

## Support information

### **Amino- and sulfo-bifunctionalized hyper-crosslinking organic nanotube frameworks as efficient catalysts for one-pot cascade reactions**

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## Experimental Section

**Materials.** All reagents were used as received unless stated otherwise. Dichloromethane (DCM) and N, N-dimethylformamide (DMF) were dried using CaH<sub>2</sub> and distilled. Glycidyl methacrylate (GM, Acros 97%) was purified by vacuum distillation and styrene was purified by passing over a basic alumina column. 2, 2-Azoisobutyronitrile (AIBN) was purified by recrystallization from methanol. S-1-Dodecyl-S'-( $\alpha,\alpha'$ -dimethyl- $\alpha'$ -acetic acid) trithiocarbonate (TC)<sup>1</sup>, 2-cyanoprop-2-yl-4-cyanodithiobenzoate (CPD)<sup>2</sup>, 4-(3-butenyl)styrene and Boc-aminoethyl acrylamide (BOCa)<sup>3</sup> and phenyl 4-vinylbenzene sulfonate (PVBs)<sup>4</sup> were synthesized according to literature procedures.

**Characterization.** All <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of sample were recorded with a Bruker AVANCE III™ 500 spectrometer (500 MHz) by using CDCl<sub>3</sub> as a solvent. JEM-2100F TEM instrument was used to obtain the Transmission electron microscopy (TEM) images of catalyst before and after the one-pot reaction. Samples were prepared by dip-coating a 400 mesh carbon-coated copper grid from a dilute sample solution allowing the solvent to evaporate. The infrared (IR) spectra were recorded using the FT-IR (Thermo NICOLET is 50). A nitrogen adsorption-desorption isotherm was collected on a Quantachrome Autosorb IQ adsorption analyzer. The polymer samples were degassed for more than 10h at 120 °C before measurements. GC/MS analyzed were obtained on an Agilent 6890 Series GC System with a Hewlett-Packard 5973 Mass Selective Detector (70 eV) using a HP-5MS fused silica capillary column (cross-linked 5% phenyl ethyl siloxane, 30 m ×0.25 mm ID×0.25 μm film thickness) and argon as a carrier gas (1 mL min<sup>-1</sup>). The split ratio was 1:50. The injector temperature was kept at 270 °C and detector was kept at 280 °C. The column temperature was held at 60 °C for 3 min, increased to 280 °C at a rate of 25 °C min<sup>-1</sup>, and then kept at 280 °C for 5 min. The Brunauer-Emmett-Teller (BET) surface area and the micropore surface area were determined by using the BET equation and the t-plot equation, respectively. The pore size distribution was analyzed by original density functional theory (DFT). Elemental analyses were conducted by using an elementalVario

EL III and the sample was dried in vacuo at ambient temperature. Gel permeation chromatography (GPC) data were obtained from Waters GPC system equipped with a Waters 1515 isocratic HPLC pump, a 2414 refractive index detector, and two Waters's HPLC columns. N-N dimethyl formamide was used as the solvent for polymers and eluent for GPC with a flow rate of 1 mL min<sup>-1</sup> at 30°C. The GPC instrument was calibrated with narrowly dispersed linear polystyrene standards.

### **1. Synthesis of P(GM-g-PLA-g-PBOCa)**

The P(GM<sub>300</sub>-g-PLA<sub>30</sub>-TC) was prepared according to the previous reported method.<sup>9</sup> P(GM<sub>300</sub>-g-PLA<sub>30</sub>-TC) (200 mg) was mixed with AIBN (0.2 mg), BOCa (208 mg) and 1,4-dioxane (1mL) in a reaction vessel and degassed by three freeze-pump-thaw cycles. The solution was conducted at 60 °C for 1 h and was precipitated from THF into diethyl ether three times and dried under vacuum at ambient temperature for 24 h. Yield = 300mg (10%). GPC (PS standards, DMF as eluent): M<sub>n</sub> = 5.3×10<sup>6</sup> g/mol, M<sub>w</sub>/M<sub>n</sub> = 1.11.

### **2. Synthesis of P(GM-g-PLA-g-PBOCa-g-PPVBs/PS)**

P(GM<sub>300</sub>-g-PLA<sub>30</sub>-g-PBOCa<sub>6</sub>) (120 mg) was mixed with PVBs (97 mg), styrene (3.72 mL) and 1,4-dioxane (4 mL) in a reaction vessel and degassed by three freeze-pump-thaw cycles. The solution was conducted at 60 °C for 4 h and 30 min and was precipitated from DCM into methanol three times and dried under vacuum at ambient temperature for 24 h. Yield = 280mg. GPC (PS standards, DMF as eluent): M<sub>n</sub> = 8.5×10<sup>6</sup> g/mol, M<sub>w</sub>/M<sub>n</sub> = 1.13.

### **3. Synthesis of amino- and sulfo- bifunctionalized hyper-crosslinking polymer catalyst (NH<sub>2</sub>-SO<sub>3</sub>H-H-ONTFs)**

The P(GM<sub>300</sub>-g-PLA<sub>30</sub>-g-PBOC<sub>6</sub>a-g-PPVBs<sub>13</sub>/PS<sub>116</sub>) (150 mg) was dissolved in dried DCE (15mL) under nitrogen. Formaldehyde dimethyl acetal (0.16 mL) and anhydrous FeCl<sub>3</sub> (289 mg) were then added into the above mixture solution and stirring at 90°C for 24 h. The solvent was removed and the hyper-crosslinking solid was washed with methanol. The resulting solid (160 mg) was added to a mixture of methanol (16 mL) and NaOH (16 mL)

and stirred at 60 °C for 20 h. After that, the solid was washed with water and stirred with the CH<sub>3</sub>COOH/CH<sub>3</sub>COONa buffer (PH = 6) (25 mL, 1mg/mL) to obtain sulfonic acid group via the ion-exchanging method. The product was washed with H<sub>2</sub>O and methanol and dried in a vacuum at 60 °C and obtained as brown powder.

#### **4. Catalytic Experiment**

The one-pot deacetalization-Knoevenagel cascade reactions were chosen as a typical example to test the catalytic performance of the obtained NH<sub>2</sub>-SO<sub>3</sub>H-H-ONTFs catalyst. Catalysis experiments were conducted in a 5 mL sealed vials in an oil bath. 10 mg of the catalyst (1), 75 mmol of Benzaldehyde dimethyl acetal (2), 300 mmol of ethyl cyanoacetate (3) and 0.4 mL toluene (the percentage of 1 is 10% and 2:3=1:4) were placed into the vial. The mixture was stirred at 80°C for 1 h and solution of reaction was detected by GC. For the further study of the catalytic performance of the catalyst, other reactants were also catalyzed by it and detected by GC.

The catalyst was washed with methanol and deionized water and dried under a vacuum after the one-pot reaction to conduct the recovered test to detect the reusability of the catalyst.

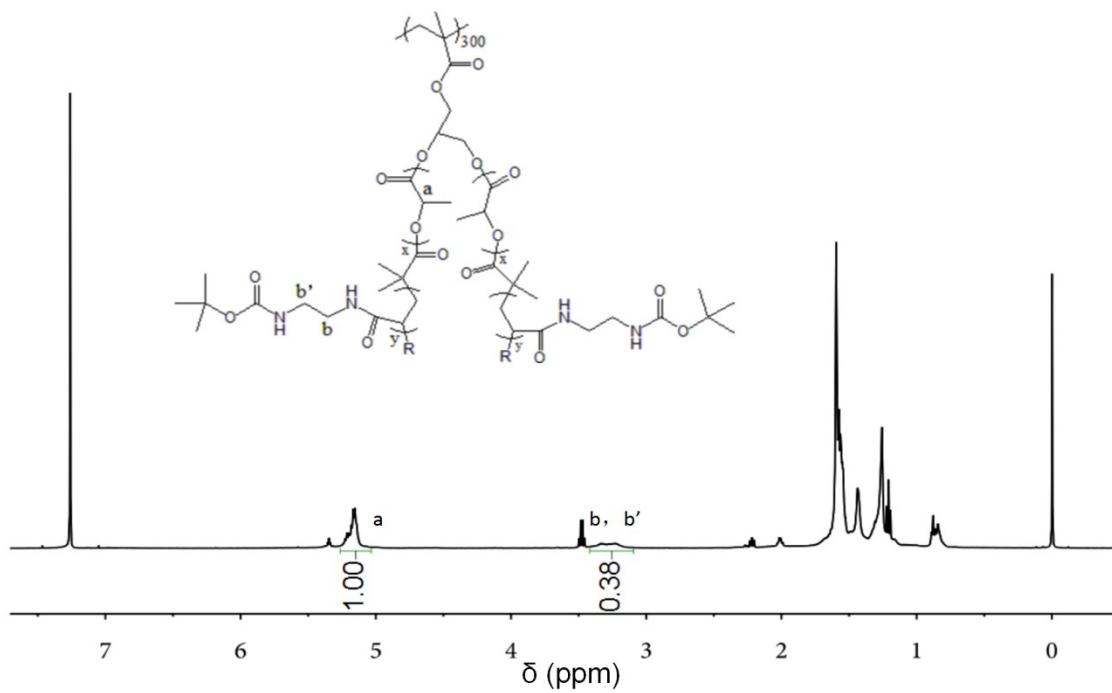


Fig. S1 <sup>1</sup>H NMR of P(GM-g-PLA-PBOCa).

