

# Supporting Information

## Consecutive reactions to construct tricarbonyl compounds and synthetic applications thereof.

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## General information:

All experiments involving air and/or moisture-sensitive compounds were conducted in an oven dried round-bottom flask capped with a rubber septum under a positive pressure of nitrogen. Air- and moisture-sensitive liquids were transferred via syringe or stainless-steel cannula. Low temperature baths were: ice/water (0 °C), CO<sub>2</sub>(s)/acetone (−78 °C). Unless otherwise noted, reaction temperatures refer to that of the bath. Concentration refers to removal of volatiles on a rotary evaporator below 35 °C. Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with silica gel (0.25-mm, 60-Å pore size, 230–400 mesh, Merck) impregnated with a fluorescent indicator (254 nm). Materials on TLC plates were visualized under an ultraviolet lamp (254 nm) and/or by submersion of the plate in a solution of phosphomolybdic acid (5%) containing a trace of ceric sulfate in aqueous sulfuric acid (5% v/v) followed by charring on a hot plate. Flash column chromatography (FCC) was performed according to Still et al. with silica gel 60 (40-63 μm). All mixed solvent eluents are reported as v/v solutions. Unless otherwise noted, all reported compounds were homogeneous by thin layer chromatography (TLC) and by <sup>1</sup>H NMR.

## Materials

All the reagents were purchased from Sigma-Aldrich and were used as received unless other thing stated. Solvents were distilled prior to use. Anhydrous solvents were distilled under nitrogen atmosphere. THF and diethyl ether were distilled on sodium benzophenone ketyl; MeOH on magnesium activated with 5% iodine. Et<sub>3</sub>N, CH<sub>3</sub>CN dichloroethane and DMF were distilled on CaH<sub>2</sub>.

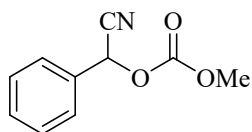
## Instrumentation

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra and carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were recorded on Agilent-Inova-300 and Varian VNMRS-400 NMR spectrometers. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to tetramethylsilane (TMS: 0.0). Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to and are referenced to tetramethylsilane (TMS: 0.0).

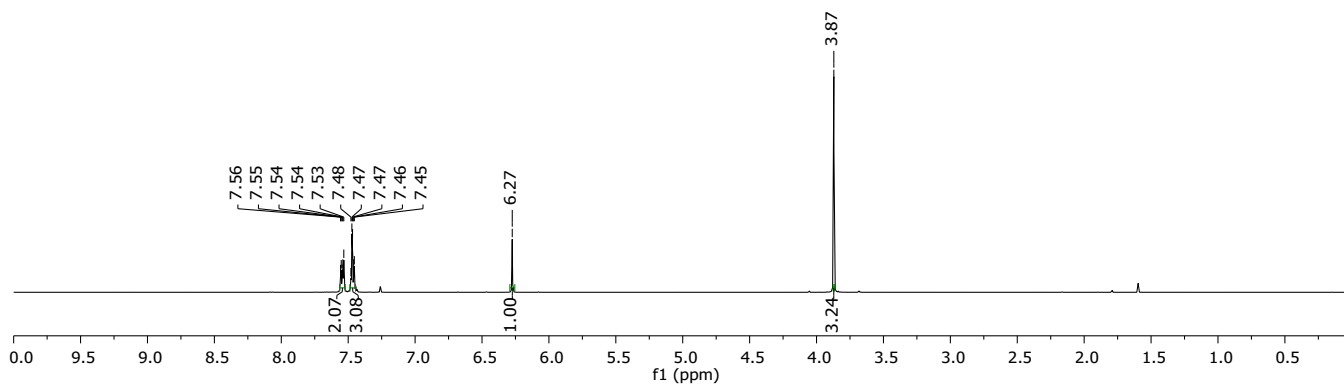
Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublets of doublets, ddt = doublet of doublets of triplets, dqd = doublet of quartets of doublets, m = multiplet, br = broad, app = apparent), integration, and coupling constant (J) in Hertz (Hz). IR spectra were recorded on a Perkin-Elmer Spectrum 400 FT-IR/FIR spectrometer with ATR. Mass spectra were carried out on a JEOL SMX-102a spectrometer. For compounds 6e, 7e, 7f, 7h, 7p, 8g, and 8n, CDCl<sub>3</sub> was used as a standard. For the rest of the analyzed compounds, TMS was the standard. This information is included in the ESI.

# NMR Spectra

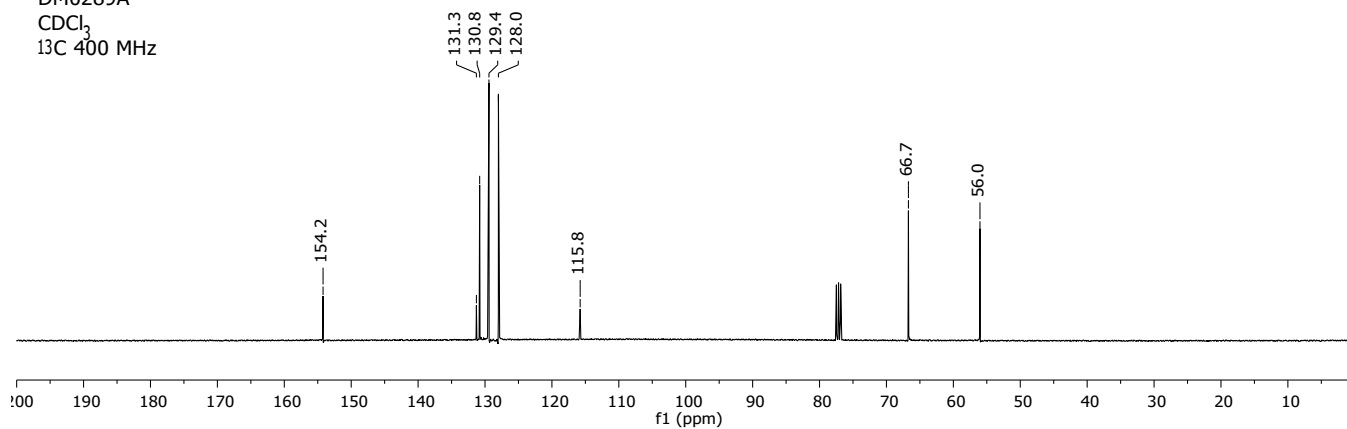
## Cyano(phenyl)methyl methyl carbonate (6a)



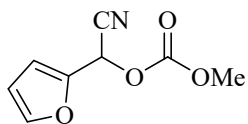
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<sup>1</sup>H 400 MHz



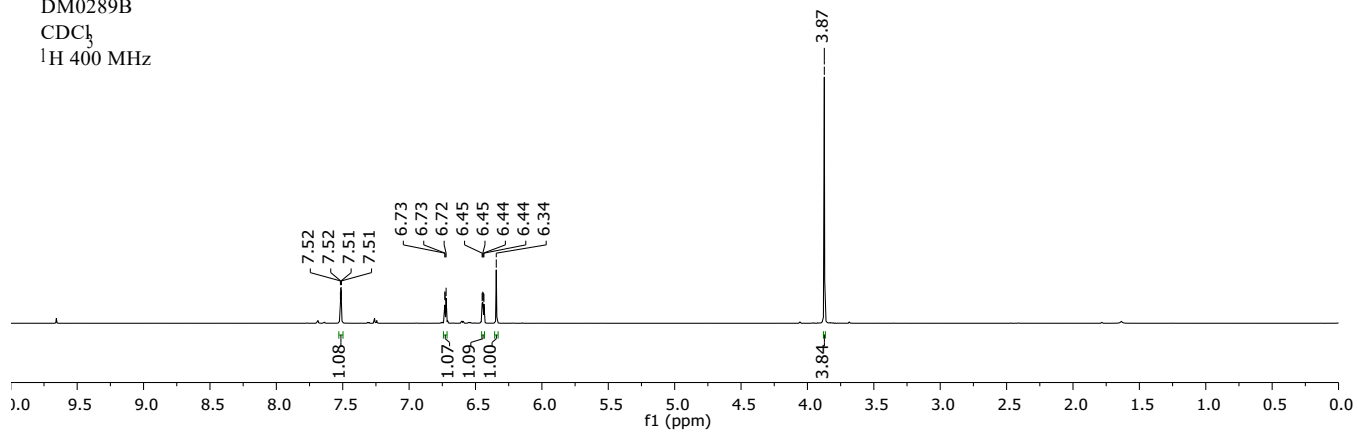
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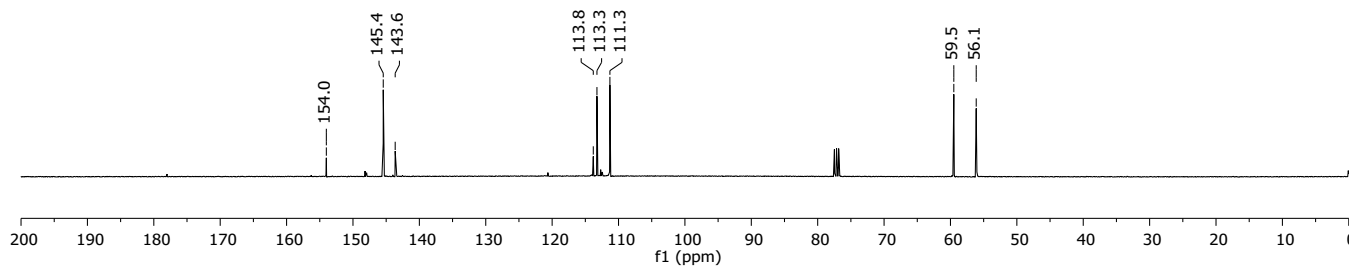
# Cyano(furan-2-yl)methyl methyl carbonate (6b)



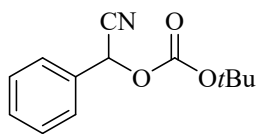
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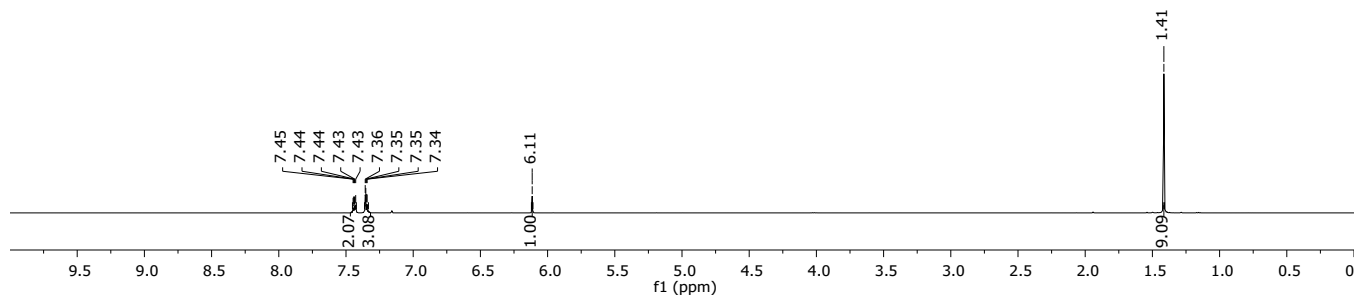
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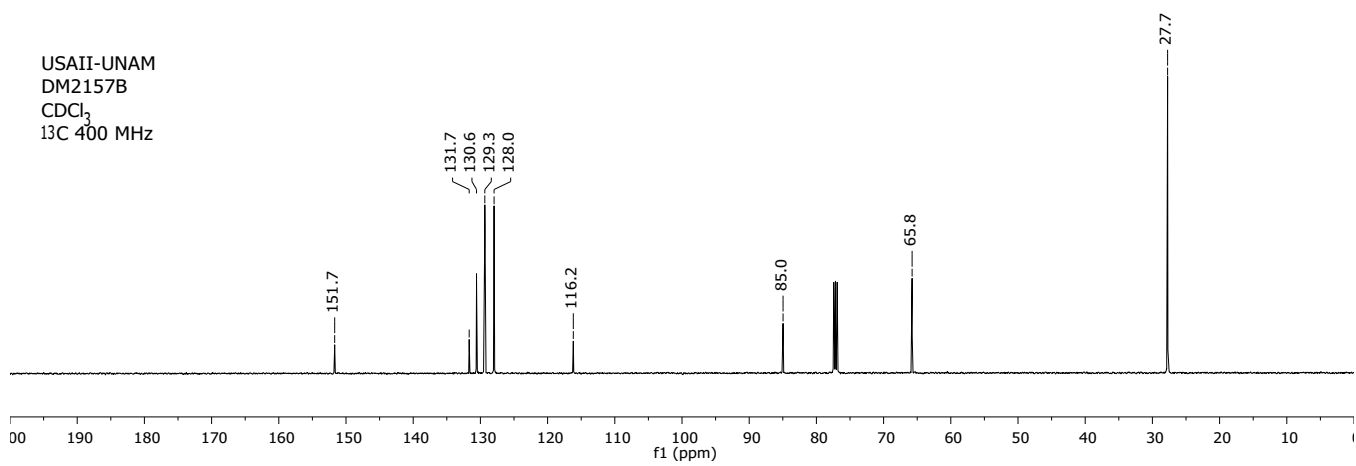
**tert-Butyl (cyano(phenyl)methyl) carbonate (6c)**



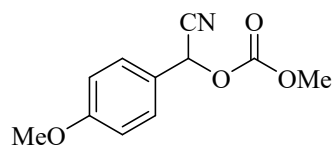
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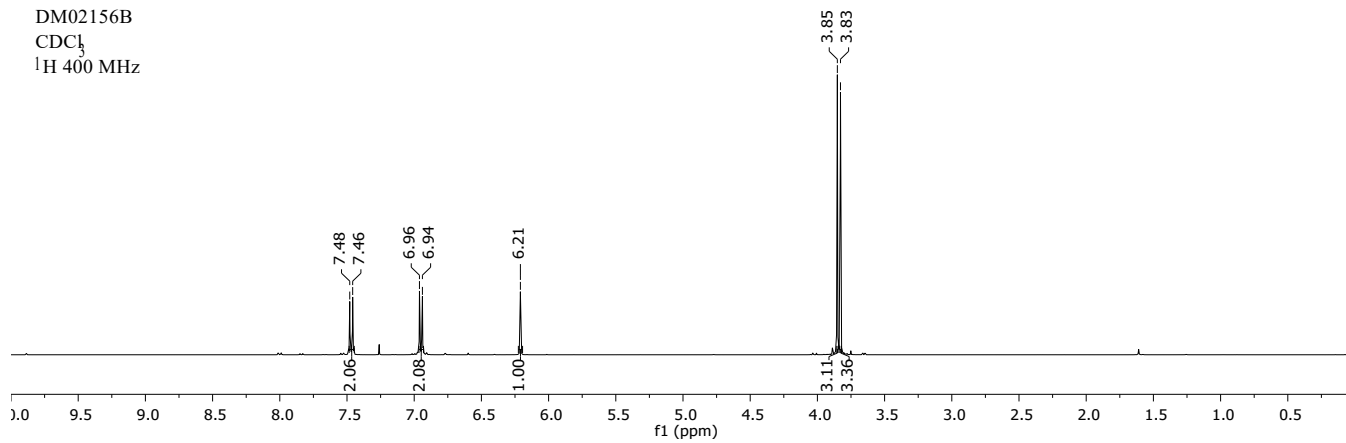
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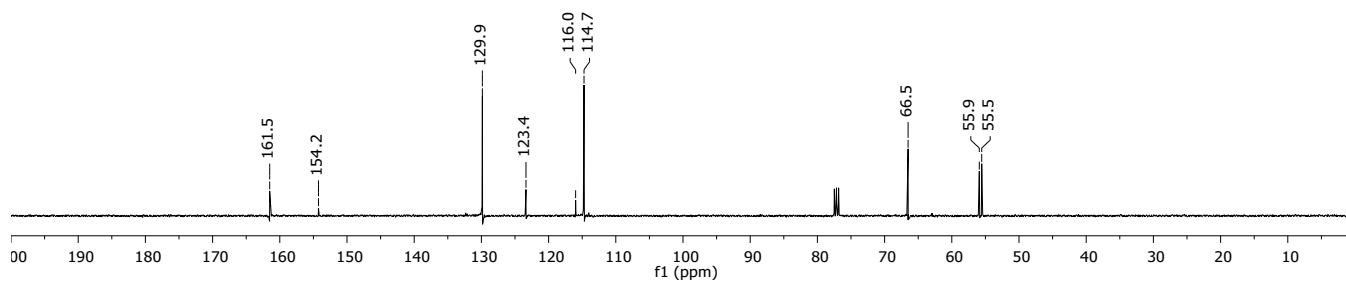
# Cyano(4-methoxyphenyl)methyl methyl carbonate (6d)



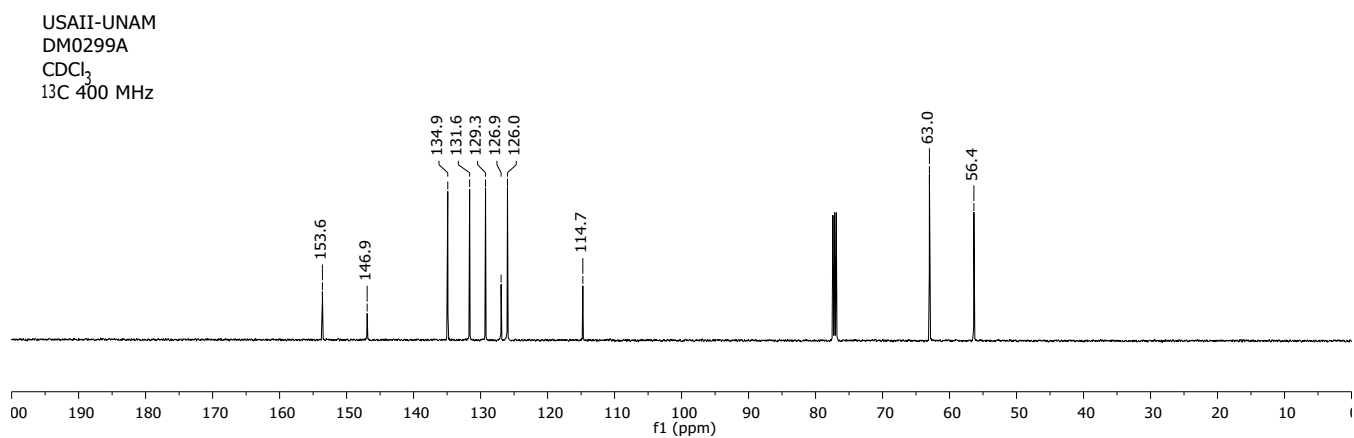
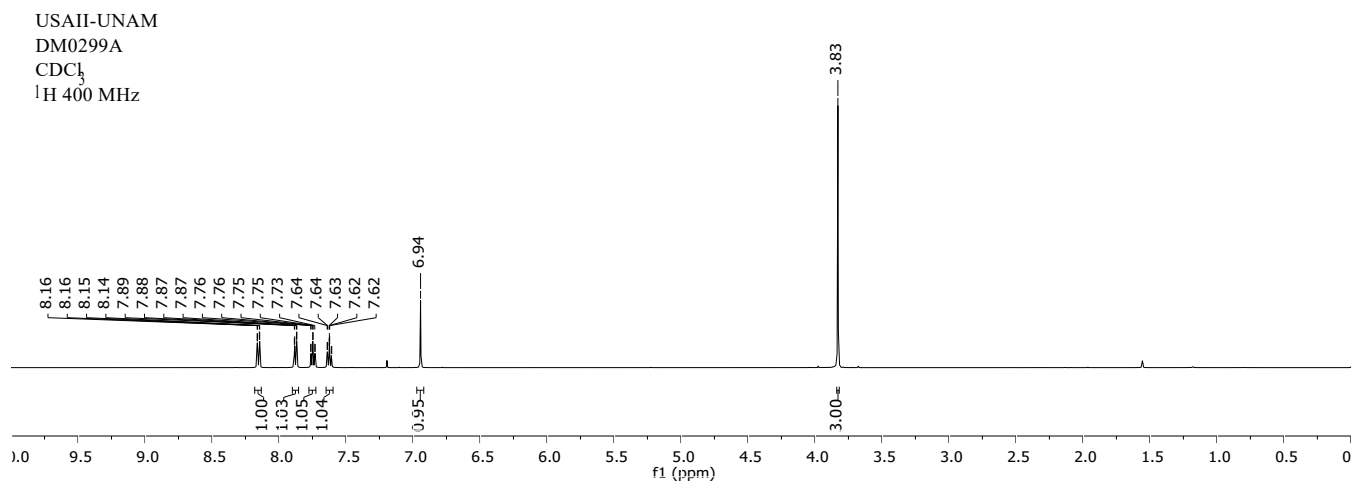
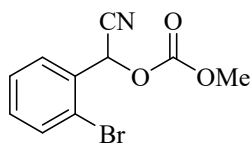
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<sup>1</sup>H 400 MHz



