Halogenoborane mediated allene cyclooligomerization

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Supporting Information

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**General Information.** All reactions involving air- or moisture-sensitive compounds were carried out under an inert gas atmosphere (Argon) by using Schlenk-type glassware or in a glovebox. All solvents were dried and degassed before use, if necessary for the respective reaction. Chemicals: Unless otherwise noted all chemicals were used as purchased. The following instruments were used for physical characterization of the compounds: elemental analyses: Foss-Heraeus CHNO-Rapid; NMR: Varian UNITY plus NMR spectrometer ($^1$H, 600 MHz; $^{13}$C, 151 MHz; $^{11}$B, 192 MHz; $^{19}$F, 564 MHz; $^{31}$P, 243 MHz). NMR chemical shifts are given relative to SiMe$_4$ and referenced to the respective solvent signals ($^1$H and $^{13}$C) or external standard [$\delta$(BF$_3$·OEt$_2$) = 0 for $^{11}$B NMR, $\delta$(CFCl$_3$·OEt$_2$) = 0 for $^{19}$F NMR]. NMR assignments were supported by additional 2D NMR experiments.

**X-Ray diffraction:** For compound 12 data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, Methods Enzymol. 1997, 276, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, Acta Crystallogr. 2003, A59, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, Acta Crystallogr. 1990, A46, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, Acta Crystallogr. 2008, A64, 112-122). Data sets for compounds 4b and 15e were collected with a D8 Venture CMOS diffractometer. For compound 4a data sets were collected with a Bruker APEX II CCD diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., 2016); cell refinement: SAINT V8.37A (Bruker AXS Inc., 2015); data reduction: SAINT V8.37A (Bruker AXS Inc., 2015); absorption correction, SADABS V2014/7 (Bruker AXS Inc., 2014); structure solution SHELXT-2015 (Sheldrick, 2015); structure refinement SHELXL-2015 (Sheldrick, 2015) and graphics, XP (Bruker AXS Inc., 2015).

$R$-values are given for observed reflections, and $wR^2$ values are given for all reflections. **Exceptions and special features:** For compounds 4a and 4b the CH$_2$-CCl=CH$_2$ and CH$_2$-CBr=CH$_2$ units were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. Moreover, for compound 4a a badly disordered half C$_3$H$_4$ (allene) molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek, A.L. (2015). Acta Cryst. C71, 9-18) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed allene molecule. For compound 15e two cyclohexyl and
one methyl groups were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. CCDC deposition numbers are 1862533 to 1862535 and 1881527.

Materials. CIB(C₆F₅)₂ and BrB(C₆F₅)₂ were prepared according to procedures described in the literature [J. Li, C. G. Daniliuc, G. Kehr and G. Erker, Chem. Commun., 2018, 54, 6344; A. Ueno, J. Li, C. G. Daniliuc, G. Kehr and G. Erker, Chem. Eur. J., 2018, 24, 10044]. Allene was purchased from abcr GmbH in 96% purity, and used as received. Compound 14e was prepared according to the procedures described in the literature [X. Tao, G. Kehr, C. G. Daniliuc and G. Erker, Angew. Chem. Int. Ed., 2017, 56, 1376].

A) Reaction of CIB(C₆F₅)₂ with excess allene

Scheme S1.

\[
\text{CIB(C}_6\text{F}_5)_2 \xrightarrow{\text{excess allene}} \begin{array}{c}
\text{1} \\
\end{array} + \begin{array}{c}
\text{3a} \\
\text{Cl} \\
\end{array}
\]

CIB(C₆F₅)₂ (22.8 mg, 0.06 mmol) was dissolved in d₈-toluene (0.5 mL) in a Young NMR tube. After evacuating the tube, the solution was exposed to allene gas for several minutes at room temperature. Then the resulting reaction mixture was characterized by NMR experiments.

The reaction after 7 hours at r.t.: a mixture with allene (ca. 75 mol%, ¹H), compound 1 (ca. 8 mol%, ¹H), compound 3a (ca. 7 mol%, ¹H), and unreacted CIB(C₆F₅)₂ (ca. 10 mol%, ¹⁹F) as major components.

The reaction after 24 hours at r.t.: a mixture with allene (ca. 68 mol%, ¹H), compound 1 (ca. 15 mol%, ¹H), compound 3a (ca. 14 mol%, ¹H), and unreacted CIB(C₆F₅)₂ (ca. 3 mol%, ¹⁹F) as major components.

The reaction after 48 hours at r.t.: a mixture with allene (ca. 70 mol%, ¹H), compound 1 (ca. 15 mol%, ¹H), compound 3a (ca. 14 mol%, ¹H) and unreacted CIB(C₆F₅)₂ (ca. < 1 mol%, ¹⁹F) as major components.

The NMR data of compound 1 in the reaction mixture are consistent with those reported in the literature [X. Tao, G. Kehr, C. G. Daniliuc and G. Erker, Angew. Chem. Int. Ed., 2017, 56, 1376]

NMR data of compound 1:
$^1$H NMR (600 MHz, 299 K, $d_8$-toluene): $\delta$ $^1$H: 4.53 (m, 2H, =CH$_2$), 2.70 (m, 2H, CH$_2$).

$^{13}$C($^1$H) NMR (151 MHz, 299 K, $d_8$-toluene): $\delta$ $^{13}$C: 145.9 (=C), 107.8 (=CH$_2$), 43.4 (CH$_2$).

Compound 3a was characterized by NMR experiments from the reaction mixture after 7 hours at r.t.: NMR data of compound 3a:

$^1$H NMR (600 MHz, 299 K, $d_8$-toluene): $\delta$ $^1$H: [5.08, 4.84](each m, each 1H, 9-CH$_2$=), [4.63, 4.48](each m, each 2H, 4,6-CH$_2$=), [2.58, 2.54](each d, $^2$$J_{HH}$ = 14.0 Hz, each 1H, 5-CH$_2$), 2.26 (s, 2H, 8-CH$_2$), [2.24, 2.00](each d, $^2$$J_{HH}$ = 14.0 Hz, each 2H, 3,7-CH$_2$), 2.18 (s, 2H, BCH$_2$).

