Electronic Supplementary Information (ESI) for

BODIPY Blocked Anthroxyl Radicals: Substituent Effect on Reactivity and Fluorescence Turn-on Detection of Hydroxyl Radical

Table of Contents

1. Experimental section

1.1 General methods

All reagents were purchased from commercial suppliers and used as received without further purification. Anhydrous dichloromethane (DCM) were distilled from CaH_2. Toluene and THF were distilled from sodium benzophenone immediately prior to use. The ^{1}H NMR and ^{13}C NMR spectra were recorded in solution of $CDCl_3$ or CD_2Cl_2 on Bruker DPX 300, DPX 400 or DRX 500 NMR spectrometers with tetramethylsilane (TMS) as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. HR-ESI mass spectra were recorded on Finnigan LCQ quadrapole ion trap mass spectrometer. High resolution APCI mass spectra were recorded on Bruker amazonX mass spectrometer. UV-vis absorption and fluorescence spectra were recorded on a Shimadzu UV-1700 spectrometer and a RF-5301 fluorometer, respectively. The electrochemical measurements on CH Instruments were carried out in dry DCM with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at a scan rate of 100 mV/s at room temperature under the protection of nitrogen. A gold disk was used as working electrode, platinum wire was used as counter electrode, and Ag/AgCl (3M KCl solution) was used as reference electrode. The potential was externally calibrated after each experiment, against the ferrocene/ferrocenium couple. Compound **3** was synthesized according to literature procedure.[1]

Density functional theory calculations (UB3LYP/6-31G(d)) were performed in

the gas phase with Gaussian 09 package.[2]

1.2 Synthesis and characterization data

Synthesis of compound **4a**: Compound **3** (285 mg, 1 mmol) was dissolved in 100 mL of dry DCM in a round bottom flask, and then it was purged with Argon for 20 minutes. To the solution, 2,5-dimethylpyrrole (234 mg, 2.2 mmol) and one drop of trifluoroacetic acid (TFA) was added. The reaction mixture was stirred for 2 hours at room temperature and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 227 mg, 1 mmol) was added. After 1 h, 2 mL of triethylamine and 2 mL of $BF_3 \cdot OEt_2$ were added and the resulting mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexanes : DCM = 5:1) and give compound **4a** as an orange solid (126 mg, 26% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 8.61 (d, *J* = 6 Hz, 2H), 7.92 (d, *J* = 9 Hz, 2H), 7.68-7.63 (m, 2H), 7.52-7.46 (m, 2H), 5.94 (s , 2H), 2.59 (s , 6H), 0.66 (s , 6H). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ (ppm) 156.8, 143.5, 138.7, 134.7, 132.9, 131.0, 131.0, 129.6, 128.5, 128.3, 127.9, 126.0, 125.3, 121.9, 15.1, 13.8. HR-MS (APCI): *m*/*z* calcd for $C_{27}H_{23}BBrF_2N_2$: 503.1105; found, 503.1102 ($[M]^+$).

For compound **4b**: the procedure was carried out similar to the synthesis of compound **4a**. Yield, 23%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.61 (d, *J* = 9 Hz, 2H), 7.90 (d, *J* = 9 Hz, 2H), 7.62-7.57 (m, 2H), 7.45-7.40 (m, 2H), 6.21 (d, *J* = 6 Hz, 2H), 6.16 (d, *J* = 6 Hz, 2H), 3.16 (q, *J* = 7 Hz, 4H), 1.37 (t, *J* = 7.5 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 164.4, 139.5, 136.1, 131.6, 130.1, 130.0, 128.0, 127.9, 127.4, 126.8,

125.2, 118.0, 118.0, 29.8, 22.3. HR-MS (APCI): m/z calcd for $C_{27}H_{23}BBrF_2N_2$: 503.1105; found, 503.1091 ($[M]^+$).

Synthesis of compound **5a**: Compound **4a** (38 mg, 0.075 mmol), bis-(pinacolato)diboron (38 mg, 0.15 mmol), KOAc (74 mg, 0.75 mmol), and [1,1'- bis (diphenylphosphino)ferrocene]dichloropalladium(II) complex with dichloromethane ($Pd(dppf)Cl_2 \cdot CH_2Cl_2$, 12.3 mg, 0.15 mmol) were dissolved in toluene and water (15 mL, 3mL). The mixture was degassed by frozen-pump-thaw cycles with liquid N_2 and then it was heated to reflux for 24 h. The reaction mixture was cooled to room temperature, washed with water, and extracted with CH_2Cl_2. The organic phases were dried and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes : DCM = 2:1) and gave a red solid (15 mg, 36% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) 8.41 (d, *J* = 10 Hz, 2H), 7.89 (d, *J* = 5 Hz, 2H), 7.54-7.50 (m, 2H), 7.44-7.41 (m, 2H), 5.93 (s , 2H), 2.58 (s , 6H), 1.61 (s , 12H), 0.64 (s , 6H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ (ppm) 156.3, 143.4, 139.7, 135.6, 132.7, 130.1, 129.5, 129.1, 127.1, 126.4, 125.7, 121.5, 121.5, 85.3, 25.5, 14.9, 13.5. HR-MS (APCI): *m/z* calcd for $C_{33}H_{35}B_2F_2N_2O_2$: 551.2858; found, 551.2865 ($[M]^+$).

For compound **5b**: the procedure was carried out similar to the synthesis of compound **5a**. From 50 mg of compound **4b**, 25 mg red solid was obtained, yield, 47%. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.38 (d, *J* = 15 Hz, 2H), 7.87 (d, *J* = 15 Hz, 2H), 7.51-7.45 (m, 2H), 7.40-7.34 (m, 2H), 6.20 (d, *J* = 5 Hz, 2H), 6.14 (d, *J* = 10 Hz, 2H),

3.14 (q, *J* = 7.5 Hz, 4H), 1.62 (s , 12H), 1.36 (t, *J* = 7.5 Hz, 6H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ (ppm) 164.4, 141.0, 136.4, 135.1, 130.7, 130.3, 129.9, 128.9, 127.1, 126.5, 126.1, 118.1, 118.1, 85.3, 30.1, 25.5, 12.9. HR-MS (APCI): *m*/*z* calcd for $C_{33}H_{35}B_2F_2N_2O_2$: 551.2858; found, 551.2860 ($[M]^+$).

Synthesis of **4Me-BO-An-O**: Compound **5a** (55 mg, 0.1 mmol) was dissolved in 20 ml THF, 1ml K_3PO_4 solution (1M) was added and stirred for 5 min, then H_2O_2 (10 eq.) was added and stirred for 30 min. After complete consumption of compound **5a** (monitored by TLC), the solution was extracted with CH_2Cl_2. The organic phases were dried and concentrated under reduced pressure. The crude compound **6a** was used for next step directly without any further purification. Compound **6a** was dissolved in 5 ml anhydrous dichloromethane. Lead dioxide (47.8 mg, 1 mmol) was added and stirred at room temperature under Argon. The reaction was monitored by TLC. When compound **6a** was completely consumed, the mixture was filtered through celite. The organic phases were dried and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexanes : DCM = 1:1) and gave a black red solid (26 mg, 60% yield for two steps). Compound **4Me-BO-An-O** is NMR silent. Thus, ^{1}H NMR and ^{13}C NMR spectra are not given. HR-MS (ESI): *m*/*z* calcd for $C_{27}H_{23}BF_2N_2O$: 440.1871; found, 440.1874 ($[M+H]^+$).

1.3 Photostability test

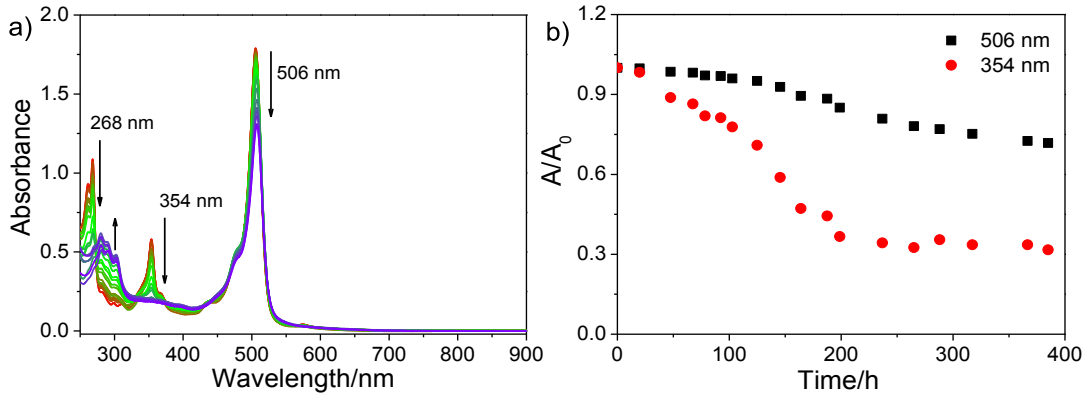


Figure S1. (a) Changes of absorption spectra of compound **4Me-BO-An-O** under ambient air and light conditions. (b) Decay curves of the optical densities at 354 nm and 506 nm.

1.4 Reaction with ROS/RNS

All the selectivity tests were performed in acetonitrile- deionized water (9:1, v:v). The absorption and fluorescence spectra were monitored after reacting 5 μM solutions of compound **4Me-BO-An-O** with 40 equivalents of reactive oxygen species (ROS) or reactive nitrogen species (RNS).

Hydroxyl radical (· OH) and *tert*-butoxy radical (· O^{t}Bu) were generated by reaction of Fe^{2+} with Hydrogen peroxide (H_2O_2) or tertbutylhydroperoxide (TBHP), respectively. Singlet oxygen ($^1O_2$) was originated from the reaction between hydrogen peroxide and hypochlorite in deionized water. Superoxide (O_2^-) was added as solid KO_2. Aqueous solution of NaClO was used as a hypochlorite (ClO^-) source. H_2O_2 and TBHP were delivered from 30% and 70% aqueous solutions, respectively. DEA/NONOate (1,1-diethyl-2-hydroxy-2-nitroso-sodium hydrazine, a commercially available nitric oxide (NO) donor) was purchased from Sigma-Aldrich. A 15 mM nitric oxide stock solution of DEA/NONOate was prepared in 0.01 M NaOH solution.

Peroxynitrite ($ONOO^-$) was obtained according to literature procedure.[3] The concentration of the $ONOO^-$ stock solution was calculated by using its molar extinction coefficient of 1670 $M^{-1}cm^{-1}$ at 302 nm. The aqueous solutions of $NaNO_2$ and $NaNO_3$ were freshly prepared and used as nitrite (NO_2^-) and nitrate (NO_3^-) sources, respectively. The aquous solution of other analytes was freshly prepared in deionized water. All the spectra were obtained in a quartz cuvette (path length = 1 cm). All measurements were made at room temperature.

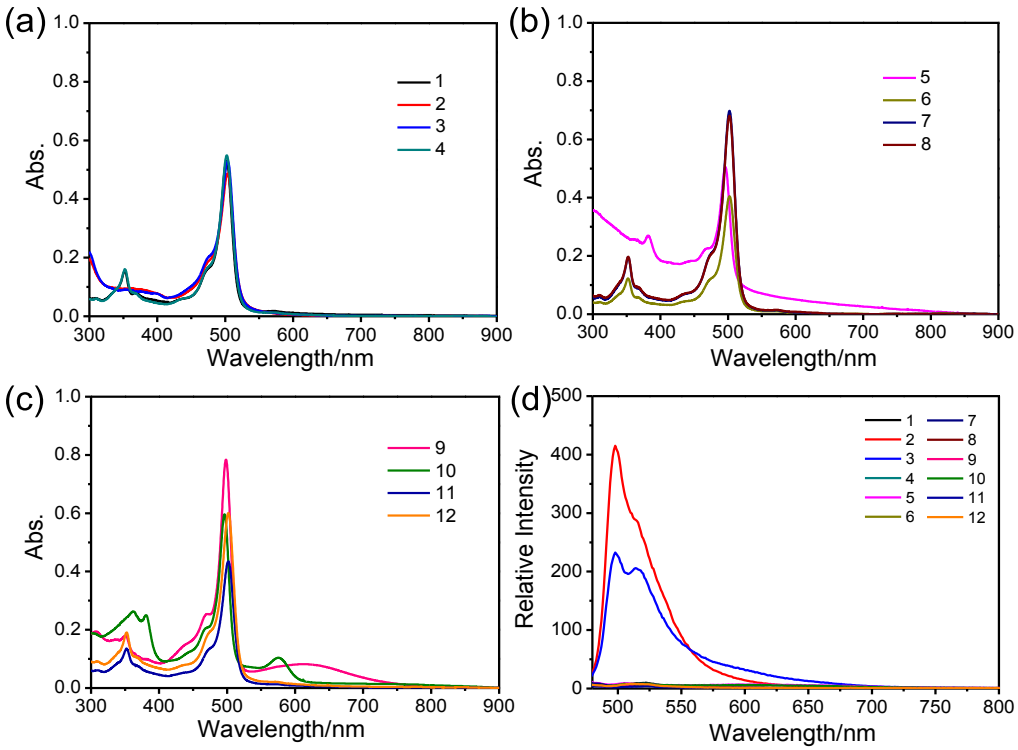


Figure S2. Absorption spectra (a, b, c) and fluorescence spectra (d) of **4Me-BO-An-O** (5 μM) with various analytes (200 μM): (1) **4Me-BO-An-O** only; (2) ·OH; (3) ·O^{t}Bu; (4) $^1O_2$; (5) O_2^-; (6) OCl^-; (7) H_2O_2; (8) TBHP; (9) NO; (10) $ONOO^-$; (11) NO_2^-; (12) NO_3^-; λ_{ex} = 450 nm.

