Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Diiron species containing a cyclic $P^{ph}{}_2N^{Ph}{}_2$ diphosphine related to the [FeFe]H_2ases active site

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Fig a. VT $^{31}P\{^1H\}$ NMR study of complex 1 in CD_2Cl_2

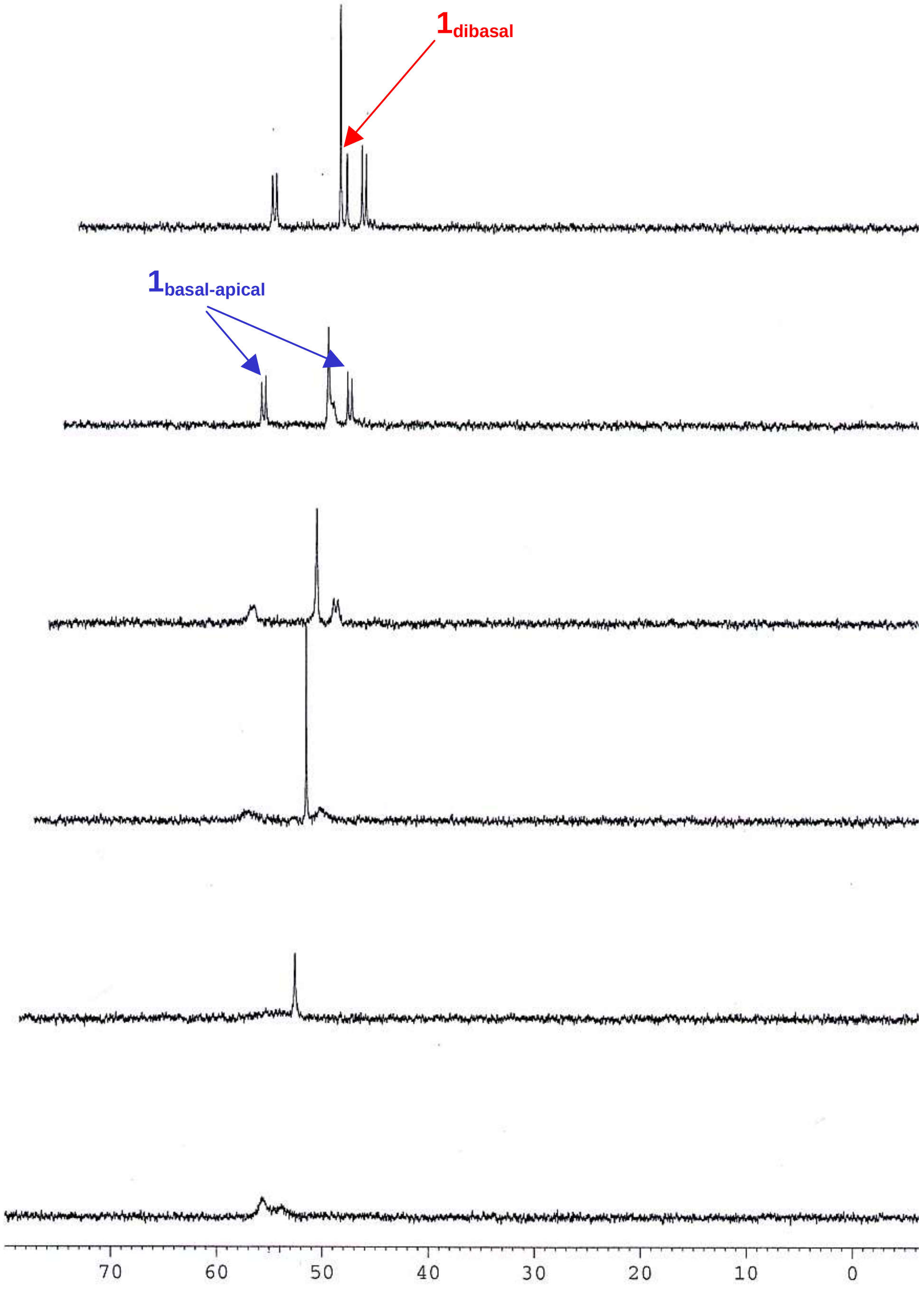
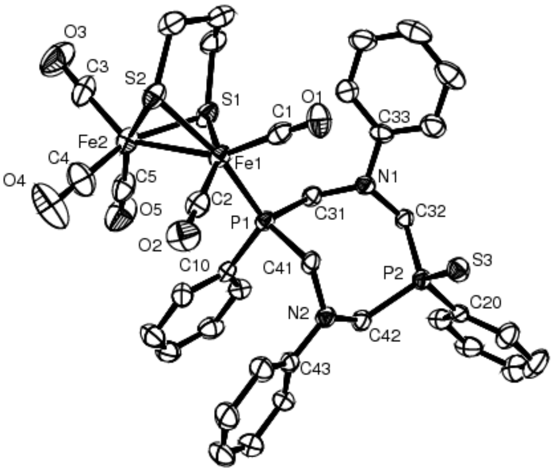


