Supplementary Information

GCMS analysis of products.

The number of ^{12}C and ^{13}C atoms in a labelled compound is given by the following equation:

$$P(n,r) = \left(\frac{(n+r)!}{n!\,r!}\right) {P_{12C}}^{n} {P_{13C}}^{r}$$

Where *P(n,r)* is the chance of finding n ^{12}C's and r ^{13}C 's in any molecule, n is the number of ^{12}C's, r is the number of ^{13}C's, P_{13C} is the abundance of ^{13}C and P_{12C} is the abundance of ^{12}C (=1-P_{13C}). The first part of the equation exists to correct for the number of times 1 (or any number of) label can be distributed throughout the molecule, and the P's give the chance for a label to occur. Applying this equation to any molecule one can assess the extent of labelling in that species as a function of the abundance of that label. Importantly it tells something about the pattern one can expect in a mass spectrum. Two examples: when butanol has 10% or 30% ^{13}C incorporated we would expect the molecular ion in the MS to have the mass patterns shown in Figure S1, assuming that the label is incorporated equally in all sites.

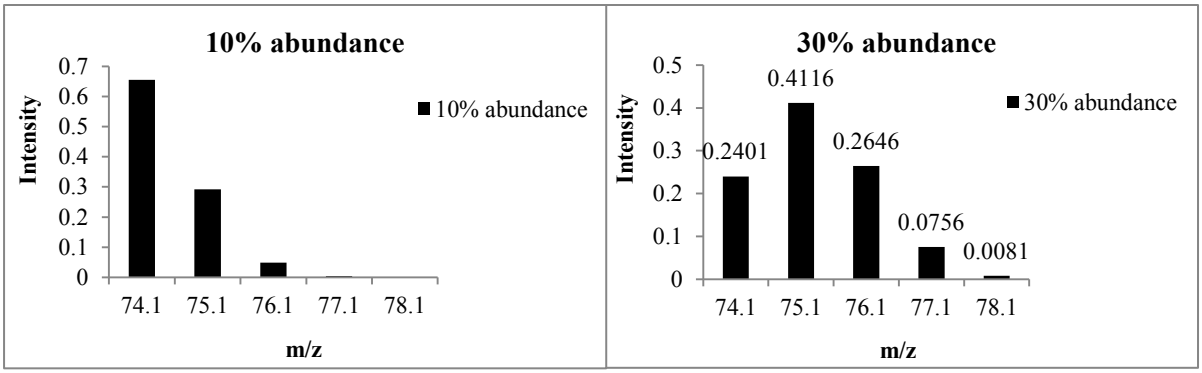

Figure S1. the expected MS patterns for the parent ion of butanol when there is either 10% or 30% ^{13}C labelling in the fragment.

As can be seen the patterns change significantly with the extent of labelling. The butanol containing 30% labelling now has a higher chance of finding a label in it than of not finding a label in it at all, while the example containing 10% label does not. Thus, if the % C incorporation is known the expected MS pattern can be calculated. This argument can be

used in reverse to derive the % of ^{13}CO incorporated into a molecule from a measured mass spectrum.

The observed labelling pattern taken from a reaction was compared with spectra simulated using a variety of % incorporation. Because the parent ion is not s ingle peak, we used a "natural pattern", N_1 from an unlabelled source, namely from the reaction where no added label was present. We then assumed that a molecule containing one ^{13}C label would have an identical pattern shifted by 1 mass unit to higher mass (N_2). The pattern for a compound containing 2 ^{13}C atoms would be shifted by 2 mass units etc. These patterns are shown in Figure S2.

