Student Handout

Procedure

Lab period 1:

Reaction:

Measure 0.75 g of solid cinnamic acid and 25 mL of your unknown alcohol in a 100 mL round bottom flask. Add a stir bar and stir solution until it is completely dissolved. Slowly add 1 mL of sulfuric acid (H_2SO_4) while stirring. (Caution: Sulfuric acid is toxic and corrosive; avoid getting on your skin.)

Attach air condenser to the round bottom flask and reflux gently for 45 minutes to 1 hour.

Carefully remove the apparatus from the heat and allow it to cool.

Work Up:

Cool in ice bath for approximately 2-3 min then transfer mixture to a separatory funnel using a Pasteur pipette. (*Make sure stopcock is closed and funnel does not leak before transfer)

Add 20 mL of ethyl acetate (makes the organic layer easier to handle) and 20 mL of aqueous sodium bicarbonate (neutralizes remaining acid) to the separatory funnel, shake thoroughly. ***Vent-Frequent release of pressure by inverting the separatory funnel and opening the stopcock pointing away from you. You will see two layers form inside the separatory funnel. The organic layer is the top (lower density) and the aqueous layer is the bottom.

Let it to settle for a few minutes and drain the bottom aqueous layer, which contains unreacted excess alcohol. Label and set aside.

Wash the organic layer in the separatory funnel with saturated sodium chloride solution. Drain the bottom aqueous layer, label and set aside. Collect the top organic layer (which has your ester) in a labeled Erlenmyer flask and dry the solution over anhydrous calcium chloride. Add sufficient calcium chloride pellets so that they no longer clump together on the bottom of the flask. After few minutes, decant the dry organic solution into a round bottom flask.

Rotovap the organic layer at 40^0C. Check the purity of the product by TLC. Label the TLC plate with cinnamic acid and the crude ester. Develop the TLC plate in 90% hexane and 10% ethyl acetate, visualize under UV light.

Lab period 2:

Column Chromatography:

In a small beaker, prepare a slurry of silica gel in hexane. Gently stir the slurry to remove air bubbles and pour the slurry into the column. Open the stopcock, rinse with hexane, and allow solvent to drain slowly into an Erlenmeyer flask. Tap the column with a small rubber tubing for packing. Allow the solvent to drain just to the surface of the silica layer. Using a Pasteur pipette, add the sample to the column and let it run into the silica. Fill the column with 100 mL of 5%

ethyl acetate and 95 % hexane. Collect fractions in clean small test tubes, checking the purity of the even fractions by TLC with the crude and the *trans*- cinnamic acid. (Develop TLC plate in 90% hexane and 10% ethyl acetate)
*Try not to let the column run dry – always stop before the top of the liquid reaches the top of the solid.

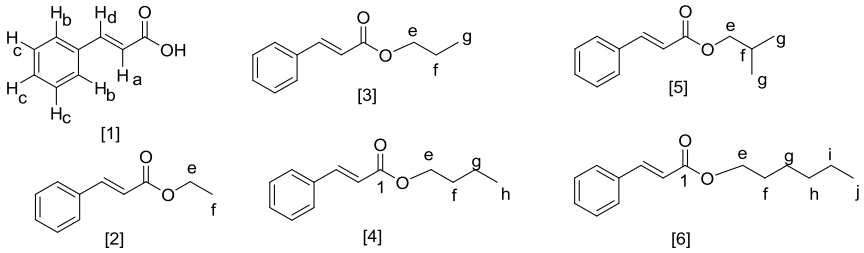
Once all of the compounds have been eluted from the column according to the TLC plates, pour the ester fractions into a preweighed round bottom flasks and rotovap at 40^0C. Allow to cool to room temperature and make sure outer flask is dry. Weigh the flask and calculate the percent yield of your ester.

Analysis of the Product:

As in previous labs, set up NMR sample in $CDCl_3$ and run ^{1}H-NMR, ^{13}C-NMR, DEPT 135 and DEPT 90 to determine the structure of the cinnamic acid ester you synthesized. Be sure to identify all signals and report your findings in the report. Include the identity of the unknown alcohol that was originally used in the synthesis.

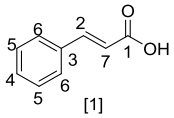
Teacher Supporing materials

Table 1: ^{1}H-NMR data (300 MHz, $CDCl_3$); *J* value in Hz

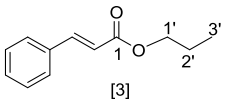


H	**[1]**	**[2]**	**[3]**	**[4]**	**[5]**	**[6]**
a	7.85, 7.80 (1H) *d*	7.71, 7.66 (1H) *d*	7.68, 7.62 (1H) *d*	7.72, 7.67 (1H) *d*	7.71, 7.66 (1H) *d*	7.72, 7.67 (1H) *d*
b	7.59- 7.57 (2H) *m*, Ar-H	7.51-7.48 (2H) *m*,(Ar-H)	7.47-7.44 (2H) *m*, (Ar-H)	7.53- 7.50 (2H) *m*, Ar-H	7.50- 7.46 (2H) *m*, Ar-H	7.55- 7. 53 (2H) *m*, Ar-H
c	7.44-7.42 (3H) *m*, Ar-H	7.36-7.34 (3H) *m*,(Ar-H)	7.32-7.29 (3H) *m* (Ar-H)	7.39-7.34 (3H) *m*, Ar-H	7.35-7.33 (3H) *m*. Ar-H	7.41-7.39 (3H) *m*, Ar-H
d	6.51, 6.46 (1H) *d*	6.46, 6.40 (1H) *d*	6.43, 6.38 (1H) *d*	6.47, 6.42 (1H) *d*	6.47, 6.42 (1H) *d*	6.49, 6.43 (1H) *d*
e	--	4.29-4.22 (2H) *q*	4.14 (2H) *q*	4.23 (2H) *t*	3.99, 3.97 (1H) *d*	4.23 (2H) *t*
f	--	1.33 (3H) *t*	1.71-1.65 (2H) *q*	1.74-1.65 (2H) *m*	2.07-1.93 (1H) *m*	1.74-1.76 (2H) *m*
g	--	--	0.95 (3H) *t*	1.51-1.41 (2H) *m*	0.98, 0.96 (6H) *br d*	1.43-1.41 (2H) *m*
h	--	--	--	0.97 (3H) *t*	--	1.36-1.31 (2H) *m*
j	--	--	--	--	--	0.97 (3H) *t*

Table 2: ^{13}C-NMR data (300 MHz, $CDCl_3$); (multiplicity from DEPT in parentheses)



[1]



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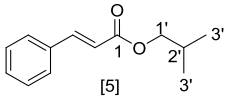

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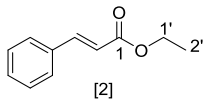

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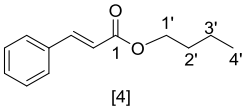
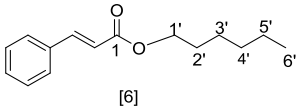


