Supplementary information

N-2,6-Di(isopropyl)phenyl 2-Azaphenalenyl Radical Cations

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1. Experimental

General: All reactions of air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Air- and moisture-sensitive liquids and solutions were transferred *via* syringe. Analytical thin-layer chromatography was performed using glass plates pre-coated with Merck Art. 7730 Kiesel-gel 60 GF-254. Thin layer chromatography plates were visualized by exposure to UV light. Organic solutions were concentrated by using rotary evaporation at *ca.* 15 Torr obtained with a diaphragm pump. Column chromatography was performed with Merck Kiesel-gel 60. All reagents were commercially available and used without further purification unless otherwise noted. THF was purchased from Wako Chemical Co. and distilled from lithium aluminum hydride at 760 Torr under a nitrogen atmosphere before use.

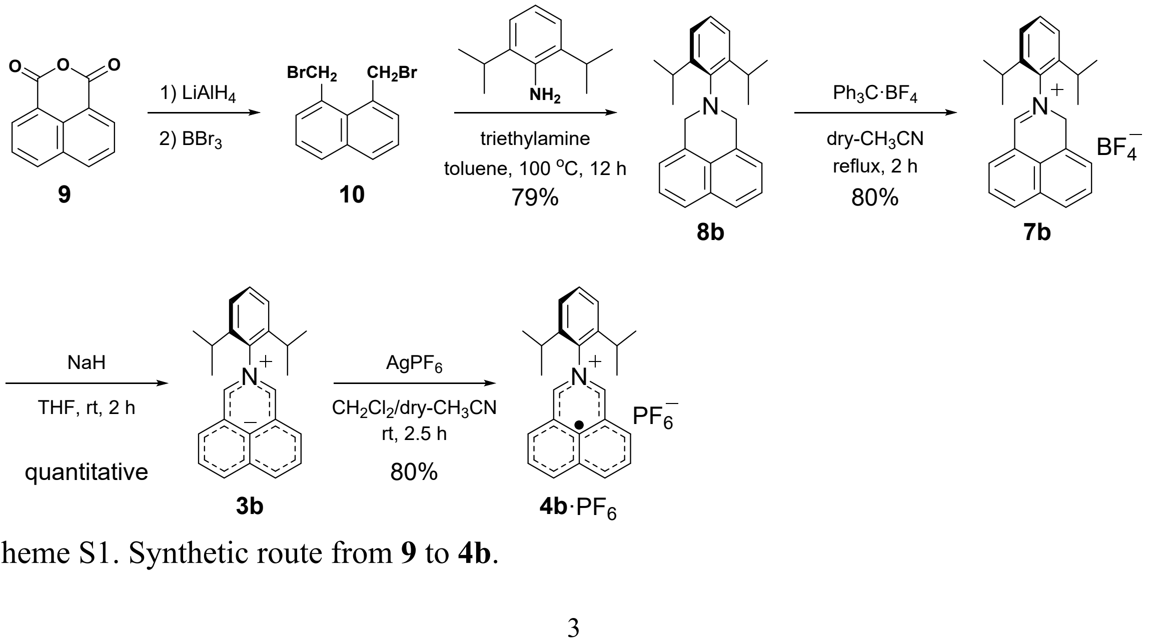
Melting points were recorded on a Yanaco MP–S3 apparatus and reported uncorrected. Positive FAB and EI mass spectra were recorded on a JEOL JMS-700 and a Shimadzu GCMS-QP2010 Ultra, respectively. High-resolution mass spectra were measured on an Applied Biosystem Japan Ltd. ^{1}H- and ^{13}C-NMR spectra of **7b** and **8** were recorded on a JEOL-JNM-ECZ Series 400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard. The NMR spectral data were measured at 20 °C. NMR spectra of **3b** were recorded on JEOL-AL400 (400 MHz for ^{1}H, and 100 MHz for ^{13}C). ^{1}H and ^{13}C NMR signals of **3b** were assigned using HSQC, HSBC, NOESY, and ^{13}C off-resonance techniques. UV-vis-NIR spectra of **3b**, **4a**, and **4b** were recorded on a SHIMAZU UV-3600 spectrophotometer. IR spectra of **3b** and **4a** were recorded as solids in a KBr pellet on a JASCO FT/IR 6200 spectrophotometer, and those of **7b** and **8** were recorded using a Shimadzu FTIR-8400 spectrometer. ESR spectra were recorded on a Bruker EMXmicro spectrometer. For recording ESR spectra at room temperature, a Bruker EMXmicro X-band EPR spectrometer equipped with a Bruker ER4119HS-W1 a high-sensitivity cavity resonator, a variable temperature control unit including a liquid N_2 cryostat, and a temperature controller was used. The magnetic field was calibrated at room temperature with a Bruker strong pitch standard ($g = 2.0028$). For the spectrum of **4a**, a CH_2Cl_2 solution of **4a** at 297 K was employed (9.63831 GHz, g-value = 2.0027, Gain = 20000, sweep time = 2 min, modulation amplitude = 0.01 mT). For the spectrum of **4b**, a CH_3CN solution of **4b** at 295 K was employed (9.59162 GHz, g-value = 2.0027, Gain = 250000, sweep time = 3.4 min, modulation amplitude = 0.01 mT). ESR spectral simulation was performed with Bruker WIN-EPR SimFonia program (Version 1.2). Cyclic voltammetric measurements of **3b** were performed with an ALS-600C electrochemical analyzer using a glassy carbon working electrode, a Pt counter electrode, and an Ag/$AgNO_3$ reference electrode at room temperature in DCM containing 0.1 M Bu_4NClO_4 as the supporting electrolyte.

All calculations were conducted using the Gaussian 09 program.[1] The geometry of **4a** was optimized with the UB3LYP functional and 6-311G(d) basis set. The geometrical optimizations of **3b**, **4b**, and **1'** were conducted by using (U)B3LYP-D3(BJ)/6-311G(d) level. From the frequency analyses, these optimized geometries locate at the local minimum giving all positive vibrational frequencies. These optimized geometries were employed for the calculations of the other physical properties.

Molecular orbitals of **4a**, **4b**, and **1'** were evaluated at the UB3LYP/6-311+G(d,p) level. Electronic excitation properties of **4a** were evaluated by the TDDFT method UB3LYP and 6-311+G(d,p) basis set. AICD plots for **3b** and **4b** were calculated by using the method developed by Herges[2] and only π-electrons are considered at the CSGT-(U)B3LYP/6-311+G(d)//(U)B3LYP-D3(BJ)/6-311G(d) level. The magnetic field is perpendicular to the molecular planes. Yellow surface is the isosurface of the induced current density under the magnetic field. Green allows with red head indicate the induced current density vectors. The clockwise and counterclockwise density vectors indicate diamagnetic and paramagnetic ring currents, respectively.

The theoretical hyperfine coupling constants (hfccs) of **4a** and **4b** for the simulation of the ESR measurements were calculated at the UB3LYP/EPR-II level.

Synthesis of 3a and 3b. Azomethine ylide **3a** was prepared from *N*-2,6-di(isopropyl)phenyl-5,8-di-*tert*-butyl-1*H*-benz[*de*]isoquinolinium tetrafluoroborate (**7a**) as literature[3]. Azomethine ylide **3b** was also synthesized from *N*-2,6-di(isopropyl)phenyl-1*H*-benz[*de*]isoquinolinium tetrafluoroborate (**7b**). The iminium ion **7b** was prepared from *N*-2,6-di(isopropyl)phenyl 2,3-dihydro-1*H*-benz[*de*]isoquinoline (**8**) in a similar manner of **7a**. The benz[*de*]isoquinoline derivative **8** were synthesized starting with 1,8-naphthalenedicarboxylic acid anhydride (**9**) via 1,8-bis(bromomethyl)naphthalene (**10**) through sequential reduction with lithium aluminum hydride, bromination with boron tribromide, and respective reaction with 2,6-diisopropylaniline (Scheme S1).



Scheme S1. Synthetic route from **9** to **4b**.

***N*-2,6-Di(isopropyl)phenyl 2,3-dihydro-1*H*-benz[*de*]isoquinoline 8b.** A solution of **10** (1.0 g, 3.2 mmol), triethylamine (1.3 mL, 9.3 mmol) and 2,6-di(isopropyl)aniline (1.0 mL, 5.3 mmol) in toluene (25 mL) was heated at 100 °C with stirring for overnight. The generated solid was removed by filtration, and the filtrate was concentrated under vacuum. The crude product was purified by column chromatography on silica gel to give **8b** (0.83 g, 2.5 mmol) from a toluene/hexane (1:1) elusion as colorless solids in 79% yield.

