

Supporting Information for

N-Nitrosamine- $\{\text{cis-Re}[\text{CO}]_2\}^{2+}$ Cobalamin Conjugates as Mixed

CO/NO-Releasing Molecules.

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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} O ₁₆ N ₁₅ P.11(H ₂ O)	2(C ₆₈ H _{93b} O ₁₆ N ₁₇ O ₁₆ P).C ₃ H ₆ O.23(H ₂ O)
Formula weight	1664.67	3465.45
Temperature/K	183(1)	183(1)
Crystal system	orthorhombic	monoclinic
Space group	P2 ₁ 2 ₁ 2 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)
$\alpha/^\circ$	90	90
$\beta/^\circ$	90	95.299(2)
$\gamma/^\circ$	90	90
Volume/Å ³	8661.3(5)	9330.0(4)
Z	4	4
$\rho_{\text{calc}}/\text{cm}^3$	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	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	5.61 to 50.69	5.57 to 52.75
Index ranges	-19 ≤ h ≤ 16, -25 ≤ k ≤ 25, -30 ≤ l ≤ 30	-19 ≤ h ≤ 19, -26 ≤ k ≤ 26, -35 ≤ l ≤ 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 ≥ 2 σ (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)

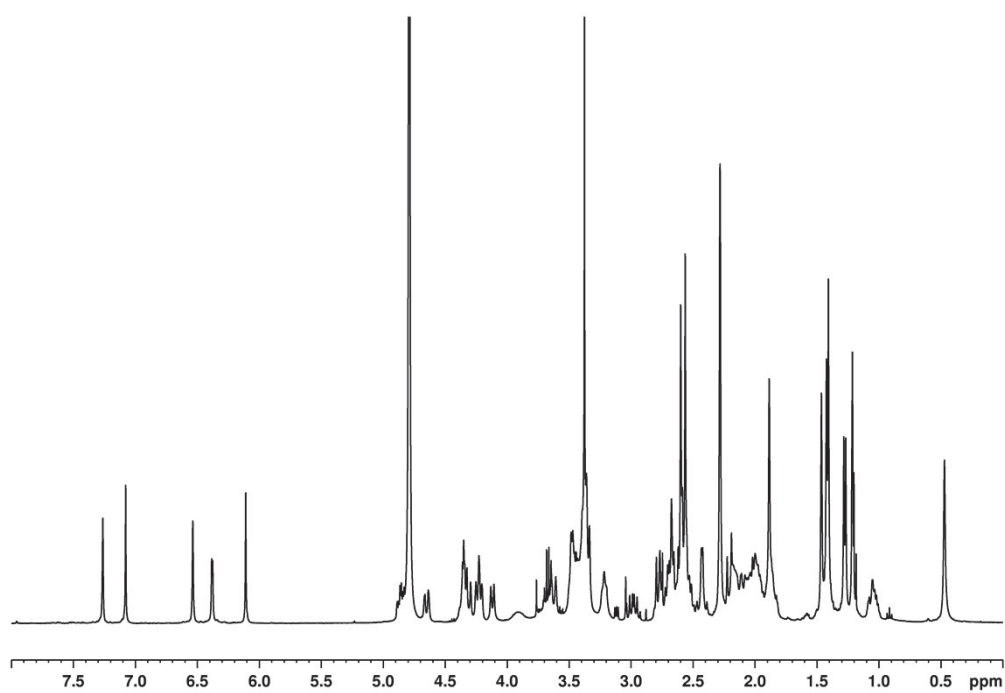


Figure S1. ^1H -NMR spectrum of **3** in D_2O .

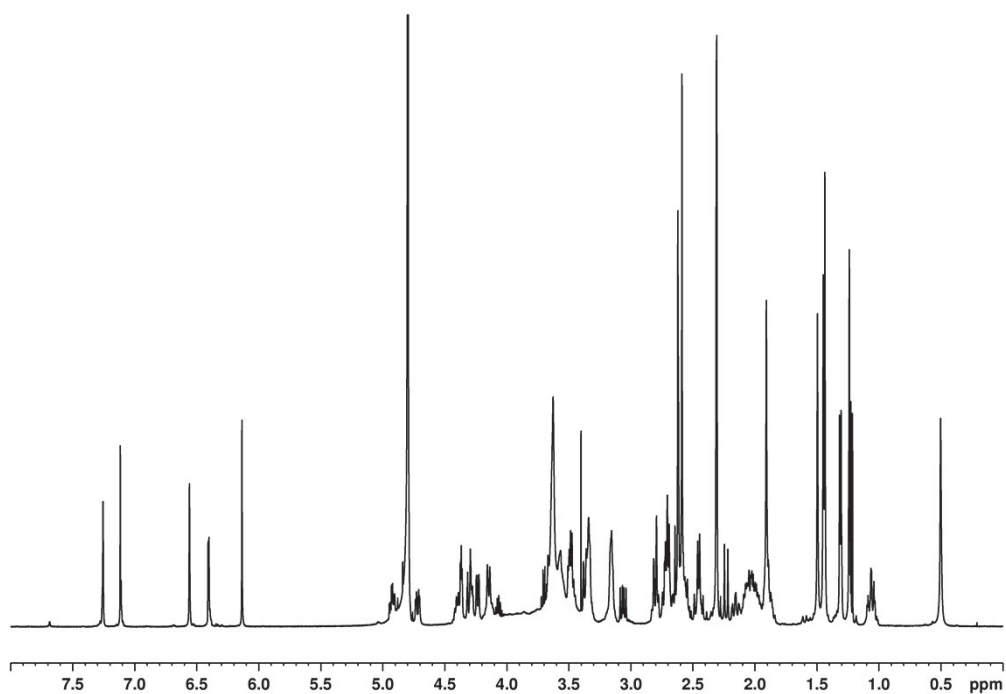


Figure S2. ^1H -NMR spectrum of **5** in D_2O .

