Electronic Supplementary Material (ESI) for Polymer Chemistry.

Chelation-assisted CuAAC of star-shaped polymers enables fast self-healing at low temperatures.

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Supporting Information

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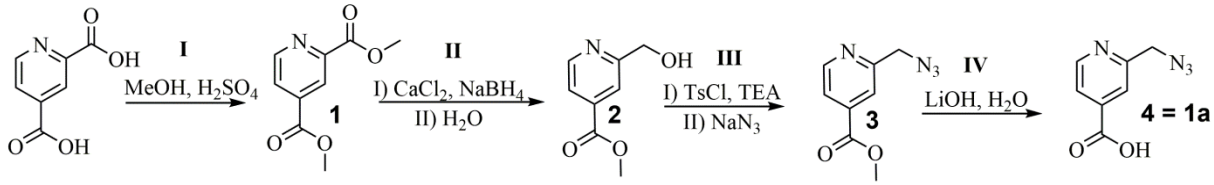
Synthetic-route to obtain 2-(6-azidomethyl)-pyridine-4-carboxylic acid (**4** = **1a**):



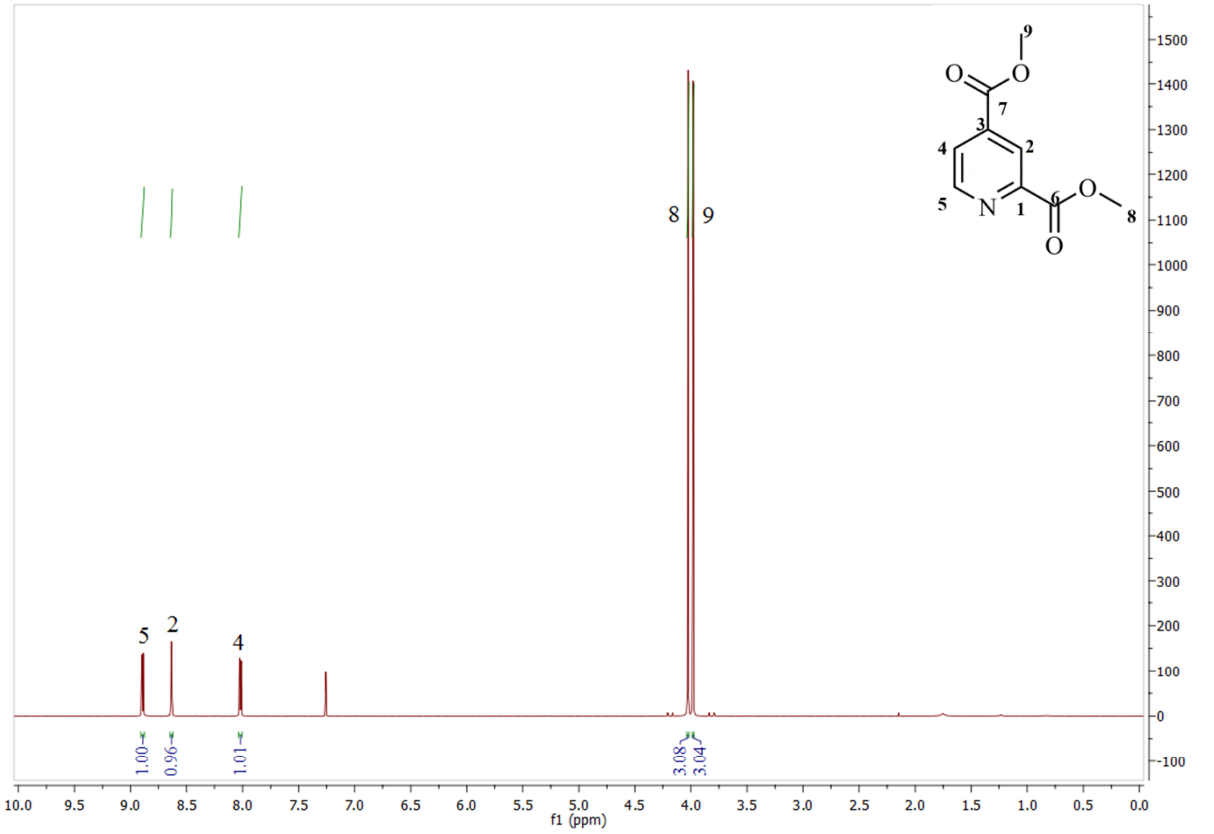


Figure **S1**. ^{1}H-NMR of pyridine-2,4-carboxylic acid dimethylester (**1**) in $CDCl_3$.

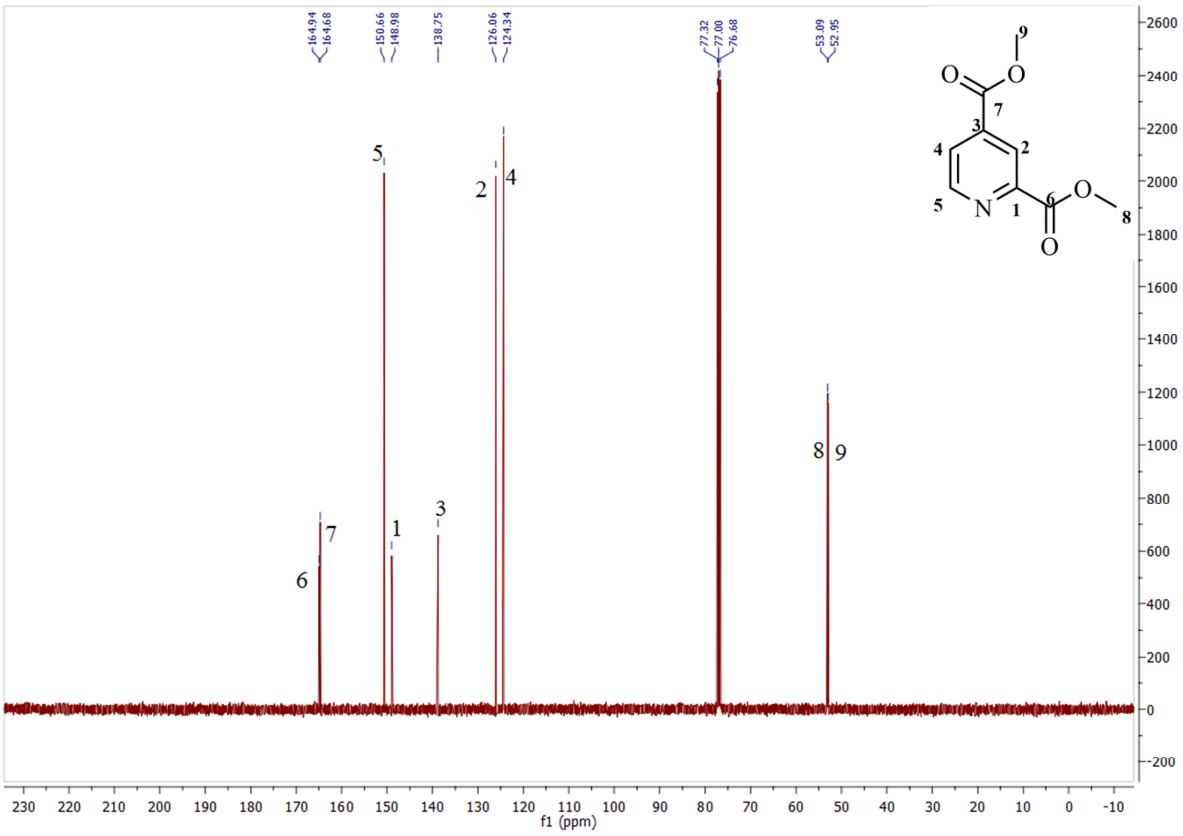


Figure **S2**. ^{13}C-NMR of pyridine-2,4-carboxylic acid dimethylester (**1**) in $CDCl_3$.

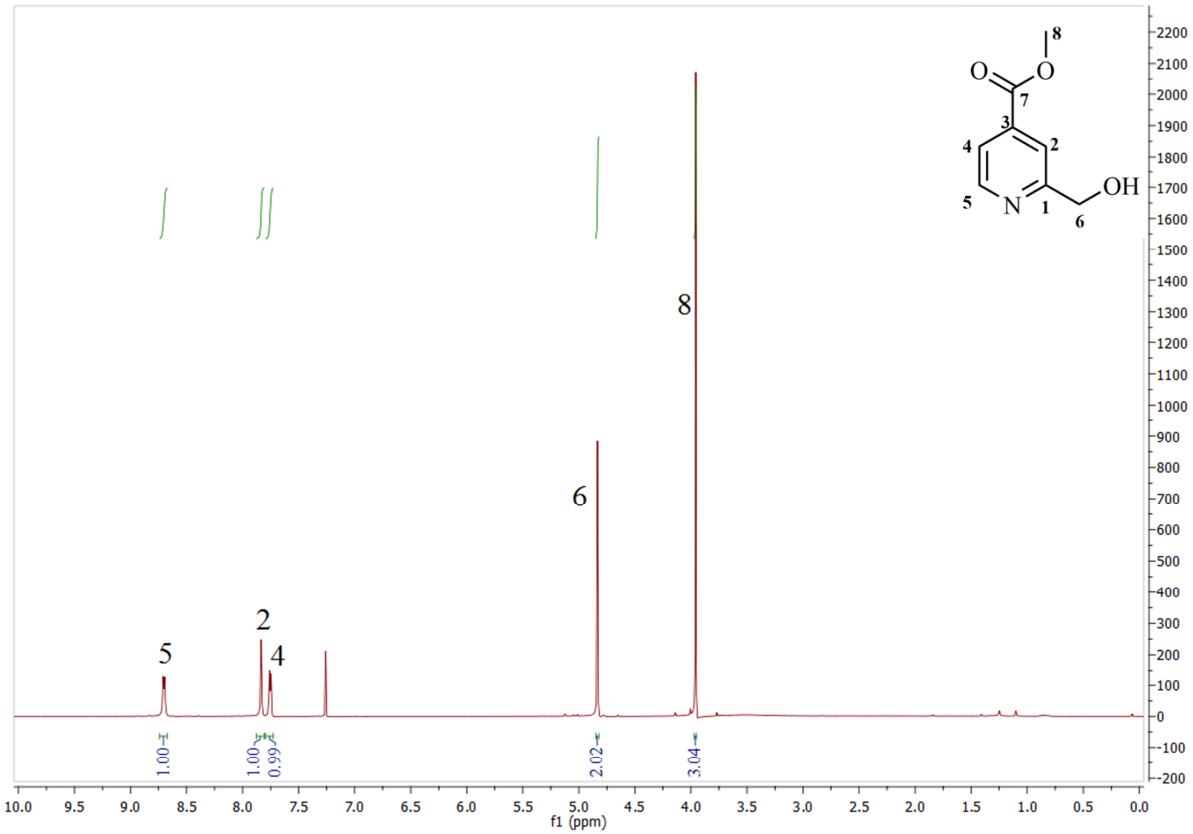


Figure **S3**. ^{1}H-NMR of 2-(6-hydroxymethyl)-pyridine-4-carboxylic acid methylester (**2**) in $CDCl_3$.

