Supporting Information

Synthesis and Chiral Self-Sorting of Spirobifluorene-Containing Boronate Ester Cages

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Content

1 Materials and Chemicals

All chemicals were purchased from commercial suppliers ABCR, ALFA AESAR, ACROS ORGANICS, FISHER CHEMICALS, MERCK and SIGMA ALDRICH, and were used without further purification. Solvents were distilled prior to use. Dichloromethane and tetrahydrofuran were dried with the solvent purification system "PureSolv MD 5" from INNOVATIVE TECHNOLOGY.

2 Technical Equipment

NMR spectroscopy: BRUKER AVANCE 300, BRUKER AVANCE 400, BRUKER AVANCE 500, BRUKER AVANCE III HD PRODIGY 500, BRUKER AVANCE 600, BRUKER AVANCE III HD CRYO 700. Chemical shifts are given in ppm in relation to the residual protonated solvent signal as internal standard (^{1}H-NMR: 3.58 ppm for THF-d_8; ^{13}C-NMR: 67.21 ppm for THF-d_8). Signal multiplicities are denoted as s (singlet), d (dublet), t (triplet) and m (multiplet). Processing of the raw data was performed with the program Topspin 4.0.[S1]

MALDI-TOF mass spectrometry: ultrafleXtreme BRUKER DALTONIC, matrix: DCTB (*trans*-2-(3-(4-*t*-Butylphenyl)-2-methyl-2-propenylidene)malononitrile).

ESI/APCI mass spectrometry: MAT 95 XL THERMO FINNIGAN, micrOTOF-Q Q/TOF BRUKER DALTONIC, Orbitrap XL THERMO FISHER SCIENTIFIC.

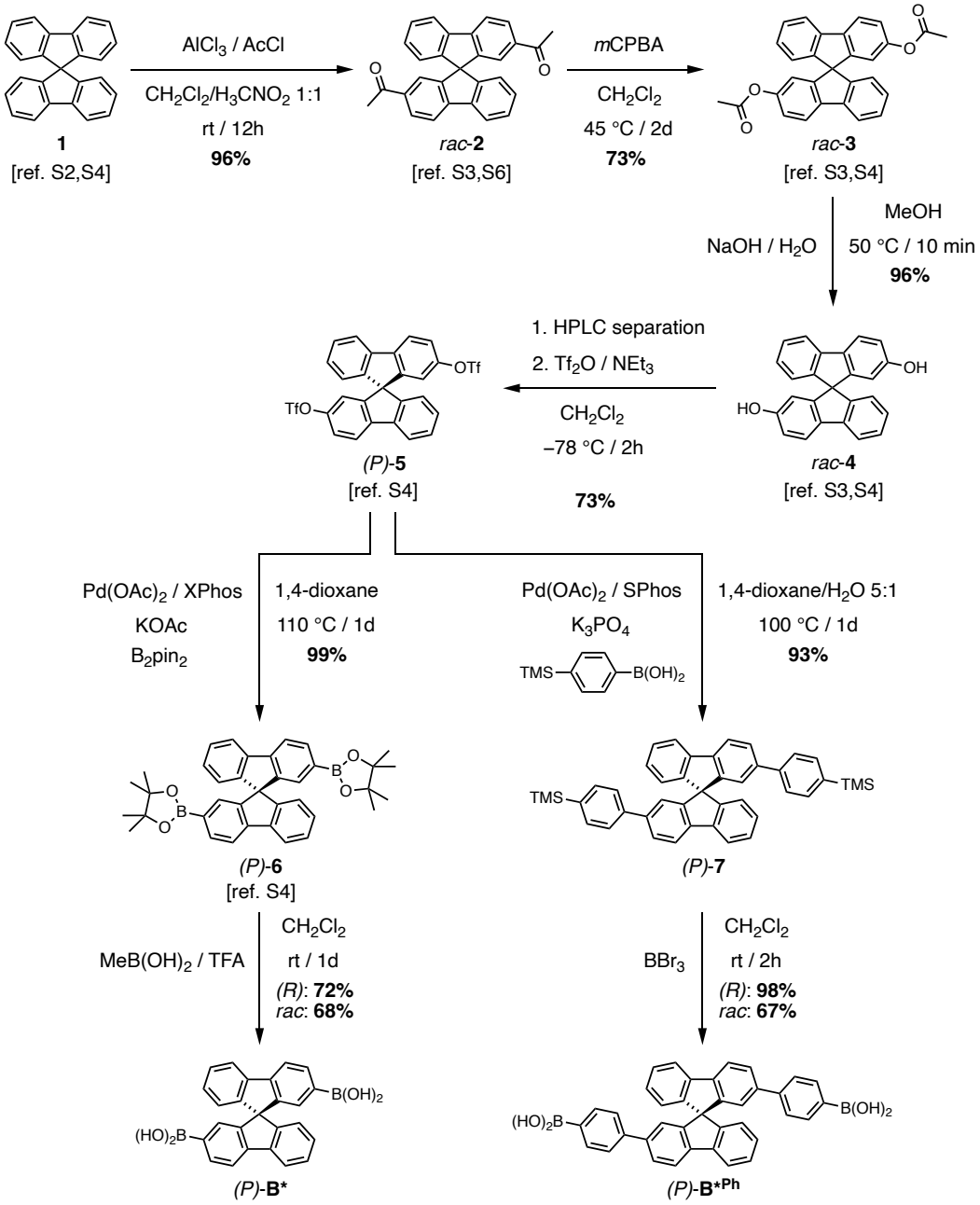
EI mass spectrometry: MAT 95 XL or MAT 90 THERMO FINNIGAN.

HPLC separations: Prominence LC-20 SHIMADZU, LC-8A SHIMADZU.

3 Synthetic Procedures and Characterization

The synthesis of 9,9'-spirobifluorene-based diboronic acids **B*** and **B*^{Ph}** (Scheme S1) largely builds on known derivatives which have been reported by us and others. Nevertheless, we give experimental details of them here besides referring to the previous work in order to provide a comprehensive collection of data for anyone interested in these compounds.

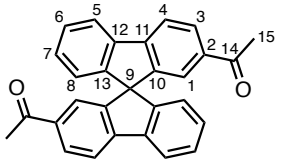
The synthesis starts with 9,9'spirobifluorene (**1**) which itself can best be prepared according to the original procedure reported by M. Gomberg.[S2] Inspired by the synthetic strategy developed by V. Prelog,[S3] we were able to report refined synthesis of key intermediate *rac*-**4** and methods for its chiral resolution either via clathrate formation with a tartaric acid derivative[S4] elaborating an initial protocol by F. Toda[S5] or more convenient via HPLC on a Chiralpak IA column.[S6] This allowed the synthesis of triflate **5**[S4] which can be converted into bis(boronic acids) **B*** and **B*^{Ph}** in both racemic and enantiomerically pure form.



Scheme S1. Synthesis of enantiomerically pure bis(boronic acids) (P)-**B** and (P)-**B*^{Ph}** (racemic **5**, **6**, **7**, **B***, and **B*^{Ph}** were prepared accordingly from *rac*-**4**).

Racemic 2,2'-bisacetyl-9,9'-spirobifluorene (*rac*-**2**)[S6]

rac-**2** was prepared according to a protocol published earlier by us.[S6]



rac-**2**

$C_{29}H_{20}O_2$

400.48 g mol^{-1}

Aluminium trichloride (2.53 g, 19.0 mmol, 3.00 eq.) was dissolved in nitromethane (6.0 mL) in a *Schlenk*-flask under argon atmosphere and the solution was cooled to 0 °C. Acetyl chloride (1.42 mL, 18.9 mmol, 3.00 eq.) was added using a syringe, taking care not to exceed a temperature of 0 °C. A solution of 9,9´-spirobifluorene (**1**, 2.00 g, 6.23 mmol, 1.00 eq.) in dichloromethane (6.0 mL) was added over a time period of 15 minutes. The reaction mixture was stirred at 0 °C for one hour and for an additional twelve hours at room temperature. Afterwards the solution was added to ice and hydrochloric acid (1.0 mol L^{-1}), the phases were separated, and the aqueous phase was extracted with dichloromethane (three times). The combined organic phases were washed with aqueous hydrochloric acid (1.0 mol L^{-1}), a saturated solution of sodium bicarbonate and water (once each) and dried with magnesium sulfate. After removal of the solvent under reduced pressure, the crude product was dissolved in a small amount of dichloromethane and precipitated by addition of an excess of cyclohexane to give *rac*-**2** (2.40 g, 96%) as a colorless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.02 (dd, H-3, $^3J_{3,4}$ = 8.0 Hz, $^4J_{3,1}$ = 1.4 Hz), 7.93 (d, 2H, H-4, $^3J_{4,3}$ = 8.0 Hz), 7.92 (ddd, 2H, H-5, $^3J_{5,6}$ = 7.5 Hz, $^4J_{5,7}$ = 1.0 Hz, $^5J_{5,8}$ = 0.6 Hz), 7.42 (ddd, 2H, H-7, $^3J_{7,8}$ = 7.7 Hz, $^3J_{7,6}$ = 7.5 Hz, $^4J_{7,5}$ = 1.0 Hz), 7.31 (d, 2H, H-1, $^4J_{1,3}$ = 1.4 Hz), 7.17 (ddd, 2H, H-6, $^3J_{6,7}$ = 7.5 Hz, $^3J_{6,5}$ = 7.5 Hz, $^4J_{6,8}$ = 1.1 Hz), 6.73 (ddd, 2H, H-8, $^3J_{8,7}$ = 7.7 Hz, $^4J_{8,6}$ = 1.1 Hz, $^5J_{8,5}$ = 0.6 Hz), 2.46 (s, 6H, H-15) ppm.

^{13}C-NMR (76 MHz, $CDCl_3$, 298 K): δ = 197.6 (C-14), 149.3 (C-12), 148.5 (C-2), 146.8 (C-11), 140.6 (C-13), 136.9 (C-10), 129.4 (C-6), 129.3 (C-3), 128.4 (C-7), 124.3 (C-8), 123.9 (C-1), 121.3 (C-5), 120.2 (C-4), 65.9 (C-9), 26.8 (C-15) ppm.

MS (EI+): *m/z* = 400.1 $[M]^{+\cdot}$, 385.1 $[M\text{-}CH_3]^+$, 357.1 $[M\text{-}C_2H_3O]^+$.

HR-MS (EI+): *m/z* calculated for $[M]^{+\cdot}$: 400.1458, found: 400.1463.

The analytical data are in accordance with the ones published in the literature.[S3]

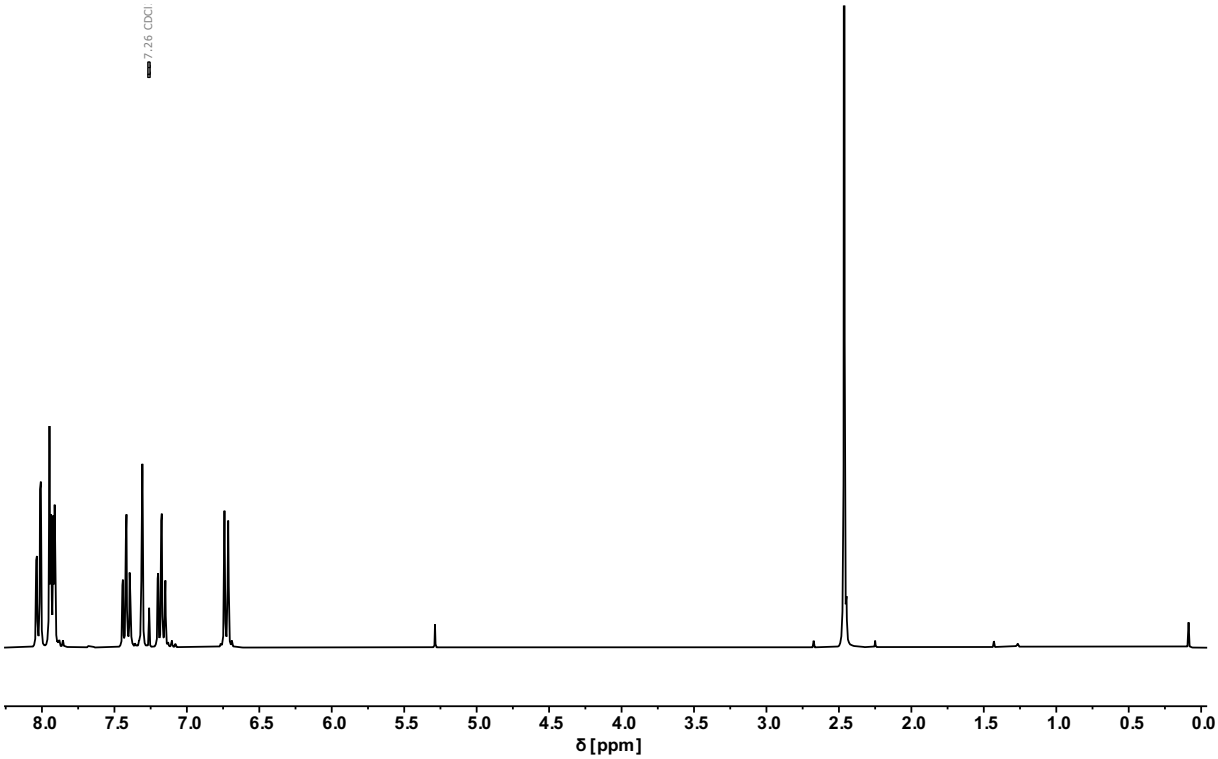


Figure S1. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) spectrum of *rac*-**2**.

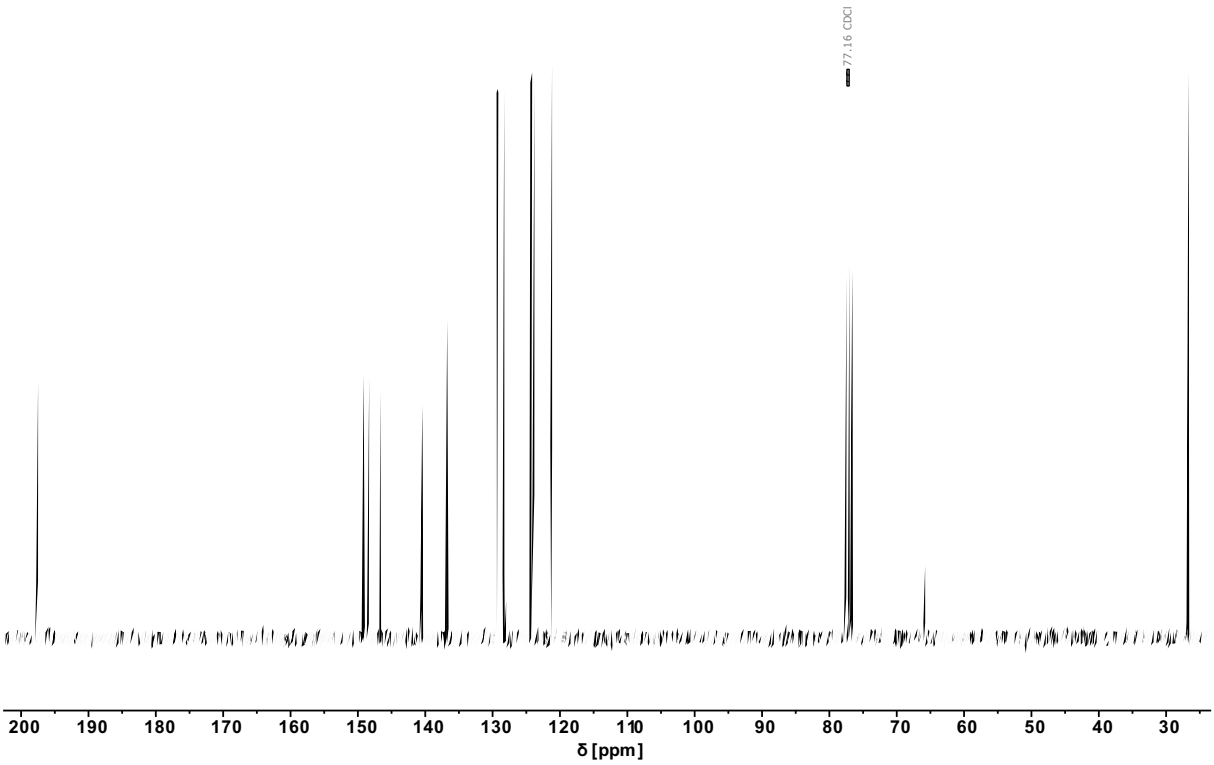
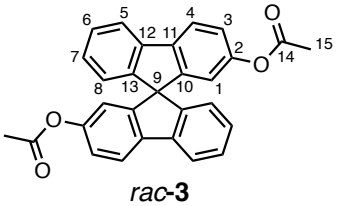


Figure S2. ^{13}C-NMR (76 MHz, $CDCl_3$, 298 K) spectrum of *rac*-**2**.

Racemic 9,9'-spirobifluorene-2,2'-diyl diacetate (*rac*-**3**)[S3,S4]

rac-**3** was prepared according to a protocol of V. Prelog.[S3]



rac-**3**

$C_{29}H_{20}O_4$

432.47 g mol^{-1}

A solution of *rac*-**2** (1.50 g, 3.75 mmol, 1.00 eq.) in dichloromethane (15.0 mL) was added dropwise to a solution of *meta*-chloroperoxybenzoic acid (4.63 g, 18.7 mmol, 5.00 eq.) in dichloromethane (120 mL). The reaction mixture was refluxed for two days while stirring. After the reaction was quenched by the addition of a saturated solution of sodium bicarbonate, the phases were separated, and the organic phase was concentrated under reduced pressure. The residue was dissolved in diethyl ether and the aqueous phase was extracted with diethyl ether (three times). The combined organic phases were washed with water, a saturated solution of sodium thiosulfate and brine (once each). After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (SiO_2, cyclohexane:dichloromethane 1:5) to give *rac*-**3** (1.18 g, 73 %) as an off-white solid.

R_f (cyclohexane/dichloromethane 1:5) = 0.52.

^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.83 (d, 2H, H-4, $^3J_{4,3}$ = 8.2 Hz), 7.80 (ddd, 2H, H-5, $^3J_{5,6}$ = 7.5 Hz, $^4J_{5,7}$ = 0.8 Hz, $^5J_{5,8}$ = 0.5 Hz), 7.37 (ddd, 2H, H-6, $^3J_{6,7}$ = 7.5 Hz, $^3J_{6,5}$ = 7.5 Hz, $^4J_{6,8}$ = 1.0 Hz), 7.15 (dd, 2H, H-3, $^3J_{3,4}$ = 8.2 Hz, $^4J_{3,1}$ = 2.0 Hz), 7.12 (ddd, 2H, H-7, $^3J_{7,8}$ = 7.6 Hz, $^3J_{7,6}$ = 7.5 Hz, $^4J_{7,5}$ = 0.8 Hz), 6.75 (ddd, 2H, H-8, $^3J_{8,7}$ = 7.6 Hz, $^4J_{8,6}$ = 1.0 Hz, $^5J_{8,5}$ = 0.5 Hz), 6.49 (d, 2H, H-1, $^4J_{1,3}$ = 2.0 Hz), 2.16 (s, 6H, H-15) ppm.

^{13}C-NMR (76 MHz, $CDCl_3$, 298 K): δ = 169.3 (C-14), 150.6 (C-2), 149.8 (C-10), 148.5 (C-13), 141.0 (C-12), 139.5 (C-C-11), 128.1 (C-6), 128.0 (C-7), 124.3 (C-8), 121.6 (C-3), 120.6 (C-4), 120.0 (C-5), 117.5 (C-1), 65.9 (C-9), 21.1 (C-15) ppm.

MS (EI+): *m/z* = 432.1 $[M]^{+\cdot}$, 390.1 $[M-CH_2O]^{+\cdot}$, 348.1 $(M-2\times CH_2O]^+$.

HR-MS (EI+): *m/z* calculated for $[M]^{+\cdot}$: 432.1362, found: 432.1365.

The analytical data are in accordance with the ones published in the literature.[S3]

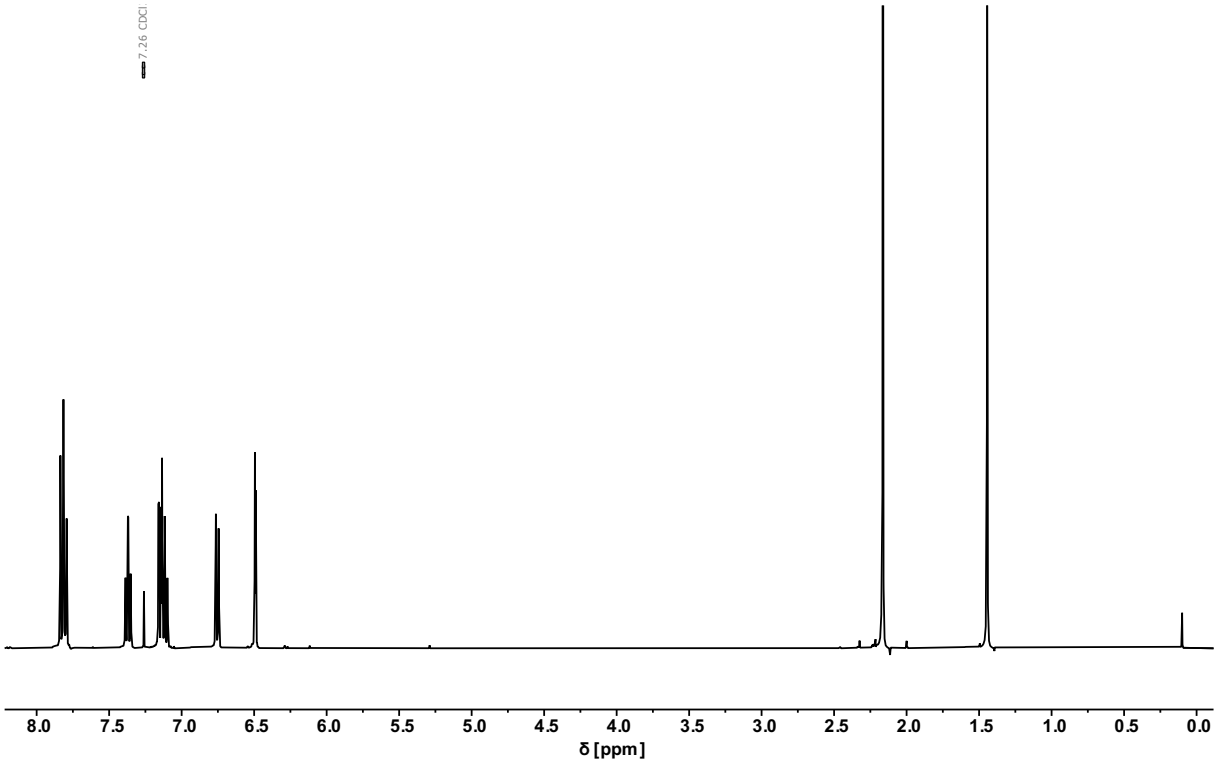


Figure S3. ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *rac*-**3**.

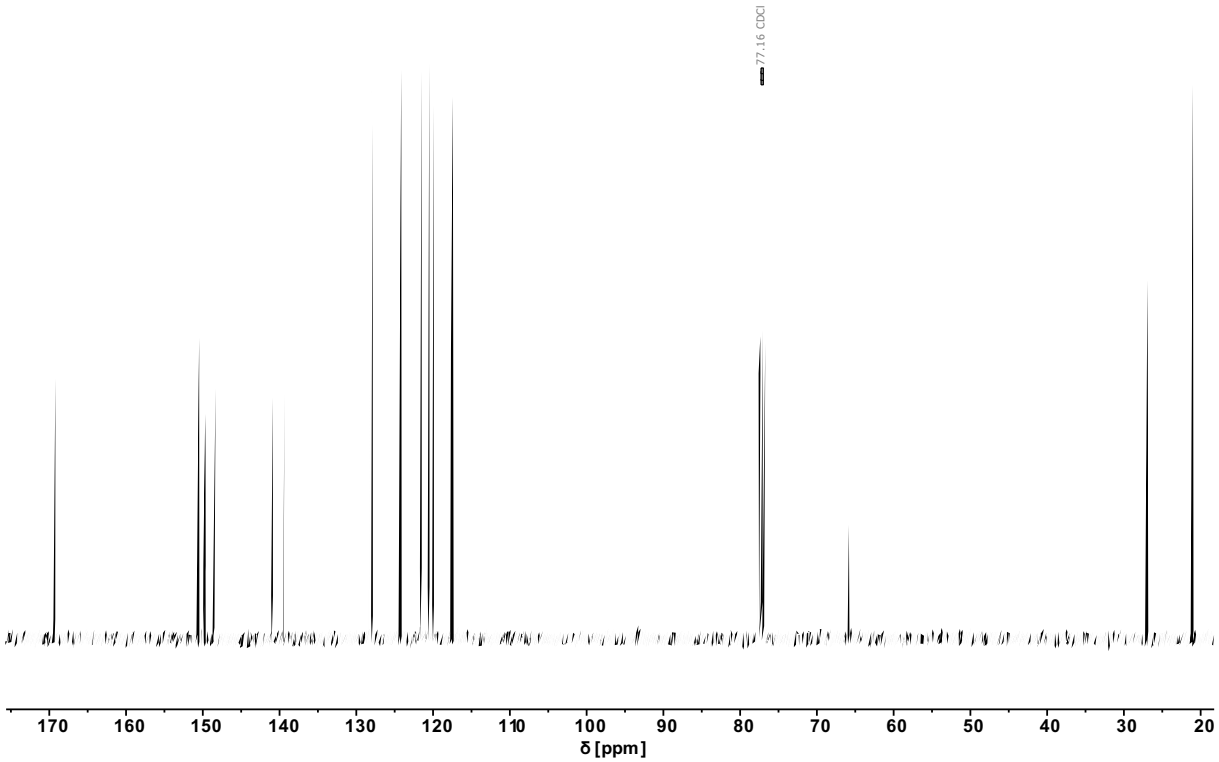
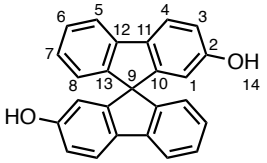


Figure S4. ^{13}C-NMR (125 MHz, $CDCl_3$, 298 K) spectrum of *rac*-**3**.

Racemic 9,9'-spirobifluorene-2,2'-diol (*rac*-**4**)[S3]

rac-**4** was prepared according to a protocol of V. Prelog.[S3]



rac-**4**

$C_{25}H_{16}O_2$

348.40 g mol^{-1}

rac-**3** (3.00 g, 6.94 mmol, 1.00 eq.) was put into a two-necked flask with reflux condenser and a dropping funnel and dissolved in methanol (200 mL). A solution of sodium hydroxide (860 mg, 15.0 mmol, 2.16 eq.) in water (30.0 mL) was added dropwise. After stirring for ten minutes at 50 °C the solution was acidified with hydrochloric acid (2.0 mol L^{-1}). The methanol was removed under reduced pressure and the aqueous phase was extracted with diethyl ether (three times). The combined organic phases were washed with brine (once) and dried with magnesium sulfate. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (SiO_2, cyclohexane:ethyl acetate 2:1) to give *rac*-**4** (2.41 g, 96 %) as a colorless solid.

R_f (cyclohexane/ethyl acetate 2:1) = 0.58.

^{1}H-NMR (700 MHz, acetone-d_6, 298 K): δ = 8.22 (s, 2H, H-14), 7.82 (dd, 2H, H-5, $^3J_{5,6}$ = 7.6 Hz, $^4J_{5,7}$ = 1.1 Hz), 7.78 (d, 2H, H-4, $^3J_{4,3}$ = 8.3 Hz), 7.33 (ddd, 2H, H-6, $^3J_{6,5}$ = 7.6 Hz, $^3J_{6,7}$ = 7.5 Hz, $^4J_{6,8}$ = 1.0 Hz), 7.04 (ddd, 2H, H-7, $^3J_{7,6}$ = 7.5 Hz, $^3J_{7,8}$ = 7.5 Hz, $^4J_{7,5}$ = 1.1 Hz), 6.88 (dd, 2H, H-3, $^3J_{3,4}$ = 8.3 Hz, $^4J_{3,1}$ = 2.3 Hz), 6.64 (dd, 2H, H-8, $^3J_{8,7}$ = 7.5 Hz, $^4J_{8,6}$ = 1.0 Hz), 6.16 (d, 2H, H-1, $^4J_{1,3}$ = 2.3 Hz).