Fig b Ortep view (elliposids at 30% of probability level) of 3. Selected bond lengths (Å): Fe(1)-Fe(2), 2.5632(8); Fe(1)-P(1), 2.2392(3) ; P(2)-S(3), 1.9533(3).



Crystal data for **2**: $C_{37}H_{36}Cl_2Fe_2N_2O_5P_2S_4$. *M* 929.40, monoclinic, $P2_1/c$, *a* = 16.7119(8), *b* = 12.2358(5), *c* = 19.4661(10) Å, β = 94.263(5), *Z* = 4, *V* = 3969.5(3) Å^3; ρ_{cal} = 1.555 g cm^{-3} ; μ(Mo-K$_\alpha$) = 1.111 mm^{-1}; λ = 0.71073 Å, *T* = 170(2) K. 29973 reflections measured, 8080 unique (R_{int} = 0.0608) used in refinement. *R*1[8080 with $I > 2\sigma(I)$] = 0.0510, *w*R2(all data) = 0.1034.CCDC 789267

Fig c. ^{31}P-{^{1}H} NMR spectrum of 2, at 298 K, in $CDCl_3$

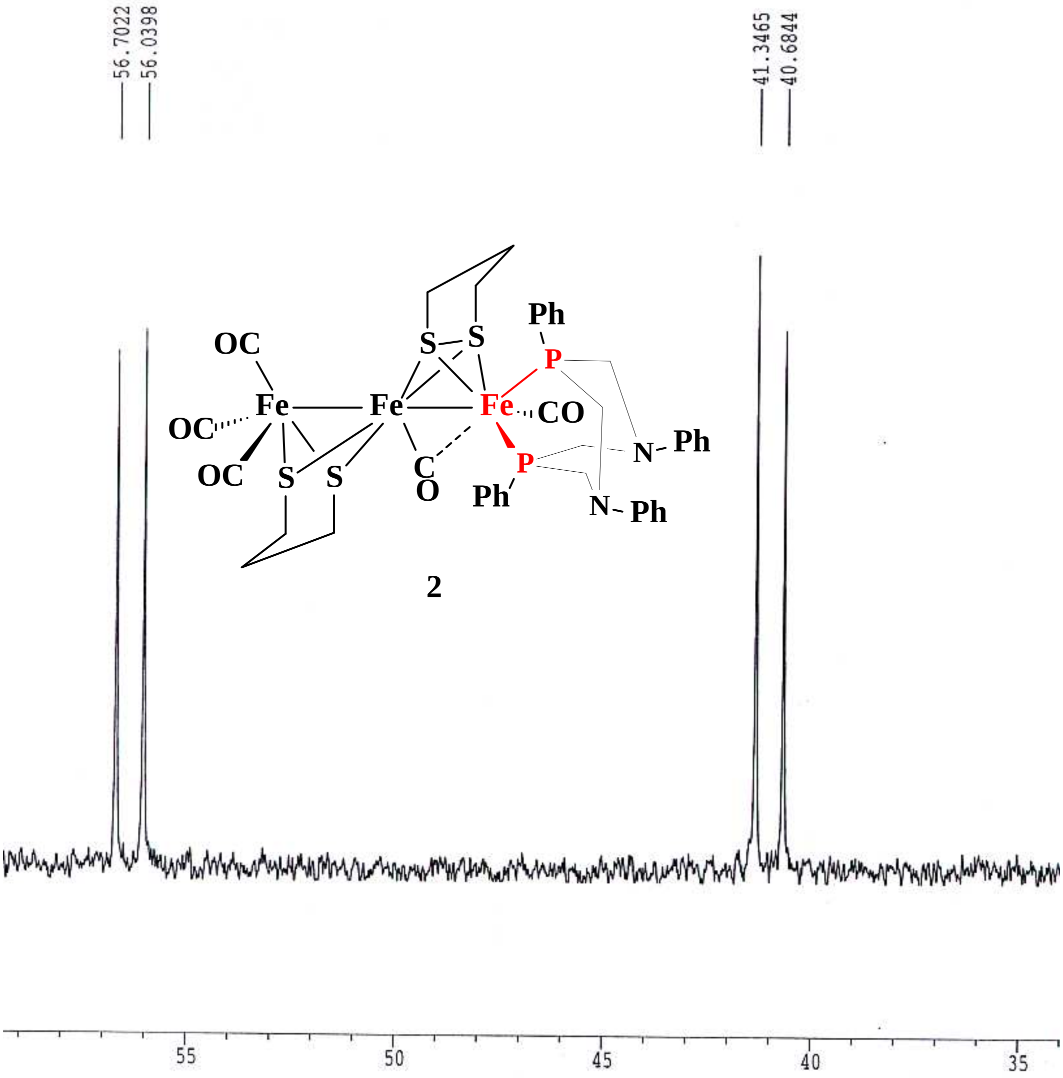


Fig d. ^{31}P-{^{1}H} NMR study of the protonation of 1 at 298 K in CD_2Cl_2. a) after addition of 1 equiv of CH_3SO_3H; b) after addition to the previous solution of 1 equiv of CF_3SO_3H.

