Supporting Information

for

High T_g Aliphatic Polyesters by the Polymerization of Spirolactide Derivatives

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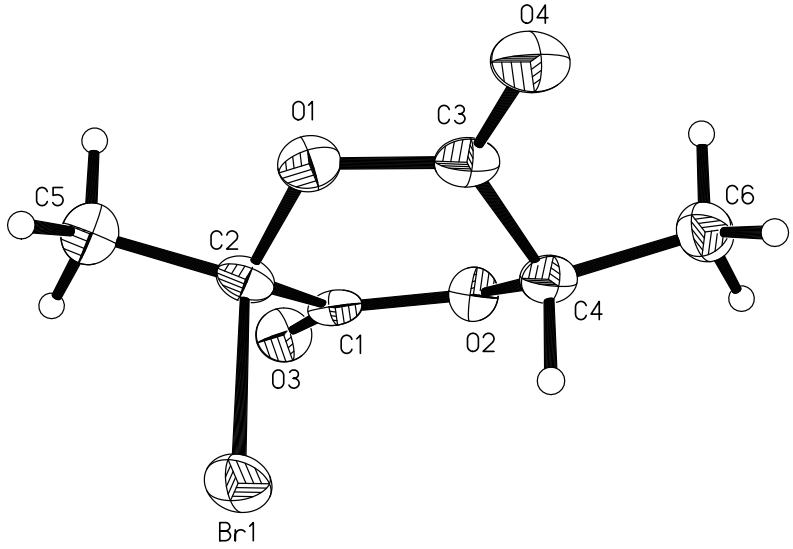


Figure S1. Crystal structures of (3*R*, 6*S*)-3-Bromo-3,6-dimethyl-1,4-dioxane-2,5-dione (bromo-lactide).

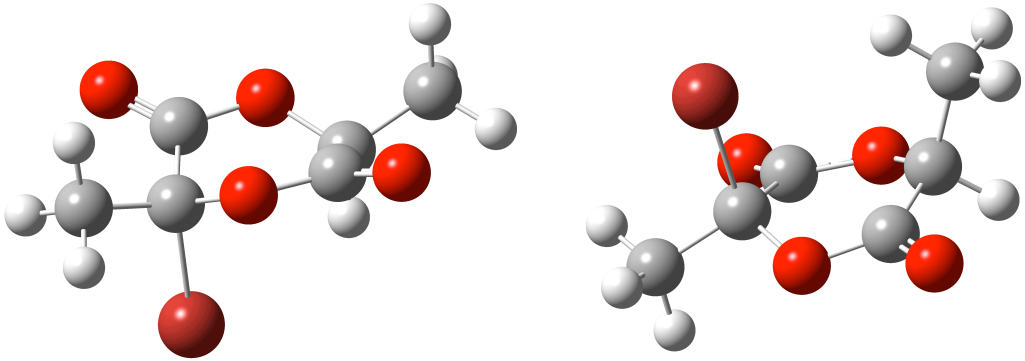


Figure S2. Stereostructures computed at the M06-L/6-31G(d) level for (3*R*,6*S*)- (left) and (3*S*,6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione (right).

Table S1. Computed electronic energies and 298 K thermal enthalpic and free energy contributions (a.u.) for bromination of lactide radical to (3*R*,6*S*) and (3*S*,6*S*) bromolactide products.

	TS Structure		Product	
	(3*R*,6*S*)	(3*S*,6*S*)	(3*R*,6*S*)	(3*S*,6*S*)
E	-5676.719 47	-5676.716 93	-3105.238 44	-3105.235 16
	-5682.007 62	-5682.003 96	-3107.897 39	-3107.893 80
H	0.143 00	0.142 94	0.142 12	0.142 21
G	0.084 65	0.084 58	0.093 33	0.093 26
Composite *G*	-5681.922 97	-5681.919 38	-3107.804 05	-3107.800 54

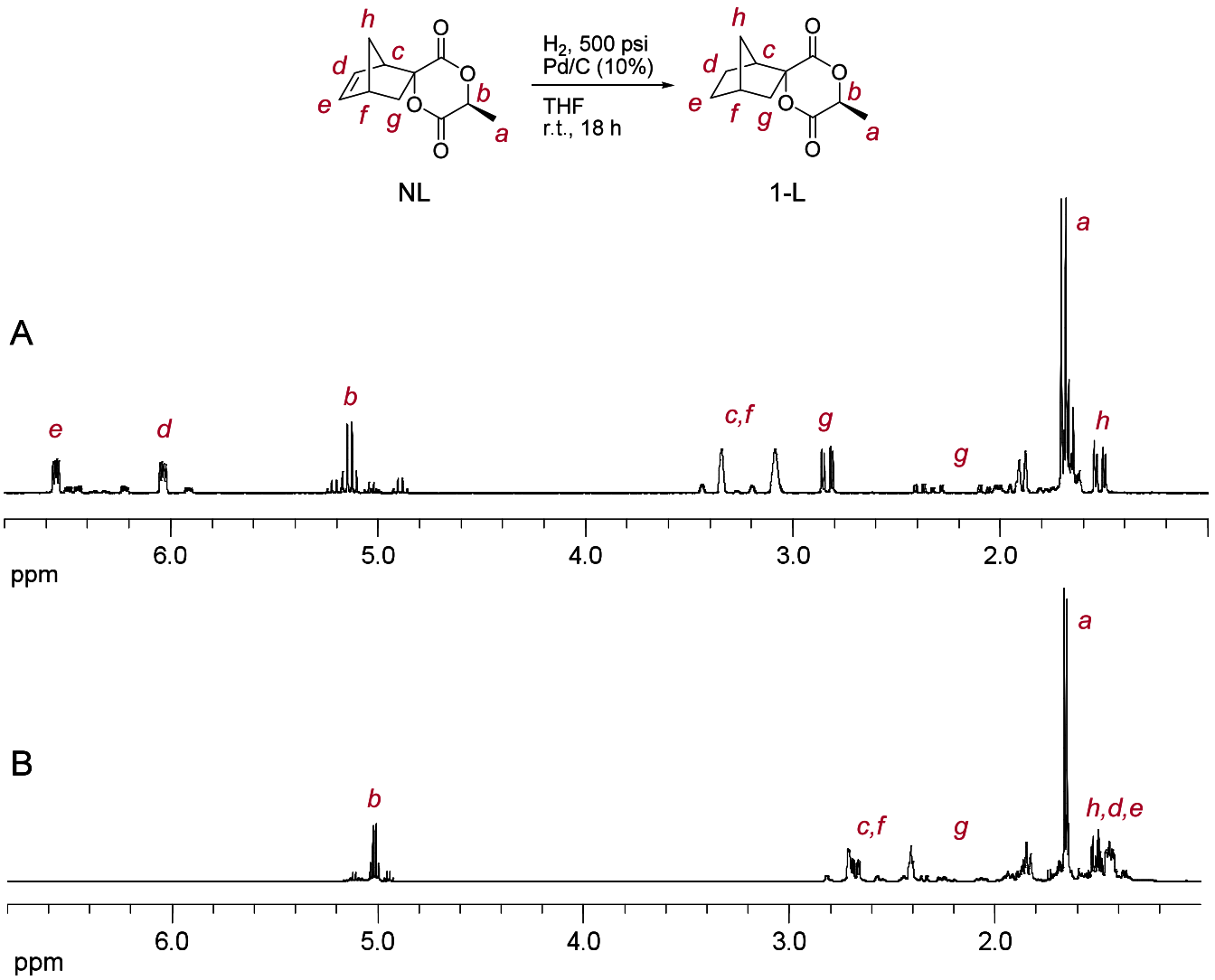


Figure S3a. [1]H NMR of spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hept[5]ene] (norbornane-lactide, NL) (A) and spiro[6-methyl-1,4-dioxane-2,5-dione-3,2′-bicyclo[2.2.1]hept[5]ane] (norbornane-lactide, **1-L**) (B) in $CDCl_3$.

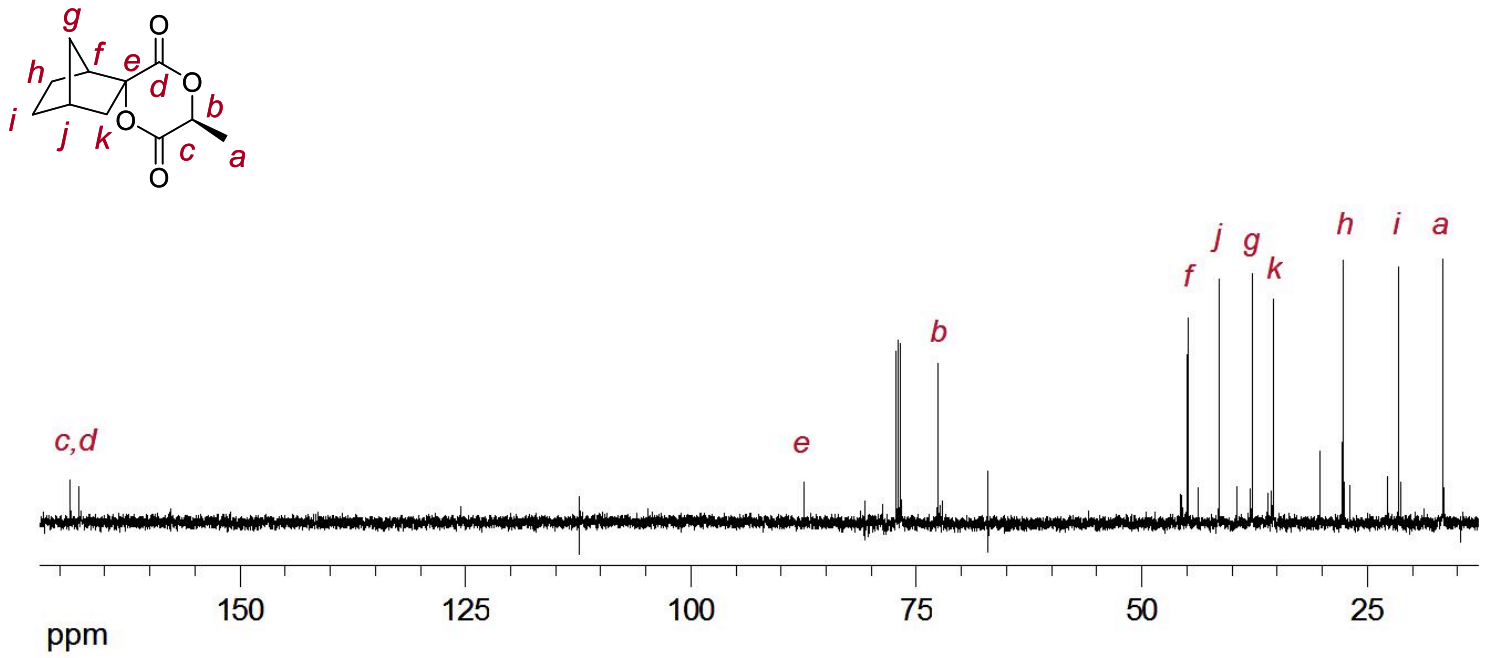


Figure S3b. 125 MHz ^{13}C NMR of **1-L** in $CDCl_3$.

