Supporting Information

Controlling the thermodynamic stability of conformational isomers of bistricyclic aromatic enes by introducing boron and silicon atoms

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Experimental section

General

For reaction solvents, toluene, benzene and Et_2O were purchased from Kanto Chemical Kanto Chemical Co., Ltd. and were distilled from calcium hydride and stored over activated molecular sieves under argon until use. All other chemicals were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. or TCI Co., Ltd. Starting materials 8,8-dimethyl-4,8-dihydrosilino[2,3-b:6,5-b']dithiophene (**1-Me**),[1] dichlorodi(1-naphthyl)silane,[2] and 8-(2,4,6-triisopropylphenyl)borinino[2,3-b:6,5-b']dithiophene-4(8H)-thione (**6**)[3] were prepared according to the literature. Room-temperature NMR spectra were recorded on Varian System 500 and 400MR spectrometers. On the other hand, variable-temperature NMR spectra were recorded on JNM-ECA500 spectrometers at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. Abbreviations Th, Tip, Ph, and Np used for the following NMR assignments stand for fused thiophene ring, tripyl group, phenyl group, naphthyl group, respectively. High-resolution APCI and ESI mass spectra were obtained on a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer at N-BARD. On the other hand, High-resolution FD mass spectra were obtained on a JMS-T2000GC "AccuTOF GC-alpha" at N-BARD. Fourier transform infrared (FTIR) spectroscopy was performed using a Shimadzu IRAffinity-1 spectrophotometer. TG/DTA analysis was carried out under gentle air flow at a heating rate of 10 ºC/min using the SII TG/DTA6200 analyzer.

DFT calculations

Geometrical optimizations were performed on a Gaussian 16 program at the B3LYP/6-31G(d) level.[4] All the optimized geometries were verified by vibrational frequency analysis at the same level of theory and found as true minima, as negative vibrational frequencies were not present. TD-DFT calculations were performed for the optimized geometries at the B3LYP/6-31+G(d) level.

Photophysical measurements

Room-temperature UV–vis absorption spectra were measured with a HITACHI U-2910 spectrophotometer. Photoluminescence spectra were measured with HORIBA FluoroMax-4 spectrophotometer. Diffuse reflection spectra of solids were measured with a Shimadzu UV-3600 plus spectrometer and converted to absorption spectra by the Kubelka–Munk theory.

Electrochemical measurements

Cyclic voltammetry measurements were performed with an AMETEK VersaSTAT 4 potentiostat/galvanostat in a 1.0 mM solution in dichloromethane containing 0.1 M nBu_4NPF_6 at a 100 mV s^{-1} scan rate using a three-electrode system which was composed of a Pt plate as the counter electrode, a Pt wire as the working electrode, and an Ag wire as the pseudo-reference electrode. The potentials were corrected using ferrocene as the internal standard.

XRD measurement

Single crystal X-ray diffraction data were collected at 100 K on a Rigaku XtaLAB Synergy R, DW diffractometer at N-BARD, Hiroshima University, using MoKα radiation monochromated with a multilayered confocal mirror. The

structure was solved by the CrysAlis Pro and expanded using Fourier techniques. Nonhydrogen atoms were refined anisotropically, whereas hydrogen atoms were included but not refined. All other calculations were performed using the OLEX2 program. Graphical crystal structures were generated using Mercury 2022.3.0 (Cambridge Crystallographic Data Centre). Deposition Numbers 2381482 (for **DTCB-SiMe**), 2381483 (for **DTCB-SiPh**), 2381484 (for **DTCB-SiNp**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformations-zentrum Karlsruhe Access Structures service. Powder XRD patterns were obtained on a Rigaku Ultima IV multipurpose X-ray diffraction system.

Determination of the activation energy ($\Delta G^{\ddagger}$) for the isomerization between the anti-folded conformers

ΔG values at 298 K were calculated using the obtained from the Van't Hoff plot derived from variable temperature ^{1}H NMR spectra. The activation energy ($\Delta G^{\ddagger}$) was calculated by the following equation.[5]

$\Delta G^{\ddagger} = 8.314Tc[22.96 + \log(Tc/\Delta\nu)]$

Tc is the coalescence temperature. $\Delta\nu$ is the difference in the chemical shifts of isopropyl groups in Tip group at −80 ℃ ($\Delta\nu$ = 400 Hz). Tc was determined to be −20 ℃ from Figure S11.

Fabrication of PVA film

PVA (0.1052 g) was dissolved in 3.5 mL of water at 90 °C. **DTCB-SiNp** (21.1 mg) was dispersed in methanol and mixed with the PVA solution. The mixed solution was poured into a mold and heated at 40 °C overnight to obtain the film.

Synthesis

Synthesis of 8,8-diphenyl-4,8-dihydrosilino[2,3-b:6,5-b']dithiophene (1-Ph)

To a solution of 2-bromo-3-((2-bromo-2,3-dihydrothiophen-3-yl)methyl)thiophene (4.03 g, 11.9 mmol) in 25 mL of Et_2O was slowly added 9.02 mL of 2.64 mol/L n-BuLi in hexane (23.8 mmol) at –80 °C for 5 min, and the mixture was stirred for 1 h at the temperature. Then 2.60 mL (12.4 mmol) of dichrolodiphenylsilane was added to the mixture at –80 °C. The mixture was warmed to room temperature and starred overnight. The resulting mixture was hydrolyzed with water and extracted with hexane. The combined organic layer was washed with water then with brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The residue was washed with a 10:1 mixture of *n*-hexane/dichloromethane to give 2.36 g (6.56 mmol, 55% yield) of **1-Ph** as an off-white solid. ^{1}H NMR (in $CDCl_3$, 500 MHz): δ = 7.71 (2H, d, *J* = 4.7 Hz, Th), 7.63–7.66 (4H, m, Ph), 7.33–7.42 (6H, m, Ph), 7.20 (2H, d, *J* = 4.7 Hz, Th), 4.37 (2H, s, CH_2).^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 149.5, 135.6, 134.6, 132.4, 130.1, 129.3, 128.1, 125.0, 32.4. HR-MS (APCI, positive) Calcd for $C_{21}H_{16}S_2Si$: M^+: 360.04267, Found: 360.04568. m.p. 142.6-144.2 °C.

Synthesis of 8,8-di(naphthalen-1-yl)-4,8-dihydrosilino[2,3-b:6,5-b']dithiophene (1-Np)

1-Np was prepared from 2.02 g (5.97 mmol) of 2-bromo-3-((2-bromo-2,3-dihydrothiophen-3-yl)methyl)thiophene, 4.40 mL (12.1 mmol) of 2.76 mol/L *n*-BuLi in hexane, and 2.10 g (5.93 mmol) of dichlorodi(1-naphthyl)silane in 30 mL of Et_2O in a manner similar to that above. The product was obtained as a light brown solid (1.89 g, 4.09 mmol, 69% yield). ^{1}H NMR (in $CDCl_3$, 500 MHz): δ = 8.06–8.09 (2H, dd, *J* = 8.5, 0.4 Hz, Np), 7.91 (2H, d, *J* = 8.2 Hz,

Np), 7.80–7.84 (4H, m, Np), 7.64 (2H, d, J = 4.7 Hz, Th), 7.38–7.43 (4H, m, Np), 7.21 (2H, d, J = 4.7 Hz, Th), 4.42 (2H, s, CH_2). ^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 149.2, 136.8, 136.4, 133.6, 133.5, 132.3, 131.2, 129.4, 129.0, 128.9, 126.4, 126.1, 125.8, 125.5, 32.6. HR-MS (APCI, positive) Calcd for $C_{29}H_{20}S_2Si$: M^+: 460.07757, Found: 460.07724. m.p. 199.8-200.9 °C.

Synthesis of 8,8-dimethylsilino[2,3-b:6,5-b']dithiophen-4(8H)-one (2-Me)

To a solution of **1-Me** (2.05 g, 8.68 mmol) in 80 mL of glacial acetic acid was added CrO_3 (1.03 g, 10.3 mmol) and heated at 75 °C overnight. The resulting mixture was hydrolyzed with water and extracted with CH_2Cl_2. The combined organic layer was washed with saturated $NaHCO_3$aq then with brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The crude product was purified by silica gel chromatography using a 1:1 mixture of *n*-hexane/dichloromethane to give 0.945 g (3.77 mmol, 43% yield) of **2-Me** as a white solid. ^1H NMR (in $CDCl_3$, 500 MHz): δ = 7.94 (2H, d, J = 4.8 Hz, Th), 7.64 (2H, d, J = 4.8 Hz, Th), 0.59 (6H, s). ^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 178.7, 148.3, 144.2, 131.5, 129.4, 0.5. HR-MS (APCI, positive) Calcd for $C_{11}H_{10}OS_2Si$: $[M+H]^+$: 251.00151, Found: 251.00194. m.p. 119.0-120.9 °C.

Synthesis of 8,8-diphenylsilino[2,3-b:6,5-b']dithiophen-4(8H)-one (2-Ph)

2-Ph was prepared from 1.79 g (4.98 mmol) of **1-Ph** and 0.861 g (8.61 mmol) of CrO_3 in 20 mL of glacial acetic acid at same temperature a manner similar to that above. The product was obtained as a white solid (0.688 g, 2.84 mmol, 37% yield). ^1H NMR (in $CDCl_3$, 400 MHz): δ = 8.01 (2H, d, J = 4.8 Hz, Th), 7.72 (2H, d, J = 4.8 Hz, Th), 7.62–7.66 (4H, m, Ph), 7.37–7.49 (6H, m, Ph). ^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 178.5, 149.3, 140.5, 135.5, 132.8, 131.6, 131.0, 129.5, 128.5. HR-MS (APCI, positive) Calcd for $C_{21}H_{14}OS_2Si$: $[M+H]^+$: 375.03281, Found: 375.03284. m.p. 169.9-171.2 °C.

Synthesis of 8,8-di(naphthalen-1-yl)silino[2,3-b:6,5-b']dithiophen-4(8H)-one (2-Np)

2-Np was prepared from 1.03 g (2.23 mmol) of **1-Np** and 0.338 g (3.38 mmol) of CrO_3 in 110 mL of glacial acetic acid at 100 °C in a manner similar to that above. The product was obtained as a white solid (0.621 g, 1.31 mmol, 59% yield). ^1H NMR (in $CDCl_3$, 500 MHz): δ = 8.02–8.06 (4H, overlapped), 7.97 (2H, d, J = 8.4 Hz, Np), 7.88 (2H, d, J = 8.1 Hz Np), 7.84 (2H, dd, J = 6.9, 1.3 Hz, Np), 7.64 (2H, d, J = 4.9 Hz, Th), 7.41–7.49 (4H, m, Np), 7.31 (2H, ddd, J = 8.3, 6.9, 1.4 Hz, Np). ^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 178.7, 148.9, 141.6, 136.6, 136.5, 133.7, 132.7, 132.1, 131.0, 129.7, 129.4, 128.3, 126.7, 126.2, 125.6. HR-MS (APCI, positive) Calcd for $C_{29}H_{18}OS_2Si$: $[M+H]^+$: 475.06411, Found: 475.06409. m.p. 284.4-286.2 °C.

Synthesis of 8,8-dimethylsilino[2,3-b:6,5-b']dithiophene-4(8H)-thione (3-Me)

To a solution of **2-Me** (0.850 g, 3.39 mmol) in 45 mL of toluene was added Lawesson's reagent (0.798 g, 1.97 mmol), and the mixture was refluxed for 5 h. The solvent was removed, and the crude product was purified by silica gel chromatography using n-hexane to give 0.636 g (2.39 mmol, 70% yield) of **3-Me** as a green solid. ^1H NMR (in $CDCl_3$, 500 MHz): δ = 8.20 (2H, d, J = 4.9 Hz, Th), 7.51 (2H, d, J = 4.9 Hz, Th), 0.58 (6H, s, Me). ^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 211.1, 154.1, 138.2, 133.4, 130.2, 0.2. HR-MS (APCI, positive) Calcd for $C_{11}H_{10}S_3Si$: $[M+H]^+$: 266.97867,

Found: 266.97897. m.p. 109.1-110.8 °C.

Synthesis of 8,8-diphenylsilino[2,3-b:6,5-b']dithiophene-4(8H)-thione (3-Ph)

3-Ph was prepared from 0.528 g (1.41 mmol) of **2-Ph** and 0.318 g (0.786 mmol) of Lawesson's reagent in 20 mL of toluene in a manner similar to that above. The product was obtained as a green solid (0.458 g, 1.17 mmol, 83% yield). ^{1}H NMR (in $CDCl_3$, 400 MHz): δ = 8.29 (d, *J* = 4.9 Hz, 2H, Th), 7.69 (m, 4H, Ph), 7.57 (d, *J* = 4.9 Hz, 2H, Th), 7.38–7.51 (m, 6H, Ph). ^{13}C NMR (in $CDCl_3$, 100 MHz): δ = 211.0, 155.2, 135.6, 134.4, 133.6, 131.6, 131.4, 131.0. 128.5. HR-MS (APCI, positive) Calcd for $C_{21}H_{14}S_2Si$: $[M+H]^+$: 391.00997, Found: 391.00928. m.p. 185.6-186.8 °C.

Synthesis of 8,8-di(naphthalen-1-yl)silino[2,3-b:6,5-b']dithiophene-4(8H)-thione (3-Np)

3-Np was prepared from 0.159 g (0.334 mmol) of **2-Np** and 0.153 g (0.377 mmol) of Lawesson's reagent in 20 mL of toluene in a manner similar to that above. The product was obtained as a green solid (0.103 g, 0.209 mmol, 57% yield). ^{1}H NMR (in $CDCl_3$, 500 MHz): δ = 8.28 (2H, s, *J* = 4.9 Hz Th), 8.01 (2H, d, *J* = 8.3 Hz, Np), 7.97 (2H, d, *J* = 8.2 Hz, Np), 7.88 (2H, d, *J* = 8.0 Hz Np), 7.82 (2H, dd, *J* = 6.9, 1.2 Hz, Np), 7.50 (2H, s, *J* = 4.9 Hz, Th), 7.41–7.47 (4H, m, Np), 7.31 (2H, ddd, *J* = 8.3, 6.9, 1.3 Hz, Np). ^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 211.0, 154.8, 136.6, 136.7, 135.3, 133.7, 132.1, 131.3, 130.7, 129.4, 128.4, 126.6, 126.2, 125.6. One peak was not observed probably due to overlapping. HR-MS (APCI, positive) Calcd for $C_{29}H_{18}S_3Si$: $[M+H]^+$: 491.04127, Found: 491.04123. m.p. 268.8-270.3 °C.

Synthesis of (8,8-dimethylsilino[2,3-b:6,5-b']dithiophen-4(8H)-ylidene)hydrazine (4-Me)

To a solution of **3-Me** (0.165 g, 0.618 mmol) in 15 mL of EtOH was added hydrazine monohydrate (0.20 mL, 4.20 mmol) and the mixture was refluxed for 80 min. The mixture was filtered, and the solvent of filtrate was removed to give 0.161 g (0.608 mmol, 98% yield) of **4-Me** as a pale yellowish solid. ^{1}H NMR (in $CDCl_3$, 500 MHz): δ = 8.13 (1H, d, *J* = 4.7 Hz, Th), 7.76 (1H, d, *J* = 4.7 Hz Th), 7.68 (1H, s, *J* = 4.7 Hz, Th), 7.56 (1H, d, *J* = 4.7 Hz, Th), 5.82 (2H, s, NH_2), 0.53 (6H, s, Me). ^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 150.1, 140.6, 140.0, 138.6, 131.2, 130.9, 130.4, 127.9, 127.5, 0.8. HR-MS (APCI, positive) Calcd for $C_{11}H_{12}N_2S_2Si$: $[M+H]^+$: 265.02839, Found: 265.02869. m.p. 102.5-104.7 °C.

Synthesis of (8,8-diphenylsilino[2,3-b:6,5-b']dithiophen-4(8H)-ylidene)hydrazine (4-Ph)

4-Ph was prepared from 0.298 g (0.763 mmol) of **3-Ph** and 0.390 mL (8.20 mmol) of hydrazine monohydrate in 15 mL of EtOH in a manner similar to that above. The product was obtained as a white solid (0.255 g, 0.656 mmol, 86% yield). ^{1}H NMR (in $CDCl_3$, 400 MHz): δ = 8.21 (1H, d, *J* = 4.8 Hz, Th), 7.83 (1H, d, *J* = 4.8 Hz, Th), 7.79 (1H, d, *J* = 4.8 Hz, Th), 7.65 (1H, d, *J* = 4.8 Hz, Th), 7.59–7.63 (4H, m, Ph), 7.34–7.46 (6H, m, Ph), 5.88 (2H, s, NH_2). ^{13}C NMR (in $CDCl_3$, 100 MHz): δ = 151.8, 141.1, 140.1, 135.6, 135.2, 133.2, 132.6, 132.2, 130.4, 128.2, 128.1, 127.8, 126.5. HR-MS (APCI, positive) Calcd for $C_{21}H_{16}N_2S_2Si$: M^+: 388.05242, Found: 388.05231. m.p. 160.7-163.0 °C.

Synthesis of 4-diazo-8,8-dimethyl-4,8-dihydrosilino[2,3-b:6,5-b']dithiophene (5-Me)

To a solution of **4-Me** (0.124 g, 0.469 g) in 10 mL of Et_2O added anhydrous magnesium sulfate (0.549 g, 4.56 mmol),

Ag_2O (0.174 g, 0.751 mmol), and five drops saturated potassium hydroxide methanol solution at –10 °C. The mixture was stirred at room temperature for 2 h while shaded from light. The solution was removed to give 0.0994 g (0.379 mmol, 81% yield) of **5-Me** as a dark reddish oil. This compound was immediately used in the next reaction. ^{1}H NMR (in $CDCl_3$, 500 MHz): δ = 7.76 (2h, d, *J* = 4.8 Hz, Th), 6.99 (2H, d, *J* = 4.8 Hz, Th), 0.57 (s, 6H, Me). ^{13}C NMR spectra could not be obtained due to the low stability. HR-MS (FD, positive) Calcd for $C_{11}H_{10}N_2S_2Si$: M+: 262.00492, Found: 262.00480. IR: Figure S41.

Synthesis of 4-diazo-8,8-diphenyl-4,8-dihydrosilino[2,3-b:6,5-b']dithiophene (5-Ph)

5-Ph was prepared from 0.173 g (0.446 mmol) of **4-Ph**, 0.800 g (6.65 mmol) of anhydrous magnesium sulfate, 0.161 g (0.695 mmol) of Ag_2O, and seven drops saturated potassium hydroxide methanol solution in 15 mL of Et_2O in a manner similar to that above. The ^{1}H NMR spectrum of the reaction solution suggested the formation of the target product, but it was decomposed during the evaporation of the solvent. ^{1}H NMR (in $CDCl_3$, 400 MHz): δ = 7.90 (2H, d, *J* = 4.8 Hz, Th), 7.76 (2H, d, *J* = 4.8 Hz, Th), 7.60–7.64 (4H, m, Ph), 7.36–7.48 (6H, m, Ph).

Synthesis of (8-(2,4,6-triisopropylphenyl)borinino[2,3-b:6,5-b']dithiophen-4(8H)-ylidene)hydrazine (7)

To a solution of **6** (0.214 g, 0.506 mmol) in 20 mL of EtOH was added hydrazine monohydrate (0.16 mL, 3.36 mmol) and the mixture was refluxed for 90 min. The mixture was filtered, and the solvent of filtrate was removed. The crude product was purified by silica gel chromatography using a 1:10 mixture of n-hexane/dichloromethane to give 0.176 g (0.419 mmol, 83% yield) of **7** as a yellowish solid. ^{1}H NMR (in $CDCl_3$, 500 MHz): δ = 8.14 (1H, d, *J* = 4.9 Hz, Th), 7.94 (1H, d, *J* = 4.9 Hz, Th), 7.91 (1H, d, *J* = 4.9 Hz, Th), 7.75 (1H, d, *J* = 4.9 Hz, Th), 7.06 (2H, s, Tip), 6.62 (2H, s, NH_2), 2.98 (1H, quint, *J* = 6.9 Hz, Tip), 2.53 (2H, quint, *J* = 6.7 Hz, Tip), 1.35 (6H, d, *J* = 6.9 Hz, Tip), 1.14 (6H, d, *J* = 6.7 Hz, Tip) 1.12 (6H, d, *J* = 6.7 Hz, Tip). ^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 150.9, 150.5, 148.9, 139.2, 137.9, 136.6, 135.8, 127.6, 126.4, 120.2, 35.7, 34.4, 24.9, 24.6, 24.2. Three signals for B−C were not detected, probably due to its low intensity as a result of quadrupolar broadening. ^{11}B NMR (in $CDCl_3$, 160 MHz): δ = 50.1. HR-MS (APCI, positive) Calcd for $C_{24}H_{29}BN_2S_2$: $[M+H]^+$: 421.19380, Found: 421.19366. m.p. 206.3-208.4 °C (decomp.).

Synthesis of 4-diazo-8-(2,4,6-triisopropylphenyl)-4,8-dihydroborinino[2,3-b:6,5-b']dithiophene (8)

To a solution of **7** (0.176 g, 0.419 mmol) in 45 mL of CH_2Cl_2 was cooled at 0 °C and added anhydrous magnesium sulfate (0.791 g, 6.57 mmol), MnO_2 (1.09 g, 12.6 mmol), and KOH (0.433 g, 7.71 mmol). The mixture was stirred at same temperature overnight while shaded from light. The solution was removed to give 0.164 g (0.392 mmol, 94% yield) of **8** as a reddish solid. This compound was immediately used in the next reaction. ^{1}H NMR (in $CDCl_3$, 500 MHz): δ = 1.12 (12H, d, *J* = 6.8 Hz, Tip), 1.37 (6H, d, *J* = 6.9 Hz, Tip), 2.55 (2H, quint, *J* = 6.7 Hz, Tip), 3.00 (1H, quint, *J* = 7.0 Hz, Tip), 7.08 (2H, s, Tip), 7.34 (2H, d, *J* = 5.0 Hz, Th), 7.93 (2H, d, *J* = 5.0 Hz, Th). ^{13}C NMR spectra were not obtained due to difficulty in purifying 8. ^{11}B NMR (in $CDCl_3$, 160 MHz): δ = 45.5. HR-MS (ESI, positive) Calcd for $C_{24}H_{27}BN_2S_2$: $[M+H]^+$: 419.17815, Found: 419.17804. decomp. 132.2 °C. IR: Figure S47.

Synthesis of DTCB-SiMe

To a solution of **5-Me** (0.124 g, 0.472 mmol) and **6** (0.211 g, 0.498 mmol) in 15 mL of benzene was added PPh_3 (0.136 g, 0.519 mmol) and refluxed for 2 h. The solution was removed and the crude was purified by silica gel chromatography using a 1:1 mixture of n-hexane/dichloromethane to give 0.176 g (0.282 mmol, 60% yield) of **DTCB-SiMe** as a yellowish-green solid. ^{1}H NMR (in $CDCl_3$, 500 MHz): δ = 7.39 (2H, d, *J* = 4.9 Hz, Th), 7.35 (2H, d, *J* = 4.7 Hz, Th), 7.08 (2H, d, *J* = 4.7 Hz, Th), 7.05 (2H, s, Tip), 7.00 (2H, d, *J* = 4.9 Hz, Th), 2.98 (1H, quint, *J* = 6.9 Hz, Tip), 2.60 (2H, br, Tip), 1.35 (6H, d, *J* = 6.9 Hz, Tip), 1.20 (12H, d, *J* = 6.7 Hz, Tip), 0.68 (6H, s, Me). ^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 152.8, 151.1, 150.4, 148.7, 144.6 (br), 136.5, 136.1 (br), 135.6 (br), 131.8, 131.7, 131.5, 130.1 (br), 129.1, 120.3, 35,8, 34.4, 24.9, 24.3, 0.7. ^{11}B NMR (in $CDCl_3$, 160 MHz): δ = 50.1. HR-MS (APCI, positive) Calcd for $C_{35}H_{37}BS_4$:Si: M^+: 624.16404, Found: 624.16449. m.p. 252.6-256.1 °C.

Synthesis of DTCB-SiPh

DTCB-SiPh was prepared from 0.103 g (0.247 mmol) of **8**, 0.112 g (0.287 mmol) of **3-Ph** and 0.0773 (0.295 mmol) of PPh_3 in 12 mL of benzene in a manner similar to that above. The product was obtained as a yellowish-green solid (0.0660 g, 0.0881 mmol, 36% yield). ^{1}H NMR (in $CDCl_3$, 500 MHz): δ = 7.74 (4H, d, *J* = 6.8 Hz, Ph), 7.40–7.50 (8H, overlapped), 7.37 (2H, d, *J* = 4.9 Hz, Th), 7.19 (2H, br, Th), 7.04 (2H, s, Tip), 7.01 (2H, br, Th), 2.96 (1H, quint, *J* = 6.9 Hz Tip), 2.58 (1H, br, Tip), 1.34 (6H, d, *J* = 6.9 Hz, Tip), 1.18 (12H, d, *J* = 6.7 Hz, Tip). ^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 153.4 (br), 151.0 (br), 150.4, 148.7, 144.6 (br), 136.0 (B-C), 135.8, 135.1 (br), 133.5, 132.62, 132.56 (br), 131.8, 131.6, 131.1 (br), 130.7, 130.3, 128.4, 120.3, 35.8, 34.4, 24.9, 24.2. ^{11}B NMR (in $CDCl_3$, 160 MHz): δ = 50.5. HR-MS (APCI, positive) Calcd for $C_{45}H_{41}BS_4Si$: M^+: 748.19534, Found: 748.19653. m.p. 284.1-285.9 °C.

Synthesis of DTCB-SiNp

DTCB-SiNp was prepared from 0.235 g (0.561 mmol) of **8**, 0.256 g (0.522 mmol) of **3-Np** and 0.143 (0.545 mmol) of PPh_3 in 40 mL of benzene in a manner similar to that above. The product was obtained as a yellowish-green solid (0.123 g, 0.144 mmol, 28% yield). ^{1}H NMR (in $CDCl_3$, 500 MHz): δ = 7.98 (d, *J* = 8.2 Hz, Np), 7.90 (4H, overlapped), 7.41–7.48 (4H, m, Np), 7.39 (2H, d, *J* = 4.7 Hz, Th), 7.33 (2H, d, *J* = 4.8 Hz, Th), 7.28 (2H, br, Np), 7.10 (2H, d, *J* = 4.7 Hz, Th), 7.03 (2H, s, Tip), 6.86 (2H, br, Th), 2.96 (1H, p, *J* = 6.9 Hz, Tip), 2.55 (2H, br, Tip), 1.33 (6H, d, *J* = 6.9 Hz, Tip), 1.17 (12H, d, *J* = 6.7 Hz, Tip). ^{13}C NMR (in $CDCl_3$, 125 MHz): δ = 153.4, 151.4, 150.3, 148.7, 144.5 (br), 137.5 (br), 137.1, 135.9 (br), 134.7, 134.4 (br), 133.7, 131.93, 131.89 (br), 131.7, 131.6, 130.6, 130.4 (br), 129.2 126.2, 125.9, 125.5, 120.3, 35.8, 34.4, 24.8, 24.2. One peak was not observed probably due to overlapping. ^{11}B NMR (in $CDCl_3$, 160 MHz): δ = 51.1. HR-MS (APCI, positive) Calcd for $C_{53}H_{45}BS_4Si$: M^+: 848.22664, Found: 848.22742. m.p. >300 °C (decomp).

Supporting figures and tables

Table S1 DFT-calculated Gibbs free energies of BAEs at the B3LYP/6-31G(d) level at 298 K.

Compound	Conformer	G^{DFT} /kJ mol^{-1}	ΔG^{DFT} [a]/ kJ mol^{-1}
Bianthrone	*anti*-folded	-3220838.80	+10.1
	twisted	-3220828.70	
Bifluorelinydene	*anti*-folded	-2625764.09	-40.4
	twisted	-2625804.51	
Biacridinylidene	*anti*-folded	-3122617.76	+37.9
	twisted	-3122579.82	
FA	*anti*-folded	-2874204.94	+4.9
	twisted	-2874200.00	
dDTCB	*anti*-folded	-12650506.85	-38.4
	twisted	-12650544.90	

[a] ΔG = G(twisted) – G(*anti*-folded).

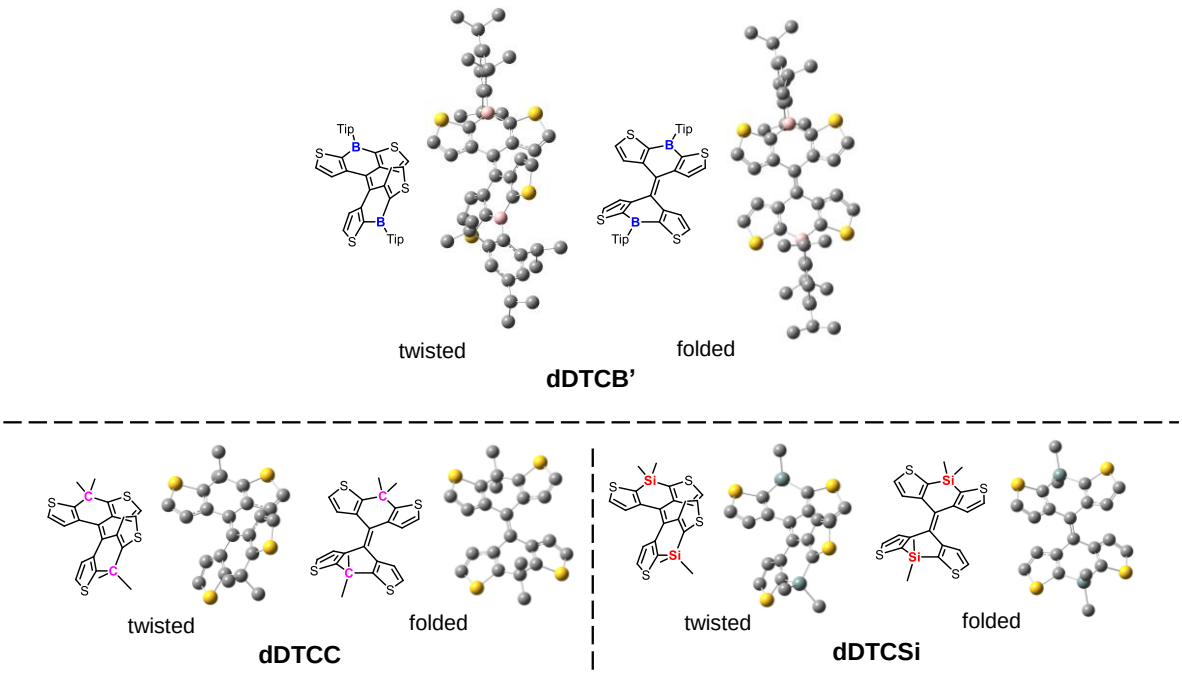
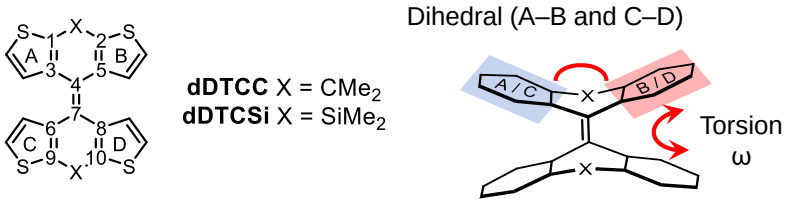


Figure S1 Optimized structures of conformational isomers of **dDTCB'**, **dDTCC**, and **dDTCSi** at the B3LYP/6-31G(d) level. Hydrogen atoms are omitted for clarity.