USAI-UNAM  
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<sup>13</sup>C 400 MHz

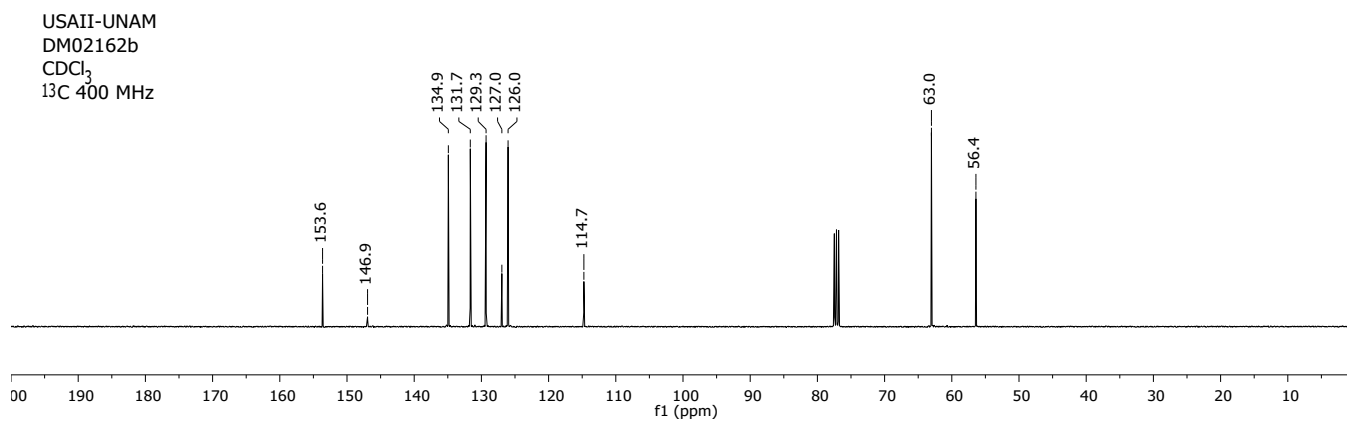
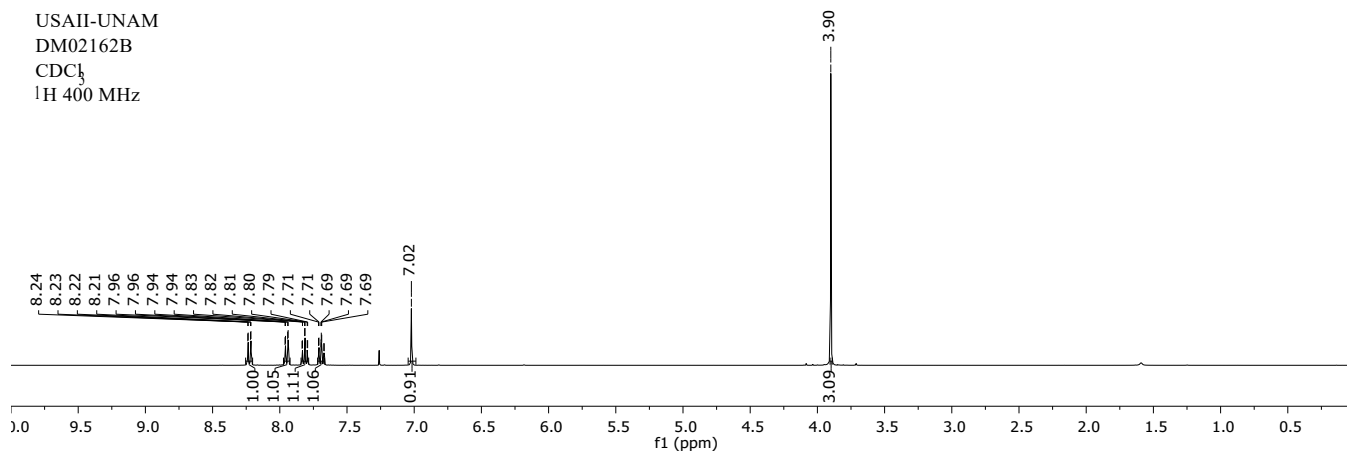
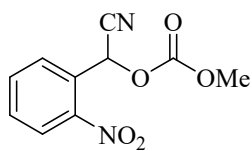


## (2-Bromophenyl)(cyano)methyl methyl carbonate (6e)

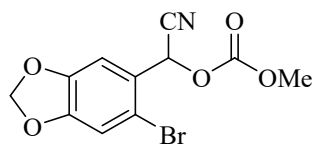




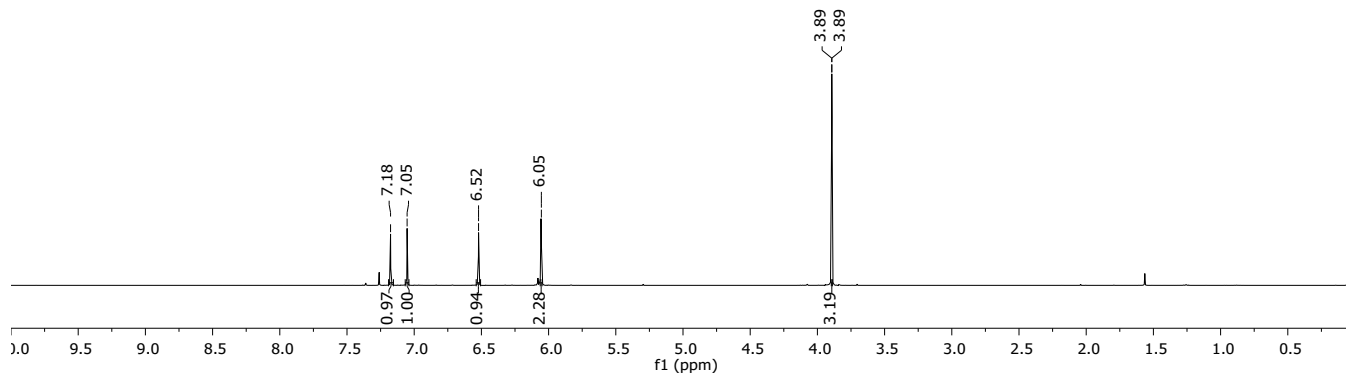
# Cyano(2-nitrophenyl)methyl methyl carbonate (6f)



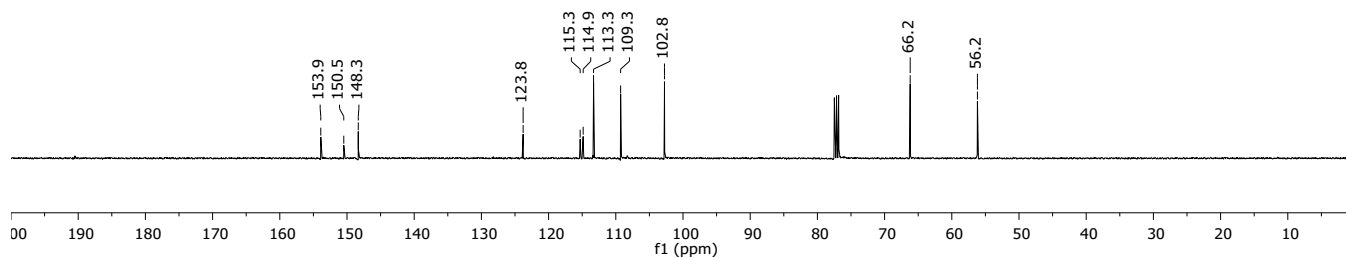
(6-Bromobenzo[d][1,3]dioxol-5-yl)(cyano)methyl methyl carbonate (6g)



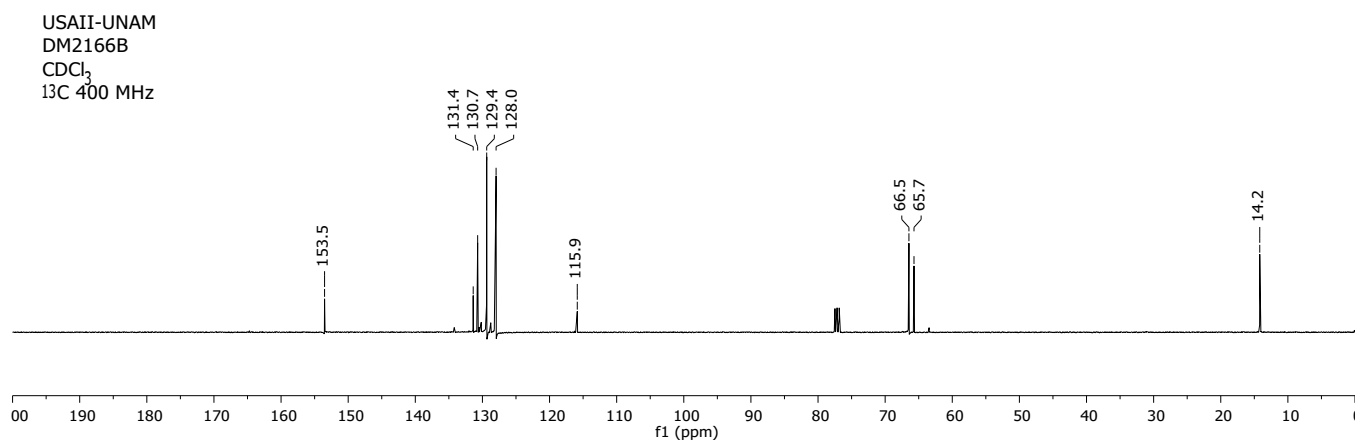
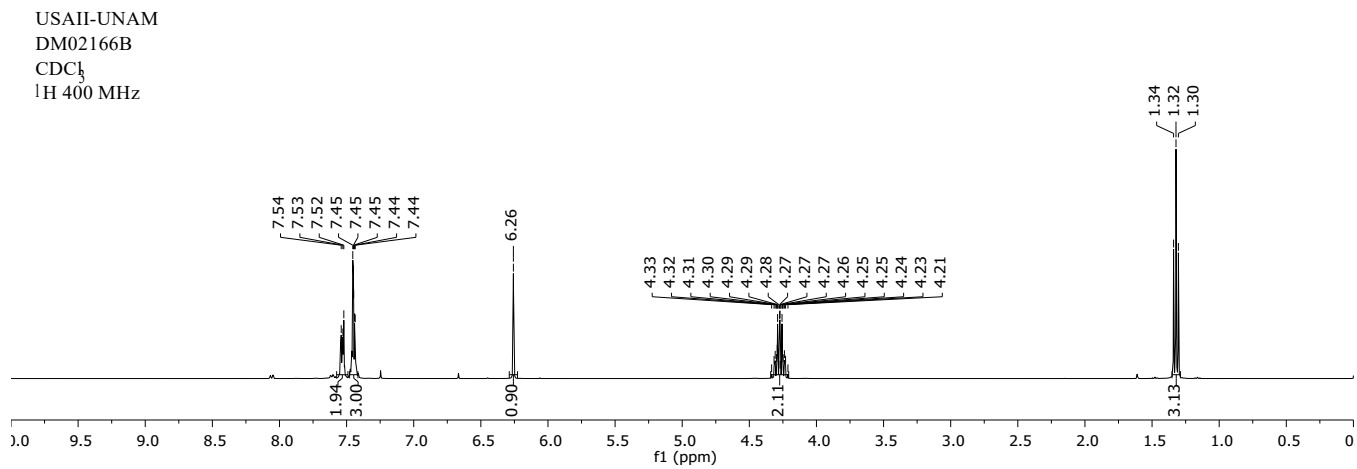
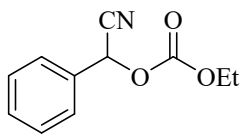
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1H 400 MHz



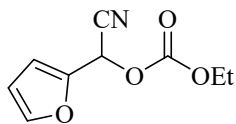
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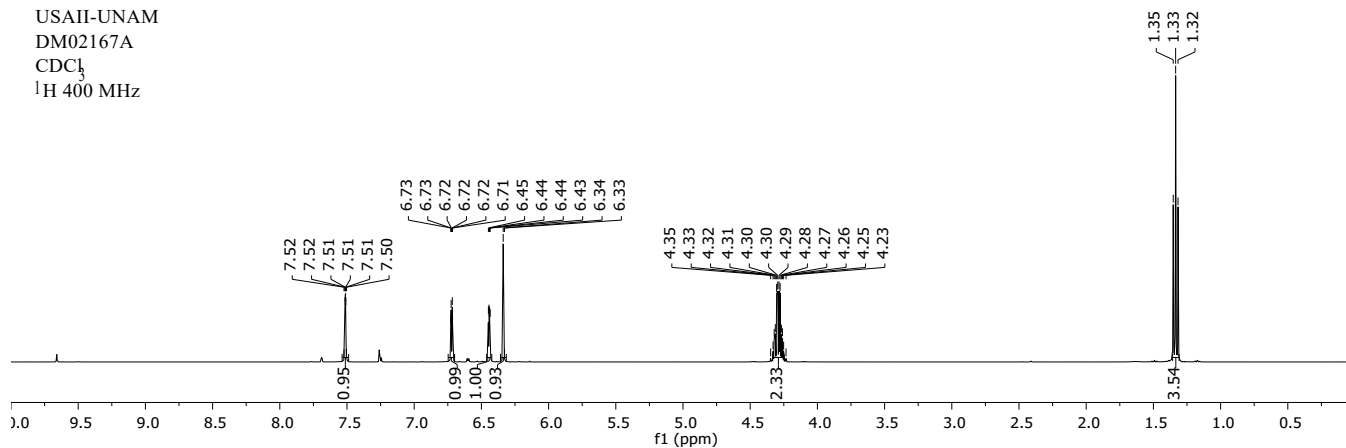
# Cyano(phenyl)methyl ethyl carbonate (7a)



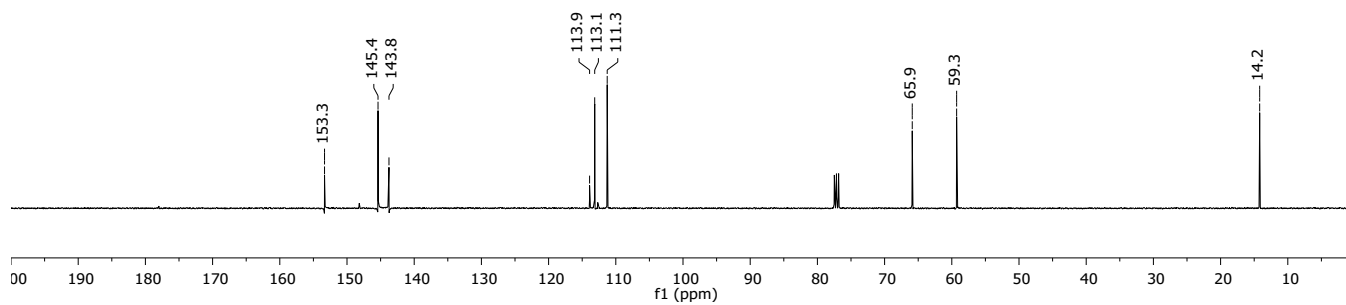
# Cyano(furan-2-yl)methyl ethyl carbonate (7b)



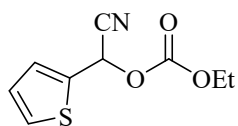
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<sup>1</sup>H 400 MHz



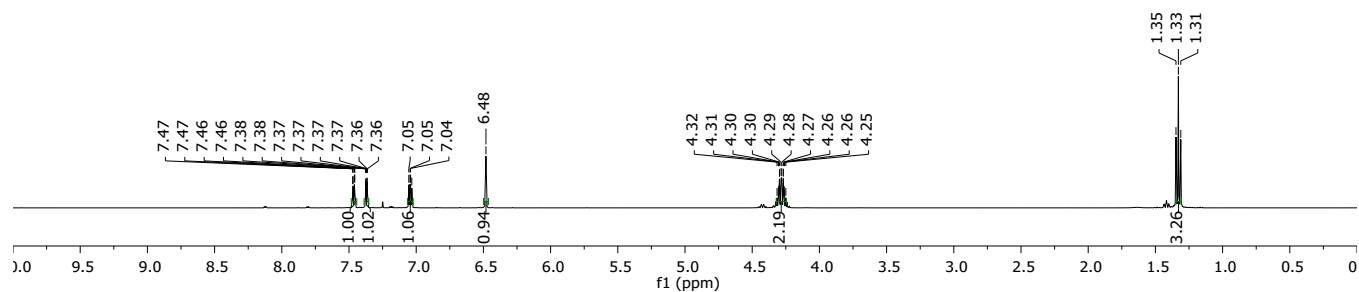
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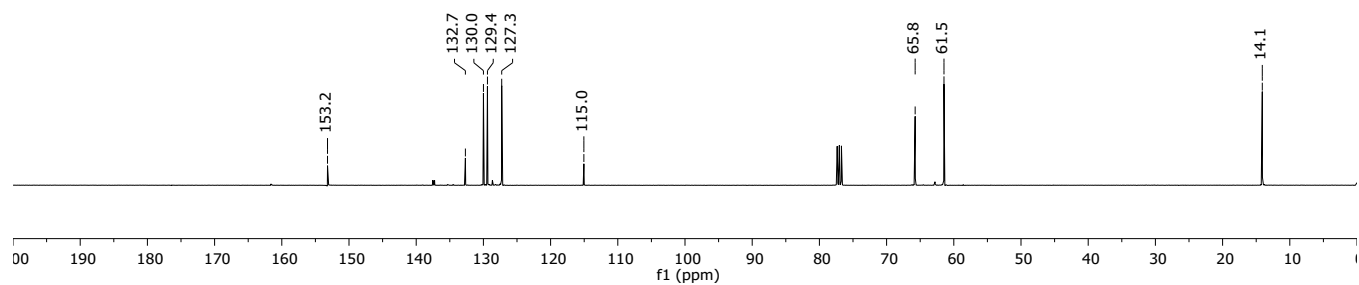
# Cyano(thiophen-2-yl)methyl ethyl carbonate (7c)