^{13}C-NMR (176 MHz, acetone-d_6, 298 K): δ = 158.6 (C-2), 152.0 (C-10), 149.3 (C-13), 142.9 (C-12), 134.2 (C-11), 128.6 (C-6), 127.1 (C-7), 124.4 (C-7), 121.9 (C-4), 119.9 (C-5), 116.0 (C-3), 111.5 (C-1), 66.6 (C-9) ppm.

MS (EI+): *m/z* = 348.1 $[M]^{+\cdot}$, 331.1 $[M\text{-}OH]^+$.

HR-MS (EI+): *m/z* calculated for $[M]^{+\cdot}$: 348.1145, found: 348.1150.

The analytical data are in accordance with the ones published in the literature.[S3]

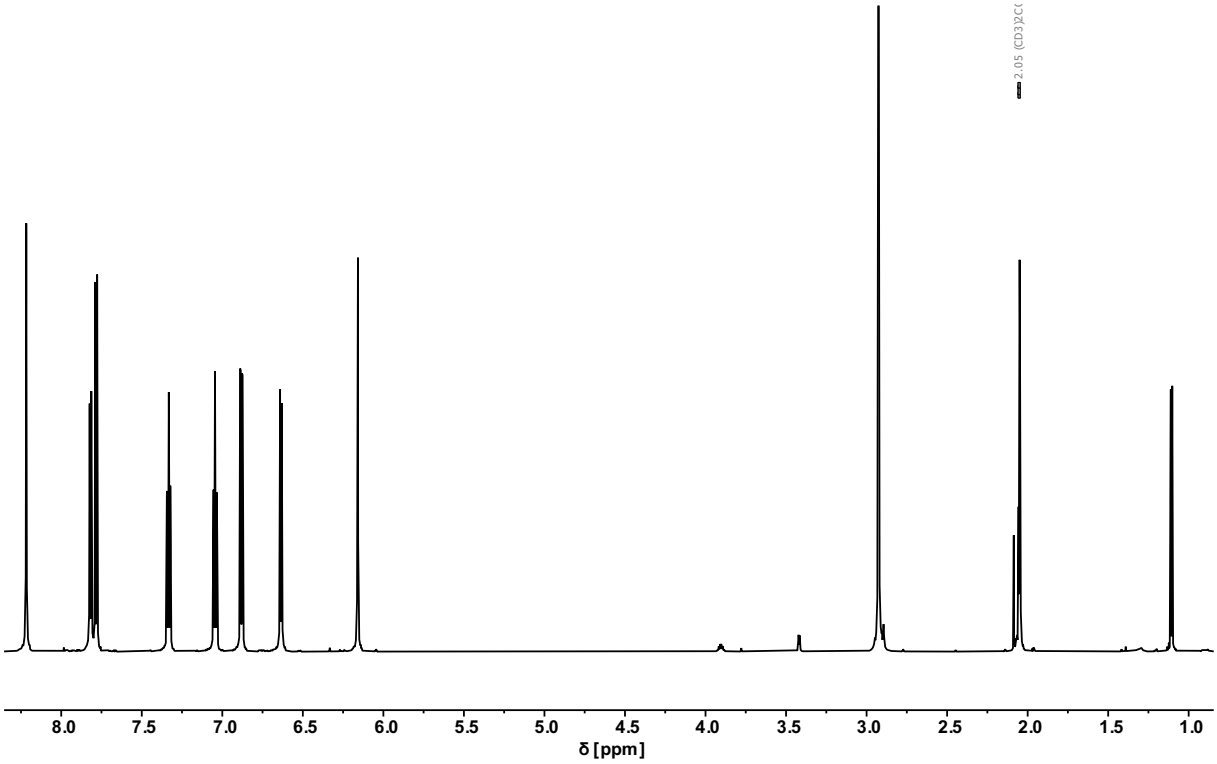


Figure S5. ^{1}H-NMR (700 MHz, acetone-d_6, 298 K) spectrum of *rac*-**4**.

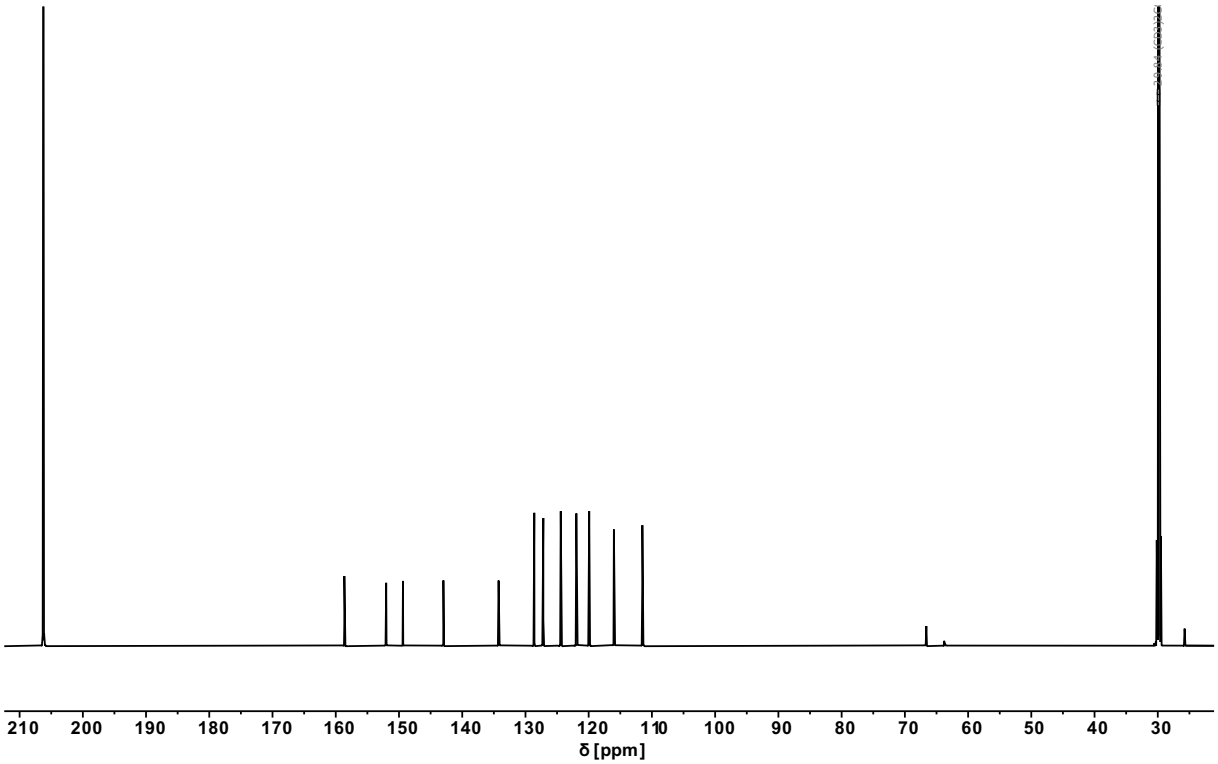


Figure S6. ^{13}C-NMR (176 MHz, acetone-d_6, 298 K) spectrum of *rac*-**4**.

Chiral resolution of racemic 9,9'-spirobifluorene-2,2'-diol (*rac*-**4**)[S6]

Chiral resolution of *rac*-**4** was achieved on a semipreparative scale via HPLC on a Chiralpak IA phase (5 µm, 250 × 10 mm) using $CHCl_3$ /iPrOH (95:5) as eluent according to the procedure published earlier by us.[S6]

Table S1. Chiral resolution of *rac*-**4** on a semipreparative scale.

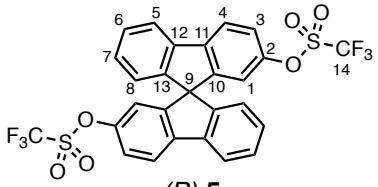
eluent	*flow rate* [mL min^{-1}]	retention time [min]		*ee* [%]	
		t_{R1}	t_{R2}	*(M)*	*(P)*
$CHCl_3$ / iPrOH (95:5)	2.3	8.5	14.6	99.9	99.9

Both enantiomers were received in excellent enantiomerical purity. The second eluting (*P*)-enantiomer of **4** was chosen as the starting material for the synthesis of the enantiomerically pure compounds literature known (*P*)-**5** and (*P*)-**6** as well as new compounds (*P*)-**7**, (*P*)-**B*** and (*P*)-**B*^{Ph}**.

Please note, that our previous studies demonstrate that chiral 9,9'-spirobifluorenes are configurationally very stable under typical transition metal catalyzed cross-coupling conditions or other functional group interconversion operations.[S4, 7-9]

(*P*)-9,9'-Spirobifluorene-2,2'-diyl bis(trifluoromethanesulfonate ((*P*)-**5**)[S4]

(*P*)-**5** was prepared according to a protocol published earlier by us.[S4]



(P)-**5**

$C_{27}H_{14}F_6O_6S_2$

612.51 g mol^{-1}

(P)-**4** (644 mg, 1.85 mmol, 1.00 eq.) and triethyl amine (1.3 mL, 9.24 mmol, 5.00 eq.) were dissolved in dichloromethane (120 mL) and cooled to −78 °C. At this temperature trifluoromethanesulfonic anhydride (1.5 mL, 9.24 mmol, 5.00 eq.) was added while stirring and the reaction mixture was allowed to reach room temperature. Hydrochloric acid (2.0 mol L^{-1}) was added, the phases were separated, and the aqueous phase was extracted with dichloromethane. The combined organic phases were washed with a saturated aqueous solution of sodium bicarbonate and brine (once each) and dried with magnesium sulfate. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (SiO_2, cyclohexane:ethyl acetate 5:1). The solid obtained was crystallized from cyclohexane to give *(P)*-**5** (844 mg, 74 %) as white crystals.

R_f (cyclohexane/ethyl acetate 5:1) = 0.28.

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.93 (d, 2H, H-4, $^3J_{4,3}$ = 8.4 Hz), 7.90-7.86 (m, 2H, H-5), 7.48-7.43 (m, 2H, H-6), 7.35 (dd, 2H, H-3, $^3J_{3,4}$ = 8.4 Hz, $^4J_{3,1}$ = 2.3 Hz), 7.24-7.18 (m, 2H, H-7), 6.78-6.74 (m, 2H, H-8), 6.62 (d, 2H, H-1, $^4J_{1,4}$ = 2.3 Hz) ppm.

^{13}C-NMR (176 MHz, acetone-d_6, 298 K): δ = 149.9 (C-12), 149.2 (C-10), 147.9 (C-13), 142.1 (C-11), 139.9 (C-2), 129.1 (C-7), 128.8 (C-6), 124.2 (C-8), 121.7 (C-3), 121.6 (C-4), 120.9 (C-5), 117.4 (C-1), 66.0 (C-9) ppm.

MS (CI+, isobutane): *m/z* = 613.3 $[M+H]^+$.

HR-MS (CI+, isobutane): *m/z* calculated for $[M]^{+\cdot}$: 613.0214, found: 613.0195.

The analytical data are in accordance with the ones published in the literature.[S4]

rac-**5** was prepared from *rac*-**4** following the same protocol.

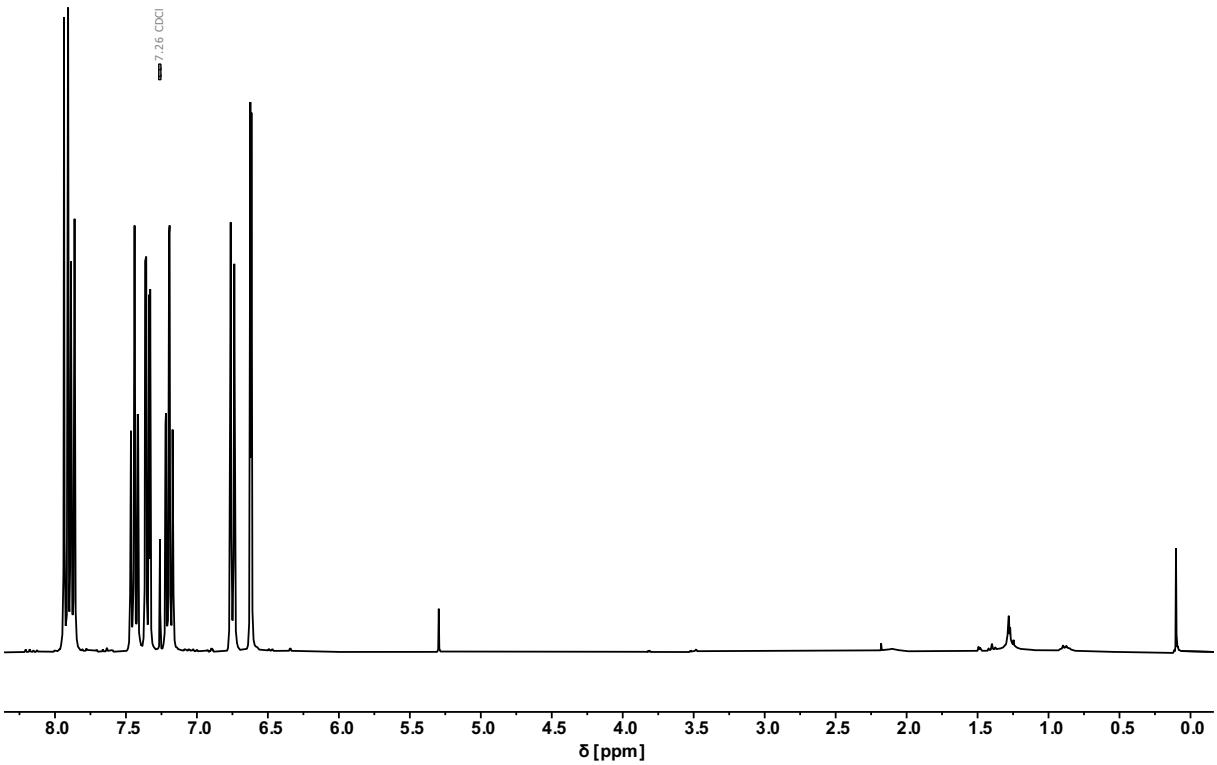


Figure S7. ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K) spectrum of *(P)*-**5**.

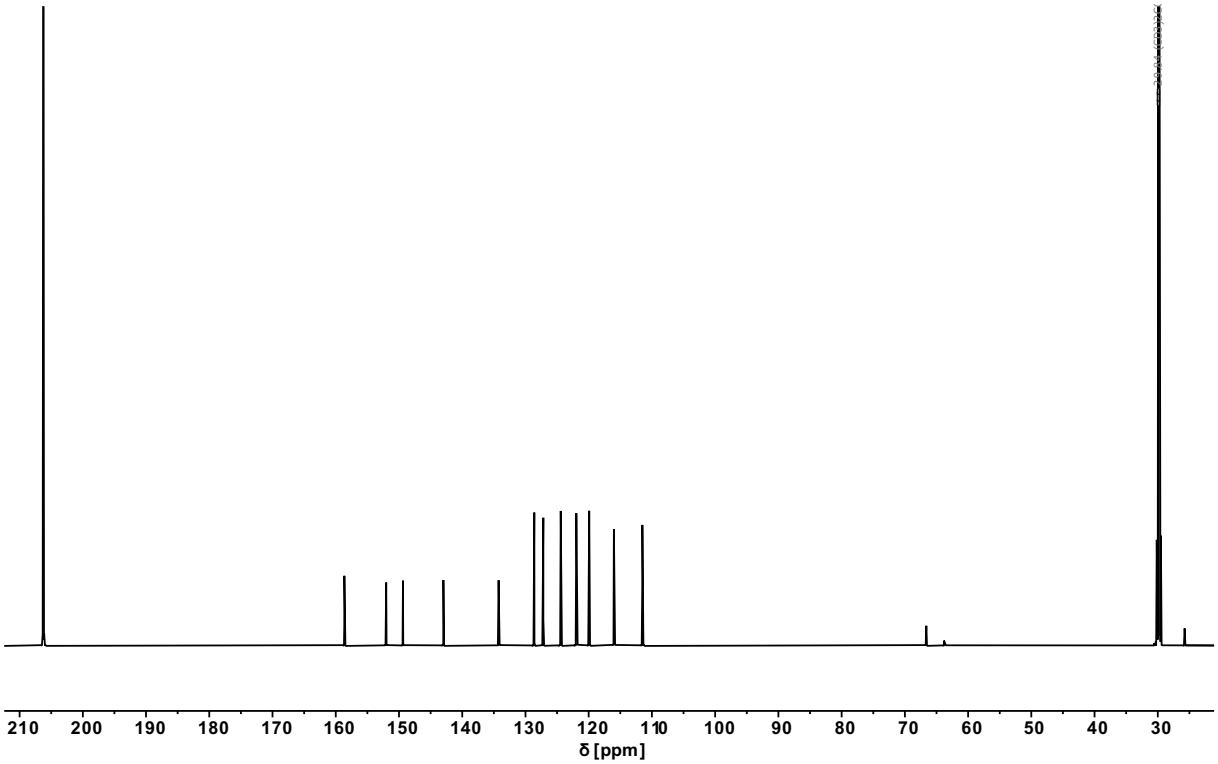
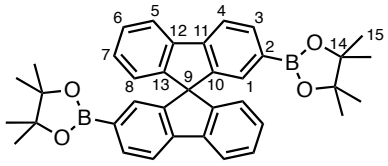


Figure S8. ^{13}C-NMR (125 MHz, $CDCl_3$, 298 K) spectrum of *(P)*-**5**.

protected short linker (*P*)-**6**[S4]

(*P*)-**6** was prepared according to a protocol published earlier by us.[S4]



(P)-**6**

$C_{37}H_{38}B_2O_4$

568.33 g mol^{-1}

(P)-**5** (500 mg, 0.816 mmol, 1.00 eq.), palladium(II) acetate (9.16 mg, 40.8 µmol, 0.05 eq.), bis(pinacolato)diboron (1.04 g, 4.08 mmol, 5.00 eq.), potassium acetate (481 mg, 4.90 mmol, 6.00 eq.) and dicyclohexyl[2′,4′,6′-tris(propan-2-yl)[1,1′-biphenyl]-2-yl]phosphin (77.8 mg, 0.163 mmol, 0.20 eq.) were put into a *Schlenk*flask under argon atmosphere. Degassed 1,4-dioxane was added and the solution was degassed several times by exchange of the atmosphere. The reaction mixture was refluxed for twelve hours while stirring. After cooling to room temperature, the mixture was filtered through a silica plug and eluted with an excess of ethyl acetate (200 mL). The crude product was purified by column chromatography (SiO_2, cyclohexane:ethyl acetate 9:1) to give protected diboronic acid *(P)*-**6** (459 mg, 99 %) as an off-white solid.

R_f (cyclohexane/ethyl acetate 9:1) = 0.27.

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.91-7.83 (m, 6H, H-3, H-4, H-5), 7.34 (ddd, 2H, H-6, $^3J_{5,6}$ = 7.3 Hz, $^3J_{6,7}$ = 7.3 Hz, $^4J_{6,8}$ = 0.7 Hz), 7.16 (m, 2H, H-1), 7.08 (ddd, 2H, H-7, $^3J_{6,7}$ = 7.3 Hz, $^3J_{7,8}$ = 7.7 Hz, $^4J_{5,7}$ = 0.7 Hz), 6.65 (dd, 2H, H-8, $^4J_{6,8}$ = 0.7 Hz, $^3J_{7,8}$ = 7.7 Hz), 1.26 (s, 24H, H-15) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ = 149.7 (C-13), 147.6 (C-10), 145.2* (C-11), 141.6 (C-12), 134.9 (C-3), 130.6 (C-1), 128.4 (C-7), 127.7 (C-6), 124.2 (C-8), 120.5 (C-5), 119.5 (C-4), 83.8 (C-14), 66.0 (C-9), 25.0 (C-15) (The signal marked with a * could not be assigned by the ^{13}C-NMR but only by HMBC due to a strong peak broadening caused by the carbon-boron coupling) ppm.

MS (ESI+): *m/z* = 586.330 $[M+NH_4]^+$.

HR-MS (CI+, isobutane): *m/z* calculated for $[M+NH_4]^{+\cdot}$: 586.3307, found: 586.3300.

The analytical data are in accordance with the ones published in the literature.[S4]

rac-**6** was prepared from *rac*-**5** following the same protocol.

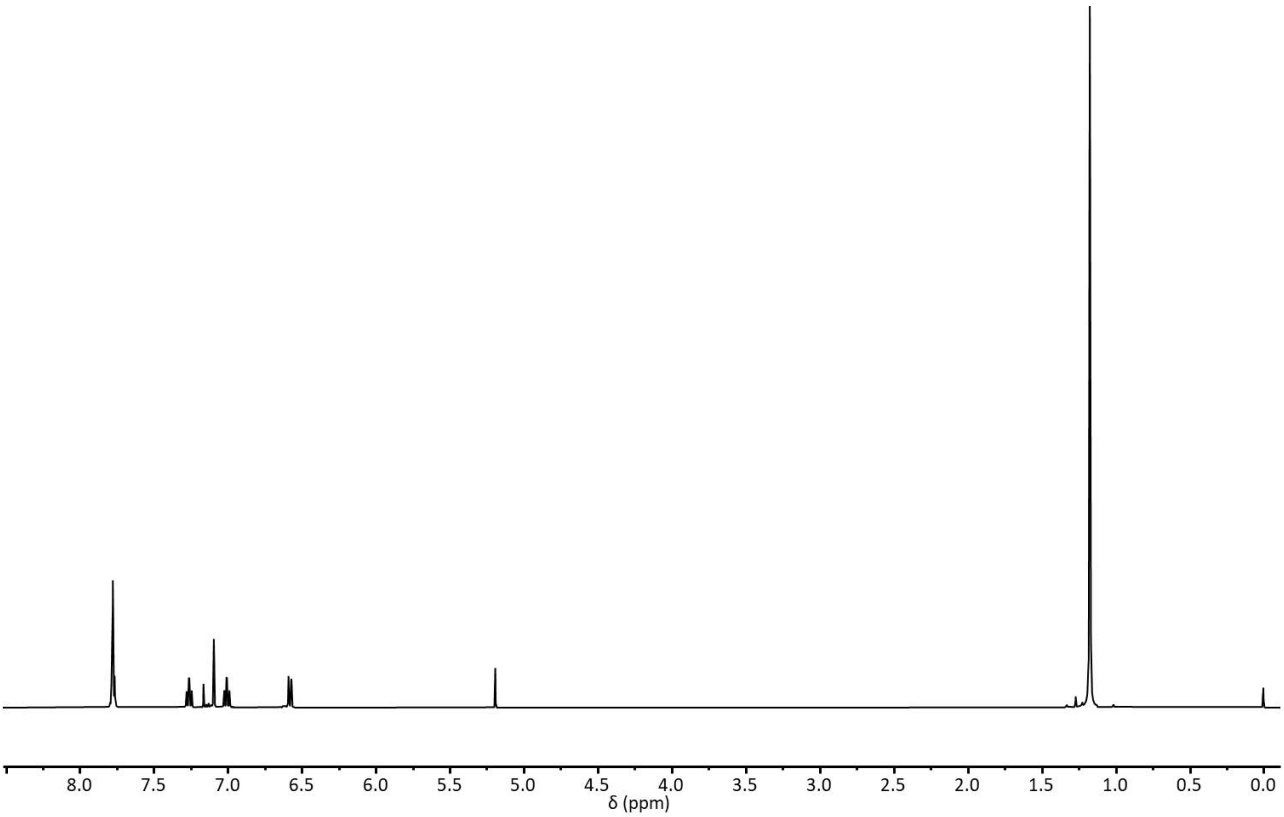


Figure S9. ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K) spectrum of *(P)*-**6**.

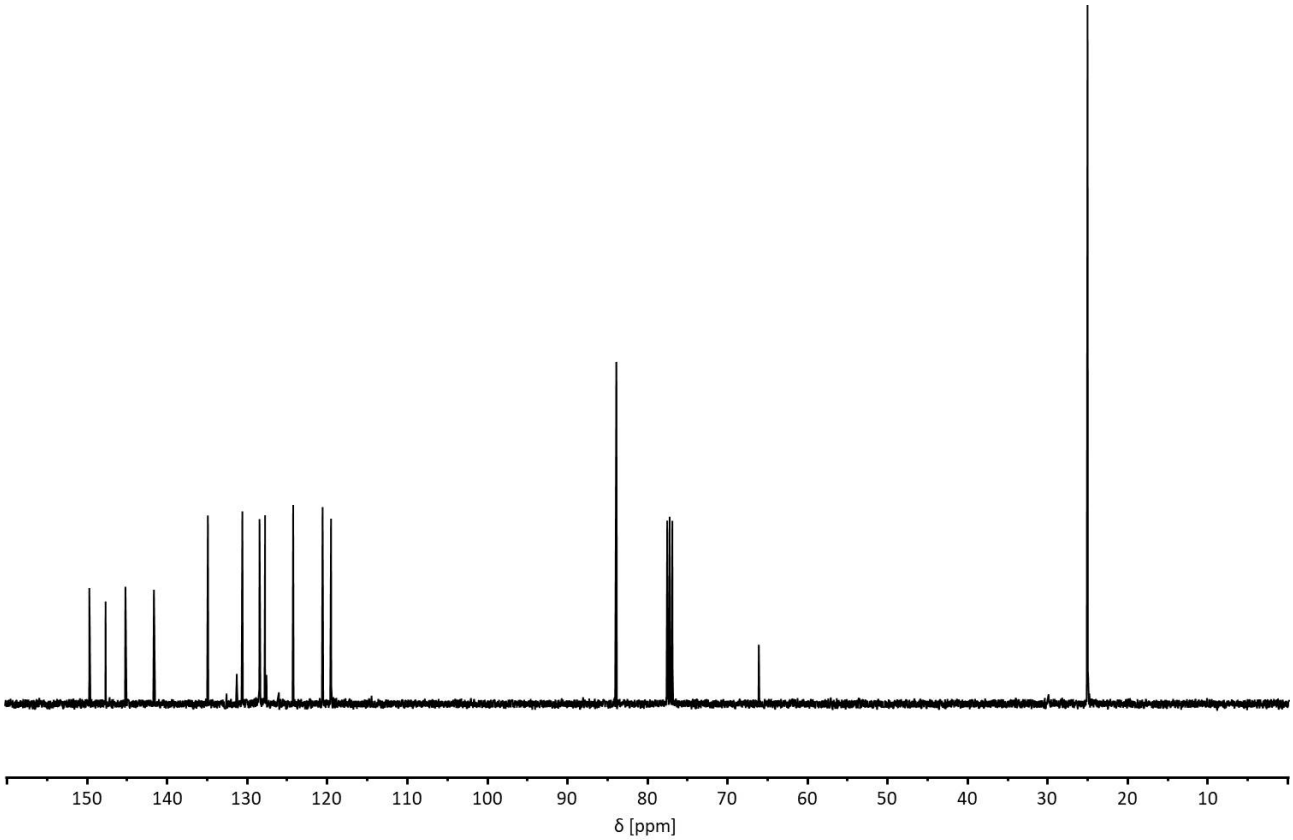
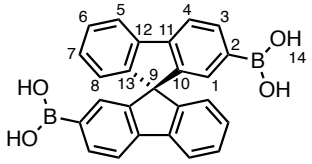


Figure S10. ^{13}C-NMR (125 MHz, $CDCl_3$, 298 K) spectrum of *(P)*-**6**.

short linker *(P)*-**B***



(P)-**B***

$C_{25}H_{18}B_2O_4$

404.03 g mol^{-1}

(P)-**6** (0.150 mg, 0.264 mmol, 1.00 eq.) and methylboronic acid (94.8 mg, 1.58 mmol, 6.00 eq.) were placed into a sealable vial. Trifluoroacetic acid (0.018 mL, 5 % v/v in dichloromethane) was added, and the reaction was stirred overnight at ambient conditions. After full conversion was confirmed by TLC analysis, all volatile components were removed under reduced pressure. The residue was dissolved in hydrochloric acid (2.6 mL, 0.1 mol L^{-1}) and the solvent was again removed. Thereafter, the crude product was purified by column chromatography (SiO_2, cyclohexane:acetone 2:1 +2 % v/v MeOH) to give *(P)*-**B*** (82 mg, 72 %) as a colorless powder.

