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Position-Specific  $^{13}\text{C}$  Fractionation during Liquid-Vapor Transition is Correlated to the Strength of Intermolecular Interaction in the Liquid Phase

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## 2 Abstract

3 The relationship between the strength of the intermolecular interaction in liquid and the position-  
4 specific  $^{13}\text{C}$  fractionation observed during distillation was investigated. A range of molecules  
5 showing different intermolecular interactions in terms of mode and intensity were incorporated in  
6 the study. Although it had previously been suggested that during evaporation the diffusive  $^{13}\text{C}$   
7 isotope effect in the thin liquid layer interfaced with vapor is not position-specific, herein we  
8 show that this is not the case. In particular, the position-specific effect was demonstrated for a  
9 series of alcohols. Our hypothesis is that intermolecular interactions in the liquid phase are the  
10 source of position-specific  $^{13}\text{C}$  fractionation observed on the molecule. A clear trend is observed  
11 between the  $^{13}\text{C}$  isotope effect of the carbon bearing the heteroatom of chemical function and the  
12 relative permittivity, the solvent hydrogen-bond acidity and the solvent hydrogen-bond basicity,  
13 while only a weak trend was observed when using the  $^{13}\text{C}$  content of the whole molecule.  
14 Furthermore two families of products appeared when using the hydrogen-bond acidity parameter  
15 for the correlation by distinguishing H-acceptors and H-donors molecules to those H-acceptors  
16 only. This strongly reinforces the hypothesis of an important role of the  $^{13}\text{C}$  positioned close to  
17 the interaction center.

18

## 19 Keywords

20 Position-specific isotope fractionation; isotope ratio monitoring  $^{13}\text{C}$  NMR spectrometry;  
21 Volatilization, Distillation, Craig-Gordon model

22

## 23 **Introduction**

24 Stable isotopes were widely used in the past to study the nature of phase transfer processes like  
25 liquid-vapor transfer (References Jancso and van Hook, book of Wolfberg et al, etc.).<sup>12</sup> Past  
26 studies used fully substituted isotopic molecules for which large isotope effects are observed  
27 which could be better measured with past analytical techniques. Progress in analytical techniques  
28 has led to the development of Compound-Specific Isotope Analysis (CSIA) capable of  
29 monitoring stable isotope ratios at natural abundance ratios. With the help of CSIA, the  
30 mechanisms of phase transfer processes were furthermore investigated and elucidated (Hunkeler  
31 and Jeannotat, Kuder, Huang, etc.). However, it has been shown that CSIA based on isotope  
32 ratio monitoring by Mass Spectrometry (irm-MS) is not always sufficient to describe the <sup>13</sup>C  
33 fractionation during the whole evaporation phenomenon. Recently, we have reported the study of  
34 several liquid-vapor transition processes using isotope ratio monitoring by <sup>13</sup>C Nuclear Magnetic  
35 Resonance spectrometry (irm-<sup>13</sup>C NMR) in order to simulate position-specific fractionation  
36 during evaporation.<sup>3</sup> We have shown that Position-Specific Isotope Analysis (PSIA) by irm-<sup>13</sup>C  
37 NMR can provide new insights into physical processes, including in circumstances in which  
38 CSIA may not detect any effect on the whole molecule.<sup>4</sup> Furthermore, bulk <sup>13</sup>C composition  
39 ( $\delta^{13}\text{C}_{\text{bulk}}$ ) analysis (CSIA), obtained by irm-MS, only indicates which isotopologue reacts  
40 preferentially in the studied process, whereas PSIA shows which isotopomer is the most sensitive  
41 (see Figure 1 for a further definition).

42 Isotope fractionation is conveniently described by the isotopic fractionation factor  $\alpha$  or the  
43 isotope effect IE and is associated with discrimination between the behavior of isotopomers.<sup>5</sup> A  
44 previous study showed that the Craig-Gordon isotope model, originally derived for water  
45 evaporation,<sup>6</sup> is also valid for organic liquids as demonstrated by Kuder and collaborators,<sup>7</sup>

46 especially for the description of the volatilization of nonpolar organic liquids with air-side  
47 limitation of the volatilization rate.<sup>4</sup> In the Craig-Gordon model in its original form, it is assumed  
48 that the diffusive effect in the stagnant liquid  $\epsilon_{\text{diff-liq}}$  (thin liquid layer interfaced with vapor, see  
49 ref 4) is not position-specific, i.e. is independent of the position of the  $^{13}\text{C}$  in the molecule.  
50 However, among the compounds studied, ethanol and propan-1-ol both showed a position-  
51 specific behavior. Working with the hypothesis that intermolecular interactions in the liquid  
52 phase were the source of position-specific  $^{13}\text{C}$  fractionation observed on the molecule collected  
53 from the vapor phase, we have therefore generated a modified Craig-Gordon equation to take  
54 these position-specific interactions into account.<sup>4</sup>

55 The most widespread non-covalent molecular interaction is hydrogen bonding. The strength of  
56 the hydrogen bond depends on the properties of both the hydrogen-bond acceptor (HBA) and the  
57 hydrogen-bond donor (HBD).<sup>8</sup> Recently, a specific methodology has been proposed by which  
58 both solvent hydrogen-bond basicity and solvent hydrogen-bond acidity can be quantified,  
59 leading to the parameters  $\beta_1$ <sup>9</sup> and ET(30),<sup>10</sup> respectively.  $\beta_1$  is linked to the original scale of  
60 Kamlet and Taft<sup>11</sup> but is specific for the solvent scales. Thus, the scale of solvent hydrogen-bond  
61 basicity was established by the method that compares the  $^{19}\text{F}$  NMR chemical shift of 4-  
62 fluorophenol and 4-fluoroanisole in hydrogen-bond acceptor solvent. In addition to the empirical  
63 parameter describing the hydrogen-bond acidity  $\alpha_1$  (from Kamlet-Taft), the quantitative solvent  
64 polarity parameter ET(30) was introduced. This is based on the negative solvachromism of 2,6-  
65 diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (known as betaine 30).<sup>12</sup> Weaker  
66 interactions are encompassed under van der Waals,  $\pi$ -bonding<sup>13</sup> or halogen-bond<sup>14</sup> interactions  
67 that explain intermolecular associations between apolar molecules, molecules possessing an

68 aromatic-ring, or halogen-containing compounds. The unit accounting for these interactions is the  
69 relative permittivity,<sup>15</sup> previously known as the dielectric constant  $\text{diE}$ .<sup>11</sup>

