

Supporting Information

Green Synthesis of Palladium Nanoparticles via Branched Polymers: The Bio-Based Nanocomposite for C-C Coupling Reactions

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1. Preparation of CMH

Hemicelluloses powder (0.66 g, approximately 5 mmol of xylose) was homodispersed in water and then was heated to 85 °C with stirring rate 500 r/min until swollen hemicelluloses were obtained (approximately 10 min). As the mixture was cooled down to room temperature, a required quantity of sodium hydroxide (accounting for 50% all amount sodium hydroxide) was added dropwise (20 drops per minute), and the mixture was swollen for 30 minutes under 85 °C. Subsequently, ethanol was added dropwise to keep the total volume up to 15 mL with the volume ratio of ethanol to water approximately 1:1 and the stirring rate was kept at 1000 r/min. Followed by the addition of MCA and remaining sodium hydroxide, the mixture was reacted at the required temperature. After the limited reaction time, the mixture was cooled down and then neutralized with diluted acetic acid. Then the resulting mixture was precipitated with ethanol, filtered and washed by ethanol for three times. The products obtained were dissolved in purified water and dialyzed for three days, followed by freezing-dried at -50 °C. Subsequently the dried sodium carboxymethyl hemicelluloses (0.33 g) were dissolved in 10 mL DMSO, and then *p*-toluenesulfonic acid (0.2 g, 1.1 mmol) that was previously dissolved in 2 mL DMSO was added. The reaction was processed at 60 °C for 30 min. After the reaction, the mixture was dialyzed for three days and freeze-dried at -50 °C, CMH was obtained. As can be seen from Table S1, six samples were prepared by changing the reaction conditions.

2. Determination of the Degree of Substitution (DS)

The DS of CMH was determined by the acidometric titration method. 0.2 g of CMH and 80 mL distilled water were added into a 250 mL conical flask and stirred for 10 min. First, two drops of phenolphthalein indicator were added into the mixture, and then acid or alkali was added dropwise with stirring until the color of the solution just changed. Besides, three drops of methyl orange was added, subsequently, the solution was titrated with 0.05 M H₂SO₄ until the color of solution was changed from colorless to red. The DS value was calculated on the basis of the equations as shown below.

$$B = \frac{2 \times M \times V}{m} \quad (1)$$

$$DS = \frac{0.132 \times B}{1 - 0.08 \times B} \quad (2)$$

Where m is weight of CMH, 0.132 (g.mmol⁻¹) is the molar mass of a xylose unit, 0.08 (g.mmol⁻¹) is the net increase in the mass of a xylose unit, M is the normality of the H₂SO₄ used, V is milliliters of H₂SO₄ used to titrate the sample, and B is the millimole per gram of H₂SO₄ consumed per gram of the products. This procedure makes the assumption that the untreated hemicelluloses do not have any carboxyl content.

3. Influences of reaction conditions on the DS of CMH

Table S1. Influences of reaction conditions on the DS of CMH.

Entry	Temp (°C)	Time (min)	Molar ratio ^a (NaOH/X)	Molar ratio ^b (MCA/X)	DS ^c
1	rt	75	1:1	2:1	0.055
2	65	75	1:1	2:1	0.082
3	65	75	2:1	1:1	0.0534
4	65	75	2:1	2:1	0.109
5	75	120	2:1	1:1	0.177
6	75	300	2:1	1:1	0.24

^a Molar ratio of NaOH/X represents the molar ratio of NaOH to anhydroxylose units in hemicelluloses. ^b Molar ratio of SMCA/X represents the molar ratio of MCA to anhydroxylose units in hemicelluloses. ^c On the basis of the assumption that all of the hemicelluloses are converted to di-etherified hemicelluloses (DS, 2.0). The DS value is 0.0 if no reaction occurred.

4. FT-IR spectra of hemicelluloses, CMH and CMH-Pd (0)

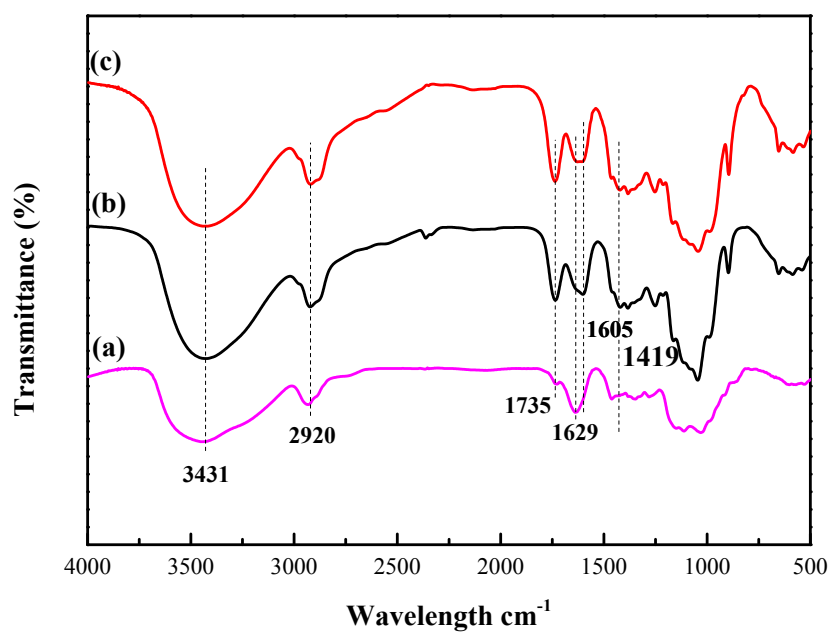
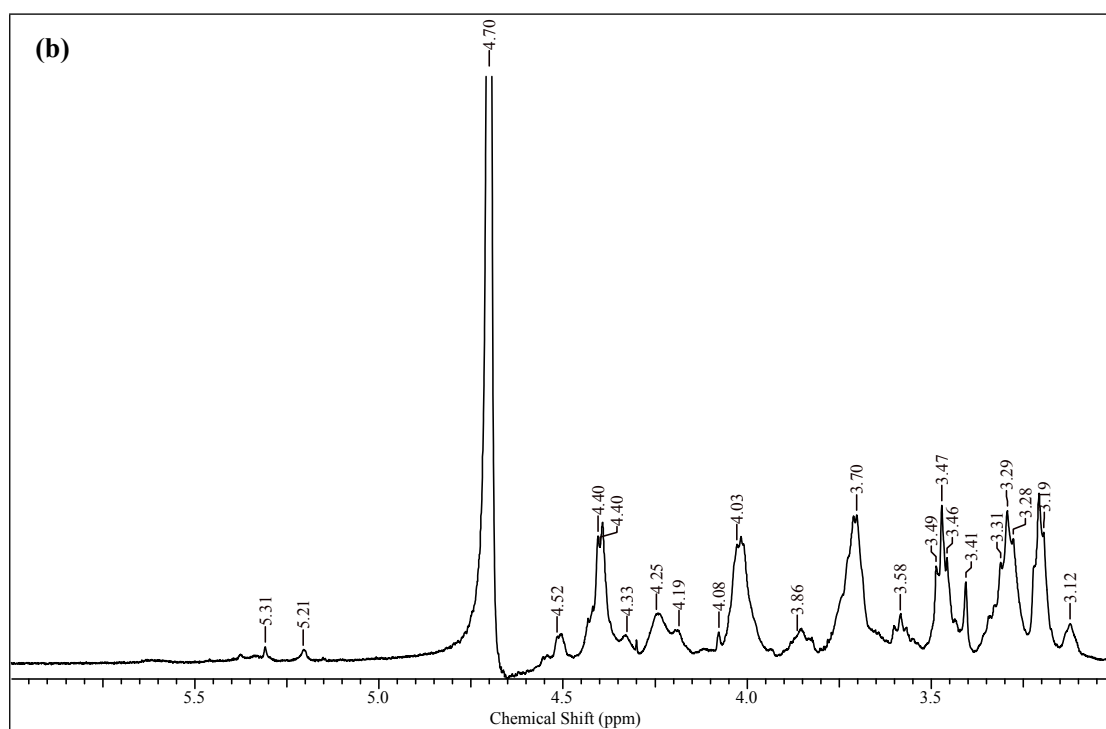
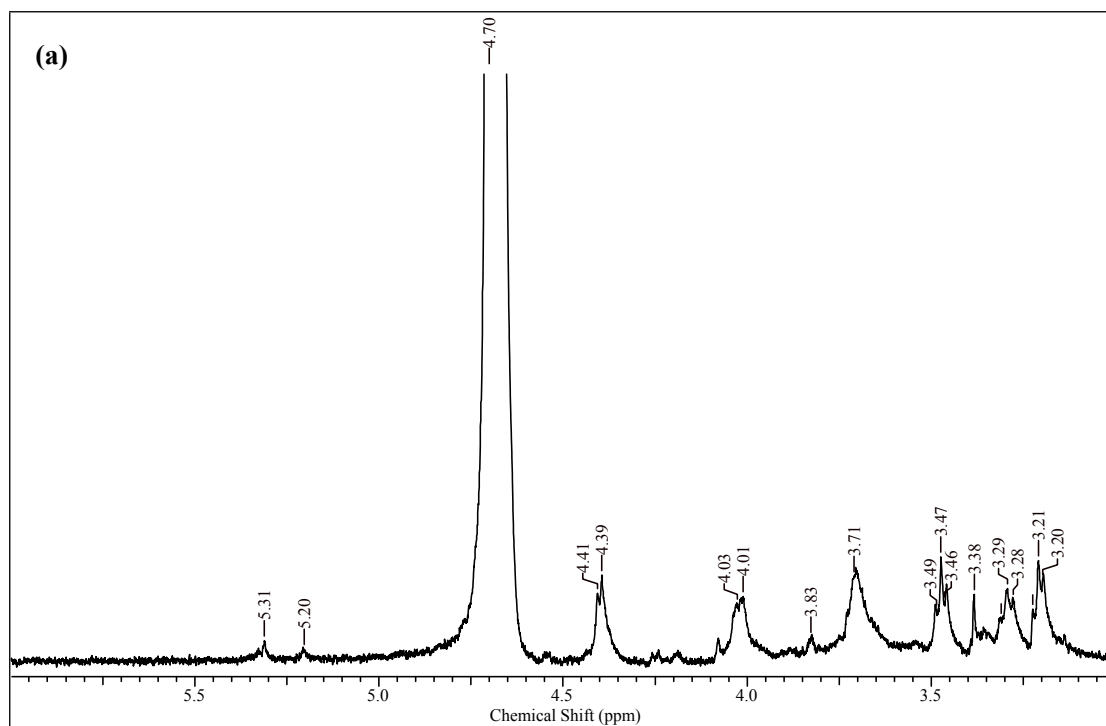


