

Dalton Transaction
Supporting Information

May 2015

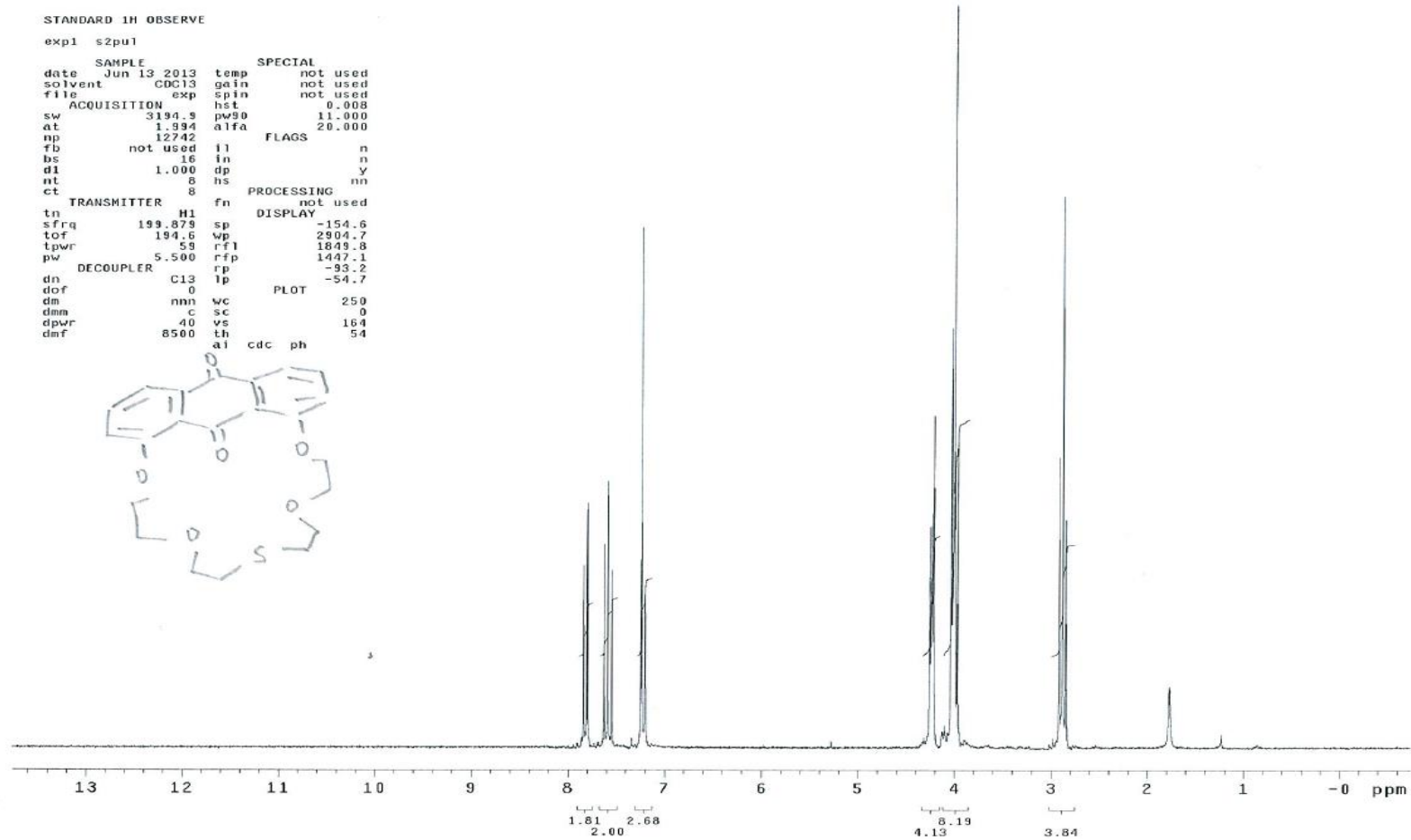
Improved Selectivity for Pb(II) by Sulfur,
Selenium and Tellurium Analogues of 1,8-
Anthraquinone-18-Crown-5: Synthesis,
Spectroscopy, X-ray Crystallography and
Computational Studies

Kadarkaraisamy Mariappan^{*}, Madhubabu Alaparthi, Mariah Hoffman, Myriam Alcantar
Rama, Vinothini Balasubramanian, Danielle M John, and Andrew G Sykes

**Contribution from the Department of Chemistry
University of South Dakota, Vermillion, SD 57069**

*Dedicated to Professor Ajai Kumar Singh, Department of Chemistry at Indian Institute of
Technology, Delhi, India*

^{*}To whom correspondence should be addressed: mkadarka@usd.edu

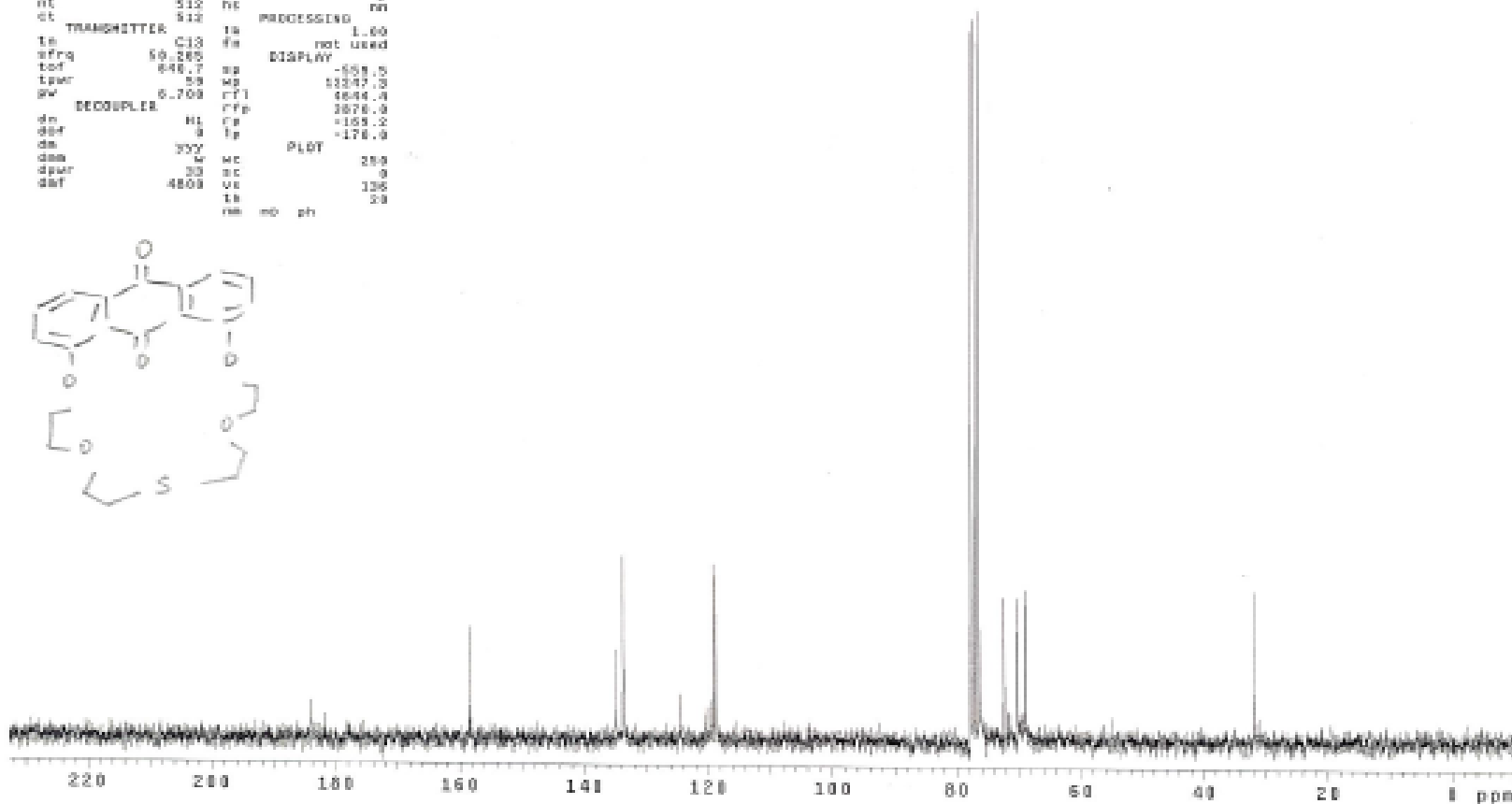
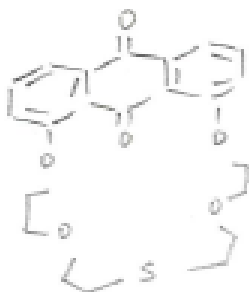


SI Fig. 1: ^1H NMR of compound 2.

13C OBSERVE

exp1 52991

SAMPLE		SPECTRA	
date	May 19 2010	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		lat	0.000
ac	12878.6	pu80	13.000
ac	1.486	shra	20.000
ap	57030	FLAG	
fa	not used	li	n
ba	0.4	ia	n
da	0.000	da	5
nt	512	hc	nn
ct	512	PROCESSING	
TRANSMITTER		fa	1.00
ta	C13	fa	not used
efrq	50.280	DISPLAY	
tof	0.00.7	ap	-0.00.0
tpwr	0.0	wp	112.07.0
pw	0.700	rfl	00.00.4
DECOUPLER		rfa	00.00.0
da	H1	ra	-100.0
def	0	fa	-170.0
da	0.00.0	PLOT	
das	0.00.0	mc	200
dpr	0.00.0	mc	0
daf	4000	va	100
		ta	0.0
		ra	0.0
		mb	ph

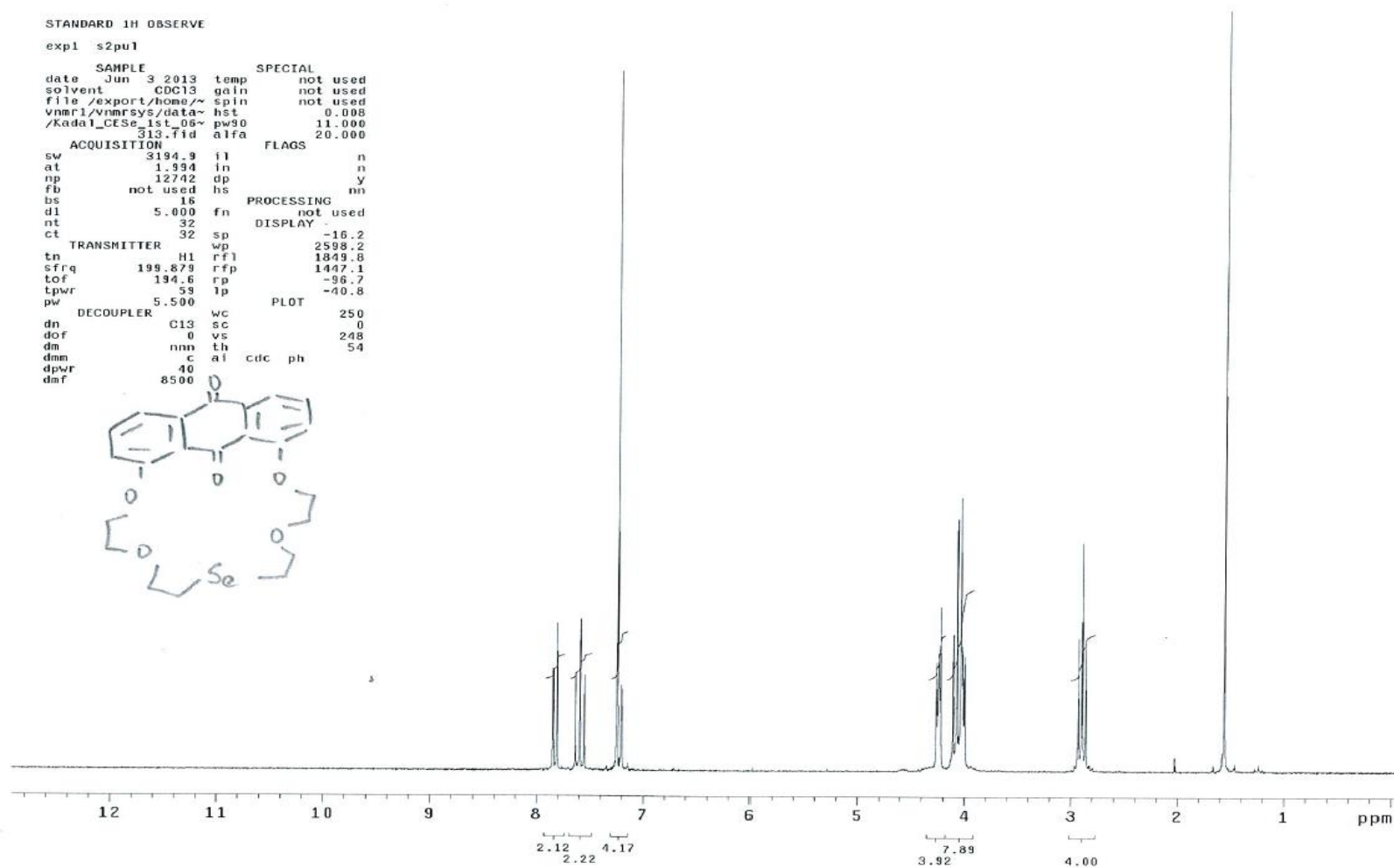
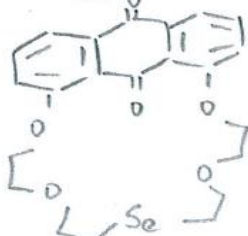


SI Fig. 2: ¹³C NMR of compound 2.