R_f (cyclohexane/acetone 9:1 + 2% v/v MeOH) = 0.43.

^{1}H-NMR (500 MHz, acetone-d_6 + 3% v/v D_2O, 298 K): δ = 8.00 (ddd, 2H, H-5, $^3J_{5,6}$ = 7.7 Hz, $^4J_{5,7}$ = 1.0 Hz, $^5J_{5,8}$ = 0.7 Hz), 7.95 (dd, 2H, H-4, $^5J_{1,4}$ = 0.8 Hz, $^3J_{3,4}$ = 7.6 Hz), 7.93 (dd, 2H, H-3, $^4J_{1,3}$ = 1.1 Hz, $^3J_{3,4}$ = 7.6 Hz), 7.40 (ddd, 2H, H-6, $^3J_{5,6}$ = 7.7 Hz, $^3J_{6,7}$ = 7.5 Hz, $^4J_{6,8}$ = 1.0 Hz), 7.20 (dd, 2H, H-1, $^4J_{1,3}$ = 1.1 Hz, $^5J_{1,4}$ = 0.8 Hz), 7.15 (ddd, 2H, H-7, $^4J_{5,7}$ = 1.0 Hz, $^3J_{6,7}$ = 7.5 Hz, $^3J_{7,8}$ = 7.6 Hz), 7.05 (s, 4H, H-14), 6.64 (ddd, 2H, H-8, $^5J_{5,8}$ = 0.7 Hz, $^4J_{6,8}$ = 1.0 Hz, $^3J_{7,8}$ = 7.6 Hz) ppm.

^{13}C-NMR (126 MHz, acetone-d_6 + 3% v/v D_2O, 298 K): δ = 150.4 (C-13), 148.9 (C-10), 144.8 (C-11), 142.7 (C-12), 134.9 (C-3), 134.2* (C-2), 130.4 (C-1), 129.0 (C-7), 128.7 (C-6), 124.6 (C-8), 121.4 (C-5), 120.2 (C-4), 66.8 (C-9). (The signal marked with a * could not be assigned by the ^{13}C-NMR but only by HMBC due to a strong peak broadening caused by the carbon-boron coupling) ppm.

MS (ESI−): *m/z* = 517.125 $[M+F_3CCO_2]^-$, 466.127 $[M+NO_3]^-$, 439.109 $[M+Cl]^-$, 403.132 $[M-H]^-$.

HR-MS (ESI−, isobutane): *m/z* calculated for $[M-H]^-$: 403.1327, found: 403.1323.

rac-**B*** was prepared from *rac*-**6** following the same protocol. The NMR data of *rac*-**B*** are in accordance with those of (*P*)-**B*** (see also Figure S41).

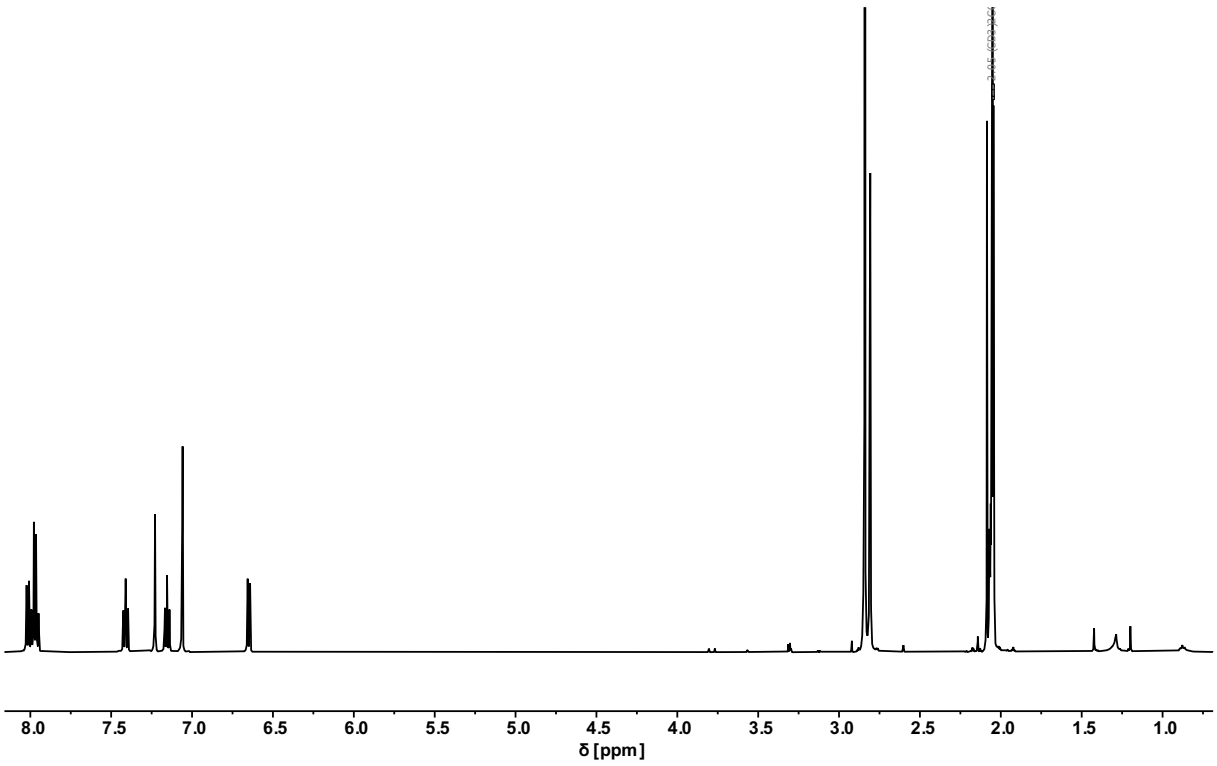


Figure S11. ^{1}H-NMR (500 MHz, acetone-d_6, 298 K) spectrum of short linker *(P)*-**B***.

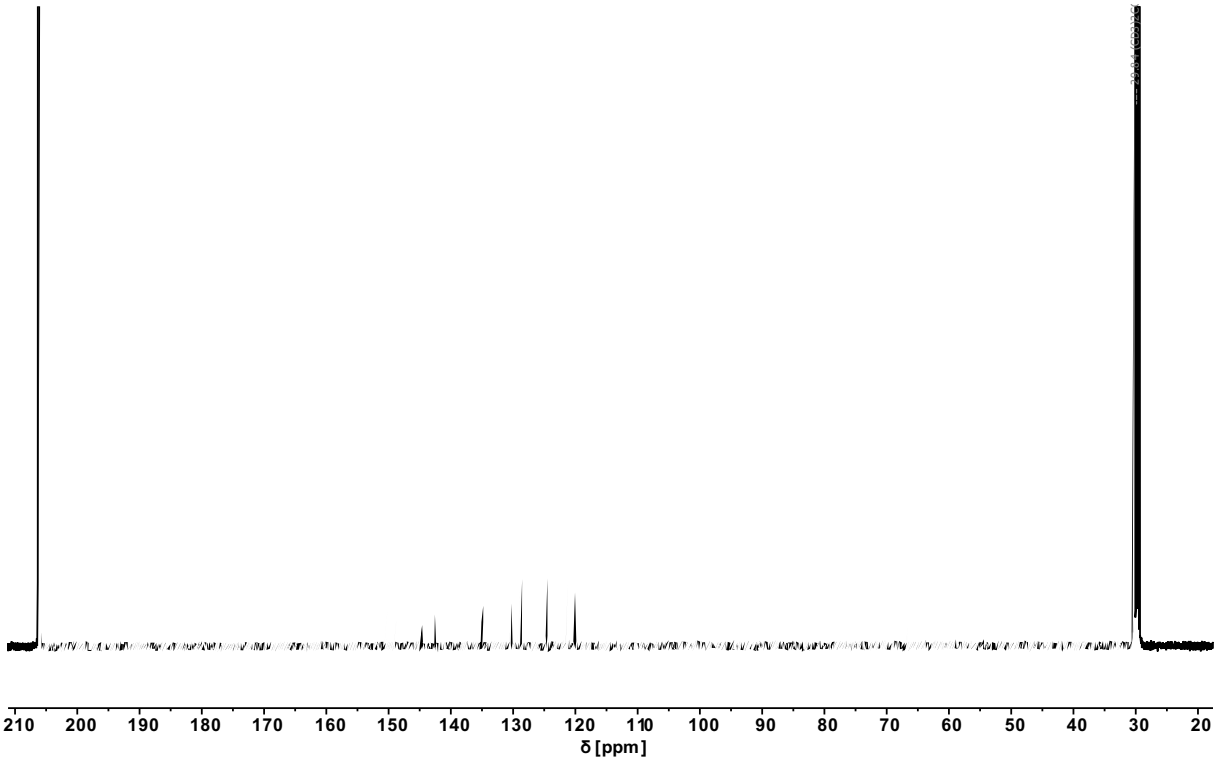


Figure S12. ^{13}C-NMR (125 MHz, acetone-d_6, 298 K) spectrum of short linker *(P)*-**B***.

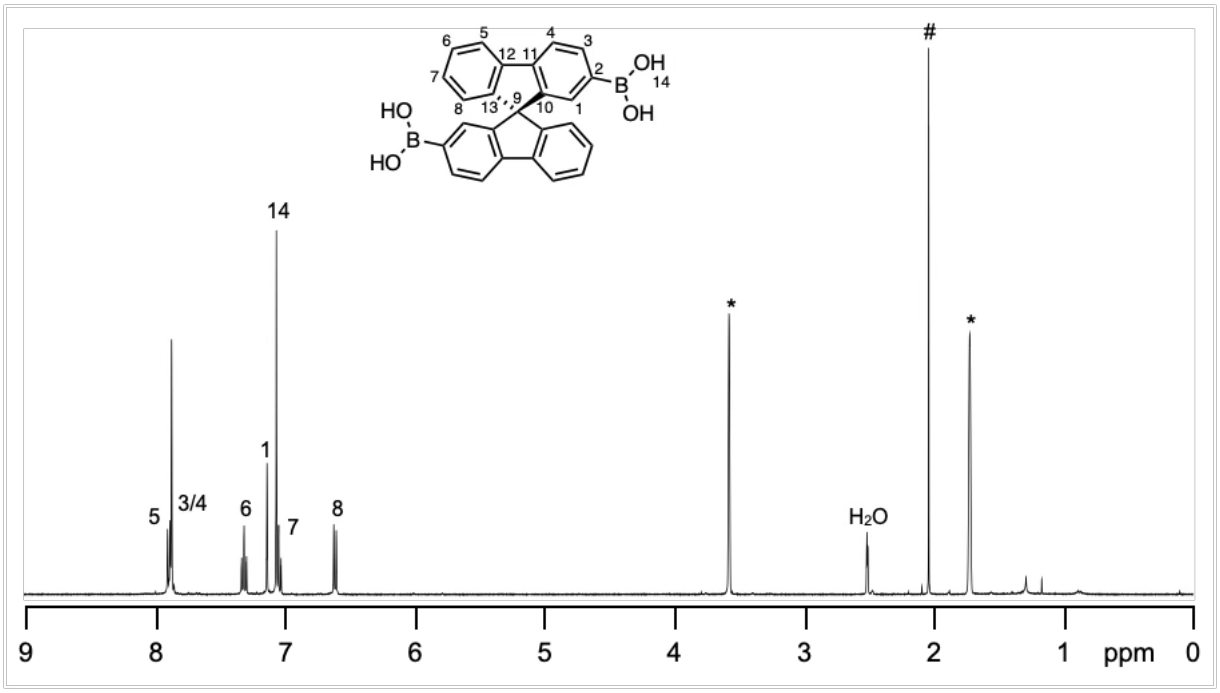


Figure S13. ^{1}H-NMR (400 MHz, THF-d_8, 298 K) spectrum of *(P)*-**B*** (* THF, # acetone).

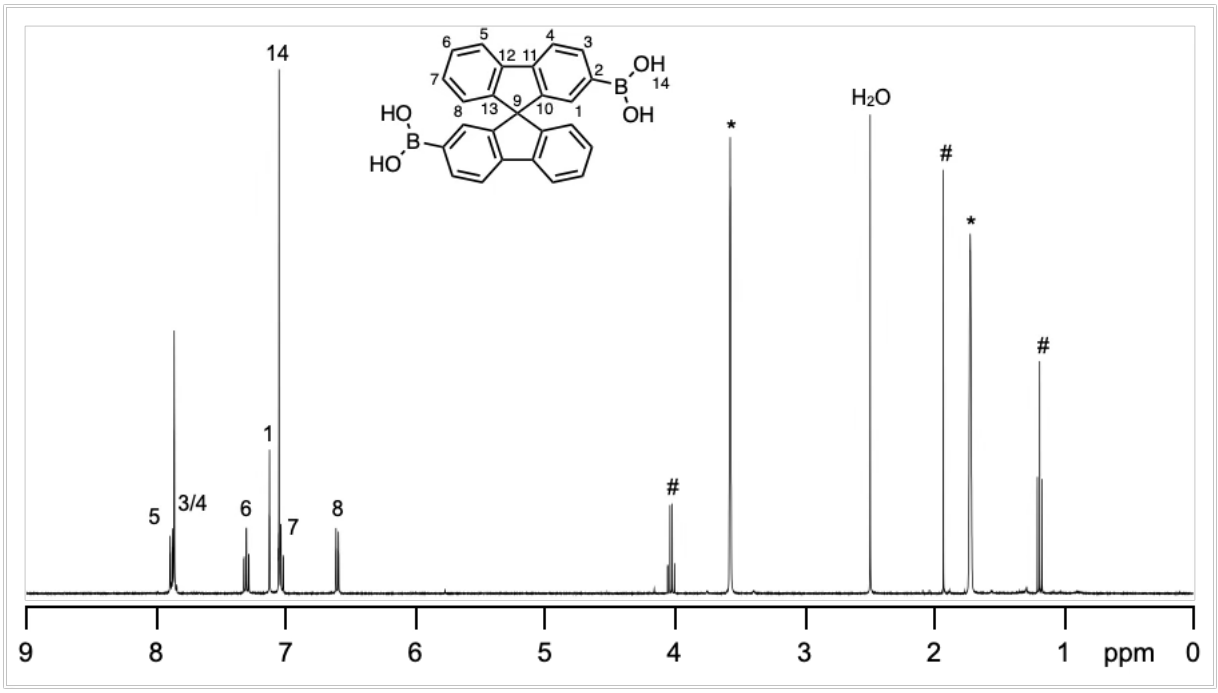


Figure S14. ^{1}H-NMR (400 MHz, THF-d_8, 298 K) spectrum of *rac*-**B*** (* THF, # EtOAc).

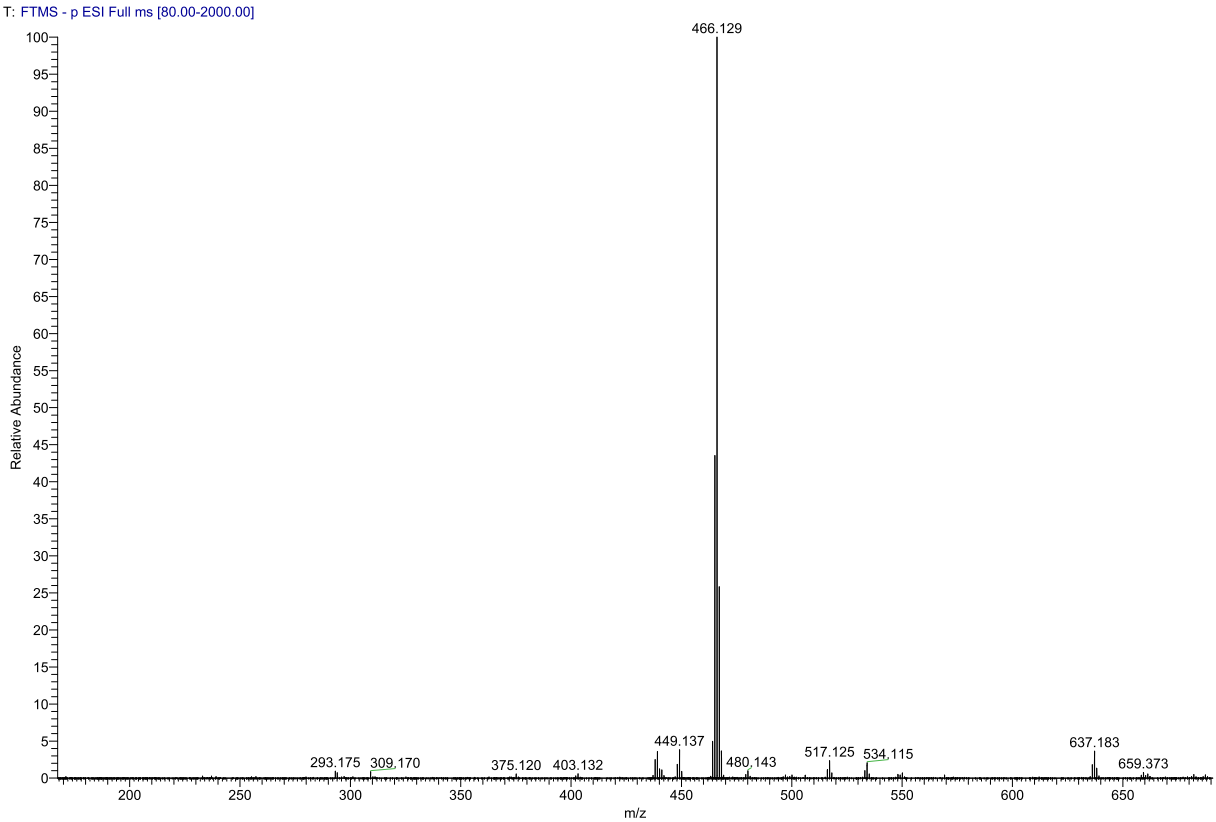
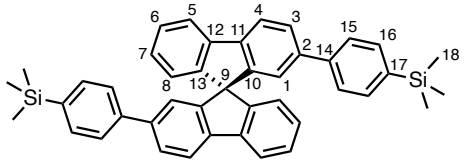


Figure S15. ESI(−) MS spectrum of short linker *(P)*-**B***.

protected elongated linker *(P)*-**7**



(P)-**7**

$C_{43}H_{40}Si_2$

612.96 g mol^{-1}

4-(Trimethylsilyl)phenylboronic acid (219 mg, 1.13 mmol, 2.30 eq.), palladium(II) acetate (5.50 mg, 24.5 µmol, 0.05 eq.), *(P)*-**5** (200 mg, 0.327 mmol, 1.00 eq.), dicyclohexyl(2′,6′-dimethoxy[1,1′-biphenyl]-2-yl)phosphin (19.2 mg, 49.0 µmol, 0.10 eq.) and potassium phosphate (624 mg, 2.94 mmol, 6.00 eq.) were put into a two-necked flask equipped with a reflux apparatus under argon atmosphere. A degassed solvent mixture (1,4-dioxane:water 5:1, 4 mL) was added and the reaction mixture was degassed several times by change of the atmosphere and then heated to reflux overnight while stirring. After cooling to room temperature, the mixture was filtered through a silica plug and eluted with an excess of ethyl acetate (100 mL). The crude product was purified by column chromatography (SiO_2, cyclohexane:dichloromethane 9:1) to give *(P)*-**7** (270 mg, 93 %) as a white foam.

R_f (cyclohexane/dichloromethane 9:1) = 0.27.

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.90 (dd, 2H, H-4, $^3J_{4,3}$ = 7.9 Hz, $^5J_{1,4}$ = 0.7 Hz), 7.88-7.87 (m, 2H, H-5), 7.62 (dd, 2H, H-3, $^3J_{3,4}$ = 7.9 Hz, $^4J_{1,3}$ = 1.7 Hz), 7.46 (m, 4H, H-16), 7.41 (m, 4H, H-15), 7.37 (ddd, 2H, H-6, $^3J_{5,6}$ = 7.5 Hz, $^3J_{6,7}$ = 7.4 Hz, $^4J_{6,8}$ = 1.1 Hz), 7.11 (ddd, 2H, H-7, $^4J_{5,7}$ = 1.1 Hz, $^3J_{6,7}$ = 7.4 Hz, $^3J_{7,8}$ = 7.5 Hz), 6.95 (dd, 2H, H-1, $^4J_{1,3}$ = 1.7 Hz, $^5J_{1,4}$ = 0.7 Hz), 6.78 (ddd, 2H, H-8, $^5J_{5,8}$ = 0.7 Hz, $^4J_{6,8}$ = 1.1 Hz, $^3J_{6,7}$ = 7.5 Hz), 0.22 (s, 18H, H-18) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ = 149.6 (C-10), 149.1 (C-13), 141.6 (C-12 or C-14), 141.5 (C-12 or C-14), 141.2 (C-11), 141.0 (C-2), 139.2 (C-17), 133.8 (C-16), 128.0 (C-6), 127.9 (C-7), 127.0 (C-3), 126.6 (C-15), 123.1 (C-1), 124.3 (C-8), 120.4 (C-4), 120.2 (C-5), 66.2 (C-9), -1.01 (C-18). (Signals of the carbon atoms C-12 and C-14 could not be definitely assigned) ppm.

MS (EI+): *m/z* = 612.2 $[M]^{+\cdot}$, 597.2 $[M-CH_3]^+$, 540.2 $[M-Si(CH_3)_3]^+$, 464.1 $[M-C_6H_4Si(CH_3)_3]^+$, 449.1 $[M-C_6H_4Si(CH_3)_3-CH_3]^+$, 291.1 $[M-2\times CH_3]^{2+}$.

HR-MS (EI+): *m/z* calculated for $[M+NH_4]^{+\cdot}$: 612.2663, found: 612.2663.

rac-**7** was prepared from *rac*-**5** following the same protocol. The NMR data of *rac*-**7** are in accordance with those of (*P*)-**7** (see also Figures S14 and S17).

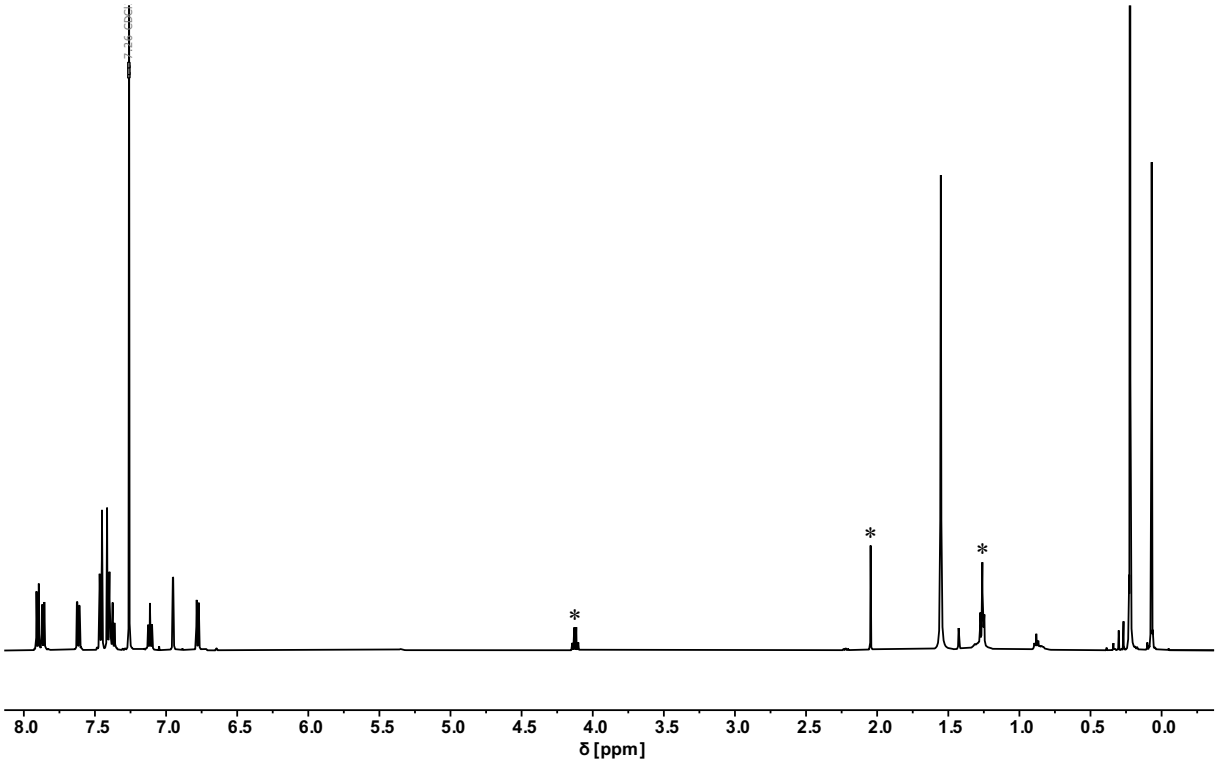


Figure S16. ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K) spectrum of *(P)*-**7** (* EtOAc).

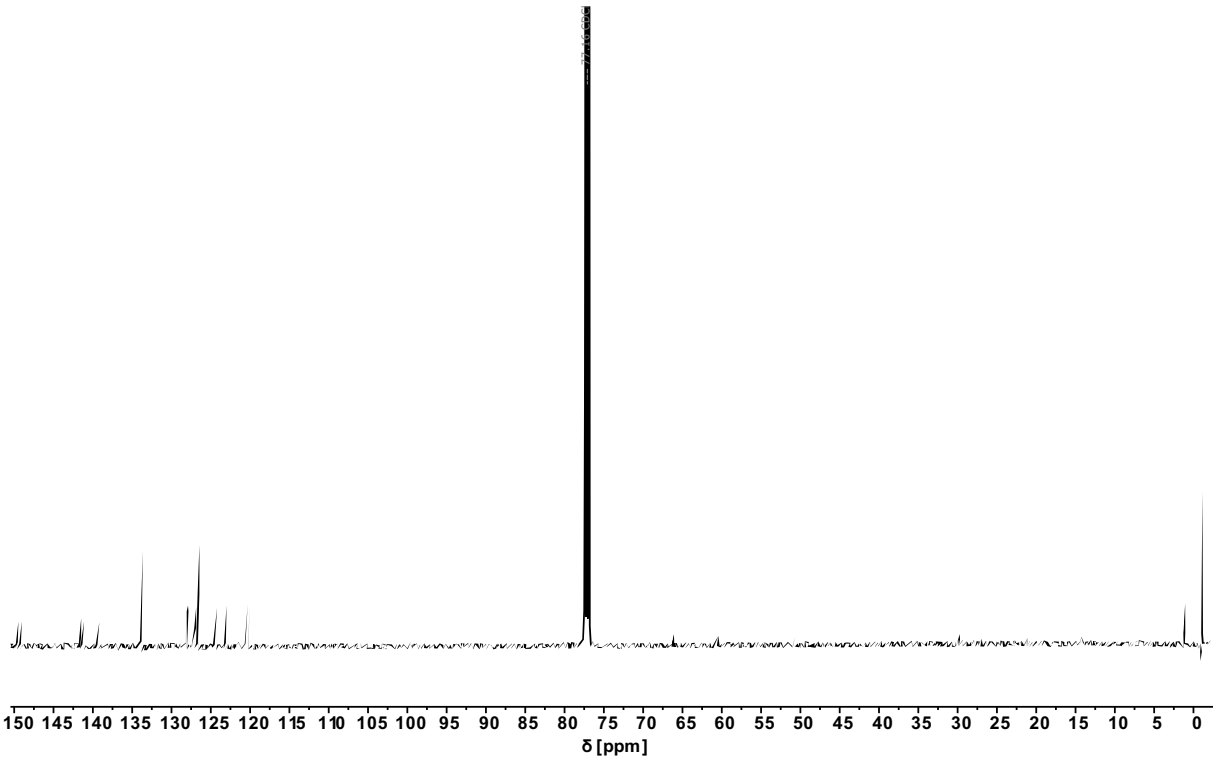


Figure S17. ^{13}C-NMR (125 MHz, $CDCl_3$, 298 K) spectrum of *(P)*-**7**.

