Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Steric Effects on Intramolecular Charge Transfer Fluorescence of Benzo[*b*]thiophene-1,1-dioxide Bridged Macrocages

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1. Details of Synthetic Studies

General. All synthetic reactions were carried out in anhydrous conditions under an argon atmosphere unless otherwise noted. The chemical shifts in the ^{1}H 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).

Materials Commercially available reagents were used without further purification unless otherwise noted. Spectroscopy grade solvents (hexane, toluene, AcOEt, CH_2Cl_2, and toluene) were used for fluorescence studies.

Synthesis of 2,5-bis(tris-9-decenylsilyl)benzo[*b*]thiophene (C10BTC10). To a 100-mL two-necked flask with a magnetic stirrer, 5-Bromobenzo[b]thiophene (2.35 g, 11 mmol) and dry THF (12 mL) were added. nBuLi solution (1.6 N, 15.4 mL, 24.2 mmol) was dropped into the flask at −78 °C for 25 min. After 1 h stirring, tris(7-octenyl)chrolosilane (13.6 g, 28.0 mmol) in THF (10 mL) was dropped into the flask at −80 °C for 1h. Then, the reaction temperature was increased to room temperature for 1h, and was stirred for 15 h. The solvents were distilled off and the reaction mixture was hydrolyzed with NH_4Cl. The organic layer was extracted with hexane and dried over Na_2SO_4. After column chromatography (silica gel, eluent: hexane) and GPC, **C10BTC10** was obtained as a colorless oil (2.83 g, 2.77 mmol, 25%).

C10BTC10: a colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.92 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.43 (s, 1H), 7.37 (d, J = 8.0 Hz, 1H), 5.79 (ddt, J = 17.0, 10.0, 6.8 Hz, 6H), 4.97 (d, J = 17.0 Hz, 6H), 4.91 (d, J = 10.0 Hz, 6H, H_2C=CH-), 2.01 (q, J = 6.8 Hz, 12H), 1.15-1.40 (br, 72H), 0.81-0.83 (br, 12H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 144.2, 140.7, 130.3, 132.9, 131.5, 129.4, 129.3, 121.4, 114.1, 33.8, 33.7, 29.4, 29.2, 29.0, 23.8, 23.8; $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$, 99 MHz): δ −1.3, −2.8; HRMS (APCI) m/z: $[M]^+$ Calcd for $C_{68}H_{118}Si_2S$ 1022.8487; Found: 1022.8493.

Synthesis of 2,5-bis(tris-11-dodecenylsilyl)benzene (C12BTC12). Using the same procedure as that for the synthesis of **1**, 5-Bromobenzo[b]thiophene (3.29 g, 15.4 mmol), tetrahydrofuran (15 mL), nBuLi solution (22 mL, 34.5 mmol), and tris(9-decenyl)chrolosilane (18 g, 32 mmol) were used to obtain **2** as a colorless oil (3.23 g, 2.71 mmol, 18%).

C12BTC12: a colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.44 (s, 1H), 7.38 (d, J = 8.0 Hz, 1H), 5.80 (ddt, J = 17.0, 10.0, 7.0 Hz, 6H), 4.99 (d, J = 17.0 Hz, 6H), 4.92 (d, J = 10.0 Hz, 6H, H_2C=CH-), 2.03 (q, J = 7.0 Hz, 12H), 1.20-1.39 (br, 96H), 0.83-0.85 (br, 12H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 144.2, 140.8, 139.2, 132.9, 131.5, 129.4, 129.3, 121.4, 114.1, 33.8, 33.7, 29.7, 29.6, 29.5, 29.3, 29.2, 29.0, 23.9, 23.8, 13.3, 12.7; $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$, 99 MHz): δ −1.4, −2.9; HRMS (APCI) m/z: $[M]^+$ Calcd for $C_{80}H_{142}Si_2S$ 1191.0365; Found: 1191.0336.

Synthesis of molecular gyrotop C18BT. To a 1000-mL three-necked flask with a magnetic stirrer, condenser, glass stopper, and dropping funnel, CH_2Cl_2 (700 mL) was added. Then, 1st generation Grubbs' catalyst (10 mg) was added to the flask, and a solution of **1** (850 mg, 0.83 mmol) in CH_2Cl_2 (250 mL) was dropped under reflux for 6 h. During the addition, Grubbs' catalyst (10 mg) was added to the flask total three times. After 18h, the reaction mixture was cooled to room temperature, and the solvent was distilled off. The residue was treated with column chromatography (silica gel, eluent: toluene) to remove metal complexes. The crude products, toluene (20 mL), and Pd/C catalyst were added to an autoclave. The vessel was heated to 60 °C and stirred for 24h under a hydrogen atmosphere (3 atm). The reaction mixture was filtered, and volatile materials were removed in vacuo. Via gel permeation crystallography (GPC) purification, **C18BT** (120 mg, 13 mmol, 15%) was obtained as colorless crystals, and **C18iBT** (240 mg, 25 mmol, 30%) was obtained as a colorless oil.

C18BT: colorless crystals; mp 85–86 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.00 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.53 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 1.15-1.40 (br, 96H), 0.81-0.83 (br, 12H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 144.4, 140.8, 139.4, 132.1, 131.5, 130.0, 129.5, 121.5, 33.5, 29.5, 29.4, 29.1, 29.0, 28.6, 23.6, 13.4, 12.6; $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$, 99 MHz): δ −0.7, −2.4; HRMS (APCI) m/z: $[M]^+$ Calcd for $C_{62}H_{112}Si_2S$ 944.8018; Found: 944.8013. **C18iBT**: a colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H), 7.38 (d, J = 8.0 Hz, 1H), 1.20-1.40 (br, 96H), 0.82-0.90 (br, 8H), 0.70-0.80 (br, 8H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 144.2, 140.8, 139.4, 133.0, 131.6, 129.5, 129.3, 121.5, 33.8, 33.7, 33.2, 33.0, 29.2, 29.1, 29.0, 28.9, 28.6, 28.5, 28.4, 28.2, 28.1, 27.7, 27.4, 23.8, 23.7, 23.4, 23.3, 14.0, 13.7, 13.0, 12.1; $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$, 99 MHz): δ −1.0, −2.6; HRMS (APCI) m/z: $[M]^+$ Calcd for $C_{62}H_{112}Si_2S$ 944.8018; Found: 944.8016.

Synthesis of molecular gyrotop C22BT. Using the same procedure as that for the synthesis of **C18BT**, bissilyldifluorobenzene **2** (1.33 g, 1.12 mmol), dichloromethane (950 mL), and toluene (10 mL) were used. **C22BT** (100 mg, 0.09 mmol, 8 %) was obtained as a colorless oil, and **C22iBT** (145 mg, 0.13 mmol, 12%) was obtained as a colorless oil.

C22BT: a colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.48 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 1.22-1.40 (br, 120H), 0.81-0.84 (br, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 144.3, 140.7, 139.3, 132.8, 131.8, 129.6, 129.4, 121.5, 33.8, 33.7, 29.7, 29.3, 29.2, 29.0, 23.8, 23.7, 14.1, 13.3, 12.6; ^{29}Si{^{1}H} NMR ($CDCl_3$, 99 MHz): δ −1.1, −2.6; HRMS (APCI) m/z: $[M]^+$ Calcd for $C_{74}H_{136}Si_2S$ 1112.990; Found: 1112.987. **C22iBT**: a colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H), 7.39 (d, J = 8.0 Hz, 1H), 1.22-1.42 (br, 120H), 0.82-0.90 (br, 8H), 0.72-0.80 (br, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 144.2, 140.8, 139.4, 133.0, 131.5, 129.4, 129.3, 121.4, 33.8, 33.7, 33.5, 33.3, 29.2, 29.1, 29.0, 28.8, 28.7, 28.5, 28.2, 28.0, 23.9, 23.8, 23.6, 23.5, 13.9, 13.5, 13.0, 12.2; ^{29}Si{^{1}H} NMR ($CDCl_3$, 99 MHz): δ −1.2, −2.7; HRMS (APCI) m/z: $[M]^+$ $C_{74}H_{136}Si_2S$ 1112.990; Found: 1112.985.

Synthesis of molecular gyrotop C18BTO2. Macrocage **C18BT** (90 mg, 0.095 mmol) and *m*CPBA (63 mg, 0.26 mmol) were dissolved in dichloromethane (20 mL). The reaction mixture was then stirred for 40 h at room temperature. The mixture was quenched with a dilute aqueous $NaHCO_3$ solution and extracted with dichloromethane. The organic layer was washed several times with dilute aqueous $NaHCO_3$ to completely remove chlorobenzoic acid. The mixture was dried over anhydrous Na_2SO_4 and filtered, and the volatile materials were removed in vacuo. Pure **C18BTO2** (60 mg, 0.061 mmol, 64% yield) was obtained as colorless crystals after recrystallization from ethanol.

C18BTO2: colorless crystals; mp 129–130 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.47 (s, 1H), 7.30 (s, 1H), 1.15-1.49 (br, 96H), 0.82-0.89 (br, 6H), 0.73-0.78 (br, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 145.8, 144.4, 141.0, 139.7, 136.1, 131.5, 130.4, 120.1, 33.4, 33.3, 29.5, 29.4(duplicated), 29.3, 29.2 (duplicated), 29.1, 29.0, 28.9, 28.7 (triplicated), 23.5, 23.3, 12.0, 11.6; ^{29}Si{^{1}H} NMR ($CDCl_3$, 99 MHz): δ 0.4, −1.5; HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{62}H_{113}Si_2SO_2$ 977.7994; Found: 977.8024.

Synthesis of molecular gyrotop isomer C18iBTO2. Using the same procedure as that for the synthesis of **C18BTO2**, **C18iBT** (103 mg, 0.11 mmol), *m*CPBA (112 mg, 0.49 mmol), and dichloromethane (20 mL) were used to obtain **C18iBTO2** as a colorless oil (70 mg, 0.072 mmol, 65%).

C18iBTO2: a colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.38 (s, 1H), 7.20 (s, 1H), 1.18-1.41 (br, 96H), 0.65-0.98 (br, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 146.1, 144.6, 140.3, 139.6, 136.1, 131.5, 129.9, 120.3, 33.8, 33.1, 12.9, 29.2, 29.1, 29.0, 28.8, 28.7, 28.6, 28.4, 28.1, 27.6, 27.3, 23.8, 23.7, 23.2, 23.0, 13.4, 12.9, 11.6, 11.3; ^{29}Si{^{1}H} NMR ($CDCl_3$, 99 MHz): δ −0.1, −2.3; HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{62}H_{113}Si_2SO_2$ 977.7994; Found: 977.8028.

Synthesis of molecular gyrotop C22BTO2. Using the same procedure as that for the synthesis of **C18BTO2**, **C22BT** (73 mg, 0.065 mmol), *m*CPBA (81 mg, 0.36 mmol), and dichloromethane (20 mL) were used to obtain **C22BTO2** as a colorless oil (55 mg, 0.048 mmol, 74%).

C22BTO2: colorless crystals; mp 81–82 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.39 (s, 1H), 7.22 (s, 1H), 1.20-1.40 (br, 120H), 0.83-0.89 (br, 6H), 0.72-0.78 (br, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 145.9, 144.6, 140.6, 139.7, 136.1, 131.5, 130.1, 120.2, 33.7, 33.6, 29.4, 29.3, 29.2, 29.1, 29.0, 23.6, 23.4, 12.2, 11.6; ^{29}Si{^{1}H} NMR ($CDCl_3$, 99 MHz): δ 0.0, −2.0; HRMS (APCI) m/z: $[M]^+$ Calcd for $C_{74}H_{136}Si_2SO_2$ 1144.979; Found: 1144.978.

Synthesis of molecular gyrotop isomer C22iBTO2. Using the same procedure as that for the synthesis of **C18BTO2**, **C22iBT** (98 mg, 0.088 mmol), *m*CPBA (126 mg, 0.56 mmol), and dichloromethane (20 mL) were used to obtain **C22iBTO2** as a colorless oil (40 mg, 0.035 mmol, 40%). **C22iBTO2**: a colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.63 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.37 (s, 1H), 7.19 (s, 1H), 1.20-1.42 (br, 120H), 0.65-0.96 (br, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 146.1, 144.8, 140.2, 139.6, 136.1, 131.5, 129.9, 120.2, 33.8, 33.7, 33.3, 33.2, 29.5, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 28.6, 28.5, 28.1, 27.9, 23.8, 23.6, 23.4, 23.1, 13.1, 12.6, 11.7, 11.4; ^{29}Si{^{1}H} NMR ($CDCl_3$, 99 MHz): δ −0.2, −2.4; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{74}H_{136}Si_2SO_2Na$ 1167.969; Found: 1167.969.

Synthesis of 2,5-bis(trimethylsilyl)benzo[b]thiophene (TMSBT). Using the same procedure as that for the synthesis of **1**, 5-Bromobenzo[b]thiophene (2.96 g, 13.9 mmol), tetrahydrofuran (15 mL), nBuLi solution (20 mL, 31.3 mmol), and chrolotrimethylsilane (4.43 g, 40.8 mmol) were used to obtain **TMSBT** as colorless crystals (1.15 g, 4.13 mmol, 30%).

TMSBT: colorless crystals; mp 79–80°C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.47 (s, 1H), 7.44 (d, J = 8.0 Hz, 1H), 0.37 (s, 9H), 0.31 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 144.2, 141.9, 140.7, 135.4, 130.8, 128.6 (duplicated), 121.6, −0.3, −0.9; ^{29}Si{^{1}H} NMR ($CDCl_3$, 99 MHz): δ −2.3, −5.4; HRMS (APCI) m/z: $[M]^+$ Calcd for $C_{14}H_{22}Si_2S$ 278.0975; Found: 279.0983.

Synthesis of 2,5-bis(trimethylsilyl)benzo[b]thiophene-1,1-dioxide (TMSBTO2). Using the same procedure as that for the synthesis of **C18BTO2**, **TMSBT** (800 mg, 2.87 mmol), *m*CPBA (2.0 g, 8.8 mmol), and dichloromethane (100 mL) were used to obtain **TMSBTO2** as a colorless oil (458 mg, 1.48 mmol, 52%).

TMSBTO2: colorless crystals; mp 80–81 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.65 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.42 (s, 1H), 7.20 (s, 1H), 0.38 (s, 9H), 0.27 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 148.1, 146.2, 139.8, 139.4, 135.4, 131.5, 129.4, 120.4, −1.4, −1.5; ^{29}Si{^{1}H} NMR ($CDCl_3$, 99 MHz): δ −2.3, −5.4; HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{23}Si_2SO_2$ 311.0952; Found: 311.0956.

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

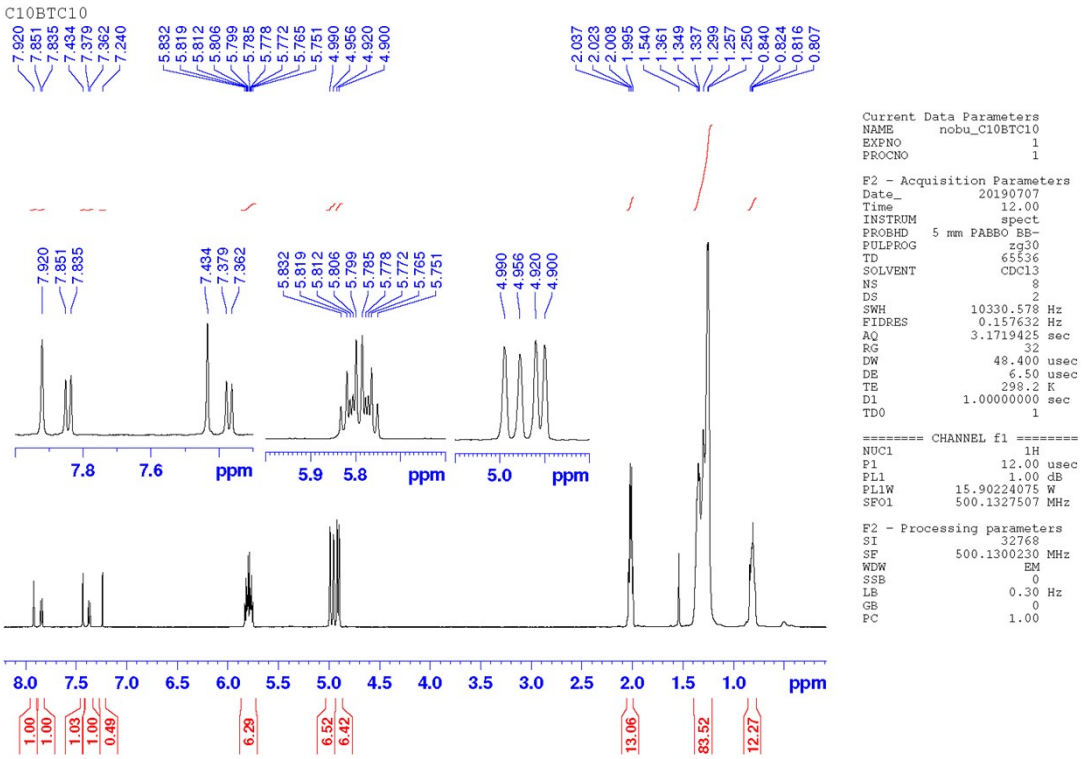


Fig. S1. ^{1}H NMR spectrum of 2,5-bis(tri(9-decenyl)silyl)benzo[b]thiophene (**C10BTC10**) in $CDCl_3$.

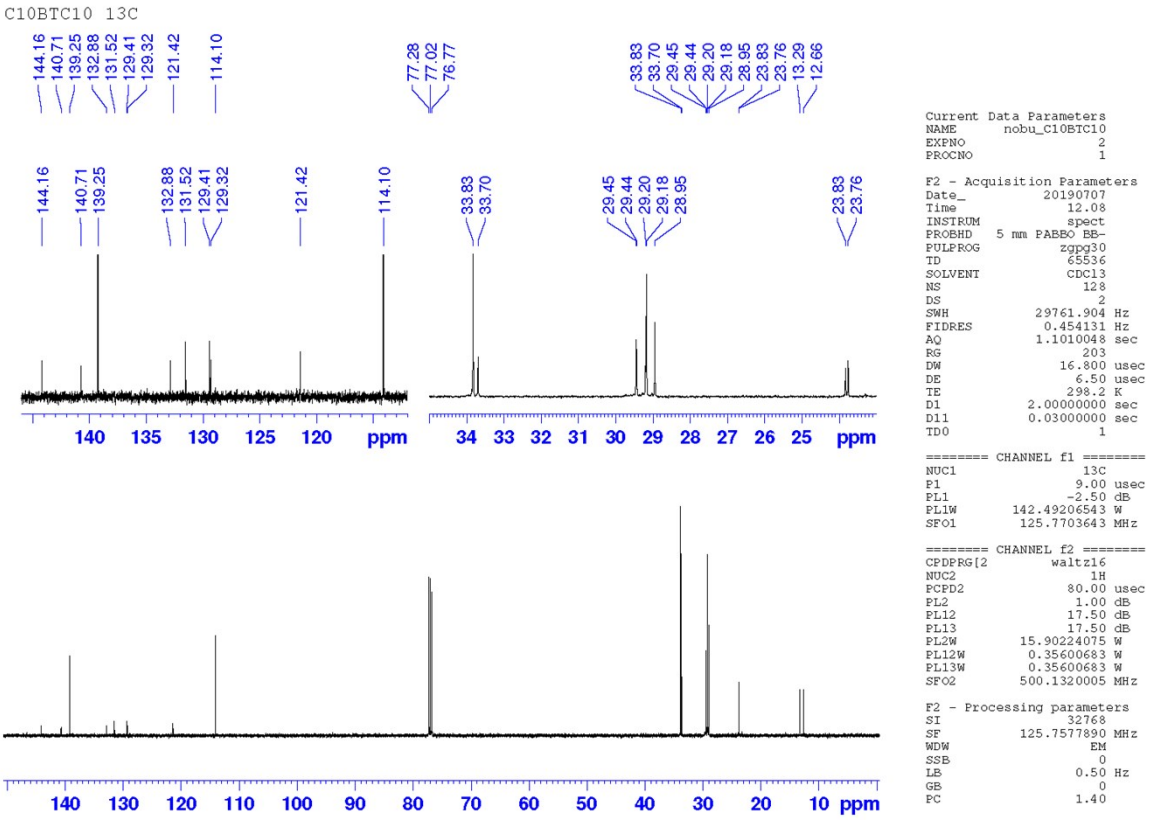


Fig. S2. ^{13}C NMR spectrum of 2,5-bis(tri(9-decenyl)silyl)benzo[b]thiophene (**C10BTC10**) in $CDCl_3$

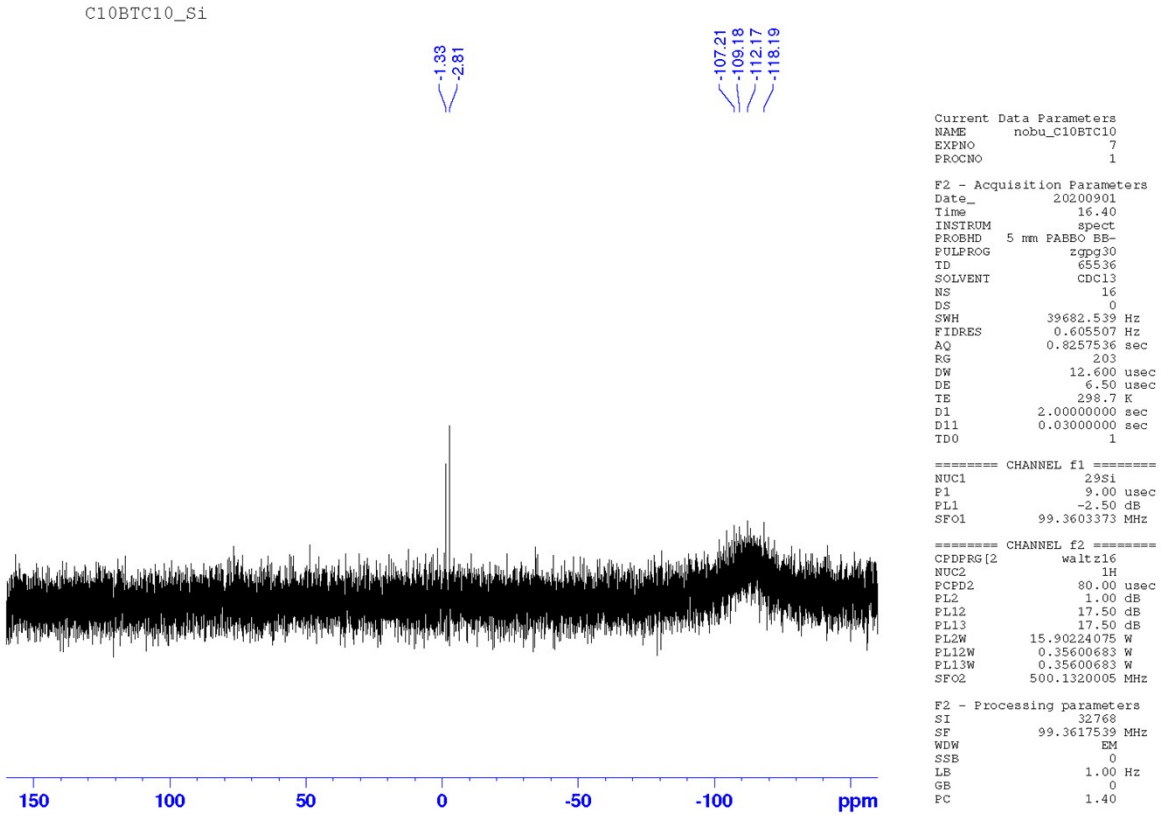


Fig. S3. ^{29}Si NMR spectrum of 2,5-bis(tri(9-decenyl)silyl)benzo[b]thiophene (**C10BTC10**) in $CDCl_3$.

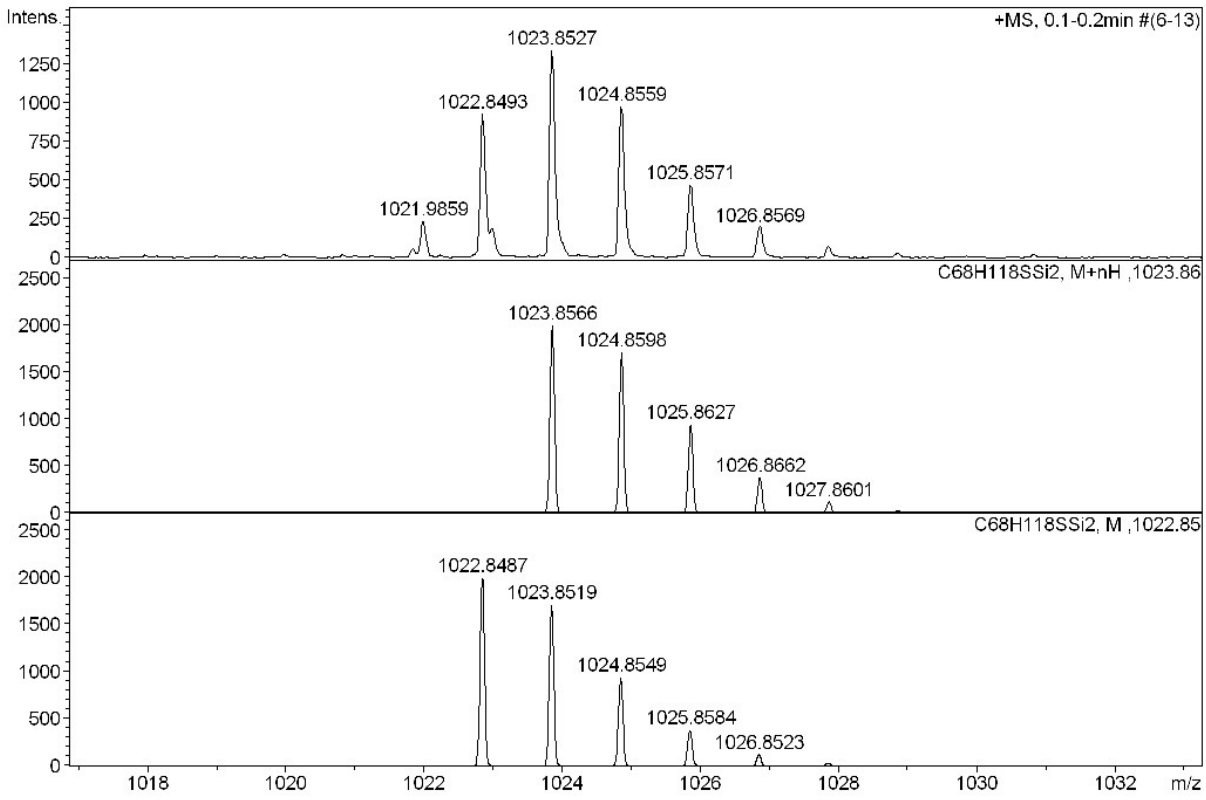


Fig. S4. HRMS spectrum of 2,5-bis(tri(9-decenyl)silyl)benzo[b]thiophene (**C10BTC10**) (APCI, positive). Top: obsd. Bottom: sim.

