

Supporting Information

Mechanistic Insights into the Nb₂O₅ and Niobium Phosphate Catalyzed In Situ Condensation of a Fluorescent Halochromic Assembly

Stefania Impellizzeri,^a Sabrina Simoncelli,^{a,b} Chiara Fasciani,^a M. Luisa Marin,^{a,c}
Geniece L. Hallett-Tapley,^a Gregory K. Hodgson,^a and Juan C. Scaiano^{a*}

^a *Department of Chemistry, Centre for Catalysis Research and Innovation, University of Ottawa, 10 Marie Curie, Ottawa, Ontario K1N 6N5, Canada*

^b *INQUIMAE and Departamento de Química Inorgánica, Analítica, y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, 1428 Buenos Aires, Argentina*

^c *Instituto Universitario Mixto de Tecnología Química (UPV-CSIC), Universitat Politècnica de València. Avenida de los Naranjos s/n, 46022 Valencia, Spain*

Hammett acidity (H_0) for the niobium catalysts employed for the condensation of 3 and 4	S2
¹ H NMR of 3 in CD ₃ CN before and after the addition of TFA	S3
¹ H NMR of 3 in CD ₃ OD before and after the addition of TFA	S4
¹ H NMR (detail) of 3a in CD ₃ CN after the addition of CD ₃ OD	S5
Normalized absorption spectra of compounds 1-4	S6
Normalized emission spectra of compounds 4 and 2	S7
Transmission, TIRF and 3D images of a T-II particle for the reaction between 3 and 4	S8
Catalytic activity of a T-II particle for the overall condensation of 3 and 4 by detection of the fluorescence of 2 by TIRFM	S8
XPS data and survey result for 3a	S9
ESI-MS spectrum of 1	S10
EI-MS spectrum of 3	S10
EI-MS spectrum of 4	S11

Table S1. Hammett acidity (H_0) for the niobium catalysts employed for the condensation of **3** and **4**.

Indicator	Max. pK_a	T-I	T-II	T-III
Methyl Red	+5.0	+	+	+
Methyl Yellow	+3.3	-	+	+
Crystal Violet	+0.8	-	+	+
Dicinnamalacetone	-3.0	-	+	+
Chalcone	-5.6	-	+	+
Anthraquinone	-8.6	-	-	-
H_0		+5.0 to +3.3	-8.6 to -5.6	-8.6 to -5.6

