Supporting Information for

A Multifunctional Photo-, Solvato-, Acido- and Ionochromic Schiff Base Probe

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Synthesis and characterization

2-[3-(4-Dimethylaminophenyl)allylideneamino]benzylalcohol (**P1**). Schiff base derivative **P1** was prepared through the condensation reaction of 4-dimethylamino-*trans*-cinnamaldehyde (1.00 g, 5.7 mmol) and (1*S*,2*R*)-(−)-*cis*-1-amino-2-indanol (0.85 g, 5.7 mmol), stirring for 2 h under reflux of methanol. The solvent and water formed during the reaction were removed with a Dean-Stark trap to yield a solid, which was washed with *n*-hexane/ethyl acetate mixtures (9:1), to give 1.67 g (5.5 mmol, 95% yield) of **P1**. m.p.: 178-180ºC. IR (ATR) $\bar{\nu}_{max}$(cm^{-1}): 3171, 2962, 2915, 1598 (CN), 1436, 1350, 1254, 1151, 989, 946. ^{1}H NMR (DMSO-δ_6, 300 MHz) δ: 8.26 (1H, d, *J* = 9.0 Hz, N_{imine} proton), 7.44 (2H, d, *J* = 9.1 Hz), 7.47-7.05 (5H, m), 7.74 (2H, d, *J* = 9.1 Hz), 6.76 (1H, d, *J* = 9.0 Hz), 4.66 (1H, d, *J* = 6.0 Hz), 3.05 (1H, dd, *J* = 21.0, 6.0 Hz), 2.97 (6H, s), (1H, t, *J* = 9.0 Hz) ppm. ^{13}C NMR (DMSO-δ_6, 75.6 MHz) δ: 164.1 (C-7), 151.4, 143.5, 143.1, 141.7, 128.1, 126.8, 125.4, 125.1, 123.7, 112.5, 76.4, 75.0, 40.2, 39.5. Anal. Calcd. for $C_{20}H_{22}N_2O$: C 78.40, H 7.24, N 9.14; found: C 78.51, H 7.21, N 9.28. HR-ESI-MS: *m*/*z* for $C_{20}H_{22}N_2O$ [M^+ +H]: 307.18048; found: 307.18047 (error 0.0586 ppm).

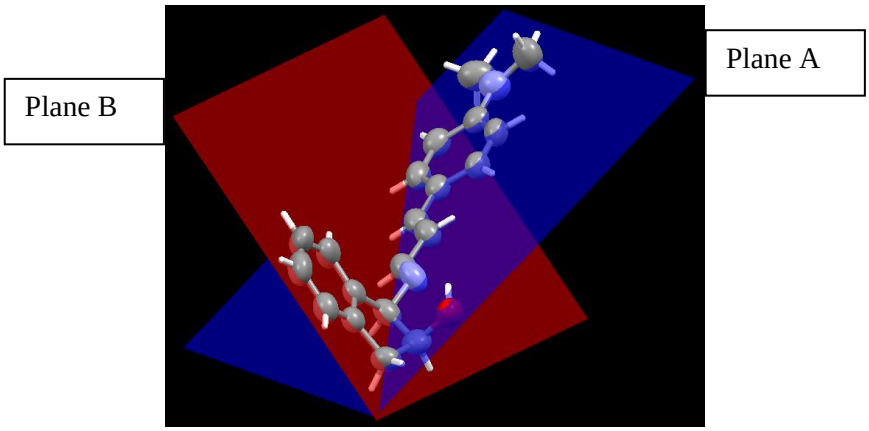


Fig. S1. Illustration of A and B planes of **P1**.

Table S1 Summary of crystal data at 293 K

Compound	P1
Crystal color	Yellow
Empirical formula	$C_{20}H_{22}N_2O$
Mol wt.	306.41
Crystal System	Monoclinic
Space group	$P2_1$
a (Å)	5.959(2)
b (Å)	8.111(3)
c (Å)	17.973(2)
α (°)	90
β (°)	96.304
γ (°)	90
V (Å^3)	863.44(5)
Z	2
$\rho_{calcd.}$ (g/cm^3)	1.180
Θ Range (°)	27.50
F(000)	328.0
Abs. Coeff. (mm$^-$	0.073
No. of reflections:	
Measured	8957
Unique	3441
Observed	2583
R [I > 2σ(I)]	0.055
Rw (all data)	0.068
Parameters	209
ρ_{min} (e Å^3)	-0.127
ρ_{max} (e Å3)	0.144
GOOF	1.098

Geometric parameters (Å, º)

C1—N1	**1.383 (4)**	**C8—C9**	**1.526 (5)**
C1—C2B	1.397 (5)	**C9—O1**	1.427 (4)
C1—C2	1.398 (4)	**C9—C10**	1.524 (6)
C2—C3	1.372 (4)	**C10—C16**	1.506 (5)
C2B—C3B	1.371 (5)	**C11—C12**	1.367 (6)
C3—C4	1.398 (4)	**C11—C16**	1.381 (5)
C3B—C4	1.400 (4)	**C12—C13**	1.369 (7)
C4—C5	1.457 (4)	**C13—C14**	1.382 (6)
C5—C6	1.309 (4)	**C14—C15**	1.376 (5)
C6—C7	1.453 (5)	**C15—C16**	1.378 (4)
C7—N2	1.274 (4)	**C17—N1**	1.419 (5)
C8—N2	1.468 (4)	**C17B—N1**	1.441 (5)
C8—C15	1.503 (5)		
N1—C1—C2B	122.4 (3)	**O1—C9—C8**	109.8 (3)
N1—C1—C2	120.9 (3)	**C10—C9—C8**	104.6 (3)
C2B—C1—C2	116.7 (3)	**C16—C10—C9**	102.3 (3)
C3—C2—C1	122.0 (3)	**C12—C11—C16**	119.0 (4)
C3B—C2B—C1	121.3 (3)	**C11—C12—C13**	120.8 (4)
C2—C3—C4	121.3 (3)	**C12—C13—C14**	120.5 (4)
C2B—C3B—C4	122.1 (3)	**C15—C14—C13**	118.9 (4)
C3—C4—C3B	116.6 (3)	**C14—C15—C16**	120.2 (4)
C3—C4—C5	122.5 (3)	**C14—C15—C8**	129.6 (3)

C3B—C4—C5	121.0 (3)	**C16—C15—C8**	110.2 (3)
C6—C5—C4	128.6 (3)	**C15—C16—C11**	120.5 (3)
C5—C6—C7	123.2 (3)	**C15—C16—C10**	110.1 (3)
N2—C7—C6	122.3 (3)	**C11—C16—C10**	129.3 (3)
N2—C8—C15	113.7 (3)	**C1—N1—C17**	121.5 (3)
N2—C8—C9	110.4 (3)	**C1—N1—C17B**	120.7 (3)
C15—C8—C9	102.0 (3)	**C17—N1—C17B**	117.1 (3)
O1—C9—C10	107.8 (3)	**C7—N2—C8**	117.7 (3)

Table S2. Catalán solvent parameters {SA, SB, SP, SdP}

Solvent	SP	SdP	SA	SB	Abs	Em	SS
Cyclohexane	0.616	0	0	0.056	28090	24876	3214
Dioxane	0.737	0.312	0	0.444	27778	23809	3969
Toluene	0.782	0.284	0	0.128	27397	24096	3301
Diethyl eter	0.617	0.385	0	0.562	27933	23866	4067
MTBE[a]	0.622	0.422	0	0.567	28090	23923	4167
Chloroform	0.783	0.614	0.047	0.071	21142	19157	1985
Buthyl acetate	0.674	0.535	0	0.525	27624	23202	4422
Ethyl acetate	0.656	0.603	0	0.542	27778	22727	5051
Tetrahydrofuran	0.714	0.634	0	0.591	27472	22472	5000
Dichloromethane	0.761	0.769	0.04	0.178	27174	22573	4601
Octanol	0.713	0.454	0.299	0.923	27174	22321	4853
i-Propanol	0.633	0.808	0.283	0.83	27472	22075	5397
Acetone	0.651	0.907	0	0.475	27624	22124	5500
Ethanol	0.633	0.783	0.4	0.658	27397	21930	5467
Methanol	0.608	0.904	0.605	0.545	27320	17668	9650
Acetonitrile	0.645	0.974	0.044	0.286	27624	21786	5838
DMF[b]	0.759	0.977	0.031	0.613	27397	21692	5705
Ethyleneglycol	0.777	0.91	0.717	0.534	26954	18868	8086
DMSO[c]	0.83	1	0.072	0.647	27472	21505	5967
Water	0.681	0.997	1.062	0.025	26881	19120	7761

[a] Methyl-tert-butyl ether, [b] N,N-dimethylformamide and [c] Dimethyl sulfoxide

Table S3. Kamlet-Taft solvent parameters for $\bar{\nu}_{abs}$, $\bar{\nu}_{em}$, and $\Delta\bar{\nu}$ (in cm^{-1})

