Supporting Information for

Counter-Ion-Regulated Fluoride Sensing by a Silyl-Protected, Highly Conjugated Molecular Wire: From On-Field Analysis to Quantification of Nerve Gas Simulants

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Experimental Section

1.1 General: All chemicals (reagents, solvents and chemicals) were bought from best-known local chemical suppliers, such as Sigma Aldrich, Spectrochem, Avra, etc and used without further purification. Solvents were distilled and dried before use. FTIR spectra were recorded on a Perkin-Elmer FTIR Spectrum BX system and were reported in wave numbers (cm^{-1}). Furthermore, ^1H nuclear magnetic resonance spectra were recorded on Bruker Avance DRX 400 spectrophotometer operating at 400 MHz for ^1H spectroscopy at 25 °C. The chemical shifts in spectra were reported in parts per million (ppm) and referenced to the residual solvent signal as the internal standard; ^1H NMR spectra (DMSO-*d6* δ 2.50 ppm). Mass spectra were recorded on Micromass Q-TOF Micro TM spectrometer.

1.2 Spectroscopic studies: The UV-Vis spectra were recorded on a JASCO V-650 UV-Vis spectrophotometer, whereas the fluorescence spectra were recorded on Shimadzu RF 6000 Spectrofluorimeter. The slit-width for the fluorescence experiment was kept at 5 nm (excitation) and 5 nm (emission), and the excitation wavelength was set at 390 nm. Sensing was carried out by adding requisite amounts of anions and nerve agents in DMF-H_2O (9:1) medium. Titrations were performed by adding requisite amounts of anions and compound 1 to the quartz cuvette (10 mm) filled with 2 mL of the solvent buffer medium. Subsequently, higher concentrations of anions were added to the probe solution and the FL was recorded.

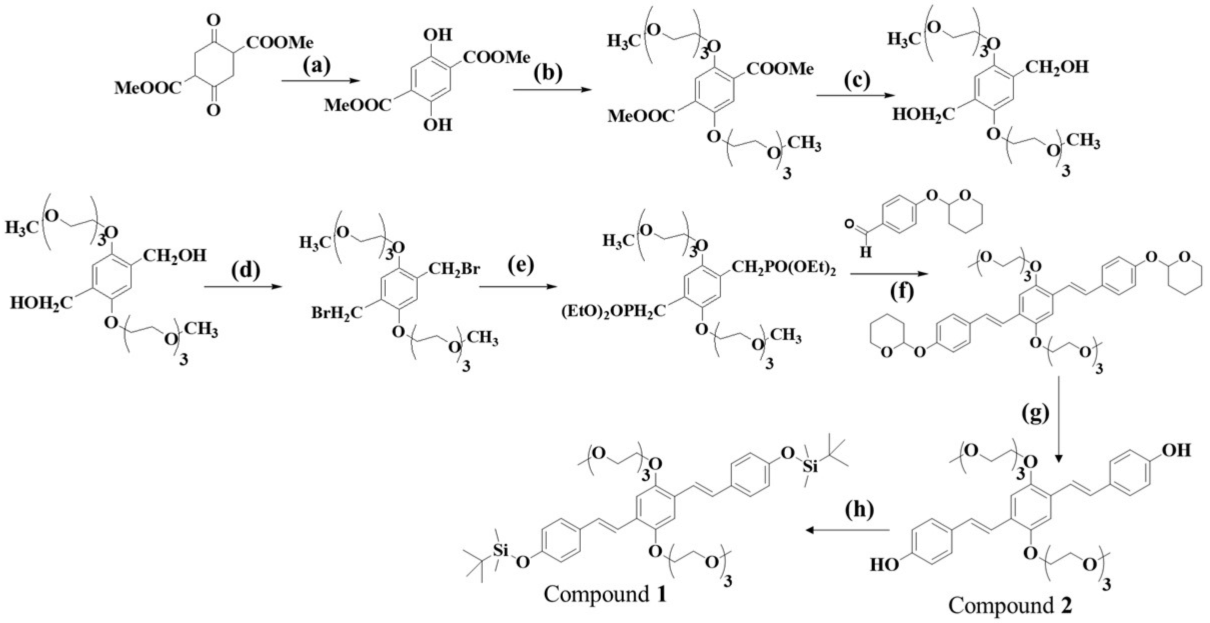
1.3 ^1H NMR Studies: ^1H NMR titration studies of compound 1 (5 mM) were performed with KF and TBAF (2 equiv..) in DMSO-d_6/D_2O (9:1) medium. The spectra were recorded using identical parameters.