70 The goal of the present work was to investigate the relationship between the strength of the  
71 intermolecular interaction in liquid and the position-specific  $^{13}\text{C}$  fractionation observed during  
72 vaporization. We asked three fundamental questions: “Does the presence of  $^{13}\text{C}$  in the molecule  
73 increase (or decrease) the interaction?”, “Is this interaction stabilized in a specific  $^{13}\text{C}$   
74 isotopomer?”, and “What is the influence of the proximity of  $^{13}\text{C}$  to the interaction site?” To  
75 answer these questions conditions are required in which the isotope fractionation measured  
76 should reflect the transition liquid-vapor only with the influence on the liquid phase, but with no  
77 further isotope effect in the vapor phase. These conditions are essentially met in distillation in  
78 which no diffusive boundary layer is occurring when the compounds are boiling. Furthermore,  
79 this process is quick, simple, and known to induce significant isotope effects in  $^2\text{H}$  and  $^{13}\text{C}$ .<sup>16</sup>  
80 Hence, this allows insight into isotope effects occurring on the liquid side. To express the isotope  
81 effect during the liquid-vapor transition we used the nomenclature already proposed for such  
82 transformation.<sup>16a</sup> In the case of a small transformation of the substrate, such as the collection of a  
83 very small distillate volume ( $\leq 3\%$ ), any associated isotope effects can readily be detected in the  
84 distillate, but impact negligibly on the isotopomer composition of the remaining liquid. The  
85 corresponding fractionation factor  $\alpha$  was defined in the classical literature as separation factor  $\alpha$   
86 (Jancso and Van Hook, 1974):

$$87 \quad \alpha = (N'/N)_{\text{vap}} / (N'/N)_{\text{liq}} \quad (1)$$

88 where  $N'$  and  $N$  are the mole fractions of light and heavy isotopomers respectively in the system  
89 at equilibrium. The specific-isotope fractionation of site  $i$  (the isotopomer with  $^{13}\text{C}$  at position  
90 isotopomer  $i$ ) is then defined as the experimental fractionation factor  $\alpha_{\text{exp}}$ :

$$\alpha_{\text{exp}, i} = (^{13}\text{C}/^{12}\text{C})_{i, \text{vap}} / (^{13}\text{C}/^{12}\text{C})_{i, \text{liq}} \quad (2)$$

92  
93 Equation 2 is adapted to more recent work on stable isotopes where ratios are measured and  
94 expressed as abundance of heavy isotopes divided by abundance of light isotopes (Aelion et al,  
95 2010). Thus, a normal isotope effect leads to  $\alpha_{\text{exp}} < 1$ : i.e. the liquid (distillate) is impoverished in  
96 heavy isotopes with respect to the vapor (starting product), while an inverse isotope effect  
97 favoring the heavy atom in the vapor gives  $\alpha_{\text{exp}} > 1$ . This is the convention that is used in the  
98 present work. Several compounds were selected with respect to their physicochemical properties  
99 in terms of hydrogen-bond capabilities, or more generally their intermolecular interactions. The  
100 code of the samples used and the carbon numbering are shown in Table 1. The alcohols are  
101 clearly hydrogen-bond acceptors and donors (amphiprotic solvents). Other chemical functions,  
102 such as those which involve heteroatoms, could be polar and/or hydrogen-bond acceptors.  
103 Furthermore, Br and Cl atoms may generate a halogen-bond. Two apolar compounds, toluene and  
104 *n*-heptane were also distilled for comparison. All the experiments were conducted at natural  
105 abundance isotope composition.

106

## 107 **Experimental**

### 108 *Chemicals*

109 Methyl *tert*-butyl ether (99.8%), *n*-heptane (99%), toluene (99.9%), bromoethane (98%),  
110 trichloroethylene (99.5%), propan-1-ol (99.7%), propan-2-ol (99%), butan-1-ol (99.7%), *tert*-  
111 butanol (99.5%), 2-methyl-2-butanol (99%), pentan-1-ol (99%), cyclohexanol (99%), ethyl  
112 acetate (99.9%), acetonitrile (99.9%), and 4-heptanone (98%), were obtained from Sigma-  
113 Aldrich. Ethanol (99.8%), methanol (98%) and chloroform (98%) were purchased from VWR

114 Prolabo and acetone (99.5%) from Alfa Aesar. DMSO- $d_6$ , dioxane- $d_8$  and  $CD_3CN$  were obtained  
115 from Eurisotop. Tris(2,4-pentadionato)chromium(III) [ $Cr(Acac)_3$ ] was from Merck.

116

### 117 *Distillation experiments*

118 For each experiment, 100 mL of pure compound was introduced into a 1 L round bottom flask  
119 and distillation was carried out using a Cadiot distillation column equipped with a Teflon  
120 spinning band (see Murray and reference therein for its characteristics<sup>17</sup>). This distillation  
121 equipment allows the reflux to be rigorously controlled. Once reflux conditions were reached, the  
122 distillate was collected up to approximately 3% maximum of the mass of the starting substrate.  
123 The distillate was then submitted to  $^{13}C$ -irm-EA/MS and irm- $^{13}C$  NMR.

124 In the present study, distillation has been chosen in order to study liquid-vapor equilibrium  
125 effects, because this method is quick and easy to perform which is perfect to study a large panel  
126 of chemical compounds in very controlled conditions. The inconvenient of this protocol is that  
127 the resulting isotope effects are magnified, especially using a spinning band distillation column  
128 which displays many theoretical plates and the capability of maintaining the system at  
129 equilibrium. Nevertheless, these overexpressed isotopic fractionations have the same direction  
130 (normal or inverse) as those observed in static phase equilibrium (Refs. Jeannotat+Hunkeler) or  
131 vapor pressure measurements (Jancso+Van Hook, 1974).

132 In the case of isotopic studies, the concept of “pure compound” needs to be further defined. The  
133 term “pure” means that there is only one chemical species present. However, it is in fact a  
134 mixture of all potential isotopologues and isotopomers of the considered compound. As an  
135 example, a sample of pure ethanol contains four types of molecules isotopically different in  $^{13}C$   
136 (see Figure 1).

