

Supporting Information

Stereoselective Ring-Opening Polymerization of Functional β -Lactones: Influence of the Exocyclic Side-Group †

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† Electronic Supplementary Information (ESI) available: complementing NMR and MS spectra, DSC thermograms of the BPL^{FG}s and PBPL^{FG}s and kinetics of the polymerizations of BPL^{FG}s. See DOI: 10.1039/x0xx00000x

‡ These authors performed all the experimental work (except the mass spectrometry (P.J.) and chiral HPLC (M.B.) analyses) and contributed to the writing of the paper.

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Table S2: Tacticity and T_g values of PBPL^{FG}s prepared by ROP of different functional BPL^{FG}s with FG = CH₂OPh, and CH₂SPh, CH₂CH₂OCH₂Ph, CH₂OCH₂Ph, using the catalytic systems **1a–1g**/iPrOH.

Table S3: Tacticity of PBPL^{FG}s prepared by ROP of different (functional) BPL^{FG}s with FG = Me, CH₂OPh, CH₂SPh, CH₂CH₂OCH₂Ph, CH₂OMe, CH₂OAll, CH₂OBn, and CO₂All, CO₂Bn, using the catalytic systems **1a–1g** /iPrOH.

Figure S1. Chiral HPLC chromatogram (column Chiralcel-OD DAICEL; 250 mm × 4.6 mm, 5 μm; 20 °C with a UV detector at 214 nm) of : (left) *racemic* phenyl glycidyl ether (*rac*-G^{CH₂OPh}), and (right) 99.97 % enantiopure phenyl glycidyl ether ((*S*)-G^{CH₂OPh}) (hexane/isopropanol 90/10; 1 mL.min⁻¹, 22 bar).

Figure S2. ¹H NMR spectrum (400 MHz, CDCl₃, 23 °C) of *racemic* 2-((phenylthio)methyl)oxirane (*rac*-G^{CH₂SPh}) (*: residual water from the deuterated solvent).

Figure S3. Chiral HPLC chromatogram (column Chiralcel-OD DAICEL; 250 mm × 4.6 mm, 5 μm; 20 °C with a UV detector at 214 nm) of : (left) *racemic* 2-((phenylthio)methyl)oxirane (*rac*-G^{CH₂SPh}), and (right) 99.87% enantiopure (*S*)-2-((phenylthio)methyl)oxirane ((*S*)-G^{CH₂SPh}) (hexane/isopropanol 99.5/0.5; 0.9 mL.min⁻¹, 23 bar).

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Figure S12. ^1H NMR (500 MHz, CDCl_3 , 25 °C) (top) and J-MOD (125 MHz, CDCl_3 , 25 °C) (bottom) spectra of isotactic PBPL $^{\text{CH}_2\text{OPh}}$ prepared from the ROP of (*S*)-BPL $^{\text{CH}_2\text{OPh}}$ mediated by complex **1d** in the presence of *i*PrOH and precipitated twice in cold pentane (Table 1, entry 13).

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Figure S23. DSC thermogram (heating rate of $10 \text{ }^\circ\text{Cmin}^{-1}$, second heating cycle, from -80 to $200 \text{ }^\circ\text{C}$) of: (left) syndiotactic $\text{PBPL}^{\text{CH}_2\text{OPh}}$ (P_r 0.75) synthesized by ROP of *rac*-BPL $^{\text{CH}_2\text{OPh}}$ with $\text{Y}\{\text{ONNO}^{\text{Cl}_2}\}/(i\text{PrOH})$ (Table 1, entry 4); (right) syndiotactic $\text{PBPL}^{\text{CH}_2\text{OPh}}$ (P_r 0.83) synthesized by ROP of *rac*-BPL $^{\text{CH}_2\text{OPh}}$ with $\text{Y}\{\text{ONNO}^{\text{tBu}_2}\}/(i\text{PrOH})$ (Table 1, entry 12).

Figure S24. DSC thermogram (heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, second heating cycle -80 to $200\text{ }^{\circ}\text{C}$) of: (left) syndiotactic PBPL^{CH₂SPh} (P_r 0.76) synthesized by ROP of *rac*-BPL^{CH₂SPh} with Y{ONNO^{Me₂}}/(*i*PrOH) (Table 1, entry 15); (right) syndiotactic PBPL^{CH₂SPh} (P_r 0.86) synthesized by ROP of *rac*-BPL^{CH₂SPh} with Y{ONNO^{tBu₂}}/(*i*PrOH) (Table 1, entry 21).

Figure S25. DSC thermogram (heating rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$, second heating cycle -60 to $200\text{ }^{\circ}\text{C}$) of : (left) syndiotactic PBPL^{CH₂CH₂OCH₂Ph} (P_r 0.86) synthesized by ROP of *rac*-BPL^{CH₂CH₂OCH₂Ph} with Y{ONNO^{cumyl₂}}/(*i*PrOH) (Table 1, entry 36); (right) atactic PBPL^{CH₂CH₂OCH₂Ph} (P_r 0.49) synthesized by ROP of *rac*-BPL^{CH₂CH₂OCH₂Ph} with Y{ONNO^{Cl₂}}/(*i*PrOH) (Table 1, entry 31).

Table S1. Kinetic data for the monitoring of the ROP of *rac*-BPL^{CH2ZPh}s with various **1**/*i*PrOH (1:1) catalytic systems ($[\text{BPL}^{\text{CH2ZPh}}]_0/[\mathbf{1}]_0/[i\text{PrOH}]_0 = 60:1:1$; Figure 1).

BPL ^{CH2ZPh} Catalyst 1	Time (h)	Conv. (%)	$\ln([\text{BPL}^{\text{CH2ZPh}}]_0/[\text{BPL}^{\text{CH2ZPh}}]_t)$	$M_{n,\text{theo}}$ (g.mol ⁻¹)	$M_{n,\text{NMR}}$ (g.mol ⁻¹)	$M_{n,\text{SEC}}$ (g.mol ⁻¹)	D_M
<i>Table 1, entry 4</i> BPL ^{CH2OPh} {ONNO} ^{Cl2} 1c	0	0	0	0	0	0	-
	1.17	19	0.21	3 000	2 500	3 500	1.09
	4	38	0.48	4 100	3 900	4 300	1.10
	7	48	0.65	5 100	5 000	5 200	1.13
	50	54	-	5 800	5 400	6 200	1.15
<i>Table 1, entry 2</i> BPL ^{CH2OPh} {ONNO} ^{Me2} 1a	0	0	0	0	0	0	-
	0.25	20	0.22	2 200	2 000	2 600	1.11
	0.50	40	0.51	4 300	5 700	5 100	1.11
	1.17	64	1.03	6 900	6 900	8 200	1.13
	2.17	83	1.78	8 900	8 000	10 400	1.13
4.17	95	3.22	10 200	10 000	11 100	1.13	
<i>Table 1, entry 11</i> BPL ^{CH2OPh} {ONNO} ^{Cumyl2} 1f	0	0	0	0	0	0	-
	0.14	100	4.61	10 700	10 000	12 200	1.12
	0.5	100	-	10 700	10 000	12 200	1.15
<i>Table 1, entry 6</i> BPL ^{CH2OPh} {ONNO} ^{tBu2} 1d	0	0	0	0	0	0	-
	0.14	100	4.61	10 700	10 600	12 200	1.11
	0.25	100	-	10 700	10 600	12 200	1.14
<i>Table 1, entry 18</i> BPL ^{CH2SPh} {ONNO} ^{Cl2} 1c	0	0	0	0	0	0	-
	24	12	0.13	1 500	1 300	1 600	1.08
	48	21	0.24	2 500	2 400	2 600	1.12
	60	28	0.33	3 300	3 200	3 600	1.14
	96	48	-	5 700	5 100	6 400	1.17
<i>Table 1, entry 15</i> BPL ^{CH2SPh} {ONNO} ^{Me2} 1a	0	0	0	0	0	0	-
	0.25	10	0.11	1 200	1 100	1 500	1.13
	0.5	20	0.22	2 400	2 400	3 200	1.14
	2	55	0.80	6 400	6 300	8 900	1.16
	4	88	2.12	10 400	10 200	12 500	1.18
8	99	4.61	11 600	11 300	13 900	1.21	
<i>Table 1, entry 25</i> BPL ^{CH2SPh} {ONNO} ^{Cumyl2} 1f	0	0	0	0	0	0	-
	0.17	100	4.61	11 700	11 300	12 700	1.08
	1	100	-	11 700	11 300	13 300	1.12
<i>Table 1, entry 20</i> BPL ^{CH2SPh} {ONNO} ^{tBu2} 1d	0	0	0	0	0	0	-
	0.17	100	4.61	15 600	15 200	16 200	1.07
	1	100	4.61	15 600	15 200	17 900	1.15

BPL ^{CH2ZPh} Catalyst 1	Time (h)	Conv. (%)	$\ln([\text{BPL}^{\text{CH2ZPh}}]_0/[\text{BPL}^{\text{CH2ZPh}}]_t)$	$M_{n,\text{theo}}$ (g.mol ⁻¹)	$M_{n,\text{NMR}}$ (g.mol ⁻¹)	$M_{n,\text{SEC}}$ (g.mol ⁻¹)	\bar{D}_M
1 BPL ^{CH2CH2OBn} {ONNO} ^{Me2} 1a	1	11	0.118	1400	1300	1400	1.05
	2	19	0.213	2400	2200	2000	1.07
	3	27	0.311	3300	3200	2700	1.07
	4	31	0.375	3900	3400	3100	1.07
	9	46	0.625	5800	5500	4300	1.07
2 BPL ^{CH2CH2OBn} {ONNO} ^{Cl2} 1c	1	8	0.081	1000	1100	1300	1.08
	2	13	0.143	1700	1600	2100	1.08
	3	19	0.211	2400	2500	2600	1.09
	4	21	0.234	2600	2700	2800	1.09
	9	33	0.402	4100	3900	3700	1.13
3 BPL ^{CH2CH2OBn} {ONNO} ^{tBu2} 1d	0.5min	35	0.439	4400	4000	3600	1.08
	1 min	66	1.07	8200	7600	6600	1.09
	2 min	90	2.31	11200	11000	8700	1.07
	3 min	96	3.27	11900	11200	9400	1.07
	5 min	100	-	12400	11900	9400	1.08
4 BPL ^{CH2CH2OBn} {ONNO} ^{Cumyl2} 1f	0.5min	8	0.088	1100	1000	1600	1.07
	1 min	17	0.19	2200	2000	2300	1.09
	2 min	35	0.428	4300	4100	3800	1.09
	3 min	50	0.687	6200	5600	4900	1.08
	4 min	61	0.952	7600	7200	6200	1.08
5 min	71	1.25	8900	8100	7200	1.08	

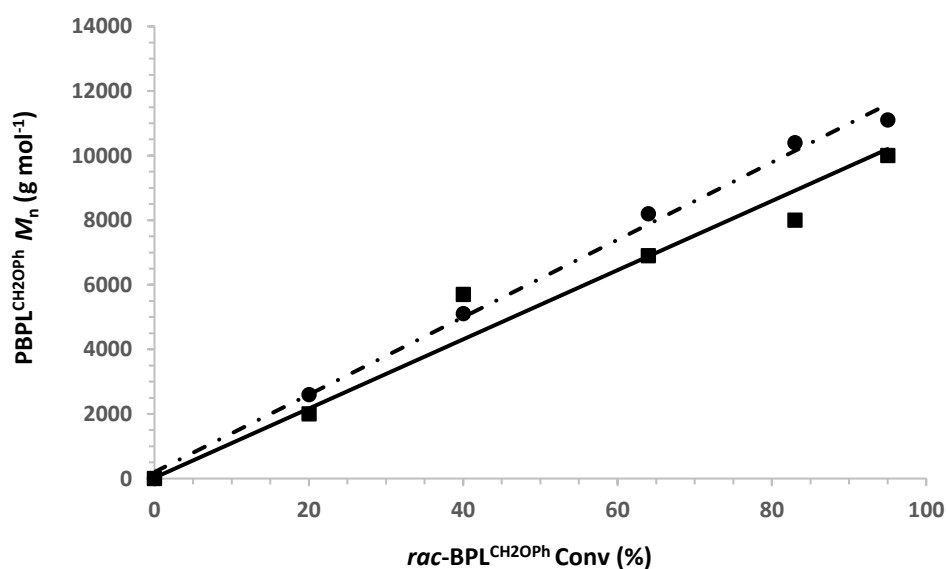


Table 1 Entry 2: Variation of $M_{n,\text{NMR}}$ ■, $M_{n,\text{SEC}}$ ●, and $M_{n,\text{theo}}$ (solid line) values of PBPL^{CH2OPh}s synthesized from the ROP of *rac*-BPL^{CH2OPh}s mediated by **1a**/(iPrOH) (1:1) catalytic system as a function of the monomer conversion.