1.4 Scanning Electron Microscopy (SEM): Samples for SEM analysis were drop-cast onto a silicon wafer at the desired concentrations, followed by overnight solvent evaporation. The silicon wafer was subsequently sputter-coated using a Leica Ultra Microtome EM UC7. The prepared stubs were then imaged at 1 µm magnification using an FEI Apreo LoVac.

1.5 Dynamic Light Scattering (DLS) Study: Anton Paar Litesizer 500 at 25 °C was used for DLS analysis. The samples were thoroughly mixed to ensure uniform suspension before recording.

Design and Synthesis of Probe Molecule

Synthesis of compound 1



Reagents, conditions and yield: (a) NCS, HOAc, 80 ^{0}C, 1h, 85%;(b) K_2CO_3, Dry DMF, 60 ^{0}C, 48 h, 60%;(c) LAH, Dry THF, 80 ^{0}C, 4h, 70%;(d) PBr_3, Dry THF, Reflux, 2 h, 25%; (e) $P(OEt)_3$, reflux, 2 h, 95% (f) K^{t}BuO, Dry THF, 5 minute, rt, 95% (g) H^+, MeOH/THF, rt, 30 min., 90%; (h) TBDMSCl, Imidazole, DMAP, Dry DCM, rt, 2h, 85%.

To a solution of the dimethyl cyclohexanedione derivative (1.0 equiv.) in HOAc, NCS (1.2 equiv.) was added, and the reaction mixture was stirred at 80 °C for 1 h to afford the aromatic diol (a, 85%). The obtained intermediate was reacted with K_2CO_3 (3.0 equiv.) and PEG methyl ether bromide (2.5 equiv.) in dry DMF at 60 °C for 48 h to yield the dialkoxy derivative (b, 60%).

Reduction with $LiAlH_4$ (3.0 equiv.) in dry THF at 80 °C for 4 h furnished the corresponding diol (c, 70%), which on treatment with PBr_3 (2.5 equiv.) in dry THF under reflux for 2 h gave the dibromide (d, 25%). Subsequent reaction with $P(OEt)_3$ (5.0 equiv.) under reflux for 2 h afforded the bis-phosphonate ester (e, 95%).

The phosphonate intermediate underwent Horner–Wadsworth–Emmons olefination with the 4-((Tetrahydro-2H-pyran-2-yl)oxy)benzaldehyde (2.2 equiv.) in the presence of KOtBu (3.0 equiv.) in dry THF at room temperature for 5 min to yield the conjugated product (f, 95%). Acidic deprotection in MeOH/THF (1:1) at room temperature for 30 min furnished **Compound 2** (g, 90%).

Finally, protection of the phenolic hydroxyl groups was achieved using TBDMSCl (2.5 equiv.), imidazole (3.0 equiv.), and catalytic DMAP in dry DCM at room temperature for 2 h to afford the target **Compound 1** (h, 85%).