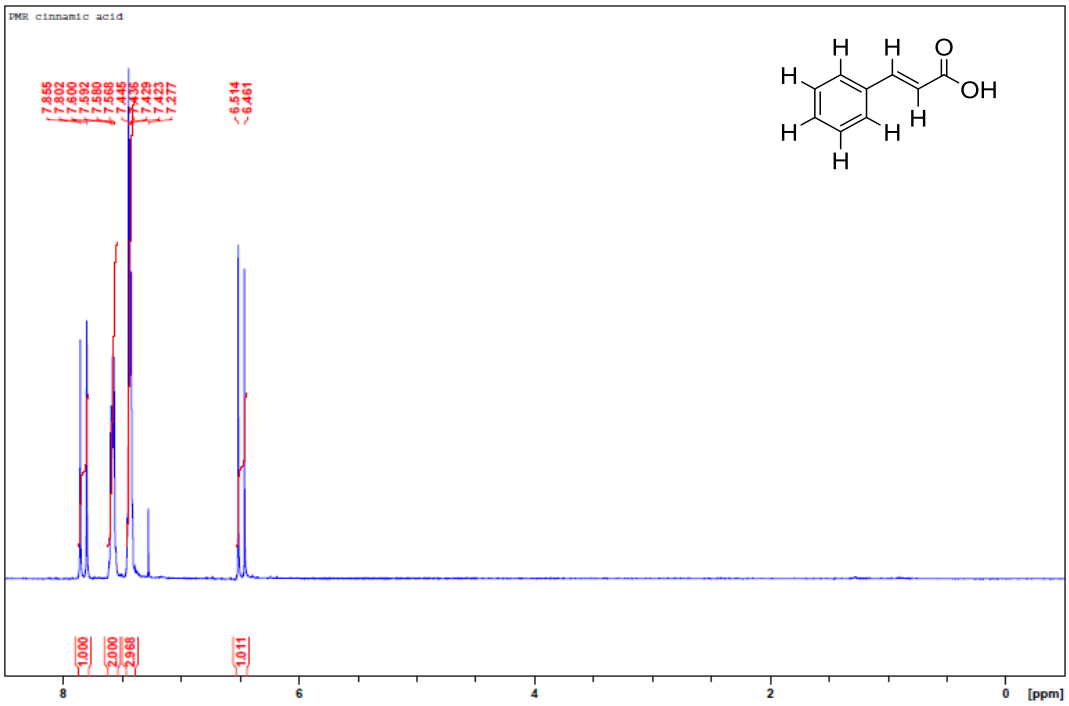
[4]



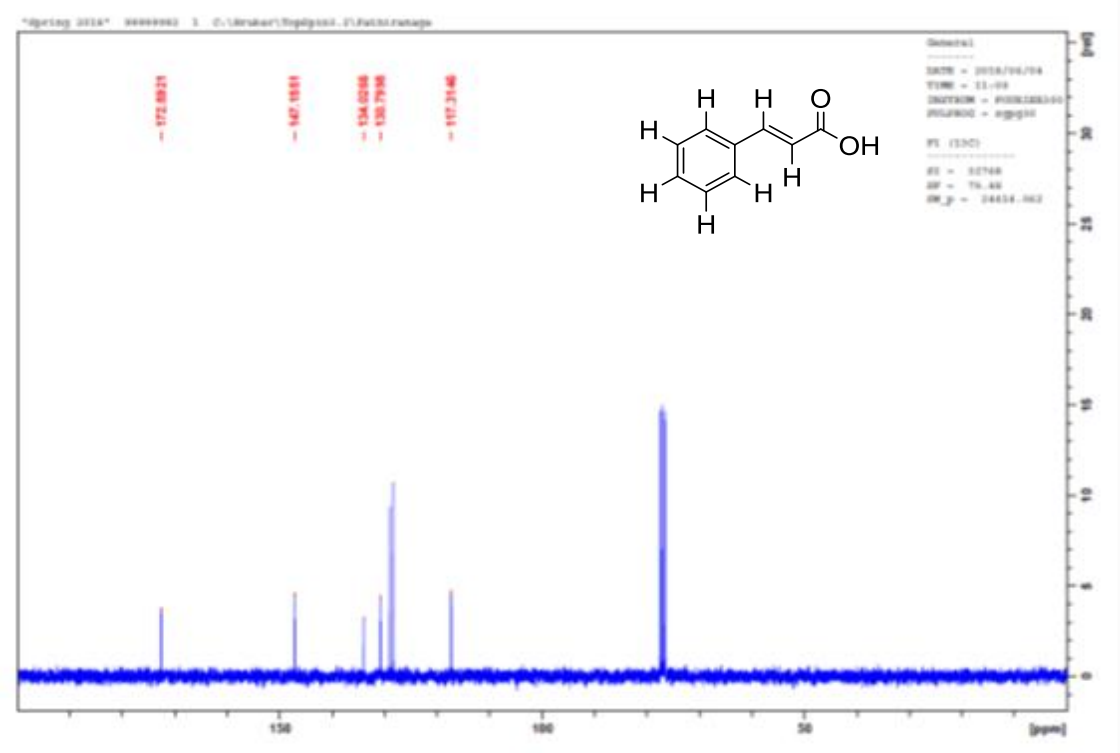
[6]

C	**[1]**	**[2]**	**[3]**	**[4]**	**[5]**	**[6]**
1	172.59 (C=O)	166.92 (C=O)	166.92 (C=O)	167.04 (C=O)	166.92 (C=O)	167.17 (C=O)
2	147.16 (CH)	144.55 (CH)	144.49 (CH)	144.53 (CH)	144.52 (CH)	144.59 (CH)
3	134.03 (C) Ar-C	134. 43 (C) Ar-C	134.40 (C) Ar-C	134.46 (C) Ar-C	134.44 (C) Ar-C	134.46(CH) Ar-C
4	130.79 (CH) Ar-C	130.21 (CH) Ar-C	130.16 (CH) Ar-C	130.21 (CH) Ar-C	130.19 (CH) Ar-C	130.22 (CH) Ar-C
5	128.99 (CH) Ar-C	128.86 (CH) Ar-C	128.81 (CH) Ar-C	128.86 (CH) Ar-C	128.84 (CH) Ar-C	128.88 (CH) Ar-C
6	128.41 (CH) Ar-C	128.04 (CH) Ar-C	128.01 (CH) Ar-C	128.05 (CH) Ar-C	128.04 (CH) Ar-C	128.06 (CH) Ar-C
7	117.31 (CH)	118.24 (CH)	118.18 (CH)	118.26 (CH)	118.23 (CH)	118.27 (CH)
1’		60.45 (CH_2)	66.01 (CH_2)	64.39 (CH_2)	70.56 (CH_2)	64.78 (CH_2)
2’		14.33(CH_3)	22.07 (CH_2)	30.79 (CH_2)	27.84 (CH)	31.49 (CH_2)
3’		--	10.41 (CH_3)	19.29 (CH_2)	19.16 (CH_3)	28.69 (CH_2)
4’		--	--	13.77 (CH_3)	--	22.67 (CH_2)
5’		--	--	--	--	22.57 (CH_2)
6’		--	--	--	--	14.04 (CH_3)

