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Supplementary Information

Ring-closing metathesis for the synthesis of a molecular gyrotop

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1. Synthetic Details

The complete synthetic route to molecular gyrotop 2 is shown in Scheme S1.

Scheme S1



General

All the reactions were carried out under anhydrous conditions using argon, unless otherwise noted. ¹H (400 MHz), ¹³C (100 MHz), and ²⁹Si (79 MHz) NMR spectra were recorded using a Bruker AVANCE 400 spectrometer. The chemical shifts are based on the residual solvent resonances. Preparatory GPC was also carried out using a JAI LC-9201 recycling preparative chromatograph with two Jaigel H Series Columns (1-H and 2-H) connected in series; chloroform stabilized with ethanol was used as the eluent.

Materials

Commercially available reagents were used as received without further purification. Anhydrous THF and dichloromethane were purchased from WAKO Chemical, Japan. Grubbs' catalysts (1st and 2nd generation), which are commercially available at Aldrich Chemicals, were used for the RCM reactions.

a. Synthesis of 1,4-Bis(tris-9-decenylsilyl)benzene (3)

In a Schlenk flask (50 mL) were placed p-dibromobenzene (0.9 g, 3.8 mmol) and dry THF (20 mL). A tert-BuLi solution (1.6 M in pentane, 9.5 mL, 15 mmol, 4.0 equiv.) was added dropwise to the solution at -78 °C. The reaction mixture turned yellow and was stirred for an additional 1 h at -78 °C. The reaction mixture was warmed to 0 °C, and then, chlorotris(9decenyl)silane^{S1} 6 (4.2 g, 10.6 mmol) was added. After stirring for 12 h at room temperature, the mixture was hydrolyzed using dilute HCl (aq) and extracted with hexane. The organic layer was washed with saturated NaHCO₃(aq) and dried over anhydrous Na₂SO₄. Concentration of the organic layer in vacuo and purification of the residue by column chromatography [Merck silica gel 60, particle size $63-200 \mu m$, hexane as an eluent (Rf = 0.5)] afforded **3** as a colorless oil (3.1 g) containing small amounts of monosilyl compounds. GPC purification of the crude product afforded pure compound 3 (2.4, 2.5 mmol, 65% yield) as a colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ 0.71–0.79 (m, 12H, Si-CH₂-), 1.25–1.38 (m, 72H), 2.019 (tddd, J = 6.8, 6.8, 1.6, 1.25 Hz, 12H, H₂C=CH-CH₂-), 4.910 (ddt, J = 10.4, 2.2, 1.25 Hz, 6H, terminal $H_2C=$), 4.974 (ddt, J = 16.9, 2.2, 1.6 Hz, 6H, terminal $H_2C=$), 5.794 (ddt, J = 16.9, 10.4, 6.8 Hz, 6H, H₂C=CH-), 7.410 (s, 4H, C₆H₄); ¹³C NMR (CDCl₃, 100 MHz): δ12.45, 23.79, 28.93, 29.16, 29.42, 33.79, 114.06 (-CH=CH₂), 133.19 (aromatic CH), 138.43 (SiC), 139.21 (-CH=CH₂); ²⁹Si NMR (CDCl₃, 79.5 MHz): δ -2.41; Anal. Calcd. for C₆₆H₁₁₈Si₂: C, 81.91; H, 12.29. Found: C, 81.57; H, 12.58.

Reference:

S1) W. Setaka, A. Koyama, K. Yamaguchi, Org. Lett., 2013, 15, 5092.

