

## Supplementary information

### Rapid degradation of cyclic peroxides by titanium and antimony chlorides

Mark S. Bali<sup>a</sup>, David Armitt<sup>b</sup>, Lynne Wallace<sup>a</sup>, Anthony I. Day<sup>\*a</sup>.

<sup>a</sup> School of Physical, Mathematical and Environmental Sciences, University of New South Wales at the Australian Defence Force Academy, Northcott Drive, Campbell ACT 2612, AUSTRALIA.

<sup>b</sup> Weapons & Combat Systems Division, Defence Science and Technology Organisation, Edinburgh, Adelaide SA 5111 AUSTRALIA.

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**Fig. S1.**  $^1\text{H}$  NMR of TPTP 1:3  $\text{TiCl}_4$  Immediate reaction

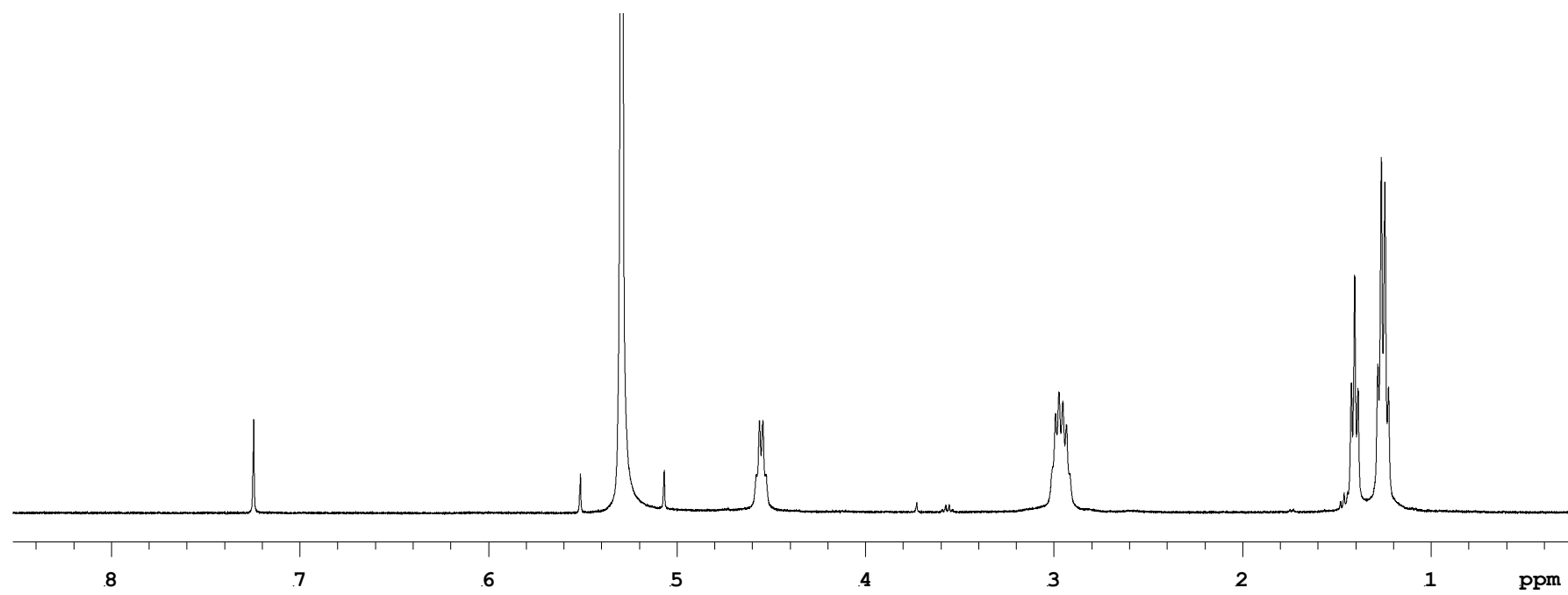


Fig. S2. ethyl propanoate (EP) 3:1 TiCl<sub>4</sub> – Variable Temp experiment

