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Light-Activated Oxidation of the Ligand of an Iron(III) Complex

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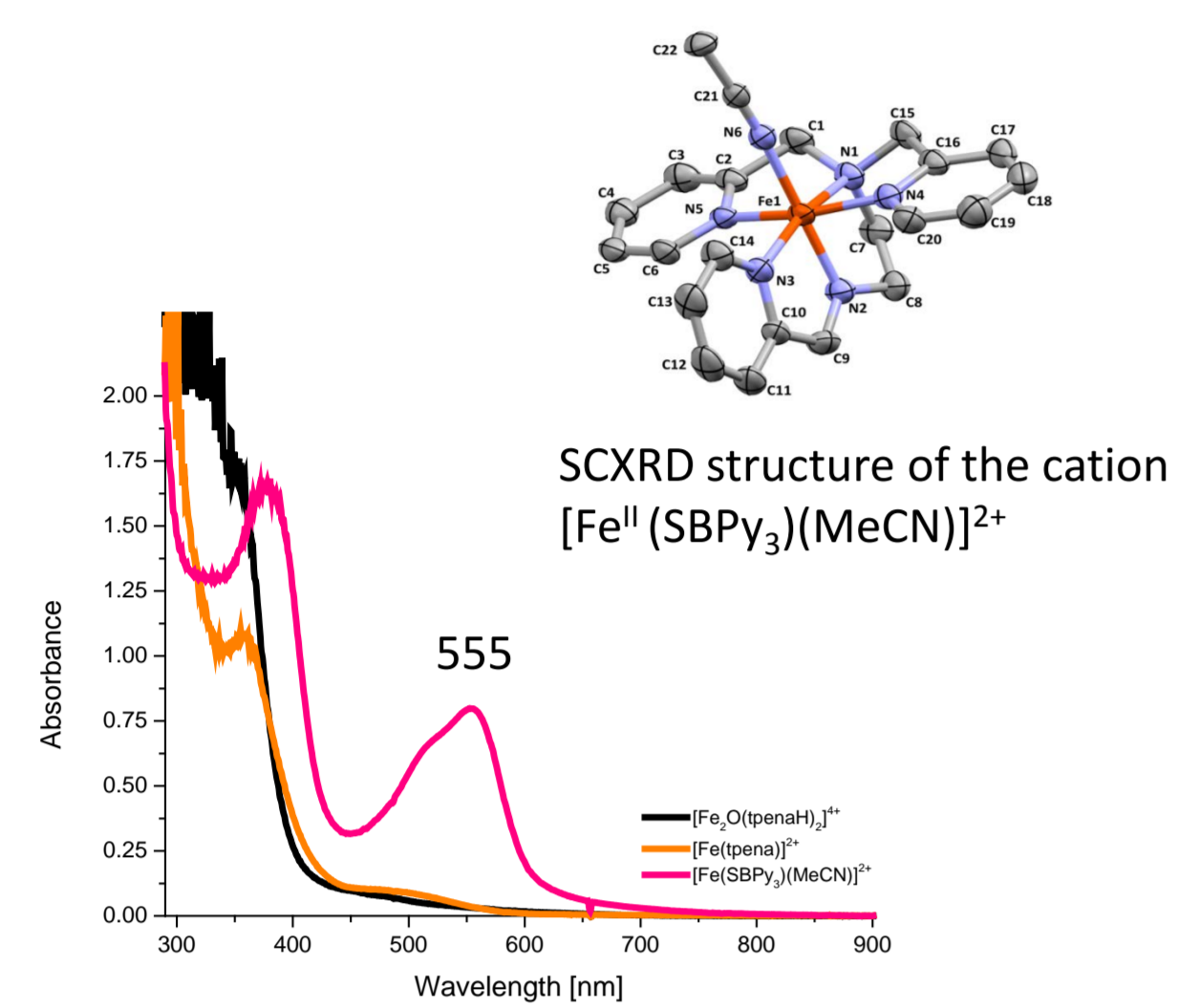
