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Supporting Information

Large-bite diboranes for the $\mu(1,2)$ complexation of hydrazine and cyanide

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Experimental section.

General Methods. ⁿButyllithium (2.65 M in hexane), LiHBEt₃ (1 M in THF) and TBAF·3H₂O were purchased from Alfa Aesar and used without further purification. TASF and TBAT were purchased from Sigma-Aldrich and used without further purification. Dimesitylboron fluoride (Mes₂BF) was purchased from TCI and used as received. 1, 8-Dibromobiphenylene and 1, 8-dibromotriptycene were synthesized by following the literature procedures.¹ All preparations were carried out under a dry N₂ atmosphere employing either a glovebox or standard Schlenk techniques. Solvents were dried by passing through an alumina column (n-pentane and CH₂Cl₂) or by refluxing under N₂ over Na/K (Et₂O and THF). All other solvents were ACS reagent grade and used as received. NMR spectra were recorded on an Inova 500 FT NMR (499.41 MHz for ¹H) spectrometer, Varian NMRS 500RM NMR spectrometer (499.69 MHz for ¹H) or an Inova 400 FT NMR (399.46 MHz for ¹H) spectrometer at room temperature. Chemical shifts are given in ppm and are referenced to residual ¹H or ¹³C solvent signals. Elemental analyses were performed by Atlantic Microlab (Norcross, GA).

Stability test for $1-\mu_2-N_2H_4$ in the presence of benzaldehyde. A solution of $1-\mu_2-N_2H_4$ (5 mg,7.3 µmol) in CDCl₃ (0.25 ml) was combined in an NMR tube with a solution of benzaldehyde (1 mg, 9.0 µmol) in CDCl₃ (0.25 ml). The mixture was allowed to react at room temperature for 24 h, at which point no reaction was observed by ¹H NMR spectrometry. The same reaction mixture was then warmed to 60 °C for 20 h. The quantitative formation of diborane **1** and benzaldehyde hydrazone was confirmed by ¹H NMR spectroscopy.

Reactivity of 1 toward ⁿ**Bu**₄**NF.** Diborane **1** (3.5 mg, 5.4 µmol) was added into a solution of tetrabutylammonium fluoride trihydrate (1.7 mg, 5.4 µmol, TBAF·3H₂O) in CDCl₃/CD₃OD (0.25 ml/0.25 ml) in an NMR tube at room temperature. No reaction was observed by ¹H NMR spectroscopy after 1 h and 12 h.

Reactivity of 2 toward ⁿ**Bu**₄**NF.** Diborane **2** (3.0 mg, 4.0 µmol) was added into a solution of tetrabutylammonium fluoride trihydrate (1.3 mg, 4.0 µmol, TBAF·3H₂O) in CDCl₃/CD₃OD (0.25 ml/0.25 ml) in an NMR tube at room temperature. No reaction was observed by ¹H NMR spectroscopy after 1 h and 12 h.

Reactivity of 1 toward ["Bu₄N][Ph₃SiF₂]. ["Bu₄N][Ph₃SiF₂] (4.2 mg, 7.7 μ mol) was added into a solution of diborane **1** (5.0 mg, 7.7 μ mol) in dry CDCl₃ (0.5 ml) in an NMR tube at room temperature. No reaction was observed by ¹H NMR spectroscopy after 5 h.

Reactivity of 2 toward [ⁿ**Bu**₄**N][Ph**₃**SiF**₂**].** [ⁿBu₄**N**][Ph₃SiF₂] (4.0 mg, 6.7 µmol) was added into a solution of diborane **2** (5.0 mg, .6.7 µmol) in dry CDCl₃ (0.5 ml) in an NMR tube at room temperature. No reaction was observed by ¹H NMR spectroscopy after 5 h.

Reactivity of 2 toward [(Me₂N)₃S][Me₃SiF₂]. [(Me₂N)₃S][Me₃SiF₂] (1.9 mg, 6.7 μ mol) was added into a solution of diborane **2** (5.0 mg, 6.7 μ mol) in dry CDCl₃ (0.5 ml) in an NMR tube at room temperature. No reaction was observed by ¹H NMR spectroscopy after 5 h.

Reactivity of 1 toward LiHBEt₃. A solution of diborane **1** (3.0 mg, 4.6 µmol) in dry CDCI₃ (0.5 ml) was added a solution of LiHBEt₃ in THF (1 M, 20 µL, 20 µmol) in an NMR tube at room temperature. No reaction was observed by ¹H NMR spectroscopy after 1 h. Note: ¹H NMR

spectroscopy indicated that LiHBEt₃ does not react with the chlorinated solvent within the timeframe of the experiment.

