

## Supplementary Information

### **Continuous flow esterification of a *H*-phosphinic acid, and transesterification of *H*-phosphinates and *H*-phosphonates under MW conditions**

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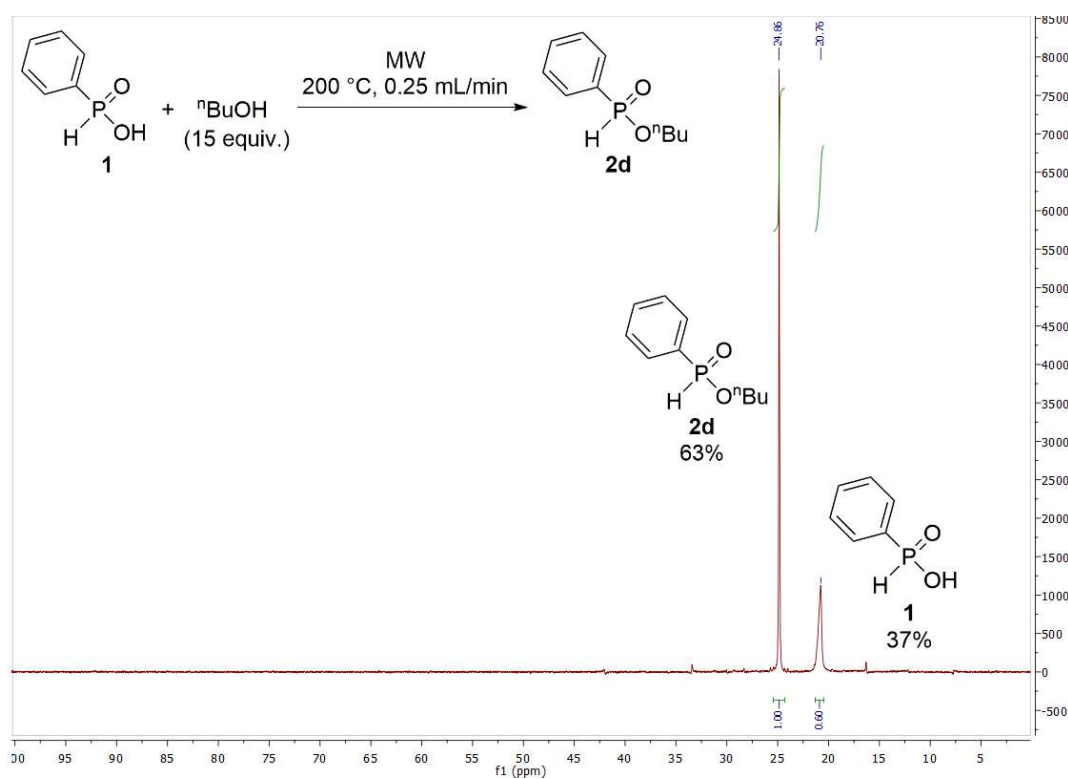
- 1) Representative examples for the calculation of the conversions in the esterifications and transesterifications .....pg. S1–S3
- 2) <sup>31</sup>P, <sup>13</sup>C and <sup>1</sup>H NMR spectra of the new dialkyl phosphites with different alkoxy groups (**4a-d**) .....pg. S4–S9

## 1) Representative examples for the calculation of the conversions in the esterifications and transesterifications

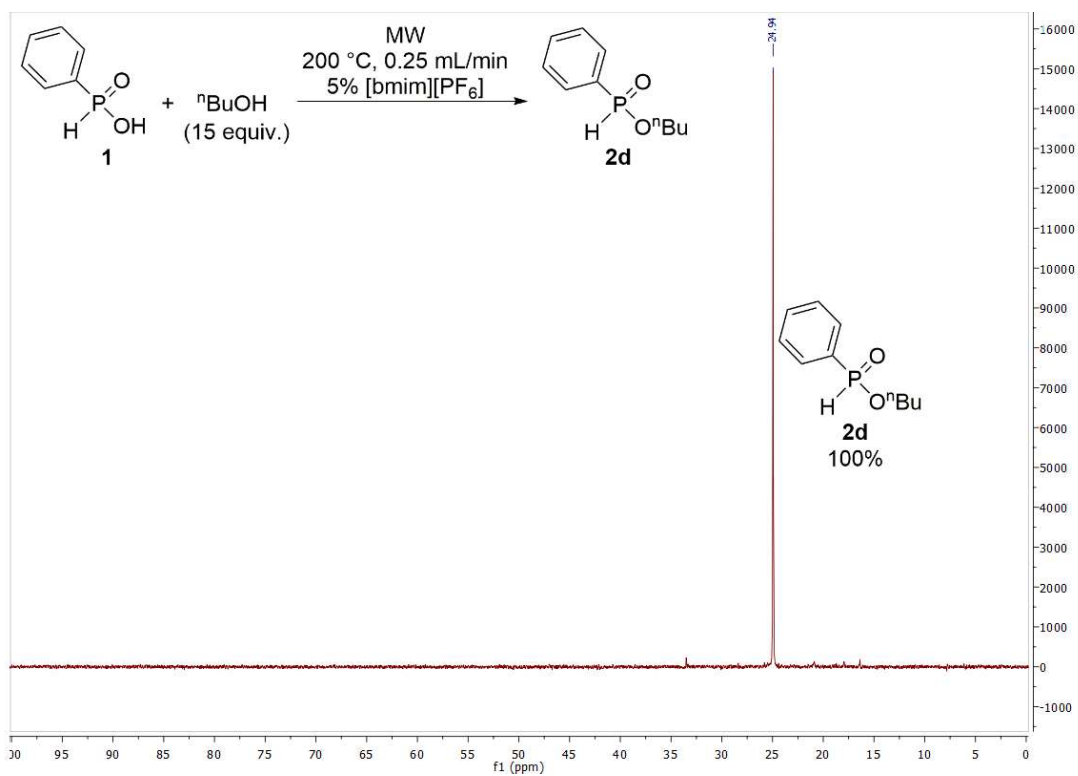
Conversions were obtained based on relative  $^{31}\text{P}$  NMR integrals. Typical examples are illustrated below. However, conversions and compositions shown in Tables 1-7 are the results of 3 parallel experiments with a pointing error of <5%. Peaks listed in Tables 8 and 9 show the shifts of the purified compounds.

