

Supporting Information

for

**Concise formal synthesis of (-)-7-deoxyloganin via *N*-Heterocyclic
Carbene Catalyzed Rearrangement of α,β -Unsaturated Enol
Esters**

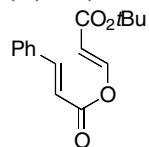
Lisa Candish and David W. Lupton*

School of Chemistry, Monash University, Clayton 3800, Victoria, AUSTRALIA

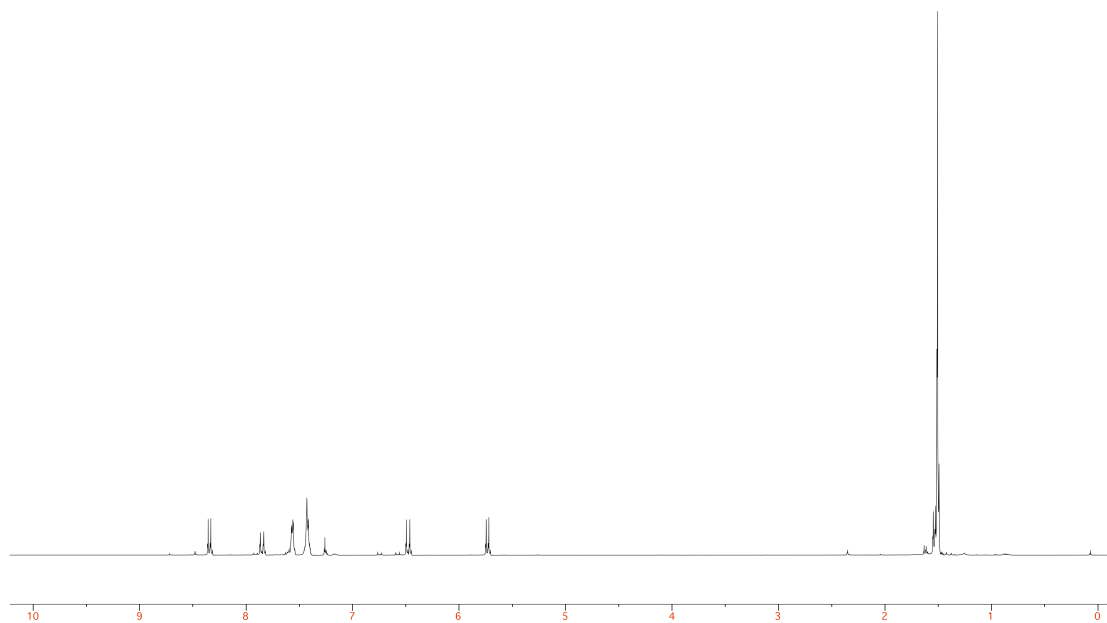
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I	$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra	SI-2
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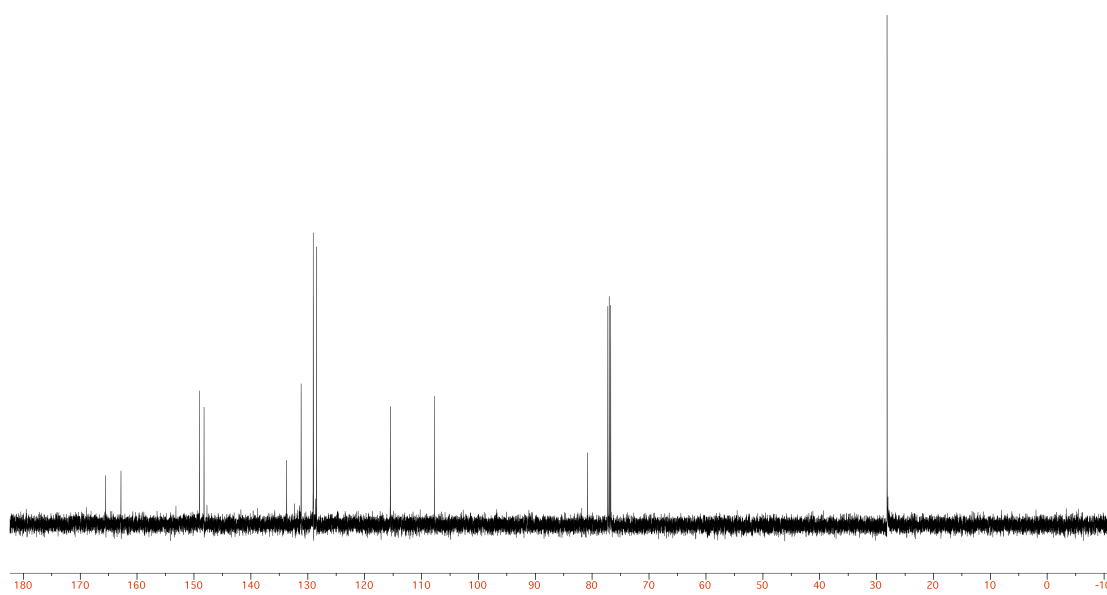
(E)-3-(tert-Butoxy)-3-oxoprop-1-enyl cinnamate (8a)



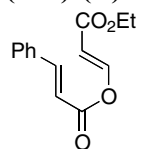
$^1\text{H-NMR}$ (500 MHz, CDCl_3)



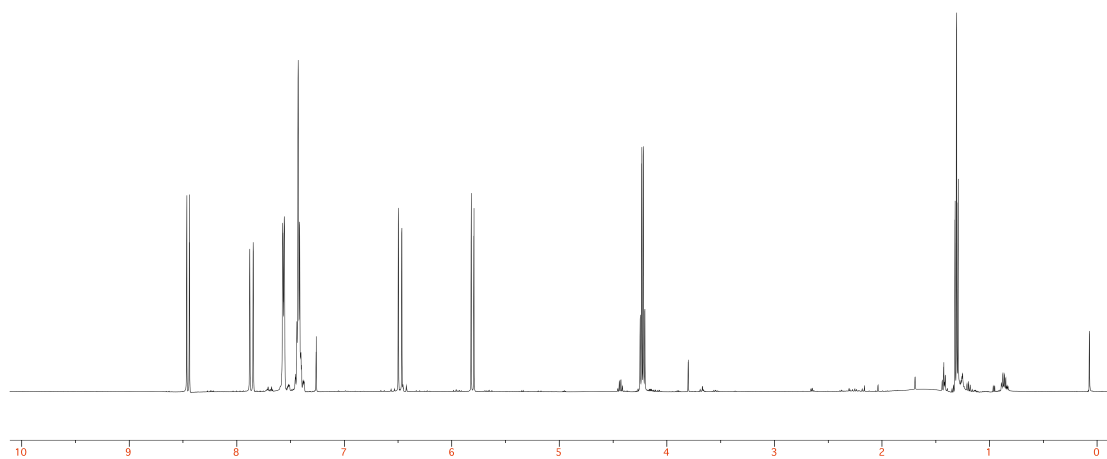
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3)



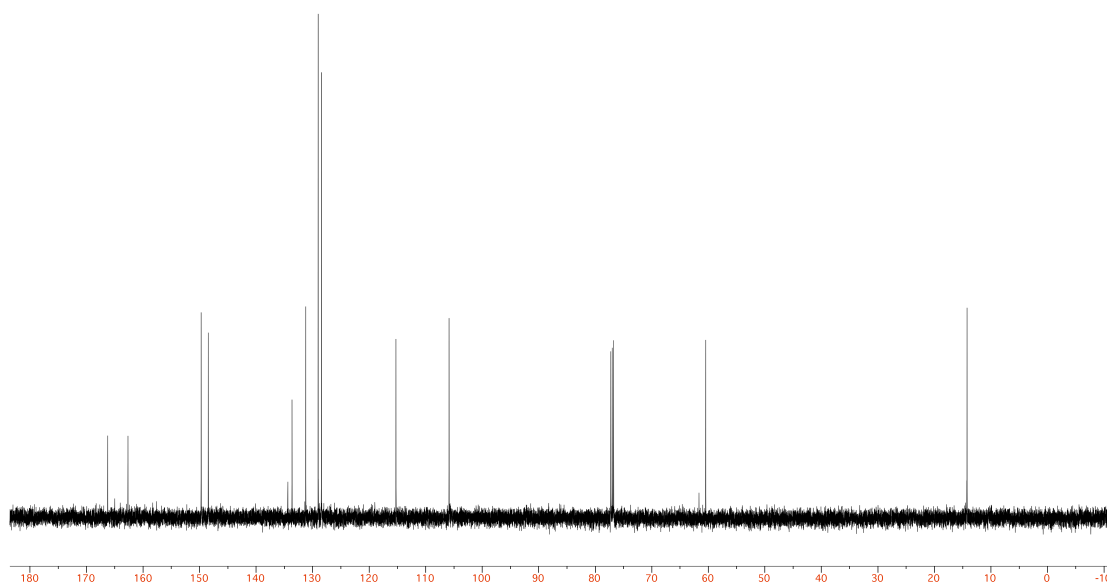
(S/R)-(E)-3-Ethoxy-3-oxoprop-1-enyl cinnamate (8b)