Reactivity of 2 toward LiHBEt₃. A solution of diborane **2** (5.0 mg, 4.0 μ mol) in dry CDCl₃ (0.5 ml) was added a solution of LiHBEt₃ in THF (1 M, 20 μ L, 20 μ mol) in an NMR tube at room temperature. No reaction was observed by ¹H NMR spectroscopy after 1 h. Note: ¹H NMR spectroscopy indicated that LiHBEt₃ does not react with the chlorinated solvent within the timeframe of the experiment.

Reactivity of 1 toward HCO₃⁻, **HSO**₄⁻, **H**₂**PO**₄⁻, **CH**₃**COO**⁻, **CI**⁻, **Br**⁻, **I**⁻, and **N**₃⁻. A solution of **1** (6.2 × 10⁻⁵ M, 3 ml) in CHCI₃/CH₃OH (v/v =1/1) was allowed to react with excess amount of [ⁿBu₄N][CI] (1 mg), [ⁿBu₄N][Br] (1 mg), [ⁿBu₄N][I] (1 mg), [ⁿBu₄N][CH₃COO] (1 mg) and [ⁿBu₄N][N₃] (1 mg) sequentially in a cuvette. UV-Vis spectra were taken after each addition and no reaction was observed. To the same solution, the saturated aqueous solution of NaHCO₃ (20 µL), NaH₂PO₄ (20 µL) and NaHSO₄ (20 µL) were added sequentially into the cuvette. No reaction was observed after each addition by UV-Vis spectrometry.

Reactivity of 2 toward HCO₃⁻, **HSO**₄⁻, **H**₂**PO**₄⁻, **CH**₃**COO**⁻, **CI**⁻, **Br**⁻, **I**⁻, and **N**₃⁻. A solution of **2** (4.2 × 10⁻⁵ M, 3 ml) in CHCI₃/CH₃OH (v/v =1/1) was allowed to react with excess amount of [ⁿBu₄N][CI] (1 mg), [ⁿBu₄N][Br] (1 mg), [ⁿBu₄N][I] (1 mg), [ⁿBu₄N][CH₃COO] (1 mg) and [ⁿBu₄N][N₃] (1 mg) sequentially in a cuvette. UV-Vis spectra were taken after each addition and no reaction was observed. To the same solution, the saturated aqueous solution of NaHCO₃ (20 µL), NaH₂PO₄ (20 µL) and NaHSO₄ (20 µL) were added sequentially into the cuvette. No reaction was observed after each addition by UV-Vis spectrometry.

Reaction of 1 with [ⁿ**Bu**₄**N]**[**2**- μ_2 -**CN]**. Diborane **2** (2.8 mg, 3.7 µmol) was added to a solution of tetrabutylammonium cyanide (1.0 mg, 3.7 µmol, TBACN) in CDCl₃/CD₃OD (0.25 ml/0.25 ml) in an NMR tube at room temperature. The quantitative formation of [ⁿBu₄N][**2**- μ_2 -CN] was confirmed by ¹H NMR spectroscopy after 5 h. At this point, a slight excess of diborane **1** (3 mg, 4.6 µmol) was directly added into the tube as a solid and the resulting mixture was warmed to 60 °C for an addition 12 h. During this time, **1** which formed a suspension in the solvent was slowly consumed. Formation of free diborane **2** and [**1**- μ_2 -CN]⁻ was confirmed by ¹H NMR spectroscopy.

Reaction of 1 with [ⁿBu₄N][Mes₂PhBCN]. Mes₂BPh (3.2 mg, 9.7 µmol) was added to a solution of tetrabutylammonium cyanide (2.6 mg, 9.7 µmol, TBACN) in CDCl₃/CD₃OD (0.25 ml/0.25 ml) in an NMR tube at room temperature. The formation of [ⁿBu₄N][Mes₂PhBCN] was confirmed by ¹H NMR spectroscopy after 1 h. At this point, diborane **1** (6.3 mg, 9.7 µmol) was directly added into the tube as a solid and the resulting mixture was warmed to 60 °C for an addition 12 h. During this time, **1** which formed a suspension in the solvent was slowly consumed. Formation of Mes₂BPh and [**1**-µ₂-CN]⁻ was confirmed by ¹H NMR spectroscopy.