137



138  $^{13}\text{C}$  -irm-EA/MS

139 Bulk  $^{13}\text{C}$  abundance ( $\delta^{13}\text{C}_{\text{bulk}}$ ) was determined by irm-MS using an Integra2 spectrometer (Sercon  
140 Instruments, Crewe, UK) linked to a Sercon elemental analyser (EA) (Sercon Instruments,  
141 Crewe, UK). A precise amount of each compound was weighted into tin capsules (2x5 mm,  
142 Thermo Fisher scientific) using a  $10^{-6}$  g precision balance (Ohaus Discovery DV215CD) to give  
143 approx. 0.4 mg of carbon for each compound. Great care was taken to ensure that there was no  
144 leakage from the capsule. First, during the weighing of the Volatile Organic Compound (VOC)  
145 introduced into the tin-capsule, the sealed capsule was left on the balance for a short delay to  
146 verify the stability of the mass. No change in mass indicated that the capsule was effectively  
147 sealed. Secondly, the percentage of carbon was checked by the operator by comparing this value  
148 with that usually obtained on the solid working reference. This gives a check in relation to the  
149 intensity of the signal of the ions obtained from the  $\text{CO}_2$  generated from the different  
150 isotopologues ( $m/z = 44, 45, 46$ ). Moreover, each sample is analyzed three times to ensure  
151 measuring true  $\delta^{13}\text{C}$  values and a repeatability study has also been performed in a previous study  
152 (see ref 3) which demonstrates the capability of these experimental conditions to measure the  
153 bulk isotopic composition of VOCs such as MTBE. The  $\delta^{13}\text{C}$  (‰) values were expressed relative  
154 to the international reference (Vienna-Pee Dee Belemnite, V-PDB) using the relationship:  
155  $\delta^{13}\text{C}_{\text{VPDB}}(\text{‰}) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$ .<sup>18</sup> The instrument was calibrated for  $\delta^{13}\text{C}$  using the  
156 international reference materials NBS-22 ( $\delta^{13}\text{C}_{\text{PDB}} = -30.03 \text{ ‰}$ ), SUCROSE-C6 ( $\delta^{13}\text{C}_{\text{PDB}} = -$   
157  $10.80 \text{ ‰}$ ), and IAEA-CH-7 PEF-1 ( $\delta^{13}\text{C}_{\text{PDB}} = -32.15 \text{ ‰}$ ) (IAEA, Vienna, Austria) and  
158 instrumental deviation followed via a laboratory working standard of glutamic acid.

159

160 *Isotope ratio monitoring  $^{13}\text{C}$  NMR spectrometry (irm- $^{13}\text{C}$  NMR)*

161 The sample preparation consisted of the successive addition in a 4 mL vial of the compound, the  
162 lock substance and the relaxation agent  $\text{Cr}(\text{Acac})_3$  (which acts to decrease the longitudinal  
163 relaxation time  $T_1$ ).<sup>19</sup> The respective amount of each was adapted according to (i) the  $T_1$  values  
164 of the analyte, (ii) the reciprocal solubility with the deuterated solvents and/or the relaxation  
165 agent and (iii) the  $^{13}\text{C}$  NMR spectrum: no peak overlapping. The exact preparation procedures  
166 were described previously.<sup>3</sup> Quantitative  $^{13}\text{C}$  NMR spectra were recorded using an AVANCE I  
167 400 spectrometer (Bruker Biospin, Wissembourg, France), fitted with a 5 mm i.d.  $^1\text{H}/^{13}\text{C}$  dual<sup>+</sup>  
168 probe, carefully tuned at the recording frequency of 100.61 MHz, or a Bruker AVANCE III 400  
169 spectrometer fitted with a 5 mm i.d. BBFO probe tuned at the recording frequency of 100.62  
170 MHz. The temperature of the probe was set to 303 K. Spectra were acquired without tube  
171 rotation. Isotope  $^{13}\text{C}/^{12}\text{C}$  ratios were calculated from processed spectra as described previously.<sup>3,</sup>  
172 <sup>20</sup>

173

174 *Calculation of  $\mathcal{E}_{\text{bulk}}$  and  $\mathcal{E}_i$* 

175 The isotope effect IE (‰) was obtained from the equation:

176 
$$\text{IE} = (\alpha - 1) \times 1000 \quad (3)$$

177 where the isotope effect (IE) is calculated as explained in detail in the work of Julien *et*  
178 *al.*<sup>4</sup> where IE is equivalent to  $\epsilon$ .179 Here  $\text{IE} < 0$  is a normal isotope effect is observed while  $\text{IE} > 0$  indicates an inverse isotope effect.

180

181 **Results and discussion**182 *Position-specific  $^{13}\text{C}$  analysis by NMR*

183 PSIA may be performed by fragmenting the molecule in such a way that, after subsequent  
184 analysis of the resulting fragments by irm-MS,<sup>21</sup> information on the isotopomer composition is  
185 retrieved. This fragmentation can conveniently be achieved on-line by pyrolysis prior to mass  
186 spectrometry analysis.<sup>22</sup> However, this approach is not easily applicable to molecules containing  
187 more than 4 carbon atoms. In contrast, quantitative NMR gives access to all spectrally-resolved  
188 sites in the compound, i.e. relative titration of the <sup>13</sup>C isotopomers constituting the molecule  
189 when irm-<sup>13</sup>C NMR conditions are used.<sup>23</sup> It offers the advantage of directly analyzing the target  
190 molecule, hence avoiding the risk of technique-associated fractionation. The precision in irm-  
191 NMR depends primarily on the signal-to-noise ratio (SNR) and it is described in the present work  
192 by a standard deviation of 0.3‰ on the  $\delta^{13}\text{C}$  scale (‰). We have shown in a previous study that,  
193 under these conditions, the uncertainty on  $\text{IE}_i$  is  $\pm 0.2\text{‰}$  (95% confidence level)<sup>24</sup> for the  
194 evaporation processes and the molecules used.<sup>3</sup> This value is the threshold of significance that  
195 will be used for the interpretation of the results presented.

196

### 197 *Bulk <sup>13</sup>C and position-specific fractionation upon distillation*

198 Zhang *et al.* showed that distillation can be a useful tool to determine isotopic fractionation  
199 factors at equilibrium during liquid-vapor transitions.<sup>16a</sup> For a given compound heated at reflux,  
200 an equilibrium between the liquid and the vapor is established. When a very small amount of  
201 distillate is collected ( $\leq 3\%$ ) it can be assumed that the isotope profile of the distillate represents  
202 the isotopic composition of the vapor at equilibrium with the liquid. These authors measured <sup>2</sup>H  
203 the position-specific isotope effect (by irm-<sup>2</sup>H NMR) as well as isotope bulk effect (by irm-MS)  
204 on heteroatoms (<sup>13</sup>C, <sup>15</sup>N and <sup>18</sup>O) in a series of organic molecules containing typical functional  
205 groups. They observed that the isotopic fractionation enrichments varied with (i) the element, (ii)