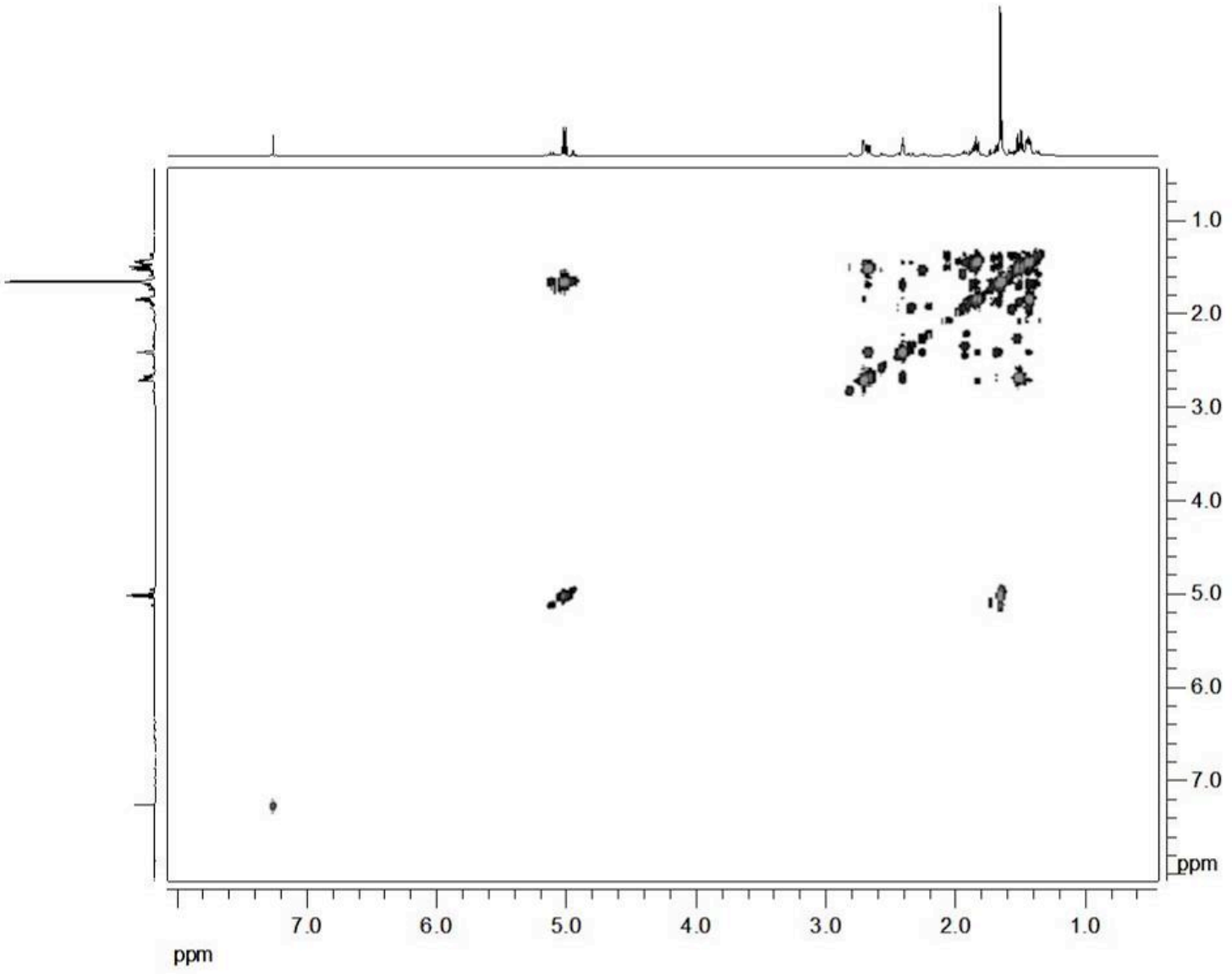


Figure S3c. 500 MHz ^{1}H–^{1}H COSY of **1-L** in $CDCl_3$.

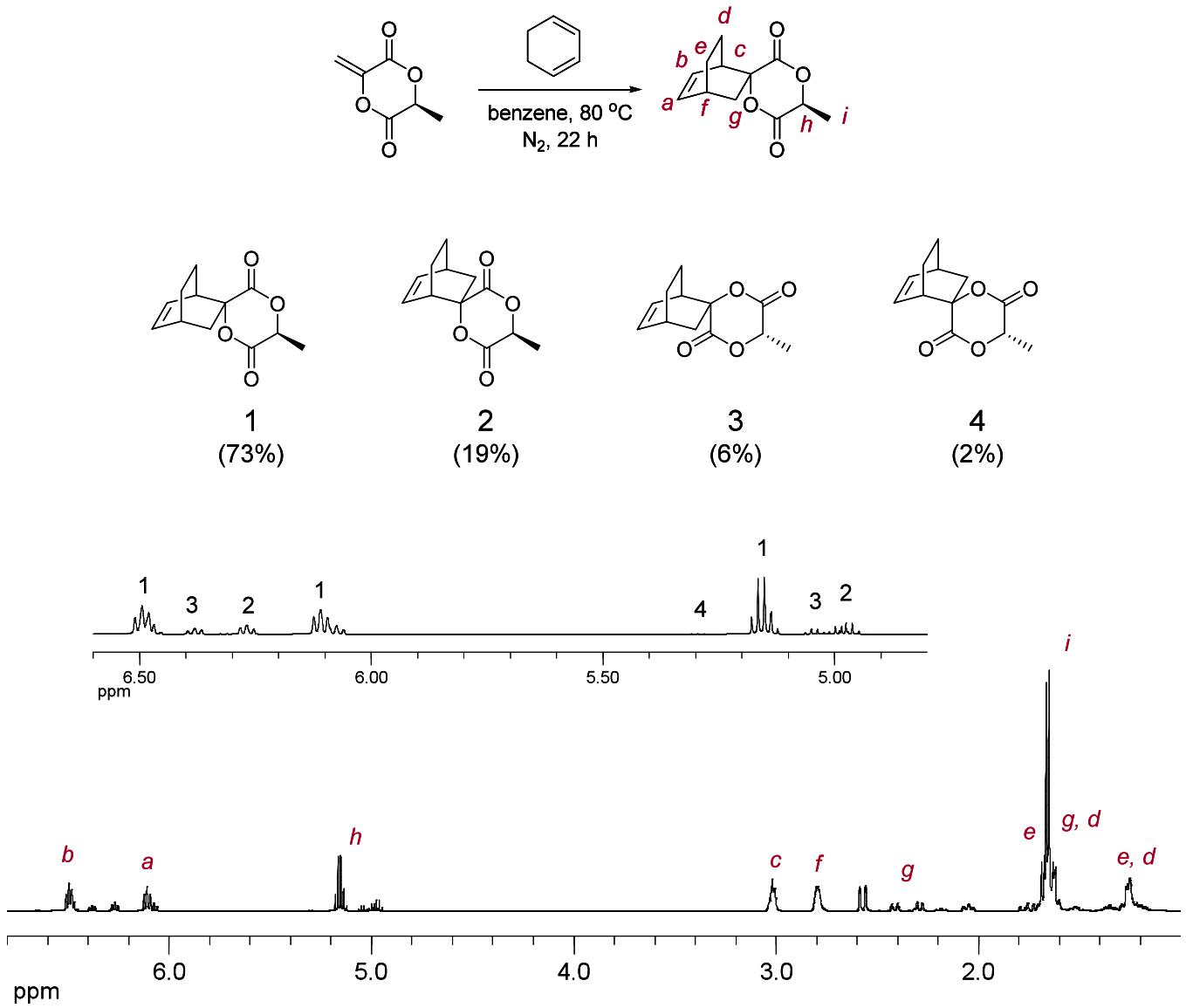


Figure S4a. ^{1}H NMR of spiro[6-methyl-1,4-dioxane-2,5-dione-3,2′-bicyclo[2.2.2]oct[5]ene] (cyclohexadiene-lactide, **2-L**) in $CDCl_3$.

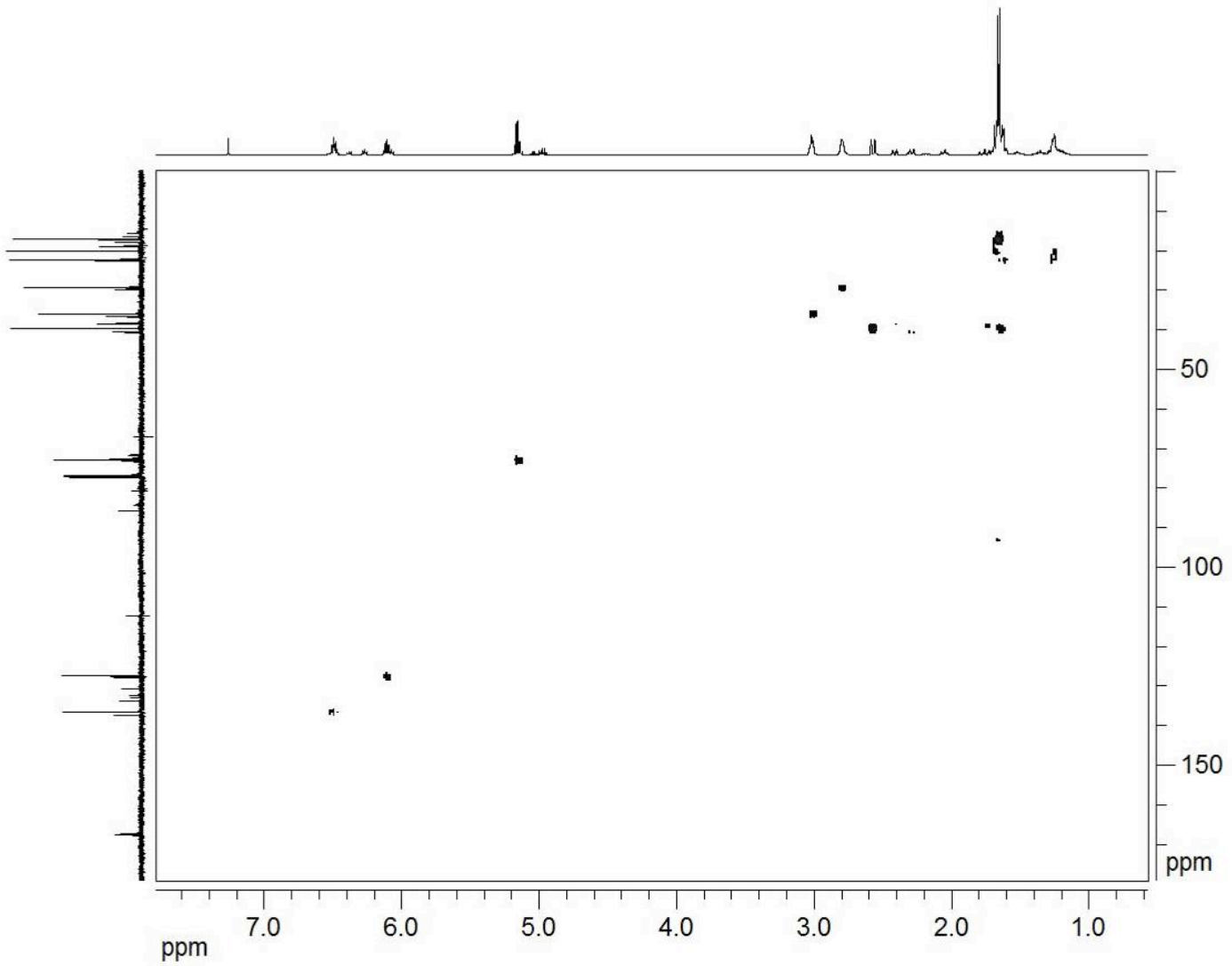


Figure S4b. 500 MHz HMQC of **2-L** in $CDCl_3$.

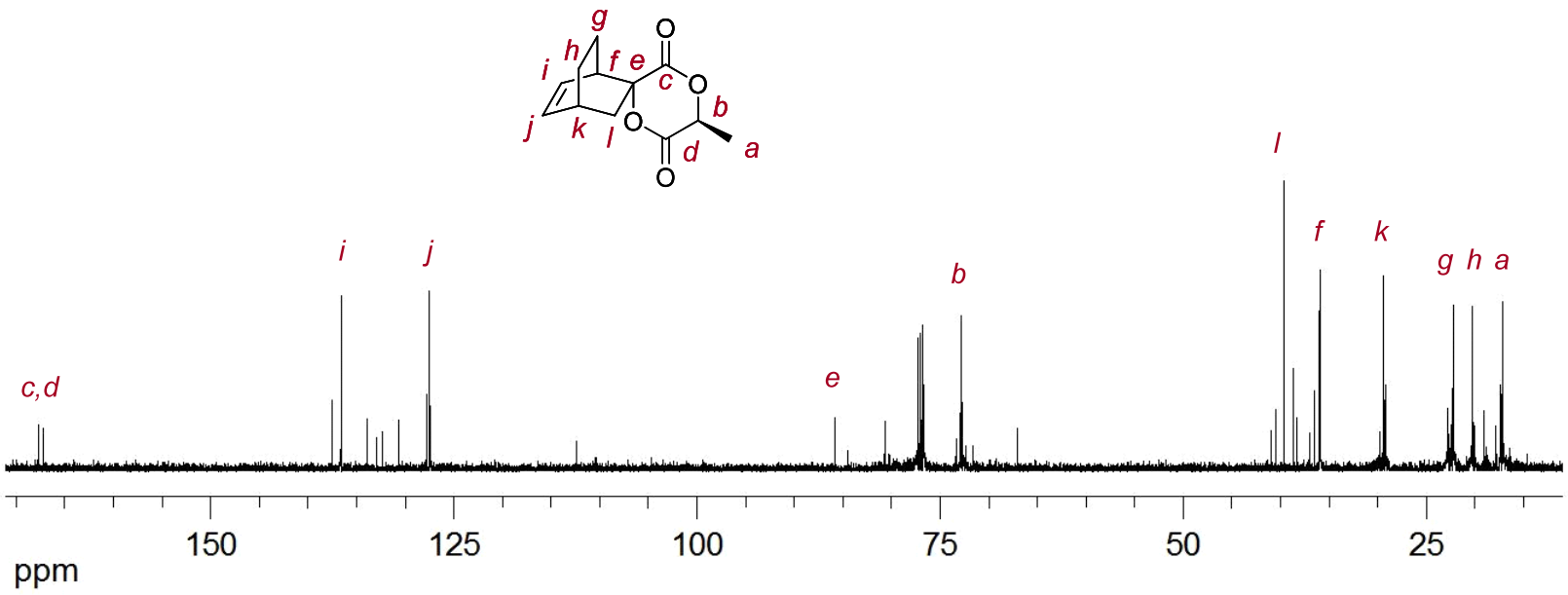


Figure S4c. 125 MHz ^{13}C NMR of **2-L** in $CDCl_3$.