Figure S1. FT-IR spectra of (a) Hemicelluloses, (b) CMH and (c) CMH-Pd (0) catalyst.

5. ^1H -NMR and ^{13}C -NMR spectra of hemicelluloses and CMH



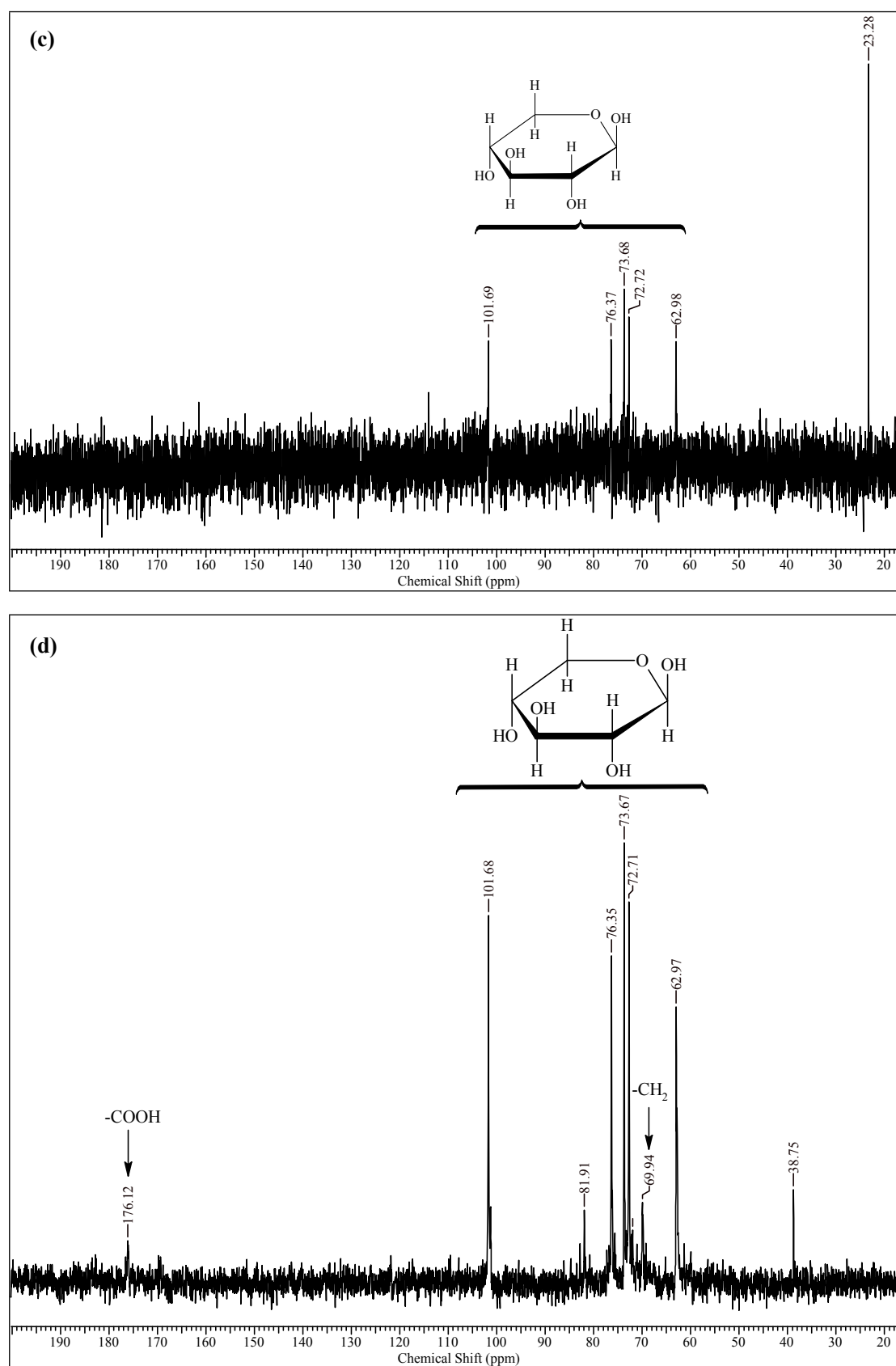
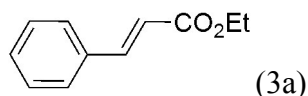


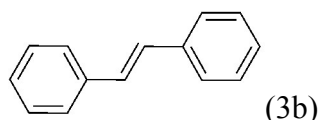
Figure S2. ^1H -NMR spectra of (a) Hemicelluloses, (b) CMH and ^{13}C -NMR spectra of (c) Hemicelluloses, (d) CMH.

6. Spectral data for synthesized compounds



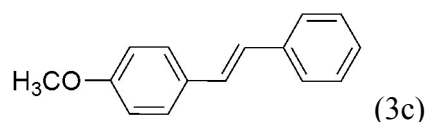
(*E*)-Ethyl Cinnamate ¹

¹H-NMR (CDCl₃, 600MHz, ppm): δ = 7.71 (d, J=12.0 Hz, 1H), 7.54-7.53 (m, 2H), 7.41-7.39 (m, 3H), 6.46 (d, J=12.0 Hz, 1H), 4.29 (q, J=6.0 Hz, 1H), 1.35 (t, J=6.0 Hz, 3H). ¹³C-NMR (CDCl₃, 150 MHz, ppm): δ =166.97, 144.55, 134.47, 130.18, 128.85, 128.02, 118.28, 60.47, 14.30.



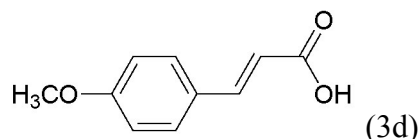
(*E*)-Stilbene ^{1, 2}

¹H-NMR (CDCl₃, 600MHz, ppm): δ=7.54-7.53 (m, 4H), 7.39-7.36 (m, 4H), 7.29-7.26 (m, 2H), 7.13 (s, 2H). ¹³C-NMR (CDCl₃, 150 MHz, ppm): δ=137.33, 128.70, 128.67, 127.61, 126.50.



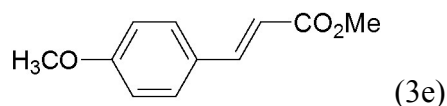
(*E*)-4-methoxy-stilbene ^{2, 4}

¹H-NMR (CDCl₃, 600 MHz, ppm): δ=7.51-7.50 (m, 2H), 7.48-7.46 (m, 2H), 7.36 (t, J=6.0Hz, 2H), 7.25 (t, J=6.0 Hz, 1H), 7.08 (d, J=12.0 Hz, 1H), 6.99 (d, J=12.0Hz, 1H), 6.92-6.91 (m, 2H), 3.85(s, 3H). ¹³C-NMR (CDCl₃, 150 MHz, ppm): δ=159.33, 137.67, 130.18, 128.63, 128.23, 127.71, 127.20, 126.64, 126.25, 114.15, 55.33.