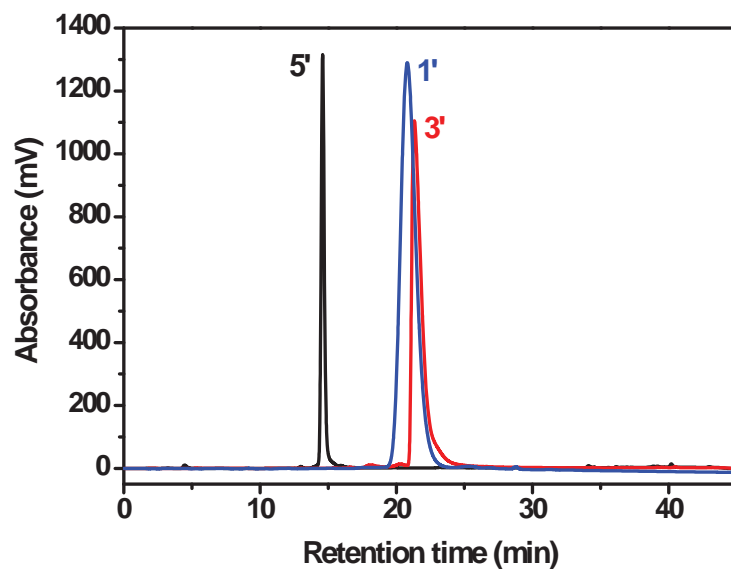


Figure S3. HPLC chromatograms of species **1a- 3a**.

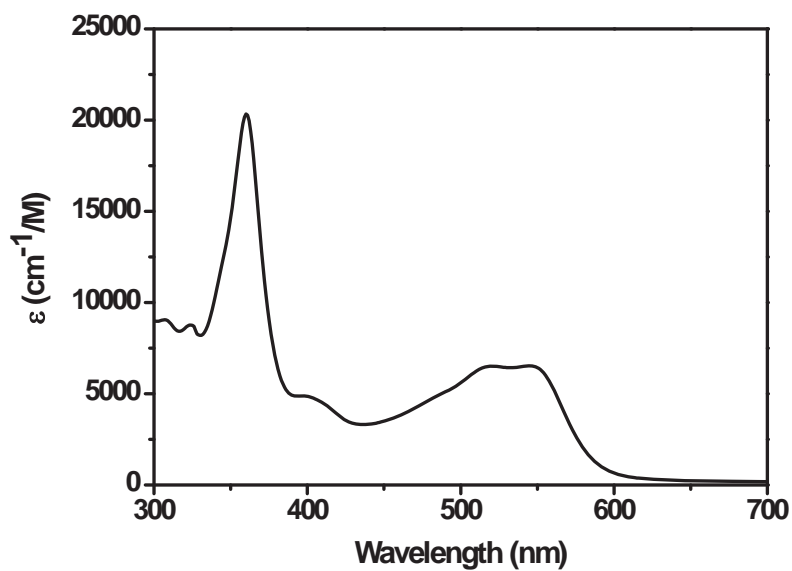


Figure S4. UV-Vis of species **1a** in methanol.

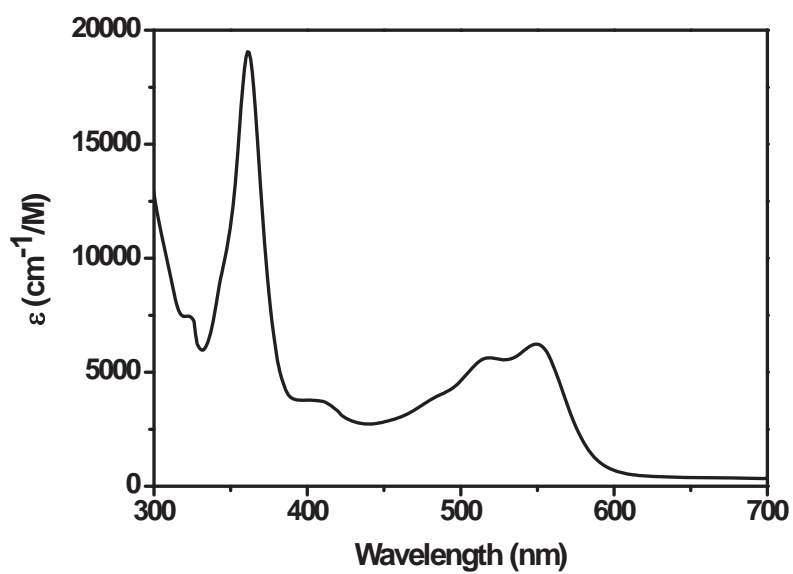


Figure S5. UV-Vis of species **2a** in methanol.

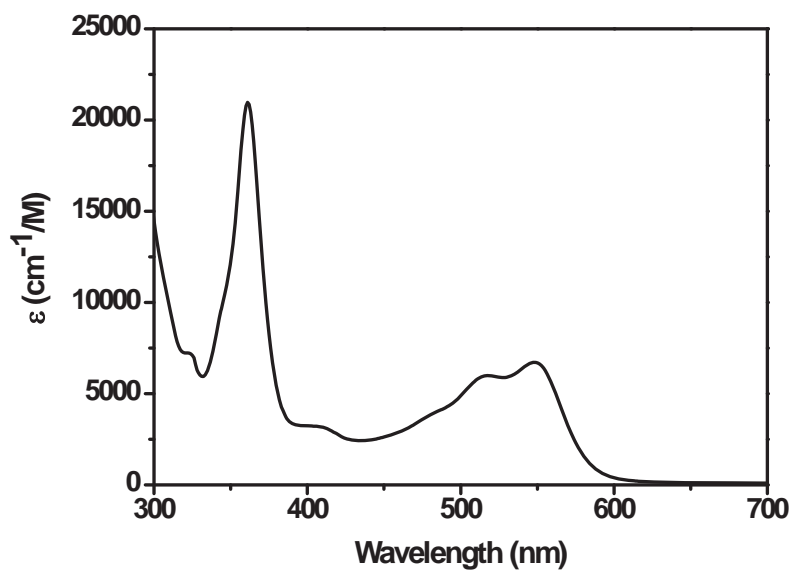


Figure S6. UV-Vis of species **3a** in methanol.