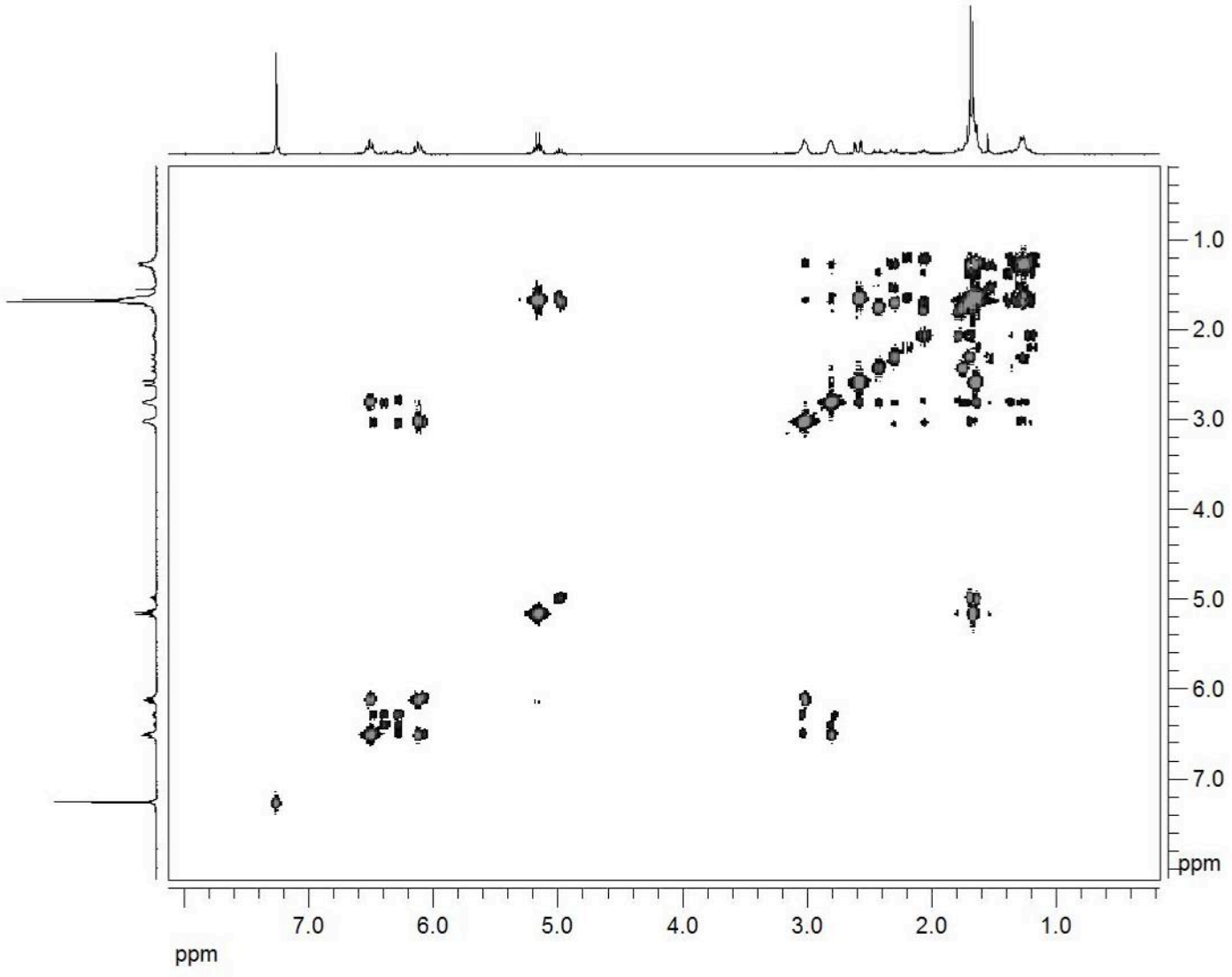


Figure S4d. 500 MHz ^{1}H–^{1}H COSY of **2-L** in $CDCl_3$.

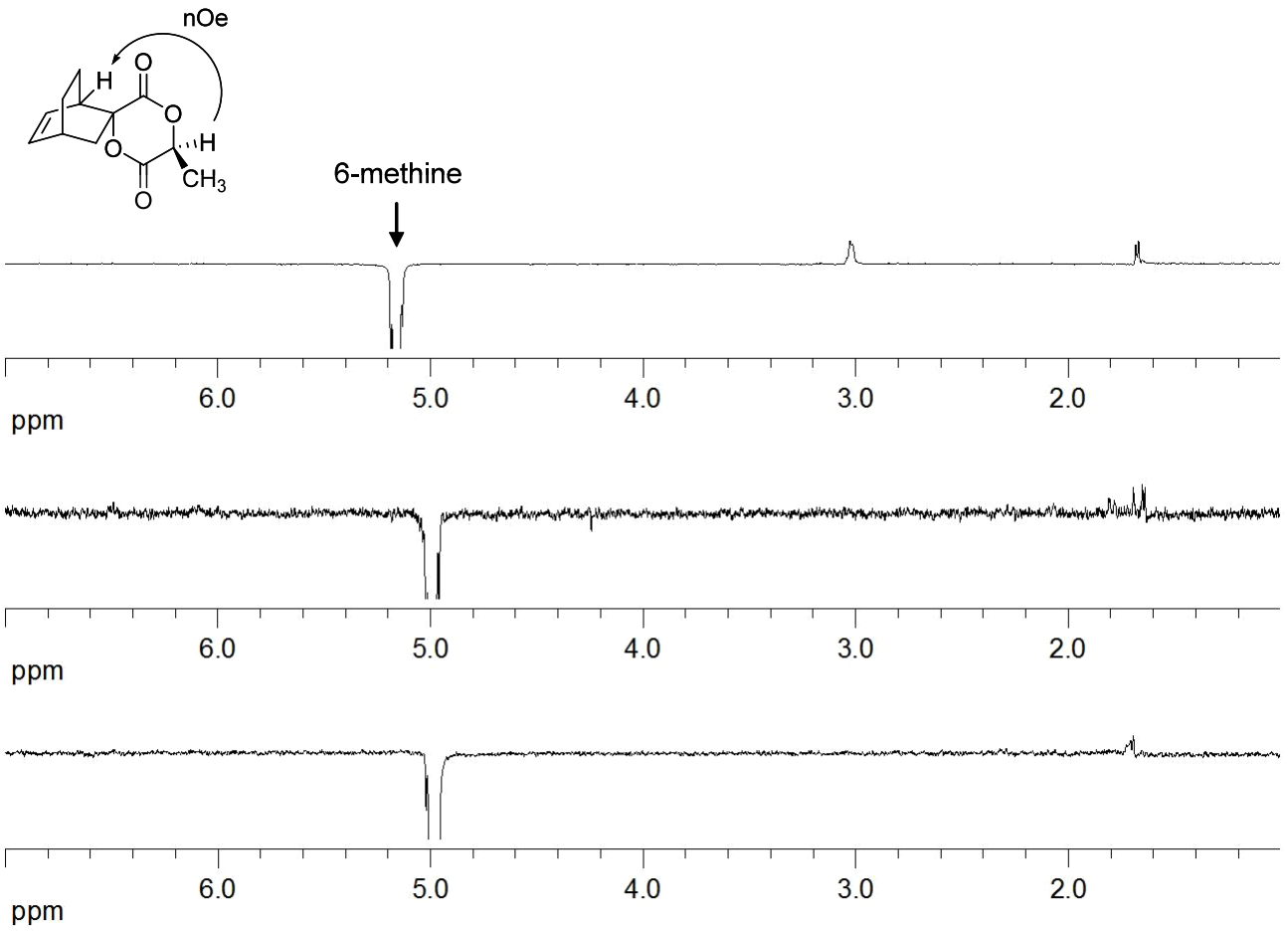


Figure S4e. 500 MHz 1D NOE spectrum of **2-L**.

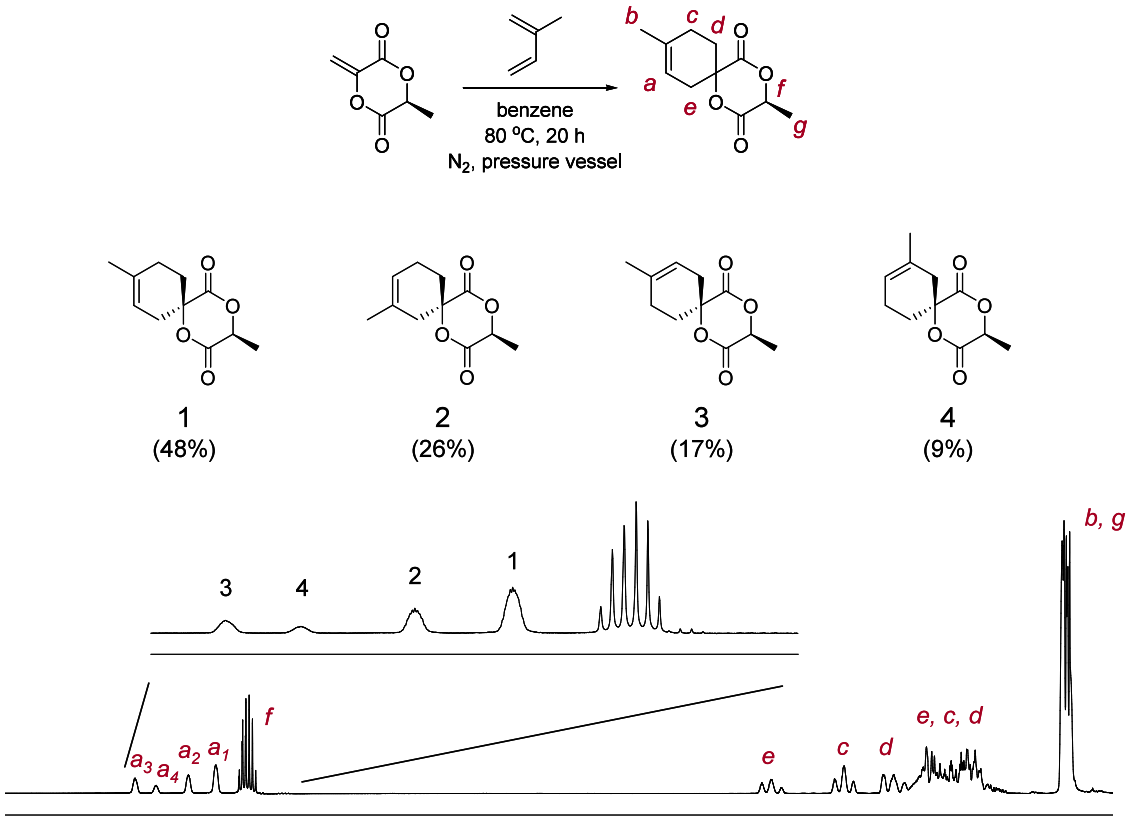
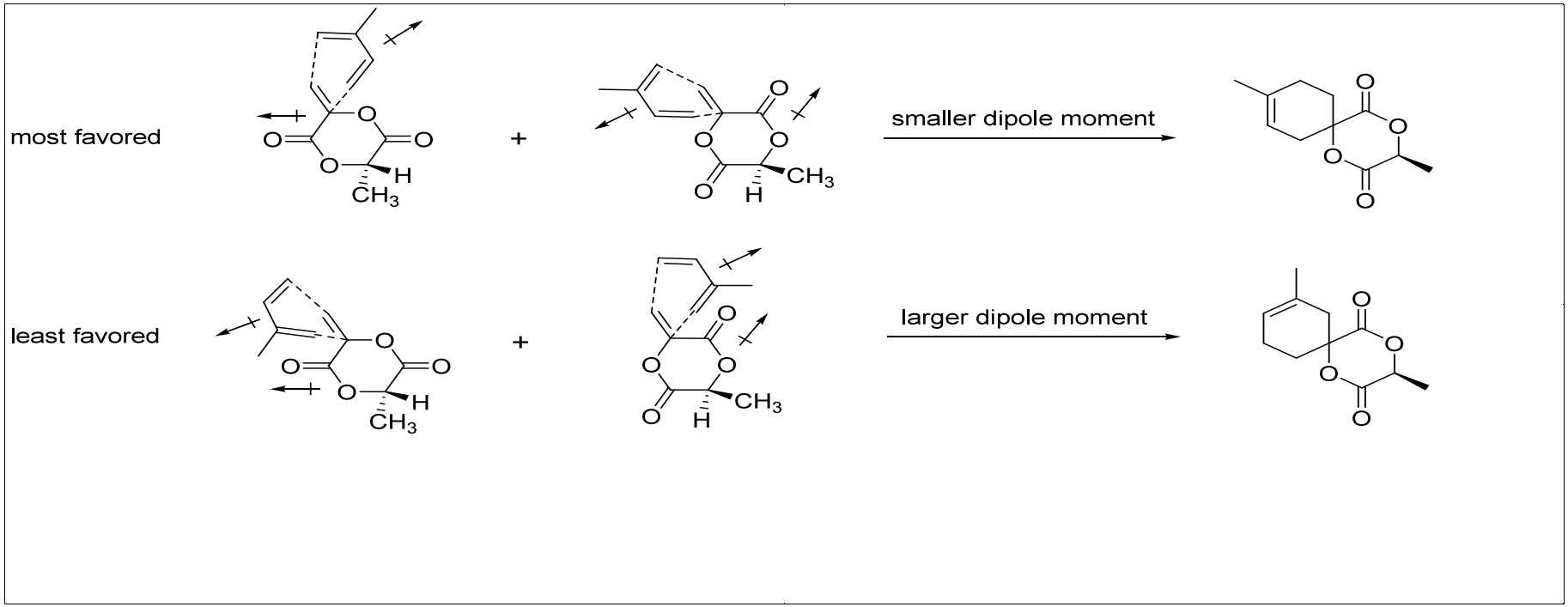


