Electronic Supplementary Information (ESI)

Encumbrance in desilylation triggered fluorogenic detection of fluoride ion – A kinetic approach

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Figure S–23. a) Plot of change in emission intensity (F^o - F) of ADDSi**1** in ACN/Water mixture (1:1) at 447 nm against concentration of fluoride ion **b)** Plot of change in emission intensity (F^o - F) of ADDSi**2** in ACN/Water mixture (1:1) at 447 nm against concentration of fluoride ion.

Figure S-24. Photograph shows the change in emission intensity upon addition different of fluoride ion (TBAF) under UV lamp (365 nm).

Materials and Methods

Preparation of Stock solution of ADDSi1

The stock solution was prepared by dissolving 1.73 mg of ADDSi**1** (0.28 mM) in HPLC grade acetonitrile with a 10 mL standard measuring flask at room temperature. UV-Vis and fluorescence measurements and titration studies were carried out by taking 0.25 mL of ADDSi**1** from this stock and diluted to 5 mL, so that the final concentration was 14 µM.

Preparation of Stock solution of ADDSi2

The stock solution was prepared by dissolving 1.38 mg of ADDSi**2** (0.28 mM) in HPLC grade acetonitrile with a 10 mL standard measuring flask at room temperature. UV-Vis and fluorescence measurements and titration studies were carried out by taking 0.25 mL of ADDSi**1** from this stock and diluted to 5 mL, so that the final concentration was 14 µM.

Preparation of Stock solution of Tetra butyl ammonium fluoride (TBAF) in ACN

The stock solution was prepared by dissolving 110 mg of TBAF in HPLC grade acetonitrile with a 5 mL (84 mM) standard measuring flask at room temperature.

Preparation of Stock solution of Sodium Fluoride (NaF) in water

The stock solution was prepared by dissolving 315 mg of NaF in deionized water in a 10 mL (0.74 M) standard measuring flask at room temperature.

Preparation of various pH buffer solutions (3 -12)

The stock solution of various pH buffer solutions ranging from 3 - 12 was prepared by mixing appropriate volume of acid (0.1 M) and conjugate base (0.1M) necessary for the required pH buffer. Calculation of the ratio of volume required for various pH buffer solutions was done by Henderson-Hasselbalch equation. The obtained stock solution (0.1 M) was further diluted to 10 mM and this was used for the fluorescence studies.

pH buffer solutions (3 - 6) – citrate buffer.

pH buffer solution (7 & 8) – phosphate buffer.

pH buffer solution (9 -12) – bicarbonate buffer.

Parameters Used for Fluorescence Measurements

Studies in ACN

Excitation wavelength = 373 nm; emission wavelength = 435 nm; excitation slit (nm) = 2; emission slit (nm) = 1.

Studies in ACN/Water (1:1)

Excitation wavelength = 380 nm; emission wavelength = 447 nm; excitation slit (nm) = 2; emission slit (nm) =1.

NMR titration studies

NMR titration studies were carried out by taking 11.56 mM of ADDSi**1** and then it was titrated against 0.5 eq, 1 eq and 2 eq of TBAF in DMSO-d_6.

NMR titration studies were carried out by taking 12.36 mM of ADDSi**2** and then it was titrated against 0.5 eq, 1 eq and 2 eq of TBAF in DMSO-d_6.

Detection limit

The detection limit of fluoride ion in acetonitrile and in mixed aqueous solution of ADDSi**1** and ADDSi**2** was calculated from the linear plot of change in emission intensity (F^o - F) against concentration of fluoride ion. To estimate detection limit we used equation $3\sigma/s$, where σ and s represent the standard deviation of blank measurements and the slope obtained from the linear plot of change in emission intensity against concentration of fluoride ion.

Kinetics

Fluoride triggered desilylation kinetics (under pseudo first order condition) were followed by monitoring the change in emission intensity using Fluoromax - 4P spectrofluorimeter in kinetics mode. In acetonitrile, time course of desilylation reaction of ADDSi**1** and ADDSi**2** (14 μM) with different concentrations of F^- were recorded by monitoring the emission intensity change at 435 nm (λ_{ex} = 373 nm), whereas in ACN/water mixture it is monitored at 447 nm (λ_{ex} = 380 nm). These pseudo first order decay kinetics were fitted by applying Guggenheim's method. The plot of **ln (I_f - I_0 / I_f - I)** Vs **time** generates a straight line and the slope of this line is the pseudo first order rate constant (where $\mathbf{I_0}$ is the intensity at zero

time t, $\mathbf{I_f}$ is the final intensity, **I** is the intensity at time t), which is a function of concentration of fluoride ion.

In acetonitrile, the plot between pseudo first order rate constant at different concentrations of fluoride ion does not generates a straight line, but a plot between ln (k_{obs}) Vs ln [F^-] produces a straight line with the slope corresponding to the order of the reaction and the intercept is the third rate constant. But in case of ACN/Water mixture the plot between k_{obs} Vs [F^-] does produces a straight line, and the slope of the line is the second order rate constant.

Detection of Fluoride ion in toothpaste

Soluble fluoride content in three commercially available toothpastes and one mouth wash were validated using the fluorescent probe ADDSi2. Tooth paste **A** (257.9 mg), Tooth paste **B** (299.5 mg), Tooth paste C (283.1 mg) and 1g of mouth wash were weighed and the samples were dispersed in 25mL of water. The resulting turbid solution was stirred for 15 min and then it was centrifuged at 4000 rpm for 15 min. After centrifuge, 0.5 mL of supernatant solution was taken from each test sample and it was titrated against ADDSi**2** solution. The extent of quenching for each samples were fitted to a calibration curve (produced from standard NaF solution) and the amount of fluoride in toothpastes **A**, **B**, **C** and mouth wash were quantitatively determined.

Dimedone, 4-hydroxybenzaldehyde, tert-butyl(chloro)diphenylsilane, tert-butyldimethylsilyl chloride, Sodium Fluoide and all anions as tetrabutylammonium salts, were purchased from Sigma Aldrich Chemicals Pvt. Ltd., and were used as received. Solvents used for the photophysical studies were of HPLC grade, purchased from Qualigens India Ltd. Analytical grade solvents were used for the synthesis and purification purpose.

IR spectra were recorded on BRUKER FTIR-VERTEX 70 spectrometer. ^1H and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz instrument. The residual solvent peaks were used as internal standards. Chemical shifts are reported in ppm and coupling constants ($J_{X\text{-}X'}$) are reported in Hz. Bruker Maxis ESI-TOF mass analyzer type was used for the HRMS measurements. Absorption spectra were recorded using Varian Cary Bio 100 UV-Vis spectrophotometer. Fluorescence spectral measurements were carried out using Horiba-Jobin

Yvon Fluoromax-4P fluorescence spectrometer. Fluorescence quantum yields were obtained from the corrected fluorescence spectra using the expression,

$$\Phi_f = (A_s/A_r)\ (a_r/a_s)\ (n_s/n_r)\ x\ 0.546$$

where A_s and A_r are the area under the corrected fluorescence spectrum, a_s and a_r are the absorbance at the wavelength of excitation (366 nm), n_s and n_r are the refractive indices of the solvent for the sample and reference respectively. Quinine sulphate in 0.1 N sulphuric acid was used as the reference (Φ_f of quinine sulphate is 0.546). The fluorescence decay measurements of dyes used in the present study were recorded using IBH **t**ime **c**orrelated **s**ingle **p**hoton **c**ounting spectrometer (TCSPC), with micro channel plate photomultiplier tube (MCP-PMT) as detector and femtosecond laser as the excitation source.

Synthesis of ADDSi1 & ADDSi2

2,2'-((4-hydroxyphenyl)methylene)bis(5,5-dimethylcyclohexane-1,3-dione)

To a solution of dimedone (2.0 g, 14.26 mmol) in aqueous methanol, 4-hydroxybenzaldehyde was added (0.87 g, 7.13 mmol) and the reaction mixture was warmed until the solution became cloudy. Then the reaction mixture was diluted with water (250 mL) the solid obtained was filtered, dried and recrystallized using methanol. (Yield : 90%) (m.p. above 200^oC)

9-(4-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione.

A mixture of tetraketone (1.0 g, 2.6 mmol) and methyl amine (0.48 g, 15.6 mmol) in acetic acid (20 mL) was kept under reflux for 8 hours. Then the reaction mixture was cooled and poured over crushed ice. The solid obtained was filtered and dried. The compound obtained was purified by silica gel column chromatography and eluted with $CHCl_3$: MeOH (96:4, v/v) to get the pure ADDOH.(83%) (m.p. above 250^oC). IR (KBr): 3267.08 (br, -OH), 2960.59 & 2869.74 (s, aromatic CH) 1629.25, (s, C=O), 1370.77 (s, -C=C-) cm^{-1}. ^1H NMR : 400MHz, DMSO-d_6: δ ppm; 0.94 and 0.99 (2s, 12H, gem- dimethyl); 2.06-2.15 (ABq, 4H, methylene proton); 2.38-2.77 (2d, 4H, J=22Hz, methylene proton); 3.25 (s, 3H, N-CH_3); 4.91(s, 1H, C_9-H) 6.50 - 6.53(d, 2H, J=10.5Hz, Ar-H); 6.85-6.87 (d, 2H, J=10.5Hz, Ar-H); 9.00(s, 1H, O-H). ^{13}C NMR: 100 MHz,

DMSO-d6; δ ppm; 28.22, 28.82, 30.16, 32.61, 33.69, 39.62, 50.04, 113.69, 114.96, 128.44, 137.11, 152.73, 155.61, 195.28.

9-(4-(tert-butyldiphenylsilyloxy)phenyl)-3,3,6,6,10-pentamethyl-3,4,6,7,9,10-hexa hydro acridine-1,8(2H,5H)-dione (ADDSi**1).**

ADDOH (400 mg, 1.05 mmol) and t-butyldiphenylchlorosilane (800 mg, 3.16 mmol) were dissolved in 20 mL of pyridine and the resulting solution was kept at 50^{o}C for 12 hours. Then the reaction mixture was poured into 30 mL of 6% HCl in an ice bath and the resulting solution was extracted with DCM (3 × 15 mL). The combined organic layer was dried over sodium sulphate and evaporated under reduced pressure. Then the crude product was purified by silica gel (100–200 mesh) column chromatography ($CHCl_3$–MeOH 98:2) to yield a yellow solid (Yiled: 80%).(m.p. above 250^{o}C). ^{1}H NMR : 400 MHz, DMSO-d_6: δ ppm; 0.81 and 0.90 (2s, 12H, gem – dimethyl proton); 0.92 (s, 9H, t-butyl proton); 1.97 – 2.06 (ABq, 4H, methylene proton); 2.28 - 2.32 (d, 2H, J=17.6 Hz, methylene proton); 2.63 – 2.67 (d, 2H, J=17.2Hz); 3.13 (s, 3H, N-CH3); 4.84 (s, 1H, C9-H) 6.43 - 6.45 (d, 2H, J=8.4 Hz, Ar-H); 6.75-6.77 (d, 2H, J=8 Hz, Ar-H); 7.30 – 7.38 (m, 6H, Ar-H); 7.53 – 7.55 (d, 4H, J = 7.2 Hz, Ar-H). ^{13}C NMR :100 MHz, DMSO -d_6; δ ppm 19.37, 26.78, 28.04, 30.20, 32.57, 33.67, 49.94, 113.31, 118.97, 128.42, 130.59, 132.59, 135.47, 139.50, 152.94, 153.28, 195.24. HRMS, m/z = 618.3398 $[M + 1]^{+}$.