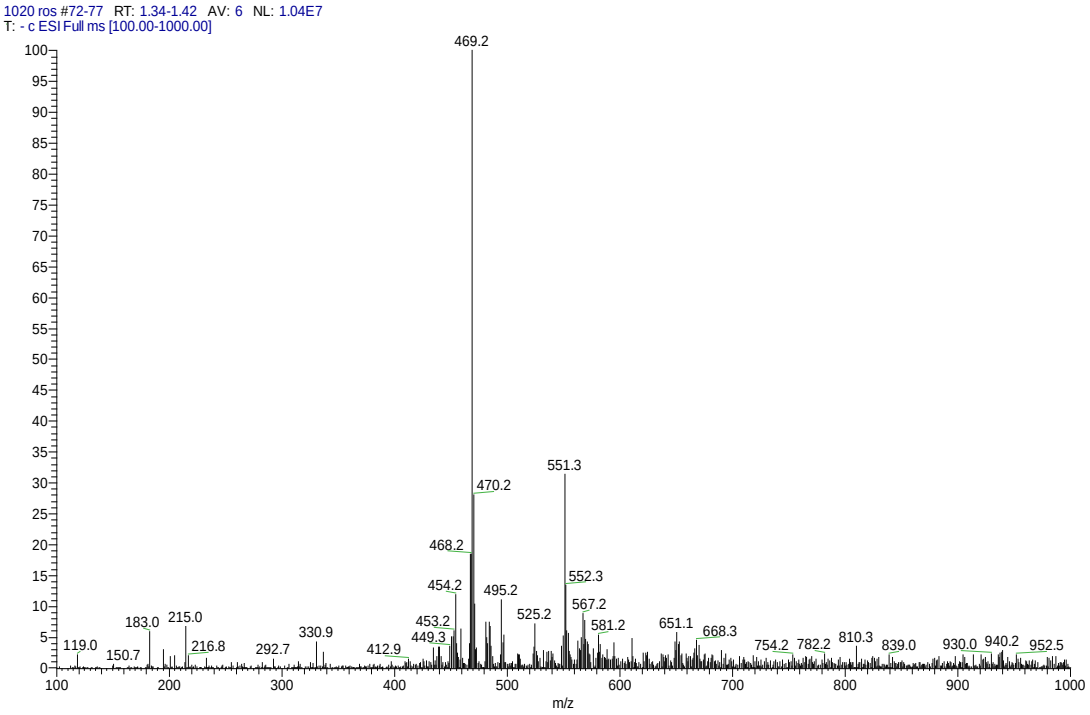


Figure S3. ESI mass spectra of the mixture of **4Me-BO-An-O** react with ·OH.

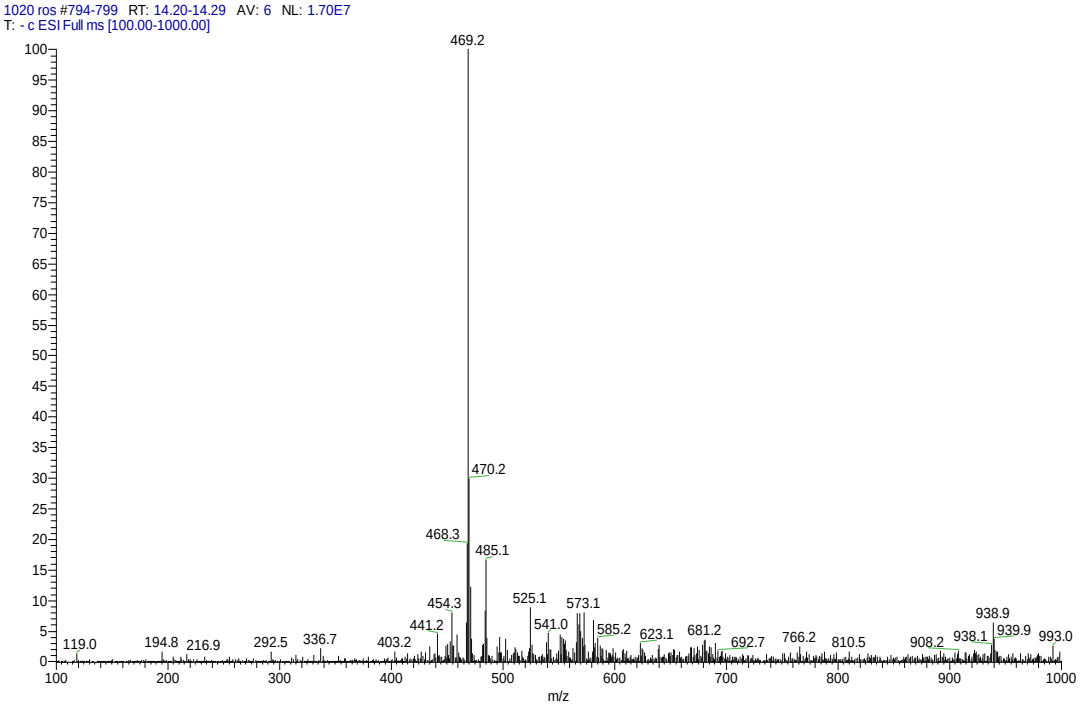
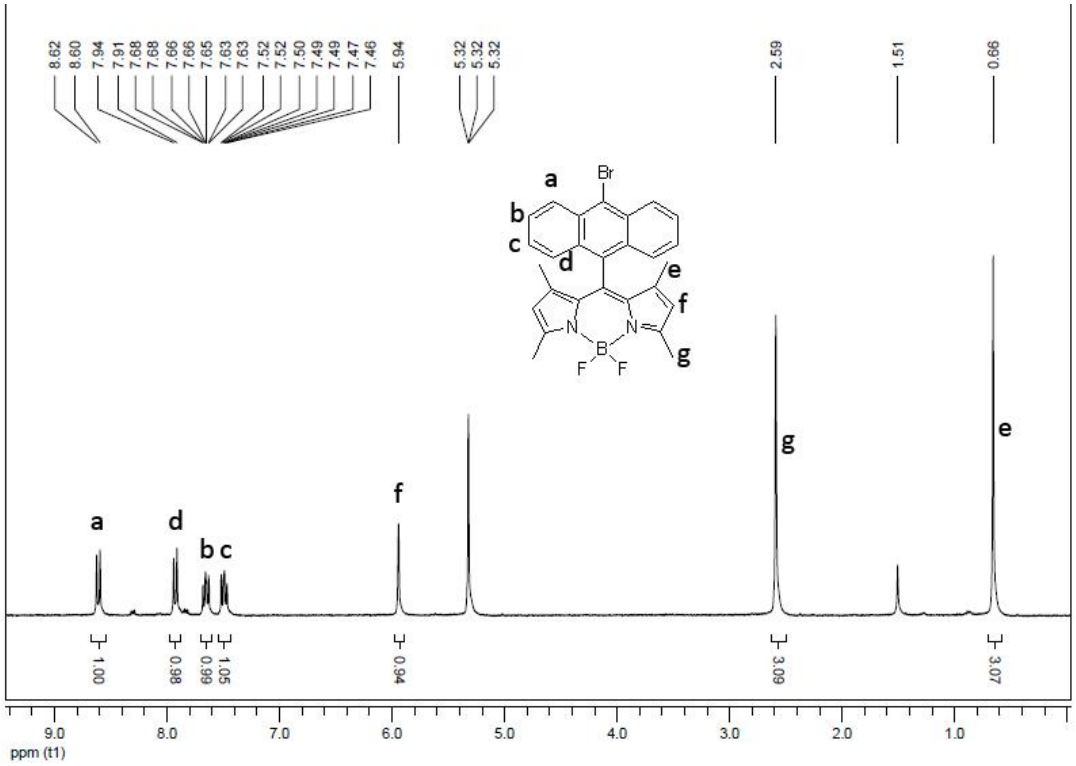
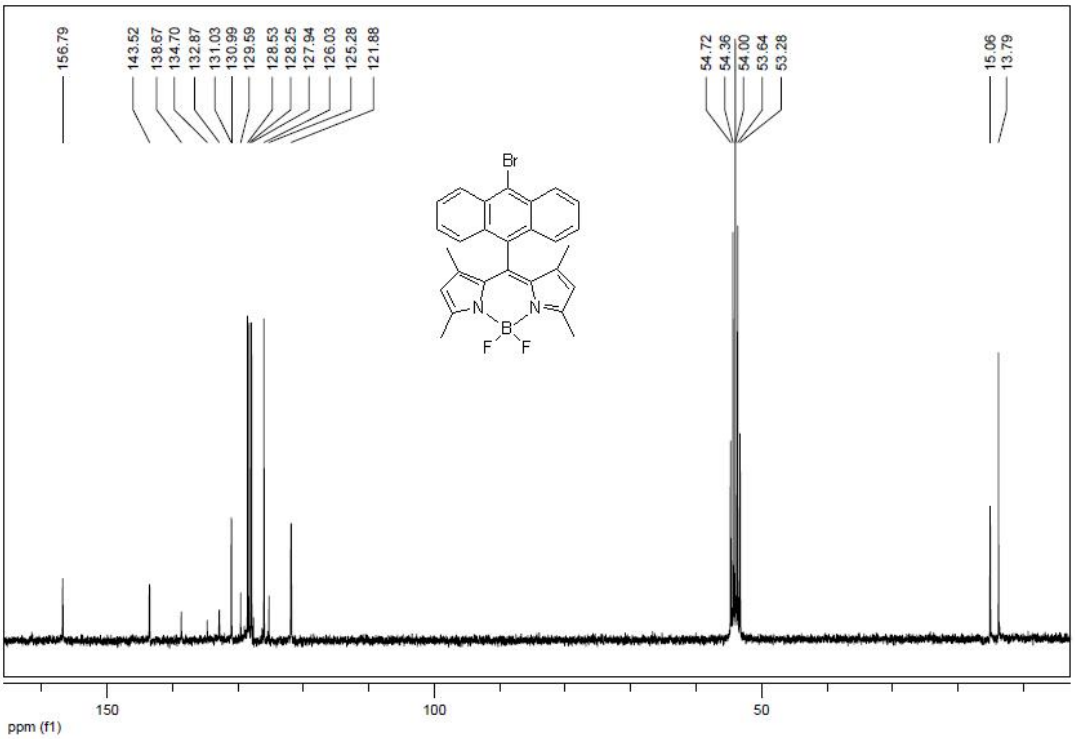


Figure S4. ESI Mass spectra of the mixture of **4Me-BO-An-O** react with ·O^{t}Bu.

1.5 NMR spectra and mass spectra



^{1}H NMR spectrum of compound **4a** in CD_2Cl_2.



^{13}C NMR spectrum of compound **4a** in CD_2Cl_2.