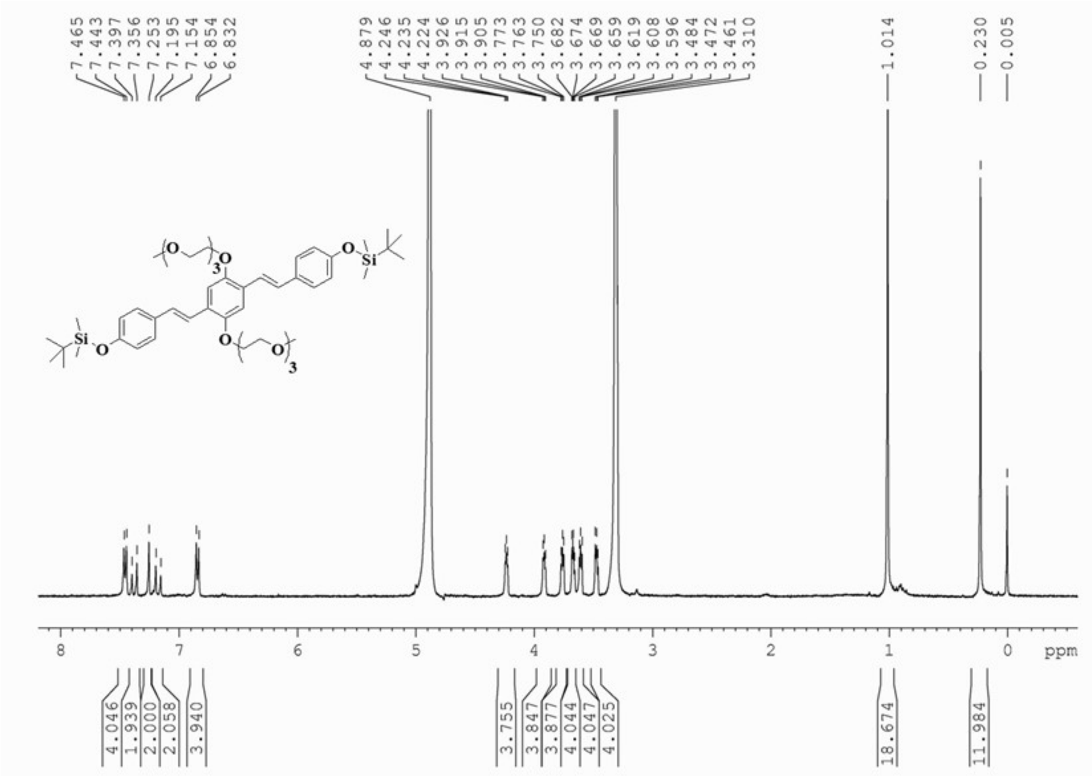


Figure S1. ^{1}H-NMR spectrum of compound 1.

Additional Spectral Data

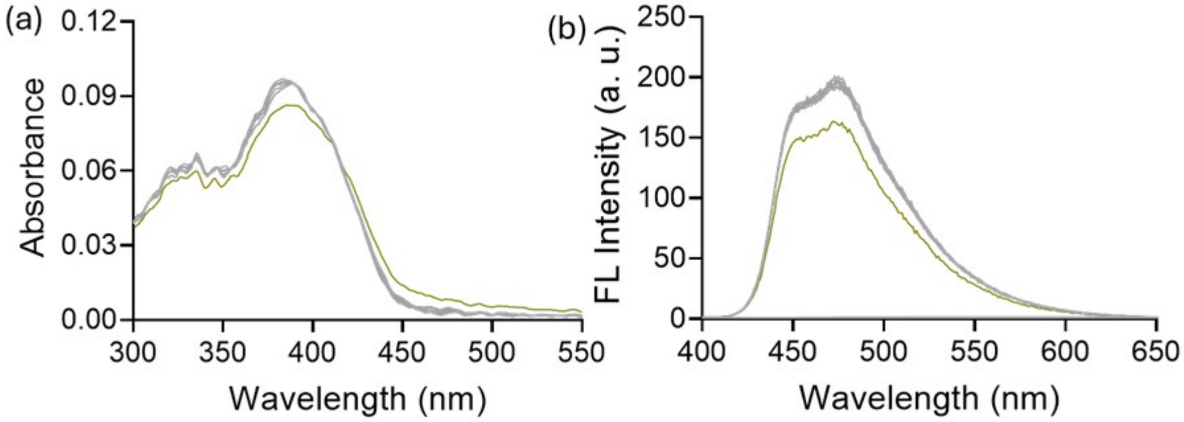


Figure S2. (a) UV-visible spectra of compound 1 (10 µM) with different anions (2 mM) in aqueous medium (pH 7.5 buffer). (b) Fluorescence spectra of compound 1 (10 µM, λex = 390 nm) with different anions (2 mM) in aqueous medium (pH 7.5 buffer).