9-(4-(tert-butyldimethylsilyloxy)phenyl)-3,3,6,6,10-pentamethyl-3,4,6,7,9,10-hexa hydroacridine-1,8(2H,5H)-dione (ADDSi**2).**

ADDOH (500 mg, 1.31 mmol) and t-butyldimethylchlorosilane (490 mg, 3.29 mmol) were dissolved in 20 mL of pyridine and the resulting solution was kept at 50^{o}C for 12 hours. The completion of the reaction was monitored by TLC. The reaction mixture was poured into 30 mL of 6% HCl in an ice bath and the resulting solution was extracted with DCM (3 × 15 mL). The combined organic layer was dried over sodium sulphate and evaporated under reduced pressure. Then the crude product was purified by silica gel (100–200 mesh) column chromatography ($CHCl_3$–MeOH 98:2) to yield a yellow solid (Yield: 78%). ^{1}H NMR :400 MHz, DMSO-d_6: δ ppm; 0.11 (1s, 6H, Si-CH3); 0.891 (s, 9H, t-butyl proton); 0.919 and 0.988 (2s, 12H, gem – dimethyl proton); 2.060 – 2.154 (ABq, 4H, methylene proton); 2.386 - 2.429 (d, 2H, J=17.2 Hz,

methylene proton); 2.728 – 2.772 (d, 2H, J=17.6Hz); 3.250 (s, 3H, N-CH3); 4.957 (s, 1H, C9-H) 6.588 - 6.609 (d, 2H, J=8.4 Hz, Ar-H); 6.933-6.954 (d, 2H, J=8.4 Hz, Ar-H). ^{13}C NMR : 100 MHz, DMSO -d_6; δ ppm; -4.03, 18.33, 26.02, 28.05, 28.87, 30.32, 32.57, 33.70, 50.02, 113.47, 119.37, 128.54, 139.52, 152.88, 153.35, 195.23. HRMS, m/z = 494.3086 [M + 1]+.

