

**Supporting Information
Experimental**

***Highly Enantioselective Borane Reduction of Heteroaryl and Heterocyclic
Ketoximes Ethers Catalyzed by Novel Spiroborate Ester derived from Diphenyl
Valinol: Application to the Synthesis of Nicotine Analogues***

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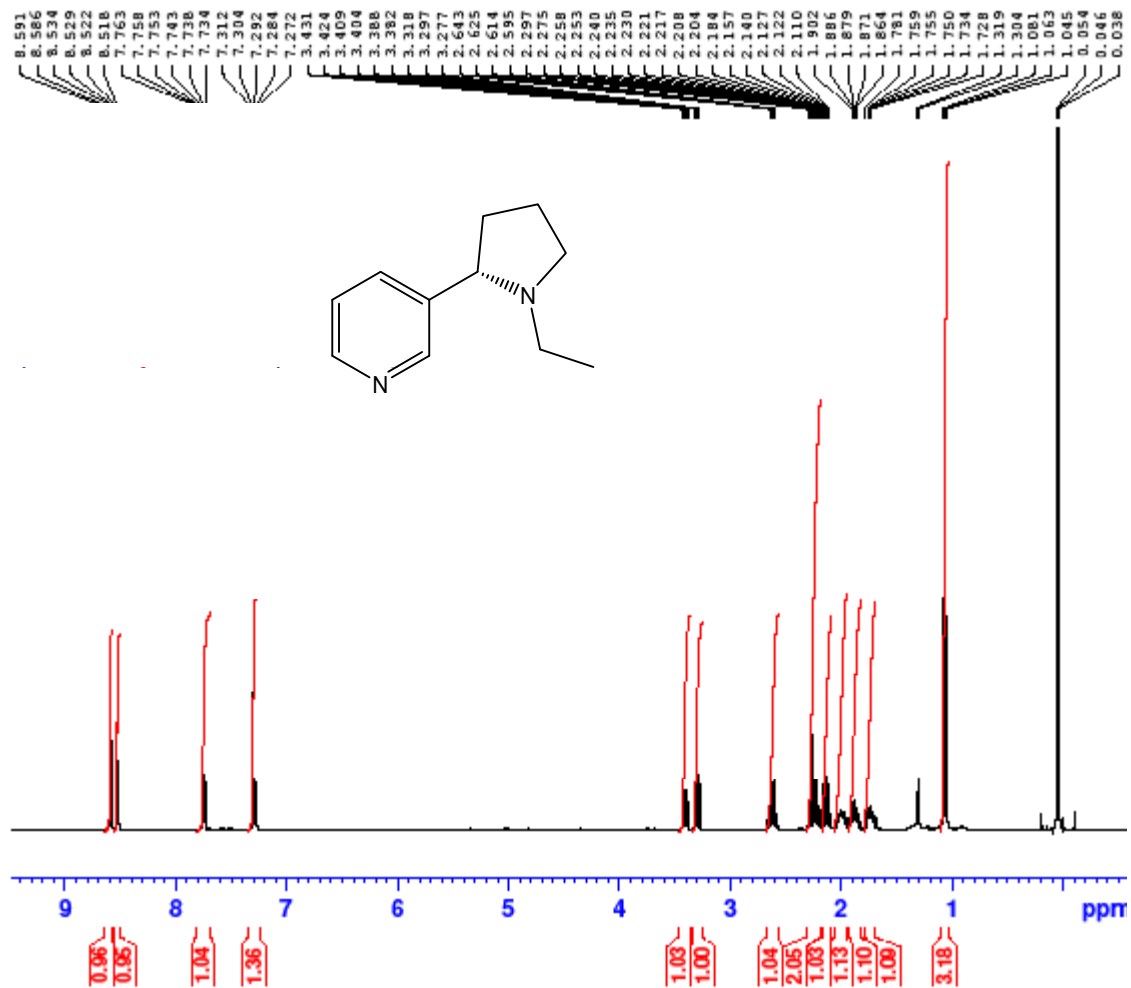
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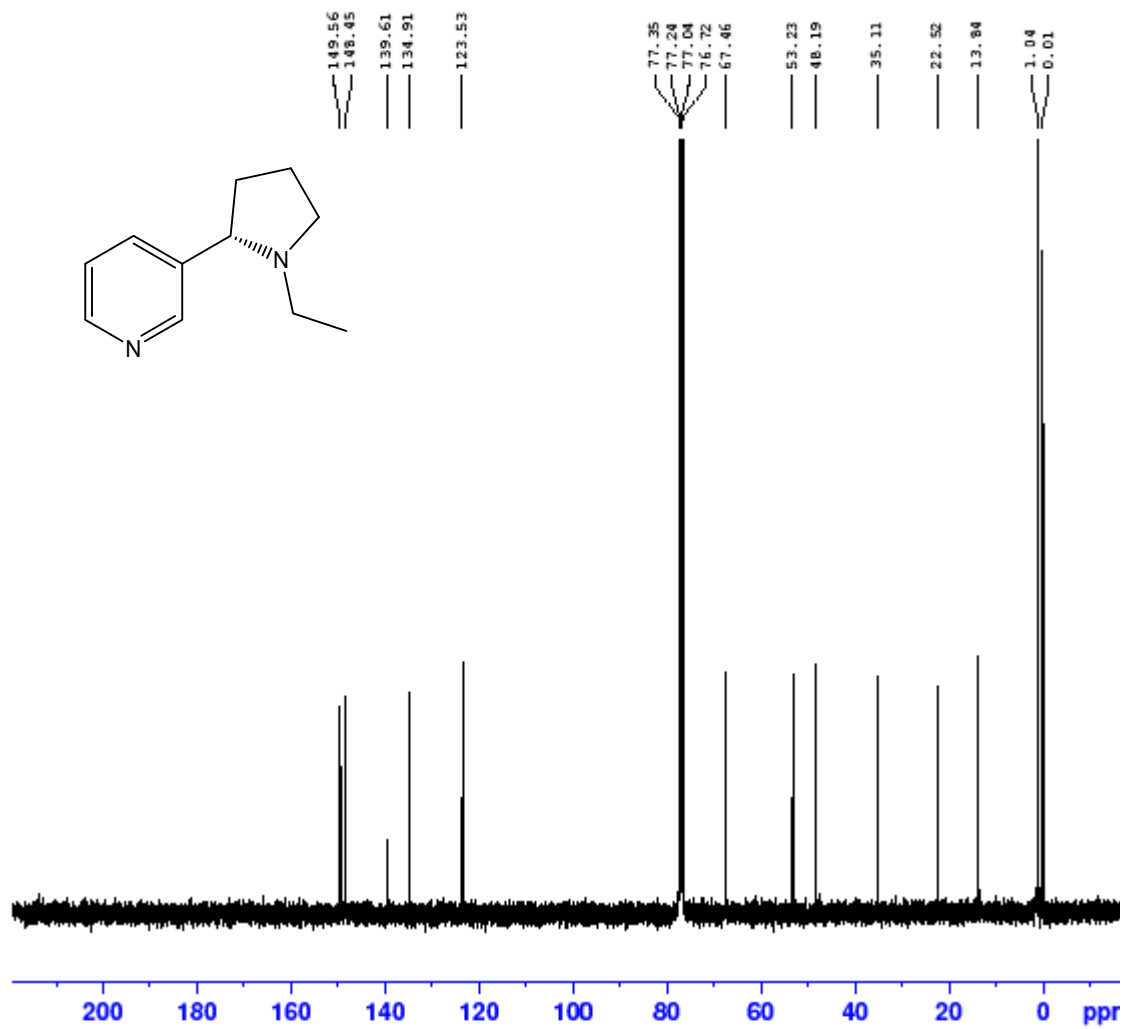
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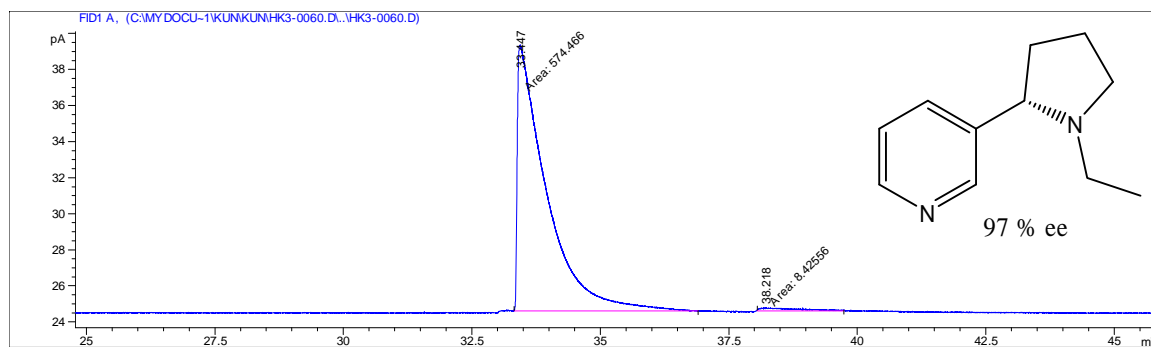
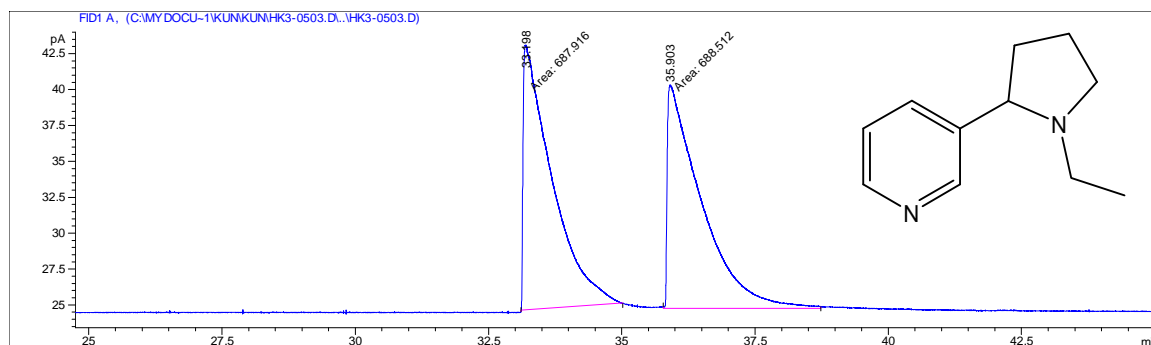
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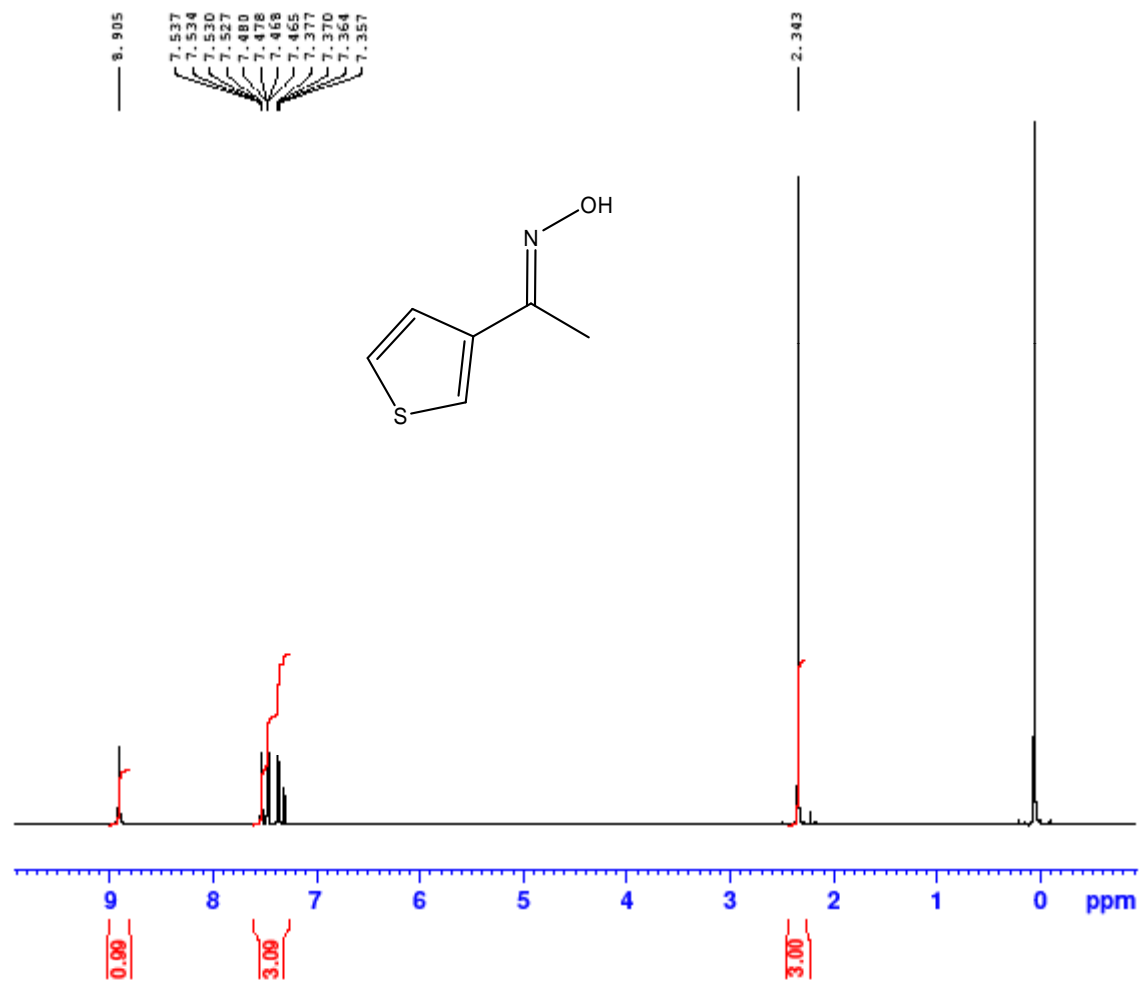
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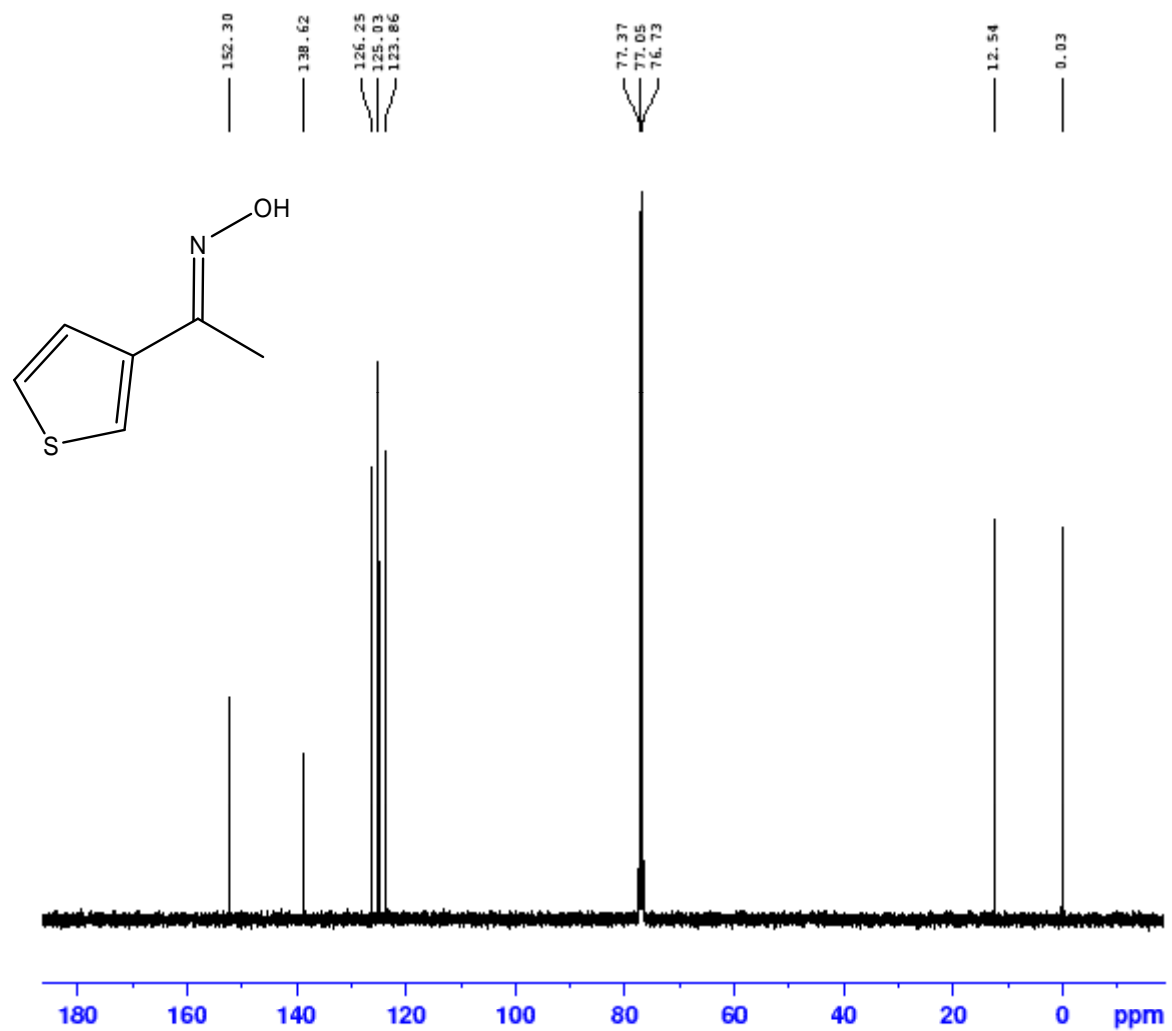
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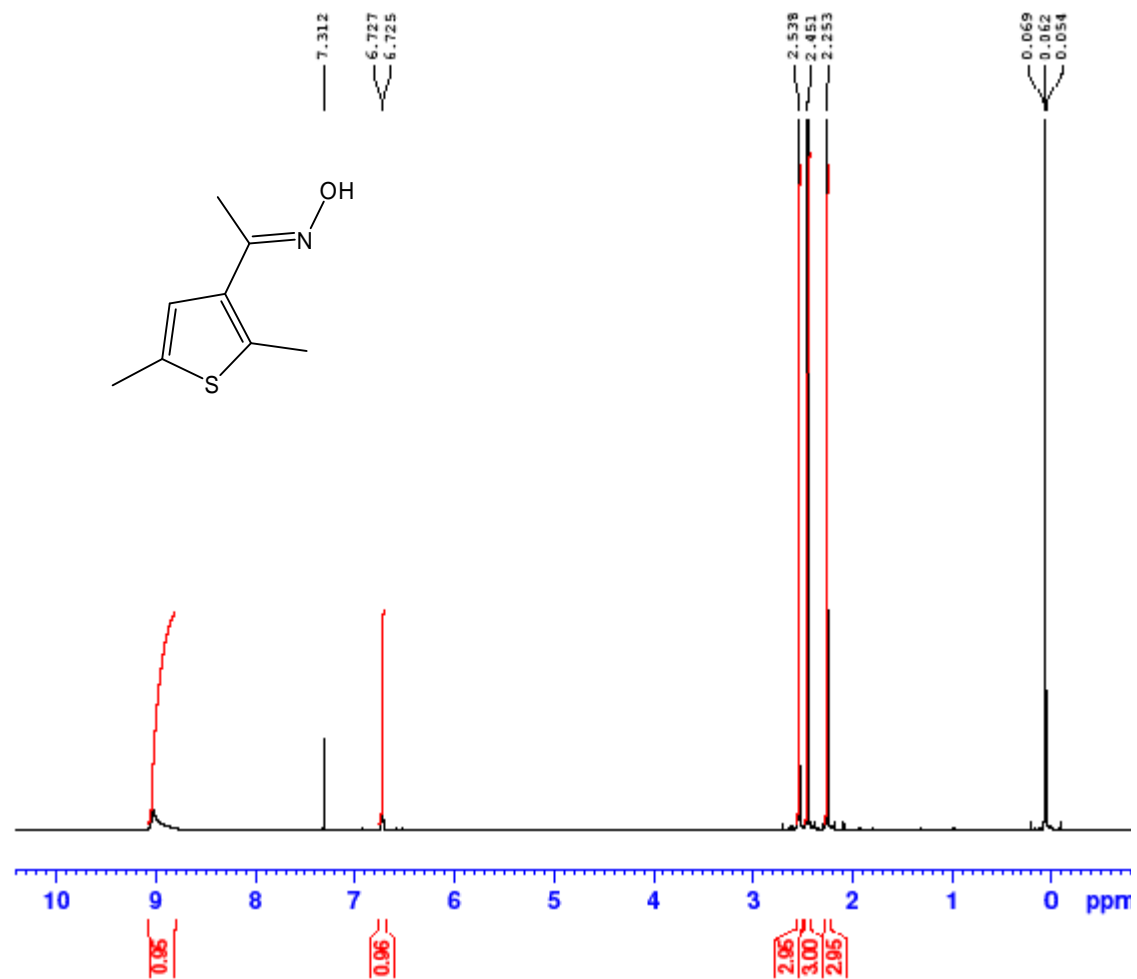
(E)-1-(Thiophen-3yl)ethanone oxime (13a)



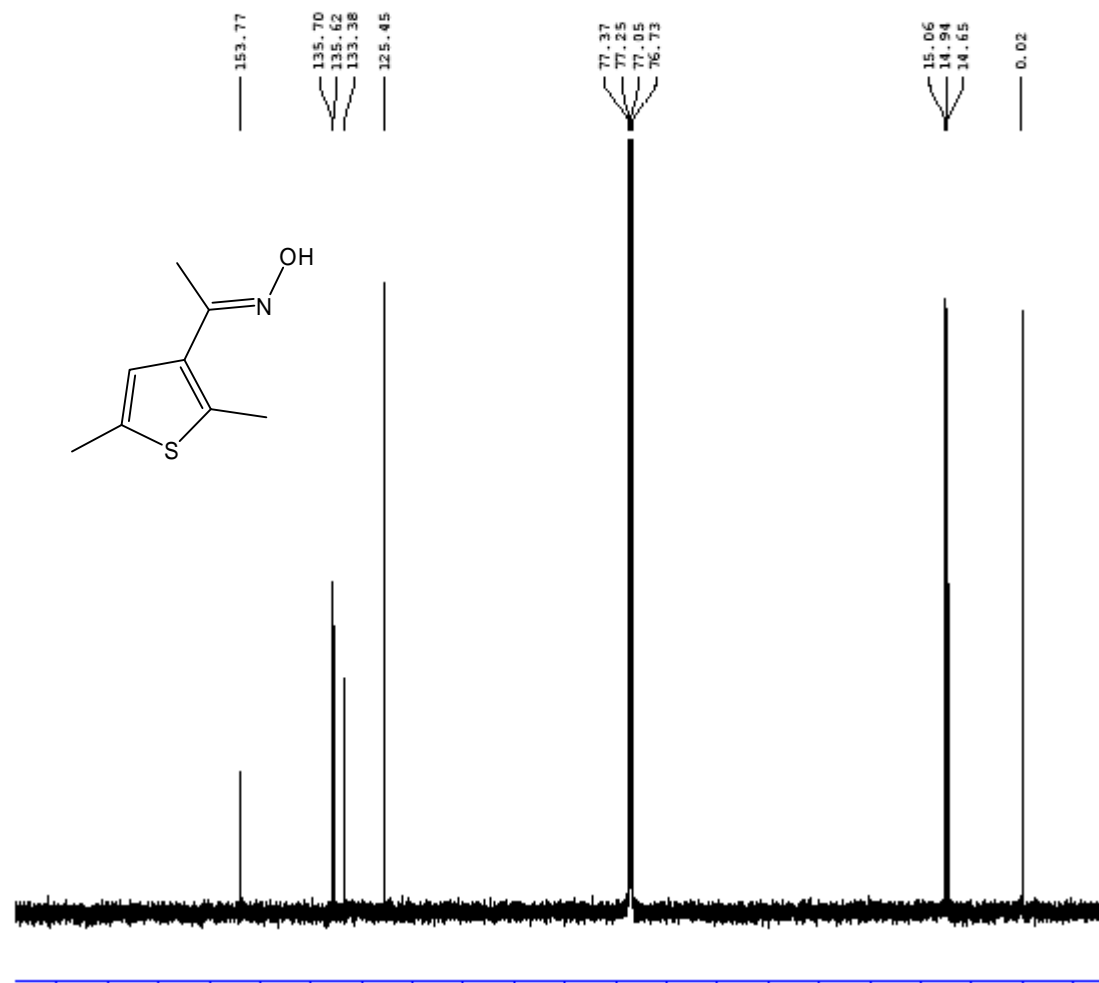
(E)-1-(Thiophen-3yl)ethanone oxime (13a)