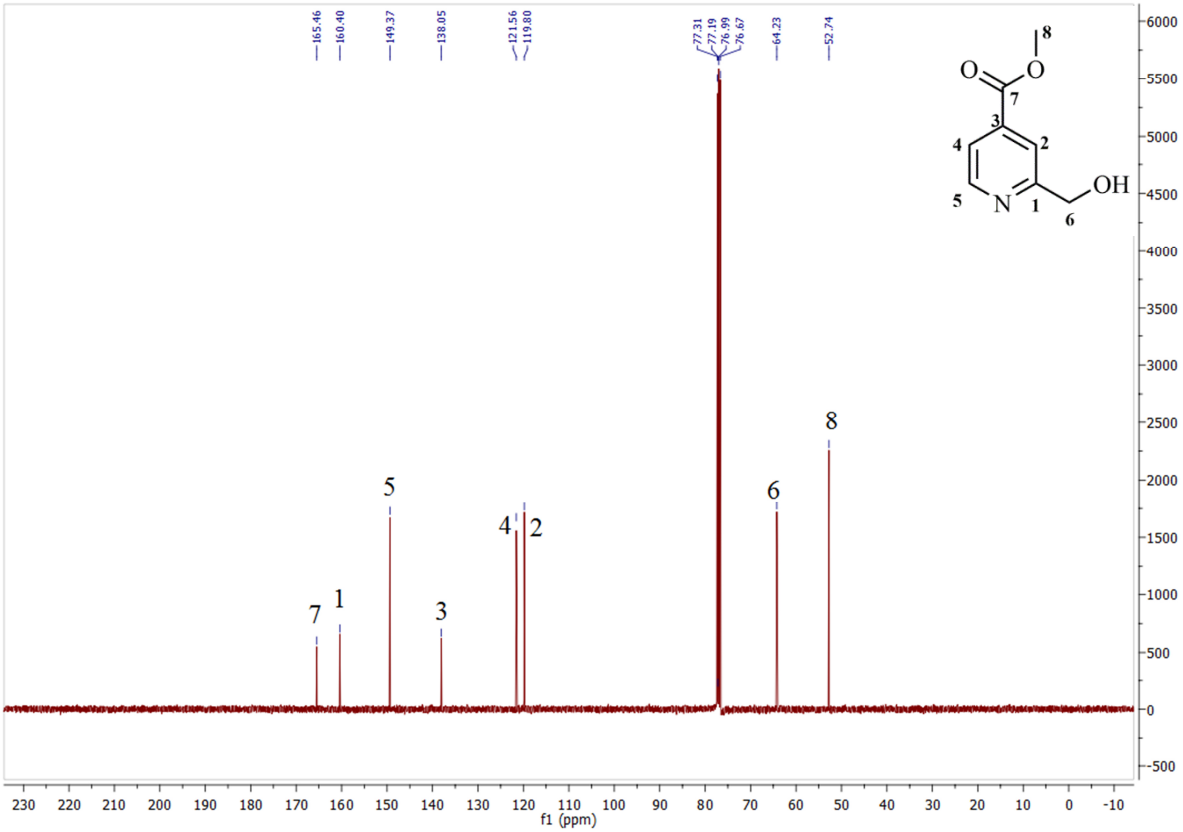


Figure **S4**. ^{13}C-NMR of 2-(6-hydroxymethyl)-pyridine-4-carboxylic acid methylester (**2**) in $CDCl_3$.

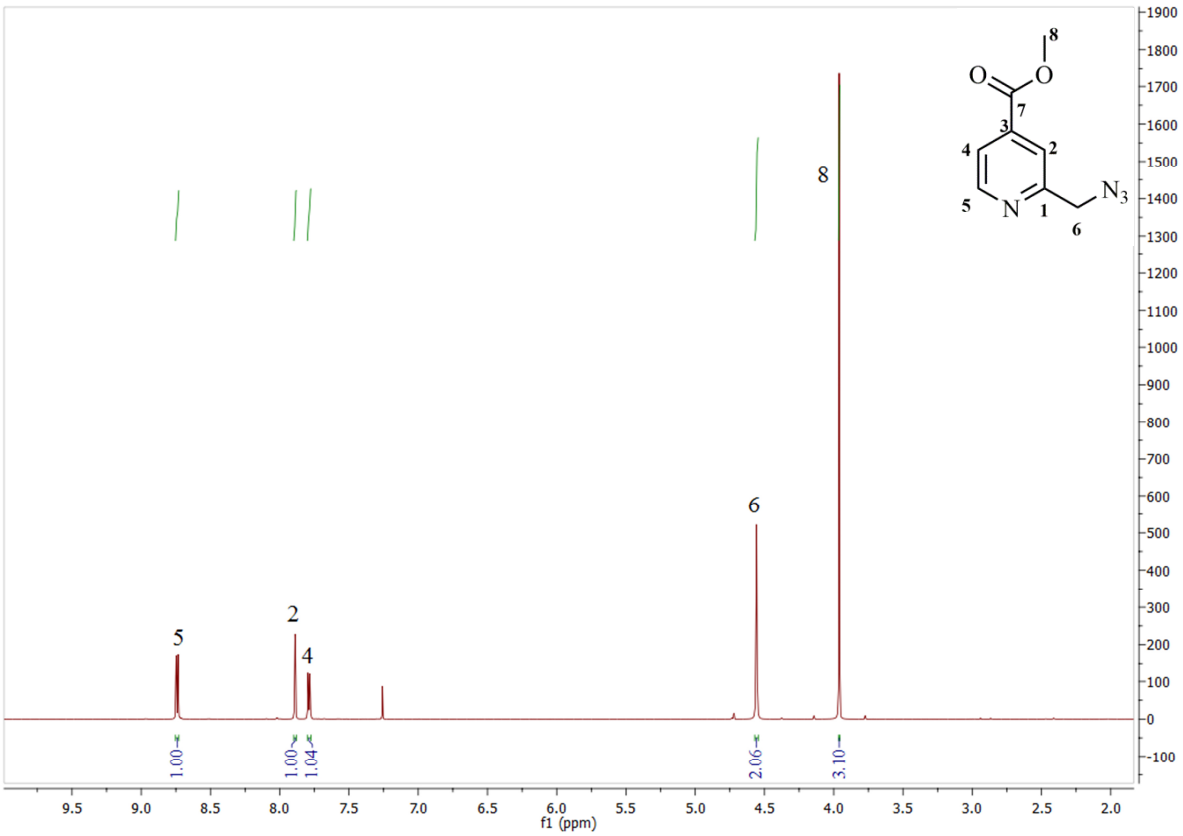


Figure **S5**. ^{1}H-NMR of 2-(6-azidoymethyl)-pyridine-4-carboxylic acid methylester (**3**) in $CDCl_3$.

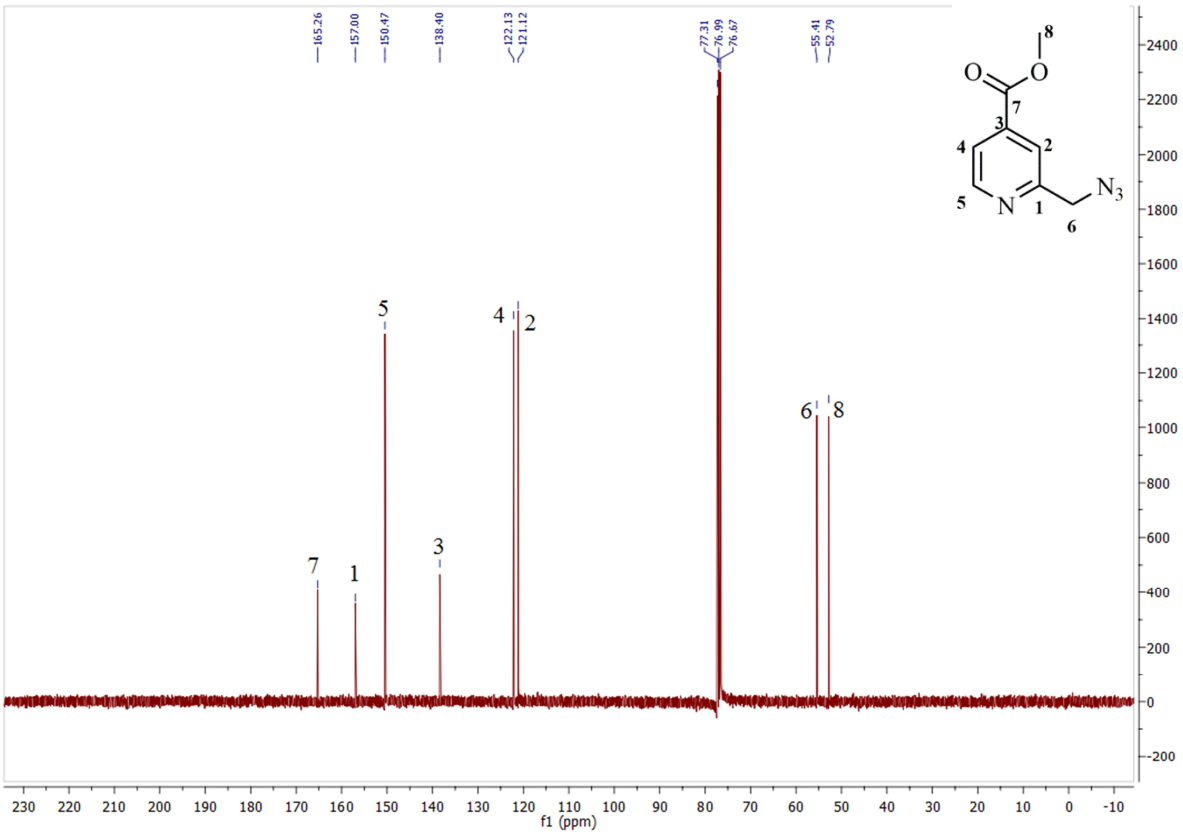


Figure **S6**. ^{13}C-NMR of 2-(6-azidomethyl)-pyridine-4-carboxylic acid methylester (**3**) in $CDCl_3$.

