

## **CIDNP as a tool to unveil the reaction mechanism: Interaction of mixed phosphonium-iodonium ylide with *p*-methoxyphenylacetylene**

Irina I. Levina,<sup>a</sup> Valery F. Tarasov,<sup>b</sup> Tatyana A. Podrugina<sup>a,c</sup> and Tatiana D. Nekipelova<sup>a\*</sup>

<sup>a</sup> *Emanuel Institute of Biochemical Physics RAS, Kosygin st. 4, Moscow, 119334 Russia.*

E-mail: [nekip@sky.chph.ras.ru](mailto:nekip@sky.chph.ras.ru)

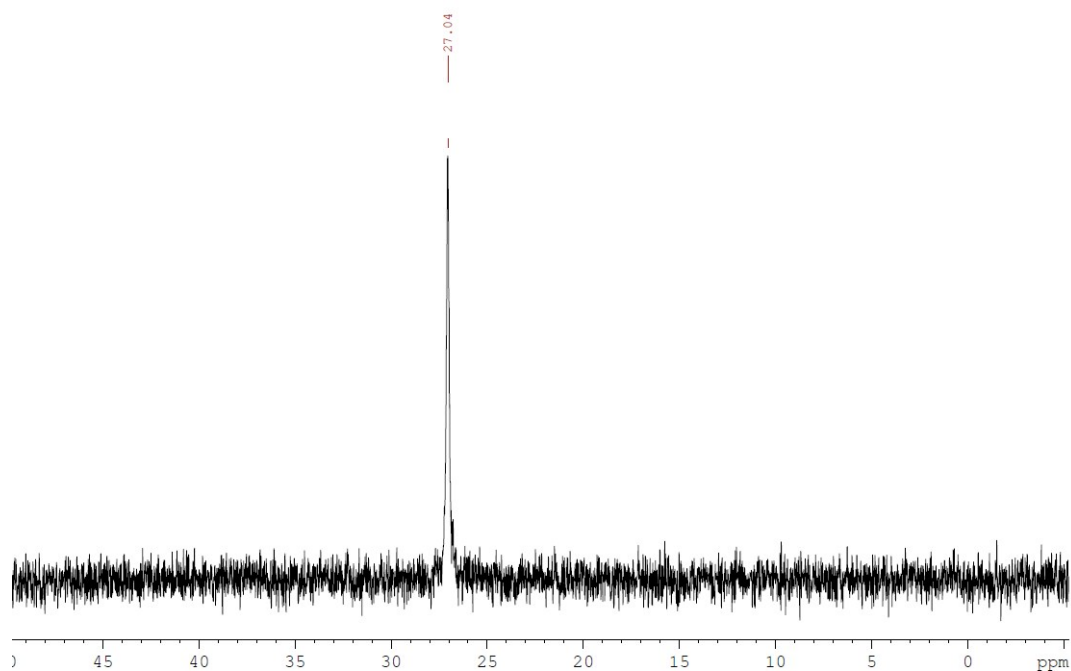
<sup>b</sup> *Semenov Institute of Chemical Physics RAS, Kosygin st. 4, Moscow, 119991 Russia*

<sup>c</sup> *Department of Chemistry, Lomonosov Moscow State University, Lenin Hills 1, Moscow, 119991 Russia*

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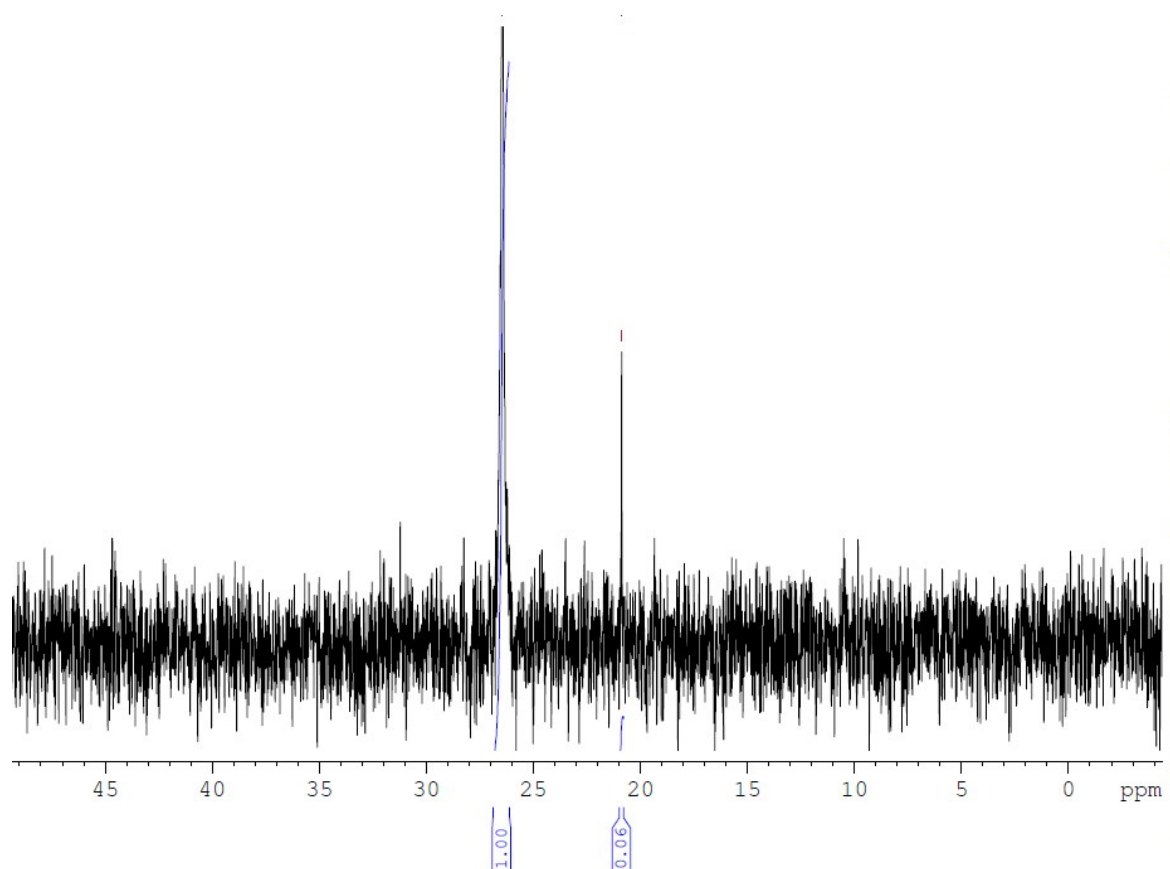
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1. Time-evolution of the  $^{31}\text{P}$  NMR spectra after mixing ylide **1** and acetylene **2**