### Direct esterification of phenyl-*H*-phosphinic acid (**1**) with butanol

Conversion: 63% (Table 2/Entry 5)

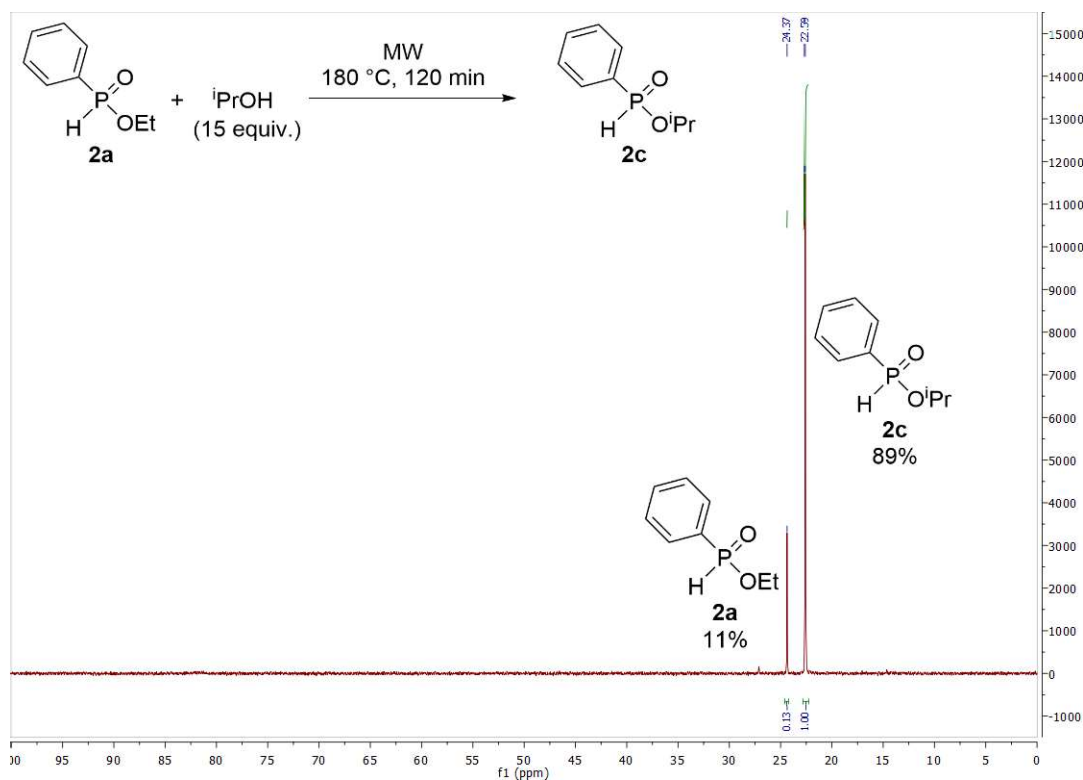


Conversion: 100% (Table 2/Entry 11)