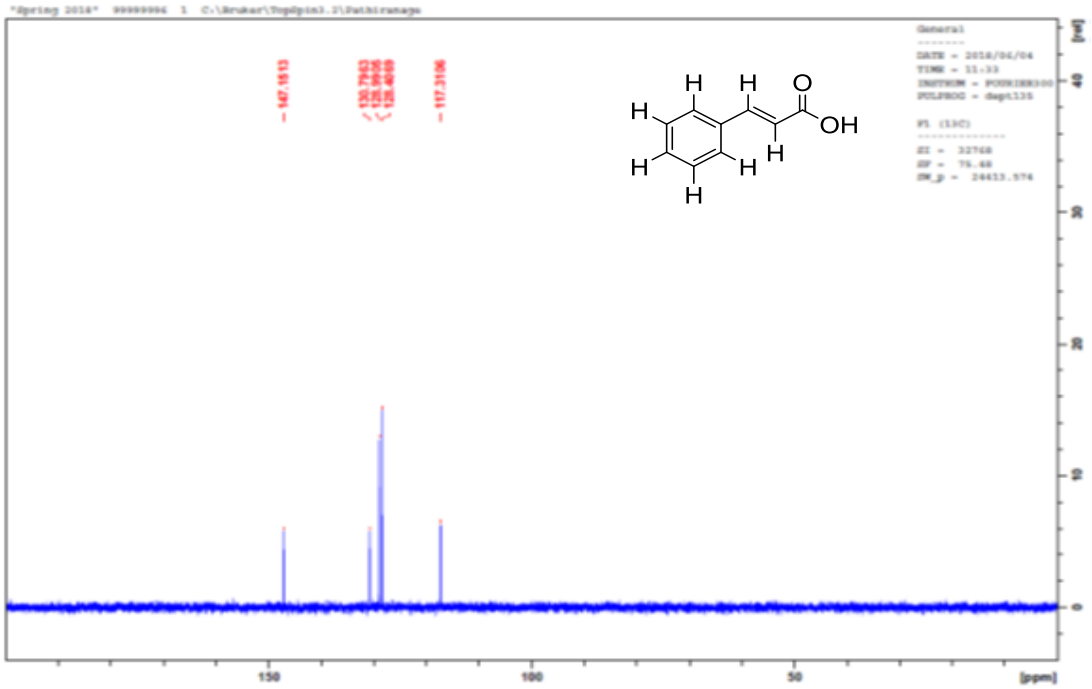
trans- cinnamic acid ^{1}H-NMR



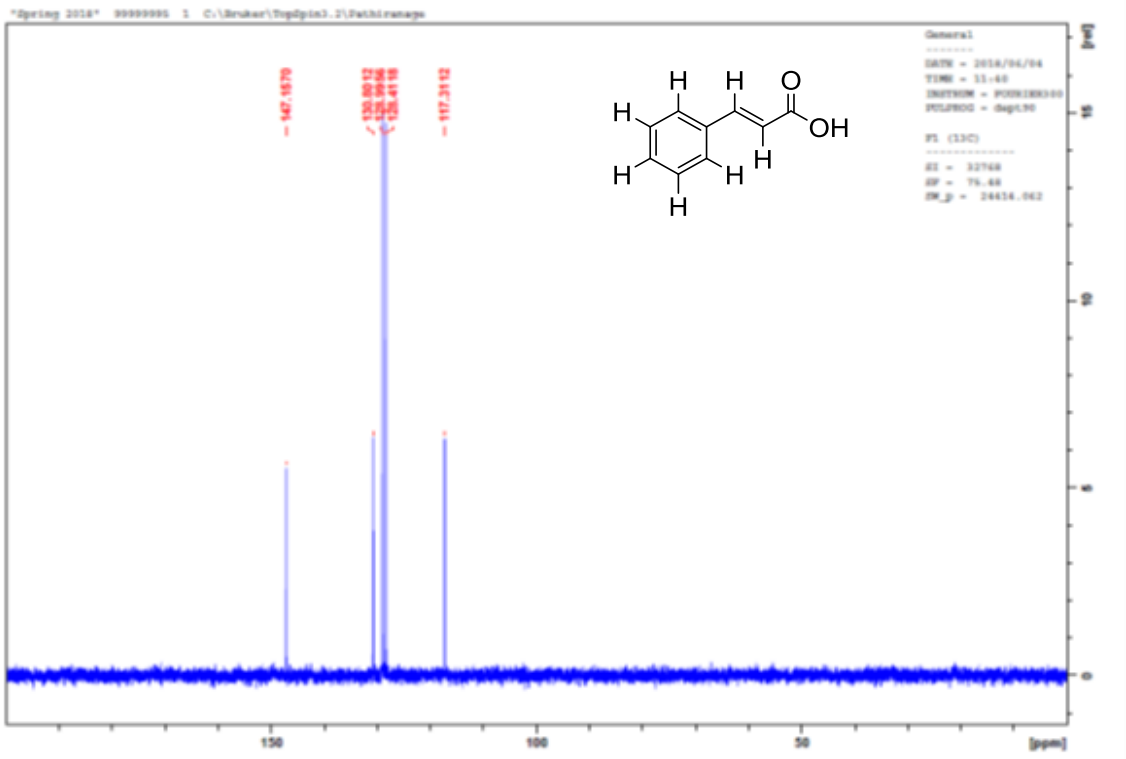
trans- cinnamic acid ^{13}C-NMR



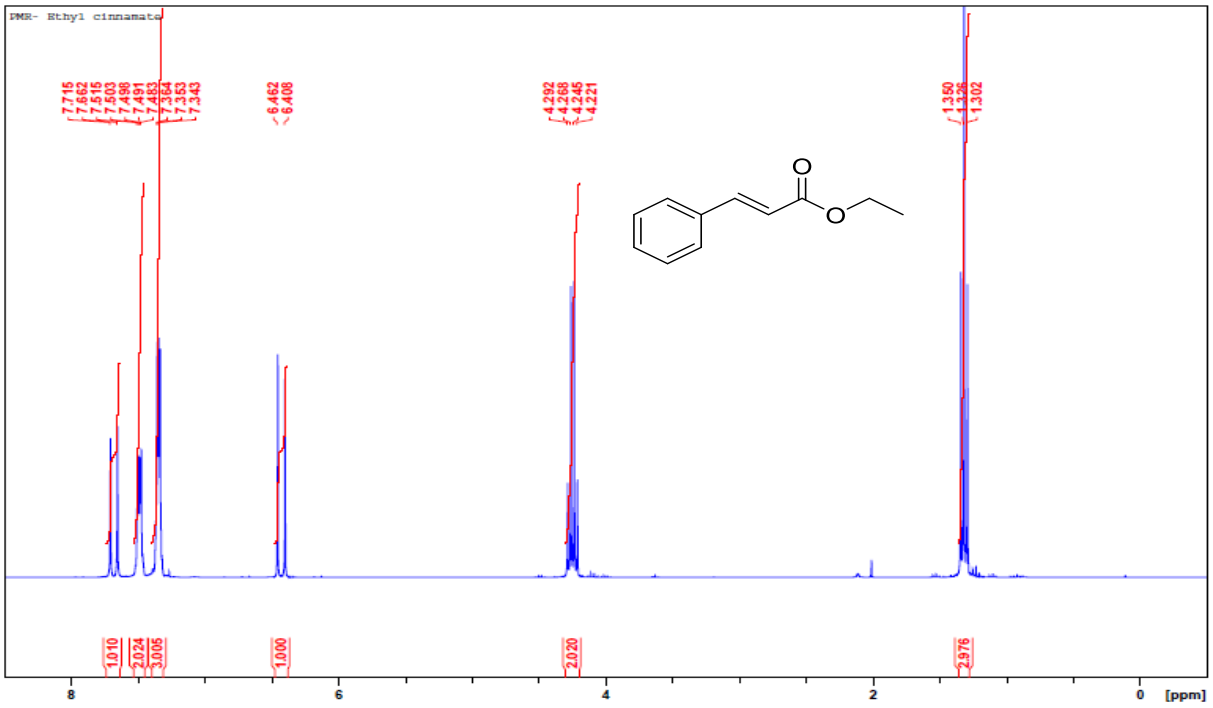
trans- cinnamic acid DEPT 135