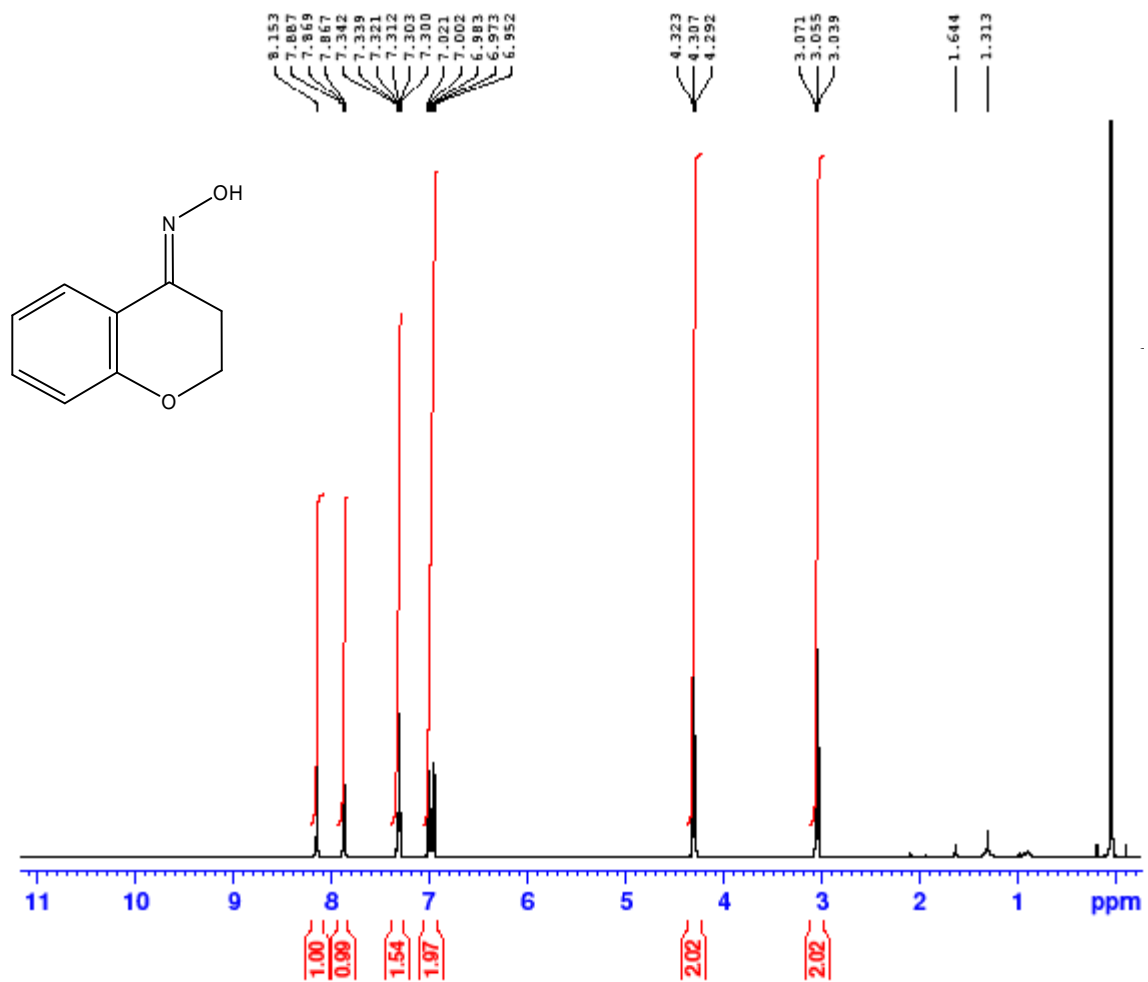
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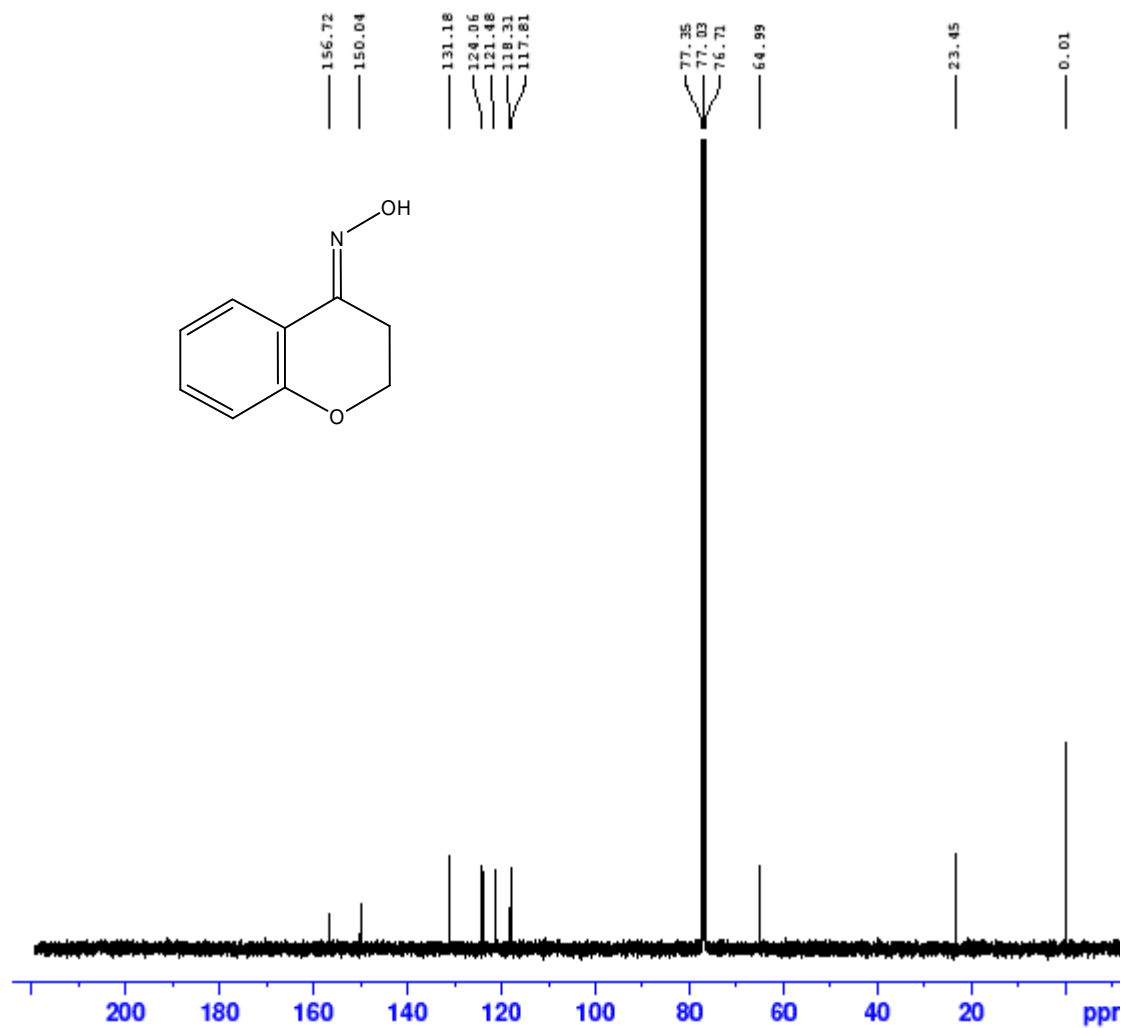
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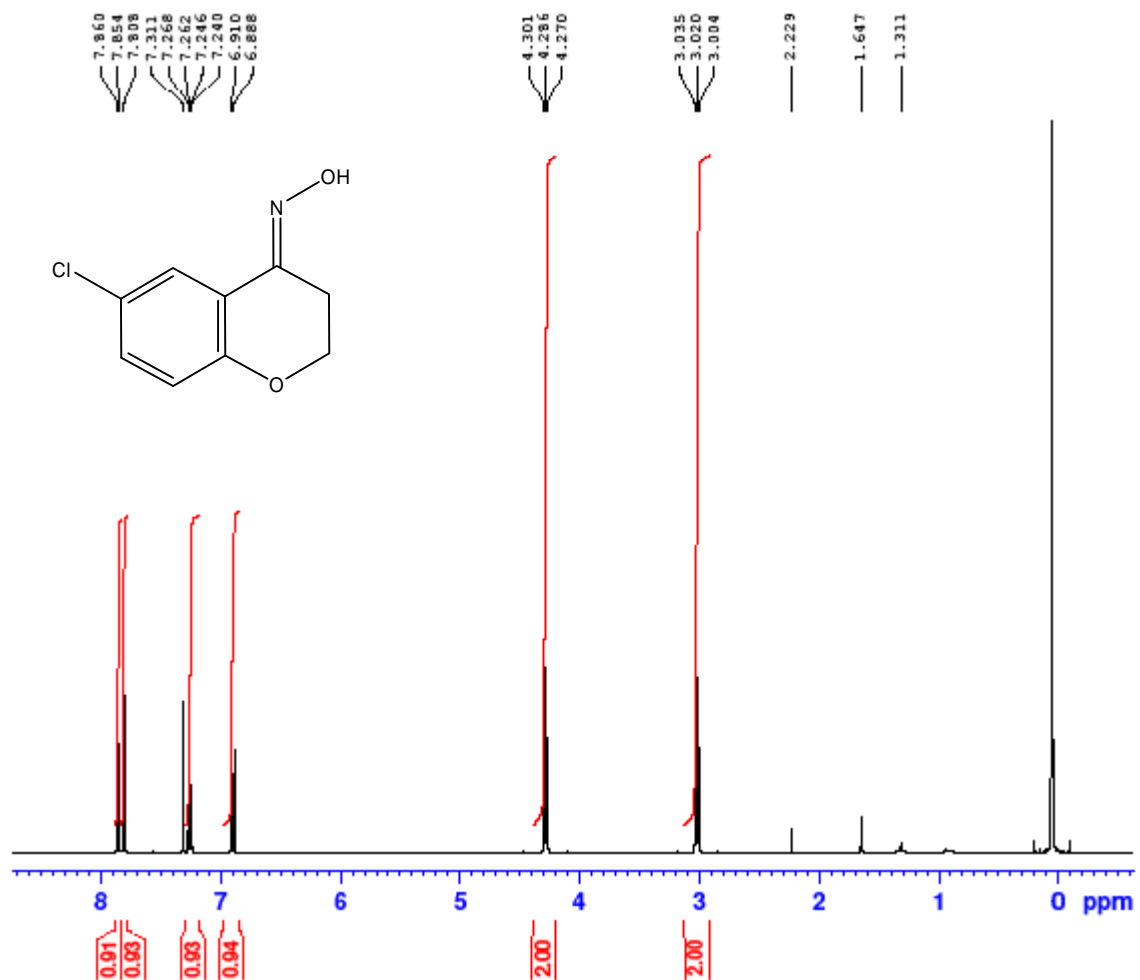
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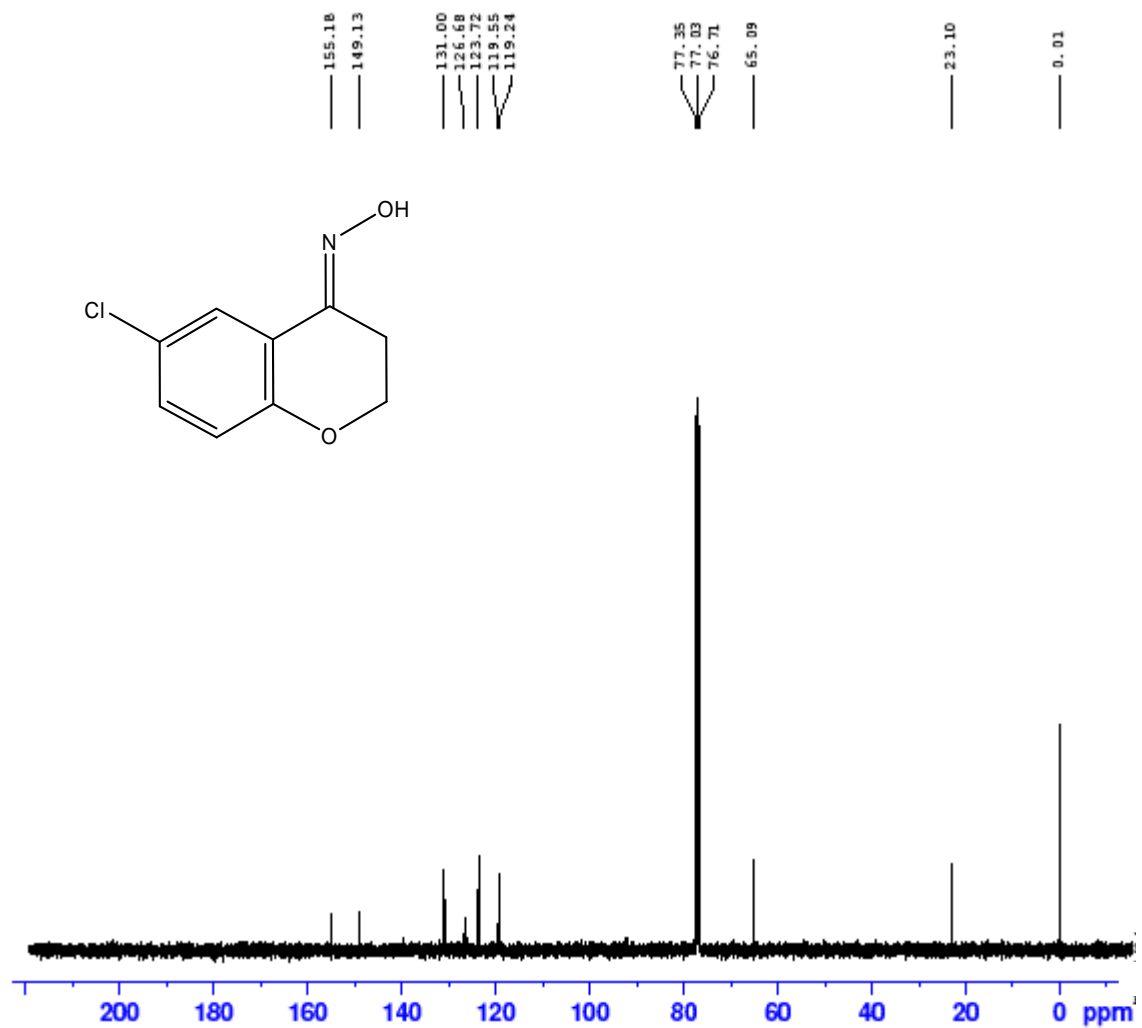
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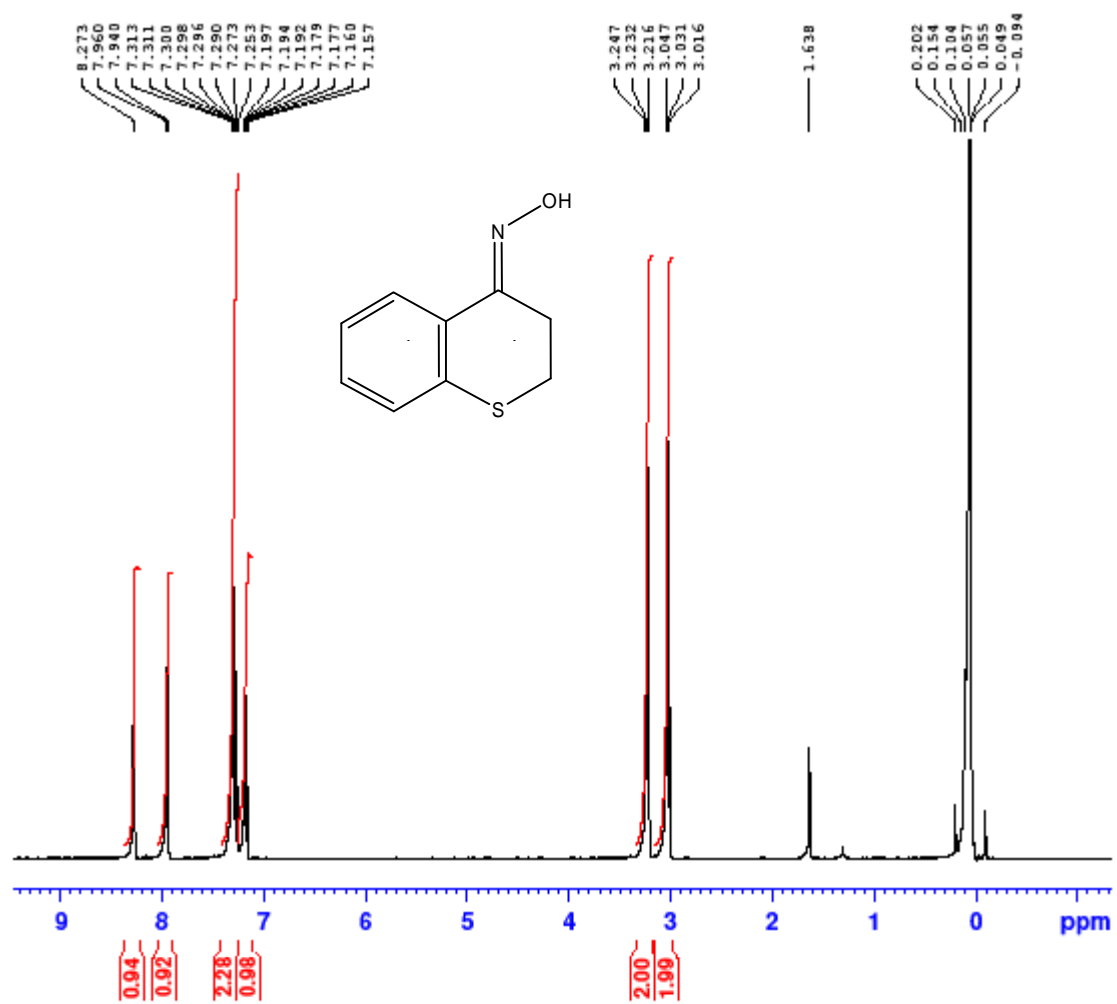
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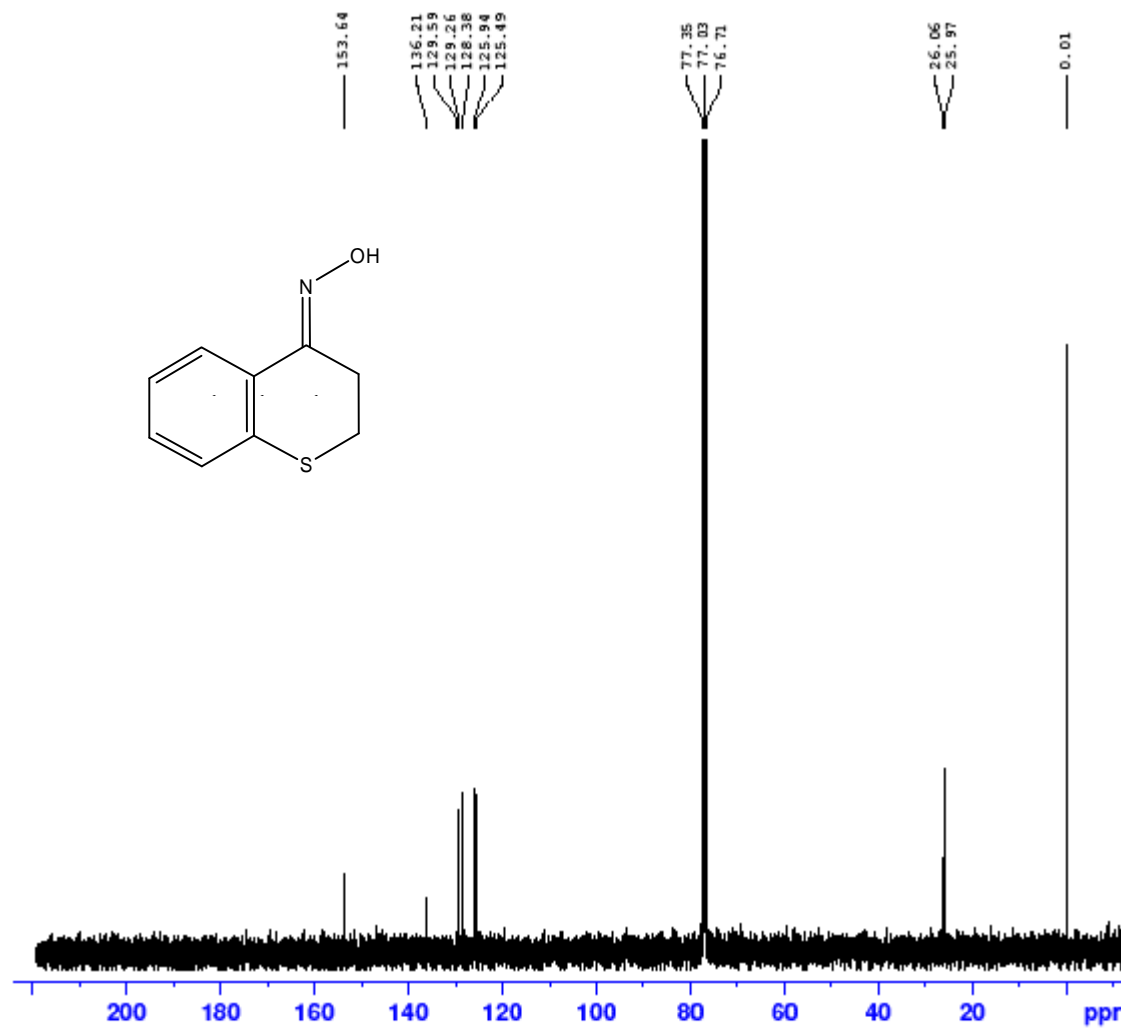
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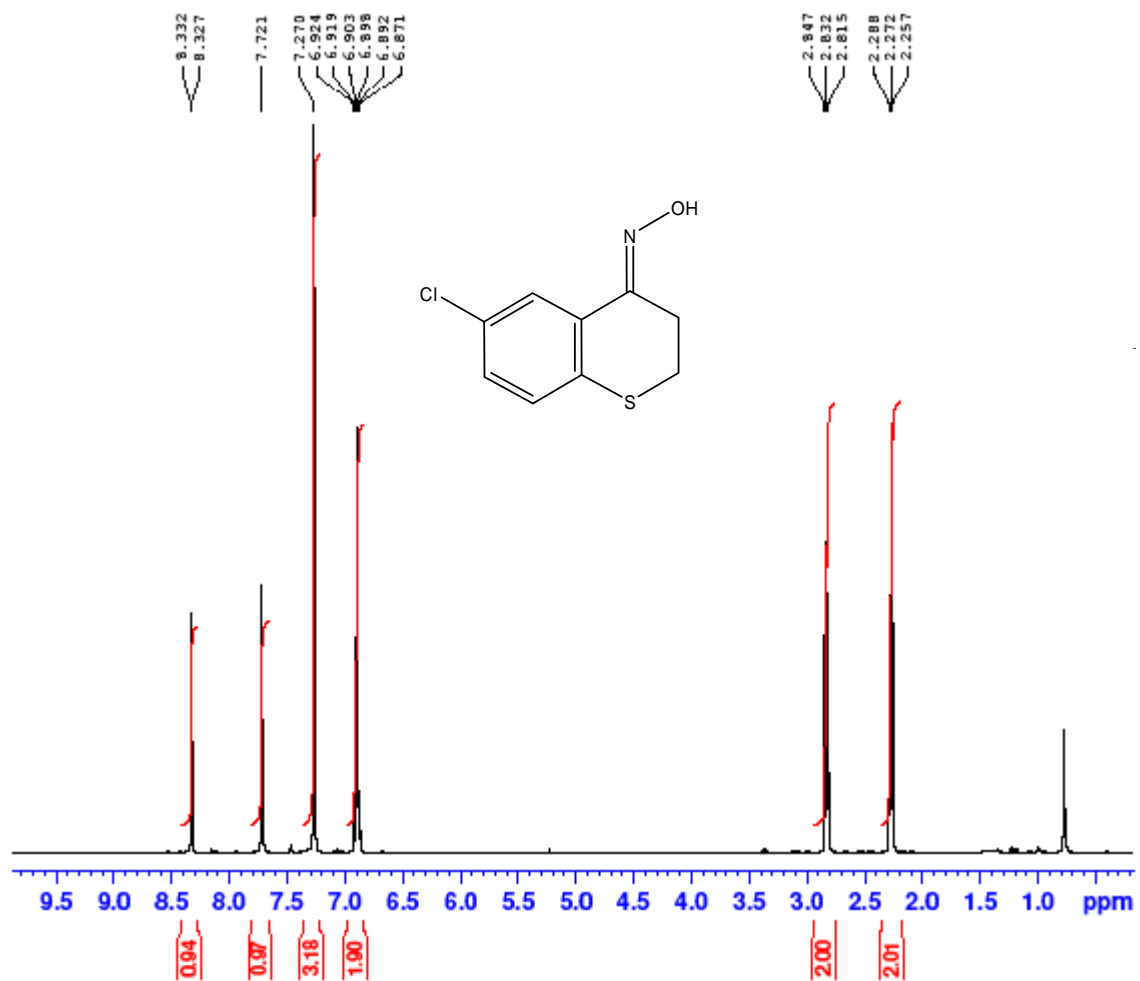
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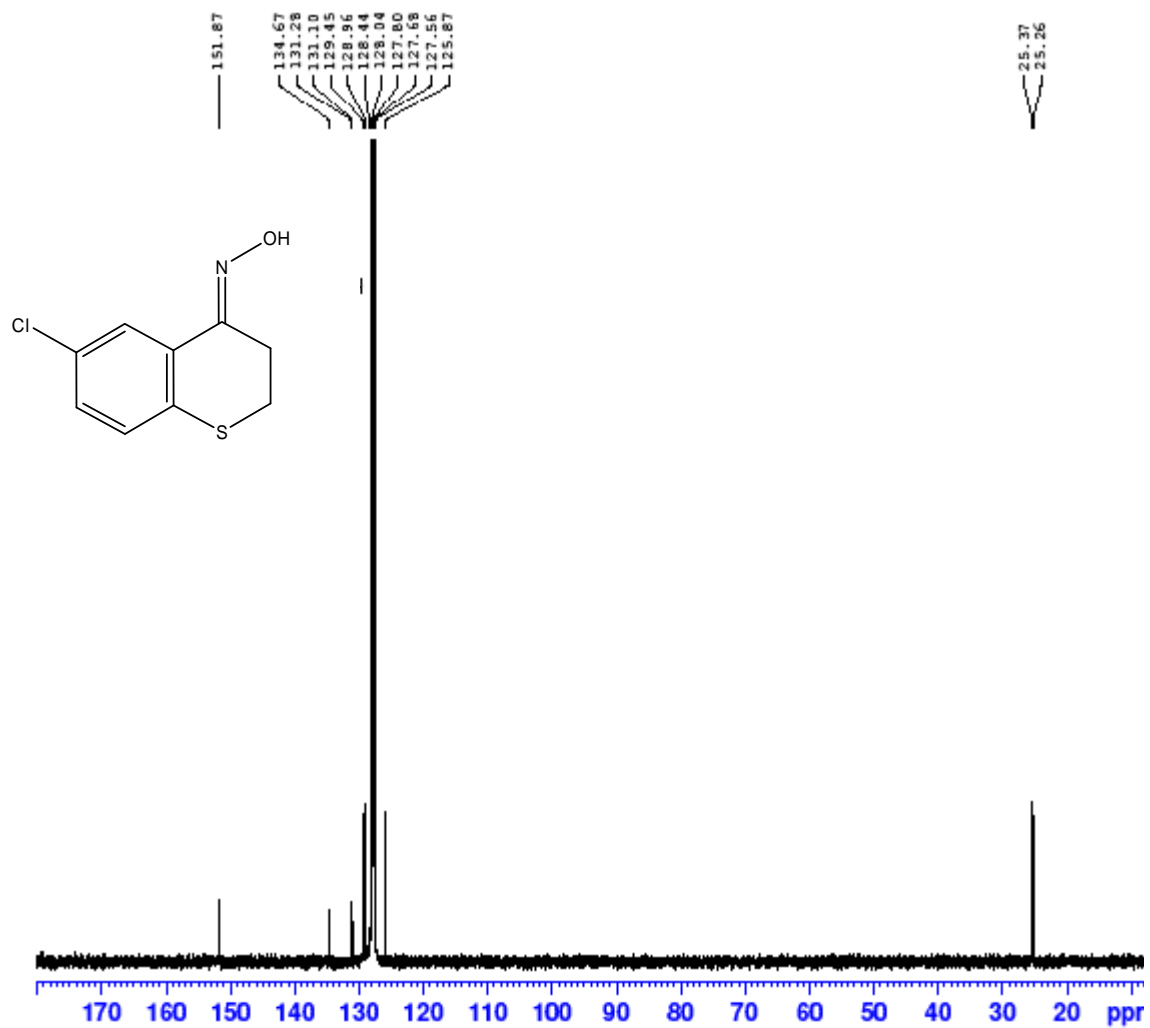
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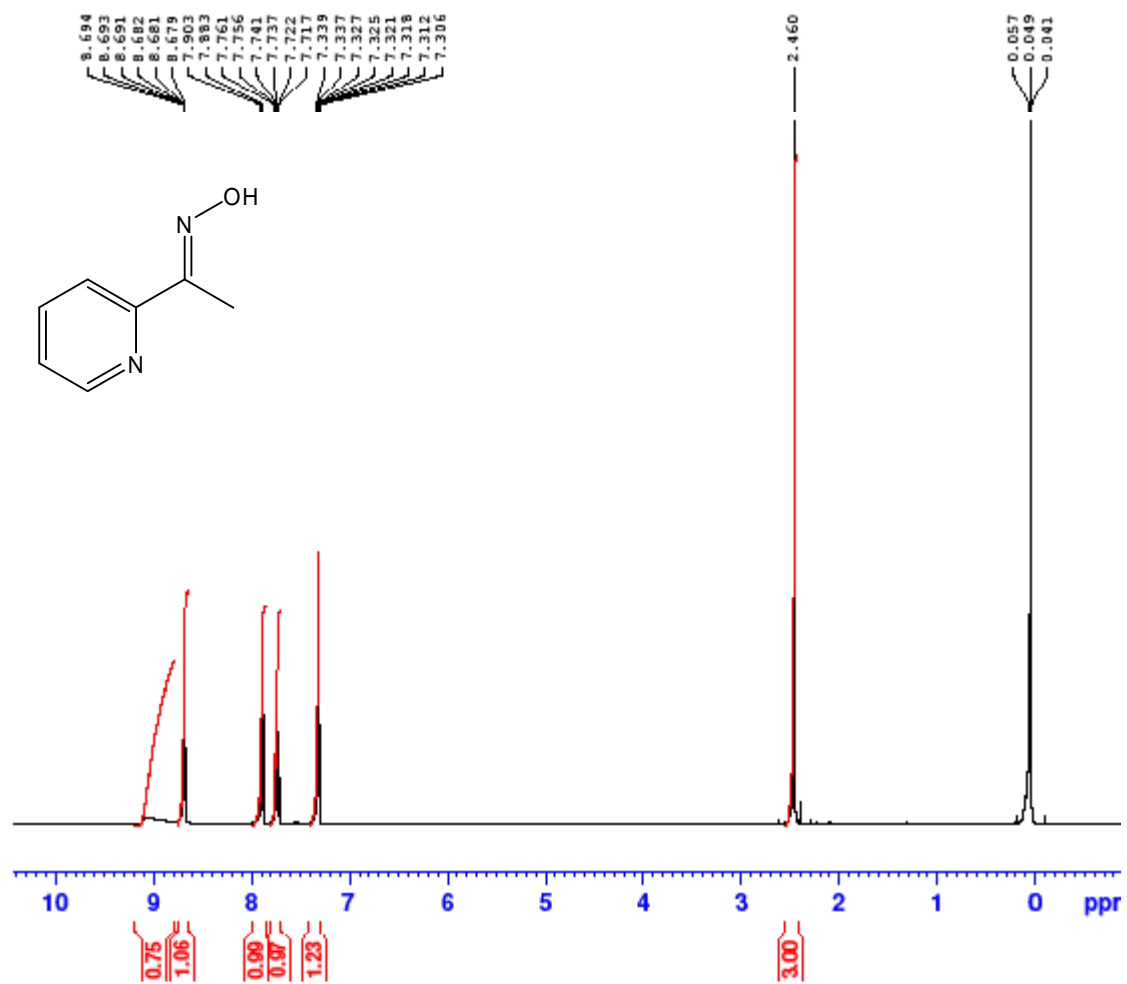
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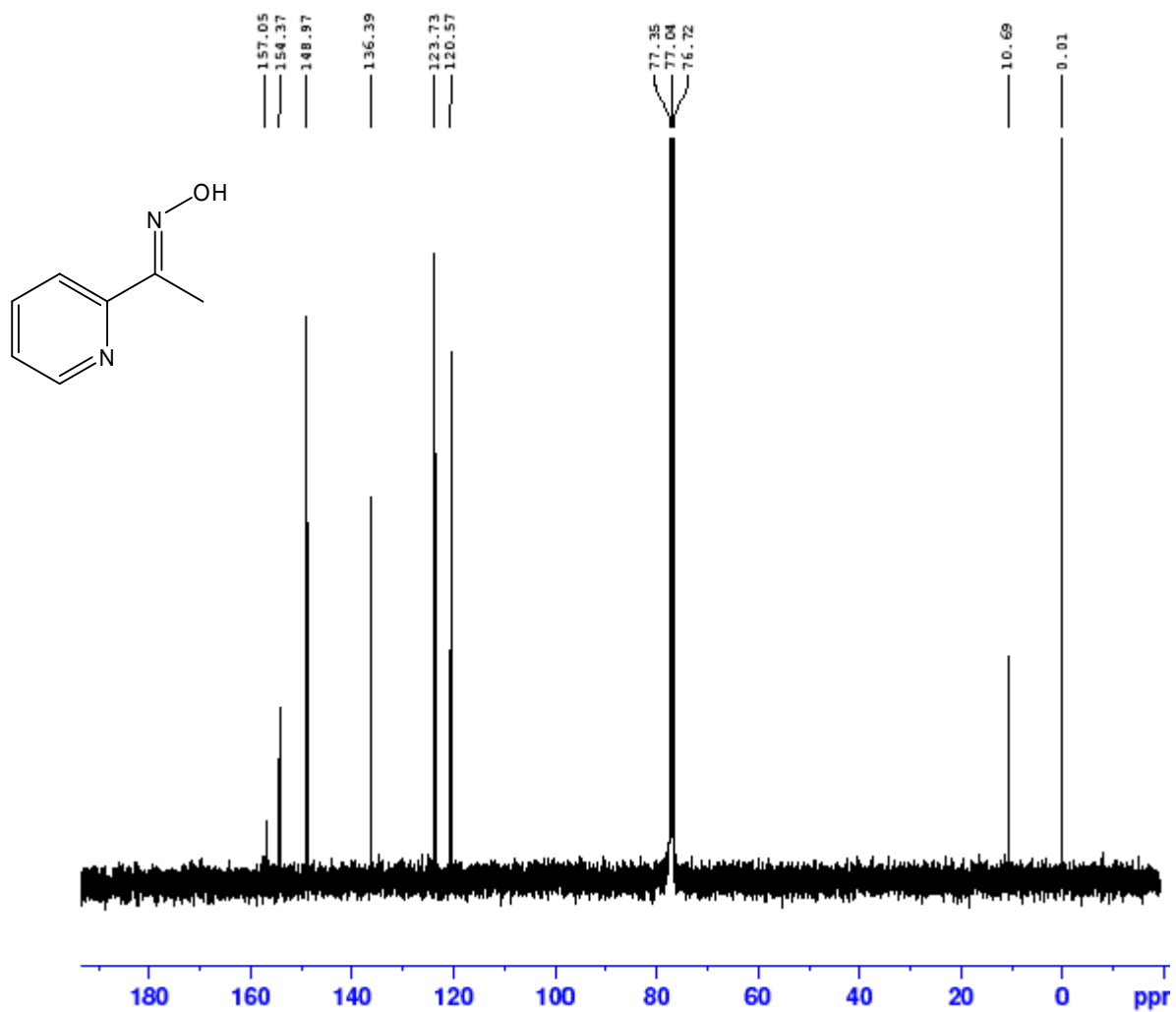
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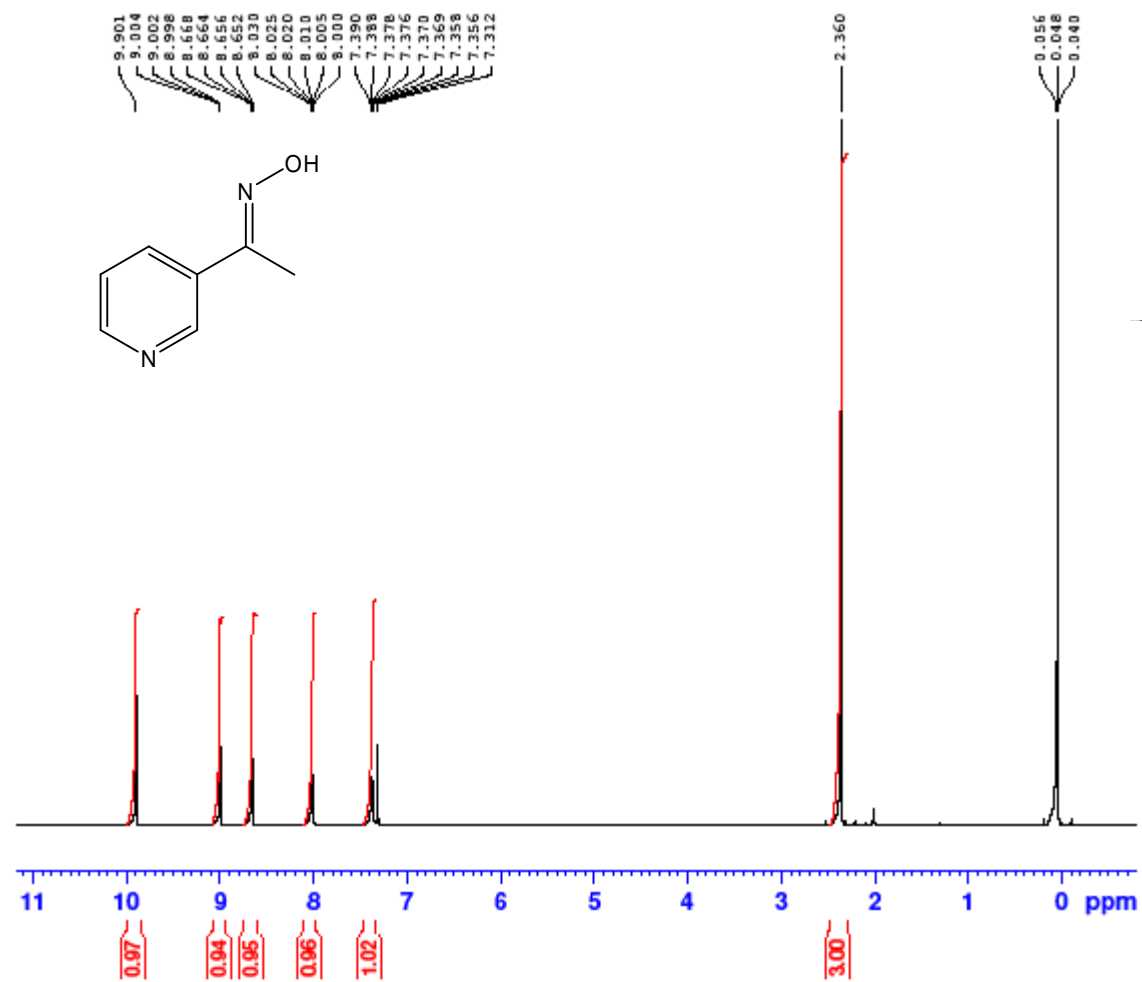
1-(pyridin-2-yl)ethanone oxime (14)



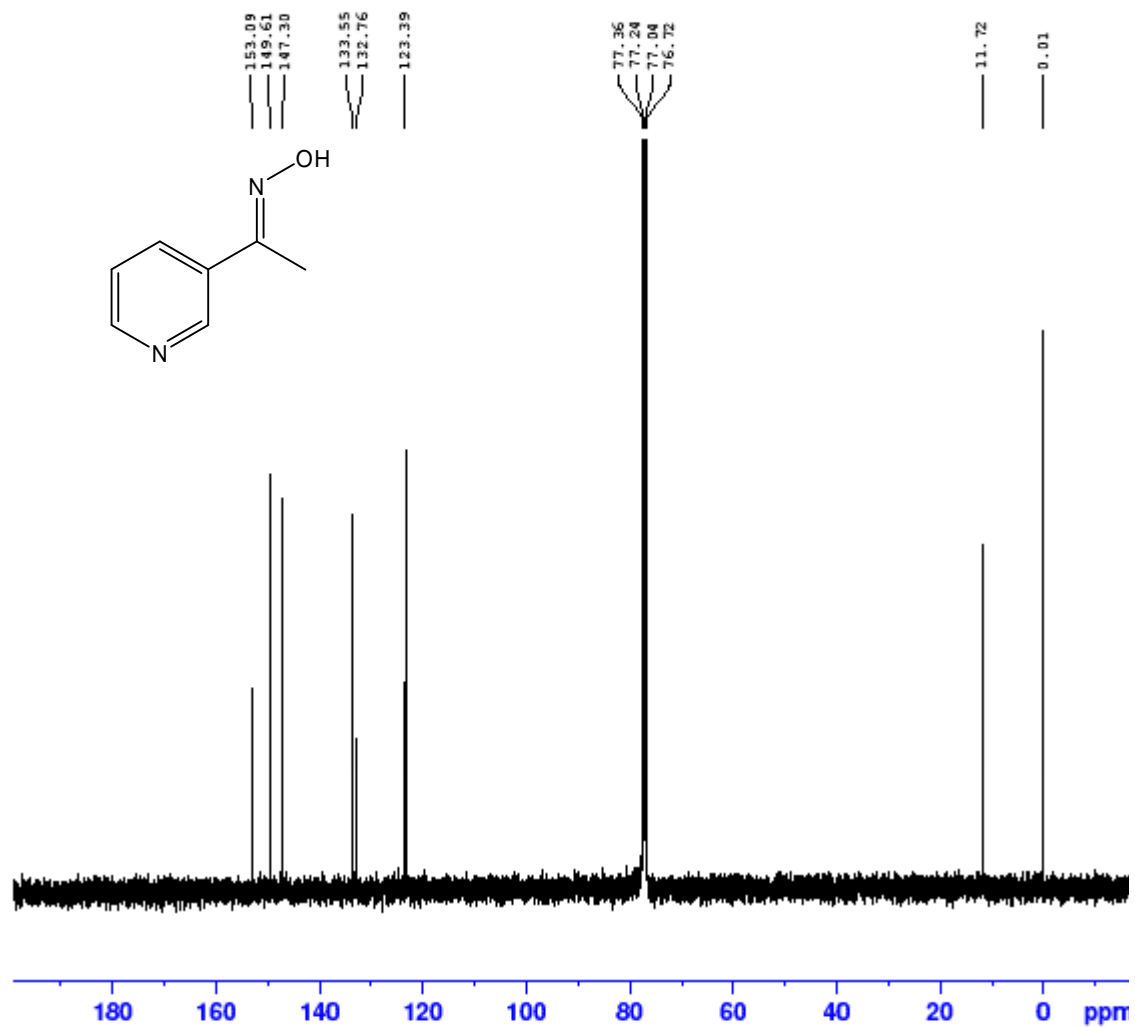
1-(pyridin-2-yl)ethanone oxime (14)



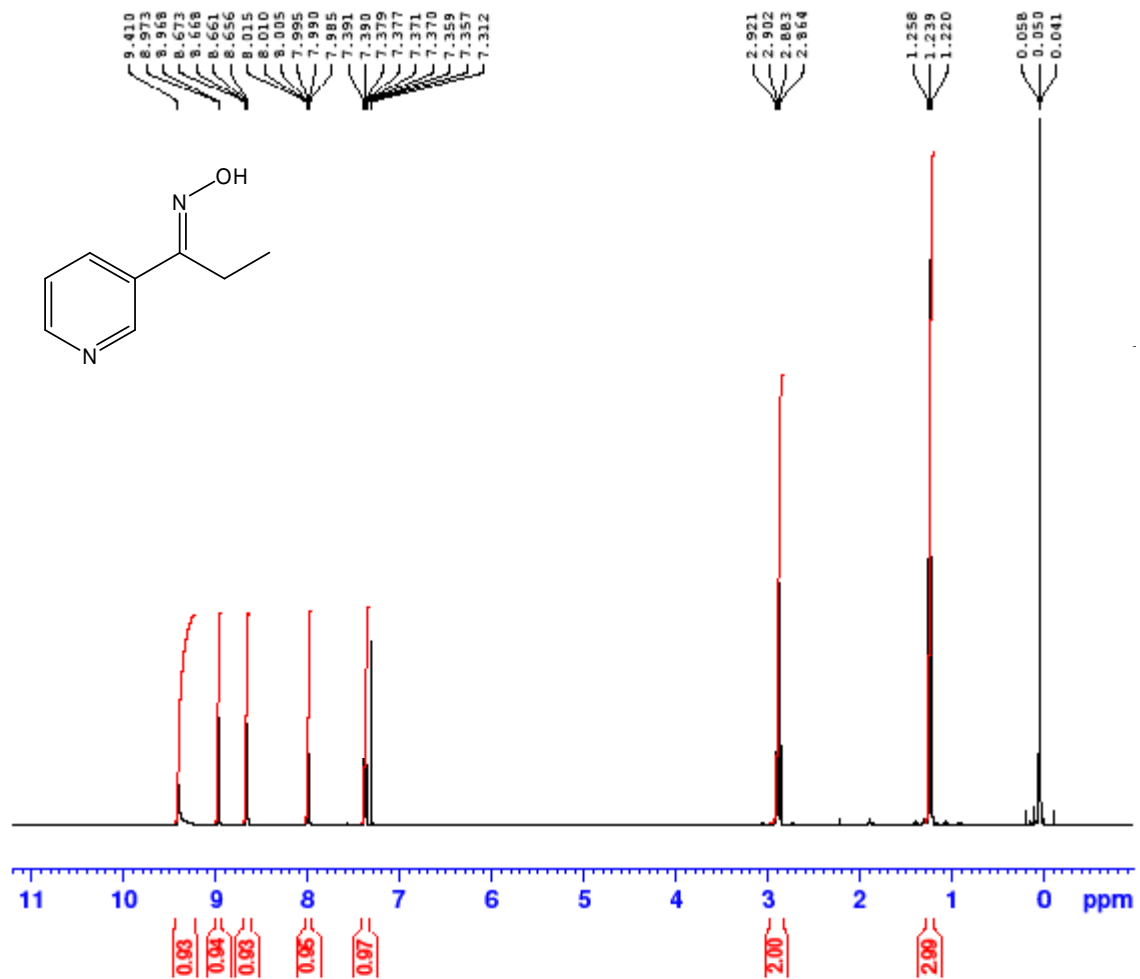
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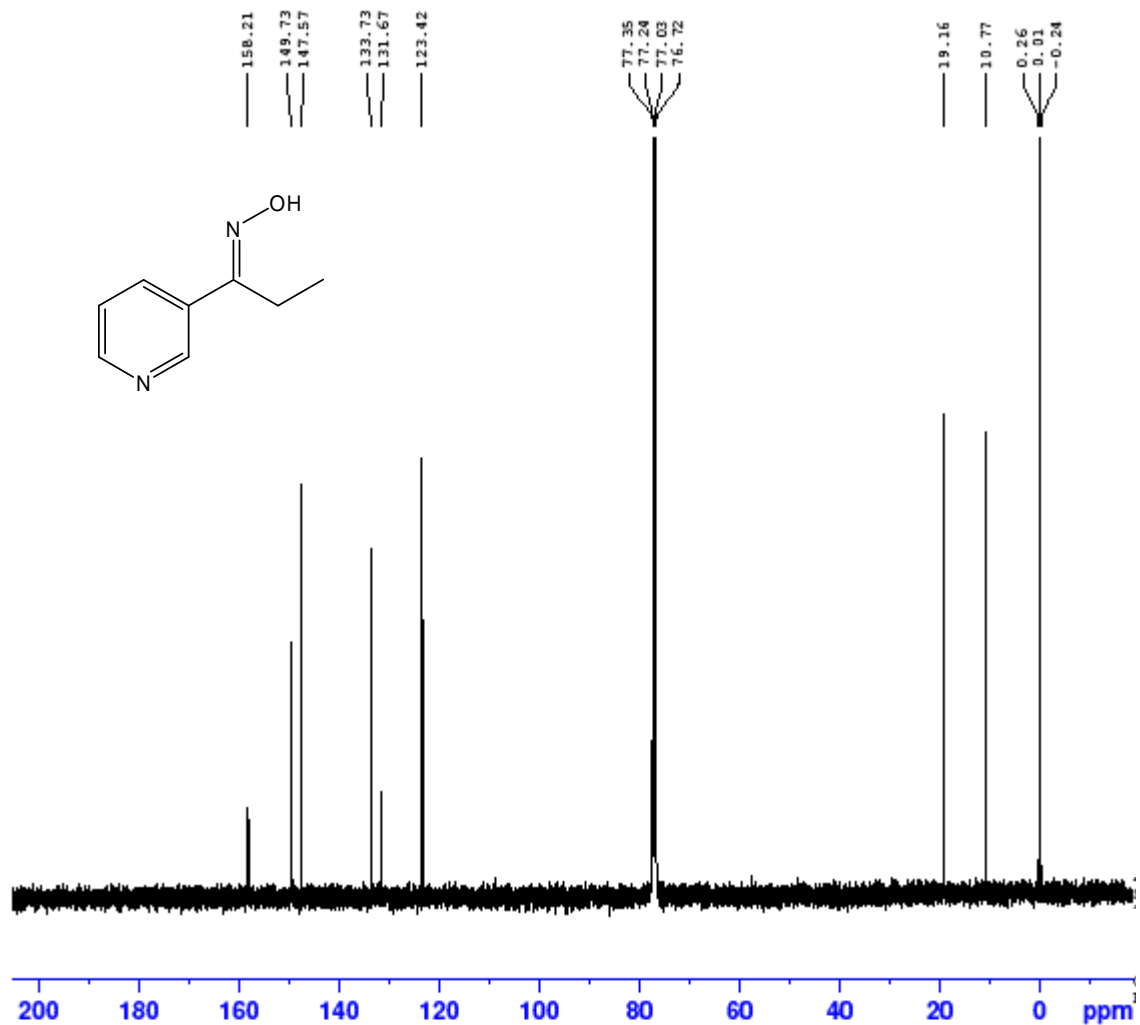
1-(pyridin-3-yl)ethanone oxime (14a)