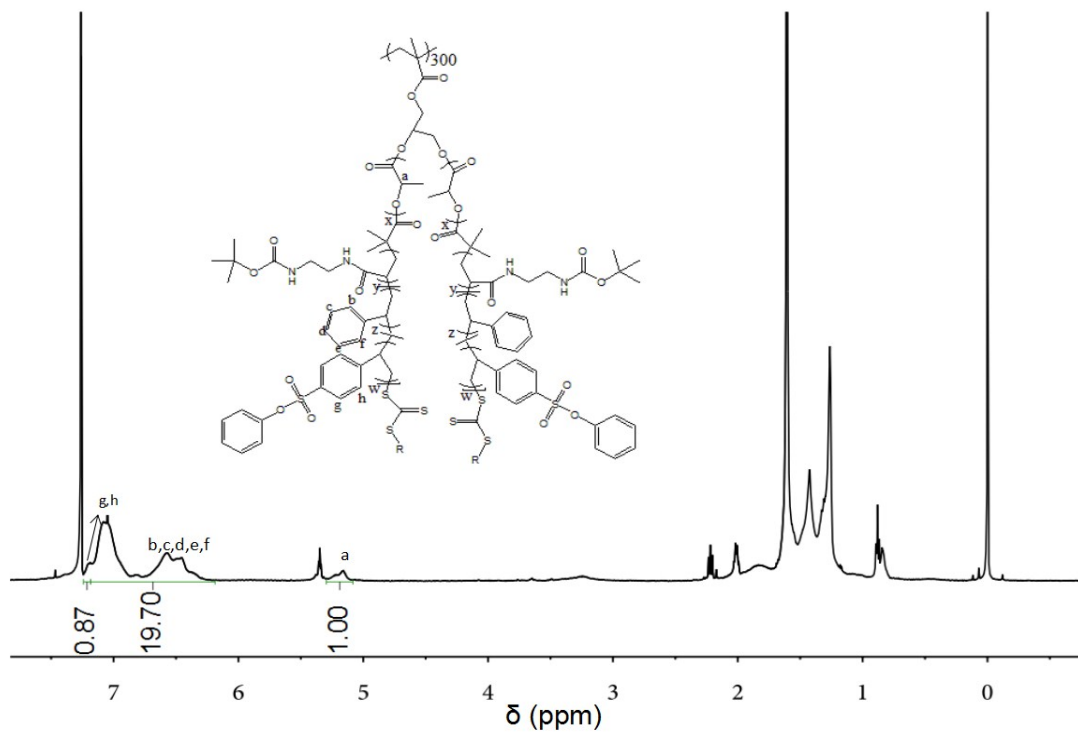


Fig. S2  $^1\text{H}$  NMR of P(GM-g-PLA-g-PBOCa-g-PPVBs/PS)

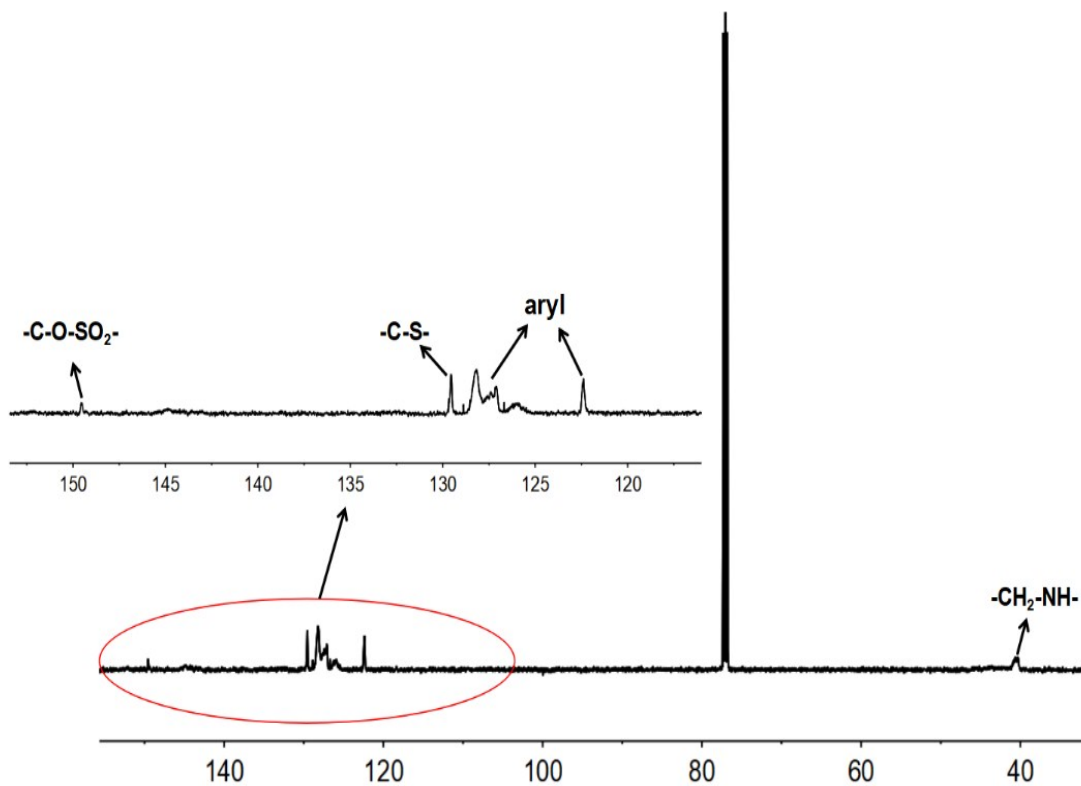


Fig. S3  $^{13}\text{C}$  NMR of P(GM-g-PLA-g-PBOCa-g-PPVBs/PS)

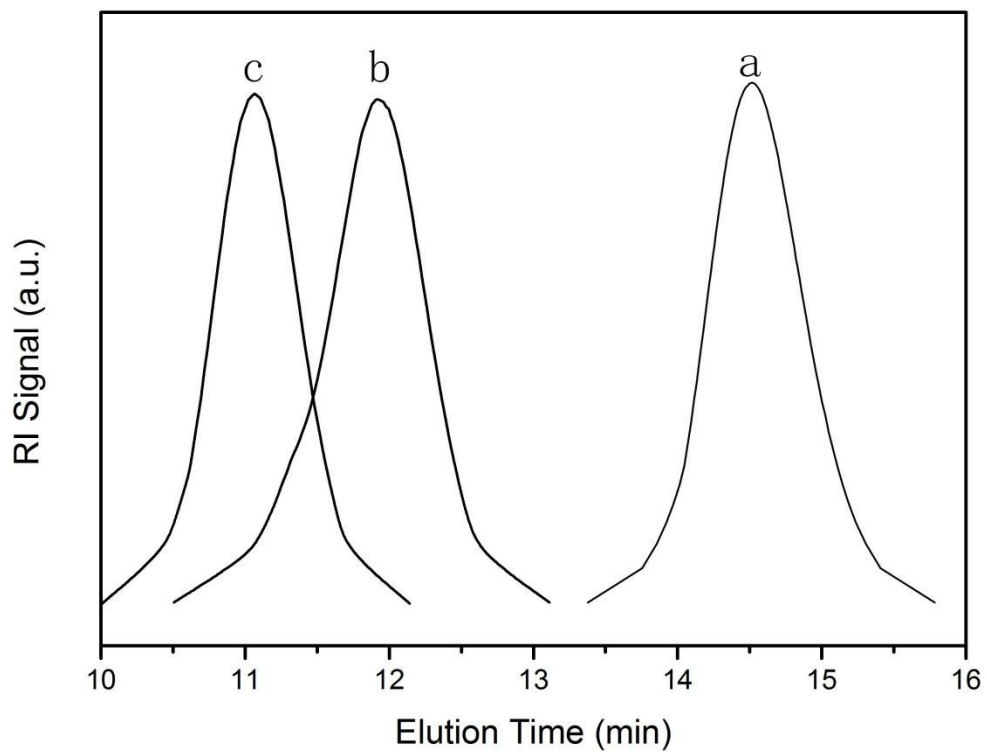


Fig. S4 GPC characterization of (a). P(GM-g-PLA-Tc) (b). P(GM-g-PLA-PBOCa)  
(c). P(GM-g-PLA-g-PBOCa-g-PPVBs/PS).



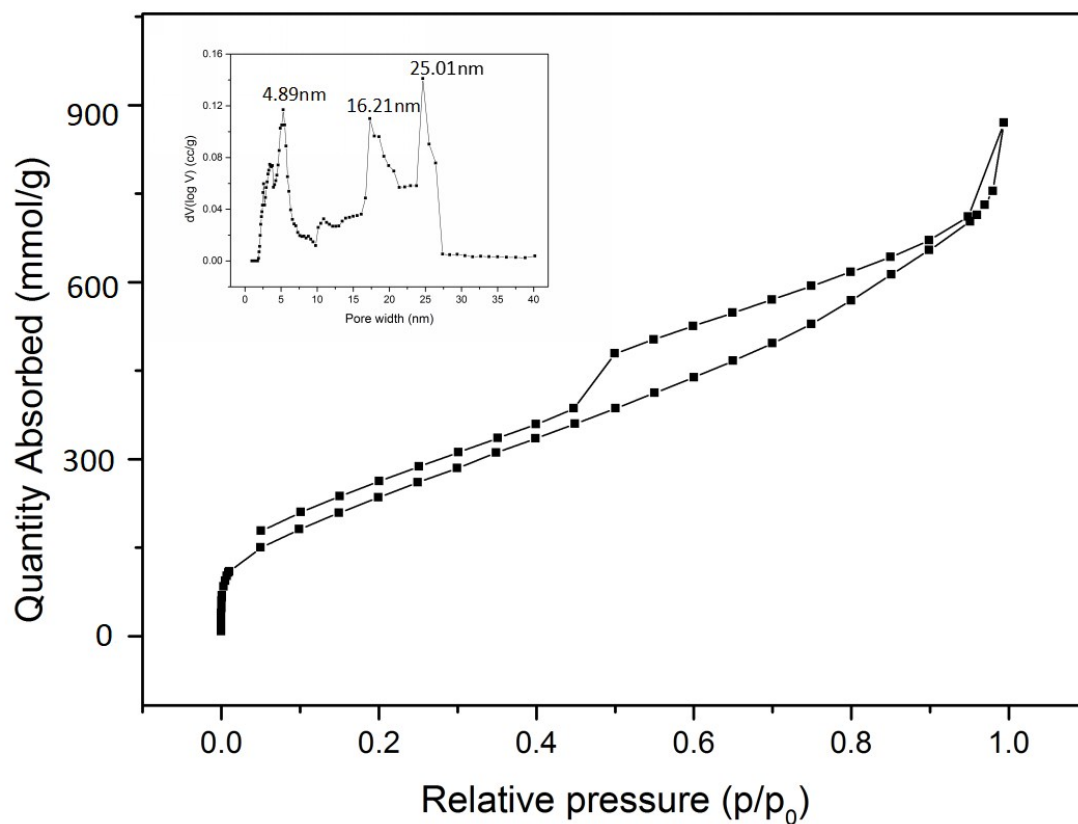


Fig. S5 N<sub>2</sub> adsorption-desorption isotherms and pore size distributions (inset) of the NH<sub>2</sub>-SO<sub>3</sub>H-H-ONTFs after recycle tests.