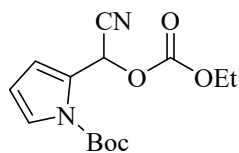
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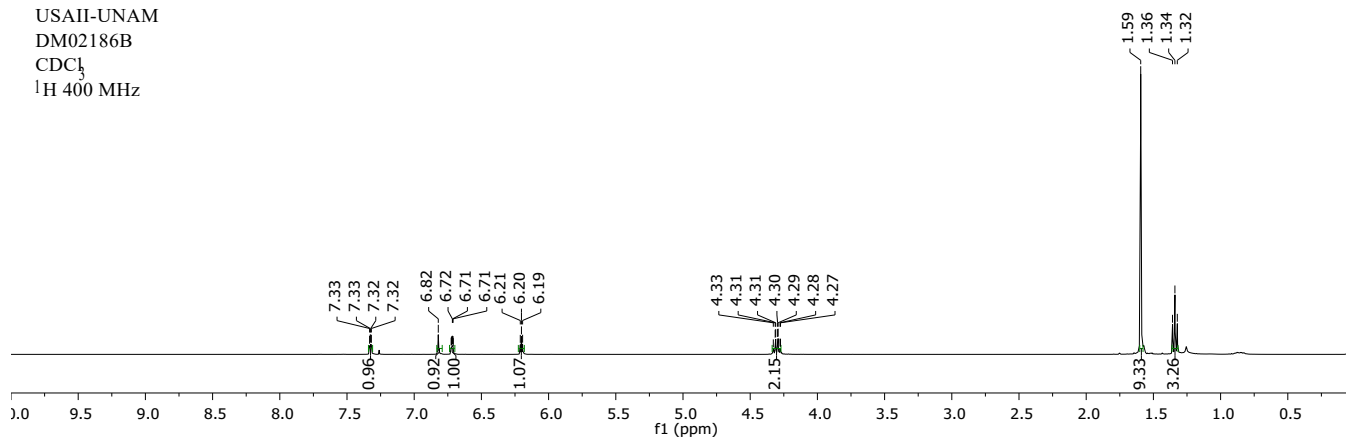
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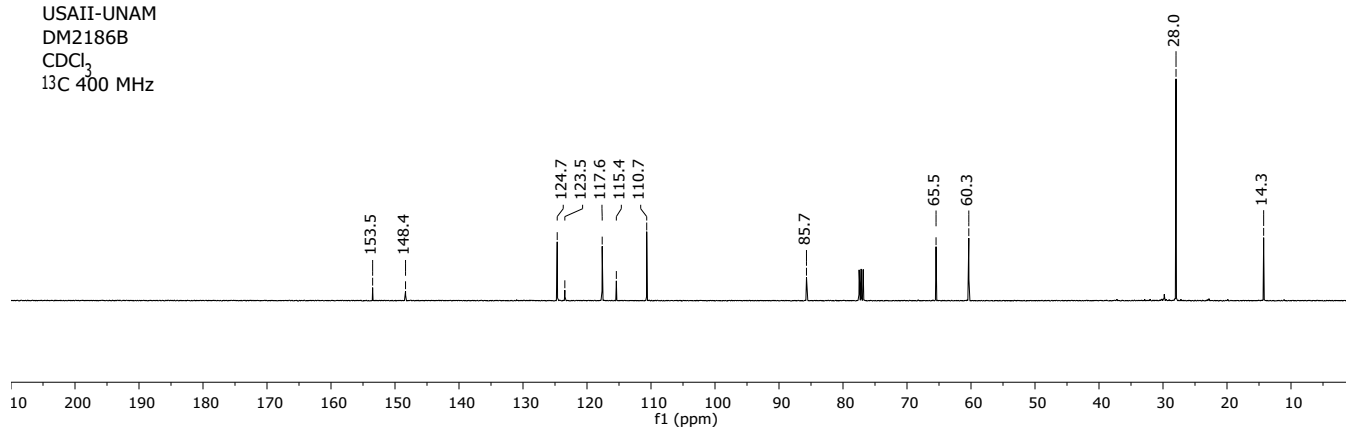
**tert-Butyl 2-(cyano((ethoxycarbonyl)oxy)methyl)-1H-pyrrole-1-carboxylate (7d)**



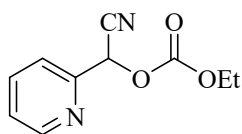
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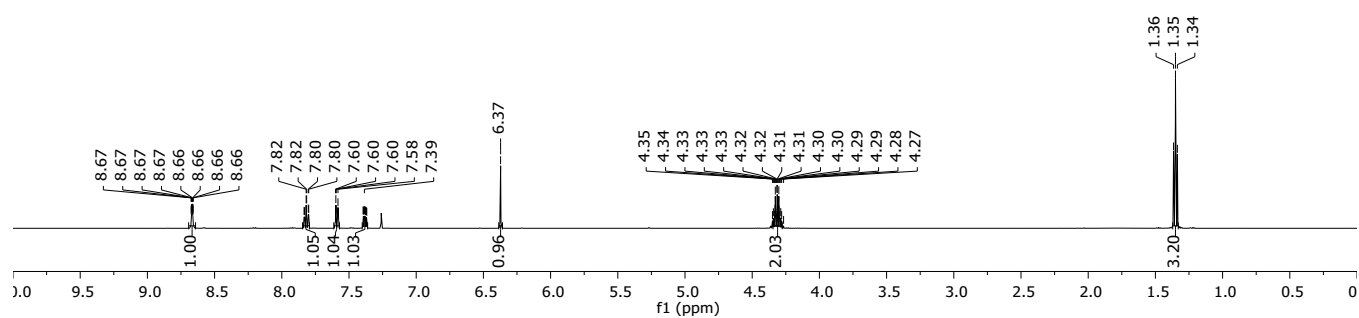
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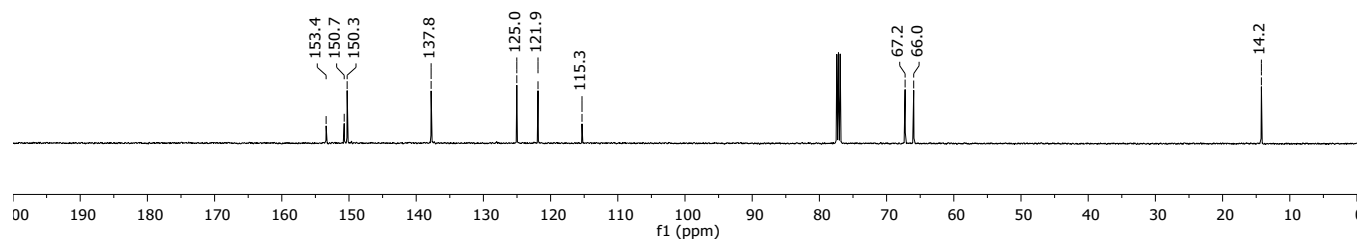
# Cyano(pyridin-2-yl)methyl ethyl carbonate (7e)



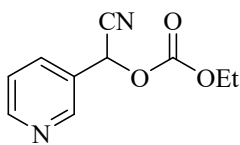
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<sup>1</sup>H 400 MHz



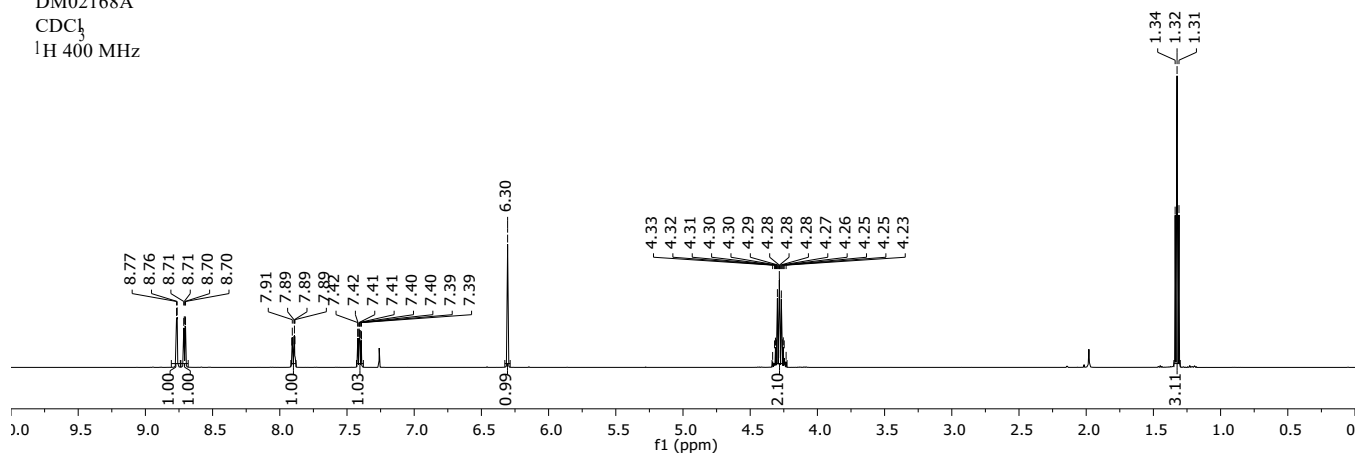
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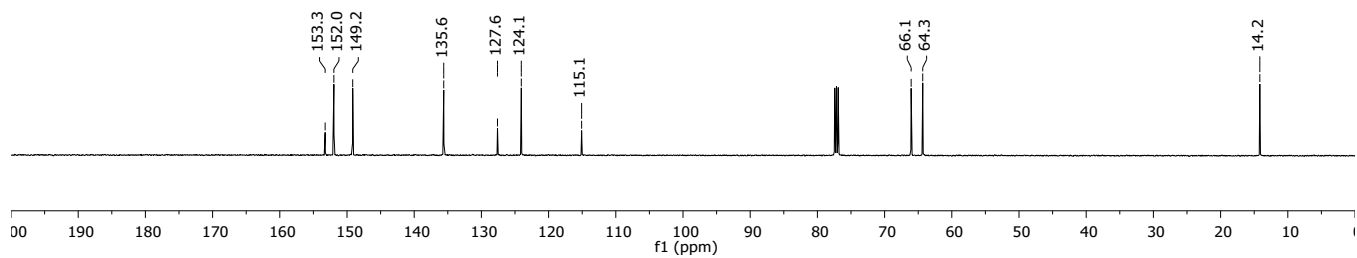
# Cyano(pyridin-3-yl)methyl ethyl carbonate (7f)



USAII-UNAM  
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1H 400 MHz

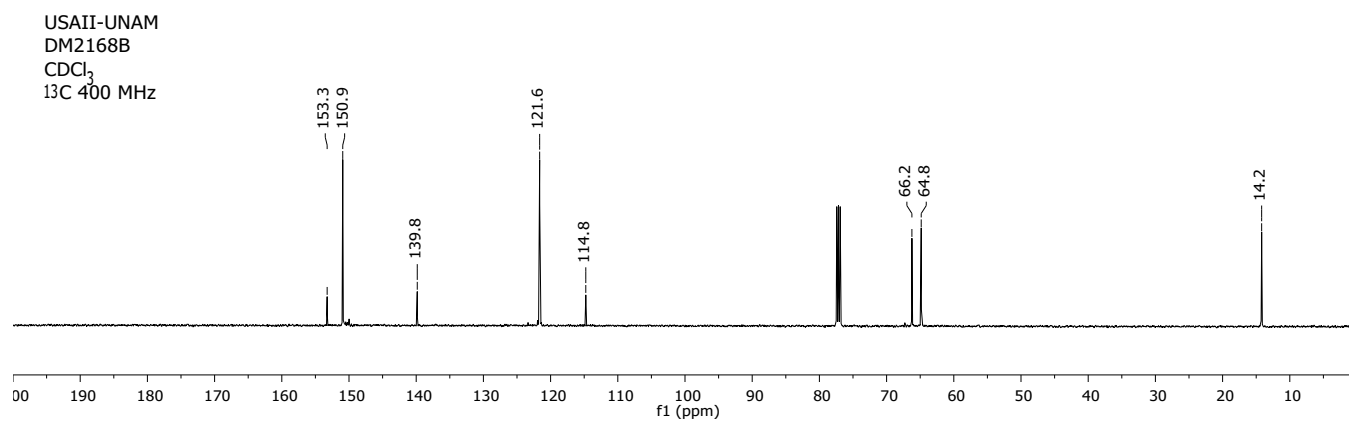
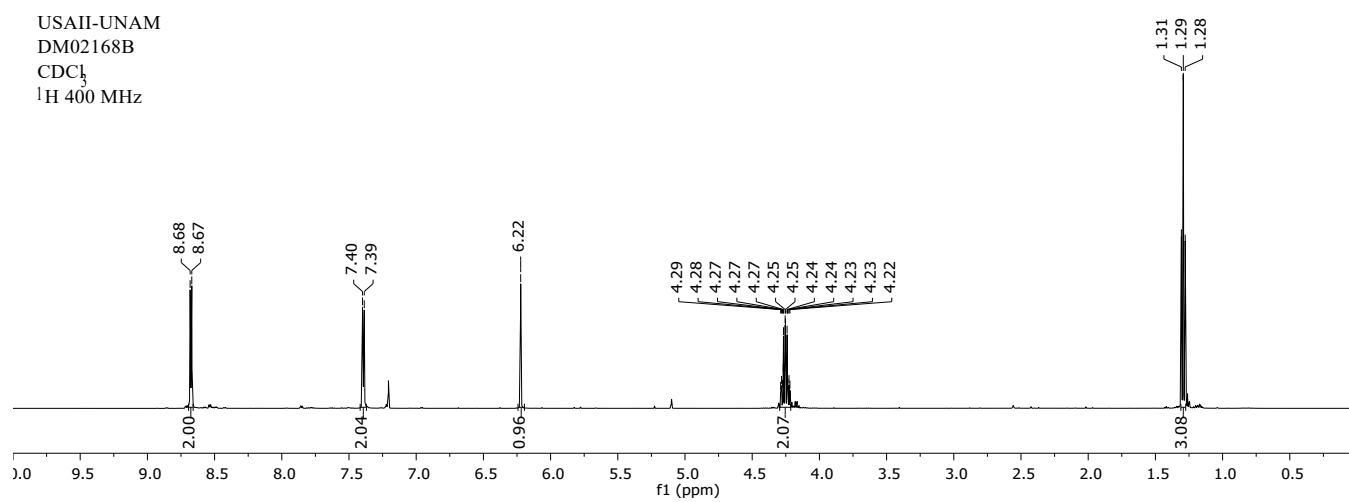
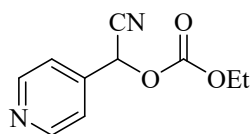


USAII-UNAM  
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CDCl<sub>3</sub>  
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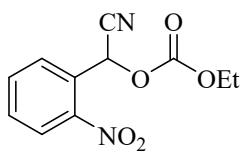




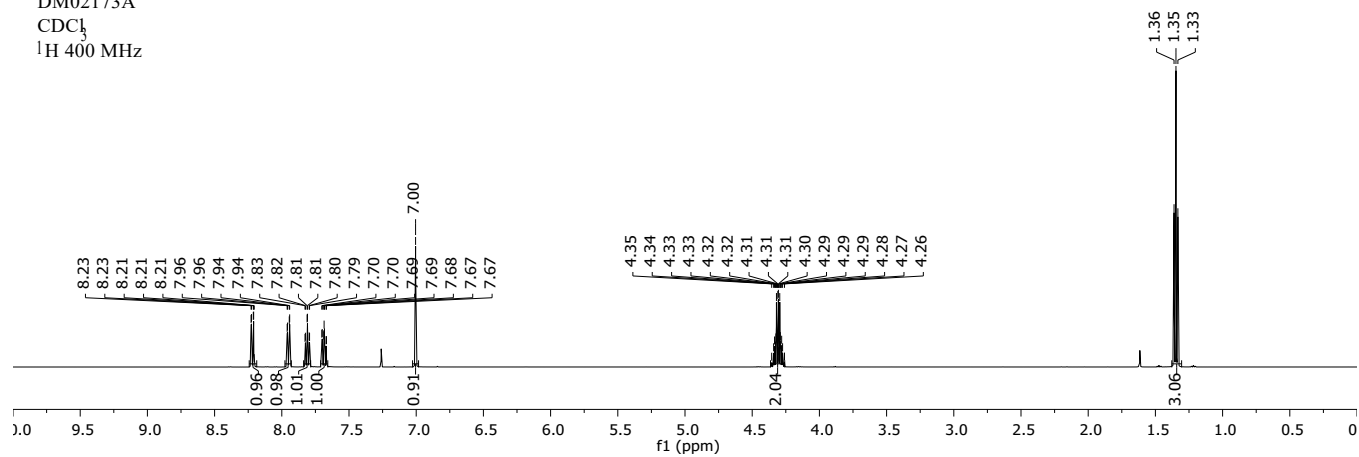
# Cyano(pyridin-4-yl)methyl ethyl carbonate (7g)



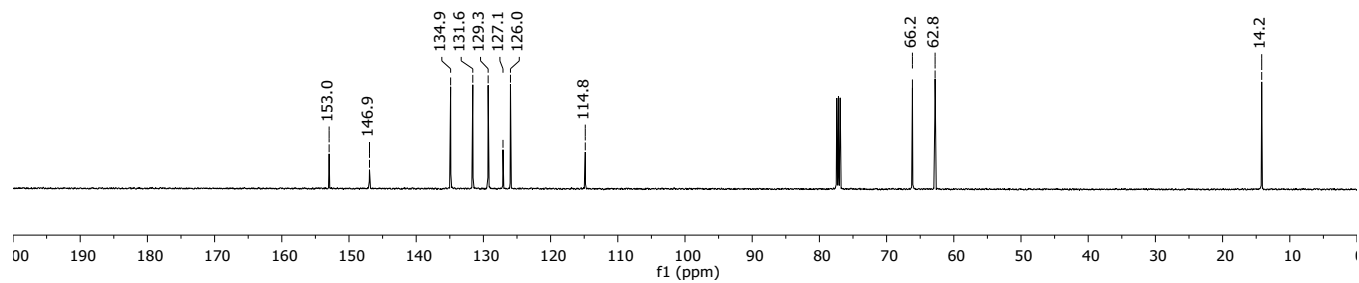
# Cyano(2-nitrophenyl)methyl ethyl carbonate (7g)



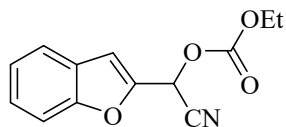
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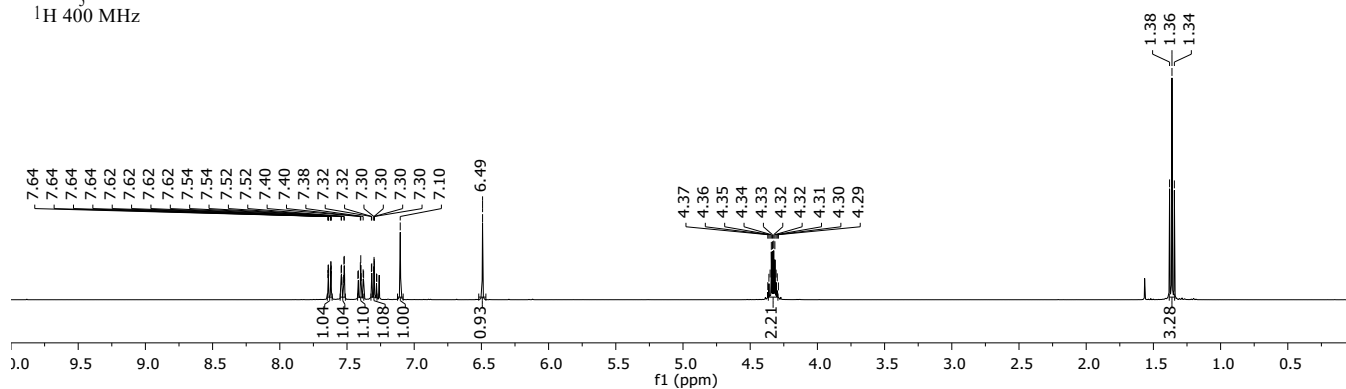
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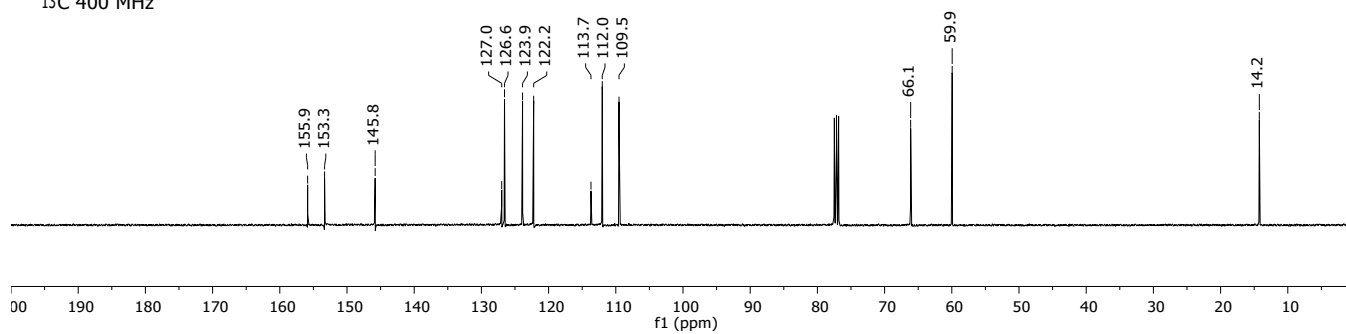
### Benzofuran-2-yl(cyano)methyl ethyl carbonate (7h)



