

Supplementary Information

Crystalline Thieno[3,2-*b*]thiophene-dioxide-diyl bridged Molecular Gyrotops as Fluorescent Dielectric Materials

Daiki Hayashi ^a Yusuke Inagaki ^a and Wataru Setaka^{*a}

^a *Division of Applied Chemistry, Faculty of Urban Environmental Sciences, Tokyo Metropolitan
University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan*

- 1. Details of Synthetic Studies**
- 2. Copies of ¹H, ¹³C, ²⁹Si NMR, and HRMS Spectra for All New Compounds**
- 3. Details of X-Ray Diffraction Studies**
- 4. Details of DSC Studies**
- 5. Details of Fluorescence Studies**
- 6. Details of Temperature Dependent Dielectric Relaxation Studies**
- 7. Details of DFT Calculations**

1. Details of Synthetic Studies

General All the reactions were carried out under an argon or nitrogen atmosphere. The chemical shifts in the ^1H and ^{13}C NMR spectra were based on the residual solvent resonances, while those in ^{29}Si NMR spectra were referenced to external tetramethylsilane. HRMS analyses were carried out using a time-of-flight mass spectrometry (TOF-MS) system with atmospheric pressure chemical ionization (APCI). Preparatory GPC was carried out using chloroform stabilized with ethanol as the eluent. Commercially available reagents were used as received without further purification.

Synthesis of 2,5-bis(tri(7-octenyl)silyl)thieno[3,2-*b*]thiophene (C8TTC8) A solution of *n*-BuLi (1.6 M in hexane, 20 mL, 2.2 equiv) was added to a THF (20 mL) solution of thieno[3,2-*b*]thiophene (1.9 g, 13.5 mmol) slowly at $-78\text{ }^\circ\text{C}$, and then the reaction temperature was raised to room temperature and stirring was continued for 3 h. To the mixture was added tri(7-octenyl)chlorosilane (13.2 g, 31.3 mmol) at $-78\text{ }^\circ\text{C}$, and then the reaction was stirred for 20 h at room temperature. The mixture was then hydrolyzed and extracted with hexane. The organic layer was washed with a saturated aqueous NaCl solution and dried over anhydrous Na_2SO_4 . Silica gel column chromatography (hexane as the eluent) of the concentrated residue afforded the crude product as a colorless oil. Pure **C8TTC8** (4.2 g, 4.1 mmol, 30% yield) was obtained as a colorless oil after GPC purification. **C8TTC8**: a colorless oil; ^1H NMR (CDCl_3 , 500 MHz): δ 7.27 (s, 1H, thienothiophene (TT)), 5.79 (ddt, $J = 17.0, 10.2, 6.8$ Hz, 3H, $\text{H}_2\text{C}=\text{CH}-$), 4.98 (d, $J = 20.0$ Hz, 3H, $\text{H}_2\text{C}=\text{CH}-$), 4.91 (d, $J = 10.0$ Hz, 3H, $\text{H}_2\text{C}=\text{CH}-$), 2.01 (q, $J = 7.0$ Hz, 6H, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-$), 1.27-1.37 (br, 24H), 0.79 (t, $J = 8.0$ Hz, 6H, $-\text{Si}-(\text{CH}_2)-$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz): δ 146.6 (C_{Ar}), 142.0 (C_{Ar}), 139.2, 125.7 (C_{Ar}), 114.1, 33.8, 33.6, 28.9, 28.7, 23.7, 13.4; $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 99 MHz): δ -3.2 ; HRMS (APCI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{54}\text{H}_{92}\text{Si}_2\text{S}_2$ 860.6173; Found: 860.6177.

Synthesis of 2,5-bis(tri(9-decenyl)silyl)thieno[3,2-*b*]thiophene (C10TTC10) Bissilylnaphthalene **C10TTC10** was synthesized by the same procedure as **C8TTC8**. In this case, the following reagents were used: thieno[3,2-*b*]thiophene (2.0 g, 14.5 mmol), THF (20 mL), *n*-BuLi solution (1.6 M in hexane, 20.6 mL, 2.2 equiv.), and tri(9-decenyl)chlorosilane (16.4 g, 32.0 mmol). Pure compound **C10TTC10** (5.6 g, 5.2 mmol, 37% yield) was obtained as a colorless oil after GPC purification of the crude products. **C10TTC10**: a colorless oil; ^1H NMR (CDCl_3 , 500 MHz): δ 7.27 (s, 1H, TT), 5.84 (ddt, $J = 17.2, 10.1, 6.7$ Hz, 3H, $\text{H}_2\text{C}=\text{CH}-$), 5.02 (d, $J = 16.9$ Hz, 3H, $\text{H}_2\text{C}=\text{CH}-$), 4.95 (d, $J = 10.1$ Hz, 3H, $\text{H}_2\text{C}=\text{CH}-$), 2.02 (q, $J = 7.3$ Hz, 6H, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-$), 1.25-1.35 (br, 36H), 0.79 (t, $J = 6.5$ Hz, 6H, $\text{Si}-\text{CH}_2-$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz): δ 146.6 (C_{Ar}), 142.1 (C_{Ar}), 125.7 (C_{Ar}), 139.2, 114.1, 33.8, 33.7, 29.4, 29.2, 29.0, 23.8, 13.4; $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 99 MHz): δ -3.2 ; HRMS (APCI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{66}\text{H}_{116}\text{S}_2\text{Si}_2$ 1029.8080; Found 1029.8130.

Synthesis of 2,5-bis(tri(9-decenyl)silyl)thieno[3,2-*b*]thiophene (C12TTC12) Bissilylnaphthalene **C12TTC12** was synthesized by the same procedure as **C8TTC8**. In this case, the following reagents were used: thieno[3,2-*b*]thiophene (1.9 g, 13.8 mmol), THF (20 mL), *n*-BuLi solution (1.6 M in hexane, 20.5 mL, 2.2 equiv.), and tri(9-decenyl)chlorosilane (22.5 g, 31.8 mmol). Pure compound **C12TTC12** (4.6 g, 3.9 mmol, 28% yield) was obtained as a colorless oil after GPC purification of the crude products. **C12TTC12**: a colorless oil; ^1H NMR (CDCl_3 , 500 MHz): δ 7.27 (s, 1H, TT), 5.59 (ddt, $J = 17.0, 10.5, 6.8$ Hz, 3H, $\text{H}_2\text{C}=\text{CH}-$), 4.97 (d, $J = 17.1$ Hz, 3H, $\text{H}_2\text{C}=\text{CH}-$), 4.91 (d, $J = 10.4$ Hz, 3H, $\text{H}_2\text{C}=\text{CH}-$), 2.02 (q, $J = 7.0$ Hz, 6H, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-$), 1.12-1.35 (br, 48H), 0.78 (t, $J = 6.6$ Hz, 6H, $\text{Si}-\text{CH}_2-$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz): δ 146.6 (C_{Ar}), 142.1 (C_{Ar}), 139.3, 125.7 (C_{Ar}), 114.1, 33.8, 33.7, 29.6(duplicated), 29.5, 29.2(duplicated), 29.0, 23.8, 13.4; $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 99 MHz): δ -3.2 ; HRMS (APCI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{78}\text{H}_{140}\text{S}_2\text{Si}_2$ 1196.9930; Found 1196.9947.

Synthesis of molecular gyrotop C14TT and its isomer, C14iTT To dichloromethane (500 mL) containing the first-generation Grubbs' catalyst (0.05 g, 0.06 mmol) under reflux was added 2,5-bissilylthieno[3,2-*b*]thiophene **C8TTC8** (750 mg, 0.87 mmol) in dichloromethane (200 mL) dropwise with stirring over 8 h, and then the mixture was stirred further for 12 h. The volatile materials were removed in vacuo, and the metal catalyst was removed from the toluene-soluble fraction following flash column chromatography (silica gel, toluene). Hydrogen gas (3 atm) was then introduced to a solution of toluene (5 mL) and the reaction mixture in the presence of 10% Pd/C (0.10 g) in an autoclave, and the mixture was allowed to stand for 72 h at $60\text{ }^\circ\text{C}$. After the excess H_2 gas was released, the mixture was filtered to remove

Pd/C. The volatile materials were removed in vacuo. The fractions containing **C14TT** (85 mg, 0.11 mmol, 12% yield) and **C14iTT** (49 mg, 0.062 mmol, 7% yield) were collected separately using GPC (chloroform) and the solvents were evaporated. **C14TT**: mp 300 °C (decomp.); colorless crystals; ¹H NMR (CDCl₃, 500 MHz): δ 7.33 (s, 1H, TT), 1.19-1.45 (br, 36H), 0.73-0.76 (br, 6H, Si-CH₂-); ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 146.6 (C_{Ar}), 141.0 (C_{Ar}), 126.1 (C_{Ar}), 32.0, 29.9, 29.7, 28.1, 27.7, 22.4, 13.6; ²⁹Si{¹H} NMR (CDCl₃, 99 MHz) δ -2.2; HRMS (APCI) *m/z*: [M]⁺ Calcd for C₄₈H₈₆Si₂S₂ 782.5704; Found: 782.5687. **C14iTT**: a colorless oil; a colorless oil; ¹H NMR (CDCl₃, 500 MHz): δ 7.28 (s, 1H, TT), 1.06-1.39 (br, 36H), 0.79-0.91 (br, 4H, Si-CH₂-), 0.69-0.72 (br, 2H, Si-CH₂-); ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 146.5 (C_{Ar}), 142.1 (C_{Ar}), 125.7 (C_{Ar}), 31.8, 31.5, 29.4, 29.3, 27.8, 27.9, 27.0, 26.9, 26.8, 26.3, 22.4, 22.3, 13.2, 12.7; ²⁹Si{¹H} NMR (CDCl₃, 99 MHz): δ -2.4; HRMS (APCI) *m/z*: [M]⁺ Calcd for C₄₈H₈₆Si₂S₂ 782.5704; Found: 782.5699.

Synthesis of the molecular gyrotop C18TT and its isomer C18iTT Molecular gyrotop **C18TT** and its isomer **C18iTT** were synthesized from **C10TTC10** by the same procedure as **C14TT**. In this case, the following reagents were used: 2,5-bissilylthieno[3,2-b]thiophene **C10TTC10** (1.0 g, 0.82 mmol), first-generation Grubbs' catalyst (0.05 g, 0.06 mmol), and dichloromethane (total 900 mL). Pure compounds **C18TT** (47 mg, 0.41 mmol, 5% yield) and **C18iTT** (270 mg, 0.22 mmol, 27% yield) were obtained after GPC separation and purification of the crude products. **C18TT**: colorless crystals; mp 68.1-68.5 °C; colorless crystals; ¹H NMR (CDCl₃, 500 MHz): δ 7.34 (s, 1H, TT), 1.12-1.38 (br, 48H), 0.76-0.83 (br, 6H, Si-CH₂-); ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 146.7 (C_{Ar}), 141.9 (C_{Ar}), 126.0 (C_{Ar}), 33.3, 29.4, 29.3, 29.2, 28.8, 28.7, 28.3, 23.6, 13.7; ²⁹Si{¹H} NMR (CDCl₃, 99 MHz): δ -2.8; HRMS (APCI) *m/z*: [M + H]⁺ Calcd for C₆₀H₁₁₁S₂Si₂: 951.7660; Found 951.7638. **C18iTT**: a colorless oil; ¹H NMR (CDCl₃, 500 MHz) δ 7.29 (s, 1H, TT), 1.20-1.40 (br, 48H), 0.79-0.90 (br, 4H, Si-CH₂-), 0.71-0.74 (br, 2H, Si-CH₂-); ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 146.6 (C_{Ar}), 142.2 (C_{Ar}), 125.8 (C_{Ar}), 33.6, 33.0, 29.3, 29.1, 28.8 (Two signals are overlapped.), 28.7, 28.4, 28.1 (Two signals are overlapped.), 27.7, 27.4, 23.7, 23.3, 14.1, 13.0; ²⁹Si{¹H} NMR (CDCl₃, 99 MHz): δ -2.8; HRMS (APCI) *m/z*: [M]⁺ Calcd for C₆₀H₁₁₀S₂Si₂: 951.7582; Found 951.7546.

Synthesis of the molecular gyrotop C22TT and its isomer C22iTT Molecular gyrotop **C22TT** and its isomer **C22iTT** were synthesized from **C12TTC12** by the same procedure as **C14TT**. In this case, the following reagents were used: 2,5-bissilylthieno[3,2-b]thiophene **C12TTC12** (1.0 g, 0.84 mmol), first-generation Grubbs' catalyst (0.05 g, 0.06 mmol), and dichloromethane (total 900 mL). Pure compounds **C22TT** (160 mg, 0.14 mmol, 16% yield) and **C22iTT** (66 mg, 0.059 mmol, 7% yield) were obtained after GPC separation and purification of the crude products. **C22TT**: colorless crystals; mp 98.4-100.4 °C; colorless crystals; ¹H NMR (CDCl₃, 500 MHz): δ 7.32 (s, 1H, TT), 1.24-1.36 (br, 60H), 0.76-0.80 (br, 6H, Si-CH₂-); ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 146.6 (C_{Ar}), 142.0 (C_{Ar}), 125.9 (C_{Ar}), 33.7, 29.3 (quintuplicated), 29.1(duplicated), 29.0, 28.9, 23.8, 13.5; ²⁹Si{¹H} NMR (CDCl₃, 99 MHz): δ -3.1; HRMS (APCI) *m/z*: [M + H]⁺ Calcd for C₇₂H₁₃₅S₂Si₂: 1119.9538; Found 1119.9507. **C22iTT**: a colorless oil; ¹H NMR (CDCl₃, 500 MHz) δ 7.28 (s, 1H, TT), 1.15-1.40 (br, 60H), 0.84-0.87 (br, 4H, Si-CH₂-), 0.73-0.83 (br, 2H, Si-CH₂-); ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 146.6 (C_{Ar}), 142.3 (C_{Ar}), 125.7 (C_{Ar}), 33.7, 33.3, 29.2(duplicated), 29.1(duplicated), 29.0(duplicated), 28.8, 28.7(duplicated), 28.5, 28.2, 28.0, 23.8, 23.5, 14.0, 13.0; ²⁹Si{¹H} NMR (CDCl₃, 99 MHz): δ -3.0; HRMS (APCI) *m/z*: [M + H]⁺ Calcd for C₇₂H₁₃₅S₂Si₂: 1119.9538; Found 1119.9511.

Synthesis of molecular gyrotop C14TTO2 Macrocycle **C14TT** (60 mg, 0.077 mmol) and *m*CPBA (140 mg, 0.63 mmol) were dissolved in dry dichloromethane (50 mL). The reaction mixture was then stirred for 48 h at room temperature. The mixture was quenched with a dilute aqueous NaHCO₃ solution and extracted with dichloromethane. The organic layer was washed 10 times with dilute aqueous NaHCO₃ to completely remove chlorobenzoic acid. The mixture was dried over anhydrous Na₂SO₄ and filtered, and the volatile materials were removed in vacuo. Pure **C14TTO2** (40 mg, 0.049 mmol, 64% yield) was obtained as colorless crystals after recrystallization from ethanol. **C14TTO2**: colorless crystals; mp 380 °C (decomp.); ¹H NMR (CDCl₃, 500 MHz): δ 7.27 (s, 1H, TT), 7.04 (s, 1H, TT), 1.18-1.46 (br, 72H), 0.76-0.79 (br, 6H, Si-CH₂-), 0.72-0.75 (br, 6H, Si-CH₂-); ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 12.6, 13.3, 22.1, 22.4, 27.7, 27.9, 28.0, 28.4, 29.5, 29.9, 29.9, 29.95, 32.0, 32.1, 126.7 (C_{Ar}), 132.1 (C_{Ar}), 144.1 (C_{Ar}), 146.9 (C_{Ar}), 147.4 (C_{Ar}), 149.6 (C_{Ar}); ²⁹Si{¹H} NMR (CDCl₃, 99 MHz) δ -0.5, -0.8; HRMS (APCI) *m/z*: [M]⁺ Calcd for C₄₈H₈₆S₂Si₂O₂: 815.5681; Found 815.5668.

Synthesis of molecular gyrotop C18TTO2 Macrocycle **C18TT** was synthesized via the same procedure as that for **C14TTO2**. In this case, molecular gyrotop **C18TT** (136 mg, 0.14 mmol), *m*CPBA

(257 g, 1.14 mmol), and dichloromethane (50 mL) were used. Pure **C18TTO2** (120 mg, 0.12 mmol, 83% yield) was obtained as colorless crystals after recrystallization from ethanol. **C18TTO2**: colorless crystals; mp 85.3-86.7 °C; ¹H NMR (CD₂Cl₂, 500 MHz): δ 7.27 (s, 1H, TT), 7.10 (s, 1H, TT), 1.26-1.42 (br, 96H), 0.78-0.84 (br, 12H, Si-CH₂-); ¹³C{¹H} NMR (CD₂Cl₂, 126 MHz): δ 149.2 (C_{Ar}), 148.3 (C_{Ar}), 147.3 (C_{Ar}), 143.9 (C_{Ar}), 132.5 (C_{Ar}), 125.8 (C_{Ar}), 33.2, 33.1, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 28.8, 28.7, 28.6, 28.3, 28.2, 23.4, 23.1, 13.3, 11.9; ²⁹Si{¹H} NMR (CD₂Cl₂, 99 MHz) δ -1.6, -1.8; HRMS (APCI) *m/z*: [M + H]⁺ Calcd for C₆₀H₁₁₁S₂Si₂O₂: 983.7559; Found 983.7581.

Synthesis of molecular gyrotop C22TTO2 Macrocycle **C22TTO2** was synthesized via the same procedure as that for **C14TTO2**. In this case, molecular gyrotop **C22TT** (130 mg, 0.12 mmol), *m*CPBA (213 mg, 0.95 mmol), and dichloromethane (50 mL) were used. Pure **C18TTO2** (130 mg, 0.11 mmol, 97% yield) was obtained as colorless crystals after recrystallization from ethanol. **C18TTO2**: colorless crystals; mp 104.1-105.3 °C; ¹H NMR (CDCl₃, 500 MHz): δ 7.25 (s, 1H, TT), 7.05 (s, 1H, TT), 1.24-1.38 (br, 120H), 0.83-0.86 (br, 6H, Si-CH₂-), 0.74-0.81 (br, 6H, Si-CH₂-); ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 149.3 (C_{Ar}), 148.2 (C_{Ar}), 147.2 (C_{Ar}), 143.8 (C_{Ar}), 132.4 (C_{Ar}), 126.2 (C_{Ar}), 33.7, 33.6, 29.5, 29.4(triplicated), 29.3(triplicated), 29.2, 29.1(triplicated), 28.9(duplicated), 23.7, 23.4, 13.3; ²⁹Si{¹H} NMR (CD₂Cl₂, 99 MHz) δ -2.2; HRMS (APCI) *m/z*: [M + H]⁺ Calcd for C₇₂H₁₃₅S₂Si₂O₂: 1119.9538; Found 1119.9511.

Synthesis of 2,5-bis(trimethylsilyl)thieno[3,2-b]thiophene (TMSTT) Bissilylnaphthalene **TMSTT** was synthesized by the same procedure as **C8TTC8**. In this case, the following reagents were used: thieno[3,2-b]thiophene (1.50 g, 10.7 mmol), THF (20 mL), *n*-BuLi solution (1.6 M in hexane, 15.2 mL, 2.3 equiv.), and trimethylchlorosilane (3.30 g, 29.9 mmol). Pure compound **TMSTT** (1.1 g, 3.9 mmol, 36% yield) was obtained as colorless crystals after column chromatography purification of the crude products. **TMSTT**: colorless crystals; mp 119.4-120.8 °C; colorless crystals; ¹H NMR (CDCl₃, 500 MHz): δ 7.30 (s, 1H, TT), 0.32 (s, 9H, Si-CH₃-); ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 146.6 (C_{Ar}), 144.9 (C_{Ar}), 125.2 (C_{Ar}), 0.2 (Me); ²⁹Si{¹H} NMR (CDCl₃, 99 MHz): δ -5.8; HRMS (APCI) *m/z*: [M]⁺ Calcd for C₁₂H₂₀S₂Si₂: 284.0539; Found 284.0529.

Synthesis of 2,5-bis(tri(7-octenyl)silyl)thieno[3,2-b]thiophene-1,1-dioxide (TMSTTO2) Thienothiophene-dioxide **TMSTTO2** was synthesized by the same procedure as **C14TTO2**. In this case, thienothiophene **TMSTT** (0.20 g, 0.70 mmol), *m*CPBA (1.3 g, 5.6 mmol), and CH₂Cl₂ (30 mL) were used. Pure compound of **TMSTT** (0.092 g, 0.29 mmol, 42% yield) was obtained as colorless crystals after recrystallization from ethanol solution. **TMSTTO2**: mp 141.4-143.0 °C; colorless crystals ¹H NMR (CDCl₃, 500 MHz): δ 7.25 (s, 1H, TT), 7.02 (s, 1H, TT), 0.36 (s, 9H, Si-CH₃), 0.31 (s, 9H, Si-CH₃); ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 150.9 (C_{Ar}), 150.8 (C_{Ar}), 147.3 (C_{Ar}), 143.9 (C_{Ar}), 131.4 (C_{Ar}), 125.5 (C_{Ar}), -0.4, -1.5; ²⁹Si{¹H} NMR (CDCl₃, 99 MHz): δ -4.6, -5.6; HRMS (APCI) *m/z*: [M + H]⁺ Calcd for C₁₂H₂₁S₂Si₂O₂: 317.0516; Found 317.0503.

2. Copies of ^1H , ^{13}C , ^{29}Si NMR, and HRMS Spectra for All New Compounds

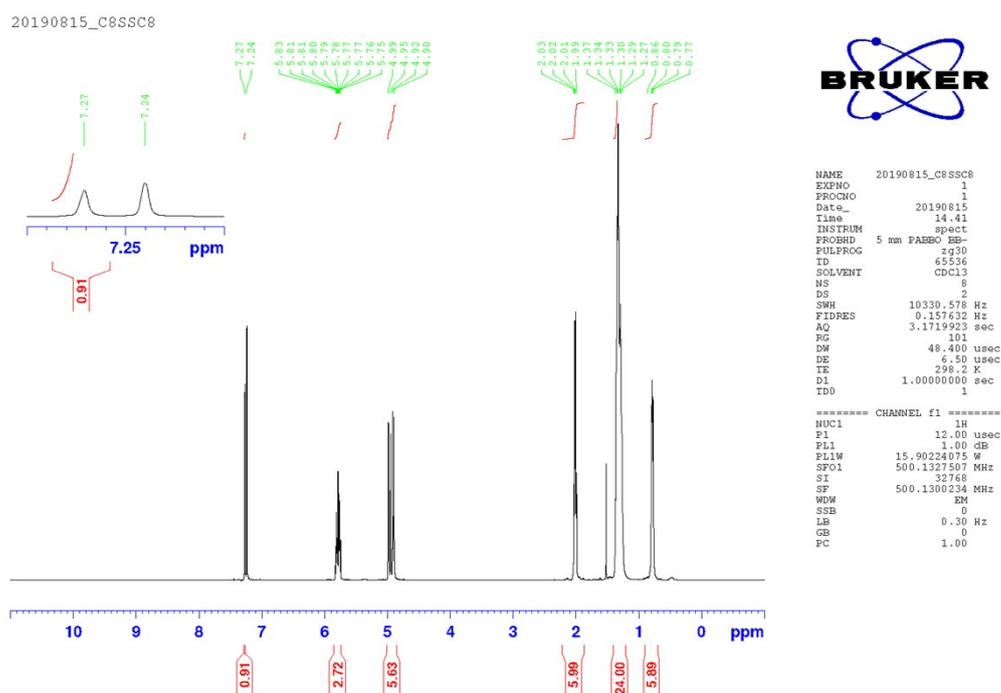


Fig. S1. ^1H NMR spectrum of 2,5-bis(tri(7-octenyl)silyl)thieno[3,2-b]thiophene (**C8TTC8**) in CDCl_3 .