Mass Spectrum SmartFormula Report

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Comment	A/P Wu Jishan		

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Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
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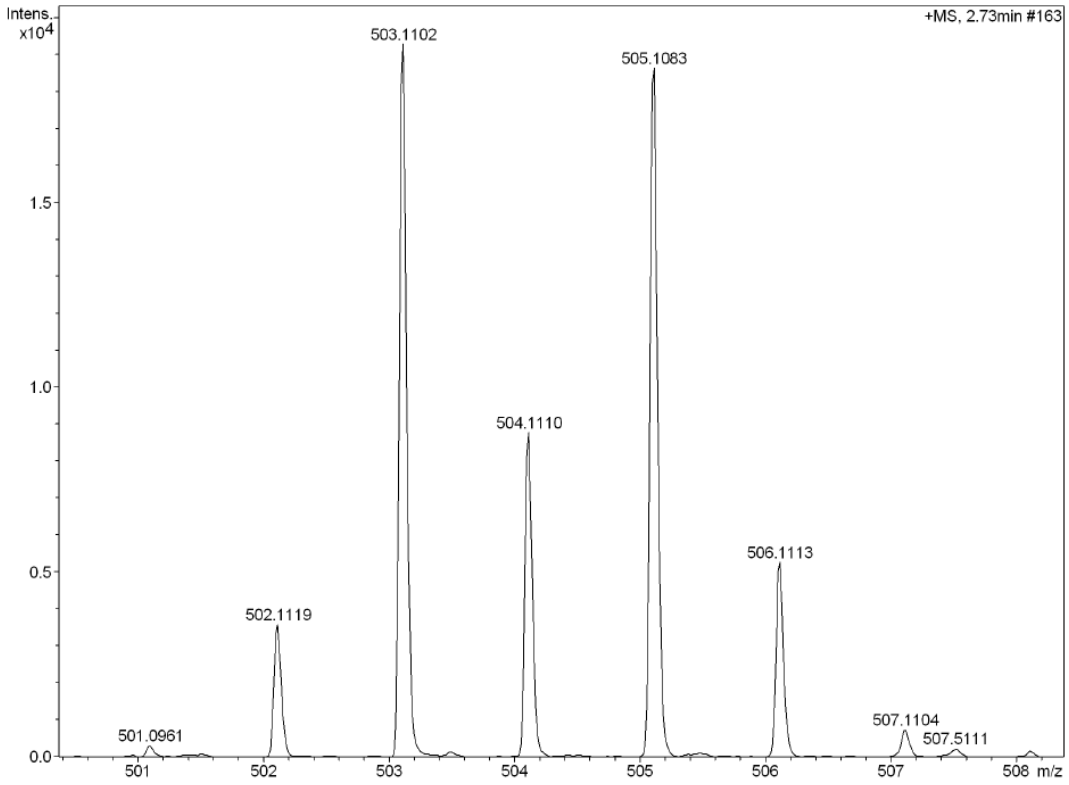
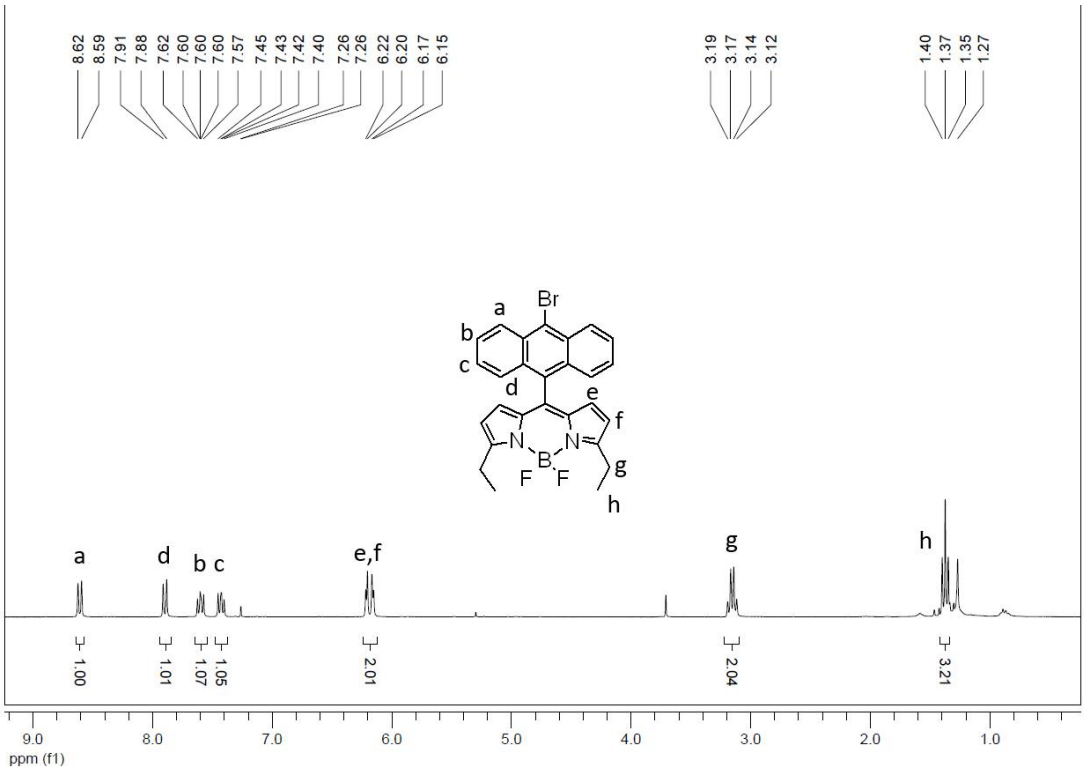
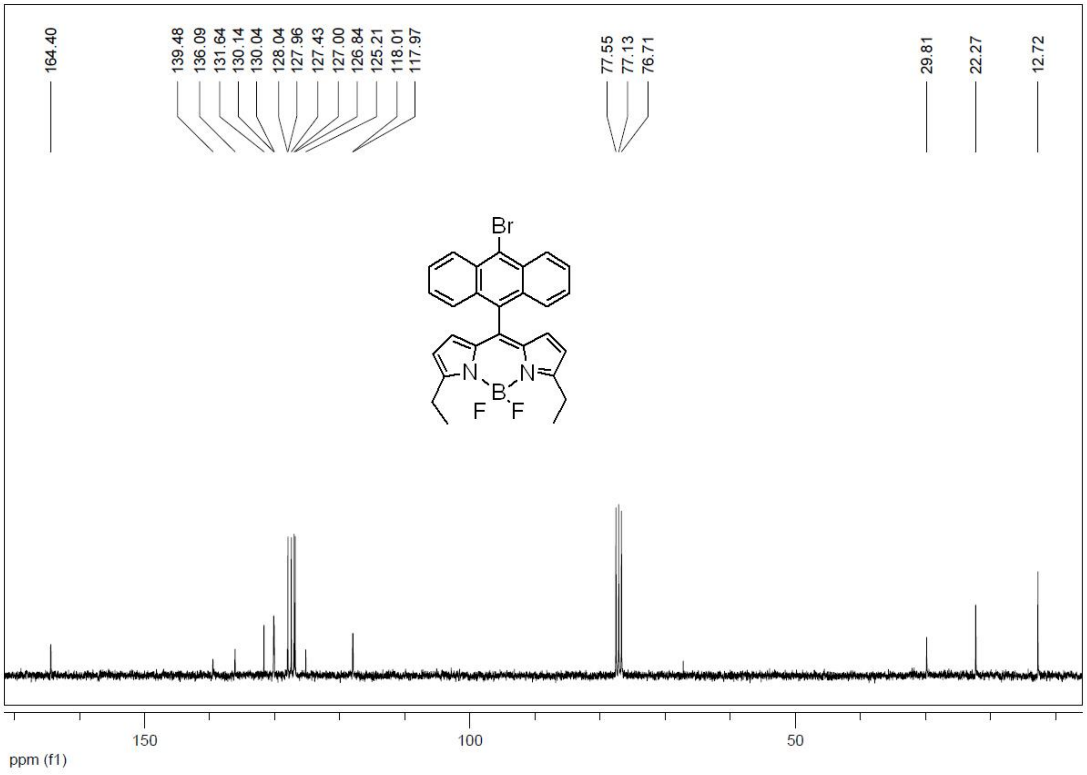


HR mass spectrum of compound **4a**.



^{1}H NMR spectrum of compound **4b** in $CDCl_3$.



^{13}C NMR spectrum of compound **4b** in $CDCl_3$.

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Comment	A/P Wu Jishan		

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Scan End	3000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
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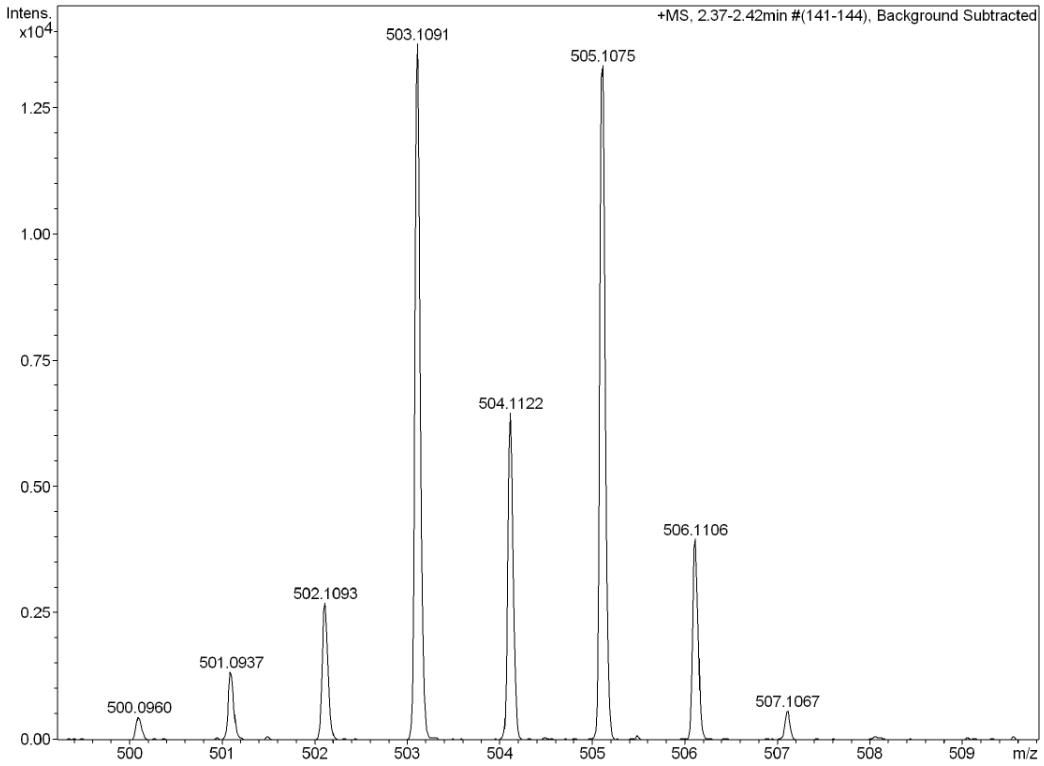
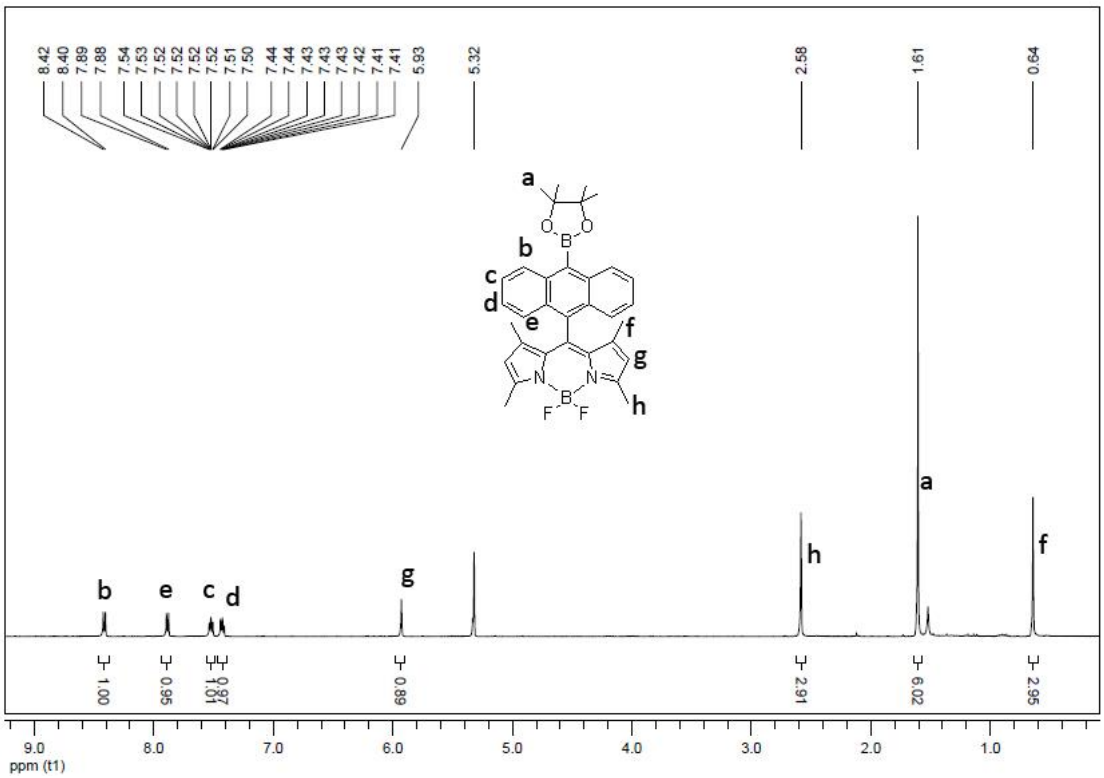
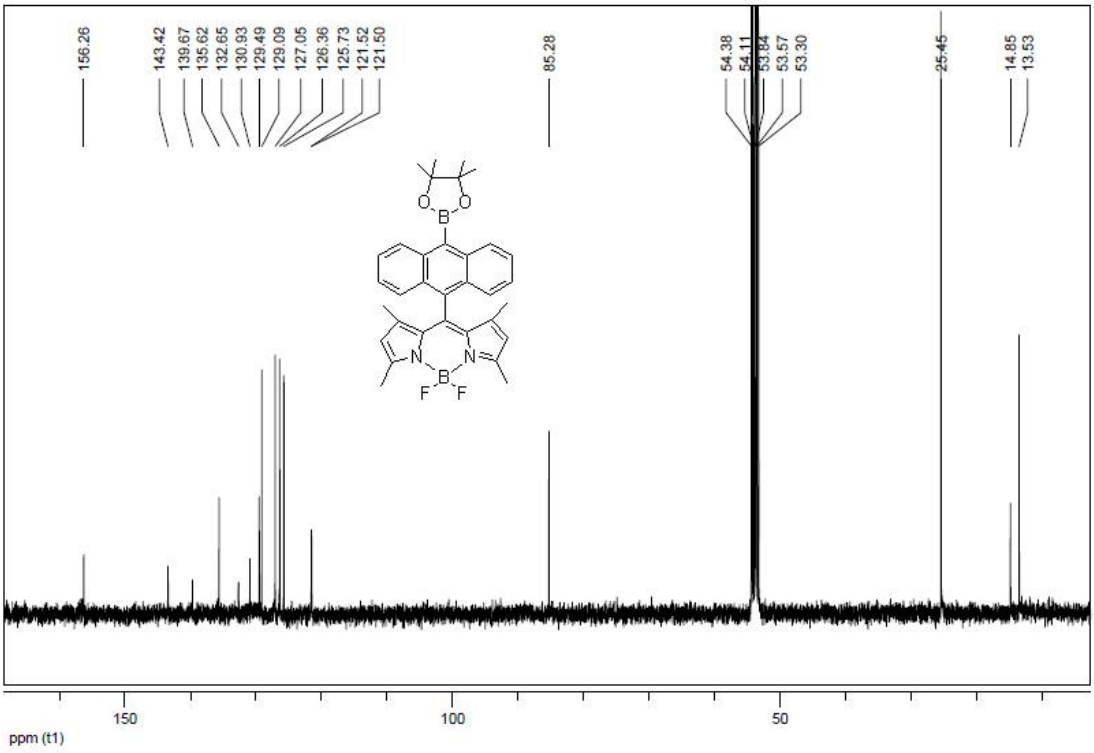