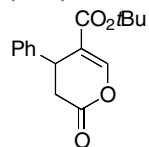
$^1\text{H-NMR}$ (500 MHz, CDCl_3)



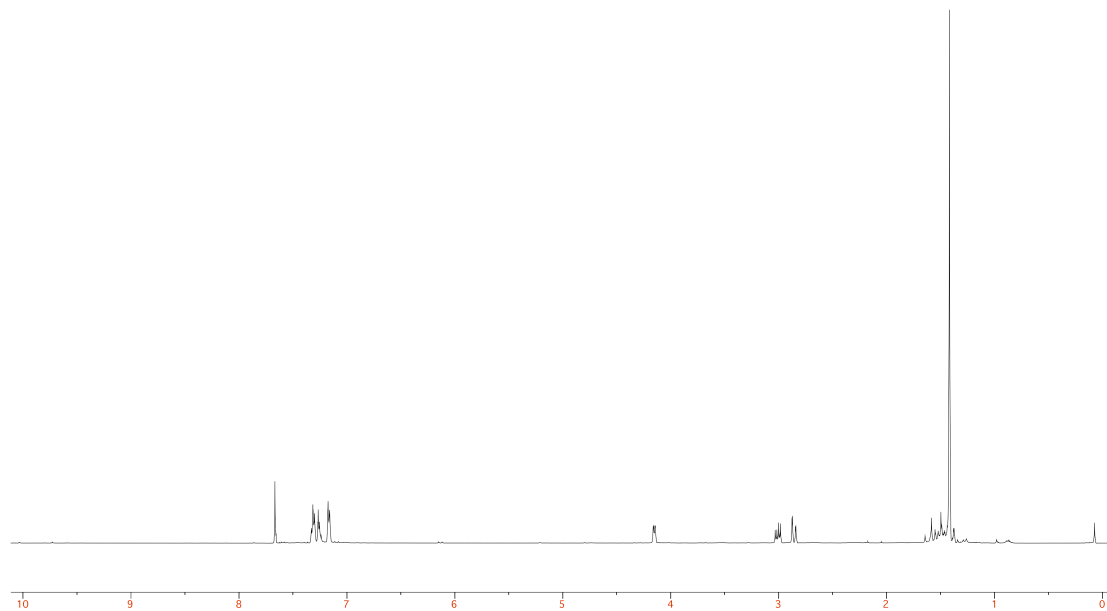
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3)



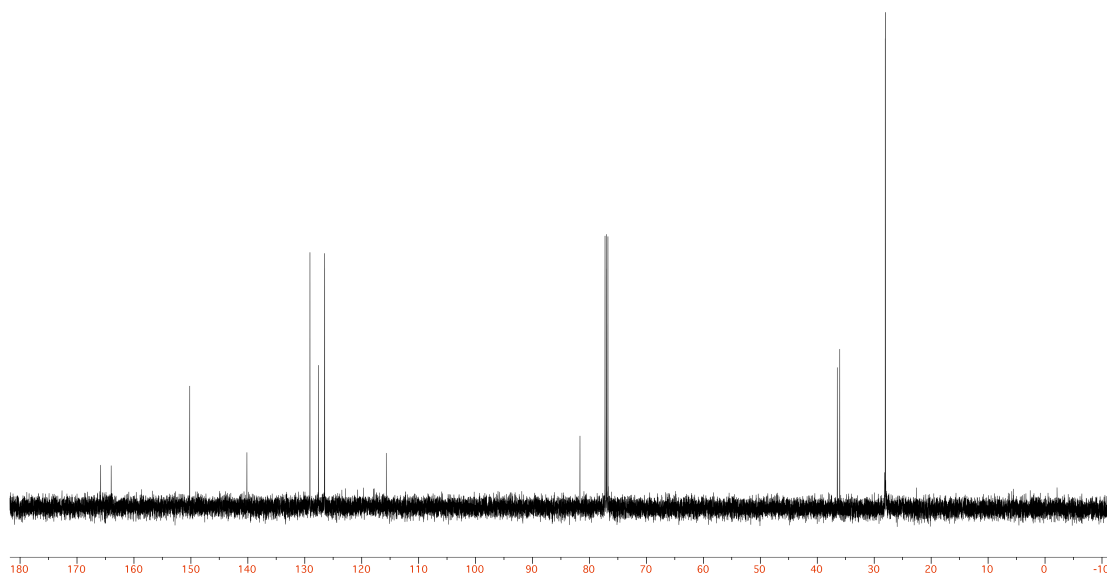
(*S/R*)-*tert*-Butyl 2-oxo-4-phenyl-3,4-dihydro-2H-pyran-5-carboxylate (9a)



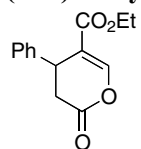
$^1\text{H-NMR}$ (500 MHz, CDCl_3)



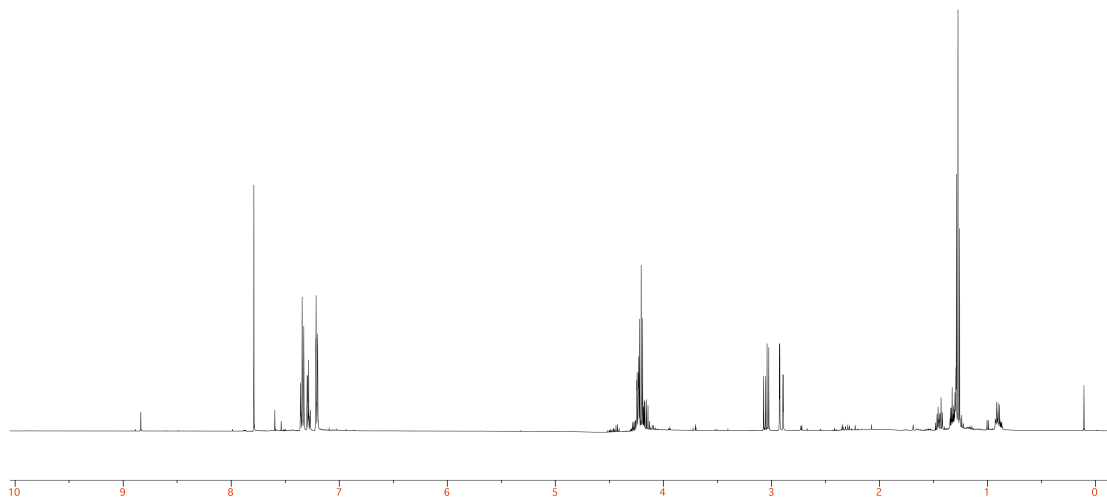
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3)



