Supporting Information for

Zinc Thiolate Reactivity toward Nitrogen Oxides: Insights into the Interaction of Zn^{2+} with *S*-Nitrosothiols and Implications for Nitric Oxide Synthase

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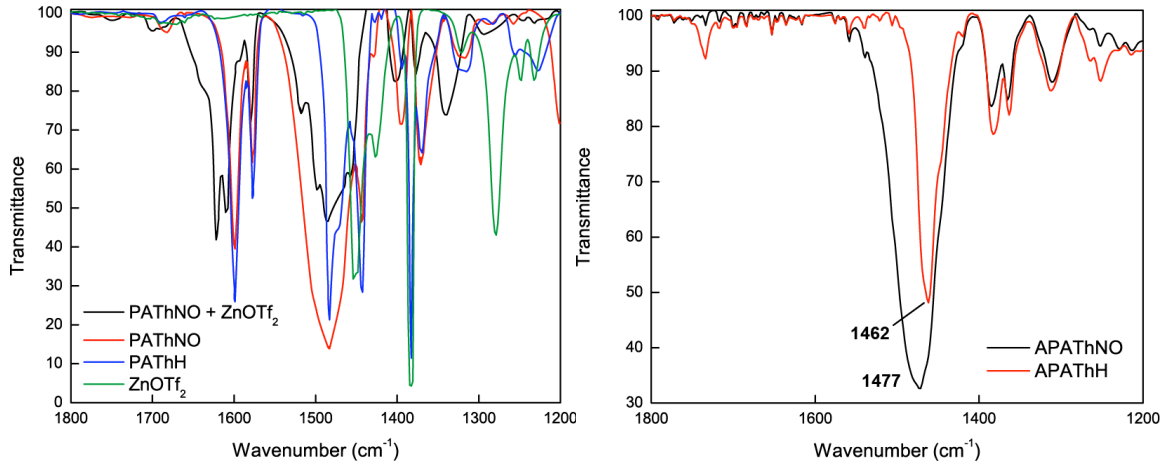

Figure S1. *Left:* Infrared spectral comparison of $Zn(OTf)_2$, PAThH, PAThNO, and PAThNO + $Zn(OTf)_2$ in MeCN. Strong absorbance bands between 1550 cm^{-1} and 1650 cm^{-1} obscure features arising from the reaction products of Zn^{2+} with PAThNO. *Right:* The infrared spectra of APAThH and APAThNO are shown for comparison.

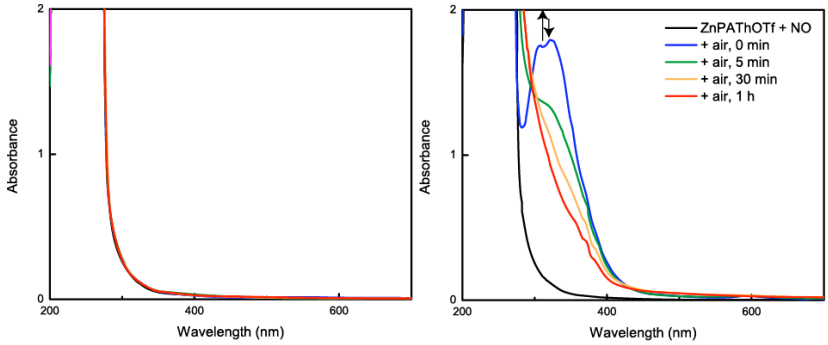

Figure S2. UV-Vis spectral profiles for reactions of anaerobic 7.5 mM ZnPAThOTf with excess NO (g), left, and of 7.5 mM ZnPAThOTf with excess NO (g) + air, right. Recorded in acetonitrile.