Table S2 Calculated geometrical parameters of **dDTCC** and **dDTCSi** at the B3LYP/6-31G(d) level of theory.

Compound	Conformer	Bond length /Å			Dihedral angle[a] /°		Torsions / °	
		C1-X/ C2-X	C9-X/ C10-X	C4-C7	A-B	C-D	τ(C3-C4-C7-C6)/ τ(C5-C4-C7-C8)	ω[b] /°
dDTCC	*anti*-folded	1.521/ 1.521	1.521/ 1.521	1.370	43.5	43.5	-1.2/1.2	0
	twisted	1.514/ 1.514	1.514/ 1.514	1.400	0.3	0.3	43.9/43.9	43.9
dDTCSi	*anti*-folded	1.873/ 1.873	1.873/ 1.873	1.370	48.0	48.0	0.6/-0.6	0
	twisted	1.861/ 1.861	1.861/ 1.861	1.416	6.3	6.3	49.3/49.3	49.3



[a] Dihedral angle between the two mean planes (A–B and C–D) is defined as the dihedral angle between the least-square planes of the atoms in the thiophene rings of each tricyclic structure. [b] Torsion angle (ω) around C4=C7 is defined as the absolute value of average of the dihedral angles (τC3–C4–C7-C6) and τ(C5–C4–C7–C8).

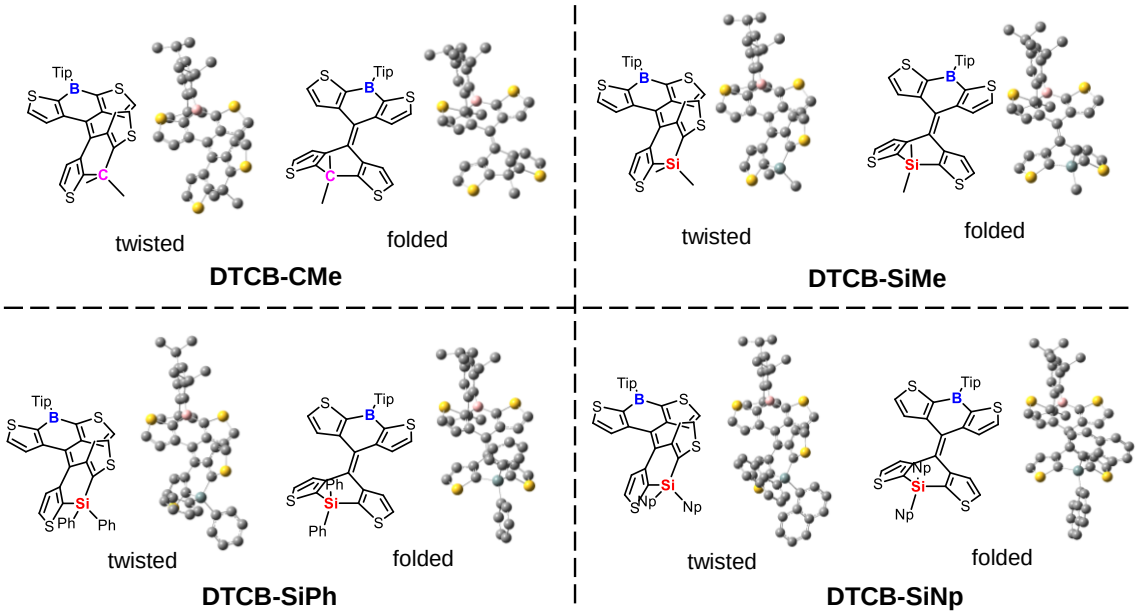


Figure S2 Optimized structures of conformational isomers of **DTCB-CMe**, **DTCB-SiMe**, **DTCB-SiPh**, and **DTCB-SiNp** at the B3LYP/6-31G(d) level. Hydrogen atoms are omitted for clarity.

Table S3 Calculated geometrical parameters of **DTCB-CMe**, **DTCB-SiMe**, **DTCB-SiPh** and **DTCB-SiNp** at the B3LYP/6-31G(d) level of theory.

Compound	Conformer	Bond length /Å			Dihedral angle[a] /°		Torsions / °	
		C1-B/ C2-B	C9-X/ C10-X	C4-C7	A-B	C-D	τ(C3-C4-C7-C6)/ τ(C5-C4-C7-C8)	ω[b] /°
DTCB-CMe	*anti*-folded	1.538/ 1.538	1.522/ 1.522	1.378	32.1	49.0	-2.7/2.7	0
	twisted	1.529/ 1.529	1.512/ 1.512	1.413	2.5	0.8	46.7/46.7	46.7
DTCB-SiMe	*anti*-folded	1.538/ 1.538	1.878/ 1.878	1.376	29.9	55.8	-1.8/1.8	0
	twisted	1.530/ 1.530	1.863/ 1.863	1.419	1.9	6.2	49.3/49.3	49.3
DTCB-SiPh	*anti*-folded	1.538/ 1.538	1.876/ 1.876	1.375	30.2	55.6	-1.8/1.8	0
	twisted	1.530/ 1.530	1.864/ 1.864	1.419	2.0	6.8	49.2/49.2	49.2
DTCB-SiNp	*anti*-folded	1.539/ 1.538	1.879/ 1.883	1.375	30.3	54.8	-2.8/0.8	1.0
	twisted	1.530/ 1.530	1.865/ 1.874	1.420	1.9	8.0	49.4/49.1	49.3

[a] Dihedral angle between the two mean planes (A–B and C–D) is defined as the dihedral angle between the least-square planes of the atoms in the thiophene rings of each tricyclic structure. [b] Torsion angle (ω) around C4=C7 is defined as the absolute value of average of the dihedral angles (τC3–C4–C7-C6) and τ(C5–C4–C7–C8).

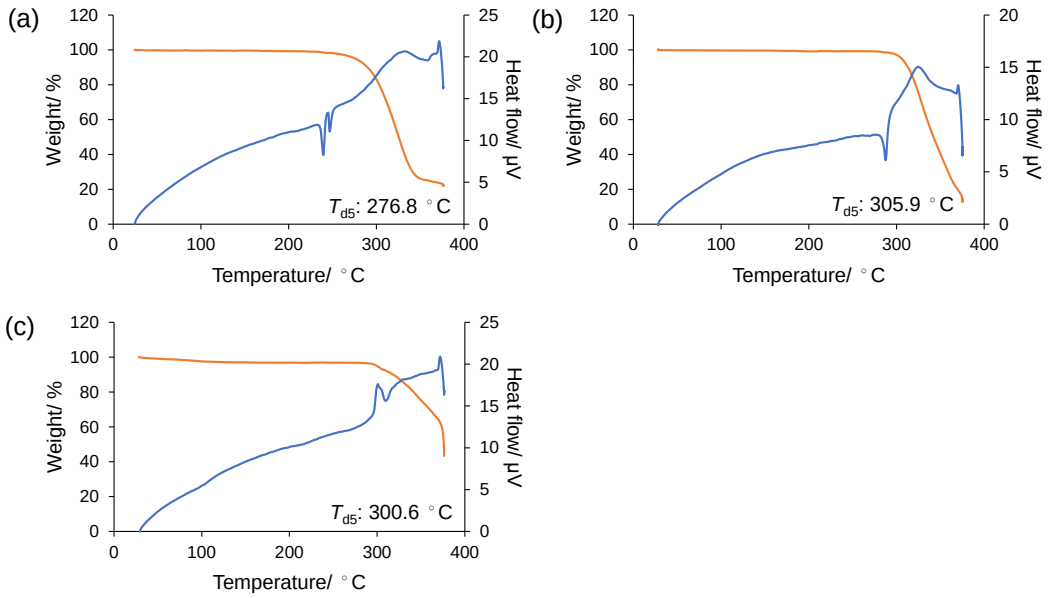


Figure S3 TG-DTA curves of (a) **DTCB-SiMe**, (b) **DTCB-SiPh**, and (c) **DTCB-SiNp** at a heating rate of 10 °C/min in air.

Table S4 Optical properties of **DTCB-SiMe**, **DTCB-SiPh** and **DTCB-SiNp** in toluene.

Compound	λ^{abs}(max) / nm	λ^{PL}(max)[a] / nm
DTCB-SiMe	596, 399	470
DTCB-SiPh	601, 401	472
DTCB-SiNp	608, 402	473

[a] excited at the absorption maxima around 400 nm.

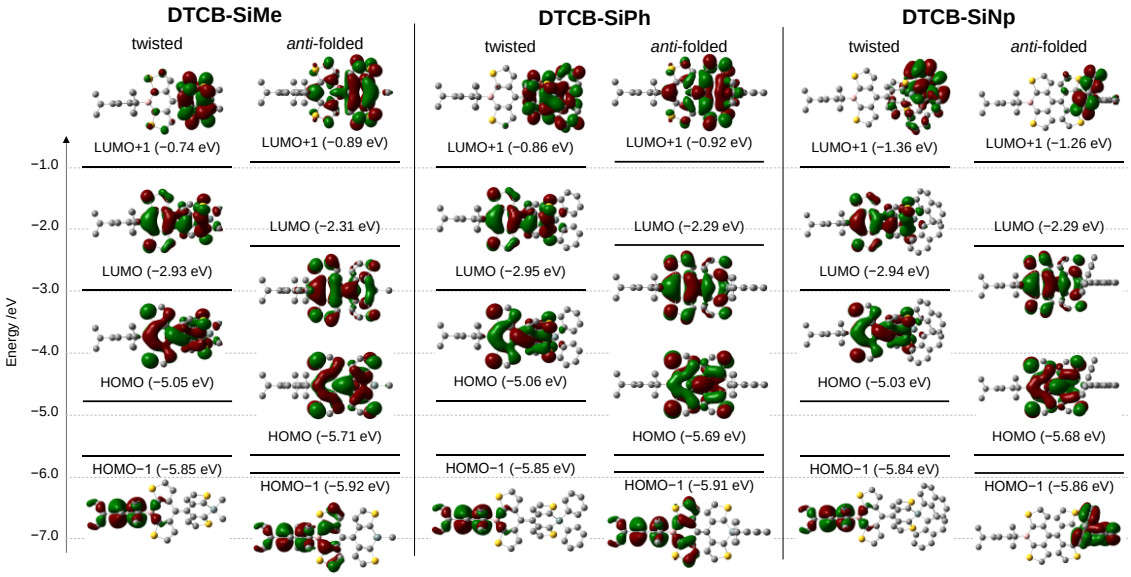


Figure S4 Kohn–Sham orbitals of the twisted and *anti*-folded conformers of **DTCB-SiMe**, **DTCB-SiPh**, and **DTCB-SiNp** at the B3LYP/6-31G(d) level. Hydrogen atoms are omitted for clarity.

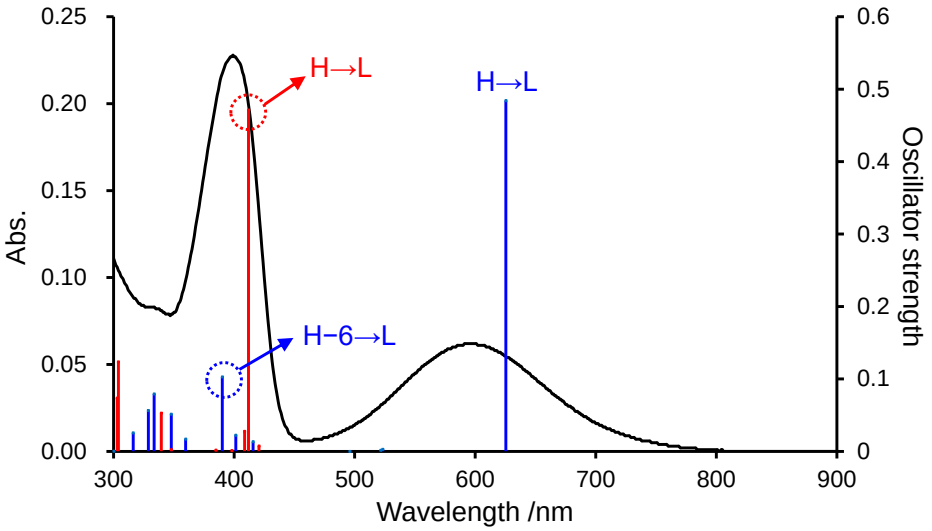


Figure S5 Experimental absorption spectrum in toluene (black line) and TD-DFT (red line: *anti*-folded, blue line: twisted) results at the B3LYP/6-31+G(d) level for **DTCB-SiMe**. H and L denote HOMO and LUMO, respectively.

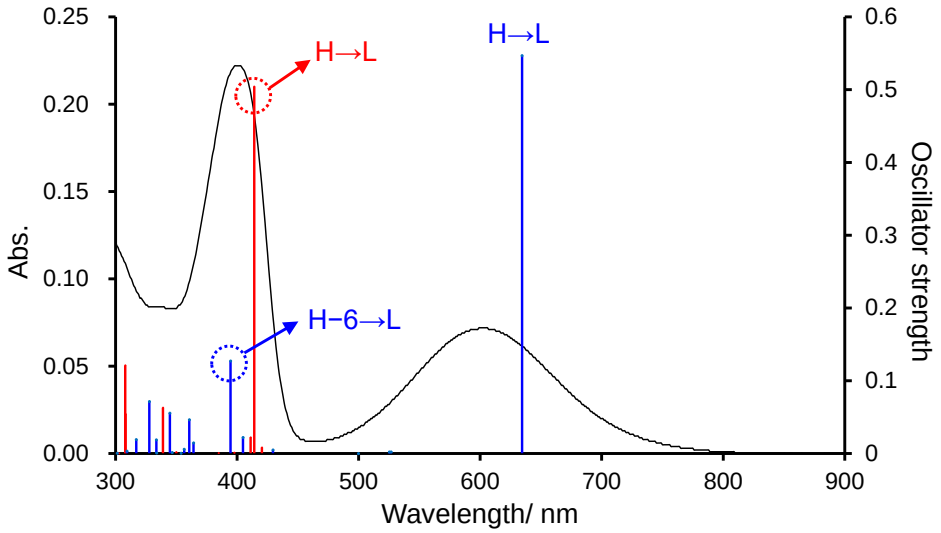


Figure S6 Experimental absorption spectrum in toluene (black line) and TD-DFT (red line: *anti*-folded, blue line: twisted) results at the B3LYP/6-31+G(d) level for **DTCB-SiPh**. H and L denote HOMO and LUMO, respectively.

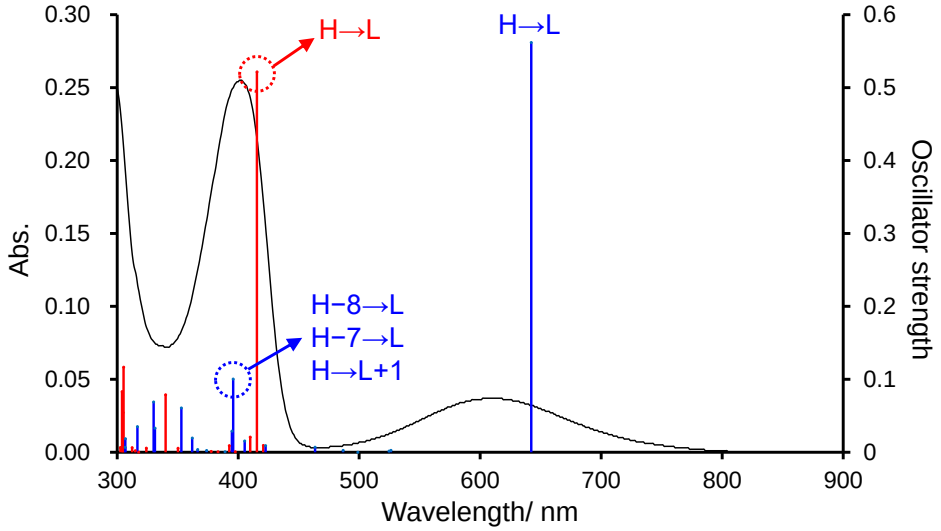


Figure S7 Experimental absorption spectrum in toluene (black line) and TD-DFT (red line: *anti*-folded, blue line: twisted) results at the B3LYP/6-31+G(d) level for **DTCB-SiNp**. H and L denote HOMO and LUMO, respectively.

Table S5 TD-DFT data for the *anti*-folded conformer of **DTCB-SiMe**.

Excited state	Composition[a]	CI	Excitation energy /eV	Wavelength /nm	f[b]
$S_0 \rightarrow S_1$	H−1→L	0.690	2.95	421	0.01
$S_0 \rightarrow S_2$	H→L	0.699	3.01	412	0.47
$S_0 \rightarrow S_3$	H−3→L	0.524	3.03	409	0.03
	H−2→L	0.464			
$S_0 \rightarrow S_7$	H−6→L	0.696	3.65	340	0.05
$S_0 \rightarrow S_8$	H−9→L	0.105	4.08	304	0.12
	H−7→L	0.545			
	H→L+1	-0.412			
$S_0 \rightarrow S_9$	H−8→L	0.698	4.09	303	0.07

[a] H and L denote HOMO and LUMO, respectively. [b] Oscillator strength.

Table S6 TD-DFT data for the twisted conformer of **DTCB-SiMe**.

Excited state	Composition[a]	CI	Excitation energy /eV	Wavelength /nm	f[b]
$S_0 \rightarrow S_1$	H→L	0.712	1.98	625	0.48
		-0.136			
$S_0 \rightarrow S_5$	H−5→L	-0.164	2.98	416	0.01
	H−4→L	0.675			
	H→L+1	0.114			
$S_0 \rightarrow S_6$	H−5→L	0.670	3.09	401	0.02
	H−4→L	0.178			
	H→L+1	-0.114			
$S_0 \rightarrow S_7$	H−6→L	0.695	3.18	390	0.10
$S_0 \rightarrow S_8$	H−7→L	0.688	3.45	360	0.02
	H→L+2	-0.117			
$S_0 \rightarrow S_9$	H−8→L	0.659	3.56	348	0.05
	H→L+1	0.235			
$S_0 \rightarrow S_{10}$	H−8→L	-0.238	3.72	334	0.08
	H−5→L	0.124			
	H→L+1	0.643			
$S_0 \rightarrow S_{11}$	H−9→L	-0.215	3.77	329	0.06
	H−7→L	0.106			
	H→L+2	0.653			
$S_0 \rightarrow S_{12}$	H−9→L	-0.261	3.92	316	0.03
	H→L+3	0.647			

[a] H and L denote HOMO and LUMO, respectively. [b] Oscillator strength.

Table S7 TD-DFT data for the *anti*-folded conformer of **DTCB-SiPh**.

Excited state	Composition[a]	CI	Excitation energy /eV	Wavelength /nm	f[b]
$S_0 \rightarrow S_1$	H−1→L	0.695	2.95	420	0.01
$S_0 \rightarrow S_2$	H→L	0.699	2.99	414	0.50
$S_0 \rightarrow S_3$	H−3→L	-0.411	3.02	411	0.02
	H−2→L	0.559			
$S_0 \rightarrow S_7$	H−6→L	0.696	3.66	339	0.06
$S_0 \rightarrow S_8$	H−12→L	-0.223	4.02	308	0.05
	H−10→L	0.150			
	H−8→L	0.156			
	H−7→L	0.627			
$S_0 \rightarrow S_9$	H−11→L	0.141	4.03	308	0.12
	H−9→L	0.564			
	H→L+1	-0.368			

[a] H and L denote HOMO and LUMO, respectively. [b] Oscillator strength.

Table S8 TD-DFT data for the twisted conformer of **DTCB-SiPh**.

Excited state	Composition[a]	CI	Excitation energy /eV	Wavelength /nm	f[b]
$S_0 \rightarrow S_1$	H→L	0.712	1.95	634	0.55
		-0.134			
$S_0 \rightarrow S_5$	H−4→L	0.692	2.89	430	0.01
$S_0 \rightarrow S_6$	H−5→L	0.687	3.06	405	0.02
	H−4→L	-0.102			
$S_0 \rightarrow S_7$	H−6→L	0.695	3.14	395	0.13
$S_0 \rightarrow S_8$	H−10→L	-0.240	3.4	364	0.01
	H−8→L	-0.274			
	H−7→L	0.593			
$S_0 \rightarrow S_9$	H−12→L	0.101	3.44	361	0.05
	H−11→L	0.107			
	H−9→L	0.631			
	H→L+1	-0.256			
$S_0 \rightarrow S_{10}$	H−10→L	0.635	3.48	356	0.01
	H−7→L	0.284			
$S_0 \rightarrow S_{13}$	H−9→L	0.257	3.60	345	0.06
	H→L+1	0.643			
$S_0 \rightarrow S_{15}$	H−12→L	0.691	3.72	334	0.02
$S_0 \rightarrow S_{16}$	H−13→L	-0.155	3.78	328	0.07

	H→L+2	0.163			
	H→L+3	0.650			
	H→L+5	0.116			
$S_0 \rightarrow S_{17}$	H−13→L	0.241	3.91	317	0.02
	H→L+2	-0.115			
	H→L+3	0.640			

[a] H and L denote HOMO and LUMO, respectively. [b] Oscillator strength.

Table S9 TD-DFT data for the *anti*-folded conformer of **DTCB-SiPh**.

Excited state	Composition[a]	CI	Excitation energy /eV	Wavelength /nm	f[b]
$S_0 \rightarrow S_1$	H−4→L	0.118	2.95	421	0.01
	H−2→L	0.632			
	H−1→L	0.273			
$S_0 \rightarrow S_2$	H→L	0.697	2.98	416	0.52
$S_0 \rightarrow S_3$	H−4→L	0.457	3.02	410	0.02
	H−3→L	0.524			
$S_0 \rightarrow S_5$	H−6→L	-0.133	3.16	393	0.01
	H−5→L	0.114			
	H−2→L	-0.275			
	H−1→L	0.623			
$S_0 \rightarrow S_8$	H−7→L	0.696	3.54	350	0.01
$S_0 \rightarrow S_9$	H−8→L	0.694	3.65	340	0.08
$S_0 \rightarrow S_{10}$	H→L+1	0.670	3.83	324	0.01
$S_0 \rightarrow S_{13}$	H−11→L	-0.116	3.97	312	0.01
	H−10→L	0.597			
	H−9→L	0.348			
$S_0 \rightarrow S_{14}$	H−10→L	0.152	4.06	305	0.12
	H−12→L	0.558			
	H→L+3	0.340			
$S_0 \rightarrow S_{15}$	H−5→L+1	-0.125	4.07	305	0.05
	H−2→L+1	-0.230			
	H−1→L+1	0.591			
	H−1→L+2	-0.220			
$S_0 \rightarrow S_{16}$	H−12→L	0.524	4.08	304	0.08
	H−11→L	-0.322			
	H−1→L+2	-0.119			
	H→L+3	0.264			

$S_0 \rightarrow S_{17}$	H−12→L	0.138	4.10	303	0.01
	H−5→L+1	-0.113			
	H−5→L+2	0.228			
	H−2→L+2	-0.221			
	H−1→L+1	0.222			
	H−1→L+2	0.541			

[a] H and L denote HOMO and LUMO, respectively. [b] Oscillator strength.

Table S10 TD-DFT data for the twisted conformer of **DTCB-SiNp**.

Excited state	Composition[a]	CI	Excitation energy /eV	Wavelength /nm	f[b]
$S_0 \rightarrow S_1$	H→L	0.712	1.93	642	0.56
		-0.133			
$S_0 \rightarrow S_6$	H−5→L	0.700	2.67	464	0.01
$S_0 \rightarrow S_7$	H−7→L	-0.114	2.93	423	0.01
	H−6→L	0.676			
$S_0 \rightarrow S_8$	H−7→L	0.643	3.06	405	0.02
	H−6→L	0.153			
	H→L+1	-0.202			
$S_0 \rightarrow S_9$	H−8→L	0.584	3.13	396	0.10
	H−7→L	-0.188			
	H→L+1	-0.325			
$S_0 \rightarrow S_{10}$	H−8→L	0.359	3.14	395	0.03
	H−7→L	0.141			
	H→L+1	0.579			
$S_0 \rightarrow S_{14}$	H−11→L	0.673	3.42	362	0.02
	H−10→L	0.143			
	H→L+4	-0.108			
$S_0 \rightarrow S_{15}$	H−12→L	0.689	3.50	353	0.06
	H→L+3	0.116			
$S_0 \rightarrow S_{16}$	H−12→L	-0.112	3.74	331	0.03
	H→L+3	0.668			
$S_0 \rightarrow S_{17}$	H−13→L	-0.207	3.76	330	0.07
	H→L+4	0.648			
$S_0 \rightarrow S_{18}$	H−13→L	-0.228	3.91	317	0.04
	H→L+5	0.436			
	H→L+6	0.420			
	H→L+7	-0.233			

$S_0 \rightarrow S_{19}$	H−5→L+1	-0.108	4.04	307	0.02
	H−3→L+1	0.493			
	H−3→L+2	0.112			
	H→L+5	0.359			
	H→L+6	-0.289			
$S_0 \rightarrow S_{20}$	H−5→L+1	-0.134	4.04	307	0.01
	H−3→L+1	0.427			
	H−3→L+2	0.124			
	H→L+5	-0.383			
	H→L+6	0.333			

[a] H and L denote HOMO and LUMO, respectively. [b] Oscillator strength.

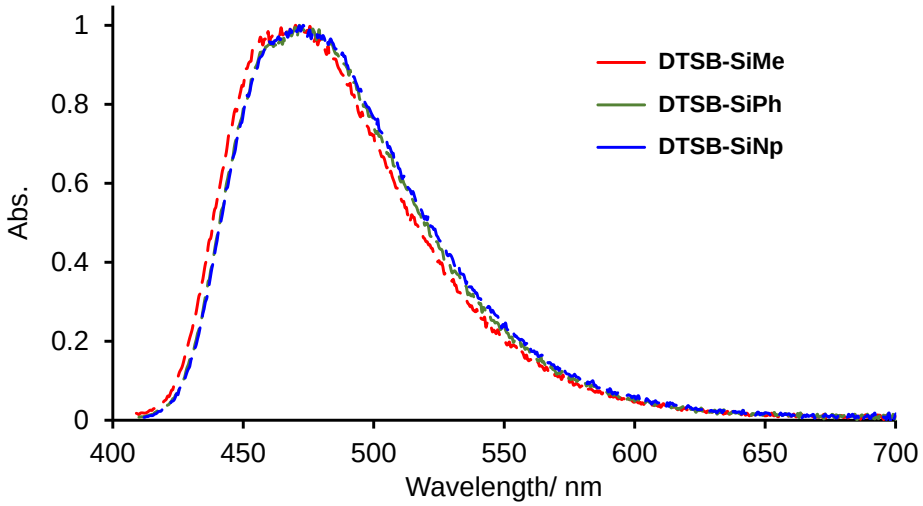


Figure S8 Photoluminescence spectra of **DTCB-SiMe**, **DTCB-SiPh**, and **DTCB-SiNp** in toluene at the concentration of 10 μmol/L.

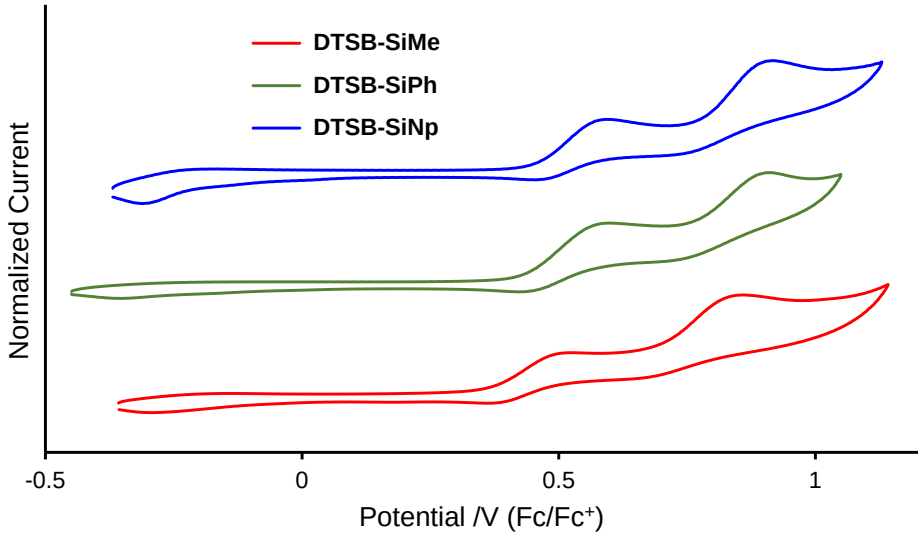


Figure S9 Anoic cyclic voltammetry data of boron-silicon hybrid BAEs in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 at the scan rate of 100 mV/s.

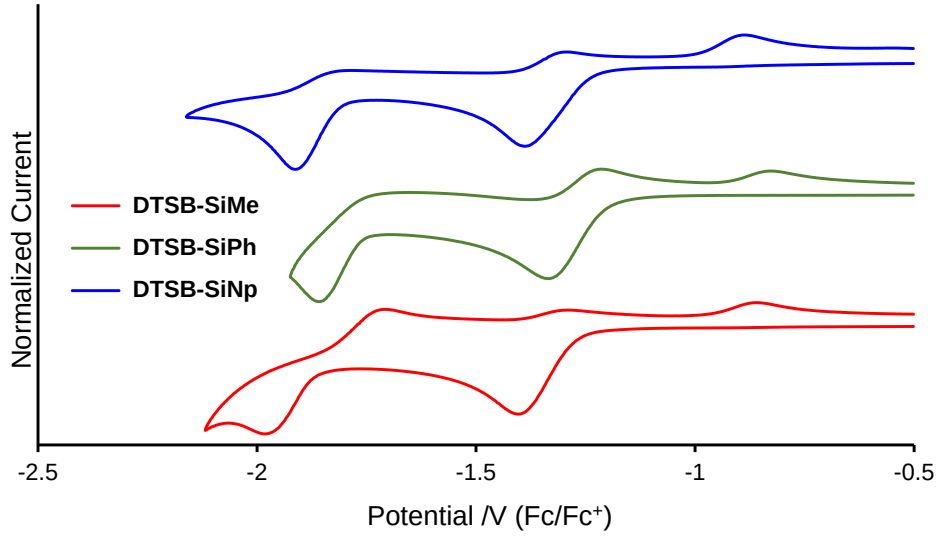


Figure S10 Cathodic cyclic voltammetry data of boron-silicon hybrid BAEs in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 at the scan rate of 100 mV/s.

Table S11 Optical and electrochemical properties of **DTCB-SiMe**, **DTCB-SiPh**, and **DTCB-SiNp** in solution.

