

Supporting Information

OFF-ON Fluorescence Sensing of Fluoride by Donor–Antimony(V) Lewis Acids

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Table S1. Crystallographic data and parameters for [3a]OTf.

Compd	([3a]OTf) ₂ ·0.5(CH ₂ Cl ₂)
formula	C _{64.5} H ₅₁ ClF ₆ N ₂ O ₈ S ₂ Sb ₂
formula weight	1439.14
crystal system	triclinic
space group	<i>P</i> −1
<i>a</i> (Å)	13.768(2)
<i>b</i> (Å)	14.800(2)
<i>c</i> (Å)	15.370(2)
α (°)	76.320(7)
β (°)	84.711(6)
γ (°)	77.513(6)
<i>V</i> (Å ³)	2968.3(7)
<i>Z</i>	2
ρ_{calc} (g cm ^{−3})	1.610
μ (mm ^{−1})	1.103
<i>F</i> (000)	1442
<i>T</i> (K)	110(2)
scan mode	<i>multi-scan</i>
<i>hkl</i> range	−19→17, −21→20, −21→22
measd reflns	81660
unique reflns [<i>R</i> _{int}]	17876 [0.0335]
reflns used for refinement	17876
refined parameters	823
<i>R</i> 1 ^{<i>a</i>} (<i>I</i> > 2σ(<i>I</i>))	0.0316
w <i>R</i> 2 ^{<i>b</i>} all data	0.0940
GOF on <i>F</i> ²	1.045
ρ_{fin} (max/min) (e Å ^{−3})	1.928, −1.586

^{*a*} $R1 = \sum ||Fo| - |Fc|| / \sum |Fo|$. ^{*b*} $wR2 = [(\sum w(Fo^2 - Fc^2)^2) / (\sum w(Fo^2)^2)]^{1/2}$.

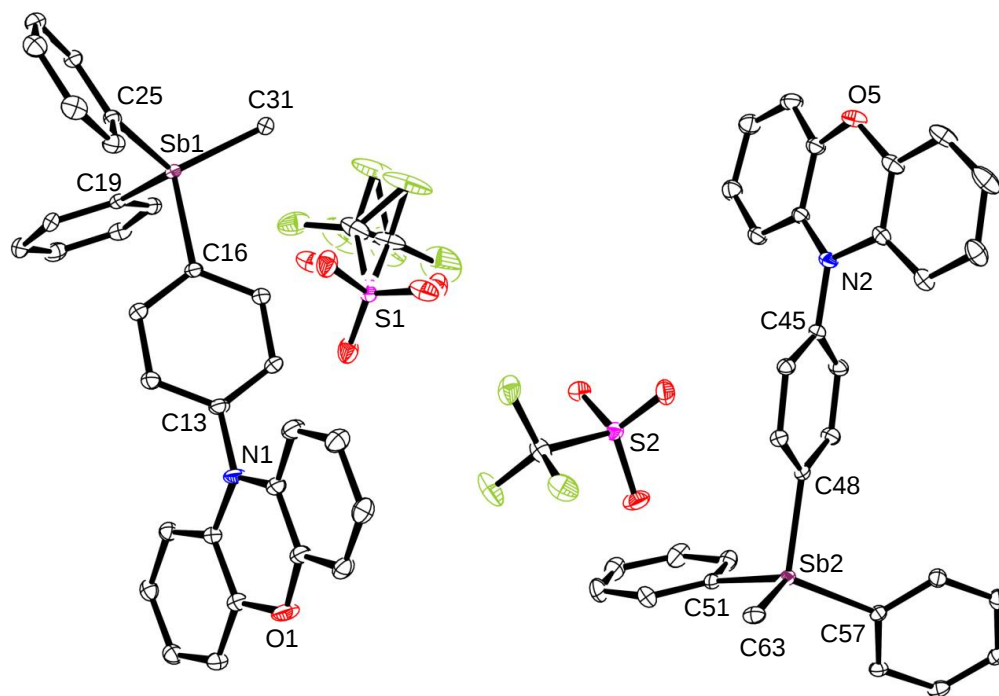


Figure S1. Crystal structures of [3a]OTf (left: molecule **A**, right: molecule **B**) (30% thermal ellipsoids). H atoms and solvent molecules were omitted for clarity.

Table S2. Selected bond lengths (Å) and angles (deg) for [3a]OTf.

A		B	
Lengths			
Sb(1)–C(16)	2.112(2)	Sb(2)–C(48)	2.1050(19)
Sb(1)–C(19)	2.102(2)	Sb(2)–C(51)	2.098(2)
Sb(1)–C(25)	2.104(2)	Sb(2)–C(57)	2.0972(19)
Sb(1)–C(31)	2.092(2)	Sb(2)–C(63)	2.096(2)
Angles			
C(16)–Sb(1)–C(19)	99.73(8)	C(48)–Sb(2)–C(51)	102.63(8)
C(16)–Sb(1)–C(25)	104.71(8)	C(48)–Sb(2)–C(57)	105.04(7)
C(16)–Sb(1)–C(31)	109.22(8)	C(48)–Sb(2)–C(63)	105.56(8)
C(19)–Sb(1)–C(25)	113.85(8)	C(51)–Sb(2)–C(57)	109.26(8)
C(19)–Sb(1)–C(31)	110.95(10)	C(51)–Sb(2)–C(63)	112.59(9)
C(25)–Sb(1)–C(31)	116.67(9)	C(57)–Sb(2)–C(63)	119.93(8)
∠PXZ–Phenylene ^a	67.29	∠PXZ–Phenylene ^a	66.28

^a PXZ = phenoxazine ring.