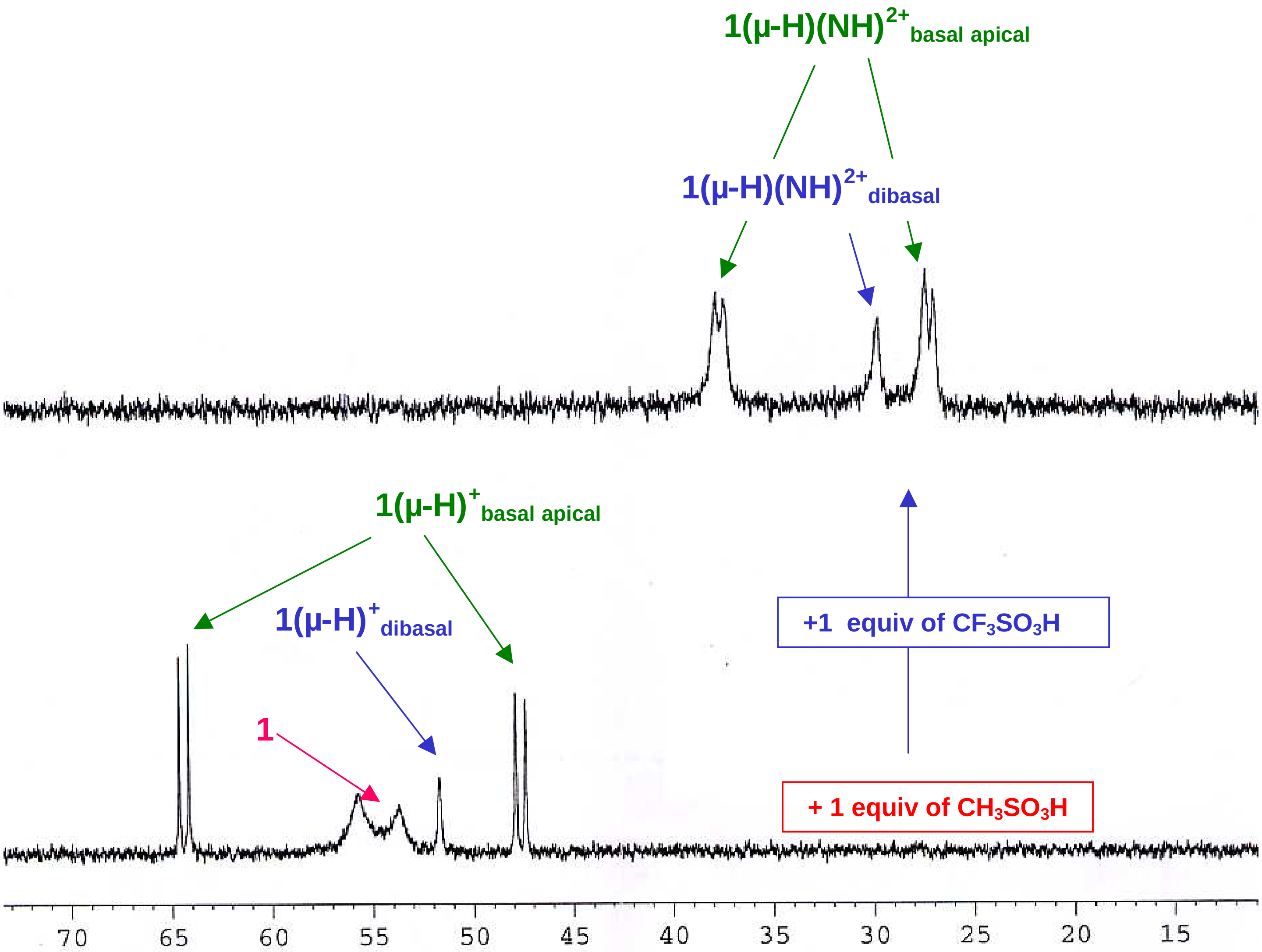