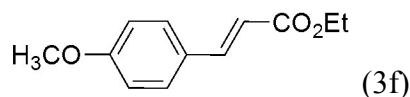
(*E*)-3-(4-methoxyphenyl)-acrylic acid ⁵

¹H-NMR (d₆-DMSO, 600 MHz, ppm): δ=12.18 (s, 1H), 7.64-7.62 (m, 2H), 7.55-7.53 (m, 1H), 6.97-6.96 (m, 2H), 6.38-6.35 (m, 1H), 3.79 (s, 3H). ¹³C-NMR (d₆-DMSO, 150 MHz, ppm): δ=167.71, 160.89, 143.63, 129.84, 126.78, 116.47, 114.30, 55.25.



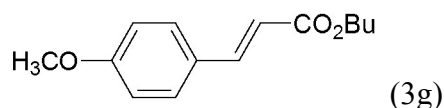
(*E*)-Methyl-3-(4-methoxyphenyl)-acrylate ²

¹H-NMR (CDCl₃, 600 MHz, ppm): δ=7.67 (d, J=18.0Hz, 1H), 7.48-7.47 (m, 2H), 6.92-6.90 (m, 2H), 6.33 (d, J=18.0 Hz, 1H), 3.84 (s, 1H), 3.80 (s, 1H). ¹³C-NMR (CDCl₃, 600 MHz, ppm): δ=167.69, 161.40, 144.47, 129.67, 127.15, 115.31, 114.33, 55.33, 51.49.



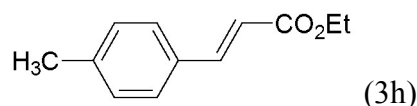
(*E*)-Ethyl 3-(4-methoxyphenyl) acrylate ^{1,2}

¹H-NMR (CDCl₃, 600 MHz, ppm): δ=7.64-7.62 (m, 1H), 7.46-7.44 (m, 2H), 6.89-6.87 (m, 2H), 6.31-6.28 (m, 1H), 4.25 (q, J=6.0 Hz, 2H), 3.80 (s, 3H), 1.32 (t, J=6.0 Hz, 3H). ¹³C-NMR (CDCl₃, 150 MHz, ppm): δ=167.17, 161.22, 144.10, 129.55, 127.07, 115.63, 114.19, 60.16, 55.19, 14.23.



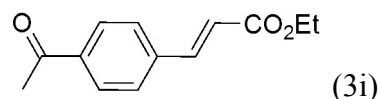
(*E*)-Butyl-3-(4-methoxyphenyl) acrylate ²

¹H-NMR (CDCl₃, 600 MHz, ppm): δ=7.64 (d, J=12.0 Hz, 1H), 7.46-7.45 (m, 2H), 6.89-6.88 (m, 2H), 6.31 (d, J=12.0 Hz, 1H), 4.19 (t, J=6.0 Hz, 2H), 3.81 (s, 3H), 1.68 (m, 2H), 1.44 (m, 2H), 0.96 (t, J=6.0 Hz, 3H). ¹³C-NMR (CDCl₃, 150 MHz, ppm): δ=167.24, 161.25, 144.05, 129.55, 127.14, 115.72, 114.21, 64.09, 55.19, 30.74, 19.10, 13.61.



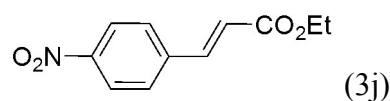
(*E*)-Ethyl-3-(4-methylphenyl) acrylate¹

¹H-NMR (CDCl₃, 600 MHz, ppm): δ=7.69-7.66 (m, 1H), 7.43-7.41 (m, 2H), 7.19-7.18 (m, 2H), 6.41-6.39 (m, 1H), 4.29-4.25 (m, 2H), 2.37 (s, 3H), 1.36-1.33 (m, 3H). ¹³C-NMR (CDCl₃, 150 MHz, ppm): δ=167.05, 144.47, 140.49, 131.69, 129.51, 127.95, 117.13, 60.27, 21.33, 14.25.



(*E*)-Ethyl 3-(4-acetylphenyl) acrylate ¹

¹H-NMR (CDCl₃, 600MHz, ppm): δ=7.97-7.96 (m, 2H), 7.71-7.68 (m, 1H), 7.61-7.60 (m, 2H), 6.53-6.51 (m, 1H), 4.30-4.26 (m, 2H), 2.61 (s, 3H), 1.36-1.33 (m, 3H). ¹³C-NMR (CDCl₃, 150 MHz, ppm): δ=197.25, 166.44, 142.95, 138.77, 137.95, 128.81, 128.07, 120.81, 60.72, 26.62, 14.25.



(*E*)-Ethyl 3-(4-nitrophenyl) acrylate ¹

¹H-NMR (CDCl₃, 600MHz, ppm): δ=8.25-8.24(m, 2H), 7.72-7.69(m, 1H), 7.72-7.66(m, 3H), 6.57-6.54(m, 1H), 4.29 (q, J=6.0 Hz, 2H), 1.35 (t, J=6.0 Hz, 3H).

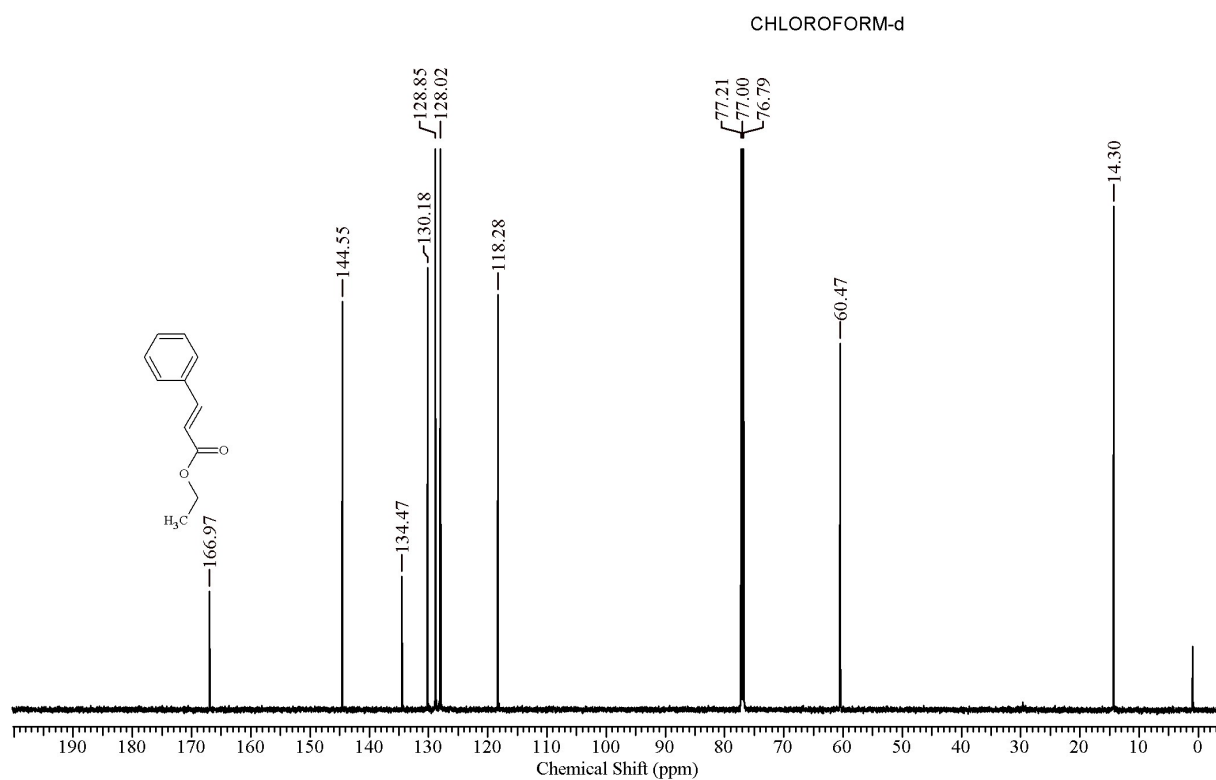
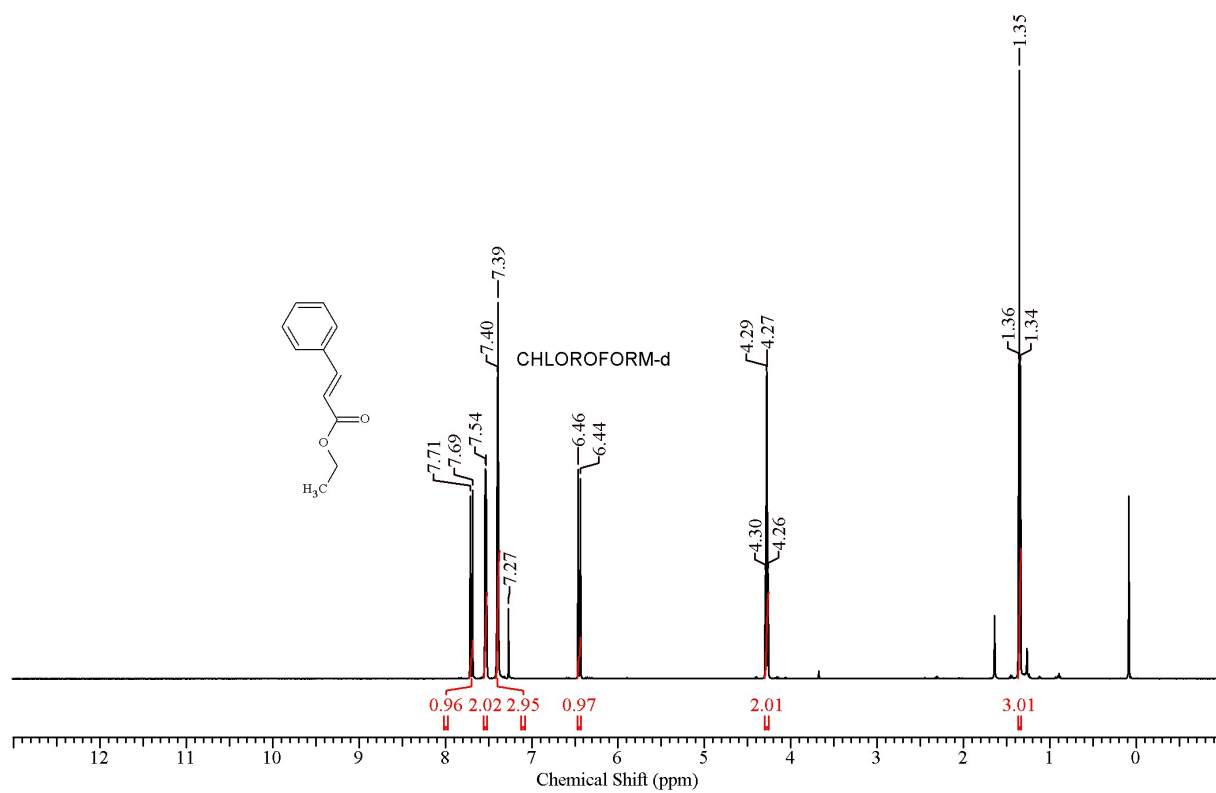
^{13}C -NMR (CDCl_3 , 150 MHz, ppm): δ =166.01, 148.49, 141.59, 140.59, 128.60, 124.16, 122.60, 60.99, 14.25.