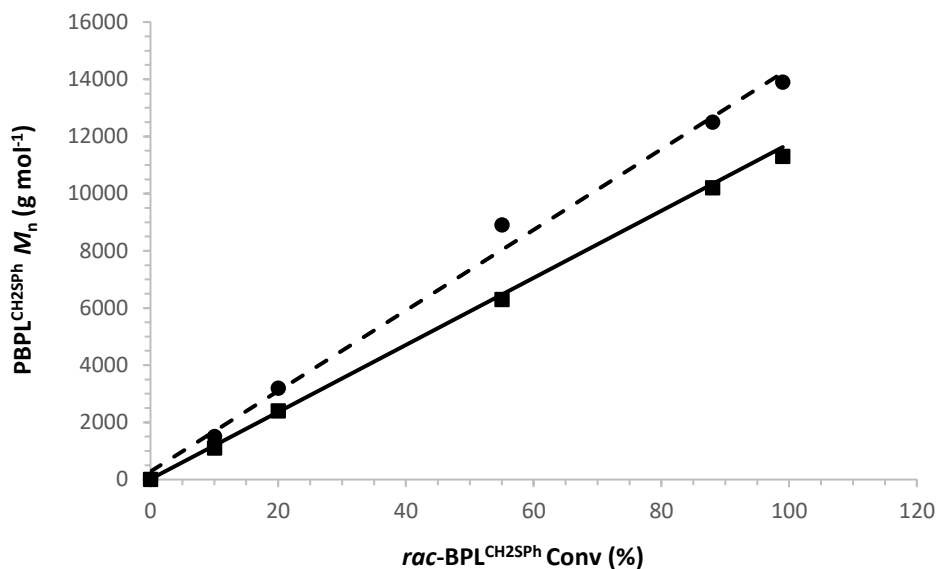


Table 1 Entry 15: Variation of $M_{n,NMR}$ ■, $M_{n,SEC}$ ●, and $M_{n,theo}$ (solid line) values of PBPL^{CH2SPh}s synthesized from the ROP of *rac*-BPL^{CH2SPh}s mediated by **1a**/(iPrOH) (1:1) catalytic system as a function of the monomer conversion.

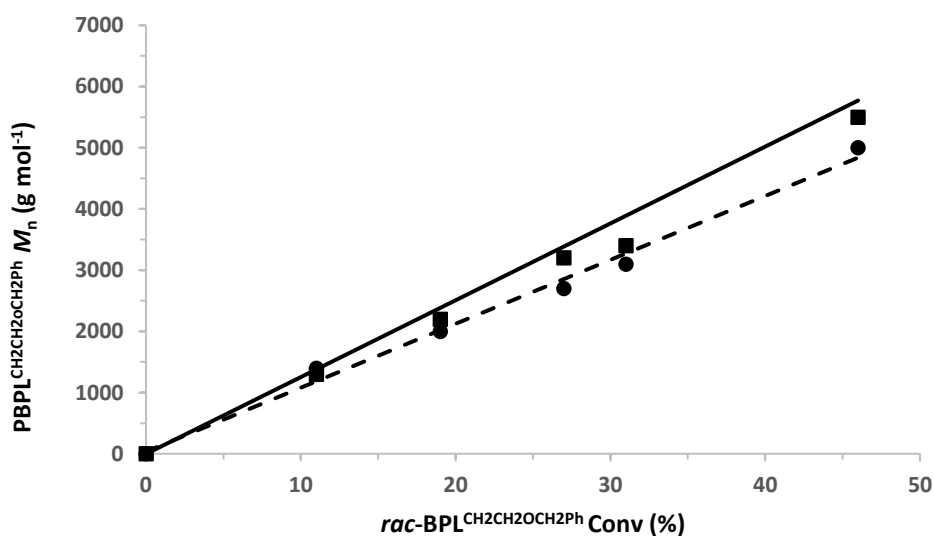
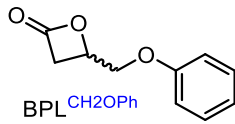
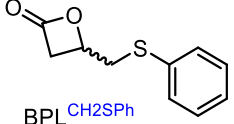
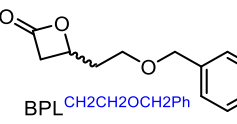
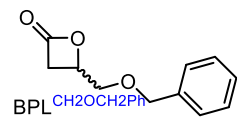


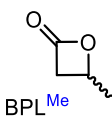
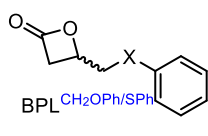
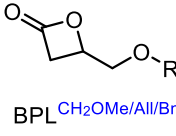
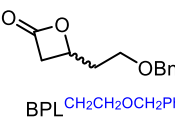
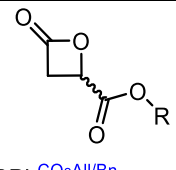
Table S1 Entry 1: Variation of $M_{n,NMR}$ ■, $M_{n,SEC}$ ●, and $M_{n,theo}$ (solid line) values of PBPL^{CH2CH2OCH2Ph}s synthesized from the ROP of *rac*-BPL^{CH2CH2OCH2Ph}s mediated by **1a**/(iPrOH) (1:1) catalytic system as a function of the monomer conversion.

Table S2: Tacticity and T_g values of PBPL^{FG}s prepared by ROP of different functional BPL^{FG}s with FG = CH₂OPh, and CH₂SPh, CH₂CH₂OCH₂Ph, CH₂OCH₂Ph, using the catalytic systems **1a–1g**/iPrOH.

Cat. \ BPL ^{FG}	 BPL ^{CH₂OPh}	 BPL ^{CH₂SPh}	 BPL ^{CH₂CH₂OCH₂Ph}	 BPL ^{CH₂OCH₂Ph}
1a,b	Syndiotactic $P_r = 0.76\text{--}0.79$ $T_g = 30\text{ }^\circ\text{C}$	Syndiotactic $P_r = 0.74\text{--}0.76$ $T_g = 8, 9\text{ }^\circ\text{C}$	Atactic $P_r = 0.49\text{--}0.52$ $T_g = -11\text{ }^\circ\text{C}$	Atactic * $P_r = 0.50$ $T_g = -6\text{ }^\circ\text{C}$
1c	Syndiotactic $P_r = 0.75\text{--}0.77$ $T_g = 21, 22\text{ }^\circ\text{C}$	Syndiotactic $P_r = 0.73\text{--}0.74$ $T_g = 9\text{ }^\circ\text{C}$	Atactic $P_r = 0.49$ $T_g = -13\text{ }^\circ\text{C}$	Isotactic * $P_r = 0.10$ $T_g = -1\text{ }^\circ\text{C}$
1d–1g	Syndiotactic $P_r = 0.81\text{--}0.87$ $T_g = 36\text{--}40\text{ }^\circ\text{C}$	Syndiotactic $P_r = 0.83\text{--}0.87$ $T_g = 12\text{--}14\text{ }^\circ\text{C}$	Syndiotactic $P_r = 0.77\text{--}0.86$ $T_g = -8\text{--}-13\text{ }^\circ\text{C}$	Syndiotactic * $P_r = 0.85\text{--}0.90$ $T_g = 0\text{ }^\circ\text{C}$

* (a) Ligny, R.; Hanninen, M. M.; Guillaume, S. M.; Carpentier, J. F. *Angew. Chem. Int. Ed.* **2017**, *56* (35), 10388-10393; (b) Ligny, R.; Hanninen, M. M.; Guillaume, S. M.; Carpentier, J.-F., *Chem. Commun.* **2018**, *54* (58), 8024-8031.

Table S3: Tacticity of PBPL^{FG}s prepared by ROP of different (functional) BPL^{FG}s with FG = Me, CH₂OPh, CH₂SPh, CH₂CH₂OCH₂Ph, CH₂OMe, CH₂OAll, CH₂OBn, and CO₂All, CO₂Bn, using the catalytic systems **1a–1g** /iPrOH.

BPL^{FG} Cat.	 BPL ^{Me}	 BPL ^{CH₂OPh/SPh}	 BPL ^{CH₂OMe/All/Bn}	 BPL ^{CH₂CH₂OCH₂Ph}	 BPL ^{CO₂All/Bn}
Crowded	Syndiotactic ‡ $P_r = 0.70\text{--}0.96$	Syndiotactic $P_r = 0.81\text{--}0.87$	Syndiotactic * $P_r = 0.78\text{--}0.90$	Syndiotactic $P_r = 0.77\text{--}0.86$	Syndiotactic † $P_r = 0.68\text{--}0.87$
Non-crowded	Atactic ‡ $P_r = 0.56$	Syndiotactic $P_r = 0.74\text{--}0.79$	Atactic * $P_r = 0.49\text{--}0.51$	Atactic $P_r = 0.49\text{--}0.52$	Syndiotactic † $P_r = 0.92\text{--}0.95$
Halogenated non-crowded	Atactic ‡ $P_r = 0.42\text{--}0.45$	Syndiotactic $P_r = 0.73\text{--}0.77$	Isotactic * $P_r = <0.05\text{--}0.12$	Atactic $P_r = 0.49$	Syndiotactic † $P_r = 0.91\text{--}0.98$

‡ (a) Chapurina, Y.; Klitzke, J.; Casagrande Ode, L., Jr.; Awada, M.; Dorcet, V.; Kirillov, E.; Carpentier, J. F. *Dalton Trans* **2014**, 43 (38), 14322-14333; (b) Bouyahyi, M.; Ajellal, N.; Kirillov, E.; Thomas, C. M.; Carpentier, J.-F. *Chem. –Eur. J.*, **2011**, 17, 1872-1883; (c) Amgoune, A.; Thomas, C. M.; Ilinca, S.; Roisnel, T.; Carpentier, J.-F. *Angew. Chem. Int. Ed.* **2006**, 118 (17), 2848-2850.

* (a) Ligny, R.; Hanninen, M. M.; Guillaume, S. M.; Carpentier, J. F. *Angew. Chem. Int. Ed.* **2017**, 56 (35), 10388-10393; (b) Ligny, R.; Hänninen, M. M.; Guillaume, S. M.; Carpentier, J.-F. *Chem. Commun.* **2018**, 54 (58), 8024-8031; (c) Ligny, R.; Guillaume, S. M.; Carpentier, J. F., *Chem. –Eur. J.*, **2019**, 25, 6412–6424.

† (a) Jaffredo, C. G.; Chapurina, Y.; Kirillov, E.; Carpentier, J. F.; Guillaume, S. M. *Chem. –Eur. J.*, **2016**, 22 (22), 7629-7641; (b) Jaffredo, C. G.; Chapurina, Y.; Guillaume, S. M.; Carpentier, J. F. *Angew Chem. Int. Ed.* **2014**, 53 (10), 2687-2691.

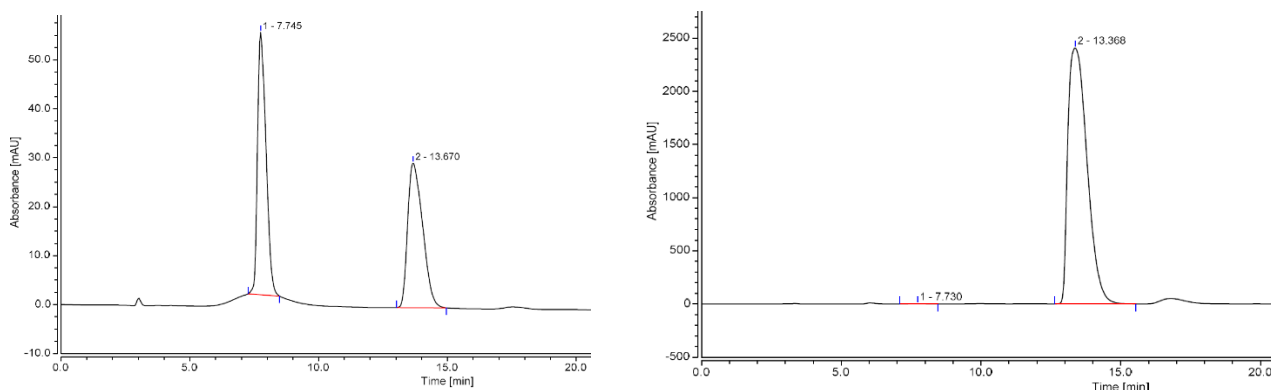


Figure S1. Chiral HPLC chromatogram (column Chiralcel-OD DAICEL; 250 mm × 4.6 mm, 5 μ m; 20 °C with a UV detector at 214 nm) of : (left) *racemic* phenyl glycidyl ether (*rac*-G^{CH₂O}Ph), and (right) 99.97 % enantiopure phenyl glycidyl ether ((*S*)-G^{CH₂O}Ph) (hexane/isopropanol 90/10; 1 mL.min⁻¹, 22 bar).

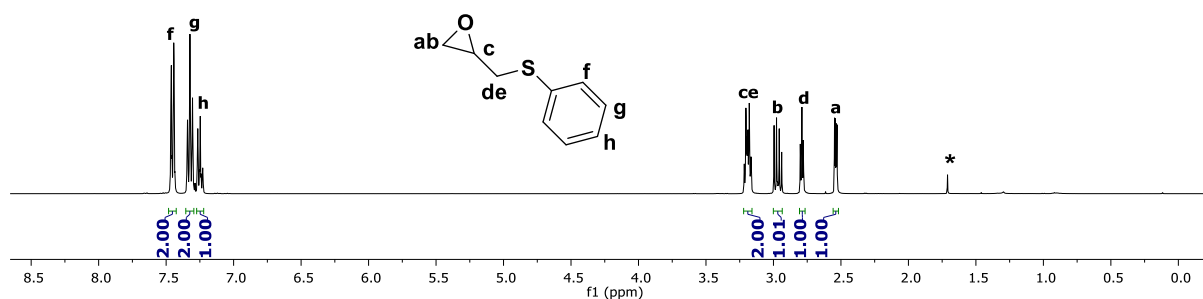


Figure S2. ¹H NMR spectrum (400 MHz, CDCl₃, 23 °C) of *racemic* 2-((phenylthio)methyl)oxirane (*rac*-G^{CH₂S}Ph) (*: residual water from the deuterated solvent).