Solvent	*a*	*β*	*π**	Abs	Em	SS
Cyclohexane	0	0	0	28090	24876	3214
Dioxane	0	0.37	0.55	27778	23809	3969
Toluene	0	0.11	0.54	27397	24096	3301
Diethyl eter	0	0.47	0.27	27933	23866	4067
MTBE[a]	0	0.49	0.46	27624	23202	4422
Buthyl acetate	0	0.45	0.55	27778	22727	5051
Ethyl acetate	0	0.55	0.58	27472	22472	5000
Tetrahydrofuran	0.3	0	0.82	27174	22573	4601
Dichloromethane	0.77	0.81	0.4	27174	22321	4853
Octanol	0.76	0.95	0.48	27472	22075	5397
i-Propanol	0.08	0.48	0.71	27624	22124	5500
Acetone	0.83	0.77	0.54	27397	21930	5467
Ethanol	0.93	0.62	0.6	27248	17668	9580
Acetonitrile	0.19	0.31	0.75	27624	21786	5838
DMF[b]	0	0.69	0.88	27397	21692	5705
Ethyleneglycol	0.9	0.52	0.92	26954	18868	8086
DMSO[c]	0	0.76	1	27472	21505	5967
Water	1.17	0.47	1.09	26881	19120	7761

[a] Methyl-tert-butyl ether, [b] N,N-dimethylformamide and [c] Dimethyl sulfoxide

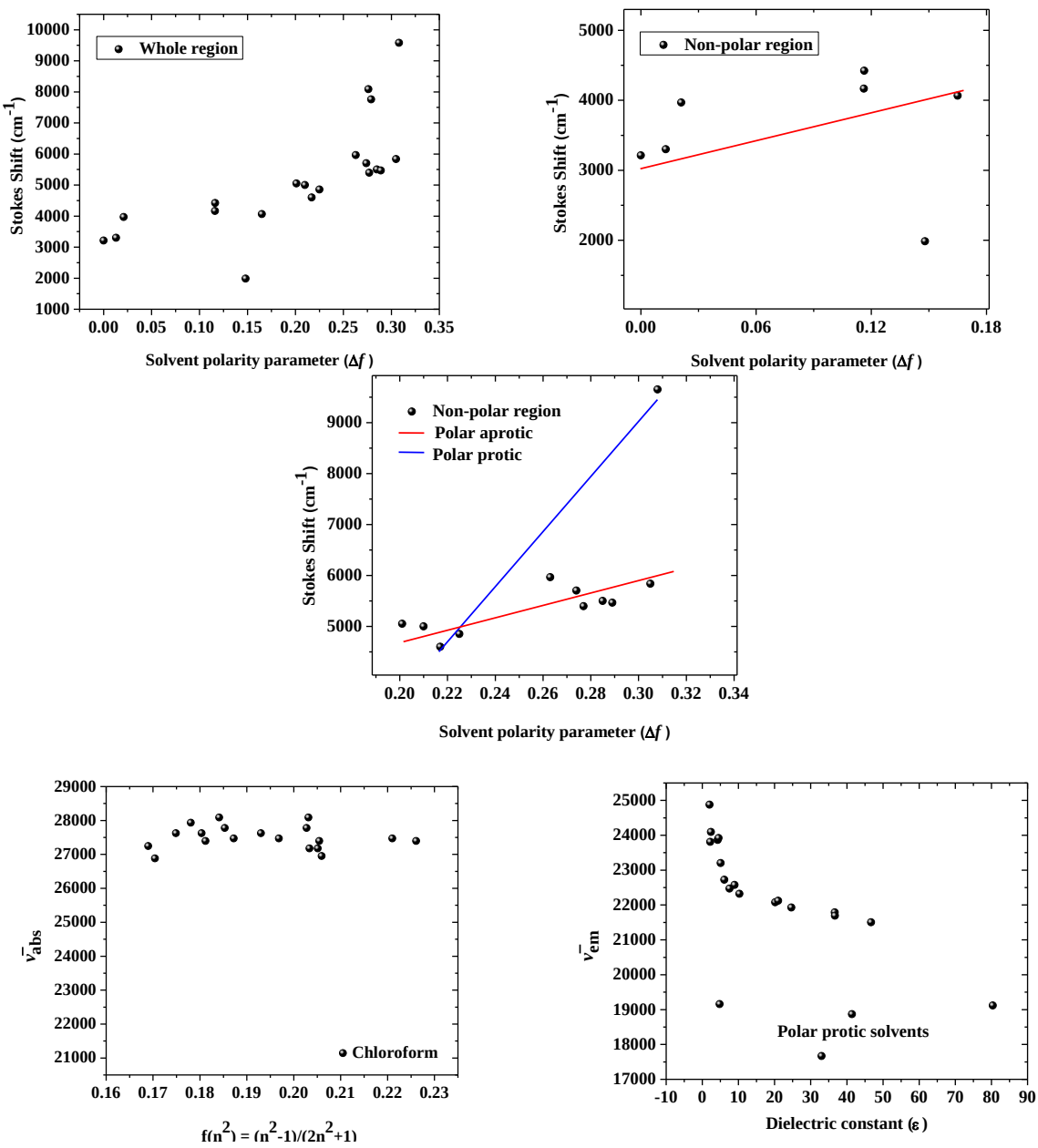


Figure S2 Lippert-Mataga Plots for compound **P1**:

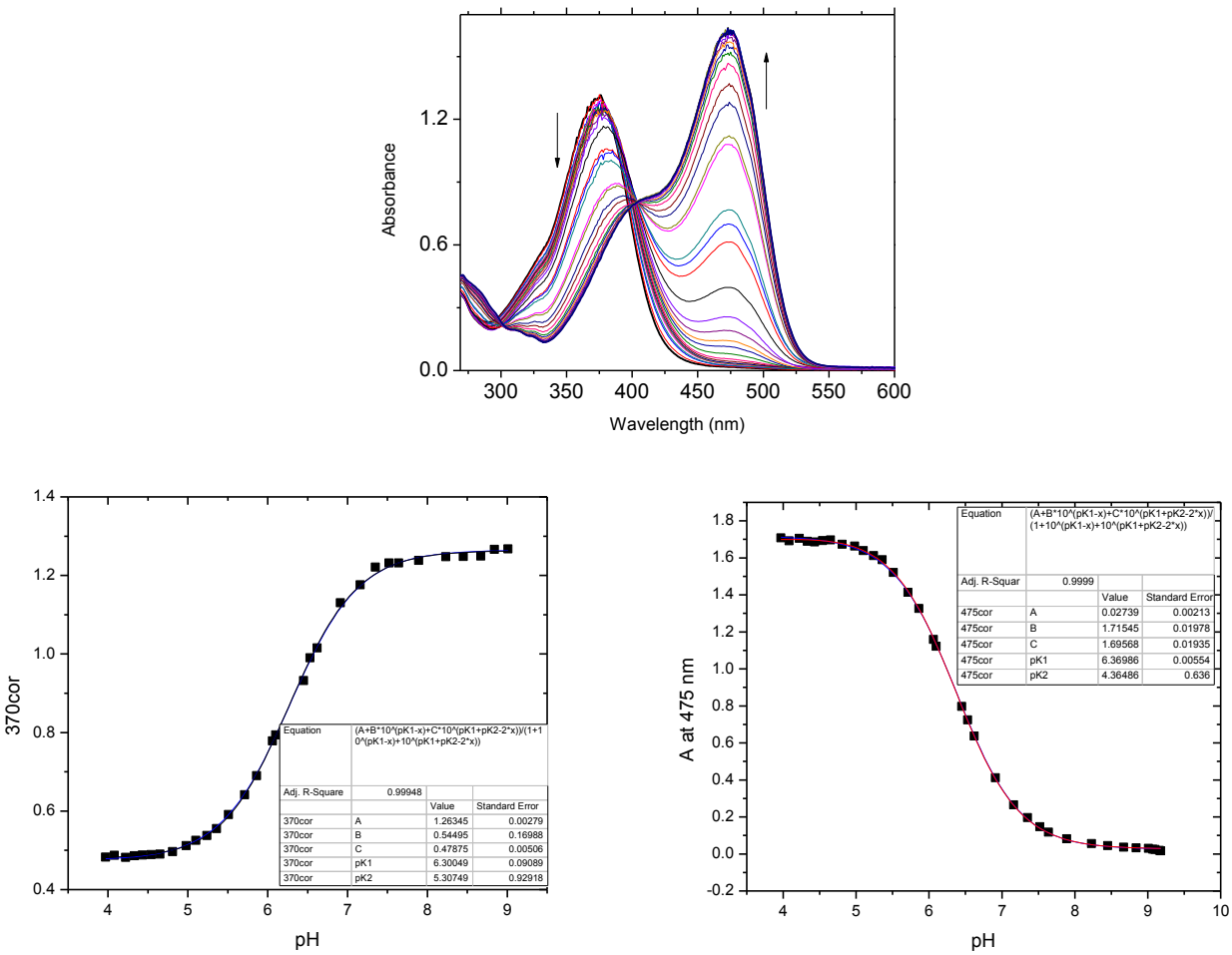
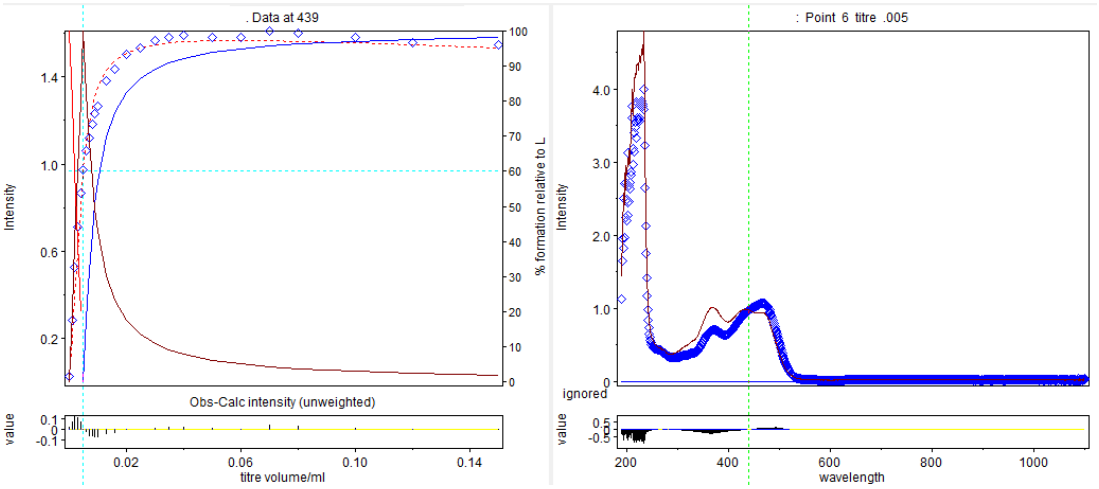