$^{13}$C($^1$H) NMR (151 MHz, 299 K, $d_8$-toluene): $\delta$ $^{13}$C: 146.6 (dm, $^1$$J_{FC}$ $\sim$ 240 Hz, C$_6$F$_5$), 144.1 (4,6-C=), 143.4 (dm, $^1$$J_{FC}$ $\sim$ 250 Hz, C$_6$F$_5$), 140.0 (CCl=), 137.7 (dm, $^1$$J_{FC}$ $\sim$ 250 Hz, C$_6$F$_5$), 117.1 (9-CH$_2$=), 115.7 (br, i-C$_6$F$_5$), 111.2 (4,6-CH$_2$=), 48.5 (8-CH$_2$), 46.6 (3,7-CH$_2$), 43.38 (5-CH$_2$), 42.9 (2-C), 42.2 (br, BCH$_2$).

$^{19}$F NMR (564 MHz, 299 K, $d_8$-toluene): $\delta$ $^{19}$F: $[-129.3$ (m, 2F, o), $-147.9$ (tt, $^3$$J_{FF}$ = 21.0 Hz, $^4$$J_{FF}$ = 4.4 Hz, 1F, $p$), $-161.1$ (m, 2F, m)](C$_6$F$_5$)$[\Delta\delta^{19}$F$_{m,p} = 13.2]$.  

$^{11}$B($^1$H) NMR (192 MHz, 299 K, $d_8$-toluene): $\delta$ $^{11}$B: 71.5 ($\nu_{J_{11B}}$ $\sim$ 1000 Hz).
Figure S1. $^1$H NMR (600 MHz, 299 K, $d_8$-toluene*) spectra of the mixture of the reaction of ClB(C$_6$F$_5$)$_2$ with excess allene after different reaction times at r.t.: 7 hours (spectrum 1); 24 hours (spectrum 2); 48 hours (spectrum 3). [a: allene]

Figure S2. $^{13}$C($^1$H) NMR (151 MHz, 299 K, $d_8$-toluene*) spectrum of the mixture of the reaction of ClB(C$_6$F$_5$)$_2$ with excess allene after 7 hours at r.t. [a: allene]
Figure S3. $^1$H/$^{13}$C GHSQC (600 MHz/151 MHz, 299 K, d$_8$-toluene*) spectrum of the mixture of the reaction of ClB(C$_6$F$_5$)$_2$ with excess allene after 7 hours at r.t. [a: allene]

Figure S4. $^{11}$B[$^1$H] NMR (192 MHz, 299 K, d$_8$-toluene) spectra of (1) ClB(C$_6$F$_5$)$_2$ and the mixture of the reaction of ClB(C$_6$F$_5$)$_2$ with excess allene after different reaction times at r.t.: (2) 7 hours, (3) 24 hours, and (4) 48 hours.
Figure S5. $^{19}$F NMR (564 MHz, 299 K, d$_8$-toluene) spectra of (1) ClB(C$_6$F$_5$)$_2$ and the mixture of the reaction of ClB(C$_6$F$_5$)$_2$ with excess allene after different reaction times at r.t.: (2) 7 hours, (3) 24 hours, and (4) 48 hours.

B) Reaction of BrB(C$_6$F$_5$)$_2$ with excess allene

Scheme S2.

BrB(C$_6$F$_5$)$_2$ (25.4 mg, 0.06 mmol) was dissolved in d$_8$-toluene (0.5 mL) in a Young NMR tube. After evacuating the tube, the solution was exposed to allene gas for several minutes at room temperature. Then the resulting reaction mixture was characterized by NMR experiments after 4 hours at room temperature: a mixture with allene (ca. 91 mol%, $^1$H), compound 1 (ca. 3 mol%, $^1$H), and compound 3b (ca. 6 mol%, $^1$H) as major components.

The NMR data of compound 1 in the reaction mixture are consistent with those reported in the literature [X. Tao, G. Kehr, C. G. Daniliuc and G. Erker, Angew. Chem. Int. Ed., 2017, 56, 1376.]

NMR data of compound 1:
$^{1}$H NMR (600 MHz, 299 K, d$_8$-toluene): $\delta$ H: 4.53 (m, 2H, =CH$_2$), 2.70 (m, 2H, CH$_2$).

$^{13}$C{$^1$H} NMR (151 MHz, 299 K, d$_8$-toluene): $\delta$ C: 145.9 (=C), 107.8 (=CH$_2$), 43.44 (CH$_2$).

Compound 3b was characterized by NMR spectroscopy from the reaction mixture after 7 hours at r.t., NMR data of compound 3b:

$^{1}$H NMR (600 MHz, 299 K, d$_8$-toluene): $\delta$ H: [5.34, 5.27](each m, each 1H, 9-CH$_2$), [4.62, 4.48](each m, each 2H, 4,6-CH$_2$), [2.57, 2.53](each d, 2$J_{HH}$ = 14.0 Hz, each 1H, 5-CH$_2$), 2.38 (s, 2H, 8-CH$_2$), [2.27, 1.97](each d, 2$J_{HH}$ = 14.0 Hz, each 2H, 3,7-CH$_2$), 2.21 (s, 2H, BCH$_2$).

$^{13}$C{$^1$H} NMR (151 MHz, 299 K, d$_8$-toluene): $\delta$ C: 146.6 (dm, 1$J_{FC}$ ~ 240 Hz, C$_6$F$_5$), 144.1 (4,6-C=), 143.4 (dm, 1$J_{FC}$ ~ 260 Hz, C$_6$F$_5$), 137.7 (dm, 1$J_{FC}$ ~ 250 Hz, C$_6$F$_5$), 130.3 (CBr=), 121.7 (9-CH$_2$), 115.7 (br, i-C$_6$F$_5$), 111.2 (4,6-CH$_2$), 50.6 (8-CH$_2$), 46.5 (3,7-CH$_2$), [43.36, 43.35](2-C, 5-CH$_2$), 42.2 (br, BCH$_2$).

$^{19}$F NMR (564 MHz, 299 K, d$_8$-toluene): $\delta$ F: [-129.3 (m, 2F, o), -147.9 (t, 3$J_{FF}$ = 21.0 Hz, 1F, p), -161.1 (m, 2F, m)]C$_6$F$_5$)[$\Delta \delta^{19}$F$_{m,p}$ = 13.1].