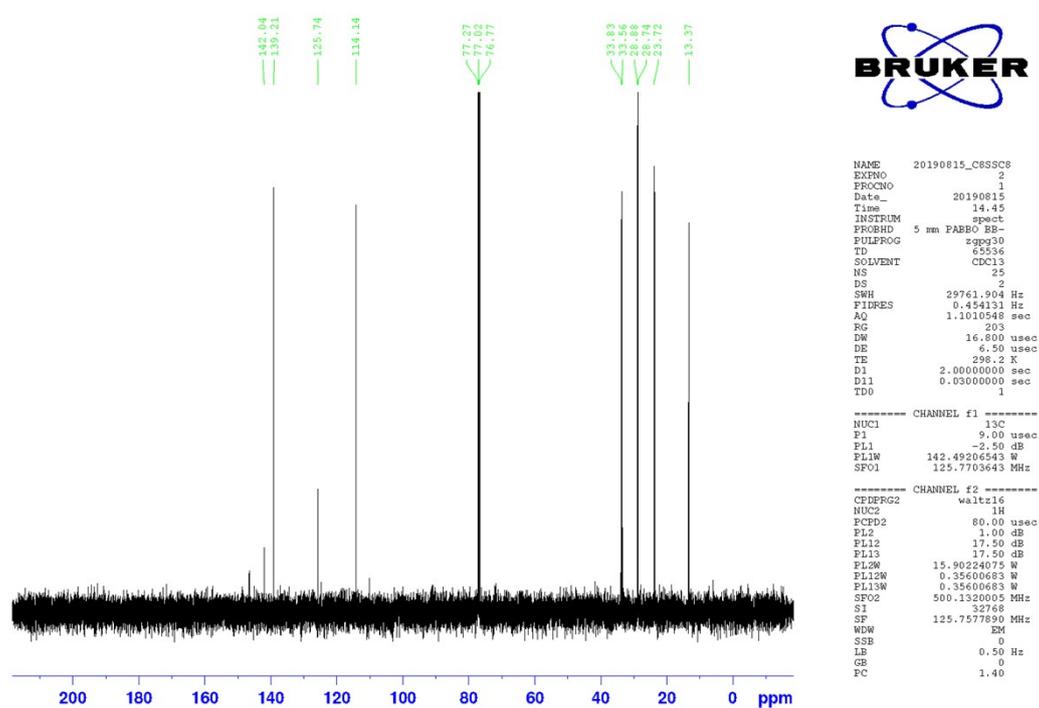
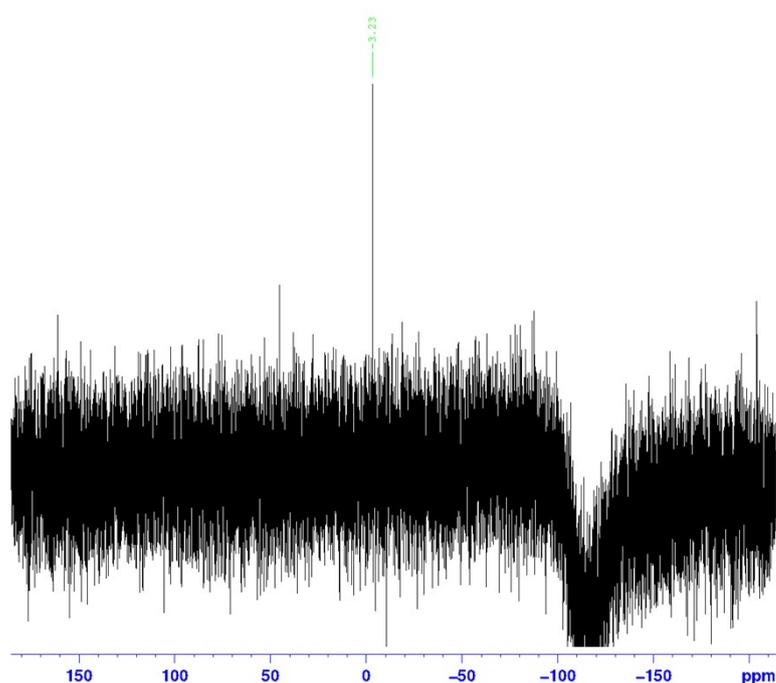


Fig. S2. ^{13}C NMR spectrum of 2,5-bis(tri(7-octenyl)silyl)thieno[3,2-b]thiophene (**C8TTC8**) in CDCl_3 .



```

NAME      20190815_C8SSCS
EXPNO     7
PROCNO    1
Date_     20190815
Time      14.47
INSTRUM   spect
PROBHD    5 mm F4BBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         18
DS         0
SWH        39682.539 Hz
FIDRES     0.605507 Hz
AQ         0.8258036 sec
RG         203
DM         12.600 usec
DE         6.50 usec
TE         298.4 K
D1         2.0000000 sec
D11        0.03000000 sec
TD0        1
----- CHANNEL f1 -----
NUC1       29Si
P1         9.00 usec
PL1        -2.50 dB
SFO1       99.3603373 MHz
----- CHANNEL f2 -----
CPDPRG2   waltz16
NUC2       1H
PCPD2     80.00 usec
PL2        1.00 dB
PL12       17.50 dB
PL13       17.50 dB
PL2W       15.90224075 W
PL12W      0.35600683 W
PL13W      0.35600683 W
SFO2       500.1320005 MHz
SI         32768
SF         99.3617539 MHz
WDW        EM
SSB         0
LB         1.00 Hz
GB         0
PC         1.40

```

Fig. S3. ^{29}Si NMR spectrum of 2,5-bis(tri(7-octenyl)silyl)thieno[3,2-b]thiophene (**C8TTC8**) in CDCl_3 .

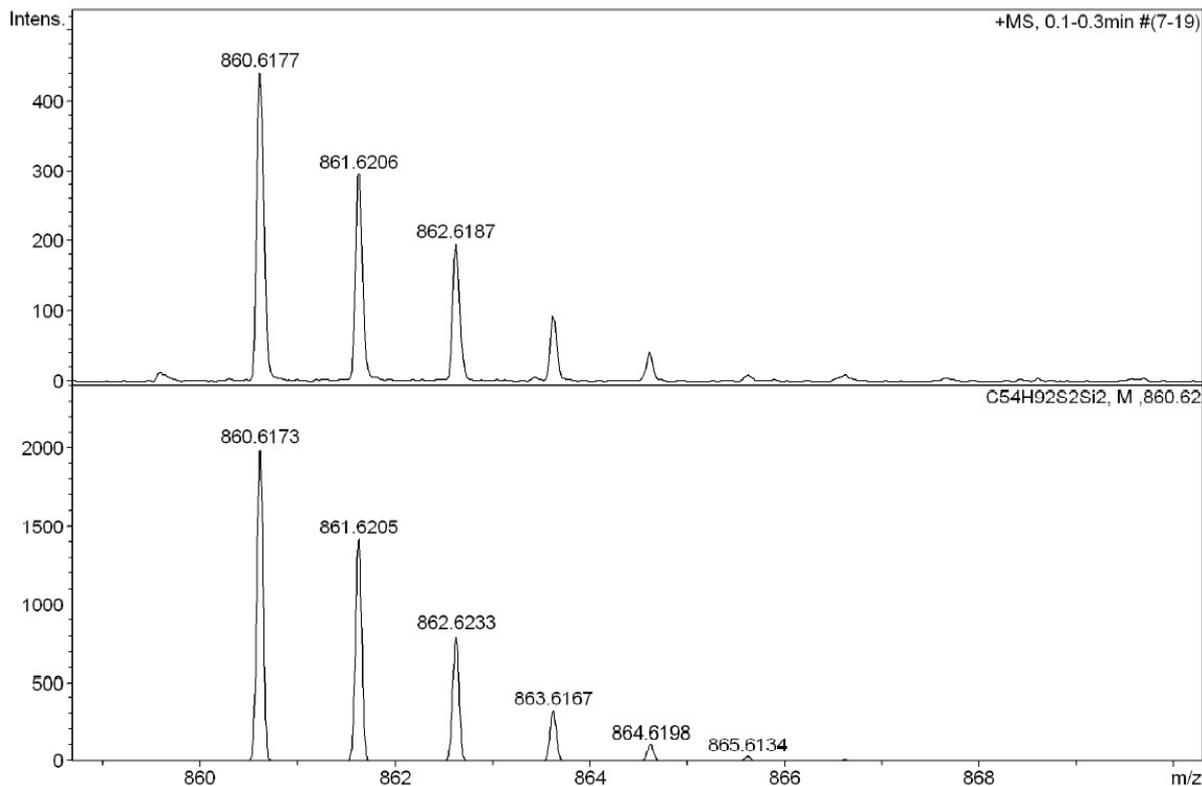


Fig. S4. HRMS spectrum of 2,5-bis(tri(7-octenyl)silyl)thieno[3,2-b]thiophene (**C8TTC8**) (APCI, positive). Top: obsd. Bottom: sim.

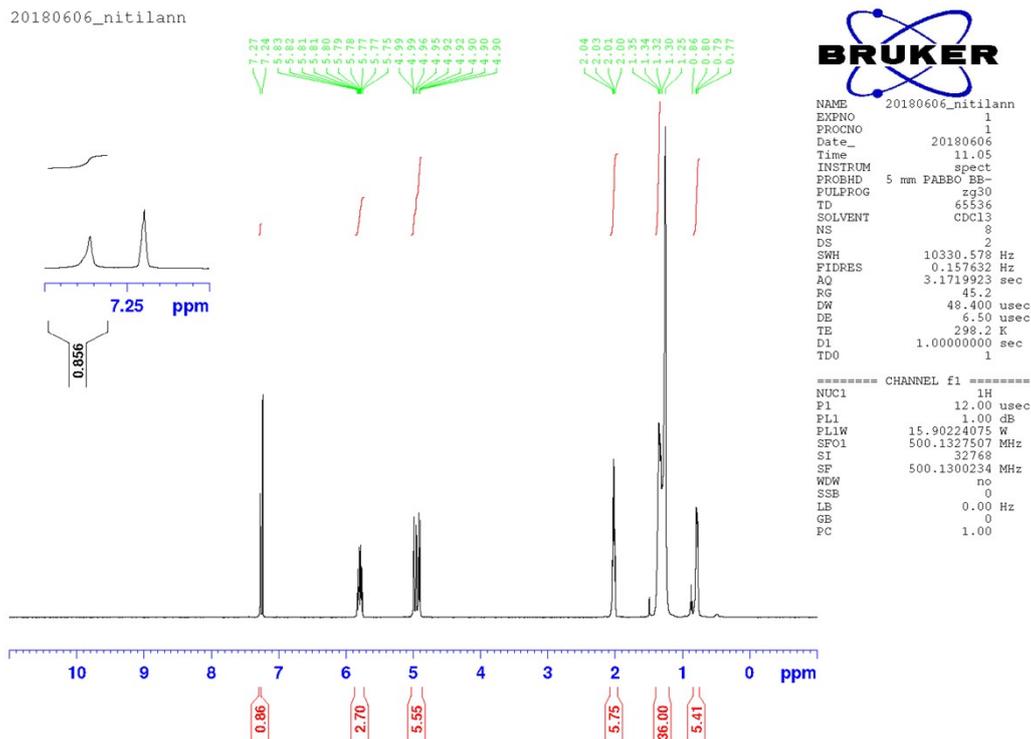


Fig. S5. ^1H NMR spectrum of 2,5-bis(tri(9-deceny)silyl)thieno[3,2-b]thiophene (**C10TTC10**) in CDCl_3 .

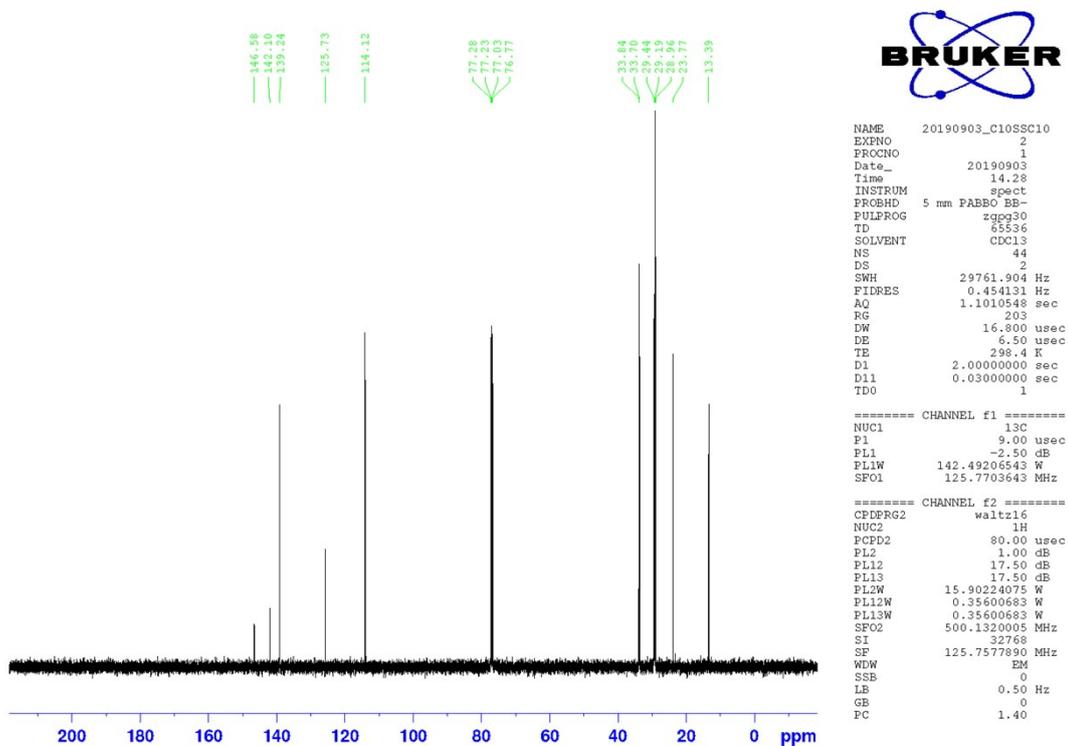


Fig. S6. ^{13}C NMR spectrum of 2,5-bis(tri(9-deceny)silyl)thieno[3,2-b]thiophene (**C10TTC10**) in CDCl_3 .

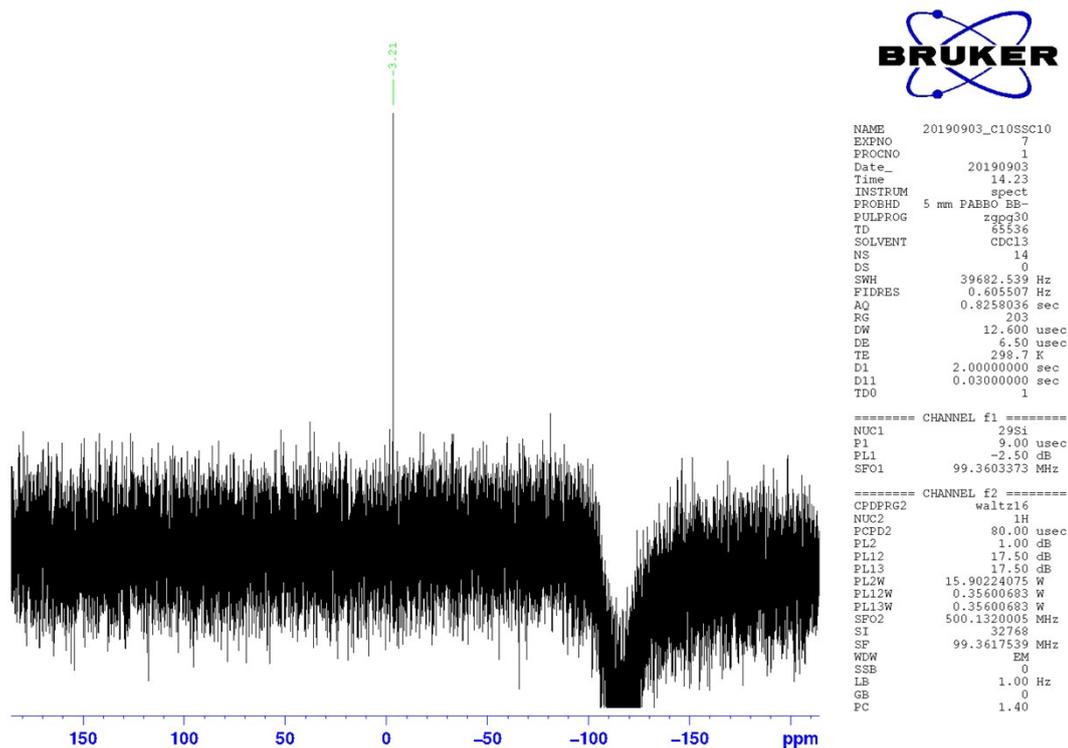


Fig. S7. ^{29}Si NMR spectrum of 2,5-bis(tri(9-decenyl)silyl)thieno[3,2-b]thiophene (**C10TTC10**) in CDCl_3 .

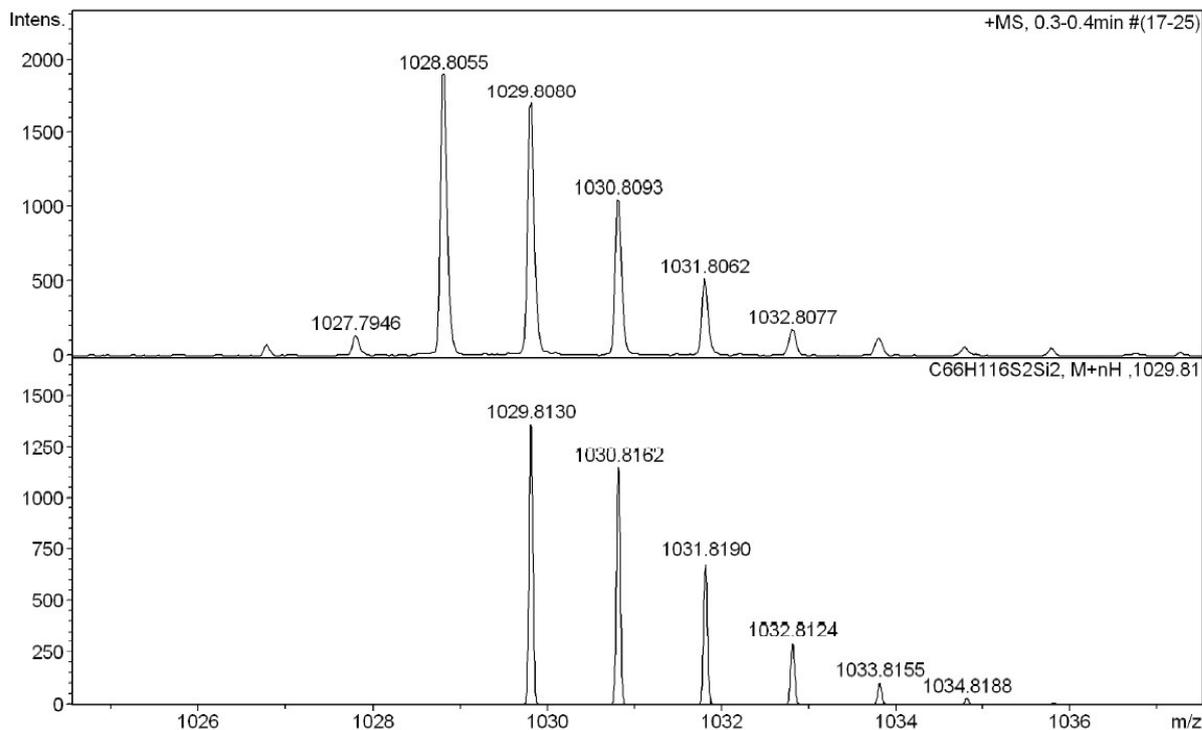


Fig. S8. HRMS spectrum of 2,5-bis(tri(9-decenyl)silyl)thieno[3,2-b]thiophene (**C10TTC10**) (APCI, positive). Top: obsd. Bottom: sim.

20190904_C12SSC12

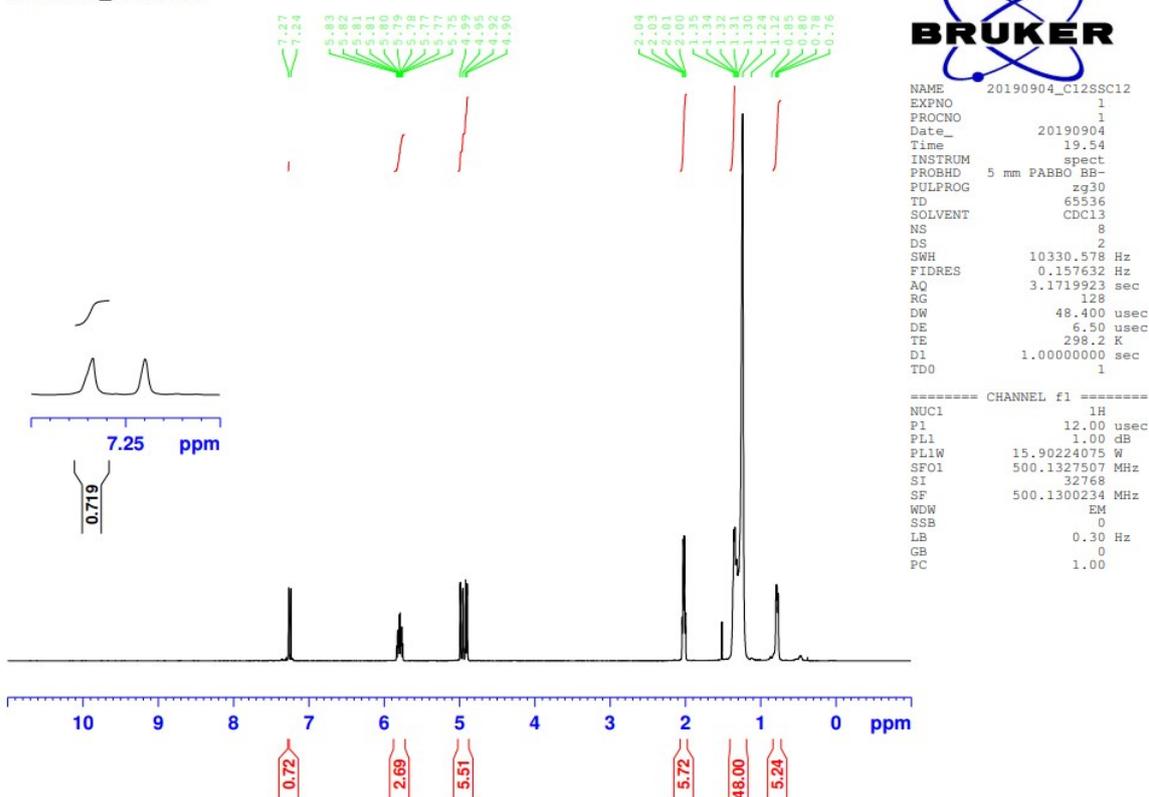


Fig. S9. ^1H NMR spectrum of 2,5-bis(tri(9-deceny)silyl)thieno[3,2-b]thiophene (C12TTC12) in CDCl_3 .

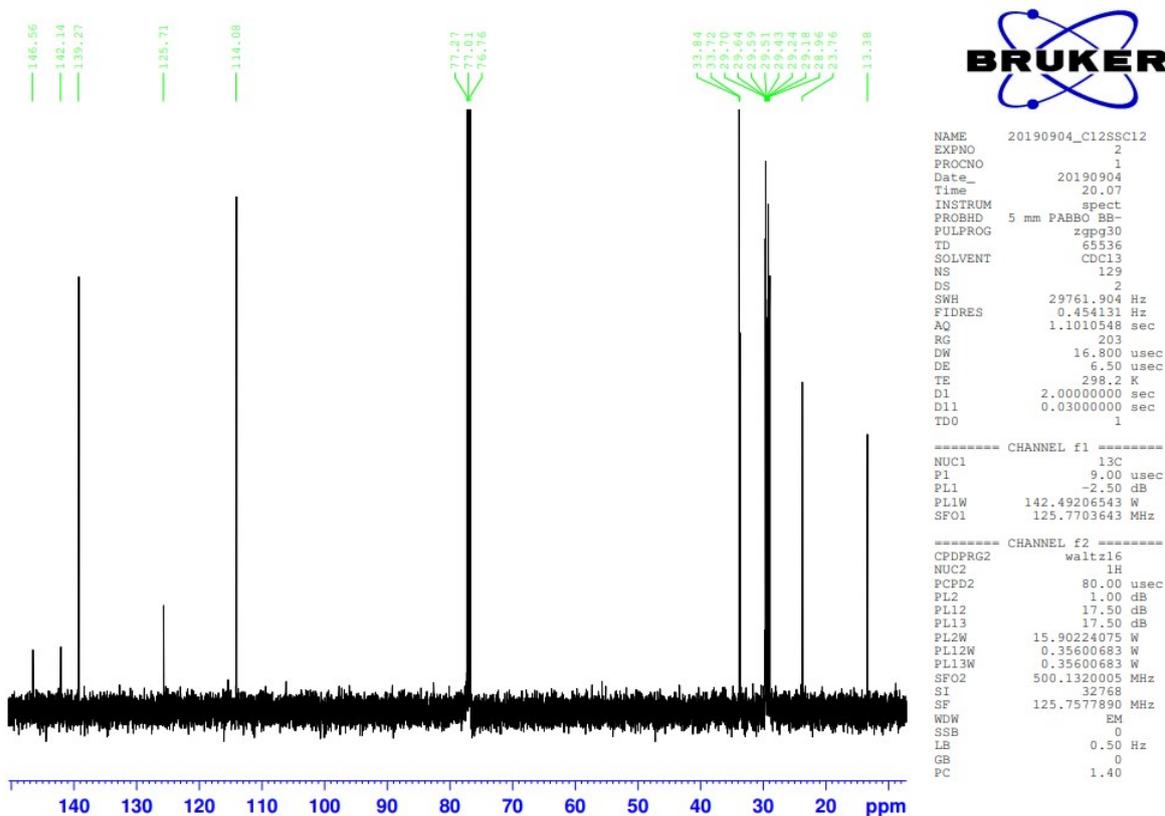


Fig. S10. ^{13}C NMR spectrum of 2,5-bis(tri(9-deceny)silyl)thieno[3,2-b]thiophene (C12TTC12) in CDCl_3 .

