Electronic Supplementary Information

Impact of Deboronation on the Electronic Characteristics of Closo-o-carborane: Intriguing Photophysical Changes in Triazole-appended Carboranyl Luminophores

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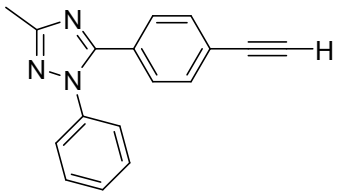
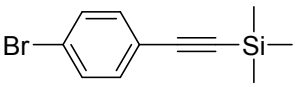
Contents

Synthesis of 5-(4-ethynylphenyl)-3-methyl-1-phenyl-1*H*-1,2,4-triazole, A1



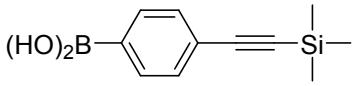
Toluene (23.0 mL) and triethylamine (15.0 mL) were added via cannula to a mixture of **Br1** (1.57 g, 5.0 mmol), CuI (76.2 mg, 0.4 mmol), and $Pd(PPh_3)_2Cl_2$ (0.31 g, 0.44 mmol) at 90 °C. After stirring for 10 min, trimethylsilylacetylene (2.77 mL, 20.0 mmol) was added. Subsequently, the reaction mixture was heated under reflux for 24 h. After this time, the volatiles were removed by rotary evaporation to afford a dark brown residue. The crude product was purified by column chromatography on silica gel (ethyl acetate:*n*-hexane = 1:4, v/v) to yield 3-methyl-1-phenyl-5-(4-((trimethylsilyl)ethynyl)phenyl)-1*H*-1,2,4-triazole (1.61 g, 97%) as a white solid. The product was then used *in situ* for the next step without characterization. After dissolving the obtained 3-methyl-1-phenyl-5-(4-((trimethylsilyl)ethynyl)phenyl)-1*H*-1,2,4-triazole (1.44 g, 4.3 mmol) with K_2CO_3 (2.40 g, 17.4 mmol) in methanol (25.0 mL) and stirring for 2 h at ambient temperature, the resulting mixture was extracted with DCM (20.0 mL × 3). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and the solvent was removed under reduced pressure. Purification of the crude product by column chromatography on silica gel (ethyl acetate:*n*-hexane = 1:4, v/v) afforded **A1** (1.10 g, 98%) as an ivory solid. ^{1}H NMR ($CDCl_3$): δ 7.45 (s, 5H), 7.42 (d, J = 2.4 Hz, 2H), 7.32 (m, 2H), 3.15 (s, 1H, –CC*H*), 2.51 (s, 3H, –CH_3). ^{13}C NMR ($CDCl_3$): δ 161.06, 153.44, 138.18, 132.35, 129.59, 129.02, 128.77, 128.24, 125.43, 123.84, 82.94 (acetylene-*C*), 79.26 (acetylene-*C*), 14.00 (–*C*H_3). Anal. Calcd for $C_{17}H_{13}N_3$: C, 78.74; H, 5.05; N, 16.20. Found: C, 78.54; H, 5.04; N, 16.11.

Synthesis of ((4-bromophenyl)ethynyl)trimethylsilane, Br2



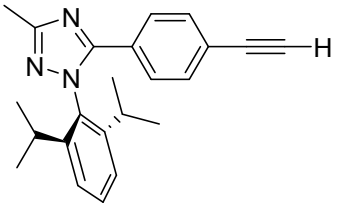
THF (30.0 mL) and triethylamine (20.0 mL) were added via cannula to a mixture of 1-bromo-4- iodobenzene (2.83 g, 10.0 mmol), CuI (95.2 mg, 0.5 mmol), and $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.5 mmol) at 60 ℃. After stirring for 10 min, trimethylsilylacetylene (1.66 mL, 12.0 mmol) was added, and the reaction mixture was heated under reflux for 30 min. The solvents were then removed under vacuum to obtain the crude product as a dark brown residue. Purification by column chromatography on silica gel (*n*-hexane) and recrystallization from methanol gave **Br2** (2.16 g, 85%) as an ivory solid. ^{1}H NMR ($CDCl_3$): δ 7.43 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 0.25 (s, 9H, –Si(CH_3)$_3$). ^{13}C NMR ($CDCl_3$): δ 133.52, 131.61, 122.88, 122.24, 104.00 (acetylene-*C*), 95.73 (acetylene-*C*), 0.03 (–Si(*C*H_3)$_3$). Anal. Calcd for $C_{11}H_{13}BrSi$: C, 52.18; H, 5.18. Found: C, 52.15; H, 5.14.

Synthesis of (4-((trimethysilyl)ethynyl)phenyl)boronic acid, B2



An *n*-hexane solution of *n*-BuLi (1.6 M, 7.98 mL, 12.8 mmol) was added dropwise to a solution of **Br2** (2.16 g, 8.5 mmol) in THF (85.0 mL) at −78 ℃ and the mixture was stirred for 1 h. After cooling once again to −78 ℃, trimethylborate (3.78 mL, 30.1 mmol) was slowly added to the mixture. After stirring for 1 h, the reaction was slowly allowed to ambient temperature and stirred for a further 12 h. After quenching using a saturated aqueous NH_4Cl solution (100 mL), the mixture was subsequently extracted with DCM (50.0 mL × 3), the organic layer was dried over anhydrous $MgSO_4$, filtered, and the volatiles were removed by rotary evaporation. The crude product was recrystallized from *n*-hexane, affording **B2** (1.30 g, 70%) as an ivory solid. ^{1}H NMR ($CDCl_3$): δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 0.29 (s, 9H, –Si(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$): δ 135.48, 131.55, 127.54, 105.09 (acetylene-*C*), 96.89 (acetylene-*C*), 0.09 (–Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{11}H_{15}BO_2Si$: C, 60.57; H, 6.93. Found: C, 60.55; H, 6.90.

Synthesis of 1-(2,6-diisopropylphenyl)-5-(4-ethynylphenyl)-3-methyl-1*H*-1,2,4-triazole, A2



Toluene (20.0 mL) and distilled water (10.0 mL) were added via cannula to the mixture of **TB2** (1.30 g, 6.0 mmol), 5-bromo-1-(2,6-diisopropylphenyl)-3-methyl-1*H*-1,2,4-triazole (1.60 g, 5.0 mmol), $Pd(PPh_3)_4$ (0.57 g, 0.5 mmol) and K_2CO_3 (2.06 g, 14.9 mmol). The resulting mixture was then heated at reflux at 120 °C for 12 h, after which it was extracted with ethyl acetate (20.0 mL × 3), the organic layer was dried over anhydrous $MgSO_4$, and the solvents were removed using a rotary evaporator. Purification by column chromatography on silica gel (ethyl acetate:*n*-hexane = 1:4, v/v) yielded 1-(2,6-diisopropylphenyl)-3-methyl-5-(4-((trimethylsilyl)ethynyl)phenyl)-1*H*-1,2,4-triazole (0.31 g, 15%) as a white solid. The product was then used *in situ* for the next step without characterization. Thus, the obtained 1-(2,6-diisopropylphenyl)-3-methyl-5-(4-((trimethylsilyl)ethynyl)phenyl)-1*H*-1,2,4-triazole (0.31 g, 0.7 mmol) and K_2CO_3 (0.41 g, 2.9 mmol) were dissolved in methanol (7.0 mL), and the mixture was stirred for 2 h at ambient temperature. After this time, the mixture was extracted with DCM (10.0 mL × 3), the combined organic extracts were dried over anhydrous $MgSO_4$ and filtered, then the solvent was removed under reduced pressure. The product was recrystallized from *n*-hexane, affording **A2** (0.23 g, 92%) as a white solid. ^{1}H NMR (CD_2Cl_2): δ 7.51 (t, *J* = 7.7 Hz, 1H), 7.43 (dd, *J* = 8.2, 2.4 Hz, 2H), 7.36 (dd, *J* = 8.2, 2.4 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 3.19 (s, 1H, –CC*H*), 2.46 (s, 3H, –C*H*$_3$), 2.36 (m, 2H, –C*H*(CH$_3$)$_2$), 1.11 (d, *J* = 6.8 Hz, 6H, –CH(C*H*$_3$)$_2$), 0.89 (d, *J* = 6.9 Hz, 6H, –CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2): δ 160.95, 154.37, 146.50, 134.96, 132.50, 131.01, 128.46, 127.84, 124.78, 123.72, 83.10 (acetylene-*C*), 79.26 (acetylene-*C*), 28.84 (–*C*H(CH$_3$)$_2$), 24.77 (–CH(*C*H$_3$)$_2$), 22.84 (–CH(*C*H$_3$)$_2$), 14.17 (–*C*H$_3$). Anal. Calcd for $C_{23}H_{25}N_3$: C, 80.43; H, 7.34; N, 12.23. Found: C, 80.37; H, 7.25; N, 12.01.

Photophysical measurements

An Agilent VARIAN Cary 100Conc spectrophotometer and a HORIBA Fluoromax-4P Luminescence spectrophotometer were used to obtain the UV/vis absorption and PL spectra of **CB1**, **CB2**, *nido*-**CB1**, and *nido*-**CB2**, respectively. The solution-phase UV–Vis absorption experiments were performed in degassed THF. The PL measurements were carried out in degassed organic solvents (*n*-hexane, THF, and MeCN) with a 1 cm quartz cuvette (5.0×10^{-5} M) at 298 K. The PL measurements were also performed in THF (5.0×10^{-5} M) at 77 K, and in the film form (5 wt% doped in PMMA) on 1.5 × 1.5 cm quartz plates (thickness = 1 mm) at 298 K. The absolute PL quantum yields (PLQYs) in THF (5.0×10^{-5} M) and in the film form were obtained at 298 K on a Fluoromax-4P spectrophotometer (HORIBA) equipped with a 3.2 inch integrating sphere (FM-sphere, HORIBA). The fluorescence decay lifetimes in THF (5.0×10^{-5} M) and in the film form were measured at 298 K using a time-correlated single-photon counting (TCSPC) spectrometer (FLS920–EDINBURGH instrument at the Central Laboratory of Kangwon National University) equipped with a EPL-372 nm pulsed semiconductor diode laser excitation source and a microchannel plate photomultiplier tube detector (MCP-PMT, 200–850 nm).

X-ray crystallography

Single X-ray quality **CB1** and **CB2** crystals were grown from mixtures of MeOH and *n*-hexane. Each single crystal was coated with Paratone oil and mounted on a glass capillary for X-ray diffractometry measurements. Crystallographic measurements were performed using a Bruker D8QUEST CCD area detector diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structures of **CB1** and **CB2** were assessed using direct methods, and all nonhydrogen atoms were subjected to anisotropic refinement with a full-matrix least-squares method on F^2 using the SHELXTL/PC software package. The X-ray crystallographic data of **CB1** and **CB2** are available in CIF format (CCDC–2045310 and 2045311, respectively), provided free of charge by The Cambridge Crystallographic Data Centre. The hydrogen atoms were placed at their geometrically calculated positions and refined using a riding model on the corresponding carbon atoms with isotropic thermal parameters. Detailed crystallographic data are given in Tables S1 and S2.

Cyclic voltammetry measurement

Cyclic voltammetry (CV) measurements using a WPG100e instrument (WonATech) were carried out in acetonitrile (0.5 mM) using a three-electrode cell configuration (Pt working and counter electrodes and a $Ag/AgNO_3$ (0.1 M in acetonitrile) reference electrode) at room temperature. Tetrabutylammonium hexafluorophosphate (n-Bu_4PF_6, 0.1 M in acetonitrile) was used as a supporting electrolyte after nitrogen bubbling for 1 h to remove oxygen. The oxidative potentials were observed at a scan rate of 100 mV/s and measured with reference to the ferrocene/ferrocenium (Fc/Fc^+) redox couple.

Computational studies

The geometries of the *closo*- and *nido*-*o*-carboranyl compounds in their ground (S_0) and first-excited (S_1) states in THF were optimized at the B3LYP/6-31G(d)[1] level of theory. The vertical excitation energies in the optimized S_0 and S_1 state geometries were calculated using the time-dependent density functional theory (TD-DFT) method[2] at the same level of theory. Solvent effects were evaluated using the self-consistent reaction field (SCRF) method based on the conductor-like polarizable continuum model (CPCM) with THF as the solvent.[3,4] All geometry optimizations were performed using the Gaussian 16 program.[5] The percent contribution (%) of a group in a molecule to each molecular orbital was calculated using the GaussSum 3.0 software program.[6] Visualizations were prepared using GaussView 6.[7]

Reference

1. J. S. Binkley, J. A. People and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.
2. E. Runge and E. K. U. Gross, *Phys. Rev. Lett.*, 1984, **52**, 997.
3. M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669–681.
4. V. Barone and M. Cossi, *J. Phys. Chem. A*., 1998, **102**, 1995.
5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16 Revision B.01*, Gaussian. Inc., Wallingford, CT, 2016.
6. N. M. O'Boyle, A. L. Tenderholt and K. M. Langner, *J. Comp. Chem*., 2008, **29**, 839.
7. R. Dennington, T. A. Keith and J. M. Millam, *GaussView 6*, Semichem Inc., Shawnee Mission, KS, 2016.