Synthesis of Molecular Gyrotop 2 and Its Isomer 2i To a solution of dichloromethane (300 mL) in the presence of Grubbs' 1st generation catalyst (0.02 g, 0.02 mmol), a dichloromethane solution (200 mL) of 3 (0.300 g, 0.3 mmol) was added dropwise with stirring over 12 h at 40 °C. During the reaction, the catalyst (0.02 g, 0.06 mmol) was added to the flask two times (every 2h). The mixture was further stirred for 8 h. The volatile materials were removed in vacuo, and the benzene soluble fraction was treated by flash column chromatography (silica gel, benzene) to remove the metal catalysts. The fraction contains unsaturated cyclized mixtures that have *E*/*Z*-alkenyl junctions (see, Fig. S12). Then, 3 atm of hydrogen gas was introduced into a toluene (5 mL) solution of the reaction mixture in the presence of 10% Pd/C (0.03 g) in an autoclave, and the mixture was filtered to remove Pd/C. The volatile materials were removed in vacuo. Using GPC with chloroform as the solvent, fractions containing 1 and 1i were collected. Pure compound 1 (62 mg, 0.07 mmol, 23% yield) and 1i

(104 mg, 0.12 mmol, 39% yield) were obtained after removal of the solvent in vacuo. Compound 1: colorless crystals, mp 82–83 °C; ¹H NMR (CDCl₃, 400 MHz): δ 0.72–0.80 (m, 12H, Si-CH₂-), 1.20–1.40 (m, 96H), 7.49 (s, 4H, aromatic CH); ¹³C NMR (CDCl₃, 100 MHz): δ 13.52, 23.63, 28.29, 28.40, 28.66, 28.74, 28.85, 28.94, 33.41, 133.45 (aromatic CH), 138.30 (SiC); ²⁹Si NMR (CDCl₃, 79.5 MHz): δ -2.29; Anal. Calcd. for C₆₀H₁₁₂Si₂: C, 81.00; H, 12.69. Found: C, 81.07; H, 13.05.

1i: colorless crystals, mp 53–55 °C; ¹H NMR (CDCl₃, 400 MHz): δ 0.66–0.74 (m, 4H, Si-CH₂-), 0.75–0.88 (m, 8H, Si-CH₂-), 1.17–1.42 (m, 96H), 7.44 (s, 4H, aromatic CH); ¹³C NMR (CDCl₃, 100 MHz): δ 12.00(4C), 13.28(2C), 23.37(4C), 23.76(2C), 27.38(6C), 27.69(6C), 28.11(4C), 28.16(4C), 28.25(2C), 28.33(2C), 28.45(4C), 28.48(4C), 28.67(2C), 28.75(2C), 33.20(4C), 33.57(2C), 133.24 (aromatic CH), 138.51 (SiC); ²⁹Si NMR (CDCl₃, 79.5 MHz): δ -2.10; Anal. Calcd. for C₆₀H₁₁₂Si₂: C, 81.00; H, 12.69. Found: C, 81.29; H, 13.05.



2. Copies of ¹H and ¹³C NMR Spectra of All New Compounds

Fig. S1. ¹H NMR spectrum of 1,4-Bis(tris-9-decenylsilyl)benzene (3) in CDCl₃.



Fig. S2. ¹³C NMR spectrum of 1,4-Bis(tris-9-decenylsilyl)benzene (3) in CDCl₃.



Fig. S3. ¹H NMR spectrum of the molecular gyrotop 2 in CDCl₃.



Fig. S4. ¹³C NMR spectrum of the molecular gyrotop 2 in CDCl₃.



Fig. S5. ¹H NMR spectrum of the isomer 2i in CDCl₃.



Fig. S6. ¹³C NMR spectrum of the isomer 2i in CDCl₃.