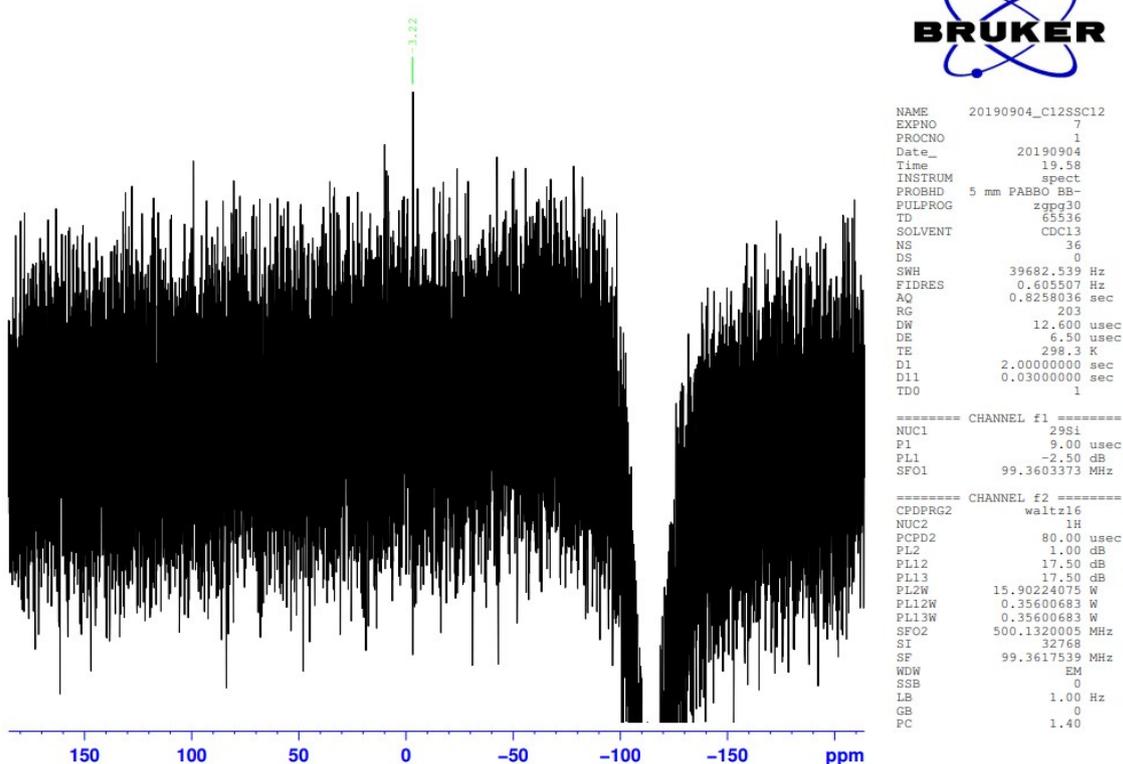


Fig. S11. ^{29}Si NMR spectrum of 2,5-bis(tri(9-decenyl)silyl)thieno[3,2-b]thiophene (C12TTC12) in CDCl_3 .

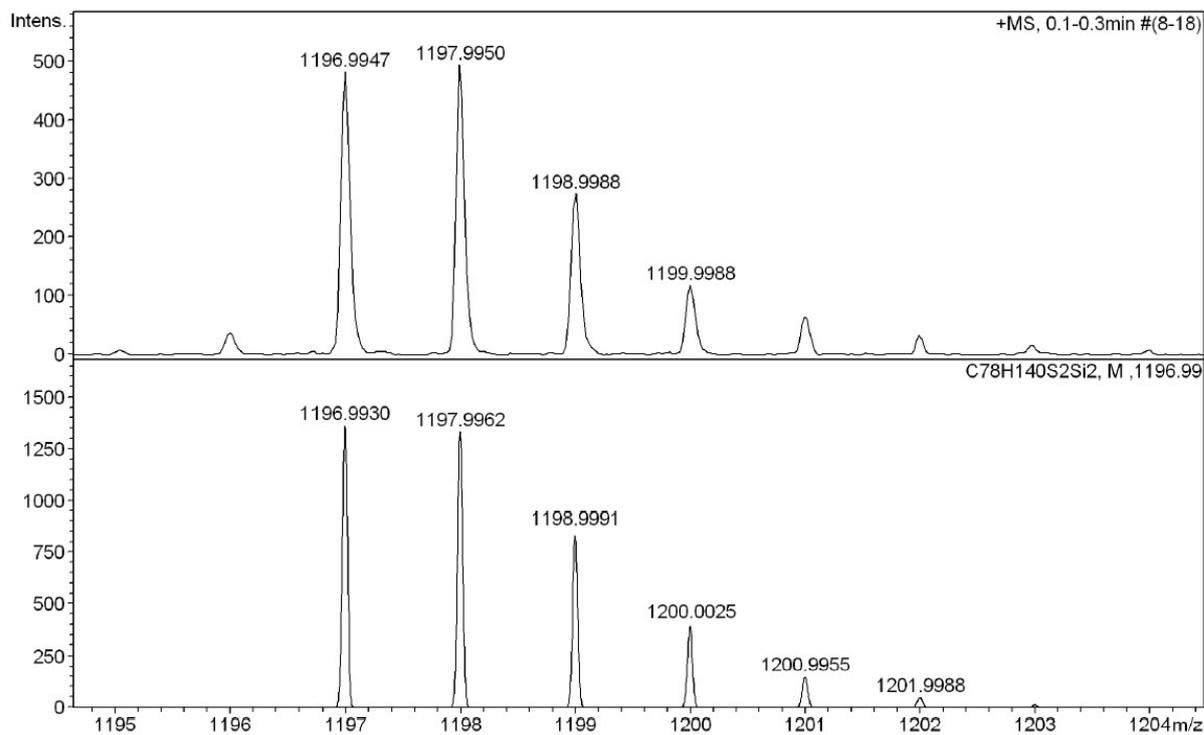


Fig. S12. HRMS spectrum of 2,5-bis(tri(9-decenyl)silyl)thieno[3,2-b]thiophene (C12TTC12) (APCI, positive). Top: obsd. Bottom: sim.

20190622_c14SS

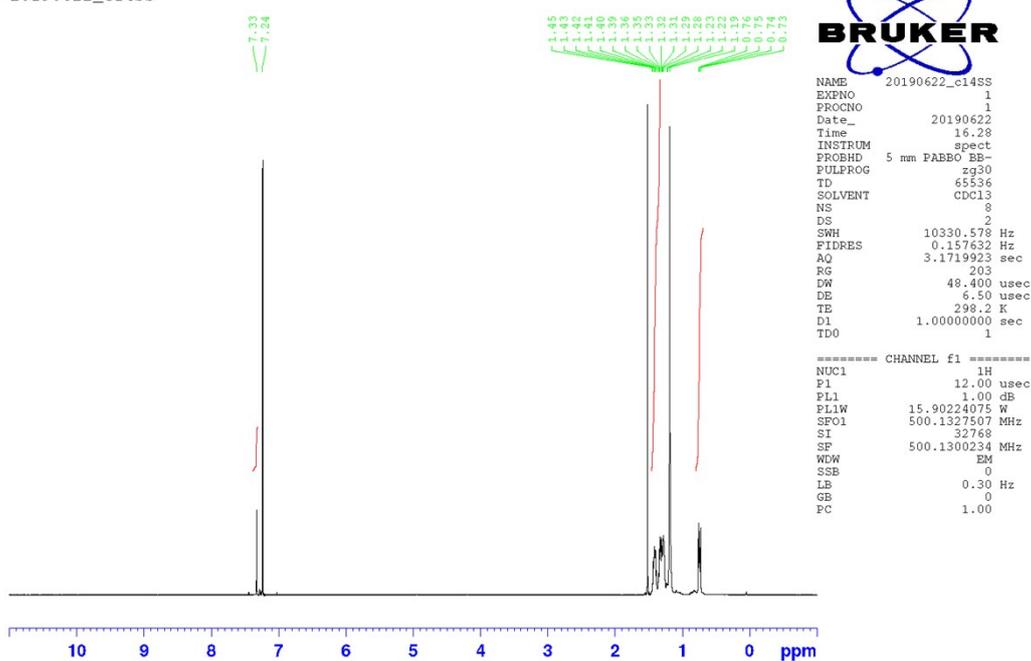


Fig. S13. ^1H NMR spectrum of Molecular Gyrotop (**C14TT**) in CDCl_3 .

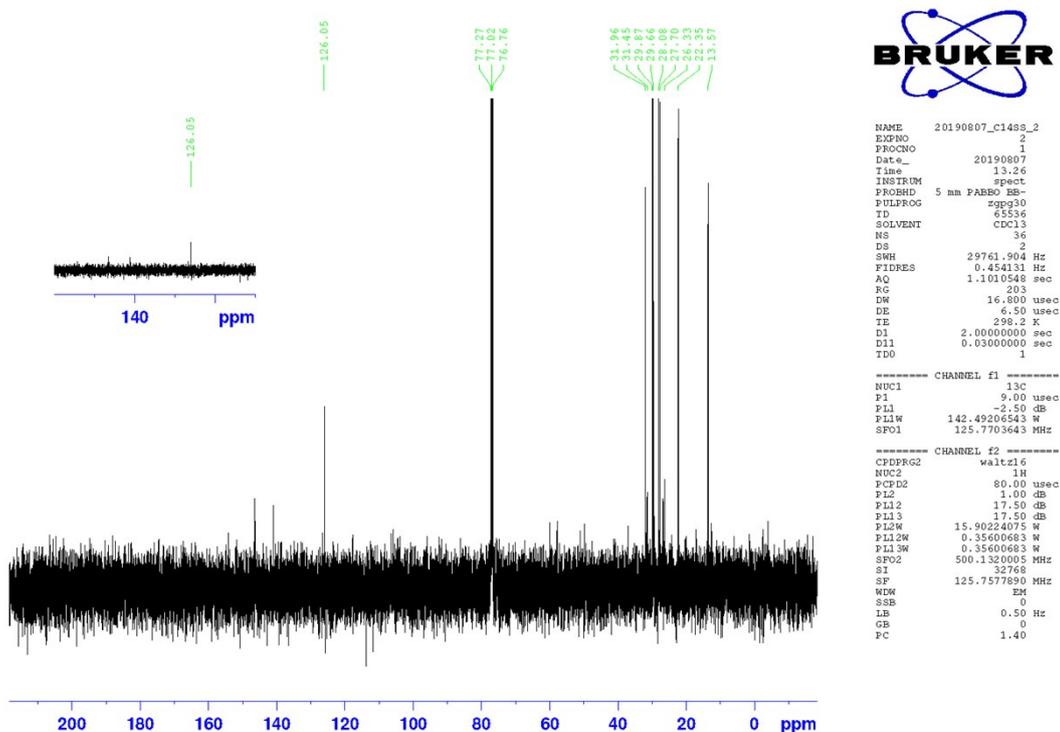


Fig. S14. ^{13}C NMR spectrum of Molecular Gyrotop (**C14TT**) in CDCl_3 .

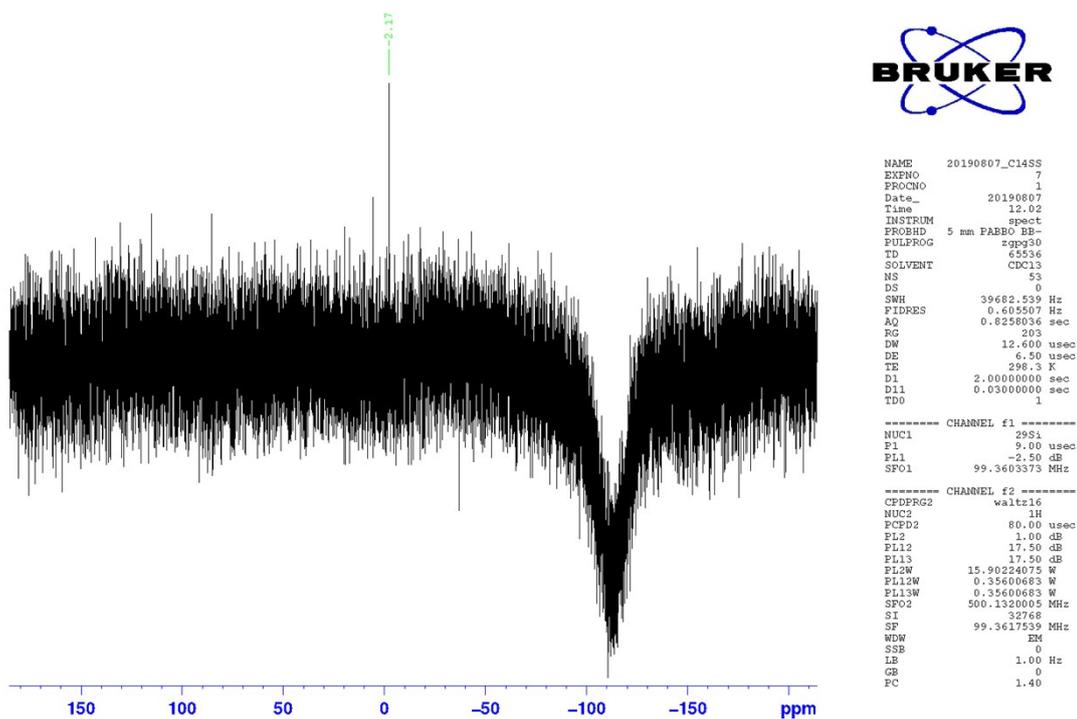


Fig. S15. ^{29}Si NMR spectrum of Molecular Gyrotop (**C14TT**) in CDCl_3 .

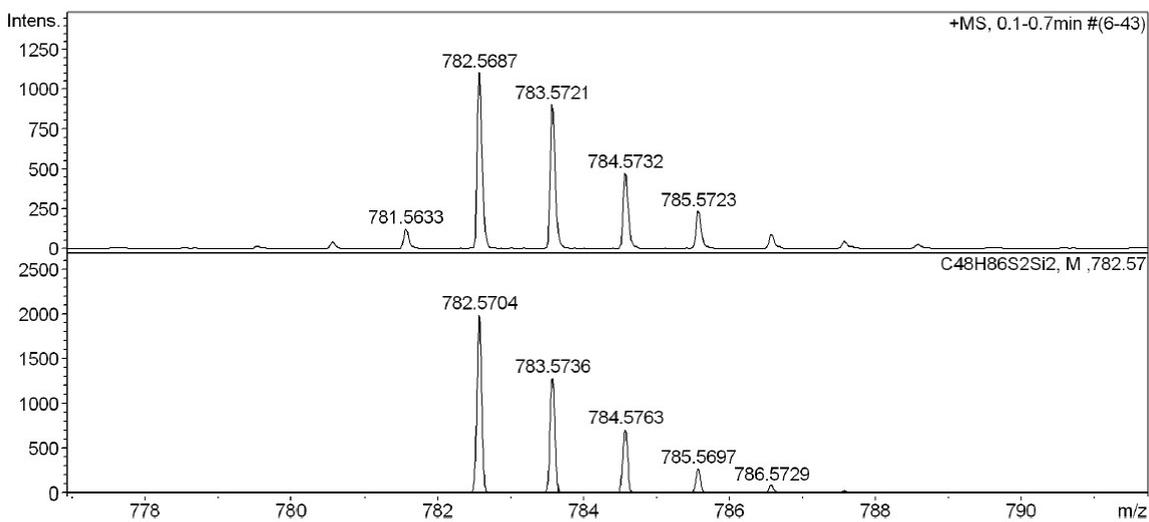


Fig. S16. HRMS spectrum of Molecular Gyrotop (**C14TT**) (APCI, positive). Top: obsd. Bottom: sim.

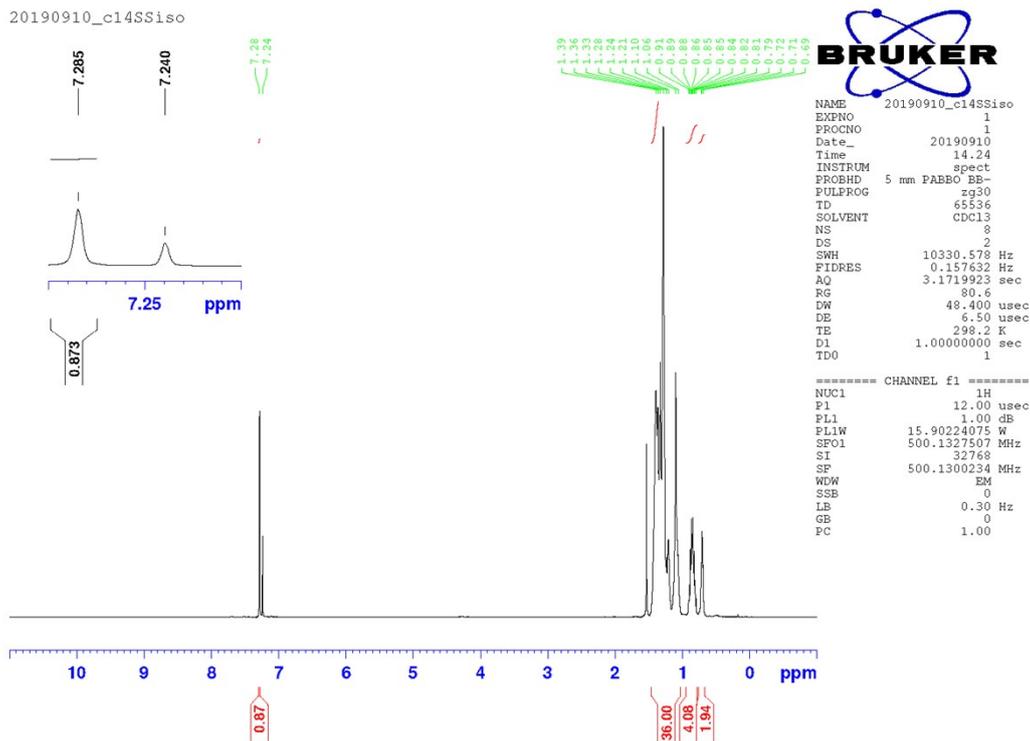


Fig. S17. ^1H NMR spectrum of Molecular Gyrotop Isomer (C14iTT) in CDCl_3 .

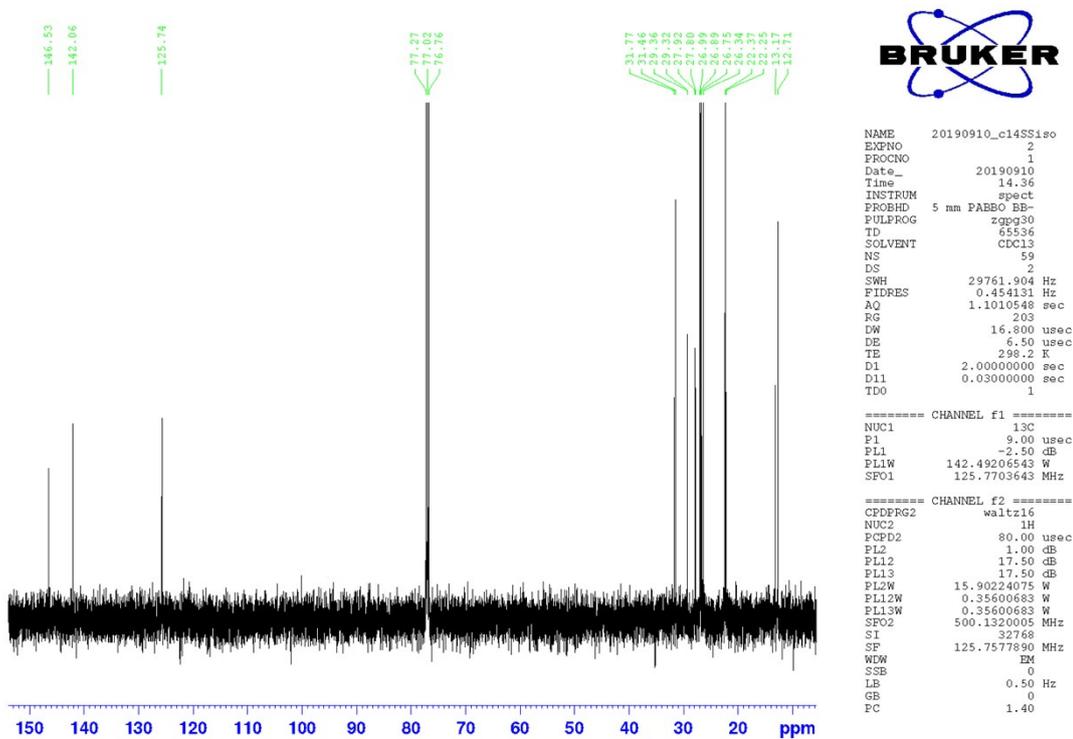


Fig. S18. ^{13}C NMR spectrum of Molecular Gyrotop Isomer (C14iTT) in CDCl_3 .

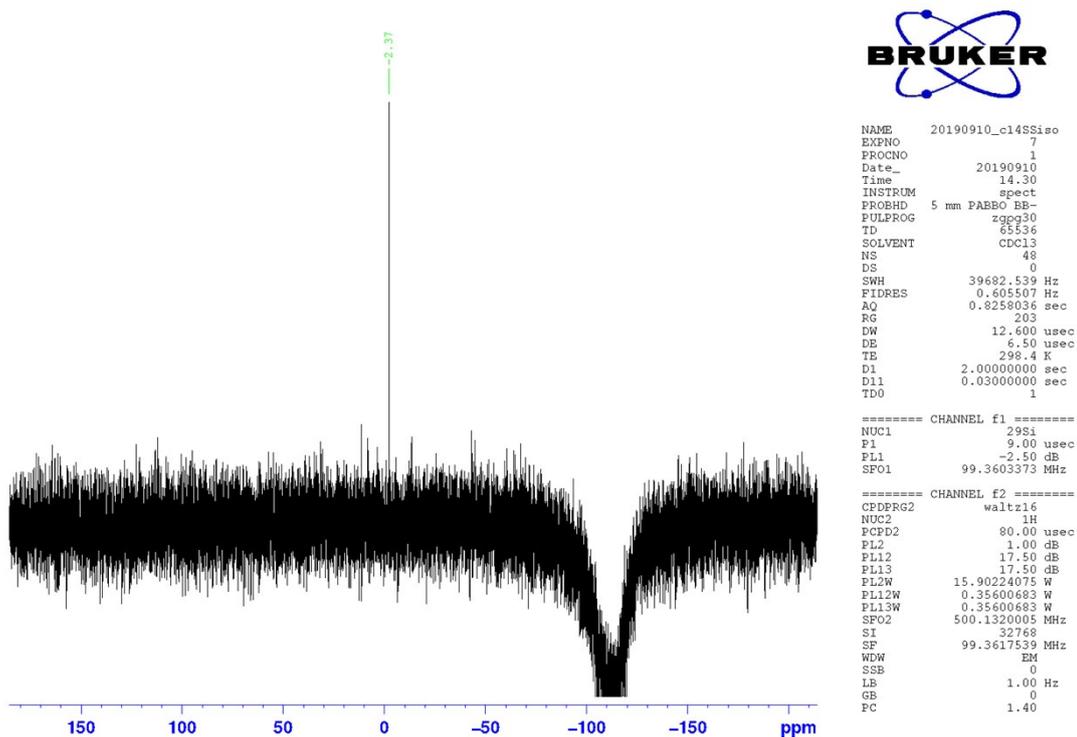


Fig. S19. ^{29}Si NMR spectrum of Molecular Gyrotop Isomer (**C14iTT**) in CDCl_3 .