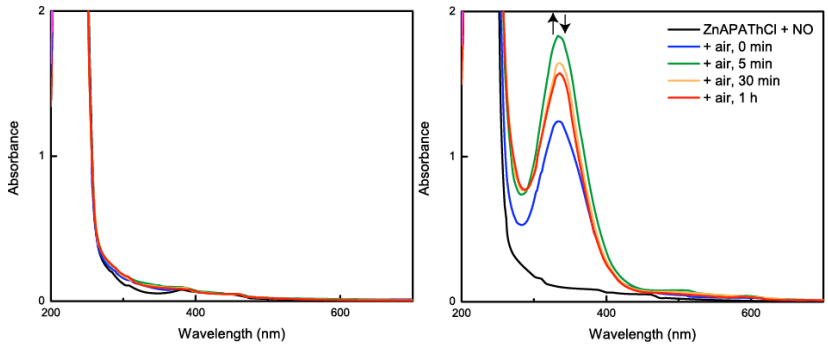

Figure S3. UV-Vis spectral profiles for reactions of anaerobic 7.5 mM ZnAPAThCl with excess NO (g), left, and of 7.5 mM ZnAPAThCl with excess NO (g) + air, right. Recorded in acetonitrile.

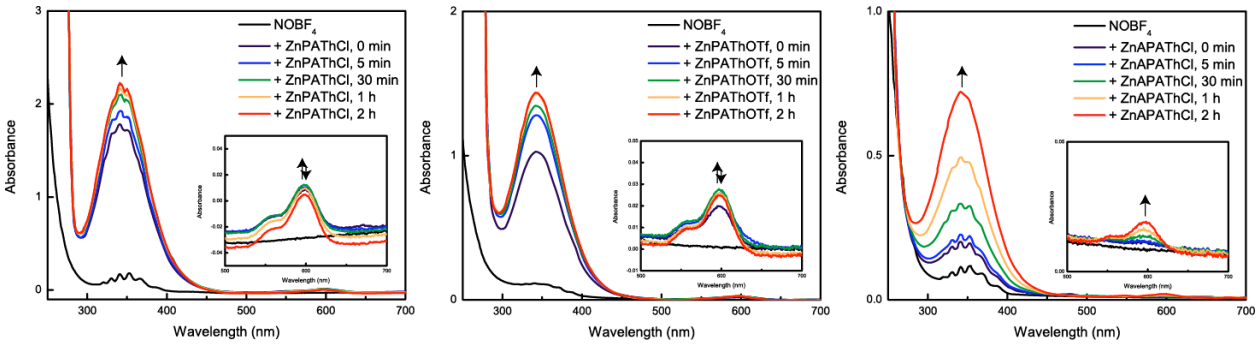

Figure S4. Spectral profiles for reactions of 1 equiv of $NOBF_4$ with 7.5 mM zinc thiolate complexes. From left to right: ZnPAThCl, ZnPAThOTf, and ZnAPAThCl. The low-intensity features observed between 300 nm and 400 nm result from NO_2BF_4 contamination of commercially available $NOBF_4$.