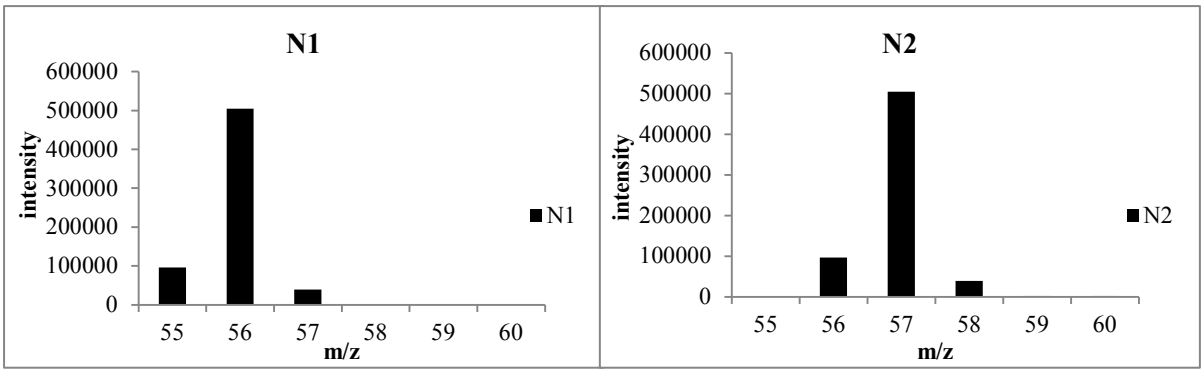

Figure S2. N_1 (left) and N_2 (right). N_1 is the pattern for the $C_4H_{7\text{-}9}^+$ fragments from butanol. Note that N_1 and N_2 look exactly the same but are in fact shifted by m/z = 1.

Then a constructed pattern is $C = k1\ N_1 + k2\ N_2 + k3\ N_3 \ldots k_n\ N_n$, where n goes up to the number of carbon atoms in the compound + 1. The constants, k, have to fit the patterns derived above in Figure S1 and must sum up to 1. So the sample with abundance 30% could be constructed using N_1 which is a pattern for butanol without label, N_2, which is N_1 but every mass shifted 1 up, etc. and the constants follow the pattern seen above in Figure S1, k1= 0.2401, k2= 0.4116, k3 = 0.2646, k4 = 0.0756 and k5= 0.0081. As follows then the constructed pattern is: $C = 0.2401\ N_1 + 0.4116\ N_2 + 0.2646\ N_3 + 0.0756\ N_4 + 0.0081\ N_5$. A construct can be easily made for all values of abundance (going from 0% abundance and up) and can then be compared to the real labelled pattern that was obtained. A good fit should match the real signal exactly in relative intensity, therefore the construct with a good fit correlates to the correct level of incorporation of ^{13}C. An example below shows the natural pattern and the pattern of the labelled compound after carrying out the reaction in the presence of some ^{13}CO (Figure S3 a) on the left hand side, and the constructed pattern that matches the labelled pattern on the right hand side and bottom left hand side (Figure S3 b and

c). The final plot shows the corresponding abundance pattern for a C_4 species that has 7.4 % ^{13}C incorporation. The constants in Figure S3 d where used to build Figure S3 b and c).