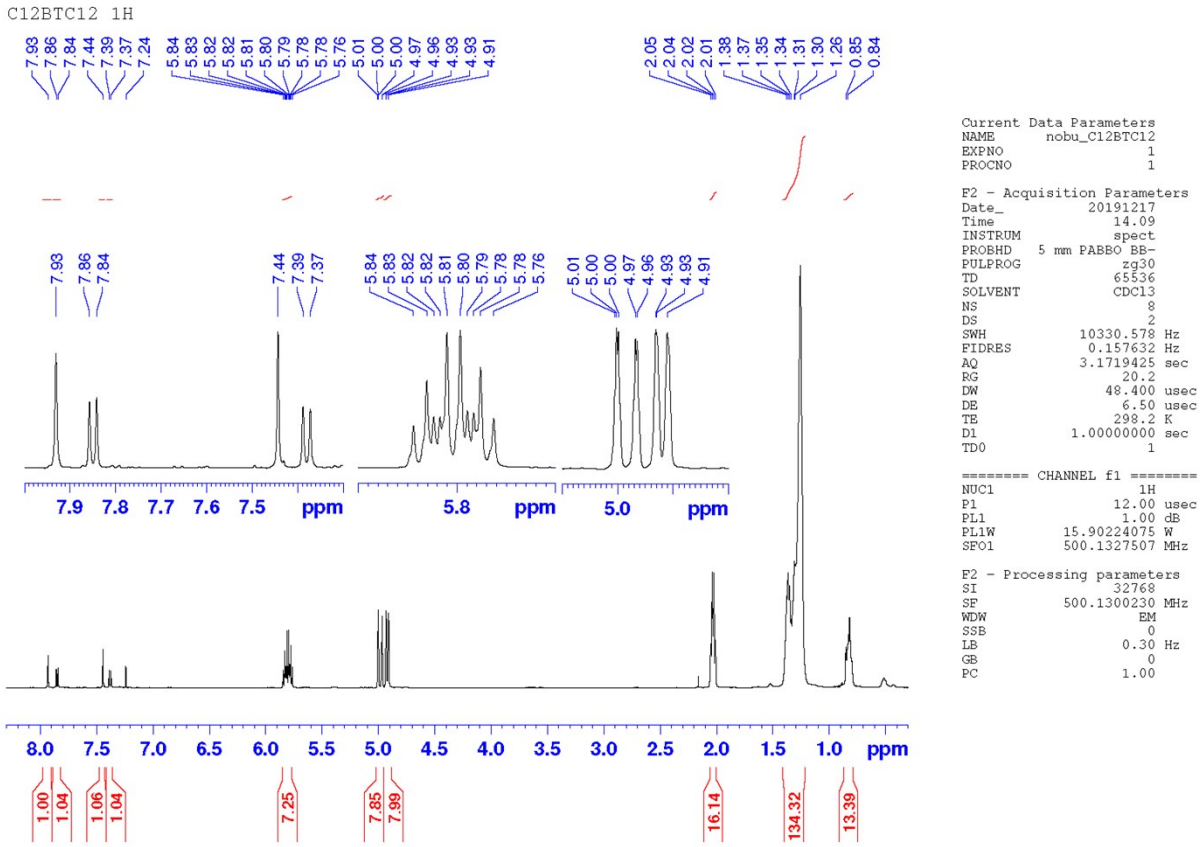


Fig. S5. ^{1}H NMR spectrum of 2,5-bis(tri(11-dodecenyl)silyl)benzo[b]thiophene (**C12BTC12**) in $CDCl_3$.

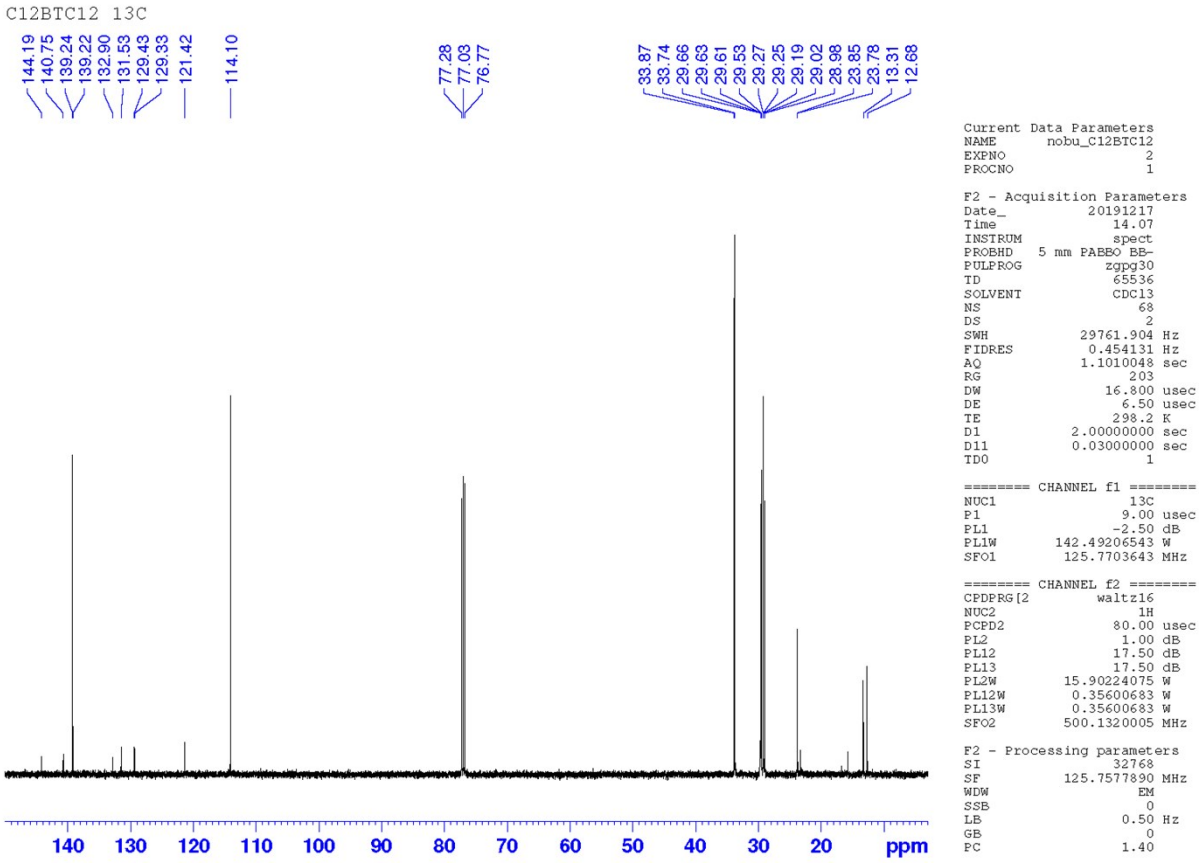


Fig. S6. ^{13}C NMR spectrum of 2,5-bis(tri(11-dodecenyl)silyl)benzo[b]thiophene (**C12BTC12**) in $CDCl_3$.

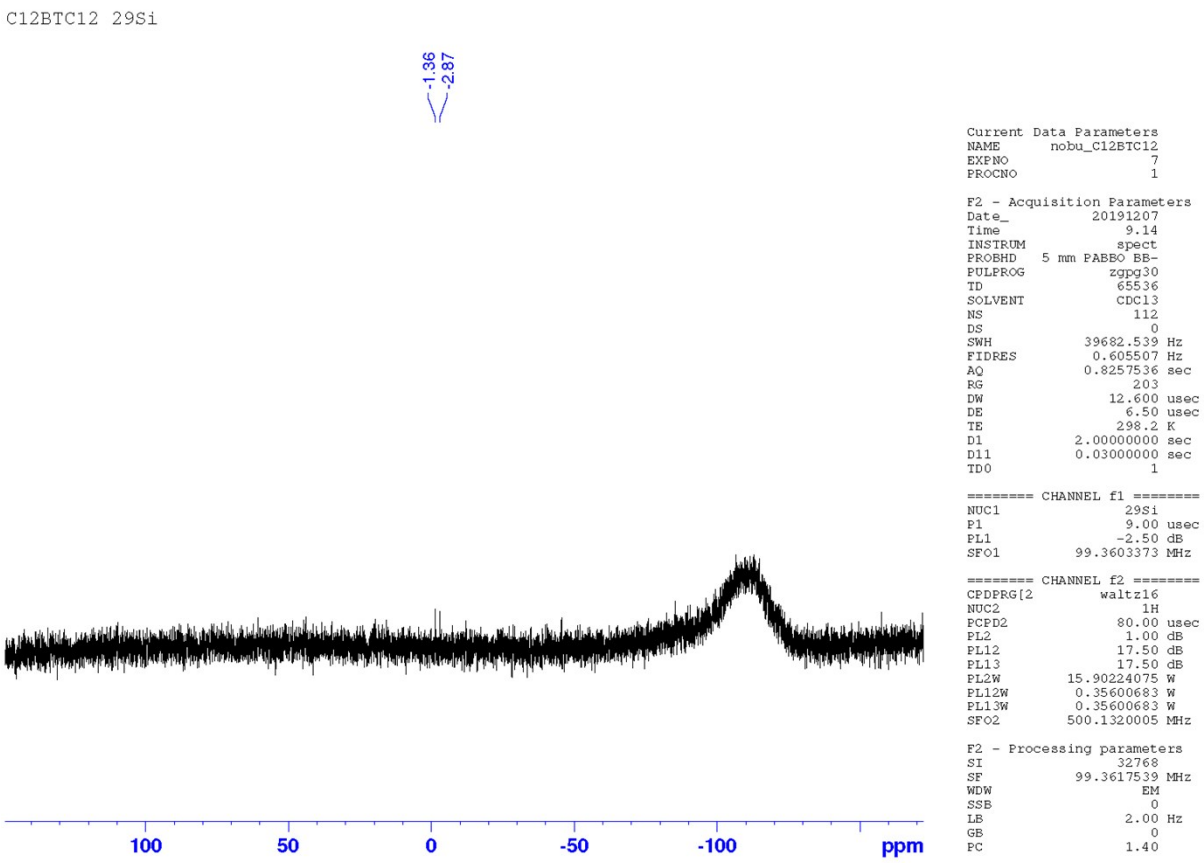


Fig. S7. ^{29}Si NMR spectrum of 2,5-bis(tri(11-dodecenyl)silyl)benzo[b]thiophene (**C12BTC12**) in $CDCl_3$.

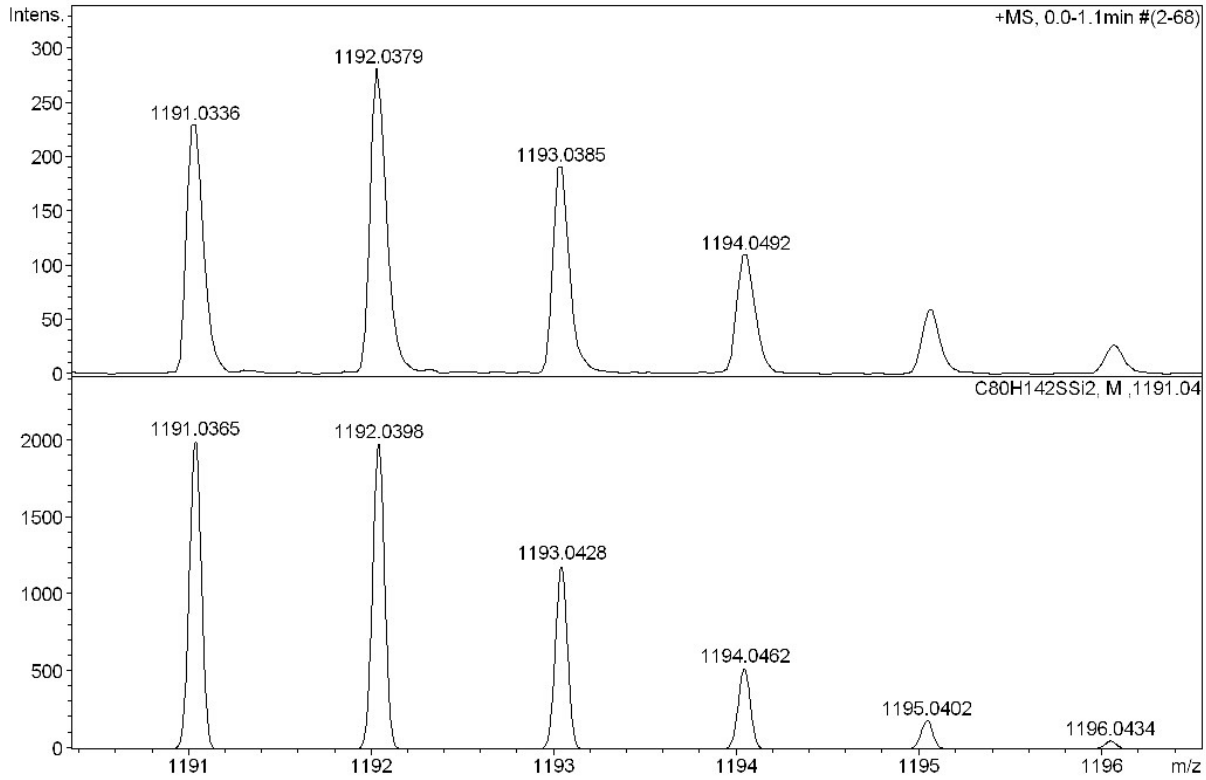


Fig. S8. HRMS spectrum of 2,5-bis(tri(11-dodecenyl)silyl)benzo[b]thiophene (**C12BTC12**) (APCI, positive). Top: obsd. Bottom: sim.

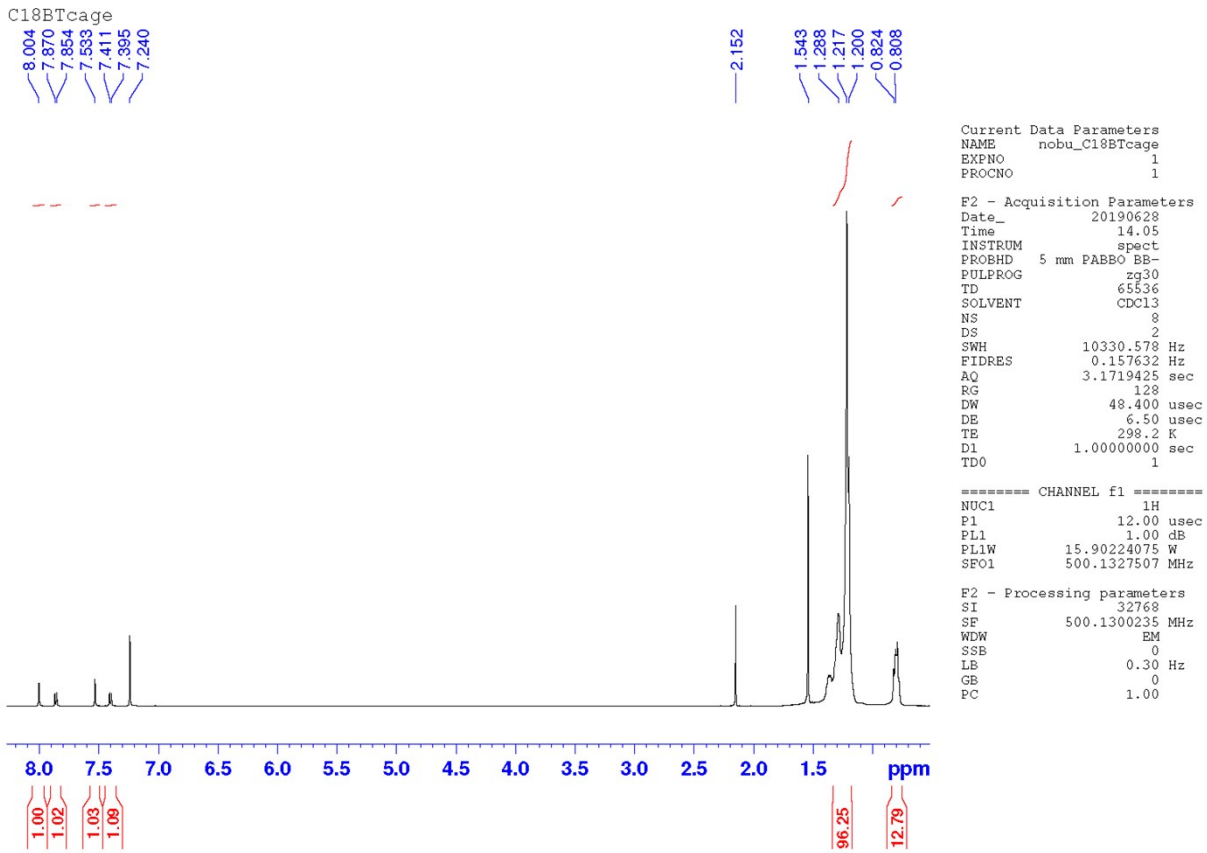


Fig. S9. ^{1}H NMR spectrum of Molecular Gyrotop (**C18BT**) in $CDCl_3$.

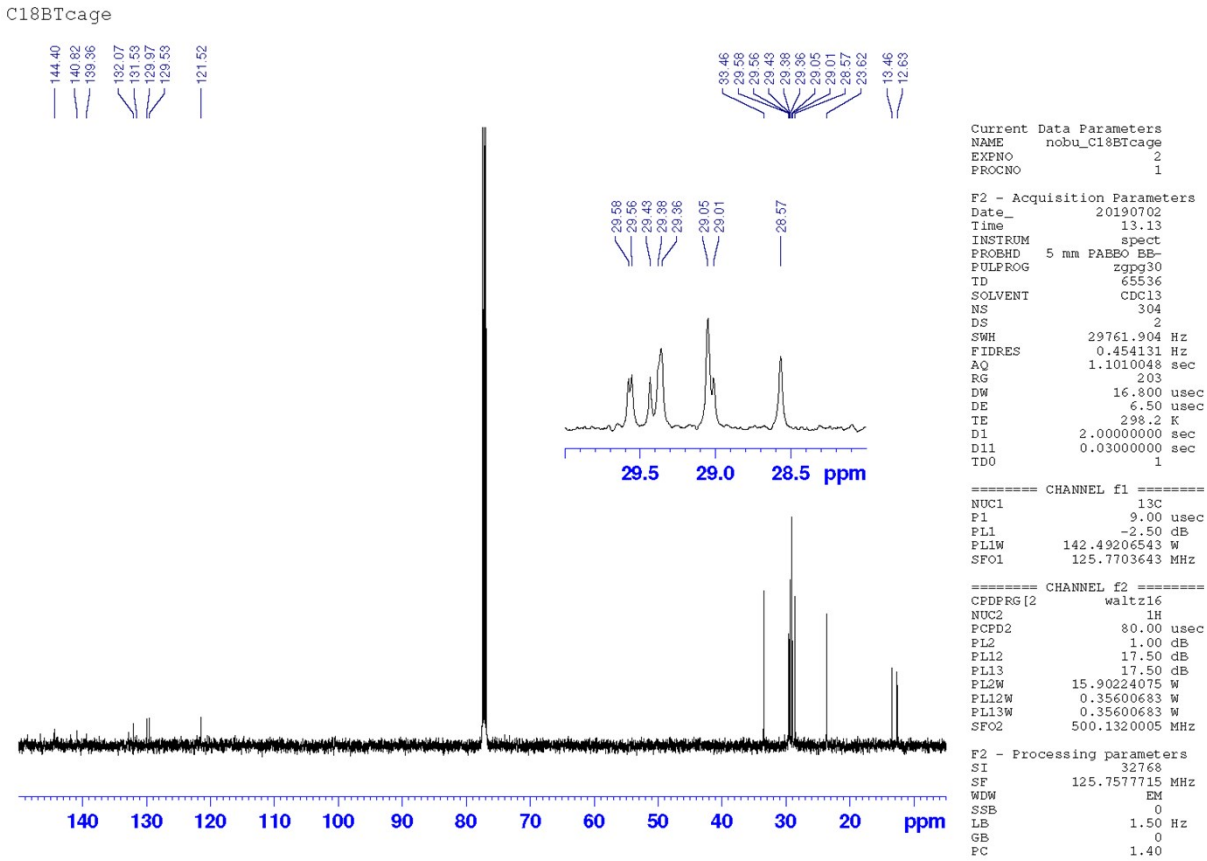


Fig. S10. ^{13}C NMR spectrum of Molecular Gyrotop (**C18BT**) in $CDCl_3$.

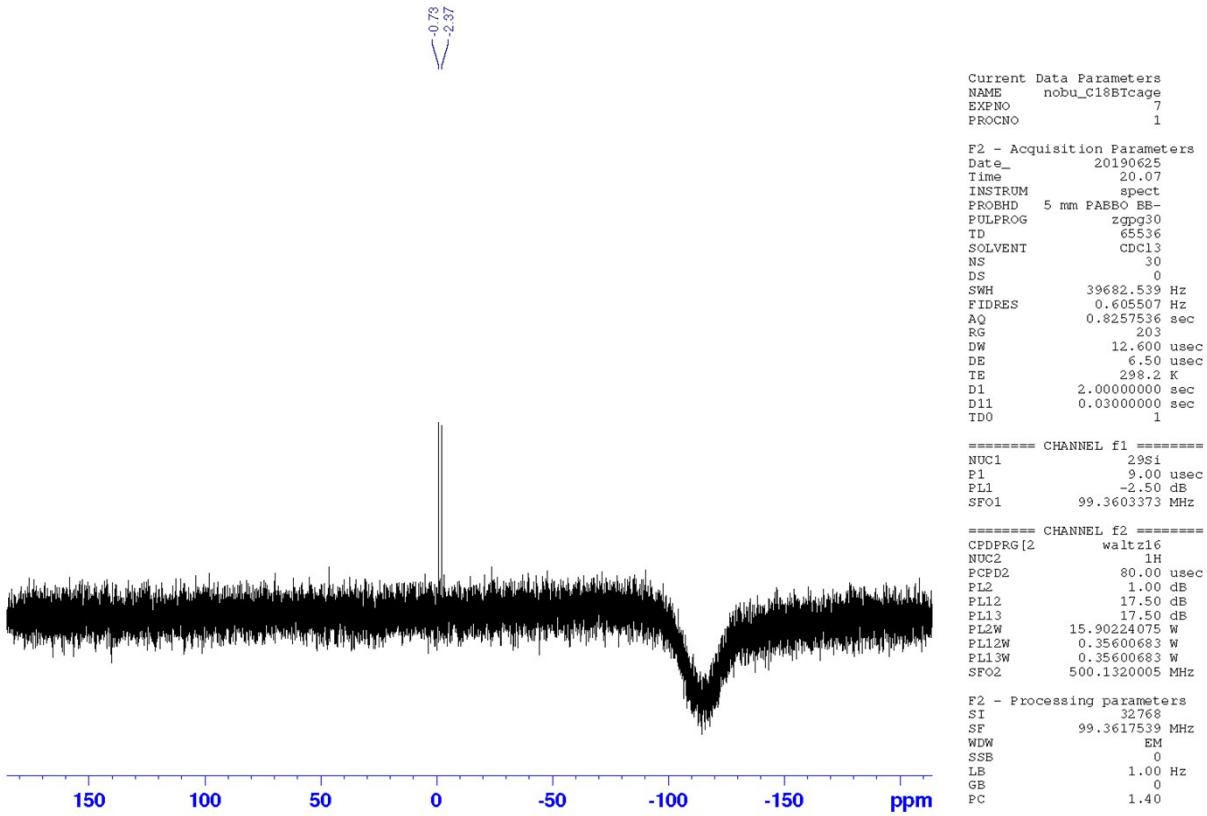


Fig. S11. ^{29}Si NMR spectrum of Molecular Gyrotop (**C18BT**) in $CDCl_3$.

