Electronic Supporting Information

Boron complexes of π-extended nitroxide ligands exhibiting three-state redox processes and near-infrared-II (NIR-II) absorption properties

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General remarks

All the manipulations were performed under a dry Ar atmosphere using Schlenk techniques or using a MBraun MB150B-G-II glovebox. Unless otherwise noted, compounds obtained from commercial suppliers (Tokyo Chemical Industries Co., Ltd., KANTO CHEMICAL Co., Inc., FUJIFILM Wako Pure Chemical Corp., or Sigma-Aldrich) were used without further purifications. Column chromatography was performed using Wako Silicagel 70 PF254, Kanto Silica Gel 60 (spherical, particle size 100-210 μm). ^{1}H, ^{13}C and ^{19}F NMR spectra were measured on a Bruker Avance-III 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{19}F 376 MHz) and chemical shifts were reported as the delta scale in ppm relative to the residual solvent signals (^{1}H and ^{13}C) or an external reference ($CFCl_3$, ^{19}F). UV-vis-NIR spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. Spectroelectrochemical measurements were conducted on a BAS SEC-2000-UV/vis spectrometer and a BAS Electrochemical Analyzer Model 1140A. ESR spectra were recorded at the X-band frequency using a JEOL JES-X320 spectrometer equipped with a 100 kHz magnetic-field modulation. ESR microwave power low enough to prevent the saturation and distortion of the spectrum. ESR spectra were recorded at 25 °C or –150 °C. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTF or a timsTOF (IMS-QTOF) spectrometer using ESI or APPI mode. Electrochemical measurements were performed under a dry Ar atmosphere using a BAS Electrochemical Analyzer Model 1210C or a BAS Electrochemical Analyzer Model 1140A. Elemental analysis was carried out using a YANACO MT-6 microanalyzer. $(C_6F_5)_2BOEt$ was prepared according to a literature.[S1]

Single crystal X-ray diffraction (XRD) measurements were carried out on a Bruker D8 VENTURE System (PHOTONIII 14 with IμS Diamond) (**4a**) or a Rigaku MicroMax-007HF diffractometer equipped with a VariMax DW light source and a Pilatus P200 detector ([**5a**]$SbCl_6$ and [**5b**]$SbCl_6$). A Mo-Kα radiation (λ = 0.71073Å) that was mono-chromated by the multilayer confocal mirror was used for the measurement of the diffractions. The crystals were kept at –173 °C (**4a**) or –100 °C ([**5a**]$SbCl_6$ and [**5b**]$SbCl_6$) while the data collections. The collected data were processes using the Bruker SAINT v8.40A (Bruker Nano, Inc., 2019) (**4a**) or CrysAlisPro ver. 1.171.41.117a program package (Rigaku Oxford Diffraction, 2021) ([**5a**]$SbCl_6$ and [**5b**]$SbCl_6$). Using Olex2,[S2] the structures were solved with the SHELXT and refined with the SHELXL program packages.[S3] The full-matrix least-squares refinements were performed on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. For [**5a**]$SbCl_6$, the following level B CheckCIF alert was pointed, which may stem from the specific beamstop alignment of the Pilatus P200 detector.

PLAT910_ALERT_3_B Missing # of FCF Reflection(s) Below Theta (Min). 15 Note

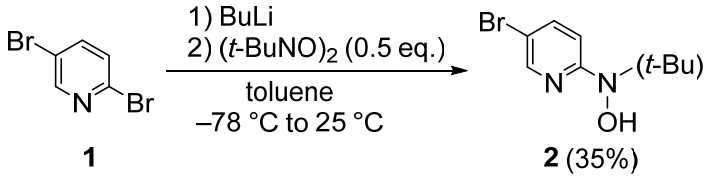
In addition, the crystals of [**5a**]$SbCl_6$ contained two CH_2Cl_2 molecules per one [**5a**]$SbCl_6$ unit, and one of the two CH_2Cl_2 molecules was highly disordered over four positions (occupancy ratio = 0.30:0.30:0.20:0.20), resulting in the relatively strong residual electron density (1.310 e Å^{-3}) around the disordered CH_2Cl_2 molecules. In order to refine the disordered CH_2Cl_2 molecule, DFIX and SIMU restraints were applied to the bond lengths and anisotropic parameters of this CH_2Cl_2 molecule. These crystallographic problems may not have substantial effects on the structural features of the main part. CCDC-2182062 (**4a**), 2182063 ([**5a**]$SbCl_6$) and 2182064 ([**5b**]$SbCl_6$) contain the supplementary crystallographic data for this paper.

Density functional theory (DFT) calculations were performed using Gaussian 16, Revision C.02[S4] program package. CAM-B3LYP density functional with 6-31G(d) and 6-31+G(d) base were employed for the geometry optimizations and single point energy calculations, respectively. ESR *g*-tensors were calculated using ORCA 5.0.3[S5] program suite at the B3LYP/EPR-II level of theory. Natural Bond Orbital (NBO) analyses were performed using NBO 7.0.[S6] The computation was performed using Research Center for Computational Science, Okazaki, Japan (Project: 19-IMS-C235, 20-IMS-C151, 21-IMS-C164, and 22-IMS-C164).

High resolution mass spectrum (HRMS) measurements and elemental analyses were carried out at the Microanalytical Laboratory, Institute for Chemical Research (ICR), Kyoto University and at University of Tsukuba, respectively.

Syntheses and copies of spectra of new compounds

*N-(5-bromopyridin-2-yl)-N-(tert-butyl)hydroxylamine (**2**)*

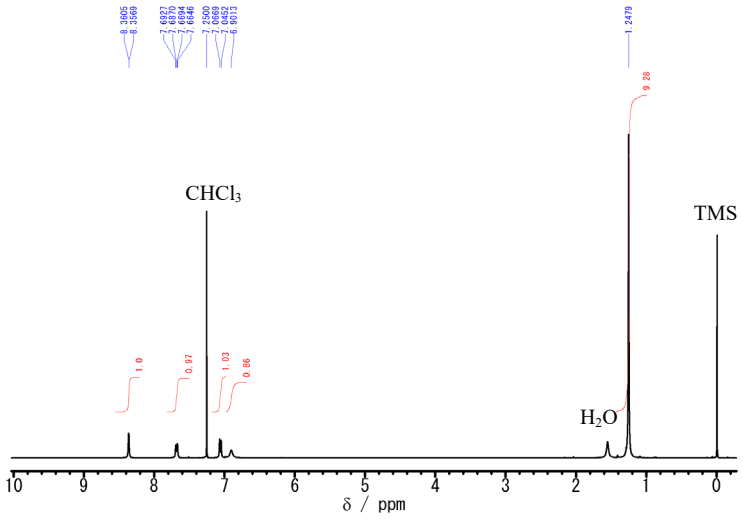


1 **2** (35%)

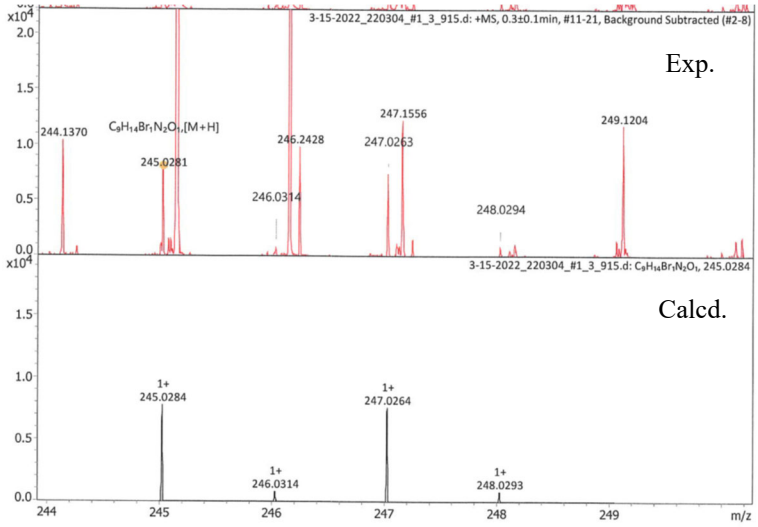
To a toluene solution (50 mL) of 2,5-dibromopyridine (**1**) (3.6 g, 15 mmol) was added n-butyl lithium (1.57 M in hexane, 11 mL, 18 mmol) at –78 °C, and the mixture was stirred for 2 h at –78 °C. This mixture was treated with 2-methyl-2-nitrosopropane dimer (1.70 g, 9.8 mmol) in toluene (20 mL) and stirred for 12 h at 25 °C. The reaction was quenched with aq. NH4Cl, and the mixture was extracted with ethyl acetate. The organic layer was dried with Na_2SO_4, and the solvents were evaporated. The crude product was separated by column chromatography (SiO_2, eluent: hexane/ethyl acetate = 9:1, v/v) to give **2** as a yellow solid (1.3 g, 5.3 mmol, 35%). Compound **2** was rapidly oxidized under air to give the corresponding nitroxide radical, and thus satisfactory ^{13}C NMR spectrum could not be recorded due to the substantial signal broadening.

^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 1.6 Hz, 1H, Ar*H*), 7.67 (dd, J = 8.7,1.6 Hz, 1H, Ar*H*), 7.06 (d, J = 8.7 Hz, 1H, Ar*H*), 6.91 (brs, 1H, O*H*), 1.25 (s, 9H, C(C*H*$_3$)$_3$); HRMS (ESI): *m*/*z* calcd for $C_9H_{14}{}^{79}BrN_2O$ 245.0284, $C_9H_{19}{}^{81}BrN_2O$ 247.0264. Found: 245.0281, 247.0263 ($[M+H]^+$).

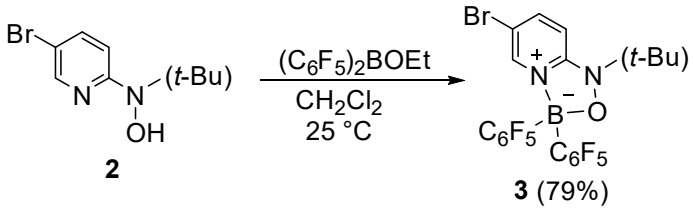
^1H NMR of **2** (400 MHz, $CDCl_3$)



HRMS (ESI) of **2**



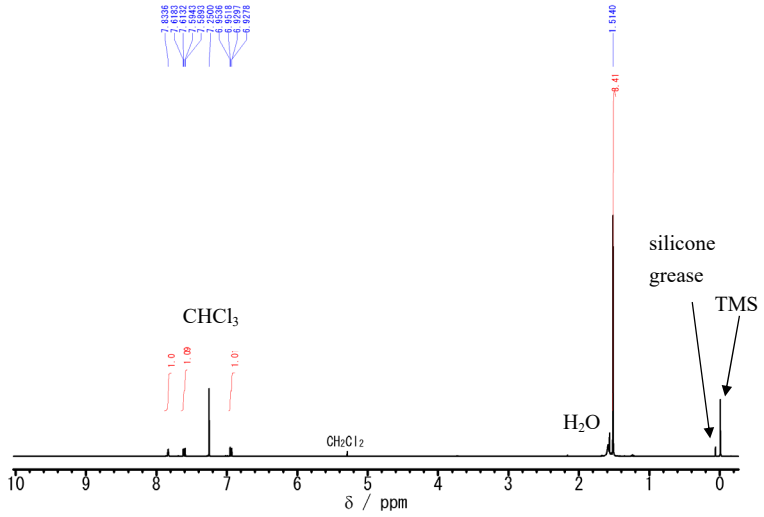
*Aminoxide-substituted borane compound **3***



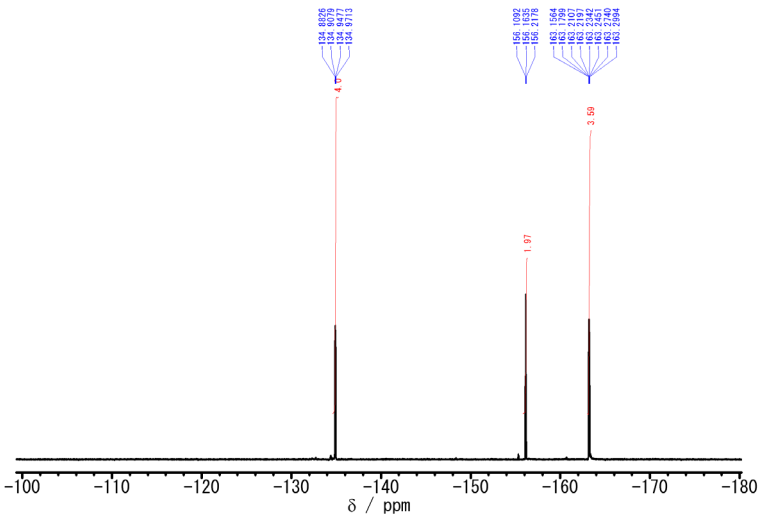
To a CH_2Cl_2 (10 mL) solution of **2** (0.40 g, 1.4 mmol) was added $(C_6F_5)_2BOEt$ (0.71 g, 1.8 mmol) at 25 °C, and the mixture was stirred for 1 h. The solvent was evaporated. The crude product was separated by column chromatography (SiO_2, eluent: hexane/ethyl acetate = 7:3, v/v) to give **3** as a yellow solid (0.78 g, 1.3 mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (brs, 1H, Ar*H*), 7.61 (dd, J = 9.6, 2.0 Hz, 1H, Ar*H*), 6.95 (dd, J = 9.6, 2.0 Hz, 1H, Ar*H*), 1.51 (s, 9H, C(C*H*$_3$)$_3$); ^{19}F NMR (376 MHz, $CDCl_3$): δ −134.92 (dd, J = 24.5, 9.4 Hz, 4F), −156.16 (t, J = 20.4 Hz, 2F), −163.15~−163.30 (m, 4F); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 27.80 (s, C(*C*H$_3$)$_3$), 62.02 (s, *C*(CH$_3$)$_3$), 105.69 (s, *C*(Ar)), 108.94 (s, *C*(Ar)), 116.12 (br, *C*B), 135.70~138.56 (m, *C*F) 139.06~141.83 (m, *C*F), 139.39 (brt, J = 3.4 Hz, *C*(Ar)), 143.20 (s, *C*(Ar)), 146.82-149.51 (m, *C*F), 151.59 (s, *C*(Ar)); HRMS (APCI): *m*/*z* calcd for $C_{21}H_{13}B^{79}BrF_{10}N_2O$ 589.0143, $C_{21}H_{13}B^{81}BrF_{10}N_2O$ 591.0125. Found: 589.0143, 591.0124 ([M+H]$^+$).