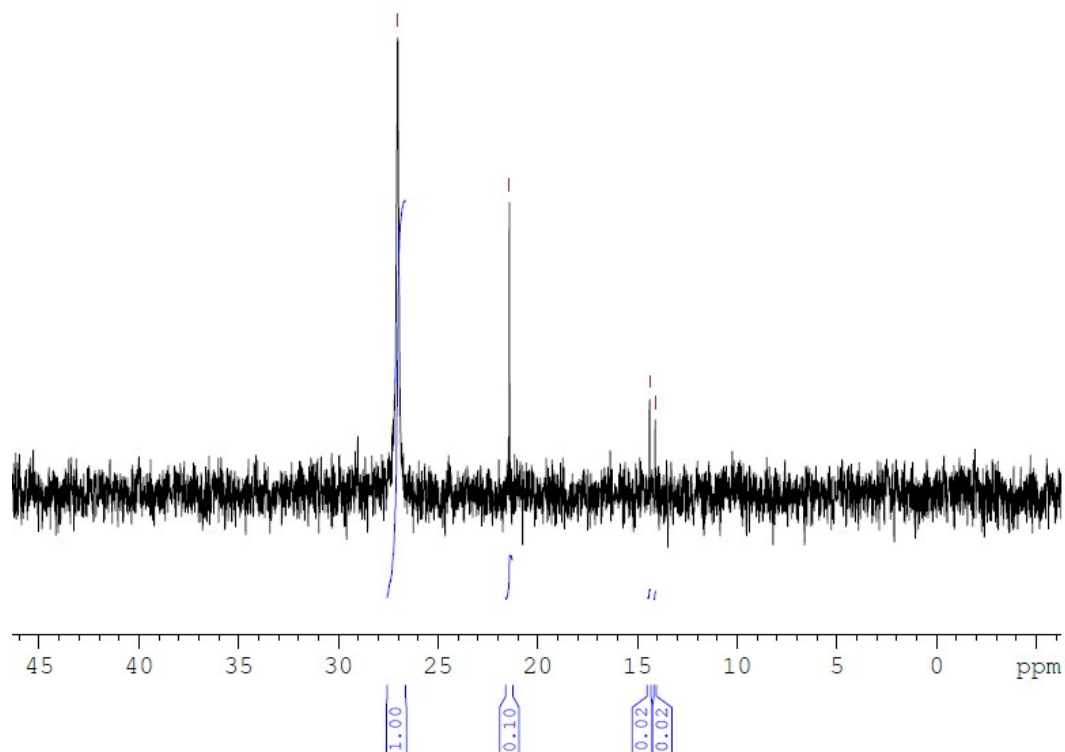
**Fig. S1.**  $^{31}\text{P}$  NMR spectrum of ylide **1**.

Phosphonium salt **5** ( $\delta$  21.4 ppm) is the first product detected in 120 s after mixing the reagents. (Fig. S2)



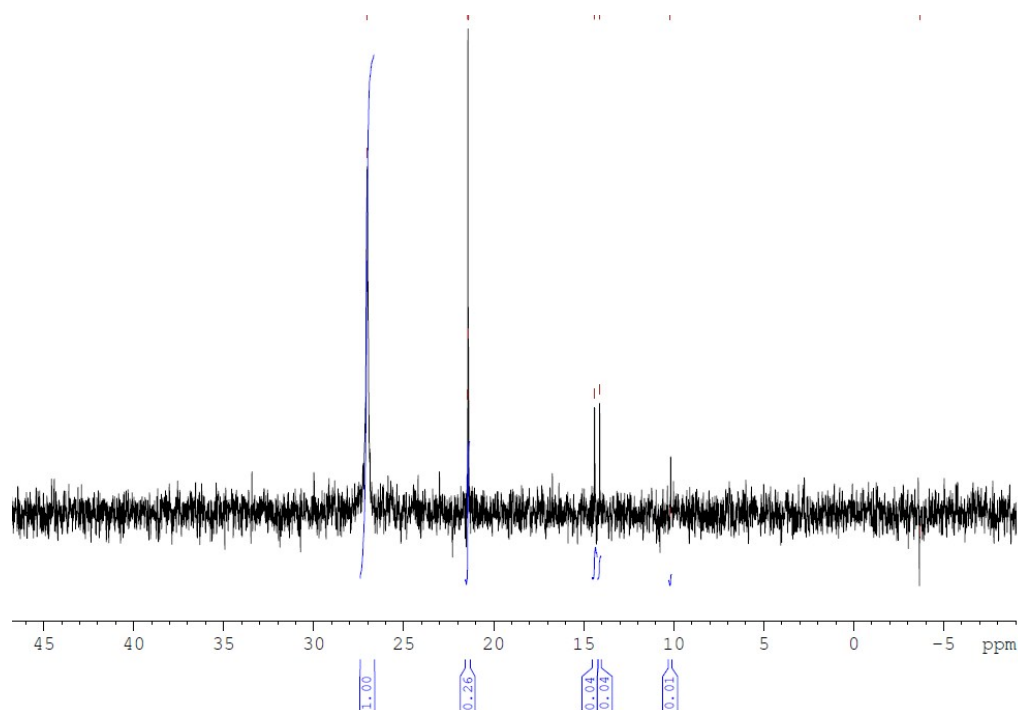
**Fig. S2.**  $^{31}\text{P}$  NMR spectrum of the mixture **1** + **2** at 120 s after mixing

In 6 s two more products appear ( $\delta$  14.4 and 14.1 ppm), with the increasing signal of salt **5**. The product with  $\delta$  14.4 ppm is unidentified, and the signal at 14.1 ppm belongs to **4**. (Fig. S3)