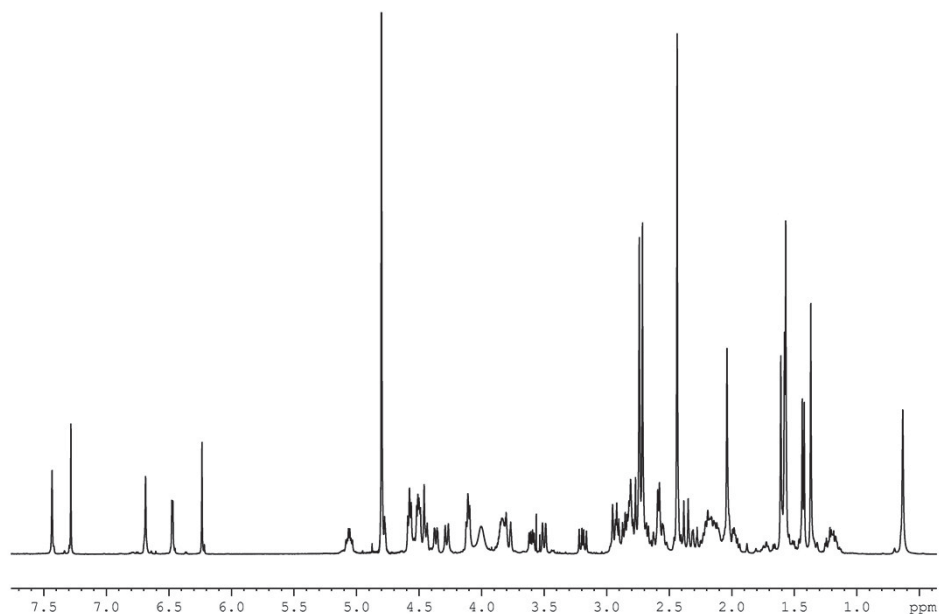


Figure S7. ^1H -NMR spectrum of **1a** in D_2O .

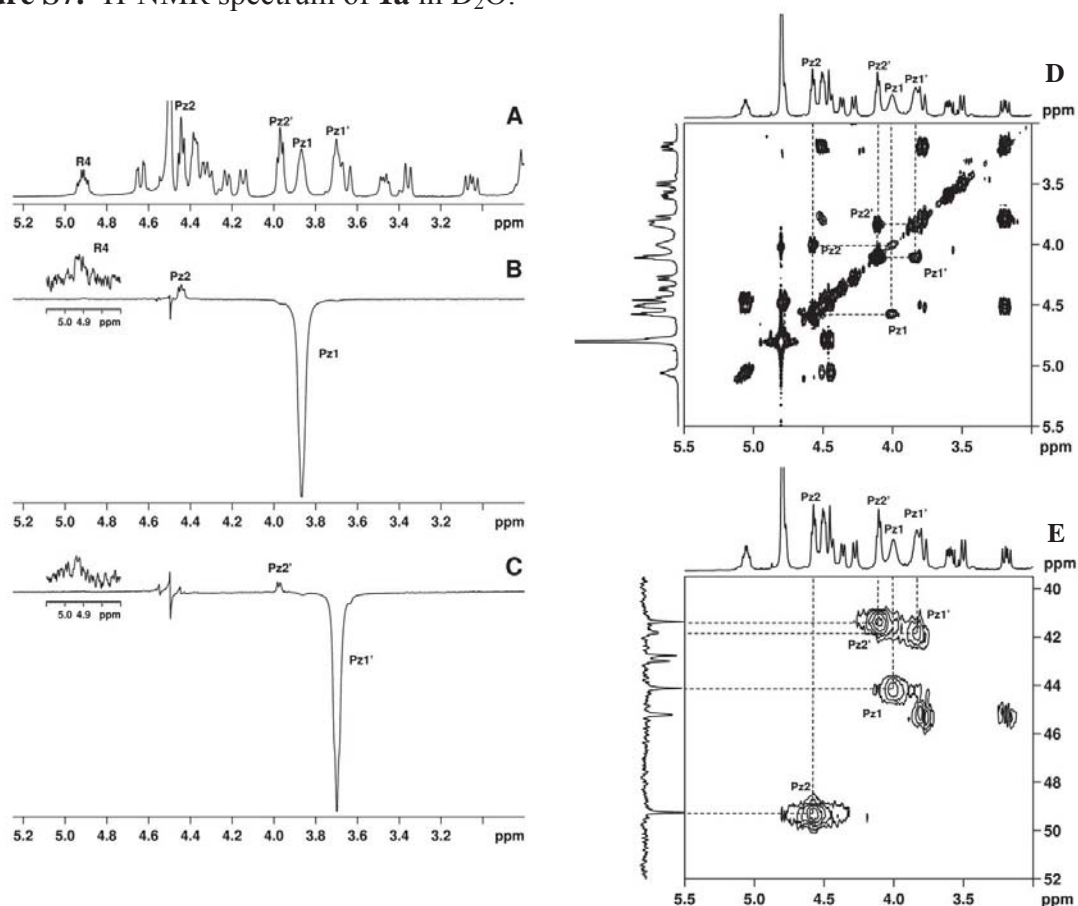


Figure S8. Right: Selected region (5.2-3.0 ppm) of NOESY 1D NMR spectra of **1a**. **A**: irradiation of Pz1 gives NOE effects on proton R4 and Pz2. **B**: Irradiation of Pz1a gives weak NOE effect on R4 and Pz2'. Left: **D**: 2D COSY of **1a** highlighting the coupling between Pz1 and Pz2 and Pz1a and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