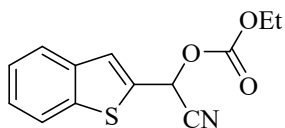
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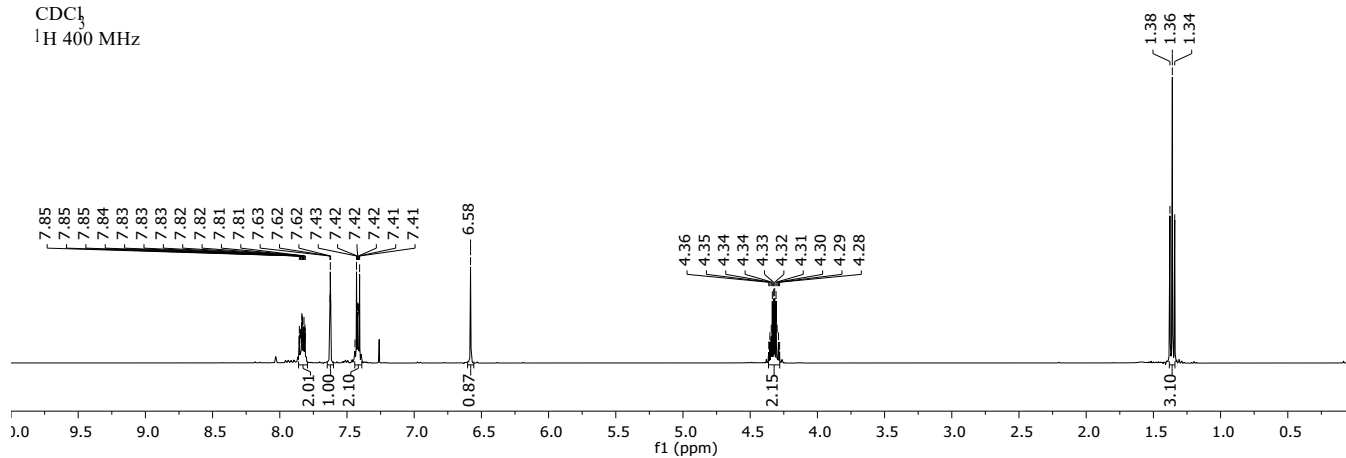
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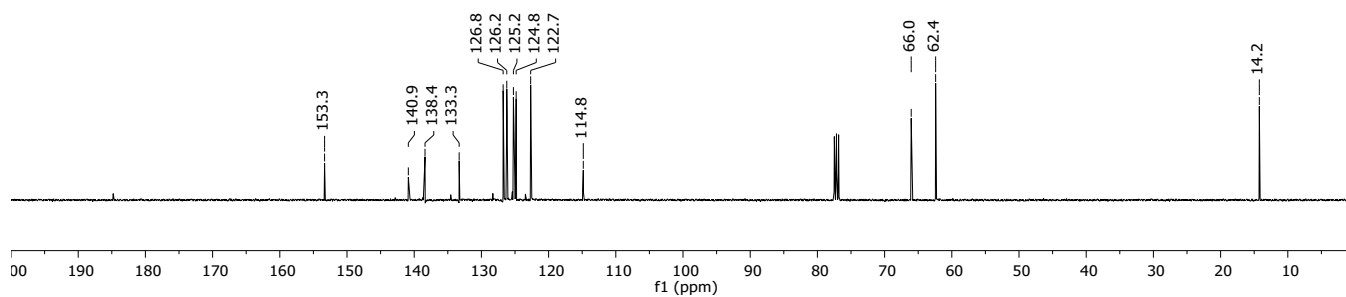
# Benzo[b]thiophen-2-yl(cyano)methyl ethyl carbonate (7i)



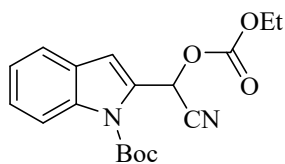
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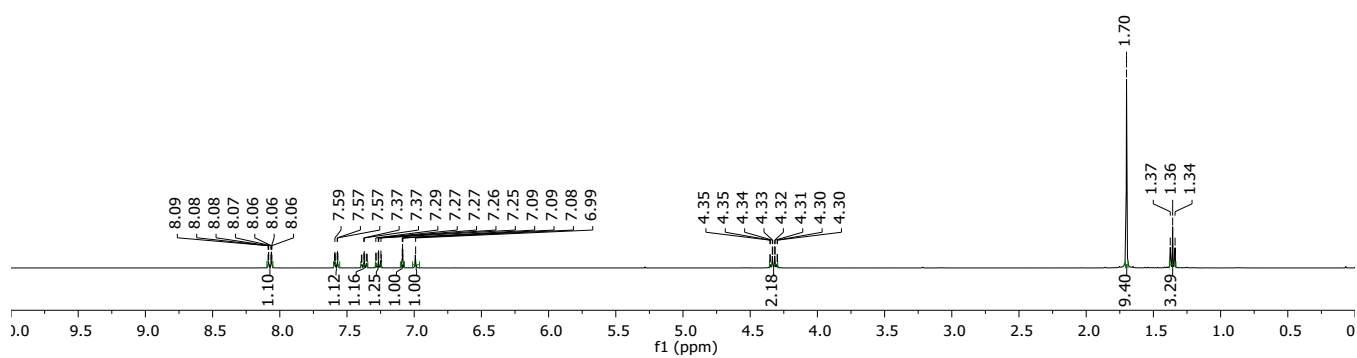
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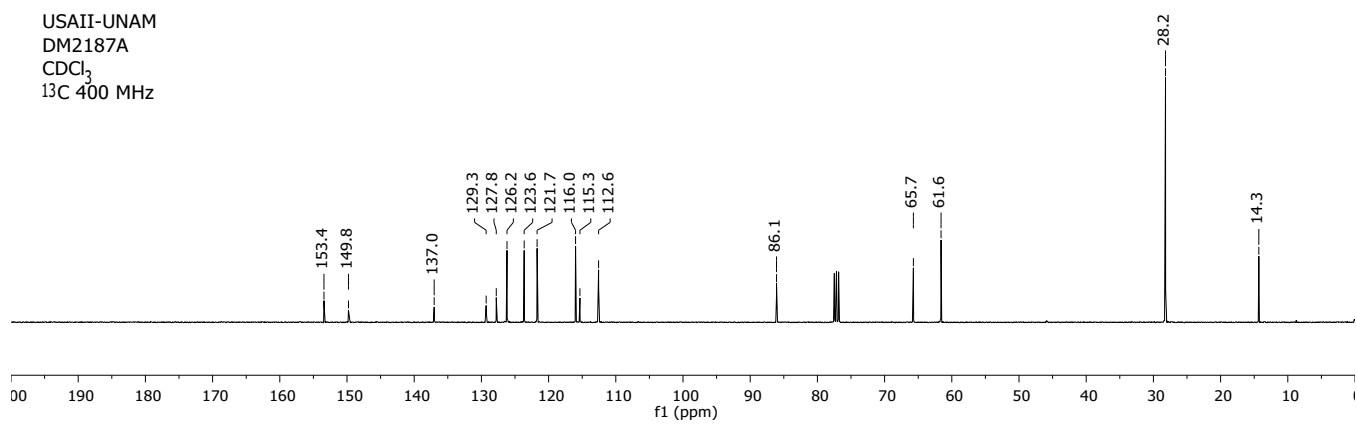
***tert*-Butyl 2-(cyano((ethoxycarbonyl)oxy)methyl)-1*H*-indole-1-carboxylate (7j)**



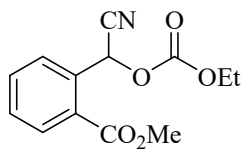
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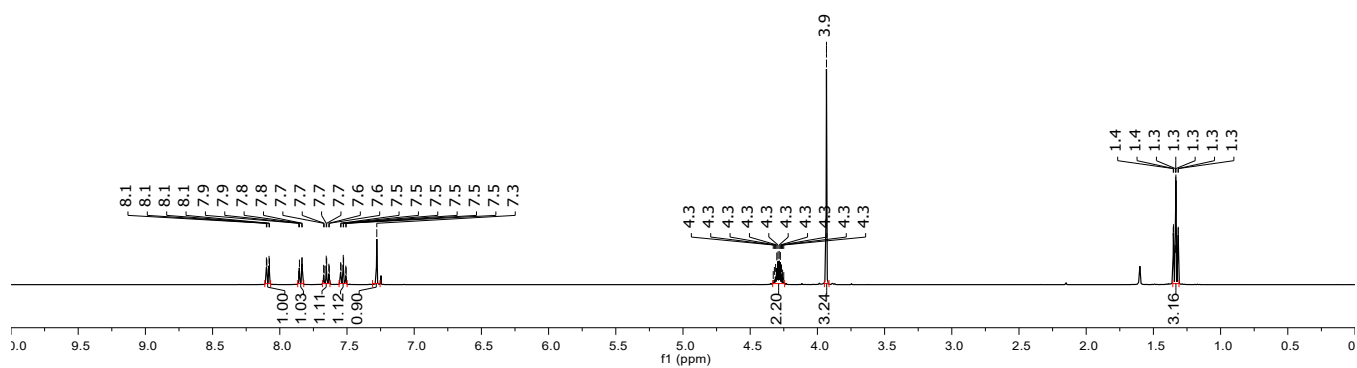
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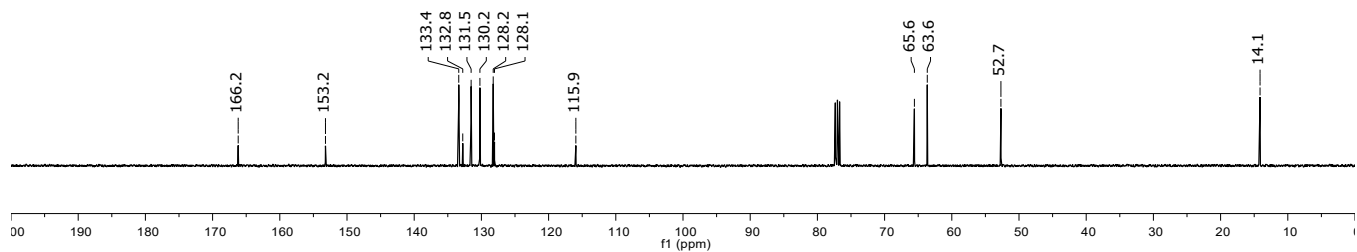
# Methyl 2-(cyano((ethoxycarbonyl)oxy)methyl)benzoate (7k)



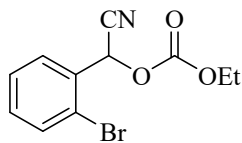
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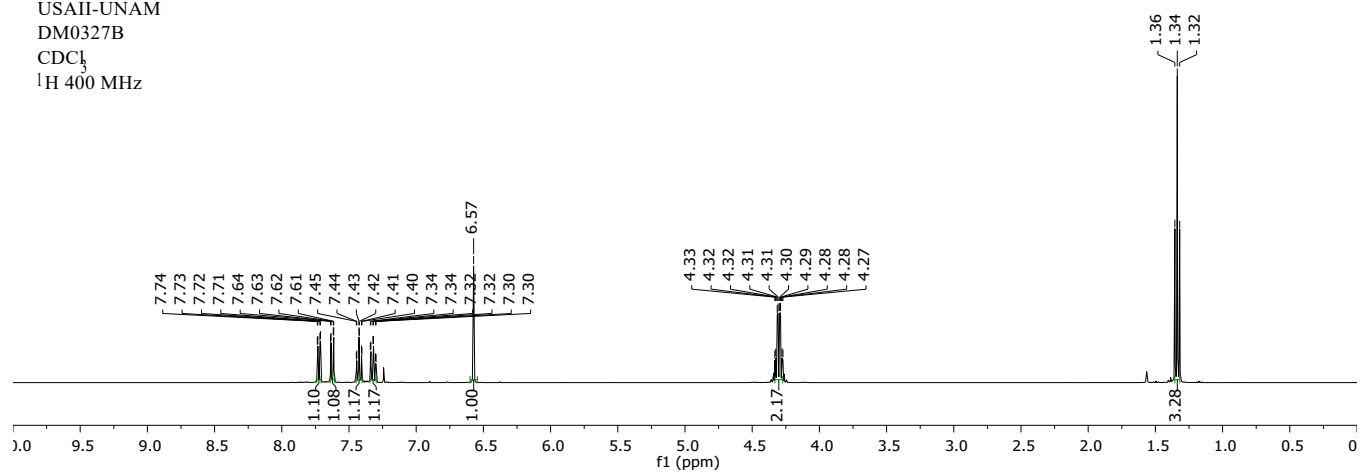
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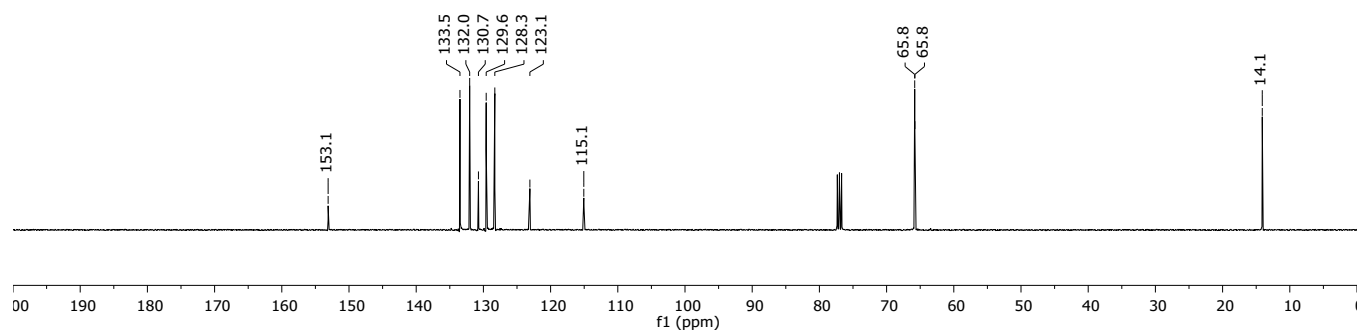
### (2-Bromophenyl)(cyano)methyl ethyl carbonate (7I)



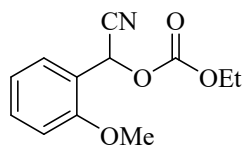
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<sup>1</sup>H 400 MHz



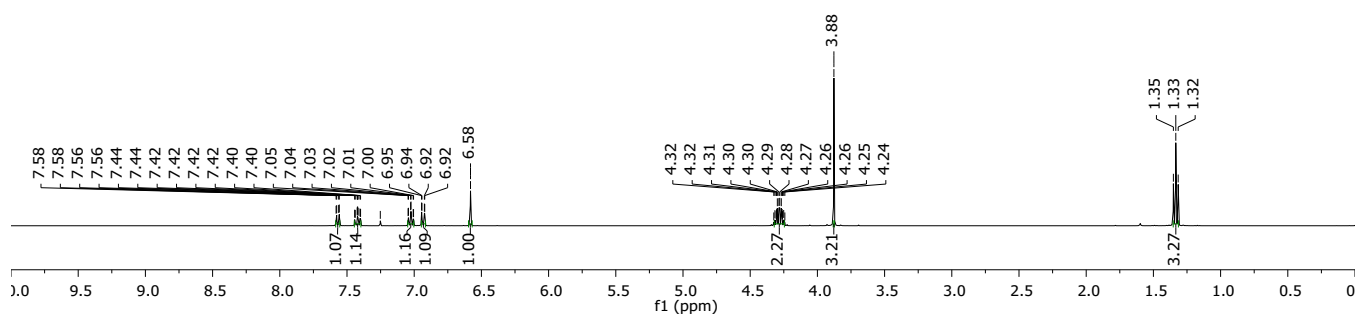
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<sup>13</sup>C 400 MHz



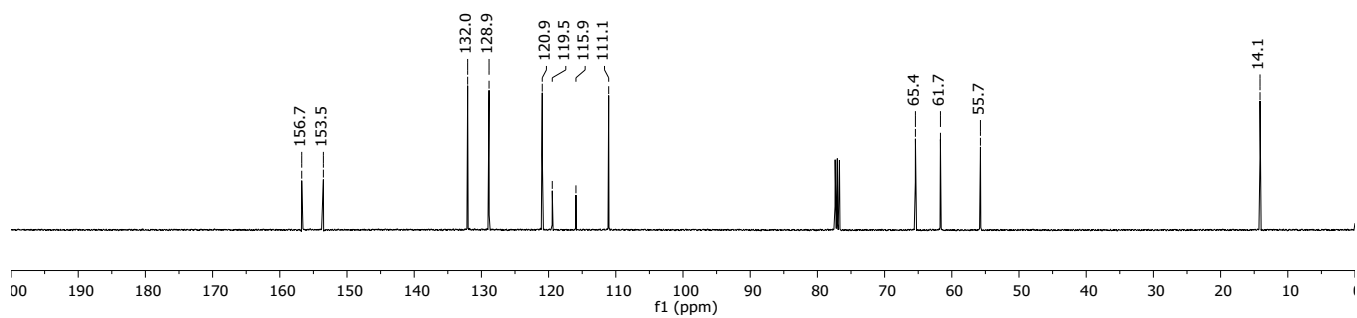
# Cyano(2-methoxyphenyl)methyl ethyl carbonate (7m)



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DMO1oOMe  
CDCl<sub>3</sub>  
1H 400 MHz