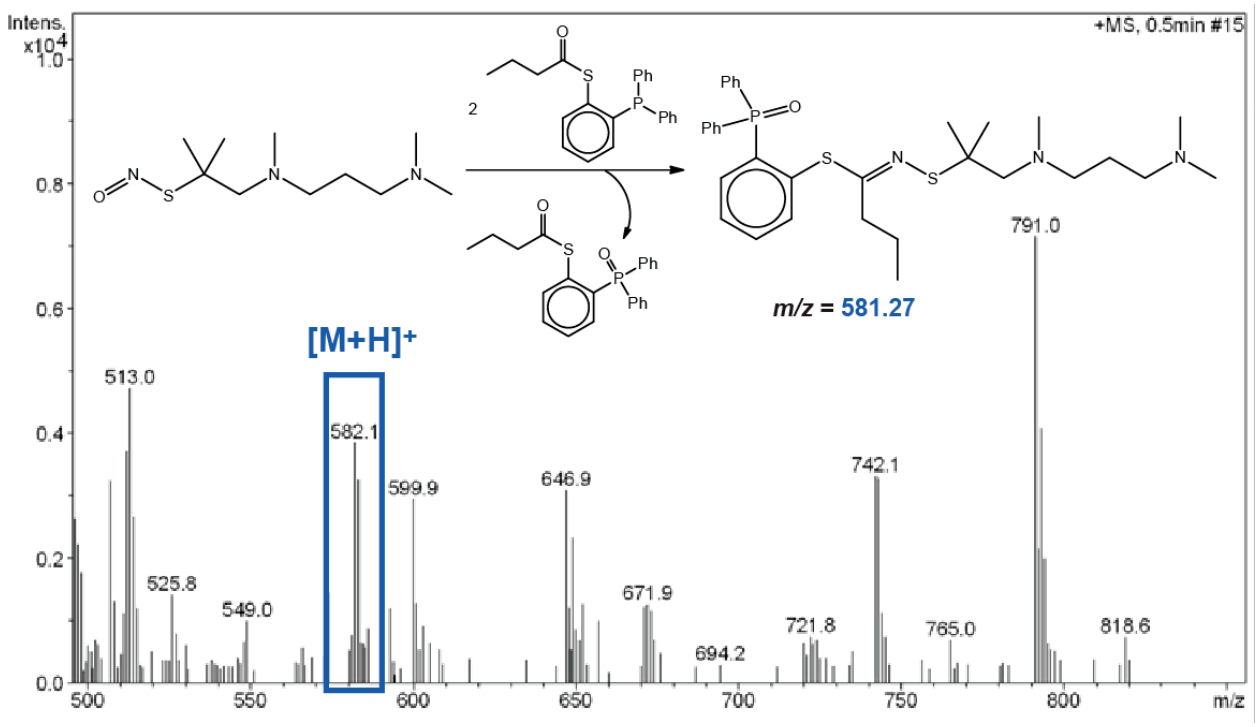

Figure S5. ESI-MS spectrum of ZnAPAThCl + 0.9 equiv $NOBF_4$ + PPh_2R.

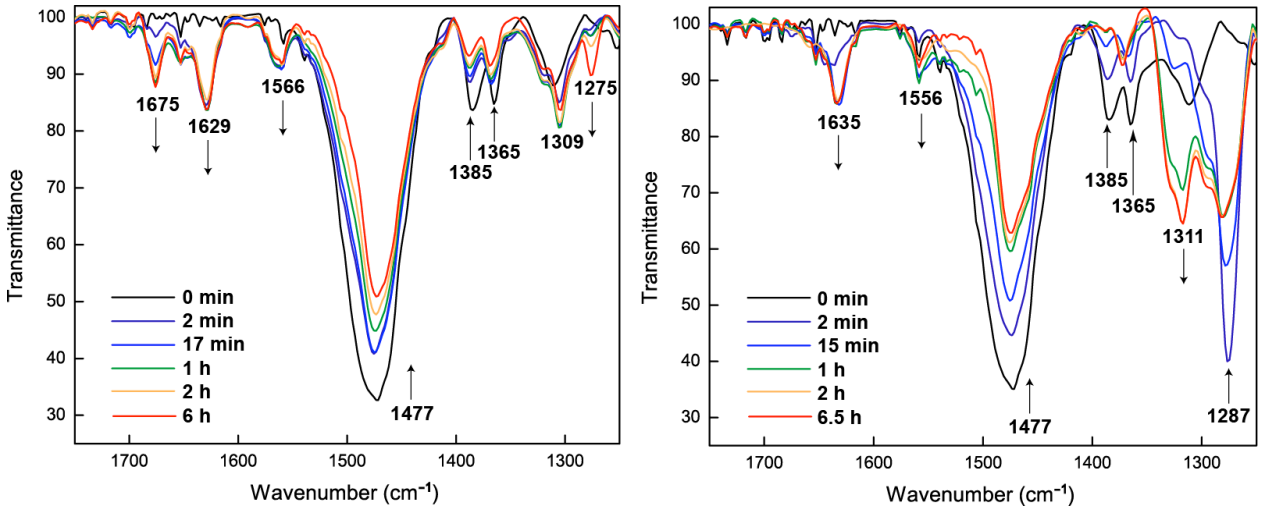

Figure S6. Solution IR spectral timecourse for the reactions of APAThNO with 1 equiv of $ZnCl_2$ (left) and $Zn(OTf)_2$ (right) in MeCN-d_3. The υ_{NO} band at 1477 cm^{-1} for APAThNO disappears upon addition of zinc(II) salt to the nitrosothiol. Because υ_{NO} of APAThNO overlaps the C–H rocking and/or bending modes, some intensity remains after the *S*-nitrosothiol N=O stretch at 1477 cm^{-1} disappears. For comparison see Figure S1, *right*.

