Supplementary Information

Sensing the chirality of various organic solvents by helically arranged π-blades

Yuki Shimizu, Yoshiaki Shoji,* Daisuke Hashizume, Yuuya Nagata and Takanori Fukushima*

*To whom correspondence should be addressed.
E-mail: yshoji@res.titech.ac.jp (Y.S.), fukushima@res.titech.ac.jp (T.F.)

Table of Contents

1. **Materials** S2
2. **Methods** S2
3. **Synthesis** S3
4. **Optical Resolution of 1_{OSi} by Chiral HPLC (Figs. S1–S4)** S6
5. **Single-Crystal X-Ray Crystallography** S8
6. **Theoretical Calculations** S9
7. **Supplementary Tables (Tables S1–S3)** S9
8. **Supplementary Figures (Figs. S5–S16)** S22
9. **Supplementary References** S32
10. **Analytical Data (Figs. S17–S23)** S33

1. Materials

Unless otherwise noted, all commercial reagents were used as received. 2,7-Di-*tert*-butyl-9-chloro-9-borafluorene,[1] compound **4**,[2] compound **6**,[2] 1,3,5-tris(phenylethynyl)benzene,[3] 1,3,5-tris(4-methoxyphenylethynyl)benzene,[3] and 1,3-bis(phenylethynyl)benzene[4] were prepared according to previously reported procedures. Anhydrous CH_2Cl_2 and DMF were dried by passage through an activated alumina column and a Q-5 column (Nikko Hansen & Co., Ltd.). 1,2-Dichloroethane (1,2-DCE) and $MeNO_2$ were dried over CaH_2 and distilled prior to use.

2. Methods

Air- and/or moisture-sensitive compounds were handled either in an argon-filled glove box or by applying a standard Schlenk-line technique. Column chromatography was carried out using Wakogel silica C-200 (particle size: 75–150 μm). Chiral HPLC was carried out on a Japan Analytical Industry model LC-9210 NEXT recycling preparative HPLC system equipped with a YMC ChiralART Cellulose-SC column (20 × 250 mm). Melting points (M.p.) and decomposition points (D.p.) were recorded on a Yanaco MP-500D model melting-point apparatus. Infrared (IR) spectra were recorded at 25 °C on a JASCO model FT/IR-660$_{Plus}$ Fourier transform IR spectrometer. Nuclear magnetic resonance (NMR) spectroscopy measurements were carried out on a Bruker model AVANCE-400 spectrometer (^{1}H: 400.0 MHz, ^{13}C: 100.6 MHz) or on a Bruker model AVANCE III HD-500 spectrometer (^{1}H: 500.0 MHz, ^{13}C: 125.7 MHz). Chemical shifts (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ^{1}H ($CDCl_3$: ^{1}H(δ) = 7.26 ppm, residual solvent in ODCB-d_4: ^{1}H(δ) = 7.19 and 6.94 ppm), the resonances of the residual solvent for ^{13}C ($CDCl_3$: ^{13}C(δ) = 78.0 ppm, ODCB-d_4: ^{13}C(δ) = 132.2, 129.9 and 127.1 ppm). Absolute values of the coupling constants are given in Hertz (Hz), regardless of their sign. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Mass spectrometry measurements were carried out on a Bruker model micrOTOF II mass spectrometer, equipped with an atmospheric pressure chemical ionization (APCI) probe. Electronic absorption spectra were recorded using a quartz cell on a JASCO model V-670 UV/VIS spectrophotometer. Circular dichroism spectra were measured using a quartz cell on a JASCO model J-820 spectropolarimeter.

3. Synthesis

Compound $\mathbf{1_H}$. Under argon, a dry 1,2-DCE solution (2.0 mL) of a mixture of 2,7-di-*tert*-butyl-9-chloro-9-borafluorene[1] (296 mg, 0.952 mmol) and 1,3,5-tris(phenylethynyl)benzene[3] (100 mg, 0.264 mmol) was stirred for 12 h at 80 °C and then allowed to cool to 25 °C. After the addition of a dry $MeNO_2$ solution (1.0 mL) of $FeCl_3$ (133 mg, 0.830 mmol), the reaction mixture was stirred for 30 min at 25 °C and then poured into MeOH (150 mL). The white precipitate thus formed was collected by filtration and subjected to column chromatography on SiO_2 (CH_2Cl_2), which allowed the isolation of $\mathbf{1_H}$ as a white solid (126 mg, 0.107 mmol) in 41% yield. M.p.: 317 °C. FT-IR (KBr): ν (cm^{-1}) 3080, 3054, 3033, 2962, 2868, 1615, 1487, 1462, 1407, 1363, 1262, 1201, 1118, 1072, 1026, 892, 813, 764, 734, 704, 658, 592. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.66 (dd, J = 8.9, 5.3 Hz, 6H), 7.94 (d, J = 1.5 Hz, 3H), 7.65 (td, J = 7.7, 1.5 Hz, 6H), 7.43–7.27 (m, 15H), 7.31 (d, J = 2.0 Hz, 3H), 7.10 (s, 3H), 6.09 (d, J = 7.7 Hz, 3H), 1.22 (s, 27H), 1.08 (s, 27H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.8, 148.7, 140.0, 137.9, 137.1, 136.2, 134.5, 131.9, 131.8, 131.3, 130.9, 129.3, 128.0, 127.8, 127.0, 126.1, 124.9, 124.5, 123.9, 123.0, 122.2, 122.0, 34.9 (two peaks) 31.5, 31.3. APCI-TOF mass: calcd. for $C_{90}H_{90}$ $[M]^+$: m/z = 1170.7037; found: 1170.7042.

Compound $\mathbf{1_{OMe}}$. Under argon, a dry 1,2-DCE solution (1.2 mL) of a mixture of 2,7-di-*tert*-butyl-9-chloro-9-borafluorene[1] (342 mg, 1.10 mmol) and 1,3,5-tris(4-methoxyphenylethynyl)-benzene[3] (149 mg, 0.319 mmol) was stirred for 48 h at 80 °C and then allowed to cool to 25 °C. After the addition of a dry $MeNO_2$ solution (2.0 mL) of $FeCl_3$ (155 mg, 0.956 mmol), the reaction mixture was stirred for 10 min at 25 °C and then poured into MeOH (300 mL). The white precipitate thus formed was collected by filtration, washed with MeOH, and dried under reduced pressure to afford $\mathbf{1_{OMe}}$ as a white solid (218 mg, 0.173 mmol) in 54% yield. D.p.: 469 °C. FT-IR (KBr): ν (cm^{-1}) 3078, 3031, 2961, 2904, 2869, 2834, 1611, 1511, 1487, 1463, 1407, 1363, 1285, 1244, 1175, 1106, 1037, 892, 836, 813, 734, 660, 576. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.65 (d, J = 8.7 Hz, 6H), 7.92 (s, 3H), 7.66 (d, J = 8.6 Hz, 3H), 7.63 (d, J = 8.6 Hz, 3H), 7.41 (s, 3H), 7.23 (d, J = 8.6 Hz, 3H), 7.11 (s, 3H), 6.96 (d, J = 8.3 Hz, 3H), 6.84 (d, J = 8.3 Hz, 3H), 6.09 (d, J = 8.3 Hz, 3H), 3.92 (s, 9H), 1.25 (s, 27H), 1.05 (s, 27H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 158.0, 148.7, 148.6, 138.1, 136.8, 136.7, 134.5, 132.5, 132.4, 132.2, 131.0, 130.9, 127.9, 127.8, 124.8, 124.4, 123.9, 122.9, 122.2, 122.0, 116.4, 110.6, 55.4, 34.9 (two peaks), 31.4 (two peaks). APCI-TOF mass: calcd. for $C_{93}H_{96}O_3$ $[M]^+$: m/z = 1260.7354; found: 1260.7331.

Compound $\mathbf{1_{OH}}$. A CH_2Cl_2 solution (1.0 M) of BBr_3 (260 μL, 0.26 mmol) was added to a CH_2Cl_2 solution (1.0 mL) of $\mathbf{1_{OMe}}$ (100 mg, 0.079 mmol) at 0 °C. After being allowed to warm to 25 °C, the reaction mixture was stirred for 24 h at 25 °C and then poured into water (10 mL). The white precipitate thus formed was collected by filtration, washed with water, and dried under reduced pressure to afford $\mathbf{1_{OH}}$ as a white solid (83 mg, 0.068 mmol) in 86% yield. D.p.: 412 °C. FT-IR (KBr): ν (cm^{-1}) 3533, 3419, 3078, 3034, 2962, 2904, 2869, 1611,

1513, 1487, 1461, 1363, 1323, 1260, 1223, 1171, 1118, 1099, 994, 967, 894, 838, 814, 734, 661, 574, 543. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.65 (dd, J = 8.8, 4.5 Hz, 6H), 7.93 (d, J = 1.4 Hz, 3H), 7.66 (dd, J = 8.8, 1.7 Hz, 3H), 7.64 (dd, J = 8.8, 1.7 Hz, 3H), 7.41 (d, J = 1.8 Hz, 3H), 7.22 (dd, J = 5.1, 2.0 Hz, 3H), 7.14 (s, 3H), 7.02 (dd, J = 5.5, 2.5 Hz, 3H), 6.80 (dd, J = 5.5, 2.5 Hz, 3H), 6.19 (dd, J = 5.1, 2.0 Hz, 3H), 5.88 (s, 3H), 1.24 (s, 27H), 1.06 (s, 27H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 153.7, 148.8, 148.6, 138.3, 136.7 (2 peaks), 134.4, 132.8 (2 peaks), 132.7, 132.1, 130.9, 127.9, 127.8, 124.9, 124.6, 123.8, 122.9, 122.2, 122.0, 116.2, 113.8, 34.9 (2 peaks), 31.4, 31.3. APCI-TOF mass: calcd. for $C_{90}H_{90}O_3$ $[M]^+$: m/z = 1218.6884; found: 1218.6859.

Compound $\mathbf{1_{OSi}}$. Under argon, imidazole (10 mg, 0.15 mmol) and *tert*-butyldiphenylsilyl chloride (38 μL, 0.25 mmol) were added successively to a dry DMF solution (0.5 mL) of $\mathbf{1_{OH}}$ (30 mg, 0.025 mmol) at 25 °C, and the resultant mixture was stirred at 150 °C for 72 h. After being allowed to cool to 25 °C, the reaction mixture was poured into water (20 mL) and extracted with CH_2Cl_2. The combined organic layer was washed successively with water and brine, dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure. The obtained residue was subjected to column chromatography on SiO_2 (CH_2Cl_2/Hexane; v/v = 1:4), which allowed the isolation of $\mathbf{1_{OSi}}$ as a white solid (44 mg, 0.023 mmol) in 92% yield. D.p.: 442 °C. FT-IR (KBr): ν (cm^{-1}) 3073, 3046, 2960, 2932, 2858, 1895, 1607, 1508, 1487, 1461, 1428, 1362, 1253, 1189, 1172, 1114, 1014, 920, 892, 839, 814, 734, 701, 659, 612, 567. ^{1}H NMR (400 MHz, $CDCl_3$) : δ (ppm) 8.69 (d, J = 8.8 Hz, 6H), 7.97 (d, J = 2.0 Hz, 3H), 7.88 (dd, J = 8.3, 2.7 Hz, 3H), 7.79–7.74 (m, 6H), 7.39-7.33 (m, 3H), 7.29–7.23 (m, 3H), 7.04 (s, 3H), 6.93–6.88 (m, 3H) , 6.85 (dd, J = 8.3, 2.2 Hz, 3H), 6.55 (t, J = 7.6 Hz, 3H), 6.32 (dd, J = 8.3, 2.2 Hz, 3H), 6.27 (dd, J = 8.3, 2.7 Hz, 3H) 1.17 (s, 27H), 1.16 (s, 27H), 1.10 (s, 27H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 153.9, 148.7, 148.6, 138.0, 137.4, 136.2, 135.7, 135.0, 134.3, 133.0, 132.9, 132.8, 132.2 (two peaks), 132.1, 131.2, 129.8, 129.7, 128.1, 127.9, 127.8, 127.7, 124.6, 124.5, 124.0, 123.1, 122.3, 122.1, 121.9, 117.0, 34.9 (two peaks), 31.5, 31.4, 26.3, 19.4. APCI-TOF mass: calcd. for $C_{138}H_{144}O_3Si_3$ $[M]^+$: m/z = 1933.0423; found: 1933.0918.

Compound 5. Under argon, a dry 1,2-DCE solution (1.5 mL) of a mixture of 2,7-di-*tert*-butyl-9-chloro-9-borafluorene[1] (257 mg, 0.827 mmol) and 1,3-bis(phenylethynyl)benzene[4] (100 mg, 0.359 mmol) was stirred for 12 h at 80 °C and then allowed to cool to 25 °C. After the addition of a dry $MeNO_2$ solution (1.0 mL) of $FeCl_3$ (134 mg, 0.826 mmol), the resulting mixture was stirred for 30 min at 25 °C and then poured into MeOH (200 mL). The white precipitate thus formed was collected by filtration, washed with MeOH, and dried under reduced pressure to afford **5** (a mixture of two conformational isomers) as a white solid (347 mg, 0.430 mmol) in 52% yield. M.p.: 317 °C. FT-IR (KBr): ν (cm^{-1}) 3433, 3079, 3057, 3029, 2962, 2903, 2869, 1615, 1486, 1461, 1442, 1405, 1393, 1363, 1320, 1263, 1201, 1118, 1072, 1029, 994, 894, 813, 764, 735, 715, 703, 647, 625, 591, 530, 438, 423. ^{1}H NMR (400 MHz,

ODCB-d_4): δ (ppm) 8.65–8.47 (m, 4H), 8.01 (d, J = 1.8 Hz, 1.5H), 7.71–7.64 (m, 2H), 7.64–7.52 (m, 4H), 7.49–7.31 (m, 4H), 7.31–7.20 (m, 4H), 7.16–6.96 (m, 7H), 6.61 (d, J = 7.6 Hz, 1.5H). 1.35 (s, 5H), 1.27 (s, 13H), 1.20 (s, 13H), 1.17 (s, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.9, 148.8, 148.7, 140.1, 140.0, 139.4, 138.8, 137.3 (two peaks), 137.1, 136.7, 135.2, 131.7, 131.5, 131.4 (two peaks), 131.3, 131.1, 130.8, 130.2, 129.7, 129.2, 128.4, 128.1, 128.0 (two peaks), 127.9, 128.7, 127.7, 127.5, 127.1, 126.8, 126.6, 126.4, 125.8, 125.4, 124.8, 124.7, 124.6, 124.5, 123.8, 123.6, 123.3, 122.2, 122.1, 122.0, 35.0 (two peaks), 34.9 (two peaks), 31.5, 31.4, 31.3 (two peaks). APCI-TOF mass: calcd. for $C_{62}H_{62}$ $[M]^+$: m/z = 806.4846; found: 806.4843.