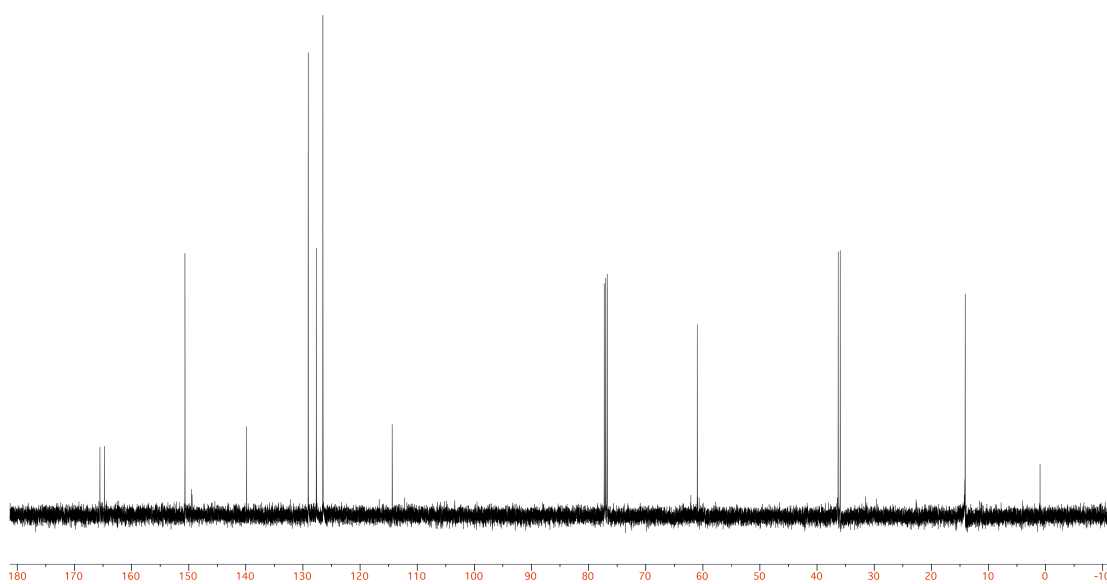
(*S/R*)-Ethyl 2-oxo-4-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (9b)



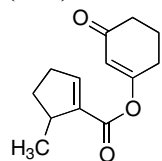
¹H-NMR (500 MHz, CDCl₃)



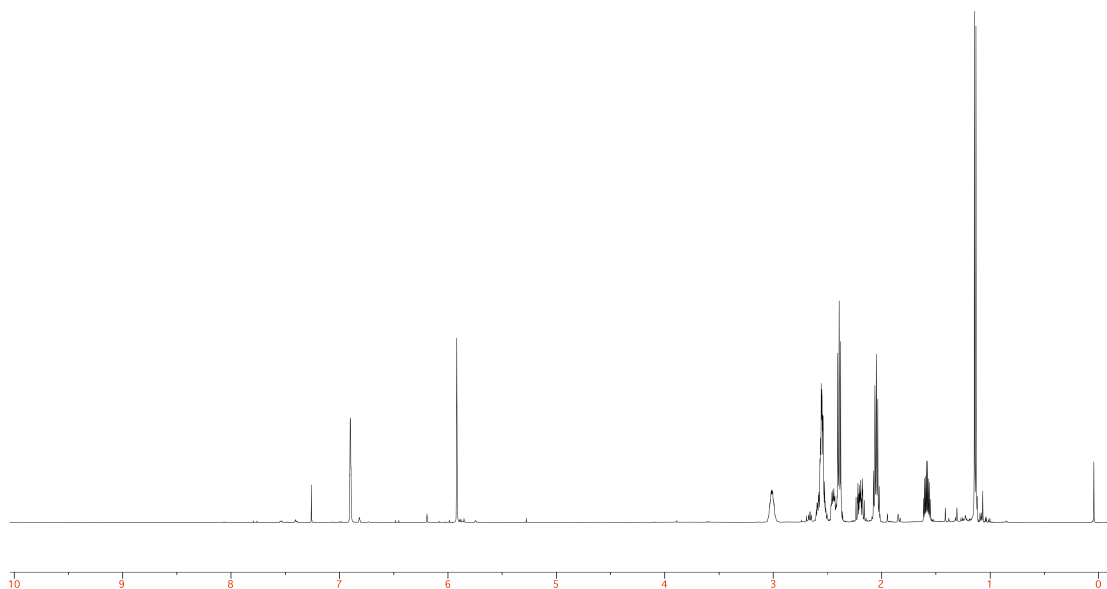
¹³C-NMR (125 MHz, CDCl₃)



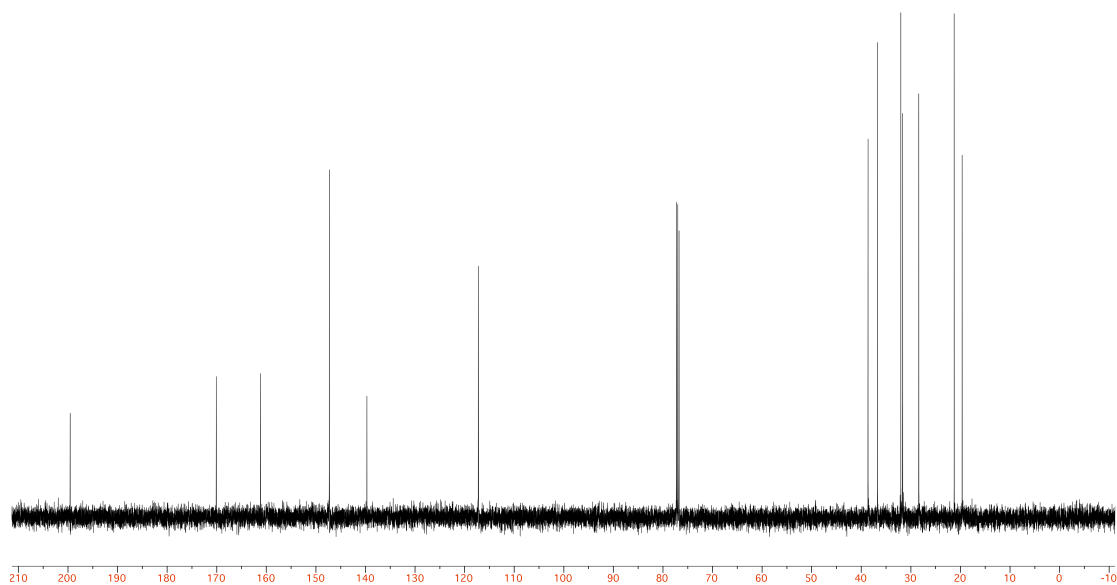
(S/R)-3-Oxocyclohex-1-enyl 5-methylcyclopent-1-enecarboxylate (10)



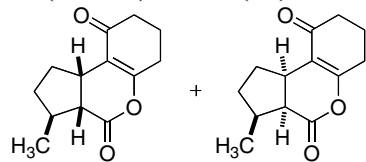
$^1\text{H-NMR}$ (500 MHz, CDCl_3)



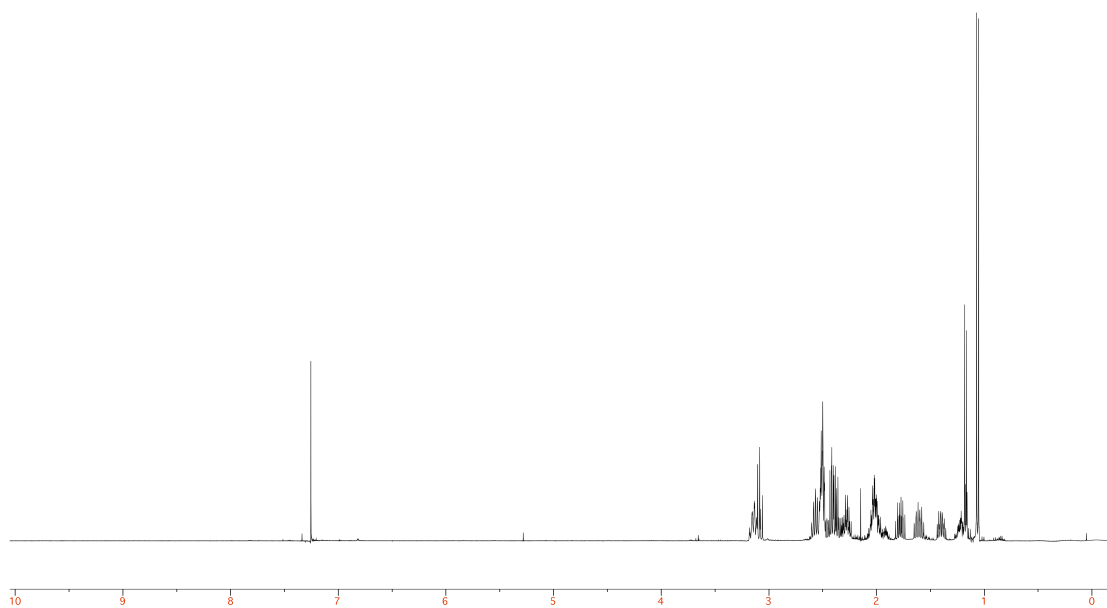
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3)