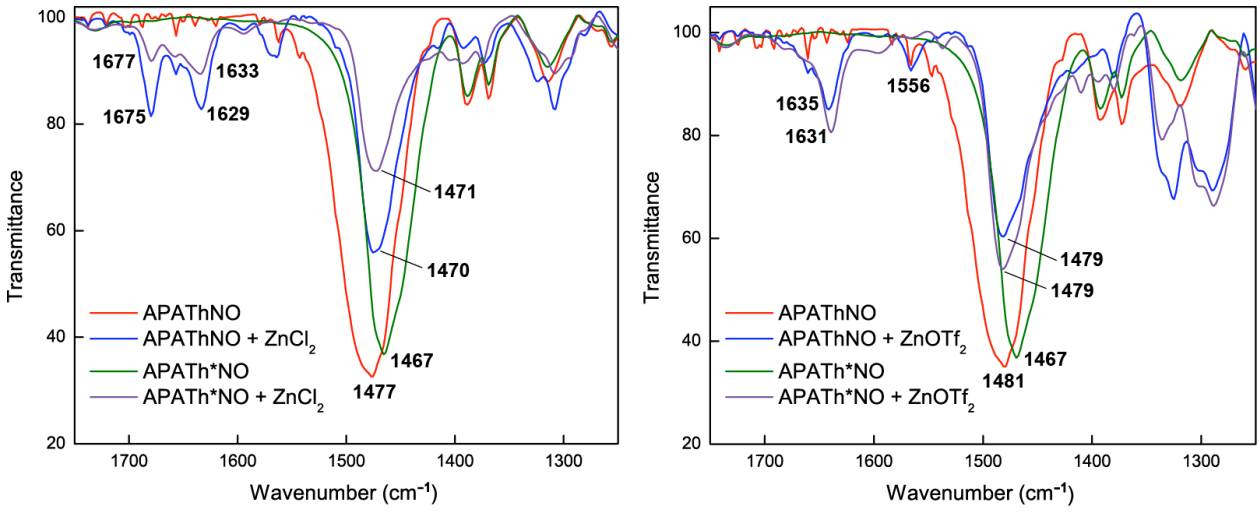

Figure S7. ^{15}N (designated *N) vs. ^{14}N spectral comparison of reactions of APATh*NO and APAThNO with $ZnCl_2$ (left) and $Zn(OTf)_2$ (right). Recorded in acetonitrile-d_3.