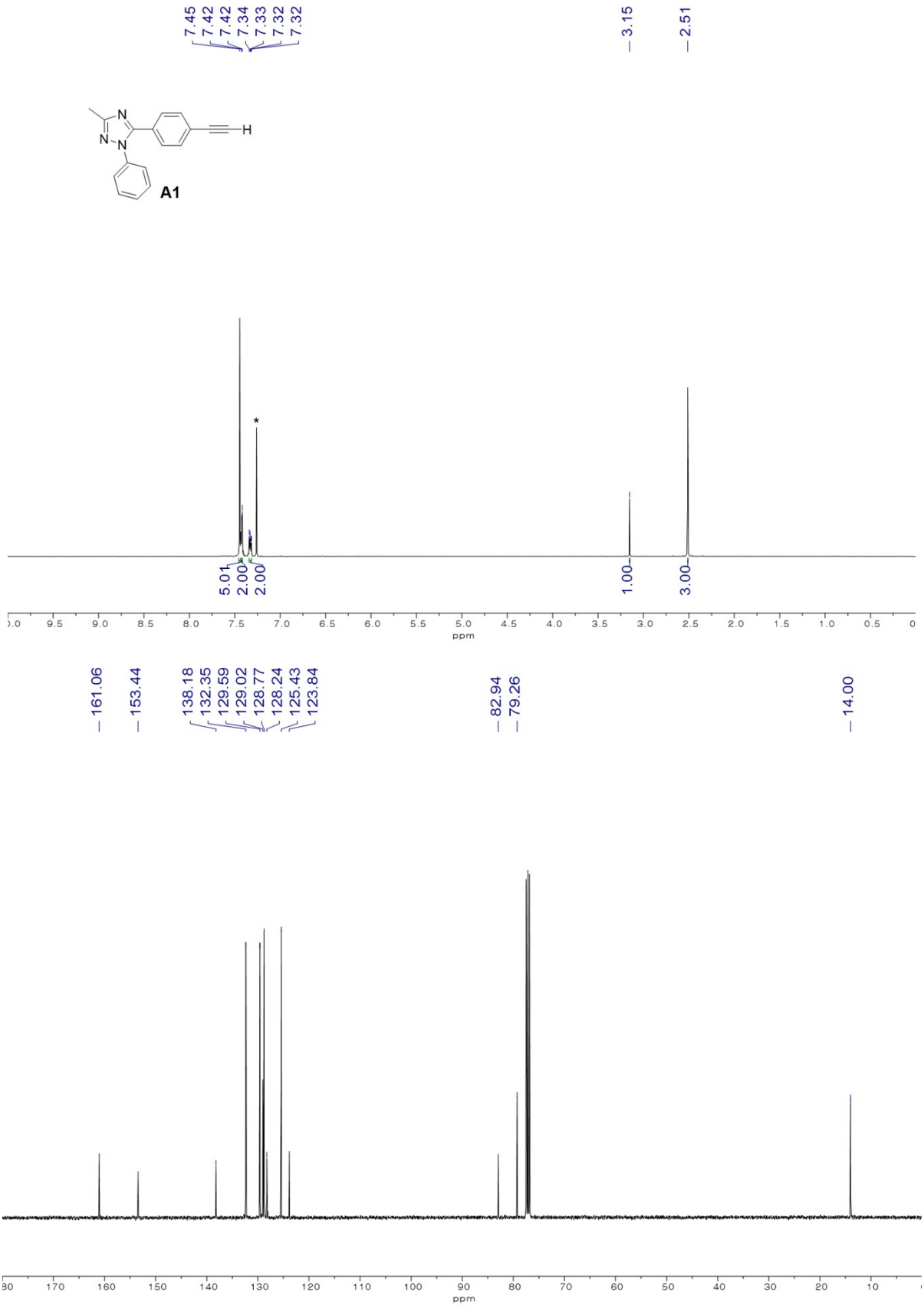


Fig. S1 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **A1** in $CDCl_3$ (* from residual $CHCl_3$ in $CDCl_3$).

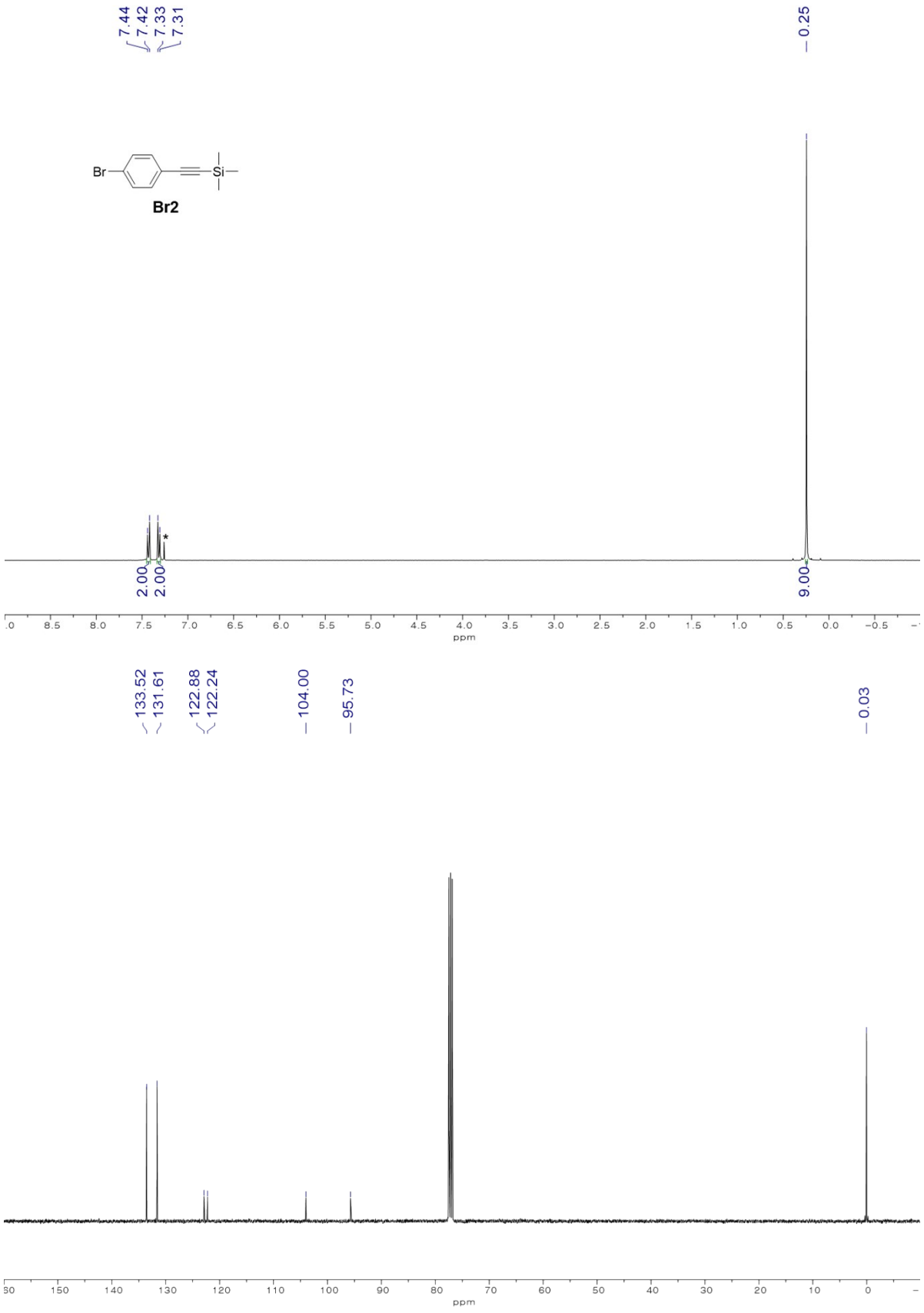


Fig. S2 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **Br2** in $CDCl_3$ (* from residual $CHCl_3$ in $CDCl_3$).

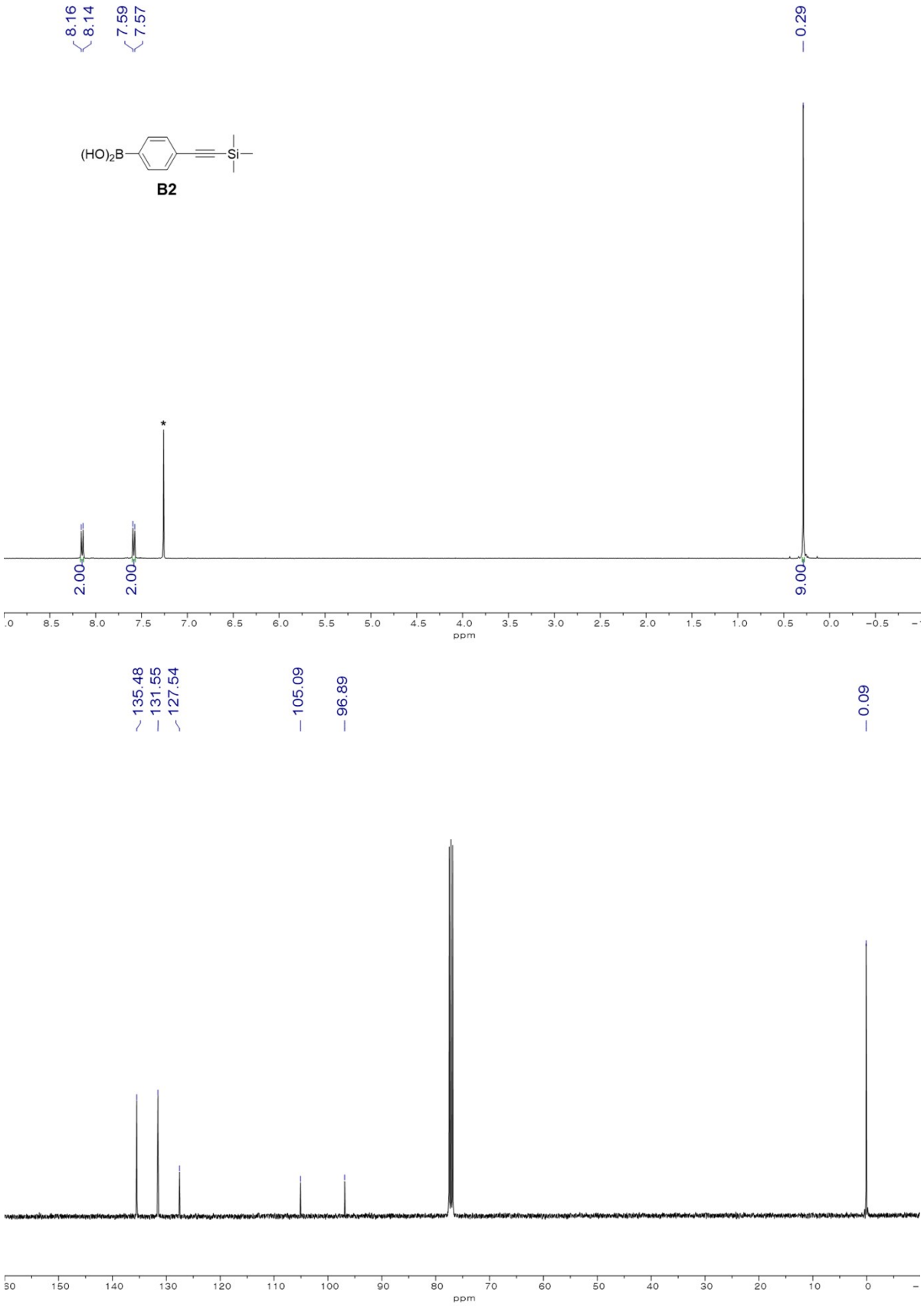


Fig. S3 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **B2** in $CDCl_3$ (* from residual $CHCl_3$ in $CDCl_3$).

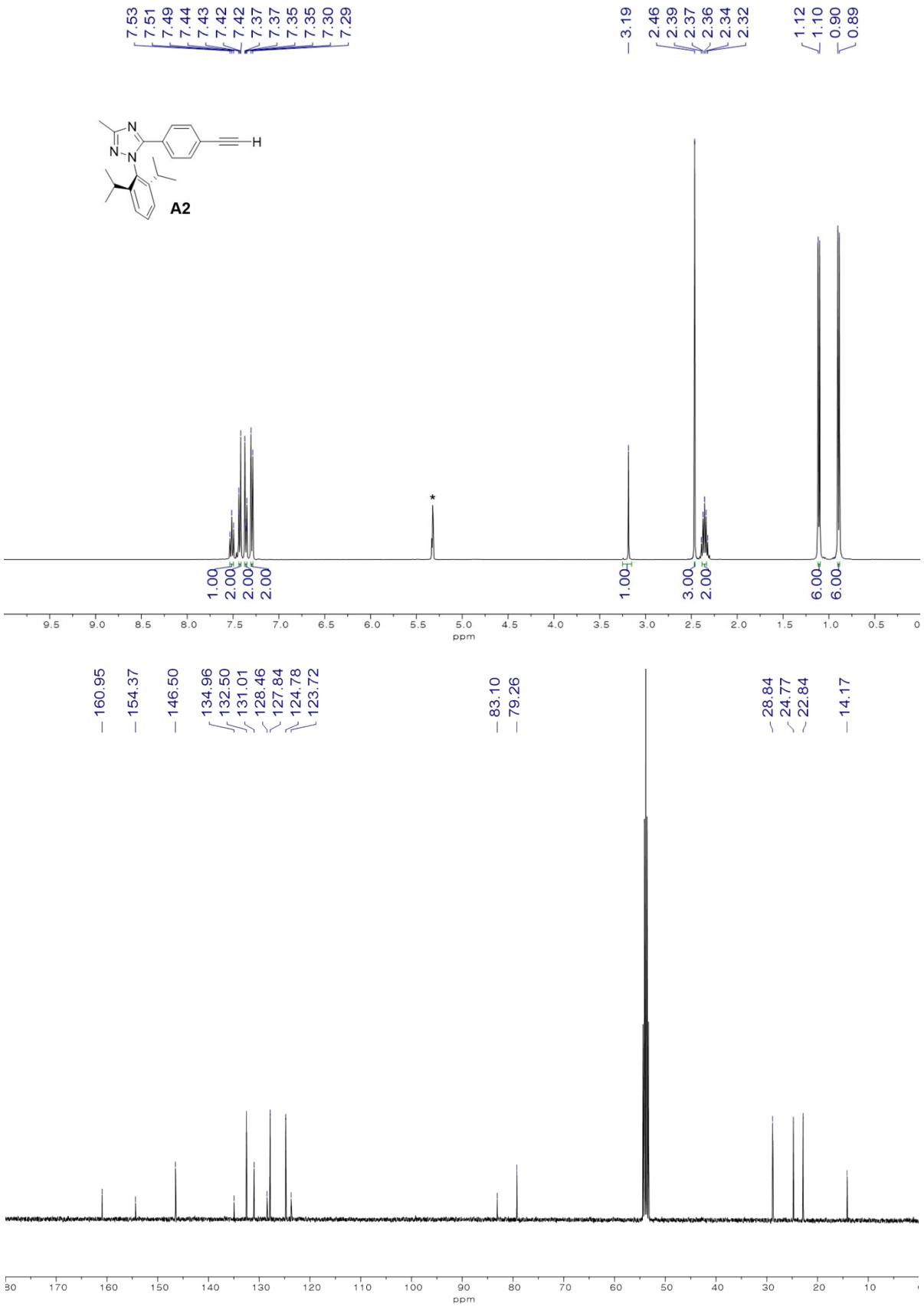


Fig. S4 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **A2** in CD_2Cl_2 (* from residual CH_2Cl_2 in CD_2Cl_2).