206 the type of chemical function and (iii) the  $^2\text{H}$  isotopomers ( $^2\text{H}$  position in the molecule). We  
207 previously confirmed that distillation under similar conditions also led to position-specific  $^{13}\text{C}$   
208 fractionation in ethanol: the distillate is enriched in  $^{13}\text{C}$  mainly on the  $\text{CH}_2$  moiety.<sup>3, 16b</sup> In the  
209 present work we have extended this protocol to other organic compounds that have several  
210 specific chemical characteristics in terms of substituent, heteroatoms and chemical functions. The  
211 isotopomer profiles expressed as  $\delta^{13}\text{C}_{\text{bulk}}$ ,  $\delta^{13}\text{C}_i$  and  $\Delta\delta^{13}\text{C}$  (difference between the  $\delta^{13}\text{C}$  in  
212 distillate and  $\delta^{13}\text{C}$  in starting material) are summarized in Table 2. Two key observations can be  
213 made. First, in the majority of cases the distillate is enriched in  $^{13}\text{C}$ . Second, a large variability of  
214  $\Delta\delta^{13}\text{C}_i$  within and between molecules is seen. In a previous study (ref 4),  $^{13}\text{C}$  isotopic  
215 fractionation associated with distillation has been determined analyzing the remaining substrate  
216 after distillation of 93 to 98% of pure compound. Under these conditions, it can be assumed that  
217 the detected isotopic fractionation corresponds to the isotope effect associated with the liquid-  
218 vapor transformation without contribution of the diffusion. In the present case, the distillate has  
219 been analyzed in order to study the isotopic fractionation associated with distillation. The low  
220 distillation yields (around 3%) along with the presence of multiple theoretical plates both induce  
221 the detection of larger isotope effects than the analysis of the remaining substrate. However, this  
222 overestimation of the isotopic fractionation associated with distillation is not misleading for the  
223 interpretation because the intramolecular distribution of the fractionation is conserved. As an  
224 example, the analysis of the distillation tail of TCE showed an isotope effect of +0.8‰ mostly  
225 located on the carbon bearing two chlorine atoms (see ref 4) and this isotope effects is about  
226 +5.1‰ in the present study but still mostly located on the same carbon position (see Table 3).  
227 The distillation protocol employed in this study doesn't allow obtaining true values of liquid-  
228 vapor equilibrium isotope effect but it is still available to study its mechanism. Table 1 shows the

229 numbering of the carbon positions, according to the shielding order of the peak in the  $^{13}\text{C}$  NMR  
230 spectrum. This shielding (or deshielding) is associated with the electron density surrounding the  
231 given carbon atom and depends to some degree on the polarity of the neighboring heteroatoms  
232 (or chemical functions). The isotopomer 'C-1' which contains the  $^{13}\text{C}$  directly linked to this  
233 heteroatom is clearly identified in alcohols. It is, however, less straightforward for other chemical  
234 species, such as ester, ketone, nitrile, etc. (see Table 1 for the attribution of C-1 in each  
235 molecule). In general, the  $^{13}\text{C}$  ratio at the C-1 is seen to be the most effected by the liquid-vapor  
236 transition, i.e. it is the isotopomer containing  $^{13}\text{C}$  at that position which distils first. Exceptions  
237 are notable for acetonitrile (acni), for which  $\delta^{13}\text{C}_{\text{C-1}}$  is depleted, and for *n*-heptane (hept) and  
238 toluene (tol) for which there is a homogeneous enrichment effect for each carbon. In the series of  
239 alcohols, a further effect is observed: the preference of the  $^{13}\text{C}$  isotopomer for the vapor phase is  
240 diminished, stabilized or even increased according to the distance from the OH function along the  
241 carbon chain. Thus, in butan-1-ol (al-5) and pentan-1-ol (al-8)  $\Delta\delta^{13}\text{C}$  upon distillation is large for  
242 the carbon-bearing OH (C-1): +5‰ and +4.1‰, lower for the inner carbon(s) of the chain:  
243 +3.0/+2.6‰ and +2.7/+2.0‰ and slightly larger for the terminal carbon positions: +2.9 and  
244 +2.7‰ respectively (Table 2). This is clear evidence that the presence of  $^{13}\text{C}$  close to the OH  
245 function influences strongly the facility for the molecule to be transformed into vapor.  
246 Interestingly, a remote effect is associated with the terminal carbon.

247

#### 248 *Position-specific $^{13}\text{C}$ fractionation versus intermolecular interactions*

249 The above discussion of the alcohol series addresses the issue of interactions within the liquid. As  
250 a first deduction, it appears that the proximity of  $^{13}\text{C}$  to the OH function favors the distillation of  
251 the corresponding isotopomer. Therefore the question is: does  $\varepsilon_{\text{C-1}}$  (the amplitude of the  $^{13}\text{C}$

252 fractionation or the discrimination between the isotopomer C-1 and the other isotopomers)  
253 represent the strength of the interaction between alcohol molecules in the liquid state? Among  
254 several parameters used for describing the potential level of intermolecular associations, the  
255 relative permittivity (diE) is the most commonly used. Table 3 reports the isotope effects ( $IE_{\text{bulk}}$   
256 and  $IE_{\text{C-1}}$ ), diE, ET(30) and  $\beta_1$  (see Introduction for a definition of these terms). Unfortunately,  
257 these parameters are not available in the literature for all the molecules studied, but sufficient  
258 values are available to establish trend lines. These lines have been drawn according to the visual  
259 distribution of data points, which means that Figures 2 and 3 do not present real correlations  
260 between isotope effects and the physical properties of compounds but, rather, lines drawn without  
261 *a priori* to make the discussion easier. Trend lines have been drawn using Microsoft Excel so  
262 they have an equation and a root mean square ( $R^2$ ) which also are detailed in Figures captions in  
263 order to help the discussion the results. Figures 2 and 3 illustrate the potential trends between the  
264 isotope effects and diE, ET(30) and  $\beta_1$ , respectively. A clear trend is observed between  $IE_{\text{C-1}}$  and  
265 diE, ET(30) and a weaker for  $\beta_1$  (Figures 2), while a loose trend can even be discerned between  
266  $IE_{\text{bulk}}$  and diE, ET(30) and  $\beta_1$  (Figures 3). This strongly reinforces the deduction of an important  
267 role of the  $^{13}\text{C}$  isotopomer C-1 in the interaction between molecules.

268 Nevertheless, there are some exceptions which deserve comment. In all cases, toluene (tol) and  
269 even more so *n*-heptane (hept) do not follow these trends: this is readily explained by the lack of  
270 polarity (no diE) and an inability to form H-bonds or, more generally, interactions involving a  
271 specific position in the molecule. Both *n*-heptane and toluene are only able to form van der Waals  
272 and  $\pi$  bonding interactions, respectively, that do not induce any significant position-specific  
273 isotope effect during distillation. Interestingly, the data for bromoethane (brom) do not fit with  
274 the  $\beta_1$  values either (Figure 2c) when it appears to have a behavior similar to alcohols concerning

275 ET(30) trends (Figure 2b). Since the parameters  $\beta_1$  and ET(30) describe the potential interaction  
276 of the molecule as a solvent,<sup>9</sup> it can be seen here that the molecule acts both as solute and solvent,  
277 i.e. in a self-association. Therefore, a molecule may be in a state to give or to receive H (or  
278 another interaction) but not to do both at the same time. Thus bromoethane shows a weak base-  
279 property, with a halogen-type association likely to be occurring.