HR mass spectrum of compound **4b**.



^{1}H NMR spectrum of compound **5a** in CD_2Cl_2.



^{13}C NMR spectrum of compound **5a** in CD_2Cl_2.

Mass Spectrum SmartFormula Report

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Comment	A/P Wu Jishan		

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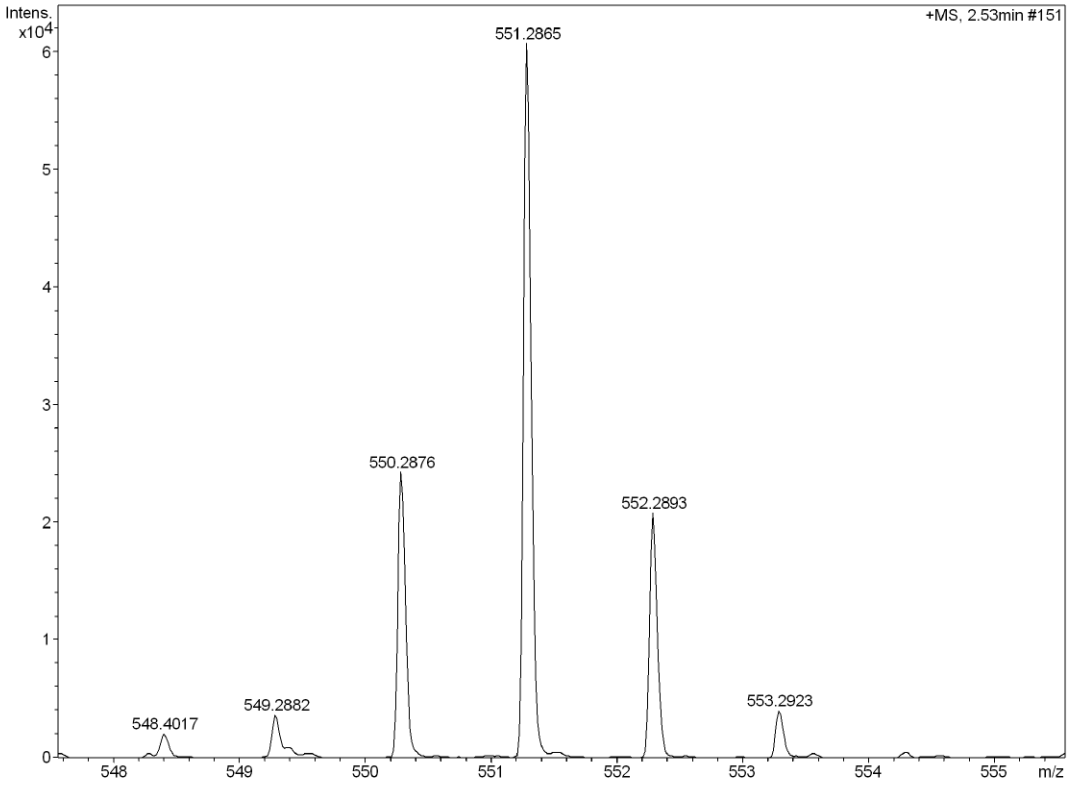
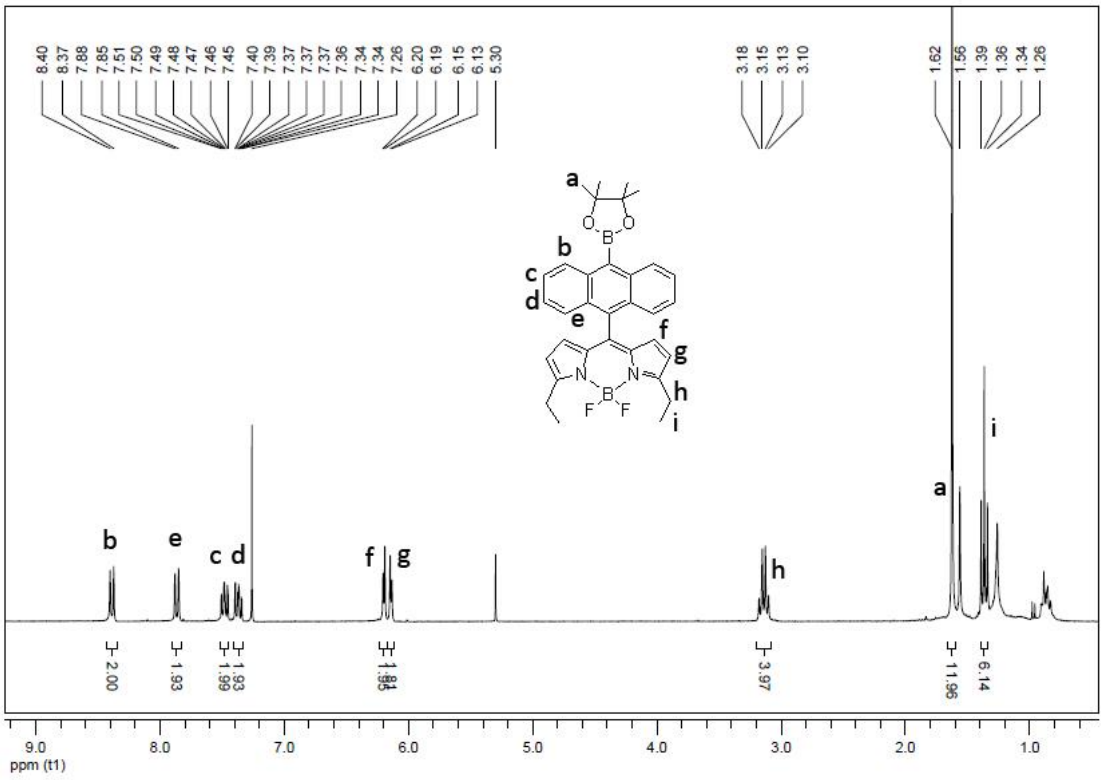
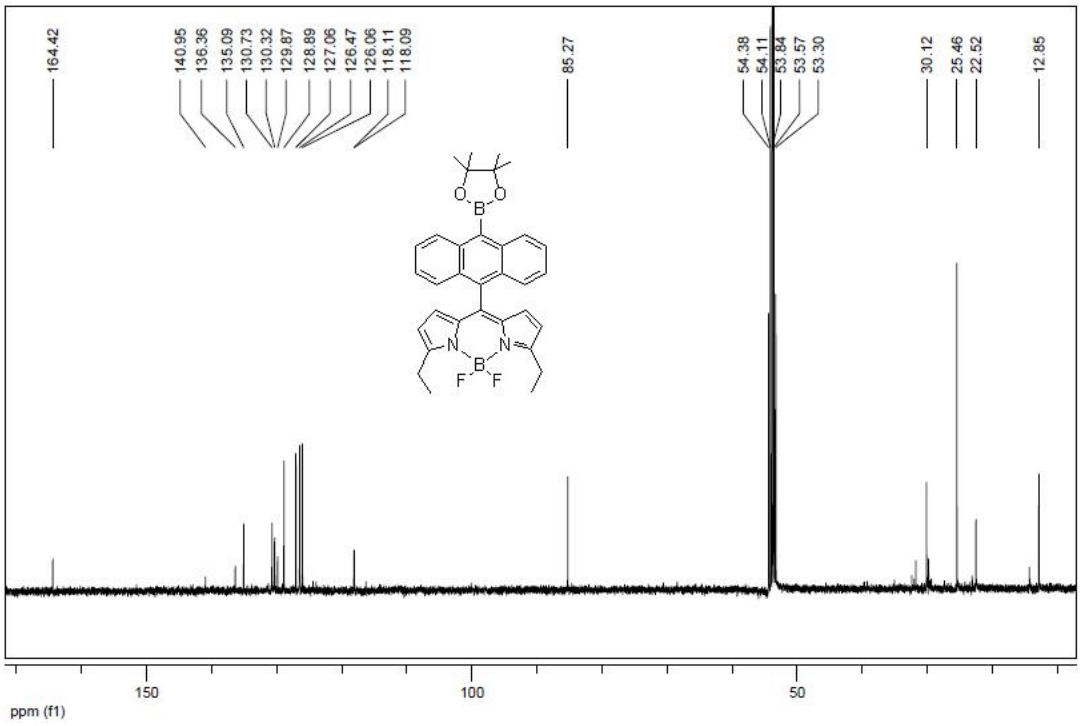


HR mass spectrum of compound **5a**.



^{1}H NMR spectrum of compound **5b** in CD_2Cl_2.



^{13}C NMR spectrum of compound **5b** in CD_2Cl_2.

