Supporting Information

Colorimetric and Ratiometric Fluorescent Chemodosimeter for Selective Sensing of Fluoride and Cyanide Ion: Tuning Selectivity in Proton Transfer and C-Si Bond Cleavage

Ajit Kumar Mahapatra*,[a] Saikat Kumar Manna,[a] Bhaskar Pramanik,[b] Kalipada Maiti,[a] Sanchita Mondal,[a] Syed Samim Ali [a] and Debasish Mandal [c]

[a] Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, Howrah-711103, West Bengal, India,

Email: akmahapatra@rediffmail.com, Fax: +913326684564

[b] Indian Institute of Science Education and Research, Kolkata, India.

[c] Institute of Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel.

1. **^{1}H NMR spectrum of LHSi (400 MHz, $CDCl_3$):**

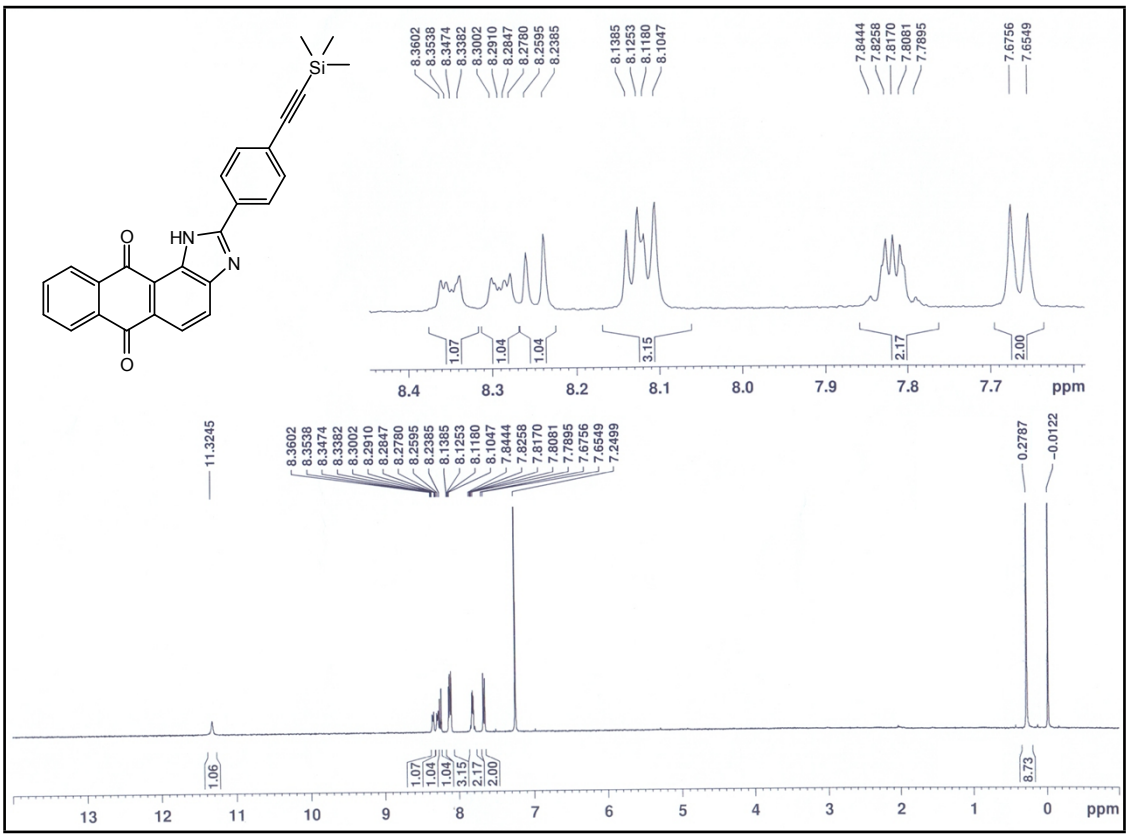

Figure S1: ^{1}H NMR spectrum of **LHSi** in $CDCl_3$ solution.