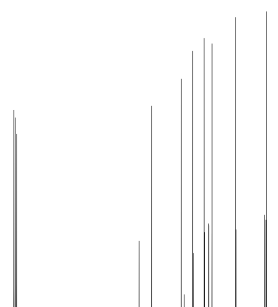
(3*S*,3*aR*,9*bS*)-3-methyl-1,3,3*a*,7,8,9*b*-hexahydrocyclopenta[*c*]chromene-4,9(2*H*,6*H*)-dione and (3*R*,3*aS*,9*bR*)-3-methyl-1,3,3*a*,7,8,9*b*-hexahydrocyclopenta[*c*]chromene-4,9(2*H*,6*H*)-dione
(3*S*,3*aS*,9*bR*)-3-methyl-1,3,3*a*,7,8,9*b*-hexahydrocyclopenta[*c*]chromene-4,9(2*H*,6*H*)-dione and (3*R*,3*aR*,9*bS*)-3-methyl-1,3,3*a*,7,8,9*b*-hexahydrocyclopenta[*c*]chromene-4,9(2*H*,6*H*)-dione (11)



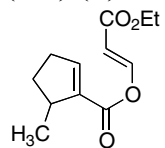
¹H-NMR (400 MHz, CDCl₃)



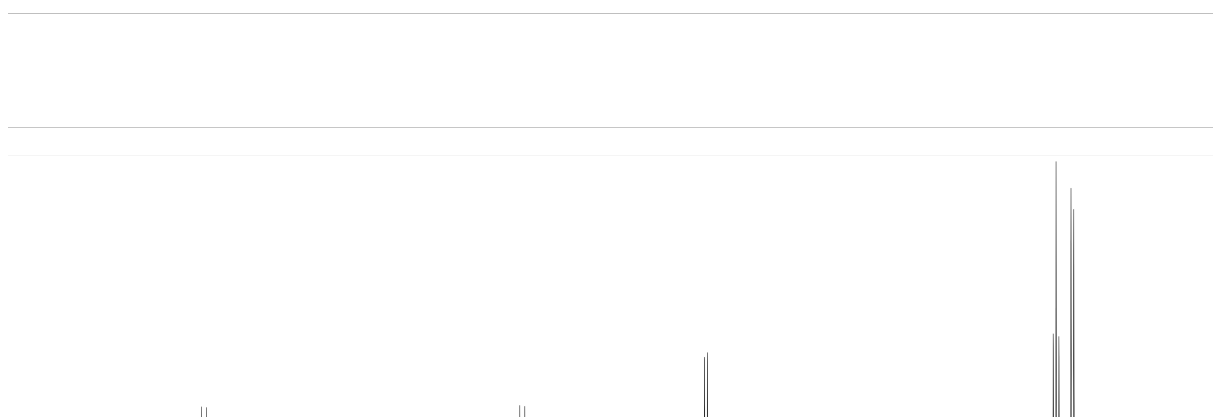
¹³C-NMR (100 MHz, CDCl₃)



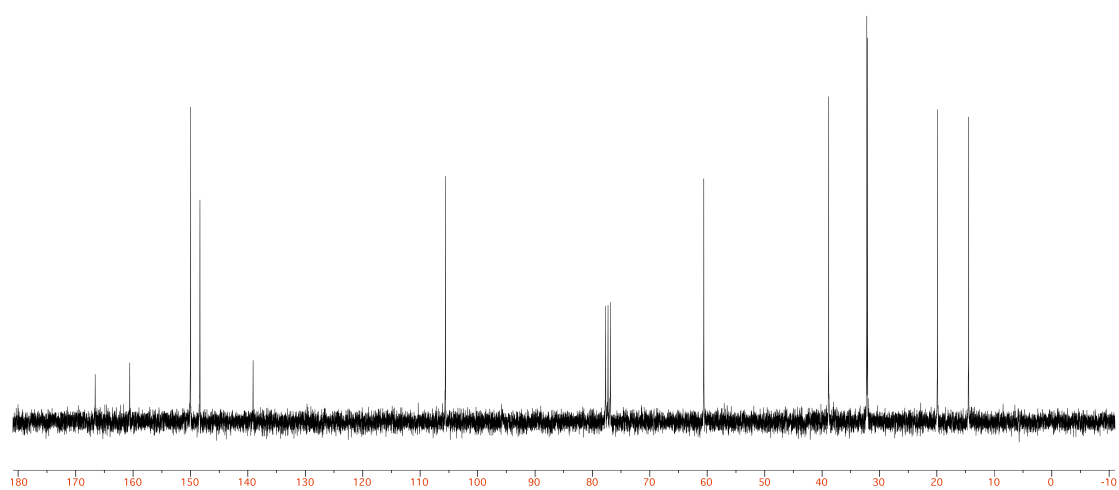
(S/R)-(E)-3-Ethoxy-3-oxoprop-1-en-1-yl 5-methylcyclopent-1-enecarboxylate (3b)



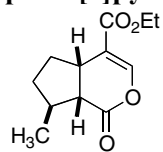
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



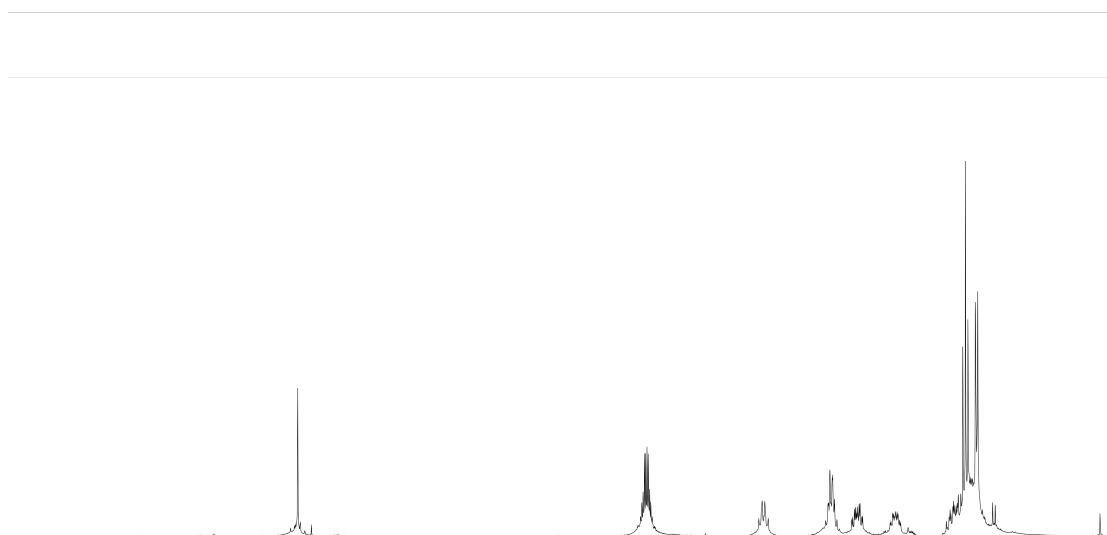
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3)