Reaction of $(C_6F_5)_3B$ with [nBu_4N][1- μ_2 -CN]. Diborane 1 (3.0 mg, 4.6 µmol) was added to a solution of tetrabutylammonium cyanide (1.2 mg, 4.6 µmol, TBACN) in CDCl₃/CD₃OD (0.25 ml/0.25 ml) in an NMR tube at room temperature. The quantitative formation of [nBu_4N][1- μ_2 -CN] was confirmed by ¹H NMR spectroscopy after 5 h. At this point, a slight excess of (C₆F₅)₃B (3 mg, 5.9 µmol) was directly added into the tube and the mixture was sonicated for an additional hour. No reaction was observed by ¹H NMR spectroscopy after 1 h and 12 h.

Reaction of $(C_6F_5)_3B$ with ["Bu₄N][2-µ₂-CN]. Diborane 2 (2.6 mg, 3.5 µmol) was added to a solution of tetrabutylammonium cyanide (1.0 mg, 3.7 µmol, TBACN) in CDCl₃/CD₃OD (0.25 ml /0.25 ml) in an NMR tube at room temperature. The quantitative formation of ["Bu₄N][2-µ₂-CN] was confirmed by ¹H NMR spectroscopy after 5 h. At this point, a slight excess of (C₆F₅)₃B (2 mg, 3.9 µmol) was directly added into the tube and the mixture was sonicated for an additional hour. Formation of free diborane 2 was confirmed by ¹H NMR spectroscopy.

Electrochemistry. Electrochemical experiments were performed with an electrochemical analyzer from CH Instruments (model 610A) with a glassy-carbon working electrode and a platinum auxiliary electrode. The reference electrode was built from a silver wire inserted into a small glass tube fitted with a porous Vycor frit at the tip and filled with a THF solution containing tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) and AgNO₃ (0.005 M). All three electrodes were immersed in a deoxygenated THF solution (5 mL) containing TBAPF₆ (0.1 M) as a support electrolyte and the diboranes (**1** and **2**) (0.003 M). Ferrocene was used as an internal standard, and all potentials are reported with respect to $E_{1/2}$ of the Fc/Fc⁺ redox couple.

Crystallographic details. The crystallographic measurements were performed at 110(2) K using a Bruker APEX-II CCD area detector diffractometer, with a graphite-monochromated Mo-K α radiation (λ = 0.71073 Å). A specimen of suitable size and quality was selected and mounted onto a nylon loop. The semi-empirical method SADABS was applied for absorption correction. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 6.1) allowed location of the remaining non-hydrogen atoms.

Determinations of quantum yield.² Quantum yields were determined relative to fluorescein (λ_{ex} = 470 nm) in 0.1 M NaOH as a standard (Φ =0.91). Absorbance measurements were taken on a Shimadzu UV-2502PC UV-Vis spectrophotometer. Fluorescence measurements were taken on samples in capped quartz cuvettes under air on a PTI QuantaMaster spectrofluorometer with entrance and exit slit widths of 2 nm and an integration time of 1 s. Fluorescence quantum yields were calculated based on the gradients of integrated emission (IE) versus absorbance at λ_{ex} (Abs) for a series of measurements on the sample or fluorescence standard, according to the following equation:³

$$\Phi_{sample} = \Phi_{std} \times \frac{IE_{sample}}{IE_{std}} \times \frac{Abs_{std}}{Abs_{sample}} \times \left(\frac{\eta_{sample}}{\eta_{std}}\right)^2$$

$$= \Phi_{std} \times \frac{Grad_{sample}}{Grad_{std}} \times \left(\frac{\eta_{sample}}{\eta_{std}}\right)^2$$

where η was 1.334 for 0.1 M NaOH and 1.407 for THF solutions. The resulting gradient plots obtained are shown in Figure S26 for compound **1** and **2**.







Figure S2. ¹³C{¹H} NMR spectrum of 2 in CDCI₃.



Figure S3. $^{11}B{^1H}$ NMR spectrum of 2 in CDCl₃.



Figure S5. ¹³C{¹H} NMR spectrum of $1-\mu_2-N_2H_4$ in CD₂Cl₂.



Figure S6. ¹H NMR spectrum of [K(dibenzo-18-crown-6)][1- μ_2 -CN] in CDCI₃ at rt.



Figure S7. ¹H NMR spectrum of [K(dibenzo-18-crown-6)][1- μ_2 -CN] in CDCl₃ at -50 °C.