2. **^{13}C NMR spectrum of LHSi (400 MHz, $CDCl_3$):**

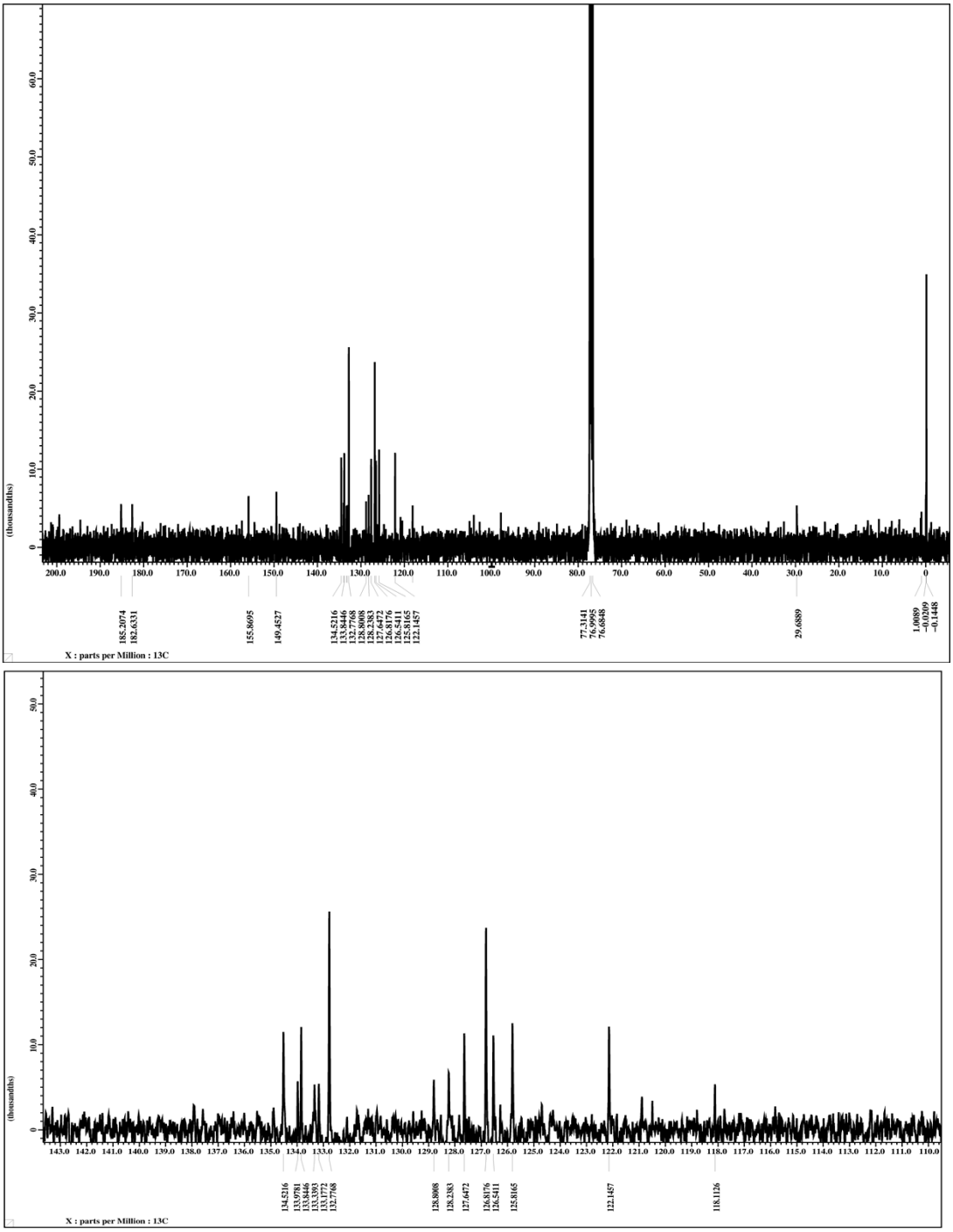

Figure S2: ^{13}C NMR spectrum of **LHSi** in $CDCl_3$ solution.