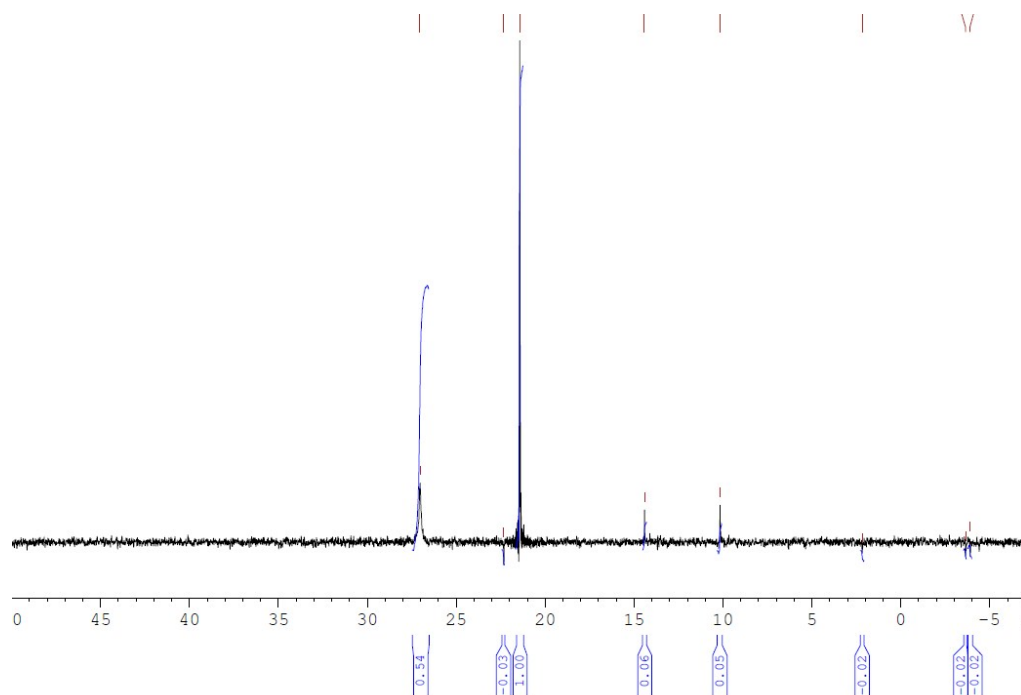
**Fig. S3.** <sup>31</sup>P NMR spectrum of the mixture **1 + 2** at 126 s after mixing.

The signal of **5** continues to grow and at 150 s new intermediates with  $\delta$  10.2 and  $-3.65$  ppm appear, with the latter signal being emissive. (Fig. S4)



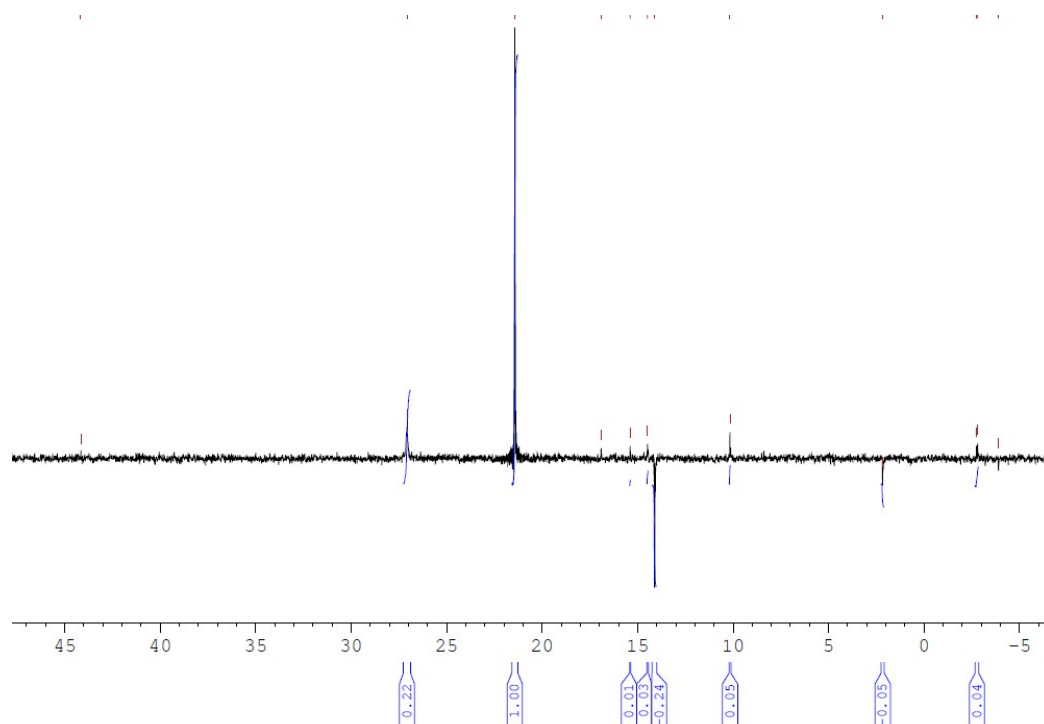
**Fig. S4.** <sup>31</sup>P NMR spectrum of the mixture **1 + 2** at 150 s after mixing.

During the following 48 s the ylide concentration decreases, the signal of salt **5** drastically increases, the signals at 14.4 and 14.1 ppm pass their maxima and the signal of **4** becomes zero at 198 s. By this time several signals of low negative intensity appear at  $\delta$  22.3, 2.2 and -3.9 ppm. (Fig. S5)



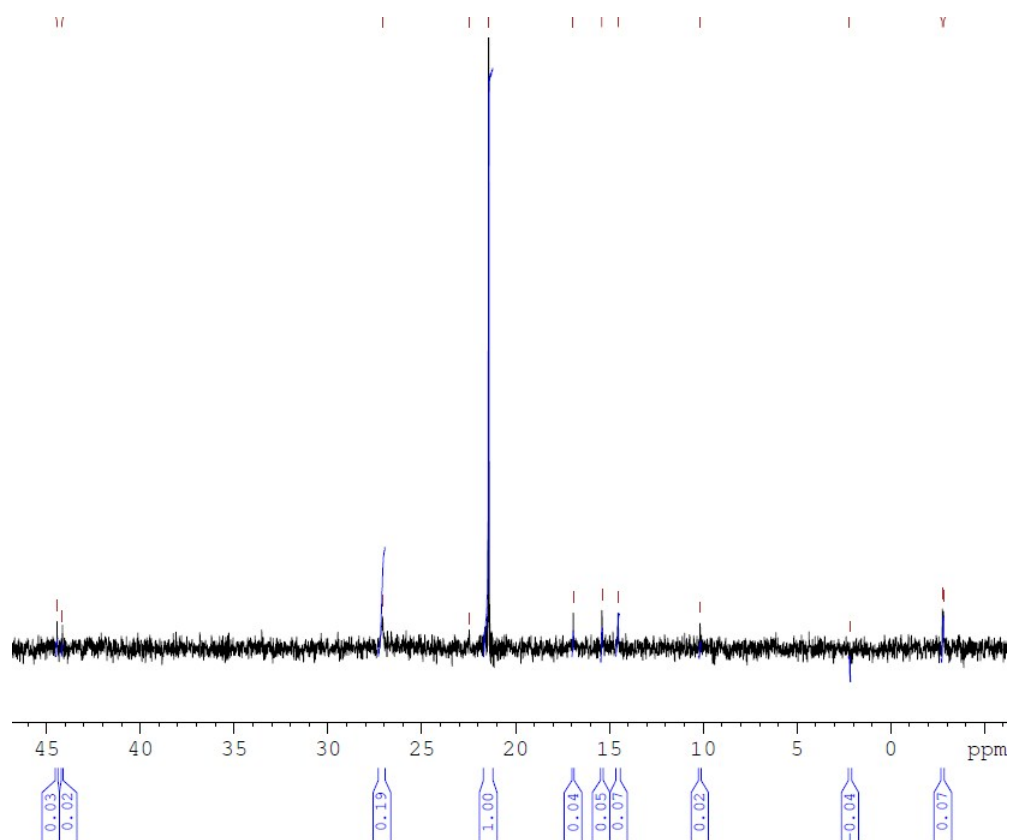
**Fig. S5.** <sup>31</sup>P NMR spectrum of the mixture **1 + 2** at 198 s after mixing.