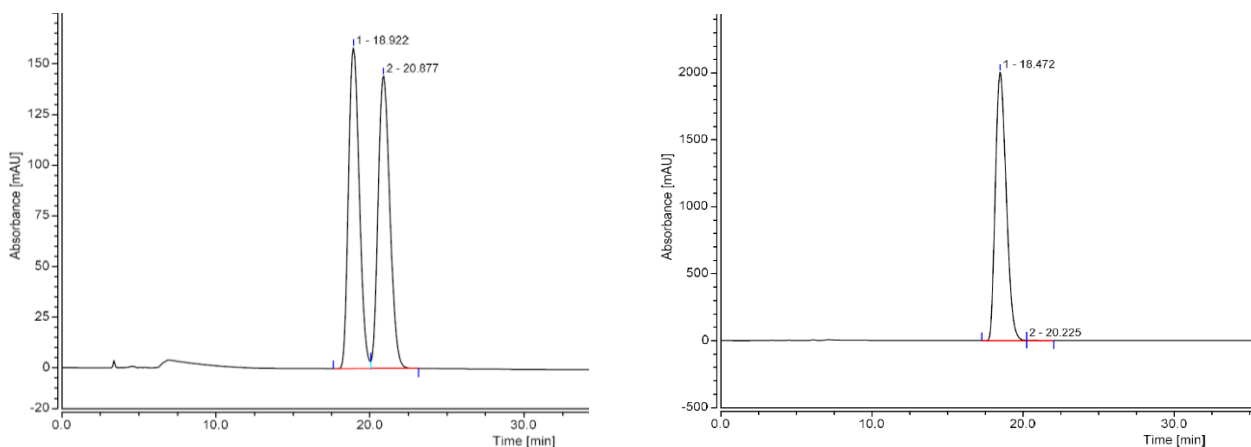


Figure S3. Chiral HPLC chromatogram (column Chiralcel-OD DAICEL; 250 mm × 4.6 mm, 5 μm; 20 °C with a UV detector at 214 nm) of : (left) *racemic* 2-((phenylthio)methyl)oxirane (*rac*-G^{CH₂SPh}), and (right) 99.87% enantiopure (*S*)-2-((phenylthio)methyl)oxirane (*S*-G^{CH₂SPh}) (hexane/isopropanol 99.5/0.5; 0.9 mL.min⁻¹, 23 bar).

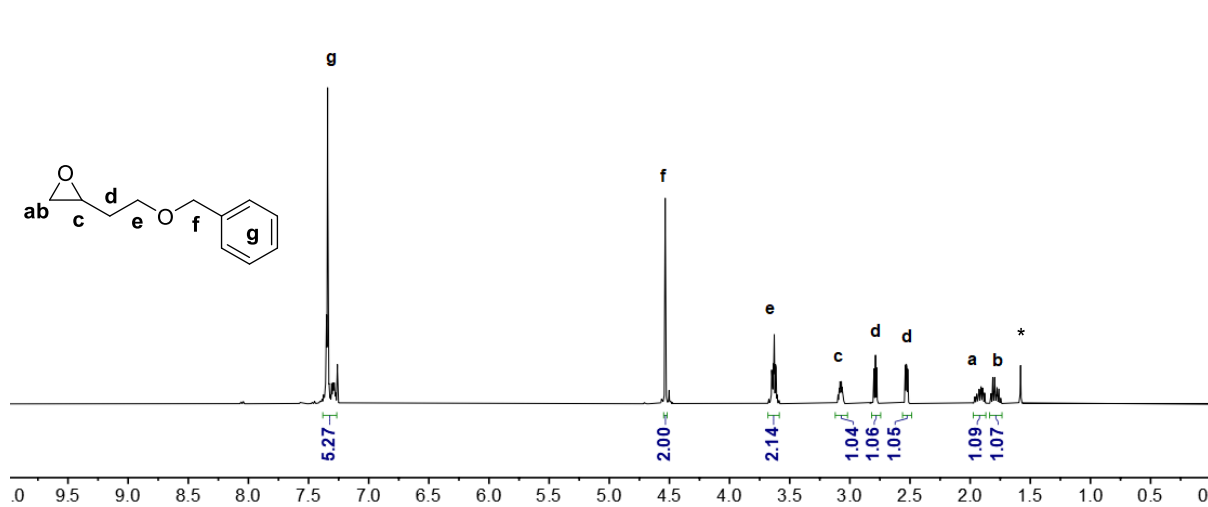


Figure S4. ¹H NMR spectrum (400 MHz, CDCl₃, 23 °C) of *racemic* 2-(2-(benzyloxy)ethyl)oxirane (*rac*-G^{CH₂CH₂OBn}) (*: residual water from the deuterated solvent).

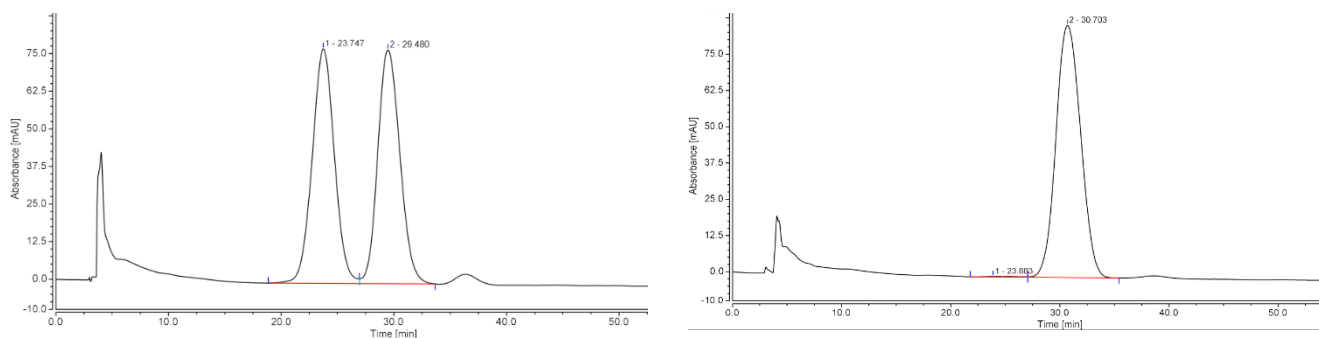


Figure S5. Chiral HPLC chromatogram (column Chiralcel-OD DAICEL; 250 mm × 4.6 mm, 5 μm; 20 °C with a UV detector at 214 nm) of : (left) 2-(2-(benzyloxy)ethyl)oxirane (*rac*-G^{CH₂CH₂OBn}), and (right) of 99.69% enantiopure (*R*)-2-(2-(benzyloxy)ethyl)oxirane ((*R*)-G^{CH₂CH₂OBn}) (hexane/isopropanol 99.7/0.3; 1 mL·min⁻¹, 25 bar) .

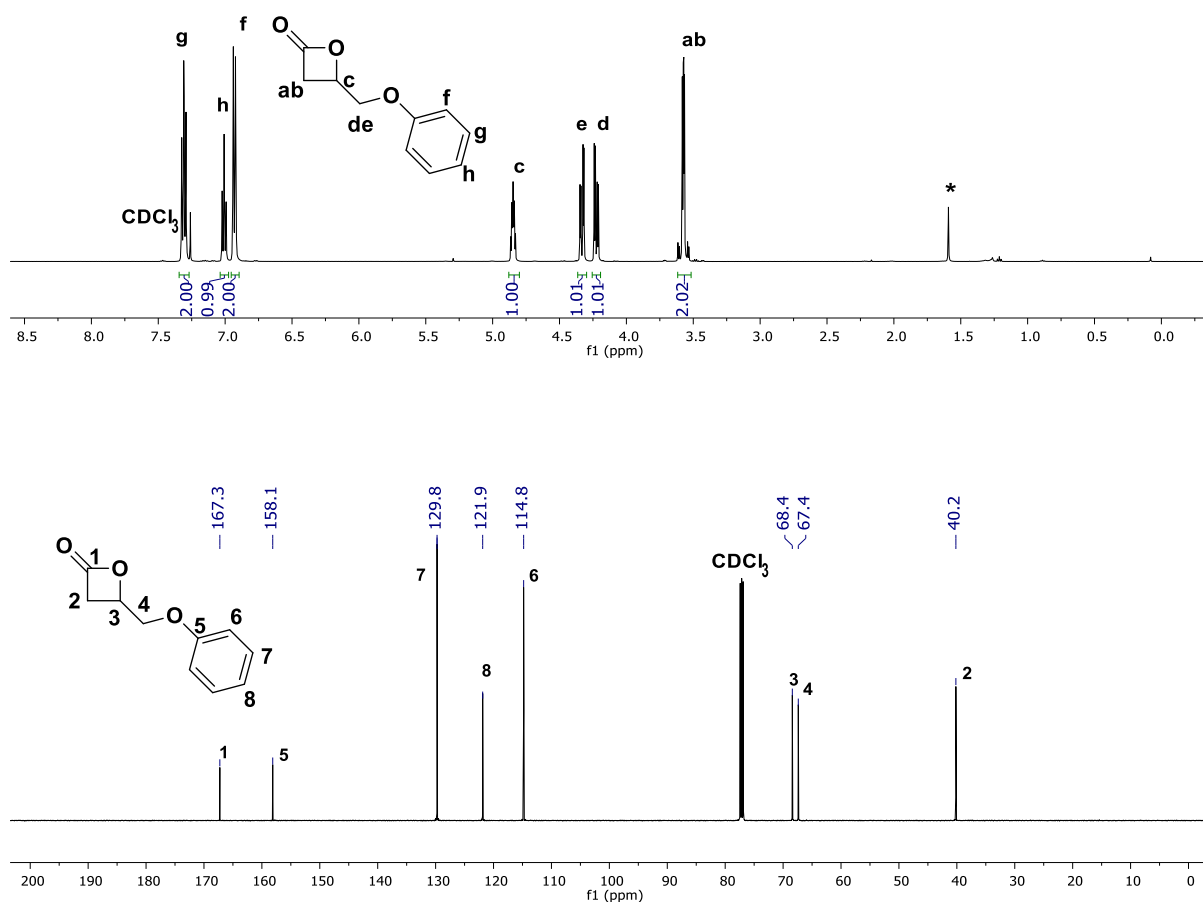


Figure S6. ¹H NMR spectrum (500 MHz, CDCl₃, 23 °C) (top) and ¹³C (125 MHz, CDCl₃, 25 °C) (bottom) of *racemic* 4-phenyloxymethylene-β-propiolactone (*rac*-BPL^{CH₂O^{Ph}}) (*: residual water from the deuterated solvent).

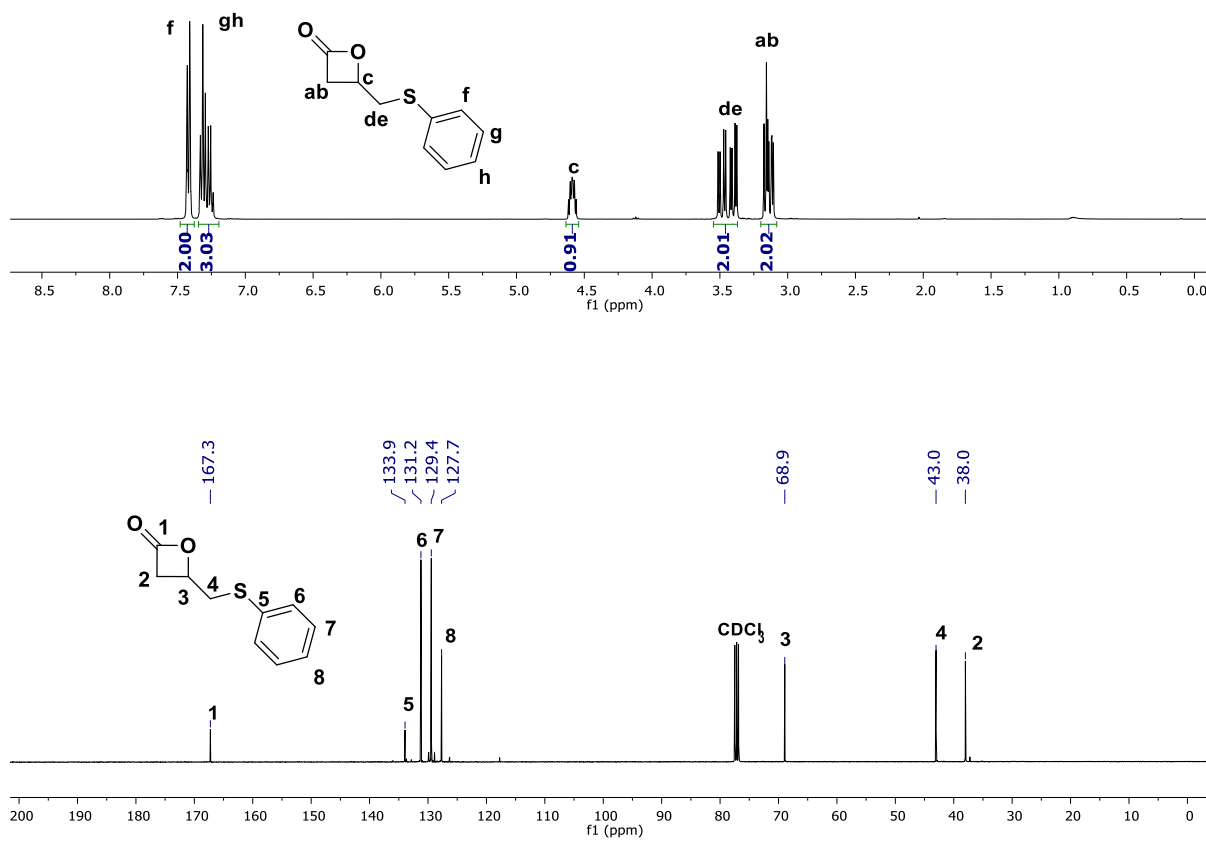


Figure S7. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) (top) and ¹³C (100 MHz, CDCl₃, 25 °C) (bottom) of *rac*-BPL^{CH₂SPh}.