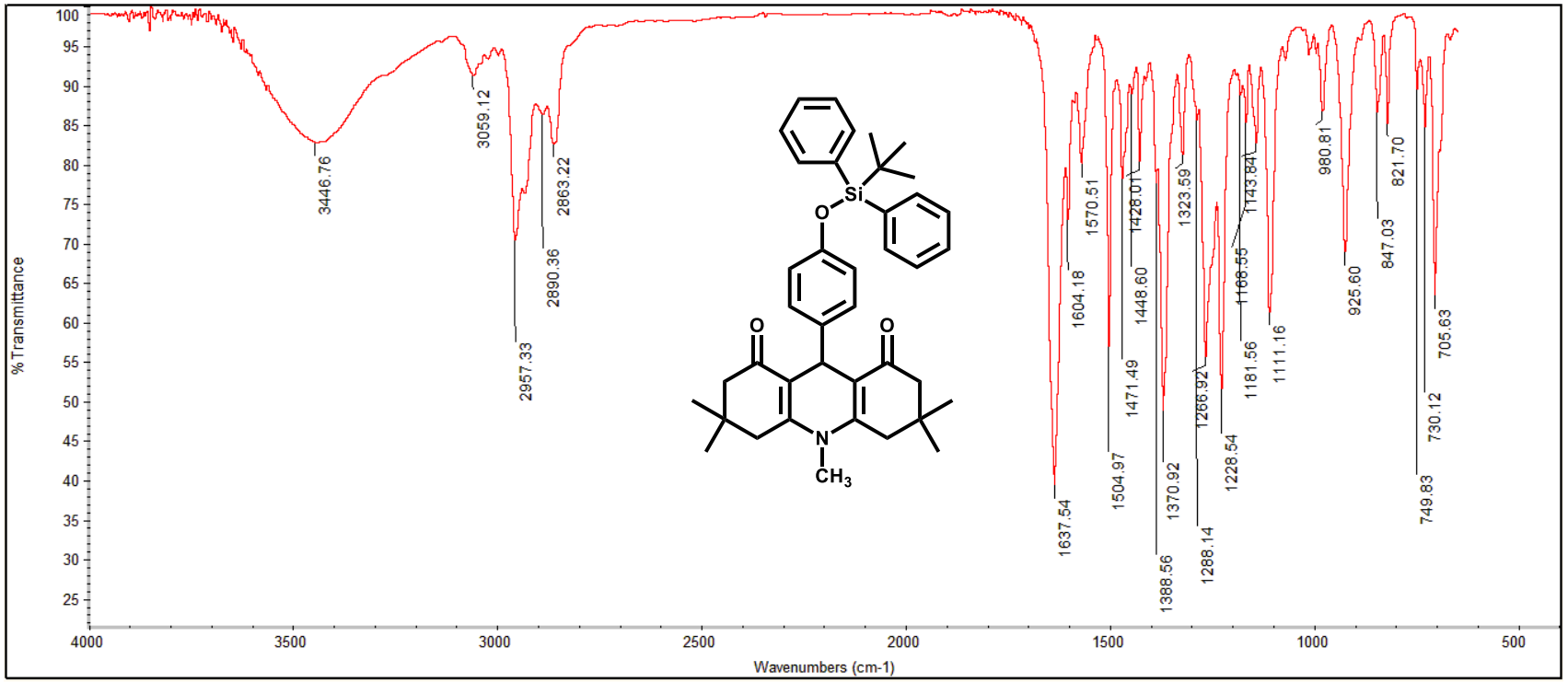

Figure S-1. IR Spectrum of ADDSi**1**

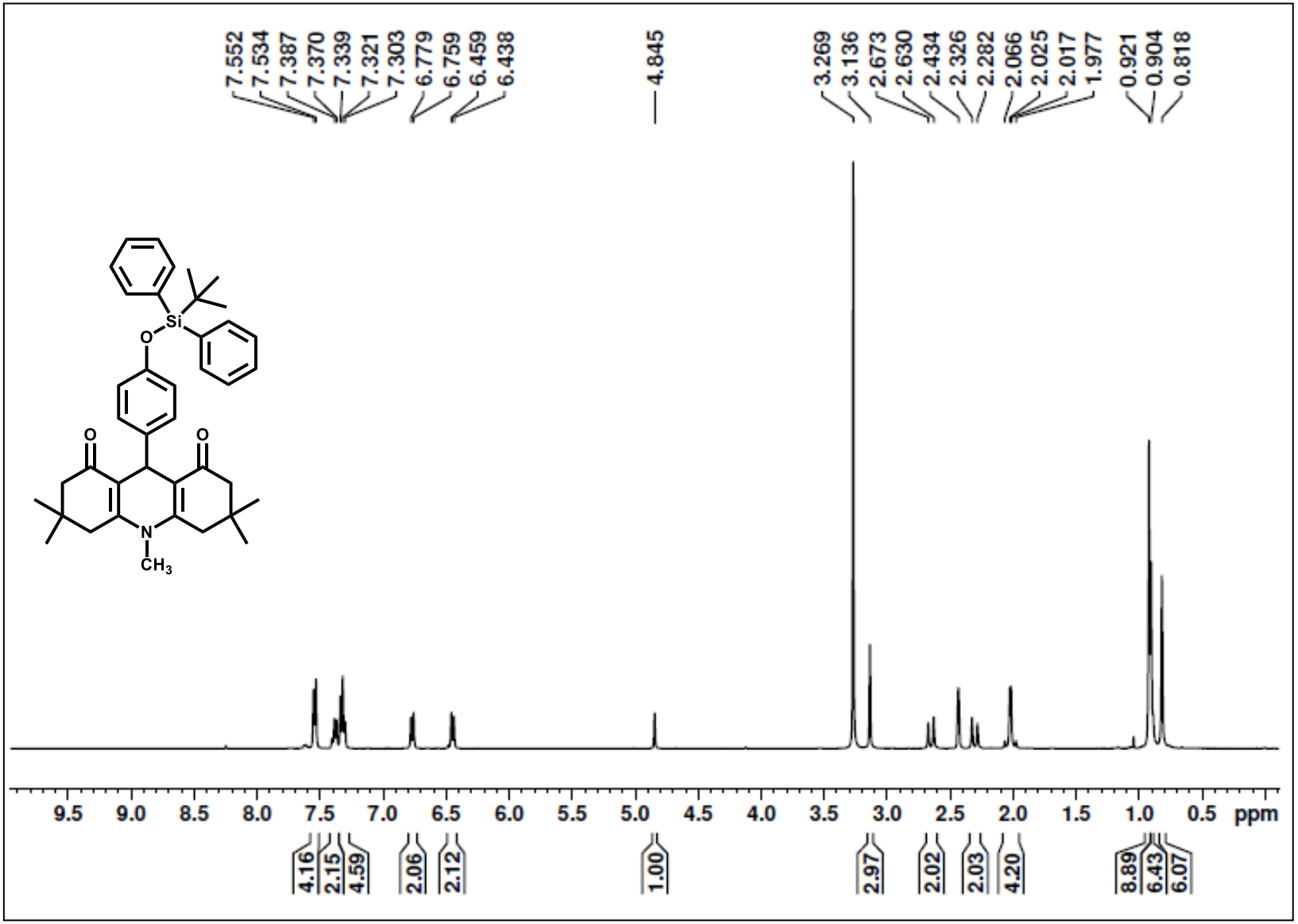

Figure S-2. ^{1}H NMR Spectrum of ADDSi**1** in DMSO-d_6

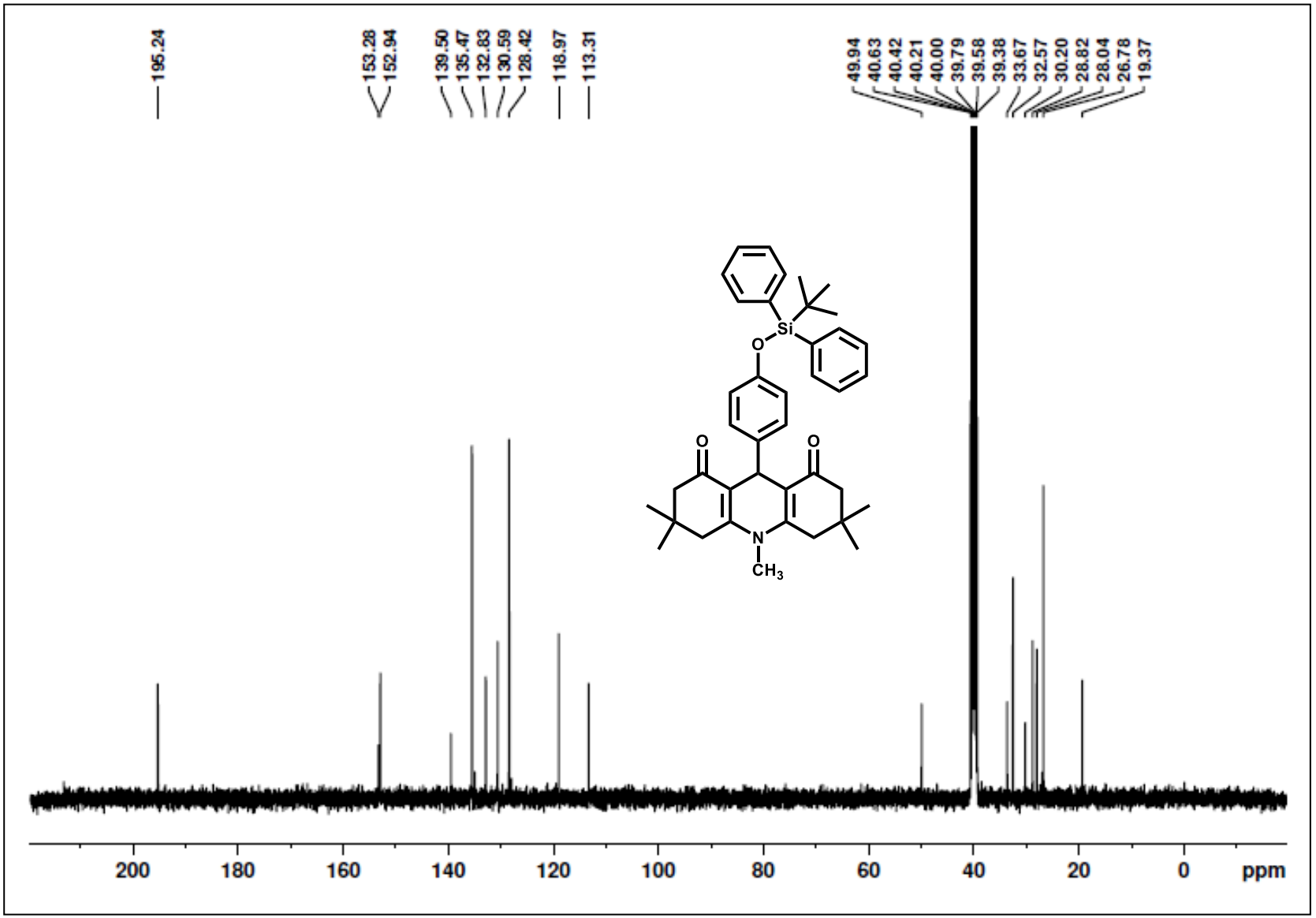

Figure S-3. ^{13}C NMR Spectrum of ADDSi**1** in DMSO-d_6

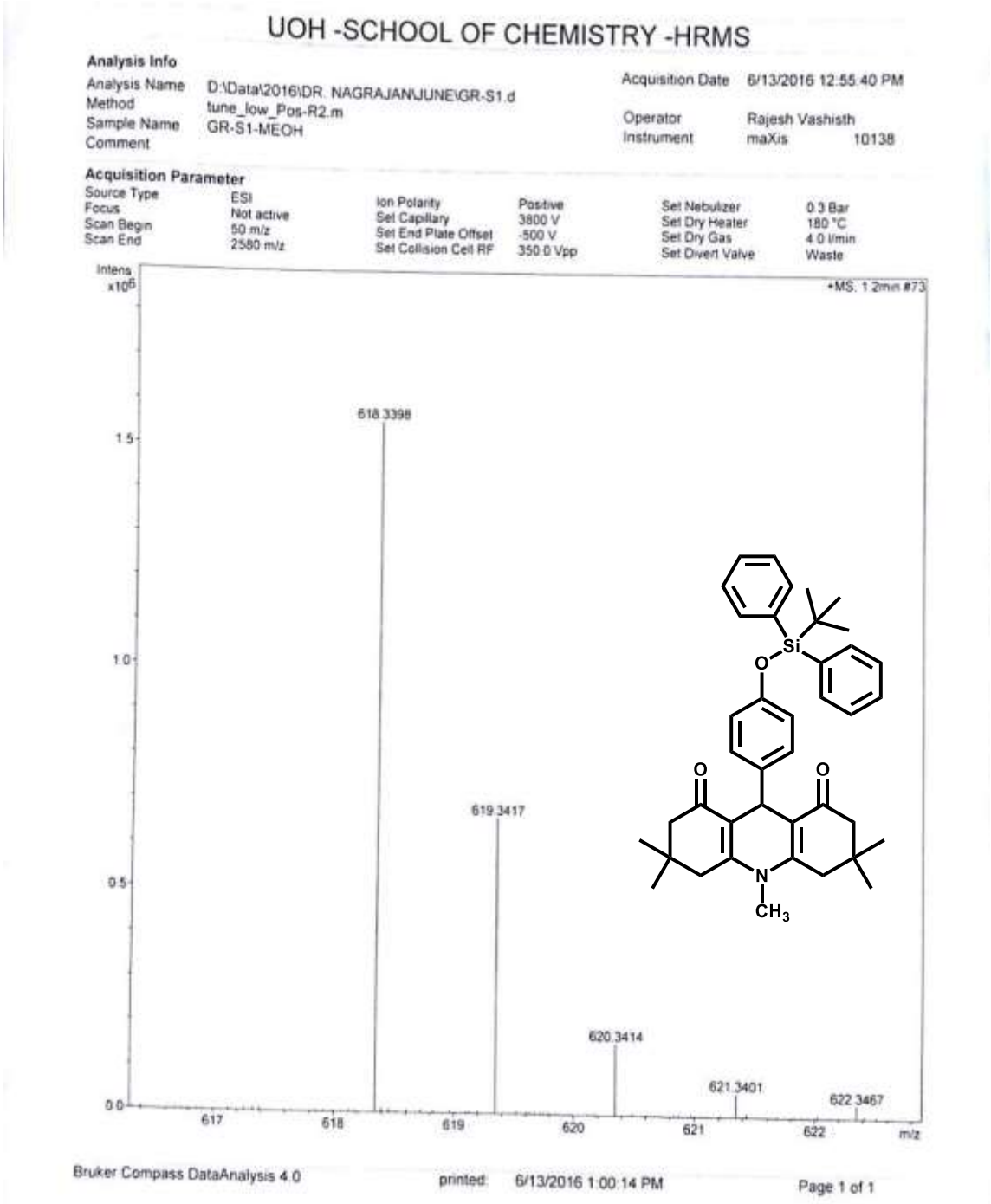

Figure S-4. HRMS of ADDSi**1**

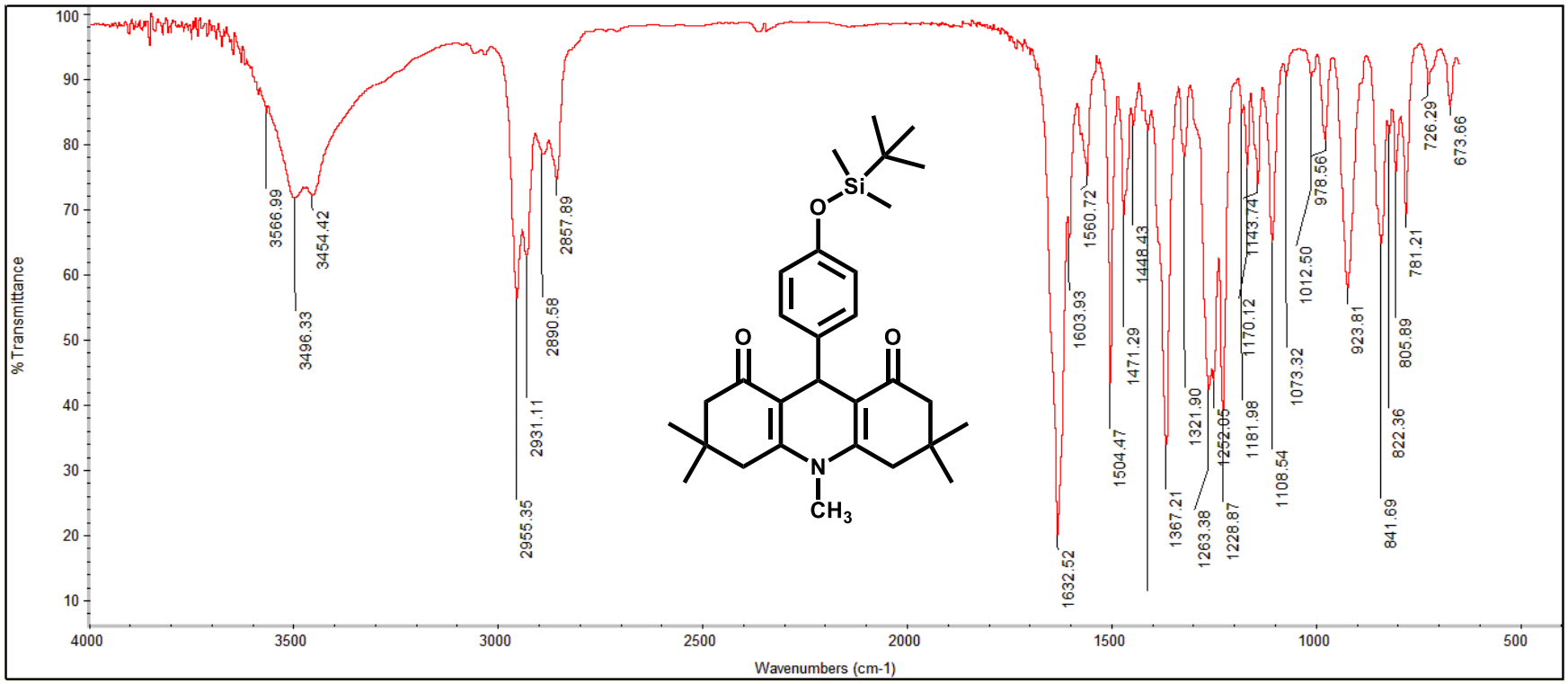

Figure S-5. IR Spectrum of ADDSi**2**

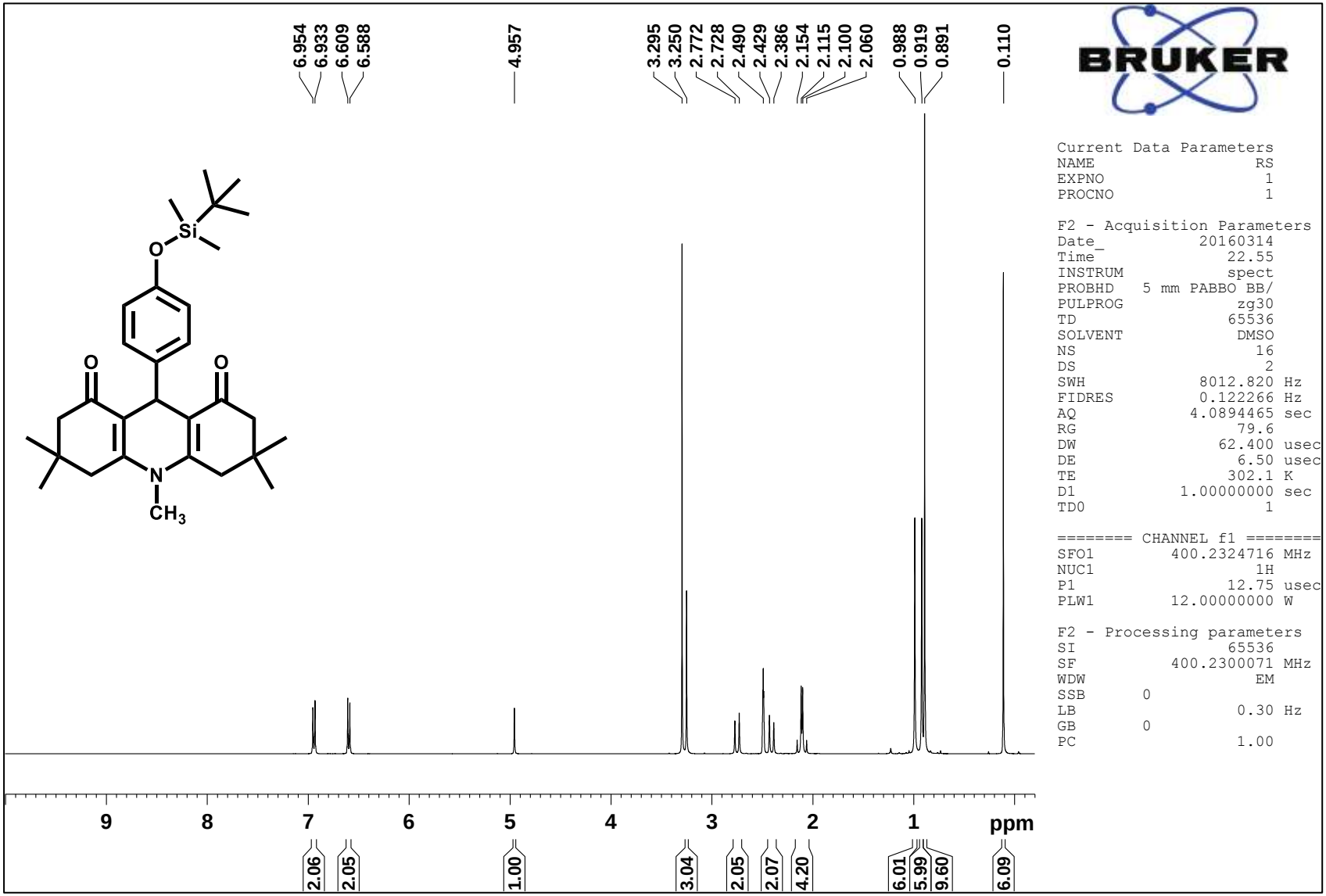

Figure S-6. ^{1}H NMR Spectrum of ADDSi**2** in DMSO-d_6