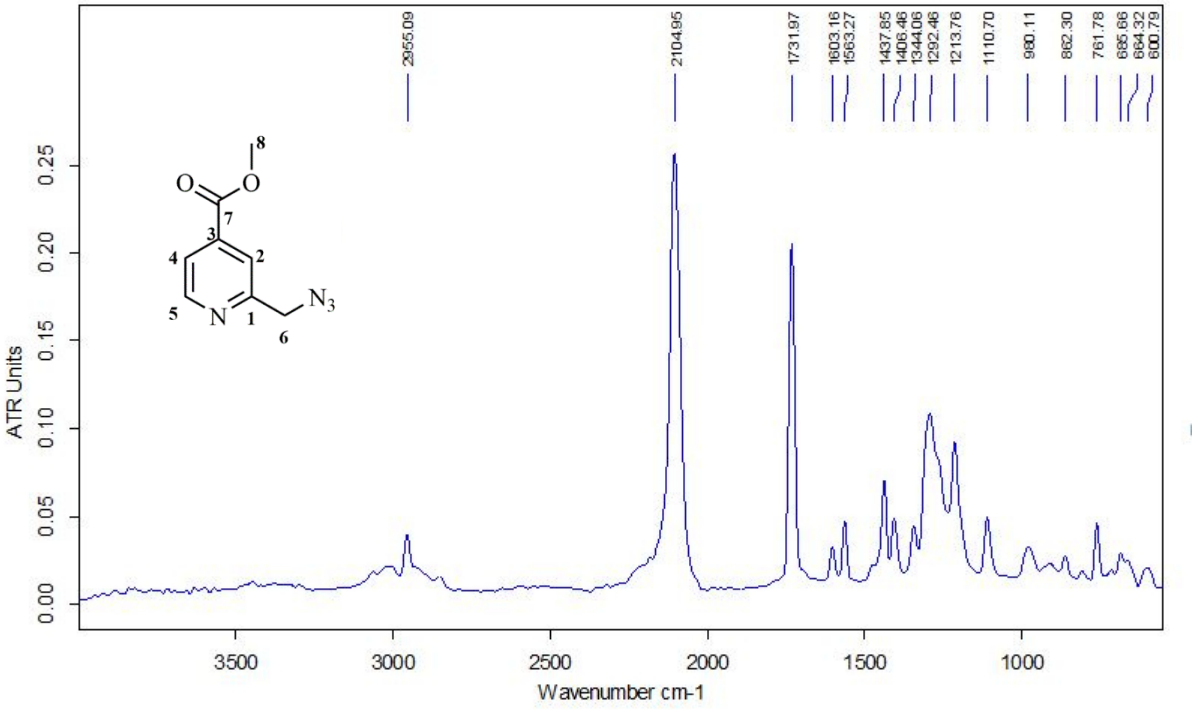


Figure **S7**. IR-spectrum of 2-(6-hydroxymethyl)-pyridine-4-carboxylic acid methylester (**3**).

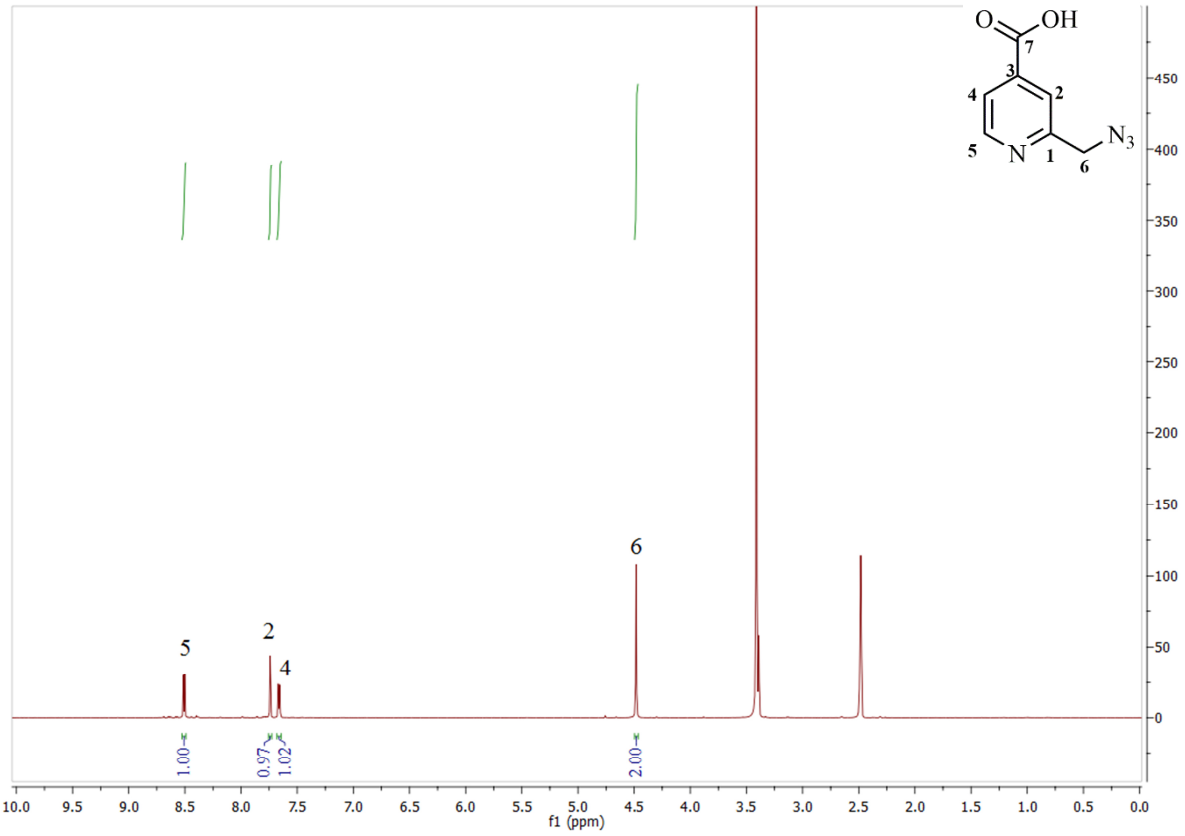


Figure **S8**. ^{1}H-NMR of 2-(6-azidomethyl)-pyridine-4-carboxylic acid (**4** = **1a**) in DMSO-d_6.

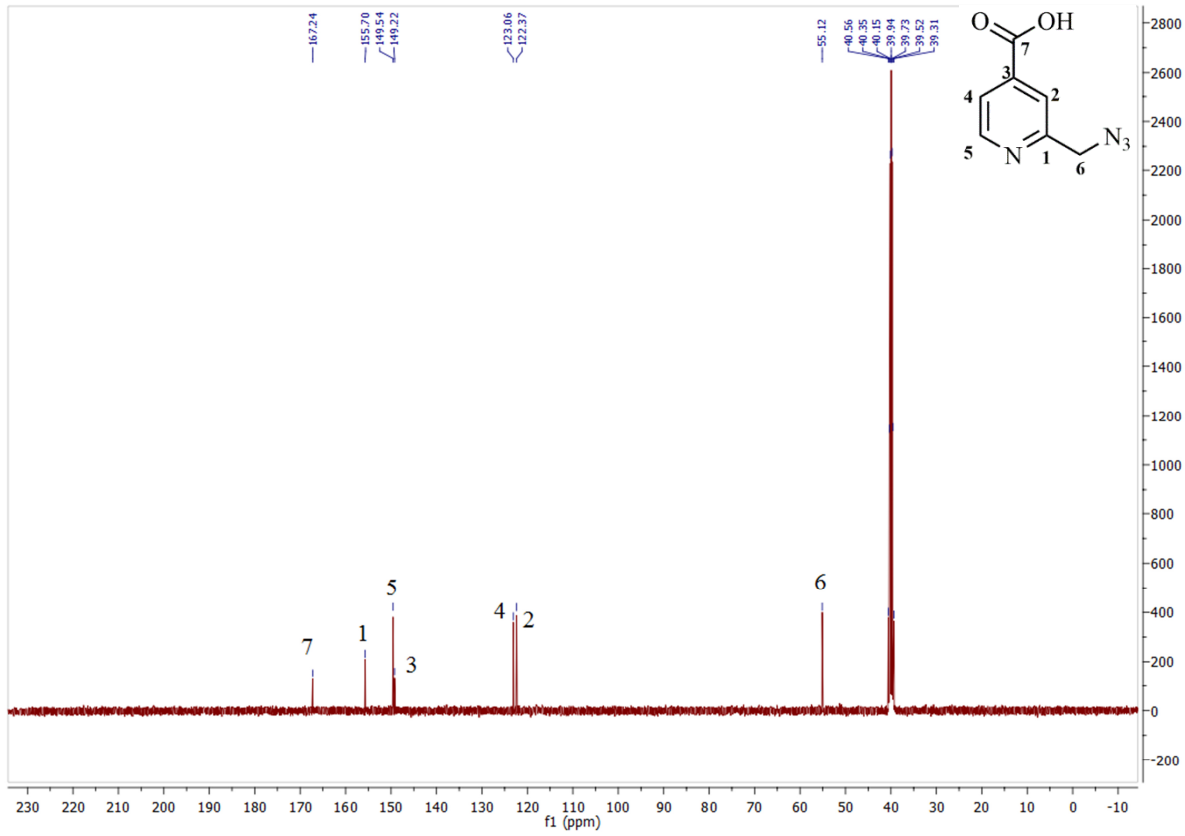


Figure **S9**. ^{13}C-NMR of 2-(6-azidomethyl)-pyridine-4-carboxylic acid (**4** = **1a**) in DMSO-d_6.