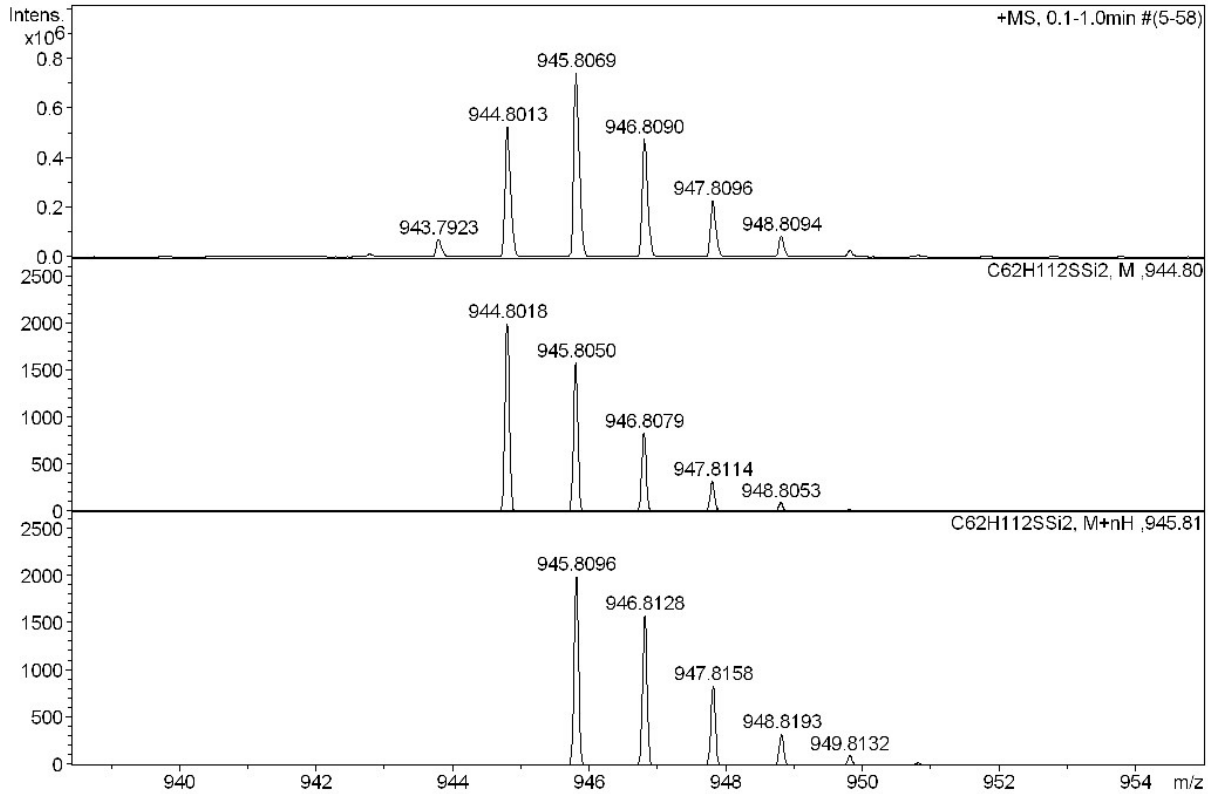


Fig. S12. HRMS spectrum of Molecular Gyrotop (**C18BT**) (APCI, positive). Top: obsd. Bottom: sim.

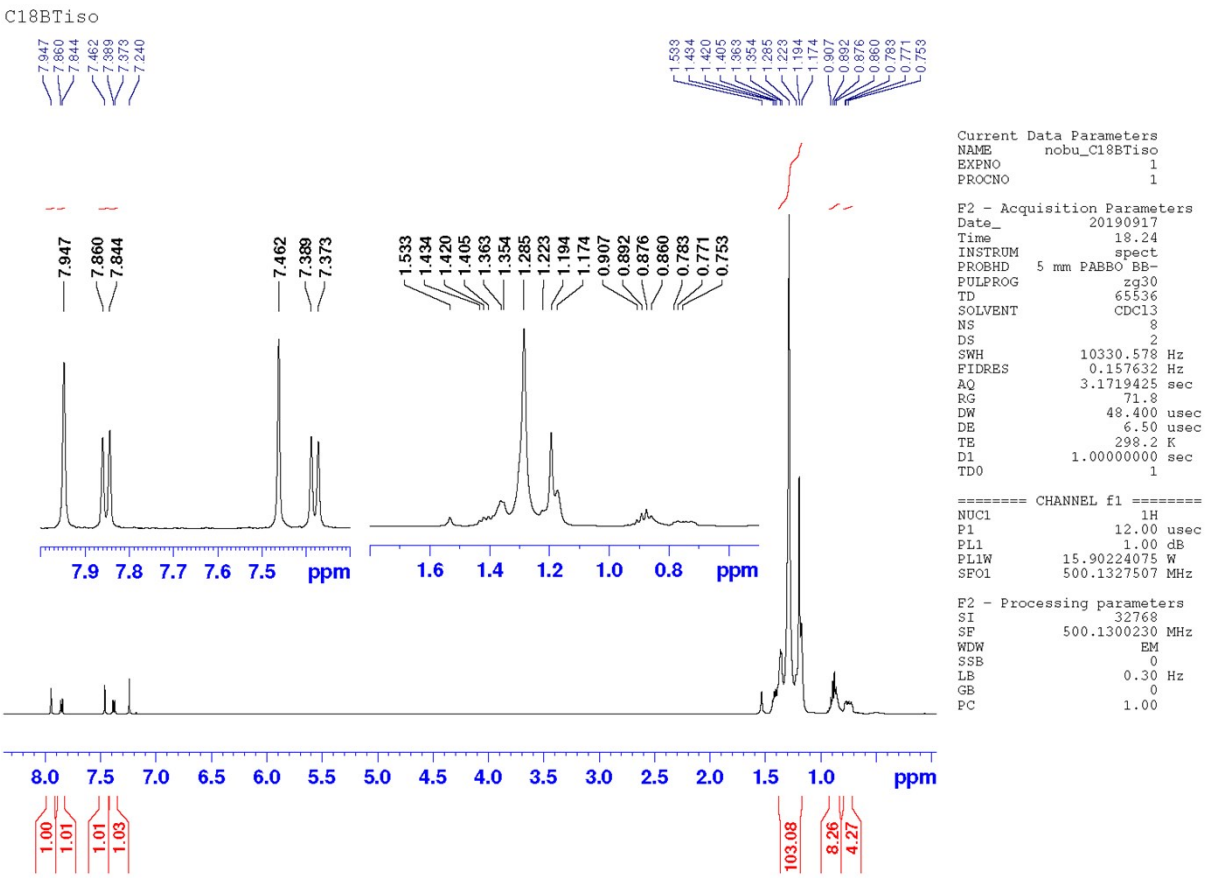


Fig. S13. ^{1}H NMR spectrum of Molecular Gyrotop Isomer (**C18iBT**) in $CDCl_3$.

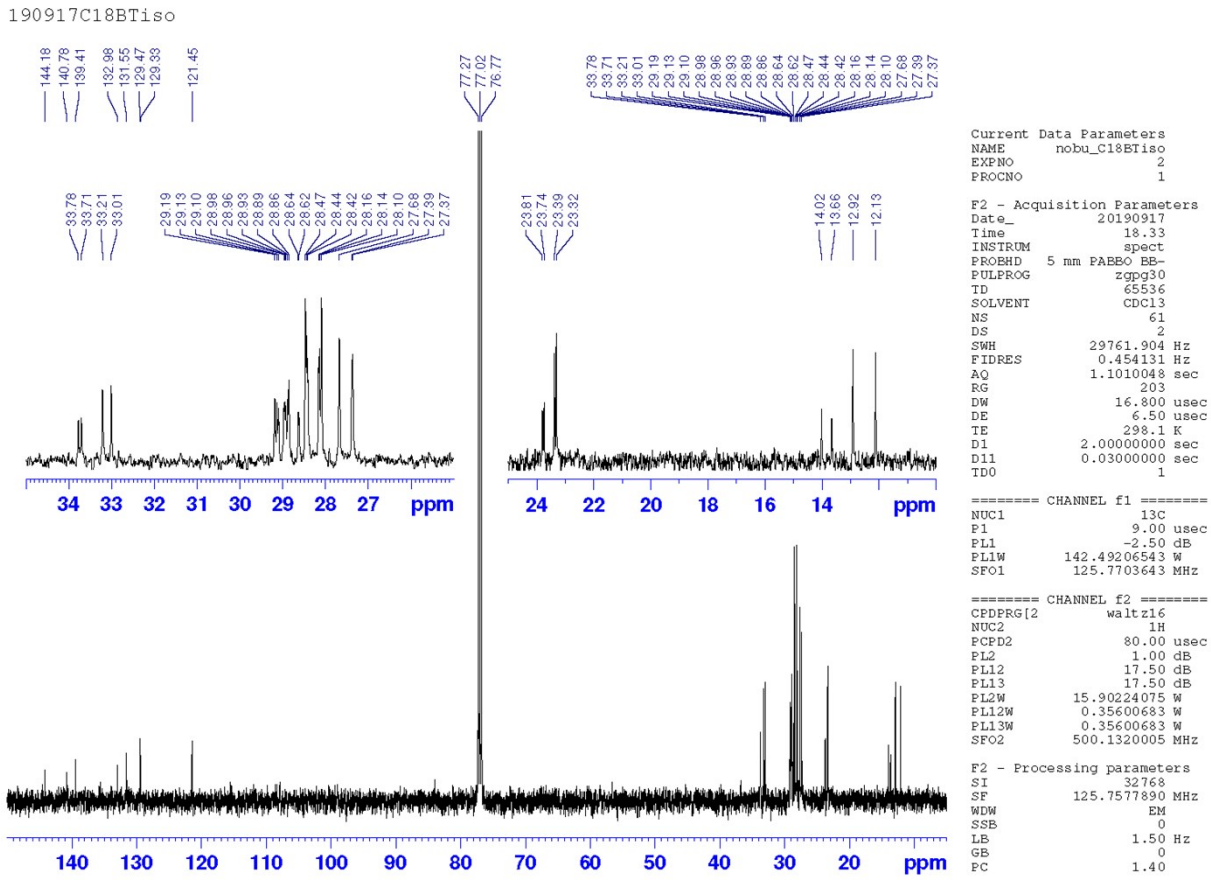


Fig. S14. ^{13}C NMR spectrum of Molecular Gyrotop Isomer (**C18iBT**) in $CDCl_3$.

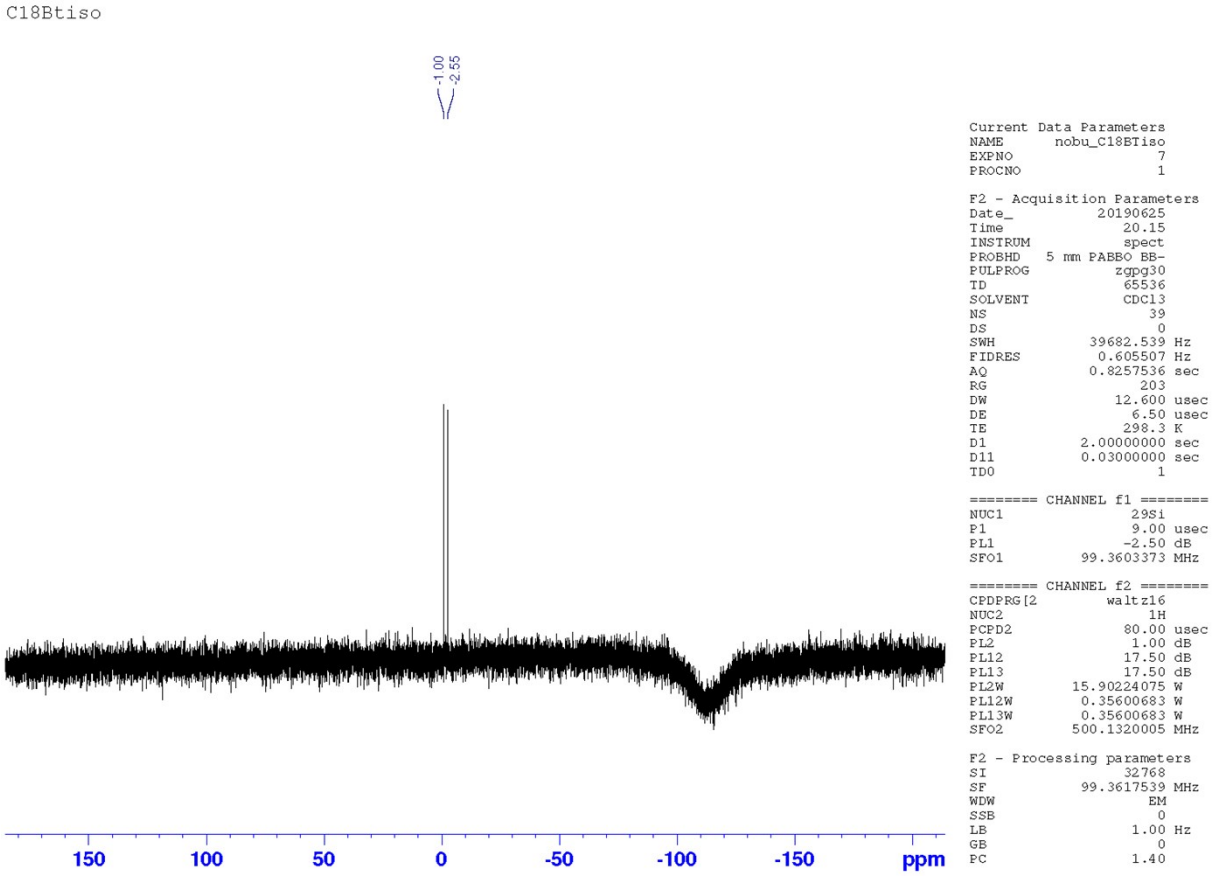


Fig. S15. ^{29}Si NMR spectrum of Molecular Gyrotop Isomer (**C18iBT**) in $CDCl_3$.

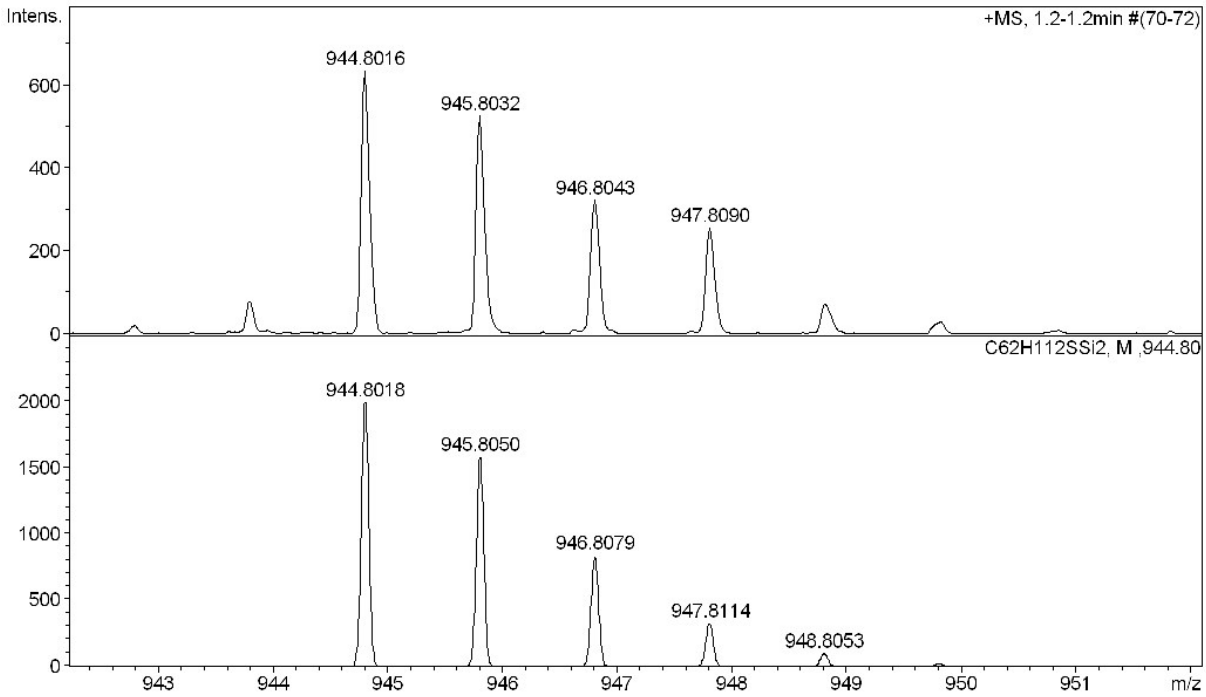


Fig. S16. HRMS spectrum of Molecular Gyrotop Isomer (**C18iBT**) (APCI, positive). Top: obsd. Bottom: sim.

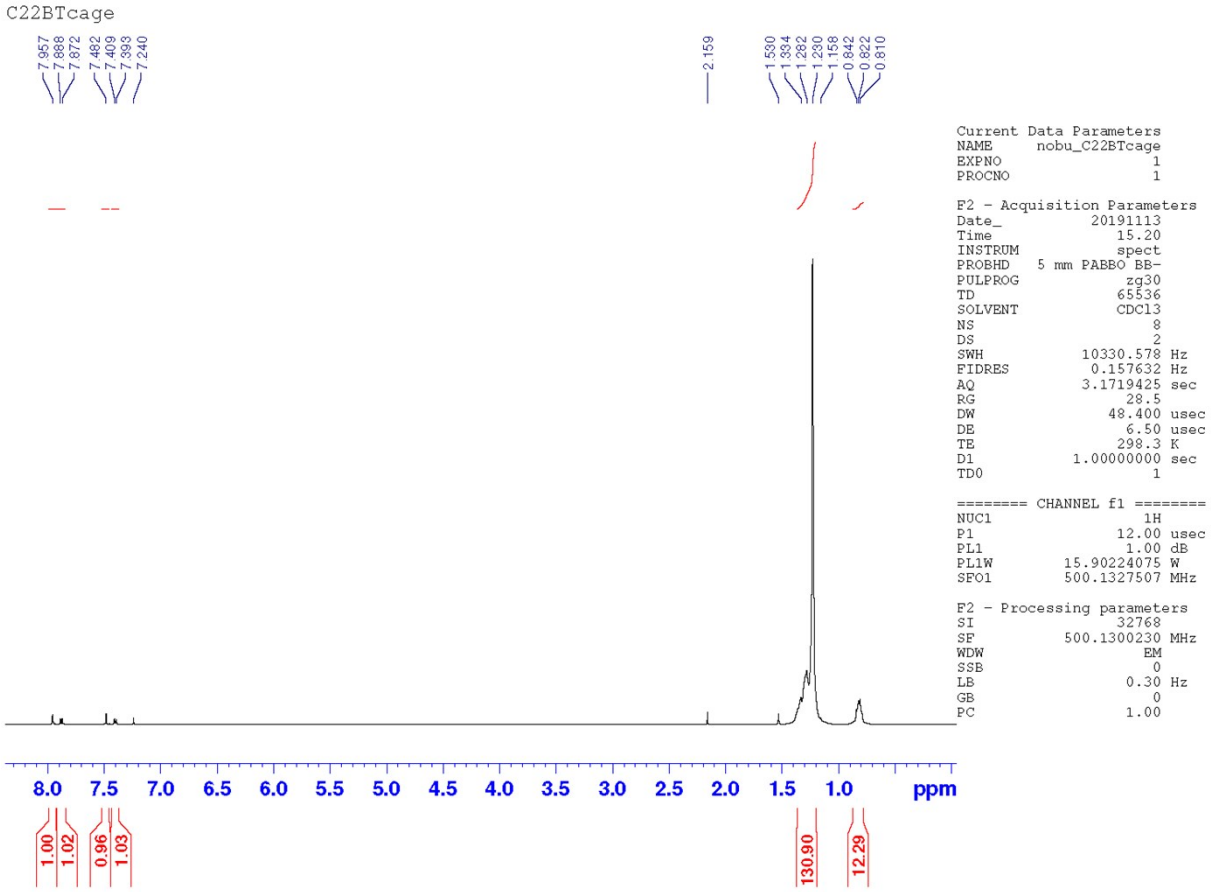


Fig. S17. ^{1}H NMR spectrum of Molecular Gyrotop (**C22BT**) in $CDCl_3$.

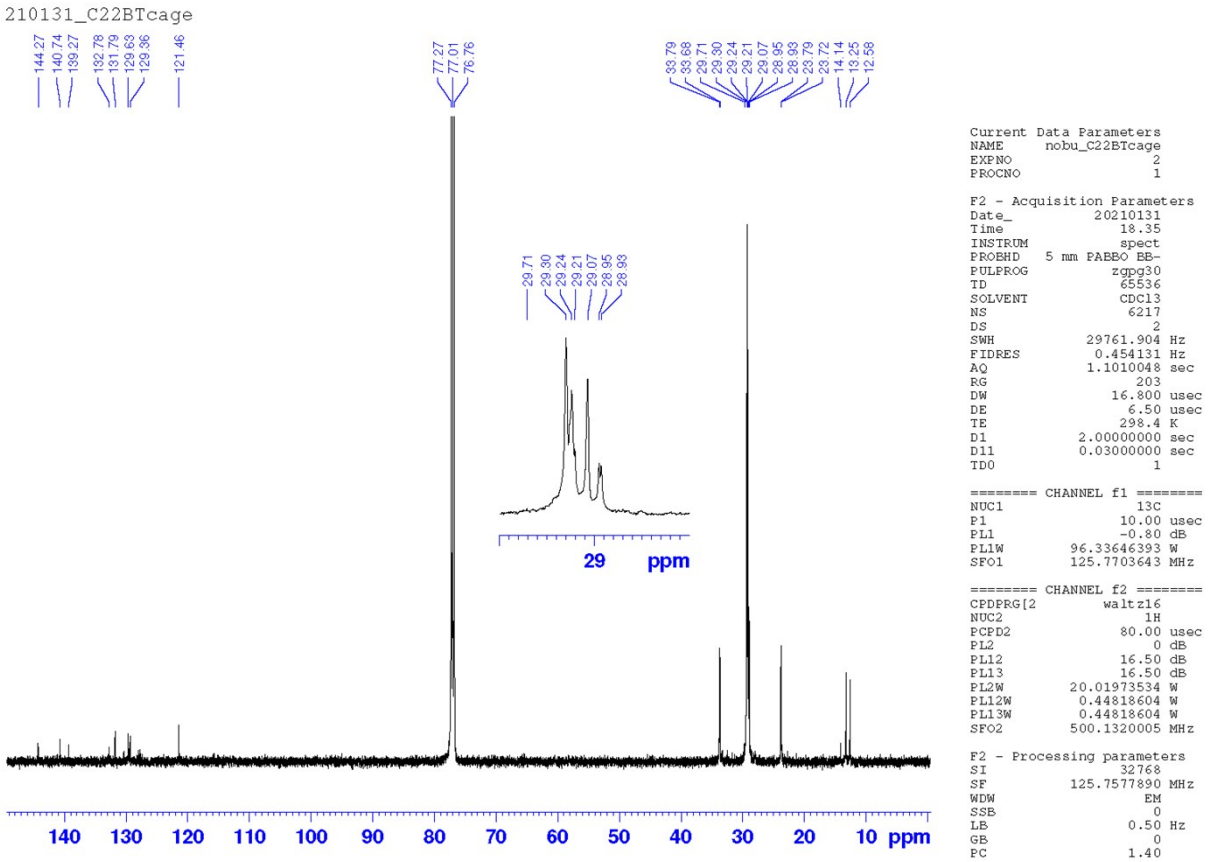


Fig. S18. ^{13}C NMR spectrum of Molecular Gyrotop (**C22BT**) in $CDCl_3$.

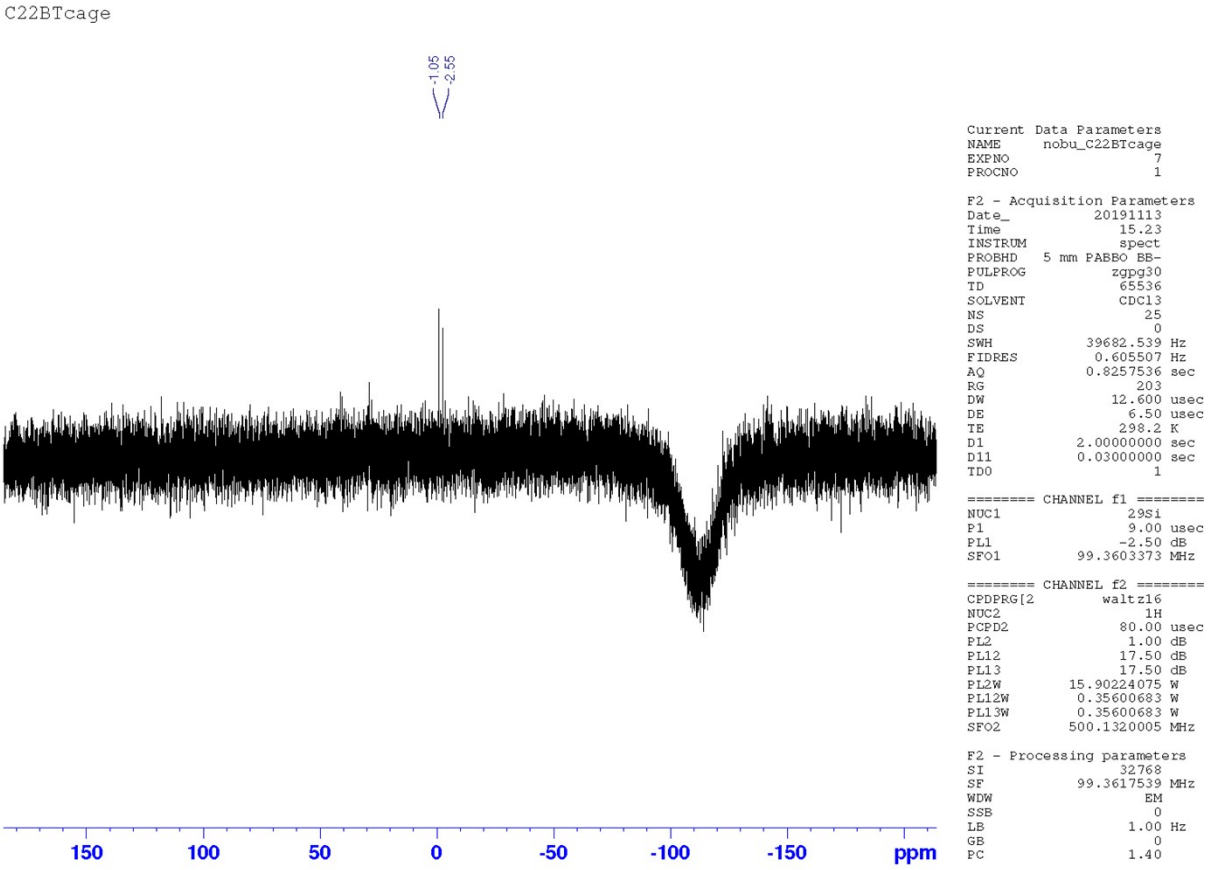


Fig. S19. ^{29}Si NMR spectrum of Molecular Gyrotop (**C22BT**) in $CDCl_3$.