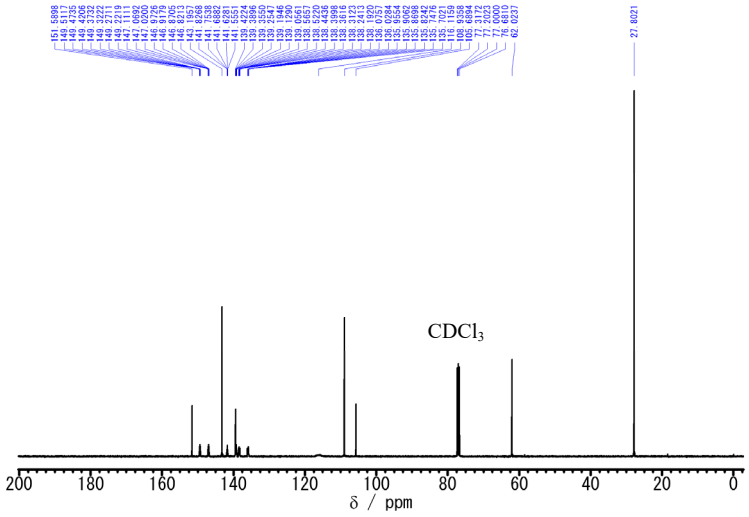
^{1}H NMR (400 MHz, $CDCl_3$) of **3**



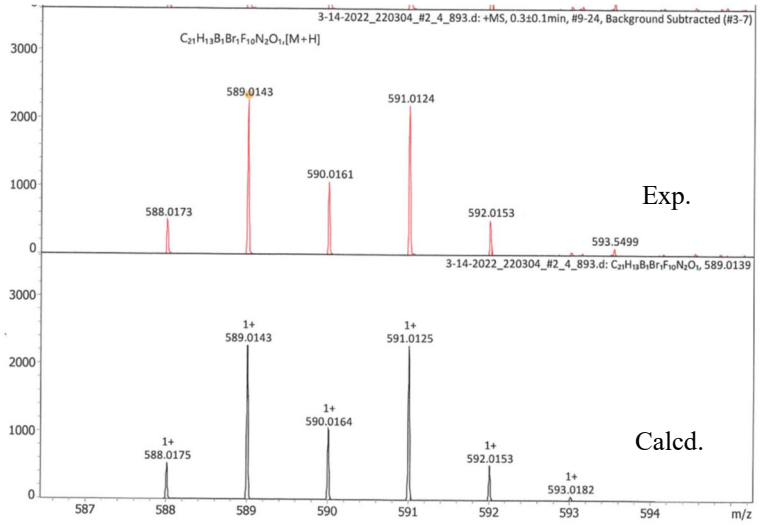
^{19}F NMR (376 MHz, $CDCl_3$) of **3**



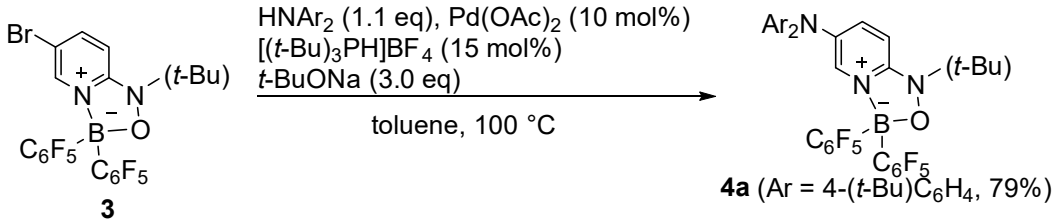
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of **3**



HRMS (APCI) of **3**



Aminoxide-substituted borane compound ***4a***



3

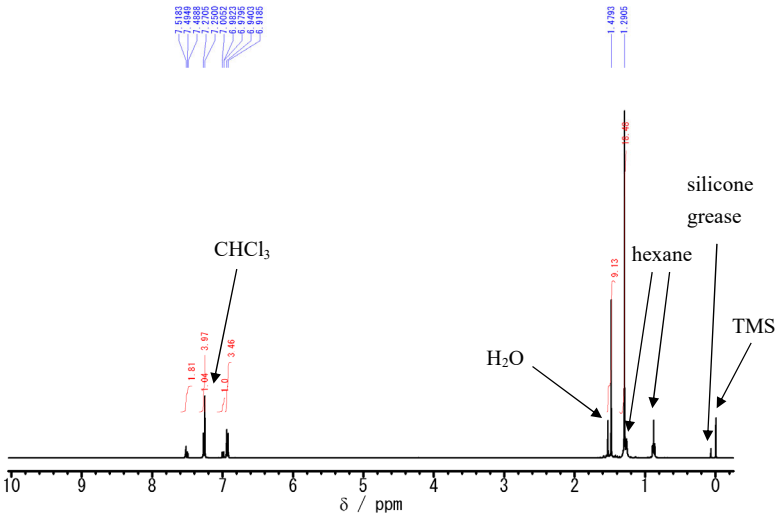
4a (Ar = 4-(*t*-Bu)C_6H_4, 79%)

A mixture of **3** (0.30 g, 0.51 mmol), bis(4-*tert*-butylphenyl)amine (0.15 g, 0.53 mmol), $Pd(OAc)_2$ (10 mg, 0.05 mmol), $[(t\text{-}Bu_3)PH]BF_4$ (20 mg, 0.080 mmol), *t*-BuONa(0.15 g, 1.5 mmol), and toluene (20 mL) was stirred at 100 °C for 20 h. The reaction was quenched with aq. NH_4Cl, and the mixture was extracted with $CHCl_3$. The organic layer was dried with $MgSO_4$, and the solvents were evaporated. The crude product was separated by column chromatography (SiO_2, eluent: hexane/ethyl acetate = 8:2,

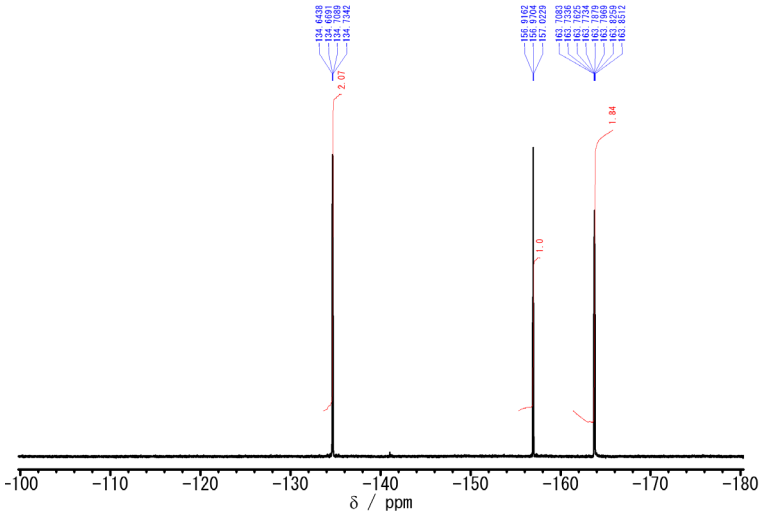
v/v) to give **4a** as a yellow solid (0.32 g, 0.40 mmol, 79%). Compound **4a** was stable in the solid state but was gradually oxidized in air-saturated solutions to give purple-coloured and NMR-silent materials, which may contain the corresponding radical and oxoammonium species.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.49 (m, 2H, Ar*H*), 7.26 (d, J = 8.7 Hz, 4H, Ar*H*), 7.04 (d, J = 9.2 Hz, 1H, Ar*H*), 6.93 (d, J = 8.7 Hz, 4H, Ar*H*), 1.47 (s, 9H, C(CH_3)$_3$), 1.29 (s, 18H, C(CH_3)$_3$); ^{19}F NMR (400 MHz, $CDCl_3$): δ −134.70 (dd, J = 24.4, 9.5 Hz, 4F), −156.97 (t, J = 20.1 Hz, 2F), −163.71~−163.85 (m, 4F); ^{13}C{^{1}H} (100 MHz, $CDCl_3$): δ 27.74 (s, C(*C*H$_3$)$_3$), 31.30 (s, C(*C*H$_3$)$_3$), 34.33 (s, *C*(CH$_3$)$_3$), 61.48 (s, *C*(CH$_3$)$_3$), 109.05 (s, *C*(Ar)), 122.98 (s, *C*(Ar)), 126.46 (s, *C*(Ar)), 133.16 (t, J = 6.7 Hz, *C*(Ar)), 135.60~138.43 (m, *C*F), 137.73 (s, *C*(Ar)), 137.80 (s, *C*(Ar)), 138.78~141.68 (m, *C*F), 143.49 (s, *C*(Ar)), 146.89 (s, *C*(Ar)), 146.95~149.51 (m, *C*F), 150.71 (s, *C*(Ar)) (the *C*B signal could not be observed probably because of the signal broadening); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.54-7.51 (m, 2H, Ar*H*), 7.28 (d, J = 6.7 Hz, 4H, Ar*H*), 7.04 (d, J = 8.4 Hz, 1H, Ar*H*), 6.94 (d, J = 6.7 Hz, 4H, Ar*H*), 1.47 (s, 9H, C(CH_3)$_3$), 1.29 (s, 18H, C(CH_3)$_3$); ^{19}F NMR (400 MHz, CD_2Cl_2): δ −135.07 (dd, J = 24.6, 10.0 Hz, 4F), −158.00 (t, J = 20.5 Hz, 2F), −164.52~−164.66 (m, 4F); UV-vis (CH_2Cl_2, rt): λ_{max} 424 nm (ε 2.4×10^3 M^{-1} cm^{-1}); HRMS (APCI): m/z calcd for $C_{41}H_{39}BF_{10}N_3O$ 790.3028. Found: 790.3027 ([M+H]$^+$).

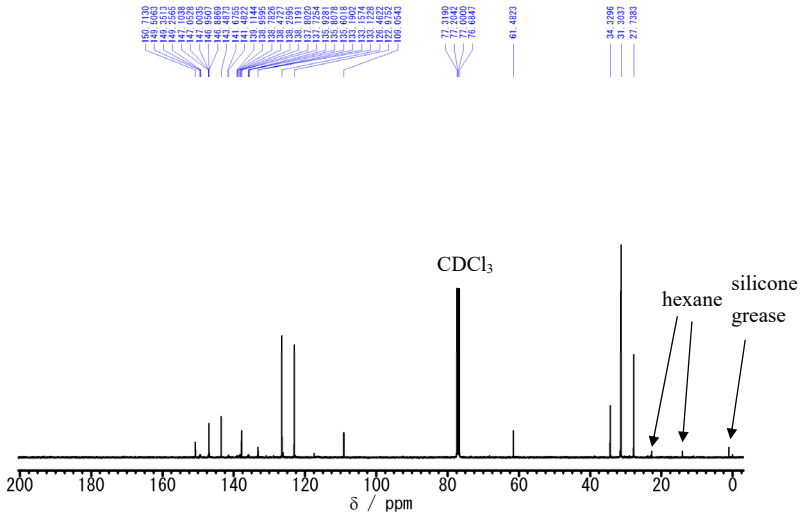
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



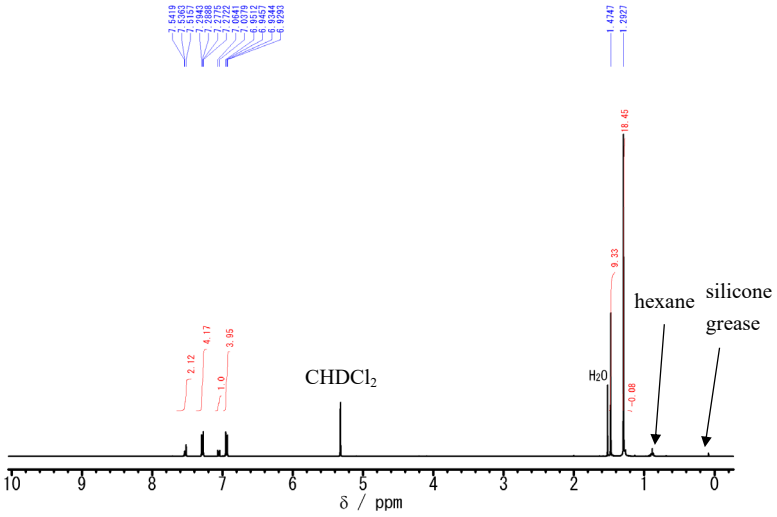
^{19}F NMR (376 MHz, $CDCl_3$) of **4a**



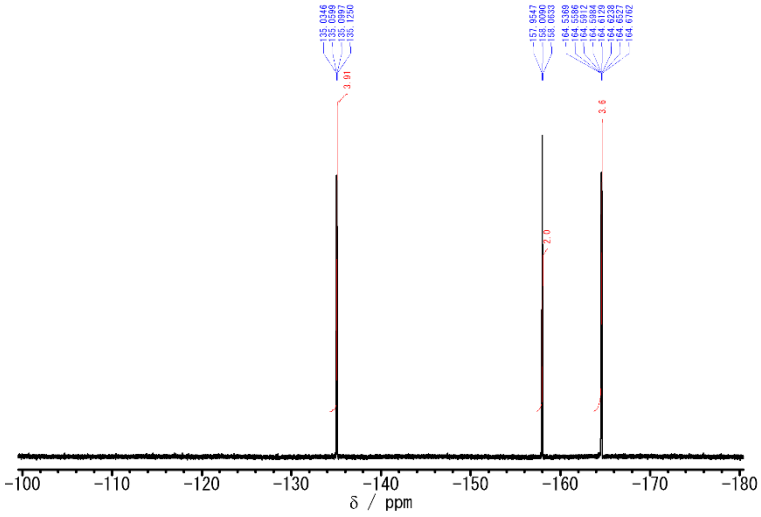
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4a**