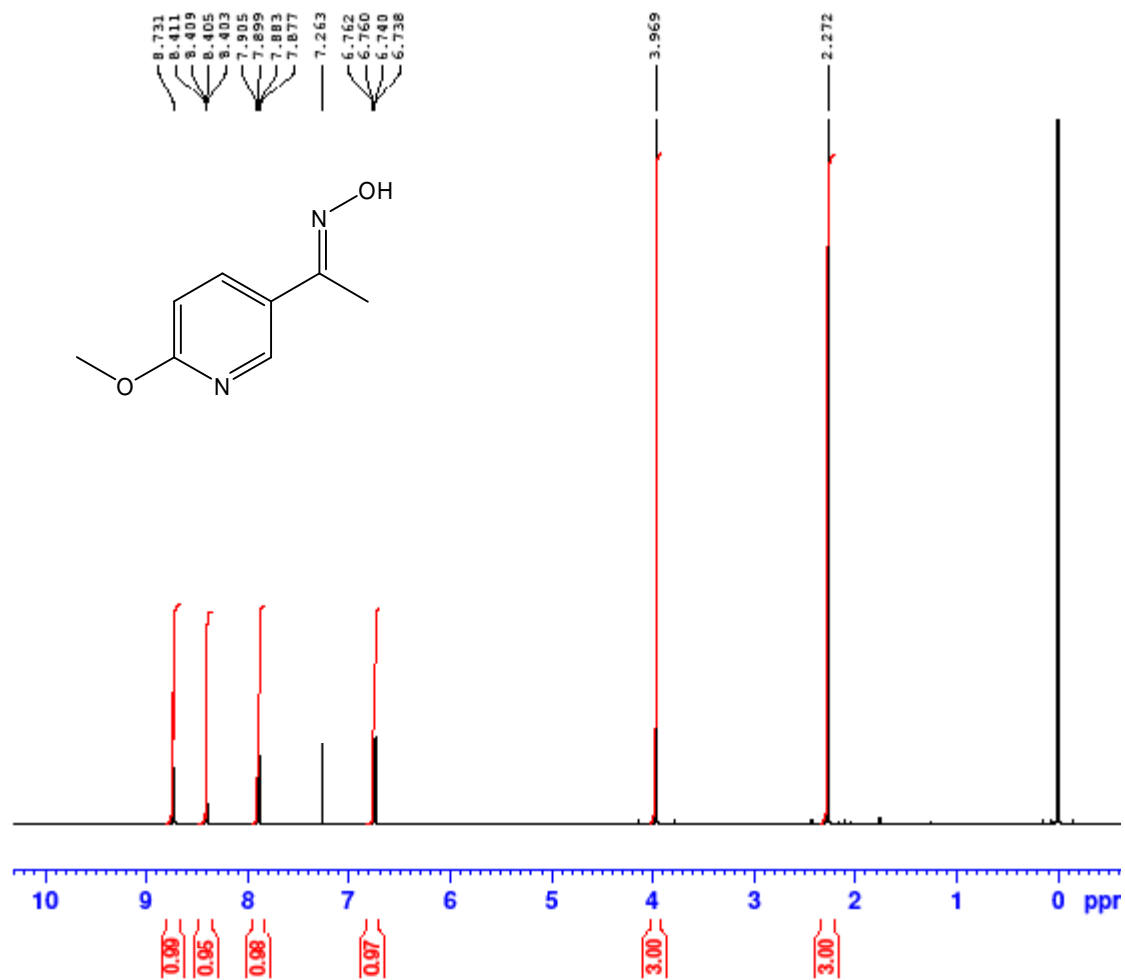
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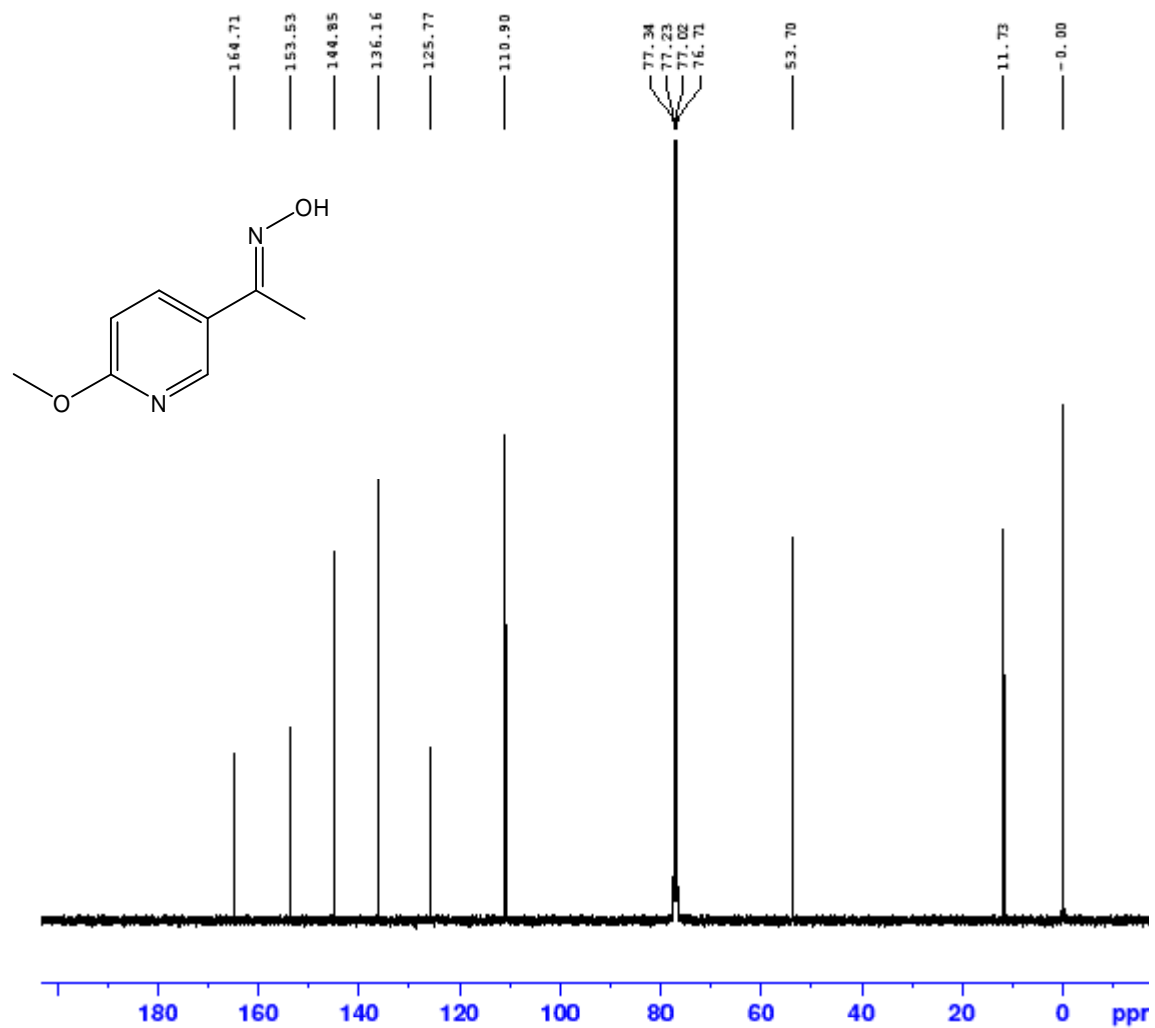
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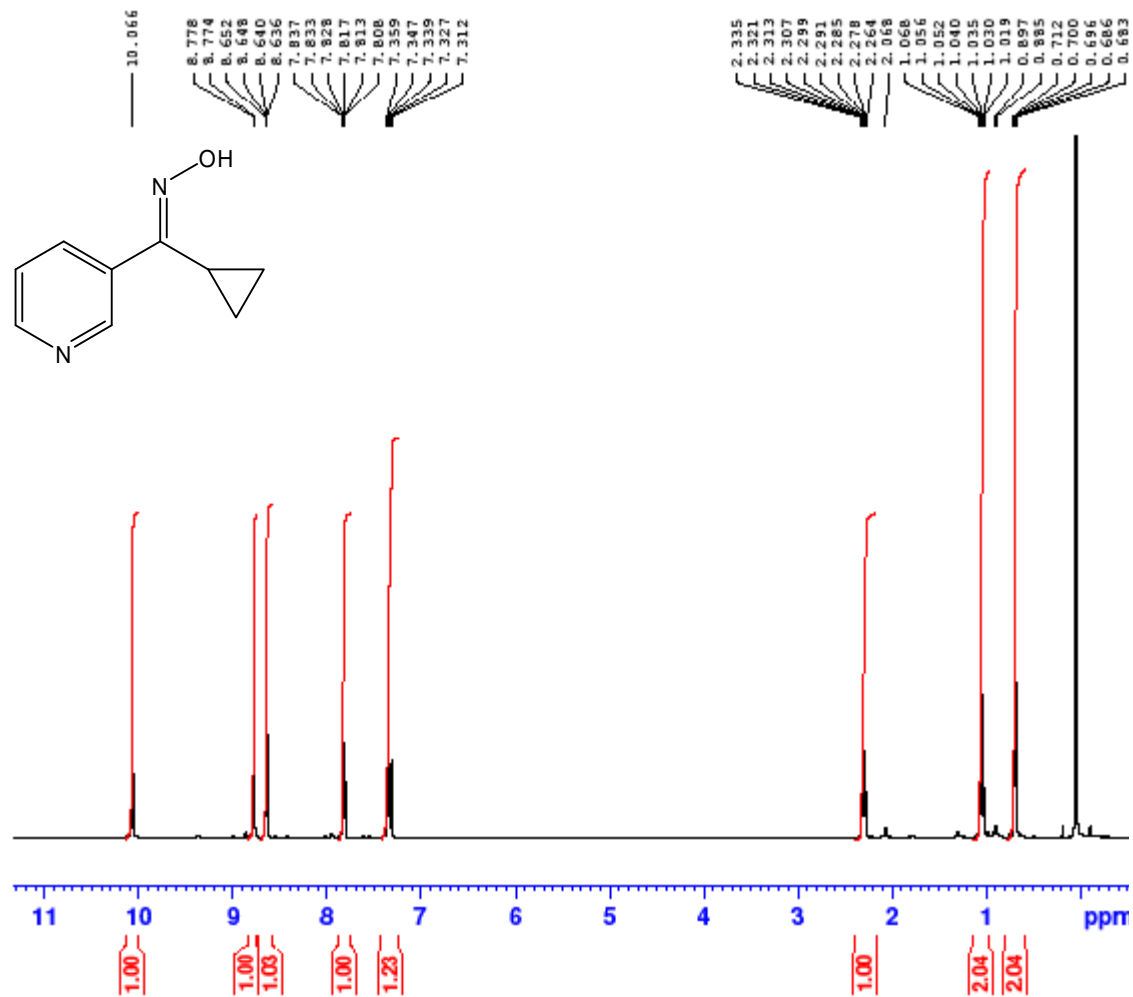
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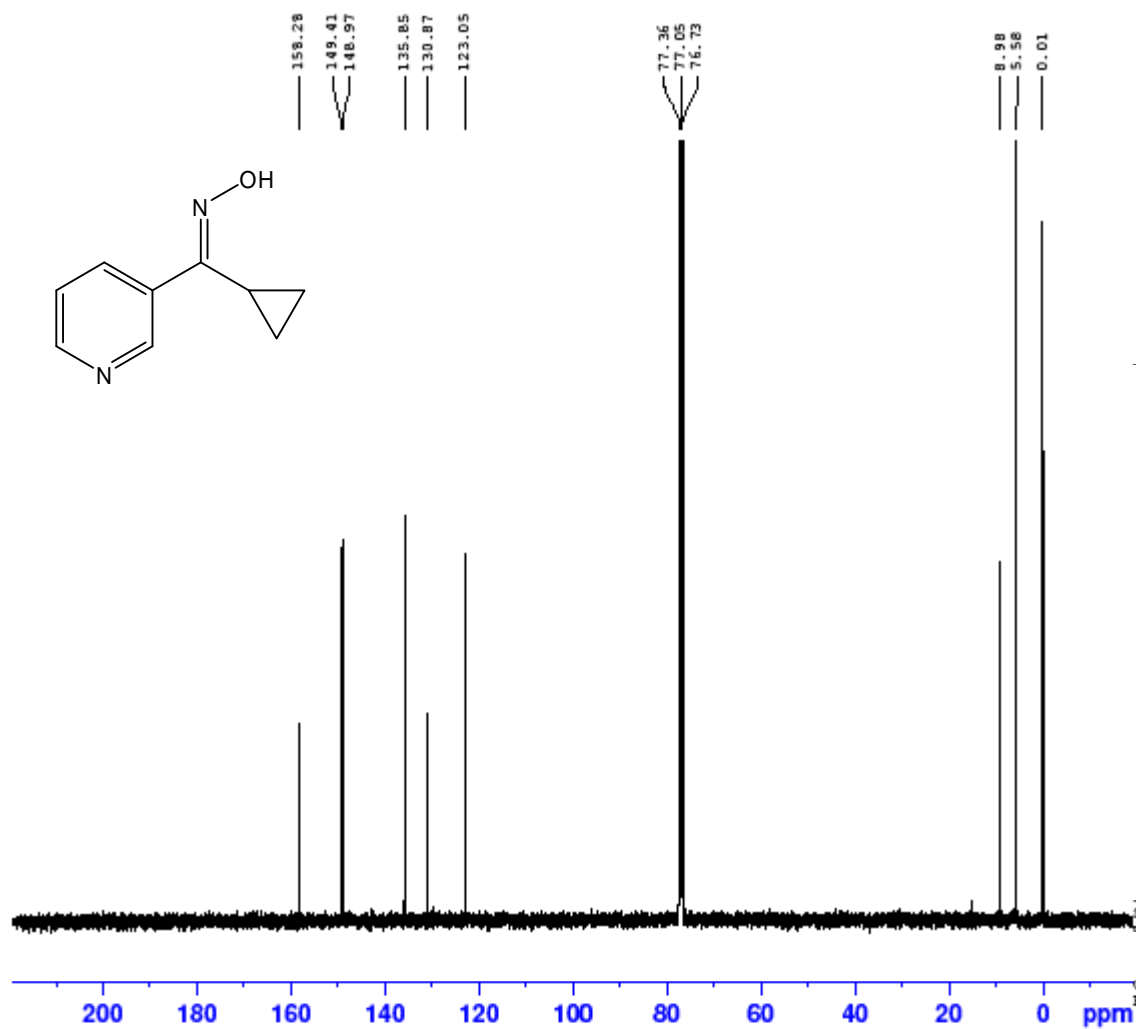
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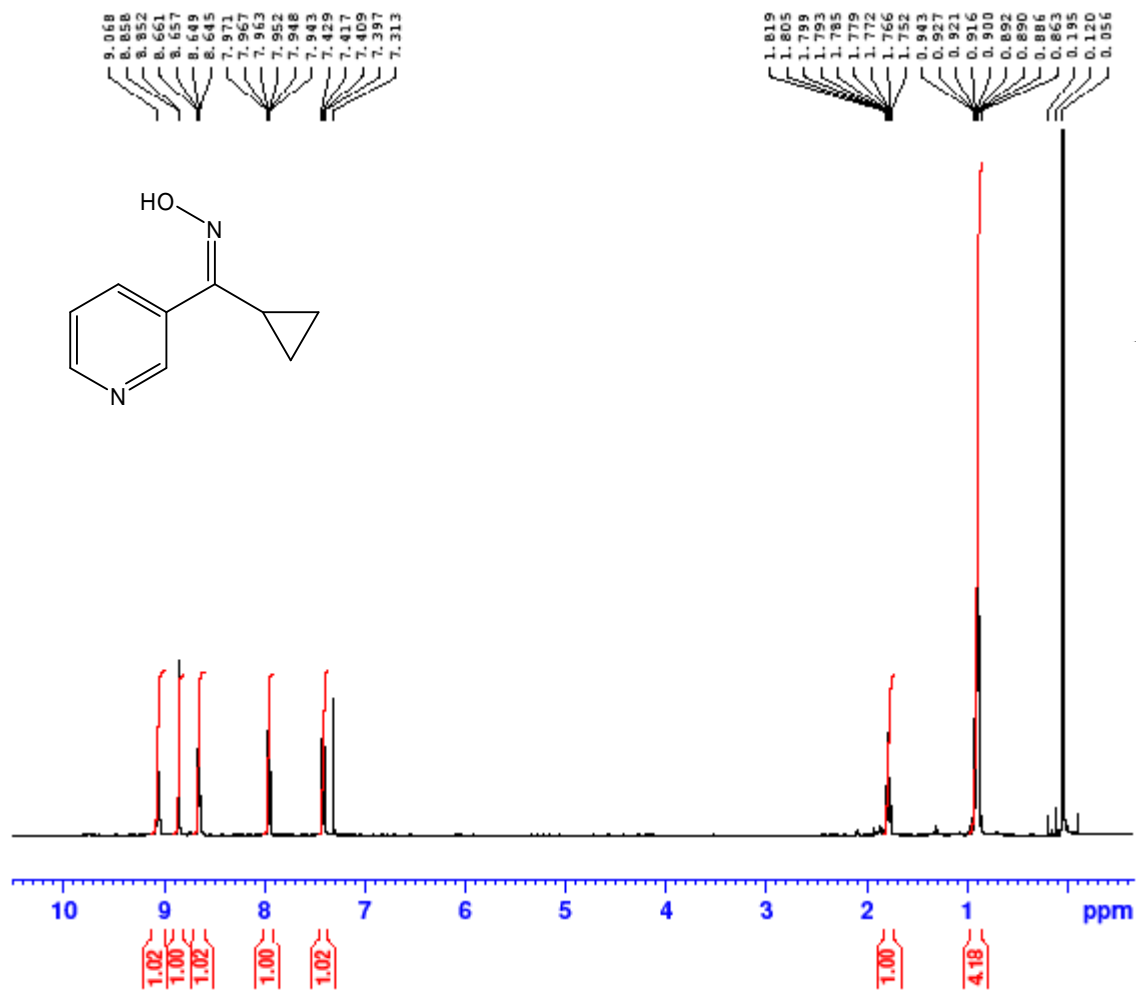
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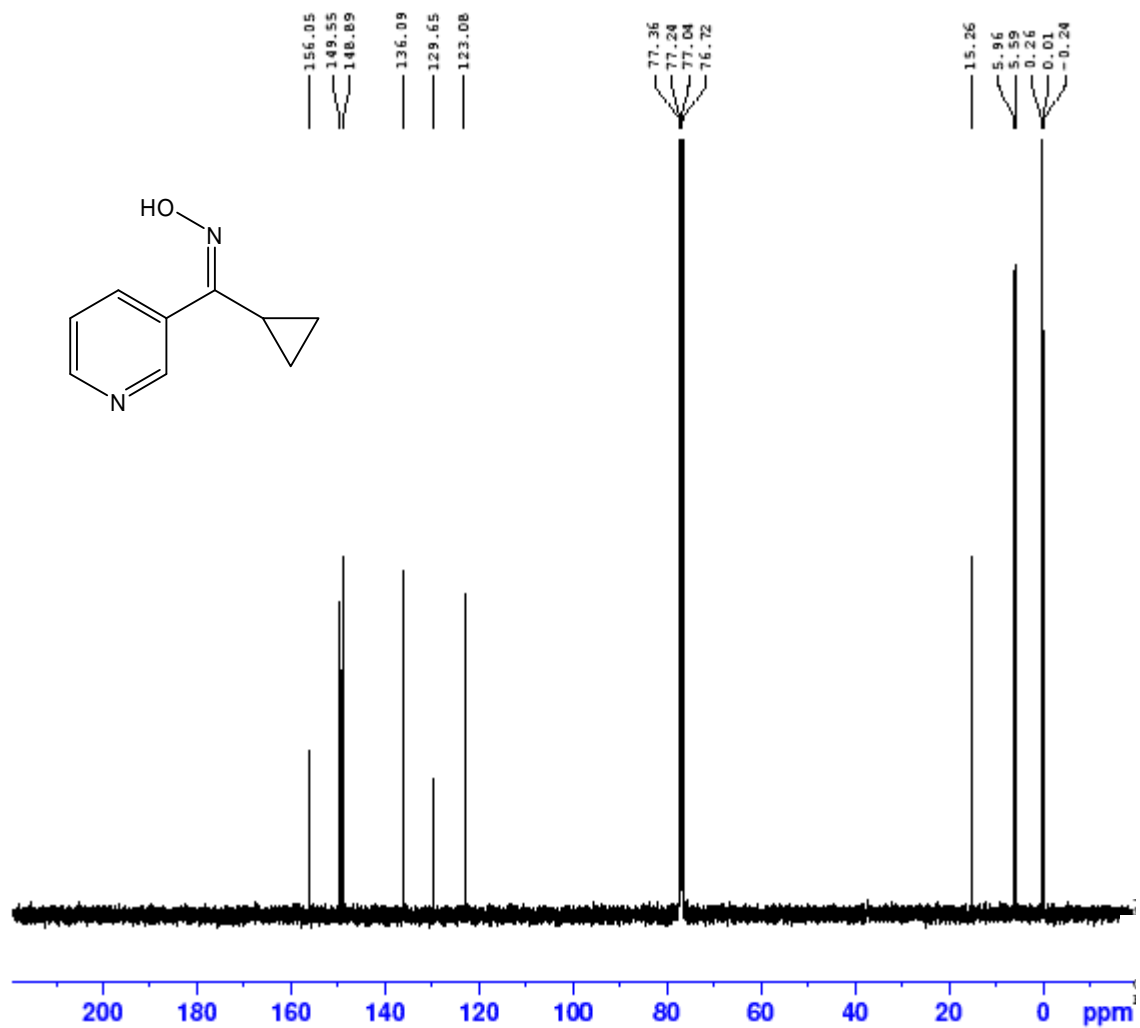
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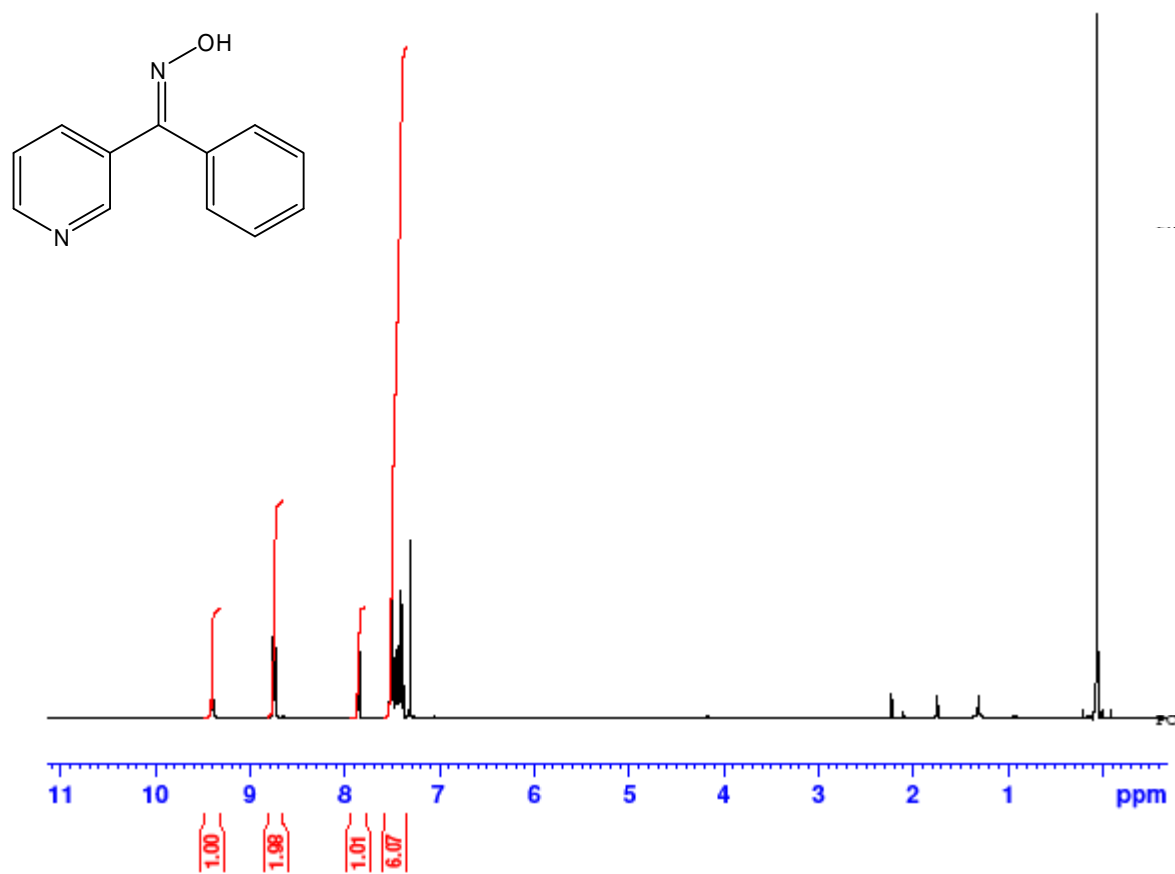
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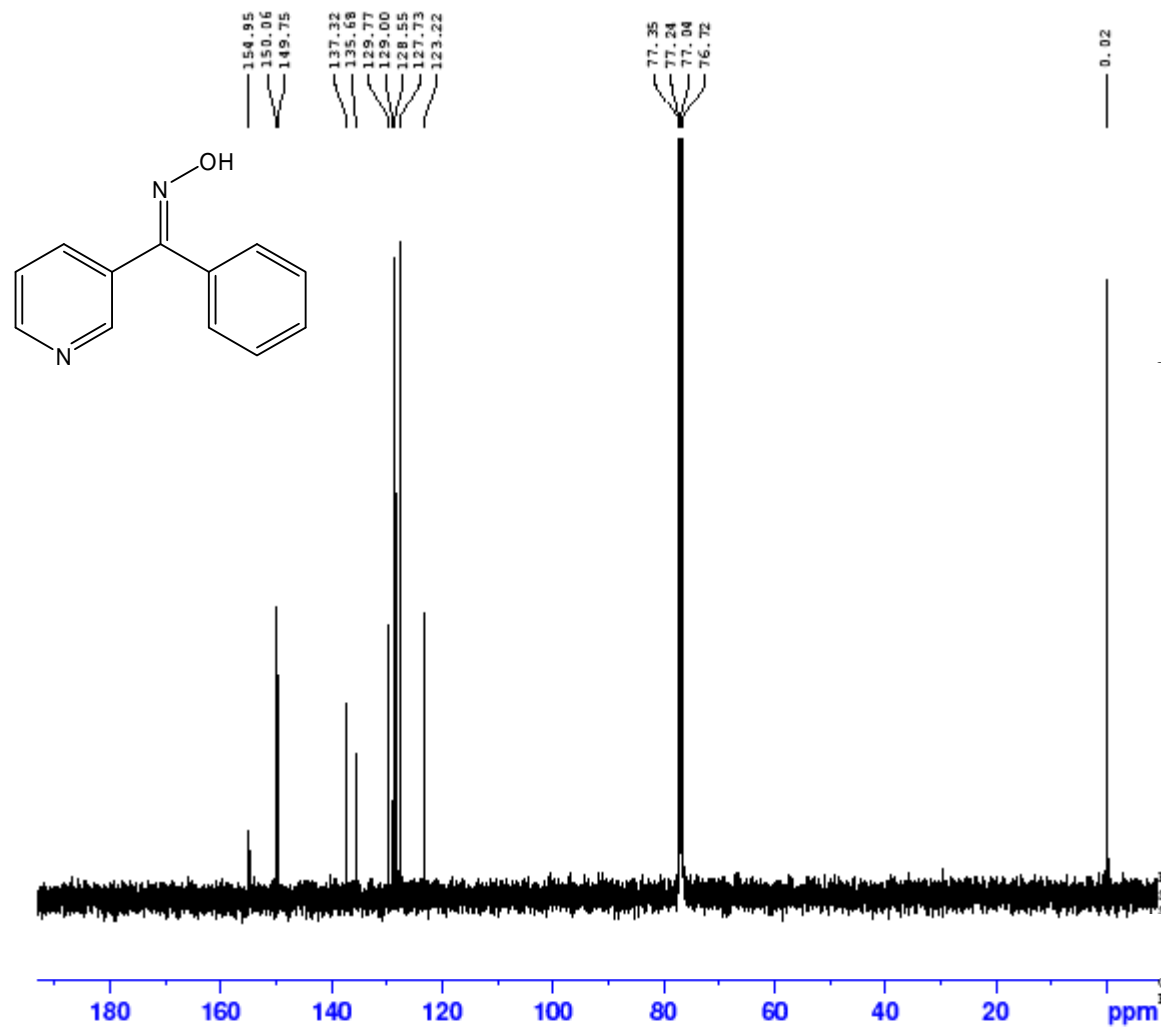
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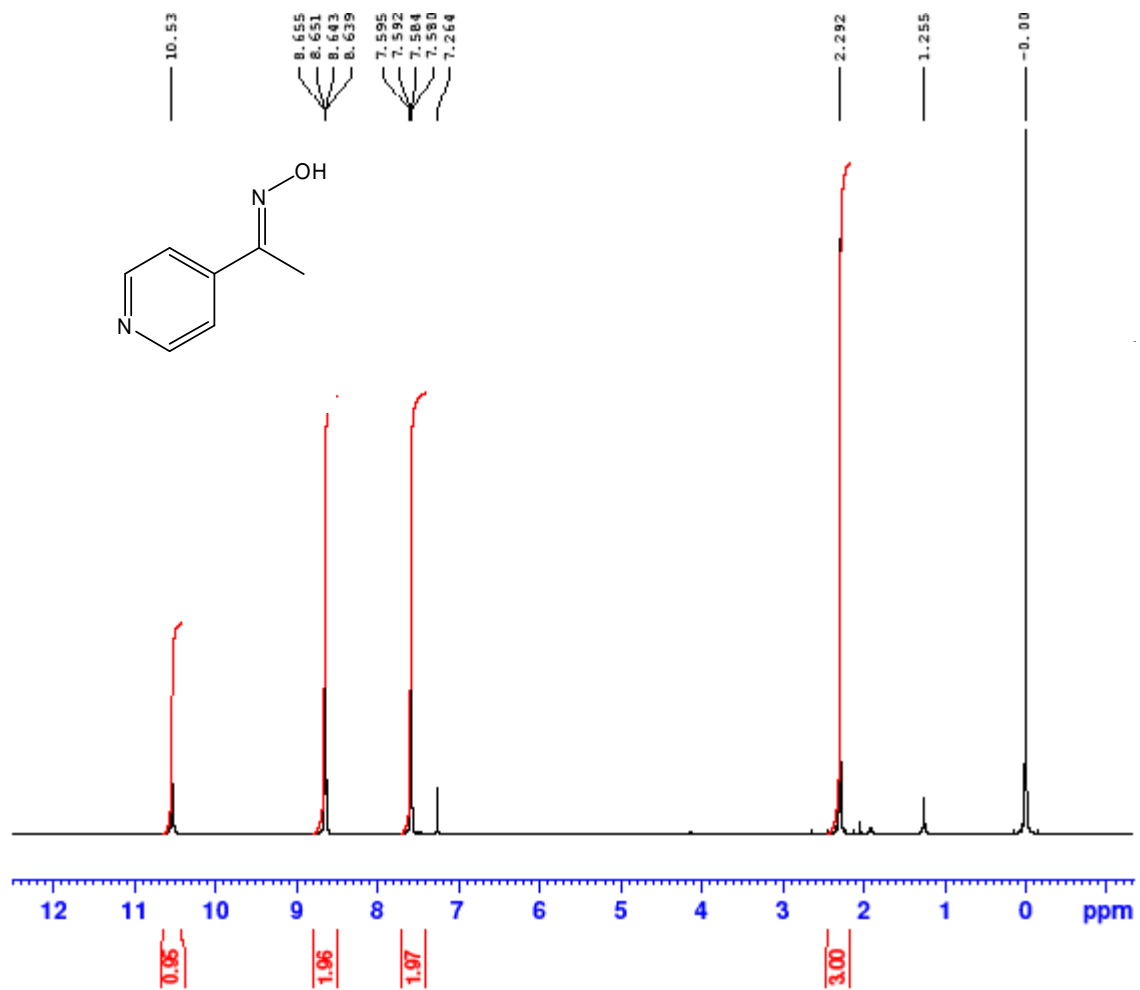
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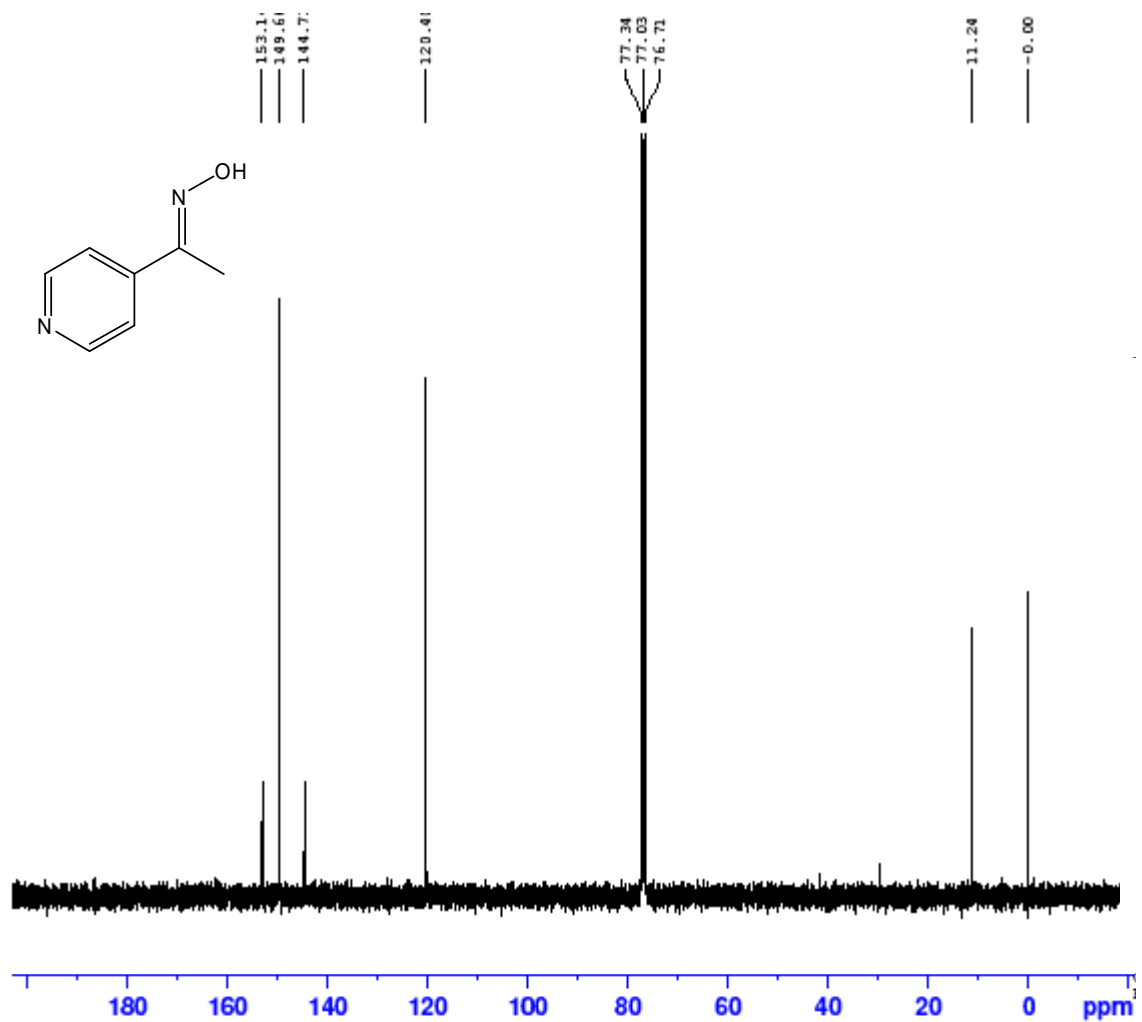
Phenyl(pyridin-3-yl)methanone oxime (14e)