(+) = observable color change; (-) = no observable color change

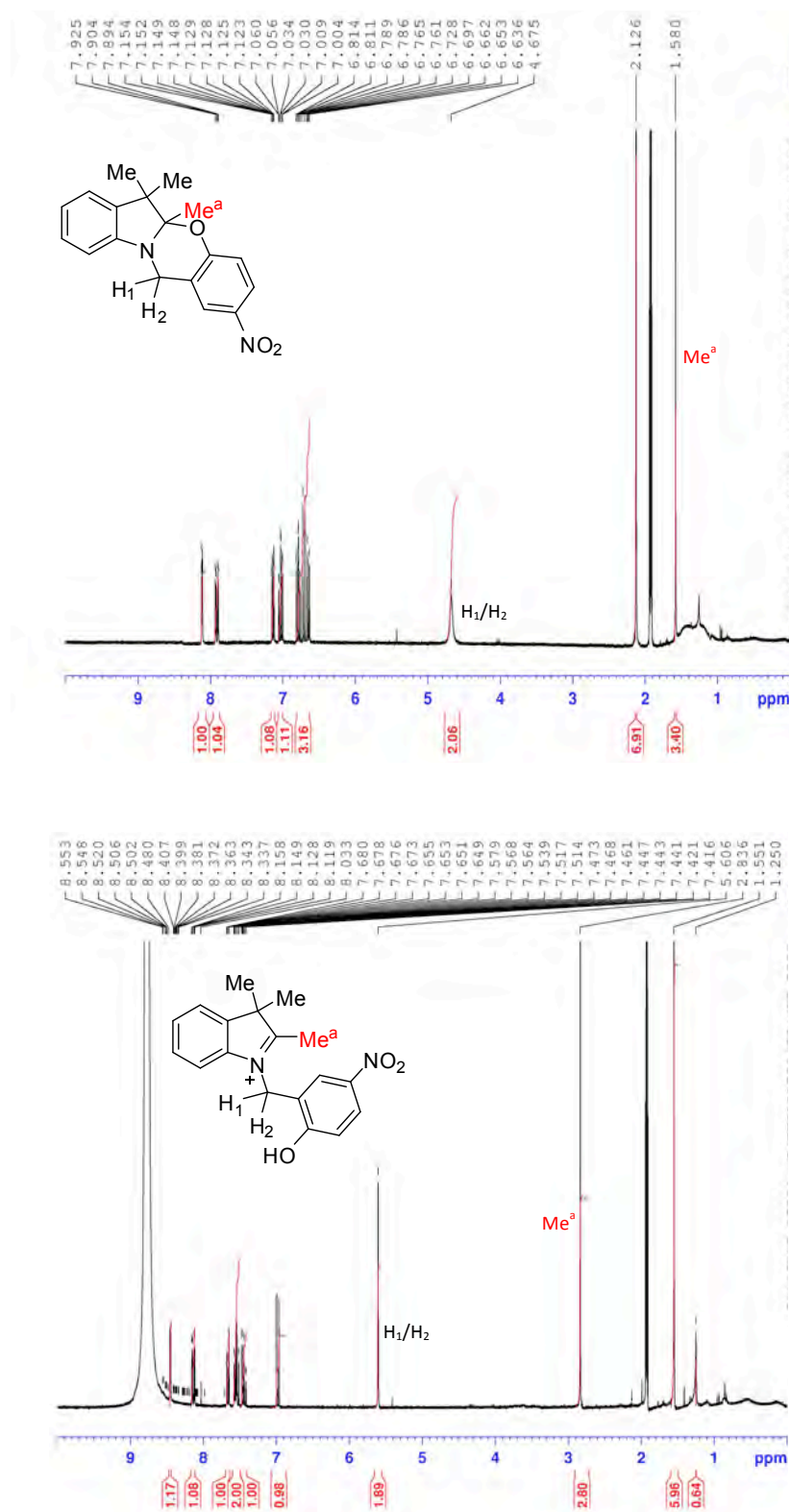


Figure S1: ^1H NMR of **3** in CD_3CN before (top) and after (bottom) addition of TFA.