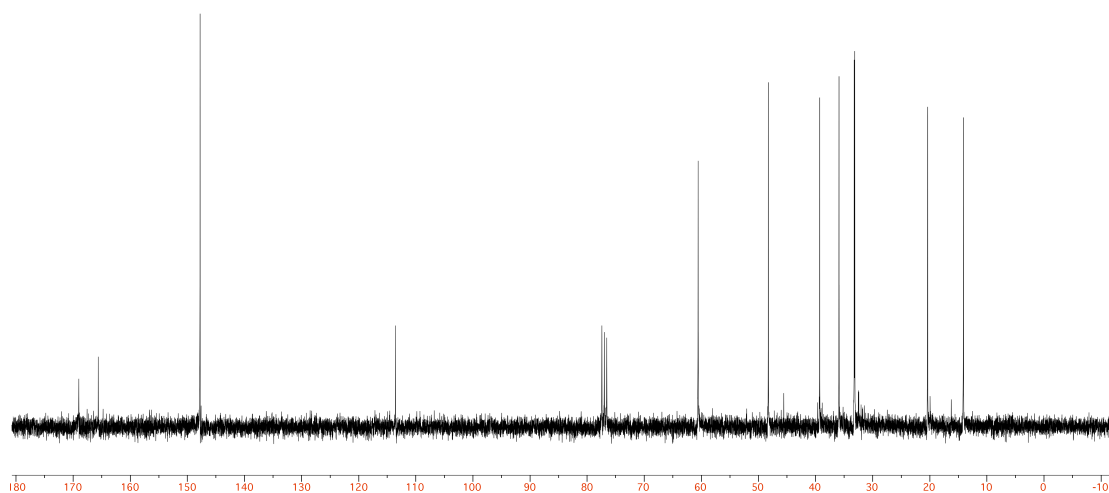
(4a*S*,7*S*,7a*R*)-Ethyl 7-methyl-1-oxo-1,4a,5,6,7,7a hexahydrocyclo penta[*c*]pyran-4-carboxylate and (4a*R*,7*R*,7a*S*)-Ethyl 7-methyl-1-oxo-1,4a,5,6,7,7a hexahydrocyclo penta[*c*]pyran-4-carboxylate (4b)



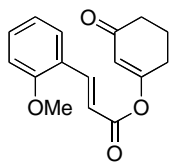
¹H-NMR (300 MHz, CDCl₃)



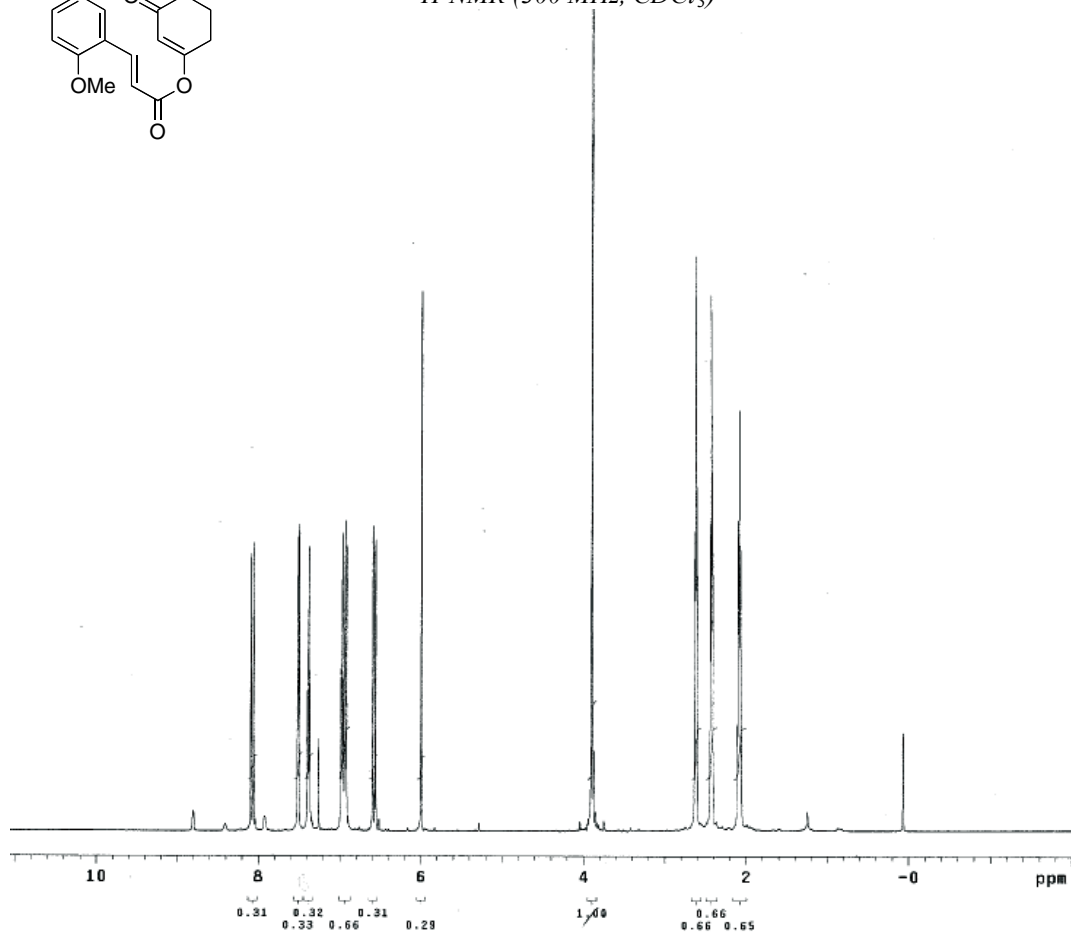
¹³C-NMR (75 MHz, CDCl₃)



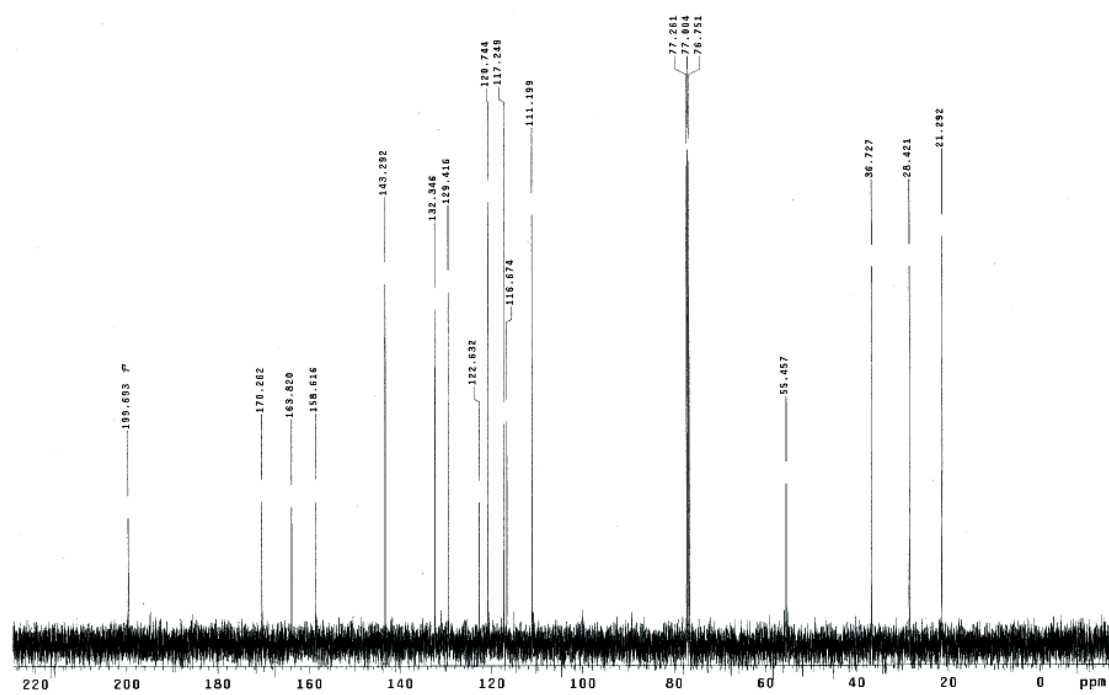
(E)-3-Oxocyclohex-1-en-1-yl 3-(2-methoxyphenyl)acrylate 12a.



