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One-Pot Synthesis of Boron Diketonate Complexes: Photophysical Properties and Sensor for Picric Acid

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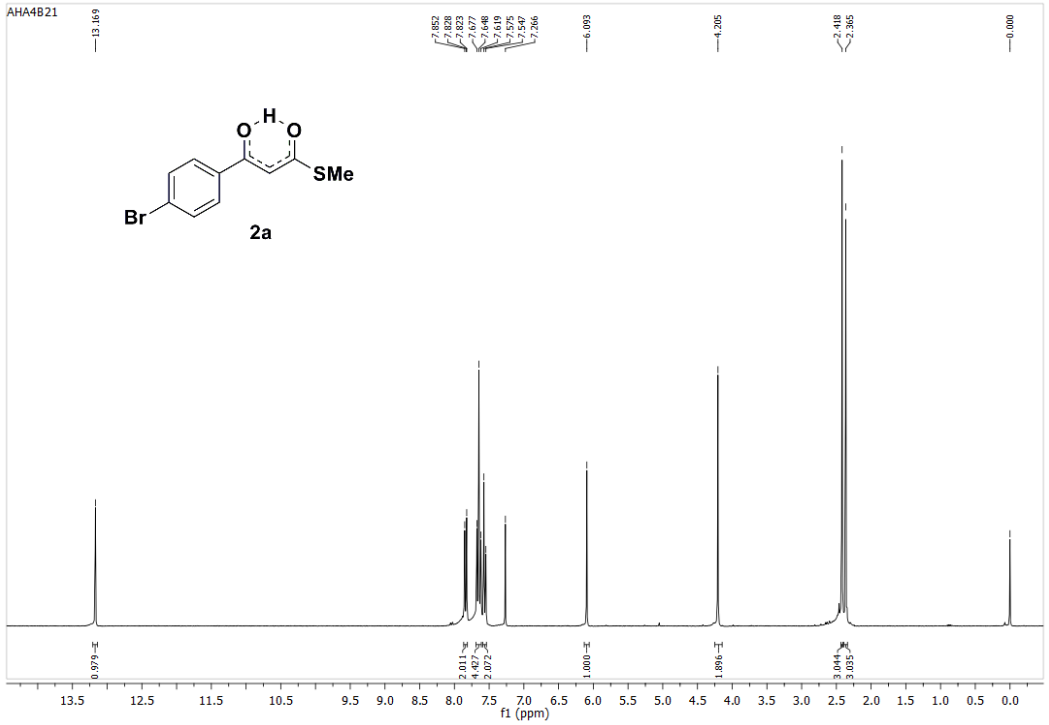