Figure S5a. ^{1}H NMR of spiro[6-methyl-1,4-dioxane-2,5-dione-3,4′-(1-methyl)cyclohex-1-ene] (isoprene-lactide, **3-L**).

Scheme S1. Schematic explanation of the *para* selectivity in the Diels-Alder reaction of exomethylene-lactide and isoprene



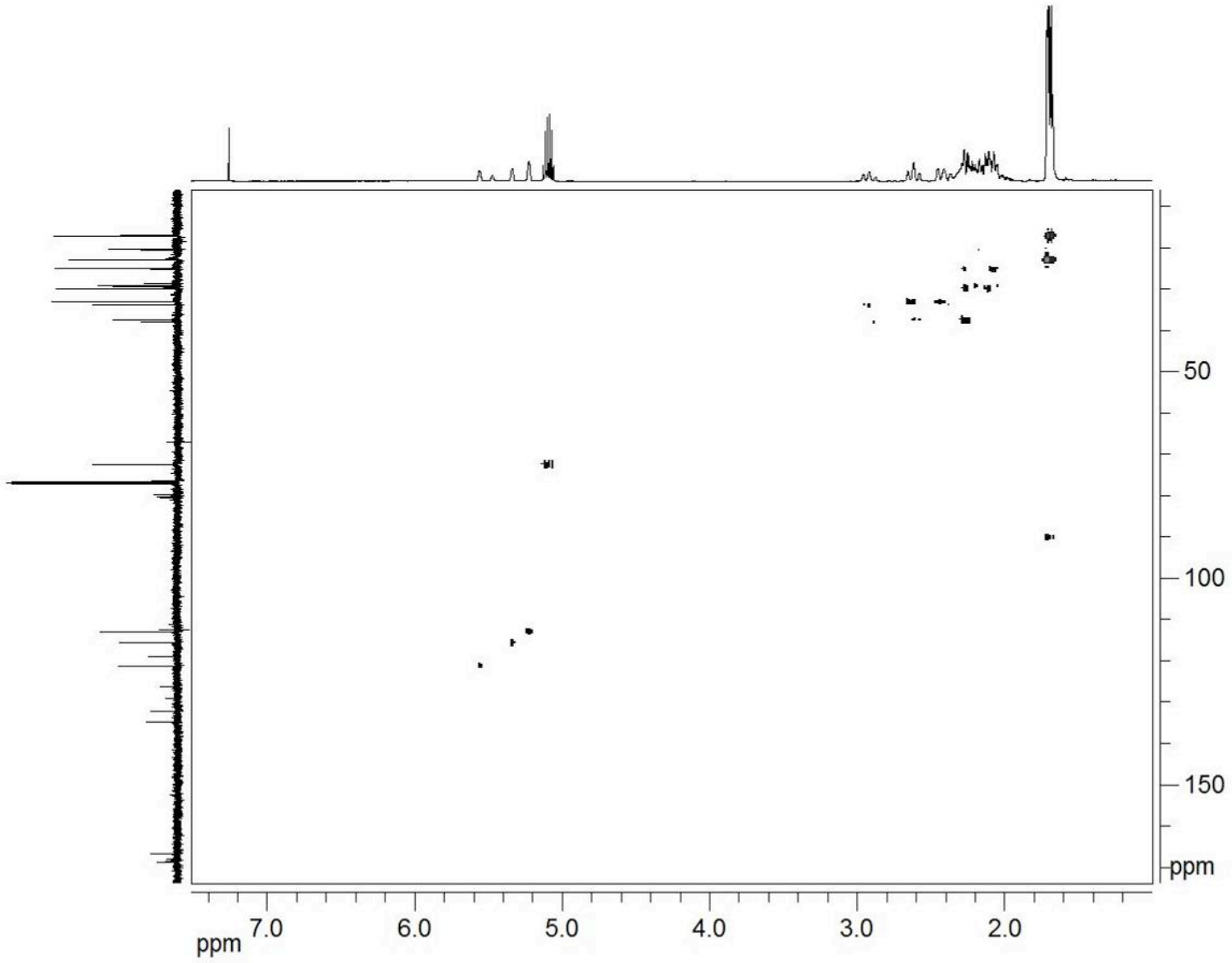


Figure S5b. 500 MHz HMQC spectrum of **3-L** in $CDCl_3$.

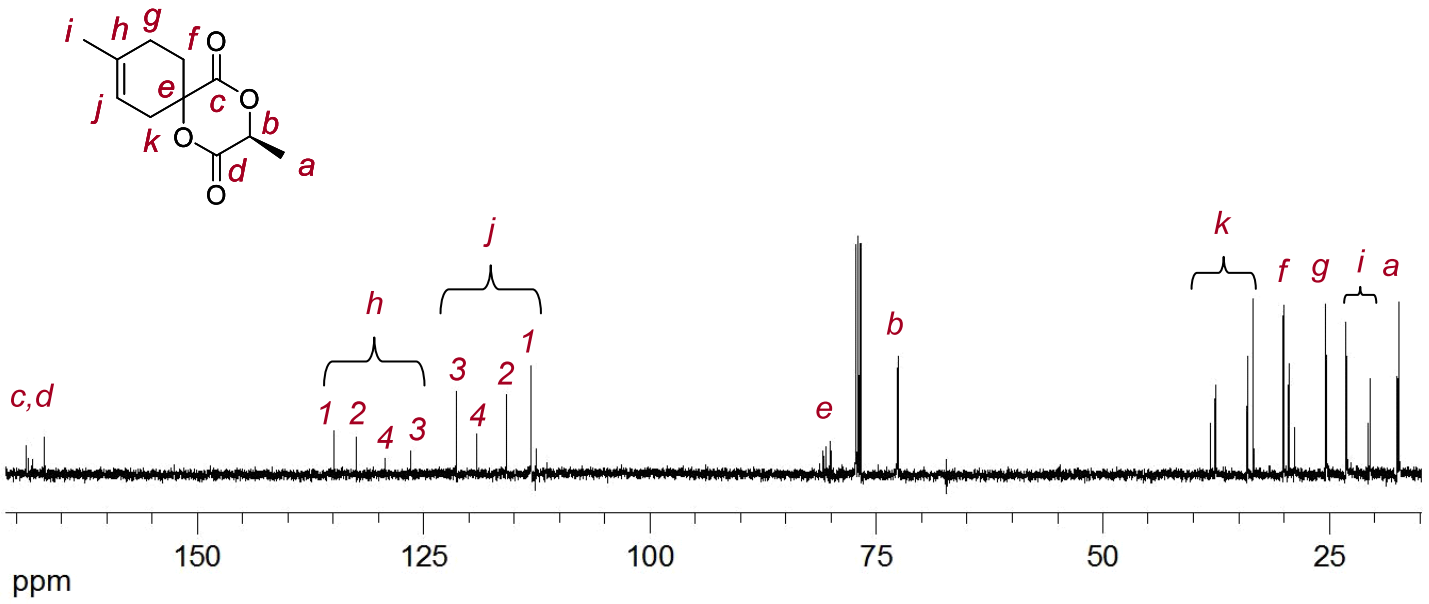


Figure S5c. 125 MHz ^{13}C NMR of **3-L** in $CDCl_3$.

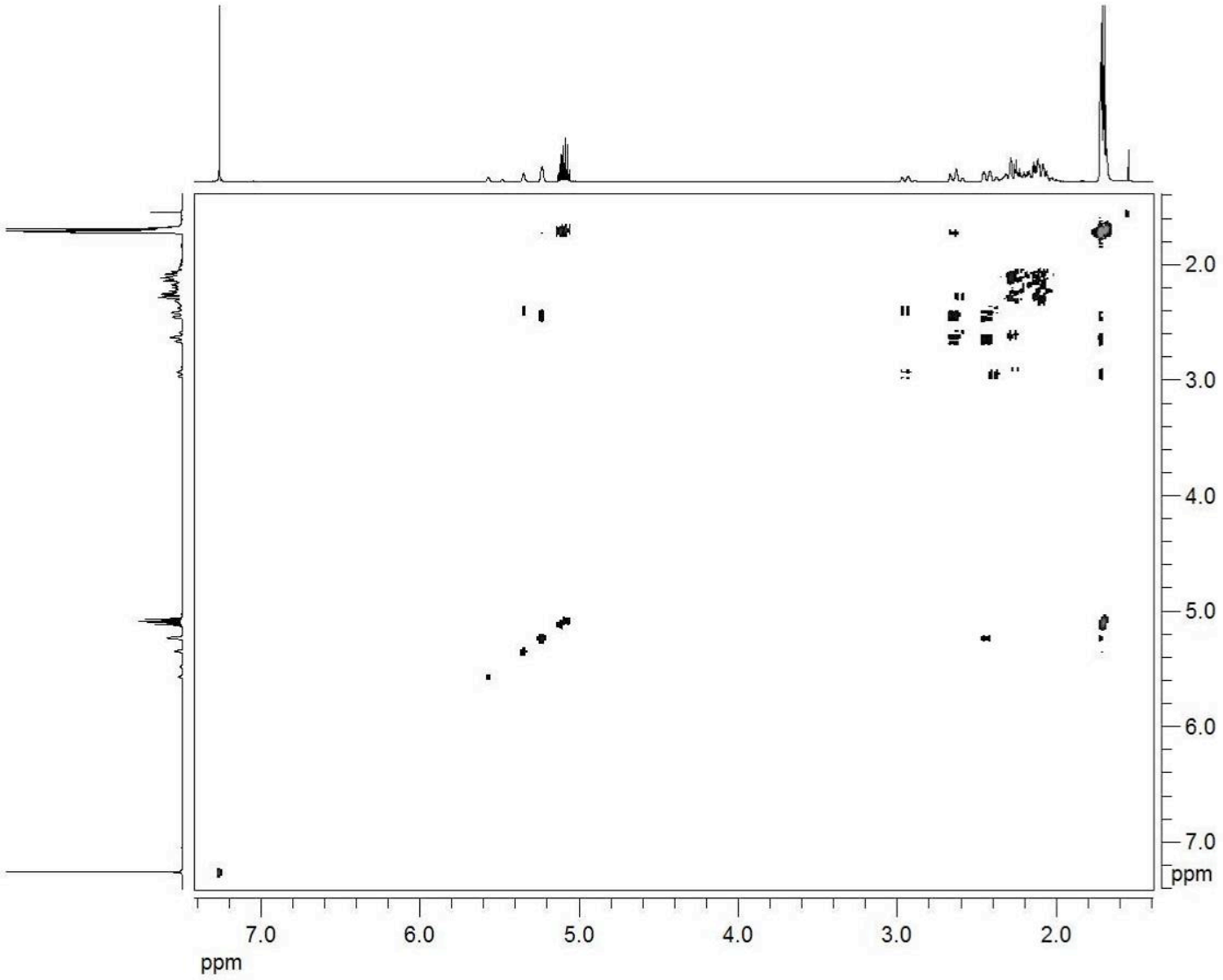


Figure S5d. 500MHz ^{1}H–^{1}H COSY of **3-L** in $CDCl_3$.