Figure S8. $^{13}C{^{1}H}$ NMR spectrum of [K(dibenzo-18-crown-6)][1- μ_2 -CN] in CDCl₃.



Figure S9. ¹¹B{¹H} NMR spectrum of [K(dibenzo-18-crown-6)][1-µ₂-CN] in CDCl₃.



Figure S10. ¹H NMR spectrum of [K(dibenzo-18-crown-6)][2-µ₂-CN] in CD₂Cl₂.



Figure S11. ¹³C{¹H} NMR spectrum of [K(dibenzo-18-crown-6)][2-µ₂-CN] in CD₂Cl₂.



Figure S12. ¹¹B{¹H} NMR spectrum of [K(dibenzo-18-crown-6)][$2-\mu_2$ -CN] in CD₂Cl₂.



Figure S13. ¹H NMR monitoring of the reaction of $1-\mu_2-N_2H_4$ with benzaldehyde in CDCl₃ at 60 °C.



Figure S14. ¹H NMR monitoring of the reaction of **1** with [$^{n}Bu_{4}N$][**2**- μ_{2} -CN] in CDCI₃/CD₃OD (1/1 vol.).



Figure S15. ¹H NMR monitoring of the reaction of 1 with [$^{n}Bu_{4}N$][Mes₂PhBCN] in CDCl₃/CD₃OD (1/1 vol.).



Figure S16. ¹H NMR monitoring of the reaction of $(C_6F_5)_3B$ with $[^nBu_4N][1-\mu_2-CN]$ in CDCl₃/CD₃OD (1/1 vol.).



Figure S17. ¹H NMR monitoring of the reaction of $(C_6F_5)_3B$ with $[^nBu_4N][2-\mu_2-CN]$ in CDCl₃/CD₃OD (1/1 vol.).



Figure S18. IR spectrum of [K(dibenzo-18-crown-6)][1- μ_2 -CN] in the solid state.



Figure S19. IR spectrum of [K(dibenzo-18-crown-6)][$2-\mu_2$ -CN] in the solid state.



Figure S20. LUMO+1 of diborane 2.

Excitations	Oscillator strength	MOs involved in the excitation	Contributions
$E_a(S_0 \rightarrow S_1)$	0.0741	174 → 175	0.69070
415.48 nm (2.9841 eV)	0.0741	174 → 177	-0.11545
$E_b (S_0 \rightarrow S_2)$ 348.03 nm (3.5625 eV)	0.0018	174 → 176	0.69825
$E_c (S_0 \rightarrow S_3)$	0.0097	172 → 176	-0.22815
342.68 nm (3.6181 eV)	0.0087	173 → 175	0.64838
		172 → 175	0.62739
$E_d(S_0 - 5_4)$	0.1448	173 → 176	-0.21573
342.47 nm (3.6203 eV)		174 → 177	0.15674
		165 → 175	-0.11294
$E_{e}(S_{0} \rightarrow S_{5})$	0.0597	172 → 175	-0.15557
338.80 nm (3.6596 eV)		174 → 177	0.65550

Table S1. Calculated low-energy electronic transitions of **1**, obtained from the TD-DFT analysis. The HOMO and LUMO orbitals are 174 and 175, respectively.



Figure S21. Results from the NTO analysis of the $S_0 \rightarrow S_1$ transition in **1**. The relevant orbitals (isovalue = 0.05) as well as the NTO contributions from the individual electronic excitations are provided.



Figure S22. Results from the NTO analysis of the $S_0 \rightarrow S_4$ transition in **1**. The relevant orbitals (isovalue = 0.05) as well as the NTO contributions from the individual electronic excitations are provided.

Table S2. Calculated low-energy electronic transitions of 2,	obtained from the TD-DFT analysis.
The HOMO and LUMO orbitals are 201 and 202, respective	ely.

Excitations	Oscillator strength	MOs involved in the excitation	Contributions
F		199 → 203	-0.12271
E_a	0.0768	200 → 202	0.61862
529.98 IIII (5.7575 eV)		200 → 203	0.28855
		199 → 202	-0.40735
Eb	0 1 4 2 0	199 → 203	0.49568
325.84 nm (3.8051 eV)	0.1450	200 → 202	0.10301
		201 → 202	-0.20426
		196 → 202	-0.11440
		196 → 203	-0.11629
Г		197 → 203	-0.13769
E_c	0.1378	198 → 202	0.18628
520.90 mm (5.8050 eV)		199 → 202	-0.16371
		199 → 203	0.16007
		201 → 202	0.58536
		196 → 202	0.40501
	0.0865	196 → 203	0.16993
		197 → 202	0.24059
Ed		197 → 203	0.13633
313.92 nm (3.9496 eV)		198 → 202	-0.34262
		198 → 203	-0.15872
		201 → 202	0.23240
		201 → 203	-0.10862
		196 → 203	0.10934
		197 → 202	-0.24500
Г		197 → 203	0.21486
E_e	0.0922	198 → 202	-0.28276
212.91 IIII (2.9023 EV)		198 → 203	0.34915
		201 → 202	0.19951
		201 → 203	0.31969