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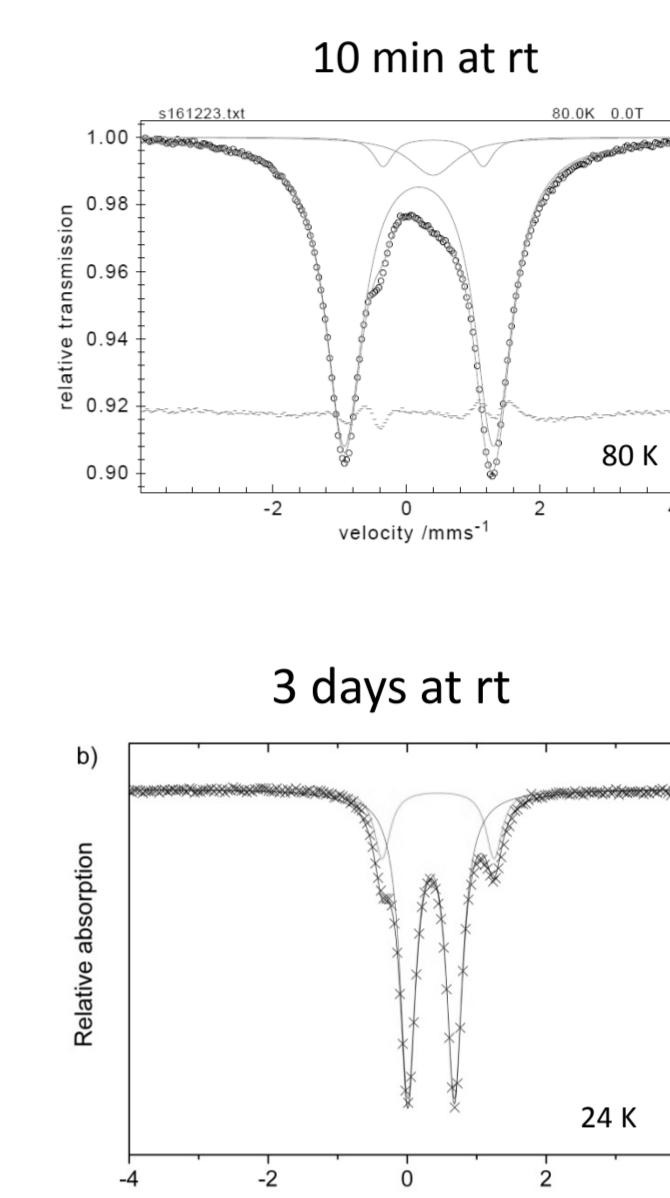
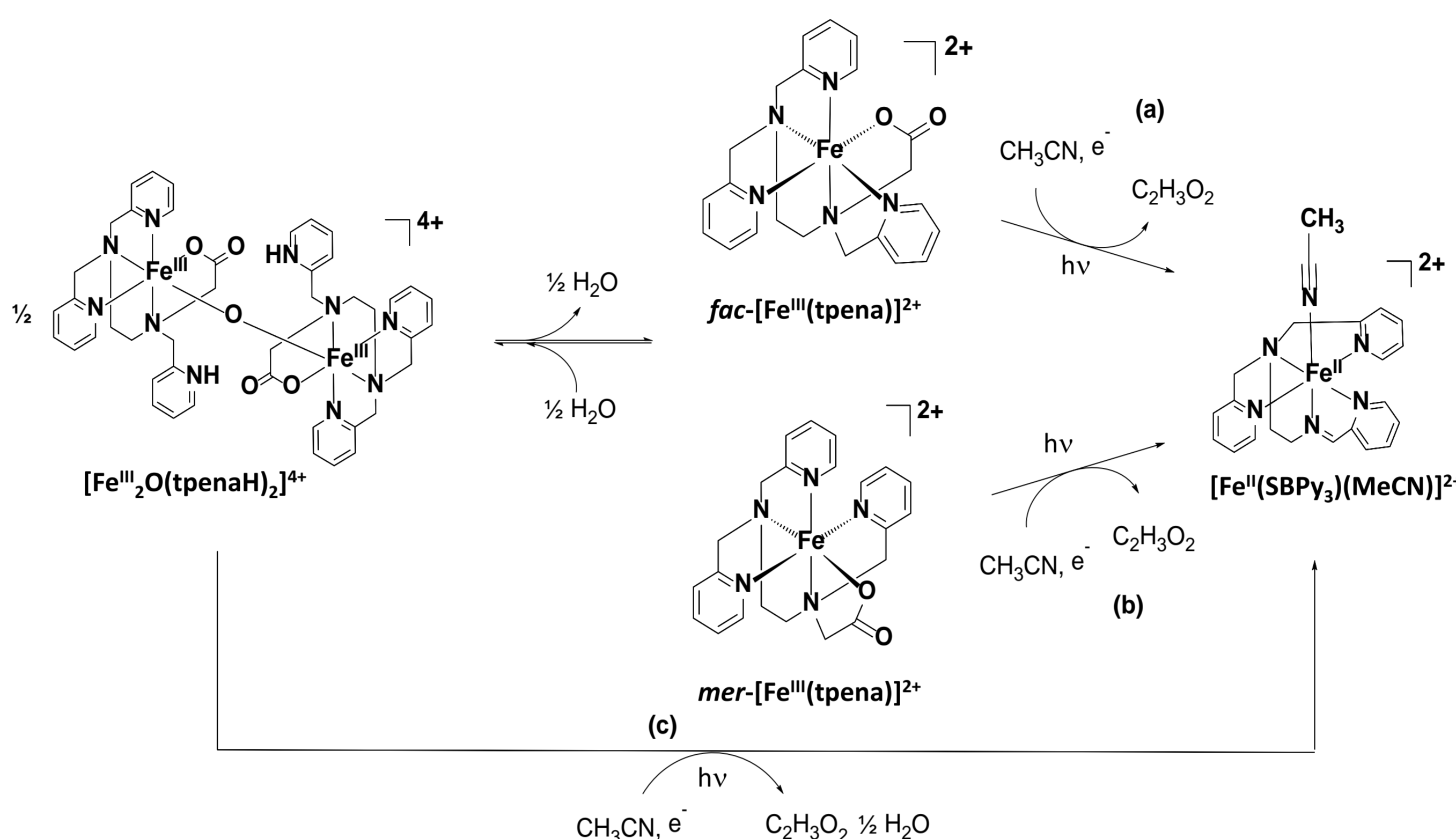
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Oxidative C-N Cleavage in a Carboxylato Ligand



