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Electronic Supplementary Information for

Variations in the Fuel Structure Control the Rate of the Back and Forth Motions of a Chemically Fuelled Molecular Switch

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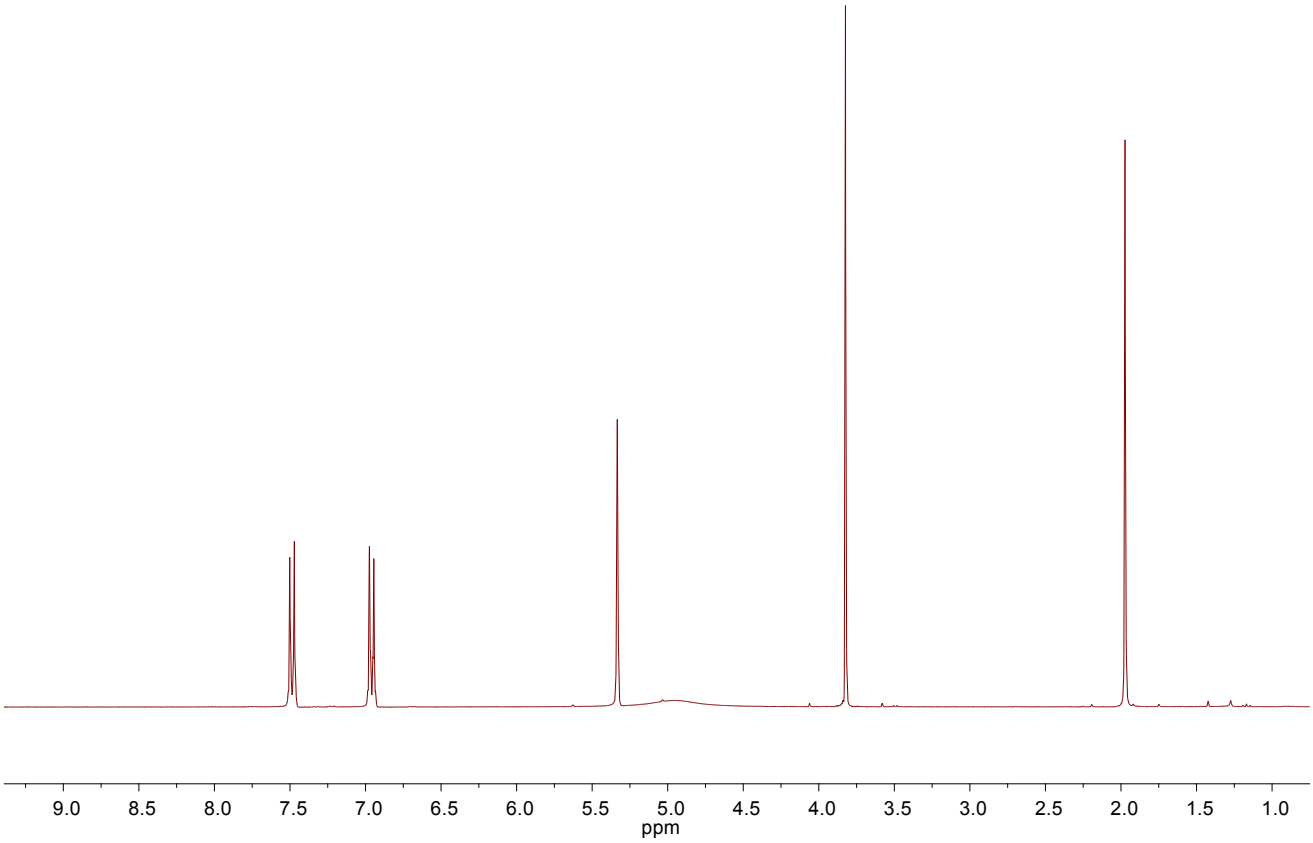
Contents

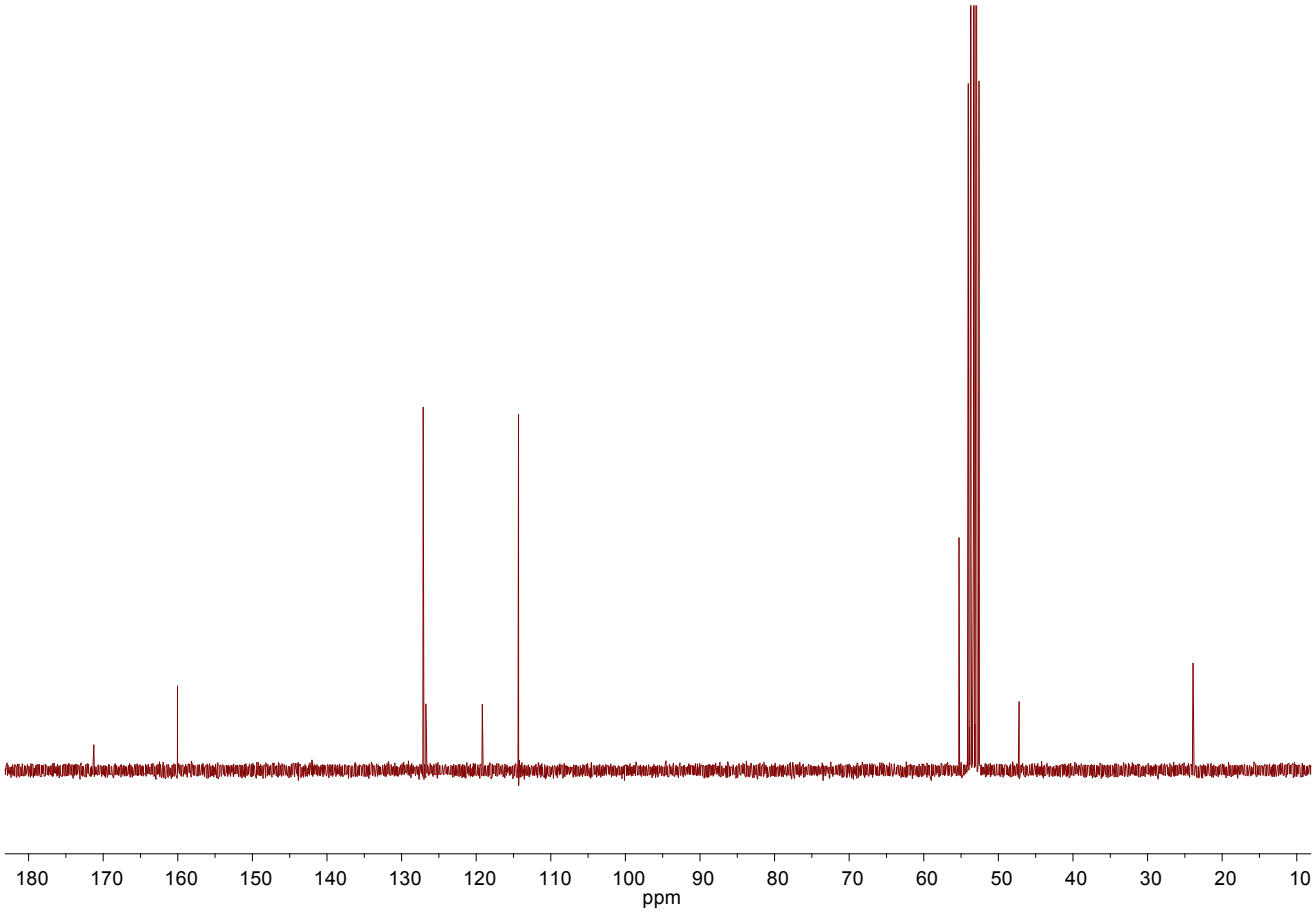
^{1}H NMR spectrum acid **2**, X = OCH_3



^{1}H NMR (300 MHz, CD_2Cl_2)

δ: 7.51-7.46 (m, 2H), 6.99-6.93 (m, 2H), 4.95 (br. s, 1H), 3.82 (s, 3H), 1.97 (s, 3H).