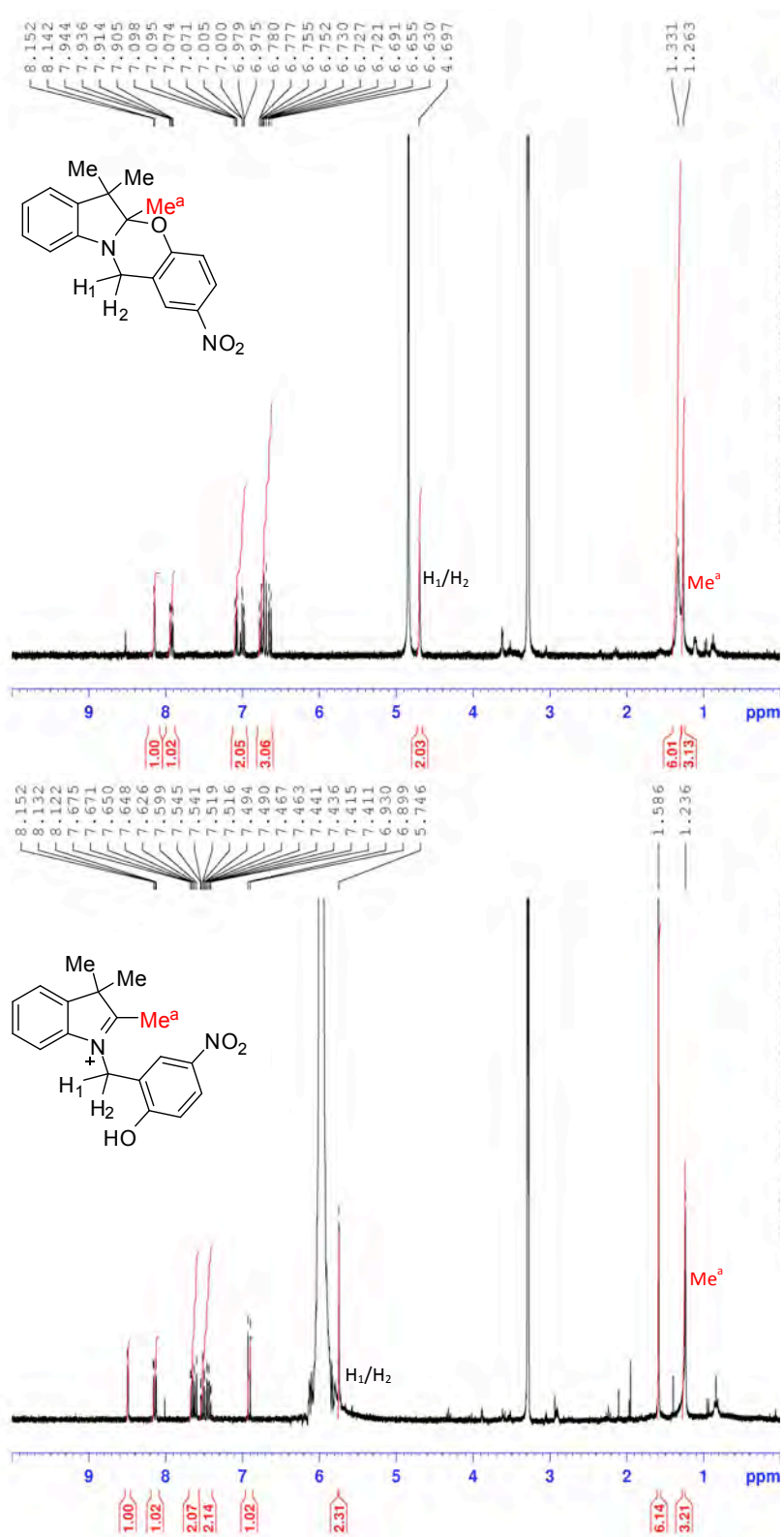


Figure S2: ¹H NMR of **3** in CD₃OD before (top) and after (bottom) addition of TFA.

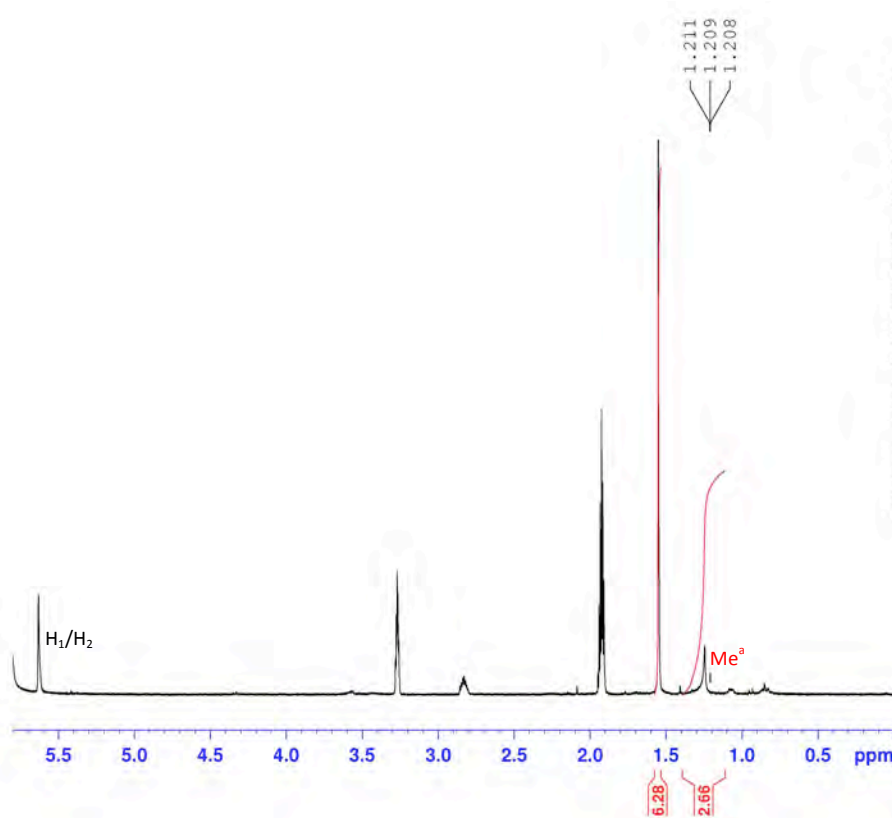


Figure S3: ^1H NMR (detail) of **3a** in CD_3CN after the addition of CD_3OD .