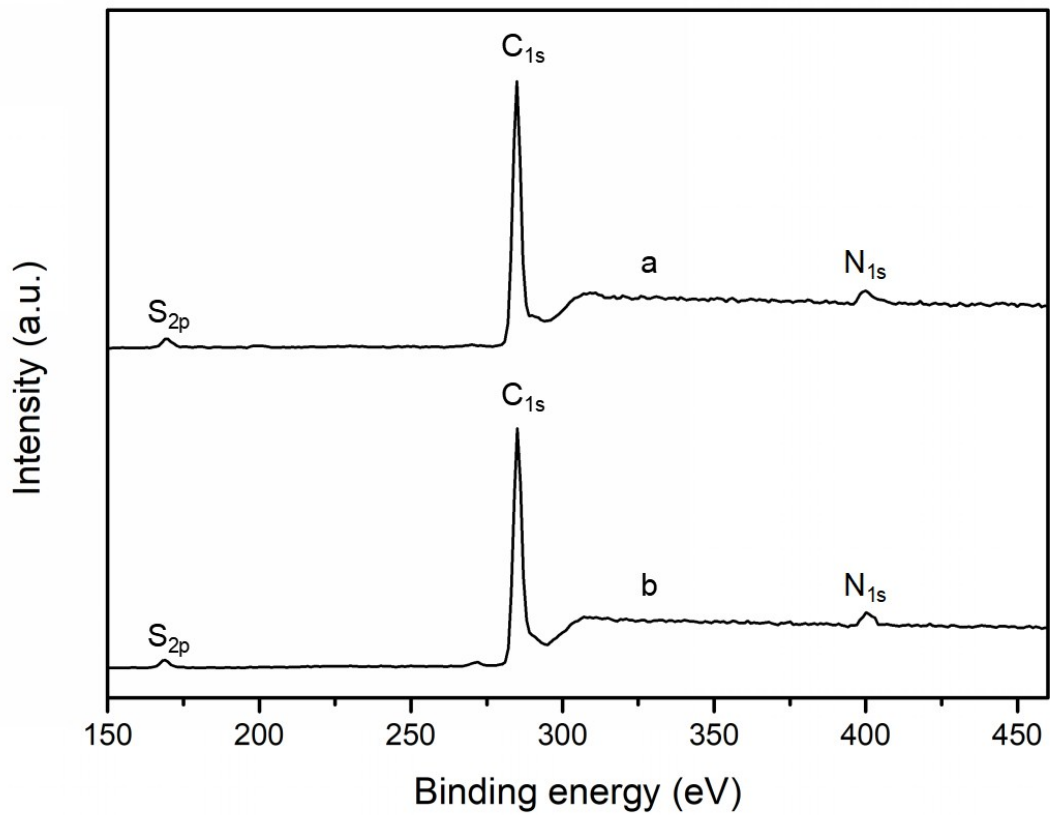


Fig. S6 XPS spectra of NH<sub>2</sub>-SO<sub>3</sub>H-H-ONTFs before(a) and after(b) use (C<sub>1s</sub>;N<sub>1s</sub>;S<sub>2p</sub>)

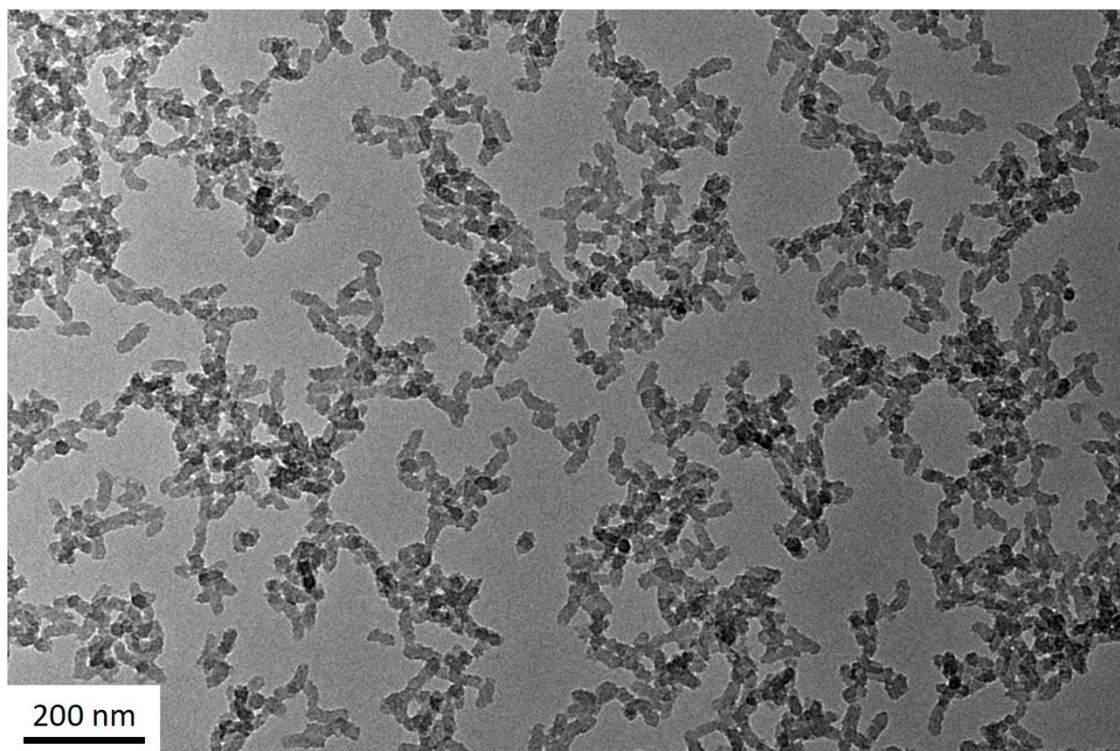


Fig. S7 TEM image of  $\text{NH}_2\text{-SO}_3\text{H-H-ONTFs}$  after recycle.

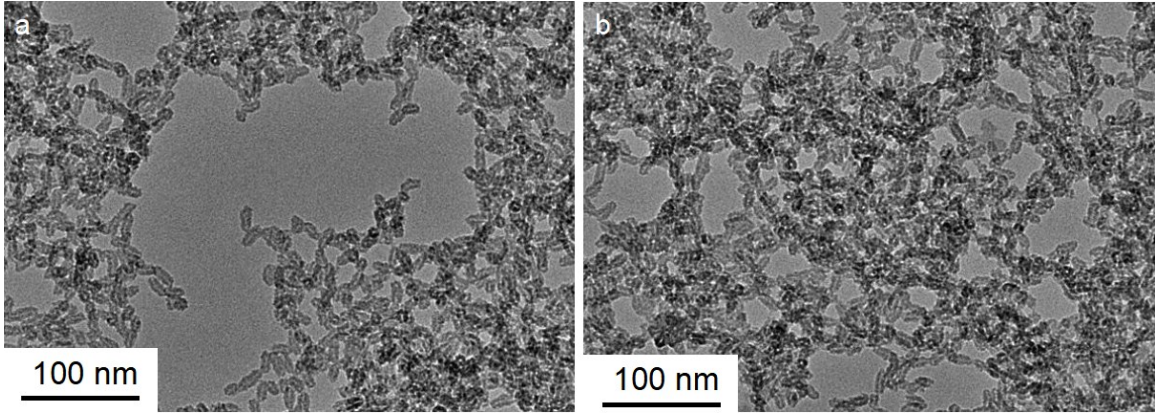


Fig. S8 TEM image of monofunctionalized ONTFs before (a) and after(b) use.

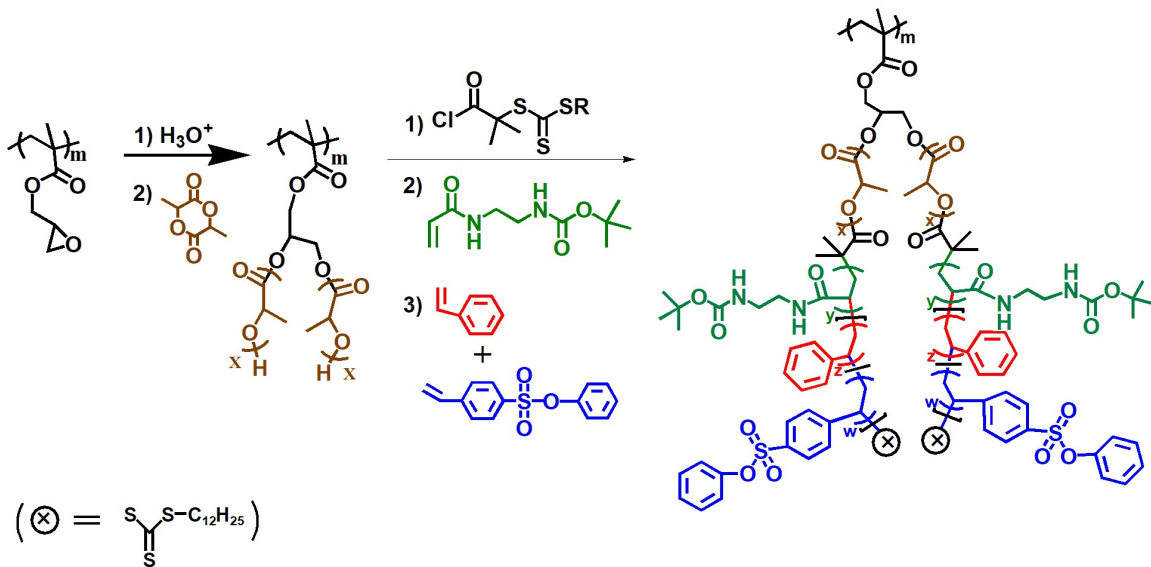
Table S1. Porous properties of NH<sub>2</sub>-SO<sub>3</sub>H-H-ONTFs(1), and NH<sub>2</sub>-SO<sub>3</sub>H-H-ONTFs after recycles(2).

