Supporting Information for

Distannoxane speciation during esterification catalysis: revealing insights provided by electrospray ionization mass spectrometry

*Evan Crawford,[a] Tracy Lohr,[a] Erin M. Leitao,[a] Samantha Kwok [a] and J. Scott McIndoe [a]**

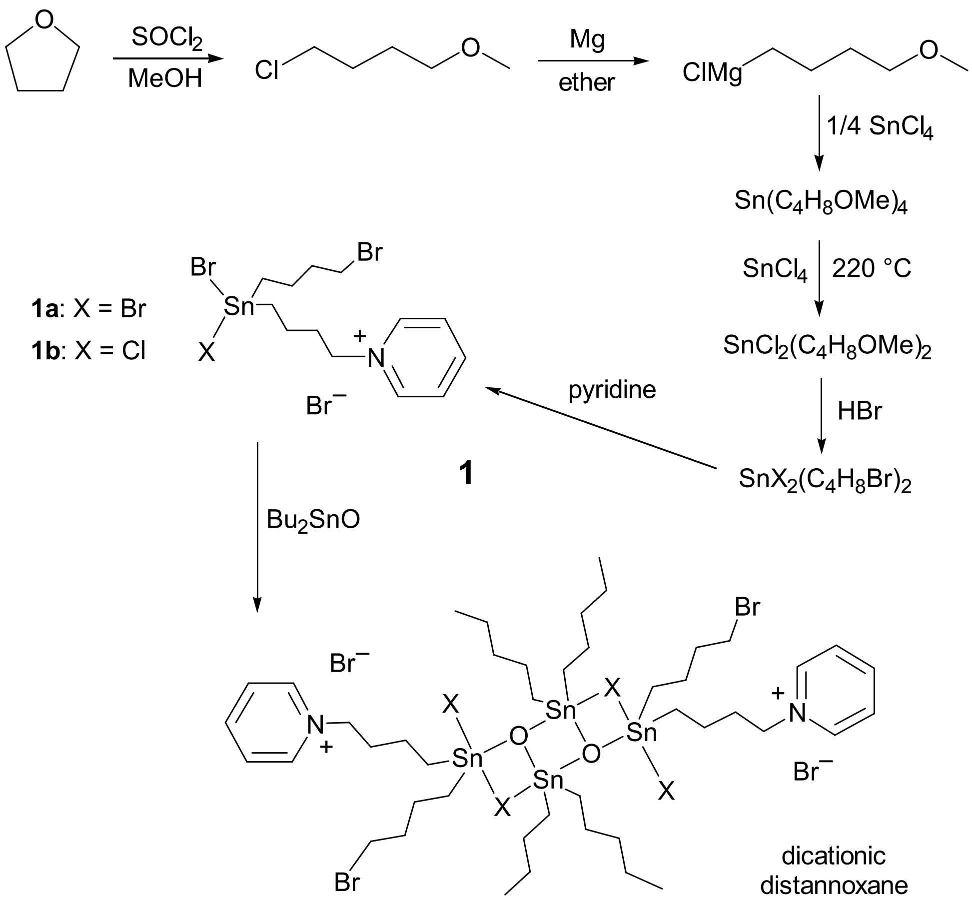
Experimental details

Dry solvents were obtained by distillation or from an MBraun solvent purification system. Solvents were HPLC grade. Reagents were purchased from Aldrich and used without further purification. Reactions were performed under nitrogen using standard Schlenk techniques. Electrospray ionization mass spectra were collected using a Micromass QTof *micro* instrument. Capillary voltage was set at 2900 V, source and desolvation gas temperatures were at 80 and 150°C, respectively. Samples were infused via syringe pump at 5-10 μL min^{-1}. NMR spectra were recorded on AC-250 or AC-300 Bruker spectrometers.

