Electronic Supplementary Information (ESI)

A Ferrocenyl-Guanidine Derivative as Highly Selective Electrochemical and Colorimetric Chemosensor Molecule for Acetate Anion.

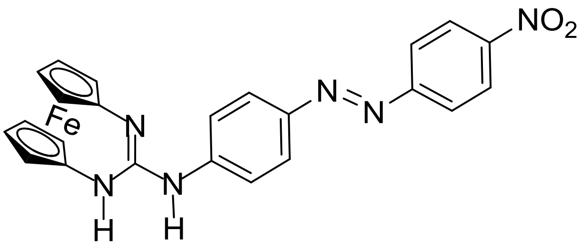
Antonia Sola, Alberto Tárraga* and Pedro Molina*

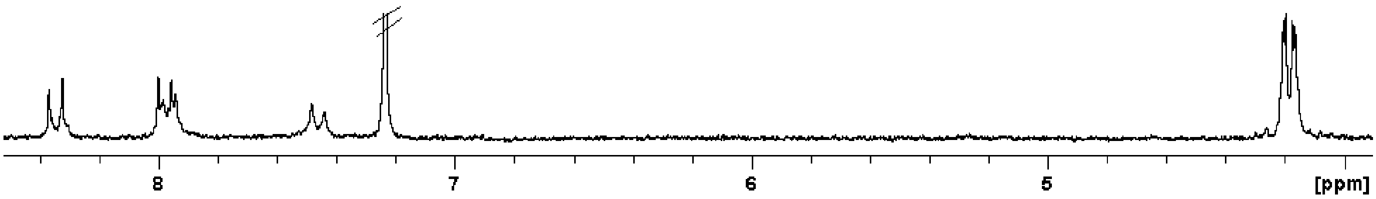
Departamento de Química Orgánica; Universidad de Murcia; Campus de Espinardo; 30100 Murcia, Spain. Fax: +34 868 884 149; Tel: +34 868 887 496 and +34 868 887 499; E-mail: pmolina@um.es; E-mail: atarraga@um.es

Table of contents

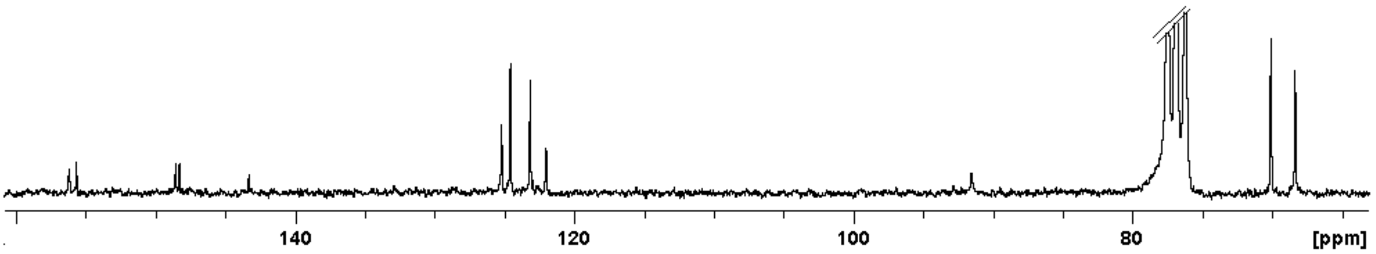
2{(*E*)-4-[2-(4-nitrophenyl)diazenyl]phenylamino-1,3-diaza[3]ferrocenophane, 1

^{1}H NMR (200MHz, $CDCl_3$)





^{13}C NMR (50 MHz, $CDCl_3$)



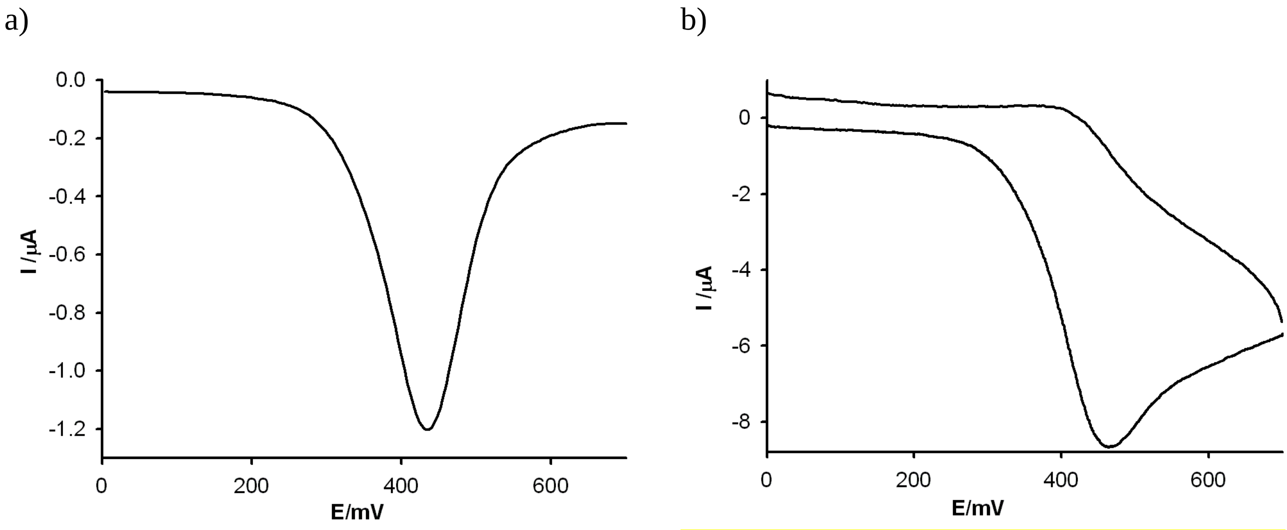


Figure ESI 1. a) OSWV and b) CV, from 0-700 mV of compound **1** (c = $1x10^{-4}$ M in CH_3CN) using $[(n\text{-}C_4H_9)_4N]PF_6$ (0.1 M) as supporting electrolyte, scanned at 0.1 V s^{-1}.

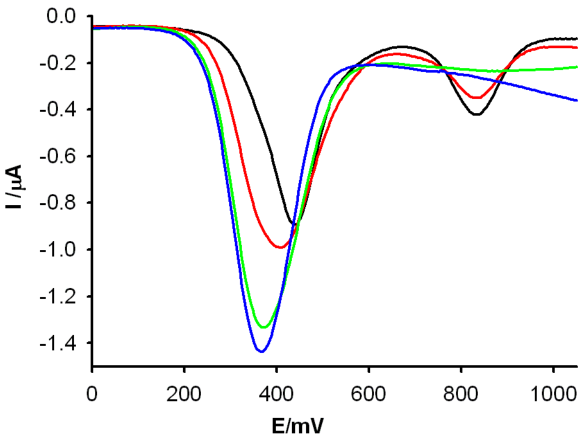


Figure ESI 2. Evolution of the OSWV of **1** (c = $1x10^{-4}$ M in CH_3CN) using $[(n\text{-}Bu)_4N]PF_6$ scanned at 0.1 V s^{-1} in the presence of 20 equiv of AcOH, upon adition of AcO^- from 0 (black) to 3 (blue) equiv.