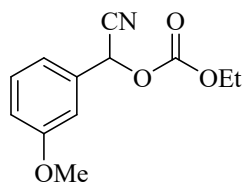


USAI-UNAM  
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13C 400 MHz

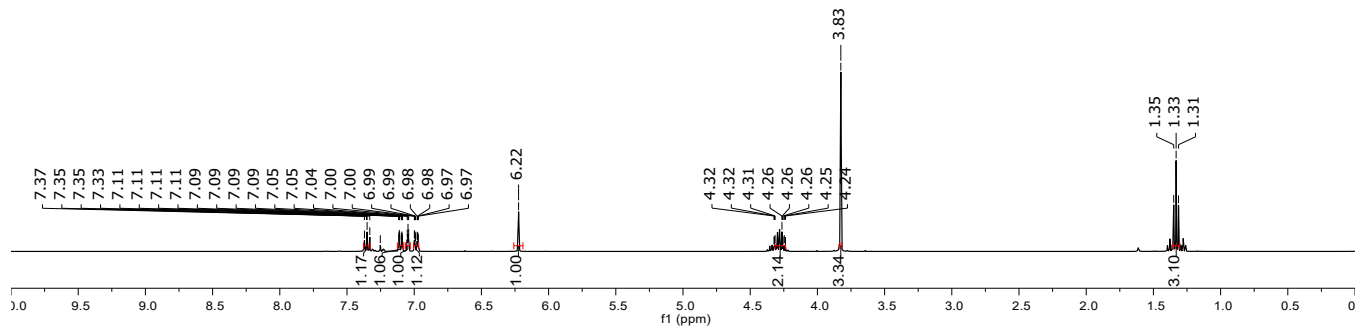




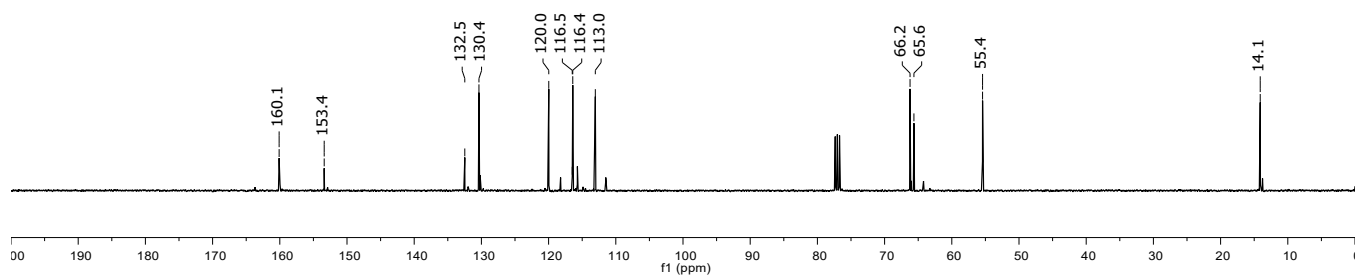
# Cyano(3-methoxyphenyl)methyl ethyl carbonate (7n)



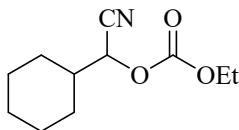
USAII-UNAM  
DM021mOMe  
CDCl<sub>3</sub>  
<sup>1</sup>H 400 MHz



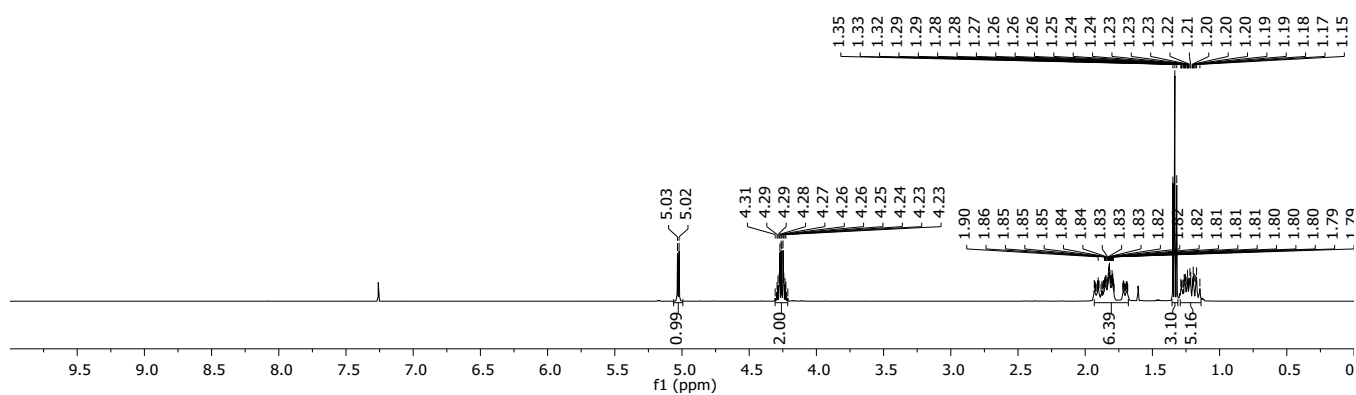
USAII-UNAM  
DM21mOMe  
CDCl<sub>3</sub>  
<sup>13</sup>C 400 MHz



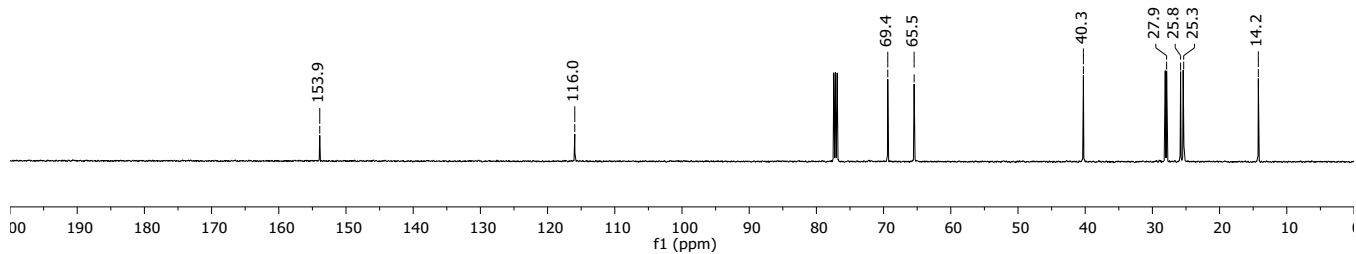
### Cyano(cyclohexyl)methyl ethyl carbonate (7o)



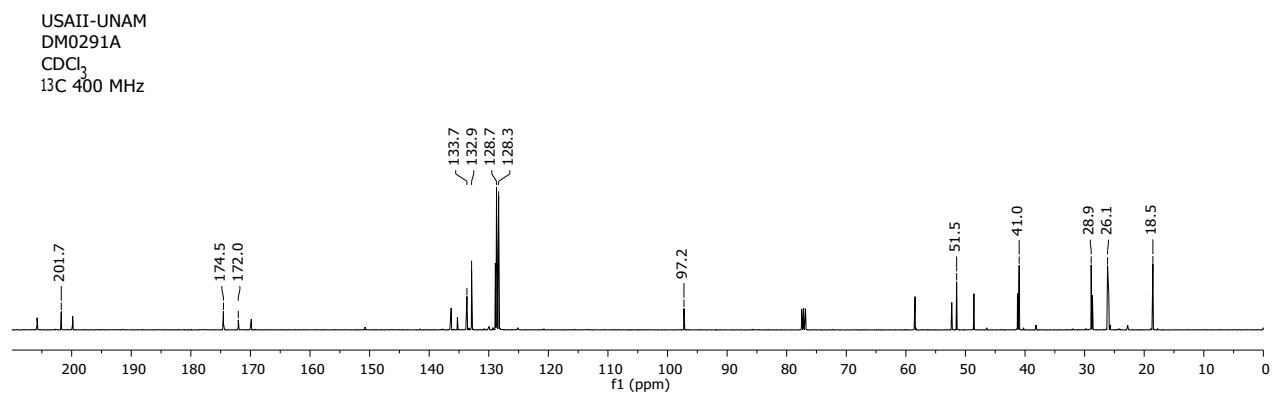
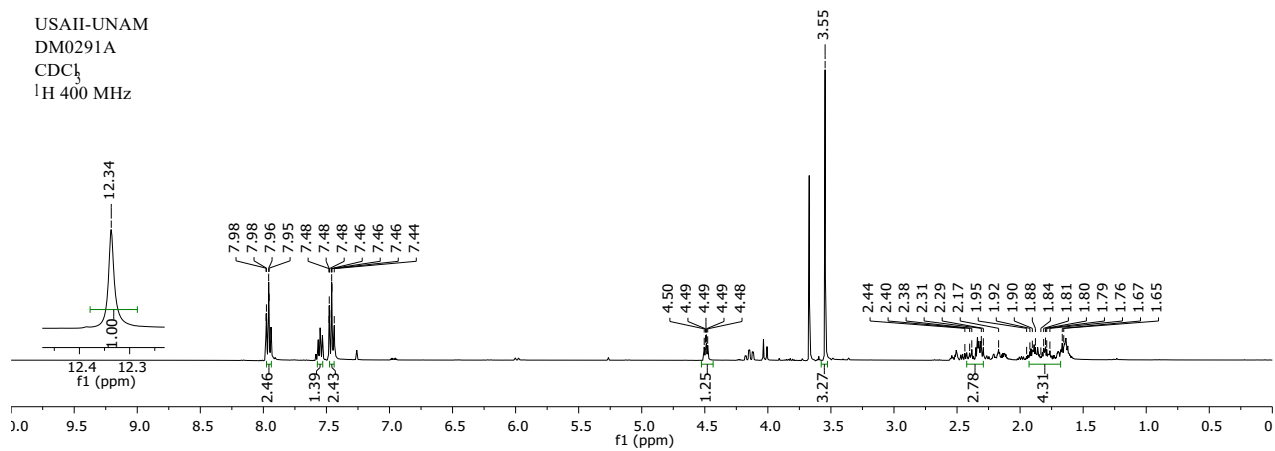
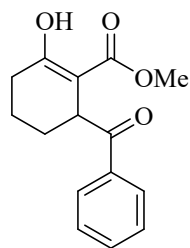
USAII-UNAM  
DM02171B  
CDCl<sub>3</sub>  
1H 400 MHz



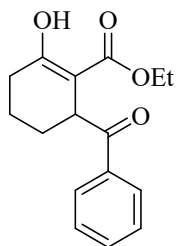
USAII-UNAM  
DM2171B  
CDCl<sub>3</sub>  
13C 400 MHz



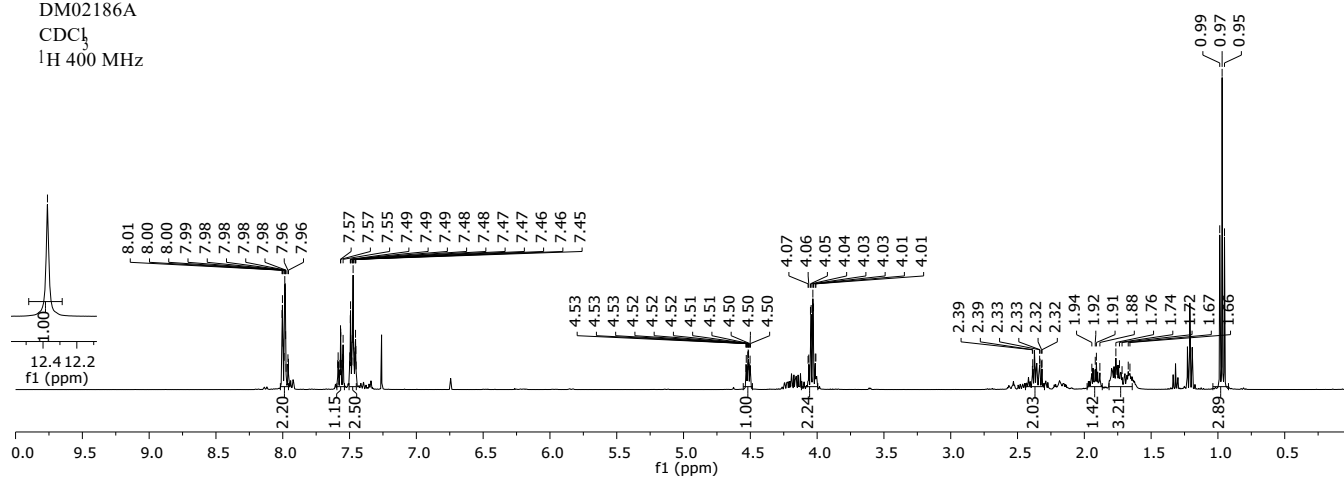
# Methyl 6-benzoyl-2-hydroxycyclohex-1-ene-1-carboxylate (8a)



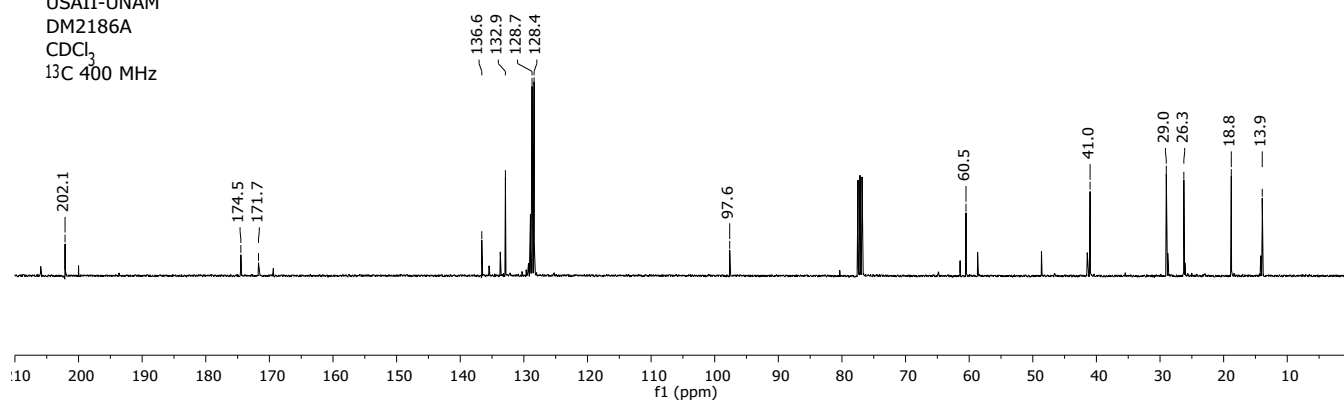
# Ethyl 6-benzoyl-2-hydroxycyclohex-1-ene-1-carboxylate (8b)



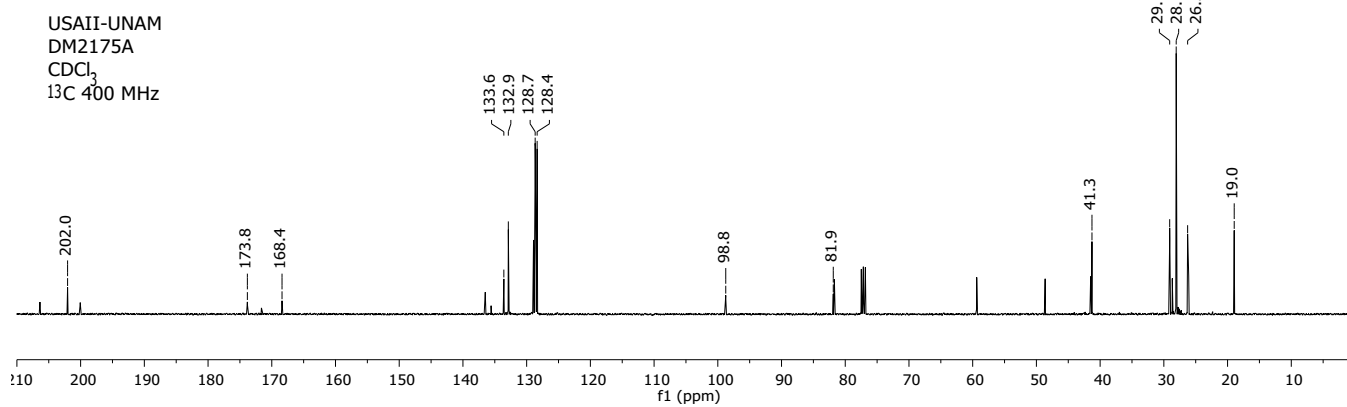
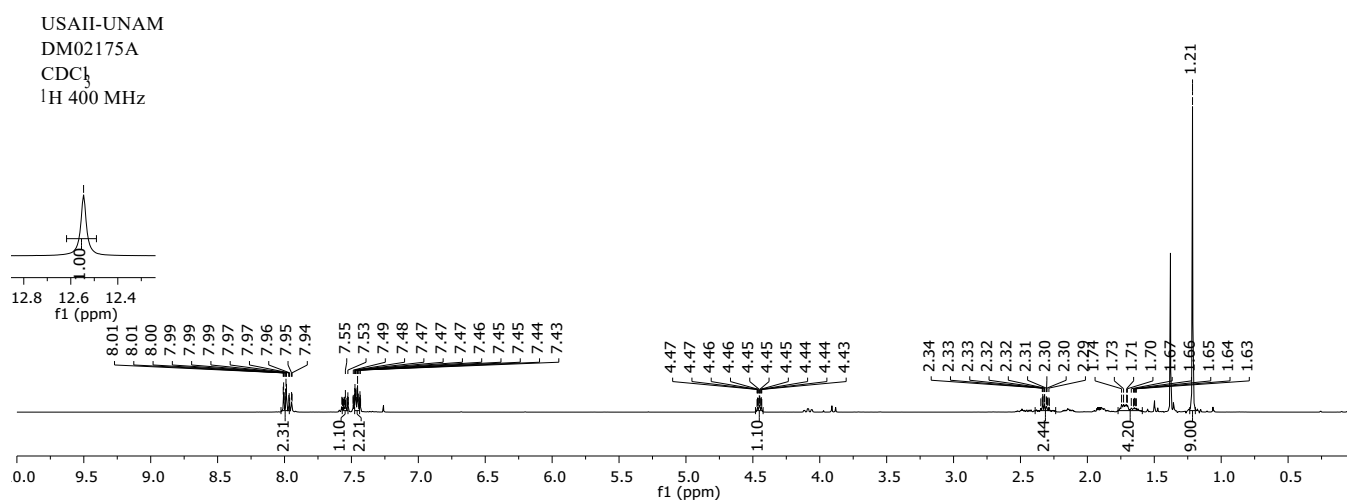
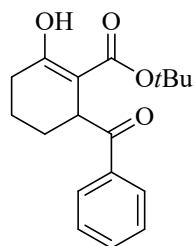
USAII-UNAM  
DM02186A  
CDCl<sub>3</sub>  
1H 400 MHz



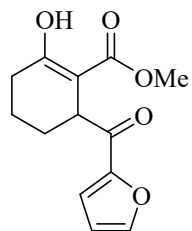
USAII-UNAM  
DM2186A  
CDCl<sub>3</sub>  
13C 400 MHz



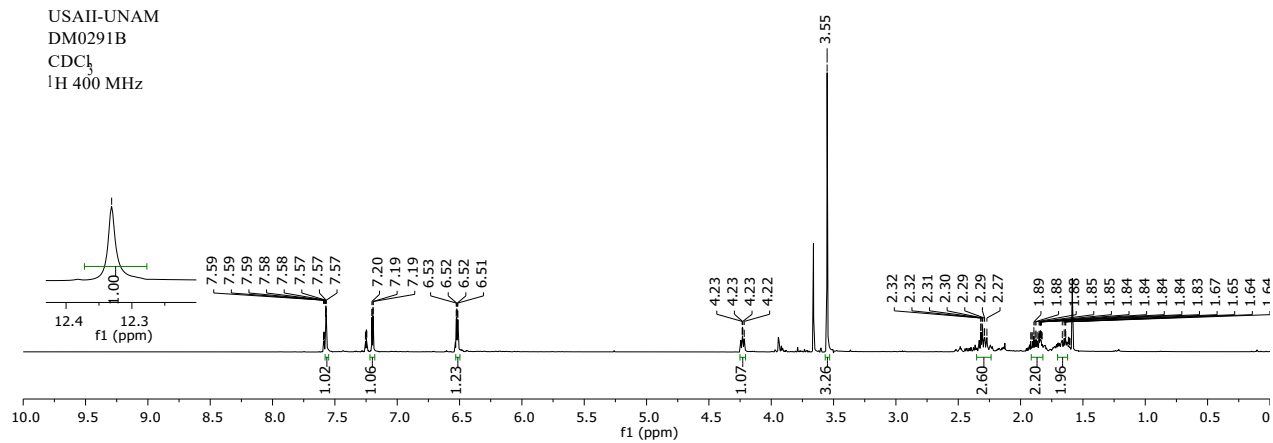
***tert*-Butyl 6-benzoyl-2-hydroxycyclohex-1-ene-1-carboxylate (8c)**