280 As can be seen from Figure 2b, a clear double trend is observed. One encompasses the alcohols  
281 (al-x), but also chloroform (chlo), which are both H-acceptors and H-donors (a proton can readily  
282 be exchanged with deuterium<sup>25</sup>), and to some extent bromoethane (brom). The case of  
283 chloroform, with the isotope effect associated with its distillation correlating very well with those  
284 for alcohols (See Figure 2b), is interesting. This could be explained by (i) the high electron  
285 density in this molecule and (ii) the resulting presence of the acidic hydrogen. These two features  
286 of chloroform can interact forming a halogen bond and its strength seems to be dependent of the  
287 presence of a <sup>13</sup>C on the central carbon position. Trichloroethene (TCE) presents an isotope effect  
288 mostly located on the carbon bearing the acidic hydrogen that can form hydrogen bonds, but this  
289 compound better correlates with H-acceptors (Figure 2b). Of the remaining products studied, that  
290 are H-acceptors only, acetonitrile (acni), acetone (acet) and ethyl acetate (etac) all show good  
291 correlation with amphiprotic molecules (alcohols) (Figures 2 and 3).

292 A change in the solvation shell of ethanol modifies the <sup>13</sup>C position-specific fractionation. As an  
293 illustration, the distillation of a dilute acidic aqueous ethanol solution (10% v/v with 1 M H<sub>2</sub>SO<sub>4</sub>),  
294 using the same device, leads to the following isotope effect IE, measured on the distillate: bulk,  
295 +3.4‰, C-1, +6.3‰, C-2, +0.5‰. By increasing the H-bond network around the ethanol  
296 molecule, the  $\epsilon_{C-1}$  is accentuated, thus confirming that the isotopomer containing a <sup>12</sup>C at the C-1  
297 position reinforces the intermolecular interaction. Interestingly, the reverse is found for the

298 position C-2 for which it is the isotopomer with a  $^{12}\text{C}$  on the  $\text{CH}_3$  that distils first. The  
299 significance of such behaviors is beyond the scope of this paper, but it is clear that the  $^{13}\text{C}$   
300 position-specific fractionation is sensitive to the types of interaction and to the models of  
301 association: most probably a large network (complex) for alcohols and chloroform versus a  
302 binary association (simple) for the other compounds investigated.

303

### 304 **Conclusion**

305 The main outcomes of this study are two-fold. First, it is shown that position-specific  
306 fractionation in liquid-vapor transitions can occur in a range of molecules. When the molecular  
307 architecture within the liquid enables interactions, then the isotope effect of diffusion  $\epsilon_{\text{diff-liq}}$  (ref  
308 4) is position-specific. This is a novel finding, since up to now it has been considered that  $^{13}\text{C}$   
309 fractionation during diffusion shows a mass effect only, i.e. is not position-specific. These new  
310 data now need to be included in the model of fractionation during the process of volatilization  
311 according to the Craig-Gordon isotope model for organic liquids.<sup>4,7</sup> Second,  $^{13}\text{C}$  position-specific  
312 fractionation appears to be exploitable as a marker of the strength of interactions in the liquid  
313 phase within the self-association framework. Fundamentally, the presence of a  $^{13}\text{C}$  atom in a  
314 molecule according to its position decreases the interaction strength. How the presence of a  $^{13}\text{C}$   
315 acts to (de)stabilize the H-bond in alcohols now needs to be further investigated by theoretical  
316 modelling. Other intermolecular interactions such as the dimerization of carboxylic acids could  
317 also be studied using the same approach. Moreover, more complex systems such as VOCs  
318 diffusive transport in soil could be studied in the same way where the presence of heavy carbon  
319 isotopes should also have an influence on isotopic fractionation associated with diffusion.

320



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325 help with irm-MS measurements and Jérôme Graton and Jean-Yves Lequestel for fruitful  
326 discussions on inter-molecular interactions.

327

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433 **Figure Captions**

434

435 **Figure 1.** Definition of isotopologues and isotopomers: example of ethanol.

436

437 **Figure 2.** Relationship between the isotope effect located on position C-1 ( $IE_{C-1}$ ) and (a) the  
438 relative permittivity (diE), (b) the hydrogen bond acidity (ET(30)),  $y=-0.31x+19.89$ ,  $R^2=0.853$  for  
439 both H-acceptors and H-donors,  $y=-0.80x+34.69$ ,  $R^2=0.938$  for H-acceptors only and (c) the  
440 hydrogen bond basicity ( $\beta_1$ ),  $y=16.1x-6.37$ ,  $R^2=0.619$ .

441

442 **Figure 3.** Relationship between the bulk isotope effect ( $IE_{Bulk}$ ) and (a) the relative permittivity  
443 (diE), (b) the hydrogen bond acidity (ET(30))  $y=-0.20x+13.39$ ,  $R^2=0.359$  for both H-acceptors  
444 and H-donors,  $y=-0.36x+15.65$ ,  $R^2=0.643$  for H-acceptors only and (c) the hydrogen bond  
445 basicity ( $\beta_1$ ).

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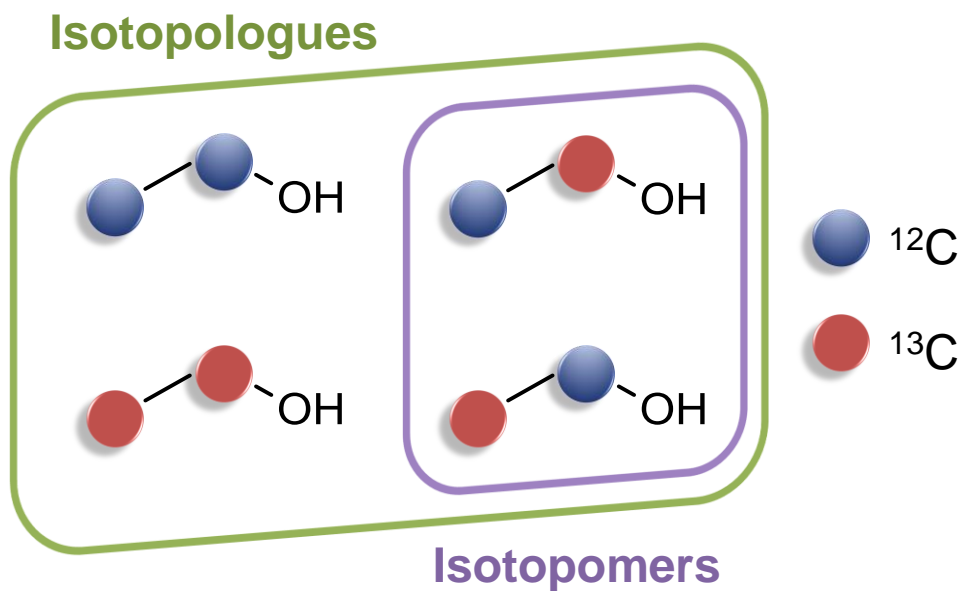
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457 **Figures**