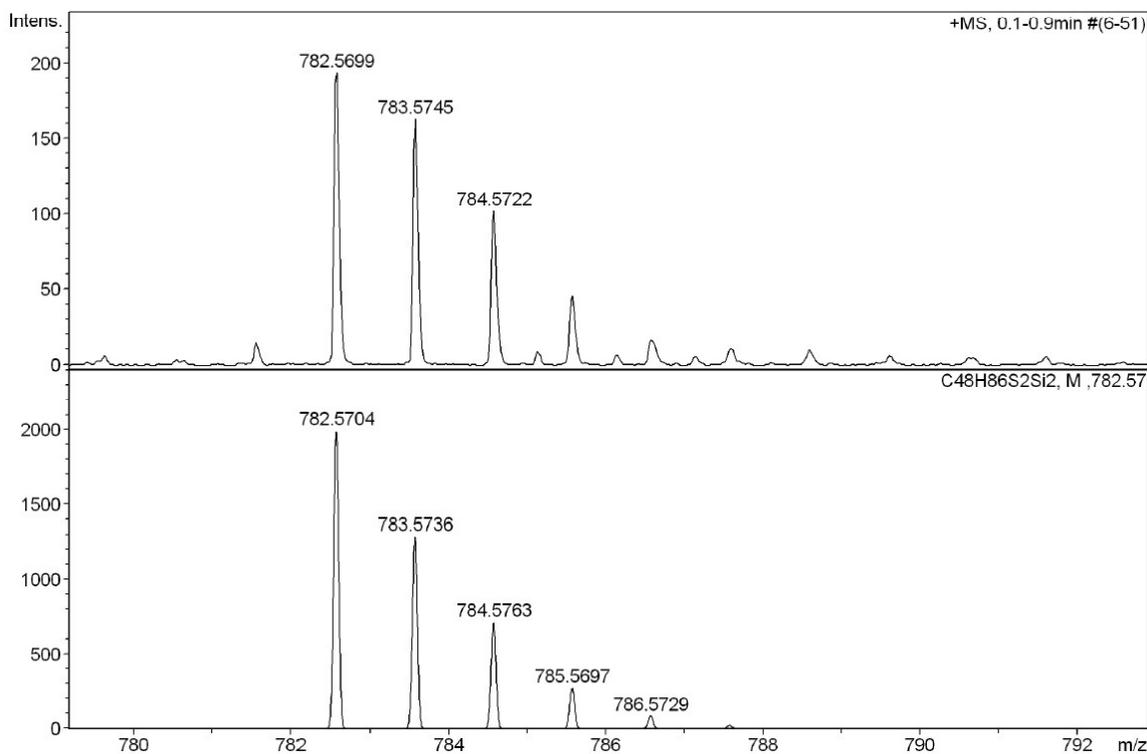


Fig. S20. HRMS spectrum of Molecular Gyrotop Isomer (**C14iTT**) (APCI, positive). Top: obsd. Bottom: sim.

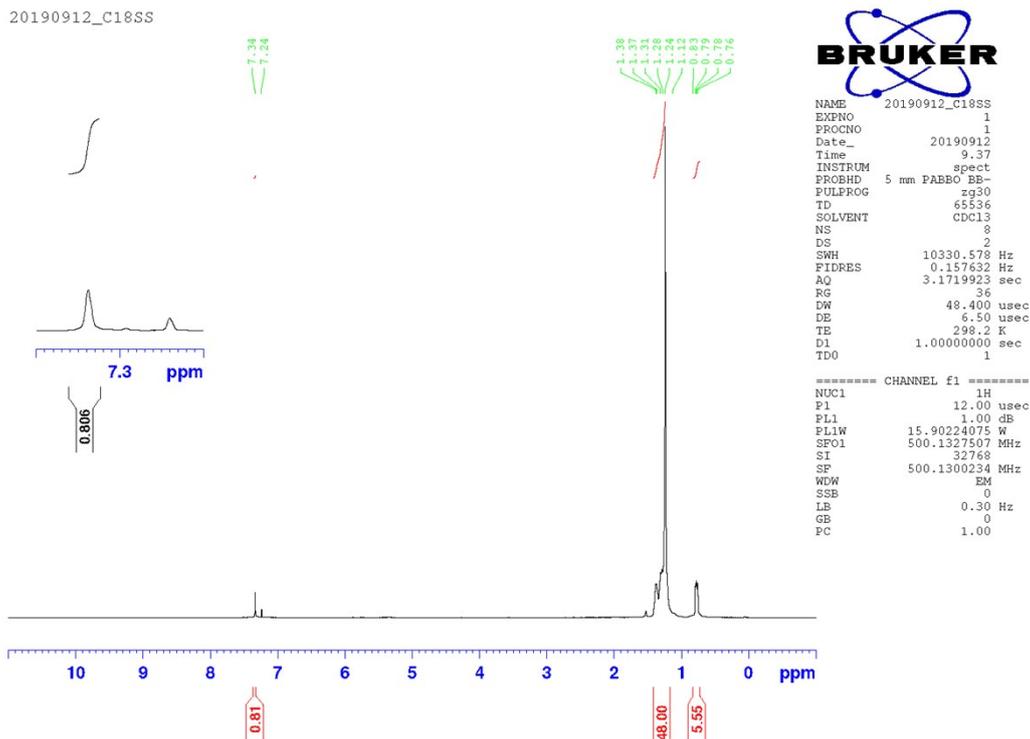


Fig. S21. ^1H NMR spectrum of Molecular Gyrotop (C18TT) in CDCl_3 .

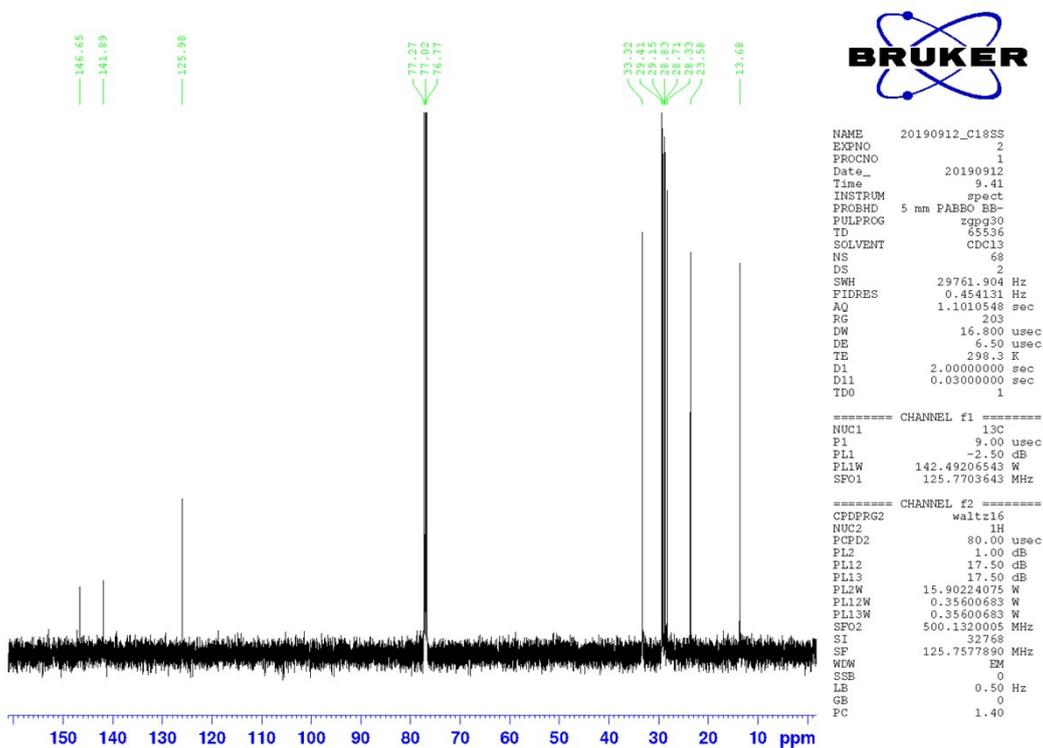


Fig. S22. ^{13}C NMR spectrum of Molecular Gyrotop (C18TT) in CDCl_3 .

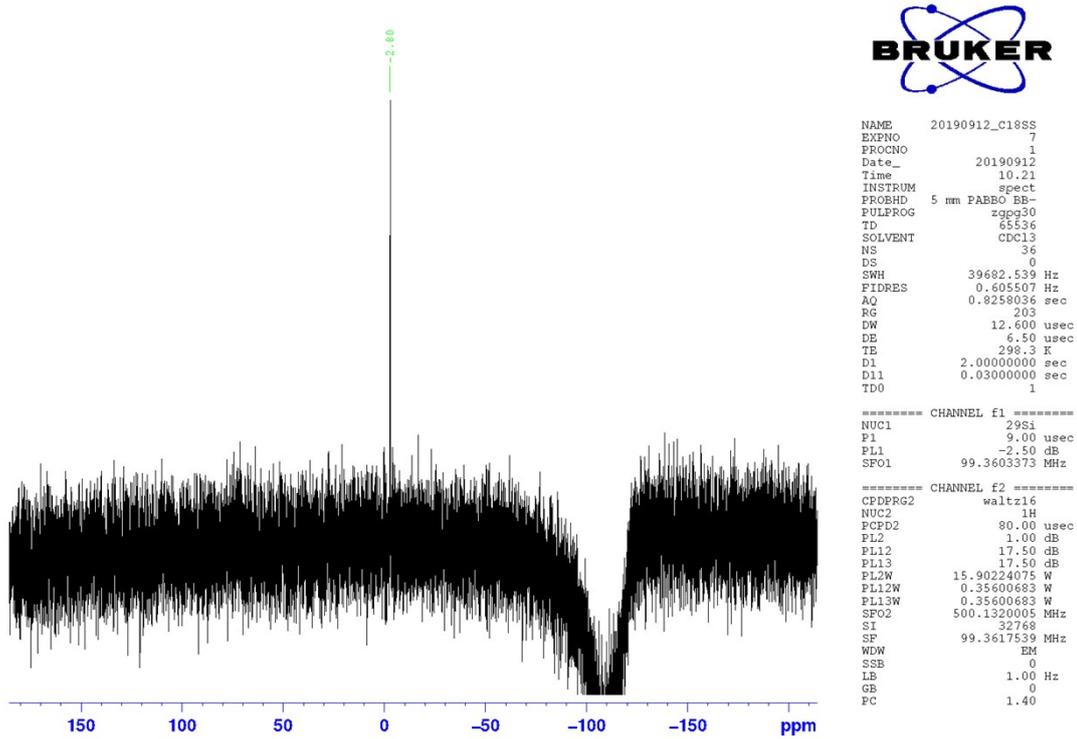


Fig. S23. ^{29}Si NMR spectrum of Molecular Gyrotop (**C18TT**) in CDCl_3 .

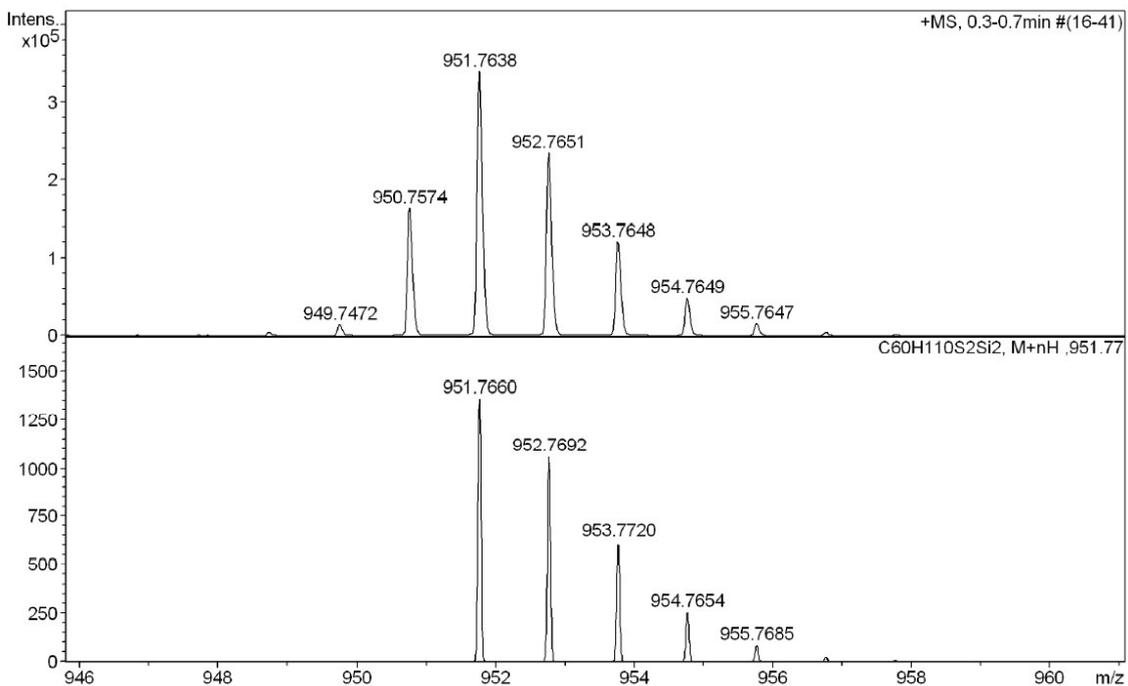


Fig. S24. HRMS spectrum of Molecular Gyrotop (**C18TT**) (APCI, positive). Top: obsd. Bottom: sim.

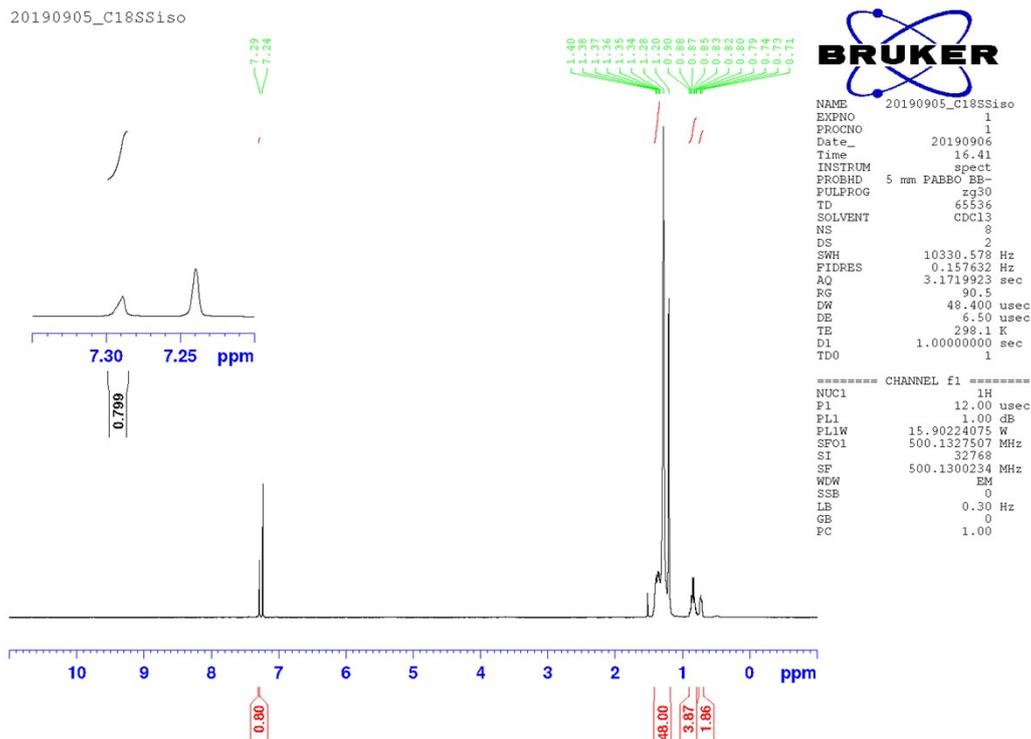


Fig. S25. ^1H NMR spectrum of Molecular Gyrotop Isomer (**C18iTT**) in CDCl_3 .

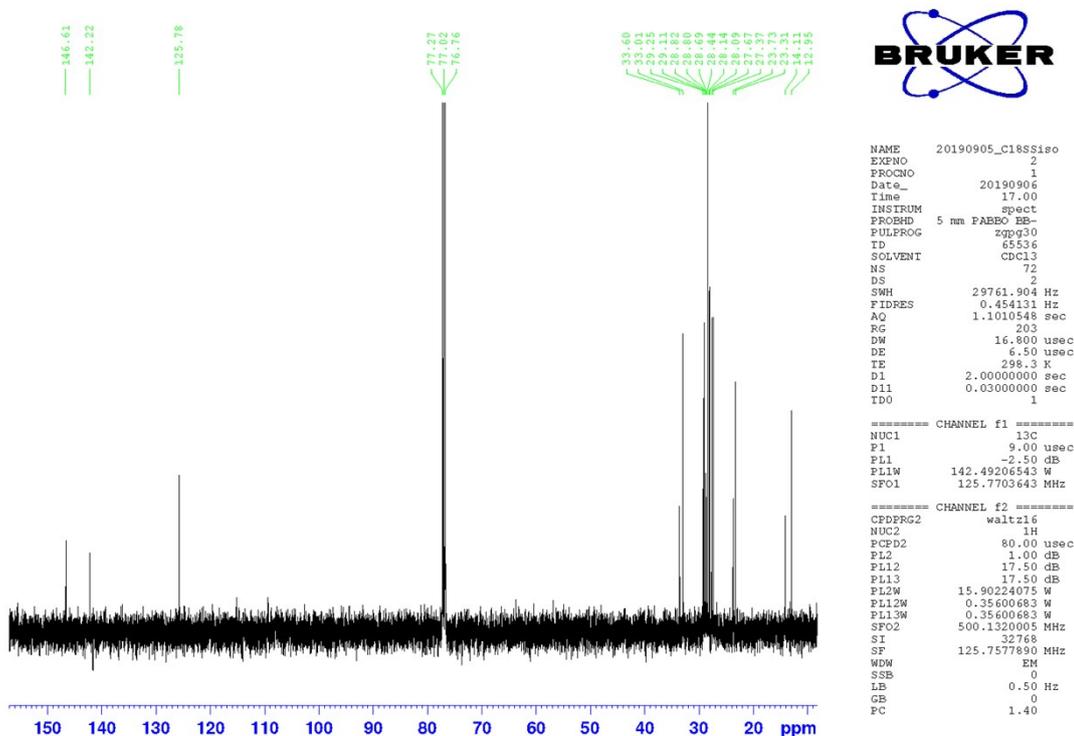


Fig. S26. ^{13}C NMR spectrum of Molecular Gyrotop Isomer (**C18iTT**) in CDCl_3 .

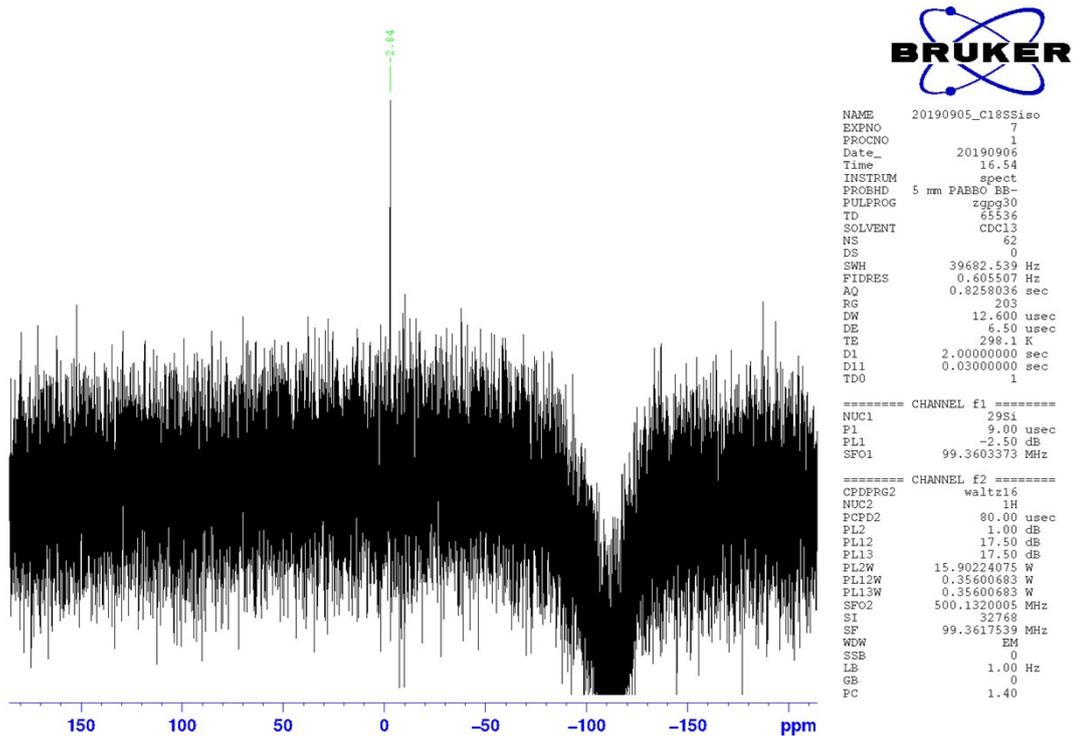


Fig. S27. ^{29}Si NMR spectrum of Molecular Gyrotop Isomer (**C18iTT**) in CDCl_3 .

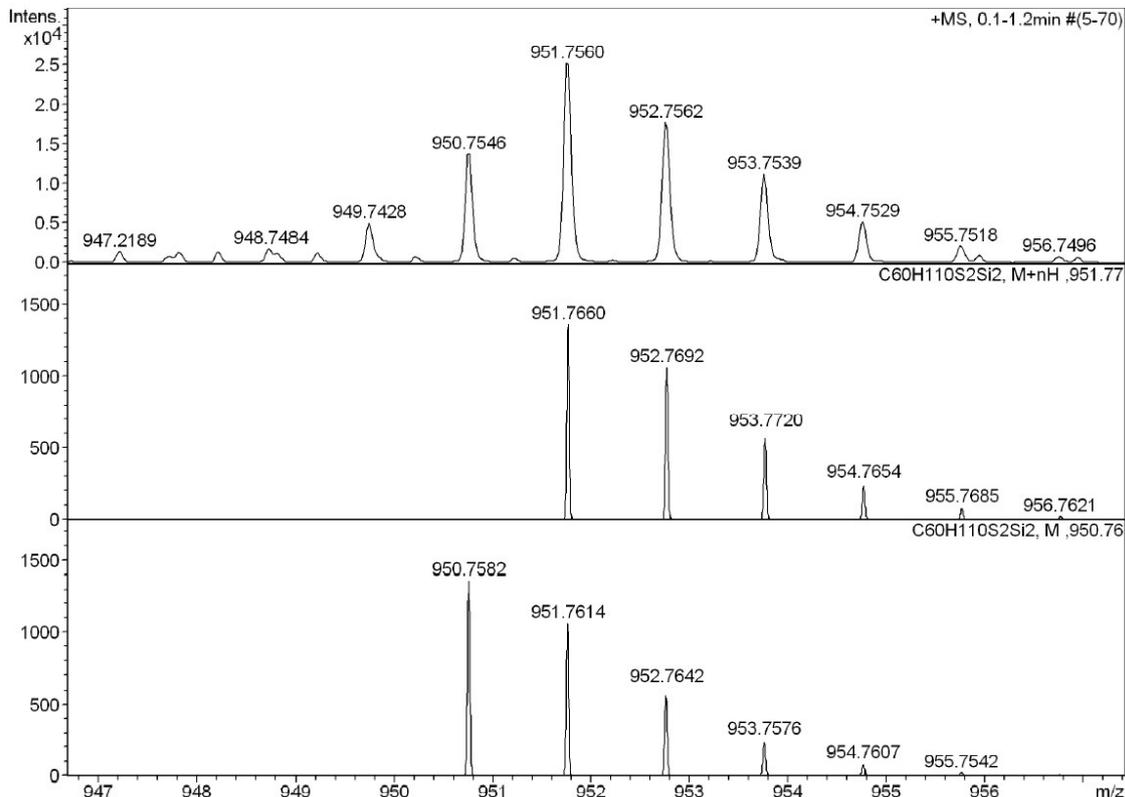


Fig. S28. HRMS spectrum of Molecular Gyrotop Isomer (**C18iTT**) (APCI, positive). Top: obsd. Bottom: sim.

