Supplementary Information

Kinetic stabilization against oxidation reaction induced by a silaalkane cage in thiophene-bridged molecular gyroscope

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1. **Synthetic Details**

2. **Copies of ^{1}H and ^{13}C NMR Spectra of All New Compounds**

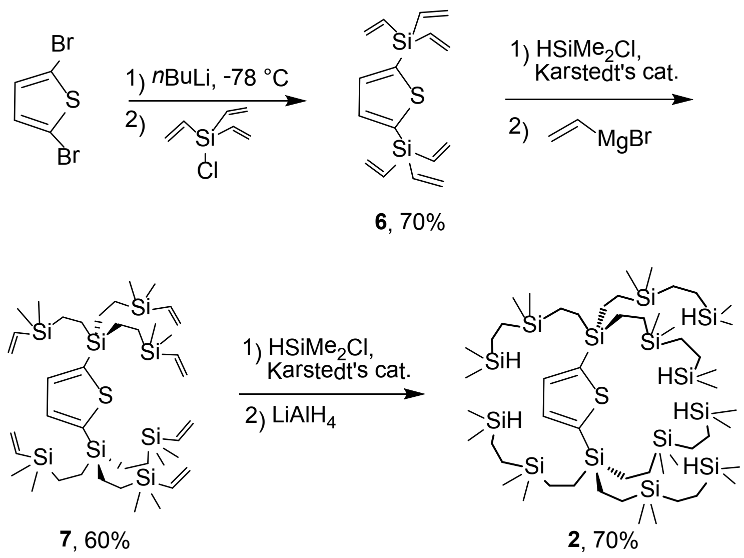
3. **Details of X-Ray Crystallography of Molecular Gyroscopes 1 and 3**

4. **The structural formula of compound 5**

1. Synthetic Details

The entire route for the synthesis of precursor **2** is shown in Scheme S1.

Scheme S1



General

All the reactions were carried out under anhydrous conditions using argon, unless otherwise noted. The ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{29}Si (79 MHz) NMR spectra were recorded using a Bruker AVANCE 400 spectrometer. The chemical shifts are based on the residual solvent resonances. The mass spectra and high-resolution mass spectra were recorded using a Bruker Daltonics APEX-III FT mass spectrometer.

Materials

Commercially available reagents were used as received without further purification, unless otherwise noted. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et$_2$O) were obtained by distillation from the corresponding sodium benzophenone ketyl solutions. Hexane was distilled from sodium under argon before use

a. Synthesis of 2,5-Bis(trivinylsilyl)thiophene (6)

2,5-Dibromothiophene (5.50 g, 22.7 mmol) and anhydrous THF (100 mL) were placed in a Schlenk flask (200 mL). An *n*-BuLi solution (1.6 M in hexanes, 31.0 mL, 49.6 equiv) was added dropwise to the solution at −50 °C. The reaction mixture was stirred for 0.5 h at −50 °C. Trivinylchlorosilane (10.62 g, 73.4 mmol) was added over 0.5 h. The reaction mixture was stirred for an additional 0.5 h at −50 °C and then warmed up to ambient temperature. After stirring for 12 h at room temperature (rt), the mixture was hydrolyzed by water and extracted with diethyl ether. The organic layer was washed with saturated $NaHCO_3$ (aqueous) and dried over anhydrous sodium sulfate (Na_2SO_4). Concentration and Kugelrohr distillation (100 °C/0.05 mm Hg) of the residue afforded **6** as a colorless oil (4.74 g, 15.8 mmol, 70% yield). **6**: a colorless oil; bp 100 °C/0.05 mmHg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85 (dd, J = 4.0, 20 Hz, 6H), 6.18 (dd, J = 4.0, 14.4 Hz, 6H), 7.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.6, 136.1, 137.5, 140.8; ^{29}Si NMR (79 MHz, $CDCl_3$): δ −29.2; HRMS (ESI) calcd for $C_{16}H_{20}SSi_2Na$, 323.0716 ($[M + Na]^+$); found, 323.0716 ($[M + Na]^+$); Anal. Calcd for $C_{16}H_{20}SSi_2$: C, 63.94; H, 6.71. Found: C, 63.67; H, 6.79.

b. Synthesis of 2,5-Bis[tris(3,3-dimethyl-3-sila-4-pentenyl)silyl]thiophene (7)

Dimethylchlorosilane (4.76 g, 50.3 mmol) was added from a dropping funnel to a mixture of 2,5-bis(trivinylsilyl)thiophene (**6**, 1.33 g, 4.41 mmol) and a catalytic amount of Karstedt's reagent[S1] dissolved in anhydrous hexane (6 mL). After the mixture was stirred at rt for 1 h, the volatile materials were removed in vacuo. A solution of vinylmagnesium bromide in THF (1.0 M, 35.0 mL, 35.0 mmol) was added dropwise to the residue and refluxed for 5 h. The mixture was poured onto crushed ice and extracted with hexane. The combined organic layers were washed with water, brine, and dried (anhydrous Na_2SO_4). Concentration and column chromatography (Merck silica gel 60, particle size 63–200 µm, hexane as the eluent) of the residue afforded the pure title compound **7** as a colorless oil (0.635 g, 0.538 mmol, 60% yield). **7**: a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (s, 36 H), 0.45-0.50 (m, 12 H), 0.69-0.73 (m, 12 H), 5.65 (dd, J = 4.0, 20 Hz, 6H), 5.94 (dd, J = 4.0, 14.4 Hz, 6H), 6.12 (dd, J = 14.4, 20 Hz, 6H), 7.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -4.0, 4.5, 7.4, 131.6, 135.5, 138.9, 142.3; ^{29}Si NMR (79 MHz, $CDCl_3$): δ -4.0, 0.4; HRMS (ESI) calcd for $C_{40}H_{80}SSi_8Na$, 840.4027 ($[M + Na]^+$); found, 840.4036 ($[M + Na]^+$); Anal. Calcd for $C_{40}H_{80}SSi_8$: C, 58.75; H, 9.86. Found: C, 58.88; H, 9.99.