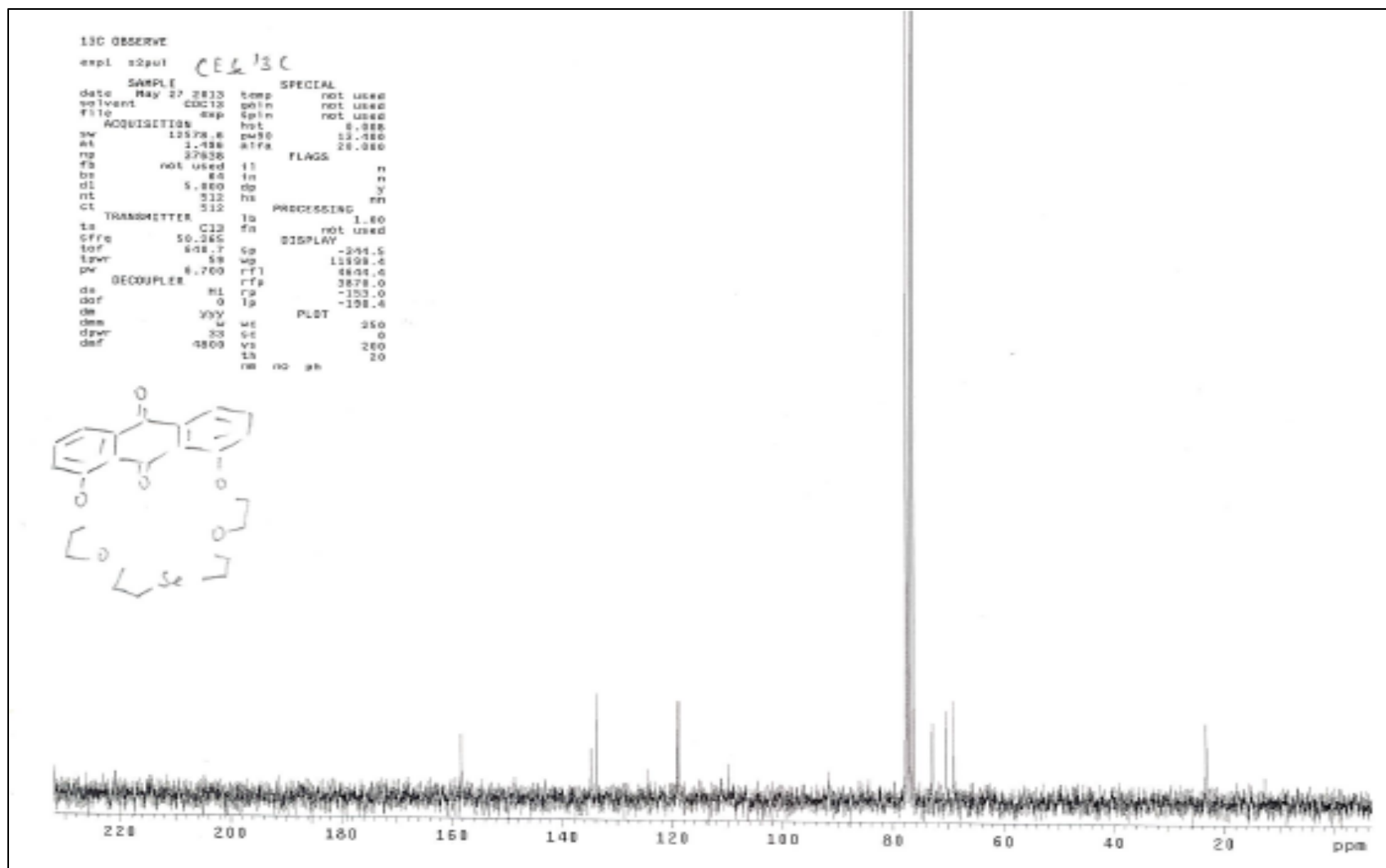
STANDARD 1H OBSERVE

expl s2pu1

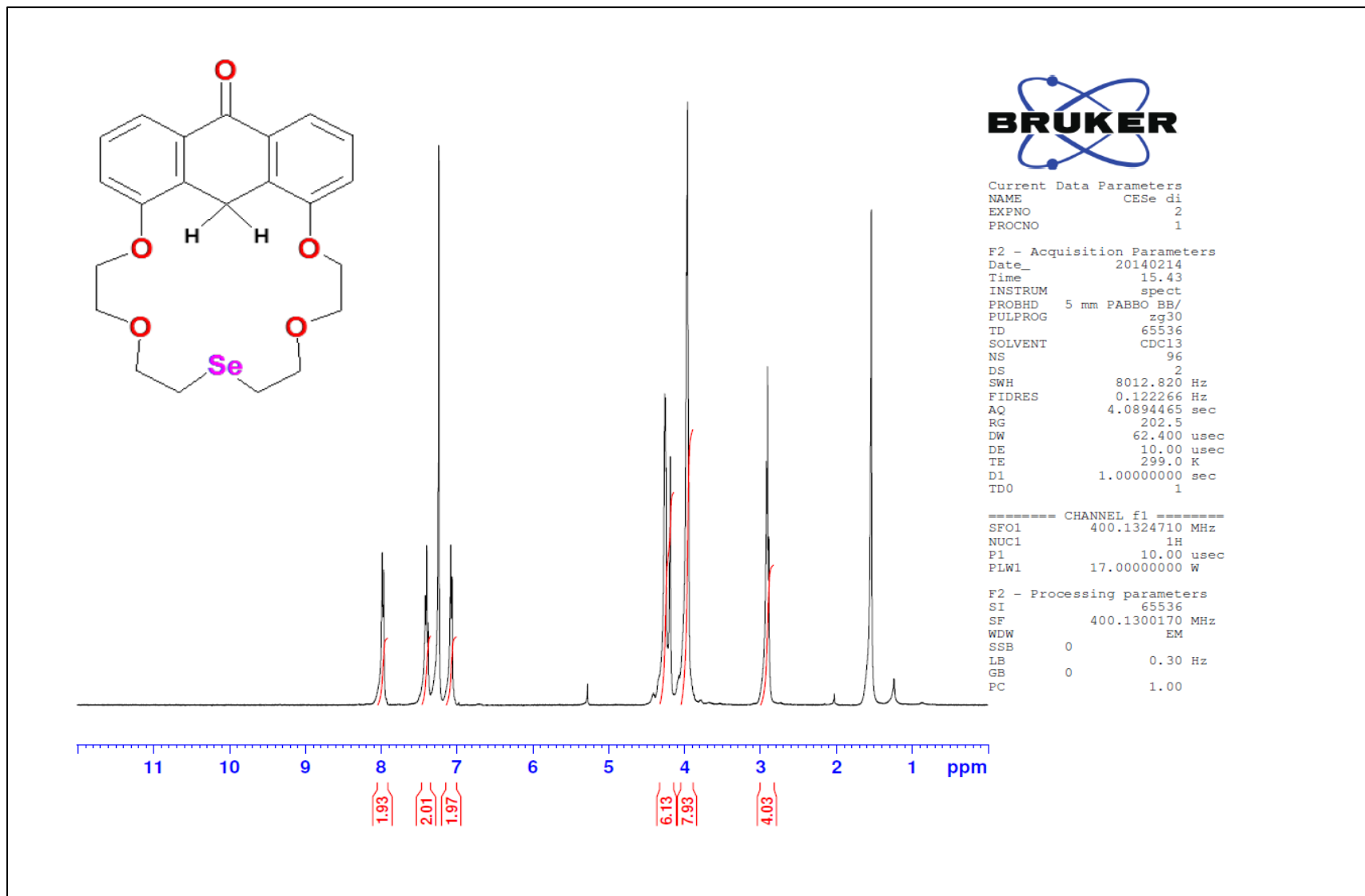
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solvent	CDCl3	gain	not used
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nmr1/vnmr/sys/data/~		hst	0.008
/kadal_CESe_1st_06~		pw90	11.000
313.fid		alfa	20.000
ACQUISITION		FLAGS	
sw	3194.9	il	n
at	1.994	in	n
np	12742	dp	y
fb	not used	hs	nn
bs	16	PROCESSING	
dl	5.000	fn	not used
nt	32	DISPLAY	
ct	32	sp	-16.2
TRANSMITTER		wp	2598.2
tn	H1	rfl	1849.8
sfrq	199.879	rfl	1447.1
lof	194.6	rp	-96.7
tpwr	59	lp	-40.8
pw	5.500	PLOT	
DECOUPLER		wc	250
dn	C13	sc	0
dof	0	vs	248
dm	nm	ch	54
dmm	c	al	cdc ph
dpwr	40		
dmf	8500		

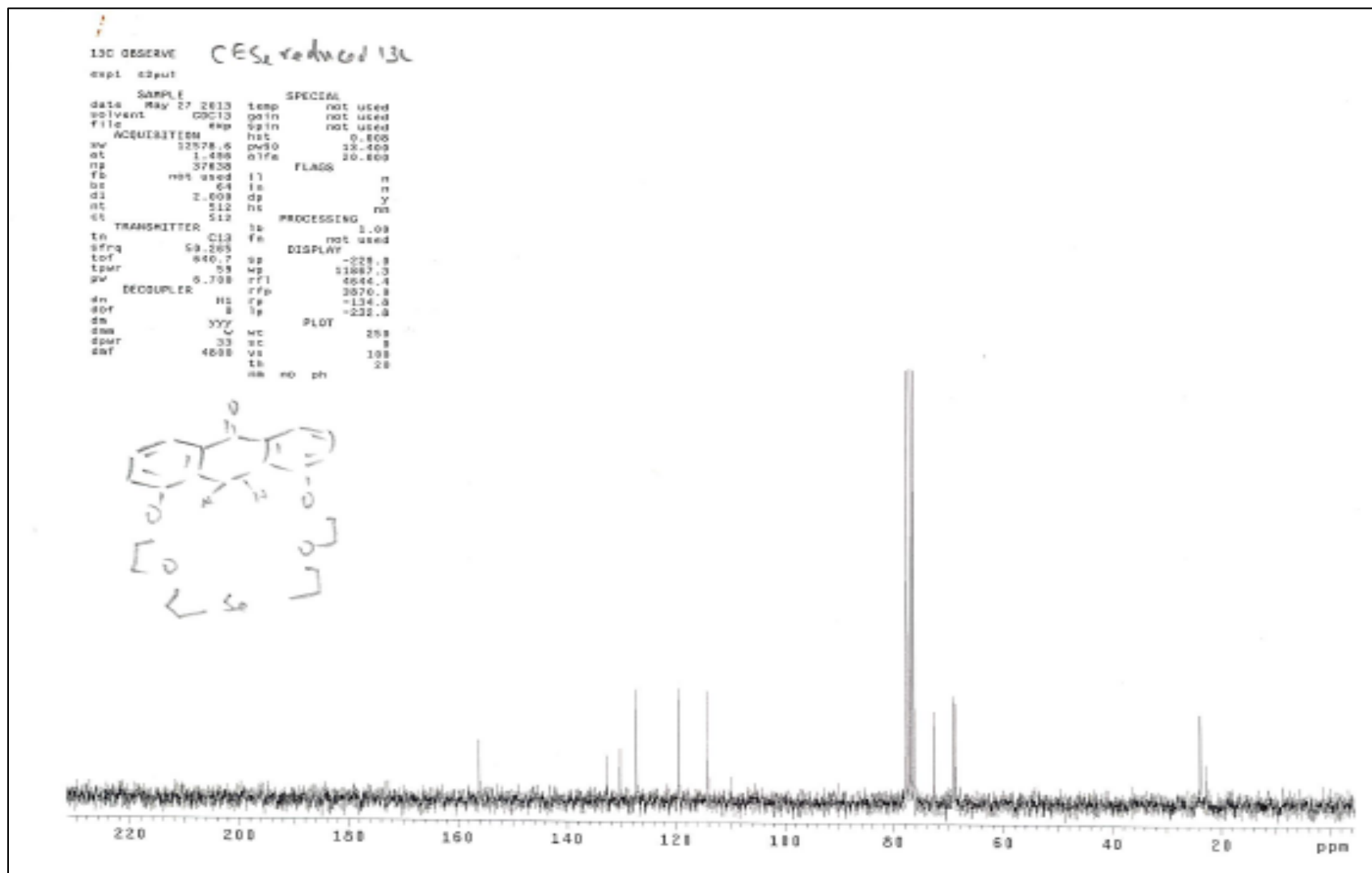


SI Fig. 3: ¹H NMR of compound **3**.