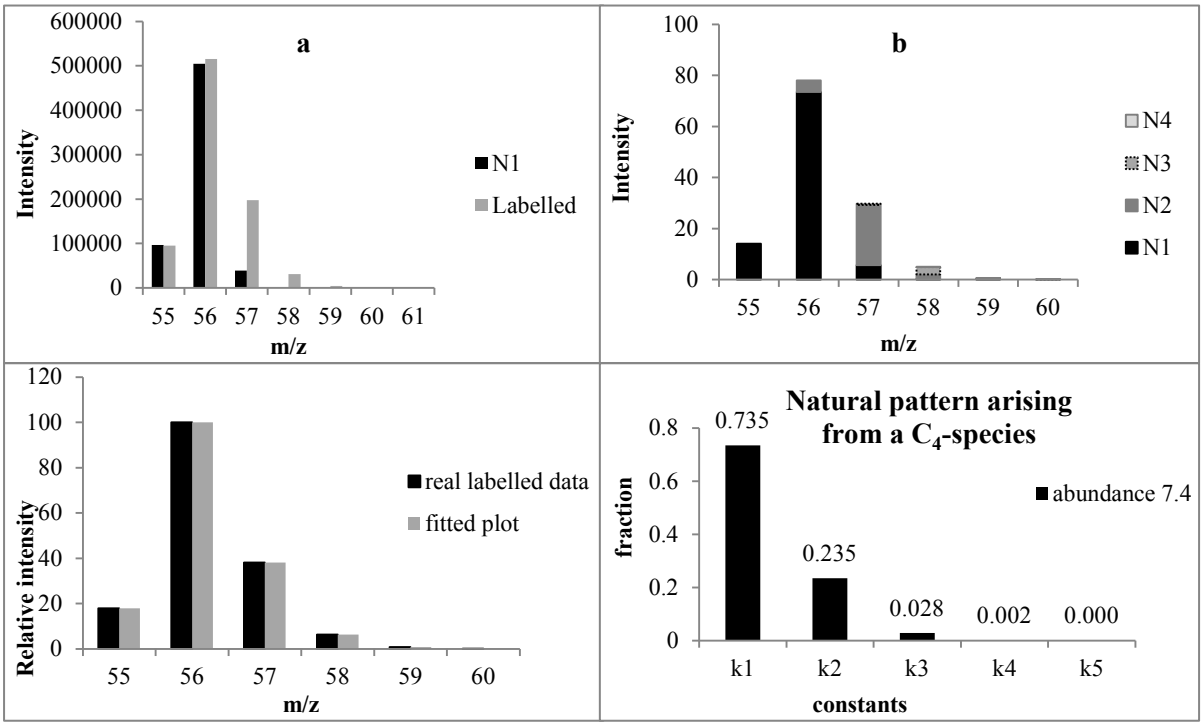

Figure S3 a) the spectra of butanol from natural abundance and from partially labelled CO (this is the $C_4H_{7\text{-}9}^+$ -fragment); b) a constructed pattern to match the labelled pattern in a); c) A comparison of the constructed pattern (fit) with the labelled pattern, it shows a very good, but not perfect fit d) the constants used for constructing b and c, they themselves form a pattern equal to a theoretical C_4-species that contains 7.4% ^{13}C abundance.

Applying the fit

We automated the fitting process defining the goodness of fit by the following equation:

$$fitness = \frac{\sqrt{\sum_N (Yreal - Yfit)^2}}{N}$$

In other words we calculated the average distance between the real value and the fitted value. In this way, a perfect match would have a fitness of 0 (average difference between fit and real is 0 per mass), and a bad fit would be higher than 5 (the average distance of the fit against the real plot would be more than 5 points off). Then the fit was re-iterated around the minimum fit for refinement to the decimal point. The best fit was used to determine the incorporation of ^{13}C into that compound. For this to work it is important that the fitness values of a comparison show a significant convergence approaching a good match.

In other words, when the constructed plot is different from the real plot the fitness value has to be significantly higher than when a construct matches very well. Figure S4 shows that it does:

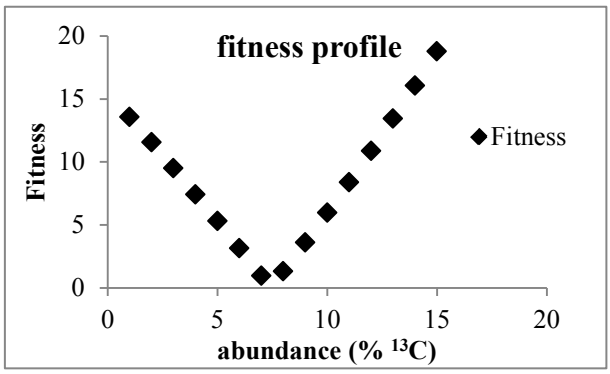

Figure S4 A fitness profile over a range of tried abundances. The values change significantly when the tried abundance does not correspond to the real abundance present.

Visual inspection of the matches also shows that bad fits really are different from the real plots. Only around the very minimum some ambiguity can occur and that is why we used the fitness value to determine the minimum.