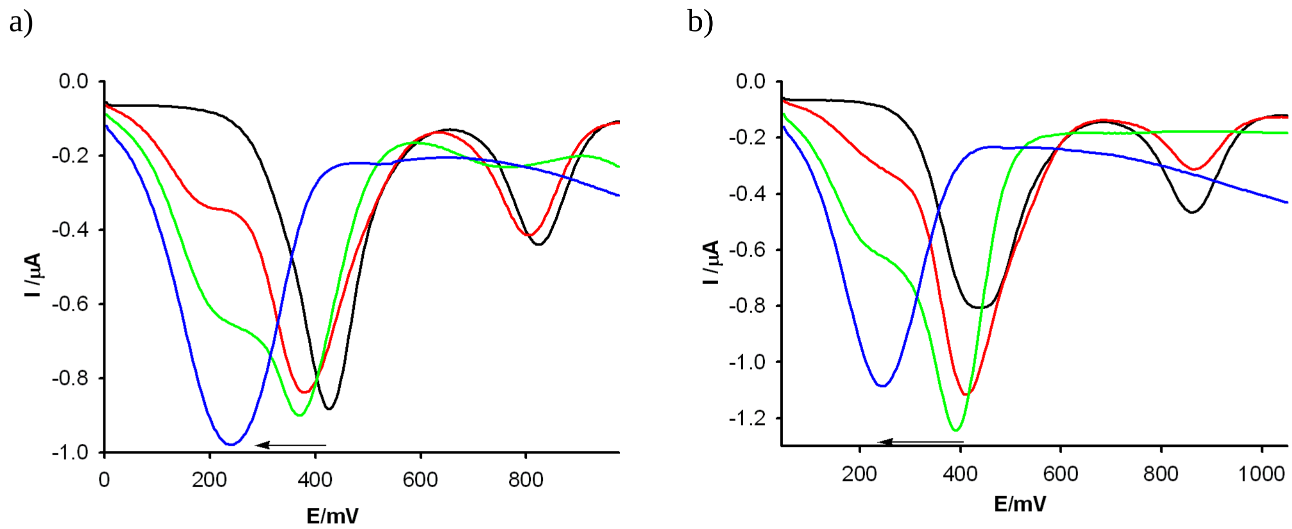
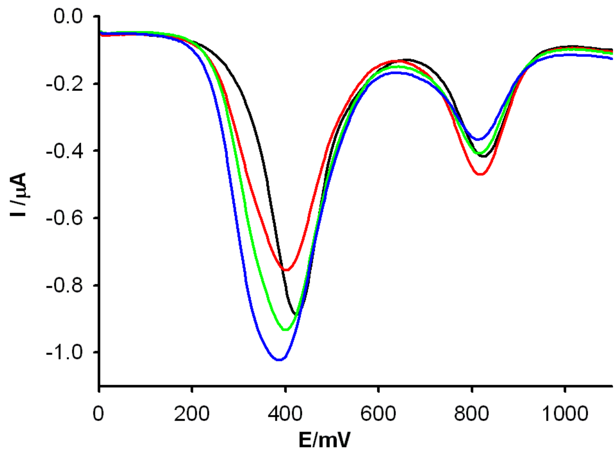


Figure ESI 3. Evolution of the OSWV of **1** (c = 1x10^{-4} M in CH_3CN) using [(*n*-Bu)$_4$N]PF_6 scanned at 0.1 V s^{-1} upon adition of a) F^- and b) Bu_4NOH , from 0 (black) to 6 (blue) equiv.



Figur ESI 4. a) Evolution of the OSWV of **1** (c = 1x10^{-4} M in CH_3CN) using [(*n*-Bu)$_4$N]PF_6 scanned at 0.1 V s^{-1} in the presence of 20 equiv. of AcOH upon adition of F^-, from 0 (black) to 3 equiv (blue).

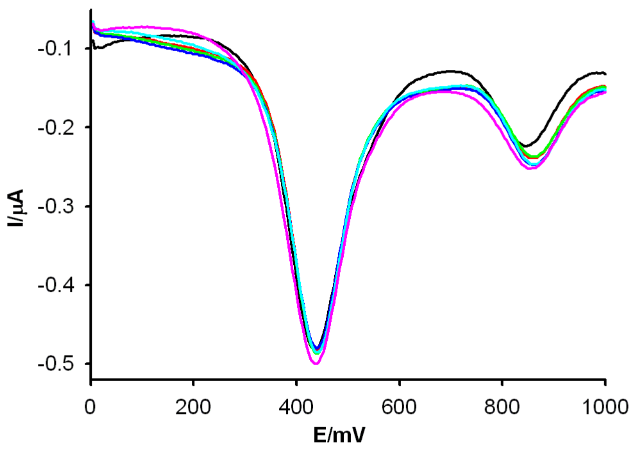


Figure ESI 5. a) Evolution of the OSWV of **1** (c = $1\cdot10^{-4}$ M) in $CH_3CN/[(n\text{-}Bu)_4N]PF_6$ scanned at 0.1 V s^{-1} upon adition of $(Bu_4N)_2CO_3$ (c = $2.5\cdot10^{-2}$ M in CH_3CN), from 0 (black) to 1 (pink) equiv.