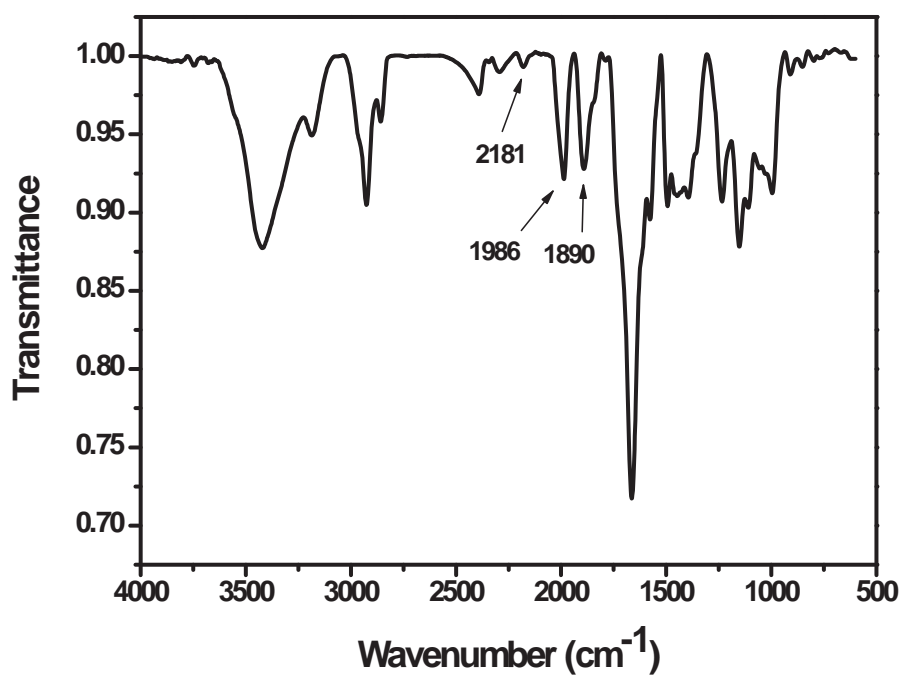


Figure S9. IR spectrum of **1b** (KBr).

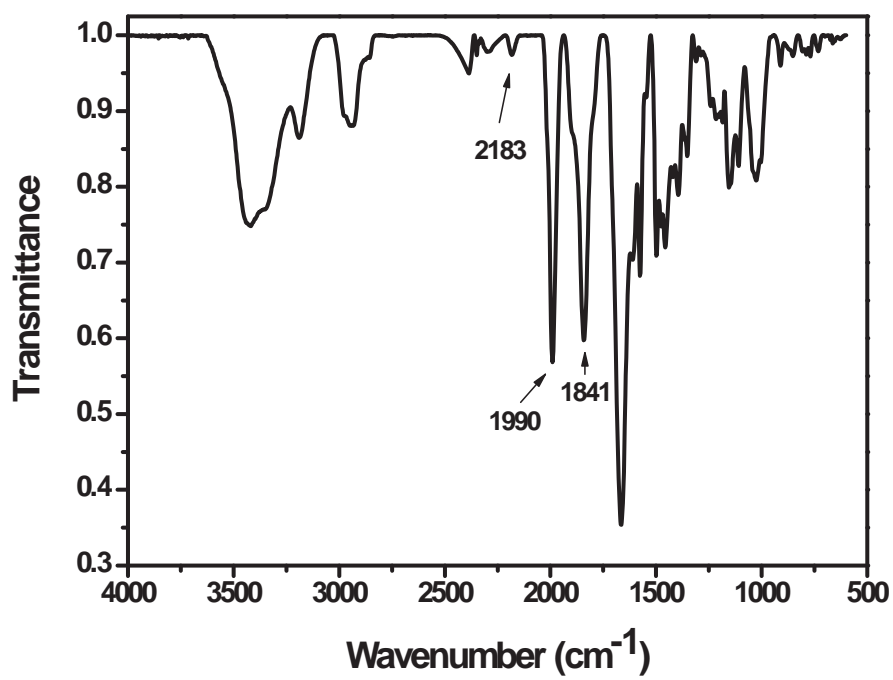


Figure S10. IR spectrum of **2b** (KBr).

