Dalton Transaction

Supporting Information

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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

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

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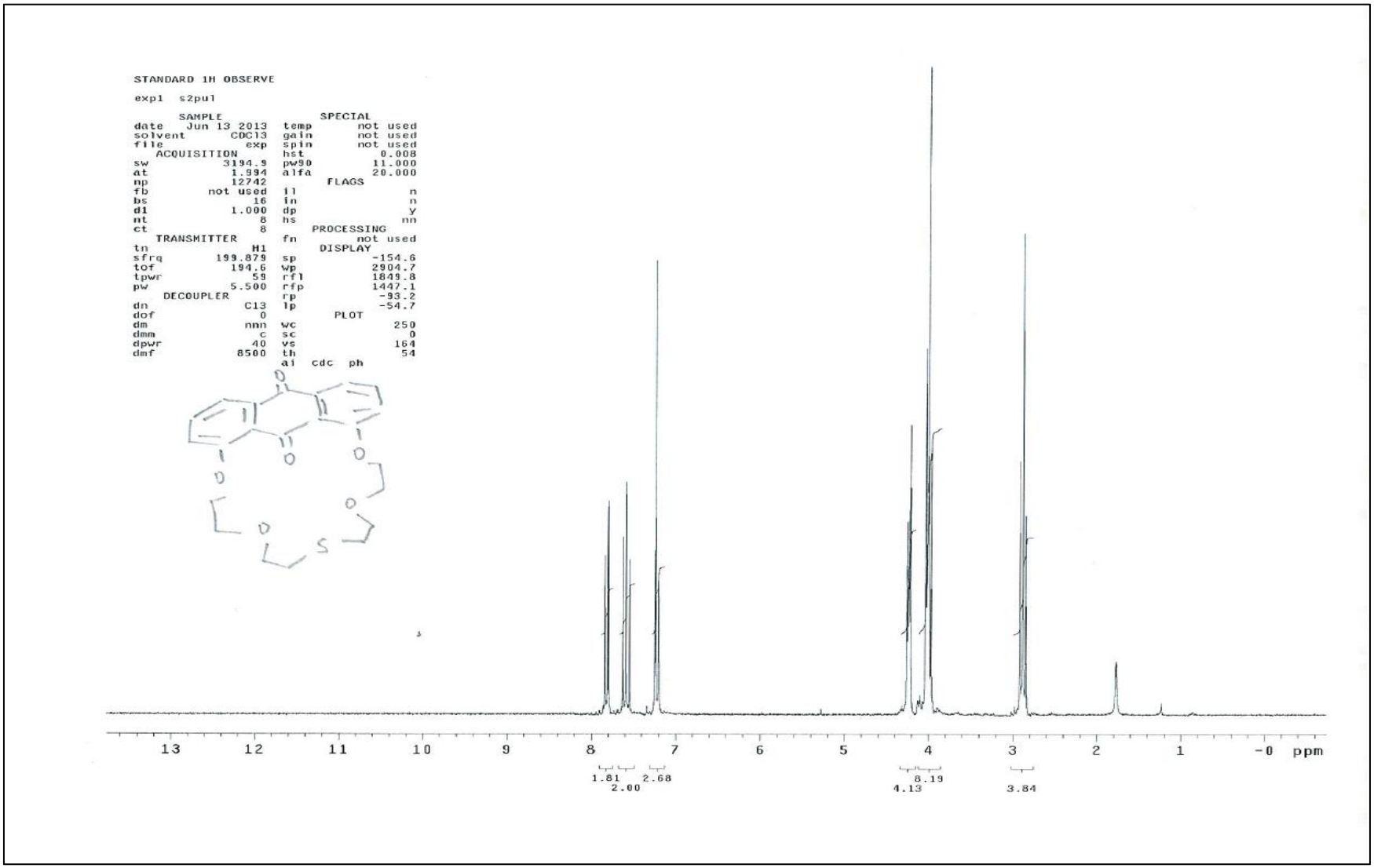
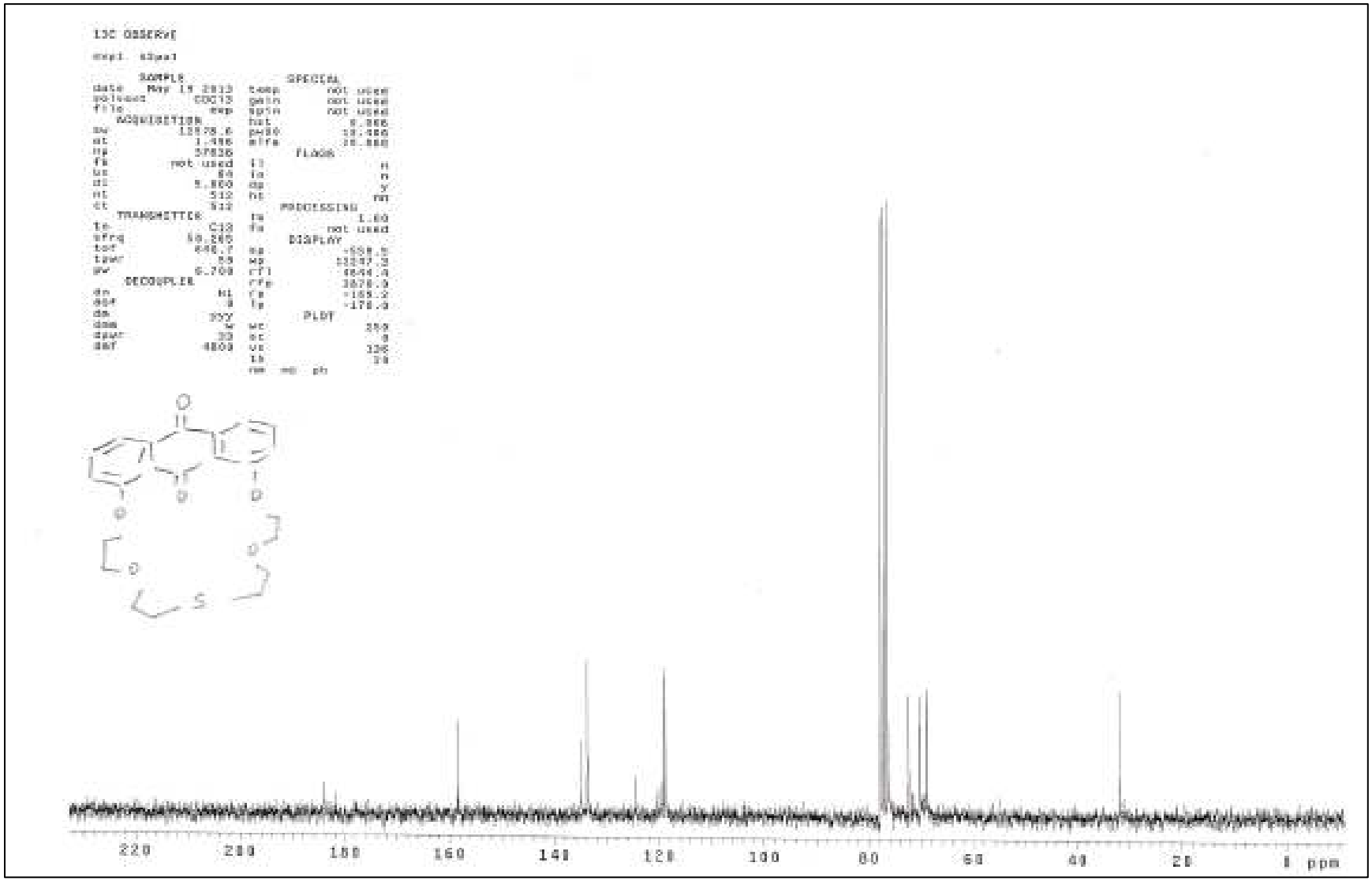
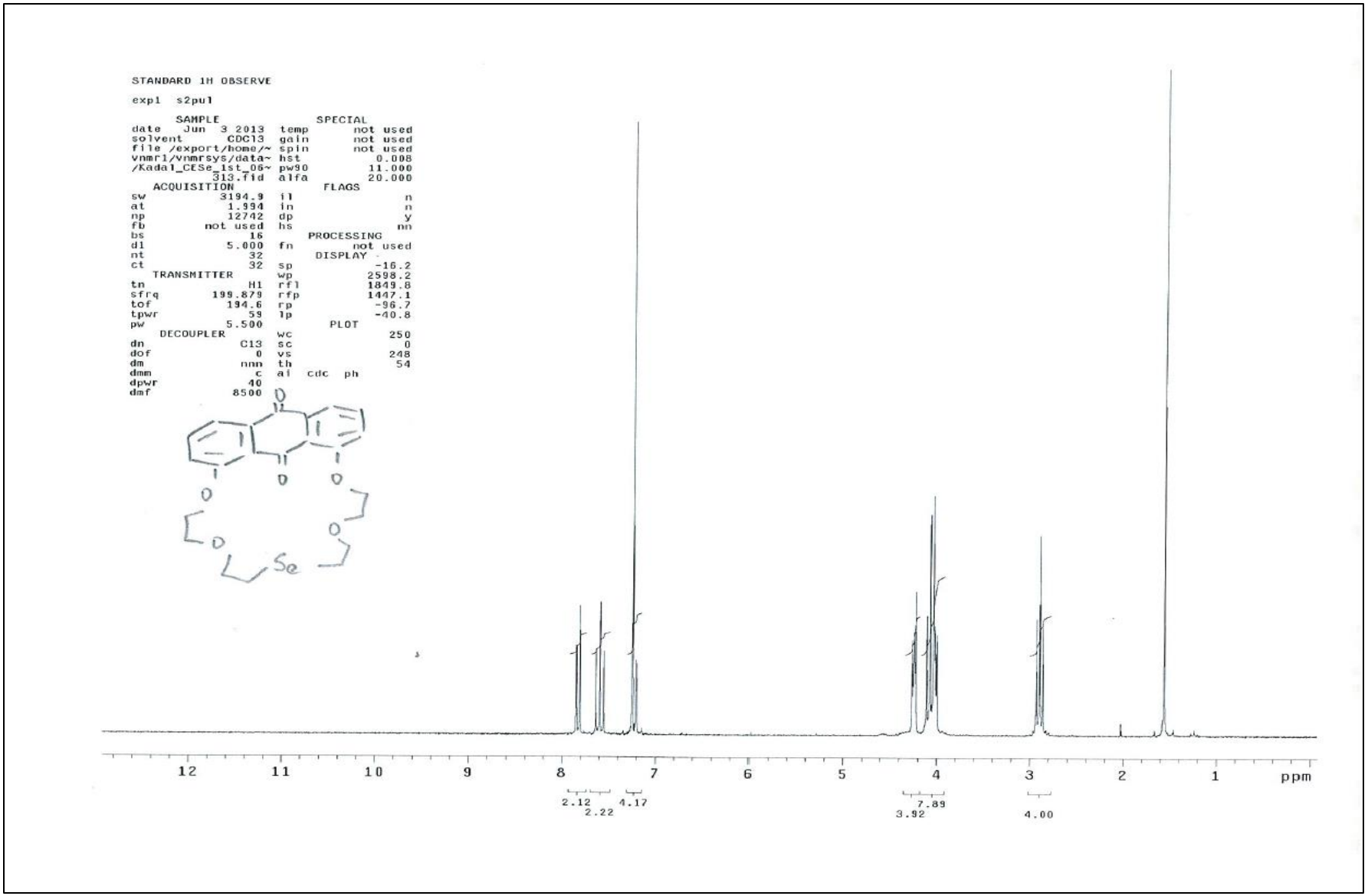