7. References for synthesized compounds

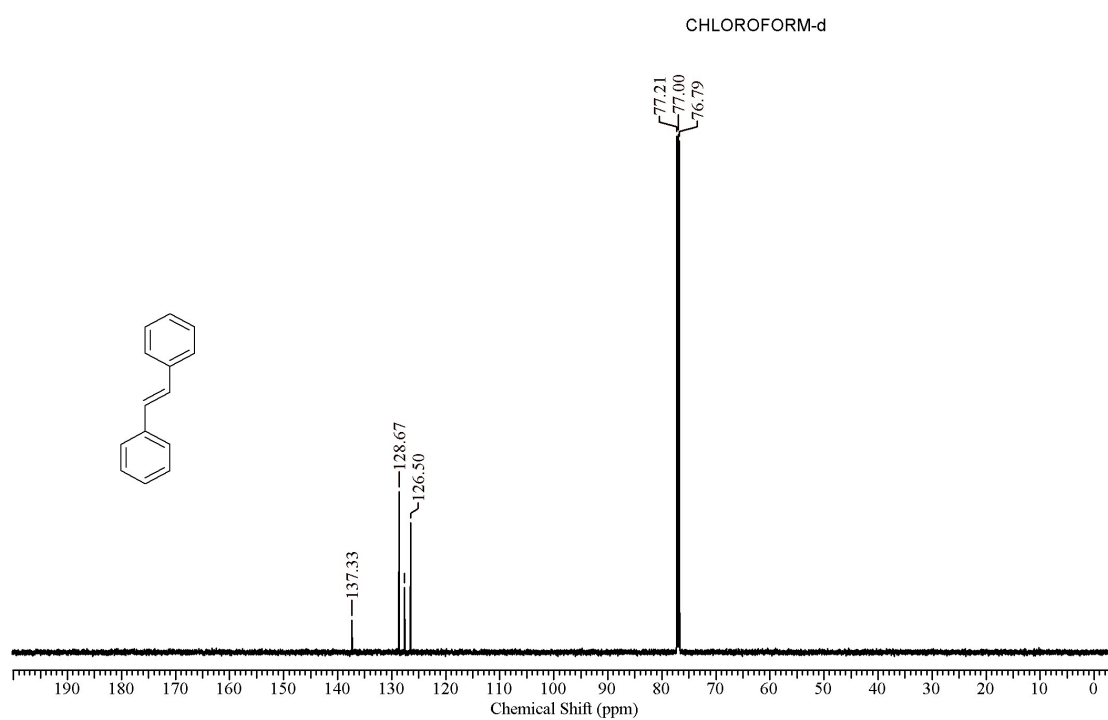
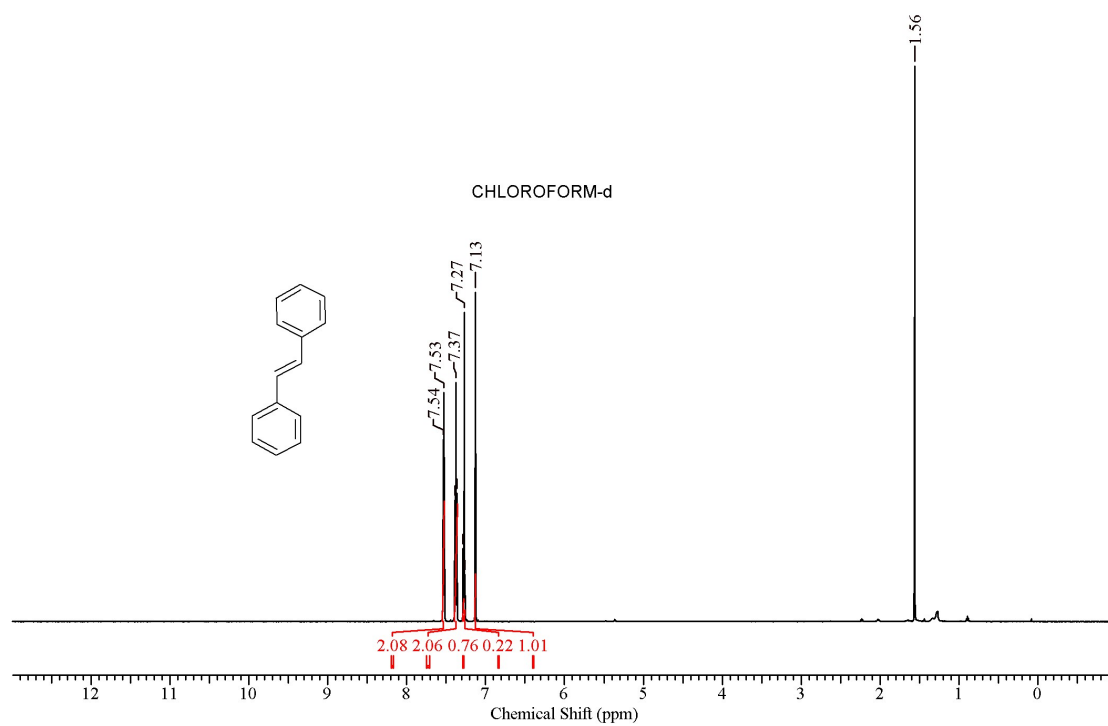
1. Y. Wang, J. Luo and Z. Liu, *J. Organomet. Chem.*, 2013, **739**, 1-5..
- 2 P. Li, L. Wang, L. Zhang, G. W. Wang, *Adv. Synth. Catal.* 2012, **354**, 1307-1318.
- (3) H. Q. Yang, X. J. Han, G. Li, Y. W. Wang, *Green Chem.* 2009, **11**, 1184-1193.
- (4) B. Tamami, H. Allahyari, F. Farjadian, S. Ghasemi, *Iranian Polymer Journal* 2011, **20**, 699-712.
- (5) X. Ma, Y. Zhou, J. Zhang, A. Zhu, T. Jiang, B. Han, *Green Chem.* 2008, **10**, 59-66.