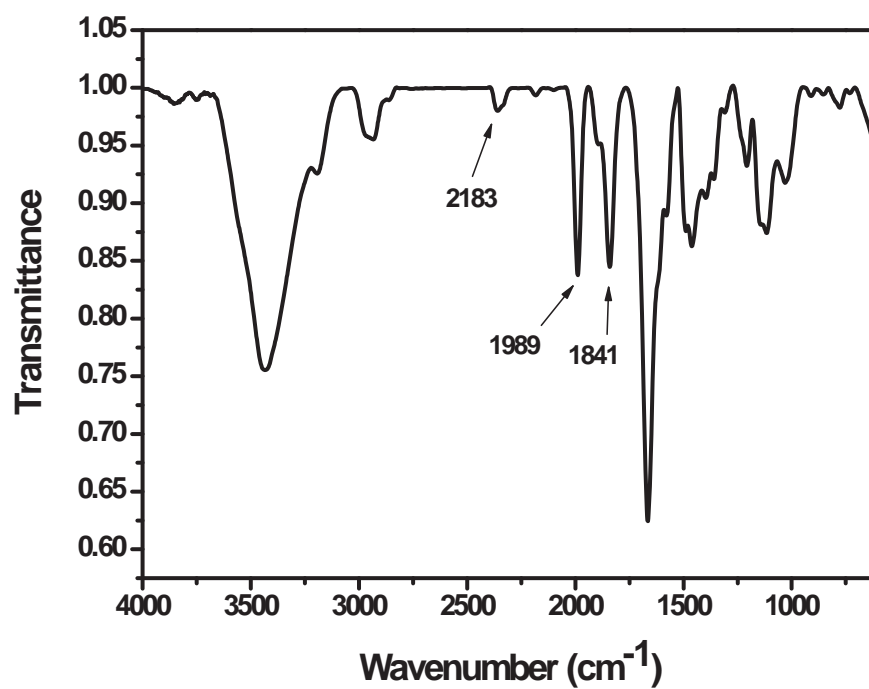


Figure S11. IR spectrum of **3b** (KBr).

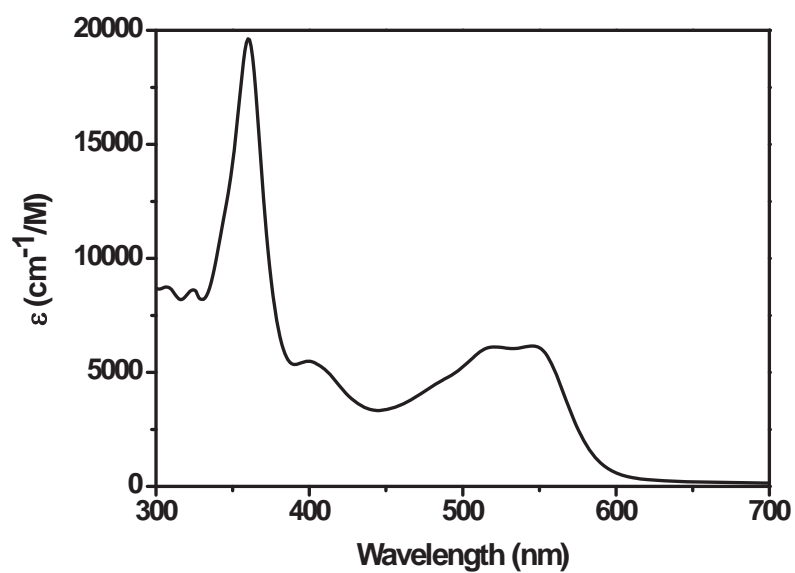


Figure S12. UV-Vis of species **1b** in methanol.

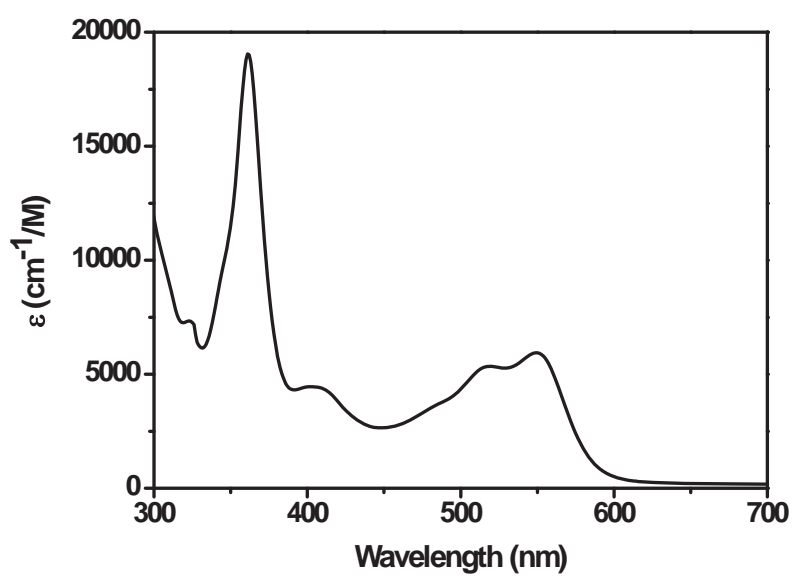


Figure S13. UV-Vis of species **2b** in methanol.