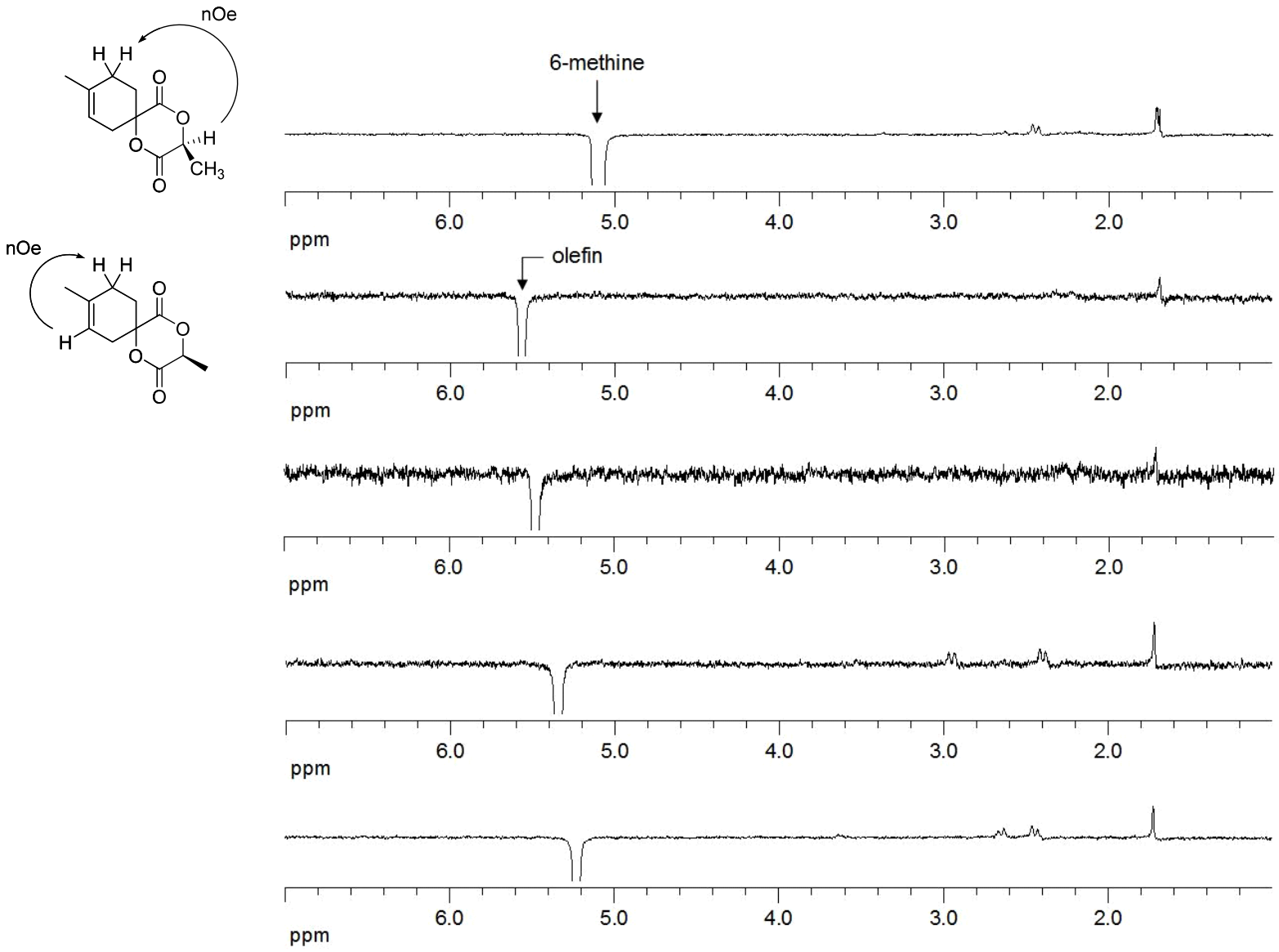


Figure S5e. 500 MHz 1D NOE spectra of **3-L**.

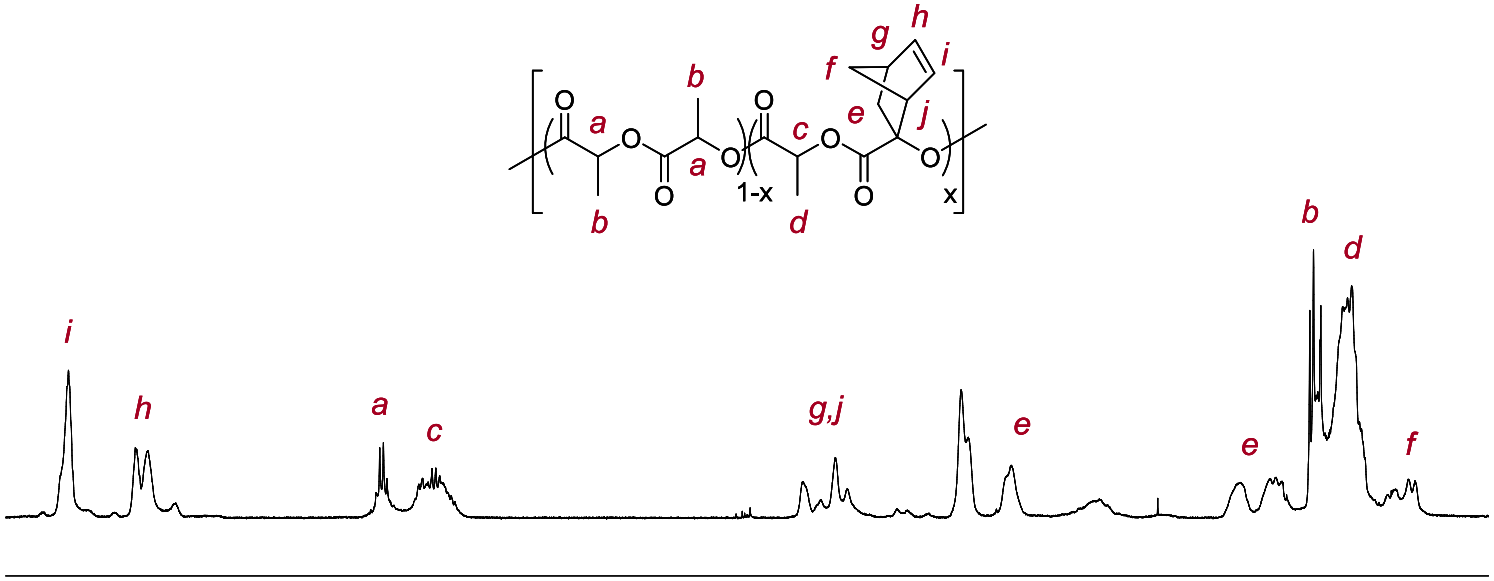


Figure S6. Representative 500 MHz ^{1}H NMR spectrum of poly(norbornene-s-L-lactide) (P(NL-s-L)) copolymer in $CDCl_3$.

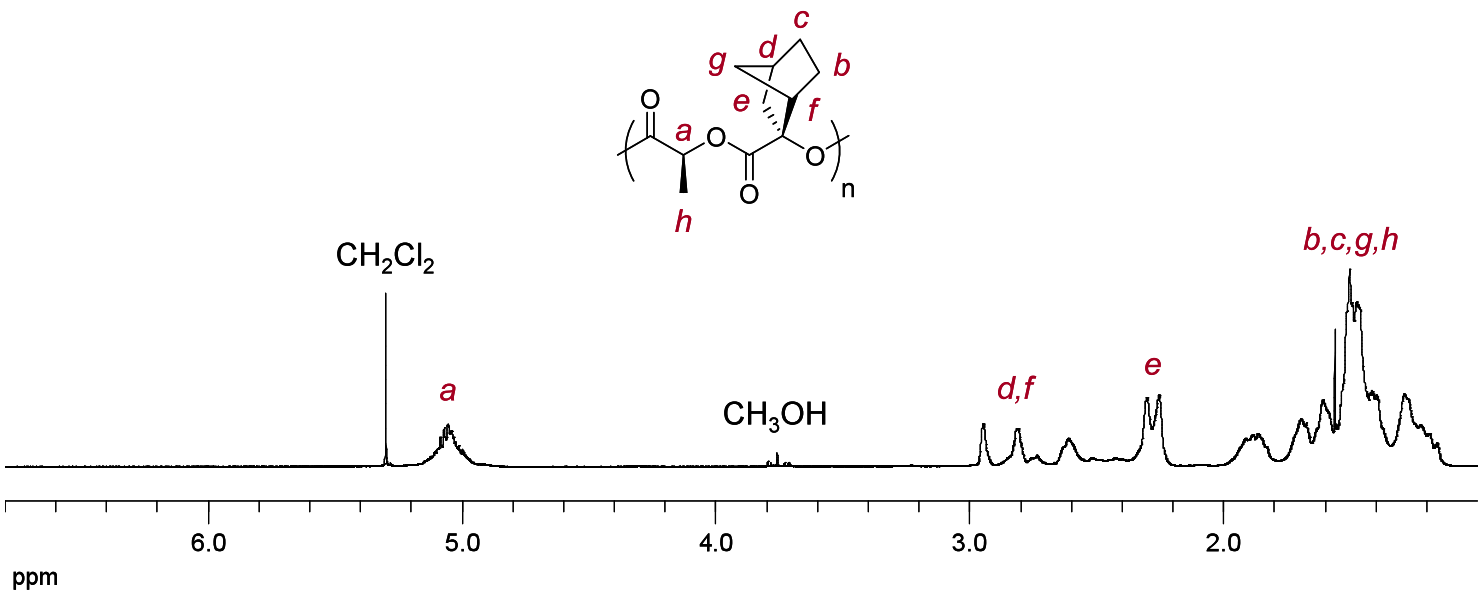


Figure S7. 500 MHz ^{1}H NMR spectrum of poly(norbornane-lactide) (**P(1-L)**).