8. Copy of ^1H -NMR, and ^{13}C -NMR of some of the synthesized compounds

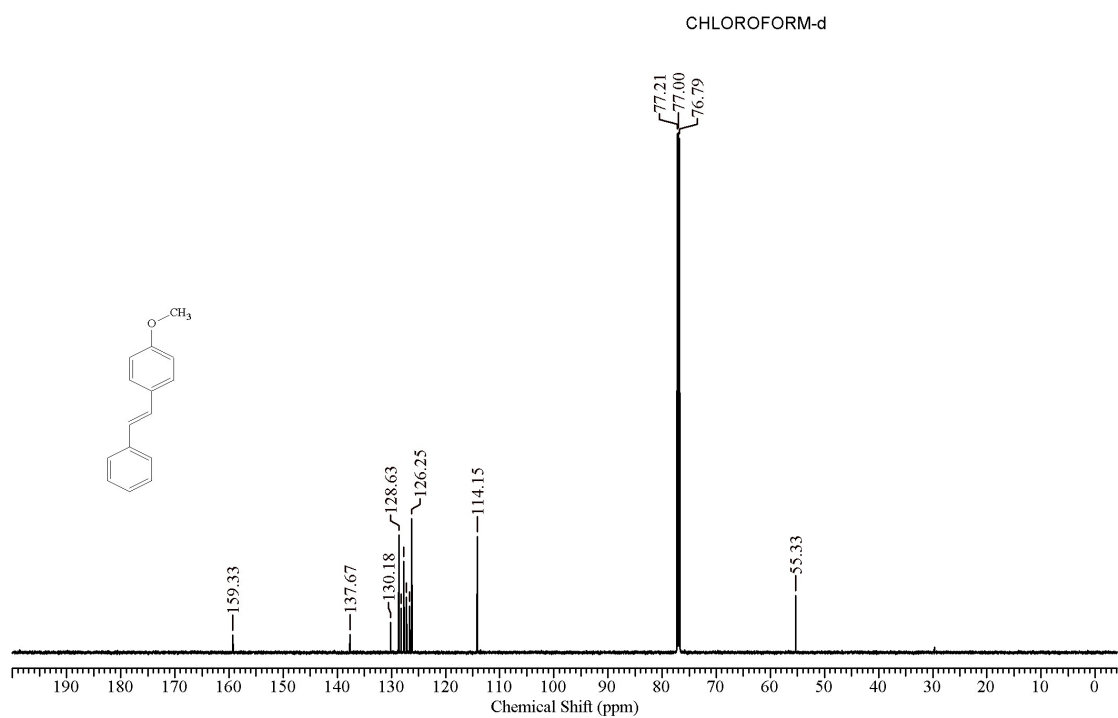
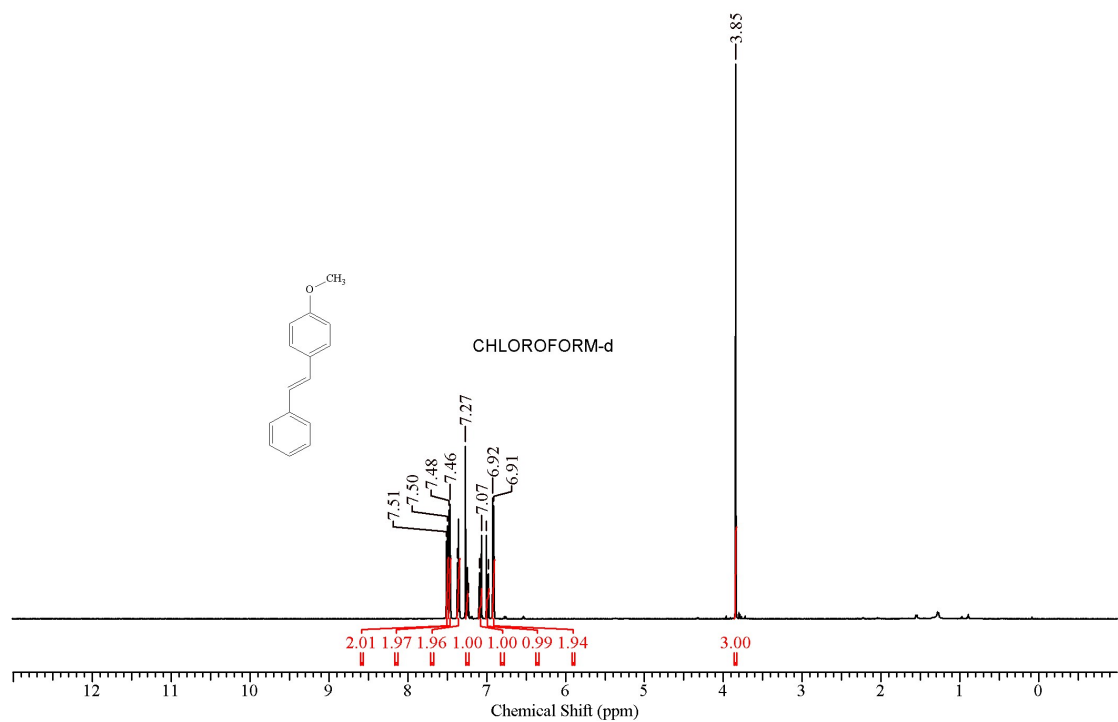
1. (*E*)-Ethyl Cinnamate (3a)



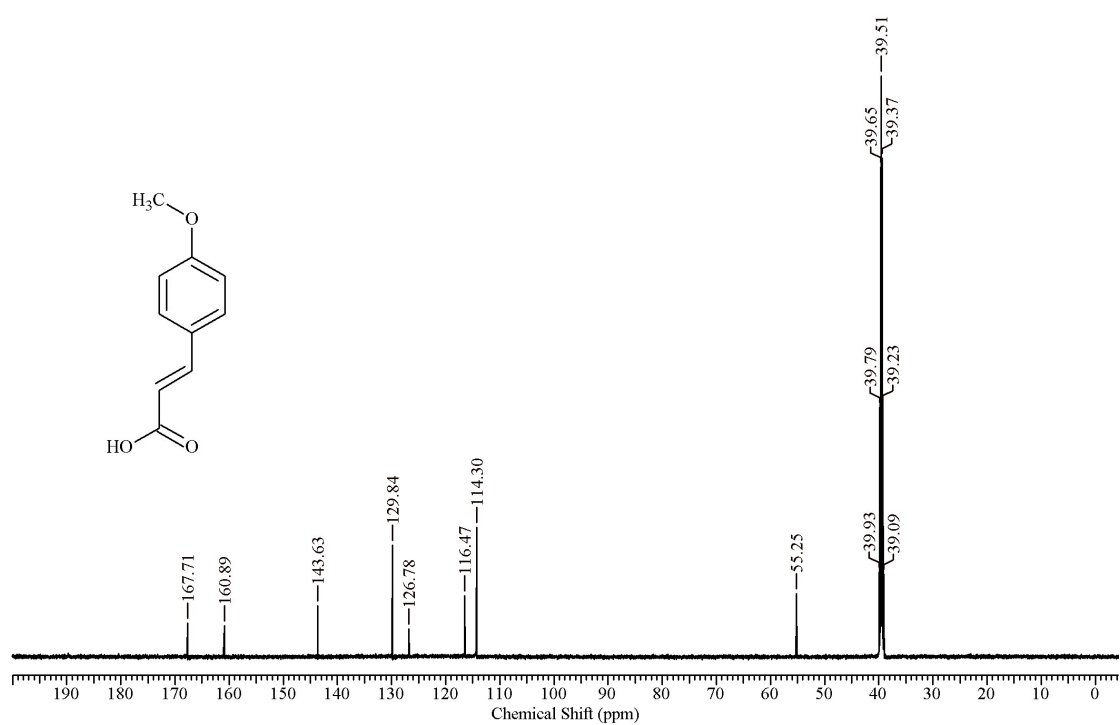
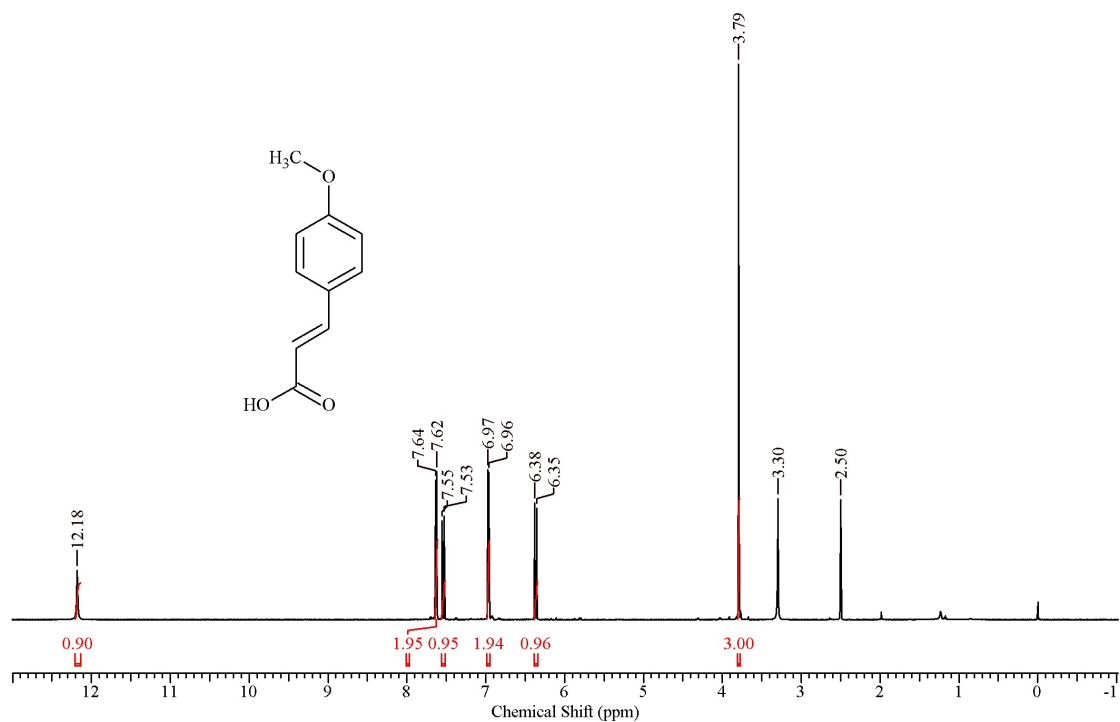
2. (*E*)-Stilbene (3b)