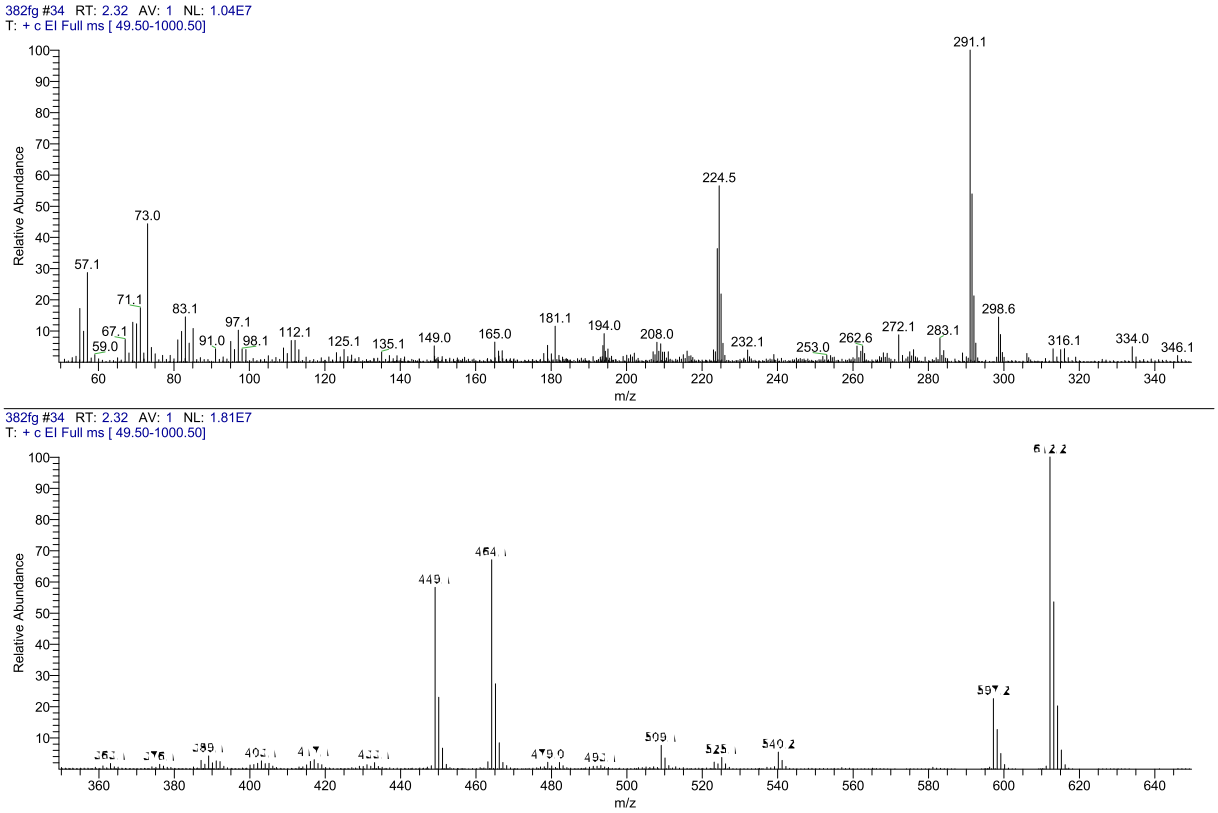


Figure S18. EI-MS spectrum of *(P)*-**7**.

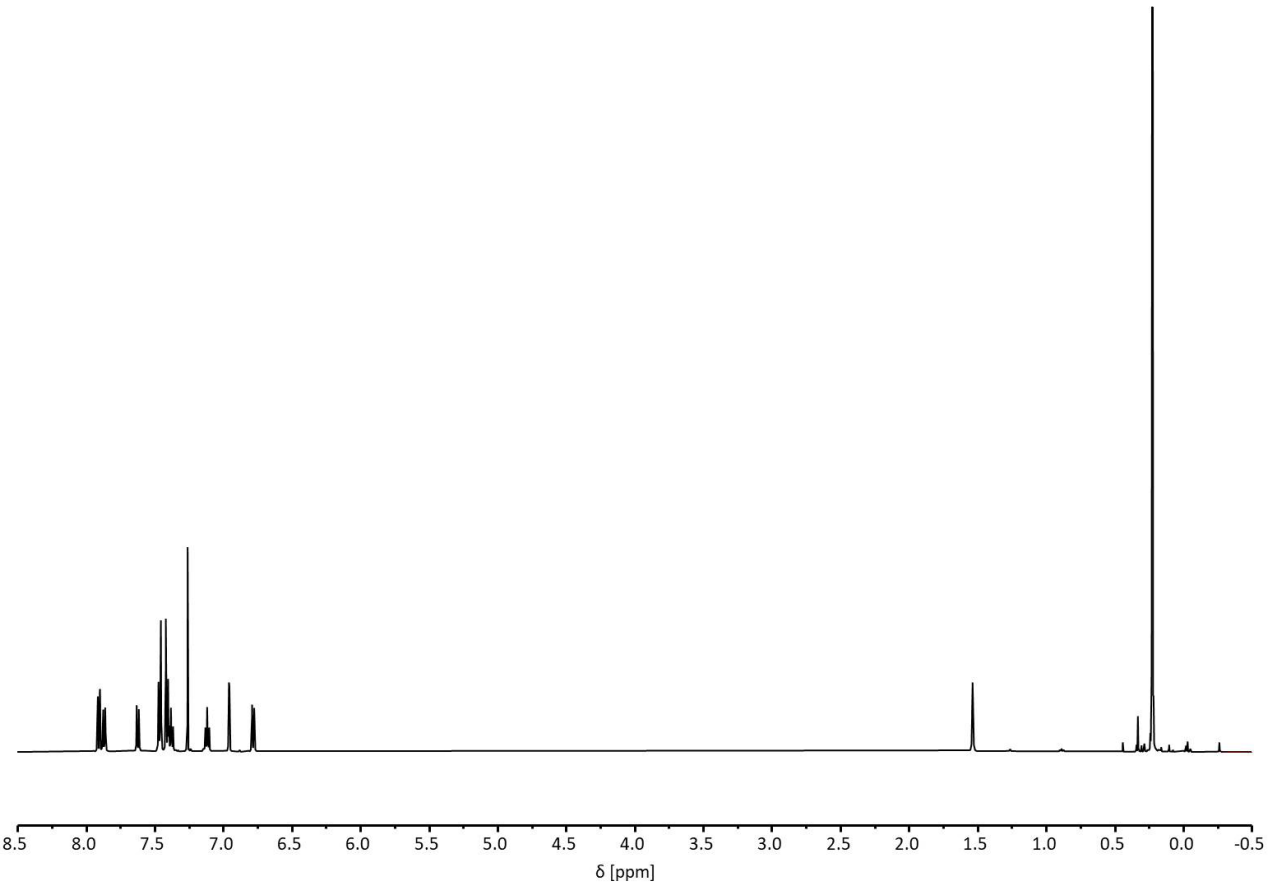
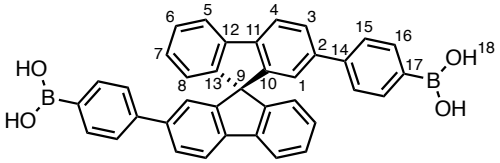


Figure S19. ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K) spectrum of *rac*-**7**.

elongated linker *(P)*-**B*^{Ph}**



(P)-**B*^{Ph}**

$C_{37}H_{26}B_2O_4$

556.23 g mol^{-1}

(P)-**7** (143 mg, 0.233 mmol, 1.00 eq.) was put into an oven-dried Schlenk flask under argon atmosphere. Boron tribromide (0.8 mL, 0.776 mmol, 3.33 eq., 1.0 mol/L in dichloromethane) was added and the mixture was stirred for two hours at room temperature. Afterwards solvent and excess boron tribromide was removed by high vacuum and the residue was dissolved in dichloromethane (1.0 mL). While stirring water was slowly added. The resulting suspension was filtered, washed with water and the residue was purified by column chromatography (SiO_2, cyclohexane/acetone 2:1 + 2% v/v MeOH) to give *(P)*-**B*^{Ph}** (128 mg, 98 %) as a white powder.

R_f (cyclohexane/acetone 2:1 + 2% v/v MeOH) = 0.12.

^{1}H-NMR (500 MHz, acetone-d_6 + 3% v/v D_2O, 298 K): δ = 8.12 (dd, 2H, H-4, $^3J_{4,3}$ = 7.9 Hz, $^5J_{4,1}$ = 0.7 Hz), 8.08-8.03 (m, 2H, H-5), 7.84-7.80 (m, 4H, H-16), 7.78 (dd, 2H, H-3, $^3J_{3,4}$ = 7.9 Hz, $^4J_{3,1}$ = 1.7 Hz), 7.48-7.40 (m, 3H, H-6, H-15), 7.22-7.15 (m, 2H, H-7), 7.02 (dd, 2H, H-1, $^4J_{1,3}$ = 1.7 Hz, $^5J_{1,4}$ = 0.7 Hz), 6.76-6.70 (m, 2H, H-8) ppm.

^{13}C-NMR (126 MHz, acetone-d_6 + 3% v/v D_2O, 298 K): δ = 150.4 (C-10), 149.8 (C-13), 142.8 (C-14), 142.2 (C-11), 142.1 (C-12), 141.5 (C-2), 135.5 (C-16), 133.4 (C-17), 128.92 (C-6), 128.85 (C-7), 127.8 (C-3), 126.4 (C-15), 122.6 (C-1), 121.7 (C-4), 121.3 (C-5), 66.9 (C-9) (Signals of the carbon atoms C-12 and C-14 could not be definitely assigned. The signal marked with * could not be assigned by the ^{13}C-NMR but only by HMBC due to a strong peak broadening caused by the carbon-boron coupling) ppm.

MS (ESI−): *m/z* = 618.192 $[M+NO_3]^-$, 590.129 $[M+Cl]^-$.

HR-MS (ES−): *m/z* calculated for $[M-H]^-$: 555.1957, found: 555.1949.

rac-**B*^{Ph}** was prepared from *rac*-**7** following the same protocol. The NMR data of *rac*-**B*^{Ph}** are in accordance with those of (*P*)-**B*^{Ph}** (see also Figure S42).

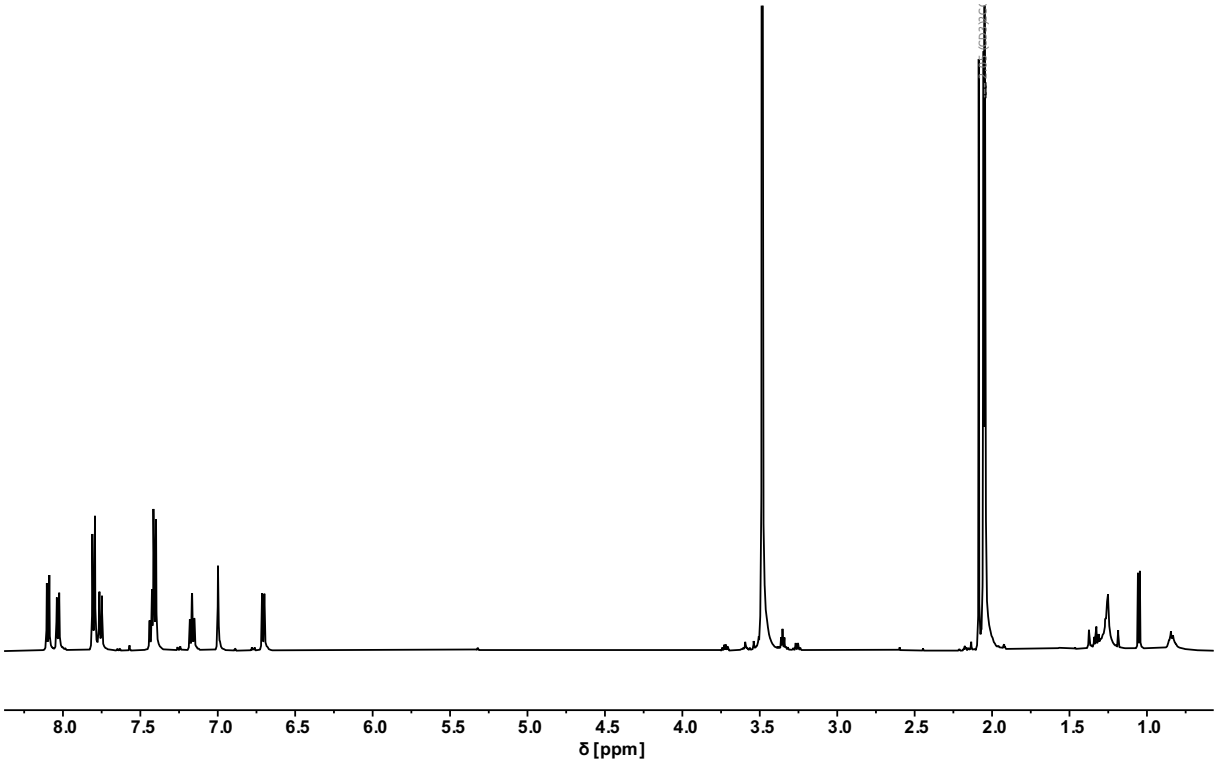


Figure S20. ^{1}H-NMR (500 MHz, acetone-d_6/D_2O (97:3)) spectrum of elongated linker *(P)*-**B*^{Ph}**.

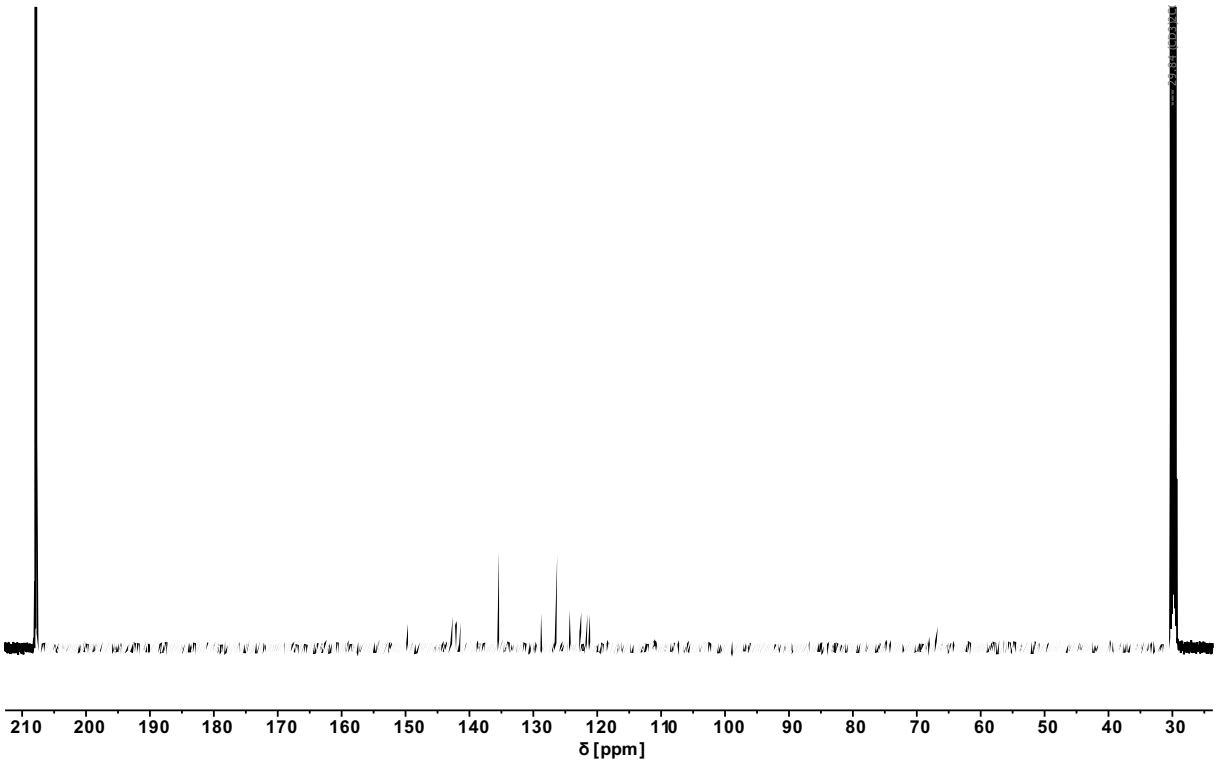


Figure S21. ^{13}C-NMR (125 MHz, acetone-d_6/D_2O (97:3)) spectrum of elongated linker *(P)*-**B*^{Ph}**.

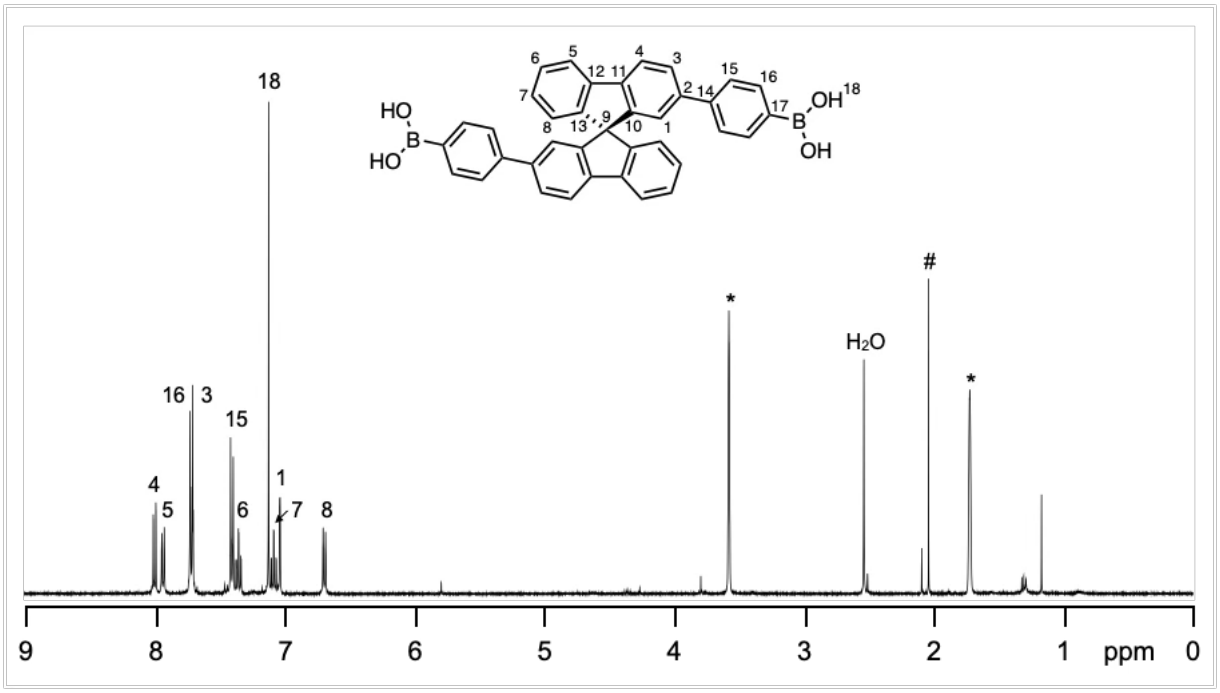


Figure S22. ^{1}H-NMR (400 MHz, THF-d_8, 298 K) spectrum of *(P)*-**B*^{Ph}** (* THF, $^{\#}$ acetone).

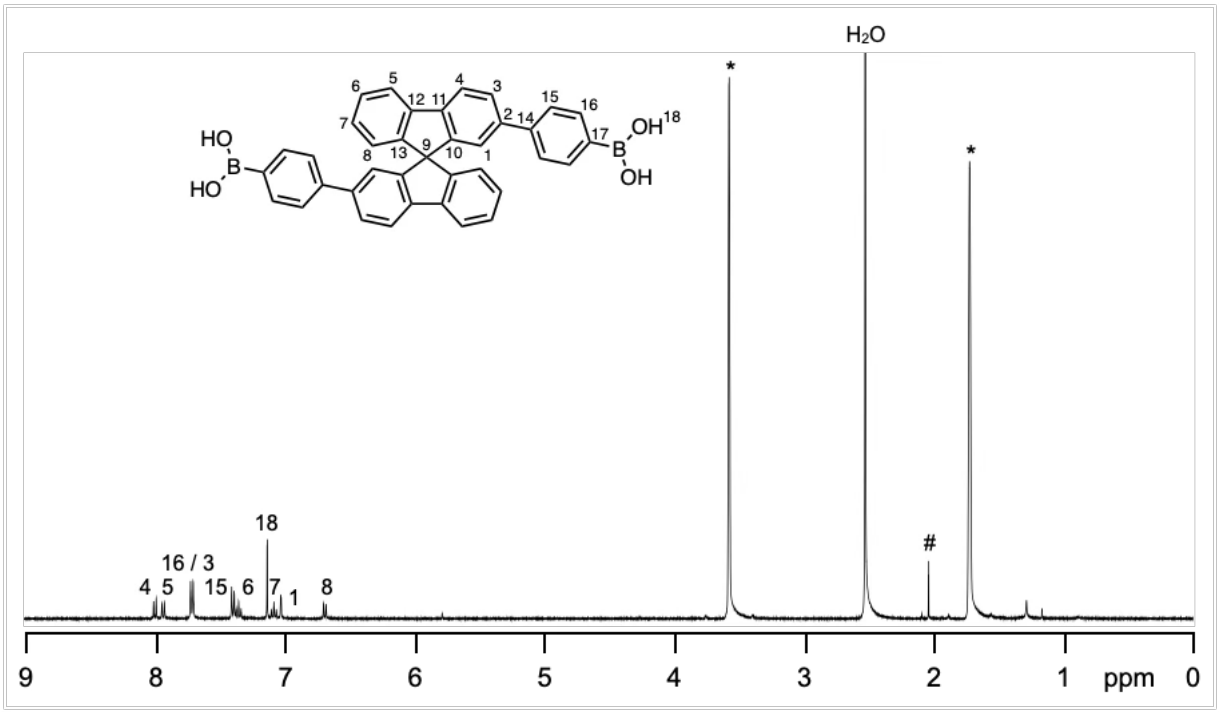


Figure S23. ^{1}H-NMR (400 MHz, THF-d_8, 298 K) spectrum of *rac*-**B*^{Ph}** (* THF, $^{\#}$ acetone).

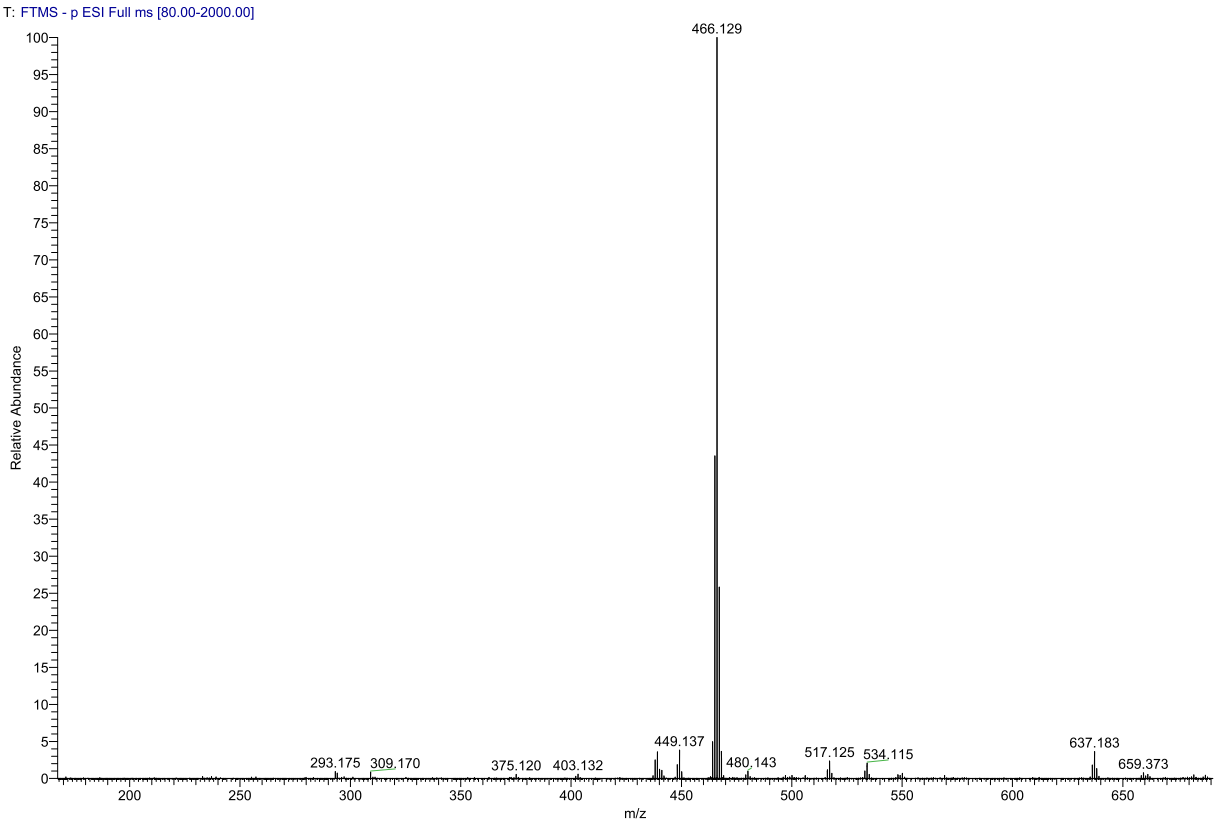
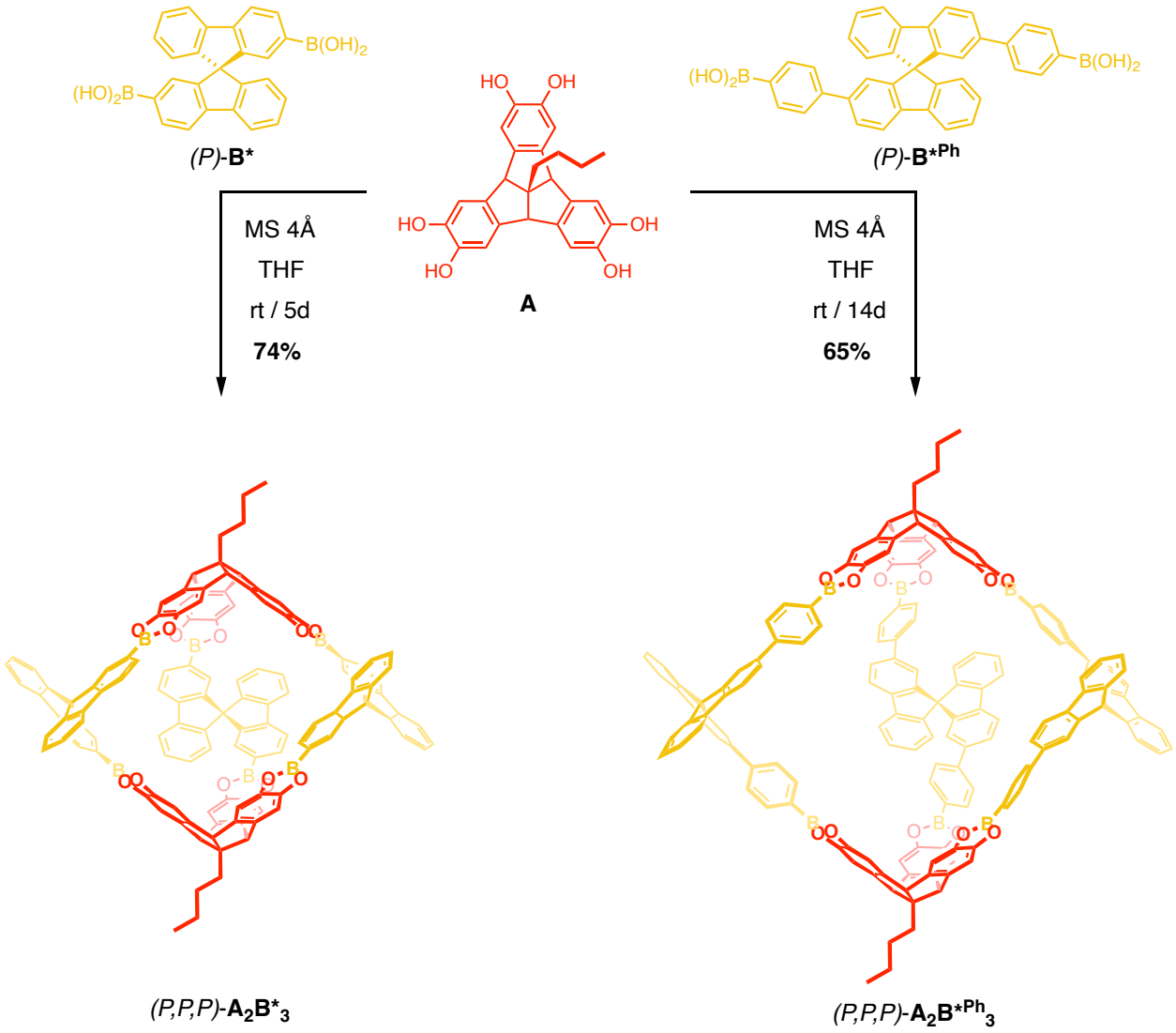


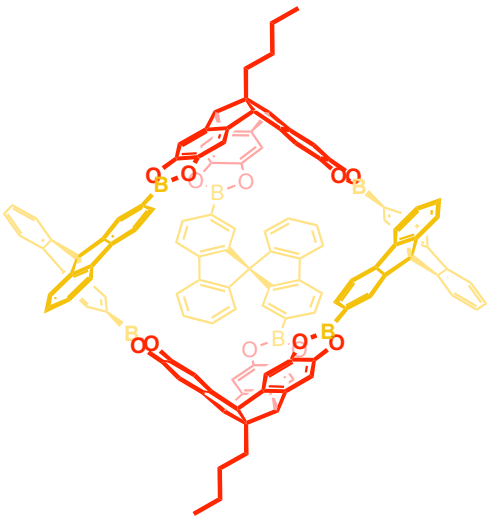
Figure S24. ESI(−)-MS spectrum of elongated linker *(P)*-**B*^{Ph}**.