Figure S3. Spectrophotometric pH titration of **P1** in using hexadecyltrimethylammonium chloride (HTAB, 5 mM) and *N*-Cyclohexyl-2-aminoethanesulfonic acid (CHES) buffer at pH 9.2

a) Spectrophotometric titration: 2:1 complex



b) Spectrophotometric titration: 1:1 complex

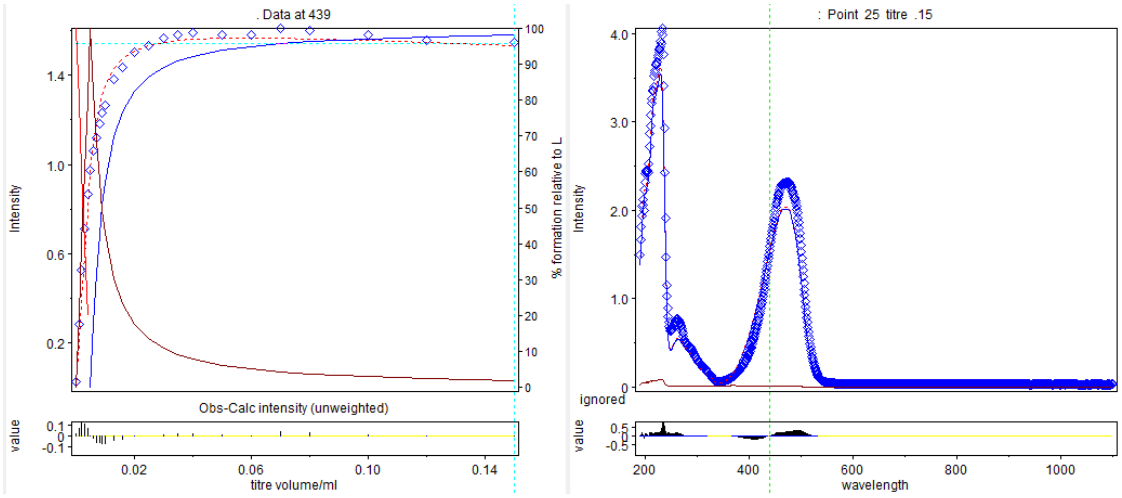
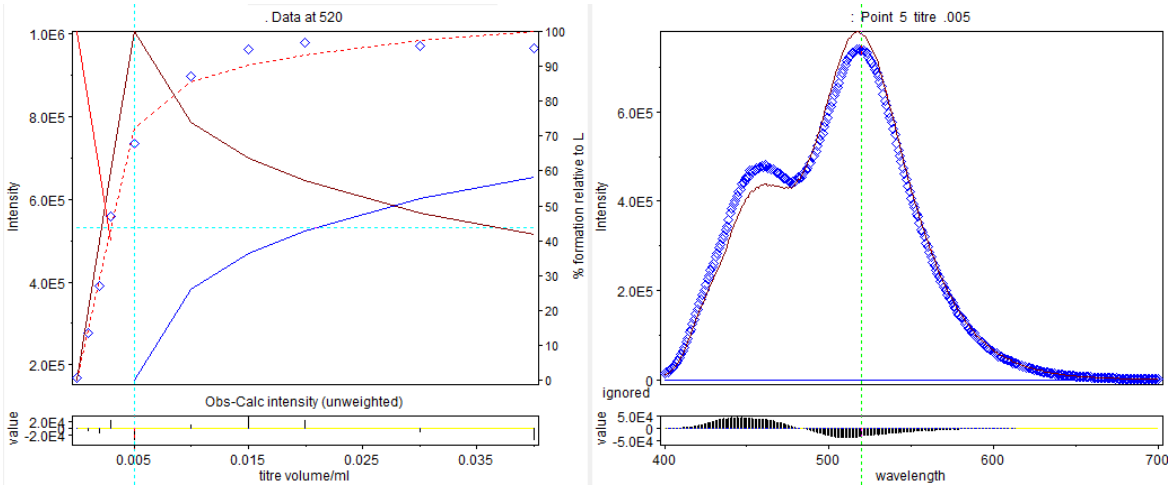


Figure S4A. Spectrophotometric for $4x10^{-5}$ M **P1** with (0 to $5.6x10^{-4}$ M) $SnPh_2^{2+}$ in acetonitrile : water (4 : 96, v/v) solution. The maroon line accounts for [**P1** : Sn] = 2 : 1 complex, observed in a); while the blue line for 1 : 1 complex observed in b).

a) Fluorimetric titration: 2:1 complex



b) Fluorimetric titration: 1:1 complex

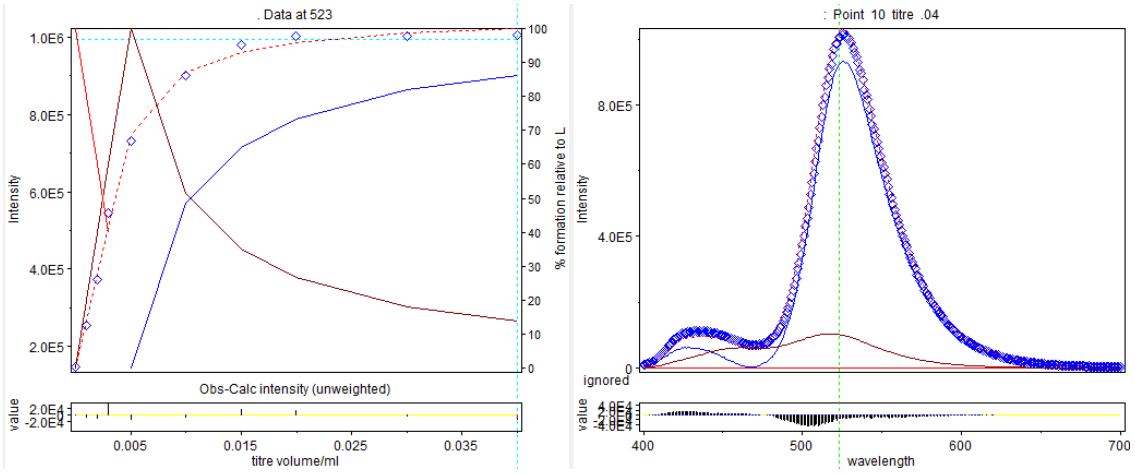


Figure S4B. Fluorimetric titration of $4x10^{-5}$ M **P1** with (0 to $5.6x10^{-4}$ M) $SnPh_2^{2+}$ in acetonitrile : water (4 : 96, v/v) solution. The maroon line accounts for [**P1** : Sn] = 2 : 1 complex, observed in a); while the blue line for 1 : 1 complex, observed in b).