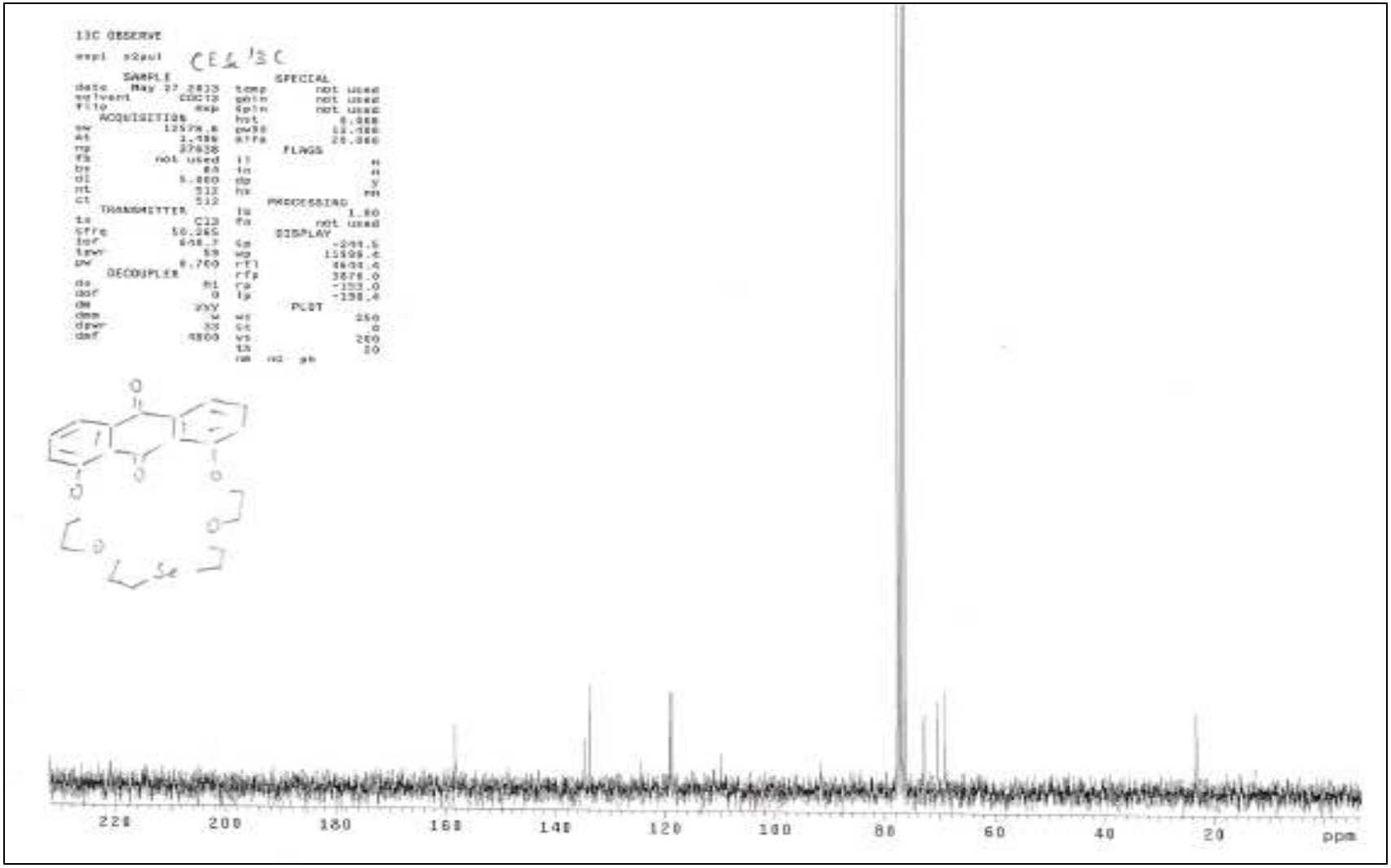
SI Fig. 1: ^{1}H NMR of compound **2**.



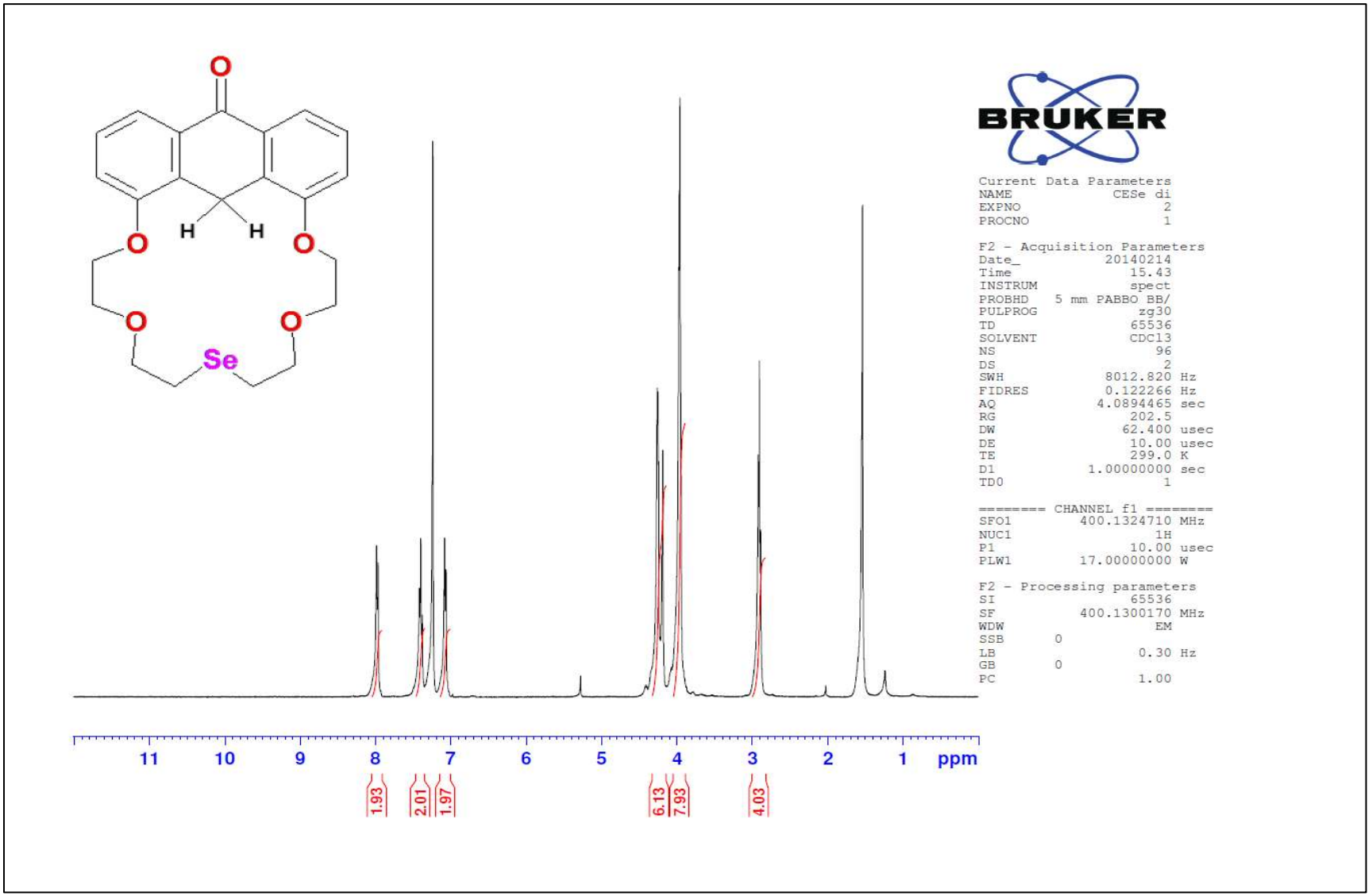
SI Fig. 2: ^{13}C NMR of compound **2**.



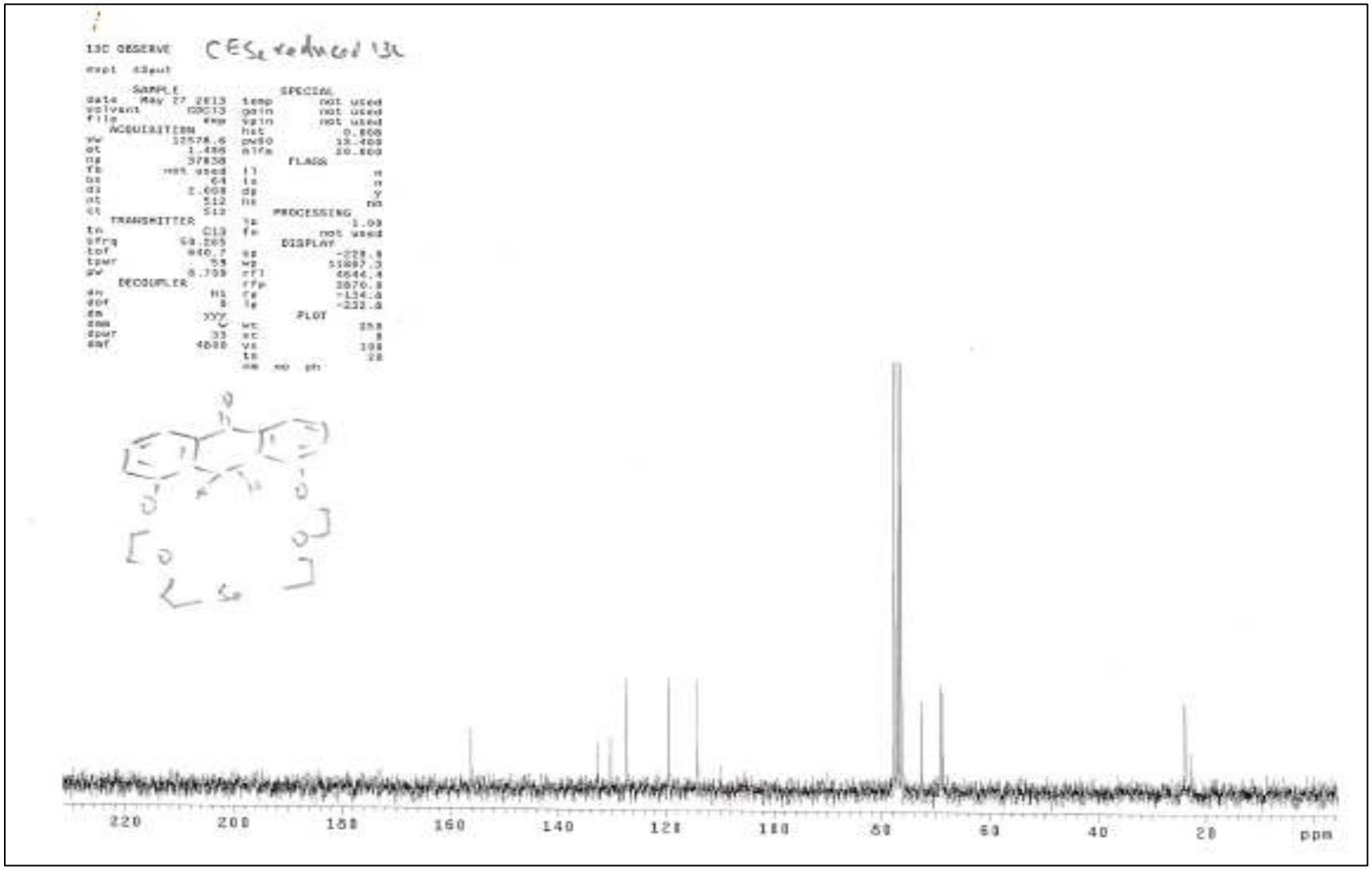
SI Fig. 3: ^{1}H NMR of compound **3**.



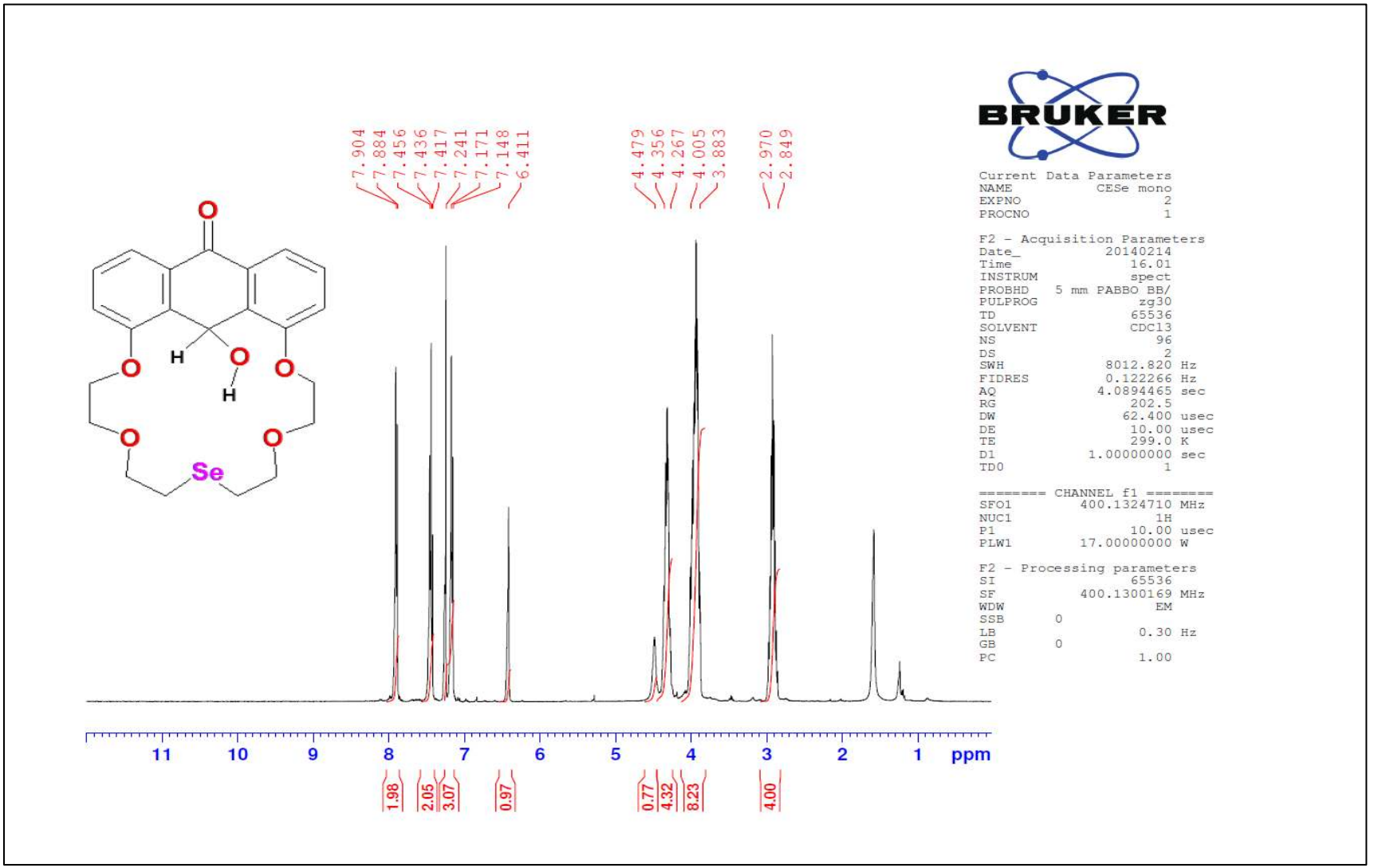
SI Fig. 4: ^{13}C NMR of compound **3**.