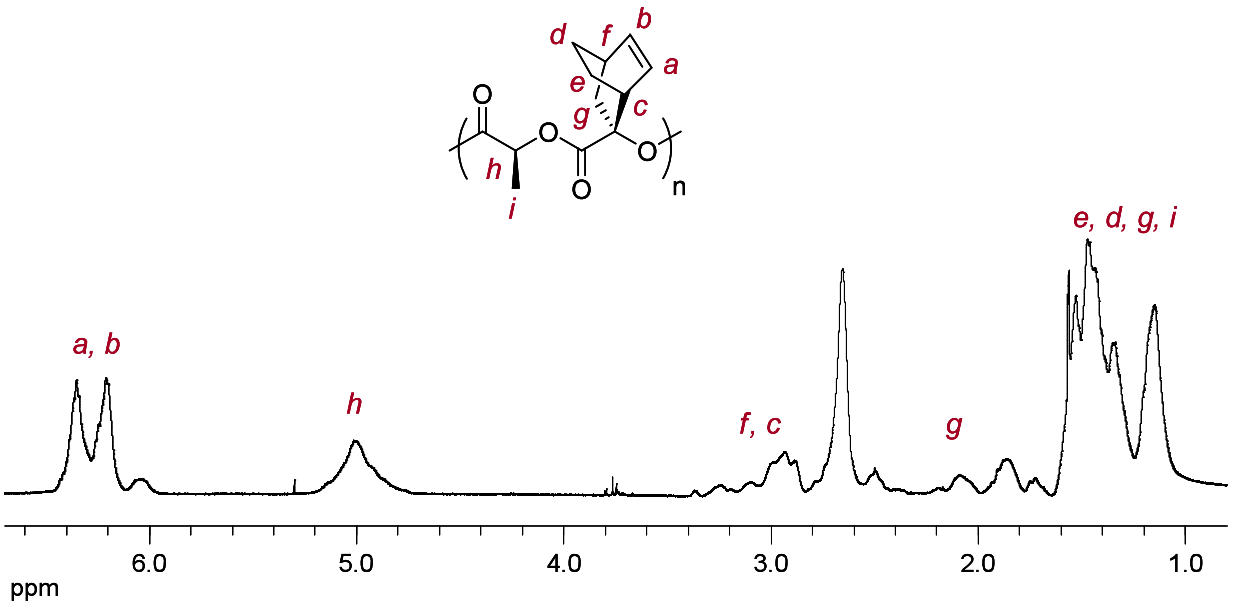


Figure S8. 500 MHz ^{1}H NMR of poly(cyclohexadiene-lactide) (**P(2-L)**).

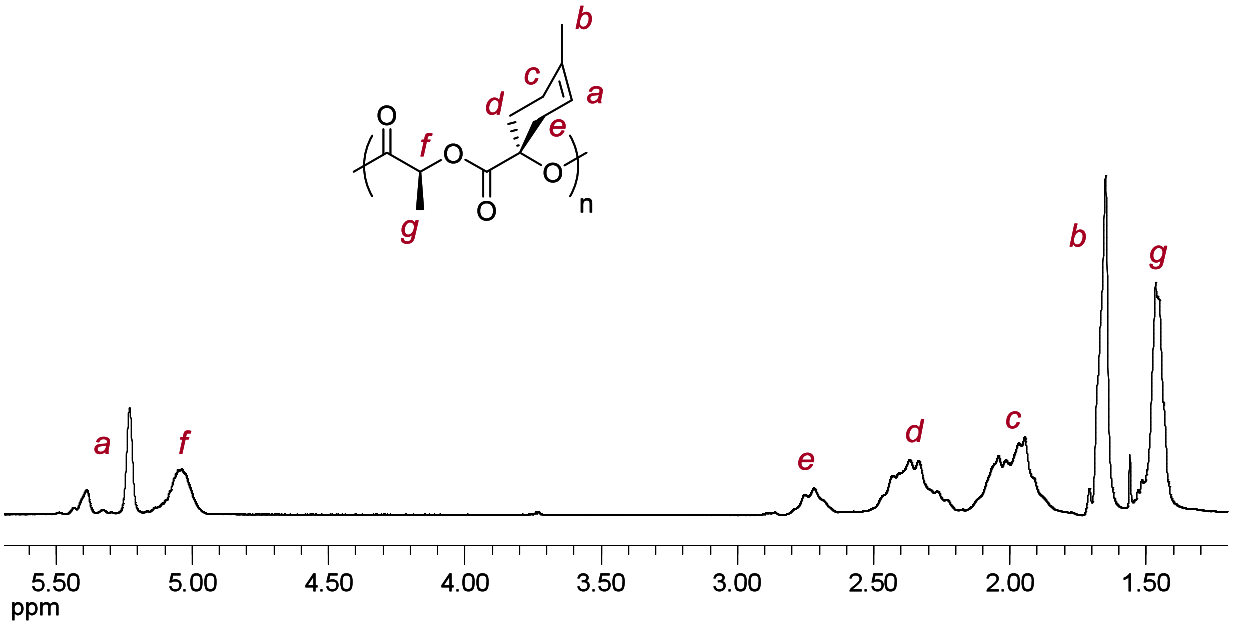


Figure S9. 500 MHz ^{1}H NMR of poly(isoprene-lactide) (**P(3-L)**).

Cartesian coordinates for computed structures (Å, M06-L/6-31G(d))

TS leading to (3*R*,6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.788781	-1.342047	0.437333
2	6	-2.198190	-0.947185	-0.961848
3	6	-1.387186	1.212165	-0.372728
4	6	-1.744121	0.977017	1.055279
5	1	-0.694991	-1.478967	0.427815
6	8	-2.083337	-0.285634	1.383006
7	8	-1.924692	0.378456	-1.302579
8	8	-2.689393	-1.657884	-1.787741
9	8	-1.799596	1.880294	1.854978
10	6	-2.489933	-2.587925	0.909884
11	1	-3.574851	-2.447819	0.910131
12	1	-2.251558	-3.422793	0.246354
13	1	-2.163715	-2.832919	1.923685
14	6	-1.215583	2.600599	-0.857299
15	1	-0.684457	3.197280	-0.113651
16	1	-0.678601	2.614633	-1.809450
17	1	-2.203025	3.057711	-1.017354
18	35	0.975754	0.579633	-0.166545
19	35	3.171963	-0.599197	0.080472

TS leading to (3*S*,6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.827899	1.650891	0.571091
2	6	-1.843505	1.335277	-0.906705
3	6	-1.725200	-0.970160	-0.395134
4	6	-1.977509	-0.734673	1.047976
5	1	-2.693720	2.311743	0.718633
6	8	-2.076884	0.542344	1.459206
7	8	-2.020136	0.009647	-1.289470
8	8	-1.781703	2.172926	-1.757621
9	8	-2.126664	-1.653786	1.819419
10	6	-0.570843	2.390219	0.992890
11	1	0.320750	1.770157	0.866920
12	1	-0.459710	3.294132	0.387234
13	1	-0.657601	2.674257	2.044956
14	6	-1.839700	-2.337295	-0.945879
15	1	-1.446835	-3.063425	-0.231744
16	1	-2.897465	-2.580686	-1.126147
17	1	-1.311215	-2.414556	-1.900106
18	35	0.751889	-0.736387	-0.232242
19	35	3.016591	0.205923	0.095172

(3*R*,6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.692705	-0.049037	-0.595863
2	6	1.507008	-0.631803	0.790377
3	6	-0.679194	0.341821	0.672668
4	6	-0.105961	1.488558	-0.153785
5	1	1.152353	-0.696696	-1.304150
6	8	1.109753	1.274958	-0.689063
7	8	0.311649	-0.347146	1.398968
8	8	2.316167	-1.307830	1.362940
9	8	-0.675817	2.540595	-0.285577
10	6	3.145600	0.071102	-0.974764
11	1	3.676686	0.719695	-0.271911
12	1	3.616396	-0.914577	-0.951532
13	1	3.235841	0.489768	-1.980442
14	6	-1.748728	0.776818	1.632455
15	1	-2.537879	1.307753	1.098173
16	1	-2.166086	-0.092937	2.145246
17	1	-1.312550	1.454274	2.374720
18	35	-1.515067	-0.901047	-0.675279

(3*S*,6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.937028	0.448960	-0.369455
2	6	-1.593746	-0.170145	0.968239
3	6	0.680228	0.454207	0.618328
4	6	0.267441	1.482437	-0.428778
5	1	-2.859429	1.014769	-0.187081
6	8	-1.009979	1.450819	-0.841497
7	8	-0.357800	0.087421	1.495540
8	8	-2.390983	-0.811142	1.596007
9	8	1.037226	2.304978	-0.853715
10	6	-2.197272	-0.586456	-1.447794
11	1	-1.290254	-1.154208	-1.672580
12	1	-2.973724	-1.277975	-1.107627
13	1	-2.538709	-0.087267	-2.358722
14	6	1.858466	0.891651	1.440311
15	1	2.691689	1.156295	0.788197
16	1	1.580329	1.773445	2.028465
17	1	2.155957	0.089688	2.120021
18	35	1.215368	-1.168437	-0.441898