4. Optical Resolution of $\mathbf{1}_{OSi}$ by Chiral HPLC

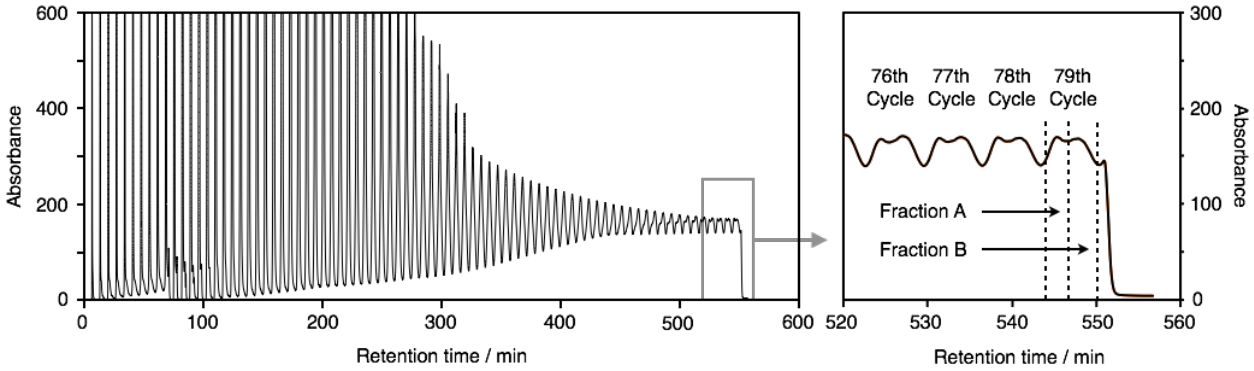


Fig. S1. Recycling preparative chiral HPLC profile of a racemic mixture of $\mathbf{1}_{OSi}$ monitored by a UV-Vis detector at 250 nm. A CH_2Cl_2/hexane (v/v = 1/1) solution of a racemic mixture of $\mathbf{1}_{OSi}$ (4.0 x 10^{-4} M) was subjected to recycling preparative HPLC on a ø20 x 250 mm CHIRALART Cellulose-SC column (YMC co. ltd.) with CH_2Cl_2/hexane (v/v = 1/4) as an eluent at a flow rate of 3.5 mL min^{-1}, where the former (fraction A) and the latter (fraction B) elution peaks at the 79th cycle were collected. The $\Delta\varepsilon$ values of $\mathbf{1}_{OSi}$ in fractions A and B were +186.3 and –152.1 M^{-1} cm^{-1} at 268 nm in hexane at 25 °C, respectively.

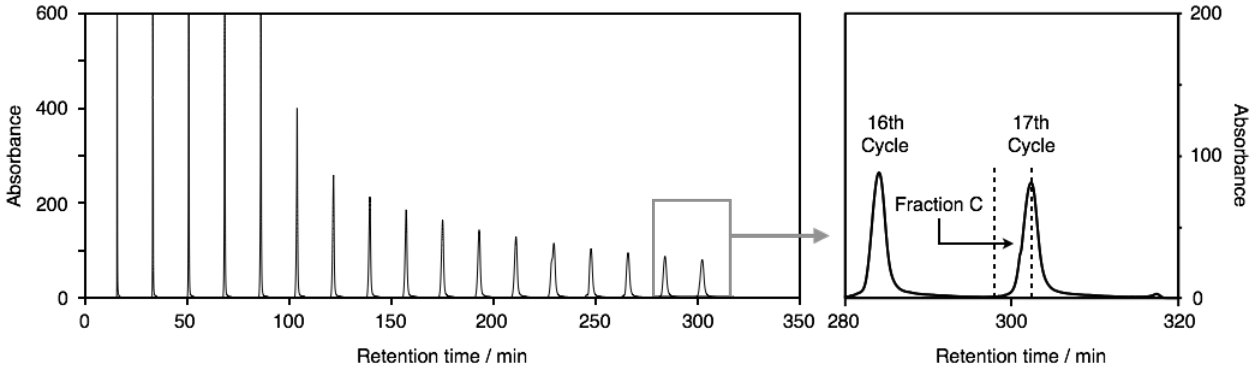


Fig. S2. Recycling preparative chiral HPLC profile of fraction A monitored by UV-Vis detector at 250 nm. Fraction A was subjected to recycling preparative HPLC on a ø20 x 250 mm CHIRALART Cellulose-SC column (YMC co. ltd.) with CH_2Cl_2/hexane (v/v = 1/4) as an eluent at a flow rate of 3.5 mL min^{-1}, where the former half of the elution peak at the 17th cycle was collected as fraction C. The $\Delta\varepsilon$ value of $\mathbf{1}_{OSi}$ in fraction C were +270 M^{-1} cm^{-1} at 268 nm in hexane at 25 °C.

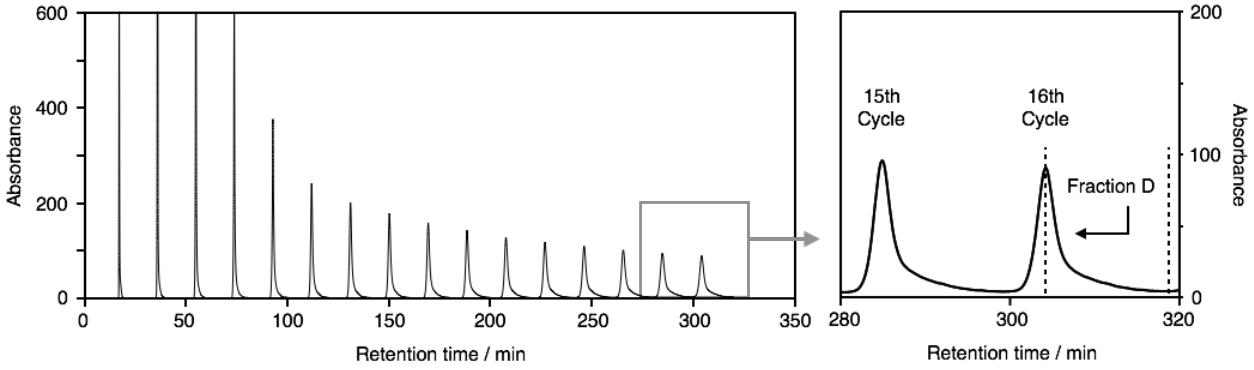


Fig. S3. (a) Preparative chiral HPLC profile of fraction B monitored by a UV-Vis detector at 250 nm. Fraction B was subjected to recycling preparative HPLC on a ø20 x 250 mm CHIRALART Cellulose-SC column (YMC co. ltd.) with CH_2Cl_2/hexane (v/v = 1/4) as an eluent at a flow rate of 3.5 mL min^{-1}, where the latter half of the elution peak at the 16th cycle was collected as fraction D. The $\Delta\varepsilon$ value of $\mathbf{1}_{OSi}$ in fraction D was –211.4 M^{-1} cm^{-1} at 268 nm in hexane at 25 °C.

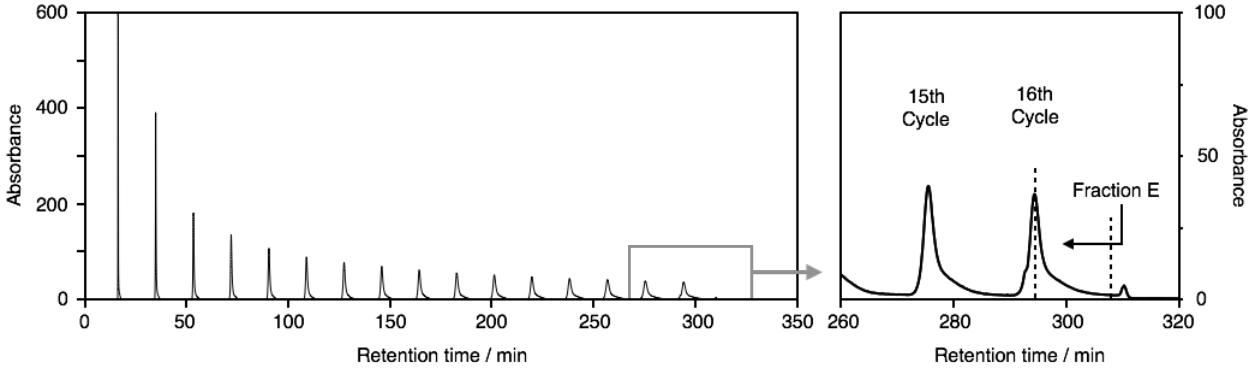


Fig. S4. (a) Preparative chiral HPLC profile of fraction D monitored by a UV-Vis detector at 250 nm. Fraction D was subjected to preparative HPLC on a ø20 x 250 mm CHIRALART Cellulose-SC column (YMC co. ltd.) with CH_2Cl_2/hexane (v/v = 1/4) as an eluent at a flow rate of 3.5 mL min^{-1}, where the latter half of the elution peak at the 16th cycle was collected as fraction E. The $\Delta\varepsilon$ values of $\mathbf{1}_{OSi}$ in fraction E was –268.5 M^{-1} cm^{-1} at 268 nm in hexane at 25 °C.

5. Single-Crystal X-ray Crystallography

Compound $\mathbf{1_H}$. A colorless plate single crystal of $\mathbf{1_H}$, obtained by recrystallization from a mixture of $CHCl_3$ and hexane at 25 °C, was coated with immersion oil (type B: Code 1248, Cargille Laboratories, Inc.) and mounted on a MicroMount (MiTeGen, LLC.). Diffraction data were collected at 90 K under a cold nitrogen gas stream on a Bruker model APEX2 platform-CCD X-ray diffractometer system, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data were collected by an ω-scan with 0.5° oscillations for each frame. Bragg spots were integrated using the ApexII program package,[5] and the empirical absorption corrections (multi-scan) were applied using the SADABS program.[6] Structure was solved by a direct method (SHELXT Version 2014/4)[7] and refined by full-matrix least squares (SHELXL Version 2014/5).[8] Anisotropic temperature factors were applied to all non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and refined by applying riding models.

Compound $\mathbf{\mathit{M}\text{-}1_{OSi}}$. A colorless needle single crystal of $\mathbf{\mathit{M}\text{-}1_{OSi}}$, obtained by recrystallization from a mixture of $CHCl_3$ and pentane at 25 °C, was coated with Parabar 10312 (Hampton Research Corp.) and mounted on a glass capillary. The diffraction data were collected at 90 K using a RIGAKU model AFC-8 diffractometer equipped with a Saturn70 CCD detector using Mo-Kα radiation (λ = 0.71073 Å) monochromated and focused by a multi-layer confocal mirror. Intensity data were collected by an ω-scan with 0.3° oscillations for each frame. Bragg spots were integrated and scaled using the CrysAlisPro (ver. 1.171.38.43) program,[9] and empirical absorption corrections (multi-scan) were applied using the CrysAlisPro program. Structure was solved by a direct method with the program of SHELXT (ver. 2014/4)[7] and refined by a full-matrix least squares method with the program of SHELXL (ver. 2014/5).[8] The highly disordered solvent contributions to the calculated structure factors, except for those of a $CHCl_3$ molecule, were calculated and omitted using the SQUEEZE software.[10] Anisotropic temperature factors were applied to all non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and refined by applying riding models. CCDC-1854763 ($\mathbf{1_H}$) and 1854764 ($\mathbf{1_{OSi}}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for $\mathbf{C_{99}H_{111}}$ ($\mathbf{1_H}$•1.5hexane): colorless plate, 0.27 x 0.12 x 0.05 mm^3, triclinic, $P\bar{1}$, a = 12.352(2) Å, b = 14.495(3) Å, c = 24.020(5) Å, α = 98.958(3)°, β = 92.578(3)°, γ = 111.662(2)°, V = 3923.7(13) $Å^3$, Z = 2, ρ_{calcd} = 1.101 g cm^{-3}, T = 90 K, $2\theta_{max}$ = 55.9 °, Mo$K\alpha$ radiation, λ = 0.71073 Å, μ = 0.062 mm^{-1}, 26074 reflections measured, 12042 unique reflections, 913 parameters, GOF = 1.003, $R1$ = 0.0529 ($I > 2\sigma(I)$), w$R2$ = 0.1471 (all data), $\Delta\rho_{min, max}$ = –0.233, 0.389 e $Å^{-3}$, CCDC-1854763.

Crystal data for $C_{139}H_{145}O_3Cl_3Si_3$ (Compound $\mathbf{1}_{OSi}$•$CHCl_3$): colorless needle, 0.20 x 0.06 x 0.03 mm^3, orthorhombic, $P2_12_12_1$, a = 15.27587(13) Å, b = 24.1176(2) Å, c = 37.3535(3) Å, V = 13761.7(2) $Å^3$, Z = 4, ρ_{calcd} = 0.991 g cm^{-3}, T = 90 K, $2\theta_{max}$ = 55.0 °, Mo$K\alpha$ radiation, λ = 0.71073 Å, μ = 0.138 mm^{-1}, 404394 reflections measured, 31595 unique reflections, 1449 parameters, GOF = 1.025, $R1$ = 0.0398 ($I > 2\sigma(I)$), w$R2$ = 0.1016 (all data), $\Delta\rho_{min, max}$ = –0.337, 0.431 e $Å^{-3}$, Flack χ = 0.054(9), CCDC-1854764.

6. Theoretical Calculations

Density functional theory (DFT) calculations were performed using Gaussian 09 program package.[11] Geometry optimizations of $\mathbf{1}_{OSi}$, $\mathbf{1}_H$, and model $\mathbf{1}_H$ ($\mathbf{1}_H$') were performed at the ωB97X-D/6-31G(d,p) level. The CD spectral patterns of $\mathbf{1}_{OSi}$, $\mathbf{1}_H$, and $\mathbf{1}_H$' were investigated using time-dependent density functional theory (TDDFT). Cartesian coordinates and energies of the computed structures are listed in Tables S1–S3.