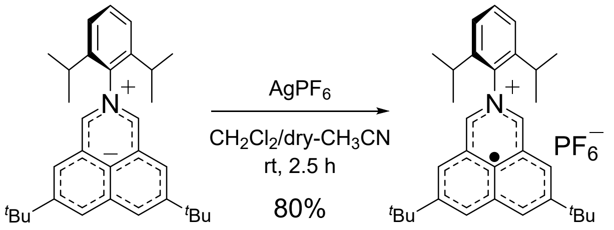
M.p. 156−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.43 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 6.8 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 4.60 (s, 4H), 3.34 (sep, *J* = 6.9 Hz, 2H), 1.16 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.42, 145.20, 134.54, 133.52, 127.94, 126.93, 125.88, 125.33, 124.21, 120.93, 53.94, 28.44, 23.99 ppm; IR (KBr): ν 2959 (s), 2925 (m), 2867 (m), 2794 (m), 1447 (s), 1375 (m), 1362 (m), 1323 (m), 797 (s), 765 (s) cm^{-1}; HRMS (EI) m/z: calcd. for [$C_{24}H_{27}N$]: 329.2143; found: 329.2142.

***N*-2,6-Di(isopropyl)phenyl-1*H*-benz[*de*]isoquinolinium tetrafluoroborate 7b.** A mixture of **8b** (0.10 g, 0.33 mmol) and Ph_3CBF_4 (0.18 g, 0.55 mmol) in dry-acetonitrile (10 mL) was stirred at reflux for 2 h. After cooling to rt, the mixture was diluted with ethyl acetate to afford **7b** (91 mg, 0.22 mmol) as an yellow precipitate in 67% yield.

D.p. 207−208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 9.54 (s, 1H), 8.73 (d, *J* = 6.8 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 5.58 (s, 2H), 2.94 (sep, *J* = 6.8 Hz, 2H), 1.34 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.61, 142.81, 140.55, 139.82, 137.31, 132.04, 131.98, 128.97, 128.29, 127.96, 126.47, 125.63, 124.32, 121.01, 58.33, 28.96, 24.64, 24.04 ppm; IR (KBr): ν 1643 (m), 1609 (m), 1516 (m), 1181 (m), 1109 (m), 1059 (s), 769 (m) cm$^{-1;}$ HRMS (FAB, NBA) m/z: calcd. for [$C_{24}H_{26}N^+$]: 328.2074; found: 328.2060.

***N*-2,6-Di(isopropyl)phenyl-2-azaphenalenyl 3b.** In a nitrogene-filled glovebox, a solution of **9b** (52 mg, 0.13 mmol) and NaH (183 mg, 7.6 mmol) in THF (4 mL) was stirred at rt for 2 h. Filtration of the mixture gave a filtrate that was concentrated in vácuo to afford **3b** as a green solid (41 mg, 0.13 mmol).

^{1}H NMR (400 MHz, THF-d8) : δ 7.35 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 2H), 6.36 (t, *J* = 8.0 Hz, 2H) , 6.03 (d, *J* = 8.0 Hz, 2H), 5.61 (s, 2H), 5.51 (d, *J* = 7.2 Hz, 2H), 3.49 (sep, *J* = 7.4 Hz, 2H), 1.25 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, THF-d8) δ 144.42, 141.02, 140.65, 140.15, 138.68, 130.49, 129.51, 125.08, 118.31, 115.13, 105.75, 28.88, 26.20 ppm; HRMS (ESI$^+$) m/z: calcd. for [$C_{24}H_{26}N^+$]: 328.20598; found: 328.20448.



3a **4a**$\cdot$PF$_6$

***N*-2,6-Di(isopropyl)phenyl-5,8-di-*tert*-butyl-2-azaphenalenyl radical cation 4a$\cdot$PF$_6$.** In a nitrogene-filled glovebox, a solution of **3a** (75 mg, 0.17 mmol) and $AgPF_6$ (65 mg, 0.26 mmol) in acetonitrile (2 mL) and CH_2Cl_2 (2 mL) was stirred at rt for 2 h. Filtration of the mixture gave a filtrate that was concentrated in vácuo to afford **4a** as a brown solid (100 mg, 0.17 mmol). M.p. 165−166 °C; IR (KBr): ν 2966 (s), 1607 (m), 1468 (m), 1369 (m), 1084 (m), 1060 (m), 843 (s), 558 (s) cm^{-1}; HRMS (MALDI-TOF-MASS$^+$) m/z: calcd. for [$C_{32}H_{41}N$]: 439.3234 ([M+H]$^+$); found: 439.3248.

Table S1. Oxidation of **3a** at rt in CH_3CN and CH_2Cl_2.

Oxidant	Time (h)	result	yield	melting point
Magic Blue	0.5	No isolable product	—	—
$Fe(C_5H_5)_2$ PF_6	2	No reaction	—	—
$AgPF_6$	2.5	Generation of **4a**	quant	165—166 ℃
$AgBF_4$	2.5	Generation of **4a**, but unstable	quant	88.5—89.0 ℃
$AgSbF_6$	2.5	Generation of **4a**	46 %	＞300 ℃

***N*-2,6-Di(isopropyl)phenyl-2-azaphenalenyl radical cation 4b$\cdot$PF$_6$.** In a nitrogene-filled glovebox, a solution of **3b** (92 mg, 0.28 mmol) and $AgPF_6$ (107 mg, 0.42 mmol) in acetonitrile (3 mL) and CH_2Cl_2 (3 mL) was stirred at rt for 2.5 h. Filtration of the mixture gave a filtrate that was concentrated in vácuo to afford **4b** as a brown solid (138 mg, 0.28 mmol).

M.p. 48.1−48.9 °C; IR (KBr); ν 3091 (w), 2969 (m), 1646 (w), 1469 (m), 1450 (m), 832 (s), 560 (s); HRMS (ESI$^+$) m/z: calcd. for [$C_{24}H_{26}N$]: 328.20598; found: 328.20995.

References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C.

Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O.; Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels,O. Farkas, J. B. Foresman, J. Ortiz, J. V. Cioslowski, D. J. Fox, *Gaussian 09 (Revision D.01)*, Gaussian, Inc., Wallingford CT, **2009**.

[2] D. Geuenich, K. Hess, F. Köhler, R. Herges, *Chem. Rev.* 2005, **105**:3758.

[3] K. Katayama, A. Konishi, K. Horii, M. Yasuda, C. Kitamura, J. Nishida, T. Kawase, *Commun. Chem.* 2019, **2**:136.

2. Energy diagram of 1' and 4b.

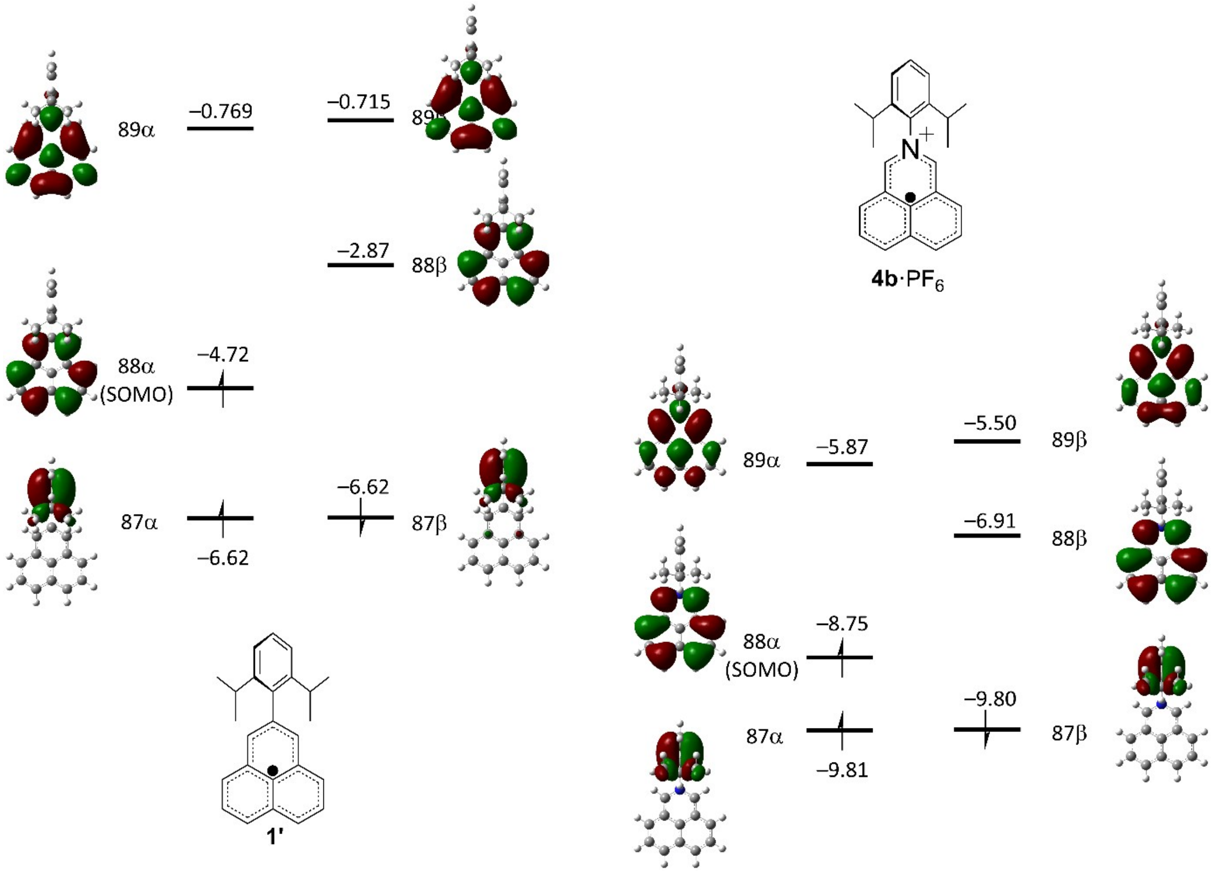


Fig. S1. Calculated orbital energy diagram (/eV) for **1'** and **4b** at the UB3LYP/6-311+G(d,p)//UB3LYP-D3(BJ)/6-311G(d) level.