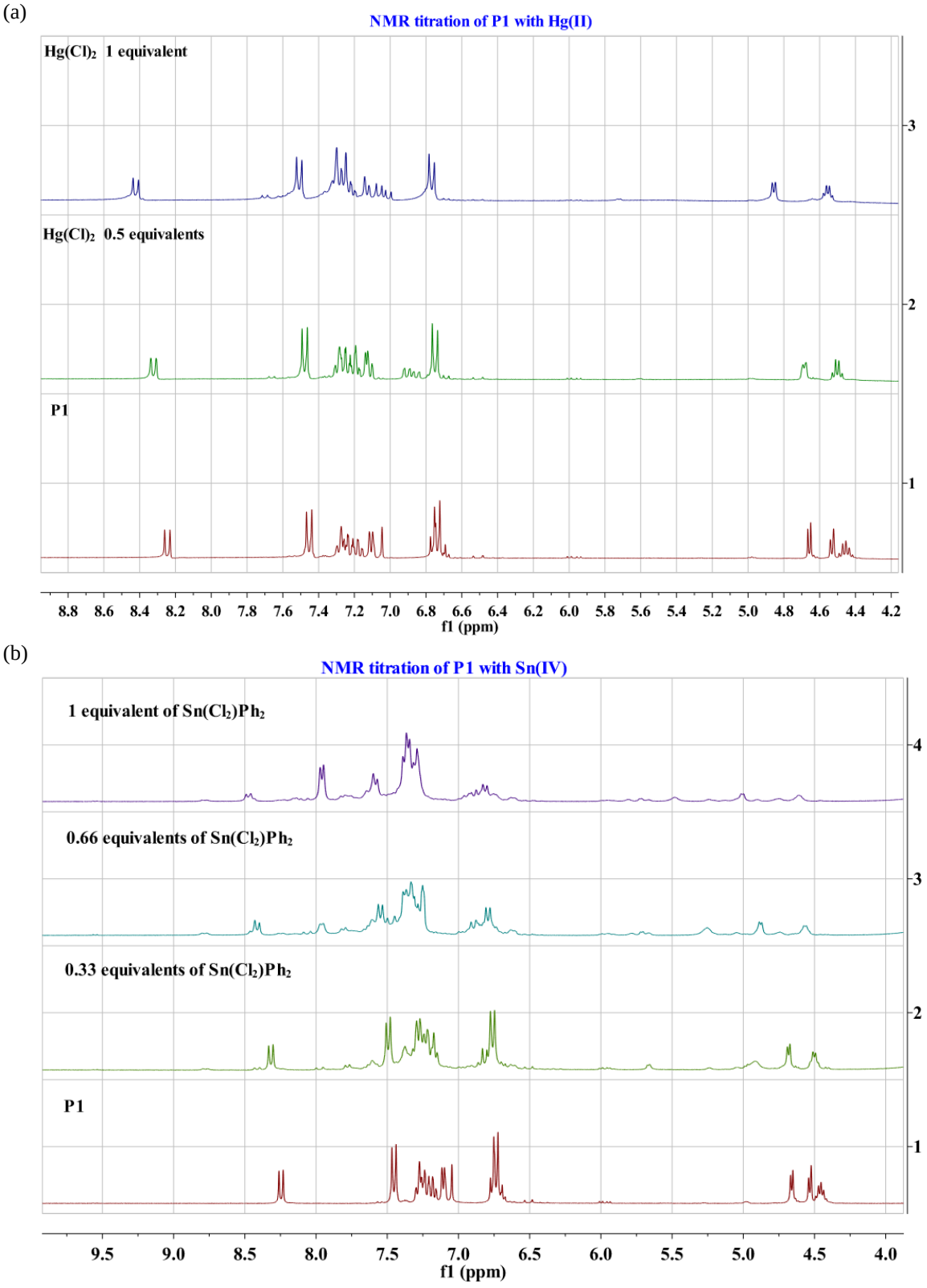


Figure S5. ^{1}H-NMR titration of **P1** with (a) $HgCl_2$ and (b) $SnPh_2Cl_2$ in DMSO-δ_6.

a)

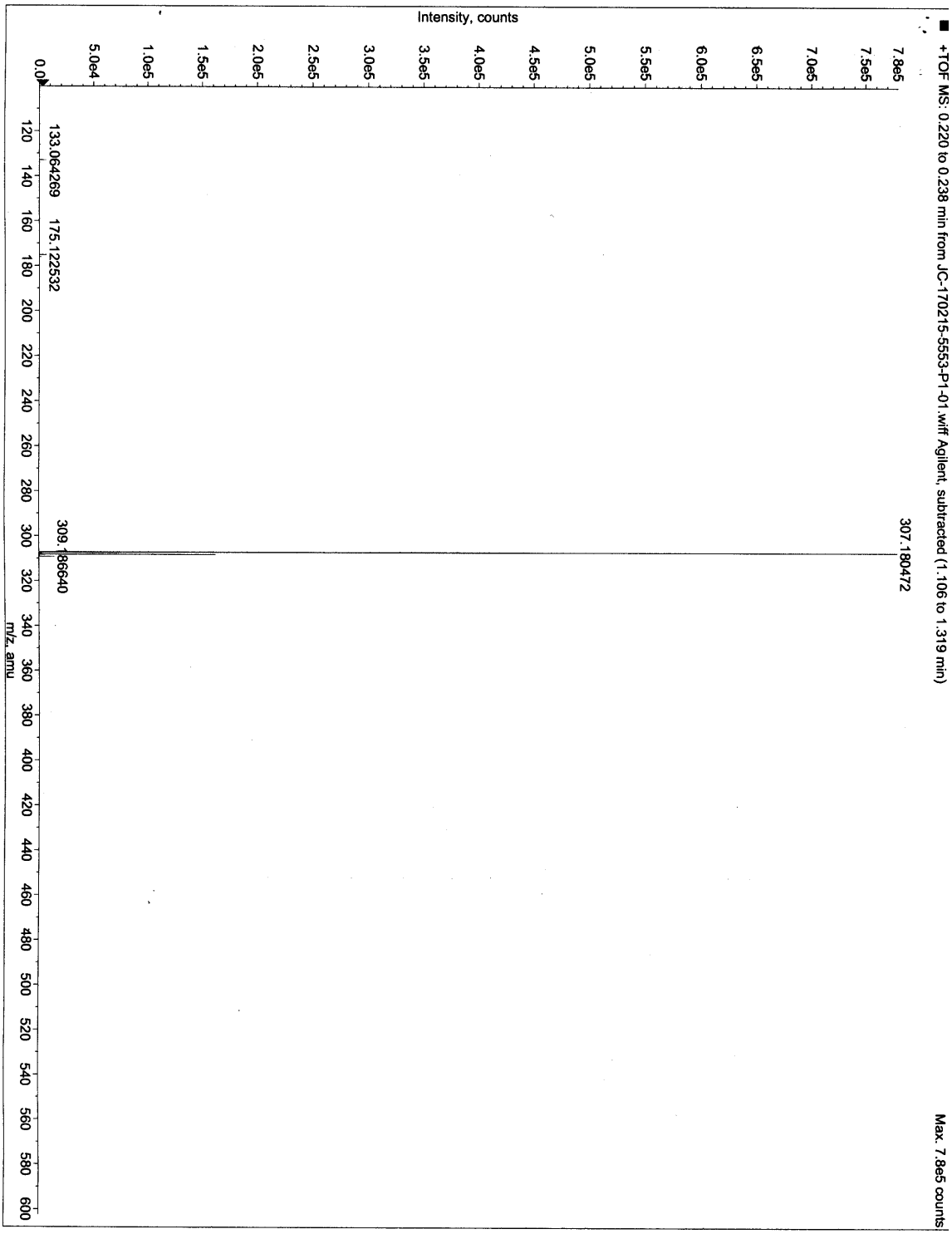


Figure S6. Continue…

…a)

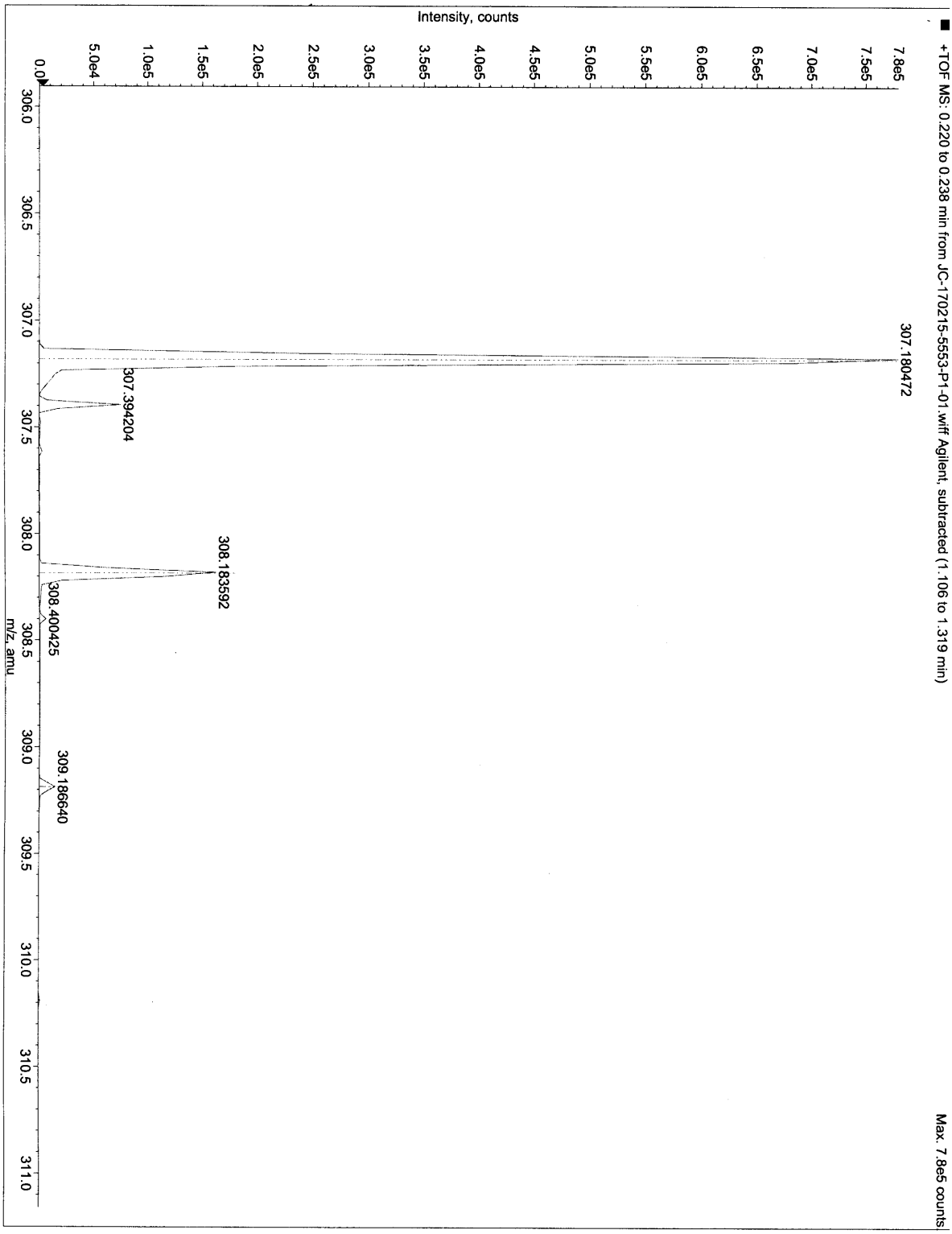


Figure S6. Continue…

b)