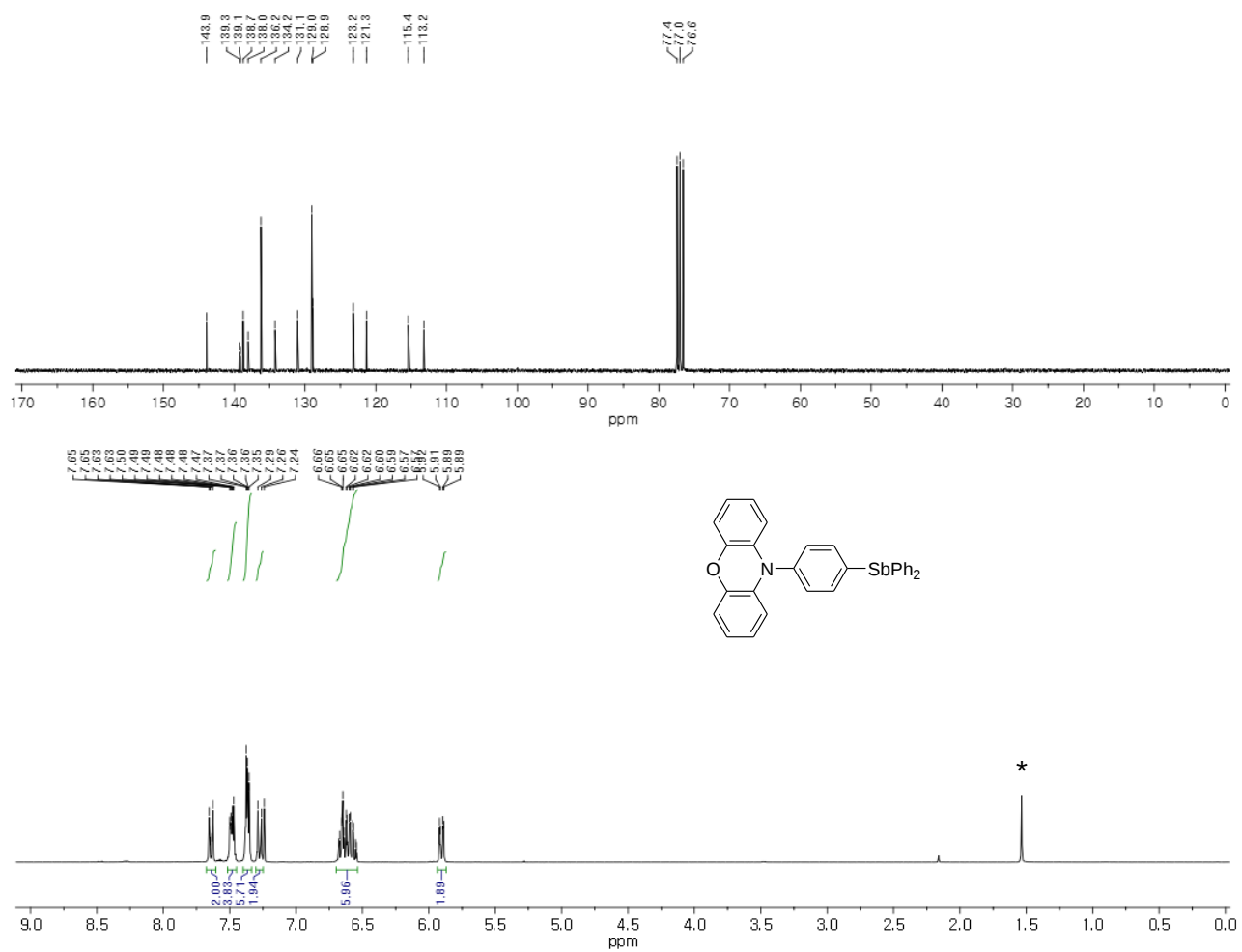


Figure S2. ¹H (bottom) and ¹³C (top) NMR spectra of **2a** (* from residual H₂O in CDCl₃).

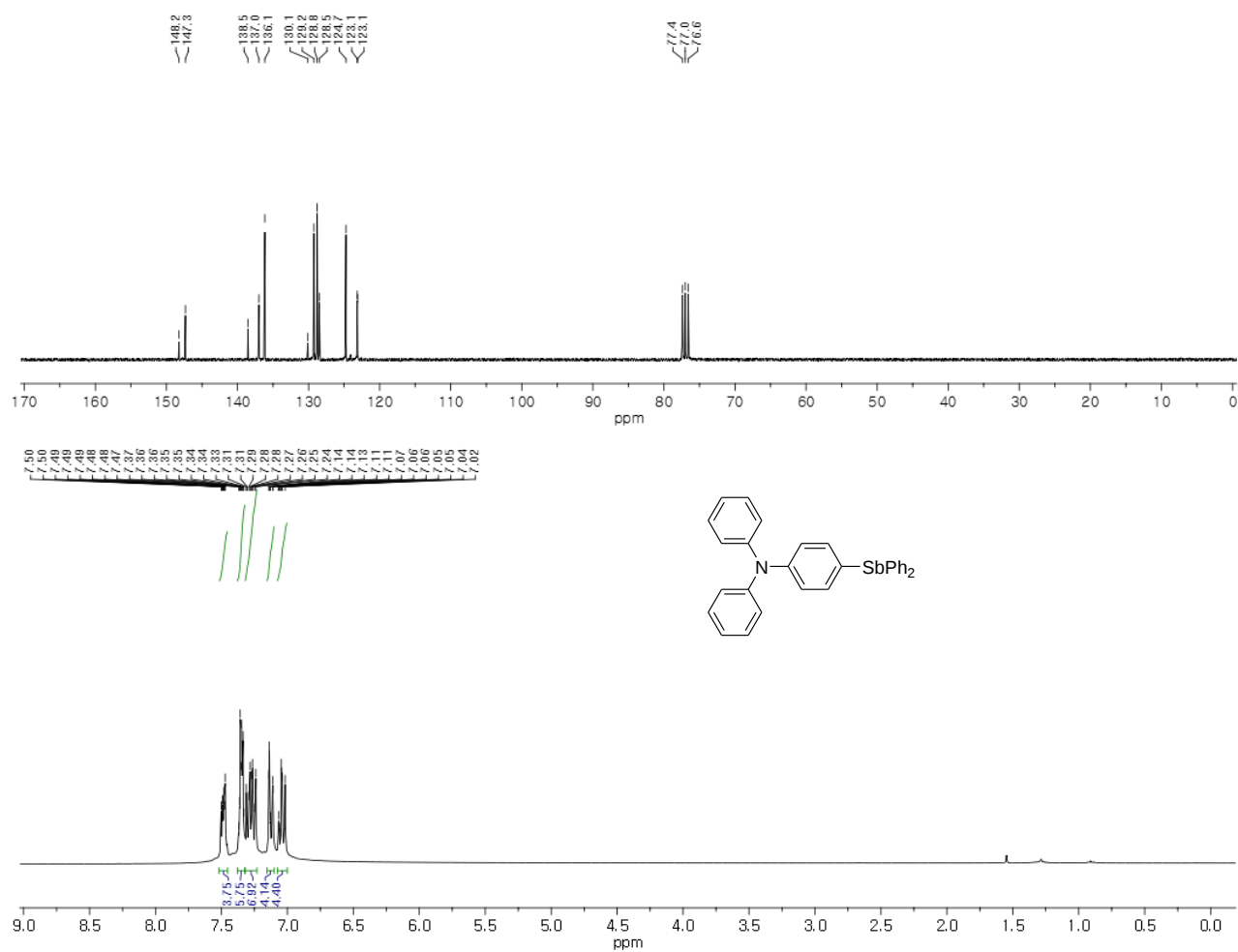


Figure S3. ¹H (bottom) and ¹³C (top) NMR spectra of **2b**.