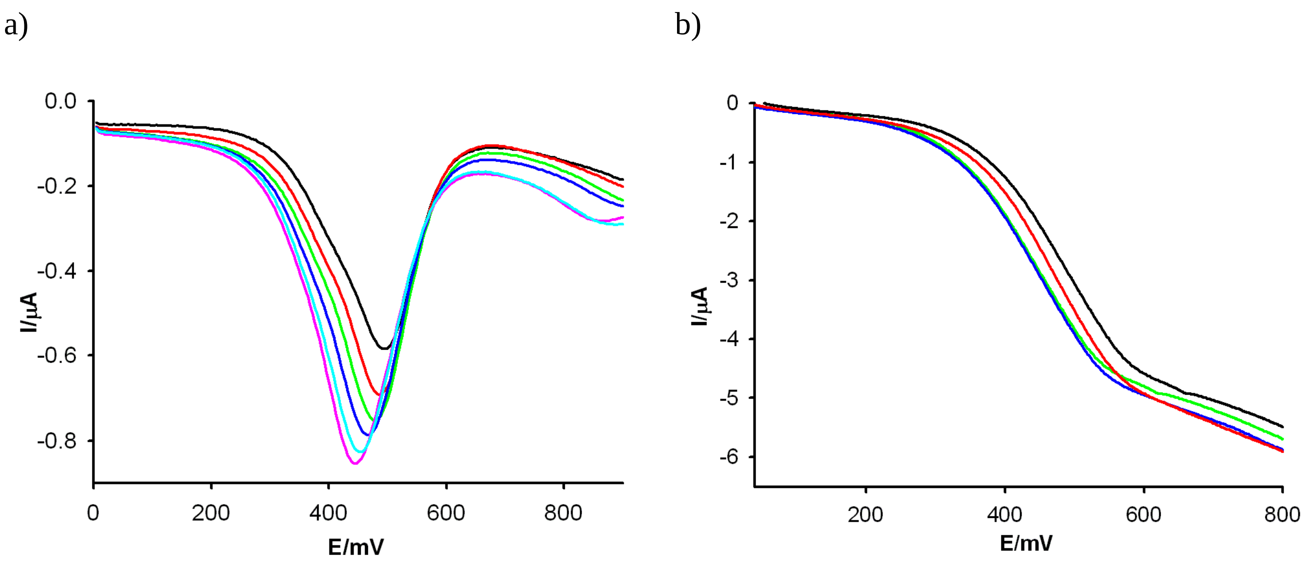


Figure ESI 6. a) Evolution of the OSWV of **1** (c = $1\cdot10^{-4}$ M) in $DMF/[(n\text{-}Bu)_4N]PF_6$ scanned at 0.1 V s^{-1} upon adition of NaClO (c = $2.5\cdot10^{-2}$ M in DMF), from 0 (black) to 5 (pink) equiv. b) Evolution of the linear sweep voltammetry (LSV) of **1** ($1x10^{-4}$ M) in $DMF/[(n\text{-}Bu)_4N]PF_6$ obtained using a rotating disk electrode at 100 mVs^{-1} and 1000 rpm., upon addition of increasing amounts [from 0 (black) to 5 equiv (blue)] of NaClO.

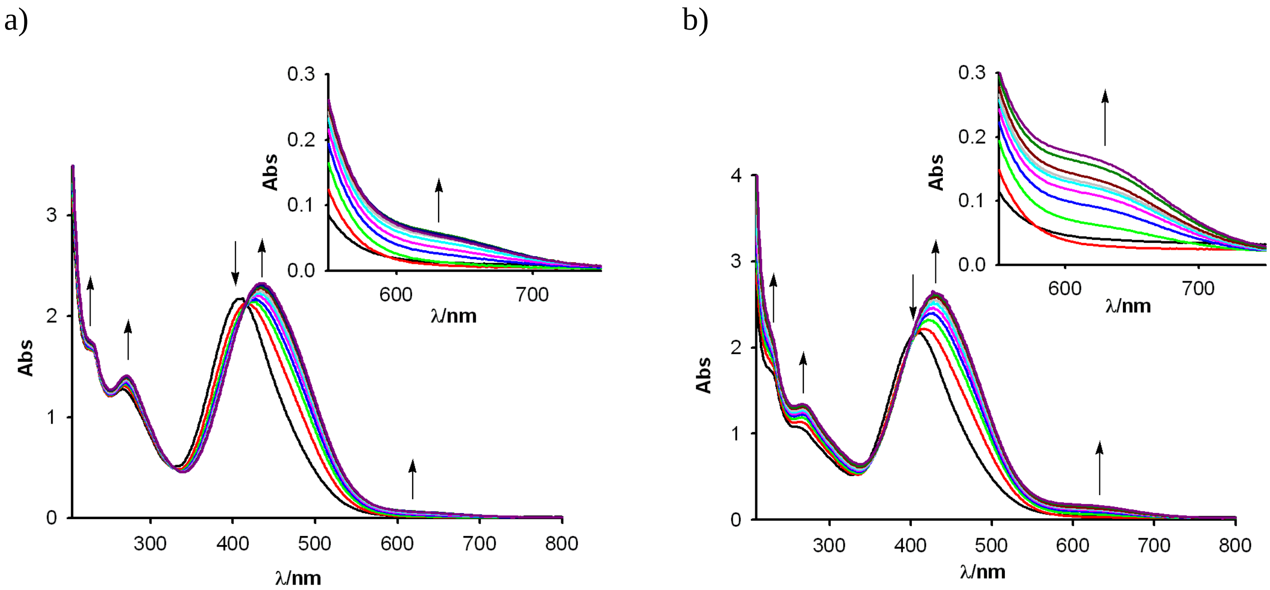


Figure ESI 7. Changes in the absorption spectra of **1** (c =1x10^{-4} M) in CH_3CN upon addition of: a) F^-, and b) Bu_4NOH, from 0 to 5 equiv. Arrows indicate the absorptions that increase or decrease during the titration process.

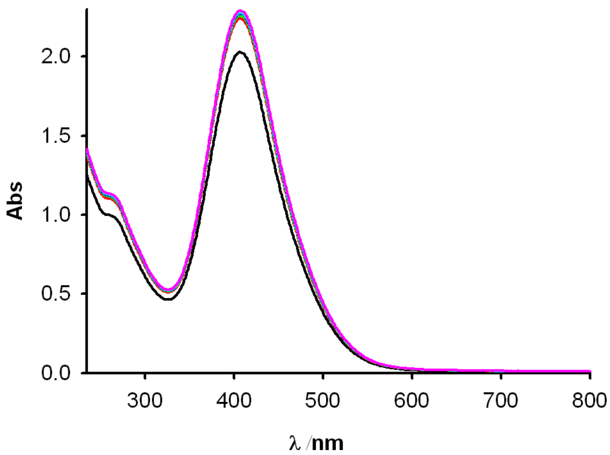


Figure ESI 8. Changes in the absorption spectra of **1**, (c = 1·10^{-4} M in CH_3CN) (black), upon addition of increasing amounts of $(Bu_4N)_2CO_3$ (c = 2.5·10^{-2} M in CH_3CN)until 1 equiv (pink line).

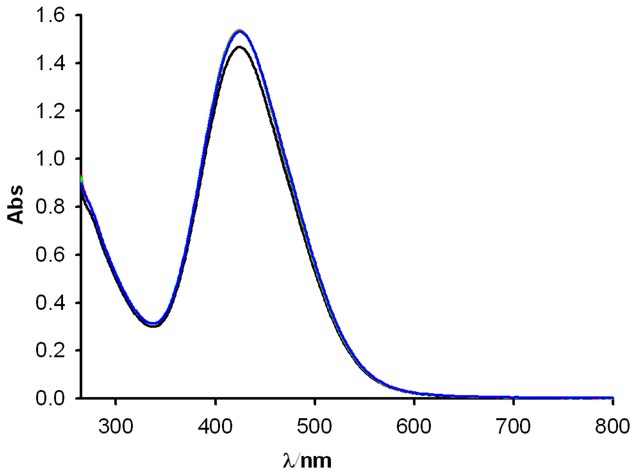


Figure ESI 9. Changes in the absorption spectra of **1**, (c = $1\cdot10^{-4}$ M in DMF) (black), upon addition of increasing amounts of NaClO (c = $2.5\cdot10^{-2}$ M in DMF)until 3 equiv (blue line).