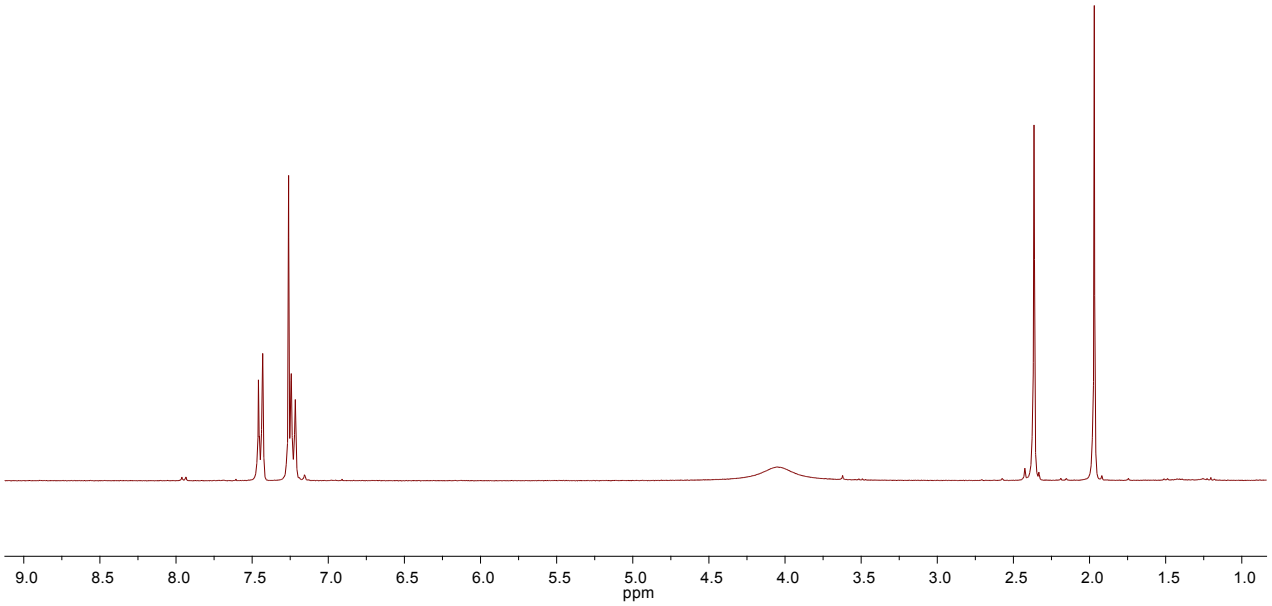
^{13}C NMR spectrum of acid **2**, X = OCH_3



^{13}C NMR (75 MHz, CD_2Cl_2)

δ: 171.3, 160.0, 127.1, 126.7, 119.2, 114.3, 55.3, 47.1, 23.8.

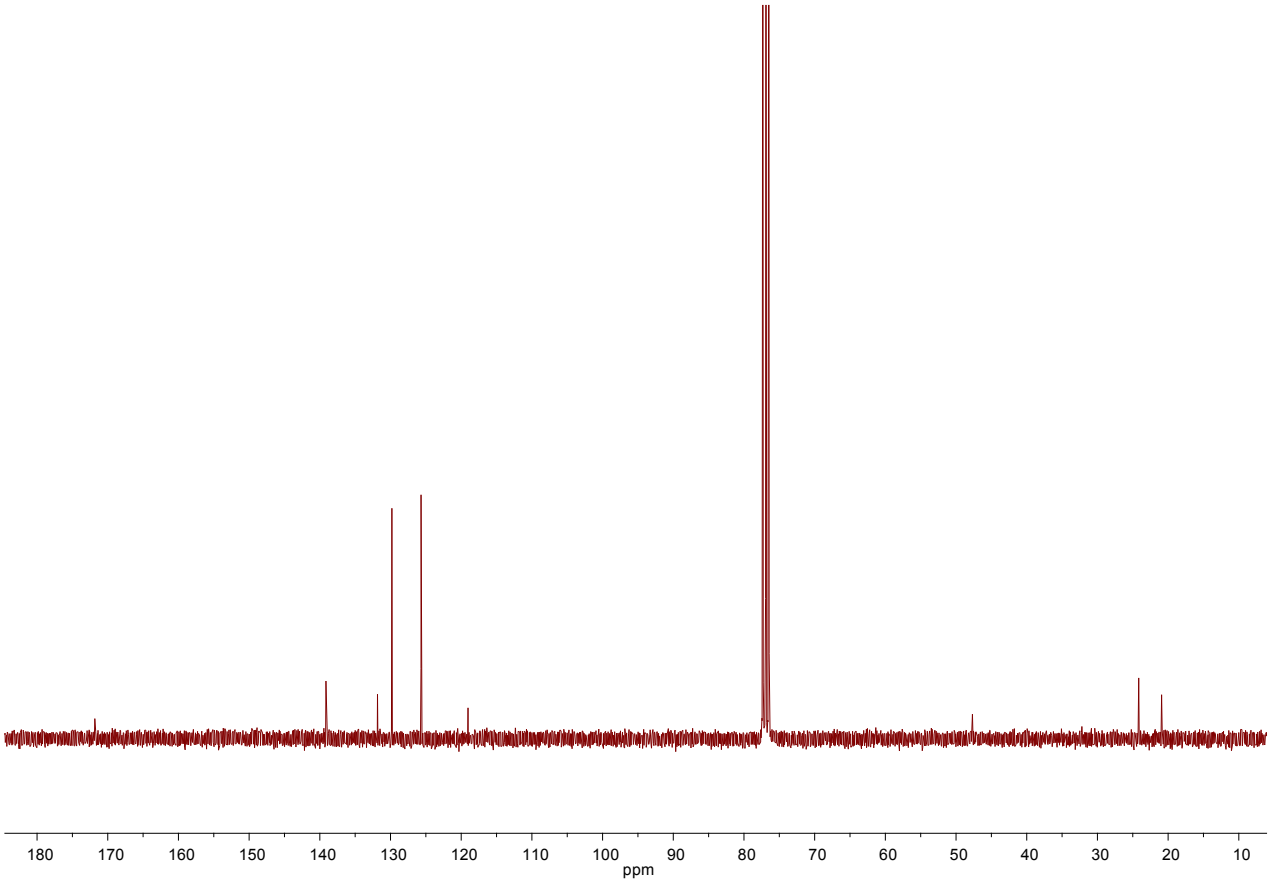
^{1}H NMR spectrum acid **2**, X = CH_3



^{1}H NMR (300 MHz, $CDCl_3$)

δ: 7.46-7.43 (m, 2H), 7.24-7.22 (m, 2H), 4.05 (br. s, 1H), 2.36 (s, 3H), 1.97 (s, 3H).