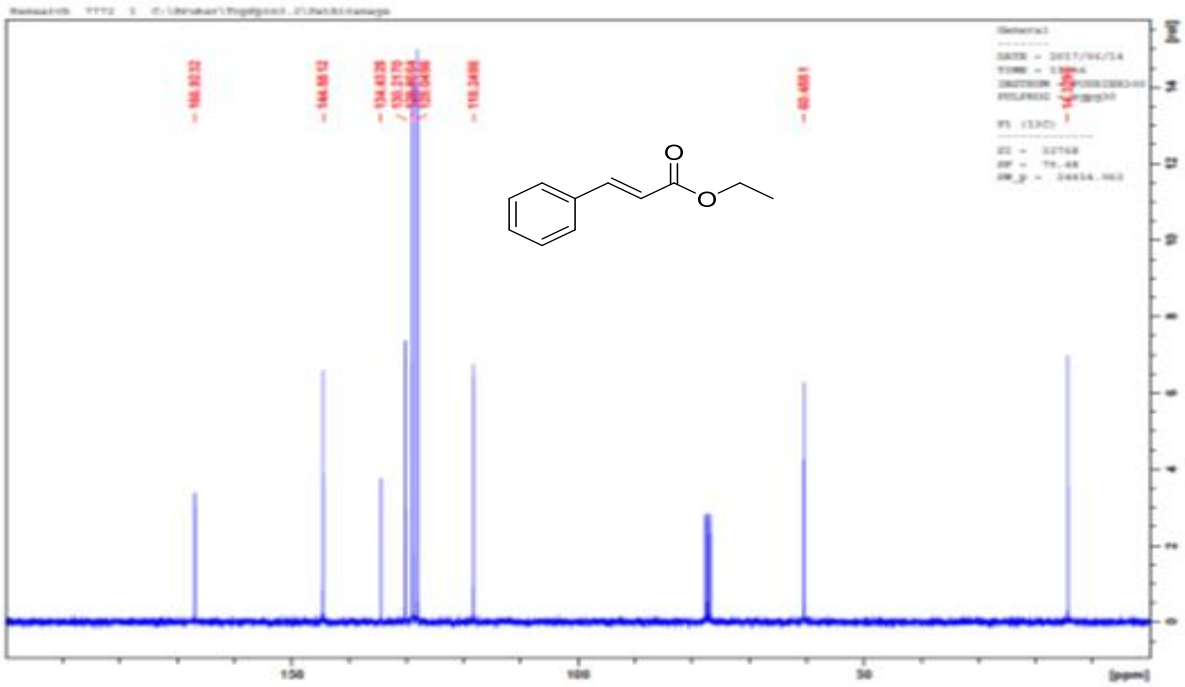
trans- cinnamic acid DEPT 90



Ethyl cinnamate ^{1}H-NMR

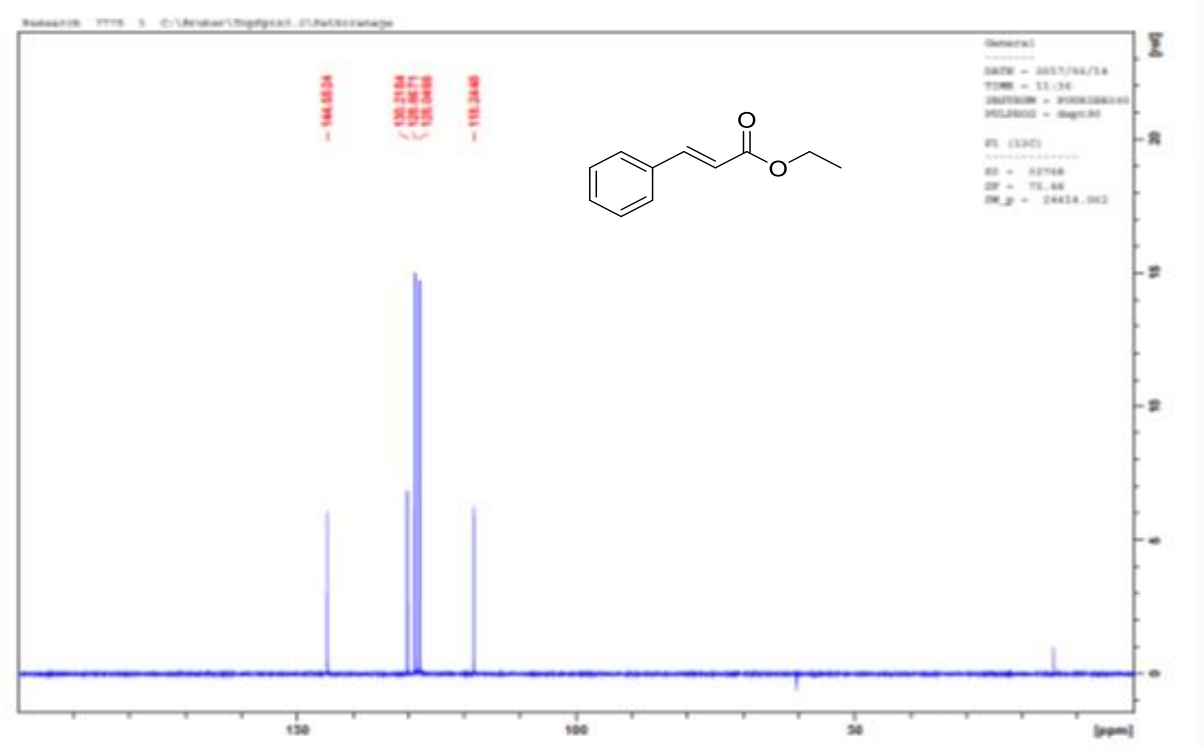


Ethyl cinnamate ^{13}C-NMR

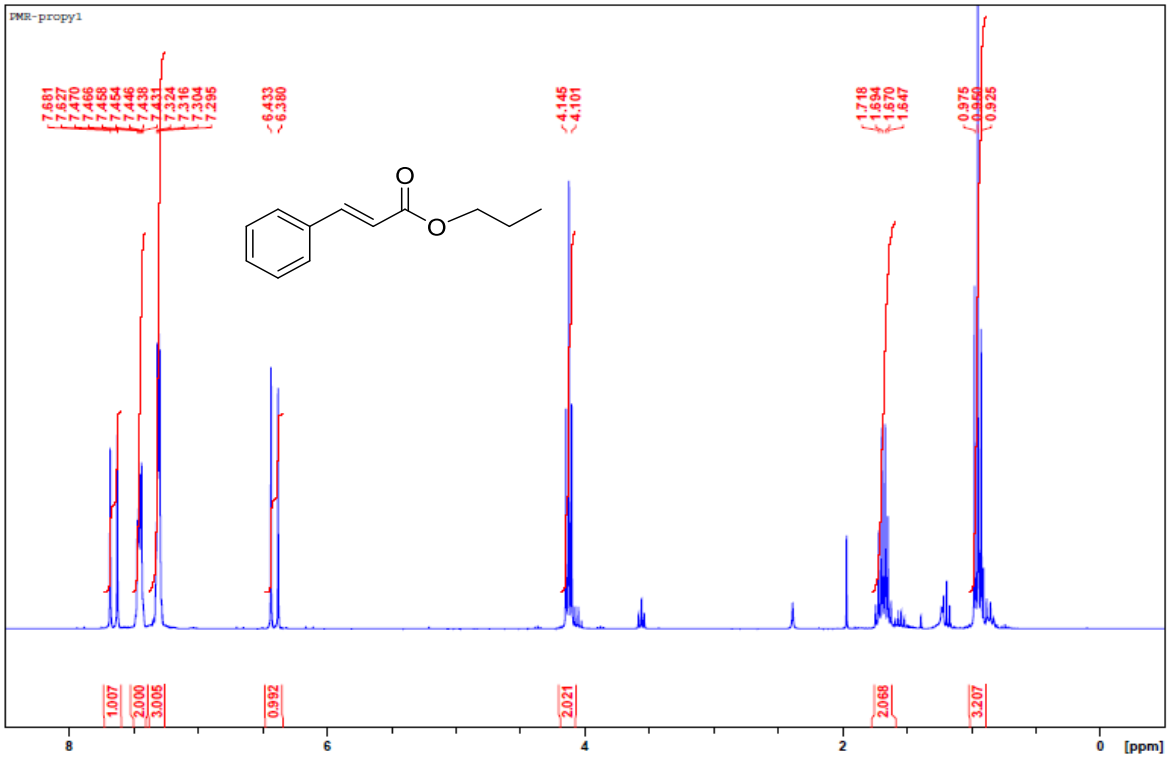


Ethyl cinnamates DEPT 135