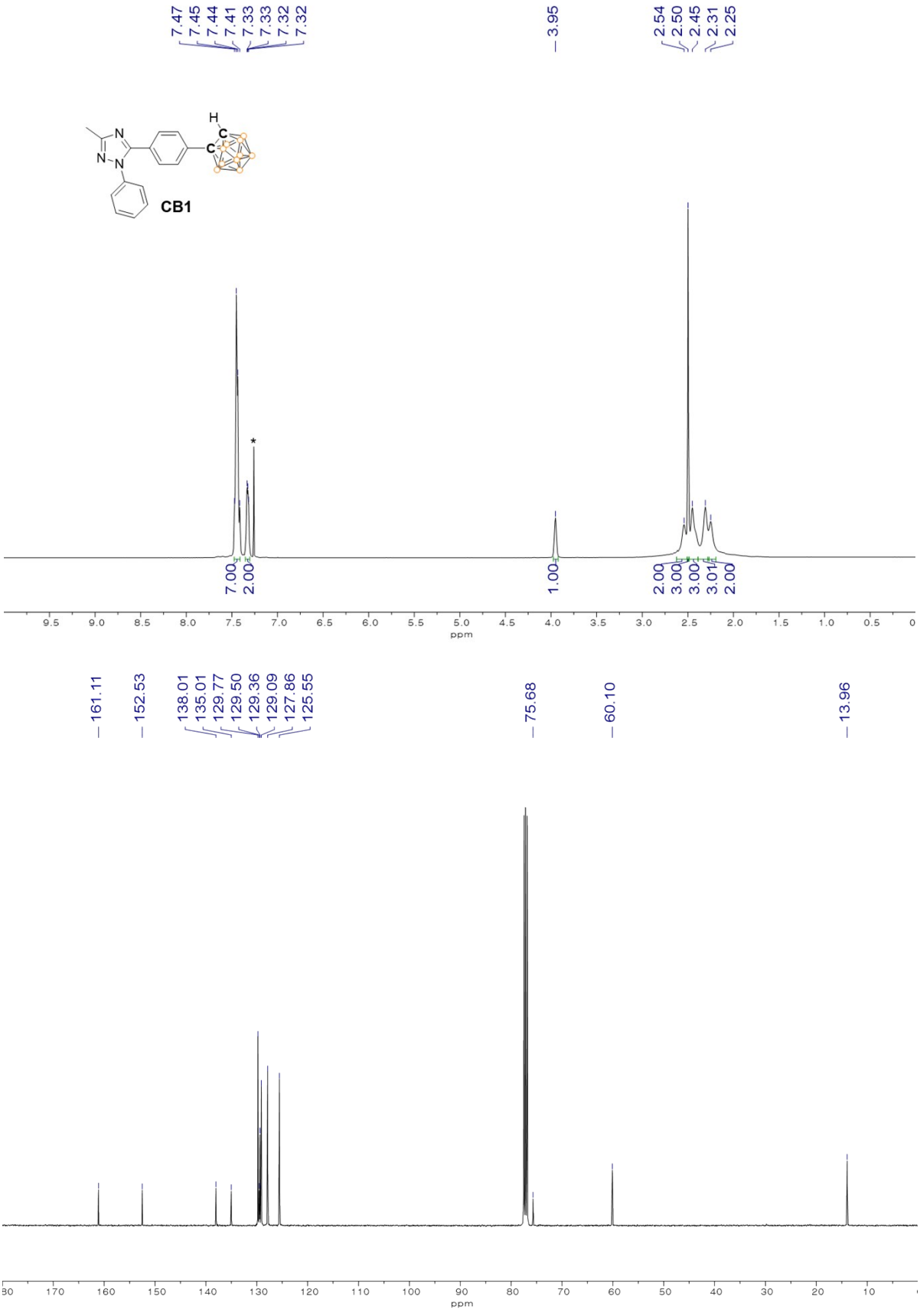


Fig. S5 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of **CB1** in $CDCl_3$ (* from residual $CHCl_3$ in $CDCl_3$).

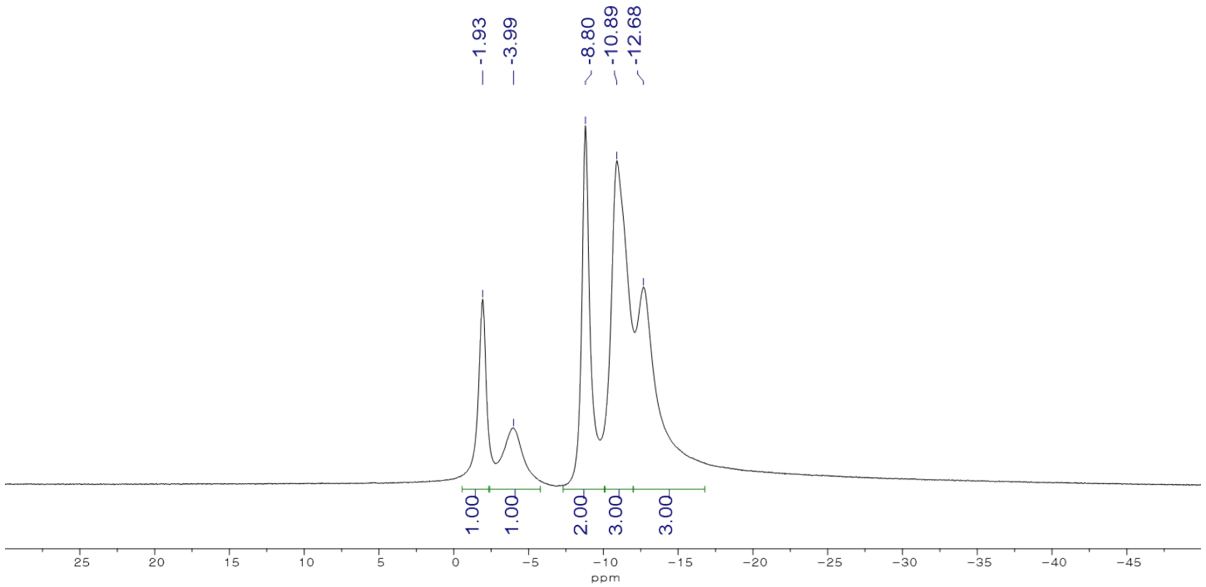


Fig. S6 $^{11}B\{^{1}H\}$ NMR spectra of **CB1** in $CDCl_3$.

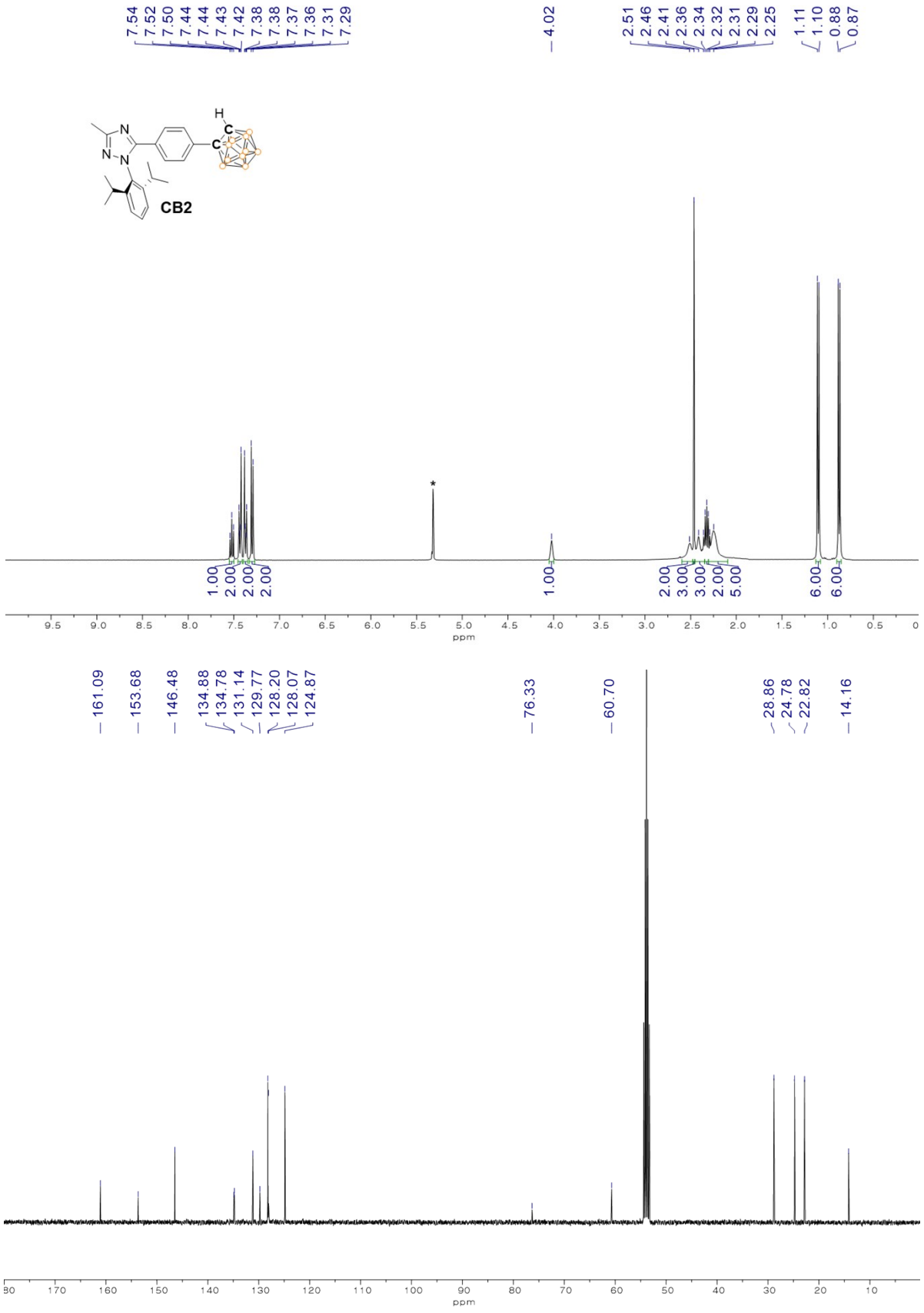


Fig. S7 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of **CB2** in CD_2Cl_2 (* from residual CH_2Cl_2 in CD_2Cl_2).

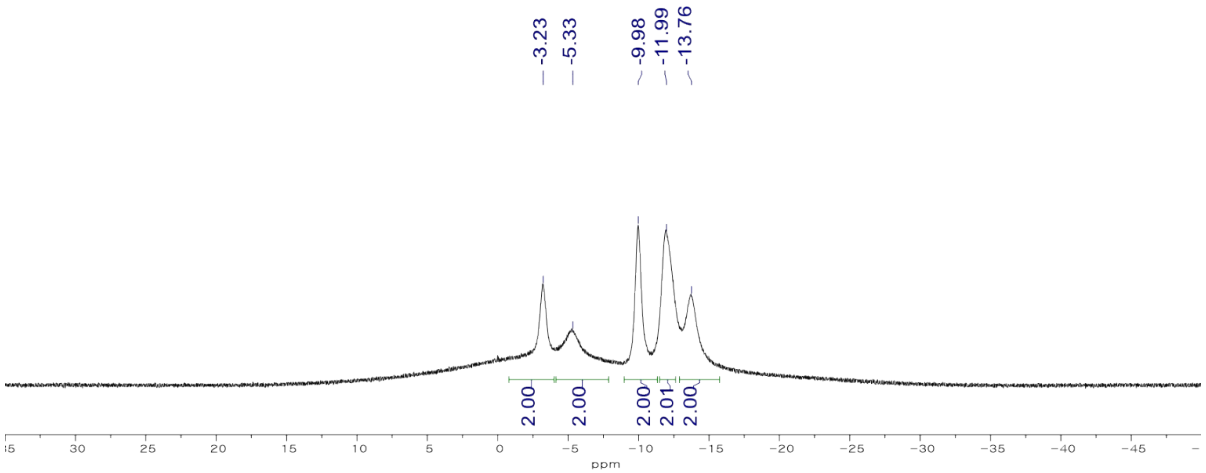


Fig. S8 $^{11}B\{^{1}H\}$ NMR spectra of **CB2** in CD_2Cl_2.

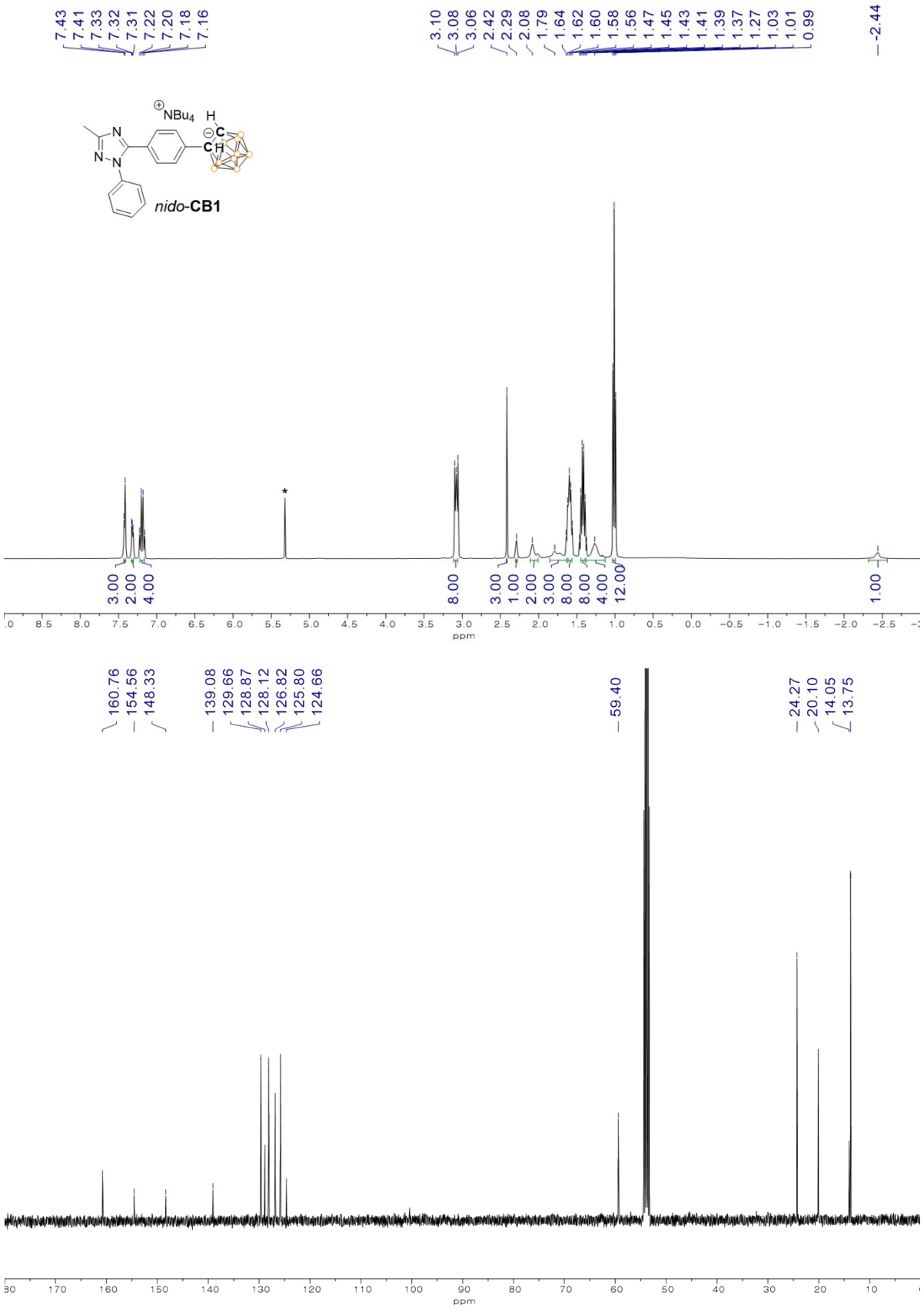


Fig. S9 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of *nido*-**CB1** in CD_2Cl_2 (* from residual CH_2Cl_2 in CD_2Cl_2).