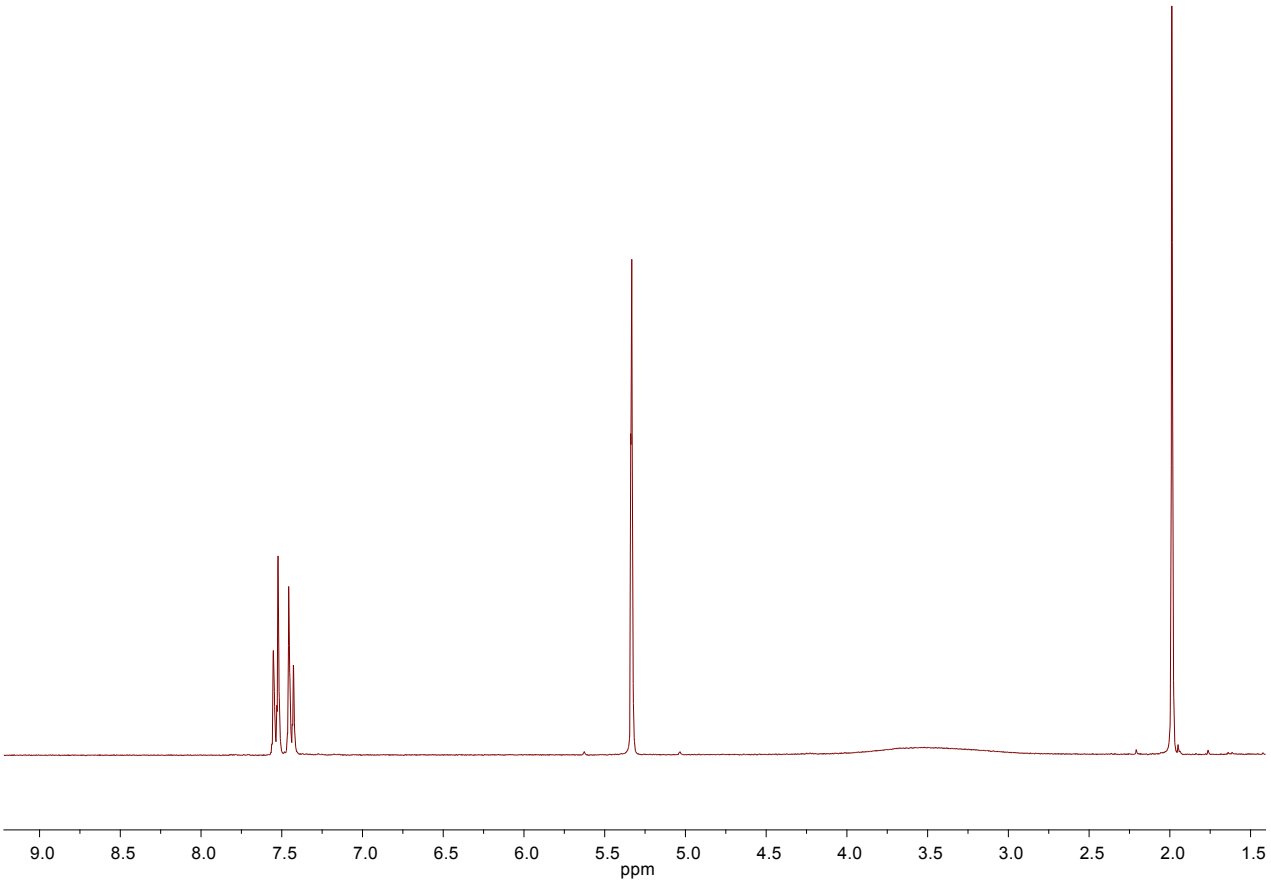
^{13}C NMR spectrum of acid **2**, X = CH_3



^{13}C NMR (75 MHz, $CDCl_3$)

δ: 171.2, 139.1, 131.8, 129.8, 125.7, 119.0, 47.7, 24.2, 20.9.

^{1}H NMR spectrum acid **2**, X = Cl



^{1}H NMR (300 MHz, CD_2Cl_2)

δ: 7.55–7.52 (m, 2H), 7.46-7.43 (m, 2H), 3.52 (br s, 1H), 1.99 (s, 3H).

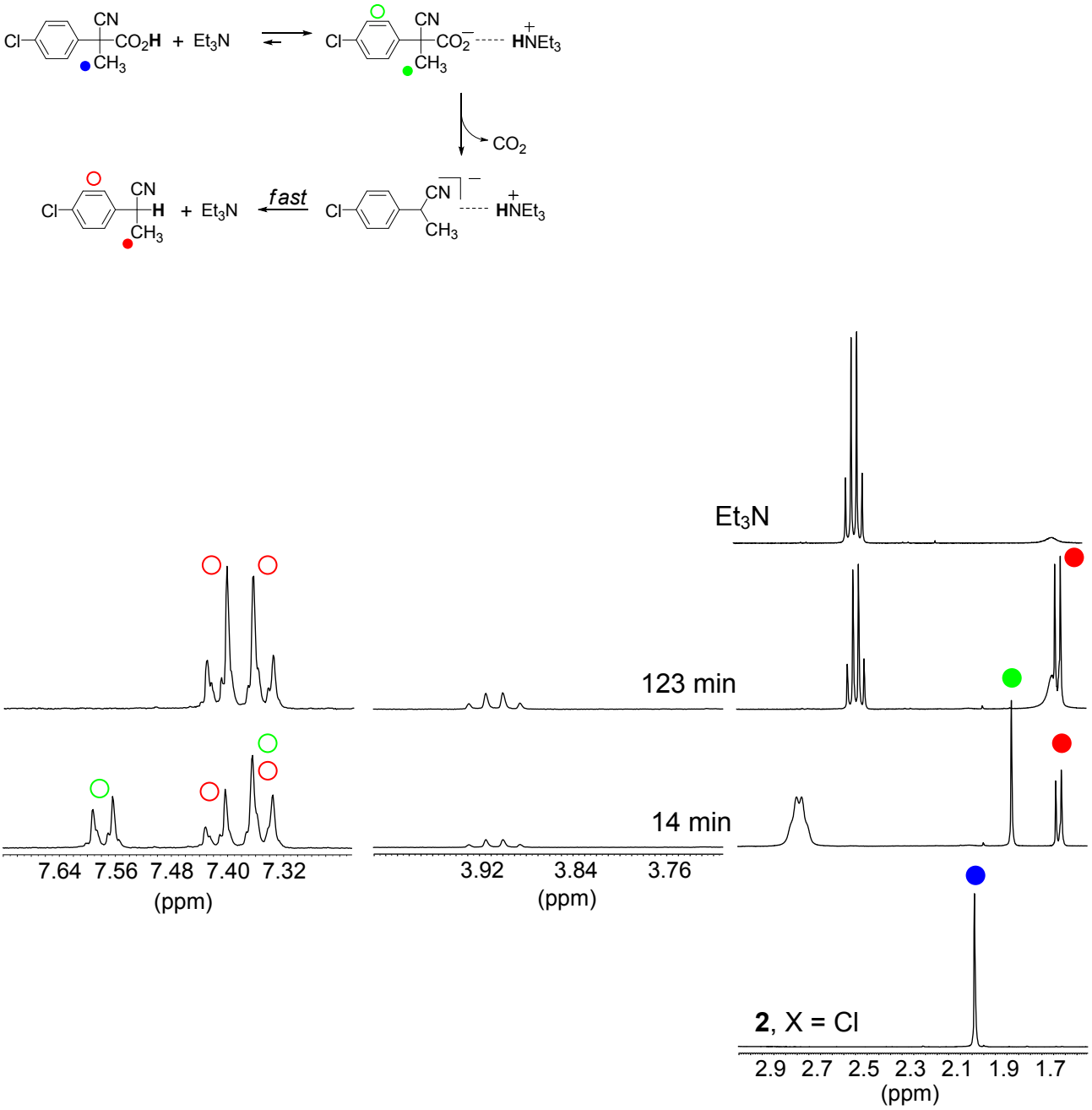


Fig. S1. Decarboxylation of 10 mM **2**, X = Cl promoted by 10 mM Et_3N in CD_2Cl_2 at 25 °C. Portion of ^1H NMR spectra recorded at t ≈ $t_{½}$ (14 min) and t = ∞ (123 min). Portions of the spectra of the pure reactants are shown for comparison. The broad signal is due to adventitious H_2O.

