

Supporting Information

Synthesis, Crystal Structure, Solid-State Optical Property and C–H Activation of sp^3
Carbon of Highly-Stable 1-(2',6'-Dimesitylphenyl)-2,3,4,5-tetraphenylborole

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4. Experimental Section

4.1 General

^1H (400 MHz), ^{11}B (128 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on JEOL JNM-EX400 and AL400 spectrometers. In ^1H and ^{13}C NMR spectra, tetramethylsilane (TMS) and $\text{C}_6\text{D}_5\text{H}$ was used as an internal standard in CDCl_3 and C_6D_6 , and ^{11}B NMR spectra were referenced externally to $\text{BF}_3\cdot\text{OEt}_2$ (sealed capillary). The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; dd, double doublet. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher Scientific EXACTIVE for atmospheric pressure chemical ionization (APCI). UV-vis absorption spectra and diffuse reflection spectra were recorded on a SHIMADZU UV-3600 spectrophotometer.

4.2 Materials

All syntheses were carried out under an argon atmosphere with standard Schlenk and glovebox techniques. 1-Chloro-2,3,4,5-tetraphenylborole (**5**) and 2,5-dimesitylphenyllithium (**6**) were prepared according to the published procedures.^{1,2} Deoxidized toluene (Wako), deoxidized benzene (Wako), deoxidized hexane (Wako), deoxidized diethyl ether (Wako) were used as received. CDCl_3 (Eur isotop) and C_6D_6 (Eur isotop) were distilled under argon and stored over molecular sieves.

4.3 Synthetic Procedures and Characterization

Synthesis of **7**

Compounds **5** (55 mg, 0.13 mmol) and **6** (44 mg, 0.13 mmol) were mixed in benzene (1 mL) at ambient temperature. The reaction mixture was stirred for 10 min resulting in

a dark blue solution and a colorless precipitate. After the filtration, the solution was concentrated to give dark green crystals of **7** by slow evaporation of solvent. The crystals were triturated by hexane (2 mL×2) and dried over vacuum to yield crystal **7-ben**^{1/6} (54 mg, 52%, co-crystal with 0.1 eq. benzene) as a dark green, crystalline solid. Crystal **7-ben**^{1/2} (co-crystal with 0.5 eq. benzene) was obtained by recrystallization from benzene-hexane mixed-solvent solution for the X-ray diffraction analysis. Crystal **7-hex**^{3/10} (co-crystal with 0.3 eq. hexane) was obtained by recrystallization from Et₂O-hexane mixed-solvent solution for the X-ray diffraction analysis. No partial evaporation was observed in crystal **7-hex**^{3/10} *in vacuo*.

¹H NMR (CDCl₃) δ: 7.43 (1H, t, *J* = 7.6 Hz, *p*-H-BAr), 7.36 (1H, s, 0.1 eq. benzene), 7.11 (2H, d, *J* = 7.6 Hz, *m*-H-BAr), 6.96–6.72 (12H, m, C₆H₅), 6.55 (4H, s, *m*-H-Mes), 6.39 (4H, d, *J* = 7.6 Hz, C₆H₅), 6.27 (4H, d, *J* = 7.2 Hz, C₆H₅), 2.16 (6H, s, *p*-CH₃-Mes), 2.02 (12H, s, *o*-CH₃-Mes) ppm.

¹³C NMR (CDCl₃) δ: 162.5, 144.4, 138.9, 138.8, 136.8, 136.6, 136.1, 130.2, 129.4, 128.5, 128.4, 128.3, 128.2, 126.8, 126.7, 126.5, 124.8, 23.0, 20.1 ppm.

¹¹B NMR (CDCl₃) δ: 79.59 (br.)

HRMS (APCI) *m/z* calcd. [M–H] : 679.3535, found: 679.3542.