$^{11}$B{$^1$H} NMR (192 MHz, 299 K, d$_8$-toluene): $\delta$ B: 72.3 ($\nu_{3/2}$ ~ 1200 Hz).
Figure S6. $^1$H NMR (600 MHz, 299 K, d$_8$-toluene*) spectrum of the mixture of the reaction of BrB(C$_6$F$_5$)$_2$ with excess allene after 4 hours at r.t. [a: allene]

Figure S7. $^1$H/$^{13}$C GHSQC (600 MHz/151 MHz, 299 K, d$_8$-toluene*) spectrum of the mixture of the reaction of BrB(C$_6$F$_5$)$_2$ with excess allene after 4 hours at r.t. [a: allene]
Figure S8. $^{13}\text{C}^1\text{H}$ NMR (151 MHz, 299 K, $d_8$-toluene*) spectrum of the mixture of the reaction of BrB(C$_6$F$_5$)$_2$ with excess allene after 4 hours at r.t. [a: allene]

Figure S9. $^{11}\text{B}^1\text{H}$ NMR (192 MHz, 299 K, $d_8$-toluene) spectra of (1) BrB(C$_6$F$_5$)$_2$ and (2) the mixture of the reaction of BrB(C$_6$F$_5$)$_2$ with excess allene after 4 hours at r.t.
Figure S10. $^{19}$F NMR (564 MHz, 299 K, $d_8$-toluene) spectra of (1) BrB(C$_6$F$_5$)$_2$ and (2) the mixture of the reaction of ClB(C$_6$F$_5$)$_2$ with excess allene after 4 hours at r.t.

C) Synthesis of compound 4a

Scheme S3.

ClB(C$_6$F$_5$)$_2$ (120 mg, 0.320 mmol) was dissolved in $d_8$-toluene (2.0 mL) in a Schlenk tube. After evacuating the Schlenk tube, the solution was exposed to allene gas for several minutes at room temperature. Then the resulting reaction mixture was stirred for 48 hours at room temperature. Subsequently, pyridine (30.0 mg, 0.380 mmol) was added. After stirring the reaction mixture for 10 min. at room temperature, all volatiles were removed in vacuo and the residue was washed with pentane (1 mL × 3). Drying of the remaining solid in vacuo gave compound 4a (105 mg, 0.170 mmol, 53%) as a white powder.

**Anal. Calc.** for C$_{29}$H$_{21}$BClF$_{10}$N: C, 56.20; H, 3.42; N, 2.26. Found: C, 56.77; H, 3.62; N, 2.24.
NMR data of compound 4a:

\[ \text{1H NMR } (600 \text{ MHz, } 299 \text{ K, } \text{CD}_2\text{Cl}_2) \]: δ \text{1H}: 8.77 (m, 2H, o-Py), 8.07 (m, 1H, p-Py), 7.64 (m, 2H, m-Py), [5.32, 5.12](each m, each 1H, 9-CH\_2=), [4.67, 4.47](each m, each 2H, 4,6-CH\_2=), [2.73, 2.57](each dm, \text{2J}_{HH} = 14.0 \text{ Hz, each 1H, 5-CH}_2), 2.39 (s, 2H, 8-CH\_2), [2.21, 1.68](each d, \text{2J}_{HH} = 13.5 \text{ Hz, each 2H, 3,7-CH}_2), 1.74 (s, 2H, BCH\_2).

\[ \text{13C}^{\text{1H}} \text{NMR } (151 \text{ MHz, } 299 \text{ K, } \text{CD}_2\text{Cl}_2) \]: δ \text{13C}: 148.6 (dm, \text{1J}_{FC} \sim 240 \text{ Hz, C}_6\text{F}_5), 146.2 (4,6-C=), 145.5 (o-Py), 141.9 (p-Py), 141.1 (CCl=), 140.0 (dm, \text{1J}_{FC} \sim 250 \text{ Hz, C}_6\text{F}_5), 137.7 (dm, \text{1J}_{FC} \sim 250 \text{ Hz, C}_6\text{F}_5), 126.7 (m-Py), 121.5 (br, i-C\_6\text{F}_5), 116.6 (9-CH\_2=), 109.6 (4,6-CH\_2=), 48.7 (8-CH\_2), 44.4 (3,7-CH\_2), 43.9 (5-CH\_2), 39.9 (2-C), 31.2 (br, BCH\_2).

\[ \text{19F NMR } (564 \text{ MHz, } 299 \text{ K, } \text{CD}_2\text{Cl}_2) \]: δ \text{19F}: [−129.4 (m, 2F, o), −158.4 (t, \text{3J}_{FF} = 21.0 \text{ Hz, 1F, p}), −164.0 (m, 2F, m)](\text{C}_6\text{F}_5)[\Delta \delta^{19F}_{m,p} = 5.6].

\[ \text{11B}^{\text{1H}} \text{NMR } (192 \text{ MHz, } 299 \text{ K, } \text{CD}_2\text{Cl}_2) \]: δ \text{11B}: −1.4 (\text{v}_\text{zz} \sim 250 \text{ Hz}).

Figure S11. \text{1H NMR } (600 \text{ MHz, } 299 \text{ K, } \text{CD}_2\text{Cl}_2*) spectrum of compound 4a. [P: pentane; Py: pyridine]
Figure S12. $^{11}$B($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 4a.

Figure S13. $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 4a.[Py: pyridine]
Single crystals suitable for the X-ray crystal structure analysis were obtained from diffusion of pentane vapor to a solution of the white powder in CH₂Cl₂ at room temperature.

**X-ray crystal structure analysis of compound 4a (erk9164):** A colorless plate-like specimen of C₂₉H₂₁BCIF₁₀N, approximate dimensions 0.020 mm x 0.060 mm x 0.100 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1882 frames were collected. The total exposure time was 34.10 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 20385 reflections to a maximum θ angle of 66.76° (0.84 Å resolution), of which 4780 were independent (average redundancy 4.265, completeness = 98.3%, R_int = 9.58%, R_sig = 10.26%) and 2842 (59.46%) were greater than 2σ(F²). The final cell constants of a = 10.2284(12) Å, b = 11.0264(13) Å, c = 12.5397(13) Å, α = 88.589(8)°, β = 80.364(7)°, γ = 79.511(8)°, volume = 1371.0(3) Å³, are based upon the refinement of the XYZ-centroids of 2983 reflections above 20σ(I) with 8.155° < 2θ < 129.2°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.823. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8210 and 0.9600. The
structure was solved and refined using the Bruker SHELXTL Software Package, using the space group \( P \bar{1} \), with \( Z = 2 \) for the formula unit, \( \text{C}_{29}\text{H}_{21}\text{BClF}_{10}\text{N} \). The final anisotropic full-matrix least-squares refinement on \( F^2 \) with 408 variables converged at \( R_1 = 5.70\% \), for the observed data and \( wR_2 = 16.70\% \) for all data. The goodness-of-fit was 0.972. The largest peak in the final difference electron density synthesis was \( 0.267 \text{ e/Å}^3 \) and the largest hole was \(-0.255 \text{ e/Å}^3 \) with an RMS deviation of \( 0.059 \text{ e/Å}^3 \). On the basis of the final model, the calculated density was \( 1.501 \text{ g/cm}^3 \) and \( F(000), 628 \text{ e}^- \). CCDC deposition number 1862533.