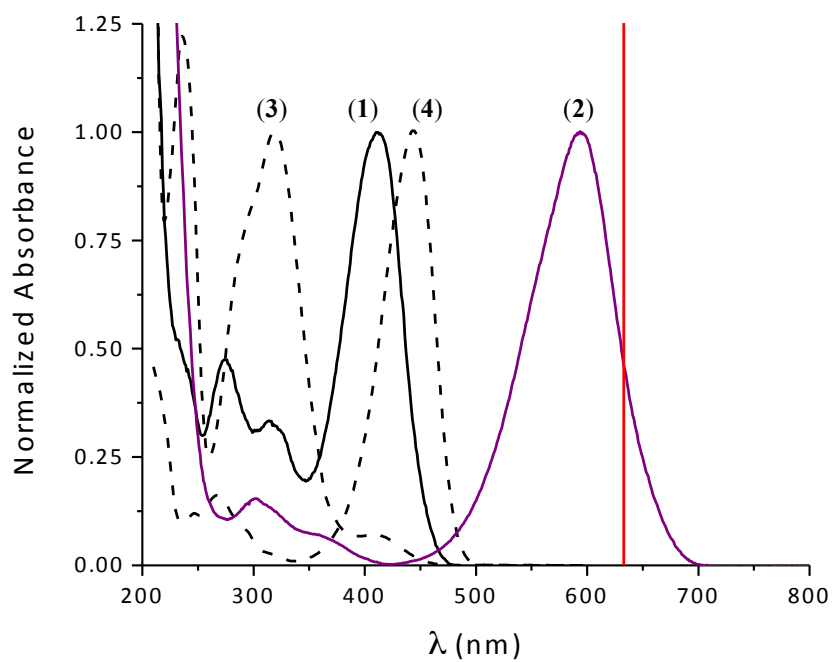


Figure S4. Normalized absorption spectra of **1-4**. The spectrum of **2** was recorded upon addition of 10 equivalents of trifluoroacetic acid to a solution of **1** in MeCN. The line in red represents the laser excitation wavelength (633 nm) used for TIRFM experiments.

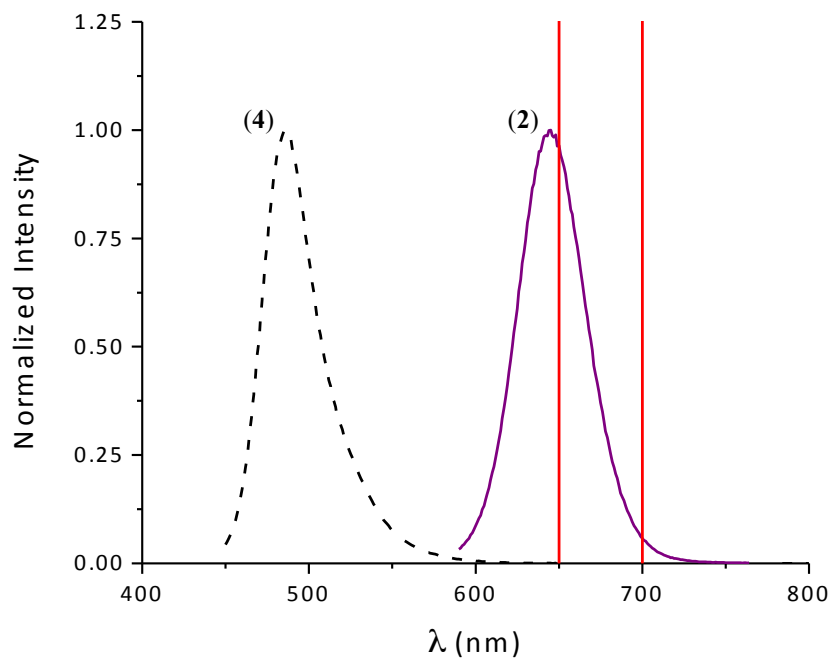


Figure S5. Normalized emission spectra of **4** and **2**. The spectrum of **2** was recorded upon addition of 10 equivalents of trifluoroacetic acid to a solution of **1** in MeCN. The lines in red represents the band pass region of the emission filter used for TIRFM experiments (675/50 nm band pass).