3. Hyper fine coupling constants (hfccs) of 4a and 4b.

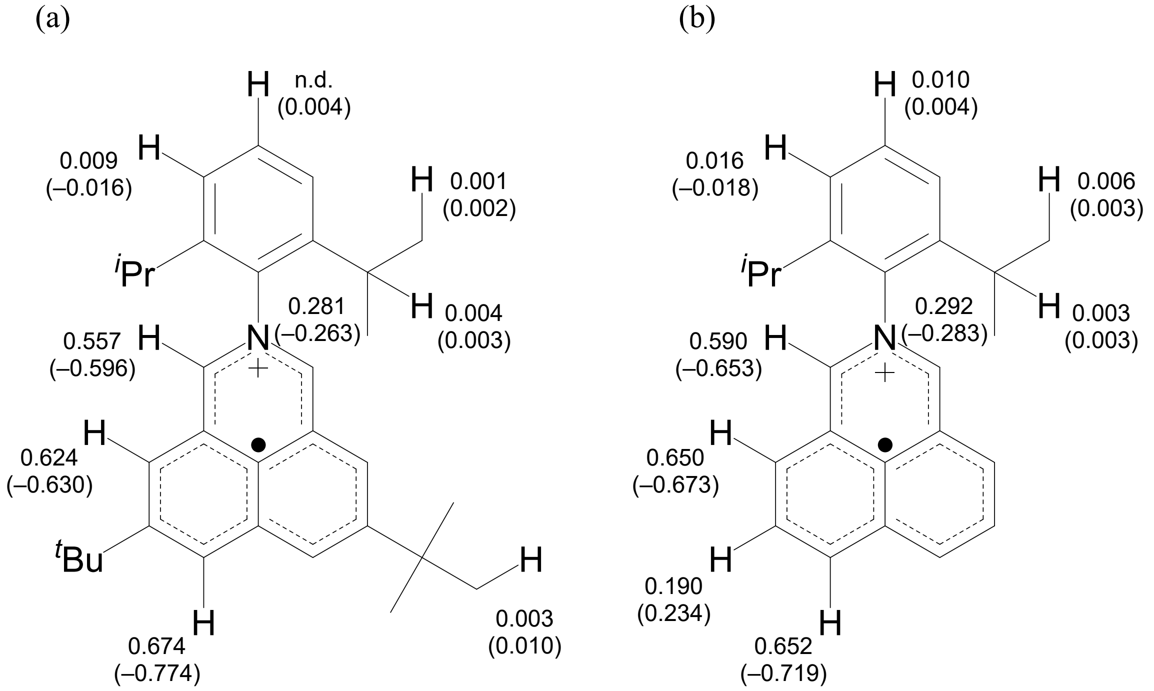


Fig. S2. Summary for simulated hyper-fine coupling constants ($|A_{\mathrm{H\ or\ N}}|$ /mT) for (a) **4a** and (b) **4b**. The values in the parentheses were calculated by the UB3LYP/EPR-II//UB3LYP/6-311G(d) method.

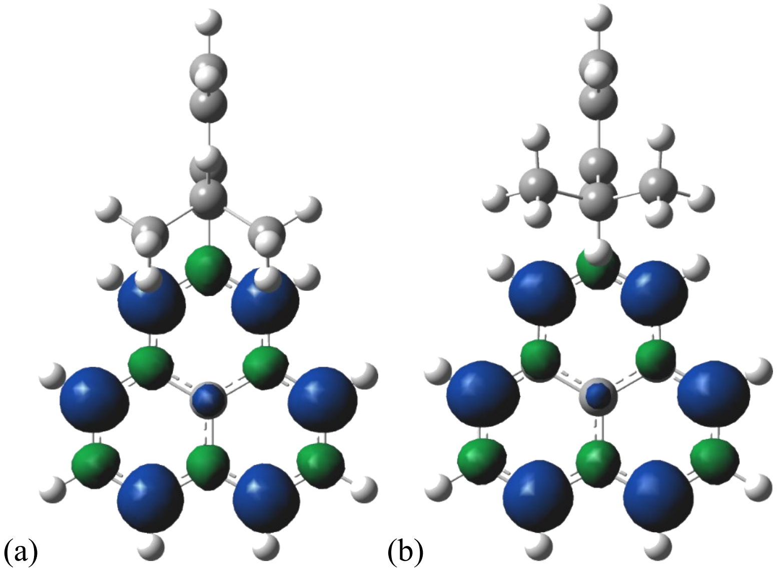


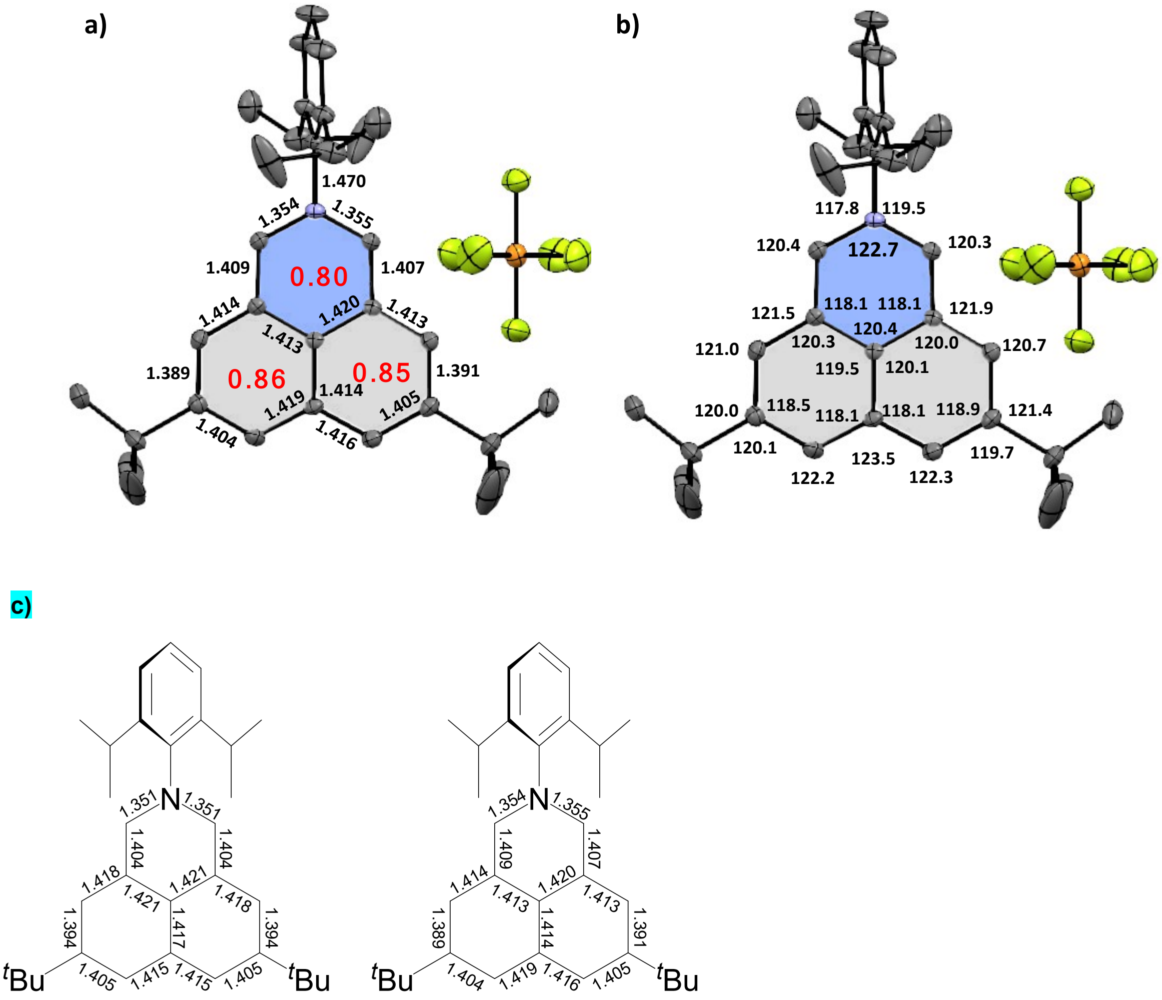
Fig. S3. Spin density distribution for (a) **1'** and (b) **4b** at the UB3LYP/6-311+G(d,p)//UB3LYP-D3(BJ)/6-311G(d) level. Positive (blue) and negative (green) spin densities are shown.