Further on the signal of **4** becomes emissive and attains a negative minimum and the signal of salt **5** attains an absorption maximum at 288 s. By this time the signal at 14.4 ppm decreases and low positive signals at 16.9, 15.4, -2.75 and -2.8 ppm appear.(Fig. S6)

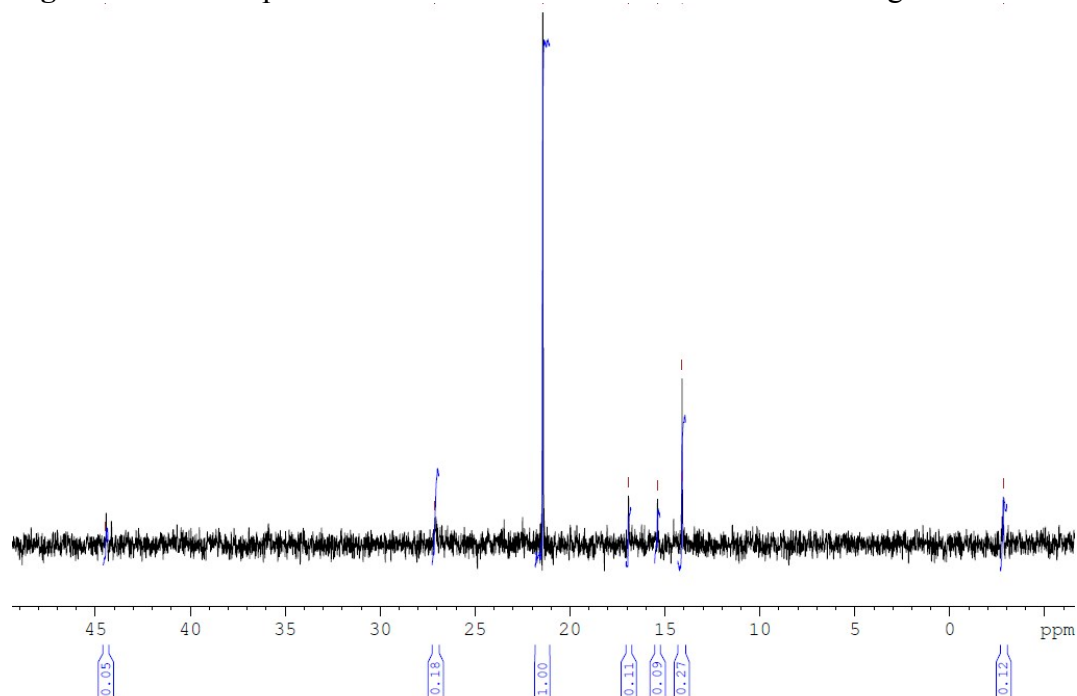


**Fig. S6.** <sup>31</sup>P NMR spectrum of the mixture **1 + 2** at 288 s after mixing.

The signal of **4** begins to grow and at 360 s crosses a zero point and continues to grow further, whereas the signal of salt **5** decreases. (Figs. S7, S8)



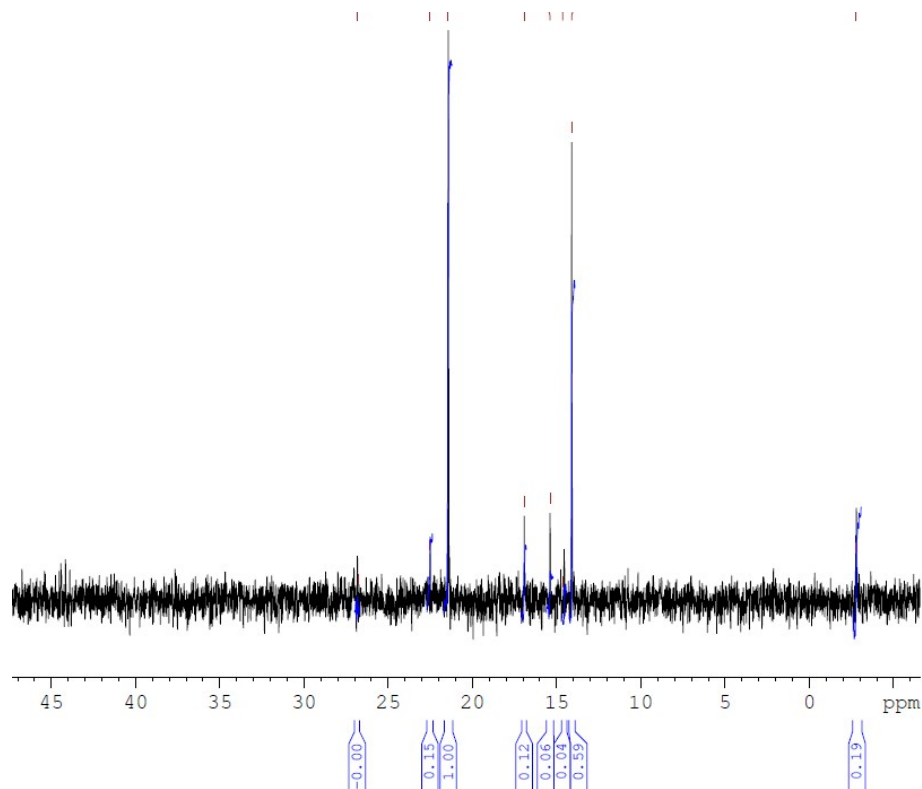
**Fig. S7.** <sup>31</sup>P NMR spectrum of the mixture **1 + 2** at 360 s after mixing.



