Supporting Information for

N-Nitrosamine-{cis-Re[CO]$_2$}$^{2+}$ Cobalamin Conjugates as Mixed CO/NO-Releasing Molecules.

Giuseppe Santoro,[a] Ruben Beltrami,[b] Emmanuel Kottelat,[b] Olivier Blacque,[a] Anna Bogdanova [c] and Fabio Zobi*[a]

[a] *Department of Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland.*

[b] *Departement of Chemistry, University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg, Switzerland.*

[c] *Institute of Veterinary Physiology, University of Zürich, Winterthurerstrasse 260, CH-8057 Zürich, Switzerland.*

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Table S1. Crystal data and structure refinement for **1** and **1a**.

CCDC number	1054820	1054821
Empirical formula	$C_{68}H_{93b}oN_{16}O_{15}P.11(H_2O)$	$2(C_{68}H_{93b}oN_{17}O_{16}P).C_3H_6O.23(H_2O)$
Formula weight	1664.67	3465.45
Temperature/K	183(1)	183(1)
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1$
a/Å	16.2518(4)	15.6019(4)
b/Å	21.2575(8)	21.4078(4)
c/Å	25.0707(10)	28.0537(7)
α/°	90	90
β/°	90	95.299(2)
γ/°	90	90
Volume/Å^3	8661.3(5)	9330.0(4)
Z	4	4
ρ_{calc}g/cm^3	1.277	1.234
μ/mm^{-1}	0.297	0.280
F(000)	3548.0	3692.0
Crystal size/mm^3	0.33 × 0.23 × 0.14	0.35 × 0.25 × 0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.61 to 50.69	5.57 to 52.75
Index ranges	$-19 \le h \le 16$, $-25 \le k \le 25$, $-30 \le l \le 30$	$-19 \le h \le 19$, $-26 \le k \le 26$, $-35 \le l \le 34$
Reflections collected	72378	85003
Independent reflections	15847 [R_{int} = 0.0894, R_{sigma} = 0.0911]	37195 [R_{int} = 0.0489, R_{sigma} = 0.0730]
Data/restraints/parameters	15847/483/949	37195/760/1927
Goodness-of-fit on F^2	1.046	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.1037, wR_2 = 0.2782	R_1 = 0.0717, wR_2 = 0.1836
Final R indexes [all data]	R_1 = 0.1458, wR_2 = 0.3167	R_1 = 0.0834, wR_2 = 0.1928

Largest diff. peak/hole / e $Å^{-3}$	0.68/-0.78	0.90/-0.64
Flack parameter	0.026(10)	0.049(6)

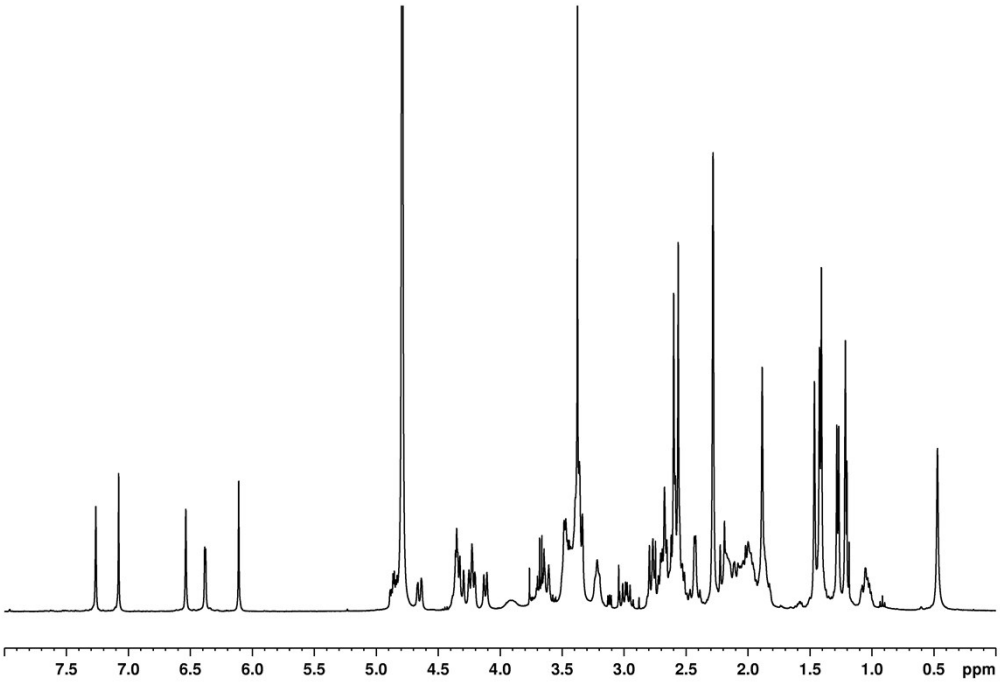


Figure S1. ^{1}H-NMR spectrum of **3** in D_2O.