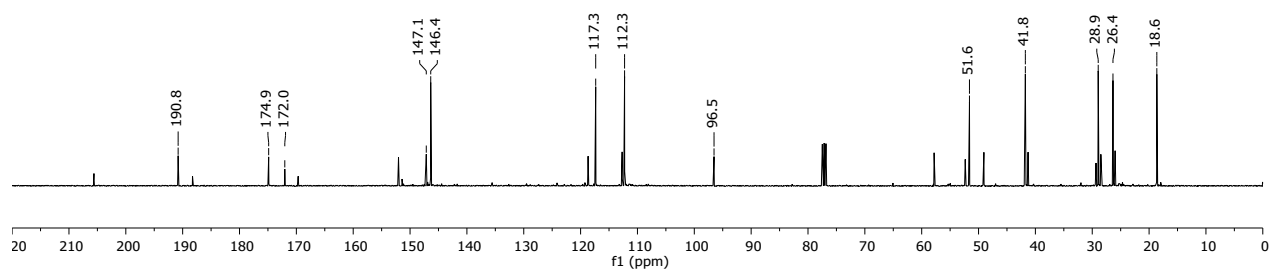
# Methyl 6-(furan-2-carbonyl)-2-hydroxycyclohex-1-ene-1-carboxylate (8d)



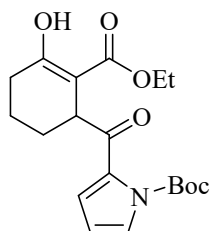
USAII-UNAM  
DM0291B  
CDCl<sub>3</sub>  
1H 400 MHz



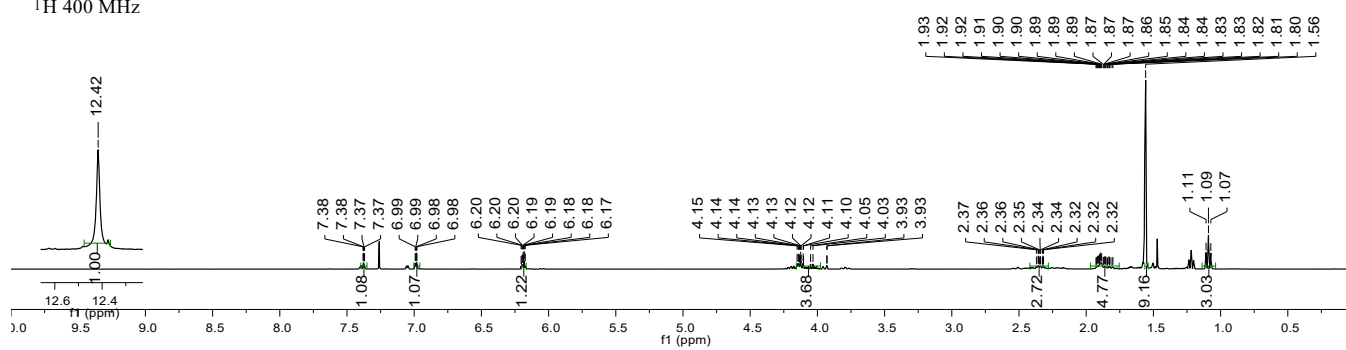
USAII-UNAM  
DM0291B  
CDCl<sub>3</sub>  
13C 400 MHz



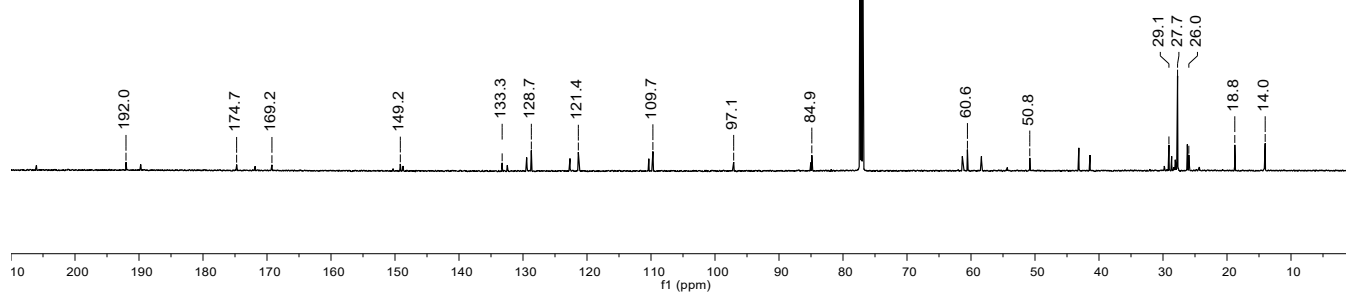
**tert-Butyl 2-(3-hydroxy-2-(methoxycarbonyl)cyclohex-2-ene-1-carbonyl)-1H-pyrrole-1-carboxylate (8e)**



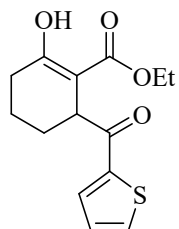
USAII-UNAM  
DM02189B  
CDCl<sub>3</sub>  
<sup>1</sup>H 400 MHz



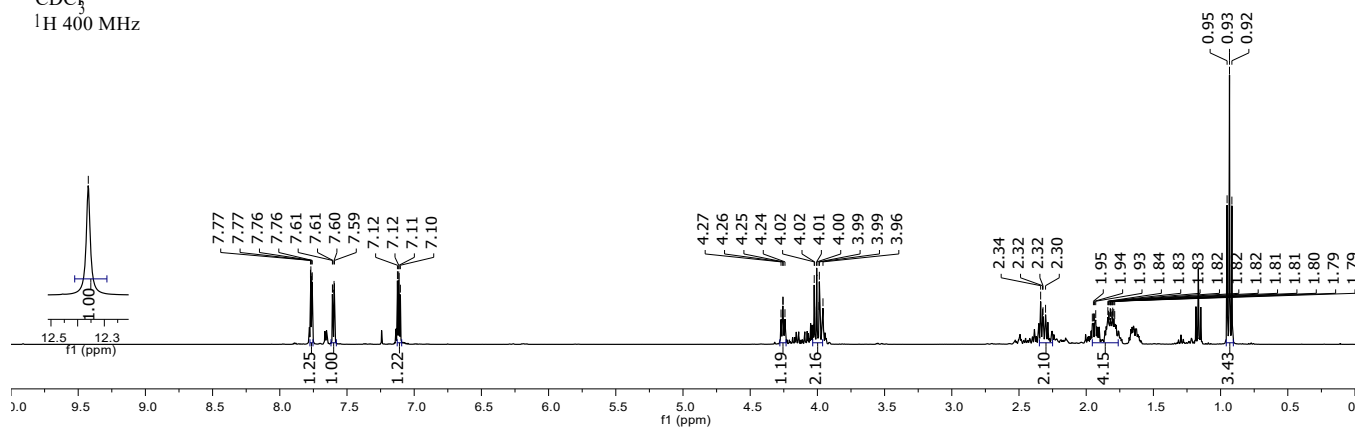
USAII-UNAM  
DM2189B  
CDCl<sub>3</sub>  
<sup>13</sup>C 400 MHz



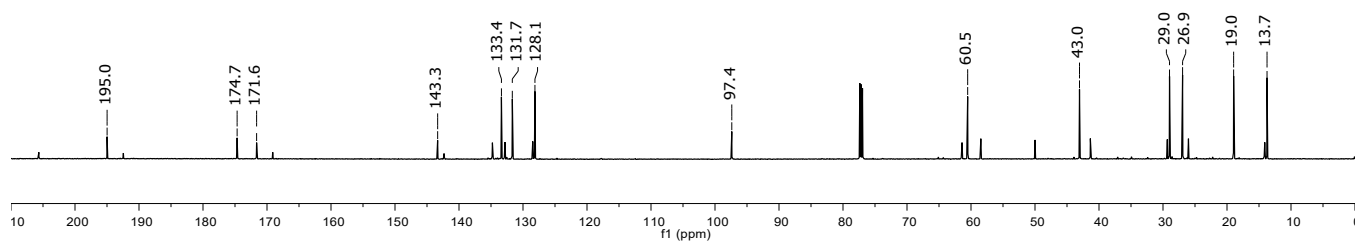
## Methyl 6-(thiophen -2-carbonyl)-2-hydroxycyclohex-1-ene-1-carboxylate (8f)



USAII-UNAM  
DM317B  
CDCl<sub>3</sub>  
<sup>1</sup>H 400 MHz

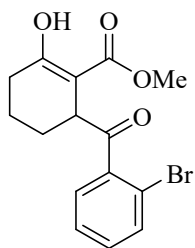


USAII-UNAM  
DM317B  
CDCl<sub>3</sub>  
<sup>13</sup>C 400 MHz

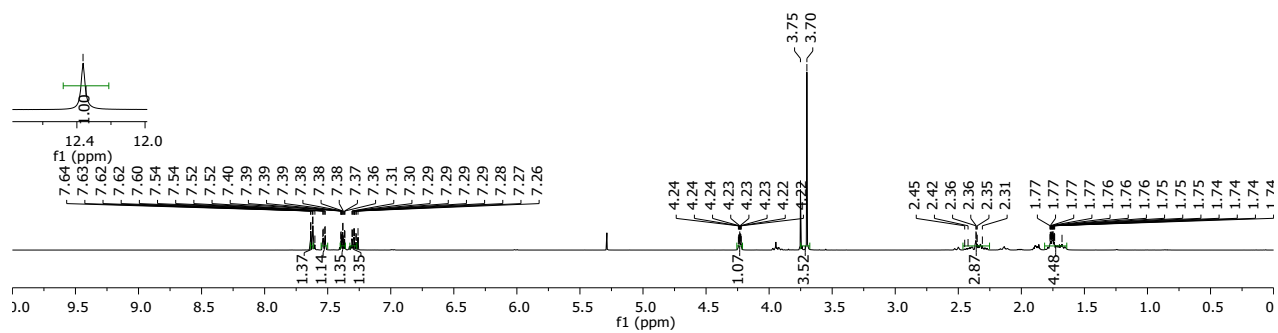




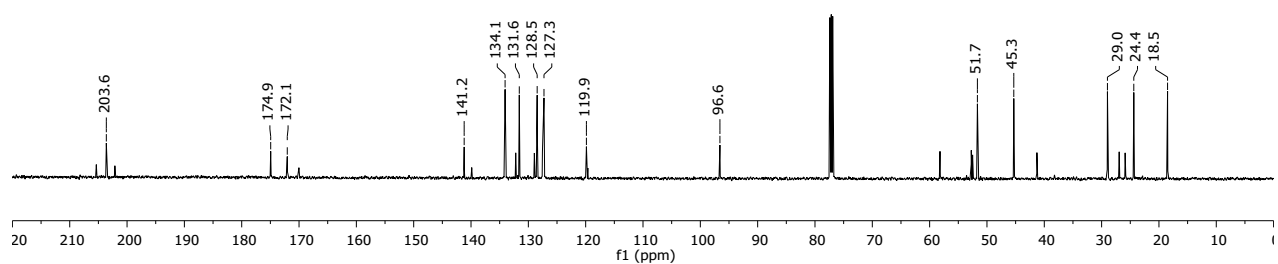
# Methyl 6-(2-bromobenzoyl)-2-hydroxycyclohex-1-ene-1-carboxylate (8g)



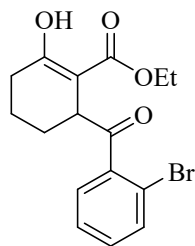
USAII-UNAM  
DM00299B  
CDCl<sub>3</sub>  
1H 400 MHz



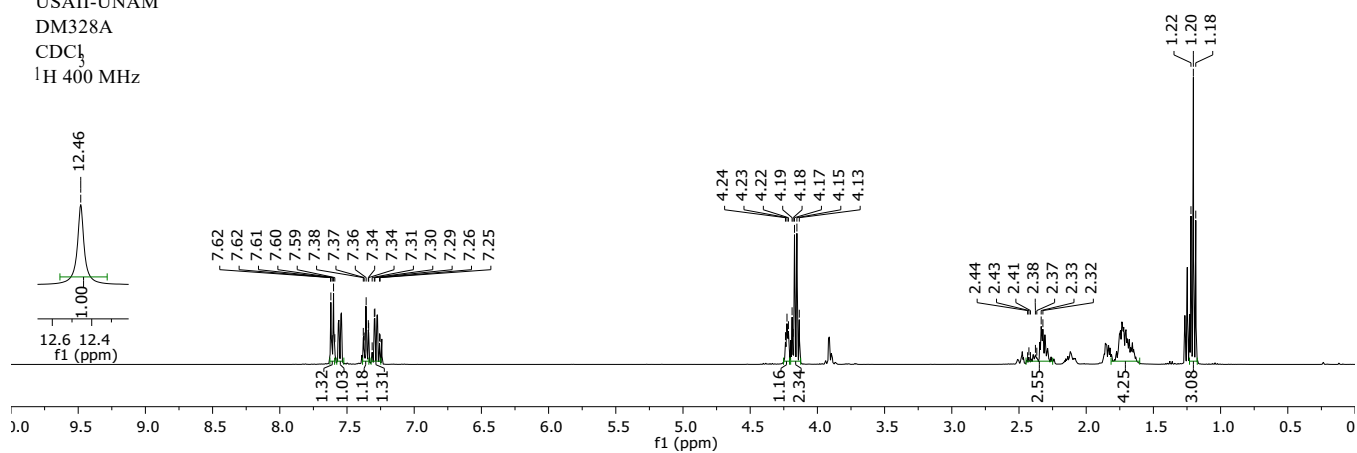
USAII-UNAM  
DM0299B  
CDCl<sub>3</sub>  
13C 400 MHz



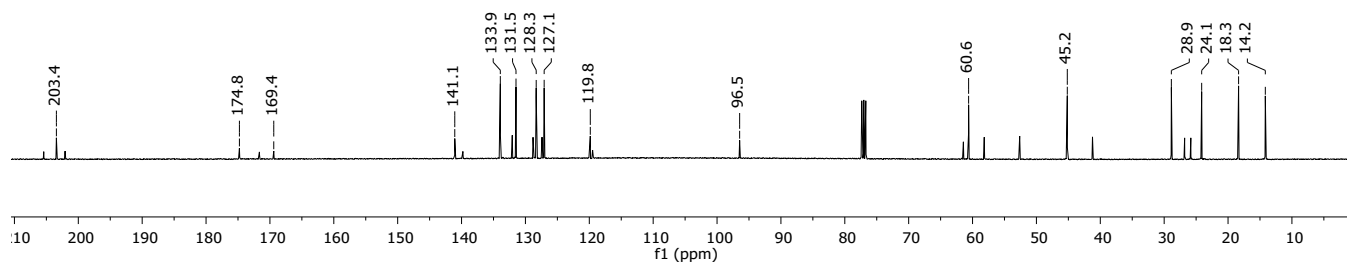
# Ethyl 6-(2-bromobenzoyl)-2-hydroxycyclohex-1-ene-1-carboxylate (8h)



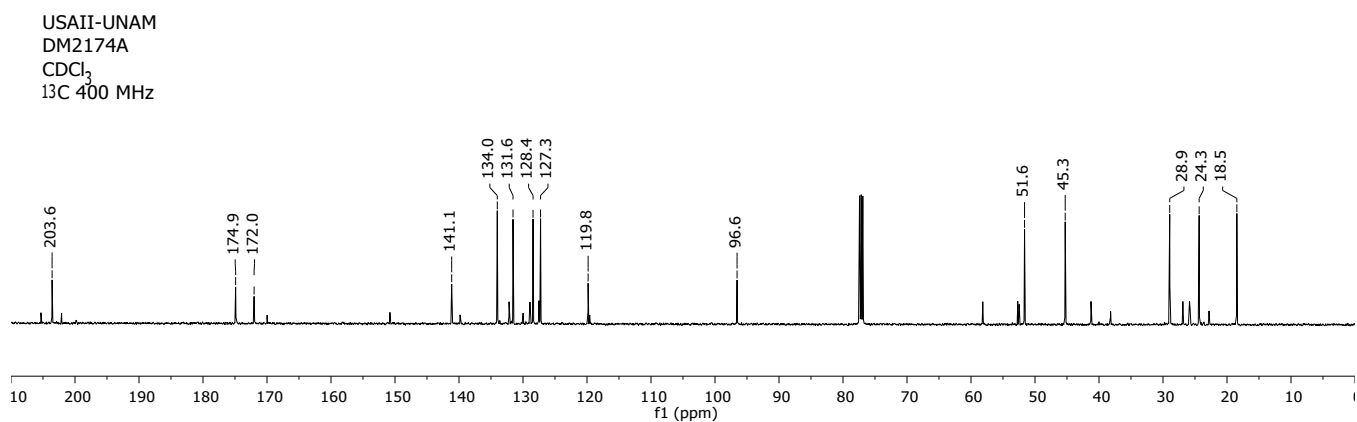
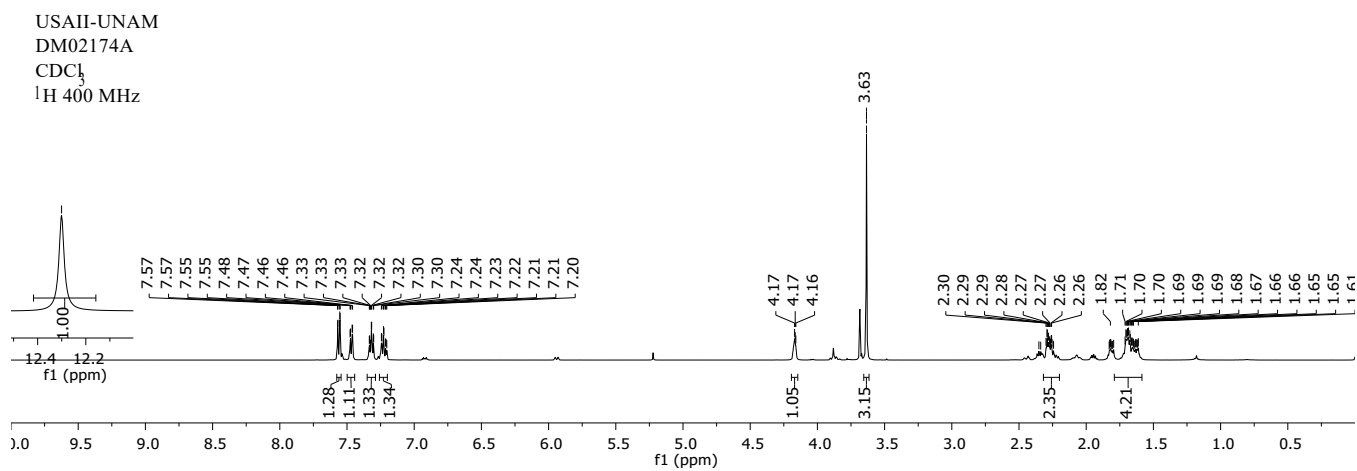
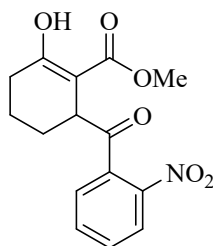
USAII-UNAM  
DM328A  
CDCl<sub>3</sub>  
1H 400 MHz



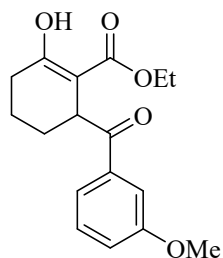
USAII-UNAM  
DM328A  
CDCl<sub>3</sub>  
13C 400 MHz