4-methoxy-1-chlorobutane was prepared by treatment of tetrahydrofuran with thionyl chloride in methanol.[1] The tetrasubstituted tin compound $Sn(C_4H_8OMe)_4$ was prepared by reacting 4-methoxy-1-chlorobutane with magnesium to form the Grignard reagent, which was subsequently reacted with 0.25 equivalents of $SnCl_4$.[2] $SnCl_2(C_4H_8OMe)_2$ was prepared by reaction of $Sn(C_4H_8OMe)_4$ with $SnCl_4$ in a high temperature comproportionation reaction, and purified by vacuum distillation.[3] $SnX_2(C_4H_8Br)_2$ was prepared by refluxing $SnCl_2(C_4H_8OMe)_2$ with HBr in concentrated sulfuric acid, followed by an aqueous acidic workup and distillation.[4]

---

[1] Ferrari, T.; Vogel, P. *Synlett.* **1991**, 233.
[2] Thoonen, S. H. L.; Deelman, B. J.; van Koten, G. *J. Organomet. Chem.* **2004**, *689*, 2145-2157.
[3] Melnichenko, L.S.; Zemlyanski, N. N.; Kocheshkov, K. A. *Russ. Chem. Bull.* **1972**, *21*, 1993-1996.
[4] Mitchell, R.H.; Lai, Y.H. *J. Org. Chem.*, **1984**, *49*, 2534-2540.



Scheme SI1. Synthesis for the production of charged tetrasubstituted distannoxanes.

The preparation results in a mixture of $SnBr_2(C_4H_8Br)_2$ and $SnBrCl(C_4H_8Br)_2$ and the presence of the chlorine is carried forward. The mixture might be avoided if $SnBr_4$ were used in place of $SnCl_4$ for the comproportionation, but we were unsuccessful in making this reaction work in reasonable yield.

(4-bromobutyl)(4-pyridiniumbutyl)dihalotin bromide (mixture of 1a and 1b). Under nitrogen, a solution of bis(4-bromobutyl)dibromotin (31.5 g, 57 mmol) and pyridine (15 mL, 185 mmol) in dichloromethane (175 mL) was heated to reflux for 16 h. The mixture was filtered and the solid washed with dichloromethane. The solid was extracted using Soxhlet extraction apparatus in dichloromethane for 30 h. The mixture was filtered to collect a white powder, yield: 31.4 g, 50 mmol, 88%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.10 (d, 2H, Py^+ C*H*), 8.62 (t, 1H, Py^+ C*H*), 8.18 (t, 2H, Py^+ C*H*), 4.64 (t, 2H, -C*H*$_2$-Py^+), 3.55 (t, 2H, -C*H*$_2$Br), 2.00-1.65 (m, 12H, -C*H*$_2$-). ESI-MS(+) (MeCN) *m/z* (relative intensity): **1a** $[C_{13}H_{21}NBr_3Sn]^+$ (100%) calcd. 549.8267; found 549.8218, **1b** $[C_{13}H_{21}NBr_2ClSn]^+$ (18%) calcd. 505.9758; found 505.9763. ESI-MS(–) (MeCN) *m/z*: $[Br]^-$ (100%) 78.92.

