Supplemental Information to:

New Insights into Poly(Lactic-*co*-glycolic acid) Microstructure: Using Repeating Sequence Copolymers to Decipher Complex NMR and Thermal Behavior

*Ryan M. Stayshich and Tara Y. Meyer**

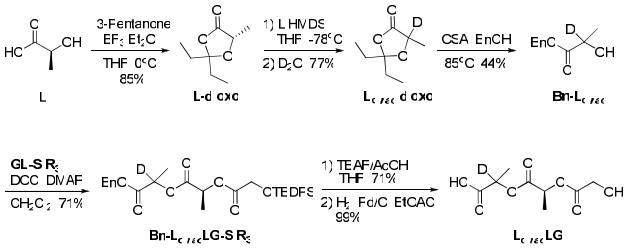
Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260

Corresponding author: tmeyer@pitt.edu

Results for Deuterium Labeled RSC PLGAs

A complementary subset of deuterium labeled segmers was prepared by incorporation of deuterium labeled monomers. Racemic α-deuterated benzyl lactate (**Bn-L$_{d,rac}$**) was prepared in three steps from lactic acid (Scheme S1). Adapting methods from Seebach, Greiner and Petasis, condensation of the acid with 3-pentanone using boron triflouride generated lactic acid dioxolanone, **L-dioxo**, in an 85% yield.[1] **L-dioxo** was treated with lithium hexamethyldisilazide to generate a lactic enolate that was quenched with deuterium oxide to afford **L$_{d,rac}$-dioxo** in a 77% yield with >85% deuterium incorporation.[2,3] Camphosulfonic acid mediated transesterification with benzyl alcohol gave **Bn-L$_{d,rac}$** in 44% yield and segmer **L$_{d,rac}$LG** was prepared similarly to **LLG** in a 50% yield.

Scheme S1.



Deuterium labeled 2-bromopropionic acid and bromoacetic acid (**L$_{d,rac}$-Br** and **G$_{d2}$-Br**) were prepared in three steps according to the procedure of Hoberman (Scheme S2).[4,5] Commercially available methylmalonic acid and *per*-deuterated malonic acid were treated with bromine in dry ether to generate the bromomalonic acids in quantitative yields. Treatment with deuterium oxide facilitated deuterium exchange. Decarboxylation followed by distillation under reduced pressure gave **L$_{d,rac}$-Br** and **G$_{d2}$-Br** in 99 and 65% yields, respectively, with > 99% deuterium incorporation. **L$_{d,rac}$-Br** and **G$_{d2}$-Br** were coupled with **L-Bn** under mild esterification conditions to give bromo-dimers **Bn-LL$_{d,rac}$-Br** and **Bn-LG$_{d2}$-Br** in 89 and 85% yields, respectively. The bromo-dimers were treated with cesium carbonate, potassium iodide and deuterated **G-SiR$_3$** in dry acetonitrile to give **Bn-LL$_{d,rac}$G-SiR$_3$** and **Bn-LG$_{d2}$G-SiR$_3$** in 48 and 46% yields, respectively. After subsequent deprotections, segmers **LL$_{d,rac}$G** and **LG$_{d2}$G** were isolated in 92 and 90% yields, respectively.

Scheme S2.

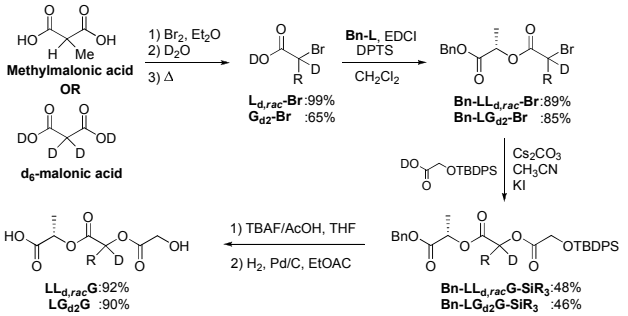


Table S1. ^{1}H NMR chemical shifts of specific sequences from RSCs standards

		Methine[a]				Methylene[b]		Methine[c]		
Sequence	Polyad	L^O	L	L^C	G	$H^{downfield}$	$H^{upfield}$	L^O	L	L^C
LG	all *i*		5.225			4.860	4.626		1.568	
	all *s*		5.239			4.807	4.686		1.560	
GLG	all *i*		5.244		G^C	4.864	4.686		1.57	
					G^O	4.804	4.720			
LLG	all *i*[d]	5.205		5.175		4.853	4.602	1.572		1.561
	iis[e]	5.215		5.176		4.852	4.611	1.567		1.557
	sii[f]	5.212		5.182		4.818	4.613	1.571		1.548
	ssi[e]	5.176		5.219		4.806	4.634	1.557		1.529
	iss[f]	5.187		5.221		4.785	4.686	1.554		1.528
	all *s*[g]	5.182		5.216		4.813	4.652	1.559		1.532

[a] quartet ^{3}J = 7.0- 7.2 Hz; [b] pair of doublets, ^{3}J = 15.6 – 16.2 Hz; [c] doublet ^{3}J = 7 – 7.2 Hz; [d]from **poly LLG**; [e]central tetrads from **poly LLGLL$_R$G** sequences *ssiissi* and *iissiis*; [f]central tetrads from **poly L$_R$LGLLG** sequences *issiiss* and *siissii*; [g]from **poly L$_R$LG** and **LL$_R$G**

Table S2. ^{13}C NMR chemical shifts of specific sequences from RSCs standards

		L Carbonyl			G Carbonyl			Methine		
Sequence	Polyad	L^O	L	L^C	G^O	G	G^C	L^O	L	L^C
LG	all *i*		169.38			166.43			69.15	
	all *s*		169.24			166.38			69.19	
GLG	all *i*		169.28		166.37		166.47		69.24	
LLG	all *i*[a]	169.50		169.37		166.49		68.98		69.18
	iis[b]	169.36		169.32		166.53		69.02		69.16
	sii[c]	169.46		169.30		166.47		68.98		69.17
	ssi[b]	169.36		169.14		166.31		69.11		69.39
	iss[c]	169.18		169.14		166.31		69.17		69.29
	all *s*[d]	169.22		169.14		166.36		69.17		69.35

[a] from **poly LLG**; [b]central tetrads from **poly LLGLL$_R$G** sequences *ssiissi* and *iissiis* ; [c]central tetrads from **poly L$_R$LGLLG** sequences *issiiss* and *siissii*; [d]from **poly L$_R$LG** and **LL$_R$G**

Experimental Section

Materials. 4-(Dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) was synthesized according to reported literature procedure.[6] Ethyl acetate, methylene chloride, acetonitrile and triethylamine were distilled under nitrogen from calcium hydride. THF was passed through activated alumina using a SPS 400 (Innovative Technology). Lactic acid was purified for

dioxolanone synthesis by vacuum distillation of a commercially available 90% solution (Acros) followed by recrystallization in benzene with ether and hexanes. All other reagents were purchased and used without further purification. Column chromatography was performed using EMD 60 Å, 40-63 μm standard grade silica.

NMR Spectroscopy. ^{1}H (300, 600 and 700 MHz) and ^{13}C (75, 150 and 175 MHz) NMR spectra were recorded with Bruker spectrometers in $CDCl_3$ and calibrated to the residual solvent peaks (δ 7.24 and δ 77.0, respectively). 2D NMR experiments were recorded with Bruker 600 and 700 MHz NMR spectrometers equipped with a 5 mm gradient probe using HMBC and HMQC gradient pulse sequences.

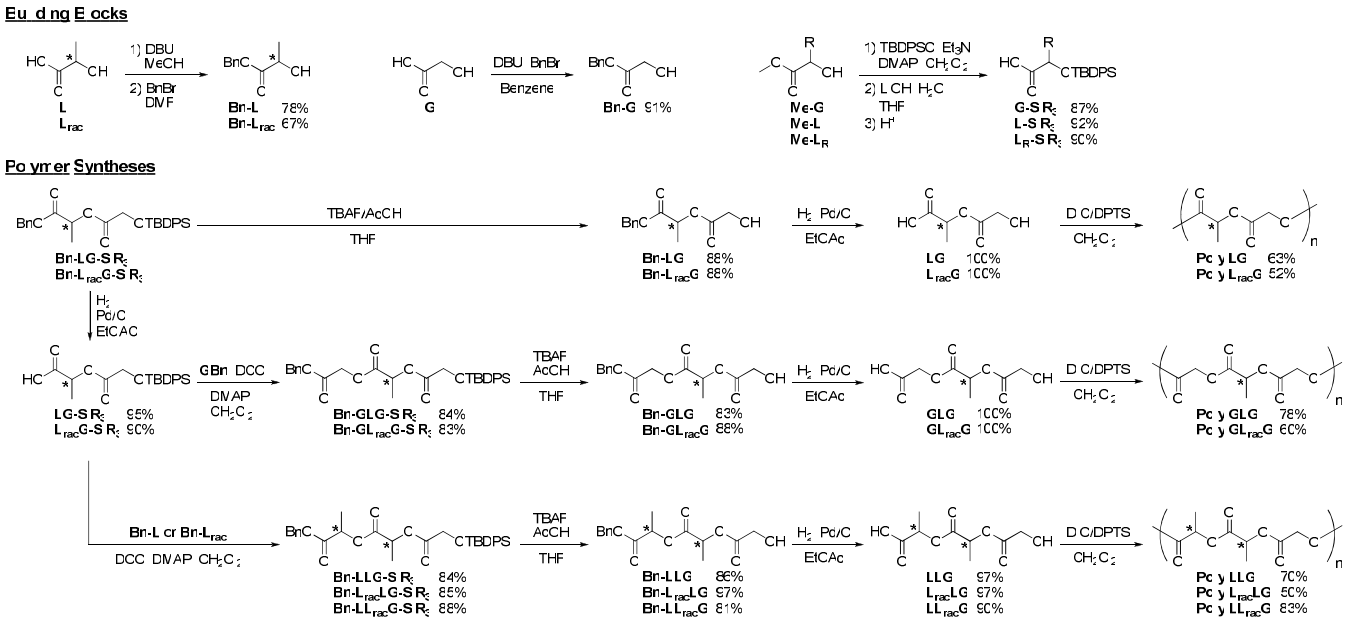
Molecular weight analysis. Molecular weights and polydispersities were acquired on a Waters GPC (THF and $CHCl_3$) with Jordi 500 Å, 1000 Å and 10000 Å divinylbenzene (DVB) columns and refractive index detector (Waters) was calibrated to polystyrene standards. Absolute molecular weights were performed by Impact Analytical, Inc using Waters Alliance Separations Module 2695, PLGel 5 μm Mixed-C column, Waters 2414 DRI and Wyatt Dawn EOS (690 nm) detectors. MALDI-TOF MS analysis was performed with a Voyager DE-STR instrument (Applied Biosystems) equipped with a 337-nm nitrogen laser. An accelerating voltage of 25 kV was applied. Mass spectra were recorded in the reflection mode (1000 shots). The polymer samples were dissolved in THF at a concentration of 1 mg/ml. The cationization agents used were potassium trifluoroacetate or sodium trifluoroacetate dissolved in THF at a concentration of 1 mg/ml. The matrix trans-2-(3-(4-tert-butylphenyl)-2-methyl-2-propenylidene)malononitrile(DCTB) was dissolved in THF at a concentration of 40 mg/ml. Solutions of matrix (10 mL), salt (1 mL), and polymer (5 mL) were mixed, and the mixture was

spotted by hand onto a stainless-steel MALDI target and left to dry. Baseline corrections and data analysis were performed by using Data Explorer version 4.0 from Applied Biosystems.[7]

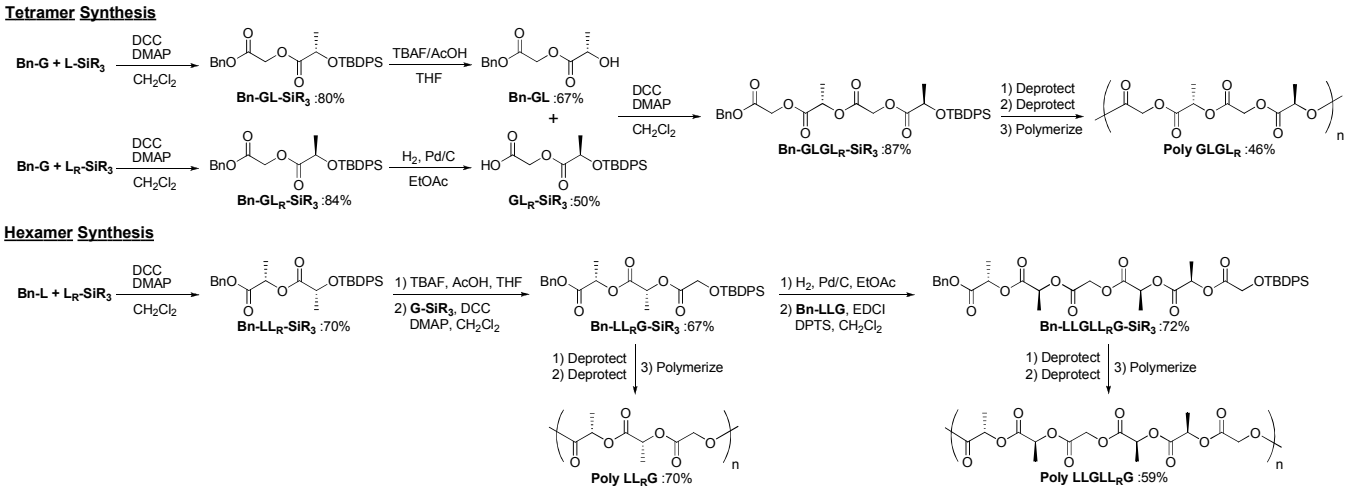
Thermal Analysis. Differential scanning calorimetry (DSC) measurements were performed with a Perkin Elmer Pyris 6 DSC. Standard data were collected with a heating and cooling rate of 10°C/min and data was collected from the second cycle. Annealed samples were prepared by drop- casting (CH_2Cl_2) into DSC pans, drying under vacuum for 24 h, and annealing at 85 °C for 3 h. The data for annealed samples was collected on the first run.

Synthesis

Scheme S3

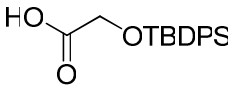


Scheme S4



Building Blocks

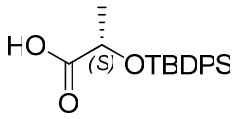
General procedures for the preparation of TBDPS-protected acids. The silyl-protected acids were prepared according to previous literature procedures.[8,9]



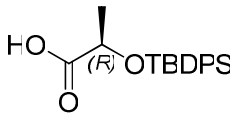
G-SiR$_3$. Methyl glycolate (4.63 g, 51.4 mmol), Et_3N (15.7 ml, 113 mmol) and 4-(dimethylamino)pyridine (DMAP) (3.05 g, 25 mmol) were combined in 200 ml of dry CH_2Cl_2 under N_2. After cooling the reaction mixture to 0 °C, *t*-butyldiphenylchlorosilane (TBDPSCl) (15.5 g, 56.5 mmol) was added and the reaction mixture was stirred at room temperature for 18 h. The reaction mixture was filtered and the filtrate was washed with 10% HCl (2 × 150 ml) and H_2O (2 × 100 ml). The organic layer was dried with $MgSO_4$ and concentrated *in vacuo* to yield a colorless oil (18.0 g, 97%). The ^{1}H NMR spectrum revealed that the resultant oil contained up to 10% TBDPSCl.

The resultant oil (11.0 g, 33.4 mmol) was dissolved in 550 ml of THF and cooled in an ice bath. $LiOH{\cdot}H_2O$ (5.6 g, 134 mmol) in 205 ml of H_2O was added dropwise over 15 min. The

ice bath was removed and the reaction was allowed to stir for 10 min. Water (100 ml) was added and the THF was removed *in vacuo*. The aqueous phase was extracted with Et_2O (2 × 150 ml) to remove starting material, acidified using 1.0 M HCl, and then extracted with Et_2O (2 × 150 ml). The second ethereal phase was dried with $MgSO_4$ and concentrated *in vacuo* to yield a colorless oil (8.07 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8-7.6 (m, 4H), 7.5-7.3 (m, 6H), 4.39 (s, 2H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 135.7, 132.4, 130.3, 128.1, 62.0, 26.9, 19.3; MS (EI) m/z 257 (M- *t*-butyl).

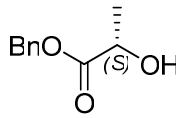


L-SiR$_3$. The product was a colorless solid (17.58 g, 92%). MP 73.5-75°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.2 (s, 1H), 7.8-7.6 (m, 4H), 7.5-7.3 (m, 6H), 4.33 (q, J = 6.78 Hz, 1H), 1.48 (d, J = 6.81 Hz, 3H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.2, 135.9, 135.8, 133.1, 132.5, 130.2, 128.0, 69.0, 27.0, 21.2, 19.3; MS (EI) *m/z* 271 (M-t-butyl).

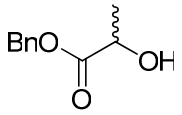


L$_R$-SiR$_3$ The product was a colorless solid (17.3 g, 90%). MP 69-70°C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.69- 7.64 (m, 4H), 7.5- 7.24 (m, 6H), 4.32 (q, J= 6.7 Hz, 1H), 1.34 (d, J= 6.9 Hz, 3H), 1.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 135.7, 132.8, 132.2, 130.2, 130.1, 127.8, 127.7, 69.1, 26.8, 21.0, 19.2; MS (EI) m/z 271 (M-*t*-butyl).

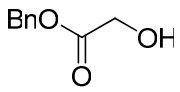
General procedure for benzyl protection of α-hydroxy acids. Benzyl protection of lactic acids was accomplished according to previous literature.[8,10]



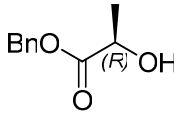
Bn-L. 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) (85.3 g, 0.56 mol) was added dropwise to a stirring solution of 90% (s)-lactic acid (50.0 g, 0.56 mol) and methanol (230 ml) in an ice bath. The reaction mixture was stirred at RT for 30 min and then the solvent was removed by distillation under reduced pressure. DMF (230 ml) was added to the reaction mixture, followed by the dropwise addition of benzyl bromide (80.4 g, 0.47 mol). After 20 h, DMF was removed by vacuum distillation and the resulting residue was taken up in brine and EtOAc. The layers were separated and the aqueous layer was extracted EtOAc (2 × 300 ml). The organic layers were combined and washed with 1.0 M HCl (3 × 250 ml), sat. $NaHCO_3$ (3 × 250 ml), and H_2O (2 × 250 ml). The organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. The product was purified by vacuum distillation (85 °C at 0.15 mm Hg) to yield a colorless liquid (65.61 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.5-7.3 (m, 5H), 5.19 (s, 2H), 4.30 (q, J= 6.90 Hz, 1H), 3.00 (s, 1H), 1.42 (d, J= 6.90 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 135.2, 128.4, 128.1, 67.1, 66.8, 20.2, MS (GC) m/z 180 (M+).



Bn-L$_{rac}$. The product was distilled under vacuum (78 °C at 0.1 mm Hg) to yield a colorless liquid (56.0 g, 67%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4-7.3 (m, 5H), 5.19 (s, 2H), 4.30 (quartet, J= 6.90 Hz, 1H), 3.00 (s, 1H), 1.42 (d, J= 6.90 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 135.2, 128.5, 128.4, 128.1, 67.1, 66.8, 20.2, MS (GC) m/z 180 (M+).



Bn-G. Glycolic acid (11.4 g, 0.15 mol) and DBU (22.84 g, 0.15 mol) were added to 300 mL of dry benzene and allowed to stir for 15 min. Benzyl bromide (30.8 g, 0.18 g) was added dropwise and the reaction mixture was refluxed for 6 h. The reaction mixture was then extracted with 1.0 M HCl (2 x 200 mL) followed by H_2O (1 x 200 mL). The organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. The concentrate was chromatographed (silica, 20% EtOAc in hexanes) to yield a colorless liquid (22.66 g, 91% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4-7.3 (m, 5H), 5.20 (s, 2H), 4.18 (d, J= 5.66 Hz, 2H), 2.66 (t, J= 5.68 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 135.0, 128.6, 128.5, 128.4, 67.2, 60.6; MS (GC) *m/z* 166 (M+).

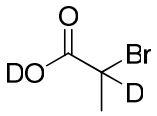


Bn-L$_R$. Benzyl alcohol (5.95 g, 55 mmol), **L$_R$-SiR$_3$** (16.5 g, 50 mmol), 1,3-dicyclohexylcarbodiimide (DCC) (11.35 g, 55 mmol) and DMAP (3.05 g, 25 mmol) were combined in 250 ml of methylene chloride (CH_2Cl_2) and stirred for 4 h at RT. The reaction mixture was filtered and concentrated *in vacuo*. The concentrate was chromatographed (silica, 2.5-5% EtOAc in hexanes) to yield a colorless oil (18.1 g, 86%). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.65- 7.62 (m, 4H), 7.42-7.2 (m, 11H), 5.03 (d, J= 12.3 Hz, 1H), 4.96 (d, J= 12.3 Hz, 1H), 4.31 (q, J= 6.7 Hz, 1H), 1.37 (d, J= 6.9 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 135.9, 135.7, 135.6, 133.5, 133.1, 129.7, 128.4, 128.2, 127.6, 127.5, 68.9, 66.3, 26.8, 21.2, 19.2; HRMS (M+Na) calc mass 441.1862, mass found 441.1883.

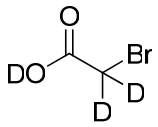
Di-protected **Bn-L$_R$-SiR$_3$** (18.0 g, 43 mmol) was added to 430 ml of dry THF under N_2. Acetic acid (4.4 ml, 77 mmol) was added followed by *t*-butyl ammonium fluoride (TBAF) (1.0

M, 64.5 ml, 64.5 mmol). After 1 h, the reaction mixture was added to 500 ml brine and 200 ml of Et_2O and the layers were separated. The aqueous layer was washed with Et_2O (1 x 200 ml). The organic layers were combined, dried with $MgSO_4$ and concentrated *in vacuo*. The concentrate was chromatographed (silica, 10-15% EtOAc in hexanes) to yield a colorless liquid (6.91 g, 89%). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.36-7.32 (m, 5H), 5.19 (s, 2H), 4.35-4.26 (m, 1H), 2.88 (d, J= 4.8 Hz, 1H), 1.42 (d, J= 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 135.2, 128.6, 128.5, 128.2, 67.3, 66.8, 20.3; HRMS (M+Na) calc mass 180.0786, mass found 180.0779.

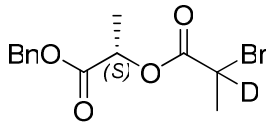
Deuterated Building Blocks and Oligomers



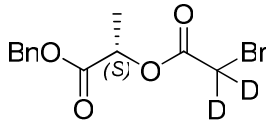
α-d-bromopropionic acid ($L_{d,rac}$-Br). Methyl malonic acid (20.0 g, 0.17 mol) was dissolved in 500 ml of dry Et_2O under N_2 and cooled to 0 °C. Bromine (8.7 ml, 0.17 mol) was added dropwise and upon completion of the addition the reaction mixture was concentrated by vacuum distillation. The pale orange colored solid was dried under vacuum overnight. Deuterium oxide (200 ml, 20 mol) was added and the reaction mixture was allowed to stir for 1 h. D_2O was removed by vacuum distillation and the product was dried under vacuum for 5 d. Decarboxylation was achieved by heating the reaction mixture at 150 °C for 1 h until gas bubbles were no longer observed. The red liquid was distilled under reduced pressure (105-110 °C) to yield a colorless liquid (25.9 g, 99%). ^{1}H NMR (300 MHz, DMSO) δ 1.93 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 168.7, 58.5, 26.9; MS (EI) m/z 155 (M+).



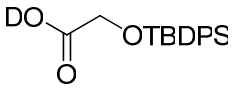
α-d,d-bromo acetic acid (G_{d2}-Br). Per-deuterated malonic acid (20 g, 0.18 mol) was dissolved in 500 ml of dry Et_2O under N_2 and cooled to 0 °C. Bromine (9.53 ml, 0.18 mol) was added dropwise and upon completion the reaction mixture was concentrated by vacuum distillation. The pale orange solid was dried under vacuum overnight. Decarboxylation was achieved by heating the reaction mixture at 140 °C for 2 h until gas bubbles were no longer observed. The red liquid was distilled under reduced pressure (112 °C) to yield a colorless liquid (16.94 g, 65%). ^{13}C NMR (75 MHz, DMSO) δ 168.5, 27.5 (m); MS (EI) m/z 142 (M+).



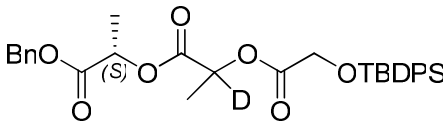
Bn-LL$_{d,rac}$-Br. The acid **L$_{d,rac}$-Br** (8.0 g, 51.6 mmol), **Bn-L** (10.8 g, 60 mmol) and DPTS (3.04 g, 10 mmol) were combined in 200 ml of dry CH_2Cl_2 under N_2. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (11.5 g, 60 mmol) was added and the reaction mixture was stirred at RT for 16 h. The reaction mixture was washed with water (2 x 300 ml) to remove the urea. The organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. The concentrate was chromatographed (silica, CH_2Cl_2) to yield a colorless oil (14.52 g, 89%). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.34-7.31 (m, 10H), 5.22-5.11 (m, 6H), 1.82-1.79 (m, 3H), 1.68-1.66 (m, 3H), 1.55-1.51 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 169.9, 169.7, 169.4, 135.1, 128.6, 128.5, 128.4, 128.2, 128.1, 69.8, 69.7, 67.2, 21.4, 21.3, 16.7, 16.6; MS (EI) m/z 317 (M+).



Bn-LG$_{d2}$-Br. Procedure as described above for **Bn-LL$_{d,rac}$-Br**. The crude was chromatographed (silica, CH_2Cl_2) to yield a colorless oil (13.64 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.31 (m, 5H), 5.24-5.13 (m, 3H), 1.52 (d, J= 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 169.7, 135.2, 128.7, 128.6, 128.5, 128.2, 77.1 (t), 70.1, 67.3, 16.8; MS (EI) m/z 303 (M+).

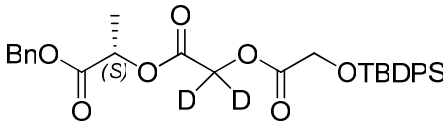


D-G-SiR$_3$. Deuterium oxide was added to silyl-protected glycolic acid (**G-SiR$_3$**) and the mixture was allowed to stir for 1 h. D_2O was removed by vacuum distillation and the product was dried under vacuum overnight. The compound was used without further purification.

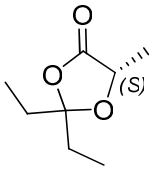


Bn-LL$_{d,rac}$G-SiR$_3$. The bromo-dimer, **Bn-LL$_{d,rac}$-Br** (4.52 g, 14.3 mmol) was combined with **D-G-SiR$_3$** (5.0 g, 15.9 mmol), Cs_2CO_3(7.0 g, 21.5 mmol) and KI (0.24 g, 1.4 mmol) in 200 ml dry CH_3CN under N_2. The reaction mixture was stirred at RT for 24 h, quenched with D_2O and extracted with Et_2O (2 x 150 ml). The organic layers were dried with $MgSO_4$ and concentrated *in vacuo*. The concentrate was chromatographed (silica, 5% EtOAc in hexanes) to yield a colorless oil (3.74 g, 48%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.66 (m, 8H), 7.4-7.3 (m, 22H), 5.21-5.11 (m, 6H), 4.34 (d, J= 16.8 Hz, 1H), 4.32 (d, J=16.8 Hz, 1H), 4.28 (d, J= 16.8 Hz, 1H), 4.27 (d, J= 16.8 Hz, 1H), 1.51 (d, J= 7.2 Hz, 3H), 1.45 (d, J= 6.6 Hz, 3H), 1.43 (s, 6H), 1.073 (s, 9H), 1.069 (s, 9H); ^{13}C (150 MHz, $CDCl_3$) δ 170.6, 170.4, 170.0, 169.83, 169.82,

169.7, 135.58, 135.55, 135.54, 135.2, 135.1, 132.74, 132.71, 129.9, 128.6, 128.5, 128.4, 128.2, 127.8, 127.7, 69.3, 69.1, 68.3 (m), 67.2, 67.1, 62.0, 61.9, 26.6, 19.3, 16.76, 16.74, 16.71, 16.6; MS (EI) m/z 536 (M+).

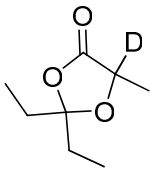


Bn-LG$_{d2}$G-SiR$_3$. Procedure as described above for **Bn-LL$_{d,rac}$G-SiR$_3$**. The crude was chromatographed (silica, 5% EtOAc in hexanes) to yield a colorless oil (3.55 g, 46%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.7-7.65 (m, 4H), 7.41-7.3 (m, 11H), 5.20 (q, J= 6.9 Hz, 1H), 4.72 (d, J= 18 Hz, .05H), 4.64 (d, J= 14.4 Hz, .05H), 4.35 (d, J= 16.8 Hz, 1H), 4.32 (d, J= 17.4 Hz, 1H), 1.48 (d, J= 6.6 Hz, 3H), 1.06 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 169.9, 166.8, 135.5, 135.1, 132.7, 132.6, 129.9, 128.6, 128.4, 128.2, 127.8, 69.4, 67.2, 61.9, 60.1 (m), 26.6, 19.3, 16.8; MS (ES) m/z 559 (M+Na).

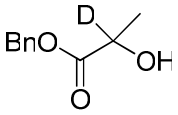


L-Dioxo. Lactic acid (solid, not aqueous solution) (23.7 g, 263 mmol) was added to 300 ml of dry THF and cooled to -78 °C. While cooling, BF_3•Et_2O (49 ml, 400 mmol) was added dropwise over 10 min followed by the dropwise addition of 3-pentanone (56 ml, 400 mmol) over 10 min. Once the additions were completed the reaction mixture was warmed to 0 °C. After 6 h, Et_3N (60 ml, 430 mmol) was added dropwise and the reaction mixture was poured into 250 ml of ice water. The aqueous layer was extracted with Et_2O (3 × 150 ml). The ethereal layers were dried with $MgSO_4$ and concentrated *in vacuo*. The concentrate was chromatographed (silica, 5% EtOAc in hexanes) to yield a colorless liquid (35.3 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.43

(q, J= 6.7 Hz, 1H), 1.85-1.65 (m, 4H), 1.40 (d, J= 6.6 Hz, 3H), 0.93-0.86 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 113.9, 70.8, 30.7, 30.0, 17.4, 7.4, 6.7; MS (EI) m/z 159 (M+1).



$L_{d,rac}$-Dioxo. Lithium hexamethyldisilazide (46.9 g, 280 mmol) was dissolved in 500 ml of dry THF and cooled to -78 °C. **L-Dioxo** (22.2 g, 140 mmol) was dissolved in 30 ml of THF and added dropswise. The reaction mixture was allowed to stir at -78 °C for 30 min and quenched with D_2O (11.2 g, 560 mmol). Once at RT, the reaction mixture was added to a brine solution and extracted with Et_2O (3 × 300 ml). The ethereal layers were dried with $MgSO_4$ and concentrated *in vacuo*. The concentrate was chromatographed (silica, 10% EtOAc in hexanes) to yield a colorless liquid (17.1 g, 77%) with > 85% deuterium incorporation. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.45 (q, J= 6.9 Hz, 0.14 H), 1.82-1.69 (m, 4H), 1.43-1.4 (m, 3H), 0.95-0.86 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 114.1, 70.8, 70.5 (t), 30.8, 30.1, 17.4, 7.5, 6.8; HRMS (M+) calc mass 159.1005 mass found 159.1006.

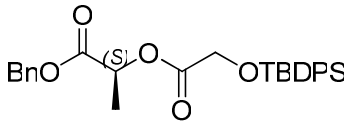


Bn-$L_{d,rac}$. Dioxolanone **$L_{d,rac}$-Dioxo** (5.0 g, 31.4 mmol) was dissolved in benzyl alcohol (BnOH, 34 g, 314 mmol) with camphorsulfonic acid (3.48 g, 15 mmol) and heated at 85 °C for 6 h. After cooling, the mixture was taken up in CH_2Cl_2 and washed with saturated $NaHCO_3$ (2 × 100 ml) and brine (75 ml). The organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. The concentrate was chromatographed (silica, 15% EtOAc in hexanes) followed by removal of excess BnOH by vacuum distillation to yield a colorless oil (2.52 g, 44%). ^{1}H NMR (600 MHz,

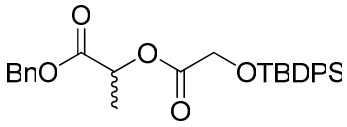
$CDCl_3$) δ 7.38-7.31 (m, 5H), 5.19 (s, 2H), 3.08 (s, 1H), 1.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.5, 135.2, 128.6, 128.5, 128.2, 67.3, 66.5 (t), 20.3; HRMS (M+) calc mass 181.0849 found 181.0850.

General procedure for DCC/DMAP coupling reactions. One equivalent of TBDPS-acid was combined with 1-1.2 equivalents of benzyl protected alcohol, 1.2 equivalents of DCC and 0.5 equivalents of DMAP. The reaction mixture was let stir at RT for 4 h under N_2 and then filtered to remove dicyclohexylurea. The filtrate was concentrated *in vacuo* and chromatographed (silica, 2.5-5% EtOAc in hexanes).

Dimer synthesis. Diprotected dimers were prepared according to previous literature.[8]

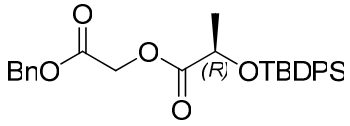


Bn-LG-SiR$_3$. The product was a colorless oil (9.25 g, 87%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.7-7.6 (m, 4H), 7.4-7.3 (m, 11H), 5.2-5.1 (m, 3H), 4.34 (d, J= 16.8 Hz, 1H), 4.27 (d, J= 16.8 Hz, 1H), 1.29 (d, J= 7.2 Hz, 3H), 1.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.2, 135.5, 135.2, 129.8, 128.5, 128.3, 128.1, 128.0, 127.8, 68.7, 66.9, 61.9, 26.6, 19.2, 16.8; MS (Q-Tof) m/z 499 (M+Na), 445, 399; HRMS (M+Na) calc mass 499.1917, found 499.1883; elemental analysis calc. C 70.56, H 6.77, found C 70.89, H 6.83.

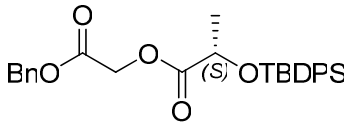


Bn-L$_{rac}$G-SiR$_3$. The product was a colorless oil (8.76 g, 82%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.8- 7.6 (m, 4H), 7.5- 7.3 (m, 11H), 5.2- 5.1 (m, 3H), 4.37 (d, J= 16.5 Hz, 1H), 4.31 (d, J= 13.2 Hz, 1H), 1.45 (d, J= 7.2 Hz, 3H), 1.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.2,

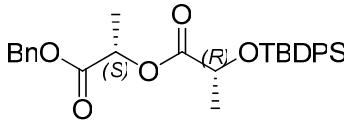
135.6, 135.3, 134.8, 132.7, 129.9, 128.6, 128.4, 128.0, 127.4, 68.7, 67.0, 62.0, 26.7, 19.3, 16.9; MS (ES) m/z 499.1 (M+Na).



Bn-GL$_R$-SiR$_3$. The product was a colorless oil (18.2 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.64 (m, 4H), 7.43-7.31 (m, 6H), 5.15 (s, 2H), 4.60 (d, J= 15.9 Hz, 1H), 4.44 (d, J= 15.9 Hz, 1H), 4.38 (q, J= 6.8 Hz, 1H), 1.39 (d, J= 6.9 Hz, 3H), 1.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 167.3, 135.9, 135.7, 135.0, 133.4, 133.0, 19.8, 128.6, 128.5, 128.4, 127.7, 127.6, 68.7, 67.0, 60.6, 26.8, 21.3, 19.2; MS (EI) m/z 419 (M-*t*-butyl).



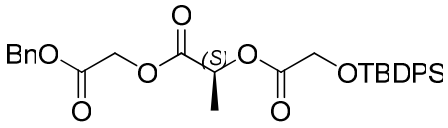
Bn-GL-SiR$_3$. The product was a colorless oil (9.5 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.66 (m, 4H), 7.43-7.30 (m, 11H), 5.16 (s, 2H), 4.60 (d, J= 15.9 Hz, 1H), 4.44 (d, J= 15.9 Hz, 1H), 4.38 (q, J= 6.8 Hz, 1H), 1.39 (d, J= 6.9 Hz, 3H), 1.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 167.3, 135.9, 135.7, 135.0, 134.8, 133.4, 132.9, 129.8, 129.6, 128.6, 128.5, 128.4, 127.7, 127.6, 127.5, 68.6, 67.0, 60.6, 26.8, 21.2, 19.2; HRMS (M+Na) calc mass 499.1917, found 499.1965.



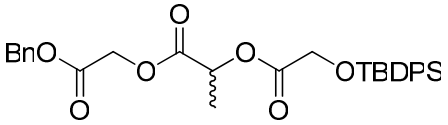
Bn-LL$_R$-SiR$_3$. The product was a colorless oil (10.5 g, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67- 7.63 (m, 4H), 7.43- 7.30 (m, 11H), 5.14 (s, 2H), 5.00 (q, J= 7.0 Hz, 1H), 4.37 (q, J= 6.6 Hz, 1H), 1.42 (d, J= 7.2 Hz, 3H), 1.35 (d, J= 6.6 Hz, 3H), 1.08 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$)

δ 173.0, 170.2, 135.8, 135.7, 135.3, 133.5, 133.0, 129.8, 128.5, 128.3, 128.1, 127.6, 127.5, 68.9, 68.7, 66.9, 26.8, 21.2, 19.2, 16.8; HRMS (M+Na) calc mass 513.2073, found 513.2075.

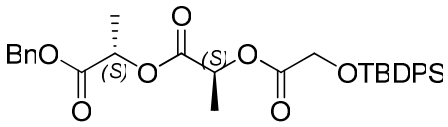
Trimer Synthesis. Di-protected trimers were prepared by coupling of **LG-SiR$_3$** or **L$_{rac}$G-SiR$_3$** with desired benzyl-protected alcohol using general DCC/DMAP coupling procedures unless otherwise stated.



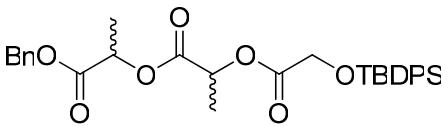
Bn-GLG-SiR$_3$. The product was a colorless oil (6.39 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.7-7.6 (m, 4H), 7.5-7.3 (m, 11H), 5.16 (s, 2H), 5.15 (q, J= 7.2 Hz, 1H), 4.77 (d, J= 15.6 Hz, 1H), 4.59 (d, J= 15.0 Hz, 1H), 4.33 (d, J= 16.2 Hz, 1H), 4.28 (d, J= 16.8 Hz, 1H), 1.46 (d, J= 7.8 Hz, 3H), 1.06 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 169.9, 167.0, 135.6, 135.5, 134.9, 132.7, 129.9, 128.6, 128.5, 127.8, 127.7, 68.5, 67.2, 61.9, 60.9, 26.6, 19.2, 16.8; HRMS (M+Na) calc mass 557.197, found 557.196.



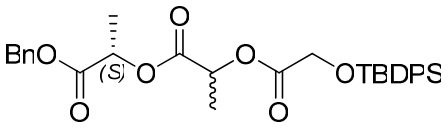
Bn-GL$_{rac}$G-SiR$_3$. The product was a colorless oil (5.8 g, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.7-7.6 (m, 4H), 7.5-7.3 (m, 11H), 5.16 (s, 2H), 5.15 (q, J= 7.2 Hz, 1H), 4.76 (d, J= 16.2 Hz, 1H), 4.59 (d, J= 16.8 Hz, 1H), 4.33 (d, J= 16.8 Hz, 1H), 4.28 (d, J= 16.8 Hz, 1H), 1.46 (d, J= 7.8 Hz, 3H), 1.06 (s, 9H), ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 169.9, 167.0, 135.6, 135.5, 134.9, 132.7, 129.9, 128.6, 128.5, 127.8, 68.5, 67.2, 61.9, 61.0, 26.6, 19.2, 16.8; HRMS (M+Na) calc mass 557.197, found 557.192.



Bn-LLG-SiR$_3$. The product was a colorless oil (35.3 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.7-7.6 (m, 4H), 7.5-7.3 (m, 11H), 5.21-5.1 (m, 4H), 4.34 (d, J= 17.4 Hz, 1H), 4.28 (d, J= 16.8 Hz, 1H), 1.51 (d, J= 7.2 Hz, 3H), 1.44 (d, J= 6.6 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 170.0, 169.8, 135.6, 135.5, 135.1, 134.8, 132.7, 129.9, 128.6, 128.5, 128.2, 127.8, 127.7, 69.1, 68.4, 67.1, 61.9, 26.6, 19.3, 16.8, 16.7; HRMS (M+Na) calc mass 571.212, found 571.213.

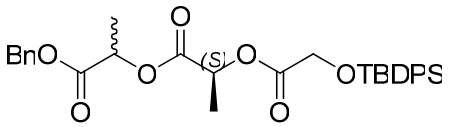


Bn-L$_{rac}$L$_{rac}$G-SiR$_3$. The product was a colorless oil (6.74 g, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.66 (m, 16H), 7.41-7.30 (m, 44H), 5.21-5.10 (m, 16H), 4.36-4.27 (m, 8H), 1.51 (d, J= 7.2 Hz, 3H), 1.45-1.43 (m, 21H), 1.07 (s, 36H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 170.4, 170.0, 169.83, 169.82, 169.7, 135.6, 135.5, 135.2, 135.1, 132.7, 129.9, 128.6, 128.5, 128.4, 128.2, 127.8, 127.7, 69.3, 69.1, 68.7, 68.5, 67.14, 67.13, 61.98, 61.96, 26.6, 19.3, 16.8, 16.76, 16.74, 16.66; HRMS (M+Na) calc mass 571.2128, found 571.2093.

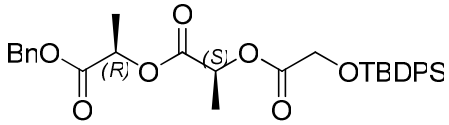


Bn-LL$_{rac}$G-SiR$_3$. The product was a colorless oil (33.6 g, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.7-7.6 (m, 4H), 7.5-7.3 (m, 22H), 5.21-5.1 (m, 8H), 4.34 (d, J= 16.8 Hz, 1H), 4.32 (d, J= 16.8 Hz, 1H), 4.282 (d, J= 16.8 Hz, 1H), 2.281 (d, J= 17.4 Hz, 1H), 1.51 (d, J= 7.2 Hz, 3H), 1.45 (d, J= 7.2 Hz, 3H), 1.44 (d, J= 7.2 Hz, 3H), 1.43 (d, J=7.2 Hz, 3H), 1.07 (s, 18H); ^{13}C NMR (150

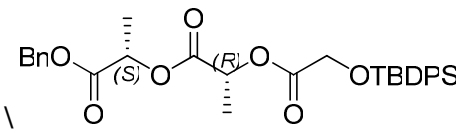
MHz, $CDCl_3$) δ 170.6, 170.4, 170.0, 169.84, 169.82, 169.7, 135.57, 135.53, 135.14, 135.1, 132.7, 132.67, 129.9, 128.6, 128.57, 128.47, 1218.43, 128.24, 128.22, 127.8, 69.2, 69.1, 68.6, 68.4, 67.14, 67.13, 61.96, 61.93, 26.6, 19.2, 16.82, 16.75, 16.73, 16.65; HRMS (M+Na) calc mass 571.213, found 571.213.



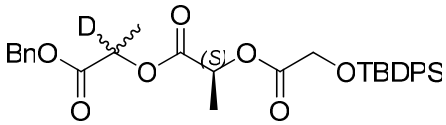
Bn-L$_{rac}$LG-SiR$_3$. The product was a colorless oil (12.53 g, 88%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.7- 7.6 (m, 8H), 7.4-7.3 (m, 22H), 5.21-5.1 (m, 8H), 4.35 (d, J= 16.8 Hz, 1H), 4.32 (d, J= 16.8 Hz, 1H), 4.28 (d, J= 17.4 Hz, 4H), 1.51 (d, J= 7.2 Hz, 3H), 1.45 (d, J= 7.2 Hz, 3H), 1.44 (d, J= 7.8 Hz, 6H), 1.08 (s, 9H), 1.07 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 170.4, 170.0, 169.83, 169.81, 169.68, 135.57, 135.53, 135.15, 135.1, 132.7, 132.6, 129.9, 128.6, 128.5, 128.4, 128.2, 127.8, 69.3, 69.1, 68.6, 68.4, 67.1, 62.0, 61.9, 26.6, 19.2, 16.8, 16.75, 16.74, 16.7; MS (EI) m/z 491 (M-tbutyl).



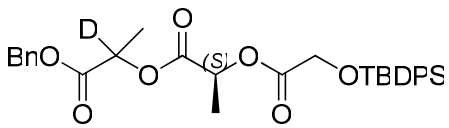
Bn-L$_R$LG-SiR$_3$. The product was a colorless oil (4.79 g, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.66 (m, 4H), 7.42-7.30 (m, 11H), 5.17 (q, J= 7.2 Hz, 1H), 5.169 (d, J= 12.0 Hz, 1H), 5.14 (q, J= 7.2 Hz, 1H), 5.12 (d, J= 12.6 Hz, 1H), 4.31 (d, J= 16.8 Hz, 1H), 4.27 (d, J= 16.8 Hz, 1H), 1.44 (d, J= 7.8 Hz, 3H), 1.43 (d, J= 7.2 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 169.8, 169.7, 135.6, 135.5, 135.2, 132.7, 129.9, 128.6, 128.4, 128.2, 127.8, 69.3, 68.3, 67.1, 62.0, 26.6, 19.2, 16.8, 16.7; HRMS (M+Na) calc mass 571.2128, found 571.2090.



Bn-LL$_R$G-SiR$_3$. Benzyl-protected dimer **Bn-LL$_R$** (4.8 g, 19 mmol), **G-SiR$_3$** (7.23 g, 23 mmol), DCC (4.75 g, 23 mmol) and DMAP (1.22 g, 10 mmol) were combined in 200 ml of CH_2Cl_2 and stirred at room temperature for 4 h under N_2. The reaction mixture was filtered and concentrated *in vacuo*. The concentrate was chromatographed (silica, 2.5-5% EtOAc in hexanes) to yield a colorless oil (7.3 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68- 7.65 (m, 4H), 7.43- 7.30 (m, 11H), 5.19- 5.12 (m, 4H), 4.32 (d, J= 16.8 Hz, 1H), 4.28 (d, J= 16.8 Hz, 1H), 1.45 (d, J= 7.8 Hz, 3H), 1.43 (d, J= 7.2 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 169.8, 169.7, 135.6, 135.5, 135.1, 132.7, 129.9, 128.6, 128.4, 128.2, 127.8, 69.3, 68.7, 67.1, 61.9, 26.6, 19.3, 16.9, 16.7; HRMS (M+Na) calc mass 571.2128, found 571.2087.

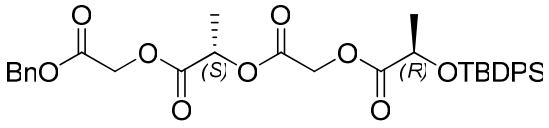


Bn-L$_{d,rac}$LG-SiR$_3$. The product was a colorless oil (4.68 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.65 (m, 8H), 7.42-7.29 (m, 22H), 5.17-5.10 (m, 6H), 4.33 (d, J= 16.8 Hz, 1H), 4.31 (d, J= 16.2 Hz, 1H), 4.272 (d, J= 16.2 Hz, 1H), 4.270 (d, J=16.8 Hz, 1H), 1.50 (s, 3H), 1.43 (s, 3H), 1.42 (d, J= 7.8 Hz, 6H), 1.063 (s, 9H), 1.060 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 170.4, 170.0, 169.83, 169.8, 169.7, 135.6, 135.5, 135.1, 132.7, 129.9, 128.6, 128.2, 127.8, 69.1 (t), 68.6, 68.4, 67.1, 61.94, 61.92, 26.6, 19.2, 16.8, 16.64, 16.62, 16.61; MS (EI) m/z 493 (M-tbutyl).



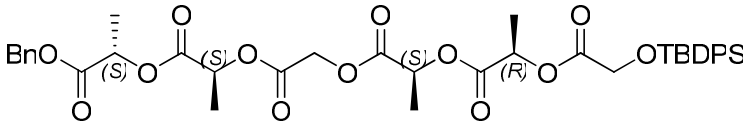
Bn-L$_{d,rac}$LG-SiR$_3$. See General Procedures for DCC/DMAP Coupling Reactions. The crude was chromatographed (silica, 5% EtOAc in hexanes) to yield a colorless oil (4.68 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.65 (m, 8H), 7.42-7.29 (m, 22H), 5.17-5.10 (m, 6H), 4.33 (d, J= 16.8 Hz, 1H), 4.31 (d, J= 16.2 Hz, 1H), 4.272 (d, J= 16.2 Hz, 1H), 4.270 (d, J=16.8 Hz, 1H), 1.50 (s, 3H), 1.43 (s, 3H), 1.42 (d, J= 7.8 Hz, 6H), 1.063 (s, 9H), 1.060 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 170.4, 170.0, 169.83, 169.8, 169.7, 135.6, 135.5, 135.1, 132.7, 129.9, 128.6, 128.2, 127.8, 69.1 (t), 68.6, 68.4, 67.1, 61.94, 61.92, 26.6, 19.2, 16.8, 16.64, 16.62, 16.61; MS (EI) m/z 493 (M-*t*-butyl).

Tetramer Synthesis.

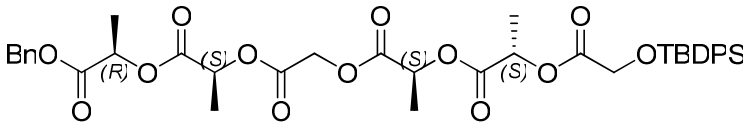


Bn-GLGL$_R$-SiR$_3$. Benzyl-protected **Bn-GL** (1.67 g, 7 mmol), **GL$_R$-SiR$_3$** (2.5 g, 6.5 mmol), DCC (1.65 g, 8 mmol) and DMAP (0.37 g, 3 mmol) were combined in 50 ml of CH_2Cl_2 and stirred at room temperature for 4 h under N_2. The reaction mixture was filtered and concentrated *in vacuo*. The crude was chromatographed in 5-10% EtOAc in hexanes to yield a colorless oil (3.41 g, 87%).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66-7.64 (m, 4H), 7.4-7.31 (m, 11H), 5.21 (q, J= 7.2 Hz, 1H), 5.17 (s, 2H), 4.78 (d, J= 16.2 Hz, 1H), 4.60 (d, J= 16.2 Hz, 1H), 4.59 (d, J= 16.2 Hz, 1H), 4.36 (q, J= 7.2 Hz, 1H), 1.51 (q, J= 7.2 Hz, 1H), 1.39 (d, J= 7.2 Hz, 1H), 1.07 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7, 169.5, 166.9, 166.8, 135.9, 135.7, 134.9, 133.4, 132.9, 129.8, 128.6, 128.5, 127.6, 69.0, 68.7, 67.2, 61.1, 60.3, 26.8, 21.3, 19.2, 16.8; MS (EI) m/z 549 (M-tbutyl).

Hexamer Synthesis.



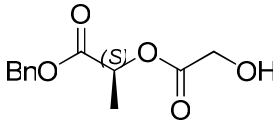
Bn-LLGLL$_R$G-SiR$_3$. Benzyl-proteceted **Bn-LLG** (0.97 g, 3.11 mmol), **LL$_R$G-SiR$_3$** (1.3 g, 2.83 mmol), DPTS (0.17 g, 0.57 mmol) and EDCI (0.65 g, 3.4 mmol) were combined in 30 ml of dry CH_2Cl_2 under N_2. The reaction mixture was stirred at room temperature for 4 h and then washed with brine (2 x 50 ml) and $NaHCO_3$ (2 x 50 ml). The organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. The concentrate was chromatographed (silica, 10% EtOAc in hexanes) to yield a colorless oil (1.76 g, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68- 7.66 (m, 4H), 7.43- 7.30 (m, 11H), 5.2- 5.1 (m, 6H), 4.84 (d, J= 15.6 Hz, 1H), 4.61 (d, J= 16.2 Hz, 1H), 4.32 (d, J= 16.2 Hz, 1H), 4.28 (d, J= 16.8 Hz, 1H), 1.512 (d, J= 7.2 Hz, 3H), 1.508 (d, J= 7.2 Hz, 3H), 1.499 (d, J= 7.2 Hz, 3H), 1.47 (d, J= 7.2 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 169.9, 169.7, 169.42, 169.4, 166.7, 135.6, 135.5, 135.0, 132.7, 132.6, 129.9, 128.6, 128.5, 128.2, 127.8, 69.3, 69.2, 68.9, 68.6, 67.2, 62.0, 60.7, 26.6, 19.2, 16.8, 16.73, 16.7, 16.6; HRMS (M+Na) calc mass 773.2605, found 773.2568.



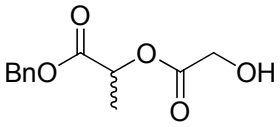
Bn-L$_R$LGLLG-SiR$_3$. Benzyl-protected **Bn-L$_R$LG** (0.87 g, 2.7 mmol), **LLG-SiR$_3$** (1.26 g, 2.7 mmol), DPTS (0.16 g, 0.55 mmol) and EDCI (0.58 g, 3 mmol) were combined in 20 ml of dry CH_2Cl_2 under N_2. The reaction mixture was stirred at RT for 4 h and then washed with brine (2 x 50 ml) and $NaHCO_3$ (2 x 50 ml). The organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. The concentrate was chromatographed (silica, 10% EtOAc in hexanes) to yield a colorless oil (1.76 g, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.66 (m, 4H), 7.43-7.31 (m,

11H), 5.23 (q, J= 7.2 Hz, 2H), 5.18 (d, J= 12 Hz, 1H), 5.16 (q, J= 7.2 Hz, 1H), 5.13 (d, J= 12.6 Hz, 1H), 5.129 (q, J= 7.2 Hz, 1H), 4.81 (d, J= 16.2 Hz, 1H), 4.60 (d, J= 16.2 Hz, 1H), 4.34 (d, J= 16.8 Hz, 1H), 4.29 (d, J= 16.8 Hz, 1H), 1.57 (d, J= 7.2 Hz, 3H), 1.50 (d, J= 6.6 Hz, 3H), 1.49 (d, J= 7.2 Hz, 6H), 1.07 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.8, 169.7, 169.6, 169.2, 166.3, 135.6, 135.5, 135.1, 132.7, 129.9, 128.6, 128.5, 128.2, 127.8, 69.5, 69.3, 68.8, 68.4, 67.2, 61.9, 60.7, 26.6, 19.2, 16.69, 16.67; HRMS (M+K) calc mass 789.2345, found 789.2358.

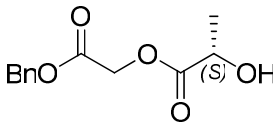
General Procedure for TBDPS deprotection. The deprotection was prepared according to previous literature.[8] For primary alcohols, 1.5 equivalents of TBAF (1.0 M in THF) buffered by 8 equiv of acetic acid was added to the di-protected oligomer in dry THF. The reaction mixture was allowed to stir for 1.5 to 2 h and then poured into brine. The product was extracted using Et_2O, dried with $MgSO_4$ and concentrated *in vacuo*. The concentrate was chromatographed (silica, 15% EtOAc in hexanes) to yield a clear liquid. For secondary alcohols, 1.5 equiv of TBAF was buffered with 1.2-2 equivalents of acetic acid.



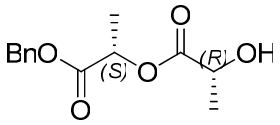
Bn-LG. The product was a colorless liquid (18.1 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4-7.3 (m, 5H), 5.24 (quartet, J= 7.1 Hz, 1H), 5.17 (s, 2H), 4.27 (dd, J= 17.4 Hz, J= 5.4 Hz, 1H), 4.20 (dd, J= 17.4 Hz, J= 6.0 Hz, 1H), 2.26 (t, J= 5.6 Hz, 1H), 1.52 (d, J= 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 170.1, 134.9, 128.4, 128.3, 128.0, 69.0, 67.0, 60.3, 16.6; MS (EI) m/z 238 (M+); elemental analysis calc. C 60.50, H 5.92, found C 60.11, H 6.05.



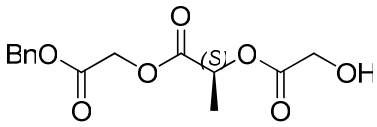
Bn-L$_{rac}$G. The product was a colorless liquid (2.20 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4-7.3 (m, 5H), 5.24 (quartet, J= 7.1 Hz, 1H), 5.17 (s, 2H), 4.27 (dd, J= 17.1 Hz, J= 5.4 HZ, 1H), 4.20 (dd, J= 17.4 HZ, J= 5.7 Hz, 1H), 2.26 (t, J= 5.6 Hz, 1H), 1.52 (d, J= 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 170.0, 135.0, 128.4, 128.3, 128.0, 69.0, 67.0, 60.3, 16.6; MS (EI) m/z 238 (M+).



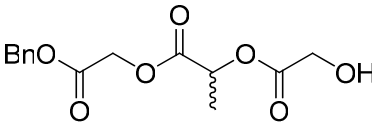
Bn-GL. The product was a colorless liquid (3.3 g, 67% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.30 (m, 5H), 5.17 (s, 2H), 4.76 (d, J= 15.9 Hz, 1H), 4.66 (d, J= 15.9 Hz, 1H), 4.39 (q, J= 7.0 Hz, 1H), 1.44 (d, J= 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 167.2, 134.7, 128.6, 67.3, 66.7, 61.1, 20.2; HRMS (M+Na) calc mass 261.0739, found 261.0738.



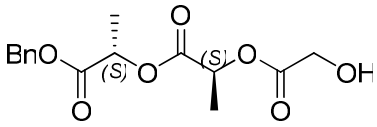
Bn-LL$_{R}$. The product was a colorless liquid (4.97 g, 94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.31 (m, 5H), 5.19 (q, J= 7.0 Hz, 1H), 5.18 (d, J= 12.0 Hz, 1H), 5.15 (d, J= 12.6 Hz, 1H), 4.36 (dq, J= 6.0 Hz, J= 1.8 Hz, 1H), 2.81 (d, J= 5.4 Hz, 1H), 1.52 (d, J= 7.2 Hz, 3H), 1.42 (d, J= 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.9, 170.0, 135.1, 128.6, 128.5, 128.2, 69.5, 67.2, 66.7, 20.0, 16.8; HRMS (M+Na) calc mass 275.0895, found 275.0912.



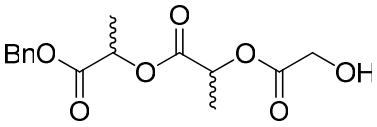
Bn-GLG. The product was a colorless liquid (6.37 g, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.32 (m, 5H), 5.28 (q, J= 6.9 Hz, 1H), 5.18 (s, 2H), 4.79 (d, J= 15.6 Hz, 1H), 4.63 (d, J= 15.6 Hz, 1H), 4.27 (dd, J= 17.4 Hz, 3.6 Hz, 1H), 4.22 (dd, J= 17.4 Hz, 4.8 Hz, 1H), 2.29 (s, 1H), 1.55 (d, J= 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.6, 169.6, 166.9, 134.8, 128.7, 128.5, 69.2, 67.4, 61.1, 60.5, 16.8; HRMS (M+Na) calc mass 319.079, found 319.080.



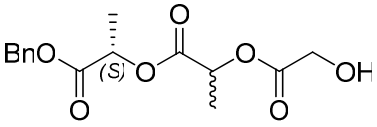
Bn-GL*rac*G. The product was a colorless liquid (6.81 g, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.32 (m, 5H); 5.27 (q, J= 6.9 Hz, 1H), 5.17 (s, 2H), 4.79 (d, J= 15.6 Hz, 1H), 4.63 (d, J= 15.6 Hz, 1H), 4.26 (d, J= 17.4 Hz, 1H), 4.22 (d, J= 17.4 Hz, 1H), 2.41 (s, 1H), 1.55 (d, J= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.6, 169.6, 166.9, 134.8, 128.7, 69.1, 67.3, 61.1, 60.5, 16.8; MS (EI) m/z 296 (M+).



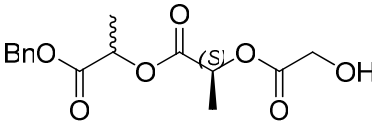
Bn-LLG. The product was a colorless liquid (7.72 g, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.30 (m, 5H), 5.22-5.18 (m, 2H), 5.16 (d, J= 12 Hz, 1H), 5.12 (d, J= 12 Hz, 1H), 4.26 (d, J= 17.4 Hz, 1H), 4.20 (d, J= 17.4 Hz, 1H), 2.53 (s, 1H), 1.51 (d, J= 7.2 Hz, 3H), 1.50 (d, J= 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.6, 169.8, 169.6, 135.1, 128.6, 128.5, 128.2, 69.3, 69.1, 67.2, 60.4, 16.7, 16.6; HRMS (M+Na) calc mass 333.095, found 333.096.



Bn-L*rac*L*rac*G. The product was a colorless liquid (3.56 g, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.29 (m, 20H), 5.27 (q, J= 6.6 Hz, 2H), 5.21-5.12 (m, 14H), 4.27-4.18 (m, 8H), 2.60 (s, 4H), 1.52-1.48 (m, 24H); ^{13}C (600 MHz, $CDCl_3$) δ 172.6, 172.5, 169.9, 169.7, 169.6, 169.4, 135.1, 135.0, 128.6, 128.5, 128.4, 128.2, 69.5, 69.3, 69.2, 69.1, 67.2, 60.4, 16.78, 16.73, 16.68, 16.63; HRMS (M+Na) calc mass 333.0950, found 333.0966.

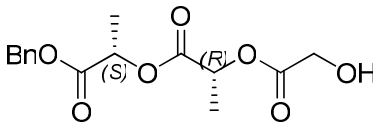


Bn-LL*rac*G. The product was a colorless liquid (7.55 g, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.3 (m, 10H), 5.27 (q, J= 7.2 Hz, 1H), 5.22-5.11 (m, 7H), 4.27-4.19 (m, 4H), 2.49 (s, 2H), 1.513 (d, J= 6.6 Hz, 3H), 1.51 (d, J= 7.2 Hz, 6H), 1.49 (d, J= 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7, 172.5, 169.9, 169.7, 169.6, 169.4, 135.1, 135.0, 128.6, 128.57, 128.51, 128.4, 128.23, 128.22, 69.4, 69.3, 69.2, 69.1, 67.2, 16.75, 16.73 (2), 16.6; HRMS (M+Na) calc mass 333.095, found 333.096.

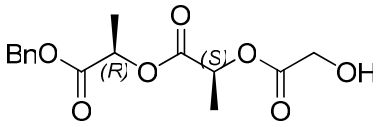


Bn-L*rac*LG. The product was a colorless liquid (4.93 g, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.30 (m, 10H), 5.28 (q, J= 7.2 Hz, 1H), 5.22-5.11 (m, 7H), 4.26 (d, J= 18.0 Hz, 1H), 4.24 (d, J= 17.4 Hz, 1H), 4.21 (d, J= 18.6 Hz, 1H), 4.20 (d, J= 17.4 Hz, 1H), 2.42 (s, 2H), 1.52 (d, J= 6.6 Hz, 3H), 1.51 (d, J= 7.2 Hz, 6H), 1.49 (d, J= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ

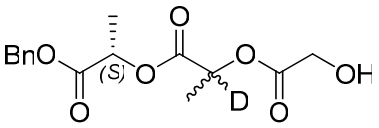
172.7, 172.5, 169.9, 169.7, 169.6, 169.4, 135.1, 135.0, 128.6, 128.5, 128.4, 128.3, 128.2, 69.5, 69.3, 69.2, 69.1, 67.2, 60.5, 16.8, 16.7 (2), 16.6; MS (EI) m/z 310 (M+).



Bn-LL$_R$G. The product was a colorless liquid (1.40 g, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (m, 5H), 5.27 (q, J= 7.2 Hz, 1H), 5.19 (d, J= 12.0 Hz, 1H), 5.16 (q, J= 7.2 Hz, 1H), 5.13 (d, J= 12.0 Hz, 1H), 4.24 (d, J= 17.4 Hz, 1H), 4.20 (d, J= 17.4 Hz, 1H), 2.54 (s, 1H), 1.51 (d, J= 7.2 Hz, 3H), 1.49 (d, J= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.5, 169.7, 169.5, 135.1, 128.6, 128.5, 128.2, 69.5, 69.2, 67.2, 60.4, 16.75, 16.73; HRMS (M+Na) calc mass 333.0950, found 333.0935.

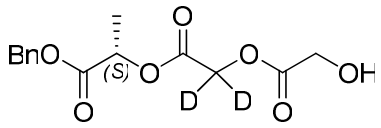


Bn-L$_R$LG. The product was a colorless liquid (1.84 g, 69%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.31 (m, 5H), 5.27 (q, J= 7.2 Hz, 1H), 5.19 (d, J= 12.0 Hz, 1H), 5.16 (q, J= 7.2 Hz, 1H), 5.13 (d, J= 12.0 Hz, 1H), 4.24 (d, J= 16.8 Hz, 1H), 4.20 (d, J= 18.0 Hz, 1H), 2.50 (s, 1H), 1.51 (d, J= 7.2 Hz, 3H), 1.49 (d, J= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.5, 169.8, 169.5, 135.1, 128.6, 128.5, 128.3, 69.5, 69.3, 67.3, 60.5, 16.8, 16.78; HRMS (M+Na) calc mass 333.0950, found 333.0921.

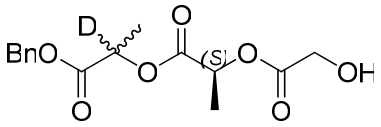


Bn-LL$_{d,rac}$G. The product was a colorless liquid (1.67 g, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.4-7.3 (m, 10H), 5.21-5.12 (m, 6H), 4.27 (d, J= 17.4 Hz, 1H), 4.26 (d, J=17.4 Hz, 1H), 4.21 (dd, J= 16.8 Hz, 6.6 Hz, 1H), 4.20 (dd, J= 16.8 Hz, 6.0 Hz, 1H), 2.26 (t, J= 6.0 Hz, 1H), 2.22 (t, J=6.0

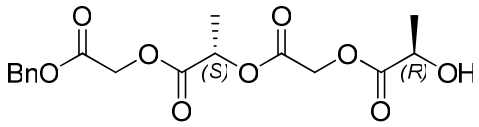
Hz, 1H), 1.51 (d, J= 7.2 Hz, 3H), 1.45 (d, J= 6.6 Hz, 3H), 1.43 (s, 6H), 1.073 (s, 9H), 1.069 (s, 9H); ^{13}C (150 MHz, $CDCl_3$) δ 172.7, 172.5, 169.9, 169.7, 169.6, 169.4, 135.1, 135.0, 128.6, 128.5, 128.4, 128.3, 128.2, 69.5, 69.3, 69.0 (m), 67.2, 60.5, 16.8 (2), 16.7, 16.6; HRMS (M+) calc mass 311.1115, found 311.1107.



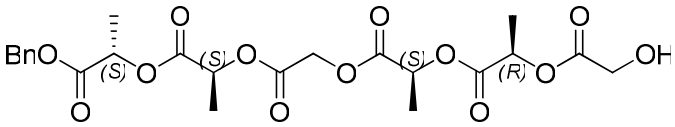
Bn-LG$_{d2}$G. The product was a colorless liquid (1.53 g, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34-7.31 (m, 5H), 5.22 (q, J=6.6 Hz, 1H), 5.18 (d, J= 12.6 Hz, 1H), 5.5 (d, J= 12.0 Hz, 1H), 4.28 (s, 2H), 2.25 (s, 1H), 1.51 (d, J= 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.6, 169.8, 166.7, 155.1, 128.6, 128.5, 128.2, 69.6, 67.3, 60.5 (m), 60.4, 16.8; HRMS (M+) calc mass 298. 1021, found 298.1019.



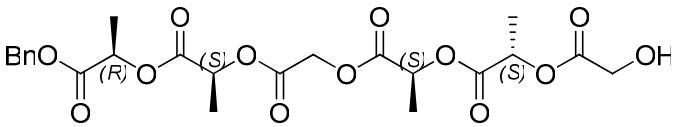
Bn-L$_{d,rac}$LG. The product was a colorless liquid (1.72 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.30 (m, 10H), 5.28 (q, J= 6.8 Hz, 1H), 5.23-5.12 (m, 5H), 4.27 (dd, J= 17.4 Hz, 5.4 Hz 1H), 4.24 (dd, J= 19.8 Hz, 6.0 Hz, 1H), 4.21 (dd, J= 18.0 Hz, 6.0 Hz, 1H), 4.20 (dd, J= 17.4 Hz, 6.0 Hz, 1H), 2.29 (t, J= 5.7 Hz, 1H), 2.26 (t, J= 5.7 Hz, 1H), 1.52 (d, J= 7.2 Hz, 6H), 1.51 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.6, 172.4, 169.8, 169.7, 169.5, 135.0, 134.9, 128.5, 128.4, 128.3, 128.2, 69.2 (t), 69.1, 68.9, 67.1, 60.4, 16.7, 16.6, 16.57, 16.5; MS (EI) m/z 311 (M+).



Bn-GLGL$_R$. The product was a colorless liquid (1.37 g, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.4-7.3 (m, 5H), 5.25 (q, J= 7.2 Hz, 1H), 5.17 (s, 2H), 4.795 (d, J= 16.2 Hz, 1H), 4.792 (d, J= 15.6 Hz, 1H), 4.75 (d, J= 15.6 Hz, 1H), 4.62 (d, J= 16.2 Hz, 1H), 4.40 (dq, J= 6.0 Hz, J= 6.6 Hz, 1H), 2.66 (dd, J= 3.0 Hz, J= 6.0 Hz, 1H), 1.55 (d, J= 7.2 Hz, 3H), 1.47 (d, J= 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.9, 169.4, 166.9, 166. 6, 134.8, 128.7, 128.5, 69.2, 67.3, 66.7, 61.1, 60.9, 20.3, 16.8; MS (EI) m/z 368 (M+).



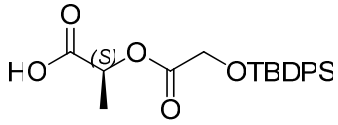
Bn-LLGLL$_R$G. The product was a colorless liquid (1.01 g, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36- 7.30 (m, 5H), 5.28 (q, J= 7.0 Hz, 1H), 5.20 (q, J= 6.8 Hz, 1H), 5.18 (q, J= 7.0 Hz, 1H), 5.162 (d, J= 12.6 Hz, 1H), 5.160 (q, J= 7.2 Hz, 1H), 5.12 (d, J= 12.0 Hz, 1H), 4.87 (d, J= 16.2 Hz, 1H), 4.62 (d, J= 16.2 Hz, 1H), 4.25 (d, J= 17.4 Hz, 1H), 4.21 (d, J= 17.4 Hz, 1H), 2.40 (s, 1H), 1.56 (d, J= 7.2 Hz, 3H), 1.55 (d, J= 7.2 Hz, 3H), 1.51 (d, J= 7.2 Hz, 3H), 1.50 (d, J= 7.2 Hz, 3H); ^{13}C NMR (600 MHz, $CDCl_3$) δ 172.5, 169.9, 169.42, 169.4, 169.3, 166.5, 135.0, 128.6, 128.5, 128.2, 69.3, 69.2 (2), 69.1, 67.2, 60.8, 60.4, 16.74, 16.7 (2), 16.6; HRMS (M+Na) calc mass 535.1428, found 535.1451.



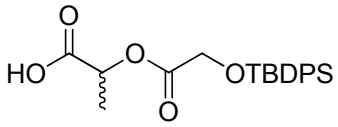
Bn-L$_R$LGLLG. The product was a colorless liquid (1.05 g, 96%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.30 (m, 5H), 5.24-5.19 (m, 3H), 5.17 (d, J= 12.6 Hz, 1H), 5.15 (q, J= 7.2 Hz, 1H), 5.12 (d, J= 12.6 Hz, 1H), 4.80 (d, J= 16.2 Hz, 1H), 4.61 (d, J= 15.6 Hz, 1H), 4.25 (d, J= 17.4 Hz, 1H),

4.20 (d, J= 17.4 Hz, 1H), 2.56 (s, 1H), 1.57 (d, J= 7.8 Hz, 3H), 1.56 (d, J= 7.2 Hz, 3H), 1.49 (d, J= 7.2 Hz, 3H), 1.48 (d, J= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.6, 169.7, 169.6, 169.4, 169.2, 166.3, 135.1, 128.5, 128.4, 128.2, 69.4, 69.3, 69.0, 68.9, 67.1, 60.7, 60.4, 16.7; HRMS (M+Na) calc mass 535.1428, found 535.1420.

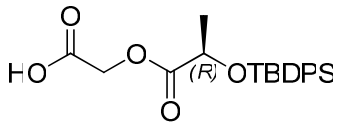
General procedures for benzyl deprotections. The deprotections accomplished using methods previously described.[8] The benzyl protected oligomer was combined with 10% Pd/C (5% w/w) in dry EtOAc. The reaction mixture was stirred 16- 18 h under 1 atm of hydrogen, filtered through celite and concentrated *in vacuo*. No further purification was used unless stated.



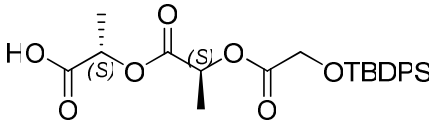
LG-SiR$_3$. The crude was chromatographed (silica, 15% EtOAc in hexanes) to yield a colorless oil (30.6 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.7-7.6 (m, 4H), 7.5-7.3 (m, 6H), 5.14 (quartet, J= 7.1 Hz, 1H), 4.36 (d, J= 16.8 Hz, 1H), 4.29 (d, J=16.8 Hz, 1H), 1.48 (d, J= 7.2 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 170.6, 135.6, 135.5, 132.7, 132.6, 129.9, 127.8, 68.2, 61.9, 26.6, 19.3, 16.7; MS (EI) m/z 329 (M-*t*butyl).



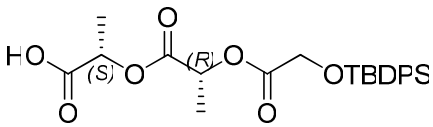
L$_{rac}$G-SiR$_3$. The crude was chromatographed (silica, 15% EtOAc in hexanes) to yield a colorless oil (28.8 g, 90%). ^{1}H NMR(300 MHz, $CDCl_3$) δ 7.7-7.6 (m, 4H), 7.5-7.3 (m, 6H), 5.13 (quartet, J= 7.0 Hz, 1H), 4.35 (d, J= 16.8 Hz, 1H), 4.29 (d, J=17.1 Hz, 1H), 1.48 (d, J= 7.5 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 170.6, 135.6, 135.5, 132.7, 132.6, 129.9, 127.9, 68.3, 61.9, 26.7, 19.3, 16.7; MS (EI) m/z 329 (M-*t*-butyl).



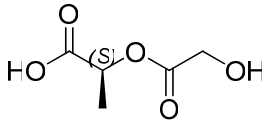
GL$_R$-SiR$_3$. The crude was chromatographed (silica, 15% EtOAc in hexanes) to yield a colorless oil (2.85 g, 50%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67-7.64 (m, 4H), 7.42-7.33 (m, 6H), 4.58 (d, J= 16.2 Hz, 1H), 4.48 (d, J= 16.8 Hz, 1H), 4.38 (q, J= 6.6 Hz, 1H), 1.40 (d, J= 7.2 Hz, 3H), 1.08 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.1, 173.0, 135.9, 135.7, 133.4, 132.9, 129.9, 129.8, 127.9, 127.7, 127.6, 68.6, 60.0, 26.8, 21.2, 19.2; MS (EI) m/z 329 (M-*t*-butyl).



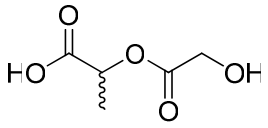
LLG-SiR$_3$. The crude was chromatographed (silica, 15% EtOAc in hexanes) to yield a colorless oil (2.32 g, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.56 (m, 4H), 7.43-7.36 (m, 6H), 5.16 (q, J= 7.2 Hz, 1H), 5.12 (q, J= 7.2 Hz, 1H), 4.34 (d, J= 16.8 Hz, 1H), 4.29 (d, J= 16.8 Hz, 1H), 1.54 (d, J= 7.2 Hz, 3H), 1.48 (d, J= 7.2 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.8, 170.7, 169.8, 135.6, 135.5, 132.7, 132.6, 129.9, 127.8, 127.7, 68.6, 68.4, 62.0, 26.6, 19.2, 16.67, 16.64; HRMS (M+Na) calc mass 481.1659, found 481.1616.



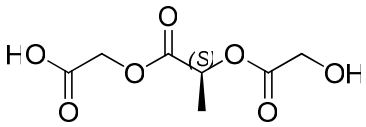
LL$_R$G-SiR$_3$. The crude was chromatographed (silica, 15% EtOAc in hexanes) to yield a colorless oil (1.46 g, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.66 (m, 4H), 7.43- 7.35 (m, 6H), 5.17 (q, J=7.2 Hz, 1H), 5.12 (q, J= 7.0 Hz, 1H), 4.33 (d, J= 16.8 Hz, 1H), 4.29 (d, J= 16.8 Hz, 1H), 1.48 (d, J= 7.8 Hz, 3H), 1.46 (d, J= 7.2 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.2, 170.6, 169.7, 135.6, 135.5, 132.6, 129.9, 127.8, 68.8, 68.7, 62.0, 26.6, 19.3, 16.8, 16.6; HRMS (M+Na) calc mass 481.1659, found 481.1678.



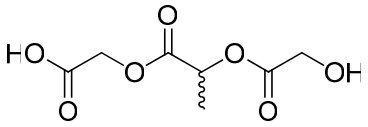
LG. The filtrate was concentrated *in vacuo* to yield a colorless oil (4.35 g, 100%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.18 (quartet, J= 7.1 Hz, 1H, CH), 4.29 (d, J= 17.4 Hz, 1H, CH_2), 4.22 (d, J= 17.4 Hz, 1H, CH_2), 1.49 (d, J= 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4 (C=O), 172.6 (C=O), 68.9, 60.2, 16.6; MS (EI) m/z 131 (M- H_2O), 117; HRMS (M-H_2O) calc mass 131.0344, found 131.0348.



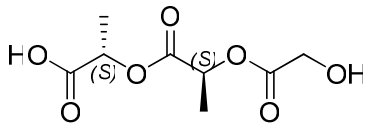
L$_{rac}$G. The filtrate was concentrated *in vacuo* to yield a colorless oil (4.35 g, 100%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.17 (quartet, J= 7.1 Hz, 1H), 4.29 (d, J= 17.4 Hz, 1H), 4.22 (d, J= 17.4 Hz, 1H), 1.52 (d, J= 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 172.8, 69.0, 60.4, 16.7; MS (EI) m/z 149 (M+).



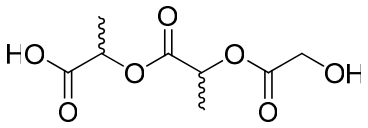
GLG. The filtrate was concentrated *in vacuo* to yield a colorless oil (4.33 g, 100%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.28 (q, J= 7.2 Hz, 1H), 4.77 (d, J= 15.6 Hz, 1H), 4.65 (d, J= 16.8 Hz, 1H), 4.29 (d, J= 18 Hz, 1H), 4.24 (d, J= 17.4 Hz, 1H), 1.57 (d, J= 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8, 171.3, 169.7, 69.1, 60.7, 60.4, 16.7; MS (EI) m/z 207 (M+).



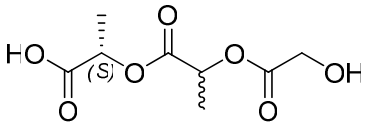
GL$_{rac}$G. The filtrate was concentrated *in vacuo* to yield a colorless oil (4.63 g, 100%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.27 (q, J= 6.9 Hz, 1H), 4.76 (d, J= 16.2 Hz, 1H), 4.64 (d, J= 16.8 Hz, 1H), 4.29 (d, J= 17.4 Hz, 1H), 4.24 (d, J= 17.4 Hz, 1H), 1.56 (d, J= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8, 171.3, 169.7, 69.1, 60.7, 60.4, 16.7; MS (EI) m/z 207 (M+).



LLG. The filtrate was concentrated *in vacuo* to yield a colorless oil (4.90 g, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.22 (q, J= 7.2 Hz, 1H), 5.17 (q, J= 7.2 Hz, 1H), 4.28 (d, J= 16.8 Hz, 1H), 4.23 (d, J= 17.4 Hz, 1H), 1.56 (d, J= 7.2 Hz, 3H), 1.55 (d, J= 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.0, 172.8, 169.7, 69.2, 68.9, 60.4, 16.66, 16.63; MS (EI) m/z 203 (M-H_2O).

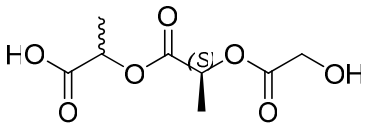


L$_{rac}$L$_{rac}$G. The filtrate was concentrated *in vacuo* to yield a colorless oil (0.70 g, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.27-5.10 (m, 8H), 4.30-4.21 (m, 8H), 1.56-1.51 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.3, 174.1, 172.8, 169.8, 169.7, 69.3, 69.2, 69.0, 60.42, 60.39, 16.66, 16.63; HRMS (M+Na) calc mass 243.0481, found 243.0484.

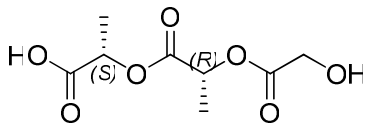


LL$_{rac}$G. The filtrate was concentrated *in vacuo* to yield a colorless oil (4.60 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.27 (q, J= 7.2 Hz, 1H), 5.23 (q, J= 7.2 Hz, 1H), 5.18 (q, J= 7.2 Hz, 1H),

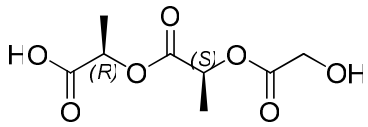
5.15 (q, J= 7.2 Hz, 1H), 4.29 (d, J= 18.0 Hz, 1H), 4.28 (d, J= 18.0 Hz, 1H), 4.24 (d, J= 17.4 Hz, 1H), 4.23 (d, J= 16.8 Hz, 1H), 1.57 (d, J= 7.2 Hz, 3H), 1.56 (d, J= 6.6 Hz, 3H), 1.54 (d, J= 7.2 Hz, 3H), 1.53 (d, J= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.1, 174.8, 172.9, 172.8, 169.7, 169.6, 69.3, 69.2, 69.0, 68.9, 60.4, 16.7, 16.6 (2), 16.5; MS (EI) m/z 203 (M-H_2O).



L_{rac}LG. The filtrate was concentrated *in vacuo* to yield a colorless oil (3.22 g, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.26 (q, J= 7.2 Hz, 1H), 5.22 (q, J= 7.2 Hz, 1H), 5.17 (q, J= 7.2 Hz, 1H), 5.13 (q, J= 7.2 Hz, 1H), 4.29 (d, J= 17.4 Hz, 1H), 4.28 (d, J= 17.4 Hz, 1H), 4.24 (d, J= 17.4 Hz, 1H), 4.23 (d, J= 17.4 Hz, 1H), 1.57 (d, J= 7.2 Hz, 3H), 1.55 (d, J= 6.6 Hz, 1H), 1.54 (d, J= 6.6 Hz, 1H), 1.53 (d, J= 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.1, 174.9, 172.9, 172.8, 169.7, 169.6, 69.3, 69.2, 69.1, 68.9, 60.5, 60.4, 16.72, 16.7 (2), 16.6; MS (EI) m/z 221 (M+).

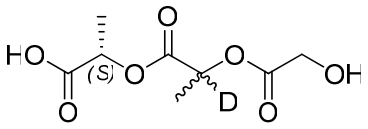


LL_RG. The filtrate was concentrated *in vacuo* to yield a colorless oil (0.91 g, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.26 (q, J= 7.0 Hz, 1H), 5.14 (q, J= 7.0 Hz, 1H), 4.29 (d, J= 17.4 Hz, 1H), 4.24 (d, J= 17.4 Hz, 1H), 1.54 (d, J= 7.2 Hz, 3H), 1.53 (d, J= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.6, 173.0, 169,6, 69.3, 69.2, 60.4, 16.7; HRMS (M+Na) calc mass 243.0481, found 243.0488.

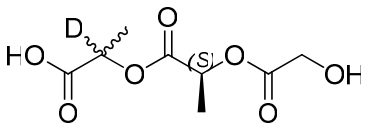


L_RLG. The filtrate was concentrated *in vacuo* to yield a colorless oil (0.59 g, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.23 (q, J= 7.2 Hz, 1H), 5.13 (q, J= 7.2 Hz, 1H), 4.28 (d, J= 17.4 Hz, 1H),

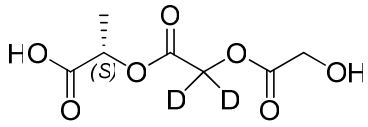
4.23 (d, J= 17.4 Hz, 1H), 1.53 (d, J= 6.6 Hz, 3H), 1.52 (d, J= 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.4, 173.0, 169.7, 69.3, 69.2, 60.4, 16.7; HRMS (M+Na) calc mass 243.0481, found 243.0487.



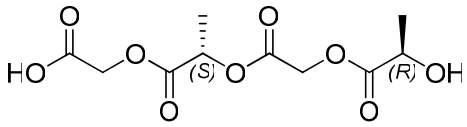
LL$_{d,rac}$G. The filtrate was concentrated *in vacuo* to yield a colorless oil (1.0 g, 94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.17 (q, J= 7.2 Hz, 1H), 5.13 (q, J= 7.2 Hz, 1H), 4.282 (d, J= 16.8 Hz, 1H), 4.276 (d, J= 16.8 Hz, 1H), 4.23 (d, J= 17.4 Hz, 2H), 1.55 (s, 3H), 1.54 (d, J= 7.2 Hz, 3H), 1.53 (s, 3H), 1.52 (d, J= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.7, 174.5, 172.9, 172.8, 169.8, 169.7, 69.4, 69.2, 69.1, 68.9, 68.8, 68.7, 60.4, 60.3, 16.6, 16.5; MS (EI) m/z 204 (M-H_2O).



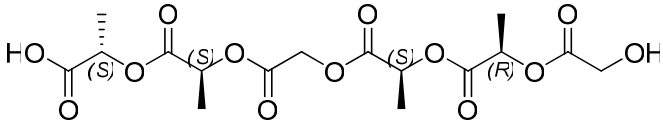
L$_{d,rac}$LG. The filtrate was concentrated *in vacuo* to yield a colorless oil (1.05 g, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.2-5.1 (m, 2H), 4.4-4.1 (m, 4H), 1.6-1.3 (m, 12H); MS (EI) m/z 204 (M-H_2O).



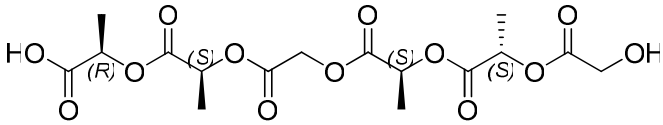
LG$_{d2}$G. The filtrate was concentrated *in vacuo* to yield a colorless oil (0.95 g, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.19 (q, J= 7.2 Hz, 1H), 4.3 (s, 2H), 1.55 (d, J= 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.5, 172.9, 166.8, 69.2, 60.5 (t), 60.4, 16.7; MS (EI) m/z 206 (M+).



GLGL$_R$. The filtrate was concentrated in vacuo to yield a colorless oil (0.84 g, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.26 (q, J= 7.2 Hz, 1H), 4.80 (d, J= 15.6 Hz, 1H), 4.78 (d, J= 15.6 Hz, 1H), 4.75 (d, J= 15.6 Hz, 1H), 4.64 (d, J= 16.2 Hz, 1H), 4.41 (q, J= 7.2 Hz, 1H), 1.57 (d, J= 7.2 Hz, 3H), 1.47 (d, J= 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.9, 171.5, 169.4, 166.7, 69.2, 66.8, 60.9, 60.7, 20.2, 16.7; MS (EI) m/z 279 (M+).



LLGLL$_R$G. The filtrate was concentrated *in vacuo* to yield a colorless oil (0.68 g, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.26 (q, J= 7.0 Hz, 1H), 5.22 (q, J= 7.0 Hz, 1H), 5.17 (q, J= 7.0 Hz, 1H), 5.16 (q, J= 7.0 Hz, 1H), 4.84 (d, J= 16.2 Hz, 1H), 4.67 (d, J= 15.6 Hz, 1H), 4.27 (d, J= 17.4 Hz, 1H), 4.22 (d, J= 17.4 Hz, 1H), 1.56 (d, J= 7.2 Hz, 3H), 1.55 (d, J= 7.2 Hz, 1H), 1.54 (d, J= 6.6 Hz, 3H), 1.53 (d, J= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.3, 172.9, 169.5, 169.4, 169.3, 166.6, 69.4, 69.3, 69.1, 69.0, 60.0, 60.4, 16.7 (2), 16.6 (2); HRMS (M+Na) calc mass 445.0958, found 445.0998.

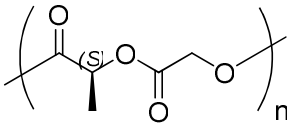


L$_R$LGLLG. The filtrate was concentrated *in vacuo* to yield a colorless oil (0.61 g, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.26-5.21 (m, 3H), 5.13 (q, J= 6.6 Hz, 1H), 4.82 (d, J= 15.7 Hz, 1H), 4.64 (d, J= 16.2 Hz, 1H), 4.27 (d, J= 16.8 Hz, 1H), 4.22 (d, J= 16.8 Hz, 1H), 1.58 (d, J= 7.2 Hz, 3H), 1.57 (d, J= 6.6 Hz, 3H), 1.53 (d, J= 7.7 Hz, 3H), 1.52 (d, J= 7.2 Hz, 3H); ^{13}C NMR (150

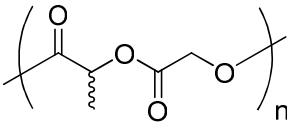
MHz, $CDCl_3$) δ 174.1, 172.7, 169.6, 169.4, 169.3, 166.4, 69.4, 69.2, 69.1, 60.8, 60.5, 16.69 (2), 16.66, 16.64; HRMS (M+Na) calc mass 445.0958, found 445.0930.

Polymers

General procedures for DIC/DPTS polymerizations. Polymerization was adapted from Stupp and coworkers.[6] The oligomer and 0.2 equivalents of DPTS were dissolved in CH_2Cl_2 and chilled to 0°C. DIC (1.5 equiv) was added dropwise by syringe and the reaction mixture was stirred at RT for 3 h. The polymers were precipitated twice in MeOH and dried under vacuum.

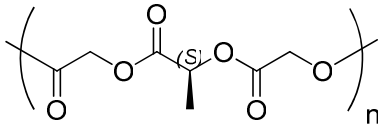


Poly LG. A white solid was collected (2.14 g, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.23 (q, J= 7.2 Hz, 1H), 4.86 (d, J= 15.6 Hz, 1H), 4.63 (d, J= 16.2 Hz, 1H), 1.57 (d, J= 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 166.4, 69.2, 60.8, 16.7; SEC (THF): M_n – 27.4 kDa, M_w – 36.3 kDa, PDI – 1.3; SEC ($CHCl_3$): M_n – 33.3 kDa, M_w – 44.0 kDa, PDI – 1.3; SEC-MALLS ($CHCl_3$): M_n – 13.4 kDa, M_w – 14.5 kDa, PDI – 1.08.

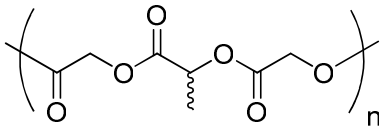


Poly L*rac*G. A white solid was collected (0.62 g, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.26-5.21 (m, 4H), 4.86 (d, J= 15.6 Hz, 1H), 4.85 (d, J= 16.2 Hz, 1H), 4.814 (d, J= 16.2 Hz, 1H), 4.809 (d, J= 16.8 Hz, 1H), 4.808 (d, J= 16.2 Hz, 1H), 4.804 (d, J= 15.6 Hz, 1H), 4.684 (d, J= 16.2 Hz, 1H), 4.680 (d, J=15.6 Hz, 2H), 4.677 (d, J= 16.2 Hz, 1H), 4.63 (d, J= 15.6 Hz, 1H), 1.567 (d, J= 7.2 Hz, 3H), 1.564 (d, J= 7.2 Hz, 3H), 1.562 (d, J= 6.6 Hz, 1H), 1.558 (d, J= 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.38, 169.31, 169.28, 169.22, 166.44, 166.40(2), 166.36, 69.19, 69.17,

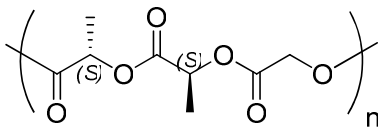
69.15, 60.8, 16.77, 16.76, 16.74; SEC (THF): M_n – 28.8 kDa, M_w – 37.1 kDa, PDI – 1.3; SEC ($CHCl_3$): M_n – 34.3 kDa, M_w – 47.2, PDI – 1.4.



Poly GLG. A white solid was collected (0.85 g, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.24 (q, J= 7.2 Hz, 1H), 4.86 (d, J= 16.2 Hz, 1H), 4.80 (d, J- 15.6 Hz, 1H), 4.72 (d, J= 15.6 Hz, 1H), 4.69 (d, J= 15.6 Hz, 1H), 1.57 (d, J= 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 166.5, 166.4, 69.2, 60.9, 60.7, 16.7; SEC (THF): M_n – 26.2 kDa, M_w – 36.2 kDa, PDI – 1.2; SEC ($CHCl_3$): M_n – 36.2 kDa, M_w – 49.7 kDa, PDI – 1.4; SEC-MALLS ($CHCl_3$): M_n – 19.4 kDa, M_w – 21.3 kDa, PDI – 1.10.

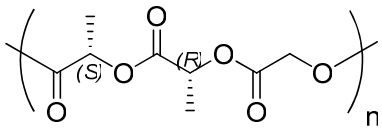


Poly GL$_{rac}$G. A white solid was collected (0.56 g, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.24 (q, J= 7.2 Hz, 2H), 4.86 (d, J= 16.2 Hz, 1H, 2i), 4.84 (d, J= 16.2 Hz, 1H), 4.80 (d, J= 16.2 Hz, 1H), 4.78 (d, J= 16.2 Hz, 1H), 4.73 (d, J= 16.2, 1H), 4.72 (d, 16.8 Hz, 1H), 4.70 (d, J= 16.2 Hz, 1H), 4.68 (d, J= 15.6 Hz, 1H), 1.57 (d, J= 7.2 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3 (2), 166.46, 166.44, 166.35 (2), 69.2, 60.9, 60.7, 16.7; SEC (THF): M_n – 21.4 kDa, M_w – 26.6 kDa, PDI – 1.3; SEC ($CHCl_3$): M_n – 27.5 kDa, M_w – 38.6 kDa, PDI – 1.4.

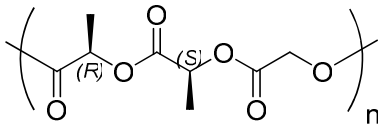


Poly LLG. White fibers were collected (3.0 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.21 (q, J= 7.2 Hz, 1H), 5.18 (q, J= 7.2 Hz, 1H), 4.85 (d, J= 16.2 Hz, 1H), 4.60 (d, J= 16.2 Hz, 1H), 1.57 (d,

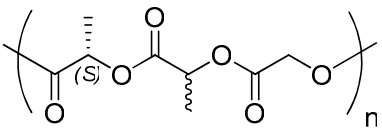
J= 7.2 Hz, 3H), 1.56 (d, J= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 169.4, 166.5, 69.2, 69.0, 60.8, 16.7, 16.6; SEC (THF): M_n – 41.2 kDa, M_w – 50.5 kDa, PDI – 1.2; SEC ($CHCl_3$): M_n – 41.8 kDa, M_w – 53.7 kDa, PDI – 1.3; SEC-MALLS ($CHCl_3$): M_n – 23.1 kDa, M_w – 25.3 kDa, PDI – 1.10.



Poly LL$_R$G. White fibers were collected (0.56 g, 71%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.22 (q, J= 7.0 Hz, 1H), 5.18 (q, J= 7.0 MHz, 1H), 4.81 (d, J= 16.1 Hz, 1H), 4.65 (d, J= 16.1 Hz, 1H), 1.56 (d, J= 7.0 Hz, 3H), 1.53 (d, J= 7.7 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.23, 169.15, 166.4, 69.4, 69.2, 60.8, 16.74, 16.70; SEC (THF): M_n – 29.0 kDa, M_w – 39 kDa, PDI – 1.4; SEC ($CHCl_3$): M_n – 42.3 kDa, M_w – 55.8 kDa, PDI – 1.3.

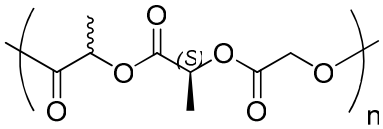


Poly L$_R$LG. White fibers were collected (0.30 g, 59%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.22 (q, J= 7.0 Hz, 1H), 5.19 (q, J= 7.0 Hz, 1H), 4.81 (d, J= 16.1 Hz, 1H), 4.65 (d, J= 16.1 Hz, 1H), 1.56 (d, J= 7.0 Hz, 3H), 1.53 (d, J= 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 169.1, 166.4, 69.4, 69.2, 60.8, 16.74, 16.71; SEC (THF): M_n – 30.6 kDa, M_w – 43.1 kDa, PDI – 1.4; SEC ($CHCl_3$): M_n – 39.8 kDa, M_w – 54.7 kDa, PDI – 1.4.



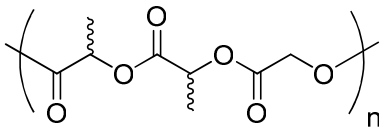
Poly LL$_{rac}$G. A white solid was collected (2.03 g, 50%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.24-5.16 (m, 8H) [possible interpretation: 5.22 (q, J= 7.0 Hz, 1H), 5.218 (q, J= 7.0 Hz, 2H), 5.212 (q,

J= 7.0 Hz, 1H), 5.187 (q, J= 7.0 Hz, 1H), 5.185 (q, J= 7.0 Hz, 1H), 5.177 (q, J= 7.0 Hz, 1H), 5.175 (q, J= 7.0 Hz, 1H)], 4.87 (d, J= 16.1 Hz, 1H), 4.85 (d, J= 16.1 Hz, 3H), 4.813 (d, J= 16.1 Hz, 3H), 4.811 (d, J= 16.1 Hz, 1H), 4.808 (d, J= 16.1 Hz, 3H), 4.806 (d, J= 16.1 Hz, 1H), 4.652 (d, J= 16.1 Hz, 1H), 4.650 (d, J= 16.1 Hz, 1H), 4.63 (d, J= 16.1 Hz, 2H), 4.62 (d, J= 16.1 Hz, 2H), 4.60 (d, J= 16.1 Hz, 2H), 1.572 (d, J= 7.0 Hz, 3H), 1.569 (d, J= 7.0 Hz, 3H), 1.562 (d, J= 7.0 Hz, 3H), 1.560 (d, J= 7.0 Hz, 3H), 1.559 (d, J= 7.0 Hz, 3H), 1.556 (d, J= 7.0 Hz, 3H), 1.53 (d, J= 7.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 169.4, 169.35 (m), 169.31, 169.30, 169.2, 169.18, 169.15, 169.12, 169.1, 166.52, 166.48, 166.34, 166.29, 69.3, 69.2, 69.1, 69.0, 68.9, 60.76, 60.74, 16.72, 16.65, 16.63, 16.61; SEC (THF): M_n – 17.8 kDa, M_w – 25.1 kDa, PDI – 1.4; SEC ($CHCl_3$): M_n – 19.3 kDa, M_w – 30.1 kDa, PDI – 1.6.

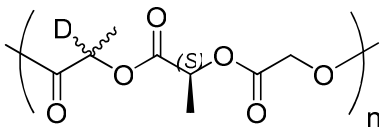


Poly L*rac*LG. A white solid was collected (2.31 g, 83%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.24-5.14 (m, 8H), 4.86 (d, J=16.1 Hz, 4H), 4.826 (d, J= 16.1 Hz, 1H), 4.824 (d, J= 16.1 Hz, 1H), 4.822 (d, J=16.1 Hz, 1H), 4.81 (d, J= 16.1 Hz, 1H), 4.79 (d, J= 15.4 Hz, 1H), 4.789 (d, J= 16.1 Hz, 1H), 4.69 (d, J= 16.1 Hz, 4H), 4.654 (d, J= 16.1 Hz, 2H), 4.652 (d, J= 16.1 Hz, 1H), 4.620 (d, J= 16.1 Hz, 1H), 4.618 (d, J= 16.1 Hz, 2H), 4.616 (d, J= 16.1 Hz, 1H), 4.604 (d, J= 16.1 Hz, 1H), 4.603 (d, J= 16.1 Hz, 2H), 4.601 (d, J= 16.1 Hz, 1H), 1.576 (d, J= 7.0 Hz, 3H), 1.573 (d, J= 7.0 Hz, 3H), 1.561 (d, J= 1.561 Hz, 3H), 1.560 (d, J= 6.3 Hz, 3H), 1.558 (d, J= 7.0 Hz, 3H), 1.556 (d, J= 7.0 Hz, 3H), 1.553 (d, J= 6.3 Hz, 3H), 1.534 (d, J= 7.7 Hz, 3H), 1.532 (d, J= 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.51, 169.50, 169.48, 169.46, 169.37, 169.32, 169.23, 169.21, 169.19, 169.18, 169.16, 169.14, 169.13, 166.50, 166.48, 166.35, 166.33, 69.34, 69.29, 69.16, 68.97, 60.76, 60.74, 16.72, 16.70, 16.67, 16.65, 16.64; SEC (THF): M_n – 27.4 kDa, M_w –

38.9 kDa, PDI – 1.4; SEC ($CHCl_3$): M_n – 40.5 kDa, M_w – 54.7 kDa, PDI – 1.4; SEC-MALLS ($CHCl_3$): M_n – 25.3 kDa, M_w – 28.5 kDa, PDI – 1.12.

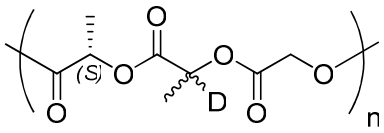


Poly $L_{rac}L_{rac}G$. A white solid was collected (0.41 g, 65%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.24 – 5.16 (m, 8H), 4.85 (d, J= 16.1 Hz, 1H), 4.818 (d, J= 16.1 Hz, 1H), 4.808 (d, J= 16.1 Hz, 1H), 4.805 (d, J= 15.4 Hz, 1H), 4.78 (d, J= 16.8 Hz, 1H), 4.686 (d, J= 15.4 Hz, 1H), 4.65 (d, J= 14.0 Hz, 1H), 4.63 (d, J= 16.1 Hz, 1H), 4.61 (d, J= 16.1 Hz, 1H), 4.60 (d, J= 16.8 Hz, 1H), 1.58-1.52 (m, 24H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.49, 169.45, 169.36, 169.3, 169.27, 169.26, 169.18, 169.17, 169.14, 169.12, 169.1, 166.52, 166.48, 166.47, 166.42, 166.34, 166.3, 69.35, 69.29, 69.16, 69.12, 69.11, 69.01, 68.97, 60.77, 60.74, 16.72, 16.69, 16.67, 16.65, 16.63, 16.61; SEC (THF): M_n – 30.5 kDa, M_w – 43.0 kDa, PDI – 1.4; SEC ($CHCl_3$): M_n – 35.1 kDa, M_w – 46.0 kDa, PDI – 1.3.

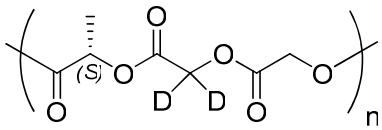


Poly $L_{d,rac}LG$. A white solid was collected (0.64 g, 99%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.25-5.15 (m, 4H), 4.86 (d, J= 16.1 Hz, 4H), 4.824 (d, J= 16.1 Hz, 1H), 4.822 (d, J= 16.1 Hz, 2H), 4.821 (d, J= 16.1 Hz, 1H), 4.81 (d, J= 16.1 Hz, 4H), 4.788 (d, J= 16.1 Hz, 2H), 4.786 (d, J= 16.1 Hz, 2H), 4.69 (d, J= 16.1 Hz, 4H), 4.652 (d, J= 16.1 Hz, 2H), 4.649 (d, J= 16.1 Hz, 2H), 4.618 (d, J= 16.1 Hz, 1H), 4.616 (d, J= 16.1 Hz, 2H), 4.614 (d, J= 16.1 Hz, 1H), 4.603 (d, J= 16.1 Hz, 1H), 4.601 (d, J= 16.1 Hz, 2H), 4.599 (d, J= 16.1 Hz, 1H). 1.58-1.53 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$) d 169.50, 169.48, 169.46, 169.45, 169.36, 169.31, 169.2, 169.18, 169.16, 169.14, 169.12, 166.47 (2), 166.34, 166. 31, 69.34, 69.29, 69.16 (2), 69-68 (m), 60.75, 60.73, 16.71,

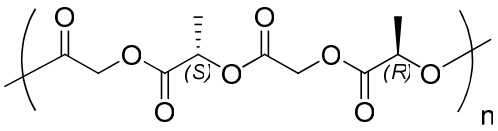
16.67, 16.63, 16.57, 16.55; SEC (THF) M_n – 32.8 kDa, M_w – 41.2 kDa, PDI – 1.3; SEC ($CHCl_3$): M_n – 31.7 kDa, M_w – 47.4 kDa, PDI – 1.5.



Poly LL$_{d,rac}$G. A white solid was collected (0.55 g, 62%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.23-5.15 (m, 4H), 4.85 (d, J= 16.1 Hz, 8H), 4.81 (d, J= 16.1 Hz, 4H), 4.807 (d, J= 16.1 Hz, 4H), 4.651 (d, J= 16.1 Hz, 2H), 4.649 (d, J= 16.1 Hz, 2H), 4.632 (d, J= 16.1 Hz, 4H), 4.615 (d, J= 16.1 Hz, 2H), 4.614 (d, J= 16.1 Hz, 2H), 4.602 (d, J= 16.1 Hz, 4H), 1.58-1.53 (m, 24H); ^{13}C NMR (150MHz, $CDCl_3$) δ 169.5, 169.39, 169.37, 169.34, 169.32, 169.31, 169.21, 169.19, 169.16, 169.13, 169.11, 166.54, 166.50, 166.35, 166.31, 69.17, 69.10, 69.0, 68.98, 60.77, 60.75, 16.70, 16.69, 16.66, 16.63, 16.53, 16.51; SEC (THF) M_n – 29.6 kDa, M_w – 40.1 kDa, PDI – 1.4; SEC ($CHCl_3$): M_n – 33.7 kDa, M_w – 48.4 kDa, PDI – 1.4.

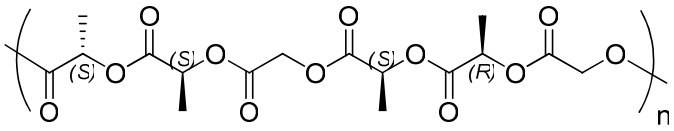


Poly GLG$_{d2}$. A white solid was collected (0.44 g, 52%). ^{1}H (600 MHz, $CDCl_3$) δ 5.25 (q, J= 7.2Hz, 1H), 4.86 (d, J= 16.2 Hz, 1H), 4.68 (d, J= 16.2 Hz, 1H), 1.57 (d, J= 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 166.5, 166.4, 69.2, 60.7, 16.7; SEC (THF) M_n – 15.2 kDa, M_w – 21.6 kDa, PDI – 1.4; SEC ($CHCl_3$): M_n – 25.3 kDa, M_w – 38.4 kDa, PDI – 1.5.

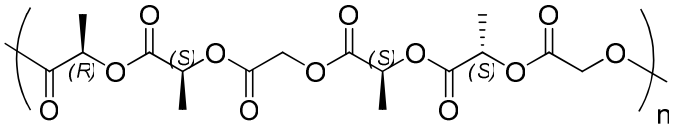


Poly GLGL$_R$. A white powder was collected (0.49 g, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.24 (q, J= 7.2 Hz, 1H), 4.81 (d, J= 16.2 Hz, 1H), 4.69 (d, J= 15.6 Hz, 1H), 1.56 (d, J= 7.2 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 166.4, 69.2, 60.8, 16.8; SEC (THF): M_n – 12.3 kDa, M_w – 17.9 kDa, PDI – 1.5; SEC ($CHCl_3$): M_n – 12.1 kDa, M_w – 17.0 kDa, PDI – 1.4.



Poly LLGLL$_R$G. A white solid was collected (0.43 g, 70%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.22 (q, J= 7.0 Hz, 1H), 5.215 (q, J= 7.2 Hz, 1H), 5.18 (q, J= 7.0 Hz, 2H), 4.85 (d, J= 16.1 Hz, 1H), 4.81 (d, J= 16.1 Hz, 1H), 4.63 (d, J= 16.1 Hz, 1H), 4.61 (d, J= 16.1 Hz, 1H), 1.57 (d, J= 7.0 Hz, 3H), 1.56 (d, J= 7.7 Hz, 6H), 1.53 (d, J= 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.36 (2), 169.32, 169.1, 166.5, 166.3, 69.4, 69.2, 69.1, 60.77, 60.75, 16.74, 16.70, 16.66, 16.62; SEC (THF): M_n – 30.0 kDa, M_w – 42.0 kDa, PDI – 1.4; SEC ($CHCl_3$): M_n – 32.0 kDa, M_w – 47.4 kDa, PDI – 1.5.



Poly L$_R$LGLLG. A white solid was collected (0.36 g, 63%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.221 (q, J= 7.0 Hz, 1H), 5.212 (q, J= 7.0 Hz, 1H), 5.187 (q, J= 7.0 Hz, 1H), 5.182 (q, J= 7.0 Hz, 1H), 4.818 (d, J= 16.1 Hz, 1H), 4.785 (d, J= 16.1 Hz, 1H), 4.686 (d, J= 16.1 Hz, 1H), 4.613 (d, J= 16.8 Hz, 1H), 1.571 (d, J= 7.0 Hz, 3H), 1.554 (d, J= 7.0 Hz, 3H), 1.548 (d, J= 7.0 Hz, 3H), 1.528 (d, J= 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 169.3, 169.2, 169.1, 166.5, 166.3, 69.3, 69.2 (2), 69.0, 60.8, 16.71 (2), 16.68, 16.65; GPC (THF): M_n – 30.1 kDa, M_w – 41.2 kDa, PDI 1.4; GPC ($CHCl_3$): M_n – 39.8 kDa, M_w – 52.7 kDa, PDI – 1.3.

Miscellaneous Figures:

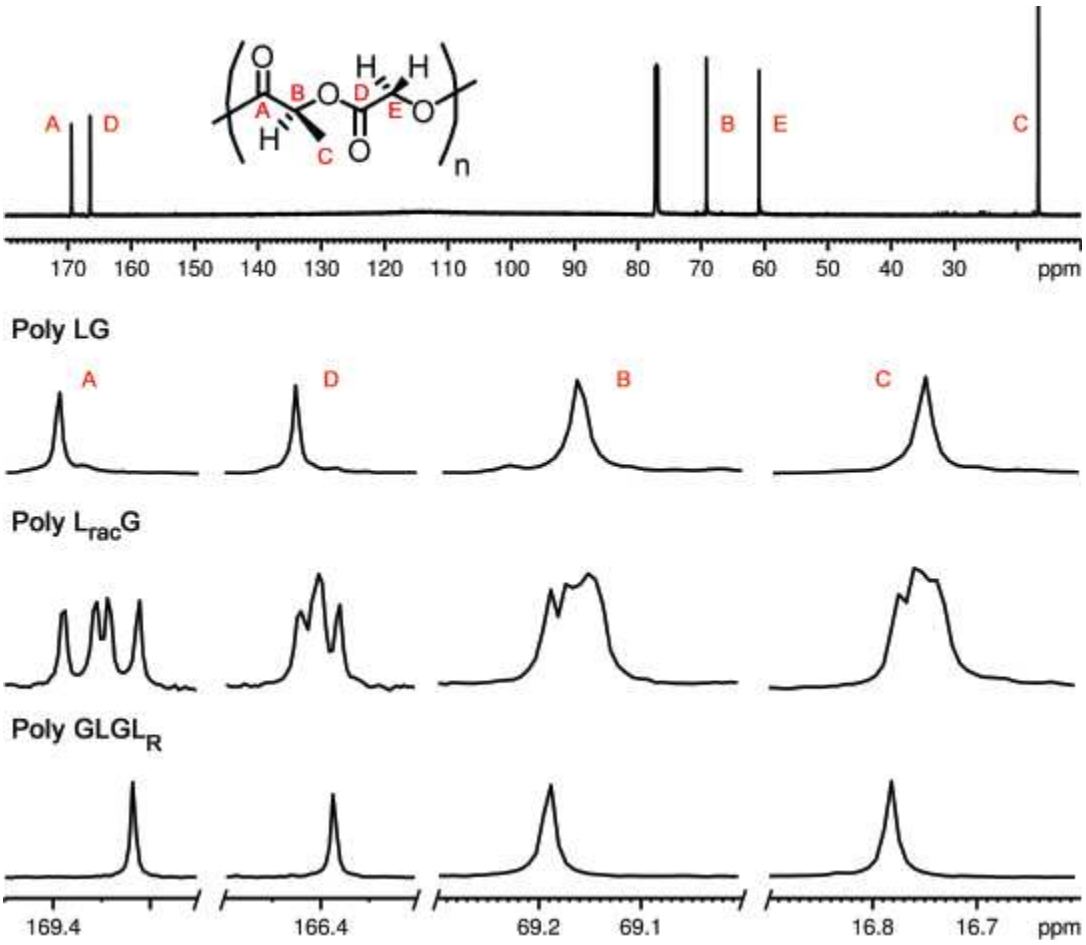


Figure S1. (Top) Full spectrum of **poly LG**; (Bottom) expansions of selected regions for **poly LG**, **L*rac*G** and **GLGL*R***. ^{13}C NMR spectra at 150 MHz in $CDCl_3$.

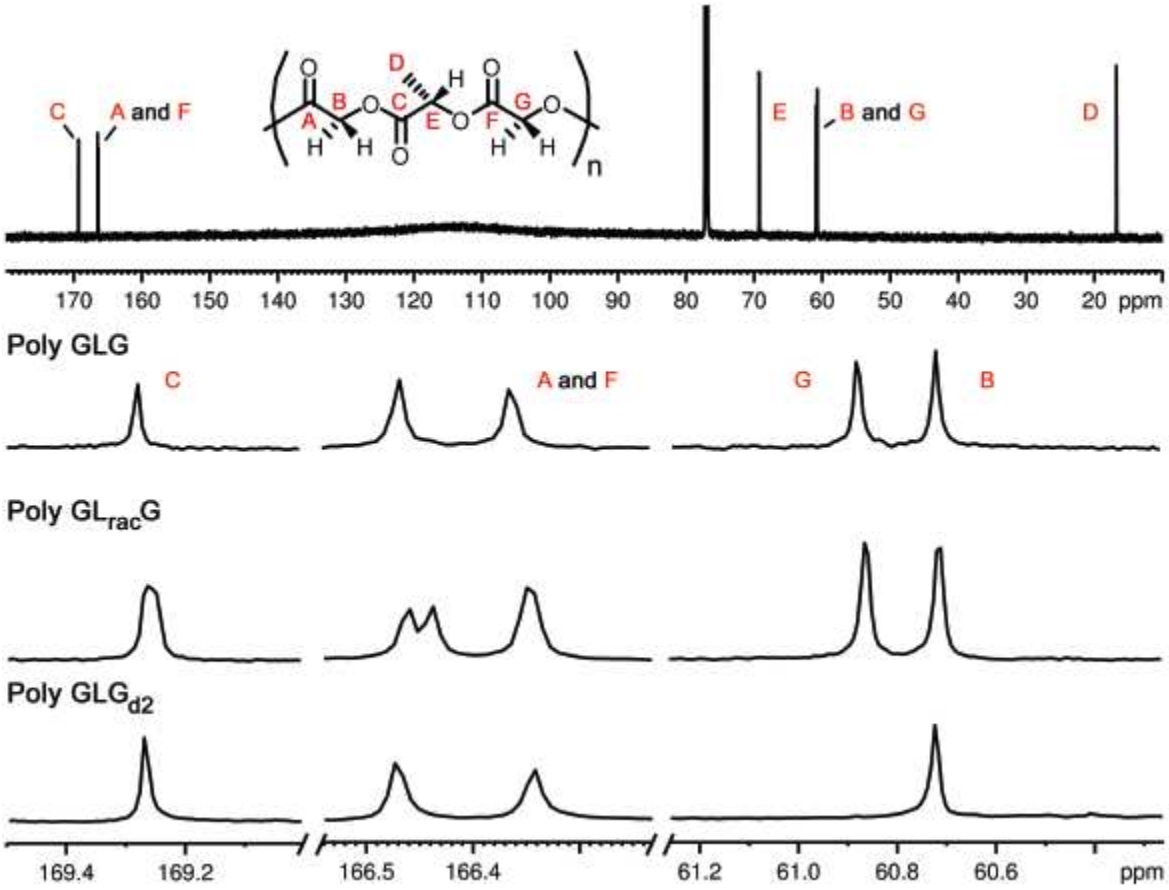


Figure S2. (Top) Full spectrum of **poly GLG**; (Bottom) expansions of selected regions for **poly GLG**, G**L**$_{rac}$**G** and **GLG**$_{d2}$. ^{13}C NMR spectra at 150 MHz in $CDCl_3$.

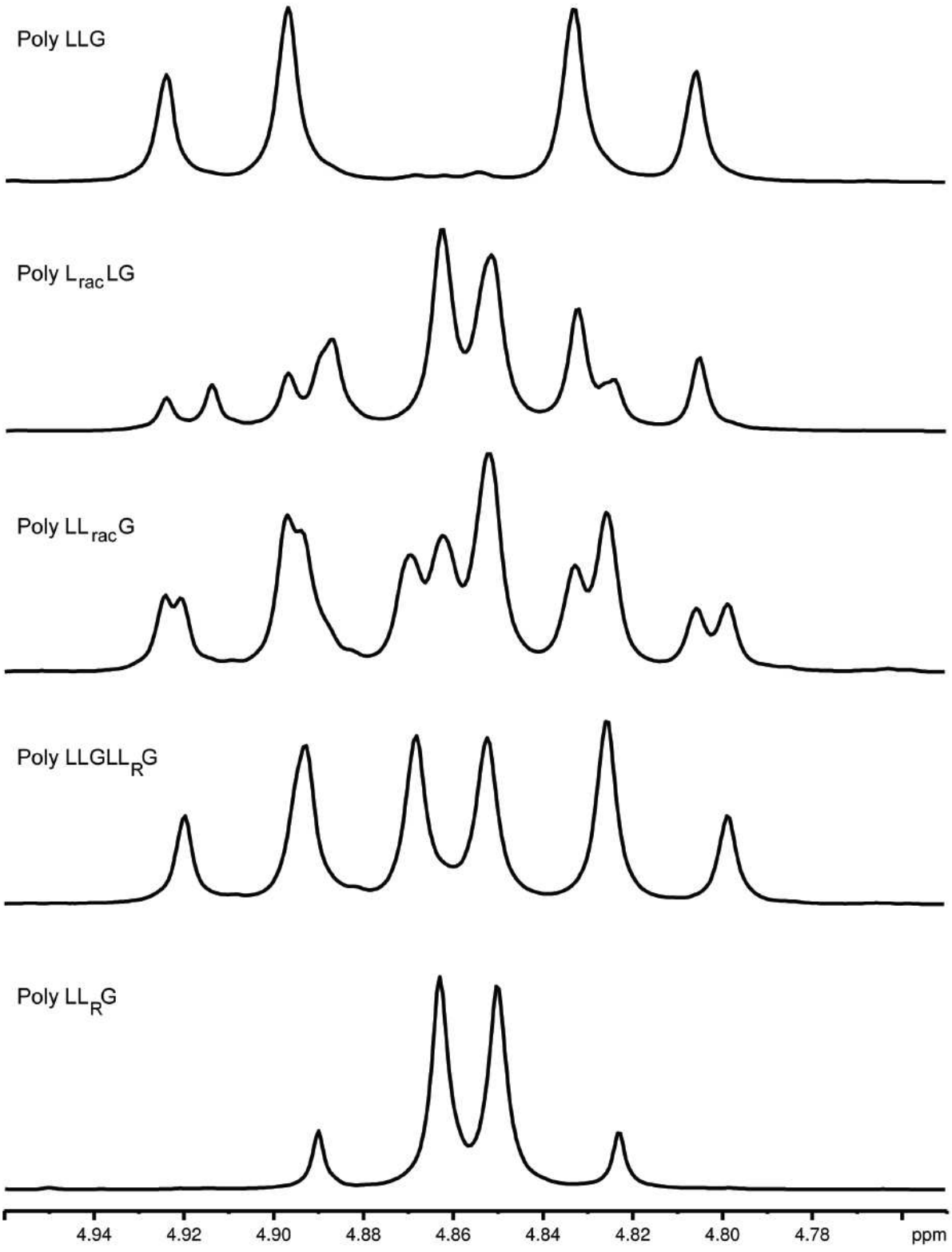


Figure S3. ^{1}H NMR spectra of the methylene region for selected LLG polymers at 600 MHz in d_6-DMSO.

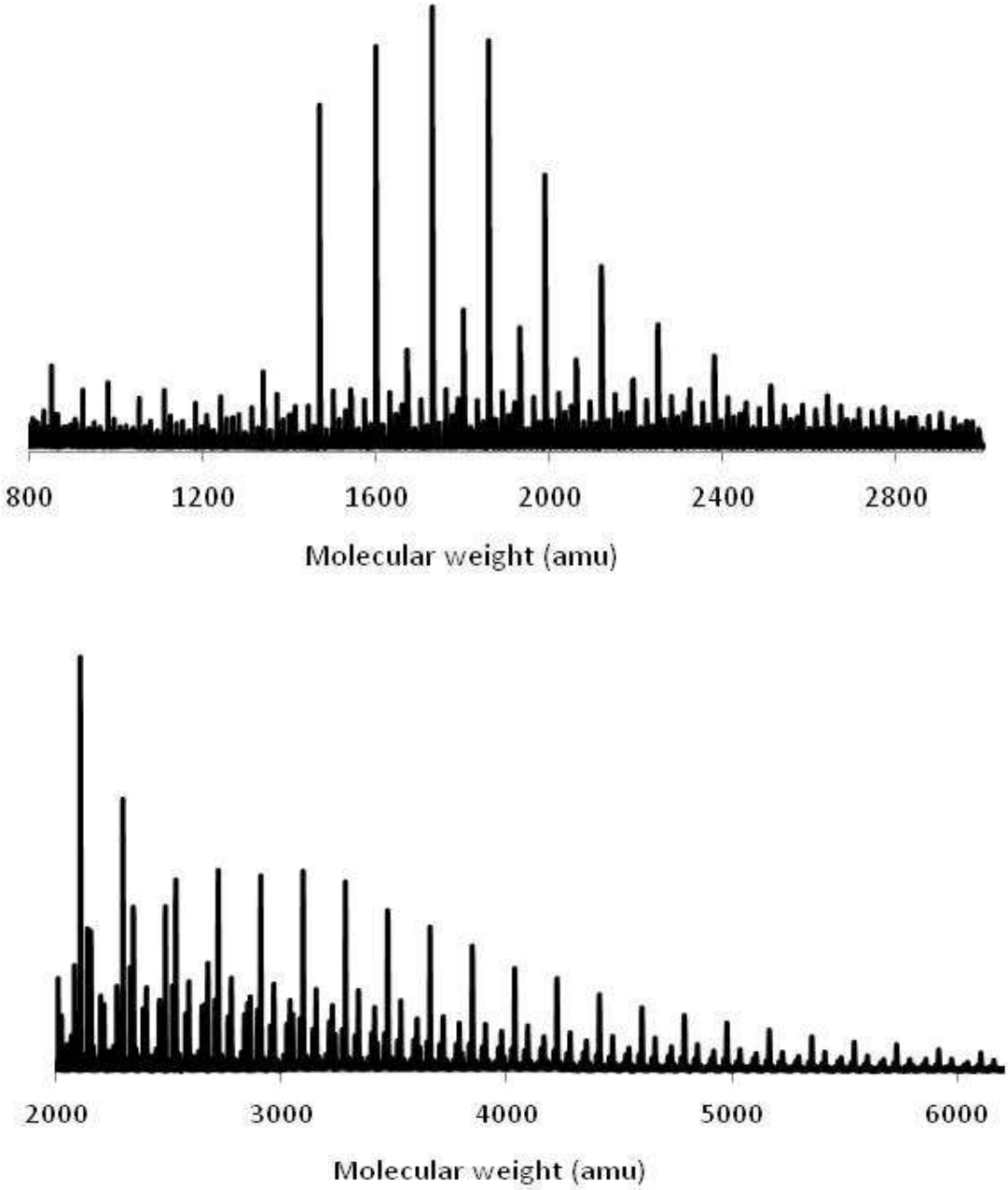


Figure S4. MALDI-TOF spectra for **poly LG** (top) and **GLG** (bottom)

References:

(1) Nakamura, K.; Baker, T. J.; Goodman, M. *Org. Lett.* **2000**, *2*, 2967-2970.
(2) Greiner, A.; Ortholand, J. Y. *Tetrahedron Lett.* **1992**, *33*, 1897-900.
(3) Laube, T.; Dunitz, J. D.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1373-93.
(4) Hoberman, H. D. *J. Biol. Chem.* **1958**, *233*, 1045-8.
(5) Hoberman, H. D.; D'Adamo, A. F., Jr. *J. Org. Chem.* **1960**, *25*, 30-1.
(6) Moore, J. S.; Stupp, S. I. *Macromolecules* **1990**, *23*, 65-70.
(7) Huijser, S.; Staal, B. B. P.; Huang, J.; Duchateau, R.; Koning, C. E. *Angew. Chem. Int. Ed.* **2006**, *45*, 4104-4108.
(8) Stayshich, R. M.; Meyer, T. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 4704-4711.
(9) Faure, S.; Piva-Le-Blanc, S.; Bertrand, C.; Pete, J. P.; Faure, R.; Piva, O. *J. Org. Chem.* **2002**, *67*, 1061-1070.
(10) Wolfe, S.; Wilson, M.-C.; Cheng, M.-H.; Shustov, G. V.; Akuche, C. I. *Can. J. Chem.* **2003**, *81*, 937-960.