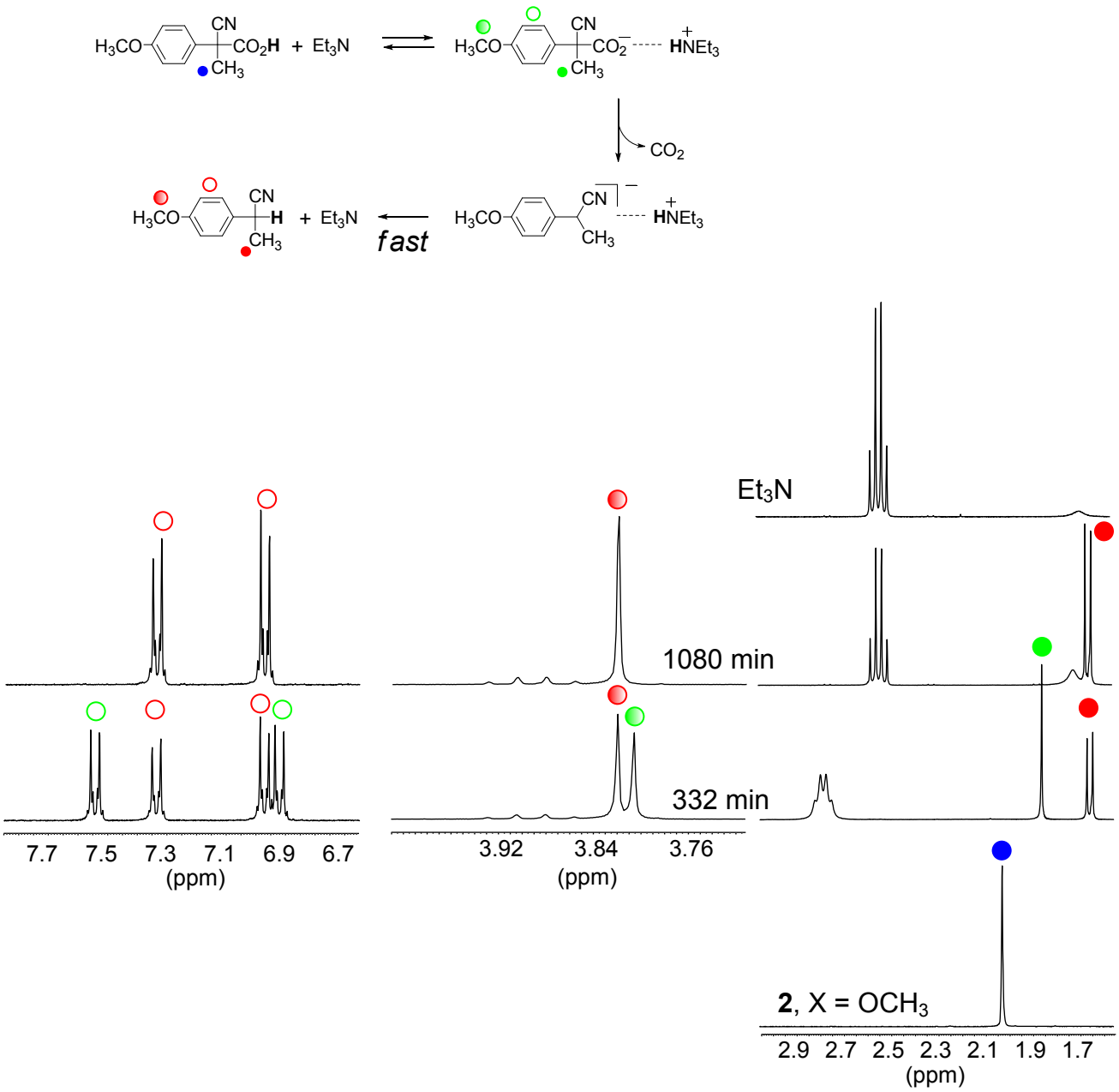


Fig. S2. Decarboxylation of 10 mM **2**, X = OCH_3 promoted by 10 mM Et_3N in CD_2Cl_2 at 25 °C. Portion of ^1H NMR spectra recorded at t ≈ $t_{½}$ (332 min) and t = ∞ (1080 min). Portions of the spectra of the pure reactants are shown for comparison. The broad signal is due to adventitious H_2O.

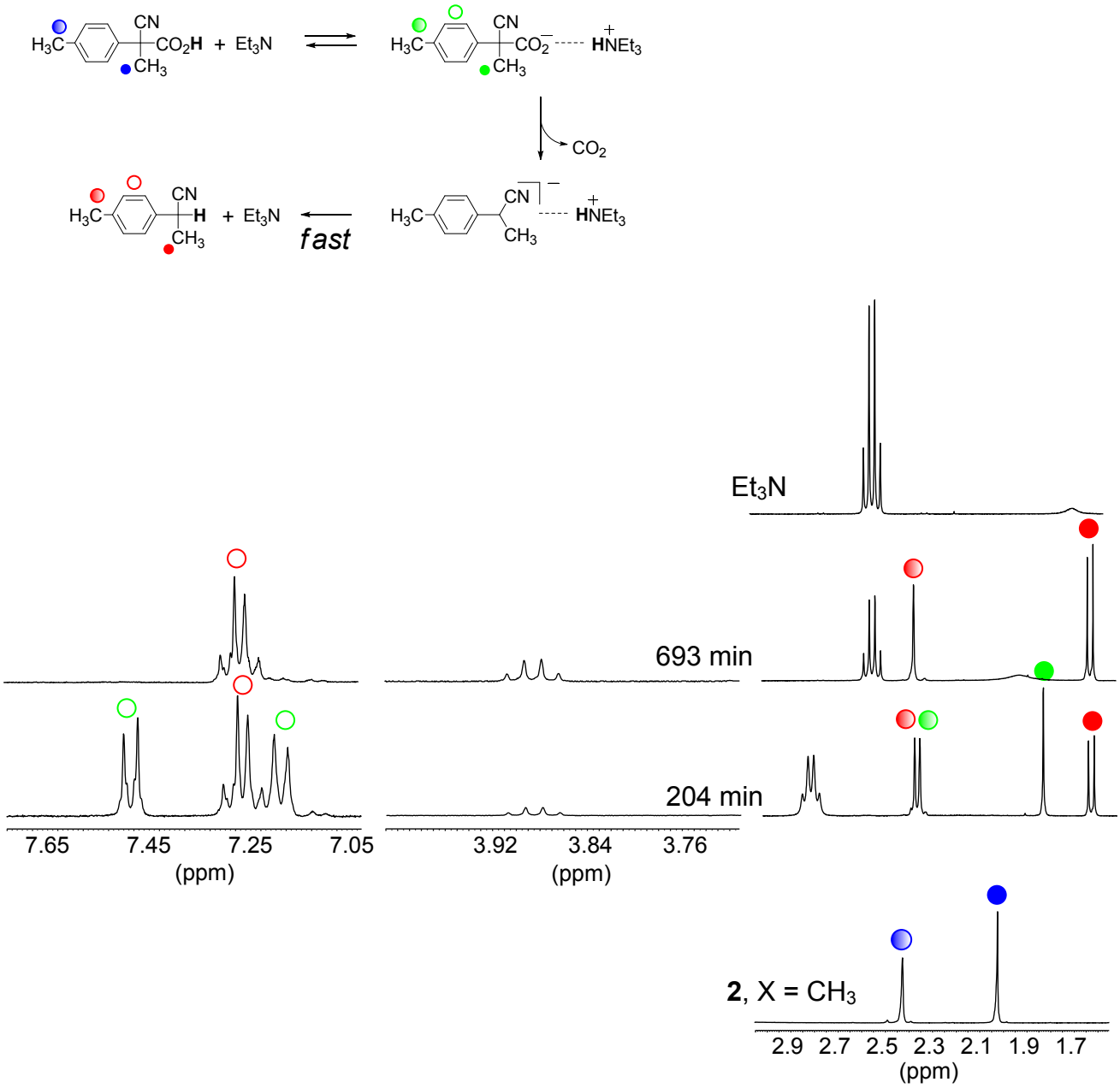
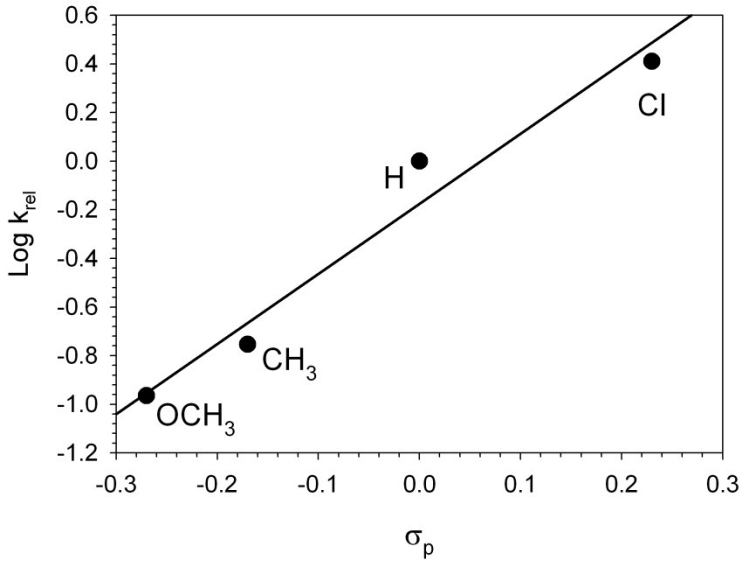