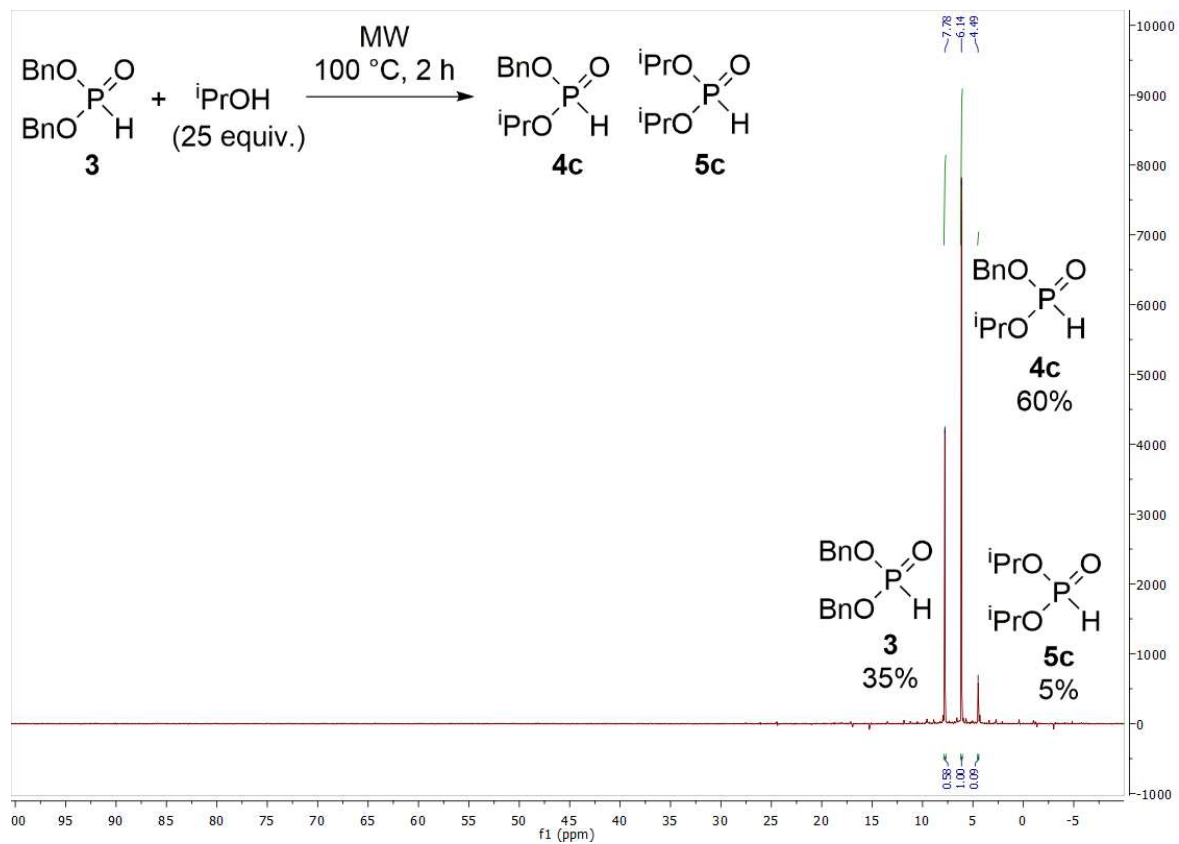
### Transesterification of ethyl phenyl-*H*-phosphinate (**2a**)

Conversion: 89% (Table 3/Entry 7)