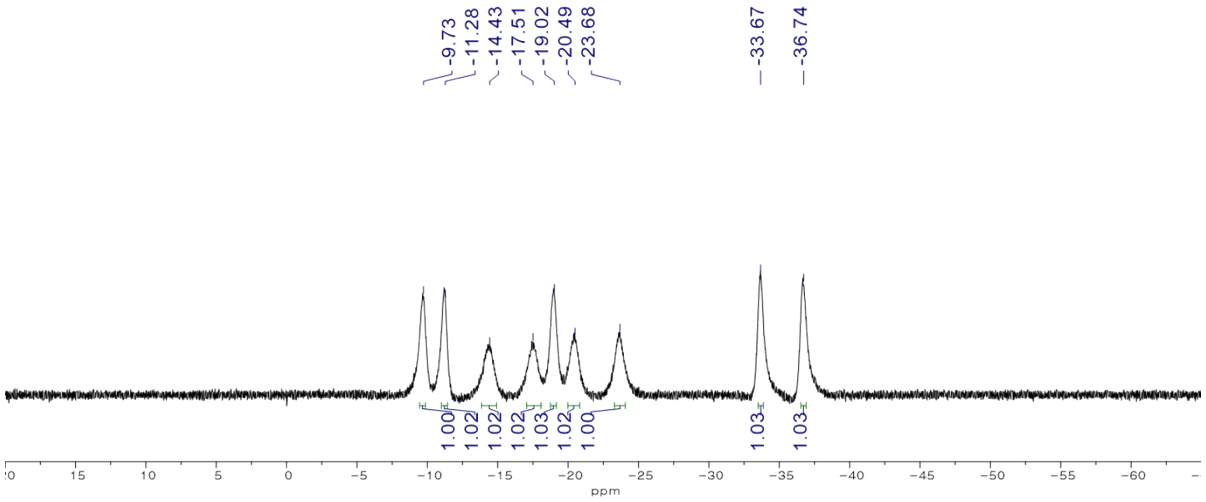


Fig. S10 $^{11}B\{^{1}H\}$ NMR spectra of *nido*-**CB1** in CD_2Cl_2.

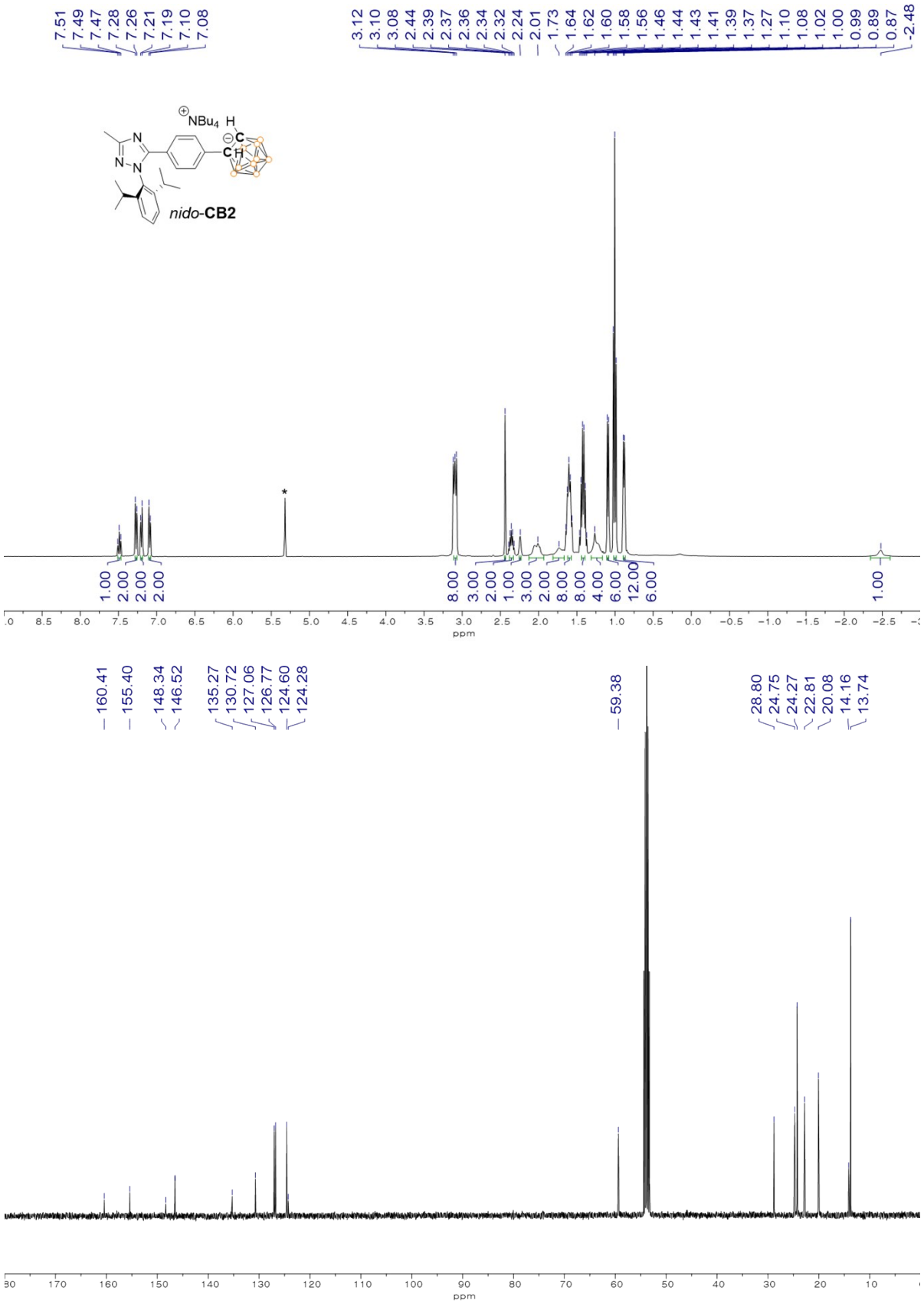


Fig. S11 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of *nido*-**CB2** in CD_2Cl_2 (* from residual CH_2Cl_2 in CD_2Cl_2).

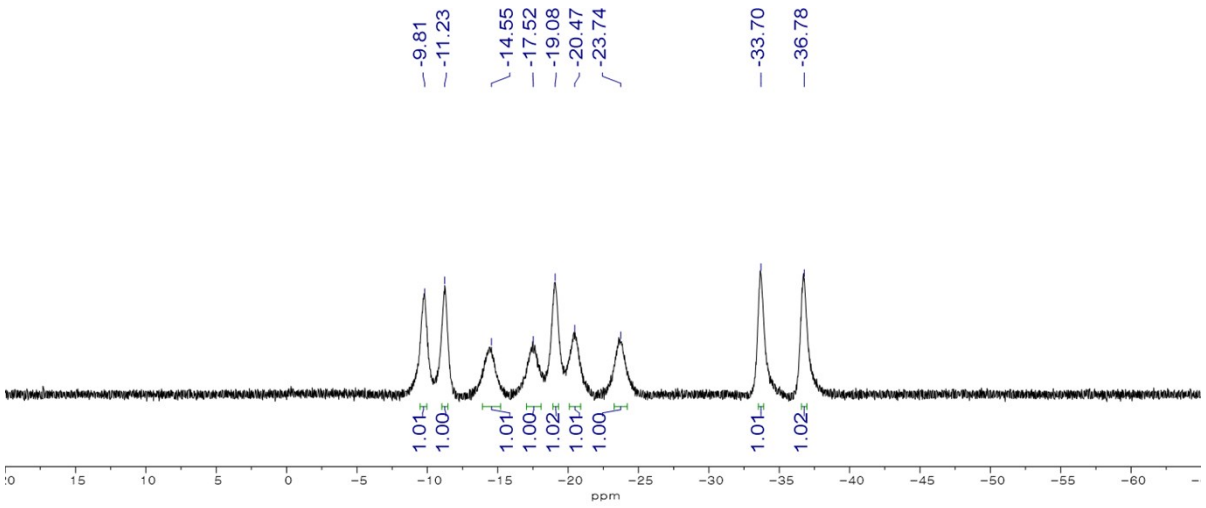


Fig. S12 $^{11}B\{^{1}H\}$ NMR spectra of *nido*-**CB2** in CD_2Cl_2.

Table S1 Crystallographic data and parameters for **CB1** and **CB2**.

Compound	(**CB1**)$_2$·CH_3OH	**CB2**
Formula	$(C_{17}H_{23}B_{10}N_3)_2$·$CH_3OH$	$C_{23}H_{35}B_{10}N_3$
Formula weight	787.01	461.64
Crystal system	Triclinic	Monoclinic
Space group	P_{-1}	C2/c
a (Å)	10.4481(4)	25.430(5)
b (Å)	14.8507(6)	14.506(3)
c (Å)	15.1867(6)	16.515(3)
α (°)	93.0616(14)	90
β (°)	109.8435(13)	100.40(3)
γ (°)	90.8587(13)	90
V (Å^3)	2211.94(15)	5992(2)
Z	2	8
ρ_{calc}(g cm^{-3})	1.182	1.023
μ (mm^{-1})	0.065	0.055
F(000)	820	1952
T (K)	173(2)	296(2)
Scan mode	*multi-scan*	*multi-scan*
hkl range	$-13 < h < 13$, $-19 < k < 19$, $-19 < l < 19$	$-32 < h < 32$, $-18 < k < 18$, $-21 < l < 21$
Measd reflns	127691	29568
Unique reflns [R_{int}]	10132 [0.0529]	6880 [0.0820]
Reflns used for refinement	10132	6880
Refined parameters	571	361
R_1[a] (I > 2σ(I))	0.0540	0.0749
wR_2[b] all data	0.1430	0.2531
GOF on F^2	1.047	1.051
ρ_{fin} (max/min) (e Å^{-3})	0.298, −0.258	0.255, −0.159

[a] $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR_2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (°) for **CB1** and **CB2**.

Compound	**CB1**	**CB2**
	length (Å)	
C1–H1	0.98(2)	0.940
C1–C2	1.642(2)	1.622(3)
C2–C3	1.5068(19)	1.492(3)
C9–N1	1.3467(19)	1.352(2)
C9–N4	1.3262(19)	1.328(3)
N1–N2	1.3749(17)	1.369(2)
C10–N2	1.314(2)	1.329(3)
C10–N4	1.3632(19)	1.351(3)
	angles (°)	
H1–C1–C2	114.0(12)	117.98
C1–C2–C3	118.16(12)	119.84(15)
C9–N1–N2	109.77(12)	109.57(15)
N1–N2–C10	102.61(12)	102.54(15)
N2–C10–N4	114.42(13)	114.5(2)
C9–N4–C10	103.86(13)	103.94(16)
N1–C9–N4	109.33(13)	09.49(17)

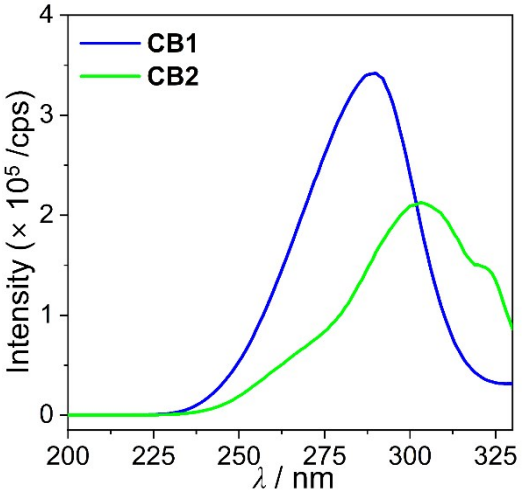


Fig. S13 Excitation graphs of **CB1** and **CB2** in THF (5.0×10^{-5} M).