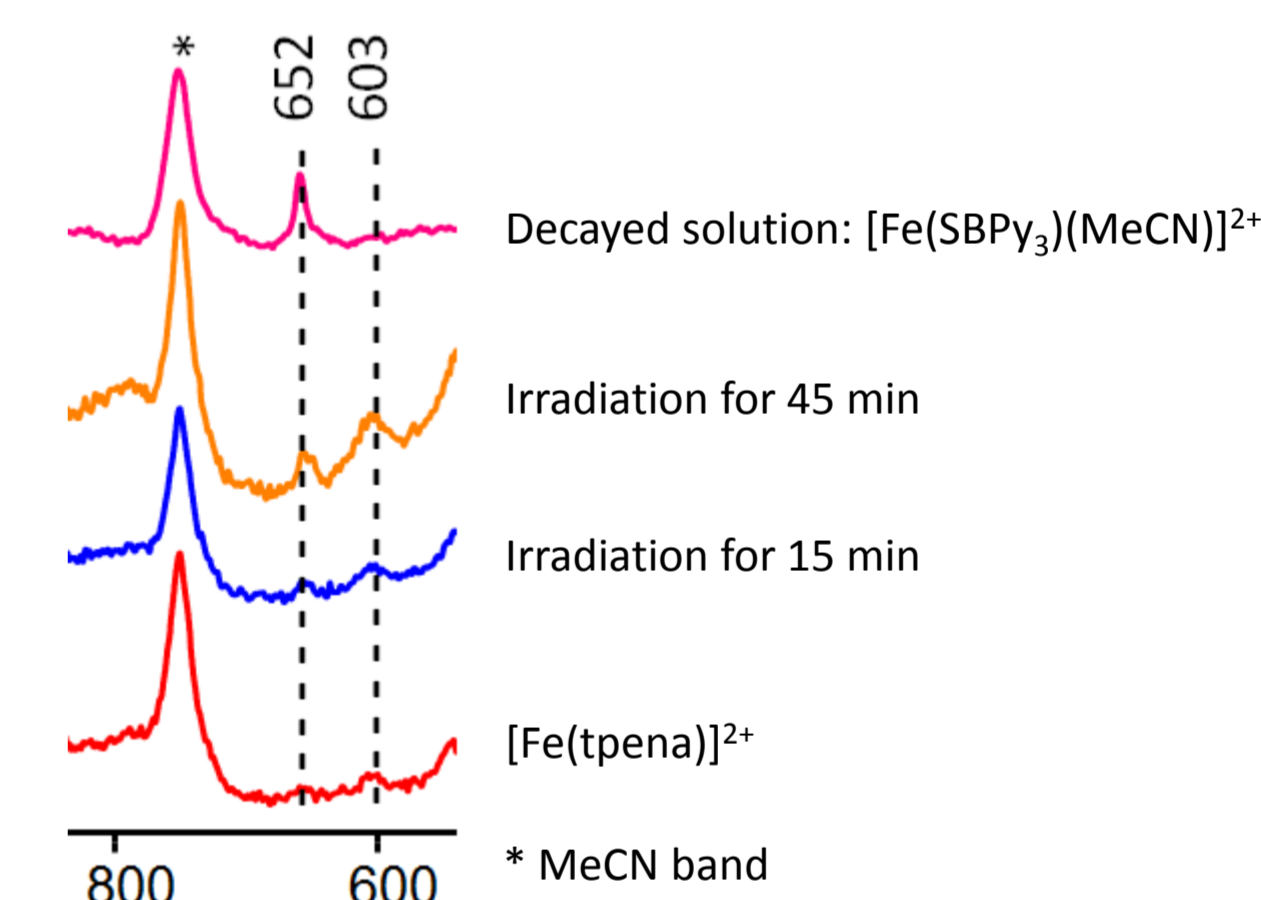
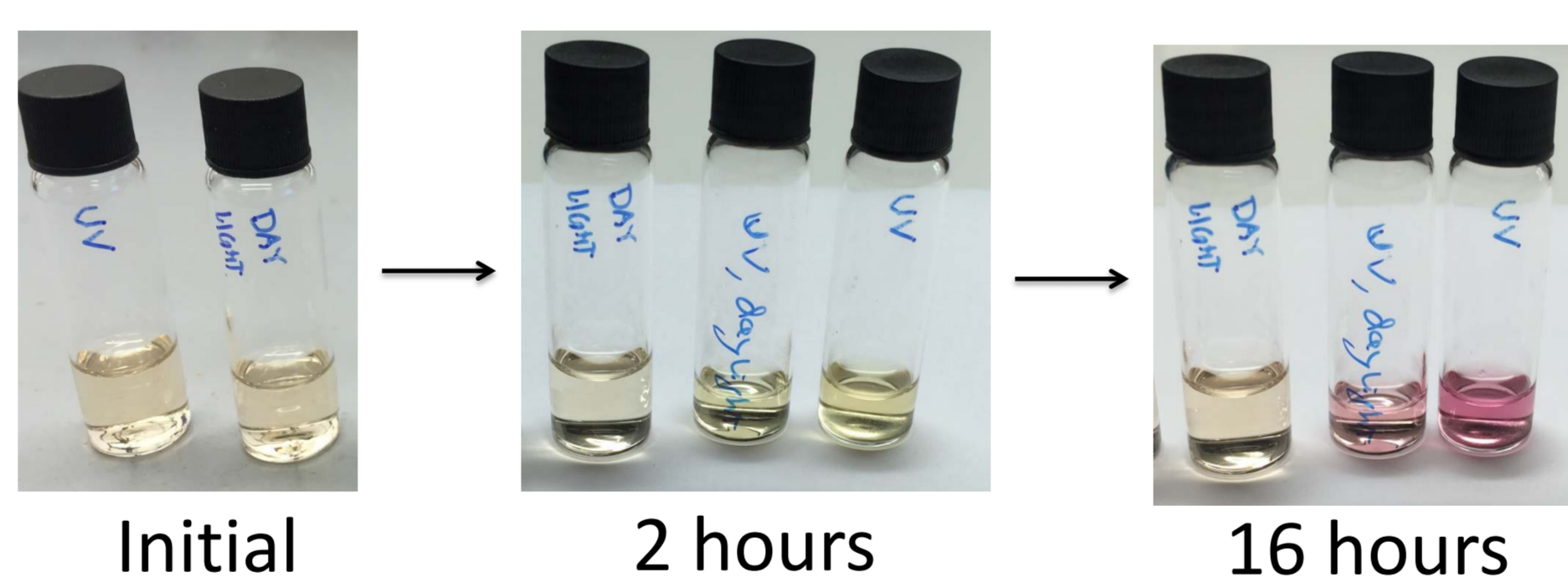
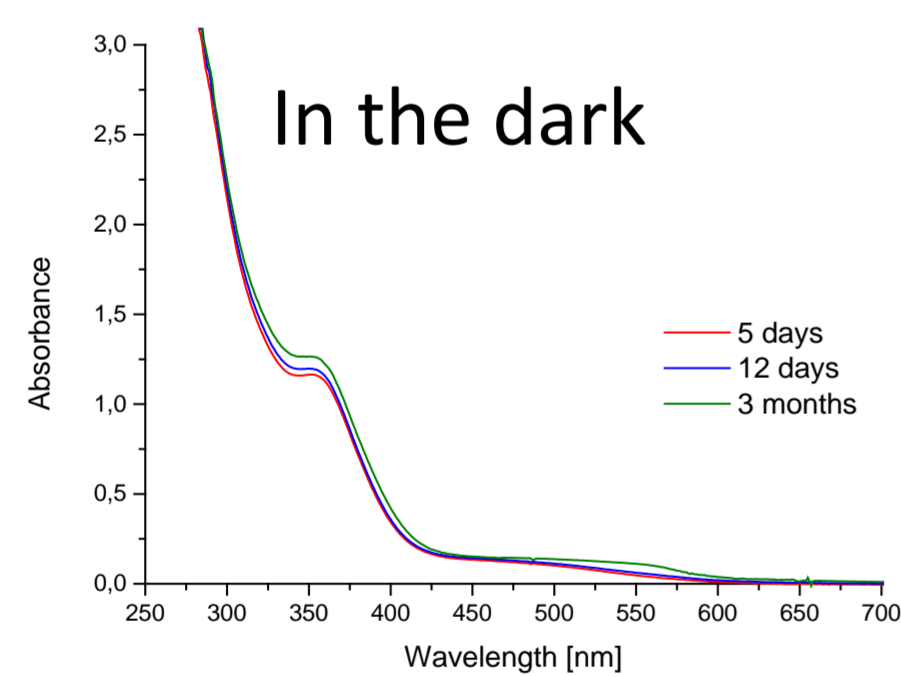
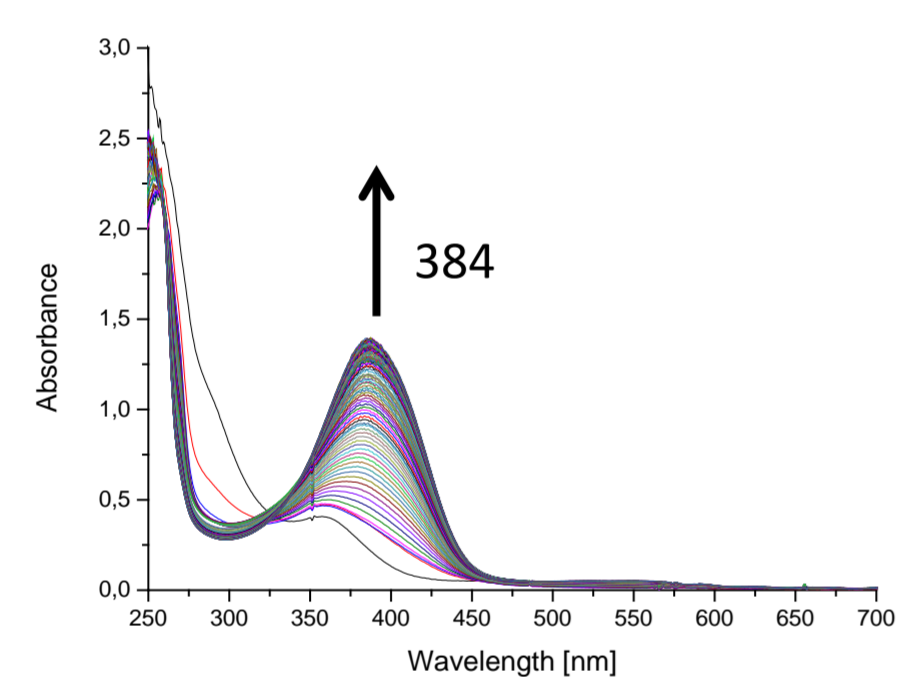
Which pathway (a), (b) or (c)?