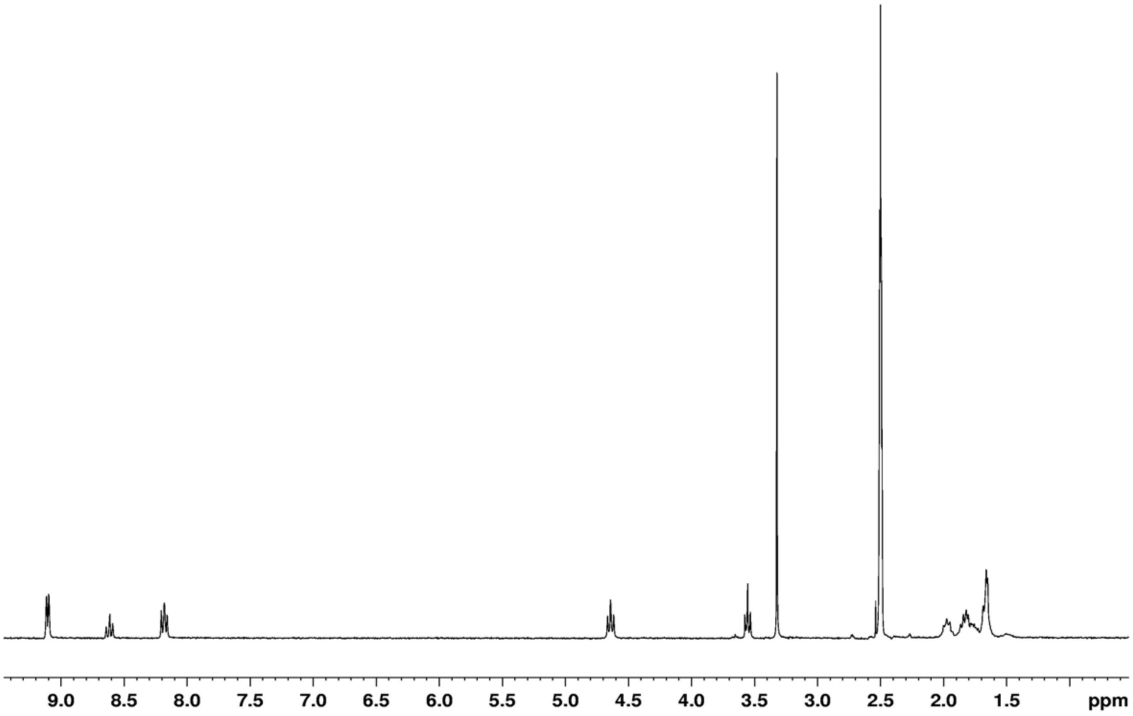


Figure SI1. ^{1}H NMR spectrum of **1a+b** in d$_6$-DMSO.

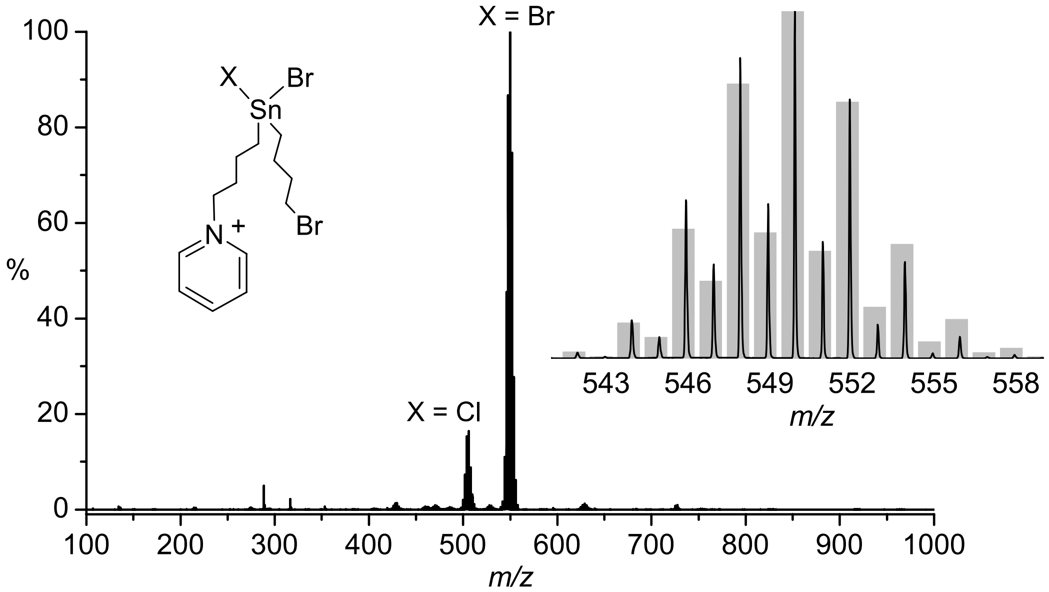


Figure SI2. Positive-ion ESI-MS of **1a+b**. The inset shows the match between calculated (histogram) and experimental (line) isotope patterns for **1b**; similar results were observed for **1a**.