Compound	E_{red}^{1}[a] /V	E_{red}^{2}[a] /V	E_{ox}^{1}[a] /V	E_{ox}^{2}[a] /V	HOMO /eV	LUMO /eV	$E_g^{1}{}_{(CV)}$[b] /eV	$E_g^{2}{}_{(CV)}$[c] /eV	λ_{onset}[d] /nm	$E_{g(Opt)}$[e] /eV
DTCB-SiMe	-1.38	-1.77	0.36	0.59	-5.16	-3.43	1.74	2.36	724	1.71
DTCB-SiPh	-1.20	-1.71	0.44	0.65	-5.24	-3.60	1.64	2.36	727	1.71
DTCB-SiNp	-1.24	-1.78	0.46	0.71	-5.26	-3.56	1.70	2.49	753	1.65

[a] Onset potential as $Fc/Fc^{0/+}$; [b] $E_g^{1}(CV) = E^{1}_{ox} - E^{1}_{red}$; [c] $E_g^{2}(CV) = E^{2}_{ox} - E^{2}_{red}$; [d] Absorption onset in toluene; [e] Obtained from the absorption onset in toluene.

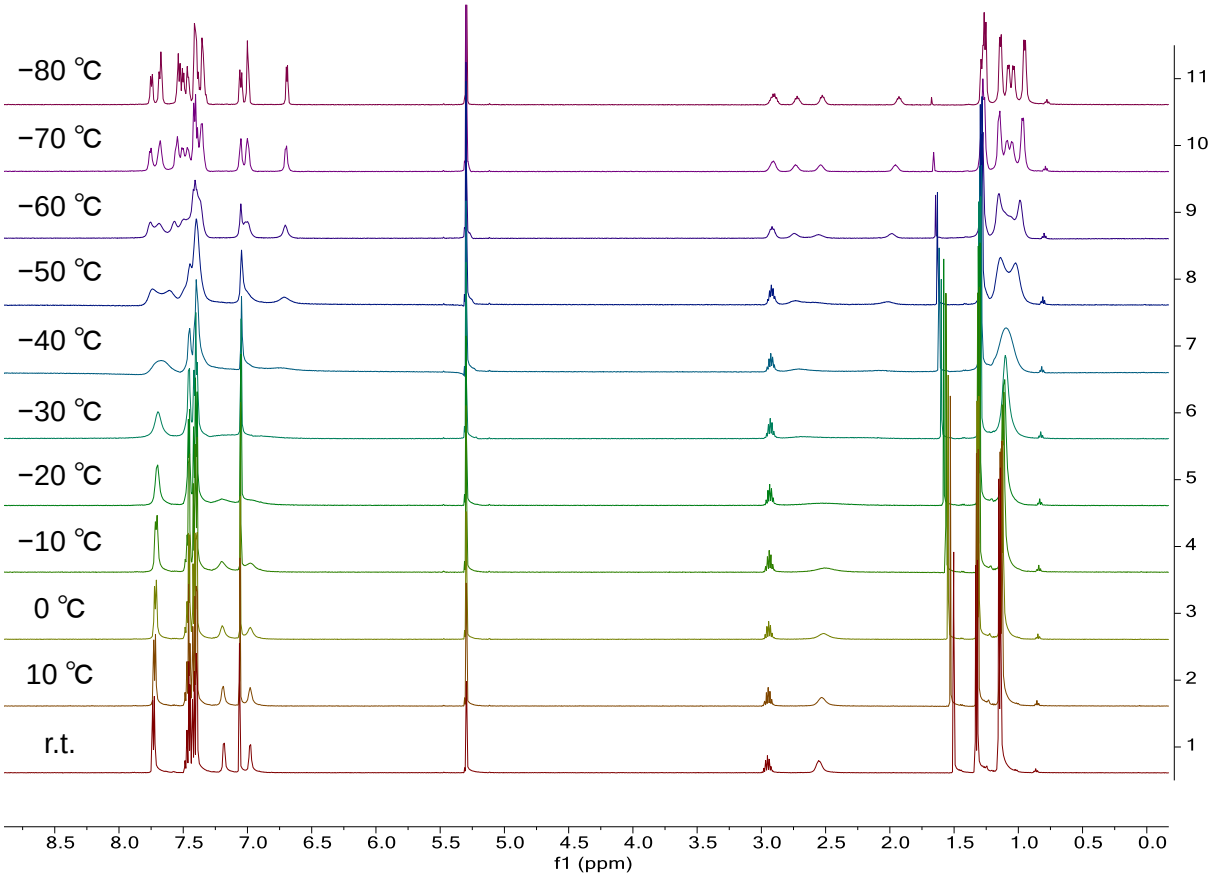


Figure S11 Variable temperature ^{1}H NMR spectra of **DTCB-SiPh** in CD_2Cl_2 from room temperature to −80 ℃.

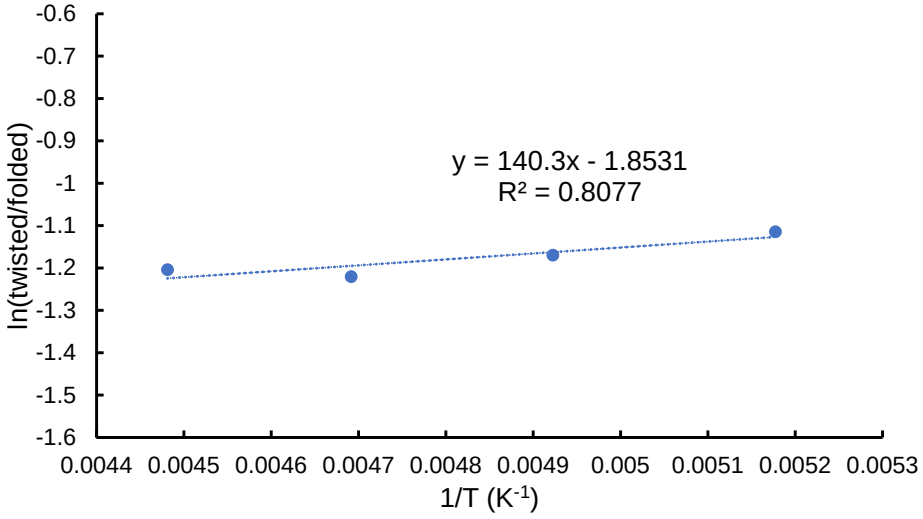


Figure S12 Van't Hoff plot derived from variable temperature ^{1}H NMR spectra of **DTCB-SiPh** of the equilibrium between the *anti*-folded and twisted conformers.

Table S12 Geometrical parameters of **DTCB-SiMe**, **DTCB-SiPh** and **DTCB-SiNp** in the crystal structures.

Compounds	Conformer	Bond length /Å			Dihedral angle[a] /°		Torsions / °	
		C1-B/ C2-B	C9-Si/ C10-Si	C4-C7	A-B	C-D	τ(C3-C4-C7-C6)/ τ(C5-C4-C7-C8)	ω[b] /°
DTCB-SiMe	*anti*-folded	1.531(2)/ 1.532(2)	1.870(1)/ 1.869(1)	1.361(2)	34.3	55.7	-5.9/-0.5	3.2
DTCB-SiPh	*anti*-folded	1.532(2)/ 1.531(3)	1.859(2)/ 1.868(2)	1.362(2)	33.6	58.3	-3.6/-2.9	3.3
DTCB-SiNp	*anti*-folded	1.540(2)/ 1.537(2)	1.861(1)/ 1.871(1)	1.361(2)	33.9	56.5	-9.3/-2.9	6.1

[a] Dihedral angle between the two mean planes of the tricyclic structures (A–B and C–D), which is defined as the dihedral angle between the least-square planes of the atoms in the thiophene rings of each tricyclic structure. [b] Torsion angle (ω) around C4=C7 is defined as the absolute value of average of the dihedral angles τ(C3–C4–C7-C6) and τ(C5–C4–C7–C8).

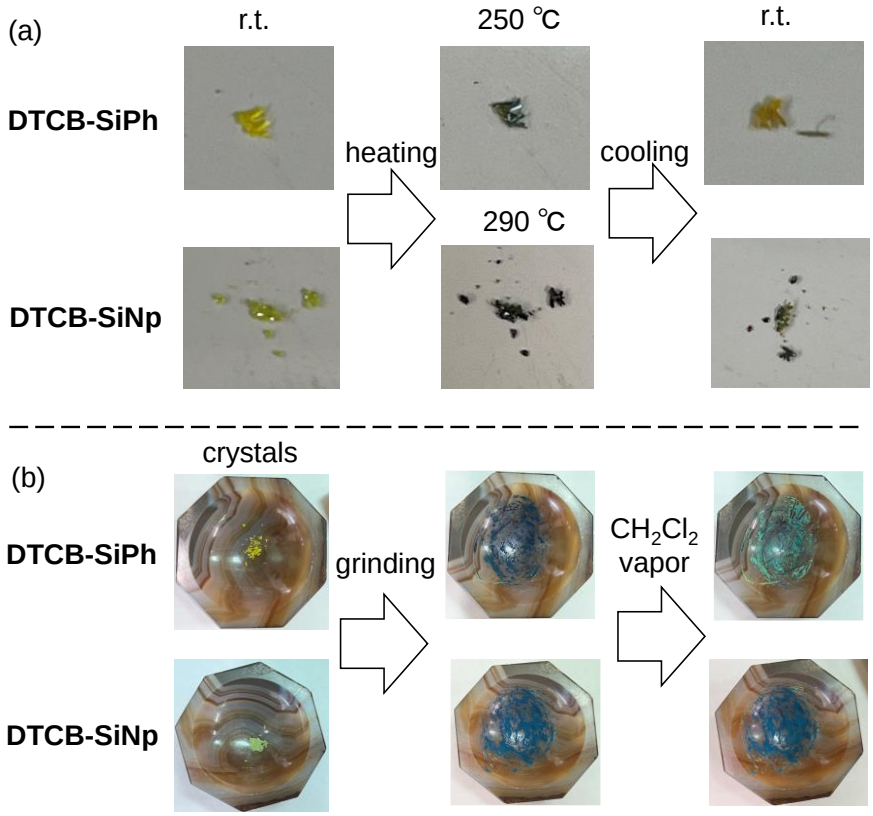


Figure S13 Thermochromism and mechanochromism of crystals of **DTCB-SiPh** and **DTCB-SiNp** in variable temperature.

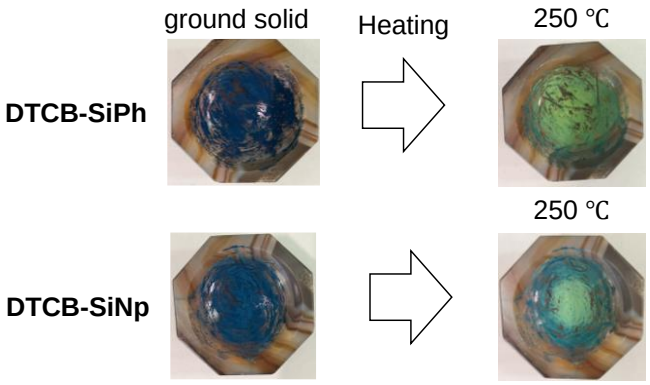


Figure S14 Thermal annealing of the ground solid of **DTCB-SiPh** and **DTCB-SiNp**.

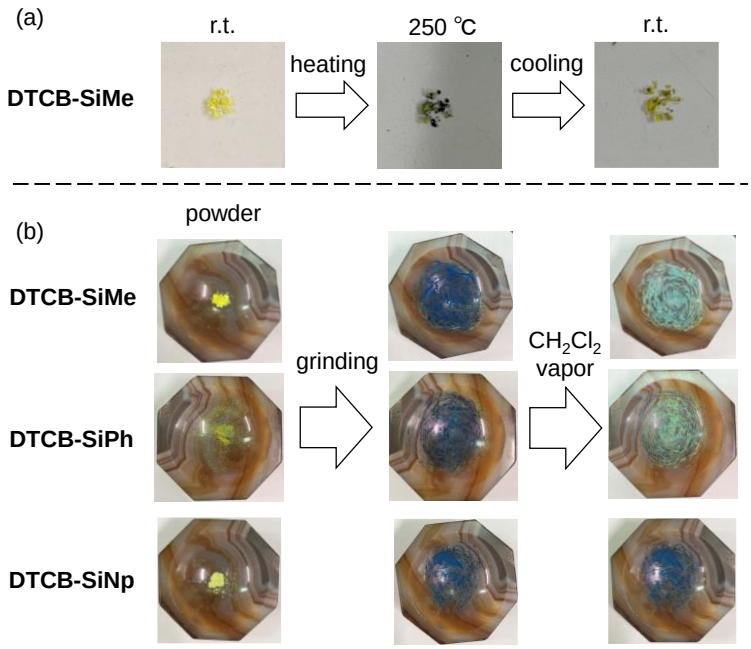


Figure S15 (a) Thermochromism and (b) mehanochromism of precipitated solid.

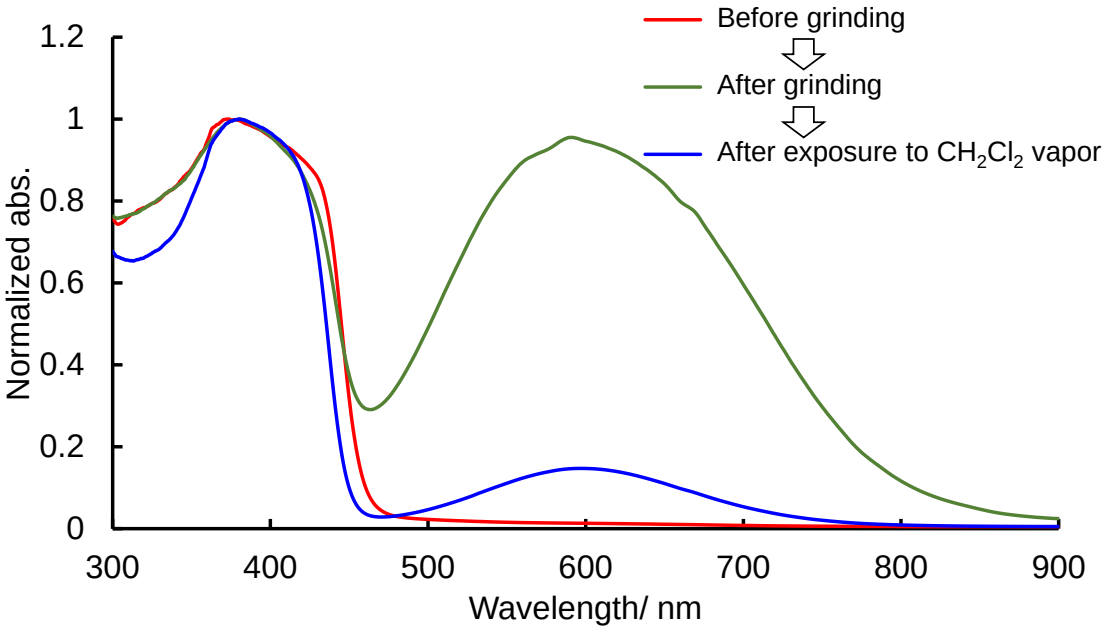


Figure S16 Normalized absorption spectra of **DTCB-SiMe** as solids converted from the diffuse reflectance spectra.

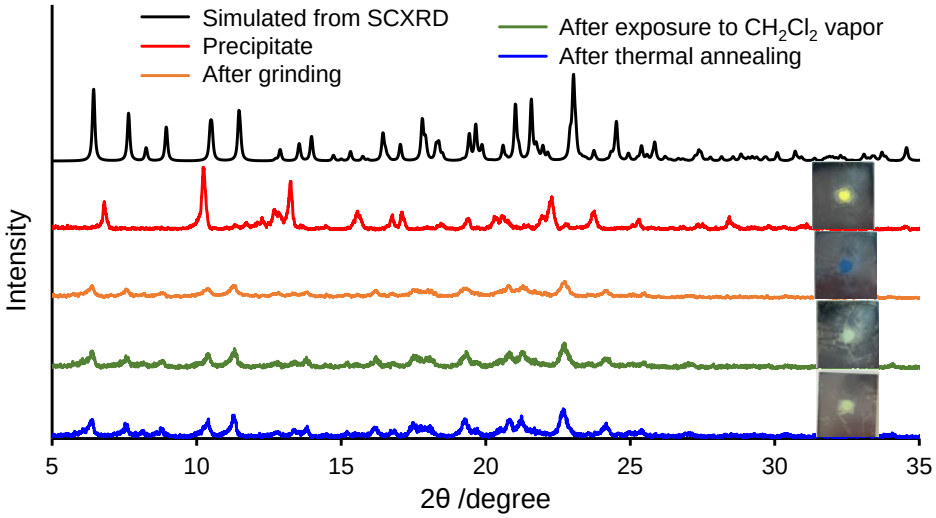


Figure S17 XRD patterns of a powder sample recorded at room temperature.

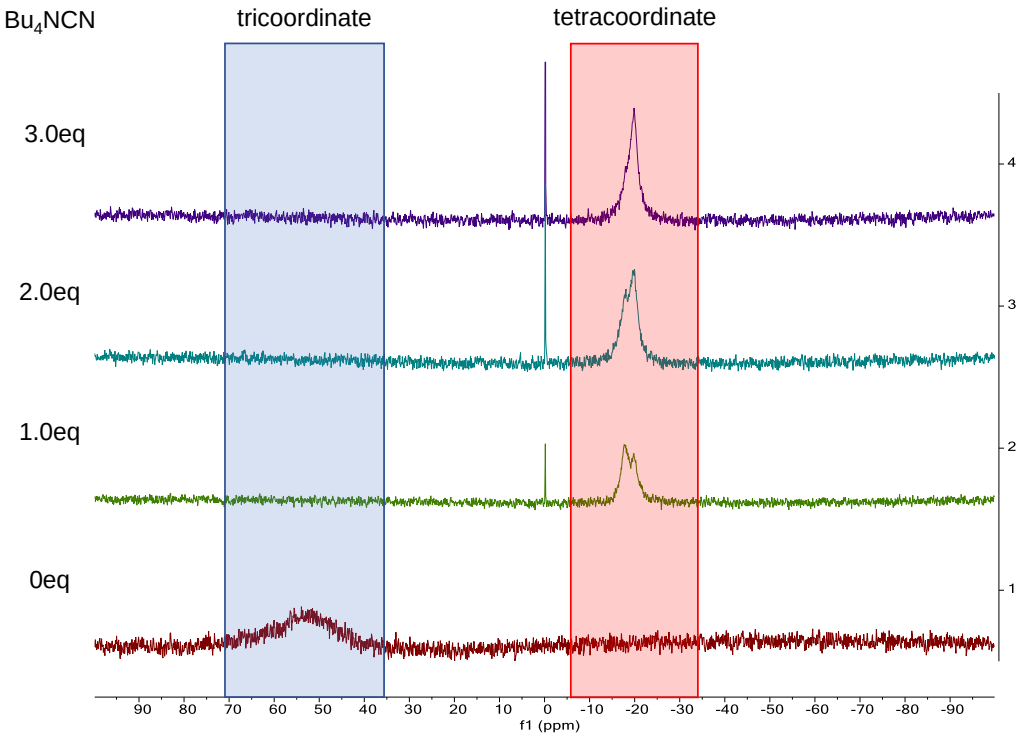


Figure S18 ^{11}B NMR spectra of **DTCB-SiPh** in C_6D_6 before and after addition of Bu_4NCN.

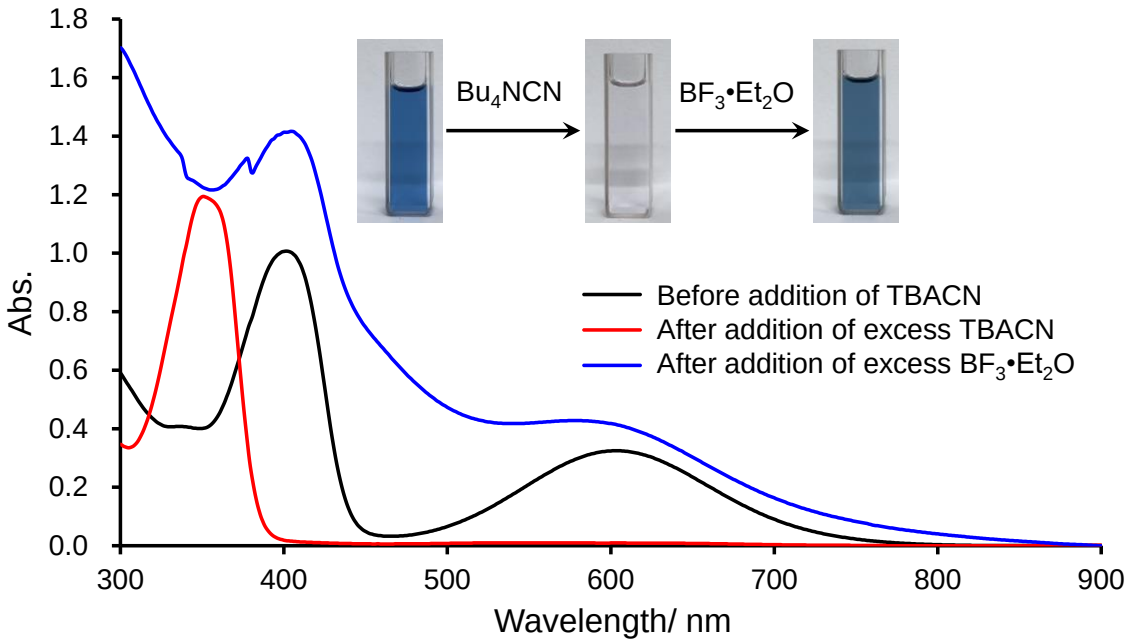


Figure S19 Reversibility of anion responsiveness of **DTCB-SiPh** at the concentration of 45 μmol/L.

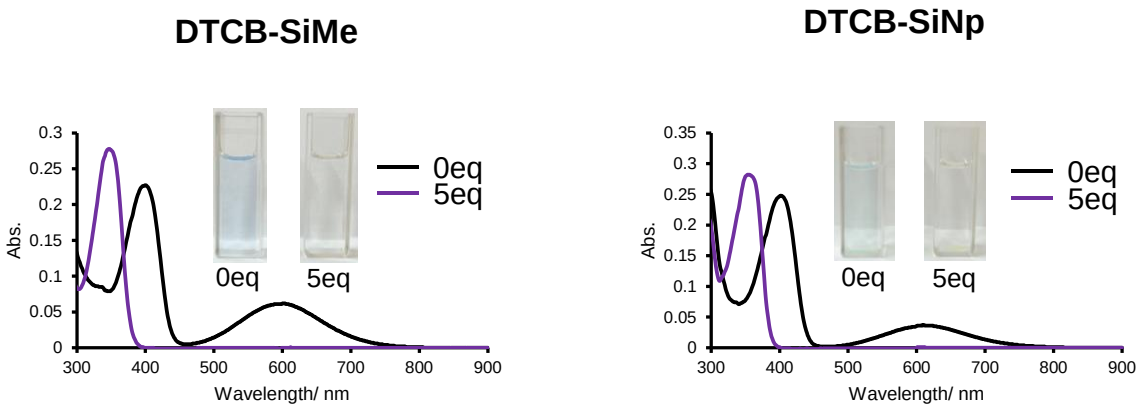


Figure S20 Absorption data for titrations of **DTCB-SiMe** and **DTCB-SiNp** with TBACN aliquots in toluene at the concentration of 10 μmol/L and 9.9 μmol/L, respectively.

Table S13 DFT-calculated Gibbs free energies of **DTCB-SiPh** before and after the coordination of cyanide ion on the boron center at the B3LYP/6-31G(d) level at 298 K.

	Conformer	G^{DFT} /kJ mol^{-1}	ΔG^{DFT} [a]/ kJ mol^{-1}
Cyanide-free	*anti*-folded	-9572388.78	-1.8
	twisted	-9572390.53	
Cyanide complex	*anti*-folded	-9816307.51	+3.5
	twisted	-9816303.96	

[a] ΔG = G(twisted) – G(*anti*-folded).

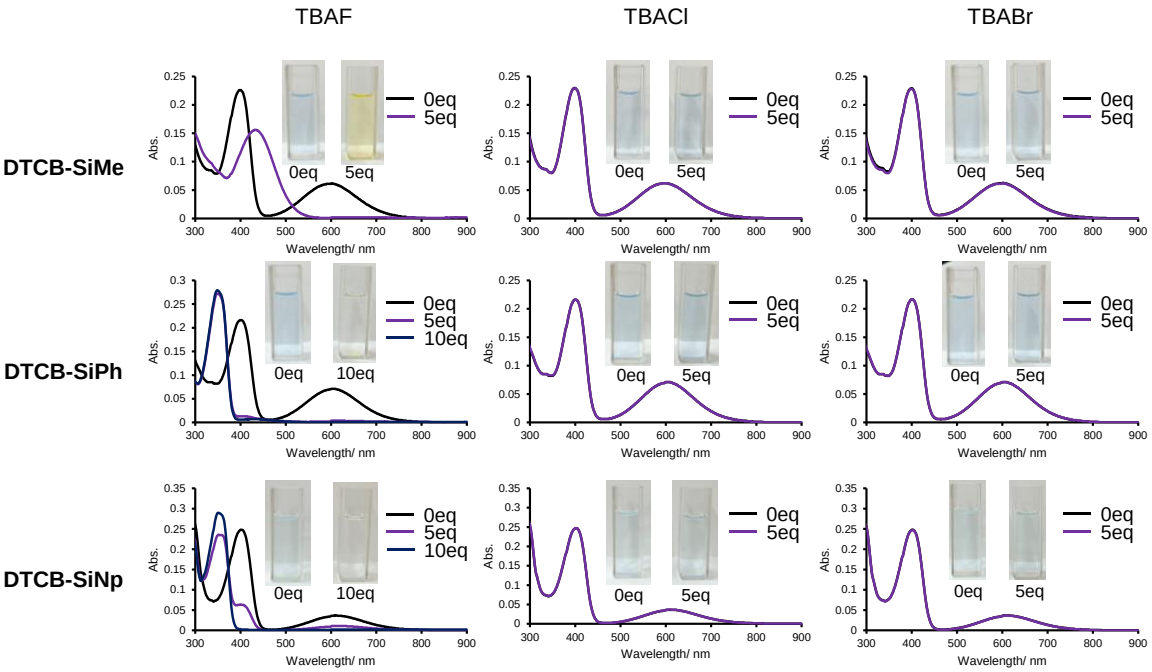


Figure S21 Absorption data for titrations of **DTCB-SiMe**, **DTCB-SiPh**, and **DTCB-SiNp** with tetrabutylammonium fluoride (TBAF), chloride (TBACl), and bromide (TBABr) aliquots in toluene at the concentration of 10 μmol/L, 10 μmol/L, and 9.9 μmol/L, respectively.

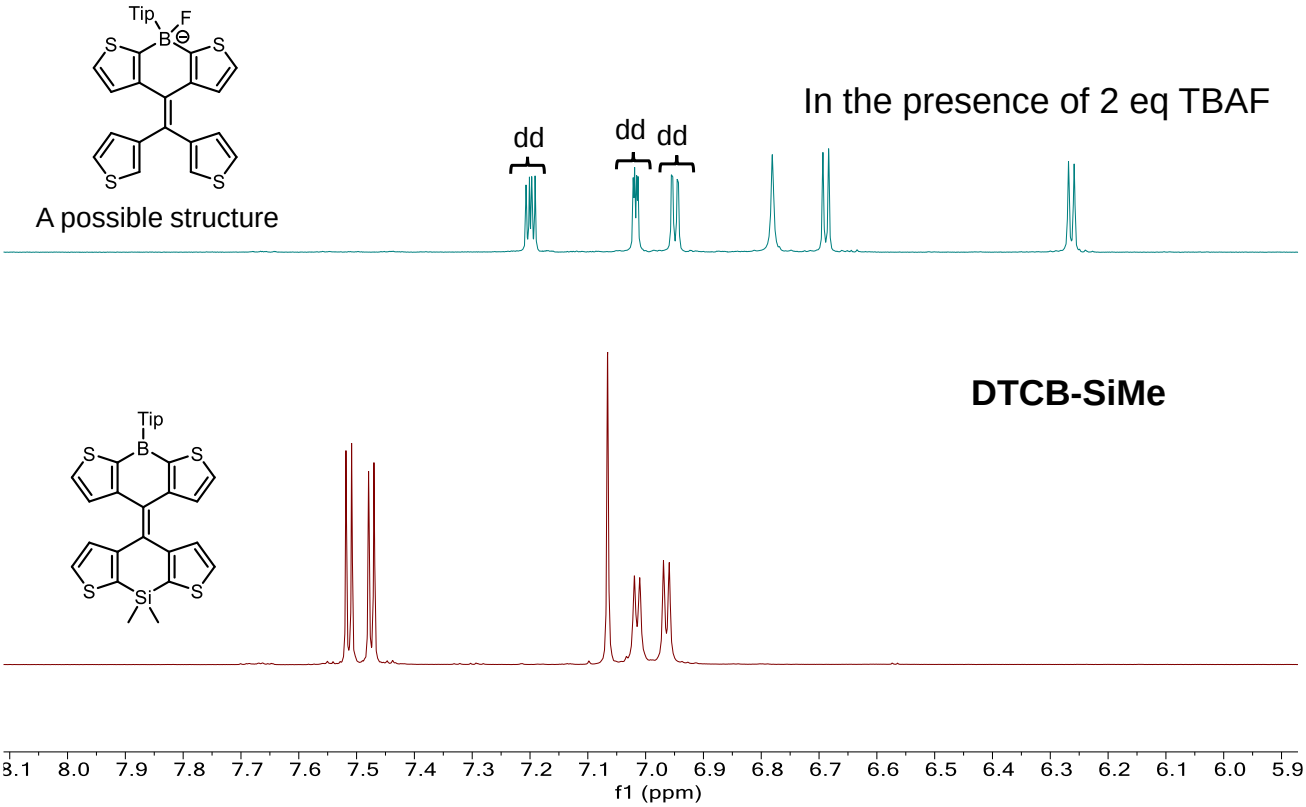


Figure S22 ^{1}H NMR spectra of **DTCB-SiMe** before and after addition of TBAF in THF-d_8 at room temperature.

