

Electronic Supplementary Information

Constraint-induced structural deformation of planarized triphenylboranes in the excited state

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1. Experimental details

General Procedures. Melting points (mp) were determined with a Yanaco MP-S3 instrument. ^1H , ^{13}C , and ^{11}B NMR spectra were measured with a JEOL AL-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , and 128 MHz for ^{11}B) in CDCl_3 or acetone- d_6 . Chemical shifts are reported in δ ppm. ^1H NMR spectra are referenced to residual protons in the deuterated solvent as an internal standard. ^{13}C NMR spectra are referenced to carbon-13 in the deuterated solvent as an internal standard. ^{11}B NMR spectra are referenced to $\text{BF}_3\cdot\text{OEt}_2$ as an external standard. Mass spectrometry was performed with a Bruker Daltonics micrOTOF Focus with the APCI ionization method. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of silica gel 60 F₂₅₄ (Merck). Column chromatography was performed using silica gel PSQ 100B (Fuji Silysia Chemical). Recycling preparative gel permeation chromatography (GPC) was performed using LC-918 equipped with polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) using chloroform as an eluent. Commercially available solvents and reagents were used as received. Dry toluene was purchased from Kanto Chemical, and degassed by bubbling of nitrogen for 30 minutes before use. Cyclohexane was dried over Na, and distilled before use. $\text{BF}_3\cdot\text{OEt}_2$ was distilled from CaH_2 . CsF was dried by heating in vacuum at 80 °C for 2 h before use. The planarized triphenylboranes **1** and **2**,¹ $[\text{Ir}(\text{OMe})\text{cod}]_2$,² and $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ ³ were prepared as described in the literature. All reactions were carried out under an argon (Ar) or nitrogen (N_2) atmosphere.

UV-visible absorption spectra were recorded on a Shimadzu UV-3510 spectrometer. The concentrations of sample solutions were $\sim 10^{-5}$ M for room temperature measurements. Fluorescence spectra were recorded on a Hitachi F-4500 spectrometer for both room temperature and varied temperature measurements. 3-Methylpentane was purified by passing through a $\text{AgNO}_3\text{-Al}_2\text{O}_3$ column.⁴ The sample solutions were degassed by three freeze-pump-thaw cycles before measurements. For the varied temperature experiments, the solution in a 1 cm square quartz cell equipped with a Teflon stopcock was cooled by an Oxford Optistat DN cryostat. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920-02 calibrated integrating sphere system.

Synthesis of 4. To a solution of **2** (402 mg, 1.20 mmol) in cyclohexane (6 mL) was added bis(pinacolato)diboron (1.01 g, 3.99 mmol), $[\text{Ir}(\text{OMe})\text{cod}]_2$ (16.1 mg, 0.024 mmol), and 4,4'-di-*t*-butyl-2,2'-bipyridine (13.1 mg, 0.049 mmol). The mixture was stirred at 80 °C for 5 h. After the addition of a saturated aqueous solution of NH_4Cl , the mixture was extracted with CH_2Cl_2 , and the extracts were dried over MgSO_4 . After filtration, volatiles were removed under reduced pressure.

The crude product was purified by column chromatography on silica gel using EtOAc as an eluent, followed by GPC to give 691 mg (0.971 mmol) of **4** in 81% yield as pale yellow solids: mp >300 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.42 (s, 36H), 1.88 (s, 12H), 4.62 (s, 2H), 7.88 (s, 2H), 8.12 (s, 2H), 8.13 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 25.11 (q), 34.56 (q), 37.27 (t), 43.09 (s), 84.02 (s), 84.10 (s), 130.09 (d), 130.31 (d), 131.36 (d), 145.43 (s), 155.62 (s), 155.87 (s), four signals for the carbon atoms bound to the boron atoms were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, CDCl_3) δ 31.0, 46.0; HRMS (APCI, pos) m/z calcd for $\text{C}_{43}\text{H}_{57}^{11}\text{B}_4\text{O}_6$ $[\text{M}+\text{H}]^+$ 713.4548, found: 713.4546.

Synthesis of 5. To a solution of **4** (70.9 mg, 0.100 mmol) in toluene (1 mL) was added bromobenzene (51.7 mg, 0.329 mmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (15.6 mg, 0.015 mmol), XPhos (28.6 mg, 0.060 mmol), and CsF (168.0 mg, 1.11 mmol). The mixture was stirred at 80 °C for 13 h. After the addition of $\text{BF}_3\cdot\text{OEt}_2$ (0.12 mL) and H_2O (6 mL), the mixture was extracted with CH_2Cl_2 , and the extracts were dried over MgSO_4 . After filtration, volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel using CHCl_3 as an eluent, followed by GPC to give 10.7 mg (0.0190 mmol) of **5** in 19% yield as pale yellow solids: mp >300 °C; ^1H NMR (400 MHz, acetone- d_6) δ 1.97 (s, 12H), 4.79 (s, 2H), 7.43–7.47 (m, 3H), 7.53–7.58 (m, 6H), 7.80 (s, 2H), 7.86–7.90 (m, 6H), 8.07 (s, 4H); ^{13}C NMR (100 MHz, acetone- d_6) δ 34.83 (q), 38.17 (t), 44.17 (s), 123.99 (d), 124.24 (d), 125.02 (d), 128.39 (d), 128.53 (d), 128.61 (d), 128.63 (d), 129.83 (d), 129.88 (d), 142.63 (s), 142.97 (s), 146.09 (s), 146.61 (s), 147.82 (s), 157.88 (s), 157.97 (s), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, CDCl_3) δ 45.4; HRMS (APCI, pos) m/z calcd for $\text{C}_{43}\text{H}_{35}^{11}\text{B}$ 562.2832, found: 562.2824.

Synthesis of 6. This compound was prepared from **4** (142 mg, 0.199 mmol) and 1-bromo-4-(hexyloxy)benzene (170 mg, 0.661 mmol) essentially in the same manner as described for **5**. The crude product was purified by column chromatography on silica gel using CHCl_3 as an eluent, followed by GPC to give 106 mg (0.123 mmol) of **6** in 61% yield as pale yellow solids: mp 64–65 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.92–0.95 (m, 9H), 1.36–1.40 (m, 12H), 1.49–1.53 (m, 6H), 1.80–1.88 (m, 6H), 1.91 (s, 12H), 4.03–4.07 (m, 6H), 4.70 (s, 2H), 7.03–7.07 (m, 6H), 7.63 (s, 2H), 7.67–7.69 (m, 6H), 7.84–7.85 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.20 (q), 22.78 (t), 25.93 (t), 29.46 (t), 31.78 (t), 34.74 (q), 37.87 (t), 43.41 (s), 68.32 (t), 115.05 (d), 122.95 (d), 123.14 (d), 123.89 (d), 128.15 (s), 128.76 (d), 128.85 (d), 129.87 (s), 134.48 (s), 134.95 (s), 144.85 (s),

145.29 (s), 146.64 (s), 156.74 (s), 156.89 (s), 159.25 (d), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, CDCl_3) δ 43.6; HRMS (APCI, pos) m/z calcd for $\text{C}_{61}\text{H}_{72}^{11}\text{BO}_3$ $[\text{M}+\text{H}]^+$ 863.5579, found: 863.5588.

2. Fluorescence lifetime profiles

For fluorescence lifetime measurements, a time-correlated single-photon counting (TCSPC) method using a home-built cavity-dumped Cr:forsterite laser⁵ with a 0.1 MHz repetition rate was employed. The fourth harmonic light at 315 nm was used for excitation. A photomultiplier tube (Hamamatsu Photonics, R3809U-50) equipped with an amplifier (Hamamatsu Photonics C5594) and a photon counting module (PicoQuanta, PicoHarp 300) was used for signal detection. A monochromator was placed in front of the photomultiplier tube. The instrumental response function was estimated by the fwhm of scattered light from a colloidal solution for the excitation light pulse. In the present measurements, the instrumental response time was 32 ps. The time profiles of fluorescence were analyzed by the deconvolution procedures with linear and nonlinear least-square methods.

Phosphorescence lifetime of **1** in 3MP at 77 K was determined with a Hamamatsu picosecond fluorescence measurement system C4780. The solution in a 1 cm square quartz cell was cooled by an Oxford Optistat DN cryostat.

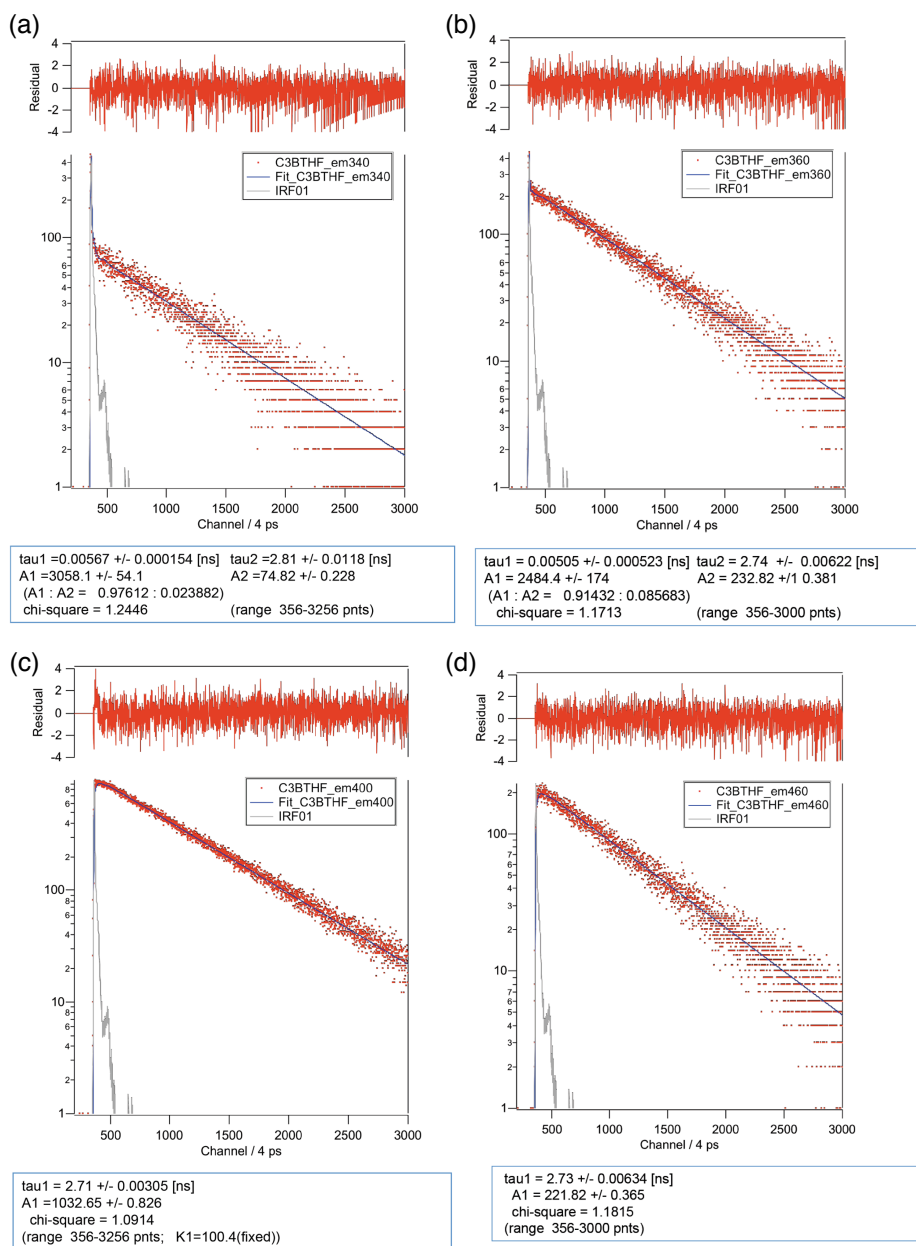


Fig. S1 Fluorescence decay profiles of the planarized triphenylborane **1** in THF at room temperature monitored at (a) 340, (b) 360, (c) 400, and (d) 460 nm ($\lambda_{\text{ex}} = 315$ nm).

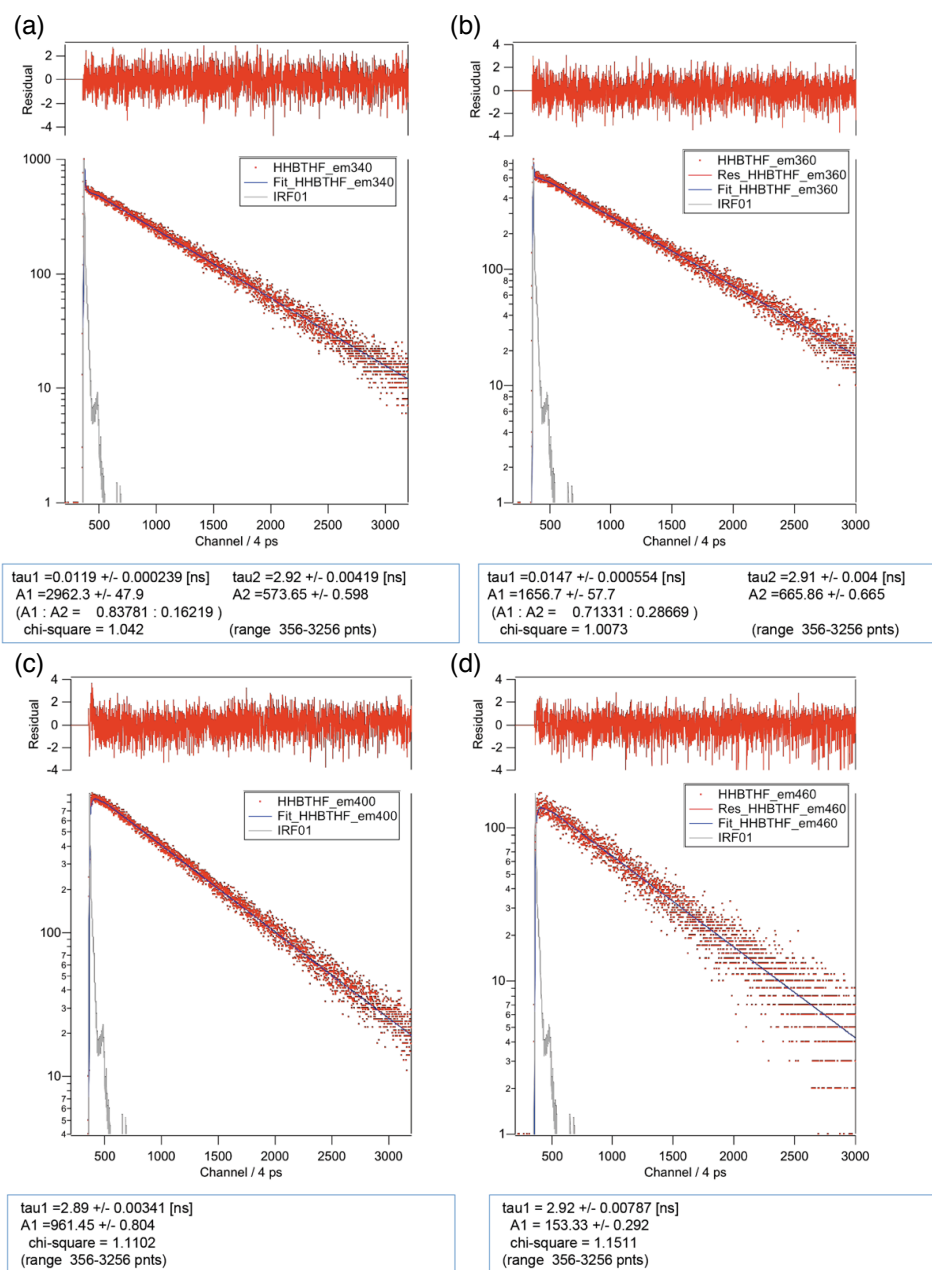


Fig. S2 Fluorescence decay profiles of the planarized triphenylborane **2** in THF at room temperature monitored at (a) 340, (b) 360, (c) 400, and (d) 460 nm ($\lambda_{\text{ex}} = 315$ nm).