4. Crystallographic analysis of 4a.

Single crystals of **4a** for X-ray analysis were obtained by slow evaporation from a CH_2Cl_2/hexane solution. X-ray diffraction data were collected on a Rigaku XtaLAB Synergy-S diffractometer requipped with HyPix-6000HE Hybrid Photon Counting (HPC) X-ray detector with graphite-monochromated CuKα (λ = 1.54187 Å) radiation, and Φ and ωscans at a maximum 2θ value of 148.236. The crystal was kept at 123 K during data collection. Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimization. CCDC 2310427 (**4a**, $C_{32}H_{41}NPF_6$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystallographic data of **4a**.

Compound	**4a**
Chemical formula	$C_{32}H_{41}NPF_6$
Formula weight	584.63
Color	Brown
Shape	Prism
Crystal system	triclinic
Space group	P–1
a (Å)	11.0504(2)
b (Å)	11.3069(2)
c (Å)	13.5760(3)
α (°)	112.089(2)
β (°)	90.039(2)
γ (°)	102.919(2)
Volume (Å^3)	1525.21(6)
Z	2
D_{calc} (g/cm^3)	1.273
R_1 ($I > 2\sigma(I)$)	0.0740
wR_2 (All reflections)	0.2138
Reflections ($I > 2\sigma(I)$)	6168
Temperature (K)	123
CCDC number	2310427



Optimized structure *Observed structure*

Fig. S4. Molecular structures of **4a** with a) bond lengths and the HOMA values, b) bond angles of the azaphenalenyl skeleton, and c) bond length comparison of the theoretically optimized structure of **4a** (UB3LYP/6-311G(d)) with the X-ray observed structure.

References

[1] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

[2] Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

[3] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

5. DFT calculations.

Table S3. TD-DFT calculations of **4a**.

Excited state number	Excitation energy / eV (wavelength / nm)	Excitation amplitudes		Oscillator strength
1 (<S^2> = 0.805)	1.82 (681)	0.969	(120α – 121α)	0.0181
3 (<S^2> = 0.806)	2.57 (482)	0.703 –0.534 –0.452	(119β – 120β) (116β – 120β) (120α – 122α)	0.0125
6 (<S^2> = 0.988)	3.33 (373)	0.719 –0.562	(120α – 122α) (116β – 120β)	0.1583

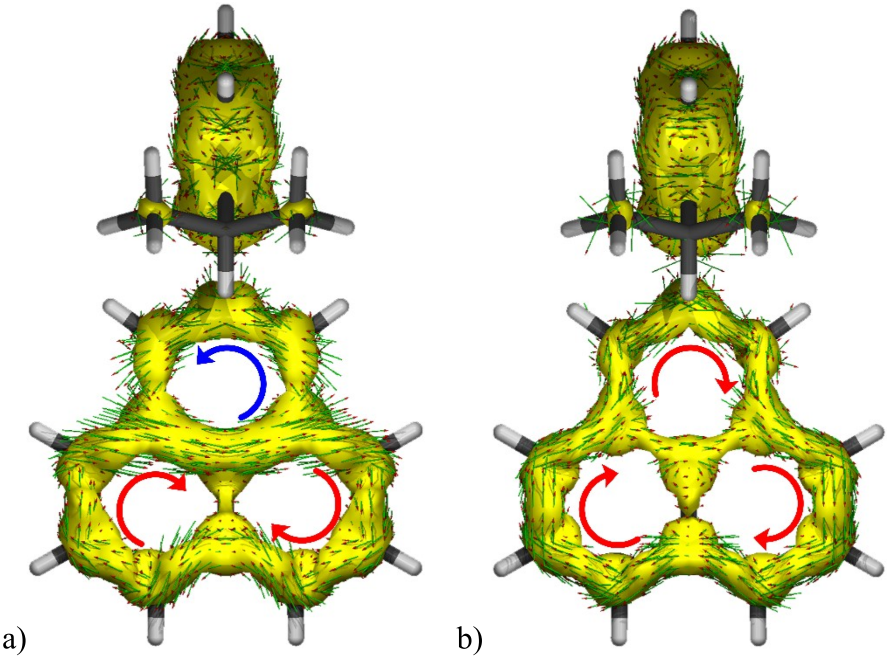


Fig. S5. ACID plots for (A) **3b** and (B) **4b** at the CSGT-(U)B3LYP/6-311+G(d)//(U)B3LYP-D3(BJ)/6-311G(d) level.

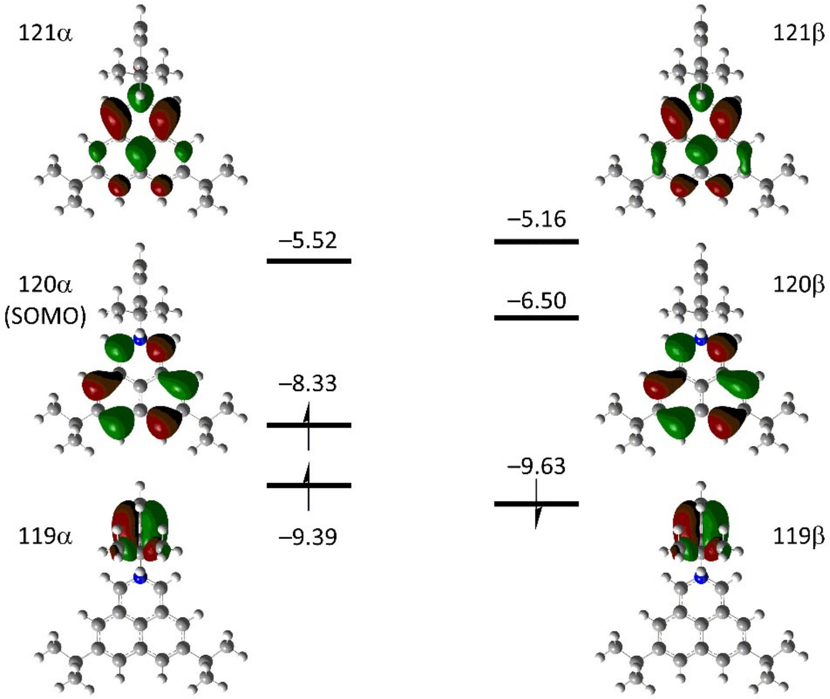


Fig. S6. Energy levels of LUMO and SOMO of **4a** and drawings of LUMO and SOMO coefficients on the optimized conformations by using the DFT calculations (UB3LYP/6-311+G(d,p)//UB3LYP/6-311G(d) level).

6. Optoelectronic properties.

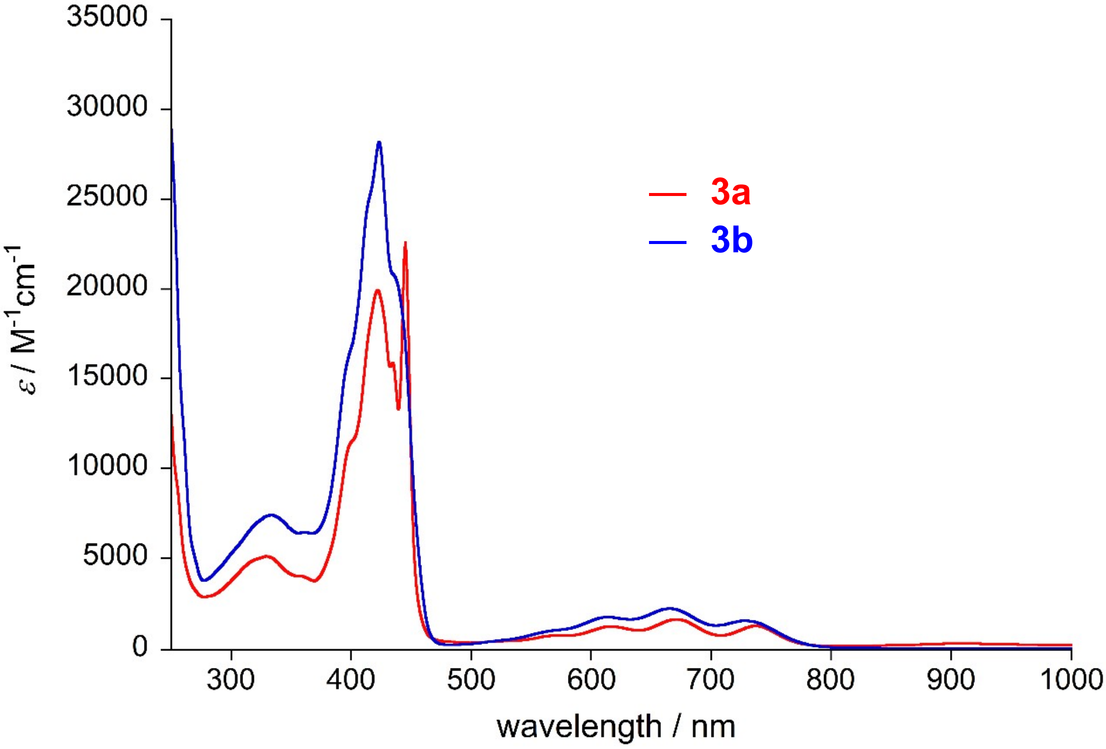


Fig. S7. UV–vis absorption spectra of **3a** and **3b** in CH_2Cl_2.