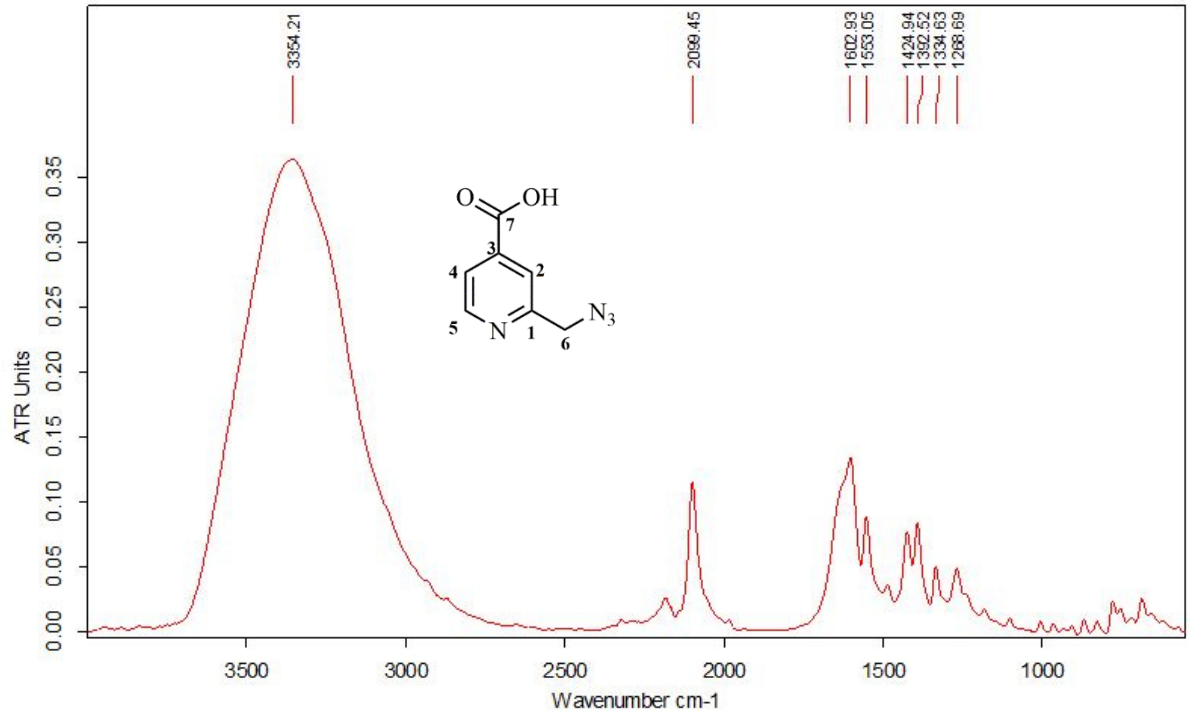
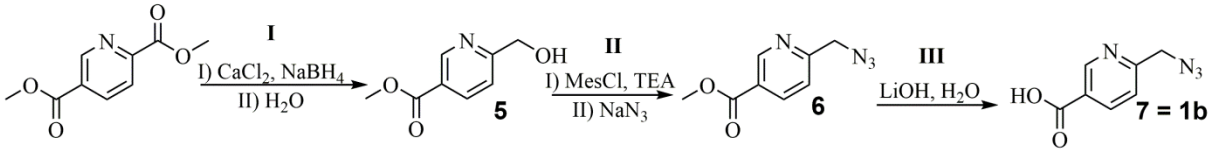


Figure **S10**. IR-spectrum of 2-(6-azidomethyl)-pyridine-4-carboxylic acid (**4** = **1a**).

Synthetic route to obtain 2-(6-azidomethyl)-pyridine-5-carboxylic acid (**7** = **1b**):



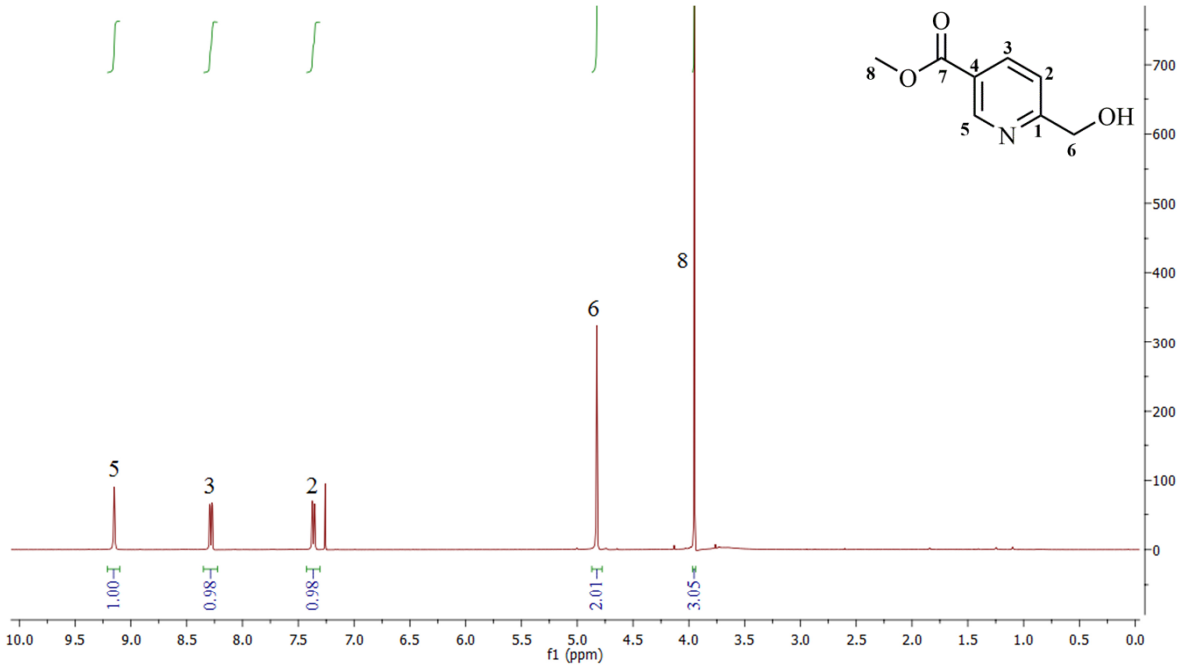


Figure **S11**. ^{1}H-NMR of 2-(6-hydroxymethyl)-pyridine-5-carboxylic acid methylester (**5**) in $CDCl_3$.

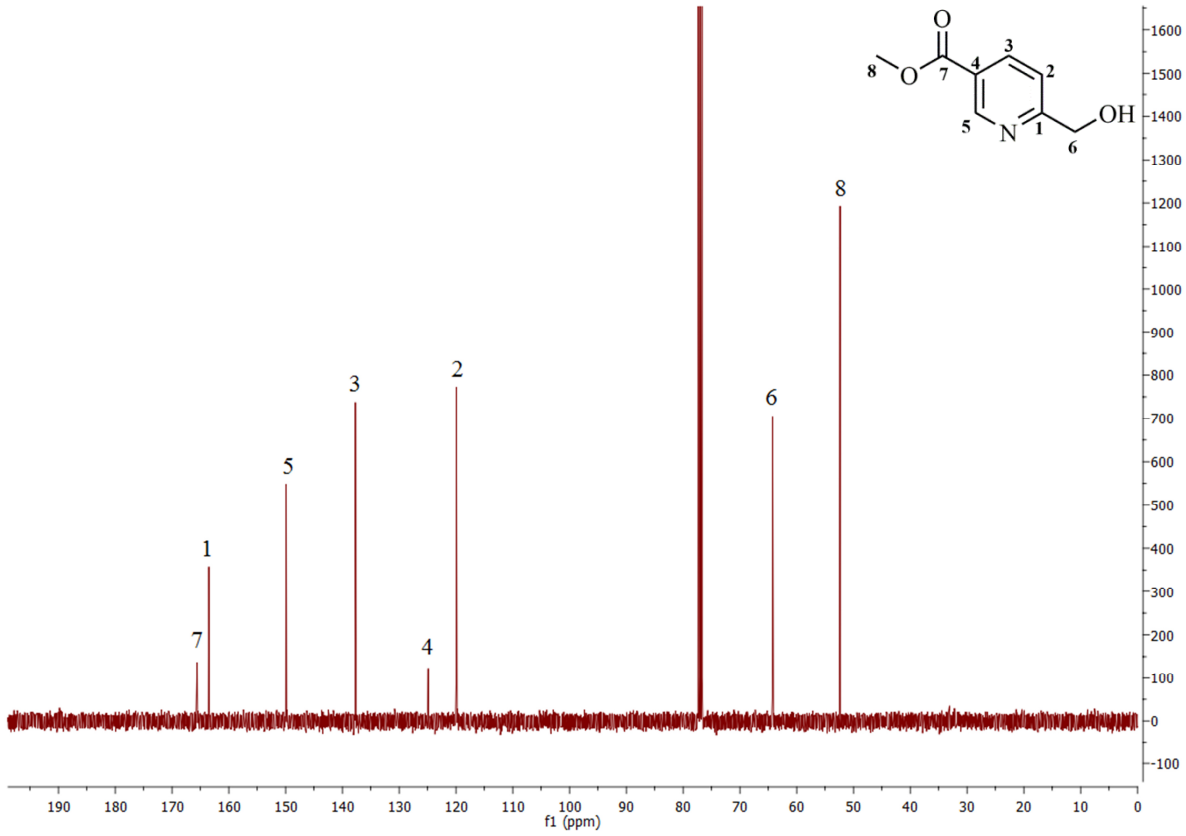


Figure **S12**. ^{13}C-NMR of 2-(6-hydroxymethyl)-pyridine-5-carboxylic acid methylester (**5**) in $CDCl_3$.