Table S1 Summary of fluorescence lifetimes of the planarized triphenylboranes **1** and **2** in THF at room temperature ($\lambda_{\text{ex}} = 315 \text{ nm}$)^a

	Monitoring wavelength	Lifetime [ns]	Pre-exponential factor	Chi-square
1	340 nm	0.0057	3058.1 (97.6%)	1.24
		2.80	74.82 (2.4%)	
	360 nm	0.0051	2484.4 (91.4%)	1.17
		2.74	232.82 (8.6%)	
	400 nm	2.71	1032.7	1.09
	460 nm	2.73	221.8	1.18
2	340 nm	0.012	2962.3 (83.8%)	1.04
		2.92	573.7 (16.2%)	
	360 nm	0.015	1656.7 (71.3%)	1.01
		2.91	665.9 (28.7%)	
	400 nm	2.89	961.5	1.11
	460 nm	2.92	153.3	1.15

^aDetermined by a picosecond time-correlated single-photon counting (TCSPC) method.

3. Time profiles of transient absorption

To study the dynamic behavior in the femtosecond–nanosecond time region, a dual NOPA/OPA laser system was used for transient absorption measurements. The details of the system were described elsewhere.⁶ Briefly, the output from a femtosecond Ti:Sapphire laser (Tsunami, Spectra-Physics) pumped by the second harmonics of a cw Nd³⁺:YVO₄ laser (Millennia Pro, Spectra-Physics) was regeneratively amplified with a 1 kHz repetition rate (Spitfire, Spectra-Physics). The amplified laser pulses (802 nm, 0.9 mJ/pulse energy, 85 fs fwhm, 1 kHz) were divided into two beams at the same energy (50%). One of these beams was guided into a NOPA (non-collinear optical parametric amplifier) system (TOPAS-white, Light-Conversion). The NOPA output can cover the wavelength region between 500 and 1000 nm with 1–40 mW output energy with ca. 20 fs fwhm. In the present study, the output wavelength was set at 620 nm and second harmonic pulses at 310 nm were used as excitation light. White light continuum was generated by focusing the fundamental light beam (802 nm) into a 1 mm CaF₂ window, which covers the wavelength region from 350 to 720 nm. Polarization of the two laser beams was set at a magic angle for all the measurements. The signal and the reference pulses were respectively detected with multichannel photodiode array systems (PMA-10, Hamamatsu Photonics) and the detected signals were sent to a personal computer for further analysis. In order to correct the transient absorption spectrum for the dispersion of probe light, we measured the optical Kerr effect of CCl₄ and determined the wavelength-dependent arrival times of femtosecond white light at the sample position. From the cross correlation trace between the NOPA output and the super-continuum at the sample position, the response pulse duration was estimated to be ca. 80 fs. A rotating sample cell with an optical pathlength of 2 mm was used and the absorbance of the sample at the excitation wavelength was set ~1.0.

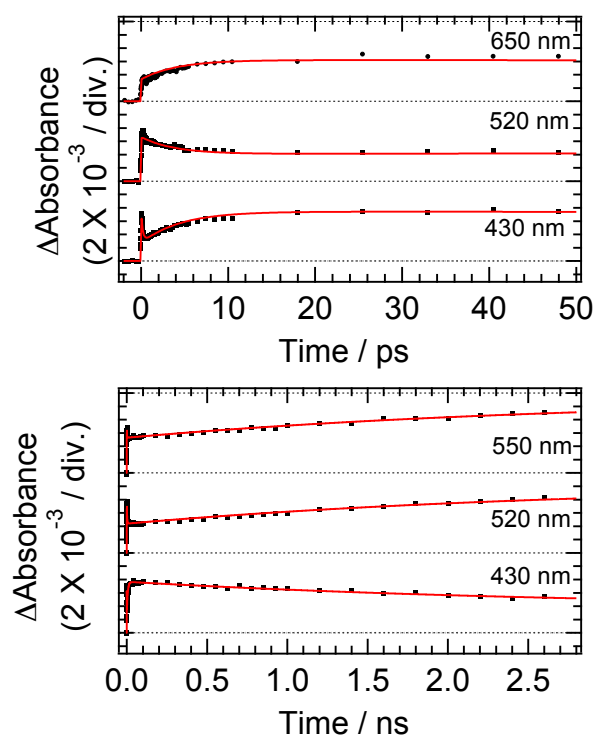


Fig. S3 Time profiles of the transient absorbance of **1** in THF following excitation with a femtosecond 310-nm laser pulse. Solid lines are curves calculated from a triple exponential function. In the analysis, the longest time constant was fixed as 2.8 ns.

Table S2 Time constants obtained for **1**

Monitoring wavelength	τ_1^a	τ_2	τ_3 (fixed)
430 nm	200±10 fs	4.5±0.2 ps	2.8 ns
520 nm	50±70 fs	3.8±0.3 ps	2.8 ns
550 nm	200±10 fs	3.2±0.5 ps	2.8 ns
650 nm		4.1±0.6 ps	2.8 ns

^aThe fastest time constant may be due to the relaxation from the excited Franck-Condon state to the S₁ state and/or the contribution from the coherent artifact.

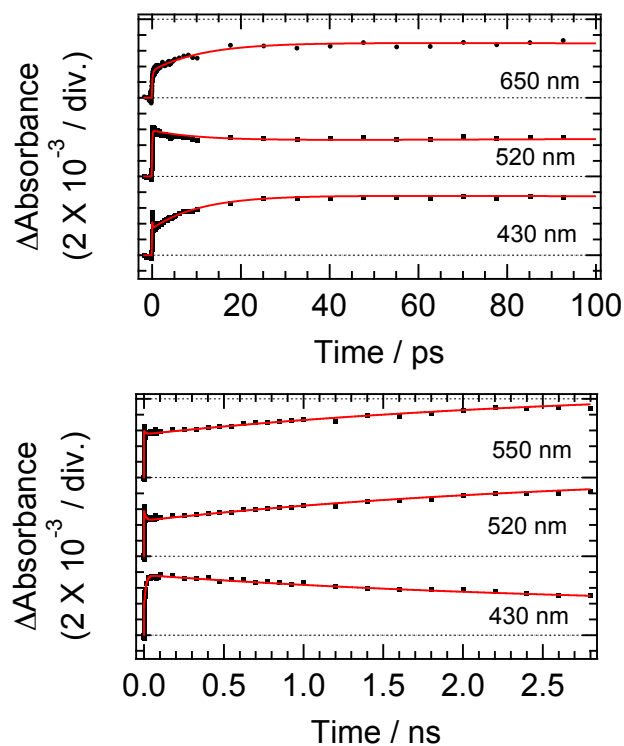


Fig. S4 Time profiles of the transient absorbance of **2** in THF following excitation with a femtosecond 310-nm laser pulse. Solid lines are curves calculated from a triple exponential function. In the analysis, the longest time constant was fixed as 2.9 ns.

Table S3 Time constants obtained for **2**

Monitoring wavelength	τ_1^a	τ_2	τ_3 (fixed)
430 nm	80±30 fs	11.0±1.0 ps	2.9 ns
520 nm	81±10 fs	11.3±0.3 ps	2.9 ns
550 nm	80±15 fs		2.9 ns
650 nm		11.6±1.6 ps	2.9 ns

^aThe fastest time constant may be due to the relaxation from the excited Franck-Condon state to the S_1 state and/or the contribution from the coherent artifact.

4. Emission spectra of **2** at low temperature

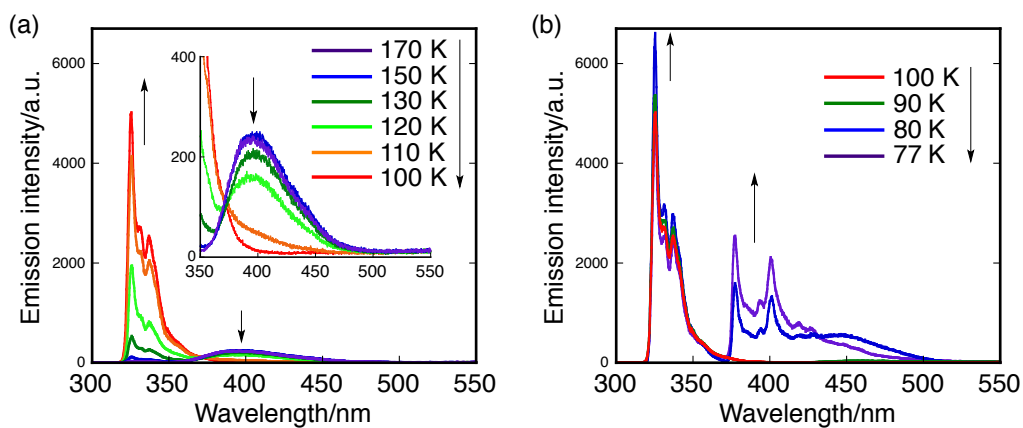


Fig. S5 Emission spectra of **2** in 3-methylpentane (3MP) at (a) 170–100 K and (b) 100–77 K.

5. Photophysical properties of **5** and **6** at room temperature

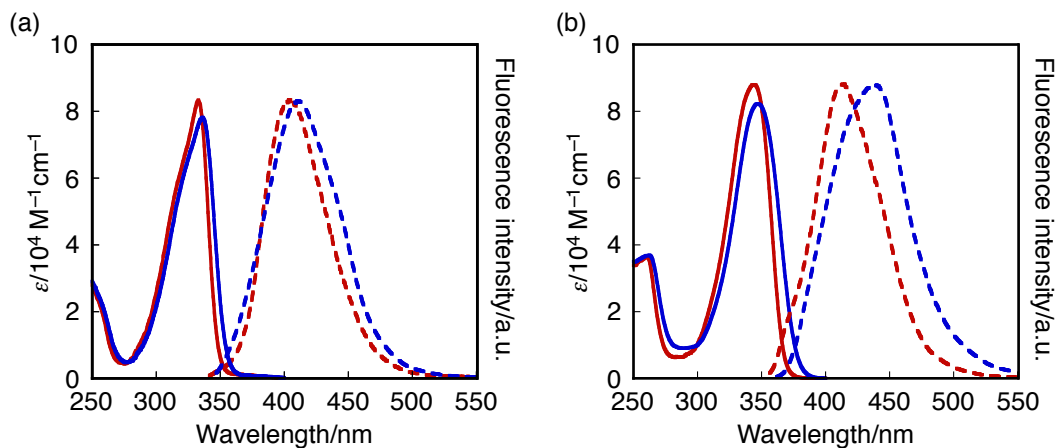


Fig. S6 Absorption (solid) and fluorescence (dash) spectra of (a) **5** and (b) **6** at room temperature in THF (blue) and 3MP (red).

Table S4 Absorption and fluorescence properties of **5** and **6** at room temperature

	Solvent	λ_{abs} [nm]	$\log \epsilon$	λ_{f} [nm]	$\nu_{\text{abs}} - \nu_{\text{f}}$ [cm^{-1}]	Φ_{f}^a
5	3MP	333	4.92	406	5400	0.70
	THF	336	4.89	413	5550	0.82
6	3MP	344	4.94	416	5030	0.84
	THF	347	4.91	438	5990	0.88

^a Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within $\pm 3\%$ error.

6. Theoretical calculations

Computational Details. We adopted the all-electron Gaussian-type double- ζ -quality polarized basis set def-SV(P) of Schäfer *et al.*⁷ for this study. After screening several choices for density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations, we selected the PBE0 exchange-correlation functional⁸ as it is in good agreement with the observed experimental excitation energies. Ground state calculations employed a Lebedev integral grid comprising 96 radial points and 590 angular points, while excited states calculations employed a Lebedev integral grid comprising 48 radial points and 110 angular points. Geometry optimizations as well as energy calculations in the ground and excited states were carried out with the GAMESS computational chemistry package.⁹ Atomic charges in the ground and excited states were computed at the previously optimized geometries by means of a fit of point charges due to an electrostatic potential approach as implemented in TURBOMOLE¹⁰ at the PBE0/def-SV(P) and TD-PBE0/def-SV(P) level.

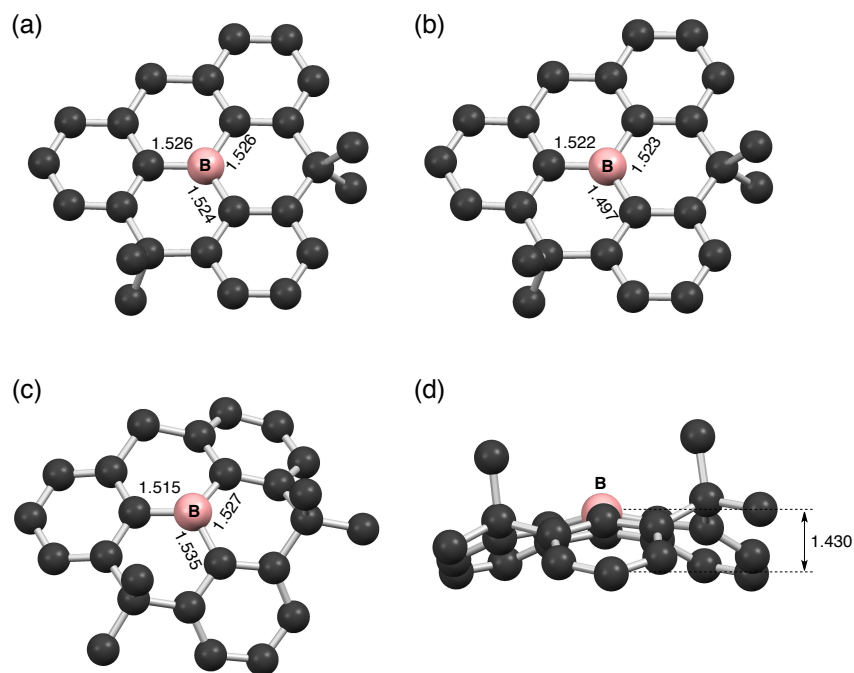


Fig. S7 Optimized structures of **2** calculated at the PBE0/def-SV(P) level of theory. Hydrogen atoms are omitted for clarity. The distances are shown in Å. (a) A planar S_0 structure, (b) a planar S_1 structure, and (c) a bowl-shaped S_1 structure and (d) its side view.

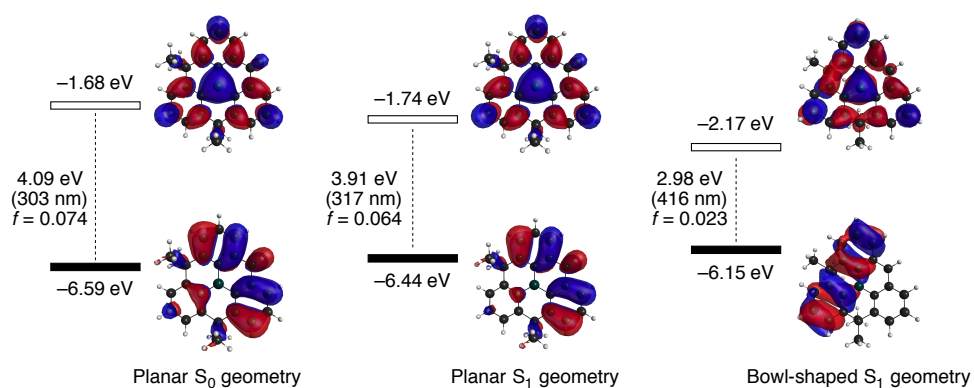


Fig. S8 Representation of HOMO and LUMO of **2** in the ground state at each optimized geometry, together with the transition energies calculated at the TD-PBE0/def-SV(P)//PBE0/def-SV(P) level of theory.