**Figure S15.** Crystal structure of compound 4a (thermal ellipsoids: 15% probability)
D) Synthesis of compound 4b

**Scheme S4.**

BrB(C₆F₅)₂ (127 mg, 0.300 mmol) was dissolved in d₈-toluene (2.0 mL) in a Schlenk tube. After evacuating the tube, the solution was exposed to allene gas for several minutes at room temperature. Then the resulting reaction mixture was stirred for 48 hours at room temperature. Subsequently, pyridine (30.0 mg, 0.380 mmol) was added to the resulting reaction mixture. After stirring for 10 min at room temperature, all volatiles were removed in vacuo and the residue was washed with pentane (1 mL × 3). Drying of the remaining solid in vacuo gave compound 4b (144 mg, 0.220 mmol, 72%) as a white powder.

**Anal. Calc.** for C₂₉H₂₁BBrF₁₀N: C, 52.44; H, 3.19; N, 2.11. Found: C, 52.47; H, 3.23; N, 2.10.

NMR data of compound 4b:

**¹H NMR** (600 MHz, 299 K, CD₂Cl₂): δ ¹H: 8.79 (m, 2H, o-Py), 8.07 (m, 1H, p-Py), 7.64 (m, 2H, m-Py), [5.60, 5.57](each m, each 1H, 9-CH₂=), [4.66, 4.47](each m, each 2H, 4,6-CH₂=), [2.73, 2.57](each dm, ²JHH = 14.0 Hz, each 1H, 5-CH₂), 2.52 (s, 2H, 8-CH₂), [2.23, 1.68](each d, ²JHH = 13.5 Hz, each 2H, 3,7-CH₂), 1.77 (s, 2H, BCH₂).

**¹³C¹H NMR** (151 MHz, 299 K, CD₂Cl₂): δ ¹³C: 148.6 (dm, ¹JC ~ 240 Hz, C₆F₅), 146.1 (4,6-C=), 145.5 (o-Py), 141.9 (p-Py), 140.0 (dm, ¹JC ~ 250 Hz, C₆F₅), 137.6 (dm, ¹JC ~ 250 Hz, C₆F₅), 131.6 (CBr=), 126.7 (m-Py), 121.5 (br, i-C₆F₅), 121.3 (9-CH₂=), 109.6 (4,6-CH₂=), 50.4 (8-CH₂), 44.3 (3,7-CH₂), 43.8 (5-CH₂), 40.4 (2-C), 31.5 (br, BCH₂).
$^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{19}$F: $[-129.4$ (m, 2F, o), $-158.4$ (t, $^{3}J_{FF} = 21.0$ Hz, 1F, p), $-164.0$ (m, 2F, m)](C$_6$F$_5$)[$\Delta\delta^{19}$F$_{m,p} = 5.6$].

$^{11}$B$^{1}$H NMR (192 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{11}$B: $-1.4$ ($\nu_{1/2} \sim 220$ Hz).

**Figure S16.** $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$*) spectrum of compound 4b. [P: pentane; Py: pyridine]

**Figure S17.** $^{11}$B$^{1}$H NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 4b.
Figure S18. $^{13}$C($^{1}$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 4b. [Py: pyridine]

Figure S19. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 4b.
Single crystals suitable for the X-ray crystal structure analysis were obtained from diffusion of pentane vapor to a solution of the white powder in CH$_2$Cl$_2$ at room temperature.

**X-ray crystal structure analysis of compound 4b (erk9170):** A colorless prism-like specimen of C$_{29}$H$_{21}$BBrF$_{10}$N, approximate dimensions 0.158 mm x 0.170 mm x 0.303 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1382 frames were collected. The total exposure time was 16.14 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 27371 reflections to a maximum θ angle of 70.23° (0.82 Å resolution), of which 5152 were independent (average redundancy 5.313, completeness = 98.8%, R$_{int}$ = 3.26%, R$_{sig}$ = 2.24%) and 4888 (94.88%) were greater than 2σ(F$^2$). The final cell constants of a = 10.2011(4) Å, b = 11.0143(4) Å, c = 12.5252(5) Å, α = 88.7430(10)°, β = 80.8650(10)°, γ = 79.6490(10)°, volume = 1366.81(9) Å$^3$, are based upon the refinement of the XYZ-centroids of 9975 reflections above 20 σ(I) with 7.148° < 2θ < 140.2°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.845. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4770 and 0.6600. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P\overline{1}$, with Z = 2 for the formula unit, C$_{29}$H$_{21}$BBrF$_{10}$N. The final anisotropic full-matrix least-squares refinement on F$^2$ with 407 variables converged at R1 = 2.95%, for the observed data and wR2 = 7.34% for all data. The goodness-of-fit was 1.039. The largest peak in the final difference electron density synthesis was 0.288 e/Å$^3$ and the largest hole was -0.416 e/Å$^3$ with an RMS deviation of 0.050 e/Å$^3$. On the basis of the final model, the calculated density was 1.614 g/cm$^3$ and F(000), 664 e$. CCDC deposition number 1862534.
E) Synthesis of compound 12

Experiment 1: isolation of a mixture of compounds 11a and 12

Scheme S5.

ClB(C₆F₅)₂ (165 mg, 0.434 mmol) was dissolved in d₈-toluene (2.0 mL) in a Schlenk tube. After evacuating the Schlenk tube, the solution was exposed to allene gas for several minutes at room temperature. Then the resulting reaction mixture was stirred for 48 hours at room temperature.
Subsequently, $^1$Bu$_3$P (175 mg, 0.868 mmol) was added. After stirring the reaction mixture for 24 hours at 60 °C, all volatiles were removed in vacuo and pentane (1 mL) was added to the residual oil. Then CH$_2$Cl$_2$ was added dropwise to the stirred mixture until it became a suspension. The liquid was removed by filtration. Drying of the remaining solid in vacuo gave a white powder (165 mg, ca. 54%).

A solution of the obtained white powder in CD$_2$Cl$_2$ showed a mixture of two main components: compounds 12 (ca. 79 mol%, $^1$H) and 11a (ca. 21 mol%, $^1$H).

NMR data of compound 11a:

$^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^1$H: 7.56 (d, $^1$J$_{PH}$ = 462.4 Hz, 1H, PH), 1.66 (d, $^3$J$_{PH}$ = 15.3 Hz, 27 H, tBu).

