**Supplementary information on:**

# Intramolecular carbon and nitrogen isotope analysis by quantitative dry fragmentation of the phenylurea herbicide isoproturon in a combined injector/capillary reactor prior to GC separation

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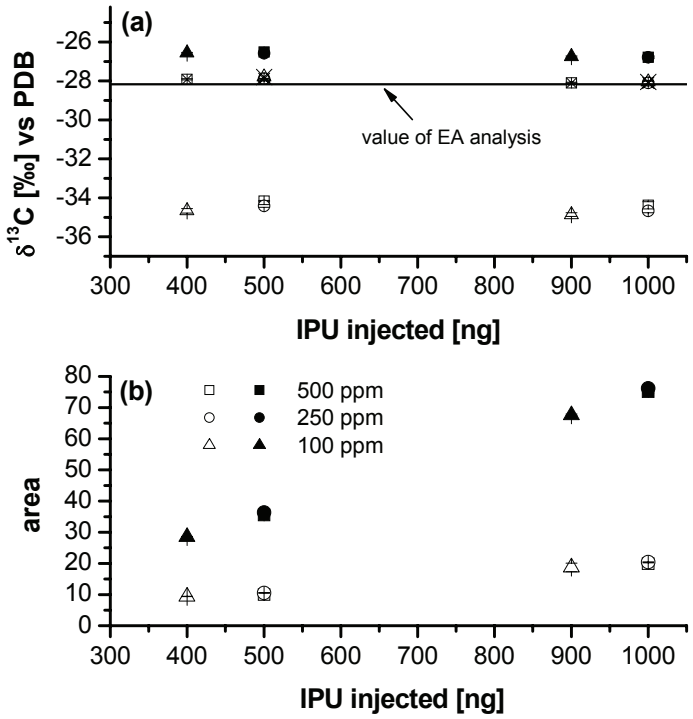
**Figure S-1:**



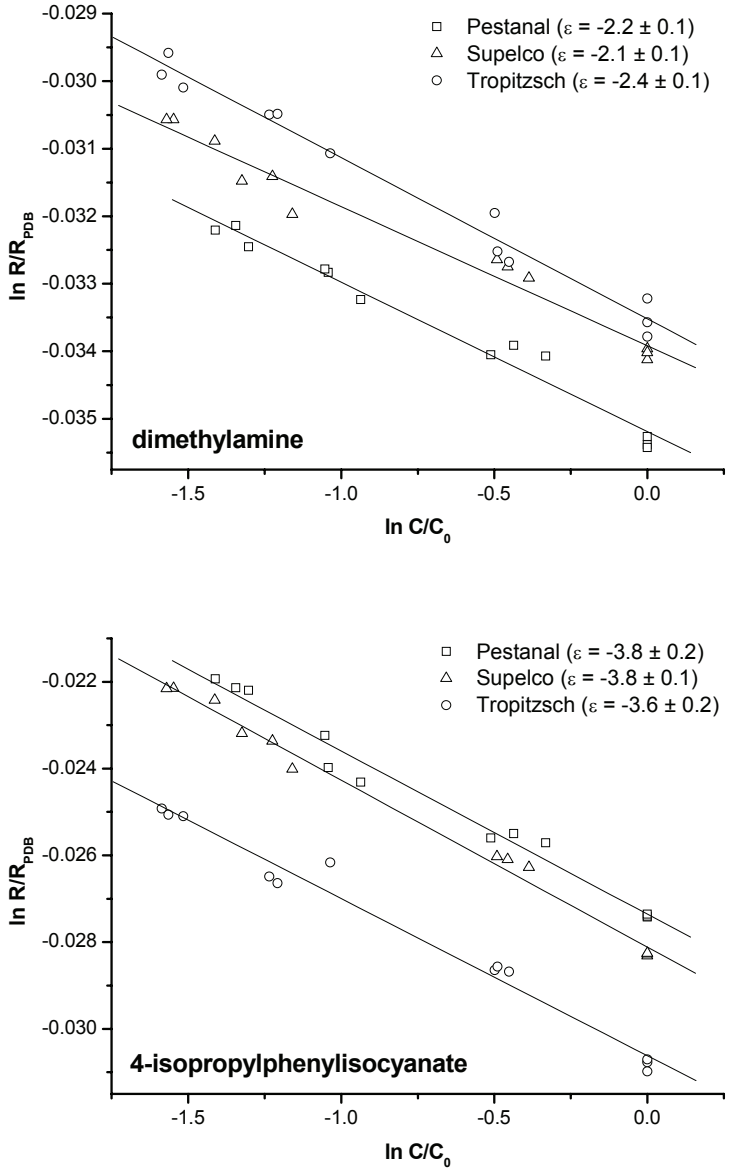

$\delta^{13}C$ values (a) and response area (b) as a function of the amount of Pestanal-isoproturon injected with solutions of different concentration varying injection volume. Open and closed symbols are dimethylamine and 4-isopropylphenylisocynante, respectively. The $CO2^{+}$ signal at m/z 44 ranged from 680 to 1600 mV for dimethylamine and from 3 to 9 V for 4-isopropylphenylisocynante. Goodness of linear fit for areas of both products were $r^2 > 0.99$. In (a) also $\delta^{13}C$ values of the Pestanal-isoproturon assessed by EA-IRMS (horizontal line) and the calculated average isotope signature of the two fragments (crossed-out open symbols) is shown.