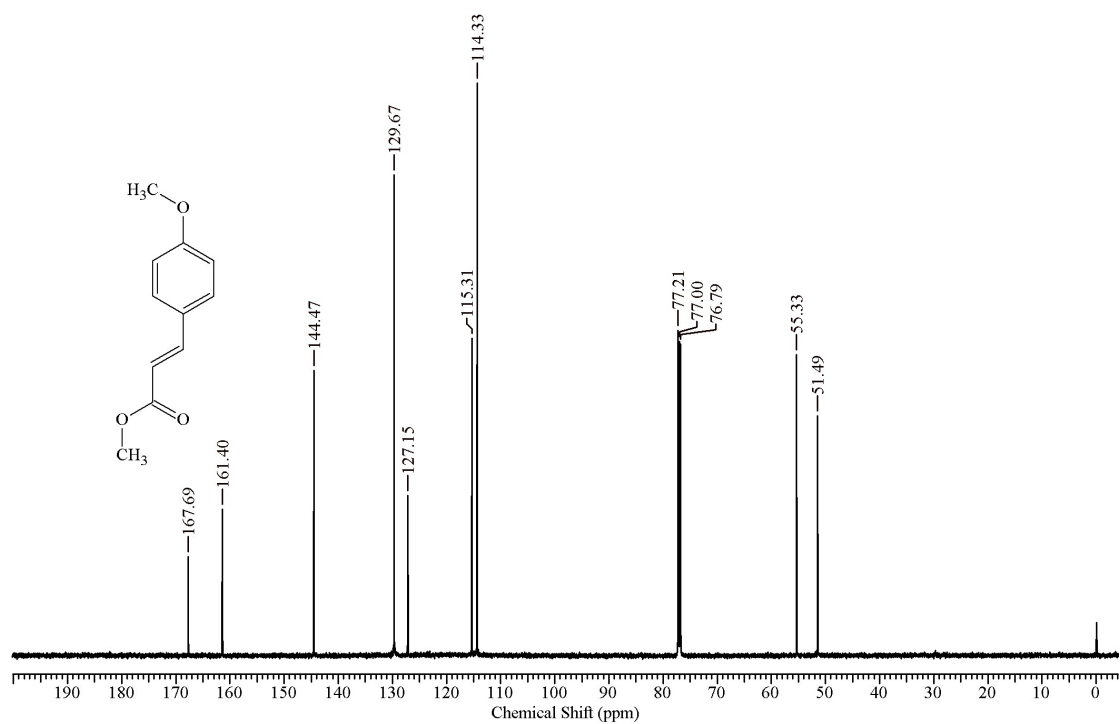
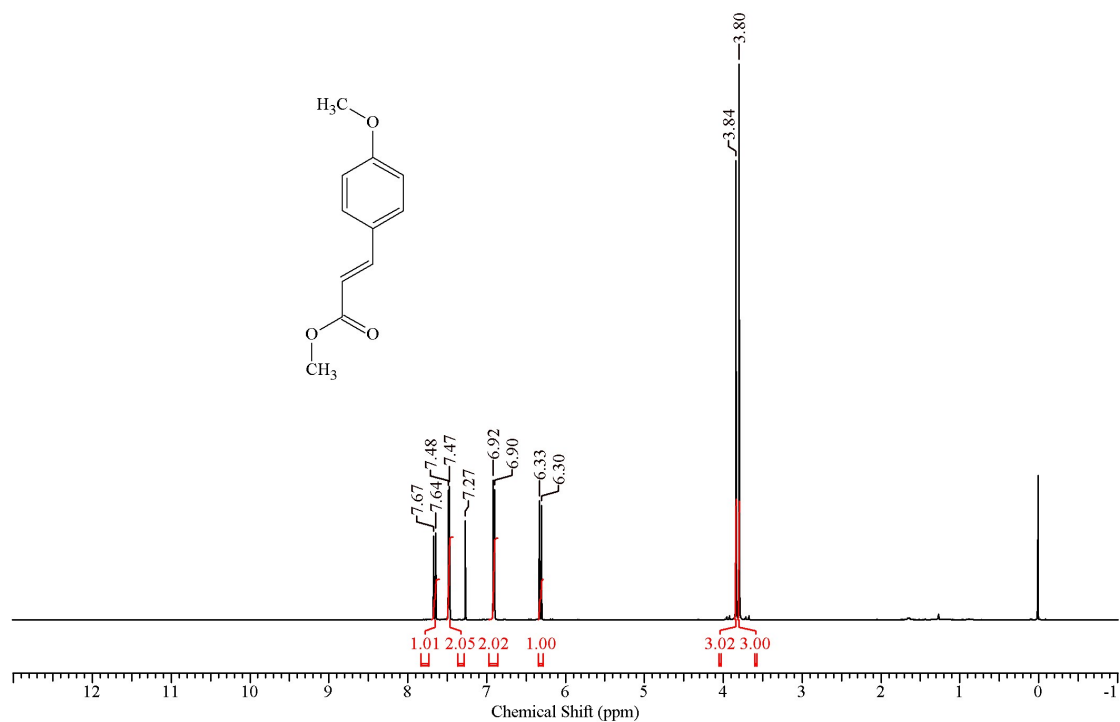
3. (*E*)-4-methoxy-stilbene (3c)



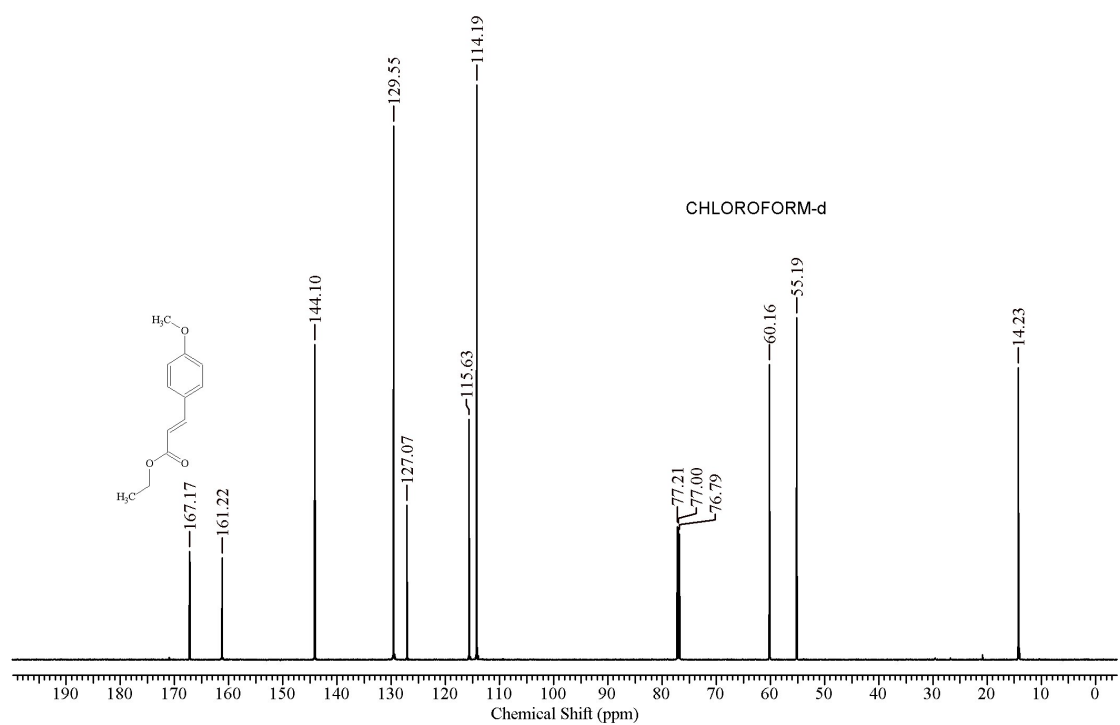
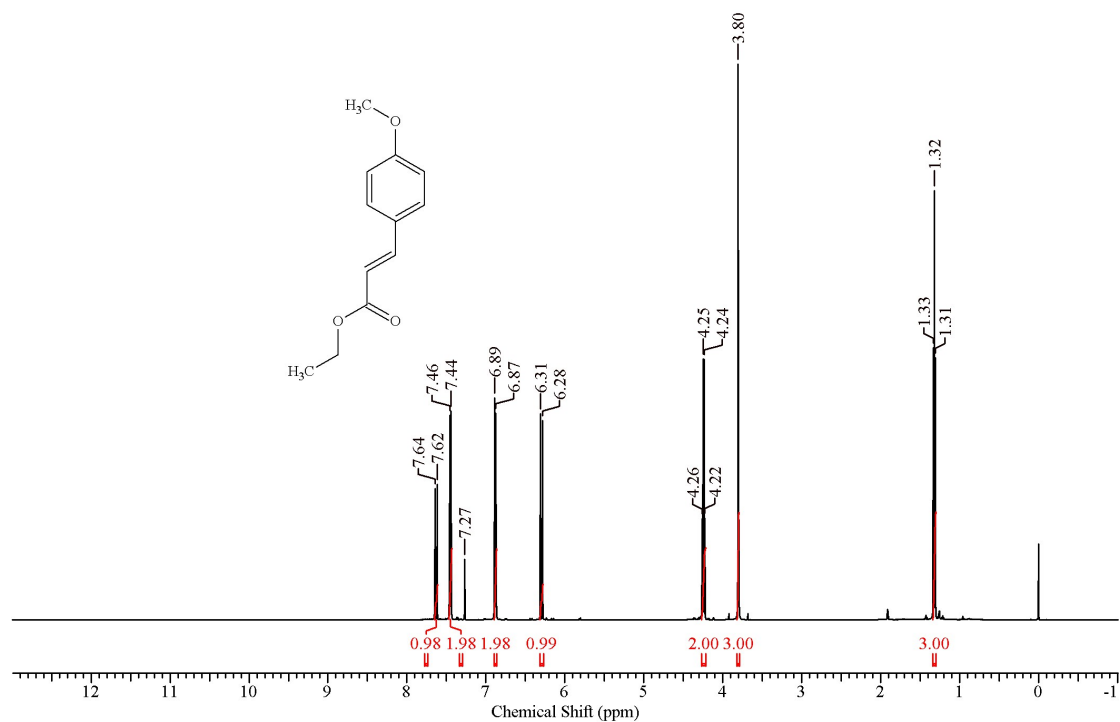
4. (*E*) –3-(4-methoxyphenyl)-acrylic acid (3d)