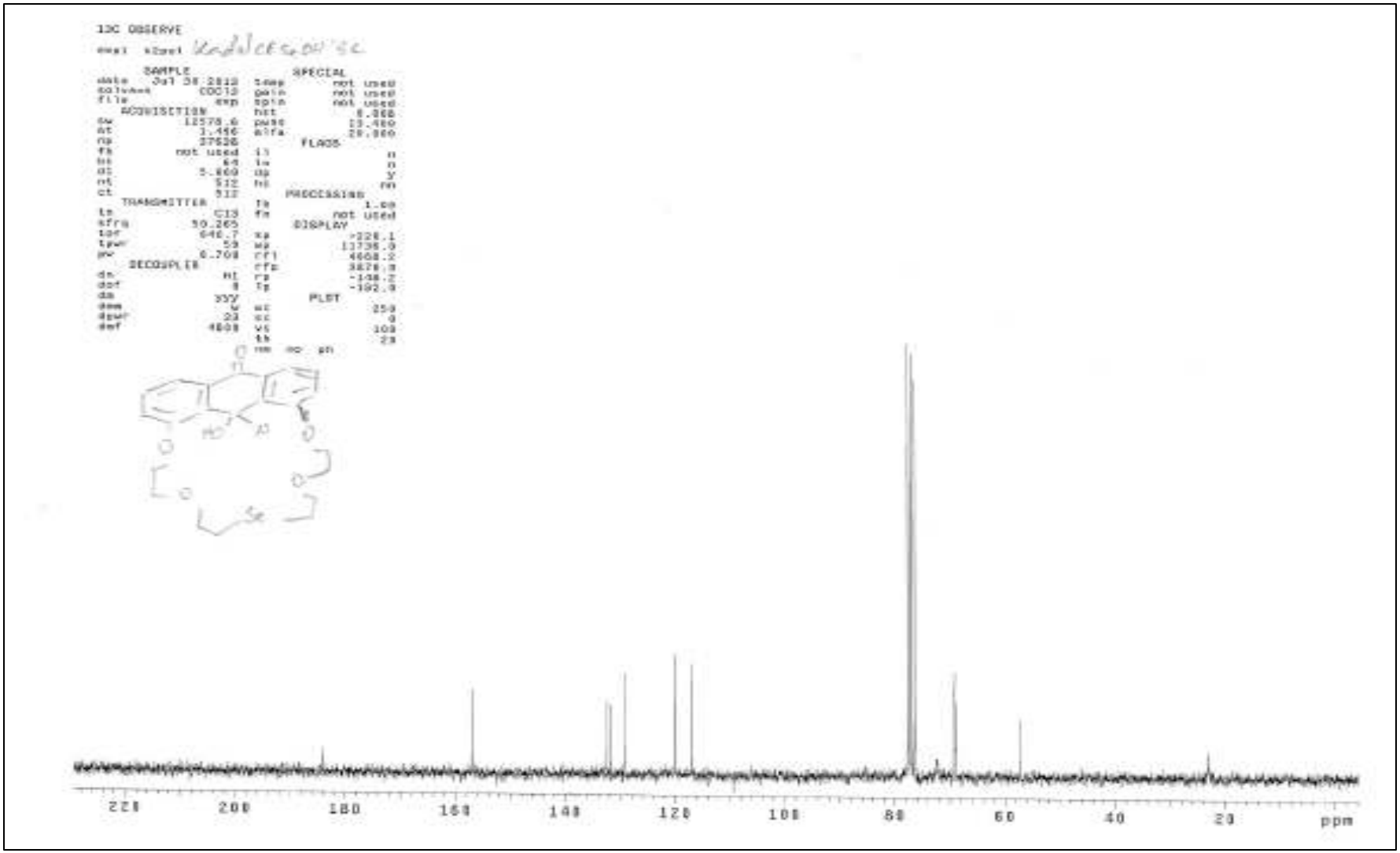
SI Fig. 5: ^{1}H NMR of compound **4**.



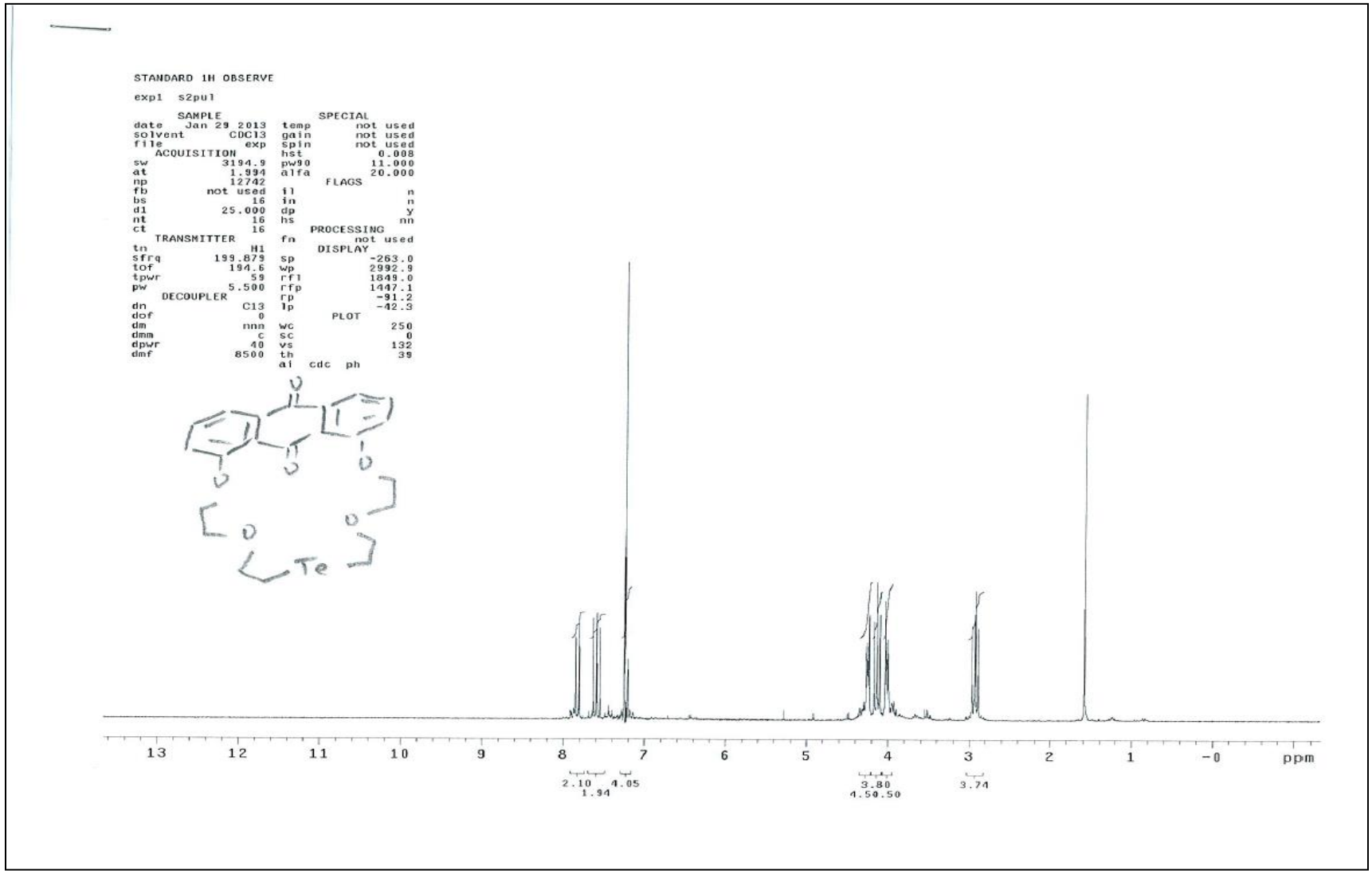
SI Fig. 6: ^{13}C NMR of compound **4**.



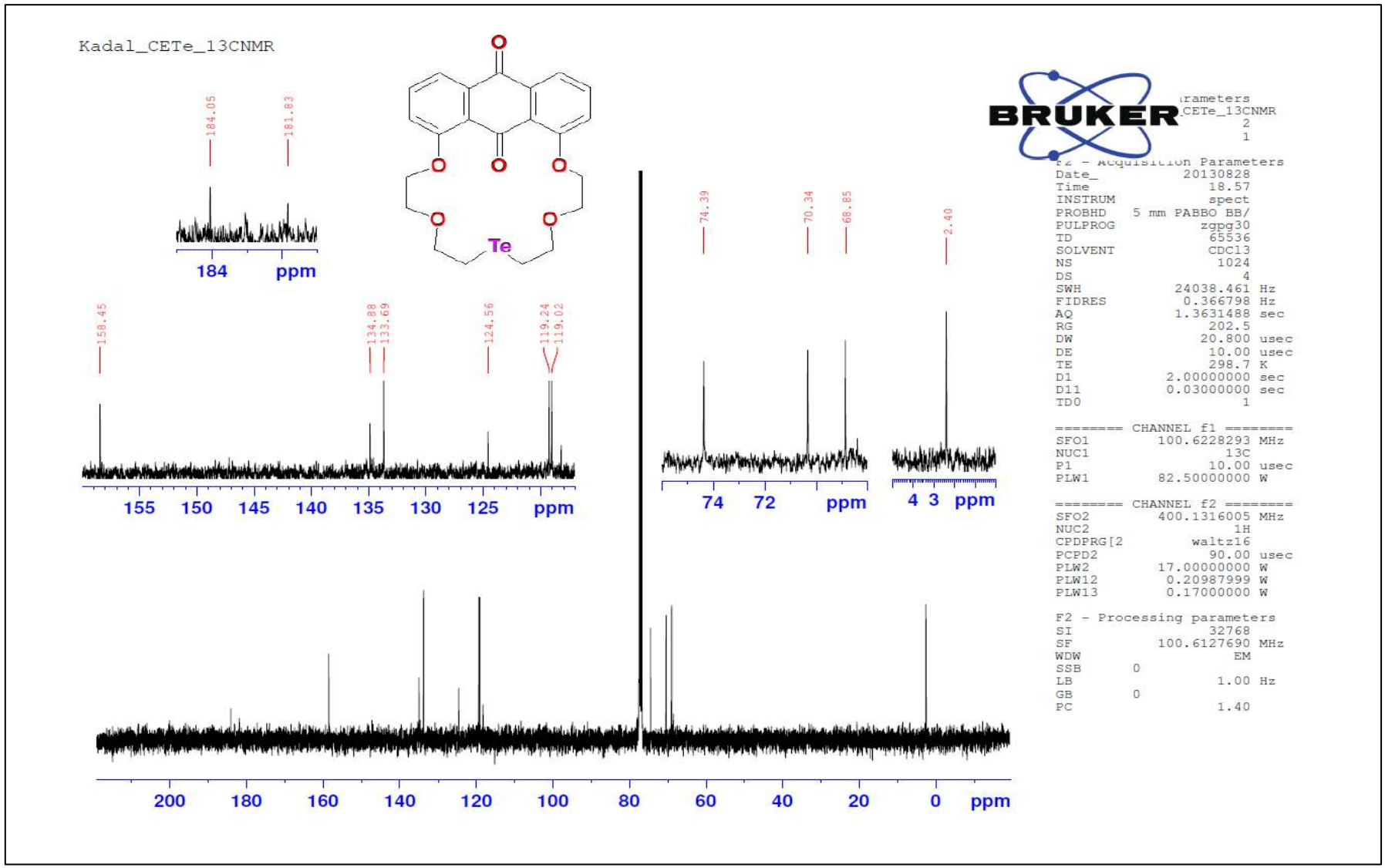
SI Fig. 7: ^{1}H NMR of compound **5**.