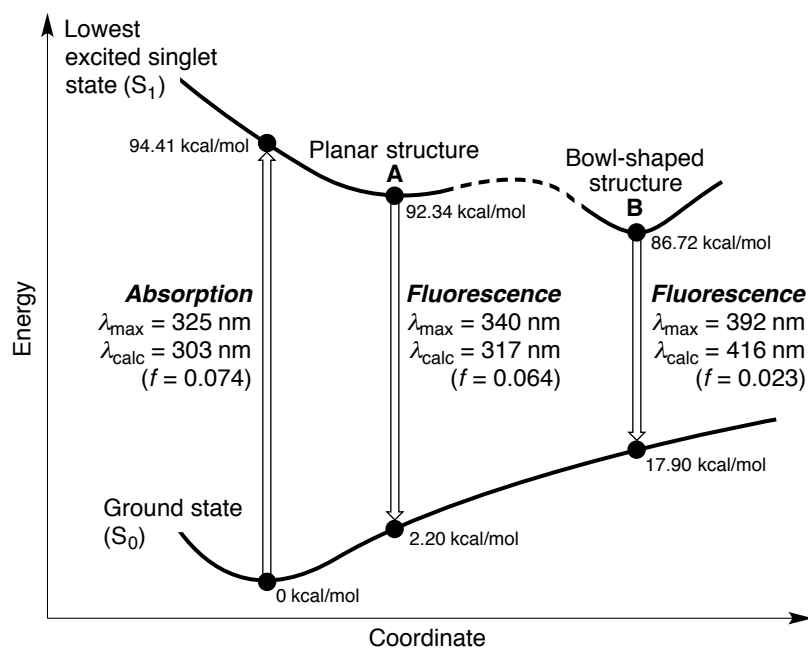


Fig. S9 Plausible potential energy surfaces for **2**, together with the calculated relative energies at each structure, and the calculated transient energies.

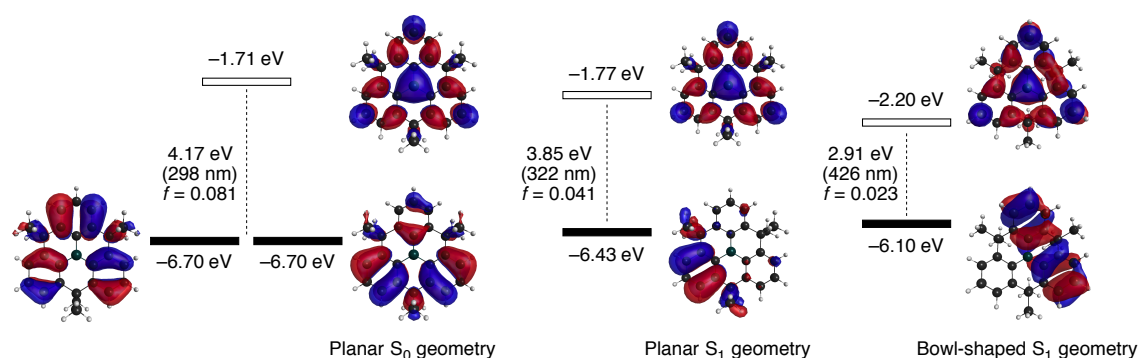


Fig. S10 Representation of HOMO and LUMO of **1** in the ground state at each optimized geometry, together with the transition energies calculated at the TD-PBE0/def-SV(P)//PBE0/def-SV(P) level of theory.

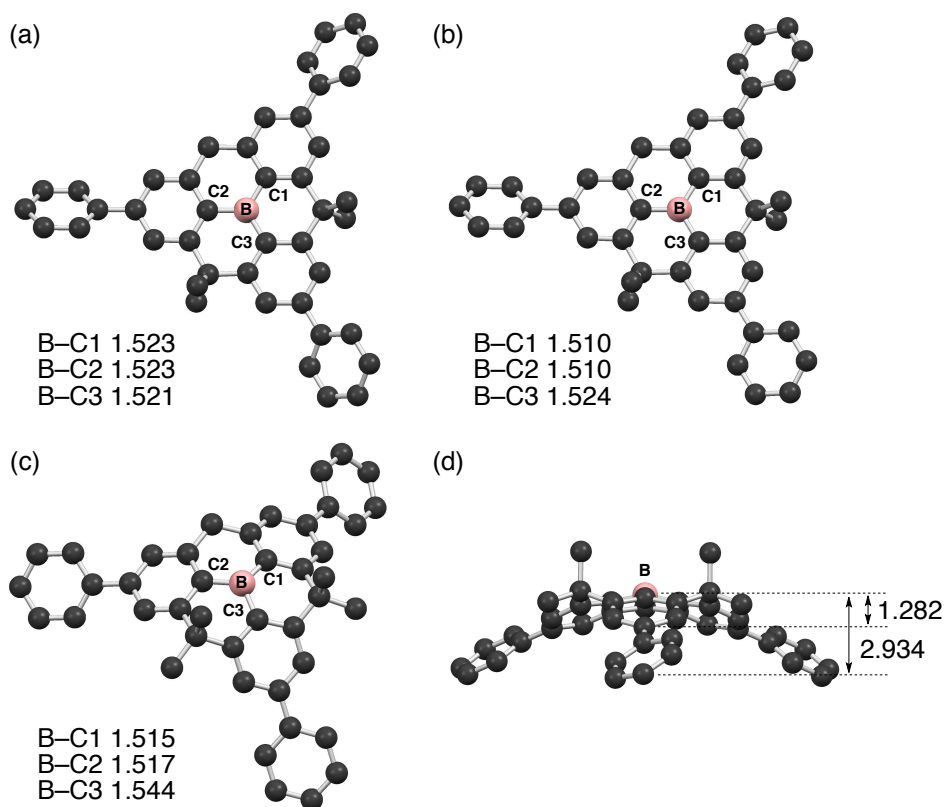


Fig. S11 Optimized structures of **5** calculated at the PBE0/def-SV(P) level of theory. Hydrogen atoms are omitted for clarity. The distances are shown in Å. (a) A planar S_0 structure, (b) a planar S_1 structure, and (c) a bowl-shaped S_1 structure and (d) its side view.

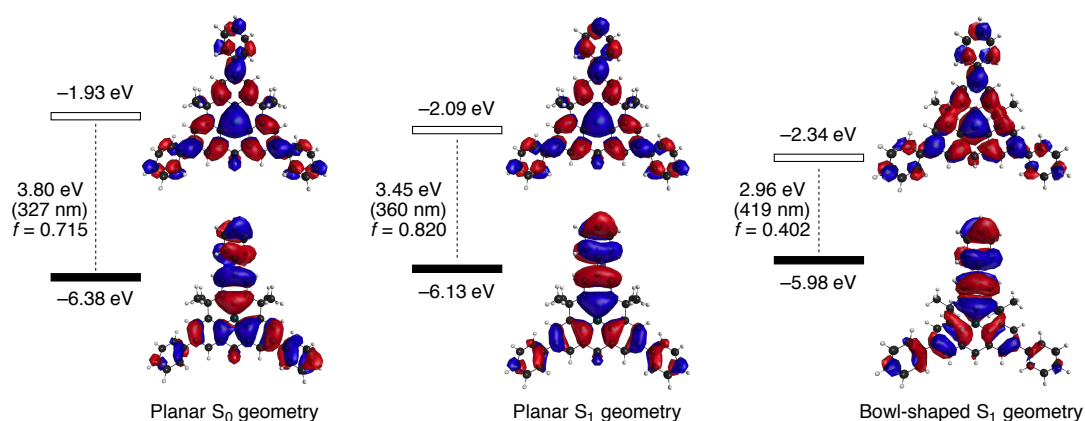


Fig. S12 Representation of HOMO and LUMO of **5** in the ground state at each optimized geometry, together with the transition energies calculated at the TD-PBE0/def-SV(P)//PBE0/def-SV(P) level of theory.

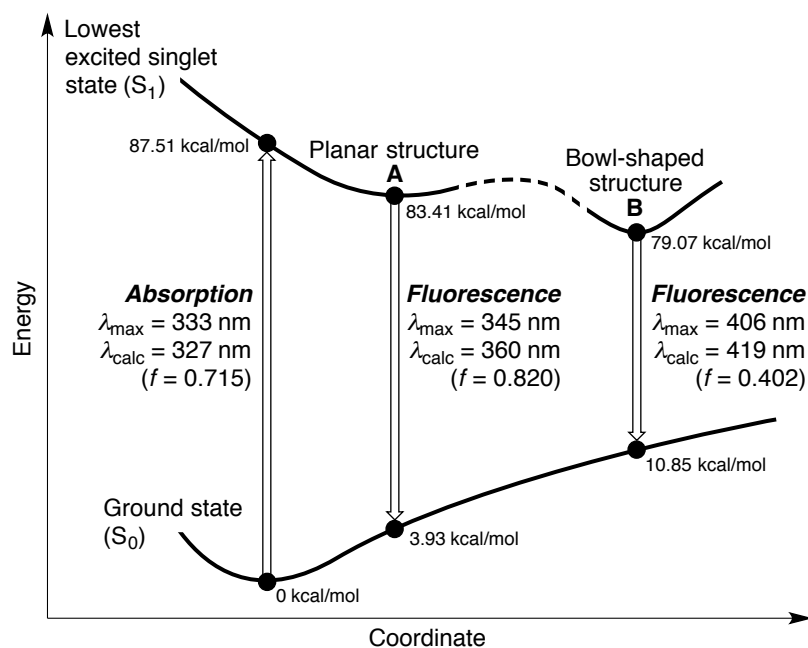


Fig. S13 Plausible potential energy surfaces for **5**, together with the calculated relative energies at each structure, and the calculated transient energies.

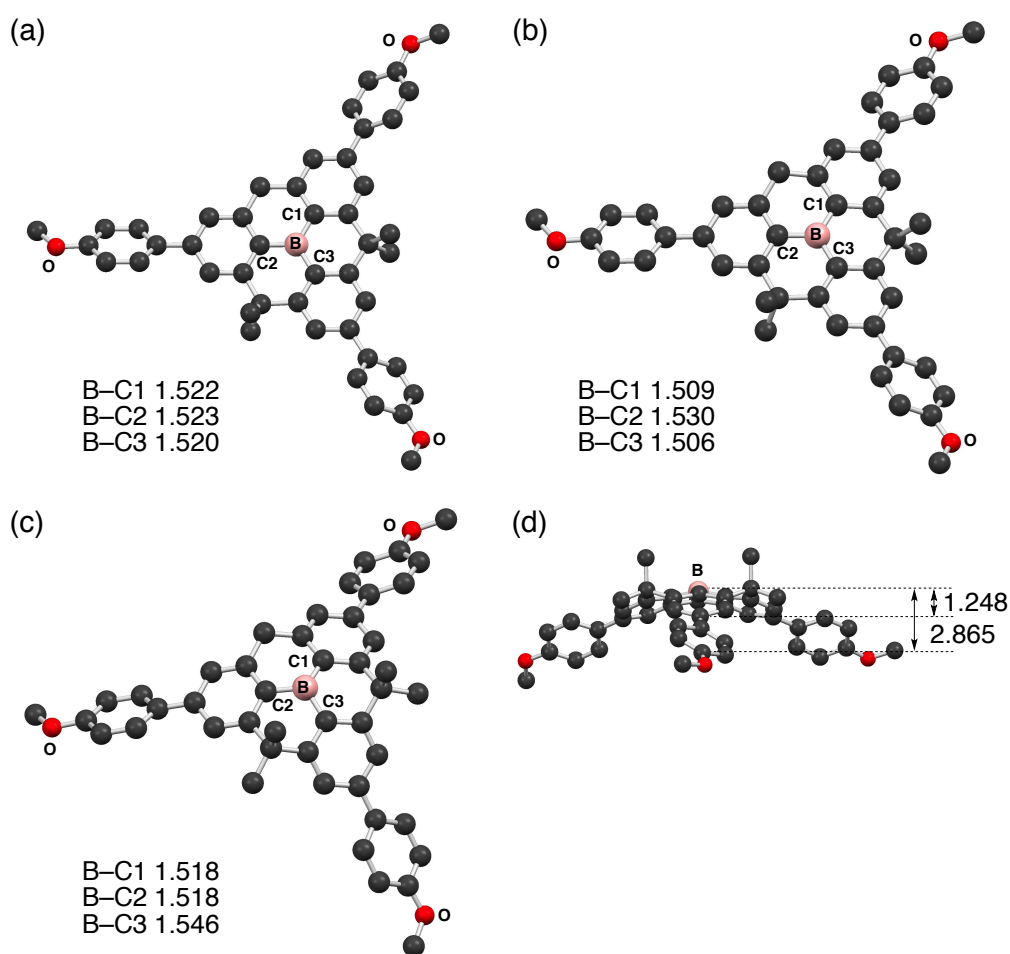


Fig. S14 Optimized structures of **6'** calculated at the PBE0/def-SV(P) level of theory. Hydrogen atoms are omitted for clarity. The distances are shown in Å. (a) A planar S_0 structure, (b) a planar S_1 structure, and (c) a bowl-shaped S_1 structure and (d) its side view.

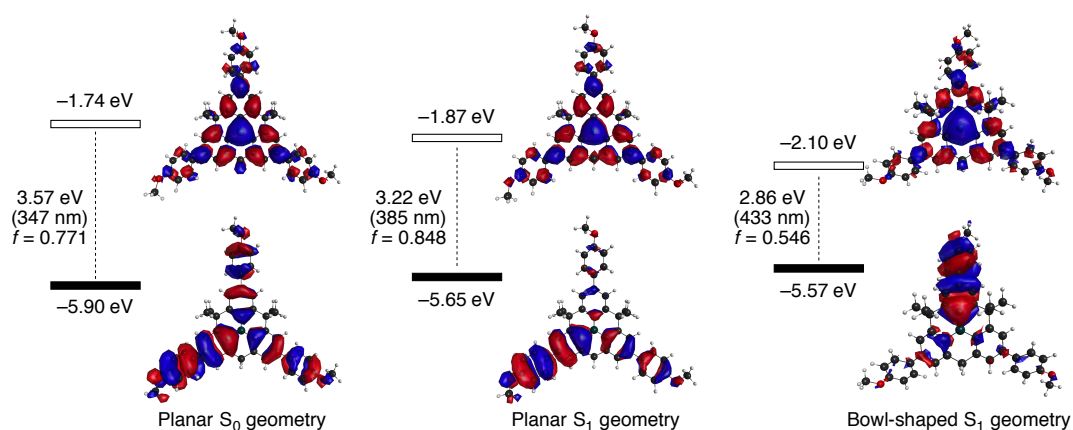


Fig. S15 Representation of HOMO and LUMO of **6'** in the ground state at each optimized geometry, together with the transition energies calculated at the TD-PBE0/def-SV(P)//PBE0/def-SV(P) level of theory.