Fig. S1 ^{1}H NMR spectrum of **2a**

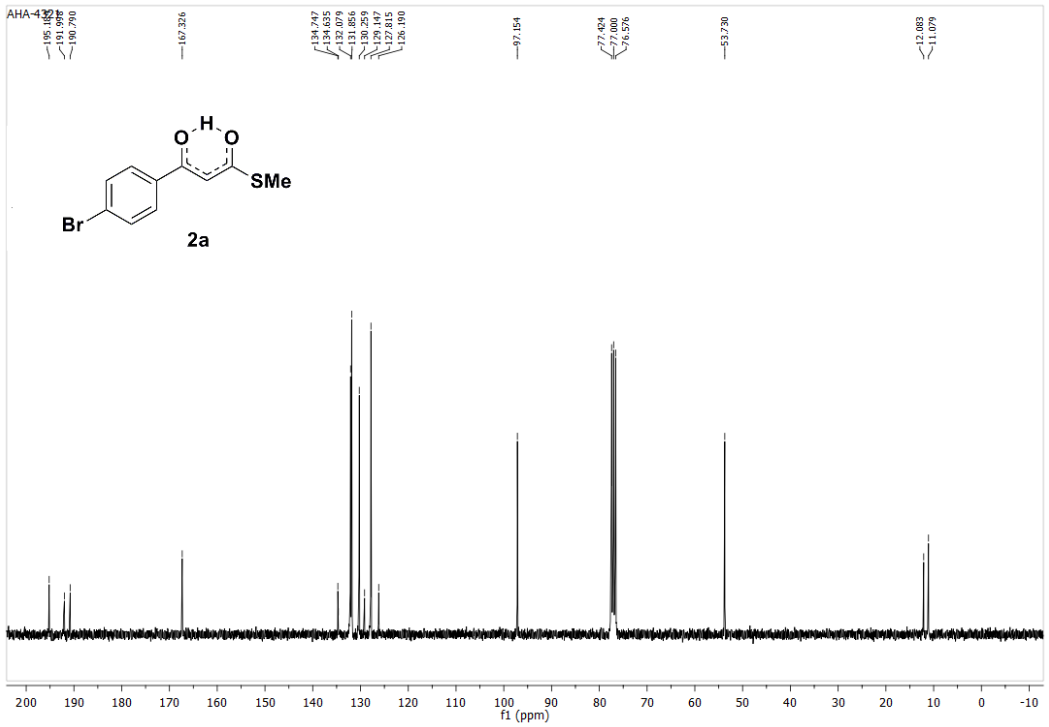


Fig. S2 ^{13}C NMR spectrum of **2a**

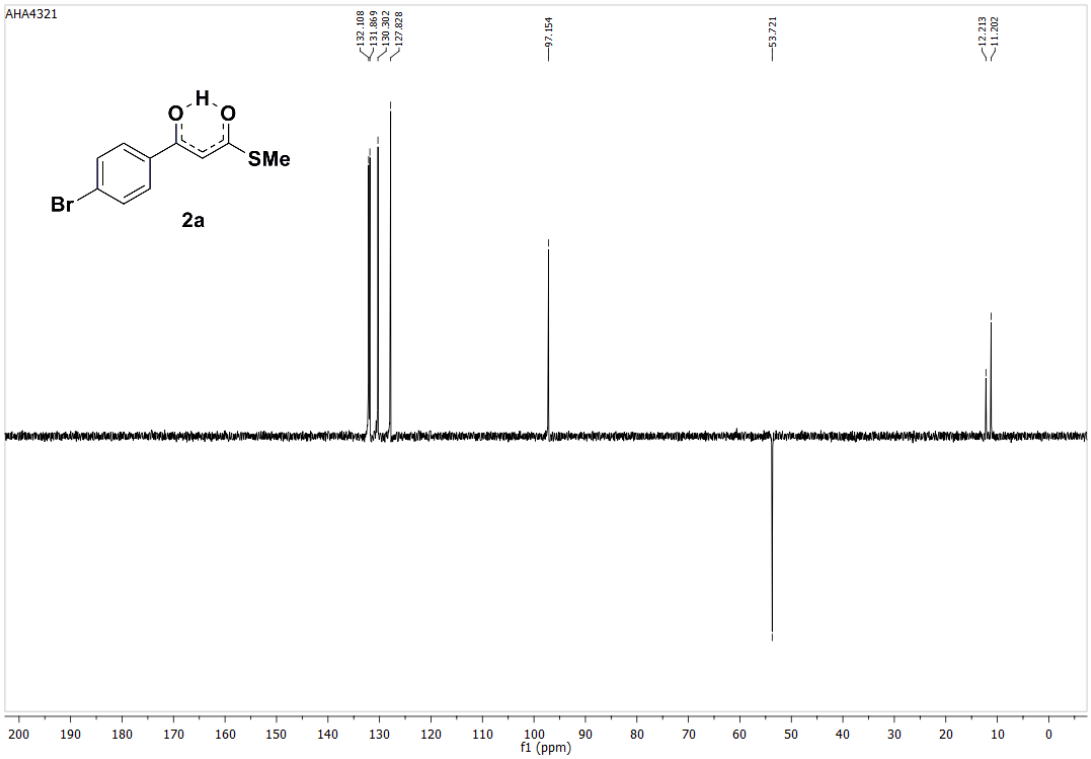


Fig. S3 DEPT-135 spectrum of **2a**

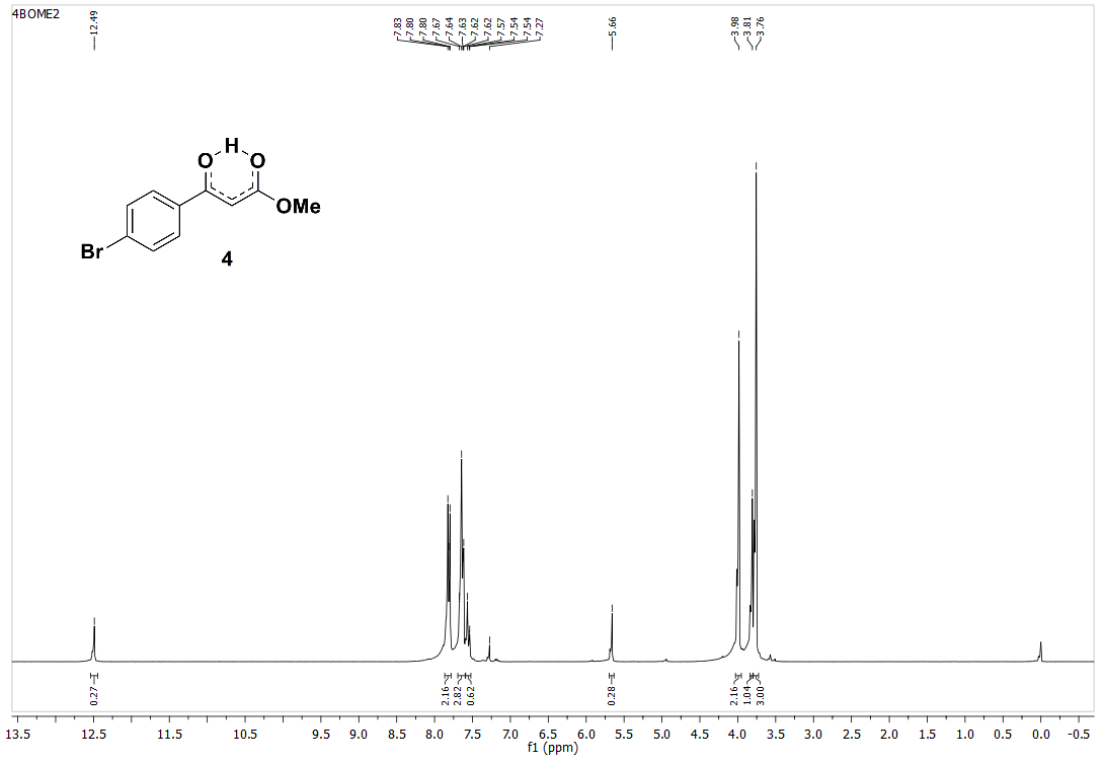


Fig. S4 ^{1}H NMR spectrum of **4**

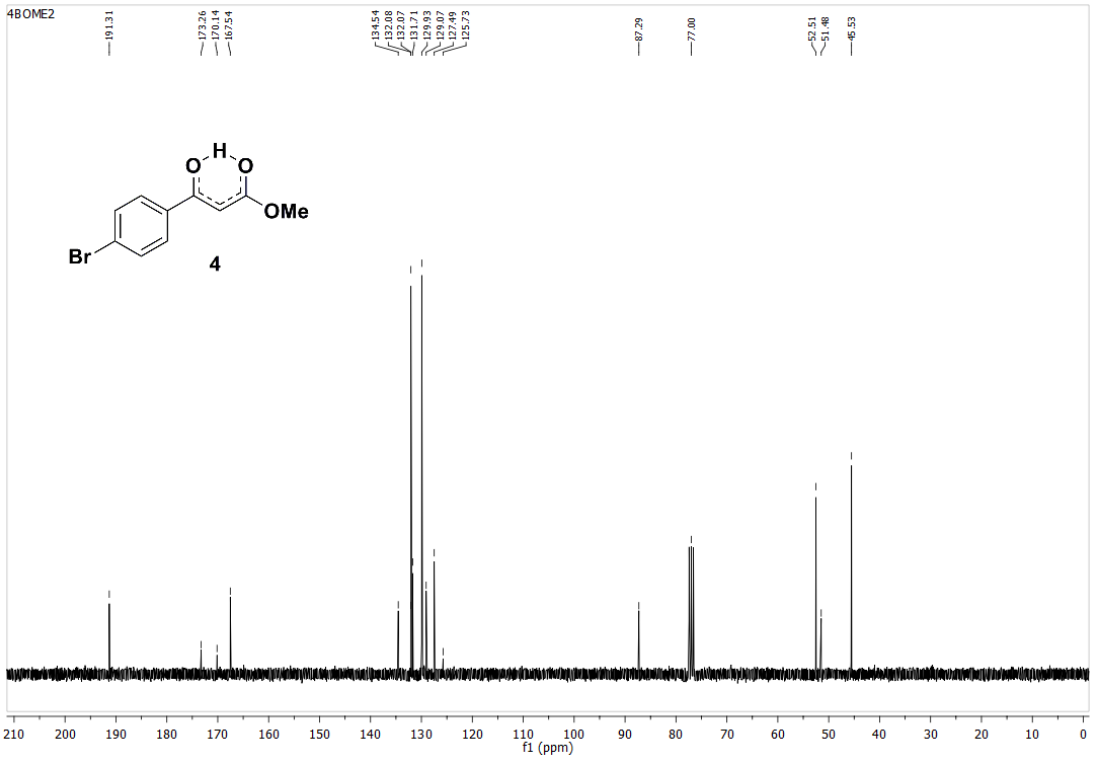


Fig. S5 ^{13}C NMR spectrum of **4**

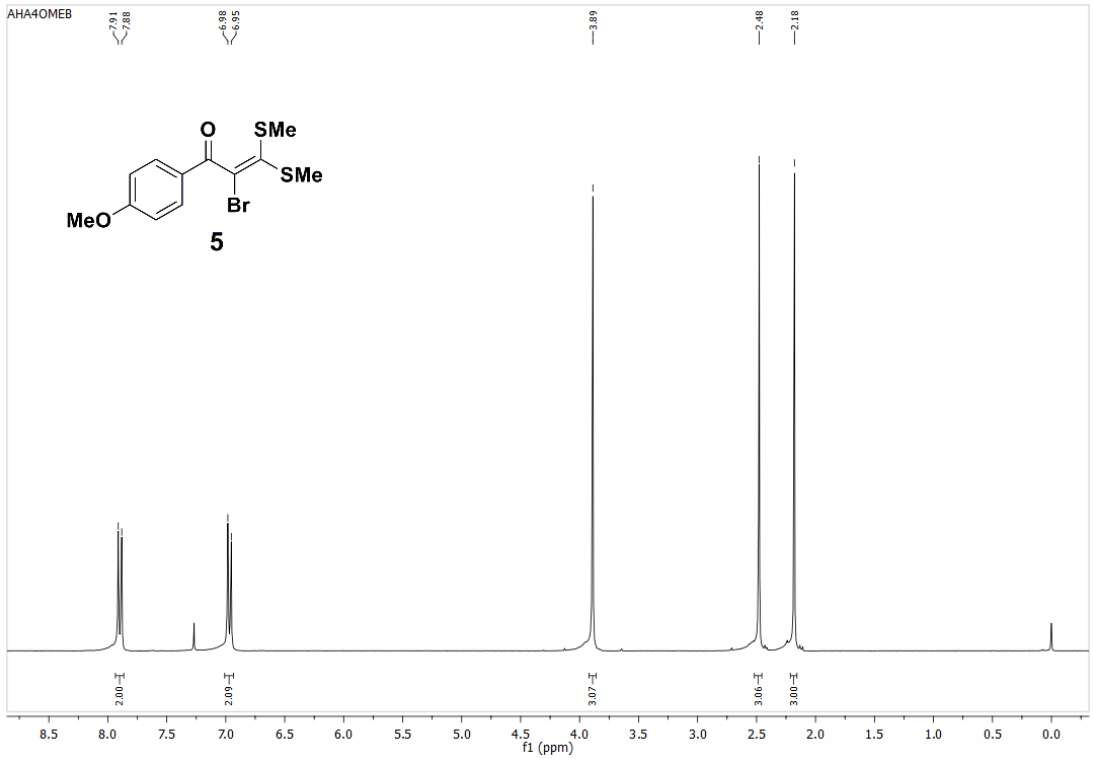


Fig. S6 ^{1}H NMR spectrum of **5**