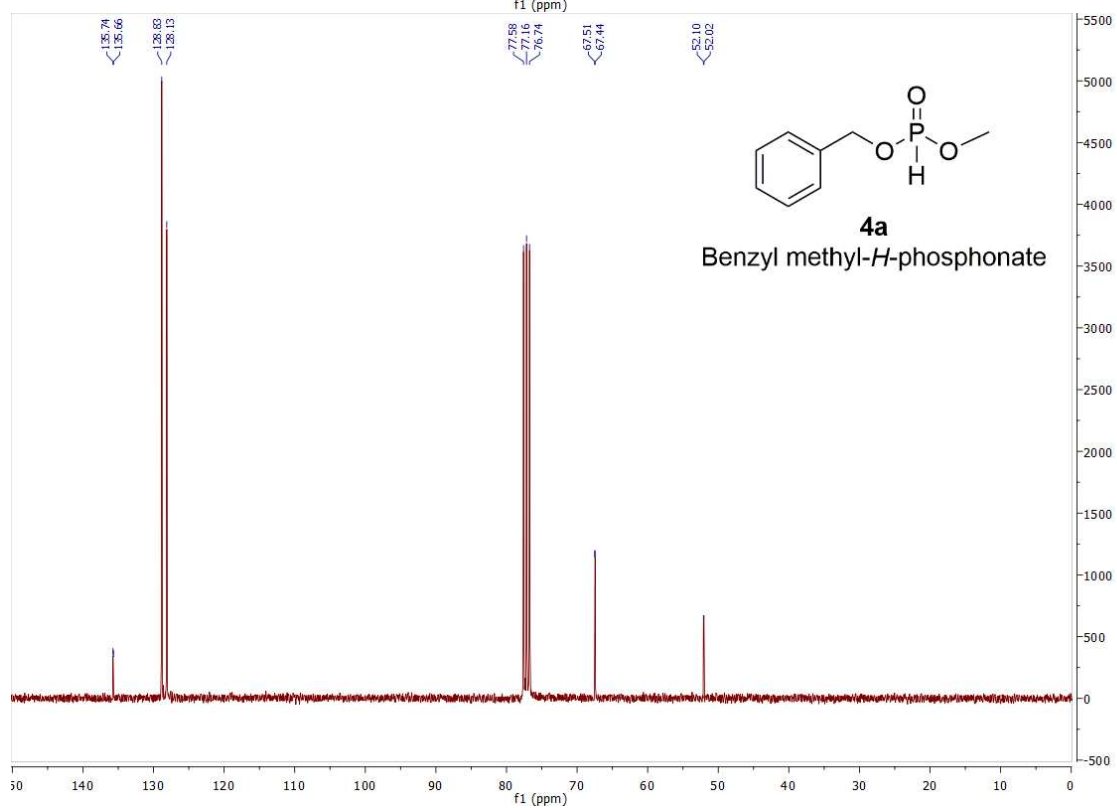
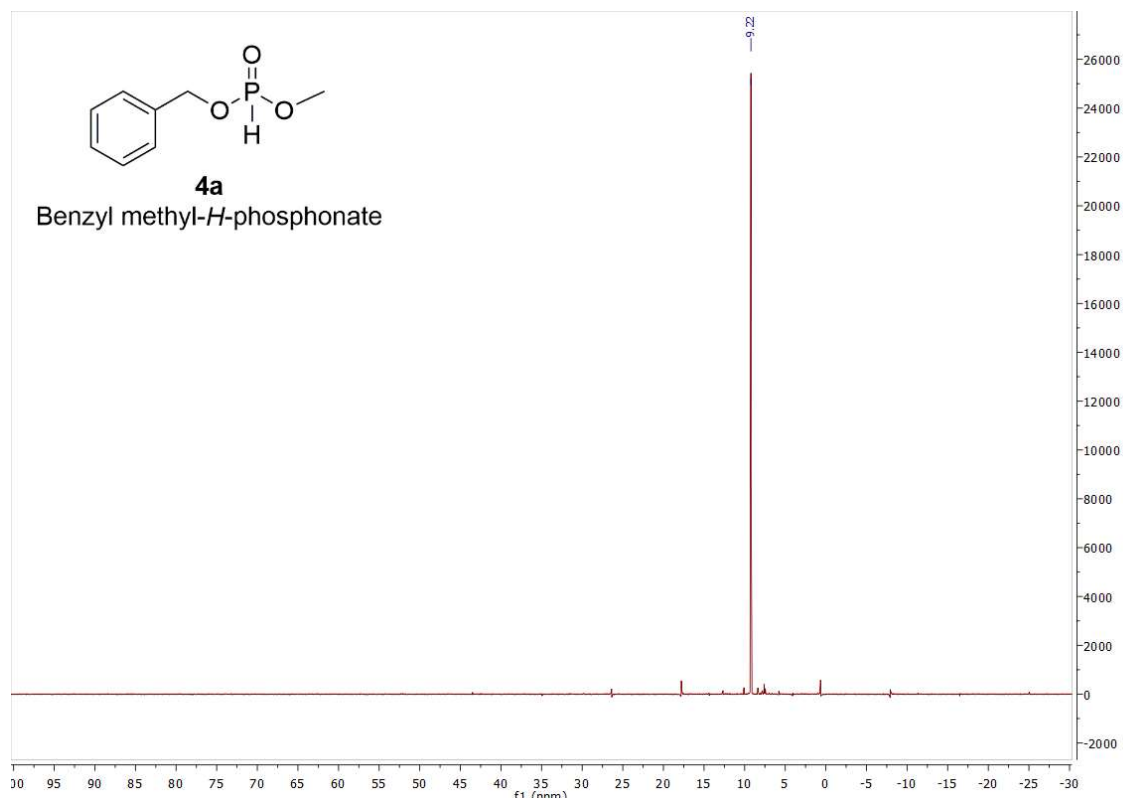
### Transesterification of dibenzyl phosphite (**3**)