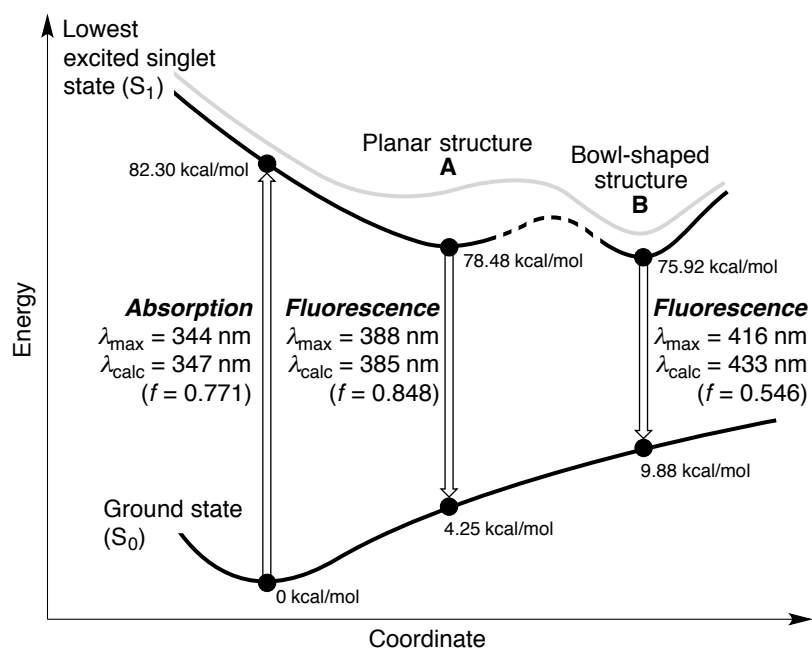


Fig. S16 Plausible potential energy surfaces for **6'**, together with the calculated relative energies at each structure, and the calculated transient energies. The gray line represents the energy surface of the S_1 state for **5**, for comparison.

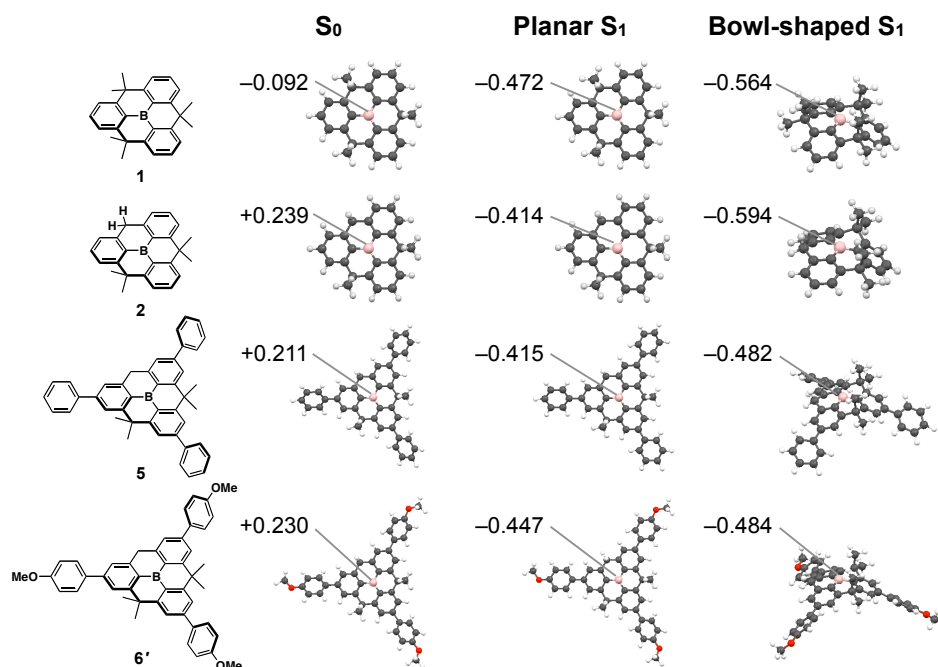


Fig. S17 Charge distributions on the boron atom of **1**, **2**, **5**, and **6'** calculated at the PBE0/def-SV(P) level of theory.

Table S5 Coordinates of the optimized structure of **1** in the ground S_0 state calculated at the PBE0/def-SV(P) level of theory

	x	y	z		x	y	z
B	0.0003186421	-0.0000368524	0.0000060109	C	0.1898362498	-2.9842097311	0.0000024481
C	0.0478262792	-0.7614053551	1.3212895307	C	-0.0943497069	1.4920164572	2.5895821018
C	0.0018020416	-0.0398708089	2.5343781126	C	-0.0943528807	1.4920219066	-2.5895660223
C	0.1365150265	-2.1706792165	1.3016909230	C	-1.0114905768	-3.9568176976	0.0000016233
C	0.0460132530	-0.7561906867	3.7350558133	H	-1.9623483464	-3.3970414713	0.0000069519
C	0.1787436103	-2.8502440670	2.5236510539	H	-0.9989005753	-4.6079241044	-0.8898445477
C	0.1335586218	-2.1456464091	3.7236413212	H	-0.9988950173	-4.6079319329	0.8898419461
H	0.0130722250	-0.2422275421	4.6997788251	C	1.5097148642	-3.7888845151	0.0000036266
H	0.2478091010	-3.9410386847	2.5603793281	H	1.5840414049	-4.4358858991	0.8899058115
H	0.1674105664	-2.6920094475	4.6718180021	H	1.5840473821	-4.4358796863	-0.8899026229
C	0.0478271160	-0.7614025614	-1.3212792108	H	2.3776511818	-3.1075627231	0.0000089694
C	0.0018032395	-0.0398652257	-2.5343660173	C	1.1386077108	2.0156851918	3.3608386388
C	0.1365169191	-2.1706764193	-1.3016836959	H	2.0677575085	1.7629079950	2.8220634577
C	0.0460166697	-0.7561819406	-3.7350453614	H	1.1004608724	3.1113366974	3.4796235042
C	0.1787479348	-2.8502381084	-2.5236456483	H	1.1977781155	1.5728573088	4.3690544674
C	0.1335638421	-2.1456375319	-3.7236342064	C	-1.3831205356	1.8571825618	3.3610477686
H	0.0130755972	-0.2422164472	-4.6997670669	H	-1.3853675026	1.4115918116	4.3696958921
H	0.2478144499	-3.9410326327	-2.5603765373	H	-1.4834174036	2.9490103229	3.4788606677
H	0.1674176570	-2.6919977511	-4.6718123987	H	-2.2732782239	1.4888269896	2.8230745313
C	-0.0958993766	1.5226342708	0.0000078697	C	-1.3831271657	1.8571843734	-3.3610274559
C	-0.1395665800	2.2102781710	1.2327216762	H	-1.4834332782	2.9490125156	-3.4788296819
C	-0.1395681632	2.2102809630	-1.2327043314	H	-1.3853704036	1.4116033188	-4.3696799706
C	-0.2277191095	3.6061538156	1.2114586270	H	-2.2732818774	1.4888161630	-2.8230579439
C	-0.2277204109	3.6061561604	-1.2114386563	C	1.1386000237	2.0156959998	-3.3608268087
C	-0.2708812632	4.2909859338	0.0000106709	H	1.1004509976	3.1113478773	-3.4796067266
H	-0.2642615940	4.1831932020	2.1396984366	H	2.0677527388	1.7629176465	-2.8220571609
H	-0.2642648846	4.1831984270	-2.1396768602	H	1.1977660283	1.5728725648	-4.3690447238
H	-0.3398226594	5.3836615474	0.0000104907				

Table S6 Coordinates of the planar optimized structure of **1** in the excited S_1 state calculated at the PBE0/def-SV(P) level of theory

	x	y	z		x	y	z
B	-0.0006796648	0.0218780242	-0.0379987342	C	0.1883427888	-2.9669530066	0.0088481293
C	0.0468645360	-0.7448384911	1.2924509109	C	-0.0933228125	1.4756957738	2.5789394337
C	0.0020839276	-0.0421453154	2.5088205915	C	-0.0946612830	1.5019245406	-2.6067212004
C	0.1348638246	-2.1474659901	1.2908992303	C	-1.0137851340	-3.9473353226	0.0419692686

C	0.0478923527	-0.7818017566	3.7492974923	H	-1.9648288335	-3.3895149564	0.0201291360
C	0.1787542369	-2.8496295954	2.5531357518	H	-0.9844404676	-4.6015441617	-0.8439855356
C	0.1352335133	-2.1701715490	3.7664472903	H	-1.0087108874	-4.5980085354	0.9339906730
H	0.0138082475	-0.2449668166	4.7000489512	C	1.5108483826	-3.7781791374	0.0420405933
H	0.2481292786	-3.9397557198	2.5629500919	H	1.5932723132	-4.4236576661	0.9341315265
H	0.1693006159	-2.7151958813	4.7123783892	H	1.5692027709	-4.4304440042	-0.8440067134
C	0.0470214343	-0.7495264985	-1.3259565498	H	2.3786415705	-3.0980414331	0.0199610853
C	0.0017472978	-0.0384670592	-2.5543019158	C	1.1432587333	1.9745343900	3.3725003443
C	0.1357767675	-2.1665441108	-1.3090908050	H	2.0710508534	1.7407748858	2.8241438610
C	0.0465833686	-0.7657369194	-3.7435896654	H	1.0893071345	3.0680597132	3.4956838370
C	0.1784220371	-2.8547225977	-2.5213522603	H	1.2103943607	1.5308802412	4.3814191519
C	0.1342367751	-2.1619440848	-3.7339555768	C	-1.3819008300	1.8155623227	3.3738714111
H	0.0141235658	-0.2554403488	-4.7115173461	H	-1.3908177718	1.3679219834	4.3831678449
H	0.2474899575	-3.9474536555	-2.5510862764	H	-1.4664533701	2.9072264574	3.4963381758
H	0.1684377087	-2.7132836684	-4.6782252901	H	-2.2735806597	1.4659876095	2.8272010412
C	-0.0958574158	1.5206565736	-0.0126566460	C	-1.3811166093	1.8677266622	-3.3792523354
C	-0.1402064158	2.2145572930	1.2253895465	H	-1.4826800050	2.9604965549	-3.4950933889
C	-0.1406924834	2.2267993712	-1.2438660187	H	-1.3833813600	1.4215698800	-4.3885668310
C	-0.2284228068	3.6063387696	1.2164823678	H	-2.2707623090	1.4981386752	-2.8411084936
C	-0.2287546828	3.6183036420	-1.2073696179	C	1.1368307135	2.0255391996	-3.3779288432
C	-0.2725656403	4.3080389322	0.0090332015	H	1.1003248835	3.1223120511	-3.4947401019
H	-0.2649394472	4.1783440567	2.1498595962	H	2.0650387917	1.7711431987	-2.8381219372
H	-0.2655408977	4.2000730314	-2.1339486277	H	1.1968845045	1.5821390644	-4.3867636639
H	-0.3416638828	5.3998094687	0.0153433671				

Table S7 Coordinates of the bowl-shaped optimized structure of **1** in the excited S₁ state calculated at the PBE0/def-SV(P) level of theory

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
B	-0.4303529778	-0.0299558129	0.0303495138	C	-0.2044458140	-2.9311757409	-0.0250705027
C	-0.1582927673	-0.7687910186	1.3234075284	C	-0.3161092097	1.4772901894	2.5176443854
C	0.0473779534	-0.0229175154	2.5128388702	C	-0.5766815098	1.4417365670	-2.5295822779
C	0.1011704488	-2.1630364314	1.2786726653	C	-1.7381044817	-3.1336994438	-0.0950787811
C	0.5183161536	-0.6866049588	3.6453991266	H	-2.2615781415	-2.1626876556	-0.0917323047
C	0.5709768643	-2.7932158824	2.4307092352	H	-2.0185546495	-3.6788330619	-1.0146256395
C	0.7766334046	-2.0598387450	3.6029462141	H	-2.0840400683	-3.7125470761	0.7791957795
H	0.7042212841	-0.1515154565	4.5795826864	C	0.4448471405	-4.3158399907	-0.0397065689
H	0.7963452191	-3.8621983488	2.4402270027	H	0.0729767648	-4.9287420444	0.7968666221
H	1.1521941124	-2.5663274616	4.4975918415	H	0.1858931987	-4.8595970466	-0.9640423746
C	-0.1504811165	-0.7382944602	-1.2977639723	H	1.5443663129	-4.2605392237	0.0385136255
C	0.0784001625	0.0603423949	-2.4685872105	C	0.2803848176	2.2080230229	3.7216264002

C	0.1955845030	-2.1127563199	-1.2608009495	H	1.3827320805	2.1555195057	3.7359085920
C	0.8658766253	-0.4676093737	-3.5060262550	H	-0.0204095645	3.2694178059	3.7230344267
C	0.9345102030	-2.6098318283	-2.3288735148	H	-0.0946135913	1.7769311647	4.6636337121
C	1.2674050074	-1.7930423549	-3.4368584998	C	-1.8574249883	1.5799018982	2.6263595908
H	1.0994726605	0.1194912806	-4.3962911628	H	-2.2042118214	1.0985684144	3.5575897226
H	1.3116147795	-3.6352806818	-2.3175165248	H	-2.1791557610	2.6371859474	2.6330048133
H	1.8225348814	-2.2321600112	-4.2716628340	H	-2.3445488577	1.0722032894	1.7767187681
C	-0.2080727171	1.4838543557	-0.0164609070	C	-2.1068523191	1.3341511745	-2.4141378493
C	0.0850291431	2.1530182460	1.1987020596	H	-2.5550702996	2.3431597389	-2.3894860089
C	0.0242798821	2.1063115296	-1.2890200223	H	-2.5128598593	0.7894594735	-3.2848095642
C	0.7781447810	3.3553338180	1.1097291244	H	-2.4060625180	0.7984344472	-1.4991289993
C	0.7651717692	3.2996720768	-1.3348140053	C	-0.2479017496	2.1923530260	-3.8159315135
C	1.1155254224	3.9191448553	-0.1447674455	H	-0.7051005203	3.1958592393	-3.7975453395
H	1.1154073739	3.8733870268	2.0106783010	H	0.8362174845	2.3127525877	-3.9749563945
H	1.0004010665	3.7856293861	-2.2836405325	H	-0.6642256474	1.6565640634	-4.6854399457
H	1.6327126119	4.8833542025	-0.1711628975				

Table S8 Coordinates of the optimized structure of **2** in the ground S_0 state calculated at the PBE0/def-SV(P) level of theory