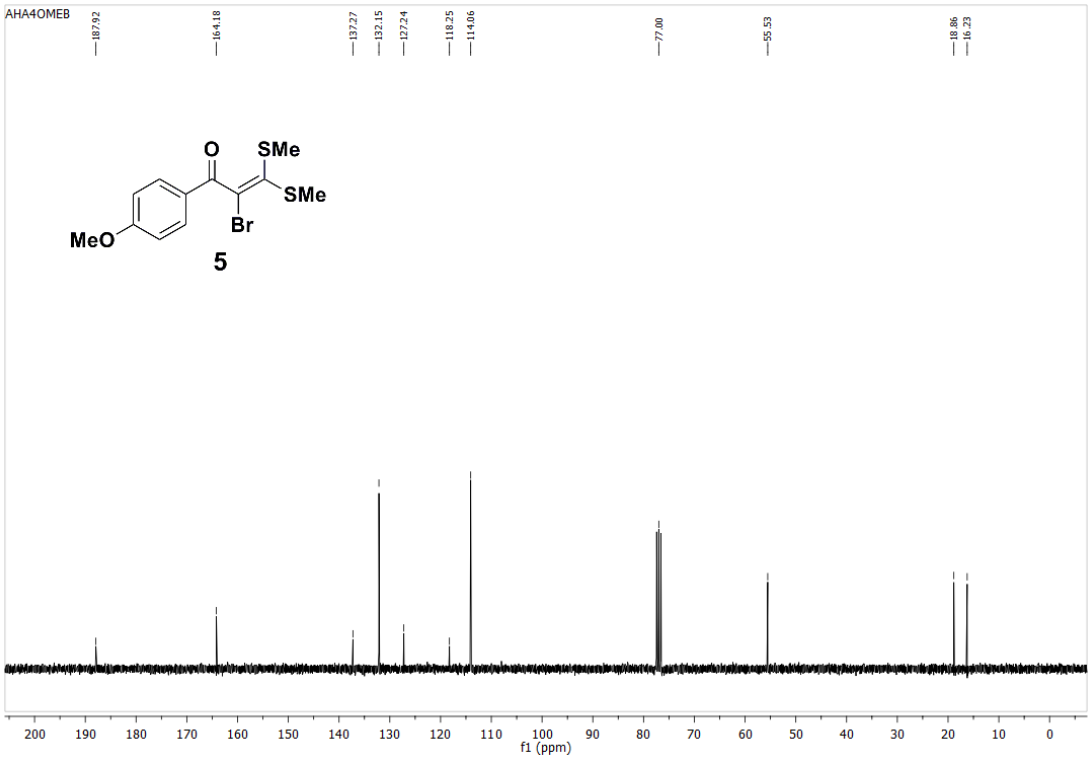


Fig. S7 ^{13}C NMR spectrum of **5**

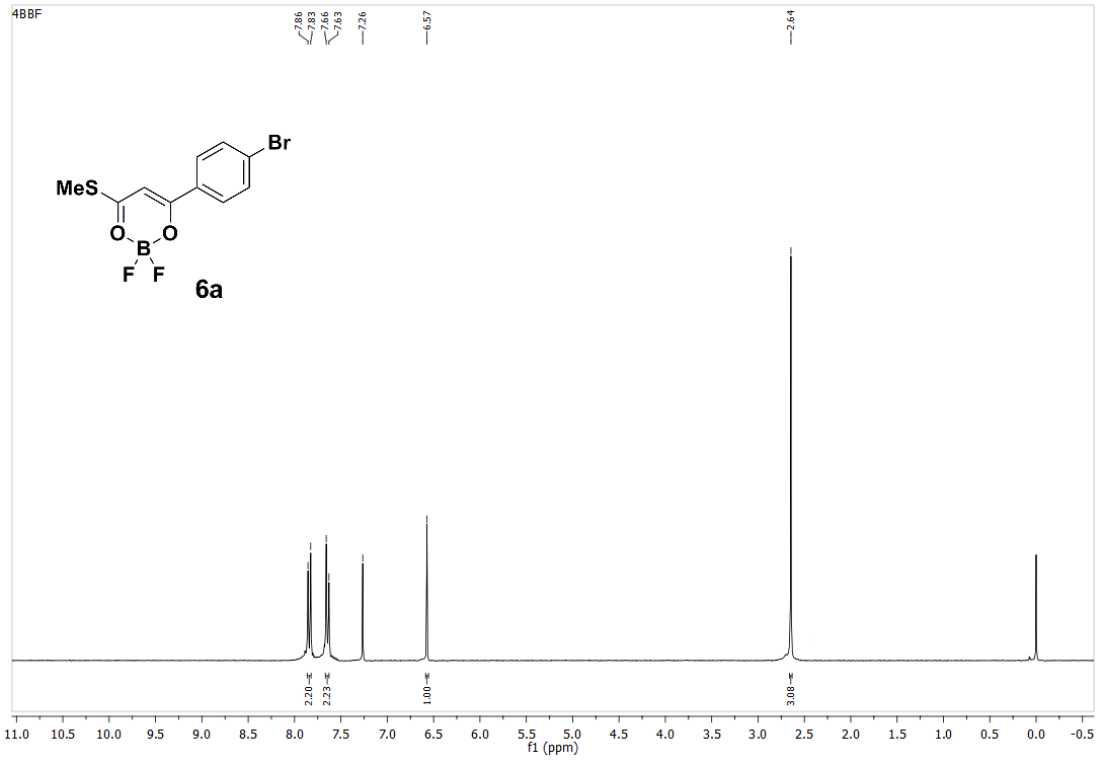


Fig. S8 ^{1}H NMR spectrum of **6a**

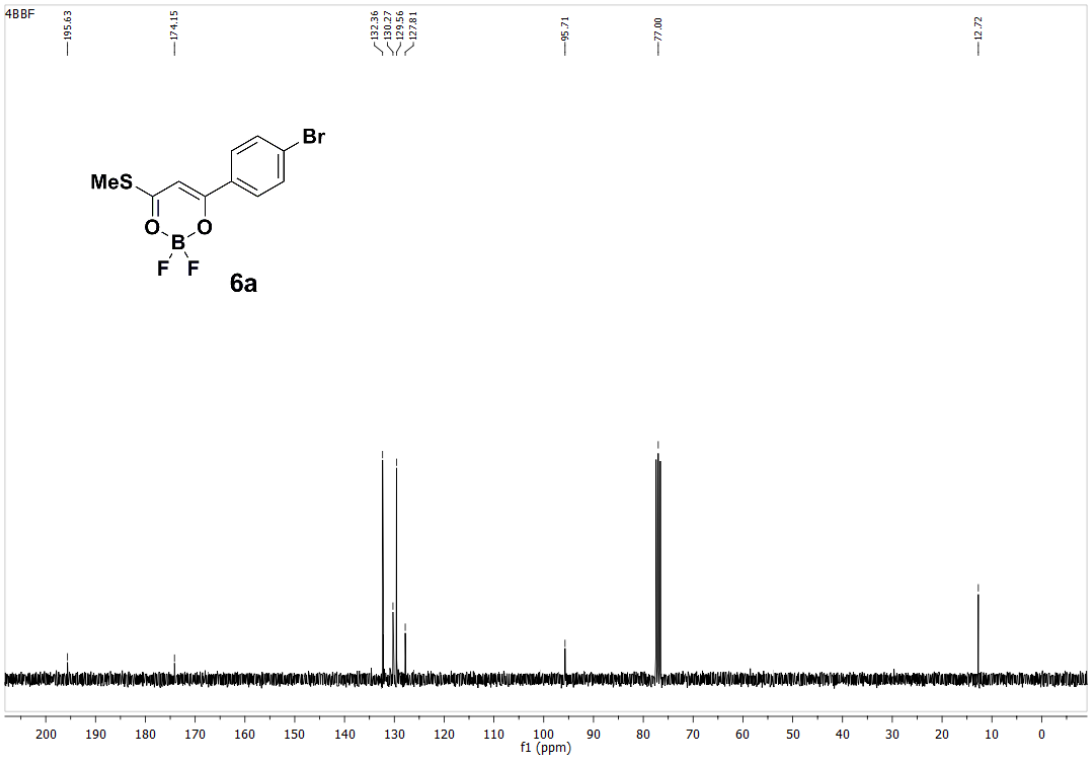


Fig. S9 ^{13}C NMR spectrum of **6a**

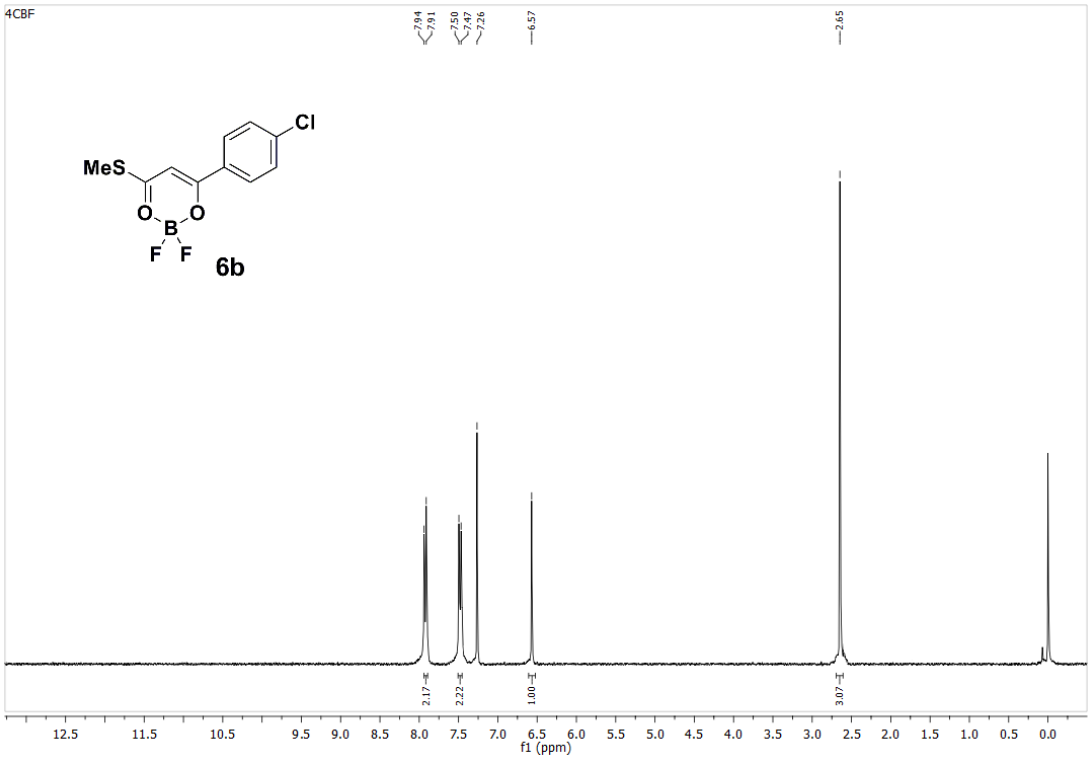


Fig. S10 ^{1}H NMR spectrum of **6b**

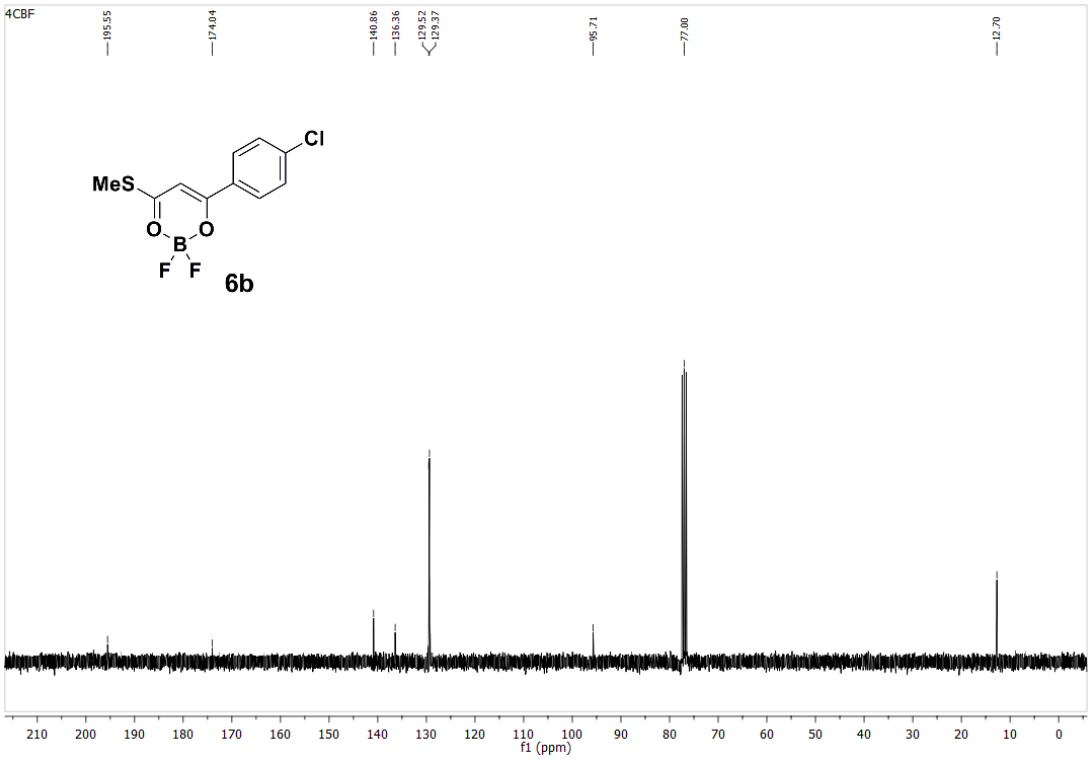


Fig. S11 ^{13}C NMR spectrum of **6b**