Fig. S3. Decarboxylation of 10 mM **2**, X = CH_3 promoted by 10 mM Et_3N in CD_2Cl_2 at 25 °C. Portion of ^1H NMR spectra recorded at $t \approx t_{½}$ (204 min) and $t = \infty$ (693 min). Portions of the spectra of the pure reactants are shown for comparison. The broad signal is due to adventitious H_2O.



$$\rho = 2.9$$

$$r = 0.9816$$

Fig. S4. Hammett plot related to reactions between 10 mM **2**, X = OCH_3, CH_3 , H, and Cl with 10 mM Et_3N in CD_2Cl_2 at 25 °C.

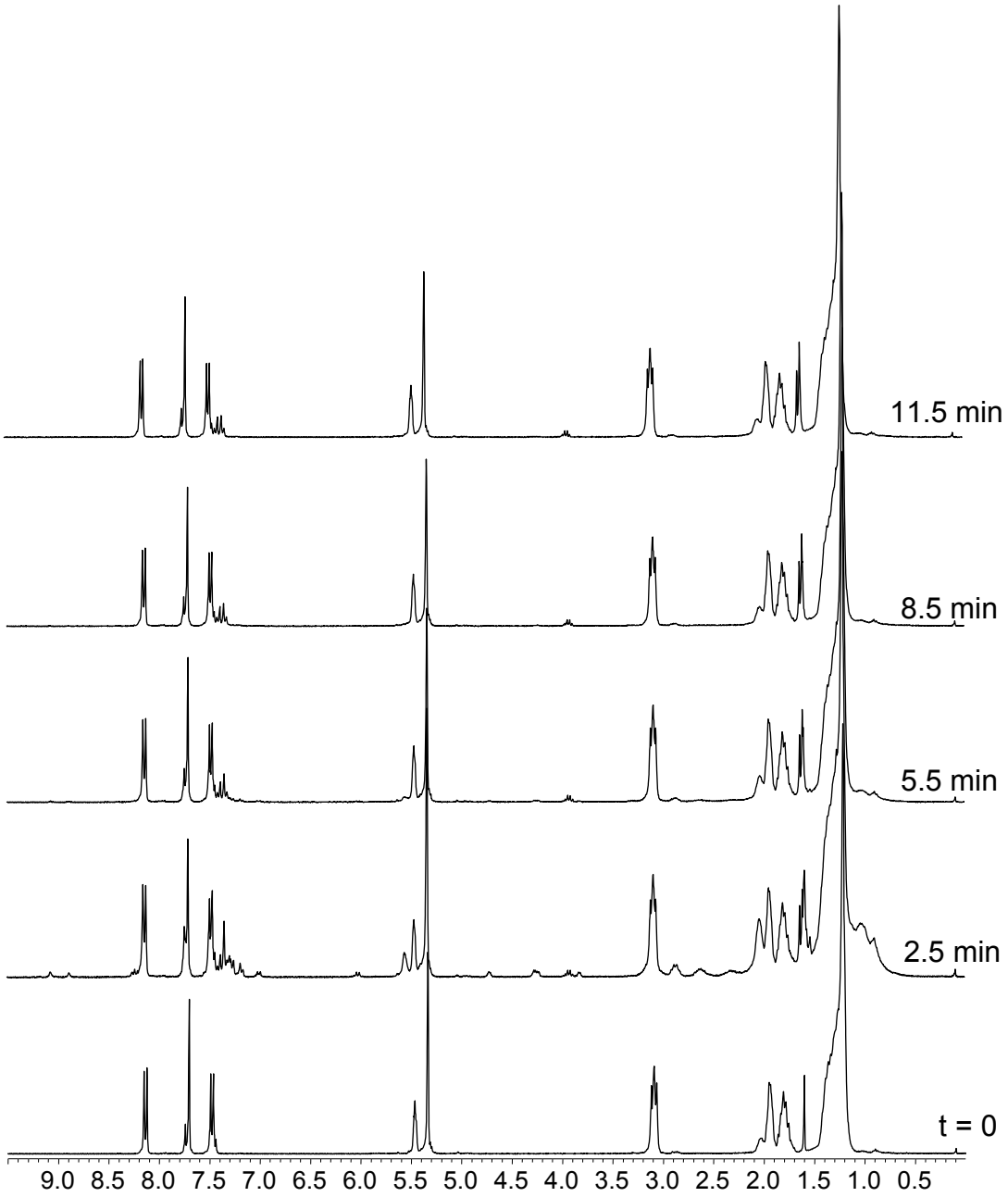


Fig. S5. ^{1}H NMR monitoring of the reaction between 5 mM **1** and 5 mM **2**, X = Cl in CD_2Cl_2 at 25 °C.