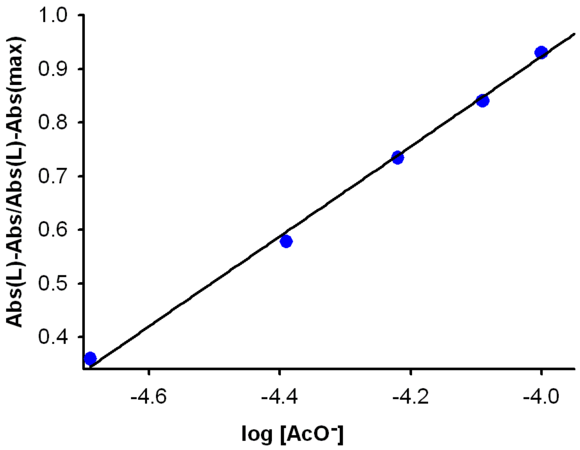


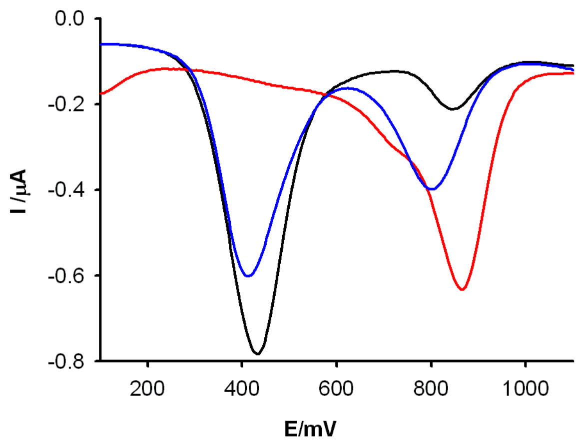
Figure ESI 10. Absorbance of **1** (c = $1\cdot10^{-4}$M in CH_3CN) at each concentration of AcO^- added, normalized between the minimum absorbance, found at zero equiv of AcO^-, and the maximum absorbance.

Table ESI 1. Elecrtochemical and UV-Vis data of **1** and [**1•H**]$^+$, and in the presence of the corresponding anions.

Compound	$E_p^{1\ a}$	$E_p^{2\ a}$	$\Delta E_p^{2\ b}$	$\lambda_{max}(10^{-3}\ \varepsilon)$ [c]	$\Delta\lambda$[d]	IP[e]	Kas
1	440	830	---	230(14.14), 270(9.55), 410(18.40)	---	---	---
[**1**•AcO$^-$]	258	---	-182	231(14.96), 272(10.78),440(20.86)	30	330, 415	$3.81x10^6 \pm 0.55$[f]
[**1•H**]$^+$	---	865	---	231(16.44),344(19.13)	66	---	---
[**1•H**]$^+$ + AcO$^-$	410	800	---	230(14.14), 270(9.55), 410(18.40)	---	---	---
[**1•H**]$^+$ + Cl$^-$	---	724	-141	231(17.81),352(19.42)	8	291, 345	$2.80x10^{11} \pm 0.91$[g]
[**1•H**]$^+$ + Br$^-$	---	683	-182	350(19.18)	6	286, 347	$3.27x10^5 \pm 0.19$d[f]
[**1•H**]$^+$ + NO_3^-	---	758	-107	350(18.85)	6	277, 350	$1.66x10^5 \pm 0.15$[f]
[**1•H**]$^+$ + HSO_4^-	---	758	-107	230(16.93),352(18.87)	8	280, 350	$1.98x10^5 \pm 0.18$[f]

[a] in mV; [b] electrochemical shifting, in mV, observed upon addition of the corresponding anion; [c] λ_{max} in nm, ε in $dm^3mol^{-1}cm^{-1}$; [d] shifting in nm from the lower energy band in the complex and in the free receptor ; [e] isosbestic points in nm; [f] in M^{-1}; [g] in M^{-2}.

a)



b)

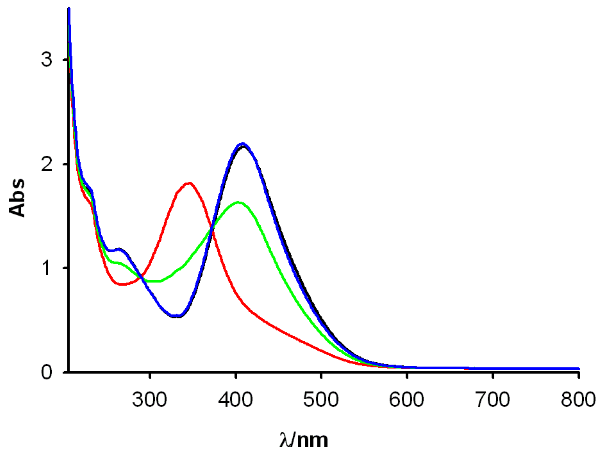


Figure ESI 11. a) Evolution of the OSWV of **1** (c = $1{\cdot}10^{-4}$ M) in CH_3CN/[(*n*-Bu)$_4$N]PF_6 scanned at 0.1 V s^{-1} containing 1 equiv. of HBF_4 (red line) when 1 equiv of:AcO^- was added (blue line). The black line corresponds to the OSWV of the neutral ligand **1**. b) Changes in the absorption spectra of [**1**·H^+], (c = $1{\cdot}10^{-4}$ M in CH_3CN) (red), upon addition of increasing amounts of AcO^- until 1 equiv (blue line). The black line, which appears superimposed to the blue one, corresponds to the neutral ligand **1**.