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459 **Figure 1.**

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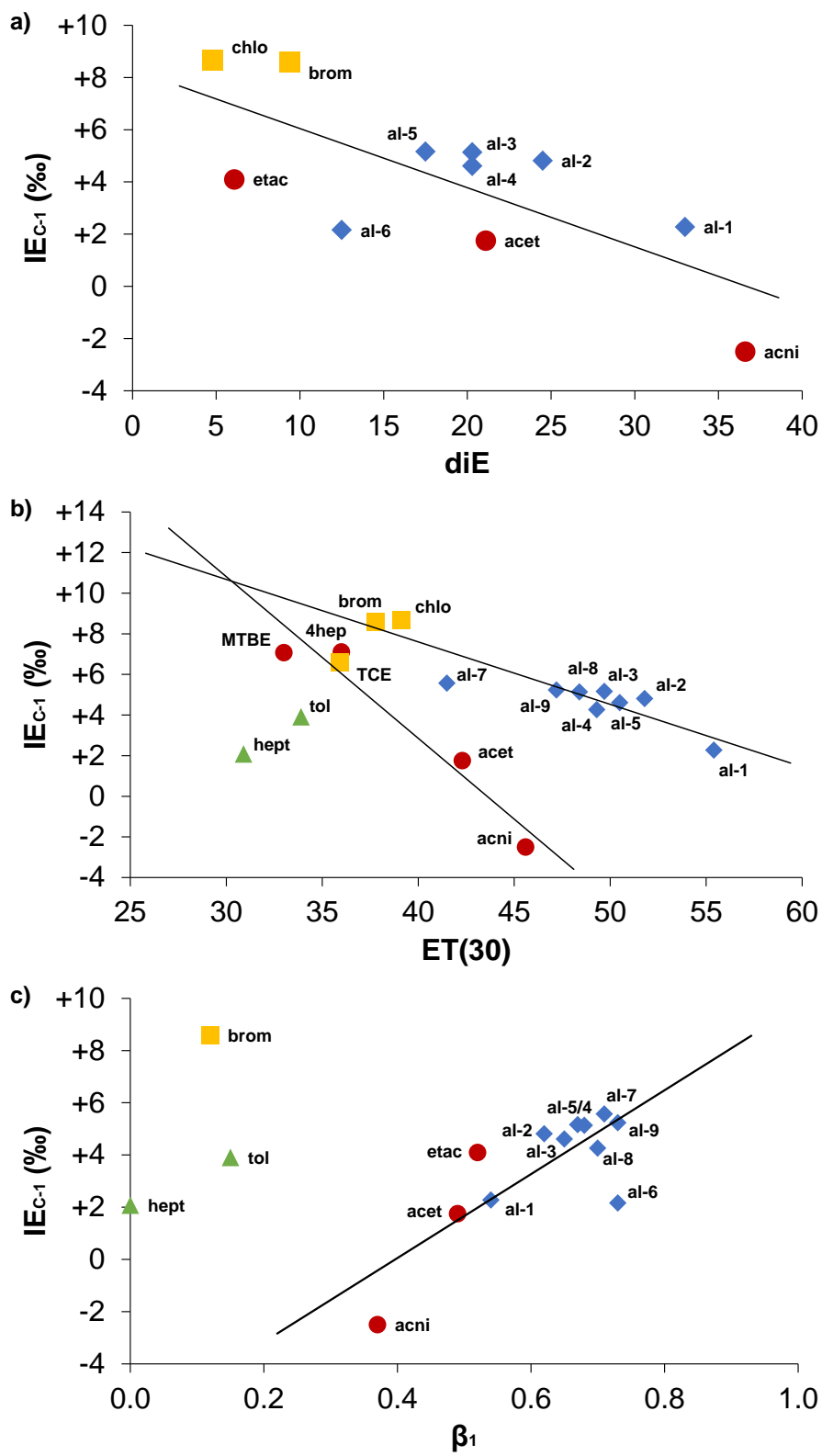
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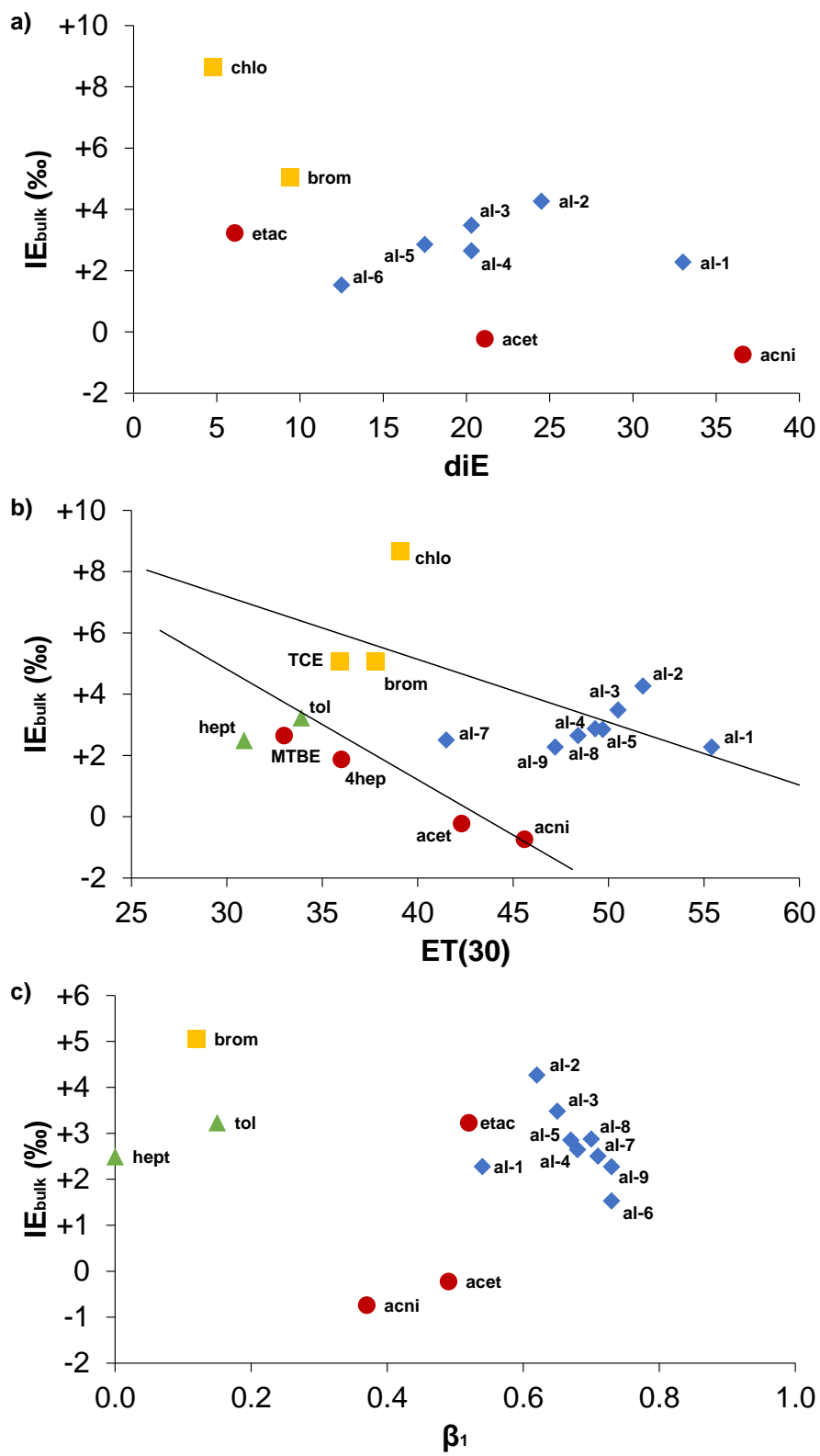
487 **Figure 2.**  
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491 **Figure 3.**  
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493