NMR and IR spectra

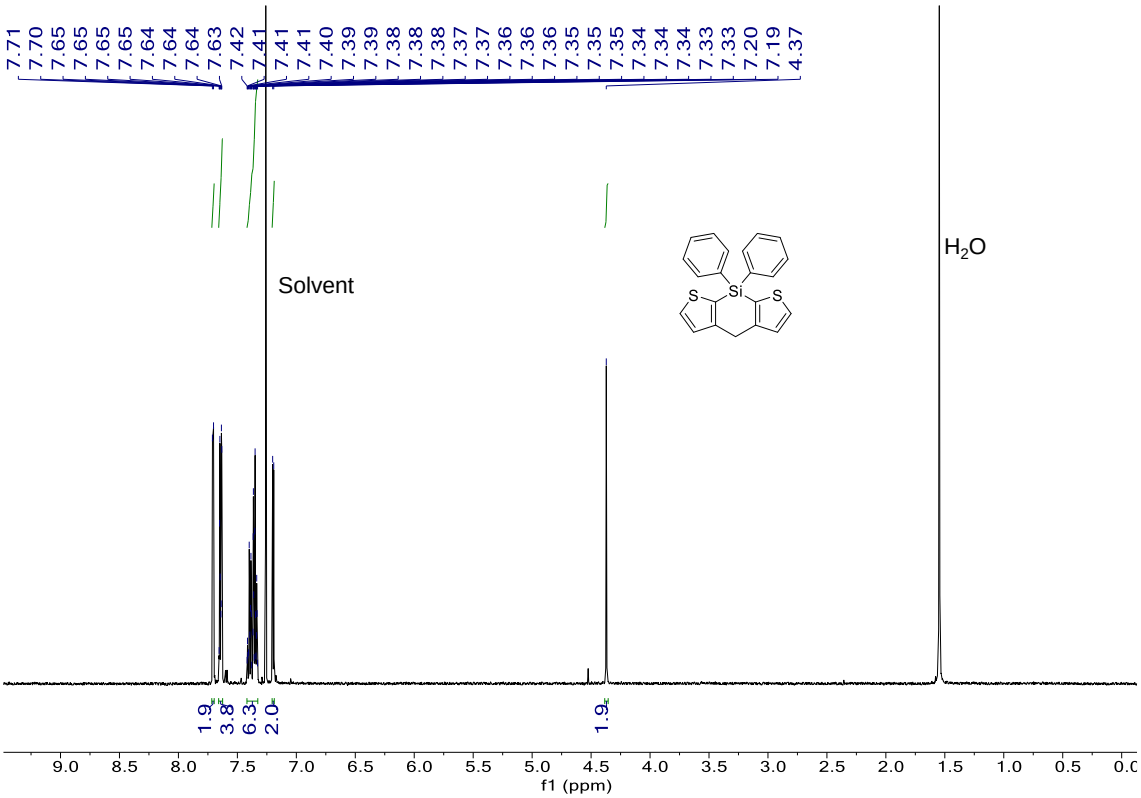


Figure S23 ^{1}H NMR spectrum of **1-Ph** in $CDCl_3$ at room temperature (500 MHz).

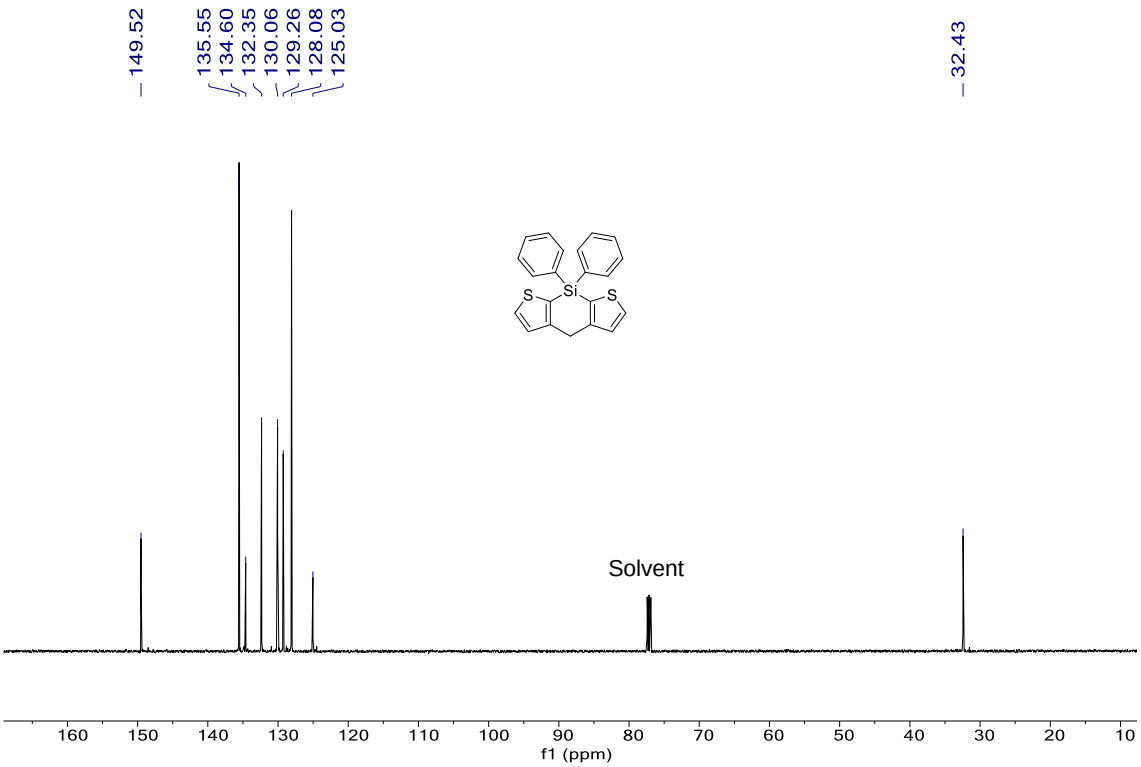


Figure S24 ^{13}C NMR spectrum of **1-Ph** in $CDCl_3$ at room temperature (125 MHz).

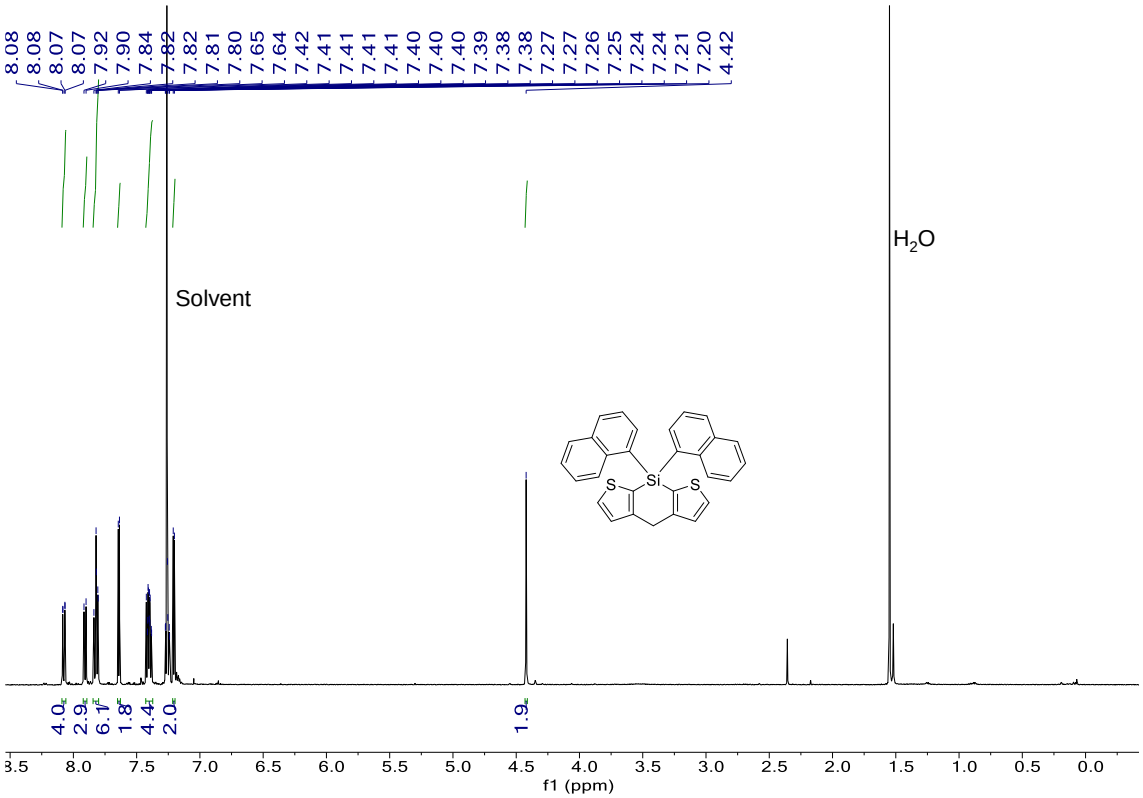


Figure S25 ^{1}H NMR spectrum of **1-Np** in $CDCl_3$ at room temperature (500 MHz).

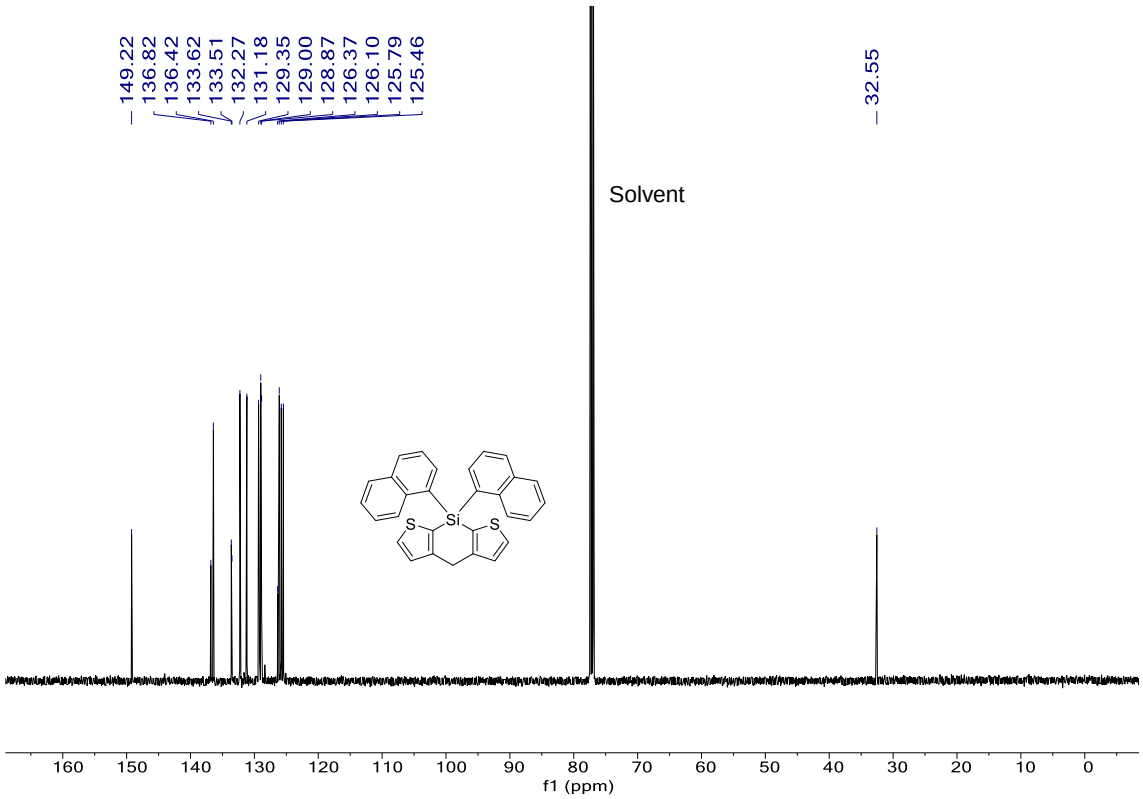


Figure S26 ^{13}C NMR spectrum of **1-Np** in $CDCl_3$ at room temperature (125 MHz).

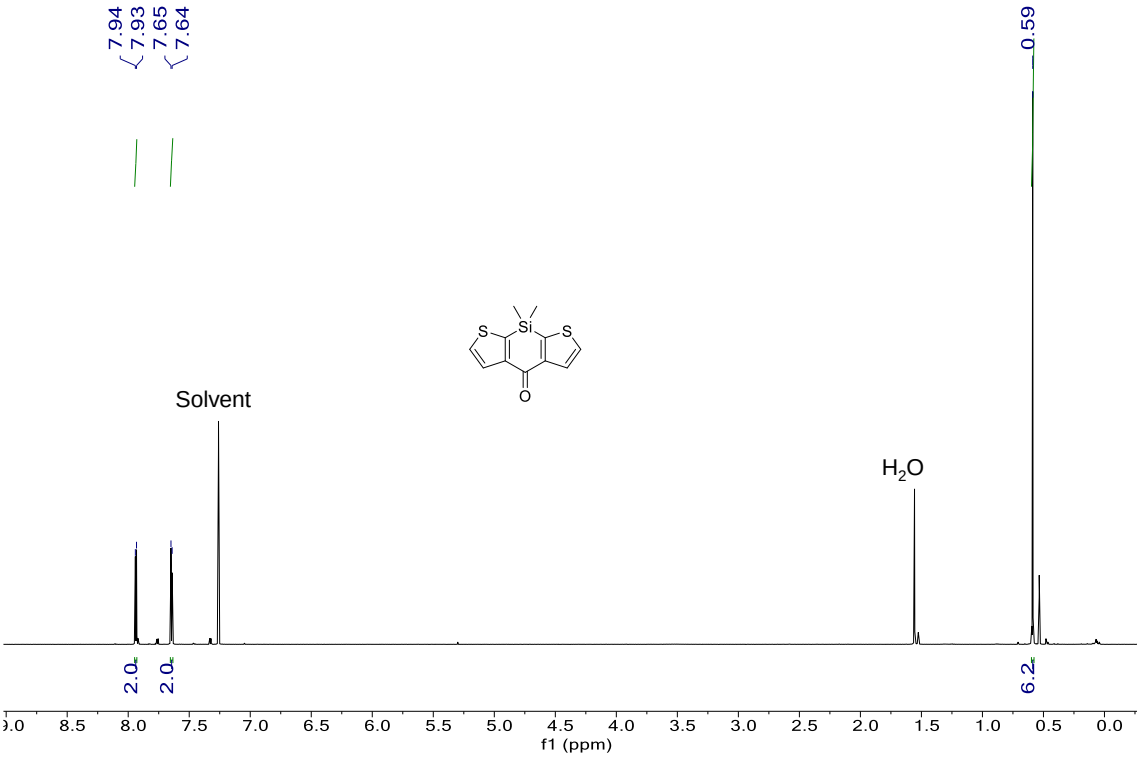


Figure S27 ^{1}H NMR spectrum of **2-Me** in $CDCl_3$ at room temperature (500 MHz).

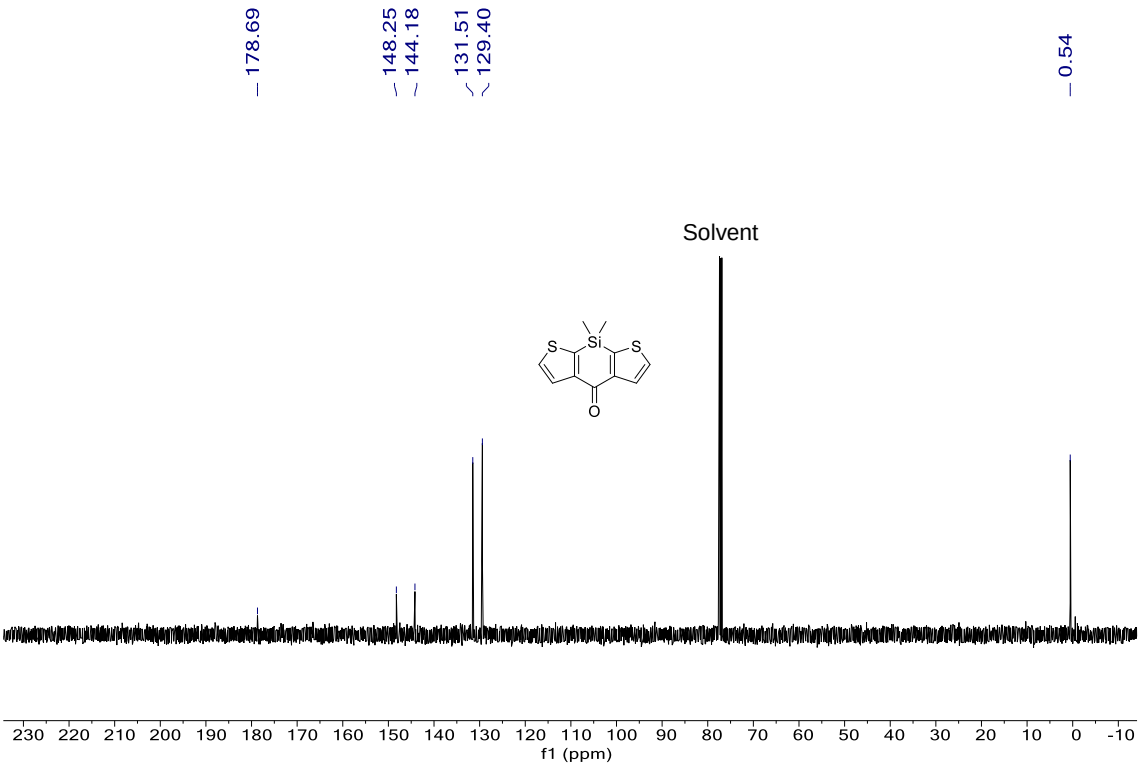


Figure S28 ^{13}C NMR spectrum of **2-Me** in $CDCl_3$ at room temperature (125 MHz).

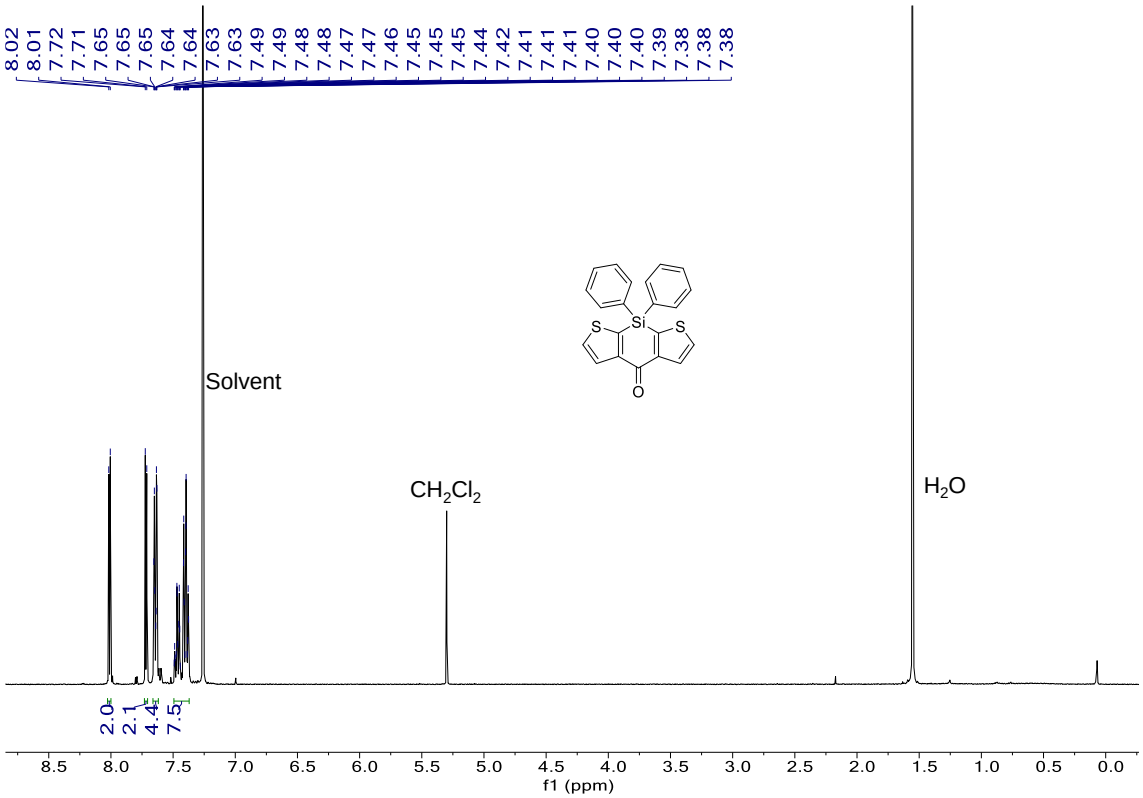


Figure S29 ^{1}H NMR spectrum of **2-Ph** in $CDCl_3$ at room temperature (400 MHz).

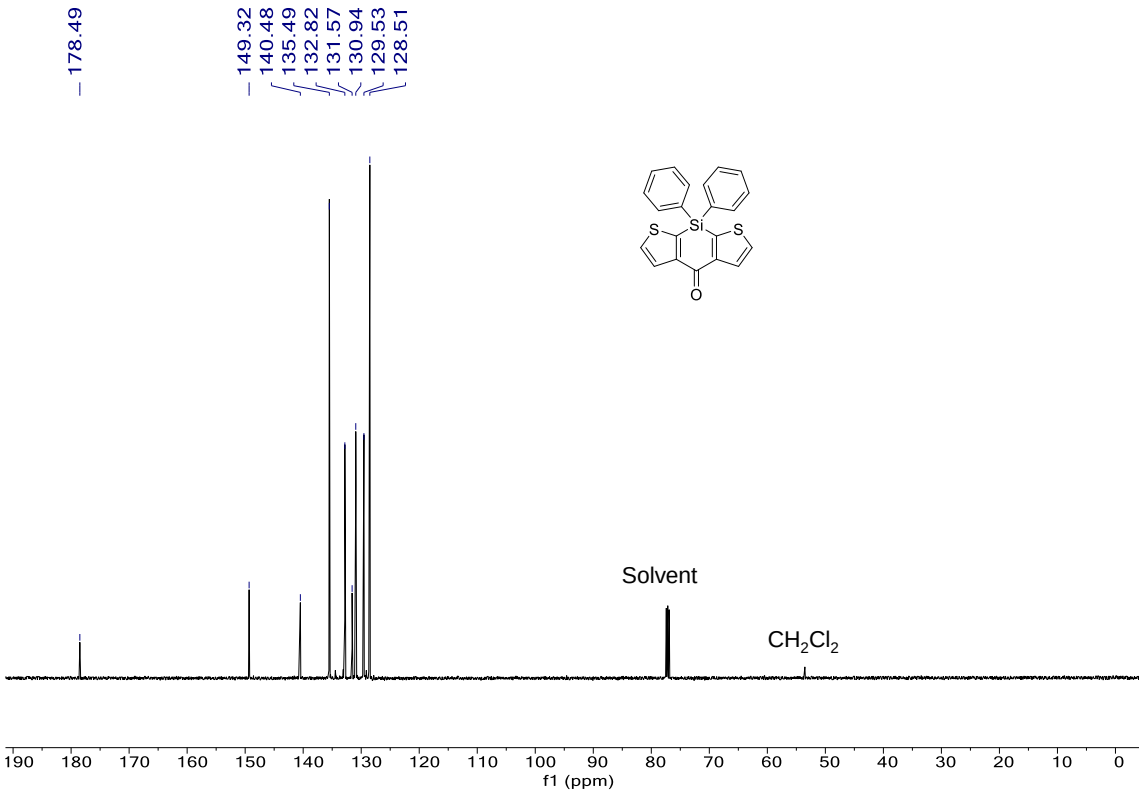


Figure S30 ^{13}C NMR spectrum of **2-Ph** in $CDCl_3$ at room temperature (125 MHz).

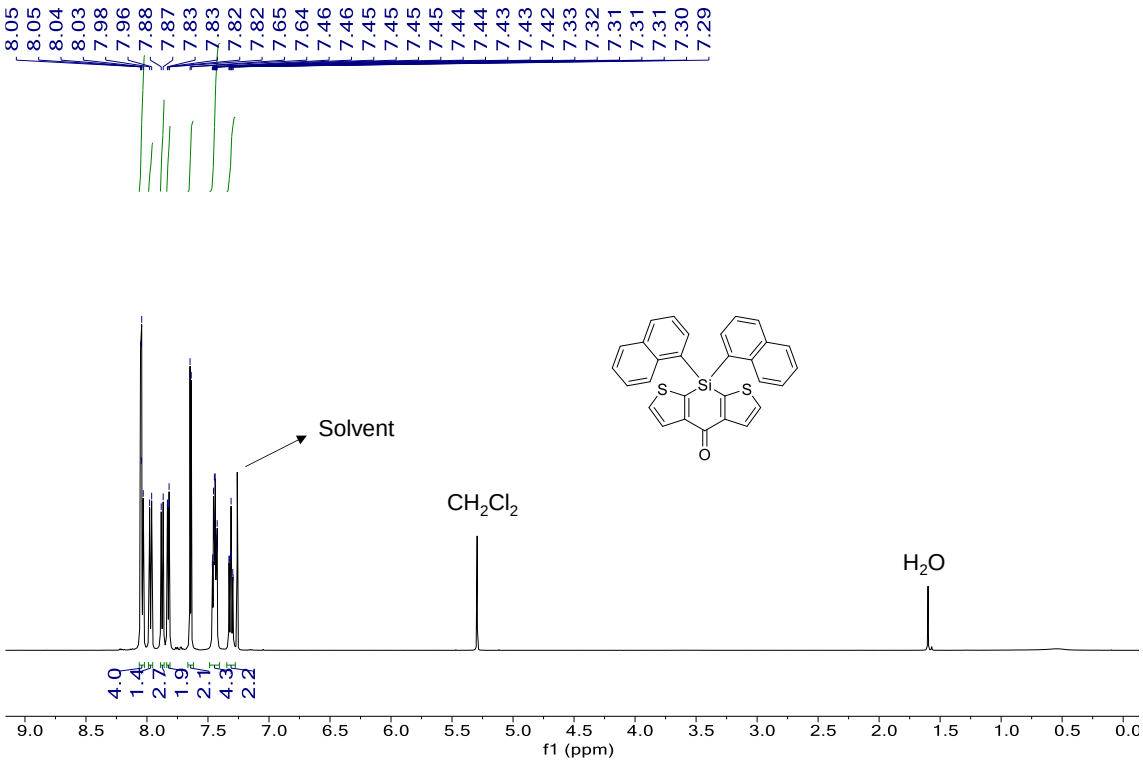


Figure S31 ^{1}H NMR spectrum of **2-Np** in $CDCl_3$ at room temperature (500 MHz).

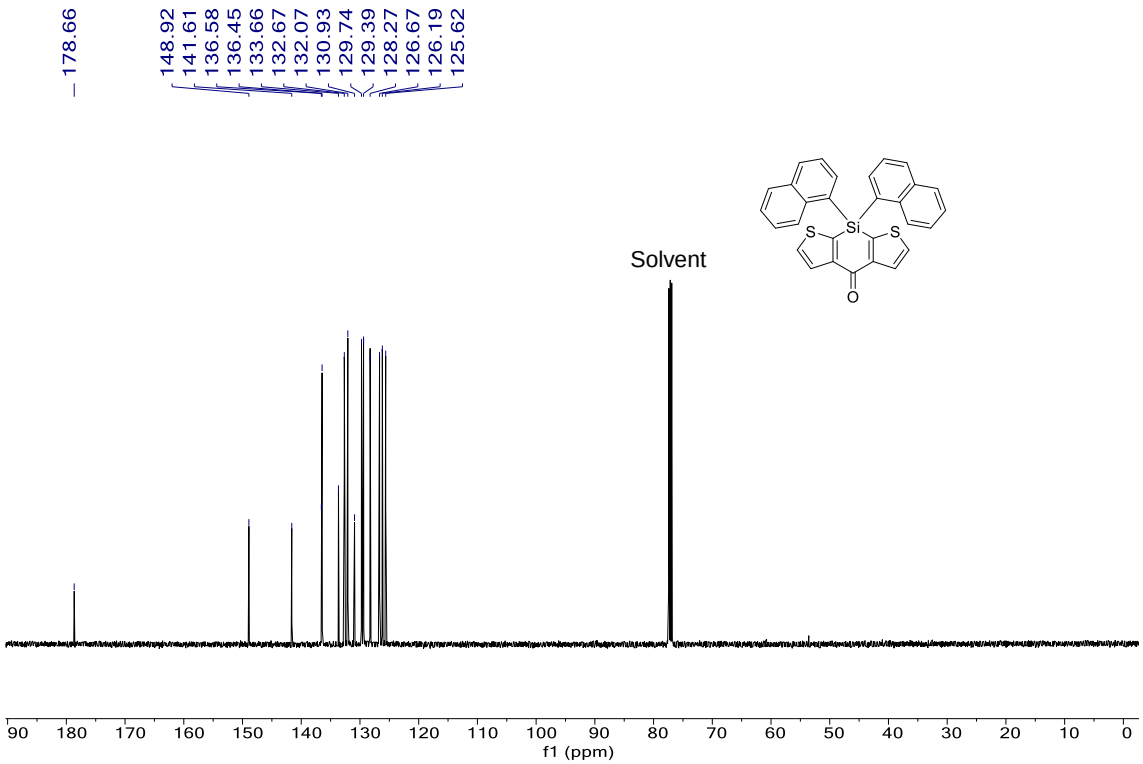


Figure S32 ^{13}C NMR spectrum of **2-Np** in $CDCl_3$ at room temperature (125 MHz).

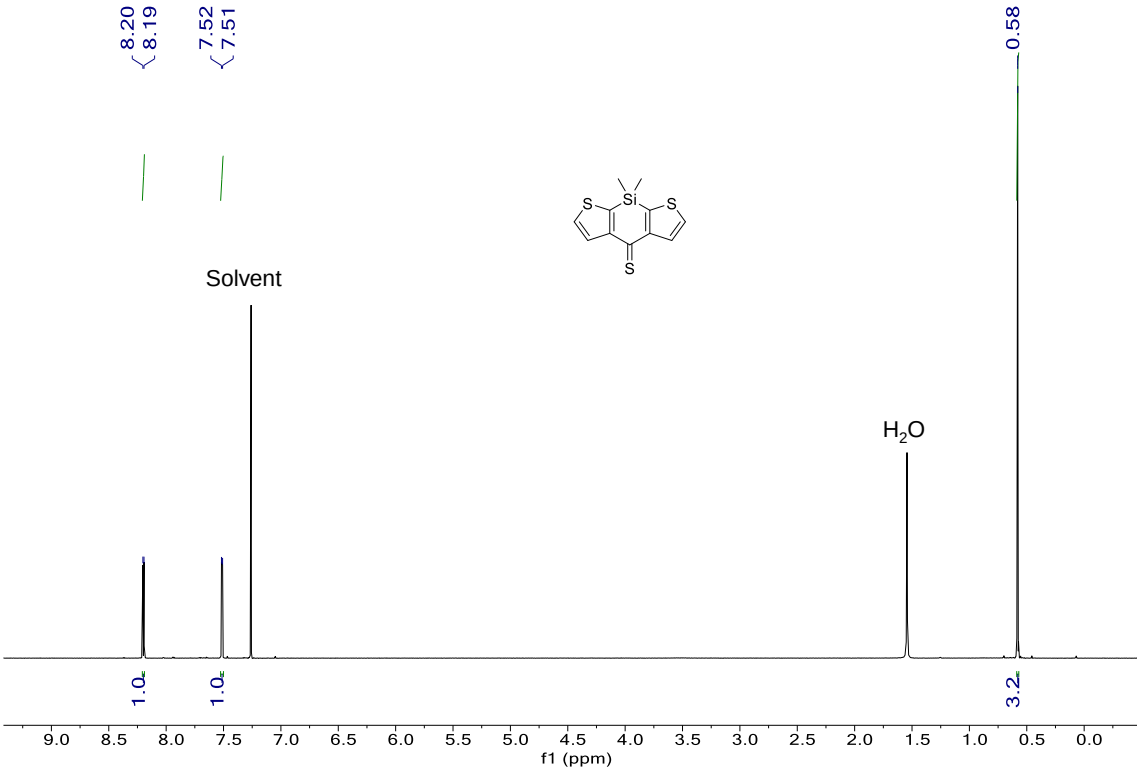


Figure S33 ^{1}H NMR spectrum of **3-Ph** in $CDCl_3$ at room temperature (500 MHz).