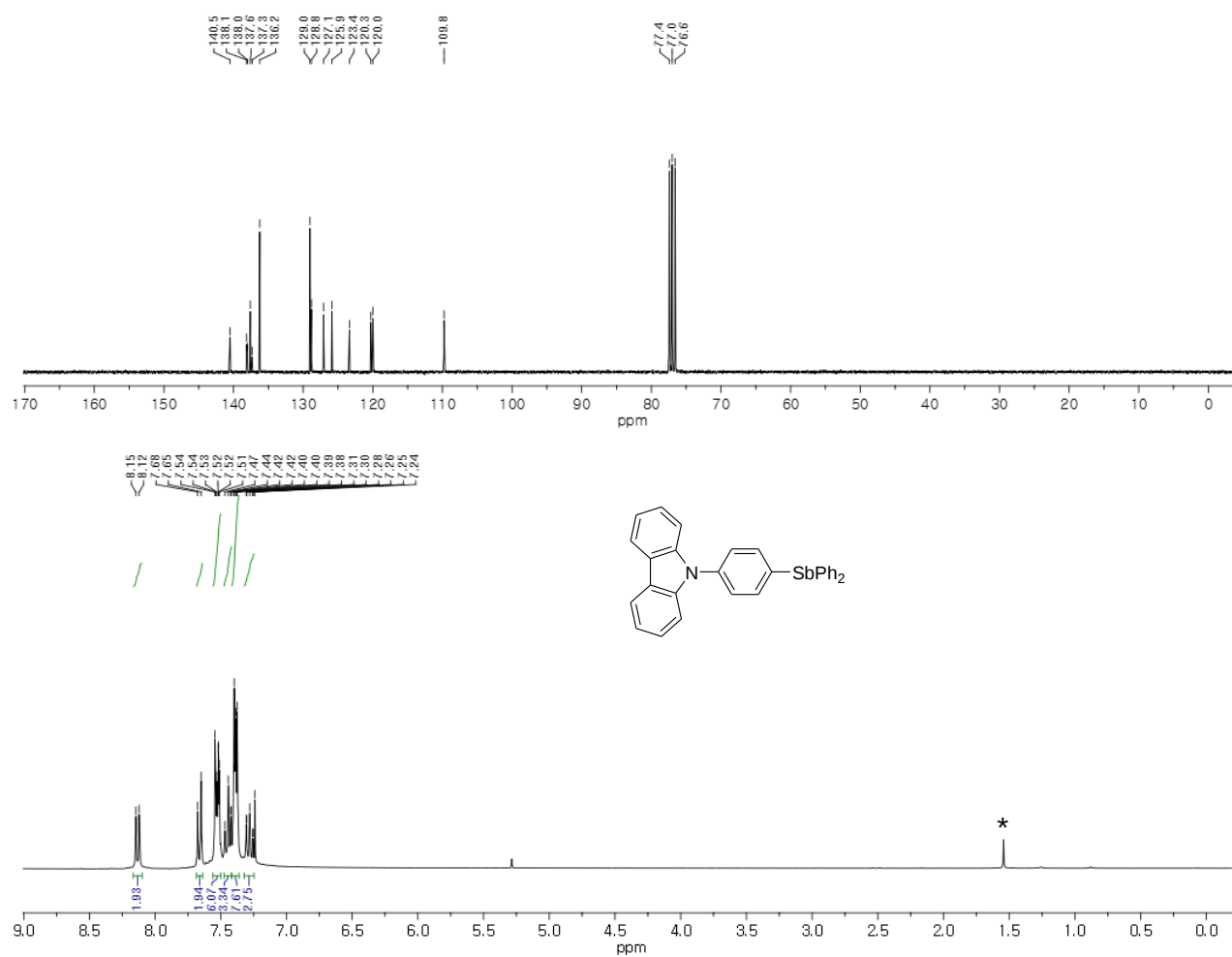


Figure S4. ¹H (bottom) and ¹³C (top) NMR spectra of **2c** (* from residual H₂O in CDCl₃).

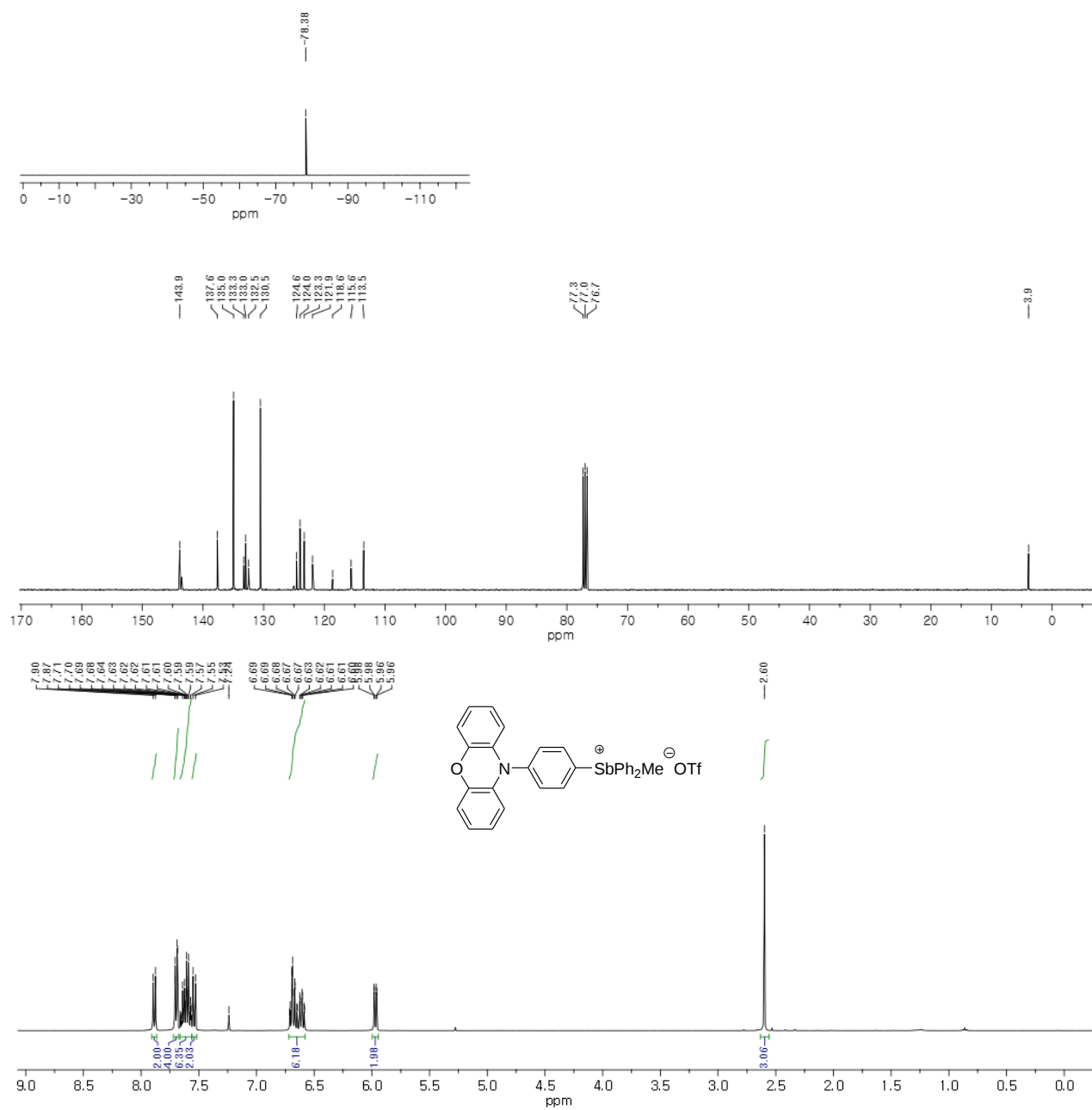


Figure S5. ¹H (bottom), ¹³C (middle), and ¹⁹F (top) NMR spectra of [3a]OTf.