20190911_c22ss

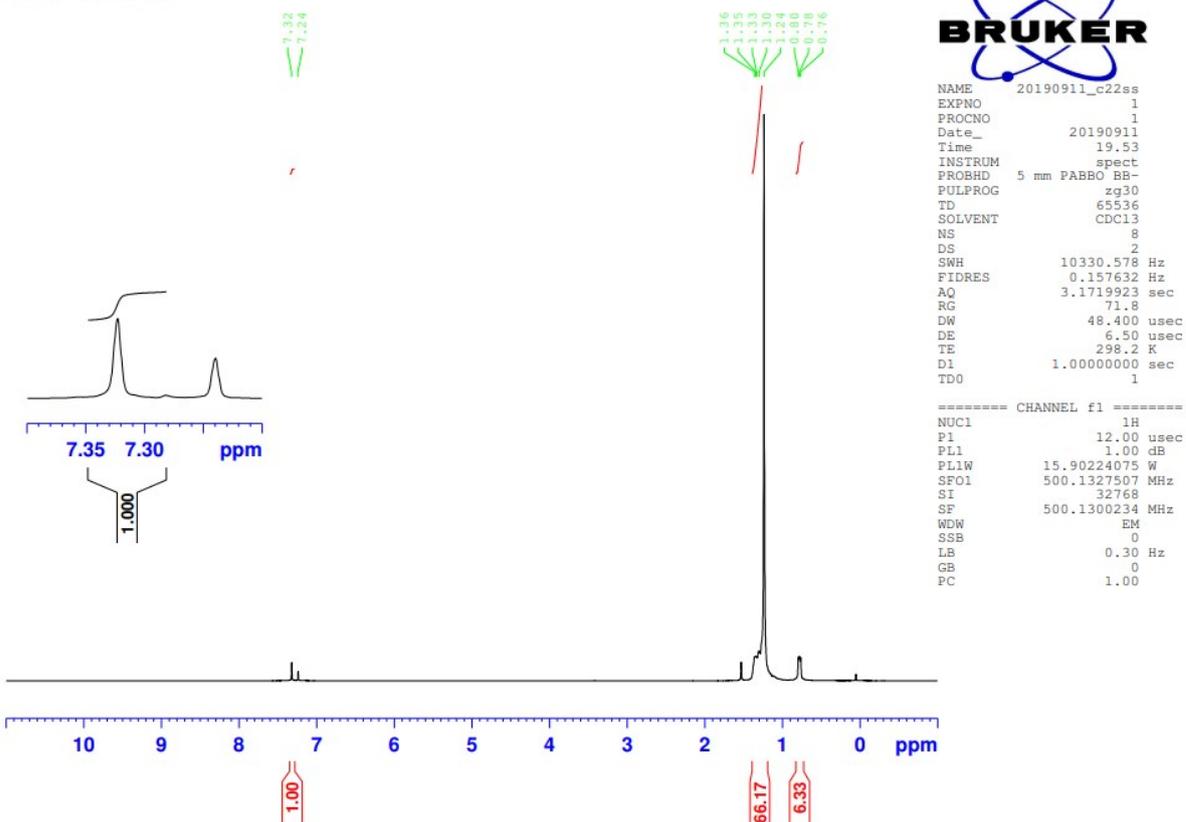


Fig. S29. ^1H NMR spectrum of Molecular Gyrotop (C22TT) in CDCl_3 .

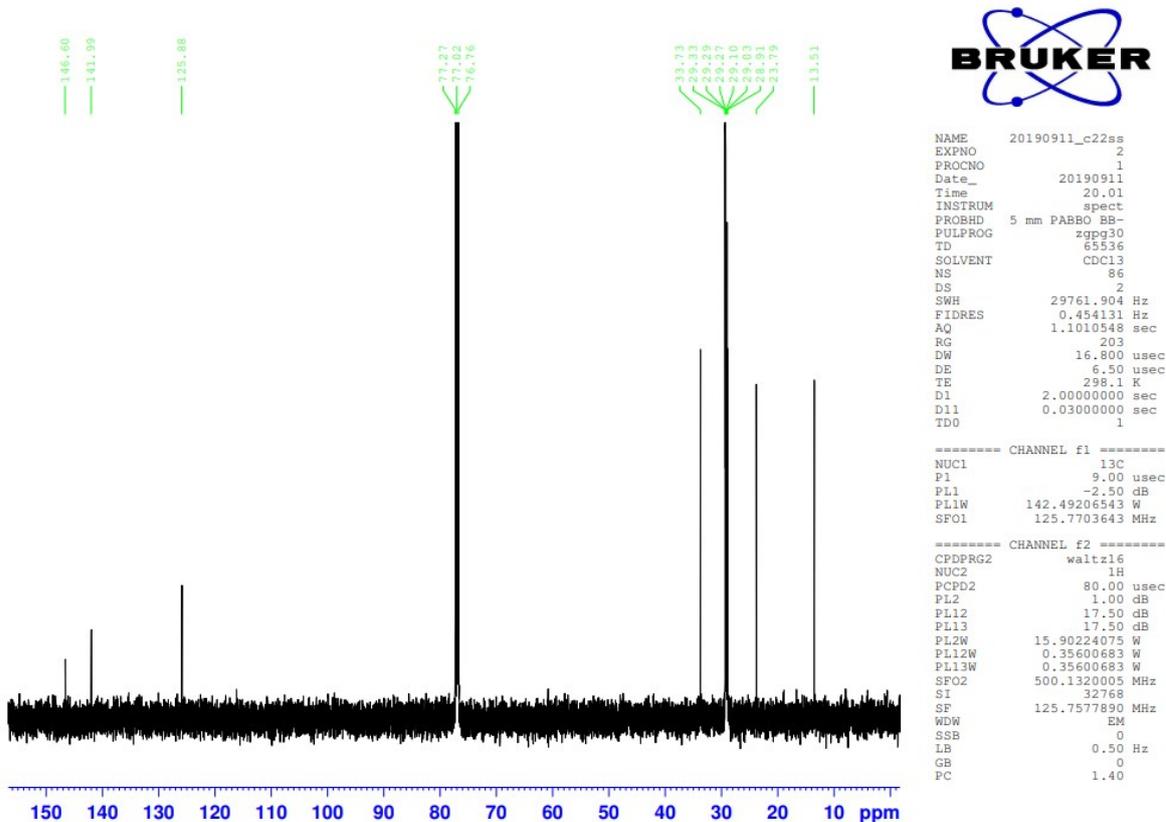


Fig. S30. ^{13}C NMR spectrum of Molecular Gyrotop (C22TT) in CDCl_3 .

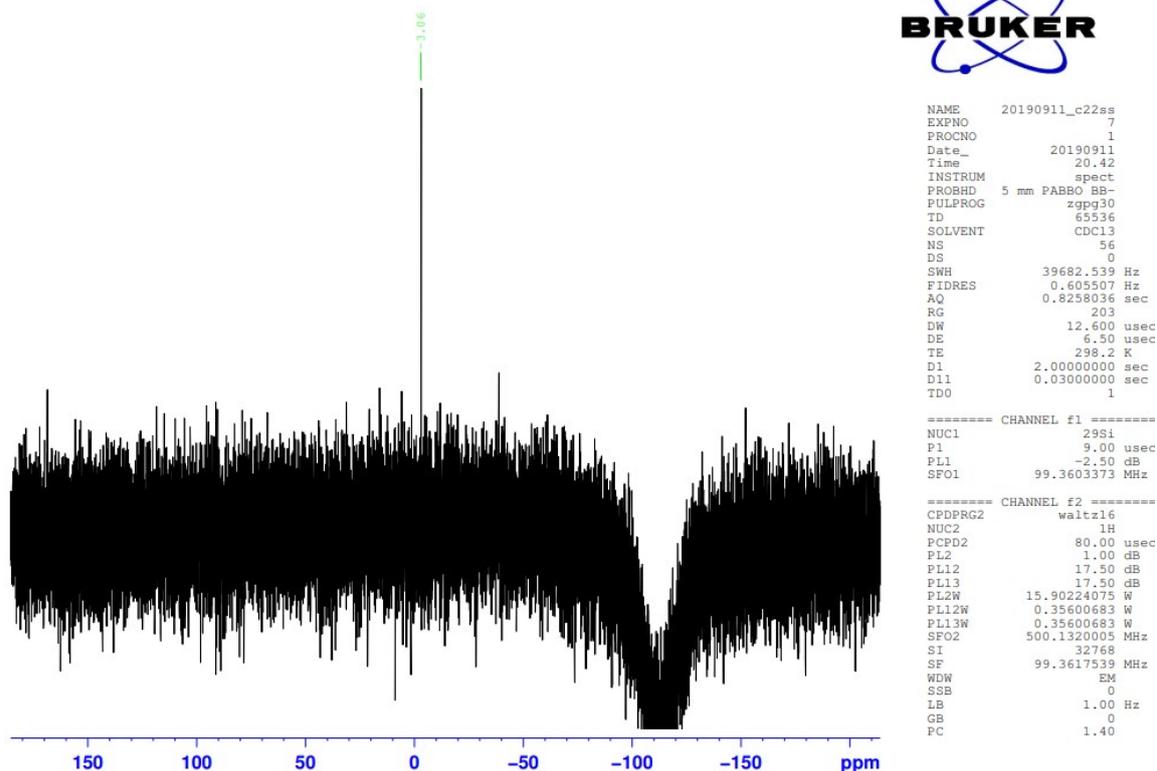


Fig. S31. ^{29}Si NMR spectrum of Molecular Gyrotop (C22TT) in CDCl_3 .

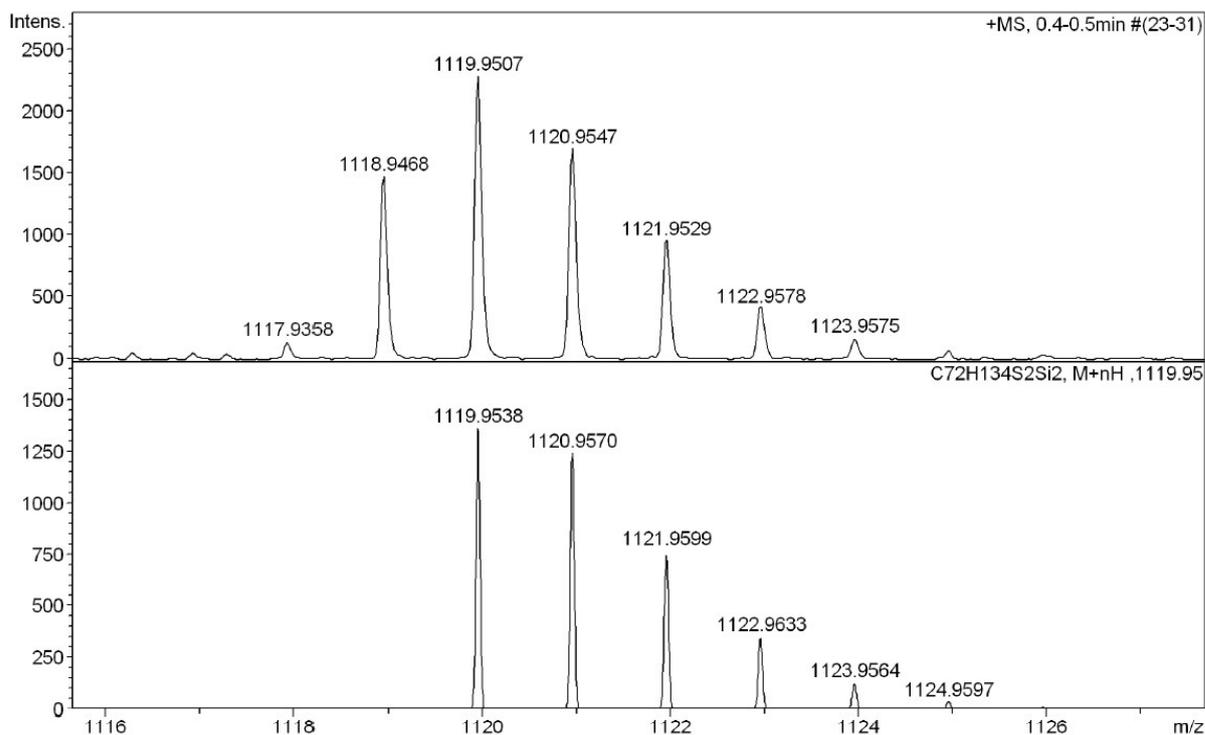


Fig. S32. HRMS spectrum of Molecular Gyrotop (C22TT) (APCI, positive). Top: obsd. Bottom: sim.

20190911_c22SSiso

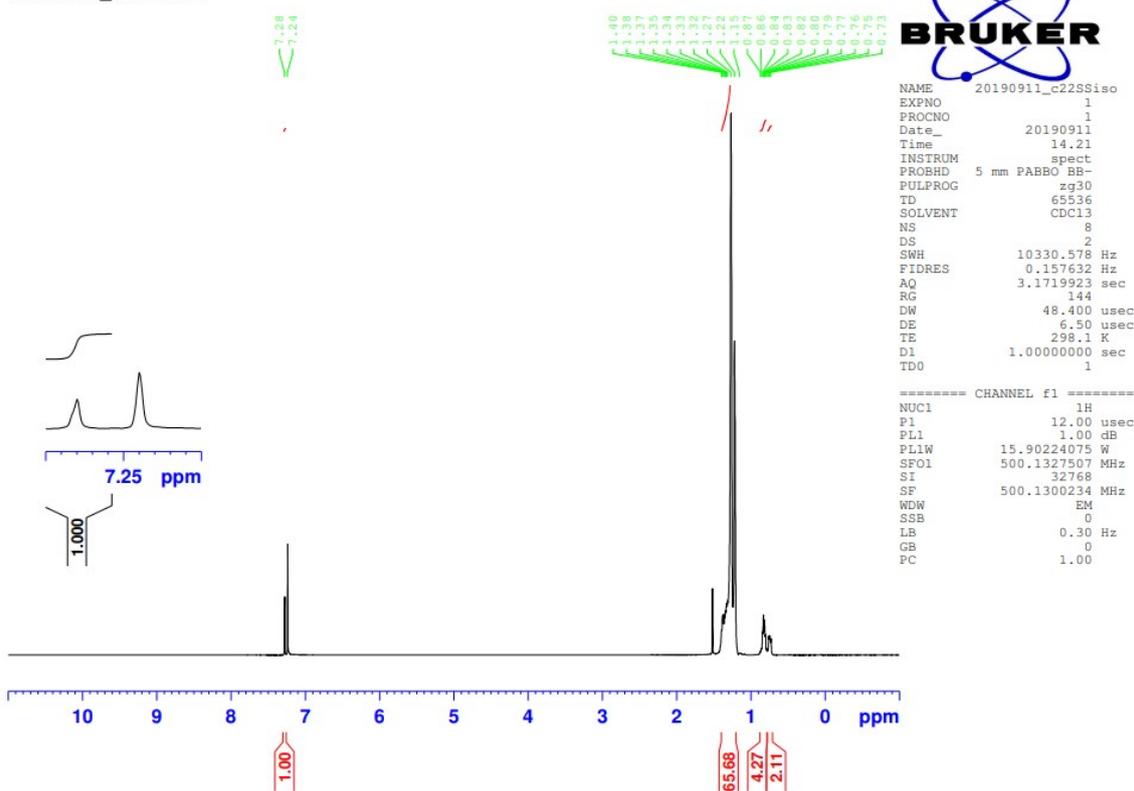


Fig. S33. ^1H NMR spectrum of Molecular Gyrotop Isomer (**C22iTT**) in CDCl_3 .

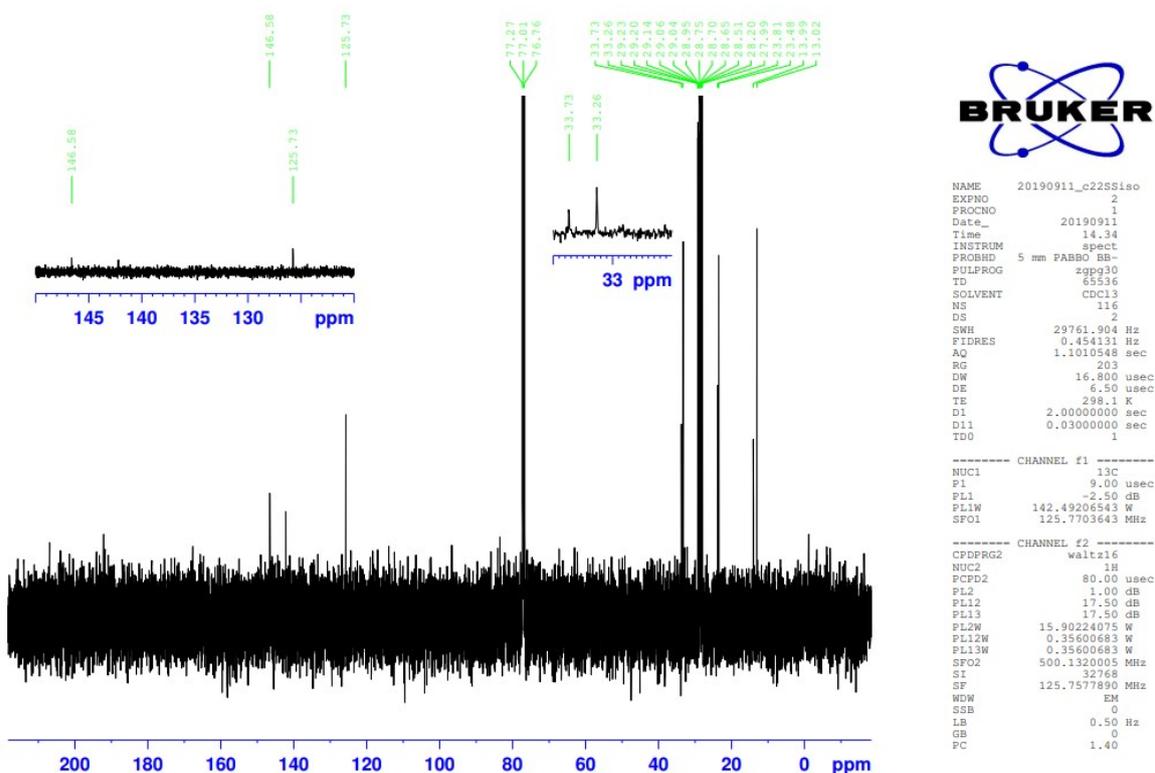


Fig. S34. ^{13}C NMR spectrum of Molecular Gyrotop Isomer (**C22iTT**) in CDCl_3 .

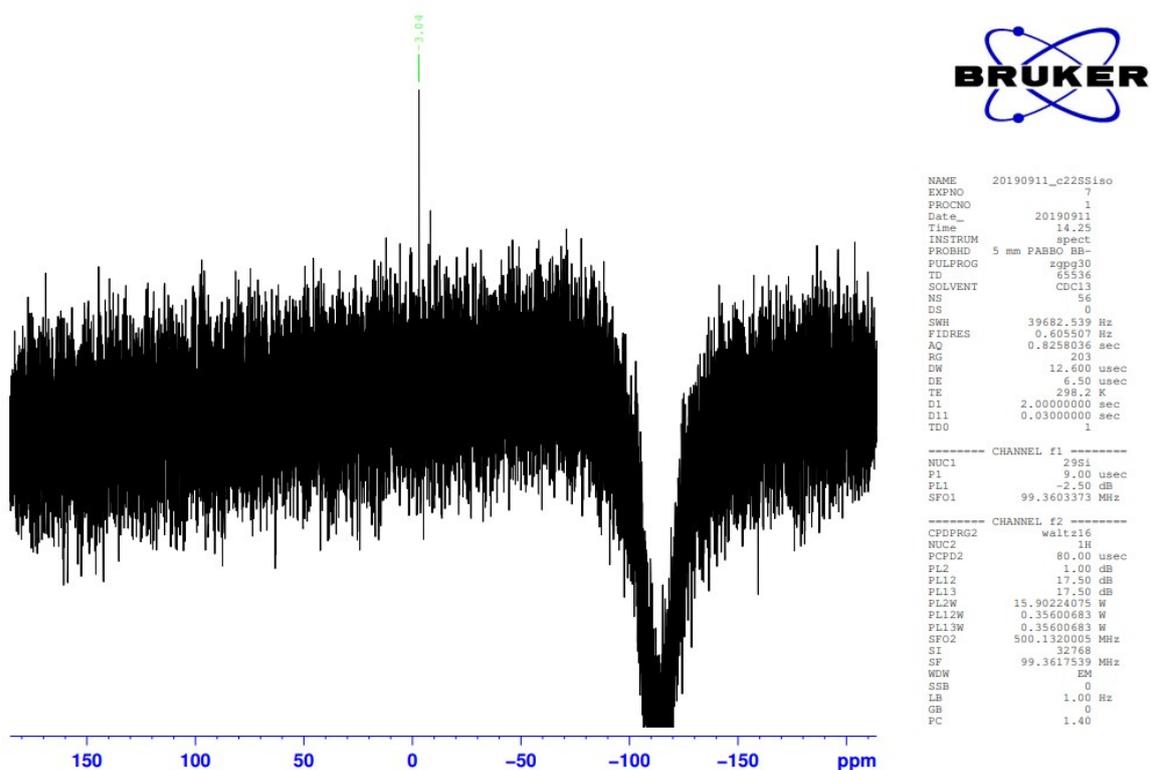


Fig. S35. ^{29}Si NMR spectrum of Molecular Gyrotop Isomer (**C22iTT**) in CDCl_3 .

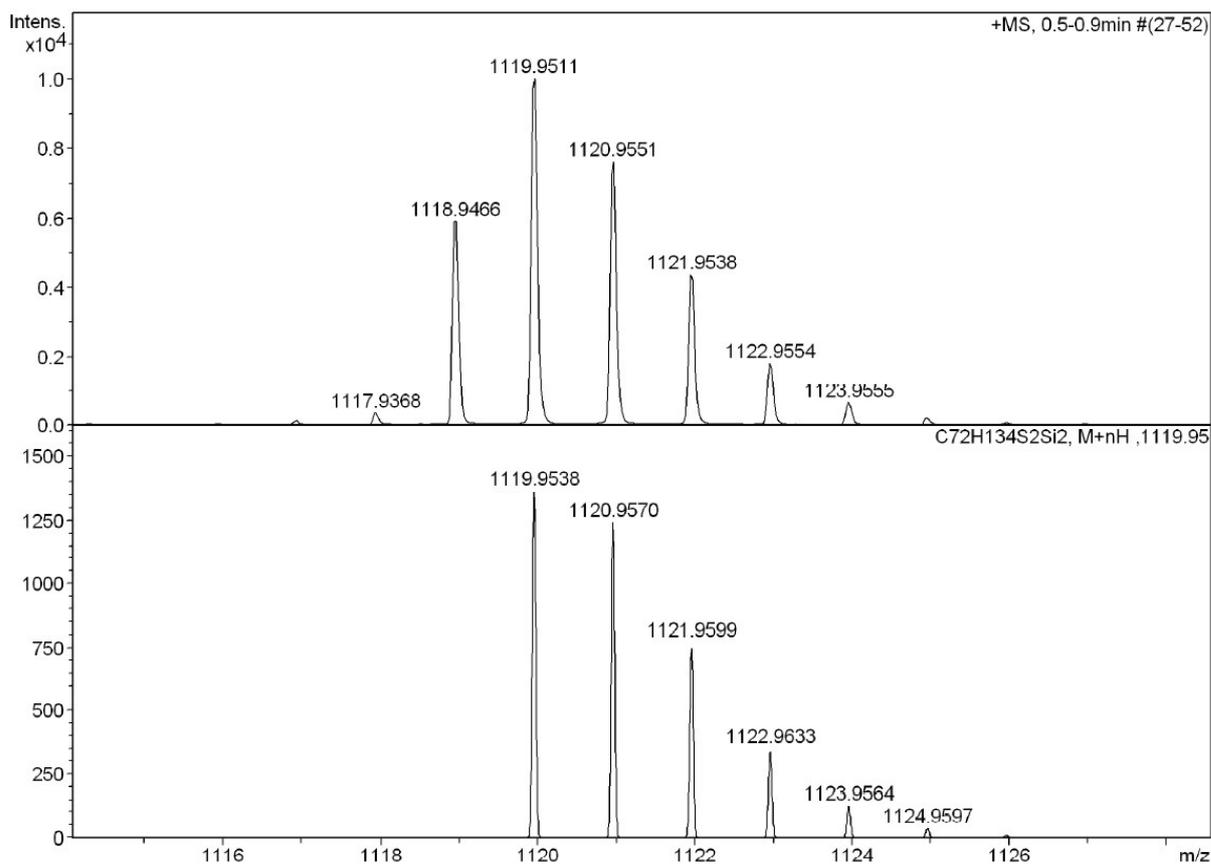


Fig. S36. HRMS spectrum of Molecular Gyrotop Isomer (**C22iTT**) (APCI, positive). Top: obsd. Bottom: sim.