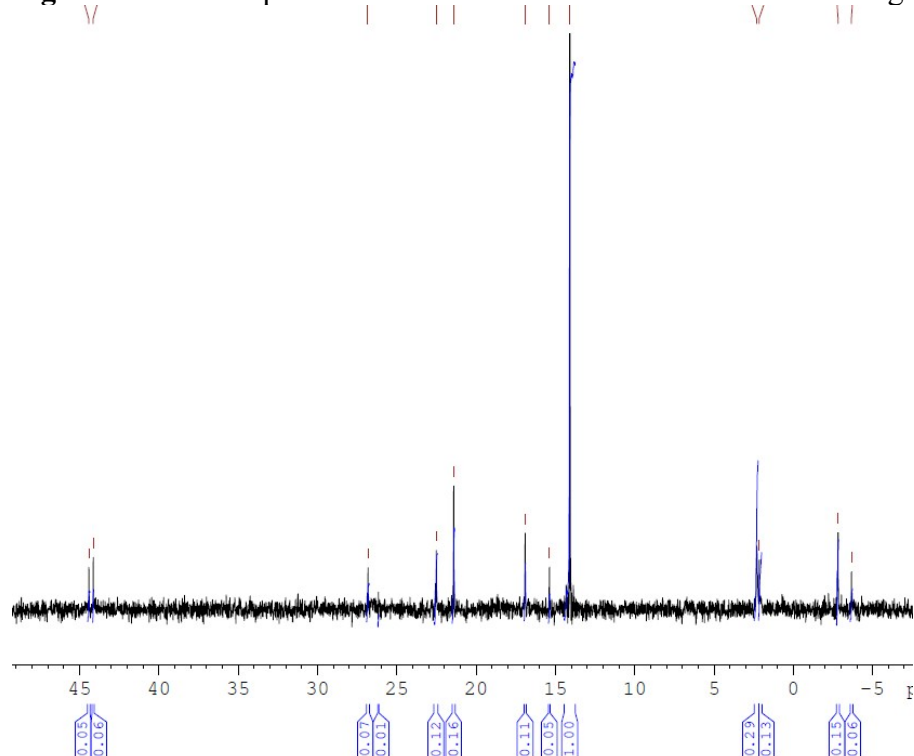
**Fig. S8.** <sup>31</sup>P NMR spectrum of the mixture **1 + 2** at 390 s after mixing.

The ylide concentration decreases and at 420 s (7 min) **1** is consumed completely. By this time the signal of **4** almost attains its final value and stops increasing, whereas the signal of **5** decreases for 2 min more and attains its final value at 9 min. All minor emission signals

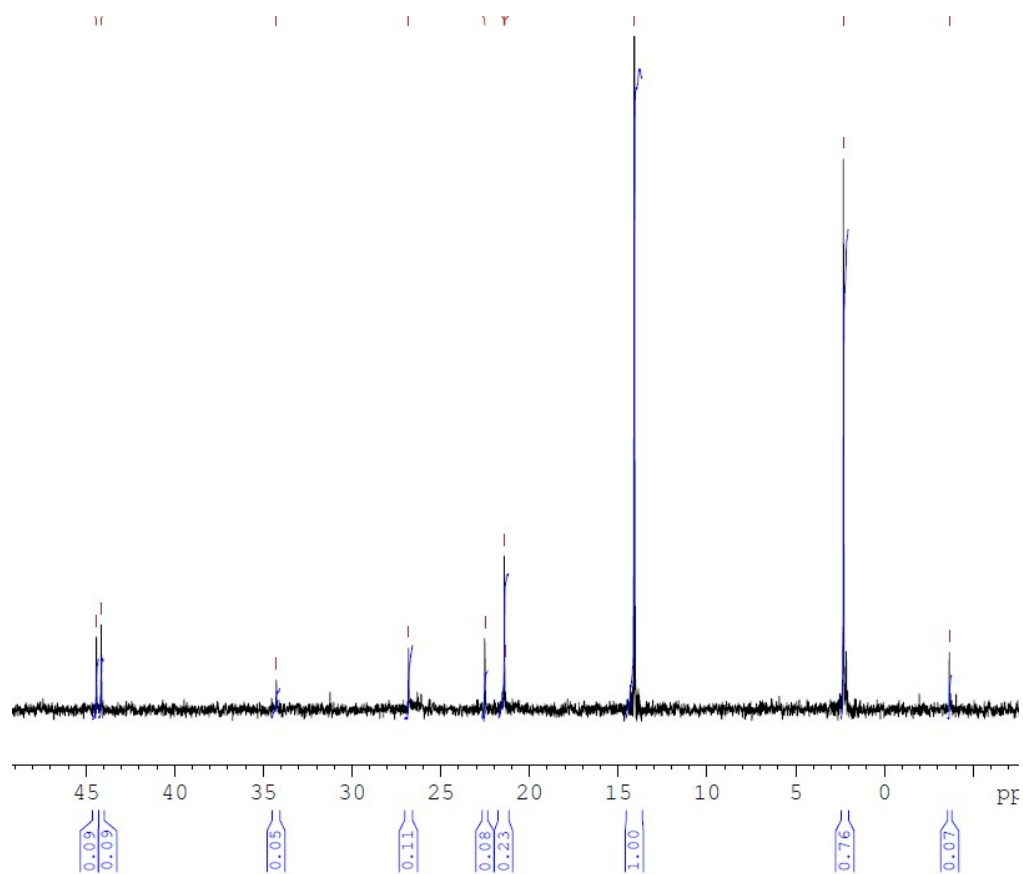
disappear by 360 s and the products with signals at 22.3, 2.2 and  $-3.9$  ppm present as minor products in the final mixture. The signals at 14.4 and 10.2 ppm disappear by 378–390 s. The signals at 16.9, 15.4,  $-2.75$  and  $-2.8$  ppm attain their highest values by 7–8 min and then slowly decrease: signals at 15.4 and  $-2.75$  ppm disappear in 30 min and the signals at 16.9 and  $-2.8$  ppm in 150 min. (Figs. S9–S11)