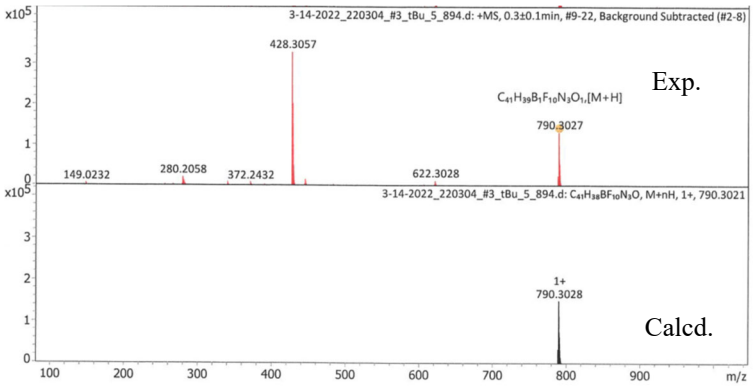
^{1}H NMR (400 MHz, CD_2Cl_2) of **4a**



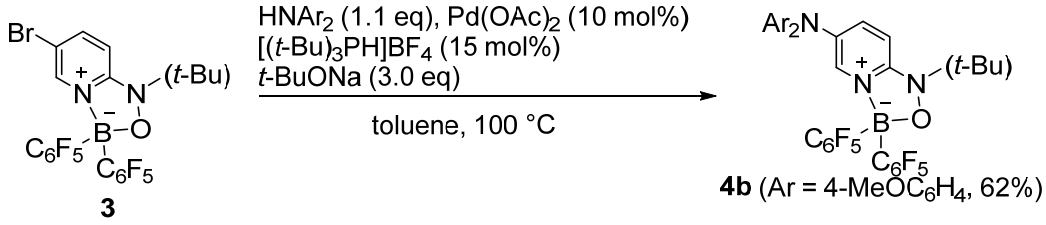
^{19}F NMR (376 MHz, CD_2Cl_2) of **4a**



HRMS (APCI) of **4a**



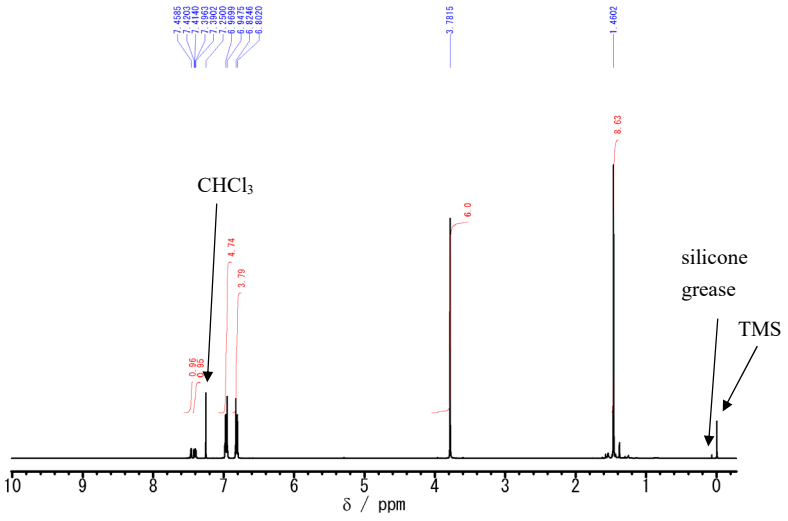
Aminoxide-substituted borane compound ***4b***



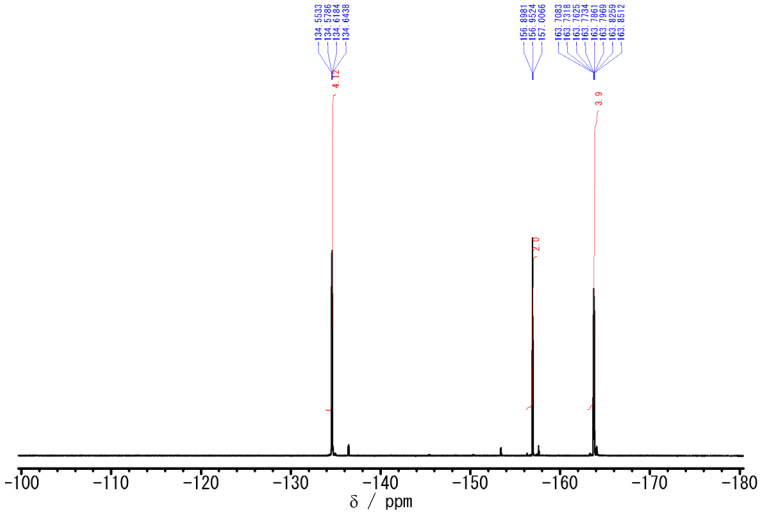
A mixture of **3** (0.15 g, 0.25 mmol), bis(4-methoxyphenyl)amine (0.07 g, 0.28 mmol), $Pd(OAc)_2$ (7 mg, 0.03 mmol), $[(t\text{-}Bu_3)PH]BF_4$ (0.012 g, 0.04 mmol), *t*-BuONa (0.07 g, 0.75 mmol), and toluene (5 mL) was stirred at 100 °C for 20 h. The reaction was quenched with aq. NH_4Cl, and the mixture was extracted with $CHCl_3$. The organic layer was dried with $MgSO_4$, and the solvents were evaporated. The crude product was separated by column chromatography (SiO_2, eluent: hexane/ethyl acetate = 8:2, v/v) to give **4b** as a yellow solid (0.11 g, 0.16 mmol, 62%). Compound **4b** was gradually oxidized under air even in the solid state and was rapidly oxidized in air-saturated solutions to give green-coloured and NMR-silent materials, which may contain the corresponding radical and oxoammonium species.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (br, 1H, Ar*H*), 7.40 (dd, J = 9.6, 2.5 Hz, 1H, Ar*H*), 7.02 (dd, J = 1.9, 8.8 Hz, 1H, Ar*H*), 6.95 (d, J = 9.0 Hz, 4H, Ar*H*), 6.93~6.98 (m, 1H, Ar*H*), 6.81 (d, J = 9.0 Hz, 4H, Ar*H*), 3.78 (s, 6H, OCH_3), 1.46 (s, 9H, C(CH_3)$_3$); ^{19}F NMR (400 MHz, $CDCl_3$): δ −135.02 (dd, J = 24.5, 9.4 Hz, 4F), −158.02 (t, J = 20.2 Hz, 2F), −164.55~−164.70 (m, 4F); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ27.68 (s, C(*C*H$_3$)$_3$), 55.49 (s, *C*(CH$_3$)$_3$), 61.43 (s, O*C*H$_3$), 109.24 (s, *C*(Ar)), 115.62 (s, *C*(Ar)), 125.50 (s, *C*(Ar)), 130.39 (t, J = 9.5 Hz, *C*(Ar)), 135.63 (s, *C*(Ar)), 135.73~138.45 (m, *C*F), 138.82 (s, *C*(Ar)), 139.24 (s, *C*(Ar)), 138.95~141.62 (m, *C*F), 146.83~149.53 (m, *C*F), 150.34 (s, *C*(Ar)), 156.44 (s, *C*(Ar)) (the *C*B signal could not be observed probably because of the signal broadening); UV-vis (CH_2Cl_2, rt): λ_{max} 427 nm (ε 2.3×10^3 M^{-1} cm^{-1}); HRMS (APCI): *m*/*z* calcd for $C_{35}H_{27}BF_{10}N_3O_3$ 738.1986. Found: 738.1984 ([M+H]$^+$).

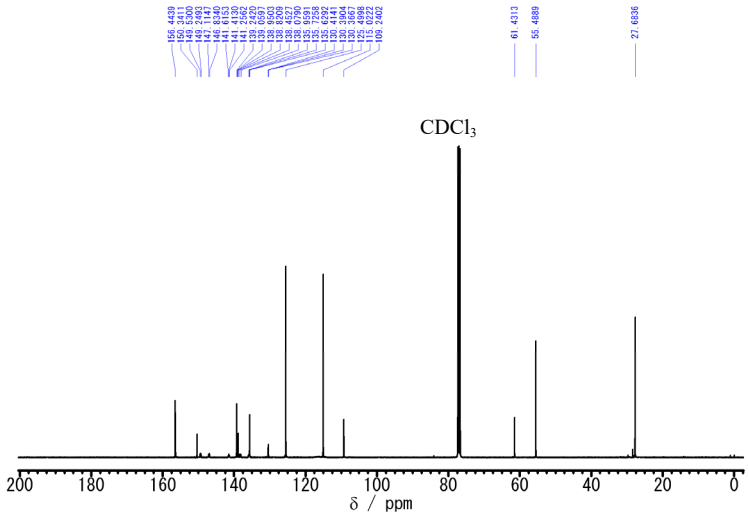
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



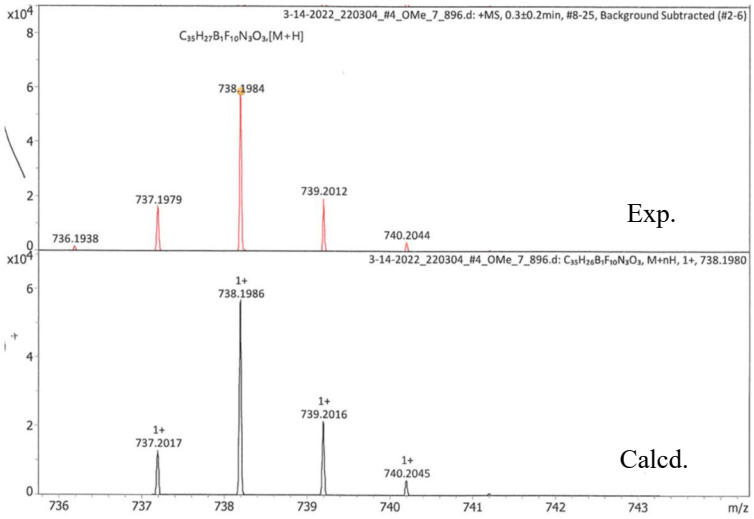
^{19}F NMR (376 MHz, $CDCl_3$) of **4b**



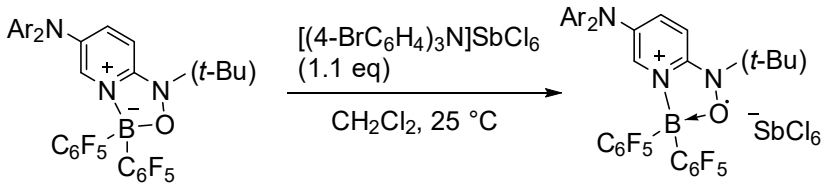
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of **4b**



HRMS (APCI) of **4b**



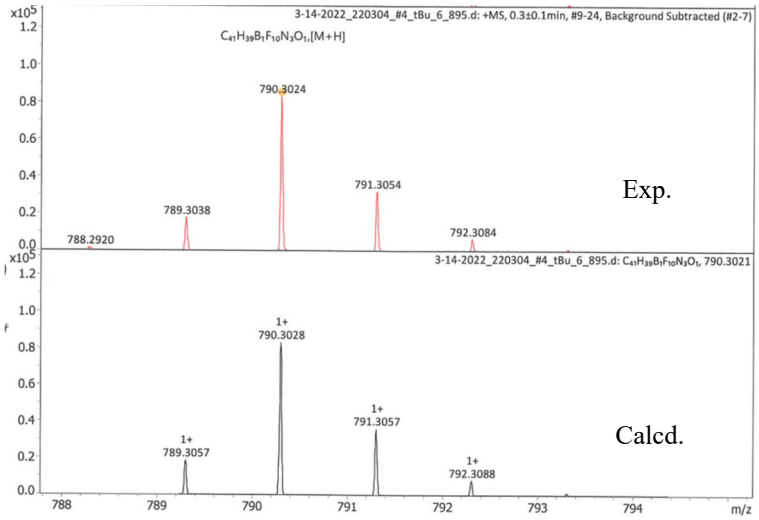
*Nitroxide radical-boranylium ion complex [**5a**]SbCl₆*



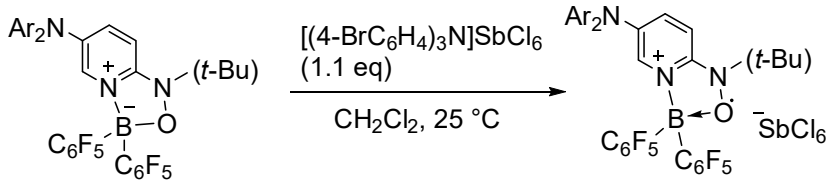
4a (Ar = 4-(*t*-Bu)C₆H₄) → [**5a**]SbCl₆ (67%)

A mixture of **4a** (0.10 g, 0.13 mmol), [(4-BrC₆H₄)₃N]SbCl₆ (0.13 g, 0.15 mmol) and CH_2Cl_2 (5 mL) was stirred at 25 °C for 1 h, and the solvent was evaporated. The residue was washed with Et_2O (2 times) and re-crystalized from CH_2Cl_2 at –10 °C to give [**5a**]SbCl₆ as a dark purple solid (0.095 g, 0.085 mmol). UV-vis-NIR (CH_2Cl_2, rt): λ_{max} 1052 nm (ε 1.7×10^4 M^{-1} cm^{-1}); ESR (X-band, CH_2Cl_2, rt): *g* 2.0037; HRMS (APCI): *m/z* calcd for $C_{41}H_{39}BF_{10}N_3O$ 790.3028. Found: 790.3024 ([**5a**+H]$^+$). Anal. calcd for $C_{41}H_{38}N_3BOCl_6Sb$: C, 43.81; H, 3.41; N, 3.74. Found: C, 43.99; H, 3.63; N, 3.84.