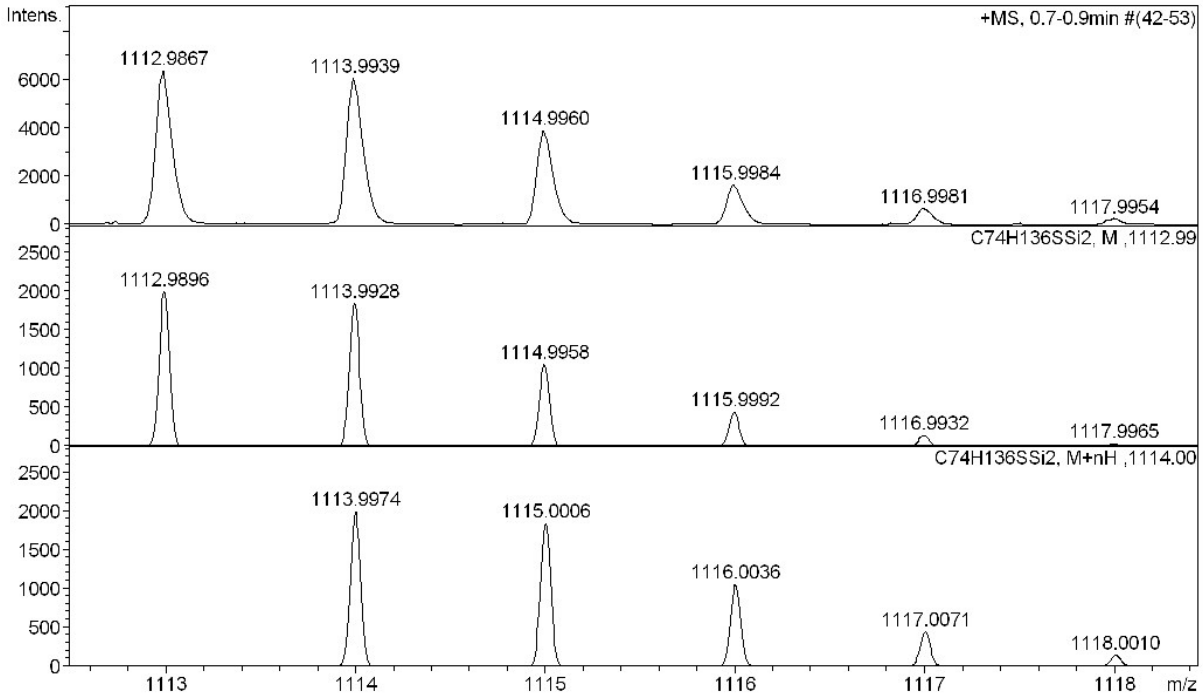


Fig. S20. HRMS spectrum of Molecular Gyrotop (**C22BT**) (APCI, positive). Top: obsd. Bottom: sim.

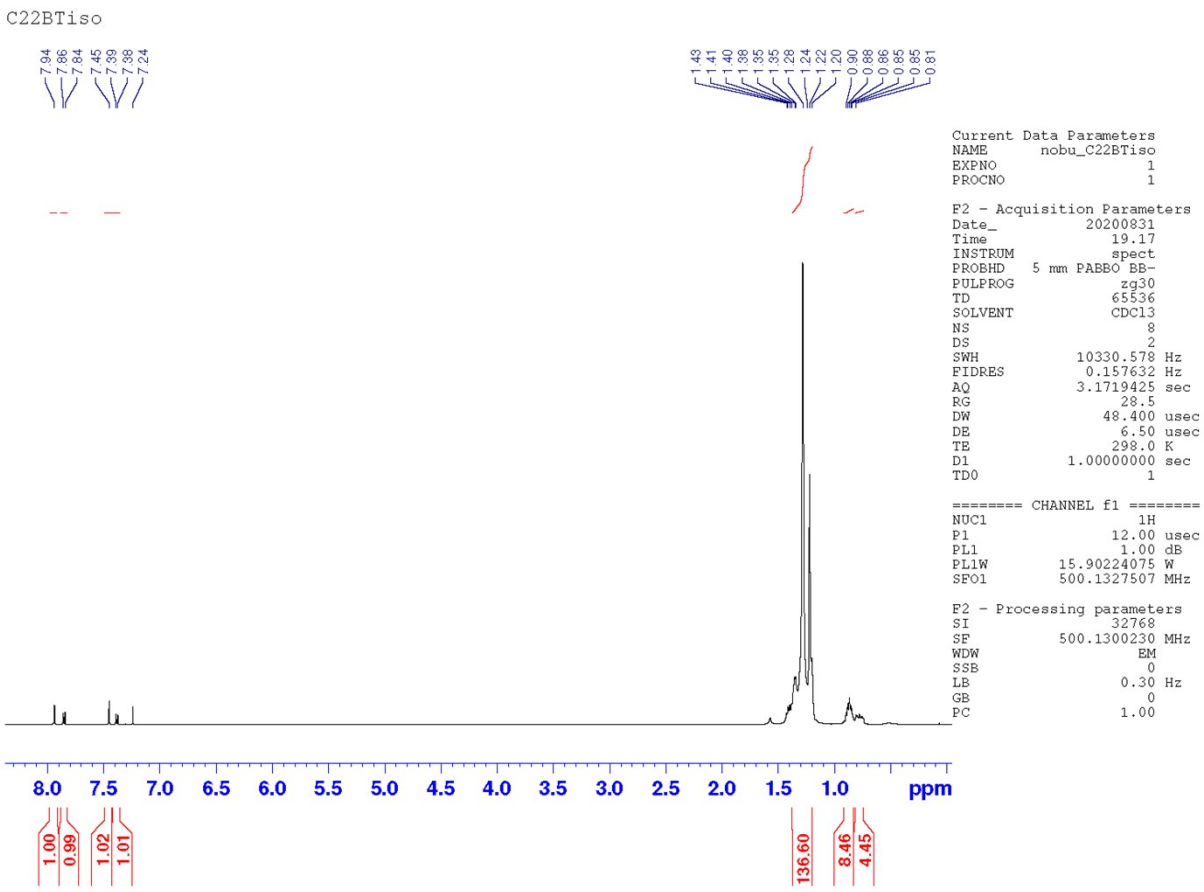


Fig. S21. ^{1}H NMR spectrum of Molecular Gyrotop Isomer (**C22iBT**) in $CDCl_3$.

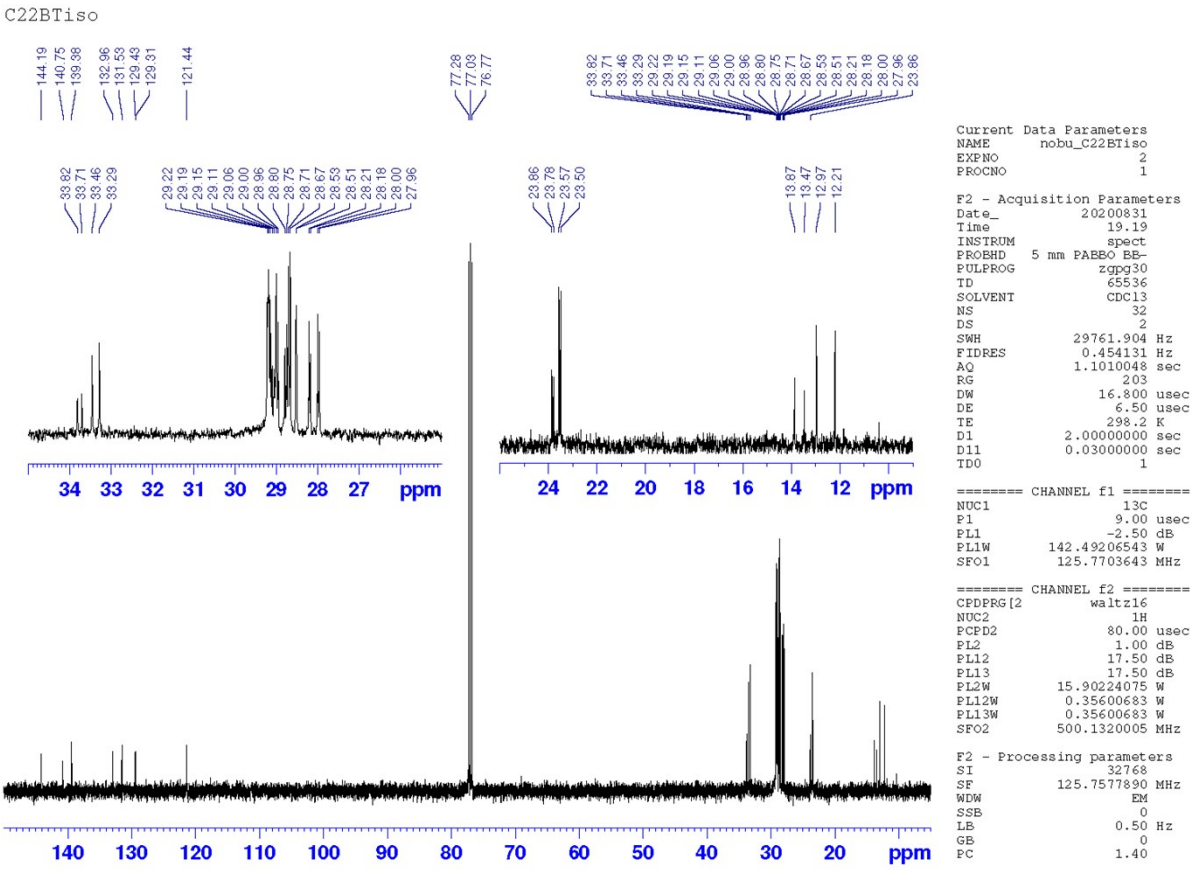


Fig. S22. ^{13}C NMR spectrum of Molecular Gyrotop Isomer (**C22iBT**) in $CDCl_3$.

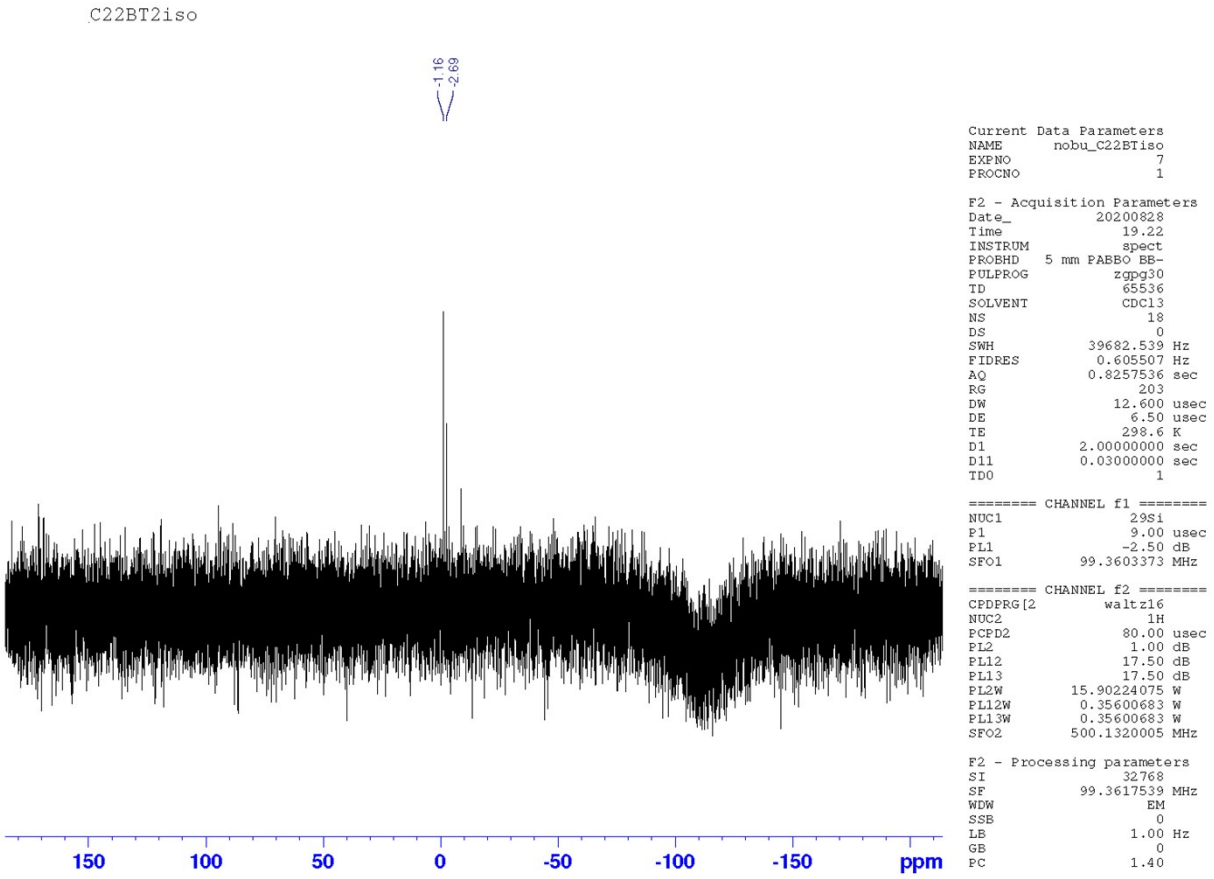


Fig. S23. ^{29}Si NMR spectrum of Molecular Gyrotop Isomer (**C22iBT**) in $CDCl_3$.

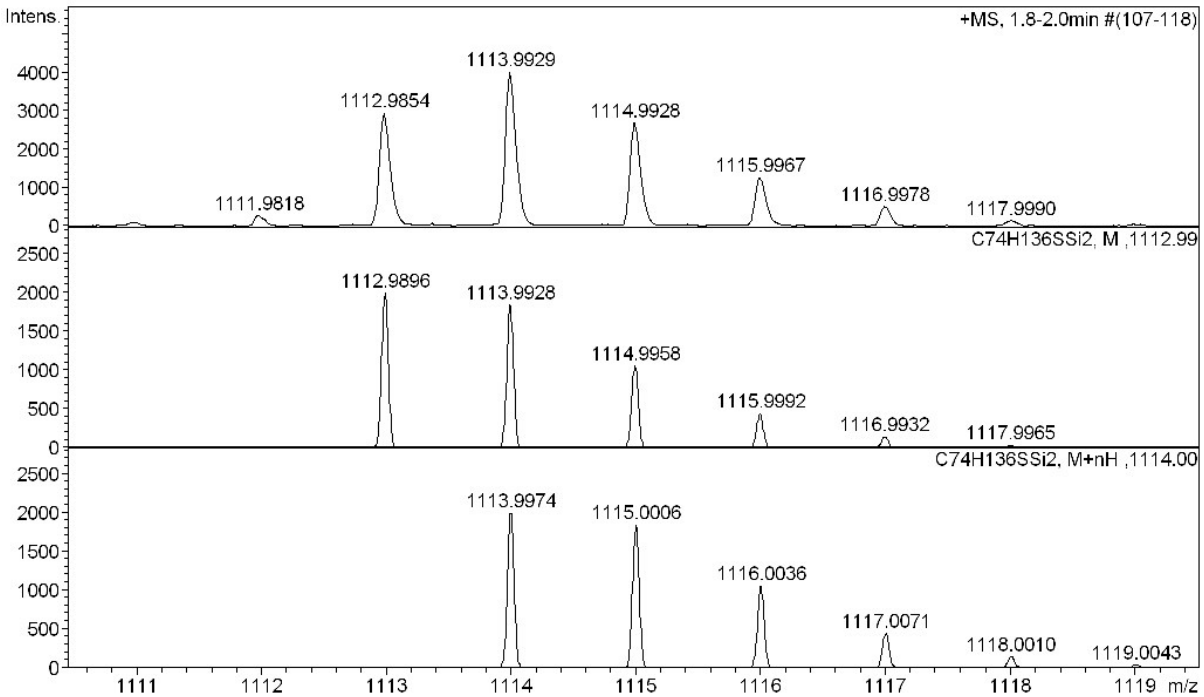


Fig. S24. HRMS spectrum of Molecular Gyrotop Isomer (**C22iBT**) (APCI, positive). Top: obsd. Bottom: sim.

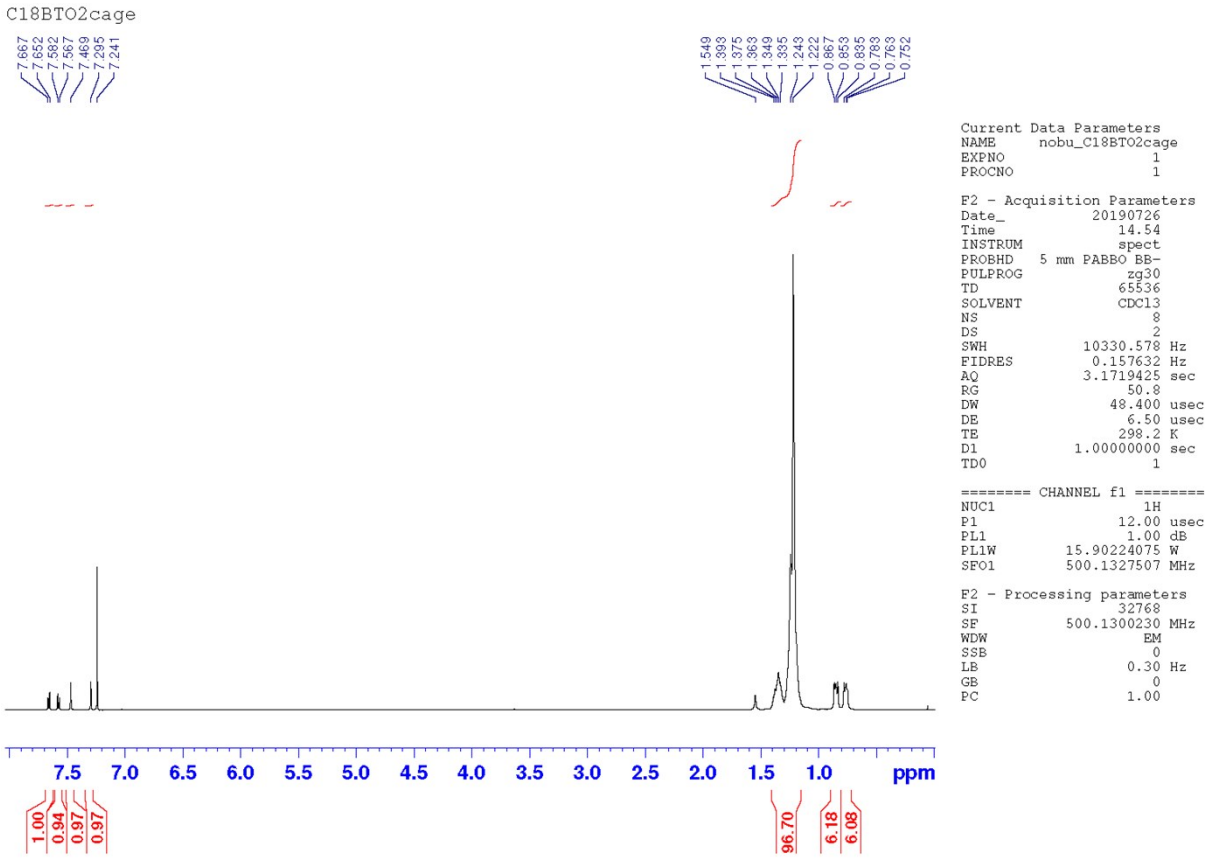


Fig. S25. ^{1}H NMR spectrum of Molecular Gyrotop (**C18BTO2**) in $CDCl_3$.

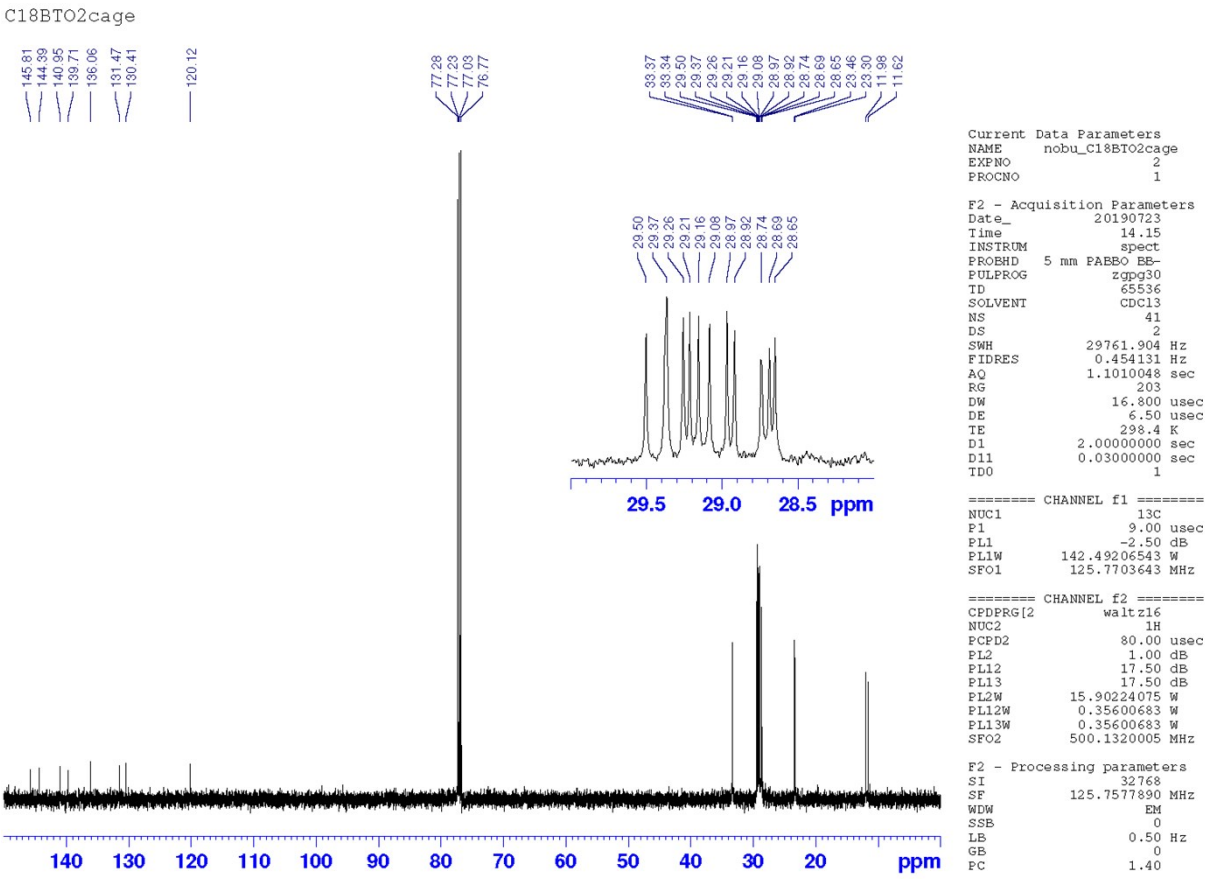


Fig. S26. ^{13}C NMR spectrum of Molecular Gyrotop (**C18BTO2**) in $CDCl_3$.

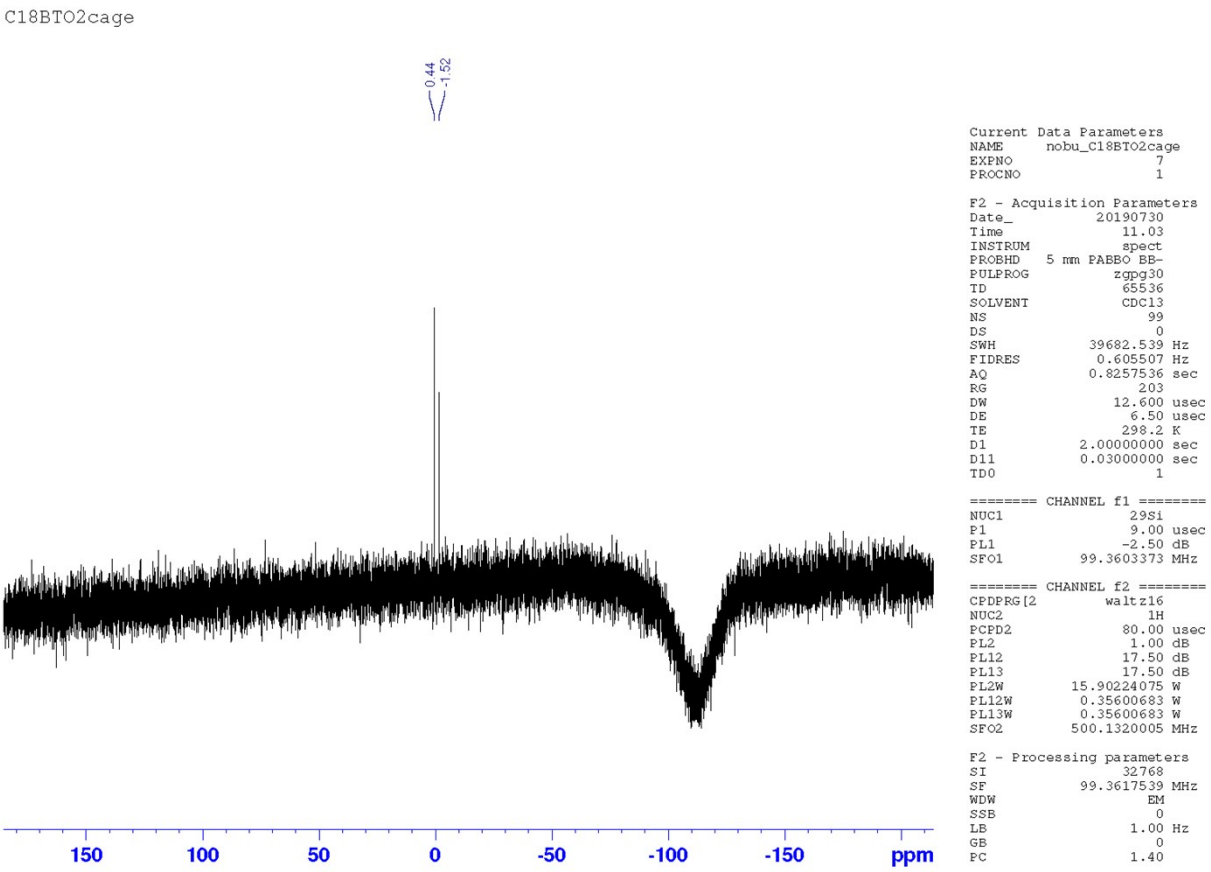


Fig. S27. ^{29}Si NMR spectrum of Molecular Gyrotop (**C18BTO2**) in $CDCl_3$.