NMR spectrum for products from a reaction using $^{13}CH_3OH$

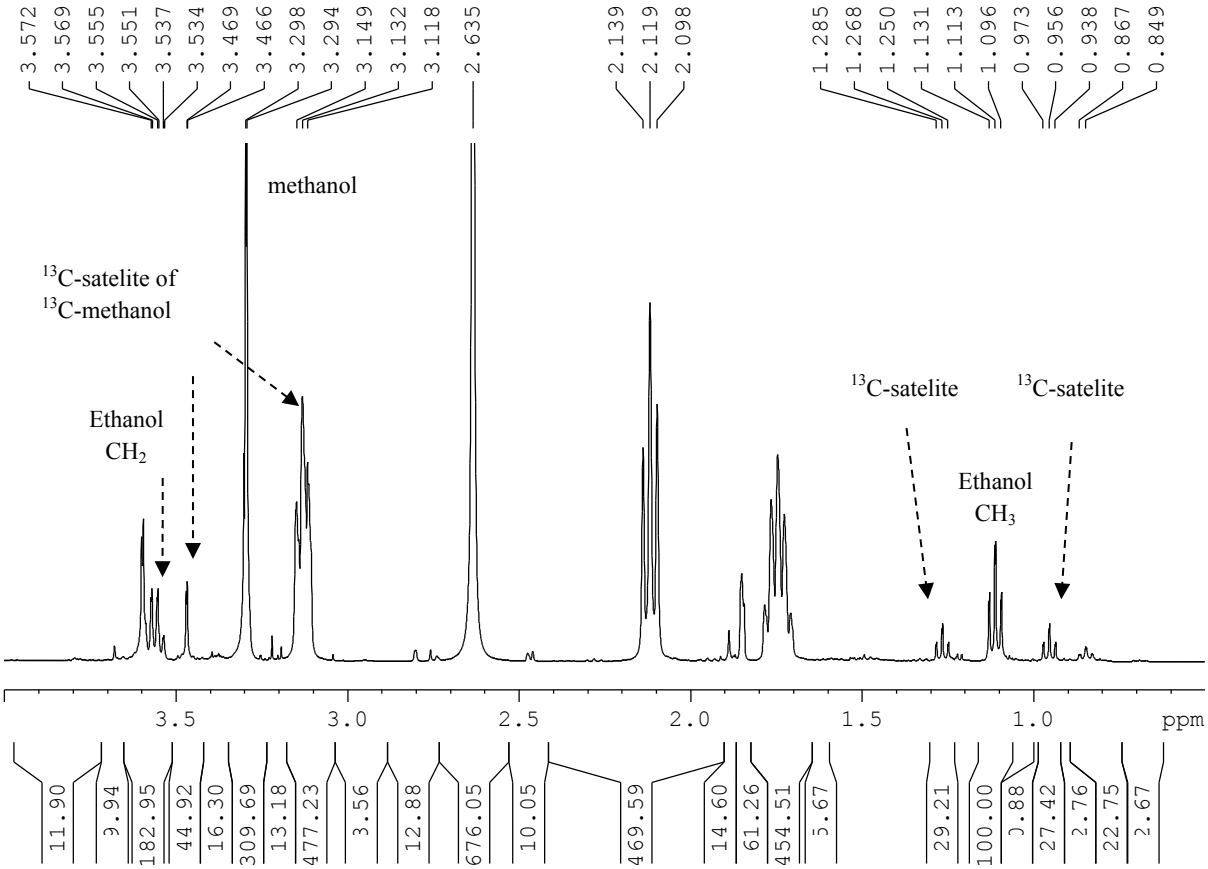

Figure S5. ^{1}H NMR of the distilled product from the reaction using $[Ru_3(CO)_{12}]$ and ^{13}C-MeOH.

Figure S5 shows a typical ^{1}H NMR spectrum for the products from a CO hydrogenation carried out in the presence of $^{13}CH_3OH$.

Labelling of propanol from reactions involving $^{13}CH_3OH$

The labelling pattern for propanol formed in reactions with added $^{13}CH_3OH$ was evaluated as follows:

Figures S6 and S7a) show that there is never more than one ^{13}C atom in each molecule of propanol.(no peak at *m/z* = 62). The extent of incorporation of the single label is 34 %