Samples	S <sub>BET</sub> <sup>[a]</sup> [m <sup>2</sup> /g]	S <sub>micro</sub> <sup>[b]</sup> [m <sup>2</sup> /g]	S <sub>meso</sub> <sup>[c]</sup> [m <sup>2</sup> /g]	V <sub>Total</sub> <sup>[d]</sup> [cm <sup>3</sup> /g]
1	885	495	390	1.39
2	881	452	429	0.57

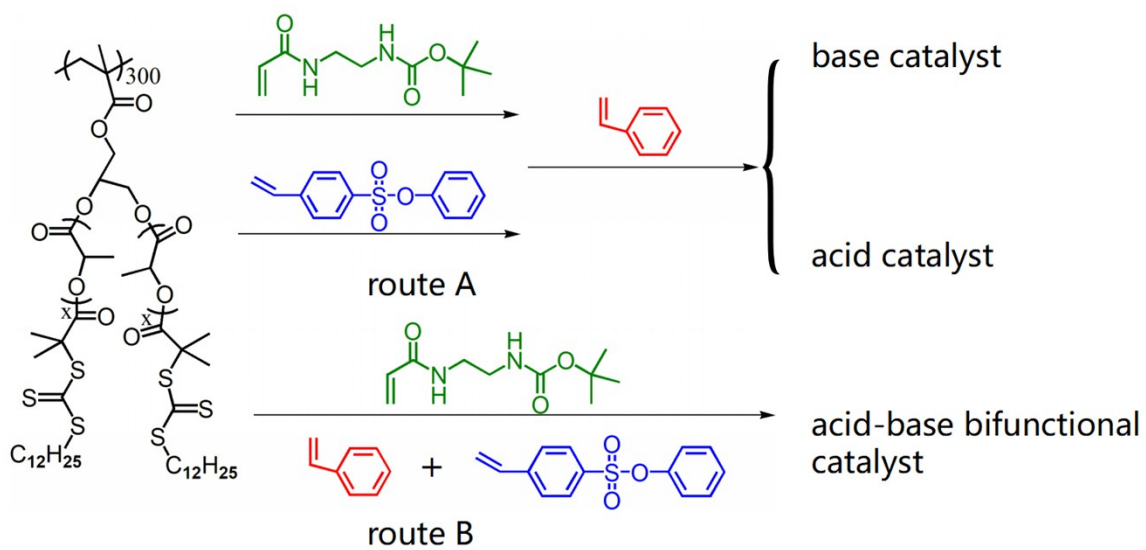
[a] BET specific surface area calculated from N<sub>2</sub> adsorption isotherm at 77.4 K; [b] Microporous surface area calculated from t-plots; [c] Mesoporous surface area; [d] Total pore volume at P/P<sub>0</sub> = 0.998.

**Table S2.** Comparison of the catalytic performance of different heterogeneous catalysts in the deacetalization-Knoevenagel cascade reactions.

Entry	Catalysts	[benzaldehyde Dimethylacetal ], Amount of catalyst	Reaction Conditions	Yield.3 (%)	TOF ( h <sup>-1</sup> )	Ref.
1	PPAF-SO <sub>3</sub> H-NH <sub>2</sub>	0.18 M, 20 mg	Toluene (2 mL), 90 °C, 1 h	100	913	5
2	PPAF (SO <sub>3</sub> H/NH <sub>2</sub> )	0.18 M, 30 mg	Toluene (2 mL), 90 °C, 1 h	87	794	6
3	MCN (COOH/NH <sub>2</sub> )	0.17 M, 30 mg	Toluene (3 mL), 80 °C, 24 h	>99	35.5	7
4	SOH-AEPTMS@MCM-41	0.004 M, 150 mg	H <sub>2</sub> O (12 ml), 80 °C, 1 h	94.9	3.8	8
5	MONNs (SO <sub>3</sub> H/NH <sub>2</sub> )	0.08 M, 9.5 mg	Toluene (0.4 mL), 80 °C, 1.5 h	>99	854	9
6	AMSA-MIL-101-NH <sub>2</sub>	0.005 M, 50 mg	Toluene (10 mL), 90 °C, 10 h	99.74	1.5	10
7	SO <sub>3</sub> H-AA@MNP	0.005 M, 20 mg	Toluene (10 mL), 90 °C, 7 h	89	4	11
8	<b>NH<sub>2</sub>-SO<sub>3</sub>H-H-ONTFs</b>	<b>0.075 M, 10 mg</b>	<b>Toluene (0.4 mL), 80 °C, 1 h</b>	<b>&gt;99</b>	<b>1141</b>	<b>This work</b>



Scheme S1 Synthesis route of the multicomponent bottlebrush copolymer precursors.

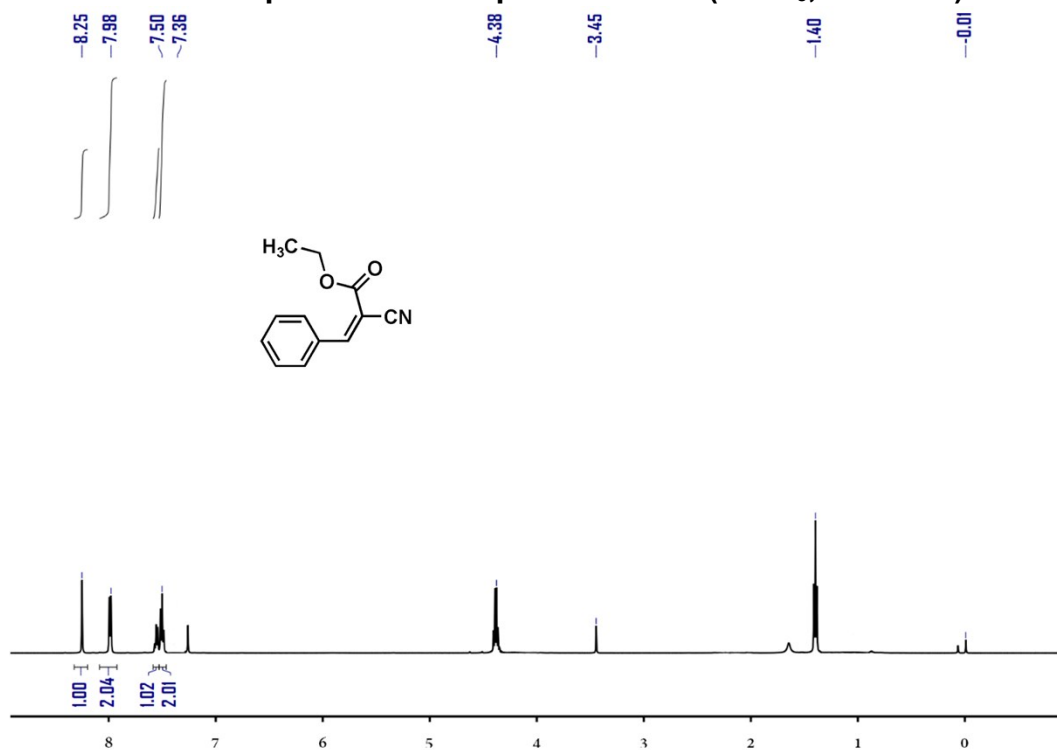


Scheme S2 Synthesis routes of base catalyst, acid catalyst, and acid-base bifunctional catalyst.