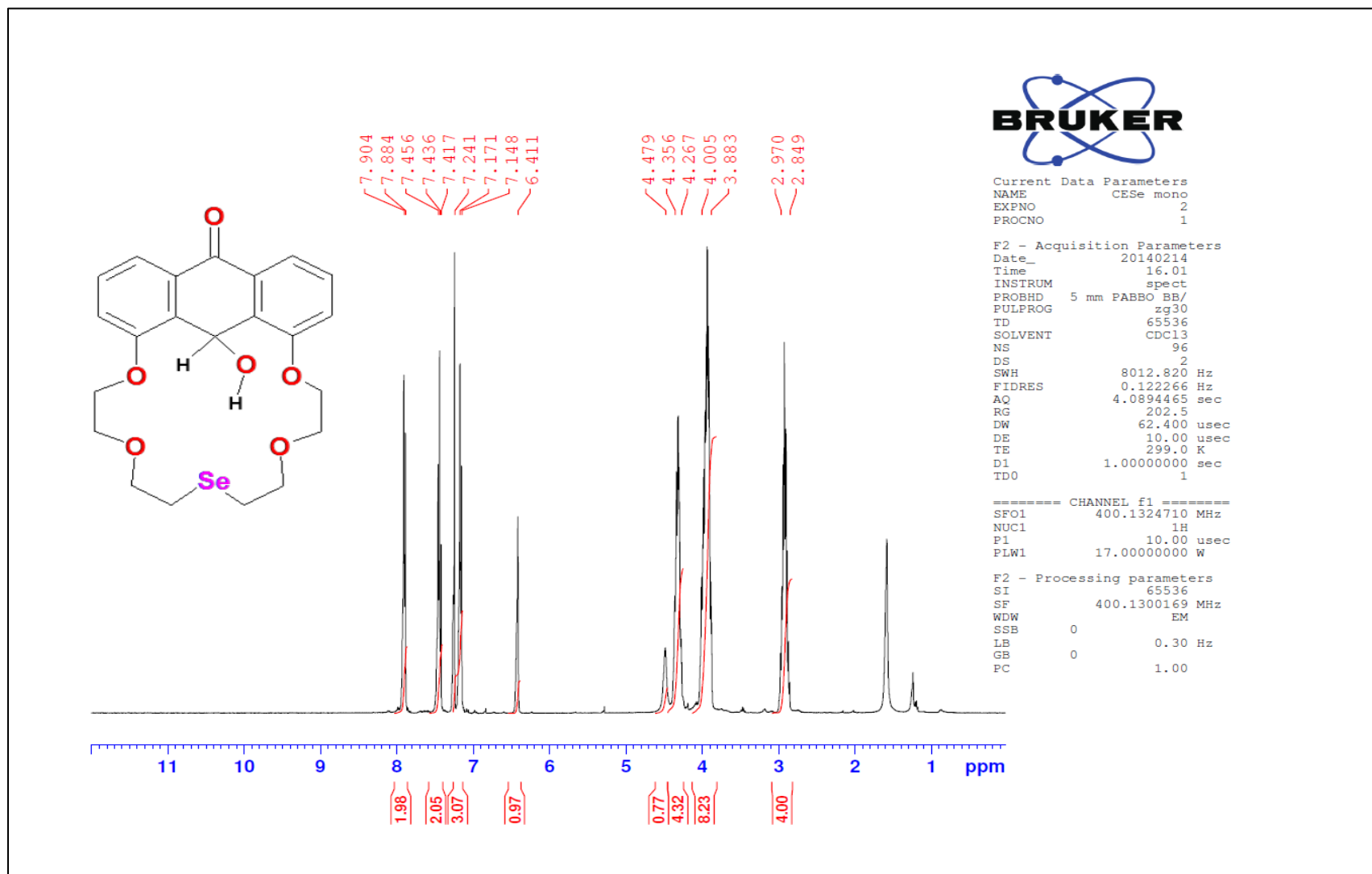


SI Fig. 4: ^{13}C NMR of compound 3.

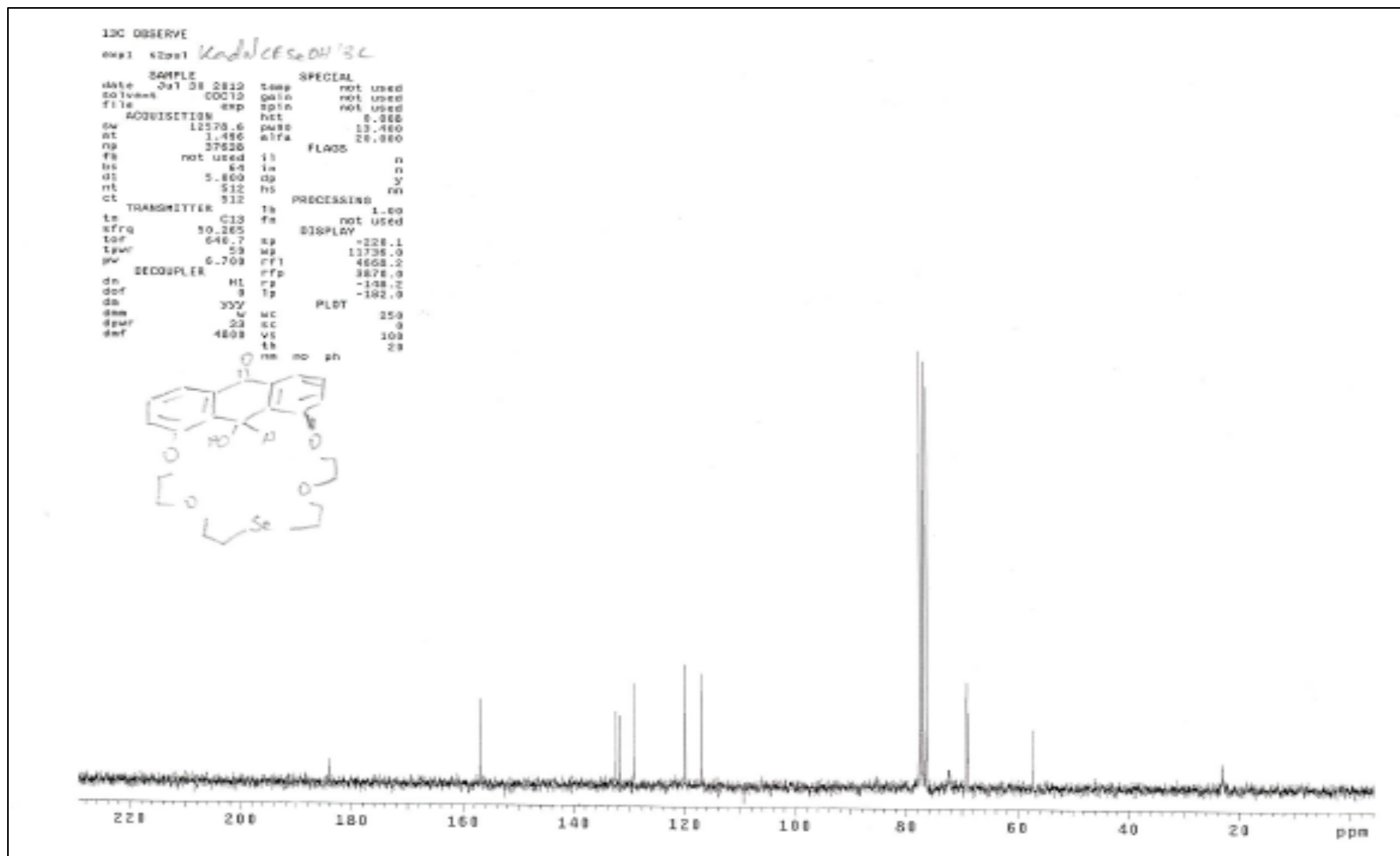




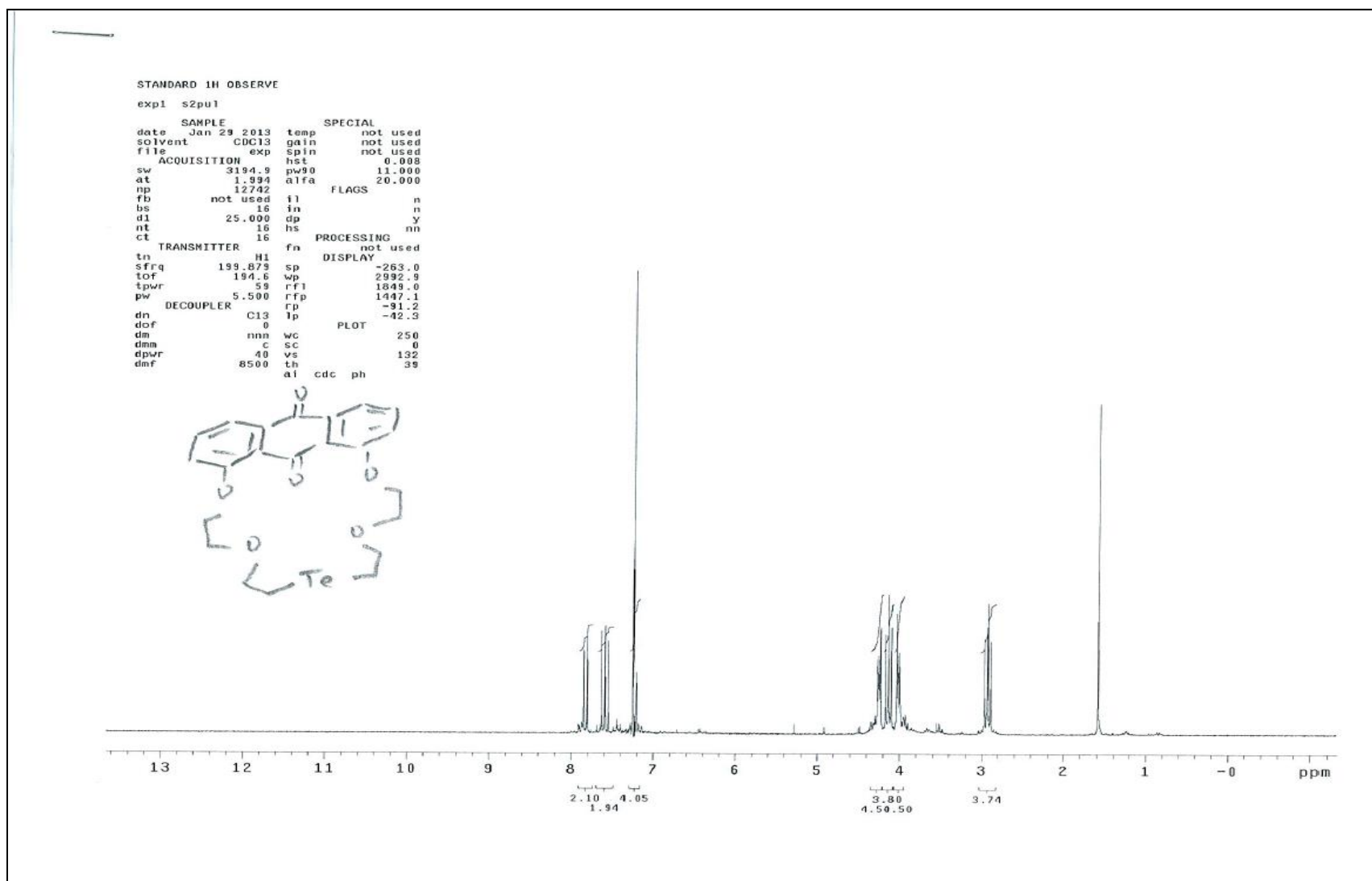
SI Fig. 6: ¹³C NMR of compound 4.