S1) B. Boury, R. J. P. Corriu, R. Nuñez, *Chem. Mater.*, 1998, **10**, 1795.

c. Synthesis of 2,5-Bis[tris(3,3,6,6-tetramethyl-3,6-disilaheptyl)silyl]thiophene (2)

Dimethylchlorosilane (0.85 g, 8.98 mmol) was added from a dropping funnel to a mixture of 2,5-bis[tris(3,3-dimethyl-3-sila-4-pentenyl)silyl]thiophene (**7**, 0.63 g, 0.77 mmol) and a catalytic amount of Karstedt's reagent[S1] dissolved in anhydrous hexane (1 mL) was added. After the mixture was stirred at rt for 1 h, the volatile materials were removed in vacuo. A solution of the residue in Et_2O (6 mL) was added dropwise to a mixture of $LiAlH_4$ (0.10 g, 2.64 mmol) in Et_2O (4 mL), and the reaction was stirred for 1.5 h. Hydrolysis of the mixture, extraction with hexane, concentration, and column chromatography (Merck silica gel 60, particle size 63–200 µm, hexane as the eluent) of the residue afforded pure title compound **2** (0.635 g, 0.538 mmol, 70% yield). **2**: a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ -0.06 (s, 36 H), 0.04 (d, J = 3.6 Hz, 36H), 0.40-0.43 (m, 36 H), 0.66-0.71 (m, 24 H), 0.80-0.84 (m, 12 H), 3.81 (br s, 6 H), 7.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -4.8, -4.4, 4.5, 6.4, 6.7, 7.3, 135.4, 142.5; ^{29}Si NMR (79 MHz, $CDCl_3$): δ -10.1, 0.2, 5.8; HRMS (ESI) calcd for $C_{52}H_{128}SSi_{14}Na$, 1199.6399 ($[M + Na]^+$); found, 1199.6394 ($[M + Na]^+$); Anal. Calcd for $C_{52}H_{128}SSi_{14}$: C, 52.98; H, 10.94. Found: C, 52.99; H, 10.73.

S1) B. Boury, R. J. P. Corriu, R. Nuñez, *Chem. Mater.*, 1998, **10**, 1795.

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

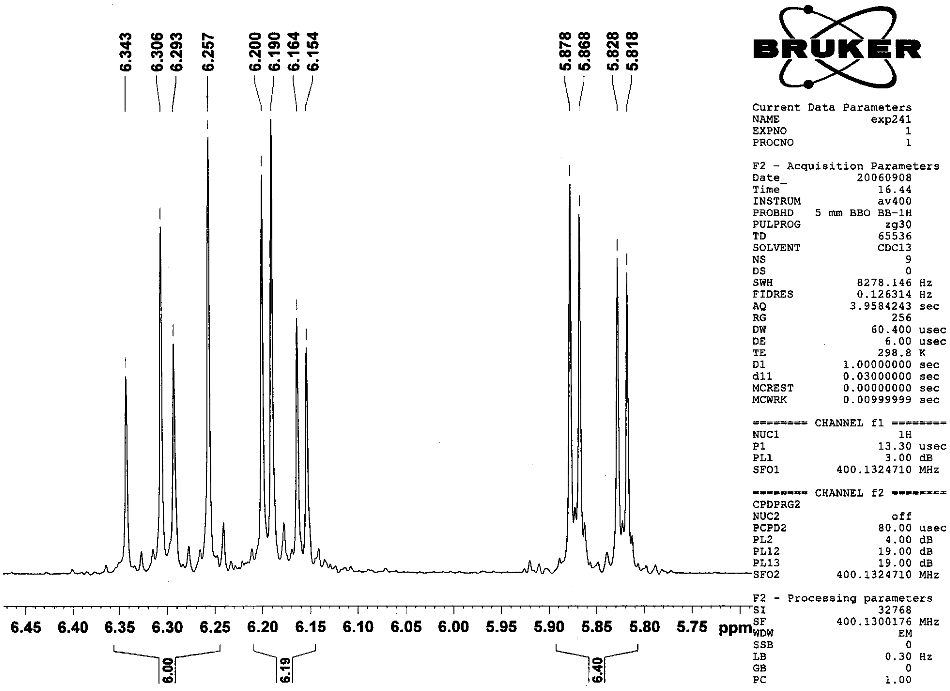


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Fig. S1. ^{1}H NMR spectrum of 2,5-Bis(trivinylsilyl)thiophene (**6**) in $CDCl_3$.