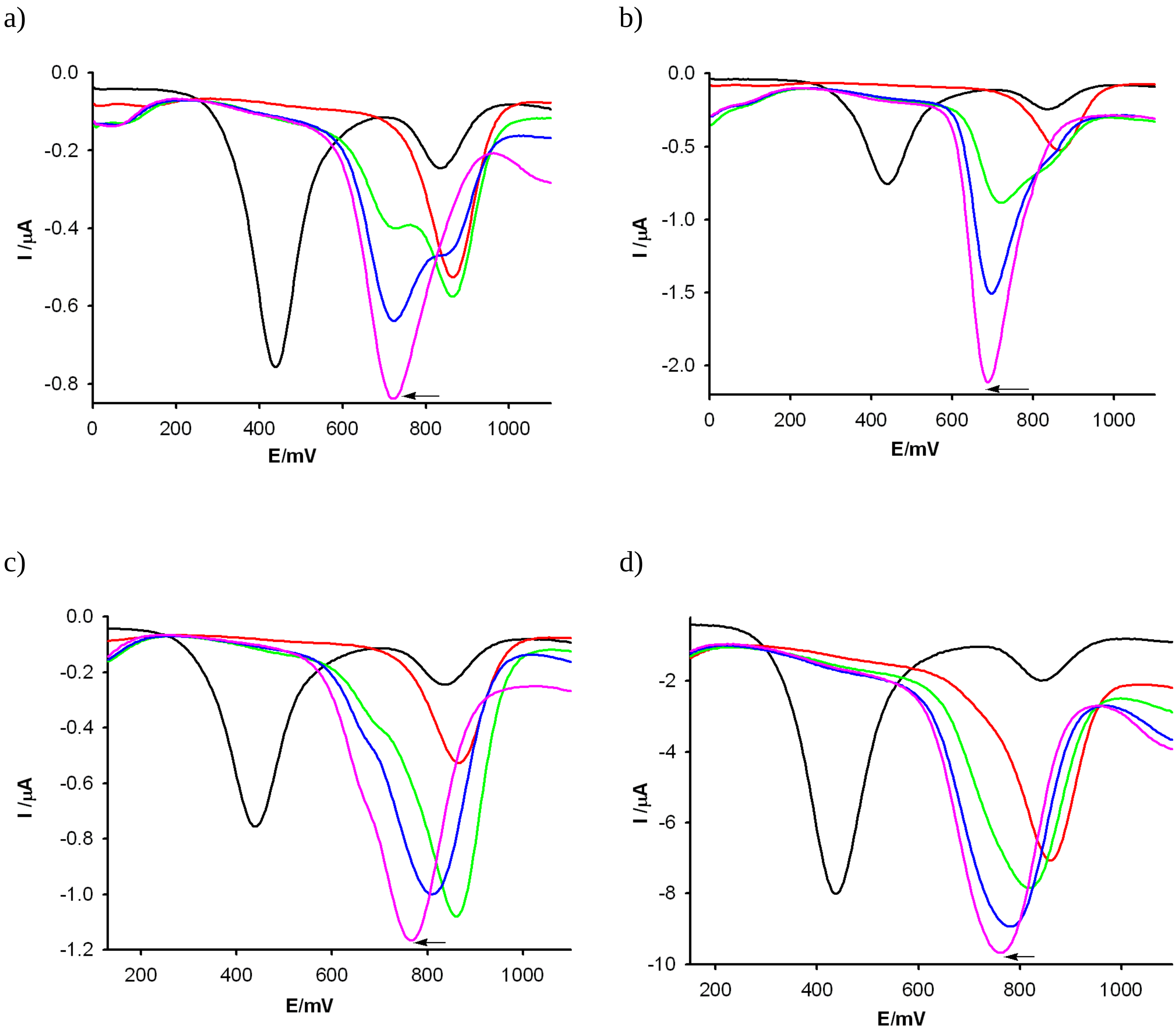


Figure ESI 12. Evolution of the OSWV of **1** (c = $1 \cdot 10^{-4}$ M) in $CH_3CN/[(n\text{-}Bu)_4N]PF_6$ scanned at 0.1 V s^{-1} containing 1 equiv. of HBF_4 (red line) when 2 equiv of: a) Cl^- , b) Br^-, c) NO_3^-, and d) HSO_4^-, were added (pink lines). The black line corresponds to the OSWV of the neutral ligand **1**.

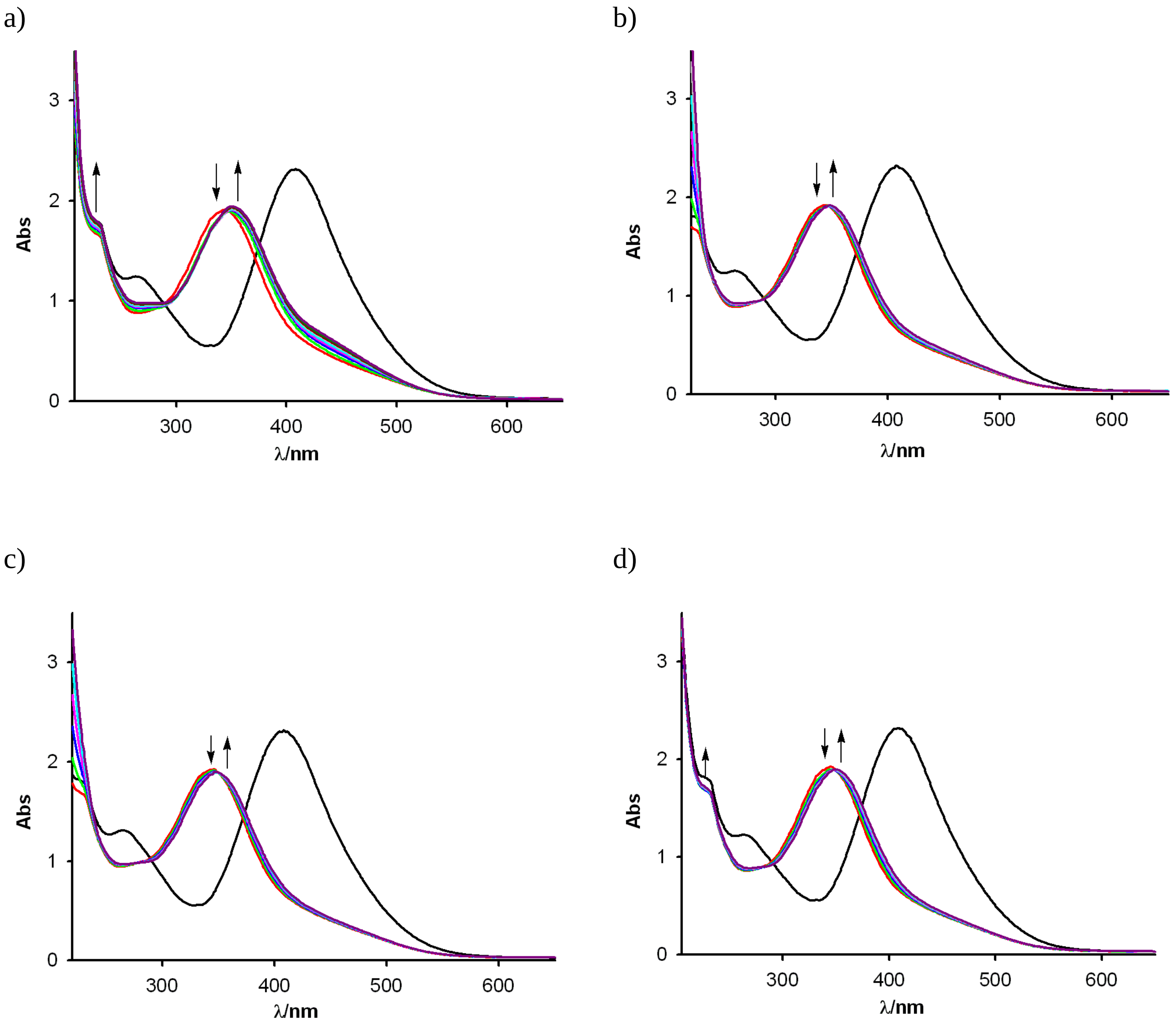


Figure ESI 13. Changes in the absorption spectra of [**1**·H^+], (c = 1·10^{-4} M in CH_3CN) (red), upon addition from 0 to 3 equiv of a) Cl^-, b) Br^-, c) NO_3^-, d) HSO_4^-, (purple lines). The black line corresponds to the neutral ligand **1.** Arrows indicate the absorptions that increase or decrease during the titration process.