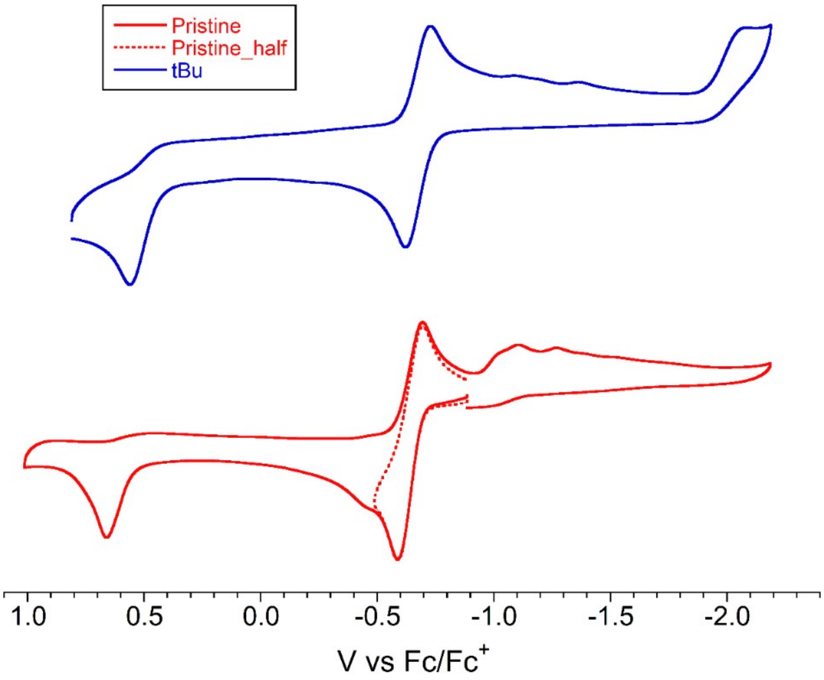


Fig. S8. Cyclic voltammograms (CV) of **3a** and **3b** in CH_2Cl_2.

Table S4. Redox properties in CH_2Cl_2 and frontier orbital energies of **3a** and **3b**.

	E_2^{ox}	E_1^{ox}	E_2^{red}
3a	+0.56[a]	–0.68	–2.06[a]
3b	+0.65[a]	–0.62	—

[a] Peak potential.

7. NMR charts.

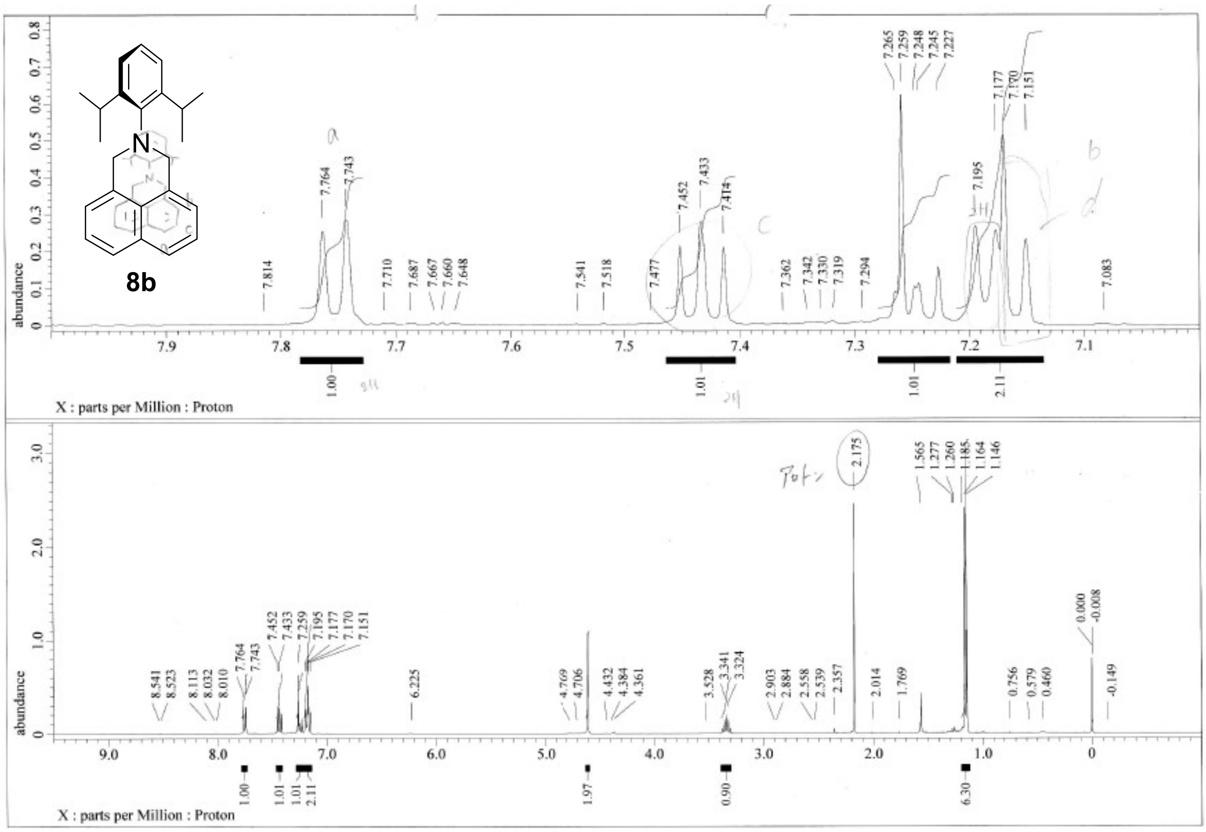


Fig. S9. ^{1}H NMR spectrum (400 MHz) of **8b** in $CDCl_3$.

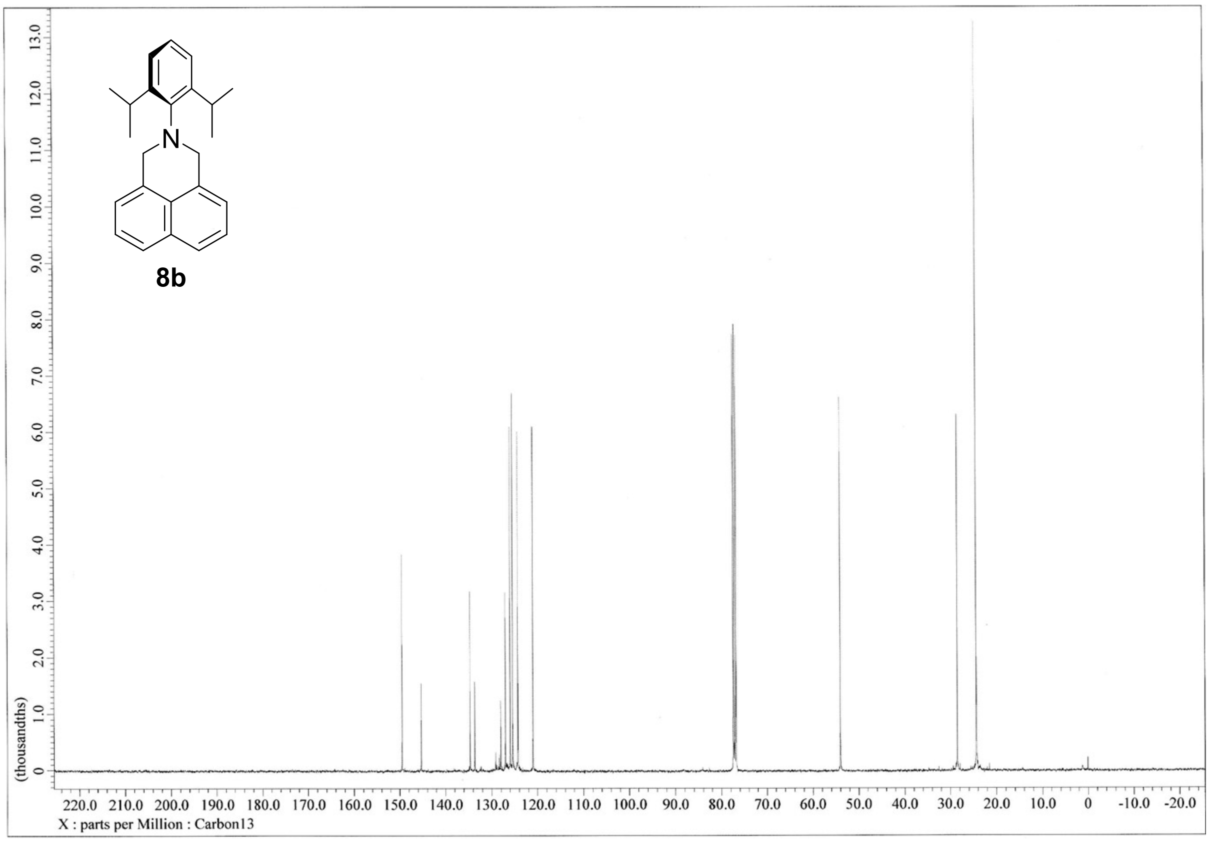


Fig. S10. ^{13}C NMR spectrum (100 MHz) of **8b** in CDCl$_3$.