HRMS (APCI) of [**5a**]SbCl₆



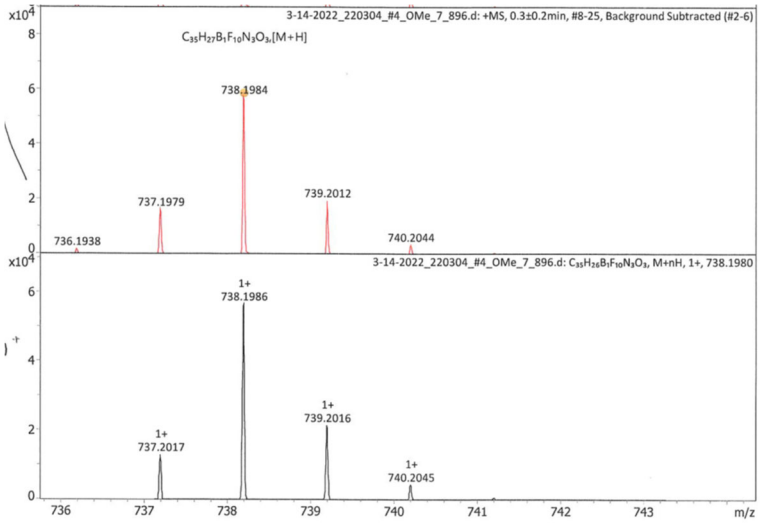
*Nitroxide radical-boranylium ion complex [**5b**]SbCl$_6$*



4b (Ar = 4-MeOC$_6$H$_4$) [**5b**]SbCl$_6$ (92%)

A mixture of **4b** (0.10 g, 0.12 mmol), [(4-BrC$_6$H$_4$)$_3$N]SbCl$_6$ (0.11 g, 0.13 mmol) and CH$_2$Cl$_2$ (5 mL) was stirred at 25 °C for 1 h, and the solvent was evaporated. The residue was washed with hexane and re-crystallized from CH$_2$Cl$_2$ at –10 °C to give [**5b**]SbCl$_6$ as a dark green solid (0.11 g, 0.10 mmol). UV-vis-NIR (CH$_2$Cl$_2$, rt): λ_{max} 1081 nm (ε 1.6×10^4 M^{-1} cm^{-1}); ESR (X-band, CH$_2$Cl$_2$, rt): g 2.0035; HRMS (APCI): m/z calcd for C$_{35}$H$_{27}$BF$_{10}$N$_3$O$_3$ 738.1986. Found: 738.1984 ([**5b**+H]$^+$). Anal. calcd for C$_{35}$H$_{26}$N$_3$BO$_3$Cl$_6$Sb: C, 39.22; H, 2.45; N, 3.92. Found: C, 39.34; H, 2.65; N, 4.00.

HRMS (APCI) of [**5b**]SbCl$_6$



XRD data

*Compound **4a***

Empirical formula	$C_{41}H_{38}BF_{10}N_3O$	
Formula weight	789.55	
Temperature	–173 °C	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 9.8688(5) Å	α= 95.144(2)°.
	b = 10.8972(6) Å	β= 100.083(2)°.
	c = 18.0044(9) Å	γ= 96.151(2)°.
Volume	1883.69(17) $Å^3$	
Z	2	
Density (calculated)	1.392 g cm^{-3}	
Absorption coefficient	0.118 mm^{-1}	
F(000)	816	
Crystal size	0.220×0.200×0.150 mm^3	
θ range for data collection	1.891 to 27.499°.	
Index ranges	-12<=h<=12, -14<=k<=14, -23<=l<=23	
Reflections collected	39509	
Independent reflections	8650 [R(int) = 0.0718]	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.910	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8650 / 0 / 514	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2σ(I)]	R_1 = 0.0538, wR_2 = 0.1436	
R indices (all data)	R_1 = 0.0689, wR_2 = 0.1594	
Largest diff. peak and hole	0.585 and –0.408 e $Å^{-3}$	
CCDC No.	2182062	

*Compound [**5a**]SbCl$_6$*

Empirical formula	$C_{43}H_{42}BCl_{10}F_{10}N_3OSb$
Formula weight	1293.85
Temperature	–100 °C
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 21.093(7) Å
	b = 11.908(5) Å β = 108.42(5)°.
	c = 23.298 (14) Å
Volume	5552(5) Å^3
Z	4
Density (calculated)	1.548 g cm^{-3}
Absorption coefficient	1.047 mm^{-1}
F(000)	2580.0
Crystal size	0.36×0.26×0.23 mm^3
θ range for data collection	5.846 to 59.528°.
Index ranges	-28<=h<=27, -15<=k<=13, -32<=l<=32
Reflections collected	46335
Independent reflections	14171 [R(int) = 0.0233]
Completeness to θ = 25.242°	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.91904
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14171/ 210 / 712
Goodness-of-fit on F^2	1.044
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0516, wR_2 = 0.1269
R indices (all data)	R_1 = 0.0757, wR_2 = 0.1383
Largest diff. peak and hole	1.307 and –0.850 e Å^{-3}
CCDC No	2182063

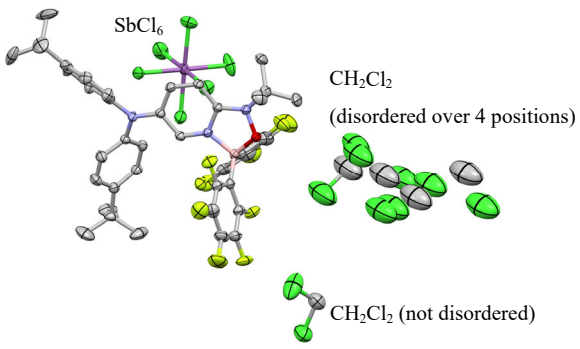


Fig. S1 Structure of [**5a**]SbCl$_6$ (50% probability level). Hydrogen atoms are omitted.

*Compound [**5b**]SbCl$_6$*

Empirical formula	$C_{35}H_{26}BF_{10}N_3O_3SbCl_6$
Formula weight	1071.85
Temperature	–100 °C
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 18.0480(11) Å
	b = 10.6917(7) Å β = 102.647(6)°.
	c = 21.8391(12) Å
Volume	4111.9(4) Å^3
Z	4
Density (calculated)	1.731 g cm^{-3}
Absorption coefficient	1.146 mm^{-1}
F(000)	2116
Crystal size	0.070×0.070×0.050 mm^3
θ range for data collection	2.767 to 27.481°.
Index ranges	-23<=h<=22, -13<=k<=13, -25<=l<=28
Reflections collected	34211
Independent reflections	9429 [R(int) = 0.0601]
Completeness to θ = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.51931
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9429 / 0 / 537
Goodness-of-fit on F^2	1.013
Final R indices [I>2σ(I)]	R_1 = 0.0513, wR_2 = 0.0841
R indices (all data)	R_1 = 0.0967, wR_2 = 0.0949
Largest diff. peak and hole	0.662 and –0.487 e Å^{-3}
CCDC No	2182064

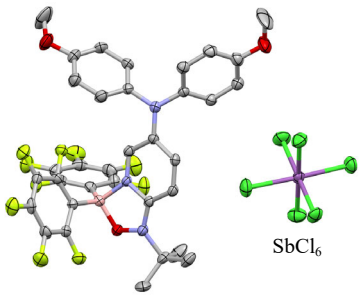


Fig. S2 Structure of [**5b**]SbCl$_6$ (50% probability level). Hydrogen atoms are omitted.

ESR spectra of ***5***

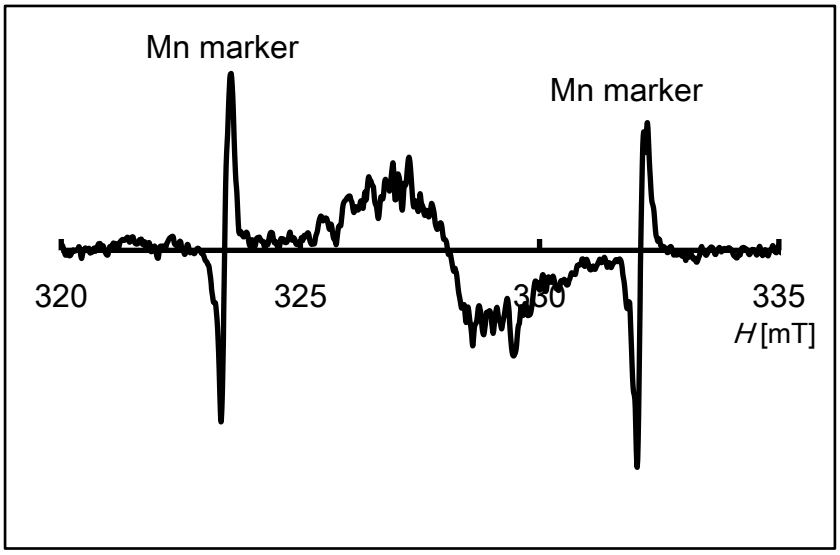


Fig. S3 ESR spectrum of [**5a**]$SbCl_6$ in CH_2Cl_2 at –150 °C.

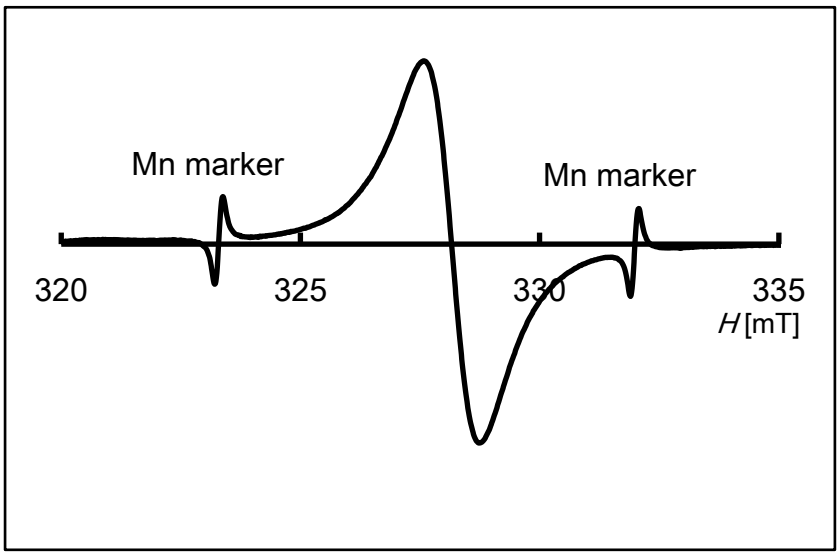


Fig. S4 ESR spectrum of [**5b**]$SbCl_6$ in CH_2Cl_2 at –150 °C.

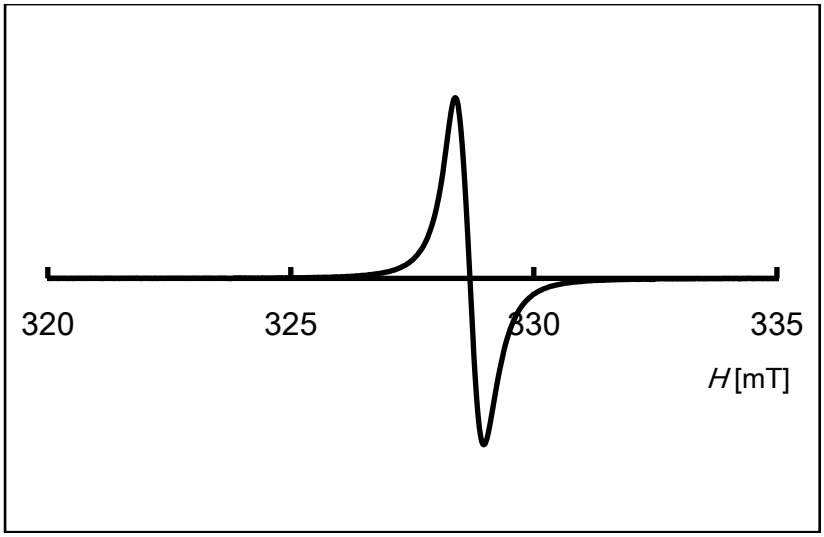


Fig. S5 ESR spectrum of [**5a**]$SbCl_6$ in the solid state at 25 °C.

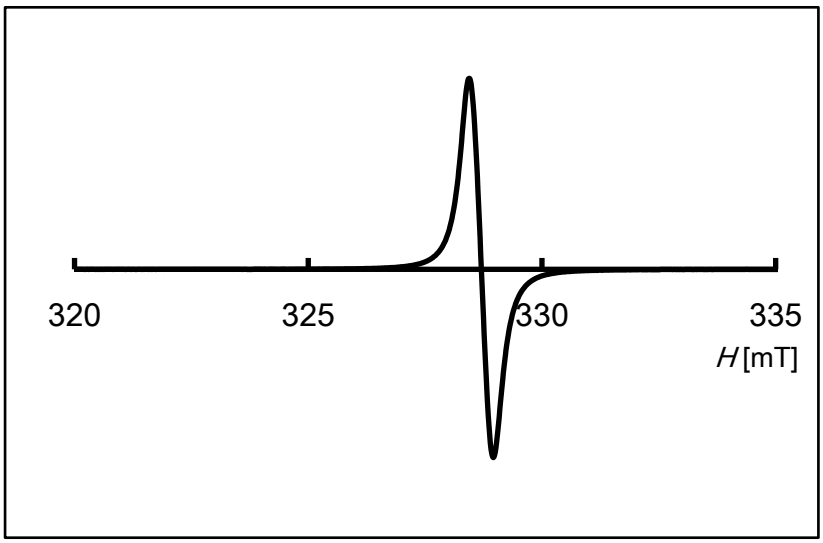


Fig. S6 ESR spectrum of [**5b**]$SbCl_6$ in the solid state at 25 °C.