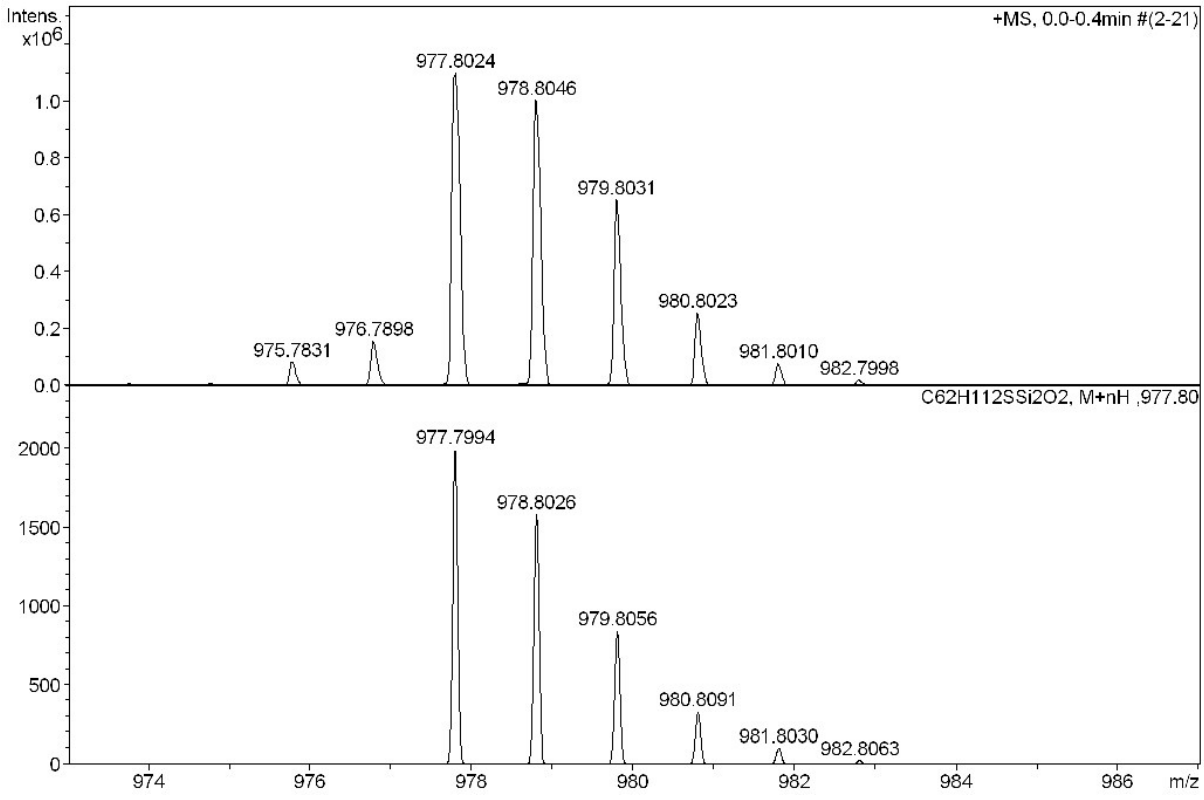


Fig. S28. HRMS spectrum of Molecular Gyrotop (**C18BTO2**) (APCI, positive). Top: obsd. Bottom: sim.

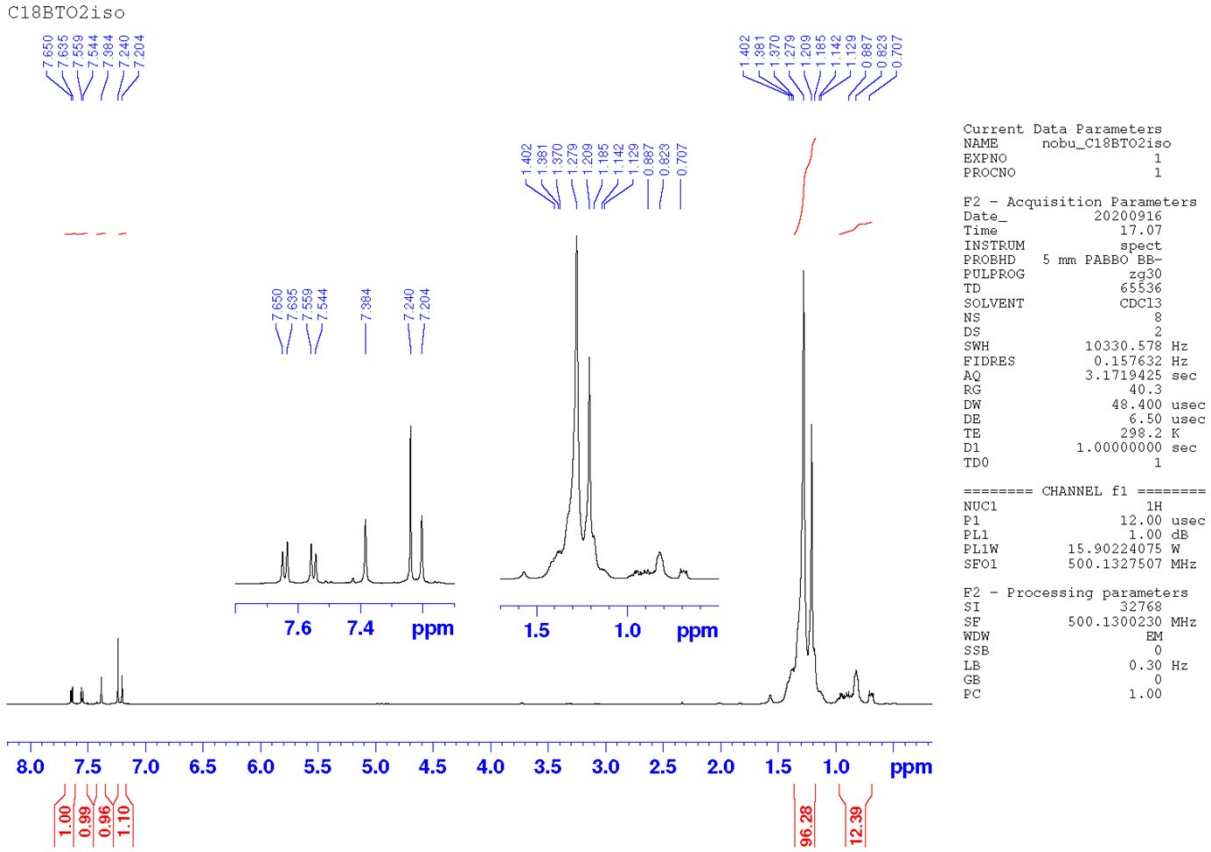


Fig. S29. ^{1}H NMR spectrum of Molecular Gyrotop Isomer (**C18iBTO2**) in $CDCl_3$.

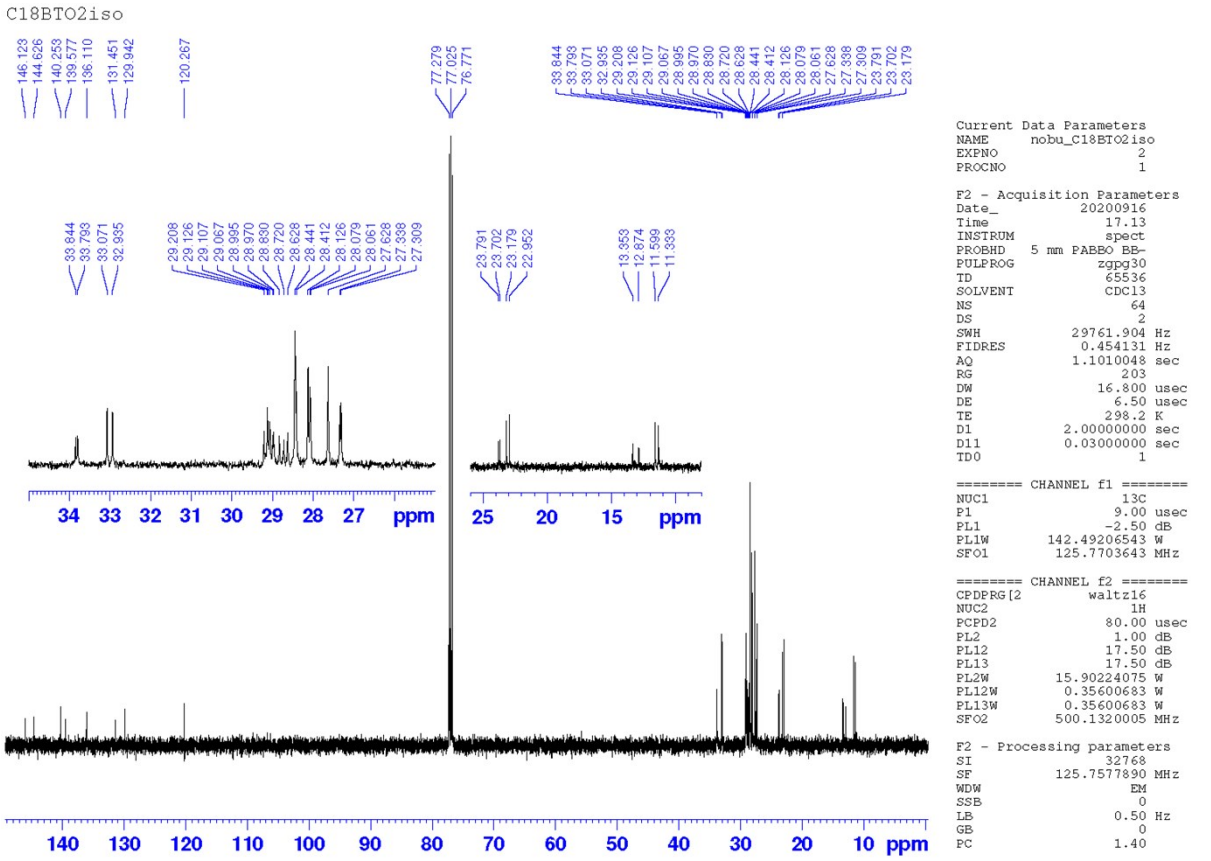


Fig. S30. ^{13}C NMR spectrum of Molecular Gyrotop Isomer (**C18iBTO2**) in $CDCl_3$.

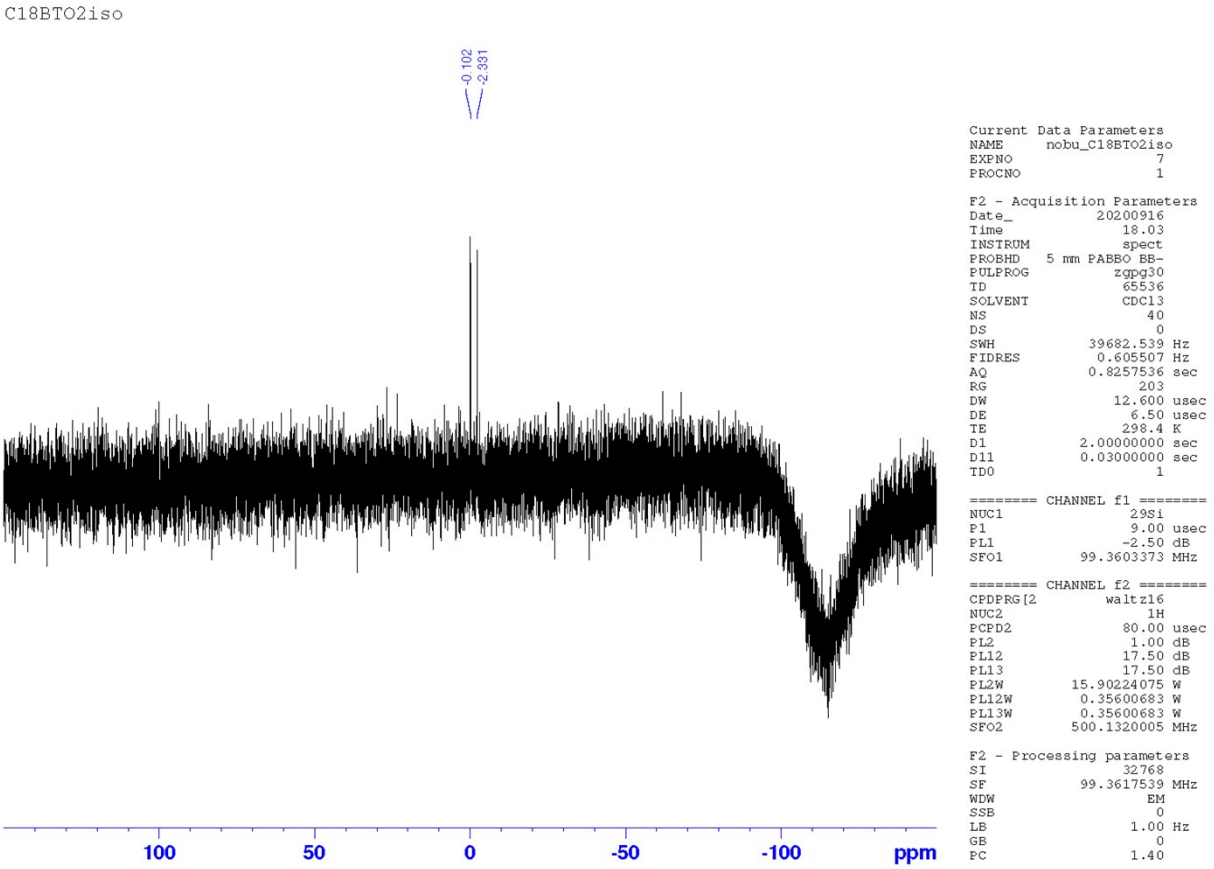


Fig. S31. ^{29}Si NMR spectrum of Molecular Gyrotop Isomer (**C18iBTO2**) in $CDCl_3$.

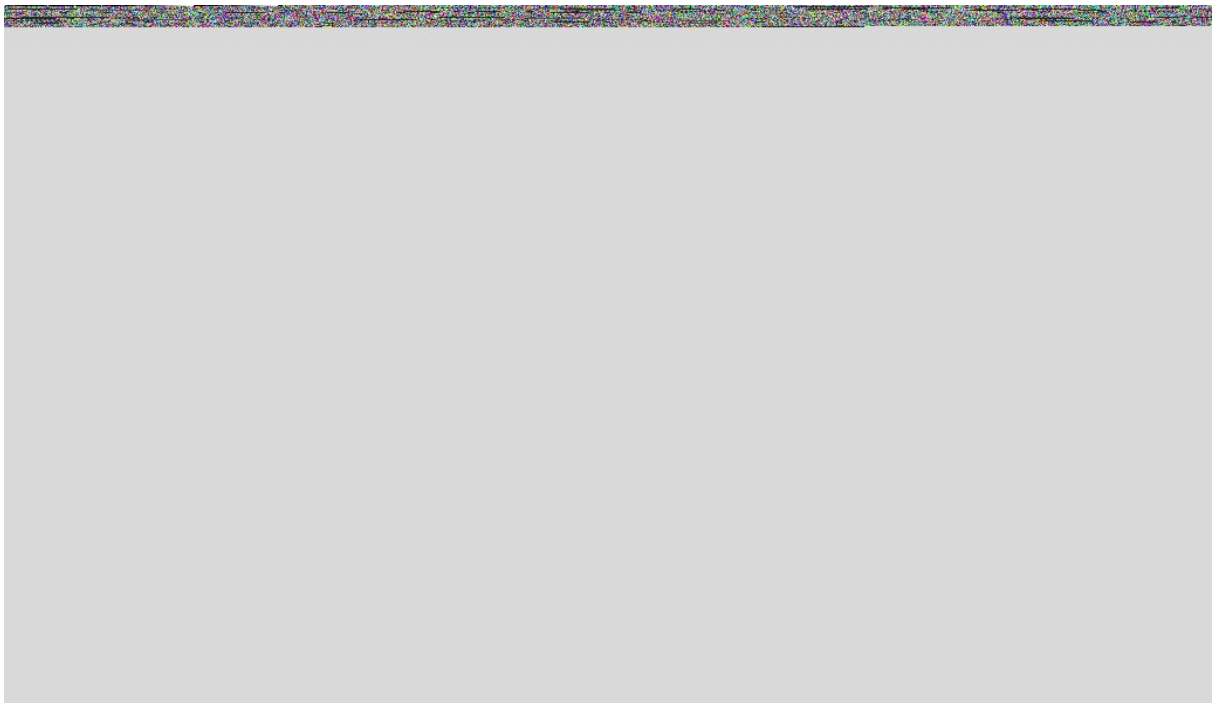


Fig. S32. HRMS spectrum of Molecular Gyrotop Isomer (**C18iBTO2**) (APCI, positive). Top: obsd. Bottom: sim.

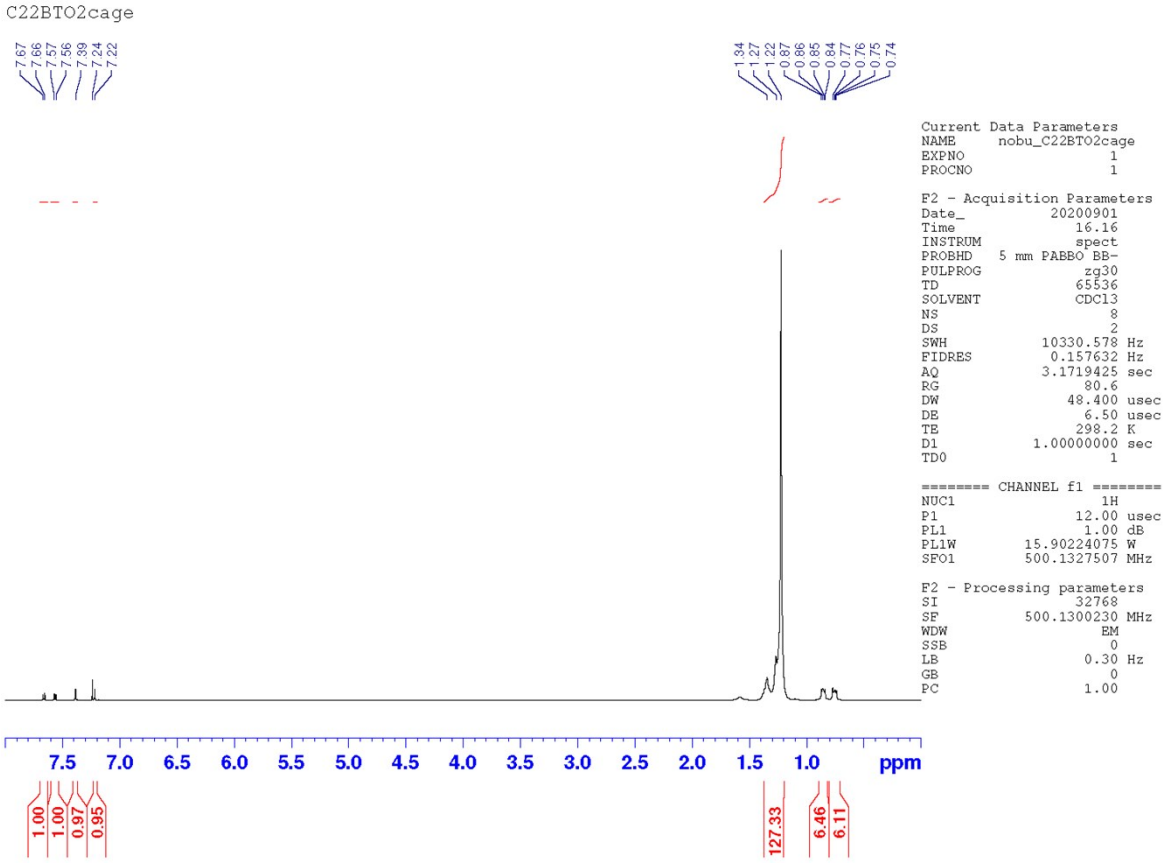


Fig. S33. ^{1}H NMR spectrum of Molecular Gyrotop (**C22BTO2**) in $CDCl_3$.

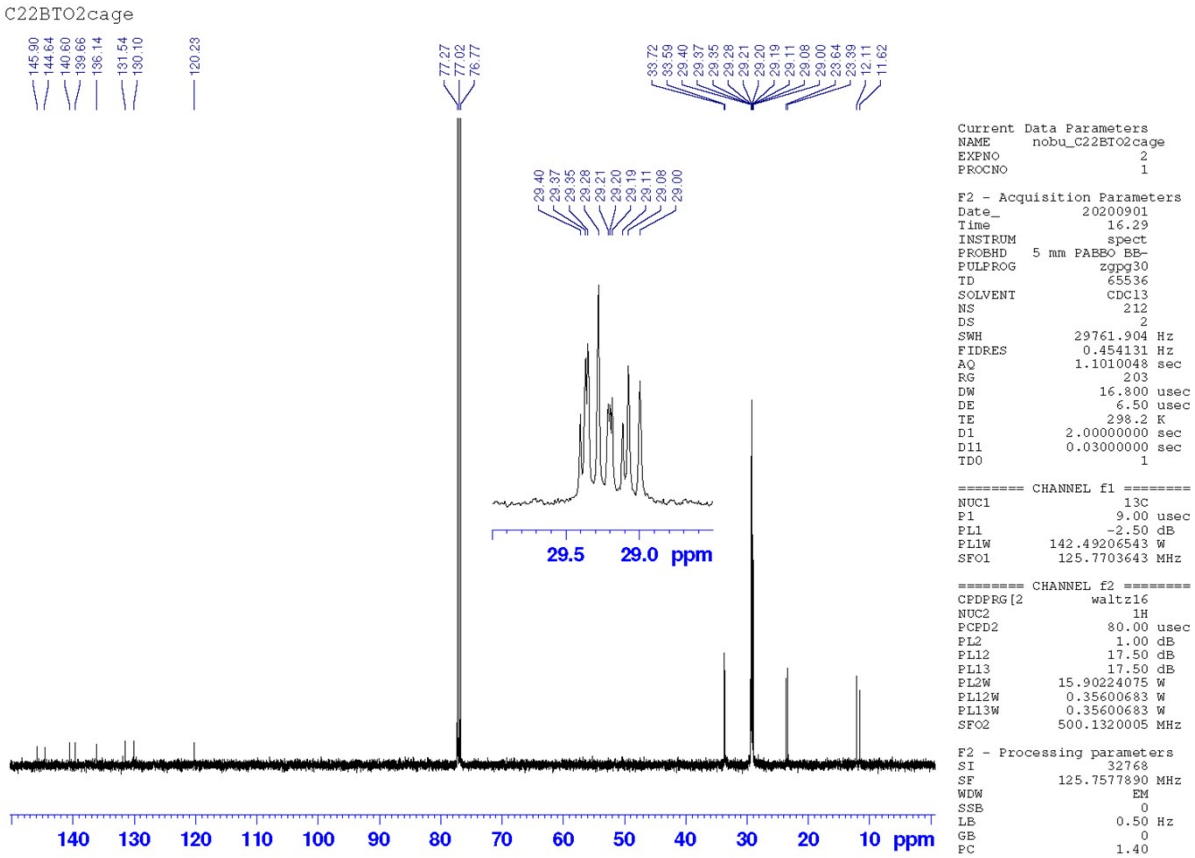


Fig. S34. ^{13}C NMR spectrum of Molecular Gyrotop (**C22BTO2**) in $CDCl_3$.

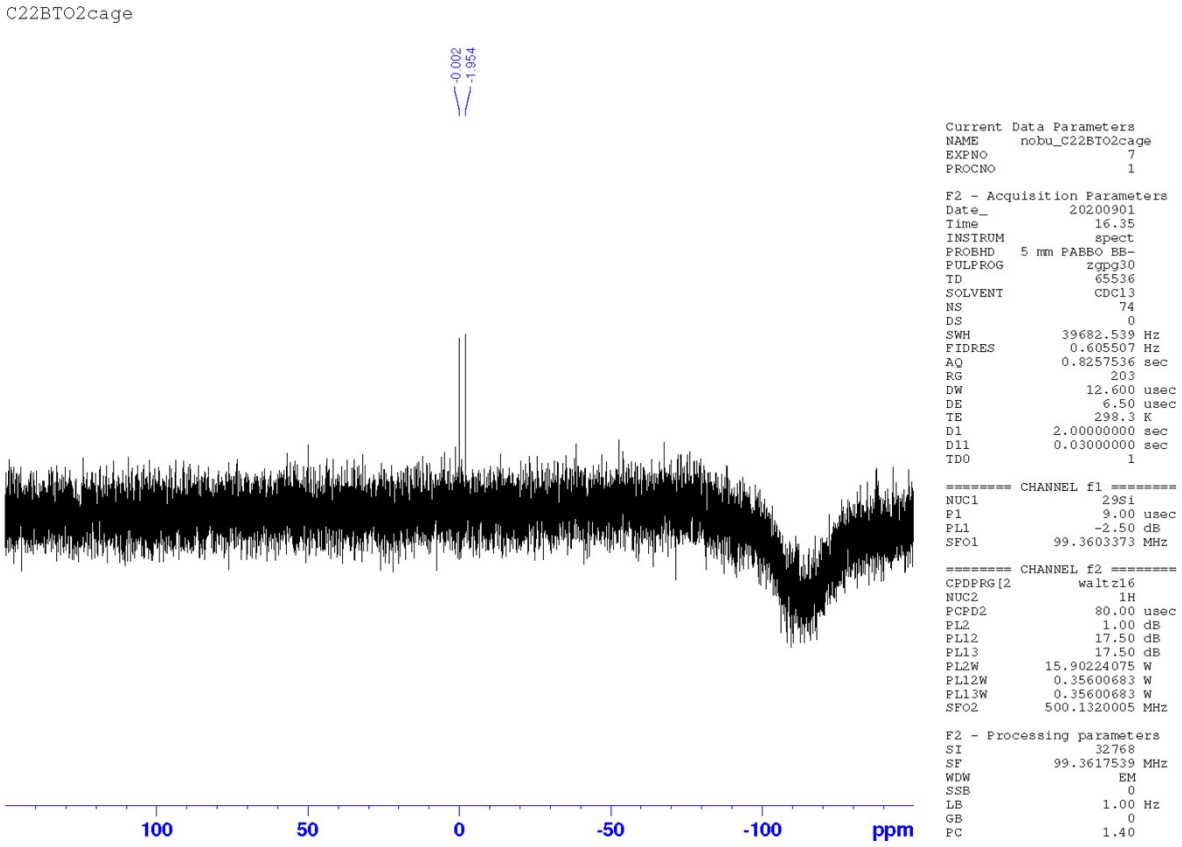


Fig. S35. ^{29}Si NMR spectrum of Molecular Gyrotop (**C22BTO2**) in $CDCl_3$.