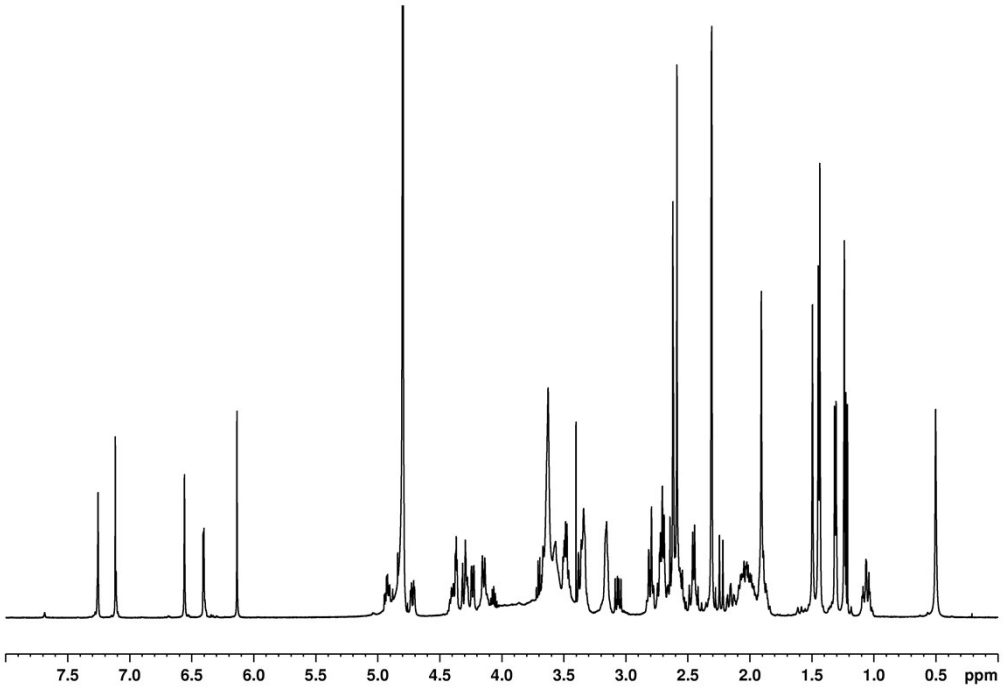


Figure S2. ^{1}H-NMR spectrum of **5** in D_2O.

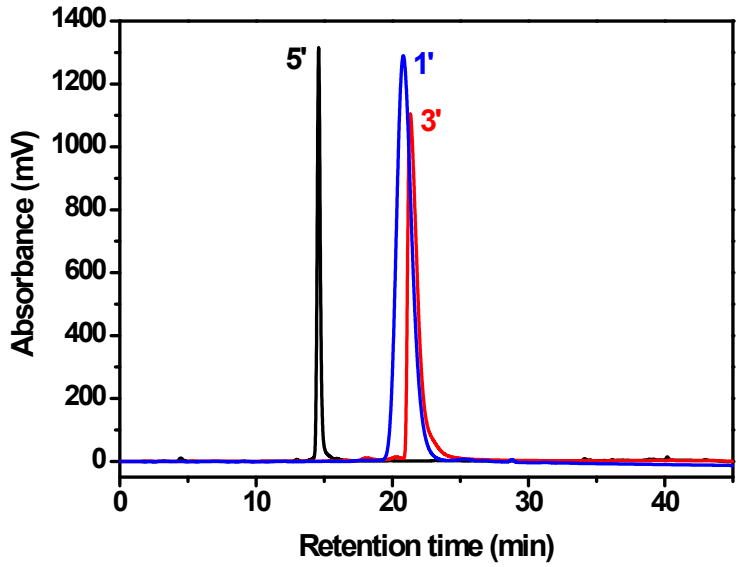


Figure S3. HPLC chromatograms of species **1a- 3a**.

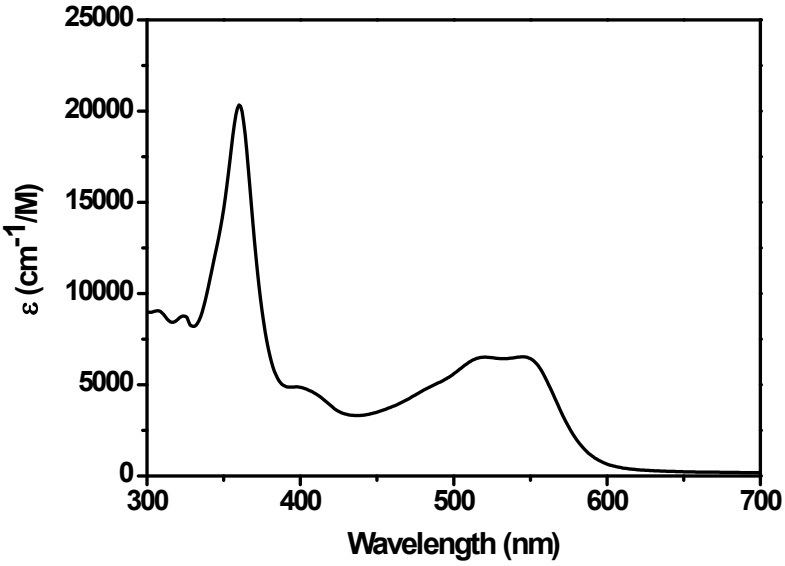


Figure S4. UV-Vis of species **1a** in methanol.

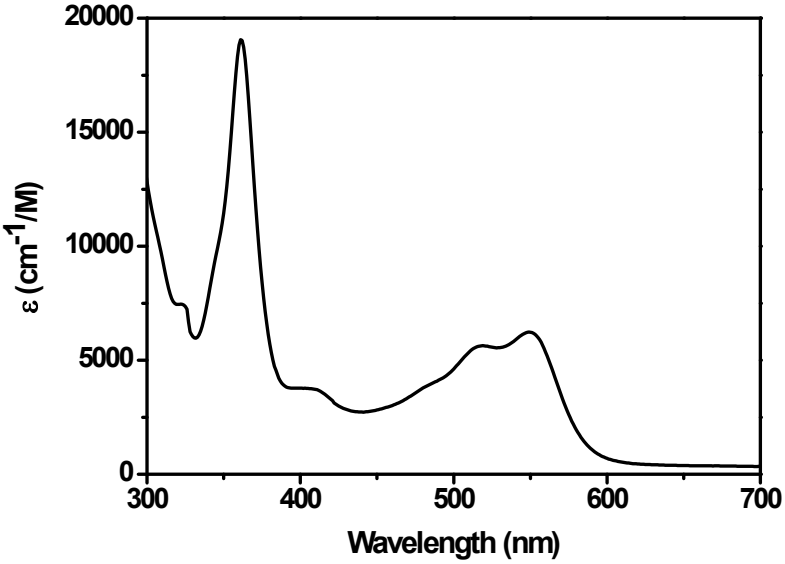


Figure S5. UV-Vis of species **2a** in methanol.