$^{31}$P{$^1$H} NMR (243 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{31}$P: 47.9 ($\nu_{12}$ ~ 8 Hz).

$^{31}$P NMR (243 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{31}$P: 47.9 (dm, $^1$J$_{PH}$ ~ 463 Hz).

Figure S21. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) compound 12 (Experiment 2) and (2) the obtained white powder (Experiment 1).
Figure S22. $^{11}$B{$^1$H} NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) compound 12 (Experiment 2) and (2) the obtained white powder (Experiment 1).

Figure S23. (1) $^{31}$P{$^1$H} and (2) $^{31}$P NMR (243 MHz, 299 K, CD$_2$Cl$_2$) spectra of the obtained white powder (Experiment 1) and (3) $^{31}$P{$^1$H} and (4) $^{31}$P NMR spectra of compound 12 (Experiment 2).
Figure S24. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) compound 12 (Experiment 2) and (2) the obtained white powder (Experiment 1).

**Experiment 2: isolation and characterization of compound 12**

Scheme S6.

BrB(C$_6$F$_5$)$_2$ (150 mg, 0.357 mmol) was dissolved in d$_8$-toluene (2.0 mL) in a Schlenk tube. After carefully evacuating the Schlenk tube, the solution was exposed to allene gas for several minutes at room temperature. Then the resulting reaction mixture was stirred for 24 hours at room temperature. Subsequently, $^1$Bu$_3$P (144 mg, 0.714 mmol) was added. After stirring the reaction mixture for 24 hours at room temperature, all the volatiles were removed in vacuo and pentane (1 mL) was added to the residual oil. Then CH$_2$Cl$_2$ was added dropwise to the stirred mixture until it became a suspension. The solution was removed by filtration. Drying of the remaining solid in vacuo gave compound 12 (165 mg, 0.234 mmol, 65%) as a white powder.

**Anal. Calc.** for C$_{36}$H$_{42}$BF$_{10}$P: C, 61.20; H, 5.99. Found: C, 60.53; H, 5.93.
NMR data of compound 12:

\[ ^1H \text{NMR} \ (600 \text{ MHz}, 299 \text{ K, } \text{CD}_2\text{Cl}_2): \delta \ ^1H: 8.21 \ (d, \ ^3J_{PH} = 27.8 \text{ Hz, 1H, BCH=}), [4.61, 4.41]\text{(each m, each 2H, 4,6-CH}_2\text{=}), [2.81, 2.72]\text{(each dm, } ^2J_{HH} = 14.0 \text{ Hz, each 1H, 5-CH}_2\text{)}, [2.22, 1.90]\text{(each d, } ^2J_{HH} = 13.0 \text{ Hz, each 2H, 3,7-CH}_2\text{)}, 2.06 \ (d, \ ^4J_{PH} = 4.5 \text{ Hz , 2H, 8-CH}_2\text{)}, 1.58 \ (d, \ ^3J_{PH} = 13.2 \text{ Hz, 27 H, tBu}), 1.20 \ (s, \ 2H, \text{BCH}_2). \]

\[ ^13C\{^1H\} \text{NMR} \ (151 \text{ MHz}, 299 \text{ K, } \text{CD}_2\text{Cl}_2): \delta \ ^13C: 177.0 \text{ (br m, BCH=), 148.3 (dm, } ^1J_{FC} \sim 240 \text{ Hz, C}_6\text{F}_5\text{), 147.7 (4,6-C=), 138.0 (dm, } ^1J_{FC} \sim 240 \text{ Hz, C}_6\text{F}_5\text{), 137.0 (dm, } ^1J_{FC} \sim 250 \text{ Hz, C}_6\text{F}_5\text{), 128.8 (i-}\text{C}_6\text{F}_5\text{), 118.9 (d, } ^1J_{PC} = 37.0 \text{ Hz, PC=), 108.4 (4,6-CH}_2\text{=), 48.0 (3,7-CH}_2\text{), 44.4 (5-CH}_2\text{), 43.6 (d, } ^2J_{PC} = 9.3 \text{ Hz, 8-CH}_2\text{), 41.5 (d, } ^1J_{PC} = 28.0 \text{ Hz), 31.8](\text{tBu), 40.7 (d, } ^3J_{PC} = 6.1 \text{ Hz, 2-C ), 32.8 (br m, BCH}_2\text{).} \]

\[ ^19F \text{NMR} \ (564 \text{ MHz, 299 K, CD}_2\text{Cl}_2): \delta \ ^19F: [-132.9 \ (m, 2F, o), -163.9 \ (t, ^3J_{FF} = 21.0 \text{ Hz, 1F, p}), -166.6 \ (m, 2F, m)](\text{C}_6\text{F}_5)[\Delta \delta ^{19F}_{m,p} = 2.7]. \]

\[ ^11B\{^1H\} \text{NMR} \ (192 \text{ MHz, 299 K, CD}_2\text{Cl}_2): \delta \ ^{11}B: -15.8 \ (\nu_{1/2} \sim 60 \text{ Hz).} \]

\[ ^31P\{^1H\} \text{NMR} \ (243 \text{ MHz, 299 K, CD}_2\text{Cl}_2): \delta \ ^{11}P: 43.9 \ (\nu_{1/2} \sim 30 \text{ Hz).} \]
Figure S26. $^{11}$B($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 12.

Figure S27. $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 12.
Single crystals suitable for the X-ray crystal structure analysis were obtained from the diffusion of pentane vapor to a solution of the white powder in CH₂Cl₂ at room temperature.

**X-ray crystal structure analysis of compound 12 (erk9169):** formula C₃₆H₄₂BF₁₀P, $M = 706.48$, colourless crystal, 0.13 x 0.13 x 0.03 mm, $a = 9.9507(3)$ Å, $b = 11.7835(3)$ Å, $c = 16.0070(5)$ Å, $\alpha = 71.517(1)^\circ$, $\beta = 86.117(1)^\circ$, $\gamma = 70.299(1)^\circ$, $V = 1674.26(8)$ Å³, $\rho_{\text{calc}} = 1.401$ g cm⁻³, $\mu = 0.164$ mm⁻¹, empirical absorption correction (0.979 ≤ $T$ ≤ 0.995), $Z = 2$, triclinic, space group $P\overline{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 173(2)$ K, $\omega$ and $\phi$ scans, 15352 reflections collected ($\pm h, \pm k, \pm l$), 5781 independent ($R_{\text{int}} = 0.047$) and 4799 observed reflections [$I > 2\sigma(I)$], 442 refined parameters, $R = 0.055$, $wR^2 = 0.127$, max. (min.) residual electron density 0.32 (-0.28) e Å⁻³, hydrogen atoms were calculated and refined as riding atoms. CCDC deposition number 1862535.
Figure S30. Crystal structure of compound 12 (thermal ellipsoids: 30% probability)

Experiment 3: compound 11b

Scheme S7.