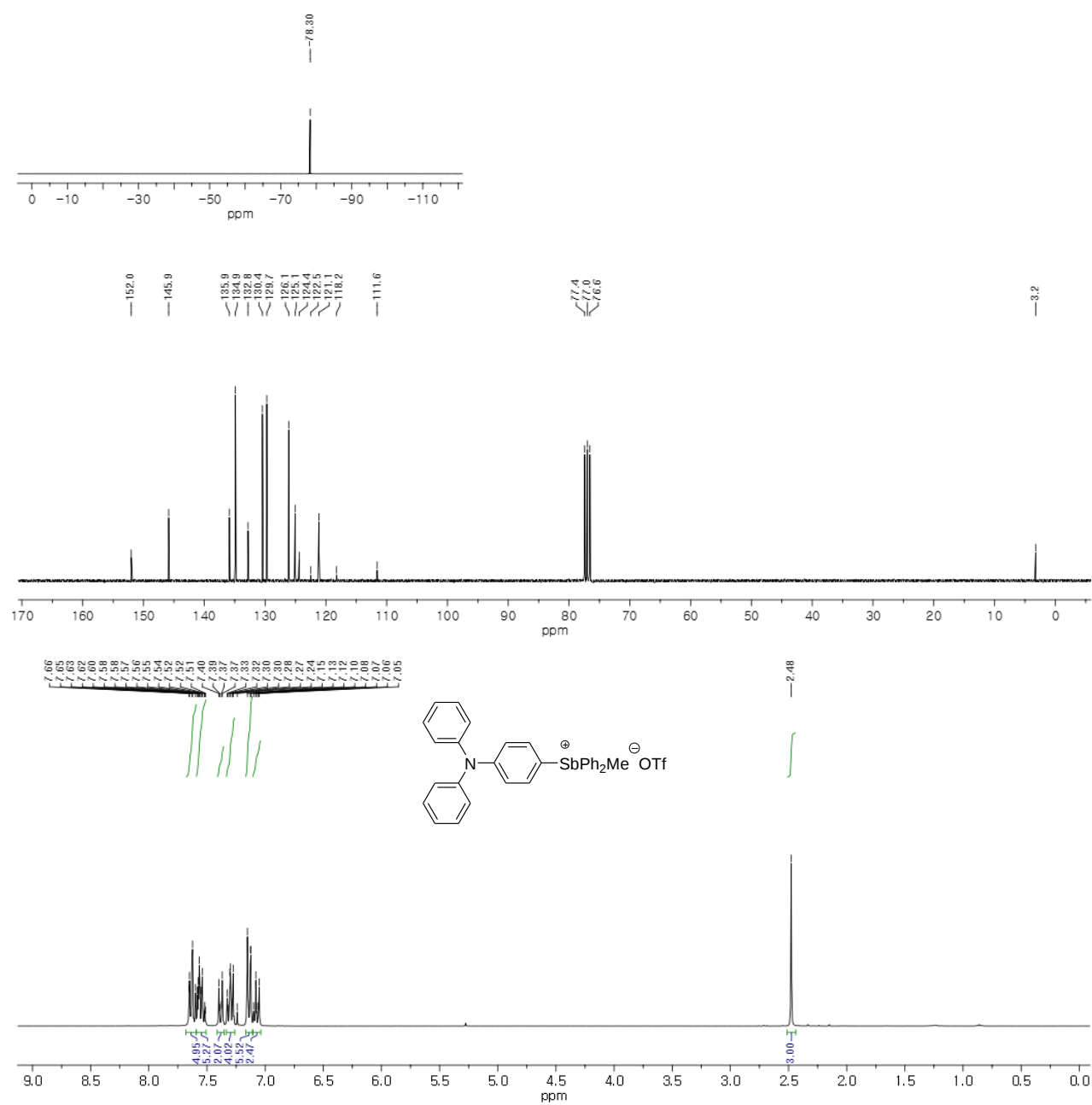


Figure S6. ¹H (bottom), ¹³C (middle), and ¹⁹F (top) NMR spectra of **[3b]OTf**.

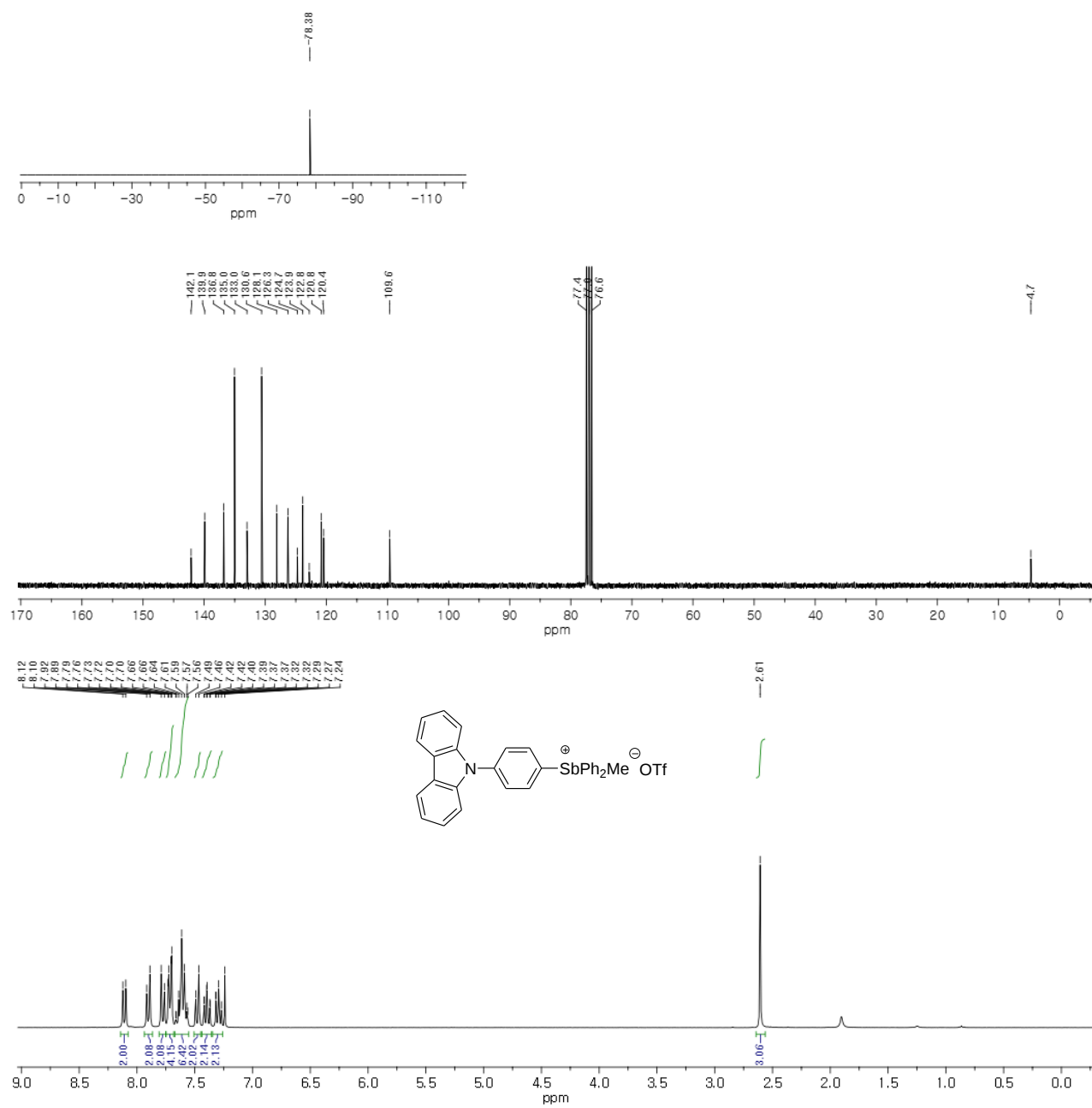


Figure S7. ¹H (bottom), ¹³C (middle), and ¹⁹F (top) NMR spectra of [3c]OTf.