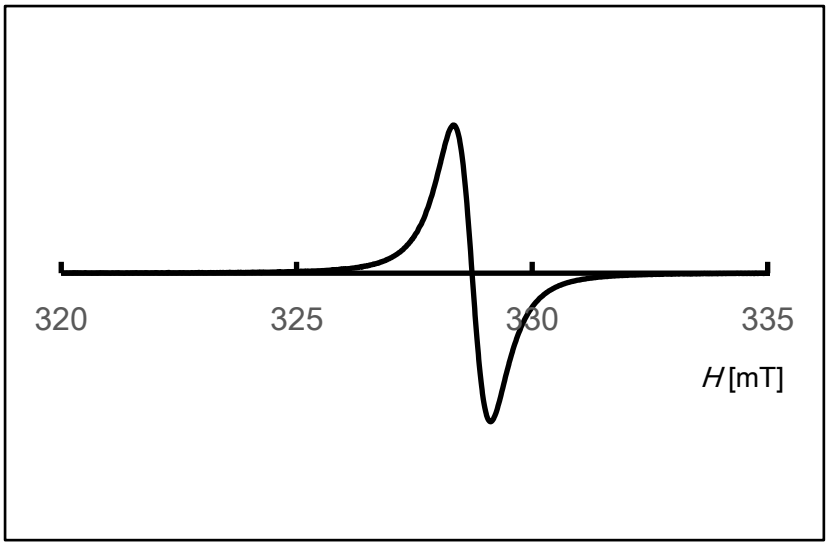


Fig. S7 ESR spectrum of [**5a**]$SbCl_6$ in the solid state at –150 °C.

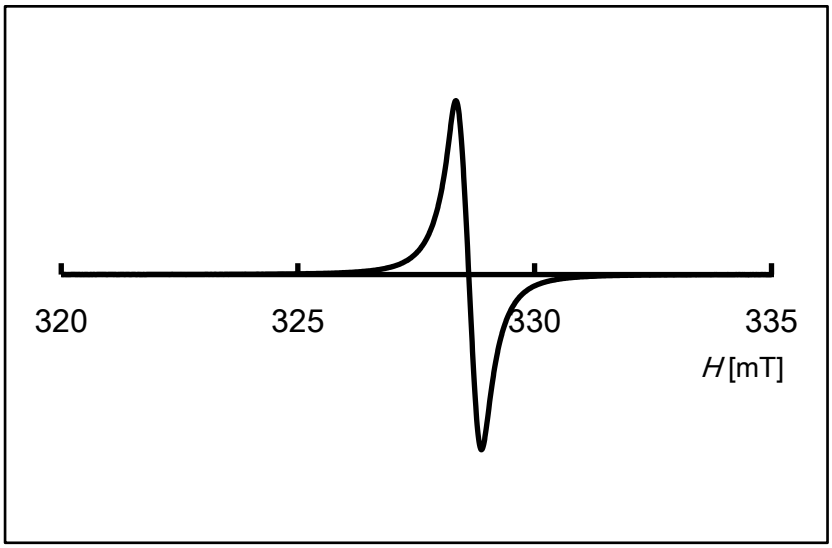


Fig. S8 ESR spectrum of [**5b**]$SbCl_6$ in the solid state at –150 °C.

Computational data

Cartesian coordinates of ***4a***

C	-0.6126	-2.31438	-1.46247
C	0.303218	-0.48229	-0.28994
C	0.616315	-2.50368	-2.12574
C	1.518538	-0.59159	-0.92914
H	0.091863	0.301294	0.423635
C	1.653593	-1.64324	-1.86
H	0.736159	-3.28518	-2.85817
H	2.596197	-1.76561	-2.38261
N	-0.71679	-1.30936	-0.57265
N	-1.81447	-2.93455	-1.63165
O	-2.66645	-2.53303	-0.58288
C	-2.06543	-4.35846	-1.96724
C	-1.35781	-4.72927	-3.27486
C	-1.59997	-5.25381	-0.81498
C	-3.57717	-4.4899	-2.18434
H	-1.49046	-3.95122	-4.03211
H	-0.29244	-4.92659	-3.13958
H	-1.79971	-5.65152	-3.66054
H	-2.08249	-4.9542	0.116963
H	-1.85003	-6.29869	-1.0221
H	-0.51596	-5.18424	-0.67703
H	-3.80774	-5.51564	-2.48544
H	-4.12835	-4.25616	-1.27462
H	-3.9105	-3.806	-2.96904
B	-2.23247	-1.22891	-0.06974
C	-2.34266	-1.26672	1.549153
C	-3.18666	-0.4901	2.334054
C	-1.59163	-2.20585	2.25197
C	-3.26959	-0.61176	3.714977
C	-1.64235	-2.36071	3.627377
C	-2.49072	-1.55192	4.366388
C	-2.90036	0.066663	-0.82313
C	-3.77086	-0.02573	-1.90231

C	-2.56574	1.364952	-0.45565
C	-4.27261	1.086717	-2.57026
C	-3.03786	2.497582	-1.09215
C	-3.903	2.356668	-2.16586
F	-4.17927	-1.21218	-2.37292
F	-1.73591	1.571334	0.59009
F	-3.99207	0.428461	1.782881
F	-0.756	-3.03204	1.594234
F	-0.88961	-3.27621	4.241627
F	-2.55855	-1.68236	5.689397
F	-4.09817	0.164255	4.415466
F	-2.66961	3.720213	-0.68671
F	-4.36912	3.43138	-2.79971
F	-5.10334	0.93638	-3.60407
N	2.53252	0.358146	-0.7135
C	2.117345	1.695515	-0.43355
C	3.877505	-0.03353	-0.52109
C	2.426053	2.312663	0.776866
C	1.321969	2.375524	-1.35089
C	4.914148	0.832889	-0.88161
C	4.210997	-1.27283	0.020782
C	1.915114	3.570188	1.064381
H	3.050047	1.795656	1.498847
C	0.801444	3.625383	-1.04258
H	1.08789	1.907507	-2.30201
C	6.234033	0.459232	-0.6984
H	4.675985	1.802067	-1.30652
C	5.543907	-1.63956	0.180246
H	3.428092	-1.95618	0.332653
C	1.074552	4.249488	0.175694
H	2.154938	4.01383	2.025243
H	0.166948	4.111865	-1.77302
C	6.589677	-0.78765	-0.16902

H	7.009075	1.161441	-0.99003
H	5.753104	-2.61405	0.60543
C	8.066655	-1.15657	0.003307
C	8.248	-2.55656	0.601175
C	8.766841	-1.12533	-1.36706
C	8.743088	-0.14238	0.942936
H	7.796085	-2.63642	1.594971
H	7.812077	-3.33158	-0.03736
H	9.314906	-2.77689	0.705433
H	8.707965	-0.13673	-1.83148
H	9.826884	-1.37987	-1.25946
H	8.312428	-1.84543	-2.05502
H	9.802465	-0.38977	1.071704
H	8.685221	0.877023	0.550624

H	8.270003	-0.14793	1.929996
C	0.437234	5.582431	0.579651
C	-0.30225	6.247897	-0.58813
C	-0.58148	5.301863	1.700833
C	1.509882	6.561337	1.085352
H	0.365956	6.439795	-1.43438
H	-1.14069	5.639898	-0.93755
H	-0.70892	7.210125	-0.26184
H	-0.09643	4.878141	2.585745
H	-1.08373	6.227567	2.002898
H	-1.34073	4.592025	1.359657
H	1.045092	7.50917	1.376425
H	2.043491	6.177319	1.959176
H	2.249246	6.772038	0.305796

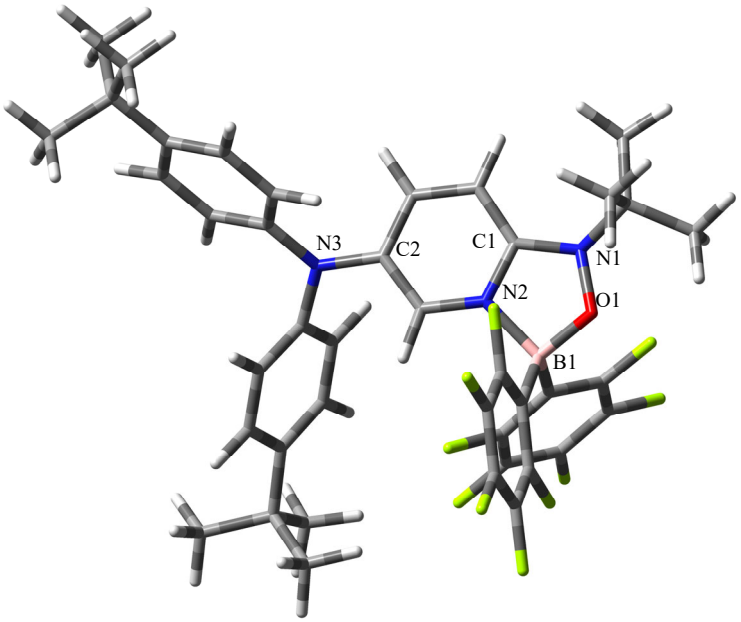


Fig. S9 DFT-optimized structure of **4a**. Selected bond lengths (Å): N1-O1 1.410, C1-N1 1.363, O1-B1 1.467, N2-B1 1.599, C2-N3 1.406.

*Cartesian coordinates of **4b***

C	-0.4726	-2.22231	-1.0556
C	0.583693	-0.33992	-0.09987
C	0.744836	-2.60473	-1.64724
C	1.800954	-0.64012	-0.67694

H	0.430763	0.538791	0.508387
C	1.851289	-1.81079	-1.46425
H	0.80879	-3.48488	-2.26631
H	2.786996	-2.08693	-1.93741

N	-0.50429	-1.09704	-0.32016
N	-1.72603	-2.76026	-1.17734
O	-2.54545	-2.14943	-0.20165
C	-2.0616	-4.20424	-1.2764
C	-1.41046	-4.81199	-2.5238
C	-1.61528	-4.93338	-0.00539
C	-3.58304	-4.28382	-1.44417
H	-1.52289	-4.15158	-3.38836
H	-0.35332	-5.0453	-2.38183
H	-1.90987	-5.75649	-2.75464
H	-2.03852	-4.44897	0.87666
H	-1.94552	-5.97626	-0.02883
H	-0.52428	-4.92573	0.089955
H	-3.87278	-5.32903	-1.58438
H	-4.09827	-3.88836	-0.57003
H	-3.90083	-3.70658	-2.31586
B	-2.03534	-0.80409	0.063105
C	-2.21797	-0.48611	1.640359
C	-2.98423	0.536749	2.186487
C	-1.61337	-1.32756	2.571406
C	-3.13506	0.727666	3.553877
C	-1.73693	-1.17274	3.942254
C	-2.50617	-0.13191	4.437345
C	-2.55271	0.337579	-0.99615
C	-3.4369	0.093263	-2.03976
C	-2.05223	1.633077	-0.95098
C	-3.78339	1.05816	-2.98028
C	-2.35789	2.620327	-1.8696
C	-3.238	2.326761	-2.89994
F	-4.01352	-1.10499	-2.20546
F	-1.20737	1.983604	0.042839
F	-3.64072	1.402314	1.40252
F	-0.85432	-2.35897	2.157827
F	-1.12622	-2.01008	4.783966
F	-2.64012	0.036914	5.751095

F	-3.88397	1.728033	4.020674
F	-1.81373	3.838745	-1.77833
F	-3.55269	3.255722	-3.80121
F	-4.63415	0.764855	-3.9664
N	2.909276	0.20418	-0.5338
C	2.715475	1.600544	-0.31922
C	4.220231	-0.3425	-0.46656
C	3.415991	2.274037	0.674302
C	1.806351	2.320432	-1.10404
C	5.257105	0.22762	-1.21419
C	4.502549	-1.44181	0.33716
C	3.226793	3.638014	0.88469
H	4.123664	1.731064	1.291664
C	1.58223	3.663316	-0.87581
H	1.254372	1.812702	-1.88811
C	6.53608	-0.28947	-1.15055
H	5.047673	1.087136	-1.84216
C	5.784419	-1.98506	0.387591
H	3.71211	-1.88463	0.934909
C	2.299157	4.337315	0.117195
H	3.79508	4.133035	1.662312
H	0.844804	4.209939	-1.45271
C	6.810363	-1.40516	-0.35351
H	7.346753	0.147083	-1.72355
H	5.967764	-2.84465	1.020228
O	8.096087	-1.8432	-0.37084
O	2.021669	5.659563	0.254247
C	2.692547	6.378516	1.265266
H	2.317088	7.400503	1.20974
H	2.478879	5.968813	2.25997
H	3.777668	6.383627	1.104306
C	8.429511	-2.95763	0.427603
H	9.493278	-3.13599	0.269373
H	8.250931	-2.75877	1.491272
H	7.86571	-3.84998	0.129392

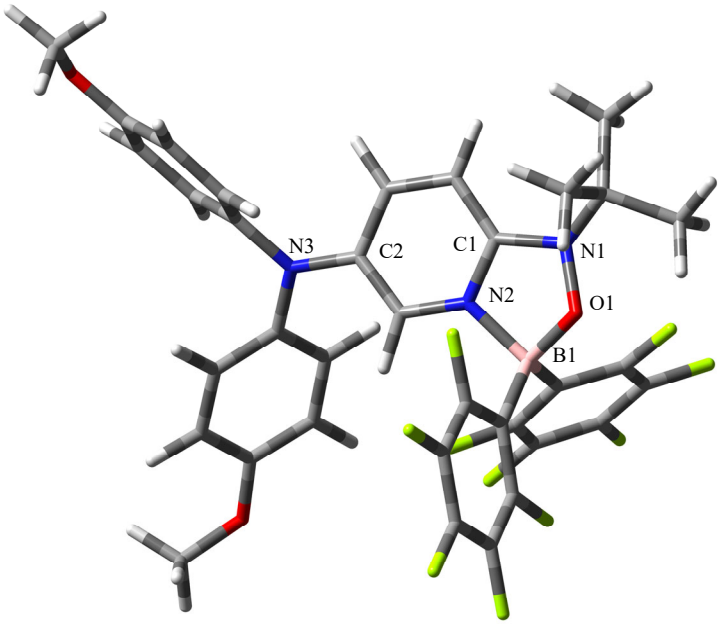


Fig. S10 DFT-optimized structure of **4b**. Selected bond lengths (Å): N1-O1 1.413, C1-N1 1.369, O1-B1 1.463, N2-B1 1.605, C2-N3 1.401.