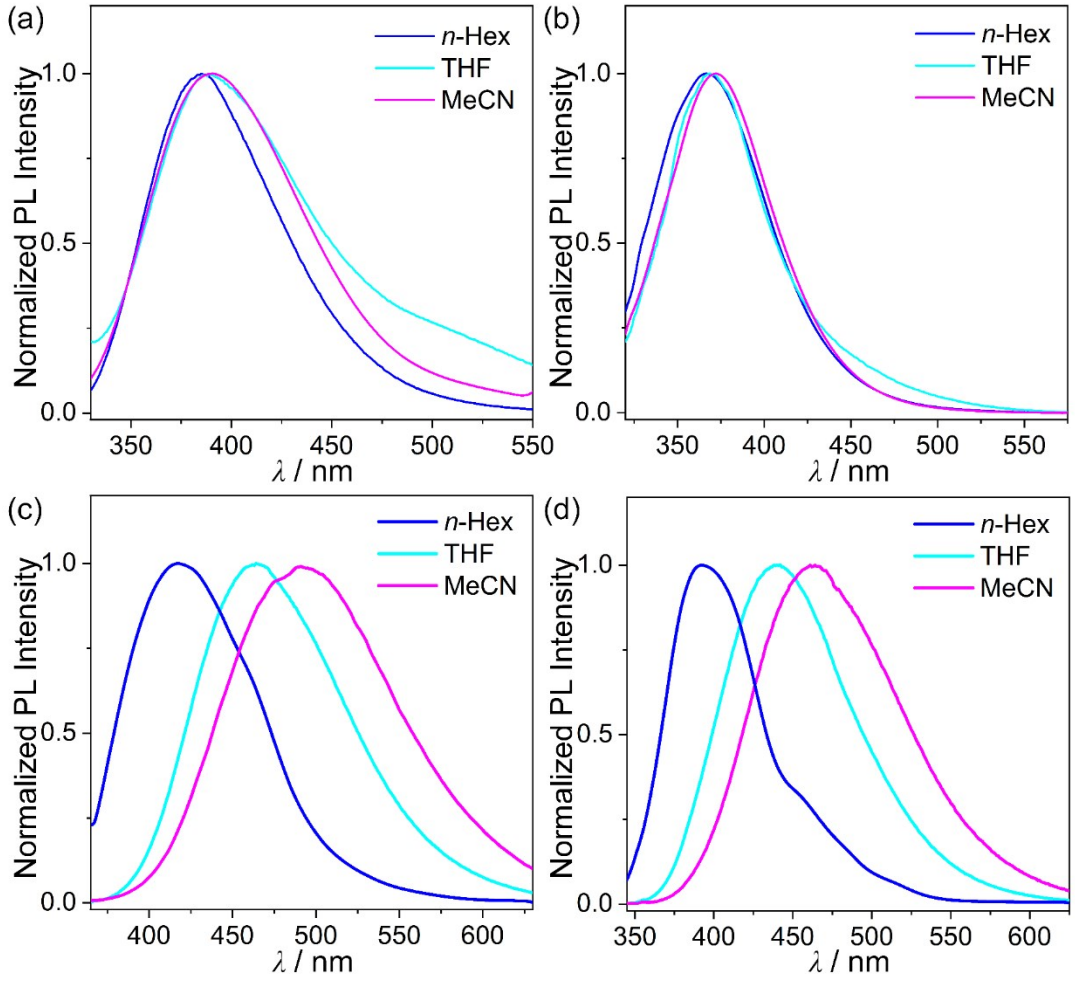


Fig. S14 PL spectra of (a) **CB1** (λ_{ex} = 290 nm), (b) **CB2** (λ_{ex} = 303 nm), (b) *nido*-**CB1** (λ_{ex} = 290 nm), and (d) *nido*-**CB2** (λ_{ex} = 303 nm) in various organic solvents (*n*-hexane (*n*-Hex), tetrahydrofuran (THF), and acetonitrile (MeCN), 5.0×10^{-5} M).

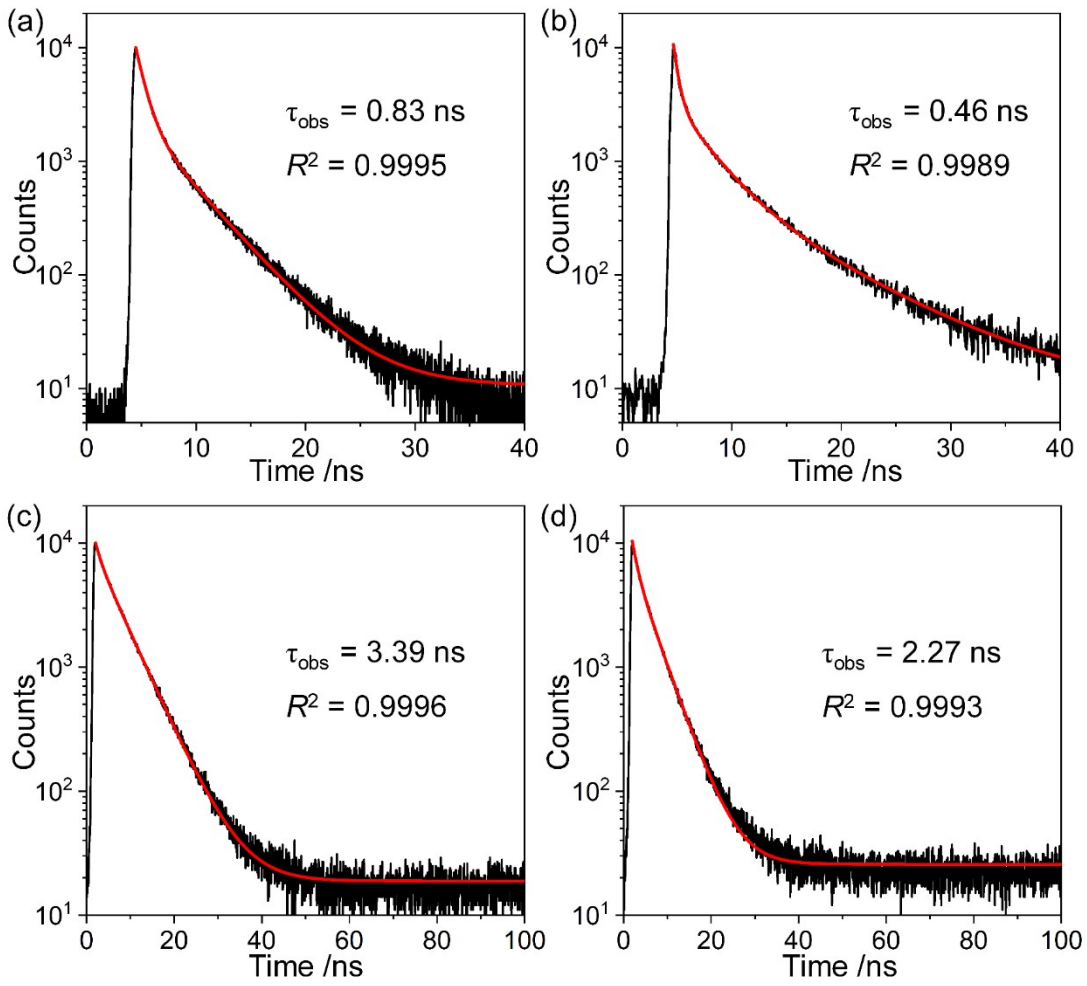


Fig. S15 Emission decay curves for (a) **CB1**, (b) **CB2**, (c) *nido*-**CB1**, and (d) *nido*-**TCB1** in THF (5.0×10^{-5} M) detected at each maximum emissive point at 298 K. Each red-line is its exponential fitting curve.

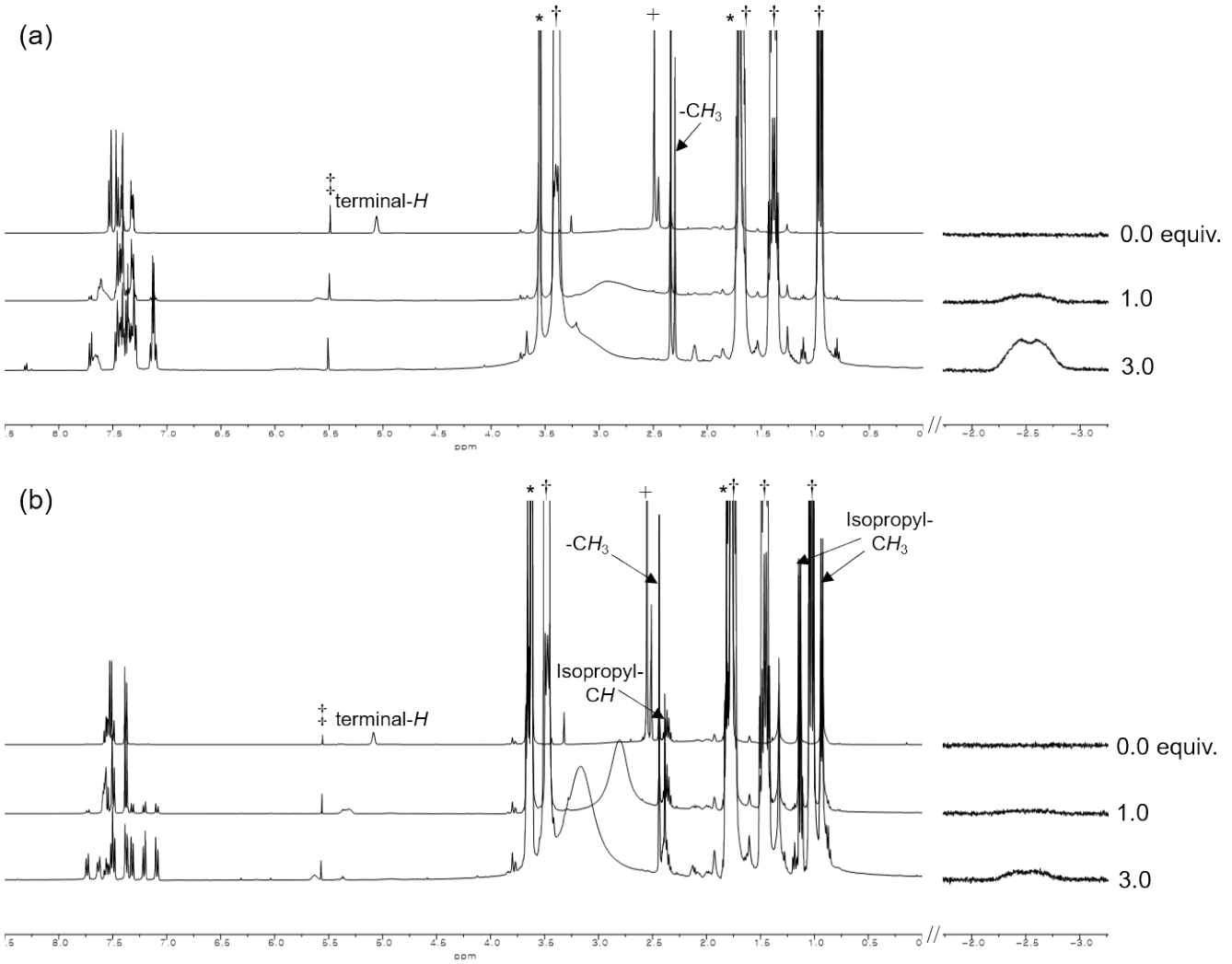


Fig. S16 ^{1}H NMR spectra of (a) **CB1** and (b) **CB2** with 3.0 equiv. of TBAF in THF-d^8 (∗ from residual THF in THF-d^8, † from *n*-butyl group of excess TBAF, ‡ from residual CH_2Cl_2, and + from residual H_2O).

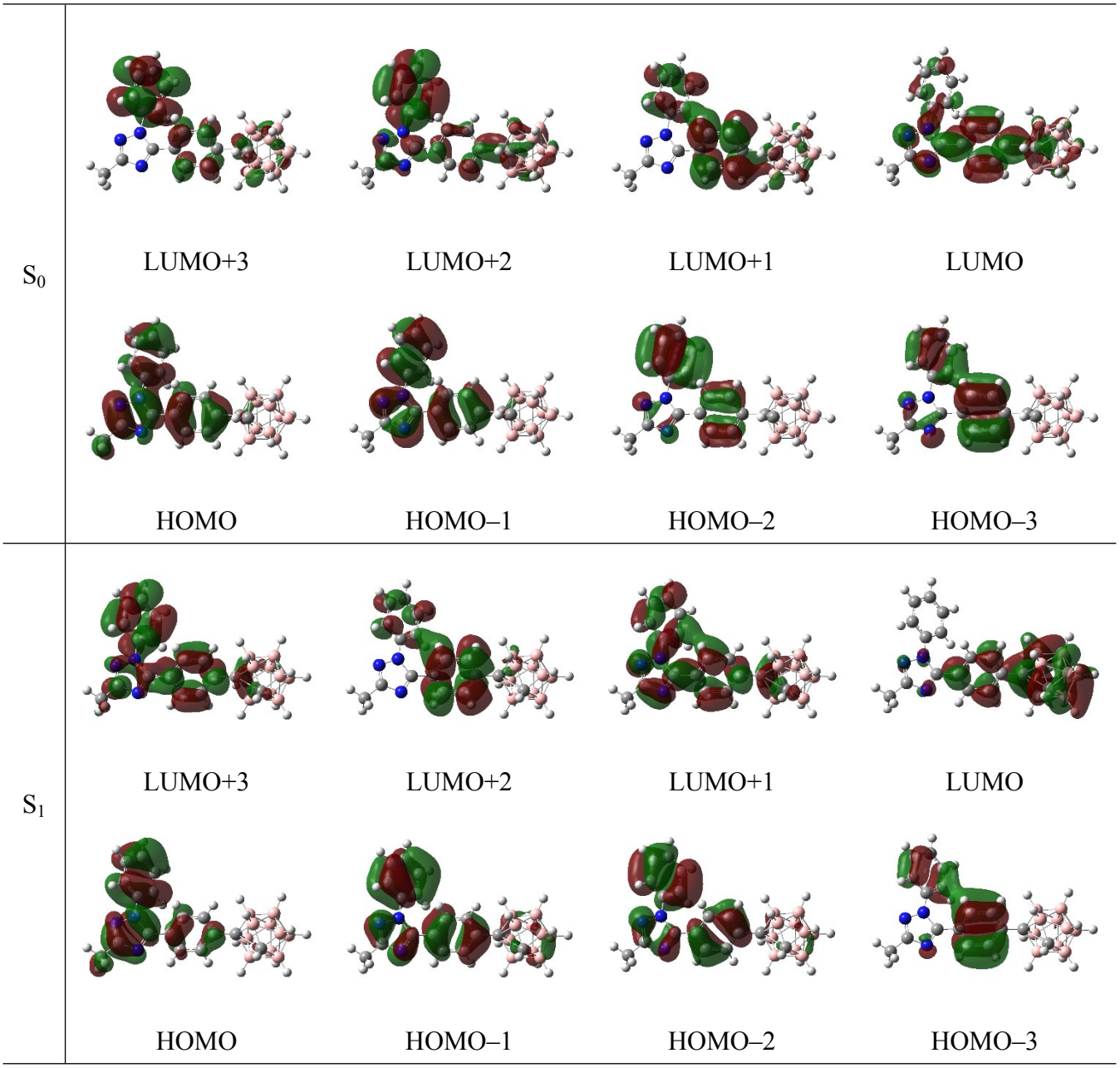


Fig. S17 The selected frontier orbitals of **CB1** from B3LYP calculations (Isovalue = 0.02 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S3 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **CB1** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	289.88	0.4424	HOMO → LUMO (97.1%)
2	260.11	0.0070	HOMO−3 → LUMO (17.0%)
			HOMO−2 → LUMO (44.6%)
			HOMO → LUMO+1 (32.8%)
3	254.17	0.2196	HOMO−1 → LUMO (81.3%)
4	248.28	0.0971	HOMO−3 → LUMO (39.0%)
			HOMO−2 → LUMO (37.2%)
			HOMO−1 → LUMO (5.8%)
			S_1
1	495.78	0.2335	HOMO → LUMO (99.6%)
2	402.50	0.4560	HOMO → LUMO+1 (96.2%)
3	392.24	0.1178	HOMO−3 → LUMO (8.72%)
			HOMO−2 → LUMO (87.7%)
4	369.91	0.0078	HOMO−4 → LUMO (25.0%)
			HOMO−3 → LUMO (59.5%)
			HOMO → LUMO+1 (11.5%)