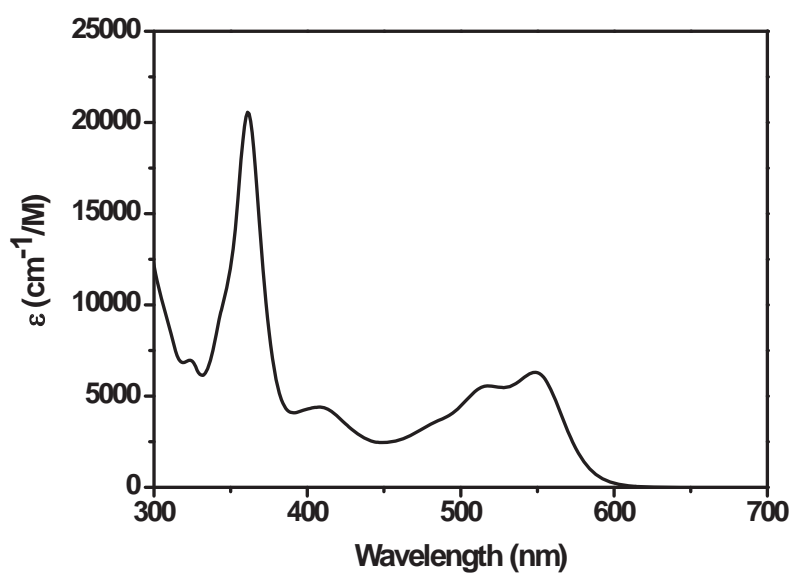
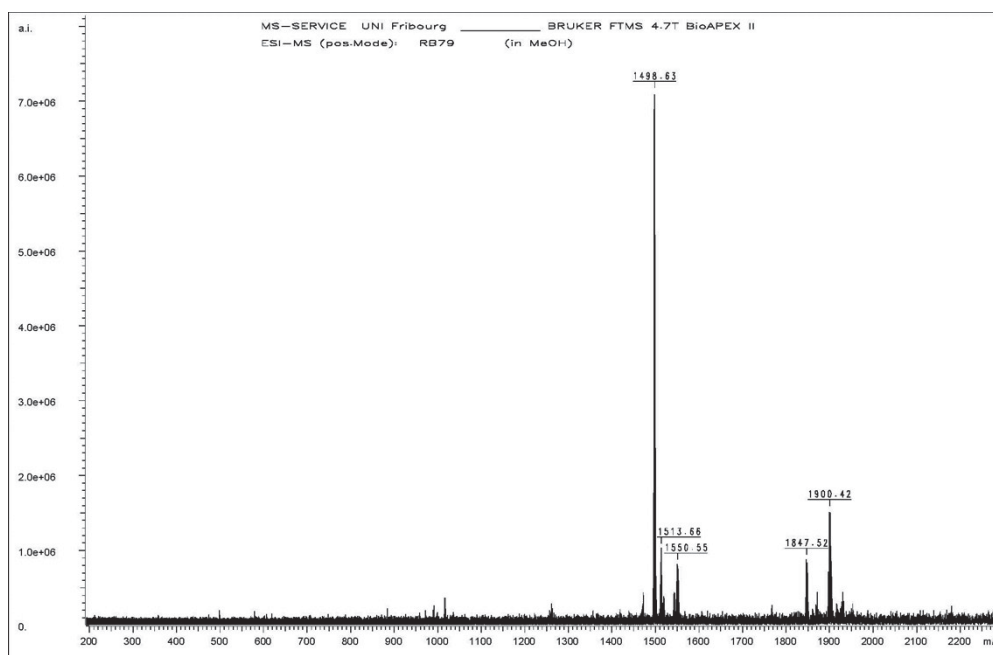


Figure S14. UV-Vis of species **3b** in methanol.



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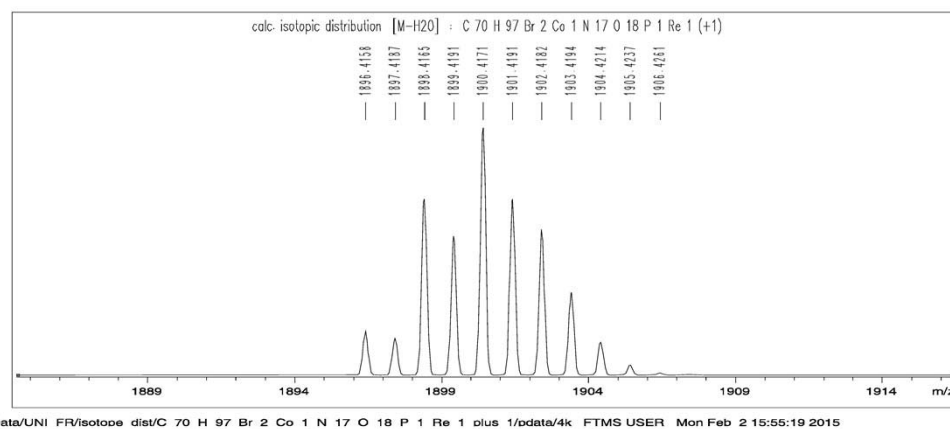
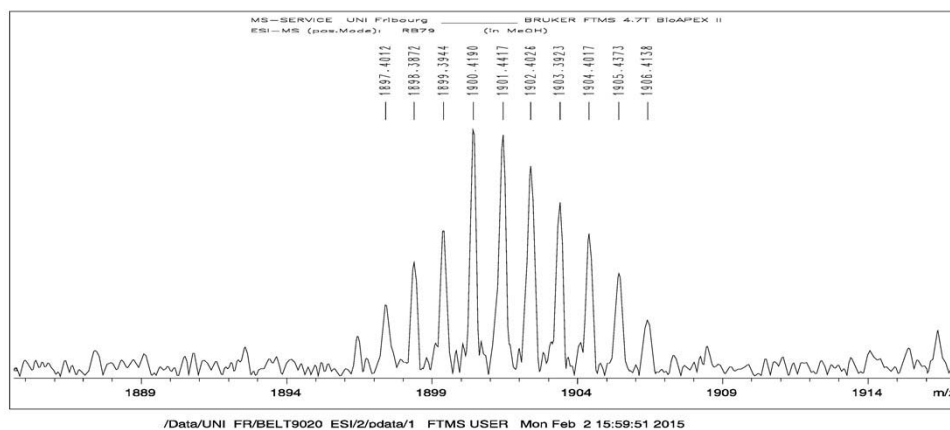
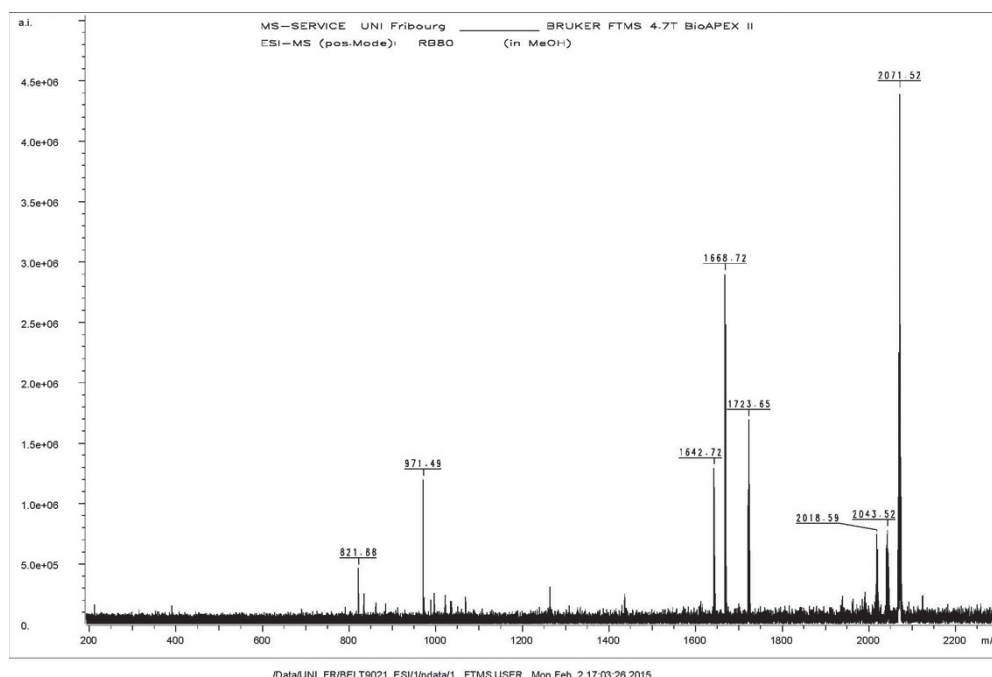
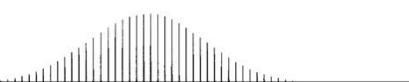


