643500	0.49107800	1.79825700
H	1.14684600	-0.25858500	2.60492400
C	1.09650900	1.91985300	2.55644500
H	0.01396800	1.97461000	2.72754800
H	1.56913000	1.97010000	3.54519900
C	1.55398100	3.09656500	1.69493500
H	1.07876100	3.07946700	0.70940900
H	1.30008900	4.04833900	2.17137200
H	2.64063000	3.07202200	1.54738700
O	0.79243700	0.44943800	0.69119200
H	-0.73763600	1.20166200	0.60166400
C	1.09966400	-0.71030300	-0.07268100
O	2.45476100	-0.90413400	-0.14615800
O	0.64117800	-1.86343200	0.55866600
O	0.48699900	-0.55194200	-1.28529300
C	-0.72709900	-2.06452300	0.56355000

C	-1.27920400	-2.92110800	-0.38561900
C	-1.52565800	-1.47284600	1.53729900
C	-2.64664100	-3.18005900	-0.36094800
H	-0.62959500	-3.36503000	-1.13233200
C	-2.89552400	-1.73140000	1.55120100
H	-1.07955400	-0.81809400	2.27830600
C	-3.45892500	-2.58352100	0.60454800
H	-3.07925700	-3.84953900	-1.09888600
H	-3.51951000	-1.26531300	2.30817200
H	-4.52545900	-2.78801900	0.62156400
C	3.16785800	0.06467400	-0.91726500
H	2.90341900	1.07562500	-0.57832000
H	2.88007400	-0.03457300	-1.97087400
C	4.65233600	-0.19544000	-0.73288500
H	5.19379400	0.59552100	-1.26714400
H	4.90161200	-0.08954600	0.33042400
C	5.09018800	-1.56829700	-1.24077800
H	4.57134300	-2.36695200	-0.70283300
H	4.86611300	-1.67984700	-2.30831800
H	6.16785700	-1.70783200	-1.10625000

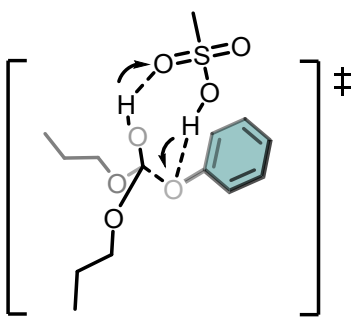
In7



S	2.73259500	-1.69948100	-0.13715700
O	1.55269900	-1.79917900	-1.20082300
O	3.87323700	-1.01978500	-0.71468500
C	3.11648000	-3.42542100	0.04329400
H	3.39349300	-3.81831400	-0.93590500
H	3.95752500	-3.49582400	0.73535700
H	2.24076900	-3.93857800	0.44130200
O	2.18384600	-1.21195200	1.13148300
H	0.96965400	0.11314600	1.50037100
C	-1.80792900	2.20467800	-0.93879100
H	-1.87524900	1.34877900	-1.62094200
H	-1.14478600	2.95230200	-1.38965200
C	-3.18528400	2.78404200	-0.67076400
H	-3.08606800	3.63809400	0.01027400
H	-3.56097400	3.17971700	-1.62328700

C	-4.17019200	1.76561700	-0.09805000
H	-3.84513100	1.41944300	0.88660000
H	-5.16760600	2.20589400	0.00562100
H	-4.25221900	0.88423900	-0.74580700
O	-1.25416500	1.78060600	0.31098400
H	0.80201200	-1.19104100	-0.95199100
C	-0.17799600	0.94141900	0.23402600
O	-0.52553200	-0.30813100	-0.39143300
O	0.82058200	1.36084900	-0.62566000
O	0.23835400	0.76319000	1.52266300
C	-1.69281500	-0.96403700	-0.03914900
C	-2.31991700	-1.65594400	-1.07171400
C	-2.21283100	-0.97375200	1.25217600
C	-3.48711900	-2.36813100	-0.81159800
H	-1.88868900	-1.62334800	-2.06804000
C	-3.38869500	-1.68045400	1.49373000
H	-1.71620100	-0.42561800	2.04300300
C	-4.02957200	-2.37808300	0.47200800
H	-3.97606700	-2.90783600	-1.61748800
H	-3.80494700	-1.68311700	2.49709800
H	-4.94492500	-2.92592300	0.67477800
C	1.50817600	2.55918300	-0.23674500
H	1.52258900	3.19429700	-1.12988000
H	0.93617500	3.07483100	0.54245100
C	2.92450500	2.26091700	0.22730800
H	2.88634600	1.62974800	1.12152100
H	3.43804200	1.67954500	-0.54577800
C	3.69108600	3.54890000	0.52639600
H	3.20411300	4.12900400	1.31962300
H	4.71091900	3.32594500	0.85476100
H	3.76015100	4.18792400	-0.36246500