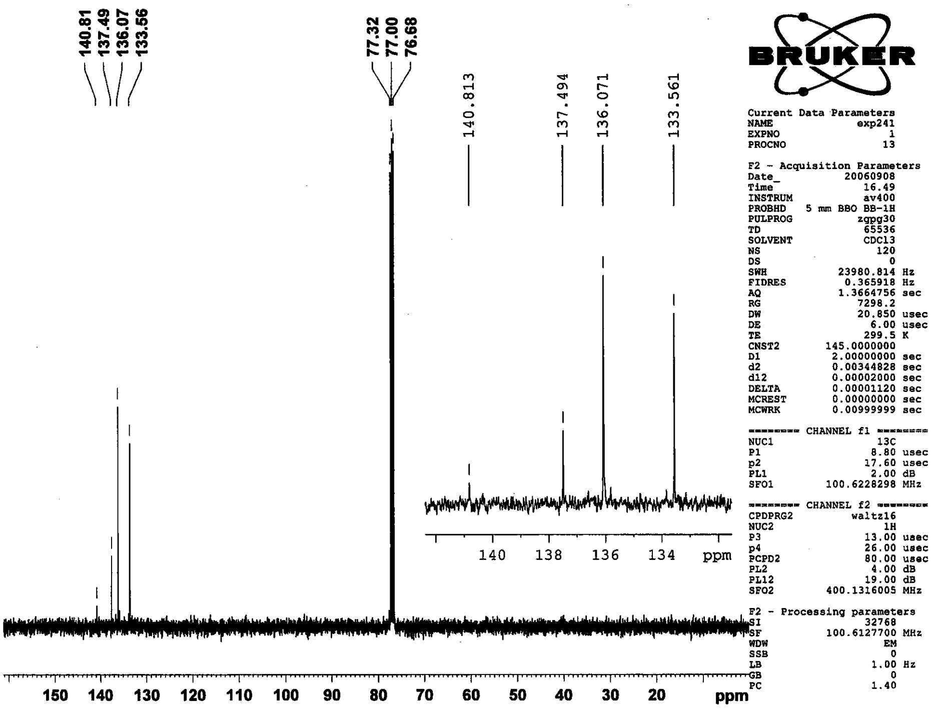

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Fig. S2. ^{13}C NMR spectrum of 2,5-Bis(trivinylsilyl)thiophene (**6**) in $CDCl_3$.

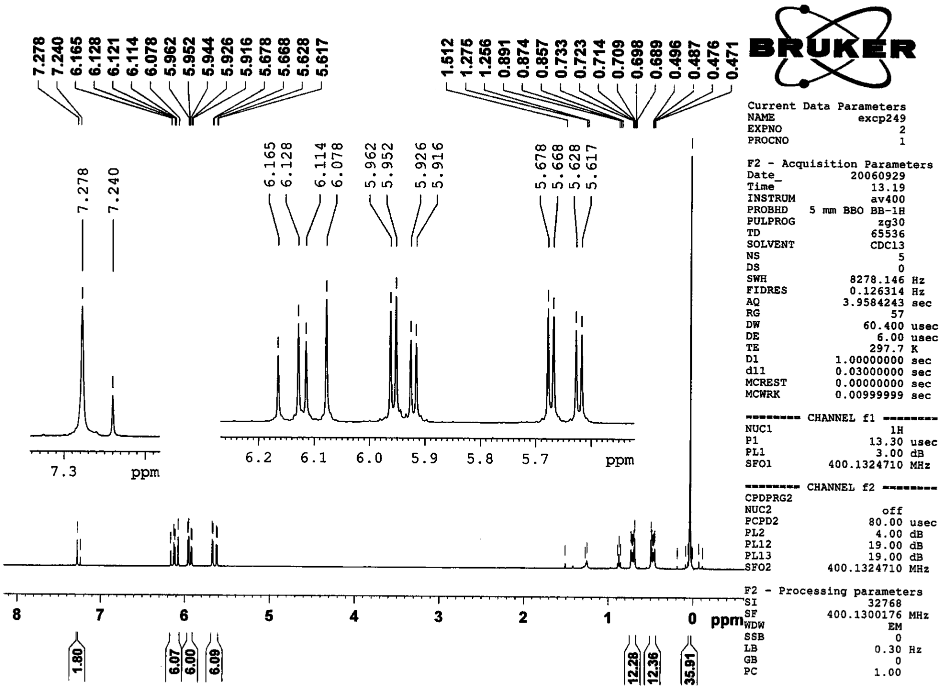


Fig. S3. ^{1}H NMR spectrum of 2,5-Bis[tris(3,3-dimethyl-3-sila-4-pentenyl)silyl]thiophene (**7**) in $CDCl_3$.

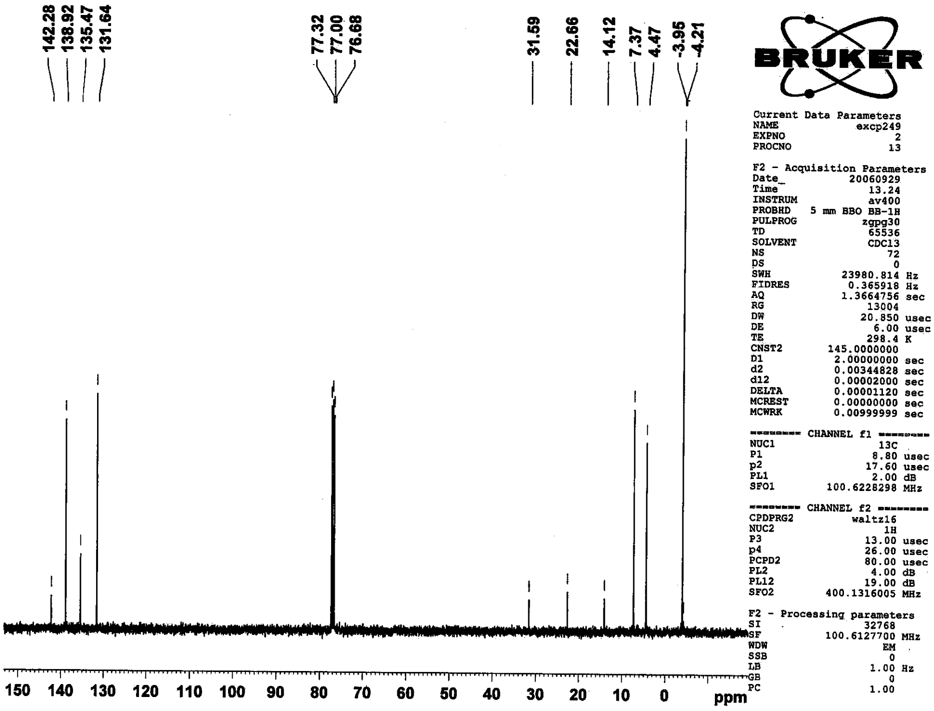


Fig. S4. ^{13}C NMR spectrum of 2,5-Bis[tris(3,3-dimethyl-3-sila-4-pentenyl)silyl]thiophene (**7**) in $CDCl_3$.