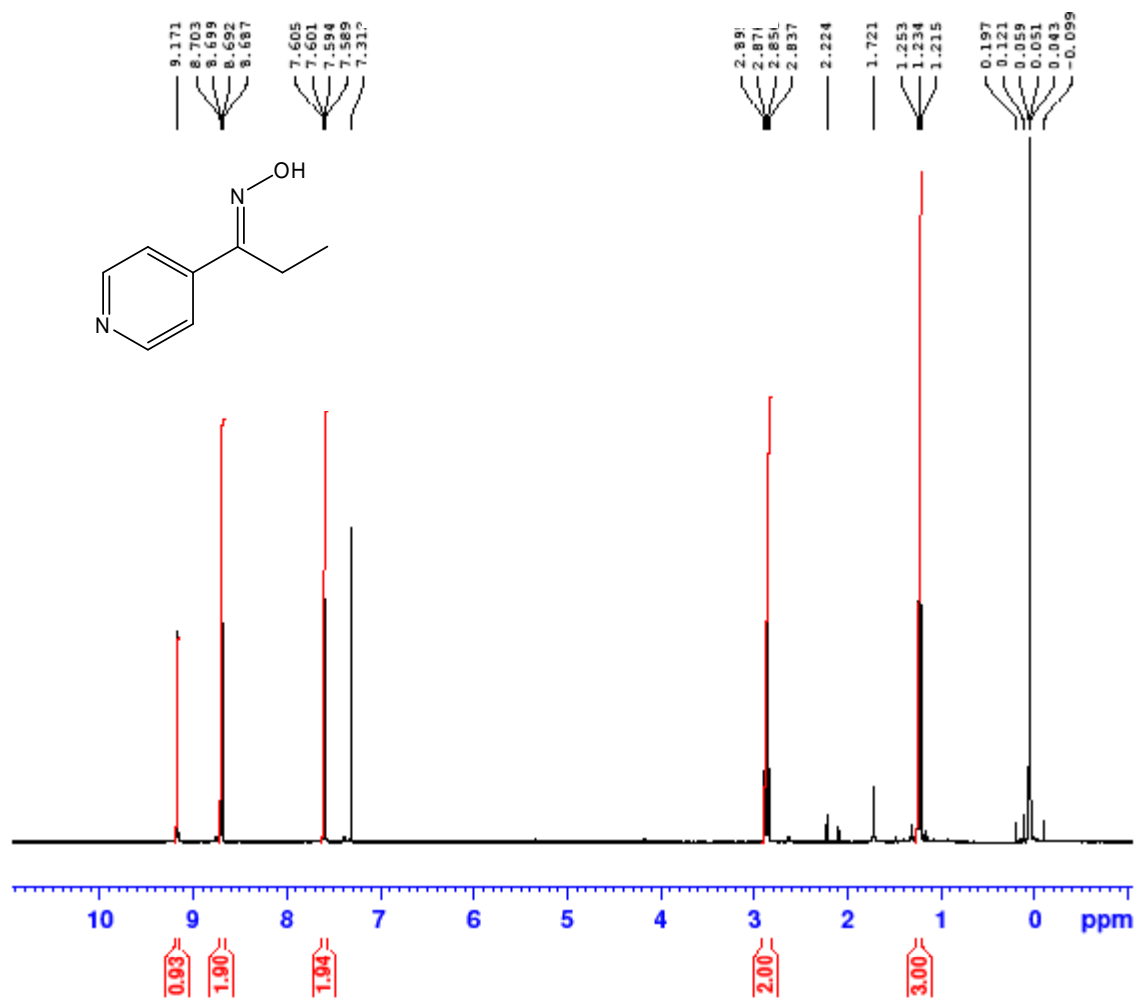
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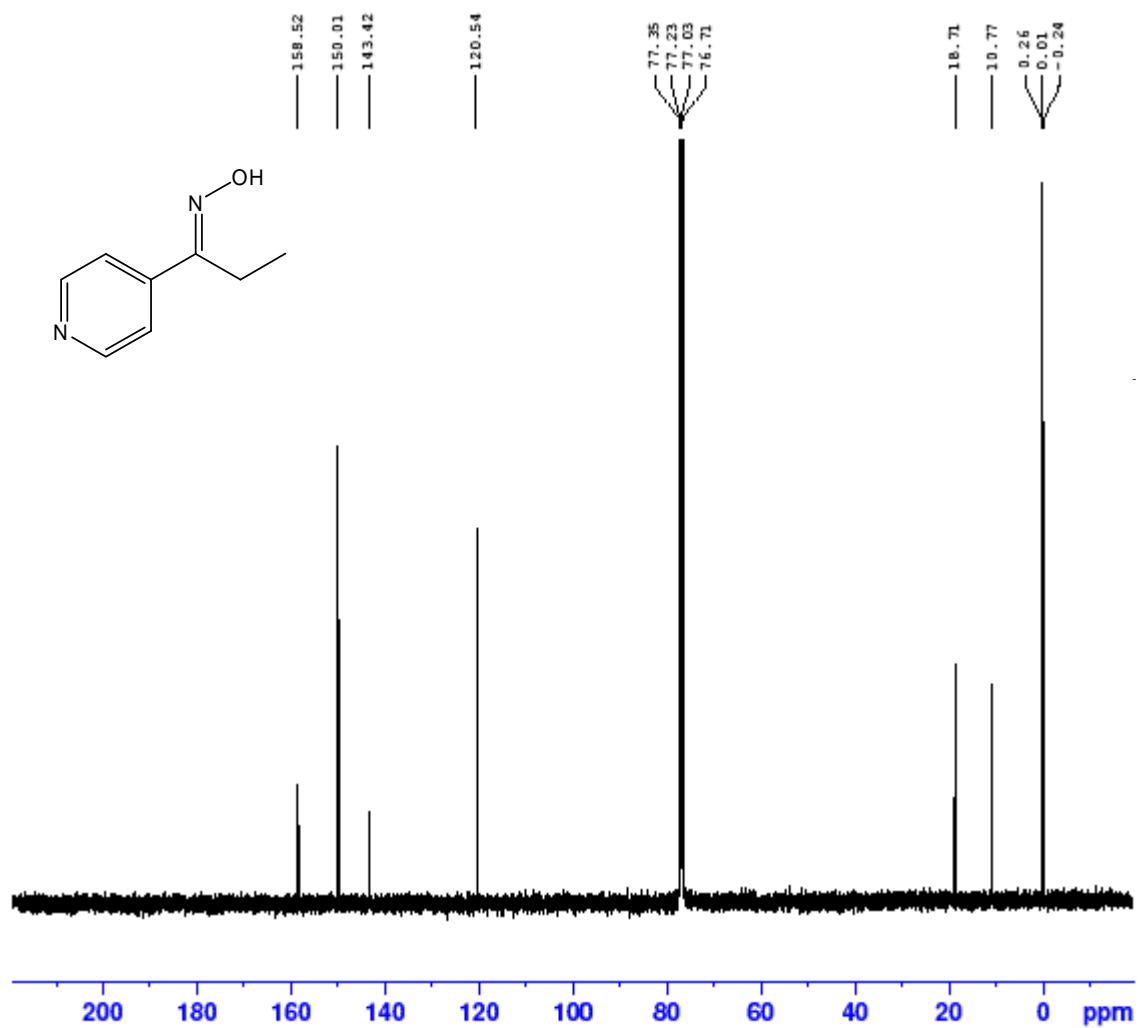
1-(pyridin-4-yl)ethanone oxime (14f)



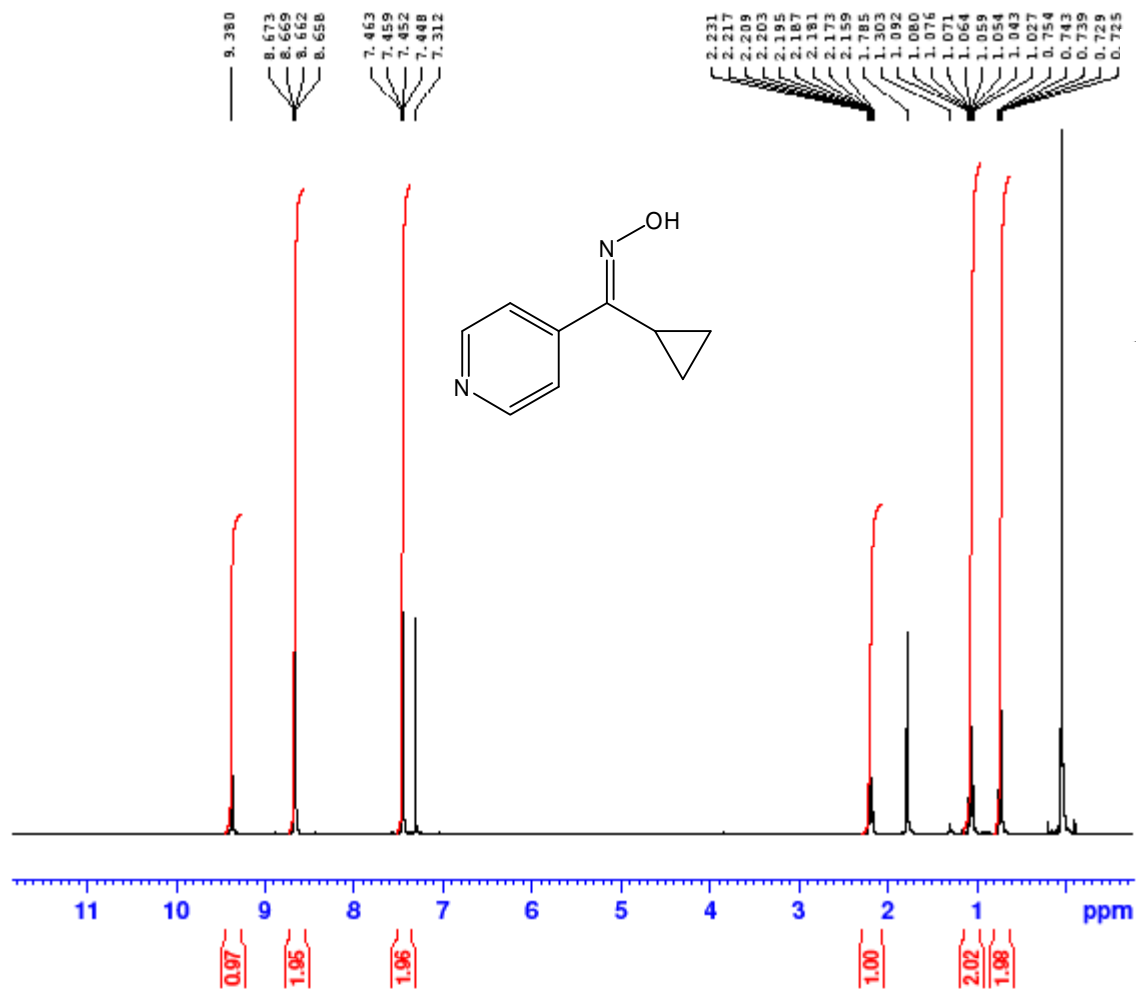
1-(pyridin-4-yl)propan-1-one oxime (14g)



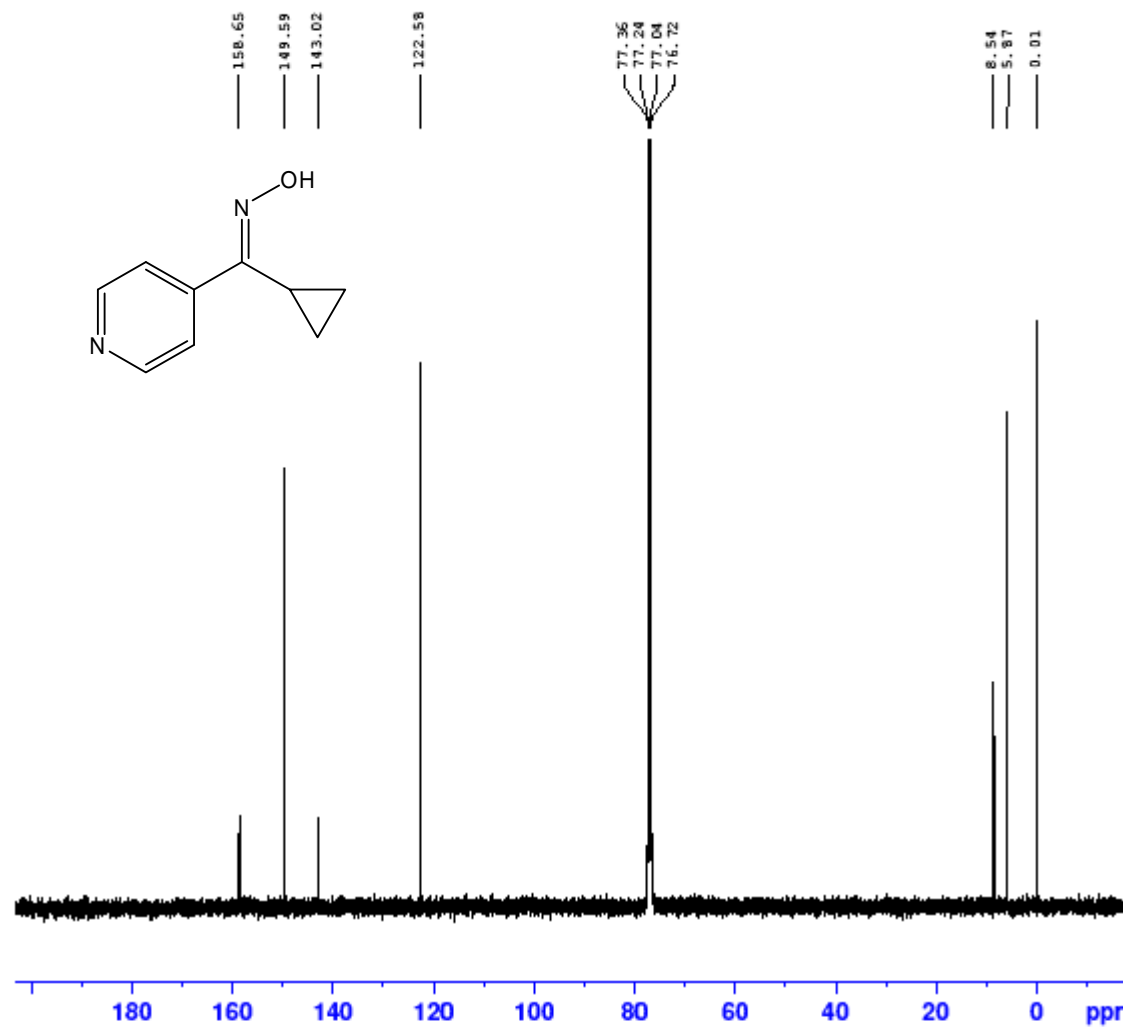
1-(pyridin-4-yl)propan-1-one oxime (14g)



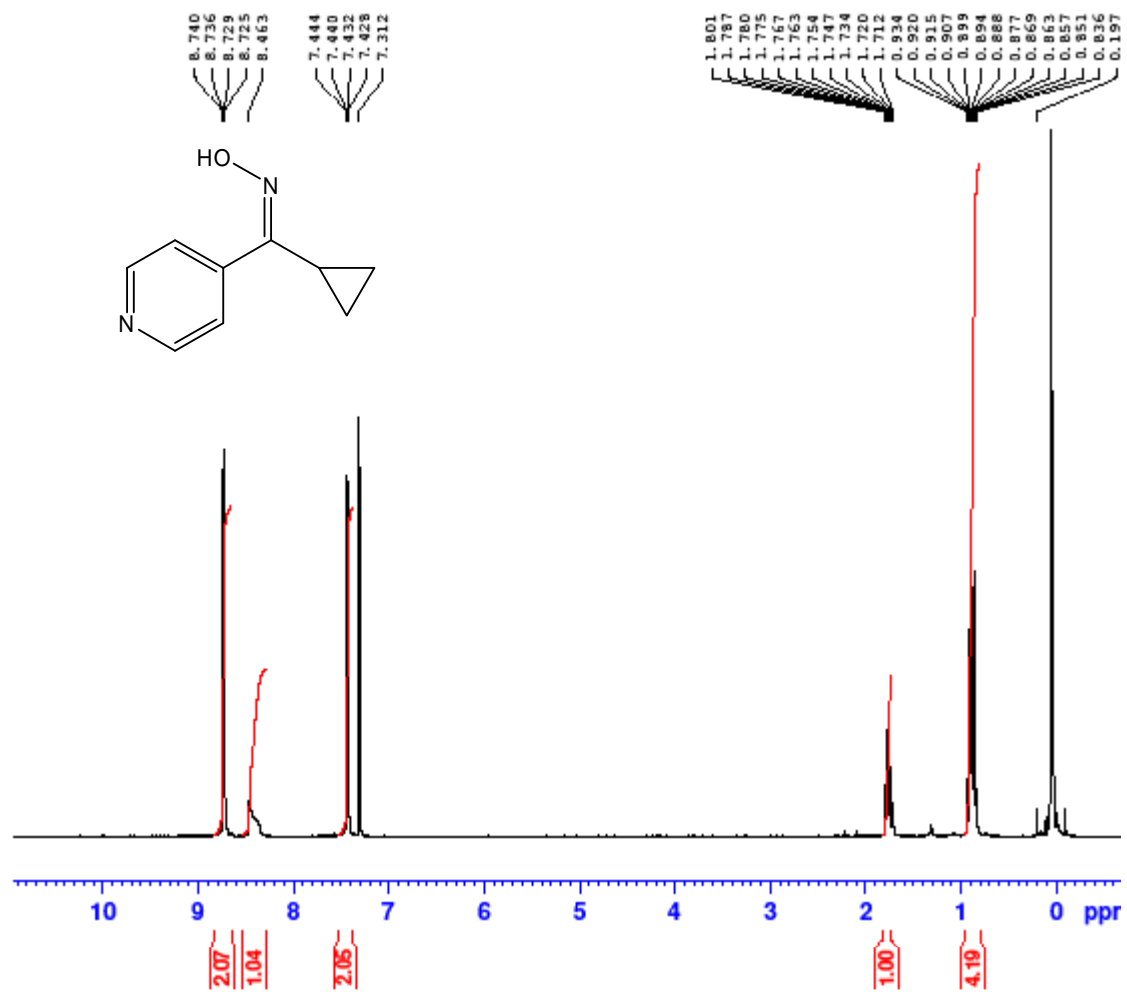
(E)-cyclopropyl(pyridin-4-yl)methanone oxime (14h_E)



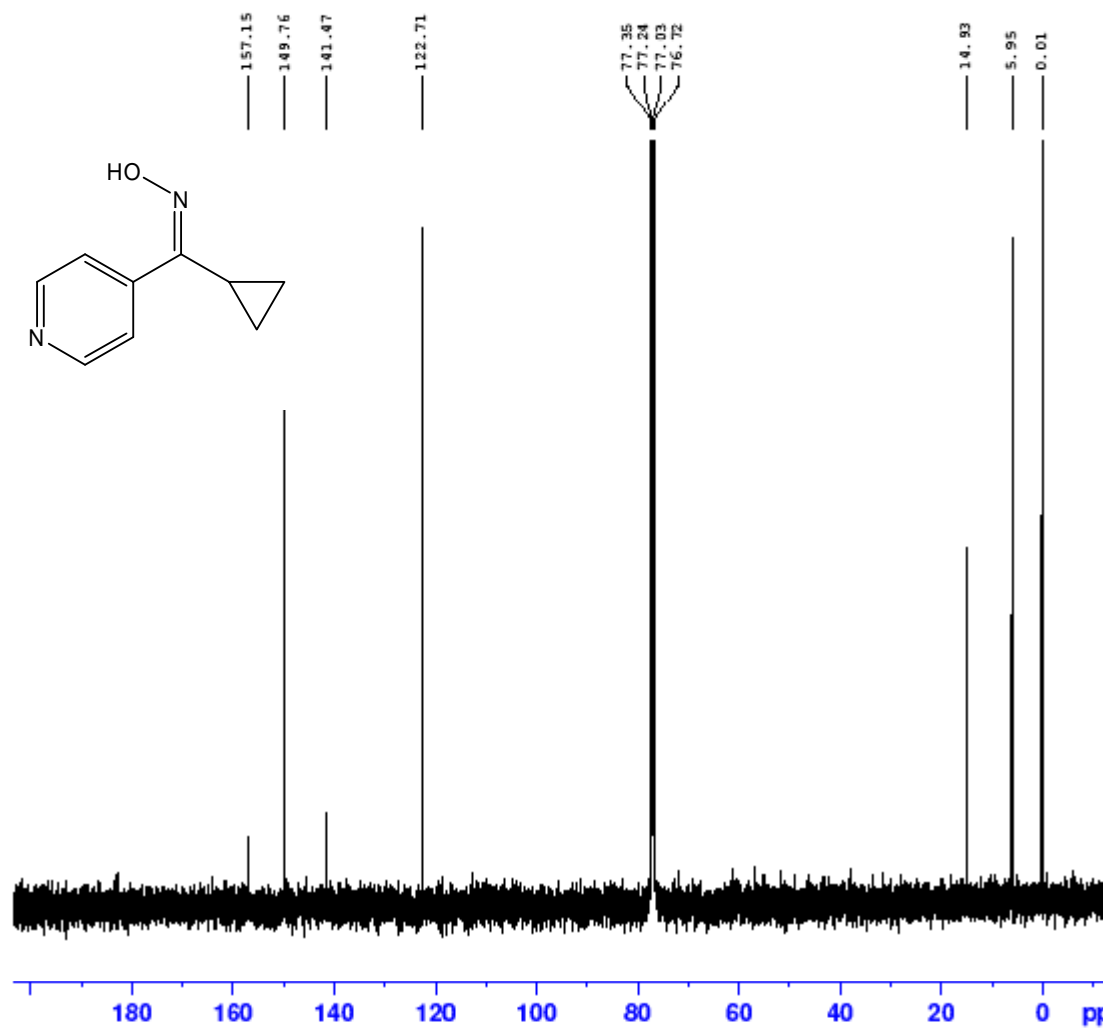
(E)-cyclopropyl(pyridin-4-yl)methanone oxime (14h_E)



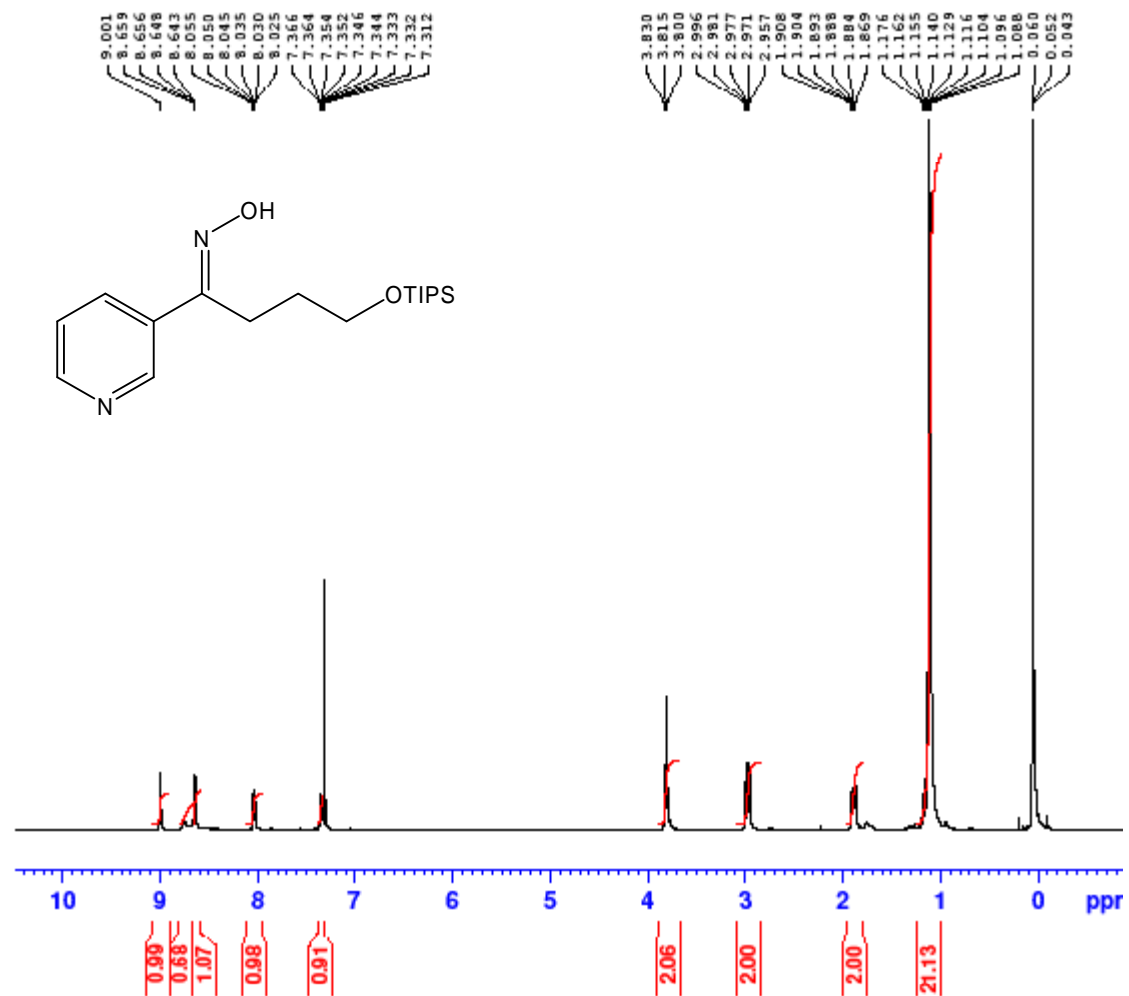
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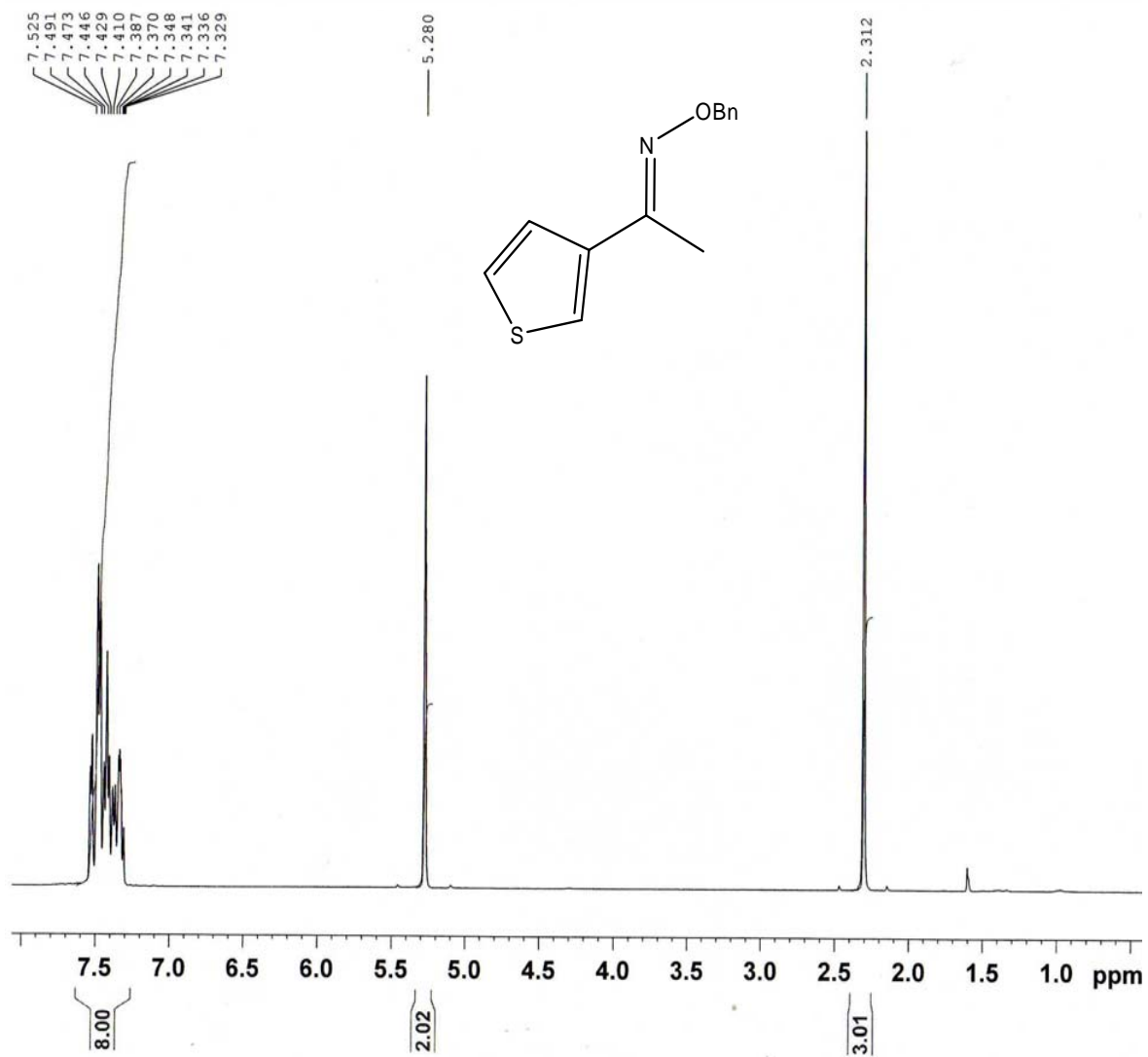
(Z)-cyclopropyl(pyridin-4-yl)methanone oxime (14h₂)



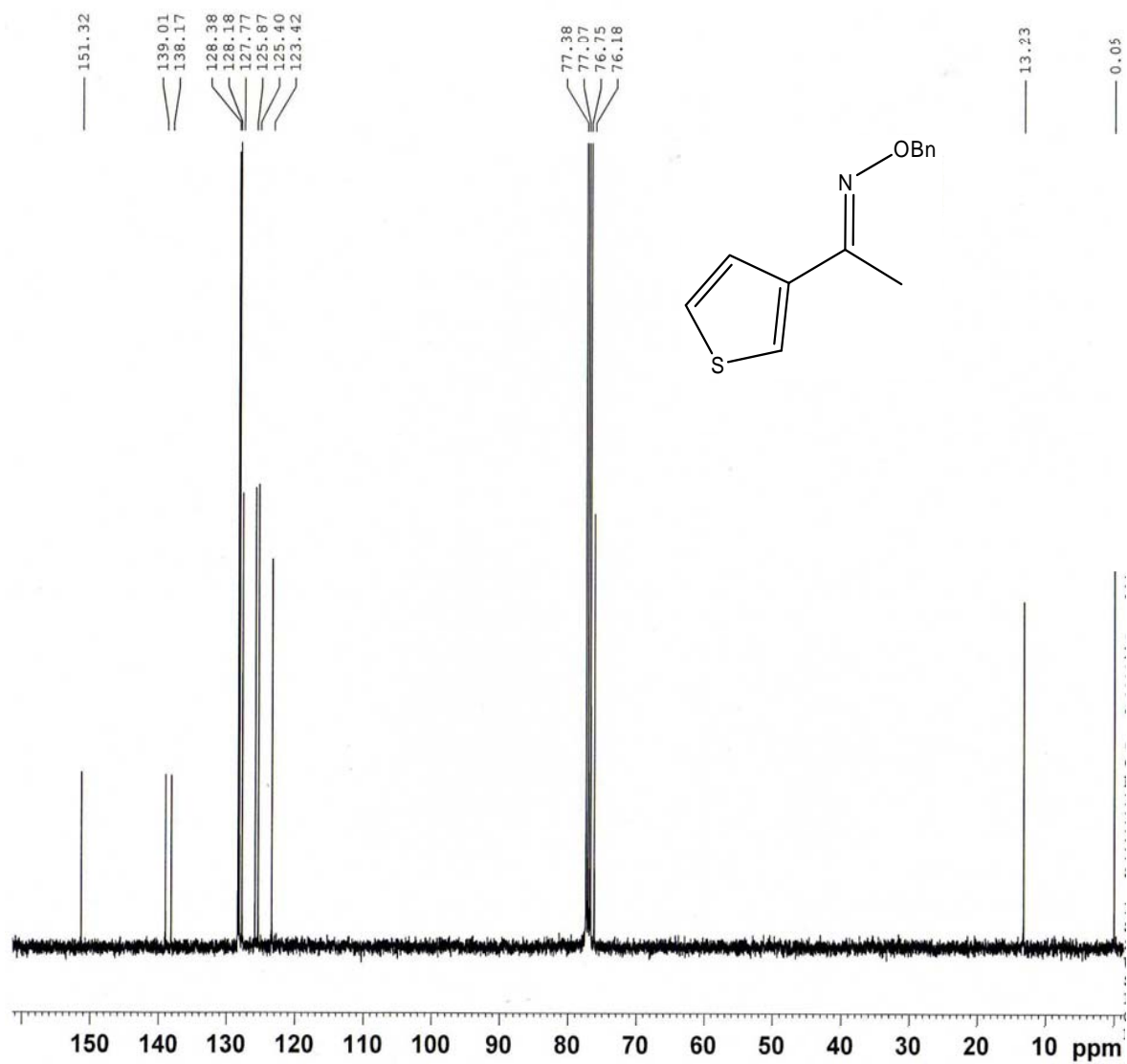
(E)-1-(pyridine-3yl)-4-(triisopropylsilyloxy)butan-1-one oxime (14i)