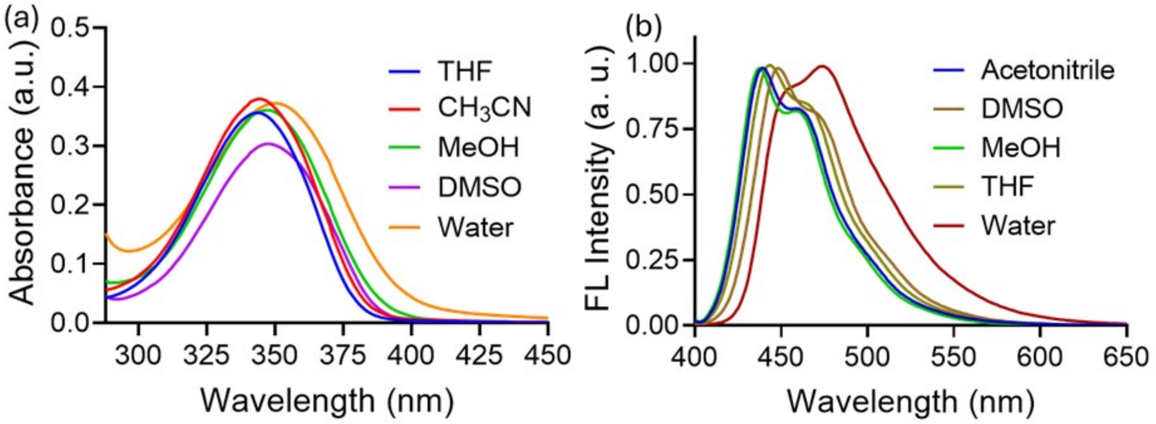


Figure S3. Normalized fluorescence spectra of compound 1 (10 μM, λex = 390 nm) in different organic solvents and in water medium.

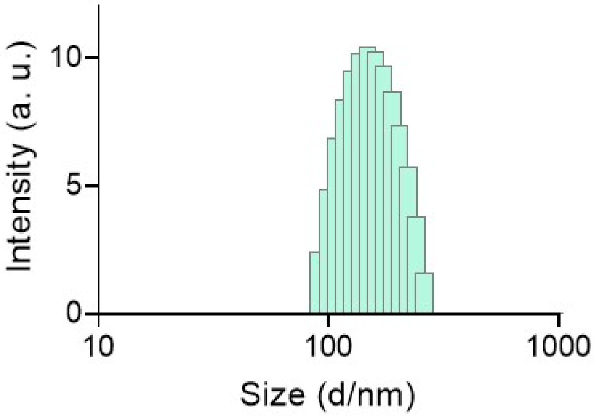


Figure S4. Average hydrodynamic diameters of compound 1 (10 μM) in water medium.

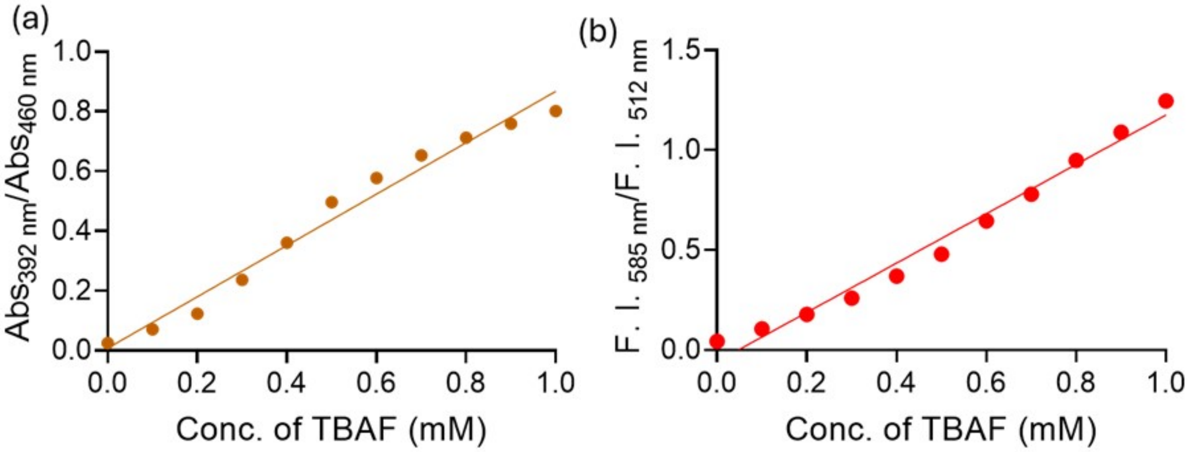


Figure S5. (a) Ratiometric changes in absorbance of compound 1 (10 μM) upon addition of TBAF (0 - 1 mM) in DMF-H_2O (9:1, pH 7.5 buffer) mixture medium. (b) Ratiometric changes in fluorescence of compound 1 (10 μM, λex = 390 nm) upon addition of TBAF (0 - 1 mM) in DMF-H_2O (9:1, pH 7.5 buffer) mixture medium.