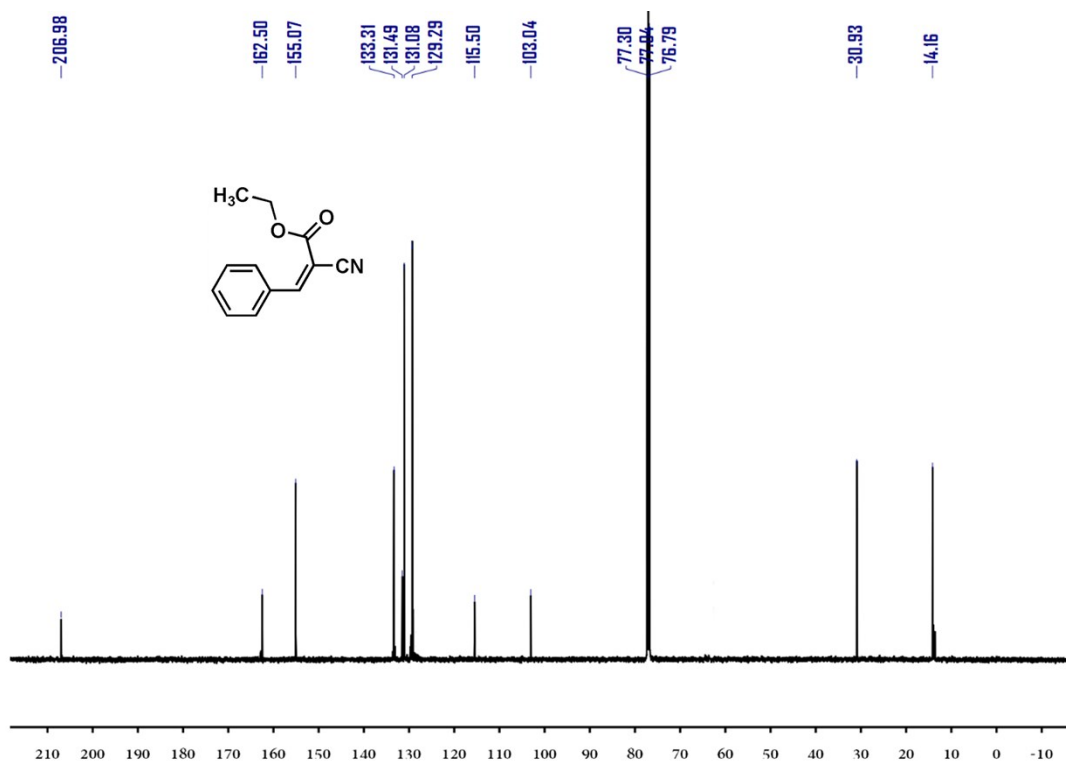


# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra of Compounds

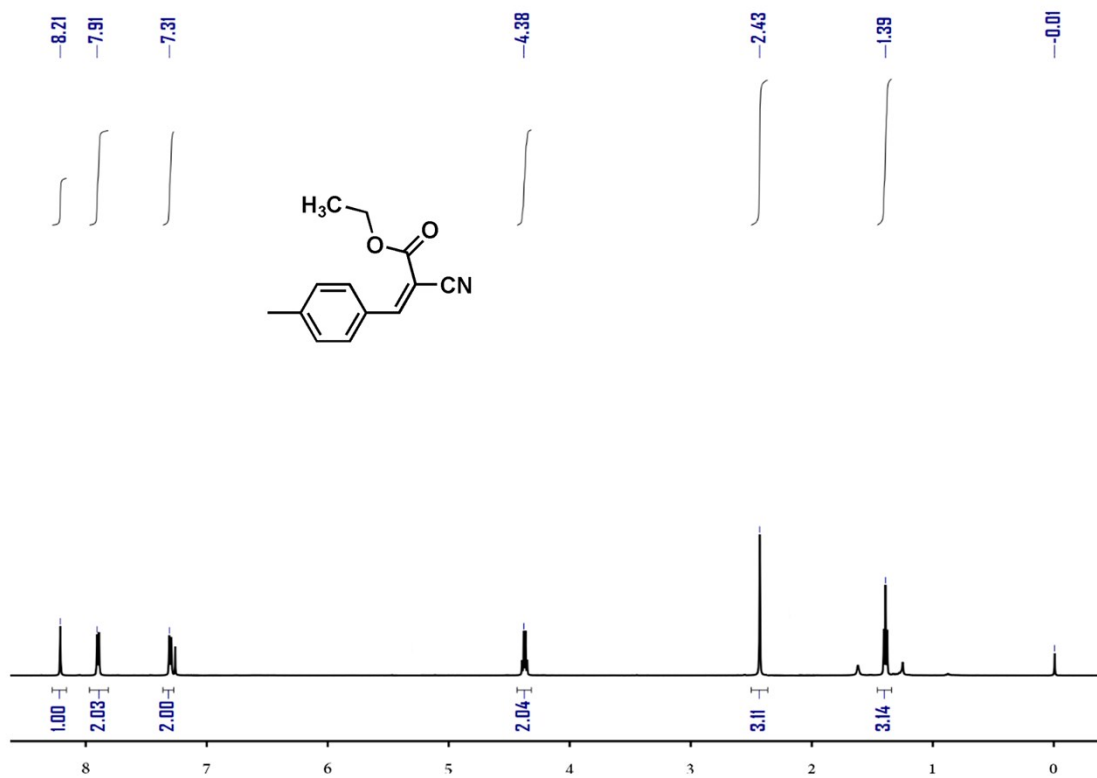
$^1\text{H}$  NMR spectrum of the product of 2a ( $\text{CDCl}_3$ , 500 MHz)



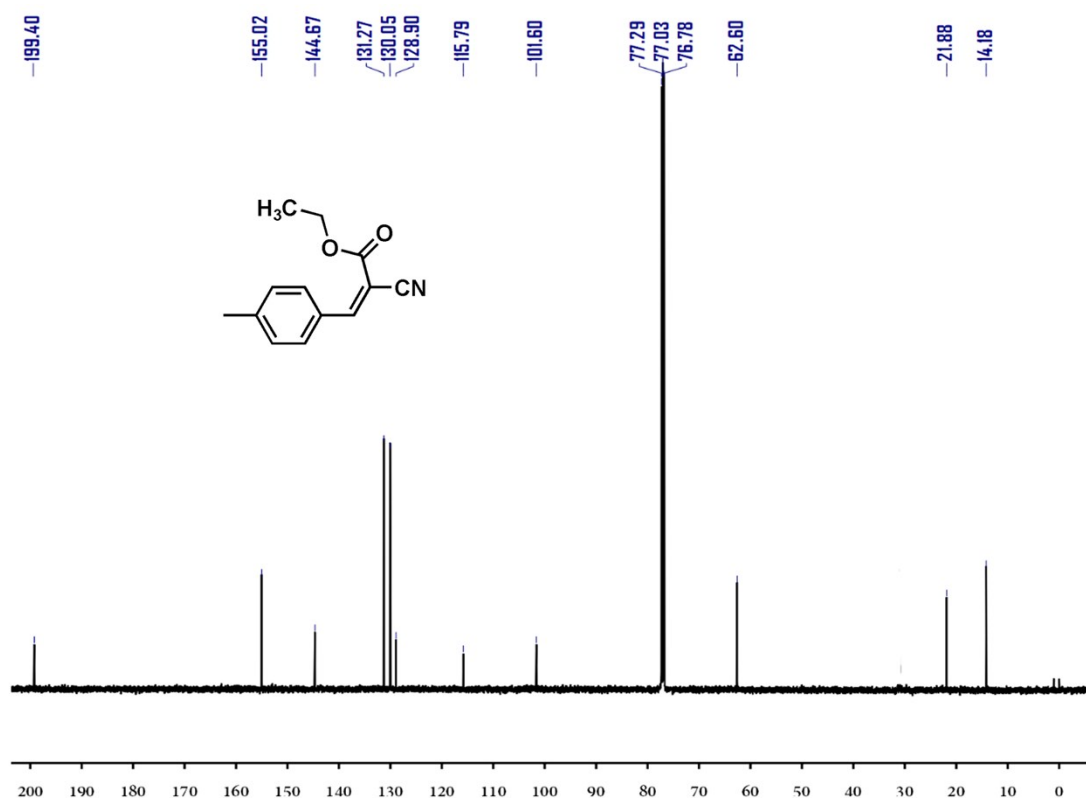
<sup>13</sup>C NMR spectrum of the product of 2a (CDCl<sub>3</sub>, 500 MHz)



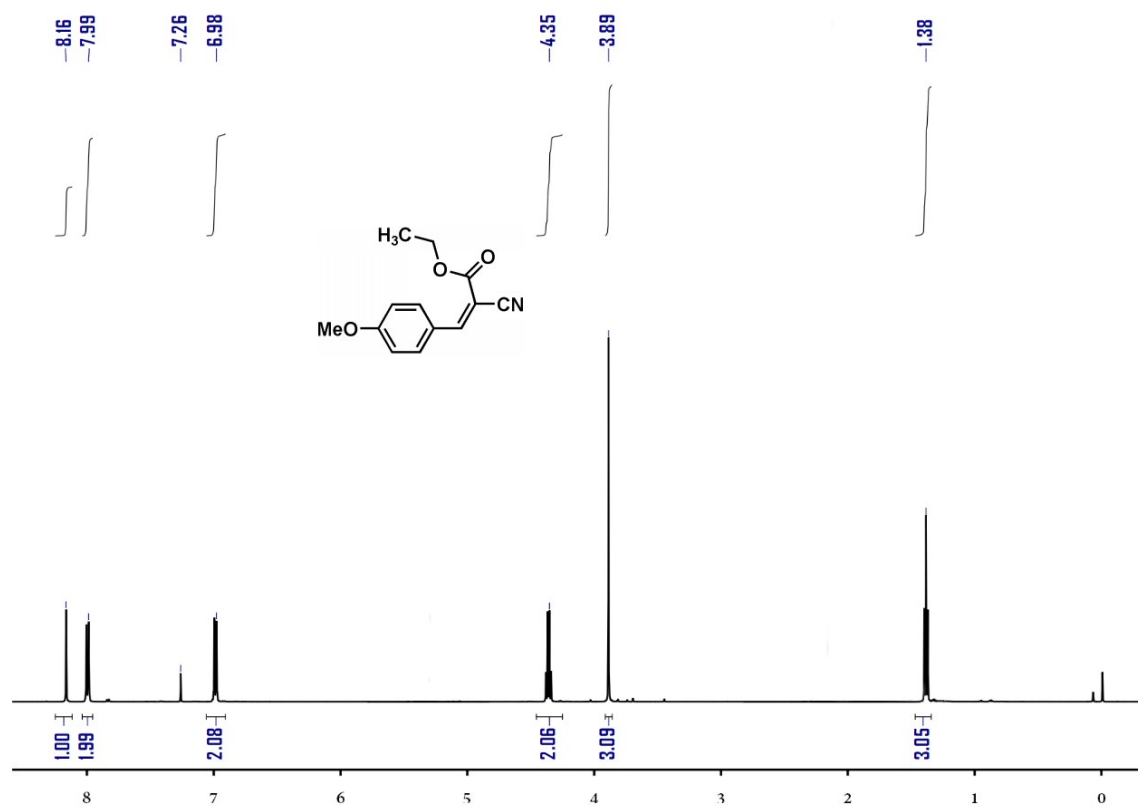
**<sup>1</sup>H NMR spectrum of the product of 2b (CDCl<sub>3</sub>, 500 MHz)**