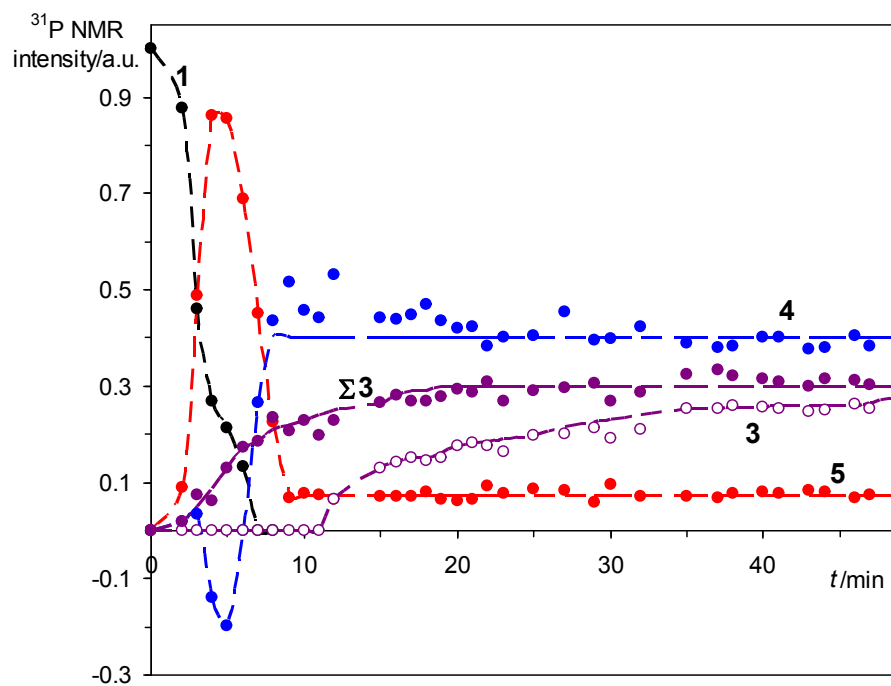
**Fig. S9.**  $^{31}\text{P}$  NMR spectrum of the mixture **1** + **2** at 420 s after mixing.



**Fig. S10.**  $^{31}\text{P}$  NMR spectrum of the mixture **1** + **2** at 15 min after mixing.



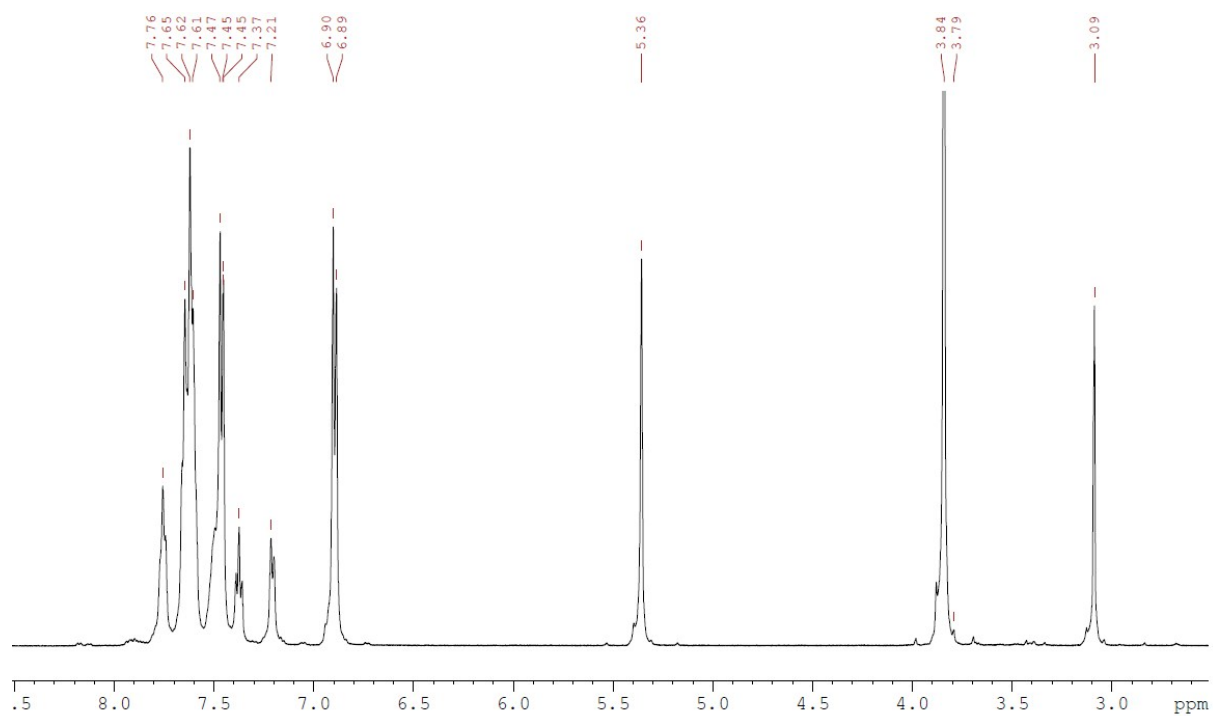
**Fig. S11.**  $^{31}\text{P}$  NMR spectrum of the mixture **1 + 2** at 150 min after mixing.



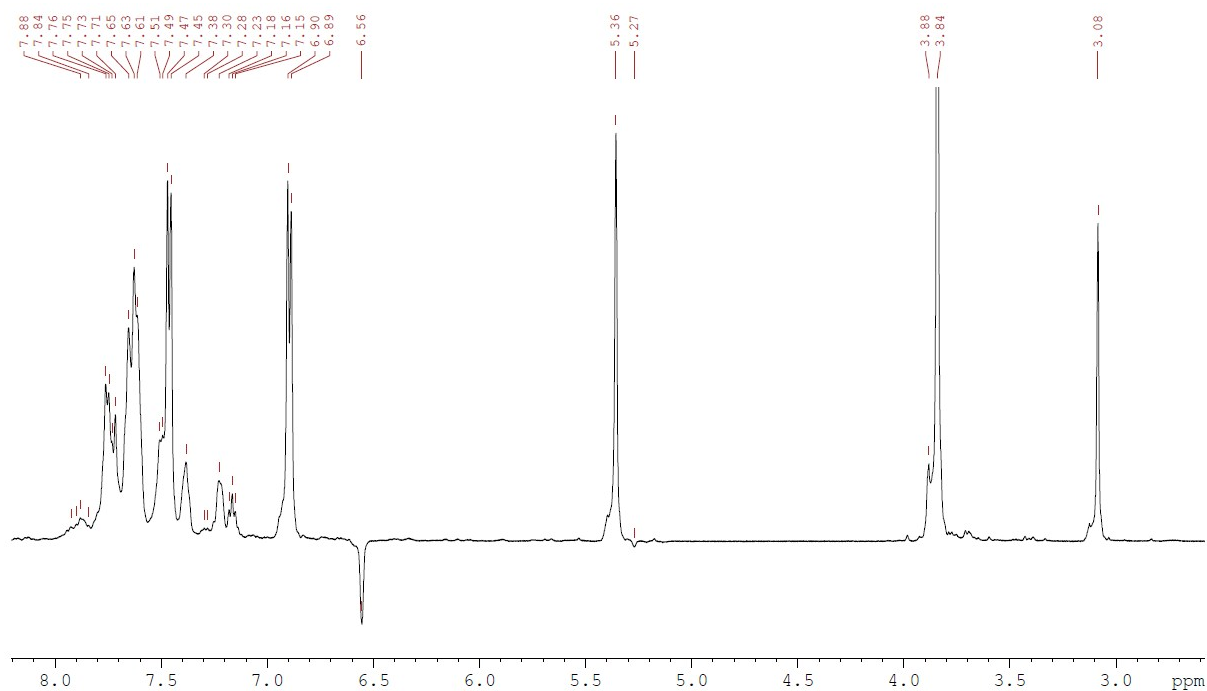
**Figure S12** Kinetics of normalized integral yields of the main products, numbers correspond to the numbers of reagents and products in Scheme 1, for  $\Sigma 3$  see the text.