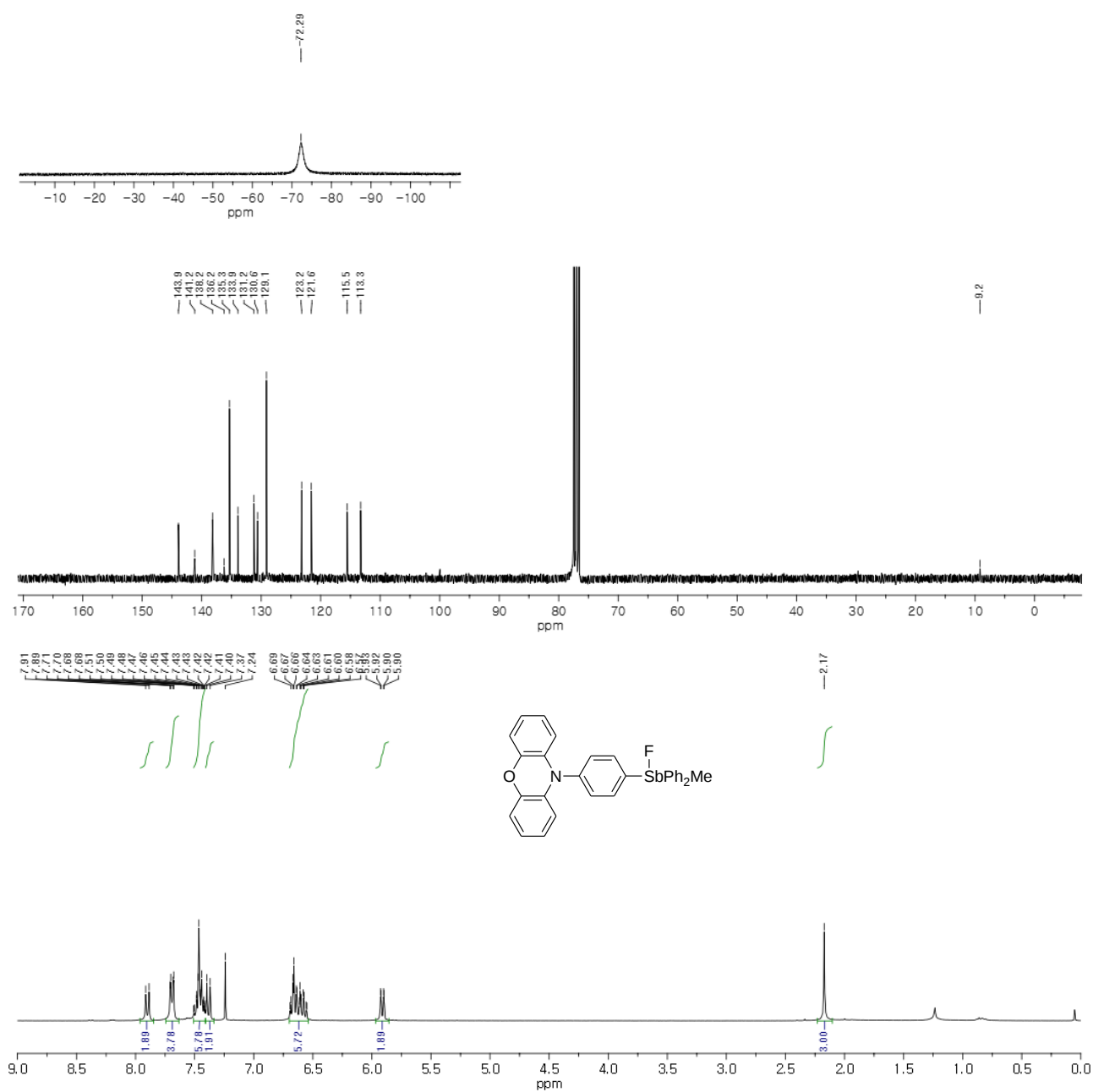


Figure S8. ¹H (bottom), ¹³C (middle), and ¹⁹F (top) NMR spectra of **3a-F**.

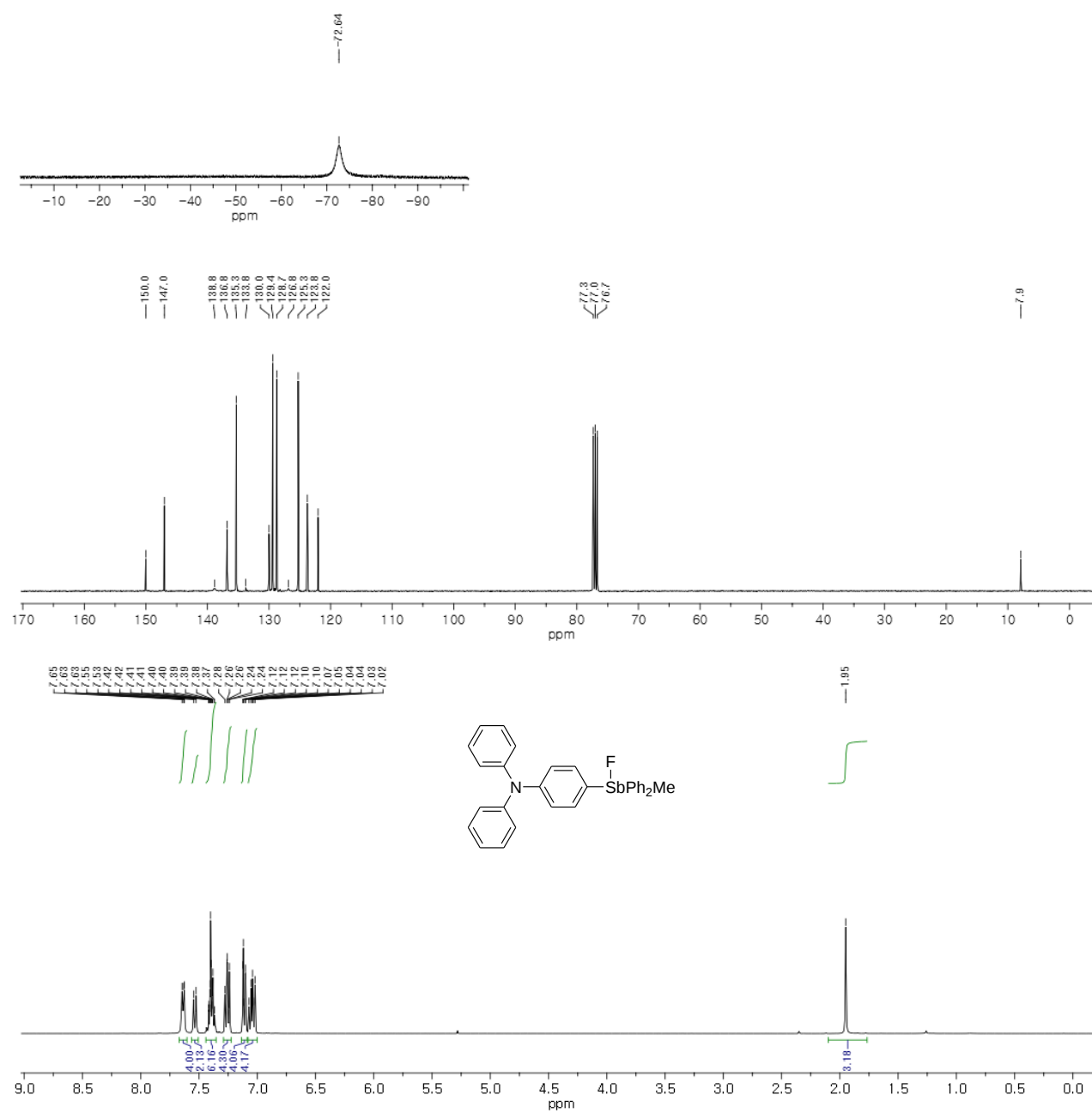


Figure S9. ¹H (bottom), ¹³C (middle), and ¹⁹F (top) NMR spectra of **3b-F**.