Supplementary Material (ESI) for Polymer Chemistry

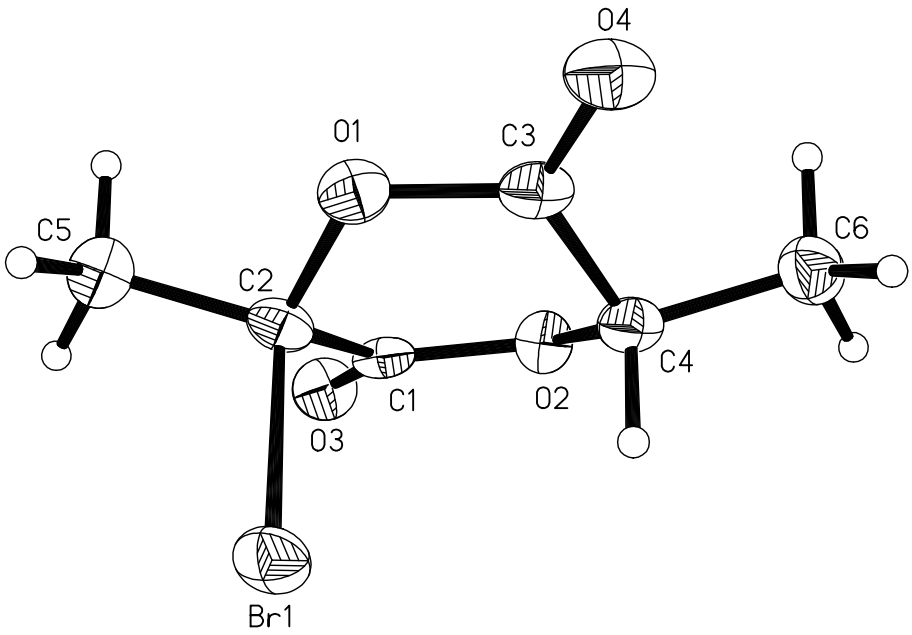
REFERENCE NUMBER: 08185b

CRYSTAL STRUCTURE REPORT

$C_6 H_7 Br O_4$

Report prepared for:
F. Jing / Prof. M. Hillmyer

September 3, 2008



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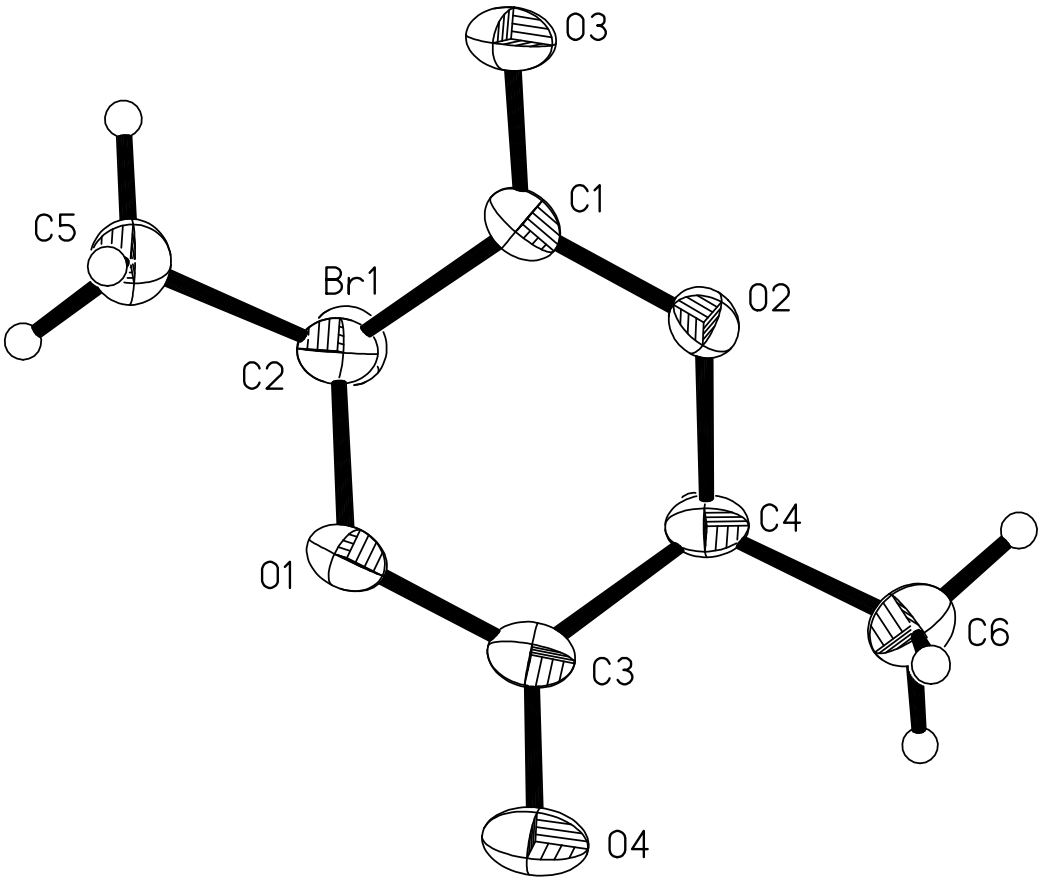
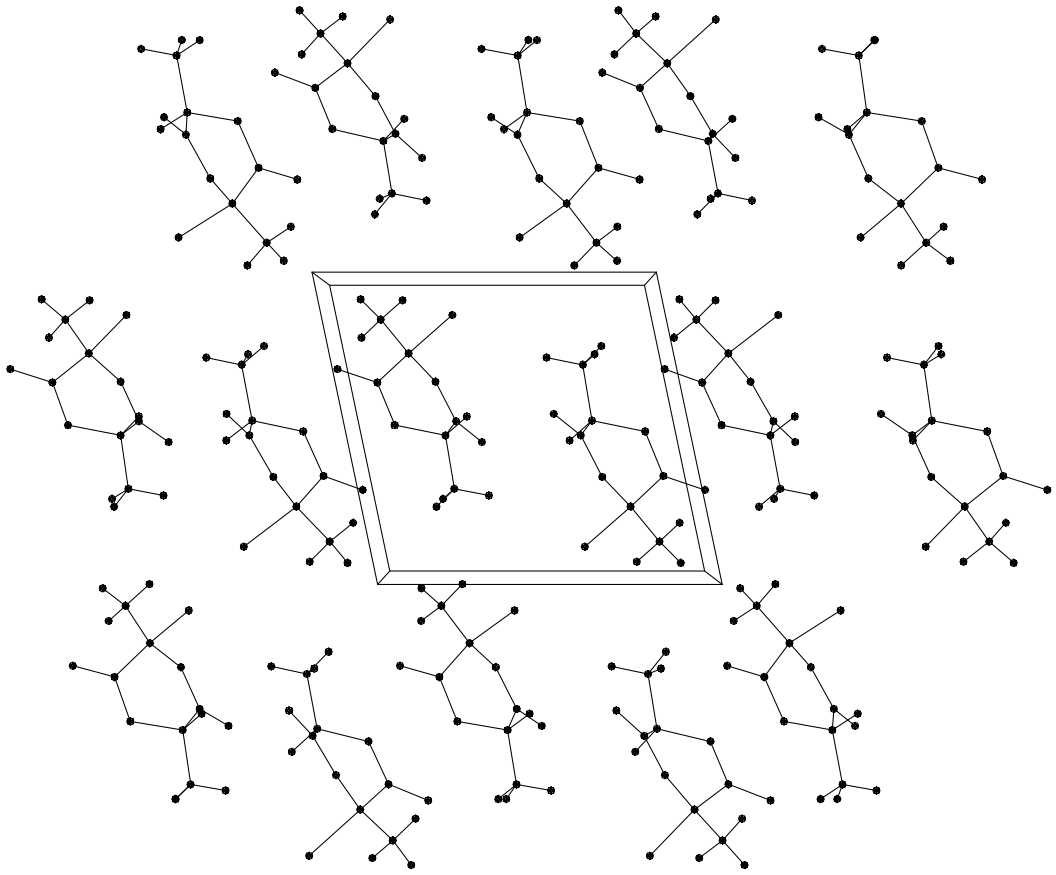




Data collection

A crystal (approximate dimensions 0.40x 0.12 x 0.05mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a CCD area detector diffractometer for a data collection at173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from four sets of 30 frames as indexed by Cell_Now.[2] The specimen indexed as a two-component, non-merohedral twin indexed on 237 reflections. The twin law by rows is [-0.99481, 0.15111, 0.00165, 0.06327, 0.99404, 0.01191, -0.00229, -0.00025, -1.00038], or a rotation about (010) by ~5 °. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.30º steps in ω at four different ϕ settings and a detector position of -28º in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2441 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR-97[5] and refined using Bruker SHELXTL.[4] The space group $P2_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0316$ and $wR2 = 0.0814$ (F^2, all data).

Structure description

The structure is the one suggested. The methyl groups are found on the same face of the six-member ring. The data were treated as a twin since a subset of reflections was affected. The ratio of twin components was 0.70:0.30.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

[1] SMART V5.054, Bruker Analytical X-ray Systems, Madison, WI (2001).

[2] An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst.* **A51**, 33-38(1995).

[3] SAINT+ V6.45, Bruker Analytical X-Ray Systems, Madison, WI (2003).

[4] SHELXTL V6.14, Bruker Analytical X-Ray Systems, Madison, WI (2000).

[5] A. Altomare, M. C. Burla, M. Camalli,G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori,R. Spagna. Sir97: a new tool for crystal structure determination andrefinement. *J. Appl. Cryst.* **32**, 115-119(1998).

[6] M. C. Burla, M. Camalli, B. Carrozzini,G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna. Sir2002: a newDirect Methods program for automatic solution and refinement of crystalstructures. *J. Appl. Cryst.* (2003), in preparation.

[7] A. L. Spek, *Acta. Cryst.***A46**, C34 (1990). PLATON, A MultipurposeCrystallographic Tool, Utrecht University, Utrecht, The Netherlands, A. L.Spek (2000).

Some equations of interest:

$$R_{int} = \Sigma|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o| - |F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma[w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2(F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 08185b.

Identification code	08185b	
Empirical formula	$C_6 H_7 Br O_4$	
Formula weight	223.03	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.349(3) Å	α = 90°
	b = 5.2884(17) Å	β = 101.900(4)°
	c = 9.007(3) Å	γ = 90°
Volume	389.1(2) $Å^3$	
Z	2	
Density (calculated)	1.903 Mg/m^3	
Absorption coefficient	5.244 mm^{-1}	
F(000)	220	
Crystal color, morphology	Colorless, Plate	
Crystal size	0.40 x 0.12 x 0.05 mm^3	
Theta range for data collection	2.31 to 27.53°	
Index ranges	$-10 \le h \le 10, -6 \le k \le 6, -11 \le l \le 11$	
Reflections collected	3488	
Independent reflections	1712 [R(int) = 0.0473]	
Observed reflections	1586	
Completeness to theta = 27.53°	99.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7795 and 0.2282	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1712 / 1 / 103	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	$R1$ = 0.0316, $wR2$ = 0.0772	
R indices (all data)	$R1$ = 0.0369, $wR2$ = 0.0814	
Absolute structure parameter	0.040(18)	
Largest diff. peak and hole	0.815 and -0.521 e.$Å^{-3}$	

Table 2. Atomic coordinates($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 08185b. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Br1	8832(1)	3907(1)	3746(1)	30(1)
O1	6629(4)	-20(6)	2725(3)	26(1)
O2	5100(3)	4213(7)	1275(3)	23(1)
O3	6990(4)	4337(7)	-109(3)	28(1)
O4	4516(4)	-638(6)	3785(3)	32(1)
C1	6553(5)	3552(10)	993(4)	21(1)
C2	7586(5)	1725(8)	2099(5)	22(1)
C3	5236(5)	818(8)	3124(4)	23(1)
C4	4753(5)	3523(10)	2750(4)	23(1)
C5	8792(6)	229(9)	1407(6)	32(1)
C6	2948(4)	3937(16)	2680(4)	31(1)

Table 3. Bond lengths [Å] and angles [°] for08185b.

Br(1)-C(2)	1.994(4)	C(3)-C(4)	1.506(7)
O(1)-C(3)	1.360(5)	C(4)-C(6)	1.512(5)
O(1)-C(2)	1.412(5)	C(4)-H(4A)	1.0000
O(2)-C(1)	1.335(5)	C(5)-H(5A)	0.9800
O(2)-C(4)	1.463(4)	C(5)-H(5B)	0.9800
O(3)-C(1)	1.200(5)	C(5)-H(5C)	0.9800
O(4)-C(3)	1.207(5)	C(6)-H(6A)	0.9800
C(1)-C(2)	1.522(6)	C(6)-H(6B)	0.9800
C(2)-C(5)	1.512(6)	C(6)-H(6C)	0.9800
C(3)-O(1)-C(2)	118.5(3)	C(3)-C(4)-C(6)	111.5(5)
C(1)-O(2)-C(4)	117.7(3)	O(2)-C(4)-H(4A)	109.0
O(3)-C(1)-O(2)	120.6(4)	C(3)-C(4)-H(4A)	109.0
O(3)-C(1)-C(2)	122.2(4)	C(6)-C(4)-H(4A)	109.0
O(2)-C(1)-C(2)	117.1(3)	C(2)-C(5)-H(5A)	109.5
O(1)-C(2)-C(5)	107.6(4)	C(2)-C(5)-H(5B)	109.5
O(1)-C(2)-C(1)	112.7(3)	H(5A)-C(5)-H(5B)	109.5
C(5)-C(2)-C(1)	113.5(4)	C(2)-C(5)-H(5C)	109.5
O(1)-C(2)-Br(1)	109.4(3)	H(5A)-C(5)-H(5C)	109.5
C(5)-C(2)-Br(1)	108.6(3)	H(5B)-C(5)-H(5C)	109.5
C(1)-C(2)-Br(1)	104.9(3)	C(4)-C(6)-H(6A)	109.5
O(4)-C(3)-O(1)	117.5(4)	C(4)-C(6)-H(6B)	109.5
O(4)-C(3)-C(4)	125.4(4)	H(6A)-C(6)-H(6B)	109.5
O(1)-C(3)-C(4)	117.0(3)	C(4)-C(6)-H(6C)	109.5
O(2)-C(4)-C(3)	110.3(3)	H(6A)-C(6)-H(6C)	109.5
O(2)-C(4)-C(6)	108.0(3)	H(6B)-C(6)-H(6C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters($Å^2 x\ 10^3$)for 08185b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	28(1)	34(1)	24(1)	-3(1)	-3(1)	-3(1)
O1	31(2)	22(1)	24(1)	5(1)	6(1)	-1(1)
O2	24(1)	26(2)	19(1)	3(1)	3(1)	3(1)
O3	35(2)	29(2)	22(1)	5(1)	10(1)	-2(1)
O4	47(2)	30(2)	22(1)	1(1)	11(1)	-10(1)
C1	26(2)	14(3)	20(2)	-2(2)	0(1)	-4(2)
C2	23(2)	25(2)	18(2)	0(2)	1(2)	-6(2)
C3	31(2)	23(2)	12(2)	-2(1)	3(2)	-6(2)
C4	30(2)	24(3)	16(2)	-2(2)	7(1)	-6(2)
C5	32(2)	31(2)	32(2)	0(2)	7(2)	2(2)
C6	29(2)	36(2)	29(2)	-4(3)	8(2)	-3(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 08185b.

	x	y	z	U(eq)
H4A	5396	4650	3547	27
H5A	8195	-918	632	47
H5B	9505	-756	2200	47
H5C	9458	1392	941	47
H6A	2645	5651	2311	47
H6B	2715	3729	3696	47
H6C	2313	2701	1988	47

Table 6. Torsion angles [°] for 08185b.