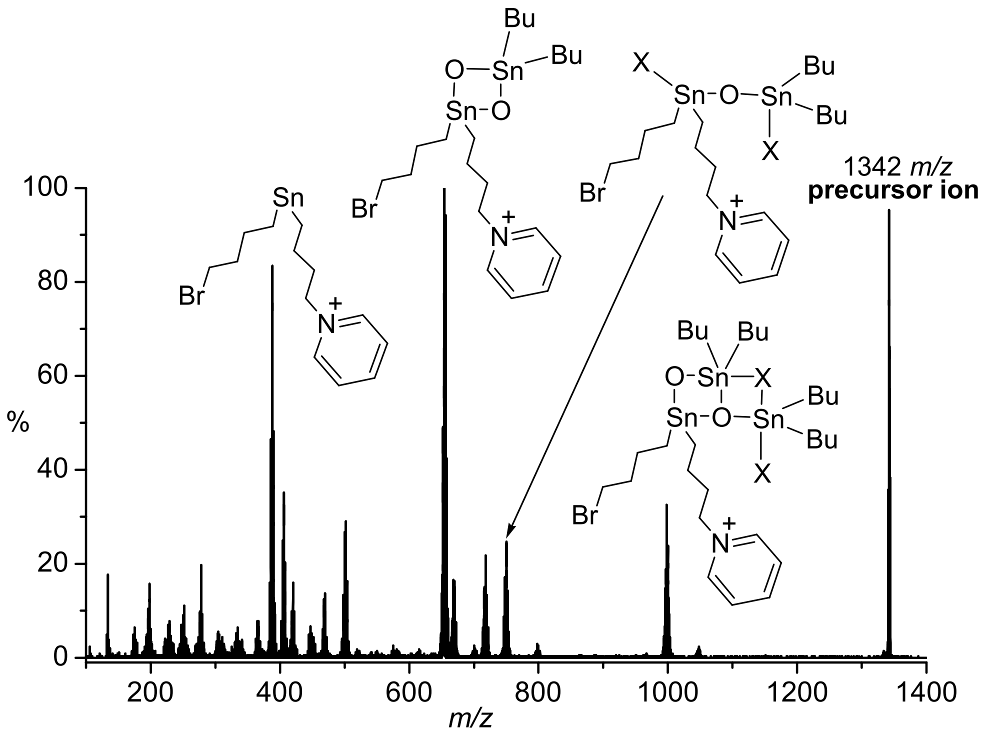
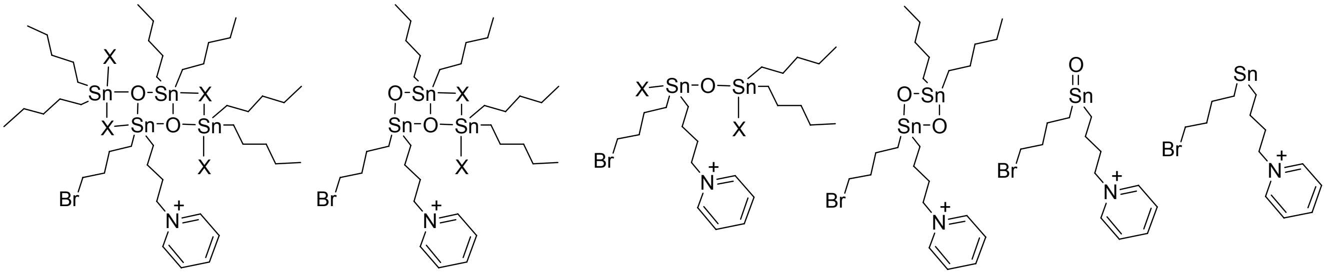


Figure SI3. MS/MS product ion spectrum of the charged distannoxane 1342 *m/z* precursor ion (see Figure 2 of paper). Spectrum compiled from data collected at collision voltages between 1-200 V. Prominent fragments appear due to neutral losses of SnX_2Bu_2 and $Sn_2OX_2Bu_4$, and at higher energies, further loss of neutral SnX_2Bu_2 and $SnOBu_2$ (X = OMe or Br). The ions $[SnO(C_4H_8Br)(C_4H_8NC_5H_5)]^+$ and $[SnX_2(C_4H_8Br)(C_4H_8NC_5H_5)]^+$ arise from the equivalent processes but where the charge resides on the other part of the ion (i.e. a neutral loss becomes a fragment ion). To account for all the ions in the spectrum, all possible isomers where OMe and Br can occupy any position and $[Sn(C_4H_8Br)\ (C_4H_8NC_5H_5)]^+$ can be in either inequivalent tin position must be invoked; however, there is no evidence of scrambling of the alkyl groups on tin, as all fragment ions contain both of $-C_4H_8Br$ and $[-C_4H_8NC_5H_5]^+$. See SI4 for all assignments.