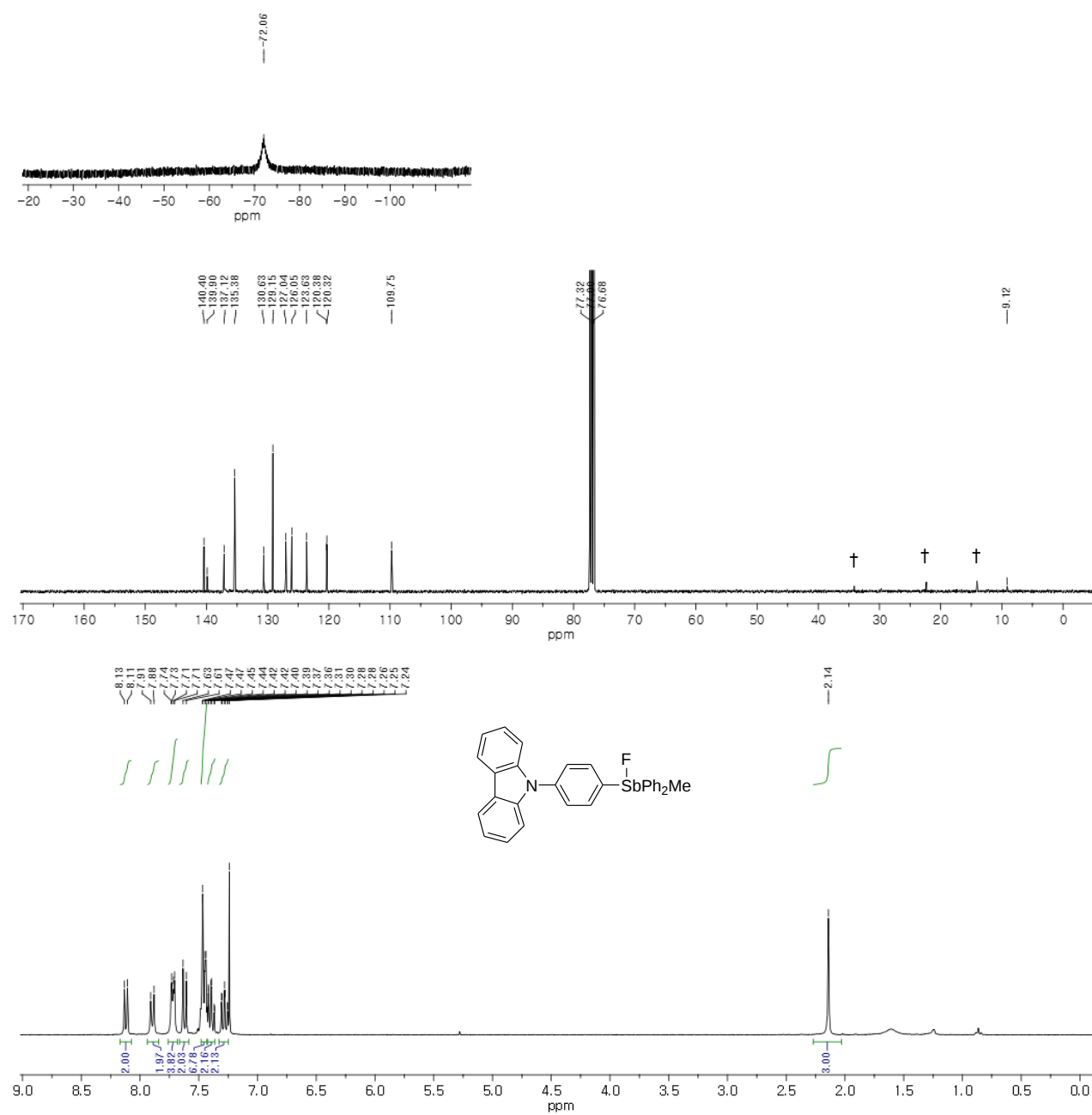


Figure S10. ¹H (bottom), ¹³C (middle), and ¹⁹F (top) NMR spectra of **3c-F**.

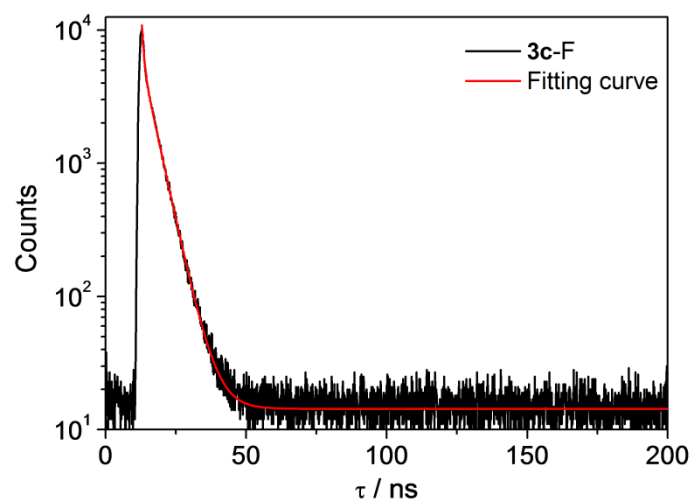


Figure S11. Transient PL decay curve of **3c-F** in MeCN at 298 K ($\lambda_{\text{ex}} = 330$ nm).

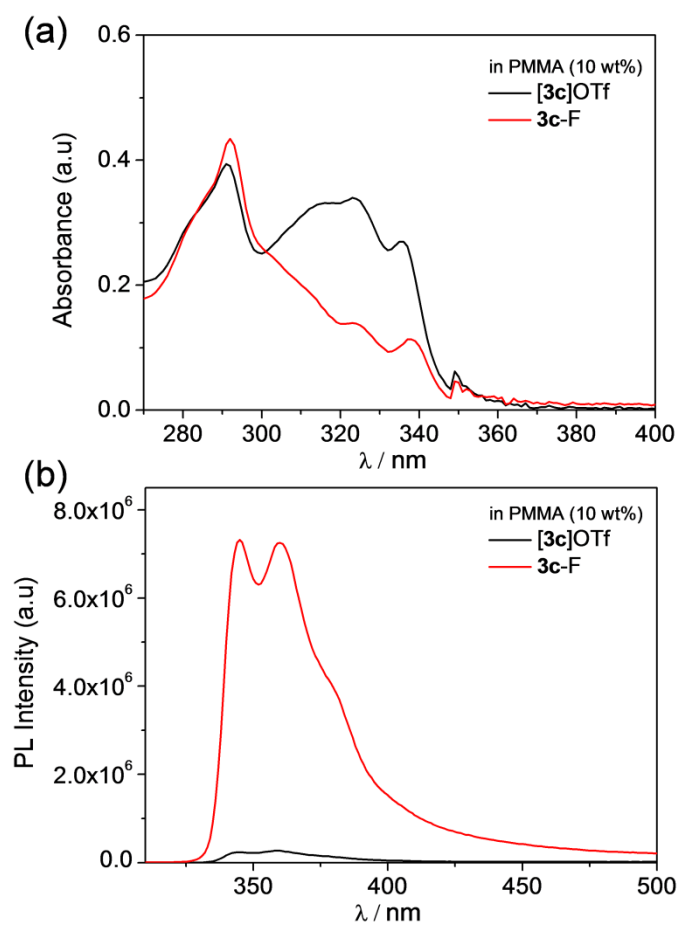


Figure S12. (a) UV/Vis absorption and (b) PL spectra of **[3c]OTf** and **3c-F** in PMMA film (10 wt%).

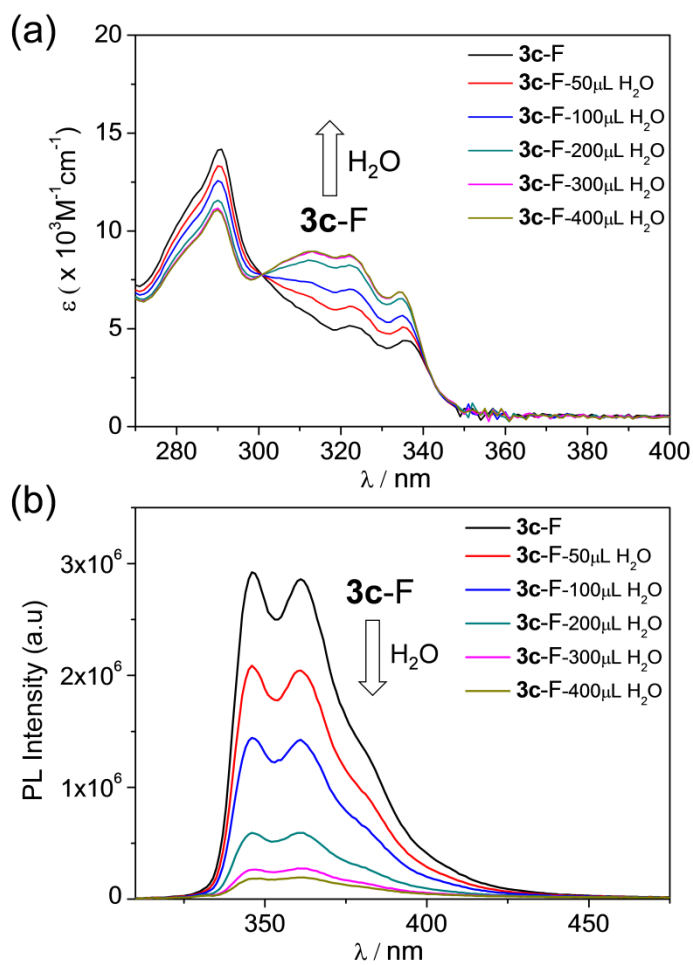


Figure S13. Changes in the (a) absorption and (b) fluorescence of 3c-F in MeCN upon addition of water.