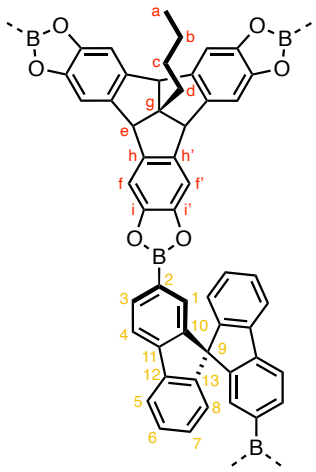


Scheme S2. Synthesis of homochiral cages *(P,P,P)*-$\mathbf{A_2B^*_3}$ and *(P,P,P)*-$\mathbf{A_2B^{*Ph}_3}$.

TBTQ **A**[S10] has been synthesized according to a previously reported procedure.

boronate ester cage *(P,P,P)*-**A$_2$B*$_3$**





(P,P,P)-**A$_2$B*$_3$**

$C_{127}H_{78}B_6O_{12}$

1860.87 g mol^{-1}

TBTQ **A** (5.00 mg, 11.6 µmol, 1 eq.) and (*P*)-**B*** (7.01 mg, 17.3 µmol, 1.5 eq.) were dissolved in 0.75 mL THF-d_8 and 4 Å molecular sieves were added. The reaction progress was monitored by ^{1}H NMR spectroscopy. After five days, the reaction was completed and the solvent was removed under reduced pressure to give cage *(P,P,P)*-**A$_2$B*$_3$** (8.0 mg, 4.3 µmol, 74%) as a pale purple solid.

^{1}H NMR (400 MHz, THF-d_8, 298 K): δ = 8.05 (m, 12H, *H*-4/5), 7.97 (dd, ^3J = 7.70 Hz, ^4J = 0.74 Hz, 6H, *H*-3), 7.45 (t, ^3J = 7.55 Hz, 6H, *H*-6), 7.19 (m, 18H, *H*-1/7, $H_{f,f'}$), 7.12 (s, 6H, $H_{f,f'}$), 6.78 (d, ^3J = 7.59 Hz, 2H, *H*-8), 4.43 (s, 6H, H_e), 1.89 (m, 4H, H_d), 1.35 (m, 8H, $H_{b,c}$), 0.84 (t, ^3J = 7.02 Hz, 6H, H_a) ppm.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.96 (m, 18H, *H*-3/4/5), 7.44 (dt, ^3J = 7.54 Hz, ^4J = 0.80 Hz, 6H, *H*-6), 7.23 (s, 6H, *H*-1), 7.19 (dt, ^3J = 7.50 Hz, ^4J = 0.88 Hz, 6H, *H*-7), 7.08, 7.03 (s, 2x6H, $H_{f,f'}$), 6.80 (d, ^3J = 7.60 Hz, 6H, *H*-8), 4.43 (s, 6H, H_e), 1.92 (m, 4H, H_d), 1.36 (m, 8H, $H_{b,c}$), 0.85 (t, 6H, H_a) ppm.

^{13}C NMR (101 MHz, THF-d_8, 298 K): δ = 149.69 (*C*-13), 149.38 (C_i), 149.22 ($C_{i'}$), 148.95 (*C*-10), 145.54 (*C*-11), 142.61 (*C*-12), 140.61 ($C_{h,h'}$), 140.51 ($C_{h,h'}$), 135.13 (*C*-3), 130.83 (*C*-1), 129.61 (*C*-7), 128.97 (*C*-6), 126.35 (*C*-2), 125.05 (*C*-8), 121.65 (*C*-5), 120.86 (*C*-4), 108.44 ($C_{f,f'}$), 108.35 ($C_{f,f'}$), 67.53 (C_g), 66.66 (C-9), 61.24 (C_e), 40.81 (C_d) 27.25 (C_c) 24.29 (C_b) 14.38 (C_a) (C_g, *C*-2 and *C*-9 were assigned with help of cross signals from HMBC experiments) ppm.

MS (MALDI-TOF, DCTB, pos. mode): *m/z* = 1804.26735 [M−C_4H_9+H]$^+$, 1860.24735 [M]$^+$.

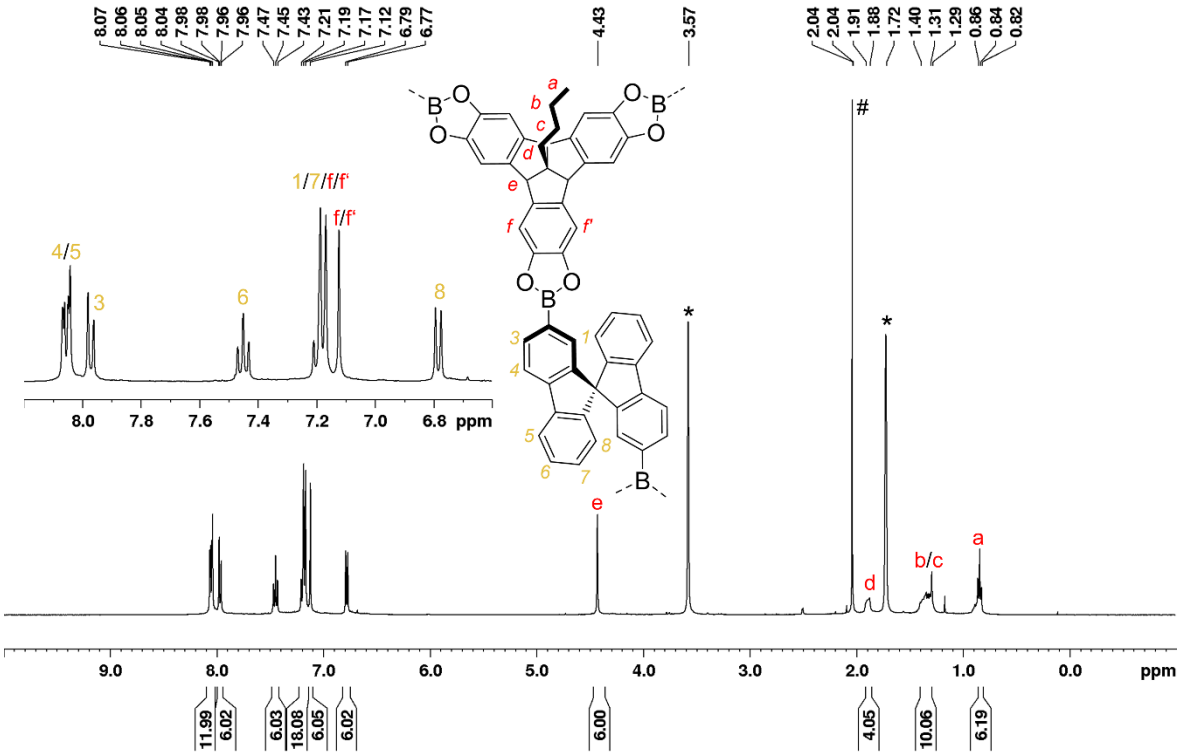


Figure S25. ^{1}H-NMR (400 MHz, THF-d_8, 298 K) spectrum of *(P,P,P)*-**$A_2B^*_3$** (* THF, # acetone).

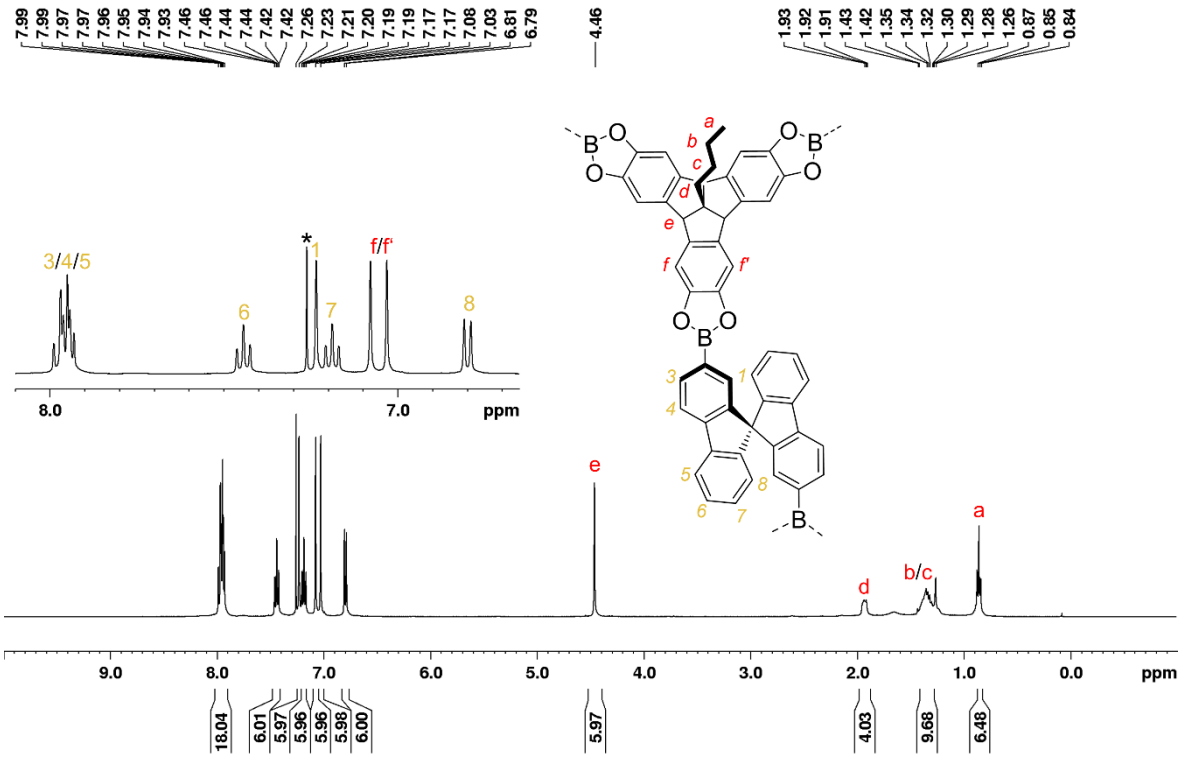


Figure S26. ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *(P,P,P)*-**$A_2B^*_3$** (* $CHCl_3$, # acetone).

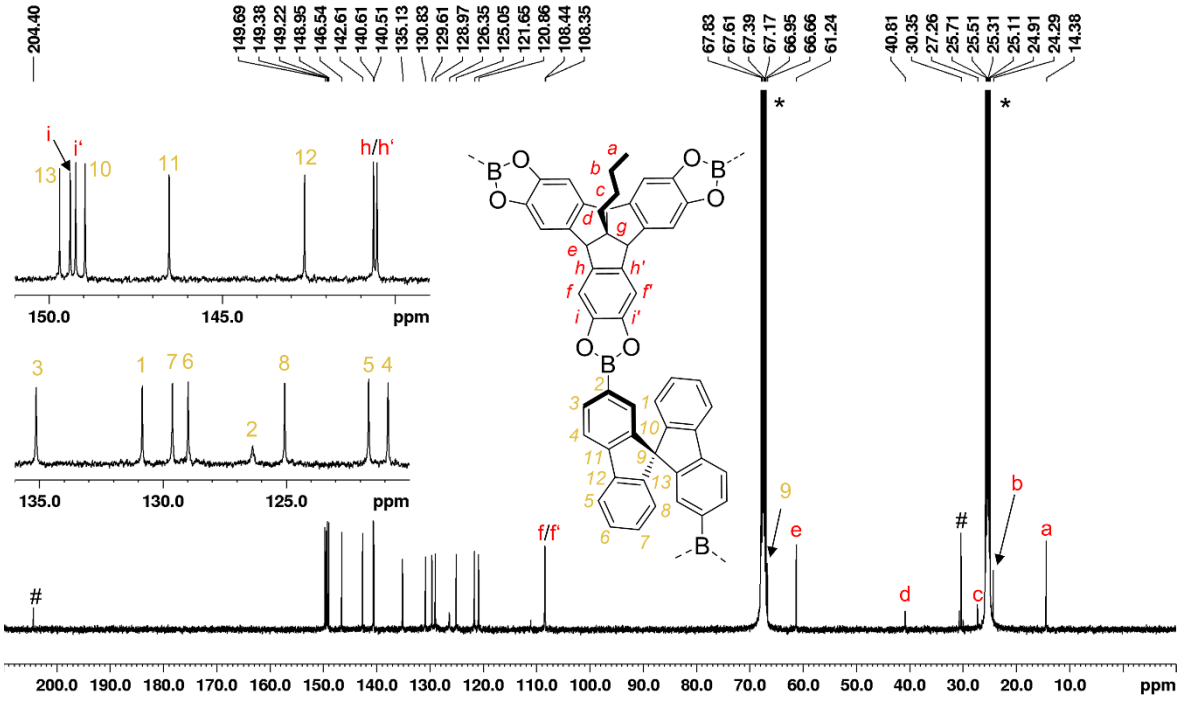


Figure S27. ^{13}C-NMR (101 MHz, THF-d_8, 298 K) spectrum of *(P,P,P)*-**A$_2$B*$_3$** (* THF, # acetone).

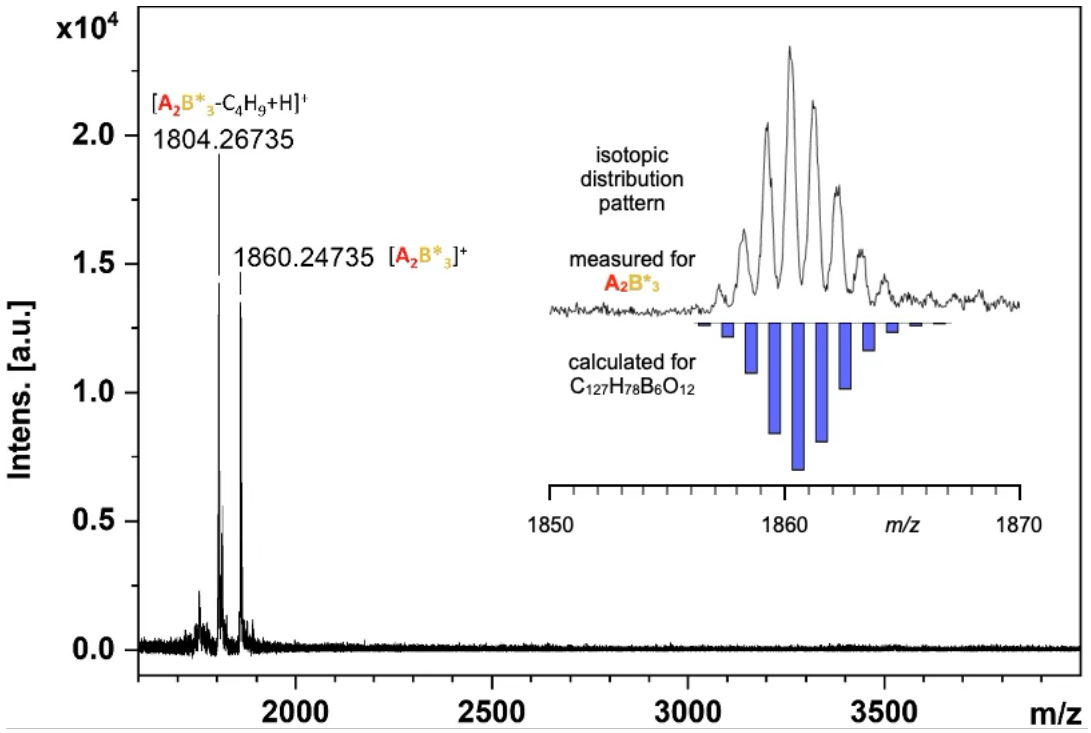
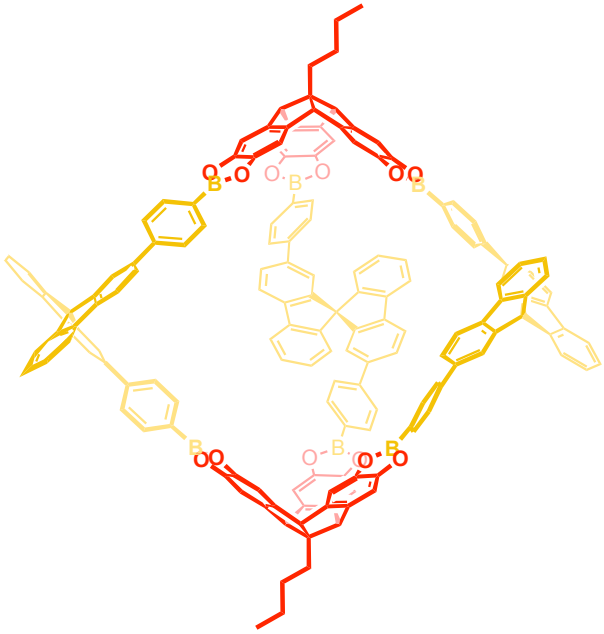
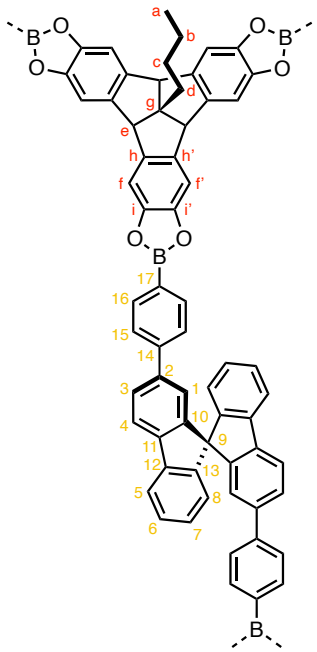


Figure S28. MS (MALDI-TOF, DCTB in $CHCl_3$, positive mode) of *(P,P,P)*-**A$_2$B*$_3$**.

boronate ester cage *(P,P,P)*-$\mathbf{A_2B^{*Ph}_3}$





(P,P,P)-$\mathbf{A_2B^{*Ph}_3}$

$C_{163}H_{102}B_6O_{12}$

2317.46 g mol^{-1}

TBTQ **A** (5.00 mg, 11.6 µmol, 1 eq.) and homochiral diboronic acid (*P*)-$\mathbf{B^{*Ph}}$ (9.65 mg, 17.3 µmol, 1.5 eq.) were dissolved in 0.75 mL THF-d_8 and 4 Å molecular sieves were added. The reaction progress was monitored by ^{1}H NMR spectroscopy. After eight days, the reaction stopped and the solvent was removed under reduced pressure. The product was purified by dissolving the residue in $C_2D_2Cl_4$, filtering off the remaining solid and removing the solvent under reduced pressure to give cage *(P,P,P)*-$\mathbf{A_2B^{*Ph}_3}$ (8.7 mg, 3.75 µmol, 65%) as a pale purple solid.

^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 298 K): δ = 7.99 (d, ^3J = 8.00 Hz, 6H, *H*-4), 7.94 (d, ^3J = 7.68 Hz, 6H, *H*-5), 7.87 (m, 18H, *H*-3/16), 7.63 (d, ^3J = 8.48 Hz, 12H, *H*-15), 7.43 (t, ^3J = 7.40 Hz, 6H, *H*-6), 7.26 (s, 12H, $H_{f,f'}$), 7.15 (m, 12H, *H*-1/7), 6.79 (d, ^3J = 7.48 Hz, 6H, *H*-8), 4.54 (s, 6H, H_e), 1.98 (m, 4H, H_d), 1.38 (m, 8H, $H_{b,c}$), 0.88 (t, ^3J = 6.83 Hz, 6H, H_a) ppm.

^{1}H NMR (400 MHz, THF-d_8, 298 K): δ = 8.05 (d, ^3J = 8.09 Hz, 6H, *H*-4), 7.97 (d, ^3J = 7.61 Hz, 6H, *H*-5), 7.91 (dd, ^3J = 8.16 Hz, ^4J = 1.35 Hz, 6H, *H*-3), 7.82 (d, ^3J = 8.15 Hz, 12H, *H*-16), 7.67 (d, ^3J = 8.20 Hz, 12H, *H*-15), 7.38 (m, 18H, *H*-6/$H_{f,f'}$), 7.21 (d, ^4J = 1.17 Hz, 6H, *H*-1), 7.10 (t, ^3J = 7.54 Hz, 6H, *H*-7), 6.70 (d, ^3J = 7.59 Hz, 6H, *H*-8), 4.56 (s, 6H, H_e), 1.99 (m, 4H, H_d), 1.43 (m, 8H, $H_{b,c}$), 0.89 (t, ^3J = 7.10 Hz, 6H, H_a) ppm.

^{13}C NMR (101 MHz, THF-d_8, 298 K): δ = 150.38 (*C*-10), 150.31 (*C*-13), 149.34 ($C_{i,i'}$), 149.32 ($C_{i,i'}$), 143.67 (*C*-14), 143.18 (*C*-2), 142.10 (*C*-12), 140.77 ($C_{h,h'}$), 139.96 (*C*-11),135.76 (*C*-16), 128.84 (*C*-7), 128.66 (*C*-6), 127.27 (*C*-3), 126.52 (*C*-15), 125.83 (*C*-17), 124.69 (*C*-8), 122.51 (*C*-1), 121.48 (*C*-

4), 121.17 (*C*-5), 108.69 ($C_{f,f'}$), 67.67 (C_g), 67.17 (*C*-9) 61.45 (C_e), 40.86 (C_d) 27.34 (C_c), 24.36 (C_b) 14.43 (C_a) (C_g, *C*-9 and *C*-17 could only be detected *via* cross signals of HMBC experiments) ppm.

MS (MALDI-TOF, DCTB, positive mode): *m/z* = 2317.08651 $[M]^+$.

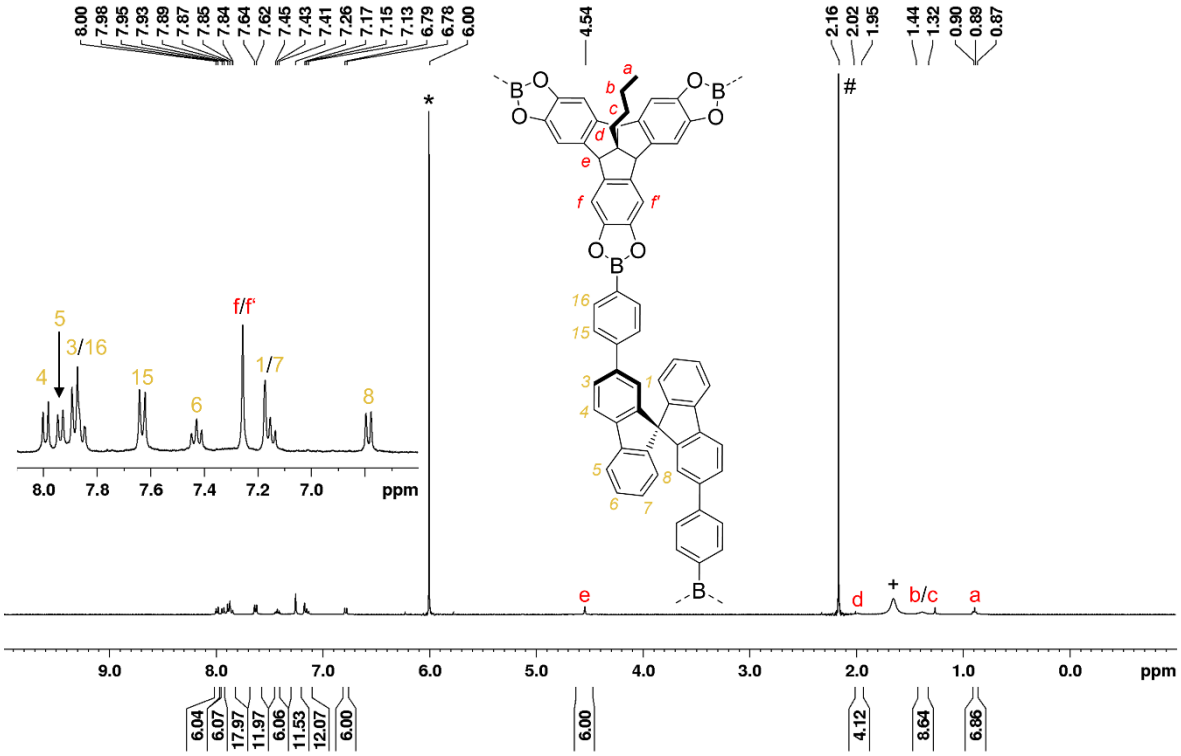


Figure S29. ^{1}H-NMR (400 MHz, $C_2D_2Cl_4$-d_8, rt) spectrum of *(P,P,P)*-$\mathbf{A_2B^{*Ph}_3}$ (* THF, # acetone).