1342 *m/z*: **precursor ion** $X_4 = Br_2(OMe)_2$

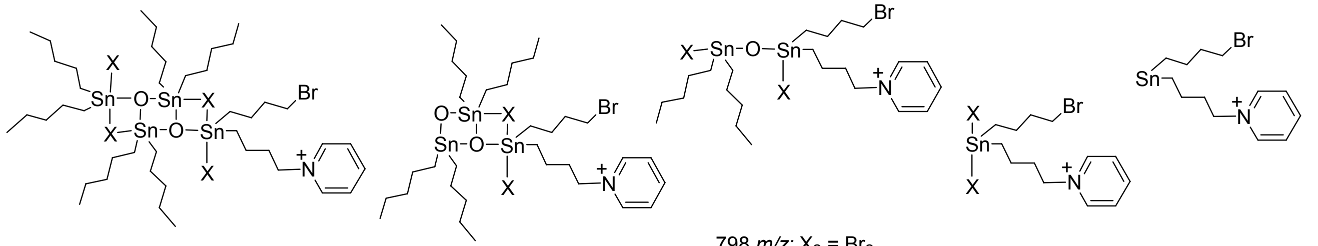
1046 *m/z:* $X_2 = Br_2$
998 *m/z:* $X_2 = Br(OMe)$

798 *m/z:* $X_2 = Br_2$
749 *m/z:* $X_2 = Br(OMe)$
700 *m/z:* $X_2 = (OMe)_2$

654 *m/z*

406 *m/z*

388 *m/z*



1342 *m/z*: **precursor ion** $X_4 = Br_2(OMe)_2$

1046 *m/z:* $X_2 = Br_2$
998 *m/z:* $X_2 = Br(OMe)$

798 *m/z:* $X_2 = Br_2$
749 *m/z:* $X_2 = Br(OMe)$
700 *m/z:* $X_2 = (OMe)_2$

500 *m/z:* $X_2 = Br(OMe)$
452 *m/z:* $X_2 = (OMe)_2$

388 *m/z*

Figure SI4. MS/MS product ion assignments from the charged distannoxane 1342 *m/z* precursor ion. See Figure 2 of paper for original MS, and Figure SI3 for MS/MS spectrum.

Catalysis

Equimolar amounts of methanol and acetic acid (79 mmol) were heated to reflux in the presence of the **1a+b** + Bu_2SnO (0.080 mmol of each, 0.05 mol% in distannoxane), in the presence of **1a+b** alone (0.022 g, 0.042 mmol, 0.05 mol%), in the presence of HBr (0.08 mmol, 0.1 mol%), or alone (i.e. no catalyst), and ^{1}H NMR spectra of samples collected at 2 and 4 hours were recorded. CH_3OH: 3.48 ppm, CH_3COOH: 2.095 ppm, CH_3COOCH_3: 3.668ppm, CH_3COOCH_3: 2.02 ppm. Conversions are based on the CH_3OH vs. CH_3COOCH_3 integrations.

The uncatalyzed reaction was repeated with brand-new glassware and stirrer, and with distilled acetic acid. Results were identical.

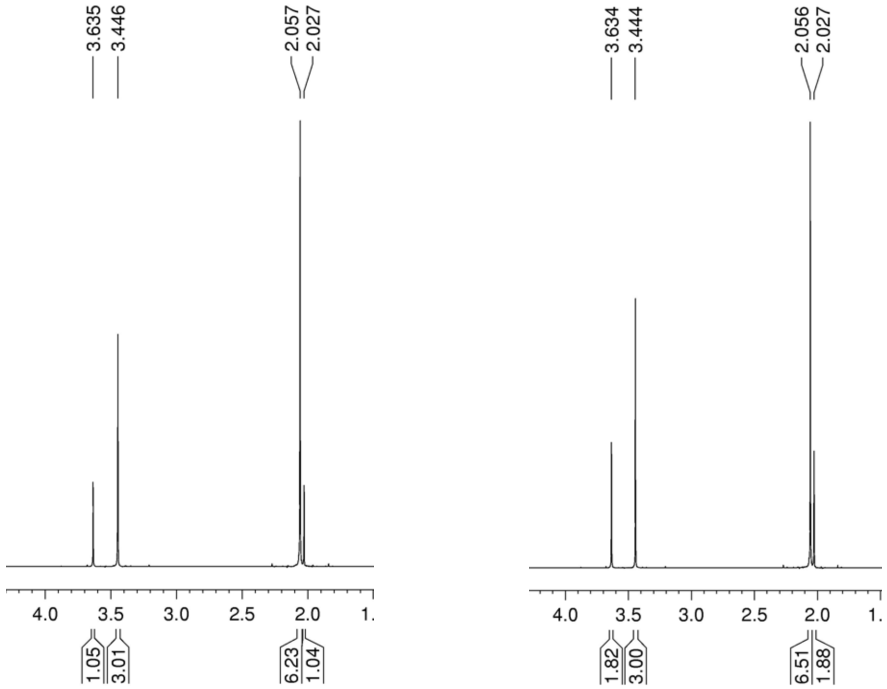


Figure SI7. ^{1}H NMR in $CDCl_3$ of the esterification of CH_3COOH with MeOH (1:1) in the presence of 0.05 mol% distannoxane (from **1a+b** + Bu_2SnO, 3 hours reflux in methanol) after 2 (left) and 4 (right) hours of reflux. Reaction has proceeded to 26% and 38% completion after 2 and 4 hours, respectively.