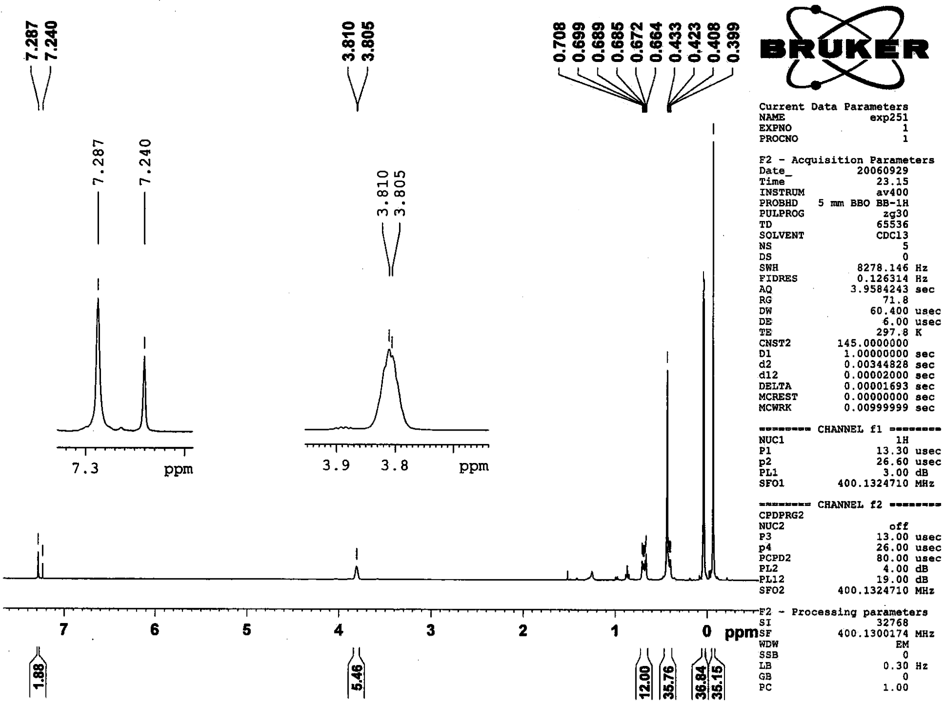


Fig. S5. ^{1}H NMR spectrum of 2,5-Bis[tris(3,3,6,6-tetramethyl-3,6-disilaheptyl)silyl]thiophene (**2**) in $CDCl_3$.

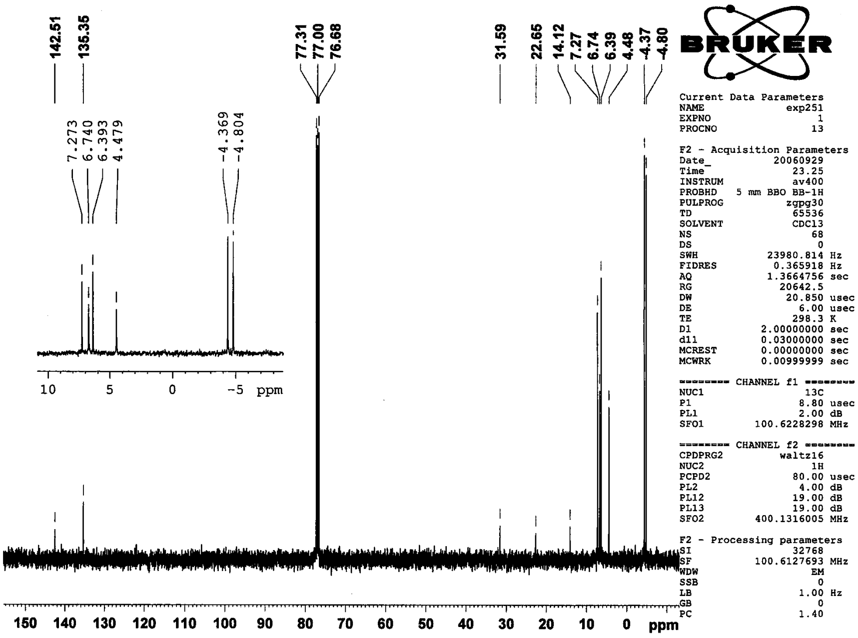
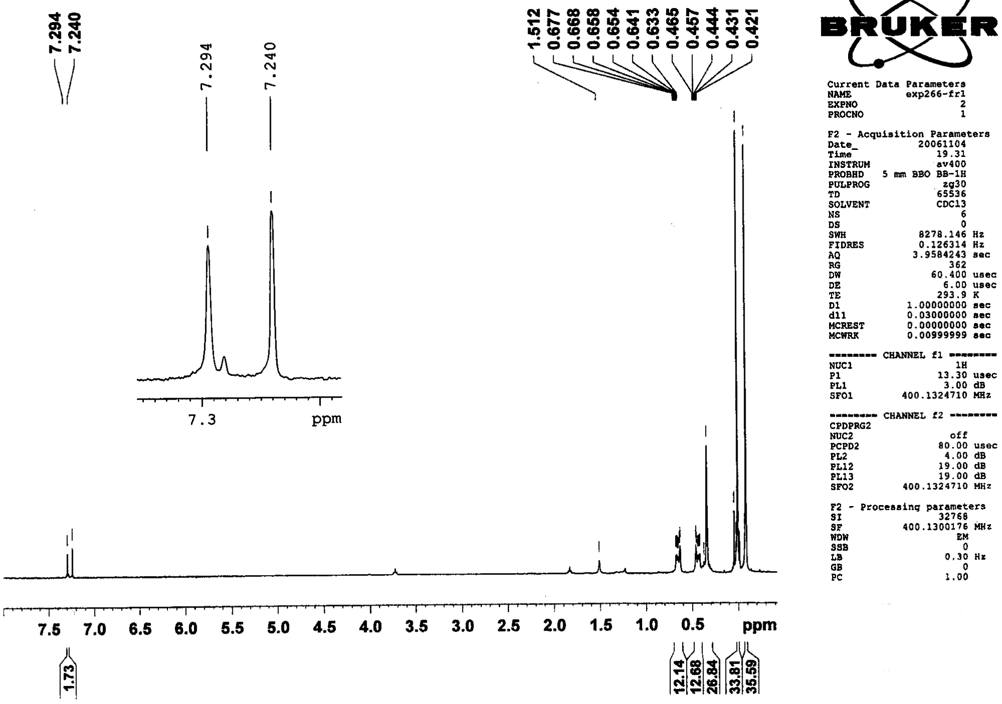