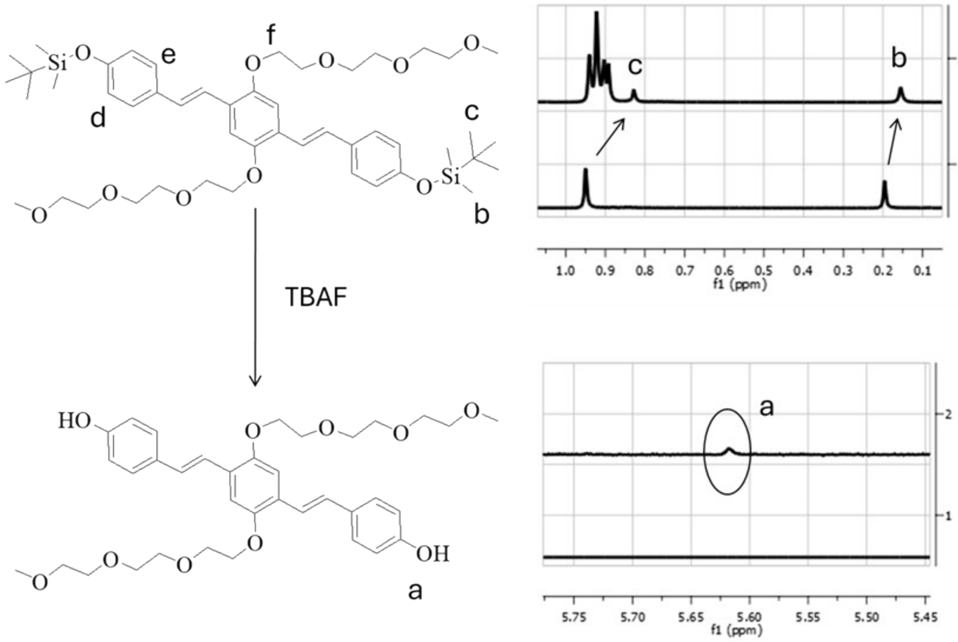


Figure S6. Partial ^{1}H-NMR spectra of compound 1 (5 mM) with TBAF (2 equiv..) in DMSO-d_6/D_2O (9:1) meidum. [inset shows the structure of compound 1 along with the concerned protons]

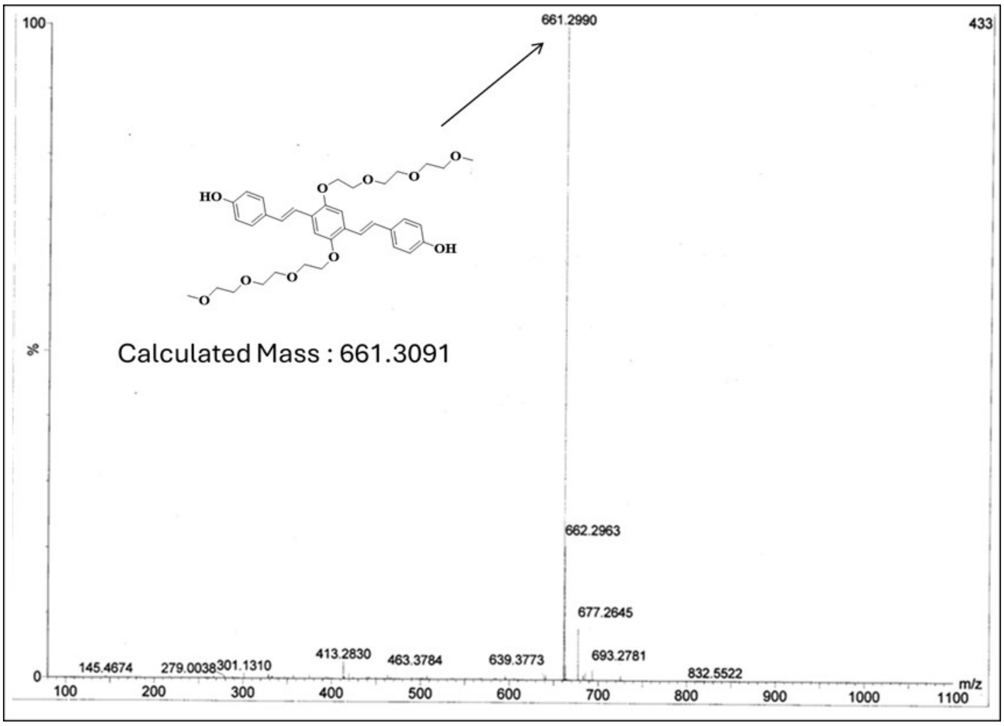


Figure S7. ESI-MS mass spectrum of compound 1 with TBAF showed formation of desilylated product.