**Calculations on Rayleigh equation for ε determination**

$$\ln\left(\frac{1000+\delta^{h}E}{1000+\delta^{h}E_{std}}\right)=\frac{\varepsilon}{1000}\ln f \qquad \text{(equ S1)}$$

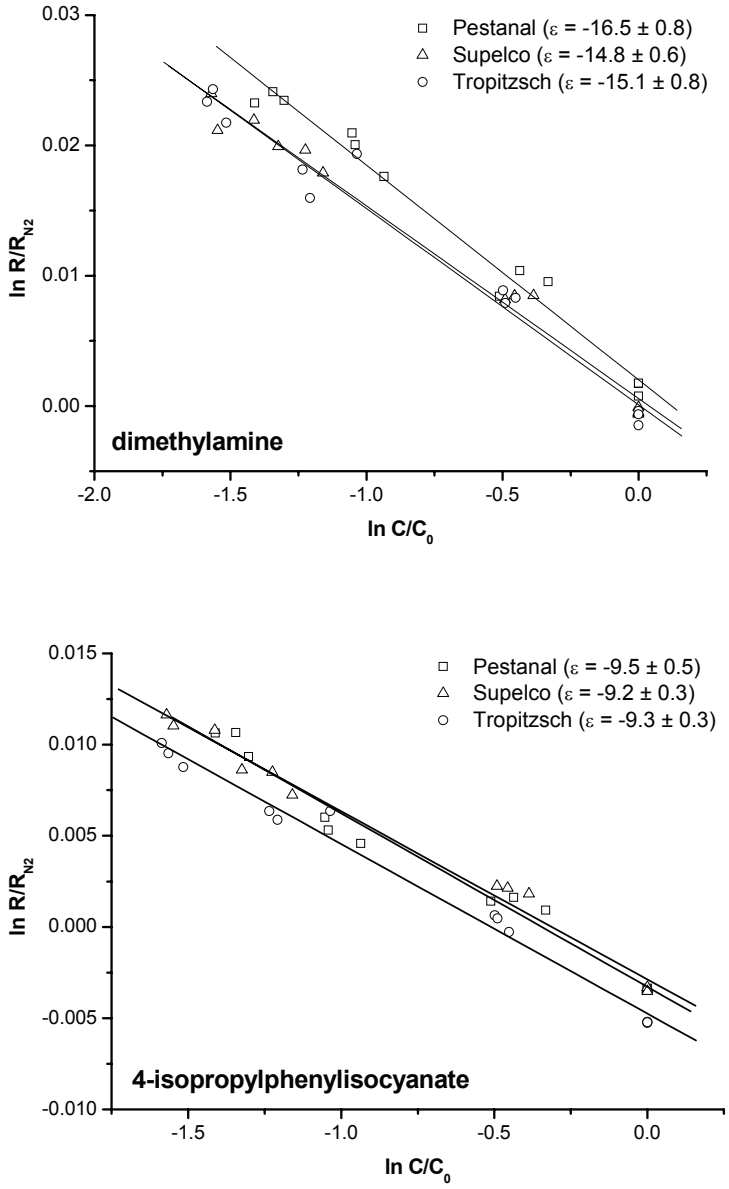
The linearized Rayleigh-equation (equ S1) was applied to derive a bulk isotopic enrichment factor, ε, which is commonly reported in per mil (‰) where *f* is the fraction of compound that has not reacted, and $\delta^{h}E$ and $\delta^{h}E_{std}$ are the isotopic signature of the compound for the element E at times t and the isotopic signature of the standard of E, respectively. The ε has a negative value for normal kinetic isotope effects. Note that we used $\delta^{h}E_{std}$ in order to discriminate the different batches of isoproturon in the linearized plots. The determination of ε is not influenced by this change.

**Figure S-2:**




Determination of carbon isotope enrichment factors ε (according to equ S1) for different batches of isoproturon during hydrolysis at 60°C and pH6 for dimethylamine and 4-isopropylphenylisocynanate.

**Figure S-3:**




Determination of nitrogen isotope enrichment factors ε (according to equ S1) for different batches of isoproturon during hydrolysis at 60°C and pH6 for dimethylamine and 4-isopropylphenylisocynanate.