Fig. S6. ^{13}C NMR spectrum of 2,5-Bis[tris(3,3,6,6-tetramethyl-3,6-disilaheptyl)silyl]thiophene (**2**) in $CDCl_3$.



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TE                    293.9 K
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PL13                  19.00 dB
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F2 - Processing parameters
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WDW                      EM
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PC                     1.00
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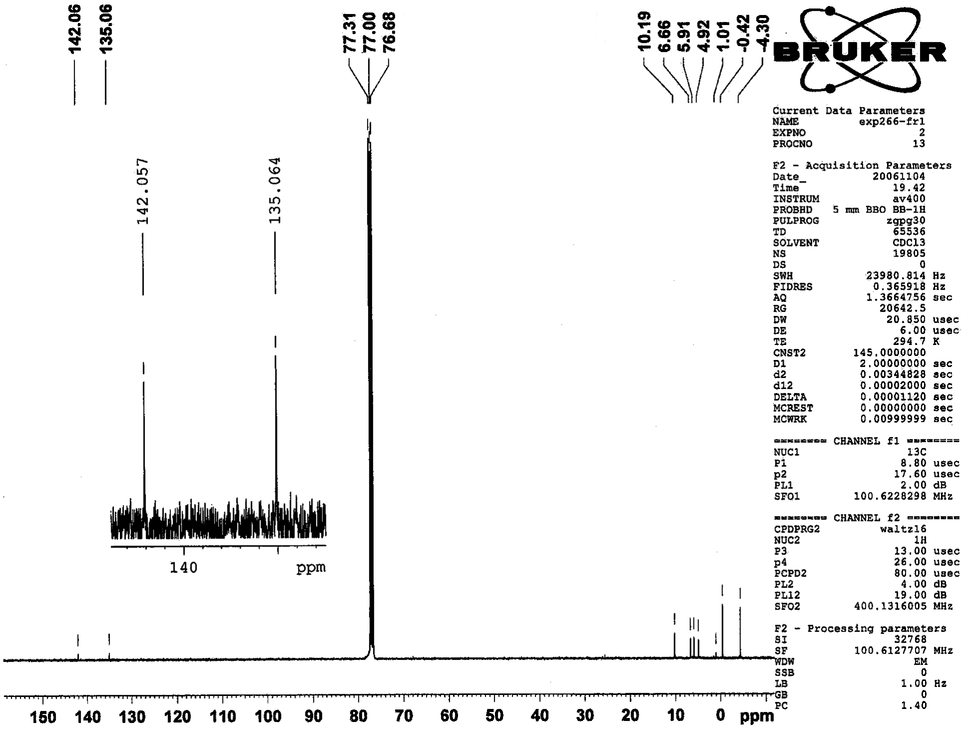
Fig. S7. ^{1}H NMR spectrum of Thiophene-Bridged Molecular Gyroscope (**1**) in CDCl$_3$.



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TE                    294.7 K
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p2                    17.60 usec
PL1                    2.00 dB
SFO1            100.6228298 MHz

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PCPD2                 80.00 usec
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PL12                  19.00 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
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WDW                      EM
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Fig. S8. ^{13}C NMR spectrum of Thiophene-Bridged Molecular Gyroscope (**1**) in CDCl$_3$.