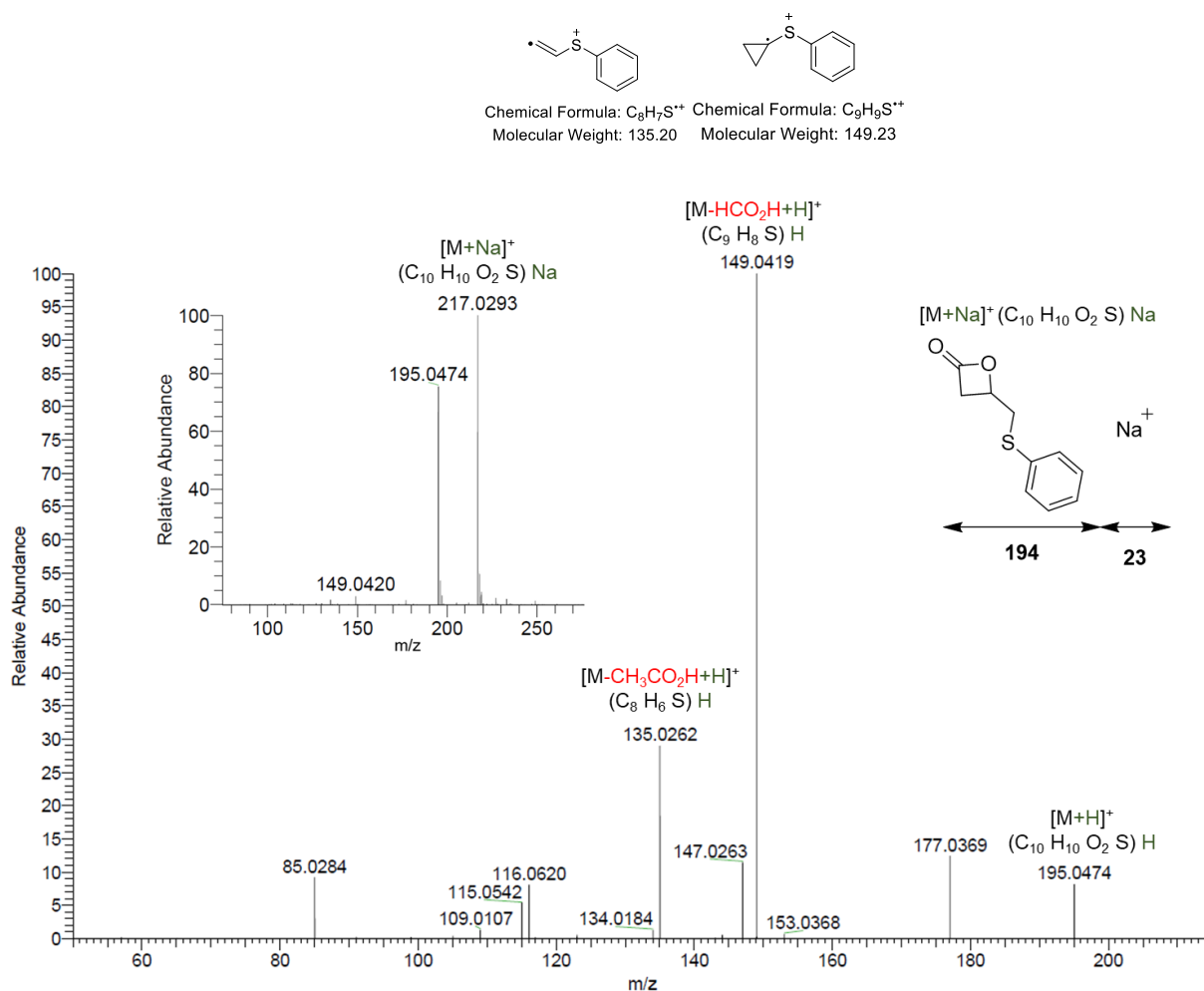


Figure S8. ESI-MS (ionized by Na^+ , solvent CH_2Cl_2/CH_3OH (95/5 v:v)) of freshly synthesized *racemic* 4-(phenylthio)methylene- β -propiolactone, *rac*-BPL^{CH₂SPh} and ESI-MSMS of $[M+H]^+$ m/z 195 with a collision energy of 10 eV. The zoomed region shows the peak for $[(COCH_2CH(CH_2SC_6H_5)O)H] \cdot Na^+$ ($m/z = 217.0293$). The two other fragmentation products depicted in red correspond to the loss of CH_2CO (m/z 149), and to the subsequent loss of CH_2 from the latter (m/z 135), or to the loss of CH_2CH_2CO from the monomer, respectively.

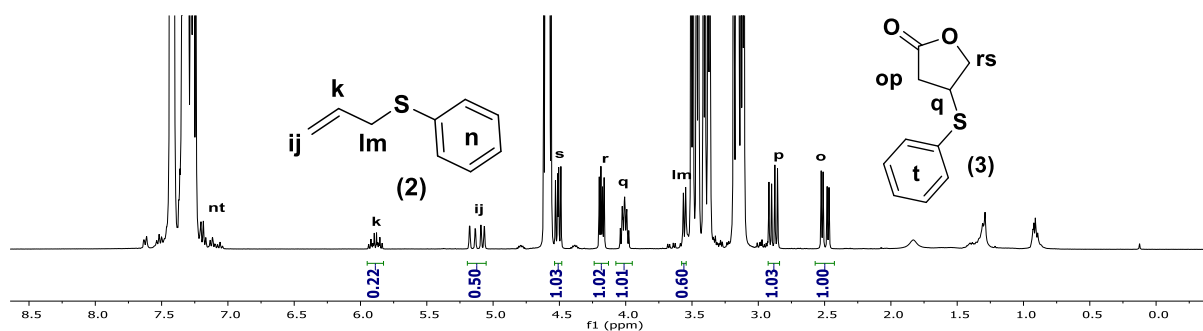


Figure S9. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) showing the decomposed (2) and the rearrangement (3) products of *rac*-BPL^{CH₂SPh}. Such rearrangements are known for β-lactones: J. W. Kramer, D. S. Treitler, G. W. Coates, Low Pressure Carbonylation of Epoxides to β-Lactones. *Organic Syntheses* **2003**, 86, 287-297.

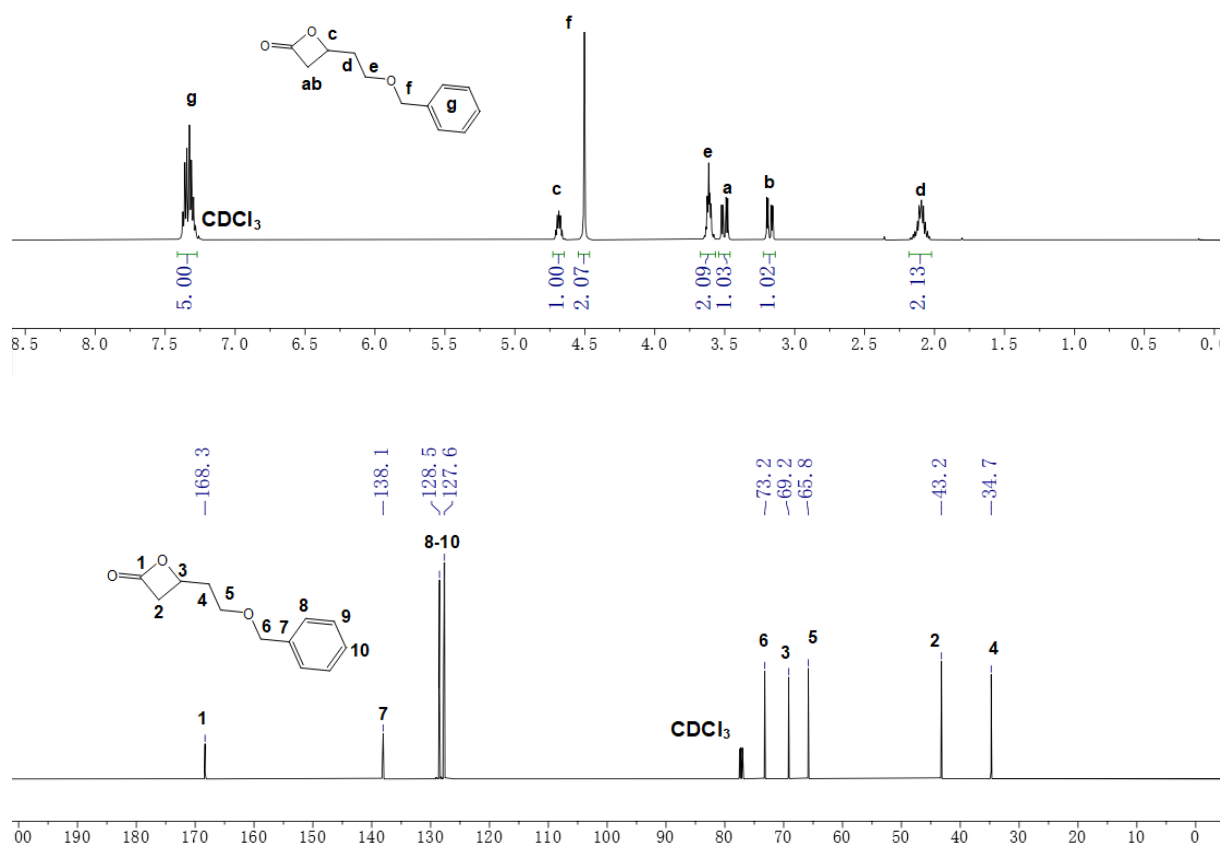


Figure S10. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) (top) and ¹³C (100 MHz, CDCl₃, 25 °C) (bottom) of *racemic* 4-(2-(benzyloxy)ethylene)-β-propiolactone, *rac*-BPL^{CH₂CH₂OCH₂Ph}.

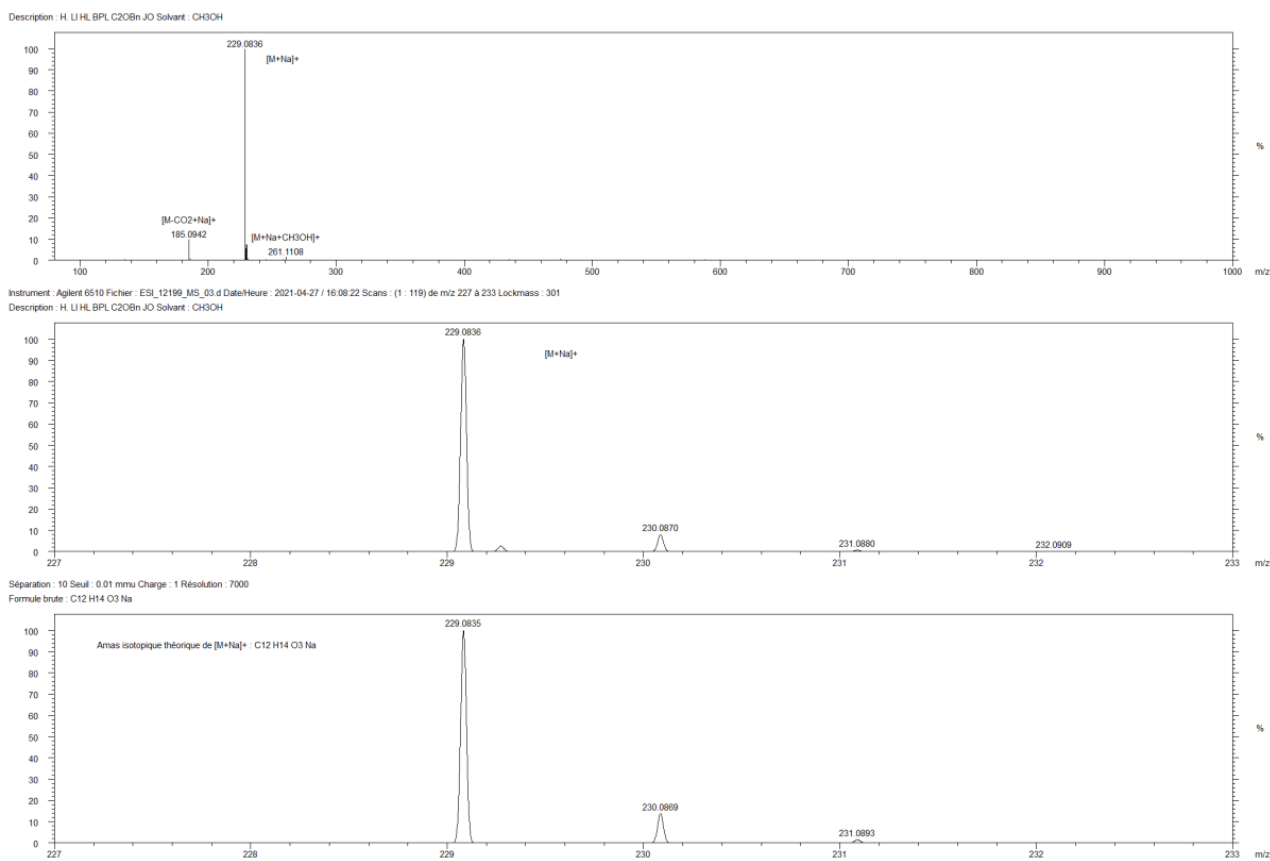


Figure S11. ESI-MS (ionized by Na^+ , solvent CH_3OH of *racemic* 4-(2-(benzyloxy)ethylene)- β -propiolactone, *rac*-BPL^{CH₂CH₂OCH₂Ph}. Zoomed regions correspond to the experimental (middle) and simulated (bottom) spectra.