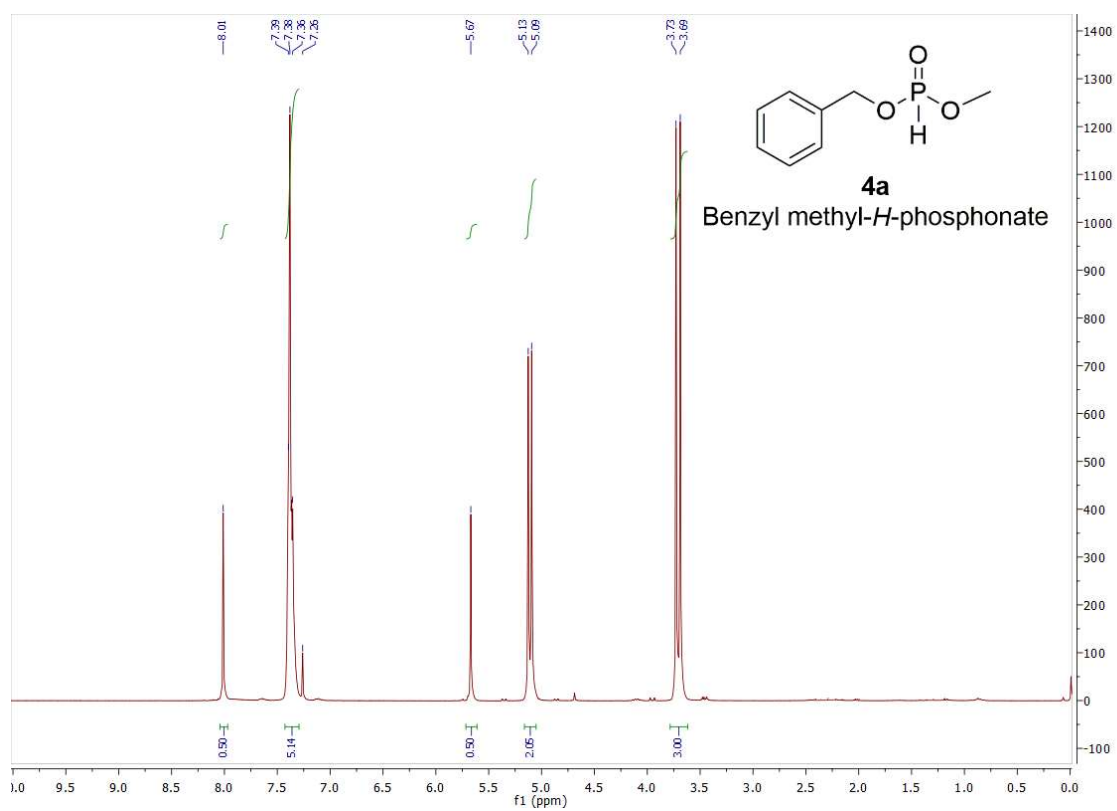
Composition: 35% (**3**), 60% (**4c**) and 5% (**5c**) (Table 5/Entry 13).



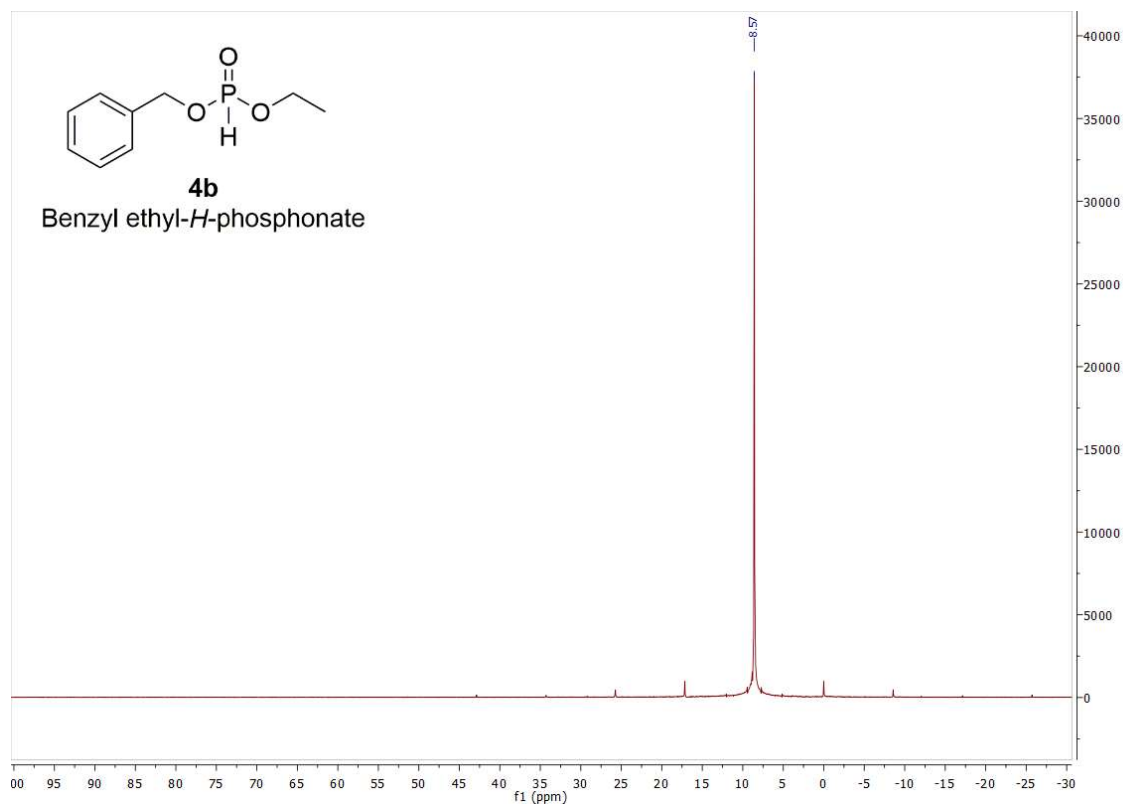
2)  $^{31}\text{P}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of the new dialkyl phosphites with different alkoxy groups (4a–d)