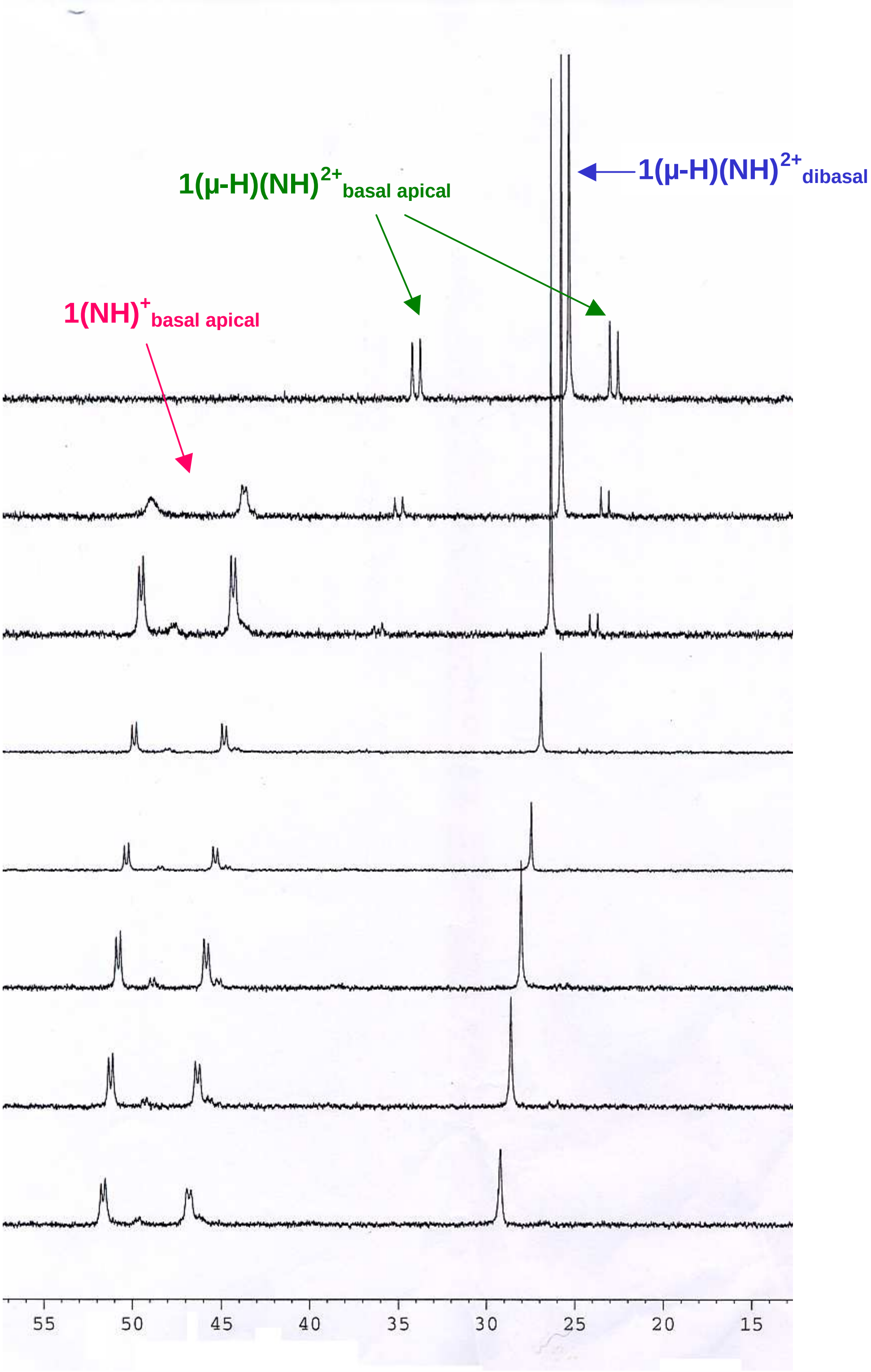