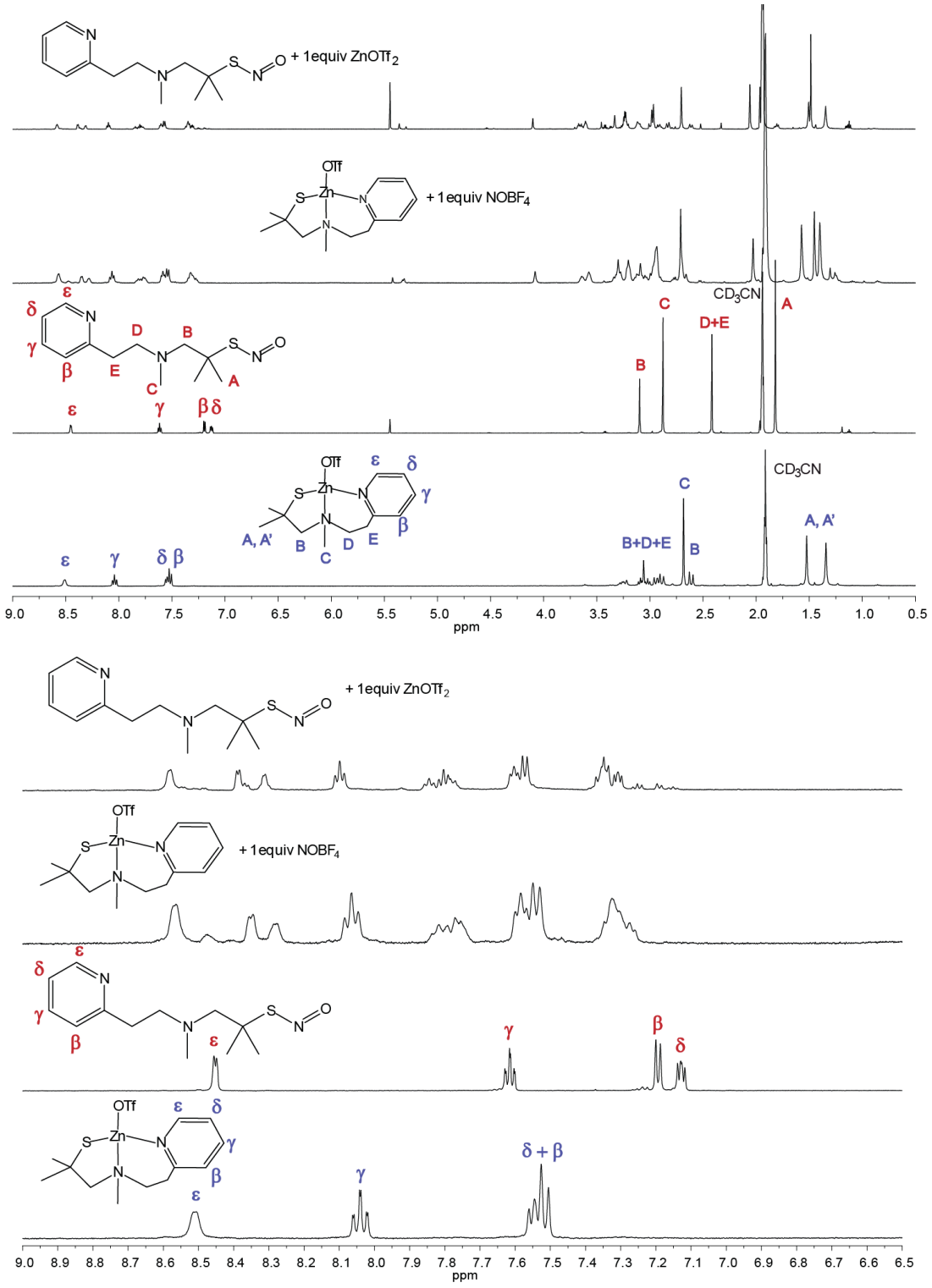

Figure S8. Comparison of ^{1}H NMR spectra for 7.5 mM ZnPAThOTf/NOBF$_4$ vs. 7.5 mM PAThNO/Zn(OTf)$_2$ reactions. Recorded in MeCN-d_3.