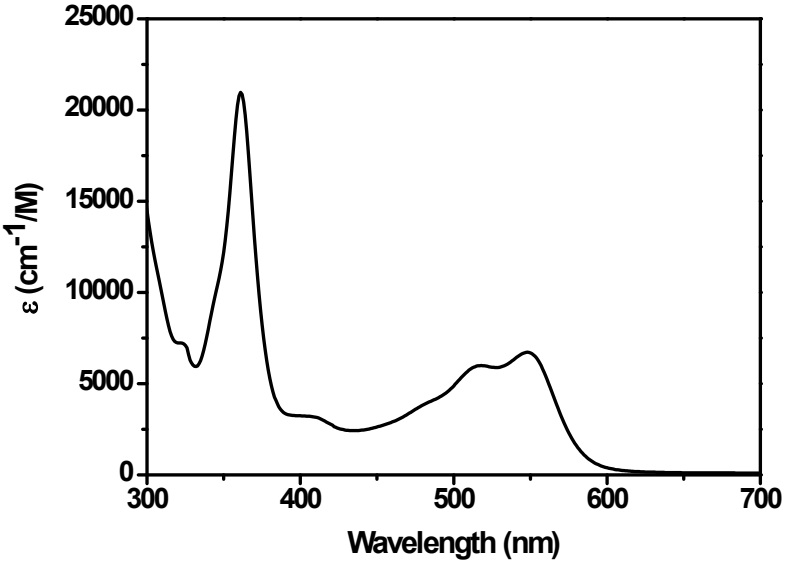


Figure S6. UV-Vis of species **3a** in methanol.

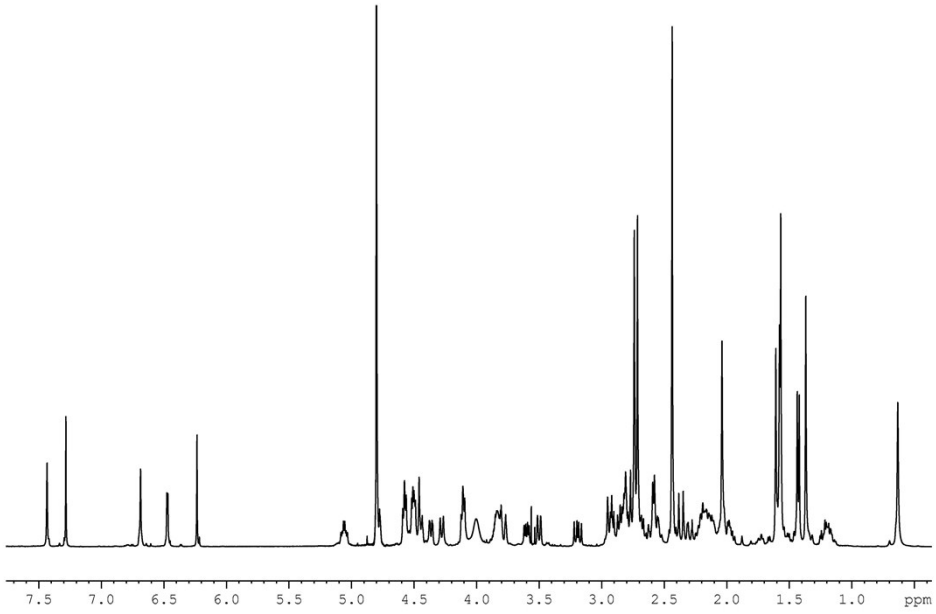


Figure S7. ^{1}H-NMR spectrum of **1a** in D_2O.