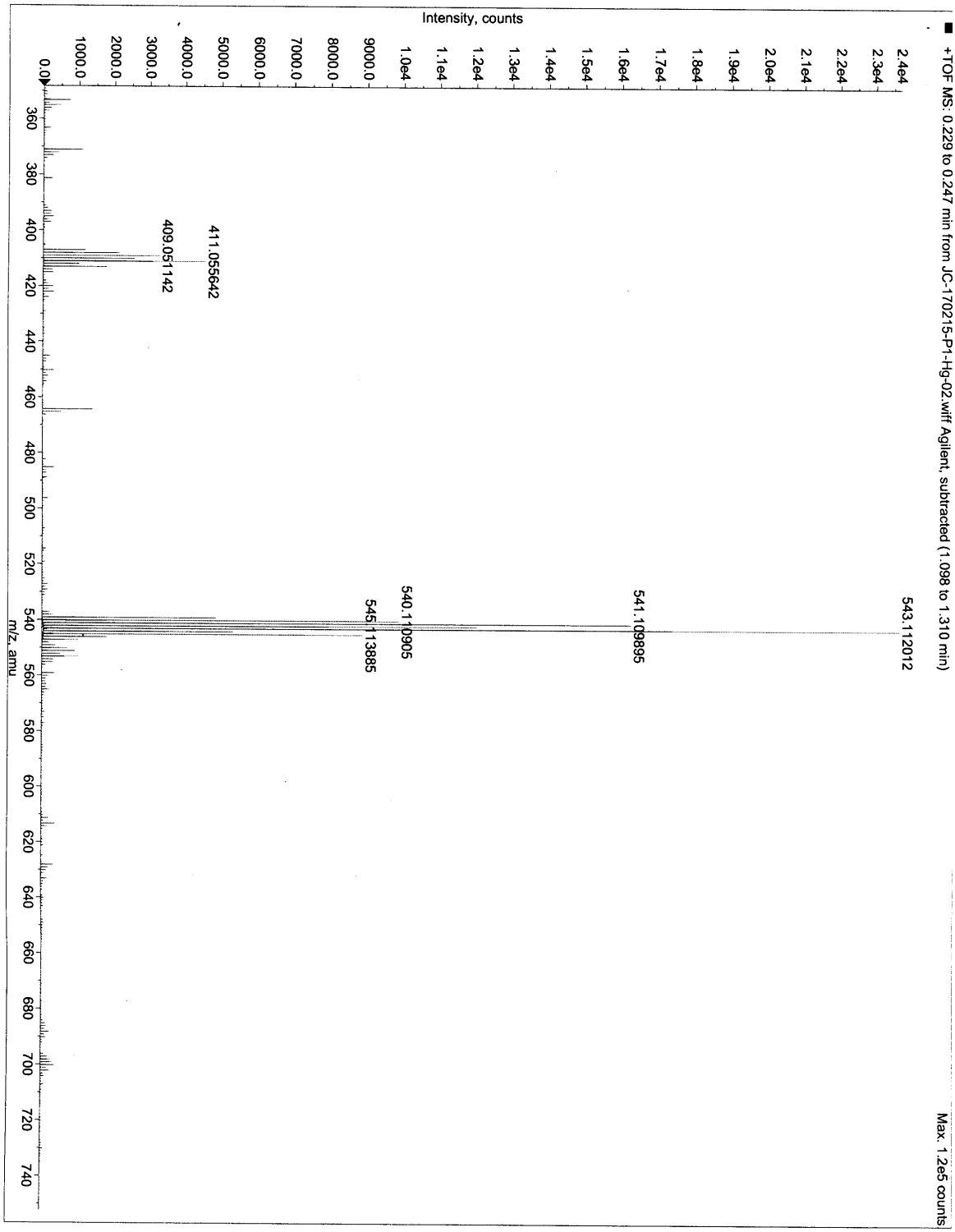


Figure S6. Continue…

…b)

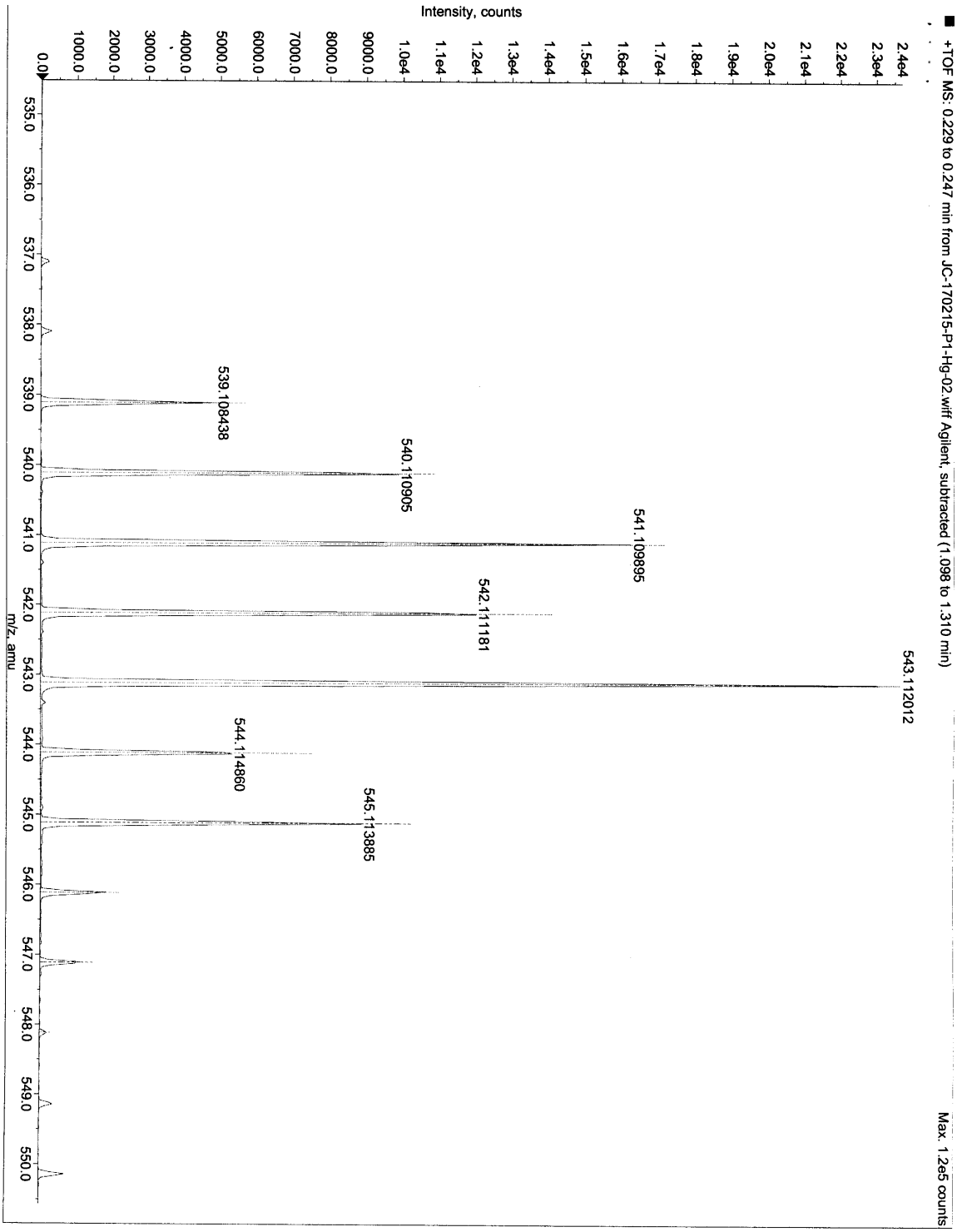


Figure S6. Continue…

c)