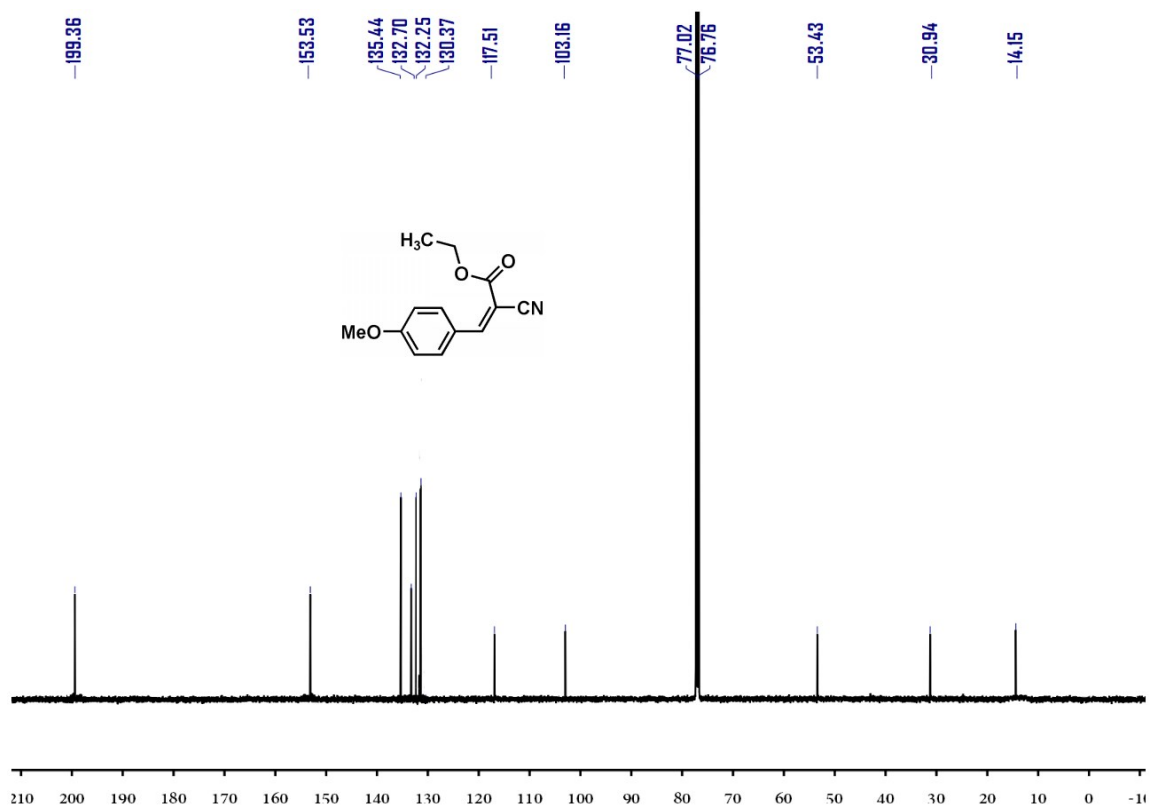
**$^{13}\text{C}$  NMR spectrum of the product of 2b ( $\text{CDCl}_3$ , 500 MHz)**



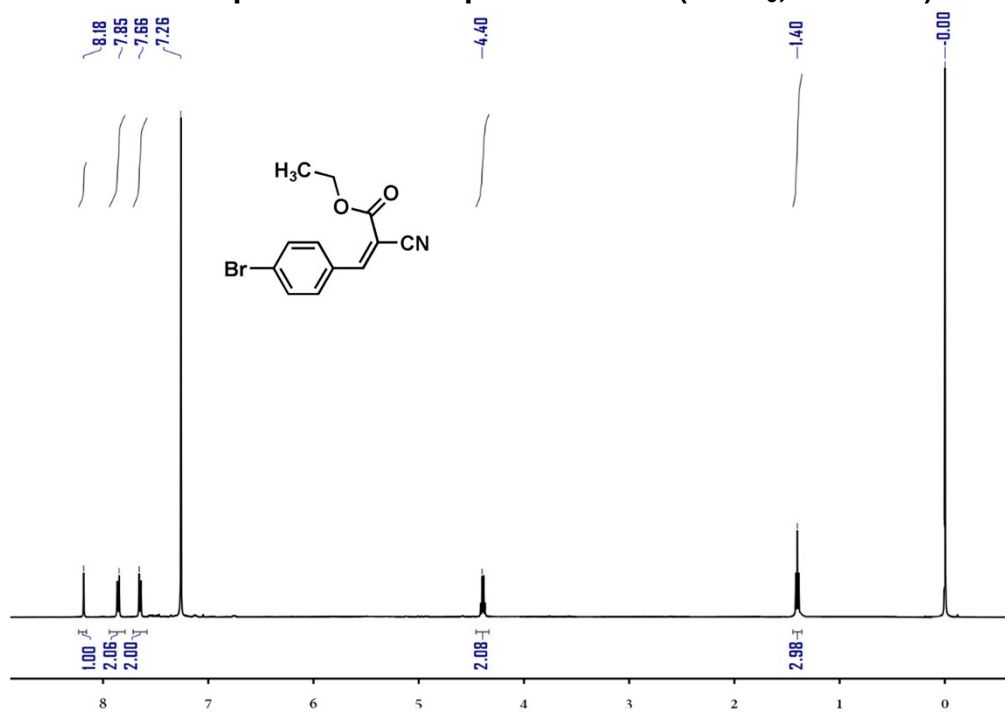
**<sup>1</sup>H NMR spectrum of the product of 2c (CDCl<sub>3</sub>, 500 MHz)**



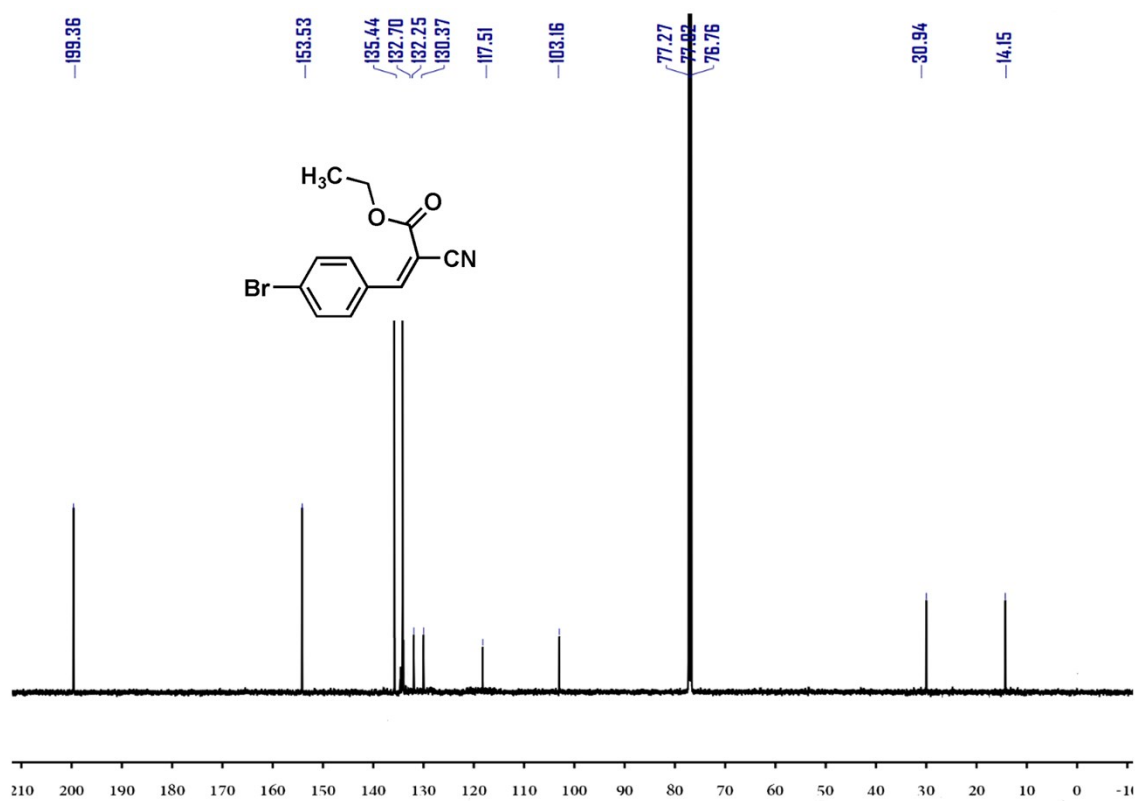
<sup>13</sup>C NMR spectrum of the product of 2c (CDCl<sub>3</sub>, 500 MHz)



**<sup>1</sup>H NMR spectrum of the product of 2d (CDCl<sub>3</sub>, 500 MHz)**

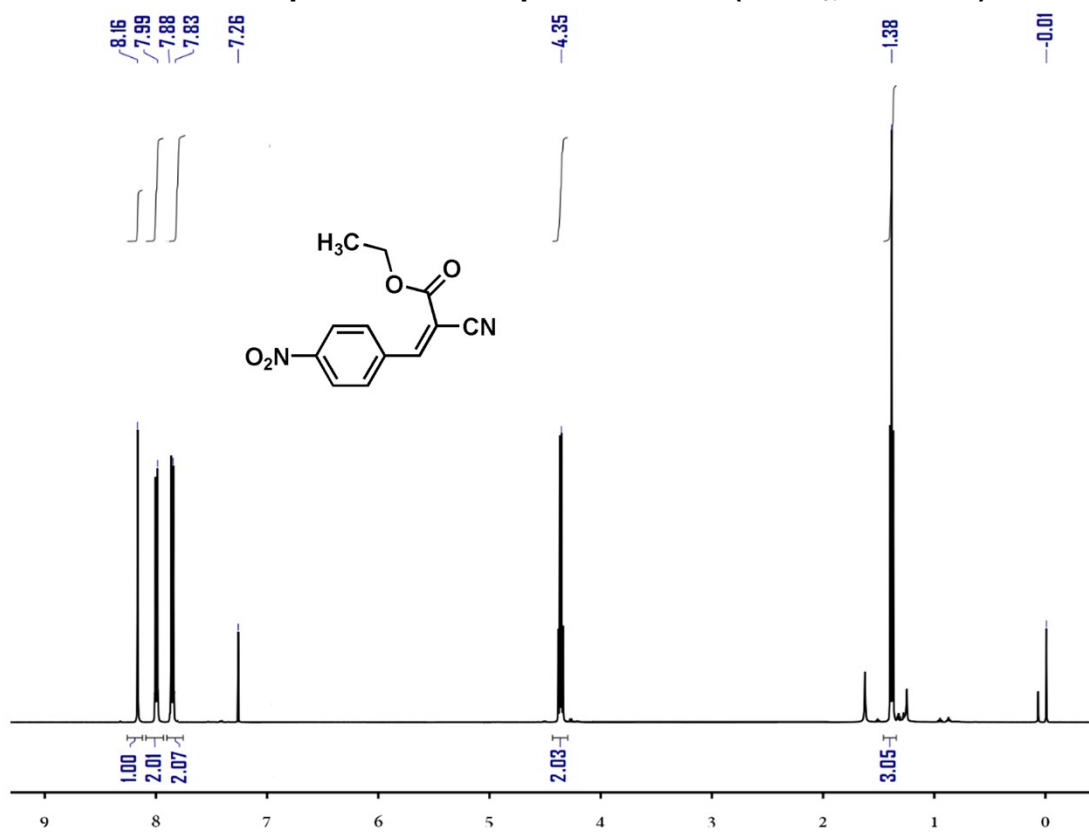


<sup>13</sup>C NMR spectrum of the product of 2d (CDCl<sub>3</sub>, 500 MHz)