Table S4 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **CB1** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

	E (eV)	*N*-phenyl	triazole +bridged phenyl	carborane
		S_0		
LUMO+3	−0.36	76.9	19.6	3.5
LUMO+2	−0.62	76.6	17.1	6.2
LUMO+1	−0.78	22.8	70.9	6.3
LUMO	−1.67	6.2	81.7	12.1
HOMO	−6.51	20.0	77.7	2.3
HOMO−1	−7.09	46.1	52.1	1.8
HOMO−2	−7.19	66.4	33.3	0.2
HOMO−3	−7.46	23.4	76.4	0.2
		S_1		
LUMO+3	−0.48	48.8	45.5	5.7
LUMO+2	−0.83	10.6	84.8	4.6
LUMO+1	−1.54	23.5	66.8	9.7
LUMO	−3.13	0.4	19.0	80.6
HOMO	−6.52	45.5	52.9	1.6
HOMO−1	−7.08	38.1	55.2	6.7
HOMO−2	−7.25	68.8	28.6	2.6
HOMO−3	−7.62	12.5	82.7	4.8

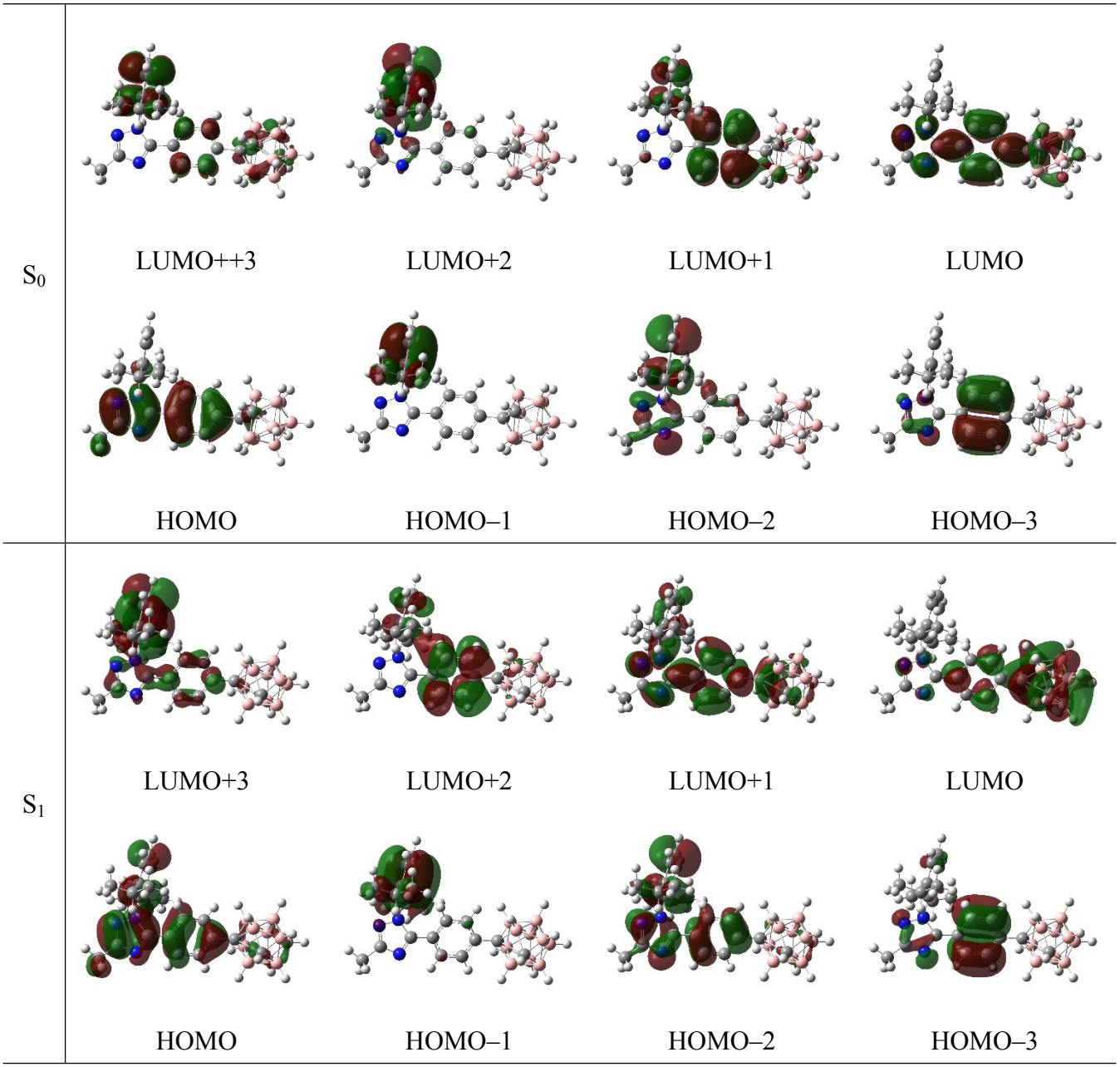


Fig. S18 The selected frontier orbitals of **CB2** from B3LYP calculations (Isovalue = 0.02 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S5 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **CB2** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	280.15	0.6336	HOMO → LUMO (92.5%)
2	278.27	0.0132	HOMO−1 → LUMO (98.1%)
3	270.78	0.0851	HOMO−2 → LUMO (90.8%)
4	259.35	0.0040	HOMO−3 → LUMO (58.7%)
			HOMO → LUMO+1 (36.0%)
			S_1
1	483.22	0.4667	HOMO → LUMO (99.4%)
2	424.89	0.0035	HOMO−1 → LUMO (99.0%)
3	380.15	0.2315	HOMO → LUMO+1 (95.2%)
4	345.33	0.0108	HOMO−4 → LUMO (12.8%)
			HOMO−2 → LUMO (84.5%)

Table S6 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **CB2** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

	E (eV)	*N*-phenyl	triazole +bridged phenyl	carborane
		S_0		
LUMO+3	−0.32	82.6	15.4	2.0
LUMO+2	−0.50	93.5	6.1	0.4
LUMO+1	−0.74	18.5	75.7	5.8
LUMO	−1.70	1.0	86.7	12.3
HOMO	−6.57	1.9	94.8	3.3
HOMO−1	−6.74	99.0	1.0	0.0
HOMO−2	−6.98	75.9	24.0	0.1
HOMO−3	−7.38	1.6	97.3	1.1
		S_1		
LUMO+3	−0.49	83.8	14.5	1.7
LUMO+2	−0.75	16.6	79.0	4.4
LUMO+1	−1.41	8.7	79.7	11.6
LUMO	−3.03	0.3	17.3	82.4
HOMO	−6.35	18.8	76.5	4.7
HOMO−1	−6.65	96.2	3.7	0.1
HOMO−2	−7.01	59.9	37.0	3.1
HOMO−3	−7.45	3.8	92.7	3.5

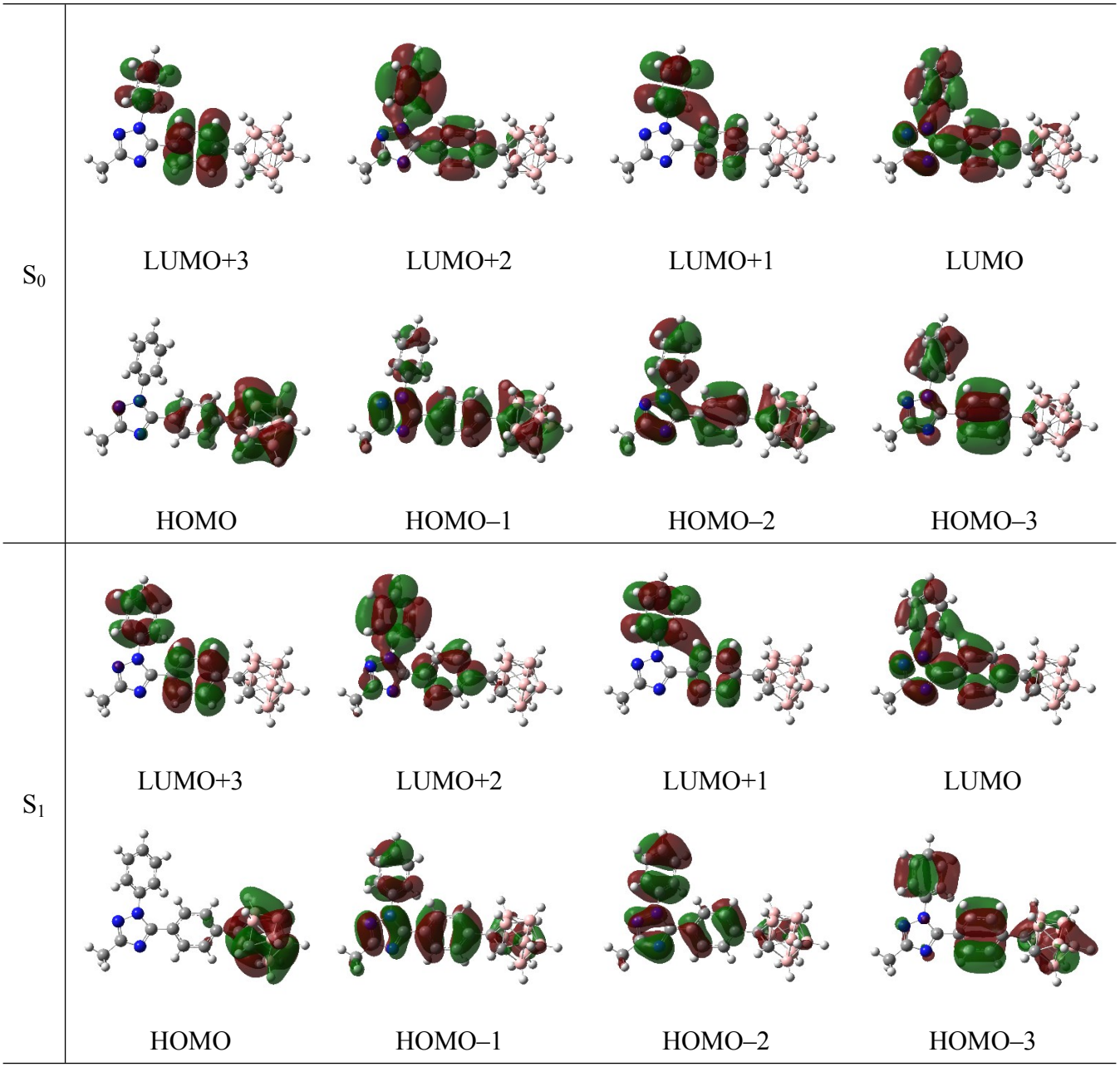


Fig. S19 The selected frontier orbitals of *nido*-**CB1** from B3LYP calculations (Isovalue = 0.02 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S7 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for *nido*-**CB1** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	325.61	0.3551	HOMO → LUMO (98.0%)
2	281.91	0.1955	HOMO−1 → LUMO (92.4%)
3	277.86	0.0336	HOMO → LUMO+1 (80.0%)
			HOMO → LUMO (12.5%)
4	267.61	0.1150	HOMO → LUMO+1 (93.4%)
			S_1
1	480.22	0.3728	HOMO → LUMO (99.1%)
2	361.55	0.0562	HOMO−1 → LUMO (97.2%)
3	336.06	0.0016	HOMO → LUMO+1 (69.5%)
			HOMO → LUMO+2 (11.2%)
			HOMO → LUMO+3 (18.5%)
4	319.56	0.0010	HOMO → LUMO+1 (11.5%)
			HOMO → LUMO+2 (86.4%)

Table S8 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of *nido*-**CB1** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

	E (eV)	*N*-phenyl	triazole +bridged phenyl	carborane
		S_0		
LUMO+3	0.21	3.1	94.7	2.2
LUMO+2	−0.10	36.8	59.7	3.5
LUMO+1	−0.22	96.5	3.4	0.1
LUMO	−0.86	57.0	41.6	1.4
HOMO	−5.17	0.1	4.1	95.8
HOMO−1	−5.81	1.2	47.3	51.5
HOMO−2	−6.46	0.3	5.2	94.5
HOMO−3	−6.65	2.6	23.7	73.7
		S_1		
LUMO+3	0.22	4.8	93.1	2.1
LUMO+2	−0.03	63.3	35.0	1.7
LUMO+1	−0.15	95.5	4.5	0.0
LUMO	−1.62	26.5	71.5	2.0
HOMO	−4.55	0.0	1.3	98.7
HOMO−1	−5.73	5.2	67.4	27.4
HOMO−2	−6.41	0.5	8.2	91.3
HOMO−3	−6.70	3.1	12.2	84.7