Synthesis of **8**

Crystal **7-ben**^{1/6} (5.0 mg, 0.0072 mmol) was dissolved in Et₂O (1 mL) at ambient temperature. The solution was left for 30 days in a glovebox. After the dark blue of solution color turned into pale yellow, hexane (1 mL) was added to the solution. **8** was recrystallized by slow evaporation and the solution was concentrated to colorless crystals. The crystals were triturated by hexane (2 mL×2) and dried over *in vacuo* to

yield **8** (3.0 mg, 58%, co-crystal with 0.5 eq. hexane) as a colorless, crystalline solid. 0.5 eq. integral value peaks of ^1H NMR at 3.64 and 3.61, 2.98 and 2.95 ppm were assigned to 2 hydrogen atoms of a diastereomeric methylene.

^1H NMR (CDCl_3) δ : 7.36–7.22 (6H, m, Ar-*H*), 7.07–6.73 (12H, m, Ar-*H*), 6.48 (4H, t, $J = 8.0$ Hz, Ar-*H*), 6.32 (2H, d, $J = 4.0$ Hz, Ar-*H*), 6.22 (2H, d, $J = 3.6$ Hz, Ar-*H*), 6.16 (1H, s, *m-H*-Mes), 3.64 (0.5 H, s, CH_2), 3.61 (0.5H, s, CH_2), 3.40 (1H, s, *CH*), 2.98 (0.5H, s, CH_2), 2.95 (0.5H, s, CH_2), 2.28 (3H, s, CH_3 -Mes), 2.20 (3H, s, CH_3 -Mes), 2.06 (3H, s, CH_3 -Mes), 1.31 (3H, s, CH_3 -Ar), 1.27 (4H, m, 0.5 eq. *hexane*), 0.88 (3H, t, $J = 2.4$ Hz, 0.5 eq. *hexane*), 0.83 (3H, s, CH_3 -Ar) ppm.

^{13}C NMR (CDCl_3) δ : 148.7, 144.9, 142.5, 141.3 (br.), 141.03, 141.01, 140.6, 139.8, 138.7, 138.4, 137.8, 137.2, 136.7, 136.4, 136.3, 136.2, 130.7, 130.4, 130.0, 129.8, 129.3, 129.2, 128.1, 128.0, 127.70, 127.69, 127.3, 127.2, 127.1, 126.4, 126.12, 126.09, 125.3, 66.3, 56.9, 35.1, 31.6 (*hexane*), 22.7 (*hexane*), 21.9, 21.5, 21.2, 20.9, 18.7, 14.1 (*hexane*) ppm.

^{11}B NMR (CDCl_3) δ : 88.23 (br) ppm.

HRMS (APCI) m/z calcd. $[\text{M}-\text{H}]^-$: 679.3535, found: 679.3542.

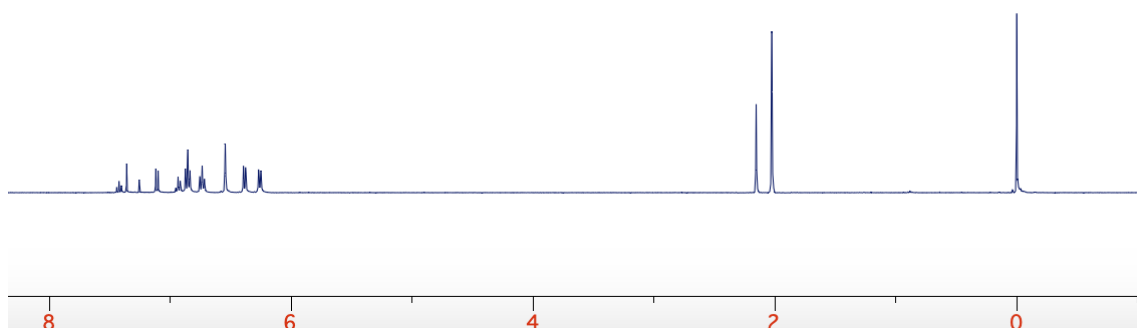


Chart S1. ¹H NMR spectrum of crystal **7-ben**^{1/10} in CDCl₃.