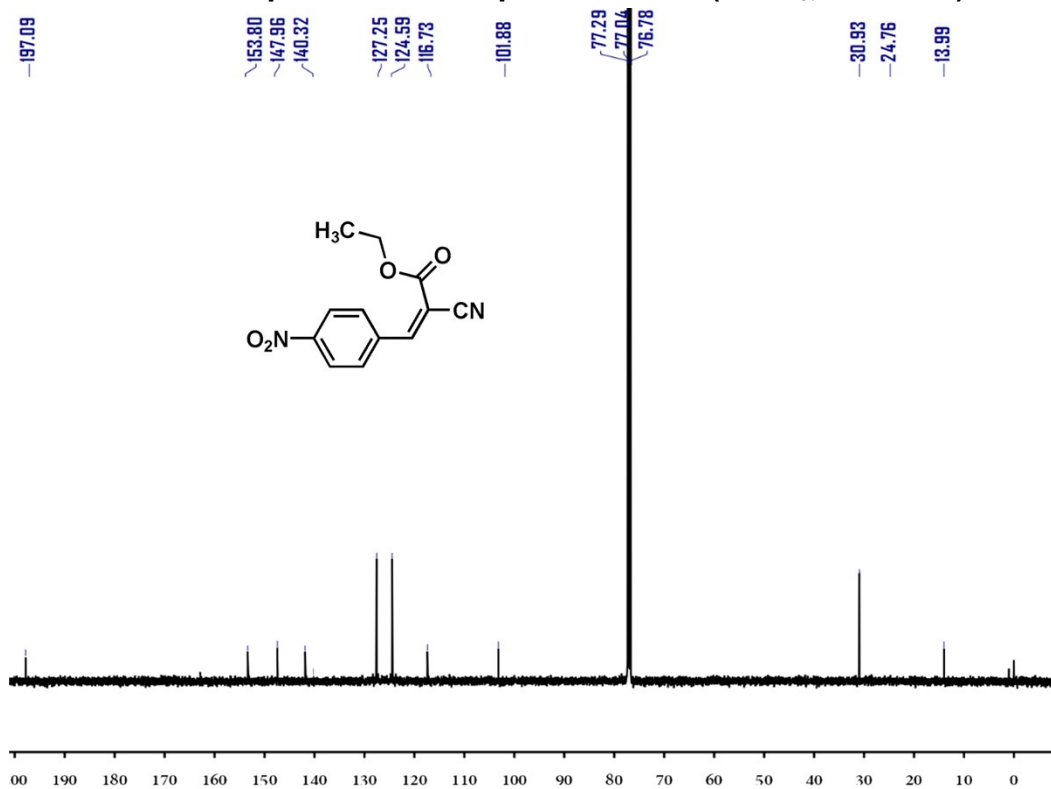




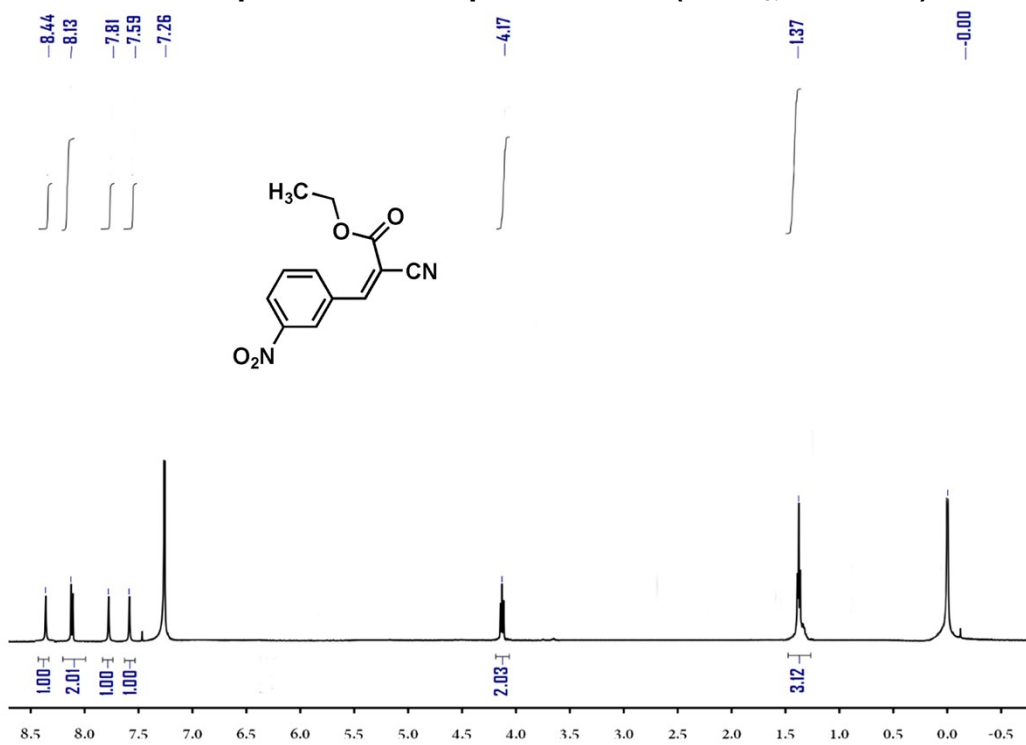
**$^1\text{H}$  NMR spectrum of the product of 2e ( $\text{CDCl}_3$ , 500 MHz)**



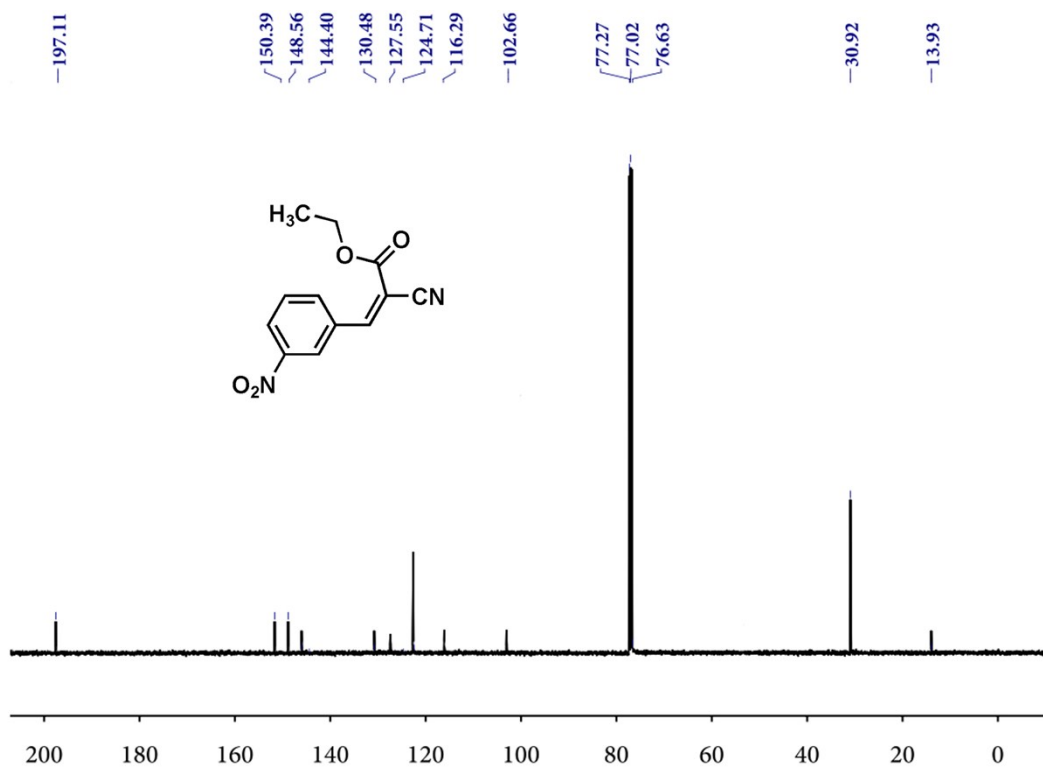
**$^{13}\text{C}$  NMR spectrum of the product of 2e ( $\text{CDCl}_3$ , 500 MHz)**



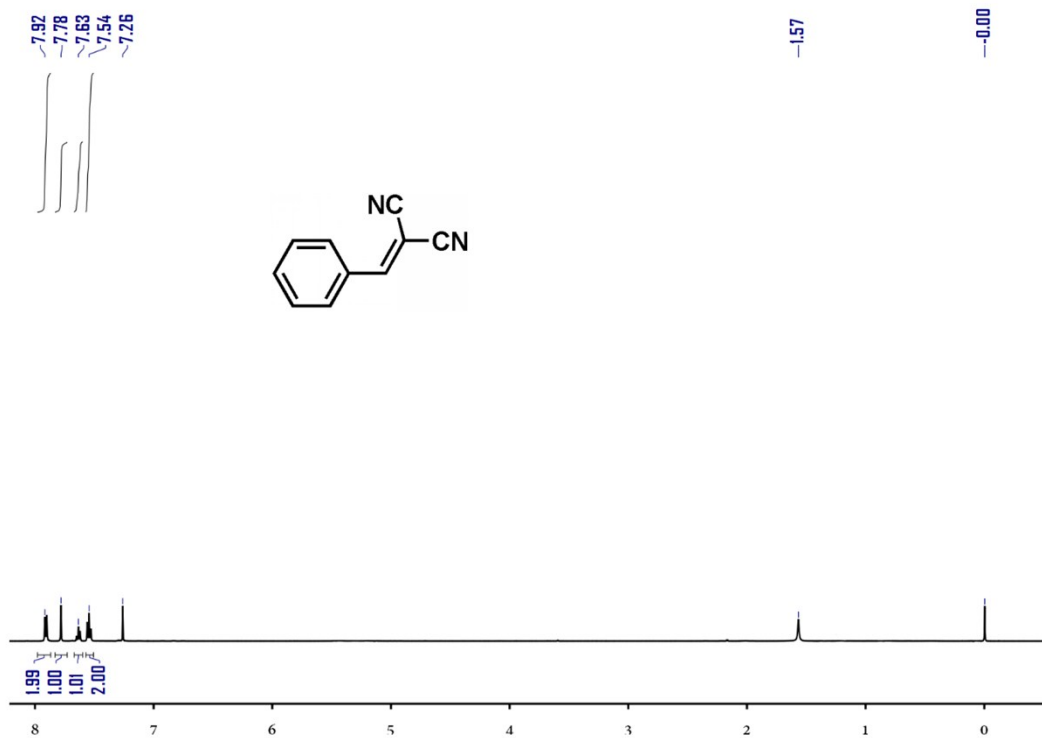
**<sup>1</sup>H NMR spectrum of the product of 2f (CDCl<sub>3</sub>, 500 MHz)**