7. Supplementary Tables.

Table S1. Cartesian coordinates of the optimized geometry of $\mathbf{1}_{OSi}$ (a singlet state in vacuum) at the ωB97X-D/6-31G(d,p) level. Total energy is −6438.47929418 hartree.

Si	4.768512	0.616754	-3.640835
Si	-1.850132	-4.43803	-3.640835
O	3.362606	0.02553	-2.911284
O	-1.659193	-2.924867	-2.911284
C	0.823149	1.149159	2.608237
C	1.384496	-0.137714	2.605241
H	2.464013	-0.244292	2.612309
C	0.583627	-1.287448	2.608237
C	-0.811512	-1.130152	2.605241
H	-1.44357	-2.011752	2.612309
C	-1.406776	0.138288	2.608237
C	-0.572984	1.267865	2.605241
H	-1.020443	2.256044	2.612309
C	1.705757	2.362128	2.65731
C	1.665532	3.313235	1.656596
C	2.562143	4.457466	1.685294
C	2.579207	5.401995	0.623809
H	1.894274	5.243015	-0.196531
C	3.433109	6.493941	0.597987
C	4.316454	6.648159	1.693343
H	5.001795	7.490487	1.723716
C	4.335967	5.742757	2.733031

H	5.040816	5.905034	3.541006
C	3.472338	4.622359	2.764189
C	3.488248	3.648121	3.837791
C	4.354908	3.763516	4.949395
H	5.038964	4.602236	5.015309
C	4.362265	2.834445	5.96635
H	5.05624	2.969456	6.791132
C	3.483735	1.726106	5.955035
C	2.623189	1.610293	4.873679
H	1.927255	0.784663	4.840133
C	2.609489	2.529329	3.789686
C	0.742498	3.185831	0.482414
C	0.987613	2.255054	-0.536409
H	1.828599	1.574101	-0.449785
C	0.165973	2.183559	-1.65894
H	0.368786	1.465067	-2.446305
C	-0.934614	3.040049	-1.788726
C	-1.198252	3.973216	-0.777634
H	-2.052971	4.636071	-0.854018
C	-0.360897	4.039721	0.336592
H	-0.571404	4.77498	1.1093
Si	-2.918381	3.821276	-3.640835
O	-1.703413	2.899337	-2.911284
C	-2.136403	5.412169	-4.297784
C	-0.746109	5.611014	-4.1987
H	-0.125538	4.859359	-3.719604
C	-0.137013	6.7593	-4.708903
H	0.938808	6.884383	-4.617137
C	-0.905218	7.740814	-5.336023
H	-0.432433	8.635395	-5.733256
C	-2.284704	7.564932	-5.454006
H	-2.891453	8.321292	-5.945558
C	-2.888445	6.415093	-4.942666
H	-3.964003	6.302943	-5.055777
C	-4.284582	4.174166	-2.383073
C	-4.857348	5.449045	-2.216767
H	-4.499391	6.286176	-2.809021
C	-5.871914	5.674211	-1.28379
H	-6.295889	6.669708	-1.177165
C	-6.332364	4.627557	-0.484922
H	-7.118216	4.801974	0.24557
C	-5.770033	3.355927	-0.617214
H	-6.108956	2.538988	0.013171
C	-4.760742	3.135818	-1.555247
H	-4.328047	2.141123	-1.627094
C	-3.50108	2.692299	-5.077341
C	-2.296008	2.380723	-5.991419
H	-1.503658	1.855036	-5.447881
H	-1.862358	3.291842	-6.419874

H	-2.612051	1.739032	-6.826421
C	-4.594684	3.404394	-5.901841
H	-5.466096	3.668165	-5.289383
H	-4.948153	2.743795	-6.706331
H	-4.220217	4.319129	-6.375029
C	-4.072983	1.368368	-4.527952
H	-4.970281	1.533536	-3.920654
H	-3.342583	0.829296	-3.914646
H	-4.356976	0.709444	-5.361211
C	3.455875	7.515724	-0.551501
C	2.450924	7.169777	-1.66641
H	2.503908	7.928708	-2.4555
H	1.418995	7.147486	-1.299587
H	2.670671	6.198242	-2.123758
C	4.871424	7.556394	-1.175978
H	4.904221	8.279586	-2.000248
H	5.153104	6.574421	-1.572909
H	5.632232	7.852424	-0.445907
C	3.100066	8.916167	0.002791
H	3.12369	9.662325	-0.801017
H	3.803615	9.238791	0.777596
H	2.09542	8.919917	0.440653
C	3.529112	0.709944	7.109092
C	2.495438	-0.418594	6.942591
H	2.571483	-1.115329	7.785474
H	2.654694	-0.994212	6.024718
H	1.471419	-0.028871	6.927004
C	4.937108	0.06846	7.163565
H	4.995479	-0.653017	7.987783
H	5.721436	0.816874	7.319253
H	5.161635	-0.462138	6.231347
C	3.244933	1.430917	8.448227
H	3.284296	0.717548	9.280593
H	2.249992	1.89046	8.440913
H	3.976291	2.219883	8.652593
C	1.192784	-2.658293	2.65731
C	2.036579	-3.099011	1.656596
C	2.579207	-4.447614	1.685294
C	3.388661	-4.934656	0.623809
H	3.593447	-4.261997	-0.196531
C	3.907363	-6.22013	0.597987
C	3.599248	-7.062238	1.693343
H	3.986054	-8.076925	1.723716
C	2.80539	-6.626436	2.733031
H	2.593501	-7.317992	3.541006
C	2.266912	-5.318312	2.764189
C	1.415242	-4.844972	3.837791
C	1.081847	-5.653219	4.949395
H	1.466171	-6.664989	5.015309

C	0.273569	-5.195055	5.96635
H	0.043504	-5.86356	6.791132
C	-0.247016	-3.880056	5.955035
C	0.08296	-3.076895	4.873679
H	-0.28409	-2.061383	4.840133
C	0.885719	-3.524548	3.789686
C	2.387762	-2.235937	0.482414
C	1.459128	-1.982825	-0.536409
H	0.448912	-2.370664	-0.449785
C	1.808031	-1.235516	-1.65894
H	1.084393	-1.051911	-2.446305
C	3.100066	-0.710625	-1.788726
C	4.040032	-0.948892	-0.777634
H	5.041441	-0.540111	-0.854018
C	3.678949	-1.707314	0.336592
H	4.420956	-1.89264	1.1093
C	5.755277	-0.855905	-4.297784
C	6.999856	-0.706079	-4.942666
H	7.440511	0.281456	-5.055777
C	7.693776	-1.803854	-5.454006
H	8.652176	-1.656574	-5.945558
C	7.156351	-3.086465	-5.336023
H	7.694687	-3.9432	-5.733256
C	5.922232	-3.260994	-4.708903
H	5.492647	-4.255224	-4.617137
C	5.232335	-2.159357	-4.1987
H	4.271097	-2.32096	-3.719604
C	5.757225	1.623474	-2.383073
C	7.147686	1.482064	-2.216767
H	7.693684	0.753499	-2.809021
C	7.849968	2.248121	-1.28379
H	8.924082	2.117546	-1.177165
C	7.173764	3.170209	-0.484922
H	7.71774	3.763569	0.24557
C	5.791334	3.319032	-0.617214
H	5.253306	4.021017	0.013171
C	5.096069	2.555015	-1.555247
H	4.01829	2.677638	-1.627094
C	4.082139	1.685875	-5.077341
C	3.221533	2.843123	-4.527952
H	2.389483	2.480114	-3.914646
H	2.792884	3.41853	-5.361211
H	3.813222	3.537622	-3.920654
C	5.245634	2.276916	-5.901841
H	5.850584	1.495251	-6.375029
H	5.909772	2.899695	-5.289383
H	4.850273	2.913329	-6.706331
C	3.20977	0.79804	-5.991419
H	3.781998	-0.033072	-6.419874

H	2.812071	1.392586	-6.826421
H	2.358337	0.374688	-5.447881
C	4.78087	-6.750738	-0.551501
C	4.983747	-5.707451	-1.66641
H	5.614508	-6.132802	-2.4555
H	5.480407	-4.802628	-1.299587
H	4.0325	-5.41199	-2.123758
C	4.108318	-7.996974	-1.175978
H	4.718221	-8.386973	-2.000248
H	3.117063	-7.749929	-1.572909
H	3.984283	-8.803868	-0.445907
C	6.171594	-7.142819	0.002791
H	6.805974	-7.536358	-0.801017
H	6.09922	-7.913423	0.777596
H	6.677165	-6.274646	0.440653
C	-1.149727	-3.411273	7.109092
C	-1.610232	-1.951816	6.942591
H	-2.251645	-1.669305	7.785474
H	-2.18836	-1.801926	6.024718
H	-0.760712	-1.25985	6.927004
C	-0.383256	-3.525653	8.448227
H	-1.020733	-3.203057	9.280593
H	0.51219	-2.89378	8.440913
H	-0.06567	-4.553511	8.652593
C	-2.409266	-4.309891	7.163565
H	-3.063268	-3.999703	7.987783
H	-2.153285	-5.363346	7.319253
H	-2.981041	-4.239038	6.231347
C	-2.898541	0.296165	2.65731
C	-3.702112	-0.214224	1.656596
C	-5.14135	-0.009852	1.685294
C	-5.967868	-0.467339	0.623809
H	-5.487721	-0.981018	-0.196531
C	-7.340472	-0.273811	0.597987
C	-7.915702	0.414079	1.693343
H	-8.98785	0.586438	1.723716
C	-7.141357	0.883678	2.733031
H	-7.634318	1.412958	3.541006
C	-5.739249	0.695953	2.764189
C	-4.90349	1.196851	3.837791
C	-5.436755	1.889703	4.949395
H	-6.505135	2.062753	5.015309
C	-4.635834	2.36061	5.96635
H	-5.099744	2.894105	6.791132
C	-3.236719	2.15395	5.955035
C	-2.70615	1.466602	4.873679
H	-1.643165	1.27672	4.840133
C	-3.495208	0.995219	3.789686
C	-3.13026	-0.949894	0.482414

C	-2.446741	-0.272229	-0.536409
H	-2.277511	0.796563	-0.449785
C	-1.974004	-0.948042	-1.65894
H	-1.453178	-0.413156	-2.446305
C	-2.165452	-2.329424	-1.788726
C	-2.84178	-3.024325	-0.777634
H	-2.98847	-4.095961	-0.854018
C	-3.318052	-2.332407	0.336592
H	-3.849552	-2.88234	1.1093
C	-3.618874	-4.556263	-4.297784
C	-4.486226	-3.451656	-4.1987
H	-4.145559	-2.538398	-3.719604
C	-5.785219	-3.498307	-4.708903
H	-6.431455	-2.62916	-4.617137
C	-6.251133	-4.654349	-5.336023
H	-7.262255	-4.692195	-5.733256
C	-5.409071	-5.761078	-5.454006
H	-5.760723	-6.664718	-5.945558
C	-4.111411	-5.709013	-4.942666
H	-3.476507	-6.584399	-5.055777
C	-1.472643	-5.79764	-2.383073
C	-2.290338	-6.931109	-2.216767
H	-3.194293	-7.039675	-2.809021
C	-1.978054	-7.922332	-1.28379
H	-2.628192	-8.787254	-1.177165
C	-0.8414	-7.797766	-0.484922
H	-0.599523	-8.565543	0.24557
C	-0.021301	-6.674958	-0.617214
H	0.85565	-6.560005	0.013171
C	-0.335327	-5.690832	-1.555247
H	0.309757	-4.81876	-1.627094
C	-0.581059	-4.378174	-5.077341
C	-0.65095	-5.68131	-5.901841
H	-1.630367	-5.81438	-6.375029
H	-0.443676	-6.56786	-5.289383
H	0.097881	-5.657124	-6.706331
C	0.85145	-4.211491	-4.527952
H	0.9531	-3.30941	-3.914646
H	1.564092	-4.127974	-5.361211
H	1.157059	-5.071158	-3.920654
C	-0.913762	-3.178763	-5.991419
H	-0.85468	-2.229724	-5.447881
H	-1.91964	-3.25877	-6.419874
H	-0.200021	-3.131618	-6.826421
C	-8.236746	-0.764986	-0.551501
C	-9.271659	-1.773348	0.002791
H	-9.929664	-2.125968	-0.801017
H	-9.902835	-1.325369	0.777596
H	-8.772585	-2.645271	0.440653

C	-8.979741	0.440579	-1.175978
H	-9.622442	0.107387	-2.000248
H	-8.270167	1.175509	-1.572909
H	-9.616514	0.951444	-0.445907
C	-7.434671	-1.462326	-1.66641
H	-8.118417	-1.795906	-2.4555
H	-6.899402	-2.344858	-1.299587
H	-6.70317	-0.786252	-2.123758
C	-2.379385	2.701329	7.109092
C	-2.861677	2.094736	8.448227
H	-2.263563	2.48551	9.280593
H	-2.762182	1.00332	8.440913
H	-3.910621	2.333627	8.652593
C	-2.527842	4.241431	7.163565
H	-1.93221	4.65272	7.987783
H	-3.568152	4.546472	7.319253
H	-2.180594	4.701176	6.231347
C	-0.885206	2.37041	6.942591
H	-0.319838	2.784634	7.785474
H	-0.466334	2.796139	6.024718
H	-0.710706	1.288722	6.927004

Table S2. Cartesian coordinates of the optimized geometry of $\mathbf{1_H}$ (a singlet state in vacuum) at the ωB97X-D/6-31G(d,p) level. Total energy is −3483.05379608 hartree.