BrB(C₆F₅)₂ (50 mg, 0.119 mmol) was dissolved in d₈-toluene (2.0 mL) in a Schlenk tube. After carefully evacuating the Schlenk tube, the solution was exposed to allene gas for several minutes at
room temperature. Then the resulting reaction mixture was stirred for 24 hours at room
temperature. Subsequently, \textsuperscript{1}Bu\textsubscript{3}P (144 mg, 0.714 mmol) was added. After stirring the reaction
mixture for 24 hours at room temperature, all the volatiles were removed in vacuo and pentane (1
mL) was added to the residual oil. Then CH\textsubscript{2}Cl\textsubscript{2} was added dropwise to the stirred mixture to give a
suspension. The liquid was separated by filtration. Drying of the remaining solid in vacuo gave
compound \textbf{12} (58 mg, 0.082 mmol, 69\%) as a white powder. The filtrate was dried in vacuo,
dissolved in CD\textsubscript{2}Cl\textsubscript{2} and characterized by NMR experiments.

NMR data of compound \textbf{11b} from the dried filtrate:

\textbf{\textsuperscript{1}H NMR} (600 MHz, 299 K, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \textsuperscript{1}H: 8.39 \) (d, \( \textsuperscript{1}J_{PH} = 470.7 \) Hz, 1H, PH), 1.65 (d, \( \textsuperscript{3}J_{PH} = 15.1 \) Hz, 27
H, tBu).

\textbf{\textsuperscript{31}P\{\textsuperscript{1}H\} NMR} (243 MHz, 299 K, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \textsuperscript{11}P: 41.4 \) (\( \nu_{1/2} \approx 5 \) Hz).

\textbf{\textsuperscript{31}P NMR} (243 MHz, 299 K, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta \textsuperscript{11}P: 41.4 \) (dm, \( \textsuperscript{1}J_{PH} \approx 470 \) Hz).

\textbf{Figure S31}. \textsuperscript{1}H NMR (600 MHz, 299 K, CD\textsubscript{2}Cl\textsubscript{2}) spectra of (1) the obtained white powder
(Experiment 3), (2) the dried filtrate of Experiment 3 and (3) compound \textbf{12} (Experiment 2).
Figure S32. $^{13}$B($^1$H) NMR (192 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) the obtained white powder (Experiment 3), (2) the dried filtrate of Experiment 3, and (3) compound 12 (Experiment 2).

Figure S33. $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) the obtained white powder (Experiment 3), (2) the dried filtrate of Experiment 3, and (3) compound 12 (Experiment 2).
Figure S34. (1) $^{31}$P{$^1$H} and (2) $^{31}$P NMR (243 MHz, 299 K, CD$_2$Cl$_2$) spectra of the obtained white powder (Experiment 3), (3) $^{31}$P{$^1$H} and (4) $^{31}$P NMR spectra of the dried filtrate of Experiment 3, and (5) $^{31}$P{$^1$H} and (6) $^{31}$P NMR spectra of compound 12 (Experiment 2).
F) XB(C₆F₅)₂ (X = Cl, Br) catalyzed cyclotrimerization of substituted allenes 13

Scheme S8.

\[
\begin{array}{c}
\text{R} \\
\text{13c,d}
\end{array}
\xrightarrow{10 \text{ mol}\% \ XB(C₆F₅)₂ (2a,b)}
\begin{array}{c}
\text{d₈-toluene} \\
60 ^\circ \text{C}, 48 \text{ h}
\end{array}
\begin{array}{c}
\text{R} \\
\text{14c,d}
\end{array}
\]

X = Cl (a), Br (b)
R = n-octyl (c), n-dodecyl (d)

**General procedure:** borane 2 (0.060 mmol) and substrate 13 (0.600 mmol) were dissolved in d₈-toluene (ca. 1 mL) in a NMR tube. After flame-sealing the NMR tube, it was placed in a steel autoclave and heated at 60 °C for 48 h. Then the tube was opened and all the volatile was removed in vacuo. The residue was purified through column chromatography (silica gel, pentane) giving the corresponding final product 14.

| Entry | Substrate (mg/mmol) | Borane (mg/mmol) | Yield (mg/mmol) | Yield (%) |
|-------|---------------------|-----------------|-----------------|-----------|
| 1     | 13c (91.2 / 0.600)  | 2a (22.8 / 0.060)| 14c (40.4 / 0.009) | 44        |
| 2     | 13c (91.2 / 0.600)  | 2b (25.4 / 0.060)| 14c (42.0 / 0.009) | 46        |
| 3     | 13d (126 / 0.600)   | 2a (22.8 / 0.060)| 14d (50.2 / 0.008) | 40        |
| 4     | 13d (126 / 0.600)   | 2b (25.4 / 0.060)| 14d (68.1 / 0.011) | 54        |

*aReaction conditions: 60 °C, 48 h; *b* isolated yield.
Entry 1:
Scheme S9.

Following the general procedure ClB(C6F5)2 (2a) (22.8 mg, 0.060 mmol) and n-octyllallene (13c) (91.2 mg, 0.600 mmol) were used as starting materials. Compound 14c (40.4 mg, 0.009 mmol, 44%) was isolated as colorless oil.

HRMS: m/z Calc. for C33H60 [M+Ag]+: 563.37405. Found 563.37454.

1H NMR (600 MHz, 299 K, CD2Cl2): δ: 4.67 (s, 2H, 1-CH2=), [4.66, 4.63](each m, each 2H, 3,5-CH2=), 2.90 (t, 3JHH = 7.1 Hz, 1H, 4-CH), 2.86 (t, 3JHH = 7.1 Hz, 2H, 2,6-CH), 1.64 (m, 2H, 4-CH2), [1.64, 1.58](each m, each 2H, 2,6-CH2), 1.31-1.28 (m, 36H, CH2octyl), 0.89 (t, 3JHH = 7.3 Hz, 9H, CH3).