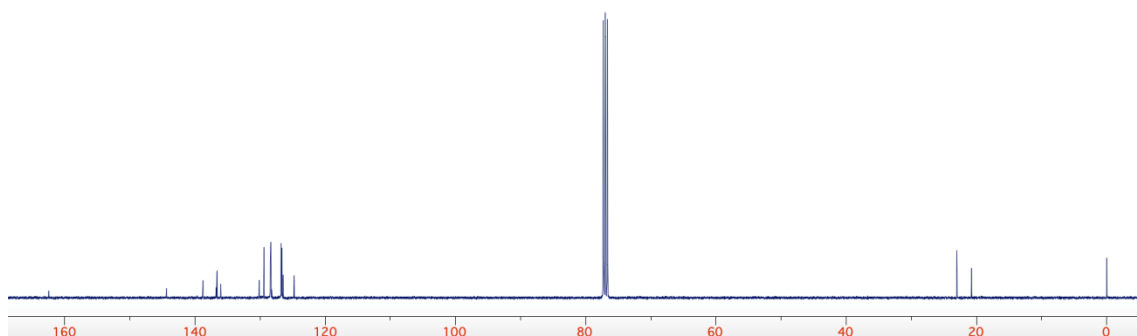


Chart S2. ¹³C NMR spectrum of crystal **7-ben**^{1/10} in CDCl₃.

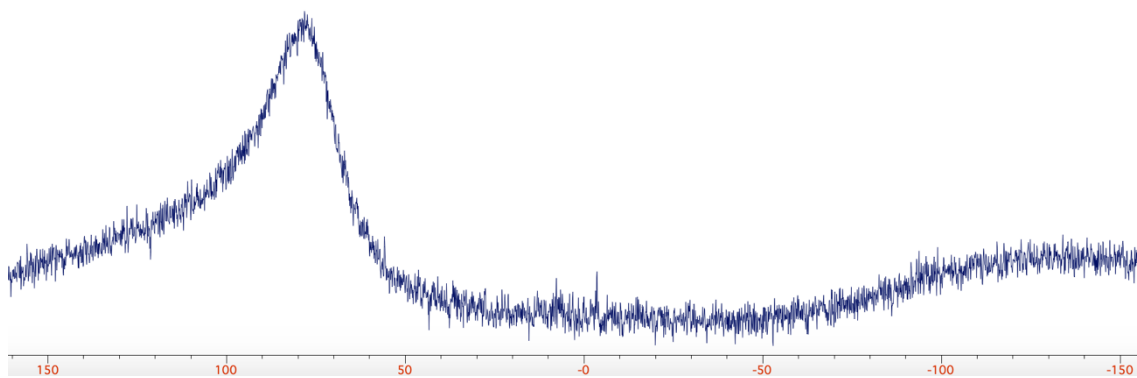


Chart S3. ¹¹B NMR spectrum of crystal **7-ben**^{1/10} in CDCl₃.

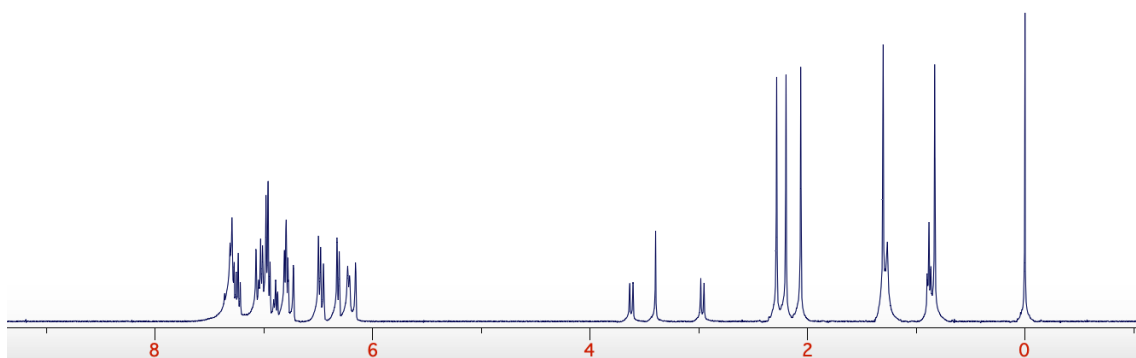


Chart S4. ^1H NMR spectrum of compound **8** in CDCl_3 .