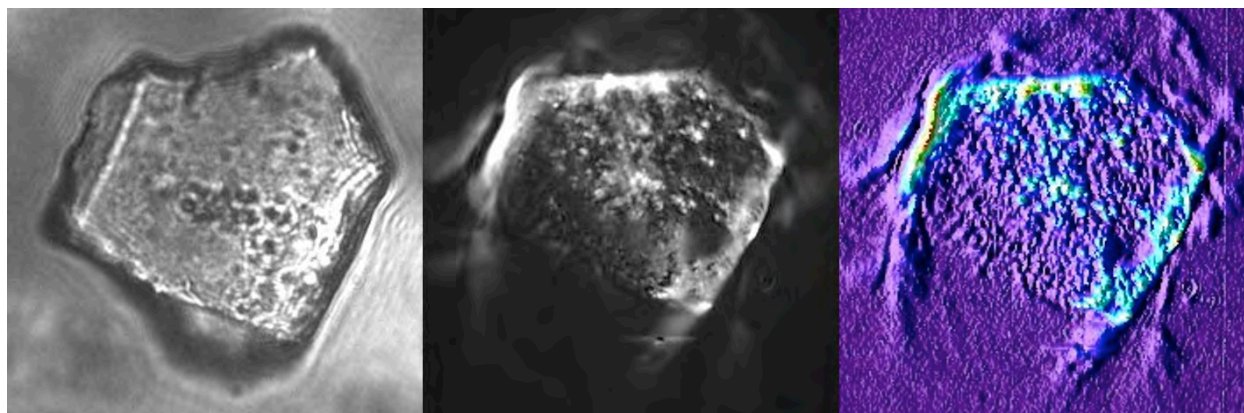


Figure S6. Transmission (left), TIRF (center) and 3D (right) images of a **T-II** particle immobilized on a cover glass and immersed in a 2 mM solution of **3** and **4** with 633 nm laser excitation and a 675/50 nm band pass emission filter (see Supplementary Video S2). The fluorescence image and the 3D representation correspond to the accumulated spot intensity reconstructed from a movie of 500 frames in length (100 ms per frame).