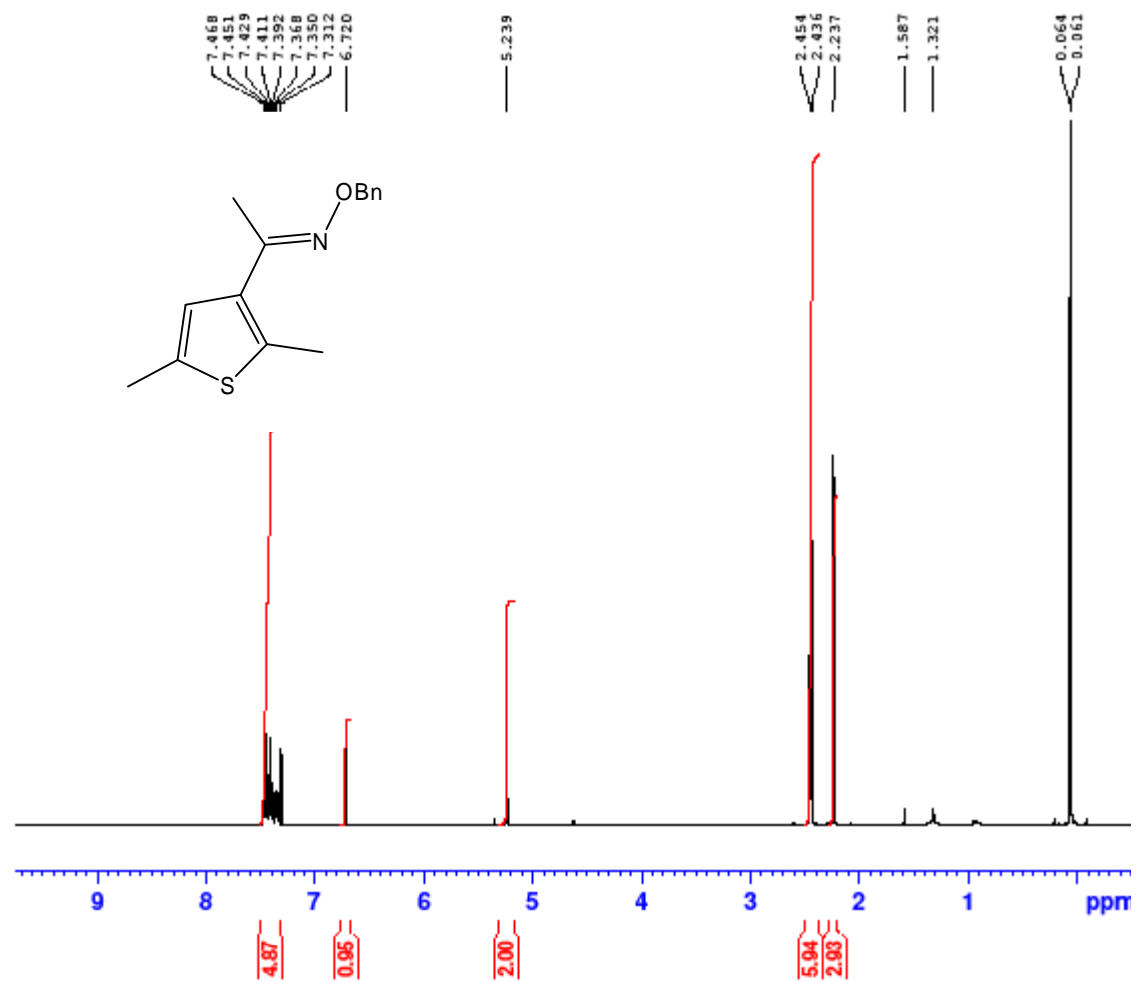
(E)-1-(Thiophen-3-yl)ethanone O-benzoyloxime (15a)



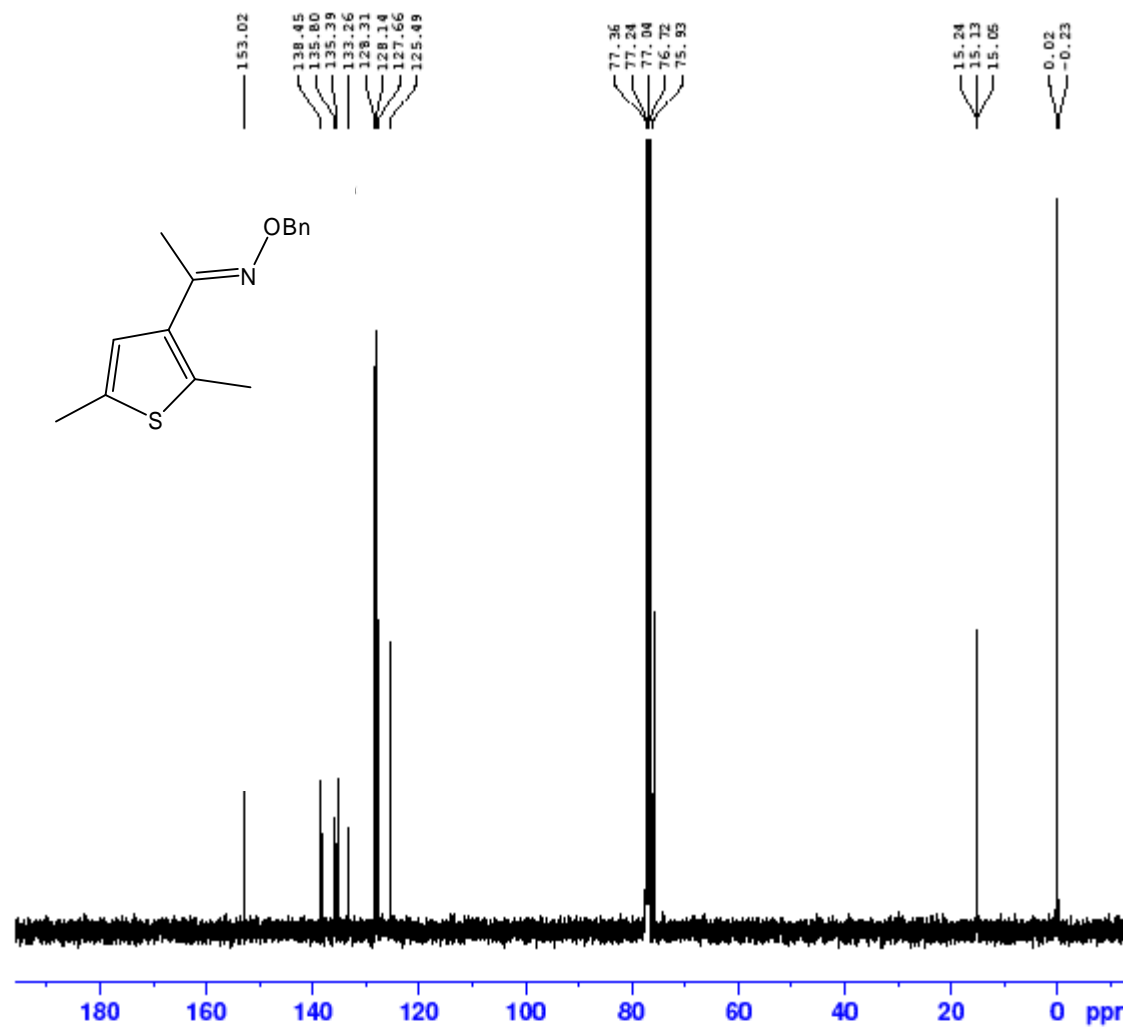
(E)-1-(Thiophen-3-yl)ethanone O-benzoyloxime (15a)



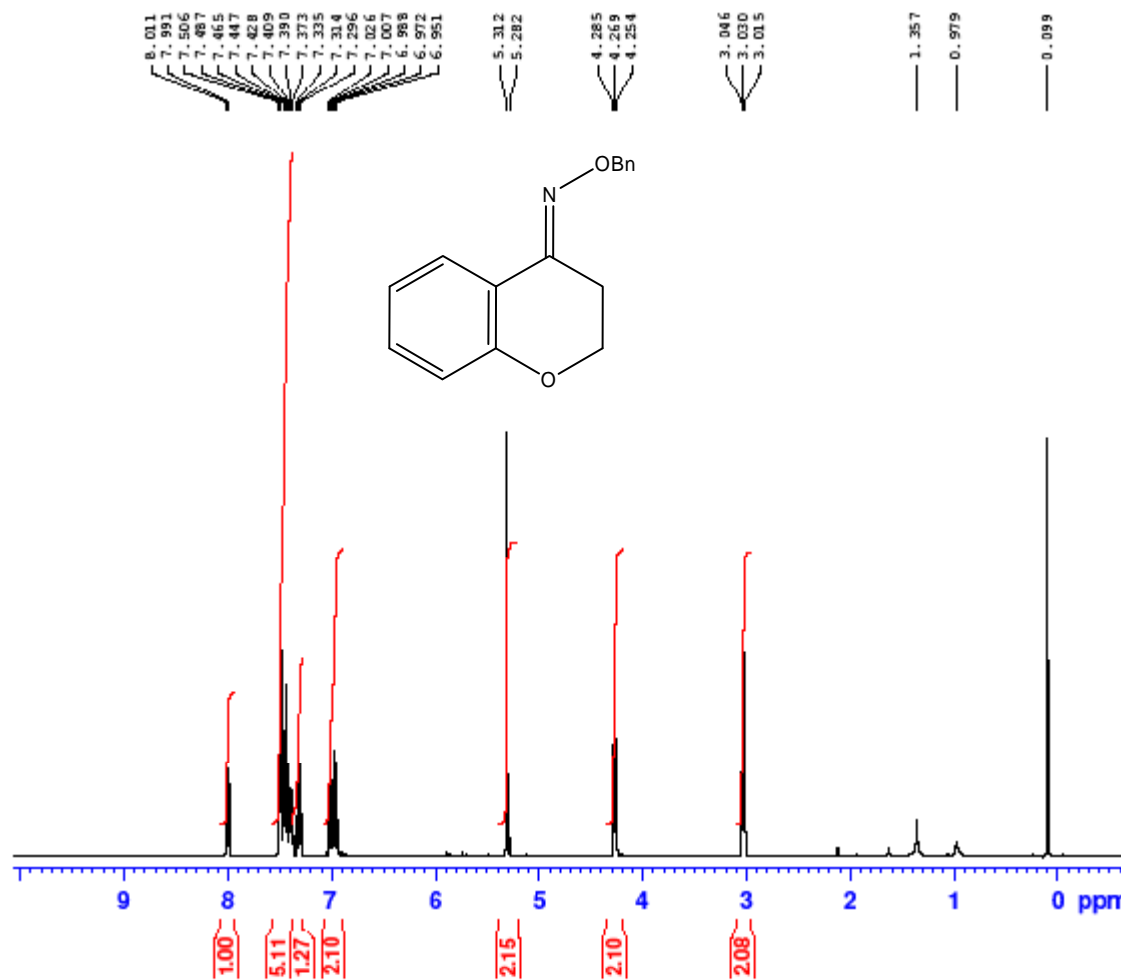
(E)-1-(2,5-dimethylthiophen-3-yl)ethanone O-benzyl oxime (15b)



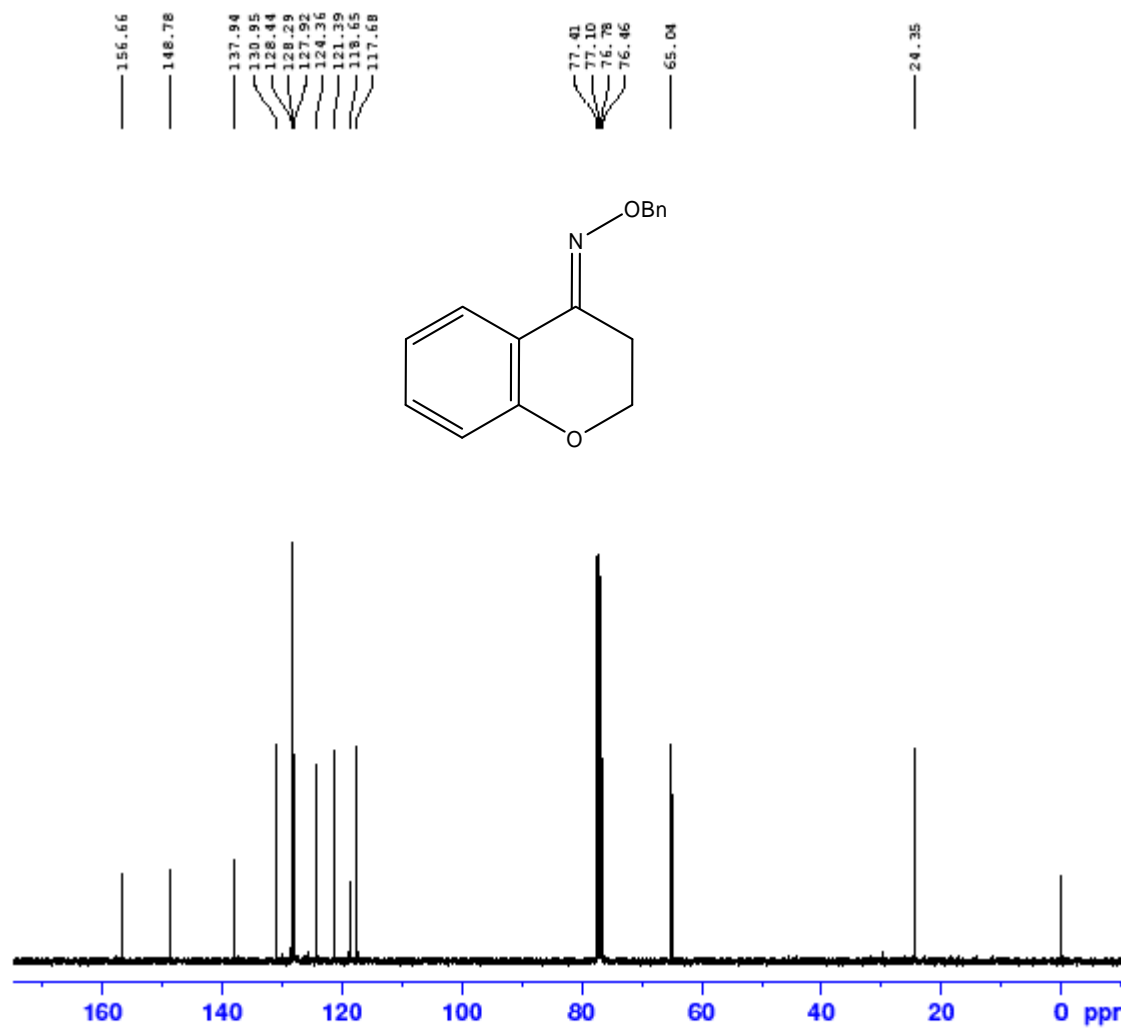
(E)-1-(2,5-dimethylthiophen-3-yl)ethanone O-benzyl oxime (15b)



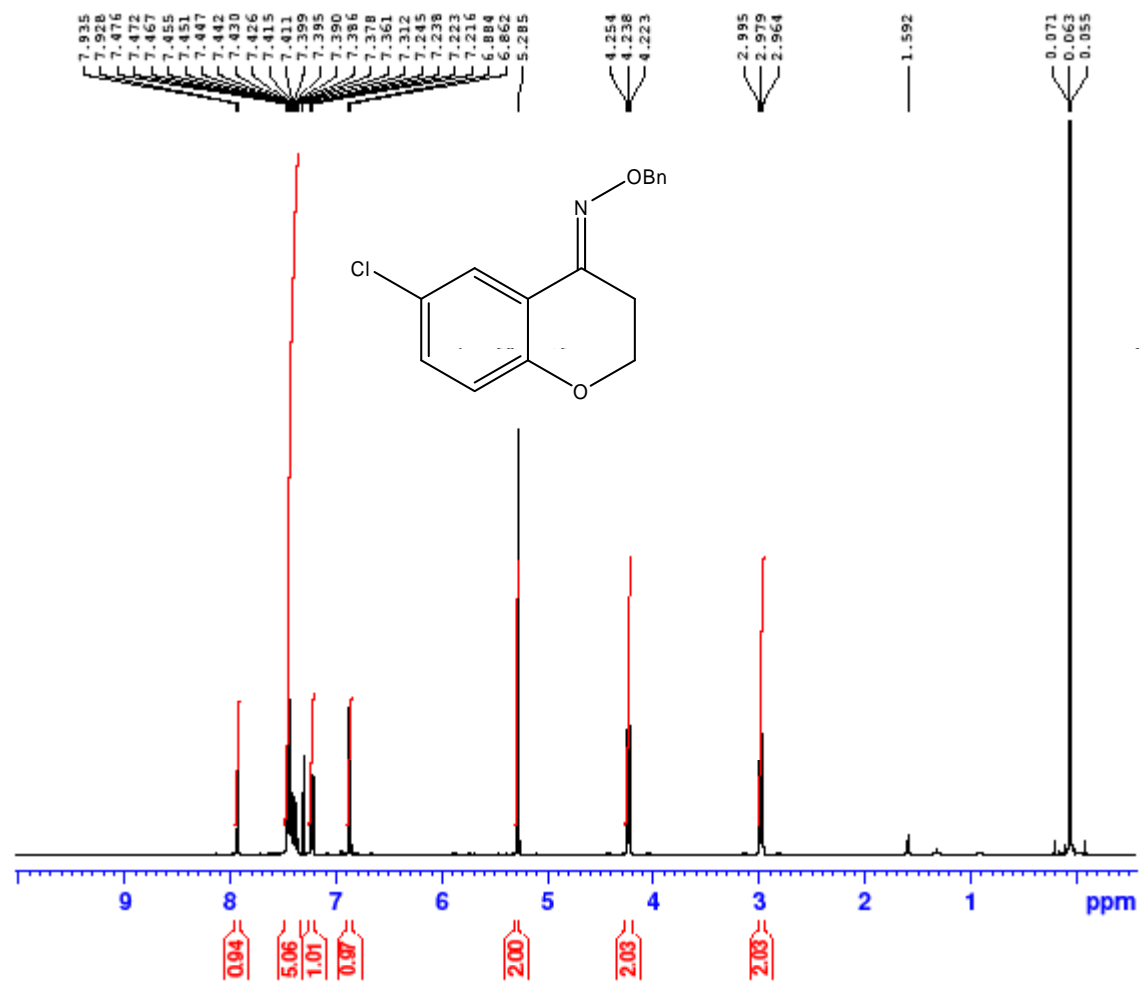
(E)-Chroman-4-one O-benzyl oxime (15c)



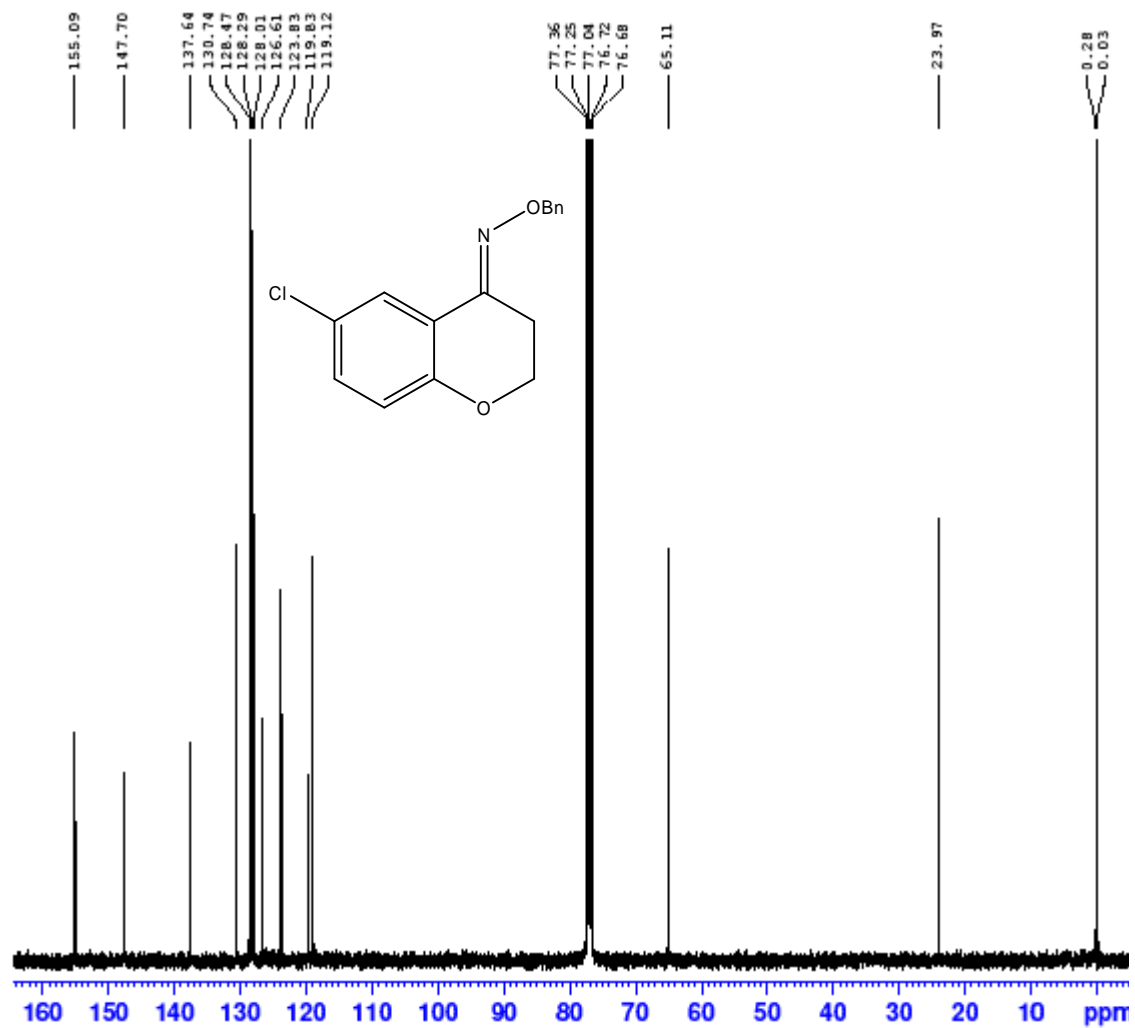
(E)-Chroman-4-one O-benzyl oxime (15c)



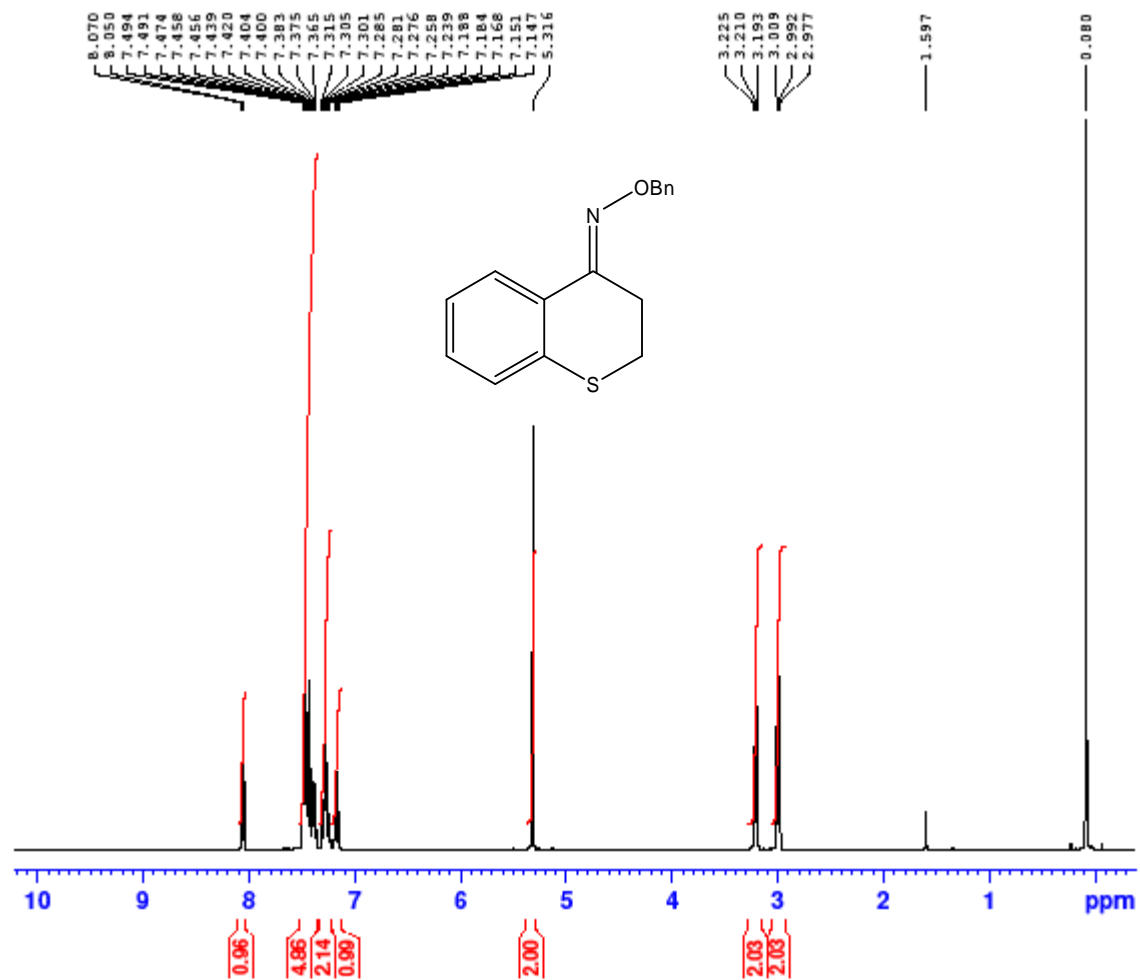
(E)-6-Chlorochroman-4-one O-benzyl oxime (15d)



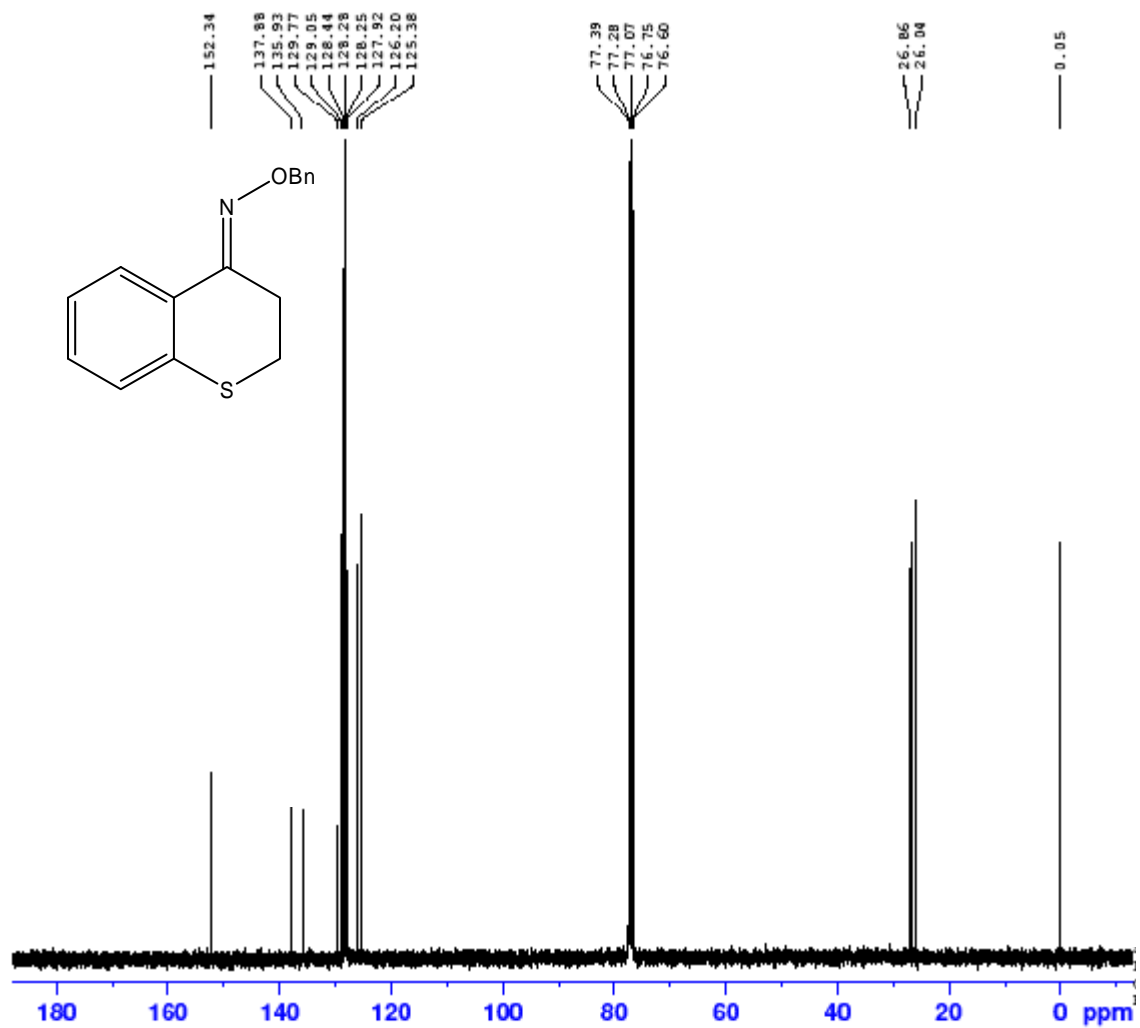
(E)-6-Chlorochroman-4-one O-benzyl oxime (15d)



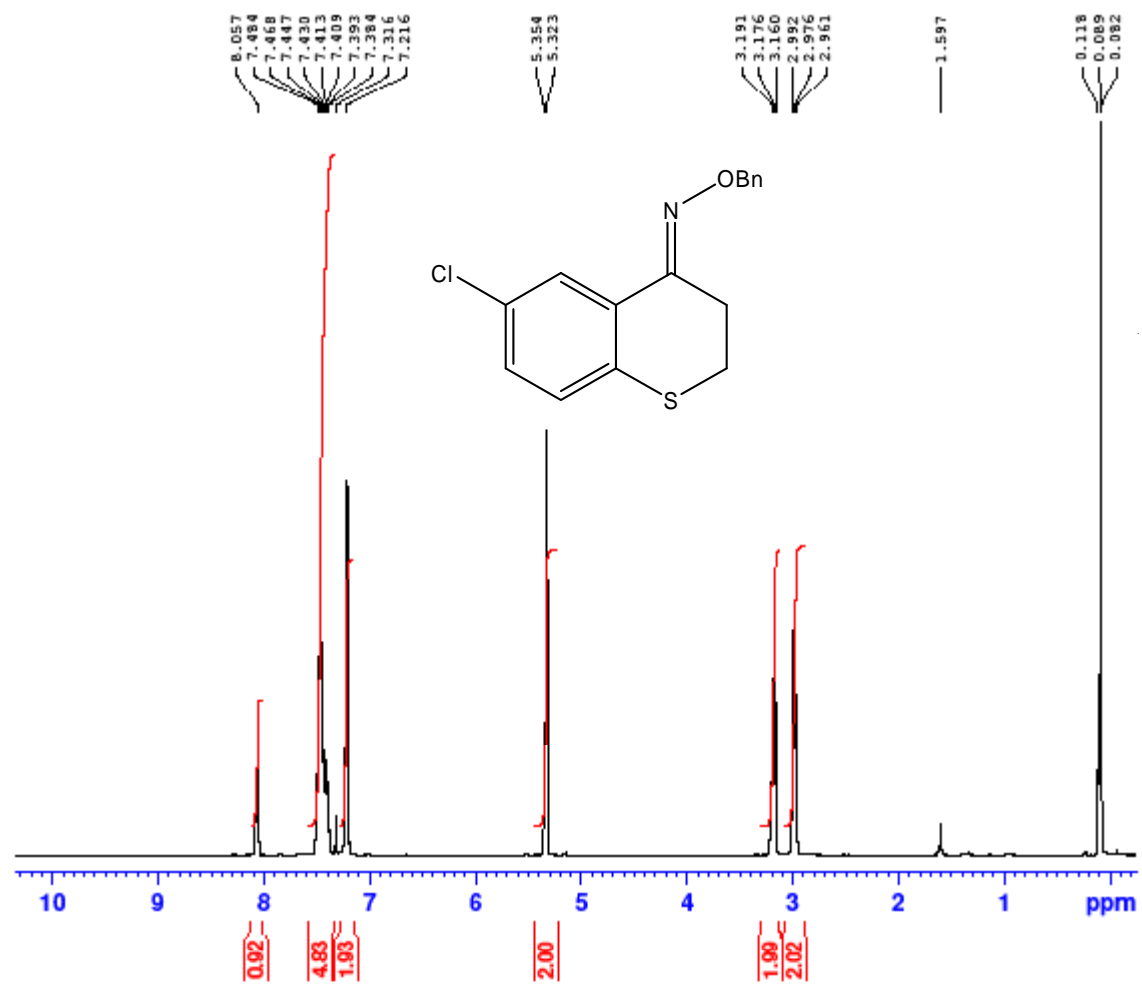
(E)-Thiochroman-4-one O-benzyl oxime (15e)



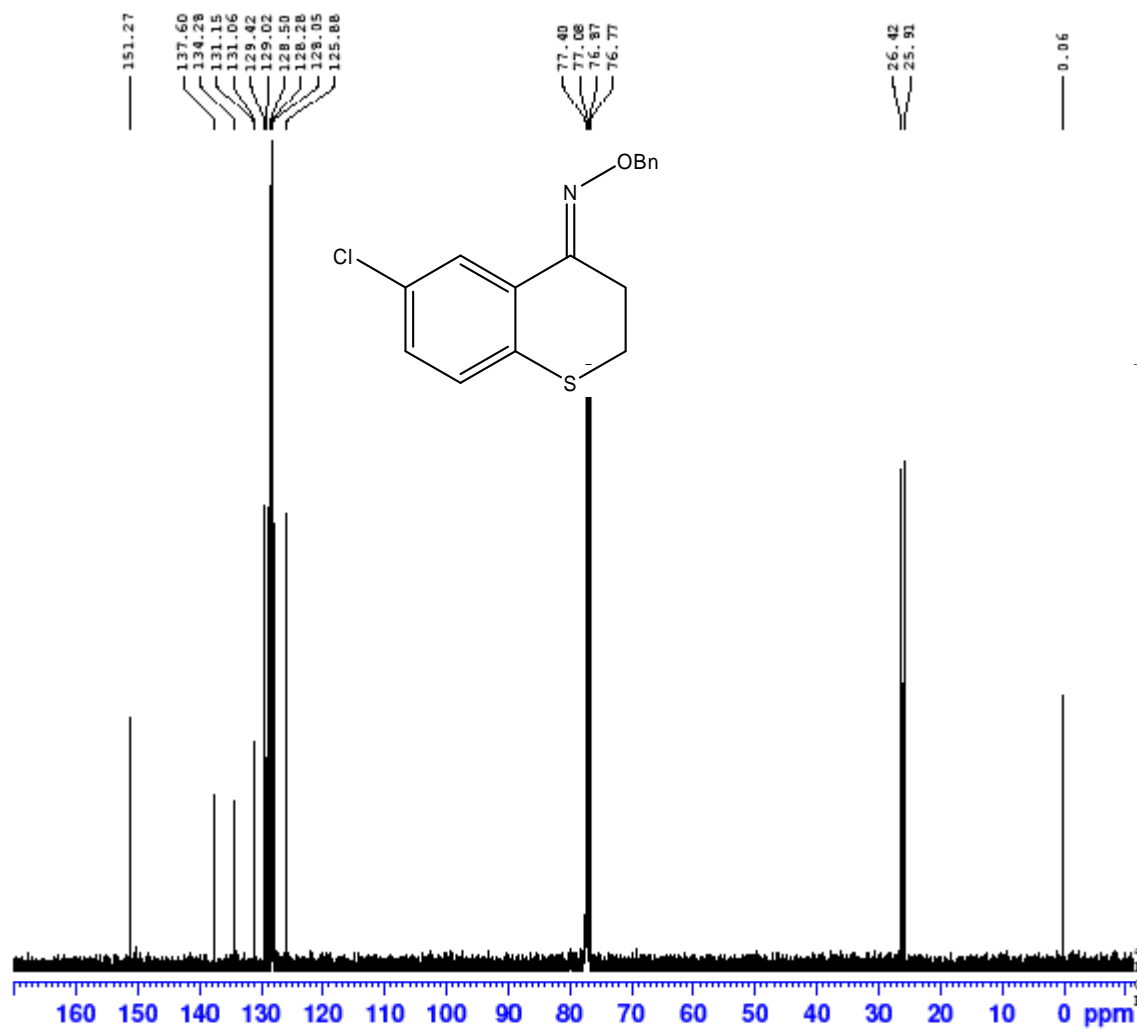
(E)-Thiochroman-4-one O-benzyl oxime (15e)