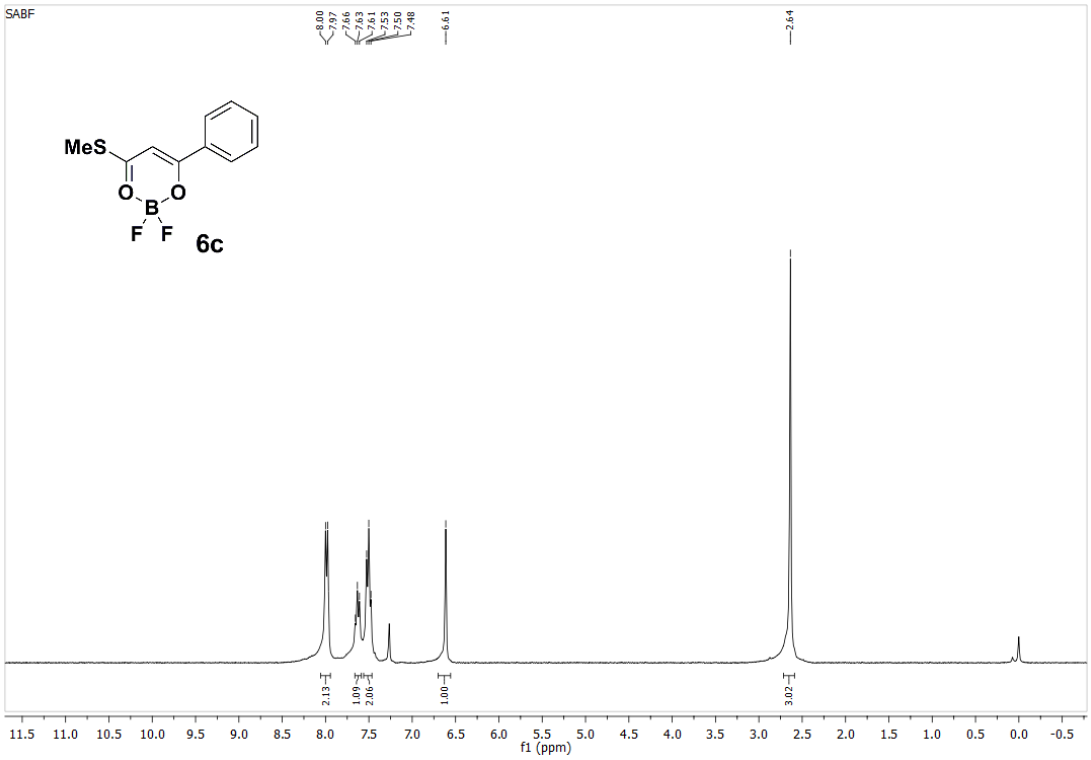


Fig. S12 ^{1}H NMR spectrum of **6c**

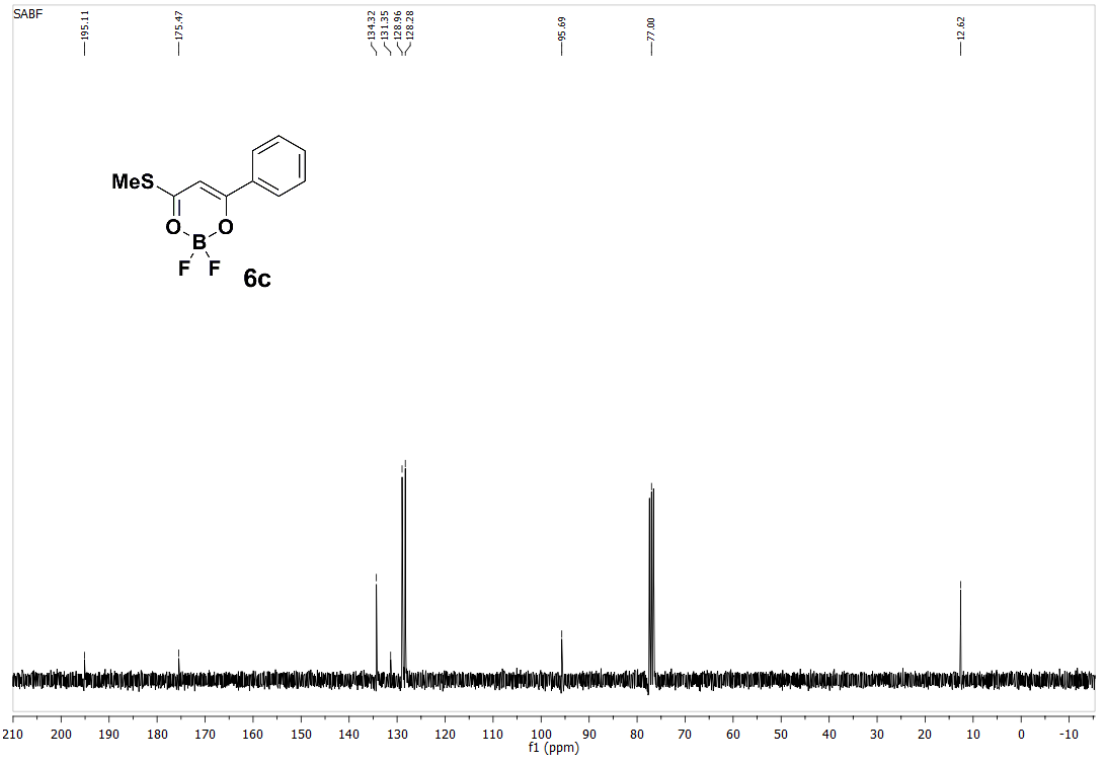


Fig. S13 ^{13}C NMR spectrum of **6c**

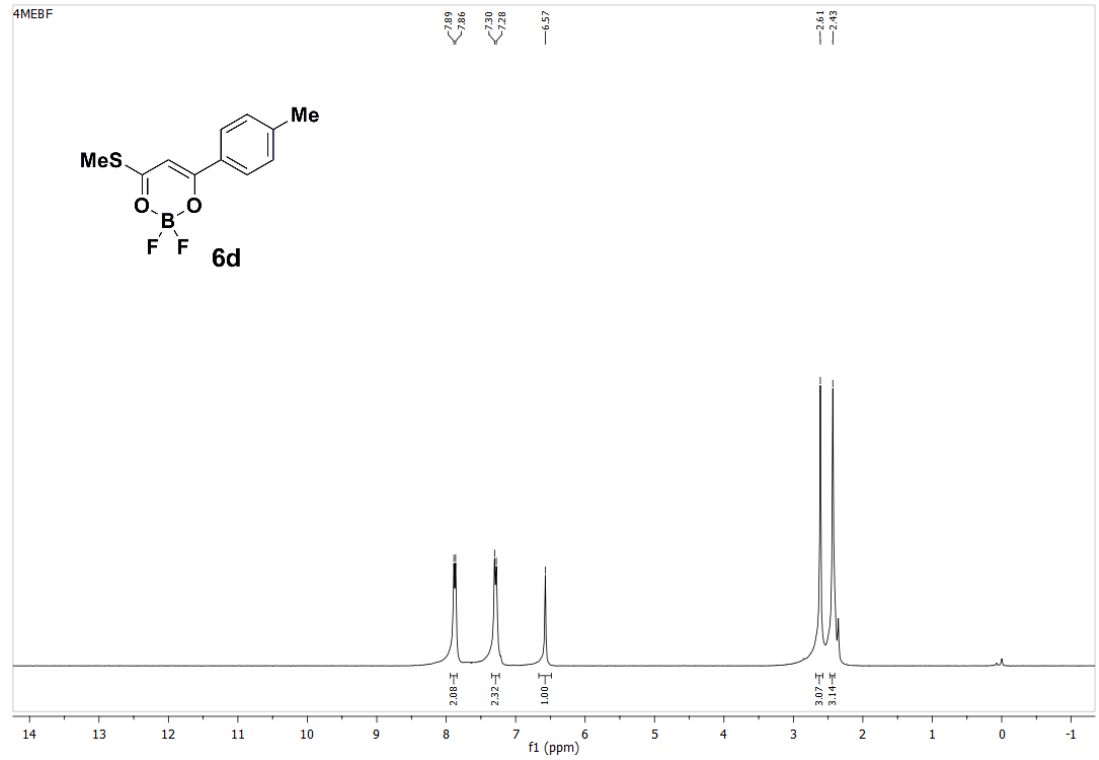


Fig. S14 ^{1}H NMR spectrum of **6d**

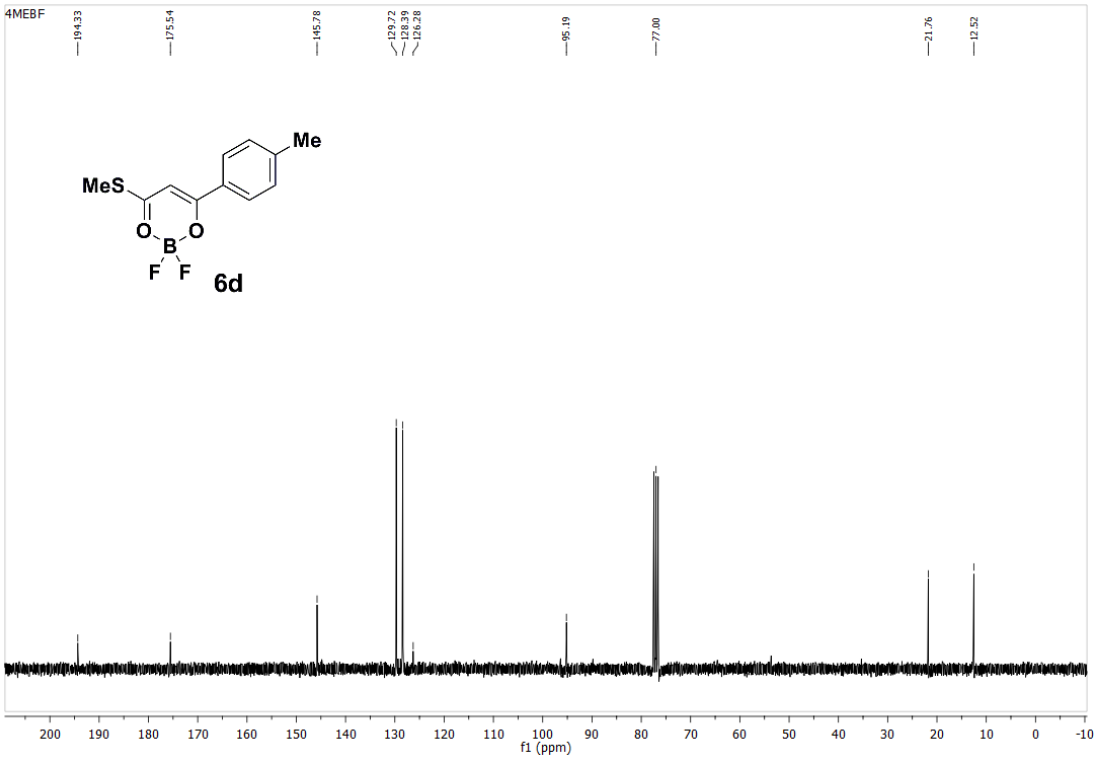


Fig. S15 ^{13}C NMR spectrum of **6d**

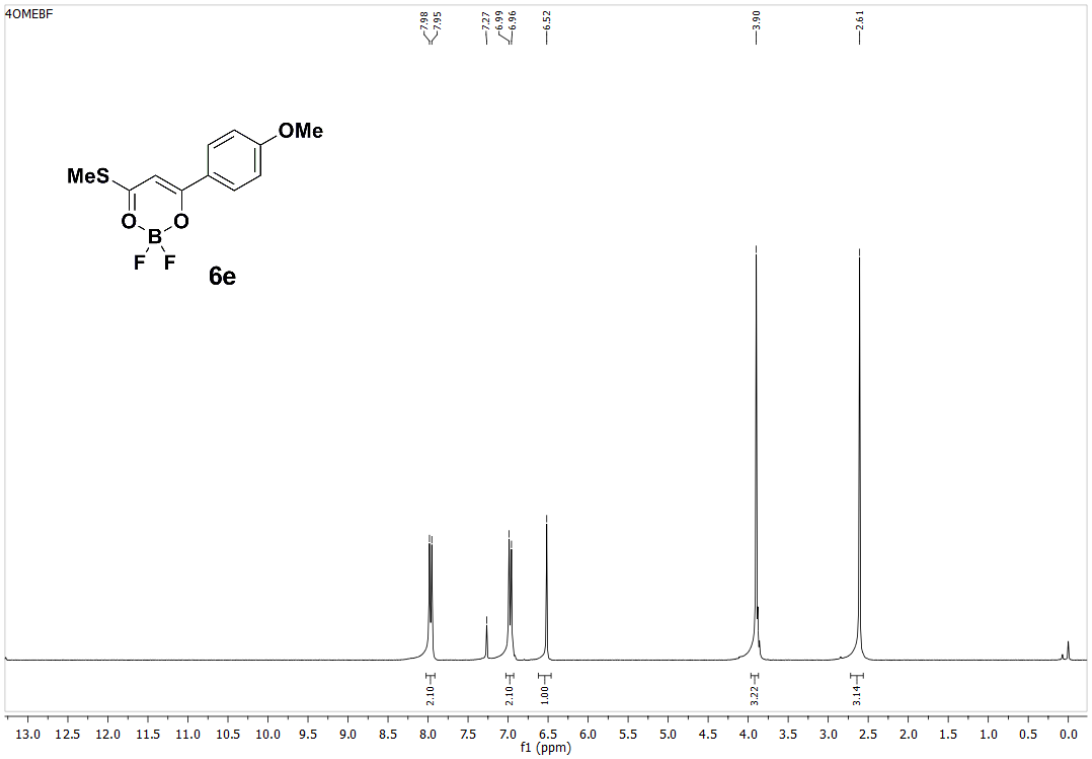


Fig. S16 ^{1}H NMR spectrum of **6e**

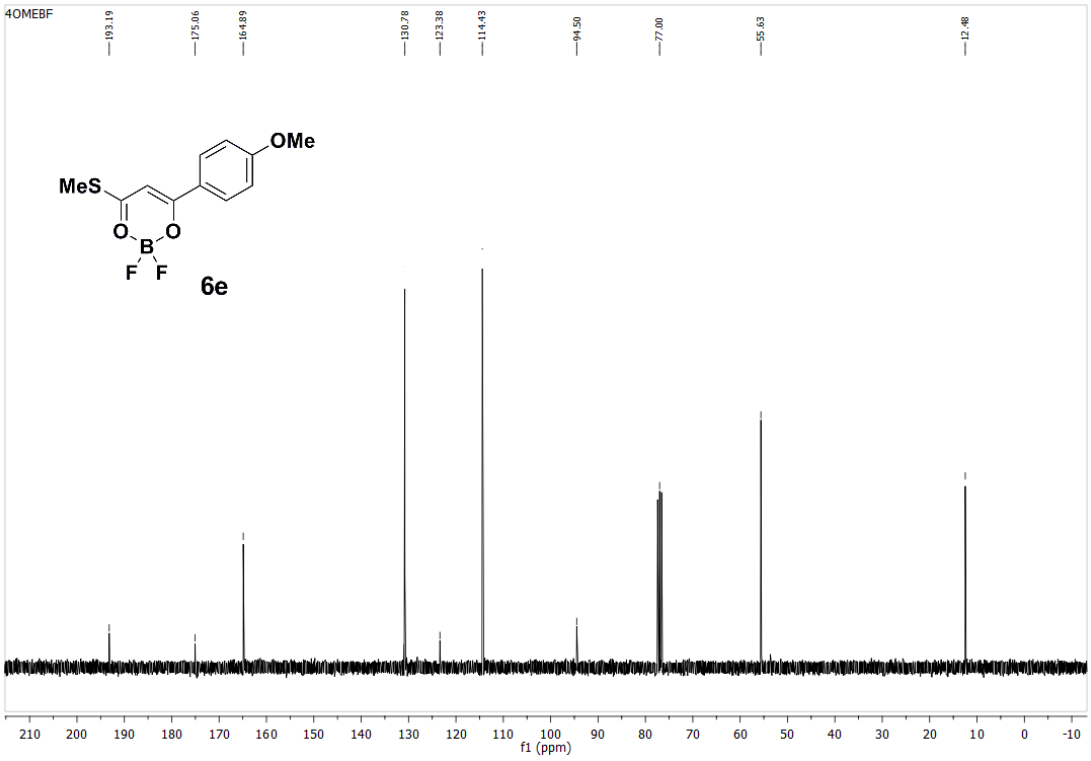