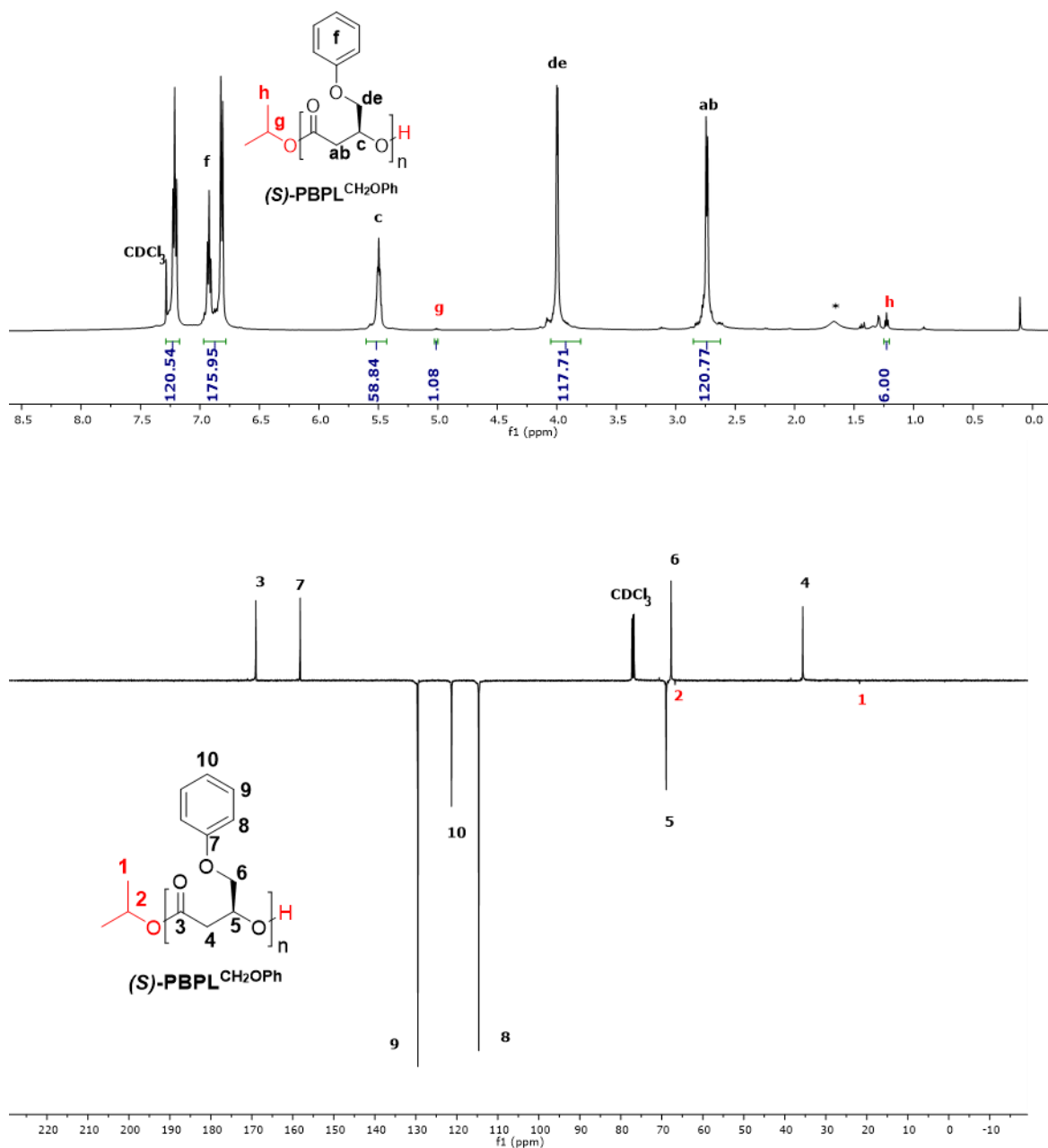


Figure S12. ¹H NMR (500 MHz, CDCl₃, 25 °C) (top) and J-MOD (125 MHz, CDCl₃, 25 °C) (bottom) spectra of isotactic PBPL^{CH₂OPh} prepared from the ROP of (*S*)-BPL^{CH₂OPh} mediated by complex **1d** in the presence of *i*PrOH and precipitated twice in cold pentane (Table 1, entry 13), * residual water.

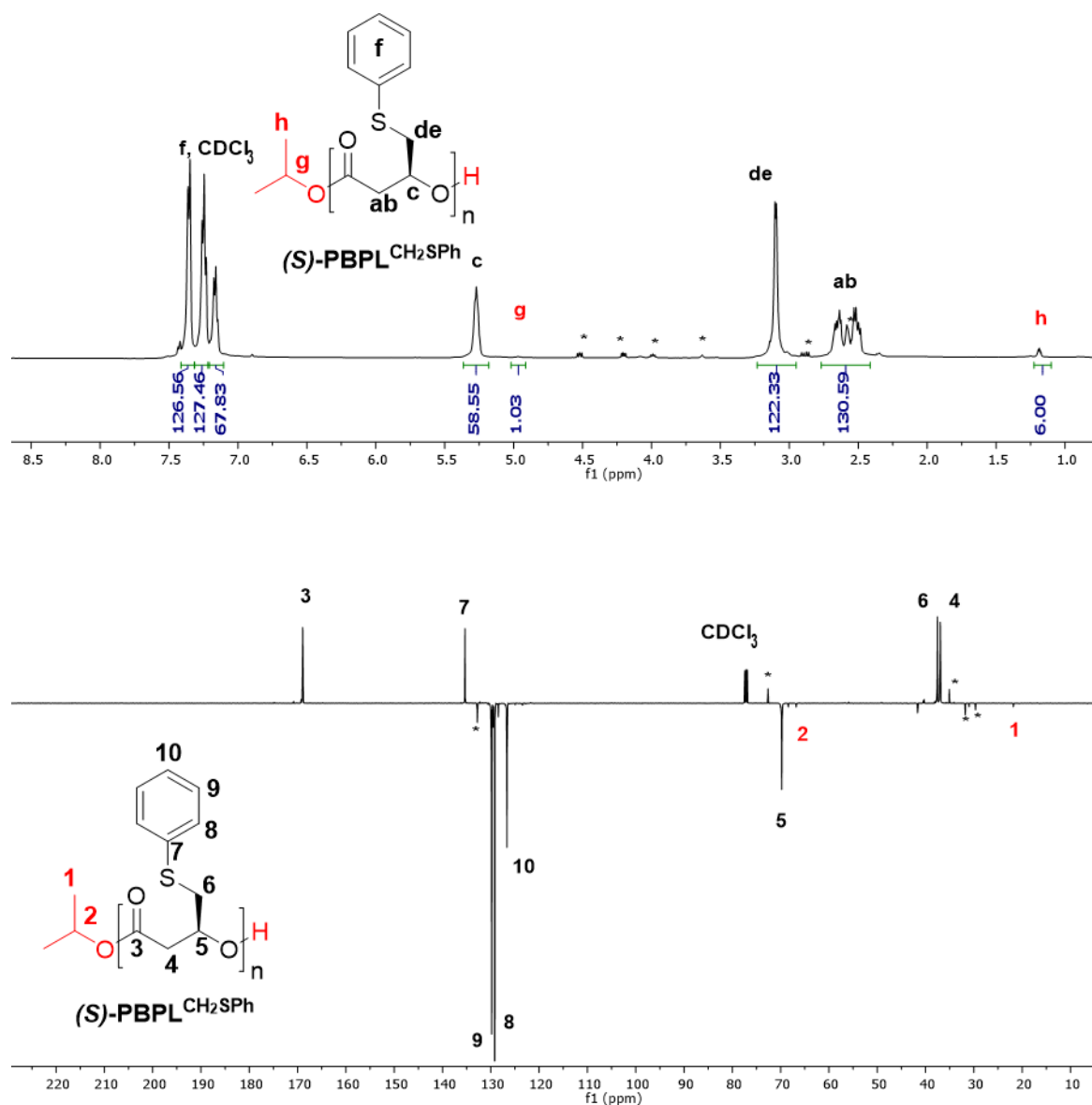


Figure S13. ¹H NMR (500 MHz, CDCl₃, 25 °C) (top) and J-MOD (125 MHz, CDCl₃, 25 °C) (bottom) spectra of isotactic PBPL^{CH₂SPh} prepared from the ROP of (*S*)-BPL^{CH₂SPh} mediated by complex **1d** in the presence of *i*PrOH and precipitated twice in cold pentane (Table 1, entry 27) (*: minor peaks correspond to the degradation product **3** of BPL^{CH₂SPh}).

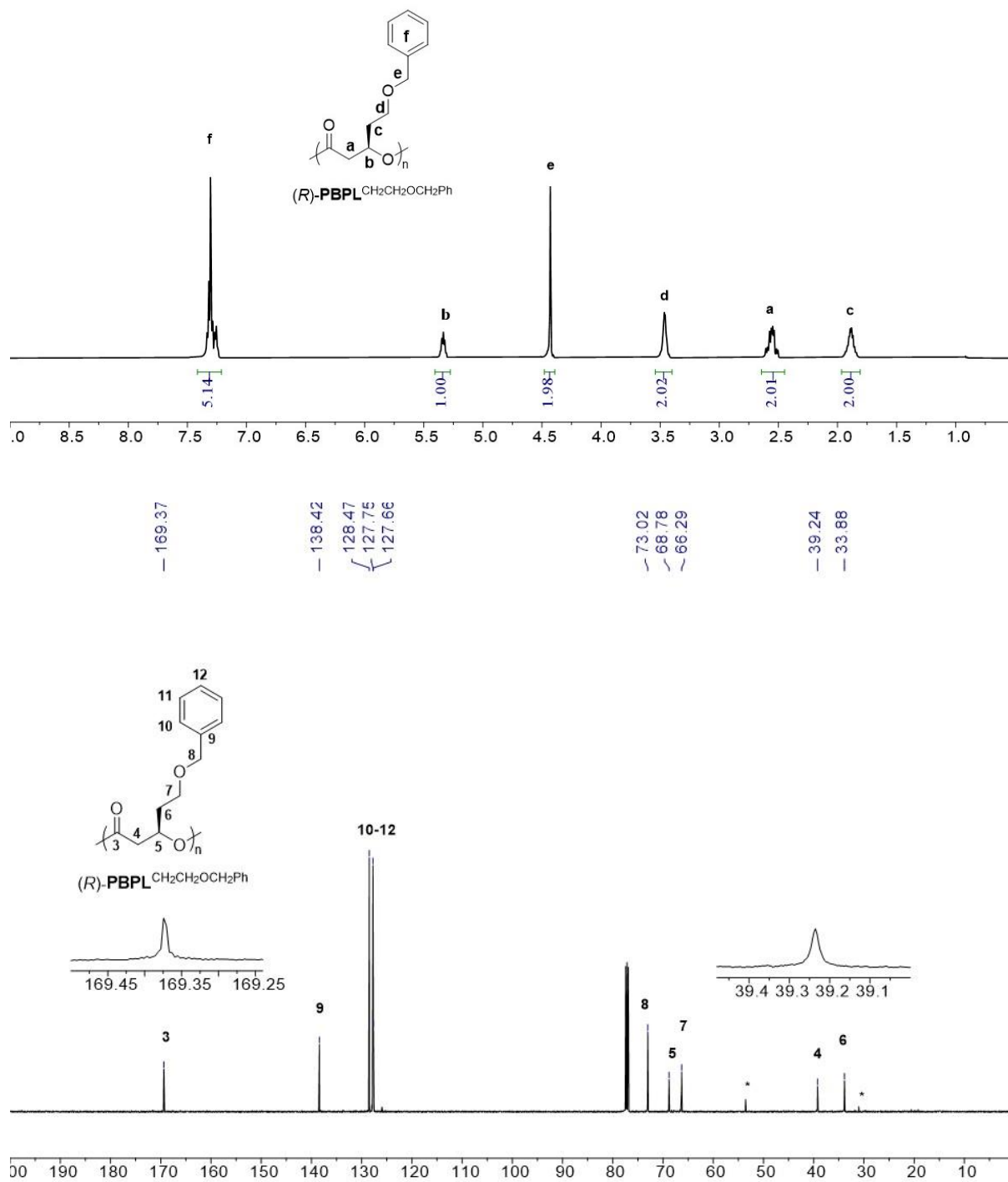


Figure S14. ^1H (top) and ^{13}C (bottom) NMR spectrum (500 and 125 MHz, CDCl_3 , 25 °C) of *isotactic* $\text{PBPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ prepared from the ROP of $(R)\text{-BPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ mediated by complex **1d** in the presence of *i*PrOH and precipitated twice in cold pentane (Table 1, entry 40).