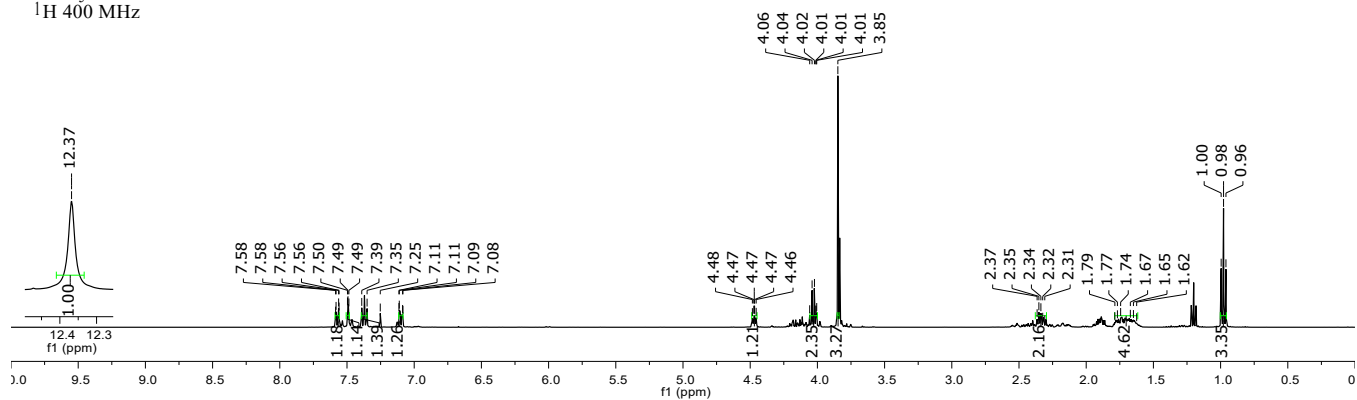
Methyl 2-hydroxy-6-(2-nitrobenzoyl)cyclohex-1-ene-1-carboxylate (8i)



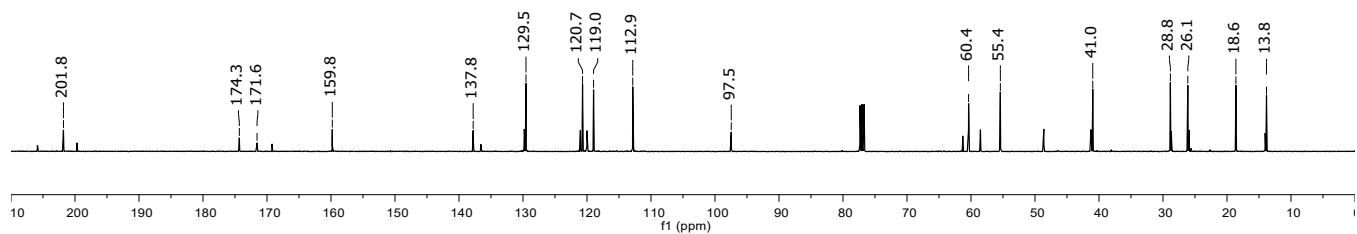
### Methyl 2-hydroxy-6-(3-methoxybenzoyl)cyclohex-1-ene-1-carboxylate (8j)



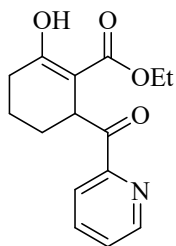
USAII-UNAM  
DM02198A  
CDCl<sub>3</sub>  
<sup>1</sup>H 400 MHz



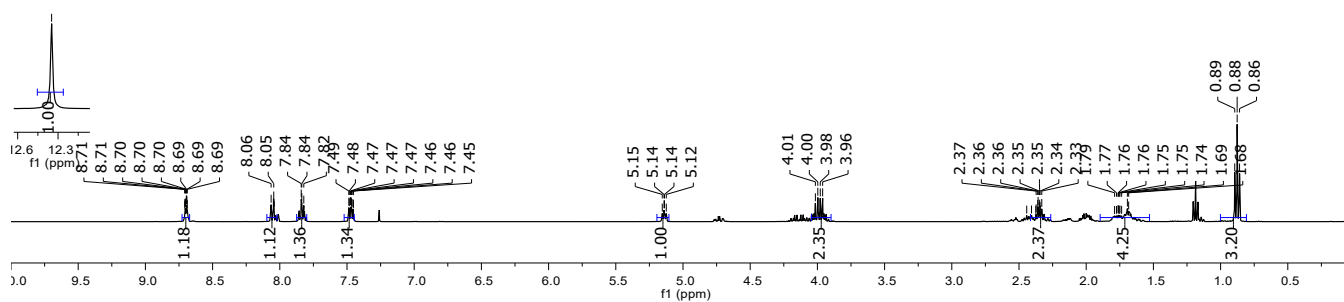
USAII-UNAM  
DM2198A  
CDCl<sub>3</sub>  
<sup>13</sup>C 400 MHz



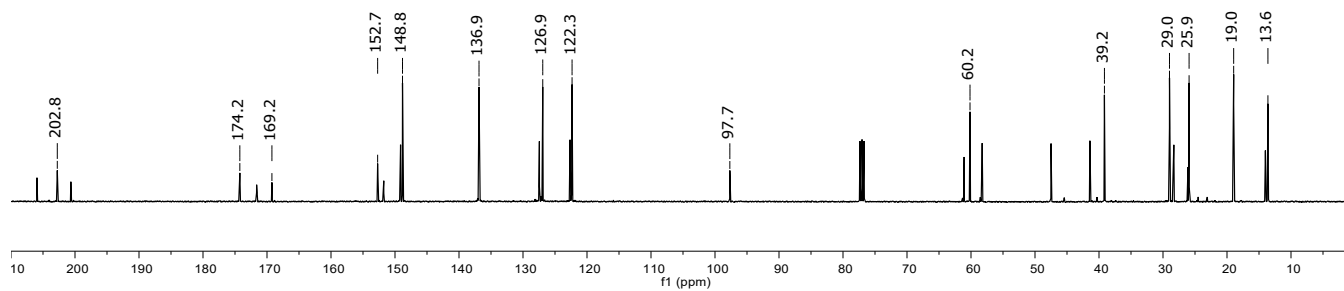
## Ethyl 2-hydroxy-6-picolinoylcyclohex-1-ene-1-carboxylate (8k)



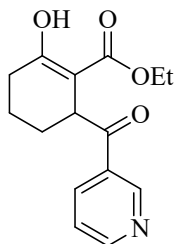
USAII-UNAM  
DM02188B  
CDCl<sub>3</sub>  
<sup>1</sup>H 400 MHz



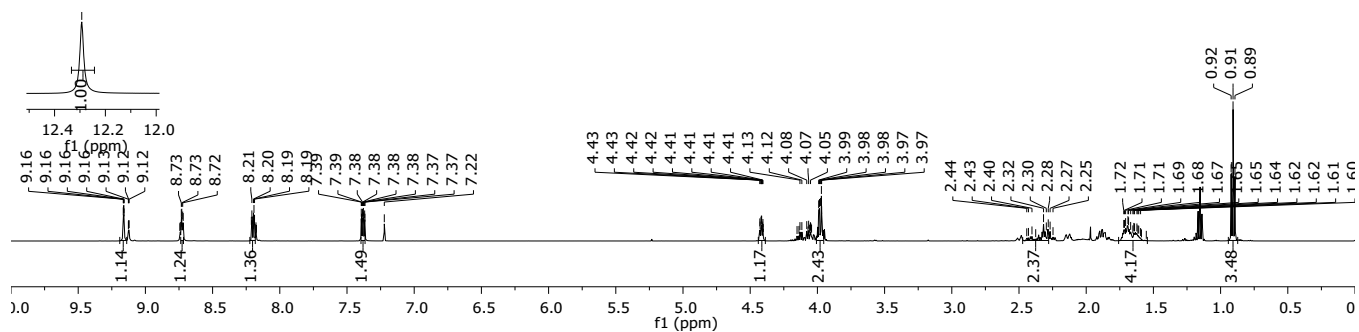
USAII-UNAM  
DM2188B  
CDCl<sub>3</sub>  
<sup>13</sup>C 400 MHz



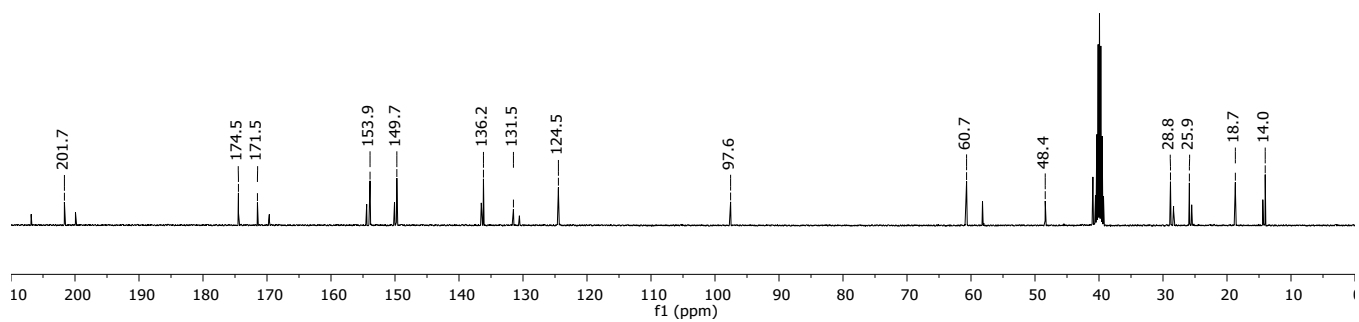
# Ethyl 2-hydroxy-6-nicotinoylcyclohex-1-ene-1-carboxylate (8l)



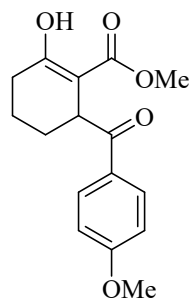
USAI-UNAM  
DM2175B  
CDCl<sub>3</sub>  
1H 400 MHz



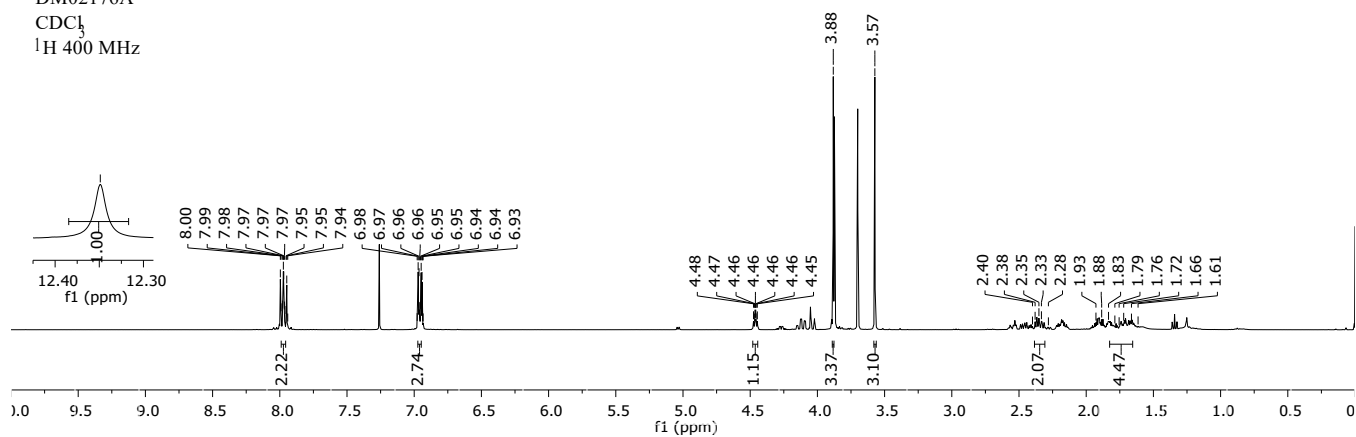
USAI-UNAM  
DM2175B  
CDCl<sub>3</sub>  
13C 400 MHz



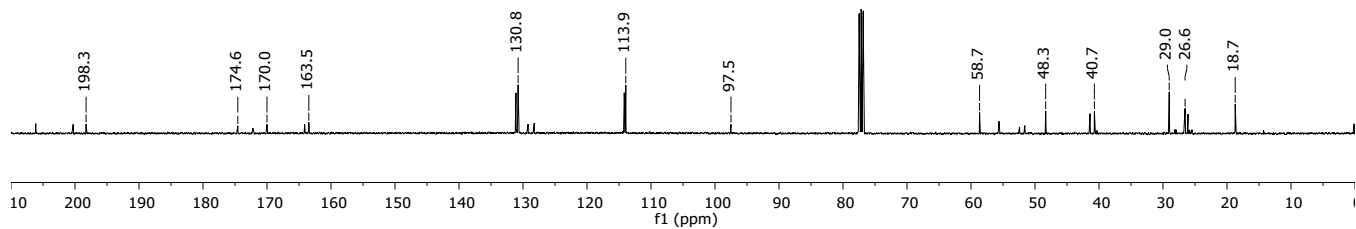
# Methyl 2-hydroxy-6-(4-methoxybenzoyl)cyclohex-1-ene-1-carboxylate (8m)



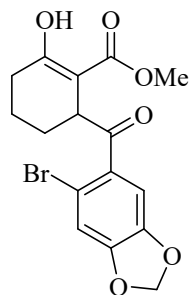
USAI-UNAM  
DM2176A  
CDCl<sub>3</sub>  
1H 400 MHz



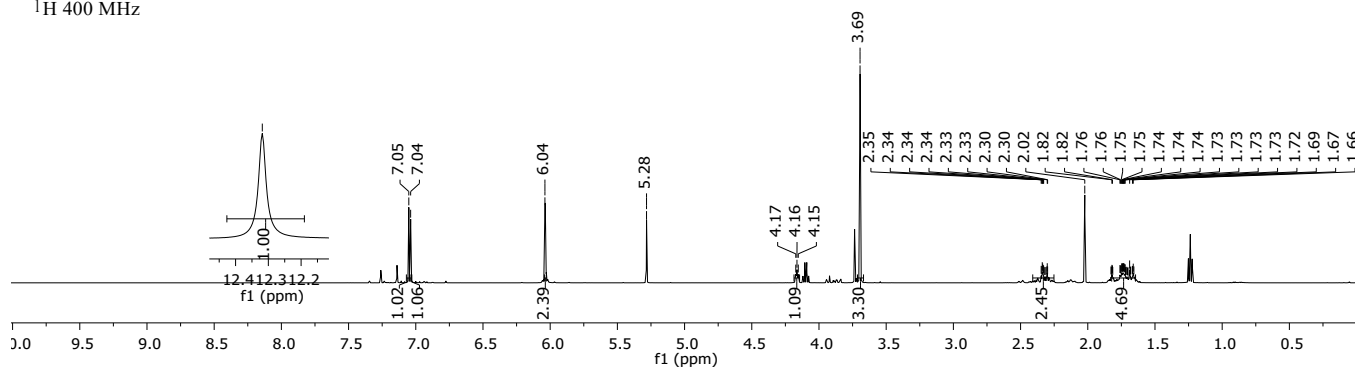
USAI-UNAM  
DM2176A  
CDCl<sub>3</sub>  
13C 400 MHz



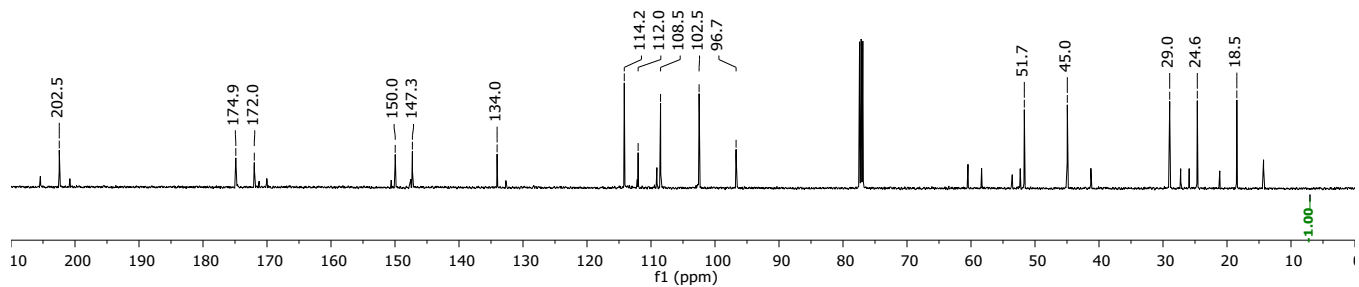
**Methyl 6-(6-bromobenzo[d][1,3]dioxole-5-carbonyl)-2-hydroxycyclohex-1-ene-1-carboxylate (8n)**



USAI-UNAM  
DM02174B  
CDCl<sub>3</sub>  
<sup>1</sup>H 400 MHz

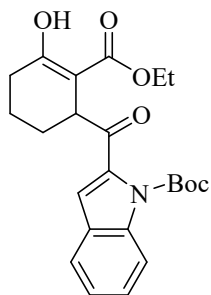


USAI-UNAM  
DM2174B  
CDCl<sub>3</sub>  
<sup>13</sup>C 400 MHz

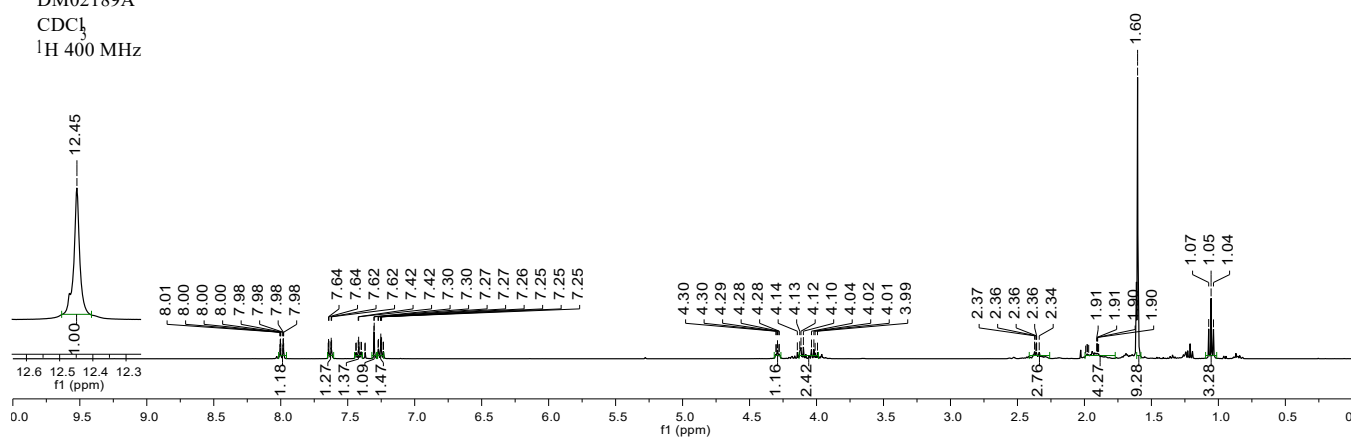




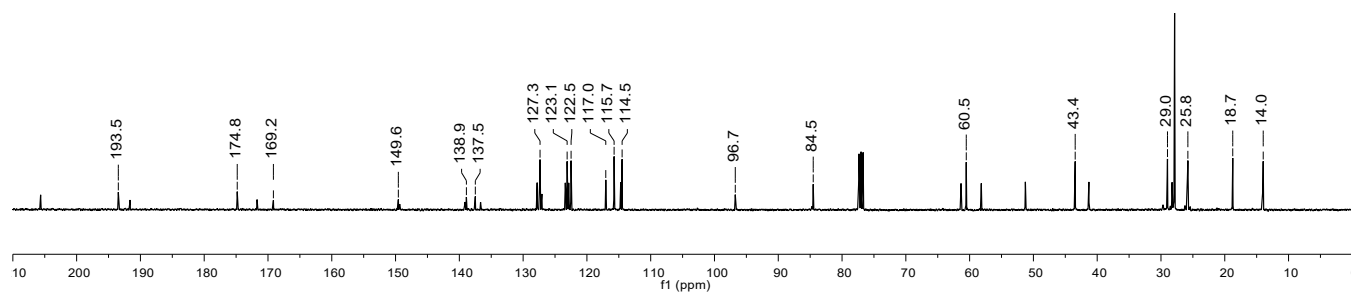
**tert-Butyl 2-(3-hydroxy-2-(methoxycarbonyl)cyclohex-2-ene-1-carbonyl)-1H-indole-1-carboxylate (8o)**