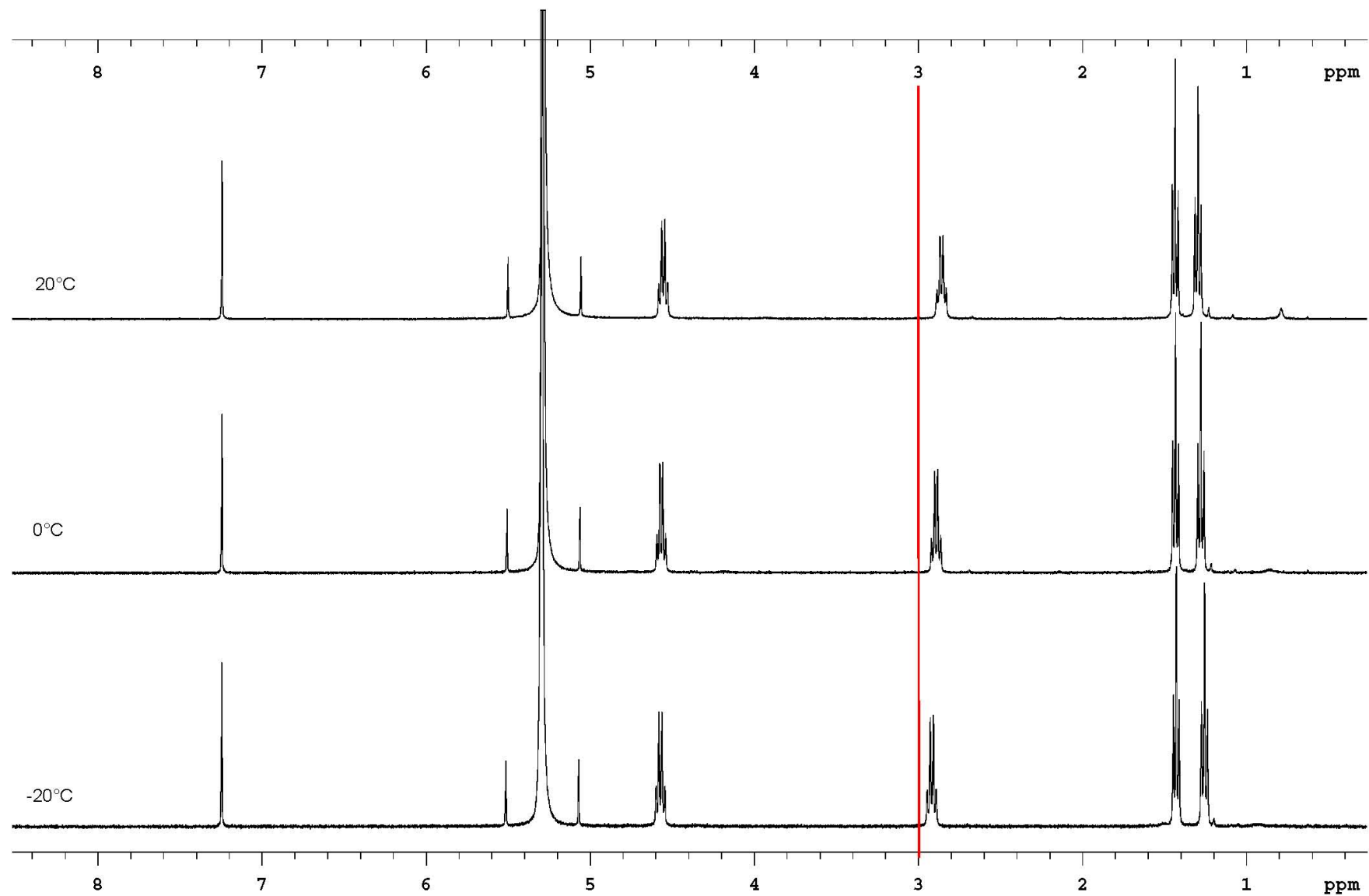


Fig. S3. 3-pentanone (3P) 3:1 TiCl<sub>4</sub>– Variable Temp experiment

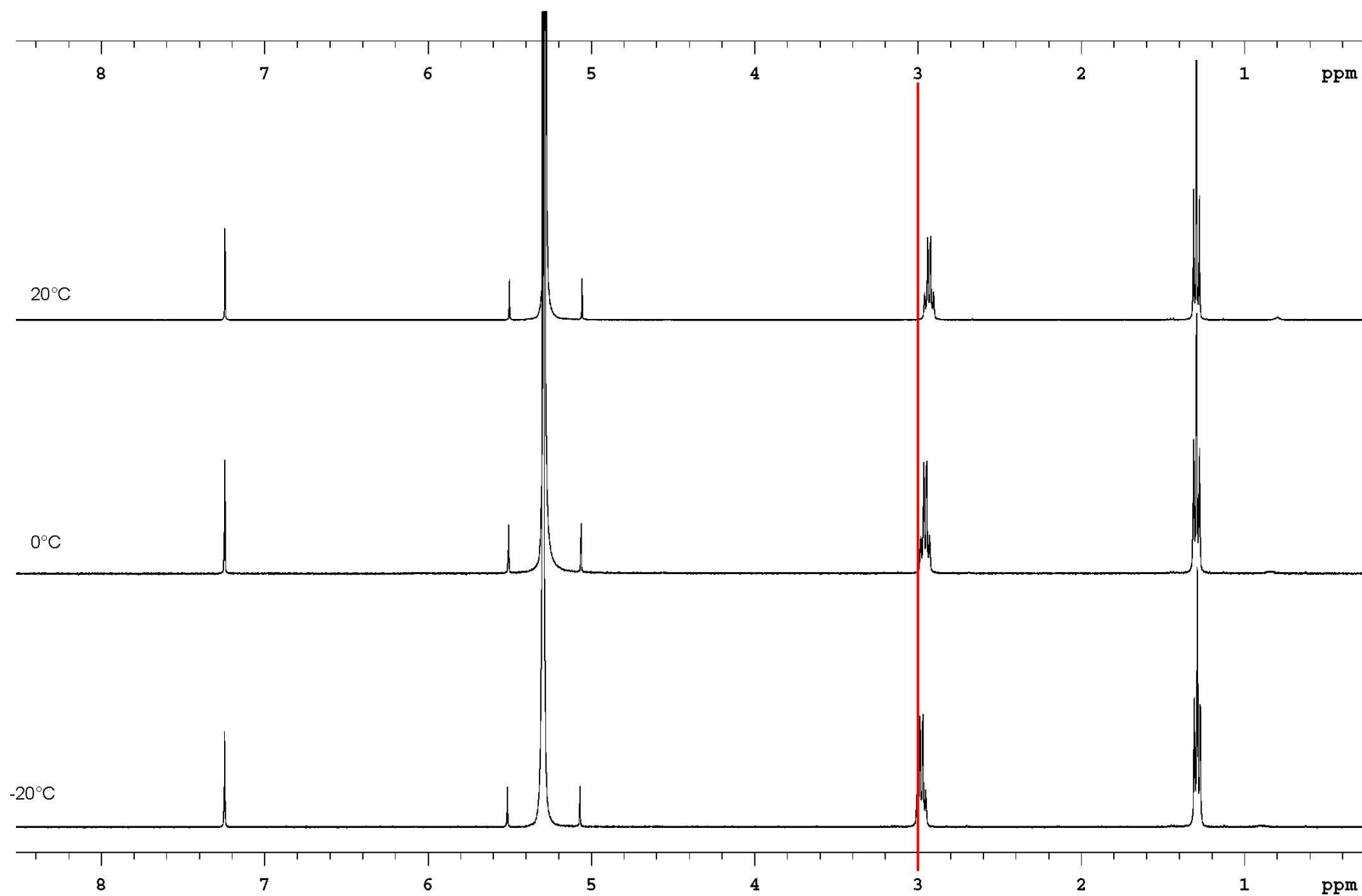


Fig. S4. TPTP 1:2 TiCl<sub>4</sub> – Variable Temp experiment

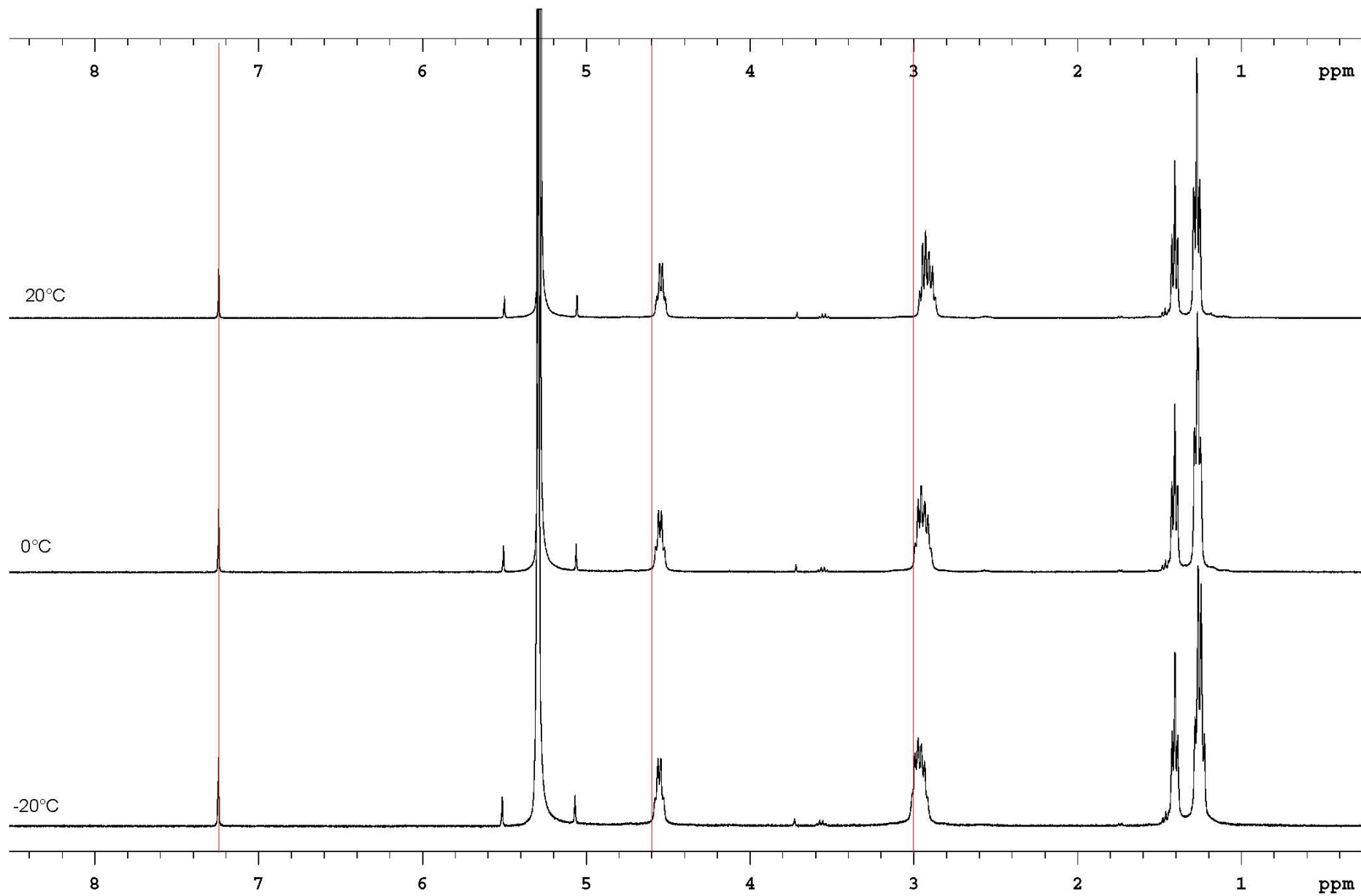


Fig. S5. TPTP 1:2 TiCl<sub>4</sub> (sealed 5 mm NMR tube sample over days) showing only trace chlorination product formation