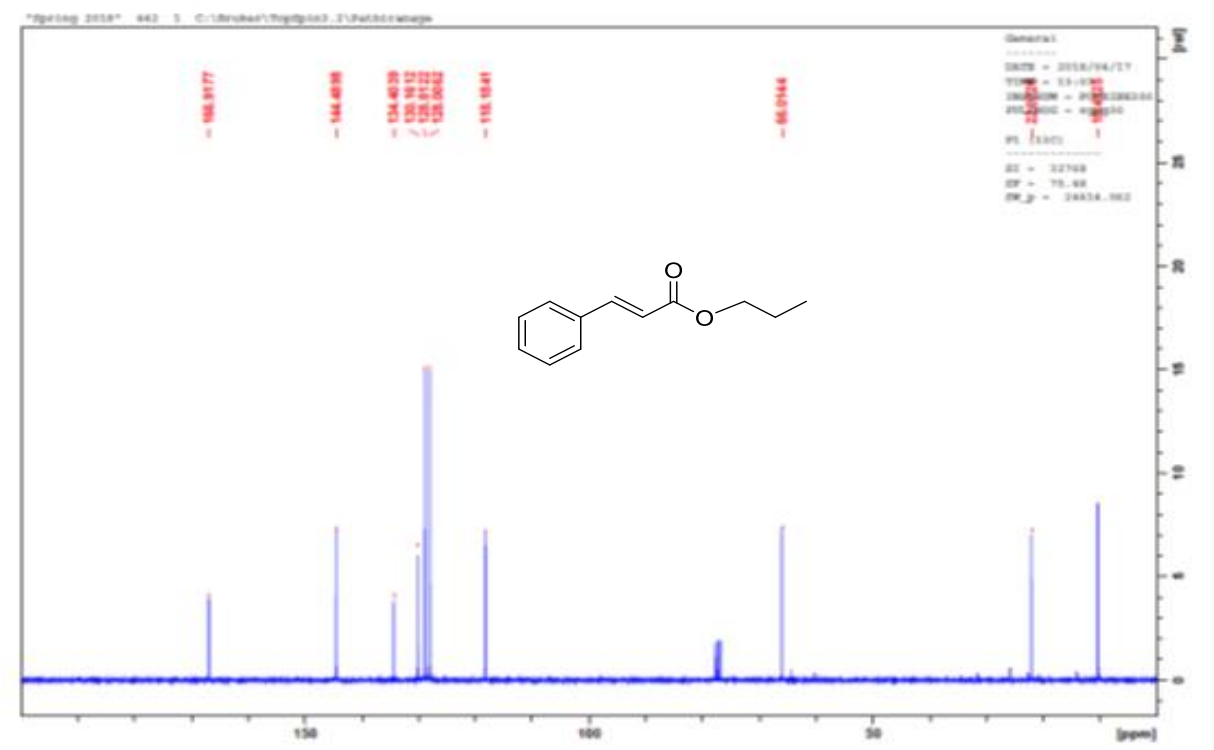
Ethyl cinnamate DEPT 90



Propyl cinnamate ^{1}H-NMR

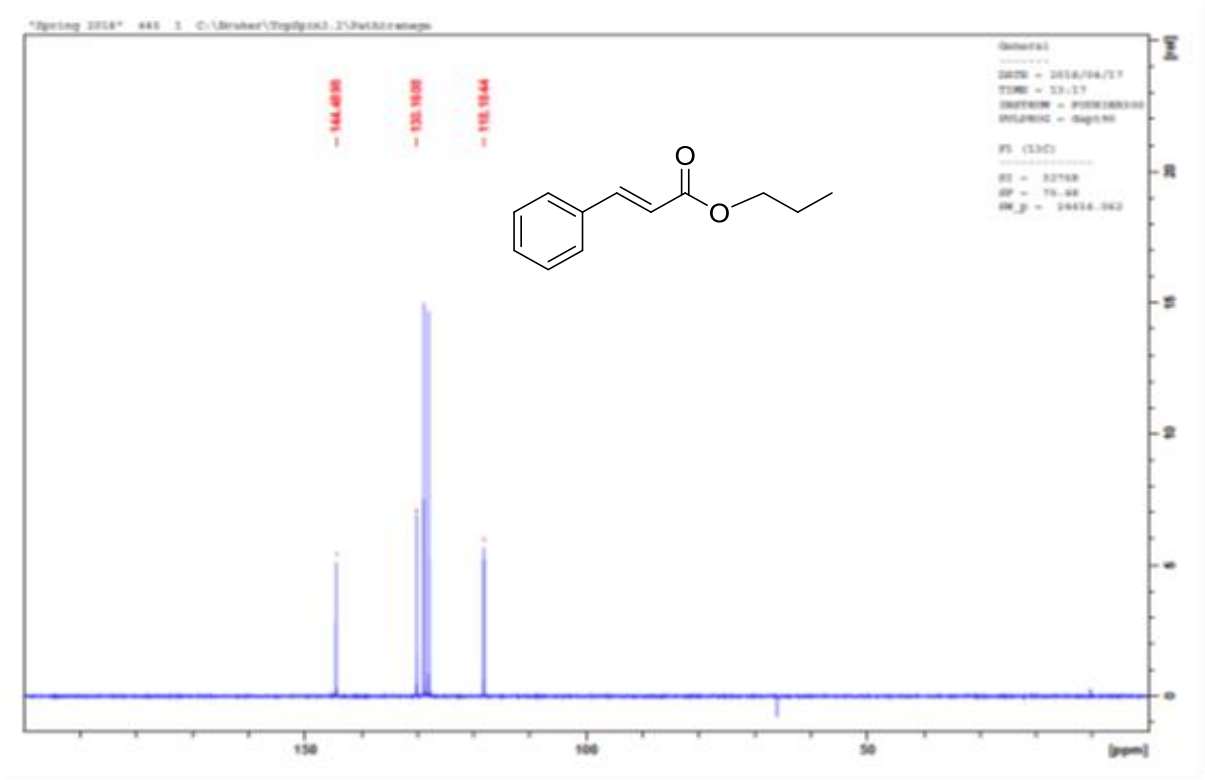


Propyl cinnamate ^{13}C-NMR

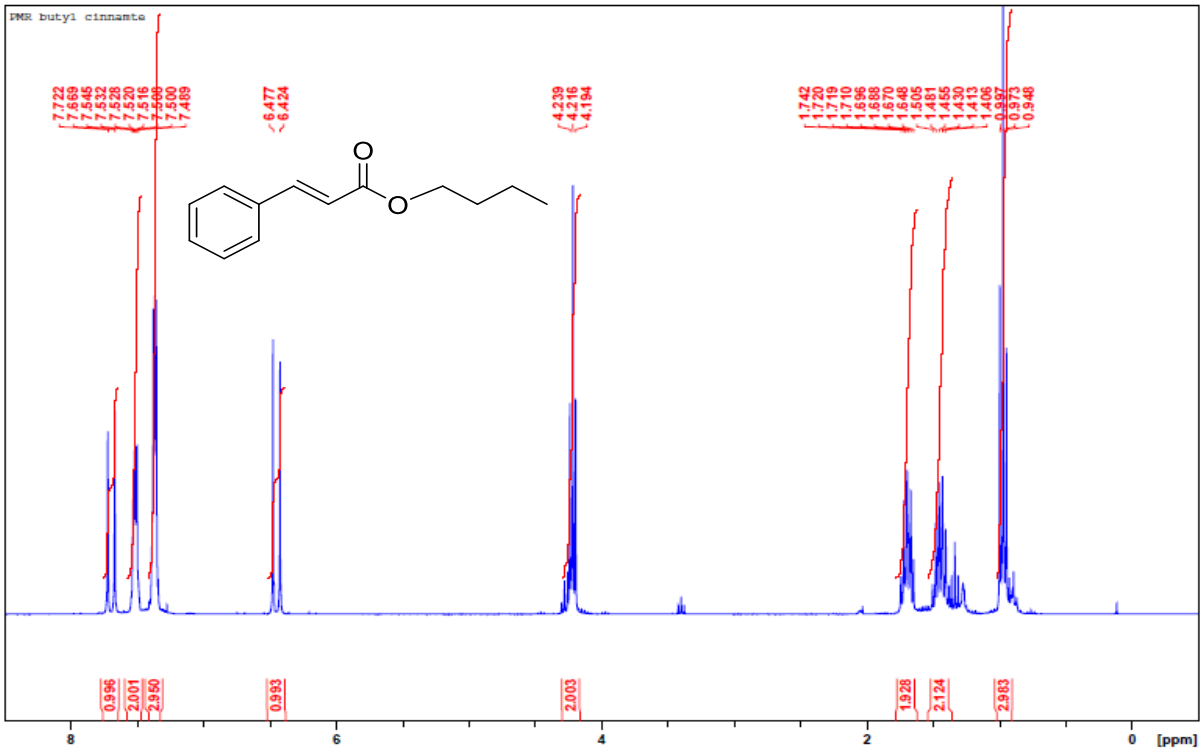