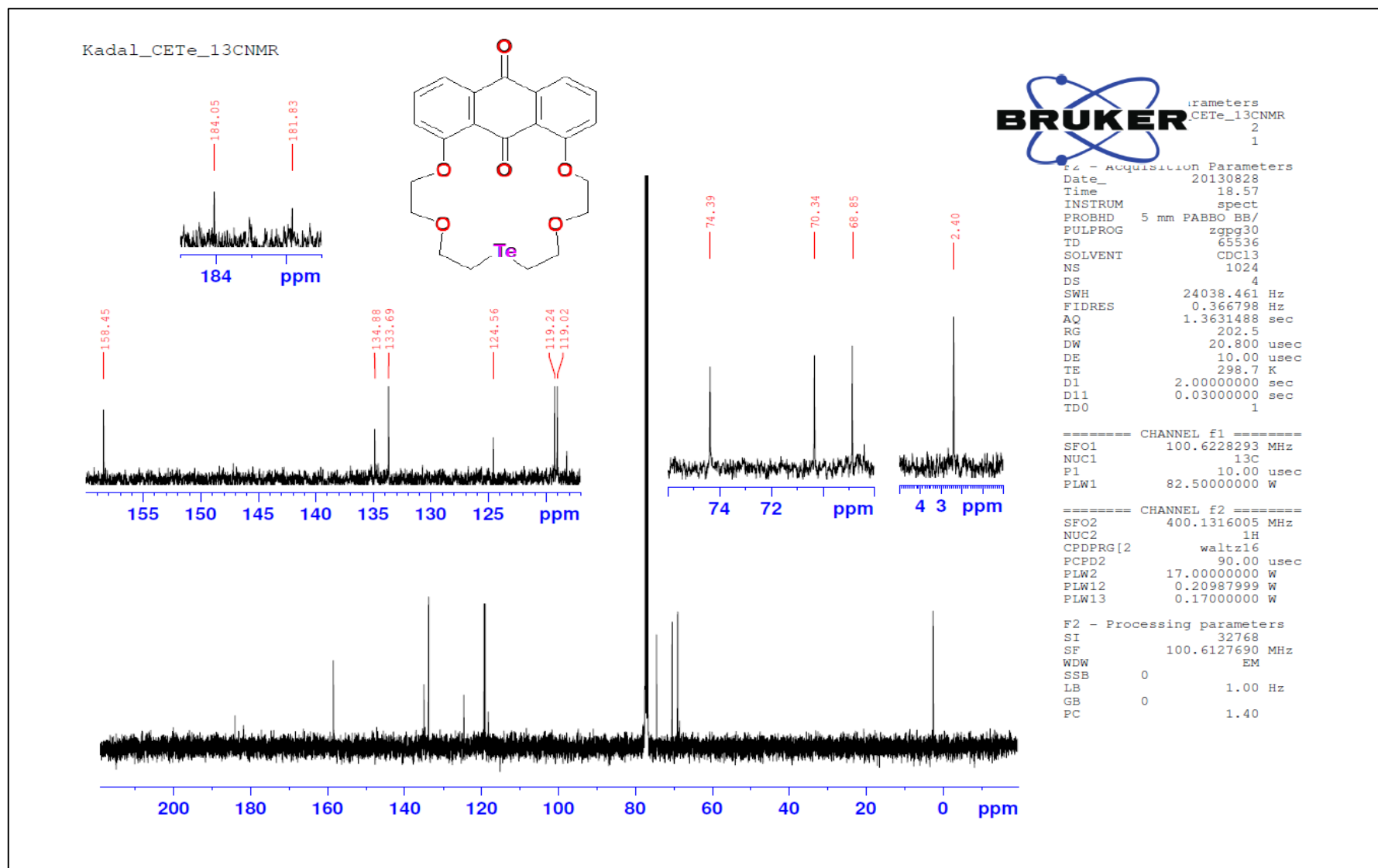
SI Fig. 7: ¹H NMR of compound **5**.



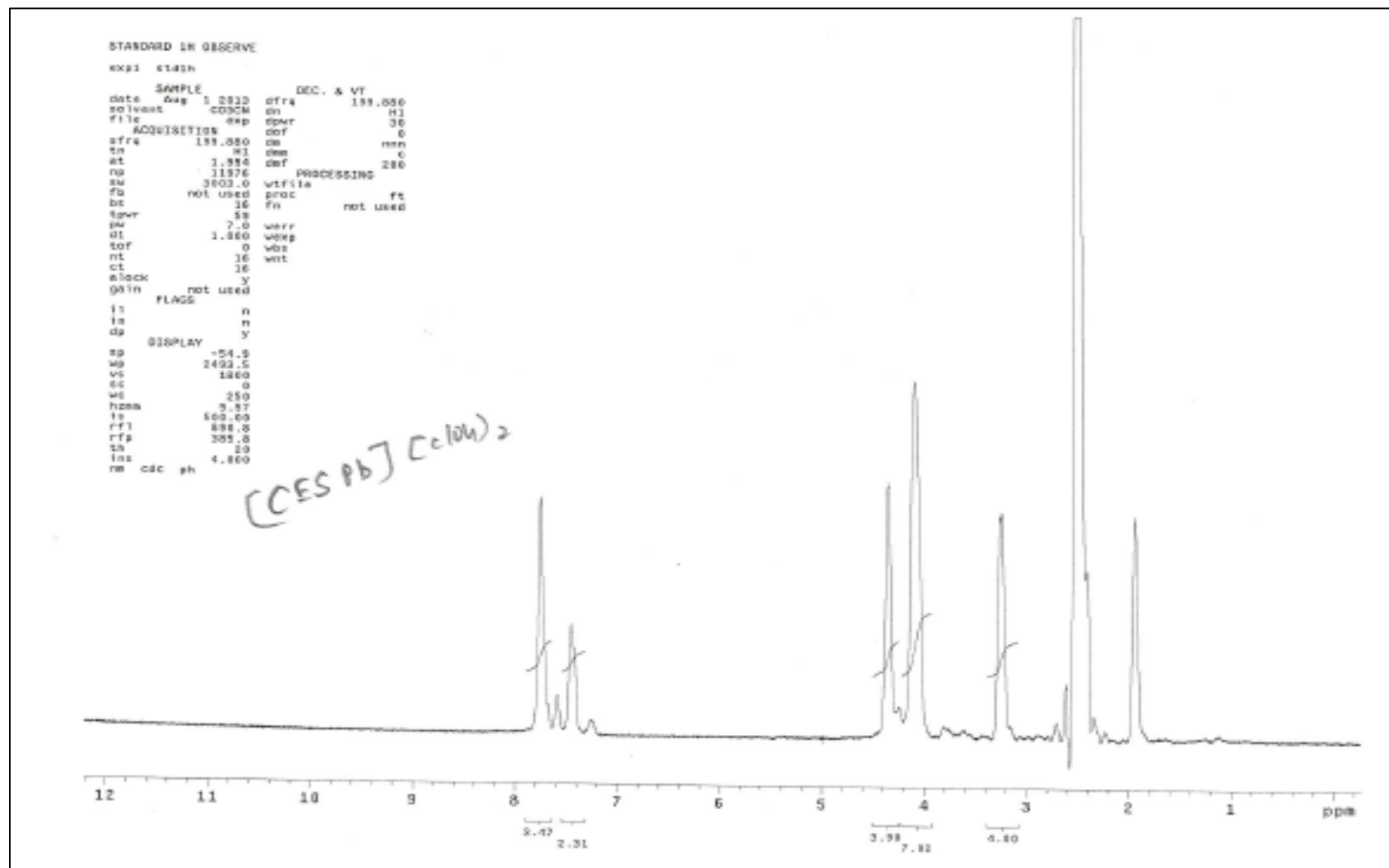
SI Fig. 8: ¹³C NMR of compound 5.



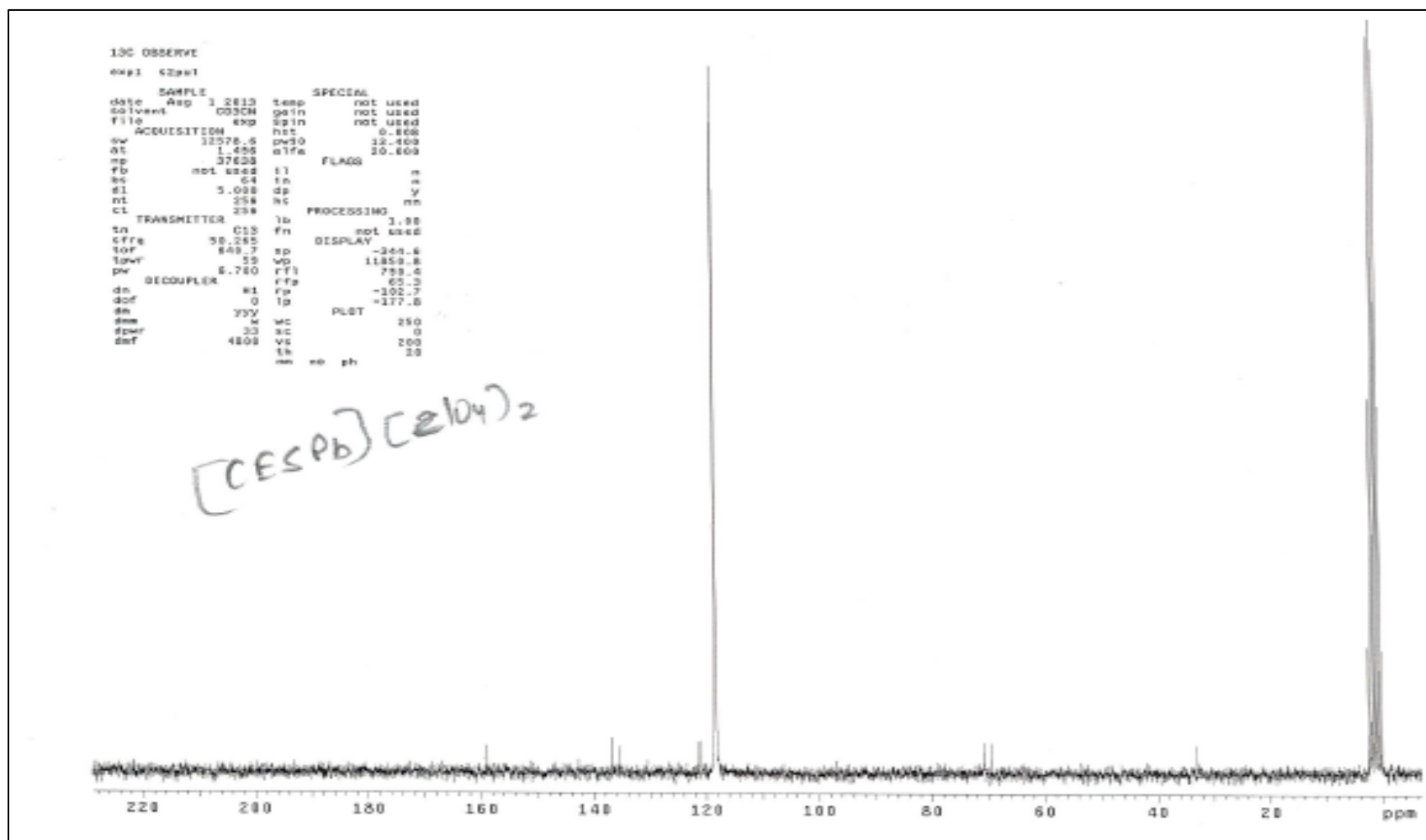
SI Fig. 9: ^1H NMR of compound 6.