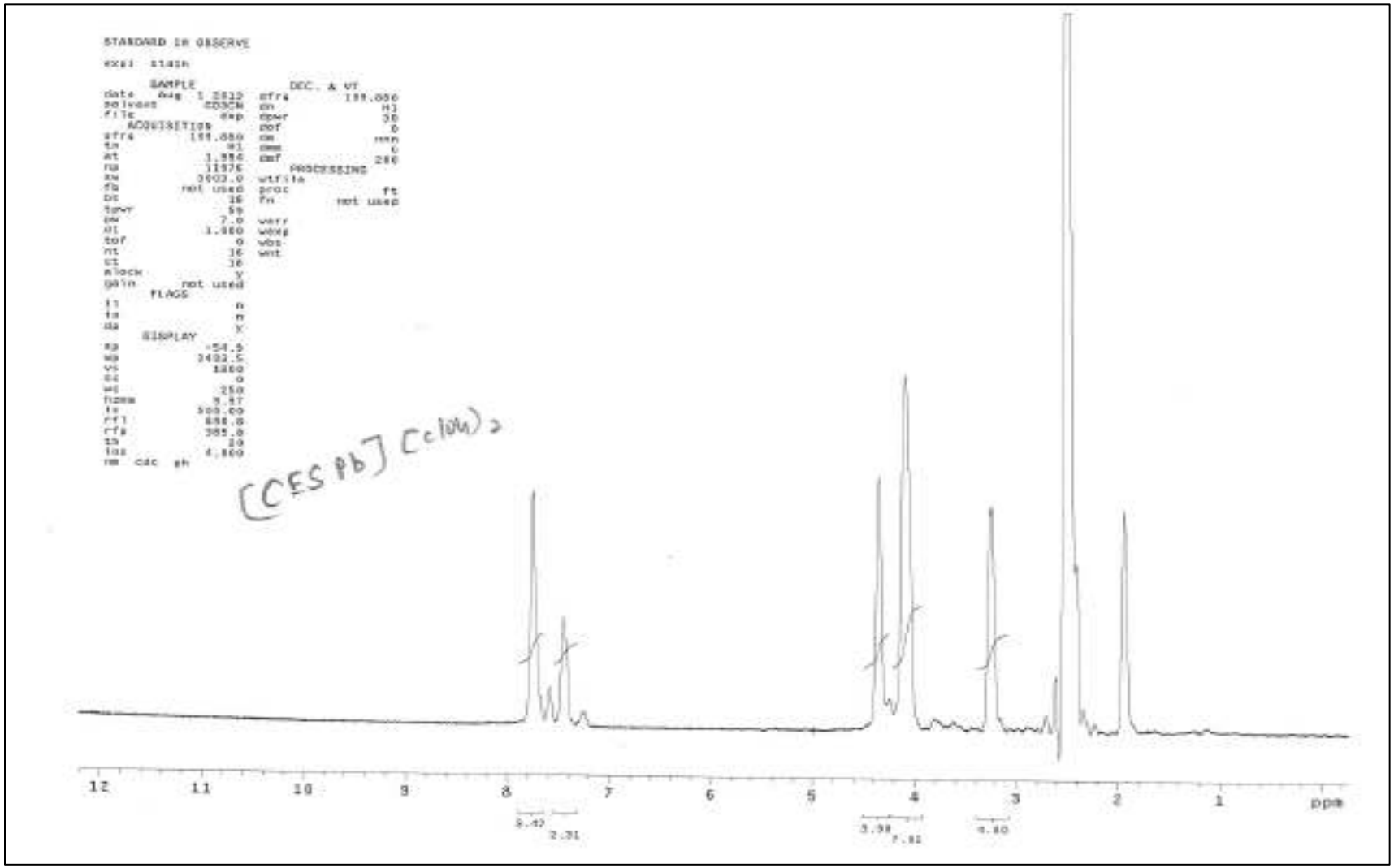
SI Fig. 8: ^{13}C NMR of compound **5**.



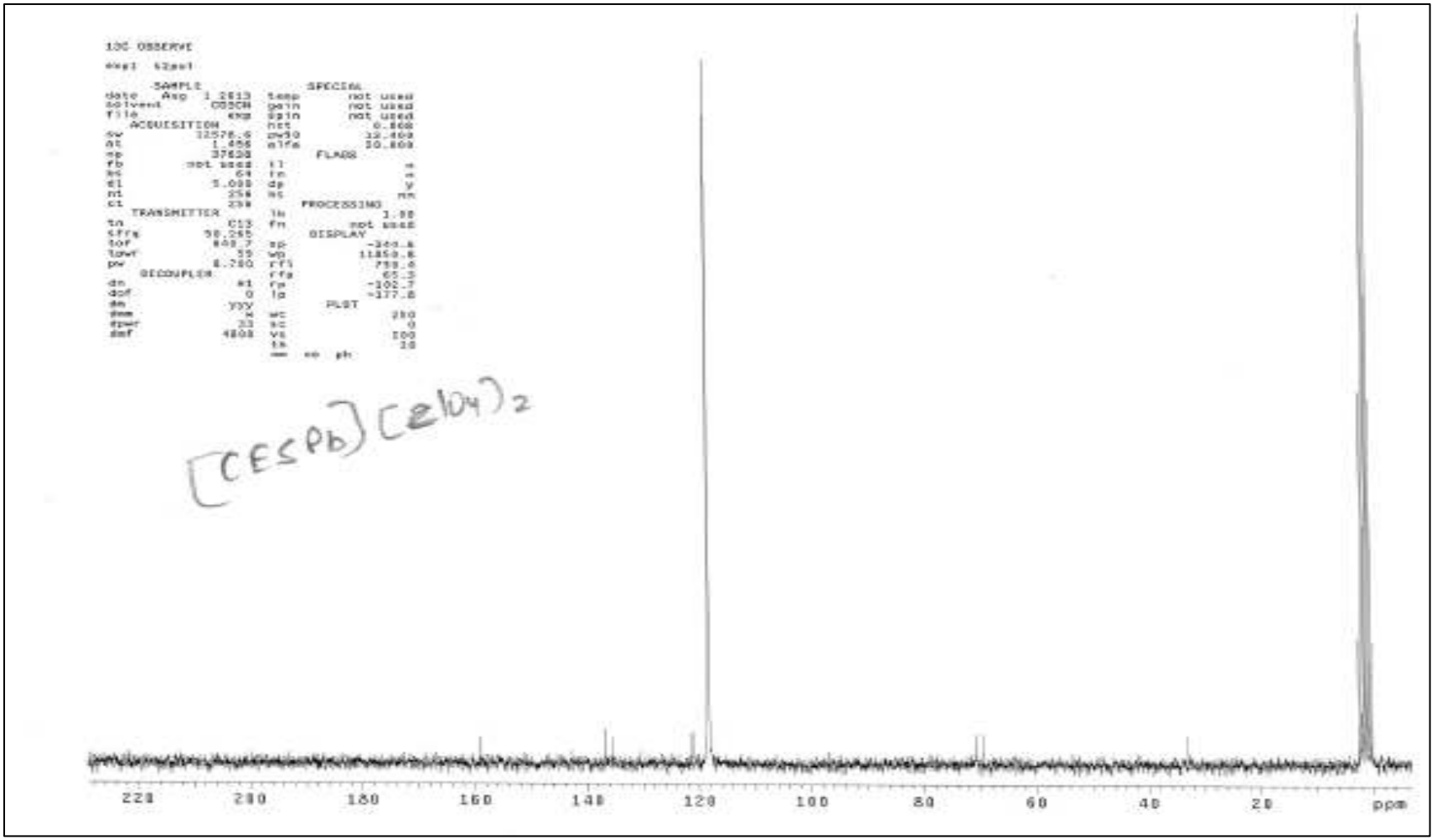
SI Fig. 9: ^{1}H NMR of compound **6**.



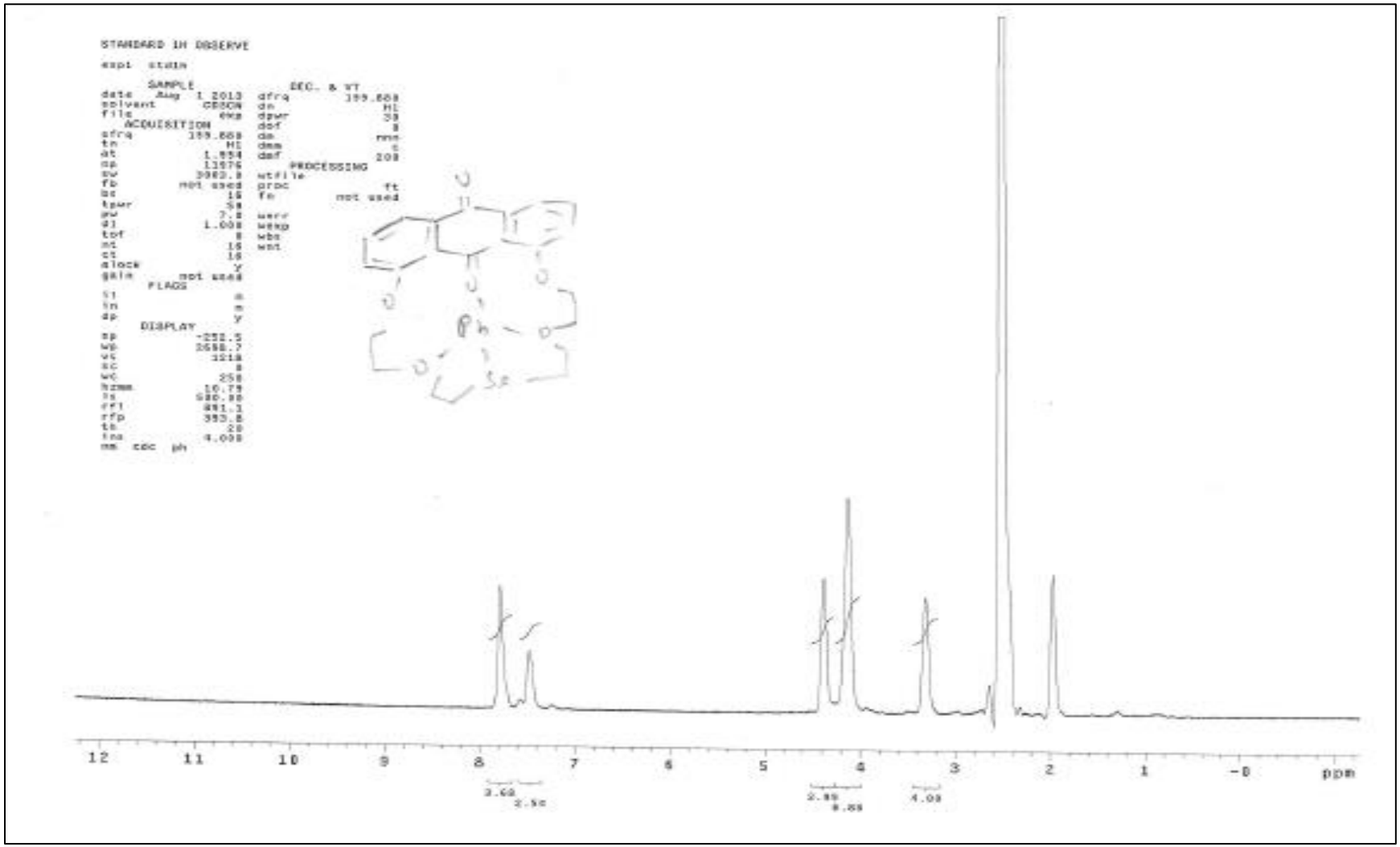
SI Fig. 10: ^{13}C NMR of compound **6**.