13C{1H} NMR (151 MHz, 299 K, CD2Cl2): δ: 154.1 (1-C=), 154.0 (3,5-C=), 108.0 (1-CH2=), 105.7 (3,5-CH2=), 51.6 (2,6-CH), 46.2 (4-CH), 34.0 (2,6-CH2), 30.7 (4-CH2), [32.3, 30.2, 30.0, 29.9 (br m), 29.7 (br m), 28.3, 27.9, 23.1](CH2octyl), 14.3 (CH3).

Figure S35. 1H NMR (600 MHz, 299 K, CD2Cl2) spectrum of isolated compound 14c.
Entry 2:

Scheme S10.

Following the general procedure BrB(C₆F₅)₂ (2b) (25.4 mg, 0.060 mmol) and n-octyllallene (13c) (91.2 mg, 0.600 mmol) were used as starting materials. A colorless oil (42.0 mg, 0.009 mmol, 46%) was isolated as colorless oil.

HRMS: m/z Calc. for C₃₃H₆₀ [M+Ag]⁺: 563.37405. Found 563.37497.
**Figure S37.** $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) isolated compound 14c (entry 1) and (2) isolated colorless oil (entry 2).

**Entry 3:**

Scheme S11.

Following the general procedure ClB(C$_6$F$_5$)$_2$ (2a) (22.8 mg, 0.060 mmol) and n-dodecylallene (13c) (126 mg, 0.600 mmol) were used as starting materials. Compound 14d (50.2 mg, 0.008 mmol, 40%) was isolated as colorless oil.

**HRMS:** m/z Calc. for C$_{45}$H$_{84}$ [M+Ag]$^+$: 731.56185. Found 731.56279.

$^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^1$H: 4.67 (s, 2H, 1-CH$_2$=), [4.66, 4.63](each m, each 2H, 3,5-...
CH$_2$=), 2.90 (t, $^3$$J_{HH} = 7.1$ Hz, 1H, 4-CH), 2.86 (t, $^3$$J_{HH} = 7.1$ Hz, 2H, 2,6-CH), 1.64 (m, 2H, 4-CH$_2$), [1.64, 1.58](each m, each 2H, 2,6-CH$_2$), 1.32-1.27 (m, 60H, CH$_2$-$\text{dodecyl}$), 0.89 (t, $^3$$J_{HH} = 7.3$ Hz, 9H, CH$_3$).

$^{13}$C{H} NMR (151 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ $^{13}$C: 154.1 (1-C=), 154.0 (3,5-C=), 108.0 (1-CH$_2$=), 105.8 (3,5-CH$_2$=), 51.6 (2,6-CH), 46.2 (4-CH), 34.0 (2,6-CH$_2$), 30.7 (4-CH$_2$), [32.3, 30.2, 30.1-30.0 (br m), 28.3, 27.9, 23.1](CH$_2$-$\text{dodecyl}$), 14.3 (CH$_3$).

**Figure S38.** $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of isolated compound 14d.
Entry 4:

Scheme S12.

Following the general procedure BrB(C₆F₅)₂ (2b) (25.4 mg, 0.060 mmol) and n-dodecylallene (13c) (126 mg, 0.600 mmol) were used as starting materials. A colorless oil (68.1 mg, 0.011 mmol, 54%) was isolated.

HRMS: m/z Calc. for C₄₅H₈₄ [M+Ag]⁺: 731.56185. Found 731.56310.
Figure S40. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectra of (1) isolated compound 14d (entry 3) and (2) isolated colorless oil (entry 4).

G) Isomerization of the cyclotrimer 1

Scheme S13.

Step 1: HBr(C$_6$F$_5$)$_2$ (20.8 mg, 0.06 mmol) was suspended in toluene-d$_8$ (0.7 mL) and the atmosphere removed. After applying allene gas for 2 min, the mixture was stirred for 10 min at room temperature. The now clear solution was transferred to a NMR tube, which was then flame-sealed and heated to 60 °C for 24 h in a steel autoclave. Then the solution was filtered through a small plug of silica and ferrocene (9.8 mg, 0.05 mmol) was added as an internal standard. The obtained solution was characterized by $^1$H NMR experiment. A yield of 0.077 mmol was estimated by integration ($^1$H) of compound 1 in relation to the ferrocene standard.
NMR data of compound 1 in solution from Step 1:

$^1H$ NMR (600 MHz, 299 K, toluene-d$_8$): $\delta$ $^1H$: 4.59 (m, 1H, =CH$_2$), 2.75 (m, 1H, CH$_2$).

Step 2: Without further workup p-toluene sulfonic acid monohydrate (0.7 mg, 0.004 mmol; 5 mol%) was added to the solution from Step 1. After 1.5 h at room temperature, the $^1H$ NMR spectrum indicated complete conversion to mesitylene.

NMR data of mesitylene in solution from Step 2:

$^1H$ NMR (600 MHz, 299 K, toluene-d$_8$): $\delta$ $^1H$: 6.66 (m, 1H, ArH), 2.14 (m, 3H, CH$_3$).

Figure S41. $^1H$ NMR (600 MHz, 299 K, toluene-d$_8$) spectra of the reaction mixture of Step 1 (spectrum 1) and Step 2 (spectrum 2).
H) Isomerization of the cyclotrimer 14c

Experiment 1: (NMR scale)

Scheme S14.

The cyclotrimer 14c (11.0 mg, 0.024 mmol) was dissolved in CD$_2$Cl$_2$ (0.7 mL) and p-toluene sulfonic acid monohydrate (0.2 mL, 0.001 mmol; 0.0055 M in CD$_2$Cl$_2$) was added. Then the solution was sealed in a NMR tube. After 22 h at room temperature, the reaction mixture was characterized by $^1$H NMR experiment.

Experiment 2: (preparative scale)

Scheme S15.

The cyclotrimer 14c (86.0 mg, 0.19 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) and p-toluene sulfonic acid monohydrate (2 mg, 0.01 mmol; 5 mol%) was added. Then the solution was stirred for 24 h at room temperature, during which it took on a brownish color. After removal of all volatiles in vacuo, the $^1$H NMR spectrum of the crude product indicated a conversion of 75%. The crude product was dissolved in CH$_2$Cl$_2$ (10 mL) and another portion of p-toluene sulfonic acid monohydrate (2 mg, 0.01 mmol; 5 mol%) was added. After stirring for additional 24 h at room temperature and removal of all volatiles in vacuo, the $^1$H NMR spectrum of the crude product indicated full conversion. Then the crude product was dissolved in pentane (10 mL) and passed through a small plug of silica. After rinsing of the silica plug with pentane (30 mL), all volatiles were removed in vacuo and compound 15c (72.0 mg, 0.15 mmol, 78%) was isolated as a yellowish oil.
HRMS: m/z Calc. for C\textsubscript{33}H\textsubscript{60} [M+Ag]\textsuperscript{+}: 563.37405. Found 563.37445.