Figure S23. Results from the NTO analysis of the $S_0 \rightarrow S_1$ transition in **2**. The relevant orbitals (isovalue = 0.05) as well as the NTO contributions from the individual electronic excitations are provided.



Figure S24. Results from the NTO analysis of the $S_0 \rightarrow S_2$ transition in **2**. The relevant orbitals (isovalue = 0.05) as well as the NTO contributions from the individual electronic excitations are provided.



Figure S25. Results from the NTO analysis of the $S_0 \rightarrow S_3$ transition in **2**. The relevant orbitals (isovalue = 0.05) as well as the NTO contributions from the individual electronic excitations are provided.



Figure S26. Plots of integrated emission (IE) vs. absorbance at λ_{ex} for **1** (top) and **2** (bottom) and fluorescein.

Table S3. Crystallographic details of 2.

Identification code	У	
Empirical formula	C56 H56 B2	
Formula weight	750.62	
Temperature	110 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.785(3) Å	α = 90° .
	b = 19.051(5) Å	β = 93.290(4) °.
	c = 19.029(5) Å	γ = 90°.
Volume	4265.4(18) Å ³	
Z	4	
Density (calculated)	1.169 Mg/m ³	
Absorption coefficient	0.065 mm ⁻¹	
F(000)	1608	
Crystal size	0.4 x 0.18 x 0.1 mm	3
Theta range for data collection	1.514 to 27.566°.	
Index ranges	-15<=h<=15, -24<=k	<=24, -24<=l<=24
Reflections collected	48875	
Independent reflections	9827 [R(int) = 0.118	8]
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from	equivalents
Max. and min. transmission	0.7456 and 0.6960	
Refinement method	Full-matrix least-squ	ares on F ²
Data / restraints / parameters	9827 / 0 / 535	
Goodness-of-fit on F ²	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0727, wR2 =	0.1230
R indices (all data)	R1 = 0.1521, wR2 =	0.1540
Extinction coefficient	n/a	
Largest diff. peak and hole	0.313 and -0.256 e.Å	<u>\</u> -3

Table S4. Crystallographic details of $1-\mu_2-N_2H_4$.

Identification code	y_sq		
Empirical formula	C48 H54 B2 N2		
Formula weight	680.55		
Temperature	110 K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	C 1 2/c 1		
Unit cell dimensions	a = 18.849(3) Å	a= 90°.	
	b = 11.5959(16) Å	b= 106.9137(18)°.	
	c = 20.422(3) Å	g = 90°.	
Volume	4270.7(10) Å ³		
Z	4		
Density (calculated)	1.058 Mg/m ³		
Absorption coefficient	0.060 mm ⁻¹		
F(000)	1464		
Crystal size	0.91 x 0.53 x 0.3 mm	3	
Theta range for data collection	2.085 to 27.548°.		
Index ranges	-24<=h<=24, -15<=k<	=15, -26<=l<=26	
Reflections collected	46117		
Independent reflections	4928 [R(int) = 0.0259]	l	
Completeness to theta = 25.242°	100.0 %		
Absorption correction	Semi-empirical from e	equivalents	
Max. and min. transmission	0.7456 and 0.6876		
Refinement method	Full-matrix least-squa	res on F ²	
Data / restraints / parameters	4928 / 0 / 241		
Goodness-of-fit on F ²	1.042		
Final R indices [I>2sigma(I)]	R1 = 0.0512, wR2 = 0).1412	
R indices (all data)	R1 = 0.0567, wR2 = 0).1471	
Extinction coefficient	n/a		
Largest diff. peak and hole	0.453 and -0.376 e.Å ⁻	-3	

Table S5. Crystallographic details of [K(dibenzo-18-crown-6)][1- μ_2 -CN]-(CH $_2$ Cl $_2$).