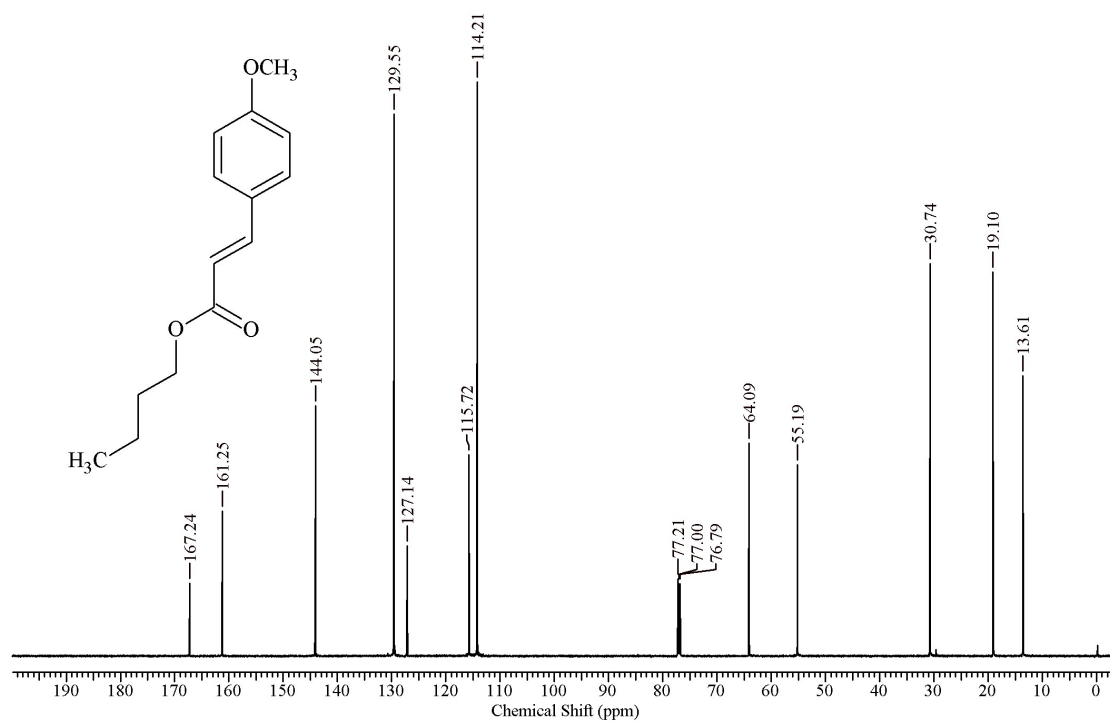
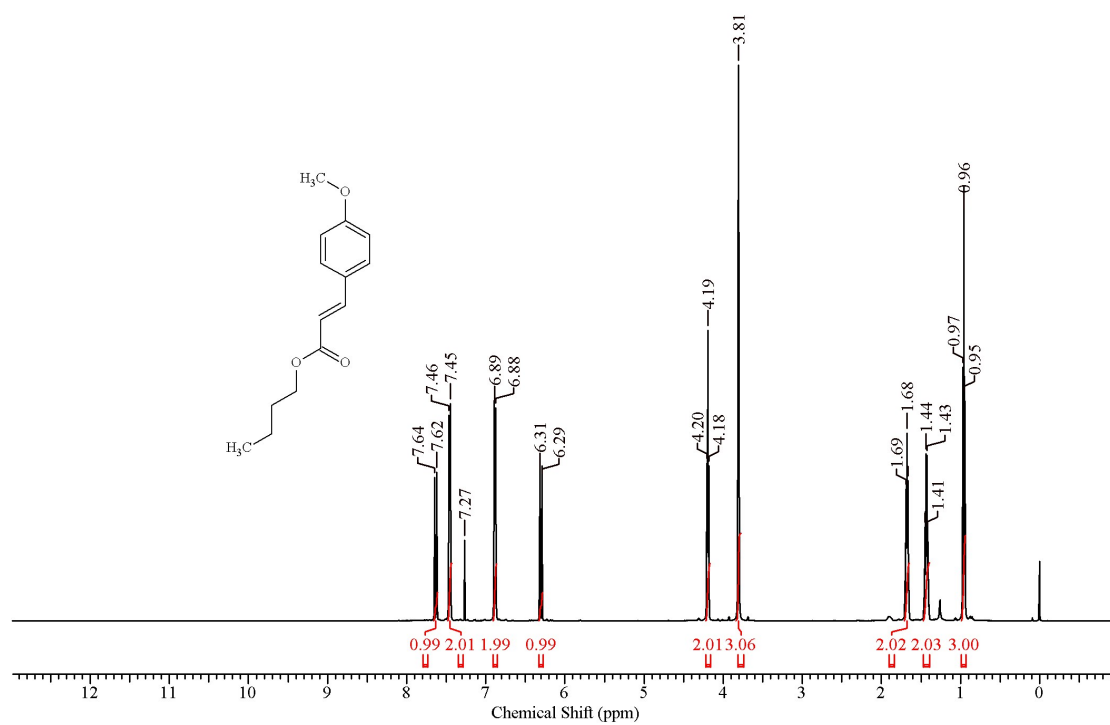
5. (*E*) –Methyl-3-(4-methoxyphenyl)-acrylate (3e)