*Cartesian coordinates of **5a***

C	-0.58405	-2.48737	-1.02083
C	0.243037	-0.50272	-0.07717
C	0.716039	-2.87456	-1.42014
C	1.561434	-0.80166	-0.4753
H	-0.00656	0.405447	0.454014
C	1.766029	-2.04774	-1.13683
H	0.879	-3.79879	-1.95433
H	2.765774	-2.32467	-1.44732
N	-0.75759	-1.31522	-0.3512
N	-1.76865	-3.09415	-1.18555
O	-2.77909	-2.42614	-0.61799
C	-2.11947	-4.3688	-1.89773
C	-1.74504	-4.19339	-3.3738
C	-1.37486	-5.52502	-1.2223
C	-3.62832	-4.57755	-1.77073
H	-2.26874	-3.33154	-3.79539
H	-0.67134	-4.06241	-3.52853
H	-2.05095	-5.0859	-3.92488
H	-1.60764	-5.56105	-0.1549

H	-1.7016	-6.46389	-1.67566
H	-0.29078	-5.4661	-1.33947
H	-3.88156	-5.49256	-2.31111
H	-3.93392	-4.69525	-0.72987
H	-4.18495	-3.74734	-2.20644
B	-2.32387	-1.08449	-0.08488
C	-2.66978	-1.03308	1.48201
C	-3.56708	-0.16205	2.091082
C	-2.09695	-1.97993	2.327222
C	-3.85413	-0.20459	3.449035
C	-2.35352	-2.05872	3.683814
C	-3.24356	-1.15674	4.249633
C	-2.77888	0.140532	-1.03988
C	-3.40444	-0.00756	-2.27222
C	-2.46067	1.450359	-0.69542
C	-3.726	1.067169	-3.09299
C	-2.7525	2.546488	-1.48429
C	-3.39939	2.353506	-2.69687
F	-3.71328	-1.22427	-2.75414

F	-1.80994	1.692733	0.46286
F	-4.21119	0.767837	1.378914
F	-1.23875	-2.88964	1.816232
F	-1.76486	-2.98367	4.43719
F	-3.50914	-1.2093	5.546183
F	-4.71405	0.656285	3.981575
F	-2.40457	3.77594	-1.09832
F	-3.68378	3.388393	-3.47397
F	-4.32519	0.863244	-4.26117
N	2.551986	0.106493	-0.24673
C	2.184713	1.484322	-0.07914
C	3.928544	-0.2629	-0.17555
C	2.484988	2.159257	1.100371
C	1.473433	2.128347	-1.08743
C	4.887315	0.518227	-0.8209
C	4.327619	-1.37424	0.561622
C	2.028172	3.456342	1.27457
H	3.048439	1.661435	1.882794
C	1.025681	3.427836	-0.89573
H	1.268717	1.611428	-2.02021
C	6.223432	0.169995	-0.73366
H	4.582293	1.390024	-1.38945
C	5.673789	-1.71075	0.632167
H	3.593609	-1.96344	1.102764
C	1.274767	4.117013	0.293877
H	2.247427	3.955408	2.211472
H	0.468021	3.903606	-1.692
C	6.653919	-0.95165	-0.0108

H	6.950132	0.789661	-1.24751
H	5.954247	-2.57602	1.219402
C	8.145192	-1.2915	0.054622
C	8.417637	-2.54698	0.891026
C	8.6716	-1.53513	-1.37183
C	8.906219	-0.1121	0.687822
H	8.09538	-2.4254	1.930098
H	7.924097	-3.43156	0.475612
H	9.492089	-2.74932	0.904659
H	8.549372	-0.65604	-2.01105
H	9.739005	-1.77427	-1.34041
H	8.151793	-2.37309	-1.84701
H	9.975189	-0.34098	0.737862
H	8.792769	0.808774	0.108703
H	8.554446	0.083855	1.70548
C	0.693408	5.506387	0.5662
C	0.145901	6.163214	-0.70799
C	-0.46753	5.332259	1.565557
C	1.761456	6.436763	1.164801
H	0.916728	6.259088	-1.47983
H	-0.70023	5.610402	-1.12481
H	-0.21144	7.169324	-0.47199
H	-0.12021	4.916905	2.516831
H	-0.9362	6.299543	1.772634
H	-1.23078	4.661206	1.159237
H	1.330317	7.426551	1.341259
H	2.143154	6.076817	2.124008
H	2.610499	6.556072	0.484386

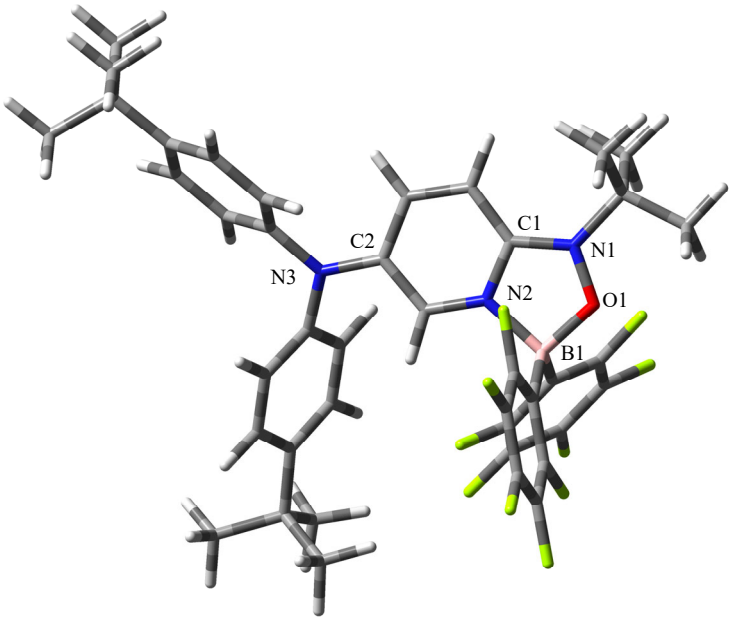


Fig. S11 DFT-optimized structure of **5a**. Selected bond lengths (Å): N1-O1 1.338, C1-N1 1.341, O1-B1 1.514, N2-B1 1.605, C2-N3 1.363.

*Cartesian coordinates of **5b***

C	-0.53966	-2.35678	-0.65342
C	0.524992	-0.3928	0.088976
C	0.705055	-2.90643	-1.06065
C	1.785194	-0.8639	-0.30668
H	0.386516	0.576058	0.548199
C	1.836212	-2.16812	-0.88443
H	0.754197	-3.88226	-1.51998
H	2.790067	-2.56613	-1.20799
N	-0.56807	-1.10689	-0.10539
N	-1.77012	-2.8562	-0.71572
O	-2.69445	-2.03443	-0.16505
C	-2.26584	-4.16658	-1.25063
C	-1.9619	-4.20666	-2.75252
C	-1.58997	-5.30343	-0.47674
C	-3.77777	-4.22412	-1.03093
H	-2.43662	-3.36012	-3.25419
H	-0.89094	-4.18841	-2.97024
H	-2.3673	-5.12997	-3.17355
H	-1.78229	-5.20647	0.59491

H	-2.00795	-6.25512	-0.81372
H	-0.50992	-5.3485	-0.63258
H	-4.13567	-5.17202	-1.43972
H	-4.0324	-4.1861	0.029334
H	-4.28682	-3.40654	-1.54108
B	-2.10903	-0.67365	0.078537
C	-2.43889	-0.23732	1.585799
C	-3.22009	0.847399	1.968428
C	-1.96997	-1.03066	2.629749
C	-3.5035	1.140631	3.295712
C	-2.22714	-0.77505	3.964751
C	-3.00399	0.325264	4.298627
C	-2.41713	0.36499	-1.13315
C	-3.09519	0.045897	-2.30313
C	-1.89706	1.654063	-1.0935
C	-3.26532	0.943021	-3.3517
C	-2.02638	2.574003	-2.11679
C	-2.72684	2.215255	-3.26015
F	-3.60889	-1.18132	-2.50042

F	-1.19541	2.050043	-0.00833
F	-3.74792	1.667569	1.053658
F	-1.21606	-2.11432	2.351302
F	-1.74152	-1.56697	4.917811
F	-3.26539	0.593524	5.570007
F	-4.2519	2.193417	3.608251
F	-1.46953	3.782941	-2.02271
F	-2.86214	3.076462	-4.25875
F	-3.92227	0.5767	-4.44753
N	2.898428	-0.07167	-0.16519
C	2.772748	1.345359	-0.13227
C	4.192932	-0.65363	-0.04473
C	3.492239	2.089014	0.803752
C	1.920285	2.006191	-1.0308
C	5.254198	-0.15072	-0.79518
C	4.411067	-1.71748	0.841021
C	3.35404	3.466336	0.86189
H	4.150296	1.584061	1.502195
C	1.764895	3.372053	-0.96593
H	1.385978	1.441438	-1.78764

C	6.520226	-0.70418	-0.68082
H	5.08564	0.672337	-1.48108
C	5.666997	-2.27188	0.95659
H	3.596377	-2.08972	1.453856
C	2.481429	4.119116	-0.01778
H	3.913466	4.022041	1.603217
H	1.08799	3.890949	-1.63434
C	6.735731	-1.77322	0.195721
H	7.328134	-0.30407	-1.2796
H	5.861309	-3.08623	1.644987
O	2.266047	5.440019	-0.03628
O	7.91513	-2.38149	0.383088
C	2.95138	6.26887	0.892246
H	2.616438	7.283838	0.685157
H	2.693777	6.00239	1.92249
H	4.035332	6.205865	0.750977
C	9.051215	-1.92553	-0.33778
H	9.87776	-2.55793	-0.01799
H	8.903702	-2.03594	-1.41717
H	9.276665	-0.88115	-0.09826

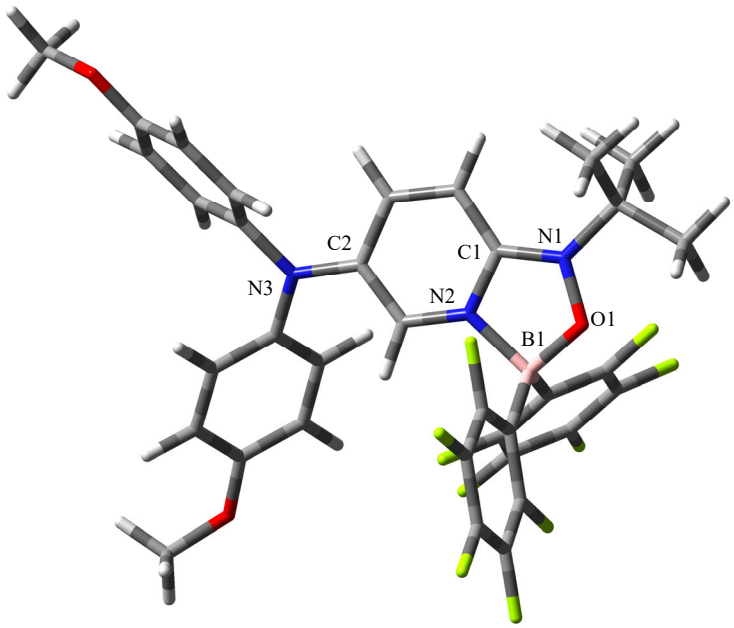


Fig. S12 DFT-optimized structure of **5b**. Selected bond lengths (Å): N1-O1 1.354, C1-N1 1.329, O1-B1 1.501,

N2-B1 1.611, C2-N3 1.374.

Cartesian coordinates of ***6a***

C	-0.6519	-2.22026	-1.44801
C	0.240758	-0.39521	-0.25438
C	0.627378	-2.53905	-1.9918
C	1.541382	-0.64502	-0.77522
H	0.045596	0.404045	0.449606
C	1.704834	-1.77377	-1.64043
H	0.741041	-3.35577	-2.68999
H	2.680778	-1.99189	-2.05885
N	-0.78184	-1.14983	-0.58308
N	-1.83437	-2.81332	-1.6111
O	-2.81728	-2.24046	-0.92336
C	-2.21966	-4.05442	-2.42265
C	-1.95207	-3.73329	-3.90514
C	-1.39073	-5.23878	-1.89176
C	-3.71582	-4.31067	-2.20177
H	-2.53121	-2.86102	-4.22241
H	-0.8956	-3.55893	-4.1277
H	-2.27416	-4.59062	-4.50307
H	-1.52536	-5.35513	-0.81239
H	-1.74793	-6.14975	-2.38019
H	-0.32251	-5.15217	-2.10771
H	-3.98836	-5.17775	-2.80959
H	-3.9418	-4.54051	-1.15812
H	-4.32558	-3.46192	-2.51732
B	-2.34706	-1.00995	-0.14302
C	-2.56587	-1.31552	1.417483
C	-3.4433	-0.62305	2.259908
C	-1.92154	-2.41554	2.000837
C	-3.63795	-0.97482	3.59611
C	-2.08146	-2.79856	3.325524
C	-2.95412	-2.06704	4.132095
C	-2.91164	0.356595	-0.79513

C	-3.74506	0.427675	-1.91581
C	-2.53319	1.589409	-0.25668
C	-4.19864	1.637264	-2.44712
C	-2.94774	2.813095	-0.76034
C	-3.79711	2.838521	-1.86745
F	-4.14412	-0.68808	-2.55428
F	-1.70136	1.61647	0.820798
F	-4.14099	0.428526	1.81052
F	-1.08363	-3.17005	1.239101
F	-1.42606	-3.84944	3.817438
F	-3.13059	-2.40713	5.399681
F	-4.466	-0.27271	4.36147
F	-2.52818	3.958052	-0.20492
F	-4.20046	3.997267	-2.3711
F	-4.99129	1.645118	-3.51454
N	2.562507	0.210847	-0.43858
C	2.250929	1.573214	-0.20073
C	3.899047	-0.23261	-0.32886
C	2.788178	2.246345	0.917076
C	1.369608	2.250179	-1.07264
C	4.952508	0.600726	-0.76804
C	4.191904	-1.49107	0.237783
C	2.396096	3.547054	1.173433
H	3.454082	1.726161	1.597869
C	1.010038	3.560492	-0.80662
H	1.022271	1.761952	-1.97845
C	6.258393	0.165597	-0.6499
H	4.731853	1.555959	-1.23269
C	5.509899	-1.89982	0.356223
H	3.394165	-2.11114	0.635599
C	1.490399	4.244122	0.331786
H	2.7803	4.033858	2.062679