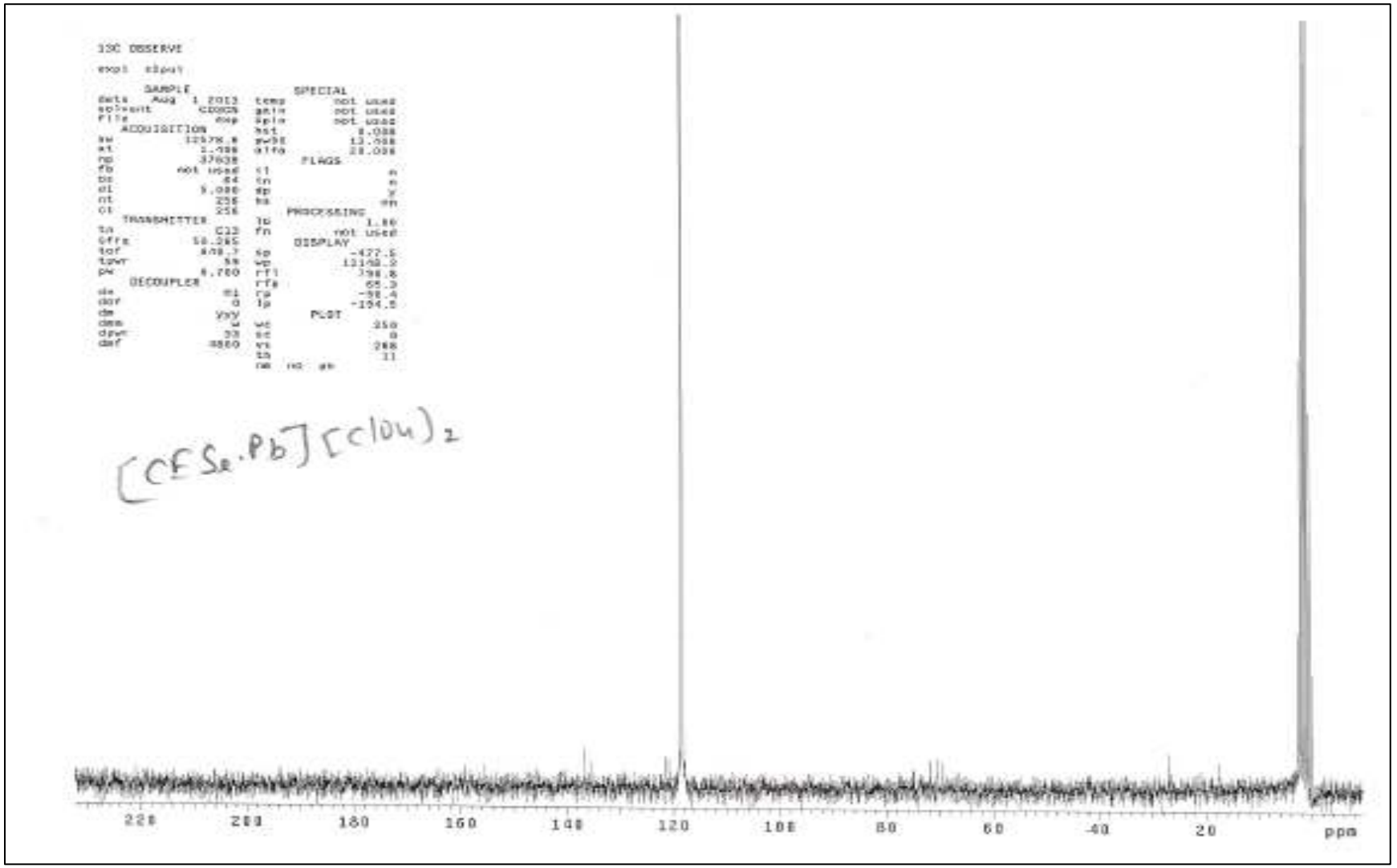
SI Fig. 11: ^{1}H NMR of compound **7**.



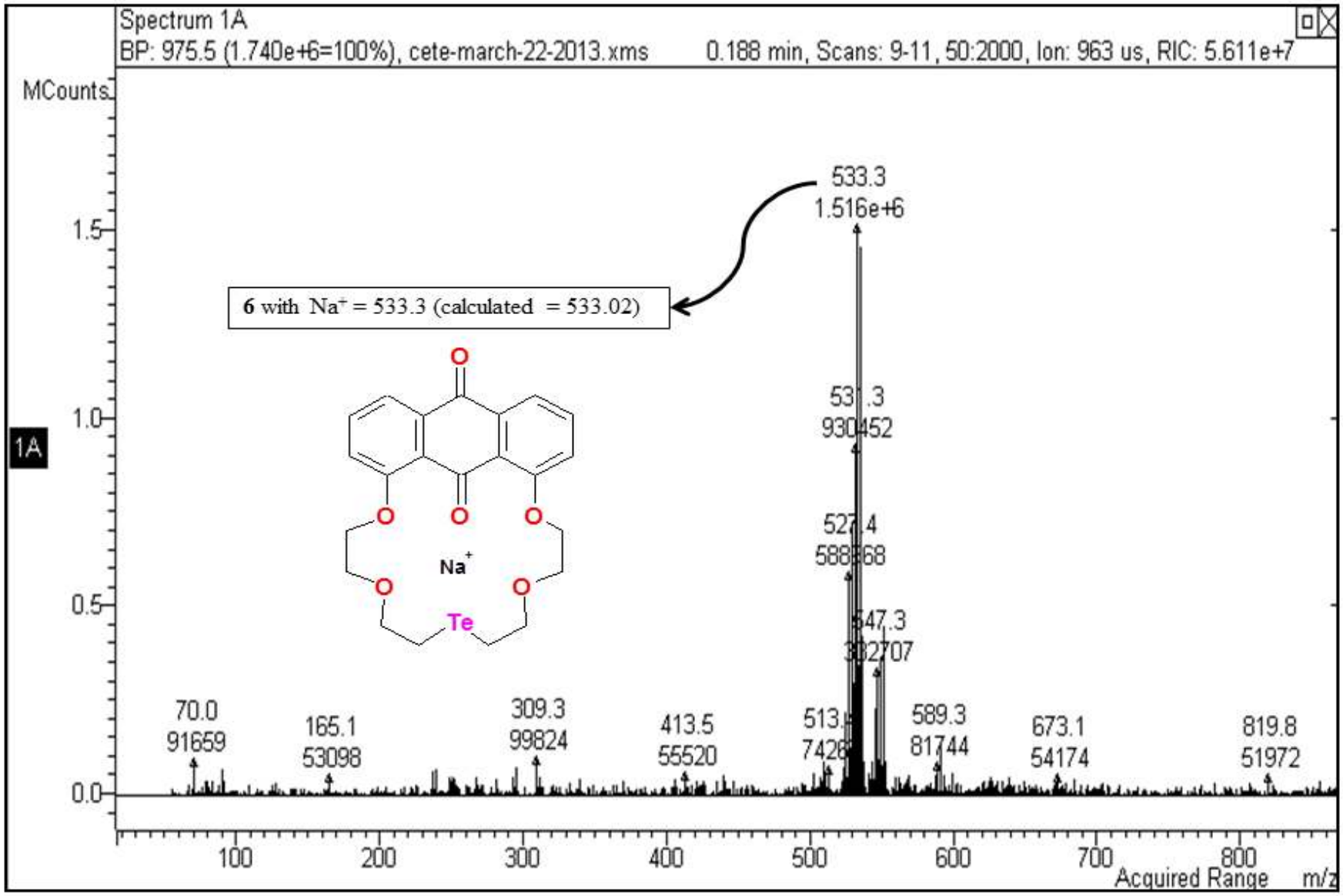
SI Fig. 12: ^{13}C NMR of compound **7**.



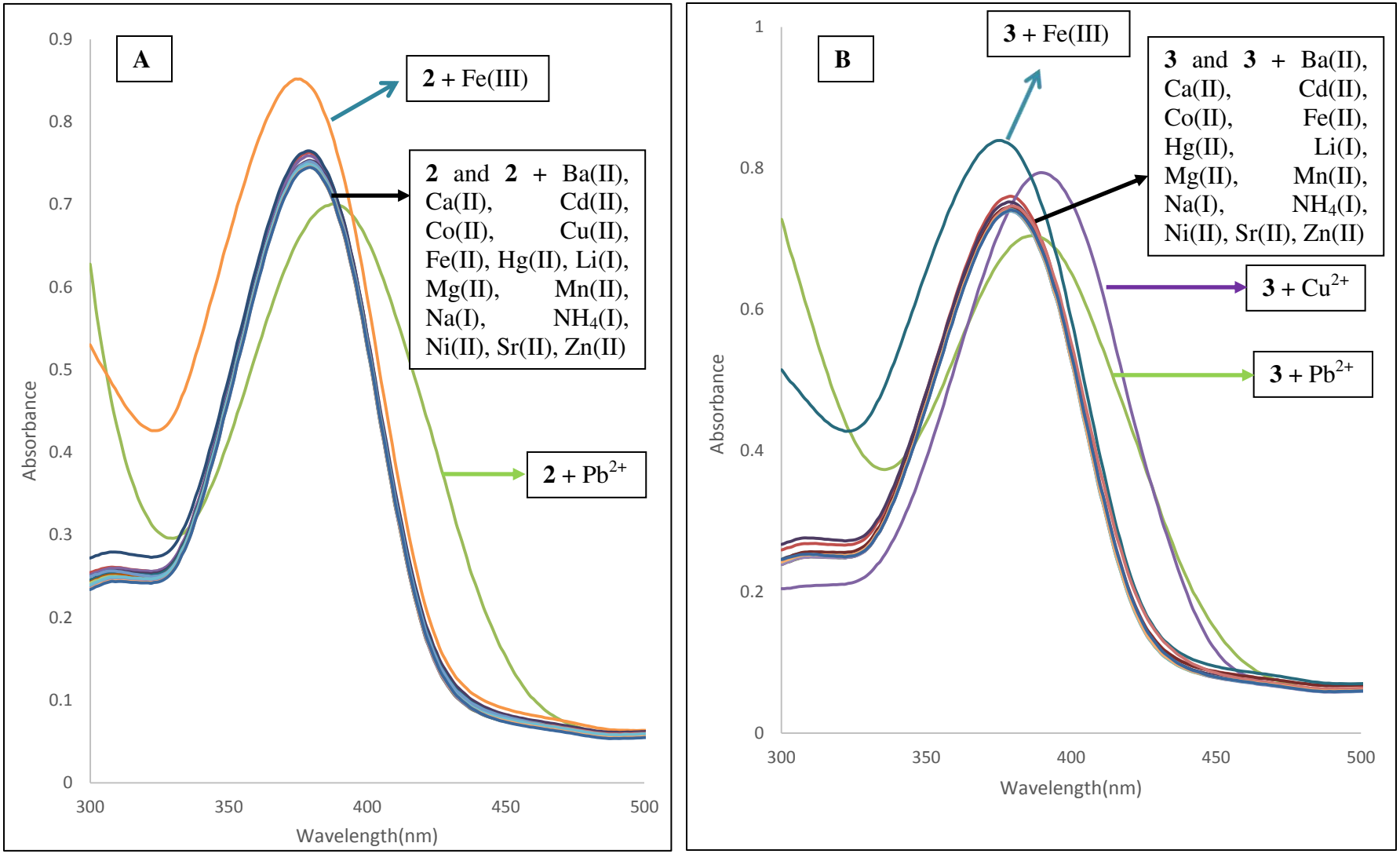
SI Fig. 13: ^{1}H NMR of compound **8**.