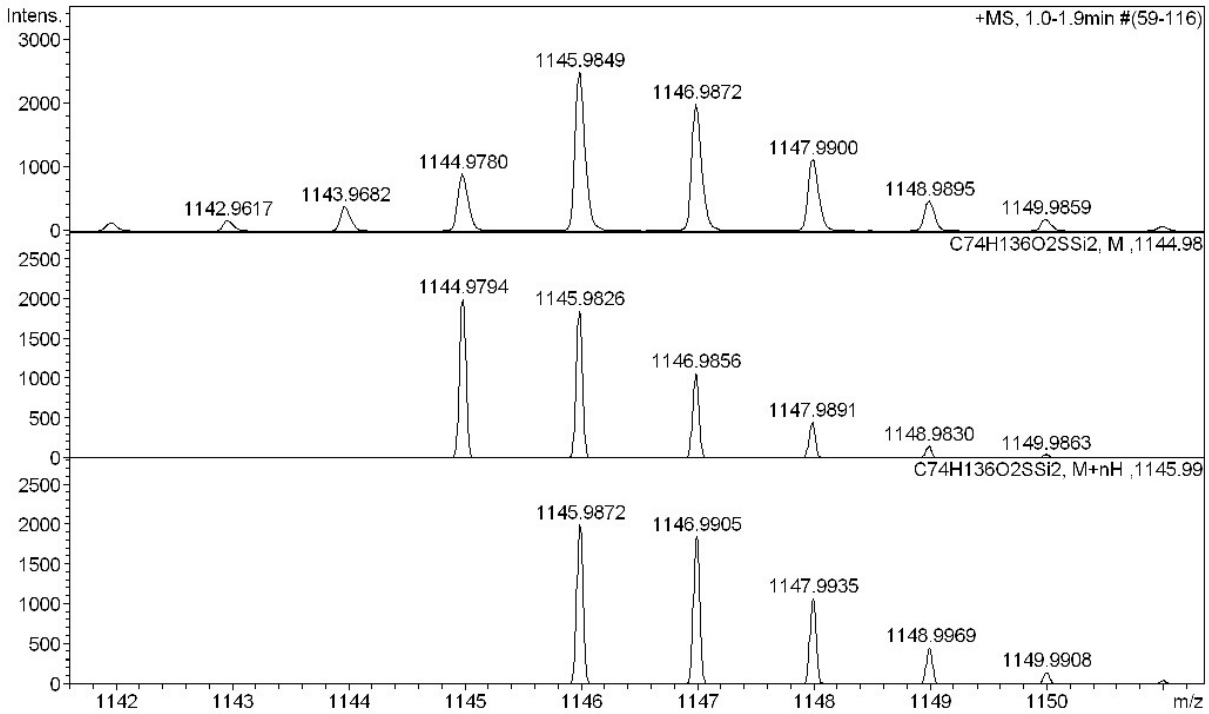


Fig. S36. HRMS spectrum of Molecular Gyrotop (**C22BTO2**) (APCI, positive). Top: obsd. Bottom: sim.

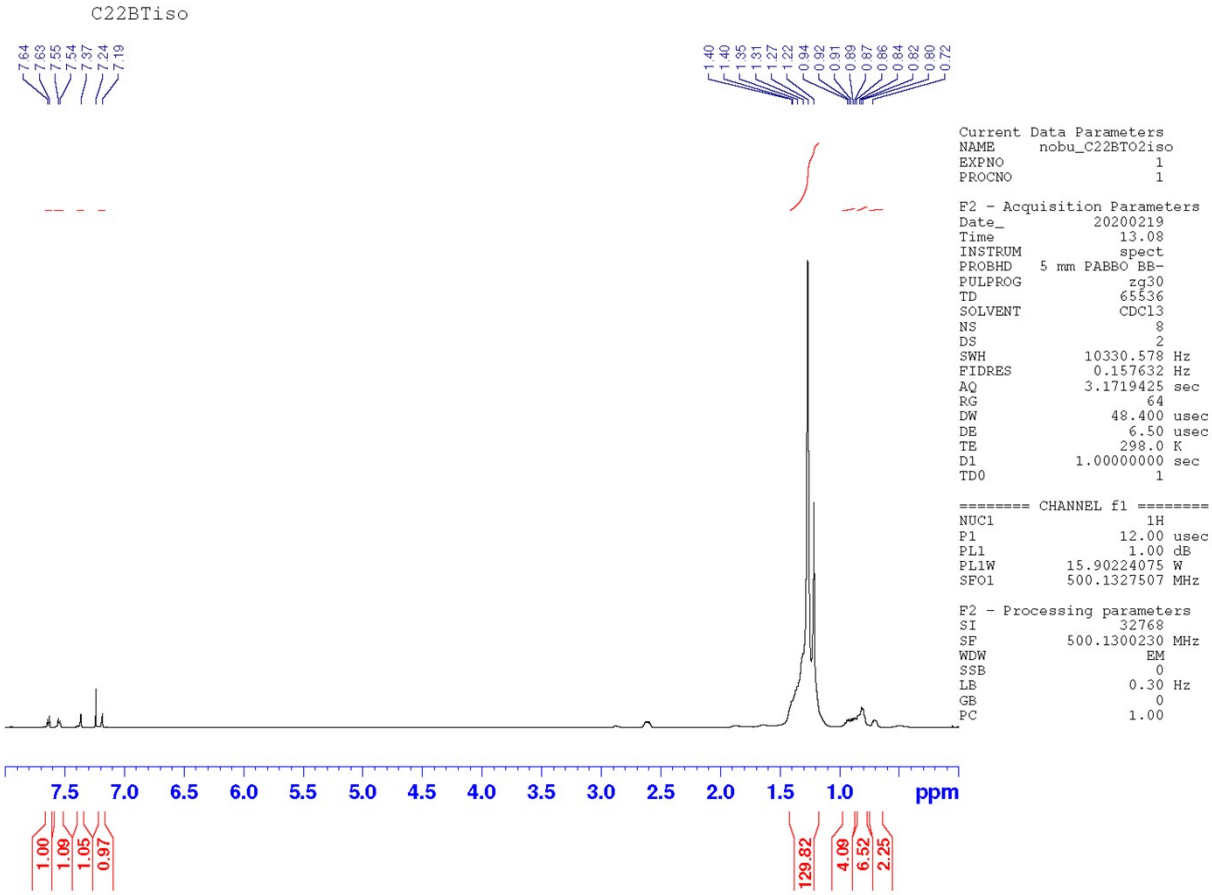


Fig. S37. ^{1}H NMR spectrum of Molecular Gyrotop Isomer (**C22iBTO2**) in $CDCl_3$.

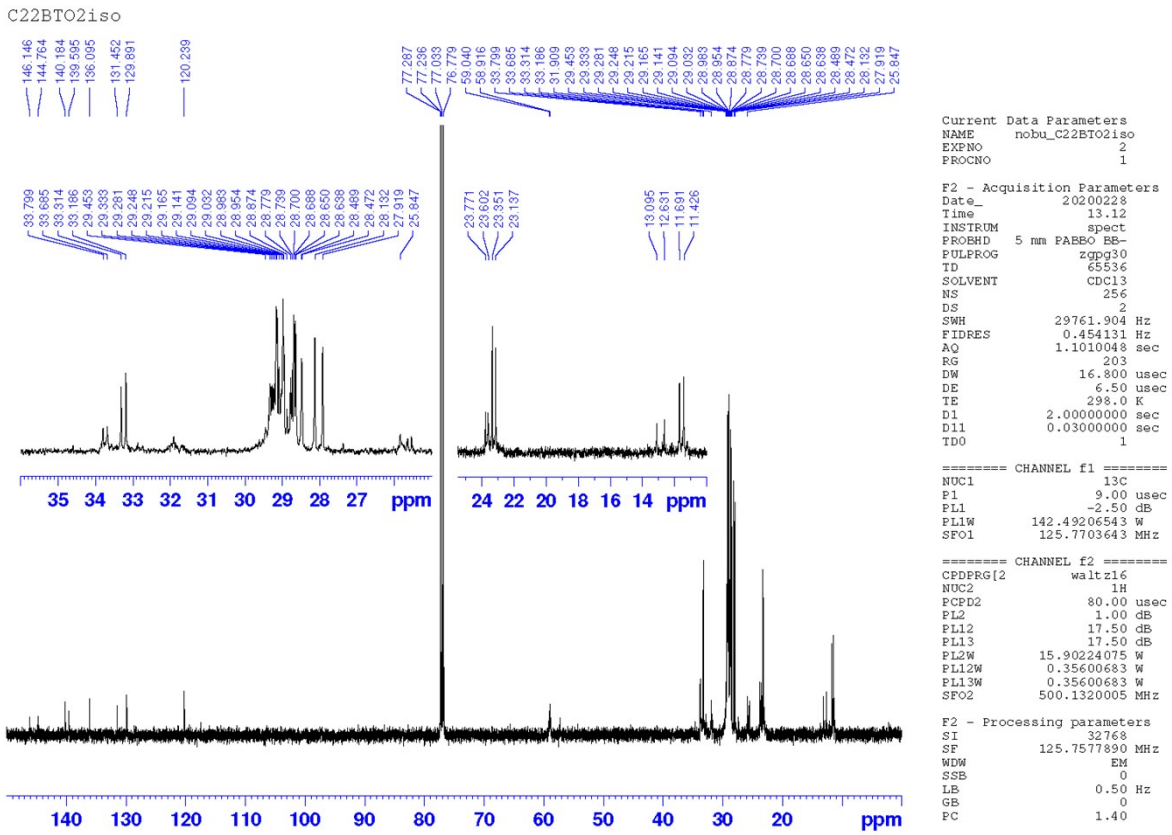


Fig. S38. ^{13}C NMR spectrum of Molecular Gyrotop Isomer (**C22iBTO2**) in $CDCl_3$.

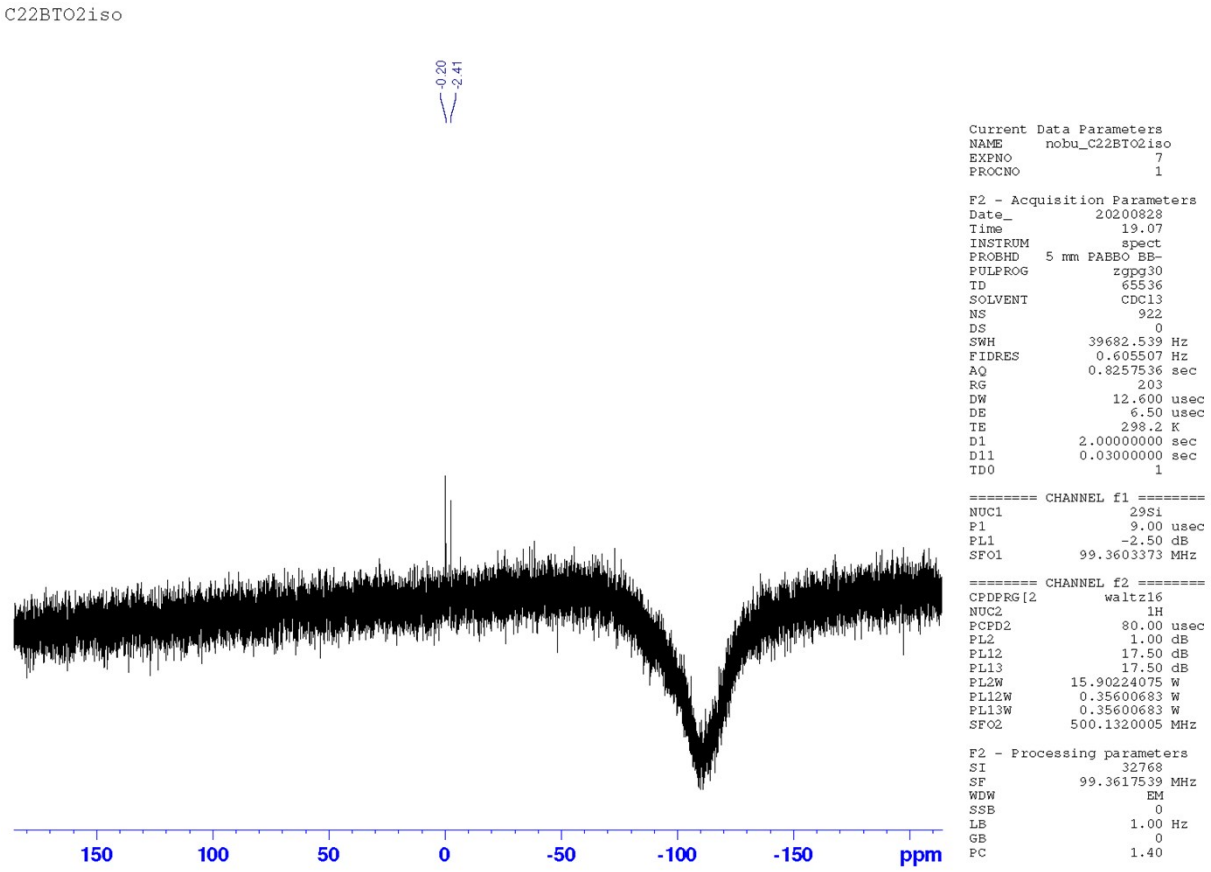


Fig. S39. ^{29}Si NMR spectrum of Molecular Gyrotop Isomer (**C22iBTO2**) in $CDCl_3$.

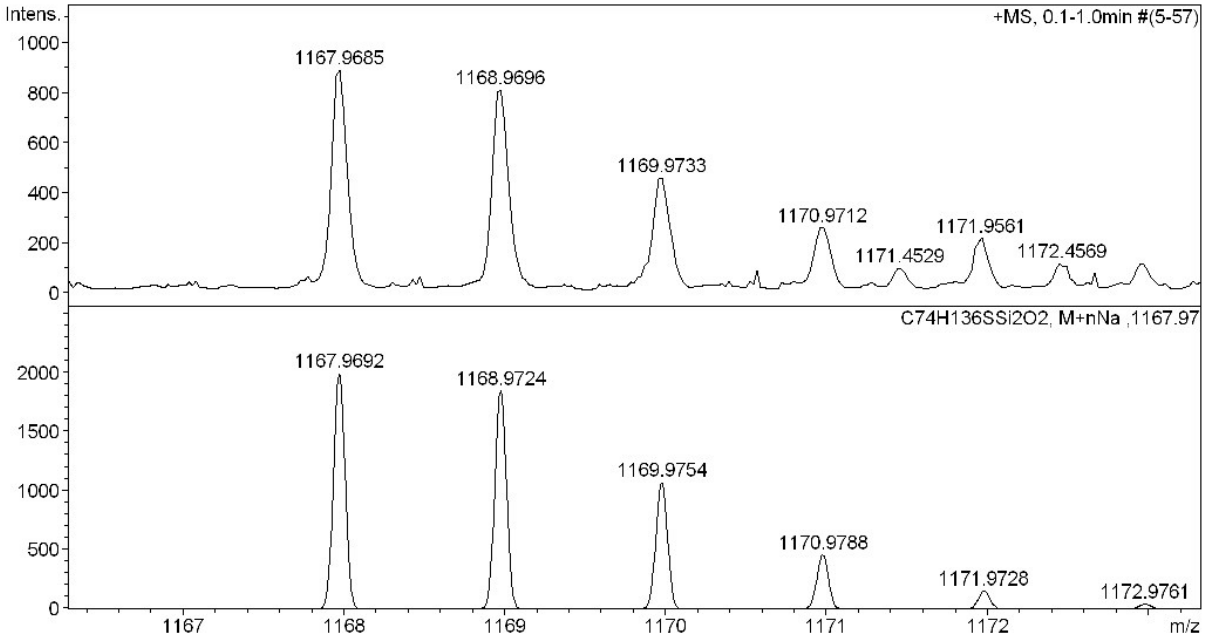


Fig. S40. HRMS spectrum of Molecular Gyrotop Isomer (**C22iBTO2**) (ESI, positive). Top: obsd. Bottom: sim.

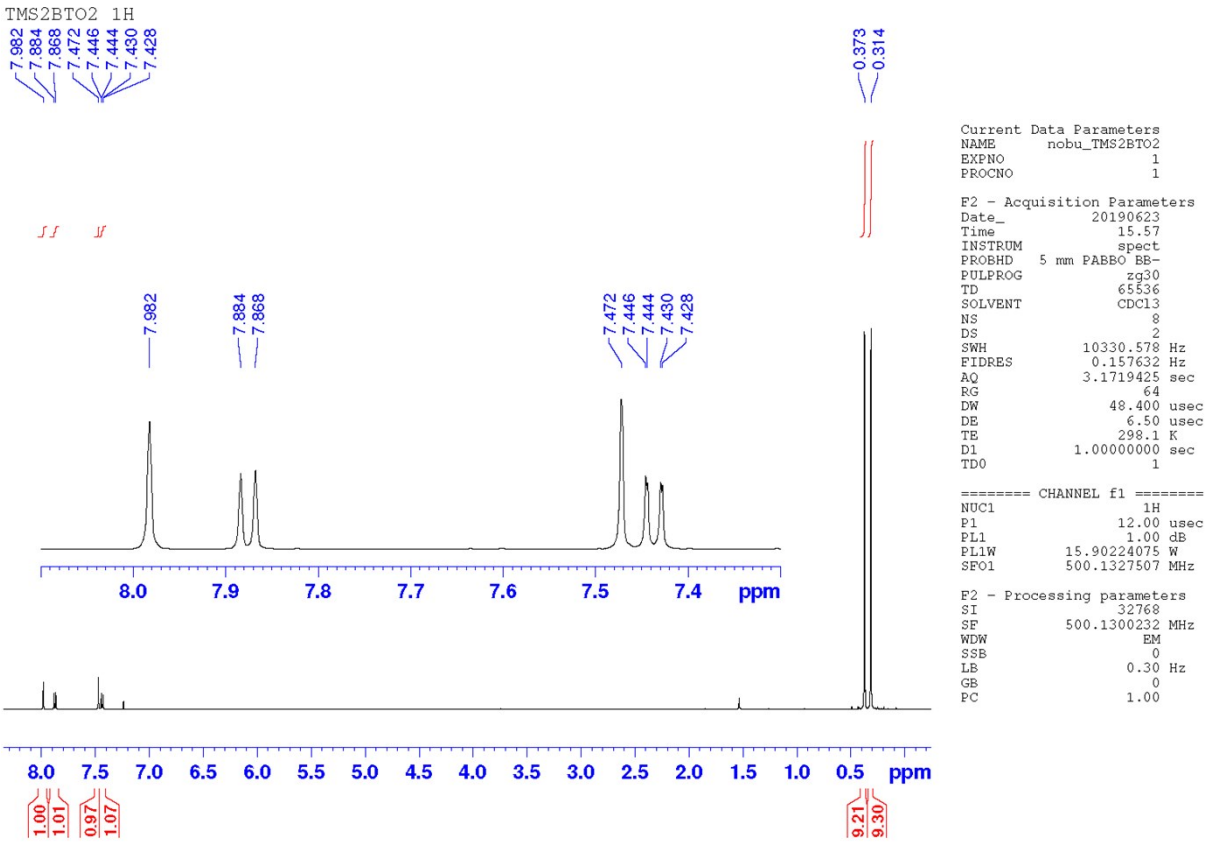


Fig. S41. ^{1}H NMR spectrum of 2,5-bis(trimethylsilyl)benzo[*b*]thiophene (**TMSBT**) in $CDCl_3$.

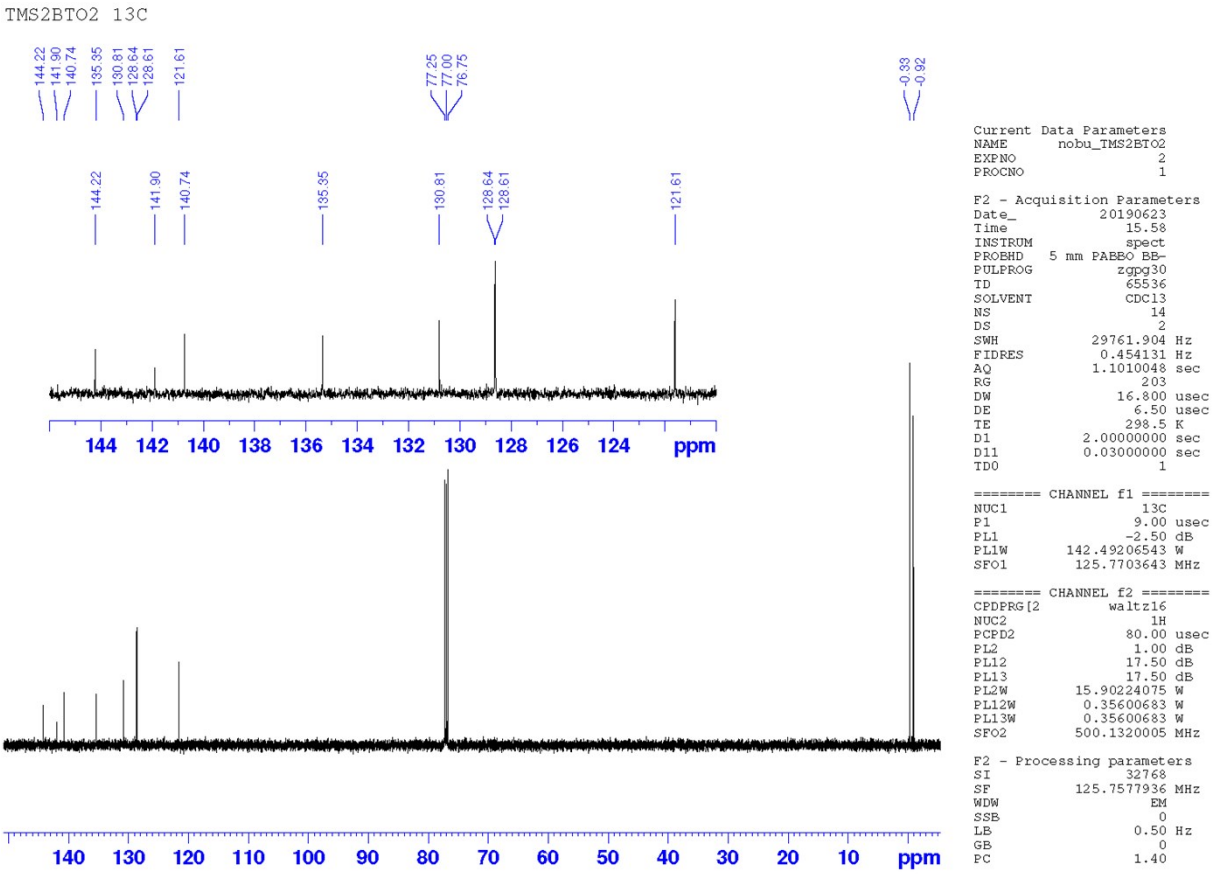


Fig. S42. ^{13}C NMR spectrum of 2,5-bis(trimethylsilyl)benzo[*b*]thiophene (**TMSBT**) in $CDCl_3$.