H	0.356953	4.06993	-1.50371
C	6.584145	-1.09239	-0.08463
H	7.050671	0.808976	-1.01596
H	5.712647	-2.85489	0.824773
C	8.043958	-1.52357	0.033155
C	8.200995	-2.91021	0.684535
C	8.665377	-1.57082	-1.39041
C	8.808373	-0.48015	0.892444
H	7.810614	-2.933	1.708334
H	7.710162	-3.69869	0.102717
H	9.263312	-3.16445	0.739447
H	8.637834	-0.59788	-1.89111
H	9.714892	-1.8719	-1.31232
H	8.151318	-2.29987	-2.02588
H	9.857802	-0.78121	0.972139

H	8.786349	0.521703	0.451914
H	8.396442	-0.41987	1.905425
C	1.030527	5.653673	0.691935
C	0.215312	6.314626	-0.43675
C	0.121352	5.52459	1.949735
C	2.247747	6.554045	1.019415
H	0.792767	6.399928	-1.36454
H	-0.71471	5.775668	-0.64499
H	-0.06269	7.327837	-0.13287
H	0.660033	5.104779	2.80576
H	-0.23775	6.518993	2.234716
H	-0.74906	4.893233	1.74188
H	1.892242	7.556215	1.278005
H	2.830328	6.189643	1.871276
H	2.917974	6.647124	0.158136

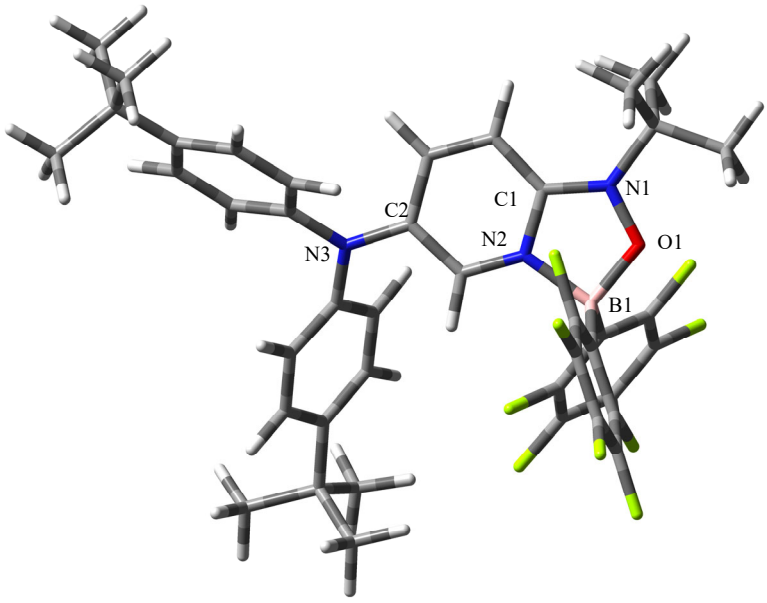


Fig. S13 DFT-optimized structure of **6a**. Selected bond lengths (Å): N1-O1 1.329, C1-N1 1.333, O1-B1 1.531, N2-B1 1.632, C2-N3 1.374.

*Cartesian coordinates of **6b***

C	-0.52975	-2.15062	-1.12506
C	0.560026	-0.34775	-0.0626
C	0.700133	-2.6115	-1.68177

C	1.816417	-0.75169	-0.58073
H	0.450897	0.507666	0.590985
C	1.847792	-1.92244	-1.40345

H	0.721866	-3.47076	-2.33634
H	2.785783	-2.2457	-1.84025
N	-0.54135	-1.00463	-0.35235
N	-1.76015	-2.6535	-1.20745
O	-2.67237	-1.93909	-0.54185
C	-2.27655	-3.9061	-1.91697
C	-2.08393	-3.67886	-3.42865
C	-1.50118	-5.12165	-1.37779
C	-3.7689	-4.0488	-1.59034
H	-2.61683	-2.77984	-3.7513
H	-1.03271	-3.59419	-3.72019
H	-2.50434	-4.5361	-3.96231
H	-1.59399	-5.19247	-0.28995
H	-1.93891	-6.0239	-1.81405
H	-0.44082	-5.1171	-1.64303
H	-4.13132	-4.93747	-2.11435
H	-3.94043	-4.18886	-0.52056
H	-4.3446	-3.187	-1.93139
B	-2.09532	-0.63438	-0.00512
C	-2.36551	-0.56924	1.569921
C	-3.15988	0.383746	2.216394
C	-1.8493	-1.57975	2.391724
C	-3.40671	0.350097	3.589106
C	-2.06591	-1.64925	3.761385
C	-2.85748	-0.67079	4.364725
C	-2.48381	0.61325	-0.96631
C	-3.29706	0.53626	-2.1015
C	-1.93709	1.874823	-0.71833
C	-3.56929	1.636645	-2.91755
C	-2.16066	2.98924	-1.51335
C	-2.99568	2.871694	-2.62514
F	-3.85323	-0.63077	-2.48227
F	-1.1132	2.041902	0.353157
F	-3.72379	1.386031	1.527715
F	-1.08563	-2.55666	1.835106
F	-1.53484	-2.63157	4.489882

F	-3.08177	-0.7104	5.670634
F	-4.15694	1.286951	4.161475
F	-1.5645	4.155787	-1.23486
F	-3.22216	3.921261	-3.40376
F	-4.35241	1.502224	-3.98409
N	2.942901	-0.00029	-0.30072
C	2.831505	1.391654	-0.10503
C	4.21065	-0.61363	-0.21192
C	3.592601	2.024808	0.907458
C	1.939251	2.164162	-0.89548
C	5.343441	0.029452	-0.76273
C	4.358633	-1.86757	0.433233
C	3.455795	3.377888	1.142051
H	4.248973	1.433692	1.537046
C	1.795154	3.509972	-0.66228
H	1.397043	1.699473	-1.71261
C	6.590551	-0.56001	-0.6867
H	5.225172	0.970597	-1.28941
C	5.599833	-2.45063	0.523595
H	3.503075	-2.34338	0.902017
C	2.549669	4.142925	0.362323
H	4.020562	3.839918	1.942649
H	1.114266	4.115267	-1.25031
C	6.738669	-1.8112	-0.03894
H	7.441663	-0.06898	-1.14253
H	5.745452	-3.39155	1.043243
O	2.336391	5.438308	0.506272
O	7.879926	-2.46479	0.09729
C	3.057492	6.212179	1.490451
H	2.694599	7.231	1.368462
H	2.829584	5.85102	2.497543
H	4.132531	6.169718	1.29346
C	9.1181	-1.91576	-0.40427
H	9.87881	-2.64831	-0.14091
H	9.069266	-1.80015	-1.49103
H	9.333544	-0.95928	0.080731

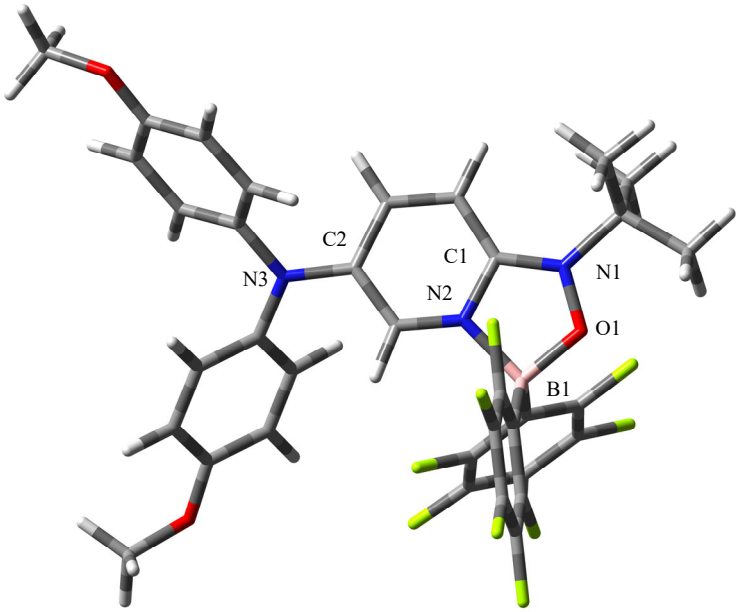


Fig. S14 DFT-optimized structure of **6b**. Selected bond lengths (Å): N1-O1 1.336, C1-N1 1.332, O1-B1 1.524, N2-B1 1.635, C2-N3 1.383.

*Cartesian coordinates of **11a***

C	-3.68884	-0.69861	-0.24835
C	-1.53983	-1.3227	-0.74379
C	-3.23131	0.450662	0.40795
C	-0.97237	-0.21159	-0.10455
H	-0.89655	-2.05776	-1.2206
C	-1.8705	0.68414	0.481284
H	-3.9038	1.162895	0.863438
H	-1.50313	1.566992	0.99222
N	-2.8392	-1.56042	-0.80621
N	-5.06497	-1.03184	-0.38901
O	-5.36489	-2.05398	-1.11284
C	-6.19442	-0.29542	0.277416
C	-6.00575	-0.29594	1.800336
C	-6.32403	1.119987	-0.30345
C	-7.48302	-1.05686	-0.04126
H	-5.94133	-1.32395	2.168001
H	-5.11411	0.236886	2.134079
H	-6.87188	0.178829	2.270978

H	-6.50298	1.064446	-1.38101
H	-7.17843	1.624822	0.157235
H	-5.44379	1.744422	-0.1422
H	-8.32163	-0.51299	0.403936
H	-7.64308	-1.13794	-1.11617
H	-7.46067	-2.06721	0.370201
N	0.418152	-0.01395	-0.0616
C	1.30619	-1.12187	-0.01674
C	0.956223	1.30011	-0.04935
C	2.443698	-1.14909	-0.82406
C	1.074953	-2.19682	0.83874
C	1.961446	1.645432	0.856212
C	0.505654	2.269983	-0.94143
C	3.320729	-2.22111	-0.76515
H	2.639489	-0.32146	-1.49765
C	1.951504	-3.27422	0.8716
H	0.200435	-2.19183	1.481078
C	2.495915	2.923535	0.855362

H	2.324237	0.901732	1.557894
C	1.037513	3.554561	-0.91756
H	-0.26739	2.01719	-1.65984
C	3.100976	-3.31394	0.080177
H	4.190273	-2.20439	-1.41369
H	1.729615	-4.08778	1.551948
C	2.047378	3.914827	-0.02528
H	3.277279	3.153712	1.573276
H	0.65539	4.276731	-1.62929
C	2.662553	5.317558	0.021062
C	2.049749	6.254851	-1.02599
C	2.428837	5.933369	1.412227
C	4.17549	5.224412	-0.2461
H	2.206105	5.885022	-2.04432
H	0.974545	6.390449	-0.87165
H	2.519708	7.24086	-0.95706
H	2.878156	5.328479	2.205101
H	2.870972	6.934299	1.465456

H	1.358866	6.022507	1.625581
H	4.630733	6.22018	-0.20966
H	4.682022	4.599926	0.49532
H	4.372412	4.796302	-1.23409
C	4.054653	-4.51431	0.070284
C	3.85802	-5.41506	1.297112
C	3.78494	-5.34594	-1.1971
C	5.520082	-4.04653	0.06359
H	4.001399	-4.86127	2.230644
H	2.863998	-5.87133	1.318899
H	4.586814	-6.23132	1.275028
H	3.944331	-4.75165	-2.10228
H	4.453551	-6.21322	-1.23873
H	2.752766	-5.7096	-1.21417
H	6.188914	-4.913	0.095896
H	5.771669	-3.47764	-0.83529
H	5.737722	-3.41771	0.932842

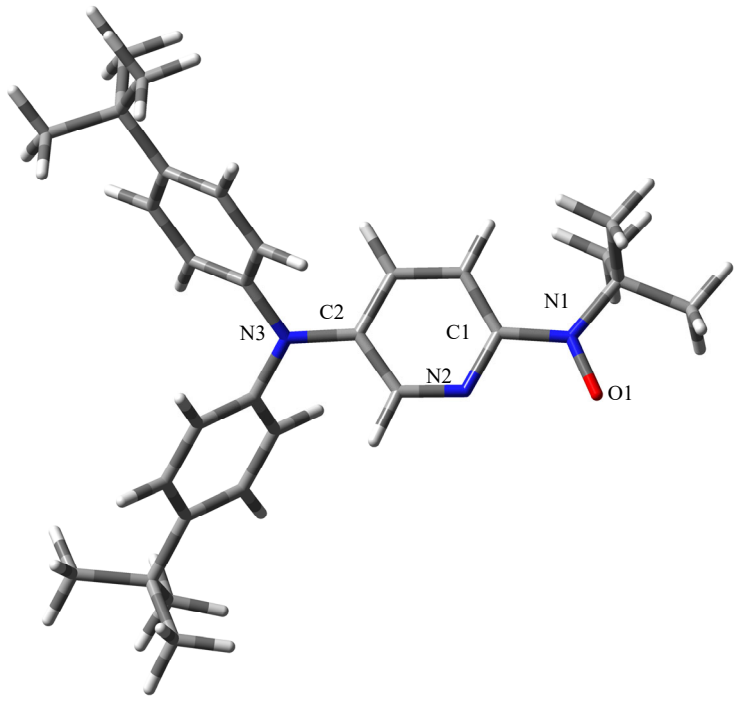


Fig. S15 DFT-optimized structure of **11a**. Selected bond lengths (Å): N1-O1 1.288, C1-N1 1.423, C2-N3 1.405.