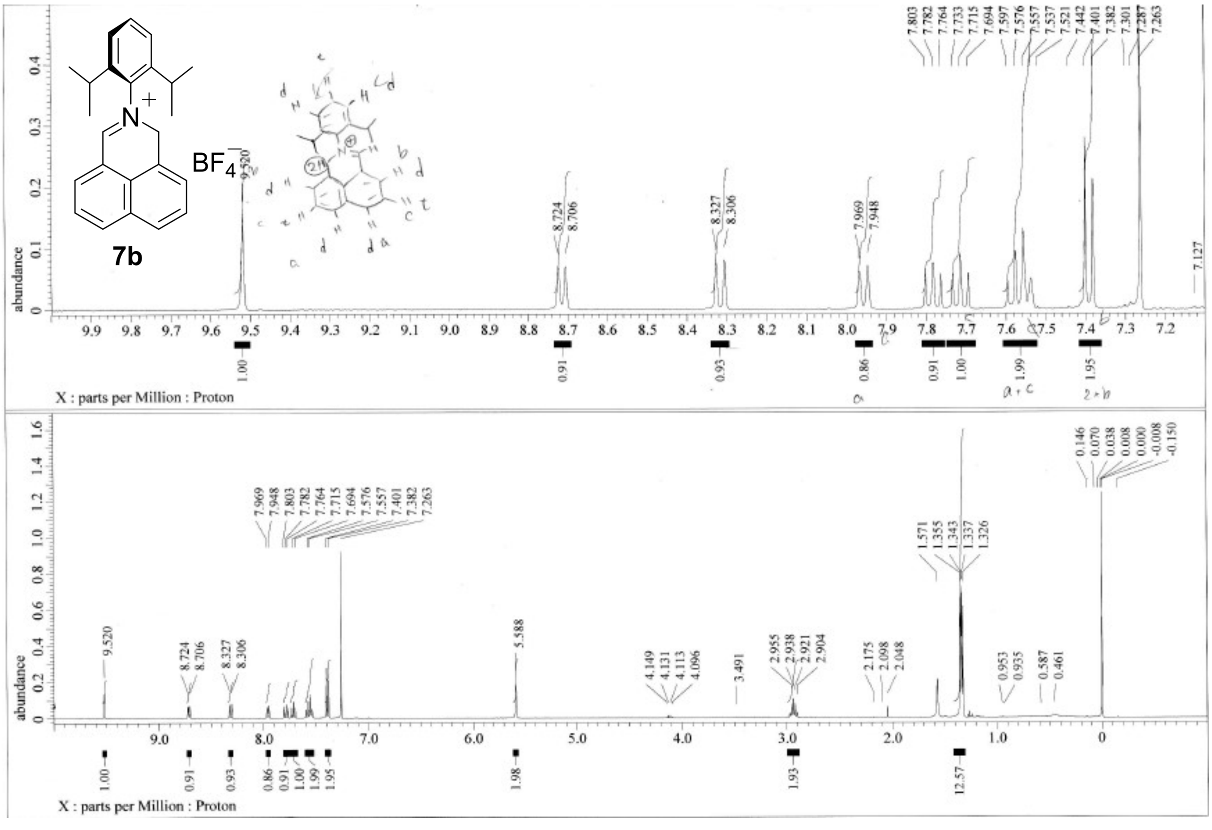


Fig. S11. ^{1}H NMR spectrum (400 MHz) of **7b** in CDCl$_3$.

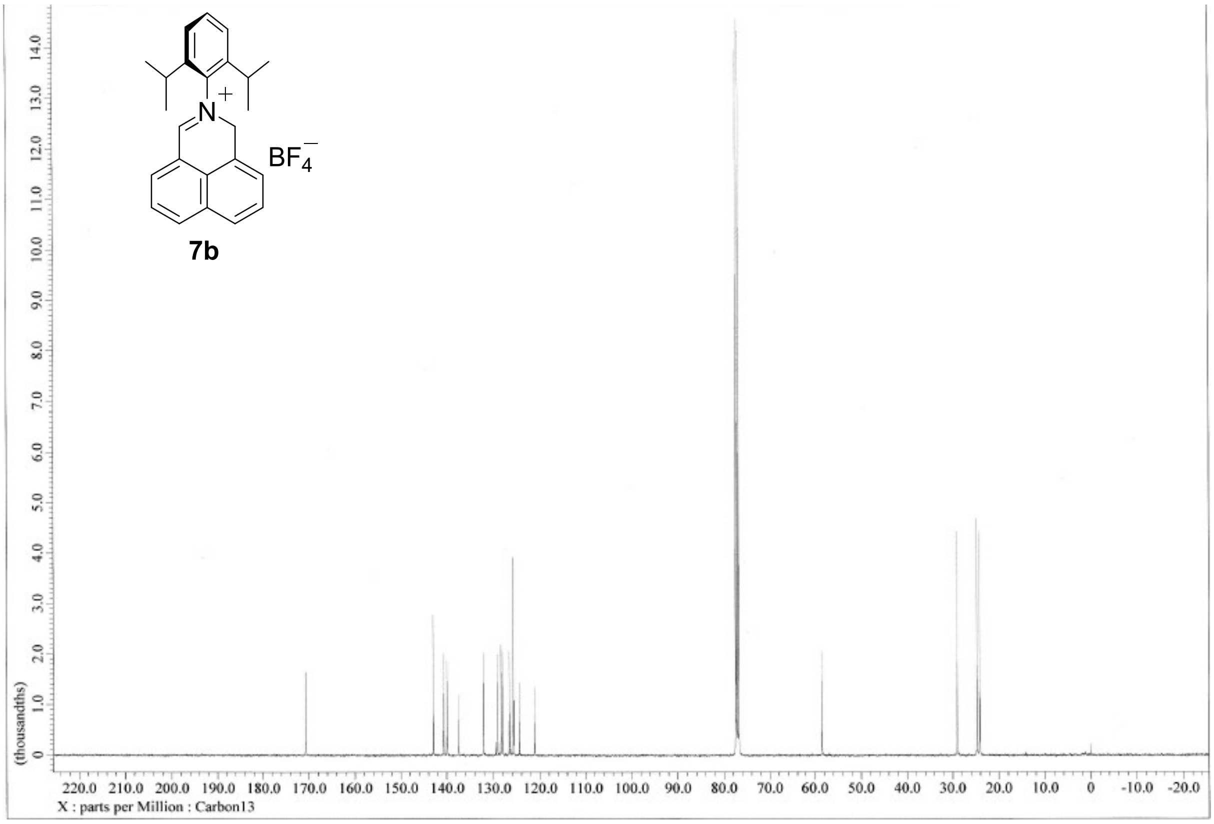


Fig. S12. ^{13}C NMR spectrum (100 MHz) of **7b** in CDCl$_3$.