Propyl cinnamate DEPT 135

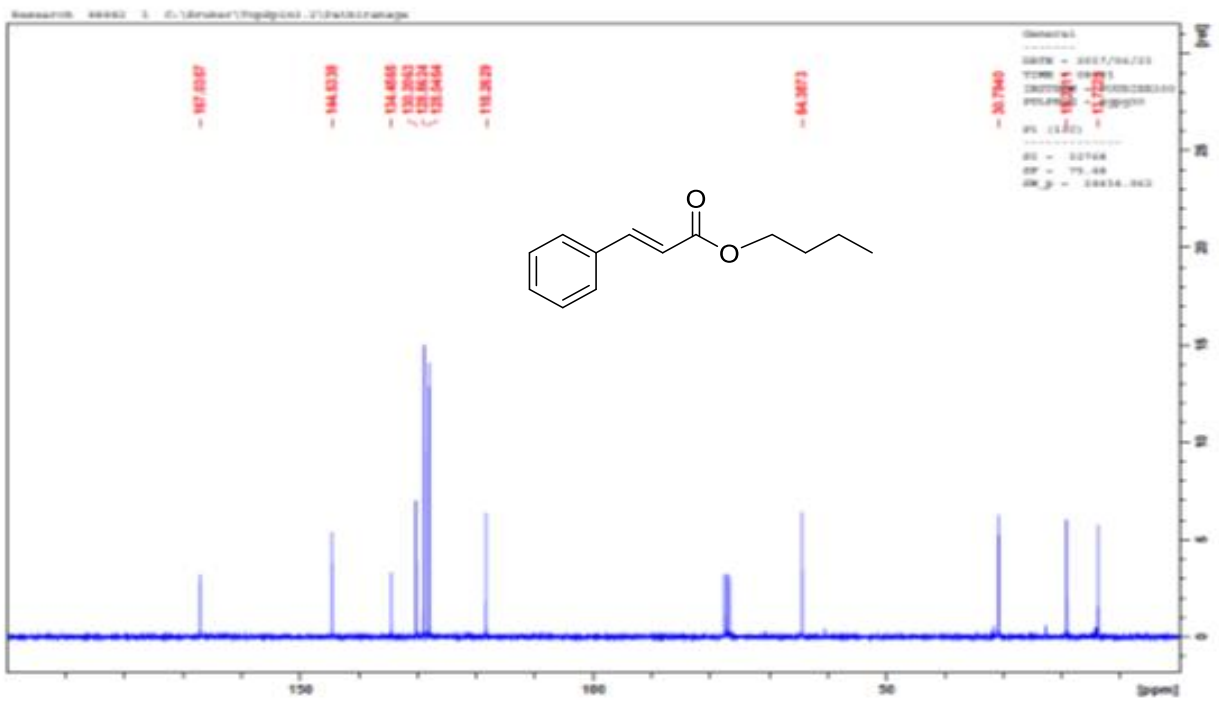
Propyl cinnamate DEPT 90



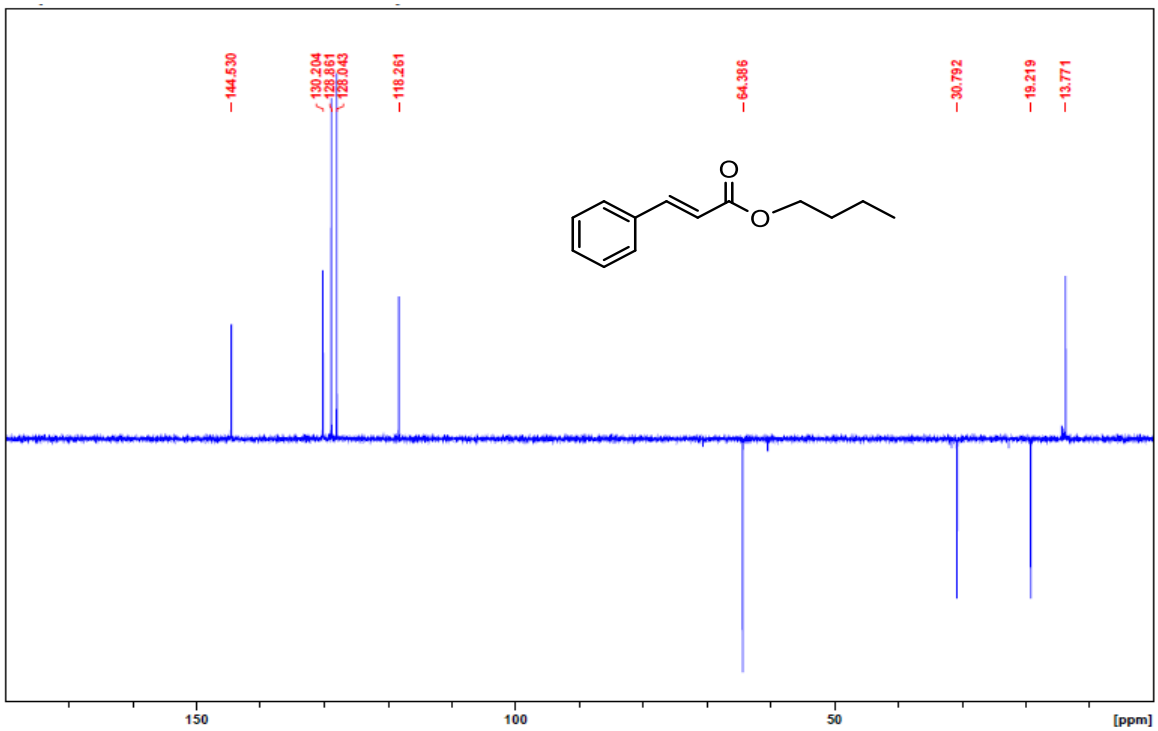
Butyl cinnamate ^{1}H-NMR



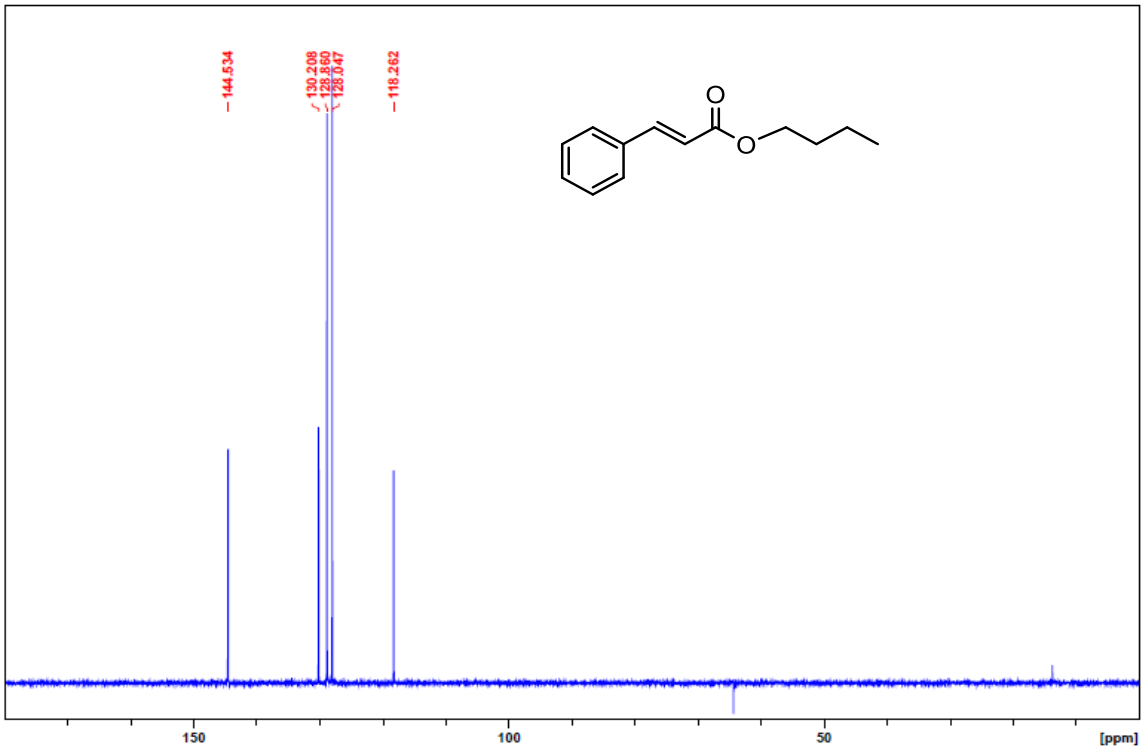
Butyl cinnamate ^{13}C-NMR