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
B	0.0603513745	0.0018508948	-0.0208573163	H	-0.2296545078	4.2150414821	2.0673977935
C	0.0006528703	-0.7553544971	1.3001075126	H	0.0555296626	4.1505711330	-2.2191229419
C	-0.1062088475	-0.0258136126	2.5051546070	H	-0.1300668315	5.3947875849	-0.0789716958
C	0.0531050049	-2.1670126999	1.2849329732	C	0.1701203748	-2.9881813310	-0.0112032704
C	-0.1605480419	-0.7402678769	3.7066291856	C	-0.1648255791	1.5111026123	2.5528741021
C	-0.0044850698	-2.8426911882	2.5085228217	C	0.1736294258	1.4609020580	-2.5664162171
C	-0.1100168559	-2.1319728890	3.7015170107	C	-1.0574533238	-3.9235079496	-0.0922318142
H	-0.2434509774	-0.2238758422	4.6671274702	H	-1.9886484129	-3.3352382907	-0.1576284462
H	0.0319652504	-3.9348540077	2.5528084846	H	-1.0031514365	-4.5761888767	-0.9795245656
H	-0.1539181570	-2.6760943932	4.6505922418	H	-1.1258070481	-4.5731406254	0.7962850970
C	0.1764991862	-0.7690776605	-1.3332923372	C	1.4609111870	-3.8332085501	0.0785413962
C	0.2308820793	-0.0485658797	-2.5445200501	H	1.4550809114	-4.4791341245	0.9722985527
C	0.2287296346	-2.1780587004	-1.3151070725	H	1.5731427245	-4.4853469506	-0.8037110624
C	0.3389918235	-0.7456366580	-3.7492652179	H	2.3482296422	-3.1798265561	0.1352489503
C	0.3372210088	-2.8484709050	-2.5391300566	C	1.0272850293	2.0045542047	3.4035194726
C	0.3913972951	-2.1375097317	-3.7382037018	H	1.9834888135	1.7239053299	2.9298445690
H	0.3826538066	-0.2038526205	-4.7004572986	H	1.0106801062	3.1016429616	3.5146670789
H	0.3814415087	-3.9406402970	-2.5802460869	H	1.0060396702	1.5663897112	4.4152895436
H	0.4763009013	-2.6844197603	-4.6829045826	C	-1.4912521567	1.9137271124	3.2360522436
C	0.0048785313	1.5273646668	-0.0246601223	H	-1.5733742008	1.4727005354	4.2435113851

C	-0.1006129947	2.2268898912	1.1950762901	H	-1.5679992831	3.0085994810	3.3438440548
C	0.0617153224	2.2084343970	-1.2583843626	H	-2.3537288965	1.5681677902	2.6409060764
C	-0.1477685870	3.6251580050	1.1498974251	H	1.0692864743	1.8330606829	-3.1013972527
C	0.0126616370	3.6035768922	-1.2708866262	H	-0.6749633010	1.7644132643	-3.2105691363
C	-0.0915118240	4.3006217087	-0.0694347903				

Table S9 Coordinates of the planar optimized structure of **2** in the excited S₁ state calculated at the PBE0/def-SV(P) level of theory

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
B	0.0591541196	-0.0119401992	0.0033211522	H	-0.2295127163	4.2265609851	2.0543034467
C	0.0005601286	-0.7556994888	1.3007197076	H	0.0567330039	4.1408118776	-2.2321150056
C	-0.1070112641	-0.0290983016	2.5189782610	H	-0.1301717324	5.4225032674	-0.0957062250
C	0.0528904689	-2.1772801915	1.2947877955	C	0.1704998321	-2.9919689691	-0.0148321104
C	-0.1608552071	-0.7428636940	3.7144809784	C	-0.1651816934	1.5161632860	2.5543277726
C	-0.0045070219	-2.8481658122	2.5147363352	C	0.1729276352	1.4447976844	-2.5382873406
C	-0.1105563723	-2.1412417453	3.7176847350	C	-1.0554047733	-3.9302216817	-0.1133869124
H	-0.2437740155	-0.2256622997	4.6761847412	H	-1.9871532188	-3.3419303126	-0.1661334812
H	0.0320749875	-3.9417735725	2.5589642708	H	-1.0061883639	-4.5811812965	-1.0038793637
H	-0.1543187406	-2.6849421720	4.6660296339	H	-1.1162466000	-4.5830025170	0.7733733675
C	0.1752379138	-0.7702743894	-1.3118578346	C	1.4620666719	-3.8401537031	0.0572377984
C	0.2303373610	-0.0544156852	-2.5304756175	H	1.4492687556	-4.4897228558	0.9482813682
C	0.2283511513	-2.1739569349	-1.3125156833	H	1.5794250899	-4.4902135463	-0.8275247151
C	0.3393968096	-0.7468246456	-3.7570841401	H	2.3483559304	-3.1869149078	0.1264475489
C	0.3383566955	-2.8427381721	-2.5625589442	C	1.0261626000	2.0263639566	3.3987706249
C	0.3934233365	-2.1416259978	-3.7699805013	H	1.9821243755	1.7350903864	2.9315307955
H	0.3816119522	-0.1877850325	-4.6986692173	H	1.0146562598	3.1251119740	3.5072758763
H	0.3819989697	-3.9352291083	-2.5967016941	H	0.9974475561	1.5914926874	4.4118001921
H	0.4779830341	-2.6841674875	-4.7152075651	C	-1.4914489486	1.9353735811	3.2311055579
C	0.0048362615	1.5095324472	-0.0127228056	H	-1.5666590493	1.4981477108	4.2407638902
C	-0.1003579921	2.2226595971	1.1928941471	H	-1.5731980393	3.0315399399	3.3355440774
C	0.0614902368	2.1993401196	-1.2462522578	H	-2.3536075909	1.5790282504	2.6422582934
C	-0.1474314661	3.6424889982	1.1330352675	H	1.0600769579	1.8287382564	-3.0953094189
C	0.0126223597	3.6108922635	-1.2739221134	H	-0.6657391045	1.7608062601	-3.2031058146
C	-0.0918224396	4.3301192353	-0.0821200616				

Table S10 Coordinates of the bowl-shaped optimized structure of **2** in the excited S_1 state calculated at the PBE0/def-SV(P) level of theory

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
B	-0.4351732551	-0.0349408035	-0.0251599336	H	0.8797690334	3.8375969316	2.2924928787
C	-0.1404585293	-0.7526513113	1.2988158226	H	0.9771302609	3.9196119415	-2.0144519572
C	0.1027076213	0.0480910947	2.4677322405	H	1.4382876481	4.9795063789	0.1852491616
C	0.2117378627	-2.1248357361	1.2492387893	C	-0.2105885068	-2.9461779557	0.0214181974
C	0.9270313960	-0.4710004085	3.4810000995	C	-0.5751115681	1.4168260607	2.5490036411
C	0.9867935246	-2.6122961795	2.2962615429	C	-0.2309316410	1.4600614160	-2.4841910084
C	1.3404228274	-1.7917787305	3.3970031998	C	-1.7420783435	-3.1502702038	0.1217931127
H	1.1755088368	0.1161903827	4.3671524273	H	-2.2666293141	-2.1797015469	0.1257803531
H	1.3783050747	-3.6322276256	2.2726175534	H	-2.1038774261	-3.7313715409	-0.7444523055
H	1.9191548571	-2.2279695331	4.2172137583	H	-2.0048055482	-3.6936376420	1.0476749877
C	-0.1734104531	-0.7812109037	-1.3167683793	C	0.4430100719	-4.3288081517	0.0246529874
C	0.0343047521	-0.0359403982	-2.5017353386	H	0.2098741217	-4.8708332062	0.9569688101
C	0.0697897086	-2.1783090832	-1.2879525242	H	0.0518563269	-4.9449848704	-0.8006714775
C	0.4598516853	-0.6878998255	-3.6559092054	H	1.5398944082	-4.2701917675	-0.0830007196
C	0.5008212284	-2.8040102839	-2.4583640751	C	-0.2406521935	2.1618291802	3.8371397531
C	0.6869374489	-2.0671996089	-3.6342799112	H	0.8428728343	2.3134924826	3.9727196342
H	0.6316706209	-0.1223060013	-4.5787815254	H	-0.7276432865	3.1512556039	3.8407192883
H	0.7097077709	-3.8763930392	-2.4814484663	H	-0.6217743354	1.6047023060	4.7094386935
H	1.0276167124	-2.5769434289	-4.5409087796	C	-2.1045481926	1.2784356177	2.4553359209
C	-0.2239573612	1.4762156646	0.0333303445	H	-2.4874837733	0.7185624117	3.3269740848
C	-0.0109533619	2.1086931365	1.3035245285	H	-2.5726452679	2.2785761897	2.4455083516
C	0.0627526041	2.1567253986	-1.1734929331	H	-2.4057984440	0.7456925771	1.5391455759
C	0.6636831485	3.3426117731	1.3435629486	H	0.3181958840	1.9532064896	-3.3044958268
C	0.6768754614	3.4005224299	-1.0974126014	H	-1.3089295113	1.6161850785	-2.7066825334
C	0.9749406010	3.9885576785	0.1548863160				

Table S11 Coordinates of the optimized structure of **5** in the ground S_0 state calculated at the PBE0/def-SV(P) level of theory

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
B	-0.0007581224	-0.2018110269	0.0112296110	H	-8.4065315335	-5.0771815308	-0.1367560593
C	-1.3245964616	-0.9550412955	-0.0026696103	C	0.0175613847	5.5958251629	0.0538389770
C	-3.7391290466	-2.3726508357	-0.0408772489	C	0.0264050630	8.4144442511	0.0742570467
C	-1.3101458954	-2.3641169568	-0.0103675688	C	-0.9148441746	6.3155478350	0.8176658514
C	-2.5390614223	-0.2409205800	-0.0126951533	C	0.9544958106	6.3207000536	-0.6995173941
C	-3.7313334440	-0.9686818453	-0.0330613665	C	0.9585481977	7.7137701453	-0.6911162189
C	-2.5174155729	-3.0598555737	-0.0272963398	C	-0.9101544136	7.7085923490	0.8294242994

H	-4.6956432603	-0.4534045742	-0.0167080309	H	-1.6385387900	5.7730251151	1.4333955695
H	-2.5163785959	-4.1545856735	-0.0598467436	H	1.6748115710	5.7826200442	-1.3230615814
C	0.0040445766	1.3186644785	0.0209963967	H	1.6922303490	8.2569640885	-1.2948201894
C	0.0128540379	4.1136497021	0.0427865458	H	-1.6404243621	8.2475634250	1.4409953292
C	-1.2257244539	2.0115373609	0.0239570801	H	0.0298384901	9.5086382456	0.0822087672
C	1.2381589321	2.0037412332	0.0281596375	C	5.0020408209	-3.1469802106	-0.0097263226
C	1.2188730097	3.3997734287	0.0371192787	C	7.4320160676	-4.5755684178	-0.0315817103
C	-1.1976435141	3.4073838896	0.0373931874	C	6.0986845089	-2.6958990544	-0.7613353090
H	2.1515679391	3.9693901625	0.0690045002	C	5.1508655385	-4.3306561836	0.7303330058
H	-2.1267296511	3.9833383215	0.0157203509	C	6.3518597457	-5.0364239595	0.7211089899
C	1.3183134078	-0.9634939062	0.0111850770	C	7.2994580159	-3.4019379357	-0.7736339406
C	3.7240199959	-2.3964898541	0.0003218942	H	5.9990833999	-1.7907231463	-1.3678394845
C	2.5373552778	-0.2571314217	0.0153174726	H	4.3188319773	-4.6892938483	1.3436308631
C	1.2949482135	-2.3724422263	0.0032700137	H	6.4470346894	-5.9513323985	1.3141480392
C	2.4978700982	-3.0758709666	-0.0004829822	H	8.1369478149	-3.0357895189	-1.3755839100
C	3.7251091442	-0.9924798824	0.0088619193	H	8.3752695993	-5.1301276109	-0.0400039732
H	2.4901293744	-4.1705677077	-0.0333003500	C	-3.3695736309	1.7298204473	1.2661241668
H	4.6924116561	-0.4834248366	0.0382080560	H	-2.8397846673	1.4076800409	2.1788032179
C	-2.5899354118	1.2959928919	0.0046147221	H	-4.3794389399	1.2870481876	1.2836911811
C	2.5977528915	1.2793542734	0.0397556198	H	-3.4852951867	2.8258506136	1.3068071861
C	-0.0100006194	-3.1367878911	-0.0131099687	C	-3.3497309149	1.7570514667	-1.2593778014
H	-0.0166977607	-3.8280516313	0.8521240964	H	-4.3594535959	1.3151659685	-1.3001862989
H	-0.0075621659	-3.8042827678	-0.8968511856	H	-2.8064377171	1.4530248760	-2.1703328038
C	-5.0216999600	-3.1150150709	-0.0659410591	H	-3.4647754618	2.8535312009	-1.2806726560
C	-7.4600393358	-4.5284631623	-0.1169428328	C	3.3467869800	1.7007319708	1.3241545972
C	-5.1869075812	-4.2973386164	0.6727804331	H	2.7909606473	1.3762694185	2.2203236631
C	-6.1062422038	-2.6574627701	-0.8310799965	H	3.4679773679	2.7956588768	1.3757977904
C	-7.3111424099	-3.3560318540	-0.8577984931	H	4.3525943573	1.2501042994	1.3650270649
C	-6.3920799860	-4.9956315370	0.6491411274	C	3.3934695378	1.7426244903	-1.2007849142
H	-4.3646460827	-4.6608663372	1.2962968962	H	3.5164284024	2.8384531000	-1.2112575616
H	-5.9936175033	-1.7532579399	-1.4367481802	H	2.8726686174	1.4478414805	-2.1278317078
H	-8.138842238	-2.9850085430	-1.4701542835	H	4.4014922978	1.2955931248	-1.2180485413
H	-6.5001624684	-5.9096469105	1.2413427029				

Table S12 Coordinates of the planar-like optimized structure of **5** in the excited S₁ state calculated at the PBE0/def-SV(P) level of theory

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
B	-0.0011227731	-0.2137317280	0.0140813935	H	-8.4226829729	-5.0829640315	-0.0904600819
C	-1.3212740296	-0.9472082372	0.0076419650	C	0.0177993143	5.5806259608	0.0390983066
C	-3.7530431373	-2.3778664168	-0.0239455257	C	0.0270170827	8.4166087293	0.0558041977