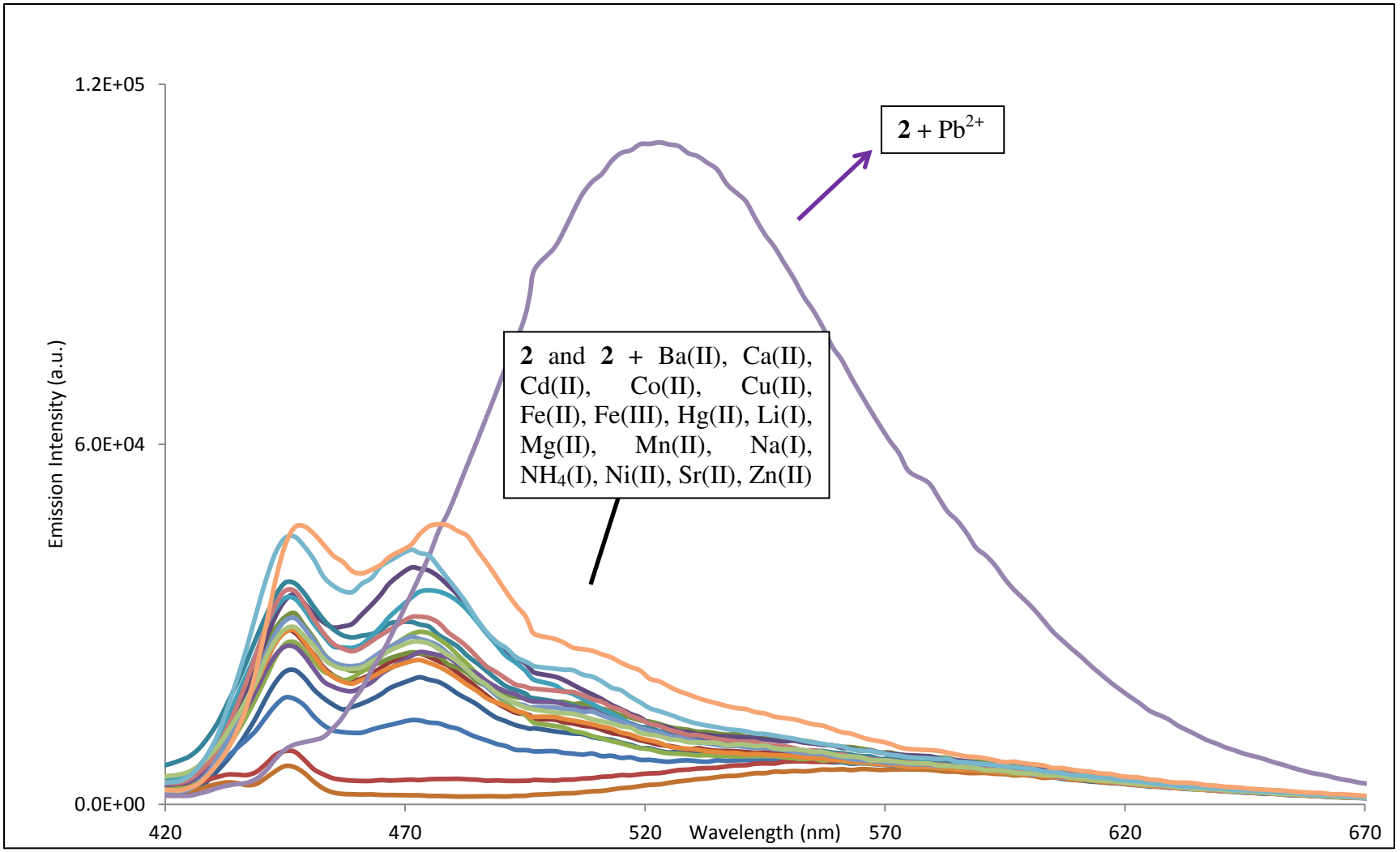
SI Fig. 14: ^{13}C NMR of compound **8**.



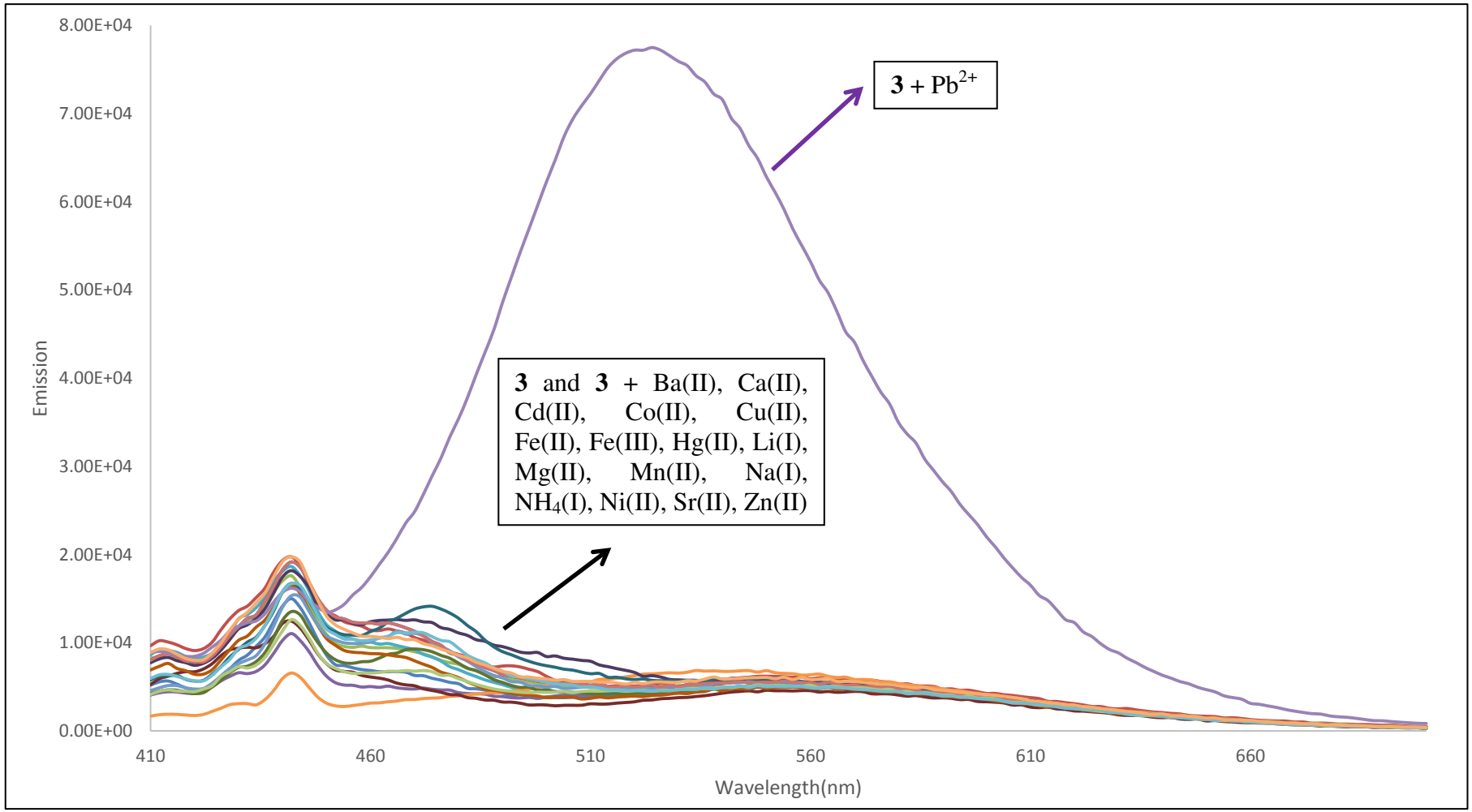
SI Fig. 15: ESI Mass spectrum of compound **6**.



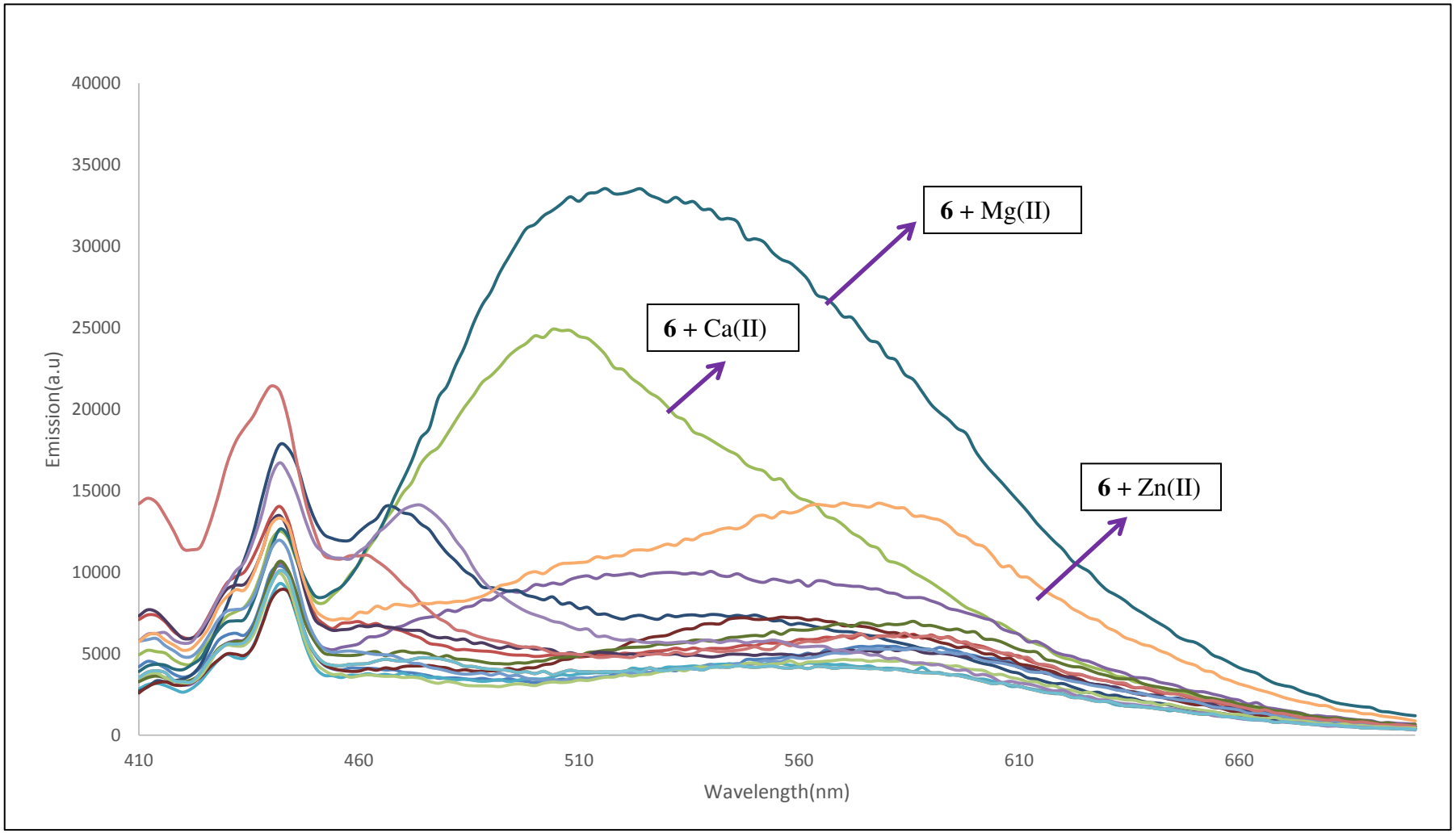
SI Fig. 16: UV-visible of compound **2** (A) and **3** (B) using $1x10^{-4}$ molar in CH_3CN mixed with 2 equivalents of metal ions.



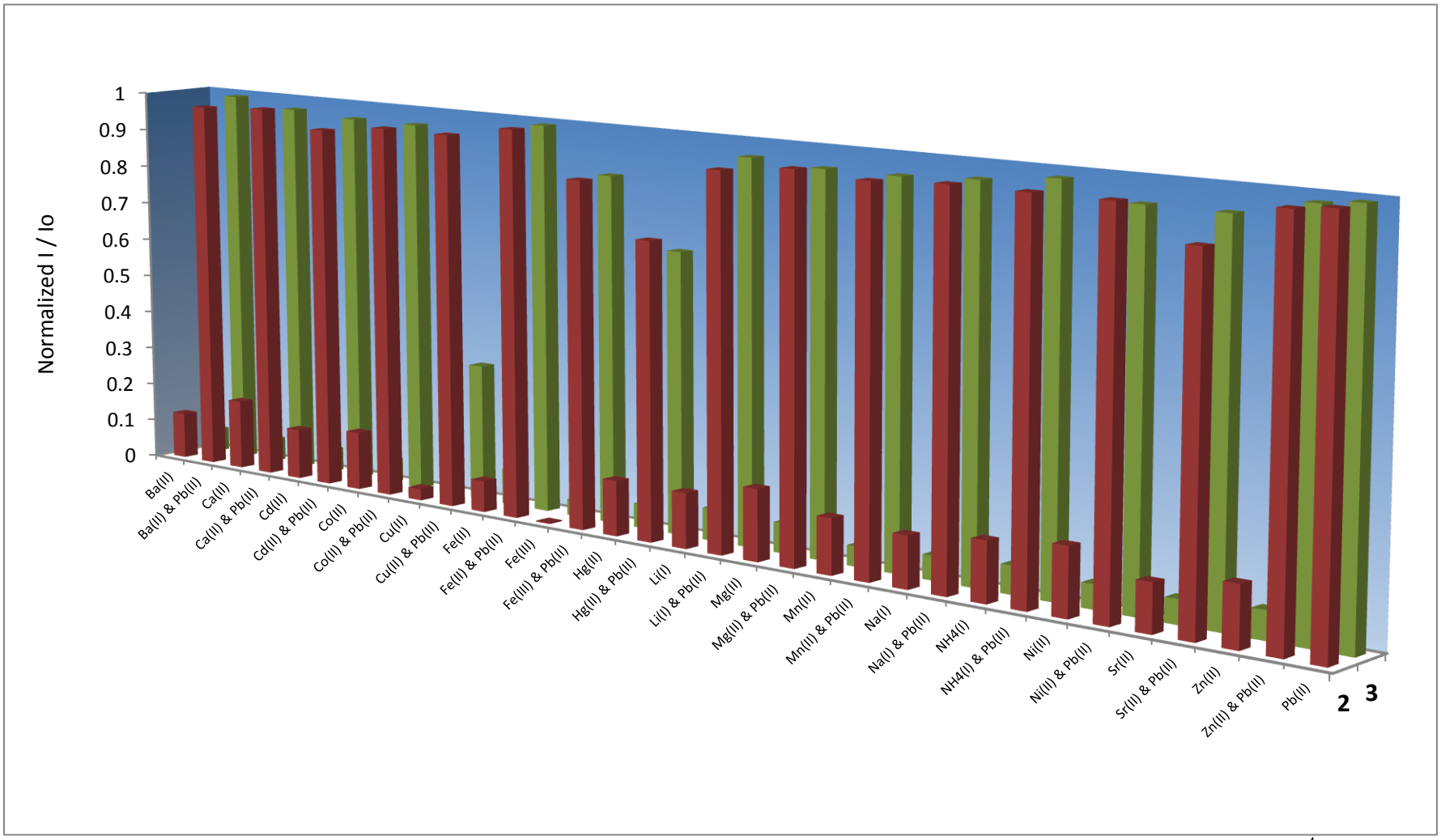
SI Fig. 17: Emission of **2** with different metal ions. 1 x 10^{-4} M of **2** in acetonitrile with two equivalents of M^{n+}. Excitation wavelength is 390 nm.