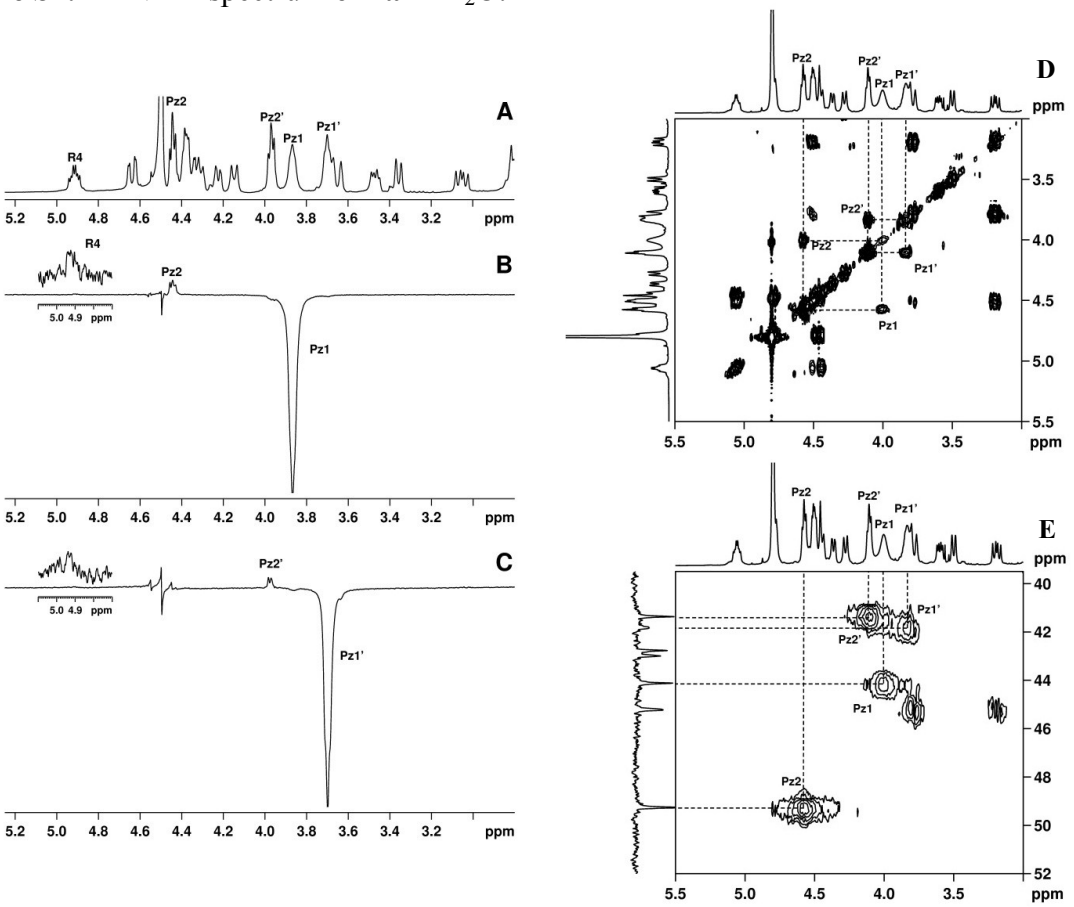


Figure S8. Right: Selected region (5.2-3.0 ppm) of NOESY 1D NMR spectra of **1a**. **A**: irradiation of Pz1 gives NOE effects on proton R4 and Pz2. **B**: Irradiation of Pz1a gives weak NOE effect on R4 and Pz2'. Left. **D**: 2D COSY of **1a** highlighting the coupling between Pz1 and Pz2 and Pz1a and Pz2' but no cross correlation. **E**: 2D HMQC (5.5-3.0 ppm) of **1a**.

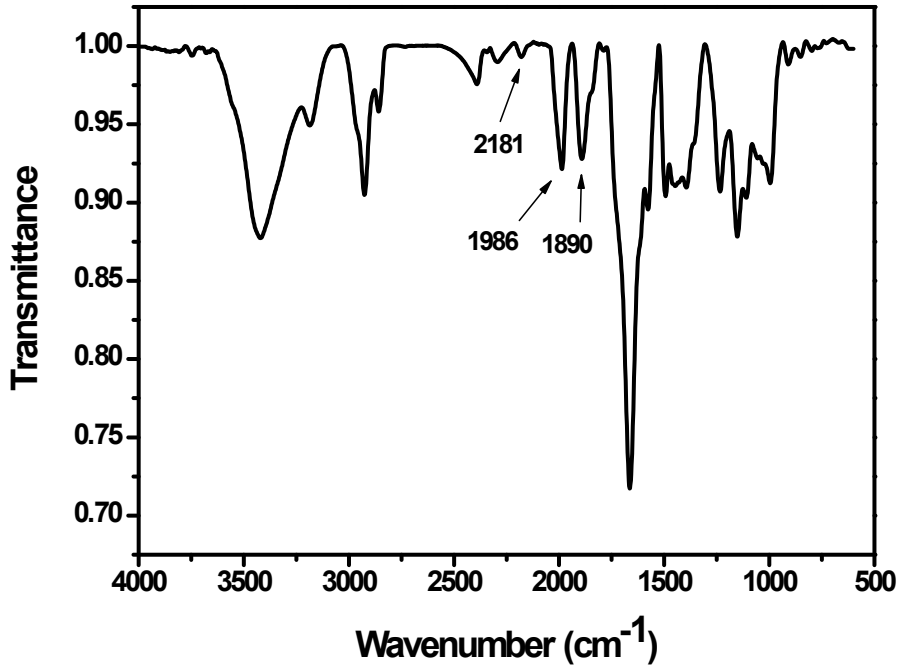


Figure S9. IR spectrum of **1b** (KBr).

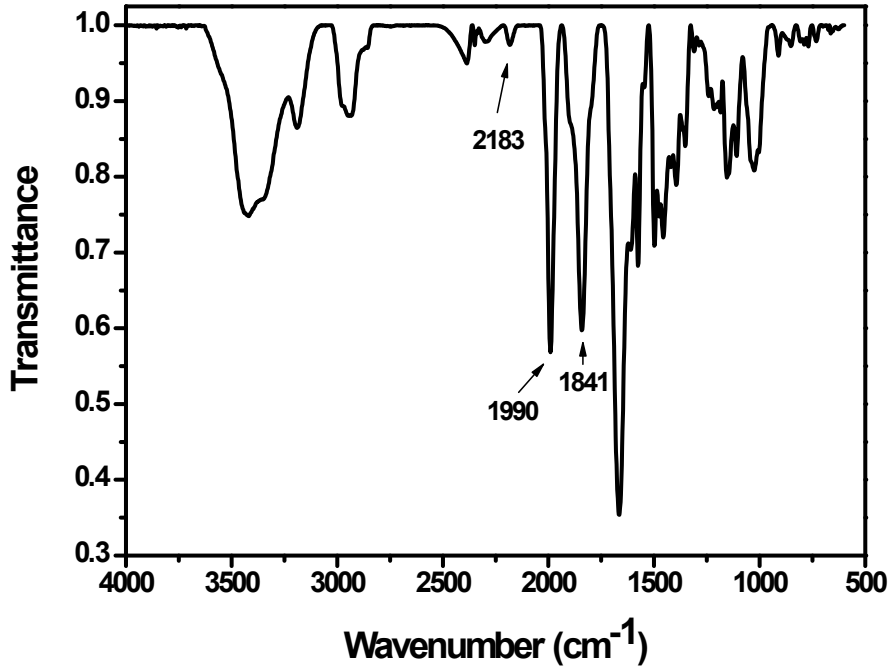


Figure S10. IR spectrum of **2b** (KBr).