C	0.007792	1.400202	-0.143664
C	1.204564	0.6859	-0.156631
H	2.148013	1.221583	-0.121013
C	1.208715	-0.706849	-0.143664
C	-0.008275	-1.386133	-0.156631
H	-0.016085	-2.471025	-0.121013
C	-1.216507	-0.693353	-0.143664
C	-1.196289	0.700233	-0.156631
H	-2.131928	1.249442	-0.121013
C	0	2.879216	0.037531
C	-0.553008	3.702709	-0.901226
C	-0.626371	5.132286	-0.672511
C	-1.169891	5.995414	-1.652234
H	-1.500177	5.553593	-2.582588
C	-1.289557	7.355844	-1.460581
C	-0.826212	7.879935	-0.234602
H	-0.902829	8.945185	-0.037622
C	-0.268419	7.070872	0.724986
H	0.078941	7.526866	1.644796
C	-0.147701	5.677076	0.539922
C	0.445834	4.802446	1.535531
C	0.960526	5.274802	2.763042

H	0.917607	6.33207	2.997798
C	1.537636	4.427954	3.679234
H	1.93129	4.845198	4.601572
C	1.626728	3.04012	3.440201
C	1.093014	2.569219	2.260421
H	1.111811	1.508236	2.061728
C	0.520606	3.41587	1.282658
C	-1.094422	3.126002	-2.167676
C	-0.246249	2.518736	-3.09616
H	0.820413	2.466481	-2.899123
C	-0.760848	1.965146	-4.263297
H	-0.084569	1.501066	-4.973841
C	-2.129119	2.000228	-4.515492
H	-2.528459	1.568298	-5.428177
C	-2.984569	2.592369	-3.589636
H	-4.054211	2.61789	-3.772531
C	-2.468632	3.154625	-2.427098
H	-3.133748	3.617646	-1.703728
C	-1.911708	8.291001	-2.502409
C	-2.32315	7.545553	-3.779192
H	-2.765578	8.250349	-4.490125
H	-3.06748	6.769262	-3.57541
H	-1.46379	7.075514	-4.267484
C	-0.897514	9.384078	-2.887363
H	-1.335454	10.061799	-3.6281
H	0.00501	8.941641	-3.320006
H	-0.596769	9.985308	-2.024569
C	-3.169111	8.945239	-1.897992
H	-3.632844	9.621469	-2.624285
H	-2.933153	9.526708	-1.001987
H	-3.904534	8.183863	-1.620182
C	2.323302	2.121222	4.449936
C	2.355895	0.662576	3.97683
H	2.887404	0.044431	4.706684
H	2.870055	0.547301	3.017681
H	1.349799	0.24502	3.868428
C	3.778358	2.596148	4.631639
H	4.300214	1.948666	5.344214
H	3.828049	3.620279	5.01293
H	4.317461	2.56324	3.680065
C	1.595534	2.178479	5.805488
H	2.111737	1.548462	6.538025
H	0.566956	1.817977	5.712475
H	1.562178	3.19607	6.206449
C	2.493474	-1.439608	0.037531
C	3.483144	-1.372436	-0.901226
C	4.757876	-2.02369	-0.672511
C	5.777126	-1.984552	-1.652234
H	5.559641	-1.477605	-2.582588

C	7.015126	-2.561133	-1.460581
C	7.23733	-3.224447	-0.234602
H	8.198172	-3.69072	-0.037622
C	6.257764	-3.302978	0.724986
H	6.478987	-3.831798	1.644796
C	4.990343	-2.710625	0.539922
C	3.936123	-2.787327	1.535531
C	4.08785	-3.469241	2.763042
H	5.02493	-3.960706	2.997798
C	3.065903	-3.545609	3.679234
H	3.23042	-4.095145	4.601572
C	1.819457	-2.928848	3.440201
C	1.678502	-2.231187	2.260421
H	0.750265	-1.716975	2.061728
C	2.697927	-2.158793	1.282658
C	3.254408	-0.615204	-2.167676
C	2.304414	-1.04611	-3.09616
H	1.725829	-1.943739	-2.899123
C	2.08229	-0.323659	-4.263297
H	1.342246	-0.677294	-4.973841
C	2.796808	0.843757	-4.515492
H	2.622415	1.405561	-5.428177
C	3.737342	1.288528	-3.589636
H	4.294265	2.202105	-3.772531
C	3.966301	0.560586	-2.427098
H	4.699847	0.905082	-1.703728
C	8.136071	-2.489913	-2.502409
C	7.696216	-1.76087	-3.779192
H	8.527801	-1.730114	-4.490125
H	7.396093	-0.728115	-3.57541
H	6.85947	-2.270078	-4.267484
C	9.33136	-1.728089	-1.897992
H	10.148859	-1.664599	-2.624285
H	9.716948	-2.223169	-1.001987
H	9.0397	-0.710506	-1.620182
C	8.575607	-3.914769	-2.887363
H	9.381501	-3.874362	-3.6281
H	7.741183	-4.475159	-3.320006
H	8.945915	-4.475837	-2.024569
C	0.675381	-3.07265	4.449936
C	1.088851	-2.471013	5.805488
H	0.285139	-2.603049	6.538025
H	1.290936	-1.399987	5.712475
H	1.986789	-2.950921	6.206449
C	0.359151	-4.570228	4.631639
H	-0.462513	-4.698428	5.344214
H	1.221229	-5.125327	5.01293
H	0.061101	-5.020651	3.680065
C	-0.60414	-2.371553	3.97683

H	-1.405224	-2.522781	4.706684
H	-0.961051	-2.759191	3.017681
H	-0.462706	-1.29147	3.868428
C	-2.493474	-1.439608	0.037531
C	-2.930136	-2.330273	-0.901226
C	-4.131505	-3.108596	-0.672511
C	-4.607235	-4.010862	-1.652234
H	-4.059464	-4.075988	-2.582588
C	-5.725569	-4.794711	-1.460581
C	-6.411118	-4.655488	-0.234602
H	-7.295343	-5.254465	-0.037622
C	-5.989345	-3.767894	0.724986
H	-6.557928	-3.695068	1.644796
C	-4.842642	-2.966451	0.539922
C	-4.381957	-2.015119	1.535531
C	-5.048376	-1.805561	2.763042
H	-5.942537	-2.371364	2.997798
C	-4.603539	-0.882345	3.679234
H	-5.16171	-0.750053	4.601572
C	-3.446185	-0.111272	3.440201
C	-2.771516	-0.338032	2.260421
H	-1.862076	0.208739	2.061728
C	-3.218533	-1.257077	1.282658
C	-2.159986	-2.510798	-2.167676
C	-1.497669	-3.715211	-2.427098
H	-1.566099	-4.522728	-1.703728
C	-0.752773	-3.880897	-3.589636
H	-0.240054	-4.819995	-3.772531
C	-0.667689	-2.843985	-4.515492
H	-0.093956	-2.973859	-5.428177
C	-1.321442	-1.641487	-4.263297
H	-1.257677	-0.823772	-4.973841
C	-2.058165	-1.472626	-3.09616
H	-2.546242	-0.522742	-2.899123
C	-6.224363	-5.801088	-2.502409
C	-5.373066	-5.784683	-3.779192
H	-5.762223	-6.520235	-4.490125
H	-4.328613	-6.041147	-3.57541
H	-5.39568	-4.805436	-4.267484
C	-6.162249	-7.21715	-1.897992
H	-6.516015	-7.95687	-2.624285
H	-6.783795	-7.303539	-1.001987
H	-5.135166	-7.473357	-1.620182
C	-7.678093	-5.469309	-2.887363
H	-8.046047	-6.187437	-3.6281
H	-7.746193	-4.466482	-3.320006
H	-8.349146	-5.509471	-2.024569
C	-2.998683	0.951428	4.449936
C	-2.684385	0.292533	5.805488

H	-2.396876	1.054587	6.538025
H	-1.857892	-0.41799	5.712475
H	-3.548967	-0.245149	6.206449
C	-4.137509	1.97408	4.631639
H	-3.837701	2.749762	5.344214
H	-5.049278	1.505048	5.01293
H	-4.378562	2.457411	3.680065
C	-1.751755	1.708977	3.97683
H	-1.48218	2.47835	4.706684
H	-1.909004	2.21189	3.017681
H	-0.887093	1.04645	3.868428

Table S3. Cartesian coordinates of the optimized geometry of model $\mathbf{1_H}$ ($\mathbf{1_H'}$) (a singlet state in vacuum) at the ωB97X-D/6-31G(d,p) level. Total energy is −2539.66594416 hartree.

C	-0.000010622	0.000006129	-0.000007484
C	0.000008966	0.000004151	0.000005681
H	-0.000004607	-0.000001387	0.000000228
C	0.000000003	-0.000012264	-0.000007484
C	-0.000008077	0.000005689	0.000005681
H	0.000003505	-0.000003296	0.000000228
C	0.000010619	0.000006134	-0.000007484
C	-0.000000888	-0.00000984	0.000005681
H	0.000001102	0.000004683	0.000000228
C	-0.000005636	0.000007365	-0.000015231
C	0.000004802	0.000000202	-0.000002037
C	-0.000008895	-0.000000882	0.000006522
C	-0.000008159	0.000009934	-0.000001805
H	-0.000005775	0.000006362	0.000000494
C	-0.000009082	0.000003996	0.000002085
C	-0.000009465	0.000009851	-0.000002872
H	-0.000011968	0.000007306	-0.000000725
C	-0.000007375	0.00000418	0.000002163
H	-0.000010774	0.000005576	-0.000002411
C	-0.000010356	0.000004389	-0.000004786
C	-0.000001082	0.000008704	0.000003589
C	-0.000008885	-0.000000754	0.000001643
H	-0.00000798	0.000006517	0.000000491
C	-0.000005703	0.00000337	0.000000105
H	-0.000007106	0.000002676	0.000001373
C	-0.000006305	0.000000305	-0.00000113
C	-0.000004325	0.000001551	-0.000001225
H	-0.000003051	-0.000001291	0.000002157
C	-0.000004674	-0.000000547	0.000008349
C	-0.000014755	0.000017037	0.000014086
C	0.000004336	0.000005917	-0.000015267

H	-0.000006978	-0.000001309	0.000003255
C	0.000004909	-0.000005948	0.000006797
H	-0.000000405	0.000003841	-0.000001424
C	-0.000010889	0.000005023	0.000001765
H	0.000000659	0.000006049	0.000000195
C	0.00000353	0.000011615	-0.000008129
H	-0.000000681	0.000006842	-0.000000735
C	0.000002718	-0.000005965	0.00000309
H	-0.000003131	0.000007038	0.00000018
H	-0.000009222	0.0000074	0.000000089
H	-0.000004528	-0.00000035	0.000000925
C	-0.00000356	-0.000008563	-0.000015231
C	-0.000002576	0.000004058	-0.000002037
C	0.000005212	-0.000007262	0.000006522
C	-0.000004523	-0.000012032	-0.000001805
H	-0.000002622	-0.000008182	0.000000494
C	0.000001081	-0.000009863	0.000002085
C	-0.000003799	-0.000013122	-0.000002872
H	-0.000000343	-0.000014018	-0.000000725
C	0.000000068	-0.000008477	0.000002163
H	0.000000558	-0.000012118	-0.000002411
C	0.000001377	-0.000011163	-0.000004786
C	-0.000006997	-0.000005289	0.000003589
C	0.000005096	-0.000007318	0.000001643
H	-0.000001654	-0.00001017	0.000000491
C	-0.000000068	-0.000006624	0.000000105
H	0.000001236	-0.000007492	0.000001373
C	0.000002888	-0.000005613	-0.00000113
C	0.00000082	-0.000004521	-0.000001225
H	0.000002644	-0.000001997	0.000002157
C	0.000002811	-0.000003774	0.000008349
C	-0.000007377	-0.000021297	0.000014086
C	-0.000007292	0.000000797	-0.000015267
H	0.000004623	-0.000005389	0.000003255
C	0.000002697	0.000007225	0.000006797
H	-0.000003124	-0.000002271	-0.000001424
C	0.000001094	-0.000011942	0.000001765
H	-0.000005568	-0.000002454	0.000000195
C	-0.000011824	-0.00000275	-0.000008129
H	-0.000005585	-0.00000401	-0.000000735
C	0.000003807	0.000005336	0.00000309
H	-0.00000453	-0.00000623	0.00000018
H	-0.000001798	-0.000011686	0.000000089
H	0.000002567	-0.000003746	0.000000925
C	0.000009196	0.000001198	-0.000015231
C	-0.000002226	-0.00000426	-0.000002037
C	0.000003683	0.000008145	0.000006522
C	0.000012682	0.000002099	-0.000001805
H	0.000008397	0.00000182	0.000000494

C	0.000008001	0.000005868	0.000002085
C	0.000013264	0.000003271	-0.000002872
H	0.000012311	0.000006711	-0.000000725
C	0.000007308	0.000004297	0.000002163
H	0.000010216	0.000006543	-0.000002411
C	0.000008979	0.000006774	-0.000004786
C	0.000008079	-0.000003415	0.000003589
C	0.000003789	0.000008072	0.000001643
H	0.000009634	0.000003653	0.000000491
C	0.00000577	0.000003253	0.000000105
H	0.000005871	0.000004816	0.000001373
C	0.000003417	0.000005308	-0.00000113
C	0.000003505	0.00000297	-0.000001225
H	0.000000407	0.000003288	0.000002157
C	0.000001863	0.000004321	0.000008349
C	0.000022132	0.00000426	0.000014086
C	-0.000006525	0.000000629	0.00000309
H	0.00000766	-0.000000808	0.00000018
C	0.000008294	-0.000008865	-0.000008129
H	0.000006265	-0.000002831	-0.000000735
C	0.000009795	0.000006919	0.000001765
H	0.000004909	-0.000003595	0.000000195
C	-0.000007606	-0.000001277	0.000006797
H	0.000003529	-0.000001569	-0.000001424
C	0.000002956	-0.000006714	-0.000015267
H	0.000002355	0.000006698	0.000003255
H	0.00001102	0.000004286	0.000000089
H	0.000001961	0.000004096	0.000000925

8. Supplementary Figures

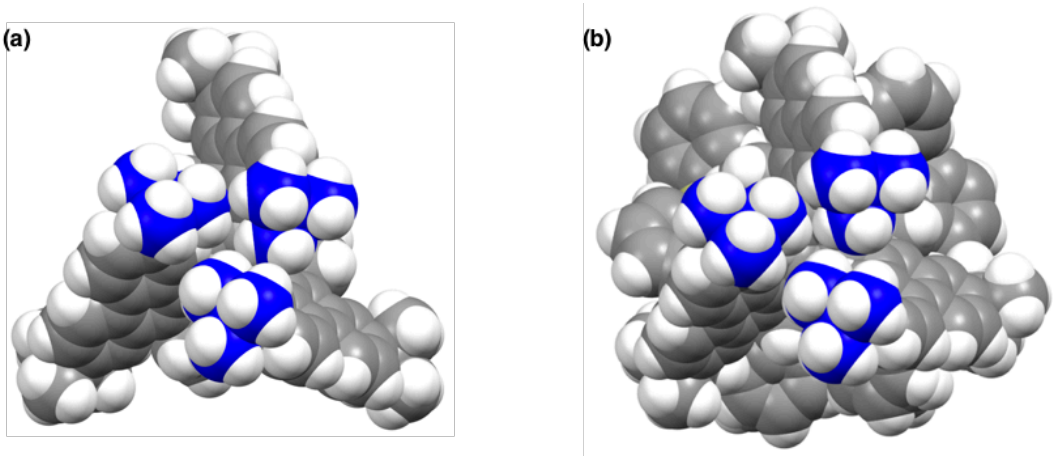


Fig. S5. Molecular structures (space-filling models) of (a) a *P*-helical conformer of $\mathbf{1_H}$ and (b) $(+)_{CD268}$-$\mathbf{1_{OSi}}$ (*M*-helicity), viewed along a direction opposite to that in Fig. 2 in the main text. In each structure, three *tert*-butyl groups, which are closely packed and arranged in a helical manner, are depicted in blue.