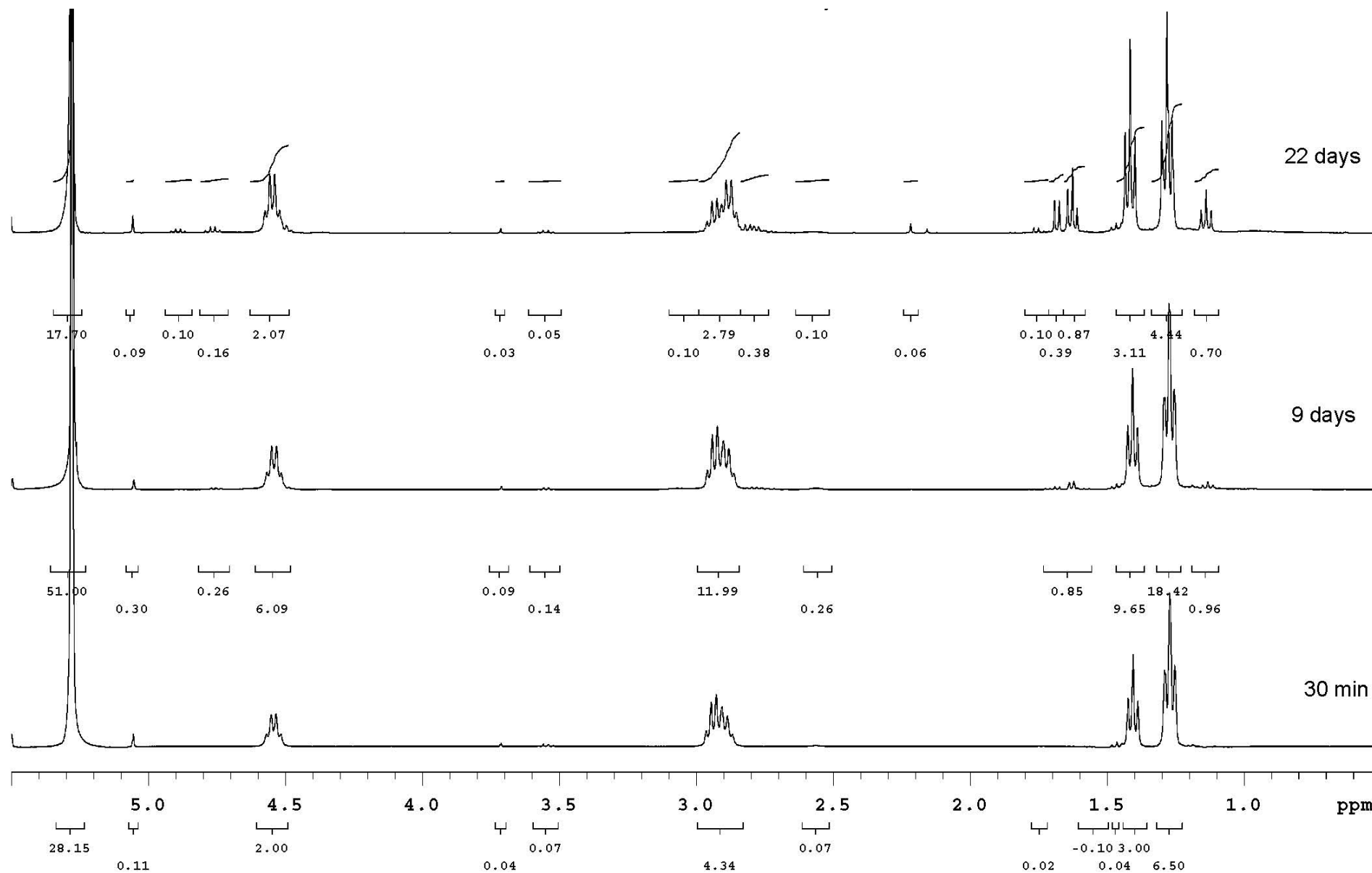


Fig. S6. TPTP 1:0.5 TiCl<sub>4</sub> (sealed 10 mm NMR tube sample for collection of precipitate)