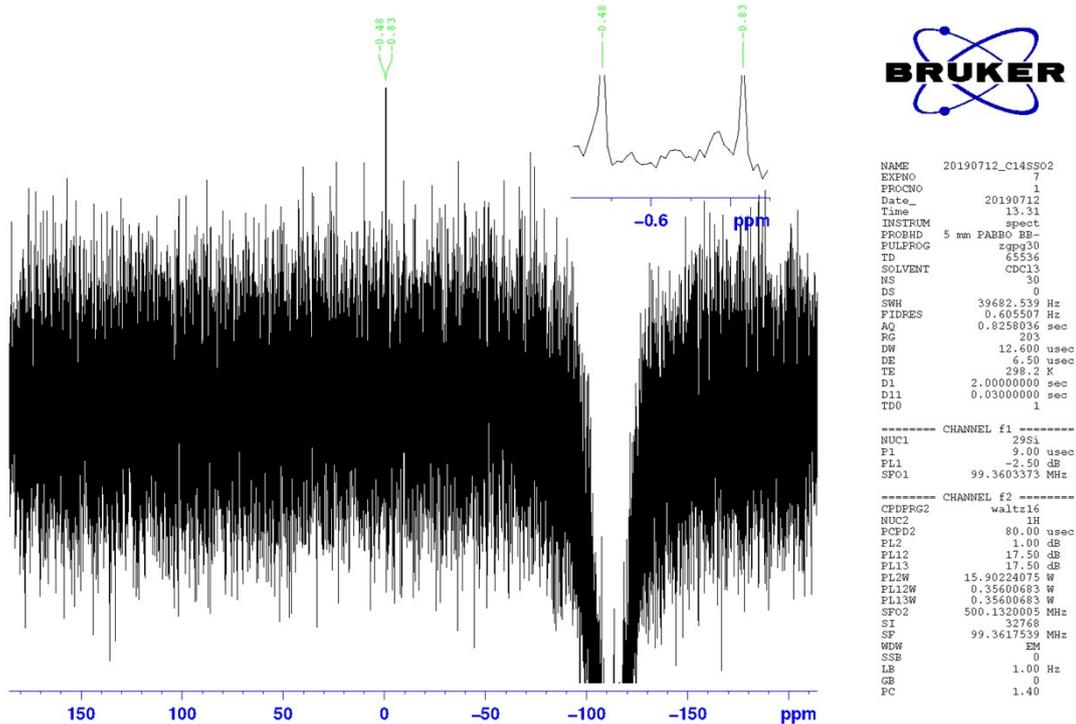


Fig. S39. ^{29}Si NMR spectrum of Molecular Gyrotop ($\text{C}_{14}\text{TTO}_2$) in CDCl_3 .

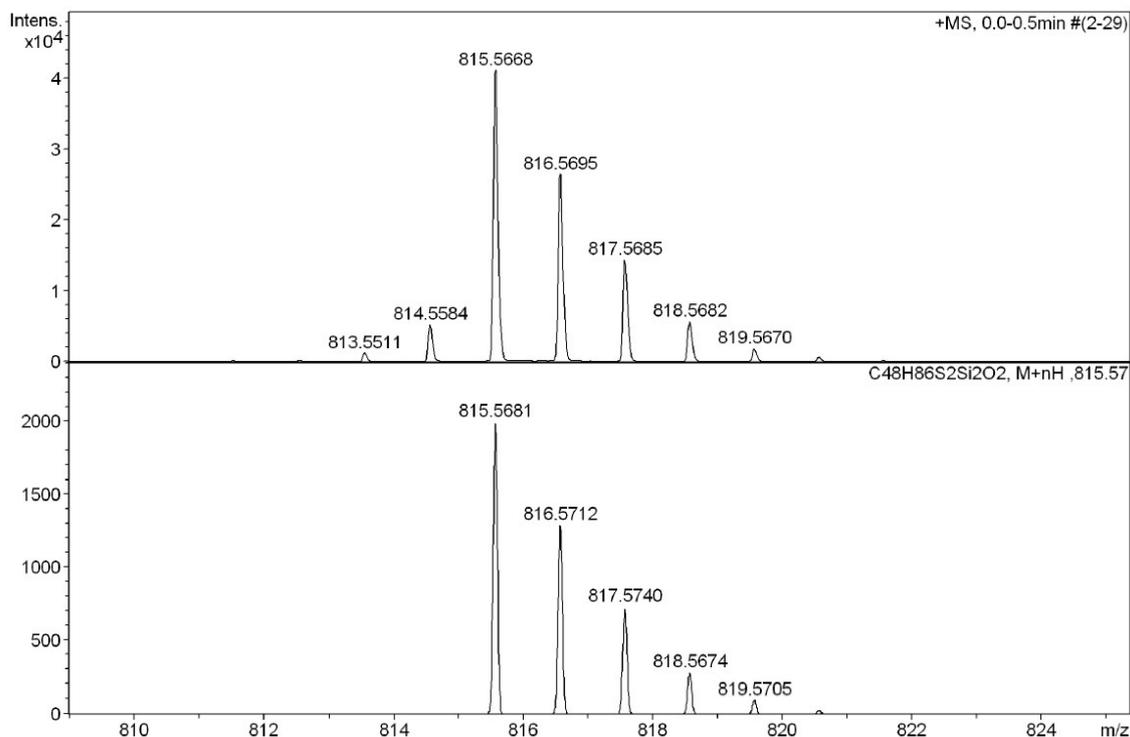


Fig. S40. HRMS spectrum of Molecular Gyrotop ($\text{C}_{14}\text{TTO}_2$) (APCI, positive). Top: obsd. Bottom: sim.

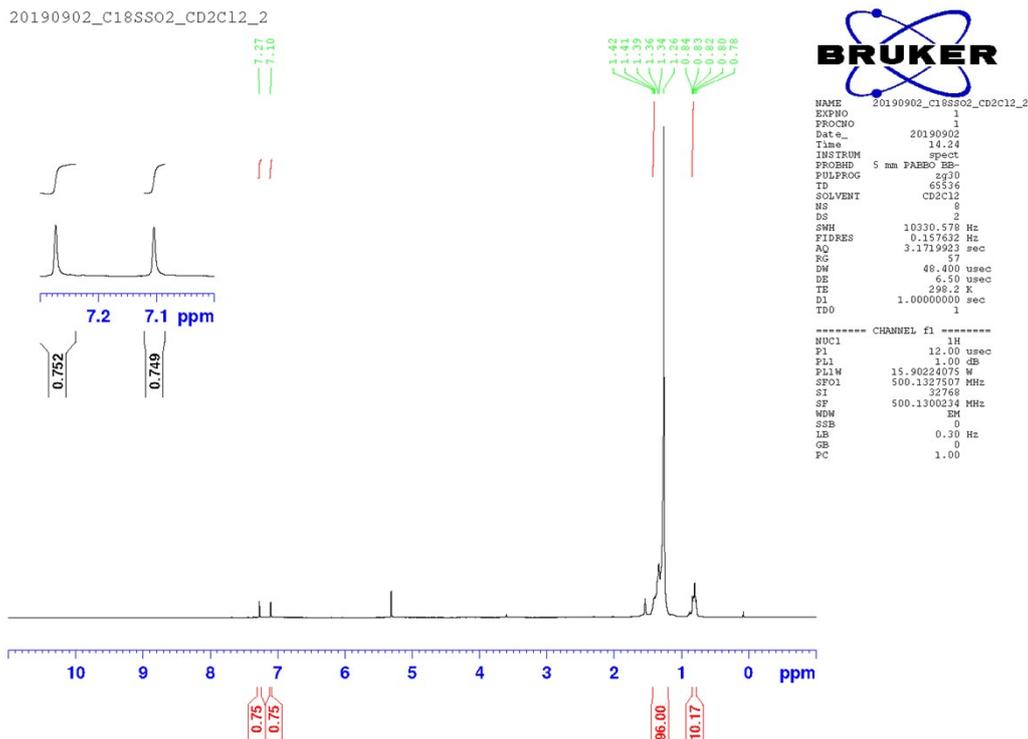


Fig. S41. ^1H NMR spectrum of Molecular Gyrotop (C18TTO2) in CD_2Cl_2 .

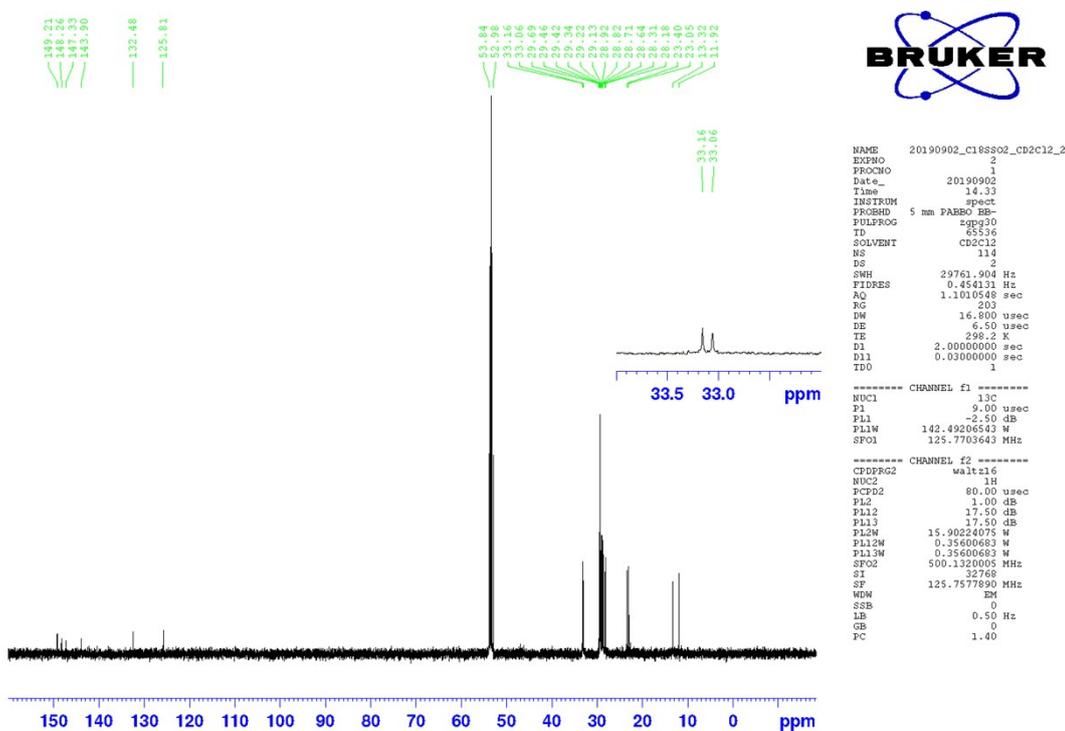


Fig. S42. ^{13}C NMR spectrum of Molecular Gyrotop (C18TTO2) in CD_2Cl_2 .

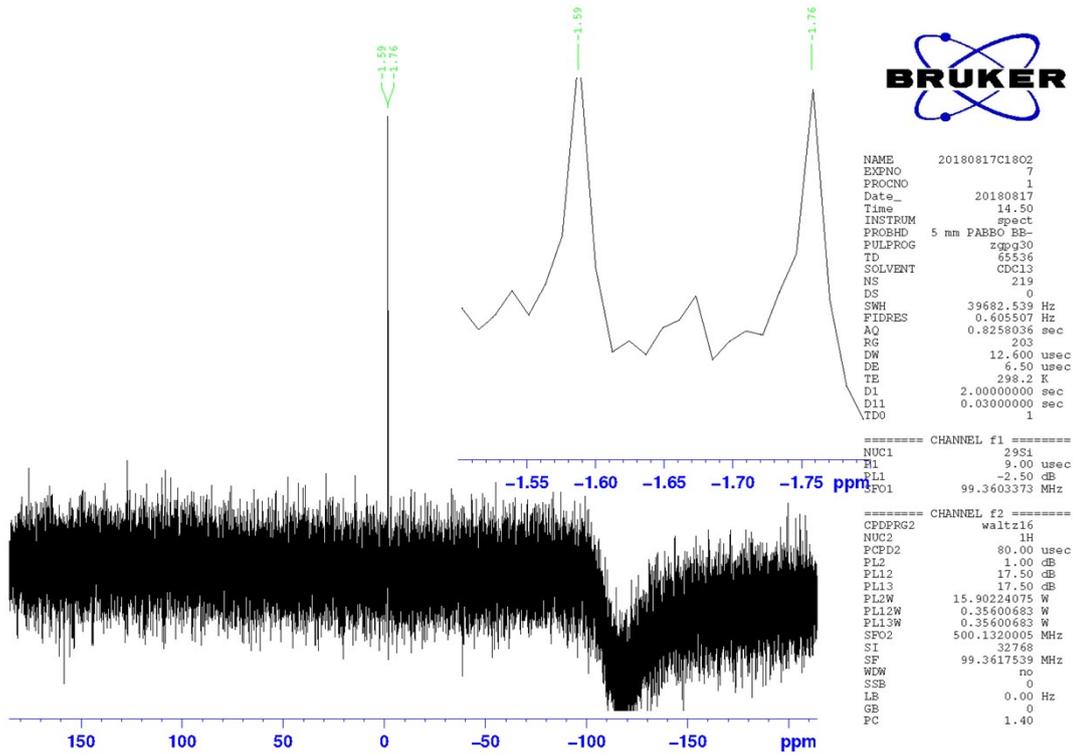


Fig. S43. ^{29}Si NMR spectrum of Molecular Gyrotop (**C18TTO2**) in CD_2Cl_2 .

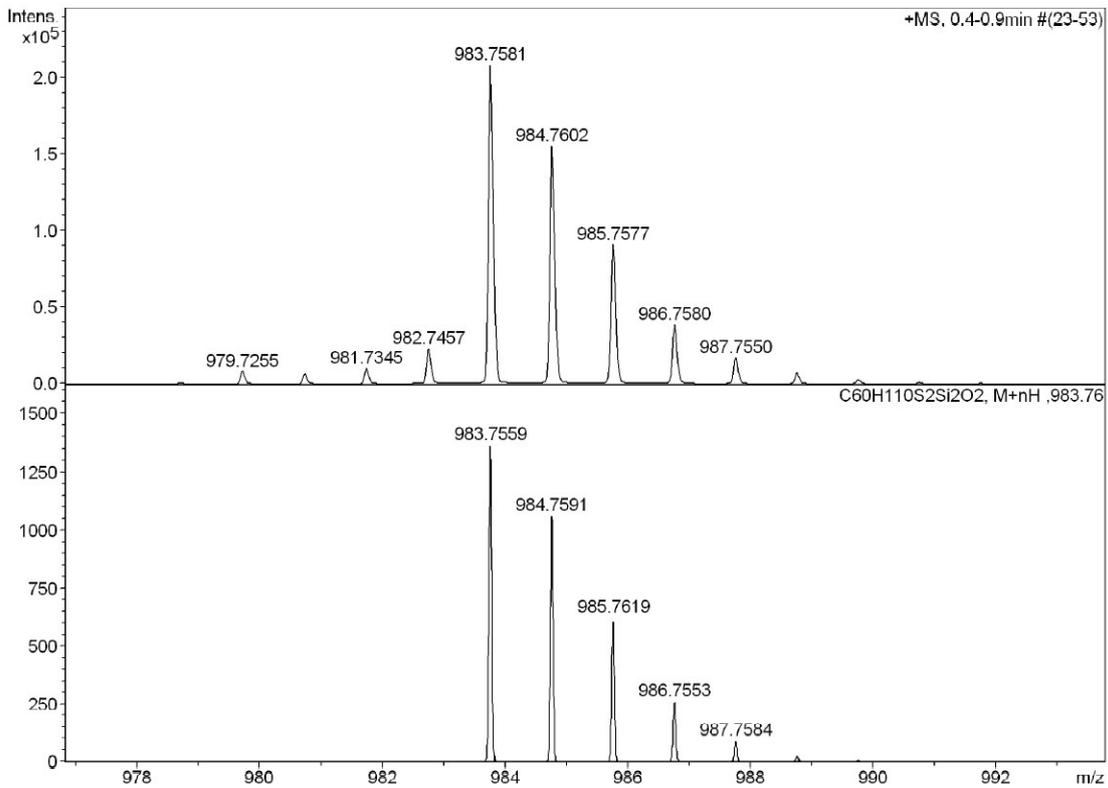


Fig. S44. HRMS spectrum of Molecular Gyrotop (**C18TTO2**) (APCI, positive). Top: obsd. Bottom: sim.

20190830_C22SSO2

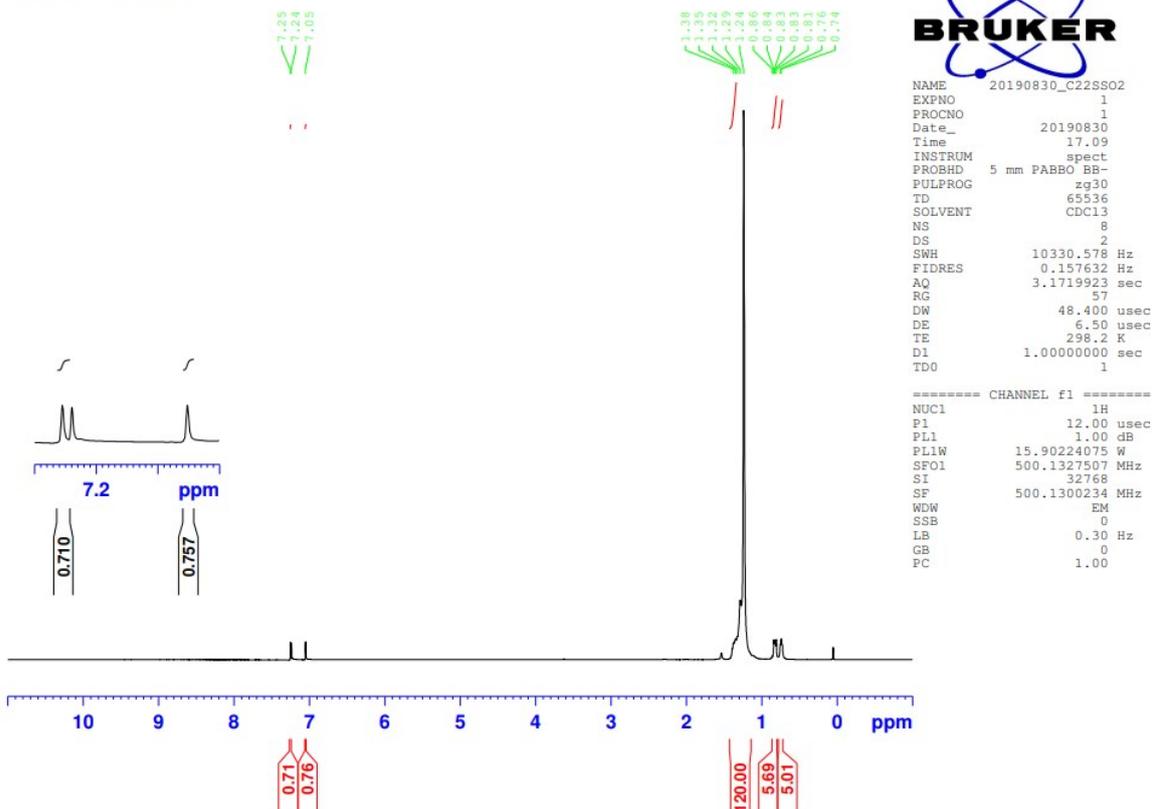


Fig. S45. ^1H NMR spectrum of Molecular Gyrotop ($\text{C}_{22}\text{TTO}_2$) in CDCl_3 .

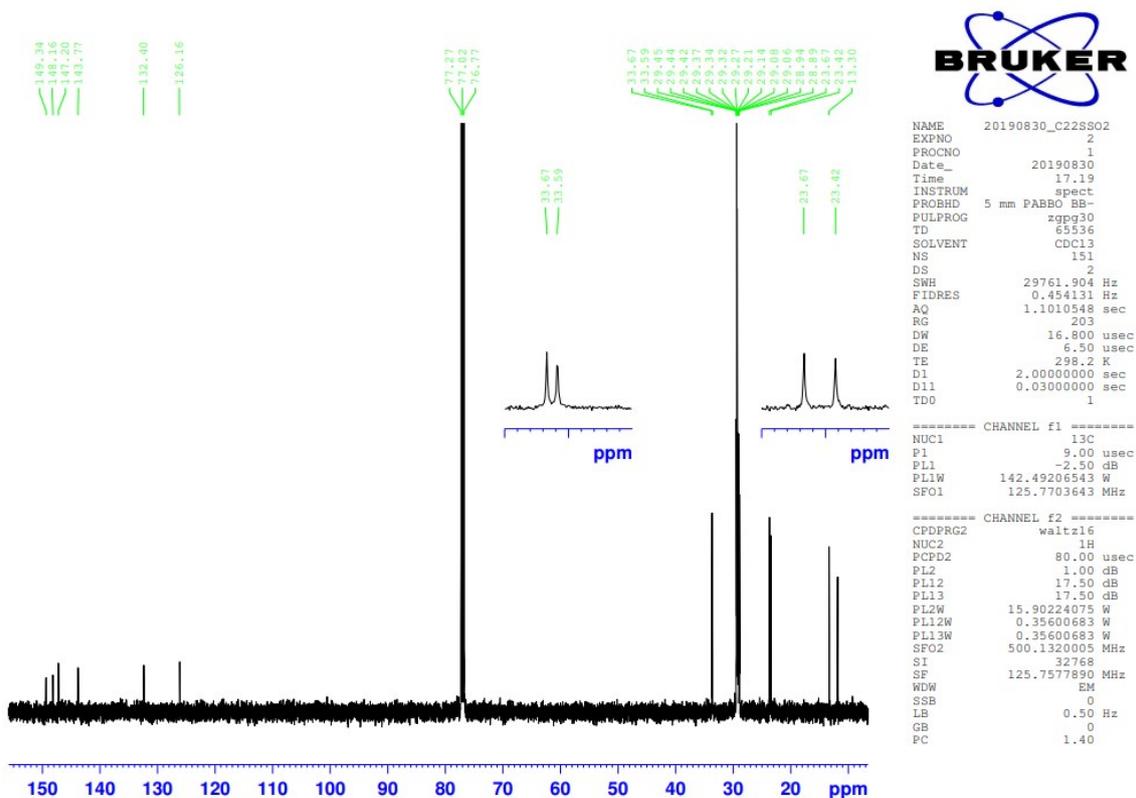


Fig. S46. ^{13}C NMR spectrum of Molecular Gyrotop ($\text{C}_{22}\text{TTO}_2$) in CDCl_3 .

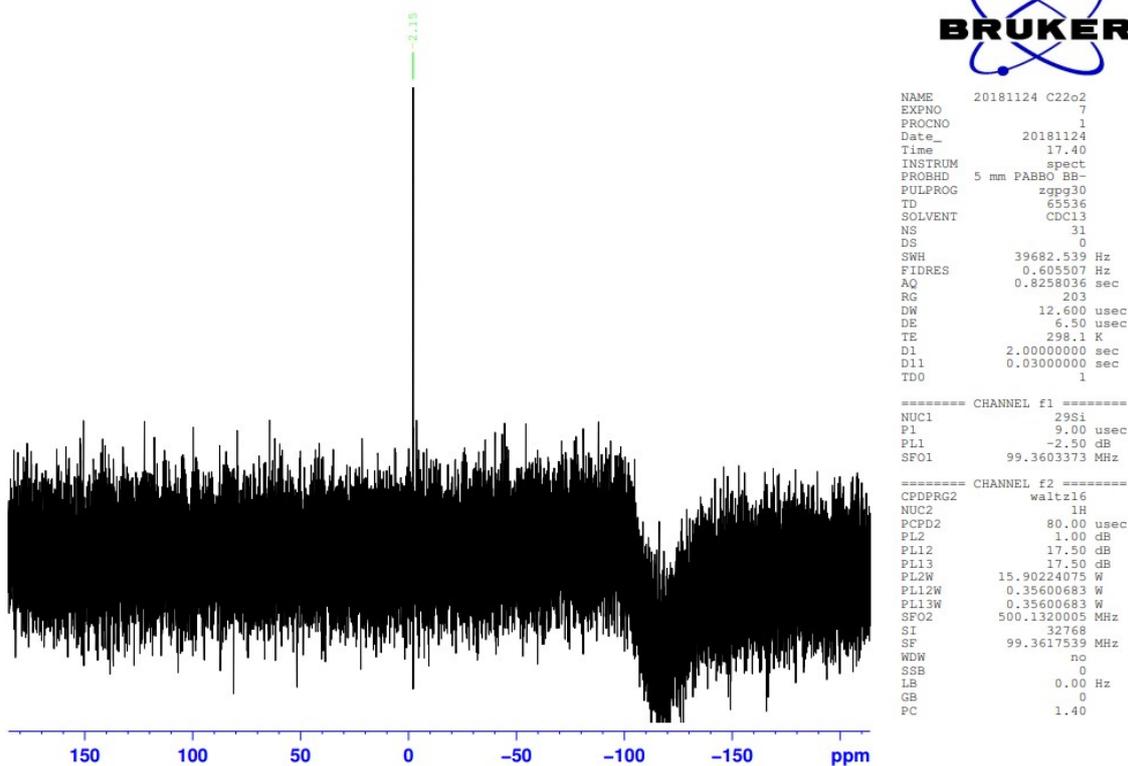


Fig. S47. ^{29}Si NMR spectrum of Molecular Gyrotop ($\text{C}_{22}\text{TTO}_2$) in CDCl_3 .