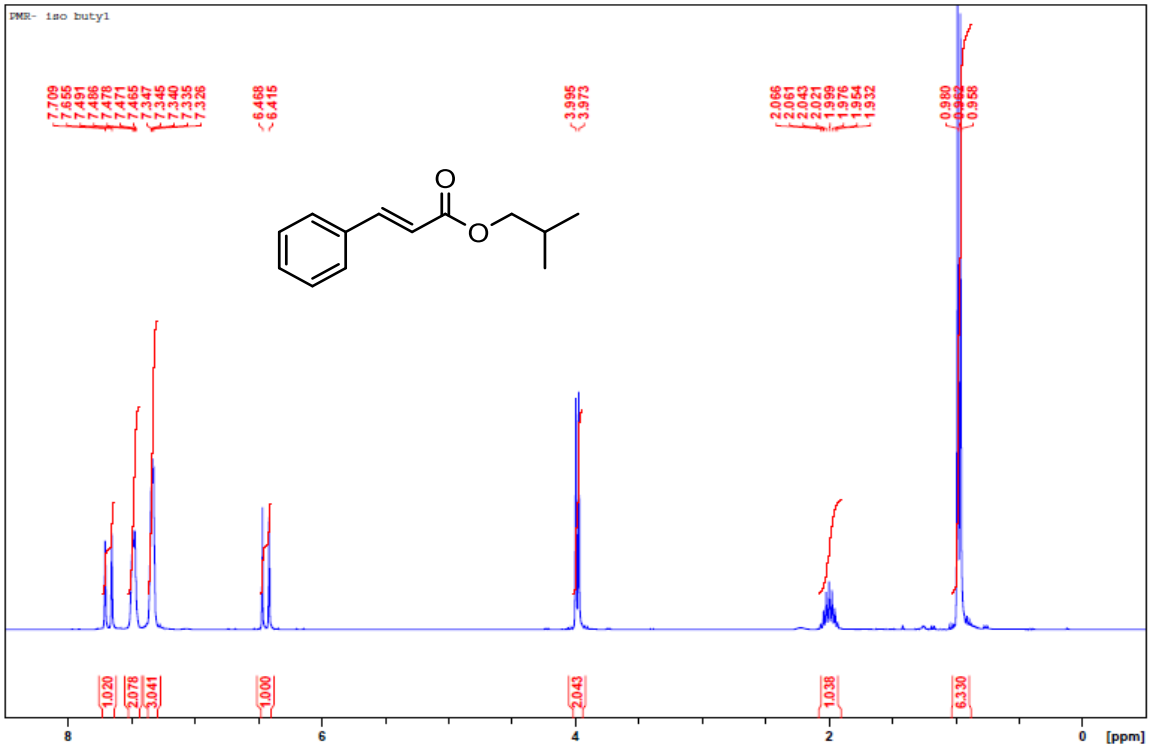
Butyl cinnamate DEPT 135



Butyl cinnamate DEPT 90

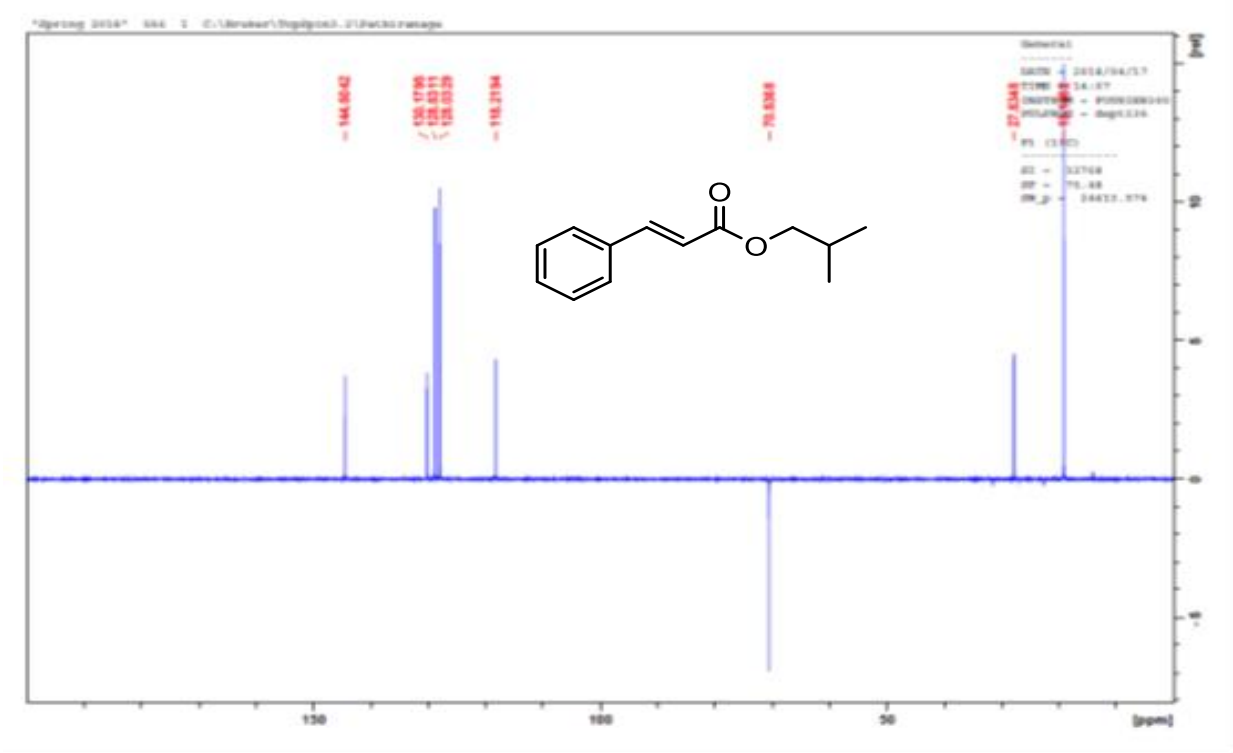


Isobutyl cinnamate ^{1}H-NMR

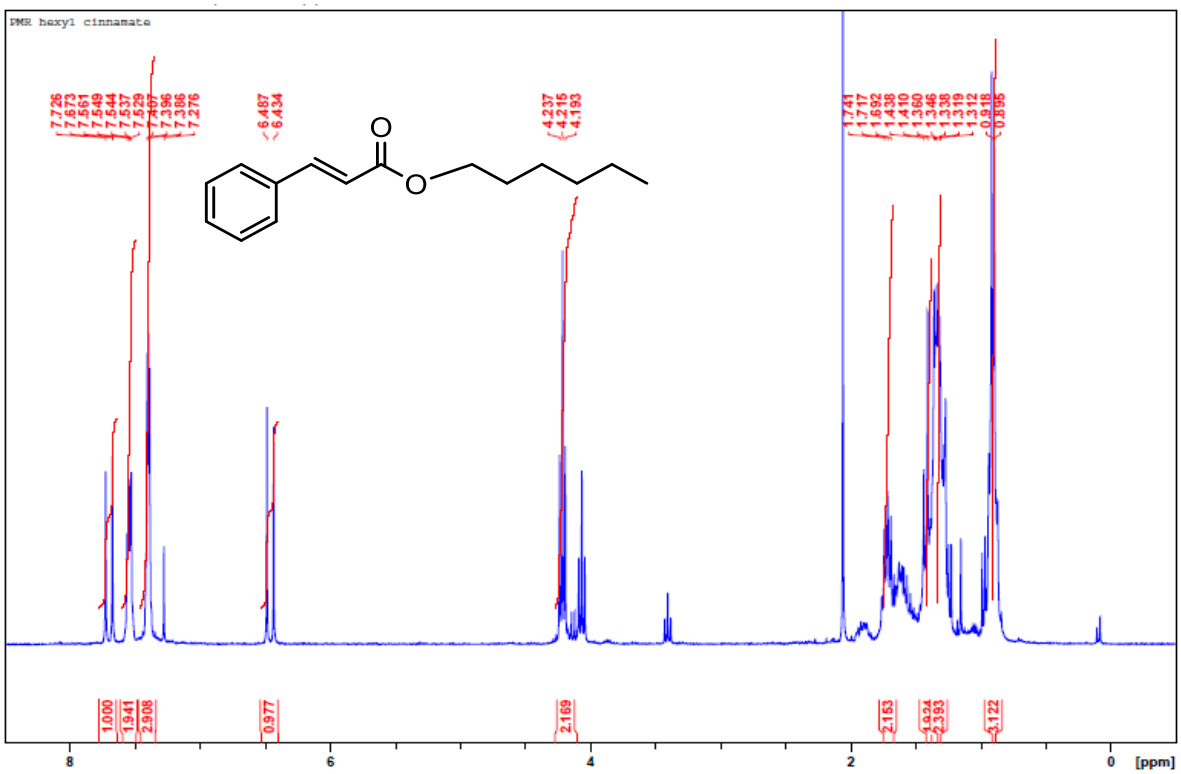


Isobutyl cinnamate ^{13}C-NMR