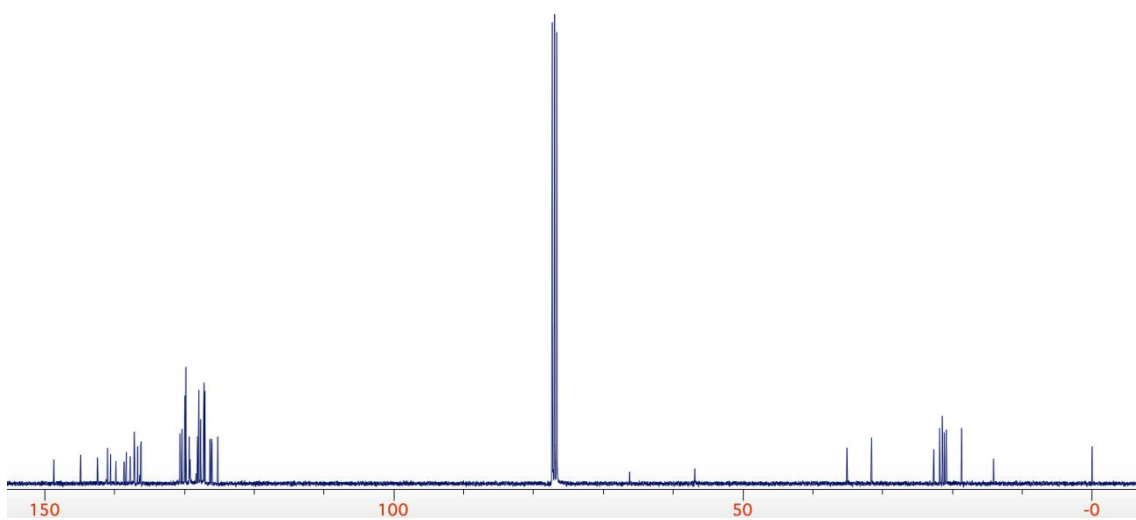


Chart S5. ^{13}C NMR spectrum of compound **8** in CDCl_3 .

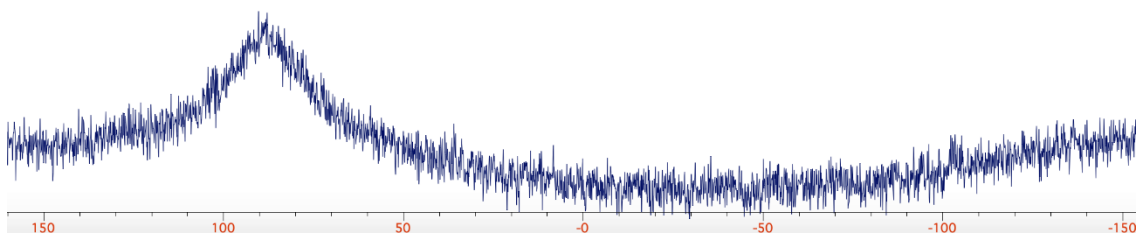


Chart S6. ^{11}B NMR spectrum of compound **8** in CDCl_3 .

4.2 Experimental details on the crystal structure determination of compounds

Single-crystal X-ray diffraction data were collected using a Rigaku R-AXIS RAPID-F and a Rigaku FR-E ++ Super Bright graphite. Data were collected with graphite-monochromated Mo K α radiation diffractometer and an imaging plate. Equivalent reflections were merged and a symmetry related absorption correction was carried out with the program ABSCOR.³ The structures were solved with SHELXT 2014⁴ and refined on F^2 with SHELXL⁵ on Yadokari-XG⁶ or Shelxle.⁷ The program ORTEP-3⁸ was used to generate the X-ray structural diagram. All non-hydrogen atoms were refined and anisotropically hydrogen atoms were assigned to idealized positions and were included in structure factor calculations.