3. **Mass spectrum of LHSi:**

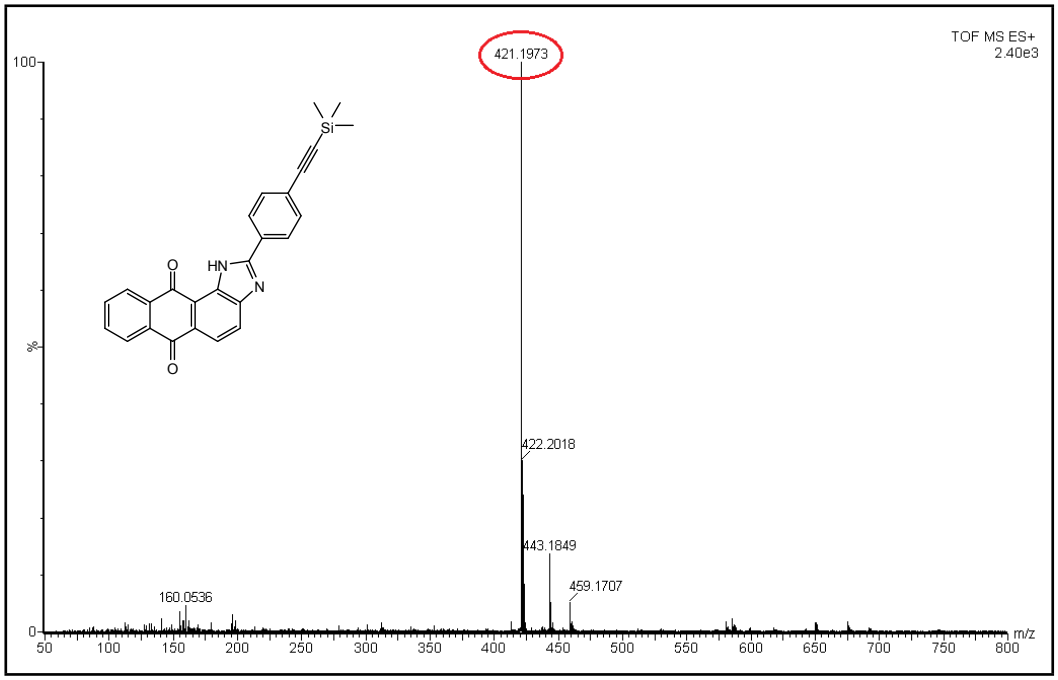

Figure S3: ESI-MS of **LHSi** .

4. UV-Vis and fluorescence spectra of LHSi in presence of TBAOH:

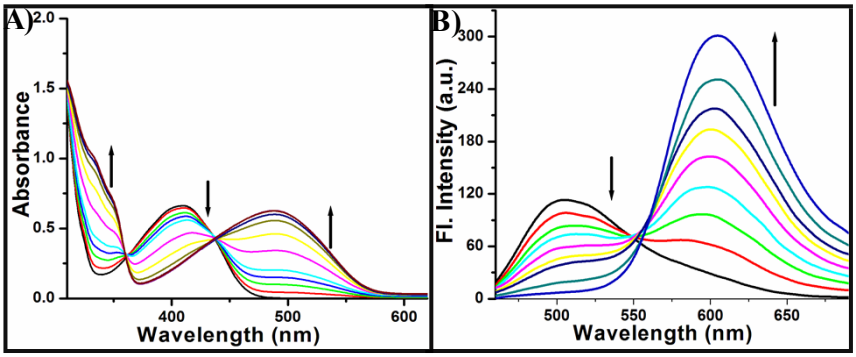

Figure S4: (A) Absorption and (B) fluorescence spectral changes of **LHSi** (c = 4× 10^{-5} M) upon addition of TBAOH in THF solution.

5. ^{1}H NMR titration of LHSi in presence of TBAF:

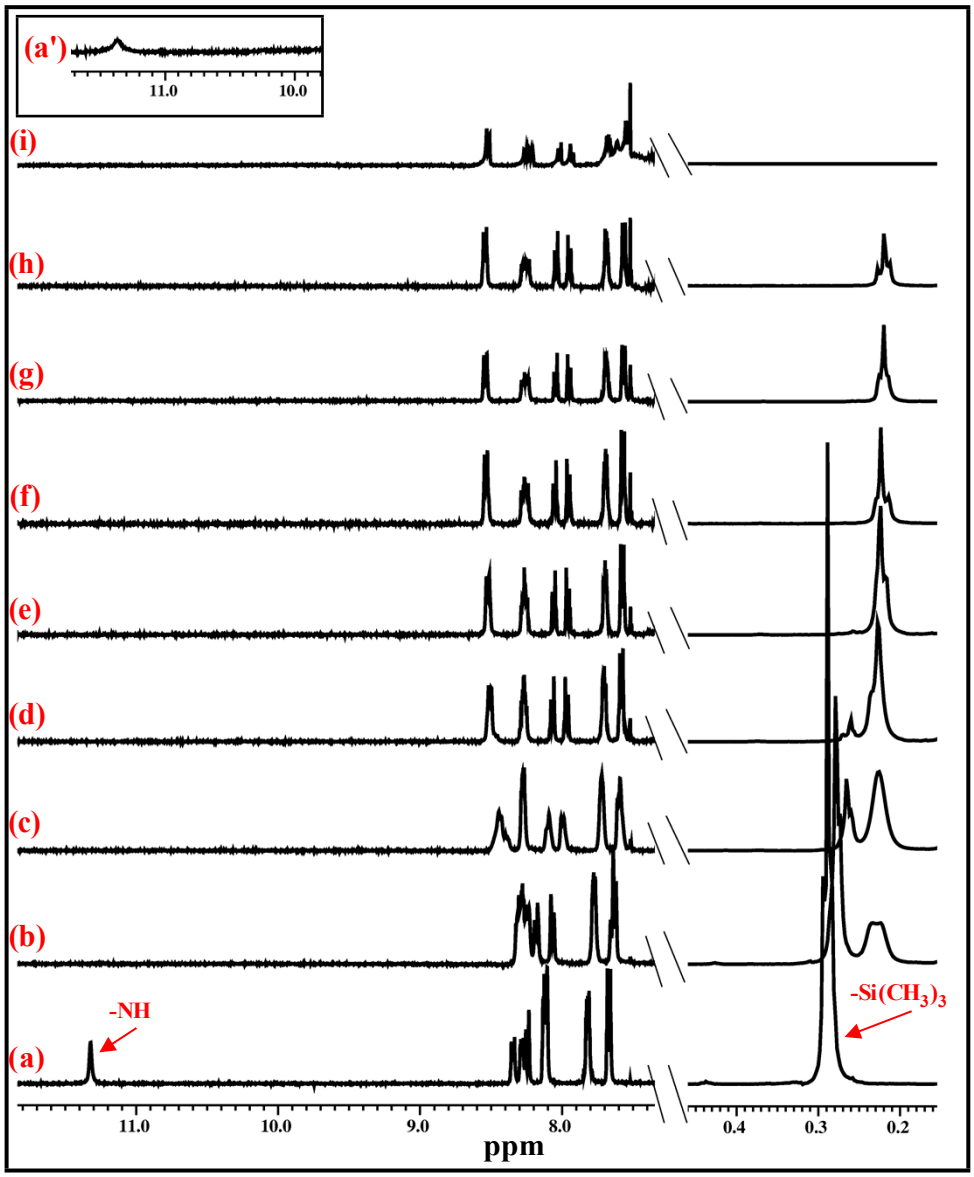

Figure S5: Partial ^{1}H NMR (400 MHz) spectra of **LHSi** in $CDCl_3$ in (a) the absence and the presence of (a') 0.5 (inset) , (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, (f) 3.0, (g) 4.0, (h) 5.0, (i) 10.0 equiv of TBAF.