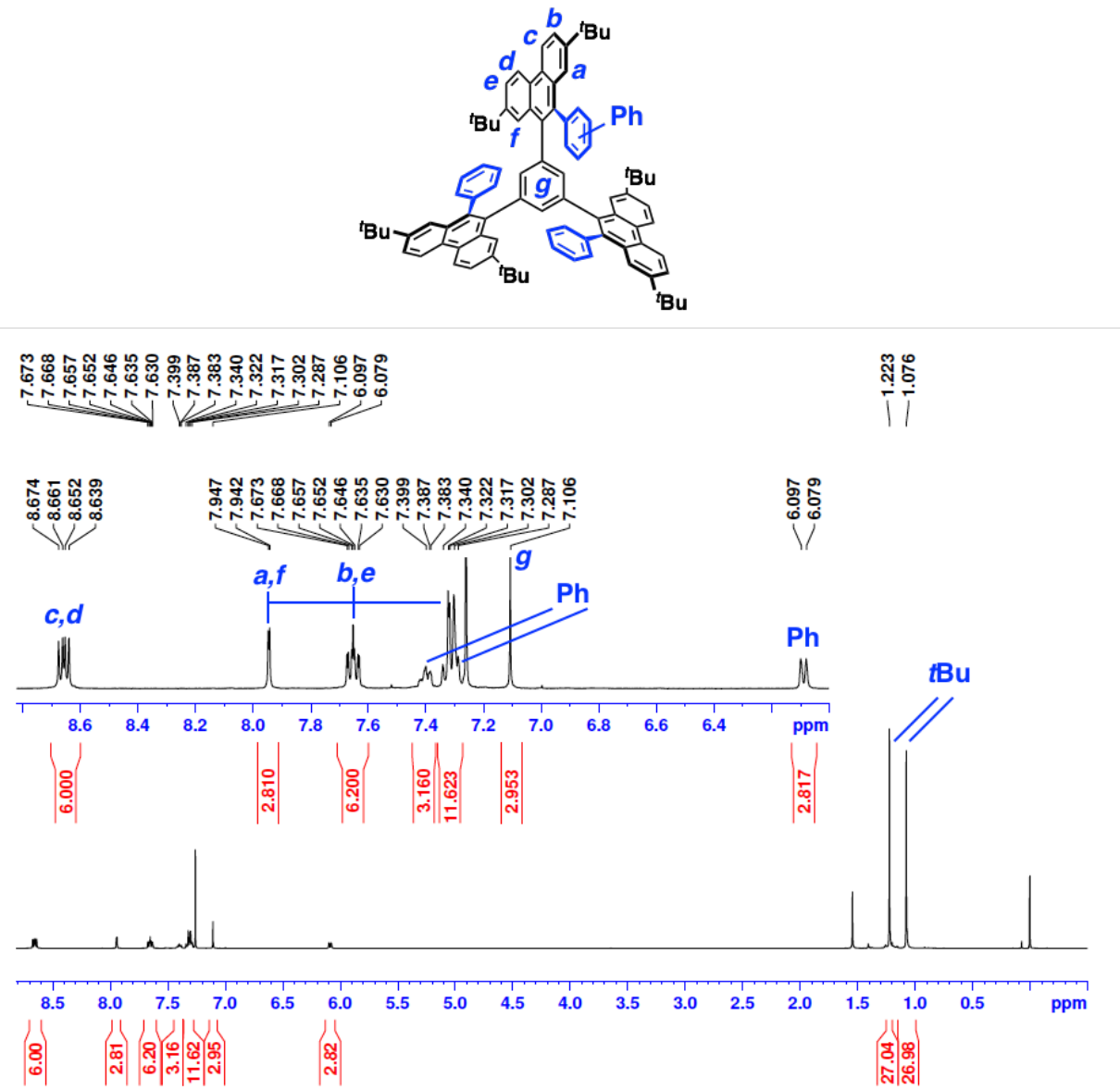


Fig. S6. ^{1}H NMR spectrum (400 MHz) of $\mathbf{1_H}$ in $CDCl_3$ at 25 °C.

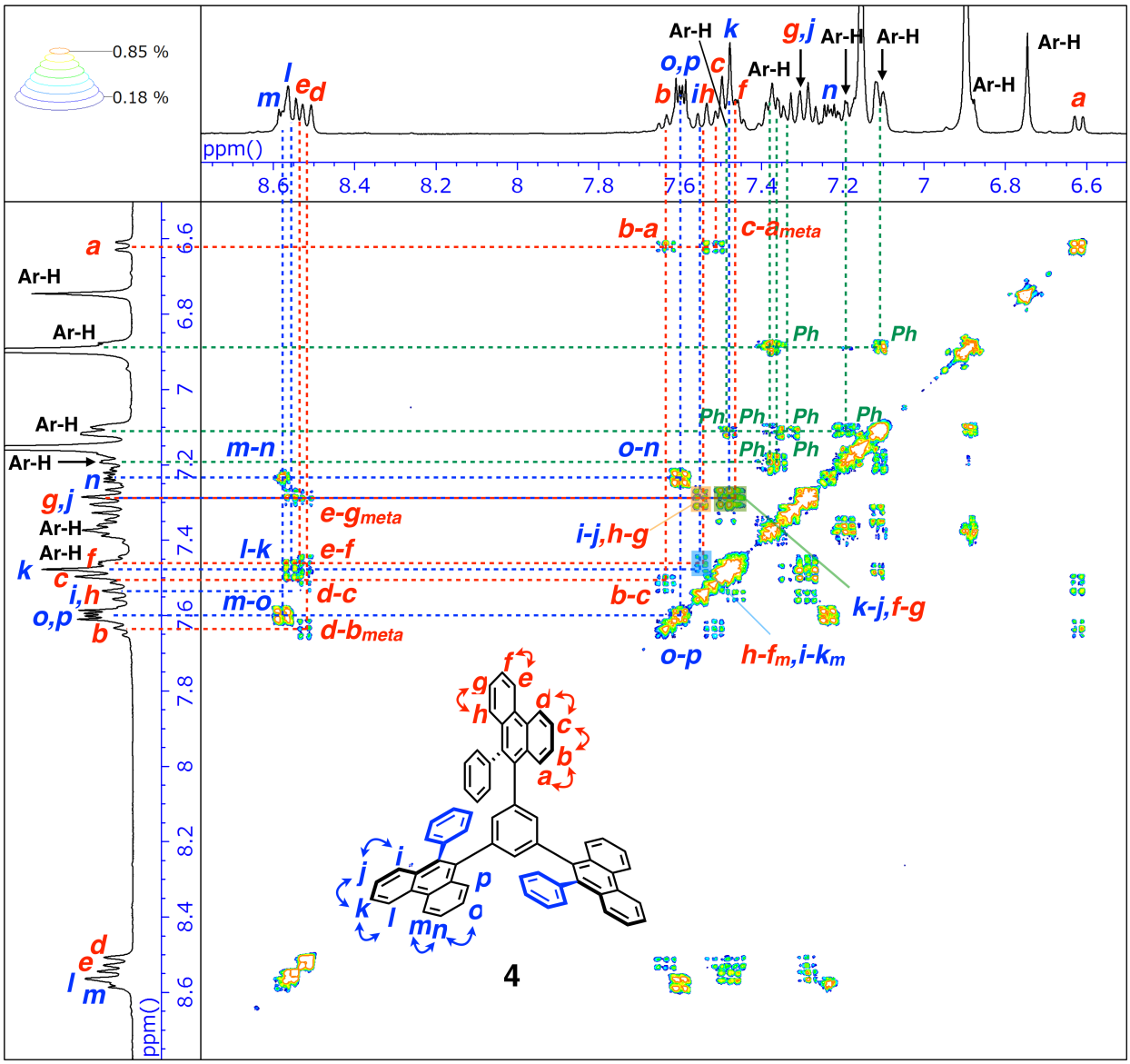


Fig. S7. ^{1}H-^{1}H COSY NMR spectrum of **4** in ODCB-d_4 at 25 °C.

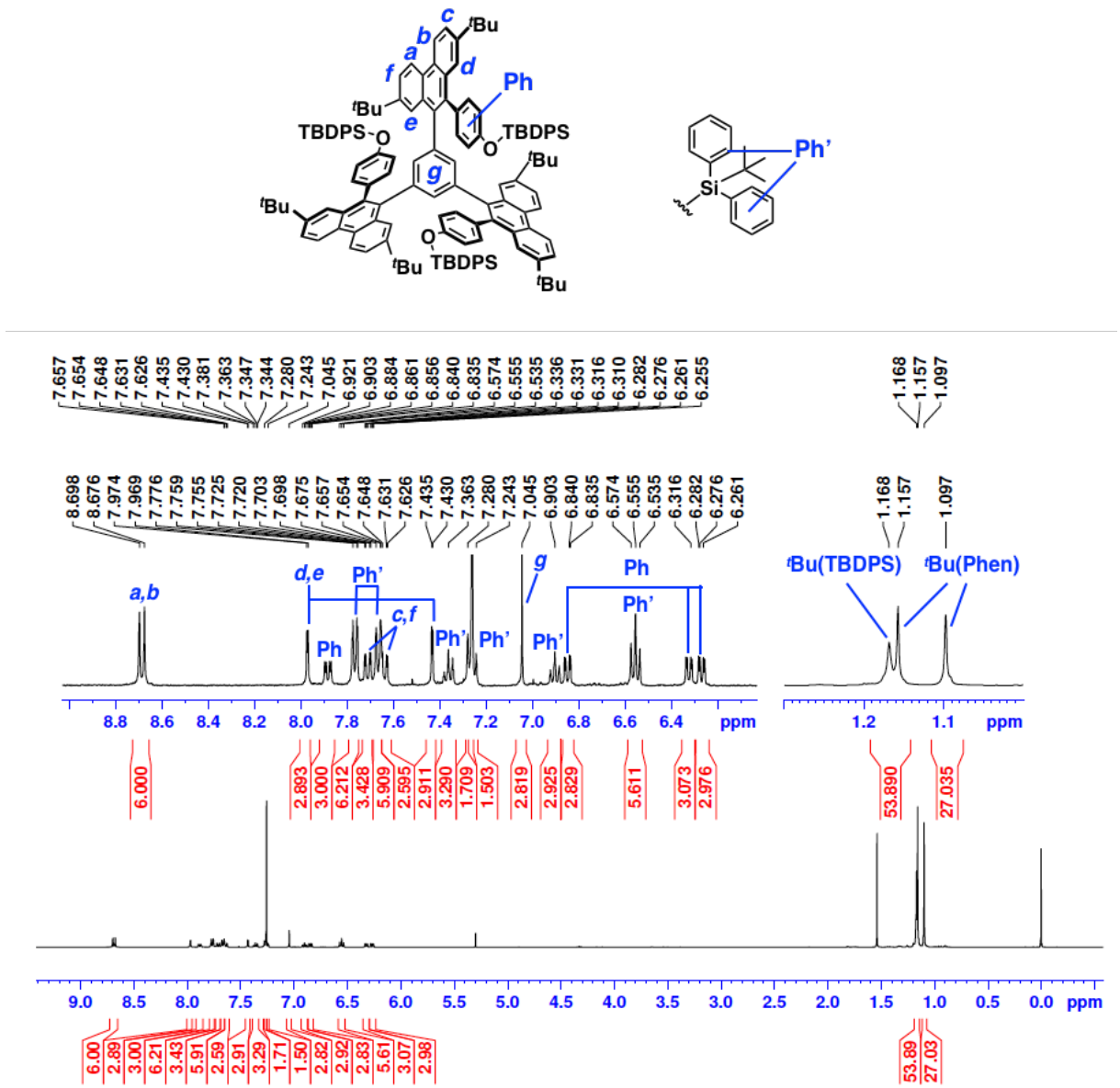


Fig. S8. ^{1}H NMR spectrum (400 MHz) of $\mathbf{1}_{OSi}$ in $CDCl_3$ at 25 °C.