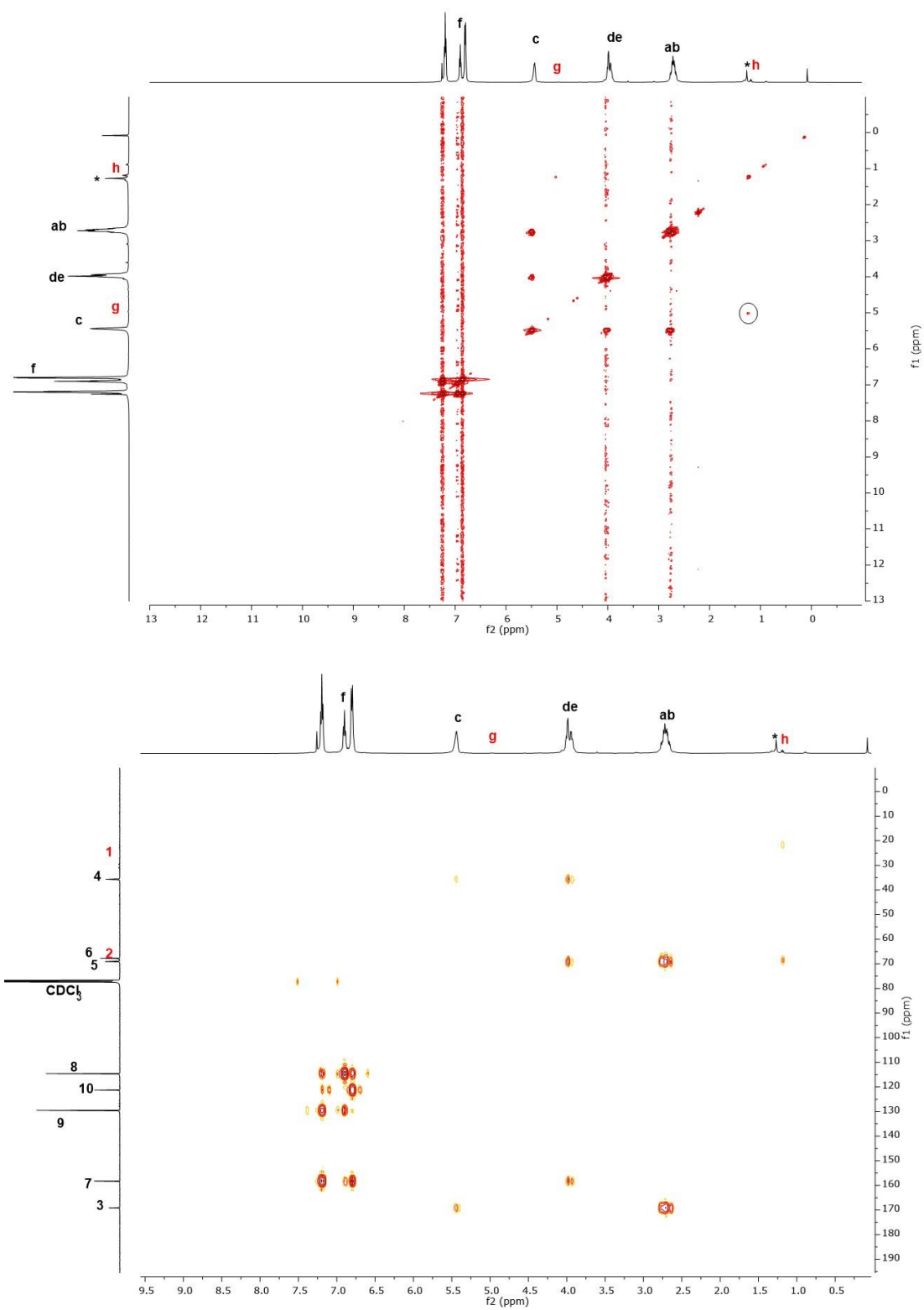


Figure S15. ¹H-¹H COSY NMR spectrum (500 MHz, CDCl₃, 25 °C) (top) and ¹H-¹³C HMBC (500 MHz, 125 MHz, CDCl₃, 25 °C) (bottom) of syndiotactic PBPL^{CH₂OPh} precipitated twice in cold pentane (Table 1, entry 6) (*: residual H-grease).

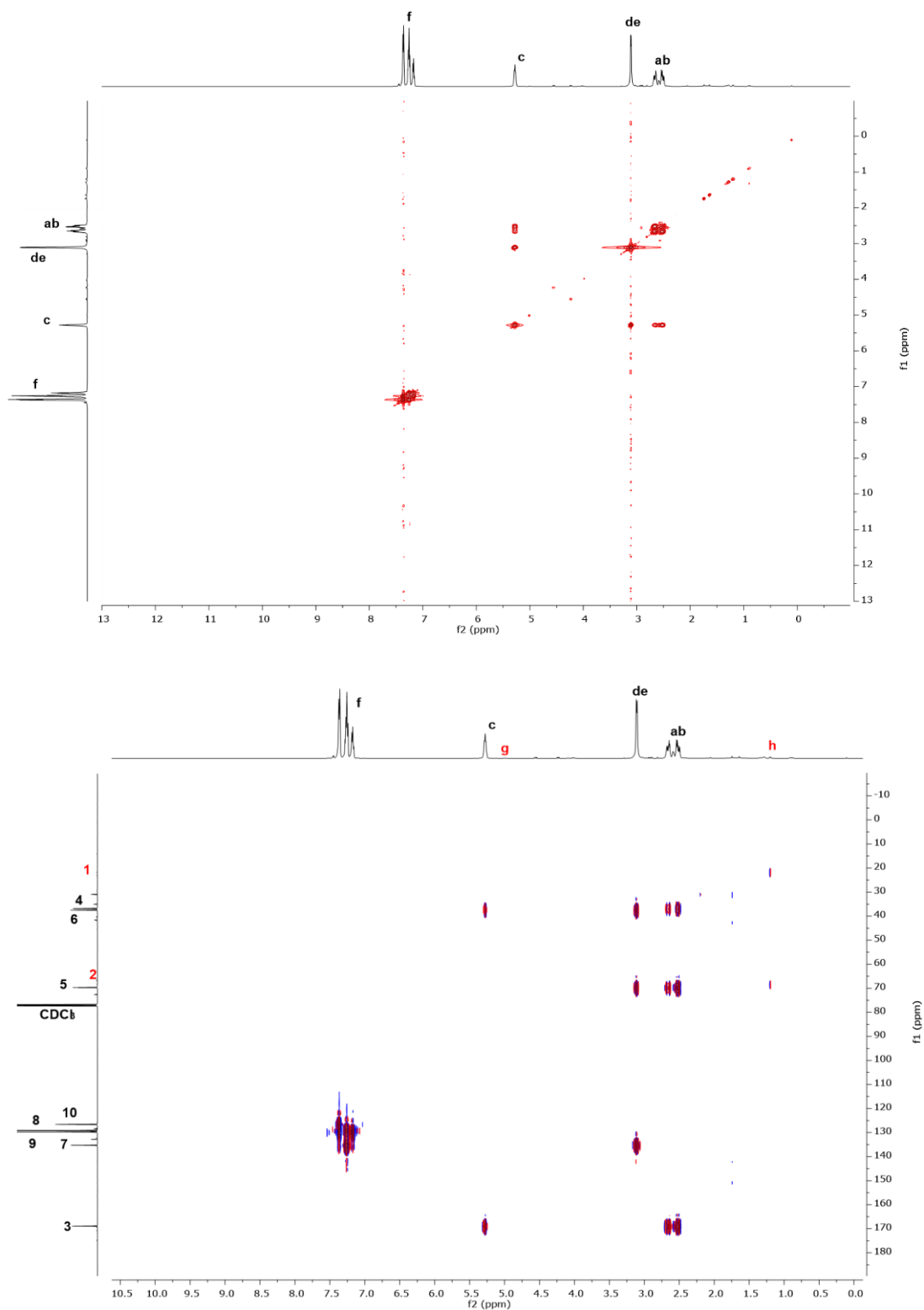


Figure S16. ^1H - ^1H COSY NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) (top) and ^1H - ^{13}C HMBC (500 MHz, 125 MHz, CDCl_3 , 25 $^\circ\text{C}$) (bottom) of syndiotactic $\text{PBPL}^{\text{CH}_2\text{SPh}}$ precipitated twice in cold pentane (Table 1, entry 26).

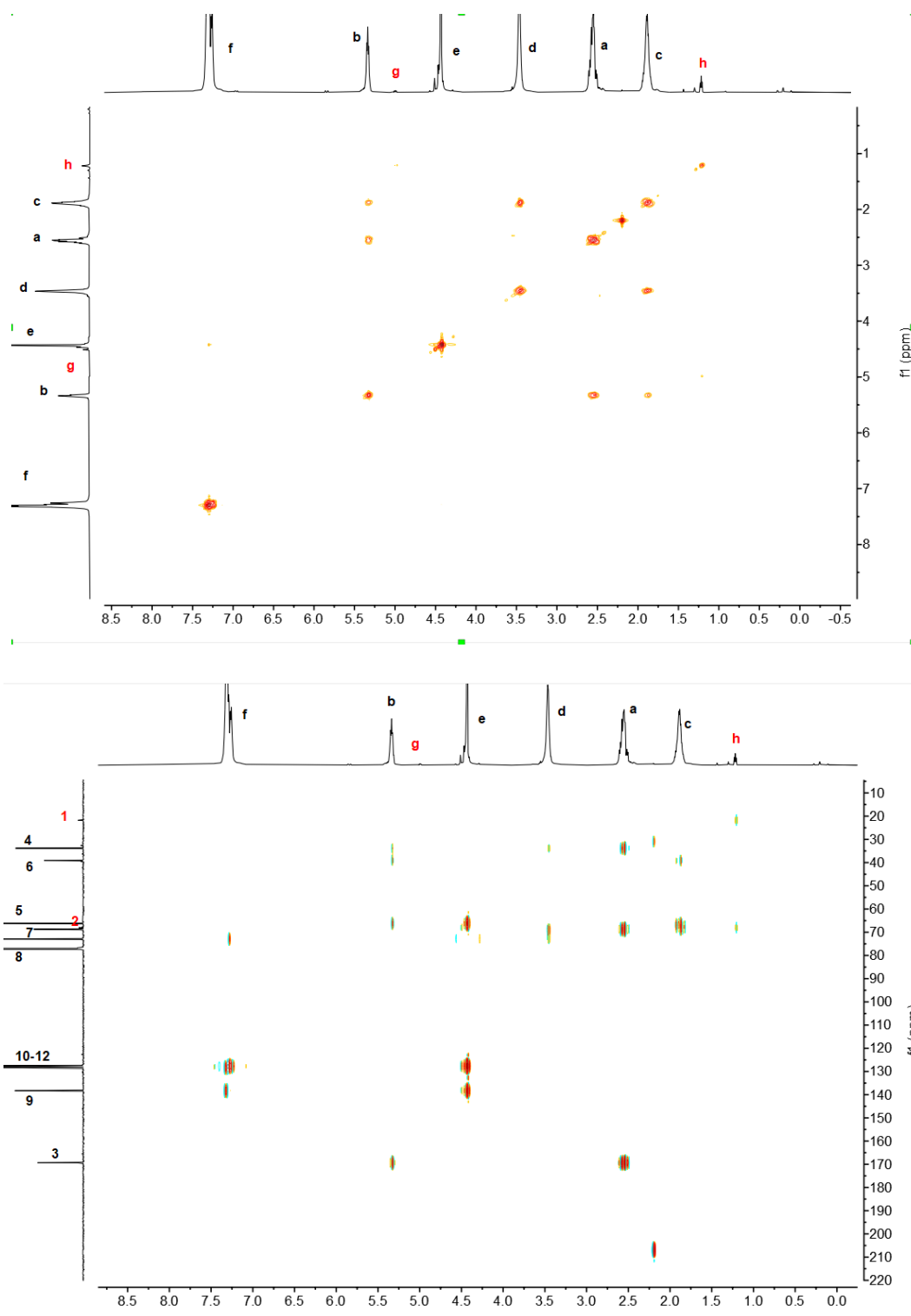


Figure S17. ^1H - ^1H COSY NMR spectrum (500 MHz, CDCl_3 , 25 °C) (top) and ^1H - ^{13}C HMBC (500 MHz, 125 MHz, CDCl_3 , 25 °C) (bottom) of syndiotactic PBPL $^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ precipitated twice in cold pentane (Table 1, entry 33).