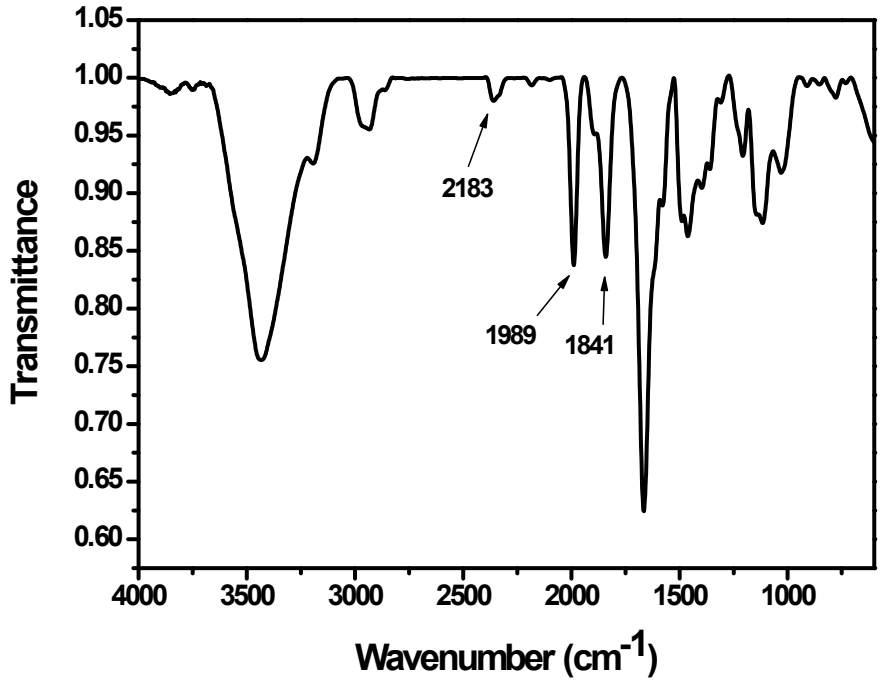


Figure S11. IR spectrum of **3b** (KBr).

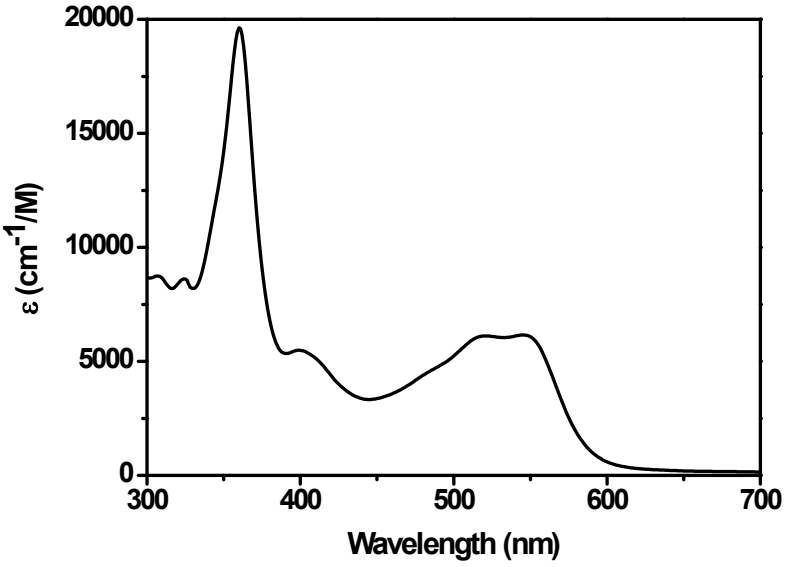


Figure S12. UV-Vis of species **1b** in methanol.

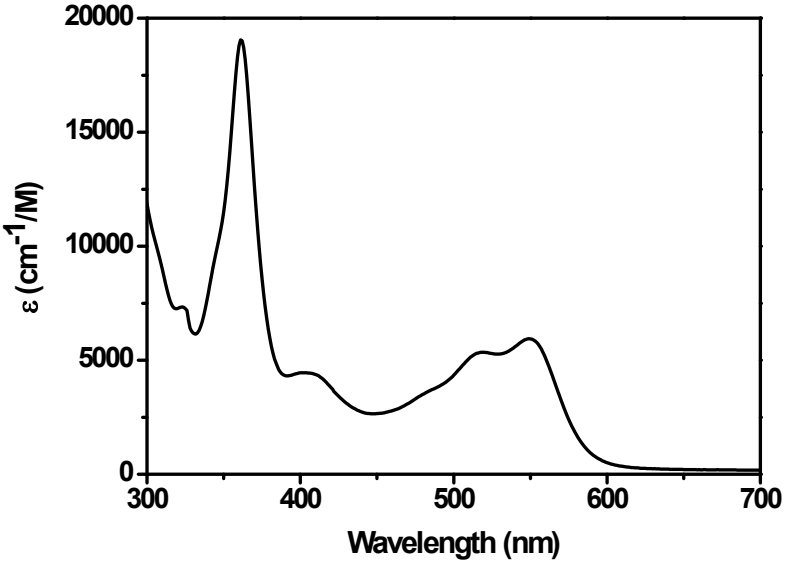


Figure S13. UV-Vis of species **2b** in methanol.