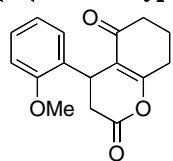
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



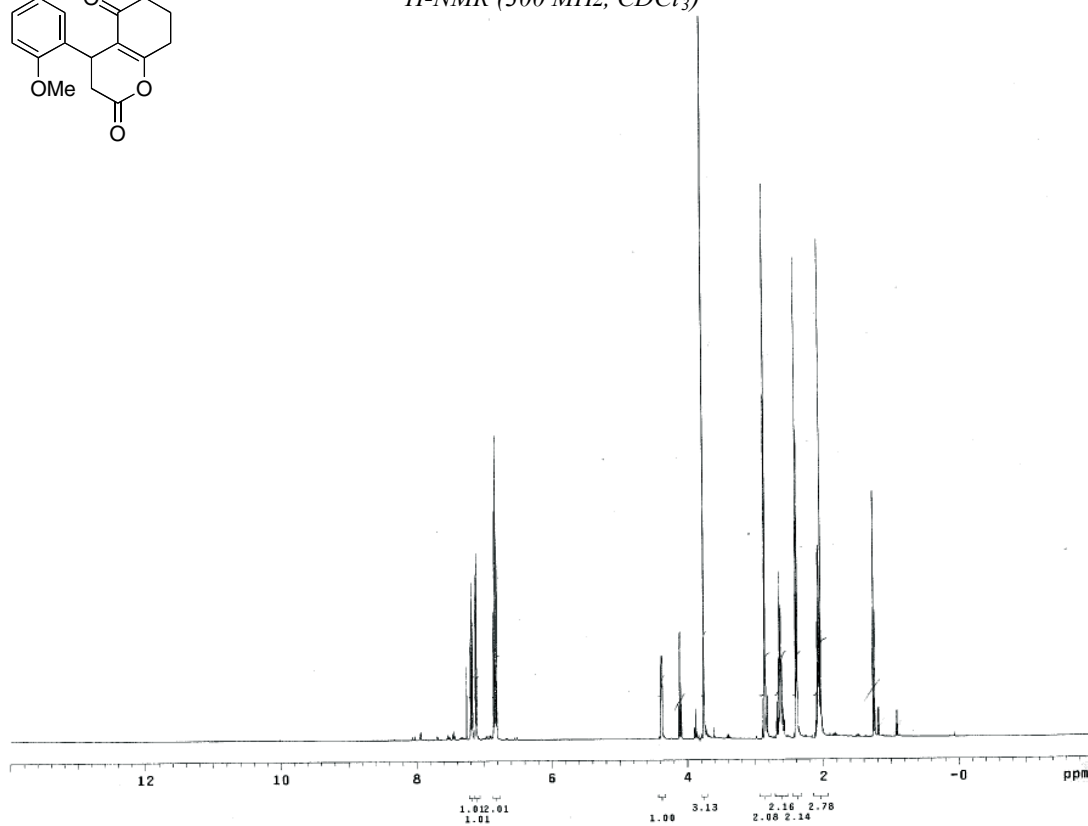
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3)



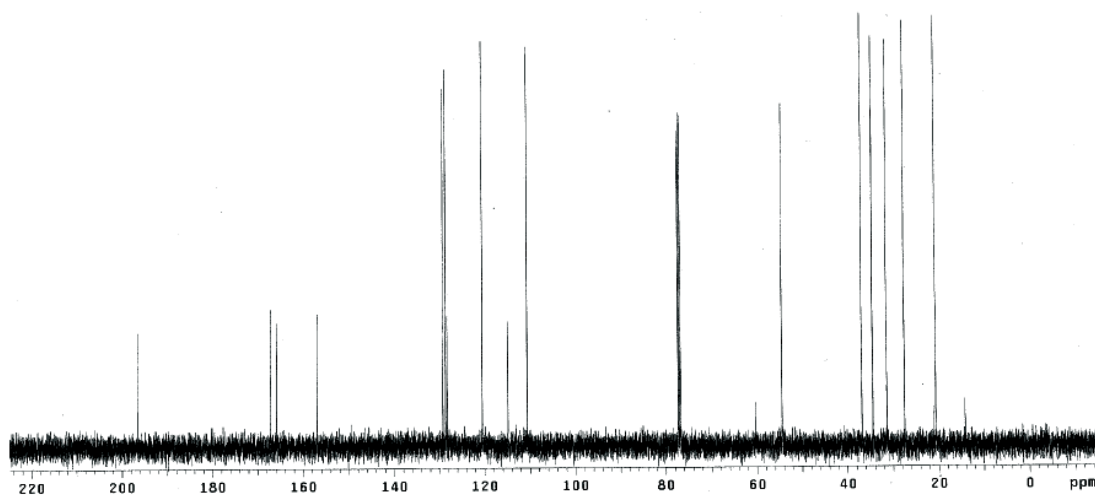
(4-(2-Methoxyphenyl)-3,4,7,8-tetrahydro-2H-chromene-2,5(6H)-dione 13a.



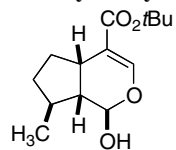
¹H-NMR (300 MHz, CDCl₃)



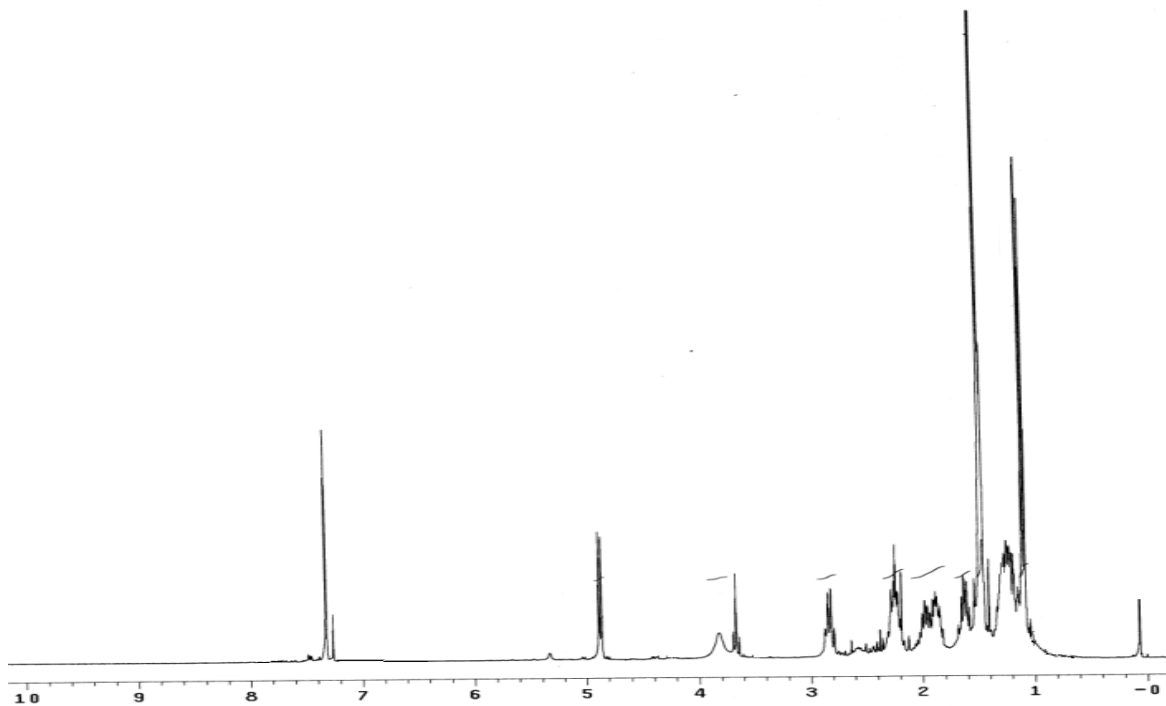
¹³C-NMR (75 MHz, CDCl₃)