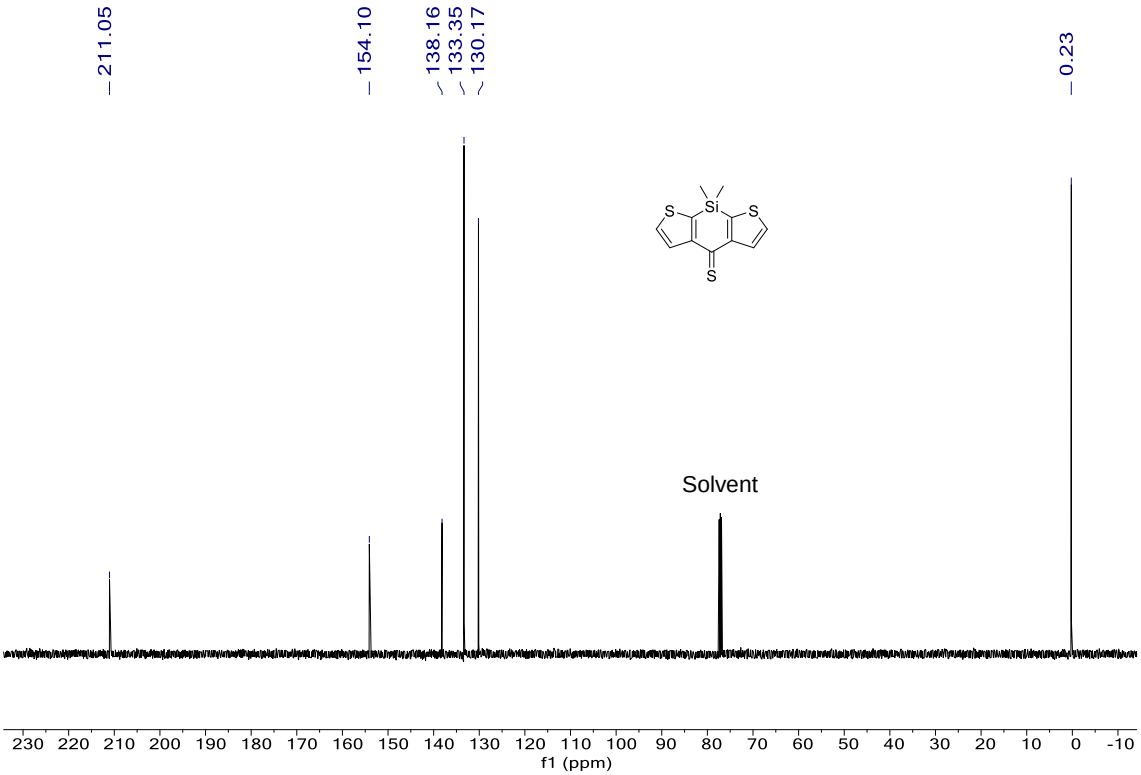


Figure S34 ^{13}CNMR spectrum of **3-Me** in $CDCl_3$ at room temperature (125 MHz).

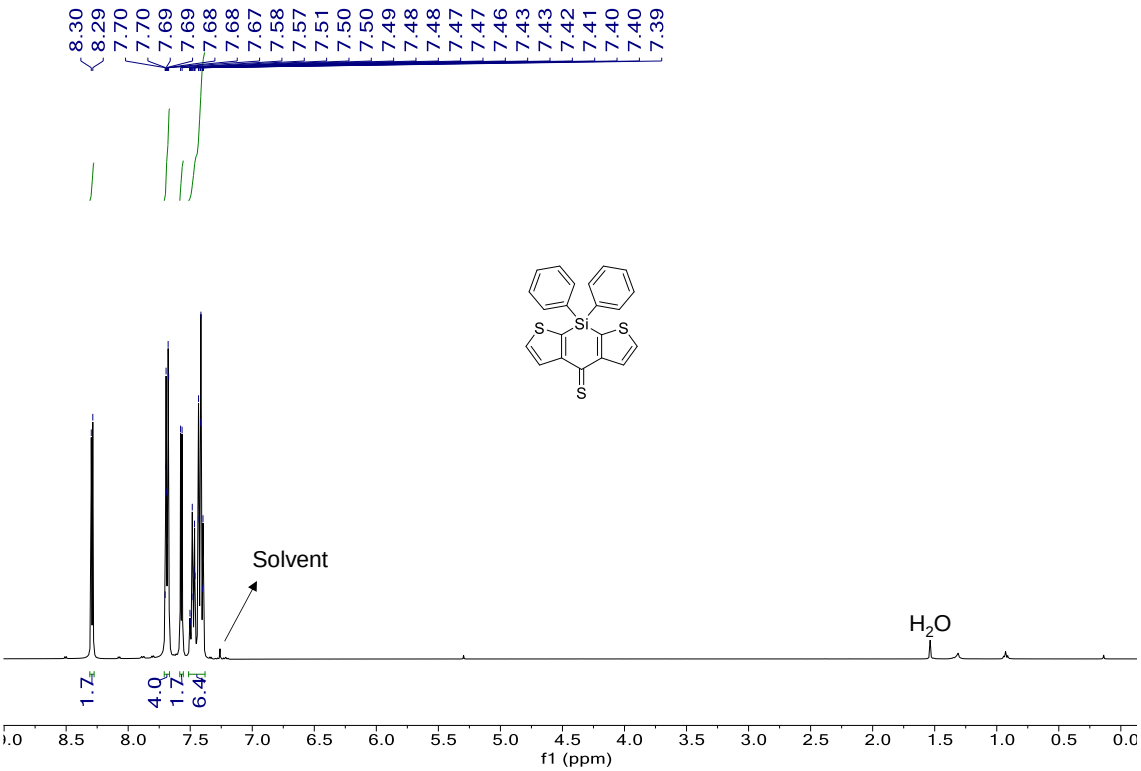


Figure S35 ^{1}H NMR spectrum of **3-Ph** in $CDCl_3$ at room temperature (400 MHz).

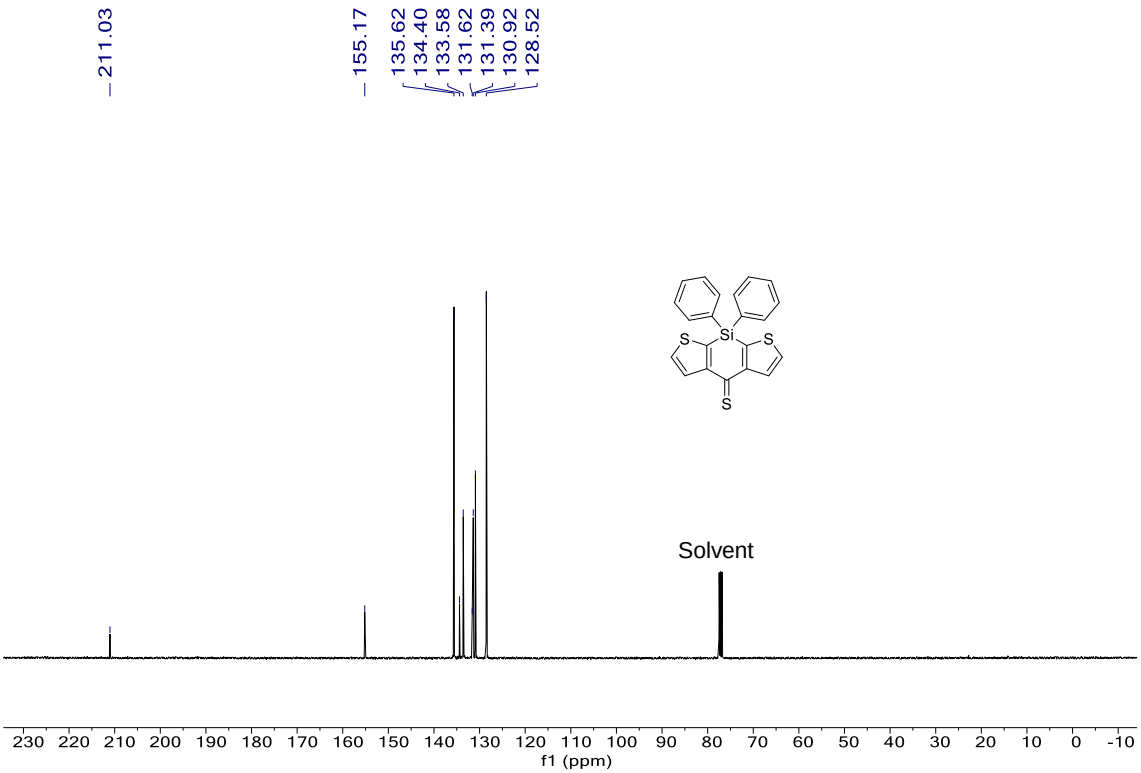


Figure S36 ^{13}CNMR spectrum of **3-Ph** in $CDCl_3$ at room temperature (100 MHz).

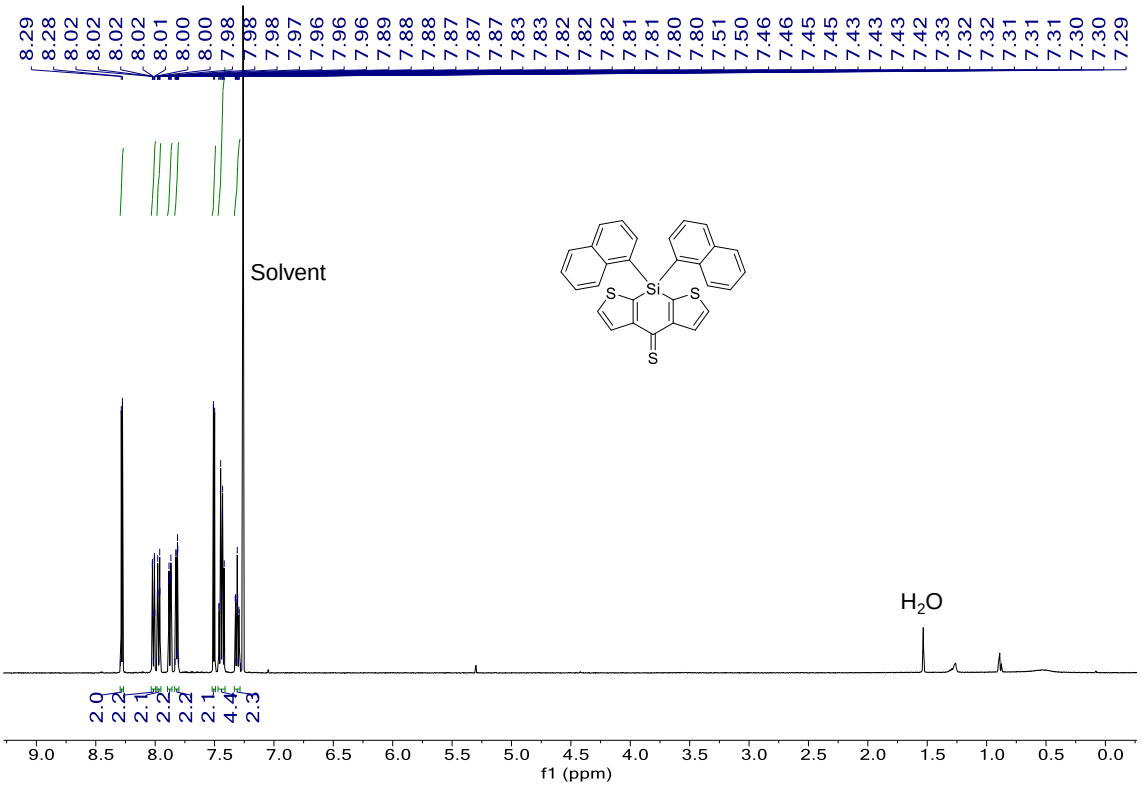


Figure S37 ^{1}H NMR spectrum of **3-Np** in $CDCl_3$ at room temperature (500 MHz).

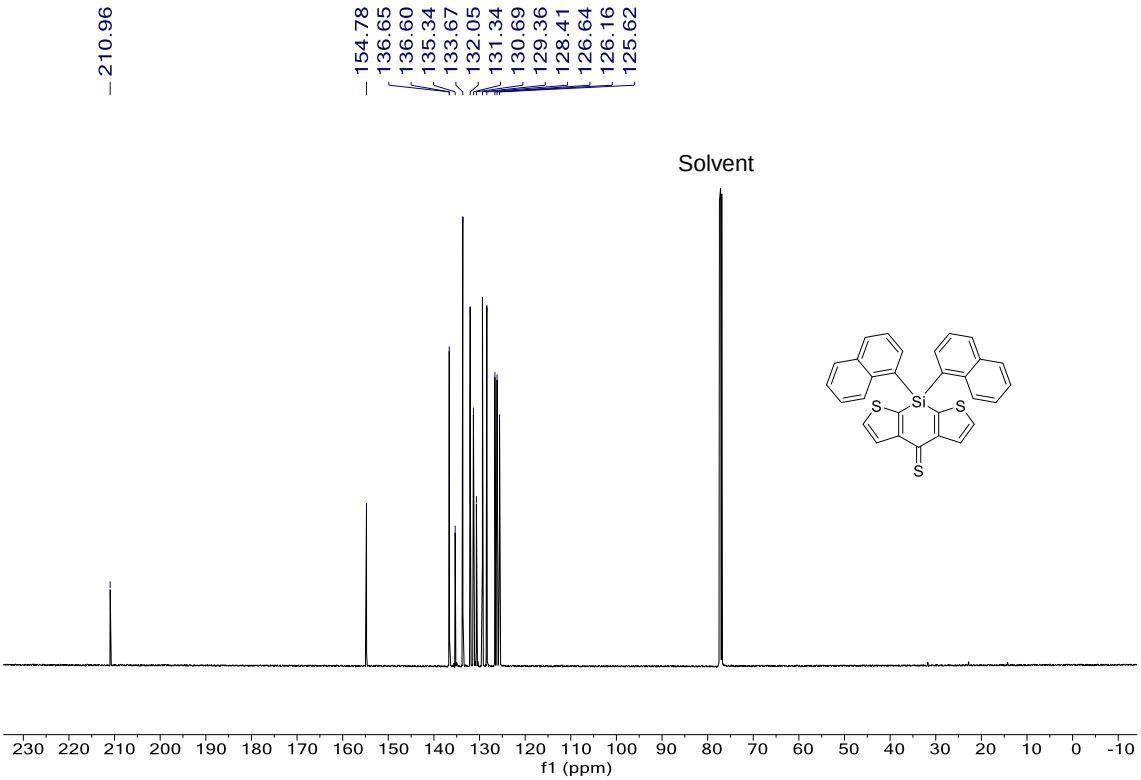


Figure S38 ^{13}C NMR spectrum of **3-Np** in $CDCl_3$ at room temperature (125 MHz).

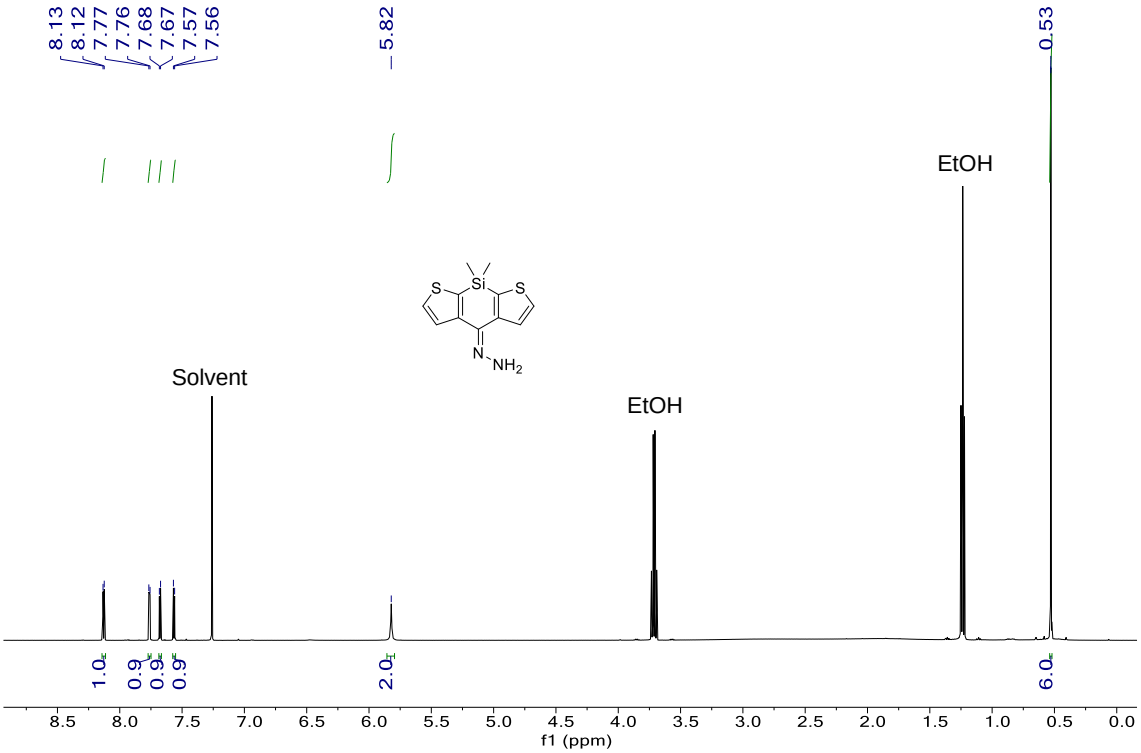


Figure S39 ^{1}H NMR spectrum of **4-Me** in $CDCl_3$ at room temperature (500 MHz).

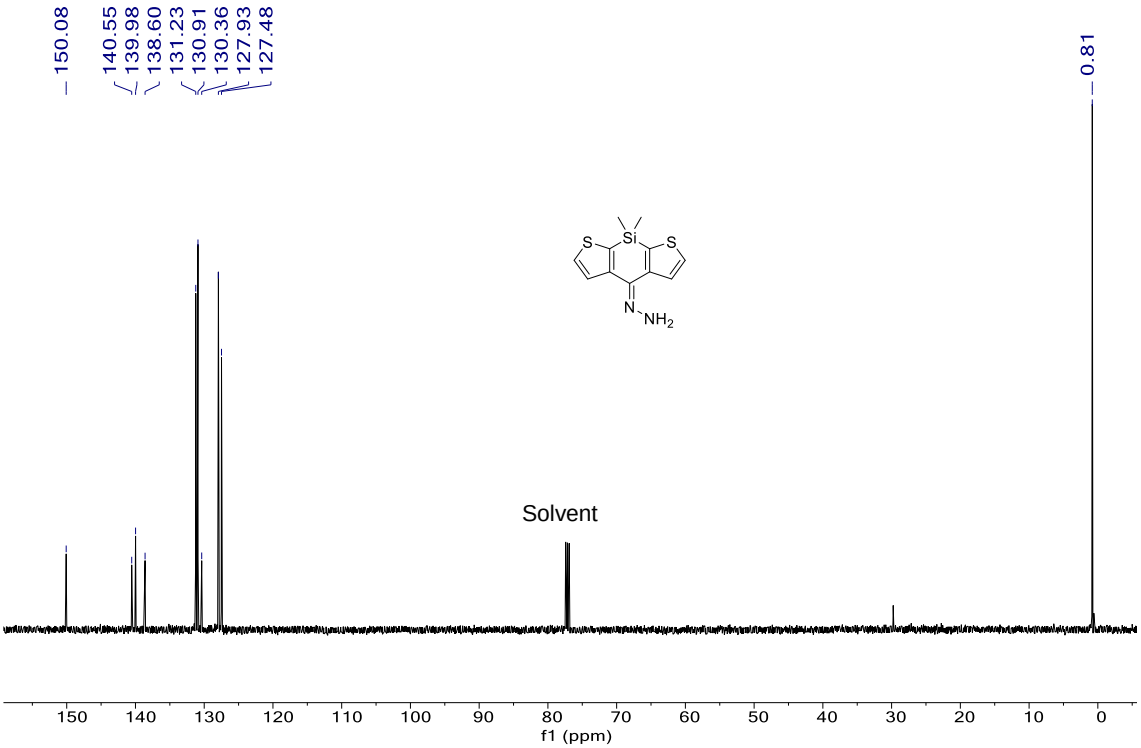


Figure S40 ^{13}C NMR spectrum of **4-Me** in $CDCl_3$ at room temperature (100 MHz).

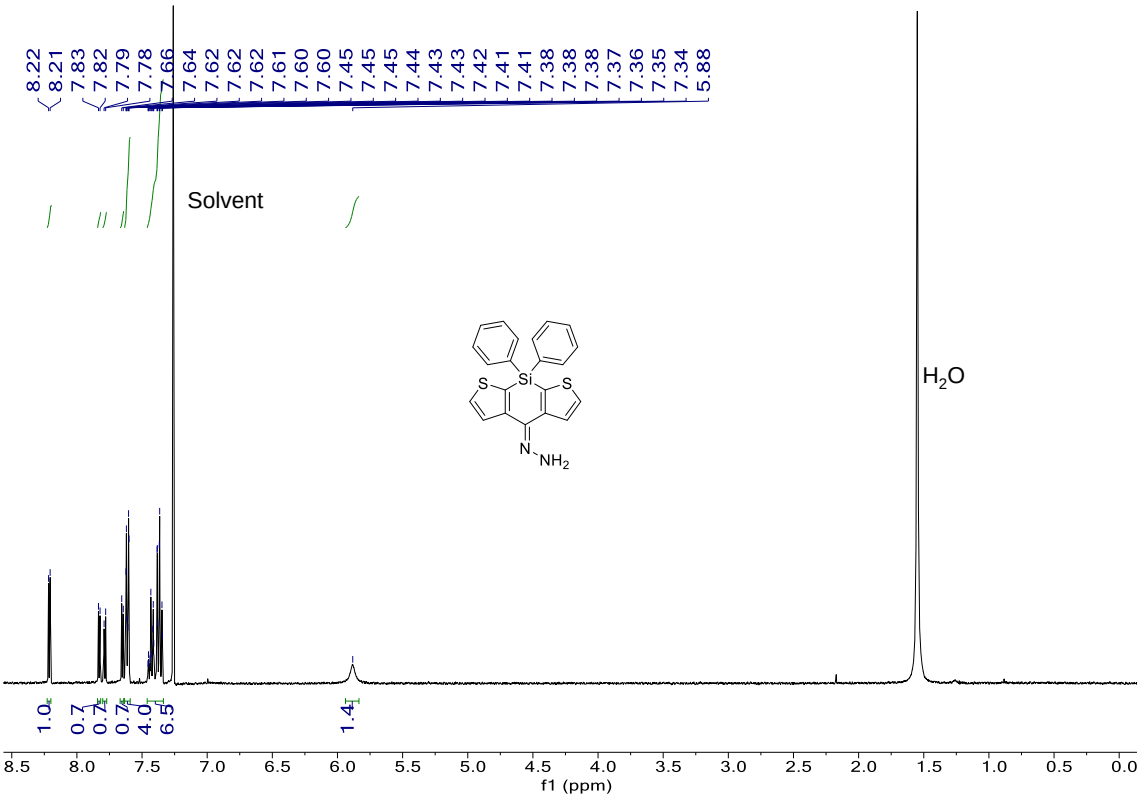


Figure S41 ^{1}H NMR spectrum of **4-Ph** in $CDCl_3$ at room temperature (400 MHz).

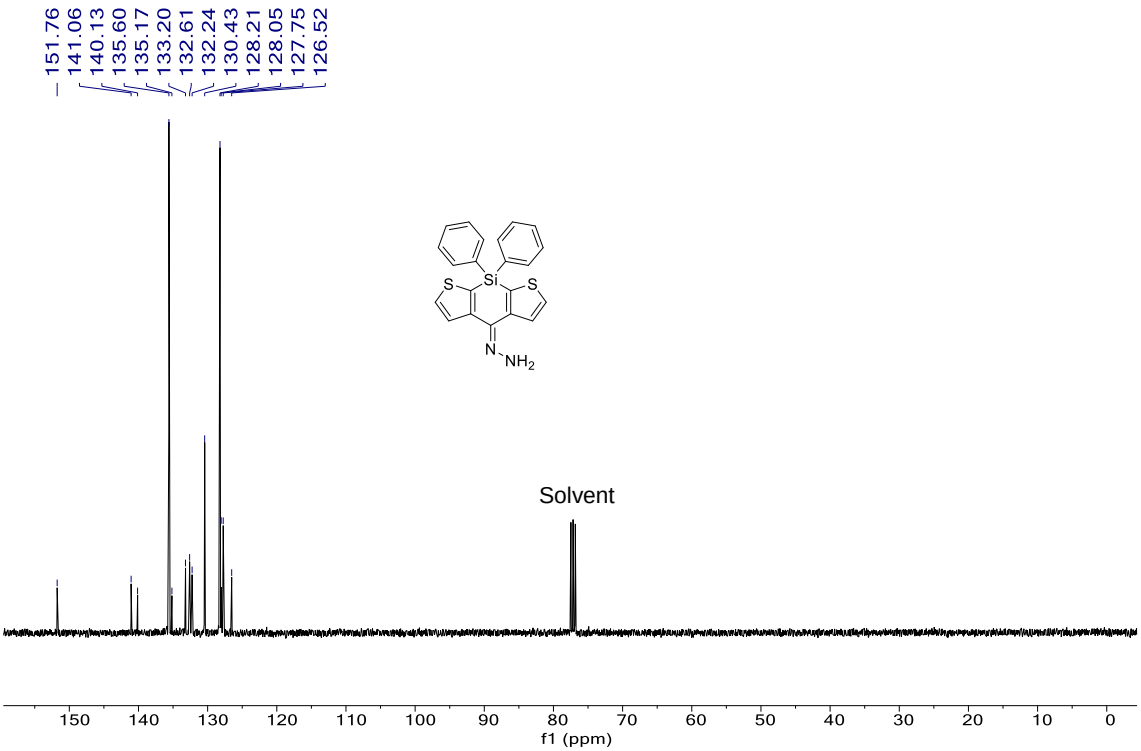


Figure S42 ^{13}C NMR spectrum of **4-Ph** in $CDCl_3$ at room temperature (100 MHz).

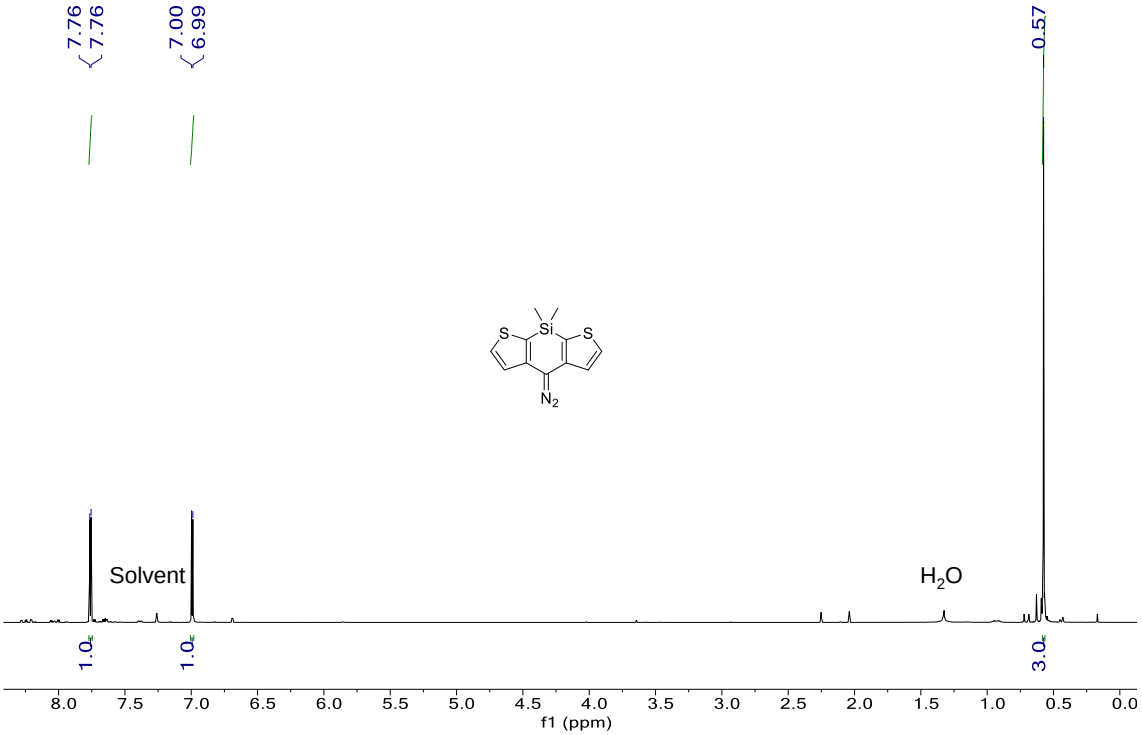


Figure S43 ^{1}H NMR spectrum of **5-Me** in $CDCl_3$ at room temperature (500 MHz).

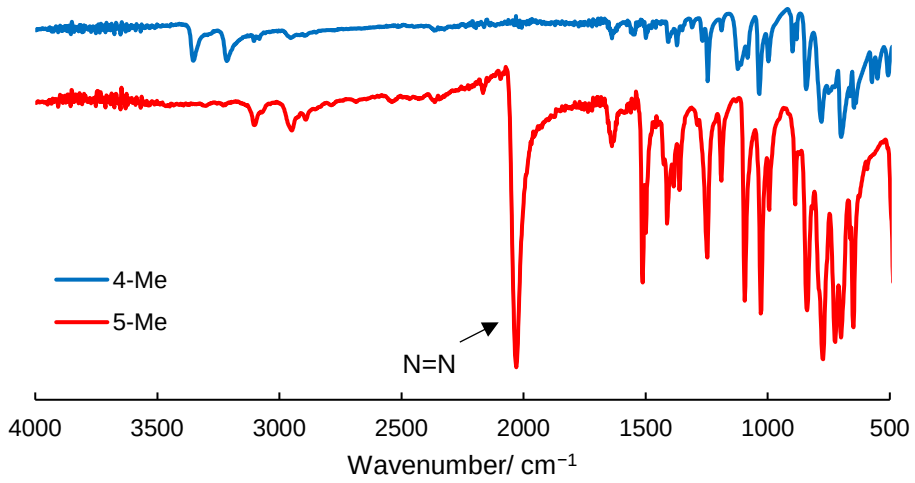


Figure S44 ATR-FTIR spectra of **4-Me** and **5-Me**.