*Cartesian coordinates of **11b***

C	-3.15902	-0.16605	-0.39608
C	-1.07929	-1.0283	-0.82993
C	-2.60692	0.899637	0.329455
C	-0.41566	-0.01993	-0.09965
H	-0.50026	-1.81212	-1.31282
C	-1.22884	0.963907	0.487216
H	-3.23482	1.679898	0.743644
H	-0.78053	1.781134	1.042545
N	-2.39865	-1.10621	-0.96783
N	-4.56153	-0.27056	-0.64452
O	-4.92304	-0.55998	-1.84168
C	-5.64889	-0.07688	0.381647
C	-5.13071	-0.35883	1.80092
C	-6.19997	1.356217	0.251417
C	-6.75887	-1.0908	0.049147
H	-4.67479	-1.35275	1.860704
H	-4.39913	0.373925	2.148497
H	-5.97739	-0.33376	2.4953
H	-6.508	1.541984	-0.78213
H	-7.0703	1.490698	0.903697
H	-5.45335	2.10861	0.528344
H	-7.57884	-0.97494	0.766065
H	-7.14064	-0.93557	-0.96025
H	-6.37955	-2.11562	0.116381
N	0.98571	-0.00208	0.02111
C	1.724562	-1.22215	0.066889
C	1.690461	1.236316	0.088096
C	2.86732	-1.39372	-0.72024
C	1.332845	-2.26895	0.919668
C	2.681634	1.440437	1.063705
C	1.422033	2.268258	-0.81736
C	3.613478	-2.57275	-0.66101
H	3.181783	-0.59432	-1.38404
C	2.05558	-3.45224	0.966653
H	0.452921	-2.14912	1.544378
C	3.381721	2.636804	1.122974
H	2.901887	0.648555	1.772877
C	2.106285	3.484152	-0.7492
H	0.667214	2.123144	-1.58436
C	3.206266	-3.61433	0.180102
H	4.495986	-2.66863	-1.28313
H	1.755324	-4.26485	1.620718
C	3.097162	3.673169	0.220731
H	4.149376	2.798611	1.8733
H	1.868711	4.262208	-1.46565
O	3.834954	4.812733	0.372135
O	3.851354	-4.81103	0.310387
C	3.593547	5.889581	-0.51855
H	4.280191	6.684299	-0.22122
H	3.796643	5.606452	-1.56007
H	2.560859	6.255368	-0.44058
C	5.013221	-5.03363	-0.47165
H	5.358791	-6.03701	-0.21617
H	4.791672	-4.9896	-1.54639
H	5.803702	-4.30788	-0.23748

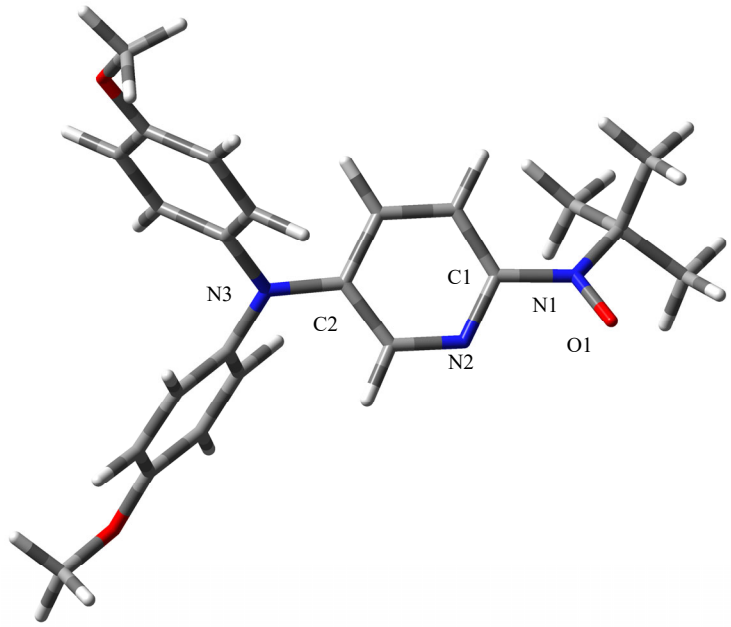


Fig. S16 DFT-optimized structure of **11b**. Selected bond lengths (Å): N1-O1 1.284, C1-N1 1.428, C2-N3 1.407.

*Cartesian coordinates of **12***

C	0.195394	2.312463	0.991988
C	0.110854	0.632649	2.612248
C	0.229828	3.319602	1.946758
C	0.157026	1.579896	3.621358
H	0.044417	-0.43365	2.791489
C	0.213302	2.92903	3.279869
H	0.272196	4.362354	1.670789
N	0.130702	1.01207	1.332328
N	0.223576	2.418288	-0.39354
O	0.198018	1.255677	-0.97632
C	0.270906	3.639384	-1.27944
C	-1.01491	4.434879	-1.02589
C	1.548327	4.418552	-0.94883
C	0.308633	3.154025	-2.72743
H	-1.8923	3.815686	-1.22983
H	-1.08613	4.825674	-0.00852
H	-1.03237	5.28884	-1.70705
H	2.428215	3.775904	-1.03665
H	1.648176	5.233347	-1.6696

H	1.53946	4.865731	0.046796
H	0.314752	4.037972	-3.36868
H	1.208347	2.572625	-2.93786
H	-0.5668	2.551925	-2.97415
B	0.042279	0.090668	0.02556
C	1.329312	-0.84058	-0.147
C	1.316794	-2.16963	-0.56295
C	2.594428	-0.2927	0.058121
C	2.478173	-2.91348	-0.72672
C	3.774237	-0.9953	-0.09515
C	3.711245	-2.32508	-0.49102
C	-1.44164	-0.51466	-0.07067
C	-2.46437	-0.00391	-0.86176
C	-1.79085	-1.59639	0.730536
C	-3.73777	-0.55595	-0.89414
C	-3.04503	-2.1773	0.73273
C	-4.02832	-1.65119	-0.0961
F	-2.26804	1.082678	-1.63304
F	-0.86652	-2.11099	1.567667

F	0.169572	-2.79325	-0.8341
F	2.696695	1.007085	0.420399
F	4.947547	-0.41269	0.121651
F	4.822684	-3.02232	-0.64771
F	2.412323	-4.17889	-1.11572

F	-3.31519	-3.21084	1.518064
F	-5.23878	-2.18228	-0.10954
F	-4.67548	-0.02978	-1.67175
H	0.145231	1.261595	4.656455
H	0.2444	3.686257	4.055618

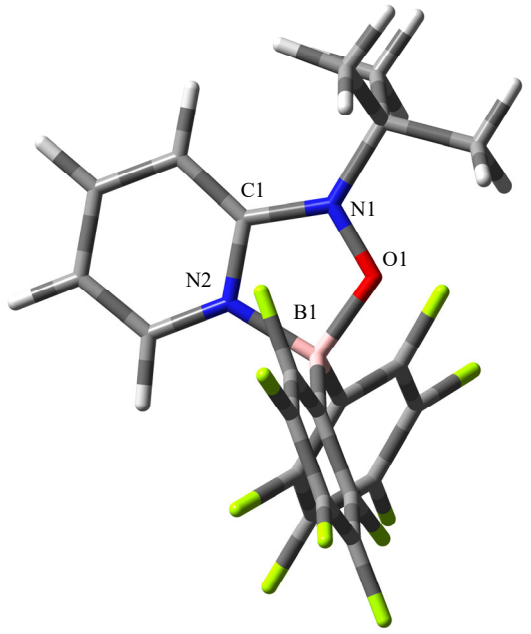


Fig. S17 DFT-optimized structure of **12**. Selected bond lengths (Å): N1-O1 1.301, C1-N1 1.390, O1-B1 1.544, N2-B1 1.601.

*Cartesian coordinates of **13***

C	-0.69671	0.232657	0.139845
C	-2.77775	0.97401	-0.40563
C	-1.17582	-1.04078	0.451358
C	-3.3579	-0.26242	-0.14603
H	-3.38793	1.808524	-0.74394
C	-2.53154	-1.28752	0.29486
H	-0.51238	-1.80449	0.836884
N	-1.47864	1.224294	-0.27363
N	0.677744	0.570261	0.311849
O	0.926823	1.66068	0.925807
C	1.842929	-0.23837	-0.16282

C	2.407569	-1.02848	1.023024
C	1.441075	-1.16034	-1.31556
C	2.891866	0.757563	-0.66863
H	2.63088	-0.34665	1.847611
H	1.701794	-1.78384	1.382151
H	3.330442	-1.54063	0.734081
H	0.960717	-0.59543	-2.11983
H	2.344081	-1.6239	-1.72264
H	0.768194	-1.96372	-1.01173
H	3.774229	0.209892	-1.01202
H	2.496942	1.341828	-1.50452

H	3.184106	1.448331	0.121297
H	-4.424	-0.40973	-0.27772
H	-2.93778	-2.26541	0.533929

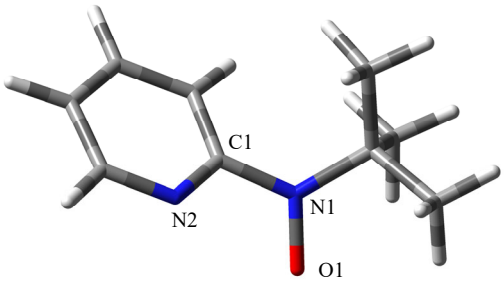


Fig. S18 DFT-optimized structure of **13**. Selected bond lengths (Å): N1-O1 1.276, C1-N1 1.426.

Cartesian coordinates of TEMPO

C	-1.3322	-0.06919	-0.02897
C	-1.24669	1.402189	-0.48352
C	0	2.128882	0.024236
H	-2.16143	1.913105	-0.15844
H	-1.24404	1.432868	-1.58186
C	1.24669	1.402189	-0.48352
H	0	2.184816	1.120185
H	0	3.16475	-0.33635
C	1.332203	-0.06919	-0.02897
H	2.161426	1.913105	-0.15844
H	1.244043	1.432868	-1.58186
N	0	-0.74339	-0.20223
C	1.767158	-0.18376	1.44764
C	2.338199	-0.82465	-0.91306
C	-2.3382	-0.82465	-0.91306
C	-1.76716	-0.18376	1.44764
O	0	-2.01956	-0.0471
H	-1.14961	0.427778	2.112554
H	-1.69316	-1.22626	1.769549
H	-2.80702	0.144137	1.558857
H	-2.01861	-0.80986	-1.96053
H	-3.32105	-0.34509	-0.84419
H	-2.42649	-1.86556	-0.5969
H	1.149614	0.427778	2.112554
H	2.80702	0.144137	1.558857
H	1.693162	-1.22626	1.769549
H	2.018612	-0.80986	-1.96053
H	2.426493	-1.86556	-0.5969
H	3.321047	-0.34509	-0.84419

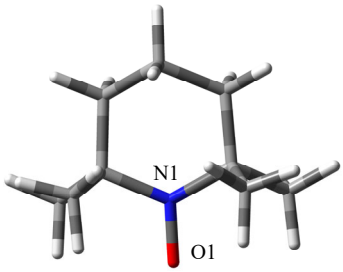


Fig. S19 DFT-optimized structure of TEMPO. Selected bond lengths (Å): N1-O1 1.286.

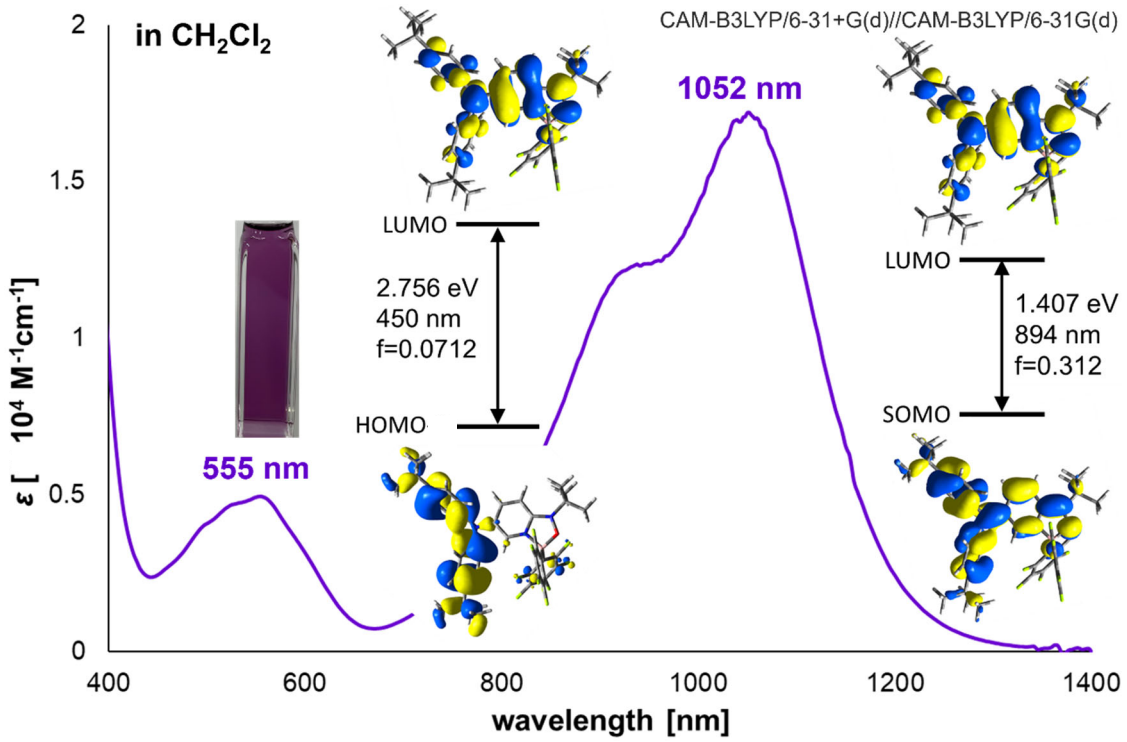


Fig. S20 UV-vis-NIR spectrum of [**5a**]$SbCl_6$ in CH_2Cl_2 and TD-DFT assignments for the longest and second longest absorption bands.

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