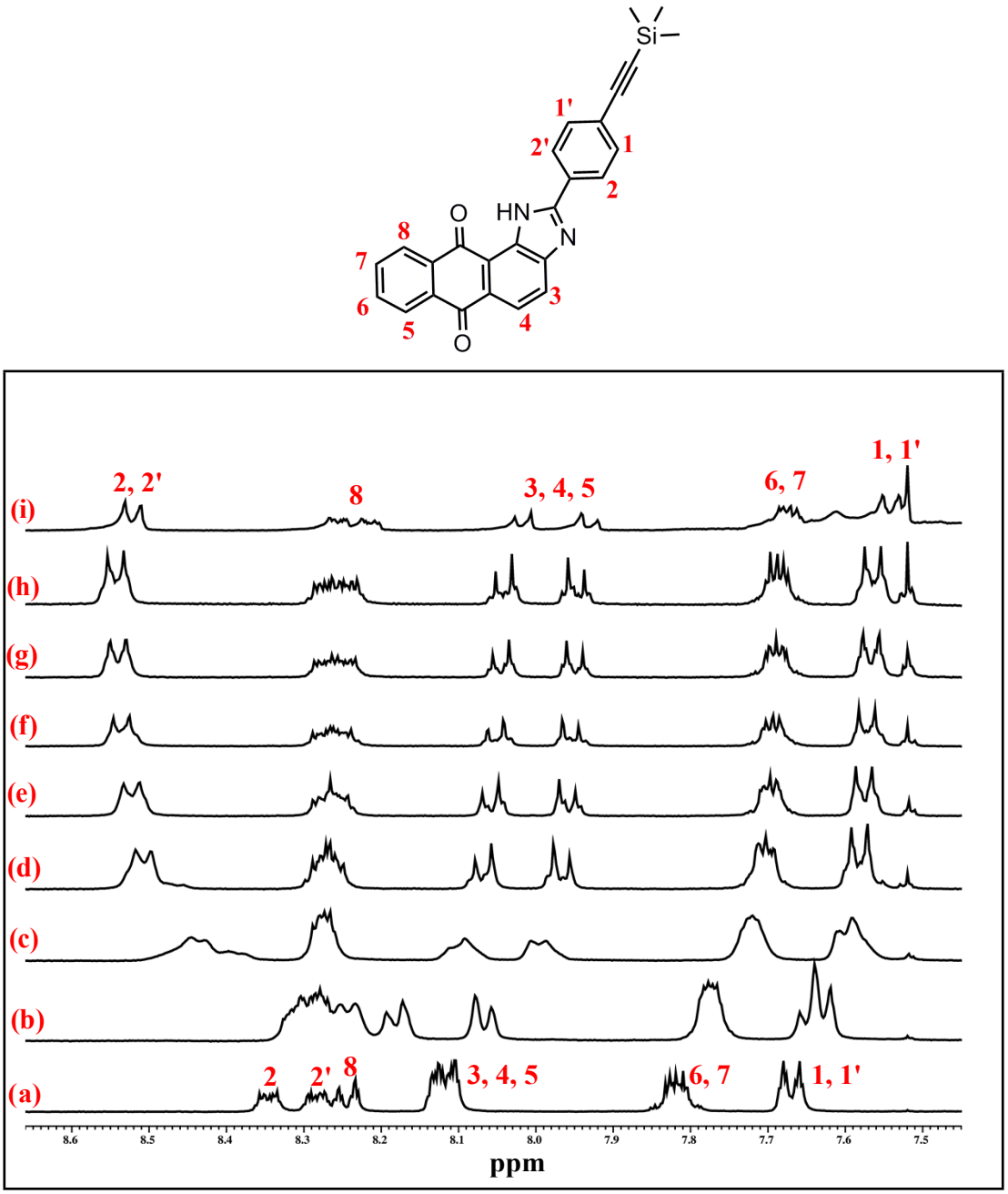

Figure S6: Partial expanded ^{1}H NMR (400 MHz) spectra of aromatic region of **LHSi** in $CDCl_3$ in (a) the absence and the presence of (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, (f) 3.0, (g) 4.0, (h) 5.0, (i) 10.0 equiv of TBAF.

6. ^{1}H NMR titration of LHSi in presence of TBACN:

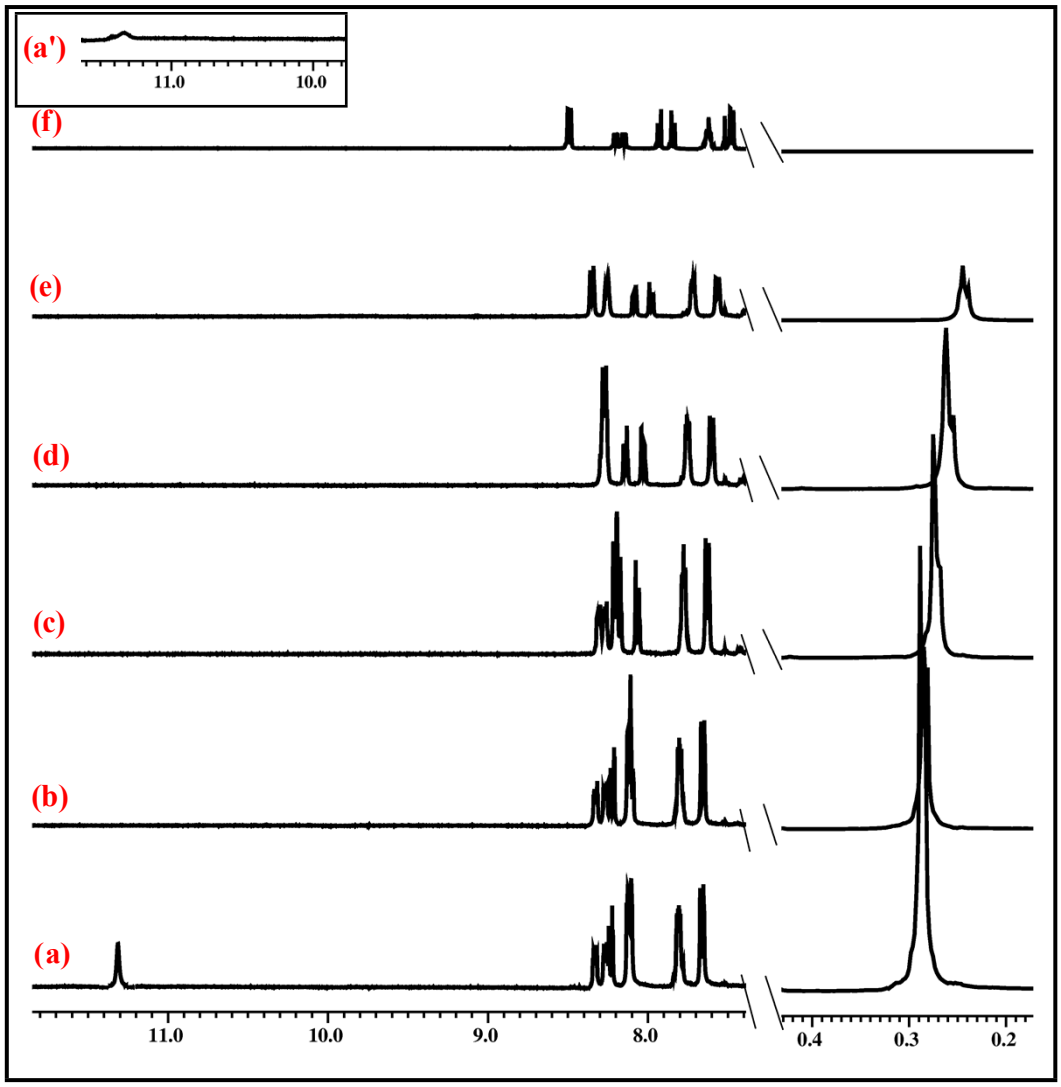

Figure S7: Partial ^{1}H NMR (400 MHz) spectra of **LHSi** in $CDCl_3$ in (a) the absence and the presence of (a') 0.5 (inset), (b) 1.0, (c) 1.5, (d) 2.0, (e) 4.0, (f) 10.0 equiv of TBACN.

7. **Mass spectrum of LHSi + TBAF:**

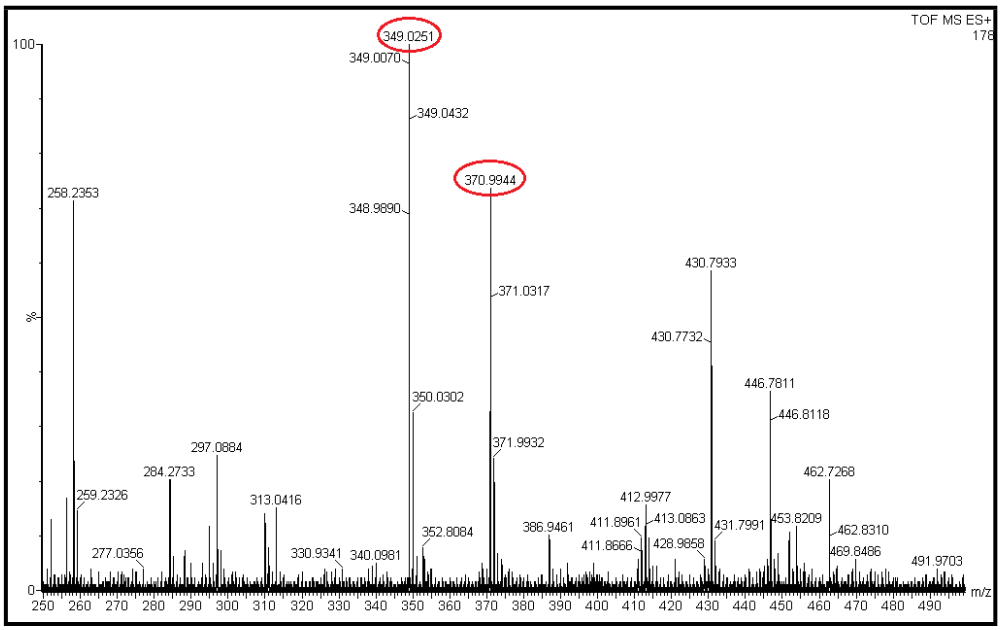

Figure S8: ESI-MS spectral evidence for desilylation of **LHSi** on treatment with TBAF.