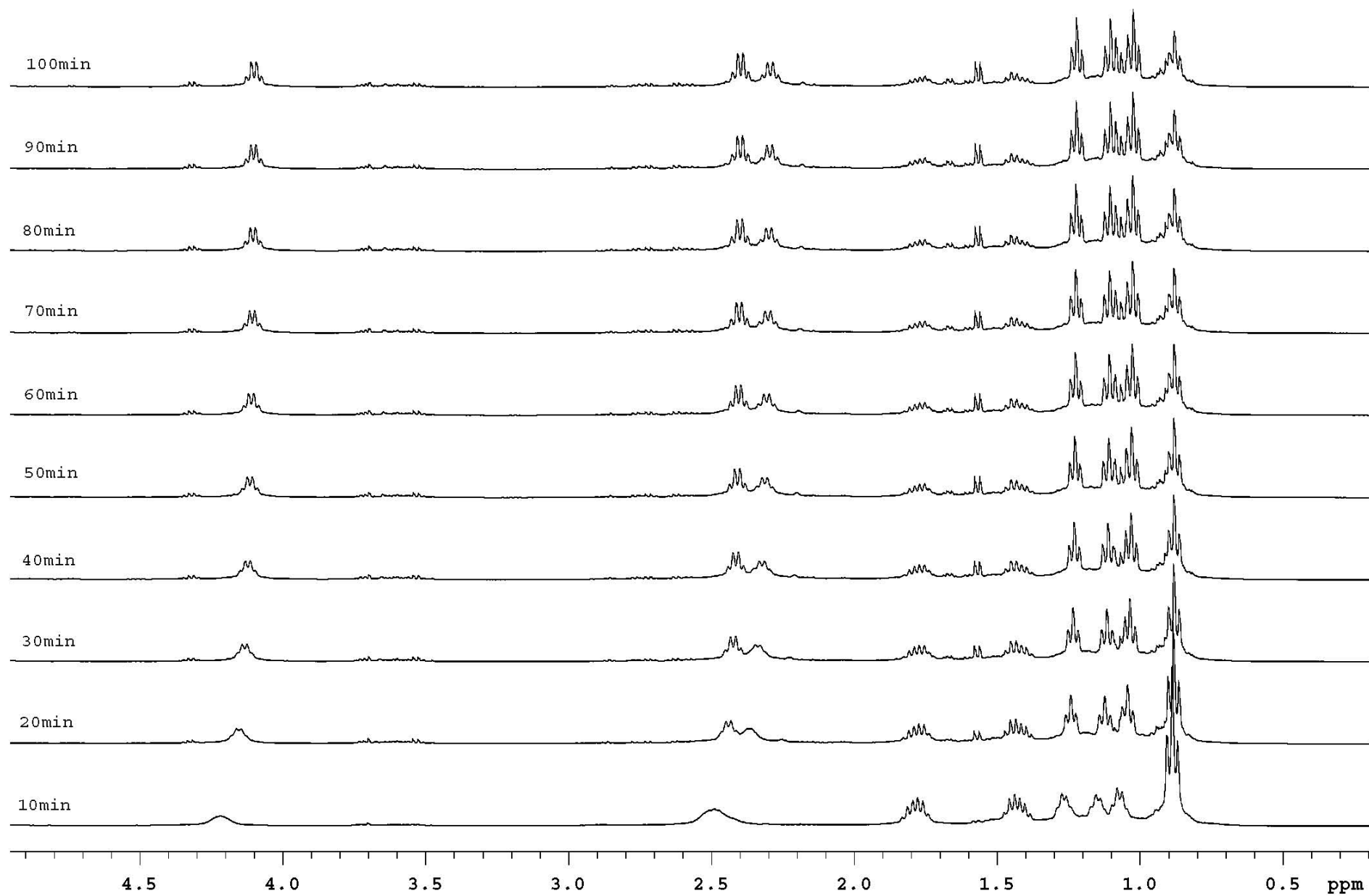
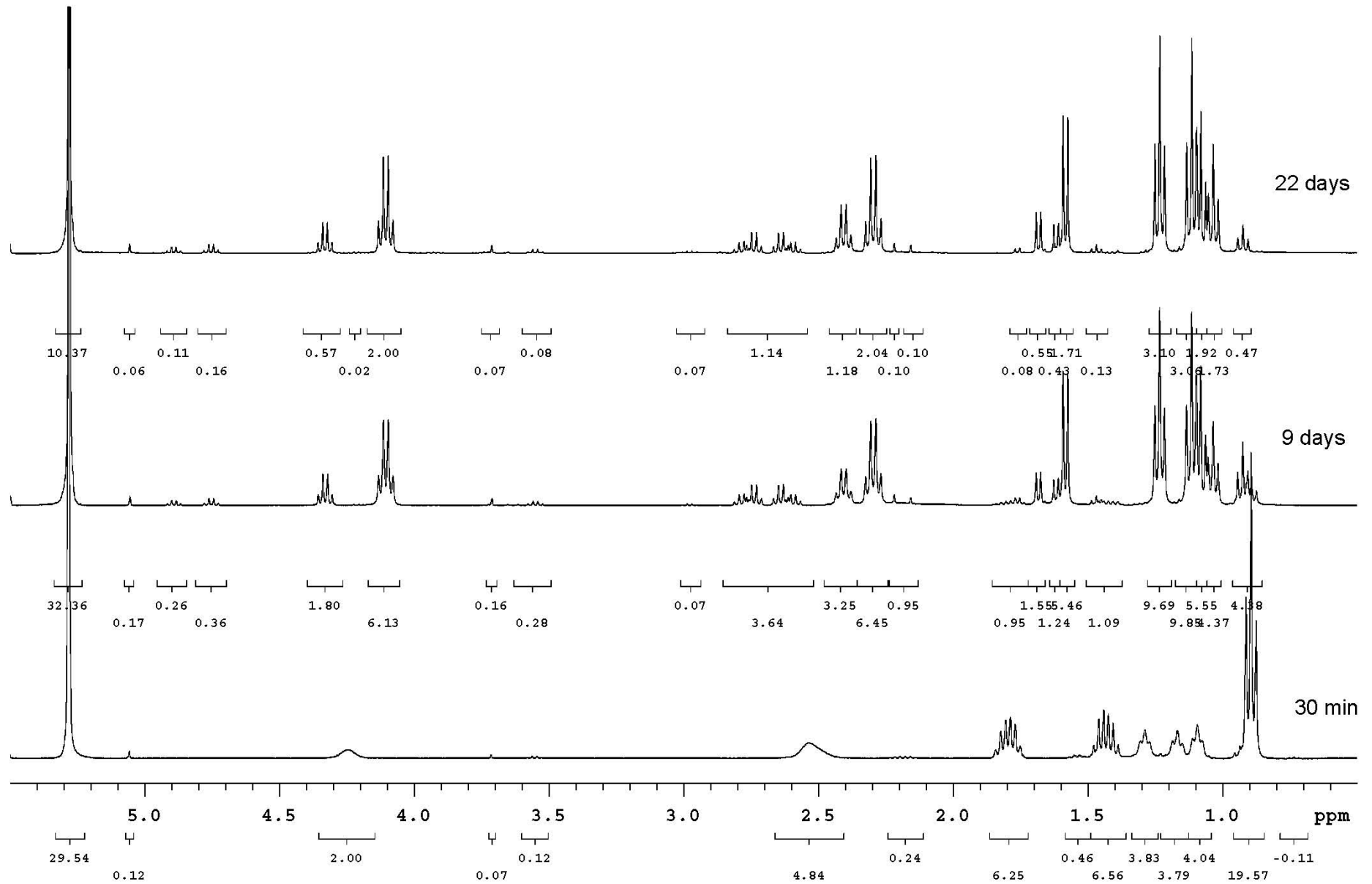


Fig. S7. TPTP 1:0.5 TiCl<sub>4</sub> (Sealed 5 mm NMR tube sample over days) showing significant chlorination product formation





**Fig. S8.** TPTP 1:0.5 TiCl<sub>4</sub> (sealed 5mm NMR tube sample after 9 days) with assignments of chlorinated products