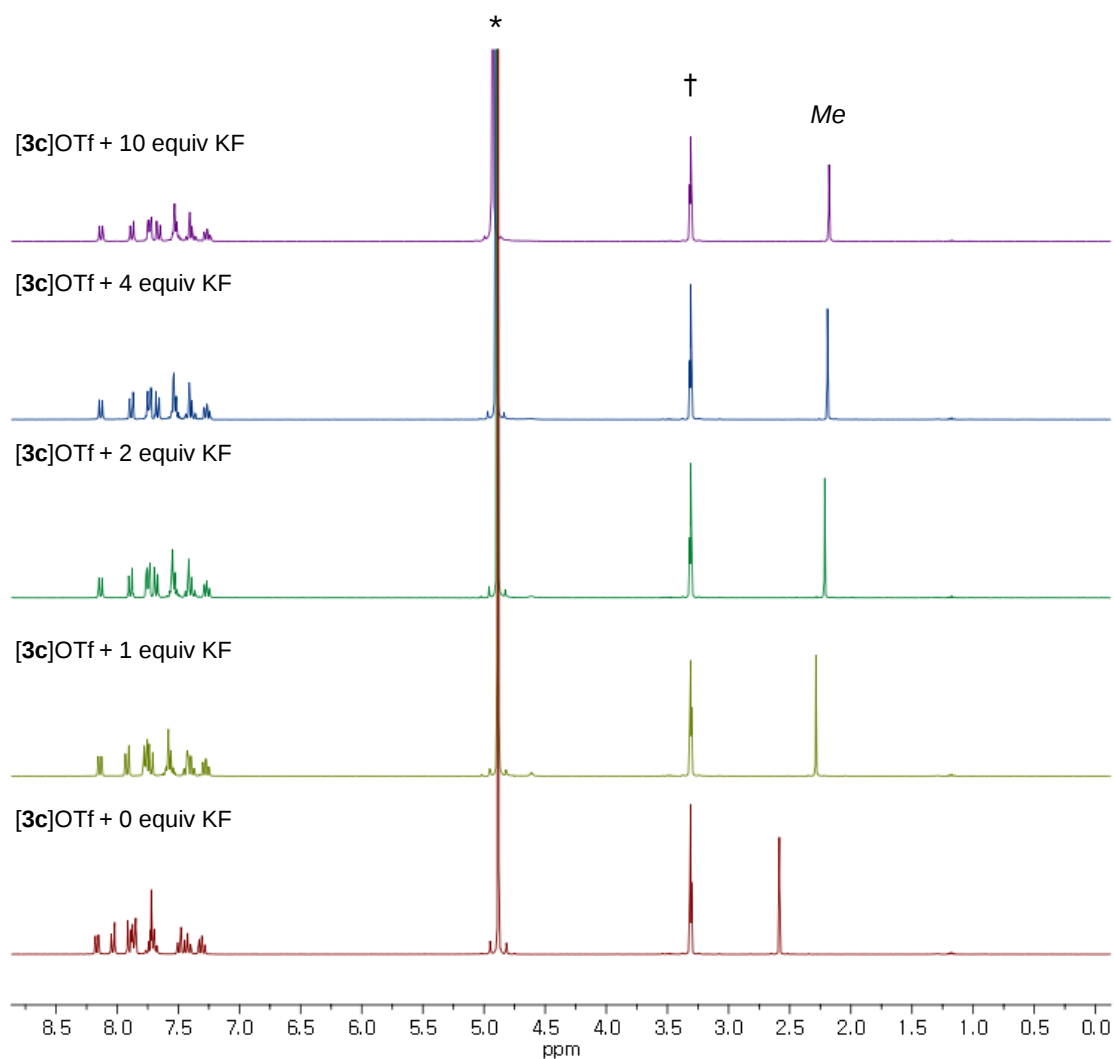


Figure S14. ^1H NMR spectral changes for $[\mathbf{3c}]\text{OTf}$ (0.015 M) upon addition of KF (0–10 equiv) in CD_3OD ($*$ and $\dagger$ from residual H_2O and CD_3OD).

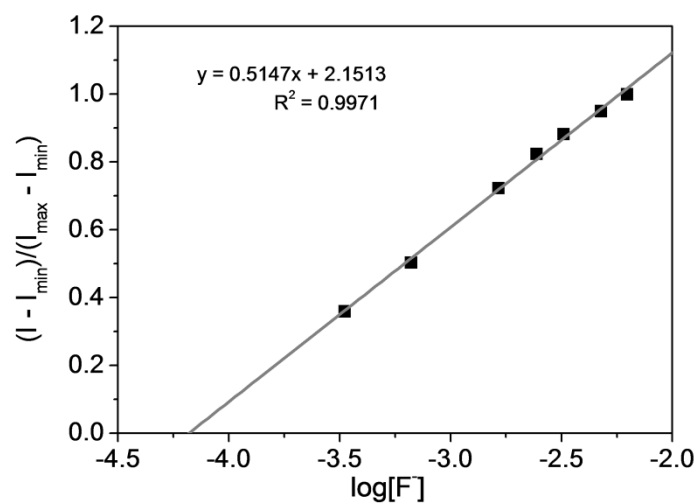


Figure S15. Linear regressions of fluorescence intensities of [3c]OTf titrated with TBAF in MeOH.

DFT Computational Results

Gas Phase Ground State Optimization

Structures for the free $[3c]^+$ and the fluoride-bound form $3c-F$ were first optimized in the gas phase. For $3c-F$, there are three possible geometries: **A**) F trans to carbazole, **B**) F trans to Ph, and **C**) F trans to Me. The crystal structure of Ph_3SbMeF^1 has shown that Ph has a stronger trans-effect than Me, so geometry **C** (F trans to Me) was first ruled out. Optimizations were performed on geometries **A** and **B**, and geometry **A** is 1.3 kcal/mol more stable than geometry **B**, thus geometry **A** (F trans to carbazole) was determined to be the geometry of compound $3c-F$.

The frontier orbitals of the free stibonium and the anion-bound compounds are shown in **Figure S16**. With HOMO localized on the carbazole π orbital and LUMO mostly localized on the Sb-Ph σ^* orbitals, the nonemissive stibonium $[3c]^+$ features a HOMO $\rightarrow$ LUMO charge transfer transition. In the anion-bound form $3c-F$, the HOMO and LUMO are localized in the carbazole π and π^* orbitals, as expected for its fluorescence.

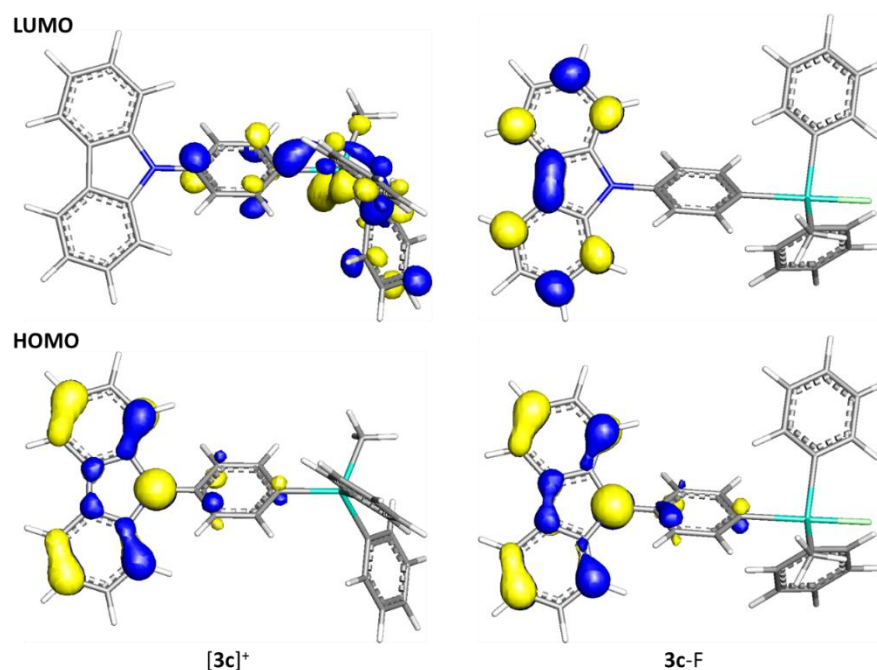


Figure S16. Frontier orbitals of $[3c]^+$ and $3c-F$. Isovalue = 0.05.