Figure S15. High-Resolution MS of **1b**.



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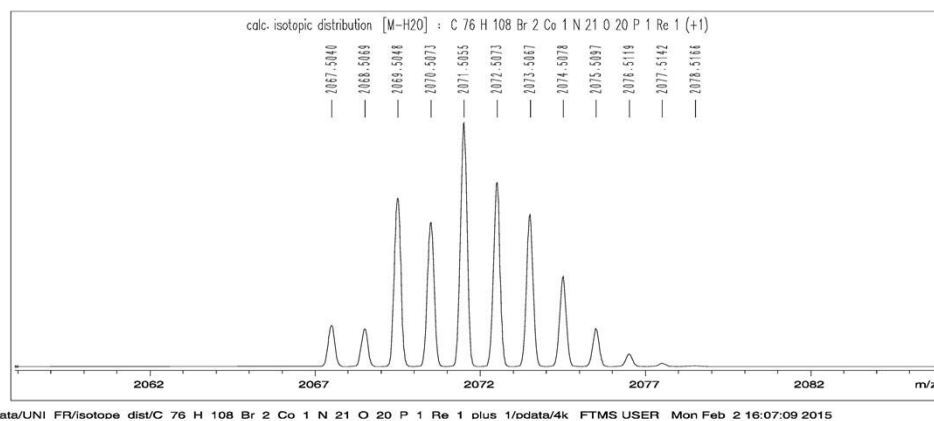
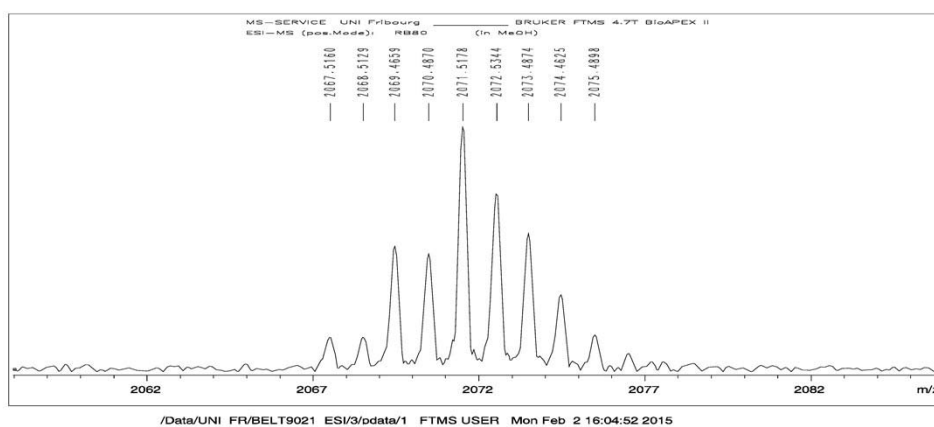
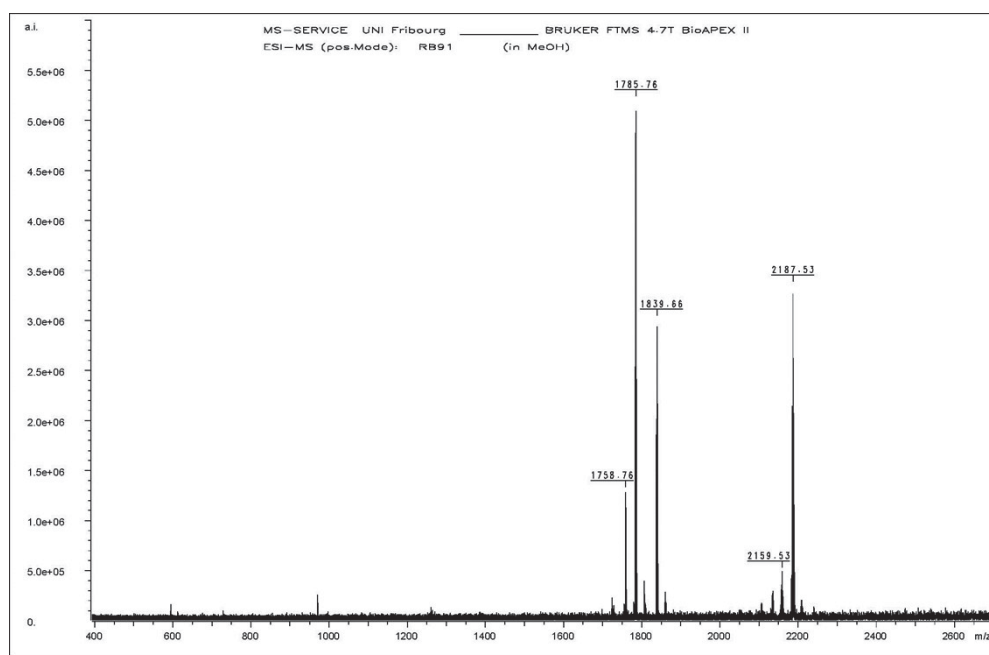