C	-1.3164782324	-2.3674863955	0.0055164943	C	-1.1203323549	6.3268406201	0.4549459425
C	-2.5483270430	-0.2403685180	-0.0057850513	C	1.1608302352	6.3243063705	-0.3677973628
C	-3.7347119258	-0.9667382710	-0.0255529598	C	1.1603771814	7.7090652144	-0.3638659381
C	-2.5183763937	-3.0585326015	-0.0050996760	C	-1.1109078538	7.7115246563	0.4671956241
H	-4.6964444197	-0.4463267768	-0.0080903755	H	-2.0106283848	5.8032510093	0.8090841972
H	-2.5096641306	-4.1533024436	-0.0354775814	H	2.0477918639	5.7991795435	-0.7279652521
C	0.0042709784	1.3101054466	0.0166383267	H	2.0503499650	8.2508846680	-0.6973087647
C	0.0130568035	4.1302115895	0.0301835201	H	-1.9973382554	8.2551447133	0.8070771927
C	-1.2407009616	2.0191419063	0.0250009125	H	0.0305617279	9.5105185425	0.0622766301
C	1.2535286256	2.0113406636	0.0137561958	C	5.0071237998	-3.1461095736	-0.0223837851
C	1.2309060507	3.3922201840	0.0095788863	C	7.4474175066	-4.5806176456	-0.0459276821
C	-1.2094218119	3.3997115494	0.0429437426	C	6.1592558333	-2.6227234521	-0.6435420856
H	2.1705493102	3.9466879425	0.0352674272	C	5.1183911387	-4.4128236231	0.5859015174
H	-2.1455734731	3.9603750747	0.0247206615	C	6.3177721692	-5.1172417117	0.5751018580
C	1.3147791128	-0.9551894312	0.0095655102	C	7.3582418944	-3.3278398145	-0.6558305611
C	3.7377427047	-2.4016026877	-0.0110781537	H	6.1030479863	-1.6583458535	-1.1562936873
C	2.5467228017	-0.2560278691	0.0026333542	H	4.2542636016	-4.8378604837	1.1040235715
C	1.3009237668	-2.3759487188	0.0083158113	H	6.3746386601	-6.0938992138	1.0660999406
C	2.4982067527	-3.0743985686	0.0026194846	H	8.2318532410	-2.8991251047	-1.1570711904
C	3.7281982616	-0.9898923711	-0.0119700805	H	8.3905326259	-5.1352418713	-0.0551181336
H	2.4823039604	-4.1690390743	-0.0276127022	C	-3.3828864871	1.7382041096	1.2711933870
H	4.6929058748	-0.4754670553	0.0130020731	H	-2.8498653684	1.4188157974	2.1829109913
C	-2.6067770007	1.3008558620	0.0090399109	H	-4.3889710065	1.2873414086	1.2922527123
C	2.6151437817	1.2846365468	0.0277605382	H	-3.5086706470	2.8341926717	1.3124784067
C	-0.0102470107	-3.1381383315	0.0011911050	C	-3.3671961227	1.7624195720	-1.2539370512
H	-0.0129247815	-3.8257161328	0.8701757346	H	-4.3729804312	1.3120015869	-1.2944638811
H	-0.0112969659	-3.8123029963	-0.8783152075	H	-2.8235526404	1.4594782399	-2.1650119834
C	-5.0275131059	-3.1148699209	-0.0417874822	H	-3.4928569571	2.8588338022	-1.2771946084
C	-7.4762088186	-4.5341673056	-0.0768130157	C	3.3601098187	1.7077330495	1.3134824760
C	-5.1519783037	-4.3758271125	0.5749202635	H	2.8009444789	1.3846763141	2.2080820267
C	-6.1701122114	-2.5890608288	-0.6774639420	H	3.4905999094	2.8026895730	1.3667854049
C	-7.3735914316	-3.2867499849	-0.6952788837	H	4.3621048703	1.2490661958	1.3573674194
C	-6.3557297589	-5.0730288474	0.5584619100	C	3.4121768259	1.7500902727	-1.2107713711
H	-4.2949854596	-4.8021156862	1.1038722787	H	3.5461578725	2.8456410923	-1.2220366407
H	-6.1029221400	-1.6288424923	-1.1967624970	H	2.8915353242	1.4577522381	-2.1386040198
H	-8.2398520853	-2.8563543512	-1.2077419004	H	4.4163781875	1.2950259755	-1.2280990349
H	-6.4230929009	-6.0455539787	1.0563188512				

Table S13 Coordinates of the bowl-shaped optimized structure of **5** in the excited S₁ state calculated at the PBE0/def-SV(P) level of theory

	x	y	z		x	y	z
B	-0.3168481368	-0.1520255679	0.2777639541	C	-1.7247252106	2.0982878679	2.3387181875
C	-0.7200504789	-0.7473644317	1.6445074478	H	-2.4415868736	1.8805130168	3.1511072075
C	-0.4651388825	0.0197215213	2.8257583009	H	-1.6700759051	3.1921824755	2.1984615377
C	-1.0375373716	-2.1434361335	1.7150542751	H	-2.1088172792	1.6547165127	1.4047367532
C	-0.3312252071	-0.6609752453	4.0199438631	H	1.9427942561	0.7893356530	-2.7580756748
C	-0.8741356432	-2.7869692960	2.9269790594	H	0.2310181988	1.2043462768	-2.6779843112
C	-0.5139299691	-2.0712210818	4.1003280587	C	1.0937895973	-4.0720561852	-3.7405859647
H	-0.0376799354	-0.1257675307	4.9233481952	C	1.2774690080	-3.7331927614	-5.0952841699
H	-1.0719003586	-3.8560973115	3.0090194197	C	1.3345086096	-5.4087297853	-3.3670314980
C	-0.1415518676	-1.1380533667	-0.8614243046	C	1.6793604279	-4.6829755132	-6.0295194699
C	0.6524877584	-0.7531152049	-1.9713007413	H	1.0720758645	-2.7112589415	-5.4261820021
C	-0.5564238817	-2.4924036012	-0.7175661303	C	1.7373022218	-6.3584688745	-4.3005579004
C	1.0445012127	-1.7088585972	-2.8947857227	H	1.2340958411	-5.6997514730	-2.3175208120
C	-0.1257505156	-3.4323139664	-1.6477000609	C	1.9120740092	-6.0026437775	-5.6391307962
C	0.6689622005	-3.0653923536	-2.7525093659	H	1.8040516380	-4.3913386973	-7.0771218062
H	1.7000872935	-1.4208876202	-3.7230603344	H	1.9276241238	-7.3869314089	-3.9777610628
H	-0.4374916342	-4.4750727315	-1.5648697612	H	2.2291405500	-6.7493534632	-6.3733823442
C	0.4728042197	1.1413861919	0.3024061927	C	3.3193814253	4.3480626113	0.5238120075
C	0.6204475161	1.8749838338	1.5107362358	C	3.6000267340	5.1566058256	-0.5937745613
C	1.2480163859	1.4828740131	-0.8331058583	C	4.0137691776	4.6248405884	1.7166993161
C	1.5584415586	2.9003615698	1.5667163802	C	4.5280004724	6.1916394935	-0.5220844735
C	2.1607827450	2.5238583599	-0.7525845871	H	3.0581685615	4.9869595112	-1.5286284059
C	2.3381119451	3.2498392598	0.4454168678	C	4.9417917583	5.6595025989	1.7892663487
H	1.6847005001	3.4862745483	2.4791528965	H	3.8443097039	3.9954973470	2.5951664405
H	2.7919454616	2.7562540679	-1.6167098132	C	5.2054749427	6.4508085970	0.6701567116
C	-1.5192602408	-2.8362190444	0.4347886014	H	4.7178328069	6.8092258639	-1.4057054435
C	-0.3227990614	1.5399870422	2.6827280189	H	5.4737486954	5.8434753892	2.7281263694
C	1.0490720777	0.7017045504	-2.1164963541	H	5.9355091109	7.2639194966	0.7266591636
C	-2.9133526811	-2.2636711272	0.0880302375	C	-0.3869022549	-2.7658410756	5.3772751233
H	-2.8687298725	-1.1711721971	-0.0556139937	C	-0.5516732102	-2.0889476125	6.6102698431
H	-3.2838729093	-2.7160050116	-0.8486959833	C	-0.0835448217	-4.1485713223	5.4314909825
H	-3.6347127917	-2.4822144477	0.8961081067	C	-0.4236676423	-2.7550150019	7.8206149189
C	-1.6724466534	-4.3438511582	0.6291834780	H	-0.8185003773	-1.0296222208	6.6148135693
H	-2.3793125489	-4.5623603865	1.4475368556	C	0.0544846281	-4.8092763965	6.6436699499
H	-2.0896558902	-4.8093507156	-0.2783308318	H	0.0866479575	-4.7012336436	4.5045881571
H	-0.7107769565	-4.8356011449	0.8553729366	C	-0.1175019396	-4.1191834848	7.8472821658
C	0.1264353051	2.1904091159	3.9905872692	H	-0.5694952824	-2.2083114603	8.7569561951

H	1.1358235324	1.8633156703	4.2938621090	H	0.3073210875	-5.8736213793	6.6537865682
H	0.1373336267	3.2878743096	3.8931825282	H	-0.0120885482	-4.6418208855	8.8025675641
H	-0.5785576621	1.9561692751	4.8063719865				

Table S14 Coordinates of the optimized structure of **6'** in the ground S_0 state calculated at the PBE0/def-SV(P) level of theory

	x	y	z		x	y	z
B	-0.0002450358	-0.1689846173	0.0390483700	H	1.6658963686	5.8161174212	1.4663744073
C	1.3223484786	-0.9235458589	0.0432569601	H	-1.6840961460	5.8395287920	-1.2412766687
C	3.7379893718	-2.3454247187	0.0357708029	H	-1.7068620262	8.2879449183	-1.2168570016
C	1.3072522894	-2.3324999101	0.0271041606	H	1.6592514884	8.2990964433	1.4743620546
C	2.5381158713	-0.2116790915	0.0572597640	C	5.0179468564	-3.0889609975	0.0258071198
C	3.7294494637	-0.9408159261	0.0542050374	C	7.4655802924	-4.5149788961	0.0007703806
C	2.5137024450	-3.0294764813	0.0238557861	C	5.1674905869	-4.2988260059	0.7285198635
H	4.6932622700	-0.4257846711	0.0938862333	C	6.1288898098	-2.6208082836	-0.6860487867
H	2.5101234899	-4.1239366694	-0.0182383903	C	7.3387661515	-3.3146563769	-0.7073982903
C	-1.3195839485	-0.9287396481	0.0114531830	C	6.3636860766	-4.9988978881	0.7210263102
C	-3.7287565022	-2.3601296384	-0.0549189410	H	4.3308276036	-4.6864260958	1.3173097449
C	-2.5381455503	-0.2217240724	-0.0029273848	H	6.0453473840	-1.6983256845	-1.2684432753
C	-1.2985011308	-2.3376399547	-0.0052350880	H	8.1709099822	-2.9127895619	-1.2890123593
C	-2.5017372287	-3.0392290904	-0.0392233211	H	6.4785645305	-5.9318686185	1.2789827909
C	-3.7262475107	-0.9555083391	-0.0350098859	C	-3.3663982873	1.7283176179	1.3058250338
H	-2.4929619727	-4.1335658805	-0.0836858368	H	-4.3732977668	1.2786912513	1.3269083402
H	-4.6925747971	-0.4439954232	-0.0172550411	H	-3.4866333548	2.8230929937	1.3637289494
C	-0.0034544063	1.3509540157	0.0562622817	H	-2.8255641290	1.3963371890	2.2083992427
C	-0.0094011000	4.1487319875	0.0923044352	C	-3.3718045800	1.7879381781	-1.2189101626
C	1.2264030669	2.0430607920	0.0835951854	H	-4.3796040679	1.3415061656	-1.2564715471
C	-1.2362920045	2.0383038704	0.0463441848	H	-2.8356467045	1.4995289328	-2.1391998087
C	-1.2154571825	3.4339838738	0.0652801527	H	-3.4936315528	2.8839957649	-1.2233564049
C	1.1996813199	3.4386919513	0.1020071795	C	3.3472407410	1.7514116904	1.3620982268
H	-2.1486326466	4.0032940324	0.0889244258	H	3.4627169420	2.8471800497	1.4112705702
H	2.1305970422	4.0121258120	0.0958796068	H	4.3562101543	1.3073624102	1.3957219486
C	0.0060323249	-3.1035738499	0.0000622682	H	2.8004974124	1.4245025782	2.2630092514
H	0.0183649241	-3.7705562235	-0.8839467131	C	3.3732946887	1.7925680910	-1.1628713328
H	-0.0033217181	-3.7952160215	0.8650636958	H	3.4901976221	2.8890154768	-1.1761671681
C	-2.5969214635	1.3150511472	0.0310061098	H	2.8459636493	1.4942541186	-2.0850512588
C	2.5901280640	1.3254568709	0.0843913912	H	4.3828546416	1.3490285762	-1.1878814229
C	-5.0058214487	-3.1077126621	-0.0931320672	O	-8.6480349856	-5.1488545027	-0.2631192011
C	-7.4491556689	-4.5394304905	-0.1675626125	O	0.0627639149	9.8055905145	0.2133215219
C	-6.1082414133	-2.6368472421	-0.8300141739	O	8.5869269057	-5.2620633713	0.0484465785

C	-5.1677456477	-4.3126825989	0.6010667320	C	-8.8495052450	-6.3594841557	0.4080597487
C	-6.3662461761	-5.0258042069	0.5734598322	H	-8.1530640485	-7.1451823585	0.0562557329
C	-7.3050271168	-3.3347107504	-0.8710637951	H	-9.8809929527	-6.6717219035	0.1853944255
H	-6.0146149122	-1.7128976392	-1.4083797743	H	-8.7383745073	-6.2456055547	1.5038665194
H	-4.3429538389	-4.6996642429	1.2068843497	C	-0.8610699110	10.5798576392	-0.4963867645
H	-6.4446321774	-5.9542626282	1.1427290531	H	-0.7885888183	10.4087114338	-1.5879790785
H	-8.1541345230	-2.9711057857	-1.4556514152	H	-0.6155854306	11.6313198465	-0.2837784738
C	-0.0118400381	5.6290453923	0.1089374269	H	-1.9004011523	10.3812115380	-0.1700759885
C	-0.0146910259	8.4616492271	0.1374915682	C	9.7212118187	-4.8288832735	-0.6460886612
C	0.9313671775	6.3544272120	0.8599646720	H	9.5356230172	-4.7624507103	-1.7357063301
C	-0.9506266000	6.3658329794	-0.6230148263	H	10.5045498095	-5.5799456773	-0.4635184185
C	-0.9611394738	7.7607532032	-0.6183532898	H	10.0757024762	-3.8451593113	-0.2817052139
C	0.9325720461	7.7403679546	0.8787863267				

Table S15 Coordinates of the planar-like optimized structure of **6'** in the excited S₁ state calculated at the PBE0/def-SV(P) level of theory

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
B	0.0067188282	-0.1258403753	-0.3166721425	H	1.7901224116	5.8010303276	1.3361118991
C	1.3069761863	-0.8933293952	-0.3064290607	H	-1.7959235538	5.9237692869	-1.0526535988
C	3.7061606867	-2.3622230469	-0.0873210822	H	-1.8198881617	8.3628382096	-0.9163352674
C	1.2935337048	-2.3093517505	-0.4083788314	H	1.7860777898	8.2750221681	1.4419238166
C	2.5316785704	-0.2037253769	-0.1200620188	C	4.9594933247	-3.1195736477	0.0304245891
C	3.7019318385	-0.9495301376	-0.0267219192	C	7.3834326385	-4.5878352386	0.2602955048
C	2.4729498457	-3.0233557146	-0.2761947361	C	4.9863227852	-4.4301436074	0.5583210936
H	4.6570543585	-0.4442288049	0.1406625718	C	6.1939204354	-2.5807727333	-0.3761746171
H	2.4569538147	-4.1142638867	-0.3727962768	C	7.3868902984	-3.2907091856	-0.2686384153
C	-1.3180327166	-0.8896979703	-0.3403045612	C	6.1638126022	-5.1479372127	0.6732015935
C	-3.7177612259	-2.3556638684	-0.1457620659	H	4.0582424588	-4.8834666765	0.9171943399
C	-2.5460995958	-0.1911685527	-0.1831023189	H	6.2241229252	-1.5828799136	-0.8221131029
C	-1.2968839987	-2.3126824327	-0.4391699755	H	8.3132053540	-2.8254037741	-0.6122326164
C	-2.4732111899	-3.0227357638	-0.3081489522	H	6.1744286592	-6.1558348802	1.0966839062
C	-3.7149152930	-0.9337063622	-0.1050659582	C	-3.3560267826	1.7358852001	1.1878087207
H	-2.4470751178	-4.1132979881	-0.3913186461	H	-4.3738984029	1.3096951272	1.2167030745
H	-4.6673703989	-0.4202048037	0.0423119090	H	-3.4551453327	2.8303225134	1.2747373312
C	-0.0069370718	1.3698094802	-0.1472161499	H	-2.8069476831	1.3754446259	2.0743615764
C	-0.0068094248	4.1795070840	0.0521213665	C	-3.4068351068	1.8369523078	-1.3331628192
C	1.2263409103	2.0663176446	-0.0460974230	H	-4.4167799856	1.3902892523	-1.3603473083
C	-1.2394543201	2.0707625604	-0.0952428405	H	-2.8862020870	1.5649139720	-2.2672189719
C	-1.2149449971	3.4588666792	-0.0093657895	H	-3.5244487338	2.9337455390	-1.3174070633
C	1.2009438347	3.4534046565	0.0475653609	C	3.3157510971	1.7223988089	1.2709996599