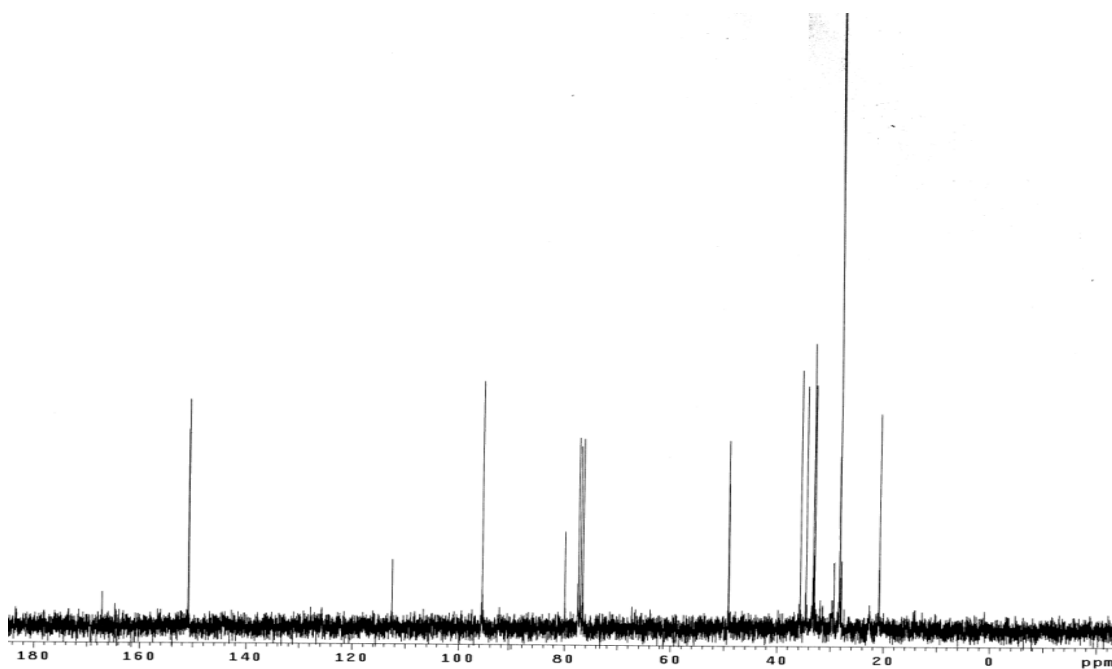
(1*R*,4*aS*,7*S*,7*aR*)-tert-Butyl 1-hydroxy-7-methyl-1,4*a*,5,6,7,7*a*-hexahydrocyclopenta [c]pyran-4-carboxylate and (1*S*,4*aR*,7*R*,7*aS*)-tert-Butyl 1-hydroxy-7-methyl-1,4*a*,5,6,7,7*a*-hexahydrocyclopenta [c]pyran-4-carboxylate (20a)



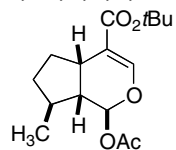
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



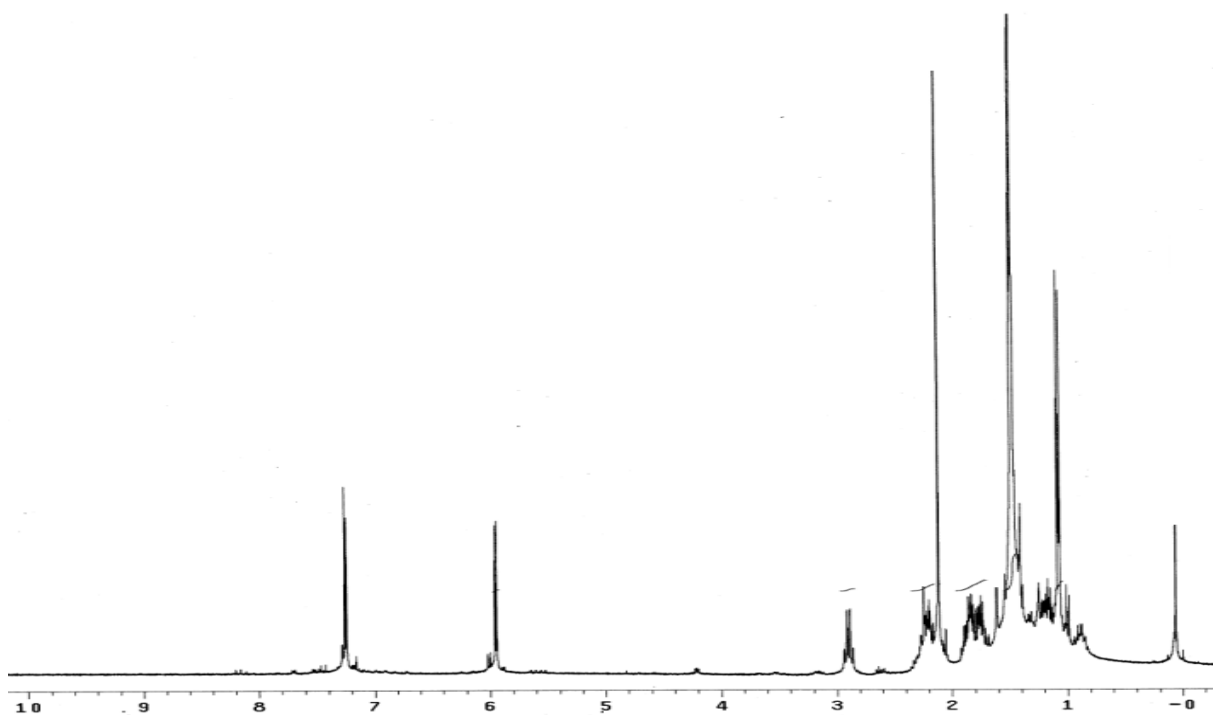
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3)



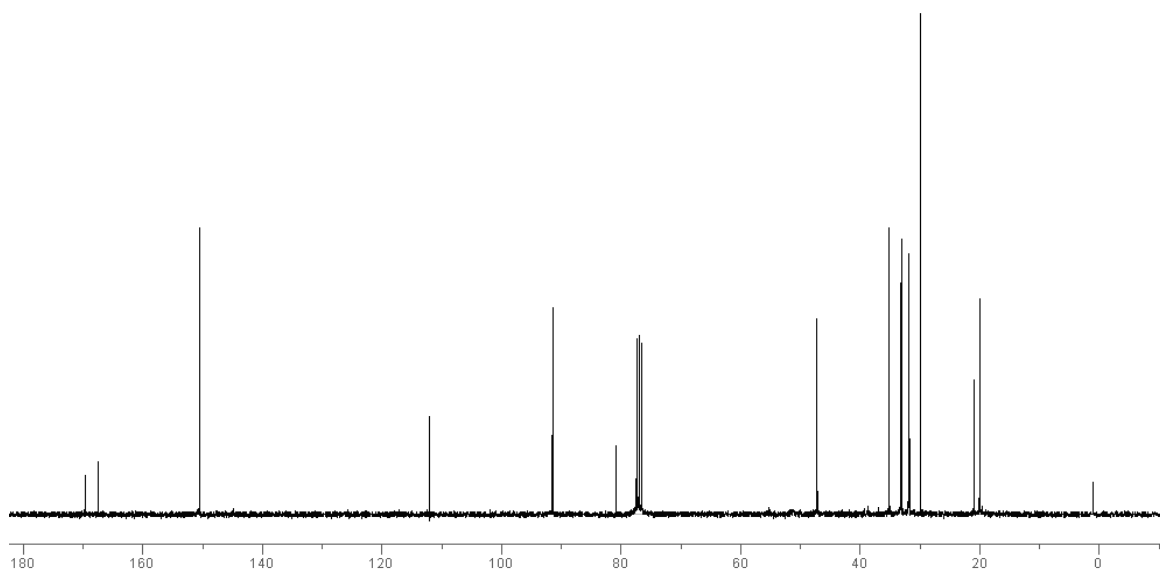
(1*S*,4*aS*,7*S*,7*aR*)-*tert*-butyl 1-Acetoxy-7-methyl-1,4*a*,5,6,7,7*a*-hexahydrocyclopenta[*c*]pyran-4-carboxylate and (1*R*,4*aR*,7*R*,7*aS*)-*tert*-butyl 1-Acetoxy-7-methyl-1,4*a*,5,6,7,7*a*-hexahydrocyclopenta[*c*]pyran-4-carboxylate (7*a*)