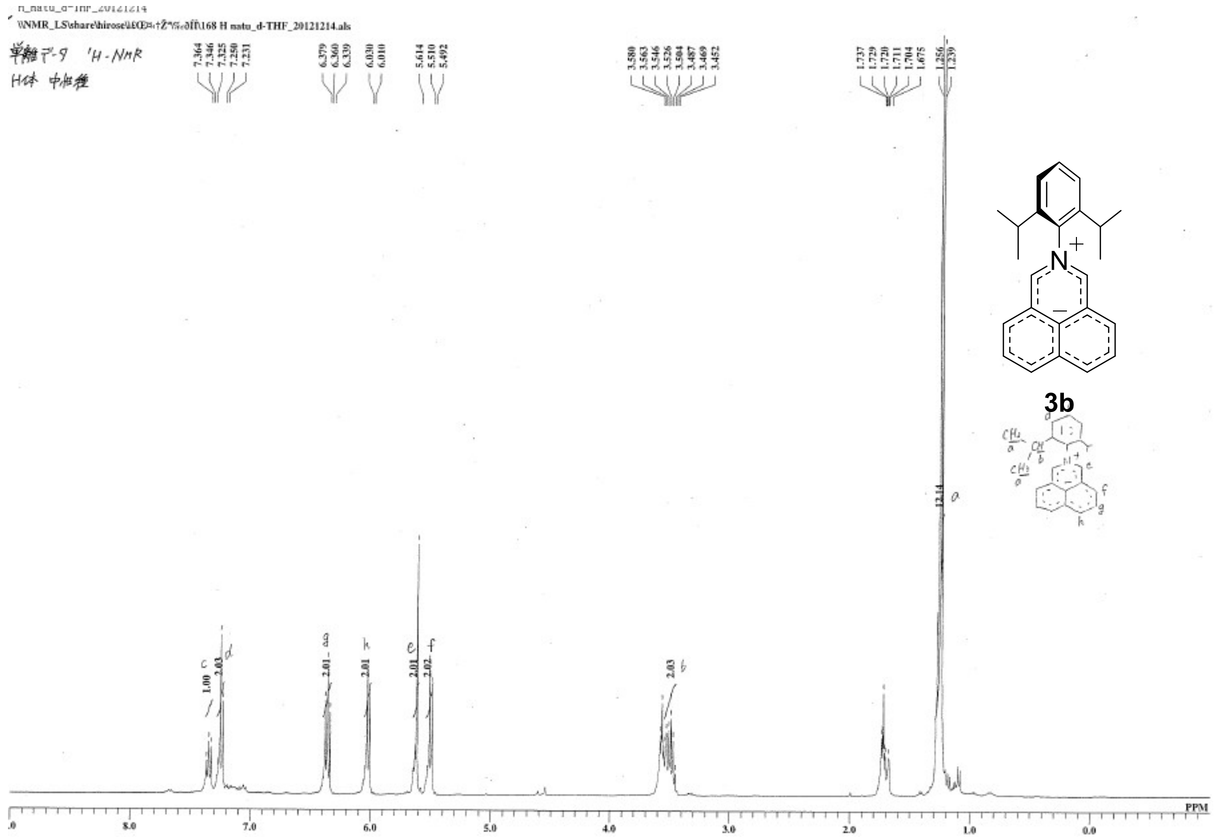
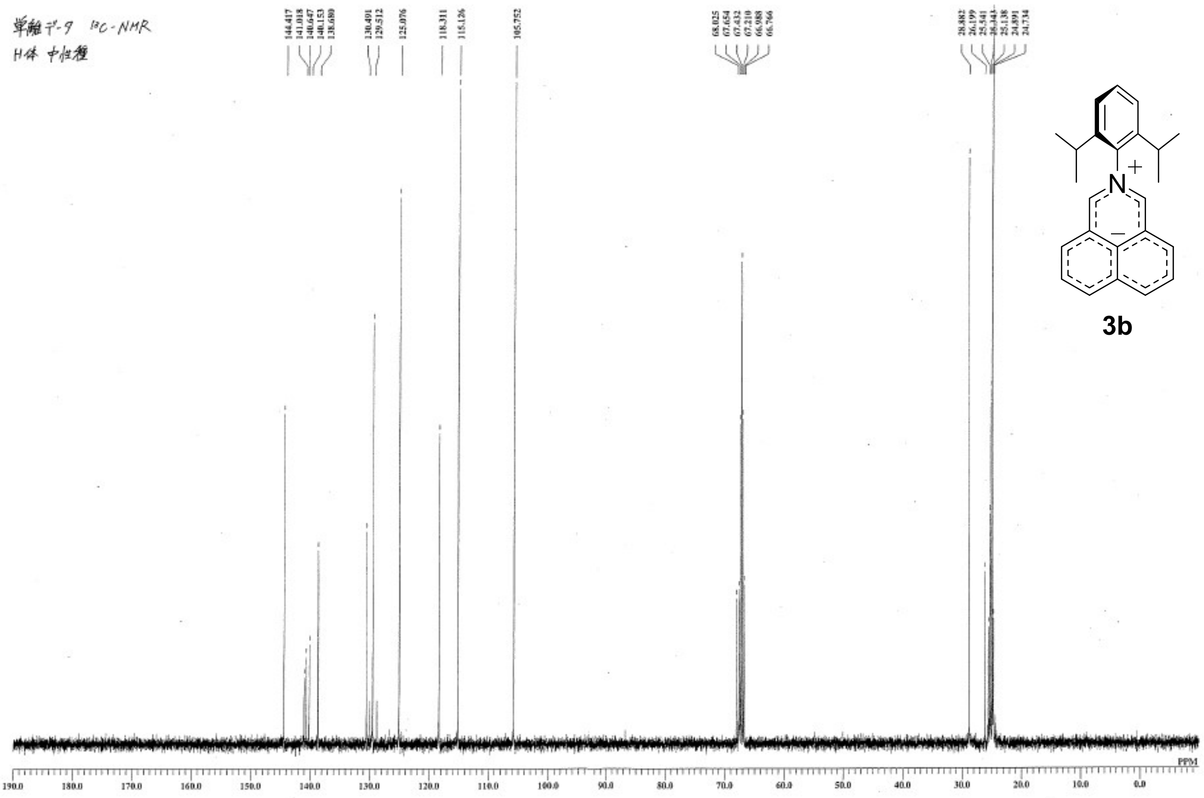


Fig. S13. ^{1}H NMR spectrum (500 MHz) of **3b** in THF-d_8.



3b

Fig. S14. ^{13}C NMR spectrum (125 MHz) of **3b** in THF-d^8.

8. Cartesian coordinates for optimized geometries.

Table S5. Optimized geometries for **3b** at the RB3LYP-D3(BJ)/6-311G(d) level.

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	1.18861902	-0.35623651	C	1.20599835	-0.00000000	3.78555809
C	-0.00000000	1.24388110	-1.77593564	C	0.00000000	0.00000000	4.47643557
C	-0.00000000	-0.00000000	-2.49278232	H	-2.13972149	0.00000000	4.33700623
C	-0.00000000	-1.24388110	-1.77593564	H	2.13972149	-0.00000000	4.33700623
C	-0.00000000	-1.18861902	-0.35623651	H	0.00000000	0.00000000	5.56147138
N	0.00000000	0.00000000	0.27560244	C	-2.55586180	0.00000000	1.63915057
C	-0.00000000	2.45007357	-2.48552422	C	-3.36491425	1.26937254	1.94419365
C	-0.00000000	2.43403591	-3.88395948	C	-3.36491425	-1.26937254	1.94419365
C	-0.00000000	1.24999192	-4.59342745	H	-2.34308423	0.00000000	0.56877459
C	-0.00000000	-0.00000000	-3.92049719	H	-2.79512072	2.16783815	1.69585121
C	-0.00000000	-1.24999192	-4.59342745	H	-4.28849027	1.28348984	1.35954138
C	-0.00000000	-2.43403591	-3.88395948	H	-3.63902168	1.32865686	3.00110647
C	-0.00000000	-2.45007357	-2.48552422	H	-2.79512072	-2.16783815	1.69585121
H	0.00000000	2.06536665	0.27292675	H	-3.63902168	-1.32865686	3.00110647
H	-0.00000000	-2.06536665	0.27292675	H	-4.28849027	-1.28348984	1.35954138
H	0.00000000	3.39124300	-1.94577291	C	2.55586180	-0.00000000	1.63915057
H	-0.00000000	3.37744228	-4.42179343	C	3.36491425	-1.26937254	1.94419365
H	-0.00000000	1.25989973	-5.67851269	C	3.36491425	1.26937254	1.94419365
H	-0.00000000	-1.25989973	-5.67851269	H	2.34308423	-0.00000000	0.56877459
H	-0.00000000	-3.37744228	-4.42179343	H	2.79512072	-2.16783815	1.69585121
H	-0.00000000	-3.39124300	-1.94577291	H	4.28849027	-1.28348984	1.35954138
C	0.00000000	0.00000000	1.72710765	H	3.63902168	-1.32865686	3.00110647
C	-1.23328284	0.00000000	2.38836035	H	2.79512072	2.16783815	1.69585121
C	1.23328284	-0.00000000	2.38836035	H	3.63902168	1.32865686	3.00110647
C	-1.20599835	0.00000000	3.78555809	H	4.28849027	1.28348984	1.35954138

Table S6. Optimized geometries for **4a** at the UB3LYP/6-311G(d) level.