Figure S16. High-Resolution MS of **2b**.



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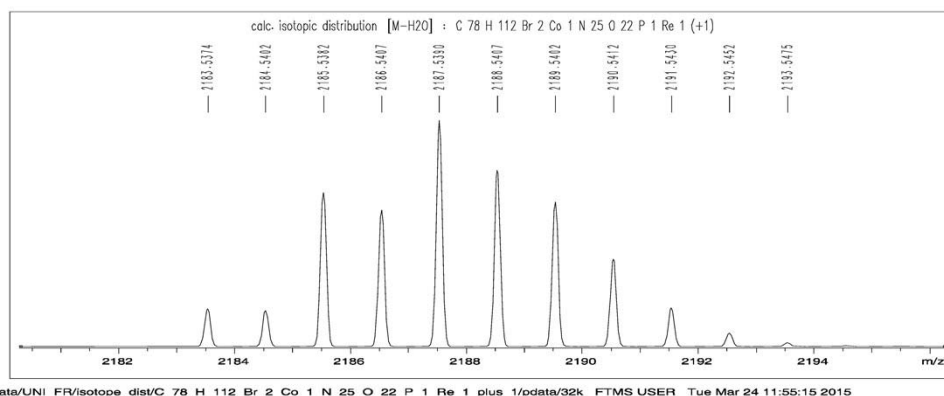
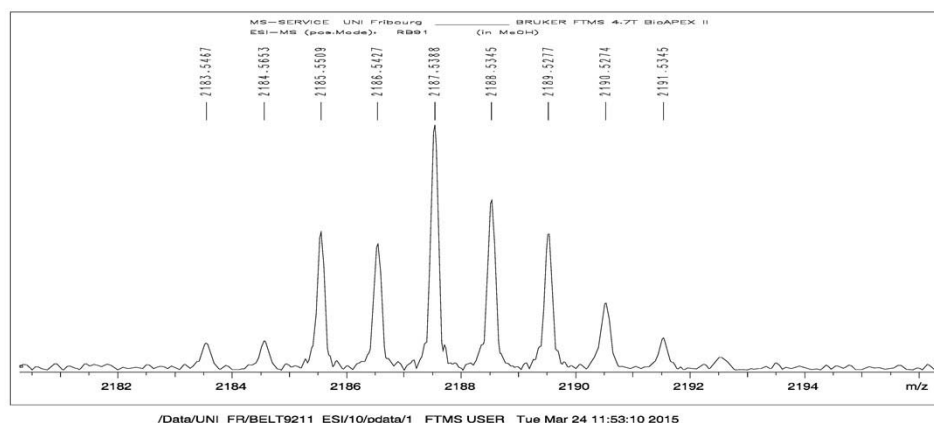


Figure S17. High-Resolution MS of **3b**.

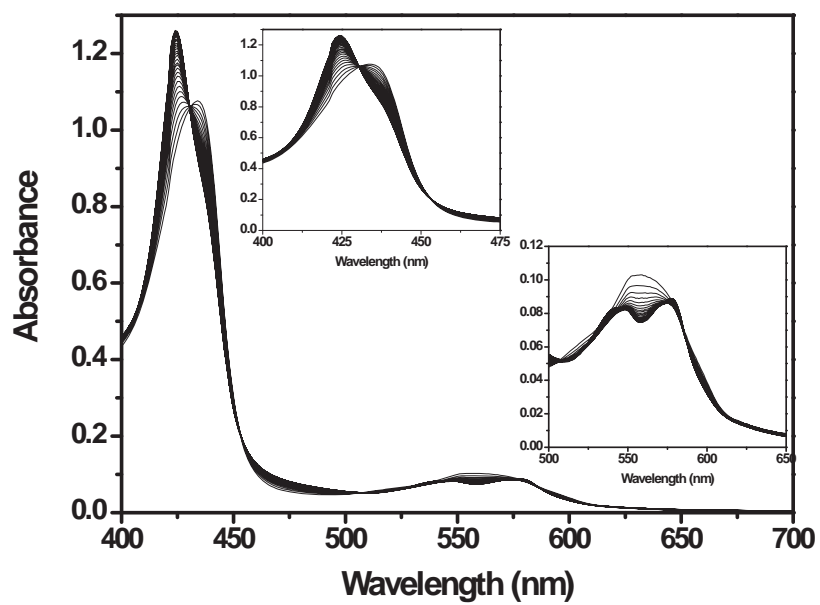


Figure S18. Typical spectrum changes on a Mb assay of mixed CO/NO releasing molecules.

Shown are the changes of **3b**.