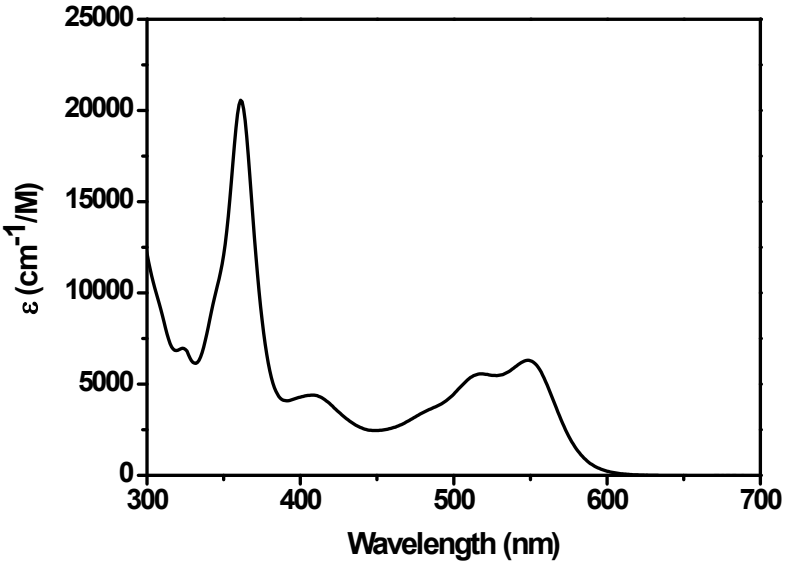


Figure S14. UV-Vis of species **3b** in methanol.