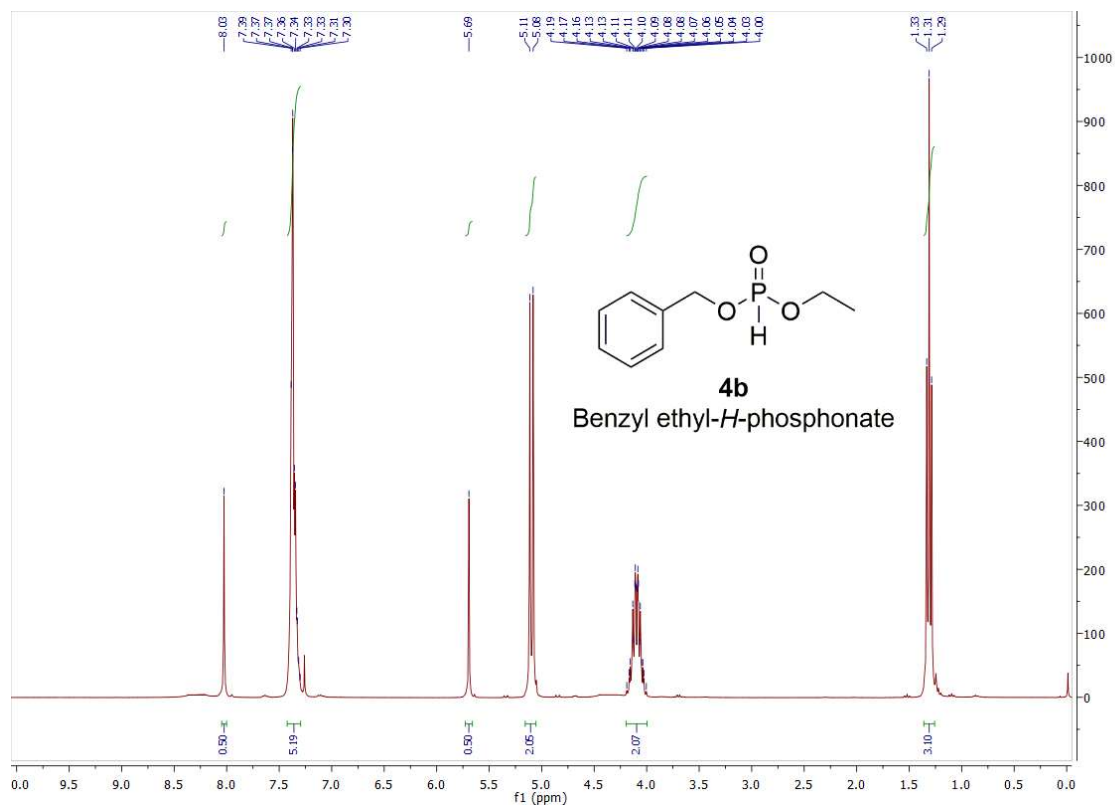
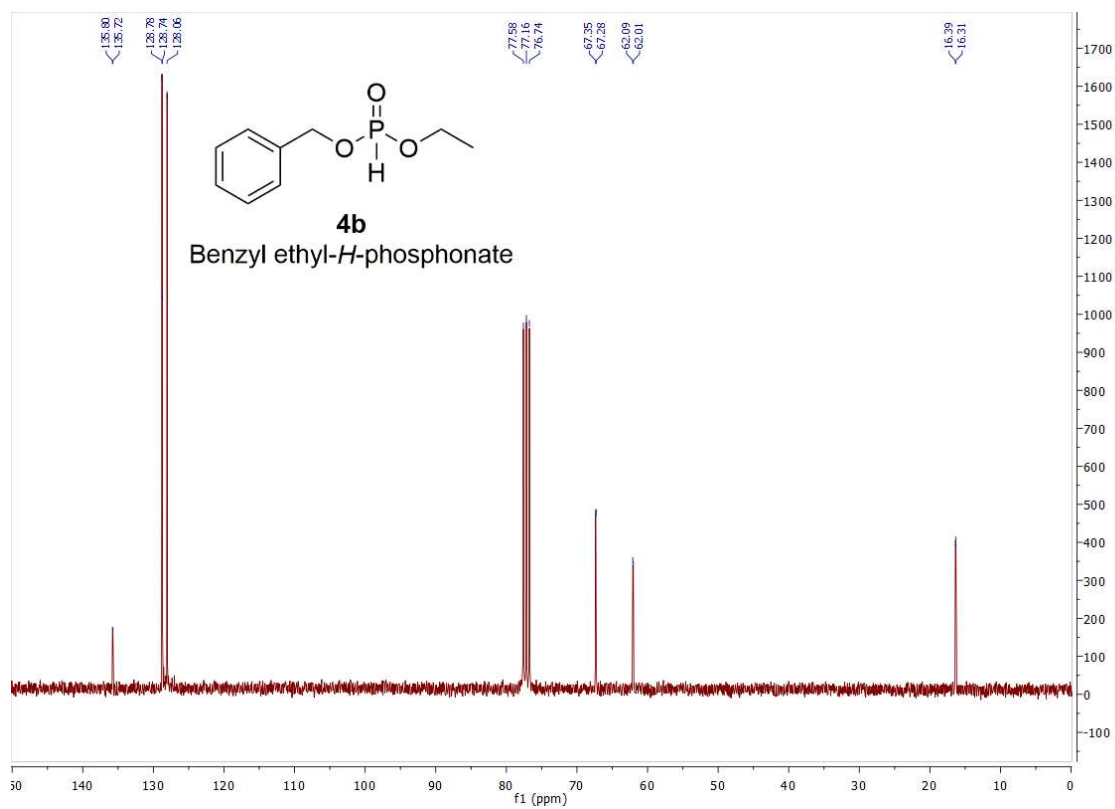
Benzyl methyl-*H*-phosphonate (4a)