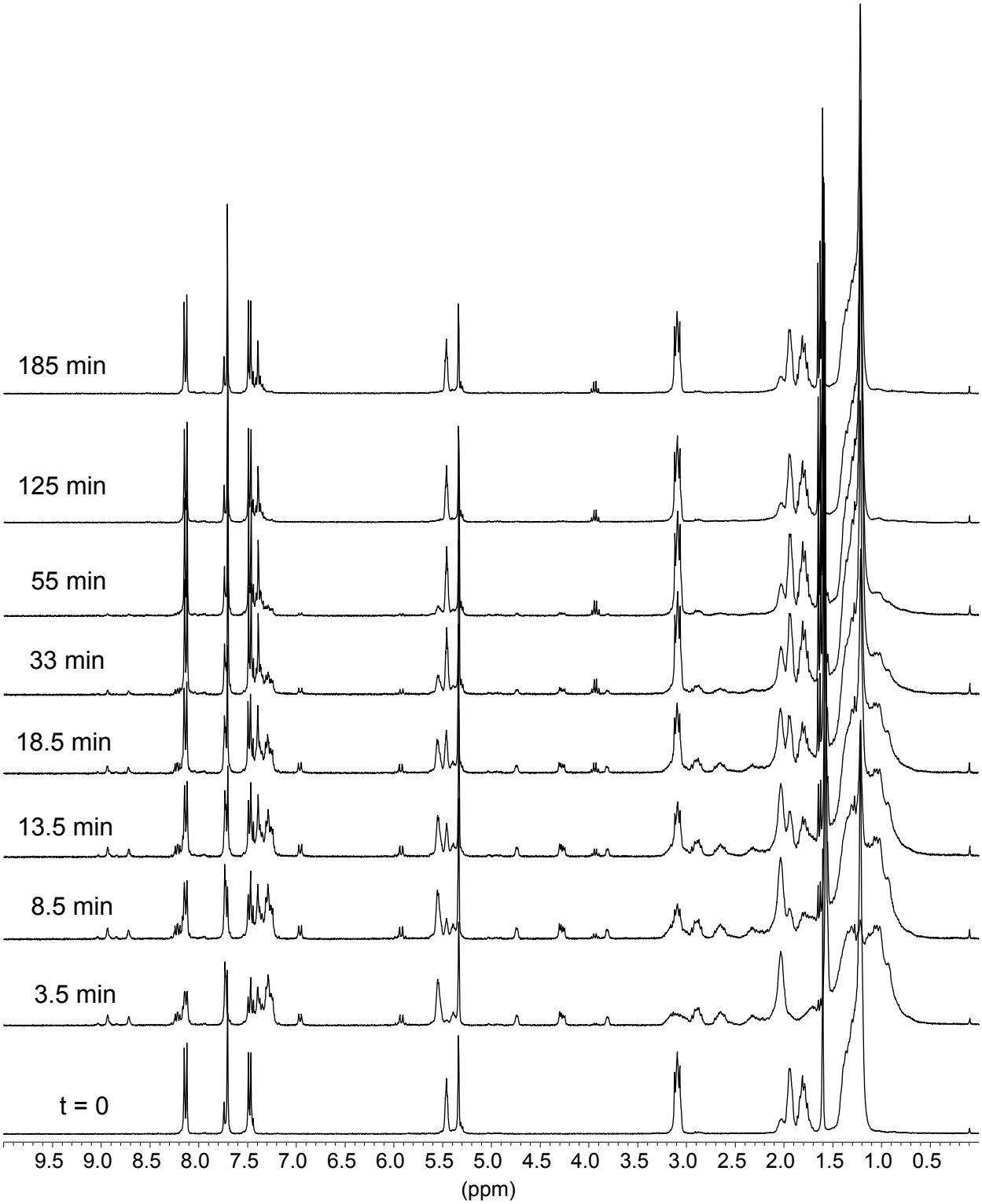


Fig. S6. ^{1}H NMR monitoring of the reaction between 5 mM **1** and 5 mM **2**, X = H in CD_2Cl_2 at 25 °C.

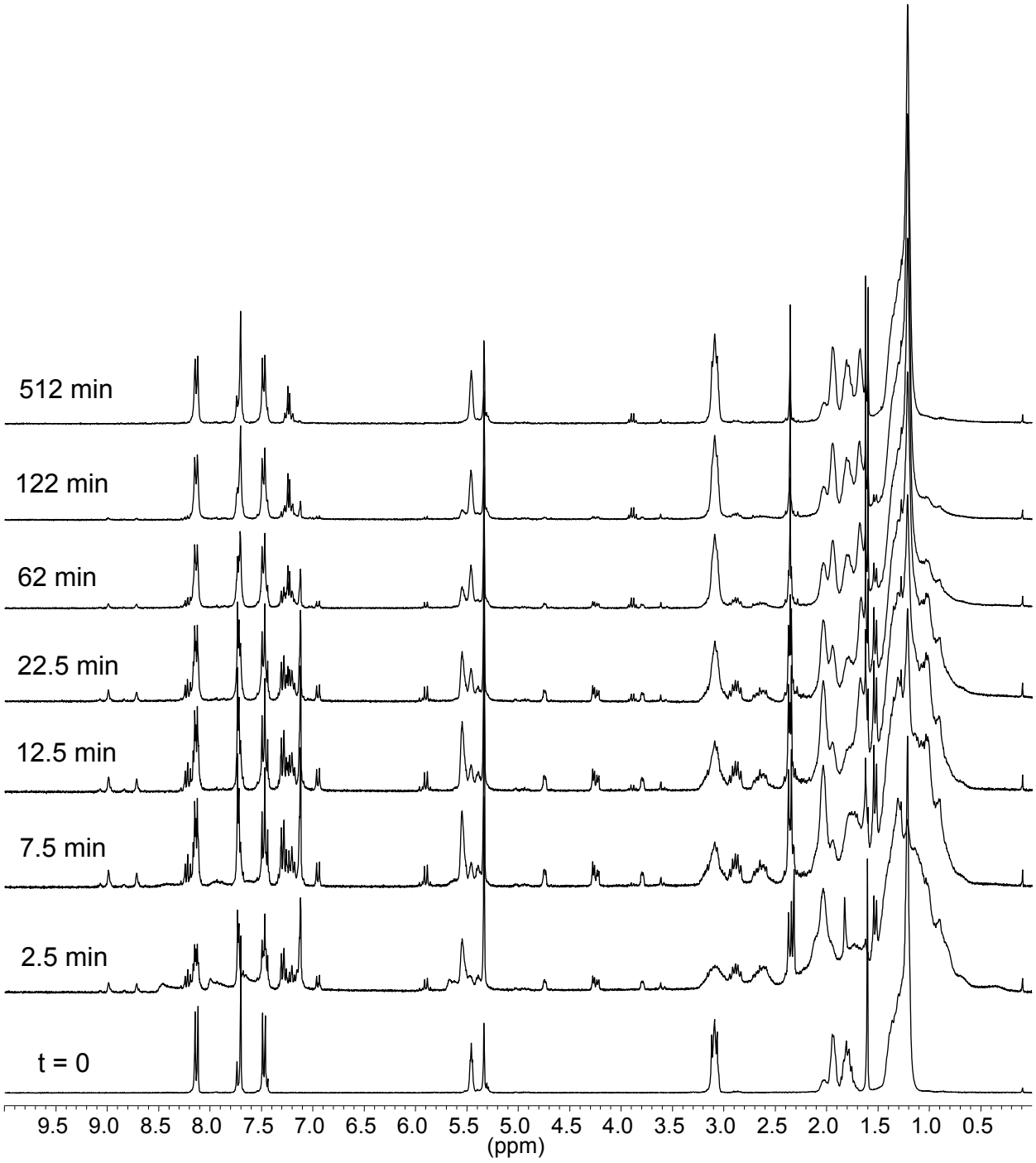


Fig. S7. ^{1}H NMR monitoring of the reaction between 5 mM **1** and 5 mM **2**, X = CH_3 in CD_2Cl_2 at 25 °C.