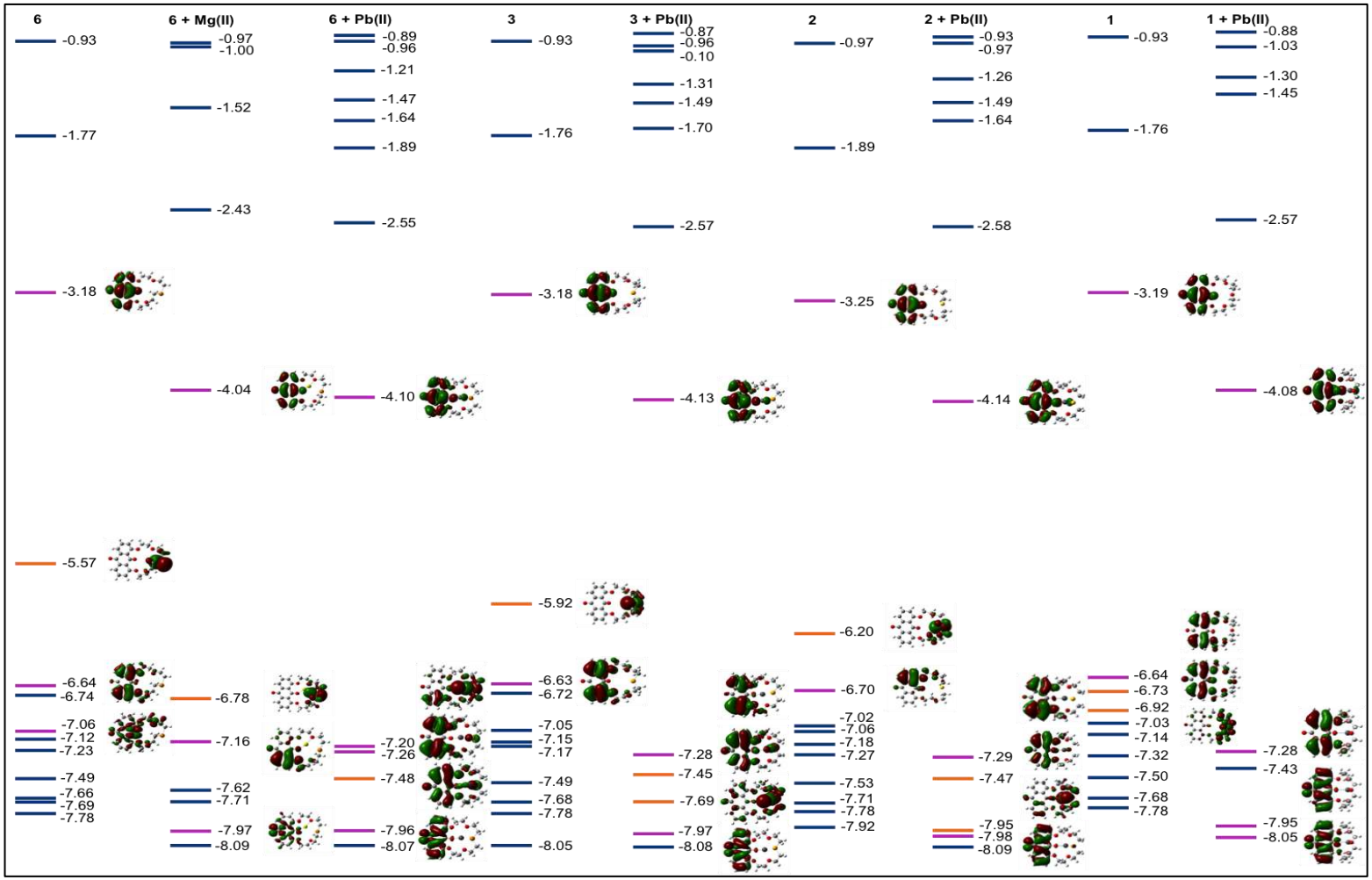
SI Fig. 18: Emission of **3** with different metal ions. 1 x 10^{-4} M of **3** in acetonitrile with two equivalents of M^{n+}. Excitation wavelength is 390 nm.



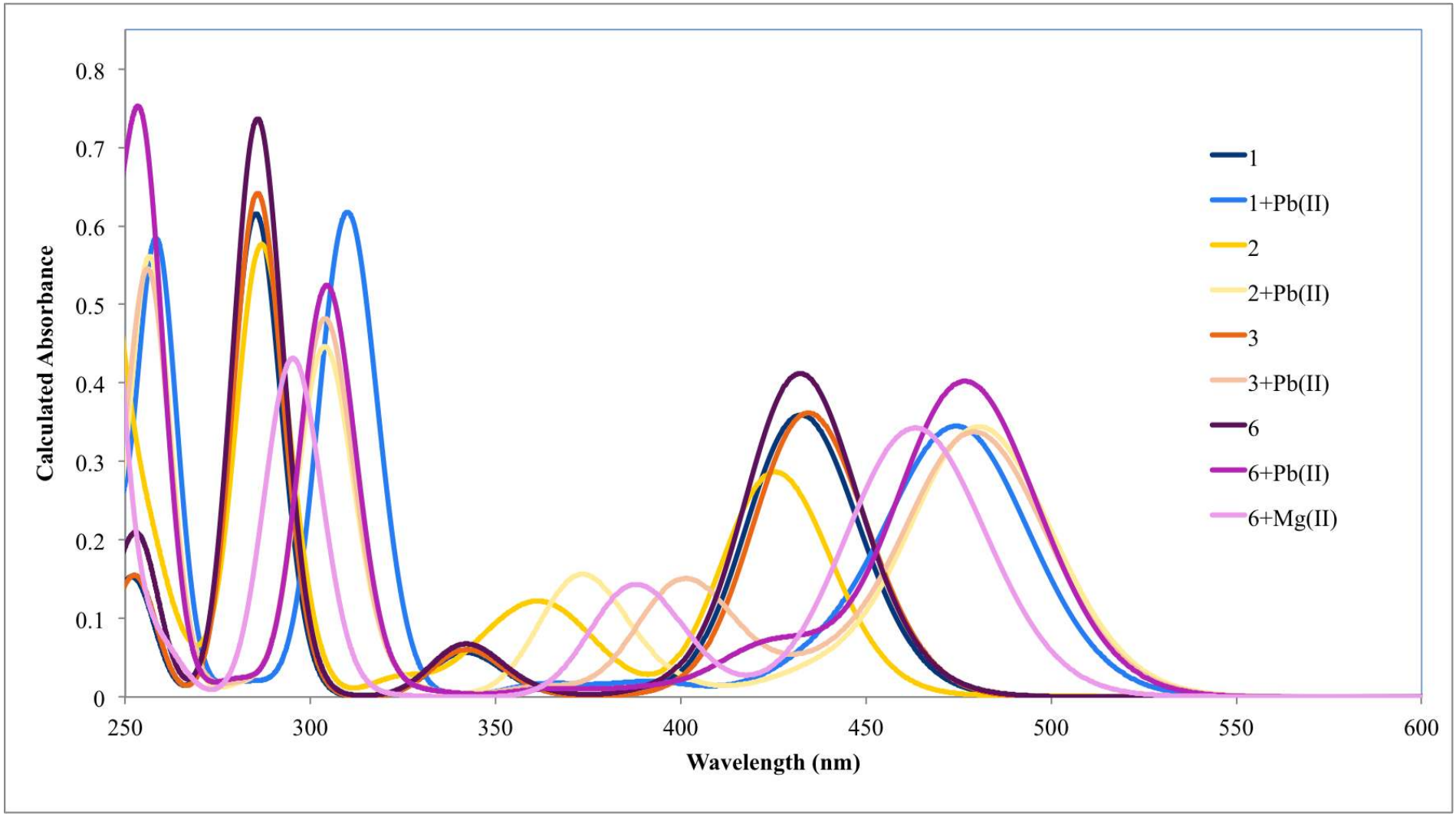
SI Fig. 19: Emission of **6** with different metal ions. 1 x 10^{-4} M of **6** in acetonitrile with two equivalents of M^{n+}. Excitation wavelength is 390 nm.



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 $1x10^{-4}$ molar concentrations with two equivalents of Pb(II) and M^{n+} in acetonitrile. Excitation wavelength is 390 nm.



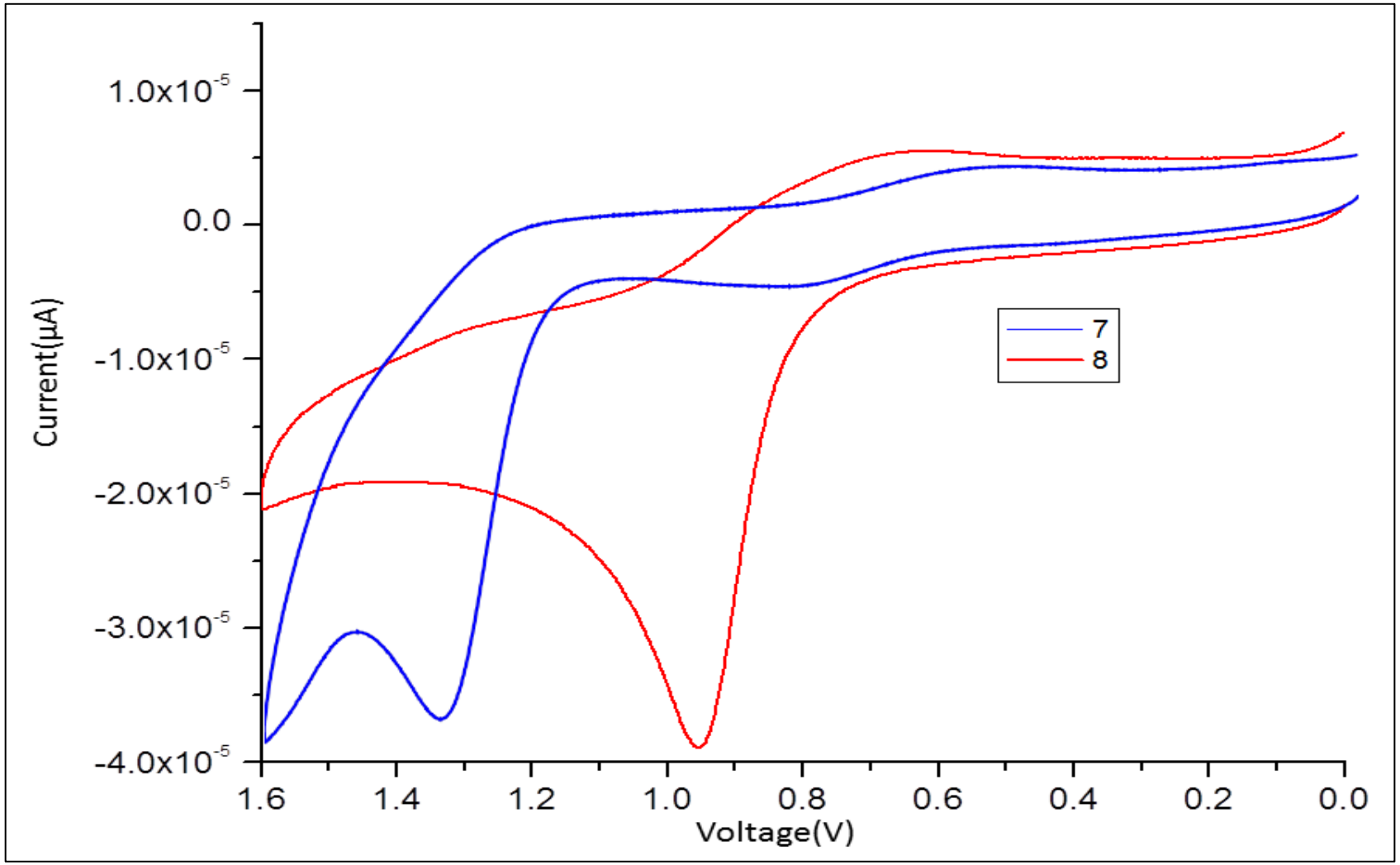
SI Fig. 21: Computationally determined molecular orbital (MO) diagram with energy values in eV. MO surfaces are only displayed for pink- and orange-labeled MOs. Pink MOs are involved in the lowest energy transition of significant oscillator strength in TDDFT calculations that correspond to absorbance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