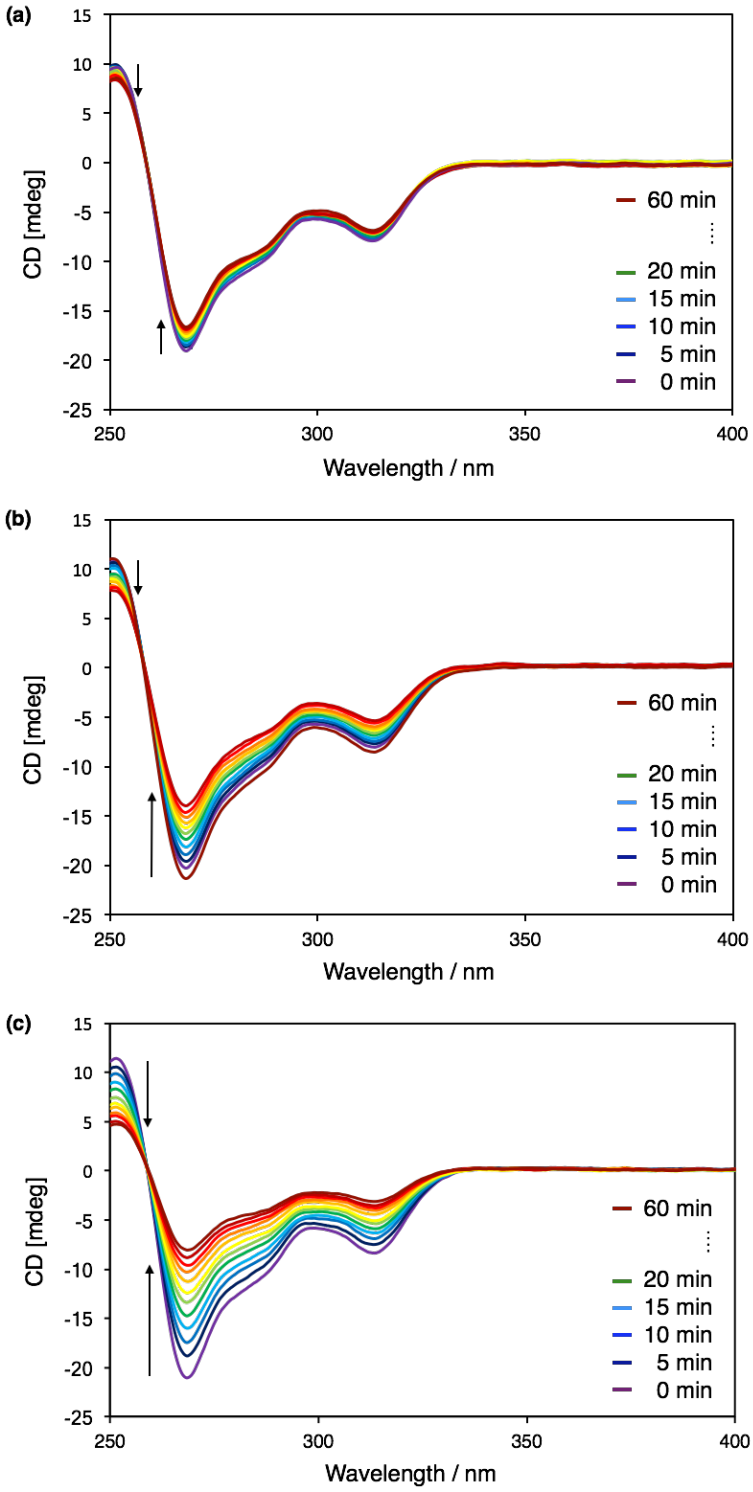


Fig. S9. Time-dependent CD spectral changes of (–)$_{CD268}$-**1**$_{OSi}$ in nonane at (a) 80 °C, (b) 90 °C, and (c) 100 °C, where the CD intensity was monitored at an interval of 5 min.

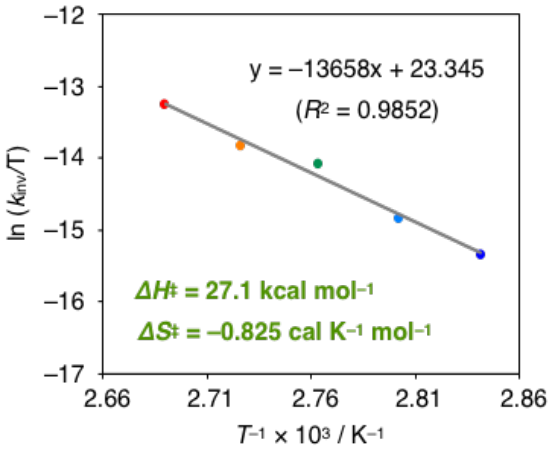


Fig. S10. Eyring plot for the helical inversion of $\mathbf{1_{OSi}}$ in *n*-nonane. The k_{inv} values were obtained from Fig. 3b in the main text.

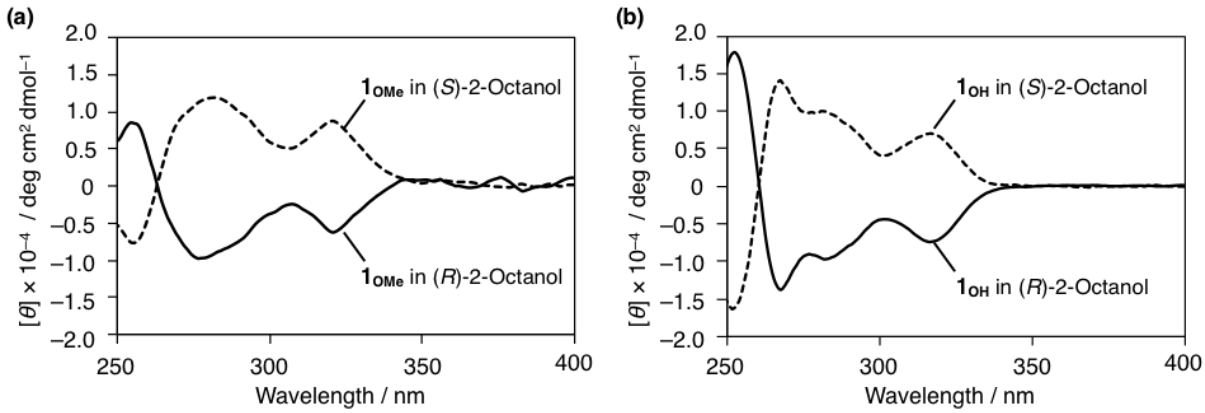


Fig. S11. CD spectra of (a) $\mathbf{1_{OMe}}$ (120 μM) and (b) $\mathbf{1_{OH}}$ (120 μM) in (*R*)- or (*S*)-2-octanol at 25 °C.

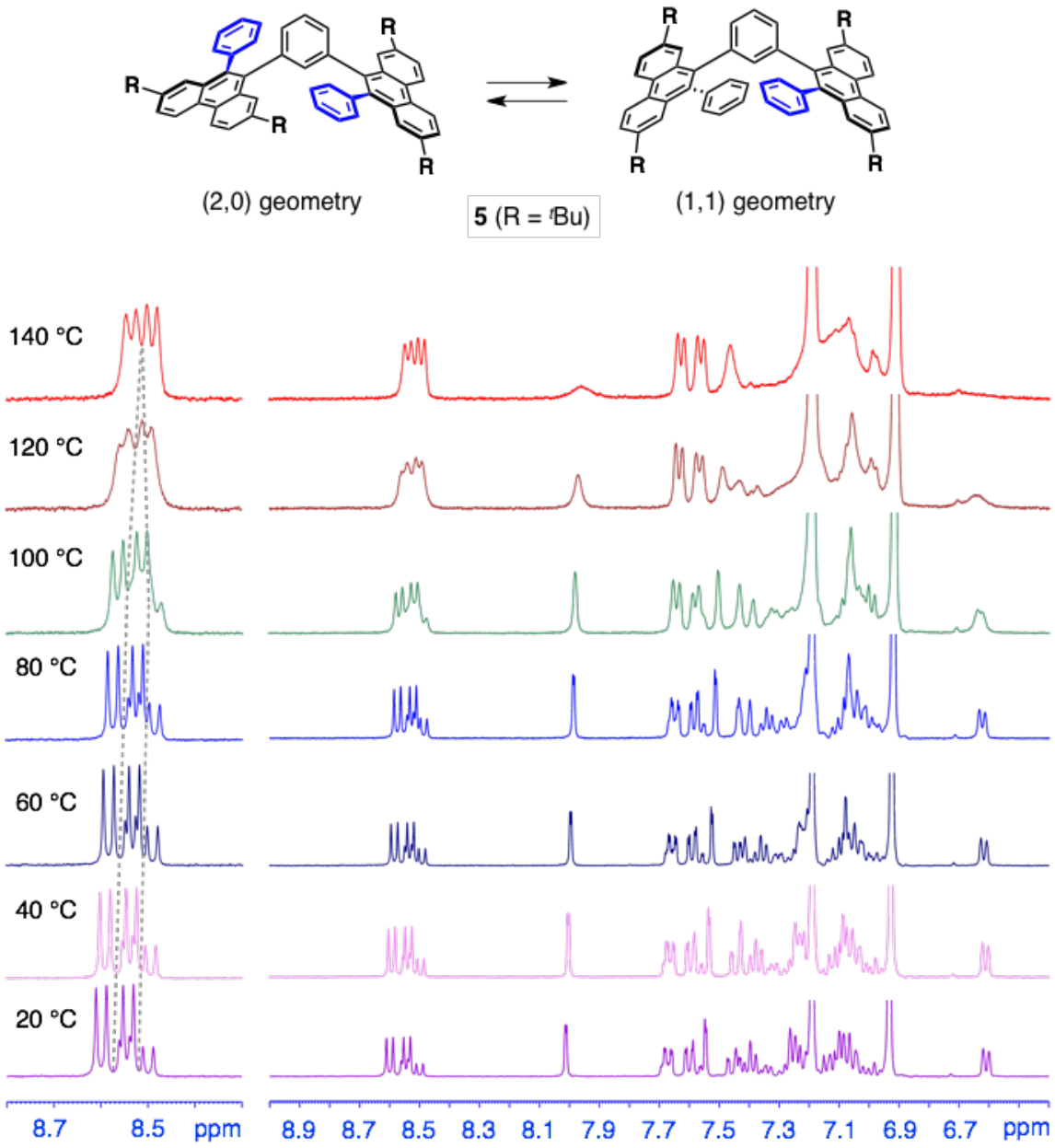


Fig. S12. Variable-temperature ^{1}H NMR (400 MHz) spectra of **5** in ODCB-d_4.

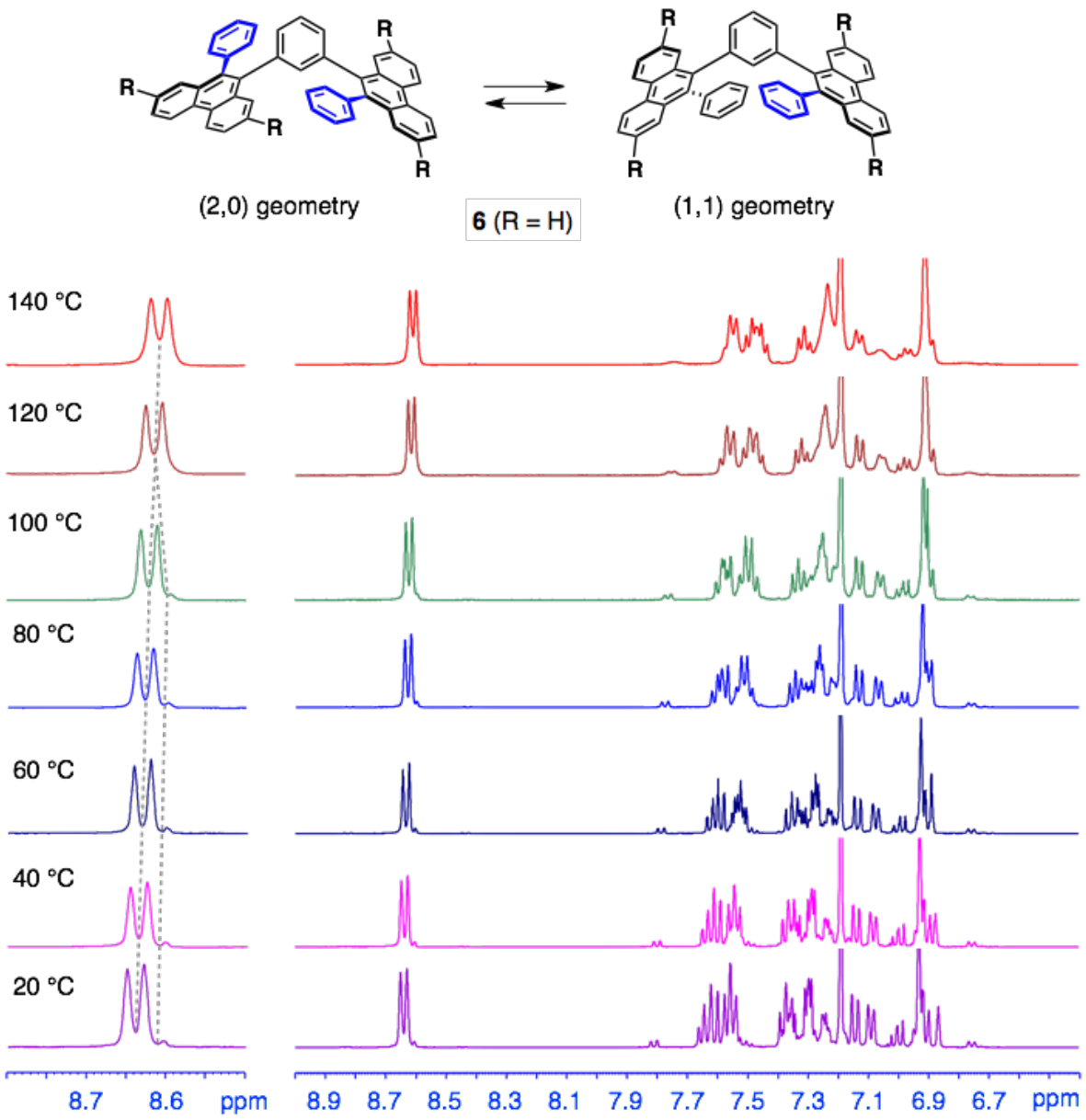


Fig. S13. Variable-temperature ^{1}H NMR (400 MHz) spectra of **6** in ODCB-d_4.