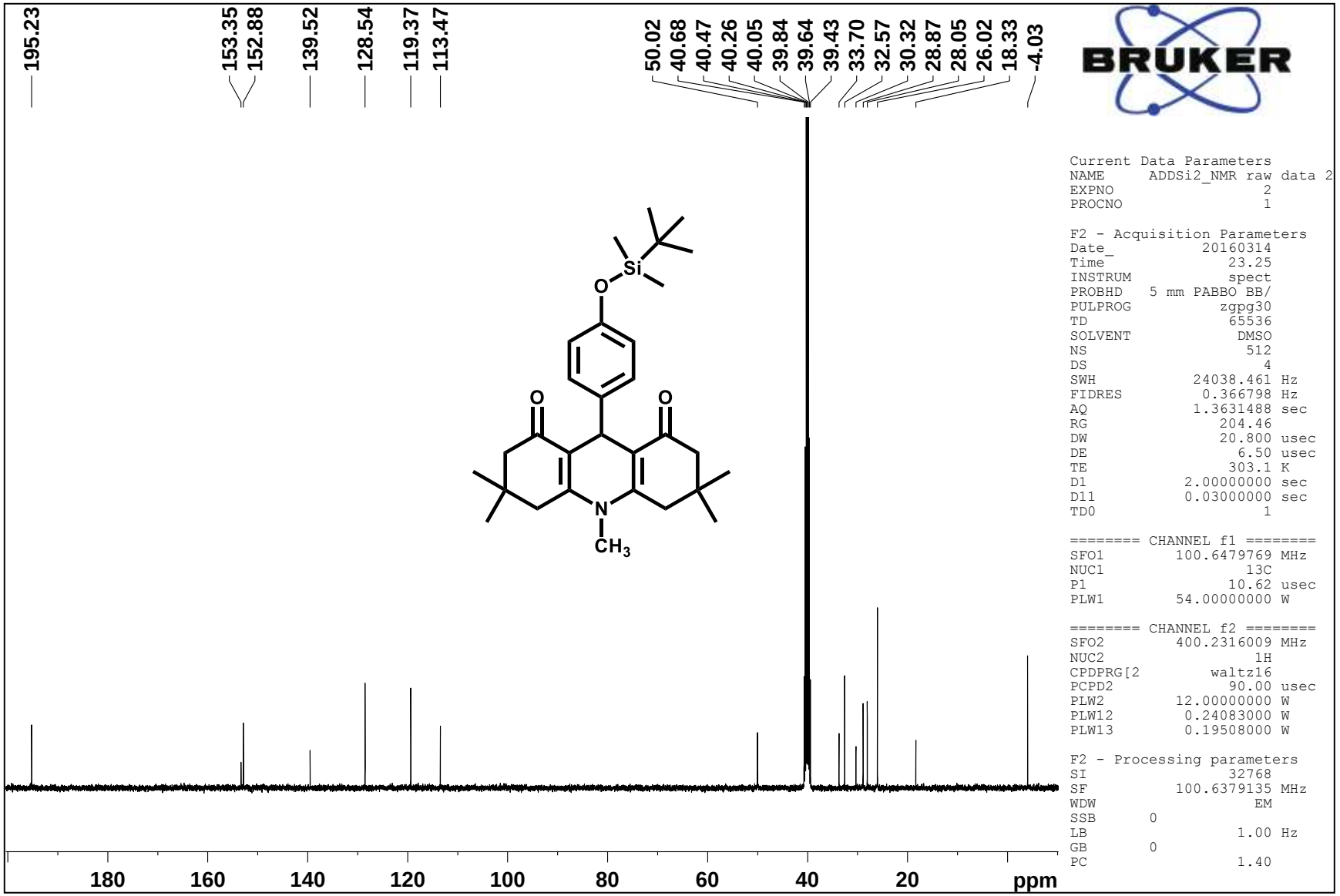

Figure S-7. ^{13}C NMR Spectrum of ADDSi**2** in DMSO-d_6

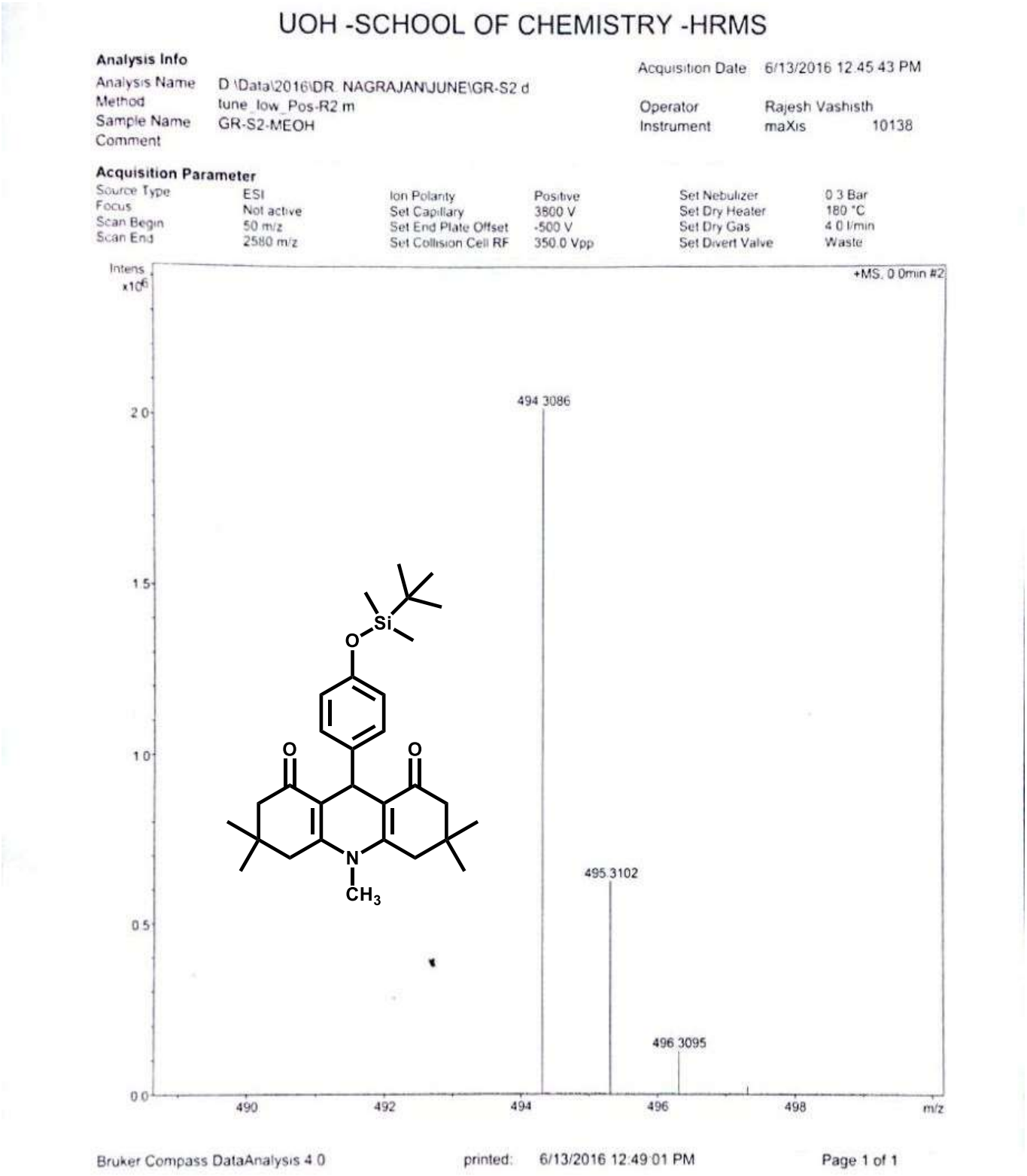

Figure S-8. HRMS of ADDSi**2**

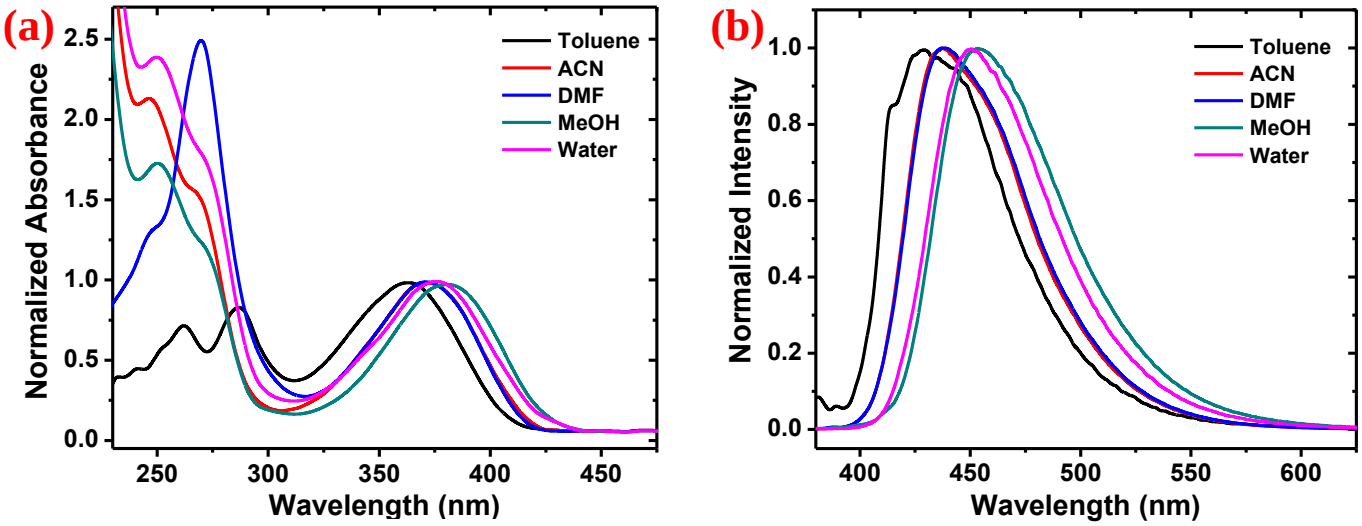

Figure S-9. a) Absorption Spectrum of ADDSi**1** in various solvents. **b)** Emission Spectrum of ADDSi**1** in various solvents.

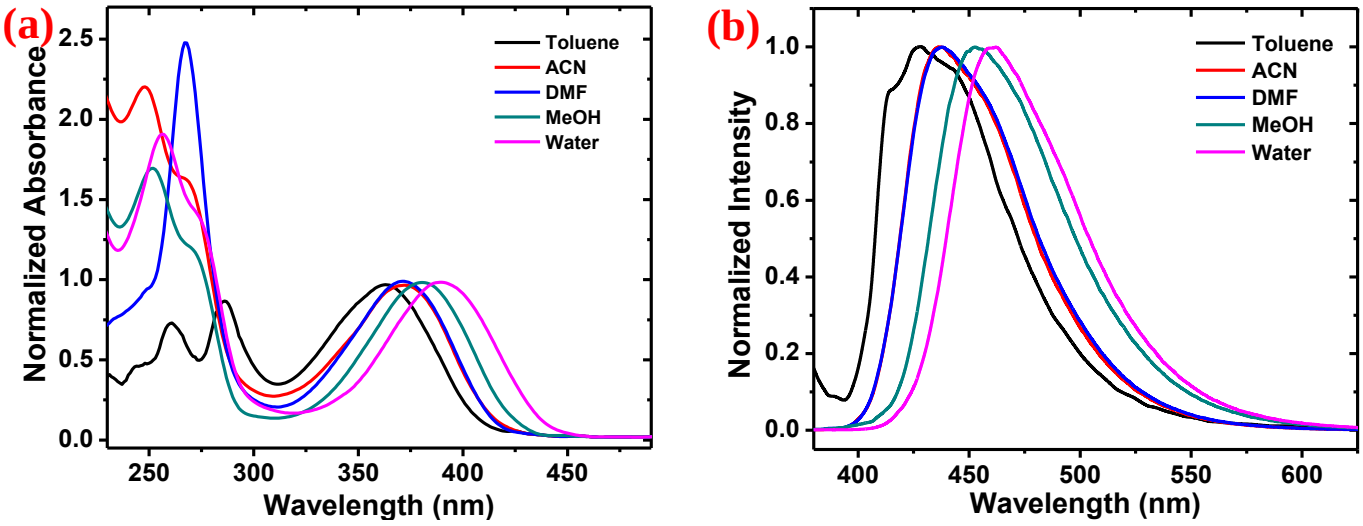

Figure S-10. a) Absorption Spectrum of ADDSi**2** in various solvents. **b)** Emission Spectrum of ADDSi**2** in various solvents.