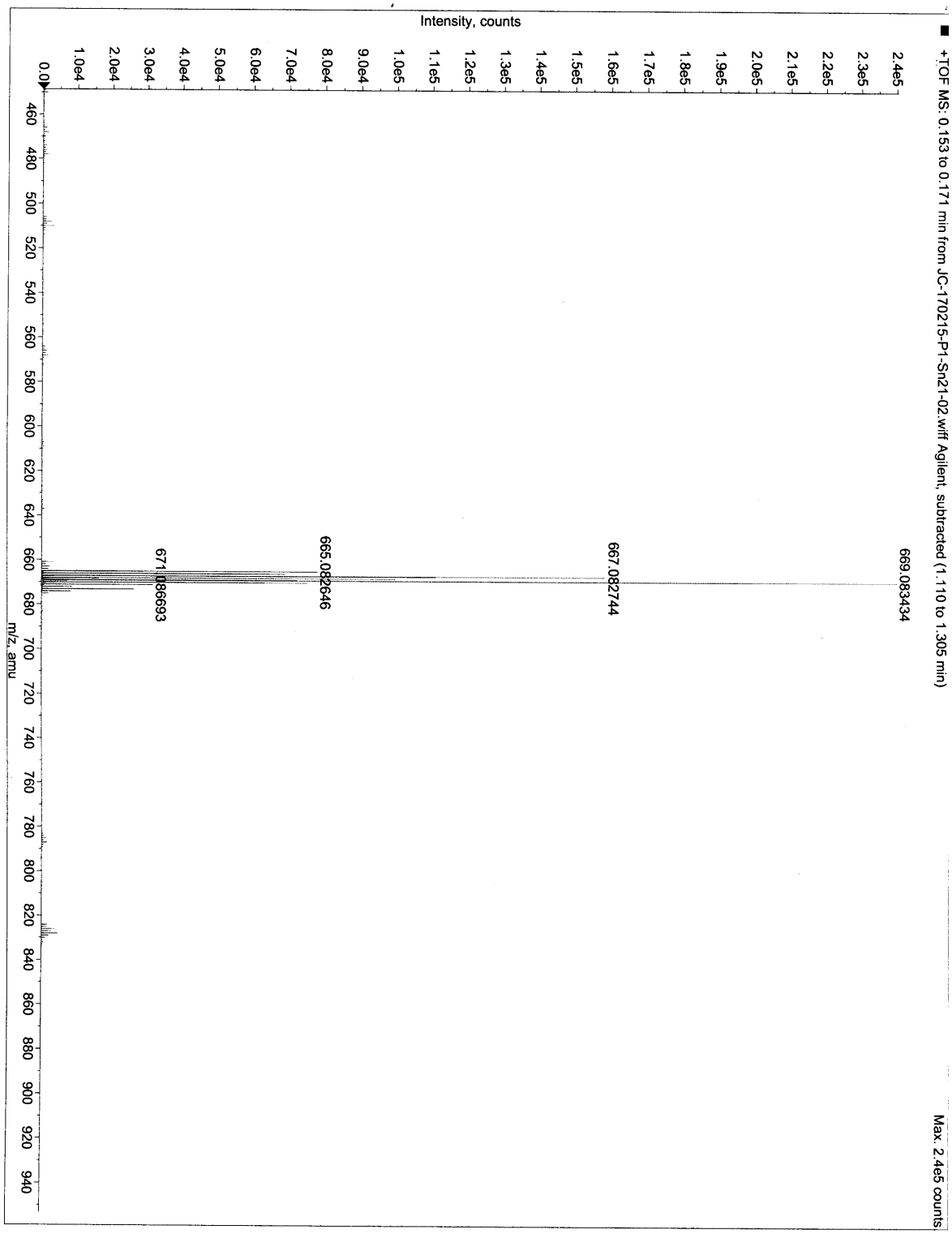


Figure S6. Continue…

…c)

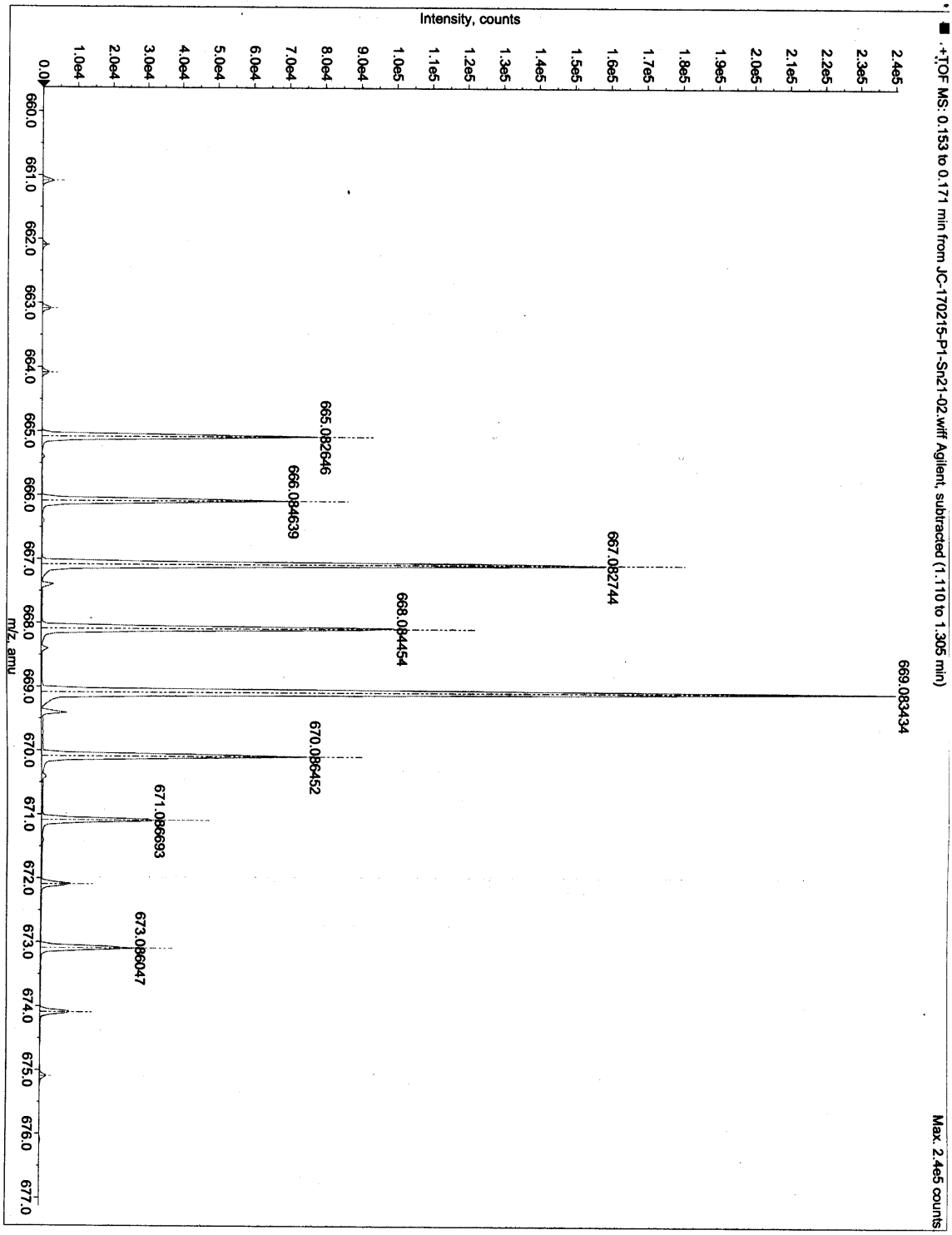


Figure S6. Continue…

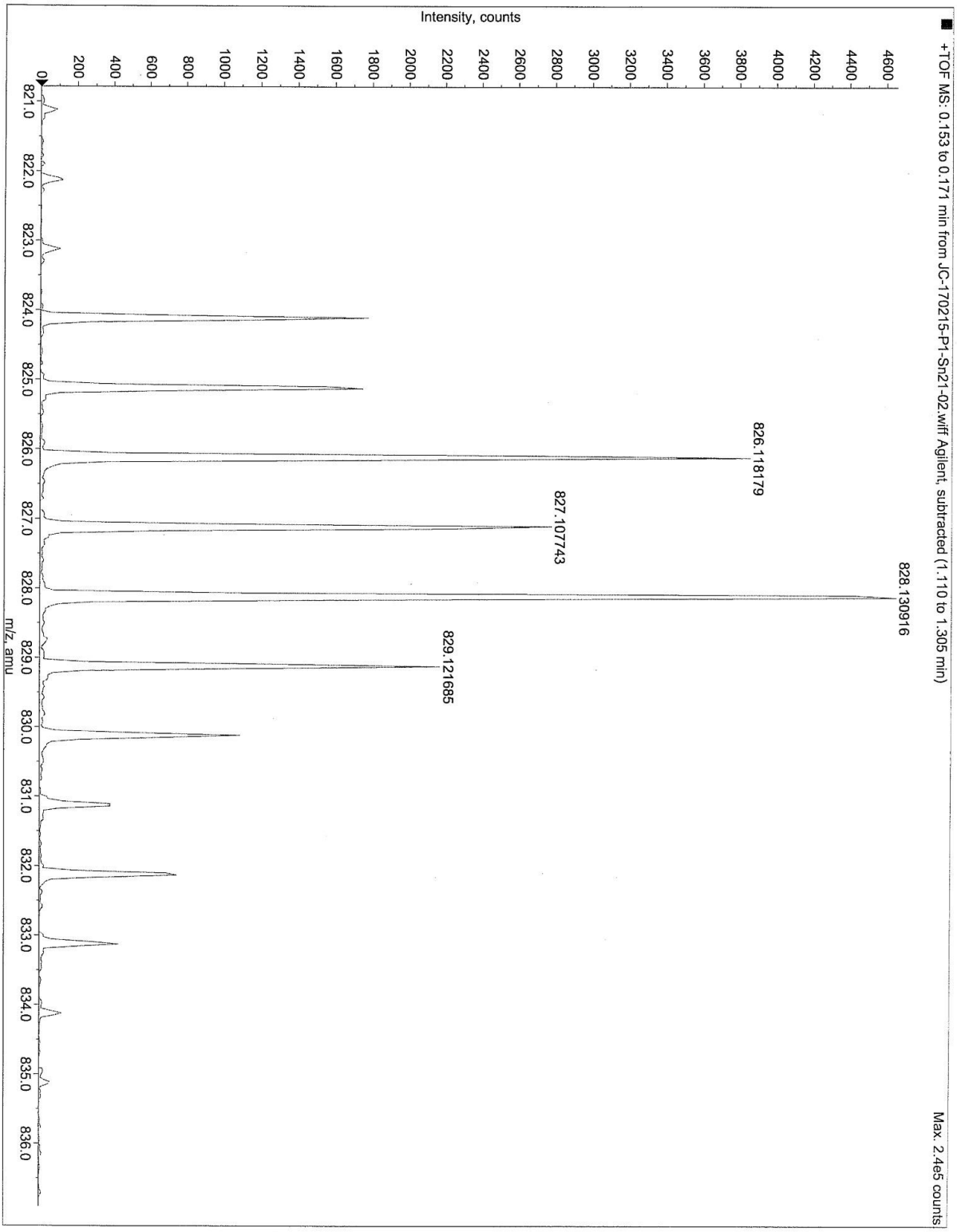


Figure S6. ESI-MS spectra of (a) **P1** and **P1** with (b) $HgCl_2$ and (c) $SnPh_2Cl_2$ in DMSO-δ_6