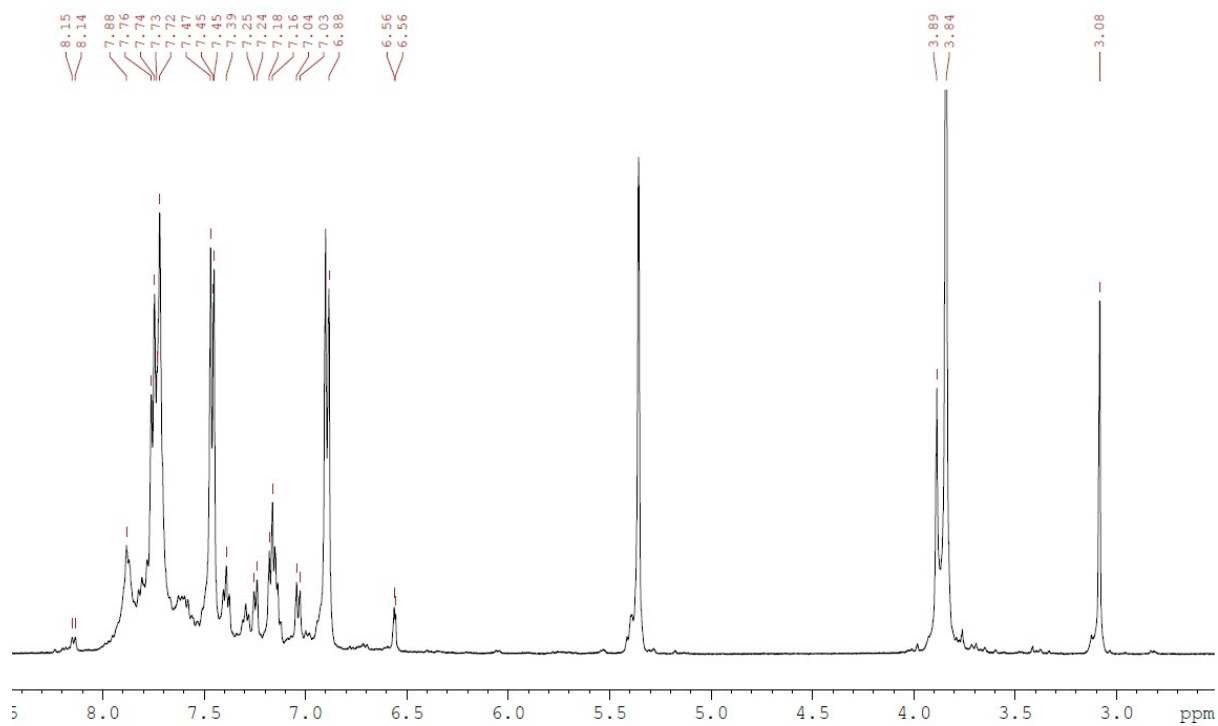
2. Time-evolution of the  $^1\text{H}$  NMR spectra after mixing ylide **1** and acetylene **2** in  $\text{DCM}_{\text{d}2}$  [1]/[2]=1/3