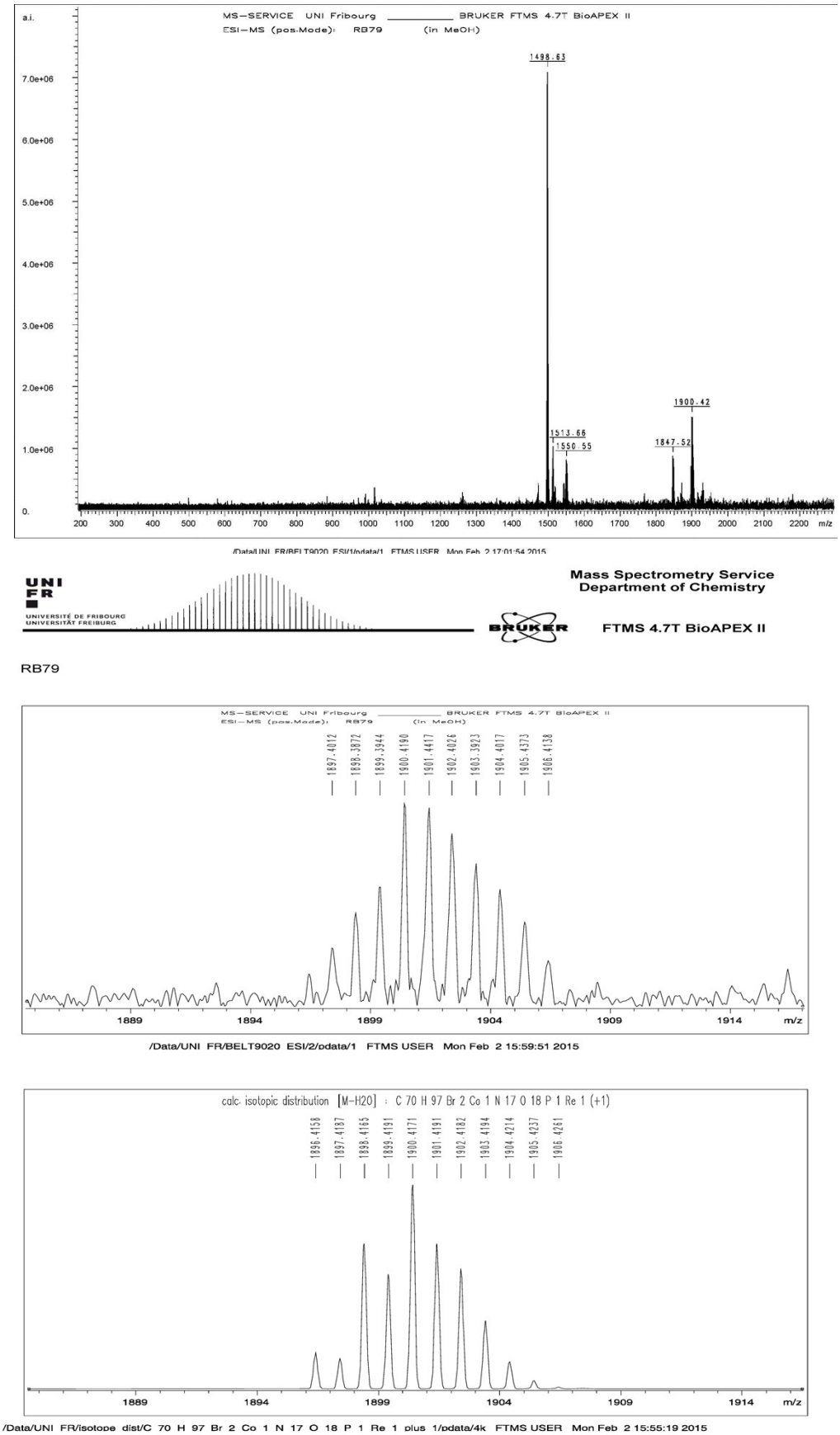
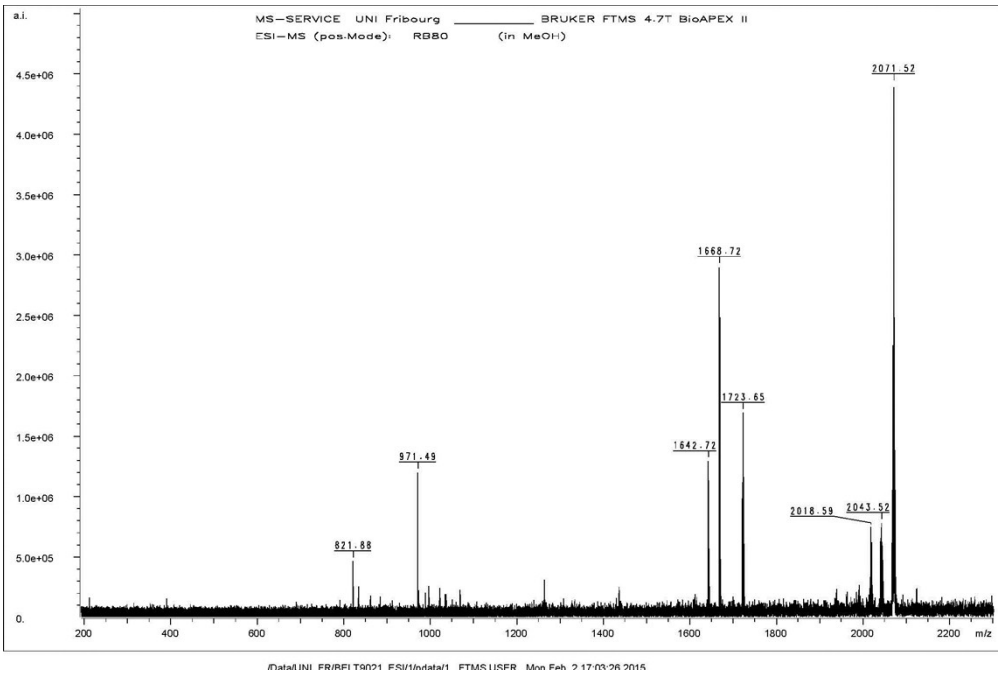
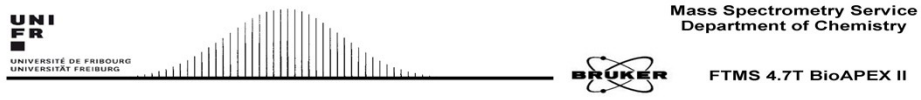
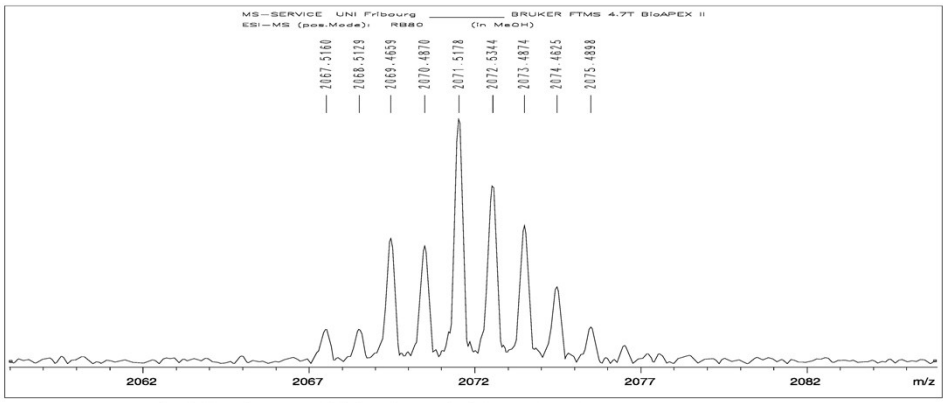


Figure S15. High-Resolution MS of **1b**.





RB80



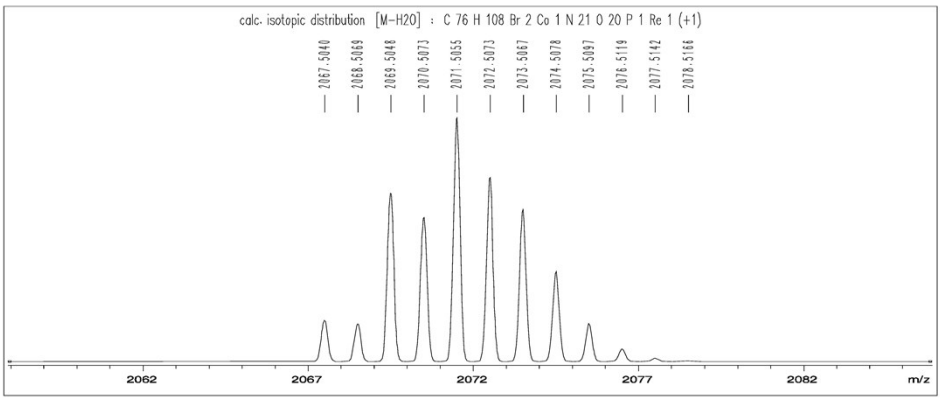


Figure S16. High-Resolution MS of **2b**.