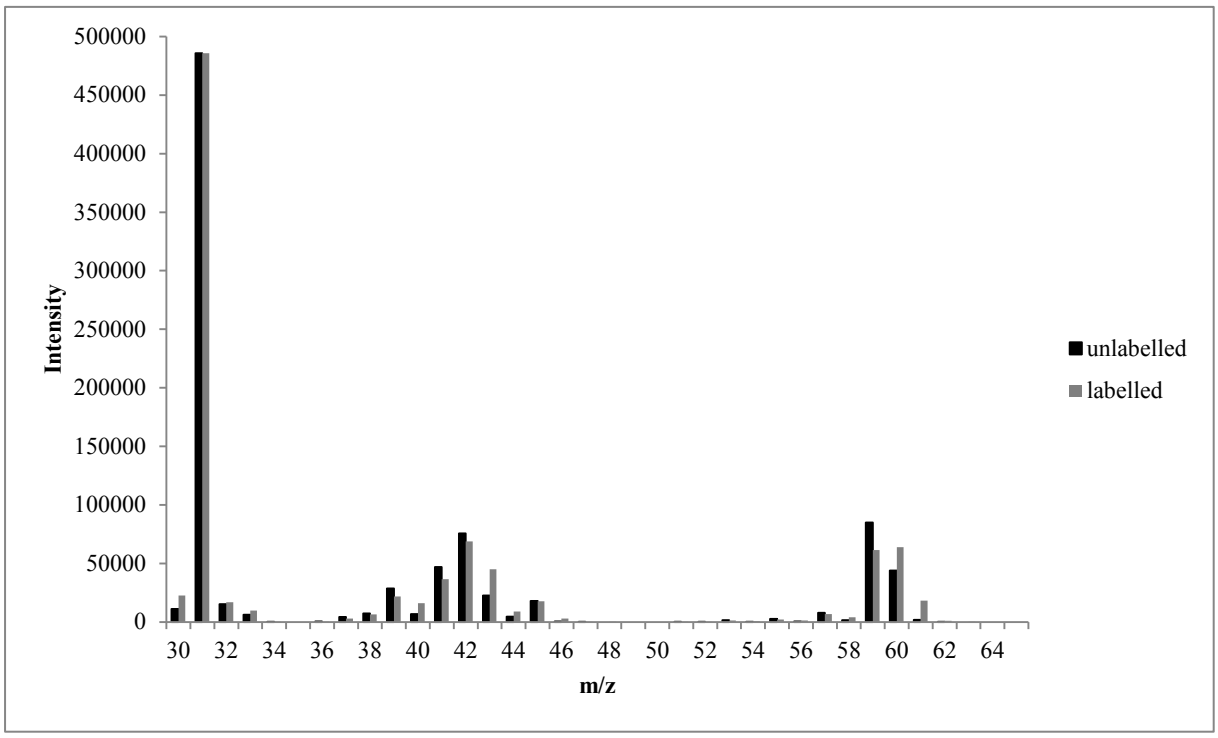

Figure S6. A comparison between the GC-MS spectra of unlabelled propanol and propanol produced when adding ^{13}C-methanol to a reaction using $[Ru_3(CO)_{12}]$. The latter spectrum has been multiplied by a normalisation constant to obtain a spectrum where the intensity of the peak with m/z =31 is the same as that from the unlabelled sample.

Further inspection of the fragmentation patterns provides more information on the exact site of the label in the monolabelled products.

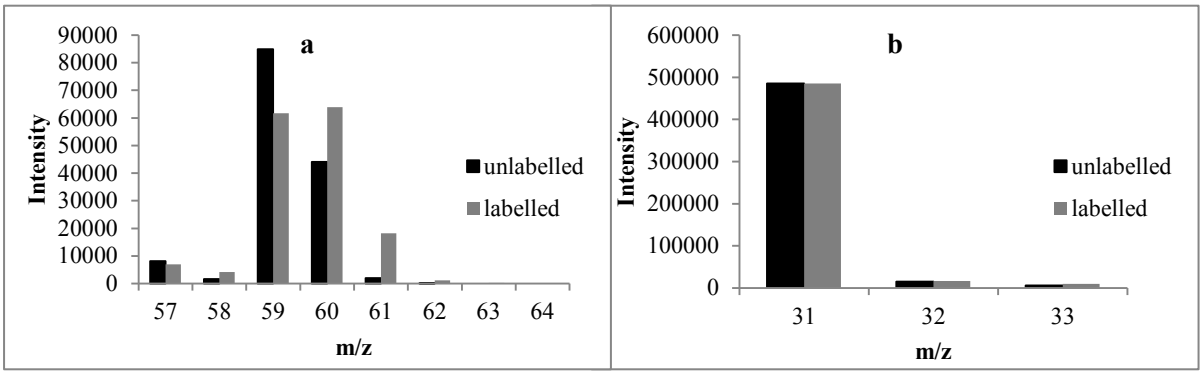

Figure S7 a) a close up of the molecular ion pattern it can clearly be seen that there is incorporation of a label, but only 1 label. b) a close up of the fragment arising from $[CH_2OH]^+$. It can be seen that there is no additional labelling in this position.