Fig. S17 ^{13}C NMR spectrum of **6e**

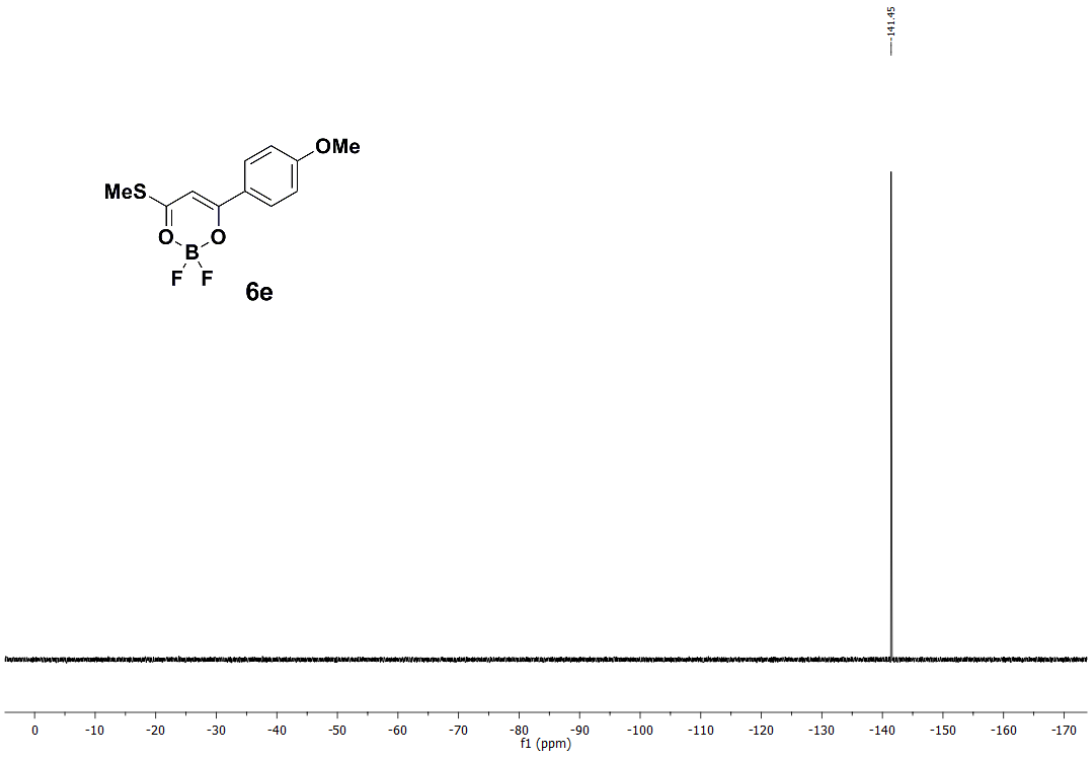


Fig. S18 ^{19}F NMR spectrum of **6e**

II. Photophysical properties of Boron diketonates 6a-e

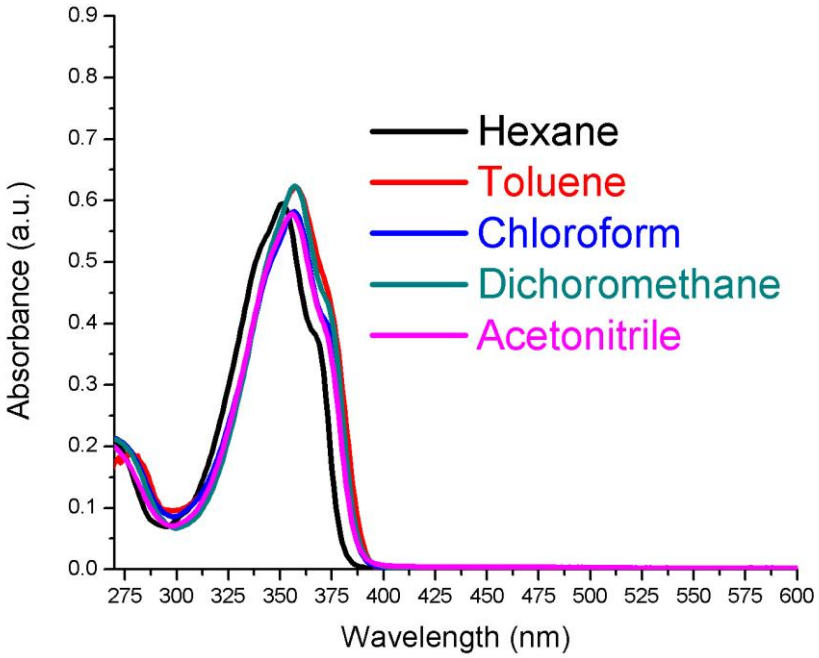


Fig. S19 UV-vis absorption spectra of **6b** in Various solvents (1×10^{-5} M)

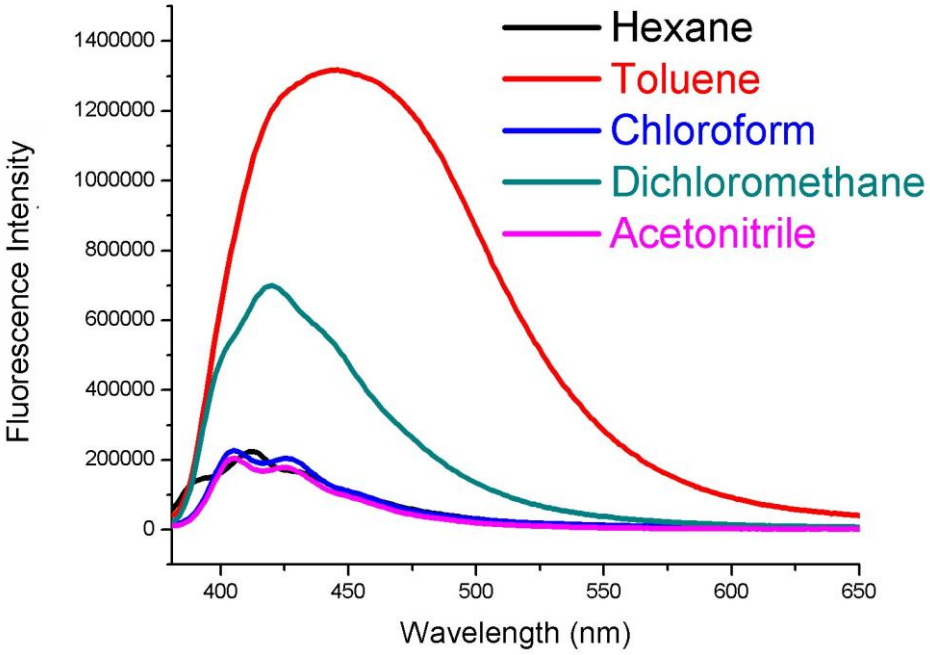


Fig. S20 Fluorescence spectra of **6b** in Various solvents (1×10^{-5} M)