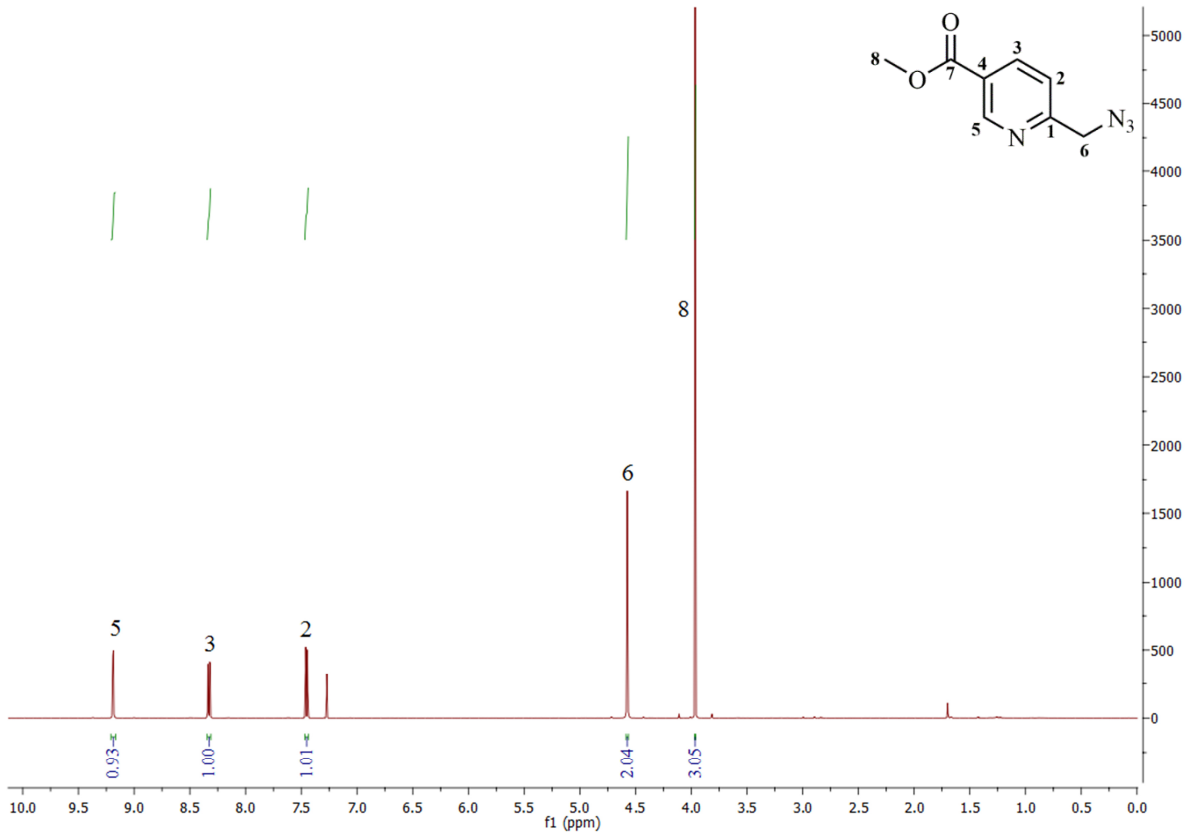


Figure **S13**. ^{1}H-NMR of 2-(6-azidomethyl)-pyridine-5-carboxylic acid methylester (**6**) in $CDCl_3$.

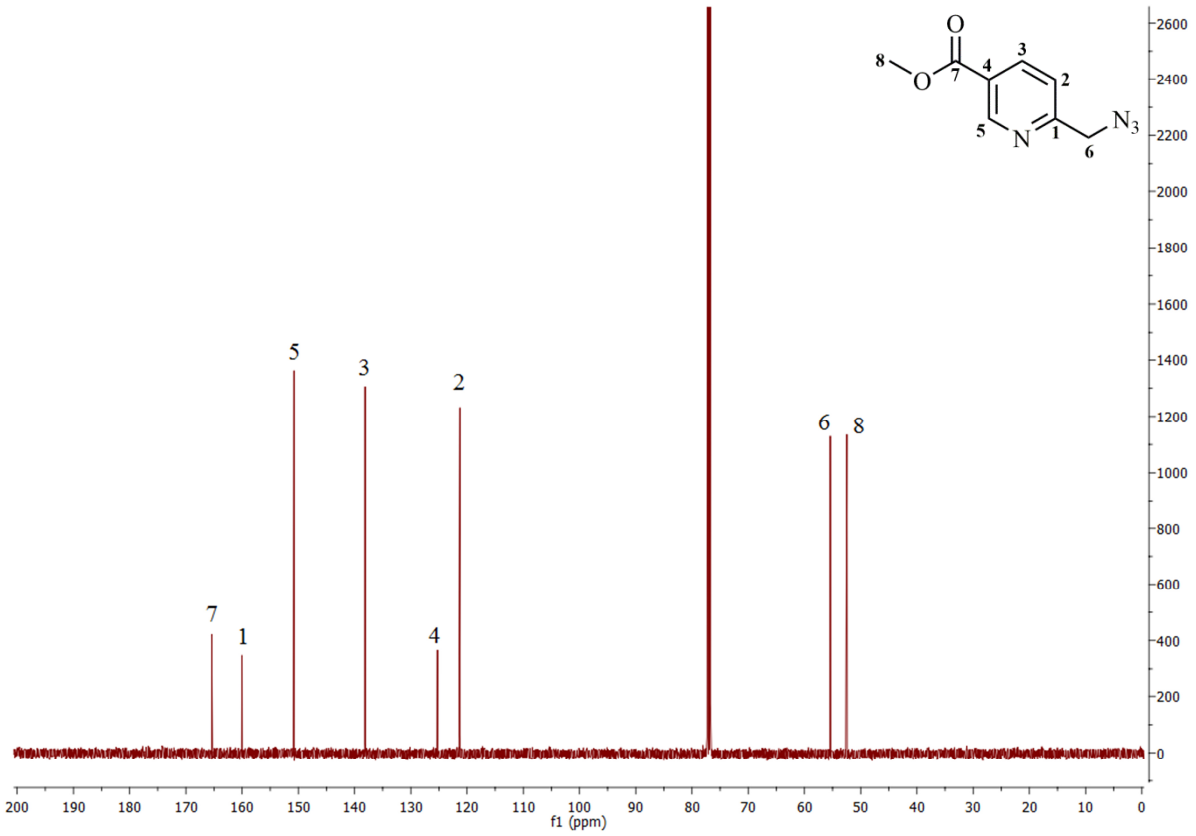


Figure **S14**. ^{13}C-NMR of 2-(6-hydroxymethyl)-pyridine-5-carboxylic acid methylester (**6**) in $CDCl_3$.

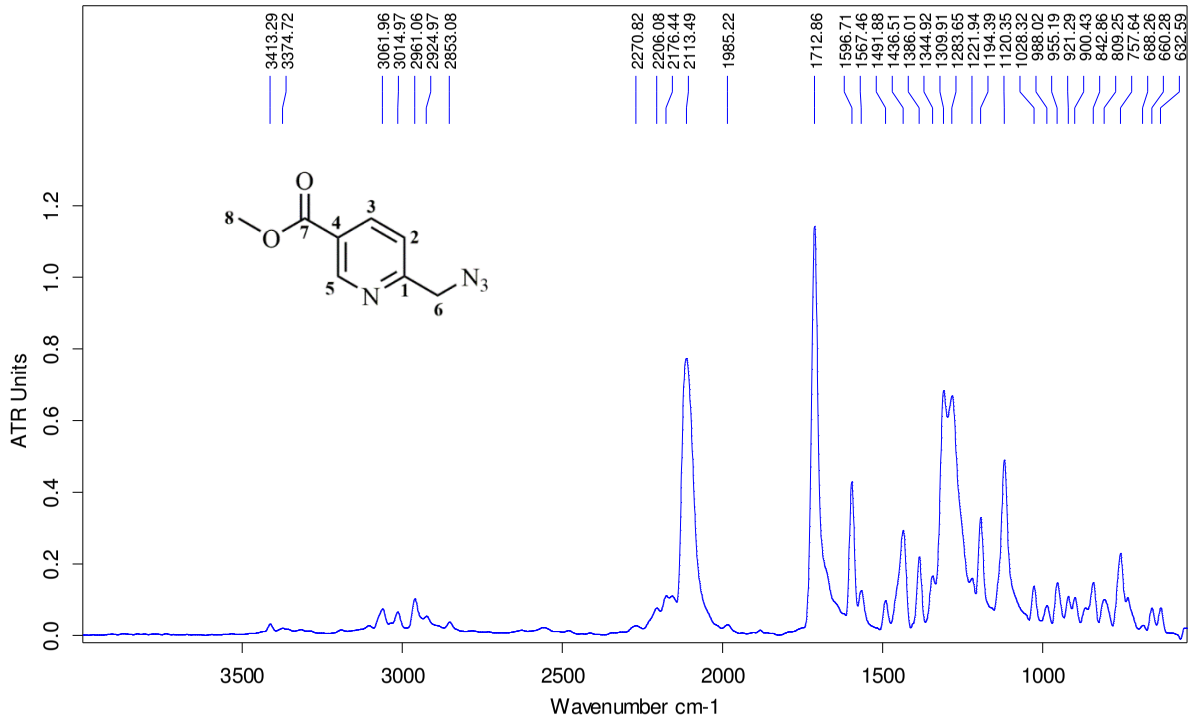


Figure **S15**. IR-spectrum of 2-(6-hydroxymethyl)-pyridine-4-carboxylic acid methylester (**6**).