8. **Mass spectrum of LHSi + TBACN:**

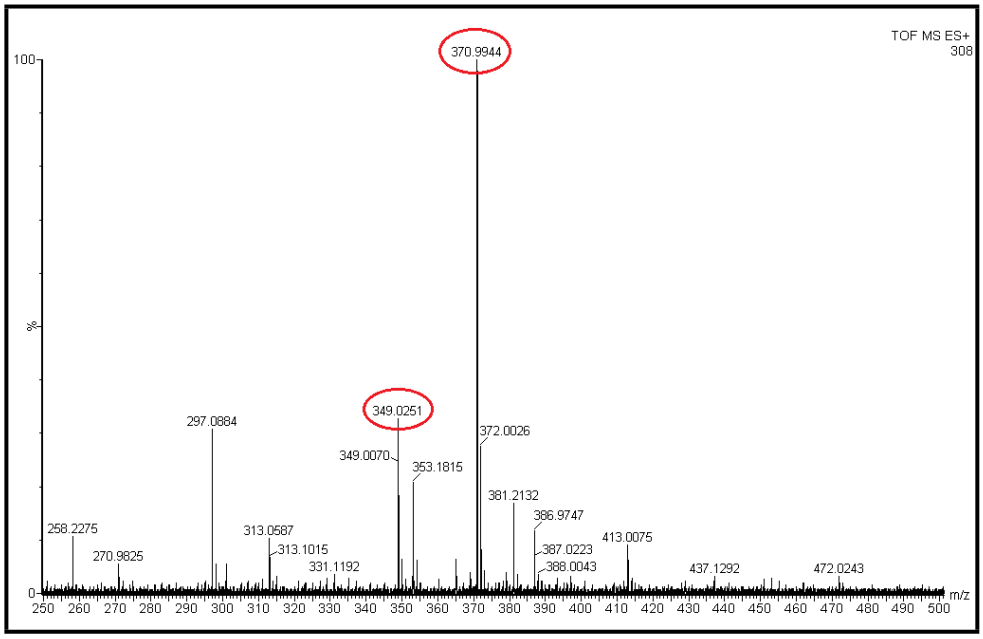

Figure S9: ESI-MS spectral evidence for desilylation of **LHSi** on treatment with TBACN.

9. **Mass spectrum of LHSi on treatment with Hg^{2+} as a countercation with fluoride:**

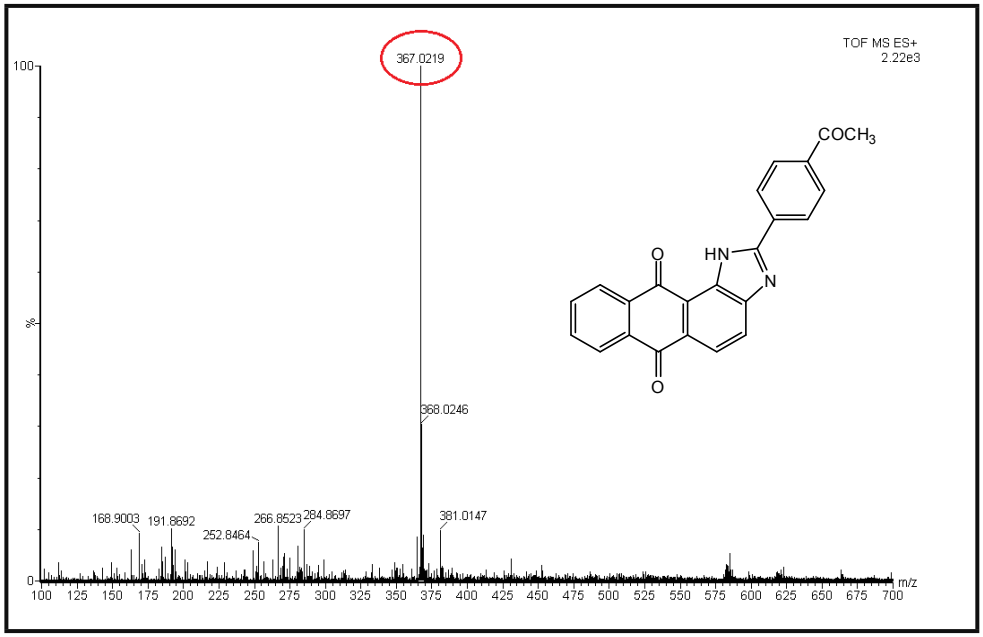

Figure S10: ESI-MS of **LHSi** on treatment with Hg^{2+} as a countercation with fluoride.