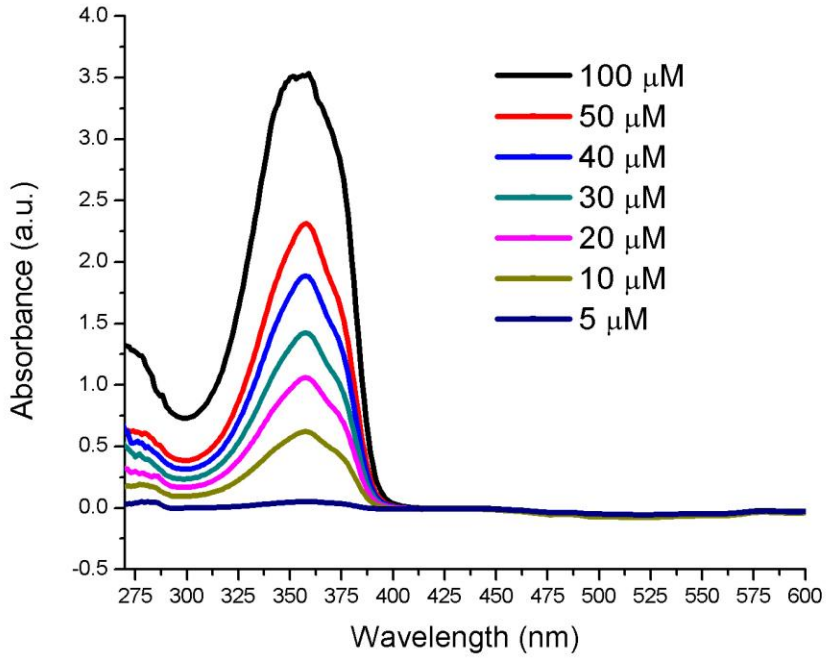


Fig. S21 UV-vis absorption spectra of **6b** in toluene at various concentrations

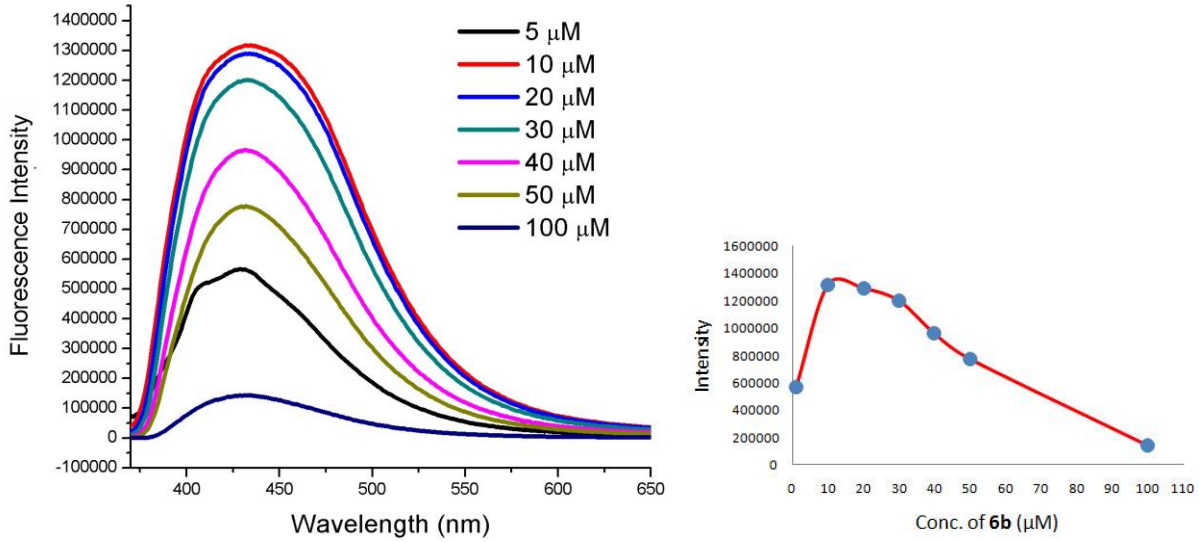


Fig. S22 Change of Fluorescence spectra of **6b** in toluene at various concentrations. Inset shows the graphical change in intensity with increase in concentration of compound **6b**.

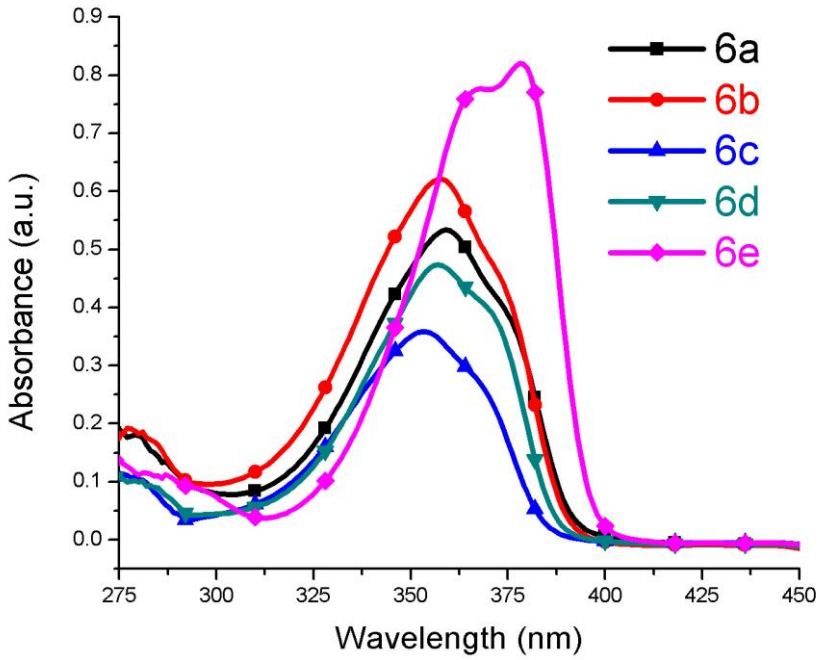


Fig. S23 UV-vis absorption spectra of **6a-e** in toluene (1×10^{-5} M)

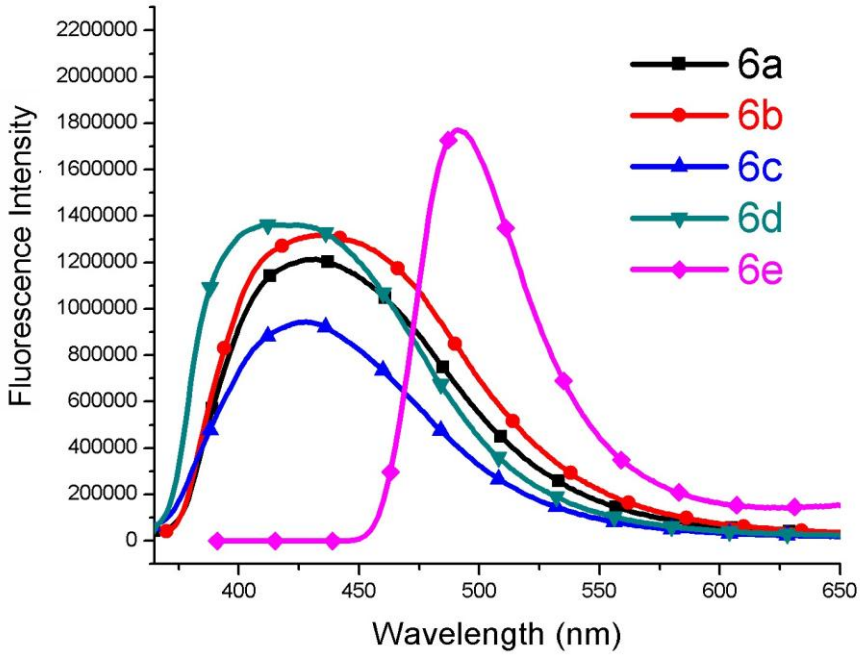


Fig. S24 Fluorescence spectra of **6a-e** in toluene (1×10^{-5} M)

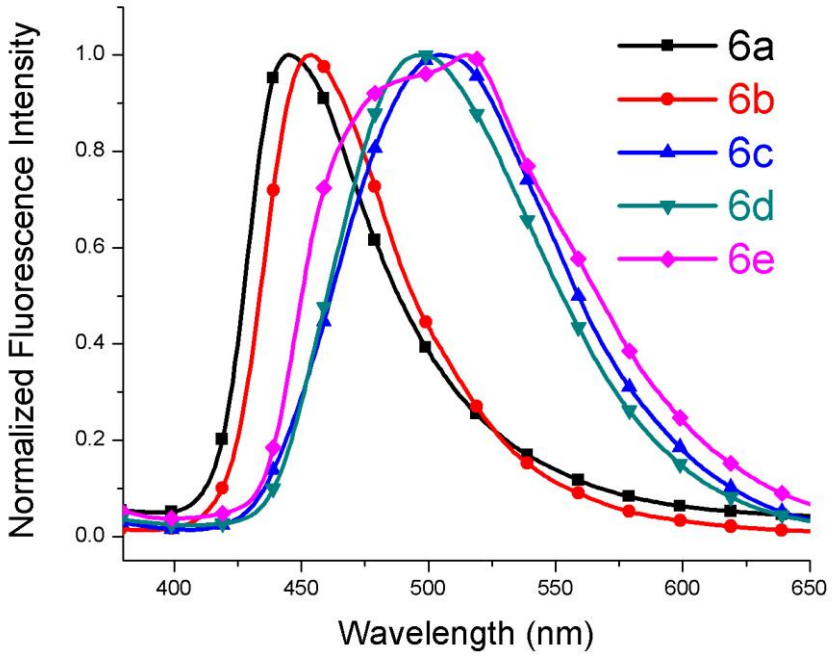
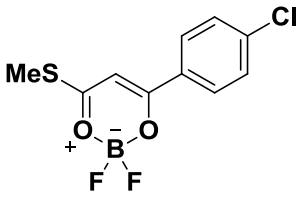


Fig. S25 Normalized fluorescence spectra of **6a-e** in the solid state, excitation at 360 nm.

Table S1 Absorption and Fluorescence properties of **6b** in various solvets[a]



solvent	λ_{abs} (ε) (nm)	F_{max} (nm)	Stokes shift [nm/cm^{-1}]	ϕ_f[b]
hexane	351 (59,500)	413	62/4276	0.06
toluene	358 (62,100)	435	77/4944	0.74
$CHCl_3$	357 (58,200)	405	48/3319	0.06
CH_2Cl_2	357 (62,300)	420	63/4201	0.22
MeCN	356 (57,800)	405	49/3398	0.04

[a]Measured at a concentration of 1×10^{-5} M. [b]Determined by comparison with quinine sulfate.