\textbf{\textsuperscript{1}H NMR} (600 MHz, 299 K, CD\textsubscript{2}Cl\textsubscript{2}): δ \textsuperscript{1}H: 2.60 (m, 2H, CH\textsubscript{2}\textsuperscript{Ar}), 2.22 (s, 3H, CH\textsubscript{3}\textsuperscript{Ar}), 1.45-1.20 (m, 12H, CH\textsubscript{2}), 0.89 (m, 3H, CH\textsubscript{3}\textsuperscript{Oct}).

\textbf{\textsuperscript{13}C{\textsuperscript{1}H} NMR} (600 MHz, 299 K, CD\textsubscript{2}Cl\textsubscript{2}): δ \textsuperscript{13}C: 137.8 and 131.5 (C\textsuperscript{Ar}), 32.3 (CH\textsubscript{2}), 31.1 (CH\textsubscript{2}\textsuperscript{Ar}), 30.7 (CH\textsubscript{2}), 30.1 (CH\textsubscript{2}), 29.9 (CH\textsubscript{2}), 29.7 (CH\textsubscript{2}), 23.1 (CH\textsubscript{2}), 15.7 (CH\textsubscript{3}\textsuperscript{Ar}), 14.3 (CH\textsubscript{3}\textsuperscript{Oct}).

**Figure S42.** \textsuperscript{1}H NMR (600 MHz, 299 K, CD\textsubscript{2}Cl\textsubscript{2}(*)) spectra (1) of compound 14c, (2) of the reaction mixture from Experiment 1 and (3) of isolated compound 15c from Experiment 2.

**Figure S43.** \textsuperscript{13}C{\textsuperscript{1}H} NMR (151 MHz, 299 K, CD\textsubscript{2}Cl\textsubscript{2}(*)) spectrum of isolated compound 15c from Experiment 2.
I) Isomerization of cyclotrimer 14e

Experiment 1: (NMR scale)

Scheme S16.

The cyclotrimer 14e (8.8 mg, 0.024 mmol) was dissolved in CD$_2$Cl$_2$ (0.7 mL) and $p$-toluene sulfonic acid monohydrate (0.2 mL, 0.001 mmol; 0.0055 M in CD$_2$Cl$_2$) was added. Then the solution was sealed in a NMR tube, which was then placed in a steel autoclave and heated up to 80 °C for 5 hours. The reaction mixture was then characterized by $^1$H NMR experiment.

Experiment 2: (preparative scale)

Scheme S17.

The cyclotrimer (88.0 mg, 0.24 mmol) and $p$-toluene sulfonic acid monohydrate (4.6 mg, 0.024 mmol; 10 mol%) were mixed in CH$_2$Cl$_2$ (10 mL) in an ampule, which was subsequently placed in a steel autoclave. The autoclave was treated with argon (ca. 10 bar) and then heated up to 80 °C for 5 hours. After the autoclave was cooled down to room temperature, the argon was carefully released. A blue solution was obtained. All the volatile was removed by rotation evaporator and the residue was purified via column chromatography (silica gel, pentane) giving product 15e (32.3 mg, 0.088 mmol, 37%) as white solid. Crystals suited for the X-ray crystal structure analysis were obtained from a solution of compound 15e in dichloromethane at -35 °C.
**HRMS:** m/z Calc. for C_{27}H_{42} [M+Ag]^+: 473.23320. Found 473.23366.

**^1H NMR** (600 MHz, 299 K, CD_2Cl_2): δ ^1H: 3.06 (tt, J_{HH} = 12.6, 3.5 Hz, 1H, CH), 2.35 (br s, 3H, CH_3), 1.99, 1.63 (each m, each 2H, 2-CH_2), 1.84, 1.39 (each m, each 2H, 3-CH_2), 1.74, 1.29 (each m, each 1H, 4-CH_2).

**^{13}C{^1H} NMR** (600 MHz, 299 K, CD_2Cl_2): δ ^13C: 142.5, 132.8 (each br, C^Ar), 41.9 (CH), 31.0 (2-CH_2), 28.3 (3-CH_2), 26.8 (4-CH_2), 19.3 (CH_3).

**Figure S44.** ^1H NMR (600 MHz, 299 K, CD_2Cl_2(*)) spectra of (1) compound 14e, (2) the reaction mixture from Experiment 1, and (3) isolated compound 15e from Experiment 2.
Figure S45. $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of isolated compound 15e from Experiment 2.

Figure S46. $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of isolated compound 15e from Experiment 2.
X-ray crystal structure analysis of 15e (erk9371): A colorless plate-like specimen of C_{27}H_{42} \cdot 0.5 x CH_2Cl_2, approximate dimensions 0.050 mm x 0.101 mm x 0.224 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1217 frames were collected. The total exposure time was 21.26 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 25656 reflections to a maximum θ angle of 66.84° (0.84 Å resolution), of which 8246 were independent (average redundancy 3.111, completeness = 98.3%, R_{int} = 5.52%, R_{sig} = 6.09%) and 5834 (70.75%) were greater than 2σ(F^2). The final cell constants of a = 10.8108(3) Å, b = 12.1099(3) Å, c = 19.1989(5) Å, α = 76.7030(10)°, β = 75.1760(10)°, γ = 87.9660(10)°, volume = 2363.95(11) Å^3, are based upon the refinement of the XYZ-centroids of 9965 reflections above 20σ(I) with 4.890° < 2θ < 133.7°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.932. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7330 and 0.9300. The structure was solved and refined using the Bruker SHELXL Software Package, using the space group P-1, with Z = 4 for the formula unit, C_{27}H_{42} \cdot 0.5 x CH_2Cl_2. The final anisotropic full-matrix least-squares refinement on F^2 with 639 variables converged at R1 = 6.90%, for the observed data and wR2 = 17.20% for all data. The goodness-of-fit was 1.030. The largest peak in the final difference electron density synthesis was 0.720 e/Å^3 and the largest hole was -0.554 e/Å^3 with an RMS deviation of 0.058 e/Å^3. On the basis of the final model, the calculated density was 1.149 g/cm^3 and F(000), 900 e.  

**Figure S47** Crystal structure analysis of compound 15e [only one of two crystallographically independent molecules is shown (mol A); thermal ellipsoids: 30% probability].