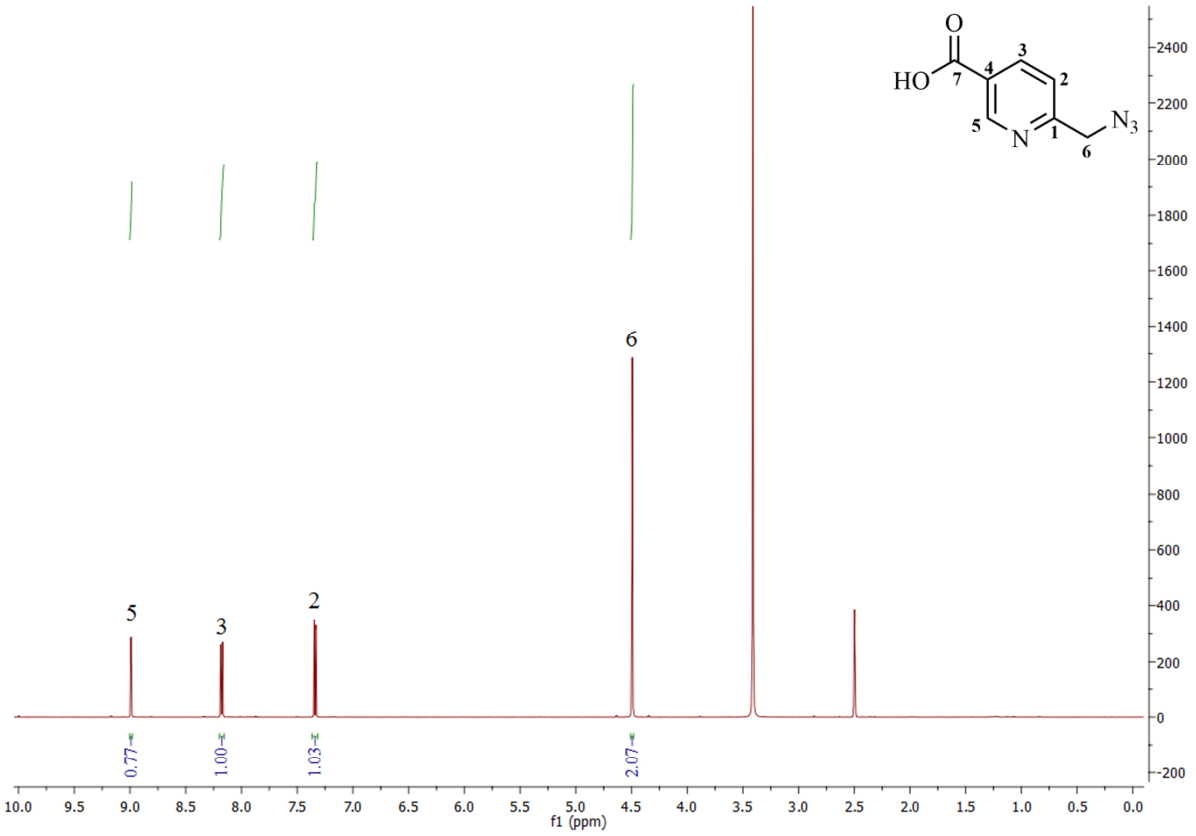


Figure **S16**. ^{1}H-NMR of 2-(6-azidomethyl)-pyridine-5-carboxylic acid (**7** = **1b**) in DMSO-d_6.

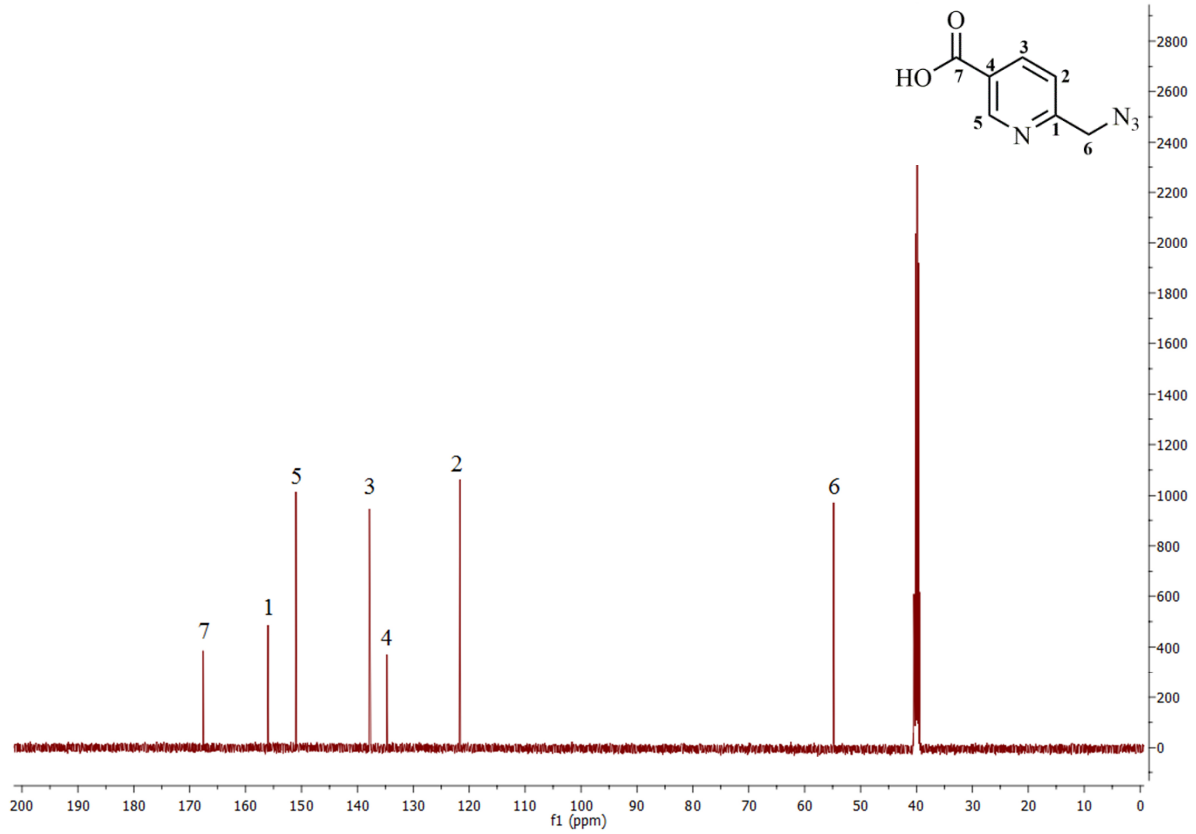


Figure **S17**. ^{13}C-NMR of 2-(6-azidomethyl)-pyridine-5-carboxylic acid (**7** = **1b**) in DMSO-d_6.

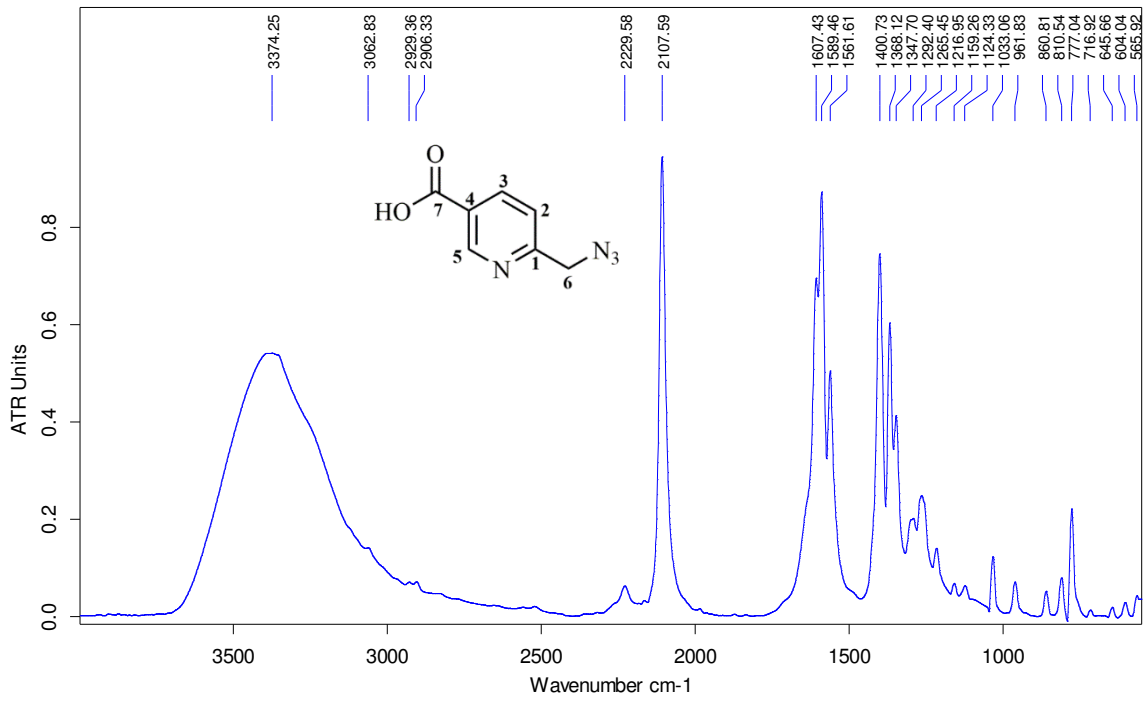


Figure **S18**. IR-spectrum of 2-(6-azidomethyl)-pyridine-5-carboxylic acid (**7** = **1b**).