The fragment arising from C_1-C_2 bond scission, $[CH_2OH]^+$, shows no label (Figure S7 b). The labelled species must come from either $^{13}\mathbf{CH_3}$-CH_2-CH_2OH or CH_3-$^{13}\mathbf{CH_2}$-CH_2OH. There are other fragments formed during the GC ionisation but most of them form overlapping masses. However, the peak at m/z 45 comes from a species, $[CH_2$-$CH_2OH]^+$, where C_2-C_3 bond scission has occurred.

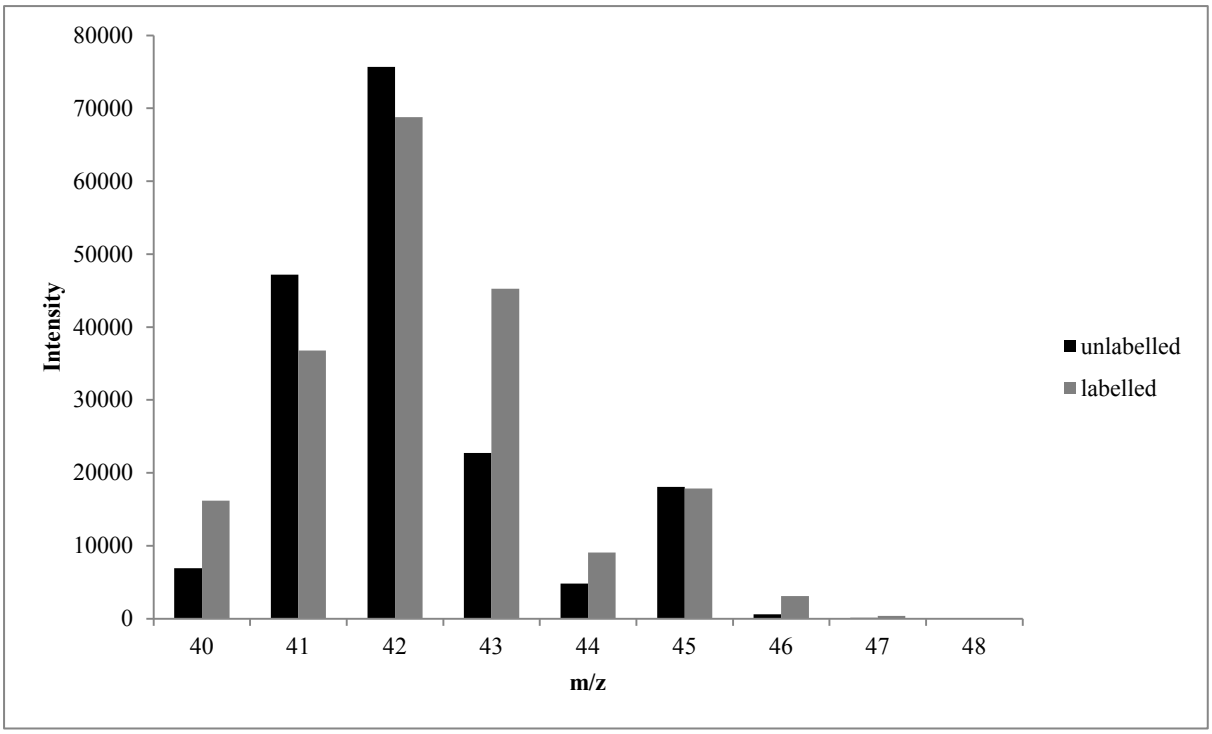

Figure S8. The GC-MS pattern of a group of species fragmented from propanol. One species is $[CH_2\text{-}CH_2OH]^+$ fragment at *m/z* 45. The singularly labelled fragment, $[^{13}CH_2CH_2OH]^+$ appears at *m/z* 46.

Figure S8 shows that this species is labelled and contains about 17.3% ^{13}C, which must all be at position 2, this is visible at *m/z* 46. However, the total amount of labelling in the propanol from this reaction is 34 % ^{13}C. Therefore, the remaining 17% must be at the C_3 position. In other words, in this reaction isotopic scrambling occurs in going from labelled ethanol to propanol, such that the label is equally distributed between C_3 and C_2.