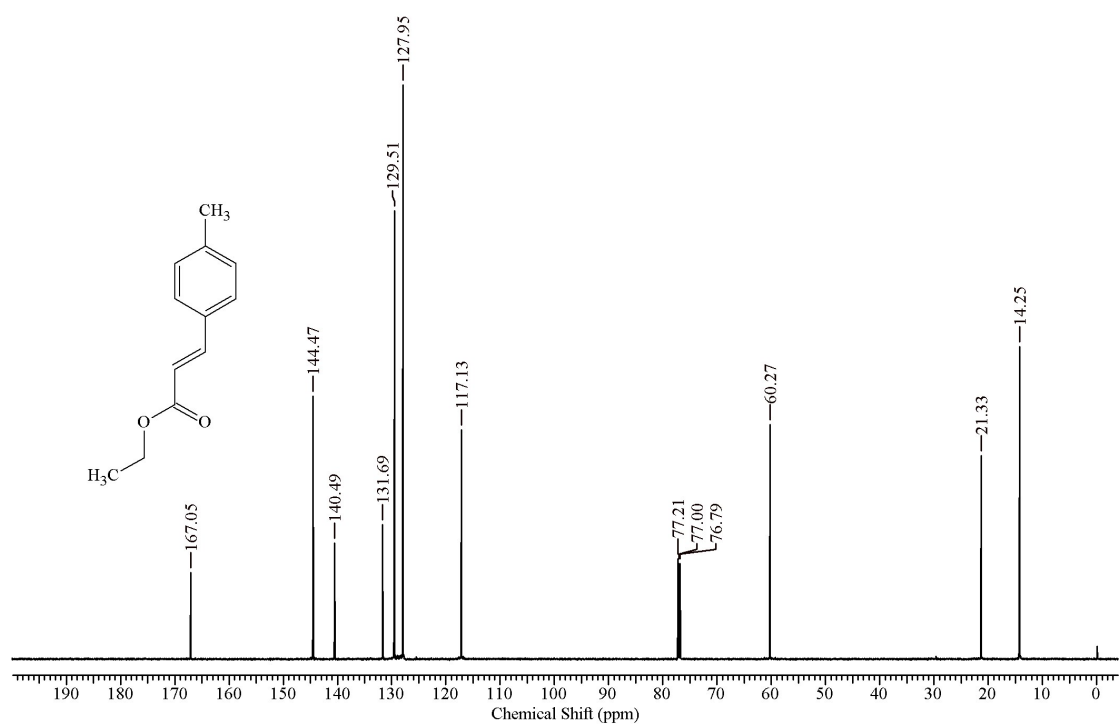
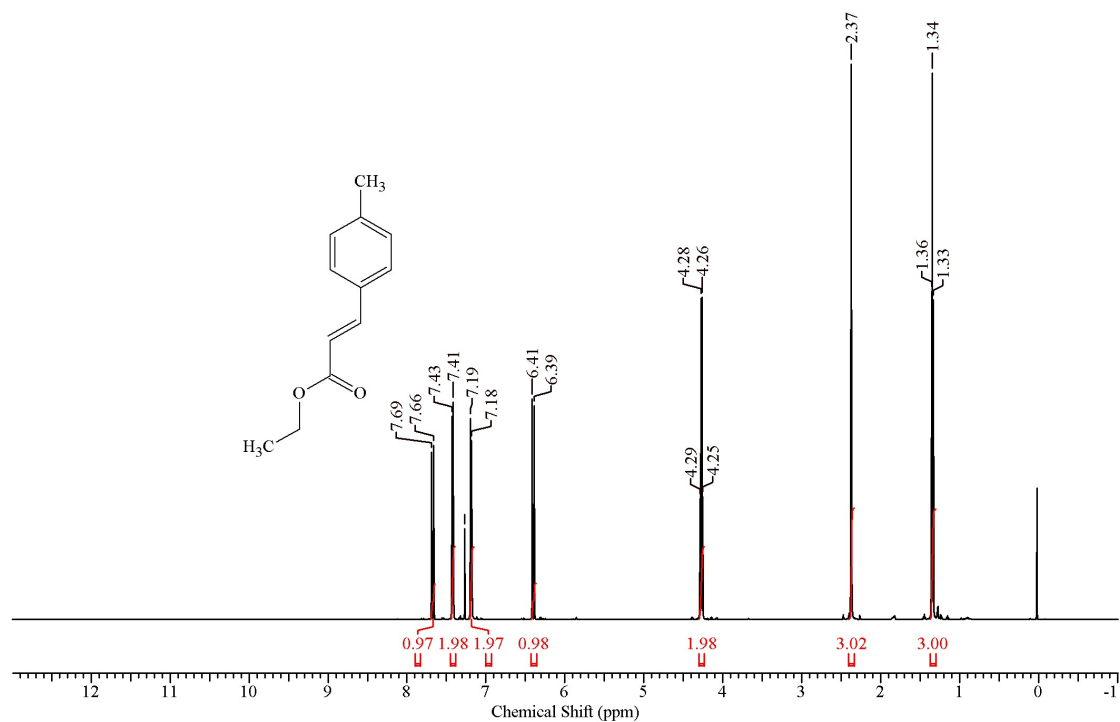
6. (*E*)-Ethyl-3-(4-methoxyphenyl) acrylate (3f)



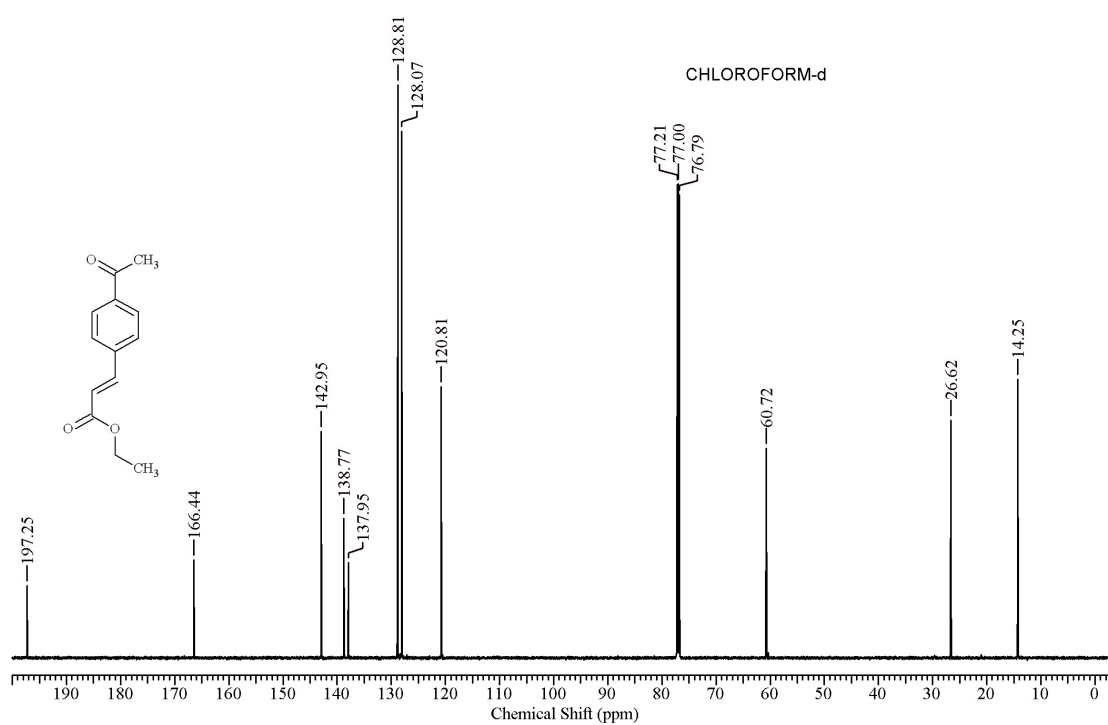
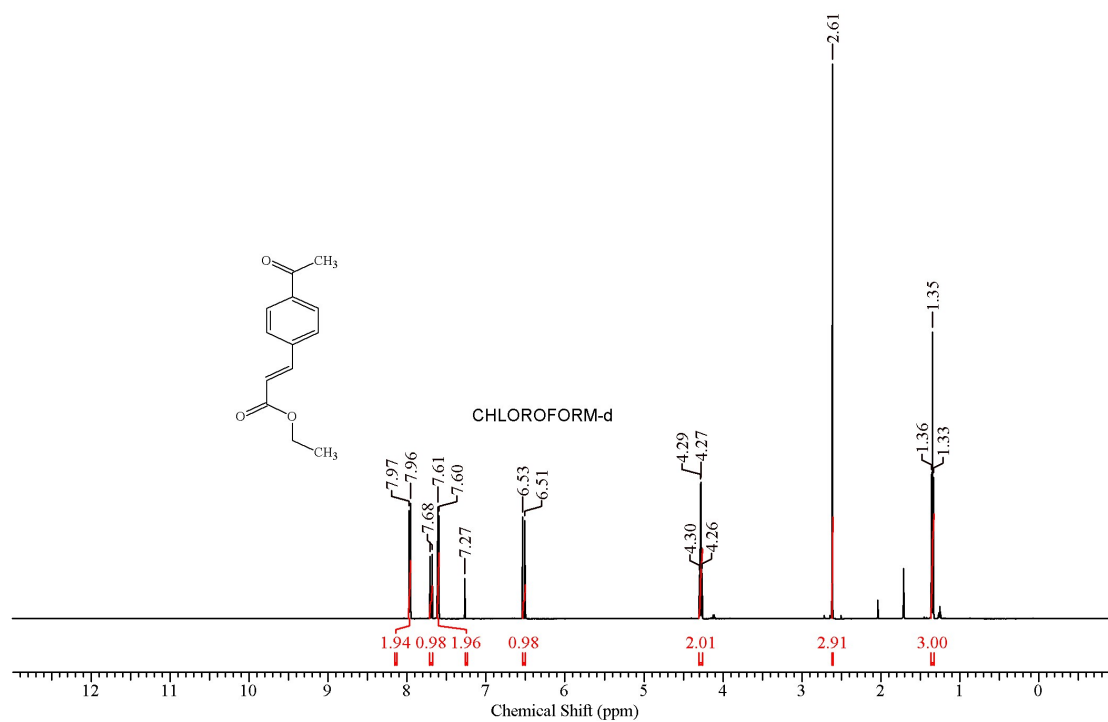
7. (*E*)-Butyl-3-(4-methoxyphenyl) acrylate (3g)



8. (*E*)-Ethyl-3-(4-methylphenyl) acrylate (3h)



9. (*E*)-Ethyl-3-(4-acetylphenyl) acrylate (3i)



10. (*E*)-Ethyl-3-(4-nitrophenyl) acrylate (3j)