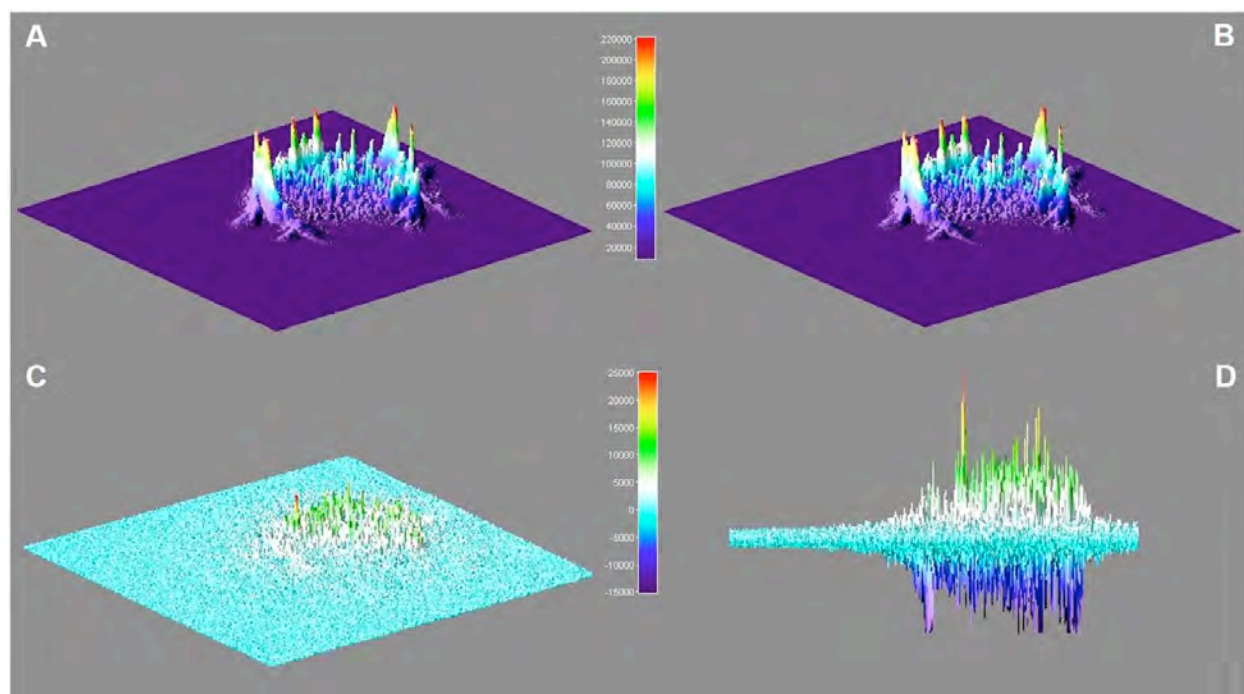
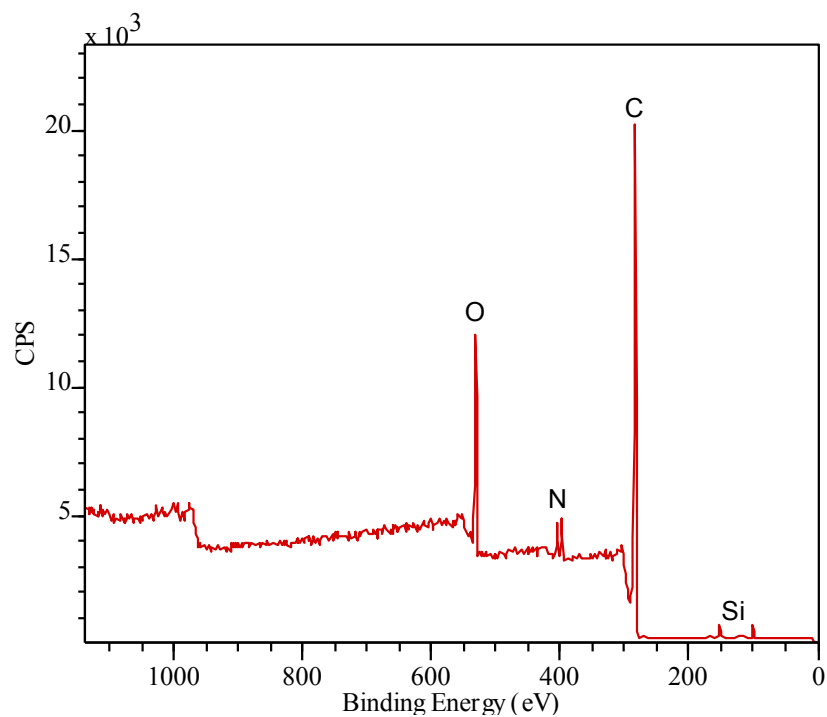


Figure S7. Catalytic activity of a **T-II** particle for the overall condensation of **3** and **4** to generate **2** by detection of the fluorescence of **2** by TIRFM. Surface maps A and B show the accumulated signal for 25 seconds and the subsequent 25 seconds, while C and D show the rescaled difference of A minus B (see color coded legend) from different perspectives.



Peak	Type	Position BE (eV)	FWHM (eV)	RawArea (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
C 1s	Reg	283.000	2.618	57911.7	0.278	12.011	79.80	74.28
O 1s	Reg	531.000	2.732	24188.3	0.780	15.999	12.36	15.32
N 1s	Reg	398.000	2.162	7478.3	0.477	14.007	6.11	6.63
Si 2p	Reg	100.000	2.480	1583.3	0.328	28.086	1.73	3.77

Figure S8. XPS data and survey result for **3a**.