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Comment	A/P Wu Jishan		

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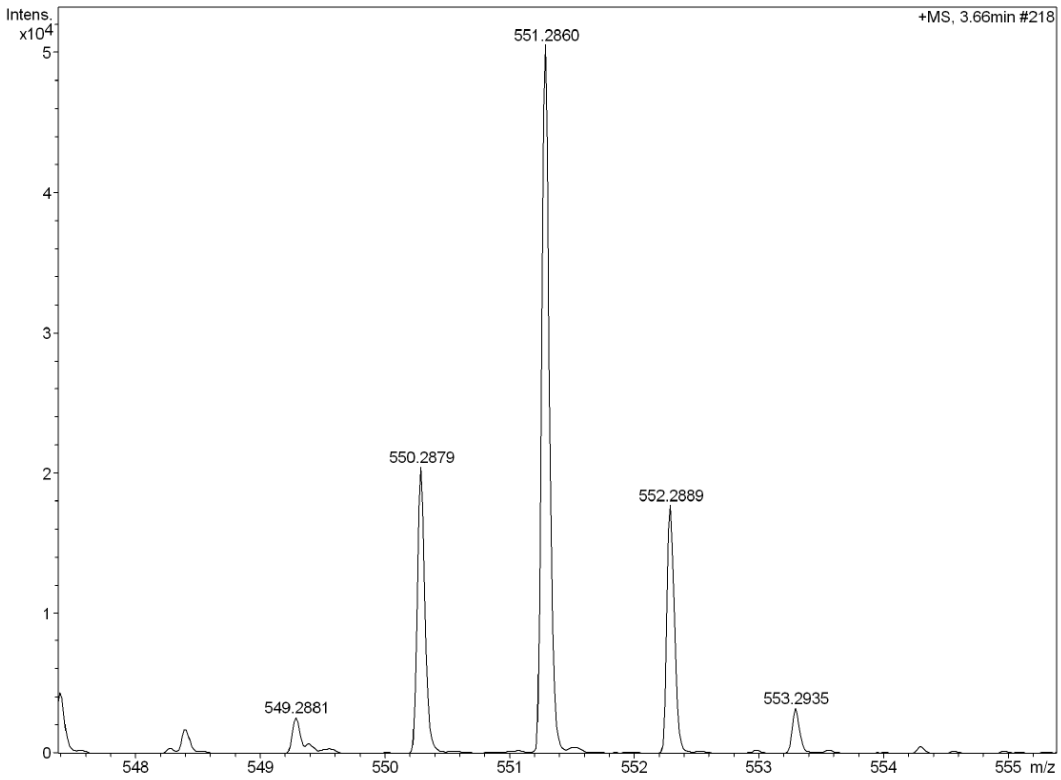

HR mass spectrum of compound **5b**.

Mass Spectrum SmartFormula Report

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Comment	A/P Wu Jishan		

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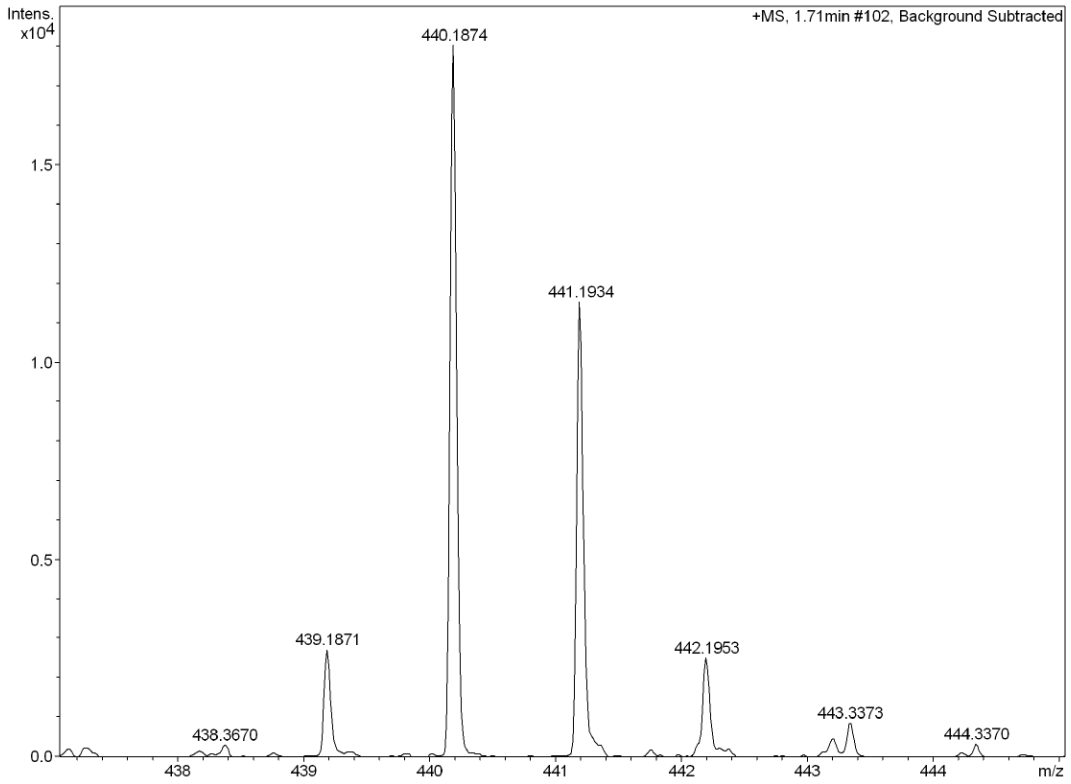

HR mass spectrum of compound **4Me-BO-An-O**.

2. X-ray crystallographic data

2.1 X-ray crystallographic data for 4Me-BO-An-O

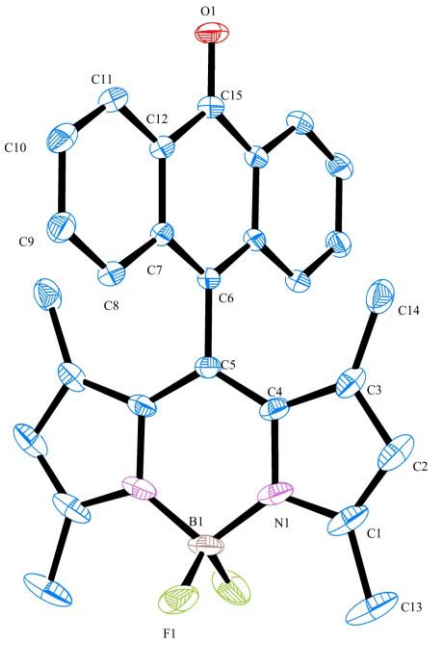

Figure S6. X-ray crystallographic structure of **4Me-BO-An-O**. Solvent molecules are omitted for clarity; ellipsoids are set to 50% probability.

Table S1. Sample and crystal data for **4Me-BO-An-O**.

Chemical formula	$C_{13.50}H_{11}B_{0.50}FNO_{0.50}$	
Formula weight	219.64 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	(0.052 x 0.125 x 0.516) mm^3	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 15.1844(5) Å	α = 90°
	b = 20.7250(6) Å	β = 100.9610(10)°
	c = 6.8775(2) Å	γ = 90°

Volume	2124.84(11) $Å^3$
Z	8
Density (calculated)	1.373 g/cm^3
Absorption coefficient	0.777 mm^{-1}
F(000)	916

Table S2. Data collection and structure refinement for **4Me-BO-An-O**.

Theta range for data collection	3.65 to 72.28°
Index ranges	-18<=h<=18, -25<=k<=24, -8<=l<=7
Reflections collected	9574
Independent reflections	2077 [R(int) = 0.0331]
Coverage of independent reflections	98.8%
Absorption correction	multi-scan
Max. and min. transmission	0.9610 and 0.6900
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2077 / 0 / 154
Goodness-of-fit on F^2	1.029
Final R indices	1838 data; I>2σ(I) R1 = 0.0450, wR2 = 0.1214
	all data R1 = 0.0501, wR2 = 0.1271
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0706P)^2+1.5525P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.221 and -0.237 $eÅ^{-3}$
R.M.S. deviation from mean	0.043 $eÅ^{-3}$

Table S3. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **4Me-BO-An-O**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
B1	0.5	0.87969(11)	0.25	0.0413(7)
F1	0.56308(7)	0.91836(5)	0.3683(2)	0.0703(5)
N1	0.45393(8)	0.83555(6)	0.3817(2)	0.0337(3)
O1	0.5	0.46437(7)	0.25	0.0409(4)
C1	0.40736(12)	0.85413(8)	0.5208(3)	0.0440(4)
C2	0.37835(12)	0.79963(8)	0.6113(3)	0.0451(4)
C3	0.40783(10)	0.74525(7)	0.5267(2)	0.0332(4)
C4	0.45562(9)	0.76788(6)	0.3807(2)	0.0268(3)
C5	0.5	0.73521(8)	0.25	0.0229(4)
C6	0.5	0.66343(8)	0.25	0.0220(4)
C7	0.57921(8)	0.62963(6)	0.33899(19)	0.0230(3)
C8	0.65883(9)	0.66259(7)	0.4276(2)	0.0259(3)
C9	0.73474(9)	0.62896(7)	0.5108(2)	0.0307(3)
C10	0.73468(10)	0.56167(7)	0.5100(2)	0.0339(4)
C11	0.65863(10)	0.52816(7)	0.4258(2)	0.0327(4)
C12	0.58036(9)	0.56105(6)	0.3396(2)	0.0262(3)
C13	0.38962(16)	0.92314(9)	0.5612(4)	0.0653(7)
C14	0.39007(12)	0.67728(8)	0.5815(2)	0.0403(4)
C15	0.5	0.52423(9)	0.25	0.0297(4)

Table S4. Bond lengths (Å) for **4Me-BO-An-O**.

B1-F1	1.3875(16)	B1-F1	1.3876(16)
B1-N1	1.5450(19)	B1-N1	1.5450(19)
N1-C1	1.349(2)	N1-C4	1.4028(17)
O1-C15	1.241(2)	C1-C2	1.400(3)
C1-C13	1.491(2)	C2-C3	1.381(2)
C2-H2	0.95	C3-C4	1.425(2)
C3-C14	1.496(2)	C4-C5	1.3968(16)
C5-C4	1.3968(16)	C5-C6	1.488(2)
C6-C7	1.4255(15)	C6-C7	1.4255(15)
C7-C8	1.4212(18)	C7-C12	1.4213(18)
C8-C9	1.3751(19)	C8-H8	0.95
C9-C10	1.395(2)	C9-H9	0.95
C10-C11	1.377(2)	C10-H10	0.95
C11-C12	1.4003(19)	C11-H11	0.95
C12-C15	1.4714(17)	C13-H13A	0.98
C13-H13B	0.98	C13-H13C	0.98
C14-H14A	0.98	C14-H14B	0.98
C14-H14C	0.98	C15-C12	1.4714(17)

Table S5. Bond angles (°) for **4Me-BO-An-O.**

F1-B1-F1	109.42(19)	F1-B1-N1	110.28(6)
F1-B1-N1	109.72(8)	F1-B1-N1	109.72(8)
F1-B1-N1	110.28(6)	N1-B1-N1	107.40(16)
C1-N1-C4	107.52(13)	C1-N1-B1	127.12(13)
C4-N1-B1	125.34(12)	N1-C1-C2	109.66(13)
N1-C1-C13	122.90(19)	C2-C1-C13	127.42(18)

C3-C2-C1	108.46(16)	C3-C2-H2	125.8
C1-C2-H2	125.8	C2-C3-C4	106.10(14)
C2-C3-C14	125.03(15)	C4-C3-C14	128.87(13)
C5-C4-N1	119.95(13)	C5-C4-C3	131.79(13)
N1-C4-C3	108.26(12)	C4-C5-C4	122.02(17)
C4-C5-C6	118.99(9)	C4-C5-C6	118.99(9)
C7-C6-C7	121.13(16)	C7-C6-C5	119.44(8)
C7-C6-C5	119.44(8)	C8-C7-C12	118.07(12)
C8-C7-C6	121.83(12)	C12-C7-C6	120.10(12)
C9-C8-C7	120.81(12)	C9-C8-H8	119.6
C7-C8-H8	119.6	C8-C9-C10	120.35(13)
C8-C9-H9	119.8	C10-C9-H9	119.8
C11-C10-C9	120.39(13)	C11-C10-H10	119.8
C9-C10-H10	119.8	C10-C11-C12	120.59(13)
C10-C11-H11	119.7	C12-C11-H11	119.7
C11-C12-C7	119.80(12)	C11-C12-C15	119.63(13)
C7-C12-C15	120.58(12)	C1-C13-H13A	109.5
C1-C13-H13B	109.5	H13A-C13-H13B	109.5
C1-C13-H13C	109.5	H13A-C13-H13C	109.5
H13B-C13-H13C	109.5	C3-C14-H14A	109.5
C3-C14-H14B	109.5	H14A-C14-H14B	109.5
C3-C14-H14C	109.5	H14A-C14-H14C	109.5
H14B-C14-H14C	109.5	O1-C15-C12	121.24(8)
O1-C15-C12	121.24(8)	C12-C15-C12	117.51(16)

Table S6. Torsion angles (°) for **4Me-BO-An-O**.