**Fig. S13** Initial  $^1\text{H}$  NMR spectrum after mixing the reagents

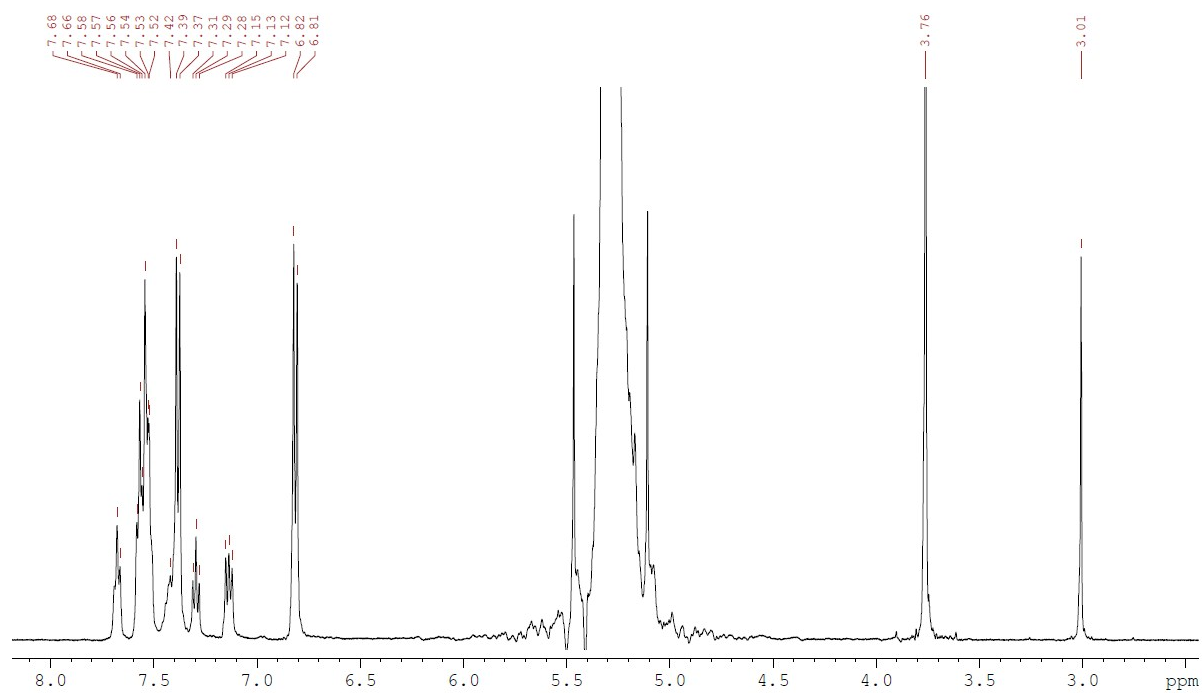


**Fig. S14**  $^1\text{H}$  NMR spectrum in 6 min after mixing the reagents.

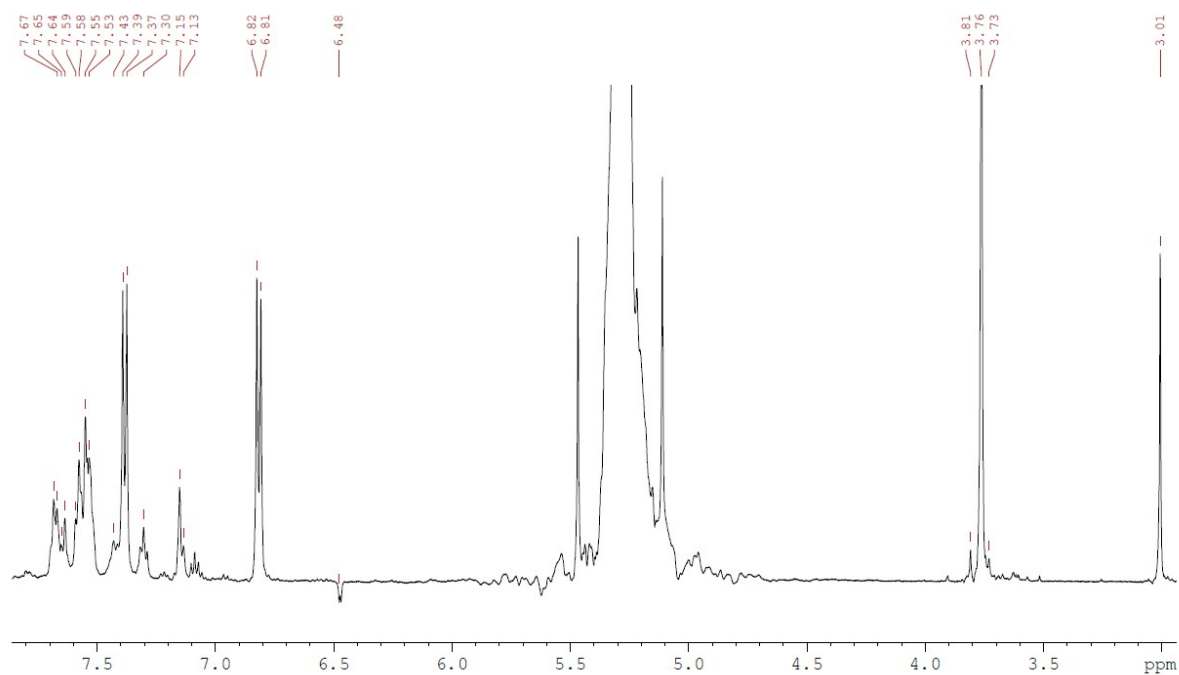


**Fig. S15**  $^1\text{H}$  NMR spectrum in 15 min after mixing the reagents.

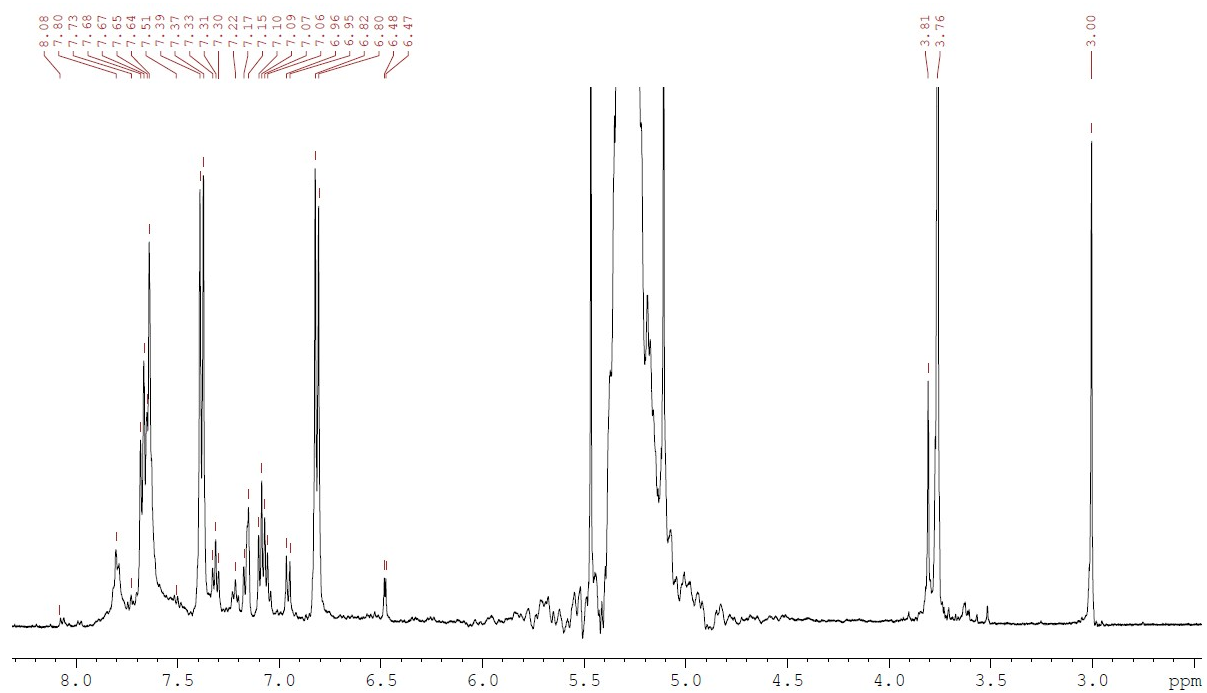
3. Time-evolution of the  $^1\text{H}$  NMR spectra after mixing ylide **1** and acetylene **2** in DCM [1]/[2] = 1/3,  $\text{C}_6\text{D}_6$  is added as a standard ( $\delta(\text{C}_6\text{H}_6) = 7.15$  ppm)



**Fig. S16** Initial  $^1\text{H}$  NMR spectrum after mixing the reagents.



**Fig. S17**  $^1\text{H}$  NMR spectrum in 5 min after mixing the reagents.



**Fig. S18**  $^1\text{H}$  NMR spectrum in 15 min after mixing the reagents.