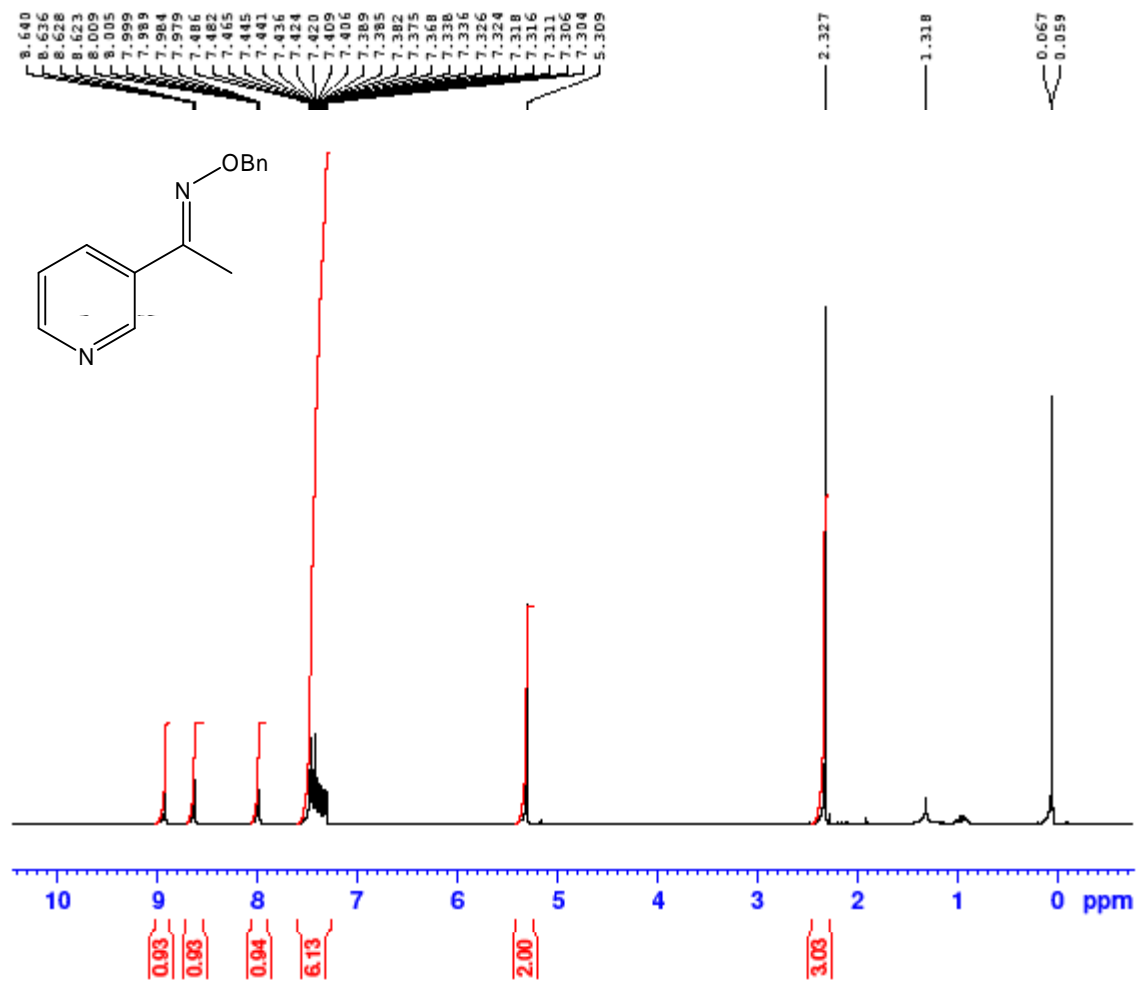
(E)-6-Chlorothiochroman-4-one O-benzyl oxime (15f)



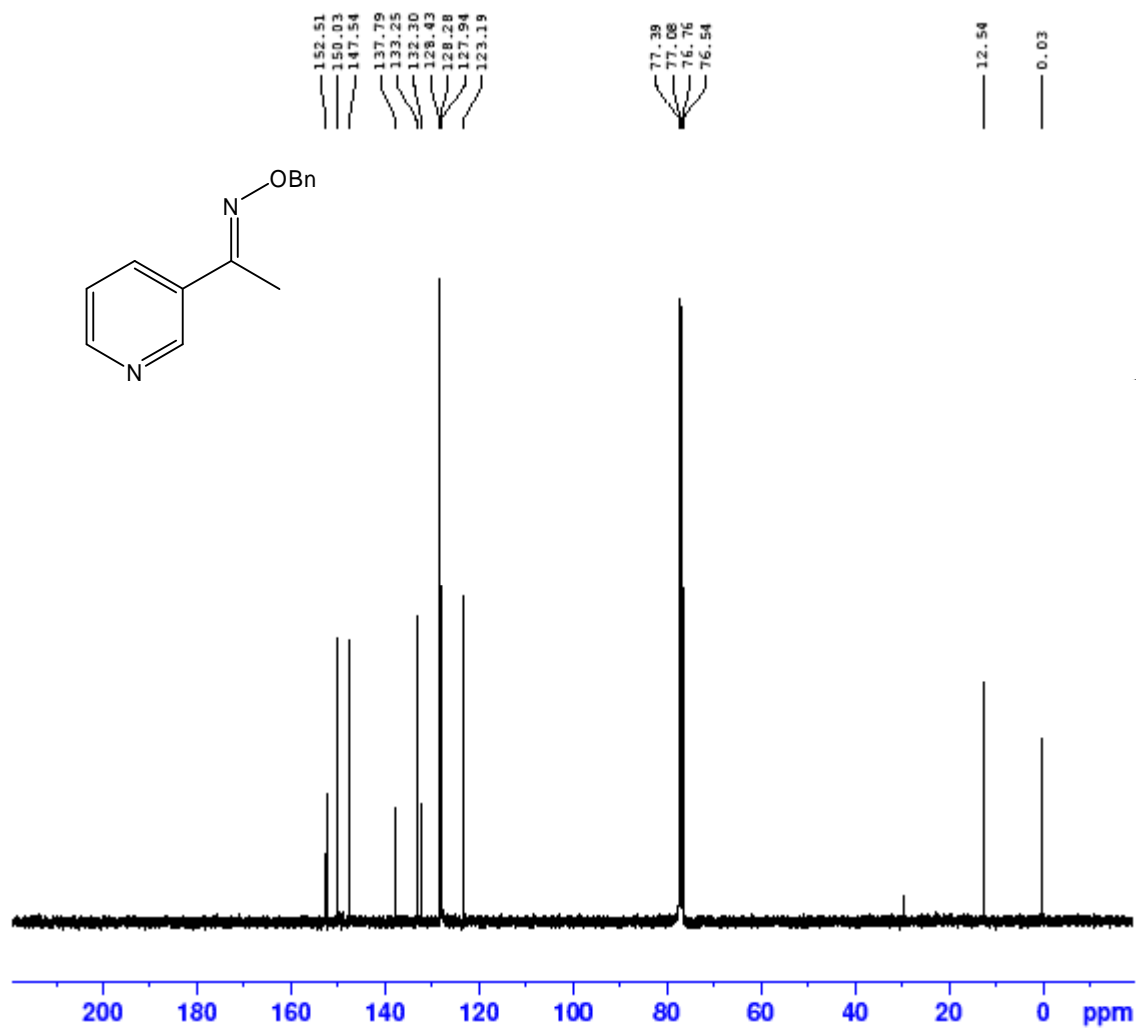
(E)-6-Chlorothiochroman-4-one O-benzyl oxime (15f)



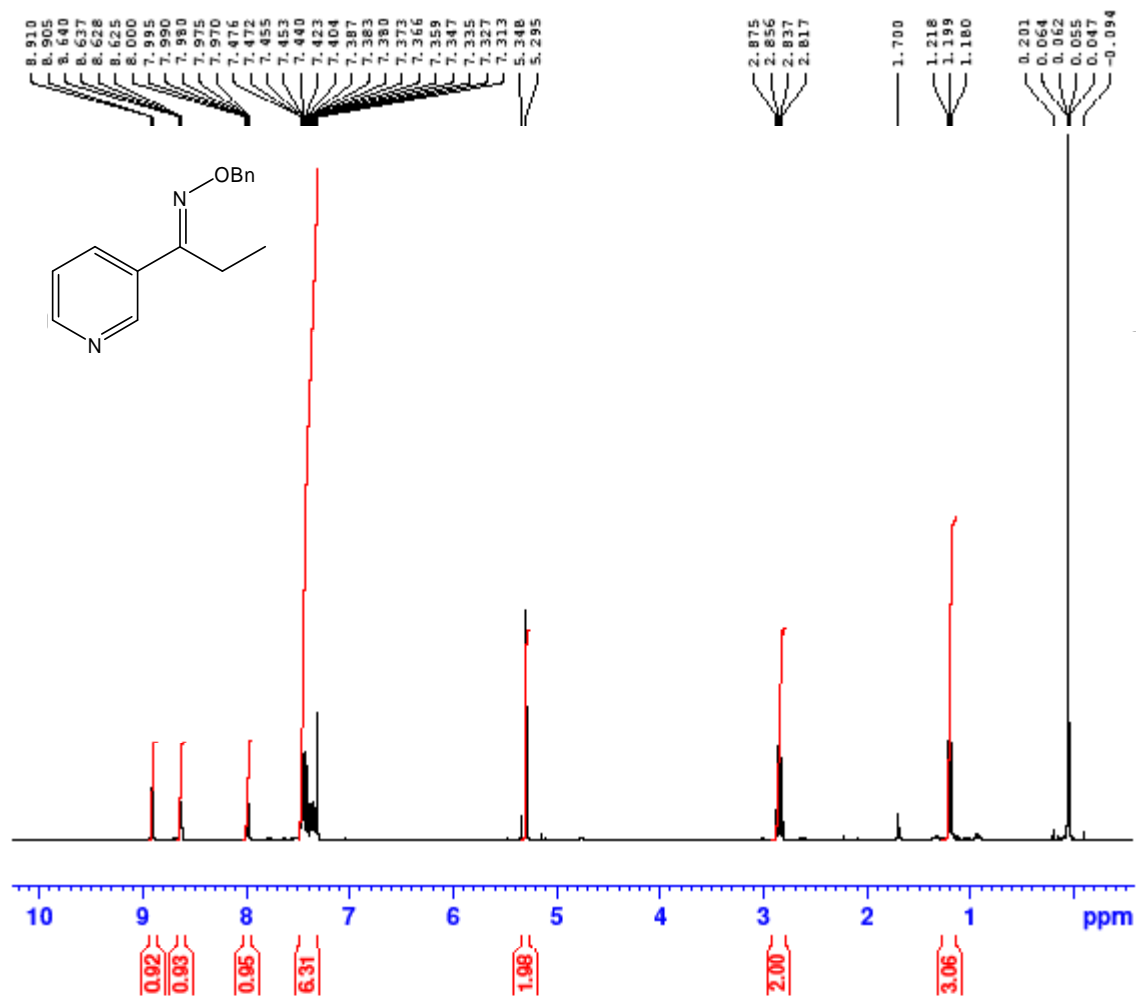
1-(pyridin-3-yl)ethanone O-benzyl oxime (16a)



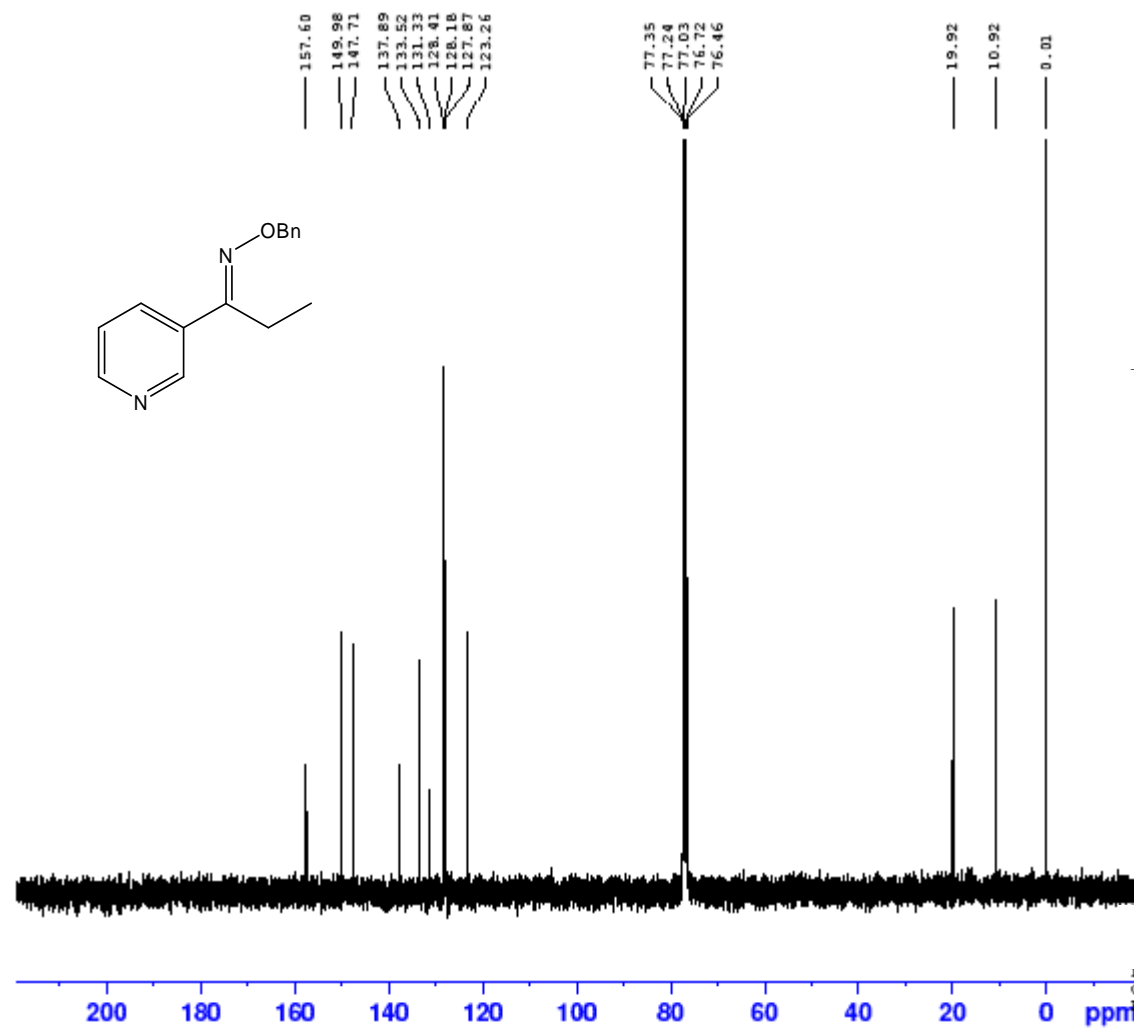
1-(pyridin-3-yl)ethanone O-benzyl oxime (16a)



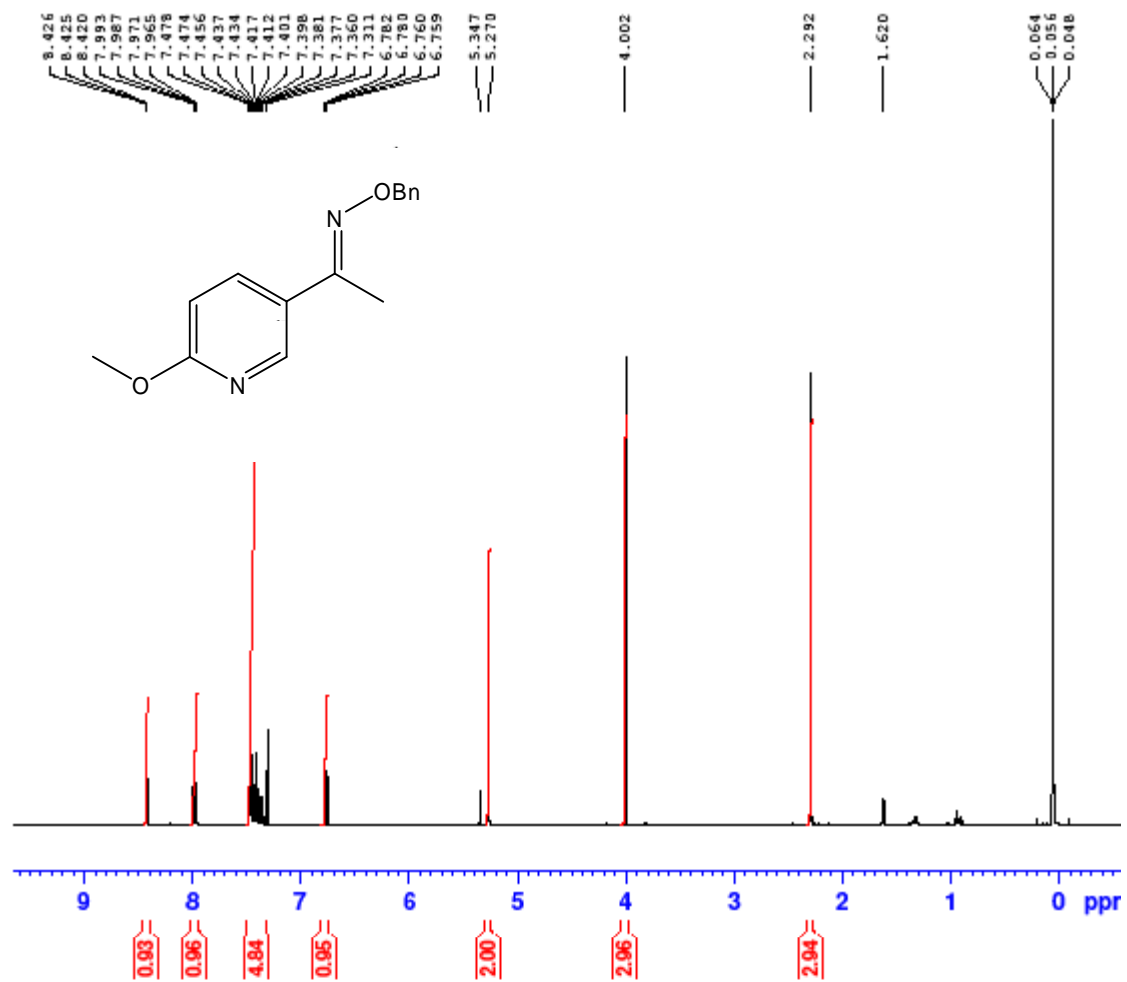
(E)-1-(Pyridine-3-yl)-propan-1-one O-benzyl oxime (16b)



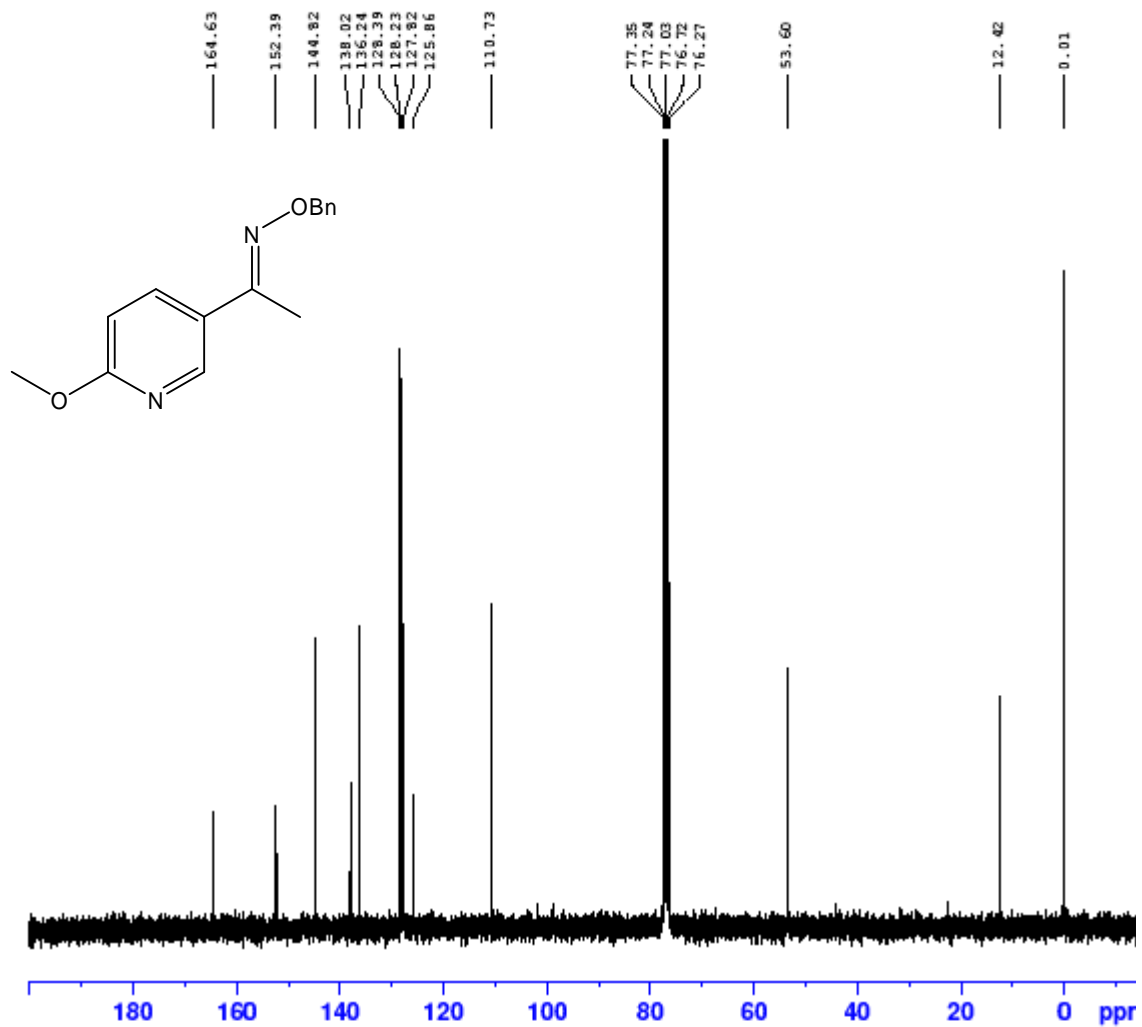
(E)-1-(Pyridine-3-yl)propan-1-one O-benzyl oxime (16b)



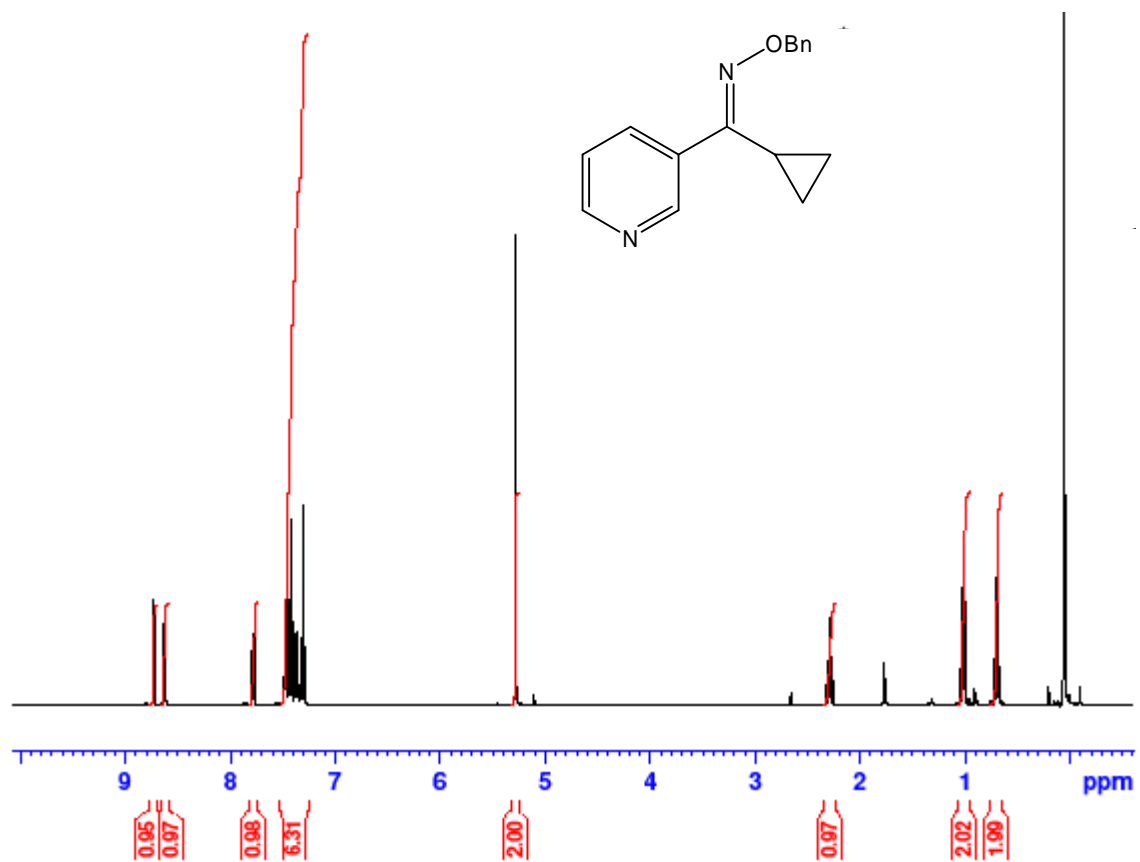
(E)-1-(6-Methoxypyridin-3-yl)-ethanone O-benzyl oxime (16c)



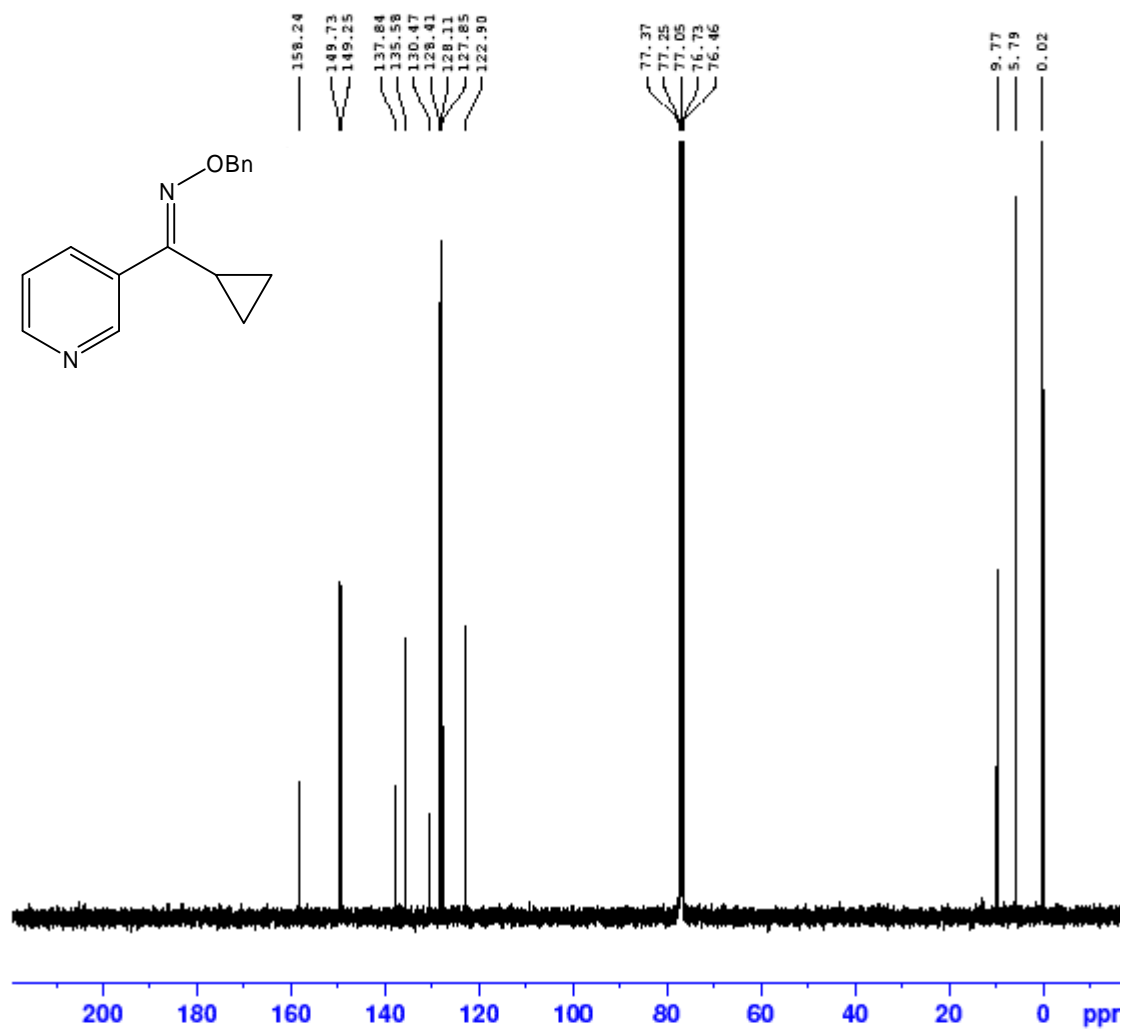
(E)-1-(6-Methoxypyridin-3-yl)-ethanone O-benzyl oxime (16c)



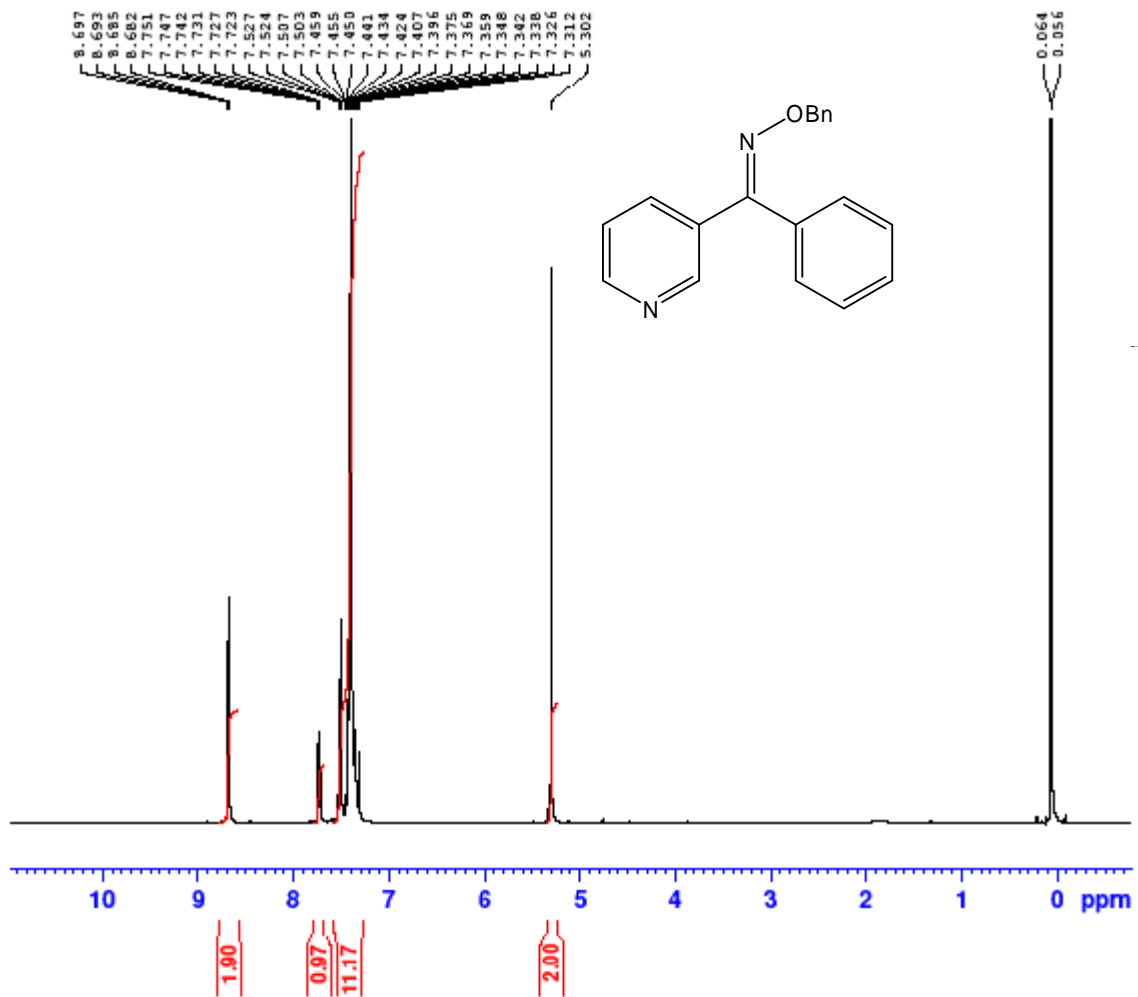
(E)-Cyclopropyl-(pyridine-3-yl)-methanone O-benzyl oxime (16d)