And how many steps?
i.e. CH_3OH , CH_2O , CO_2 , CH_3COOH are all possible C_1 and C_2 products amounting to the sum of a $\text{C}_2\text{H}_3\text{O}_2$ loss



	δ [mm ^s ⁻¹]	ΔE_Q [mm ^s ⁻¹]	Assignment
$[\text{Fe}_2\text{O}(\text{tpenaH})_2]^{4+}$	0.46	1.65	high-spin Fe(III)
$\text{fac-}[\text{Fe}^{\text{III}}(\text{tpena})]^{2+}$	0.19	2.23	low-spin Fe(III)
$\text{mer-}[\text{Fe}^{\text{III}}(\text{tpena})]^{2+}$	0.40	-	high-spin Fe(III)
$[\text{Fe}(\text{SBPY}_3)(\text{MeCN})]^{2+}$	0.34	0.67	low-spin Fe(II)

Light-Induced Intermediate

In a UV- or visible laser beam

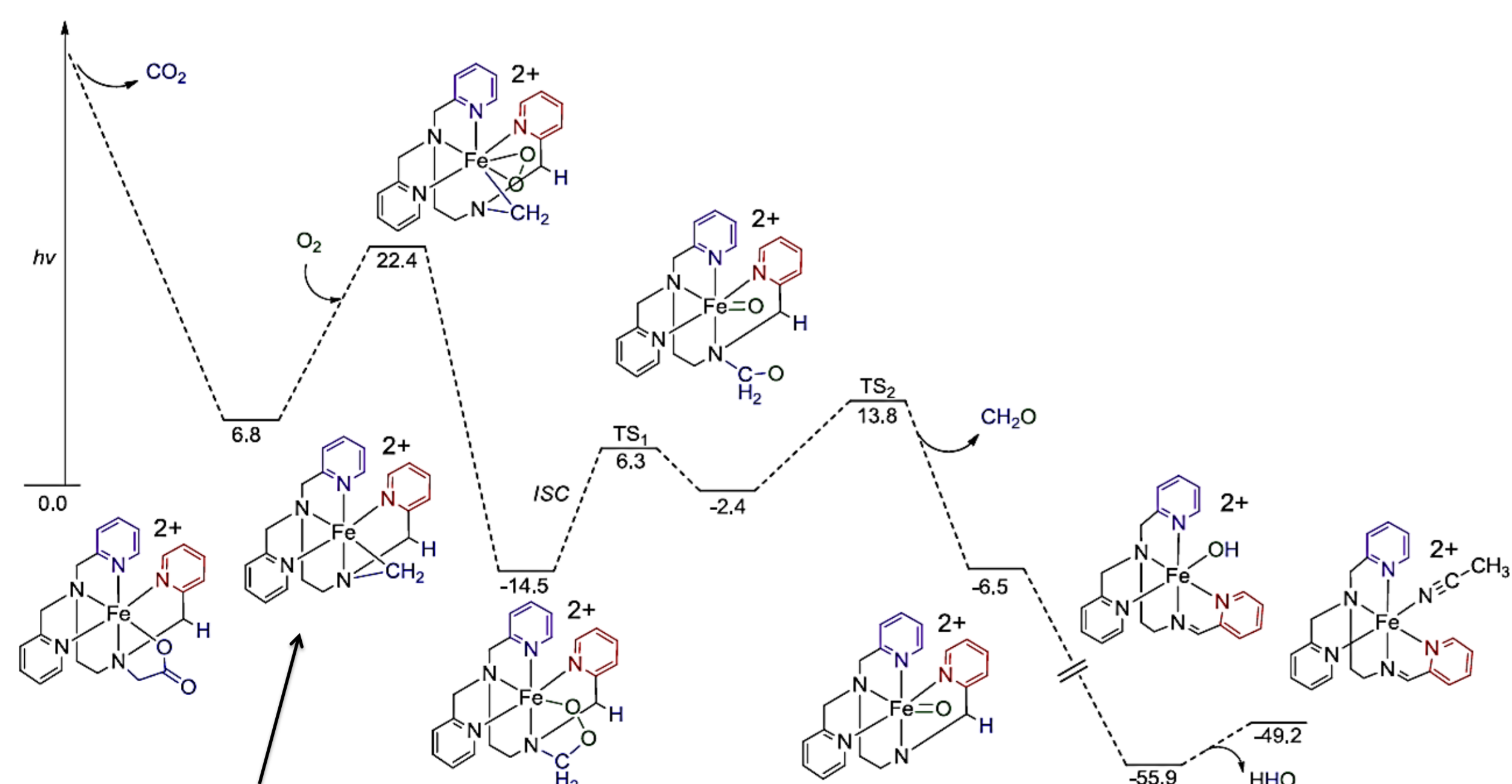


An transient yellow species with $\lambda_{\text{max}} = 384 \text{ nm}$ is formed, when solutions of $[\text{Fe}(\text{tpena})]^{2+}$ are irradiated. The 555 nm band due to $[\text{Fe}(\text{SBPY}_3)(\text{MeCN})]^{2+}$ appears subsequently.