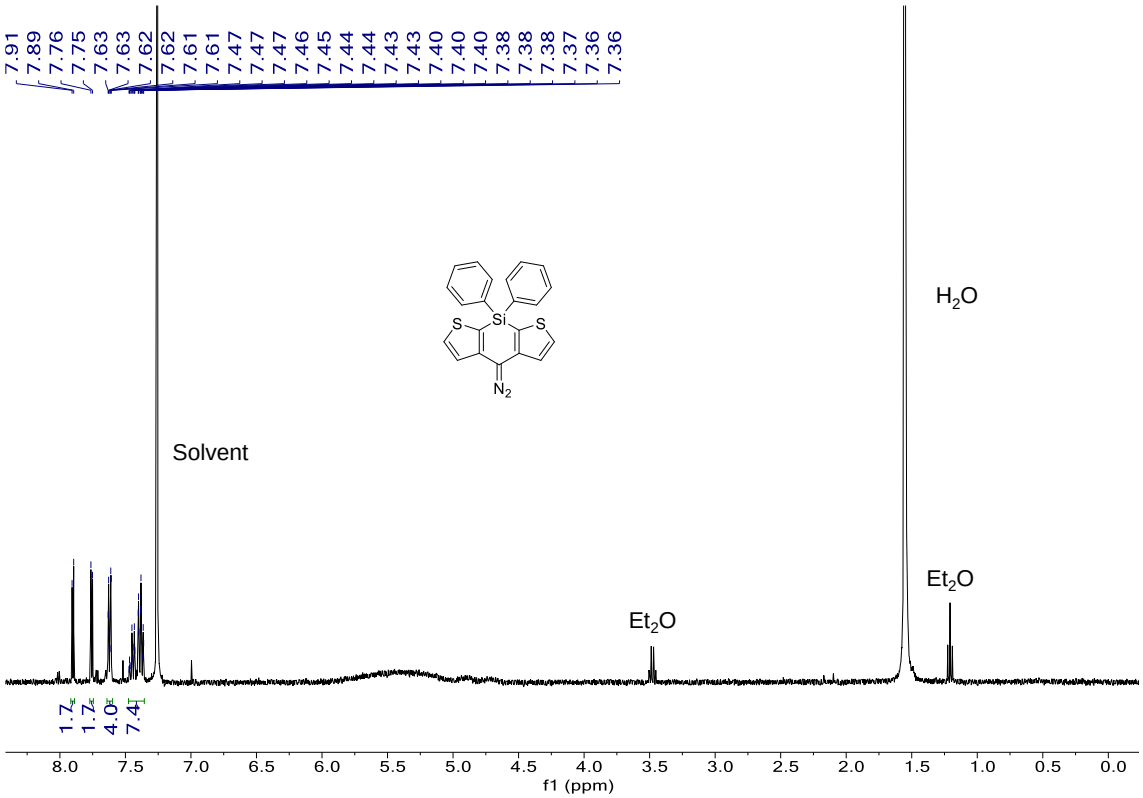


Figure S45 ^{1}H NMR spectrum of **5-Ph** in $CDCl_3$ at room temperature (400 MHz).

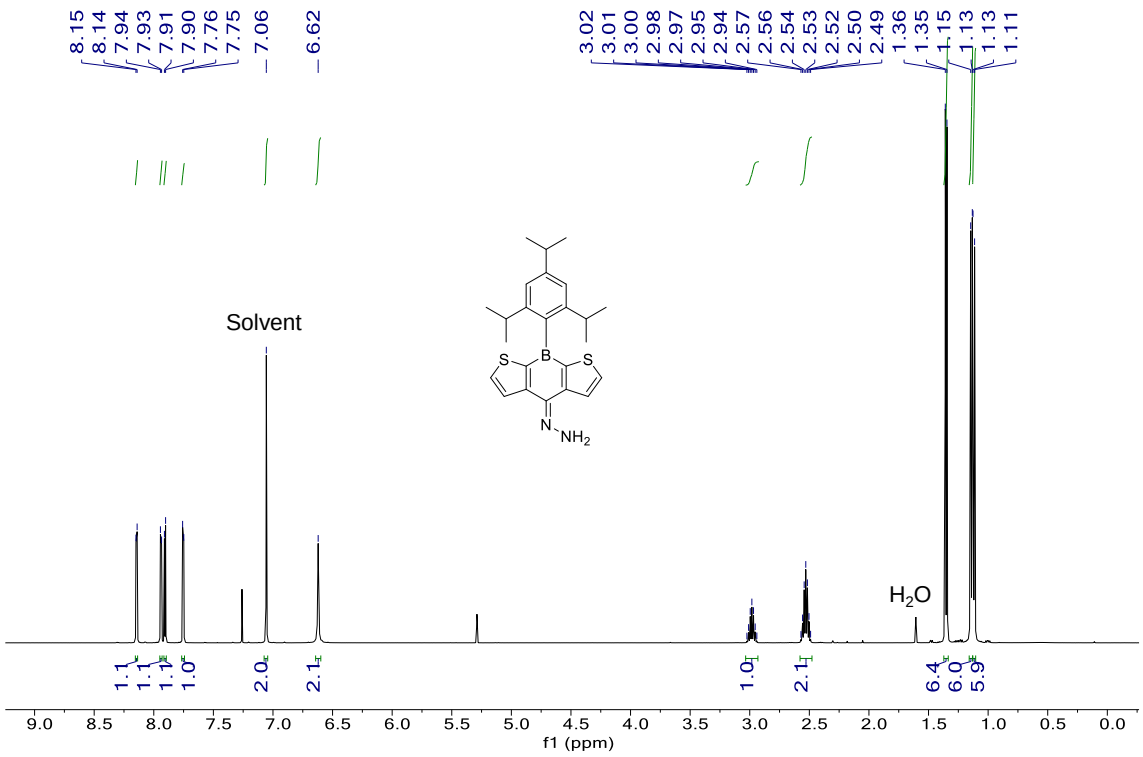


Figure S46 ^{1}H NMR spectrum of **7** in $CDCl_3$ at room temperature (500 MHz).

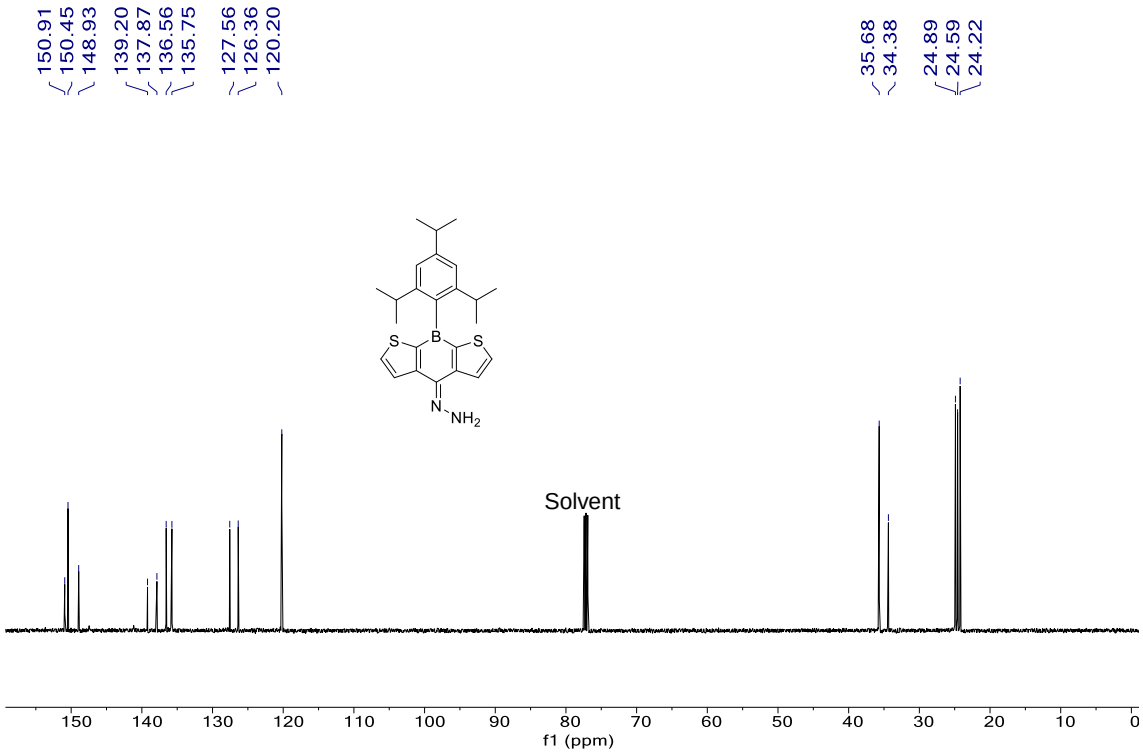


Figure S47 ^{13}C NMR spectrum of **7** in $CDCl_3$ at room temperature (125 MHz).

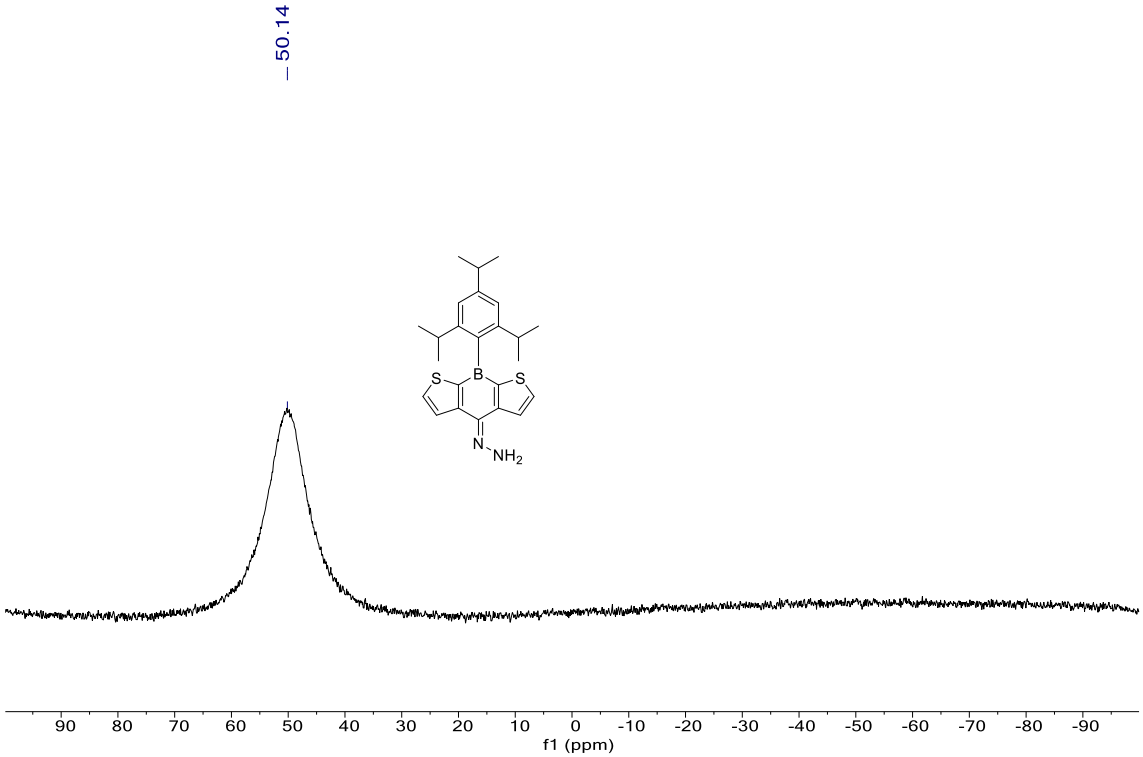


Figure S48 ^{11}B NMR spectrum of **7** in $CDCl_3$ at room temperature (160 MHz).

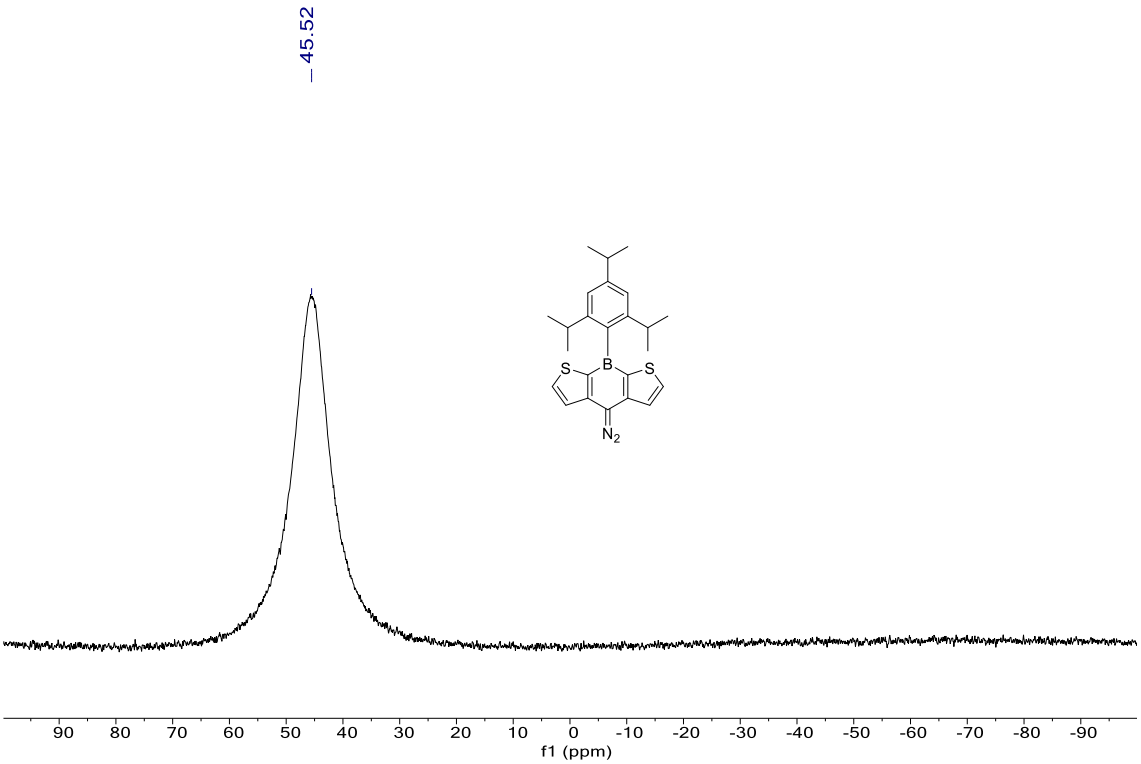


Figure S49 ^{11}B NMR spectrum of **8** in $CDCl_3$ at room temperature (160 MHz).

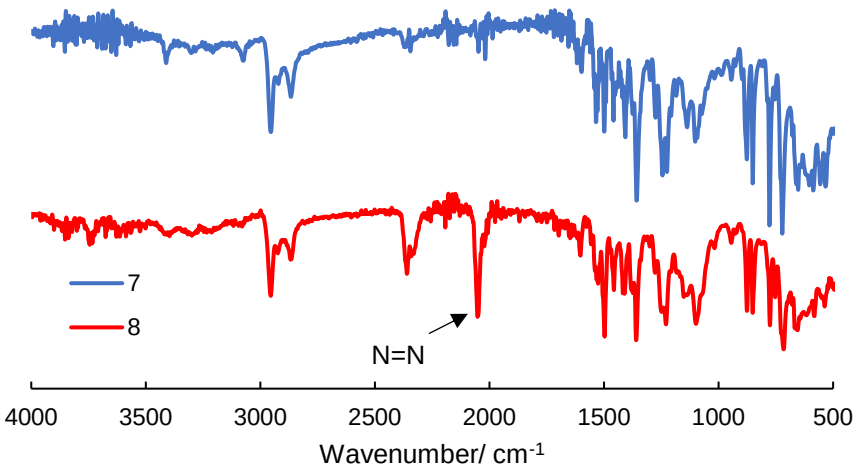


Figure S50 ATR-FTIR spectra of **4-Me** and **5-Me**.

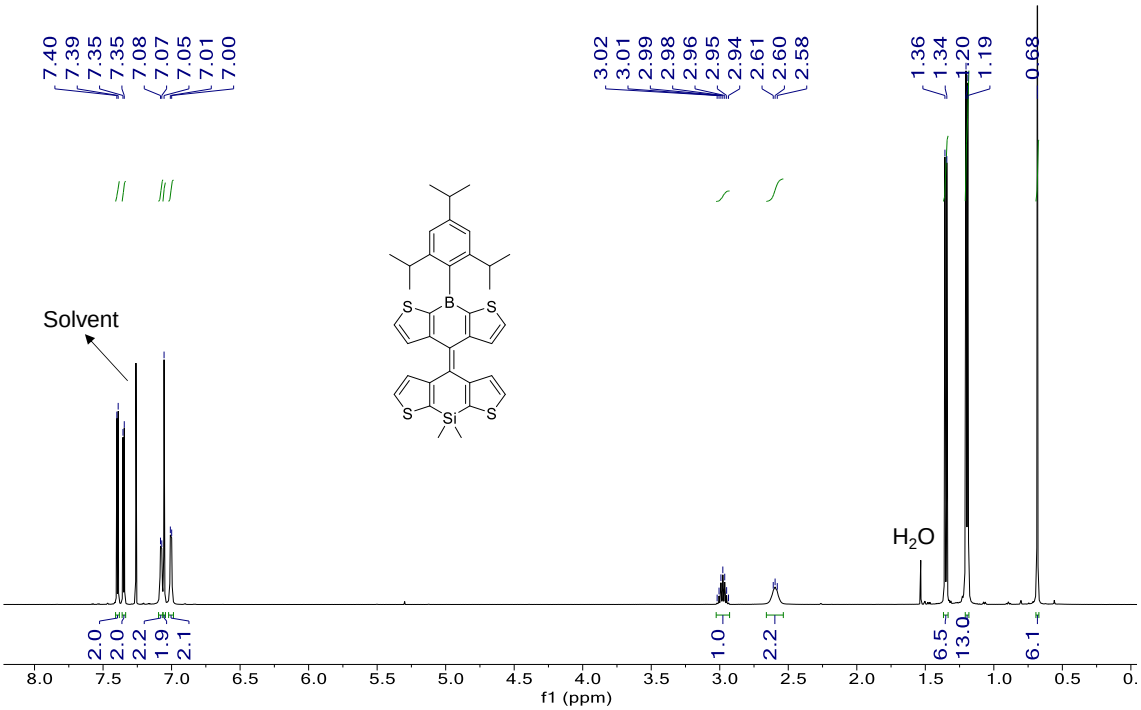


Figure S51 ^{1}H NMR spectrum of **DTCB-SiMe** in $CDCl_3$ at room temperature (500 MHz).

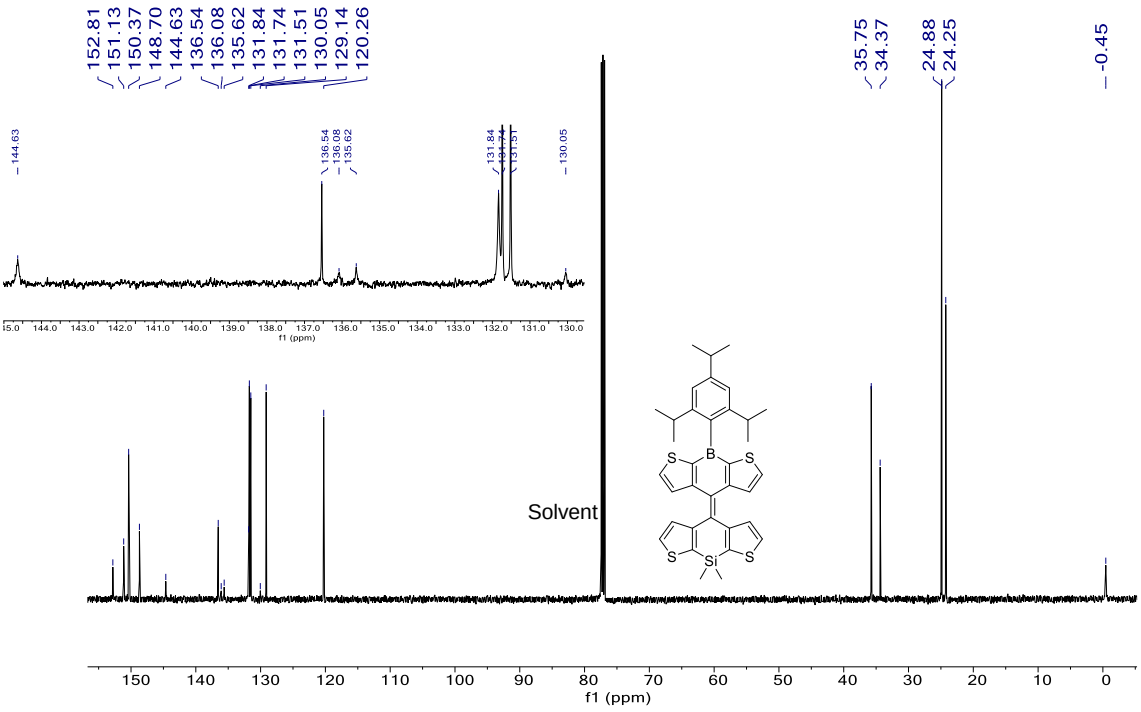


Figure S52 ^{13}C NMR spectrum of **DTCB-SiMe** in $CDCl_3$ at room temperature (125 MHz).

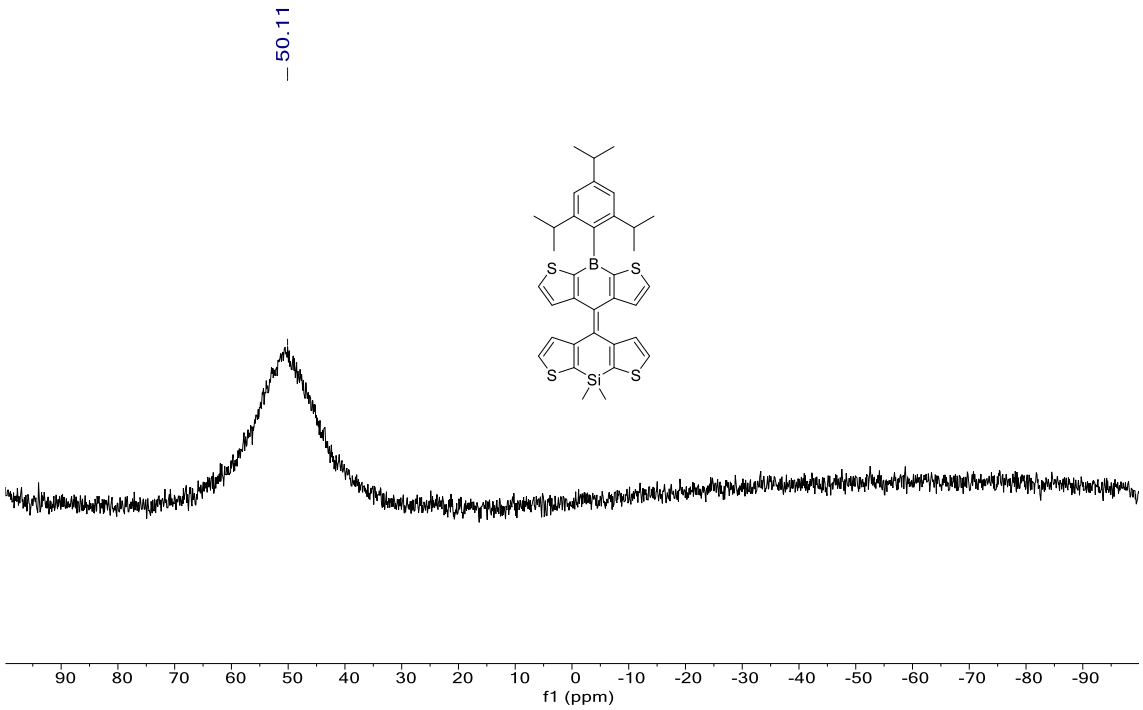


Figure S53 ^{11}B NMR spectrum of **DTCB-SiMe** in $CDCl_3$ at room temperature (160 MHz).

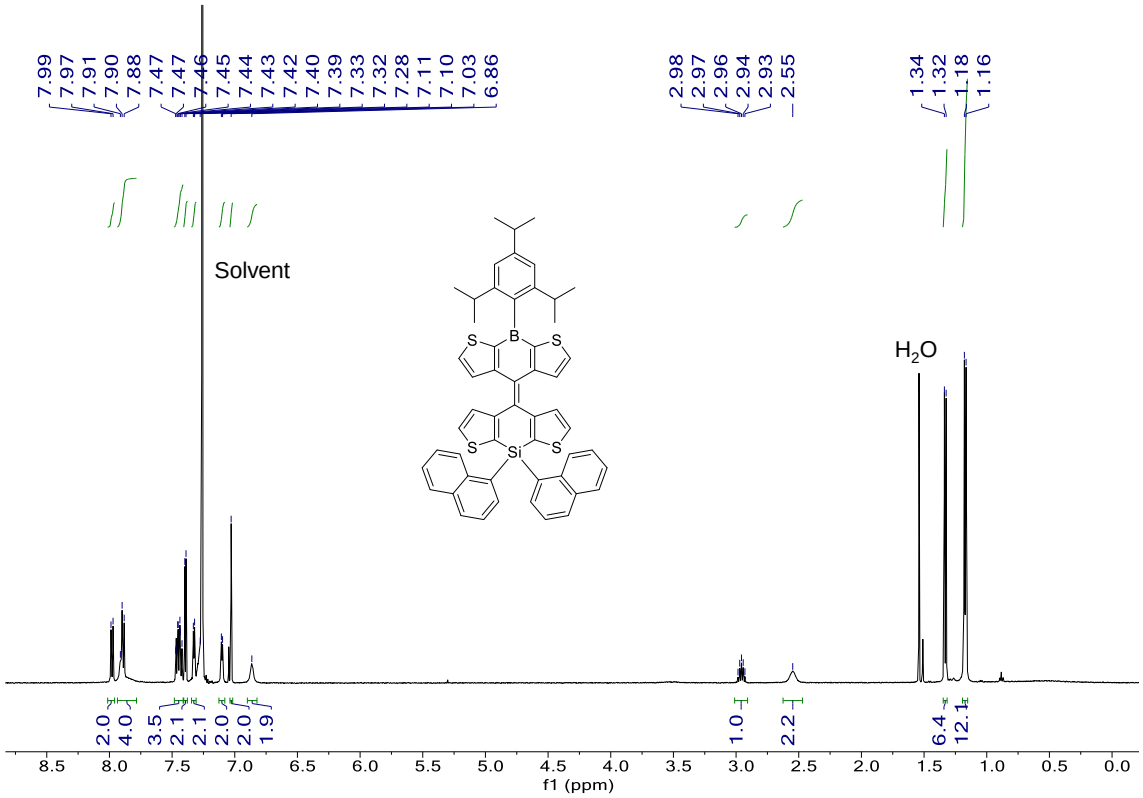


Figure S54 ^{1}H NMR spectrum of **DTCB-SiNp** in $CDCl_3$ at room temperature (500 MHz).

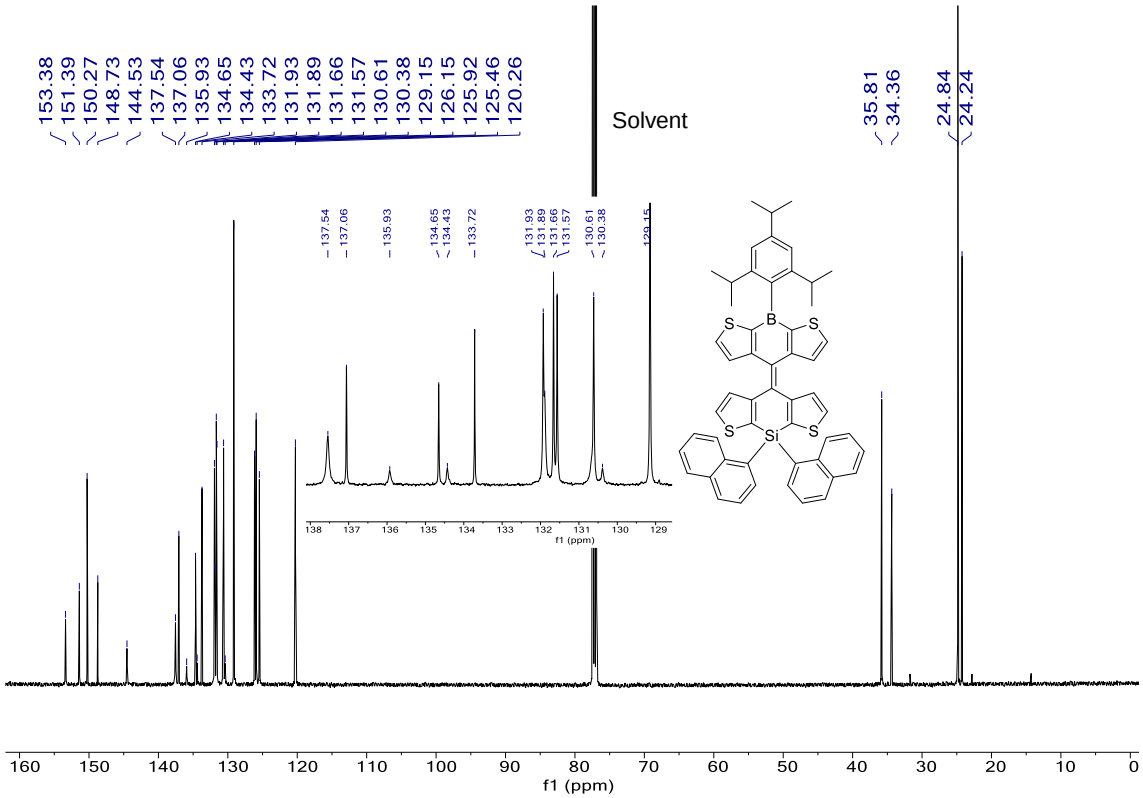


Figure S55 ^{13}C NMR spectrum of **DTCB-SiNp** in $CDCl_3$ at room temperature (125 MHz).

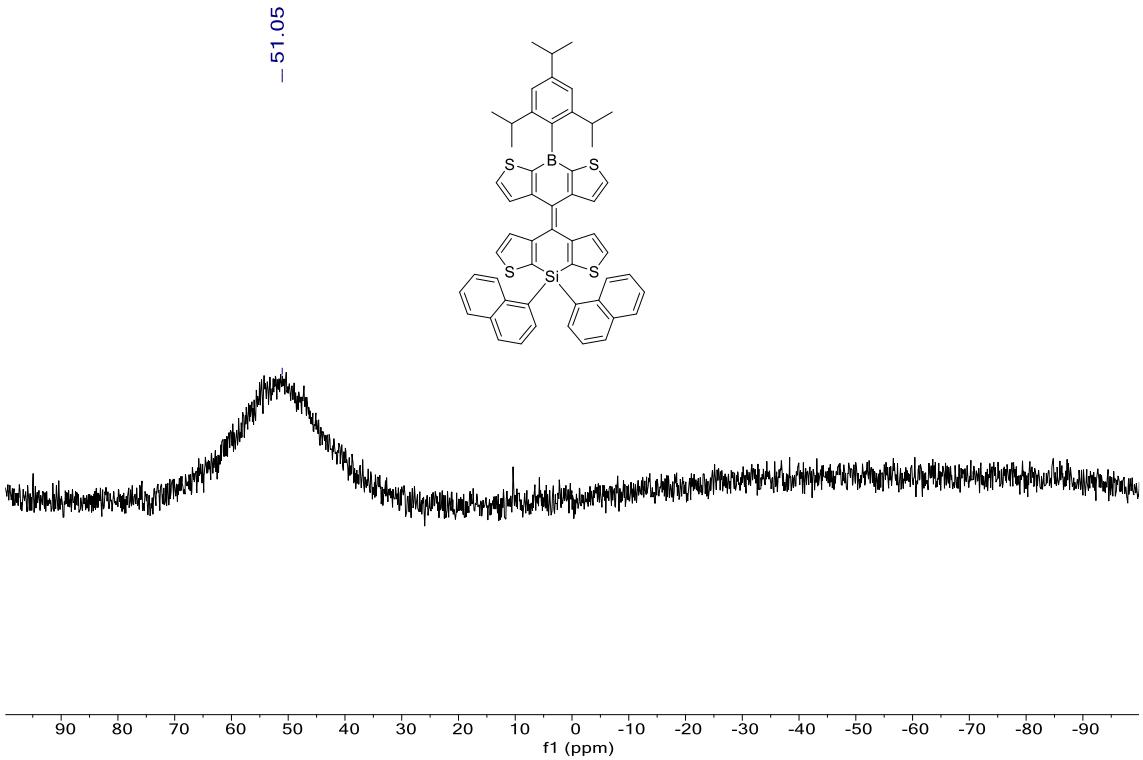


Figure S56 ^{11}B NMR spectrum of **DTCB-SiNp** in $CDCl_3$ at room temperature (160 MHz).