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.93776159	1.18306125	-0.00000504	H	-2.73453145	-1.27931698	-4.32432230
C	0.46508598	1.23361943	-0.00000454	C	-2.99139682	0.00001294	2.58294149
C	1.16997019	0.00000006	0.00000028	C	-3.30777776	-1.27013033	3.39393223
C	0.46508611	-1.23361937	0.00000414	C	-3.30778093	1.27016229	3.39392144
C	-0.93776147	-1.18306134	0.00000347	H	-1.91336064	0.00001357	2.39842144
N	-1.59035157	-0.00000009	-0.00000095	H	-3.05966026	-2.17801502	2.83778879
C	1.18400178	2.45601474	-0.00000851	H	-2.73453015	-1.27927466	4.32433182
C	2.57782345	2.47766530	-0.00000698	H	-4.36602593	-1.32640081	3.66002128
C	3.25686625	1.24710704	-0.00000211	H	-3.05966722	2.17804290	2.83776967
C	2.58733279	0.00000014	0.00000120	H	-4.36602887	1.32643163	3.66001158
C	3.25686639	-1.24710669	0.00000537	H	-2.73453203	1.27931663	4.32432012
C	2.57782371	-2.47766502	0.00000908	C	3.38324122	3.78845137	-0.00001119
C	1.18400205	-2.45601462	0.00000856	C	4.27351962	3.83698926	1.26328006
H	-1.56134077	2.06608259	-0.00000834	C	4.27355064	3.83696155	-1.26328163
H	-1.56134055	-2.06608275	0.00000636	C	2.47554654	5.03056474	-0.00003587
H	0.61992883	3.37965458	-0.00001221	H	3.67251954	3.80159709	2.17572469
H	4.34094232	1.23569499	-0.00000135	H	4.98676067	3.01043662	1.30020472
H	4.34094245	-1.23569452	0.00000572	H	4.85068191	4.76477598	1.27905275
H	0.61992919	-3.37965452	0.00001145	H	3.67257311	3.80155126	-2.17574031
C	-3.06072755	-0.00000017	-0.00000110	H	4.85071507	4.76474681	-1.27905941
C	-3.71855037	-0.00000652	-1.24116366	H	4.98679113	3.01040669	-1.30017126
C	-3.71855056	0.00000614	1.24116134	H	3.09045383	5.93266176	-0.00003389
C	-5.11630655	-0.00000637	-1.20576348	H	1.83829774	5.07773437	-0.88763880
C	-5.11630672	0.00000584	1.20576096	H	1.83826986	5.07774925	0.88754625
C	-5.80644250	-0.00000030	-0.00000130	C	3.38324162	-3.78845100	0.00001343
H	-5.67180097	-0.00001115	-2.13676152	C	4.27353825	-3.83696920	1.26329258
H	-5.67180129	0.00001057	2.13675891	C	2.47554707	-5.03056447	0.00002110
H	-6.89107626	-0.00000035	-0.00000139	C	4.27353282	-3.83698070	-1.26326910
C	-2.99139645	-0.00001326	-2.58294372	H	4.98677910	-3.01041528	1.30019440
C	-3.30777753	1.27012995	-3.39393449	H	3.67255141	-3.80156381	2.17574536
C	-3.30778039	-1.27016267	-3.39392364	H	4.85070168	-4.76475509	1.27907082
H	-1.91336030	-0.00001375	-2.39842354	H	1.83828233	-5.07774564	-0.88756977
H	-3.05966019	2.17801467	-2.83779104	H	3.09045444	-5.93266144	0.00002379
H	-2.73452988	1.27927436	-4.32433406	H	1.83828633	-5.07773758	0.88761528
H	-4.36602569	1.32640026	-3.66002358	H	4.85069630	-4.76476666	-1.27904133
H	-3.05966661	-2.17804323	-2.83777181	H	3.67254204	-3.80158376	-2.17571964
H	-4.36602832	-1.32643212	-3.66001380	H	4.98677333	-3.01042696	-1.30018158

Table S7. Optimized geometries for **4b** at the UB3LYP-D3(BJ)/6-311G(d) level.

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.37988014	-0.00000215	1.18167754	H	4.33558673	-2.13863290	-0.00000239
C	-1.78179399	-0.00000219	1.23263608	H	4.33558702	2.13863246	0.00000236
C	-2.49717655	0.00000009	0.00000000	H	5.55506474	-0.00000032	-0.00000002
C	-1.78179398	0.00000231	-1.23263609	C	1.64564059	-2.56787409	-0.00000265
C	-0.37988014	0.00000216	-1.18167755	C	1.95762348	-3.37484117	1.26995471
N	0.26896806	0.00000000	-0.00000000	C	1.95762506	-3.37484038	-1.26996009
C	-2.49488507	-0.00000442	2.45567827	H	0.56968876	-2.37218754	-0.00000331
C	-3.88260930	-0.00000435	2.44530600	H	1.71496706	-2.81004185	2.17369724
C	-4.59062830	-0.00000213	1.24675834	H	1.37953600	-4.30153811	1.28442376
C	-3.91855691	0.00000014	0.00000000	H	3.01479926	-3.64408300	1.32372381
C	-4.59062830	0.00000244	-1.24675834	H	1.71497024	-2.81004032	-2.17370257
C	-3.88260930	0.00000460	-2.44530601	H	3.01480076	-3.64408280	-1.32372785
C	-2.49488508	0.00000457	-2.45567829	H	1.37953715	-4.30153704	-1.28443062
H	0.24593341	-0.00000380	2.06245552	C	1.64564102	2.56787407	0.00000265
H	0.24593342	0.00000376	-2.06245553	C	1.95762415	3.37484116	-1.26995465
H	-1.95051072	-0.00000616	3.39285119	C	1.95762564	3.37484024	1.26996013
H	-5.67464842	-0.00000211	1.25993754	H	0.56968915	2.37218778	0.00000326
H	-5.67464842	0.00000250	-1.25993755	H	1.71496766	2.81004193	-2.17369721
H	-1.95051072	0.00000624	-3.39285121	H	1.37953685	4.30153822	-1.28442366
C	1.73391590	-0.00000004	-0.00000000	H	3.01479998	3.64408278	-1.32372367
C	2.38556441	-1.23916957	-0.00000156	H	1.71497066	2.81004020	2.17370258
C	2.38556457	1.23916940	0.00000152	H	3.01480140	3.64408239	1.32372793
C	3.78215448	-1.20702647	-0.00000142	H	1.37953795	4.30153703	1.28443068
C	3.78215467	1.20702609	0.00000138	H	-4.42373710	0.00000631	-3.38414785
C	4.47091103	-0.00000023	-0.00000002	H	-4.42373708	-0.00000604	3.38414785

Table S8. Optimized geometries for **1'** at the UB3LYP-D3(BJ)/6-311G(d) level.

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.24514200	-0.00001000	-1.20074900	H	4.60653300	-2.13468200	-0.00000800
C	-1.65892700	-0.00000800	-1.23282000	H	5.84756900	0.00003600	-0.00003300
C	-2.37599700	-0.00000600	0.00001700	C	2.02703600	2.62018700	-0.00004300
C	-1.65891300	-0.00001200	1.23284500	C	1.22401000	2.95425900	1.26755700
C	-0.24512800	-0.00001200	1.20075800	C	1.22404100	2.95424500	-1.26766700
C	-2.38798500	-0.00000200	-2.44634600	H	2.88045700	3.30668600	-0.00003900
C	-3.77762900	0.00000500	-2.43876500	H	1.77951400	2.68695800	2.17021800
C	-4.48341700	0.00000400	-1.24157500	H	1.02134400	4.02888200	1.30464700
C	-3.80320400	-0.00000300	0.00002500	H	0.26509700	2.43809900	1.29376000
C	-4.48340300	-0.00000500	1.24163400	H	1.77956300	2.68692400	-2.17031100
C	-3.77760000	-0.00001100	2.43881600	H	0.26512200	2.43809600	-1.29388600
C	-2.38795700	-0.00001500	2.44638000	H	1.02138800	4.02887000	-1.30478000
H	0.30125300	-0.00001200	-2.13742300	C	2.02706600	-2.62017800	0.00001500
H	0.30127700	-0.00001500	2.13742600	C	1.22405300	-2.95425900	-1.26758200
H	-1.84535400	-0.00000200	-3.38602900	C	1.22407200	-2.95424600	1.26762900
H	-5.56860300	0.00000700	-1.24718500	H	2.88049900	-3.30665700	0.00001500
H	-5.56858800	-0.00000200	1.24725700	H	1.77955500	-2.68696300	-2.17024700
H	-1.84531400	-0.00001900	3.38605700	H	1.02138900	-4.02888500	-1.30467200
C	1.95899300	0.00000100	-0.00000800	H	0.26513500	-2.43810800	-1.29379500
C	2.66278400	1.22683400	-0.00002500	H	1.77958300	-2.68692700	2.17028100
C	2.66280000	-1.22680700	-0.00000100	H	0.26514600	-2.43810900	1.29384500
C	4.06148800	1.19591600	-0.00003200	H	1.02142400	-4.02887400	1.30474000
C	4.06151000	-1.19589000	-0.00001200	H	-4.31840700	-0.00001300	3.37956900
C	4.76229000	0.00001700	-0.00002600	H	-4.31844700	0.00000900	-3.37951300
H	4.60651400	2.13470900	-0.00004600	C	0.46121800	-0.00000600	0.00000000