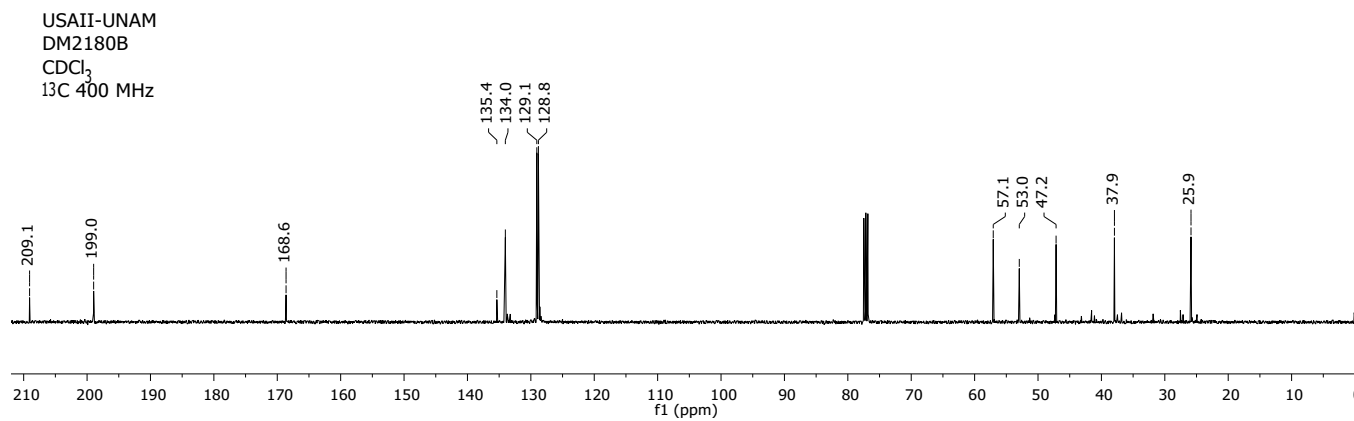
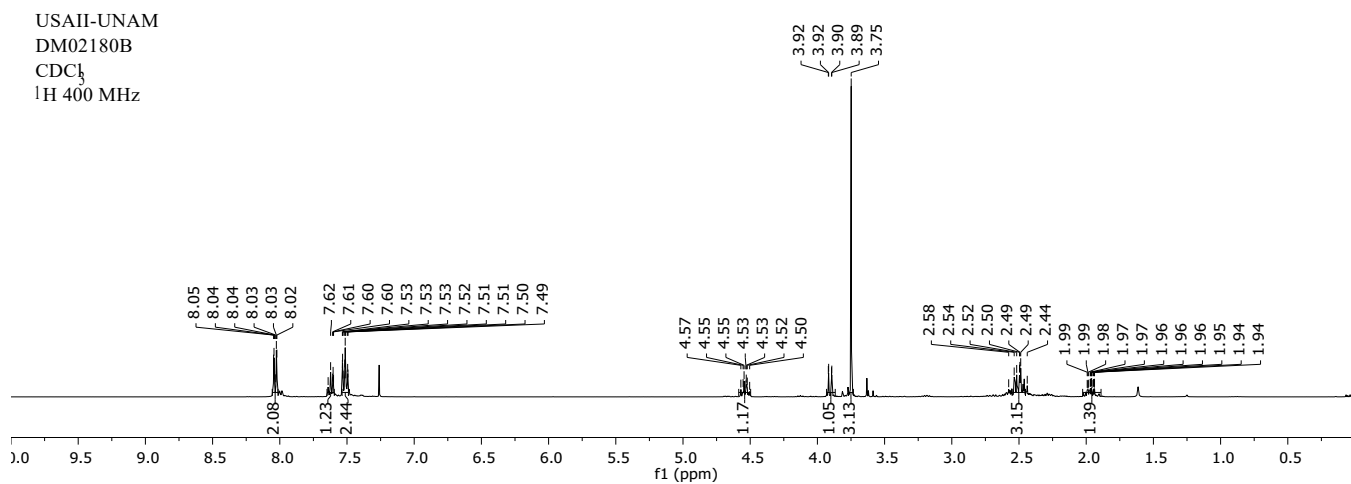
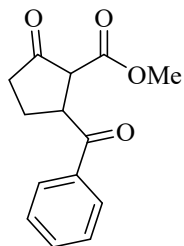
USAII-UNAM  
DM2189A  
CDCl<sub>3</sub>  
<sup>1</sup>H 400 MHz



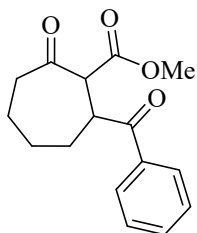
USAII-UNAM  
DM2189A  
CDCl<sub>3</sub>  
<sup>13</sup>C 400 MHz



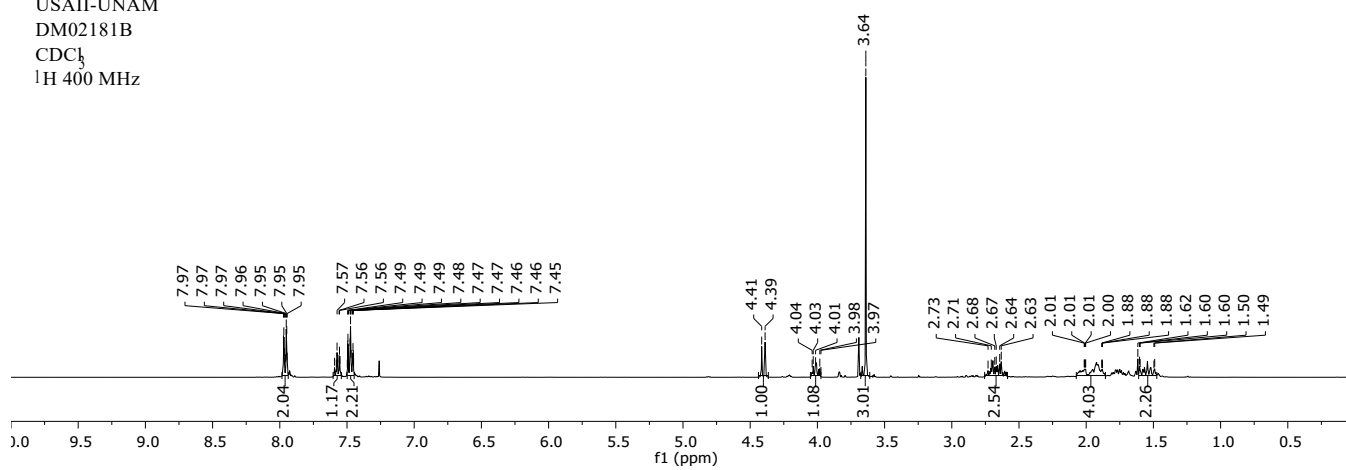
### Methyl 2-benzoyl-5-oxocyclopentane-1-carboxylate (9a)



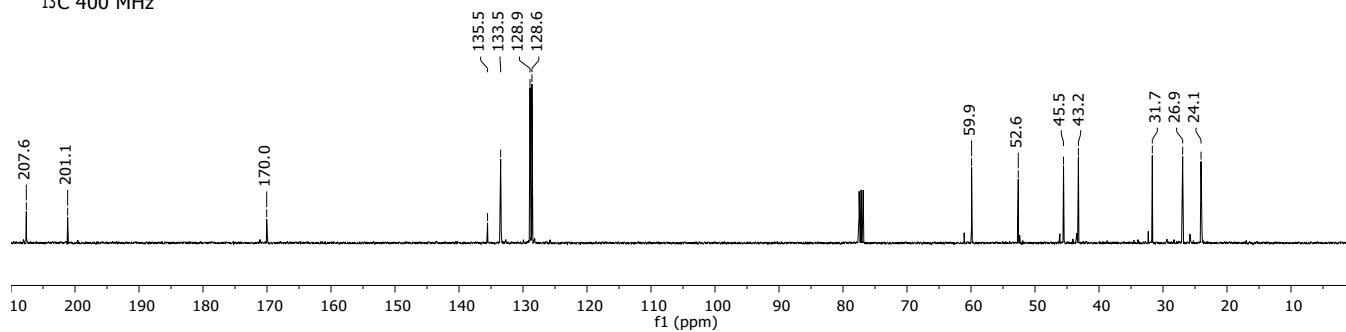
### Methyl 2-benzoyl-7-oxocycloheptane-1-carboxylate (9b)



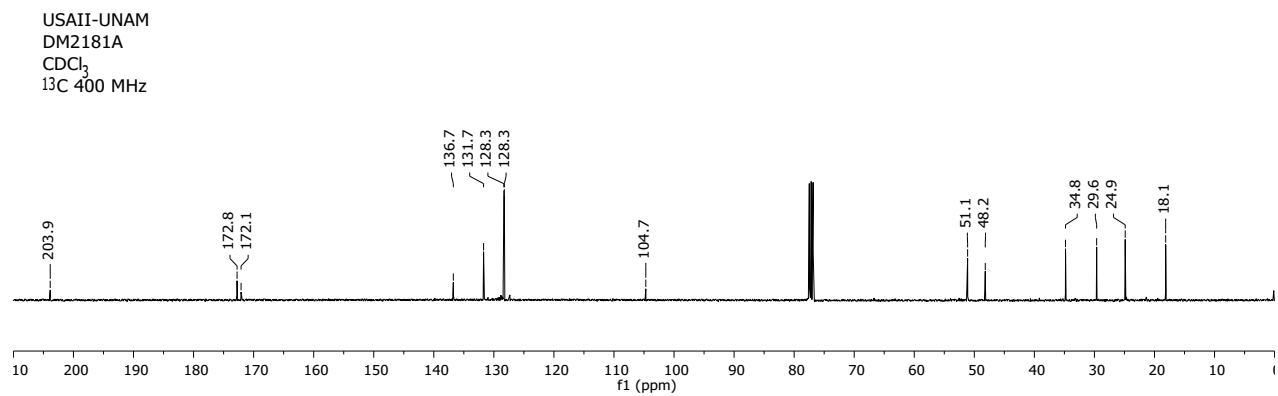
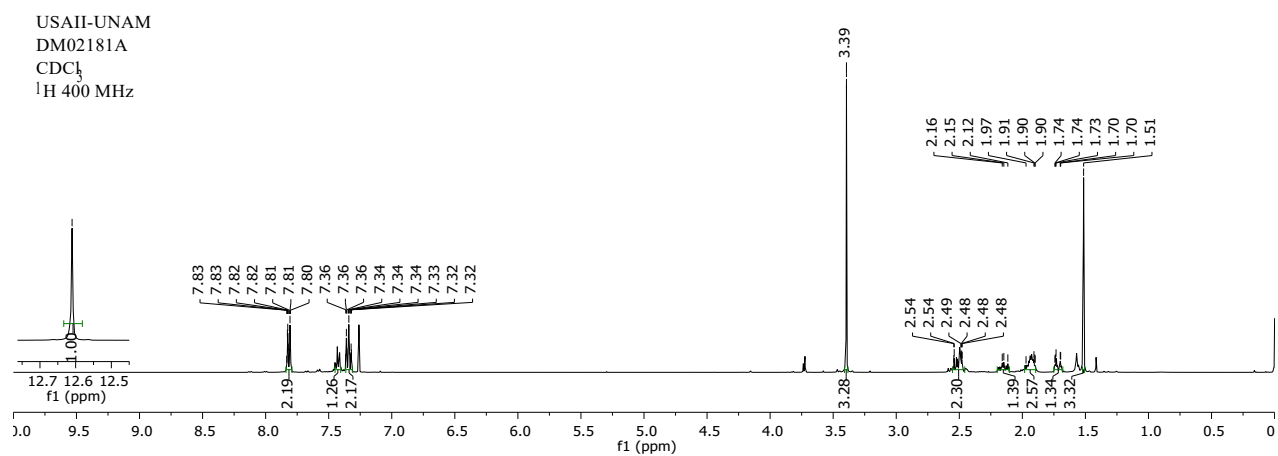
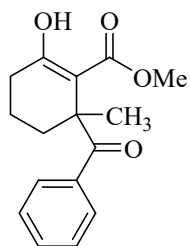
USAII-UNAM  
DM2181B  
CDCl<sub>3</sub>  
1H 400 MHz



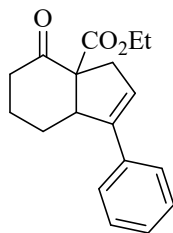
USAII-UNAM  
DM2181B  
CDCl<sub>3</sub>  
13C 400 MHz



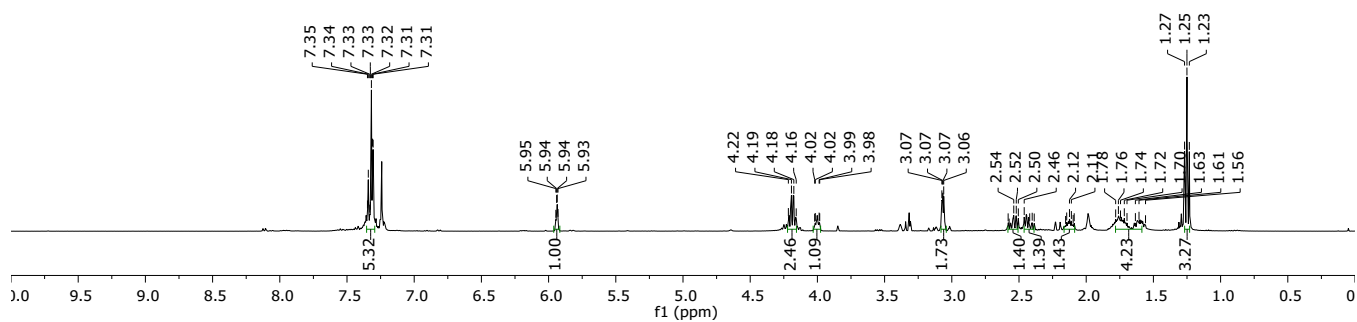
# Methyl 6-benzoyl-2-hydroxy-6-methylcyclohex-1-ene-1-carboxylate (9c)



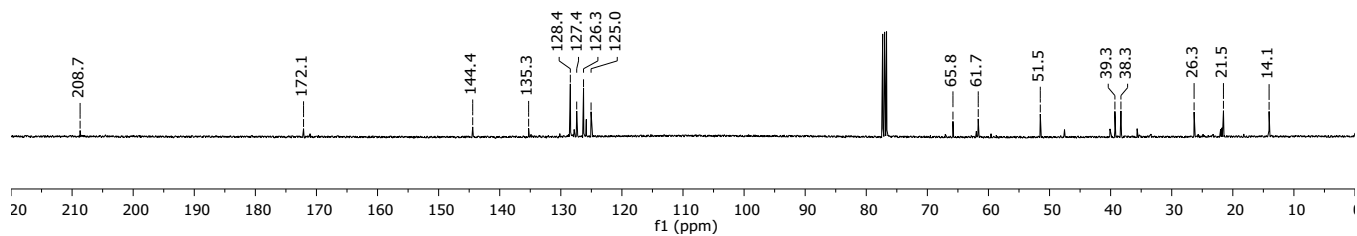
# Ethyl 4-oxo-1-phenyl-3,4,5,6,7,7a-hexahydro-3aH-indene-3a-carboxylate (10)



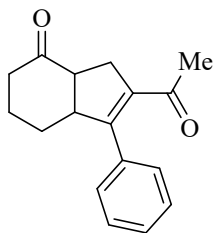
USAII-UNAM  
DM325A  
CDCl<sub>3</sub>  
<sup>1</sup>H 400 MHz



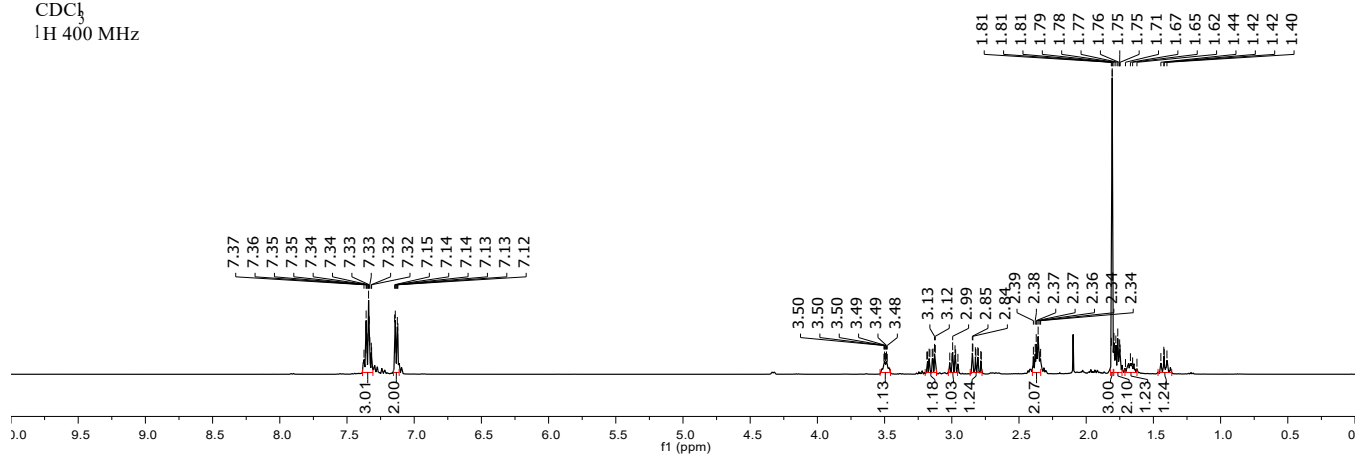
USAII-UNAM  
DM325A  
CDCl<sub>3</sub>  
<sup>13</sup>C 400 MHz



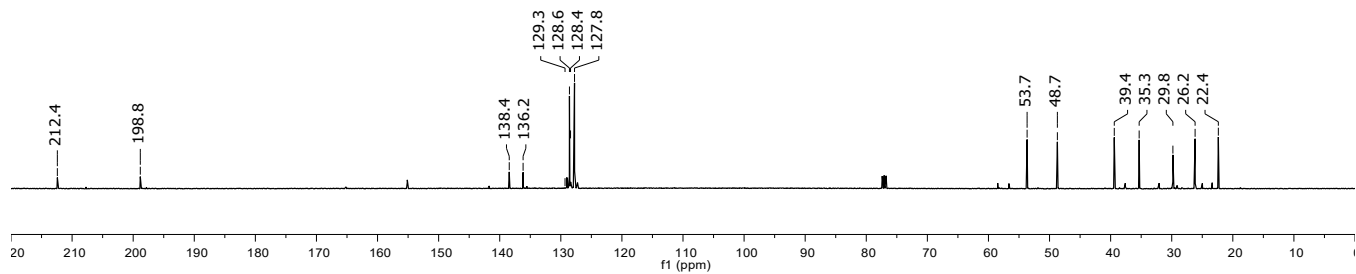
# 8-phenyl-2,3,3a,3b,5,6,7,7a-octahydrocyclopenta[a]indene-1,4-dione (11)



USAII-UNAM  
DM329A  
CDCl<sub>3</sub>  
1H 400 MHz



USAII-UNAM  
DM329A  
CDCl<sub>3</sub>  
13C 400 MHz



## 2-acetyl-1-phenyl-3,3a,5,6,7,7a-hexahydro-4H-inden-4-one (12)