Cartesian coordinates for optimized structures

Table S14 Coordinates for optimized structure of the *anti*-folded conformer of **dDTCB'** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.705780	0.577843	1.245400
2	6	0	-1.312194	0.500187	1.312119
3	6	0	-0.564997	-0.188053	0.224500
4	6	0	-1.300286	-1.360651	-0.322686
5	6	0	-2.693687	-1.313819	-0.417551
6	5	0	-3.569400	-0.243166	0.265551
7	6	0	-0.761175	-2.616777	-0.740731
8	6	0	-1.721925	-3.481215	-1.194287
9	16	0	-3.302909	-2.789745	-1.124338
10	16	0	-3.329593	1.464121	2.614455
11	6	0	-1.753723	1.634729	3.300184
12	6	0	-0.784265	1.080768	2.506964
13	6	0	-5.133333	-0.102148	0.093839
14	6	0	0.639731	0.262720	-0.279641
15	6	0	1.389440	-0.433158	-1.358886
16	6	0	2.782731	-0.504086	-1.291542
17	5	0	3.649057	0.333152	-0.321514
18	6	0	2.765720	1.396810	0.370235
19	6	0	1.371446	1.433323	0.274256
20	16	0	3.354194	2.854636	1.129994
21	6	0	1.767826	3.532986	1.206784
22	6	0	0.818893	2.674134	0.721592
23	6	0	0.861041	-1.051267	-2.535631
24	6	0	1.829440	-1.634959	-3.307155
25	16	0	3.405055	-1.444892	-2.624333
26	6	0	5.200616	0.106824	-0.103890
27	6	0	-5.630643	0.770552	-0.904289
28	6	0	-7.009091	0.917031	-1.079449
29	6	0	-7.929606	0.219100	-0.289963
30	6	0	-7.427580	-0.638546	0.690343
31	6	0	-6.053169	-0.812863	0.898231
32	6	0	6.270676	0.740078	-0.790234
33	6	0	7.587448	0.344424	-0.511642
34	6	0	7.906761	-0.633914	0.430616
35	6	0	6.848693	-1.232405	1.114435
36	6	0	5.518623	-0.885566	0.862162
37	6	0	-9.431524	0.383245	-0.484785
38	6	0	-9.892917	1.825746	-0.202996
39	6	0	-9.884160	-0.077828	-1.883142
40	6	0	-4.671390	1.559384	-1.796494
41	6	0	-4.813785	1.173409	-3.280648
42	6	0	-4.817883	3.079672	-1.597951
43	6	0	-5.584622	-1.771416	1.994278
44	6	0	-6.044951	-1.318503	3.393355
45	6	0	-6.028561	-3.221679	1.721732
46	6	0	9.348345	-1.038952	0.708677
47	6	0	10.026872	-1.641967	-0.535729
48	6	0	10.174461	0.131267	1.275544

49	6	0	4.419341	-1.594769	1.658045
50	6	0	4.393795	-3.110619	1.387413
51	6	0	4.521588	-1.296096	3.165906
52	6	0	6.158700	1.892495	-1.802224
53	6	0	4.865177	1.994492	-2.618588
54	6	0	6.473412	3.242593	-1.120363
55	1	0	0.287447	-2.877530	-0.684390
56	1	0	-1.578402	-4.493471	-1.549546
57	1	0	-1.619404	2.118512	4.259027
58	1	0	0.262993	1.066311	2.778799
59	1	0	1.614293	4.532906	1.591458
60	1	0	-0.231549	2.926815	0.664689
61	1	0	-0.185872	-1.043735	-2.808510
62	1	0	1.695494	-2.153561	-4.247673
63	1	0	-7.375486	1.591819	-1.850102
64	1	0	-8.133123	-1.187386	1.311233
65	1	0	8.392511	0.831023	-1.059858
66	1	0	7.069979	-1.995384	1.858312
67	1	0	-9.924327	-0.267887	0.250388
68	1	0	-10.983139	1.908098	-0.290059
69	1	0	-9.605467	2.143164	0.805322
70	1	0	-9.448166	2.532015	-0.914186
71	1	0	-10.974353	-0.007429	-1.980312
72	1	0	-9.590396	-1.116201	-2.071725
73	1	0	-9.439462	0.542578	-2.670369
74	1	0	-3.645697	1.298182	-1.498303
75	1	0	-4.078363	1.709754	-3.892592
76	1	0	-4.660436	0.098379	-3.424999
77	1	0	-5.810404	1.422769	-3.663515
78	1	0	-4.083150	3.622308	-2.205188
79	1	0	-4.666609	3.356655	-0.548922
80	1	0	-5.815146	3.425939	-1.893976
81	1	0	-4.486127	-1.765134	1.997987
82	1	0	-5.648010	-1.989844	4.164528
83	1	0	-5.701760	-0.303163	3.616193
84	1	0	-7.138329	-1.329029	3.474726
85	1	0	-5.632455	-3.895790	2.490931
86	1	0	-5.672740	-3.570651	0.747075
87	1	0	-7.121308	-3.311387	1.732273
88	1	0	9.318943	-1.822598	1.478463
89	1	0	11.042286	-1.980943	-0.297171
90	1	0	9.461558	-2.498553	-0.918813
91	1	0	10.103485	-0.904787	-1.343796
92	1	0	11.190594	-0.197022	1.525786
93	1	0	9.713658	0.538290	2.182248
94	1	0	10.258176	0.947928	0.548619
95	1	0	3.448416	-1.201254	1.328194
96	1	0	3.566324	-3.585717	1.928424
97	1	0	4.268324	-3.317489	0.319034
98	1	0	5.323542	-3.590973	1.713836
99	1	0	3.694047	-1.767412	3.710037
100	1	0	4.486977	-0.217959	3.356979
101	1	0	5.458225	-1.679733	3.586952
102	1	0	6.964371	1.719192	-2.529791
103	1	0	4.954374	2.815648	-3.340080
104	1	0	4.663888	1.078047	-3.179410
105	1	0	3.990700	2.214069	-1.996835

106	1	0	6.518727	4.046736	-1.865381
107	1	0	7.434552	3.208854	-0.596486
108	1	0	5.702383	3.504836	-0.388830

Table S15 Coordinates for optimized structure of the twisted conformer of **dDTCB'** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.881197	-1.179165	0.458483
2	6	0	-1.476957	-1.171109	0.484041
3	6	0	-0.708800	-0.028652	-0.012450
4	6	0	-1.458728	1.113980	-0.535666
5	6	0	-2.862983	1.122625	-0.559109
6	5	0	-3.749112	-0.027982	-0.065340
7	6	0	-0.900420	2.230102	-1.252499
8	6	0	-1.848841	3.076447	-1.747676
9	16	0	-3.454896	2.528164	-1.402692
10	16	0	-3.502766	-2.584648	1.280538
11	6	0	-1.909955	-3.133625	1.681299
12	6	0	-0.944475	-2.287592	1.219682
13	6	0	-5.328544	-0.027389	-0.092318
14	6	0	0.708799	-0.028662	0.012457
15	6	0	1.458735	1.113663	0.536336
16	6	0	2.862989	1.122290	0.559777
17	5	0	3.749112	-0.028034	0.065338
18	6	0	2.881191	-1.178902	-0.459168
19	6	0	1.476952	-1.170829	-0.484712
20	16	0	3.502754	-2.583899	-1.282059
21	6	0	1.909939	-3.132638	-1.683131
22	6	0	0.944463	-2.286876	-1.221008
23	6	0	0.900435	2.229371	1.253817
24	6	0	1.848861	3.075428	1.749476
25	16	0	3.454912	2.527344	1.404159
26	6	0	5.328545	-0.027461	0.092304
27	6	0	-6.066547	0.567292	0.959660
28	6	0	-7.464017	0.558119	0.919280
29	6	0	-8.168706	-0.024558	-0.139609
30	6	0	-7.429911	-0.607089	-1.171502
31	6	0	-6.030042	-0.620104	-1.167138
32	6	0	6.066538	0.568022	-0.959227
33	6	0	7.464008	0.558822	-0.918864
34	6	0	8.168706	-0.024662	0.139573
35	6	0	7.429921	-0.607980	1.171029
36	6	0	6.030052	-0.620993	1.166668
37	6	0	5.283713	-1.266331	2.334571
38	6	0	5.589426	-2.771035	2.456148
39	6	0	5.555438	-0.536165	3.663732
40	6	0	9.691705	-0.028572	0.175807
41	6	0	10.293115	-0.817751	-1.002551
42	6	0	10.268816	1.398415	0.236169
43	6	0	5.356296	1.211806	-2.150747
44	6	0	5.659931	2.717778	-2.261034

45	6	0	5.673577	0.483899	-3.470982
46	6	0	-9.691704	-0.028438	-0.175862
47	6	0	-10.293131	-0.818486	1.001905
48	6	0	-10.268808	1.398596	-0.235176
49	6	0	-5.356319	1.210162	2.151682
50	6	0	-5.659969	2.716045	2.263133
51	6	0	-5.673604	0.481232	3.471351
52	6	0	-5.283691	-1.264547	-2.335528
53	6	0	-5.589398	-2.769159	-2.458258
54	6	0	-5.555407	-0.533366	-3.664133
55	1	0	0.159993	2.386803	-1.401339
56	1	0	-1.686379	3.985607	-2.312014
57	1	0	-1.767652	-4.043001	2.250710
58	1	0	0.110046	-2.444807	1.405296
59	1	0	1.767630	-4.041678	-2.253078
60	1	0	-0.110059	-2.443981	-1.406708
61	1	0	-0.159977	2.385990	1.402754
62	1	0	1.686405	3.984264	2.314338
63	1	0	-8.018514	1.015959	1.735570
64	1	0	-7.965350	-1.061859	-2.002956
65	1	0	8.018499	1.017287	-1.734809
66	1	0	7.965368	-1.063384	2.002130
67	1	0	4.207361	-1.174117	2.133768
68	1	0	5.002847	-3.219966	3.267018
69	1	0	5.348671	-3.299588	1.527373
70	1	0	6.649065	-2.946892	2.676218
71	1	0	4.966259	-0.979623	4.475689
72	1	0	5.293911	0.525136	3.592216
73	1	0	6.613026	-0.601961	3.945535
74	1	0	9.990143	-0.542083	1.100249
75	1	0	11.386276	-0.859045	-0.923570
76	1	0	9.912941	-1.844888	-1.025938
77	1	0	10.046545	-0.349188	-1.962760
78	1	0	11.361908	1.371171	0.321927
79	1	0	9.871996	1.949639	1.095685
80	1	0	10.020133	1.966867	-0.667898
81	1	0	4.274309	1.115572	-1.985349
82	1	0	5.098292	3.165380	-3.090094
83	1	0	5.387277	3.244478	-1.340069
84	1	0	6.725469	2.898008	-2.446434
85	1	0	5.109091	0.925624	-4.301216
86	1	0	5.414351	-0.578540	-3.408737
87	1	0	6.739399	0.554147	-3.718658
88	1	0	-9.990133	-0.541263	-1.100686
89	1	0	-11.386291	-0.859720	0.922877
90	1	0	-9.912959	-1.845639	1.024540
91	1	0	-10.046577	-0.350631	1.962463
92	1	0	-11.361900	1.371420	-0.320963
93	1	0	-9.871978	1.950452	-1.094282
94	1	0	-10.020130	1.966379	0.669313
95	1	0	-4.274330	1.114066	1.986219
96	1	0	-5.098344	3.163009	3.092546
97	1	0	-5.387309	3.243461	1.342580
98	1	0	-6.725511	2.896122	2.448660
99	1	0	-5.109129	0.922319	4.301932
100	1	0	-5.414369	-0.581157	3.408287
101	1	0	-6.739429	0.551278	3.719071

102	1	0	-4.207342	-1.172482	-2.134645
103	1	0	-5.002812	-3.217469	-3.269466
104	1	0	-5.348648	-3.298421	-1.529885
105	1	0	-6.649035	-2.944852	-2.678469
106	1	0	-4.966215	-0.976199	-4.476423
107	1	0	-5.293888	0.527882	-3.591802
108	1	0	-6.612991	-0.598954	-3.945999

Table S16 Coordinates for optimized structure of the *anti*-folded conformer of **dDTCC** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.820939	1.201806	-0.014321
2	6	0	-1.490232	1.221779	0.350573
3	6	0	-0.665723	0.000106	0.162384
4	6	0	-1.490274	-1.221565	0.350583
5	6	0	-2.820831	-1.201458	-0.014351
6	6	0	-3.523075	0.000114	-0.628938
7	6	0	-1.123789	-2.457206	0.988874
8	6	0	-2.151409	-3.349312	1.058824
9	16	0	-3.610244	-2.708410	0.364024
10	16	0	-3.610052	2.708467	0.364195
11	6	0	-2.151392	3.349459	1.059100
12	6	0	-1.123751	2.457345	0.988945
13	6	0	0.665705	0.000055	-0.162477
14	6	0	1.490189	-1.221652	-0.350670
15	6	0	2.820736	-1.201664	0.014424
16	6	0	3.522940	-0.000072	0.629102
17	6	0	2.820876	1.201588	0.014403
18	6	0	1.490336	1.221655	-0.350727
19	16	0	3.610426	2.708326	-0.364141
20	6	0	2.151746	3.349186	-1.059304
21	6	0	1.124024	2.457202	-0.989304
22	6	0	1.123706	-2.457219	-0.989086
23	6	0	2.151280	-3.349378	-1.058983
24	16	0	3.610081	-2.708561	-0.363965
25	6	0	-3.321915	0.000030	-2.171455
26	6	0	-5.033961	-0.000015	-0.321496
27	6	0	3.321526	-0.000052	2.171586
28	6	0	5.033851	-0.000126	0.321859
29	1	0	-0.139813	-2.655398	1.393566
30	1	0	-2.149062	-4.339946	1.493260
31	1	0	-2.149153	4.339892	1.493982
32	1	0	-0.139733	2.655422	1.393574
33	1	0	2.149564	4.339790	-1.493790
34	1	0	0.140079	2.655403	-1.394077
35	1	0	0.139758	-2.655294	-1.393922
36	1	0	2.148932	-4.340032	-1.493362
37	1	0	-3.783190	0.889549	-2.615486
38	1	0	-3.783122	-0.889579	-2.615385
39	1	0	-2.257781	0.000062	-2.424048
40	1	0	-5.225062	-0.000120	0.755507

41	1	0	-5.515065	0.881715	-0.759270
42	1	0	-5.515064	-0.881668	-0.759430
43	1	0	3.782694	-0.889613	2.615646
44	1	0	2.257361	-0.000039	2.424058
45	1	0	3.782708	0.889511	2.615629
46	1	0	5.514817	-0.881862	0.759765
47	1	0	5.225122	-0.000095	-0.755114
48	1	0	5.514889	0.881540	0.759828

Table S17 Coordinates for optimized structure of the twisted conformer of **dDTCC** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.881302	-1.116432	-0.478555
2	6	0	1.495922	-1.144767	-0.461658
3	6	0	0.699958	0.000052	0.000267
4	6	0	1.496408	1.144609	0.461939
5	6	0	2.881791	1.116061	0.478014
6	6	0	3.785385	-0.000300	-0.000468
7	6	0	0.987075	2.309575	1.151297
8	6	0	1.957815	3.141891	1.607767
9	16	0	3.547241	2.528133	1.264092
10	16	0	3.546099	-2.528688	-1.264853
11	6	0	1.956379	-3.142292	-1.607456
12	6	0	0.986025	-2.309776	-1.150536
13	6	0	-0.699958	0.000261	0.000427
14	6	0	-1.496124	1.145046	-0.461197
15	6	0	-2.881510	1.116454	-0.478020
16	6	0	-3.785384	-0.000415	-0.001201
17	6	0	-2.881583	-1.116038	0.478550
18	6	0	-1.496207	-1.144329	0.462401
19	16	0	-3.546738	-2.527867	1.265297
20	6	0	-1.957169	-3.141219	1.609085
21	6	0	-0.986612	-2.308916	1.152211
22	6	0	-0.986489	2.310434	-1.149624
23	6	0	-1.957027	3.142962	-1.606141
24	16	0	-3.546603	2.528953	-1.263648
25	6	0	4.690889	0.504132	-1.160030
26	6	0	4.691168	-0.505010	1.158782
27	6	0	-4.693523	0.503438	1.156500
28	6	0	-4.688528	-0.505702	-1.162307
29	1	0	-0.066405	2.500017	1.305532
30	1	0	1.840774	4.075707	2.141087
31	1	0	1.838894	-4.076147	-2.140608
32	1	0	-0.067563	-2.500141	-1.304086
33	1	0	-1.839939	-4.074707	2.142936
34	1	0	0.066916	-2.499085	1.306455
35	1	0	0.067051	2.501072	-1.303165
36	1	0	-1.839732	4.077144	-2.138763
37	1	0	5.356486	-0.292109	-1.510373
38	1	0	5.312778	1.339982	-0.821567
39	1	0	4.084917	0.844615	-2.004813
40	1	0	4.085390	-0.845260	2.003797
41	1	0	5.312635	-1.341084	0.820101

42	1	0	5.357159	0.291019	1.508849
43	1	0	-5.315297	1.338867	0.816791
44	1	0	-4.089501	0.844325	2.002516
45	1	0	-5.359341	-0.293209	1.505498
46	1	0	-5.354293	0.289921	-1.513722
47	1	0	-4.080802	-0.845549	-2.006085
48	1	0	-5.310109	-1.342195	-0.824872

Table S18 Coordinates for optimized structure of the *anti*-folded conformer of **dDTCSi** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.711592	-1.338706	-0.152557
2	6	0	1.393612	-1.133441	-0.331324
3	6	0	0.677892	0.000043	-0.094648
4	6	0	1.393601	1.133593	-0.331306
5	6	0	2.711540	1.338830	-0.152452
6	14	0	3.800819	0.000065	0.543015
7	6	0	0.971601	2.261799	-0.930349
8	6	0	1.964379	3.151070	-1.054597
9	16	0	3.227962	2.665195	-0.502855
10	16	0	3.228165	-2.665013	-0.502973
11	6	0	1.964573	-3.151109	-1.054559
12	6	0	0.971696	-2.261683	-0.930329
13	6	0	-0.677172	0.000027	0.092045
14	6	0	-1.392488	1.134008	0.327993
15	6	0	-2.710831	1.339184	0.151903
16	14	0	-3.803409	-0.000199	-0.537125
17	6	0	-2.710661	-1.339404	0.151970
18	6	0	-1.392338	-1.134000	0.328088
19	16	0	-3.225993	-2.666573	0.500657
20	6	0	-1.961370	-3.153161	1.049233
21	6	0	-0.969123	-2.263235	0.924465
22	6	0	-0.969508	2.263489	0.924245
23	6	0	-1.961826	3.153185	1.049053
24	16	0	-3.226464	2.666368	0.500583
25	6	0	5.529302	-0.000004	-0.169556
26	6	0	3.771519	0.000121	2.414062
27	6	0	-5.527119	-0.000085	0.187315
28	6	0	-3.787318	-0.000229	-2.408273
29	1	0	-0.026382	2.452673	-1.349554
30	1	0	1.864176	4.129046	-1.545326
31	1	0	1.864225	-4.128985	-1.545293
32	1	0	-0.026296	-2.452682	-1.349488
33	1	0	-1.859879	-4.131652	1.538540
34	1	0	0.029484	-2.454761	1.341812
35	1	0	0.029114	2.455271	1.341595
36	1	0	-1.860607	4.131763	1.538303
37	1	0	5.456883	-0.000020	-1.279584
38	1	0	6.057305	-0.912270	0.185572
39	1	0	6.057387	0.912378	0.185443
40	1	0	4.293441	0.914356	2.773224

41	1	0	2.710780	0.000130	2.749885
42	1	0	4.293512	-0.914116	2.773232
43	1	0	-6.057557	-0.912455	-0.164062
44	1	0	-6.057453	0.912272	-0.164249
45	1	0	-5.446900	0.000040	1.296802
46	1	0	-4.312040	0.914071	-2.763378
47	1	0	-2.728992	-0.000120	-2.751579
48	1	0	-4.311964	-0.914461	-2.763451

Table S19 Coordinates for optimized structure of the twisted conformer of **dDTCSi** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.837522	-1.291760	0.550047
2	6	0	-1.445902	-1.159832	0.532443
3	6	0	-0.707826	0.000197	0.000507
4	6	0	-1.445455	1.160559	-0.531339
5	6	0	-2.837096	1.292316	-0.549916
6	14	0	-4.058070	-0.000026	-0.001101
7	6	0	-0.807536	2.222473	-1.282304
8	6	0	-1.675342	3.134474	-1.792624
9	16	0	-3.319467	2.720603	-1.424708
10	16	0	-3.320360	-2.719464	1.425505
11	6	0	-1.676451	-3.132877	1.794951
12	6	0	-0.808387	-2.221133	1.284612
13	6	0	0.707825	-0.000152	0.000499
14	6	0	1.445928	1.159862	0.532434
15	6	0	2.837552	1.291766	0.550015
16	14	0	4.058070	-0.000004	-0.001120
17	6	0	2.837066	-1.292311	-0.549947
18	6	0	1.445429	-1.160528	-0.531348
19	16	0	3.319396	-2.720606	-1.424748
20	6	0	1.675256	-3.134452	-1.792629
21	6	0	0.807476	-2.222436	-1.282293
22	6	0	0.808447	2.221170	1.284623
23	6	0	1.676537	3.132899	1.794945
24	16	0	3.320431	2.719463	1.425464
25	6	0	-5.156671	0.568473	1.428429
26	6	0	-5.153545	-0.569059	-1.432832
27	6	0	5.153591	0.569000	-1.432826
28	6	0	5.156625	-0.568531	1.428435
29	1	0	0.260657	2.284972	-1.440374
30	1	0	-1.445507	4.017364	-2.374409
31	1	0	-1.446962	-4.015275	2.377618
32	1	0	0.259712	-2.283310	1.443499
33	1	0	1.445395	-4.017338	-2.374410
34	1	0	-0.260723	-2.284917	-1.440337
35	1	0	-0.259646	2.283366	1.443535
36	1	0	1.447074	4.015302	2.377616
37	1	0	-5.807483	-0.243506	1.774980
38	1	0	-5.801671	1.400180	1.119448
39	1	0	-4.554916	0.905037	2.279135

40	1	0	-5.803874	0.242679	-1.780847
41	1	0	-4.549909	-0.905538	-2.282240
42	1	0	-5.798917	-1.400936	-1.125082
43	1	0	5.804002	-0.242716	-1.780741
44	1	0	5.798884	1.400945	-1.125096
45	1	0	4.549985	0.905376	-2.282295
46	1	0	5.807345	0.243475	1.775096
47	1	0	4.554841	-0.905212	2.279075
48	1	0	5.801716	-1.400160	1.119431

Table S20 Coordinates for optimized structure of the *anti*-folded conformer of **DTCB-CMe** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.675132	1.258888	-0.557459
2	6	0	-0.714176	1.245365	-0.717484
3	6	0	-1.479464	0.000086	-0.454696
4	6	0	-0.714162	-1.245142	-0.717682
5	6	0	0.675145	-1.258669	-0.557652
6	5	0	1.534232	0.000099	-0.347764
7	6	0	-1.223524	-2.500012	-1.180313
8	6	0	-0.249376	-3.452301	-1.318095
9	16	0	1.312425	-2.850938	-0.892689
10	16	0	1.312396	2.851198	-0.892261
11	6	0	-0.249414	3.452617	-1.317576
12	6	0	-1.223551	2.500298	-1.179934
13	6	0	3.092345	0.000072	-0.080502
14	6	0	3.561776	-0.000047	1.255364
15	6	0	4.935420	-0.000110	1.512490
16	6	0	5.878123	-0.000032	0.478648
17	6	0	5.403802	0.000108	-0.834277
18	6	0	4.035345	0.000155	-1.133747
19	6	0	7.374397	-0.000065	0.764916
20	6	0	7.816037	1.269372	1.517540
21	6	0	7.816007	-1.269476	1.517596
22	6	0	2.578941	-0.000298	2.426869
23	6	0	2.706413	-1.272131	3.286206
24	6	0	2.707455	1.270261	3.287918
25	6	0	3.595826	0.000339	-2.598802
26	6	0	4.061514	1.267780	-3.341130
27	6	0	4.061525	-1.266894	-3.341476
28	6	0	-2.748795	0.000029	0.080504
29	6	0	-3.541133	-1.214947	0.410706
30	6	0	-4.904196	-1.198721	0.194662
31	6	0	-5.661953	0.000045	-0.358557
32	6	0	-4.904220	1.198714	0.194908
33	6	0	-3.541156	1.214925	0.410954
34	16	0	-5.651286	2.679540	0.723717
35	6	0	-4.127802	3.297576	1.290817
36	6	0	-3.110434	2.419524	1.067320
37	6	0	-3.110383	-2.419677	1.066812
38	6	0	-4.127731	-3.297799	1.290123

39	16	0	-5.651229	-2.679676	0.723157
40	6	0	-5.598705	0.000204	-1.912747
41	6	0	-7.139039	-0.000015	0.081333
42	1	0	-2.260786	-2.682274	-1.427532
43	1	0	-0.372685	-4.469740	-1.666264
44	1	0	-0.372728	4.470105	-1.665599
45	1	0	-2.260815	2.682583	-1.427127
46	1	0	5.280020	-0.000233	2.544434
47	1	0	6.126569	0.000189	-1.648128
48	1	0	7.887706	-0.000094	-0.206634
49	1	0	8.903530	1.277131	1.660305
50	1	0	7.537074	2.173572	0.965547
51	1	0	7.350075	1.326954	2.508466
52	1	0	8.903504	-1.277261	1.660331
53	1	0	7.537001	-2.173696	0.965659
54	1	0	7.350080	-1.326993	2.508541
55	1	0	1.561980	0.000439	2.009857
56	1	0	1.955350	-1.276390	4.085632
57	1	0	2.565555	-2.173350	2.679580
58	1	0	3.694254	-1.337847	3.757447
59	1	0	1.956205	1.274141	4.087167
60	1	0	2.567578	2.172426	2.682472
61	1	0	3.695218	1.334450	3.759528
62	1	0	2.497693	0.000336	-2.618792
63	1	0	3.687319	1.268861	-4.372212
64	1	0	3.698274	2.174195	-2.846023
65	1	0	5.155731	1.324035	-3.384846
66	1	0	3.687310	-1.267707	-4.372550
67	1	0	3.698313	-2.173449	-2.846604
68	1	0	5.155741	-1.323117	-3.385232
69	1	0	-4.082274	4.266907	1.768681
70	1	0	-2.088904	2.605180	1.372604
71	1	0	-2.088845	-2.605379	1.372044
72	1	0	-4.082178	-4.267237	1.767768
73	1	0	-6.098393	-0.889143	-2.312989
74	1	0	-4.562061	0.000254	-2.261149
75	1	0	-6.098417	0.889621	-2.312807
76	1	0	-7.656203	-0.881761	-0.312920
77	1	0	-7.235547	-0.000095	1.170842
78	1	0	-7.656239	0.881766	-0.312794

Table S21 Coordinates for optimized structure of the twisted conformer of **DTCB-CMe** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.708838	0.929444	-0.850726
2	6	0	0.696145	0.902911	-0.866721
3	6	0	1.454016	0.004916	0.005735
4	6	0	0.691332	-0.872101	0.895230
5	6	0	-0.713867	-0.858593	0.911592
6	5	0	-1.583837	0.047956	0.040662
7	6	0	1.231889	-1.671698	1.964570

8	6	0	0.273297	-2.283730	2.717532
9	16	0	-1.326451	-1.880705	2.192319
10	16	0	-1.321336	1.969017	-2.117361
11	6	0	0.276739	2.326124	-2.679635
12	6	0	1.234563	1.686859	-1.948645
13	6	0	-3.166341	0.071054	0.059547
14	6	0	-3.911280	-0.833836	-0.735288
15	6	0	-5.308894	-0.798646	-0.706389
16	6	0	-6.008648	0.111309	0.093056
17	6	0	-5.264352	0.998398	0.873151
18	6	0	-3.864198	0.995568	0.870450
19	6	0	-7.531570	0.142755	0.118470
20	6	0	-8.122064	0.506774	-1.257027
21	6	0	-8.126439	-1.178301	0.641706
22	6	0	-3.209079	-1.850389	-1.636662
23	6	0	-3.522046	-3.300903	-1.223403
24	6	0	-3.527728	-1.616982	-3.125754
25	6	0	-3.114358	1.992009	1.755121
26	6	0	-3.397970	3.450673	1.349328
27	6	0	-3.405129	1.766235	3.251108
28	6	0	2.866558	-0.014203	-0.009784
29	6	0	3.635107	-1.256792	-0.059145
30	6	0	5.022713	-1.257274	-0.102595
31	6	0	5.938608	-0.055808	-0.041855
32	6	0	5.057019	1.170077	0.036349
33	6	0	3.669292	1.207179	0.022439
34	16	0	5.737604	2.756825	0.272529
35	6	0	4.153662	3.470768	0.386071
36	6	0	3.171322	2.544351	0.256581
37	6	0	3.096208	-2.579798	-0.282905
38	6	0	4.050111	-3.532370	-0.433526
39	16	0	5.654873	-2.861659	-0.353651
40	6	0	6.854242	-0.146646	1.213153
41	6	0	6.832334	0.010462	-1.313980
42	1	0	2.289144	-1.774136	2.173327
43	1	0	0.426853	-2.938027	3.566143
44	1	0	0.429292	2.975870	-3.531915
45	1	0	2.289252	1.759052	-2.181686
46	1	0	-5.867298	-1.498666	-1.324376
47	1	0	-5.795575	1.711335	1.501377
48	1	0	-7.825363	0.935064	0.820956
49	1	0	-9.215028	0.582870	-1.202791
50	1	0	-7.729670	1.465097	-1.614464
51	1	0	-7.878230	-0.253823	-2.008318
52	1	0	-9.219377	-1.112539	0.708218
53	1	0	-7.737021	-1.420455	1.636607
54	1	0	-7.883429	-2.015270	-0.023722
55	1	0	-2.126756	-1.710014	-1.515676
56	1	0	-2.967134	-4.009840	-1.850346
57	1	0	-3.247178	-3.481326	-0.178515
58	1	0	-4.589694	-3.526163	-1.332582
59	1	0	-2.968395	-2.319917	-3.755429
60	1	0	-3.261754	-0.599221	-3.430984
61	1	0	-4.594748	-1.761200	-3.333688
62	1	0	-2.039293	1.822561	1.609060
63	1	0	-2.809969	4.144004	1.963435
64	1	0	-3.142427	3.624451	0.298418