F1-B1-N1-C1	58.90(17)	F1-B1-N1-C1	-61.70(18)
N1-B1-N1-C1	178.77(15)	F1-B1-N1-C4	-119.14(15)
F1-B1-N1-C4	120.26(16)	N1-B1-N1-C4	0.74(9)
C4-N1-C1-C2	-0.04(17)	B1-N1-C1-C2	-178.36(12)
C4-N1-C1-C13	-178.52(15)	B1-N1-C1-C13	3.2(2)
N1-C1-C2-C3	0.17(19)	C13-C1-C2-C3	178.56(17)
C1-C2-C3-C4	-0.23(18)	C1-C2-C3-C14	-179.50(15)
C1-N1-C4-C5	-179.83(11)	B1-N1-C4-C5	-1.47(17)
C1-N1-C4-C3	-0.10(16)	B1-N1-C4-C3	178.26(10)
C2-C3-C4-C5	179.89(13)	C14-C3-C4-C5	-0.9(3)
C2-C3-C4-N1	0.20(16)	C14-C3-C4-N1	179.44(15)
N1-C4-C5-C4	0.71(8)	C3-C4-C5-C4	-178.95(17)
N1-C4-C5-C6	-179.29(8)	C3-C4-C5-C6	1.05(17)
C4-C5-C6-C7	-104.80(8)	C4-C5-C6-C7	75.20(8)
C4-C5-C6-C7	75.20(8)	C4-C5-C6-C7	-104.80(8)
C7-C6-C7-C8	179.75(13)	C5-C6-C7-C8	-0.25(13)
C7-C6-C7-C12	0.22(8)	C5-C6-C7-C12	-179.78(8)
C12-C7-C8-C9	0.21(19)	C6-C7-C8-C9	-179.32(11)
C7-C8-C9-C10	-0.2(2)	C8-C9-C10-C11	0.0(2)
C9-C10-C11-C12	0.1(2)	C10-C11-C12-C7	-0.1(2)
C10-C11-C12-C15	179.83(12)	C8-C7-C12-C11	-0.08(19)
C6-C7-C12-C11	179.46(11)	C8-C7-C12-C15	-179.98(10)
C6-C7-C12-C15	-0.43(16)	C11-C12-C15-O1	0.32(14)
C7-C12-C15-O1	-179.78(8)	C11-C12-C15-C12	-179.68(14)
C7-C12-C15-C12	0.22(8)		

Table S7. Anisotropic atomic displacement parameters ($Å^2$) for **4Me-BO-An-O**.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.0248(11)	0.0155(10)	0.079(2)	0	-0.0024(11)	0
F1	0.0308(5)	0.0383(6)	0.1401(12)	-0.0474(7)	0.0122(6)	-0.0087(4)
N1	0.0324(6)	0.0195(6)	0.0448(7)	-0.0070(5)	-0.0037(5)	0.0080(5)
O1	0.0370(8)	0.0152(7)	0.0712(11)	0	0.0122(7)	0
C1	0.0441(9)	0.0351(9)	0.0477(10)	-0.0141(7)	-0.0037(7)	0.0198(7)
C2	0.0505(10)	0.0468(10)	0.0390(9)	-0.0060(7)	0.0110(7)	0.0241(8)
C3	0.0340(7)	0.0340(8)	0.0321(8)	-0.0019(6)	0.0074(6)	0.0129(6)
C4	0.0261(7)	0.0186(7)	0.0339(7)	-0.0020(5)	0.0006(5)	0.0056(5)
C5	0.0193(8)	0.0177(9)	0.0300(10)	0	0.0006(7)	0
C6	0.0251(9)	0.0168(9)	0.0264(9)	0	0.0105(7)	0
C7	0.0259(7)	0.0193(7)	0.0261(7)	-0.0008(5)	0.0113(5)	0.0015(5)
C8	0.0284(7)	0.0201(6)	0.0306(7)	-0.0019(5)	0.0090(5)	0.0020(5)
C9	0.0260(7)	0.0305(8)	0.0361(8)	-0.0037(6)	0.0068(6)	0.0021(5)
C10	0.0279(7)	0.0291(8)	0.0449(9)	0.0008(6)	0.0072(6)	0.0097(6)
C11	0.0337(8)	0.0208(7)	0.0460(9)	0.0020(6)	0.0138(6)	0.0068(5)
C12	0.0278(7)	0.0189(7)	0.0346(8)	0.0010(5)	0.0128(6)	0.0033(5)
C13	0.0771(15)	0.0400(10)	0.0718(14)	-0.0214(9)	-0.0035(11)	0.0312(10)
C14	0.0472(9)	0.0420(9)	0.0377(8)	0.0094(7)	0.0235(7)	0.0132(7)
C15	0.0329(10)	0.0178(9)	0.0415(11)	0	0.0152(9)	0

Table S8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **4Me-BO-An-O**.

	x/a	y/b	z/c	U(eq)
H2	0.3442	0.8000	0.7135	0.054
H8	0.6596	0.7084	0.4294	0.031
H9	0.7875	0.6517	0.5691	0.037
H10	0.7874	0.5388	0.5678	0.041
H11	0.6593	0.4823	0.4262	0.039
H13A	0.4442	0.9485	0.5623	0.098
H13B	0.3716	0.9267	0.6902	0.098
H13C	0.3414	0.9395	0.4576	0.098
H14A	0.3720	0.6768	0.7110	0.06
H14B	0.4447	0.6515	0.5880	0.06
H14C	0.3419	0.6590	0.4815	0.06

2.2 X-ray crystallographic data for 7

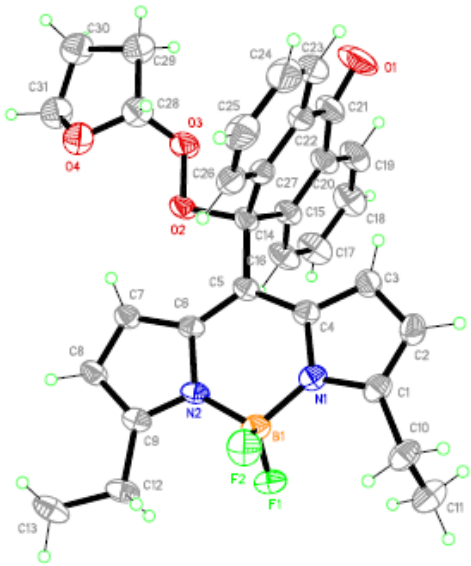

Figure S7. X-ray crystallographic structure of **7**. Solvent molecules are omitted for clarity; ellipsoids are set to 50% probability.

Table S9. Crystal data and structure refinement for **7**.

Empirical formula	C31.25 H29.50 B Cl0.50 F2 N2 O4	
Formula weight	563.60	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.3338(9) Å	α= 87.509(5)°.
	b = 12.5679(14) Å	β= 81.274(5)°.
	c = 14.0639(16) Å	γ = 75.494(5)°.
Volume	1409.5(3) $Å^3$	
Z	2	
Density (calculated)	1.328 Mg/m^3	
Absorption coefficient	1.213 mm^{-1}	
F(000)	589	
Crystal size	0.338 x 0.203 x 0.196 mm^3	
Theta range for data collection	3.179 to 66.584°.	
Index ranges	-9<=h<=9, -14<=k<=14, -16<=l<=16	
Reflections collected	15402	
Independent reflections	4923 [R(int) = 0.0486]	
Completeness to theta = 66.584°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6047	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4923 / 210 / 427	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0822, wR2 = 0.2314	
R indices (all data)	R1 = 0.0945, wR2 = 0.2449	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.130 and -0.682 e.$Å^{-3}$	

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	7695(4)	672(3)	3586(3)	28(1)
F(1)	7443(3)	-381(2)	3609(2)	40(1)

F(2)	9276(2)	626(2)	3821(2)	43(1)
N(1)	7535(3)	1189(2)	2585(2)	26(1)
N(2)	6341(3)	1414(2)	4310(2)	24(1)
O(1)	3178(5)	6016(3)	518(2)	65(1)
O(2)	3233(3)	4387(2)	3722(2)	34(1)
O(3)	2121(3)	5406(2)	3436(2)	46(1)
C(1)	8466(4)	791(3)	1740(2)	31(1)
C(2)	7994(4)	1531(3)	996(2)	35(1)
C(3)	6751(4)	2403(3)	1400(2)	32(1)
C(4)	6459(4)	2196(2)	2398(2)	27(1)
C(5)	5367(4)	2819(2)	3150(2)	25(1)
C(6)	5304(4)	2443(2)	4099(2)	24(1)
C(7)	4363(4)	2873(3)	4988(2)	27(1)
C(8)	4811(4)	2123(3)	5700(2)	30(1)
C(9)	6033(4)	1225(2)	5261(2)	26(1)
C(10)	9771(4)	-280(3)	1660(3)	38(1)
C(11)	9089(5)	-1242(3)	1430(3)	48(1)
C(12)	6903(4)	201(3)	5731(3)	33(1)
C(13)	6511(5)	216(3)	6824(3)	43(1)
C(14)	4272(4)	3919(3)	2847(2)	28(1)
C(15)	3091(4)	3743(3)	2174(2)	31(1)
C(16)	2222(4)	2931(3)	2392(3)	39(1)
C(17)	1030(5)	2806(4)	1843(3)	48(1)
C(18)	696(5)	3495(4)	1059(3)	49(1)
C(19)	1538(5)	4307(3)	846(3)	45(1)
C(20)	2739(4)	4444(3)	1392(2)	35(1)
C(21)	3610(5)	5338(3)	1146(3)	42(1)
C(22)	5014(5)	5375(3)	1667(2)	36(1)
C(23)	5985(6)	6119(3)	1367(3)	49(1)
C(24)	7296(6)	6166(3)	1831(3)	54(1)
C(25)	7651(5)	5490(3)	2625(3)	47(1)
C(26)	6683(4)	4758(3)	2935(3)	36(1)
C(27)	5372(4)	4688(2)	2453(2)	30(1)
O(4)	1965(4)	6038(3)	4969(2)	42(1)
C(28)	2383(6)	6209(4)	3977(3)	40(1)
C(29)	1158(6)	7262(4)	3697(4)	43(1)
C(30)	-117(6)	7572(4)	4638(4)	46(1)
C(31)	222(6)	6573(4)	5229(4)	45(1)

O(4A)	1009(16)	5907(8)	5044(7)	43(1)
C(28A)	919(18)	5905(10)	4062(9)	43(1)
C(29A)	180(20)	7073(10)	3733(9)	44(1)
C(30A)	230(20)	7787(9)	4546(11)	45(1)
C(31A)	1010(20)	6988(11)	5286(10)	44(1)
Cl(1)	5296(3)	944(2)	9364(2)	67(1)
C(1S)	5610(20)	-440(14)	9353(9)	42(4)

Table S11. Bond lengths [Å] and angles [°] for **7**.