494 **Table 1.** Molecular structure of each compound investigated with the carbon atoms numbered in  
 495 decreasing chemical shift in the  $^{13}\text{C}$  NMR spectrum. The code of each sample used in Fig. 3 and  
 496 4 and in the Tables is also defined.

497

code	compound	structure	code	compound	structure
al-1	methanol		brom	bromoethane	
al-2	ethanol		TCE	trichloroethylene	
al-3	propan-1-ol				
al-4	propan-2-ol		acet	acetone	
al-5	butan-1-ol		4hep	4-heptanone	
al-6	<i>tert</i> -butanol (TBA)		acni	acetonitrile	$2-1\equiv\text{N}$
al-7	2-methyl-2-butanol		etac	ethyl acetate	
al-8	pentan-1-ol		MTBE	MTBE	
al-9	cyclohexanol		tol	toluene	
chlo	chloroform		hept	<i>n</i> -heptane	

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499

500 **Table 2.**  $^{13}\text{C}$  isotope composition  $\delta$  in ‰ and the difference between  $^{13}\text{C}$  content of the starting  
 501 material and of the distillate  $\delta\Delta$  in ‰ for bulk isotopologue and each isotopomer of the studied  
 502 samples (see Table 1 for denomination and carbon numbering).

503  
 504

	Sample	Bulk	C-1	C-2	C-3	C-4	C-5
al-1	$\delta^{13}\text{C}$ initial	-30.7	-30.7				
	$\delta^{13}\text{C}$ distillate	-28.5	-28.5				
	$\Delta\delta^{13}\text{C}$	+2.2	+2.2				
al-2	$\delta^{13}\text{C}$ initial	-28.9	-32.2	-25.5			
	$\delta^{13}\text{C}$ distillate	-24.8	-27.5	-22.0			
	$\Delta\delta^{13}\text{C}$	+4.2	+4.7	+3.6			
al-3	$\delta^{13}\text{C}$ initial	-32.6	-35.5	-28.1	-34.1		
	$\delta^{13}\text{C}$ distillate	-29.2	-31.1	-25.1	-31.5		
	$\Delta\delta^{13}\text{C}$	+3.4	+4.5	+3.1	+2.6		
al-4	$\delta^{13}\text{C}$ initial	-26.9	-22.6	-29.1			
	$\delta^{13}\text{C}$ distillate	-24.4	-17.6	-27.7			
	$\Delta\delta^{13}\text{C}$	+2.6	+5.0	+1.3			
al-5	$\delta^{13}\text{C}$ initial	-31.0	-42.7	-29.1	-24.9	-28.5	
	$\delta^{13}\text{C}$ distillate	-28.3	-37.7	-26.1	-22.4	-25.6	
	$\Delta\delta^{13}\text{C}$	+2.8	+5.0	+3.0	+2.6	+2.9	
al-6	$\delta^{13}\text{C}$ initial	-25.4	-17.1	-28.2			
	$\delta^{13}\text{C}$ distillate	-23.9	-15.0	-26.9			
	$\Delta\delta^{13}\text{C}$	+1.5	+2.1	+1.3			
al-7	$\delta^{13}\text{C}$ initial	-31.2	-20.6	-28.0	-28.5	-50.5	
	$\delta^{13}\text{C}$ distillate	-28.8	-15.1	-26.3	-27.1	-48.3	
	$\Delta\delta^{13}\text{C}$	+2.4	+5.5	+1.7	+1.4	+2.1	
al-8	$\delta^{13}\text{C}$ initial	-28.3	-36.5	-23.9	-27.8	-26.2	-27.1
	$\delta^{13}\text{C}$ distillate	-25.5	-32.4	-21.3	-25.3	-24.2	-24.4
	$\Delta\delta^{13}\text{C}$	+2.8	+4.1	+2.6	+2.5	+2.0	+2.7
al-9	$\delta^{13}\text{C}$ initial	-24.4	-39.0	-17.2	-18.9	-26.9	
	$\delta^{13}\text{C}$ distillate	-22.2	-33.9	-17.8	-17.4	-23.0	
	$\Delta\delta^{13}\text{C}$	+2.2	+5.1	-0.5	+1.5	+3.9	
chlo	$\delta^{13}\text{C}$ initial	-41.7					
	$\delta^{13}\text{C}$ distillate	-33.4					
	$\Delta\delta^{13}\text{C}$	+8.4					

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507 **Table 2.** (continued)