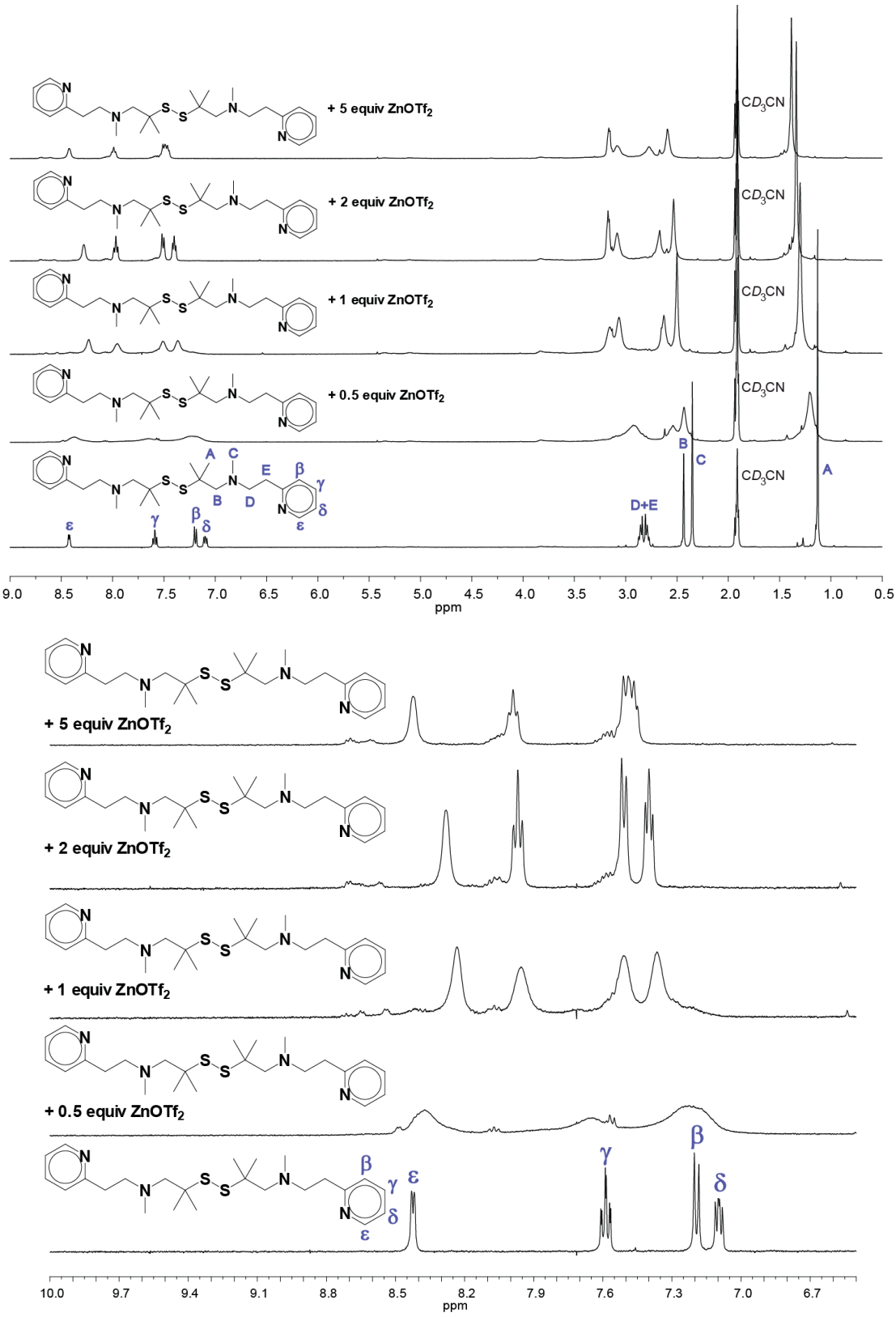

Figure S9. ^{1}H NMR spectral comparison of $PATh_2$ solutions in MeCN-d_3 containing variable amounts of $Zn(OTf)_2$.