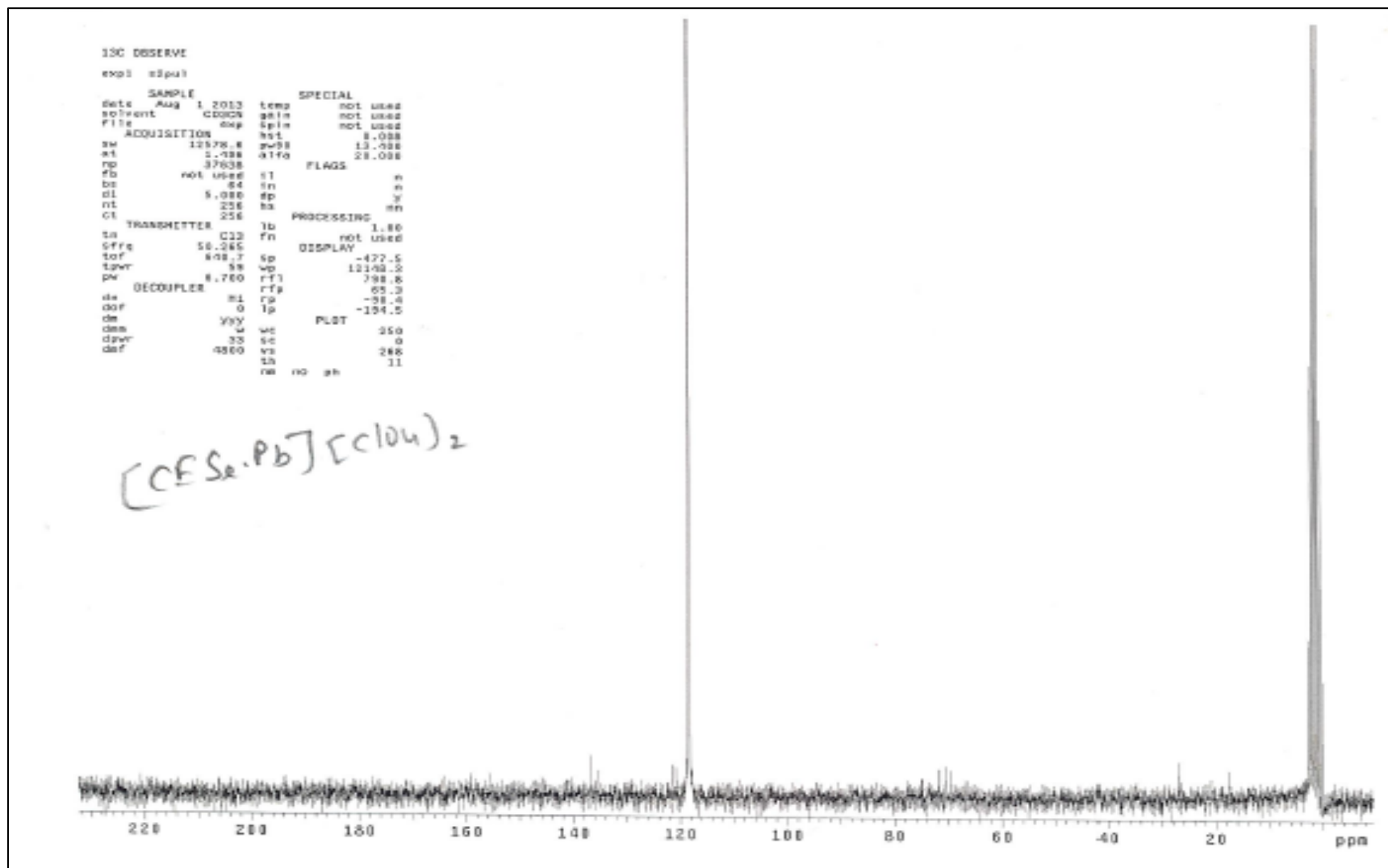
SI Fig. 10: ^{13}C NMR of compound **6**.



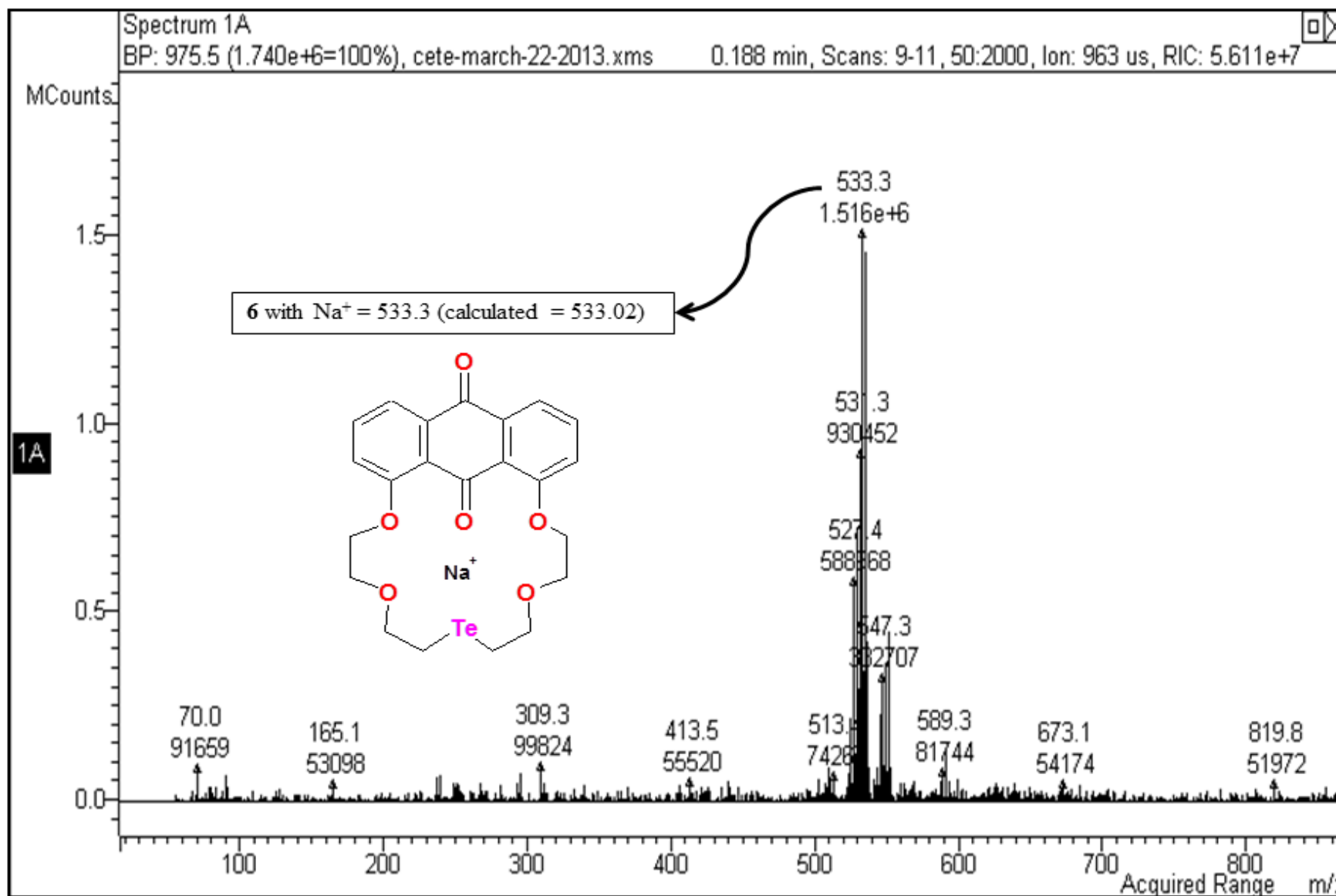
SI Fig. 11: ^1H NMR of compound **7**.



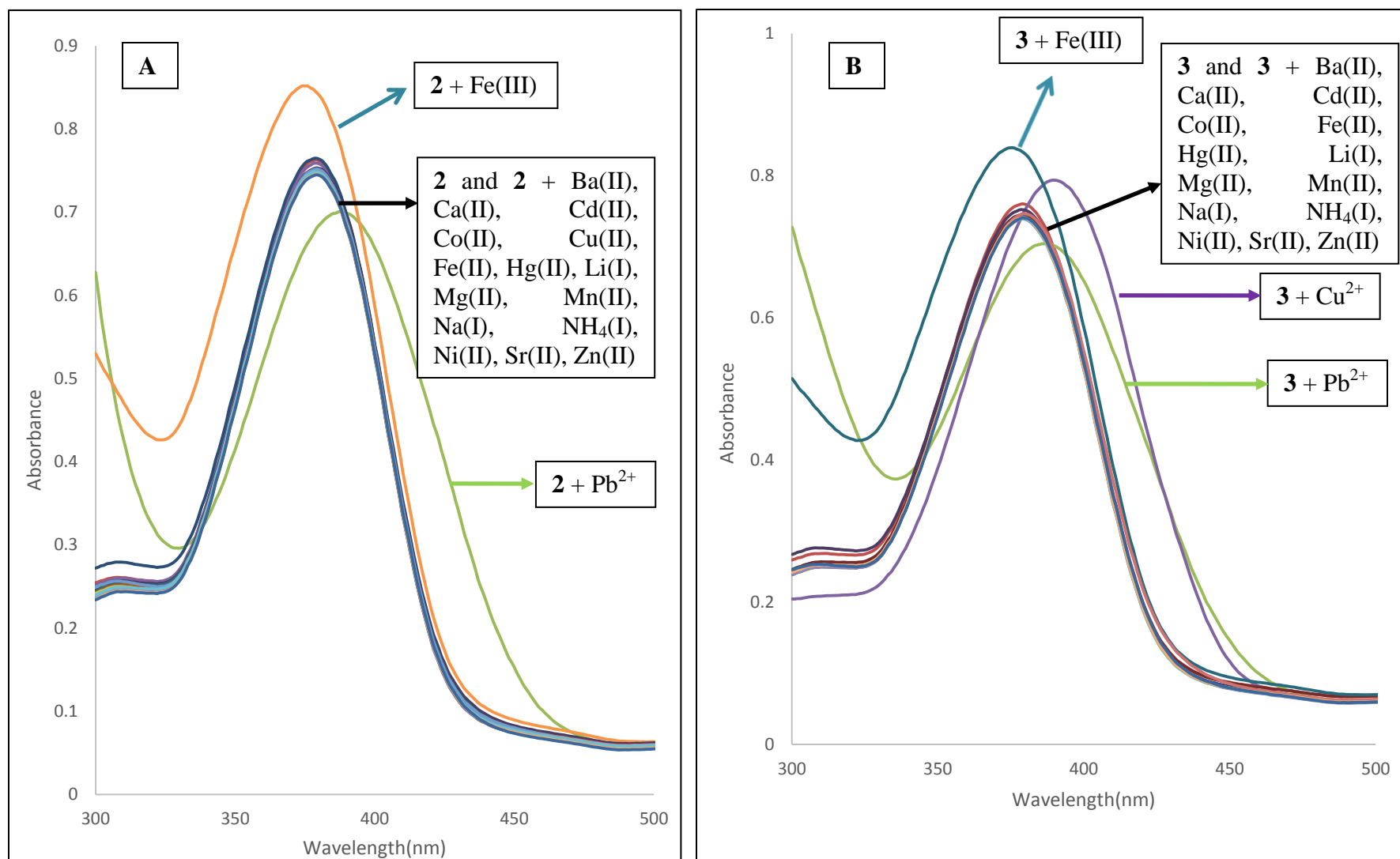
SI Fig. 12: ^{13}C NMR of compound 7.