Identification code	d			
Empirical formula	C71 H78 B2 Cl4 K N (O6		
Formula weight	1243.86			
Temperature	110 K			
Wavelength	0.71073 Å			
Crystal system	Monoclinic			
Space group	P 1 21/c 1			
Unit cell dimensions	a = 15.4096(14) Å	α= 90°.		
	b = 23.693(2) Å	β= 112.9484(11)°.		
	c = 19.0628(17) Å	$\gamma = 90^{\circ}$.		
Volume	6409.0(10) Å ³			
Z	4			
Density (calculated)	1.289 Mg/m ³			
Absorption coefficient	0.303 mm ⁻¹			
F(000)	2624			
Crystal size	0.5 x 0.3 x 0.2 mm ³			
Theta range for data collection	2.074 to 27.614°.			
Index ranges	-20<=h<=20, -30<=k<	-20<=h<=20, -30<=k<=30, -24<=l<=24		
Reflections collected	140726			
Independent reflections	14800 [R(int) = 0.0670	D]		
Completeness to theta = 25.242°	99.8 %			
Absorption correction	Semi-empirical from e	quivalents		
Max. and min. transmission	0.7456 and 0.6917			
Refinement method	Full-matrix least-squa	res on F ²		
Data / restraints / parameters	14800 / 36 / 801			
Goodness-of-fit on F ²	1.074			
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0	.1549		
R indices (all data)	R1 = 0.0805, wR2 = 0	.1724		
Extinction coefficient	n/a			
Largest diff. peak and hole	0.915 and -1.201 e.Å ⁻	-3		

Table S6. Cr	rystallographic	details of [K(dibenzo-	-18-crown-6)][2-μ ₂ -	CN]-(CH ₂ Cl ₂) ₂ .
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Identification code	У	
Empirical formula	C79 H83 B2 Cl4 K N (D6
Formula weight	1344.98	
Temperature	110 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 c 1	
Unit cell dimensions	a = 21.407(3) Å	α= 90°.
	b = 13.6932(18) Å	β = 92.4764(14)° .
	c = 23.988(3) Å	$\gamma = 90^{\circ}$.
Volume	7025.2(16) Å ³	
Z	4	
Density (calculated)	1.272 Mg/m ³	
Absorption coefficient	0.282 mm ⁻¹	
F(000)	2836	
Crystal size	0.49 x 0.36 x 0.22 mm	3
Theta range for data collection	1.942 to 26.507°.	
Index ranges	-26<=h<=26, -17<=k<	=17, -30<=l<=30
Reflections collected	70236	
Independent reflections	14546 [R(int) = 0.0661]
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from e	quivalents
Max. and min. transmission	0.7454 and 0.6939	
Refinement method	Full-matrix least-squar	res on F ²
Data / restraints / parameters	14546 / 2 / 858	
Goodness-of-fit on F ²	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0	.1119
R indices (all data)	R1 = 0.0538, wR2 = 0	.1181
Absolute structure parameter	0.002(16)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.463 and -0.555 e.Å ⁻	3

 Table S7. XYZ coordinate of the optimized structure of 1.