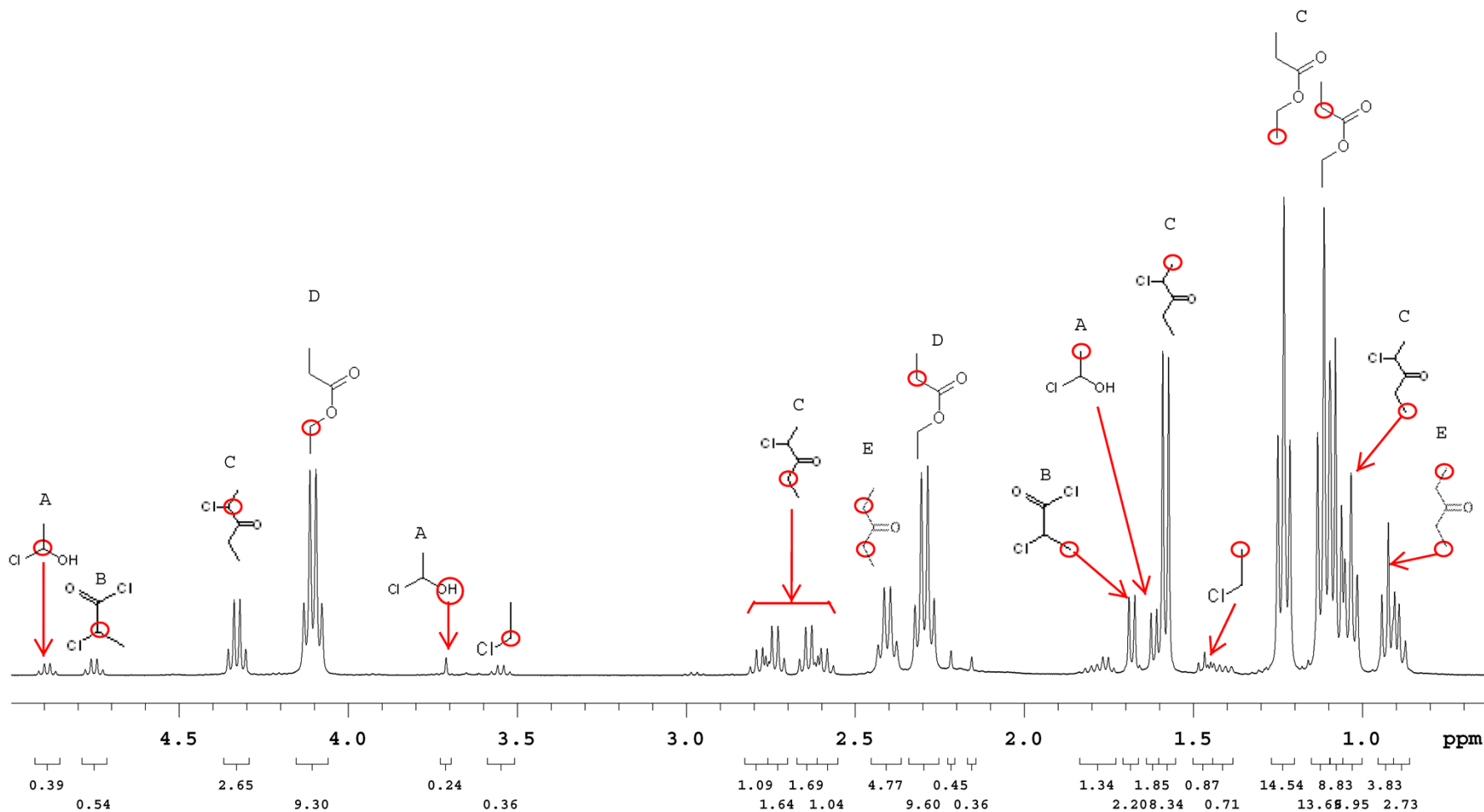
A - 1-chloroethanol(?), Ref: No ref found, reasonable match with calculated spectra (Scifinder Scholar, ChemBioDraw ChemNMR)

B - 2-chloropropionyl chloride, Ref: M. Cocivera and A. Effio, J Org Chem, 1980, 45, 415-420.

C - 2-chloro-3-pentanone, Ref: M. Marigo, S. Bachmann, N. Halland, A. Braunton and K. A. Jorgensen, Angew Chem Int Edit, 2004, 43, 5507-5510.

D - ethyl propanoate, Ref: AIST, Spectral Database for Organic Compounds, Tsukuba, Japan, 2013.

E - 3-pentanone, Ref: AIST, Spectral Database for Organic Compounds, Tsukuba, Japan, 2013.



**Fig. S9.** TPTP 1:0.5  $\text{TiCl}_4$  (Sealed 5 mm NMR tube sample after 9 days - HHgCOSY)  
For confirmation characterisation of chlorination products by literature NMR shifts