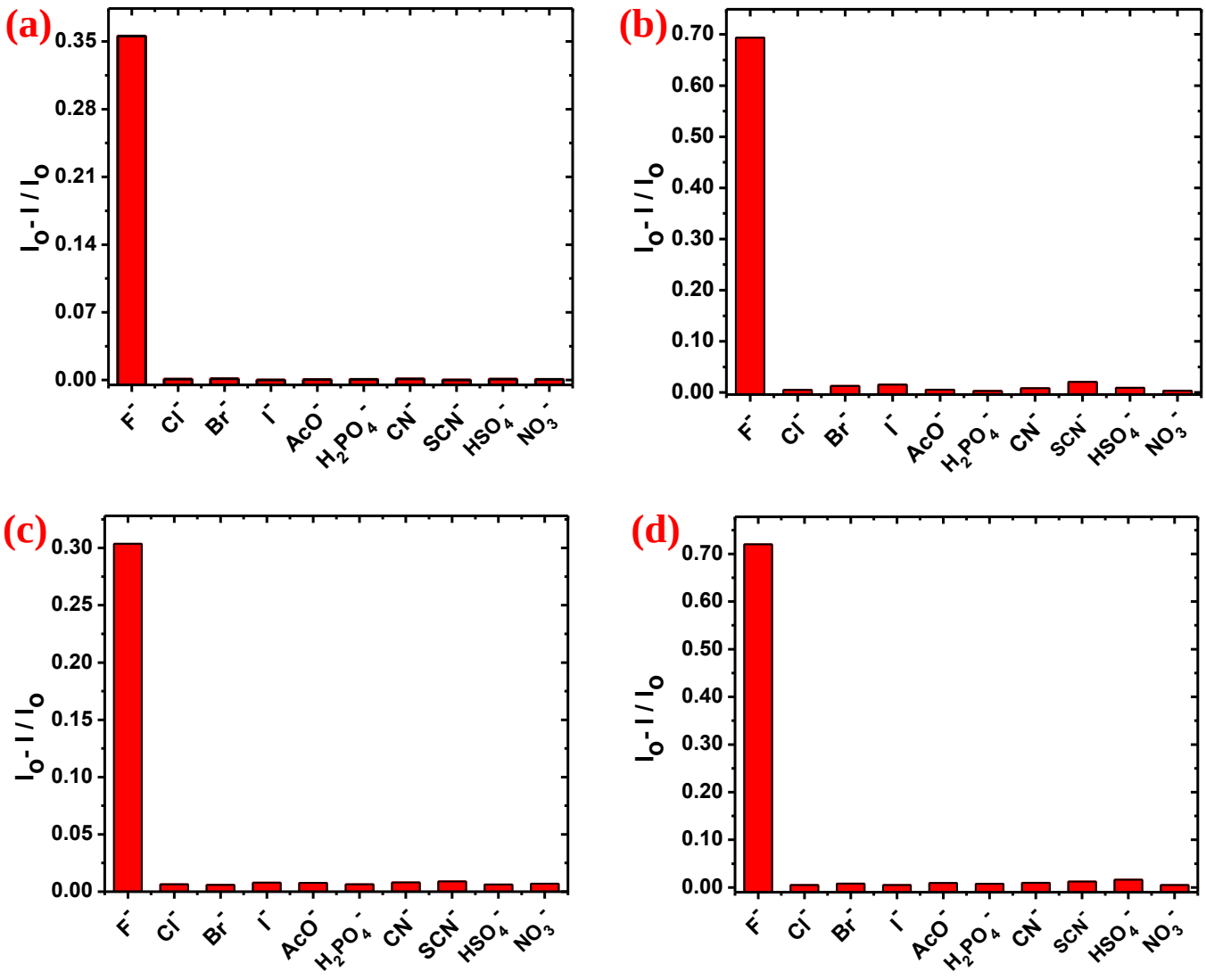

Figure S-11. Selectivity of studies **a)** ADDSi**1 (14 µM)** in ACN **b)** ADDSi**2 (14 µM)** in ACN **c)** ADDSi**1** (**14 µM**) in ACN/Water (1:1) **d)** ADDSi**2 (14 µM)** in ACN/Water (1:1). Anions Concentration (200 µM).

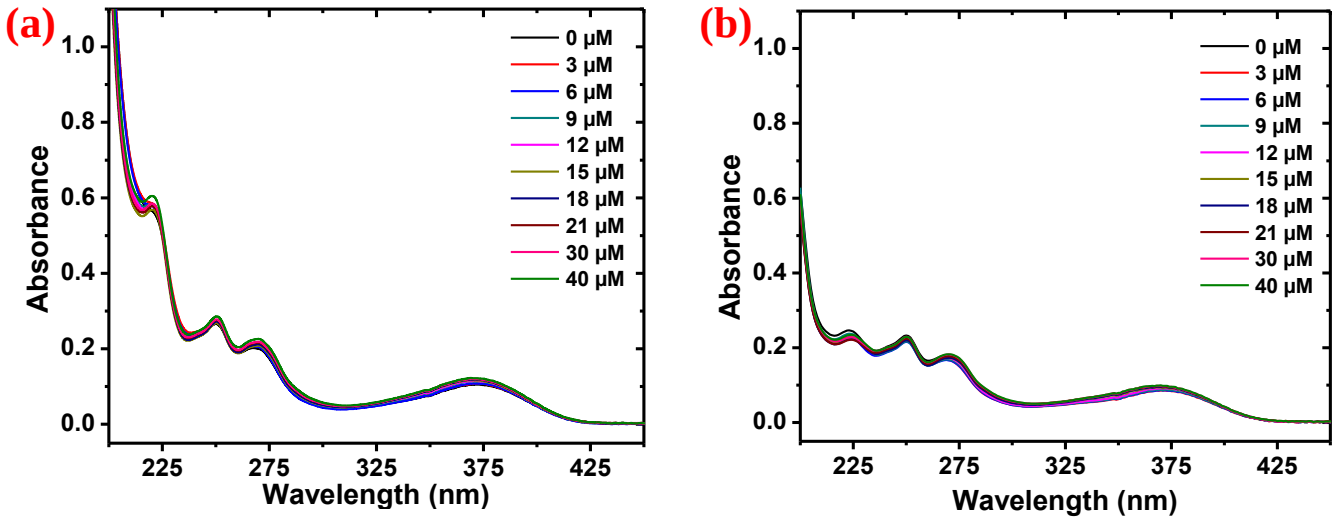

Figure S-12. a) Variation in Absorption Spectra of ADDSi**1 (14 μM)** in ACN upon addition of different concentrations of fluoride anion (TBAF). **b)** Variation in Absorption Spectra of ADDSi**2 (14 μM)** in ACN upon addition of different concentrations of fluoride anion (TBAF).

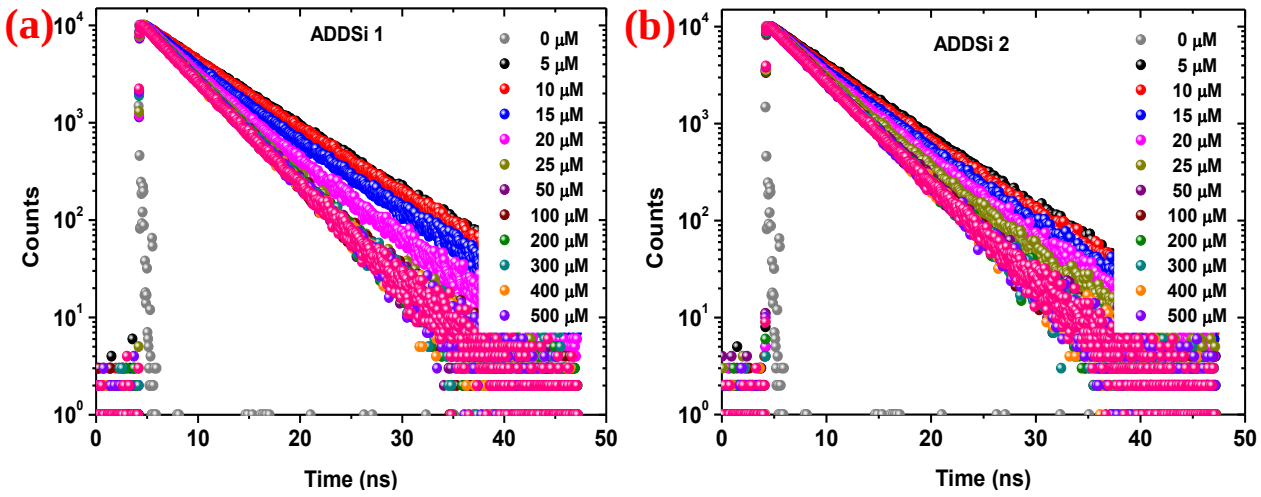

Figure S-13. a) Variation in fluorescence lifetime decay of ADDSi**1 (14 μM)** in ACN : H_2O (1:1) upon addition of different concentrations of fluoride anion (TBAF). **b)** Variation in fluorescence lifetime decay of ADDSi**2 (14 μM)** in ACN : H_2O (1:1) upon addition of different concentrations of fluoride anion (TBAF).

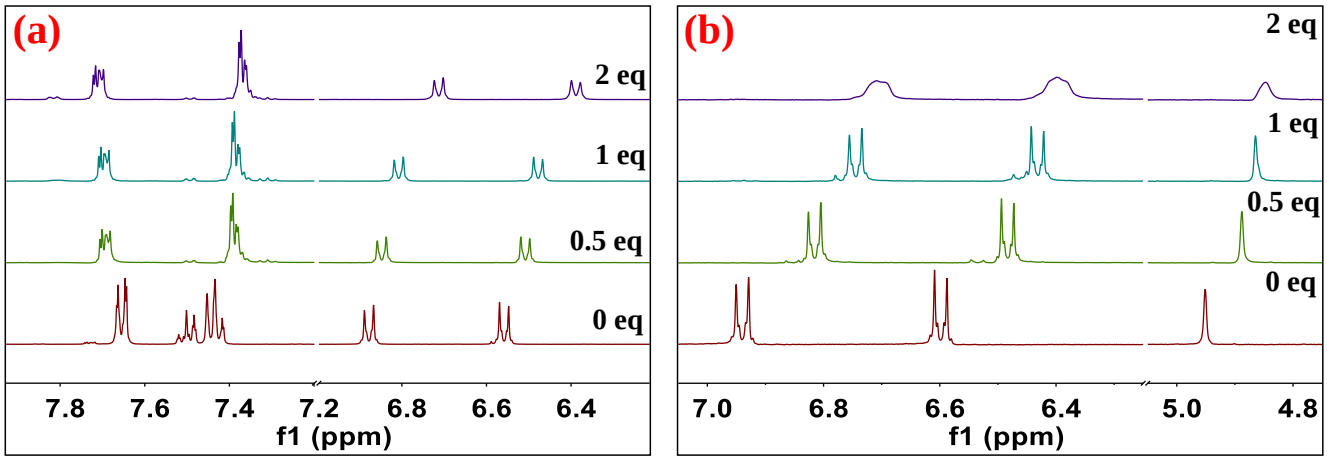

Figure S-14. Partial ^{1}H NMR Spectrum of ADDSi**1** (11.56 mM) in DMSO-d_6 upon addition of fluoride ion (0 – 2 eq)