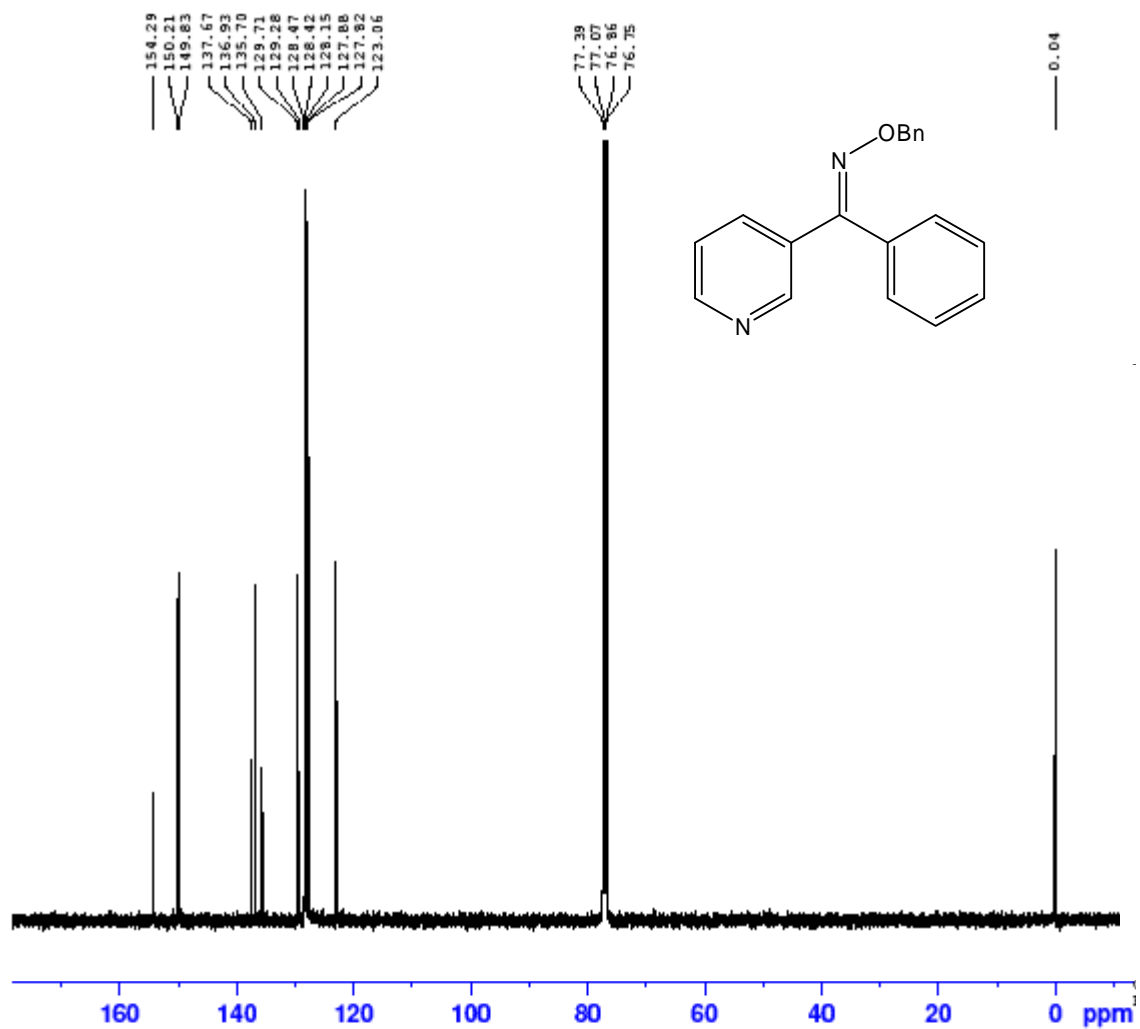
(E)-Cyclopropyl-(pyridine-3-yl)-methanone O-benzyl oxime (16d)



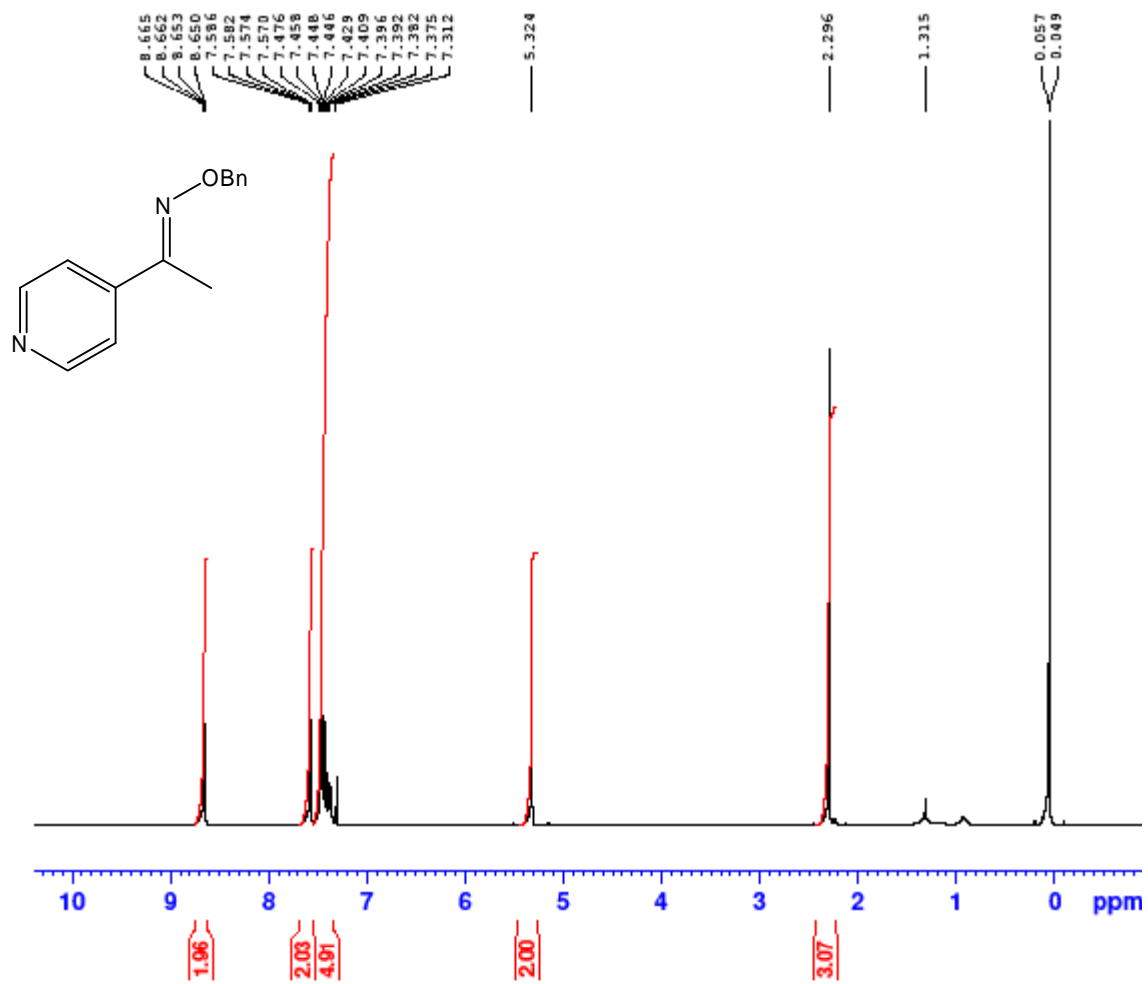
(E)-phenyl(pyridin-3-yl)methanone O-benzyl oxime (17)



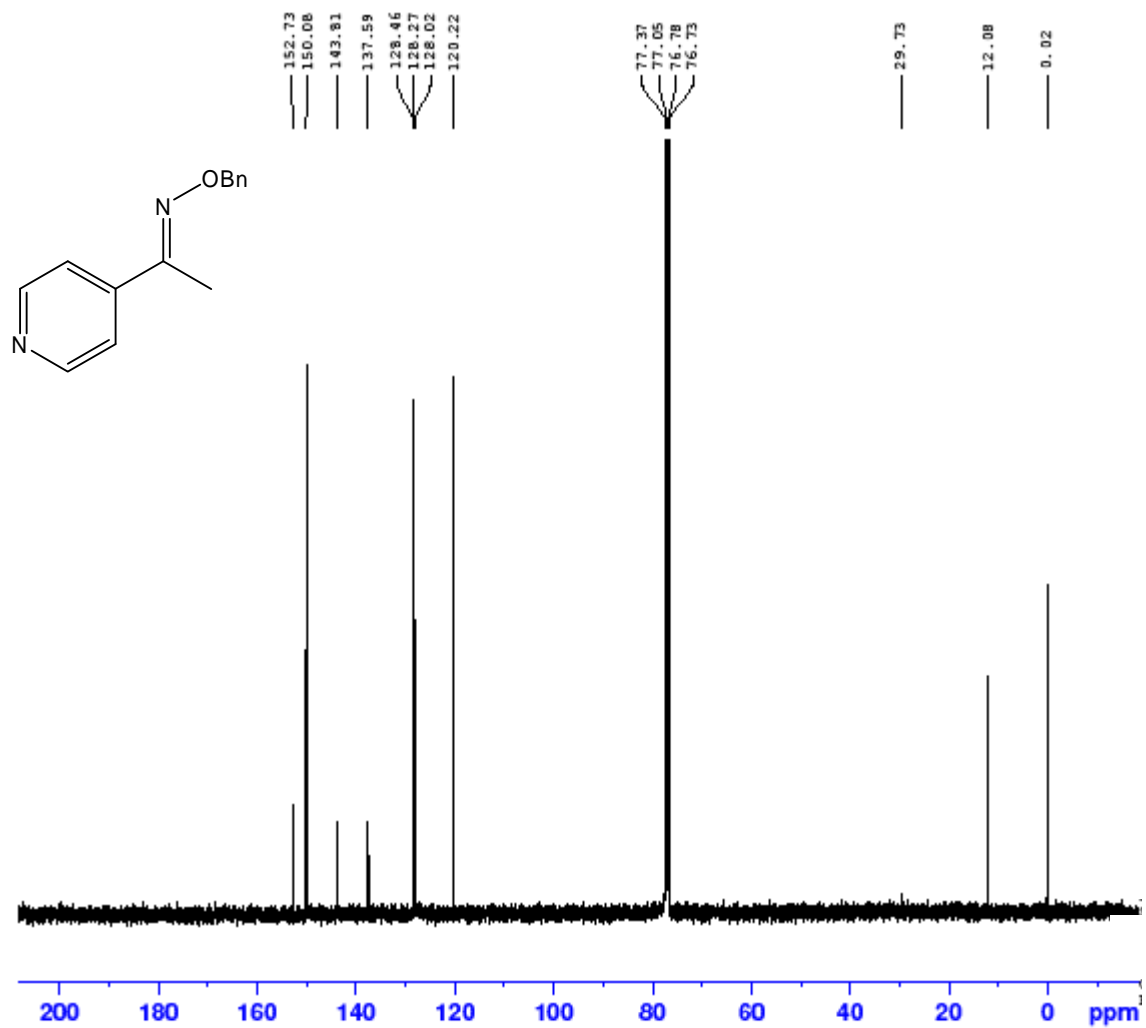
(E)-phenyl(pyridin-3-yl)methanone O-benzyl oxime (17)



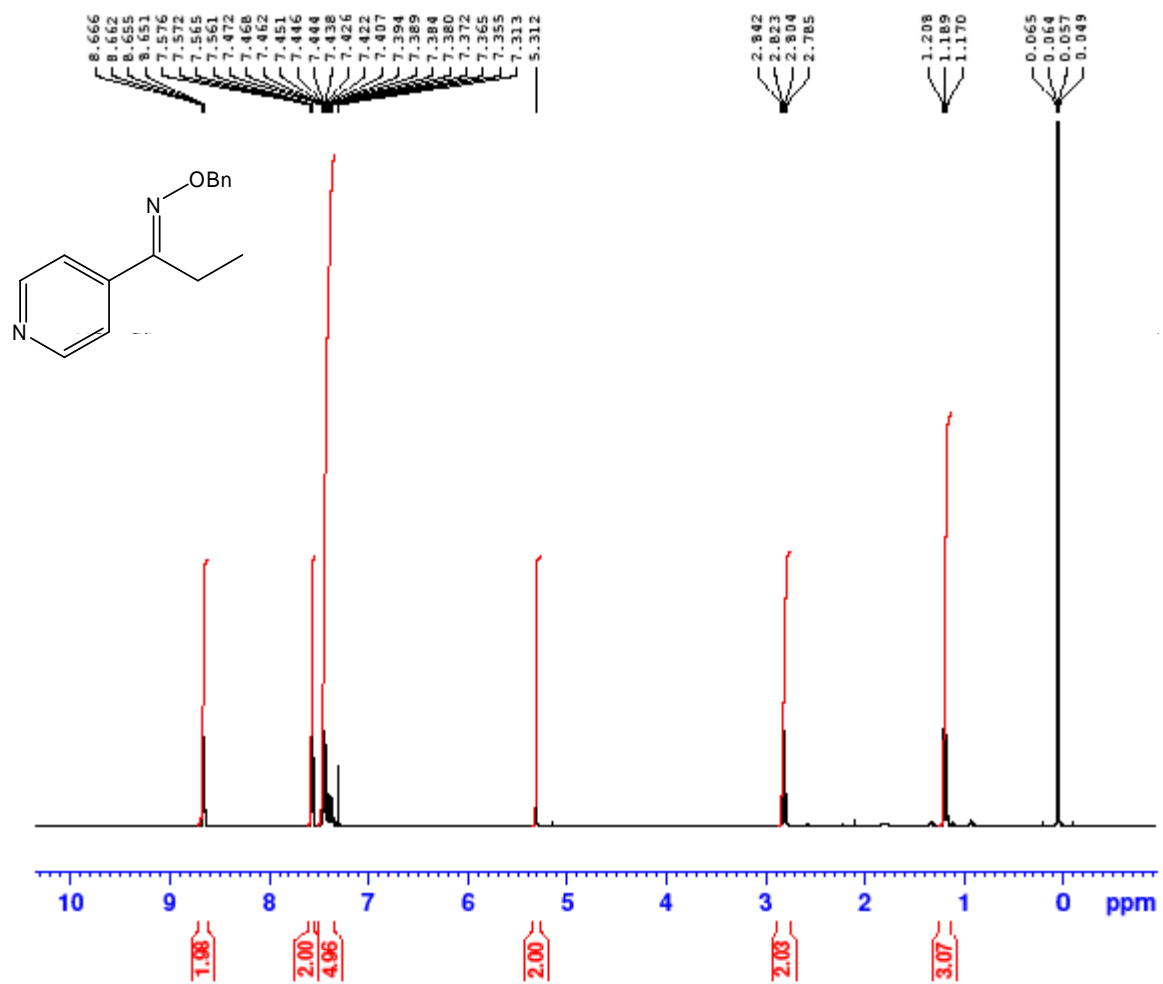
1-(pyridin-4-yl)ethanone O-benzyl oxime (18a)



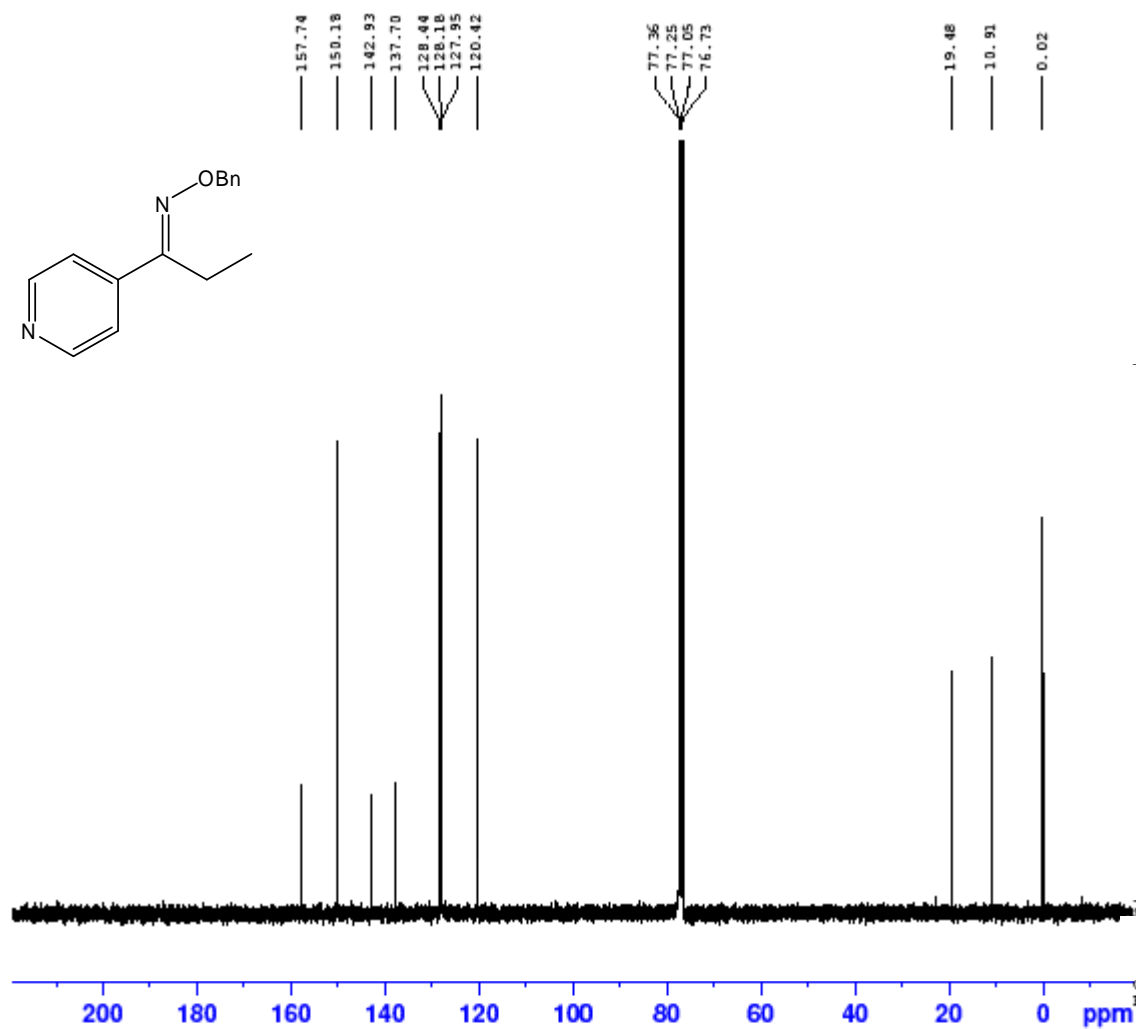
1-(pyridin-4-yl)ethanone O-benzyl oxime (18a)



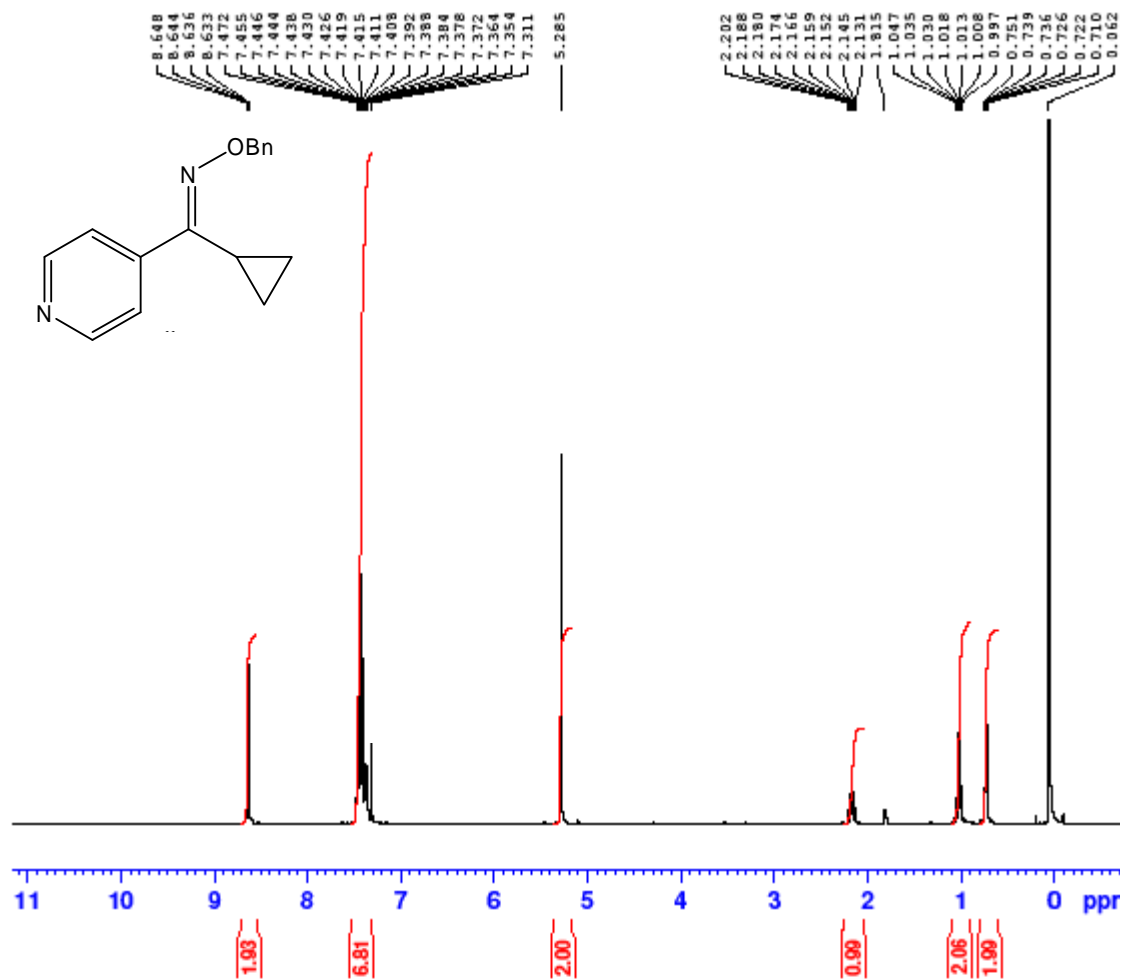
(E)-1-(Pyridine-4-yl)-propan-1-one O-benzyl oxime (18b)



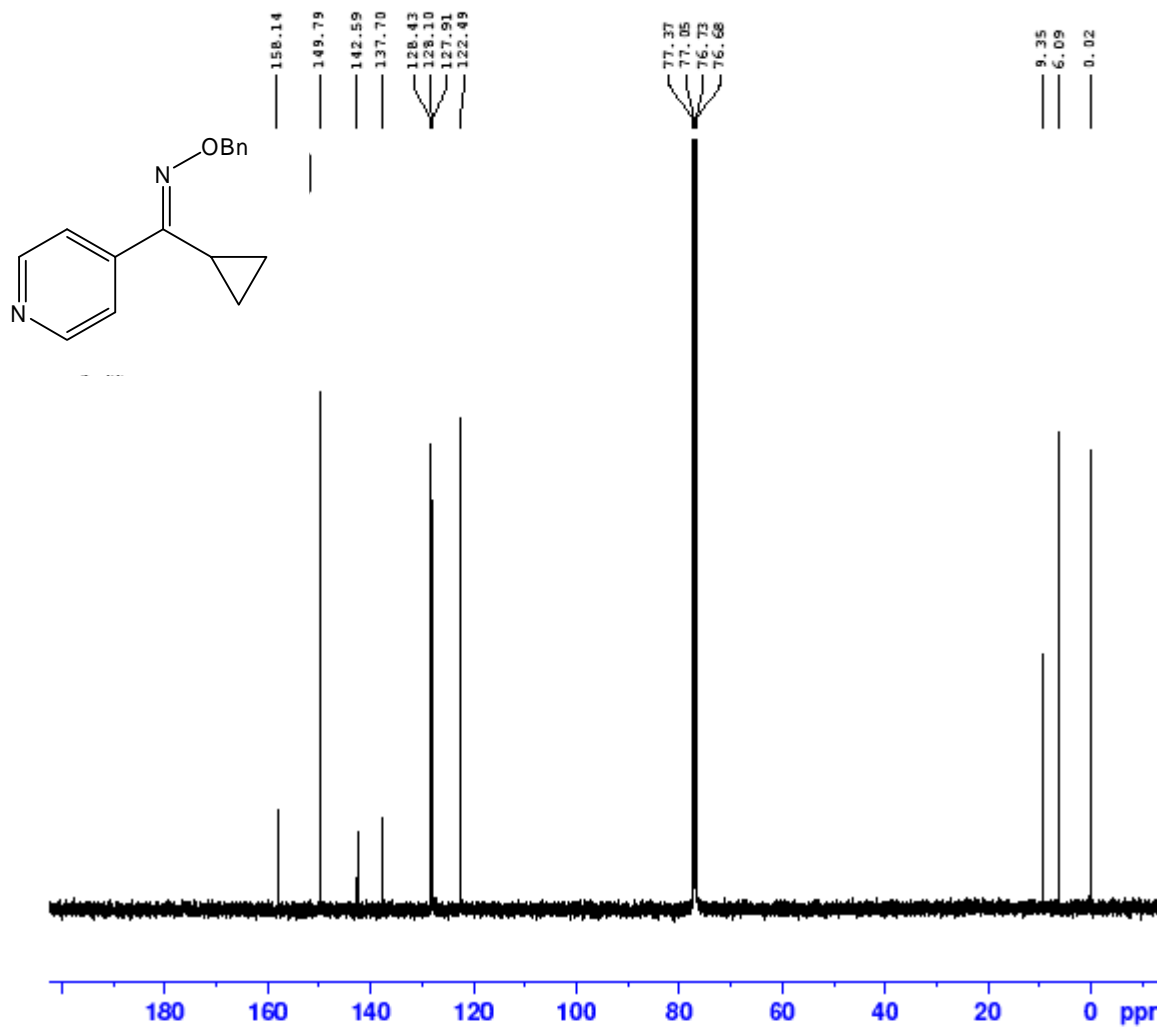
(E)-1-(Pyridine-4-yl)-propan-1-one O-benzyl oxime (18b)



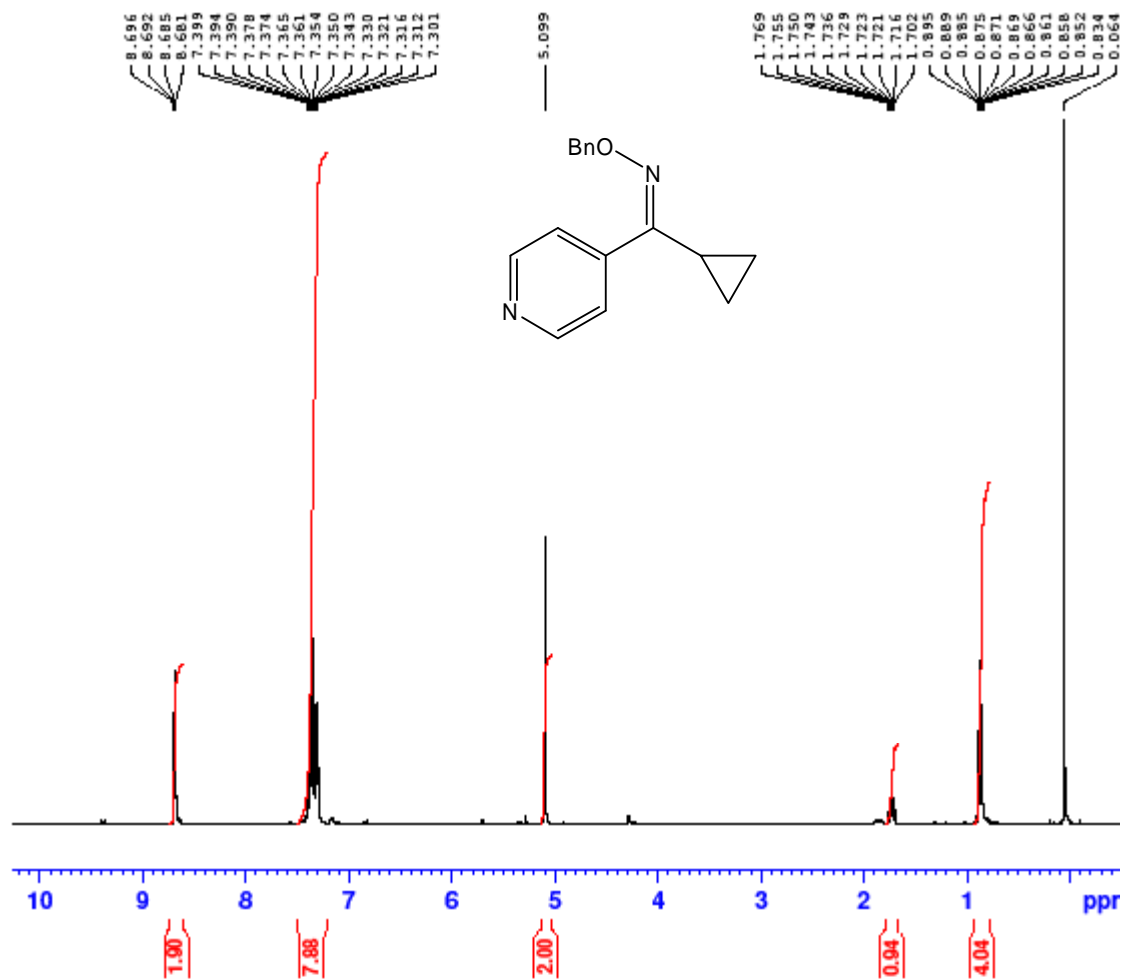
(E)-Cyclopropyl-(pyridine-4-yl)-methanone O-benzyl oxime (18c_E)



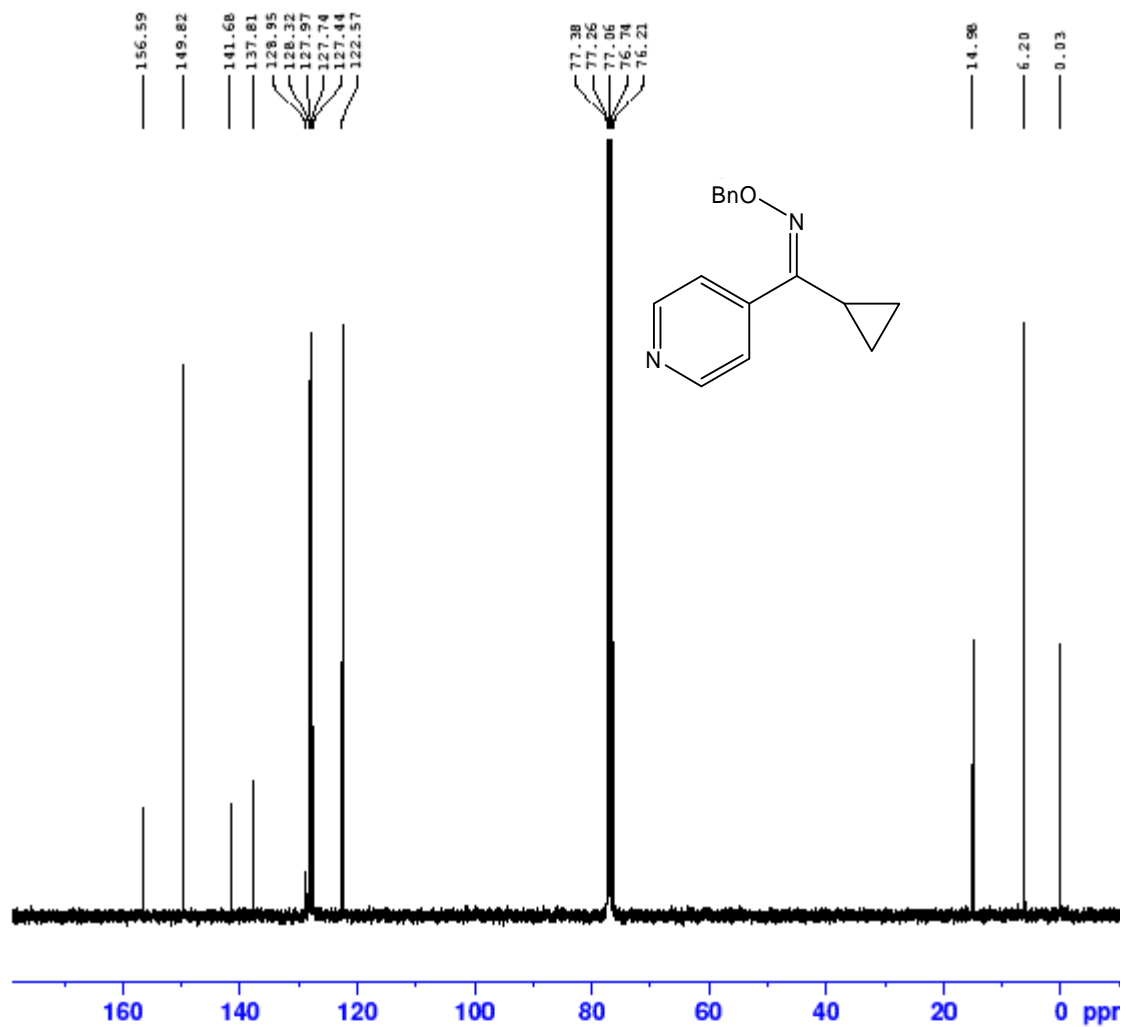
(E)-Cyclopropyl-(pyridine-4-yl)-methanone O-benzyl oxime (18c_E)



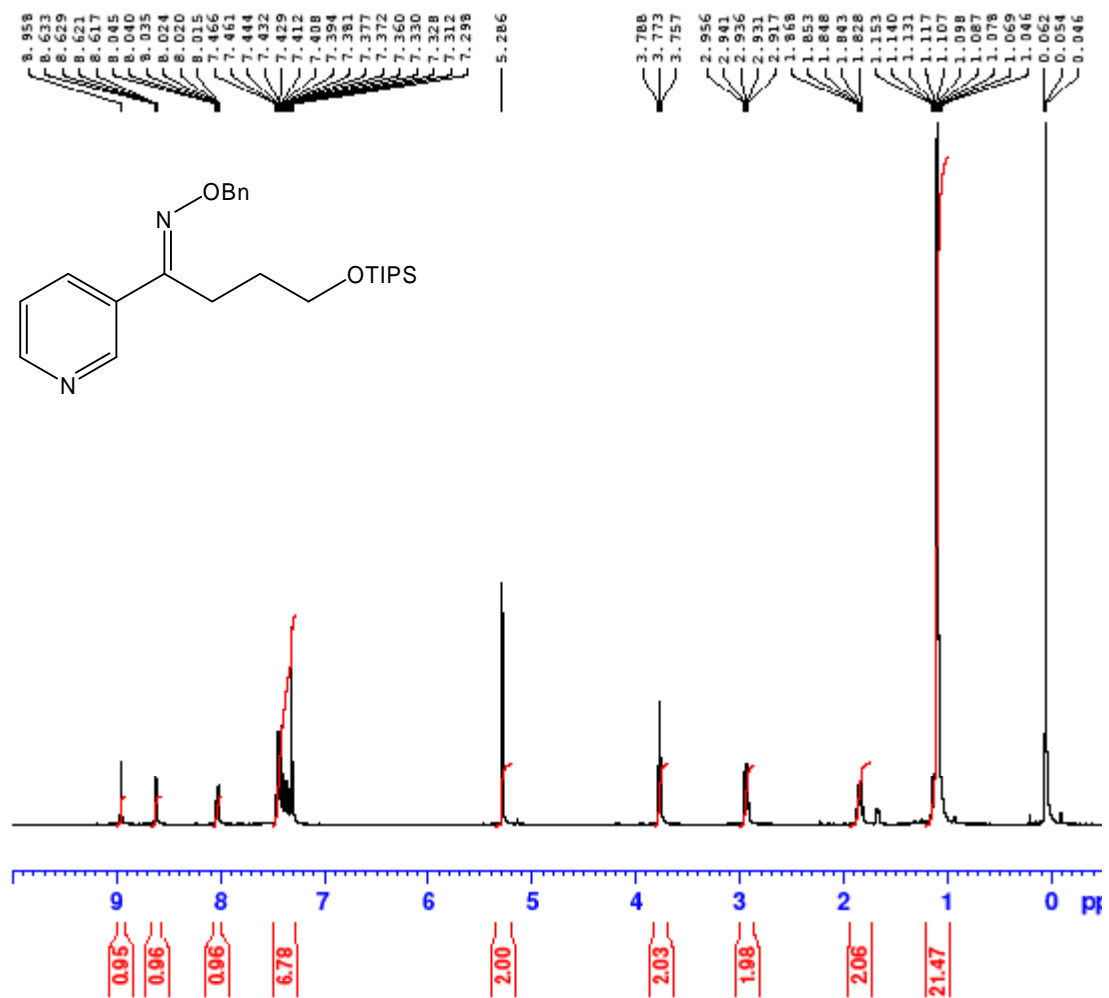
(Z)-Cyclopropyl-(pyridine-4-yl)-methanone O-benzyl oxime (18c₂)