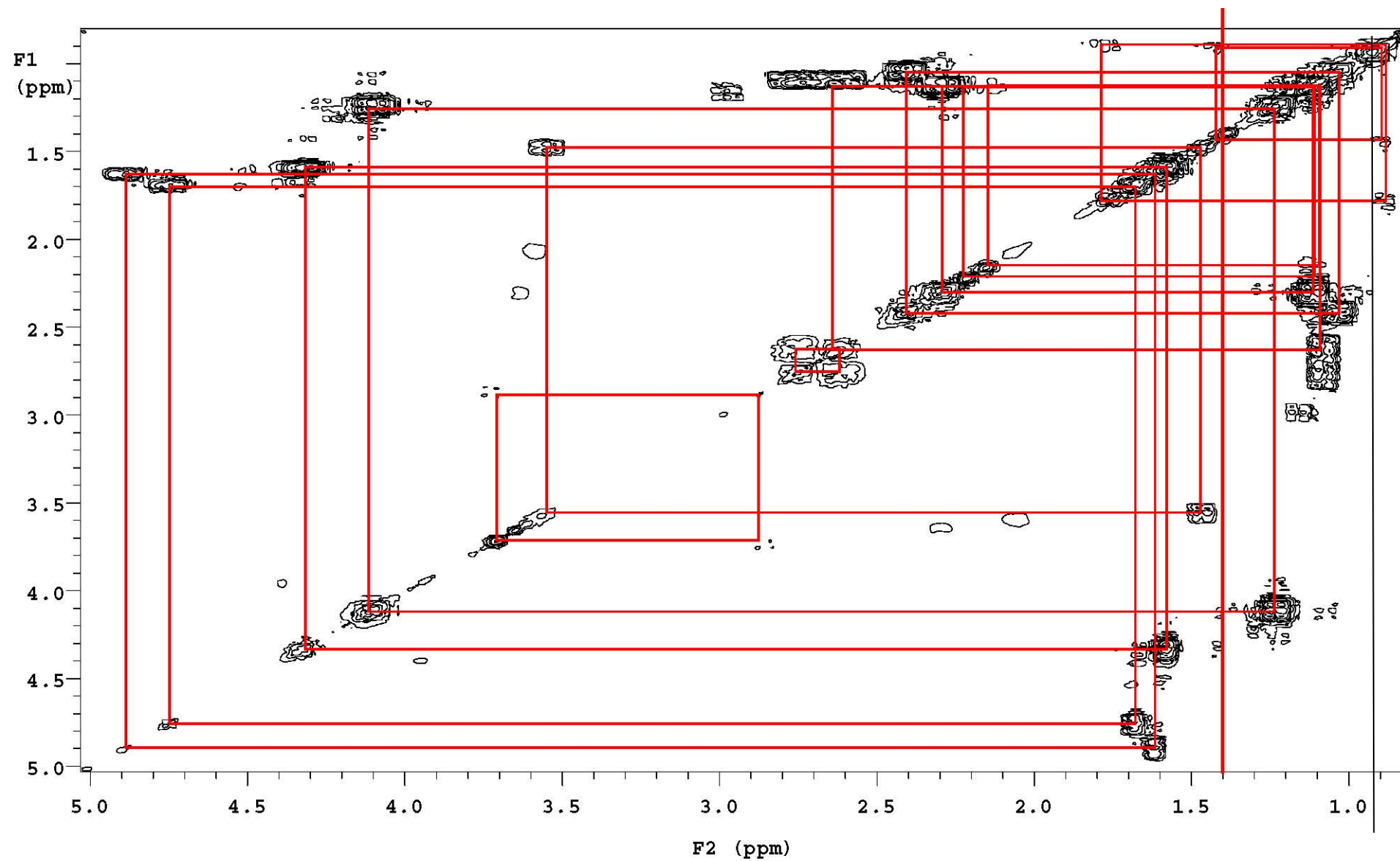


Fig. S10. FT-IR of reactions of  $\text{TiCl}_4$  with ethyl propanoate (EP) and 3-pentanone (3P). 1:1 molar ratio