С	-1.956909	-0.349389	1.843330	С	0.604832	-4.928886	-2.786070
С	-3.125818	-0.400701	2.697887	н	0.246735	-4.961486	-3.820813
Н	-4.091070	-0.519144	2.217164	н	0.463721	-5.921275	-2.344830
С	-3.087287	-0.330771	4.085295	н	1.686496	-4.738540	-2.822688
Н	-4.013730	-0.393309	4.648190	C	-1.695982	-0.472673	-2.660269
С	-1.855682	-0.187783	4.774601	н	-1.454382	0.477915	-2.178178
Н	-1.815062	-0.163836	5.858290	Н	-2.781958	-0.499037	-2.799381
С	-0.741753	-0.086535	3.978354	Н	-1.233875	-0.464244	-3.652626
С	-0.769738	-0.121161	2.544360	С	3.616042	0.180957	-0.266743
С	0.773349	0.095059	2.544980	С	3.861928	-1.220225	-0.356233
С	0.746371	0.044861	3.978544	С	5.064370	-1.693649	-0.898360
С	1.860845	0.137763	4.775044	н	5.217657	-2.767664	-0.977691
Н	1.820995	0.102223	5.858443	C	6.074294	-0.824751	-1.332208
С	3.091931	0.288466	4.086449	С	5.843733	0.551405	-1.220129
Н	4.018740	0.345185	4.649366	Н	6.616860	1.245446	-1.541918
С	3.129465	0.373370	2.699854	C	4.641584	1.066505	-0.709735
Н	4.094295	0.497230	2.219648	C	2.836772	-2.237856	0.104576
С	1.959972	0.331108	1.845639	Н	3.118523	-3.245036	-0.219261
С	-3.615054	-0.177004	-0.265895	н	1.836171	-2.036733	-0.290684
С	-4.643311	-1.058811	-0.710247	H	2.750213	-2.251458	1.197424
С	-5.849395	-0.539517	-1.206809	C	7.381436	-1.357825	-1.875688
Н	-6.627211	-1.230842	-1.523078	Н	8.073962	-1.619991	-1.063770
С	-6.079140	0.837639	-1.308959	Н	7.884180	-0.617153	-2.506546
С	-5.069468	1.702727	-0.867344	Н	7.227355	-2.263603	-2.473002
Н	-5.227719	2.777287	-0.927180	C	4.500138	2.577999	-0.641653
С	-3.862781	1.224705	-0.338686	Н	5.465545	3.059399	-0.829030
С	-4.503157	-2.570807	-0.650759	Н	4.146141	2.920446	0.337140
Н	-3.792682	-2.943130	-1.397108	Н	3.789233	2.954215	-1.385678
Н	-5.468955	-3.050344	-0.840855	C	1.413046	1.814929	-0.438779
Н	-4.149303	-2.919340	0.326002	C	0.948380	3.014507	0.190833
С	-7.367276	1.375484	-1.891847	C	0.328806	4.017625	-0.571419
Н	-7.257302	1.601233	-2.961706	Н	0.012070	4.930566	-0.073094
Н	-7.674668	2.303074	-1.396062	C	0.103629	3.881530	-1.945268
Н	-8.183616	0.651922	-1.794380	C	0.547047	2.705695	-2.562739
С	-2.838436	2.238262	0.132637	Н	0.390985	2.578081	-3.631219
Н	-2.750167	2.239412	1.225433	C	1.207445	1.693642	-1.851428
н	-3.121818	3.248753	-0.179261	C	1.130202	3.317041	1.669586
н	-1.838271	2.042810	-0.266547	Н	2.122453	3.048844	2.042425
С	-1.413040	-1.809625	-0.457194	н н	0.404417	2.775517	2.285546

С	-0.948490	-3.016033	0.159272	Н	0.983205	4.386473	1.852503
С	-0.331331	-4.011962	-0.614339	С	1.693725	0.500890	-2.655904
Н	-0.014915	-4.930377	-0.125957	Н	2.779272	0.530468	-2.797853
С	-0.108336	-3.862071	-1.987068	Н	1.228970	0.501404	-3.647046
С	-0.551428	-2.679440	-2.591685	Н	1.455059	-0.454805	-2.182569
Н	-0.396955	-2.540979	-3.659044	С	-0.612313	4.955500	-2.732105
С	-1.209593	-1.674119	-1.868882	Н	-0.469853	5.943871	-2.282363
С	-1.127855	-3.333894	1.635142	Н	-1.694075	4.765329	-2.766771
Н	-0.982091	-4.405435	1.806297	Н	-0.257706	4.997552	-3.767703
Н	-2.118883	-3.068260	2.012979	В	-2.258582	-0.739580	0.341080
Н	-0.399857	-2.800149	2.255255	В	2.260233	0.737265	0.347351

 Table S8. XYZ coordinate of the optimized structure of 2.