Crystal data for **7-ben**^{1/2}: X-ray crystallographic analysis of crystal **7-ben**^{1/2} was carried out by a Rigaku FR-E ++ Super Bright diffractometer at the Center for Scientific Instrument Renovation and Manufacturing Support, OSAKA University.

Crystal data for **7-hex**^{3/10}: X-ray crystallographic analysis of crystal **7-hex**^{3/10} was carried out by a Rigaku R-AXIS RAPID-F diffractometer. There is a void (319 Å³) and electronic density (66 electrons) in the crystal structure, containing disordered hexane (0.3 eq.) solvent molecules, which could not be refined reasonably. Hence, PLATON/SQUEEZE⁹ tool was applied, where by relevant data are given without any disordered solvent.

Crystal data for **8**: X-ray crystallographic analysis of crystal **8** was carried out by a Rigaku R-AXIS RAPID-F diffractometer. CCDC numbers: 2112954 for **7-ben**, 2112955 for **7-hex** and 2112956 for **8**.

Table S1. Crystallographic data

	7-ben ^{1/2}	7-hex ^{3/10}	8
Chemical formula	C _{19.33} H ₁₇ B _{0.33}	C₅₂H₄₅B	C₅₅H₅₂B
<i>F</i> w (g mol ⁻¹)	252.93	680.69	723.77
Crystal system, space group	Monoclinic, <i>P2/c</i>	Monoclinic, <i>P2/c</i>	Monoclinic, <i>P2₁/c</i>
Temperature (K)	103	93	93
<i>a</i> (Å)	13.734(6)	13.6520 (9)	10.8870 (5)
<i>b</i> (Å)	12.910(6)	12.8989 (6)	11.6042 (5)
<i>c</i> (Å)	12.794(6)	12.7196 (7)	32.5768 (14)
β (°)	105.017(9)	106.517 (7)	92.690 (7)
<i>V</i> (Å ³)	2190.8(17)	2147.4 (2)	4111.1 (3)
<i>Z</i>	6	2	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.06	0.06	0.07
Crystal size (mm)	0.20 × 0.10 × 0.05	0.40 × 0.30 × 0.20	0.32 × 0.30 × 0.22
<i>T</i> _{min} , <i>T</i> _{max}	0.1101, 0.9995	0.4370, 1.0000	0.547, 1.000
Reflections collected	11987	20177	36369
Independent reflections	3990	4916	9366
Observed [I > 2 σ (I)] reflections	1898	3317	6702
No. of parameters	271	244	499
<i>R</i> _{int}	0.152	0.095	0.051
($\sin\theta/\lambda$) _{max} (Å ⁻¹)	0.602	0.649	0.649
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.075 , 0.192 , 0.95	0.079, 0.204, 1.07	0.057, 0.138, 1.02

4.2 Experimental details on the crystal structure determination of compounds

Cyclic voltammetry was conducted with a tightly sealed glass cell with a Teflon screw cap and O-ring, proposed by Morita, Y. *et al.*,¹⁰ using a BASALS-Electrochemical-Analyzer Model 600D. A standard three-electrode cell configuration was employed using a glassy carbon microelectrode, platinum wire counter electrode, and an Ag/AgCl reference electrode, and the ferrocene/ferrocenium (Fc/Fc⁺) external reference at a scan rate of 0.1 V s⁻¹. A 0.1 M solution of [NBu⁴][PF⁶] in CH₂Cl₂ was used as the supporting electrolyte.