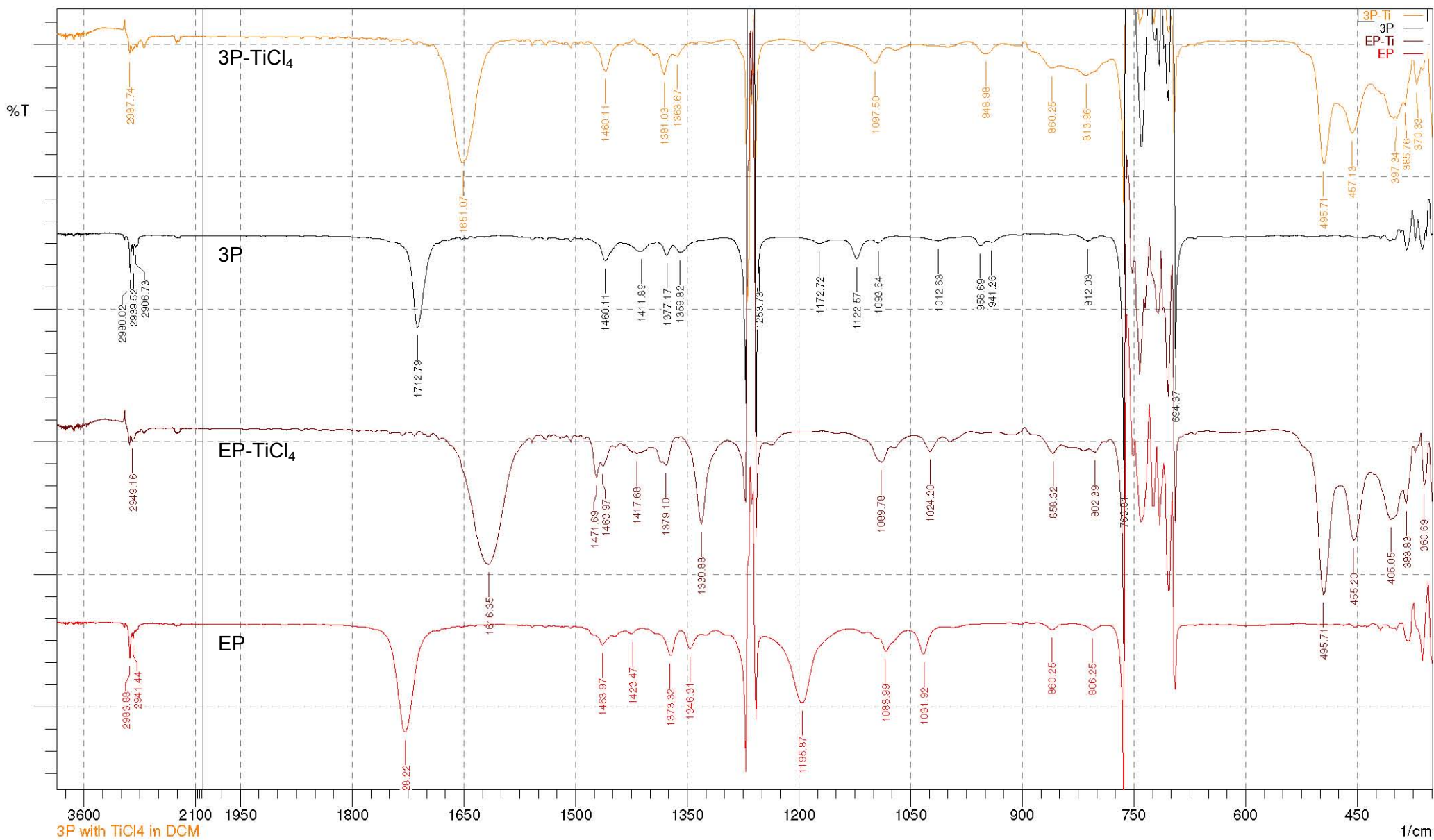
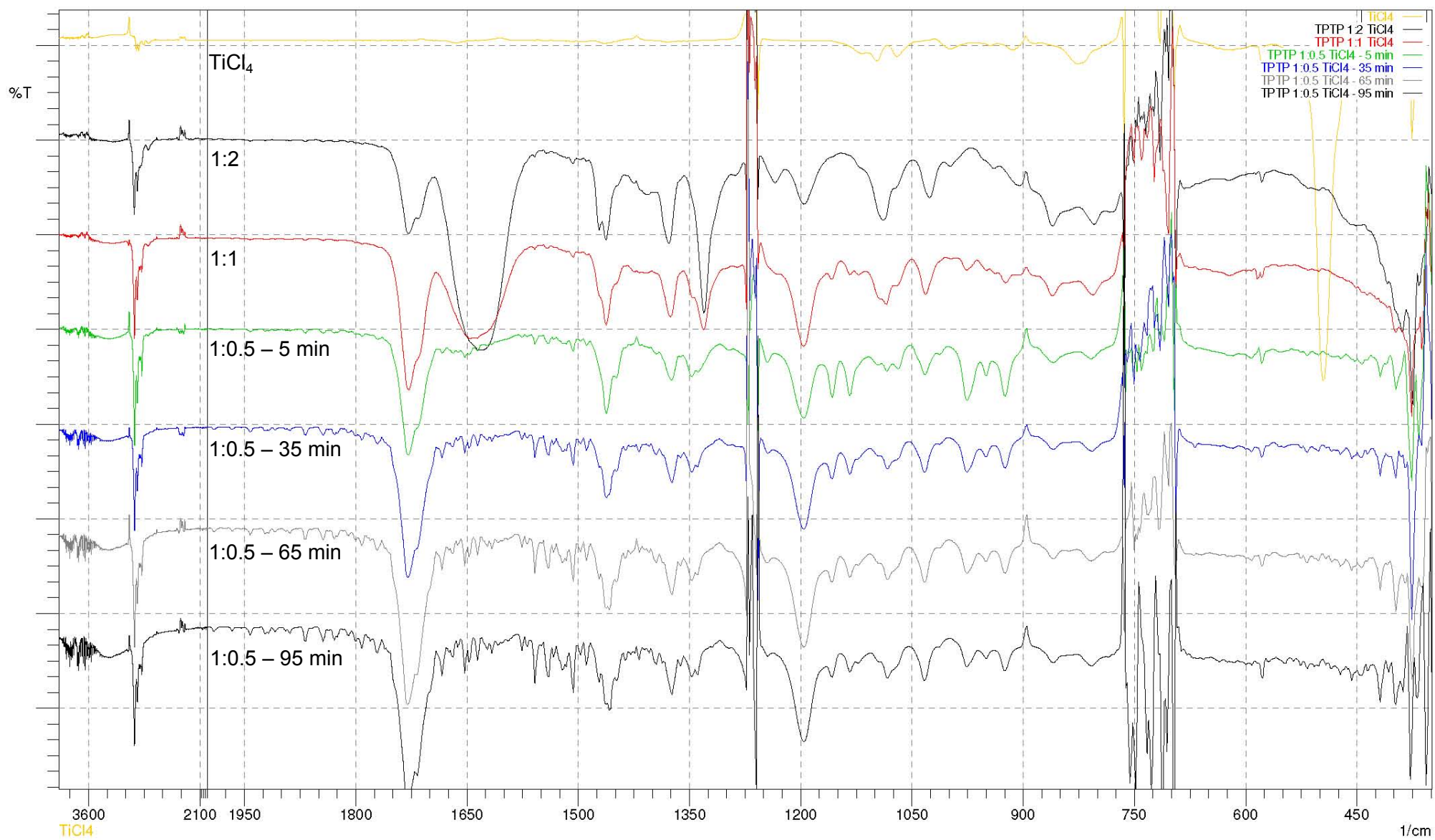


Fig. S11. FT-IR of reactions of TPTP with  $\text{TiCl}_4$ . 1:1 & 1:2 do not change over time. 1:0.5 is tracked in 30 min intervals.



**Fig. S12.** FT-IR of precipitate from reaction of TPTP with  $\text{TiCl}_4$  1:0.5, collected after 9 days (dried at  $60^\circ\text{C}$  *in vacuo*, 4 h)