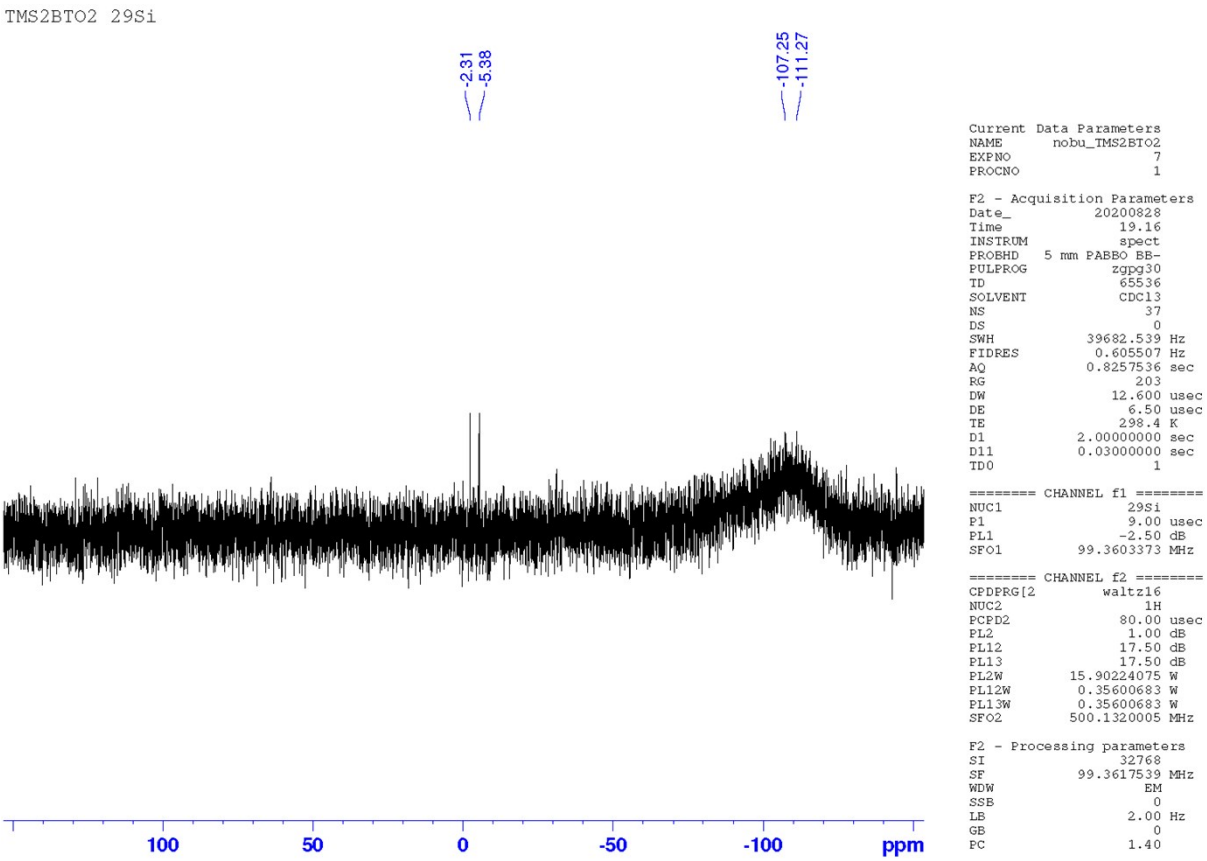


Fig. S43. ^{29}Si NMR spectrum of 2,5-bis(trimethylsilyl)benzo[*b*]thiophene (**TMSBT**) in $CDCl_3$.

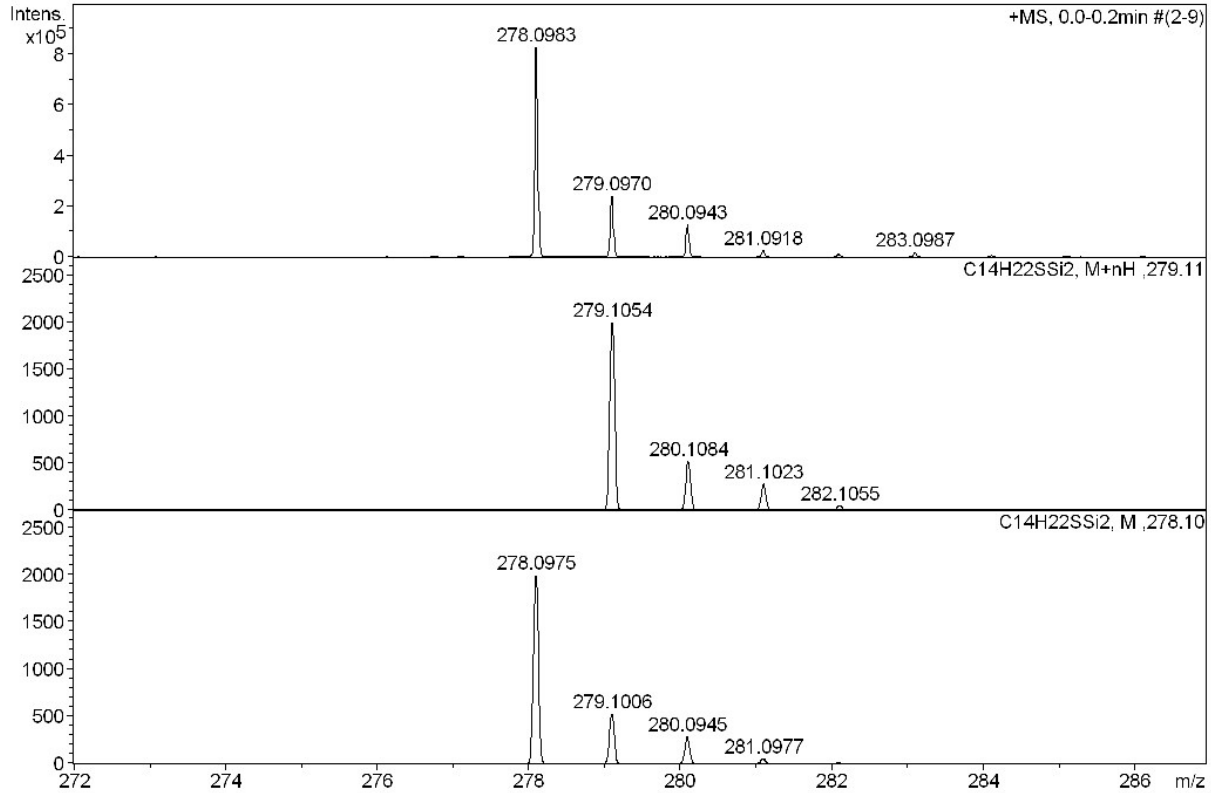


Fig. S44. HRMS spectrum of 2,5-bis(trimethylsilyl)benzo[*b*]thiophene (**TMSBT**) (APCI, positive). Top: obsd. Bottom: sim.

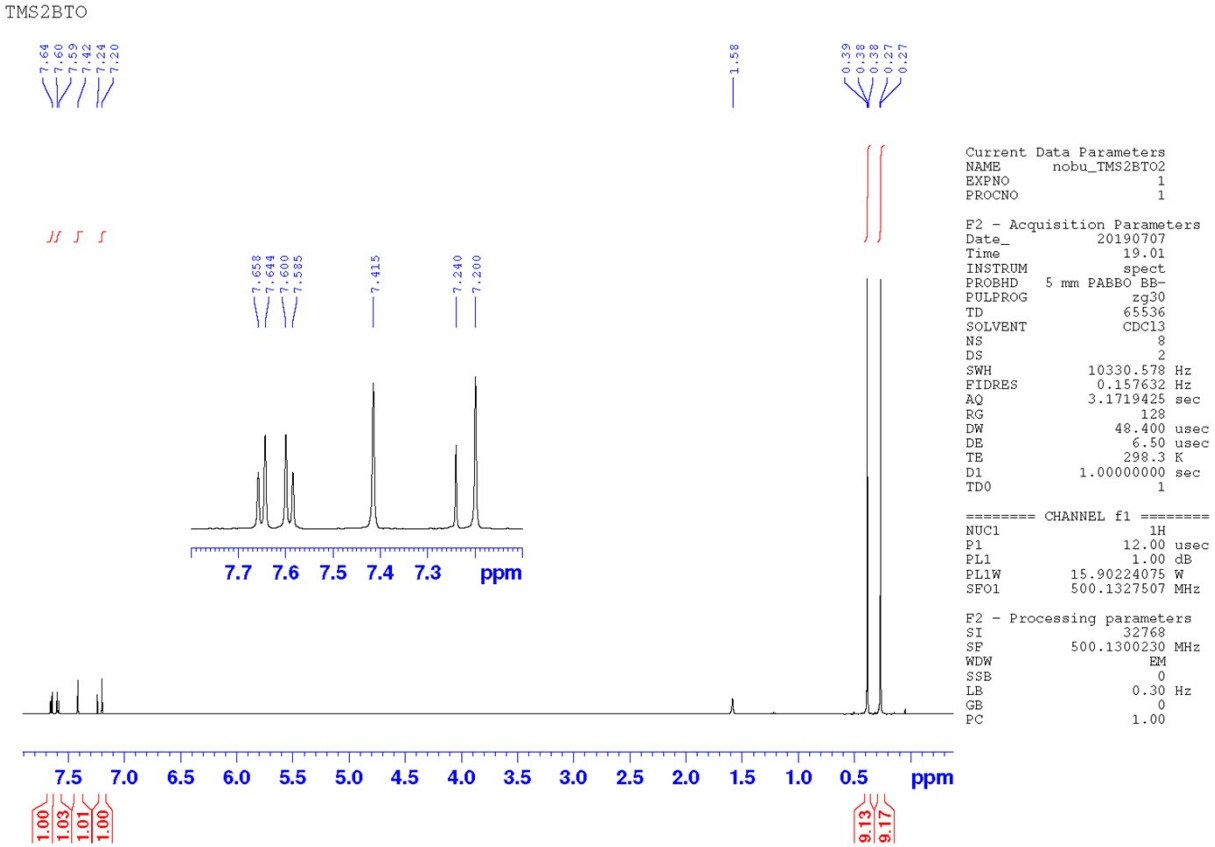


Fig. S45. ^{1}H NMR spectrum of 2,5-bis(trimethylsilyl)benzo[*b*]thiophene-1,1-dioxide (**TMSBTO2**) in $CDCl_3$.

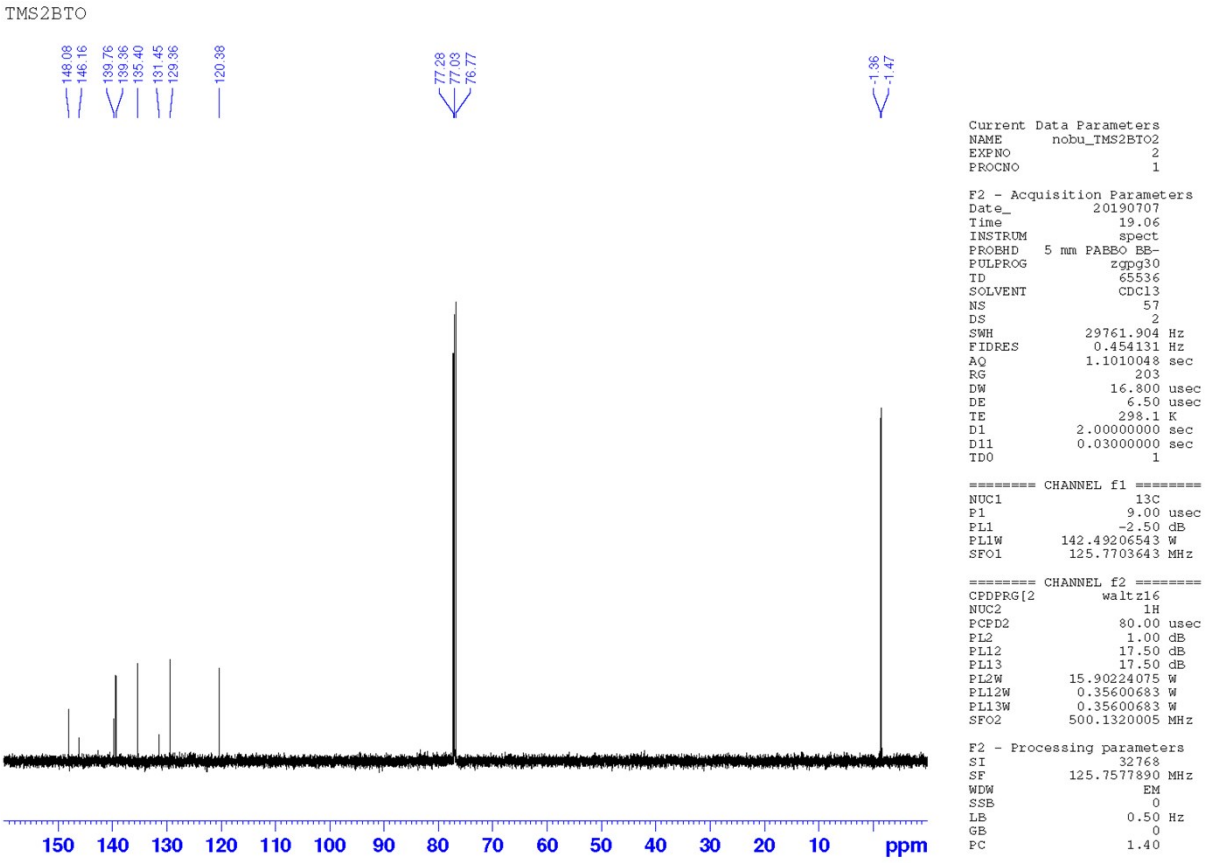


Fig. S46. ^{13}C NMR spectrum of 2,5-bis(trimethylsilyl)benzo[*b*]thiophene-1,1-dioxide (**TMSBTO2**) in $CDCl_3$.

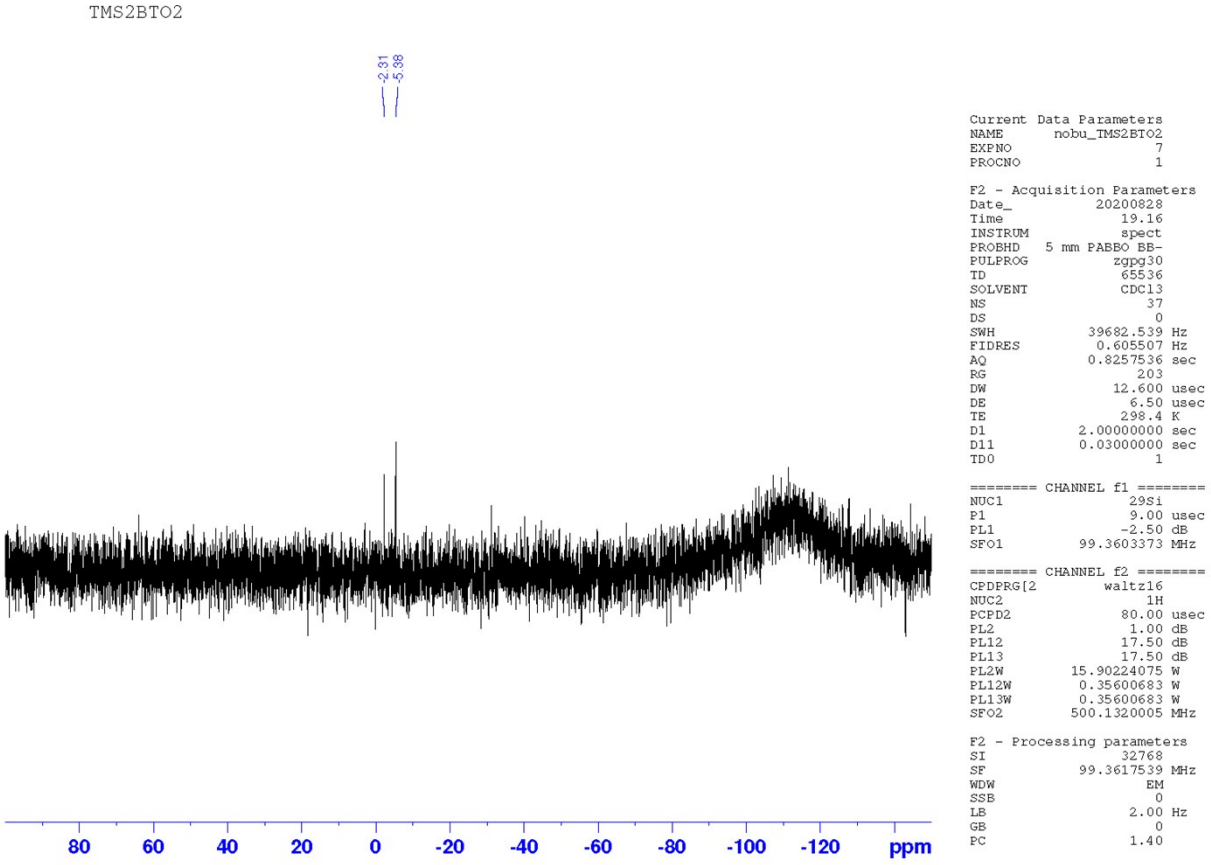


Fig. S47. ^{29}Si NMR spectrum of 2,5-bis(trimethylsilyl)benzo[*b*]thiophene-1,1-dioxide (**TMSBTO2**) in $CDCl_3$.

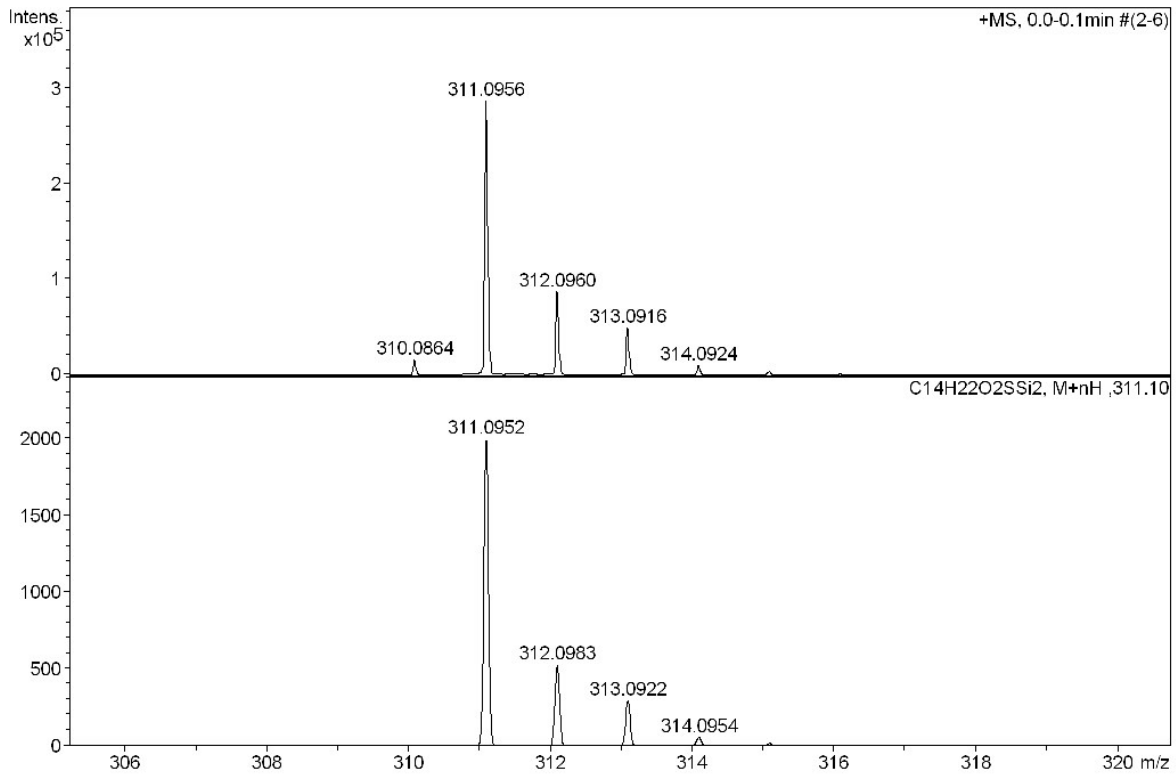


Fig. S48. HRMS spectrum of 2,5-bis(trimethylsilyl)benzo[*b*]thiophene-1,1-dioxide (**TMSBTO2**) (APCI, positive). Top: obsd. Bottom: sim.

3. Details of X-Ray Diffraction Studies

a. Crystal Data

Table S1. Crystal Data for **TMSBTO2**

Compound		**TMSBTO2**
CCDC #		2086633
Temperature		100 K
Empirical formula		C14 H22 O2 S Si2
Crystal shape		prism
Crystal color		colorless
Crystal size		0.34 x 0.31 x 0.20 mm^3
Formula weight / g mol^{-1}		310.55
Crystal system		Monoclinic
Space group		C 2/c
Z		8
Calculated density		1.218 Mg/m^3
Cell parameter	*a*	22.436(15) Å
	b	6.470(4) Å
	c	23.601(15) Å
	α	90°
	β	98.711(9)°
	γ	90°
	V	3386(4) $Å^3$
F(000)		1328
Absorption coefficient		0.329 mm^{-1}
θ range for collection (deg)		3.280 to 27.482° (Mo)
Index ranges		-28<=h<=28, -8<=k<=8, -30<=l<=30
Reflections collected		16276
Independent reflections		3888 [R(int) = 0.0401]
Completeness		99.9 %
Goodness-of-fit on F^2		1.073
Final R indices [I>2sigma(I)]		R1 = 0.0451, wR2 = 0.1166
R indices (all data)		R1 = 0.0503, wR2 = 0.1209
Largest diff. peak and hole		0.874 and -0.514 e.$Å^{-3}$

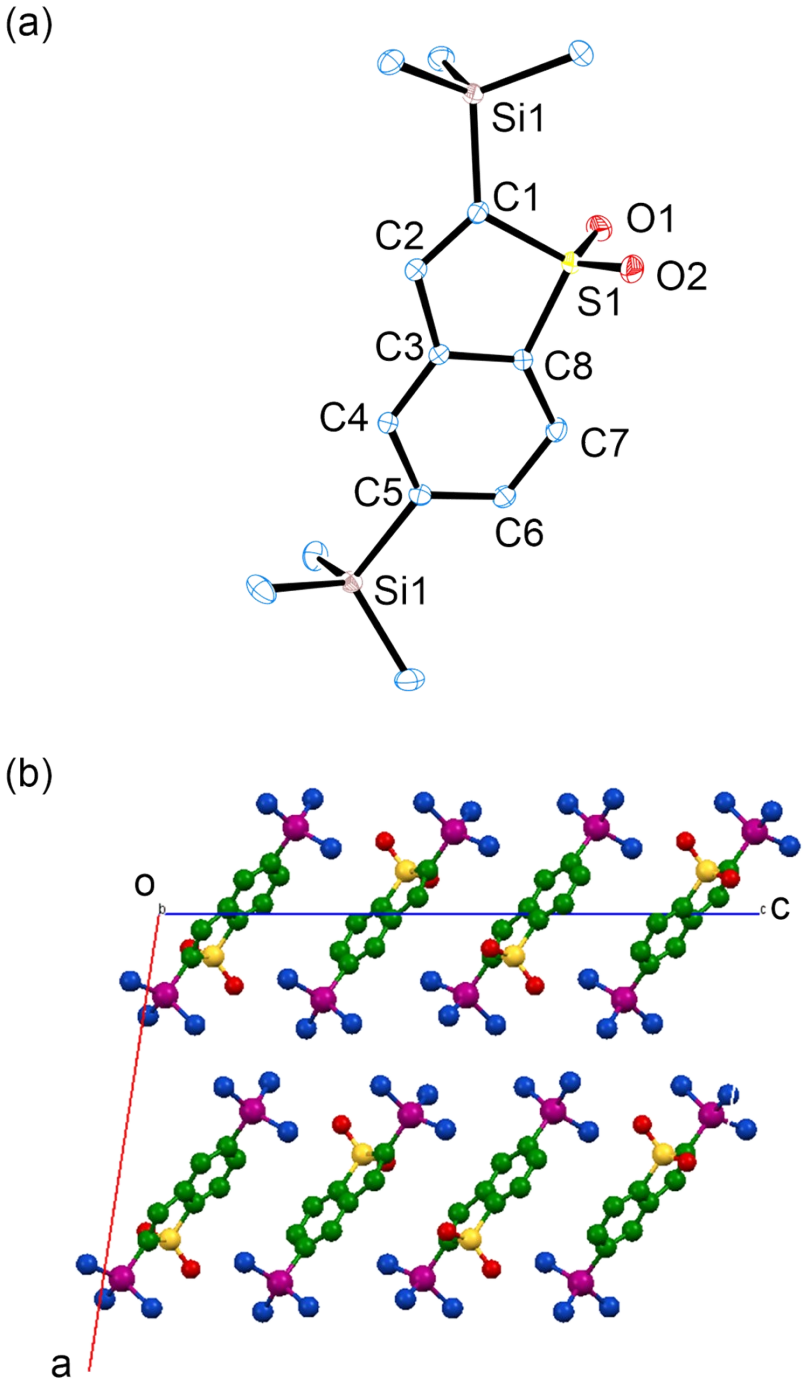


Fig. S49. Structures of **TMSBTO2** determined by X-ray crystallography (Hydrogen atoms are omitted for clarity.): (a) ORTEP drawing (50% thermal ellipsoids); (b) crystal packing structure.

4. Details of Fluorescence Studies

a. General

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 (Φ = 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.

b. Absorption Spectra of SilylBTO2s in Various Solvents

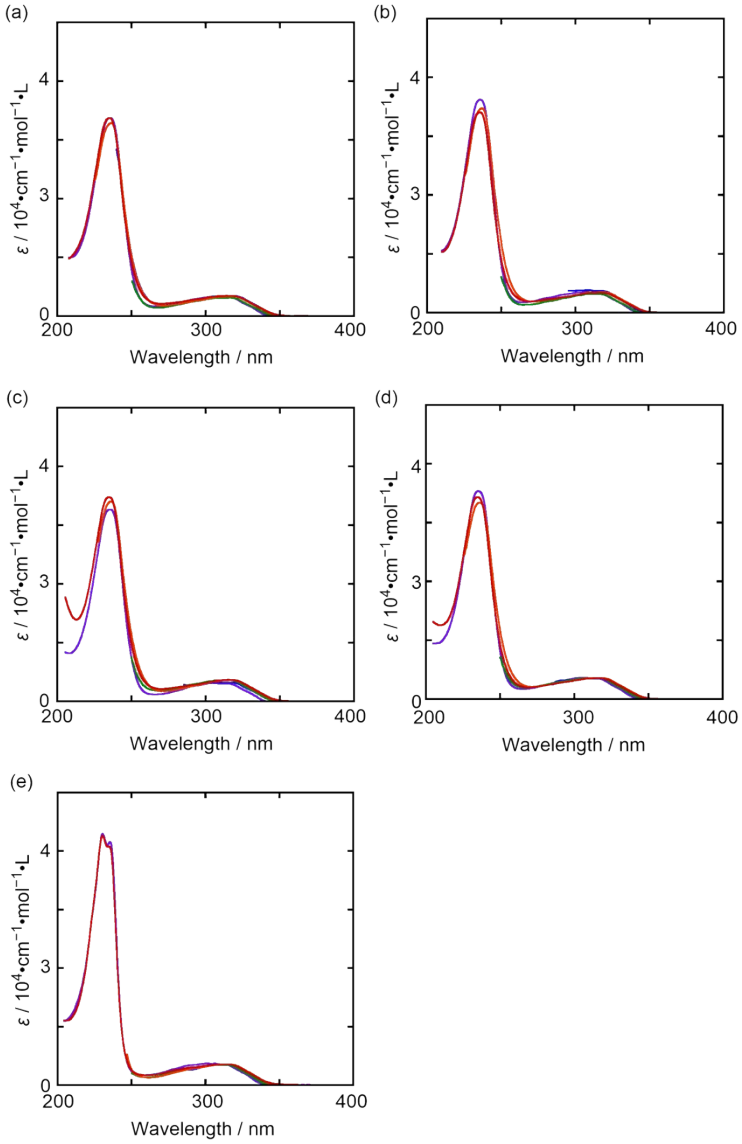


Fig. S50. Absorption spectra of silylBTO2s in various solvents (hexane (purple line), toluene (blue line), AcOEt (green line), CH2Cl2 (orange line), and EtOH (red line)) : (a) **C18BTO2**, (b) **C18iBTO2**, and (c) **C22BTO2**, (d) **C22iBTO2**, (e) **TMSBTO2** (as a control).