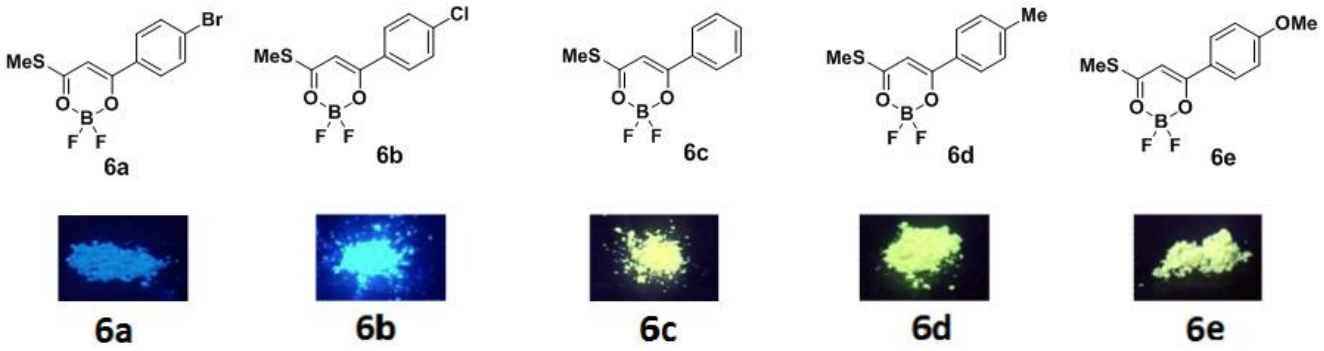


Fig. S26 Photography of boron complexes **6a-e** in solid state under (365 nm)

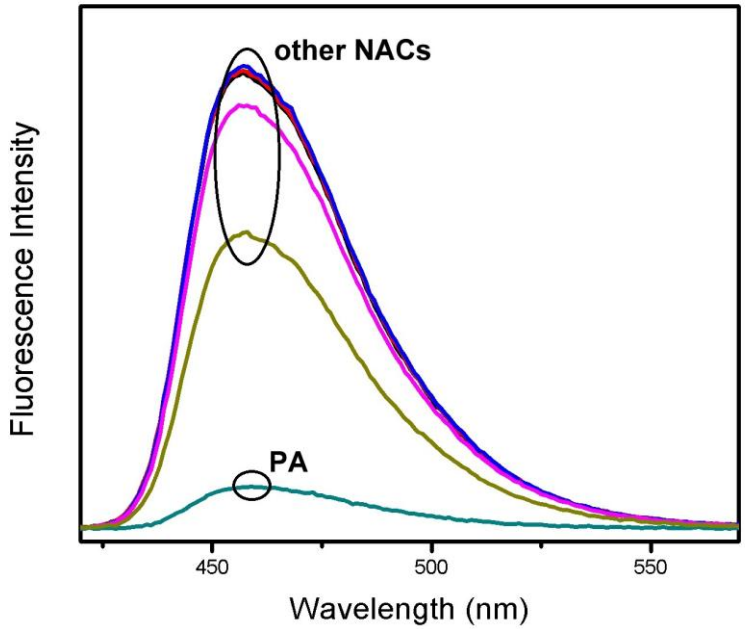


Fig. S27 Fluorescence change of **6e** in dichloromethane in the presence of other NACs.

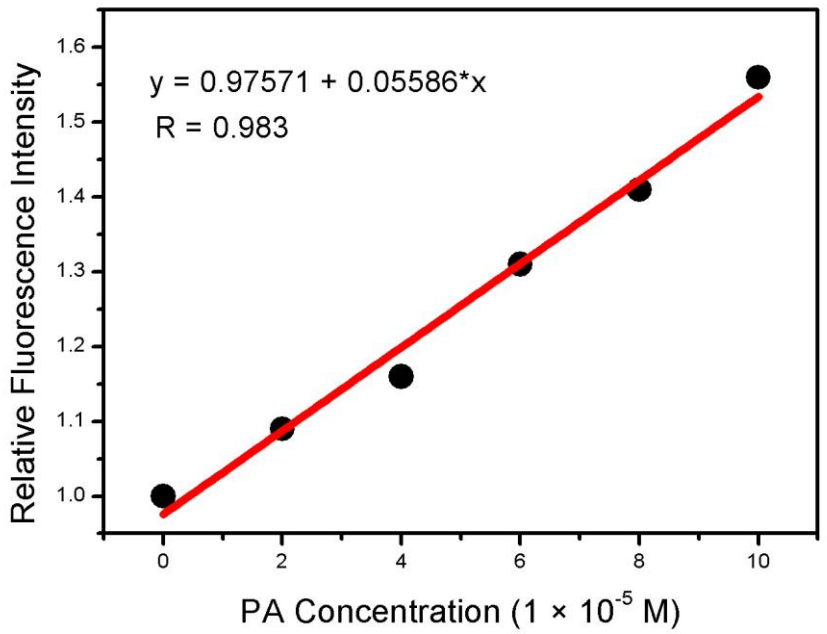


Fig. S28 Calibration plot for detection limit (LOD). The LOD was derived by using the formula 3σ/slope, where σ is the standard deviation of the blank (5 samples) and slope was obtained from linear calibration curve.

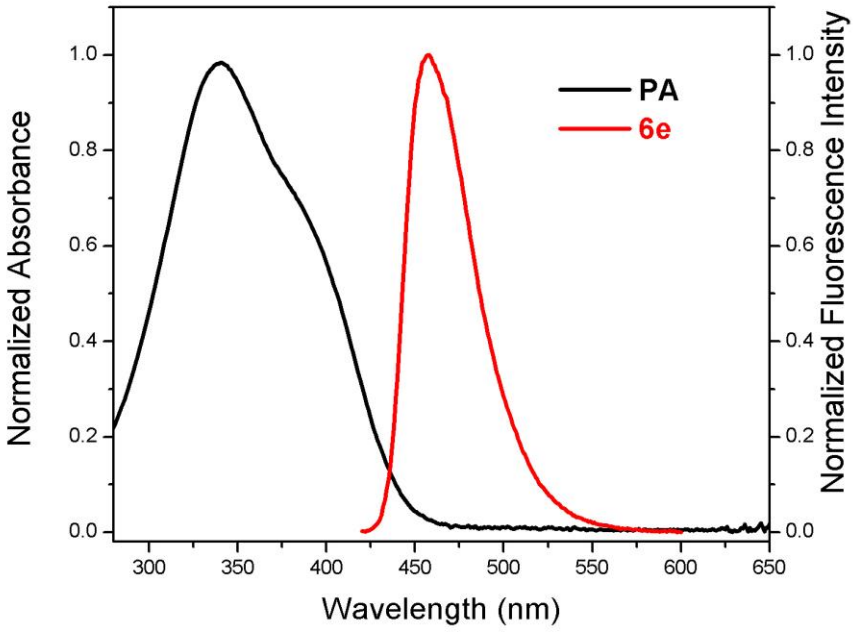


Fig. S29 Spectral overlap between absorption spectra of PA and emission spectrum of **6e.**

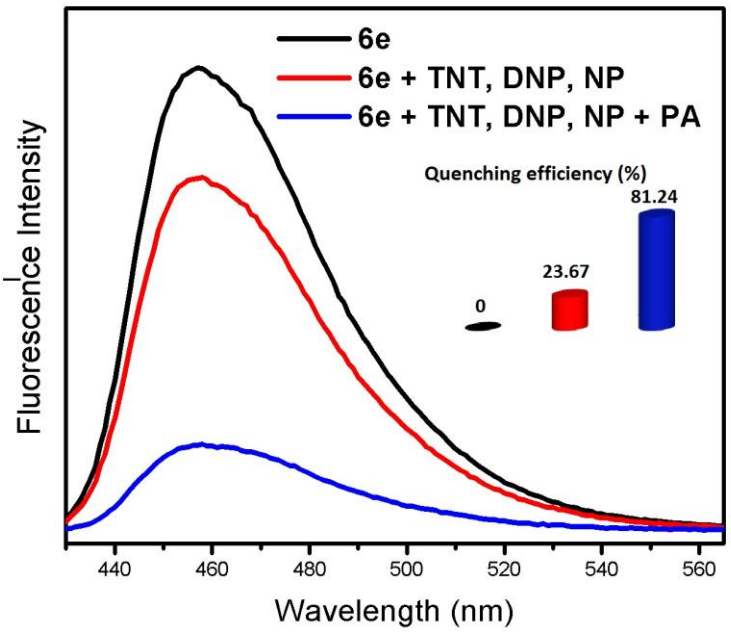


Fig. S30 Fluorescence changes of 6e in dichloromethane in the presence of other NACs coexist with PA.

III. X-ray crystal details of 6e

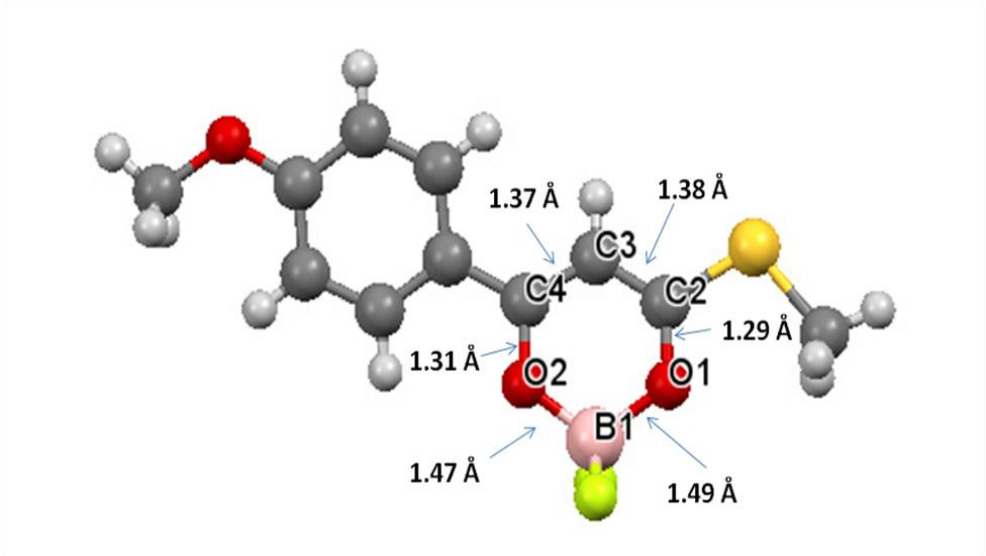


Fig. S31 X-ray crystal structure of **6e,** top view.

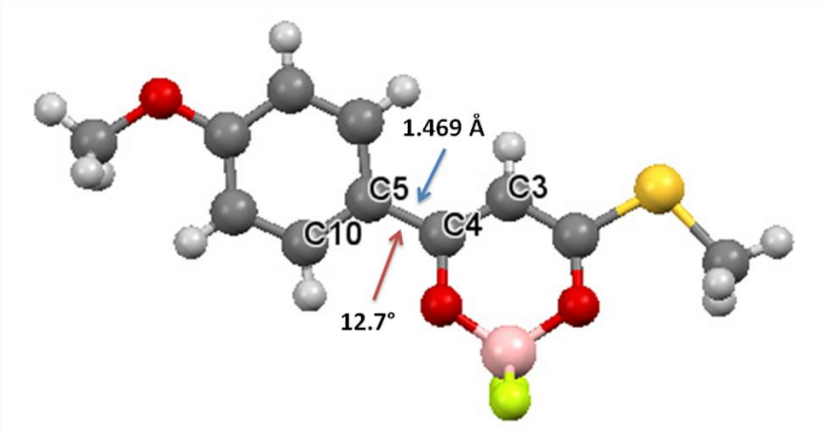


Fig. S32 The bond length of C4-C5 and the torsion angle of C3-C4-C5-C10 of **6e**.