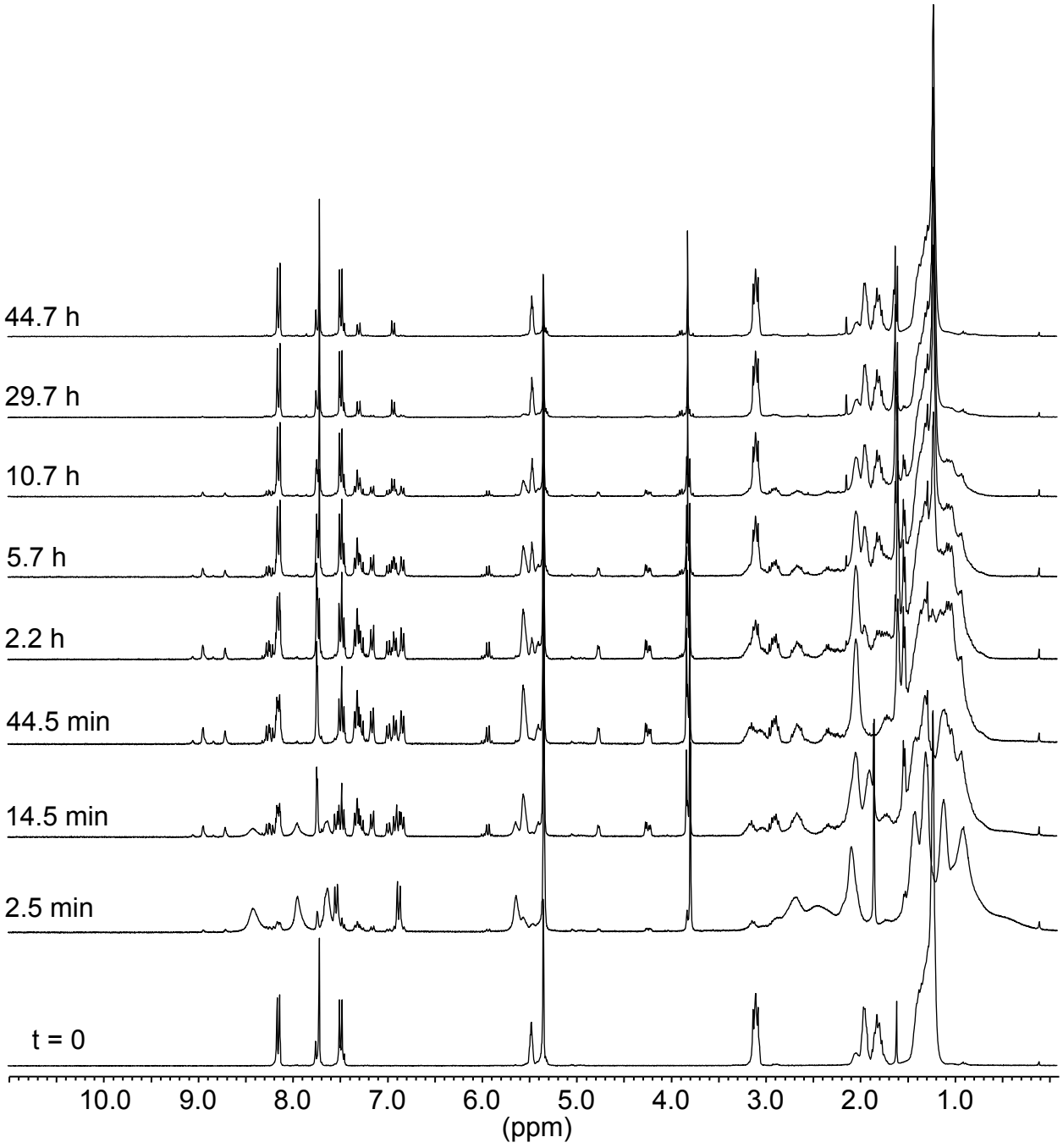


Fig. S8. ^{1}H NMR monitoring of the reaction between 5 mM **1** and 5 mM **2**, X = OCH_3 in CD_2Cl_2 at 25 °C.

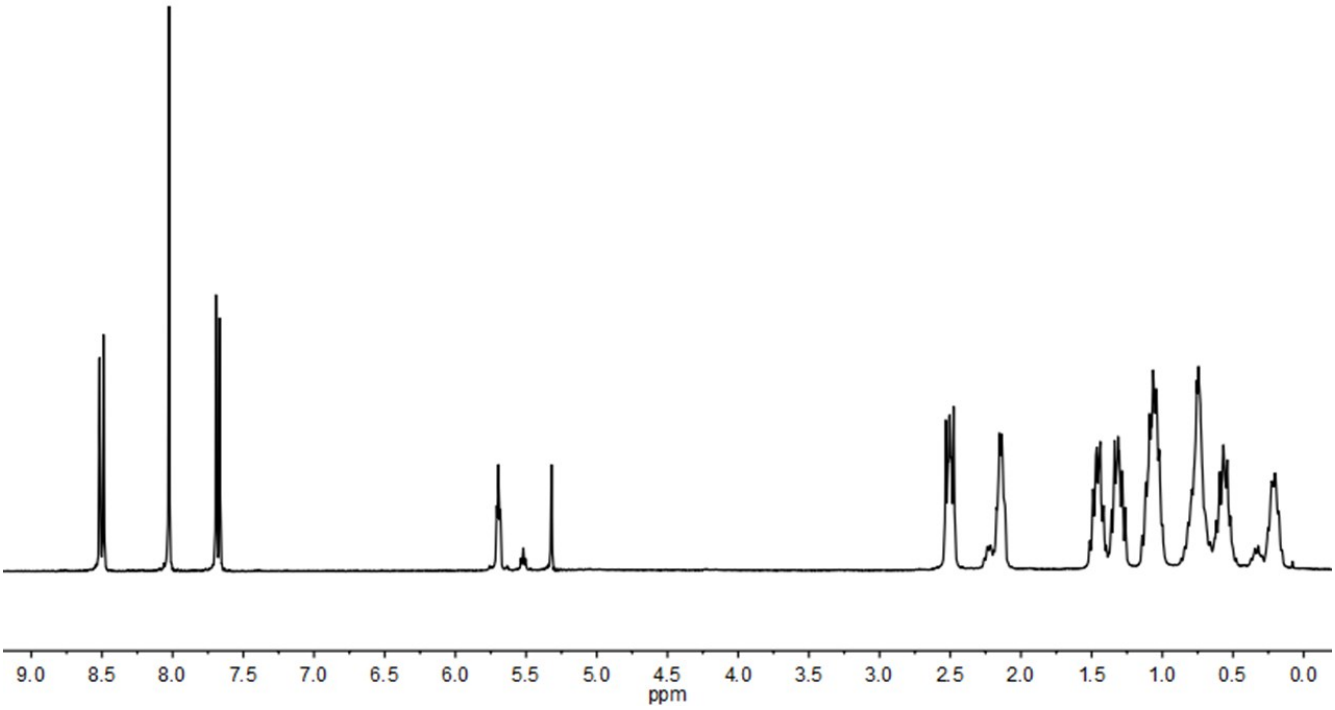


Fig. S9. ^{1}H NMR spectrum of **1**H^{+} $CF_3CO_2^-$ in CD_2Cl_2 at 25 °C (data from ref 6). Peak at 5.30 is due to $CHDCl_2$.

Consecutive first-order reactions

$$A \xrightarrow{k'} B$$

$$B \xrightarrow{k''} C$$

The integrated rate eqn (S1)[S1] reduces to the simple form of eqn (S2) when $k' >> k''$.

$$[B] = \frac{[A]_o k'}{k'' - k'}\left(e^{-k't} - e^{-k''t}\right) \quad \text{(S1)}$$

$$[B] = [A]_o\left(e^{-k''t} - e^{-k't}\right) \quad \text{(S2)}$$

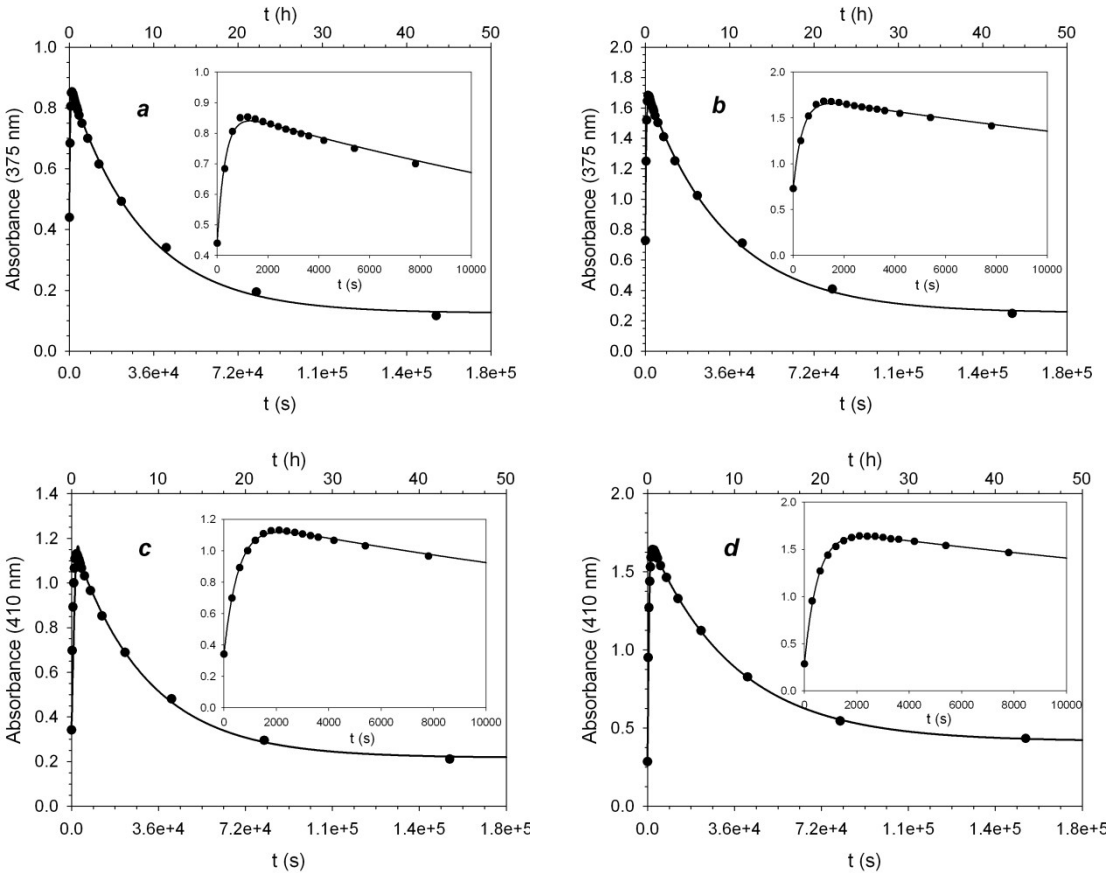
Eqn (S3) is an adaptation of eqn (S2) to the growth and subsequent decay of absorbance A in the course of the reactions of **1** with acids **2**.

$$A = A_{max}\left(e^{-k''t} - e^{-k't}\right) + A_o e^{-k't} + A_\infty\left(1 - e^{-k''t}\right) \quad \text{(S3)}$$

A_o and A_∞ are the absorbance values at t = 0 and t = ∞, respectively, and A_{max} is the maximum value in the absorbance-time profile.