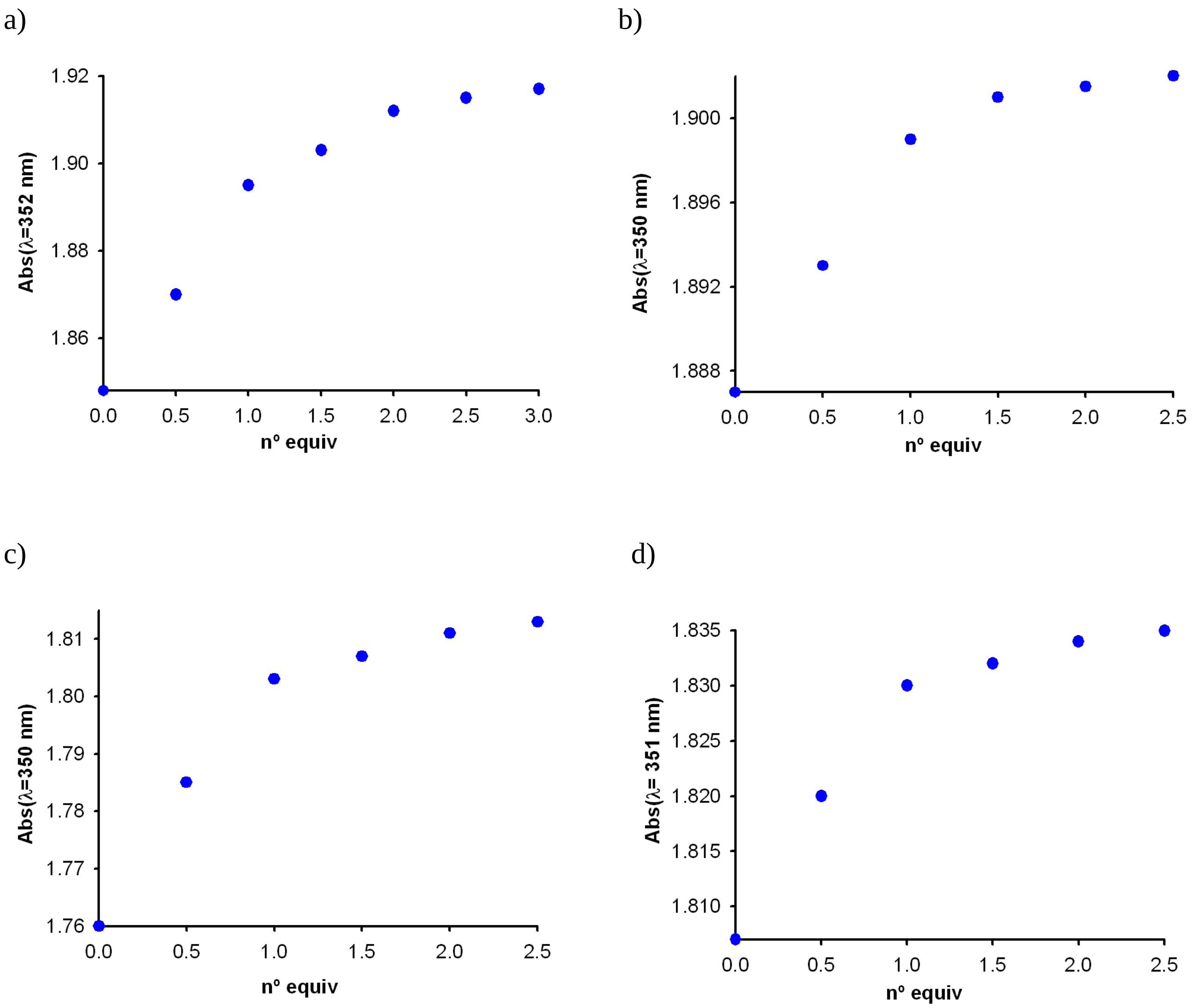


Figure ESI 14. Binding profile associated with the observed maximum absorbance of ligand [**1**·H^+] (c = 1·10^{-4} M in CH_3CN) upon addition of increasing amounts of a) Cl^-, indicating the formation of 1:2 complex and b) Br^-, c) NO_3^-, d) HSO_4^-, indicating the formation of 1:1 complexes (receptor/anion).

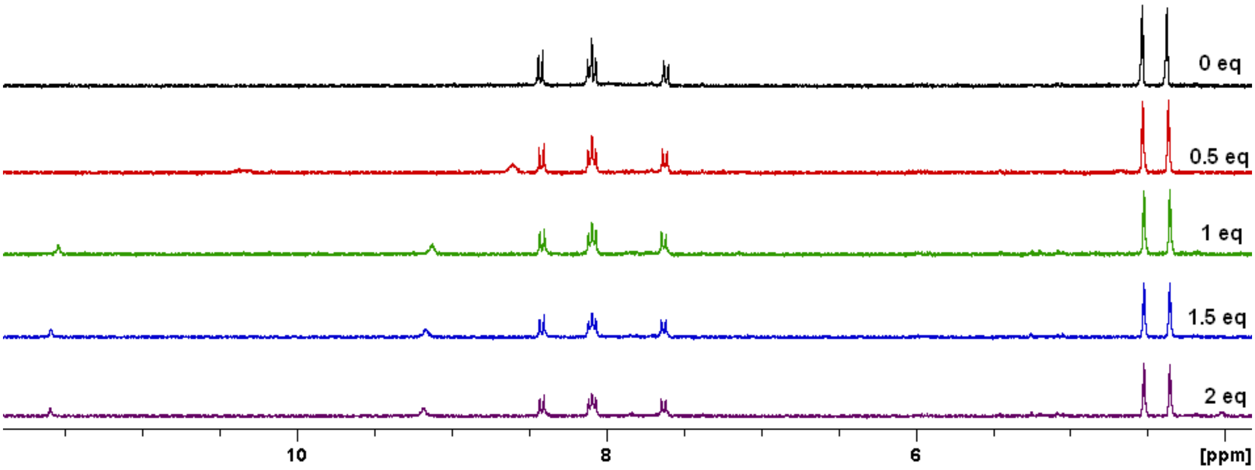


Figure ESI 15. Changes in the ^{1}H-NMR spectrum of [**1**·H^{+}] in CD_3CN upon addition of increasing amounts of Cl^- from 0 equiv (top) to 2 equiv. (bottom).