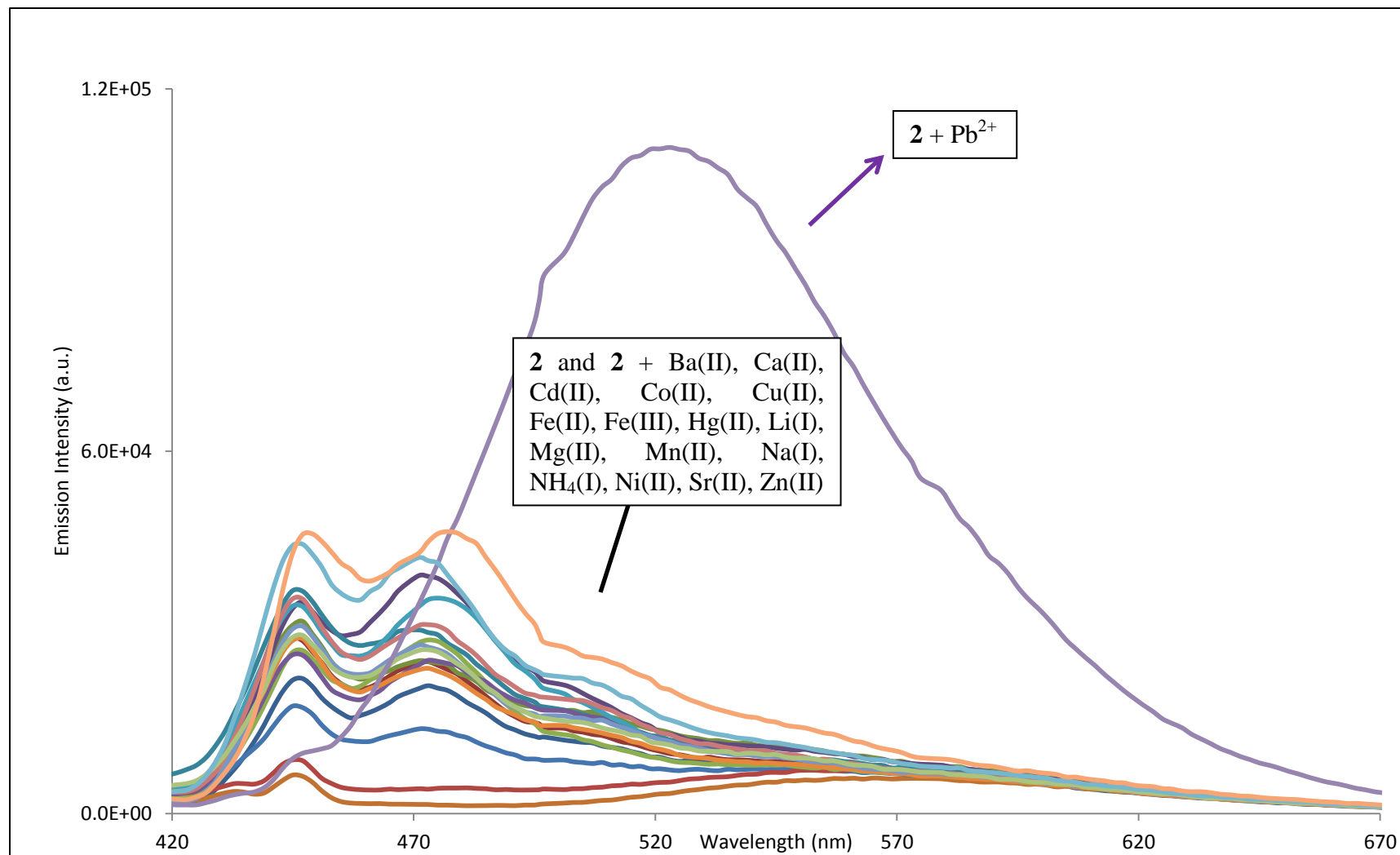
SI Fig. 14: ^{13}C NMR of compound 8.



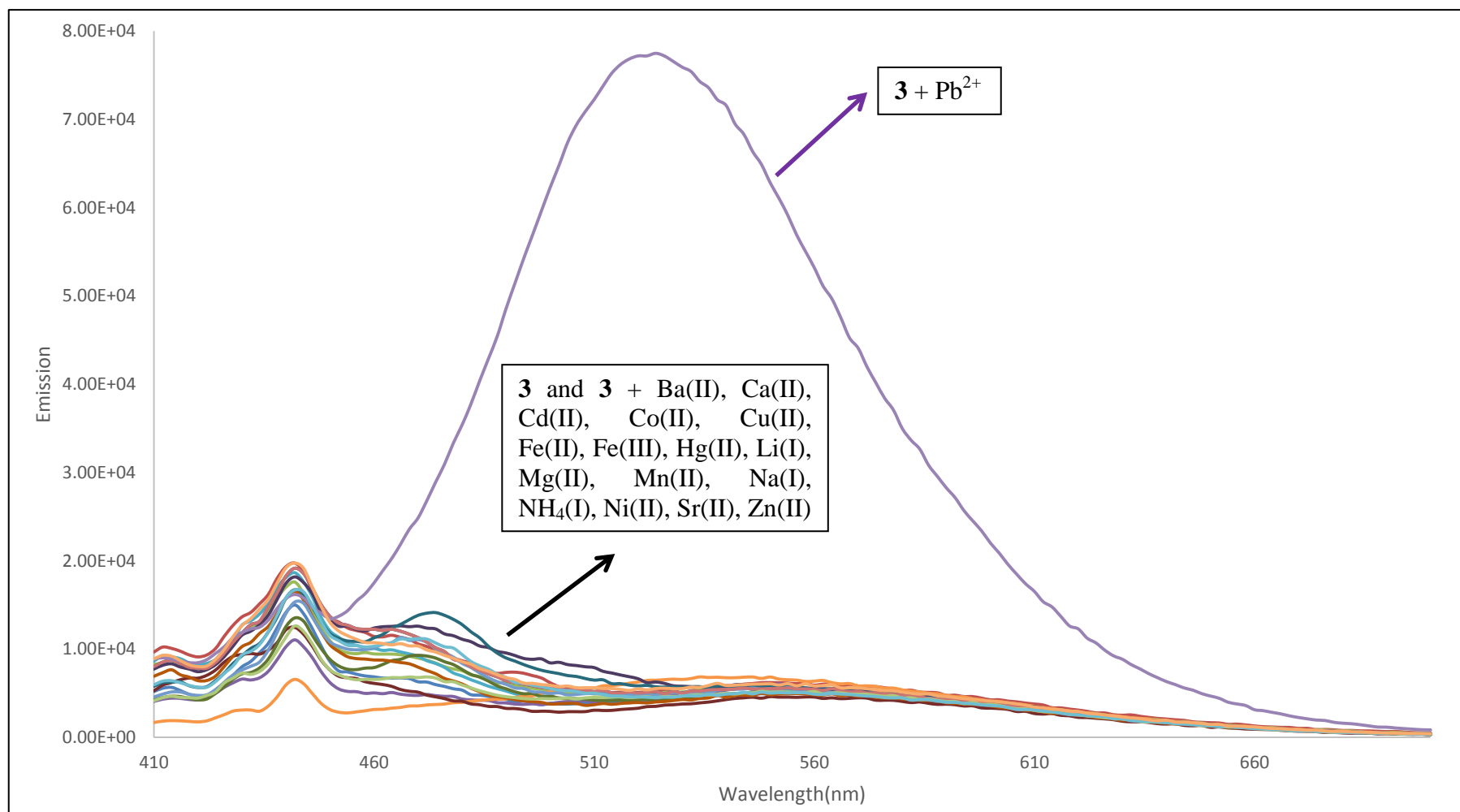
SI Fig. 15: ESI Mass spectrum of compound **6**.



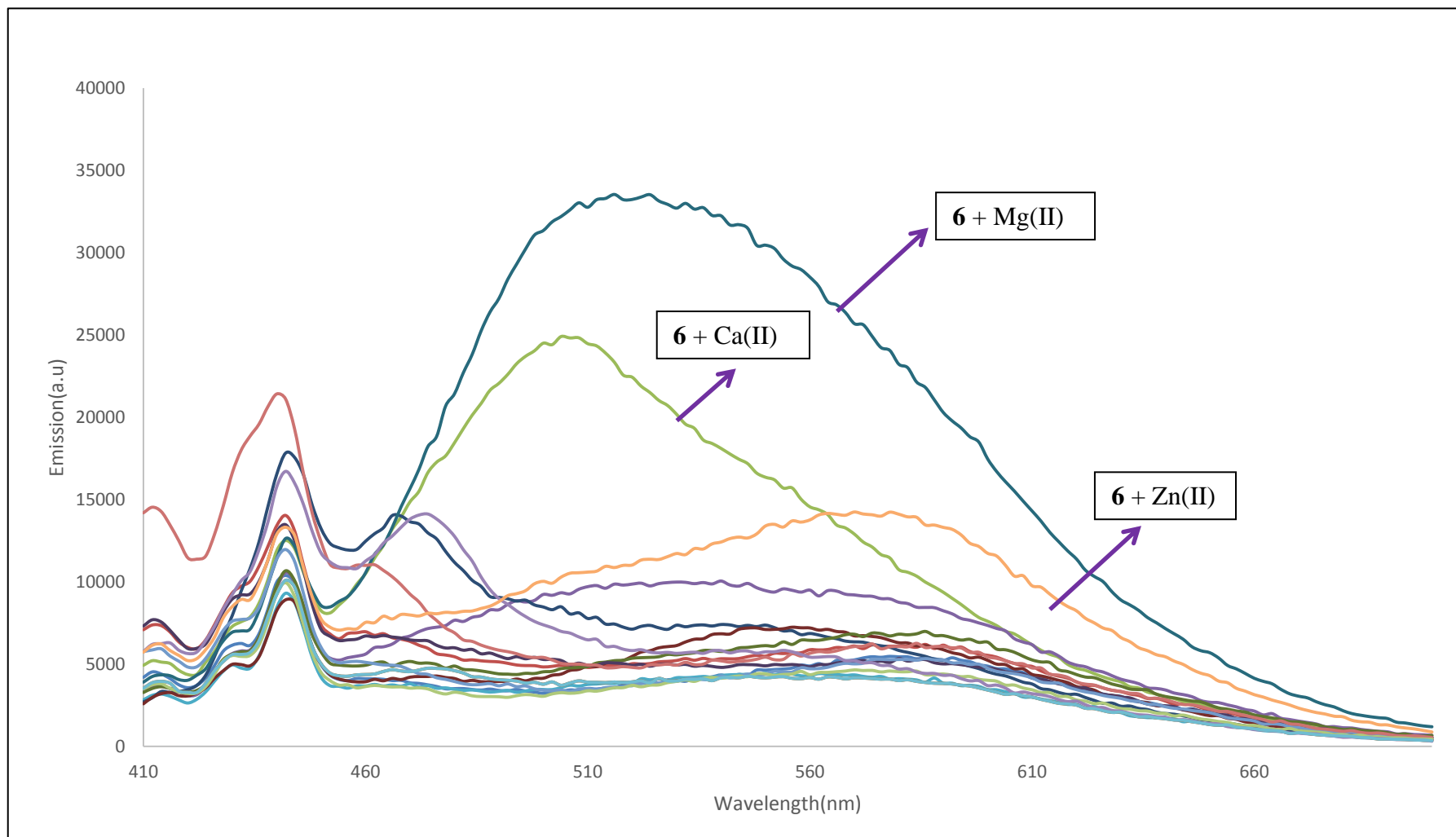
SI Fig. 16: UV-visible of compound **2** (A) and **3** (B) using 1×10^{-4} molar in CH₃CN mixed with 2 equivalents of metal ions.