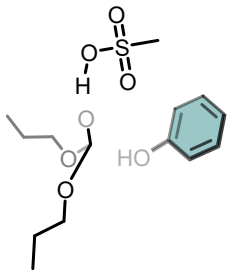
TS4



S	-1.59292200	2.57506500	0.08358800
O	-0.44691200	2.39890800	-0.88945100
O	-2.88729200	2.15123100	-0.44106100

C	-1.65446500	4.33356100	0.35990100
H	-1.87132200	4.81619900	-0.59424100
H	-2.45136900	4.53025300	1.07883800
H	-0.69025300	4.66216500	0.74948100
O	-1.22781200	1.96922500	1.40225400
H	-0.63574700	0.48795100	1.46156900
C	1.49200300	-2.38612200	1.13354800
H	0.83745600	-2.72994300	1.94134300
H	2.09478900	-1.55199900	1.49959500
C	2.36326800	-3.50810400	0.60515900
H	2.99827500	-3.11309500	-0.19693500
H	3.03361800	-3.80518900	1.42159900
C	1.56985700	-4.71642500	0.11001500
H	0.91643400	-4.44242900	-0.72357100
H	2.24260900	-5.50935500	-0.23217000
H	0.94349800	-5.12918200	0.90994000
O	0.65568100	-1.94016700	0.04061800
H	0.27401400	1.25287000	-0.77009500
C	-0.03497100	-0.81022800	0.17503100
O	0.88253600	0.35170300	-0.64775500
O	-1.08923900	-0.72507200	-0.65115300
O	-0.15347700	-0.39675600	1.42463200
C	2.14941800	0.61067400	-0.13915200
C	3.22185100	-0.05598900	-0.71922400
C	2.31697600	1.48322600	0.93058300
C	4.49892700	0.14717300	-0.20356500
H	3.03952400	-0.72160300	-1.55653100
C	3.60148900	1.68507700	1.42994500
H	1.45465300	1.98301400	1.36073800
C	4.68945500	1.01526000	0.87131700
H	5.34631700	-0.36858000	-0.64559900
H	3.74989100	2.36401600	2.26434200
H	5.68697200	1.17432900	1.26996100
C	-2.35892500	-1.16032100	-0.11885400
H	-2.24296500	-2.17310900	0.28752000
H	-2.66444500	-0.47750500	0.68044800
C	-3.35497800	-1.12187300	-1.25895400
H	-3.02158500	-1.80299600	-2.05055300
H	-3.35950400	-0.10658700	-1.66724900
C	-4.75441900	-1.50248900	-0.77730200
H	-5.46605700	-1.48154200	-1.60832000
H	-4.77449700	-2.51110800	-0.34628000
H	-5.11119300	-0.79945700	-0.01627900

In8



S	-3.10941900	-1.10768200	-0.58990600
O	-2.19836300	-1.88705300	0.25358400
O	-3.88992400	-0.06071700	0.04506000
C	-4.19035100	-2.22209800	-1.45042300
H	-4.83281400	-2.68213800	-0.69758300
H	-4.78364400	-1.64465500	-2.16045100
H	-3.58610300	-2.97393200	-1.95845800
O	-2.30847100	-0.53594100	-1.83300800
H	-1.43767300	-0.11790500	-1.55044900
C	2.68786000	0.54544600	-1.36963300
H	2.36402500	0.63186200	-2.41243700
H	2.47202000	-0.46410300	-1.01260900
C	4.15119100	0.89876800	-1.20222500
H	4.40560600	0.83176600	-0.13850200
H	4.72833400	0.11742100	-1.71248500
C	4.51692100	2.27483000	-1.75641500
H	3.96358600	3.06568200	-1.24049200
H	5.58624900	2.47370200	-1.63095400
H	4.28616700	2.34296300	-2.82648900
O	1.92363500	1.48270800	-0.57766500
H	-0.82745600	-1.22324000	1.29139200
C	0.61891600	1.31503100	-0.56248400
O	-0.09547400	-0.76340200	1.74401700
O	0.06430900	2.19842200	0.23895000
O	0.02898600	0.46592700	-1.22253500
C	1.09177600	-1.33127300	1.41836800
C	1.18893400	-2.42832300	0.55674700
C	2.24815000	-0.77232200	1.96872800
C	2.44058200	-2.96536700	0.26317000
H	0.28770500	-2.84980500	0.12016100
C	3.49091200	-1.31827900	1.66599500
H	2.15317900	0.08716900	2.62501700
C	3.59862800	-2.41673300	0.81200700
H	2.50692700	-3.82025900	-0.40452700
H	4.38456400	-0.87948400	2.10201400

H	4.57136500	-2.84046600	0.58095900
C	-1.35913100	2.09101600	0.44474000
H	-1.86544500	2.14747100	-0.52454900
H	-1.56379300	1.12110800	0.90368900
C	-1.78228100	3.22419800	1.35635100
H	-1.50958800	4.18029400	0.89406400
H	-1.22451600	3.14776800	2.29647400
C	-3.28649100	3.17143100	1.62578900
H	-3.58640000	3.98663200	2.29152600
H	-3.86068800	3.26347000	0.69719300
H	-3.57217700	2.22408500	2.09448500

Reference

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16 Rev. A.03, Wallingford, CT, 2016

2. CYLview, b. L., C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org).