3. Details of X-Ray Crystallography of the Cage 2 and the Isomer 2i

a. General

Diffraction data were collected from single crystals on a Bruker APEX-II CCD system using graphite-monochromatized MoK α radiation ($\lambda = 0.71069$ Å). The structure was solved by a direct method using SHELXS-97 (Sheldrick, 1990) program, and structural refinement was performed by using SHELXL-97 (Sheldrick, 1997) program. Crystallographic data were deposited in Cambridge Crystallographic Database Centre (CCDC-988815 for **2**, CCDC-988816 for **2**i).

b. Crystal Data of 2 and 2i

Table S1 Crystal data of 2 and 2i

		2	2i
Empirical formula		C ₆₀ H ₁₁₂ Si ₂	C ₆₀ H ₁₁₂ Si ₂
Cryst shape		plate	plate
Cryst color		colorless	colorless
Cryst size		0.20 x 0.10 x 0.05 mm ³	0.26 x 0.24 x 0.08 mm ³
Formula weight / g mol ⁻¹		889.68	889.68
Crystal system		Triclinic	Triclinic
Space group		P-1	P-1
Z		2	4
Temperature / K		120	200
Cell parameter	а	12.308(7) Å	14.530(3) Å
	b	13.358(7) Å	18.768(3) Å
	с	18.357(10) Å	21.753(4) Å
	α	76.993(7)°	95.313(2)°
	β	87.634(8)°	90.751(3)°
	γ	86.828(7)°	92.942(2)°
	V	2935(3) Å ³	5897.9(18) Å ³
Calculated density		1.007 Mg/m ³	1.002 Mg/m ³
F(000)		1000	2000
Absorption coefficient		0.094 mm ⁻¹	0.094 mm ⁻¹
$oldsymbol{ heta}$ range for collecn (deg)		1.57 to 24.00°	1.40 to 27.18°
Index ranges		-14<=h<=11, -15<=k<=15, - 20<=l<=17	-17<=h<=13, -23<=k<=22, - 27<=l<=18
Reflections collected		12042	28912
Independent reflections		8945 [R(int) = 0.1623]	22201 [R(int) = 0.0462]
Completeness		97.2 %	96.7 %
Goodness-of-fit on F ²		0.802	0.957
Final R indices [I>2sigma(I)]		R1 = 0.0927, wR2 = 0.1639	R1 = 0.0877, wR2 = 0.1959
R indices (all data)		R1 = 0.3208, $wR2 = 0.2323$	R1 = 0.2370, wR2 = 0.2645
Largest diff. peak and hole		0.308 and -0.295 e.Å ⁻³	0.571 and -0.346 e.Å ⁻³

c. Packing Diagram of the Crystal Structures



Fig. S7 Packing diagram of the crystal structure of 2.



Fig. S8 Packing diagram of the crystal structure of 2i.

4. ¹H NMR Spectrum of the Partially Cyclized Mixture 4s



Fig. S9. ¹H NMR spectrum of the partially cyclized mixture 4s in CDCl₃.

5. GPC Chart of Reaction Mixture



Fig. S10 Recycling GPC chart (refractive index detector) of RCM reaction mixture, using Grubbs' 1st generation catalyst (a) at 40 °C (entry 1 in Table 1), (b) at 20 °C (entry 2 in Table 1), and (c) at 0 °C (entry 3 in Table 1). Each fraction is indicated by the included compound number. The asterisk indicates residual solvents.



Fig. S11 Representative recycling GPC chart (refractive index detector) of RCM reaction mixture at 40 °C, using (a) Grubbs' 1st generation catalyst (entry 1 in Table 1) and (b) Grubbs' 2nd generation catalyst (entry 4 in Table 1). Each fraction is indicated by the included compound number. The asterisk indicates residual solvents.

6. ¹H NMR Spectra of Unsaturated Intermediates Formed by RCM

In the synthesis of molecular gyrotop **2** and its isomer **2i** described in experimental section, the unsaturated reaction mixture was obtained by RCM before hydrogenation. In order to reveal stereochemistry of the orefinic junctions, the mixture was treated by GPC to separate the products. Two fractions containing the cages (**6s**) and the corresponding isomers (**6is**) were obtained. Fig. S12 showed ¹H NMR spectra of the products.



Fig. S12 ¹H NMR spectra of the unsaturated intermediates of the RCM for the synthesis of **2** and **2i**: (a) unsaturated cages (**6s**); (b) unsaturated isomers (**6is**).