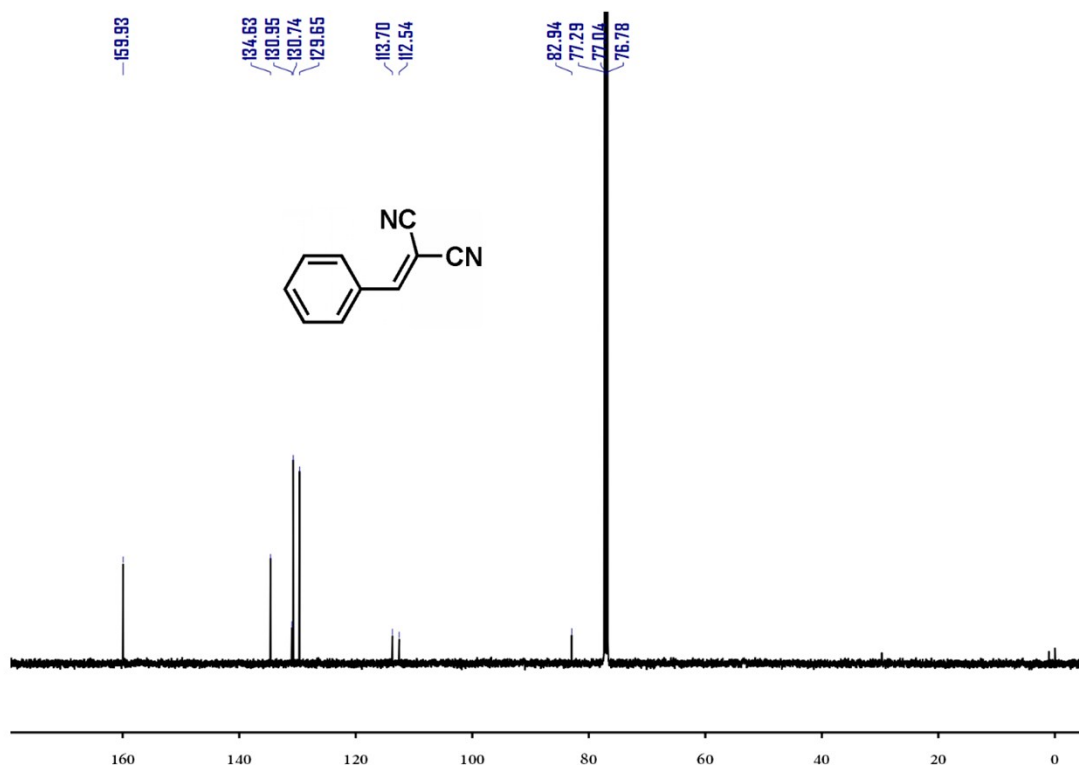
**$^{13}\text{C}$  NMR spectrum of the product of 2f ( $\text{CDCl}_3$ , 500 MHz)**



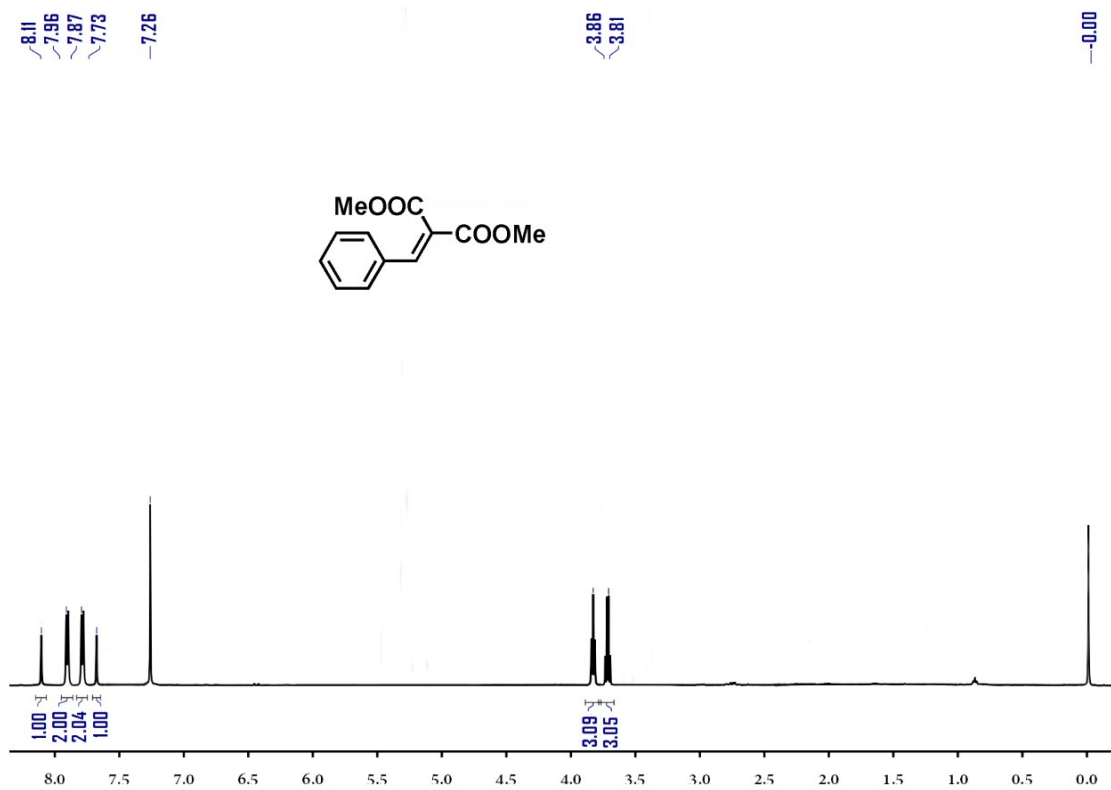
**<sup>1</sup>H NMR spectrum of the product of 2g (CDCl<sub>3</sub>, 500 MHz)**



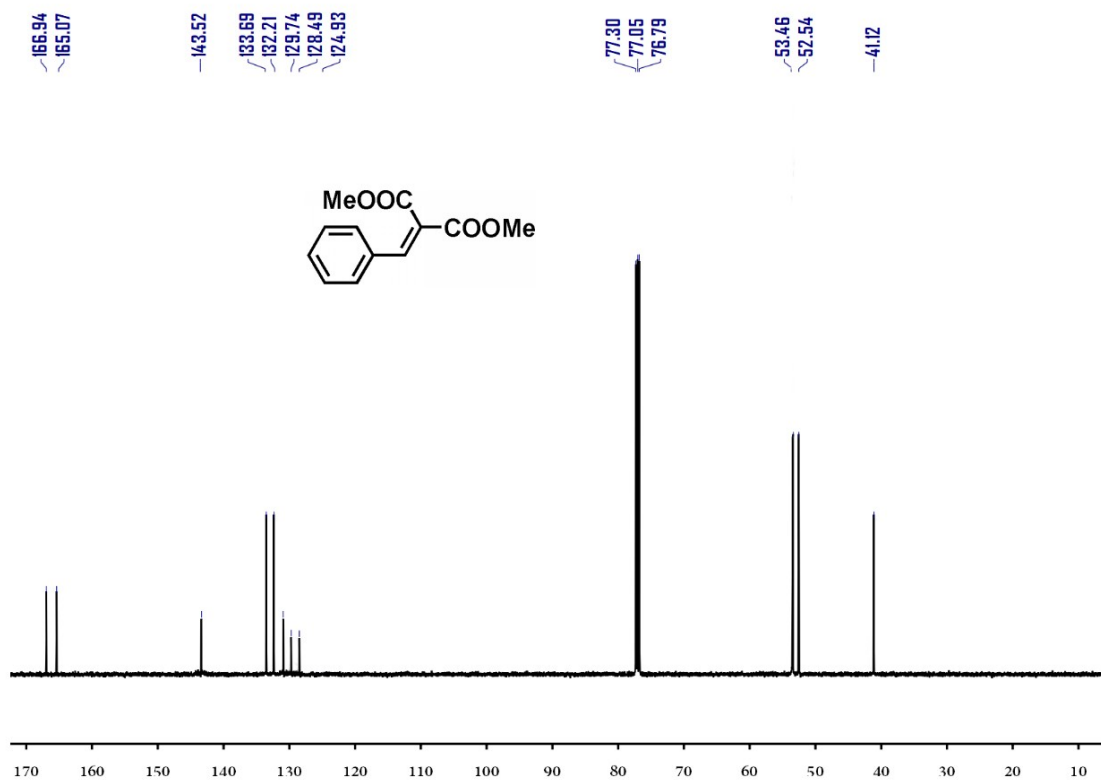
**$^{13}\text{C}$  NMR spectrum of the product of 2g ( $\text{CDCl}_3$ , 500 MHz)**



**<sup>1</sup>H NMR spectrum of the product of 2h (CDCl<sub>3</sub>, 500 MHz)**



**$^{13}\text{C}$  NMR spectrum of the product of 2h ( $\text{CDCl}_3$ , 500 MHz)**





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