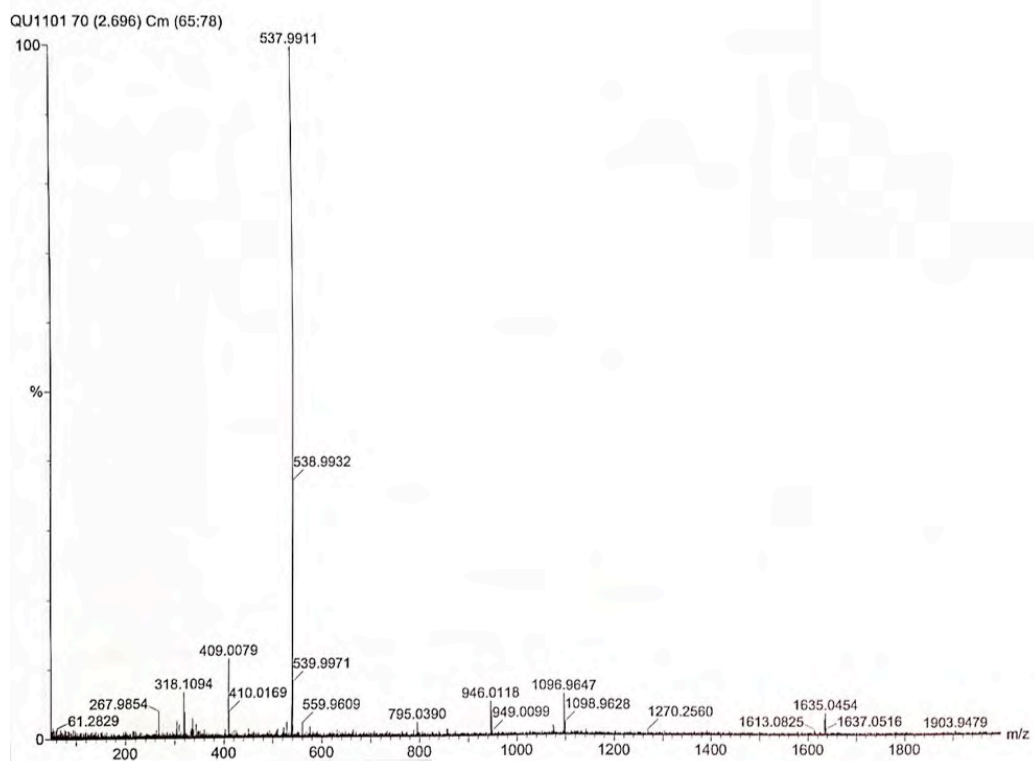


Figure S9. ESI-MS spectrum of **1**.