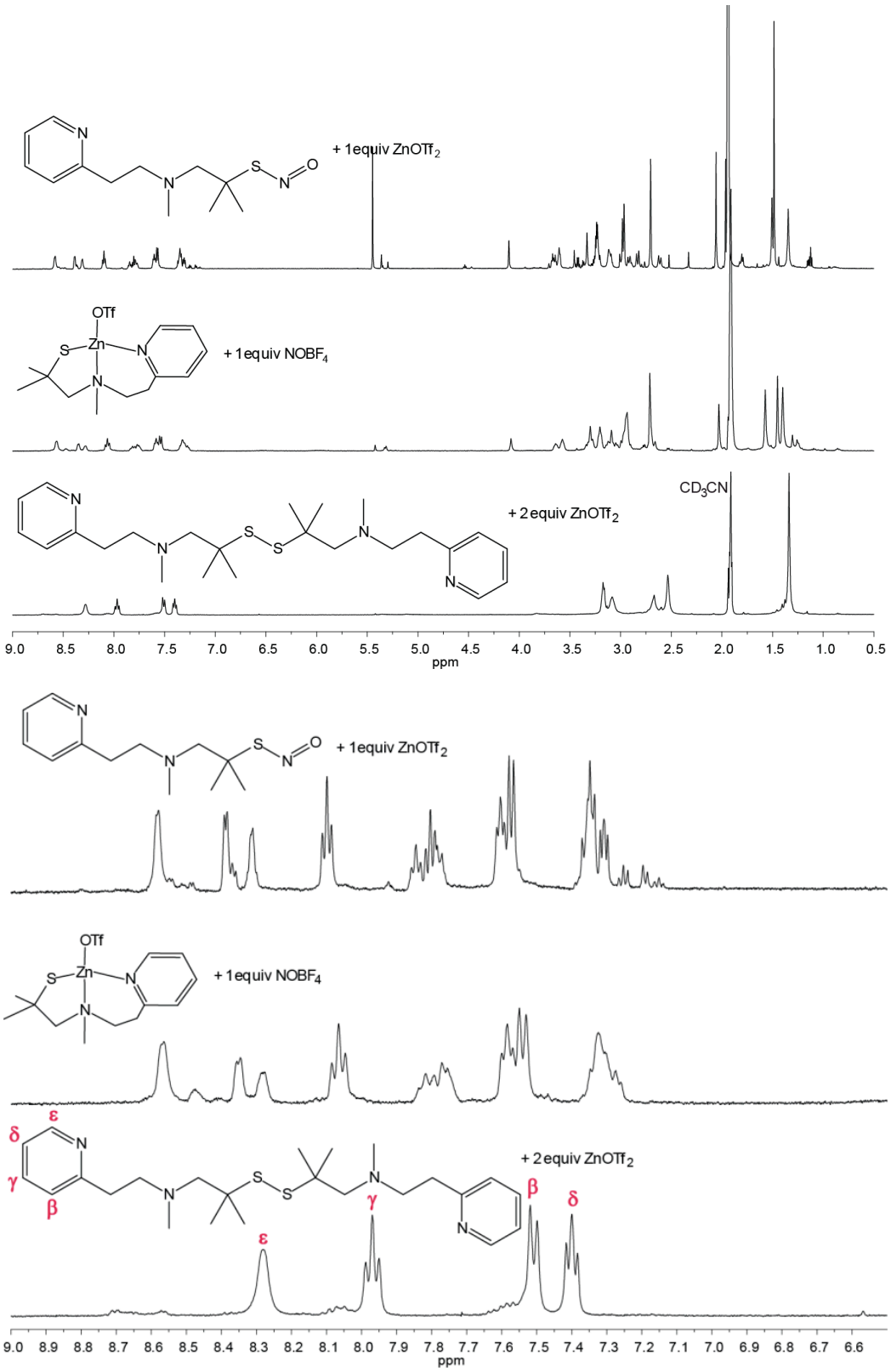

Figure S10. ^{1}H NMR comparison of a $PATh_2/Zn(OTf)_2$ solution with reaction spectra of ZnPAThOTf with $NOBF_4$ and PAThNO with $Zn(OTf)_2$. Recorded in MeCN-d_3.

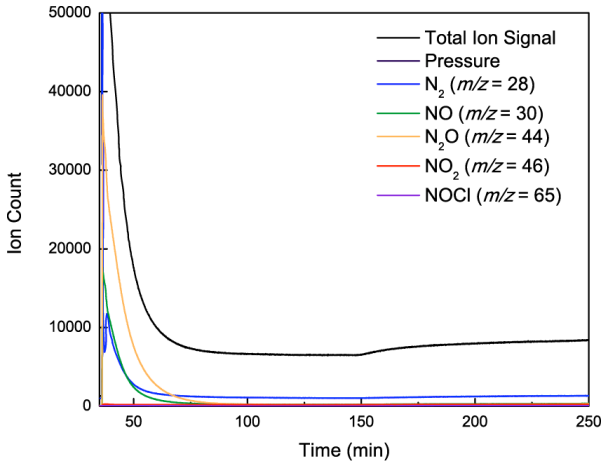

Figure S11. EI-MS analysis of the reaction headspace for ZnAPAThCl and $NOBF_4$ in CH_3CN.

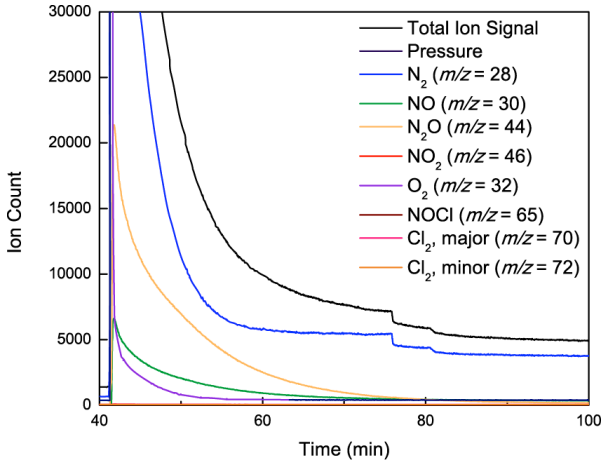

Figure S12. EI-MS analysis of the reaction headspace for APAThNO and $ZnCl_2$ in CH_3CN.