H	-2.1496749086	4.0243745954	0.0489932825	H	3.4254784658	2.8164367814	1.3583842600
H	2.1371678610	4.0175272478	0.0866633030	H	4.3264861230	1.2827976849	1.3177986717
C	0.0021109031	-3.0227925466	-0.7590809548	H	2.7477580911	1.3663310485	2.1474035740
H	0.0088408352	-3.1954638696	-1.8578600124	C	3.4081114766	1.8298914748	-1.2487984005
H	-0.0068317818	-4.0329690598	-0.3114462047	H	3.5342925682	2.9260565979	-1.2280160519
C	-2.6067417611	1.3480581472	-0.1058109622	H	2.8995793053	1.5629585950	-2.1909664414
C	2.5893022021	1.3359231957	-0.0356612368	H	4.4127091983	1.3721570698	-1.2615734648
C	-4.9585688545	-3.1017575804	-0.0380226712	O	-8.5687368221	-5.1789379216	0.2577699942
C	-7.3833971739	-4.5744827442	0.1819353030	O	0.0771053358	9.8318595675	0.4029500415
C	-6.2246952575	-2.5045503919	-0.3009591042	O	8.4789314605	-5.3594630349	0.4093053374
C	-4.9748004365	-4.4718856218	0.3380392051	C	-8.6467144448	-6.5338908372	0.6257585202
C	-6.1482617918	-5.1955306440	0.4514900789	H	-8.1043179640	-7.1767783546	-0.0916979370
C	-7.3991117737	-3.2147294157	-0.1983217953	H	-9.7144535877	-6.7949390574	0.6106772043
H	-6.2727464924	-1.4631673964	-0.6250445510	H	-8.2464131129	-6.6975307663	1.6432361847
H	-4.0352283895	-4.9721680083	0.5809227348	C	-0.9089953350	10.6279343805	-0.1852385342
H	-6.1022700451	-6.2416437410	0.7602357251	H	-0.9398532502	10.5008731938	-1.2851690570
H	-8.3649221010	-2.7517232304	-0.4153694013	H	-0.6472471038	11.6720469933	0.0448698629
C	-0.0066339946	5.6508000929	0.1303111449	H	-1.9139656330	10.4112088347	0.2271806886
C	-0.0073610404	8.4892635127	0.2782868321	C	9.7245371047	-4.8522730323	0.0251795052
C	1.0023530196	6.3564815961	0.8192861418	H	9.7565457634	-4.6172609987	-1.0564387847
C	-1.0096760966	6.4223276219	-0.4783834091	H	10.4623476243	-5.6398436810	0.2408593703
C	-1.0208030126	7.8149610252	-0.4122386566	H	9.9918122393	-3.9430174060	0.5978277314
C	1.0057027256	7.7397177155	0.8943231666				

Table S16 Coordinates of the bowl-shaped optimized structure of **6'** in the excited S₁ state calculated at the PBE0/def-SV(P) level of theory

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
B	-2.0510991391	0.4142060439	-0.0802774337	C	-6.3131263565	-3.5118296207	-0.2289786487
C	-1.9838189301	1.3556222052	-1.3042332841	C	-7.2038717038	-3.6164018118	0.8511995557
C	-1.4616106382	2.6739288304	-1.1283191392	C	-6.5603626844	-4.3505542728	-1.3359082088
C	-2.6937707974	0.9947666622	-2.4895147259	C	-8.2834307315	-4.4981777408	0.8424133610
C	-1.8123083570	3.6472467079	-2.0461536876	H	-7.0718015231	-2.9663832265	1.7207319144
C	-3.0085476676	1.9934768097	-3.3927244694	C	-7.6282369663	-5.2329413639	-1.3600782845
C	-2.6015870116	3.3404233310	-3.1871008817	H	-5.8763031596	-4.3305169346	-2.1890763788
H	-1.4502222283	4.6679848943	-1.9207751664	C	-8.5060960925	-5.3185028351	-0.2695192203
H	-3.6236101847	1.7628515066	-4.2629875481	H	-8.9507709132	-4.5268695973	1.7064080342
C	-3.0255236430	-0.7459664843	-0.1659391790	H	-7.8026350854	-5.8879449363	-2.2179443604
C	-3.4832934044	-1.3379967899	1.0377288929	C	-1.4822970015	3.0407376073	5.0547227965
C	-3.6435850495	-1.0844834214	-1.3995986512	C	-2.4498292624	2.8351675414	6.0611905135
C	-4.5422626820	-2.2324771882	1.0064537841	C	-0.4435665520	3.9373957420	5.3535917693

C	-4.7091034713	-1.9786591642	-1.3975993980	C	-2.3845725533	3.4878587558	7.2809474533
C	-5.1791982725	-2.5707344919	-0.2068534852	H	-3.2934007077	2.1668617718	5.8671607752
H	-4.8811364121	-2.6978434126	1.9381781711	C	-0.3622168478	4.6004734128	6.5769215488
H	-5.2317455338	-2.2178931896	-2.3259437098	H	0.3502800577	4.1039155673	4.6198557845
C	-1.7149564067	1.0280816111	1.2667115048	C	-1.3379183119	4.3807985159	7.5561625733
C	-1.1272838689	2.3202412556	1.3487609487	H	-3.1474831710	3.3318477260	8.0483421475
C	-2.2043643830	0.3997686625	2.4397820532	H	0.4758716346	5.2766485724	6.7587798755
C	-1.0711778440	2.9585323846	2.5830680372	C	-2.9492075851	4.3786649784	-4.1449345116
C	-2.1266229834	1.0584370170	3.6569662020	C	-2.9406673316	5.7558554175	-3.7895790220
C	-1.5602366172	2.3486615953	3.7569591585	C	-3.3207652685	4.0751468450	-5.4789368441
H	-0.6688575163	3.9702810267	2.6642850130	C	-3.2835833052	6.7415088110	-4.6882383875
H	-2.4950737162	0.5626372754	4.5613110626	H	-2.6937097082	6.0471069802	-2.7665920845
C	-3.0608305859	-0.4823972616	-2.6925509208	C	-3.6597141846	5.0561706843	-6.3956451427
C	-0.5304896176	2.9283509967	0.0658156421	H	-3.3137522766	3.0367376371	-5.8165092346
C	-2.7727924907	-1.0000665435	2.3323603086	C	-3.6478071272	6.4093324788	-6.0097764449
C	-1.7422634681	-1.2332124846	-3.0017394042	H	-3.2936449545	7.7954968405	-4.3997051860
H	-1.0228155546	-1.1218563355	-2.1732176327	H	-3.9252427402	4.7651988787	-7.4137533787
H	-1.9437080828	-2.3108122382	-3.1355895171	O	-9.5181393908	-6.2056427865	-0.3802150795
H	-1.2769360611	-0.8418372288	-3.9248231219	O	-1.3542236105	4.9695799464	8.7706452591
C	-3.9913129413	-0.6759234448	-3.8899246600	O	-3.9615543919	7.4292979916	-6.8100361178
H	-3.5309404458	-0.2830408071	-4.8125101780	C	-0.3383775706	5.8716452002	9.0994958104
H	-4.1755302499	-1.7475893876	-4.0676483120	H	-0.3203016225	6.7398809977	8.4121023174
H	-4.9667371259	-0.1805619785	-3.7442574315	H	-0.5542804305	6.2281044781	10.1181928266
C	-0.2067492139	4.4134242908	0.2274650730	H	0.6586202179	5.3893775987	9.0927402888
H	-1.1041619718	5.0133926964	0.4573795163	C	-10.4164751346	-6.3421322535	0.6818348154
H	0.5216021596	4.5635887586	1.0405767640	H	-10.9611250725	-5.3992821729	0.8845923758
H	0.2608533961	4.8151823338	-0.6874650177	H	-11.1413410570	-7.1140432493	0.3813998692
C	0.7991406049	2.1921887523	-0.2283907266	H	-9.9093896333	-6.6686963589	1.6107341282
H	1.2693879975	2.5887688932	-1.1466705104	C	-4.3457121987	7.1857943056	-8.1401021388
H	1.4999369128	2.3256606514	0.6147317861	H	-5.2564289345	6.5607195285	-8.1879461281
H	0.6290329036	1.1107104566	-0.3615627410	H	-4.5583982328	8.1691501172	-8.5833075035
H	-3.4293870977	-1.2117815035	3.1939862375	H	-3.5339783403	6.6980870319	-8.7108439153
H	-1.9188554533	-1.7062116195	2.4298214253				

7. NMR spectra

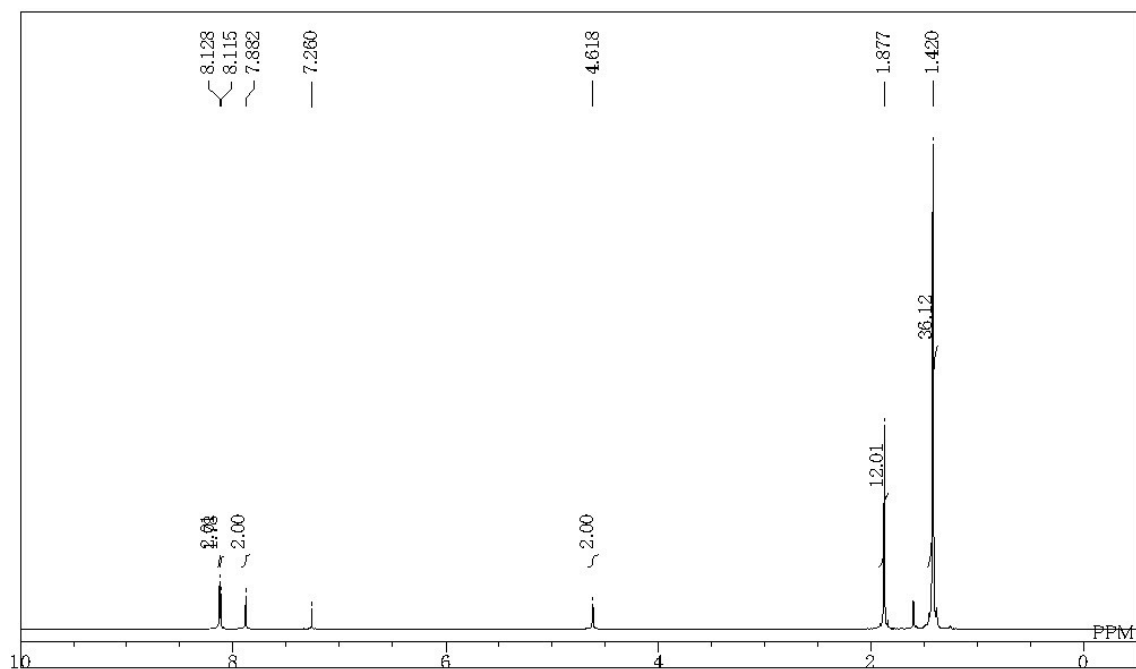


Fig. S18 ¹H NMR spectrum of **4** in CDCl₃.

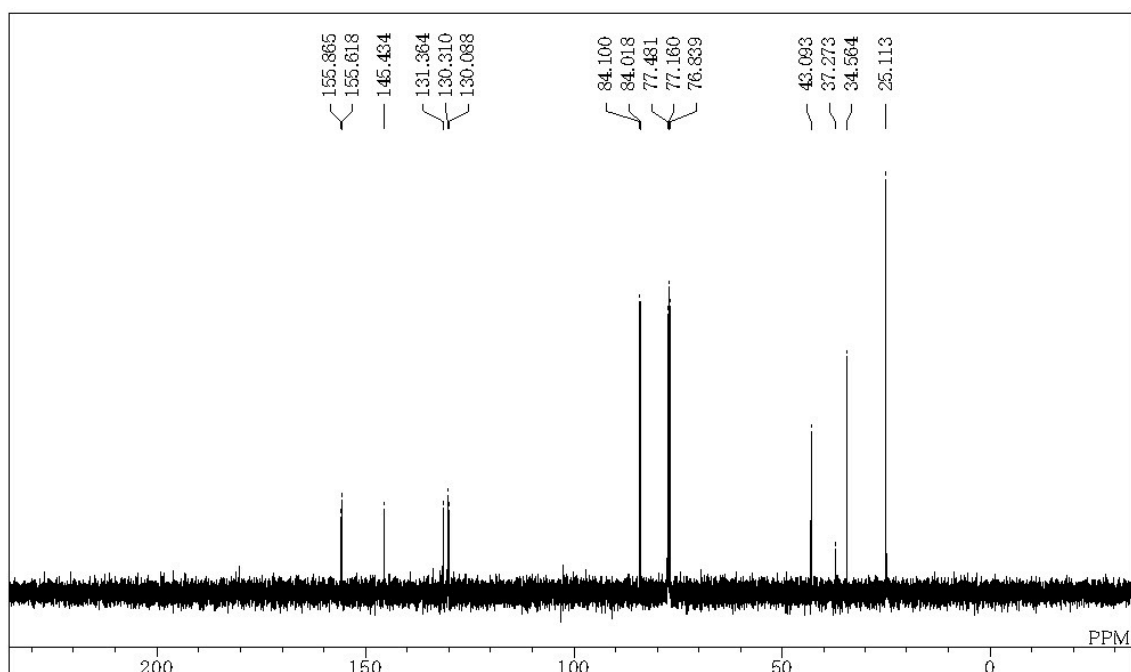


Fig. S19 ¹³C NMR spectrum of **4** in CDCl₃.

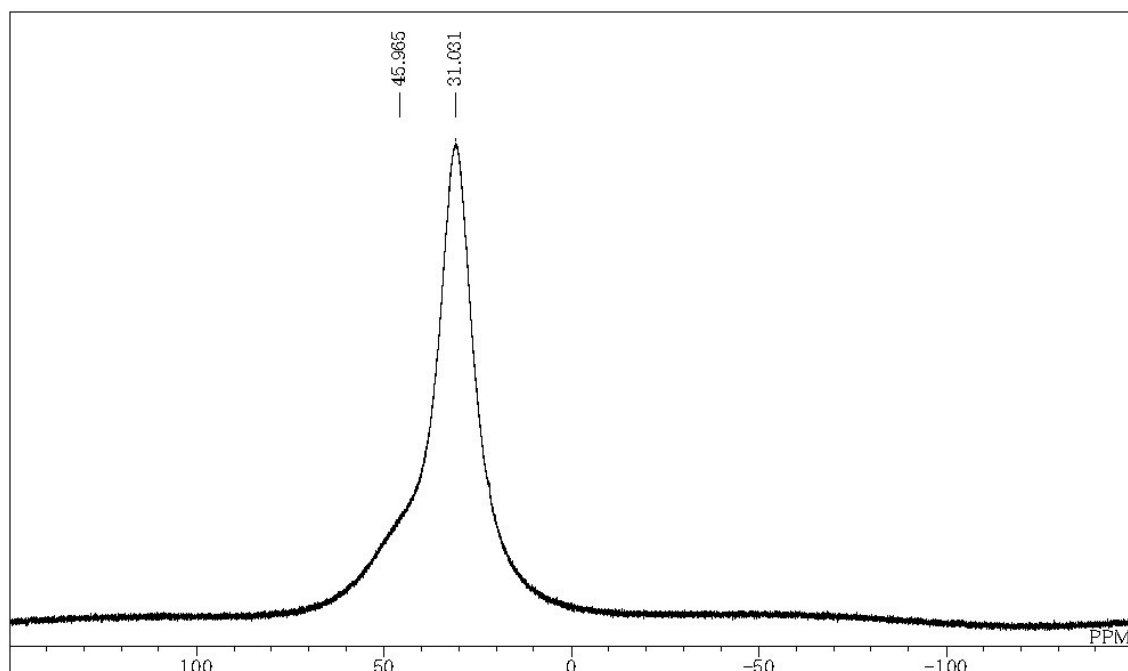


Fig. S20 ^{11}B NMR spectrum of **4** in CDCl_3 .