[S1] E. A. Frost and R. G. Pearson, Kinetics and Mechanism, 2nd Edition, John Wiley & Sons, New York 1961.

Effect of reactant concentration on the reaction of **2**, X = OCH_3 with equimolar **1** in CH_2Cl_2 at 25 °C



run	conc (mM)	10^3 k' (s^{-1})	10^5 k" (s^{-1})
a	0.30	3.2	3.2
b	0.60	2.8	3.0
c	1.00	1.9	3.3
d	1.50	2.0	2.8
	Average	2.5±0.5	3.1±0.2

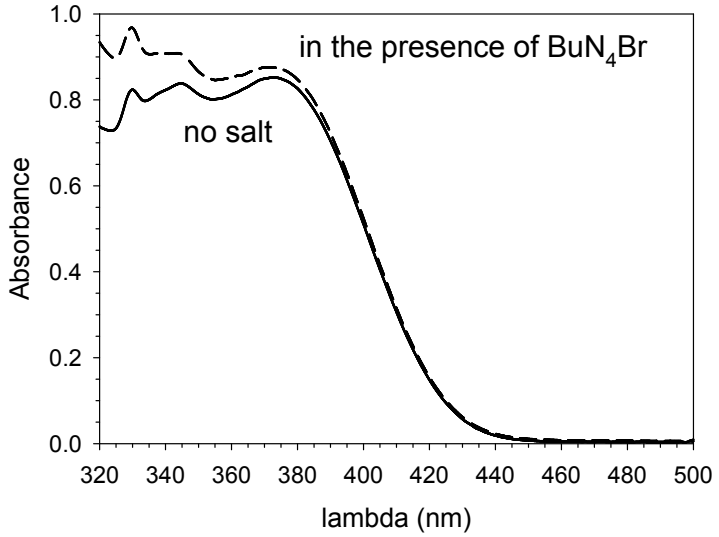
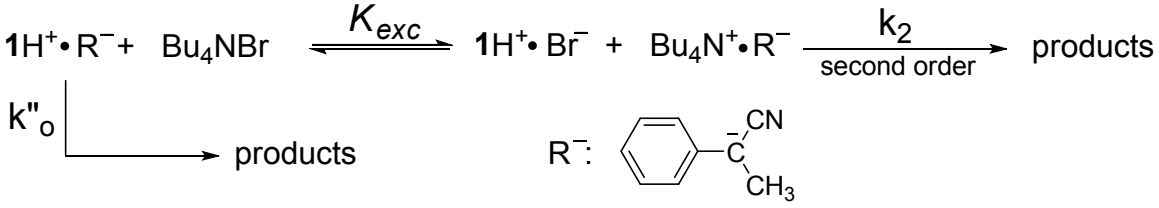


Fig. S10. Reaction between equimolar 0.30 mM **1** and **2**, X = H. Spectrum of the solution at the highest concentration of the intermediate in the absence and in the presence of 5 mM Bu_4NBr

Alternative mechanisms for reaction of 0.30 mM **2**, X = H with equimolar **1** in CH_2Cl_2 at 25 °C in the presence of increasing amounts of Bu_4NBr.

The red curve in Fig. S11 is the plot reported in the main text (Fig. 5) and is related to the association mechanism in Scheme 2

The black curve in Fig. S11 is a plot obtained from the fit of the experimental data points with the system of equations reported below, taking into account the mechanism depicted in Scheme S1. In this case, after a metathetic exchange of counterions (a sort of special salt effect), $\mathbf{1}H^+Br^-$ and $Bu_4N^+R^-$ react in a bimolecular fashion to give the products.



Scheme S1

f=k”$_o$*(((C-z)/C)+k_2*((z^2)/C)
z=(-b-(sqrt((b^2)-4*c*a)))/(2*a)
b=-K_{exc}*(C + x)
a= K_{exc} - 1
c= K_{exc}*C*x
k”$_o$ =2.5e-4 s^{-1}
fit f to y

best fit values
K_{exc} =0.99 ± 0.50
k_2=16.6 ± 2.1 M^{-1} s^{-1}
r = 0.97

The system of equations reported on the left is the one used to obtain the best fit values of K_{exc} and k_2 of Scheme S1 through the calculation software Sigma Plot 10.0.
C is the concentration of reagents **1** and **2**, X = H (3×10^{-4} M);
x is the initial concentration of $Bu_4N^+Br^-$ (ranging from 0 to 5×10^{-3} M);
z is the fraction of intermediate $\mathbf{1}H^+$ R^- exchanged with $Bu_4N^+Br^-$.

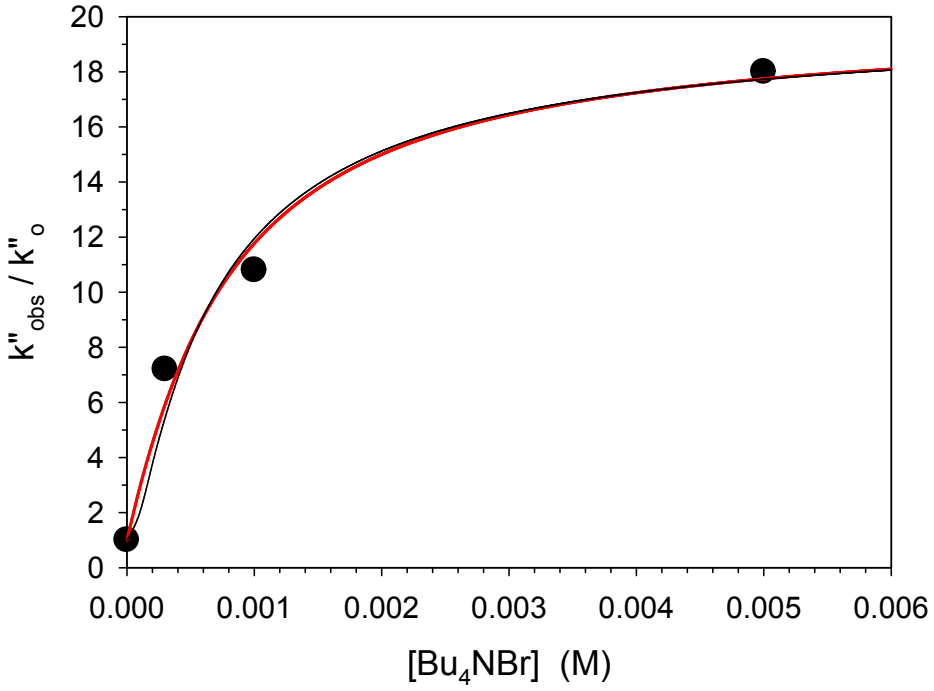


Fig. S11. Alternative fits of the data obtained for reaction of **2**, X = H with equimolar **1** in CH_2Cl_2 at 25 °C in the presence of increasing amounts of Bu_4NBr (in the case of the black fit, $k''_{obs} = k_2 \times z$).