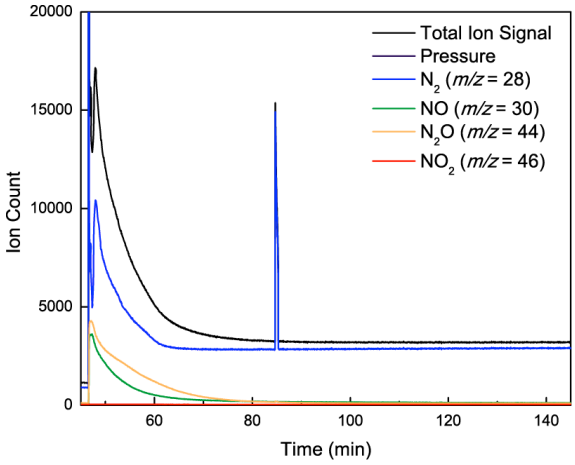

Figure S13. EI-MS analysis of the reaction headspace of the APAThNO/$ZnOTf_2$ reaction in CH_3CN.

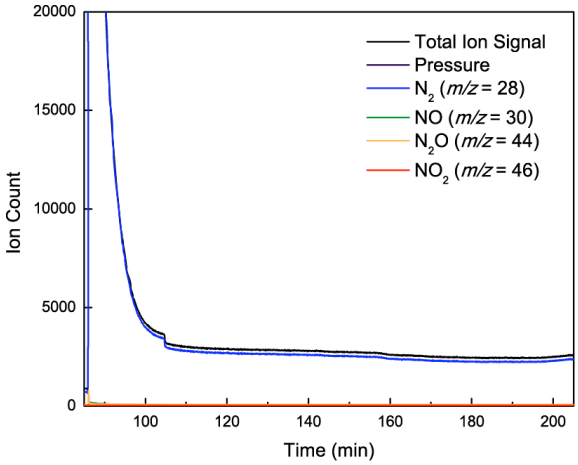

Figure S14. EI-MS control experiment: analysis of the solution headspace of APAThNO in CH_3CN.

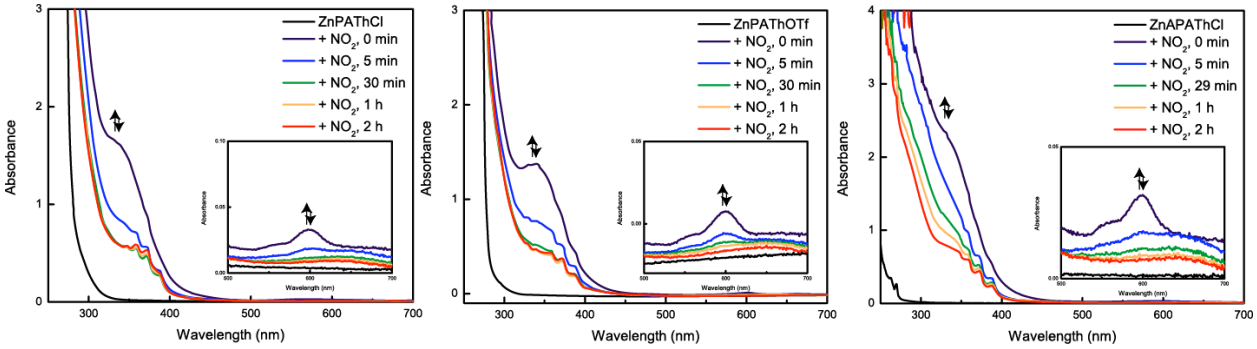

Figure S15. Acetonitrile solution spectra of NO_2 reactions with 1.5 mM ZnPAThCl (left), 1.9 mM ZnPAThOTf (middle), and 1.5 mM ZnAPAThCl (right) reactions. The lower intensity peaks appearing in the 350 – 400 nm region of the spectrum are attributed to NO_2.