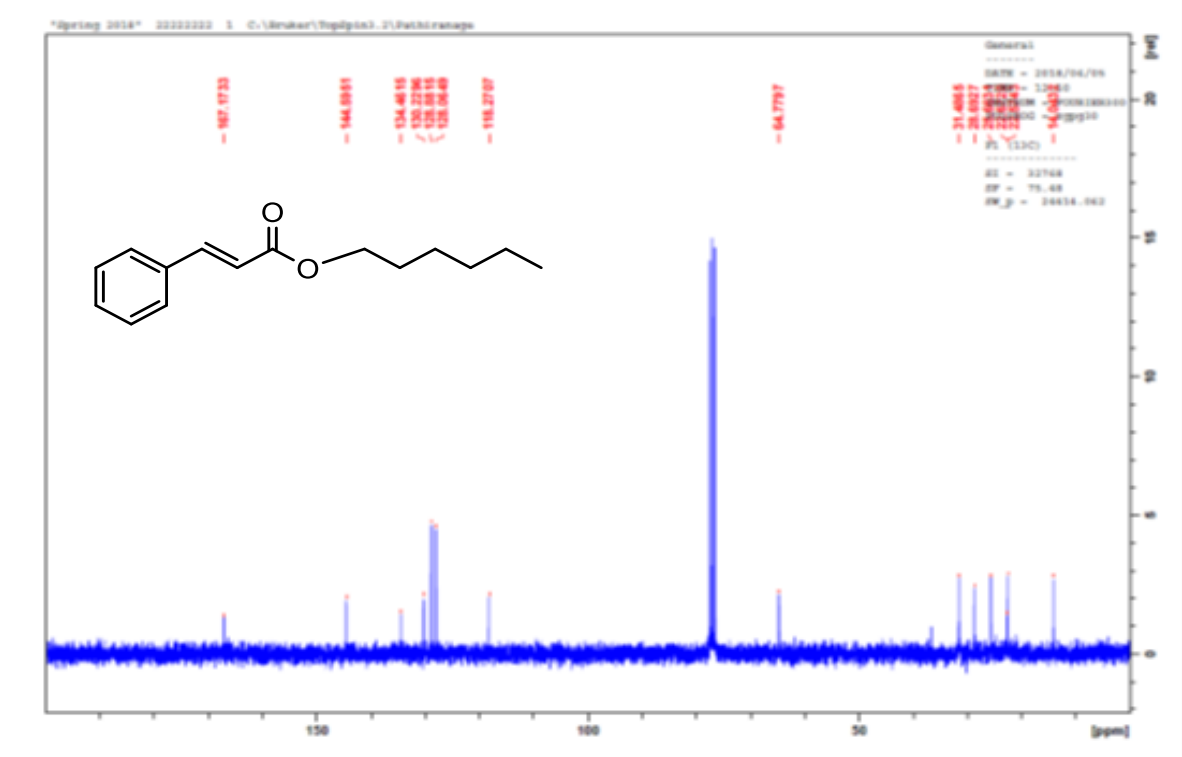
Isobutyl cinnamate DEPT 135



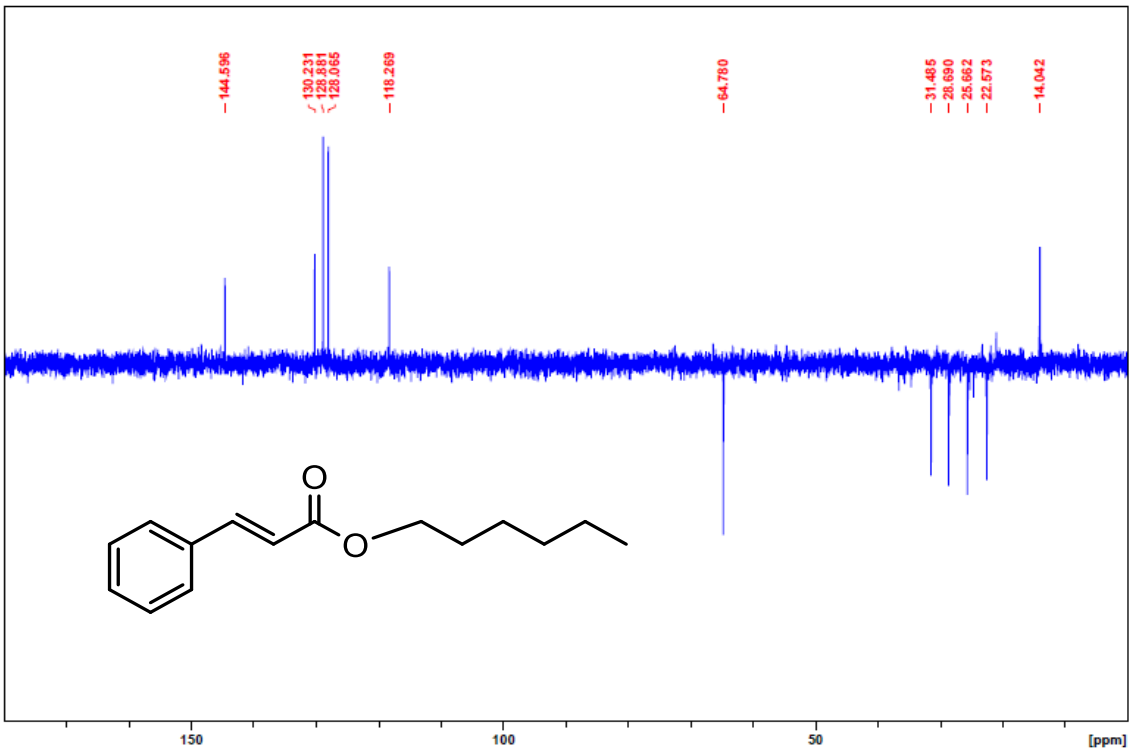
Hexyl cinnamate ^{1}H-NMR



Hexyl cinnamate ^{13}C-NMR



Hexyl cinnamate DEPT 135



Hexyl cinnamate DEPT 90