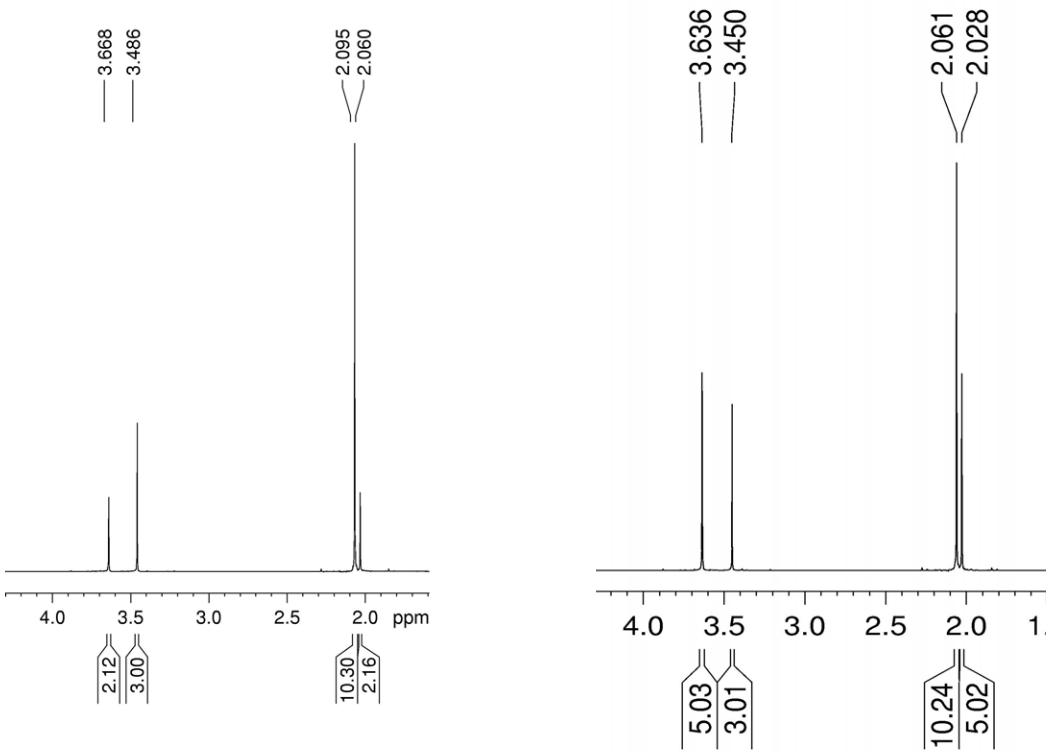


Figure SI8. ^{1}H NMR in $CDCl_3$ of the esterification of CH_3COOH with MeOH (1:1) in the presence of 0.05 mol% **1a/b** after 2 (left) and 4 (right) hours of reflux. Reaction has proceeded to 41% and 63% completion after 2 and 4 hours, respectively.