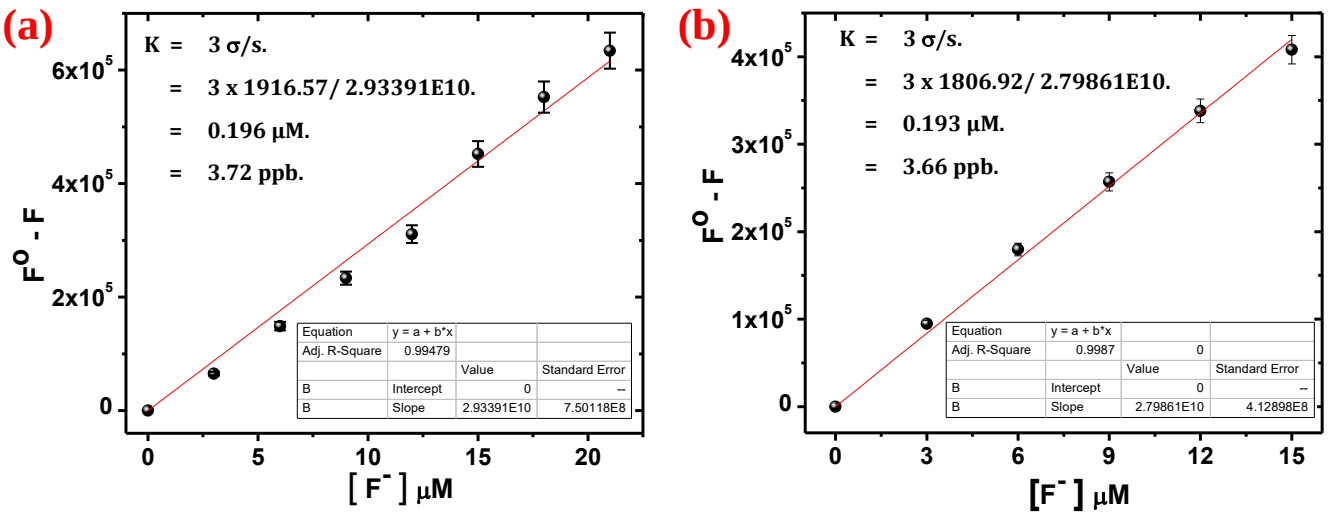

Figure S-15. a) Plot of change in emission intensity (F^{o} - F) of ADDSi**1** in ACN at 435 nm against concentration of fluoride ion. **b)** Plot of change in emission intensity (F^{o} - F) of ADDSi**2** in ACN at 435 nm against concentration of fluoride ion.

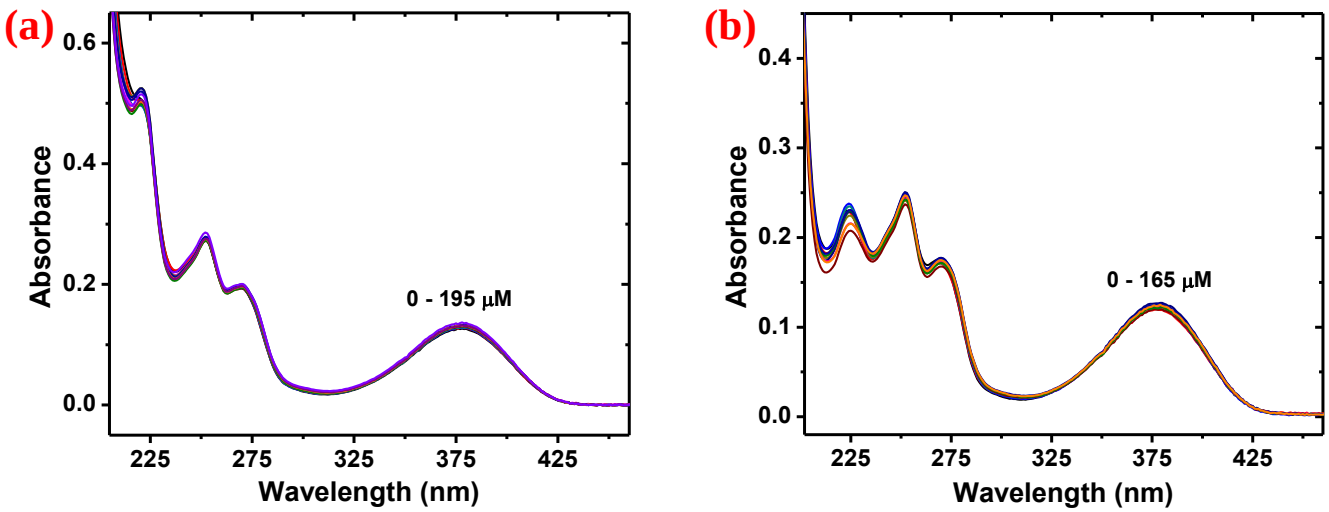

Figure S-16. a) Variation in Absorption Spectra of ADDSi**1 (14 µM)** in ACN/Water (1:1) upon addition of different concentrations of fluoride anion (TBAF). **b)** Variation in Absorption Spectra of ADDSi**2 (14 µM)** in ACN/Water (1:1) upon addition of different concentrations of fluoride anion (TBAF).

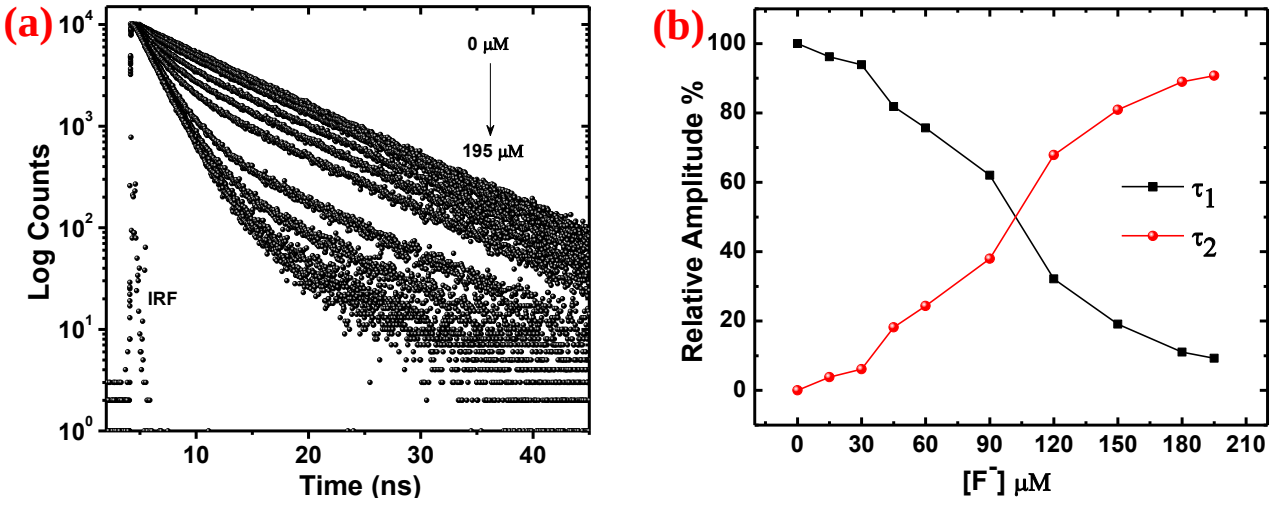

Figure S-17. a) Variation in fluorescence lifetime decay of ADDSi**1 (14 µM)** in ACN : H_2O (1 : 1) upon addition of different concentrations of fluoride anion (TBAF). **b)** Plot of relative amplitudes of two lifetimes vs fluoride ion concentration.

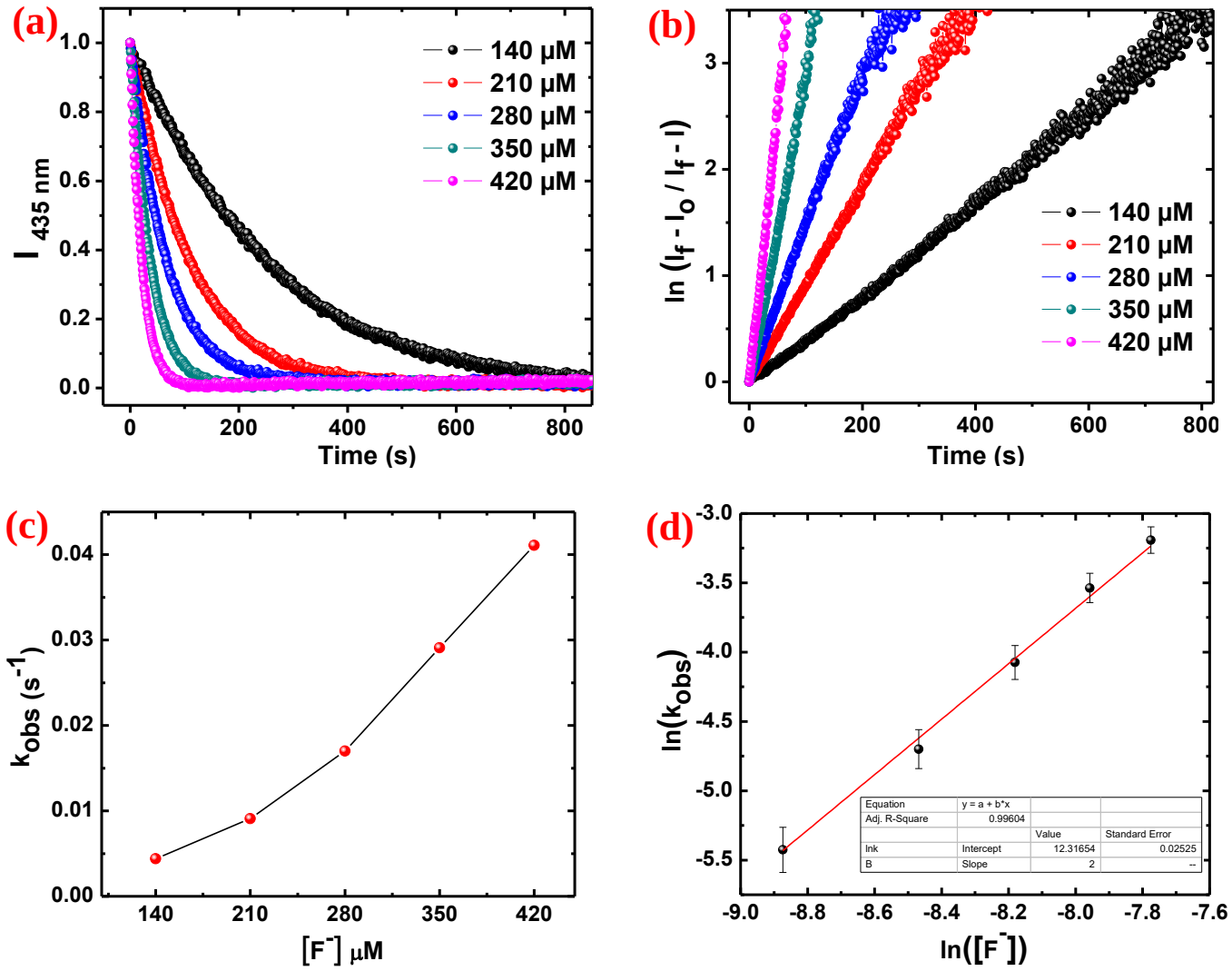

Figure S-18. a) Time course of desilylation reaction of ADDSi**1** (14 μM) upon addition of different concentrations of TBAF (140 - 420 μM) in ACN by following emission change at 435 nm. **b)** Guggenheim plot for pseudo first order kinetics of desilylation reaction of ADDSi**1** in ACN on addition of different concentrations of TBAF. **c)** Plot of fluoride concentration vs k_{obs} (ADDSi**1** in ACN). **d)** Plot of ln ($[F^-]$) vs ln (k_{obs}) (ADDSi**1** in ACN).