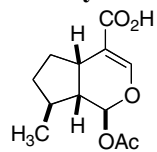
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



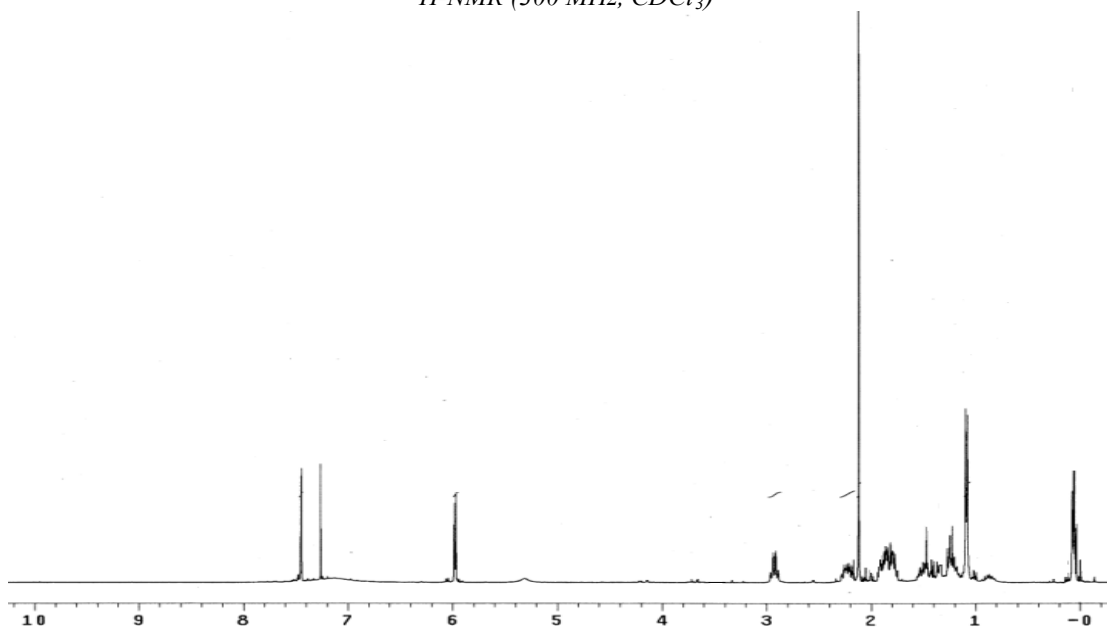
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3)



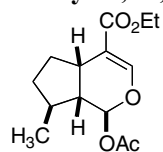
(4a*S*,7*S*,7a*R*)-1-acetoxy-7-methyl-1,4a,5,6,7,7a-hexahydrocyclopenta[*c*]pyran-4-carboxylic acid and (4a*R*,7*R*,7a*S*)-1-acetoxy-7-methyl-1,4a,5,6,7,7a-hexahydrocyclopenta[*c*]pyran-4-carboxylic acid (23)



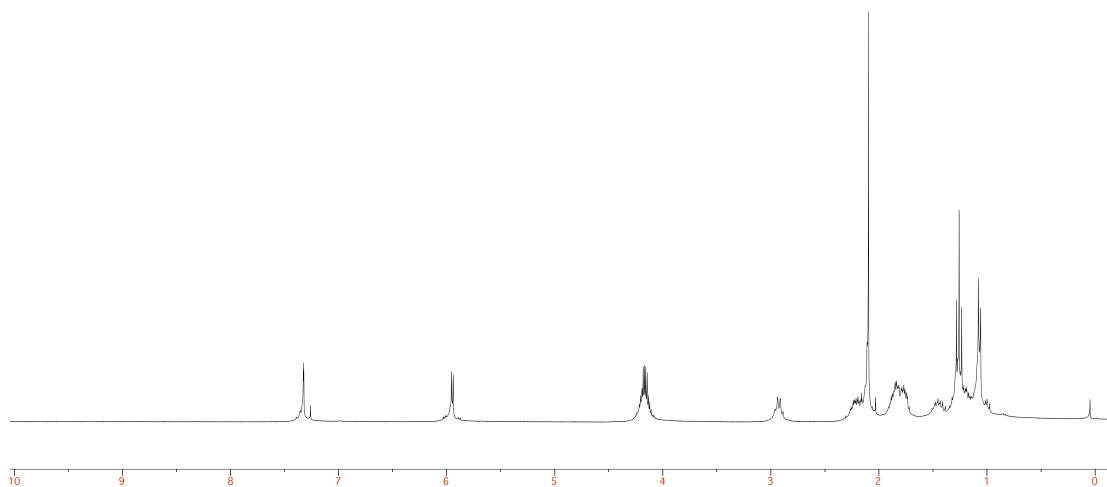
¹H-NMR (300 MHz, CDCl₃)



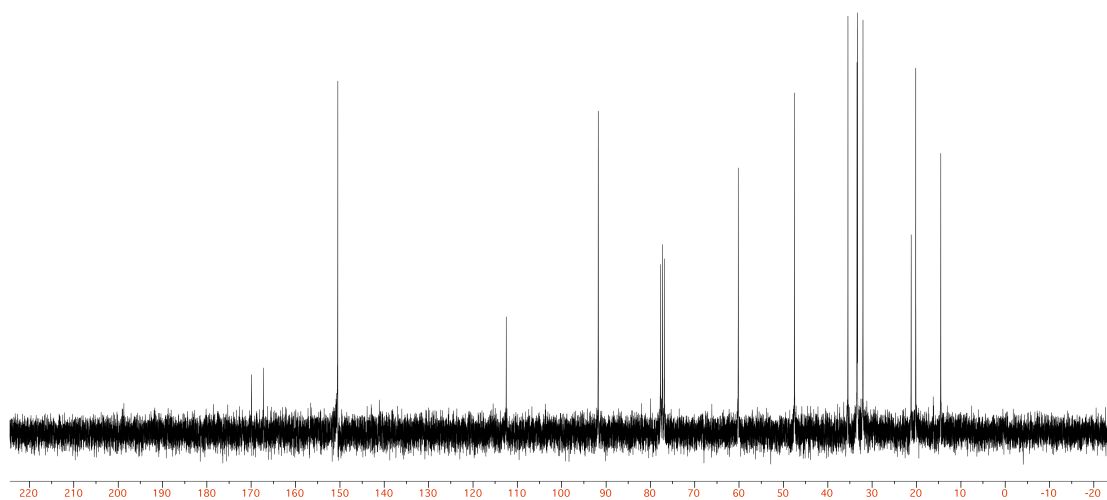
(1*S*,4*aS*,7*S*,7*aR*)-Ethyl 1-acetoxy-7-methyl-1,4*a*,5,6,7,7*a*-hexahydrocyclopenta[*c*]pyran-4-carboxylate and (1*R*,4*aR*,7*R*,7*aS*)-Ethyl 1-acetoxy-7-methyl-1,4*a*,5,6,7,7*a*-hexahydrocyclopenta[*c*]pyran-4-carboxylate (7b)



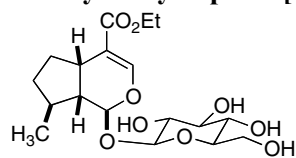
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



$^{13}\text{C-NMR}$ (75 MHz, CDCl_3)



(1*S*,4*aS*,7*S*,7*aR*)-Ethyl 7-methyl-1-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-1,4*a*,5,6,7,7*a*-hexahydrocyclopenta[*c*]pyran-4-carboxylate (25)



¹H-NMR (300 MHz, D₂O)