B(1)-F(1)	1.388(4)
B(1)-F(2)	1.393(4)
B(1)-N(1)	1.536(4)
B(1)-N(2)	1.545(4)
N(1)-C(1)	1.357(4)
N(1)-C(4)	1.396(4)
N(2)-C(9)	1.345(4)
N(2)-C(6)	1.411(4)
O(1)-C(21)	1.230(4)
O(2)-C(14)	1.448(4)
O(2)-O(3)	1.461(3)
O(3)-C(28A)	1.280(12)
O(3)-C(28)	1.370(6)
C(1)-C(2)	1.405(5)
C(1)-C(10)	1.499(4)
C(2)-C(3)	1.380(5)
C(2)-H(2)	0.9500
C(3)-C(4)	1.412(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.409(4)
C(5)-C(6)	1.394(4)
C(5)-C(14)	1.536(4)
C(6)-C(7)	1.421(4)
C(7)-C(8)	1.373(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.409(4)
C(8)-H(8)	0.9500
C(9)-C(12)	1.492(4)

C(10)-C(11)	1.524(5)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(13)	1.522(5)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(15)	1.525(5)
C(14)-C(27)	1.525(4)
C(15)-C(16)	1.391(5)
C(15)-C(20)	1.398(4)
C(16)-C(17)	1.390(5)
C(16)-H(16)	0.9500
C(17)-C(18)	1.390(6)
C(17)-H(17)	0.9500
C(18)-C(19)	1.375(6)
C(18)-H(18)	0.9500
C(19)-C(20)	1.397(5)
C(19)-H(19)	0.9500
C(20)-C(21)	1.485(5)
C(21)-C(22)	1.482(5)
C(22)-C(27)	1.394(5)
C(22)-C(23)	1.397(5)
C(23)-C(24)	1.370(7)
C(23)-H(23)	0.9500
C(24)-C(25)	1.396(6)
C(24)-H(24)	0.9500
C(25)-C(26)	1.385(5)
C(25)-H(25)	0.9500
C(26)-C(27)	1.393(5)
C(26)-H(26)	0.9500
O(4)-C(28)	1.406(6)
O(4)-C(31)	1.437(5)

C(28)-C(29)	1.533(6)
C(28)-H(28)	1.0000
C(29)-C(30)	1.563(7)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(30)-C(31)	1.467(7)
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900
O(4A)-C(28A)	1.394(13)
O(4A)-C(31A)	1.416(13)
C(28A)-C(29A)	1.523(12)
C(28A)-H(28B)	1.0000
C(29A)-C(30A)	1.496(13)
C(29A)-H(29C)	0.9900
C(29A)-H(29D)	0.9900
C(30A)-C(31A)	1.516(12)
C(30A)-H(30C)	0.9900
C(30A)-H(30D)	0.9900
C(31A)-H(31C)	0.9900
C(31A)-H(31D)	0.9900
Cl(1)-C(1S)	1.694(17)
Cl(1)-C(1S)#1	1.988(12)
C(1S)-Cl(1)#1	1.988(12)
C(1S)-H(1S1)	0.9900
C(1S)-H(1S2)	0.9900

F(1)-B(1)-F(2)	109.5(3)
F(1)-B(1)-N(1)	110.3(3)
F(2)-B(1)-N(1)	110.1(3)
F(1)-B(1)-N(2)	110.0(3)
F(2)-B(1)-N(2)	109.6(3)
N(1)-B(1)-N(2)	107.1(2)
C(1)-N(1)-C(4)	108.1(3)
C(1)-N(1)-B(1)	126.6(3)
C(4)-N(1)-B(1)	125.2(3)
C(9)-N(2)-C(6)	108.3(3)

C(9)-N(2)-B(1)	125.7(3)
C(6)-N(2)-B(1)	125.8(3)
C(14)-O(2)-O(3)	106.0(2)
C(28A)-O(3)-O(2)	118.2(6)
C(28)-O(3)-O(2)	105.1(3)
N(1)-C(1)-C(2)	109.1(3)
N(1)-C(1)-C(10)	123.3(3)
C(2)-C(1)-C(10)	127.6(3)
C(3)-C(2)-C(1)	107.6(3)
C(3)-C(2)-H(2)	126.2
C(1)-C(2)-H(2)	126.2
C(2)-C(3)-C(4)	107.5(3)
C(2)-C(3)-H(3)	126.3
C(4)-C(3)-H(3)	126.3
N(1)-C(4)-C(5)	120.8(3)
N(1)-C(4)-C(3)	107.7(3)
C(5)-C(4)-C(3)	131.5(3)
C(6)-C(5)-C(4)	121.2(3)
C(6)-C(5)-C(14)	123.4(3)
C(4)-C(5)-C(14)	115.4(3)
C(5)-C(6)-N(2)	119.4(3)
C(5)-C(6)-C(7)	134.0(3)
N(2)-C(6)-C(7)	106.5(2)
C(8)-C(7)-C(6)	108.2(3)
C(8)-C(7)-H(7)	125.9
C(6)-C(7)-H(7)	125.9
C(7)-C(8)-C(9)	107.3(3)
C(7)-C(8)-H(8)	126.3
C(9)-C(8)-H(8)	126.3
N(2)-C(9)-C(8)	109.6(3)
N(2)-C(9)-C(12)	122.7(3)
C(8)-C(9)-C(12)	127.7(3)
C(1)-C(10)-C(11)	112.9(3)
C(1)-C(10)-H(10A)	109.0
C(11)-C(10)-H(10A)	109.0
C(1)-C(10)-H(10B)	109.0
C(11)-C(10)-H(10B)	109.0
H(10A)-C(10)-H(10B)	107.8

C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(9)-C(12)-C(13)	113.7(3)
C(9)-C(12)-H(12A)	108.8
C(13)-C(12)-H(12A)	108.8
C(9)-C(12)-H(12B)	108.8
C(13)-C(12)-H(12B)	108.8
H(12A)-C(12)-H(12B)	107.7
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
O(2)-C(14)-C(15)	106.7(2)
O(2)-C(14)-C(27)	108.5(3)
C(15)-C(14)-C(27)	114.5(3)
O(2)-C(14)-C(5)	105.5(2)
C(15)-C(14)-C(5)	111.2(3)
C(27)-C(14)-C(5)	110.0(2)
C(16)-C(15)-C(20)	118.9(3)
C(16)-C(15)-C(14)	119.3(3)
C(20)-C(15)-C(14)	121.5(3)
C(17)-C(16)-C(15)	121.0(3)
C(17)-C(16)-H(16)	119.5
C(15)-C(16)-H(16)	119.5
C(16)-C(17)-C(18)	119.9(4)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(19)-C(18)-C(17)	119.3(4)
C(19)-C(18)-H(18)	120.3
C(17)-C(18)-H(18)	120.3
C(18)-C(19)-C(20)	121.4(3)
C(18)-C(19)-H(19)	119.3

C(20)-C(19)-H(19)	119.3
C(19)-C(20)-C(15)	119.4(3)
C(19)-C(20)-C(21)	119.9(3)
C(15)-C(20)-C(21)	120.7(3)
O(1)-C(21)-C(22)	121.6(4)
O(1)-C(21)-C(20)	120.2(4)
C(22)-C(21)-C(20)	118.2(3)
C(27)-C(22)-C(23)	119.5(4)
C(27)-C(22)-C(21)	121.3(3)
C(23)-C(22)-C(21)	119.2(3)
C(24)-C(23)-C(22)	120.4(4)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(23)-C(24)-C(25)	120.4(4)
C(23)-C(24)-H(24)	119.8
C(25)-C(24)-H(24)	119.8
C(26)-C(25)-C(24)	119.7(4)
C(26)-C(25)-H(25)	120.2
C(24)-C(25)-H(25)	120.2
C(25)-C(26)-C(27)	120.2(3)
C(25)-C(26)-H(26)	119.9
C(27)-C(26)-H(26)	119.9
C(26)-C(27)-C(22)	119.8(3)
C(26)-C(27)-C(14)	118.8(3)
C(22)-C(27)-C(14)	121.3(3)
C(28)-O(4)-C(31)	107.3(3)
O(3)-C(28)-O(4)	112.3(4)
O(3)-C(28)-C(29)	104.4(4)
O(4)-C(28)-C(29)	107.6(4)
O(3)-C(28)-H(28)	110.8
O(4)-C(28)-H(28)	110.8
C(29)-C(28)-H(28)	110.8
C(28)-C(29)-C(30)	103.4(4)
C(28)-C(29)-H(29A)	111.1
C(30)-C(29)-H(29A)	111.1
C(28)-C(29)-H(29B)	111.1
C(30)-C(29)-H(29B)	111.1
H(29A)-C(29)-H(29B)	109.1

C(31)-C(30)-C(29)	103.6(4)
C(31)-C(30)-H(30A)	111.0
C(29)-C(30)-H(30A)	111.0
C(31)-C(30)-H(30B)	111.0
C(29)-C(30)-H(30B)	111.0
H(30A)-C(30)-H(30B)	109.0
O(4)-C(31)-C(30)	106.8(4)
O(4)-C(31)-H(31A)	110.4
C(30)-C(31)-H(31A)	110.4
O(4)-C(31)-H(31B)	110.4
C(30)-C(31)-H(31B)	110.4
H(31A)-C(31)-H(31B)	108.6
C(28A)-O(4A)-C(31A)	107.3(10)
O(3)-C(28A)-O(4A)	123.8(11)
O(3)-C(28A)-C(29A)	110.9(11)
O(4A)-C(28A)-C(29A)	109.2(9)
O(3)-C(28A)-H(28B)	103.5
O(4A)-C(28A)-H(28B)	103.5
C(29A)-C(28A)-H(28B)	103.5
C(30A)-C(29A)-C(28A)	104.9(7)
C(30A)-C(29A)-H(29C)	110.8
C(28A)-C(29A)-H(29C)	110.8
C(30A)-C(29A)-H(29D)	110.8
C(28A)-C(29A)-H(29D)	110.8
H(29C)-C(29A)-H(29D)	108.8
C(29A)-C(30A)-C(31A)	104.3(8)
C(29A)-C(30A)-H(30C)	110.9
C(31A)-C(30A)-H(30C)	110.9
C(29A)-C(30A)-H(30D)	110.9
C(31A)-C(30A)-H(30D)	110.9
H(30C)-C(30A)-H(30D)	108.9
O(4A)-C(31A)-C(30A)	109.2(9)
O(4A)-C(31A)-H(31C)	109.8
C(30A)-C(31A)-H(31C)	109.8
O(4A)-C(31A)-H(31D)	109.8
C(30A)-C(31A)-H(31D)	109.8
H(31C)-C(31A)-H(31D)	108.3
C(1S)-Cl(1)-C(1S)#1	70.9(8)

Cl(1)-C(1S)-Cl(1)#1	109.1(8)
Cl(1)-C(1S)-H(1S1)	109.9
Cl(1)#1-C(1S)-H(1S1)	109.9
Cl(1)-C(1S)-H(1S2)	109.9
Cl(1)#1-C(1S)-H(1S2)	109.9
H(1S1)-C(1S)-H(1S2)	108.3

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+2

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	18(2)	29(2)	36(2)	0(1)	-9(1)	-2(1)
F(1)	46(1)	24(1)	46(1)	3(1)	-7(1)	-2(1)
F(2)	18(1)	60(1)	46(1)	-4(1)	-13(1)	3(1)
N(1)	17(1)	28(1)	33(1)	-1(1)	-6(1)	-3(1)
N(2)	17(1)	24(1)	33(1)	5(1)	-9(1)	-4(1)
O(1)	89(2)	55(2)	54(2)	33(2)	-28(2)	-18(2)
O(2)	31(1)	32(1)	29(1)	9(1)	1(1)	11(1)
O(3)	49(2)	37(1)	37(1)	7(1)	-5(1)	18(1)
C(1)	22(2)	32(2)	38(2)	-6(1)	-3(1)	-2(1)
C(2)	30(2)	42(2)	30(2)	-4(1)	0(1)	-6(1)
C(3)	28(2)	35(2)	29(2)	0(1)	-4(1)	-3(1)
C(4)	21(1)	28(2)	31(2)	1(1)	-6(1)	-3(1)
C(5)	18(1)	28(2)	28(2)	4(1)	-6(1)	-5(1)
C(6)	18(1)	24(1)	30(2)	4(1)	-7(1)	-2(1)
C(7)	21(1)	29(2)	28(2)	4(1)	-6(1)	-2(1)
C(8)	26(2)	34(2)	27(2)	8(1)	-5(1)	-3(1)
C(9)	20(1)	29(2)	33(2)	7(1)	-9(1)	-9(1)
C(10)	25(2)	36(2)	47(2)	-8(2)	-2(1)	2(1)
C(11)	43(2)	37(2)	59(2)	-11(2)	0(2)	-6(2)
C(12)	25(2)	31(2)	45(2)	11(1)	-15(1)	-5(1)
C(13)	38(2)	45(2)	45(2)	20(2)	-17(2)	-7(2)
C(14)	24(2)	29(2)	26(2)	6(1)	-2(1)	0(1)
C(15)	20(2)	36(2)	32(2)	7(1)	-4(1)	2(1)
C(16)	27(2)	48(2)	42(2)	17(2)	-11(2)	-9(2)