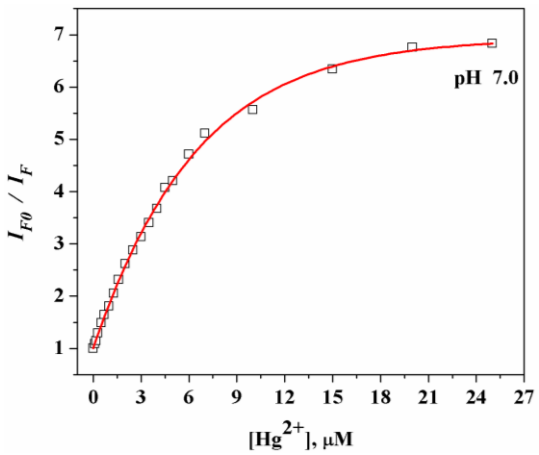
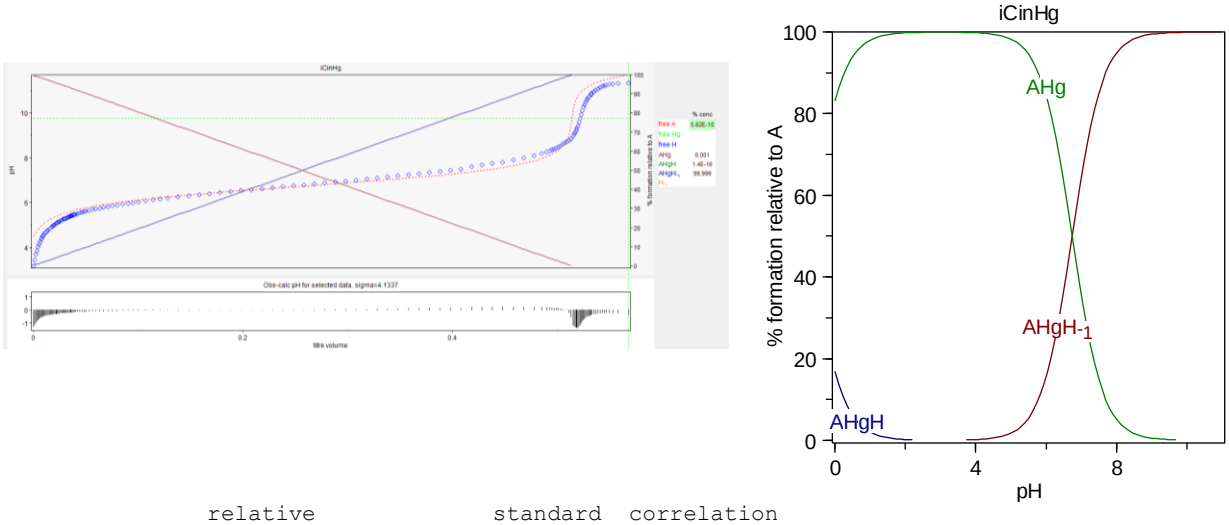


Figure S7. The concentration profile of the quenching effect of Hg^{2+} (Stern-Volmer plot) at pH 7.0



Parameter	relative shift	value	standard deviation	correlation coefficients		
Log beta AHg	0.0000	9.99	1.8E02	-		
Log beta AHgH	-0.9500	10.1303	1.4E03	0.131	-	
Log beta AHgH-1	0.0000	3.2584	1.8E02	1.000	0.131	-

Figure S8. Potentiometric titration of **P1** with Hg^{2+} ions

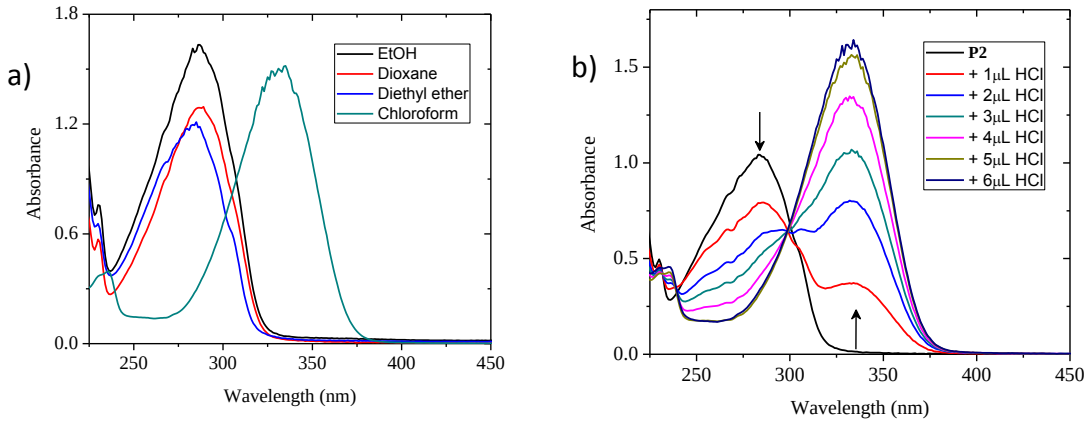


Figure S9. UV-Vis absorption spectra of compound **P1** in a) ethanol, dioxane, diethyl ether and chloroform solvents; b) HCl : ACN (1 : 99, v/v) solution.

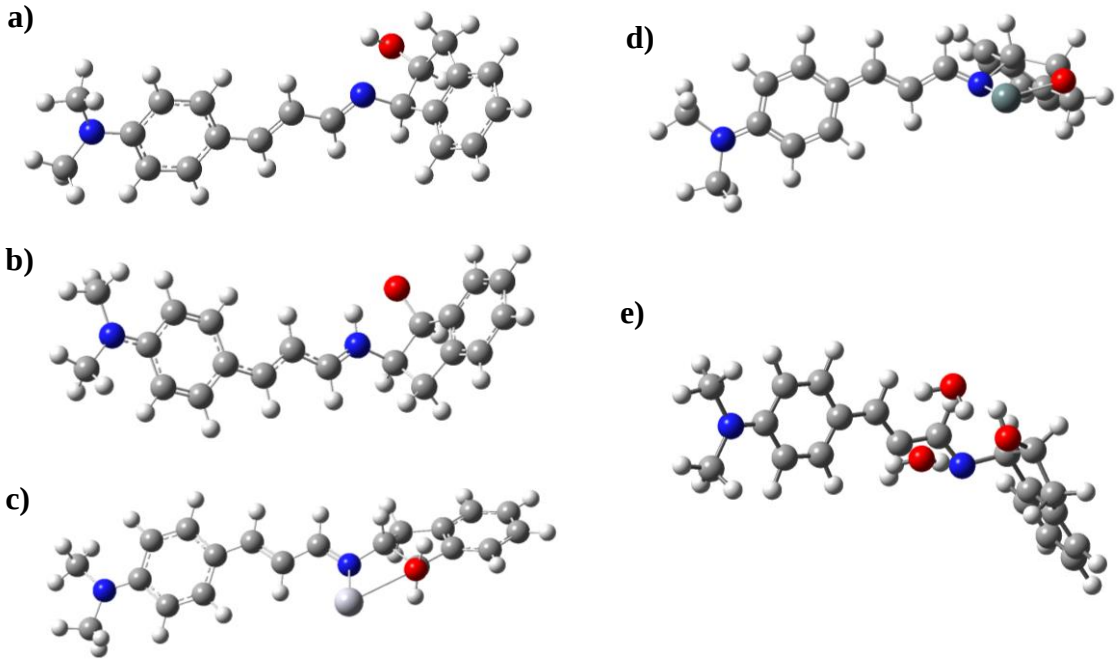


Figure S10. Molecular geometries from **P1**: a) **P1**, b) **P1-H**$^{+}$, c) **P1-Hg**, d) **P1-Sn** and e) **P1** having three water molecules, optimized at a PBE0/6-31+G(d)/IEF-PCM level of theory for the ligand and the LANL2DZ basis set for the Hg^{2+} and Sn^{2+}. For pK_a calculations zero point vibrational energies (ZPVE) were considered to account for thermal and entropic effects. We used the PBE0/6-31+G(d)/IEF-PCM level of theory. In order to determine the ΔG_{solv} the water solvent was modeled by both IEF-PCM and by an implicit (IEF-PCM)–explicit solvent model (IE). In the IE approach two water molecules were included in order to model explicit interactions and its positions were fully optimized as well.