Transient yellow species: 603 cm^{-1}
 $[\text{Fe}(\text{SBPY}_3)(\text{MeCN})]^{2+}$: 652 cm^{-1}

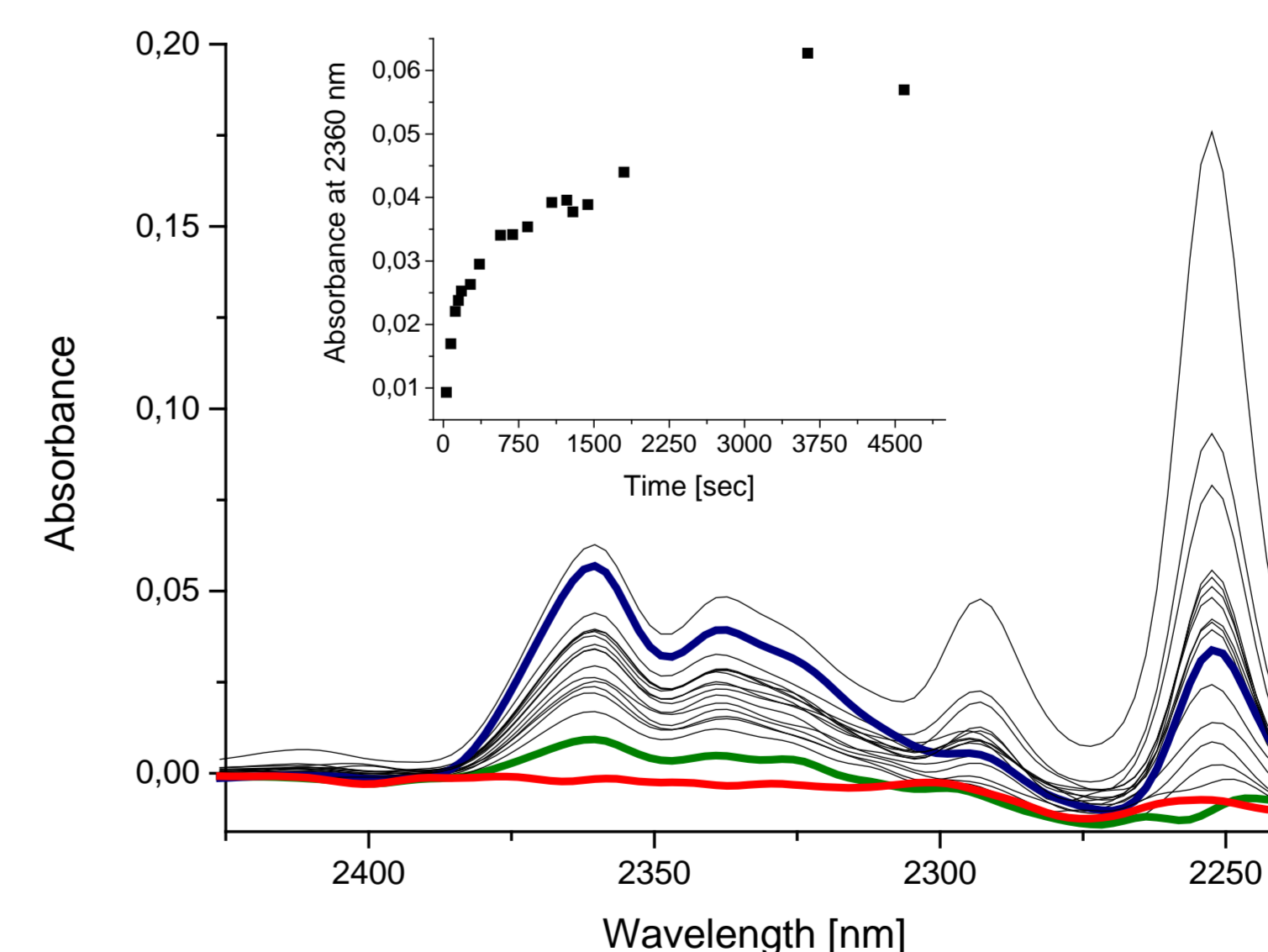
Proposed Reaction Mechanism

Detection of the Organic Products



Could this be the transient yellow species?

(1) *Angew. Chem. Int. Ed.* **2012**, *51*, 6767-6770 (2) *Chem., Eur. J.* **2016**, *22*, 3810-3820 (3) *In preparation*
tpena: *N,N,N'*-tris(2-pyridylmethyl)ethylenediamine-*N'*-acetate, SBPY₃: *N,N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-aldimine



Head-space IR spectroscopy was used to confirm the release of CO_2 (2360 nm and 2338 nm) and the Hantzsch reaction was used to detect the formation of formaldehyde. Simultaneous detection and quantification of the CO_2 and CH_2O evolution indicated a 1:1 ratio release of CO_2 and CH_2O verifying the proposed mechanism and eliminating CH_3OH and CH_3COOH as by-products.