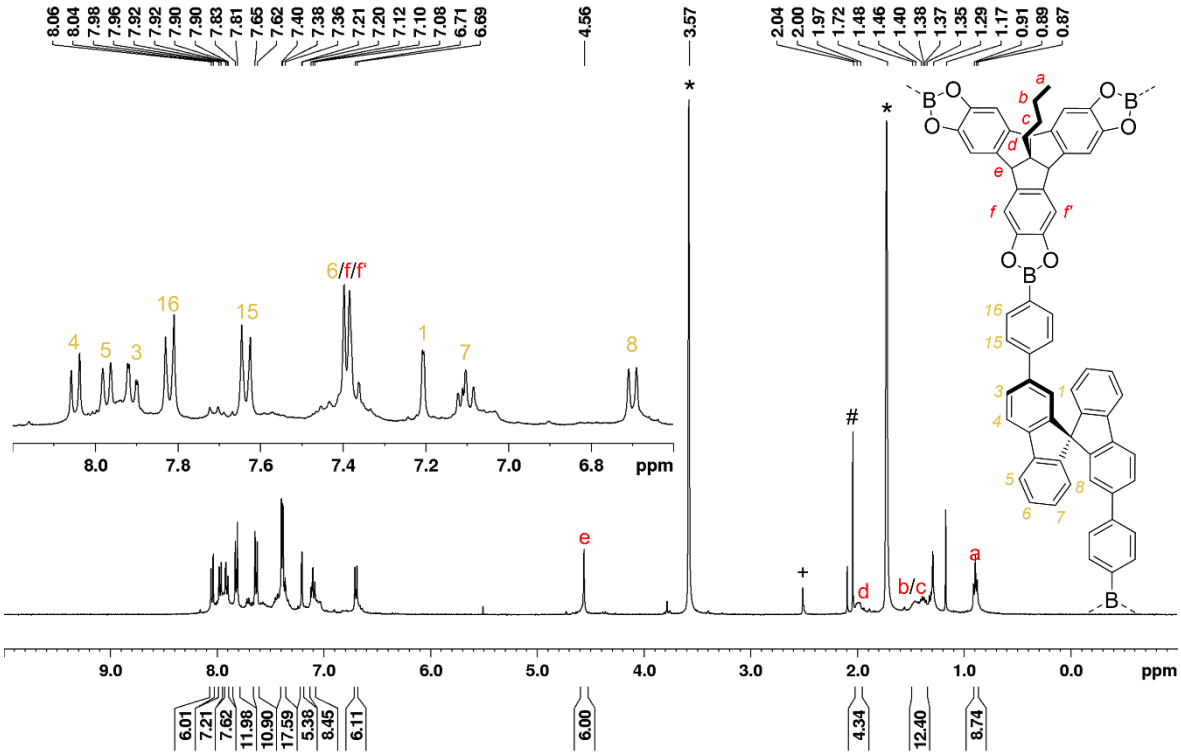


Figure S30. ^{1}H-NMR (400 MHz, THF-d_8, 298 K) spectrum of the crude product at the end of the reaction towards cage *(P,P,P)*-$\mathbf{A_2B^{*Ph}_3}$ (* THF, + H_2O. # acetone).

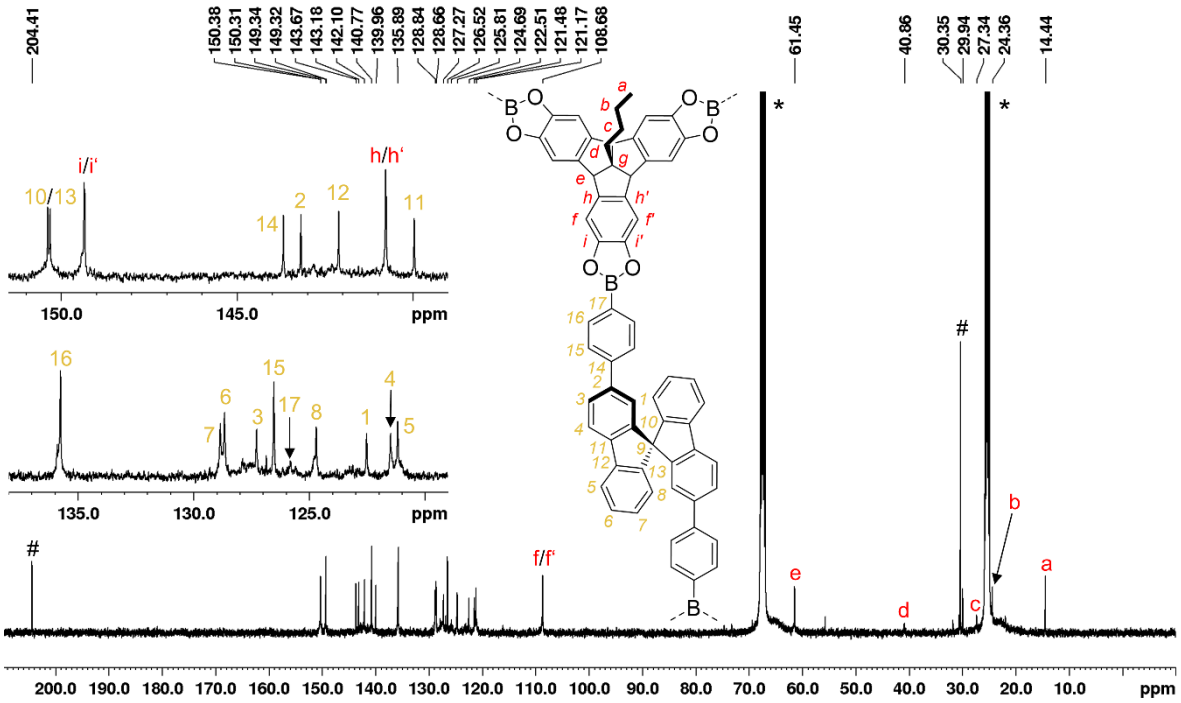


Figure S31. ^{13}C-NMR (101 MHz, THF-d_8, 298 K) spectrum of crude product at the end of the reaction towards cage *(P,P,P)*-**A$_2$B*$^{Ph}_3$** (* THF, # acetone).

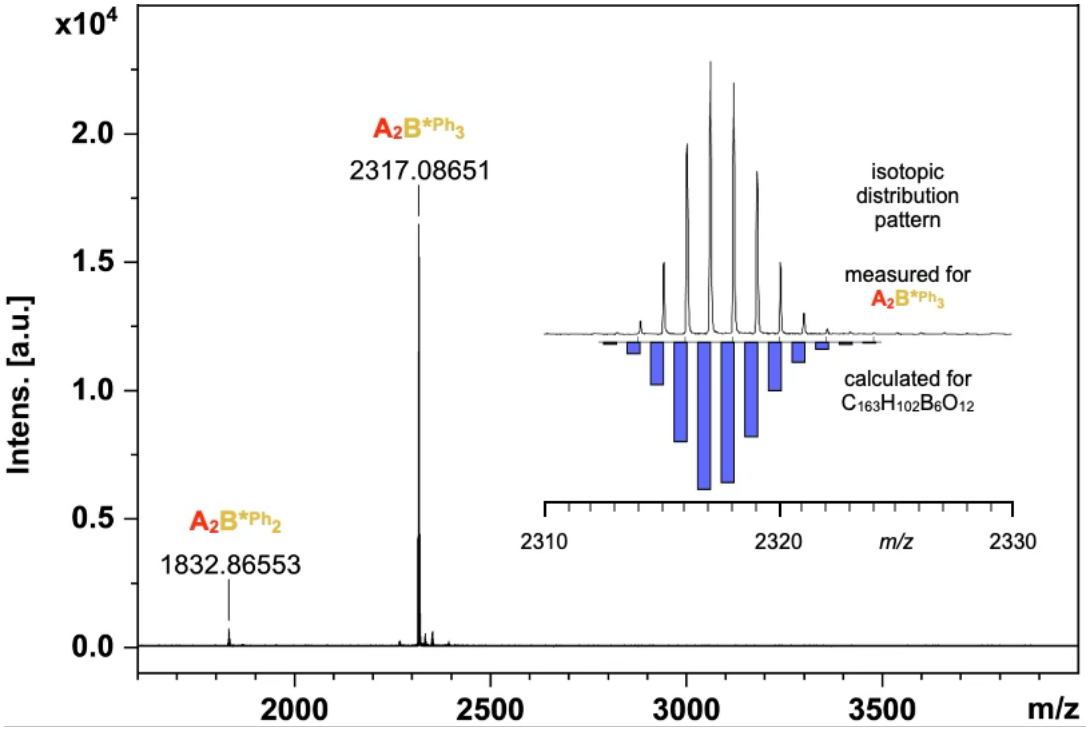


Figure S32. MS (MALDI-TOF, DCTB in $CHCl_3$, positive mode) of *(P,P,P)*-**A$_2$B*$^{Ph}_3$**.

4 Diffusion-ordered Spectroscopy (DOSY) Data

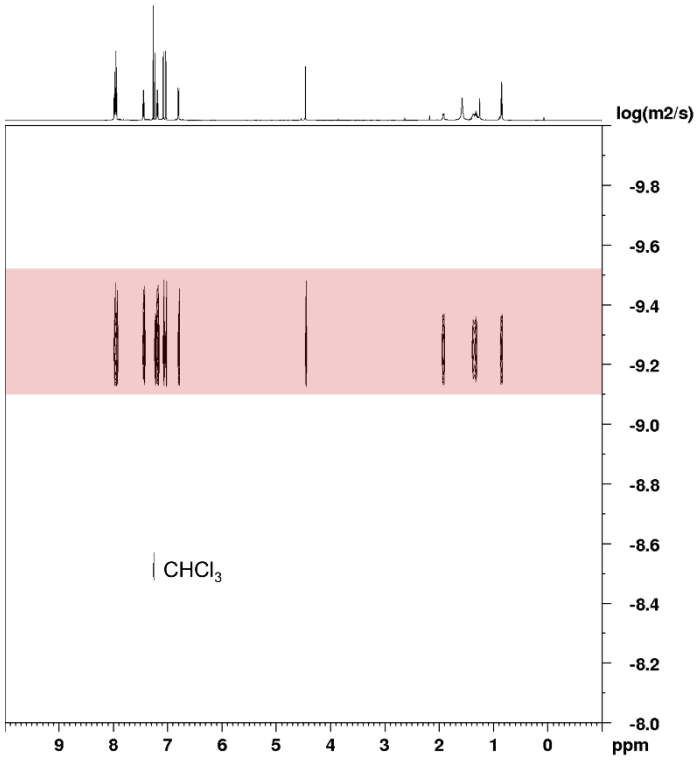


Figure S33. 2D plot of DOSY NMR (600 MHz, $CDCl_3$, 295.6 K) of (*P*,*P*,*P*)-**A$_2$B*$_3$**.

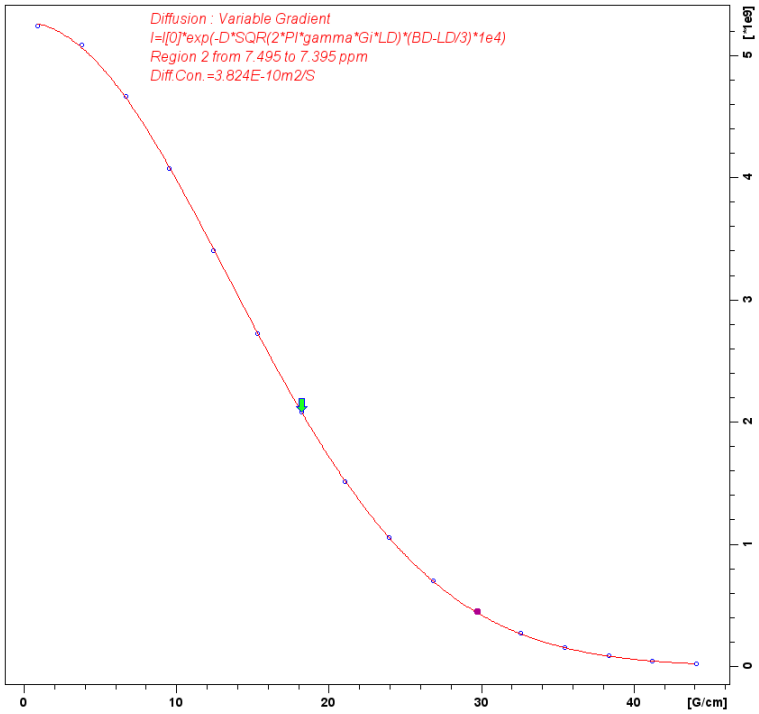


Figure S34. Monoexponential fit of the amplitude decay for selected proton signal at δ = 7.45 ppm of cage (*P*,*P*,*P*)-**A$_2$B*$_3$**.

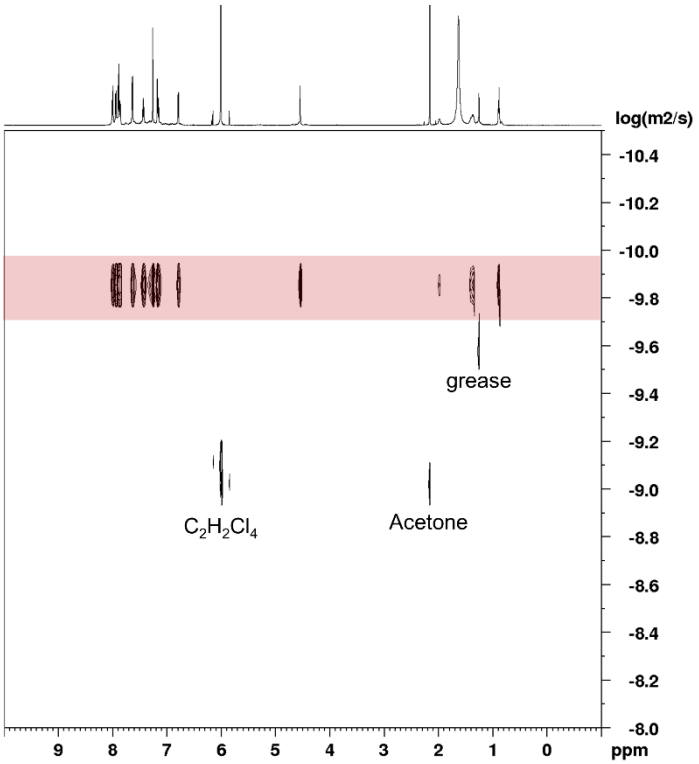


Figure S35. 2D plot of DOSY NMR (600 MHz, $C_2D_2Cl_4$, 295.6 K) of (*P*,*P*,*P*)-**A$_2$B*^{Ph}$_3$**.

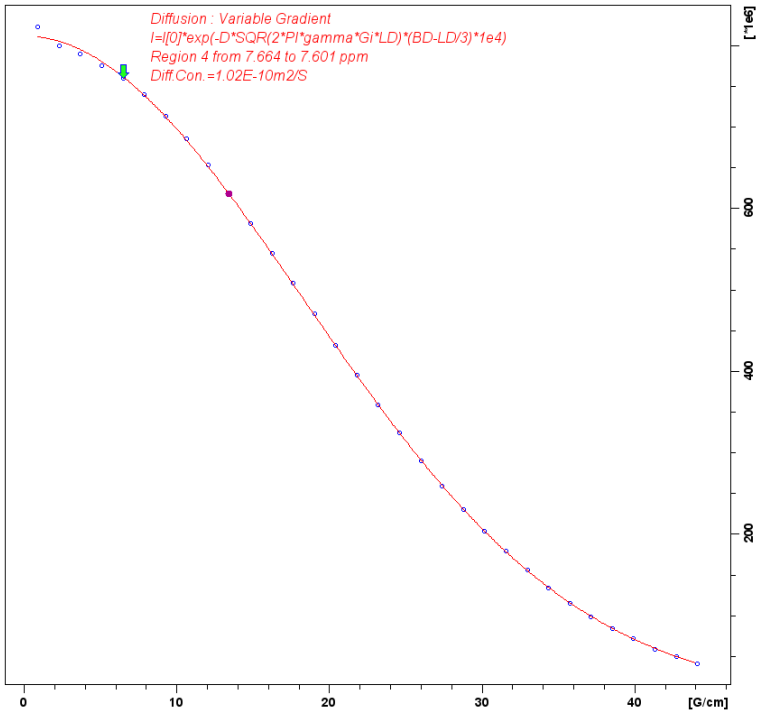


Figure S36. Monoexponential fit of the amplitude decay for selected proton signal at δ = 7.63 ppm of cage (*P*,*P*,*P*)-**A$_2$B*^{Ph}$_3$**.

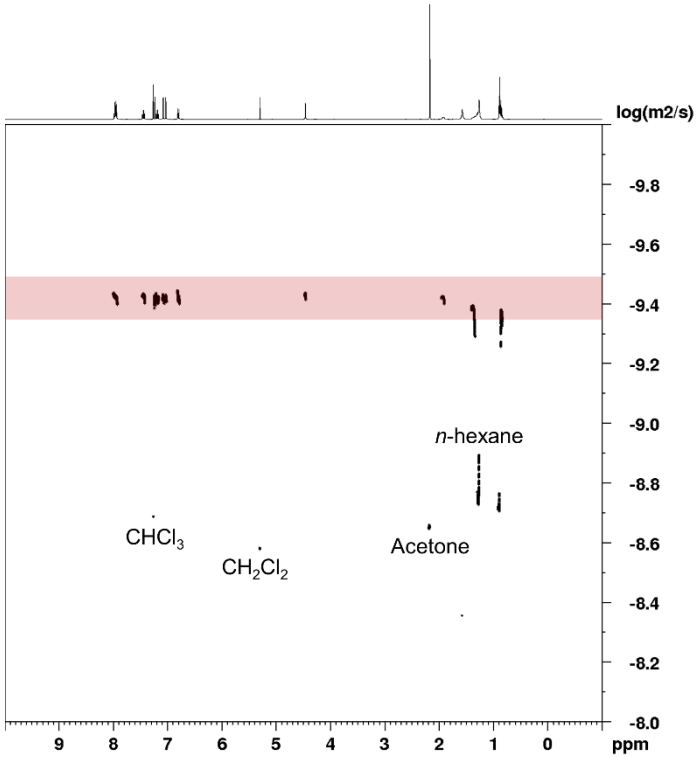


Figure S37. 2D plot of DOSY NMR (400 MHz, $CDCl_3$, 295.6 K) of racemic mixture of $\mathbf{A_2B^*_3}$ cages obtained after self-sorting experiment with **A** and *rac*-**B***.

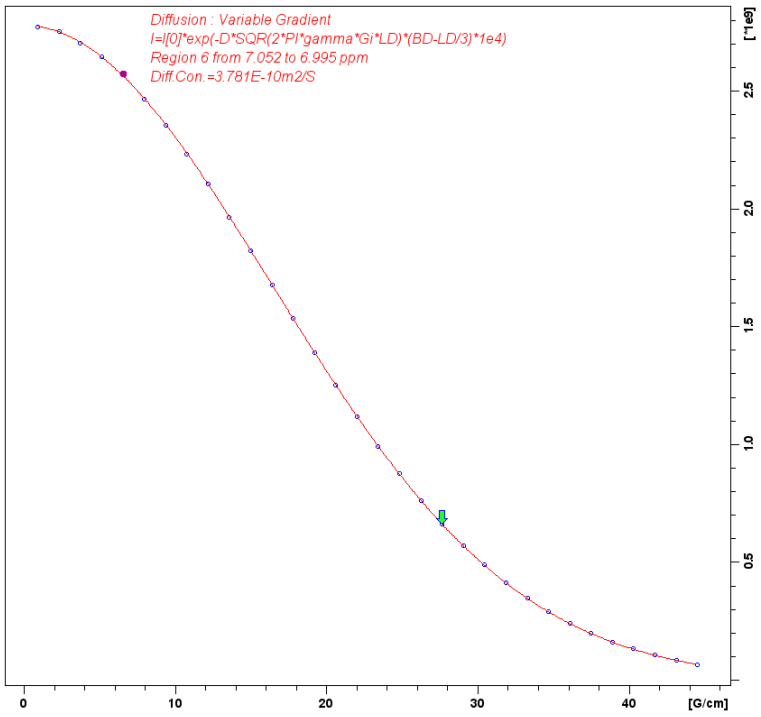


Figure S38. Monoexponential fit of the amplitude decay for selected proton signal at δ = 7.00 ppm of racemic $\mathbf{A_2B^*_3}$ cages obtained after self-sorting experiment with **A** and *rac*-**B***.

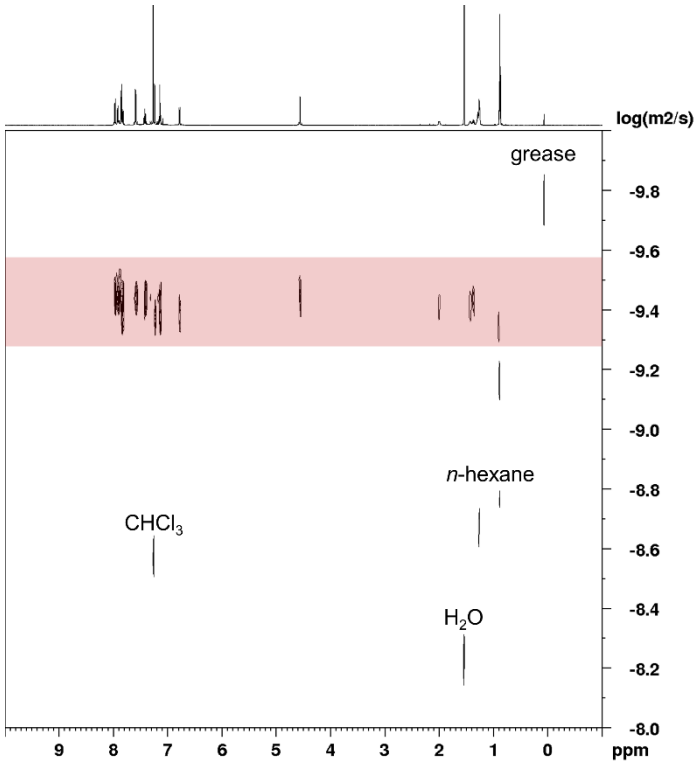


Figure S39. 2D plot of DOSY NMR (600 MHz, $CDCl_3$, 295.6 K) of the soluble mixture isolated from the self-sorting experiment with **A** and *rac*-**B**^{*Ph}.

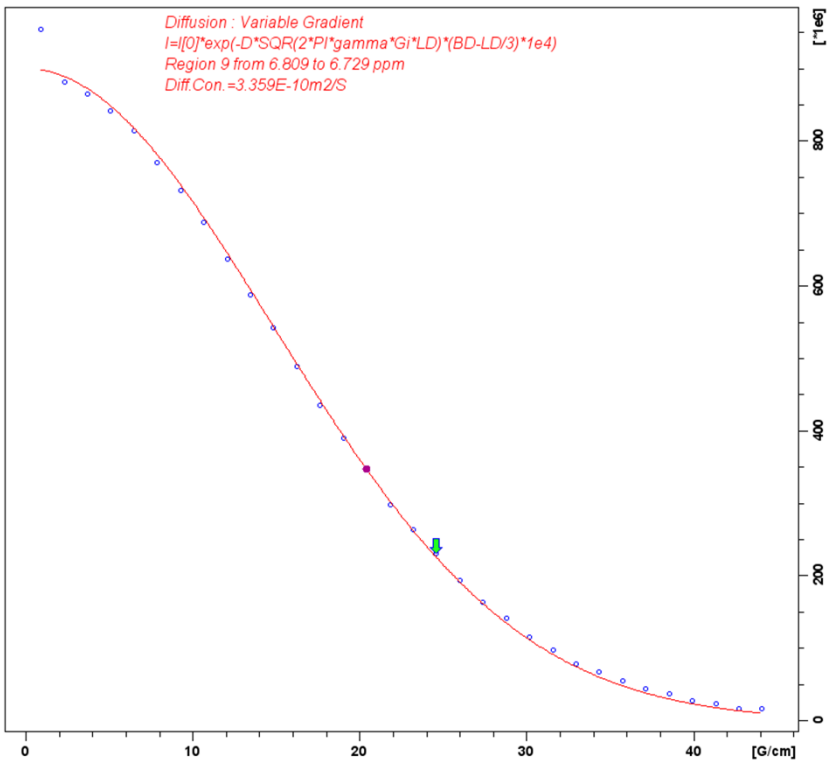
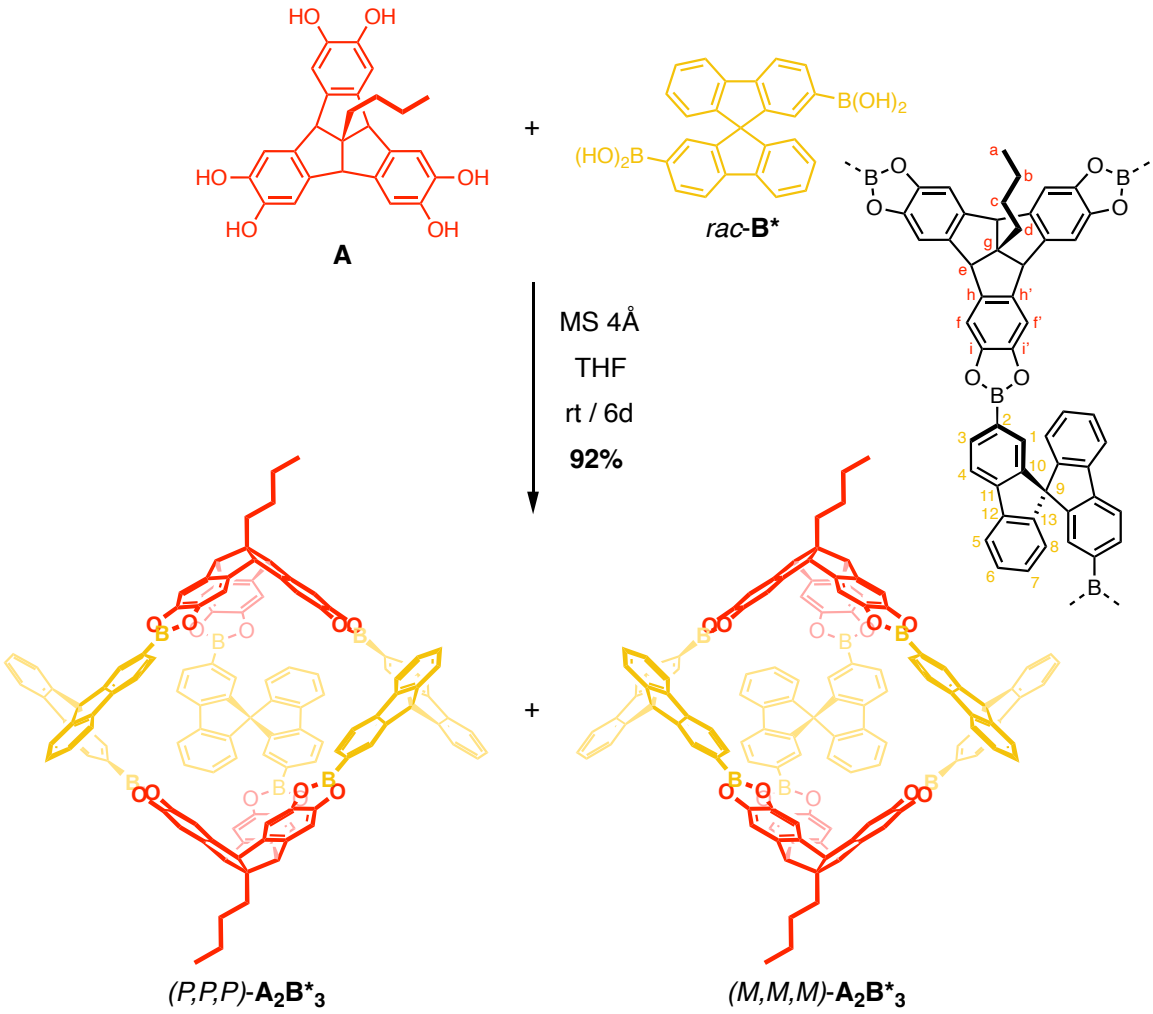


Figure S40. Monoexponential fit of the amplitude decay for selected region at δ = 6.81–6.73 ppm of the soluble mixture isolated from the self-sorting experiment with **A** and *rac*-**B**^{*Ph}.

5 Self-Sorting Experiments

narcissistic self-sorting of *rac*-**B*** into racemic mixture of *(P,P,P)*-$\mathbf{A_2B^*_3}$ and *(M,M,M)*-$\mathbf{A_2B^*_3}$



Scheme S3. Narcissistic self-sorting of *rac*-**B*** into a racemic mixture of *(P,P,P)*- and *(M,M,M)*-$\mathbf{A_2B^*_3}$.

TBTQ **A** (5.00 mg, 11.6 µmol, 1 eq.) and *rac*-**B*** (7.01 mg, 17.3 µmol, 1.5 eq.) were dissolved in THF-d_8 (0.75 mL) and 4 Å molecular sieves were added. The reaction progress was monitored by ^{1}H NMR spectroscopy. After six days, the reaction was completed and the solvent was removed under reduced pressure to give a racemic mixture of (*P,P,P*)- and (*M,M,M*)-$\mathbf{A_2B^*_3}$ (9.9 mg, 5.3 µmol, 92%) as a pale purple solid.