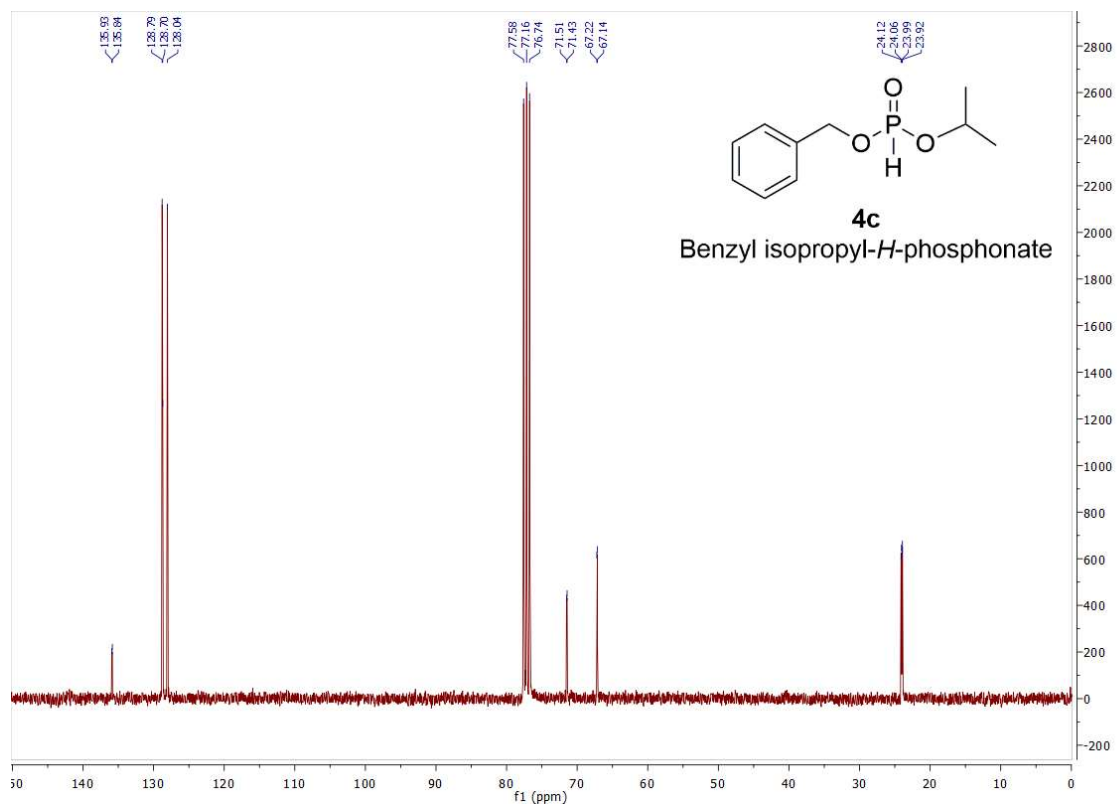
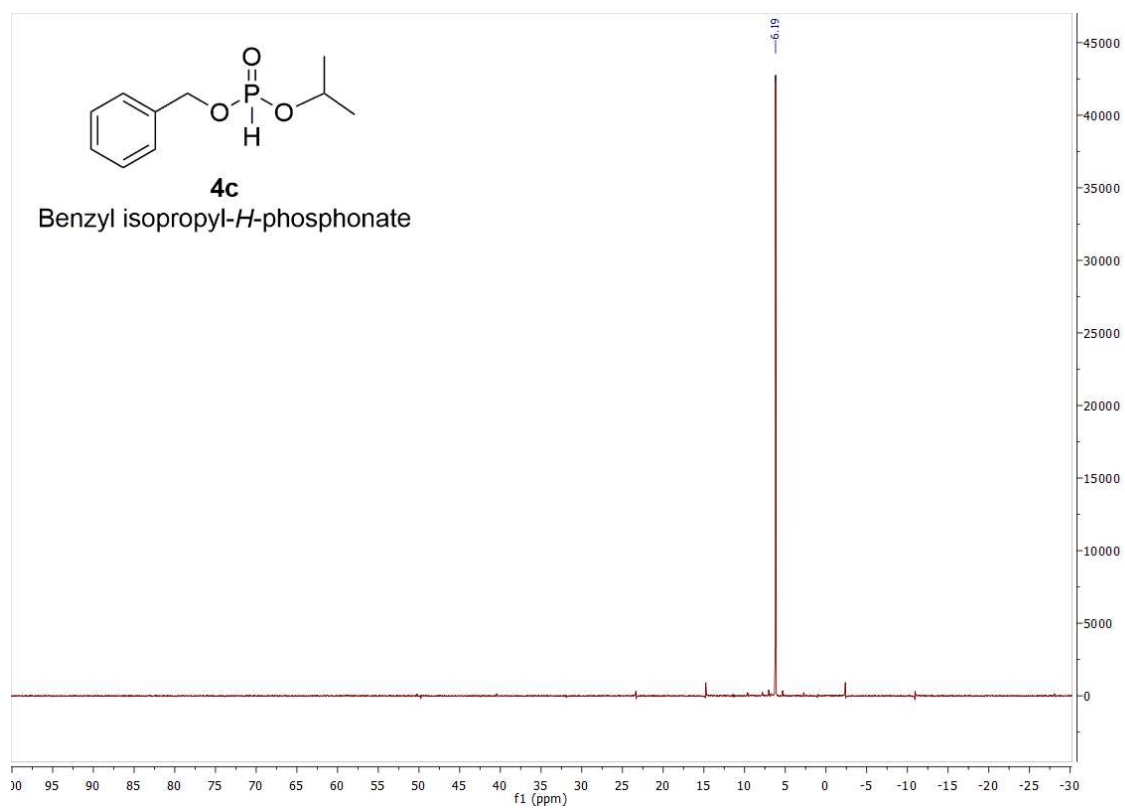