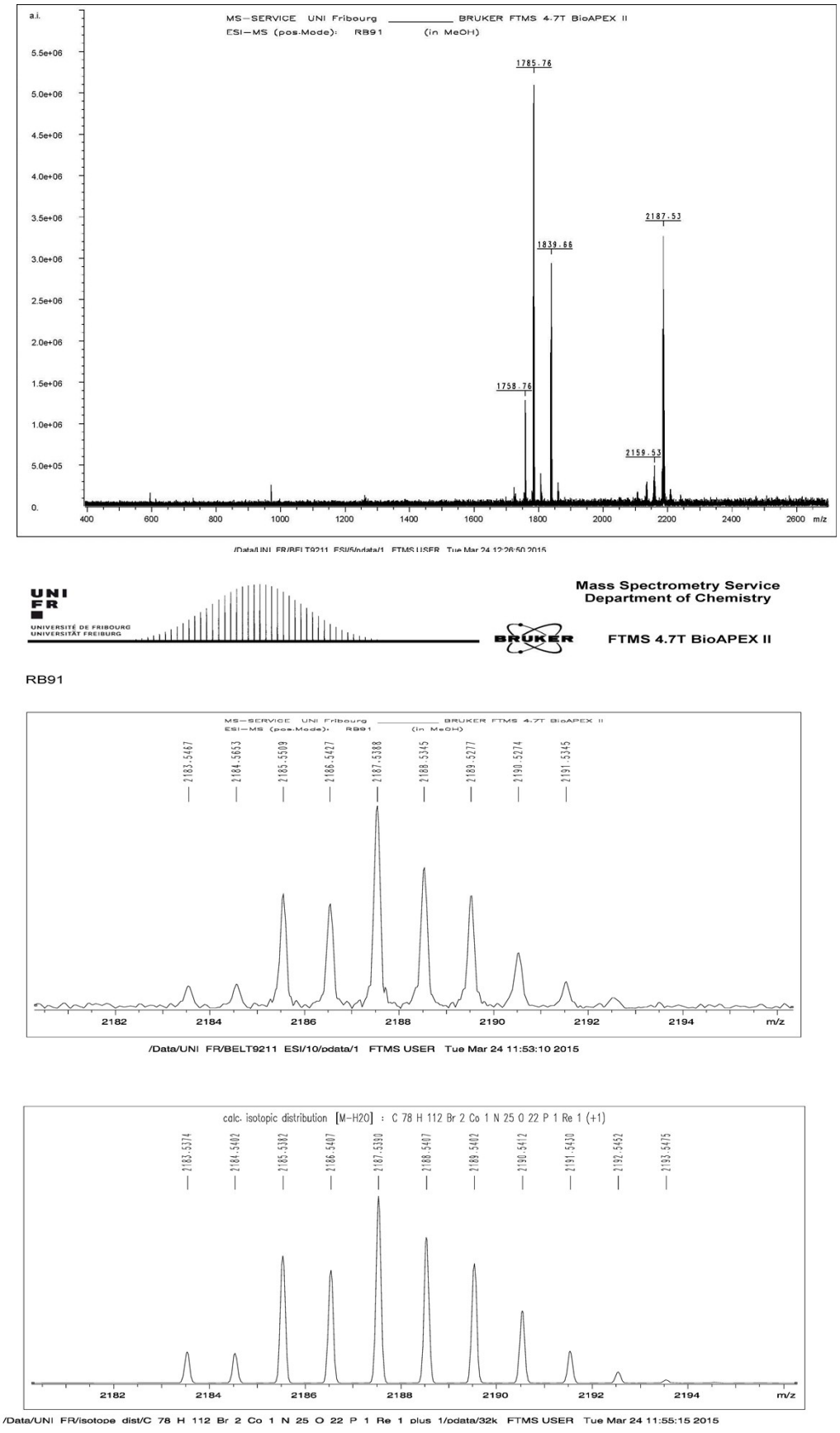


Figure S17. High-Resolution MS of **3b**.

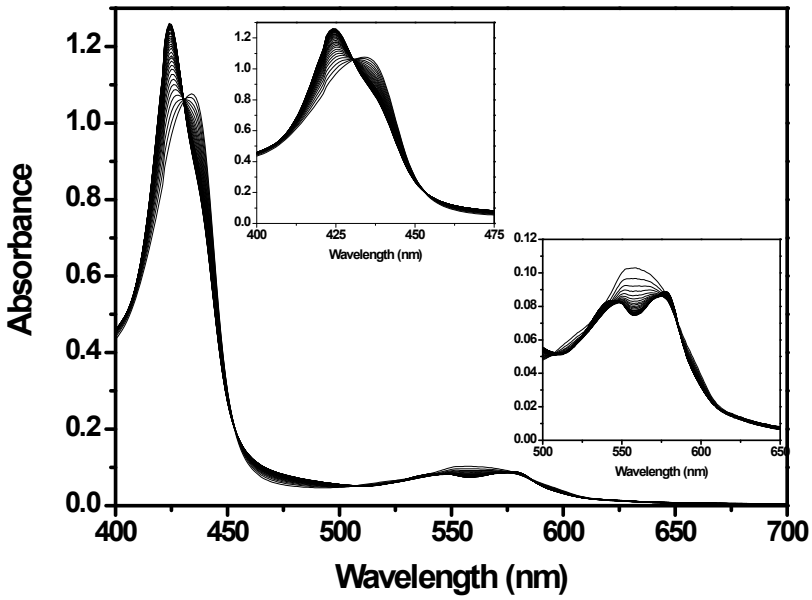


Figure S18. Typical spectrum changes oa Mb assay of mixed CO/NO releasing molecules. Shown are the changes of **3b**.