Fig e. Protonation of 1 at 203 K in the presence 4 equiv of CF_3SO_3H and VT experiment



Preliminary comparison of PNP and P_2N_2 complexes

As far as reduction of CH_3SO_3H is concerned, the efficiency of complex **1** is not much different from that of the analogue with a simple PNP-Ph ligand $[Fe_2(CO)_4(\kappa^2\text{-}PNP^{ph})(\mu\text{-pdt})]$. While the reduction of the acid occurs at a potential 0.1 V more negative when **1** is used rather than $[Fe_2(CO)_4(\kappa^2\text{-}PNP^{ph})(\mu\text{-pdt})$, the kinetics of the acid reduction appears slightly favoured in the case of **1**. The figure below shows that the ratio of the reduction peak measured in the presence of acid to the oxidation of the catalyst in acid free medium is slightly larger when the catalyst is complex **1**.

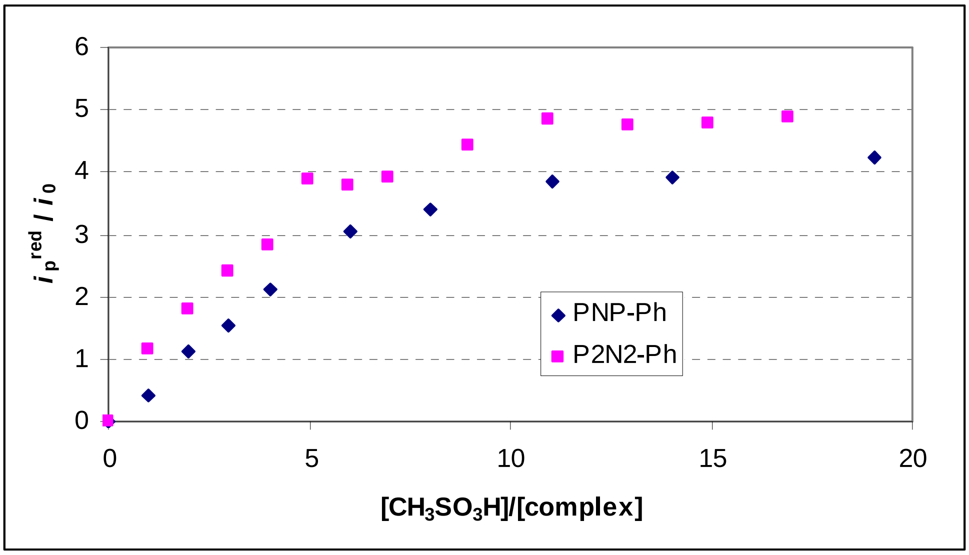


Fig g Dependence of the peak current ratio on the amounts of methane sulfonic acid added to a ca 1.8 mM solution of **1** (◆) or $[Fe_2(CO)_4(\kappa^2\text{-}PNP^{ph})(\mu\text{-pdt})]$ (■) in CH_2Cl_2-$[NBu_4][PF_6]$ (i_p^{red} and i_0 are respectively the reduction peak current in the presence of acid and the oxidation peak current of the catalyst before addition of acid measured by CV at a scan rate $v = 0.2$ V s^{-1}).