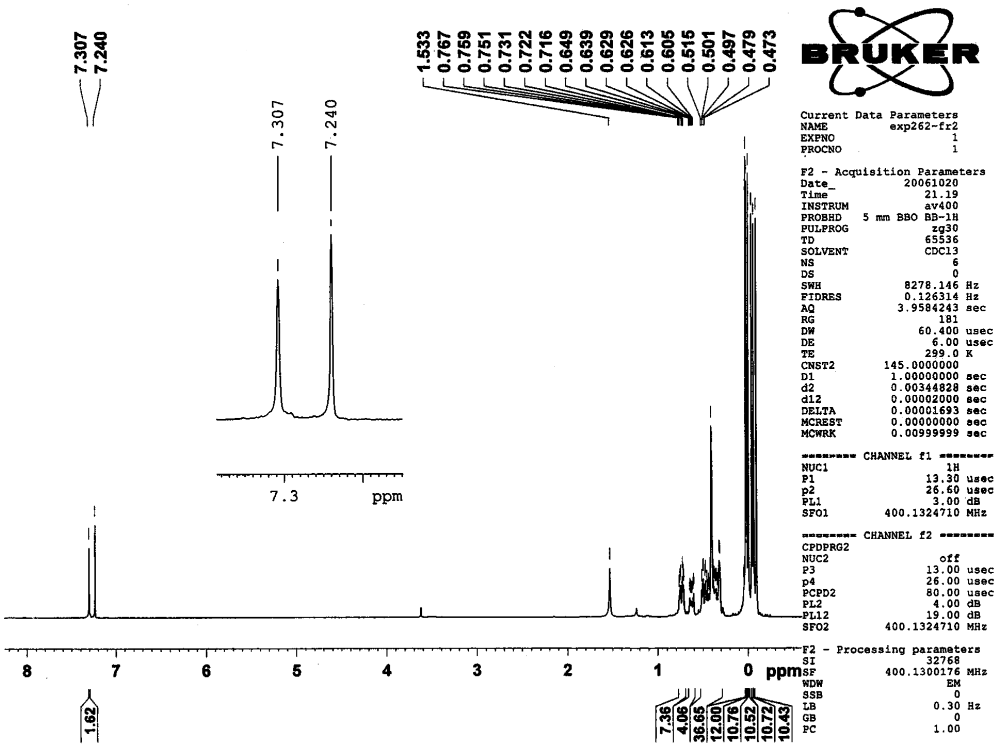


Fig. S9. ^{1}H NMR spectrum of Thiophene-Bridged Molecular Gyroscope Isomer (**1i**) in CDCl$_3$.

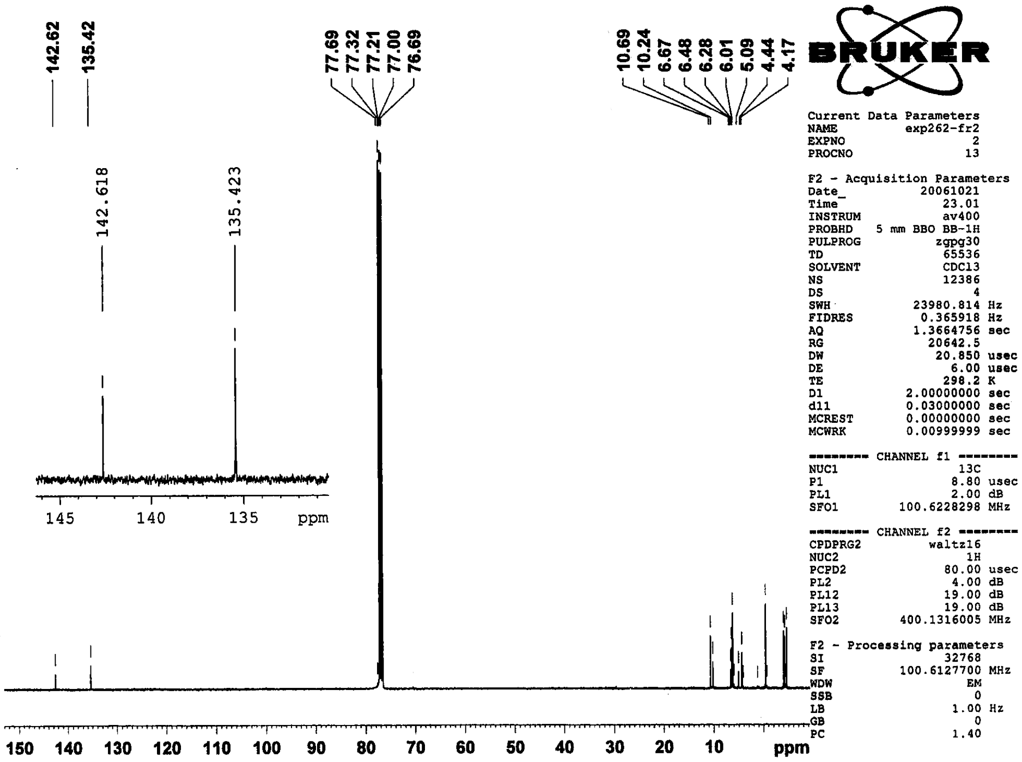
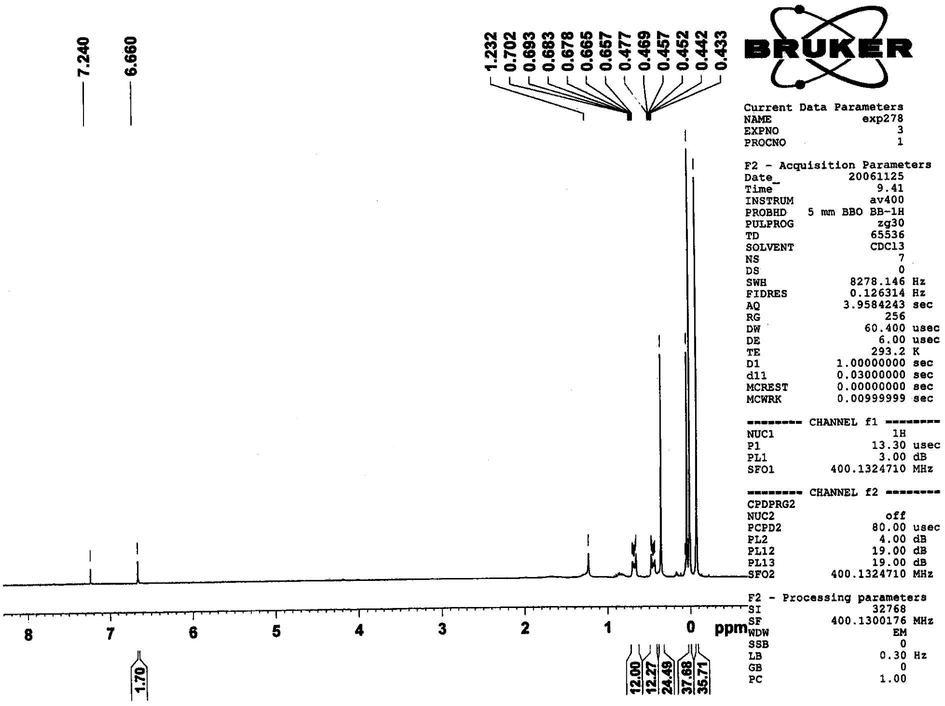


Fig. S10. ^{13}C NMR spectrum of Thiophene-Bridged Molecular Gyroscope Isomer (**1i**) in CDCl$_3$.