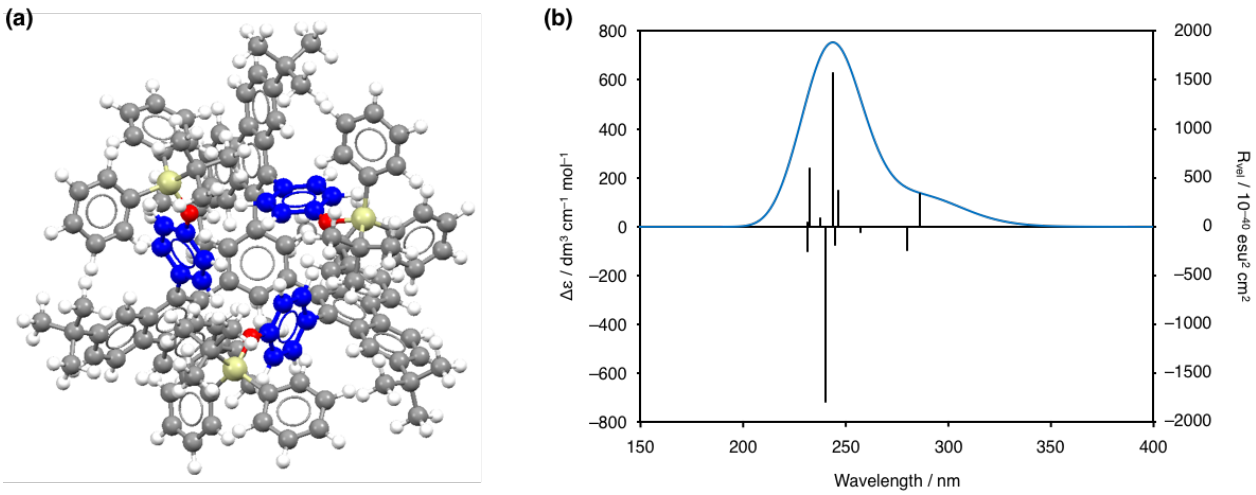


Fig. S14. (a) Optimized geometry and (b) simulated CD spectral pattern of *M*-$\mathbf{1}_{OSi}$ at the ω97X-D/6-31G(d,p) level. See also Table S1.

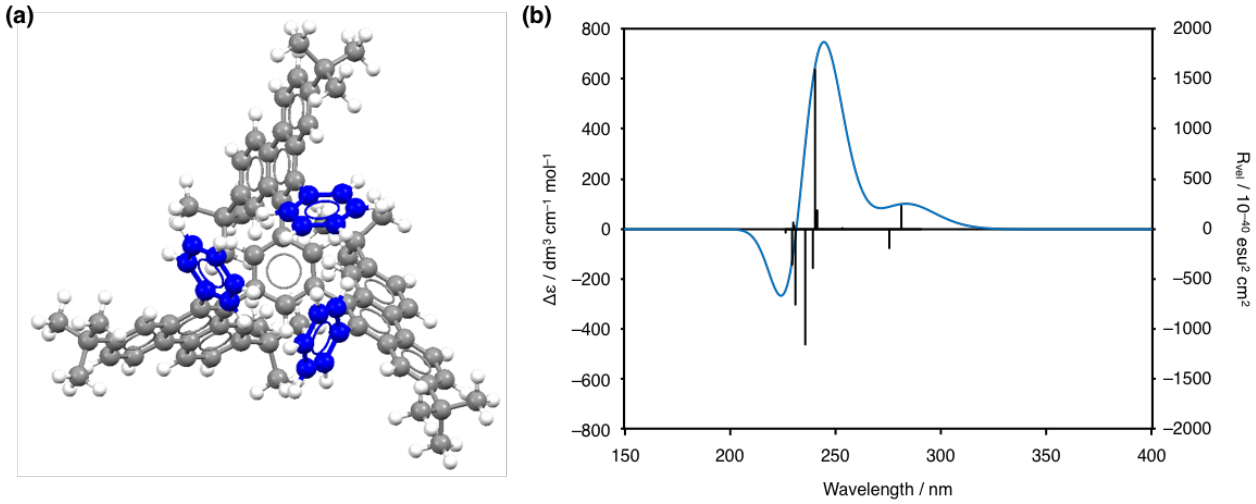


Fig. S15. (a) Optimized geometry and (b) simulated CD spectral pattern of *M*-$\mathbf{1}_{H}$ at the ω97X-D/6-31G(d,p) level. See also Table S2.

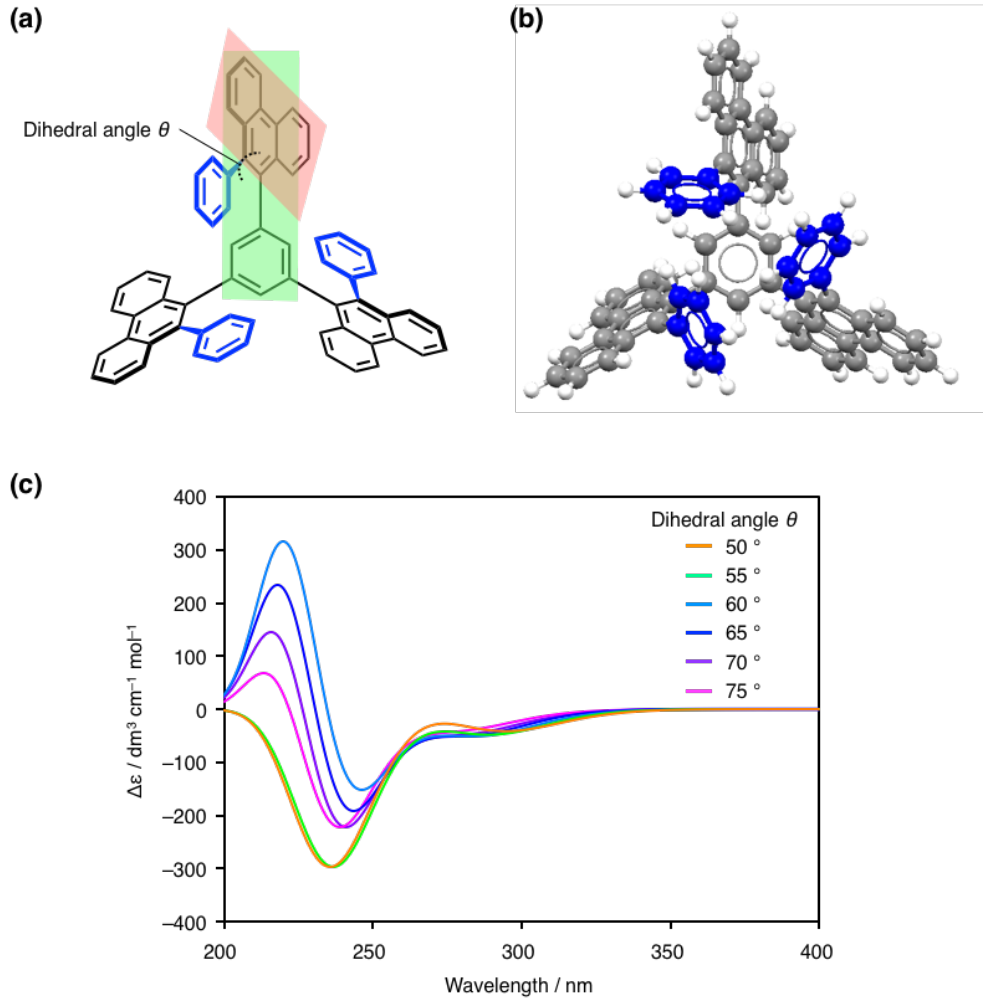


Fig. S16. (a) Schematic structure of model $\mathbf{1_H}$ ($\mathbf{1_H}$') with *P*-helicity. (b) One of the optimized structures of *P*-$\mathbf{1_H}$' with a dihedral angle (θ) between the phenanthrene blade and the central benzene plane of 70 °. See also Table S3. (c) Dihedral angle (θ)-dependence of simulated CD spectral pattern and intensity.

9. Supplementary References

1. Y. Shoji, M. Hwang, H. Sugiyama, F. Ishiwari, K. Takenouchi, R. Osuga, J. N. Kondo, S. Fujikawa, T. Fukushima, *Mater. Chem. Front.*, **2018**, *2*, 807.
2. Y. Shoji, N. Tanaka, S. Muranaka, N. Shigeno, H. Sugiyama, K. Takenouchi, F. Hajjaj, T. Fukushima, *Nat. Commun.*, **2016**, *7*, 12704.
3. Y. Yamaguchi, T. Ochi, S. Miyamura, T. Tanaka, S. Kobayashi, T. Wakamiya, Y. Matsubara, Z. Yoshida, *J. Am. Chem. Soc.*, **2006**, *128*, 4504.
4. T. Li, X. Qu, G. Xie, J. Mao, *Chem. Asian J.*, **2011**, ***6***, 1325.
5. *SAINT,* version V7.60A, Bruker, **2009**, Bruker AXS Inc., Madison, Wisconsin, USA.
6. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.*, **2015**, *48*, 3.
7. G. M. Sheldrick, *Acta Crystallogr. Sect. A*, **2015**, *A71*, 3.
8. G. M. Sheldrick, *Acta Crystallogr. Sect. C*, **2015**, *C71*, 3.
9. Rigaku Oxford Diffraction CrysAlisPro Software system, version 1.171.38.43, Rigaku Corporation, Oxford, UK, **2015**.
10. A. L. Spek, *Acta Crystallogr. Sect. C*, **2015**, *C71*, 9.
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, Jr., F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. V. Fox, Gaussian 09 (Revision A.02), Gaussian, Inc., Wallingford CT, **2009**.

10. Analytical Data

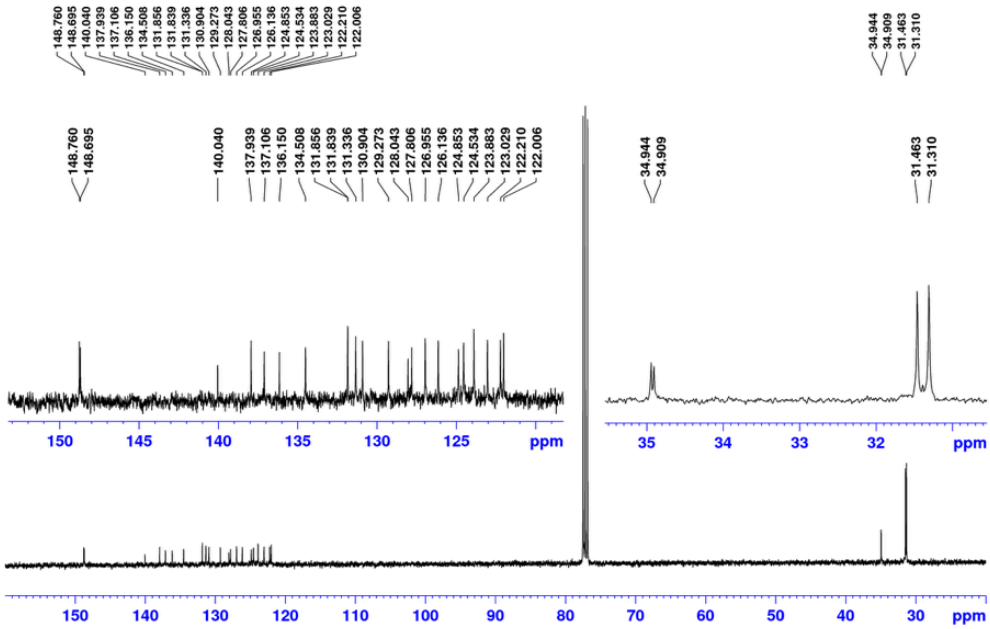


Fig. S17. ^{13}C NMR spectrum (100 MHz) of $\mathbf{1_H}$ in $CDCl_3$ at 25 °C.

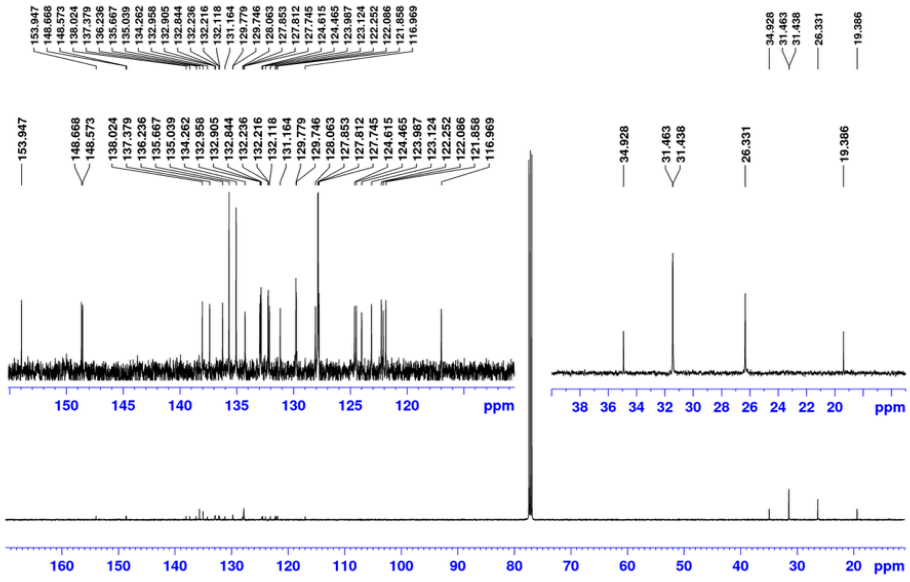
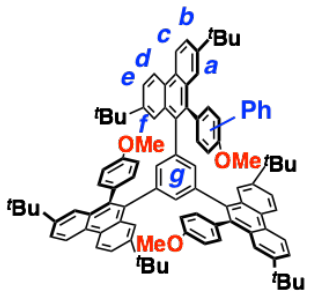


Fig. S18. ^{13}C NMR spectrum (100 MHz) of $\mathbf{1_{OSi}}$ in $CDCl_3$ at 25 °C.