Benzyl ethyl-*H*-phosphonate (**4b**)

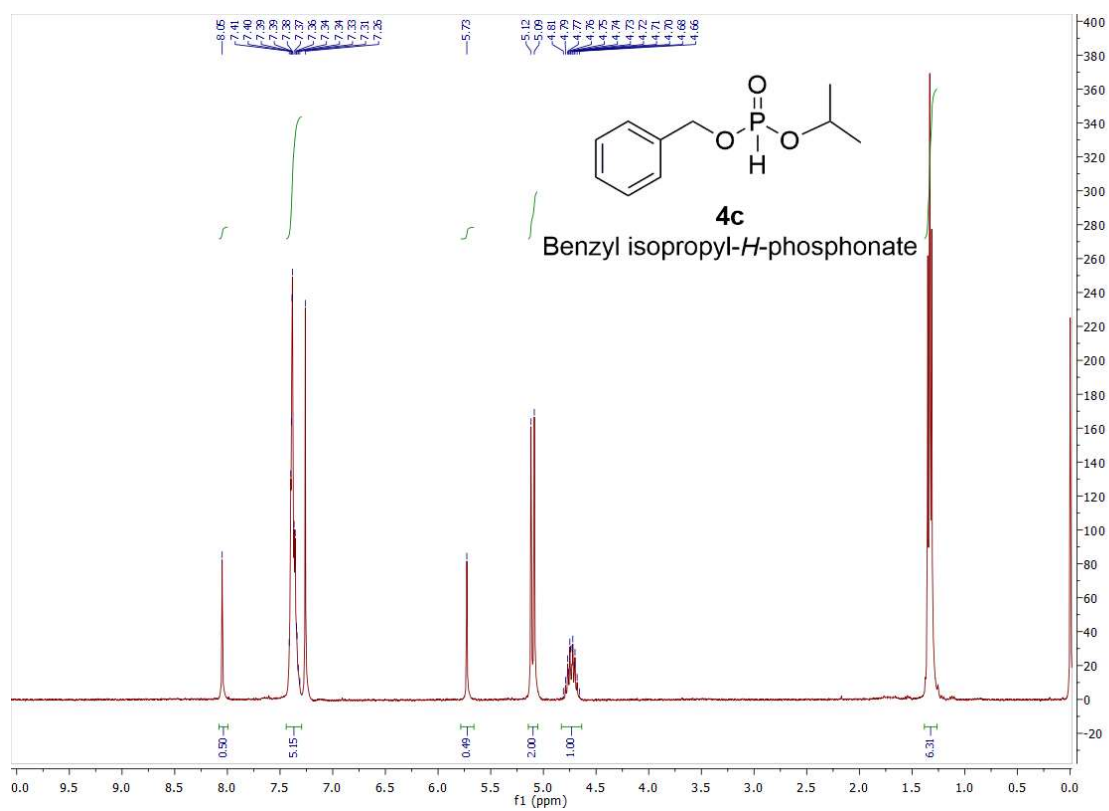




# Benzyl isopropyl-*H*-phosphonate (**4c**)







Benzyl butyl-*H*-phosphonate (**4d**)