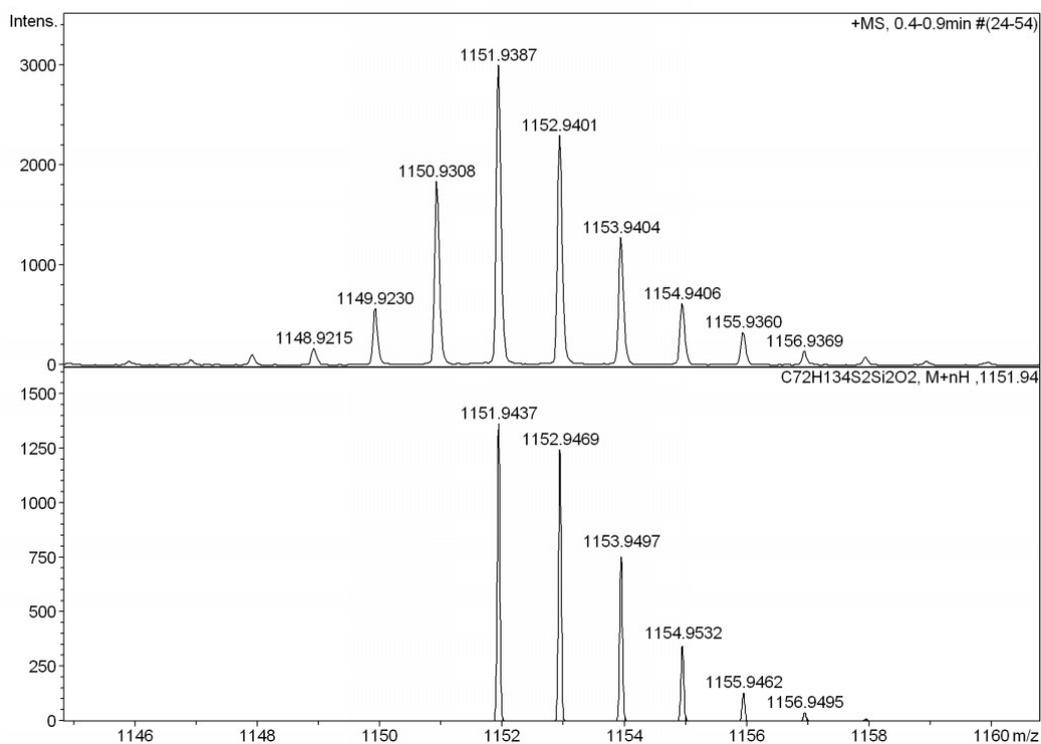
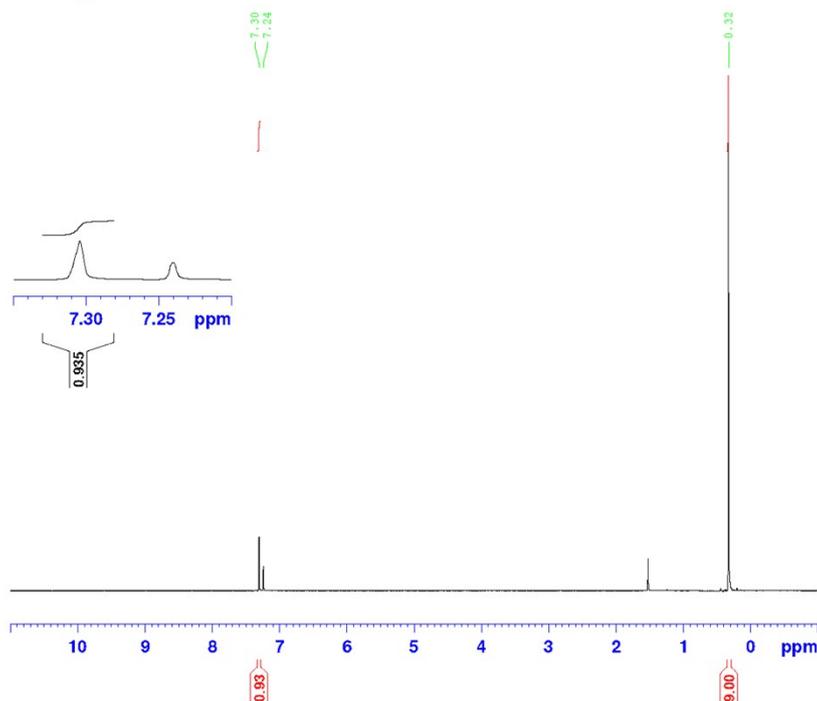


Fig. S48. HRMS spectrum of Molecular Gyrotop ($\text{C}_{22}\text{TTO}_2$) (APCI, positive). Top: obsd. Bottom: sim.

20190909_TMSSS



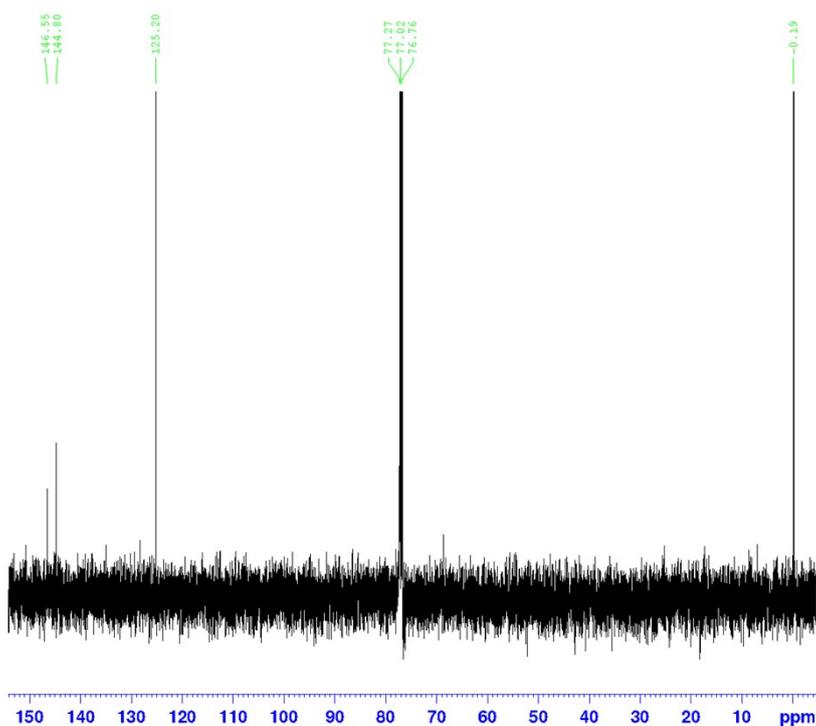
```

NAME      20190909_TMSSS
EXPNO     1
PROCNO    1
Date_     20190909
Time      13.41
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         2
DS         2
SWH       10310.578 Hz
FIDRES    0.157632 Hz
AQ         3.1719923 sec
RG         203
DW         48.400 usec
DE         6.50 usec
TE         298.2 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         12.00 usec
PL1        1.00 dB
PL1W       15.90224075 W
SFO1       500.1327507 MHz
SI         32768
SF         500.1300213 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```

Fig. S49. ¹H NMR spectrum of 2,5-bis(trimethylsilyl)thieno[3,2-b]thiophene (TMSTT) in CDCl₃.



```

NAME      20190909_TMSSS
EXPNO     2
PROCNO    1
Date_     20190909
Time      13.51
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         2
DS         2
SWH       29761.904 Hz
FIDRES    0.454131 Hz
AQ         1.1010548 sec
RG         203
DW         16.800 usec
DE         6.50 usec
TE         298.2 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.00 usec
PL1        -2.50 dB
PL1W       142.49206543 W
SFO1       125.7703643 MHz