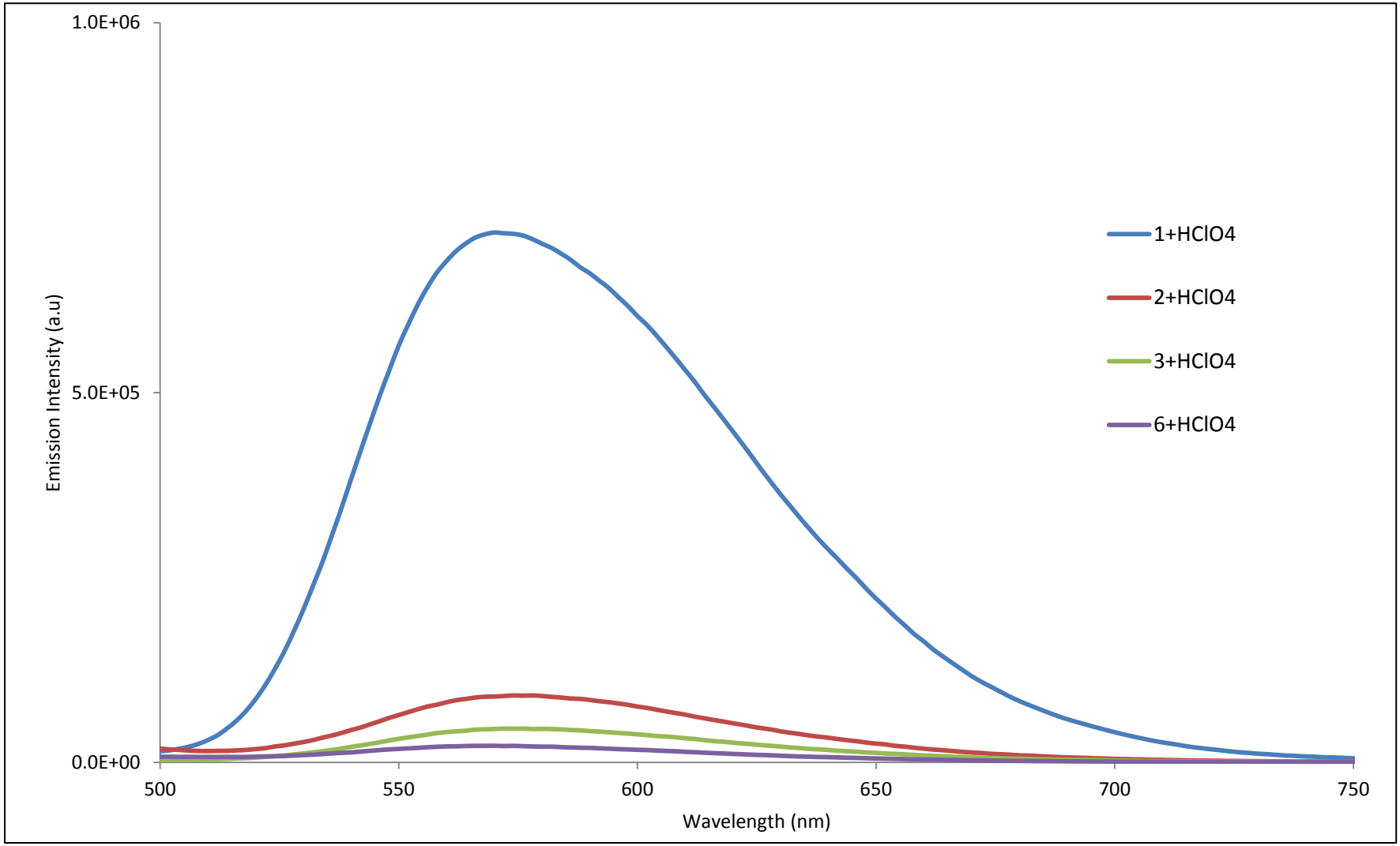
SI Fig. 22 Absorbance spectra of compounds **1**,**2**,**3**,**6** and their Pb(II) complexes determined by TDDFT. Acetonitrile solvent was modeled by IEFPCM.

	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

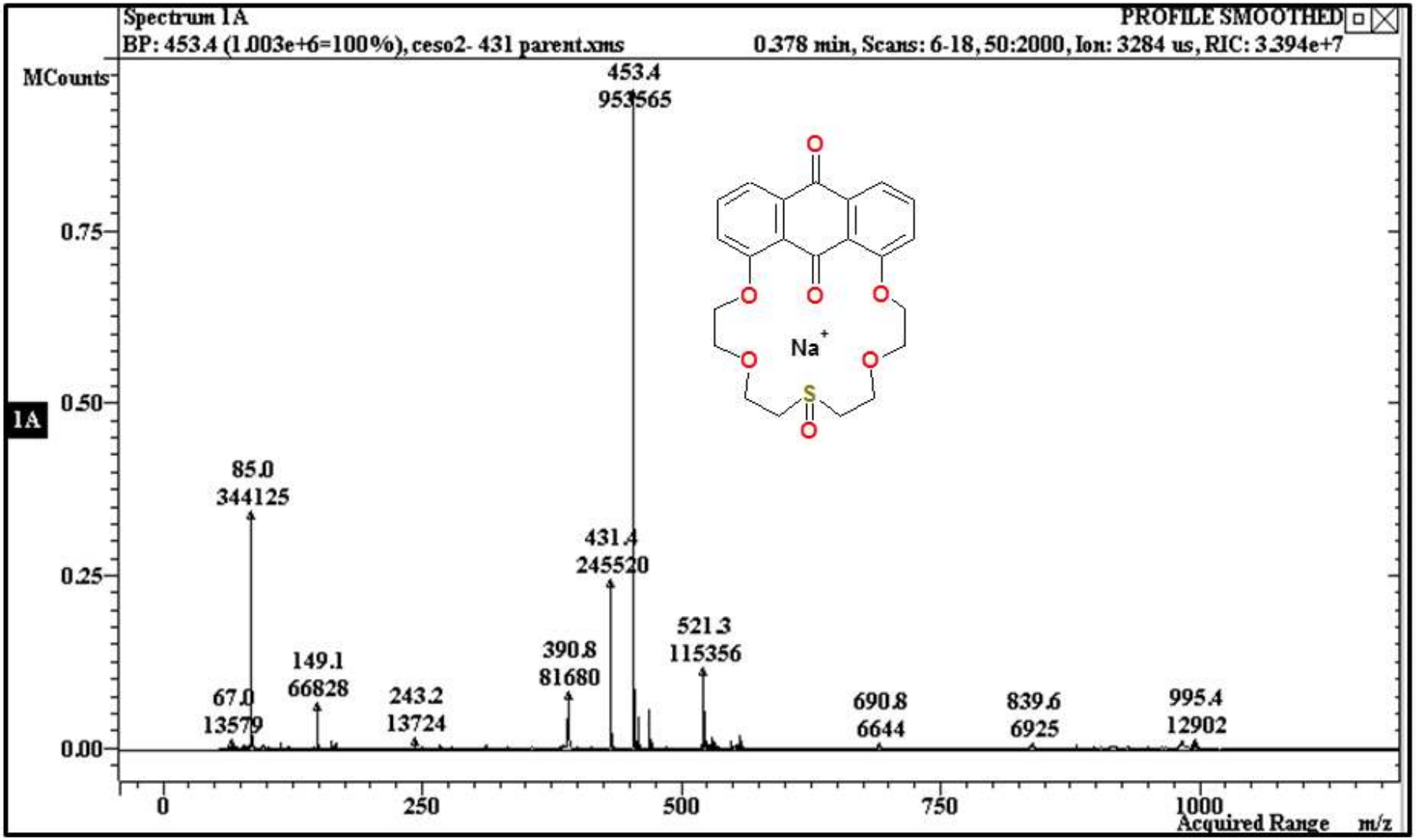
SI Fig. 23 Computationally determined IR stretching frequencies for the internal (inside the macrocycle) and external (outside the macrocycle) anthraquinone carbonyl groups.



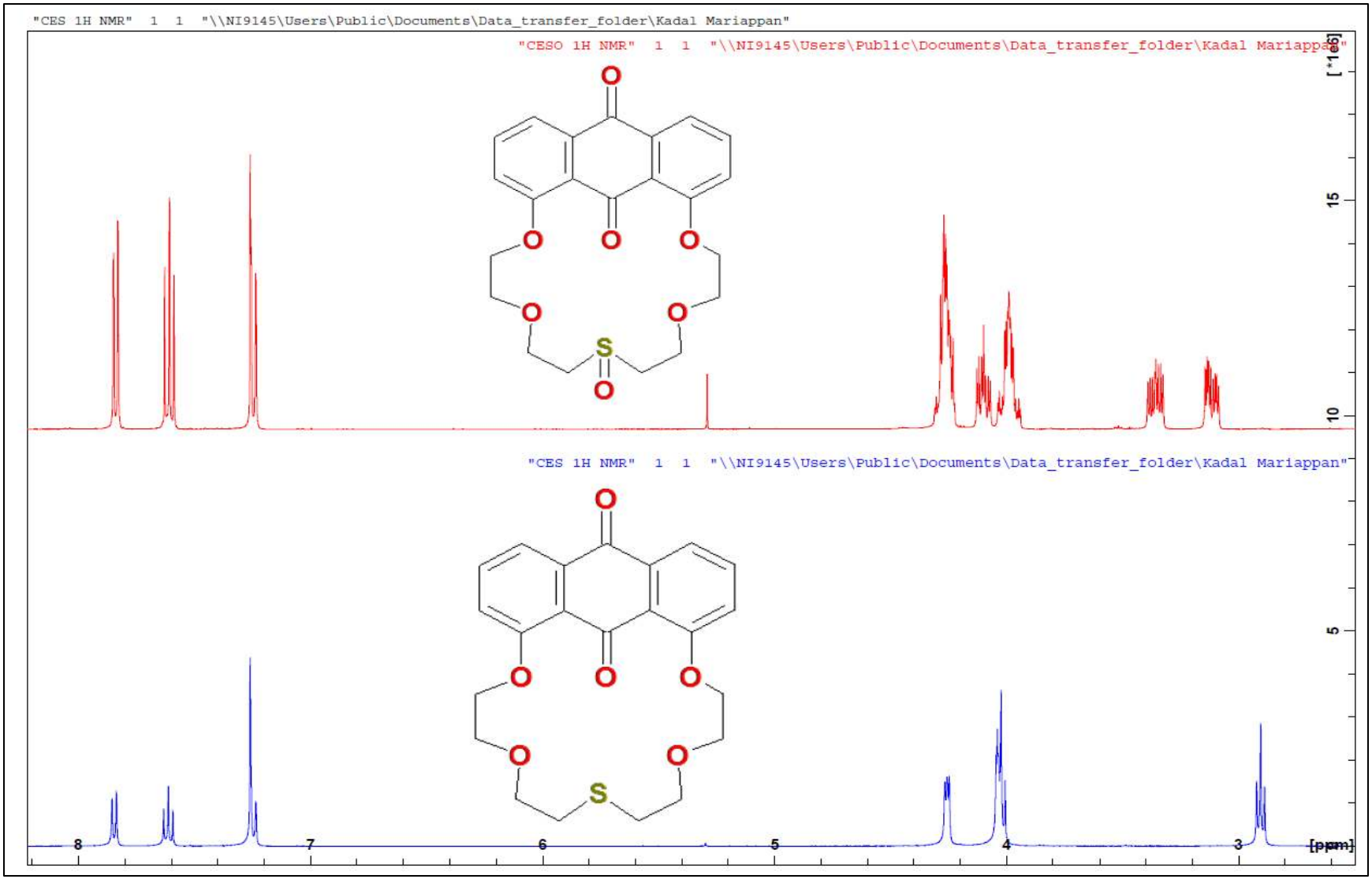
SI Fig. 24: Positive scan of compound **7** and **8** in CH_3CN using 0.1M $TBAClO_4$ vs. Ag/AgCl on glassy carbon.



SI Fig. 25: .6.5x10^{-5} Molar of **1**, **2**, **3** and **6** mixed with excess $HClO_4$. The solution excited at 390 nm.



SI Fig: 26: Mass spectrum of compound **2** as sulfoxide, and m/z s at 431.4, 453.4 are due to protonated and sodiated species of sulfoxide respectively.



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