Solution Phase Excited State Optimization

The following approach was taken to calculate the solution phase excited state geometry: First, the ground state (S_0) geometry of $[3c]^+$ was optimized with the acetonitrile solvation (PCM) and resulted in a S_0 -optimized geometry (R^{GS}) without imaginary frequencies. Then a single-point TD-DFT calculation was performed with the default non-equilibrium solvation to examine the vertical excitation energy of the first few excited states. The first excited state was confirmed to be a singlet (S_1) with significant oscillation strength ($f = 0.4625$), and has primarily HOMO $\rightarrow$ LUMO transition. Then a TD-DFT geometry optimization was done with equilibrium, linear response solvation to find the minimum energy point of the excited state potential energy surface, resulting in the S_1 -optimized geometry (R^{ES}). Unfortunately, we were not able to carry the vibrational frequencies of the optimized excited structure due to the limitations of our computing resources. Both the vertical excitation (3.98 eV) from the ground state to the excited state, and the vertical emission (3.67 eV) from the relaxed excited state geometry to the ground state, were computed with state-specific equilibrium solvation, as the energy diagram shown

in **Figure S17**. The energy difference from the relaxation of the geometry in the first excited state is 0.06 eV.

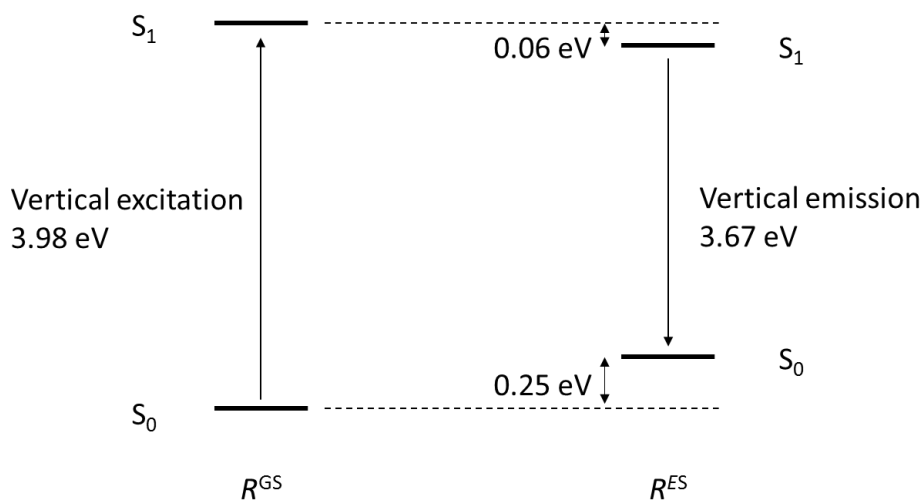


Figure S17. Energies calculated for the S_0 - (R^{GS}) and S_1 - (R^{ES}) optimized ground and excited states of $[3c]^+$.

The frontier orbitals of the S_0 -optimized (R^{GS}) and the S_1 -optimized (R^{ES}) geometries of $[3c]^+$ in solution phase are shown in **Figure S18**. Both geometries feature a tetrahedral antimony center. As in the gas phase, the HOMO of the S_0 -optimized geometry is localized at the carbazole π orbital. However, the LUMO mostly resides on the π^* orbital of the phenylene linker between the carbazole and the stibonium moieties with a small contribution of Sb-Ph σ^* orbitals in the solution phase. Note that LUMO+1 bears a large contribution from Sb-Ph σ^* orbitals. The frontier orbitals of the S_1 -optimized geometry are almost identical to those of the S_0 -optimized geometry, with a shrunk HOMO-LUMO gap as the HOMO is 0.06 eV higher and the LUMO is 0.39 eV lower in energies (**Table S3**). The HOMO $\rightarrow$ LUMO transition being the carbazole π to $[Ph_2MeSb-(p-(C_6H_4))]$ $\pi^*-\sigma^*$ charge transfer suggests that $[3c]^+$ is nonemissive in the solution phase as well. Refer to the main text for additional discussion.

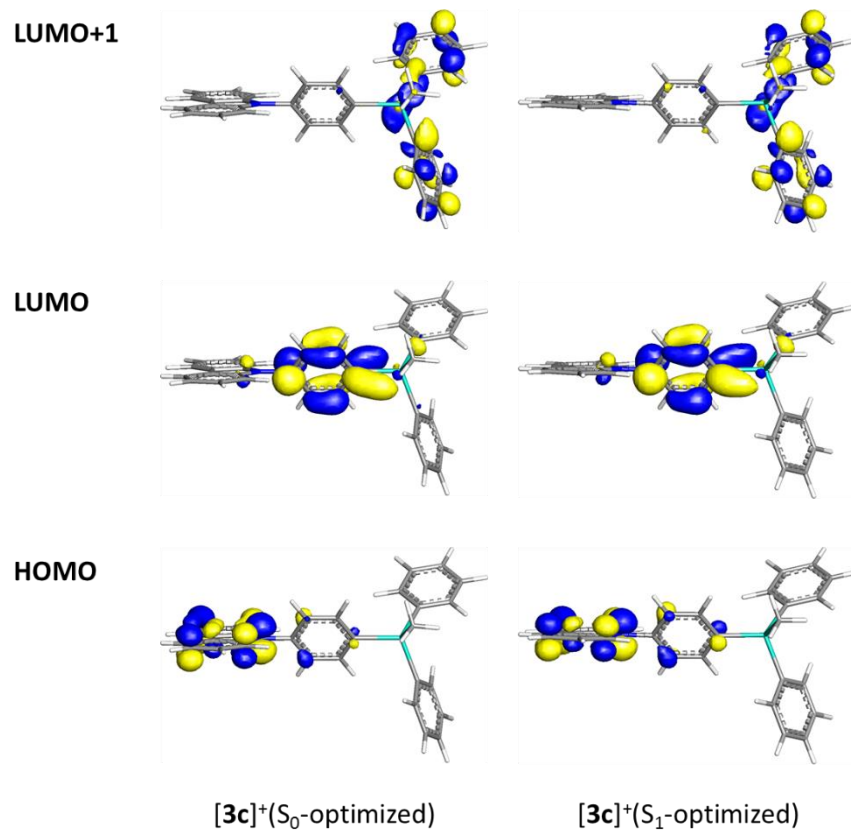


Figure S18. Frontier orbitals of S₀-optimized and S₁-optimized geometries of [3c]⁺. Isovalue = 0.05.

Table S3. Energy (eV) of the frontier orbitals of S₀-optimized and S₁-optimized geometries of [3c]⁺.

	[3c] ⁺ (S ₀ -optimized)	[3c] ⁺ (S ₁ -optimized)	Energy difference due to excited-state relaxation
LUMO+1	-0.36	-0.33	+0.03
LUMO	-0.49	-0.88	-0.39
HOMO	-7.21	-7.15	+0.06

References

- (1) Bordner, J.; Andrews, B. C.; Long, G. G. *Cryst. Struct. Commun.* **1976**, 5, 801.