^{1}H and ^{13}C NMR data of $\mathbf{A_2B^*_3}$ cages formed from TBTQ **A** and *rac*-**B*** are identical with data for homochiral cage *(P,P,P)*-$\mathbf{A_2B^*_3}$.

^{1}H NMR (400 MHz, THF-d_8, 298 K): δ = 8.06 (m, 12H, *H*-4/5), 7.97 (dd, ^3J = 7.65 Hz, ^4J = 0.90 Hz, 6H, *H*-3), 7.45 (dt, ^3J = 7.55 Hz, ^3J = 0.89 Hz, 6H, *H*-6), 7.19 (m, 18H, *H*-1/7, $H_{f,f'}$), 7.12 (s, 6H, $H_{f,f'}$),

6.78 (d, ^{3}J = 7.61 Hz, 2H, *H*-8), 4.43 (s, 6H, H_e), 1.89 (m, 4H, H_d), 1.36 (m, 8H, $H_{b,c}$), 0.84 (t, ^{3}J = 7.05 Hz, 6H, H_a) ppm.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.96 (m, 18H, *H*-3/4/5), 7.44 (dt, ^{3}J = 7.52 Hz, ^{4}J = 1.01 Hz, 6H, *H*-6), 7.23 (s, 6H, *H*-1), 7.18 (dt, ^{3}J = 7.50 Hz, ^{4}J = 1.06 Hz, 6H, *H*-7), 7.08, 7.03 (s, 2×6H, $H_{f,f'}$), 6.79 (d, ^{3}J = 7.56 Hz, 6H, *H*-8), 4.46 (s, 6H, H_e), 1.93 (m, 4H, H_d), 1.35 (m, 8H, $H_{b,c}$), 0.85 (t, ^{3}J = 7.02 Hz, 6H, H_a) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 149.02 (*C*-13), 148.36 (C_i), 148.32 ($C_{i'}$), 148.21 (*C*-10), 145.98 (*C*-11), 141.64 (*C*-12), 139.54 ($C_{h,h'}$), 134.94 (*C*-3), 130.48 (*C*-1), 128.94 (*C*-7), 128.14 (*C*-6), 124.92 (*C*-2), 124.41 (*C*-8), 120.90 (*C*-5), 120.18 (*C*-4), 107.87 ($C_{f,f'}$), 107.63 ($C_{f,f'}$), 67.07 (C_g), 65.78 (C-9), 60.38 (C_e), 39.90 (C_d) 29.85 (C_c) 23.46 (C_b) 14.19 (C_a) (C_g, *C*-2 and *C*-9 were assigned with help of cross signals from HMBC experiments) ppm.

MS (MALDI-TOF, DCTB, positive mode): *m/z* = 1860.72407 $[M+H]^+$, 1883.71508 $[M+Na]^+$.

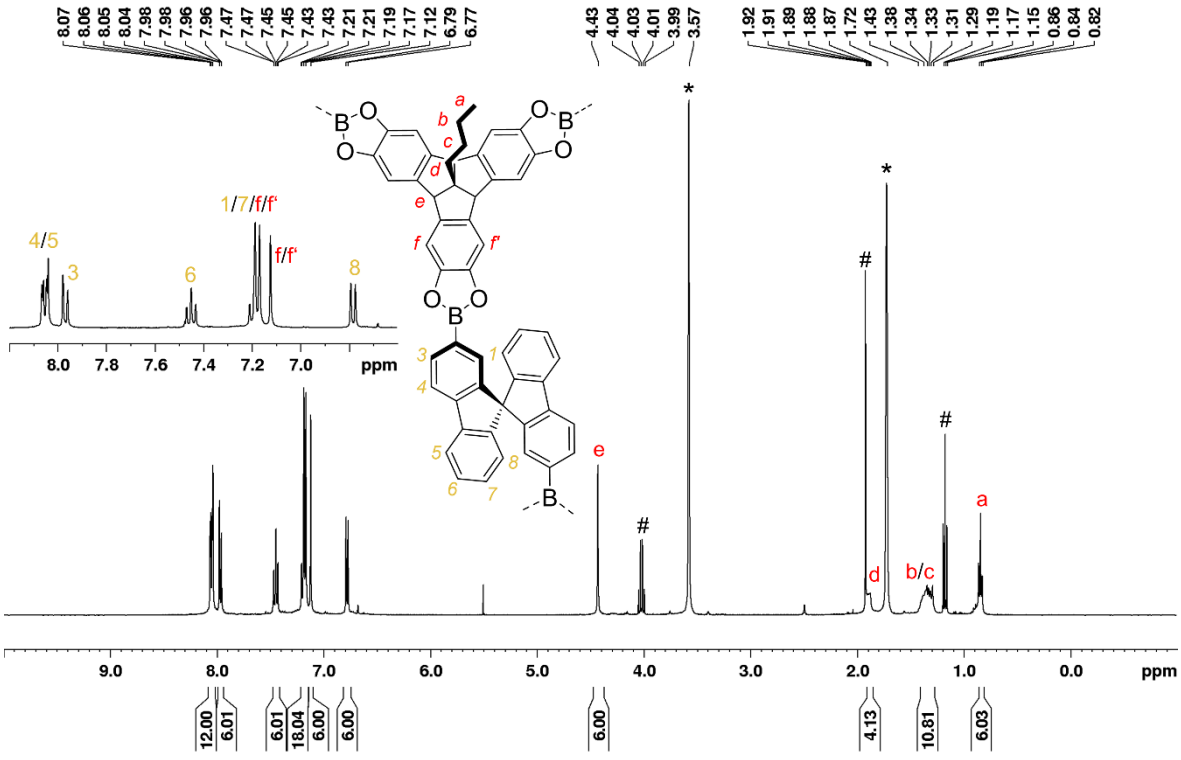


Figure S41. ^{1}H NMR (400 MHz, THF-d_8, 298 K) spectrum of racemic (*P,P,P*)- and (*M,M,M*)-**A$_2$B*$_3$** cages obtained after self-sorting experiment with **A** and *rac*-**B*** (* THF, $^{\#}$ EtOAc).

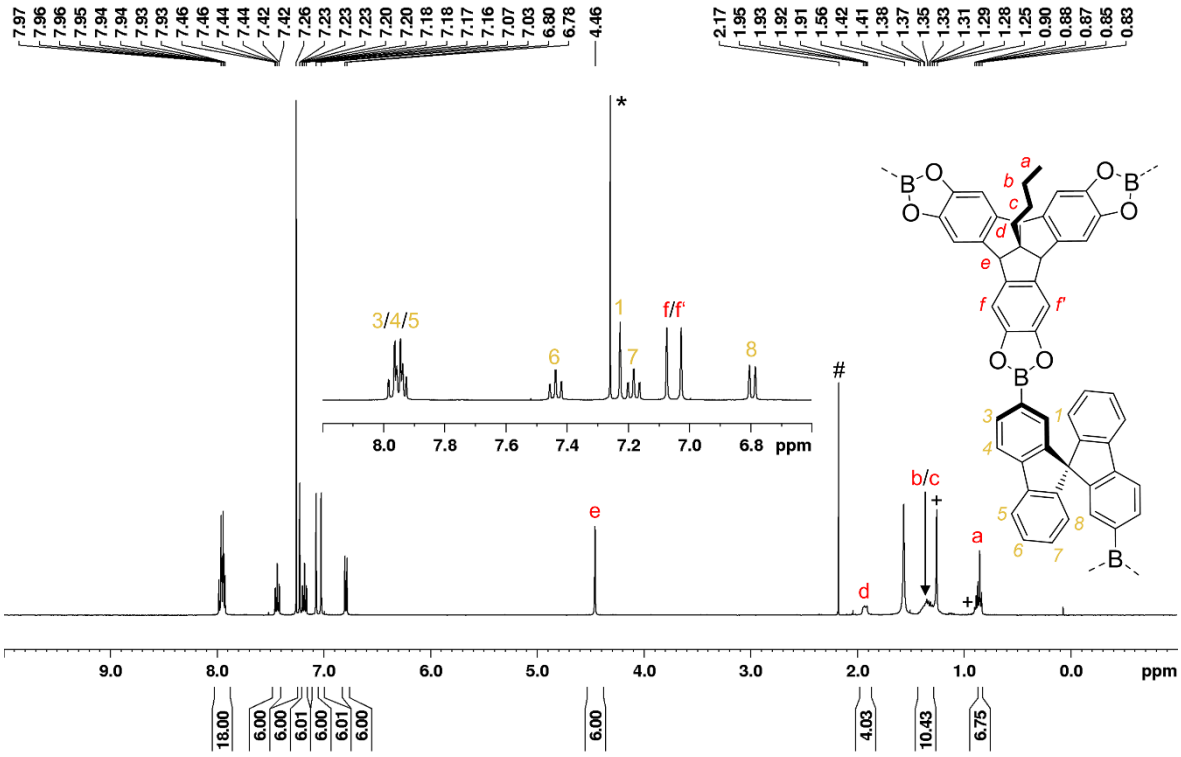


Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of a racemic mixture of *(P,P,P)*- and *(M,M,M)*-$\mathbf{A_2B^*_3}$ obtained after self-sorting experiment with **A** and *rac*-**B*** (* $CHCl_3$, $^{\#}$ Acetone, $^{+}$ H grease).

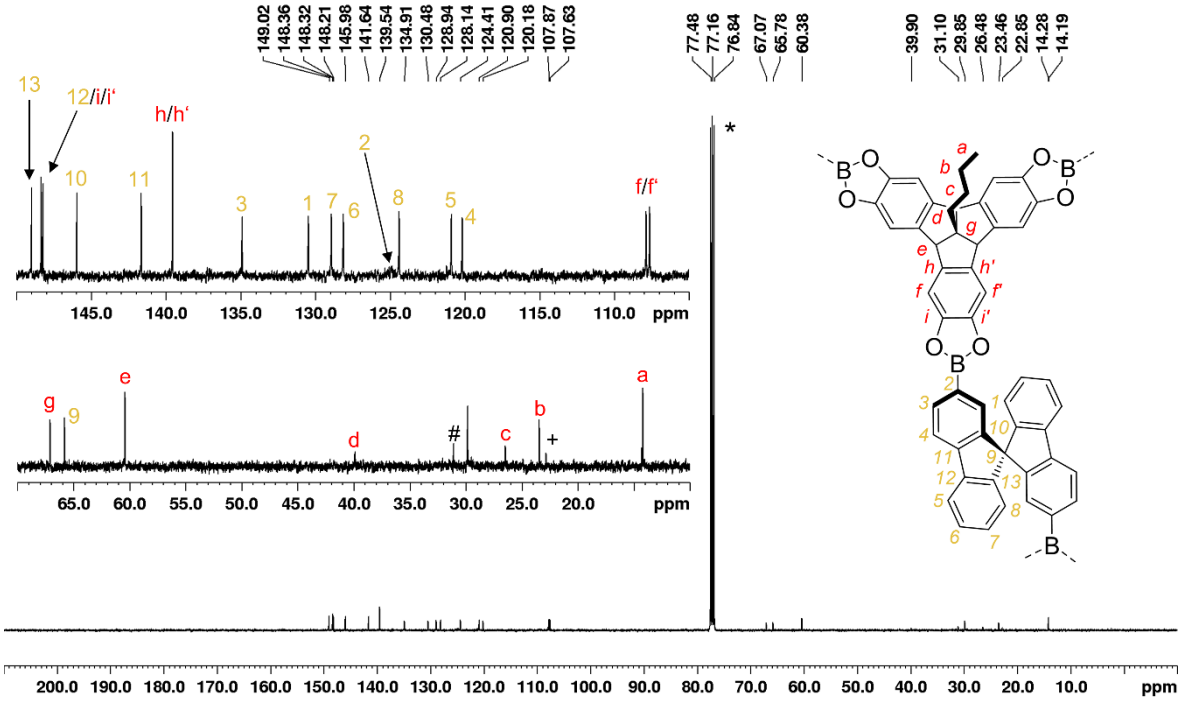


Figure S43. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of a racemic mixture of *(P,P,P)*- and *(M,M,M)*-$\mathbf{A_2B^*_3}$ obtained after self-sorting experiment with **A** and *rac*-**B*** (* $CHCl_3$, $^{\#}$ acetone, $^{+}$ H grease).

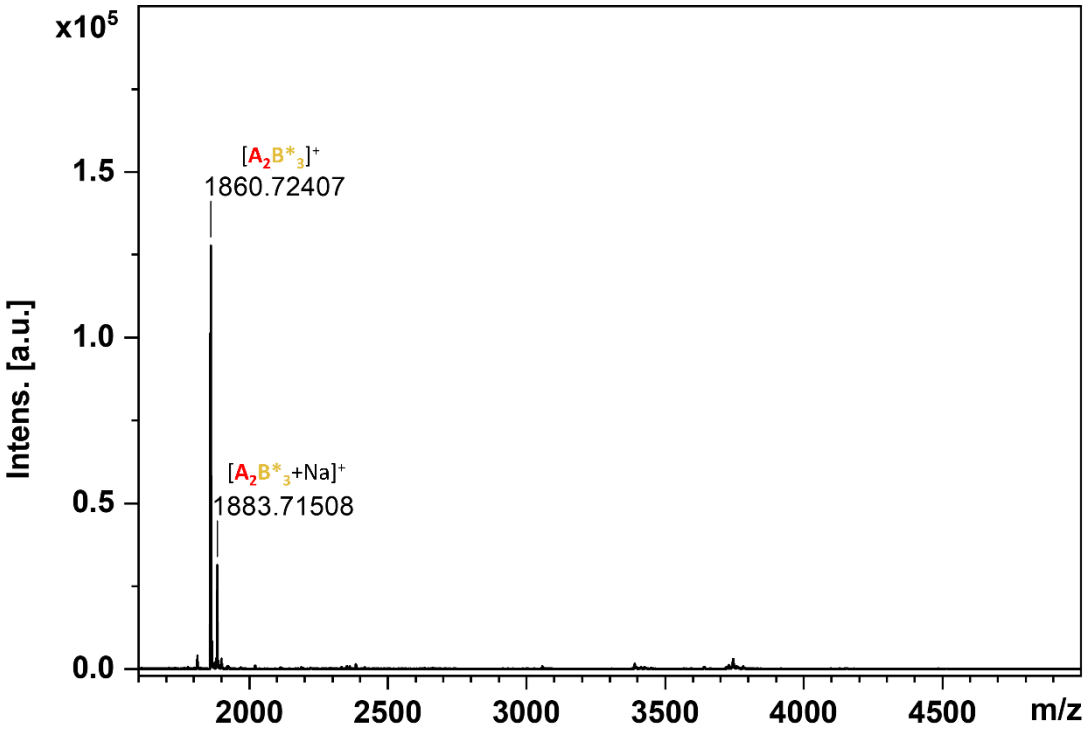


Figure S44. MS (MALDI-TOF, DCTB in $CHCl_3$, positive mode) of a racemic mixture of *(P,P,P)*- and *(M,M,M)*-**A$_2$B*$_3$** obtained after self-sorting experiment with **A** and *rac*-**B***.

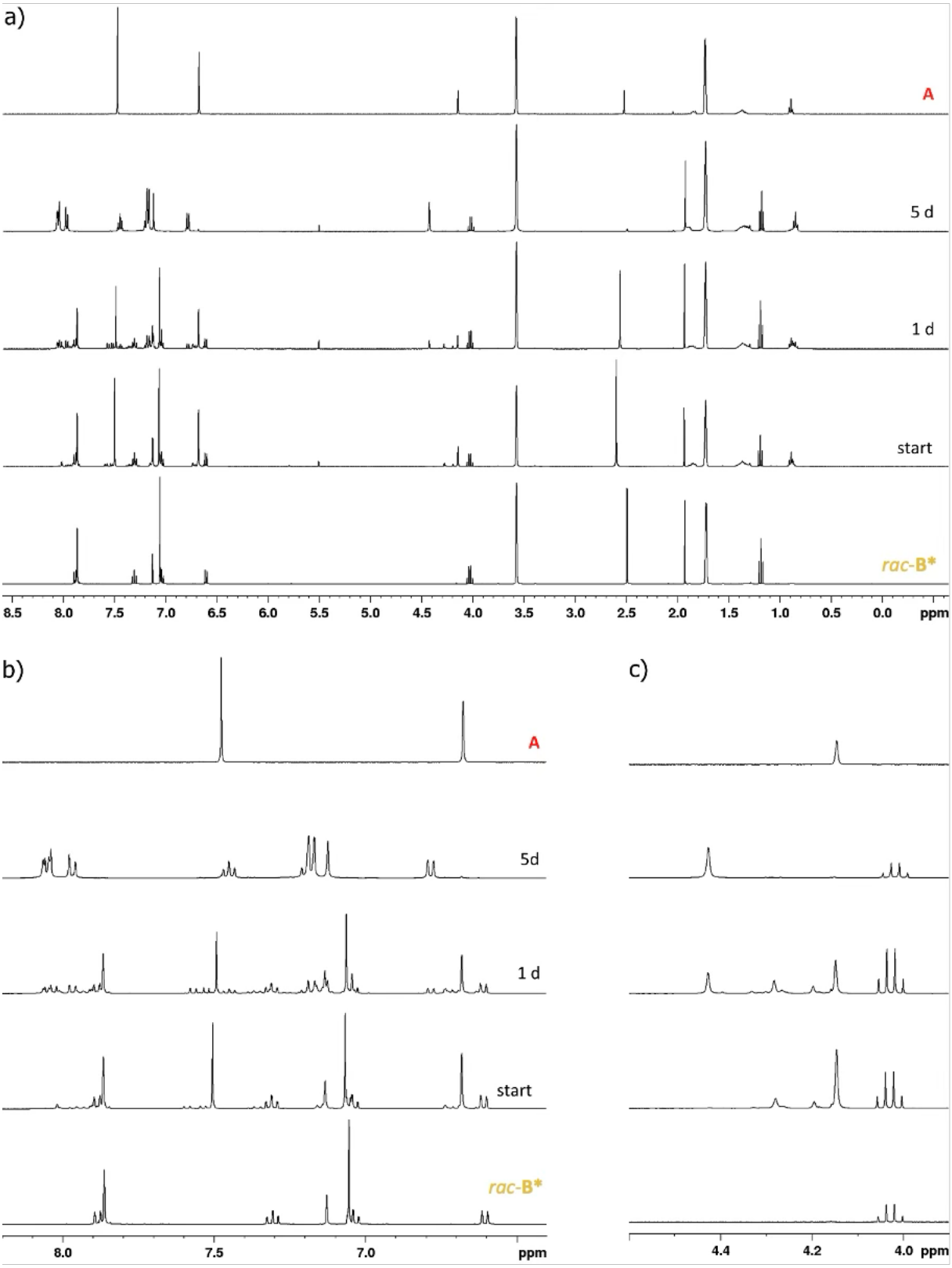
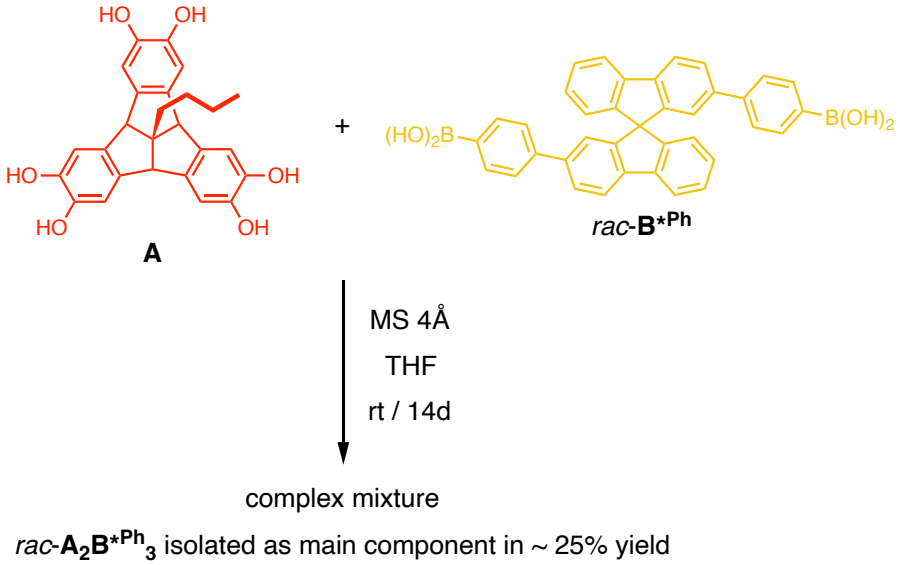


Figure S45. ^{1}H NMR (400 MHz, THF-d_8, 298 K, c(**A**) = 1.55×10^{-2} mol L^{-1}, c(*rac*-**B***) = 2.32×10^{-2} mol L^{-1}) reaction monitoring for self-sorting experiment with **A** and *rac*-**B*** directly after mixing and after one and five days: a) overview, b) details of the aromatic region, and c) details of the bridgehead region.

self-sorting experiment with TBTQ **A** and racemic elongated linker *rac*-**B*^{Ph}**



Scheme S4. Self-sorting experiment with TBTQ **A** and racemic elongated linker *rac*-**B*^{Ph}**.

TBTQ **A** (5.00 mg, 11.6 µmol, 1 eq.) and diboronic acid *rac*-**B*^{Ph}** (9.65 mg, 17.3 µmol, 1.5 eq.) were dissolved in THF-d_8 (0.75 mL) and 4 Å molecular sieves were added. The reaction progress was monitored by ^{1}H NMR spectroscopy. After no more reaction progress was observable, the precipitated material was filtrated and washed with *n*-hexane. The solid was stirred overnight at 130 °C in anhydrous $C_2D_2Cl_4$, the solvent was carefully separated from the insoluble parts and removed under reduced pressure to receive a mixture of products (3.4 mg, ~25%) as a pale purple solid.

The following NMR data corresponds to the main product of the isolated mixture.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.96 (d, ^3J = 8.10 Hz, 6H, *H*-4), 7.91 (d, ^3J = 7.68 Hz, 6H, *H*-5), 7.84 (d, ^3J = 8.40 Hz, 12H, H-16), 7.82 (dd, ^3J = 8.16 Hz, ^4J = 1.68 Hz, 6H, H-3), 7.58 (d, ^3J = 8.46 Hz, 12H, *H*-15), 7.41 (t, ^3J = 7.47 Hz, 6H, *H*-6), 7.234, 7.228 (s, 2×6H, $H_{f,f'}$), 7.14 (m, 12H, *H*-1/7), 6.77 (d, ^3J = 7.62 Hz, 6H, *H*-8), 4.55 (s, 6H, H_e), 2.00 (m, 4H, H_d), 1.39 (m, 8H, $H_{b,c}$), 0.88 (t, ^3J = 7.08 Hz, 6H, H_a) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.40, 149.39 (*C*-10, *C*-13), 148.47, 148.46 ($C_{i,i'}$), 143.16 (*C*-14), 142.16 (*C*-2), 141.21 (*C*-12), 139.76, 139.72 ($C_{h,h'}$), 139.16 (*C*-11), 135.30 (*C*-16), 128.26 (*C*-7), 128.02 (*C*-6), 126.65 (*C*-3), 126.02 (*C*-15), 125.83 (*C*-17), 124.20 (*C*-8), 122.20 (*C*-1), 120.70 (*C*-4), 120.45 (*C*-5), 107.95, 107.93 ($C_{f,f'}$), 67.18 (C_g), 66.31 (*C*-9) 60.54 (C_e), 39.96 (C_d) 26.55 (C_c), 23.52 (C_b) 14.25 (C_a) (C_g, *C*-9 and *C*-17 could only be detected *via* cross signals of HMBC experiments) ppm.

MS (MALDI-TOF, DCTB, pos. mode): *m/z* = 1832.76692 [**A$_2$B*$^{Ph}_2$**]$^+$, 2317.07676 [M]$^+$.

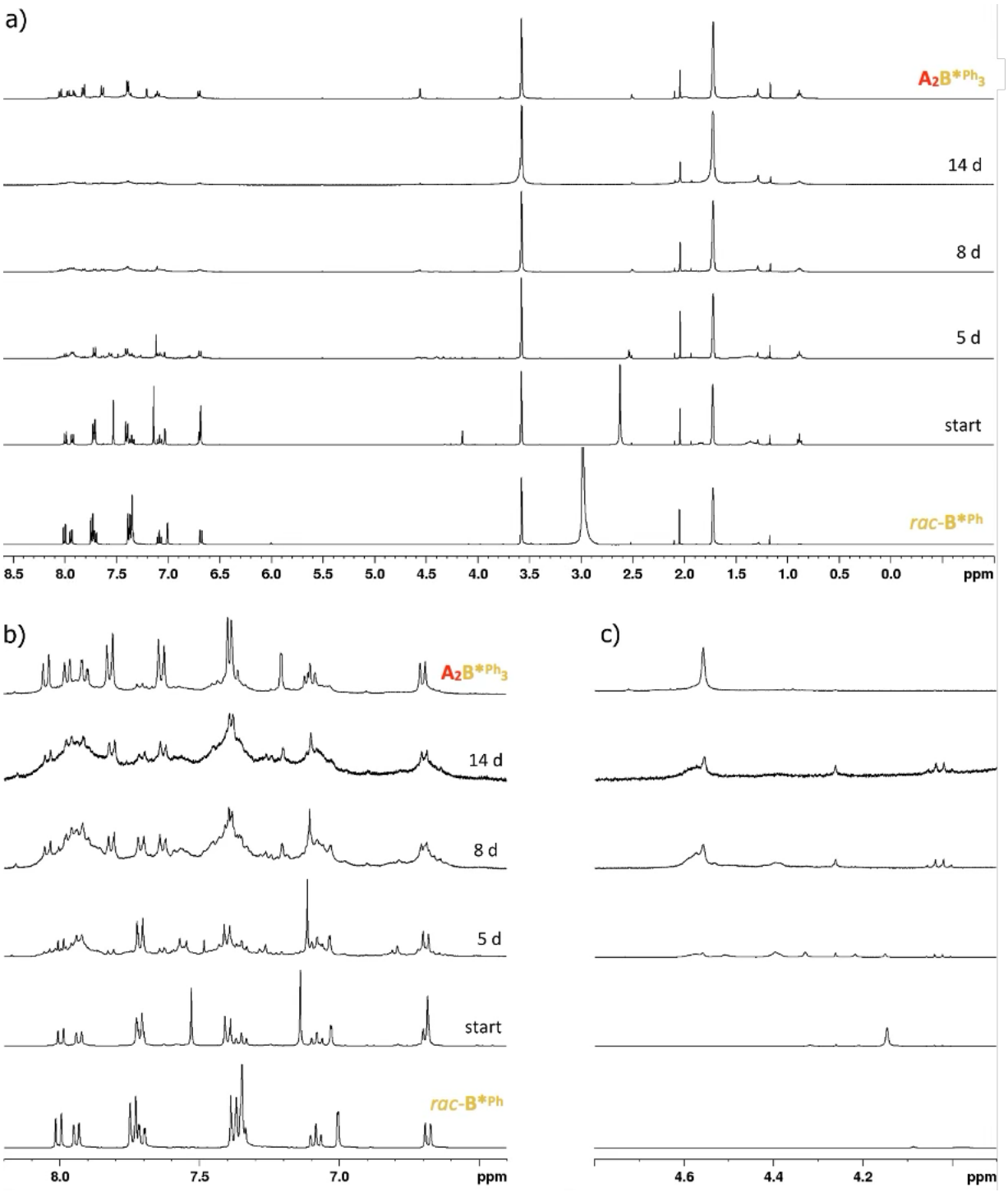


Figure S46. ^{1}H NMR (400 MHz, THF-d_8, 298 K, c(**A**) = 1.55×10^{-2} mol L^{-1}, c(*rac*-**B*^{Ph}**) = 2.32×10^{-2} mol L^{-1}) reaction monitoring for self-sorting experiment with **A** and *rac*-**B*^{Ph}** directly after mixing and after five, eight and 14 days: a) overview, b) details of the aromatic region, and c) details of the bridgehead region.