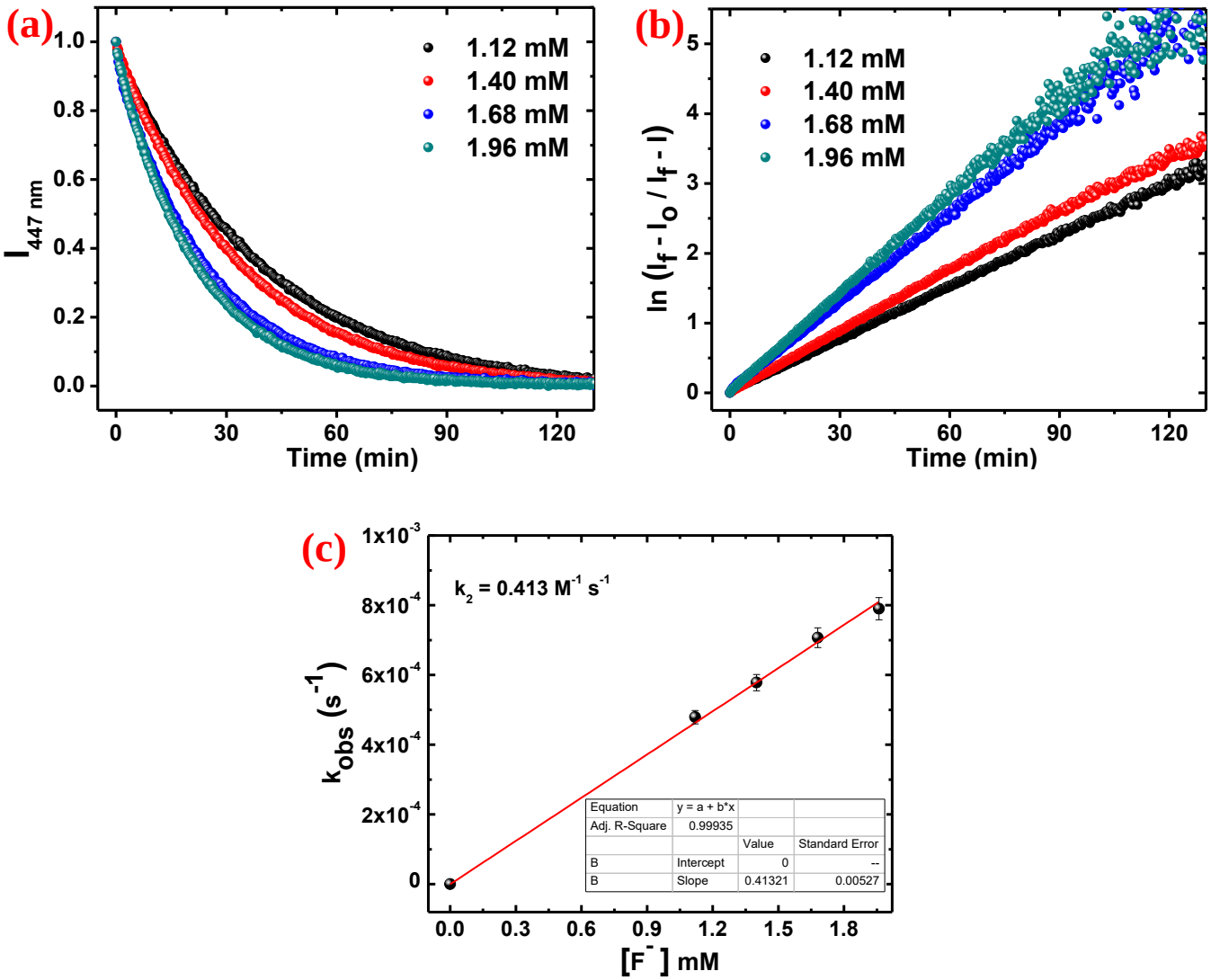

Figure S-19. a) Time course of desilylation reaction of ADDSi**1** (14 μM) upon addition of different concentrations of TBAF (140 - 420 μM) in ACN/Water (1:1) by following emission change at 447 nm. **b)** Guggenheim plot for pseudo first order kinetics of desilylation reaction of ADDSi**1** in ACN/Water (1:1) on addition of different concentrations of TBAF. **c)** Plot of fluoride concentration vs k_{obs} (ADDSi**1** in ACN/Water (1:1)).

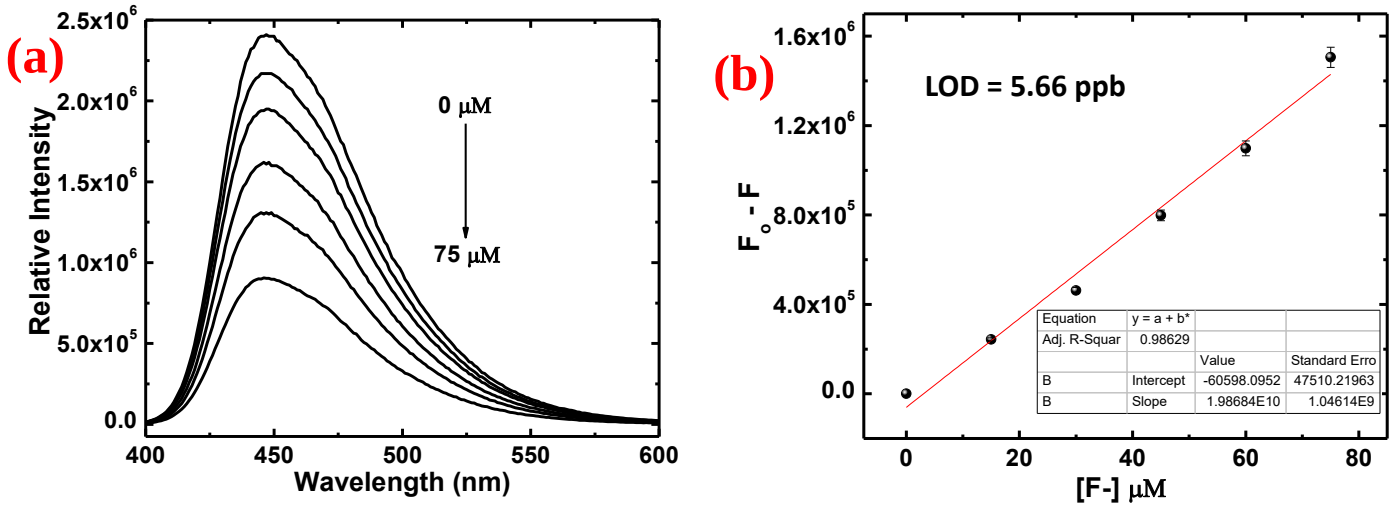

Figure-20. a) Variation in Emission Spectra of ADDSi**2** **(14 μM)** in ACN/Water (1:1) upon addition of different concentrations of fluoride anion (NaF). **b)** Plot of change in emission intensity (F^o - F) of ADDSi**2** in ACN/Water (1:1) at 447 nm against concentration of fluoride ion (NaF).

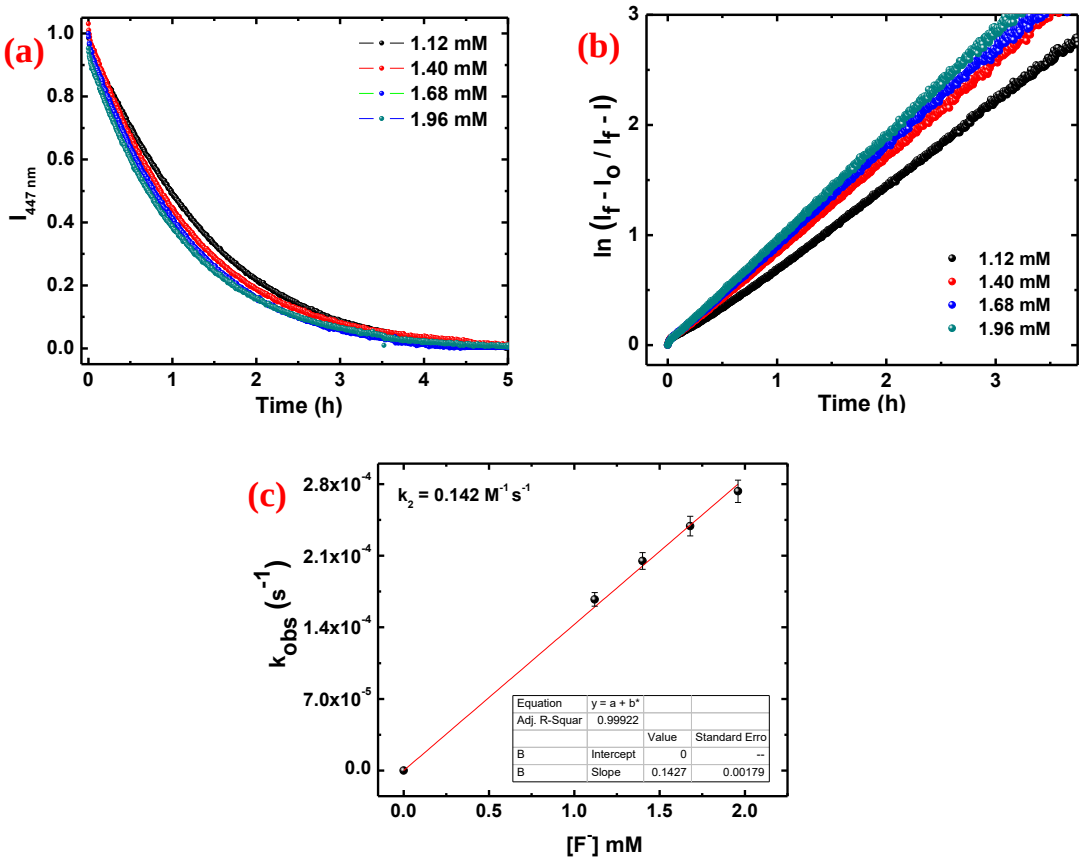

Figure S-21. a) Time course of desilylation reaction of ADDSi**2** (14 μM) upon addition of different concentrations of NaF (1.12 mM – 1.96 mM) in ACN/Water (1:1) by following emission change at 447 nm. **b)** Guggenheim plot for pseudo first order kinetics of desilylation reaction of ADDSi**2** in ACN/Water (1:1) on addition of different concentrations of NaF. **c)** Plot of fluoride concentration vs k_{obs} (ADDSi**2** in ACN/Water (1:1)).