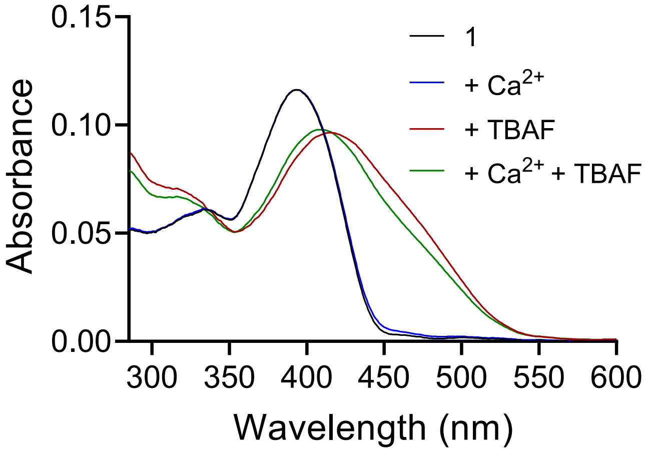


Figure S8. UV-visible spectra of compound 1 (10 µM) with Ca^{2+} ions (1 mM) when pretreated with TBAF (1 mM) in DMF-H_2O (9:1, pH 7.5 buffer).

S. No.	Solvent	Quantum Yield
1	Water	0.0616
2	DMSO	0.2638
3	Methanol	0.202
4	Acetonitrile	0.362
5	THF	0.4986

Table S1. Solvent-dependent fluorescence quantum yields (%) of compound 1

Molecule	ENERGY	HOMO	LUMO	ENERGY GAP	DIPOLE MOMENT
Comp 1 silylated	2575.6326	-0.1720	-0.0510	-0.1209	2.1219
Comp 1 desilylated (OH)	1527.8764	-0.1727	-0.0517	-0.1209	2.0386
Comp 1 desilylated (O^-)	1526.6961	+0.0582	+0.1446	0.0864	5.7809

Table S2. DFT-calculated structural and electronic parameters of the silylated, hydroxy, and phenoxide forms of compound 1, including total energies, HOMO–LUMO energies, energy gaps, and dipole moments.

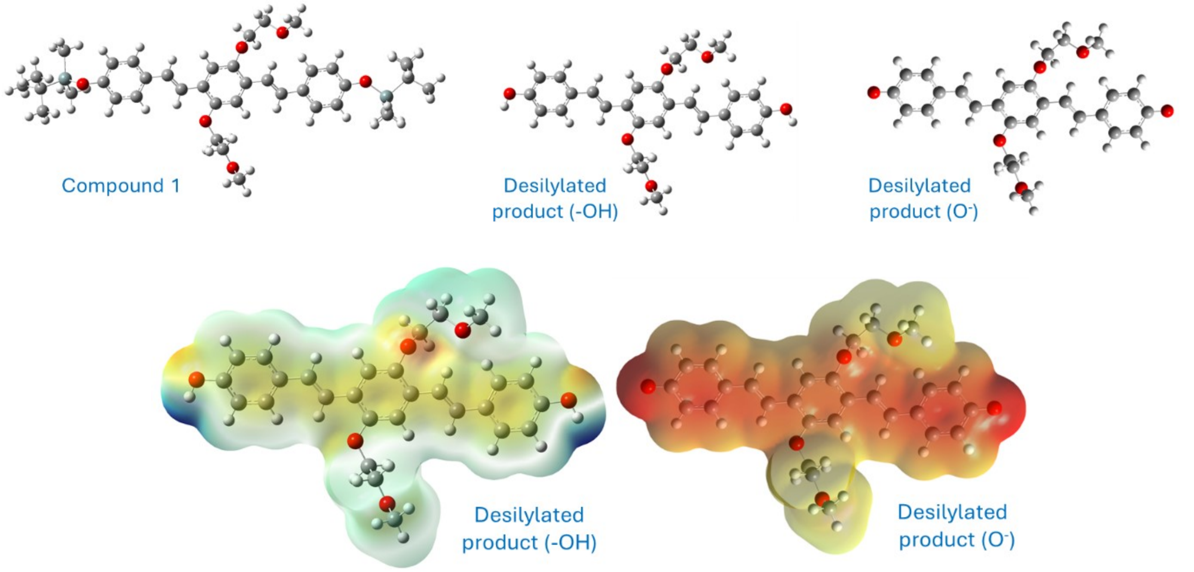


Figure S9. DFT-optimized geometries of compound 1 in its silylated, hydroxy, and phenoxide forms