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F2 - Processing parameters
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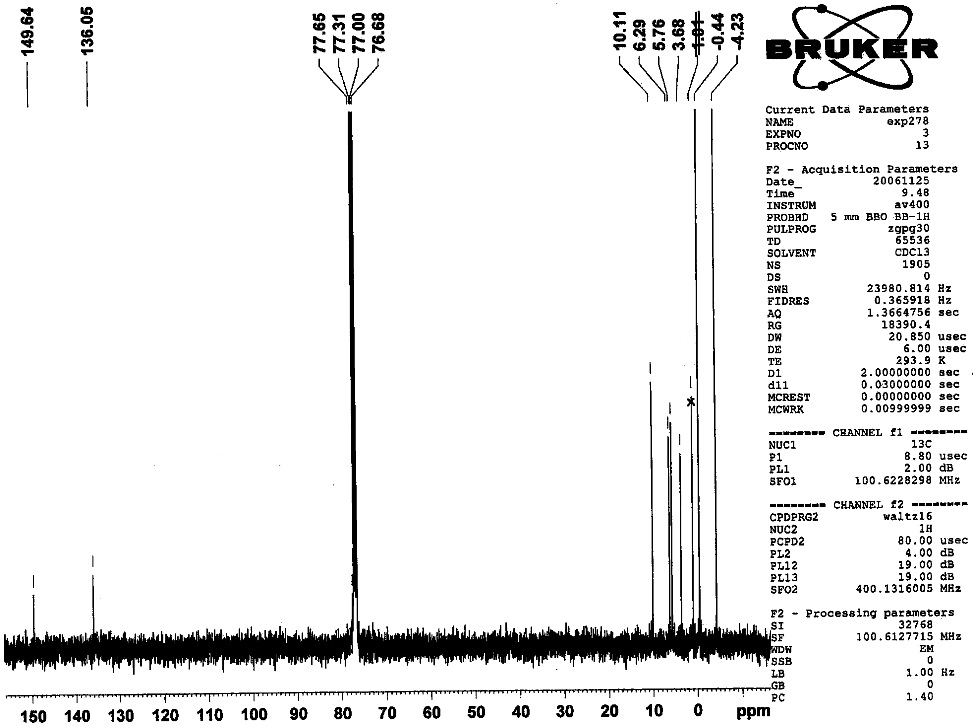
Fig. S11. ^{1}H NMR spectrum of Thiophenedioxide-Bridged Molecular Gyroscope (**3**) in CDCl$_3$.



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F2 - Processing parameters
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Fig. S12. ^{13}C NMR spectrum of Thiophenedioxide-Bridged Molecular Gyroscope (**3**) in CDCl$_3$. The asteriks indicate the signals corresponding to silicon grease.

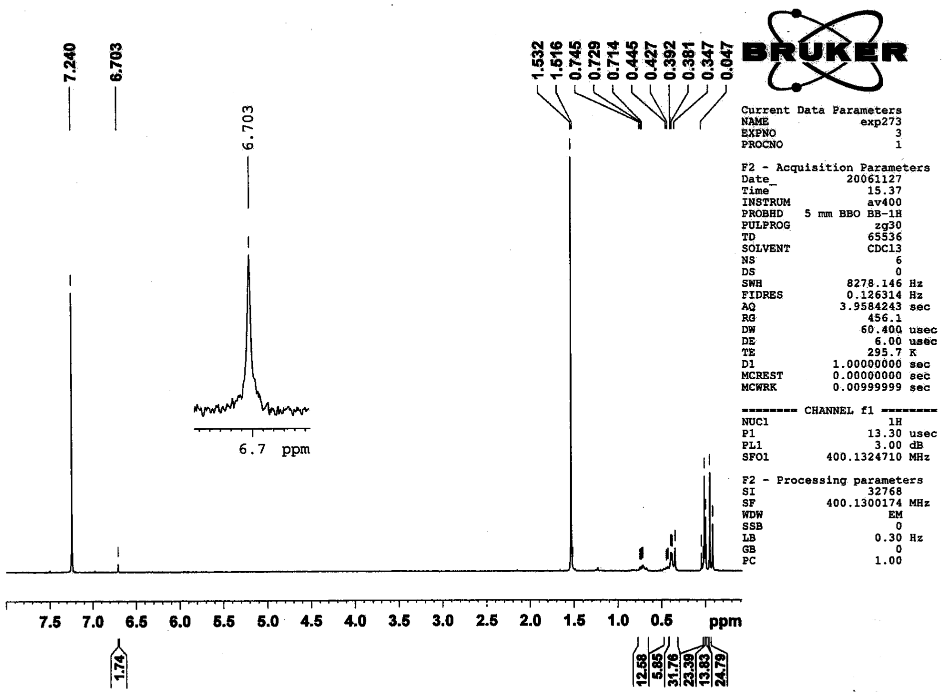

Fig. S13. ^{1}H NMR spectrum of Thiophenedioxide-Bridged Molecular Gyroscope Isomer (**3i**) in $CDCl_3$.