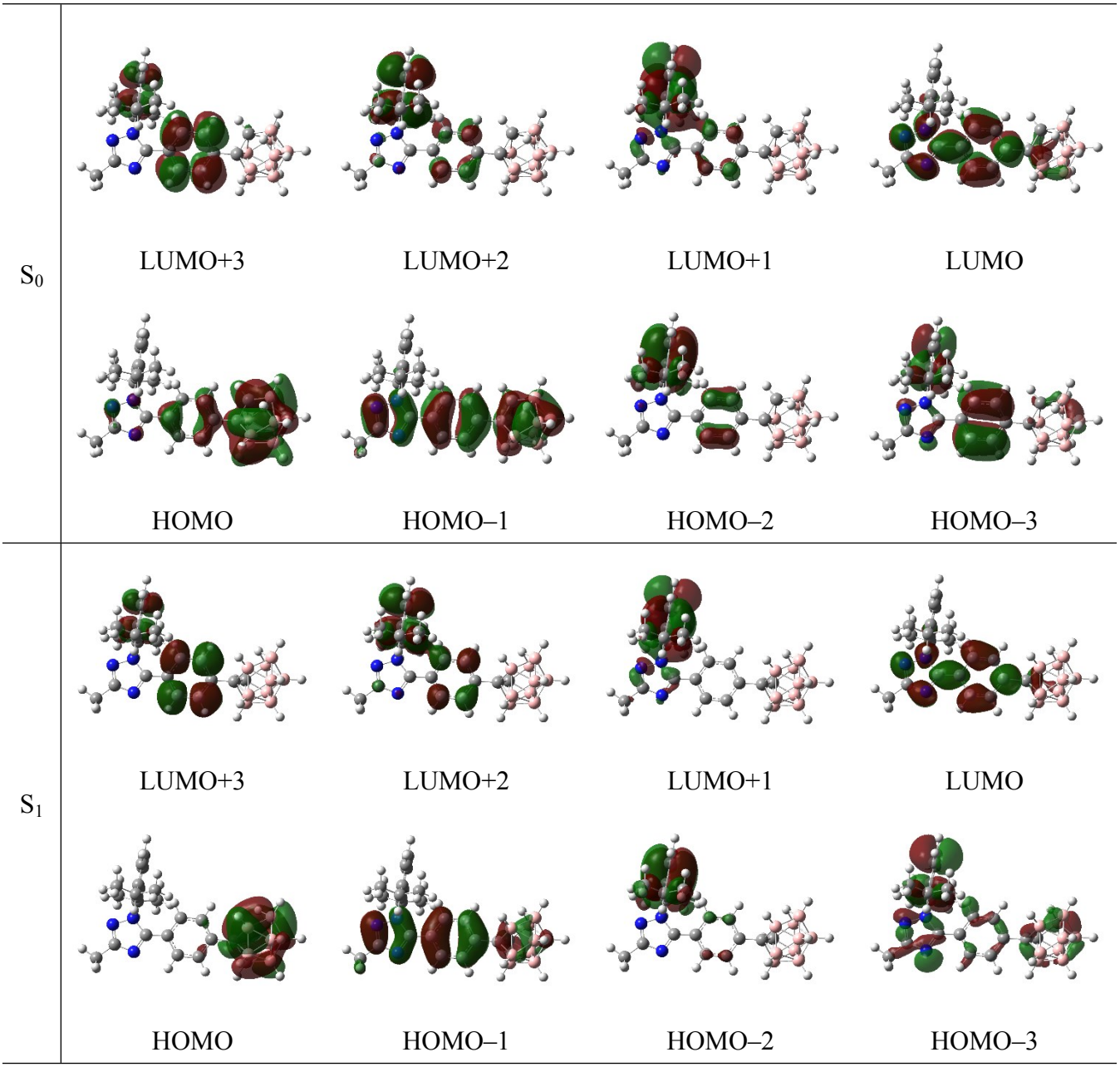


Fig. S20 The selected frontier orbitals of *nido*-**CB2** from B3LYP calculations (Isovalue = 0.02 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S9 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for *nido*-**CB2** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

state	λ_{calc} (/nm)	f_{calc}	Major contribution
		S_0	
1	321.26	0.2538	HOMO → LUMO (99.0%)
2	276.62	0.0137	HOMO → LUMO+1 (66.1%)
			HOMO → LUMO+2 (12.6%)
			HOMO → LUMO+3 (12.3%)
3	272.98	0.6141	HOMO−1 → LUMO (87.3%)
			HOMO → LUMO+2 (8.1%)
4	270.36	0.0783	HOMO−1 → LUMO (8.0%)
			HOMO → LUMO+1 (24.9%)
			HOMO → LUMO+2 (54.9%)
			HOMO → LUMO+3 (6.6%)
		S_1	
1	476.20	0.1923	HOMO → LUMO (99.3%)
2	384.22	0.0112	HOMO → LUMO+1 (72.8%)
			HOMO → LUMO+2 (22.0%)
3	338.04	0.0001	HOMO → LUMO+2 (96.1%)
4	328.98	0.0153	HOMO → LUMO+2 (23.4%)
			HOMO → LUMO+3 (76.2%)

Table S10 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of *nido*-**CB2** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

	E (eV)	*N*-phenyl	triazole +bridged phenyl	carborane
		S_0		
LUMO+3	0.20	3.0	94.9	2.1
LUMO+2	−0.15	54.5	43.3	2.2
LUMO+1	−0.24	65.5	33.1	1.4
LUMO	−0.77	74.4	24.6	1.0
HOMO	−5.17	0.0	4.6	95.4
HOMO−1	−5.78	0.3	49.6	50.1
HOMO−2	−6.47	0.0	5.0	95.0
HOMO−3	−6.60	0.3	27.2	72.5
		S_1		
LUMO+3	0.20	3.9	94.2	1.9
LUMO+2	−0.16	96.6	3.3	0.1
LUMO+1	−0.24	94.8	5.2	0.0
LUMO	−1.25	2.4	94.4	3.2
HOMO	−4.35	0.0	1.0	99.0
HOMO−1	−5.76	0.5	75.8	23.7
HOMO−2	−6.45	0.0	5.7	94.3
HOMO−3	−6.66	0.1	11.4	88.5

Table S11 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **CB1** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	-3.878242	-0.320041	-1.354704
C	-2.980470	-0.112585	0.031638
C	-1.492558	-0.384126	-0.002242
C	-0.596256	0.470491	-0.658788
H	-0.954761	1.347057	-1.181884
C	0.771253	0.209503	-0.658826
H	1.432826	0.880049	-1.194138
C	1.284700	-0.912036	0.007678
C	0.388202	-1.773527	0.658014
H	0.771035	-2.651811	1.164859
C	-0.976741	-1.512449	0.654567
H	-1.641097	-2.193234	1.172290
C	2.714449	-1.261565	0.001791
C	4.522023	-2.371058	-0.076501
C	5.465486	-3.528159	-0.123057
H	6.496524	-3.173855	-0.169298
H	5.267260	-4.154064	-0.998762
H	5.347571	-4.158468	0.763800
C	3.831345	1.028013	0.055133
C	3.185479	1.686840	1.104590
H	2.636458	1.117671	1.846566
C	3.264949	3.076958	1.188878
H	2.763241	3.592279	2.001721
C	3.998651	3.799300	0.245372
H	4.062816	4.880326	0.319077
C	4.655515	3.128641	-0.789215
H	5.230911	3.685544	-1.521928
C	4.572095	1.740432	-0.891472
H	5.074839	1.205207	-1.689078
N	3.167112	-2.512005	-0.011057
N	4.938166	-1.111231	-0.099062
N	3.772131	-0.397498	-0.042543
B	-3.932886	-0.564287	1.383580
H	-3.378454	-1.034291	2.315304
B	-3.676474	1.147607	0.968363
H	-2.940396	1.812756	1.611814
B	-5.301627	0.566007	1.402550
H	-5.802126	0.888274	2.429279
B	-5.503050	-1.076736	0.725801
H	-6.141778	-1.924190	1.255305
B	-4.018744	-1.498888	-0.126150
H	-3.506337	-2.545443	-0.300665
B	-3.608864	1.275355	-0.799824
H	-2.874262	1.968417	-1.403343
B	-5.091952	1.708105	0.046734
H	-5.437980	2.841796	0.085920
B	-6.229332	0.334982	-0.099785
H	-7.403318	0.494974	-0.163424
B	-5.430738	-0.939205	-1.045824
H	-5.898778	-1.684345	-1.836030
B	-5.175141	0.768300	-1.462882
H	-5.472356	1.174911	-2.532906
H	-3.308930	-0.618420	-2.225803

Table S12 Cartesian coordinates of the first excited state (S_1) fully optimized geometry of **CB1** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	-4.539895	-1.101781	-1.238576
C	-2.884506	-0.074274	0.106911
C	-1.447779	-0.383535	0.083868
C	-0.569116	0.311986	-0.772831
H	-0.963957	1.069069	-1.440058
C	0.791540	0.040271	-0.783752
H	1.432571	0.572325	-1.479023
C	1.328430	-0.945321	0.069570
C	0.457447	-1.668314	0.906492
H	0.860070	-2.437591	1.556706
C	-0.898948	-1.383441	0.919416
H	-1.551531	-1.934803	1.586273
C	2.744645	-1.293454	0.054414
C	4.599272	-2.337949	-0.100371
C	5.542658	-3.479182	-0.155231
H	6.567334	-3.129073	-0.277668
H	5.278387	-4.139066	-0.988293
H	5.462980	-4.073027	0.761087
C	3.879739	1.009233	0.019250
C	2.888351	1.739915	0.735751
H	2.094370	1.219098	1.249941
C	2.995570	3.114712	0.817868
H	2.257952	3.676285	1.378447
C	4.064777	3.780916	0.198328
H	4.135589	4.860804	0.261196
C	5.054906	3.055287	-0.496889
H	5.874039	3.580759	-0.973440
C	4.978429	1.682313	-0.582384
H	5.718954	1.102637	-1.116396
N	3.235885	-2.502474	0.047268
N	4.990465	-1.073642	-0.193743
N	3.836083	-0.372061	-0.054608
B	-3.765663	0.160286	1.452952
H	-3.186086	0.088835	2.488948
B	-3.514938	1.422551	0.180135
H	-2.742332	2.325103	0.235158
B	-5.062915	1.319571	1.059312
H	-5.358876	2.168275	1.842156
B	-5.421737	-0.424265	1.297563
H	-5.964085	-0.827451	2.278416
B	-4.091834	-1.312580	0.377886
H	-3.713749	-2.382669	0.730506
B	-3.753160	0.390397	-1.339831
H	-3.113947	0.633896	-2.311795
B	-5.024579	1.573880	-0.718408
H	-5.277192	2.629541	-1.209093
B	-6.282713	0.548420	0.054786
H	-7.427747	0.866159	0.144298
B	-5.837085	-1.146126	-0.264424
H	-6.571600	-2.077898	-0.340330
B	-5.589454	0.102387	-1.523850
H	-6.130957	0.144255	-2.581486
H	-4.309950	-1.875110	-1.959582

Table S13 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **CB2** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	-4.569543	-0.386817	1.242361
C	-3.820825	0.155861	-0.147978
C	-2.345227	0.484714	-0.130022
C	-1.368068	-0.510492	-0.259178
H	-1.653376	-1.548817	-0.365931
C	-0.011862	-0.192272	-0.267477
H	0.704896	-0.994746	-0.376416
C	0.413293	1.140216	-0.151790
C	-0.569085	2.140118	-0.042984
H	-0.256260	3.174443	0.032418
C	-1.919830	1.819440	-0.034024
H	-2.645295	2.619659	0.044406
C	1.821693	1.570662	-0.157012
C	3.547548	2.810634	-0.206302
C	4.407772	4.029695	-0.283886
H	5.461483	3.753434	-0.219403
H	4.172895	4.721132	0.531218
H	4.239563	4.562668	-1.224882
C	3.114832	-0.628770	0.099514
C	3.102702	-1.169485	1.400034
C	3.302781	-2.550190	1.524308
H	3.299453	-3.002517	2.511096
C	3.516465	-3.349621	0.404690
H	3.672070	-4.417746	0.524250
C	3.539950	-2.783692	-0.868155
H	3.720463	-3.417336	-1.730482
C	3.342005	-1.409963	-1.051987
C	2.912814	-0.309098	2.644843
H	2.692754	0.712083	2.322220
C	4.211448	-0.251586	3.473112
H	4.080500	0.405224	4.339508
H	5.041866	0.134065	2.874248
H	4.492375	-1.243495	3.843107
C	1.724415	-0.784920	3.500783
H	1.577834	-0.109267	4.349757
H	1.891646	-1.789438	3.903338
H	0.798183	-0.804962	2.918329
C	3.412659	-0.797747	-2.447265
H	3.035440	0.226950	-2.384747
C	4.876159	-0.714788	-2.925398
H	4.929115	-0.236022	-3.908957
H	5.320215	-1.712608	-3.011245
H	5.481643	-0.130924	-2.226427
C	2.533760	-1.543708	-3.466934
H	2.557978	-1.024015	-4.430145
H	1.491682	-1.593482	-3.136107
H	2.883132	-2.567009	-3.638514
N	2.940115	0.791866	-0.059538
N	4.052179	1.587279	-0.089076
N	2.188919	2.848681	-0.250600
B	-4.927196	1.115920	-1.035635
H	-4.484480	2.011878	-1.667057
B	-4.876873	1.214831	0.738492
H	-4.391138	2.092511	1.355632
B	-6.431913	1.131344	-0.088349
H	-7.149824	2.075352	-0.094656
B	-6.255789	0.022719	-1.479733
H	-6.855240	0.182559	-2.491481
B	-4.576790	-0.565733	-1.507723
H	-3.895665	-0.789962	-2.447906
B	-6.163805	0.180981	1.391102
H	-6.565793	0.429043	2.475391
B	-7.021419	-0.554742	0.020454
H	-8.176313	-0.816542	0.095513
B	-5.864794	-1.603553	-0.853222
H	-6.178594	-2.608004	-1.400218
B	-4.312559	-1.504452	-0.023652
H	-3.493189	-2.336505	0.121580
B	-5.813837	-1.495246	0.922560
H	-5.980421	-2.380226	1.689249
H	-3.918336	-0.491648	2.100826