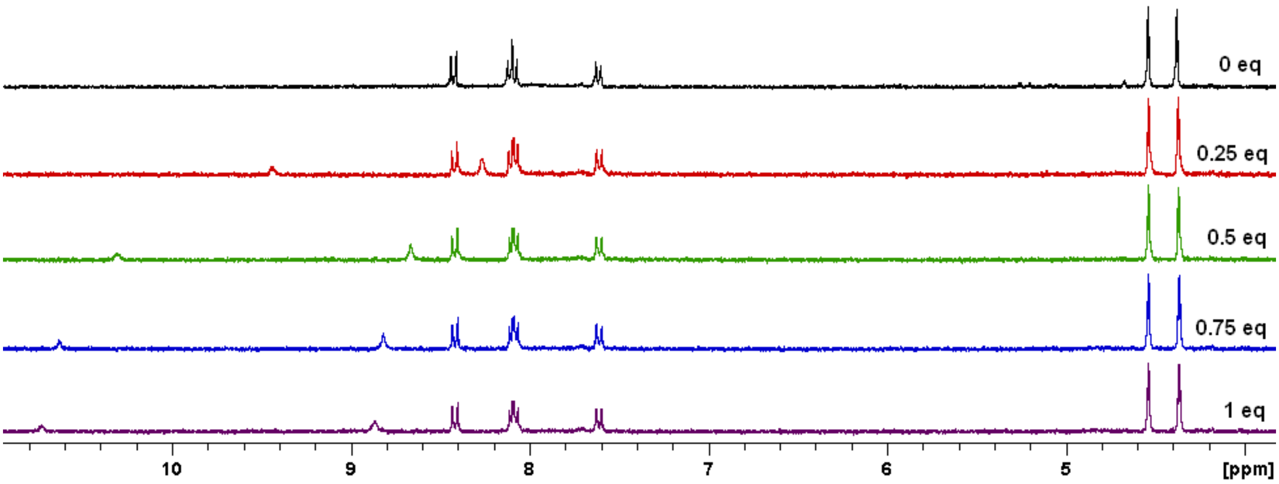


Figure ESI 16. Changes in the ^{1}H-NMR spectrum of [**1**·H^{+}] in CD_3CN upon addition of increasing amounts of NO_3^- from 0 equiv (top) to 1 equiv. (bottom).

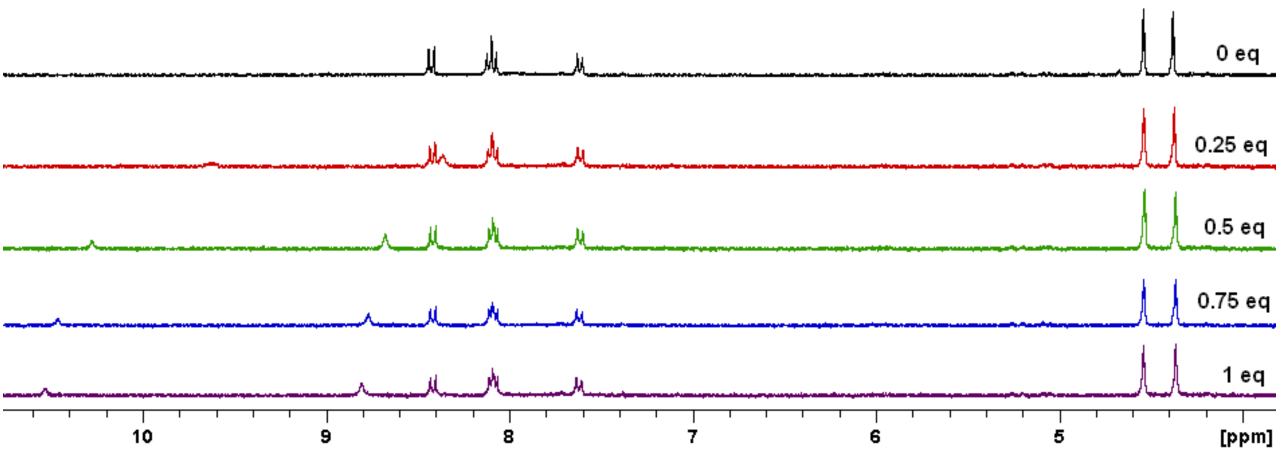


Figure ESI 17. Changes in the ^{1}H-NMR spectrum of [**1**·H^+] in CD_3CN upon addition of increasing amounts of HSO_4^- from 0 equiv (top) to 1 equiv. (bottom).

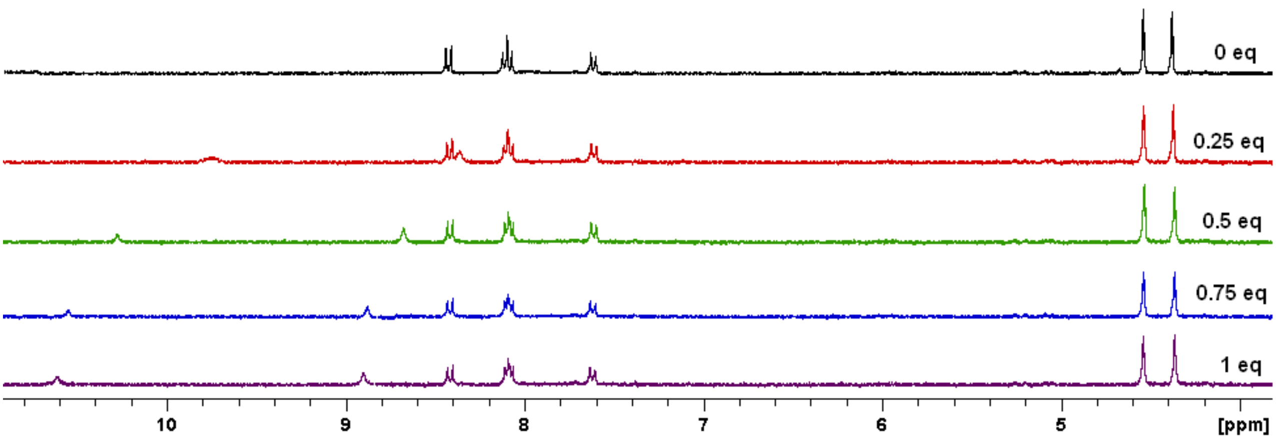


Figure ESI 18. Changes in the ^{1}H-NMR spectrum of [**1**·H^+]CD_3CN upon addition of increasing amounts of Br^- from 0 equiv (top) to 1 equiv. (bottom).