2. NMR- and IR-investigations for the synthesis of star-shaped picolinazido-telechelic PIBs (**2a**, **2b**).

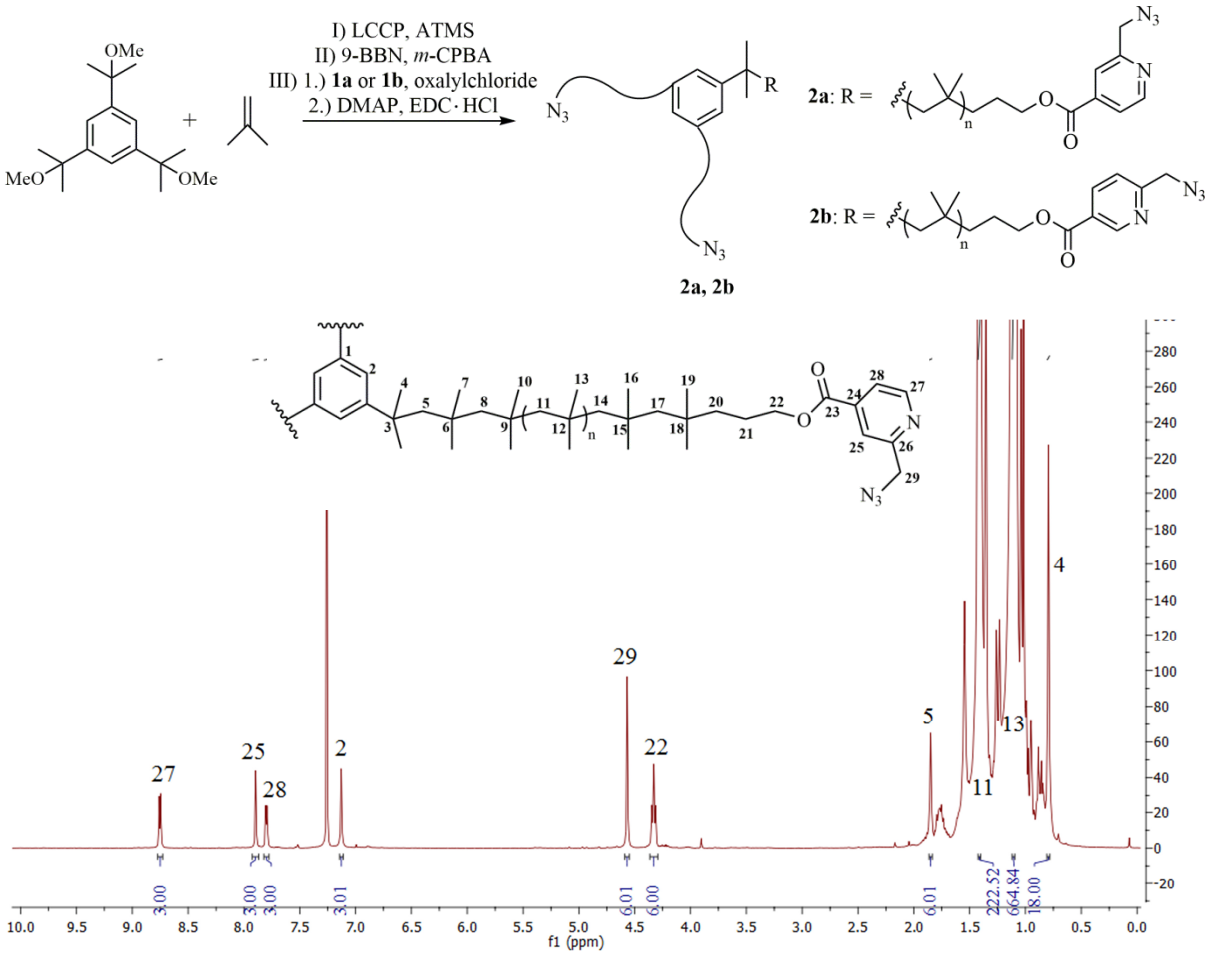


Figure **S19**. ^{1}H-NMR of star-shaped picolinazido-telechelic PIB (**2a**).

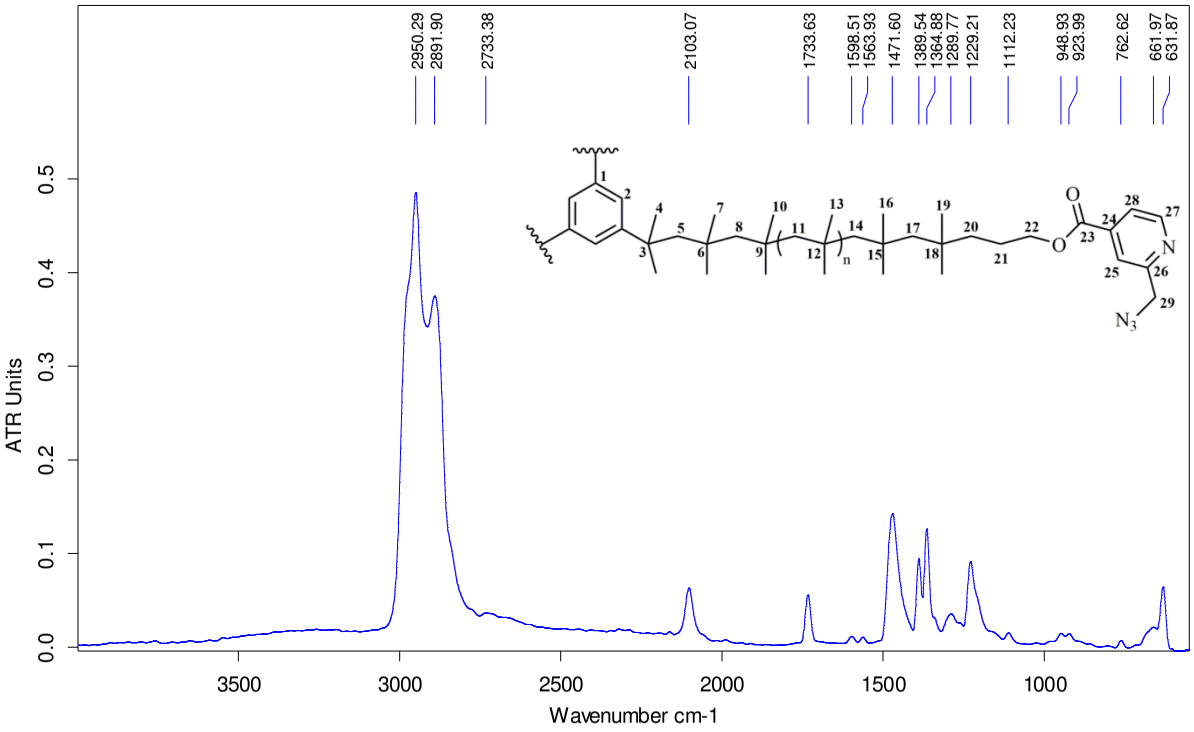


Figure **S20**. IR-spectrum of star-shaped picolinazido-telechelic PIB (**2a**).

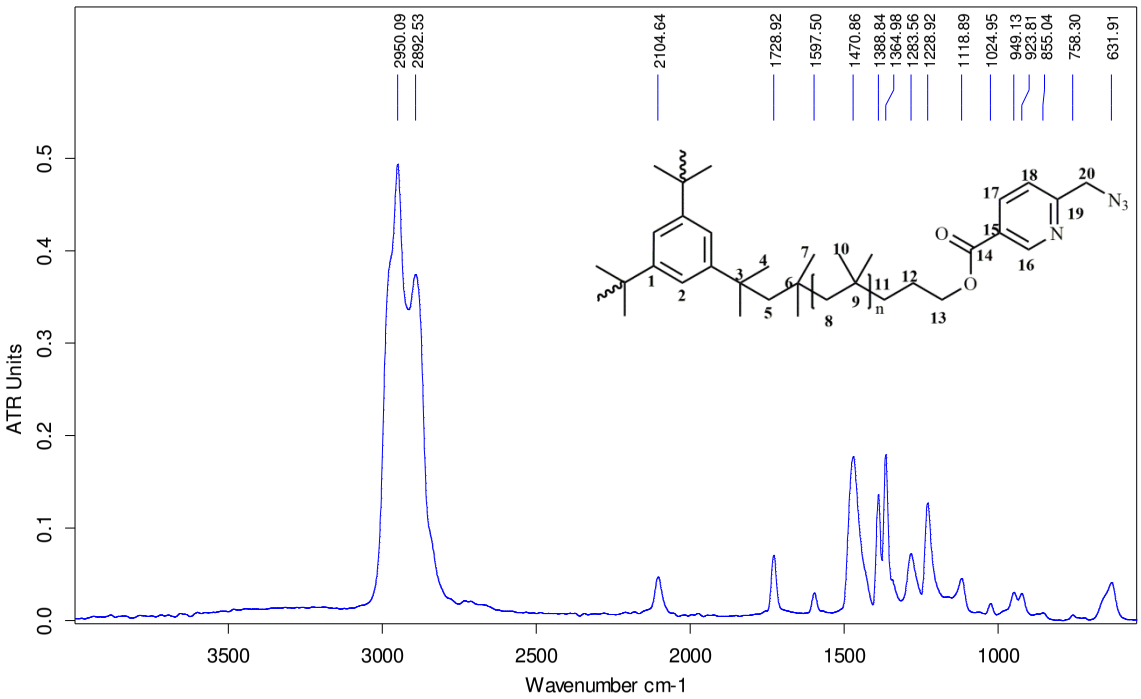


Figure **S21**. IR-spectrum of star-shaped picolinazido-telechelic PIB (**2b**).

3. *In Situ* NMR kinetic plot by conversion of 2-(6-azidomethyl)-pyridine-4-carboxylic acid methyl ester and phenylacetylene: - here shown exemplary for Table 1, entry 7: CuBr, DIPEA (0.01 eq.):

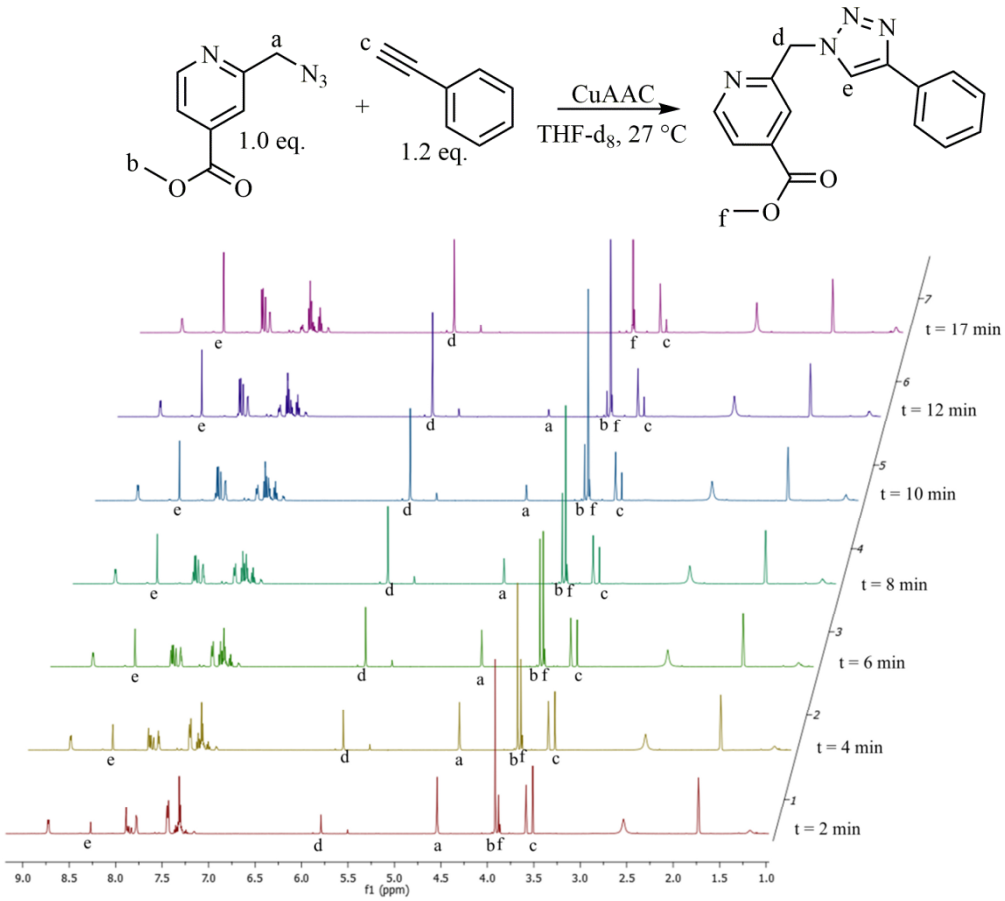


Figure **S22**. ^{1}H-NMR kinetic-plot (Table 1, entry 7) conducted in THF-d_8.