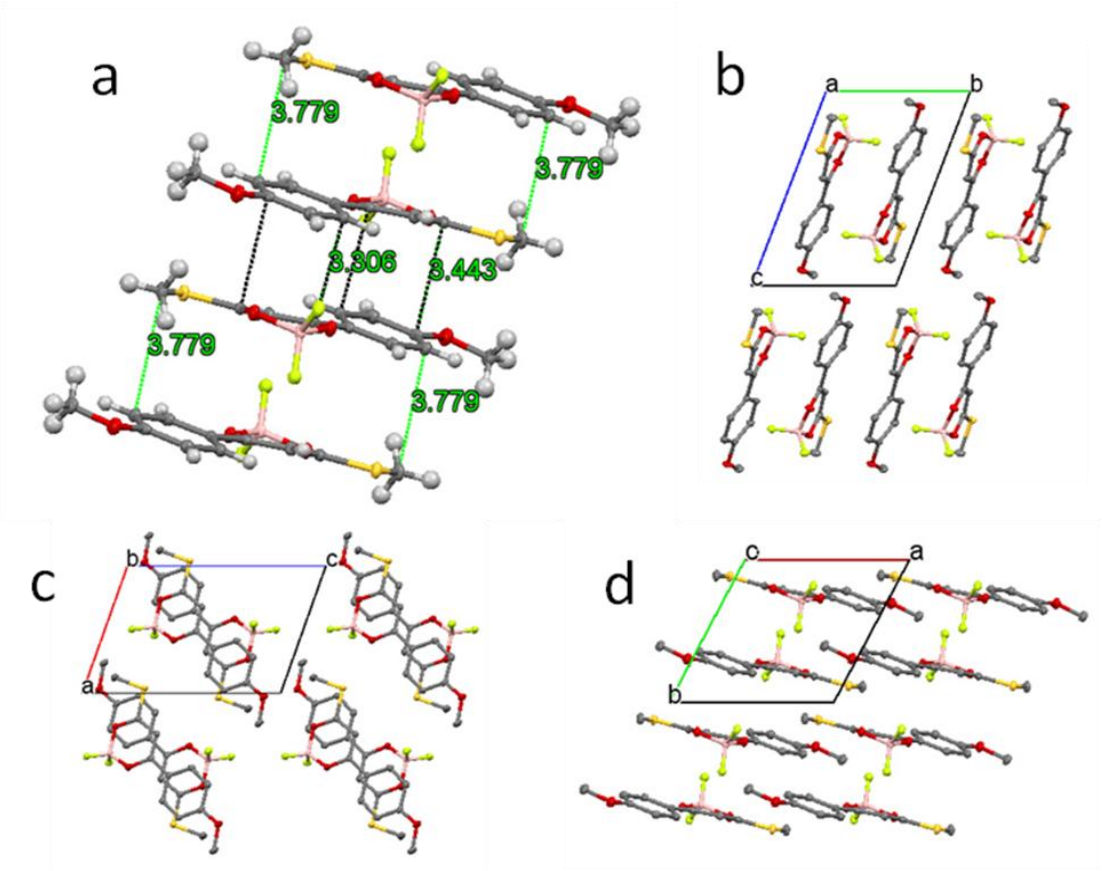


Fig. S33 Structure (a) and arrangement of the excimer formed by boron diketonate complex **6e** in the crystalline state, view along the a axis (b), the b axis (c) and the c axis (d). Ellipsoids are drawn at the 50% level, hydrogen are shown as sphere of arbitrary radius of 0.30 Å. C, grey; H, white, O, red; B, pink; F, yellow.

Table S2. Crystal data and structure refinement for **6e**

Identification code	4bmbf_070616_0m
CCDC number	1510673
Empirical formula	$C_{11}H_{11}BF_2O_3S$
Formula weight	272.07
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 7.9630(18) Å; α= 103.904(4)°.
	b = 8.0155(18) Å; β= 101.576(4)°.
	c = 10.948(2) Å; γ= 113.133(5)°.
Volume	588.7(2) $Å^3$
Z	2
Density (calculated)	1.535 Mg/m^3
Absorption coefficient	0.296 mm^{-1}
F(000)	280
Index ranges	-9<=h<=9, -9<=k<=9, -9<=l<=13

Table S3. Bond lengths [Å] for **6e**

S(1)-C(2)	1.731(2)
S(1)-C(1)	1.804(2)
F(1)-B(1)	1.381(3)
O(3)-C(11)	1.439(3)
O(3)-C(8)	1.361(2)
C(6)-H(6)	0.950
C(6)-C(7)	1.376(2)
C(6)-C(5)	1.401(3)
C(7)-H(7)	0.950
C(7)-C(8)	1.399(2)
C(9)-H(9)	0.950
C(9)-C(8)	1.390(3)
C(9)-C(10)	1.391(2)
C(5)-C(4)	1.469(2)
C(5)-C(10)	1.393(2)
C93)-H(3)	0.950
C(3)-C(4)	1.377(2)
C(3)-C(2)	1.389(2)
C(11)-H(11A)	0.980
C(11)-H(11B)	0.980
C(11)-H(11C)	0.980
F(2)-B(1)	1.372(3)

B(1)-O(2)	1.478(3)
B(1)-O(1)	1.498(3)
C(4)-O(2)	1.316(2)
C(2)-O(1)	1.297(2)
C(10)-H(10)	0.950
C(1)-H(1A)	0.980
C(1)-H(1B)	0.980
C(1)-H(1C)	0.979

Table S4. Bond angles [°] for **6e**

C(2)-S(1)-C(1)	101.90(9)
C(11)-O(3)-C(8)	117.4(1)
C(7)-C(6)-C(5)	120.9(2)
C(6)-C(7)-H(7)	120.0
C(6)-C(7)-C(8)	119.9(2)
C(8)-C(9)-C(10)	119.0(2)
C(6)-C(5)-C(4)	122.0(1)
C(6)-C(5)-C(10)	118.5(2)
C(4)-C(5)-C(10)	119.5(1)
C(4)-C(3)-C(2)	119.1(2)
O(3)-C(8)-C(7)	115.4(1)
O(3)-C(8)-C(9)	124.3(2)
C(7)-C(8)-C(9)	120.3(2)
F(1)-B(1)-F(2)	111.1(2)

F(1)-B(1)-O(2)	109.4(2)
F(1)-B(1)-O(1)	108.1(2)
F(2)-B(1)-O(2)	109.3(2)
F(2)-B(1)-O(1)	107.9(2)
O(2)-B(1)-O(1)	111.1(2)
C(5)-C(4)-C(3)	124.4(2)
C(5)-C(4)-O(2)	114.7(1)
C(3)-C(4)-O(2)	120.9(2)
S(1)-C(2)-C(3)	119.5(1)
S(1)-C(2)-O(1)	117.6(1)
C(3)-C(2)-O(1)	123.0(2)
B(1)-O(2)-C(4)	122.0(1)
B(1)-O(1)-C(2)	120.1(1)
C(9)-C(10)-C(5)	121.5(2)

Table S5. Torsion angles [°] for **6e**

C(1)-S(1)-C(2)-C(3)	-177.9(1)
C(1)-S(1)-C(2)-O(1)	2.9(2)
C(11)-O(3)-C(8)-C(7)	176.4(2)
C(11)-O(3)-C(8)-C(9)	-4.2(2)
H(6)-C(6)-C(7)-H(7)	-0.8
H(6)-C(6)-C(7)-C(8)	179.2
C(5)-C(6)-C(7)-H(7)	179.2
C(5)-C(6)-C(7)-C(8)	-0.8(3)

H(6)-C(6)-C(5)-C(4)	0.5
H(6)-C(6)-C(5)-C(10)	179.7
C(7)-C(6)-C(5)-C(4)	-179.5(2)
C(7)-C(6)-C)5)-C(10)	-0.4(2)
C(6)-C(7)-C(8)-O(3)	-179.4(2)
C(6)-C(7)-C(8)-C(9)	1.2(3)
H(7)-C(7)-C(8)-O(3)	0.6
H(7)-C(7)-C(8)-C(9)	-178.8
H(9)-C(9)-C(8)-O(3)	0.2
H(9)-C(9)-C(8)-C(7)	179.6
C(10)-C(9)-C(8)-O(3)	-179.7(2)
C(10)-C(9)-C(8)-C(7)	-0.4(3)
H(9)-C(9)-C(10)-C(5)	179.2
H(9)-C(9)-C(10)-H(10)	-0.7
C(8)-C(9)-C(10)-C(5)	-0.8(3)
C(8)-C(9)-C(10)-H(10)	179.2
C(6)-C(5)-C(4)-C(3)	-12.7(3)
C(6)-C(5)-C(4)-O(2)	166.4(2)
C(10)-C(5)-C(4)-C(3)	168.1(2)
C(10)-C(5)-C(4)-O(2)	-12.8(2)
C(6)-C(5)-C(10)-C(9)	1.2(3)
C(6)-C(5)-C(10)-H(10)	-178.8
C(4)-C(5)-C(10)-C(9)	-179.7(2)
C(4)-C(5)-C(10)-H(10)	0.3

H(3)-C(3)-C(4)-C(5)	-5.4
H(3)-C(3)-C(4)-O(2)	175.5
C(2)-C(3)-C(4)-C(5)	174.6(2)
C(2)-C(3)-C(4)-O(2)	-4.4(3)
H(3)-C(3)-C(2)-S(1)	5.2
H(3)-C(3)-C(2)-O(1)	-175.7
C(4)-C(3)-C(2)-S(1)	-174.9(1)
C(4)-C(3)-C(2)-O(1)	4.2(3)
F(1)-B(1)-O(2)-C(4)	-98.1(2)
F(2)-B(1)-O(2)-C(4)	140.1(2)
O(1)-B(1)-O(2)-C(4)	21.2(2)
F(1)-B(1)-O(1)-C(2)	99.0(2)
F(2)-B(1)-O(1)-C(2)	-140.8(2)
O(2)-B(1)-O(1)-C(2)	-21.1(2)
C(5)-C(4)-O(2)-B(1)	171.3(2)
C(3)-C(4)-O(2)-B(1)	-9.5(3)
S(1)-C(2)-O(1)-B(1)	-171.2(1)
C(3)-C(2)-O(1)-B(1)	9.7(3)