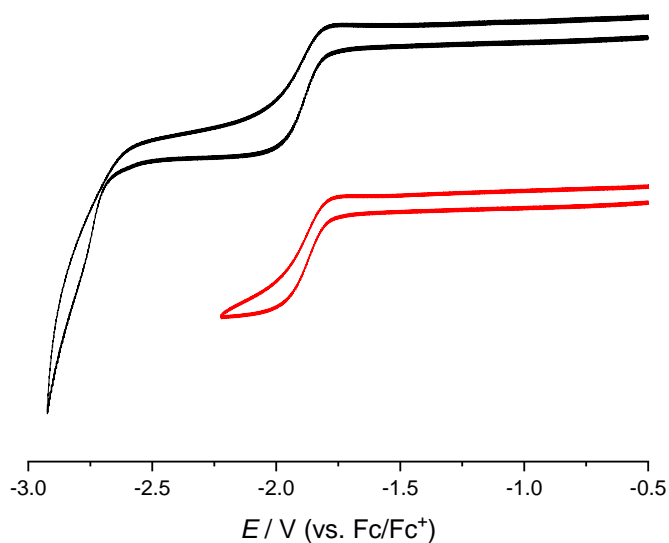


Figure S1. Cyclic voltammogram of **7** (1×10^{-4} M in CH₂Cl₂) at room temperature. The inset (red) displays the reversibility of the single-electron reduction. The first and the second reduction of **7** occurred at -1.80 V and -2.67 V ($E_{\text{red}}^{\text{onset}}$).

4.3 Experimental details on the theoretical studies

The Gaussian 16 program package¹¹ was used for computation. We optimized the structures **7** in the ground S_0 states and calculated their electric structures. The density functional theory (DFT) was applied for the optimization of the structures in the S_0 states at the PBE0/6-311G+(d,p) levels. The energy level of the optimized geometry was confirmed to be the local minima by performing frequency calculations and obtaining only positive frequencies. We also calculated the electric states and transitions from S_0 to S_1 states of **7** with the optimized geometries in the S_0 states by time-dependent DFT (TD-DFT) at the CAM-B3LYP/6-31G+(d,p) levels. The nucleus-independent chemical shift (NICS) calculations (NICS(0), NICS(1)) were also conducted at the optimized geometry using the GIAO PBE0/6-31+G(d,p) level of theory.

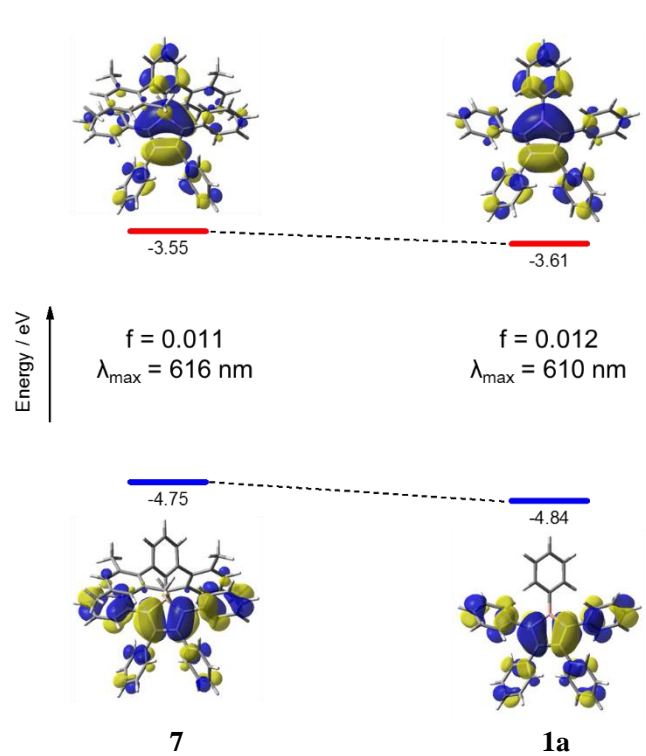


Figure S2. DFT calculated HOMOs, LUMOs and orbital energies, as well as TD-DFT calculated practical data.

Table S2. Calculated electronic transition for S₀ geometry^a

Excited State	Energy / eV	Wavelength / nm	f^b	Composition	Coefficient
1	2.0127	616	0.0113	HOMO-14 -> LUMO	-0.11738
				HOMO -> LUMO	0.68434

^a TD-DFT calculation was performed at the CAM-B3LYP/6-31+G(d,p) level of theory.

^b Oscillator strength.

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