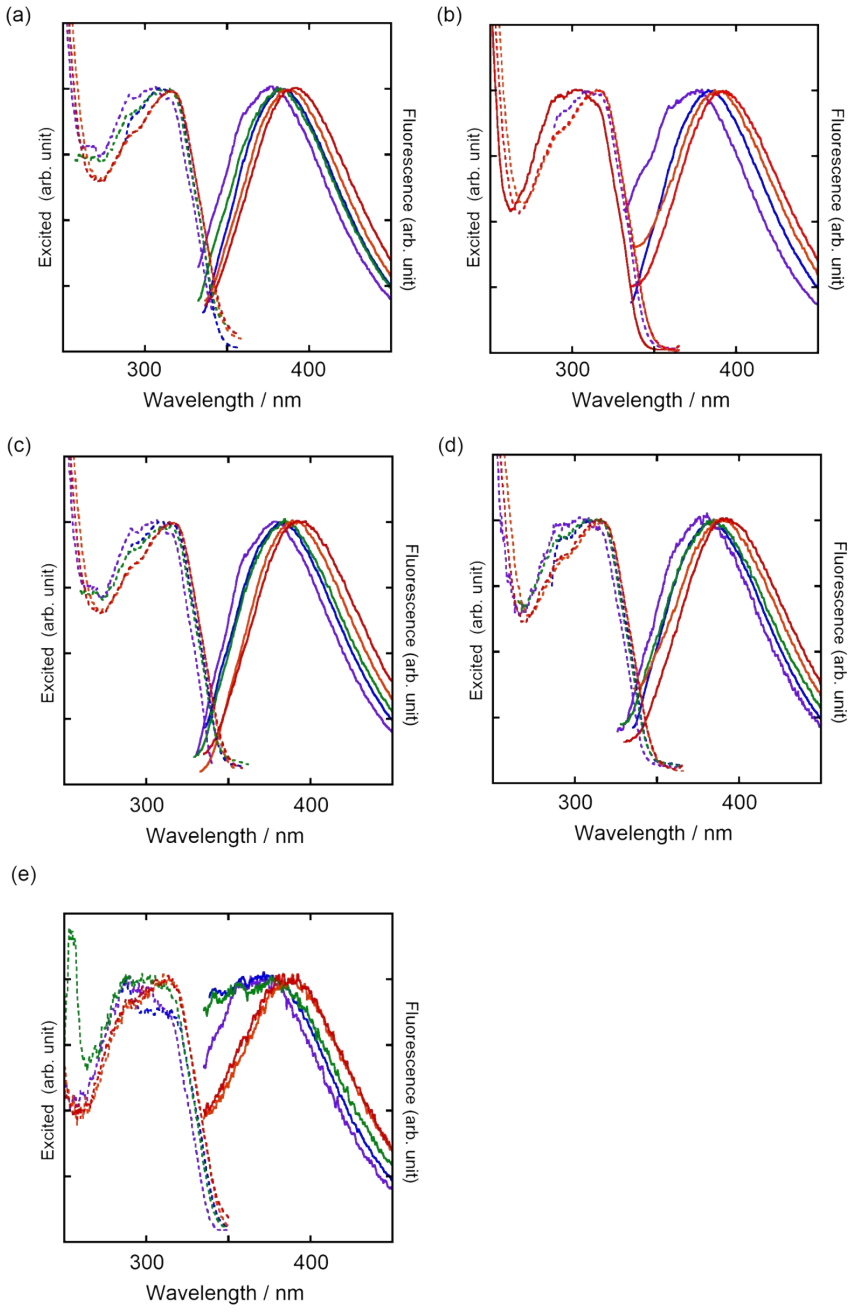


Fig. S51. Fluorescence and excited spectra of silylBTO2s in various solvents (hexane (purple line), toluene (blue line), AcOEt (green line), CH2Cl2 (orange line), and EtOH (red line)) : (a) **C18BTO2**, (b) **C18iBTO2**, and (c) **C22BTO2**, (d) **C22iBTO2**, (e) **TMSBTO2** (as a control).

Table S2. Fluorescence Parameters for Lippert-Mataga Plots of SilylBTO2

Solvent ($F_{LM}(\varepsilon,n)$)			C18BTO2		C18iBTO2		C22BTO2		C22iBTO2		TMSBTO2	
Hexane (0.00029)	ex[a] flu[b]	Δν [c]	318 376	4851	318 374.5	4744	318.5 378	4942	319 377.5	4858	317 372	4664
Toluene (0.014)	ex[a] flu[b]	Δν [c]	322.5 384	4966	322.5 383.5	4932	321.5 383	4995	322 383	4946	319 376	4752
AcOEt (0.20)	ex[a] flu[b]	Δν [c]	319.5 382	5121	-- --	--	319.5 384.5	5291	319.5 384	5257	317.5 380	5180
CH2Cl2 (0.22)	ex[a] flu[b]	Δν [c]	322.5 387	5168	322 388.5	5316	322 390	5415	322 389.5	5382	319 387	5508
EtOH (0.29)	ex[a] flu[b]	Δν [c]	322 391	5480	322 392	5546	322 393.5	5643	322 393	5611	319 387.5	5542

[a.] Excited band maxima (ex/nm), [b.] Fluorescence band maxima (flu/nm), [c.] Storks Shifts ($\Delta\nu/cm^{-1}$).

Table S3. Fluorescence Quantum Yields Φ of SilylBTO2

Solvent (Δf)	**C18BTO2**	**C18iBTO2**	**C22BTO2**	**C22iBTO2**	**TMSBTO2**
hexane	0.24	0.18	0.34	0.17	0.018
EtOH	0.26	0.20	0.24	0.17	0.031

Table S4. Fluorescence Parameters for Bakhshiev Plots of SilylBTO2

		$\Delta\nu$ ($=\Delta\nu_{abs} - \Delta\nu_{flu}$)				
Solvent	$F_B(\varepsilon,n)$[a]	C18BTO2	C18iBTO2	C22BTO2	C22iBTO2	TMSBTO2
Hexane	0.0019	4851	4744	4942	4858	4664
Toluene	0.035	4966	4932	4995	4946	4752
AcOEt	0.492	5121	4963	5291	5257	5180
CH2Cl2	0.594	5168	5316	5415	5382	5508
EtOH	0.816	5480	5546	5643	5611	5542

[a.] Bakhshiev solvent polarity function.

5. Details of DFT Calculations

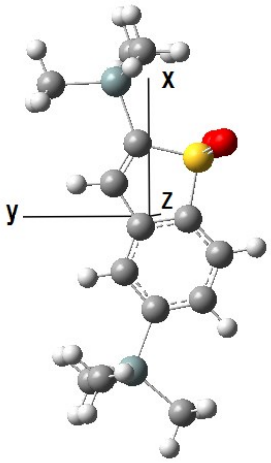
All calculations were carried out using Gaussian 16 (Revision C.01) program packages[S1] at the Research Center for Computational Science, Okazaki, Japan

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 S5. Optimized Structural Coordinate and its Total Energy for **TMSBTO2** at B3LYP/6-31+G(d) level

total energy: = `-1674.3820237 hartree` (NImag = 0)

Atomic Type	Coordinates (Angstroms) X	Y	Z
Si	3.55613028	-1.5834239922	-1.3505477041
Si	-3.824531863	0.2988866642	2.1959485412
S	1.6710690828	1.0683938931	-1.1499883812
O	1.4563521554	1.2451570449	-2.5988772119
O	2.6540656068	1.9345700533	-0.4716527732
C	3.6029614899	-1.5495969383	-3.2363984811
C	3.4244974434	-3.3595807116	-0.7118479455
C	1.9907128277	-0.678550264	-0.7635839953
C	0.096479834	1.0841303093	-0.2689398817
C	-0.7918159569	2.1306149894	-0.1100164178
C	0.9551049372	-1.1382496265	-0.0315096302
C	5.0647431531	-0.7171094785	-0.6200775093
C	-0.130286761	-0.1864785978	0.2709566803
C	-1.9616500524	1.8827626594	0.6274690812
C	-1.2978405757	-0.4116610008	1.0002496567
C	-2.2385906798	0.623669038	1.1926417708
C	-4.9110147375	1.8471804055	2.1948032157
C	-4.7608381923	-1.1455804097	1.4058472084
C	-3.3428327587	-0.1493958587	3.9720158112
H	2.740483701	-2.0727115528	-3.6665530169
H	4.5141109043	-2.0369628283	-3.6071882882
H	3.586406765	-0.5223548583	-3.6176231128
H	2.5425316619	-3.8755927179	-1.1109489206
H	4.3071371784	-3.9332049649	-1.0230383226
H	3.3783861049	-3.400407283	0.3834299479
H	-0.5958887255	3.1094536347	-0.5387254009
H	5.9892494133	-1.1963917687	-0.9676287377
H	0.9012841942	-2.1626227824	0.3306849391
H	5.0978601314	0.3389111632	-0.9108705217
H	-2.667297047	2.699280208	0.7572862103
H	-5.2098418342	2.139890787	1.1805711036
H	5.0552444849	-0.7553222178	0.4758291798
H	-5.0498460319	-0.9166161183	0.3726945111
H	-1.4741952764	-1.4012952283	1.4197276742
H	-4.4092656854	2.7049646294	2.6596631464
H	-5.8301949151	1.660093268	2.7646788161
H	-4.156246373	-2.0610083073	1.3842805781
H	-5.6769601652	-1.3704381366	1.9672053118
H	-2.7938359214	0.668269708	4.4550968068



```
 H,0,-2.7043842667,-1.0411307923,4.007145202
 H,0,-4.2338935305,-0.3579720206,4.5782908601
---------------------------------------------------------------------
```

Calculated Onsagar radius:

```
Molar volume = 3080.385 bohr**3/mol (274.890 cm**3/mol)
 Recommended a0 for SCRF calculation =  5.76 angstrom ( 10.88 bohr)
```

Table S6. Optimized Structural Coordinate and its Total Energy for **C18BTO2** at B3LYP/6-31G(d) level

total energy: = -3557.7721165 hartree (NImag = 0)

```
---------------------------------------------------------------------
   Atomic                Coordinates (Angstroms)
    Type              X           Y           Z
---------------------------------------------------------------------
 C,0,-2.5203512351,-8.3774379728,-5.4426416059
 C,0,-3.727583408,-9.1969406397,-4.9511304158
 C,0,5.8566529657,1.6583584528,-5.9302386248
 C,0,-1.3389866966,-6.1090138213,-5.5797019762
 C,0,-2.4991989002,-6.914180451,-4.9783881442
 C,0,3.7435792975,0.2054965007,-5.9293654007
 C,0,-0.0576118507,-3.8803815607,-5.6303243344
 C,0,-1.3018238518,-1.1622937501,-4.8619814266
 C,0,1.7276081294,-1.3868433188,-5.8176374659
 C,0,6.6226219284,2.8544242565,-5.3387575285
 C,0,-2.5607279527,1.0963822333,-4.7719651495
 C,0,4.5011789378,1.3666325041,-5.2703789755
 C,0,-1.2136402193,-4.6883405034,-5.0097751612
 C,0,-1.2275222311,0.350755569,-4.5744358524
 C,0,2.4813494594,-0.2134991483,-5.1607411892
 C,0,-4.9843806368,1.4692141097,-4.035038249
 C,0,-3.6865336096,0.6766500781,-3.8171344269
 C,0,-3.911544626,-9.2756090166,-3.4246159236
 C,0,-6.1712145425,1.0046052996,-3.1740914029
 C,0,6.9262736105,2.734787479,-3.8382202957
 C,0,7.9121922856,3.7927361774,-3.3187487012
 C,0,-2.7237393658,-9.8897937823,-2.6688480655
 C,0,0.9066177558,-2.509481005,-3.0558325957
 C,0,-6.0031927665,1.2421617847,-1.666927629
 C,0,-2.9617729925,-10.0915483498,-1.1621456591
 C,0,8.0445752484,3.7986576402,-1.7838365075
 C,0,2.5329439555,-3.6502897826,-1.602420414
 C,0,-7.2071857081,0.7629530134,-0.8425375012
 C,0,6.9001433184,4.5441596478,-1.0758878404
 C,0,-3.2416771656,-8.7975763012,-0.3840126335
 C,0,1.8986629249,-3.0861244452,-0.511598273
 C,0,0.7930712972,-2.239482972,-0.6352618341
 C,0,-7.050946413,0.9510865106,0.6762483796
 C,0,6.8249953076,4.3217762884,0.4449835153
 C,0,-7.1362322682,2.4112362192,1.1482220633
 C,0,-3.2684899025,-8.9854694642,1.1388887989
 C,0,6.2781606136,2.9429659138,0.8426788141
 C,0,0.3037640981,-1.7529200894,0.6705057226
 C,0,-3.6753567226,-7.711427313,1.8915721
 C,0,0.9645482227,-2.1729878919,1.7690400711
 C,0,-6.9142548571,2.6003216627,2.659104613
 C,0,6.0810049448,2.7588878172,2.3533224254
 C,0,5.4167658685,1.4216324223,2.7081578922
 C,0,-5.4568459486,2.4210507167,3.1091865094
 C,0,-3.5811704347,-7.8382605731,3.4187195324
 C,0,-3.6072168151,-5.2688392525,3.8779841276
 C,0,-1.5849464529,-3.7054991578,3.858939588
 C,0,-4.1935368662,-6.65632503,4.1932167149
 C,0,5.1273559936,1.2517813559,4.2062510079
 C,0,3.045729324,-0.2589215126,3.9723464041
 C,0,-5.2644612707,2.5964770072,4.6222186177
 C,0,-2.1352930351,-5.0792646701,4.2708011464
```

C,0,-0.4919123305,-0.3674588608,3.7743533027
C,0,-0.1365310735,-3.4526271355,4.318283254
C,0,4.4462271965,-0.0772983878,4.5781042682
C,0,2.3388336216,-1.5457042274,4.4414606119
C,0,-3.7985175841,2.5987625967,5.0861269501
C,0,-3.0393481655,1.2841069657,4.8526063938
C,0,-0.8053557839,0.0218167731,5.2355127576
C,0,-1.6059099751,1.3264146832,5.3987271185
O,0,3.6242766251,-2.6456359589,1.5025698174
O,0,2.0696881863,-4.6386694975,1.6946017657
Si,0,0.3012985645,-2.1868519374,-4.836635723
Si,0,0.6590841142,-1.8731248009,3.6250625594
C,0,0.2972882089,-1.9577868163,-1.9104911433
S,0,2.3122042254,-3.260576177,1.2301219445
C,0,2.0232179333,-3.3499678421,-2.8715213227
H,0,-2.5114342193,-8.4032376329,-6.5418053386
H,0,-1.5875700869,-8.8646953032,-5.1263025198
H,0,-3.6407076792,-10.2170478053,-5.3521182164
H,0,-4.6433989635,-8.7756156361,-5.3902854342
H,0,5.7037766273,1.8312158475,-7.0052976132
H,0,6.4865089271,0.7592127659,-5.8548830859
H,0,-1.4554942345,-6.0571540238,-6.6724315235
H,0,-0.3952126321,-6.6459169456,-5.401334476
H,0,-3.4533195972,-6.4312837939,-5.2386507481
H,0,-2.4281997363,-6.8748260536,-3.8824450004
H,0,3.4766759526,0.4760405091,-6.9617653421
H,0,4.4135690297,-0.6640221861,-6.0081369605
H,0,-0.2471557411,-3.728420093,-6.7039478046
H,0,0.86645351,-4.4766298648,-5.5813489307
H,0,-1.7296856212,-1.3076332731,-5.8669592249
H,0,-2.0158538147,-1.642913006,-4.1785064616
H,0,1.3427722873,-1.0794171512,-6.8019330711
H,0,2.44704867,-2.1927291164,-6.0323401597
H,0,7.5677579617,2.9684019584,-5.8890840253
H,0,6.0549343996,3.7796254328,-5.5181974726
H,0,-2.8968871574,0.9553661141,-5.8102674351
H,0,-2.3804374294,2.174874022,-4.6553794091
H,0,3.8767731377,2.2726781729,-5.2940379386
H,0,4.6537085704,1.1301314055,-4.2085918556
H,0,-2.1620248804,-4.1528919001,-5.1603030548
H,0,-1.0749675372,-4.7581896045,-3.9213334701
H,0,-0.4799623566,0.808610166,-5.2347978215
H,0,-0.8663800145,0.5244785328,-3.5503605871
H,0,1.8134706774,0.6530957369,-5.0610139729
H,0,2.7709763566,-0.4881655032,-4.1372885135
H,0,-5.2673859163,1.391401499,-5.0945241382
H,0,-4.7951623722,2.5372540584,-3.8503731935
H,0,-3.9031584997,-0.3934656673,-3.9431145573
H,0,-3.33990084,0.799854972,-2.7811151672
H,0,-4.1209910162,-8.2725650502,-3.0318330112
H,0,-4.8116919879,-9.8722468213,-3.2159463272
H,0,-7.0788635986,1.5236459892,-3.5134672575
H,0,-6.3500688751,-0.0660771488,-3.3551836563
H,0,7.3397219936,1.7366244486,-3.6278185427
H,0,5.988875743,2.7977018338,-3.2704467906
H,0,7.5994896319,4.7911969972,-3.659992835
H,0,8.8947635169,3.6115084122,-3.7759278297
H,0,-2.4766049978,-10.8609418522,-3.1221510158
H,0,-1.8337737713,-9.2584361985,-2.8016309933
H,0,-5.8288928771,2.3134940037,-1.4938560496
H,0,-5.1036689402,0.7246197979,-1.3048179103
H,0,-3.7986739876,-10.7903448592,-1.0140903468
H,0,-2.077204952,-10.5821301869,-0.731345667
H,0,8.9959268065,4.2658001257,-1.494211813
H,0,8.0982258181,2.7596565113,-1.4297661142
H,0,3.3932266322,-4.301880589,-1.4813088861
H,0,-8.1159161296,1.2812681923,-1.183723938
H,0,-7.3707135645,-0.3036114646,-1.0528339819
H,0,5.9360847022,4.252586801,-1.5173544686

H,0,7.0112903751,5.6179664688,-1.282308546
H,0,-4.2013827269,-8.3712545908,-0.7073910889
H,0,-2.4757985326,-8.0486994603,-0.6374906378
H,0,-6.0953205124,0.5076839359,0.9899363395
H,0,-7.833967437,0.3760718893,1.1907972815
H,0,7.8189570269,4.4730706535,0.8919711242
H,0,6.1755978594,5.0928705981,0.8835010462
H,0,-6.4077206591,3.0284281234,0.603841862
H,0,-8.1270504222,2.8036659277,0.8783718191
H,0,-3.9637934224,-9.797823898,1.3982376639
H,0,-2.2760470687,-9.3144212424,1.4808068698
H,0,6.9391255679,2.1499008151,0.4663051061
H,0,5.3107841625,2.7923125346,0.339780697
H,0,-0.5536556173,-1.0856346413,0.7192072246
H,0,-3.0429307737,-6.8803276287,1.5497467414
H,0,-4.7055379155,-7.4434130472,1.610869771
H,0,-7.2462705769,3.608060345,2.9461751592
H,0,-7.5586973622,1.9005261504,3.2122647431
H,0,7.0497341534,2.8424370293,2.8680059776
H,0,5.4610157619,3.5827959075,2.7383736304
H,0,6.0515956353,0.591708613,2.3646523171
H,0,4.4809576769,1.3377512475,2.1395152937
H,0,-4.8286942639,3.1527848943,2.5780006538
H,0,-5.094132624,1.4309805256,2.8049786948
H,0,-4.0965840412,-8.7568977529,3.7339830616
H,0,-2.5289672383,-7.9736410123,3.7049413011
H,0,-3.725085025,-5.0554174375,2.8063435263
H,0,-4.2098870732,-4.5110426184,4.3991815551
H,0,-1.6474196487,-3.6217505119,2.7641025007
H,0,-2.2421487775,-2.9200933956,4.260240959
H,0,-5.2735311673,-6.6294913041,3.9880638396
H,0,-4.0949109024,-6.8499420742,5.2710601597
H,0,6.0706976256,1.336460157,4.7646989729
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H,0,2.4306672898,0.6174838664,4.2269877325
H,0,-5.7288899414,3.5442987648,4.9302386575
H,0,-5.8141410392,1.8043351463,5.1522441303
H,0,-1.5135960722,-5.8581110722,3.8087830533
H,0,-2.0284591071,-5.2080521186,5.3583217665
H,0,-1.4244673604,-0.5682743289,3.2297813602
H,0,-0.0192484342,0.484329585,3.2639420487
H,0,0.5004411917,-4.2947606478,4.0143151468
H,0,-0.0943444383,-3.4191050675,5.4169581678
H,0,5.0804060151,-0.9169629043,4.2599995537
H,0,4.3732086685,-0.1438170061,5.6733995683
H,0,2.989484808,-2.4087202185,4.2450944892
H,0,2.1961496648,-1.5202076508,5.5322676559
H,0,-3.2632477033,3.4170564542,4.5812545623
H,0,-3.7692702201,2.8363873575,6.1591537593
H,0,-3.0182708732,1.0551272435,3.7795127132
H,0,-3.5865873011,0.458180281,5.3327350947
H,0,-1.3513469784,-0.7969102762,5.7264657866
H,0,0.1360596257,0.1310989689,5.7911147016
H,0,-1.0562307621,2.1459693928,4.9118824311
H,0,-1.6439374964,1.5806439548,6.4679801471
H,0,-0.5673794024,-1.3055503744,-2.0104329168
H,0,2.5152743881,-3.7891059124,-3.736609631

Table S7. Optimized Structural Coordinate and its Total Energy for **C22BTO2** at B3LYP/6-31G(d) level

total energy: = -4029.5283745 hartree (NImag = 0)

Atomic Type	Coordinates (Angstroms) X	Y	Z

C,0,-3.4906878846,-6.6471912169,8.4529053067
C,0,-2.3070104073,-6.8644267767,7.4930087063
C,0,-1.5576096075,-4.5029897665,-4.1851348544
C,0,-1.335139524,-6.6567092743,5.1365739674
C,0,-2.5191058531,-6.3464998483,6.0634596408
C,0,-0.3775444554,-4.6352361878,-1.8793069696
C,0,2.7206645223,-5.3140244237,-1.8586585798
C,0,-0.234782827,-6.2947386043,2.8489866225
C,0,0.9843860248,-5.8035900352,0.6403731555
C,0,-0.2828302742,-4.2350564014,-3.3654525222
C,0,-1.4237854438,-5.9744431116,3.7650977255
C,0,4.6443463834,-4.8981774985,-3.5271665055
C,0,-0.2079604705,-5.4656589847,1.5563944164
C,0,8.5018683338,-3.7761620521,-6.7414410593
C,0,6.5691035359,-4.3891443969,-5.1648531036
C,0,3.3602773453,-4.3547710318,-2.8822938181
C,0,-3.9924105531,-3.9289127738,-4.7045508061
C,0,-3.9622996469,-5.1915159483,8.6236338299
C,0,8.9707335904,-2.9989274726,-7.9835826007
C,0,5.1984817415,-3.9706633832,-4.6172035927
C,0,7.0538134415,-3.4958290476,-6.3155542188
C,0,-2.7797460878,-3.6592248999,-3.8026763097
C,0,-6.3902129376,-3.2772290203,-5.3375494122
C,0,-5.2036606044,-3.0423695644,-4.3909327867
C,0,-2.8734886112,-4.2010907833,9.0592619516
C,0,8.8708092039,-1.4714330347,-7.8600374934
C,0,1.7083886984,-2.9414182859,-0.1734087304
C,0,9.55224971,-0.7195416762,-9.0138258132
C,0,-7.617205909,-2.3914137975,-5.059808439
C,0,-3.4154138019,-2.789496467,9.3298319221
C,0,3.3606415197,-1.6535122405,1.1181260152
C,0,-7.3671829985,-0.8918415468,-5.2678306985
C,0,9.30035808,0.7999321366,-9.0014199814
C,0,7.9171310024,1.2003742458,-9.540240229
C,0,-2.3060291817,-1.7403711577,9.489460534
C,0,2.5627478125,-0.5376837024,0.9523111464
C,0,1.3542103437,-0.5658908292,0.2497318163
C,0,-8.5990150205,-0.0087017117,-5.0298383381
C,0,-2.7885332275,-0.3283246341,9.8612236885
C,0,7.590158842,2.6996954022,-9.4117188318
C,0,-3.8242394988,0.2715497955,8.8951666431
C,0,-8.2672301391,1.4869363068,-5.1086197827
C,0,0.6953242869,0.7574866948,0.2085179405
C,0,6.0349902826,2.627699562,-7.3503648334
C,0,4.4878453718,2.5458376143,-5.3159535745
C,0,7.310702298,3.2022145141,-7.9826469921
C,0,1.3229538481,1.775426083,0.8333022974
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