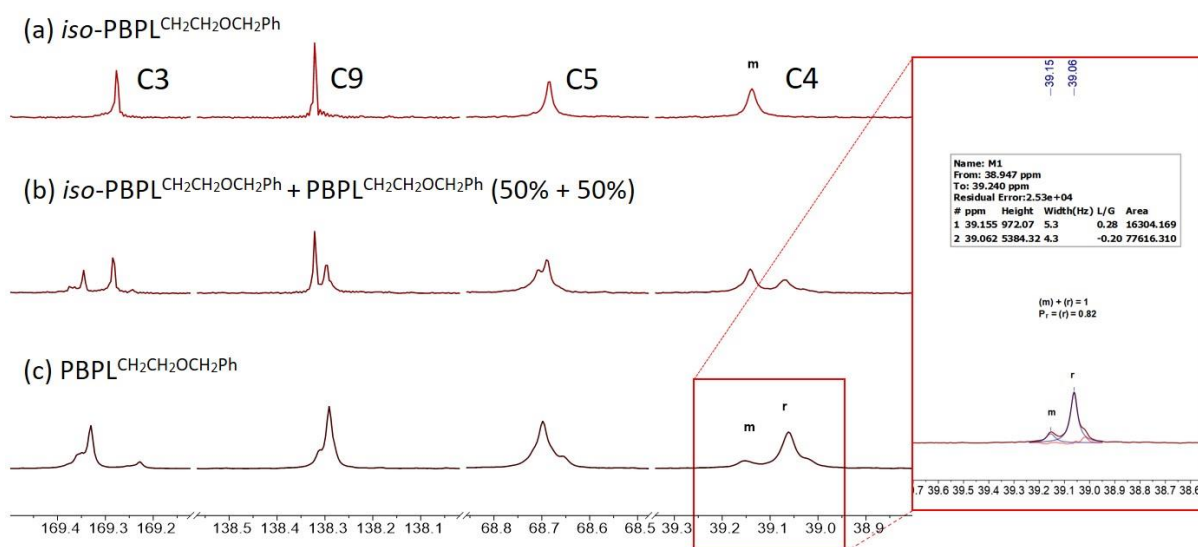


Figure S18. (a) Details of ^{13}C NMR spectrum (125 MHz, CDCl_3) of *isotactic* $\text{PBPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$; (b) a blend of *isotactic* $\text{PBPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ and $\text{PBPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ (Table 1, entries 40,39); (c) Details of ^{13}C NMR spectrum of $\text{PBPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ (Table 1, entry 39). The P_r values of $\text{PBPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ is then typically determined from the area fitting (or integration) values obtained from the NMR MestReNova software of the deconvoluted signals (labelled 1 and 2) corresponding to the *racemic* (*r*) and *meso* (*m*) diads, according to the equation: $P_r = (P_r(\text{C}_3) + P_r(\text{C}_5) + P_r(\text{C}_4)) / 3$, with $P_r(\text{C}_x) = \text{Area 1} / (\text{Area 1} + \text{Area 2})$ and C_x = corresponding carbon atom labeling.

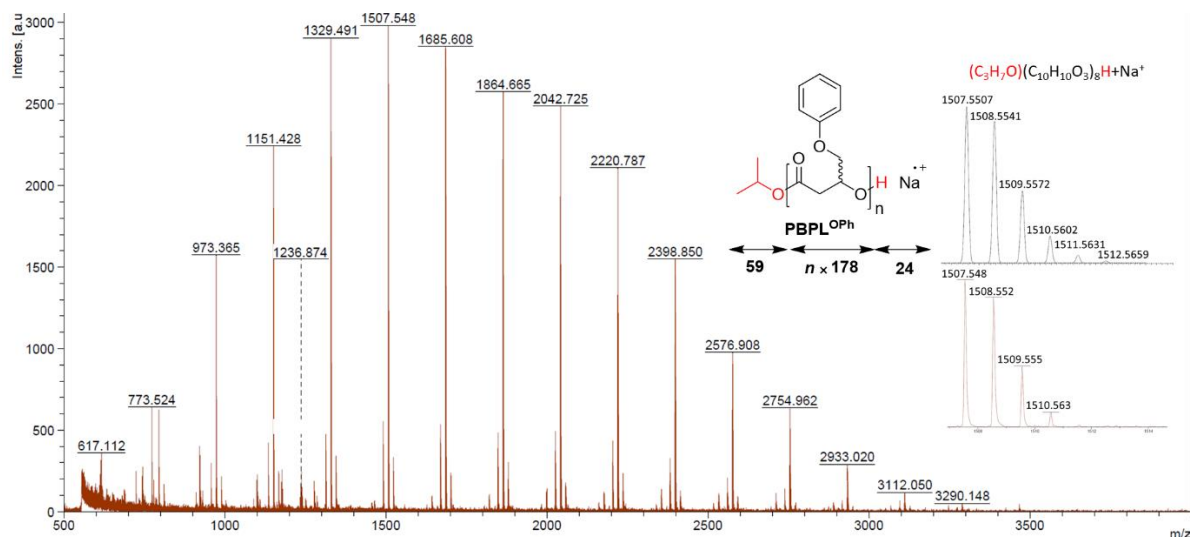


Figure S19. MALDI-ToF MS (DCTB matrix, ionized by Na^+) of $\text{PBPL}^{\text{CH}_2\text{O}}_{\text{Ph}}$ precipitated twice in cold pentane (Table 1, entry 5). Right zoomed regions correspond to the simulated (top) and experimental (bottom) spectra.

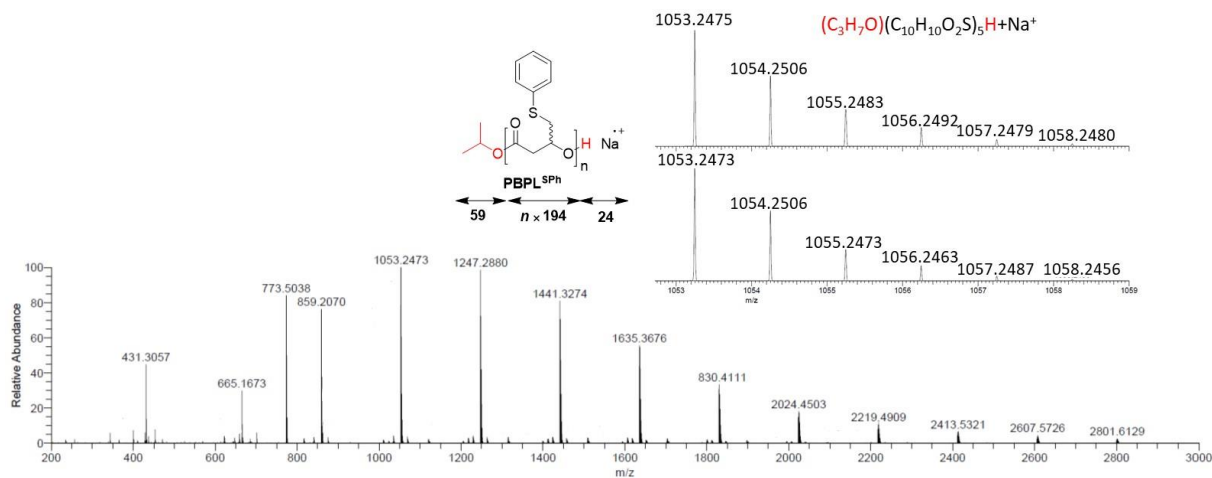


Figure S20. ESI-MS (ionized by Na^+ , solvent $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ (90/10 v:v)) of $\text{PBPL}^{\text{CH}_2\text{S}}_{\text{Ph}}$ (Table 1, entry 24) precipitated twice in cold pentane; right zoom spectra are theoretical data (top) vs. experimental (bottom).

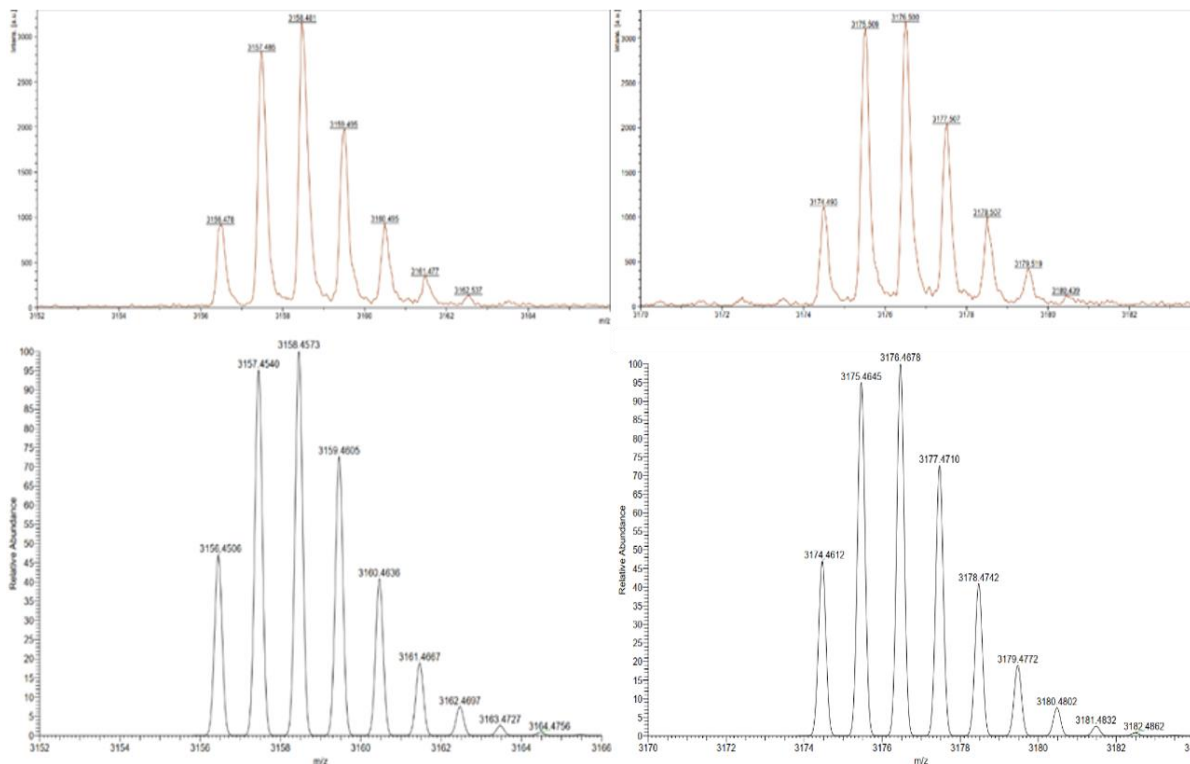
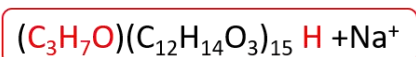
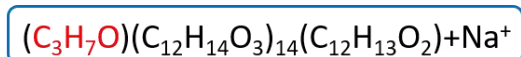
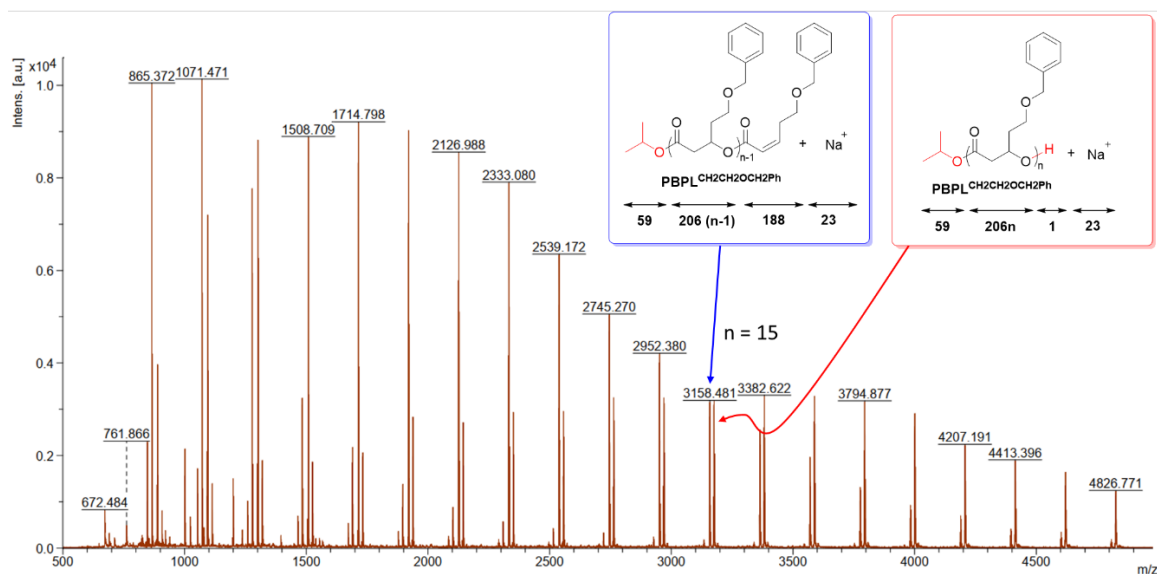


Figure S21. MALDI-ToF MS (DCTB matrix, ionized by Na^+) of $\text{PBPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ precipitated twice in cold pentane (Table 1, entry 34). Zoomed regions correspond to the simulated (top) and experimental (bottom) spectra.