С	-2.524786	-0.577613	1.396575	Н	-1.040168	0.336923	-4.398520	
В	-2.898817	0.010752	-0.021528	С	-1.459437	-1.703574	-3.859896	
С	-3.620882	-0.623049	2.308434	С	-1.977675	-2.524683	-2.851743	
н	-4.556683	-0.164600	2.007362	н	-2.054291	-3.594977	-3.028439	
В	2.640160	0.833083	0.324537	С	-2.410817	-2.010895	-1.619444	
С	-3.547659	-1.238620	3.556301	C	-1.837641	1.748783	-2.294671	
н	-4.416581	-1.259314	4.206857	н	-1.233292	2.187403	-3.094329	
С	-2.345114	-1.825851	3.963587	н	-1.422943	2.091516	-1.341238	
Н	-2.264687	-2.316418	4.929623	Н	-2.846573	2.169553	-2.367512	
С	-1.244646	-1.773685	3.111766	С	-0.951725	-2.284379	-5.160138	
С	-1.305214	-1.154587	1.843748	Н	-1.189520	-1.635103	-6.010481	
С	1.149538	-0.651059	2.035428	н	-1.385022	-3.271031	-5.354776	
C	2.120238	0.338916	1.733396	Н	0.140512	-2.402645	-5.138573	
C	2.927055	0.787985	2.820161	C	-2.992849	-2.999242	-0.622406	
Н	3.644467	1.580640	2.634474	Н	-3.914784	-2.634380	-0.158556	
C	2.859554	0.223830	4.094498	Н	-2.292357	-3.220183	0.188815	
Н	3.506972	0.587709	4.886434	Н	-3.224897	-3.946037	-1.121075	
С	1.967570	-0.826463	4.338456	C	3.176753	2.324004	0.208039	
Н	1.926605	-1.305896	5.312507	C	2.348345	3.433078	0.555043	
C	1.122303	-1.247582	3.313286	C	2.832784	4.743180	0.450783	
С	0.114135	-2.388883	3.434414	Н	2.171323	5.569781	0.700592	
Н	0.135417	-2.863062	4.418241	C	4.144127	5.016078	0.039276	
С	0.416827	-3.369188	2.296759	C	4.963278	3.930140	-0.287418	
C	0.695044	-4.728951	2.418126	Н	5.986295	4.117477	-0.605157	
Н	0.722467	-5.199955	3.396701	C	4.507147	2.603385	-0.223734	
C	0.939852	-5.484839	1.259315	C	0.915285	3.244460	1.012792	
Н	1.158220	-6.544932	1.343698	н	0.398908	4.207506	1.075885	
C	0.902728	-4.876292	0.000586	н	0.863023	2.768110	1.997554	
н	1.093198	-5.465652	-0.890973	н	0.344206	2.611983	0.323393	
C	0.621940	-3.504466	-0.121691	C	4.659589	6.436459	-0.027569	
Н	0.593619	-3.034467	-1.098362	Н	5.583699	6.499065	-0.611352	
C	0.379224	-2.754583	1.028907	Н	4.876266	6.829504	0.975206	
C	0.062377	-1.249506	1.100748	Н	3.924127	7.109005	-0.484380	
Н	0.044348	-0.780185	0.119001	C	5.489980	1.511875	-0.611571	
C	-3.976741	1.180157	-0.069439	Н	5.212326	1.030827	-1.555678	
С	-3.821464	2.363348	0.712406	Н	5.553172	0.719684	0.142137	
C	-4.769133	3.395168	0.636203	Н	6.494375	1.930709	-0.732168	
H	-4.614200	4.294722	1.227957	C C	2.815230	-0.175751	-0.883491	

I	С	-5.908683	3.297207	-0.169183	С	3.463694	-1.438661	-0.719365	
	С	-6.081330	2.122644	-0.912835	С	3.669712	-2.273296	-1.828810	
	Н	-6.968981	2.014410	-1.531810	Н	4.185535	-3.219004	-1.680755	
	С	-5.142053	1.081608	-0.891565	С	3.234301	-1.929215	-3.113241	
	С	-2.648041	2.575883	1.652699	С	2.605643	-0.688640	-3.276877	
	Н	-2.452835	3.645322	1.787064	Н	2.273027	-0.388708	-4.267875	
	Н	-1.727655	2.110297	1.295845	С	2.412346	0.191966	-2.203444	
	Н	-2.851227	2.149847	2.643183	С	4.010135	-1.929732	0.610547	
	С	-6.909411	4.428011	-0.253303	Н	4.475229	-1.134465	1.199345	
	Н	-6.688941	5.092111	-1.100630	Н	4.765225	-2.704891	0.442651	
	Н	-6.896885	5.042400	0.653293	Н	3.223503	-2.369894	1.232606	
	Н	-7.928585	4.051530	-0.394669	С	3.428066	-2.868765	-4.282630	
	С	-5.439331	-0.134811	-1.751925	Н	2.560982	-3.532235	-4.409499	
	Н	-6.462725	-0.084396	-2.137887	Н	4.306262	-3.507908	-4.141148	
	Н	-5.344289	-1.073689	-1.196261	Н	3.556028	-2.318999	-5.221739	
	Н	-4.761573	-0.202475	-2.609588	С	1.791986	1.540883	-2.516185	
	С	-2.348931	-0.606764	-1.368663	Н	2.549669	2.333117	-2.534784	
	С	-1.863437	0.234807	-2.415885	H	1.037050	1.838474	-1.784660	
	С	-1.416538	-0.323773	-3.621067	H	1.307427	1.517977	-3.497122	

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