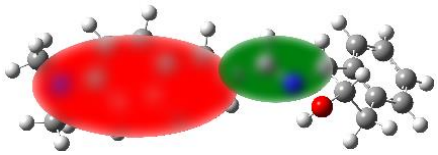


Figure S11. Calculated Density difference for **P1**. The graphical representation of D_{CT} centroids of charge $C_{+}(r)$ green /$C_{-}(r)$ red, isocontour value 0.004 au.

a)

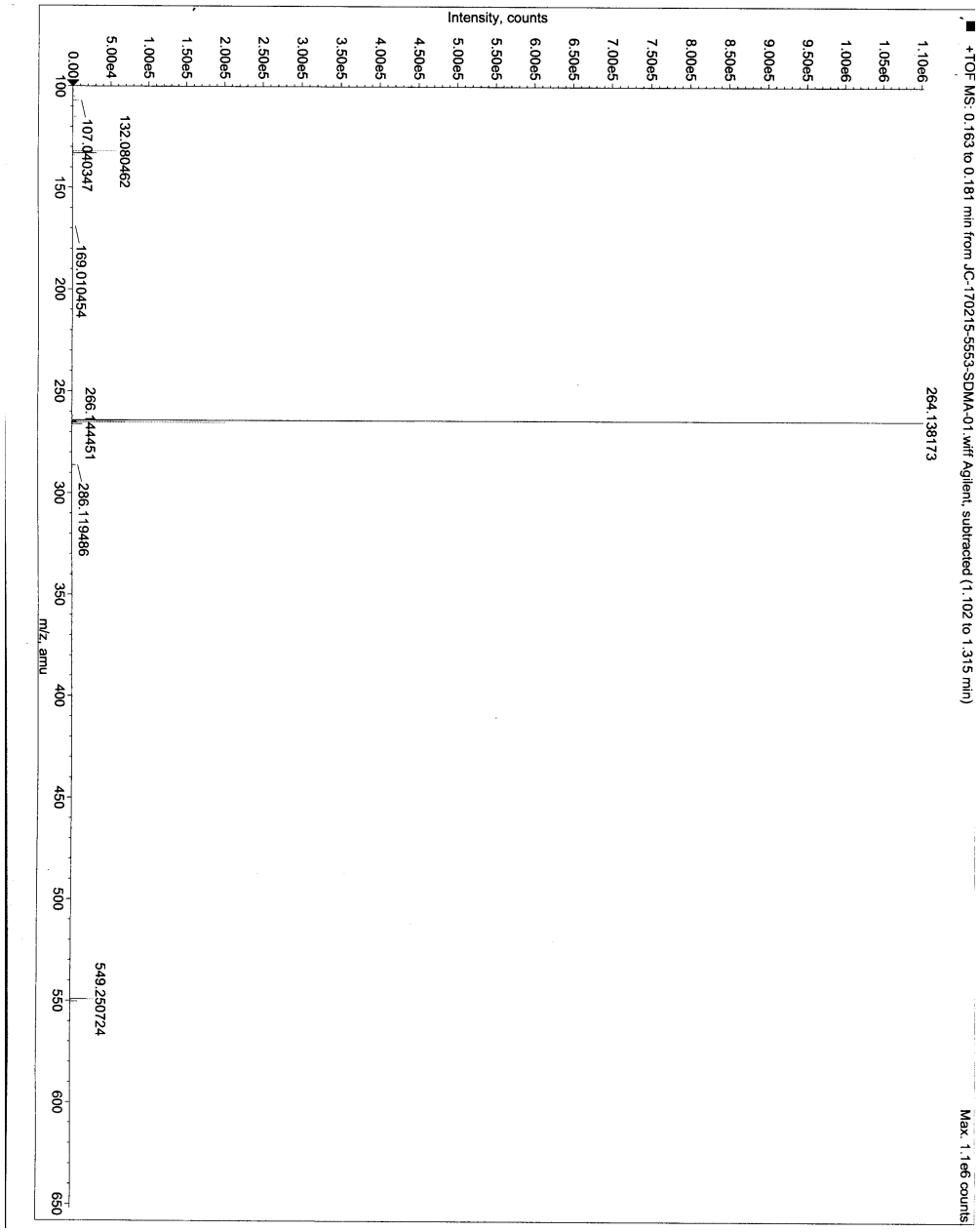


Figure S12. Continue…

…a)

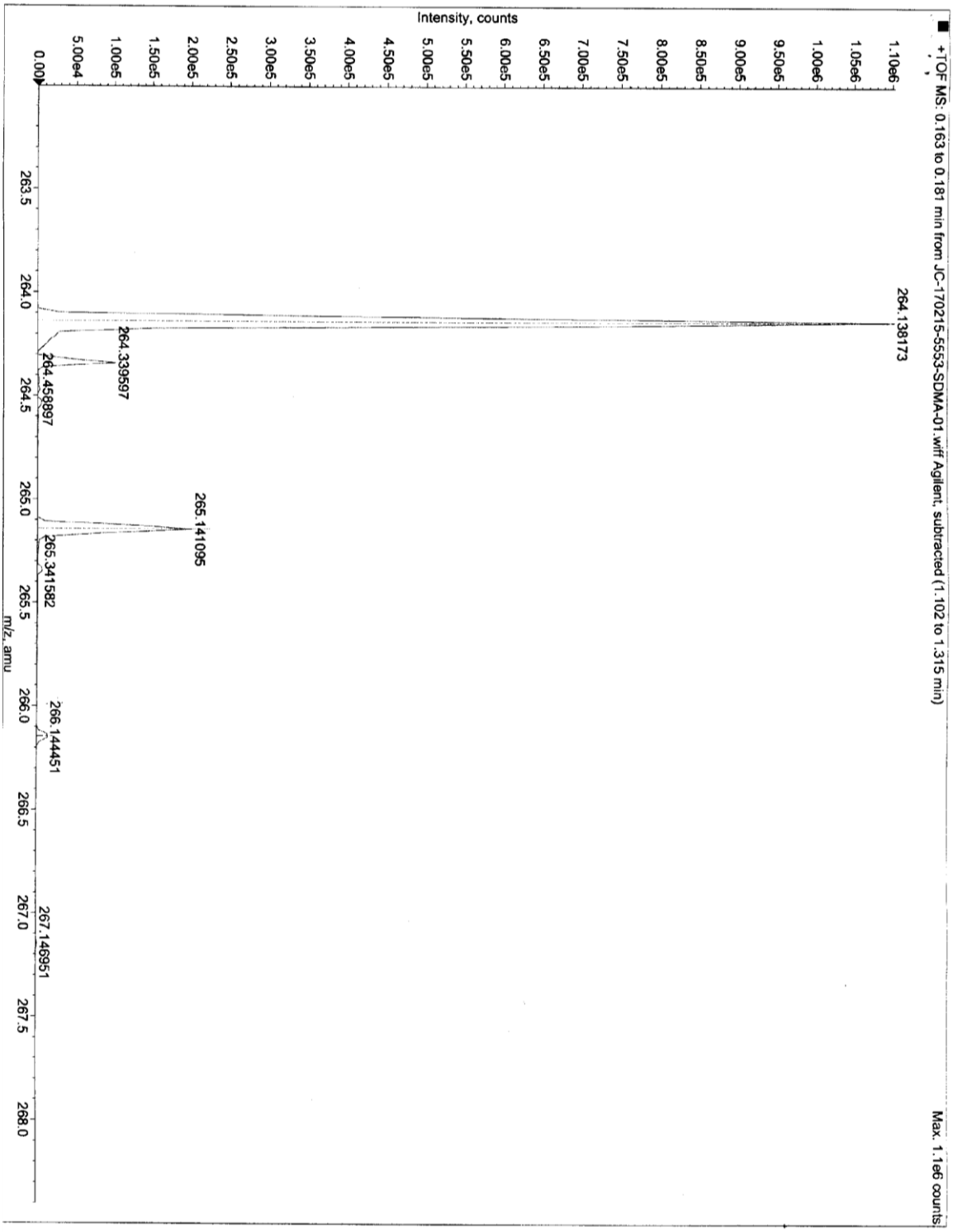


Figure S12. Continue…

b)

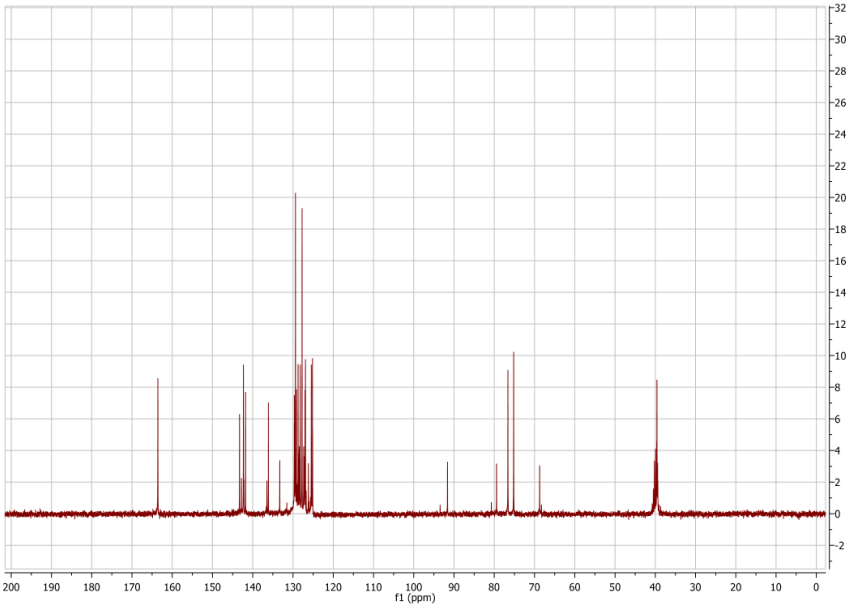


Figure S12. (a) ESI-MS and (b) ^{13}C NMR spectra of **P2** in DMSO-δ_6.

Complete author list of reference 10:

a) Melloni, A.; Paccani, R. R.; Donati, D.; Zanirato, V.; Sinicropi, A.; Parisi, M. L.; Martin, E.; Ryazantsev, M.; Ding, W. J.; Frutos, L. M.; Basosi, R.; Fusi, S.; Latterini, L.; Ferré, N; Olivucci, M. Modeling, Preparation, and Characterization of a Dipole Moment Switch Driven by Z/E Photoisomerization. *J. Am. Chem. Soc.* **2010**, 132, 9310–9319.