Synthesis of 1H$^+$: A solution of **1** (0.1g, 0.127 mmol) in dichloromethane (10 mL) was treated with 1 equiv of CF_3SO_3H. The mixture was stirred for 10 mn. and the solution was then evaporated to dryness. A red powder of **1H$^+$** was obtained (0.1g, 0.107 mmol, 84 % yield). Attempts to obtain single crystals were unsuccessful. IR and ^1H, $^{31}P\{^1H\}$ NMR data confirm that this powder was an authentic sample of the bridging hydride derivative observed in IR and NMR monitoring of protonation experiments. The IR spectrum of a solution of this powder showed the same bands ν(CO), at 2094(s), 2045(sh), 2035(s), 1978(s) cm^{-1}, than those observed during the monitoring of the protonation of **1** (see fig h). In addition, the ^1H NMR spectrum, in CD_2Cl_2 at 298 K, of this powder displayed characteristic high-field signals for $Fe_2(\mu\text{-}H)$ species with basal-apical or dibasal diphosphine : a doublet at –13.5 ppm (J_{PH} = 17.5 Hz) and a triplet at –13.6 ppm (J_{PH} = 20.0Hz). A $^{31}P\{^1H\}$ NMR recording confirmed the presence a singlet at 51.8 ppm and two doublets of equal intensities at 64.5 ppm (d, J_{PP} = 97 Hz) and 47.8 ppm (d, J_{PP} = 97 Hz).

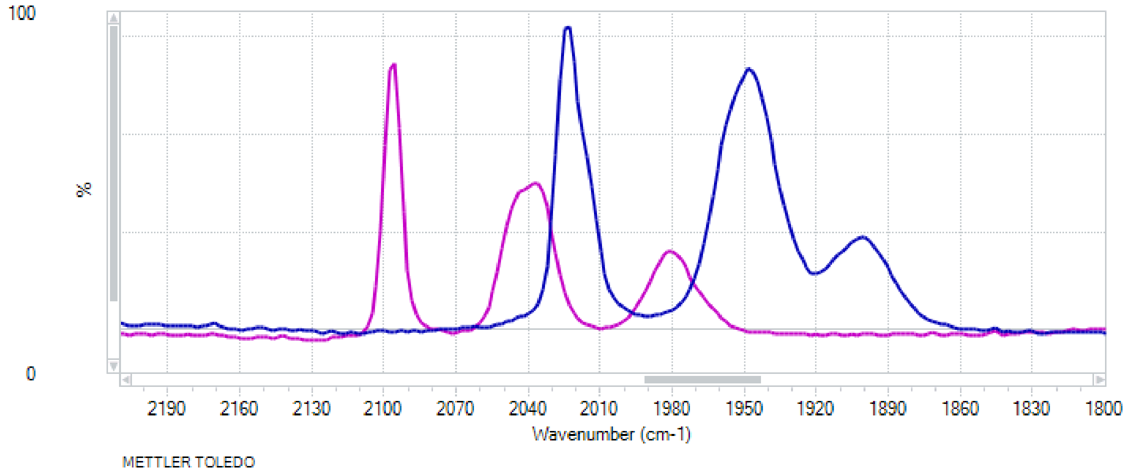


Fig h. IR in carbonyl region of a CH_2Cl_2 solution of **2** (in blue) and after addition of 1 equiv of CF_3SO_3H (purple)