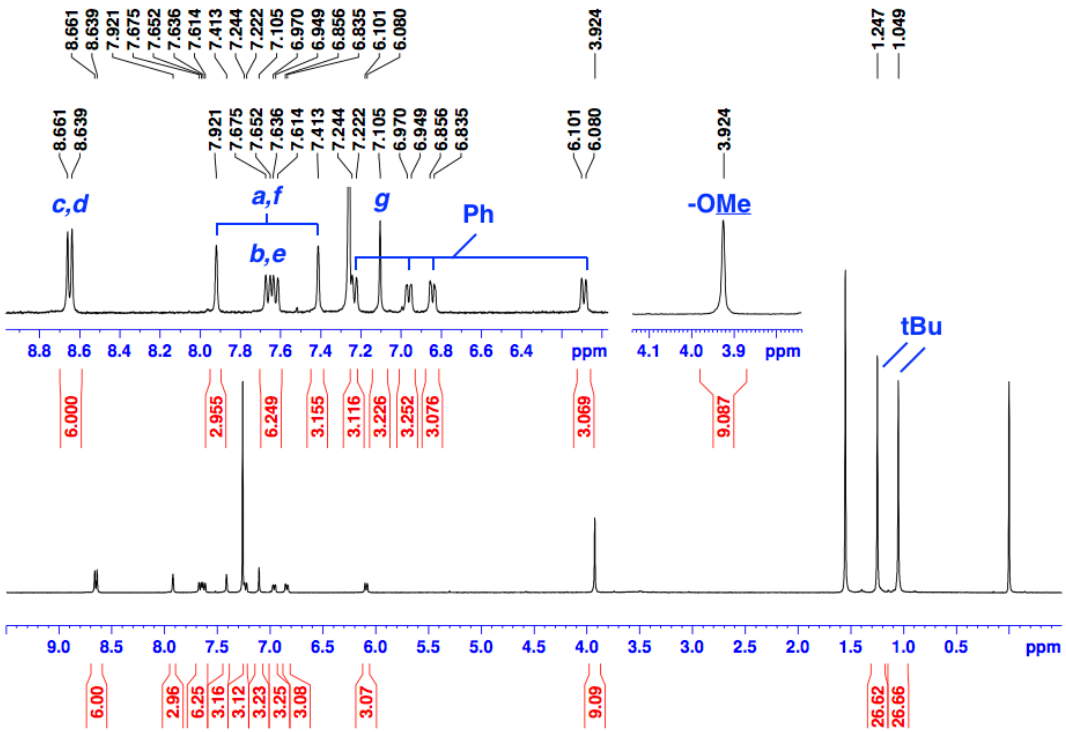


Fig. S19. ^{1}H NMR spectrum (400 MHz) of $\mathbf{1_{OMe}}$ in $CDCl_3$ at 25 °C.

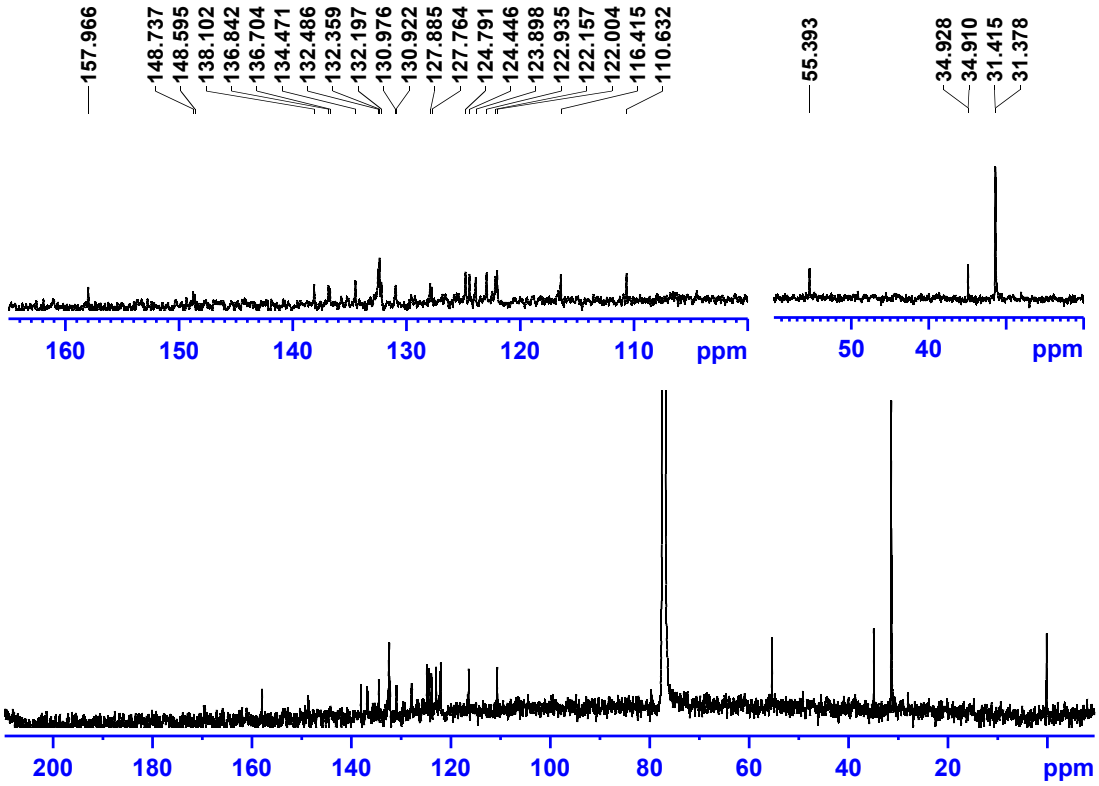


Fig. S20. ^{13}C NMR spectrum (100 MHz) of $\mathbf{1_{OMe}}$ in $CDCl_3$ at 25 °C.

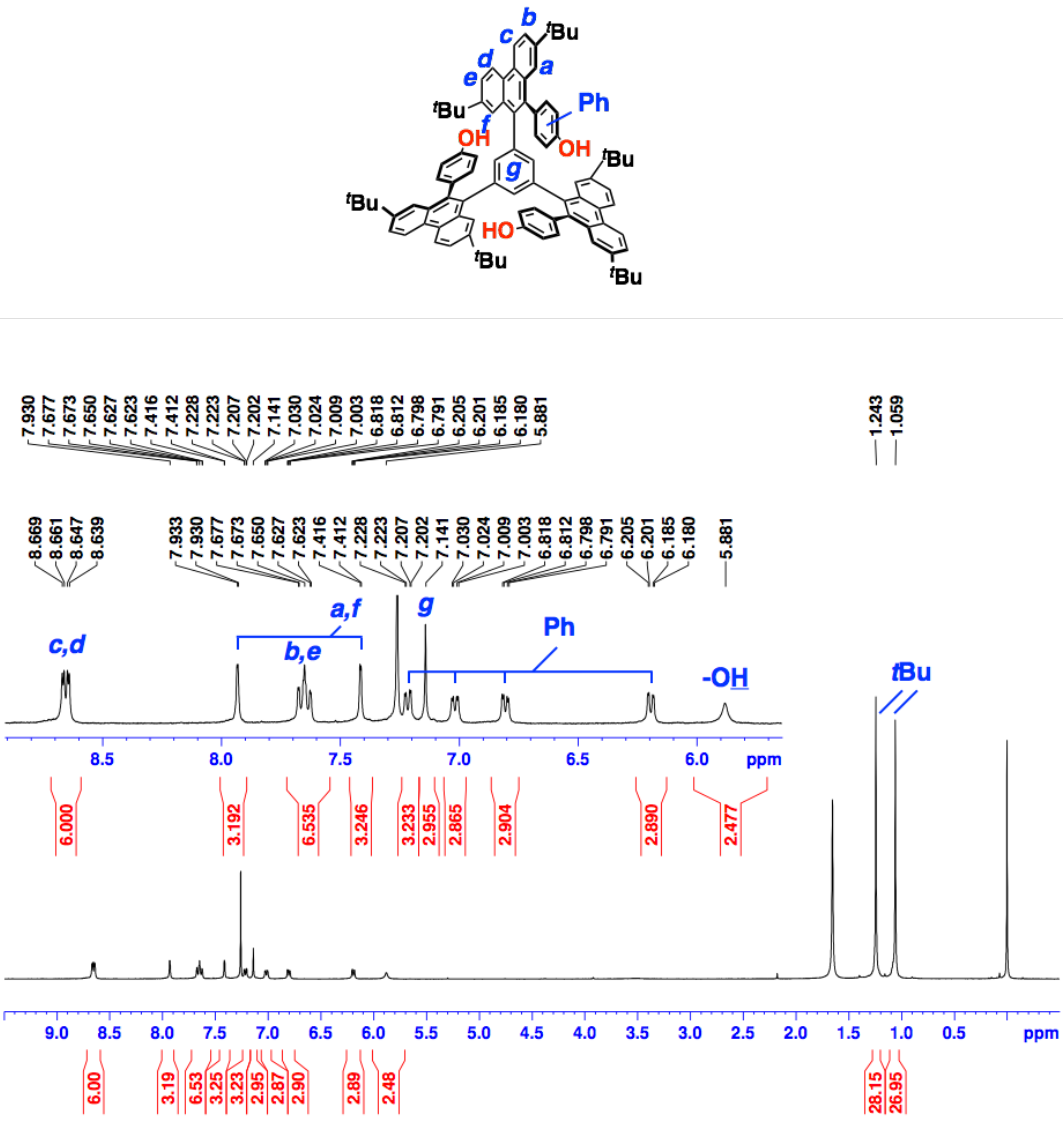


Fig. S21. ^{1}H NMR spectrum (400 MHz) of $\mathbf{1_{OH}}$ in $CDCl_3$ at 25 °C.

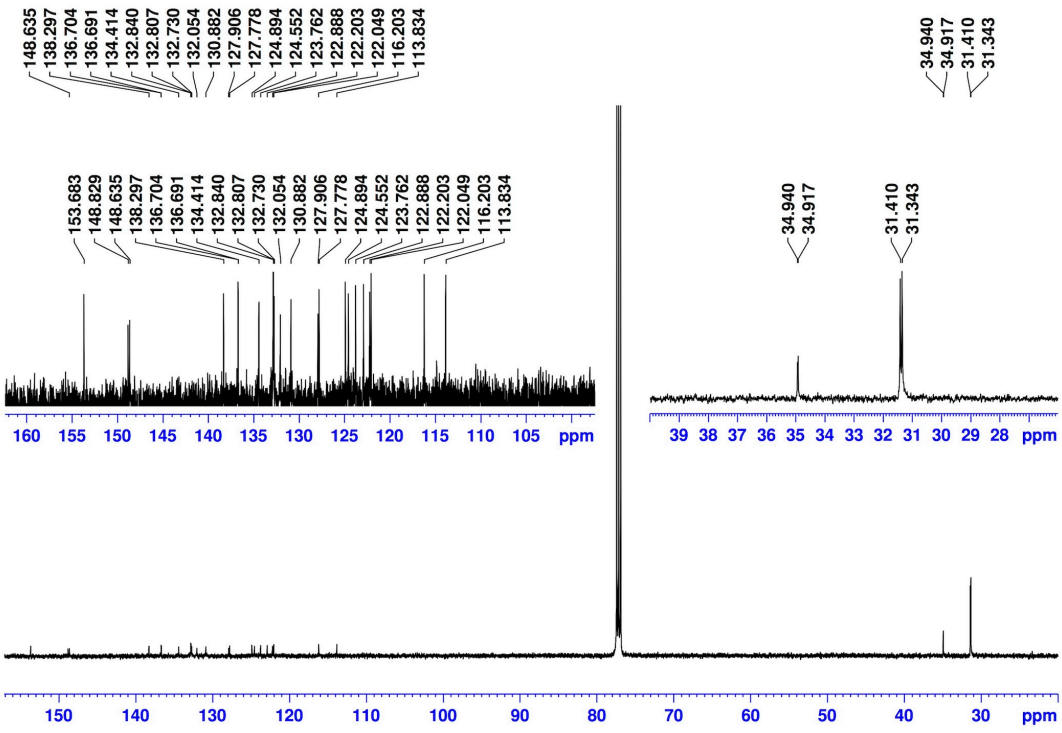


Fig. S22. ^{13}C NMR spectrum (100 MHz) of $\mathbf{1_{OH}}$ in $CDCl_3$ at 25 °C.

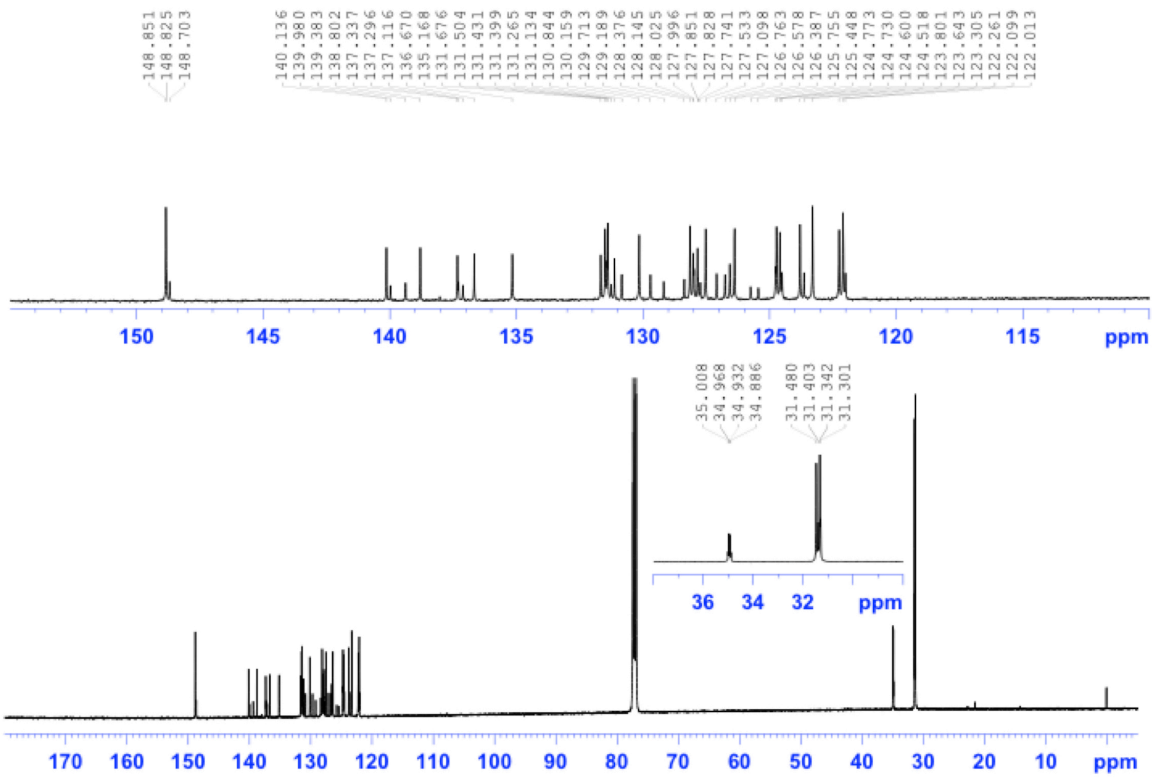


Fig. S23. ^{13}C NMR spectrum (100 MHz) of **5** in $CDCl_3$ at 25 °C.