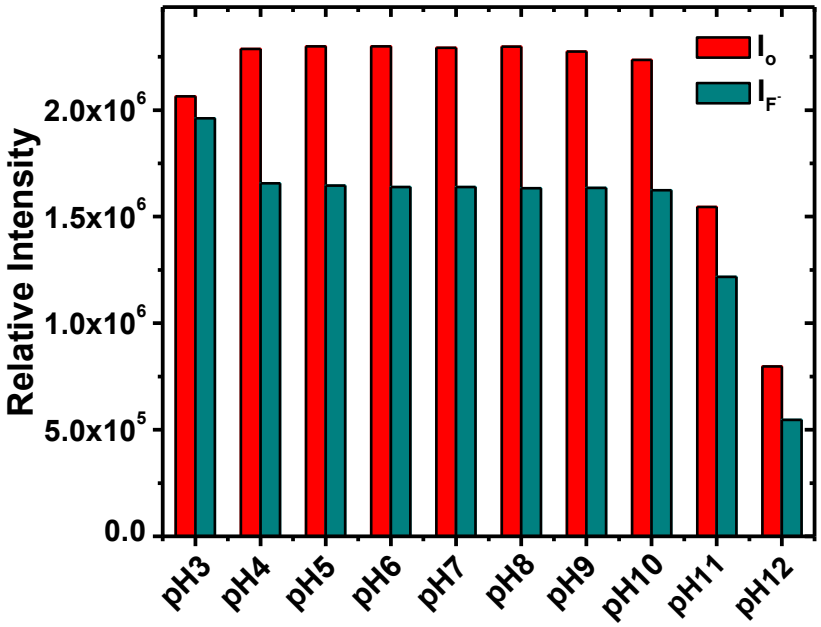

Figure S-22. Variation in fluorescence intensity of ADDSi2 (14 µM) before ($\mathbf{I_o}$) and after ($\mathbf{I_F^-}$) addition of fluoride ion (TBAF, 52.6 µM) in various pH buffer solutions - ACN/Water (1:1, 10mM buffer solutions pH 3 - 12)

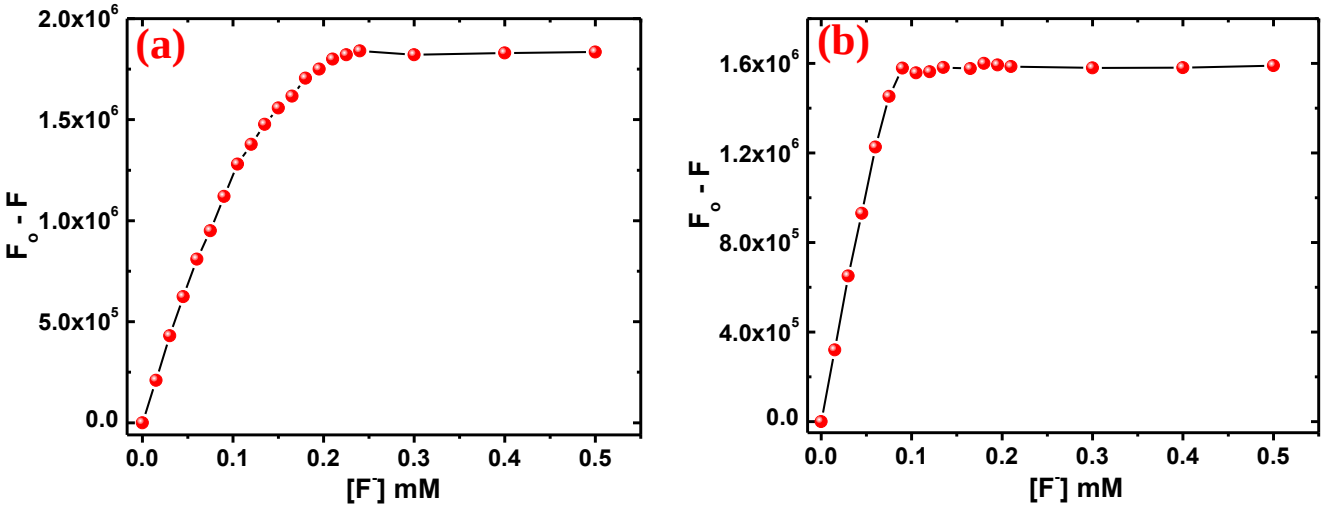

Figure S–23. a) Plot of change in emission intensity (F^o - F) of ADDSi**1** in ACN/Water mixture (1:1) at 447 nm against concentration of fluoride ion **b)** Plot of change in emission intensity (F^o - F) of ADDSi**2** in ACN/Water mixture (1:1) at 447 nm against concentration of fluoride ion.

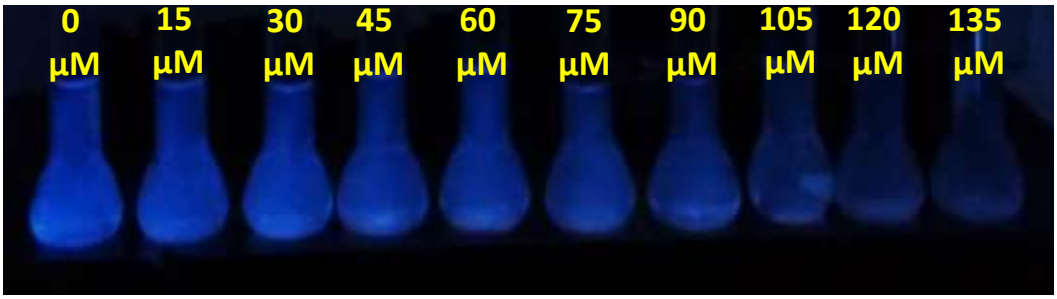

Figure S-24. Photograph shows the change in emission intensity upon addition different of fluoride ion (TBAF) under UV lamp (365 nm).

Table S-1. Photophysical data of ADDSi**1** in various solvents.

Solvent	**Abs (λ_{max})**	**Emi (λ_{max})**	**$\Delta\upsilon$(cm^{-1})**	**ϕ_f**
Toluene	363	430	4292	0.032
ACN	371	437	4071	0.40
DMF	371	438	4123	0.462
MeOH	377	453	4450	0.354
Water	378	451	4282	0.109

Table S-2. Photophysical data of ADDSi**2** in various solvents.

Solvent	**Abs (λ_{max})**	**Emi (λ_{max})**	**$\Delta\upsilon$(cm^{-1})**	**ϕ_f**
Toluene	363	427	4129	0.027
ACN	371	436	4018	0.385
DMF	371	438	4123	0.427
MeOH	382	453	4103	0.295
Water	390	463	4043	0.252

Table S-3: Fluorescence lifetime data of ADDSi**1** on addition of F^- ion (ACN) and monitored at 435 nm.

Fluorescence lifetime data of ADDSi1 on addition of F^- ion (ACN) and monitored at 436 nm					
[F^-] µM	**τ_1(ns)**	**τ_2 (ns)**	**A_1 (%)**	**A_2 (%)**	**χ^2**
0	-	6.37	-	100	1.07
5	4.11	6.49	10.36	89.64	0.94
10	4.02	6.46	34.78	65.22	1.01
15	4.08	6.70	70.40	29.60	1.04
20	4.01	6.39	92.59	7.41	1.12
25	4.09	-	100	-	1.14
50	4.05	-	100	-	1.11
100	4.06	-	100	-	1.01
200	4.05	-	100	-	1.08
300	4.09	-	100	-	1.16
400	4.03	-	100	-	1.11
500	4.02	-	100	-	1.07

Table S-4: Fluorescence lifetime data of ADDSi**2** on addition of F^- ion (ACN) and monitored at 435 nm.

Fluorescence lifetime data of ADDSi2 on addition of F^- ion (ACN) and monitored at 436 nm					
[F^-] µM	**τ_1(ns)**	**τ_2 (ns)**	**A_1 (%)**	**A_2 (%)**	**χ^2**
0	-	5.87	-	100	1.10
5	4.26	5.91	18.37	81.63	1.00
10	4.17	6.11	42.06	57.94	1.05
15	4.01	6.09	56.53	43.47	1.05
20	4.01	6.11	75.30	24.70	1.17
25	4.11	-	100	-	1.09
50	4.08	-	100	-	1.14
100	4.05	-	100	-	1.05
200	4.09	-	100	-	1.04
300	4.01	-	100	-	1.07
400	4.06	-	100	-	1.16
500	4.04	-	100	-	1.12

Table S-5: Fluorescence lifetime data of ADDSi**1** (ACN/water mixture) upon addition of F^- ion.

Fluorescence lifetime data of ADDSi1 upon addition of F^- ion					
[F^-] µM	**τ_1(ns)**	**τ_2 (ns)**	**A_1 (%)**	**A_2 (%)**	**χ^2**
0	-	8.39	-	100	1.01
15	2.04	8.47	3.85	96.15	1.06
30	1.80	8.41	6.13	93.87	1.01
45	1.98	8.40	18.17	81.83	1.02
60	1.85	8.32	24.34	75.66	1.03
75	1.92	8.30	37.95	62.05	1.01
90	1.90	8.30	51.56	48.44	1.02
105	1.90	8.31	67.88	32.12	1.01
120	1.86	8.32	80.92	19.08	1.01
135	1.87	8.41	88.93	11.07	1.09
150	1.85	8.46	90.72	9.28	1.19
165	1.85	8.38	92.57	7.23	1.04
180	1.88	8.44	95.23	4.77	1.09
195	1.85	8.30	97.25	2.75	1.06

Table S-6: Fluorescence lifetime data of ADDSi**2** (ACN/water mixture) upon addition of F^- ion.

Fluorescence lifetime data of ADDSi2 upon addition of F^- ion					
[F^-] µM	**τ_1(ns)**	**τ_2 (ns)**	**A_1 (%)**	**A_2 (%)**	**χ^2**
0		7.87		100	1.20
15	1.88	7.84	12.48	87.52	1.05
30	1.91	7.84	39.27	60.73	1.00
45	1.88	7.84	64.52	35.48	1.12
60	1.85	7.84	78.74	21.26	1.11
75	1.89	7.84	90.28	9.72	1.11
90	1.82	7.84	92.37	7.63	1.06
105	1.88	7.84	94.24	5.76	1.15
120	1.90	7.84	95.89	4.11	1.21
135	1.88	7.84	95.92	4.08	1.01
150	1.87	7.84	95.93	4.07	1.08
165	1.88	7.84	96.12	3.88	1.02

Table S-7. Limit of Detection comparison from the literature.

S.No.	Solvent Medium	LOD	Reference
1.	ACN	50 nM	1
	H_2O	16 µM	
2.	ACN	0.1 µM	2
	ACN – H_2O (1:1, v:v)	18 µM	
3.	ACN	47 nM	3
	DMF – H_2O (9:1, v:v)	7 µM	
4.	ACN	0.19 µM	Present System
	ACN-H_2O (1:1, v:v)	0.29 µM	

Table S-8. Kinetics data of ADDSi**1** in ACN.

$[F^-]$	k_{obs}	$k_{obs}/[F^-]$	$k_{obs}/[F^-]^2$
140 µM	0.0044	31.43	224489
210 µM	0.0091	43.33	206349
280 µM	0.0170	60.71	216836
350 µM	0.0291	83.14	237551
420 µM	0.0411	97.86	232993

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Table S-9. Kinetics data of ADDSi**2** in ACN.

$[F^-]$	k_{obs}	$k_{obs}/[F^-]$	$k_{obs}/[F^-]^2$
140 µM	0.022	157.14	1122449
210 µM	0.045	216.67	1031747
280 µM	0.083	295.00	1053571
350 µM	0.141	402.57	1150204
420 µM	0.203	483.33	1150794

Table S-10. Kinetics data of ADDSi**1** in ACN/Water (1:1).

$[F^-]$	k_{obs}	$k_{obs}/[F^-]$
1.12 mM	**0.000479**	**0.427679**
1.40 mM	**0.000578**	**0.412857**
1.68 mM	**0.000707**	**0.420833**
1.96 mM	**0.000790**	**0.403061**

k_2 = 0.4132

Table S-11. Kinetics data of ADDSi**2** in ACN/Water (1:1).

$[F^-]$	k_{obs}	$k_{obs}/[F^-]$
1.12 mM	**0.000821**	**0.733036**
1.40 mM	**0.001005**	**0.717857**
1.68 mM	**0.001211**	**0.720536**
1.96 mM	**0.001401**	**0.714286**

k_2 = 0.71252

Table S-12. Kinetics data of ADDSi**2** in ACN/Water (1:1) upon addition of NaF.

$[F^-]$	k_{obs}	$k_{obs}/[F^-]$
1.12 mM	**0.000167**	**0.149375**
1.40 mM	**0.000204**	**0.146286**
1.68 mM	**0.000238**	**0.142202**
1.96 mM	**0.000273**	**0.139386**

k_2 = 0.1428

Probe	k_3 (M^{-2} s^{-1}) in ACN	k_2 (M^{-1} s^{-1}) in ACN/Water (1:1)
ADDSi1 (TBAF)	**2.22×10^5**	**0.411**
ADDSi2 (TBAF)	**1.10×10^6**	**0.720**
ADDSi2 (NaF)	**-**	**0.143**

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2. A dual-channel probe for selective fluoride determination and application in live cell imaging. Z. Luo, B. Yang, C. Zhong, F. Tang, M. Yuan, Y. Xue, G. Yao, J. Zhang, Y. Zhang, *Dyes Pigm.* **2013**, 97, 52.
3. Rhodamine based dual probes for selective detection of mercury and fluoride ions in water using two mutually independent sensing pathways. N. Kumari, N. Dey, S. Bhattacharya, *Analyst*, **2014**, 139, 2370.