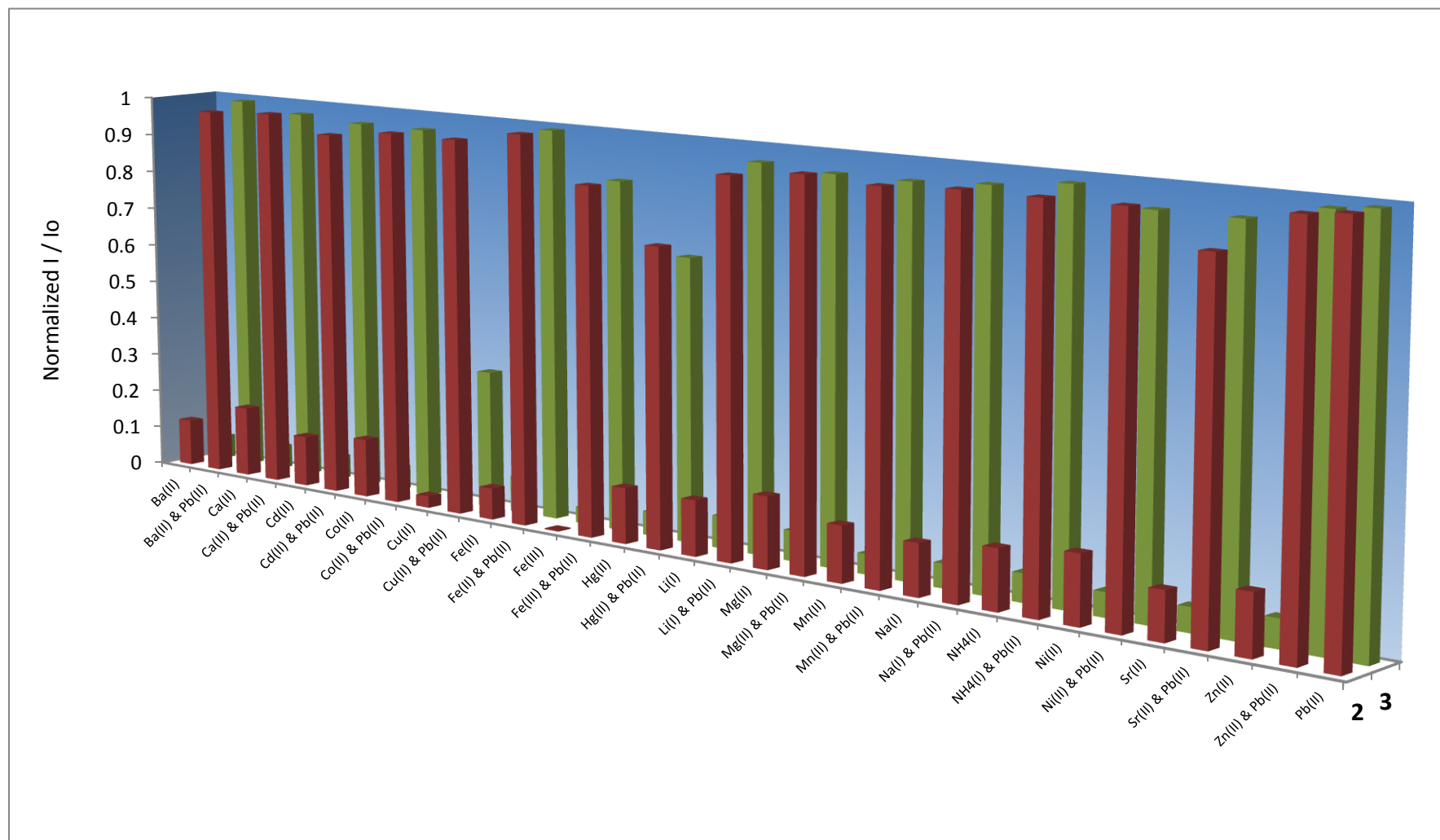
SI Fig. 17: Emission of **2** with different metal ions. 1×10^{-4} M of **2** in acetonitrile with two equivalents of M^{n+} . Excitation wavelength is 390 nm.



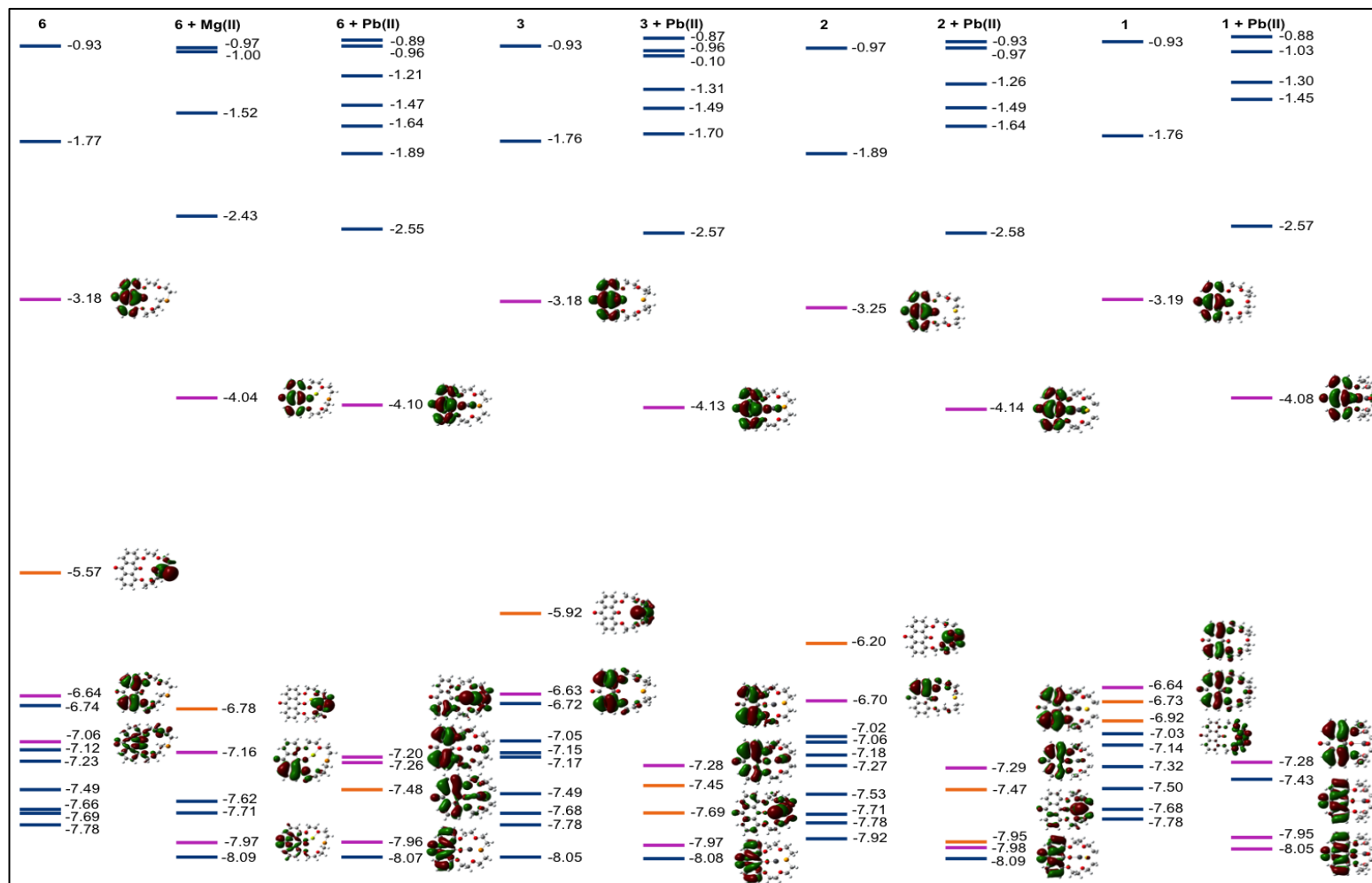
SI Fig. 18: Emission of **3** with different metal ions. 1×10^{-4} M of **3** in acetonitrile with two equivalents of M^{n+} . Excitation wavelength is 390 nm.



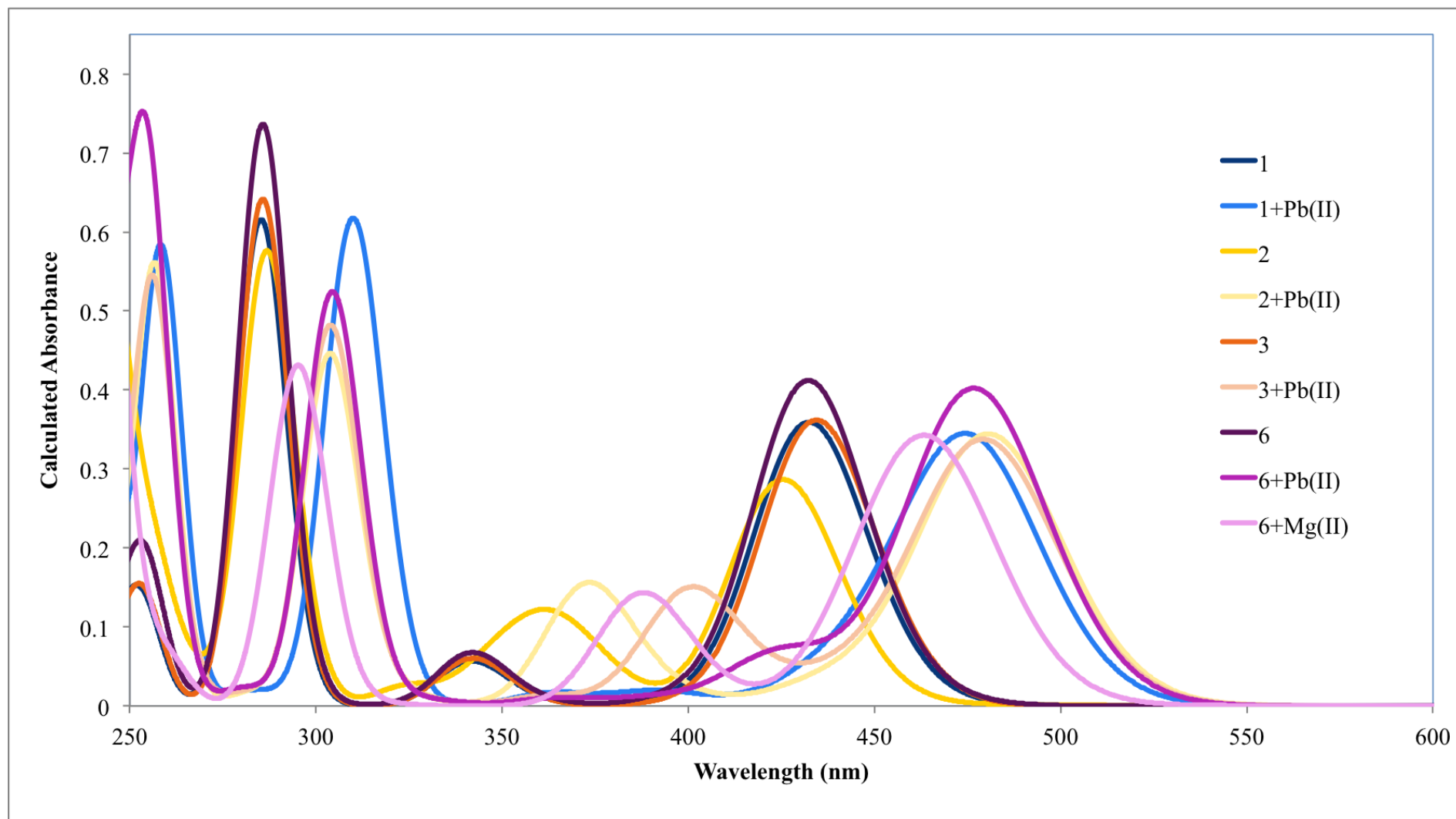
SI Fig. 19: Emission of **6** with different metal ions. 1×10^{-4} M of **6** in acetonitrile with two equivalents of M^{n+} . Excitation wavelength is 390 nm.



SI Fig. 20. Plot of normalized emission intensity at 520 nm of **2** and **3** in presence of different metal ions. **2** and **3** are in 1×10^{-4} molar concentrations with two equivalents of Pb(II) and M^{n+} in acetonitrile. Excitation wavelength is 390 nm.