C(17)	32(2)	62(2)	54(2)	14(2)	-16(2)	-17(2)
C(18)	31(2)	66(3)	50(2)	12(2)	-21(2)	-8(2)
C(19)	33(2)	59(2)	38(2)	14(2)	-14(2)	1(2)
C(20)	28(2)	39(2)	33(2)	10(1)	-6(1)	2(1)
C(21)	48(2)	41(2)	32(2)	11(2)	-8(2)	-4(2)
C(22)	45(2)	29(2)	30(2)	2(1)	2(2)	-5(1)
C(23)	69(3)	37(2)	41(2)	5(2)	3(2)	-20(2)
C(24)	69(3)	44(2)	54(2)	-4(2)	8(2)	-32(2)
C(25)	46(2)	44(2)	55(2)	-11(2)	-1(2)	-21(2)
C(26)	38(2)	31(2)	38(2)	-4(1)	-3(2)	-7(1)
C(27)	32(2)	25(2)	29(2)	-1(1)	2(1)	-3(1)
O(4)	31(1)	46(1)	45(1)	-4(1)	-9(1)	1(1)
C(28)	28(1)	42(1)	47(1)	-1(1)	-8(1)	-2(1)
C(29)	32(1)	42(1)	52(1)	-1(1)	-7(1)	-1(1)
C(30)	32(2)	46(1)	54(1)	-2(1)	-5(1)	0(1)
C(31)	32(1)	48(1)	50(1)	-3(1)	-5(1)	1(1)
O(4A)	31(2)	45(1)	48(1)	-2(1)	-7(1)	0(1)
C(28A)	31(1)	44(1)	49(1)	-2(1)	-7(1)	-1(1)
C(29A)	31(2)	44(2)	51(2)	-1(1)	-7(1)	-1(1)
C(30A)	32(2)	45(2)	52(2)	-2(1)	-6(1)	0(1)
C(31A)	32(2)	46(2)	50(1)	-2(1)	-6(1)	0(1)
Cl(1)	50(1)	92(2)	63(1)	-4(1)	-22(1)	-19(1)
C(1S)	52(9)	78(10)	11(5)	-5(6)	2(5)	-45(8)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7**.

	x	y	z	U(eq)
H(2)	8449	1446	334	42
H(3)	6194	3028	1068	38
H(7)	3562	3561	5075	32
H(8)	4377	2196	6365	36
H(10A)	10233	-433	2274	45
H(10B)	10699	-215	1149	45
H(11A)	8227	-1347	1958	71

H(11B)	10002	-1911	1352	71
H(11C)	8598	-1087	833	71
H(12A)	8127	88	5543	40
H(12B)	6578	-432	5489	40
H(13A)	6767	864	7069	64
H(13B)	7191	-451	7087	64
H(13C)	5320	246	7019	64
H(16)	2448	2455	2925	46
H(17)	443	2249	2004	57
H(18)	-104	3406	675	58
H(19)	1297	4785	316	54
H(23)	5734	6596	837	59
H(24)	7967	6662	1612	65
H(25)	8553	5531	2950	57
H(26)	6914	4302	3480	43
H(28)	3565	6275	3822	48
H(29A)	590	7127	3161	52
H(29B)	1742	7851	3505	52
H(30A)	79	8202	4961	55
H(30B)	-1284	7759	4499	55
H(31A)	-20	6762	5921	54
H(31B)	-486	6084	5104	54
H(28B)	11	5524	4026	51
H(29C)	861	7257	3137	52
H(29D)	-982	7161	3611	52
H(30C)	-907	8204	4813	54
H(30D)	928	8312	4332	54
H(31C)	2177	7037	5299	53
H(31D)	367	7176	5933	53
H(1S1)	6820	-791	9202	51
H(1S2)	5035	-653	8851	51

Table S14. Torsion angles [°] for 5b.

F(1)-B(1)-N(1)-C(1)	-59.0(4)
F(2)-B(1)-N(1)-C(1)	62.0(4)
N(2)-B(1)-N(1)-C(1)	-178.8(3)

F(1)-B(1)-N(1)-C(4)	125.1(3)
F(2)-B(1)-N(1)-C(4)	-113.8(3)
N(2)-B(1)-N(1)-C(4)	5.4(4)
F(1)-B(1)-N(2)-C(9)	57.8(4)
F(2)-B(1)-N(2)-C(9)	-62.8(4)
N(1)-B(1)-N(2)-C(9)	177.7(3)
F(1)-B(1)-N(2)-C(6)	-127.2(3)
F(2)-B(1)-N(2)-C(6)	112.2(3)
N(1)-B(1)-N(2)-C(6)	-7.3(4)
C(14)-O(2)-O(3)-C(28A)	170.8(8)
C(14)-O(2)-O(3)-C(28)	-124.0(3)
C(4)-N(1)-C(1)-C(2)	-0.5(4)
B(1)-N(1)-C(1)-C(2)	-176.9(3)
C(4)-N(1)-C(1)-C(10)	179.8(3)
B(1)-N(1)-C(1)-C(10)	3.3(5)
N(1)-C(1)-C(2)-C(3)	0.3(4)
C(10)-C(1)-C(2)-C(3)	-179.9(3)
C(1)-C(2)-C(3)-C(4)	0.0(4)
C(1)-N(1)-C(4)-C(5)	-178.3(3)
B(1)-N(1)-C(4)-C(5)	-1.8(4)
C(1)-N(1)-C(4)-C(3)	0.5(3)
B(1)-N(1)-C(4)-C(3)	177.0(3)
C(2)-C(3)-C(4)-N(1)	-0.3(4)
C(2)-C(3)-C(4)-C(5)	178.3(3)
N(1)-C(4)-C(5)-C(6)	-1.1(4)
C(3)-C(4)-C(5)-C(6)	-179.5(3)
N(1)-C(4)-C(5)-C(14)	179.1(3)
C(3)-C(4)-C(5)-C(14)	0.6(5)
C(4)-C(5)-C(6)-N(2)	-0.7(4)
C(14)-C(5)-C(6)-N(2)	179.2(3)
C(4)-C(5)-C(6)-C(7)	179.9(3)
C(14)-C(5)-C(6)-C(7)	-0.3(5)
C(9)-N(2)-C(6)-C(5)	-178.8(3)
B(1)-N(2)-C(6)-C(5)	5.5(4)
C(9)-N(2)-C(6)-C(7)	0.8(3)
B(1)-N(2)-C(6)-C(7)	-174.9(3)
C(5)-C(6)-C(7)-C(8)	179.0(3)
N(2)-C(6)-C(7)-C(8)	-0.6(3)

C(6)-C(7)-C(8)-C(9)	0.1(4)
C(6)-N(2)-C(9)-C(8)	-0.7(3)
B(1)-N(2)-C(9)-C(8)	175.0(3)
C(6)-N(2)-C(9)-C(12)	179.4(3)
B(1)-N(2)-C(9)-C(12)	-4.9(4)
C(7)-C(8)-C(9)-N(2)	0.4(4)
C(7)-C(8)-C(9)-C(12)	-179.7(3)
N(1)-C(1)-C(10)-C(11)	92.8(4)
C(2)-C(1)-C(10)-C(11)	-86.9(4)
N(2)-C(9)-C(12)-C(13)	173.4(3)
C(8)-C(9)-C(12)-C(13)	-6.5(5)
O(3)-O(2)-C(14)-C(15)	-58.6(3)
O(3)-O(2)-C(14)-C(27)	65.2(3)
O(3)-O(2)-C(14)-C(5)	-177.0(2)
C(6)-C(5)-C(14)-O(2)	-1.6(4)
C(4)-C(5)-C(14)-O(2)	178.2(3)
C(6)-C(5)-C(14)-C(15)	-117.0(3)
C(4)-C(5)-C(14)-C(15)	62.9(3)
C(6)-C(5)-C(14)-C(27)	115.2(3)
C(4)-C(5)-C(14)-C(27)	-65.0(3)
O(2)-C(14)-C(15)-C(16)	-69.8(4)
C(27)-C(14)-C(15)-C(16)	170.1(3)
C(5)-C(14)-C(15)-C(16)	44.7(4)
O(2)-C(14)-C(15)-C(20)	104.1(3)
C(27)-C(14)-C(15)-C(20)	-16.1(4)
C(5)-C(14)-C(15)-C(20)	-141.4(3)
C(20)-C(15)-C(16)-C(17)	0.5(6)
C(14)-C(15)-C(16)-C(17)	174.5(3)
C(15)-C(16)-C(17)-C(18)	0.3(6)
C(16)-C(17)-C(18)-C(19)	-1.0(7)
C(17)-C(18)-C(19)-C(20)	1.0(6)
C(18)-C(19)-C(20)-C(15)	-0.2(6)
C(18)-C(19)-C(20)-C(21)	-179.4(4)
C(16)-C(15)-C(20)-C(19)	-0.6(5)
C(14)-C(15)-C(20)-C(19)	-174.4(3)
C(16)-C(15)-C(20)-C(21)	178.6(3)
C(14)-C(15)-C(20)-C(21)	4.8(5)
C(19)-C(20)-C(21)-O(1)	6.3(6)

C(15)-C(20)-C(21)-O(1)	-172.9(4)
C(19)-C(20)-C(21)-C(22)	-172.9(3)
C(15)-C(20)-C(21)-C(22)	7.9(5)
O(1)-C(21)-C(22)-C(27)	172.4(4)
C(20)-C(21)-C(22)-C(27)	-8.5(5)
O(1)-C(21)-C(22)-C(23)	-7.1(6)
C(20)-C(21)-C(22)-C(23)	172.0(3)
C(27)-C(22)-C(23)-C(24)	0.9(6)
C(21)-C(22)-C(23)-C(24)	-179.6(4)
C(22)-C(23)-C(24)-C(25)	-1.6(6)
C(23)-C(24)-C(25)-C(26)	0.8(6)
C(24)-C(25)-C(26)-C(27)	0.7(6)
C(25)-C(26)-C(27)-C(22)	-1.3(5)
C(25)-C(26)-C(27)-C(14)	-176.7(3)
C(23)-C(22)-C(27)-C(26)	0.5(5)
C(21)-C(22)-C(27)-C(26)	-178.9(3)
C(23)-C(22)-C(27)-C(14)	175.8(3)
C(21)-C(22)-C(27)-C(14)	-3.7(5)
O(2)-C(14)-C(27)-C(26)	71.6(3)
C(15)-C(14)-C(27)-C(26)	-169.3(3)
C(5)-C(14)-C(27)-C(26)	-43.2(4)
O(2)-C(14)-C(27)-C(22)	-103.6(3)
C(15)-C(14)-C(27)-C(22)	15.5(4)
C(5)-C(14)-C(27)-C(22)	141.5(3)
O(2)-O(3)-C(28)-O(4)	-61.6(4)
O(2)-O(3)-C(28)-C(29)	-177.8(3)
C(31)-O(4)-C(28)-O(3)	-89.0(4)
C(31)-O(4)-C(28)-C(29)	25.4(5)
O(3)-C(28)-C(29)-C(30)	113.1(4)
O(4)-C(28)-C(29)-C(30)	-6.4(5)
C(28)-C(29)-C(30)-C(31)	-14.1(5)
C(28)-O(4)-C(31)-C(30)	-35.5(5)
C(29)-C(30)-C(31)-O(4)	29.8(6)
O(2)-O(3)-C(28A)-O(4A)	32.5(16)
O(2)-O(3)-C(28A)-C(29A)	165.3(8)
C(31A)-O(4A)-C(28A)-O(3)	111.2(15)
C(31A)-O(4A)-C(28A)-C(29A)	-22.2(18)
O(3)-C(28A)-C(29A)-C(30A)	-126.6(14)

O(4A)-C(28A)-C(29A)-C(30A)	13.1(18)
C(28A)-C(29A)-C(30A)-C(31A)	0.6(18)
C(28A)-O(4A)-C(31A)-C(30A)	22.7(18)
C(29A)-C(30A)-C(31A)-O(4A)	-14.0(19)
C(1S)#1-Cl(1)-C(1S)-Cl(1)#1	0.001(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+2

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