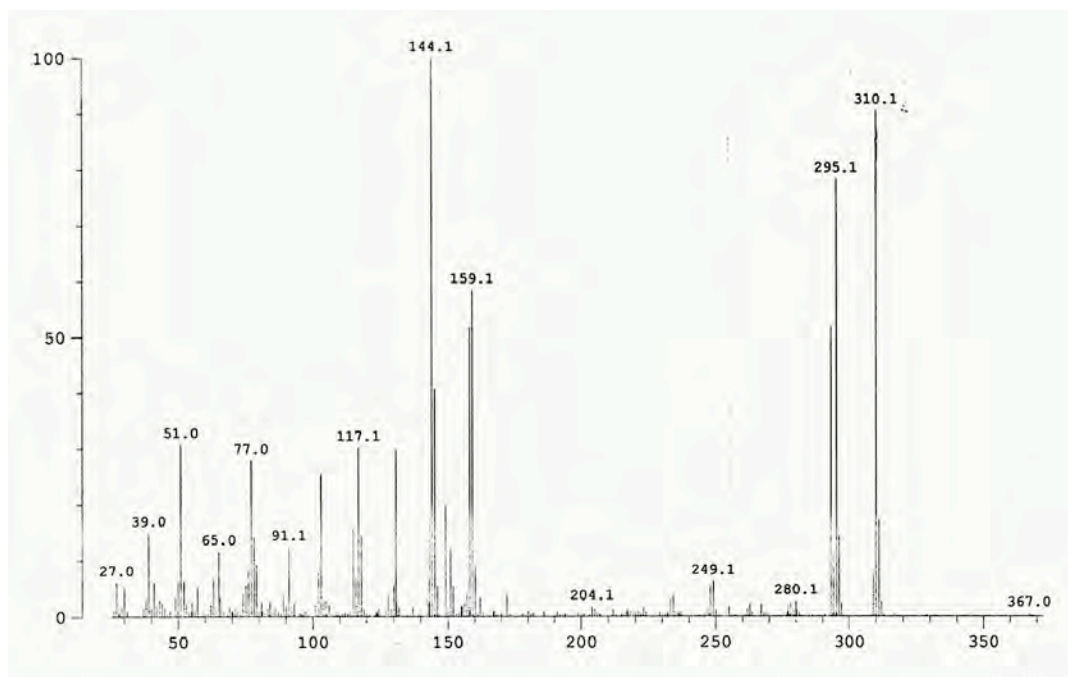


Figure S10. EI-MS spectrum of **3**. Chemical Formula: $C_{18}H_{18}N_2O_3$; Exact Mass: 310.13, Found (Hi-Res): 310.1332

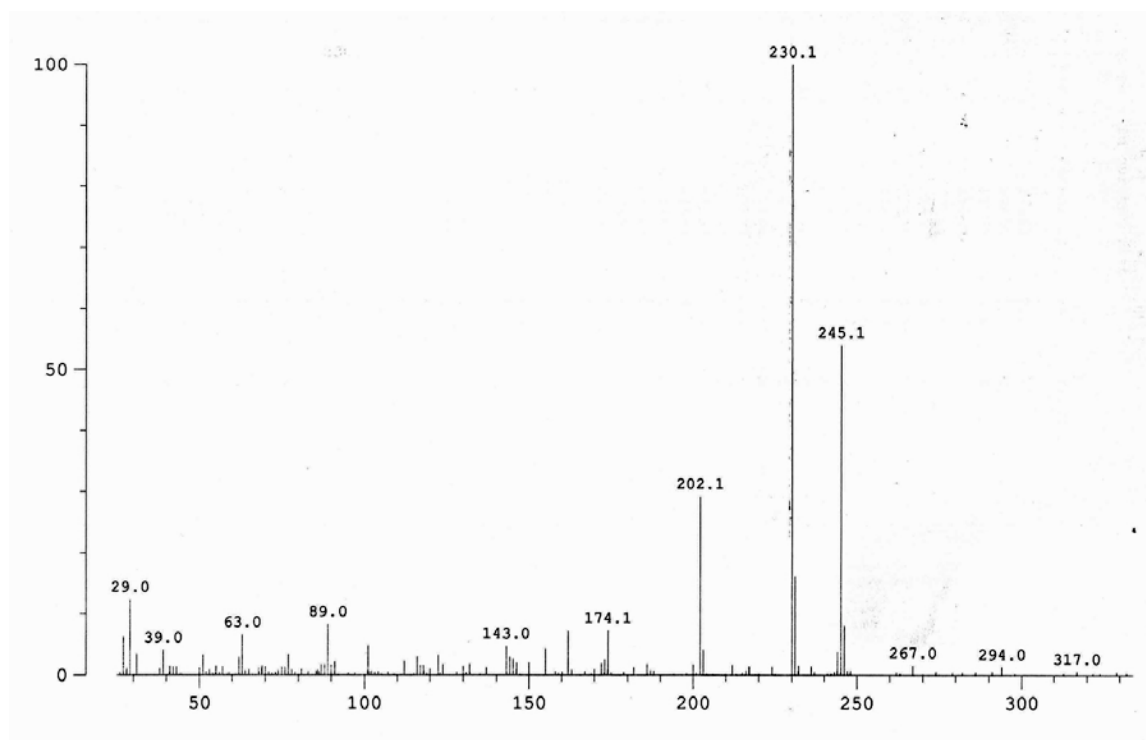


Figure S11. EI-MS spectrum of **4**. Chemical Formula: $C_{14}H_{15}NO_3$, Exact Mass: 245.11, Found (Hi-Res): 245.1036