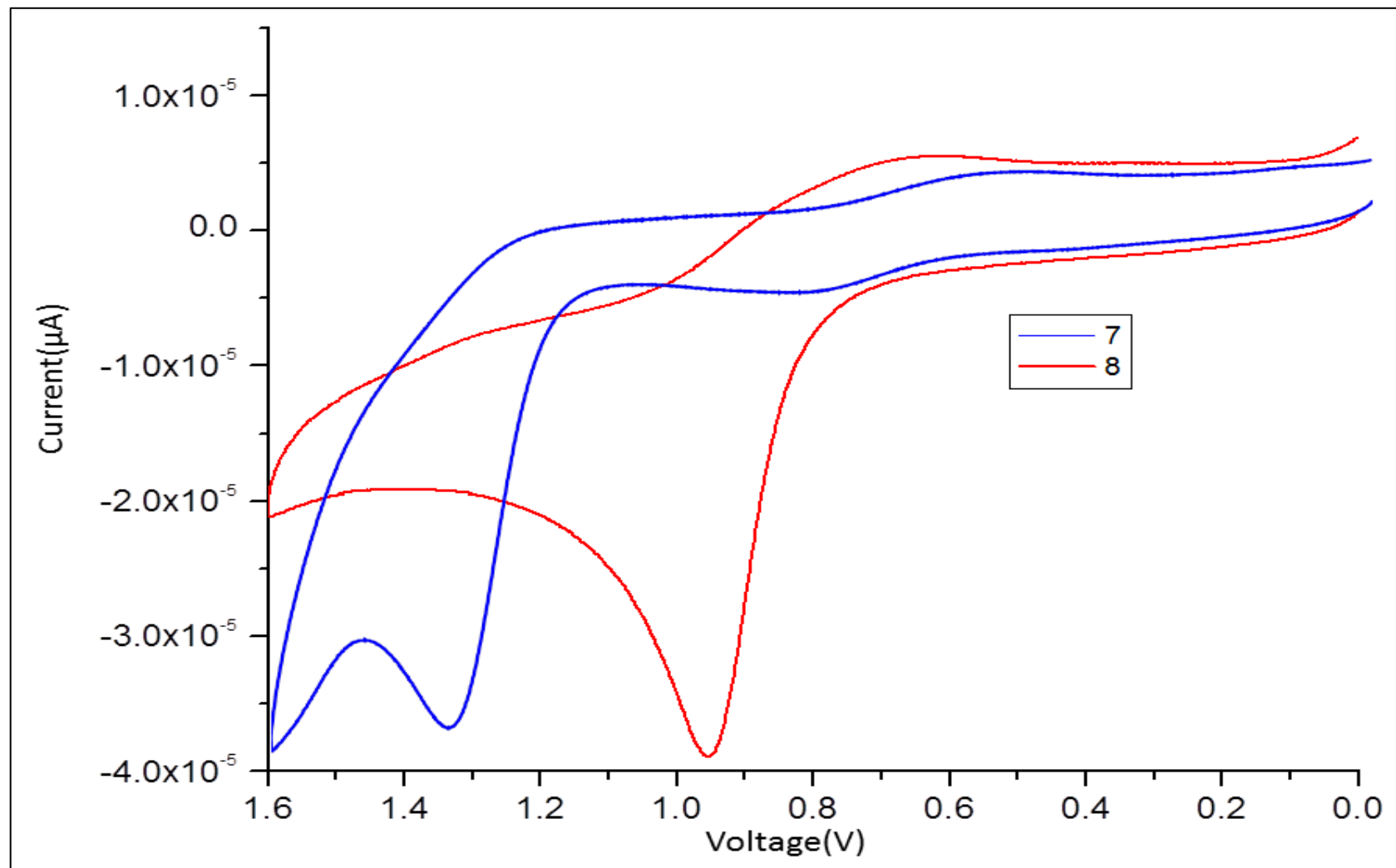
SI Fig. 21: Computationally determined molecular orbital (MO) diagram with energy values in eV. MO surfaces are only displayed for pink- and orange-labeled MOs. Pink MOs are involved in the lowest energy transition of significant oscillator strength in TDDFT calculations that correspond to absorbance peaks in the 400-550 nm range. Orange MOs are MOs near HOMO with a significant contribution from the atomic orbitals on the heteroatom.



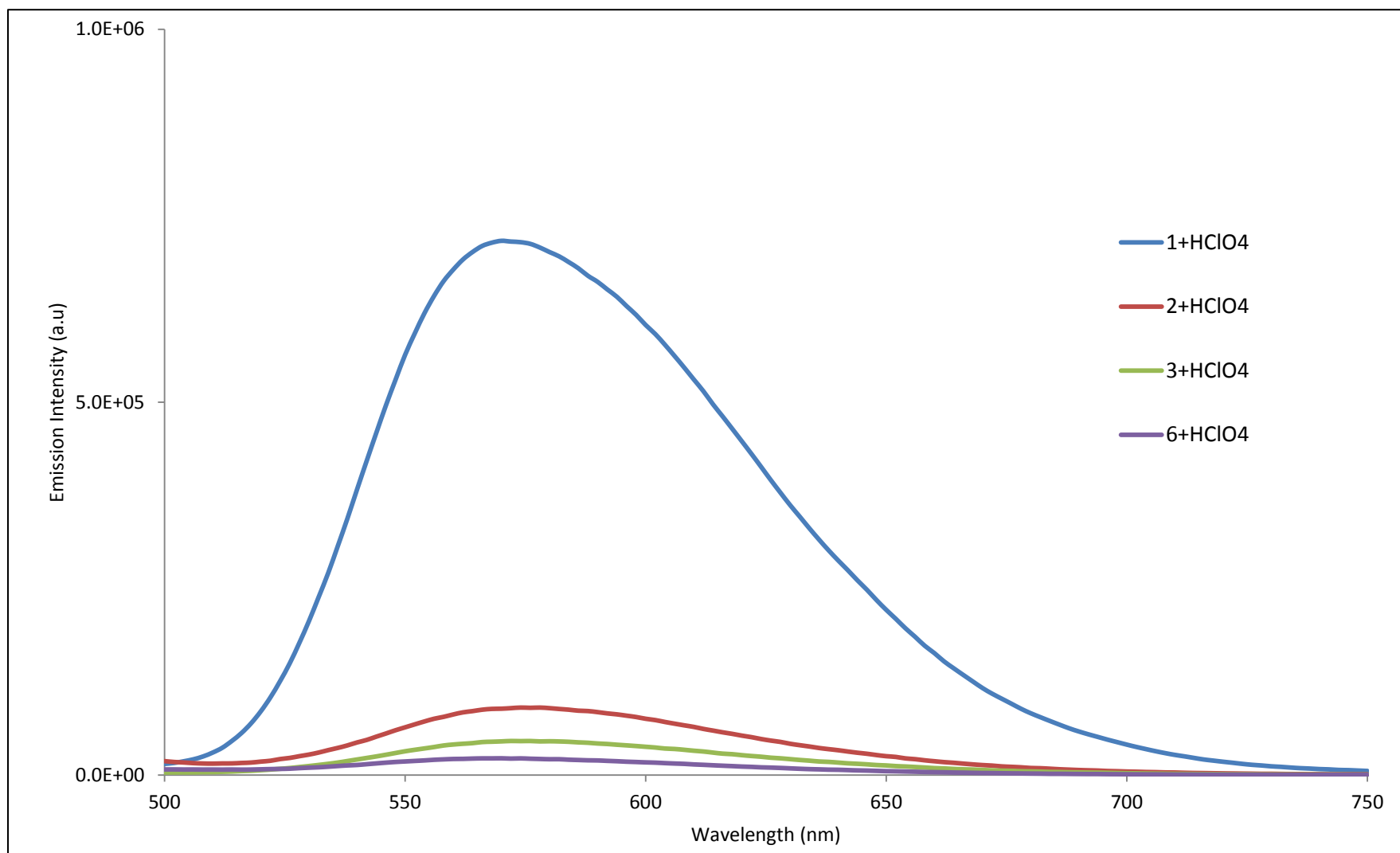
SI Fig. 22 Absorbance spectra of compounds **1,2,3,6** and their Pb(II) complexes determined by TDDFT. Acetonitrile solvent was modeled by IEFPCM.

	Internal Carbonyl (cm ⁻¹)	External Carbonyl (cm ⁻¹)
1 + Pb(II)	1535.3	1592.56
2 + Pb(II)	1534.93	1591.75
3 + Pb(II)	1536.81	1591.38
6 + Pb(II)	1537.37	1591.31
6 + Mg(II)	1563.14	1588.32

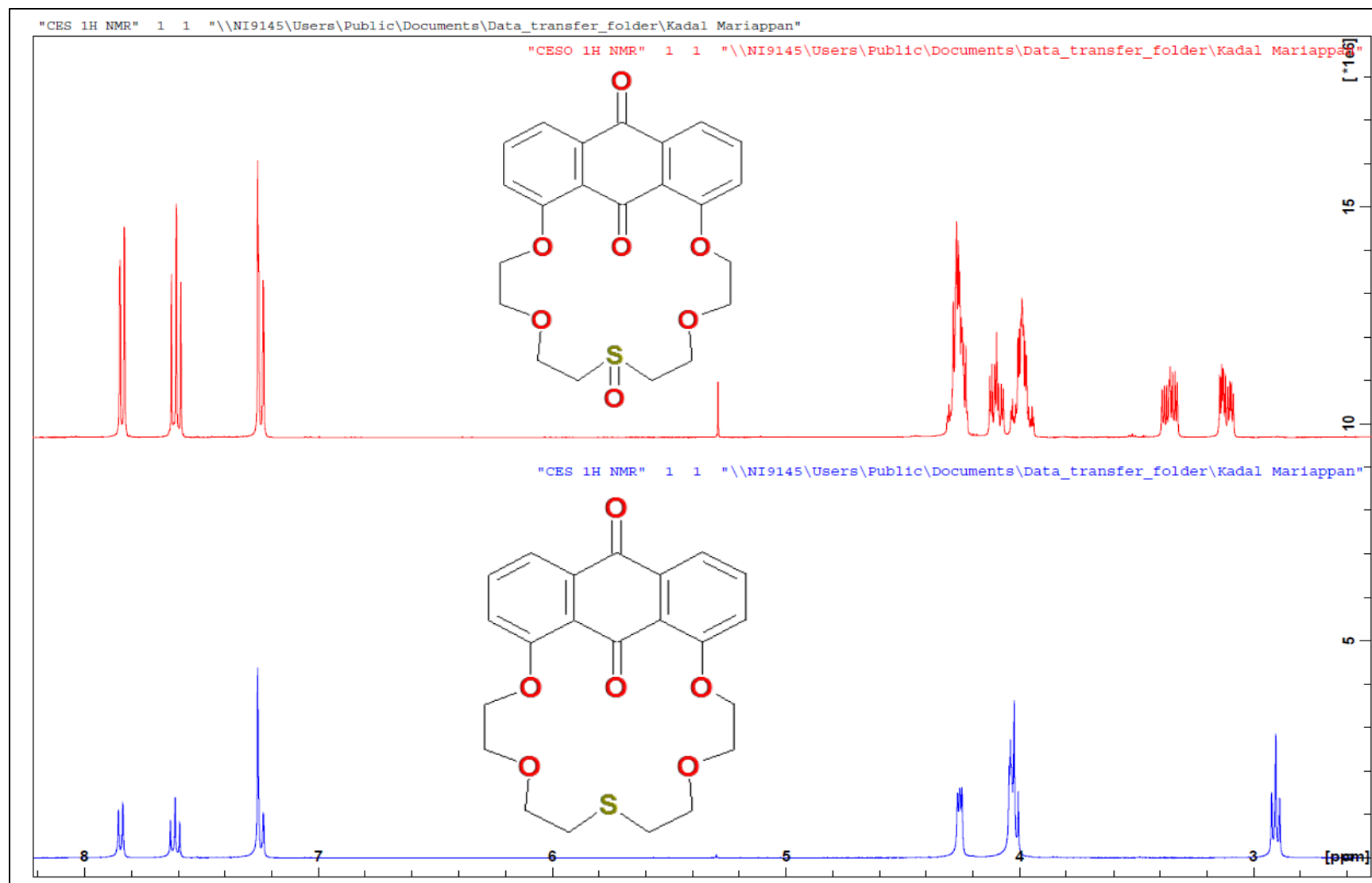
SI Fig. 23 Computationally determined IR stretching frequencies for the internal (inside the macrocycle) and external (outside the macrocycle) anthraquinone carbonyl groups.



SI Fig. 24: Positive scan of compound **7** and **8** in CH_3CN using 0.1M TBAClO_4 vs. Ag/AgCl on glassy carbon.



SI Fig. 25: $.65 \times 10^{-5}$ Molar of **1**, **2**, **3** and **6** mixed with excess HClO₄. The solution excited at 390 nm.



SI Fig. 27: ^1H NMR comparison of **2** as sulfide and sulfoxide.