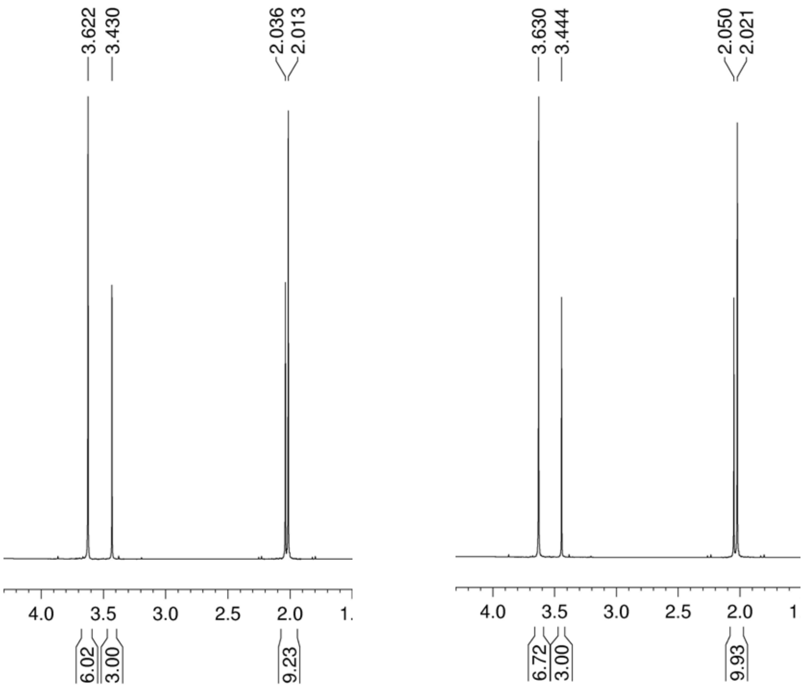


Figure SI9. ^{1}H NMR in $CDCl_3$ of the esterification of CH_3COOH with MeOH (1:1) in the presence of 0.1 mol% HBr after 2 (left) and 4 (right) hours of reflux. Reaction has proceeded to 67% and 69% completion after 2 and 4 hours, respectively.

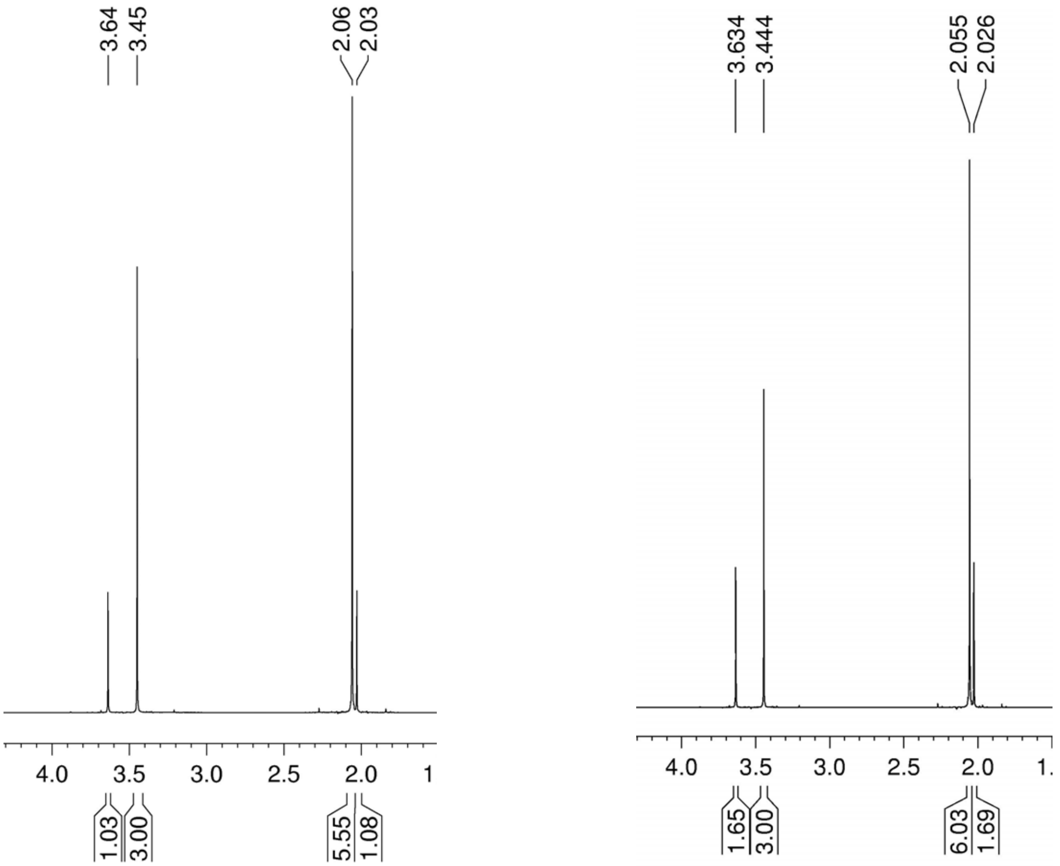


Figure SI10. ^{1}H NMR in $CDCl_3$ of the esterification of CH_3COOH with MeOH (1:1) in the absence of any catalyst after 2 (left) and 4 (right) hours of reflux. Reaction has proceeded to 25% and 35% completion after 2 and 4 hours, respectively.