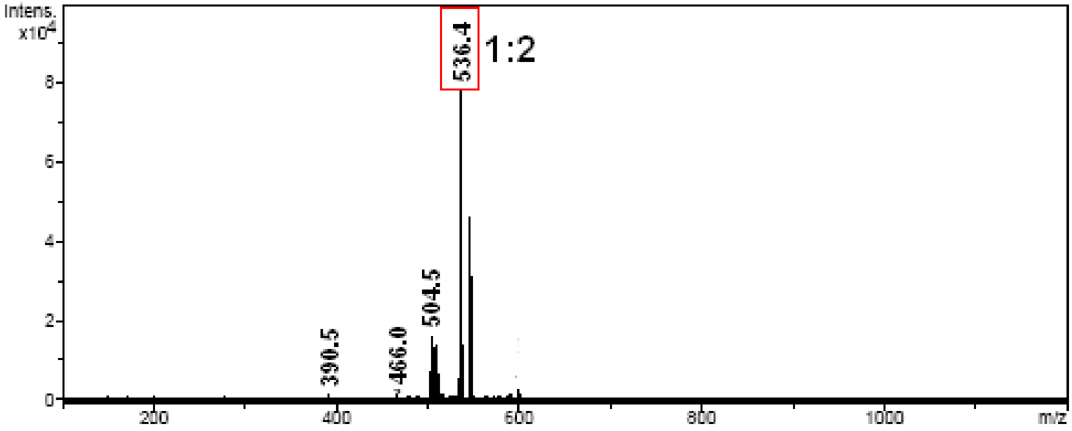


Figure ESI 19. ESI mass spectrum of the complex formed between [**1**·H$^+$] and Cl$^-$.

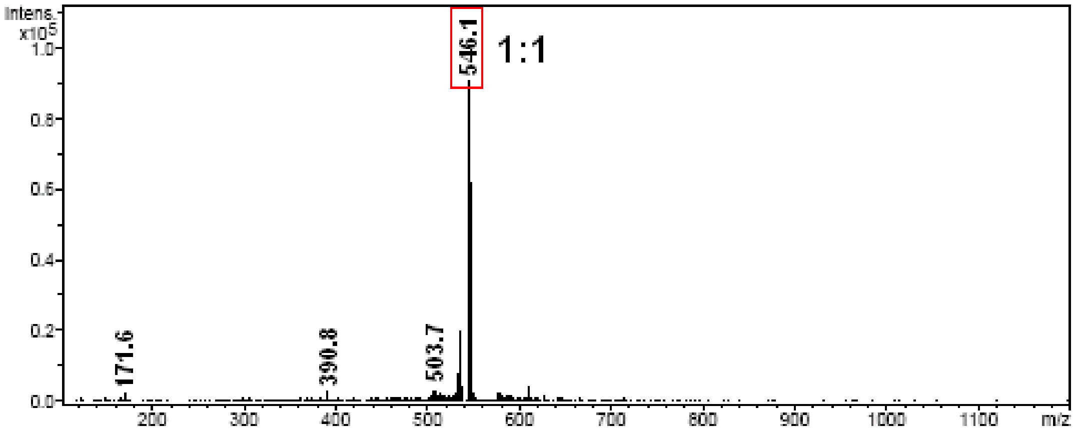


Figure ESI 20. ESI mass spectrum of the complex formed between [**1**·H$^+$] and Br$^-$.

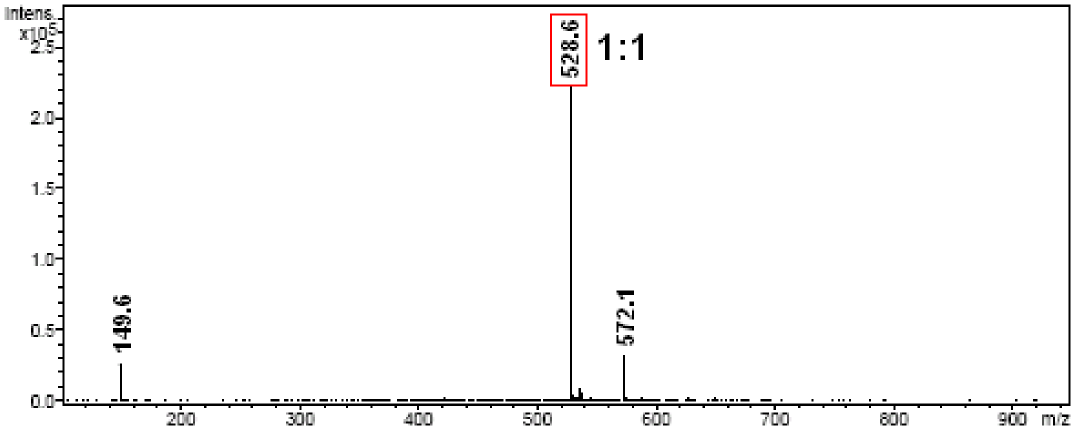


Figure ESI 21. ESI mass spectrum of the complex formed between [**1**·H$^+$] and NO_3^-.

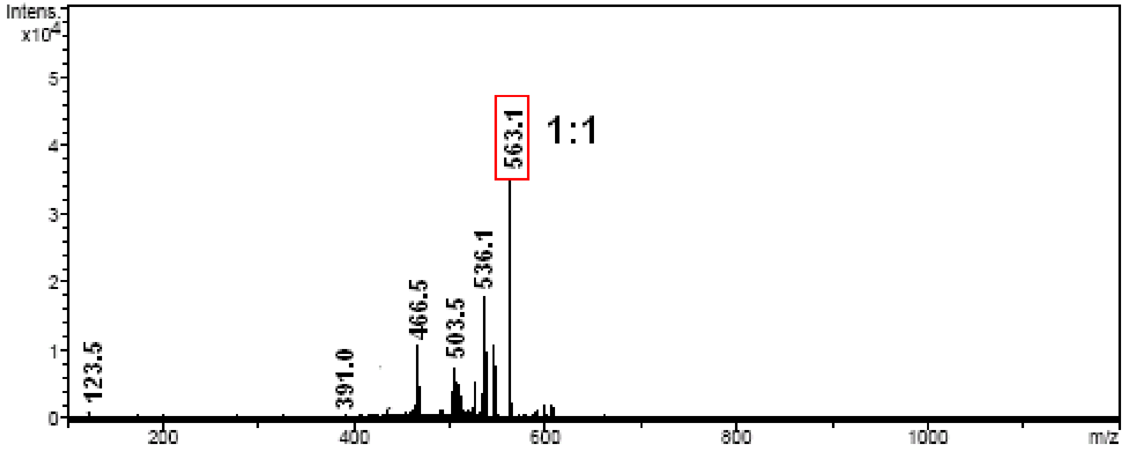


Figure ESI 22. ESI mass spectrum of the complex formed between [**1**·H^+] and HSO_4^-.