65	1	0	-4.456410	3.704221	1.483186
66	1	0	-2.813282	2.453889	3.867811
67	1	0	-3.159070	0.741668	3.550249
68	1	0	-4.463003	1.938379	3.483076
69	1	0	4.052497	4.533916	0.557725
70	1	0	2.119725	2.784757	0.331837
71	1	0	2.037104	-2.791555	-0.335727
72	1	0	3.916566	-4.592227	-0.603378
73	1	0	7.466030	-1.053925	1.171567
74	1	0	6.256613	-0.173791	2.128892
75	1	0	7.527960	0.715076	1.264231
76	1	0	7.481300	-0.869231	-1.377691
77	1	0	6.218455	0.054182	-2.218255
78	1	0	7.469316	0.900709	-1.284176

Table S22 Coordinates for optimized structure of the *anti*-folded conformer of **DTCB-SiMe** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.793052	-1.259510	-0.404053
2	6	0	-0.595277	-1.248610	-0.570355
3	6	0	-1.363268	-0.000010	-0.324556
4	6	0	-0.595322	1.248582	-0.570532
5	6	0	0.793003	1.259526	-0.404233
6	5	0	1.651147	0.000034	-0.197663
7	6	0	-1.104212	2.513030	-1.007329
8	6	0	-0.129092	3.467043	-1.124363
9	16	0	1.431488	2.857114	-0.707295
10	16	0	1.431554	-2.857131	-0.706879
11	6	0	-0.129003	-3.467138	-1.123875
12	6	0	-1.104141	-2.513122	-1.006982
13	6	0	3.208883	0.000127	0.071207
14	6	0	4.151602	-0.000139	-0.985224
15	6	0	5.519397	-0.000088	-0.691762
16	6	0	5.995821	0.000268	0.623230
17	6	0	5.055962	0.000553	1.656066
18	6	0	3.679441	0.000473	1.404180
19	6	0	7.488152	0.000167	0.929753
20	6	0	8.183148	-1.269996	0.403771
21	6	0	8.184041	1.268858	0.401456
22	6	0	3.705282	-0.000422	-2.448536
23	6	0	4.166478	1.267230	-3.193154
24	6	0	4.166802	-1.268121	-3.192851
25	6	0	2.701291	0.000716	2.579132
26	6	0	2.833043	-1.270312	3.439075
27	6	0	2.833142	1.272000	3.438679
28	6	0	-2.642793	-0.000006	0.180300
29	6	0	-3.409333	1.243016	0.498043
30	6	0	-4.727370	1.399929	0.094038
31	14	0	-5.685794	-0.000163	-0.709990
32	6	0	-4.727292	-1.400068	0.094273
33	6	0	-3.409264	-1.243014	0.498255

34	16	0	-5.366447	-2.907823	0.684133
35	6	0	-3.884471	-3.299277	1.496118
36	6	0	-2.941570	-2.329923	1.311952
37	6	0	-2.941692	2.330094	1.311543
38	6	0	-3.884639	3.299438	1.495530
39	16	0	-5.366597	2.907760	0.683618
40	6	0	-7.498922	-0.000160	-0.196085
41	6	0	-5.527492	-0.000323	-2.591228
42	1	0	-2.140623	2.701377	-1.252982
43	1	0	-0.251700	4.491761	-1.450648
44	1	0	-0.251595	-4.491907	-1.450007
45	1	0	-2.140546	-2.701516	-1.252625
46	1	0	6.233516	-0.000339	-1.512340
47	1	0	5.411379	0.000847	2.685009
48	1	0	7.591825	0.001144	2.023707
49	1	0	9.242744	-1.277965	0.687091
50	1	0	7.714167	-2.173712	0.808067
51	1	0	8.130737	-1.328356	-0.689933
52	1	0	9.243590	1.276647	0.684946
53	1	0	7.715606	2.173656	0.803966
54	1	0	8.131908	1.325209	-0.692365
55	1	0	2.607045	-0.000573	-2.463479
56	1	0	3.787317	1.268216	-4.222402
57	1	0	3.805079	2.173341	-2.696064
58	1	0	5.260434	1.324445	-3.242195
59	1	0	3.787621	-1.269437	-4.222091
60	1	0	3.805639	-2.174210	-2.695548
61	1	0	5.260772	-1.325083	-3.241920
62	1	0	1.682813	0.000693	2.165693
63	1	0	2.085698	-1.273981	4.242030
64	1	0	2.689651	-2.172137	2.833929
65	1	0	3.823018	-1.335151	3.905855
66	1	0	2.085804	1.275969	4.241638
67	1	0	2.689806	2.173645	2.833252
68	1	0	3.823124	1.336918	3.905432
69	1	0	-3.795824	-4.216014	2.064152
70	1	0	-1.948913	-2.371717	1.743554
71	1	0	-1.949033	2.372020	1.743126
72	1	0	-3.796033	4.216288	2.063387
73	1	0	-8.018415	-0.883475	-0.586742
74	1	0	-8.018477	0.883000	-0.587009
75	1	0	-7.605307	0.000000	0.893590
76	1	0	-6.005776	0.886046	-3.025033
77	1	0	-4.476110	-0.000392	-2.898109
78	1	0	-6.005849	-0.886725	-3.024884

Table S23 Coordinates for optimized structure of the twisted conformer of **DTCB-SiMe** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.845609	0.884347	-0.901021
2	6	0	0.559197	0.860008	-0.910599

3	6	0	1.316620	0.007796	0.006486
4	6	0	0.553397	-0.822499	0.938783
5	6	0	-0.851443	-0.805362	0.957916
6	5	0	-1.722458	0.052486	0.037506
7	6	0	1.097659	-1.569365	2.043601
8	6	0	0.140464	-2.137719	2.831120
9	16	0	-1.460845	-1.755893	2.292337
10	16	0	-1.453823	1.853003	-2.222883
11	6	0	0.146724	2.187286	-2.794579
12	6	0	1.102606	1.590698	-2.026585
13	6	0	-3.304206	0.075942	0.053926
14	6	0	-4.047837	-0.876984	-0.683893
15	6	0	-5.445411	-0.841178	-0.657457
16	6	0	-6.146059	0.116243	0.083729
17	6	0	-5.402801	1.050587	0.807643
18	6	0	-4.002690	1.048379	0.806018
19	6	0	-7.669012	0.146791	0.107829
20	6	0	-8.261673	0.413474	-1.288795
21	6	0	-8.260038	-1.136434	0.721918
22	6	0	-3.344153	-1.945263	-1.521996
23	6	0	-3.658305	-3.368947	-1.024901
24	6	0	-3.659584	-1.799730	-3.022895
25	6	0	-3.253602	2.096468	1.629493
26	6	0	-3.538956	3.528322	1.138449
27	6	0	-3.543331	1.959120	3.136362
28	6	0	2.735428	-0.012341	-0.007358
29	6	0	3.447775	-1.298169	-0.049362
30	6	0	4.838774	-1.448620	-0.027619
31	14	0	6.081192	-0.059969	-0.038065
32	6	0	4.878781	1.363475	-0.026849
33	6	0	3.484694	1.252739	0.020689
34	16	0	5.380917	3.010606	0.207150
35	6	0	3.744743	3.558879	0.396786
36	6	0	2.862680	2.531131	0.296391
37	6	0	2.784553	-2.558144	-0.313471
38	6	0	3.634945	-3.610568	-0.430231
39	16	0	5.289319	-3.109259	-0.270911
40	6	0	7.183039	-0.038418	1.495643
41	6	0	7.154832	-0.112395	-1.590916
42	1	0	2.156327	-1.668018	2.247262
43	1	0	0.294555	-2.749218	3.710923
44	1	0	0.300791	2.794181	-3.677568
45	1	0	2.159360	1.658066	-2.251827
46	1	0	-6.003221	-1.578571	-1.230874
47	1	0	-5.934814	1.800495	1.390449
48	1	0	-7.963875	0.985080	0.754229
49	1	0	-9.354658	0.491090	-1.238268
50	1	0	-7.871741	1.345499	-1.712346
51	1	0	-8.017579	-0.396876	-1.986017
52	1	0	-9.353115	-1.069289	0.784165
53	1	0	-7.869731	-1.307782	1.731080
54	1	0	-8.014624	-2.016860	0.116107
55	1	0	-2.261872	-1.798204	-1.407109
56	1	0	-3.102154	-4.113475	-1.607889
57	1	0	-3.386023	-3.487853	0.029420
58	1	0	-4.725691	-3.600201	-1.123247
59	1	0	-3.098988	-2.538320	-3.609064

60	1	0	-3.393388	-0.801577	-3.387045
61	1	0	-4.726183	-1.956211	-3.223791
62	1	0	-2.178233	1.919867	1.493148
63	1	0	-2.951574	4.257282	1.710379
64	1	0	-3.284134	3.640241	0.079005
65	1	0	-4.597591	3.788127	1.257697
66	1	0	-2.951524	2.682179	3.711107
67	1	0	-3.296939	0.954060	3.495440
68	1	0	-4.601156	2.144323	3.358051
69	1	0	3.531959	4.602843	0.584985
70	1	0	1.797160	2.661832	0.425841
71	1	0	1.713506	-2.658335	-0.423095
72	1	0	3.389040	-4.647938	-0.614485
73	1	0	7.844688	0.836180	1.494373
74	1	0	7.816577	-0.932893	1.533984
75	1	0	6.584444	-0.007949	2.411959
76	1	0	7.791275	-1.005445	-1.601122
77	1	0	6.539620	-0.125520	-2.496574
78	1	0	7.812783	0.763712	-1.640528

Table S24 Coordinates for optimized structure of the *anti*-folded conformer of **DTCB-SiPh** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.965958	0.311469	-1.259930
2	6	0	-0.568463	0.352400	-1.247982
3	6	0	0.172638	0.033911	-0.000047
4	6	0	-0.568435	0.352544	1.247869
5	6	0	-1.965929	0.311622	1.259866
6	5	0	-2.839250	0.182885	-0.000015
7	6	0	-0.020140	0.746348	2.509516
8	6	0	-0.979499	0.953226	3.464248
9	16	0	-2.572256	0.675493	2.857400
10	16	0	-2.572336	0.675116	-2.857493
11	6	0	-0.979603	0.952769	-3.464433
12	6	0	-0.020211	0.746029	-2.509702
13	6	0	-4.415101	0.056502	0.000014
14	6	0	-5.005047	-1.230555	0.000139
15	6	0	-6.396529	-1.360241	0.000175
16	6	0	-7.240180	-0.244106	0.000086
17	6	0	-6.647332	1.019762	-0.000038
18	6	0	-5.257190	1.191939	-0.000073
19	6	0	-8.756399	-0.392137	0.000112
20	6	0	-9.264955	-1.101326	-1.269310
21	6	0	-9.264936	-1.101228	1.269595
22	6	0	-4.133836	-2.487309	0.000228
23	6	0	-4.340167	-3.331868	1.271566
24	6	0	-4.340094	-3.331978	-1.271049
25	6	0	-4.683461	2.609707	-0.000210
26	6	0	-5.077761	3.391855	-1.267829
27	6	0	-5.077641	3.392051	1.267326
28	6	0	1.396996	-0.592165	-0.000016

29	6	0	2.128132	-0.982917	1.243257
30	6	0	3.480566	-0.712901	1.400792
31	14	0	4.498743	0.007522	-0.000025
32	6	0	3.480572	-0.712951	-1.400817
33	6	0	2.128152	-0.983010	-1.243255
34	16	0	4.059749	-1.362129	-2.908181
35	6	0	2.503220	-2.016265	-3.301934
36	6	0	1.582200	-1.742615	-2.331935
37	6	0	1.582154	-1.742382	2.332021
38	6	0	2.503167	-2.015969	3.302045
39	16	0	4.059726	-1.361934	2.908200
40	6	0	4.469677	1.890684	-0.000067
41	6	0	6.266312	-0.637479	0.000018
42	6	0	6.523196	-2.022761	-0.000194
43	6	0	7.828210	-2.513558	-0.000132
44	6	0	8.907802	-1.626828	0.000148
45	6	0	8.676098	-0.251134	0.000362
46	6	0	7.367682	0.236937	0.000295
47	6	0	4.470129	2.615944	-1.205671
48	6	0	4.478829	4.011572	-1.208117
49	6	0	4.484281	4.711583	-0.000155
50	6	0	4.479459	4.011644	1.207854
51	6	0	4.470754	2.616016	1.205493
52	1	0	1.034469	0.901961	2.692740
53	1	0	-0.827225	1.271536	4.487494
54	1	0	-0.827363	1.270939	-4.487727
55	1	0	1.034390	0.901626	-2.692984
56	1	0	-6.834914	-2.355932	0.000271
57	1	0	-7.292325	1.896487	-0.000110
58	1	0	-9.178768	0.622258	0.000077
59	1	0	-10.360947	-1.144046	-1.277165
60	1	0	-8.936600	-0.577194	-2.173502
61	1	0	-8.891540	-2.130735	-1.326853
62	1	0	-10.360928	-1.143934	1.277473
63	1	0	-8.936558	-0.577034	2.173743
64	1	0	-8.891536	-2.130639	1.327208
65	1	0	-3.083037	-2.164810	0.000245
66	1	0	-3.665710	-4.196965	1.275862
67	1	0	-4.144718	-2.740970	2.173055
68	1	0	-5.367053	-3.710607	1.336670
69	1	0	-3.665654	-4.197089	-1.275222
70	1	0	-4.144569	-2.741163	-2.172577
71	1	0	-5.366984	-3.710697	-1.336190
72	1	0	-3.588206	2.527347	-0.000255
73	1	0	-4.608277	4.383156	-1.269642
74	1	0	-4.762865	2.864042	-2.173892
75	1	0	-6.163068	3.538117	-1.323935
76	1	0	-4.608154	4.383351	1.268945
77	1	0	-4.762663	2.864376	2.173441
78	1	0	-6.162942	3.538325	1.323508
79	1	0	2.358097	-2.571321	-4.219529
80	1	0	0.551764	-2.073936	-2.374458
81	1	0	0.551706	-2.073660	2.374584
82	1	0	2.358033	-2.570932	4.219695
83	1	0	5.694571	-2.727081	-0.000412
84	1	0	8.003840	-3.586211	-0.000301
85	1	0	9.925676	-2.008399	0.000197

86	1	0	9.512667	0.442915	0.000578
87	1	0	7.202709	1.311193	0.000455
88	1	0	4.455178	2.085610	-2.155511
89	1	0	4.476243	4.552113	-2.151209
90	1	0	4.487168	5.798541	-0.000188
91	1	0	4.477366	4.552240	2.150914
92	1	0	4.456287	2.085745	2.155377

Table S25 Coordinates for optimized structure of the twisted conformer of **DTCB-SiPh** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.178246	1.033807	0.721552
2	6	0	-0.773347	1.035995	0.703260
3	6	0	-0.014619	-0.017863	0.028716
4	6	0	-0.776873	-1.080119	-0.628360
5	6	0	-2.181748	-1.092509	-0.616506
6	5	0	-3.054168	-0.033483	0.061398
7	6	0	-0.232560	-2.300357	-1.166039
8	6	0	-1.189379	-3.173091	-1.592907
9	16	0	-2.790759	-2.571168	-1.321545
10	16	0	-2.787332	2.505627	1.440723
11	6	0	-1.186848	3.123887	1.678372
12	6	0	-0.230372	2.261457	1.230307
13	6	0	-4.635965	-0.040920	0.077465
14	6	0	-5.370889	0.519200	-0.995623
15	6	0	-6.768735	0.504808	-0.964213
16	6	0	-7.477975	-0.053823	0.104359
17	6	0	-6.743165	-0.604256	1.156332
18	6	0	-5.343081	-0.606905	1.163147
19	6	0	-9.001185	-0.066160	0.129749
20	6	0	-9.587668	1.358177	0.147149
21	6	0	-9.589404	-0.890709	-1.030879
22	6	0	-4.657345	1.153387	-2.190363
23	6	0	-4.973986	0.421407	-3.508112
24	6	0	-4.958194	2.659866	-2.306459
25	6	0	-4.603230	-1.234559	2.344796
26	6	0	-4.902868	-0.504779	3.667770
27	6	0	-4.889842	-2.743392	2.466562
28	6	0	1.404350	-0.009745	0.012164
29	6	0	2.122012	-0.196792	-1.256751
30	6	0	3.514363	-0.252583	-1.394393
31	14	0	4.752948	0.014920	-0.027105
32	6	0	3.543145	0.260944	1.369576
33	6	0	2.148934	0.185776	1.264169
34	16	0	4.039731	0.317027	3.033859
35	6	0	2.403030	0.218366	3.599887
36	6	0	1.523203	0.133094	2.568291
37	6	0	1.465599	-0.155077	-2.546125
38	6	0	2.322382	-0.229966	-3.597715
39	16	0	3.972974	-0.304791	-3.069675
40	6	0	5.851645	-1.493716	0.237302

41	6	0	5.817917	1.542834	-0.317783
42	6	0	5.407704	2.806307	0.145603
43	6	0	6.163627	3.950679	-0.112049
44	6	0	7.348417	3.854633	-0.843949
45	6	0	7.774527	2.610989	-1.314039
46	6	0	7.017466	1.468551	-1.051004
47	6	0	7.070165	-1.396916	0.935767
48	6	0	7.853562	-2.525663	1.180228
49	6	0	7.435247	-3.777784	0.725948
50	6	0	6.231857	-3.896075	0.028419
51	6	0	5.449740	-2.765396	-0.210714
52	1	0	0.825948	-2.520386	-1.220853
53	1	0	-1.035270	-4.147134	-2.039227
54	1	0	-1.033292	4.099087	2.122351
55	1	0	0.826692	2.492519	1.262767
56	1	0	-7.319767	0.941745	-1.794346
57	1	0	-7.281938	-1.044218	1.993723
58	1	0	-9.303426	-0.556188	1.065709
59	1	0	-10.681274	1.326766	0.226155
60	1	0	-9.199917	1.935025	0.993911
61	1	0	-9.335885	1.903337	-0.770329
62	1	0	-10.683063	-0.935877	-0.959709
63	1	0	-9.203425	-1.915927	-1.022837
64	1	0	-9.337182	-0.447547	-2.001632
65	1	0	-3.576420	1.055403	-2.022321
66	1	0	-4.409757	0.861321	-4.339713
67	1	0	-4.713208	-0.640458	-3.442296
68	1	0	-6.039635	0.489547	-3.757440
69	1	0	-4.392145	3.104548	-3.134245
70	1	0	-4.688170	3.188104	-1.385675
71	1	0	-6.022918	2.840823	-2.496563
72	1	0	-3.526310	-1.127583	2.157427
73	1	0	-4.320642	-0.939895	4.489433
74	1	0	-4.651798	0.559129	3.597247
75	1	0	-5.963430	-0.581571	3.935518
76	1	0	-4.305788	-3.183042	3.284469
77	1	0	-4.631603	-3.269825	1.541361
78	1	0	-5.949590	-2.932719	2.675324
79	1	0	2.186714	0.212697	4.660044
80	1	0	0.457787	0.022184	2.716058
81	1	0	0.395618	-0.059452	-2.669404
82	1	0	2.081458	-0.229453	-4.652568
83	1	0	4.487815	2.896273	0.718284
84	1	0	5.829034	4.915970	0.259179
85	1	0	7.938604	4.744903	-1.045487
86	1	0	8.697624	2.529986	-1.882278
87	1	0	7.371937	0.507048	-1.415169
88	1	0	7.418605	-0.428387	1.286884
89	1	0	8.790996	-2.427350	1.721632
90	1	0	8.045863	-4.657374	0.913005
91	1	0	5.903155	-4.868044	-0.330437
92	1	0	4.515563	-2.872623	-0.756677

Table S26 Coordinates for optimized structure of the *anti*-folded conformer of **DTCB-SiNp** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.738584	0.266558	1.312664
2	6	0	1.345152	0.176907	1.387122
3	6	0	0.542246	0.073795	0.140846
4	6	0	1.249086	-0.587218	-0.986819
5	6	0	2.641485	-0.506341	-1.083364
6	5	0	3.555463	0.032120	0.029959
7	6	0	0.669981	-1.368527	-2.036561
8	6	0	1.599771	-1.828542	-2.930127
9	16	0	3.200634	-1.325373	-2.521766
10	16	0	3.425251	0.432309	2.910478
11	6	0	1.873586	0.301559	3.656589
12	6	0	0.868168	0.172379	2.736149
13	6	0	5.122114	0.207030	-0.089519
14	6	0	6.019415	-0.845501	0.213158
15	6	0	7.397207	-0.637012	0.089708
16	6	0	7.927487	0.588185	-0.327276
17	6	0	7.032041	1.618200	-0.622882
18	6	0	5.647313	1.449698	-0.511738
19	6	0	9.430097	0.802497	-0.458640
20	6	0	10.152990	0.653188	0.893403
21	6	0	10.052022	-0.122540	-1.521900
22	6	0	5.512751	-2.213312	0.674400
23	6	0	5.894357	-3.333451	-0.312349
24	6	0	5.990290	-2.555805	2.098730
25	6	0	4.719491	2.616519	-0.850874
26	6	0	4.938052	3.818639	0.086928
27	6	0	4.835055	3.033581	-2.329069
28	6	0	-0.709440	0.628040	0.008421
29	6	0	-1.488564	0.608758	-1.265490
30	6	0	-2.832349	0.259911	-1.293917
31	14	0	-3.793673	-0.055501	0.294365
32	6	0	-2.759325	1.067736	1.389680
33	6	0	-1.426807	1.338669	1.108636
34	16	0	-3.329518	2.092438	2.676037
35	6	0	-1.802315	2.901925	2.799492
36	6	0	-0.893917	2.403352	1.910193
37	6	0	-0.993394	1.028913	-2.546147
38	6	0	-1.941478	0.971176	-3.526117
39	16	0	-3.460908	0.409649	-2.910316
40	6	0	-5.601896	0.489006	0.208366
41	6	0	-3.646226	-1.848895	0.890204
42	6	0	-3.109666	-2.065198	2.151987
43	6	0	-2.928117	-3.364234	2.682998
44	6	0	-3.281366	-4.464884	1.941378
45	6	0	-3.837686	-4.315033	0.643125
46	6	0	-4.029437	-2.995867	0.107396
47	6	0	-6.571547	-0.428916	0.591123
48	6	0	-7.951583	-0.118494	0.578990
49	6	0	-8.370433	1.126803	0.179312
50	6	0	-7.431621	2.115395	-0.218692
51	6	0	-6.029244	1.803407	-0.204681

52	6	0	-4.210581	-5.447132	-0.130113
53	6	0	-4.757274	-5.300988	-1.384075
54	6	0	-4.956053	-4.006114	-1.916554
55	6	0	-4.602578	-2.890126	-1.190424
56	6	0	-7.860595	3.407243	-0.625518
57	6	0	-6.952571	4.368995	-1.003063
58	6	0	-5.570279	4.072666	-0.986614
59	6	0	-5.123875	2.828053	-0.599428
60	1	0	-0.382678	-1.607455	-2.108689
61	1	0	1.422189	-2.452229	-3.796725
62	1	0	1.777579	0.309109	4.734685
63	1	0	-0.169369	0.047222	3.014488
64	1	0	8.076141	-1.453679	0.325174
65	1	0	7.429598	2.577720	-0.948974
66	1	0	9.579054	1.837241	-0.797195
67	1	0	11.222938	0.870057	0.787242
68	1	0	9.737892	1.337358	1.641544
69	1	0	10.057492	-0.366464	1.285180
70	1	0	11.121374	0.089449	-1.642932
71	1	0	9.565000	0.009140	-2.494307
72	1	0	9.951778	-1.177266	-1.239355
73	1	0	4.415669	-2.171064	0.704409
74	1	0	5.471685	-4.292219	0.011995
75	1	0	5.521078	-3.119834	-1.319170
76	1	0	6.982364	-3.454588	-0.375893
77	1	0	5.567667	-3.513538	2.426222
78	1	0	5.685725	-1.786107	2.815320
79	1	0	7.082562	-2.642441	2.142554
80	1	0	3.685663	2.276667	-0.696280
81	1	0	4.225298	4.621159	-0.139465
82	1	0	4.806206	3.529541	1.135308
83	1	0	5.948258	4.230773	-0.021486
84	1	0	4.123147	3.834884	-2.562382
85	1	0	4.628712	2.188026	-2.994276
86	1	0	5.840545	3.403862	-2.561464
87	1	0	-1.662716	3.702585	3.514097
88	1	0	0.118029	2.777604	1.814335
89	1	0	0.022551	1.364863	-2.714420
90	1	0	-1.836580	1.232442	-4.571017
91	1	0	-2.811146	-1.215364	2.759612
92	1	0	-2.503829	-3.482712	3.676343
93	1	0	-3.140953	-5.468443	2.336654
94	1	0	-6.275033	-1.423464	0.910600
95	1	0	-8.672664	-0.871165	0.885882
96	1	0	-9.428973	1.376958	0.163922
97	1	0	-4.055896	-6.437353	0.292421
98	1	0	-5.038475	-6.174850	-1.965390
99	1	0	-5.390850	-3.890557	-2.905621
100	1	0	-4.770979	-1.908649	-1.620843
101	1	0	-8.926889	3.621832	-0.630326
102	1	0	-7.292423	5.353945	-1.311475
103	1	0	-4.852940	4.833613	-1.281778
104	1	0	-4.058205	2.627535	-0.594638

Table S27 Coordinates for optimized structure of the twisted conformer of **DTCB-SiNp** in the ground state (S0).

opt b3lyp/6-31g(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.950595	-0.754334	-1.079790
2	6	0	-1.545852	-0.738957	-1.106623
3	6	0	-0.767590	-0.013531	-0.101956
4	6	0	-1.510231	0.705584	0.933515
5	6	0	-2.914978	0.698409	0.968770
6	5	0	-3.806610	-0.036370	-0.034883
7	6	0	-0.954383	1.638303	1.880320
8	6	0	-1.900064	2.266900	2.635043
9	16	0	-3.506943	1.786988	2.201678
10	16	0	-3.578261	-1.842961	-2.294831
11	6	0	-1.984294	-2.291667	-2.803077
12	6	0	-1.016375	-1.653740	-2.085120
13	6	0	-5.388132	-0.049224	0.002594
14	6	0	-6.082614	-0.989834	0.801574
15	6	0	-7.480719	-0.987361	0.822947
16	6	0	-8.229461	-0.073904	0.073389
17	6	0	-7.534410	0.849394	-0.710178
18	6	0	-6.135442	0.877695	-0.759948
19	6	0	-9.752624	-0.077468	0.104028
20	6	0	-10.336064	-1.396170	-0.437805
21	6	0	-10.300202	0.231283	1.510370
22	6	0	-5.325026	-2.022232	1.637635
23	6	0	-5.597705	-1.858858	3.144749
24	6	0	-5.615925	-3.462390	1.174150
25	6	0	-5.440461	1.922806	-1.633130
26	6	0	-5.786931	1.753189	-3.124349
27	6	0	-5.734232	3.357815	-1.155527
28	6	0	0.651546	-0.005359	-0.145017
29	6	0	1.431212	-0.297803	1.065016
30	6	0	2.832282	-0.290383	1.151674
31	14	0	4.000360	-0.085152	-0.298869
32	6	0	2.718537	0.290387	-1.600372
33	6	0	1.333620	0.314847	-1.406113
34	16	0	3.139256	0.936297	-3.158518
35	6	0	1.480282	1.249141	-3.555949
36	6	0	0.649059	0.896595	-2.540950
37	6	0	0.828357	-0.799456	2.281039
38	6	0	1.726663	-1.091798	3.256362
39	16	0	3.353445	-0.828768	2.719874
40	6	0	5.245788	1.340810	-0.207077
41	6	0	4.875839	-1.731598	-0.659893
42	6	0	4.434595	-2.455761	-1.759643
43	6	0	4.956958	-3.729435	-2.086380
44	6	0	5.928888	-4.295506	-1.298885
45	6	0	6.425369	-3.610435	-0.158230
46	6	0	5.903408	-2.311901	0.168040
47	6	0	6.526149	1.103034	-0.690536
48	6	0	7.514336	2.114147	-0.743139
49	6	0	7.221787	3.381979	-0.304291
50	6	0	5.929442	3.696386	0.193756
51	6	0	4.922127	2.672593	0.240434

52	6	0	7.429985	-4.190551	0.661852
53	6	0	7.915544	-3.528720	1.765863
54	6	0	7.414648	-2.247417	2.090682
55	6	0	6.440832	-1.659528	1.312992
56	6	0	5.617711	5.009689	0.636477
57	6	0	4.361116	5.321906	1.101033
58	6	0	3.361145	4.323434	1.140570
59	6	0	3.635644	3.039058	0.724140
60	1	0	0.104486	1.835421	1.989010
61	1	0	-1.734962	2.998758	3.415347
62	1	0	-1.842109	-3.015439	-3.595330
63	1	0	0.039821	-1.835732	-2.237287
64	1	0	-8.000326	-1.717770	1.439524
65	1	0	-8.104125	1.567643	-1.297221
66	1	0	-10.089783	0.728174	-0.562892
67	1	0	-11.431893	-1.354448	-0.462887
68	1	0	-9.978079	-1.599147	-1.453068
69	1	0	-10.049850	-2.246639	0.192399
70	1	0	-11.395828	0.282958	1.497785
71	1	0	-9.916867	1.187624	1.882647
72	1	0	-10.011907	-0.545340	2.228779
73	1	0	-4.251130	-1.848829	1.486669
74	1	0	-5.001937	-2.574323	3.724920
75	1	0	-5.344374	-0.848734	3.484426
76	1	0	-6.653379	-2.036941	3.382013
77	1	0	-5.019603	-4.181539	1.749136
78	1	0	-5.376188	-3.591262	0.113162
79	1	0	-6.672698	-3.720436	1.312656
80	1	0	-4.357287	1.768948	-1.536875
81	1	0	-5.235157	2.479253	-3.734137
82	1	0	-5.532402	0.747751	-3.476758
83	1	0	-6.856524	1.911409	-3.306919
84	1	0	-5.181908	4.087369	-1.760619
85	1	0	-5.442699	3.492381	-0.108291
86	1	0	-6.801398	3.595670	-1.239685
87	1	0	1.217169	1.695535	-4.505857
88	1	0	-0.420067	1.055722	-2.575959
89	1	0	-0.236092	-0.941866	2.404782
90	1	0	1.529210	-1.465279	4.252493
91	1	0	3.657435	-2.043952	-2.396724
92	1	0	4.579942	-4.254649	-2.959746
93	1	0	6.333364	-5.277059	-1.535475
94	1	0	6.795232	0.110031	-1.038372
95	1	0	8.502306	1.877613	-1.128640
96	1	0	7.973951	4.167124	-0.335983
97	1	0	7.810306	-5.174492	0.396998
98	1	0	8.683487	-3.983841	2.385248
99	1	0	7.803087	-1.720011	2.957580
100	1	0	6.095297	-0.663710	1.570942
101	1	0	6.395759	5.768654	0.596098
102	1	0	4.133803	6.330812	1.434286
103	1	0	2.366839	4.571891	1.502026
104	1	0	2.853800	2.289401	0.766944

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