===== CHANNEL f2 =====
CEDEPRG2   waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        1.00 dB
PL12       17.50 dB
PL13       17.50 dB
PL2W       15.90224075 W
PL12W      0.35600683 W
PL13W      0.35600683 W
SFO2       500.1320005 MHz
SI         32768
SF         125.7577890 MHz
WDW        EM
SSB        0
LB         0.50 Hz
GB         0
PC         1.40

```

Fig. S50. ¹³C NMR spectrum of 2,5-bis(trimethylsilyl)thieno[3,2-b]thiophene (TMSTT) in CDCl₃.

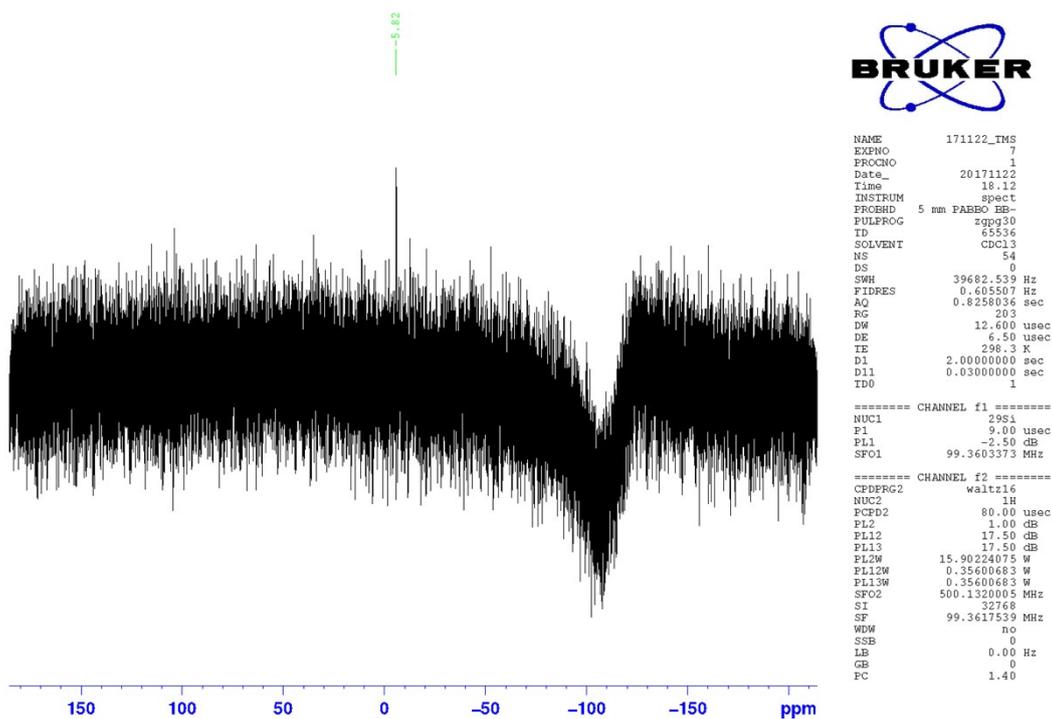


Fig. S51. ^{29}Si NMR spectrum of 2,5-bis(trimethylsilyl)thieno[3,2-b]thiophene (TMSTT) in CDCl_3 .

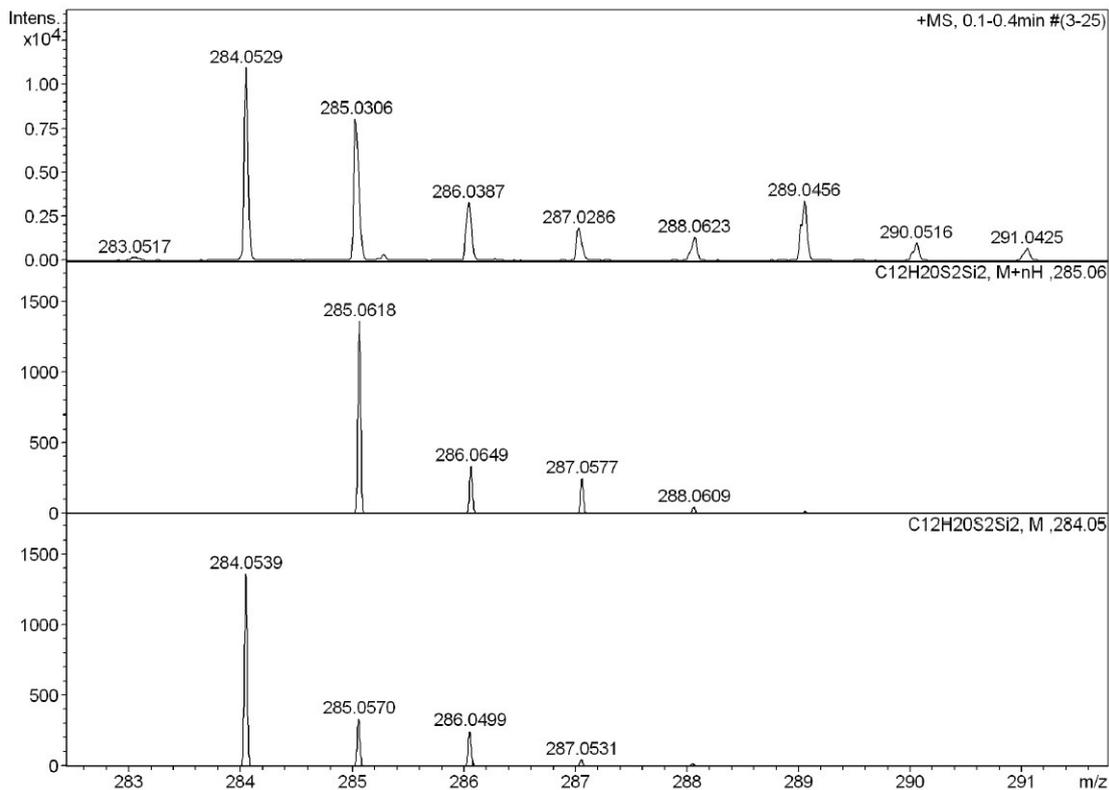


Fig. S52. HRMS spectrum of 2,5-bis(trimethylsilyl)thieno[3,2-b]thiophene (TMSTT) (APCI, positive). Top: obsd. Bottom: sim.

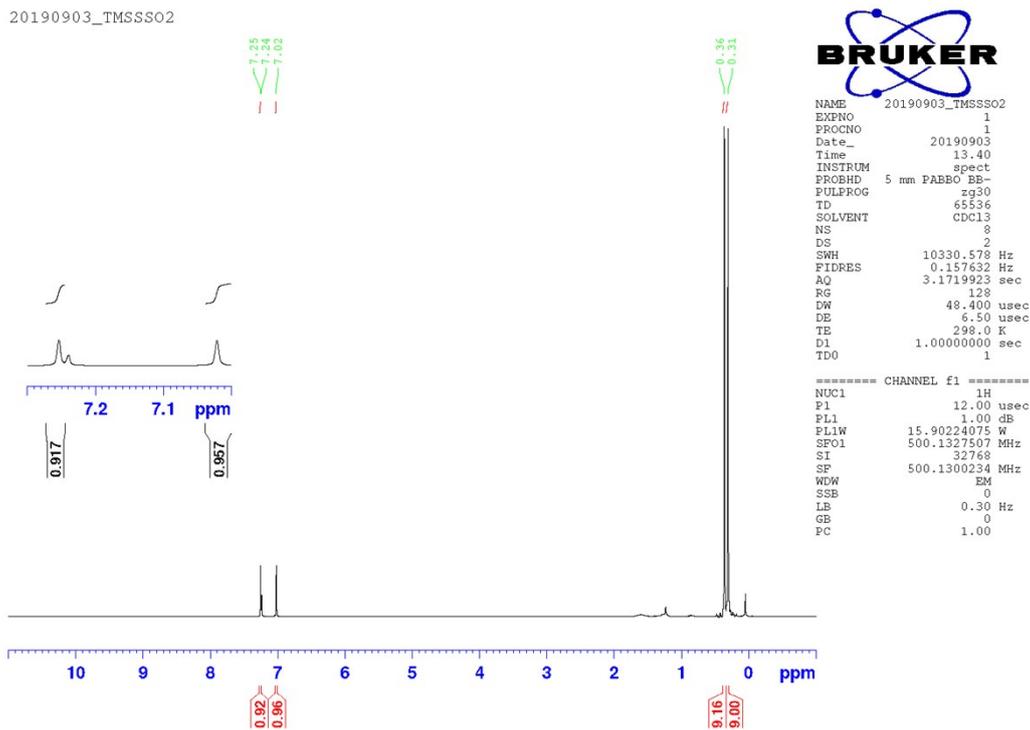


Fig. S53. ^1H NMR spectrum of 2,5-bis(trimethylsilyl)thieno[3,2-b]thiophene-1,1-dioxide (TMSTTO2) in CDCl_3 .

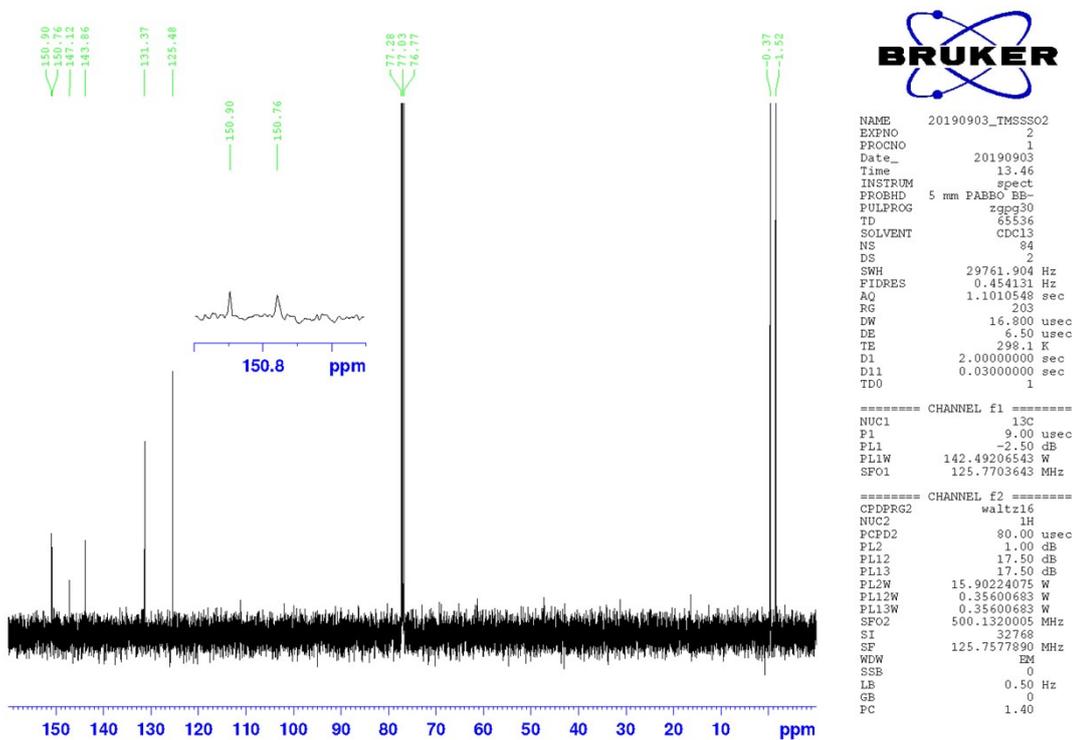


Fig. S54. ^{13}C NMR spectrum of 2,5-bis(trimethylsilyl)thieno[3,2-b]thiophene-1,1-dioxide (TMSTTO2) in CDCl_3 .

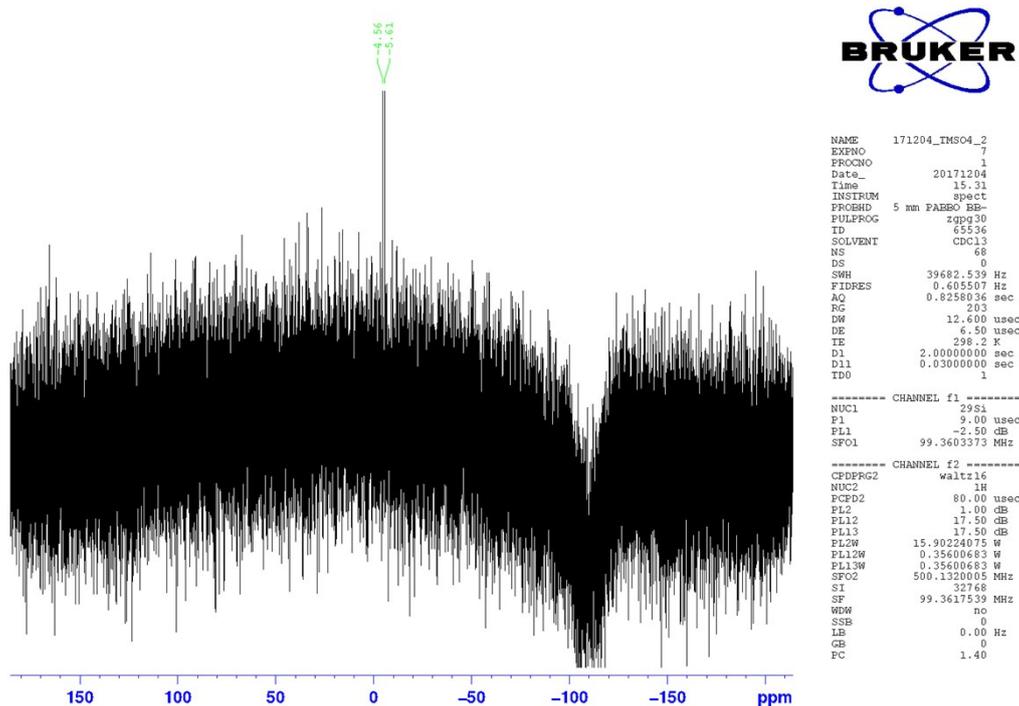


Fig. S55. ^{29}Si NMR spectrum of 2,5-bis(trimethylsilyl)thieno[3,2-b]thiophene-1,1-dioxide (TMSTTO2) in CDCl_3 .

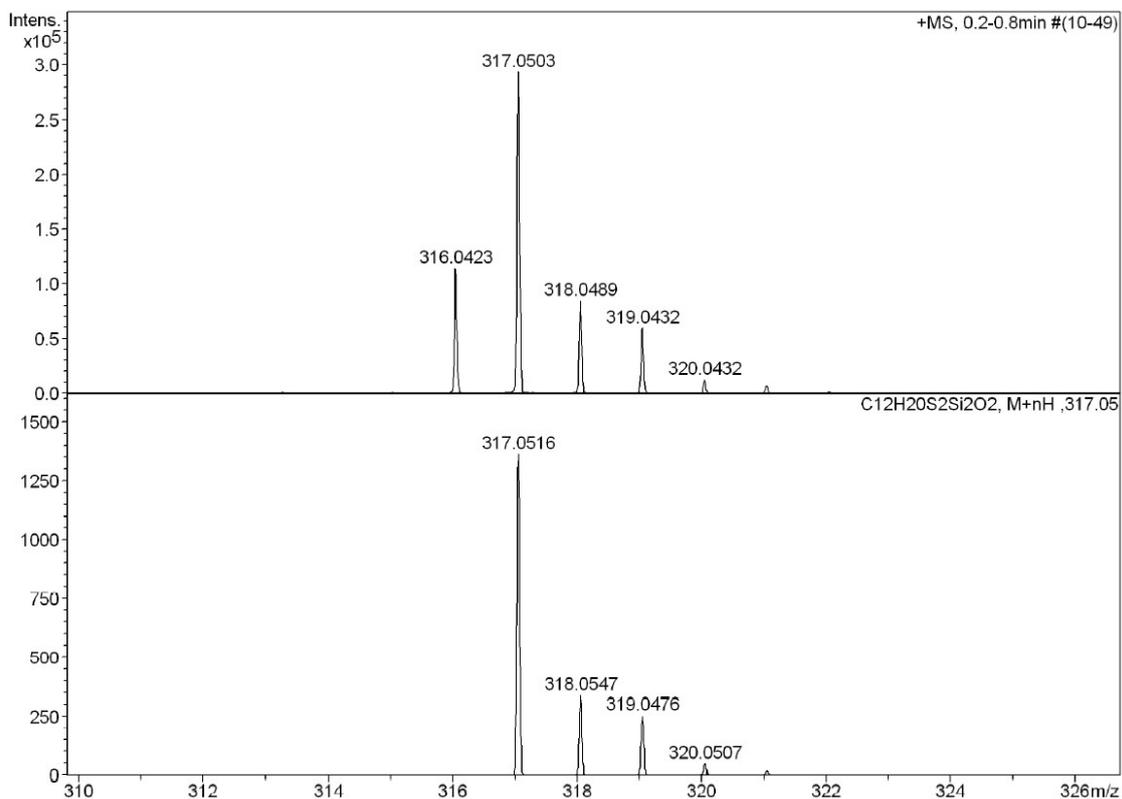


Fig. S56. HRMS spectrum of 2,5-bis(trimethylsilyl)thieno[3,2-b]thiophene-1,1-dioxide (TMSTTO2) (APCI, positive). Top: obsd. Bottom: sim.

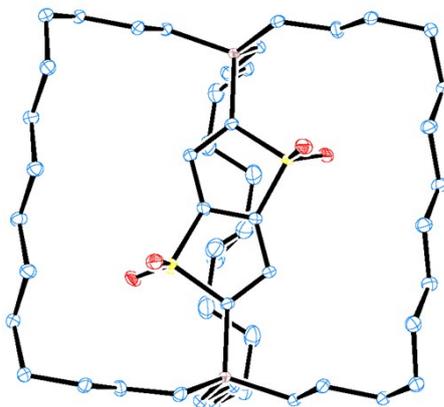
3. Details of X-Ray Diffraction Studies

a. Crystal Data

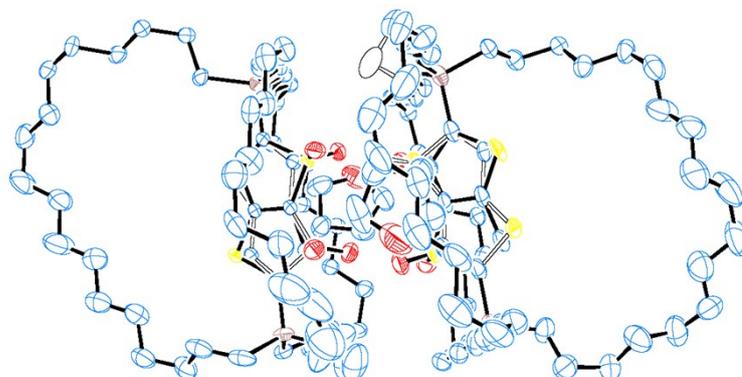
Table S1. Crystal Data

Compound	C14TTO2	C18TTO2·THF	C22TTO2·toluene	
CCDC #	2056315	2056316	2079089	
Temperature	100 K	120 K	100 K	
Empirical formula	C48 H86 O2 S2 Si2	C64 H118 O3 S2 Si2	C165 H292 O4 S4 Si4	
Crystal shape	prism	prism	plate	
Crystal color	colorless	colorless	colorless	
Crystal size	0.32 x 0.32 x 0.30 mm ³	0.35 x 0.25 x 0.10 mm ³	0.35 x 0.18 x 0.02 mm ³	
Formula weight / g mol ⁻¹	815.46	1055.88	2580.57	
Crystal system	Monoclinic	Triclinic	Triclinic	
Space group	C 2/c	P -1	P -1	
Z	4	4	1	
Calculated density	1.100 Mg/m ³	1.069 Mg/m ³	1.054 Mg/m ³	
Cell parameter	<i>a</i>	28.057(16) Å	14.1686(8) Å	14.8902(6) Å
	<i>b</i>	10.526(5) Å	18.6421(10) Å	16.5950(7) Å
	<i>c</i>	18.076(10) Å	26.5403(14) Å	19.6033(8) Å
	α	90°	92.576(3)°	102.529(2)°
	β	112.752(5)°	97.481(3)°	99.392(2)°
	γ	90°	108.562(3)°	115.908(2)°
	<i>V</i>	4923(5) Å ³	6561.0(6) Å ³	4065.7(3) Å ³
F(000)	1800	2344	1434	
Absorption coefficient	0.191 mm ⁻¹	1.379 mm ⁻¹	1.181 mm ⁻¹	
θ range for collection (deg)	3.053 to 27.533° (Mo)	4.017 to 60.000° (Cu)	4.120 to 77.490° (Cu)	
Index ranges	-36 ≤ <i>h</i> ≤ 36, -13 ≤ <i>k</i> ≤ 13, -23 ≤ <i>l</i> ≤ 23	-15 ≤ <i>h</i> ≤ 15, -20 ≤ <i>k</i> ≤ 20, -29 ≤ <i>l</i> ≤ 29	-18 ≤ <i>h</i> ≤ 17, -20 ≤ <i>k</i> ≤ 20, -23 ≤ <i>l</i> ≤ 24	
Reflections collected	25400	44497	35974	
Independent reflections	5660 [R(int) = 0.0272]	18773 [R(int) = 0.0572]	16117 [R(int) = 0.0354]	
Completeness	99.7 %	96.4 %	97.3 %	
Goodness-of-fit on F ²	1.136	1.021	1.018	
Final R indices [I > 2σ(I)]	R1 = 0.0502, wR2 = 0.1233	R1 = 0.1304, wR2 = 0.3267	R1 = 0.0998, wR2 = 0.2724	
R indices (all data)	R1 = 0.0540, wR2 = 0.1255	R1 = 0.1654, wR2 = 0.3578	R1 = 0.1114, wR2 = 0.2839	

(a)



(b)



(c)

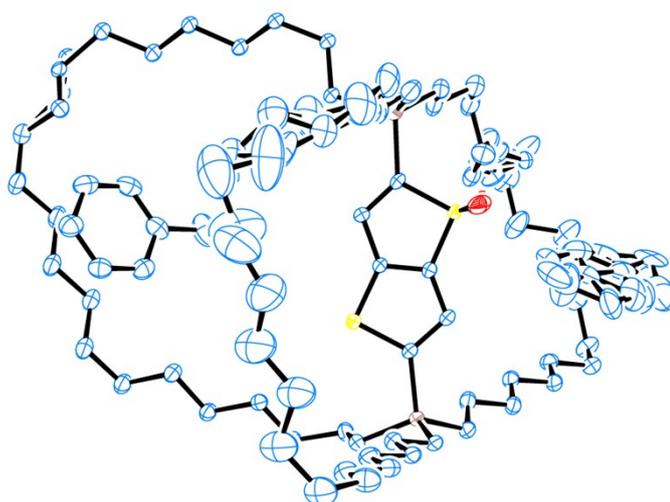
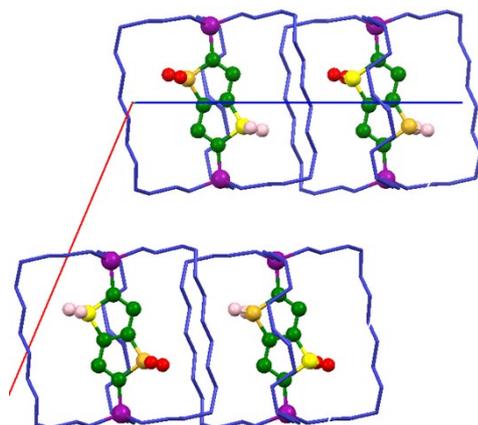
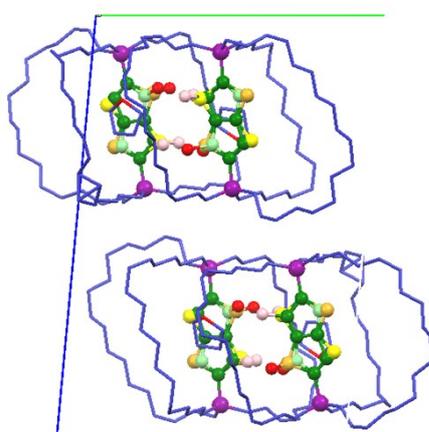


Fig. S57. ORTEP drawing (30% thermal ellipsoids) of molecular structures determined by X-ray crystallography (Hydrogen atoms are omitted for clarity. Disorder was indicated.): (a) C₁₄TTO₂; (b) C₁₈TTO₂·THF; (c) C₂₂TTO₂·toluene.

(a)



(b)



(c)

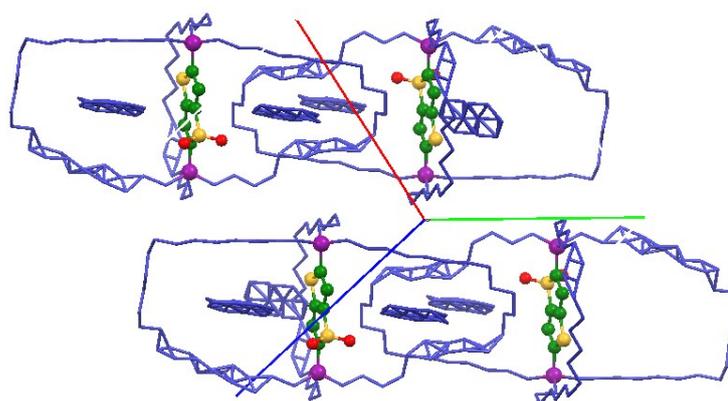
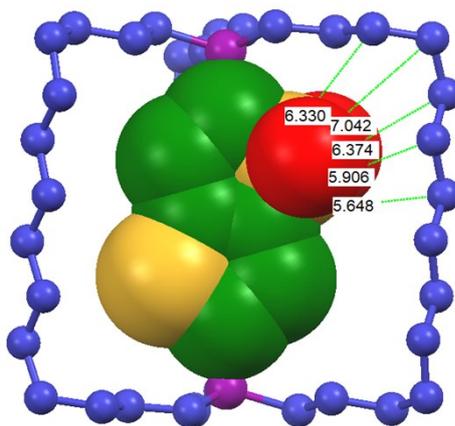
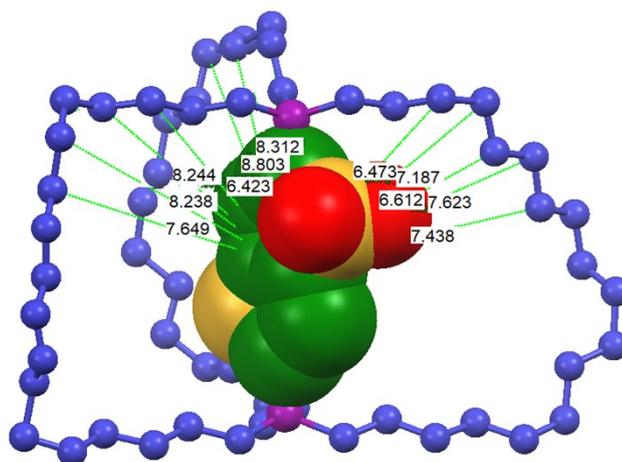


Fig. S58. Packing diagram of single crystals determined by X-ray crystallography: (a) C14TTO2; (b) C18TTO2·THF; (c) C22TTO2·toluene.

(a)



(b)



(c)

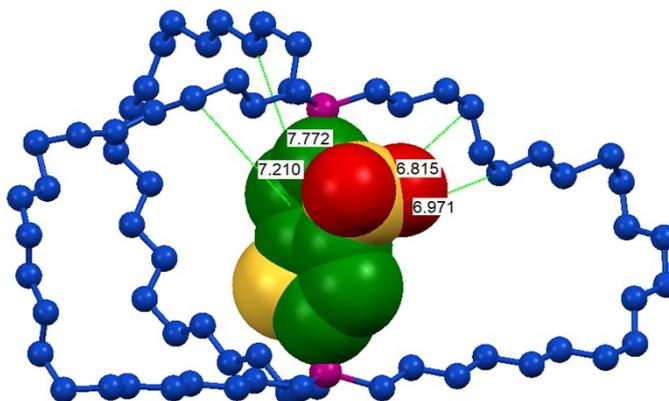


Fig. S59. Distances between center of the molecule (X) and cage carbon (C) that is contactable with oxygen (O) of the rotating TTO2 moiety: (a) **C14TTO2** crystal; (b) **C18TTO2·THF** crystal; (c) **C22TTO2·toluene** crystal.

4. Details of DSC Studies

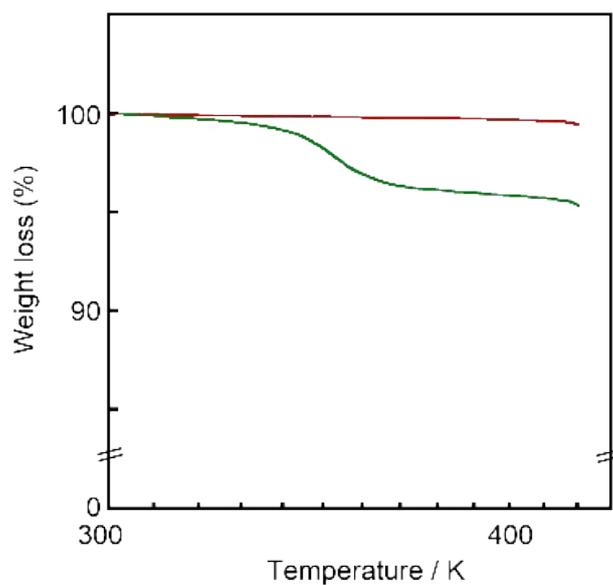


Fig. S60. Thermogravimetric analysis (TGA) data for **C18TTO2·THF** crystals (green line) and **C18TTO2** powders after melting (red line).

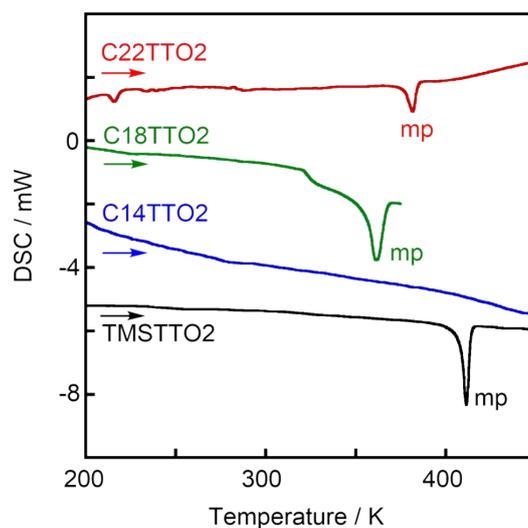


Fig. S61. DSC charts for powdered samples.

5. Details of Fluorescence Studies

Fluorescence spectra studies Sample solutions for fluorescence studies were thoroughly degassed using several freeze–pump–thaw sequences. The quantum yields of the solutions were determined by comparison with the fluorescence intensity of naphthalene in hexane ($\Phi = 0.10$, ref Weber, G.; Teale, F. W. J. *Trans. Faraday Soc.* **1957**, *53*, 646.) under irradiation by 340 nm light. The absolute quantum yields of the powders were determined using a spectrometer equipped with an integrating sphere. Lifetimes were measured under irradiation by 340 nm light (LED) with a time-correlated single-photon counting apparatus.

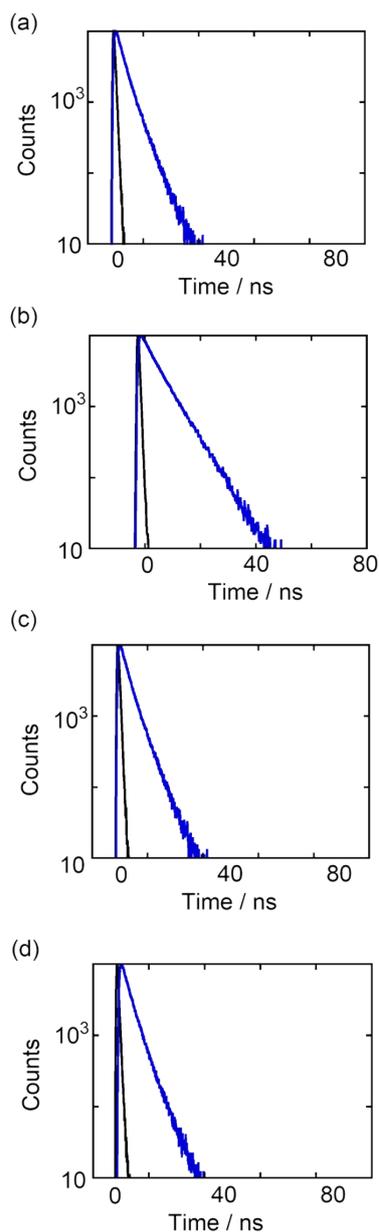


Fig. S62. Fluorescence life-time measurements for powdered silylthienothiophene-dioxide: (a) TMSTTO2 (as a control), (b) C14TTO2, (c) C18TTO2, and (d) C22TTO2.

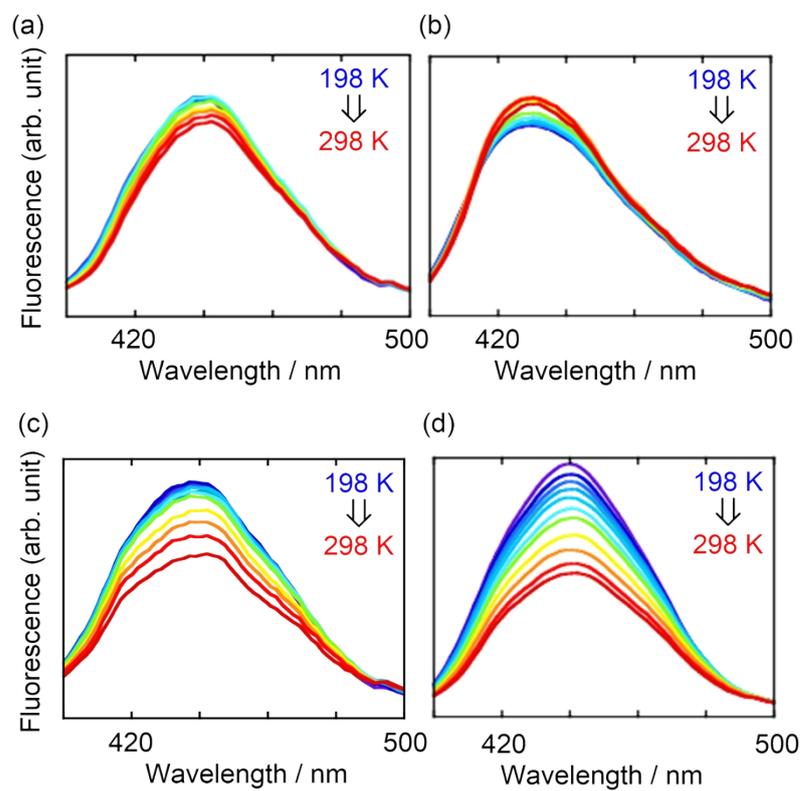


Fig. S63. Temperature dependent fluorescence spectra of powdered silylthienothiophene-dioxide: (a) TMSTTO2 (as a control), (b) C14TTO2, (c) C18TTO2, and (d) C22TTO2.

6. Details of Temperature Dependent Dielectric Relaxation Studies

Dielectric relaxation spectra studies Dielectric relaxation studies were carried out by building parallel plate capacitors with a dielectric placed between the plates. The dielectric spectra were measured using an impedance meter.

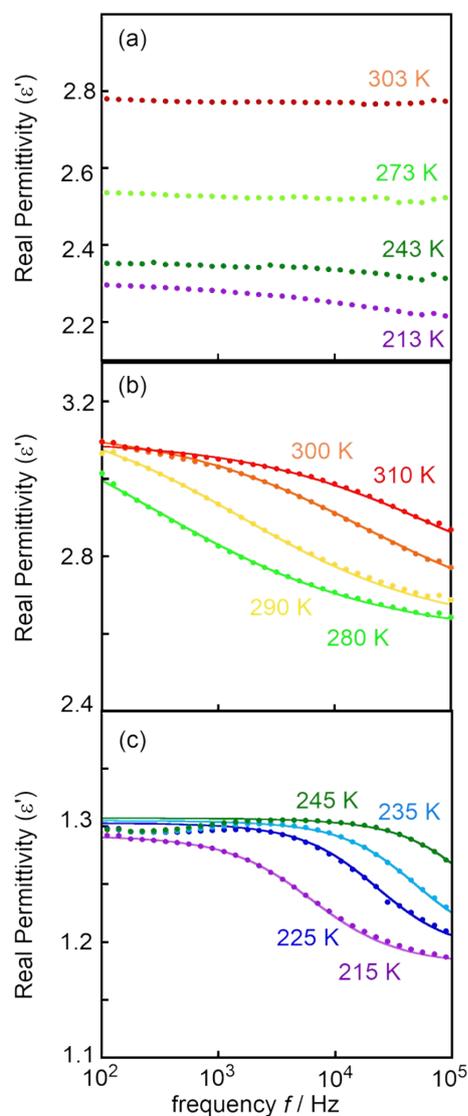
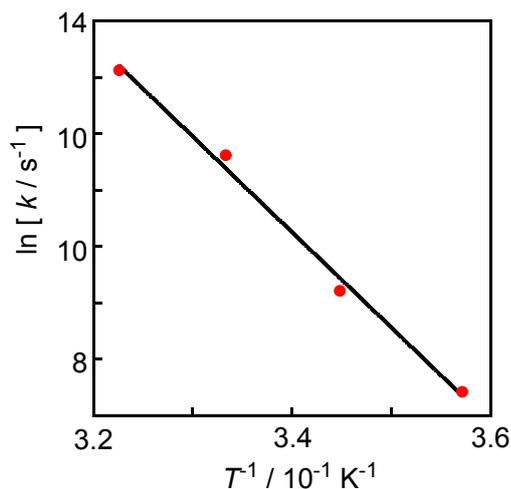


Fig. S64. Dielectric spectra (real permittivity (ϵ')) of (a) **C14TTO2** powder, (b) **C18TTO2** powder, and (c) **C22TTO2** powder: dotted lines, observed data; solid lines, fitting lines calculated using Cole–Cole model (eq. 2, $\alpha = 0.4$ for 280 K, $\alpha = 0.45$ for 290, 300, and 310 K for **C18TTO2**; $\alpha = 0.78$ for 215 K, $\alpha = 0.83$ for 225, 235, and 245 K for **C22TTO2**).

(a)



(b)

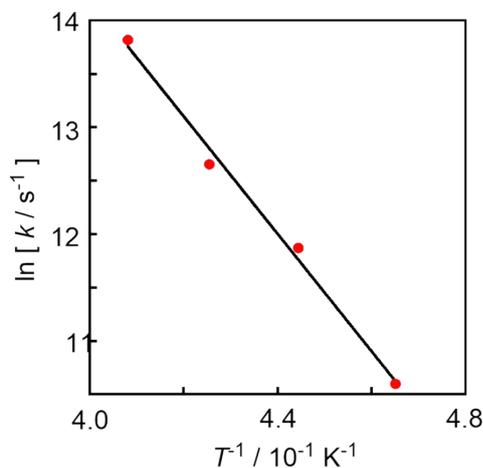


Fig. S65. An Arrhenius plot of temperature dependent reciprocal relaxation time determined by VT dielectric relaxation spectra for powdered (a) **C18TTO2** (The slope and the intercept of the fitting line are -16947 ± 942 , 67.9 ± 3.2 , respectively. The activation energy and the frequency factor were estimated to be 33.7 ± 0.19 kcal/mol and $(3.31 \pm 4.8) \cdot 10^{29}$, respectively.) and (b) **C22TTO2** (The slope and the intercept of the fitting line are -5498.3 ± 325 , 36.20 ± 1.4 , respectively. The activation energy and the frequency factor were estimated to be 10.9 ± 0.68 kcal/mol and $(5.2 \pm 16.5) \cdot 10^{15}$, respectively.).

7. Details of DFT Calculations

All calculations were carried out using Gaussian 16 (Revision C.01) program packages^{S1} at the Research Center for Computational Science, Okazaki, Japan

S1: Gaussian 16, Revision C.01,

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

Table S2. Optimized Structural Coordinate and its Total Energy for **TMSTTO2** at B3LYP/6-31G(d) level

total energy: = -1995.1241714 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	-4.093478	0.464543	0.000199
2	14	0	4.412820	-0.004557	0.000343
3	16	0	-1.350402	-1.275756	-0.000092
4	8	0	-1.601188	-1.981065	1.268041
5	8	0	-1.602755	-1.981375	-1.267741
6	16	0	1.657012	1.625026	-0.000376
7	6	0	-2.200536	0.338924	-0.000091
8	6	0	-1.264739	1.314399	-0.000528
9	6	0	0.117932	0.839215	-0.000820
10	6	0	0.278894	-0.522691	-0.000826
11	6	0	1.622031	-0.961948	-0.000383
12	6	0	2.522337	0.089507	-0.000291
13	1	0	-1.509535	2.372487	-0.000738
14	1	0	1.924711	-2.002733	-0.000473
15	6	0	-4.740645	-0.385744	1.555283
16	6	0	-4.521681	2.306644	0.000949
17	6	0	-4.741512	-0.384556	-1.555162
18	6	0	5.076284	0.853644	1.548875
19	6	0	5.076941	0.854167	-1.547669
20	6	0	4.884637	-1.833603	-0.000433
21	1	0	4.784287	1.909981	1.583056
22	1	0	6.172178	0.813248	1.577132
23	1	0	4.699842	0.375959	2.460569
24	1	0	-4.424544	0.146611	2.459614
25	1	0	4.786010	1.910812	-1.581309
26	1	0	6.172823	0.812765	-1.576032
27	1	0	-5.836850	-0.424933	1.551782
28	1	0	-4.359666	-1.409793	1.628305
29	1	0	-4.130315	2.817521	0.888447
30	1	0	4.700036	0.377324	-2.459608
31	1	0	5.976025	-1.942037	-0.000227
32	1	0	-5.610627	2.438439	0.001856
33	1	0	4.503280	-2.353823	0.885707
34	1	0	-4.131740	2.817915	-0.886949
35	1	0	4.503703	-2.352394	-0.887600
36	1	0	-4.360384	-1.408458	-1.629351
37	1	0	-5.837709	-0.423927	-1.550857
38	1	0	-4.426206	0.148685	-2.459252

Dipole moment (field-independent basis, Debye):

X= 2.2425 Y= 3.8895 Z= 0.0001 Tot= 4.4896