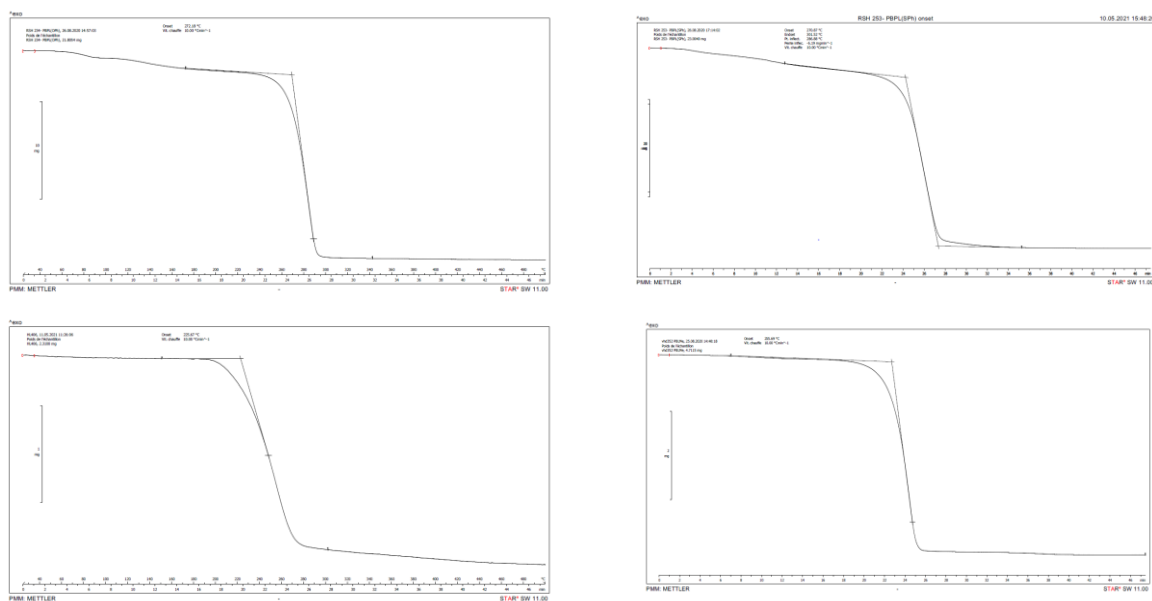


Figure S22. TGA thermograms of syndiotactic PBPL^{CH₂OPh} (top-left) (Table 1, entry 7); syndiotactic PBPL^{CH₂SPh} (top-right) (Table 1, entry 22); syndiotactic PBPL^{CH₂CH₂OCH₂Ph} (bottom-left) (Table 1, entry 38); and (bottom right) for PBPL^{Me} ($M_{n,NMR} = 7900 \text{ g mol}^{-1}$, $D_M = 1.04$; $P_r = 0.84$) prepared by ROP as previously reported (A. Amgoune, C. M. Thomas, S. Ilinca, T. Roisnel and J.-F. Carpentier, *Angew. Chem. Int. Ed.* 2006, **45**, 2782–2784).

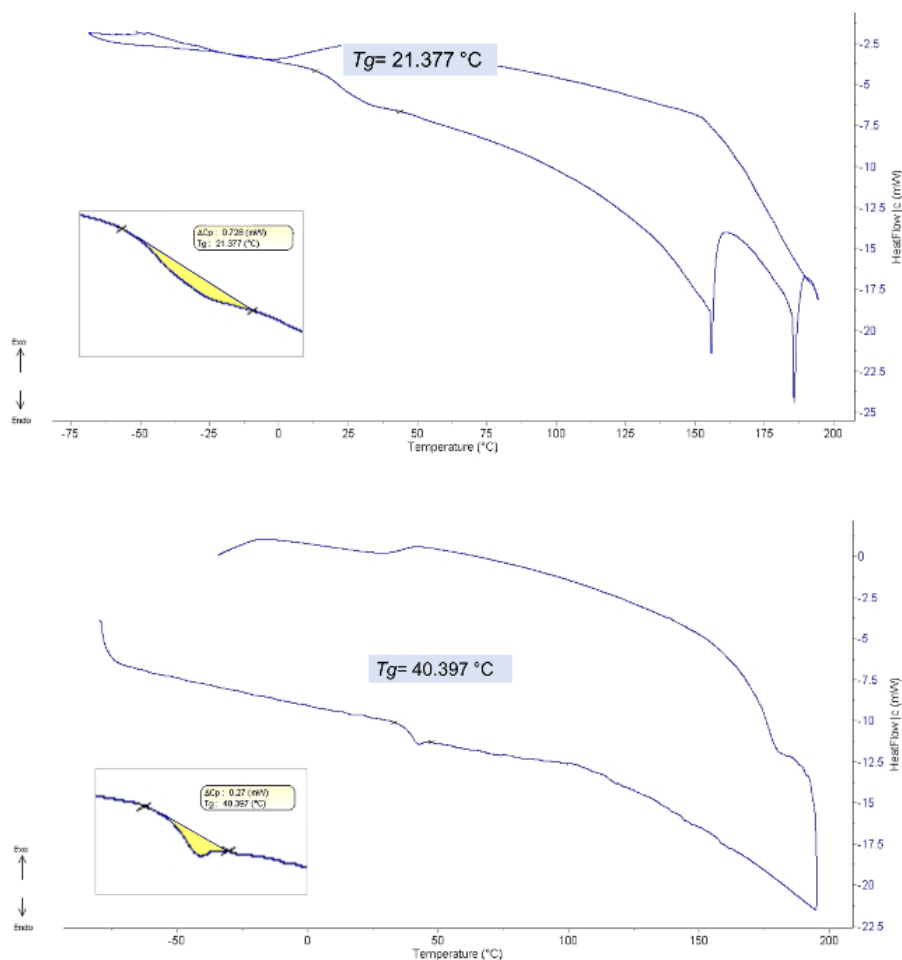


Figure S23. DSC thermogram (heating rate of 10 °Cmin⁻¹, second heating cycle, from -80 to 200 °C) of: (top) syndiotactic PBPL^{CH₂O^{Ph}} (*P_r* 0.75) synthesized by ROP of *rac*-BPL^{CH₂O^{Ph}} with Y{ONNO^{Cl2}}/(*i*PrOH) (Table 1, entry 4) - The spikes observed (ca 160° C, 190° C) arise from the cooling that sometimes occur upon filling in the liquid nitrogen fluid required to cool down the temperature; (bottom) syndiotactic PBPL^{CH₂O^{Ph}} (*P_r* 0.83) synthesized by ROP of *rac*-BPL^{CH₂O^{Ph}} with Y{ONNO^{tBu2}}/(*i*PrOH) (Table 1, entry 12).

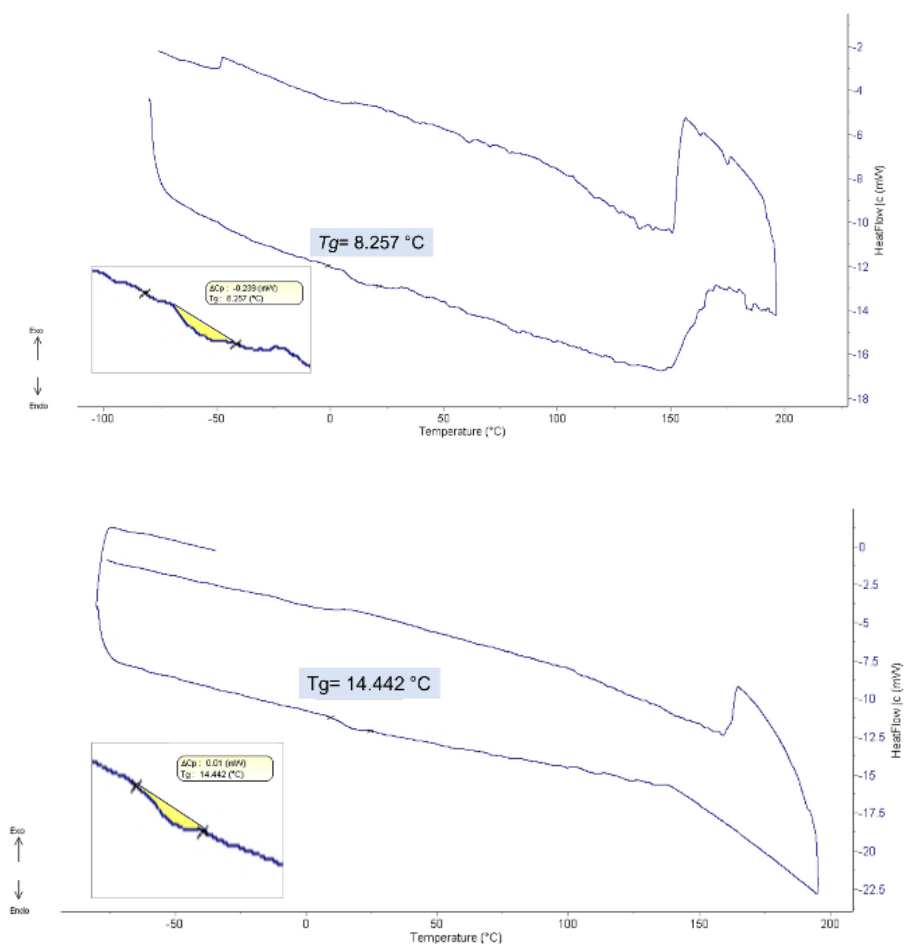


Figure S24. DSC thermogram (heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, second heating cycle -80 to $200\text{ }^{\circ}\text{C}$) of: (top) syndiotactic $\text{PBPL}^{\text{CH}_2\text{SPh}}$ (P_r 0.76) synthesized by ROP of $\text{rac-BPL}^{\text{CH}_2\text{SPh}}$ with $\text{Y}\{\text{ONNO}^{\text{Me}_2}\}/(i\text{PrOH})$ (Table 1, entry 15); (bottom) syndiotactic $\text{PBPL}^{\text{CH}_2\text{SPh}}$ (P_r 0.86) synthesized by ROP of $\text{rac-BPL}^{\text{CH}_2\text{SPh}}$ with $\text{Y}\{\text{ONNO}^{\text{tBu}_2}\}/(i\text{PrOH})$ (Table 1, entry 21).

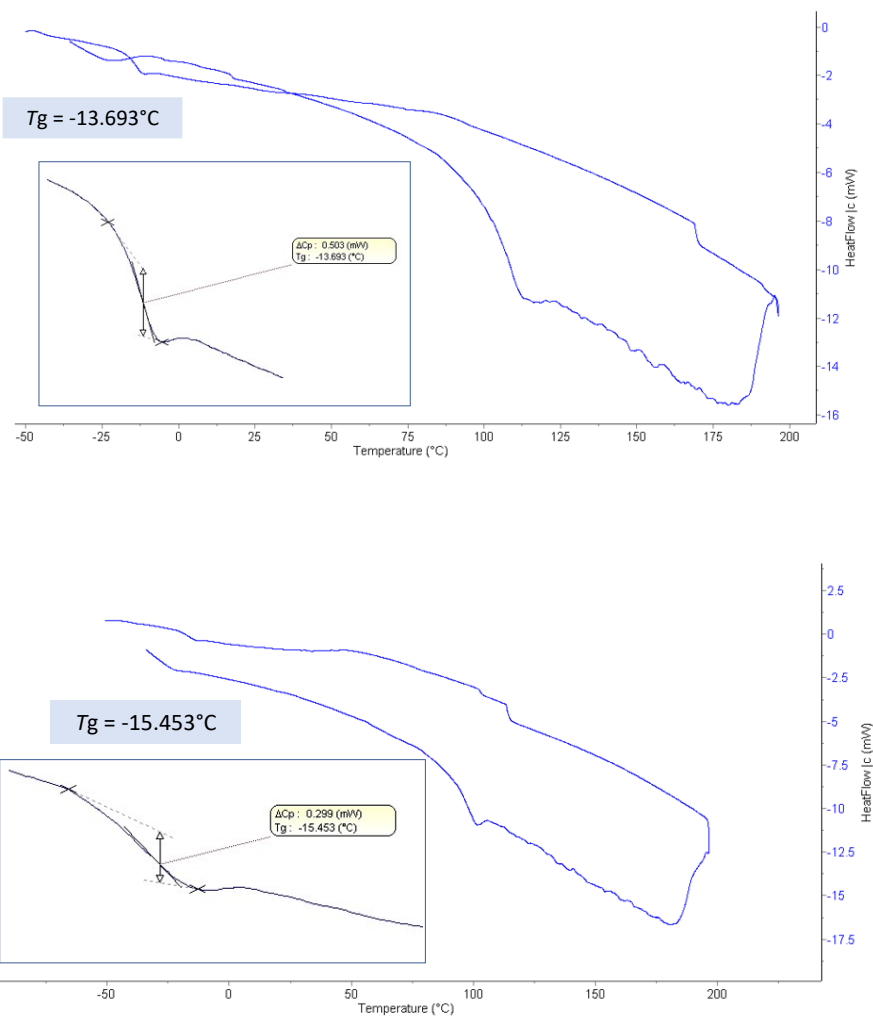


Figure S25. DSC thermogram (heating rate of 10°Cmin^{-1} , second heating cycle -60 to 200°C) of : (top) syndiotactic $\text{PBPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ (P_r 0.86) synthesized by ROP of $\text{rac-BPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ with $\text{Y}\{\text{ONNO}^{\text{cumyl}2}\}/(i\text{PrOH})$ (Table 1, entry 36); (bottom) atactic $\text{PBPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ (P_r 0.49) synthesized by ROP of $\text{rac-BPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ with $\text{Y}\{\text{ONNO}^{\text{Cl}2}\}/(i\text{PrOH})$ (Table 1, entry 31).