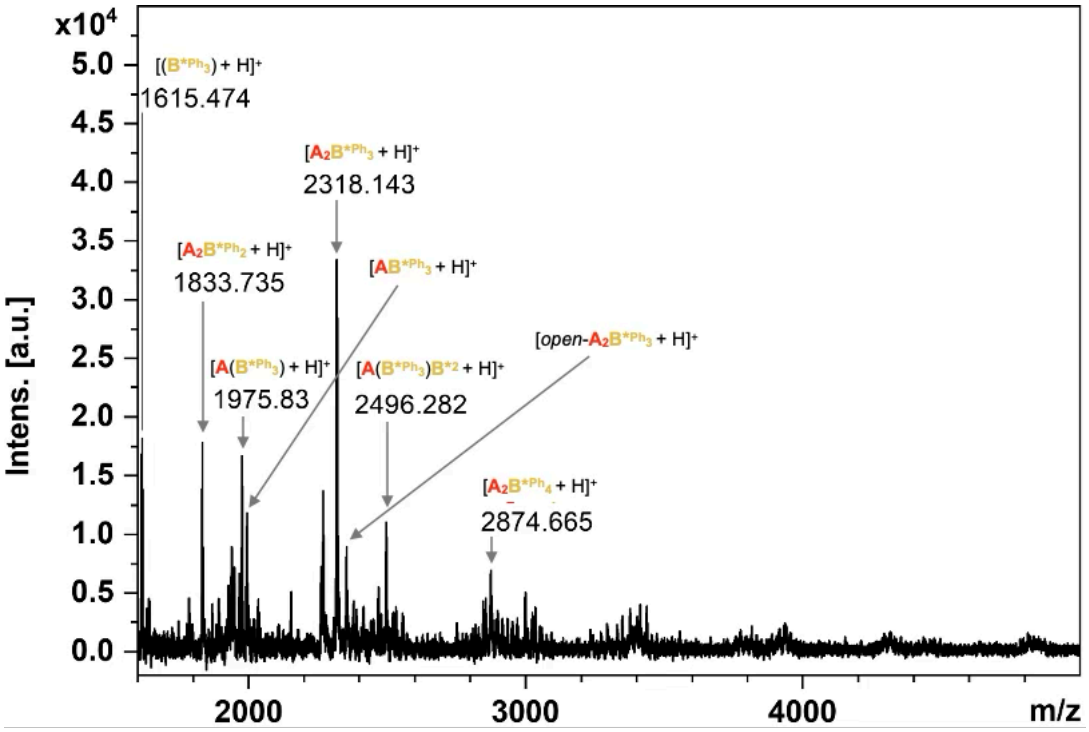


Figure S47. MS (MALDI-TOF, DCTB in $CHCl_3$, positive mode) of the reaction mixture of the self-sorting experiment with TBTQ **A** and racemic elongated linker *rac*-**B*^{Ph}** after six days.

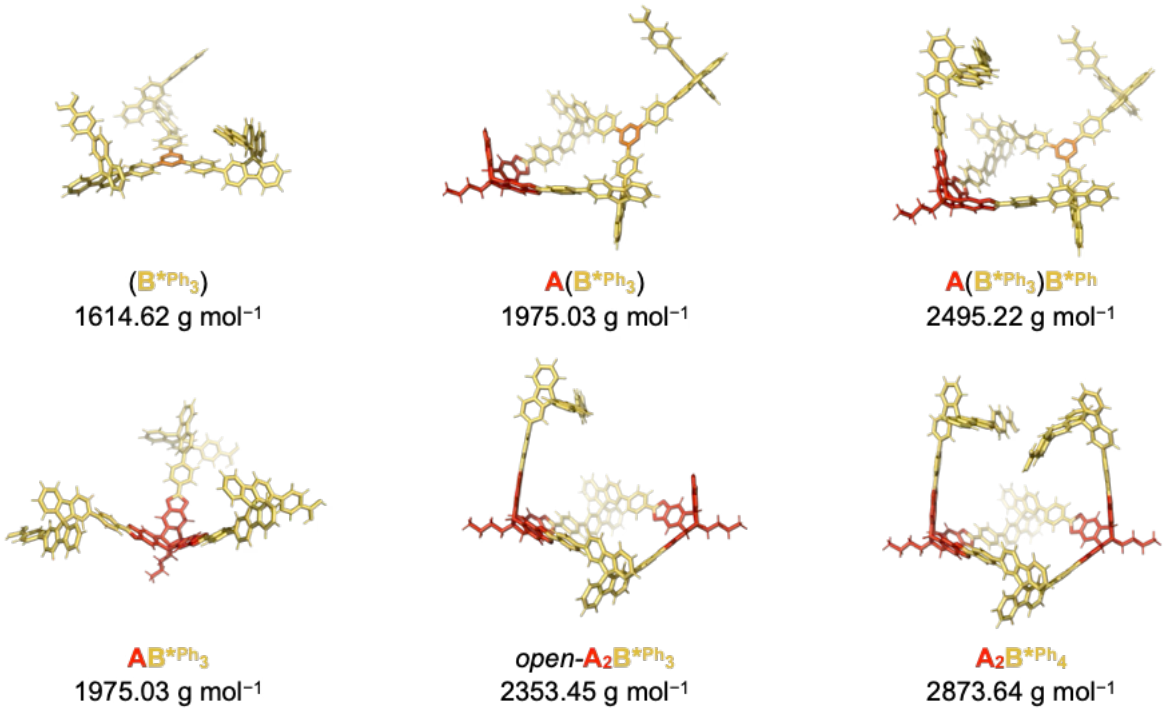


Figure S48. Molecular structures (MMFF geometry optimization with Spartan'20[S11], images generated with Pymol[S12]) and molar mass for possible side products for the self-sorting experiment with TBTQ **A** and racemic elongated linker *rac*-**B*^{Ph}**.

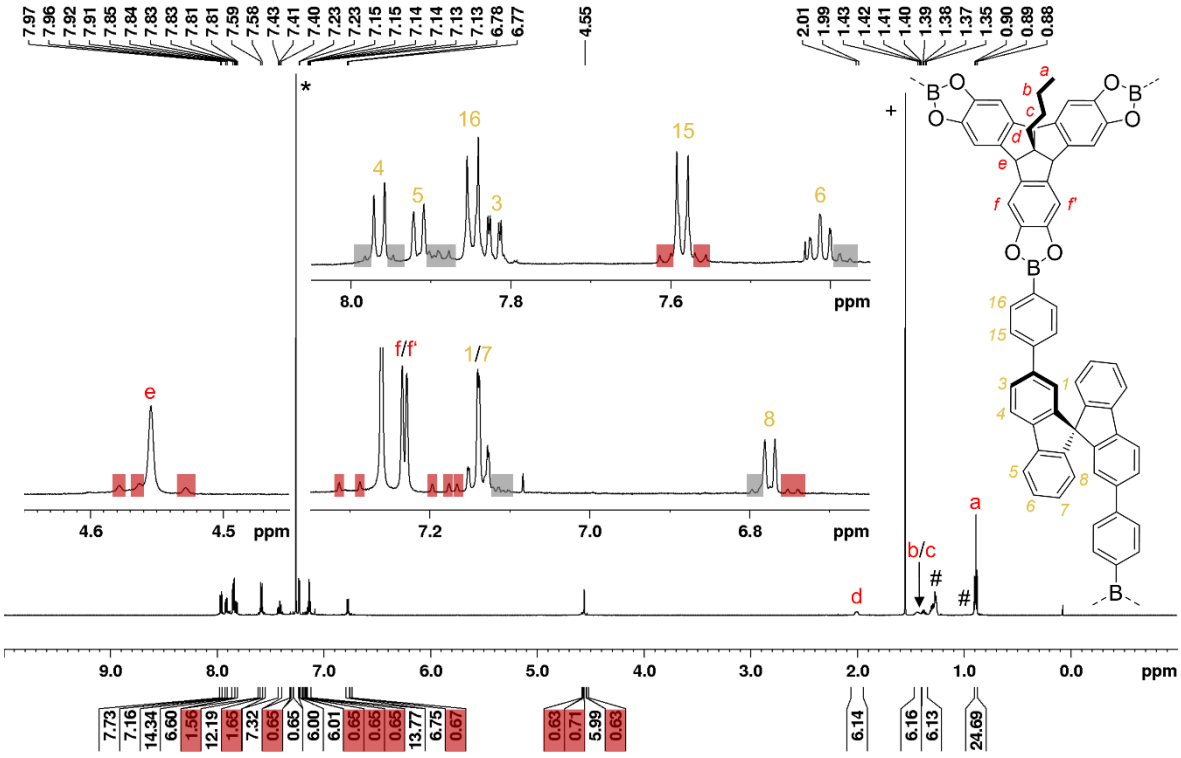


Figure S49. ^{1}H NMR (600 MHz, $CDCl_3$, rt) spectrum of the soluble mixture isolated from the self-sorting experiment of **A** with *rac*-**B*^{Ph}**; signals for the macrocyclic side product are indicated in red and grey (* $CHCl_3$, $^{+}$ H_2O, $^{\#}$ *n*-hexane, H grease).

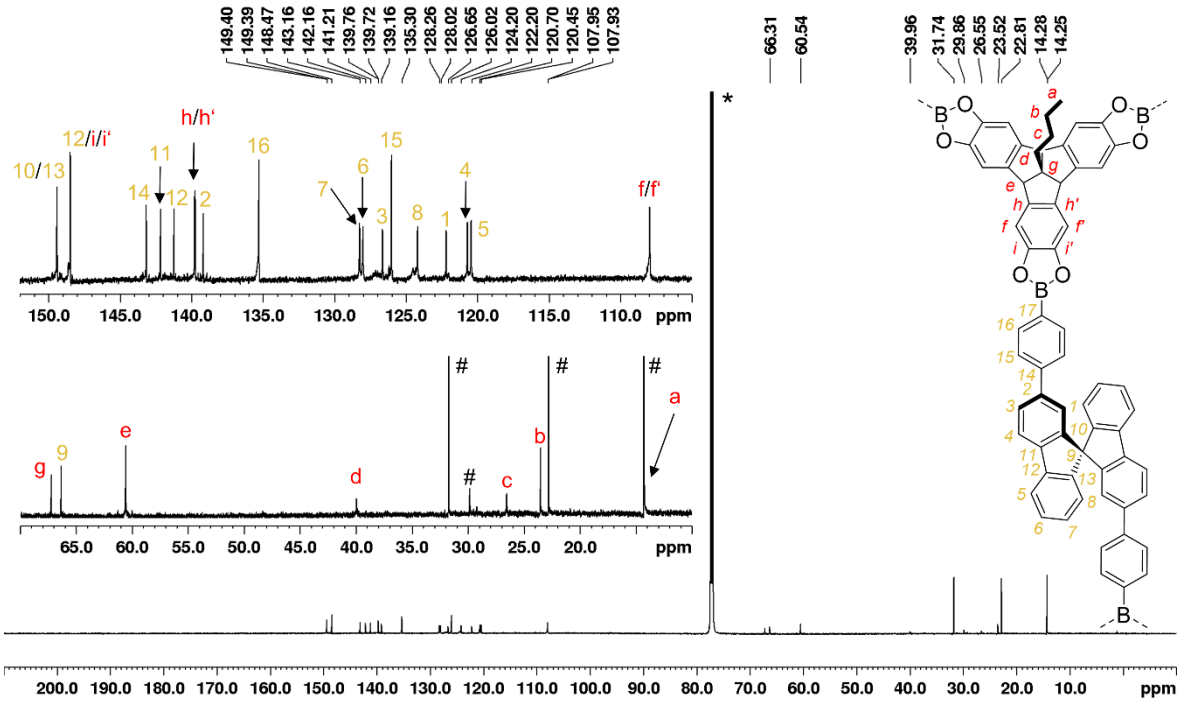


Figure S50. ^{13}C NMR (101 MHz, $CDCl_3$, rt) spectrum of the soluble mixture isolated from the self-sorting experiment of **A** with *rac*-**B*^{Ph}** (* $CHCl_3$, $^{\#}$ *n*-hexane, H grease).

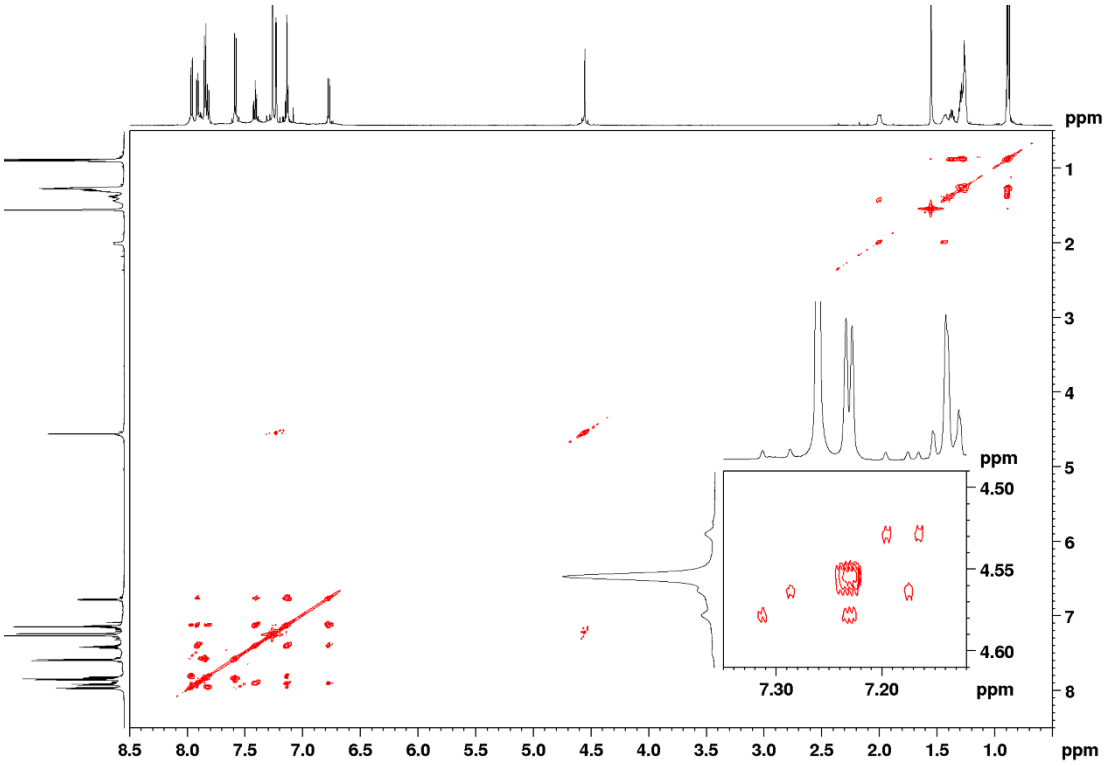


Figure S51. ^{1}H–^{1}H COSY (600 MHz, $CDCl_3$, rt) spectrum of the soluble mixture isolated from the self-sorting experiment of **A** with *rac*-**B**^{*Ph}.

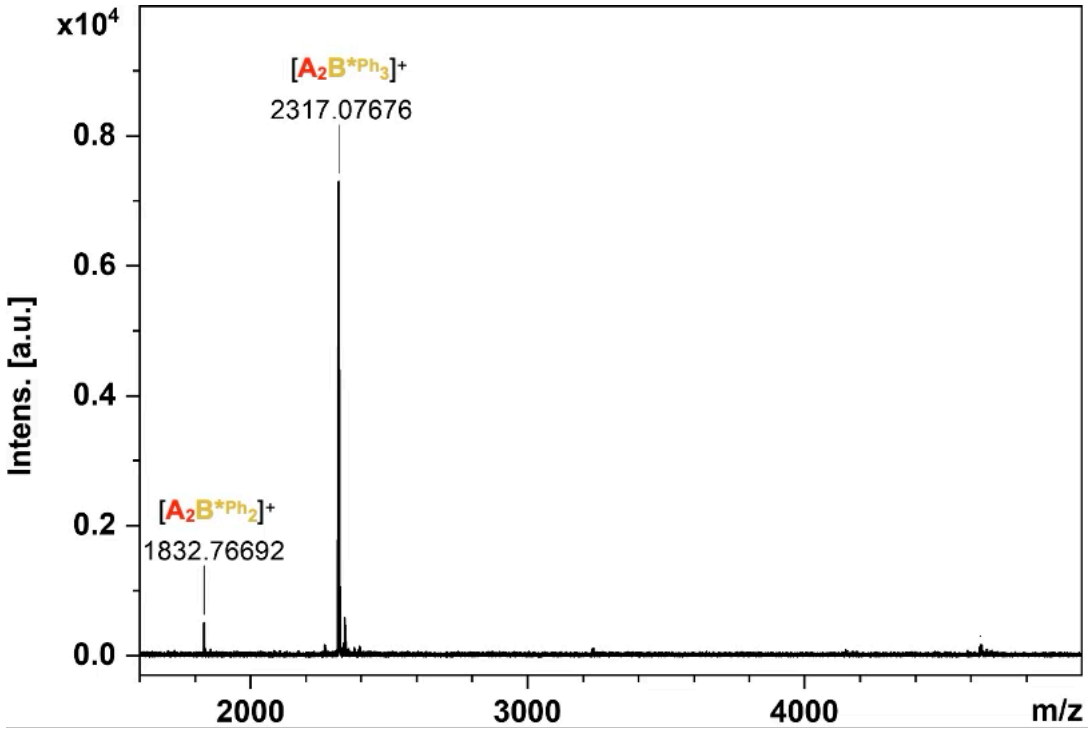


Figure S52. MS (MALDI-TOF, DCTB in $CHCl_3$, positive mode) of the soluble mixture isolated from the self-sorting experiment of **A** with *rac*-**B**^{*Ph}.

6 Molecular Modeling

For all macrocyclic and cage structures, geometry optimization in the gas phase was performed in Spartan'20[S11] with the semiempirical PM6 method. For a visualization of the solvodynamic radius derived from the DOSY measurements, a semi-transparent sphere with the corresponding size was placed at the center of gravity of the cages.

For an estimation of the inherent strain energy that is accumulated during the formation of the macrocyclic intermediates and the final cage assemblies, we defined a series of homodesmotic reaction equation, which assembles the closed structures from the individual building blocks. To account for solvent effects and any enthalpic contributions from the formation of boronate esters from free boronic acids and catechols, any unreacted sides in both the building blocks and macrocyclic intermediates were saturated by reaction with either phenylboronic acid (BPh) or pyrocatechol (cat). To balance stochiometry, the mono-condensation product (BPh)(cat) of these two stopper units was introduced. For all these structures, heats of formation were obtained after semiempirical PM6 geometry optimization in the gas phase with Spartan'20.[S11] Relative strain energies were estimated by the difference of the summed heats of formations for the products and reactants in the homodesmotic reactions.

Images of the molecular structures after geometry optimization were produced with Pymol.[S12]

homodesmotic reaction for macrocycle formation:

$$2\times\mathbf{A}(\mathrm{BPh})_3 \;+\; 2\times\mathbf{B}(\mathrm{cat})_2 \;\rightarrow\; \mathbf{A_2B_2}(\mathrm{BPh})_2 \;+\; 4\times(\mathrm{BPh})(\mathrm{cat})$$

homodesmotic reaction for cage formation:

$$2\times\mathbf{A}(\mathrm{BPh})_3 \;+\; 3\times\mathbf{B}(\mathrm{cat})_2 \;\rightarrow\; \mathbf{A_2B_3} \;+\; 6\times(\mathrm{BPh})(\mathrm{cat})$$

Table S2. Heats of formation and strain energies for homodesmotic reactions.

		short linker **B***		elongated linker **B*^{Ph}**	
		ΔH_f [kJ mol^{-1}]	**strain** [kJ mol^{-1}]	**ΔH_f** [kJ mol^{-1}]	**strain** [kJ mol^{-1}]
A(BPh)$_3$		−1059.65			
reference (BPh)(cat)		−340.06			
B(cat)$_2$		−425.25		−235.47	
homochiral macrocycles	*cis*	−1605.09	4.45	−1229.67	0.31
	trans	−1597.65	11.89	−1229.28	0.70
homochiral cage		−1349.55	5.10	−761.56	23.76
heterochiral macrocycles	*cis*	−1601.09	8.44	−1229.23	0.75
	trans-1	−1593.90	15.64	−1229.91	0.07
	trans-2	−1602.10	7.44	−1227.53	2.45
heterochiral cage		−1324.26	30.40	−755.91	29.41

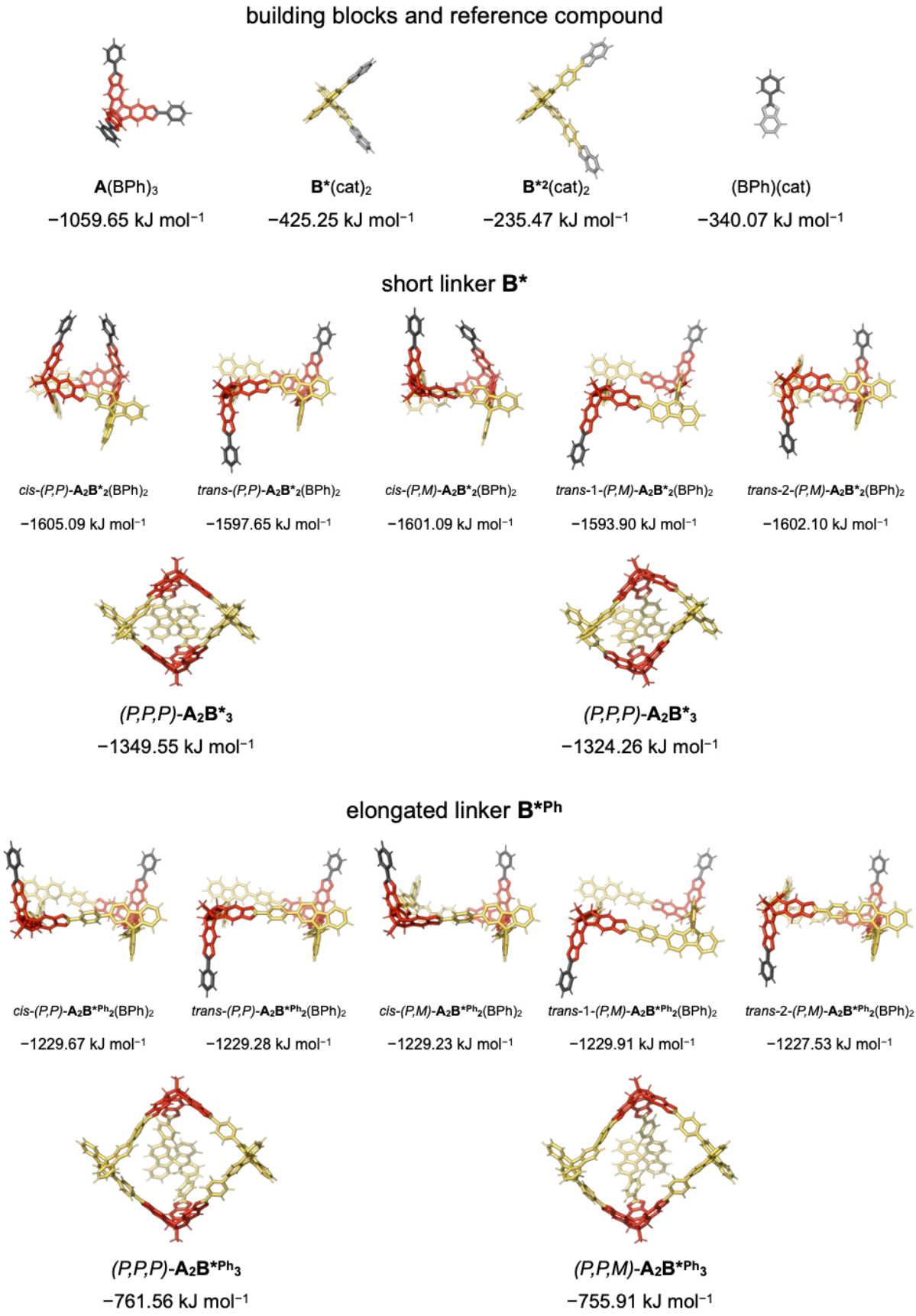


Figure S53. Molecular structures (generated with Pymol[S12]) and heats of formation (kJ mol^{-1}, gas phase, PM6, Spartan'20[S11]) for cages, saturated precursors and macrocycles, and a reference compound.

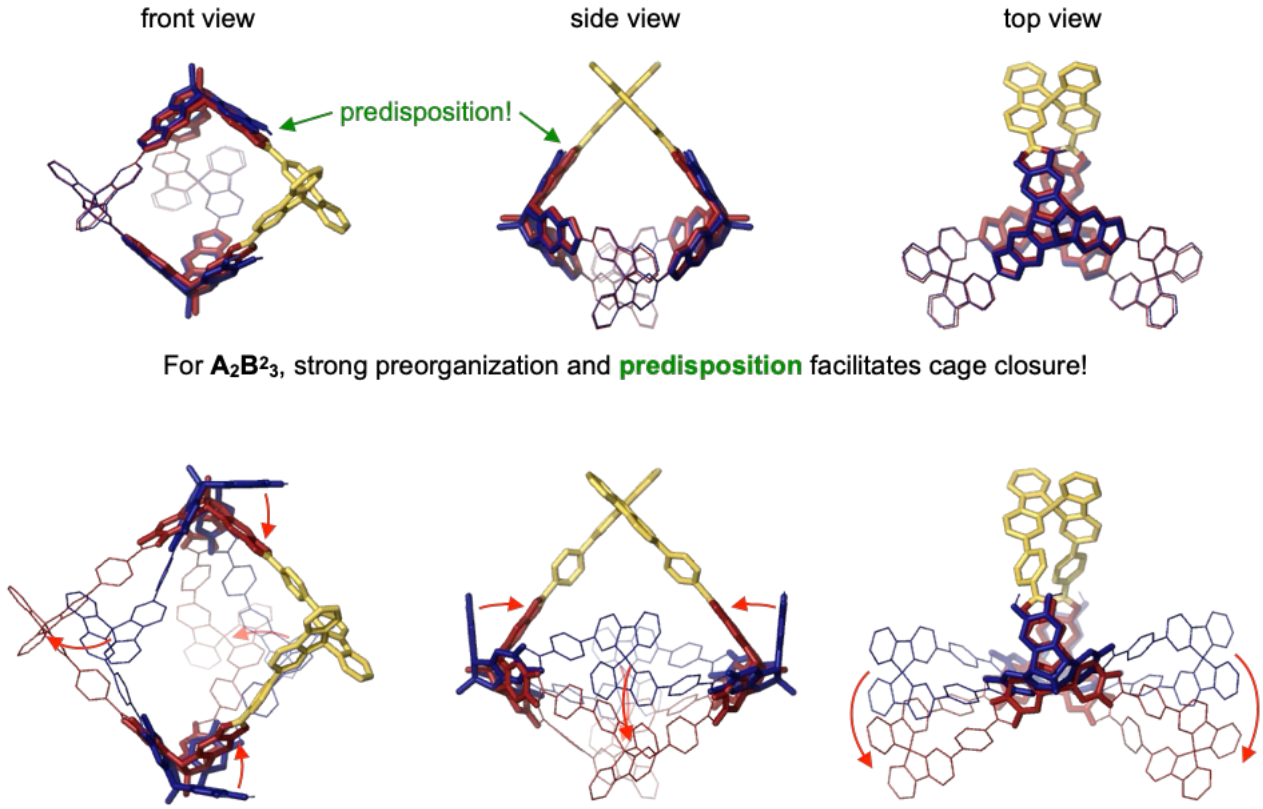


Figure S54. Overlay of PM6-geometry-optimized relaxed structures for *on-pathway* intermediates *cis-(P,P)*-$\mathbf{A_2B_2}$ (blue) and final cages *(P,P,P)*-$\mathbf{A_2B_3}$ (red, additional linker in yellow) for short linker **B*** (top) and elongated linker $\mathbf{B^{*Ph}}$ (bottom); excellent superposition of open intermediate and closed cage for **B*** indicates excellent predisposition and preorganization which facilitates cage formation; for $\mathbf{B^{*Ph}}$, significant rearrangement introduces severe macrocyclic strain during final cage closure.

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S11 *Spartan'20*, Wavefunction Inc., Irvine, CA (USA).

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