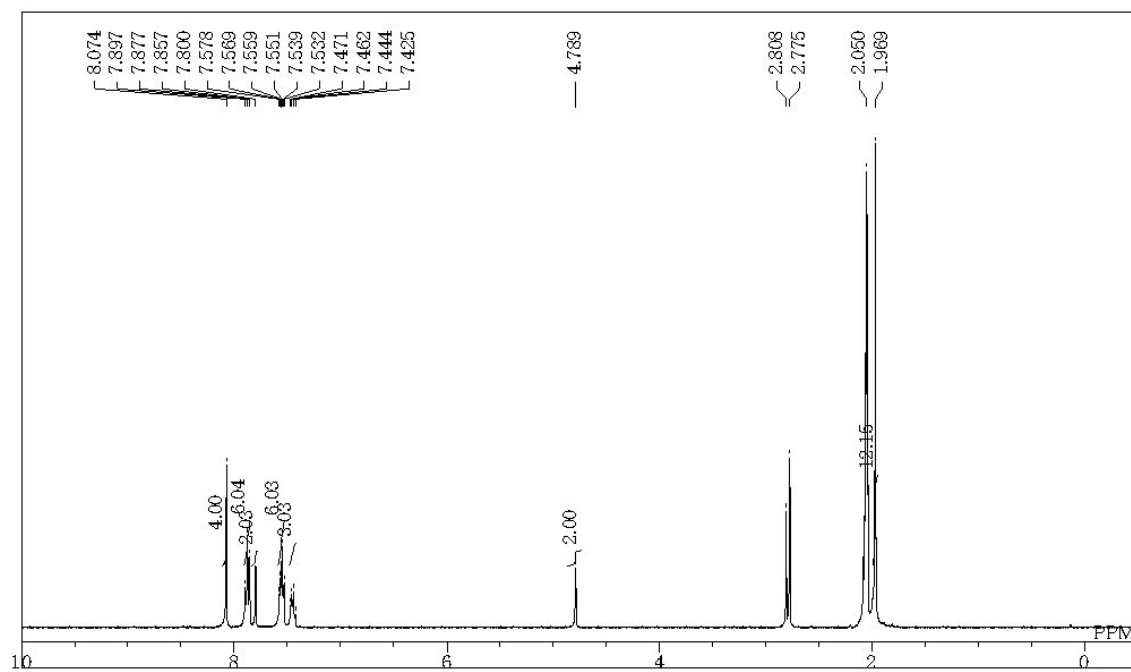


Fig. S21 ^1H NMR spectrum of **5** in $\text{acetone-}d_6$.

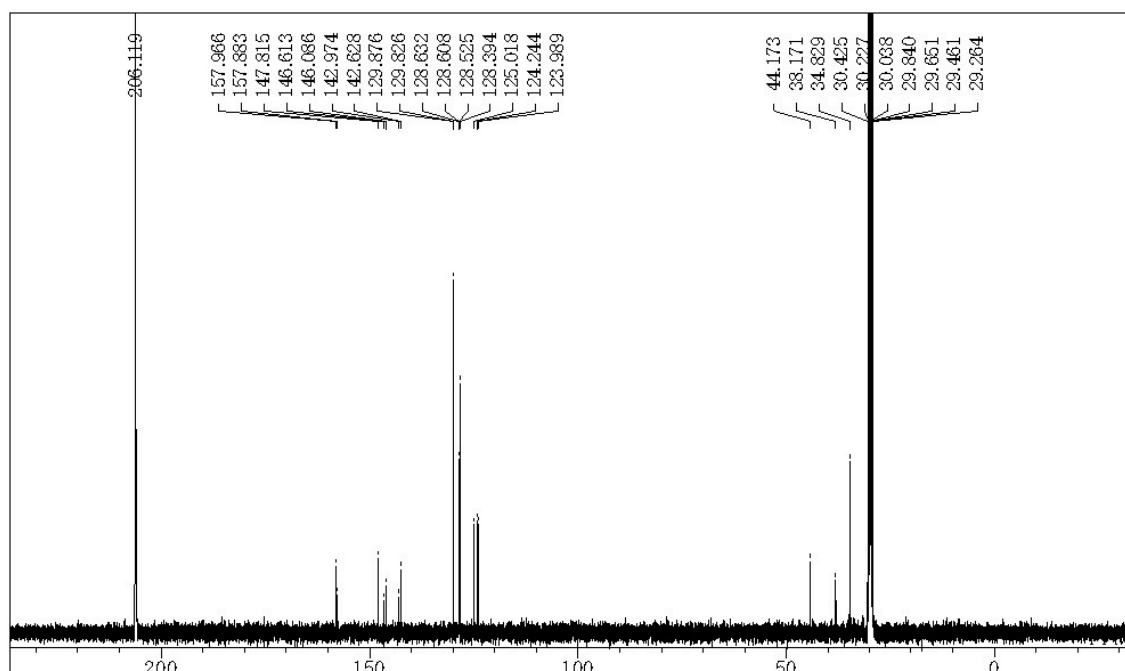


Fig. S22 ¹³C NMR spectrum of **5** in acetone-*d*₆.

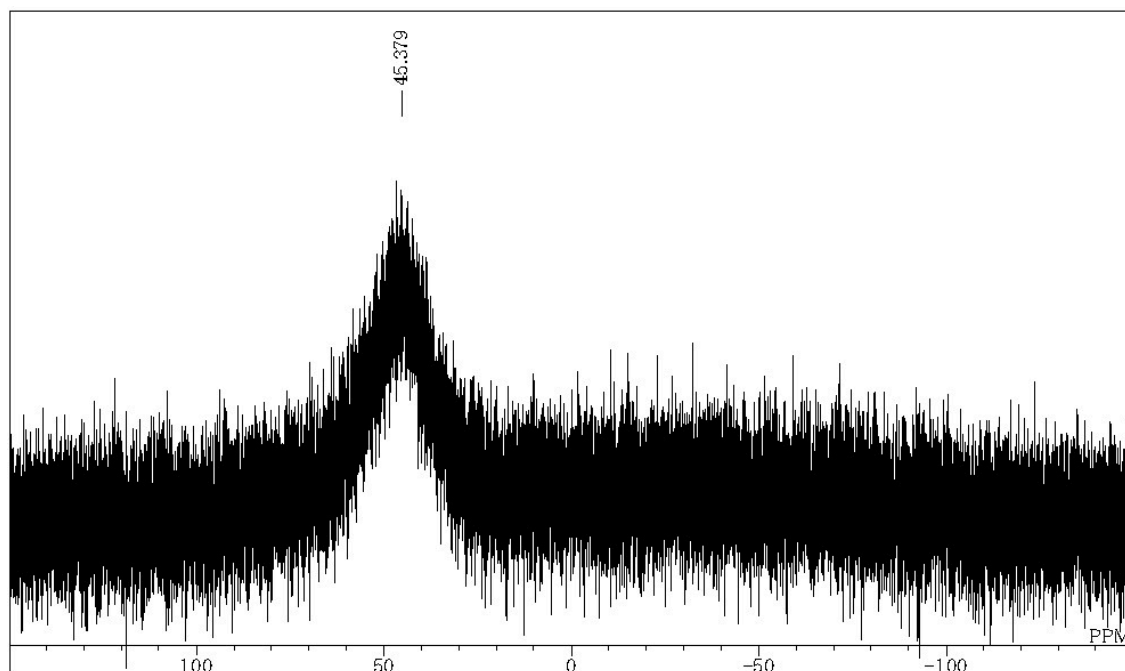


Fig. S23 ¹¹B NMR spectrum of **5** in CDCl₃.

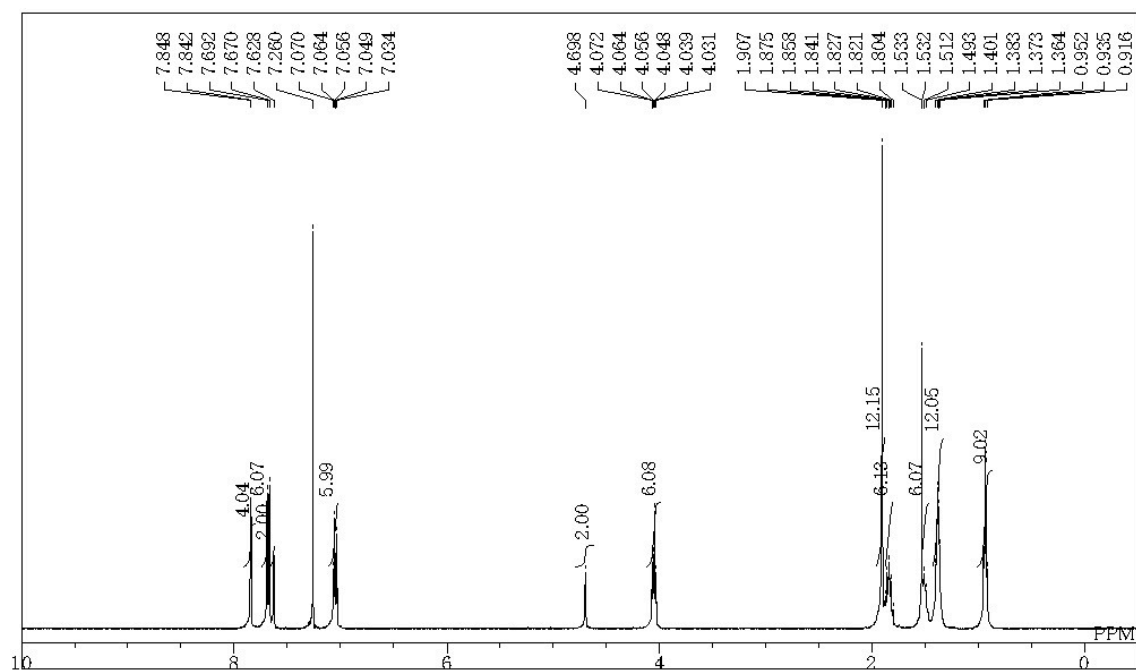


Fig. S24 ¹H NMR spectrum of **6** in CDCl₃.

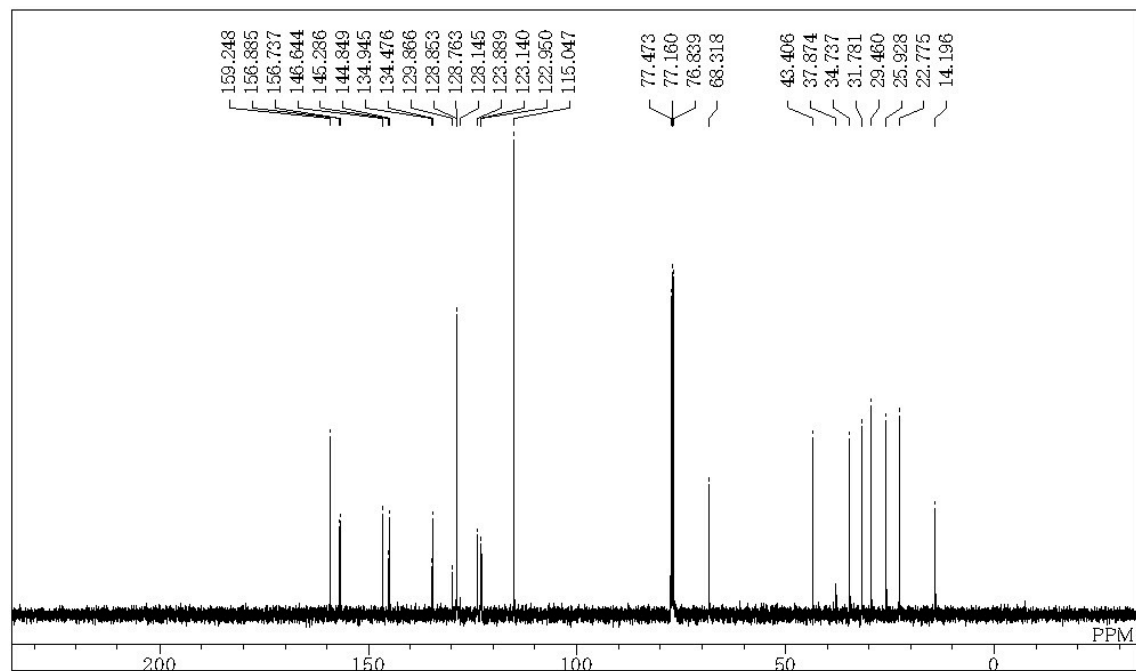


Fig. S25 ¹³C NMR spectrum of **6** in CDCl₃.

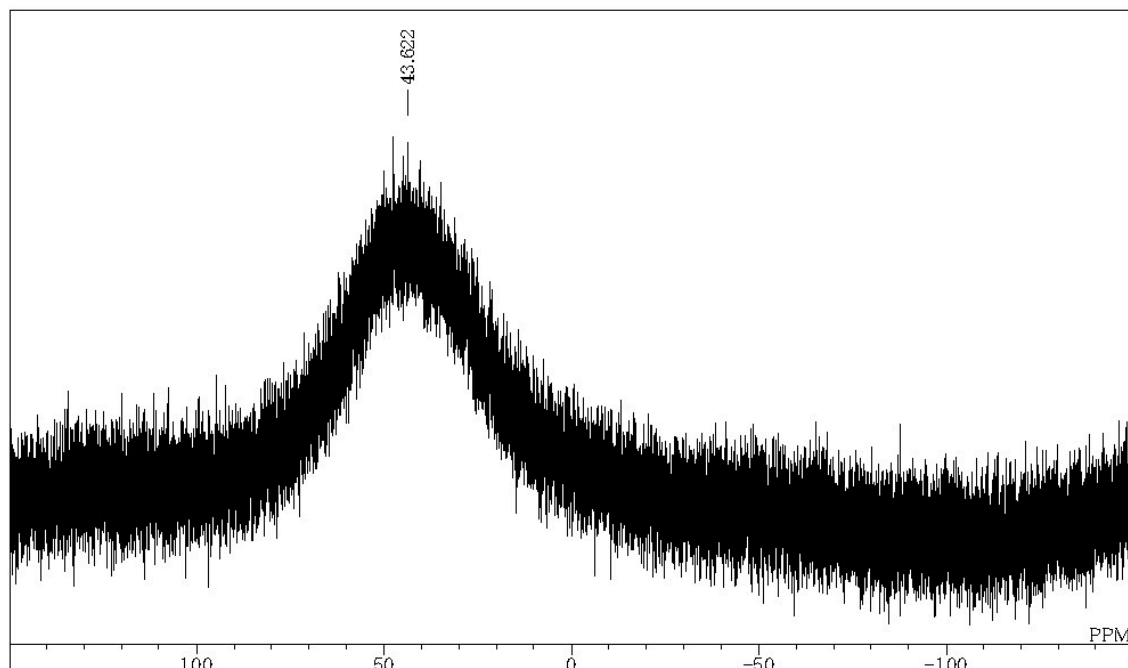


Fig. S26 ^{11}B NMR spectrum of **6** in CDCl_3 .

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