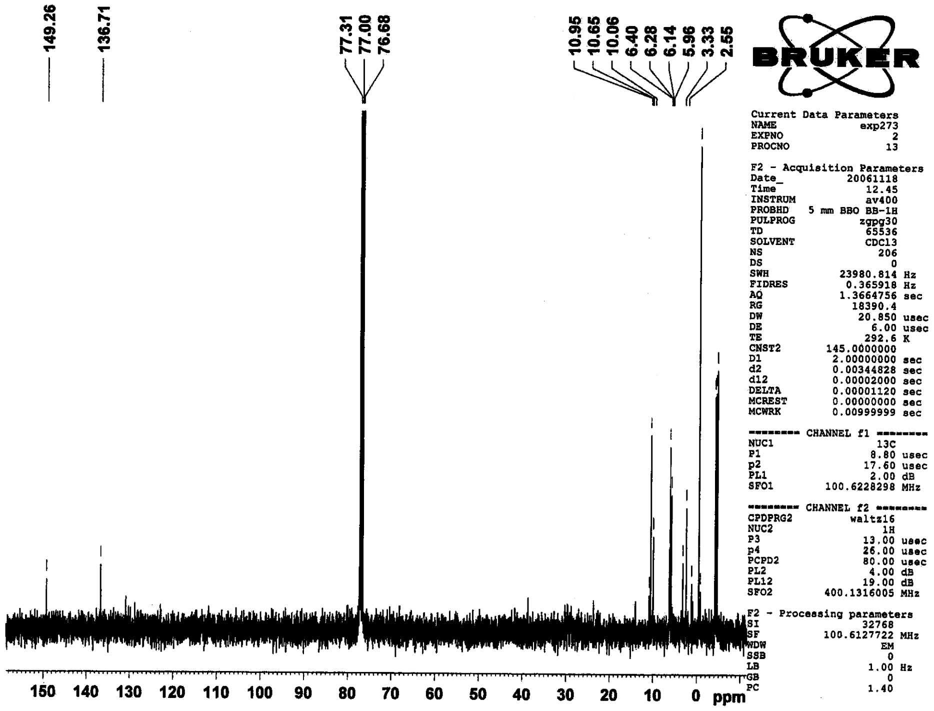

Fig. S14. ^{13}C NMR spectrum of Thiophenedioxide-Bridged Molecular Gyroscope Isomer (**3i**) in $CDCl_3$.

3. Details of X-Ray Crystallography of Molecular Gyroscopes 1 and 3

a. General

Diffraction data were collected from single crystals on a Bruker APEX-II CCD system using graphite-monochromatized MoKα radiation (λ = 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-968219 for **1**, CCDC-968220 for **3**).

b. Packing Diagram of the Crystal Structures

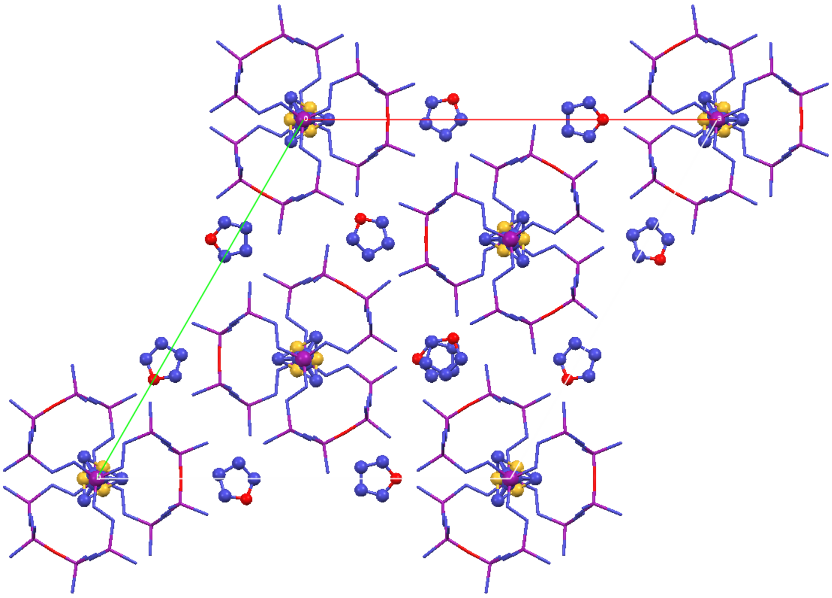

Fig. S15. Packing diagram of the crystal structure of **1**.

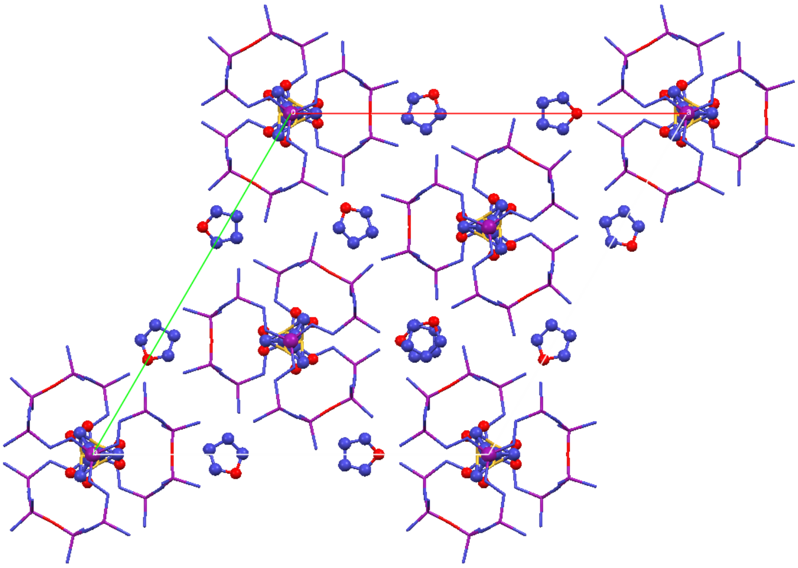

Fig. S16. Packing diagram of the crystal structure of **3**.

4. The structural formula of compound 5

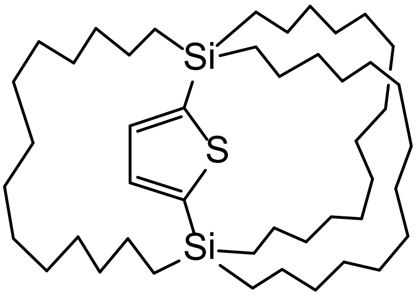

Fig. S17. The structural formula of **5**.