To determine the conversion at different defined periods of time the integrals of the corresponding resonances (a) and (d) were chosen. Calculation was done according to the following equation (S1):

$$\text{conversion} = \frac{\text{intergal of resonance d}}{(\text{integral of resonance d} + \text{integral of resonance a})} * 100\ \% \qquad \text{(S1)}$$

When resonance (a) disappears the conversion to the final click-product was seen as complete (> 99 %).

4. IR investigation of cross-linked networks after rheological investigations:
   Here shown exemplary for Table 2, entry 5 (**2a** + **3**, 20 °C, $CuF(PPh_3)_3$).

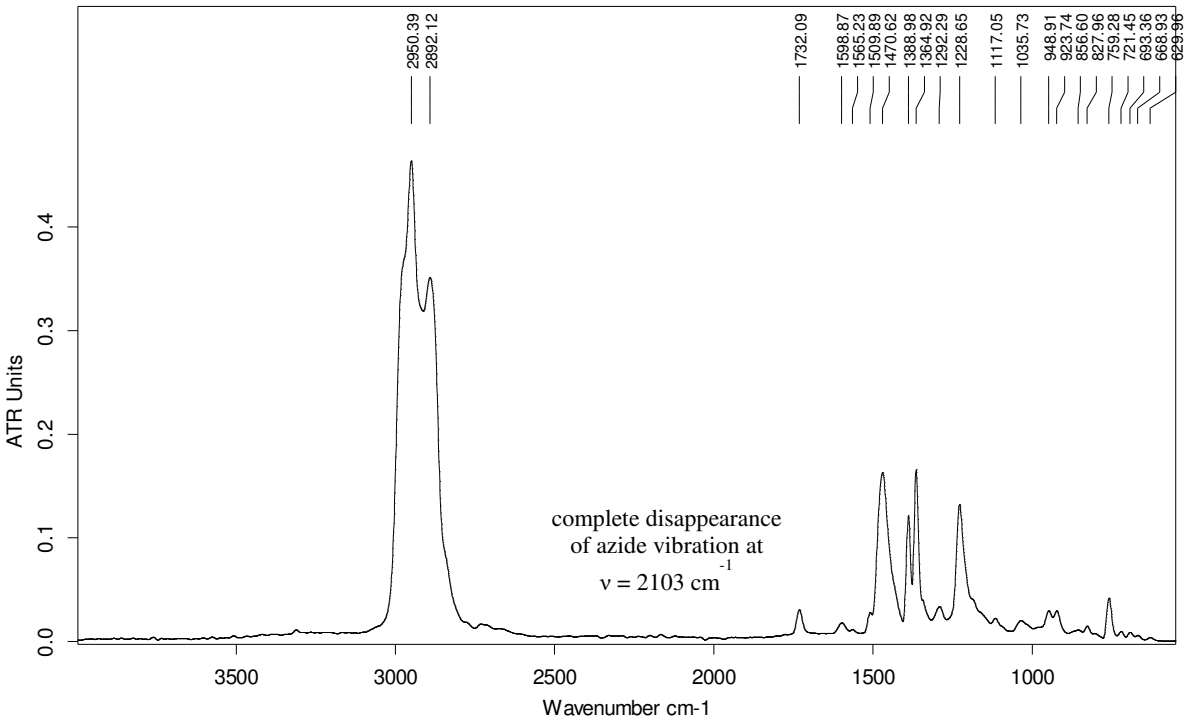


Figure **S23**. IR-spectrum of polymer network obtained by cross-linking of **2a** + **3**.

Here shown exemplary for Table 2, entry 7 (**2b** + **3**, 10 °C, $CuF(PPh_3)_3$).

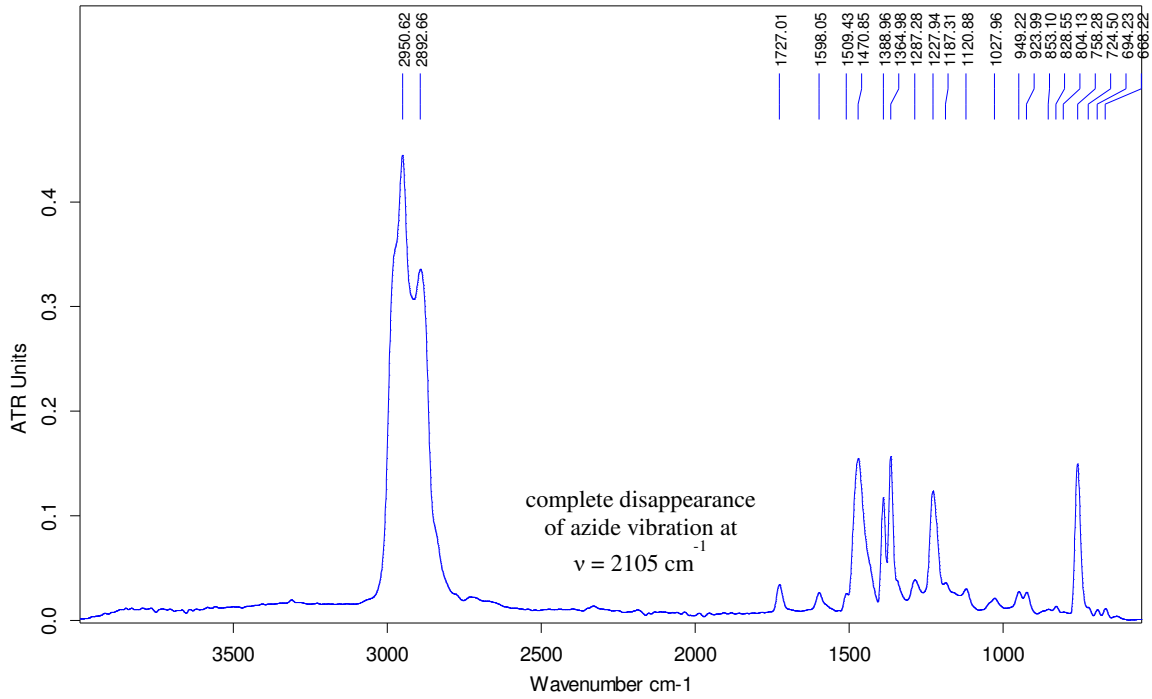


Figure **S24**. IR-spectrum of polymer network obtained by cross-linking of **2b** + **3**.

5. Fluorescence measurements of reference samples.

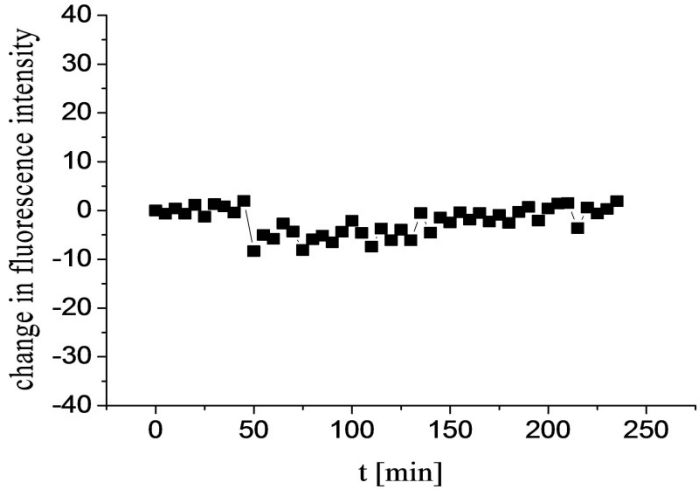


Figure **S25**. Fluorescence measurement of unscratched specimen.

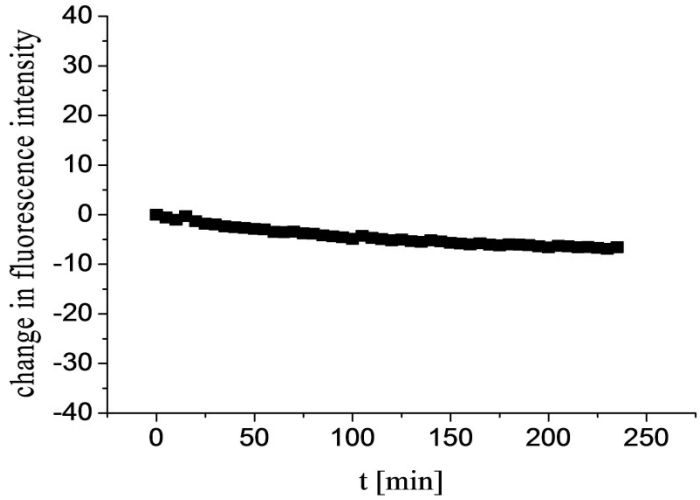


Figure **S26**. Fluorescence measurement of scratched specimen without $CuBr(PPh_3)_3$.