Table S14 Cartesian coordinates of the first excited state (S_1) fully optimized geometry of **CB2** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	-5.228999	0.572569	1.787844
C	-3.693180	0.164625	0.036534
C	-2.259248	0.526432	0.030784
C	-1.280393	-0.386791	0.475596
H	-1.587311	-1.356993	0.847303
C	0.066143	-0.055904	0.475085
H	0.779417	-0.761655	0.881744
C	0.492658	1.209654	0.007868
C	-0.486782	2.137416	-0.420893
H	-0.168903	3.111245	-0.775201
C	-1.826344	1.796328	-0.419563
H	-2.558825	2.512651	-0.772302
C	1.877175	1.625862	-0.032343
C	3.653216	2.789861	0.044061
C	4.566451	3.957324	0.094982
H	5.606793	3.634167	0.061487
H	4.394316	4.526372	1.014993
H	4.363543	4.631923	-0.742663
C	3.088388	-0.641744	-0.154386
C	3.667110	-1.341241	0.938779
C	3.726303	-2.729966	0.830875
H	4.137807	-3.310183	1.649135
C	3.251103	-3.394438	-0.303573
H	3.316284	-4.476296	-0.357454
C	2.705915	-2.681073	-1.369837
H	2.371623	-3.215347	-2.251471
C	2.615909	-1.290112	-1.333365
C	4.167745	-0.652089	2.203649
H	3.852300	0.393272	2.176208
C	5.709195	-0.660776	2.250981
H	6.058486	-0.137492	3.146653
H	6.131672	-0.162257	1.374692
H	6.097587	-1.684104	2.285531
C	3.565623	-1.271508	3.478694
H	3.880982	-0.691552	4.351357
H	3.899093	-2.302277	3.632908
H	2.471866	-1.269899	3.447678
C	2.172132	-0.518884	-2.569805
H	1.946699	0.510486	-2.279901
C	3.337964	-0.448946	-3.582124
H	3.041526	0.147196	-4.450534
H	3.611755	-1.449584	-3.931688
H	4.226380	0.010289	-3.138472
C	0.903179	-1.096265	-3.218003
H	0.587600	-0.449426	-4.041826
H	0.080810	-1.160495	-2.500072
H	1.071656	-2.093952	-3.634699
N	3.009059	0.778436	-0.088186
N	4.117898	1.516530	-0.007884
N	2.304424	2.879425	0.021630
B	-4.683700	0.347355	-1.240491
H	-4.207362	0.808723	-2.227130
B	-4.939017	1.345068	0.303295
H	-4.628244	2.491675	0.310859
B	-6.332771	0.744411	-0.754322
H	-6.981461	1.426112	-1.483614
B	-5.904557	-0.951981	-1.163666
H	-6.254397	-1.499314	-2.162396
B	-4.274725	-1.254760	-0.505480
H	-3.480634	-2.034712	-0.923306
B	-6.605058	0.871881	0.989725
H	-7.352593	1.680682	1.436520
B	-7.036787	-0.641980	0.144594
H	-8.177012	-0.975080	0.054886
B	-5.683754	-1.792791	0.408279
H	-5.859065	-2.964209	0.529403
B	-4.385294	-0.815359	1.292474
H	-3.644548	-1.335277	2.062345
B	-6.198600	-0.720680	1.720221
H	-6.627746	-1.159795	2.737927
H	-4.946035	1.066543	2.707993

Table S15 Cartesian coordinates of the ground state (S_0) fully optimized geometry of *nido*-**CB1** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	-4.057390	-1.331401	0.003999
C	-3.094261	-0.099078	-0.034677
C	-1.624942	-0.397021	-0.066707
C	-0.709946	0.434793	-0.734624
H	-1.077947	1.287850	-1.292787
C	0.657204	0.179139	-0.710199
H	1.326225	0.831776	-1.260257
C	1.167641	-0.923804	-0.006496
C	0.261437	-1.764830	0.657681
H	0.639519	-2.625262	1.199607
C	-1.104203	-1.501090	0.631833
H	-1.774186	-2.156621	1.178154
C	2.596755	-1.269123	0.013251
C	4.416281	-2.367178	-0.015587
C	5.366985	-3.520002	-0.026474
H	6.397017	-3.161114	-0.062735
H	5.186391	-4.163279	-0.893565
H	5.238889	-4.135577	0.869517
C	3.706332	1.025583	0.060053
C	3.006823	1.699758	1.064814
H	2.412850	1.141160	1.779317
C	3.084968	3.090468	1.136820
H	2.538751	3.615945	1.913754
C	3.870696	3.801023	0.226738
H	3.932387	4.882918	0.290511
C	4.580530	3.116354	-0.762524
H	5.195586	3.663147	-1.470461
C	4.498506	1.727181	-0.852858
H	5.041672	1.181673	-1.616253
N	3.061330	-2.516863	0.025619
N	4.827418	-1.107438	-0.050514
N	3.652789	-0.399652	-0.022805
B	-3.608762	1.190262	0.816687
H	-2.818992	1.944560	1.301736
B	-3.797658	1.209700	-0.947267
H	-3.161718	1.926588	-1.653374
B	-5.133589	1.651344	0.093830
H	-5.566965	2.762229	0.169574
B	-5.172125	0.678750	1.582922
H	-5.684986	1.116465	2.569923
B	-4.028327	-0.464720	-1.466423
H	-3.518099	-0.937468	-2.428346
B	-5.427243	0.612344	-1.331922
H	-6.025897	0.991680	-2.290608
B	-6.247664	0.221111	0.231826
H	-7.432382	0.341925	0.322815
B	-5.308825	-1.088005	1.016799
H	-5.835045	-1.976628	1.614448
B	-5.537100	-1.042429	-0.779789
H	-6.115242	-1.944064	-1.298274
H	-4.527544	-0.360914	1.906870
H	-3.595085	-2.305730	-0.109227

Table S16 Cartesian coordinates of the first excited state (S_1) fully optimized geometry of *nido*-**CB1** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	-4.001032	-0.712058	-1.084969
C	-3.151299	-0.010716	-0.015432
C	-1.672875	-0.276320	-0.001663
C	-0.723882	0.619662	-0.530632
H	-1.058432	1.552032	-0.977207
C	0.633908	0.345867	-0.507602
H	1.314690	1.059611	-0.954383
C	1.142146	-0.869666	0.057641
C	0.162075	-1.785999	0.560559
H	0.505442	-2.728984	0.971477
C	-1.185565	-1.493368	0.537792
H	-1.889112	-2.215844	0.945768
C	2.519634	-1.245891	0.090939
C	4.273283	-2.473209	-0.024780
C	5.154113	-3.686609	-0.028904
H	6.193464	-3.403463	-0.208487
H	4.846387	-4.394724	-0.806091
H	5.094026	-4.212711	0.929593
C	3.856028	0.933174	-0.029564
C	3.068451	1.716154	0.838653
H	2.276895	1.248484	1.410752
C	3.323011	3.079791	0.974090
H	2.706329	3.665926	1.650453
C	4.365322	3.691097	0.272235
H	4.557449	4.753743	0.384112
C	5.163659	2.907885	-0.571545
H	5.984153	3.363252	-1.119945
C	4.918098	1.547568	-0.724403
H	5.538496	0.939540	-1.371965
N	2.950064	-2.535794	0.223985
N	4.771961	-1.270018	-0.284747
N	3.642461	-0.444983	-0.181741
B	-3.985576	-0.018729	1.449873
H	-3.383533	-0.314719	2.424345
B	-3.859909	1.447441	0.460668
H	-3.182568	2.331173	0.865457
B	-5.424480	0.949236	1.188847
H	-5.918144	1.560218	2.081141
B	-5.687201	-0.787466	1.216021
H	-6.311731	-1.310139	2.076930
B	-3.851351	0.970380	-1.230519
H	-3.203340	1.464749	-2.083632
B	-5.369168	1.550539	-0.489283
H	-5.842336	2.591515	-0.805889
B	-6.408244	0.151208	-0.095922
H	-7.587536	0.251366	-0.189708
B	-5.475121	-1.344498	-0.494990
H	-5.903343	-2.340409	-0.974713
B	-5.368835	0.125315	-1.542981
H	-5.785891	-0.002249	-2.644756
H	-4.971963	-1.720184	0.701105
H	-3.451825	-1.323919	-1.789890

Table S17 Cartesian coordinates of the ground state (S_0) fully optimized geometry of *nido*-**CB2** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	4.323781	-1.228150	0.293139
C	3.918937	0.216514	-0.149557
C	2.457131	0.547595	-0.130005
C	1.486811	-0.439970	-0.368087
H	1.793522	-1.462717	-0.558679
C	0.126045	-0.141143	-0.394877
H	-0.576843	-0.939882	-0.594094
C	-0.324244	1.172182	-0.186349
C	0.643881	2.170132	0.030912
H	0.314164	3.191463	0.184275
C	1.997831	1.864516	0.056318
H	2.715924	2.657043	0.232337
C	-1.737442	1.578601	-0.202928
C	-3.495666	2.775327	-0.267387
C	-4.383903	3.973268	-0.365443
H	-5.431124	3.675182	-0.290144
H	-4.232561	4.491552	-1.317675
H	-4.161343	4.686947	0.434061
C	-2.977701	-0.640181	0.123847
C	-2.888277	-1.145271	1.435587
C	-3.058440	-2.524956	1.608747
H	-2.993037	-2.948748	2.606121
C	-3.318604	-3.359393	0.525427
H	-3.449716	-4.426028	0.682711
C	-3.416557	-2.830170	-0.759724
H	-3.628857	-3.491179	-1.593919
C	-3.248519	-1.459877	-0.991389
C	-2.642054	-0.249784	2.645297
H	-2.477821	0.769282	2.285655
C	-3.880169	-0.211779	3.562341
H	-3.709874	0.470050	4.402297
H	-4.102780	-1.201986	3.974472
H	-4.763318	0.133447	3.016265
C	-1.381609	-0.669329	3.424410
H	-1.195425	0.030776	4.245472
H	-0.499746	-0.676306	2.777113
H	-1.489478	-1.668518	3.859754
C	-3.391367	-0.888936	-2.398746
H	-3.004849	0.134131	-2.385035
C	-2.573678	-1.670016	-3.442656
H	-2.641888	-1.173751	-4.416166
H	-2.941843	-2.693209	-3.571127
H	-1.516476	-1.723804	-3.164887
C	-4.877676	-0.808758	-2.800902
H	-4.980210	-0.365619	-3.797361
H	-5.438891	-0.193446	-2.092269
H	-5.333194	-1.805014	-2.825980
N	-2.838688	0.776434	-0.084790
N	-3.973671	1.545853	-0.124147
N	-2.137813	2.846175	-0.320166
B	5.131028	1.373879	0.335577
H	4.865607	2.469520	0.717692
B	4.843781	0.846549	-1.333576
H	4.381612	1.639959	-2.098215
B	6.468446	0.894224	-0.686246
H	7.294483	1.658218	-1.087818
B	6.419904	0.358463	1.019317
H	7.174908	0.772122	1.843971
B	4.723165	0.015532	1.391679
H	4.127940	0.124054	2.413054
B	6.036005	-0.451277	-1.766644
H	6.617785	-0.599351	-2.800226
B	6.927815	-0.813016	-0.261596
H	8.058142	-1.197107	-0.295678
B	5.844117	-1.291224	1.050144
H	6.055641	-2.119331	1.878178
B	5.508052	-1.837075	-0.644243
H	5.609644	-3.003267	-0.875727
H	5.018683	-1.203348	-1.780464
H	3.529804	-1.853167	0.685838

Table S18 Cartesian coordinates of the first excited state (S_1) fully optimized geometry of *nido*-**CB2** in THF from B3LYP calculations (in Å)

Atom	X	Y	Z
C	4.567374	0.117717	1.233011
C	3.918656	0.239437	-0.157650
C	2.462401	0.585347	-0.236000
C	1.483423	-0.431118	-0.103895
H	1.803587	-1.464115	0.015011
C	0.128880	-0.160960	-0.120088
H	-0.561783	-0.987676	-0.015981
C	-0.368372	1.182954	-0.275569
C	0.639219	2.204195	-0.420590
H	0.308823	3.227995	-0.556183
C	1.984483	1.915113	-0.397988
H	2.695978	2.727788	-0.516494
C	-1.739256	1.563117	-0.307441
C	-3.527838	2.746630	-0.464452
C	-4.428089	3.933172	-0.636174
H	-5.474912	3.632930	-0.553452
H	-4.276058	4.403539	-1.613832
H	-4.220892	4.694731	0.123425
C	-3.027549	-0.632831	0.131820
C	-3.061728	-1.042426	1.482086
C	-3.244439	-2.403773	1.755933
H	-3.271553	-2.742862	2.787729
C	-3.397998	-3.329413	0.726424
H	-3.539969	-4.381413	0.958435
C	-3.371309	-2.906122	-0.600413
H	-3.494216	-3.635209	-1.396438
C	-3.188057	-1.555638	-0.923803
C	-2.913704	-0.045194	2.625306
H	-2.733557	0.937367	2.182995
C	-4.212939	0.053006	3.447484
H	-4.112126	0.808042	4.235037
H	-4.457449	-0.900924	3.928436
H	-5.056381	0.335972	2.809899
C	-1.704879	-0.375442	3.520356
H	-1.581579	0.392662	4.291750
H	-0.783262	-0.418054	2.931657
H	-1.827339	-1.338316	4.028971
C	-3.162289	-1.113396	-2.382043
H	-2.953654	-0.040887	-2.393330
C	-2.039349	-1.811068	-3.171805
H	-2.005361	-1.432414	-4.199255
H	-2.191702	-2.895019	-3.223338
H	-1.063708	-1.628176	-2.710462
C	-4.534067	-1.321883	-3.051419
H	-4.513649	-0.965139	-4.087120
H	-5.315934	-0.772749	-2.517675
H	-4.815867	-2.380885	-3.068341
N	-2.870566	0.751934	-0.173936
N	-4.026052	1.531679	-0.270519
N	-2.182318	2.842080	-0.497889
B	5.070994	0.681952	-1.315629
H	4.737134	1.280890	-2.282191
B	4.515059	-0.990564	-1.147988
H	3.737654	-1.592375	-1.805704
B	6.233916	-0.687121	-1.321270
H	6.812093	-1.008165	-2.309470
B	6.608233	0.799043	-0.413185
H	7.474472	1.541713	-0.739718
B	5.081193	1.418332	0.278530
H	4.783105	2.531685	0.530501
B	5.813786	-1.994540	-0.226477
H	6.087202	-3.122370	-0.467773
B	6.986107	-0.788269	0.314652
H	8.117636	-1.090949	0.510230
B	6.192364	0.481797	1.281152
H	6.659965	0.934929	2.271589
B	5.608811	-1.224760	1.400806
H	5.679591	-1.765528	2.453775
H	4.864091	-2.052492	0.633766
H	3.914400	0.337718	2.068463