10. Computational Study:

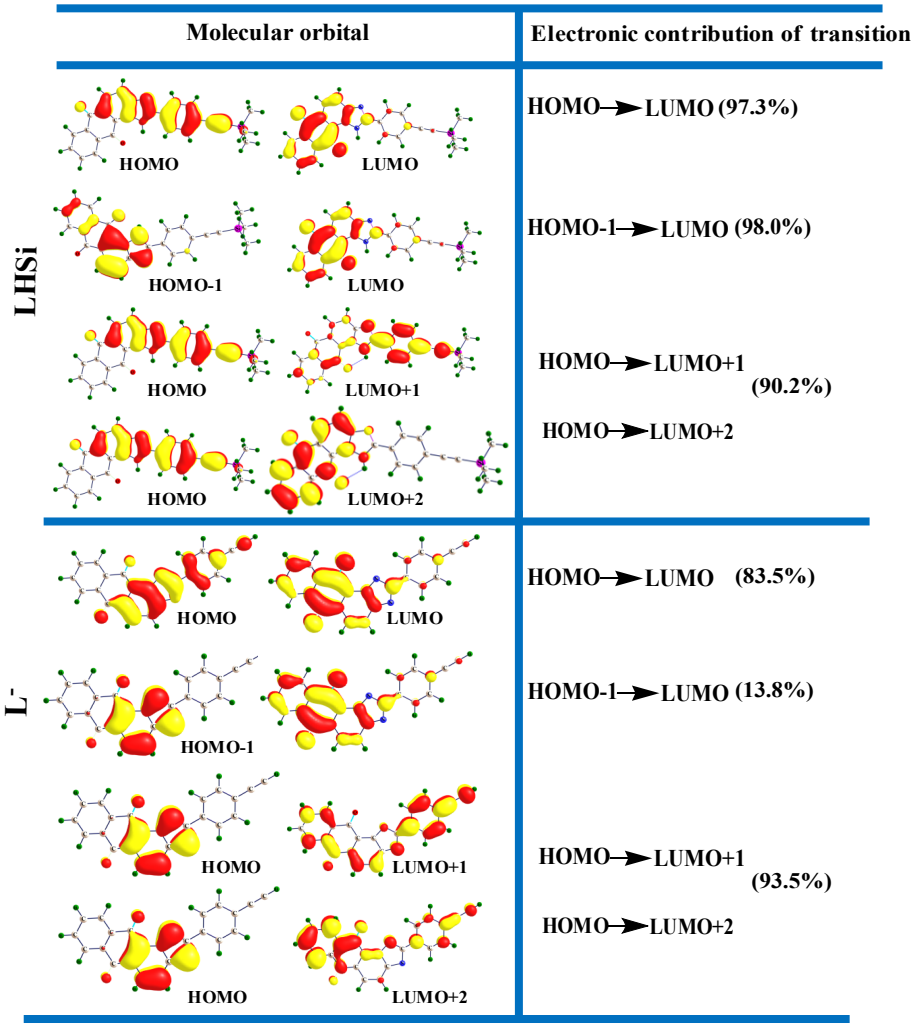

Figure S11. Molecular orbitals and electronic contribution of the relevant excitations of **LHSi** and **L**$^{-}$.

Table S1. Selected electronic excitation energies (eV), oscillator strengths (f), main configurations, and CI Coefficients of the low-lying excited states of **LHSi** and **L**$^{-}$. The data were calculated by TDDFT//B3LYP/6-31+G(*d*) based on the optimized ground state geometries.

Molecules	Electronic Transition	Excitation Energy[a]	f[b]	Composition[c]	(composition) %
LHSi	$S_0 \rightarrow S_1$	2.6362 eV 470 nm	0.3664	H → L	97.3
	$S_0 \rightarrow S_3$	3.1090 eV 398.79 nm	0.9420	H-1 → L	98.0
	$S_0 \rightarrow S_8$	3.8881 eV 318.88 nm	1.0016	H → L + 1 H → L + 2	90.2
	$S_0 \rightarrow S_{16}$	4.6356 eV 267.46 nm	0.2809	H-1 → L + 2 H → L + 3	85.1
L^{-}	$S_0 \rightarrow S_2$	2.3657 eV 524.09 nm	0.3417	H-1 → L H → L	13.8 83.5
	$S_0 \rightarrow S_6$	3.4742 eV 356.87 nm	0.5410	H → L+1 H → L+2	93.5
	$S_0 \rightarrow S_8$	3.6764 eV 337.24 nm	0.2539	H-1 → L+3	87.3

[a] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [b] Oscillator strength. [c] H stands for HOMO and L stands for LUMO.