C4-O2-C1-O3	-170.5(5)
C4-O2-C1-C2	11.2(5)
C3-O1-C2-C5	-166.1(4)
C3-O1-C2-C1	-40.3(5)
C3-O1-C2-Br1	76.0(4)
O3-C1-C2-O1	-145.6(4)
O2-C1-C2-O1	32.6(5)
O3-C1-C2-C5	-23.1(6)
O2-C1-C2-C5	155.2(4)
O3-C1-C2-Br1	95.4(4)
O2-C1-C2-Br1	-86.3(4)
C2-O1-C3-O4	-173.3(4)
C2-O1-C3-C4	4.7(5)
C1-O2-C4-C3	-45.8(5)
C1-O2-C4-C6	-167.8(5)
O4-C3-C4-O2	-144.0(4)
O1-C3-C4-O2	38.3(5)
O4-C3-C4-C6	-24.1(5)
O1-C3-C4-C6	158.2(3)

Symmetry transformations used to generate equivalent atoms:

Supplementary Material (ESI) for Polymer Chemistry

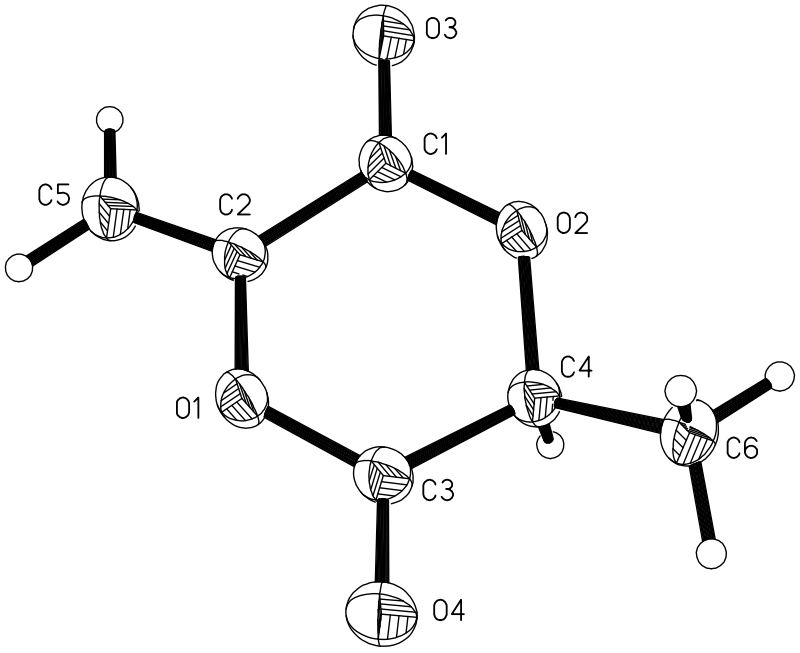
REFERENCE NUMBER: 08191a

CRYSTAL STRUCTURE REPORT

$C_6 H_6 O4$

Report prepared for:
F. Jing / Prof. M. Hillmyer

September 10, 2008



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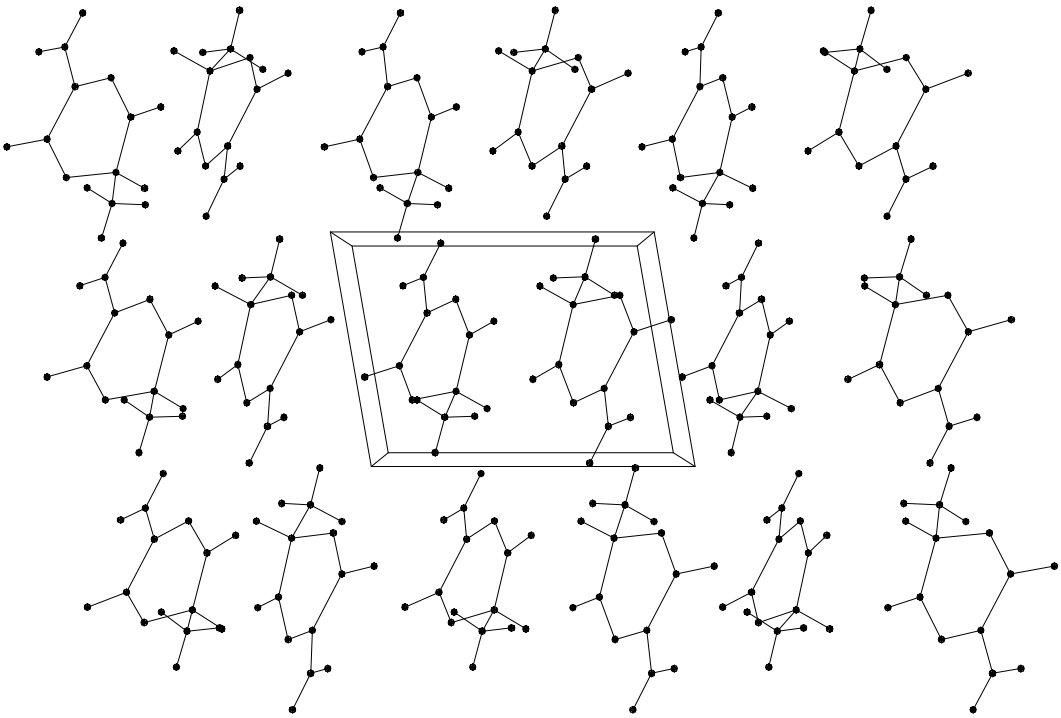

Data collection

A crystal (approximate dimensions 0.45x 0.40 x 0.30mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a CCD area detector diffractometer for a data collection at173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 33 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 15 seconds and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.30º steps in ω at four different ϕ settings and a detector position of -28º in2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2432 strong reflections from the actual data collection after integration(SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR-97[5] and refined using Bruker SHELXTL.[4] The space group $P2_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0335$ and$wR2 = 0.0953$ (F^2, obs. data).

Structure description

The structure is the one suggested. The chiral center at C4 was set as S based on chemical knowledge since no heavy atoms were present to assign the absolute configuration unambiguously. The data were merged as though it were centrosymmetric according to IUCr guidelines. Even though the structure is truly achiral and non-centrosymmetric, the data has a strong pseudosymmetry of a c-glide ⊥ the b-axis. This can be disregarded since the structure is of a single enantiomer.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All

publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

[1] SMART V5.054, Bruker Analytical X-ray Systems, Madison, WI (2001).

[2] An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst.* **A51**, 33-38(1995).

[3] SAINT+ V6.45, Bruker Analytical X-Ray Systems, Madison, WI (2003).

[4] SHELXTL V6.14, Bruker Analytical X-Ray Systems, Madison, WI (2000).

[5] A. Altomare, M. C. Burla, M. Camalli,G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna. Sir97: a new tool for crystal structure determination andrefinement. *J. Appl. Cryst.* **32**, 115-119(1998).

[6] M. C. Burla, M. Camalli, B. Carrozzini,G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna. Sir2002: a new Direct Methods program for automatic solution and refinement of crystal structures. *J. Appl. Cryst.* (2003), in preparation.

[7] A. L. Spek, *Acta. Cryst.***A46**, C34 (1990). PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, A. L.Spek (2000).

Some equations of interest:

$$R_{int} = \Sigma|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o| - |F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma[w(F_o^2)^2]]^{1/2}$$

where $w = q \,/\, [\sigma^2(F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 08191a.

Identification code	08191a	
Empirical formula	$C_6 H_6 O_4$	
Formula weight	142.11	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 5.7525(12) Å	$\alpha = 90°$
	b = 7.0293(15) Å	$\beta = 99.916(2)°$
	c = 7.8151(16) Å	$\gamma = 90°$
Volume	311.29(11) $Å^3$	
Z	2	
Density (calculated)	1.516 Mg/m^3	
Absorption coefficient	0.130 mm^{-1}	
$F(000)$	148	
Crystal color, morphology	Colorless, Block	
Crystal size	0.45 x 0.40 x 0.30 mm^3	
Theta range for data collection	2.65 to 27.49°	
Index ranges	$-7 \leq h \leq 7, 0 \leq k \leq 9, 0 \leq l \leq 10$	
Reflections collected	3225	
Independent reflections	766 [R(int) = 0.0216]	
Observed reflections	723	
Completeness to theta = 27.49°	98.6%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9620 and 0.9437	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	766 / 1 / 92	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	$R1$ = 0.0335, $wR2$ = 0.0921	
R indices (all data)	$R1$ = 0.0359, $wR2$ = 0.0953	
Absolute structure parameter	0.0(16)	
Largest diff. peak and hole	0.376 and -0.159 $e.Å^{-3}$	

Table 2. Atomic coordinates(x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 08191a. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O1	7257(2)	5656(2)	3423(2)	26(1)
O2	2724(2)	5978(2)	1445(2)	26(1)
O3	3795(2)	8550(3)	186(2)	39(1)
O4	6313(3)	2965(3)	4527(2)	41(1)
C1	4275(3)	7349(3)	1283(2)	25(1)
C2	6610(3)	7297(3)	2463(2)	26(1)
C3	5657(3)	4328(3)	3649(3)	26(1)
C4	3088(3)	4651(3)	2882(2)	25(1)
C5	8114(4)	8713(4)	2588(3)	35(1)
C6	1821(3)	2832(3)	2294(3)	30(1)

Table 3. Bond lengths [Å] and angles [°] for08191a.

O(1)-C(3)	1.344(2)	C(3)-C(4)	1.513(3)
O(1)-C(2)	1.391(2)	C(4)-C(6)	1.504(3)
O(2)-C(1)	1.334(2)	C(4)-H(4A)	1.0000
O(2)-C(4)	1.447(2)	C(5)-H(5A)	0.9500
O(3)-C(1)	1.201(3)	C(5)-H(5B)	0.9500
O(4)-C(3)	1.200(3)	C(6)-H(6A)	0.9800
C(1)-C(2)	1.493(2)	C(6)-H(6B)	0.9800
C(2)-C(5)	1.311(3)	C(6)-H(6C)	0.9800
C(3)-O(1)-C(2)	121.39(14)	C(6)-C(4)-C(3)	112.47(16)
C(1)-O(2)-C(4)	121.97(14)	O(2)-C(4)-H(4A)	107.3
O(3)-C(1)-O(2)	120.02(16)	C(6)-C(4)-H(4A)	107.3
O(3)-C(1)-C(2)	121.99(18)	C(3)-C(4)-H(4A)	107.3
O(2)-C(1)-C(2)	117.97(16)	C(2)-C(5)-H(5A)	120.0
C(5)-C(2)-O(1)	118.50(16)	C(2)-C(5)-H(5B)	120.0
C(5)-C(2)-C(1)	122.64(18)	H(5A)-C(5)-H(5B)	120.0
O(1)-C(2)-C(1)	118.82(17)	C(4)-C(6)-H(6A)	109.5
O(4)-C(3)-O(1)	118.30(16)	C(4)-C(6)-H(6B)	109.5
O(4)-C(3)-C(4)	122.39(18)	H(6A)-C(6)-H(6B)	109.5
O(1)-C(3)-C(4)	119.22(17)	C(4)-C(6)-H(6C)	109.5
O(2)-C(4)-C(6)	108.23(15)	H(6A)-C(6)-H(6C)	109.5
O(2)-C(4)-C(3)	113.88(15)	H(6B)-C(6)-H(6C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters($Å^2 x\ 10^3$)for 08191a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	20(1)	24(1)	30(1)	3(1)	-2(1)	0(1)
O2	22(1)	23(1)	30(1)	4(1)	-3(1)	-2(1)
O3	33(1)	38(1)	43(1)	17(1)	-4(1)	-3(1)
O4	34(1)	32(1)	54(1)	18(1)	-6(1)	0(1)
C1	23(1)	23(1)	27(1)	2(1)	1(1)	0(1)
C2	25(1)	24(1)	26(1)	3(1)	0(1)	-1(1)
C3	26(1)	24(1)	27(1)	3(1)	0(1)	0(1)
C4	24(1)	22(1)	27(1)	1(1)	-1(1)	-2(1)
C5	31(1)	35(1)	38(1)	5(1)	-1(1)	-7(1)
C6	31(1)	24(1)	34(1)	1(1)	1(1)	-7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 08191a.

	x	y	z	U(eq)
H4A	2310	5200	3821	30
H5A	9607	8604	3321	42
H5B	7711	9848	1945	42
H6A	185	3118	1770	45
H6B	1836	1989	3294	45
H6C	2615	2205	1434	45

Table 6. Torsion angles [°] for 08191a.

C4-O2-C1-O3	-171.72(19)
C4-O2-C1-C2	10.0(2)
C3-O1-C2-C5	165.77(19)
C3-O1-C2-C1	-16.6(3)
O3-C1-C2-C5	12.0(3)
O2-C1-C2-C5	-169.7(2)
O3-C1-C2-O1	-165.55(19)
O2-C1-C2-O1	12.7(3)
C2-O1-C3-O4	-178.15(18)
C2-O1-C3-C4	-1.7(3)
C1-O2-C4-C6	-152.75(16)
C1-O2-C4-C3	-26.9(2)
O4-C3-C4-O2	-160.98(19)
O1-C3-C4-O2	22.7(3)
O4-C3-C4-C6	-37.4(3)
O1-C3-C4-C6	146.28(18)

Symmetry transformations used to generate equivalent atoms: