Electronic Supplementary Information for:

Poly(2,7-di-*n*-pentyldibenzofulvene) Showing Chiroptical Properties in the Solid State Based Purely on a Chiral Conformation

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(1) Synthesis of 2,7-Di-n-pentyldibenzofulvene

2,7-di(1-oxopentyl)fluorene

Fluorene (30.09 g, 181.2 mmol), $AlCl_3$ (100.2 g), and CS_2 (400 ml) were mixed in a 4-necked 3-L flask filled with N_2 gas and equipped with a mechanical stirrer. To the mixture was added valeroly chloride (64 ml) dropewise from a dropping funnel in a 30-min period with vigorous stirring. The reaction mixture was stirred for 8hr at room temperature (ca. 23°C) and then slowly poured into an ice water (1 L) with stirring. The resulting mixture was extracted using CH_2Cl_2. The organic layer was washed twice with aq. NaOH (2 wt%) and once with aq. NaCl, and dried on $MgSO_4$. Removal of solvent gave the crude material as brown solid (61.01 g). Recrystallization of the crude product afforded pure 2,7-di(1-oxopentyl)fluorene (52.45g, 87%). Anal: mp 147.3-149.1°C; ^{1}H NMR (500MHz, $CDCl_3$, TMS) δ 8.18 (s, 2H), 8.04 (d, *J*=8.0Hz, 2H), 7.90 (d, *J*=8.0Hz, 2H), 4.02 (s,2H), 3.03 (t, *J*=7.0Hz, 4H), 1.76 (quint, *J*=7.0Hz, 4H), 1.44 (sextet, *J*=7.0Hz, 4H), 0.98 (t, *J*=7.0Hz, 6H); ^{13}C NMR (125MHz, $CDCl_3$) δ 200.29, 144.77, 144.46, 136.44, 127.43, 124.81, 120.59, 38.51, 36.92, 26.58, 22.49, 13.93; IR (KBr) 2957, 2937, 2895, 2870, 1680, 1605, 1213, 1137, 843, 798, 754, 731cm^{-1}; HRMS (EI) calcd for $C_{23}H_{26}O_2$ 334.1933, found 334.1933.

2,7-di-n-pentylfluorene

2,7-Di(1-oxopentyl)fluorene (30.41g, 91.06mmol) and hydrazine・monohydrate (44.2ml) were dissolved in di(ethylene glycol) (400ml), and the mixture was heated at 120°C for 2hr in a 1-L flask equipped with a Dean-Stark trap. After KOH (20.56g) was added, the reaction mixture was heated at 200°C for 3h and then quenched at room temperature by adding water. The resulting mixture was extracted with diethyl ether. The organic layer was washed twice with 1N HCl, aq. $NaHCO_3$ (saturated), water, and with aq. NaCl in this order, and dried on $MgSO_4$. Removal of solvent gave the crude product as yellow solid (27.66g). Purification by silica gel column chromatography with hexane as an eluent afforded crystalline 2,7-di-n-pentylfluorene (26.21g, 94%). Anal: mp 98.9-99.6°C; ^{1}H NMR (500MHz, $CDCl_3$, TMS) δ 7.63 (d, *J*=8.0Hz, 2H), 7.33 (s, 2H), 7.16 (d, *J*=8.0Hz, 2H), 3.83 (s, 2H), 2.67-2.64 (m, 4H), 1.68-1.62 (m, 4H), 1.53-1.33 (m, 8H), 0.91-0.88 (m, 6H); ^{13}C NMR (125MHz, $CDCl_3$) δ 143.33, 141.24, 139.43, 126.91, 124.80, 119.23, 36.70, 36.12, 31.56, 31.51, 22.59, 14.06; IR (KBr) 2953, 2925, 2870, 2855, 1467, 1420, 2397, 864, 811 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{30}$ 306.2348, found 306.2339.

9-hydoxymethyl-2,7-di-n-pentylfluorene

2,7-Di-*n*-pentylfluorene (5.04 g, 16.4 mmol) was dissolved in dry toluene (280 ml) containing *N,N,N',N'*-tetramethylethylenediamine (7.4 ml) in a flame-dried 1-L flask filled with N_2. A hexane solution of n-BuLi (1.6M, 31 ml) was added dropwise to the solution cooled at 0°C with a syringe in a 10-min period, and the mixture was stirred for additional 5 min at 0°C. Paraformaldehyde(1.58g) and toluene(20ml) were added to the solution and the resulting mixture was stirred for 80 min at 0°C. The reaction was quenched with water, and the products were extracted twice with ethyl acetate. The organic layer was washed with aq. NaCl and dried on $MgSO_4$. Removal of solvent gave the crude material as a yellow oil (8.53 g). Purification by silica gel column chromatography with hexane-ethyl acetate (15/1, v/v) as an eluent afforded crystalline 9-hydroxymethyl-2,7-di-*n*-pentylfluorene (3.14g, 57%). Anal: mp 61.3-63.7°C; ^{1}H-NMR (500MHz, $CDCl_3$, TMS) δ 7.62 (d, *J*=8.0Hz, 2H), 7.39 (s, 2H), 7.19 (d, *J*=8.0Hz, 2H), 4.05 (s, 2H), 2.68-2.65 (m, 4H), 1.69-1.63 (m, 4H), 1.36-1.33 (m, 8H), 0.91-0.89 (m, 6H); ^{13}C-NMR (125MHz, $CDCl_3$) δ 144.36, 141.69, 139.25, 127.74, 124.62, 119.45, 65.29, 50.15, 36.16, 31.61, 31.48, 22.56, 14.06; IR (KBr) 3311, 2926, 2855, 1467, 1418, 1062, 1023, 896, 809, 732 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{32}O$ 336.2453, found 336.2446.

2,7-di-n-pentyldibenzofulvene

9-Hydroxymethyl-2,7-di-*n*-pentylfluorene (1.62 g, 4.82 mmol) was dissolved in a mixture of methanol (30 mL) and THF (30 mL) in a 200-mL flask. Potassium *t*-butoxide (1.63 g, 14.5 mmol) was added to the solution cooled at 0°C, and the resulting mixture was refluxed for 5 min. The reaction was quenched with water, and the products were extracted with hexane. The organic layer was washed with aq. NaCl and dried on $MgSO_4$. Removal of solvent gave the crude product as yellow oil (1.57 g). Purification by silica gel column chromatography with hexane as an eluent afforded 2,7-di-*n*-pentyldibenzofulvene (1.40 g, 91%) as yellow oil. Anal: ^{1}H NMR (500MHz, $CDCl_3$, TMS) δ 7.56 (d, *J*=8.0Hz, 2H), 7.54 (s, 2H), 7.19 (d, *J*=8.0Hz, 2H), 6.05 (s, 2H), 2.71-2.68 (m, 4H), 1.72-1.66 (m, 4H), 1.39-1.37 (m, 8H), 0.95-0.92 (m, 6H); ^{13}C NMR (125MHz, $CDCl_3$) δ 143.66, 141.59, 138.28, 138.06, 128.98, 120.90, 119.17, 106.81, 36.16, 31.54, 31.40, 22.57, 14.04; IR (neat) 2929, 2855, 1465, 1376, 1298, 889, 817, 754 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{30}$ 318.2348, found 318.2363.

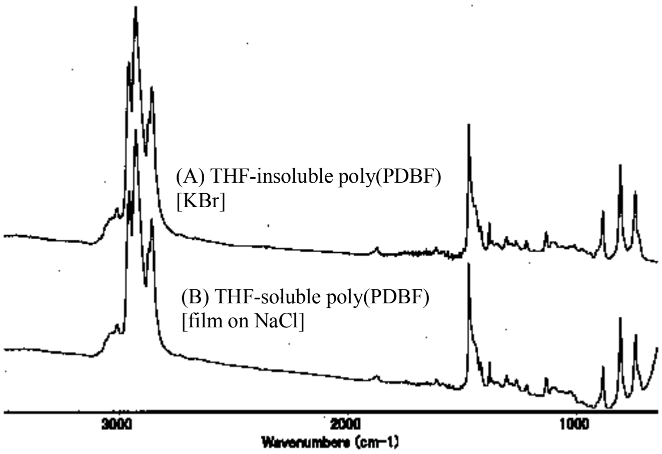
(2) Polymerization Summary

Supplementary Table 1. Anionic Polymerization of PDBF at -78^{o}C^{a}

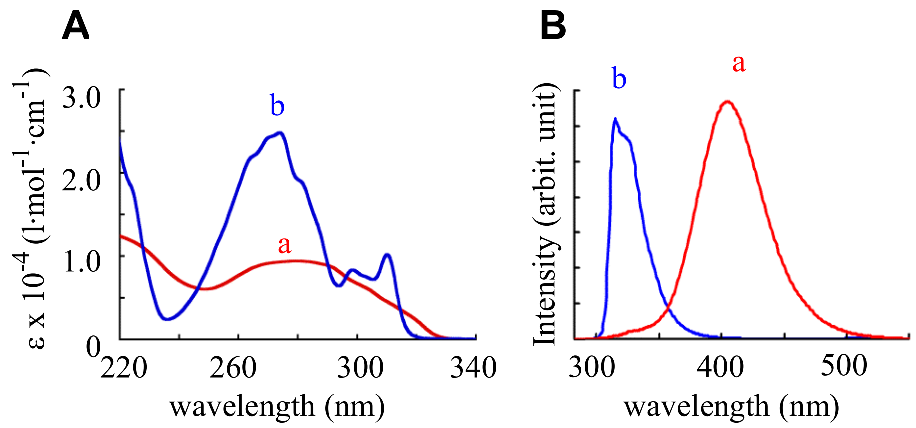
run	monomer	solvent	conv.^{b} (%)	THF-insol.^{c} part	THF -sol. part^{c}		
				yield(%)	yield(%)	Mn^{d}	Mw/Mn^{d}
1	(+)-DDB-FlLi	toluene	40	3	24	5290	1.03
2	(-)-DDB-FlLi	toluene	50	2	49	5710	1.16
3	Sp-FlLi	toluene	73	21	50	5950	1.05
4	*n*-BuLi	THF	>99	trace	84	4750	1.20

[a] Conditions: time = 24 hr; monomer amount = 1.00-1.02mmol; [monomer] = 0.20~0.21 M; [ligand]/[Li] = 1.2; $[\text{monomer}]_0/[\text{RLi}]_0 = 20$. [b] Determined by ^{1}H NMR analysis of the reaction mixture. [c] The quenched reaction mixture was first separated into MeOH-soluble and -insoblule parts and the insoluble part was then extracted using THF. [d] Determined by SEC using a Visotek TDA300 detector which collects rectangular light scattering, viscosity, and RI information.

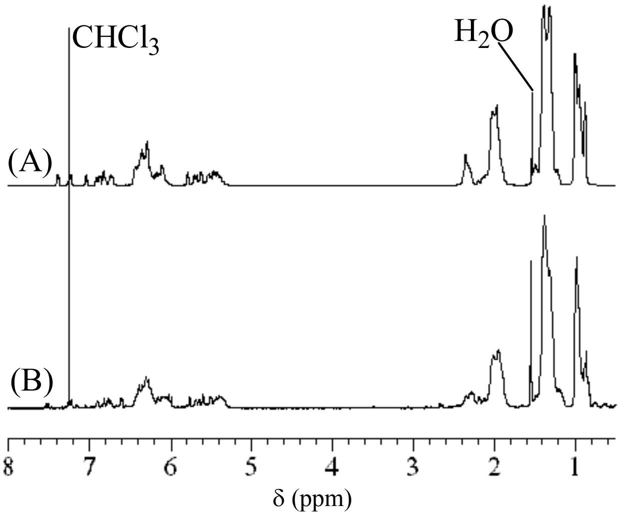
(3) Spectral and Graphical Data



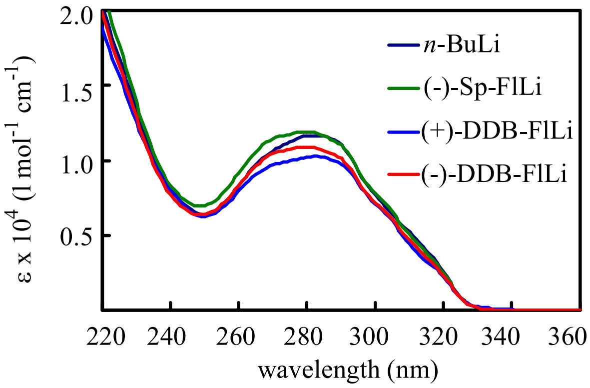
Supplementary Figure 1. IR spectra of THF-insoluble part (A) and THF-soluble part (B) of poly(PDBF) prepared using (-)-DDB-FlLi (run 2 in Supplementary Table 1). Measurement conditions: A, KBr pellet; B, film on NaCl plate.



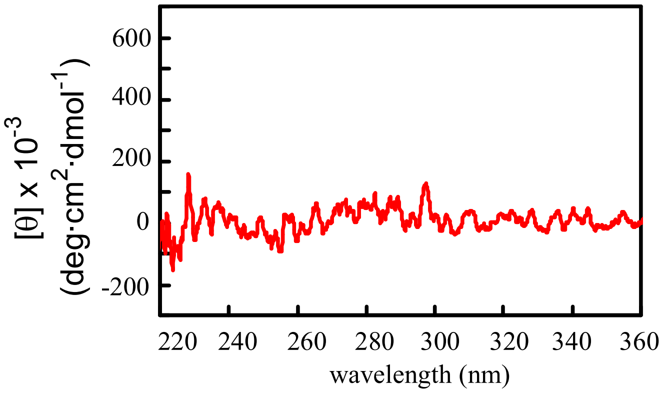
Supplementary Figure 2. Absorption (left) and emission (right) spectra of poly(PDBF)s prepared using (-)-Sp-FlLi (run 3 in Supplementary Table 1) (a) and 2,7-di-*n*-pentylfluornene (b), a model of monomeric unit in THF at room temperature. Conditions: concentration 1.8 x10^{-5} M (a), 1.7 x 10^{-5} M (per choromophore) (b); cell length 0.1 mm (absorption), 10 mm (emission); λ_{ex} for emission 282 nm.



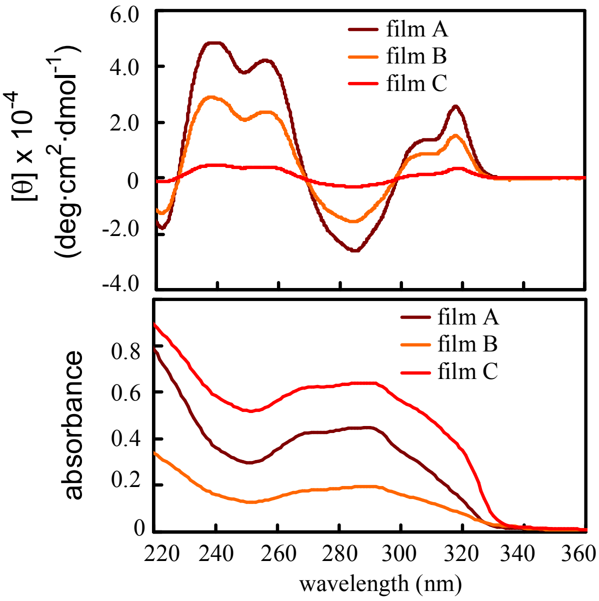
Supplementary Figure 3. ^{1}H NMR spectra of poly(PDBF)s prepared by anionic polymerization using (-)-DDB-FlLi (run 2 in Supplementary Table 1) (A) and *n*-BuLi (run 4 in Supplementary Table 1) (B). (500 MHz, CDCl$_3$, r.t.).



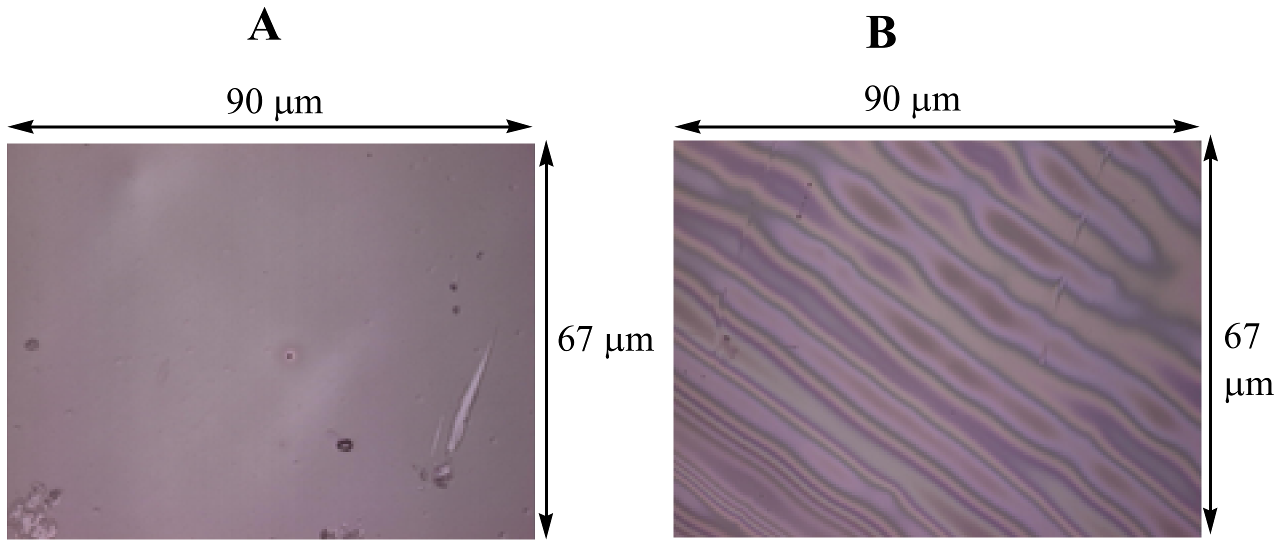
Supplementary Figure 4. Absorption spectra of poly(PDBF)s prepared by anionic initiators in a THF solution at room temperature.



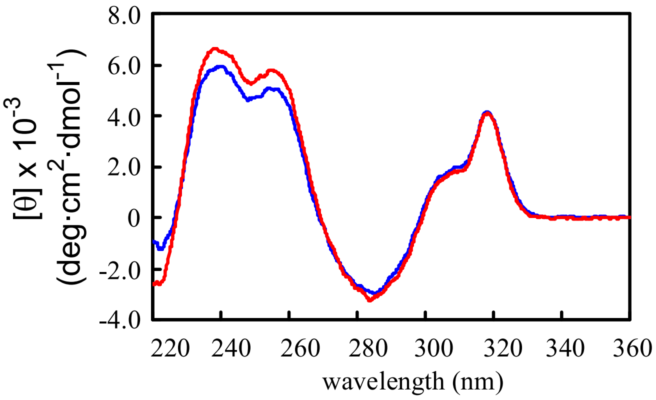
Supplementary Figure 5. CD spectrum in a THF solution of poly(PDBF) prepared using (-)-DDB-FlLi (run 2 in Supplementary Table 1). (conc. 0.01 M per residue, cell length 0.1 mm)



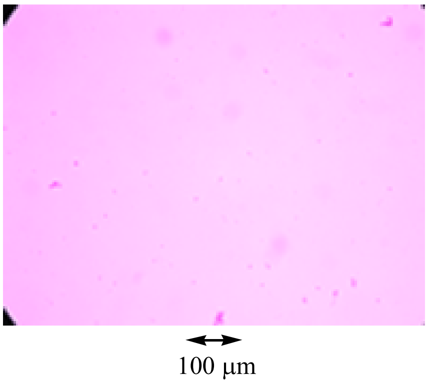
Supplementary Figure 6. CD intensity variation of films prepared from poly(PDBF) synthesized using (-)-DDB-FlLi (run 2 in Supplementary Table 1: (A) a film with a smooth surface, (B) a film with a modestly smooth surface (smoothness was between A and C), and (C) a film with a wrinkled surface. Films having wrinkles on the surface such as those in C were most often reproduced in repeated film preparation.



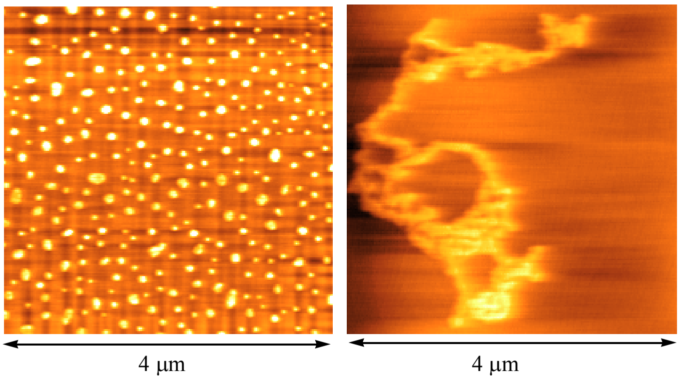
Supplementary Figure 7. Surface picture of films made from poly(PDBF) synthesized using (-)-DDB-FlLi (run 2 in Supplementary Table 1): (A) a film with a smooth surface and (B) a film with a wrinkled surface (wrinkle height 0.3~0.6 μm). Films A and B correspond to spectra A and C in Supplementary Figure 6. This analysis was preformed using a Keyence VK-9500 Laser microscope (Laser wavelength 408 nm).



Supplementary Figure 8. CD spectra of a film sample of poly(PDBF) prepared using (-)-DDB-FlLi (run 2 in Supplementary Table 1) measured at at different orientations. The two spectra were recorded at 90 degree apart.

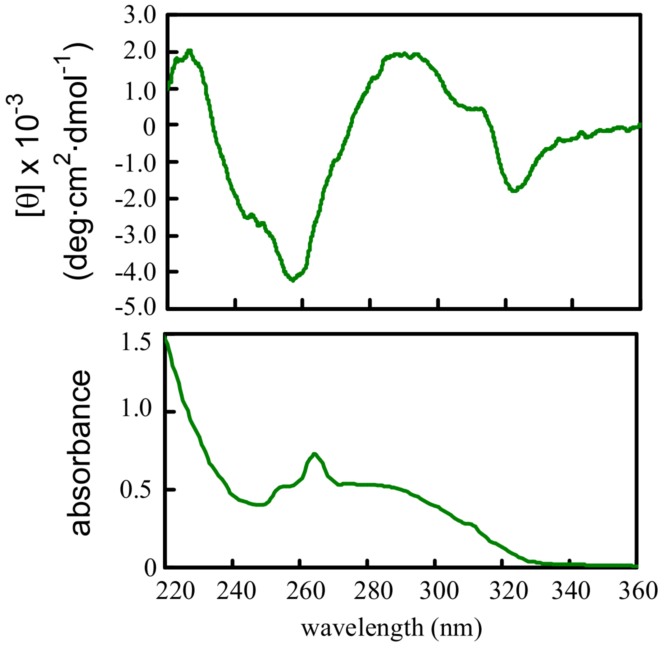


Supplementary Figure 9. Polarized microscopic picture of a film used for CD measurements. [polymer: run 2 in Supplementary Table 1]

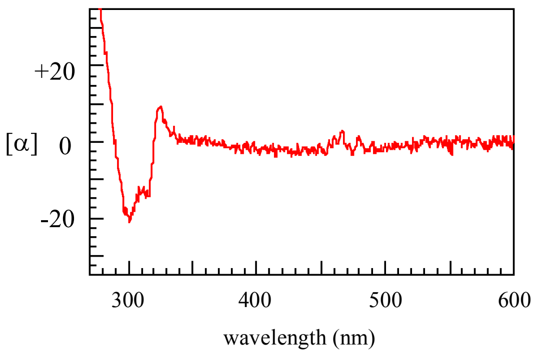


Supplementary Figure 10. Atomic force microscopic images (topographic image) of poly(PDBF)s synthesized using n-BuLi (left) and (-)-Sp-FlLi (right) (runs 4 and 3, respectively, in Supplementary Table 1). [Seiko Intruments SPA400-SPI3800N, DFM mode]

Additional explanations to this figure: The samples were prepared by dropping a dilute THF solution (1 x 10^{-4} M per residue) onto an untreated mica surface. The polymer prepared using (-)-Sp-FlLi formed long, chain-like aggregates. On the other hand, the polymer prepared by achiral n-BuLi did not from such aggregates but simple dots. These results suggest that single-handed helical chains in the solid state may tend to form large helical bundles while racemic helices do not.



Supplementary Figure 11. CD and absorption spectra of poly(PDBF) prepared using (-)-Sp-FlLi (THF-insoluble part, run 3 in Supplementary Table 1) in a decalin suspension (conc. 0.005 M per residue, cell length 0.1 mm).



Supplementary Figure 12. ORD curve of a film of poly(PDBF)s synthesized using (-)-DDB-FlLi (run 2 in Supplementary Table 1).