	Sample	Bulk	C-1	C-2	C-3	C-4	C-5
brom	$\delta^{13}\text{C}$ initial	-11.6	-12.7	-10.4			
	$\delta^{13}\text{C}$ distillate	-6.6	-4.2	-9.0			
	$\Delta\delta^{13}\text{C}$	+5.0	+8.6	+1.5			
TCE	$\delta^{13}\text{C}$ initial	-29.6	-30.9	-28.3			
	$\delta^{13}\text{C}$ distillate	-24.6	-24.5	-24.8			
	$\Delta\delta^{13}\text{C}$	+4.9	+6.4	+3.5			
acet	$\delta^{13}\text{C}$ initial	-22.3	+8.8	-37.9			
	$\delta^{13}\text{C}$ distillate	-22.6	+10.6	-39.1			
	$\Delta\delta^{13}\text{C}$	-0.2	+1.8	-1.2			
4hep	$\delta^{13}\text{C}$ initial	-28.2	-23.5	-26.7	-29.0	-31.4	
	$\delta^{13}\text{C}$ distillate	-26.4	-16.5	-26.4	-27.5	-30.2	
	$\Delta\delta^{13}\text{C}$	+1.8	+7.0	+0.3	+1.4	+1.2	
acni	$\delta^{13}\text{C}$ initial	-24.5	-2.7	-46.3			
	$\delta^{13}\text{C}$ distillate	-25.2	-5.2	-45.3			
	$\Delta\delta^{13}\text{C}$	-0.7	-2.5	+1.0			
etac	$\delta^{13}\text{C}$ initial	-30.6	-19.5	-48.1	-30.7	-29.6	
	$\delta^{13}\text{C}$ distillate	-27.5	-15.5	-42.5	-31.0	-29.0	
	$\Delta\delta^{13}\text{C}$	+3.1	+4.0	+5.6	-0.3	+0.5	
MTBE	$\delta^{13}\text{C}$ initial	-28.6	-22.1	-39.3	-27.3		
	$\delta^{13}\text{C}$ distillate	-26.1	-15.1	-37.4	-25.9		
	$\Delta\delta^{13}\text{C}$	+2.6	+7.0	+1.8	+1.4		
tol	$\delta^{13}\text{C}$ initial	-22.8	-10.4	-23.3	-26.4	-26.1	-23.5
	$\delta^{13}\text{C}$ distillate	-19.6	-6.5	-21.1	-22.9	-22.6	-20.3
	$\Delta\delta^{13}\text{C}$	+3.2	+3.9	+2.2	+3.6	+3.6	+3.2
hept	$\delta^{13}\text{C}$ initial	-27.5	-25.3	-34.3	-26.3	-27.6	
	$\delta^{13}\text{C}$ distillate	-25.1	-23.2	-31.2	-24.0	-25.0	
	$\Delta\delta^{13}\text{C}$	+2.4	+2.0	+3.1	+2.3	+2.6	

508

509 **Table 3.** Isotope effect IE in ‰ for bulk and isotopomer C-1, relative permittivity (dielectric  
 510 constant) diE, solvent hydrogen-bond acidity ET(30) and hydrogen-bond basicity  $\beta_1$  of the  
 511 studied samples (see Table 1 for denomination).

512

code	IE <sub>bulk</sub>	IE <sub>C-1</sub>	ET(30)	$\beta_1$	dielectric constant
al-1	+2.3	+2.3	55.4	0.54	33.0
al-2	+4.3	+4.8	51.8	0.62	24.5
al-3	+3.5	+4.6	50.5	0.65	20.3
al-4	+2.6	+5.1	48.4	0.68	20.3
al-5	+2.9	+5.2	49.7	0.67	17.5
al-6	+1.5	+2.2	nd	0.73	12.5
al-7	+2.5	+5.6	41.5	0.71	nd
al-8	+2.9	+4.3	49.3	0.70	nd
al-9	+2.3	+5.2	47.2	0.73	nd
chlo	+8.7	+8.7	39.1	nd	4.8
brom	+5.1	+8.6	37.8	0.12	9.4
TCE	+5.1	+6.6	35.9	nd	nd
acet	-0.2	+1.8	42.3	0.49	21.1
2hep	+1.3	-0.2	nd	nd	nd
3hep	+1.8	+1.1	nd	nd	nd
4hep	+1.9	+7.1	36.0	nd	nd
acni	-0.7	-2.5	45.6	0.37	36.6
etac	+3.2	+4.1	nd	0.52	6.1
MTBE	+2.6	+7.1	33.0	nd	nd
TAME	+3.5	+6.7	nd	nd	nd
tol	+3.2	+3.9	33.9	0.15	nd
hept	+2.5	+2.1	30.9	0.00	nd

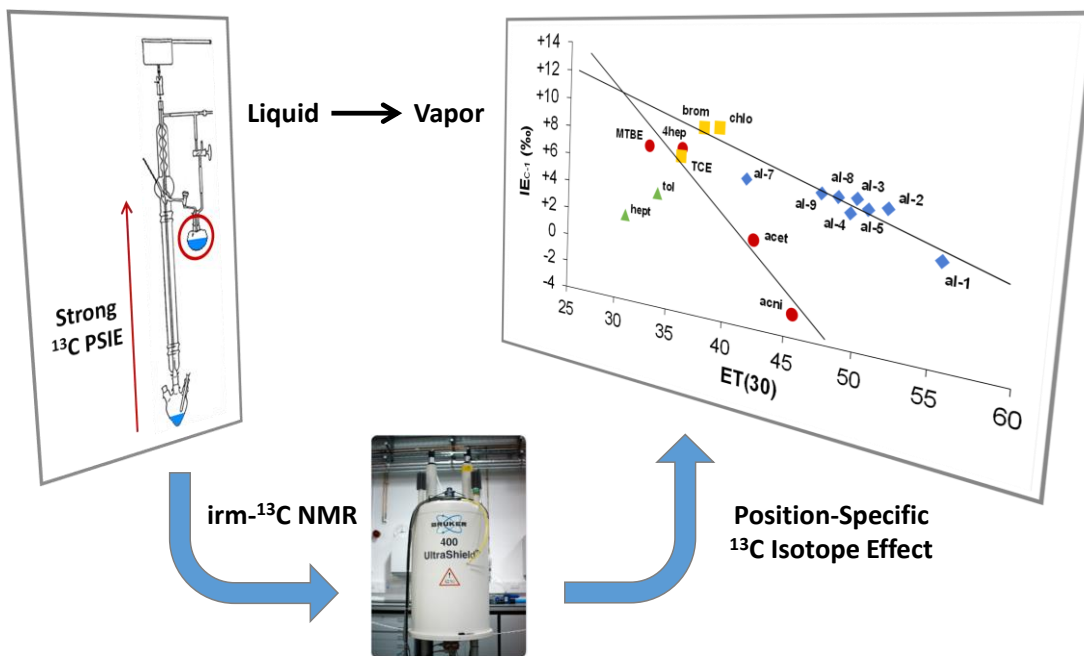
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517 **Table of Contents (TOC) graphic**  
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