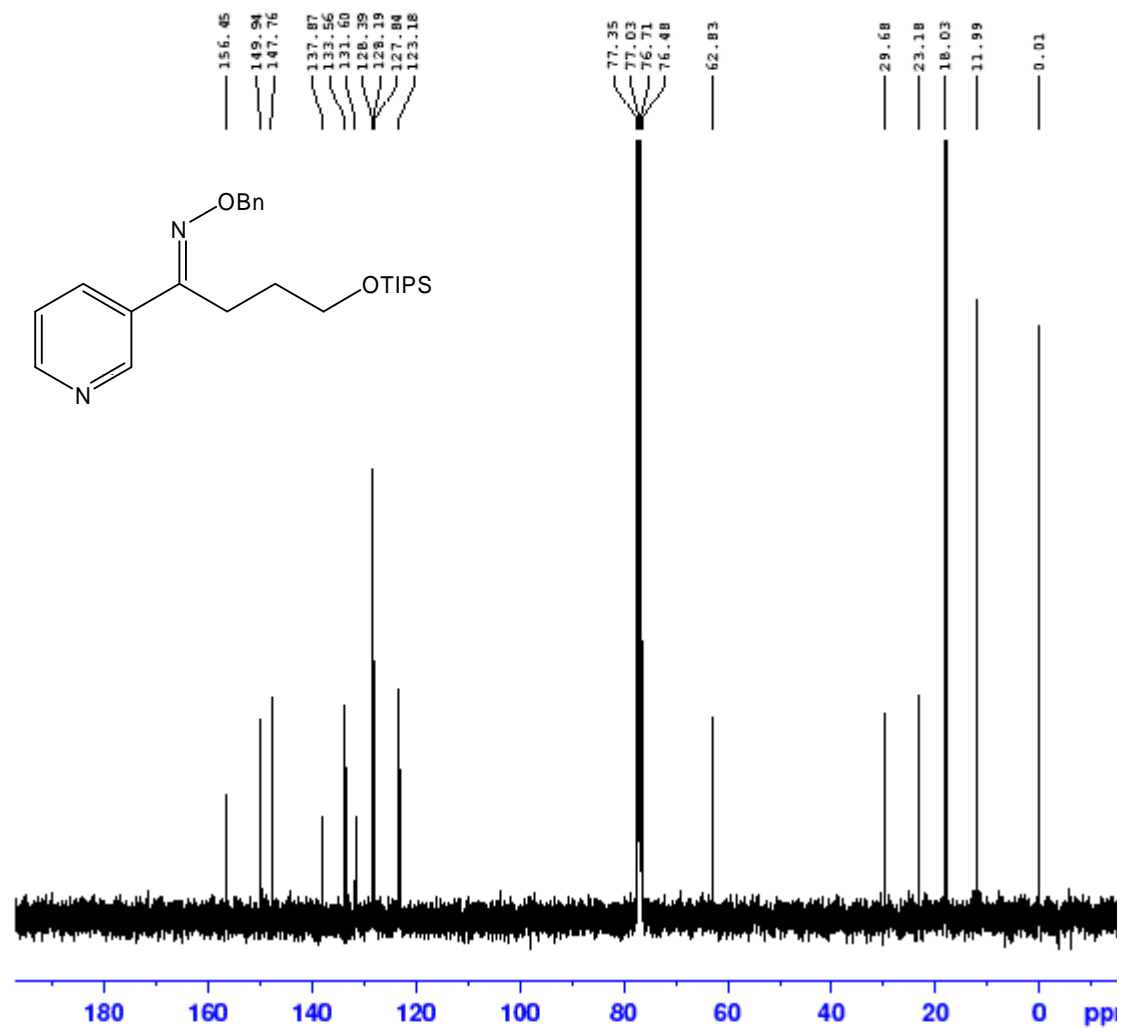
(Z)-Cyclopropyl-(pyridine-4-yl)-methanone O-benzyl oxime (18c₂)



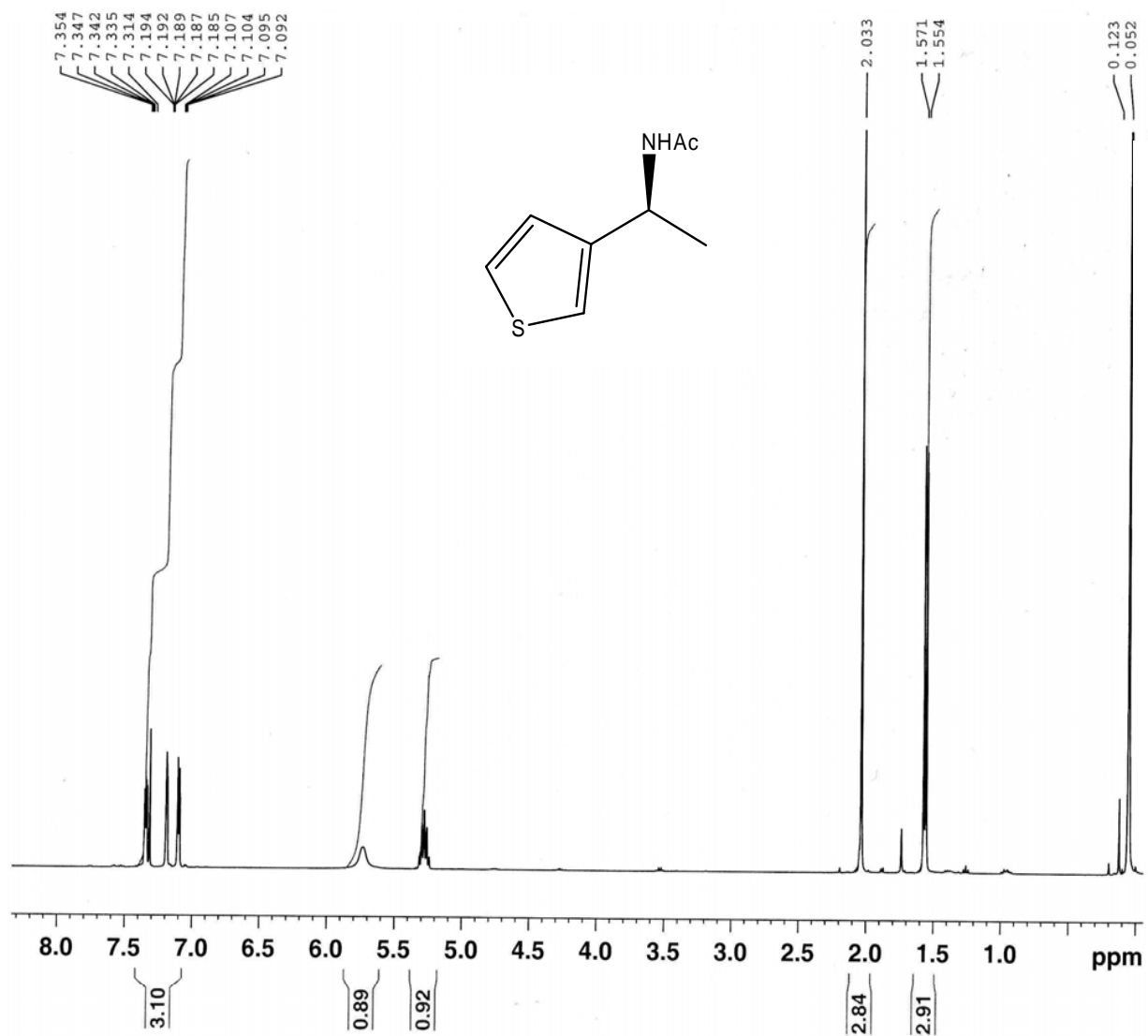
(E)-1-(pyridine-3yl)-4-(triisopropylsilyloxy)butan-1-one O-benzoyloxime (19)



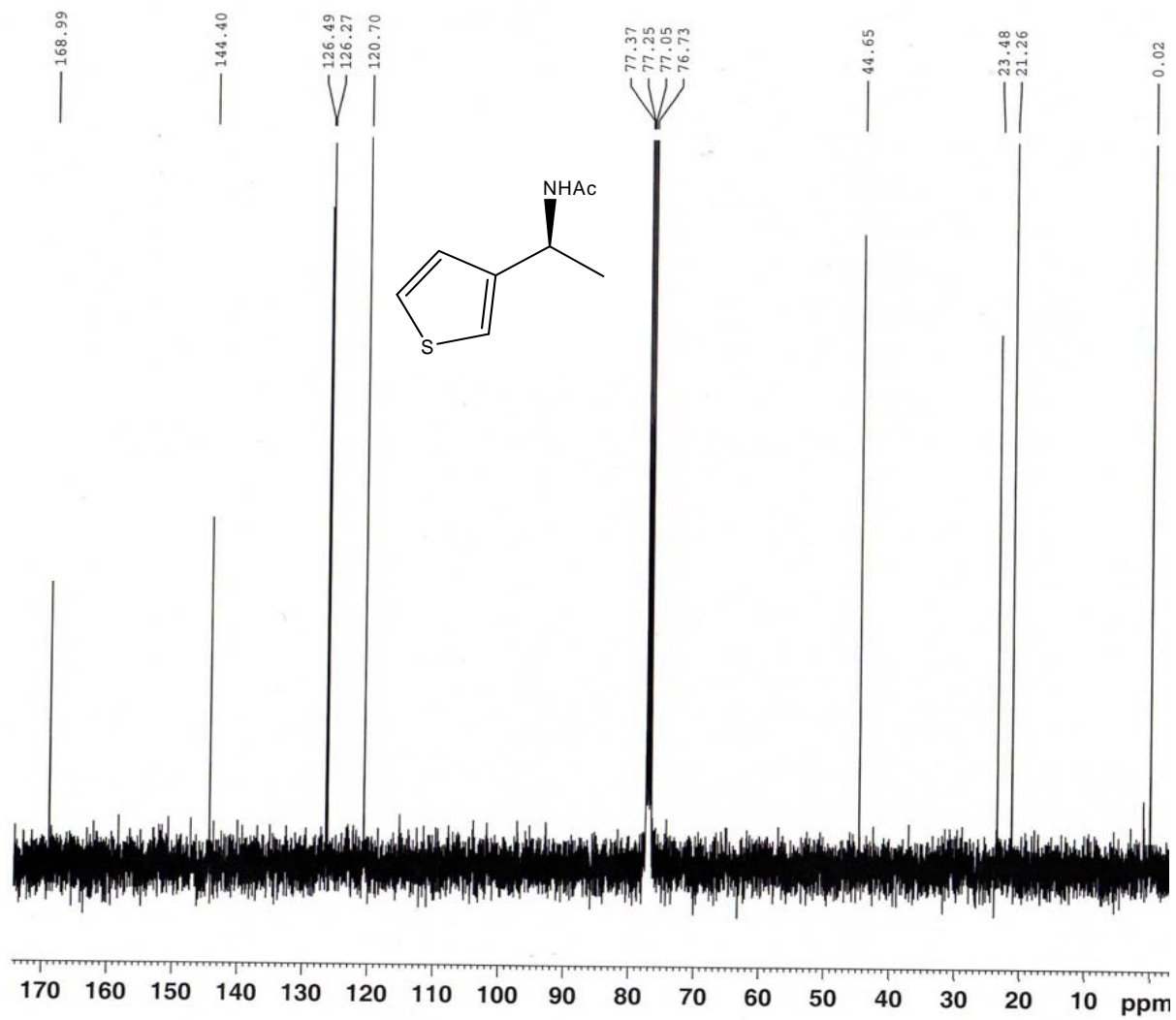
(E)-1-(pyridine-3-yl)-4-(triisopropylsilyloxy)butan-1-one O-benzoyloxime (19)



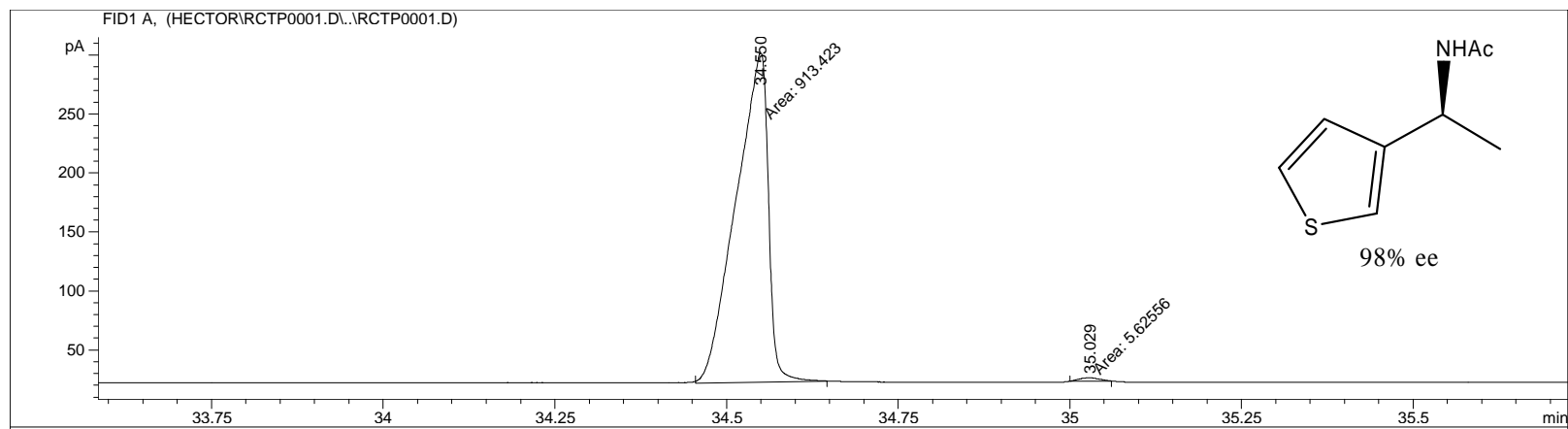
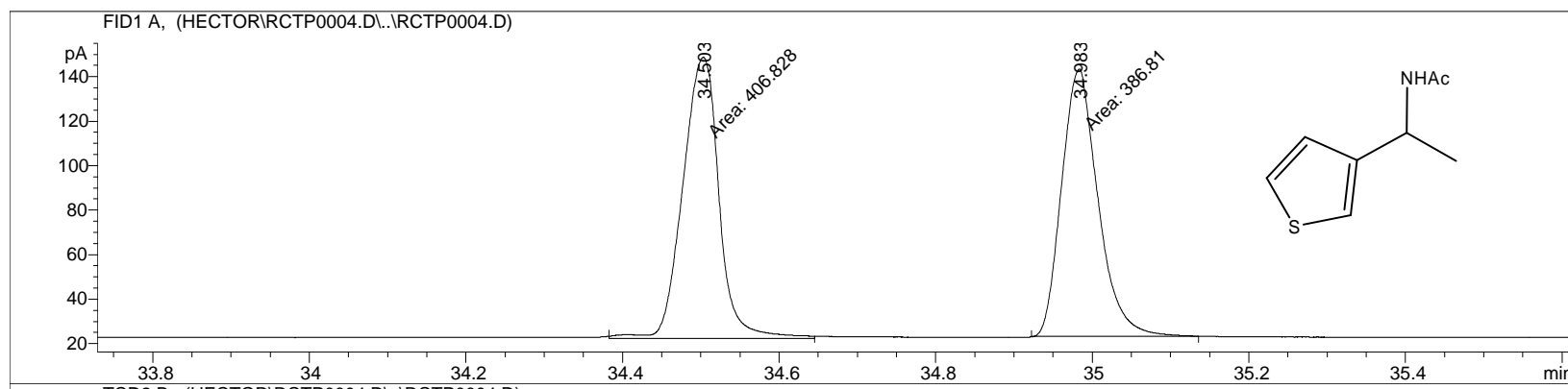
(S)-N-(1-(thiophen-3-yl)ethyl)acetamide (20a)



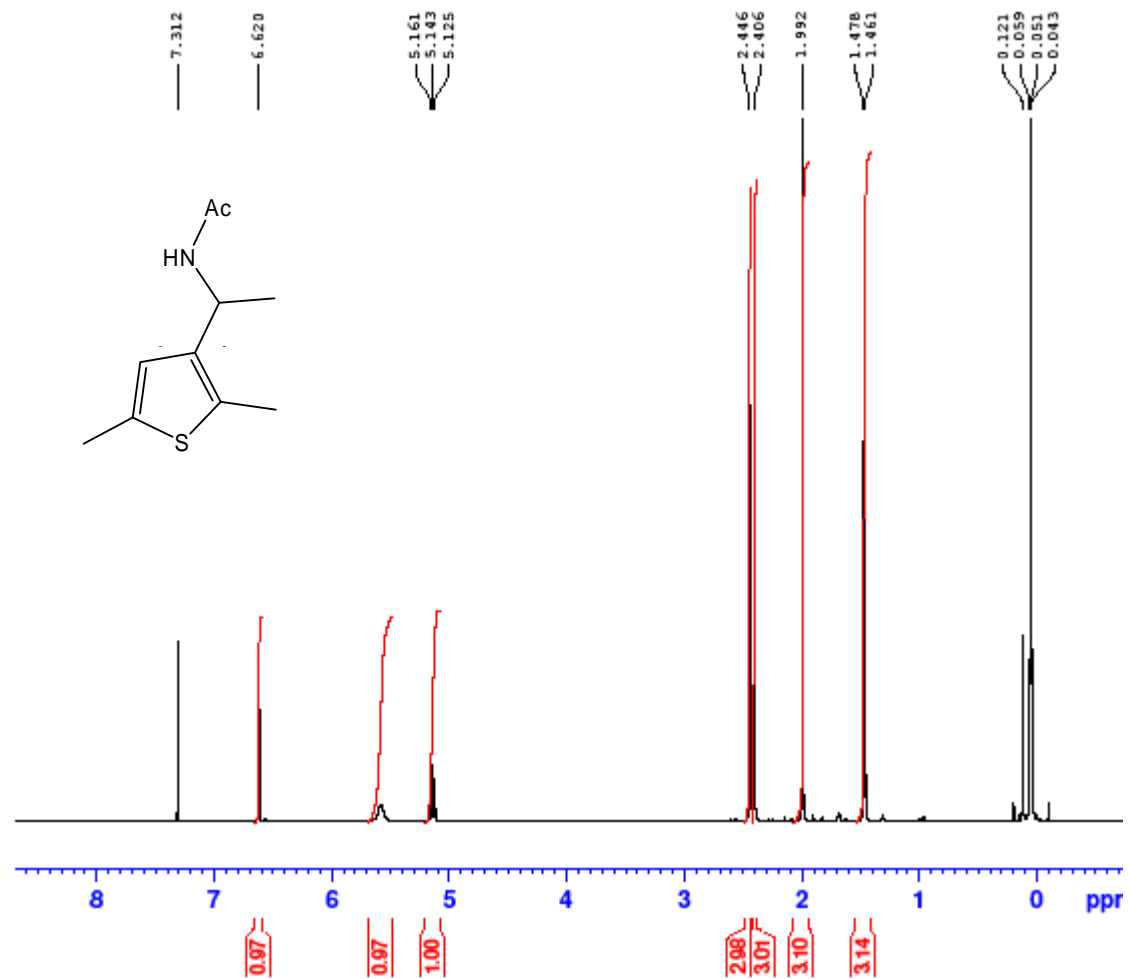
(S)-N-(1-(thiophen-3-yl)ethyl)acetamide (20a)



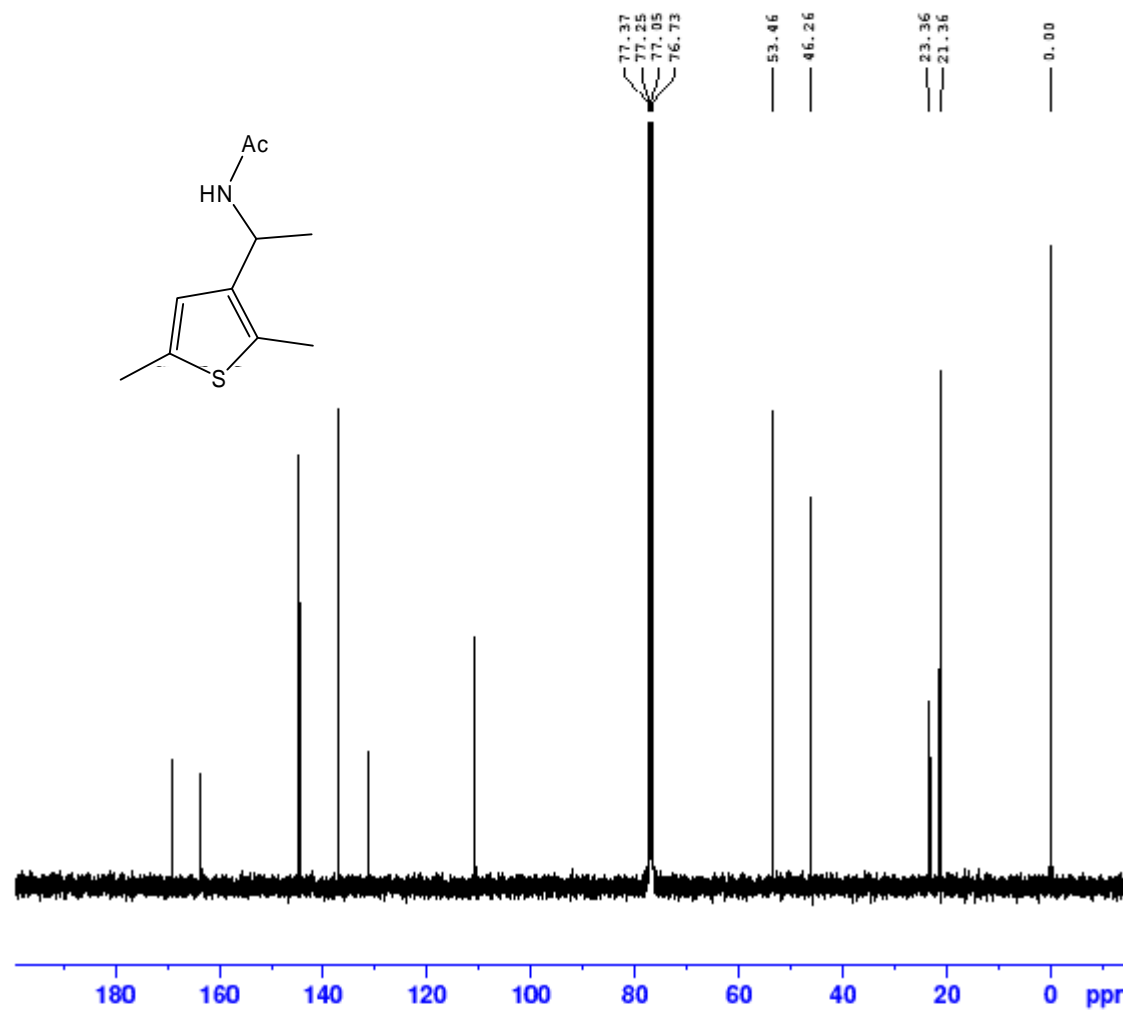
(S)-N-(1-(thiophen-3-yl)ethyl)acetamide (20a)



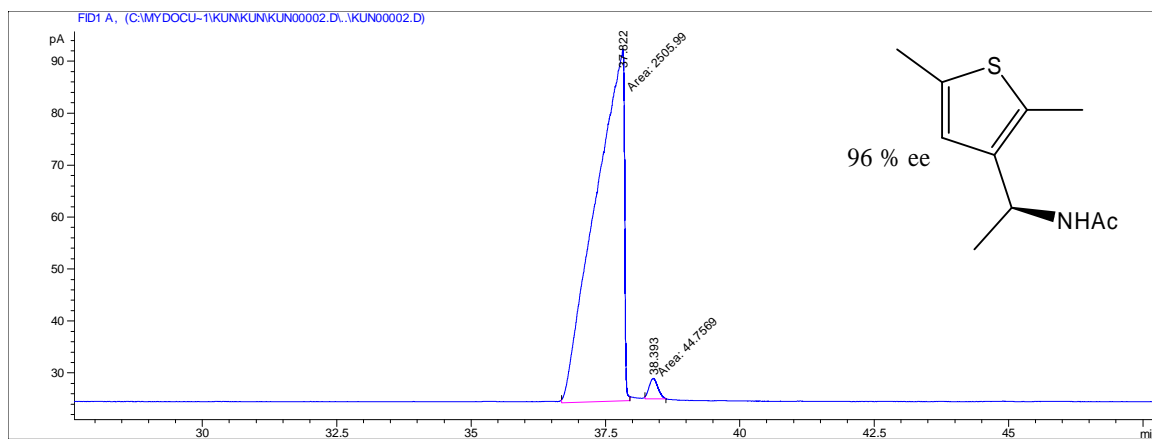
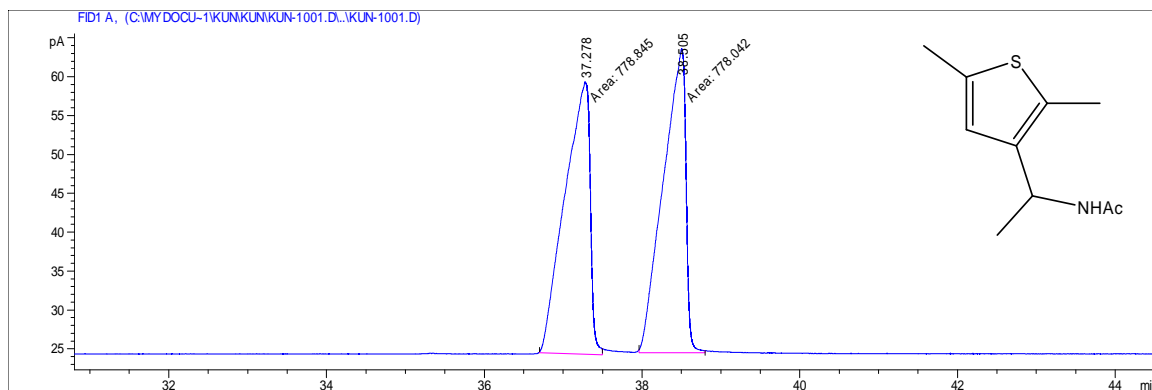
N-(1-(2,5-Dimethylthiophen-3-yl)ethyl)acetamide (20b)



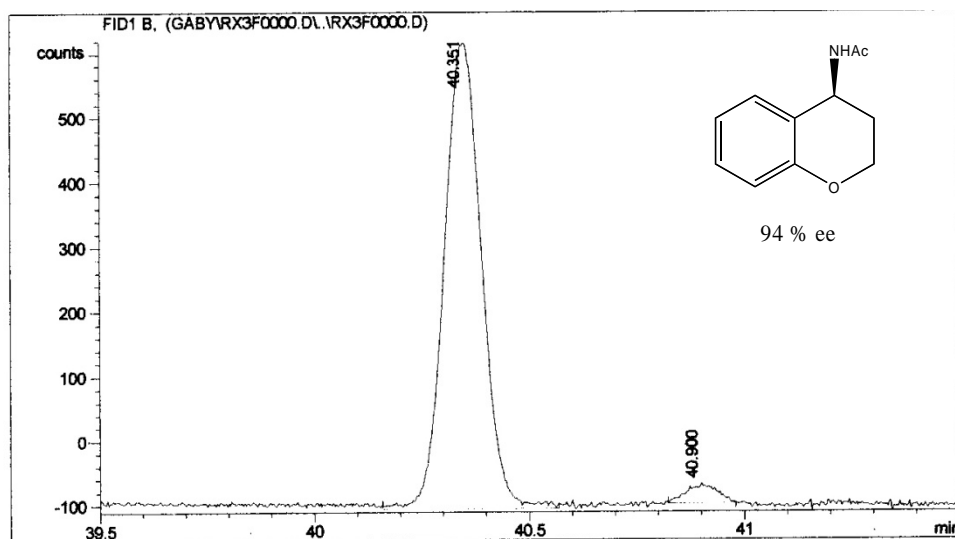
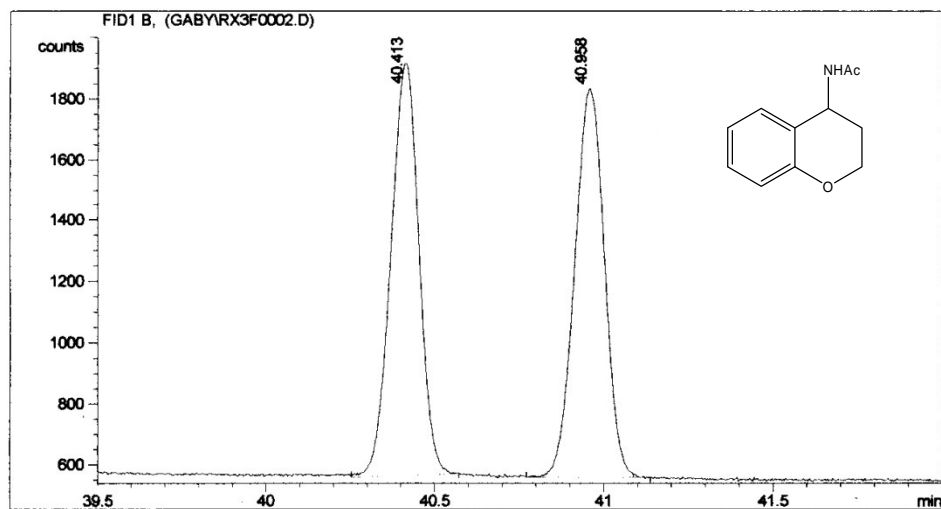
N-(1-(2,5-Dimethylthiophen-3-yl)ethyl)acetamide (20b)



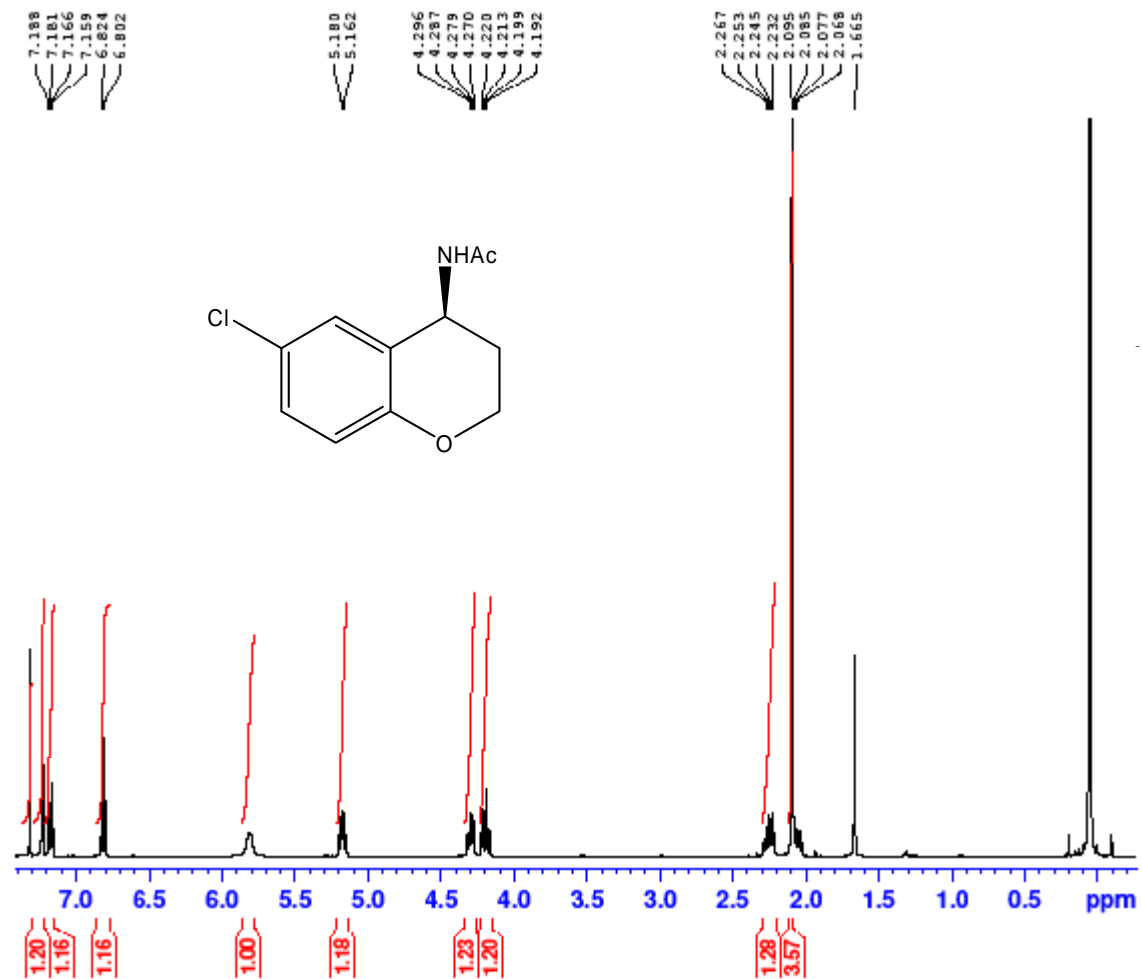
N-(1-(2,5-Dimethylthiophen-3-yl)ethyl)acetamide (20b)



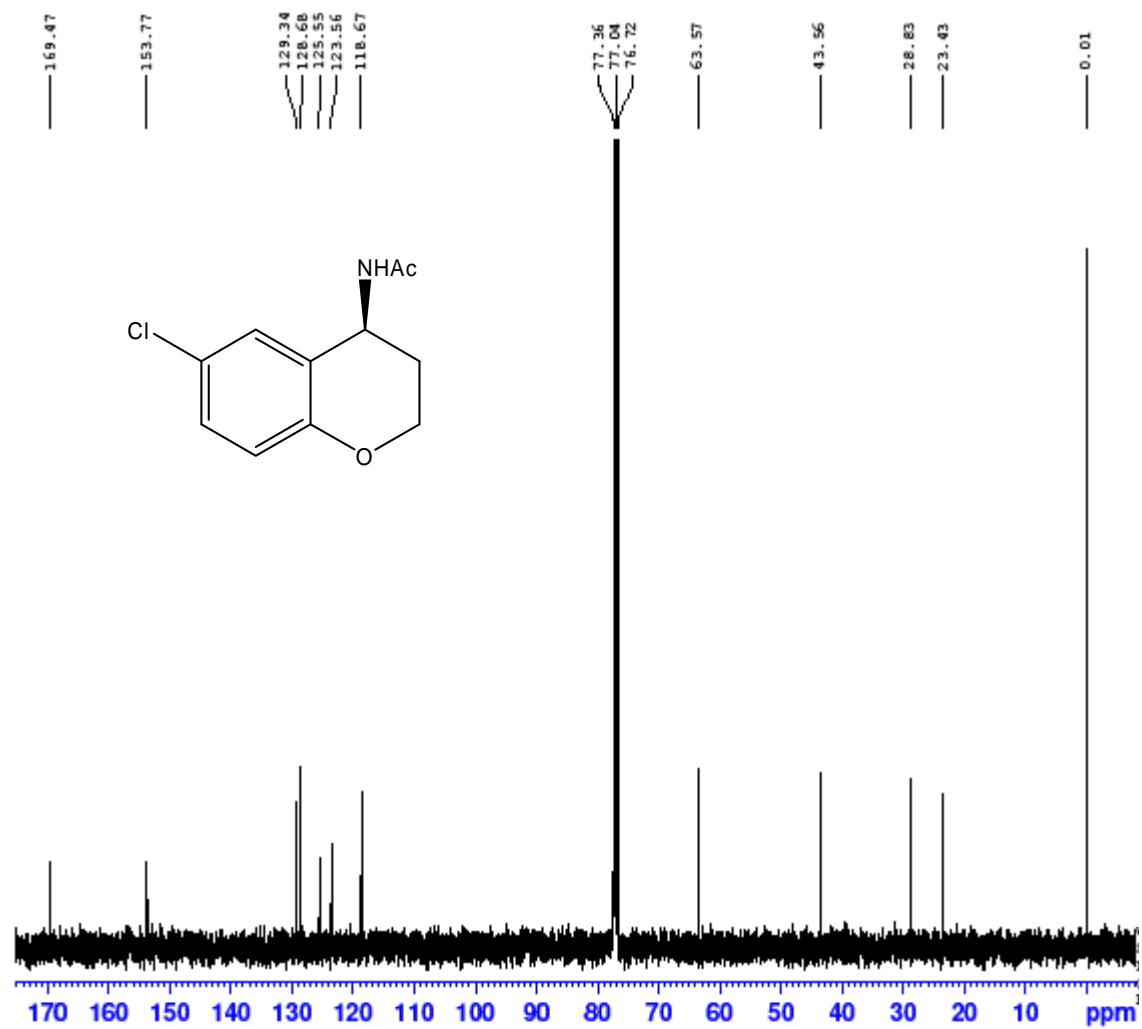
N-(chroman-4-yl)acetamide (20c)



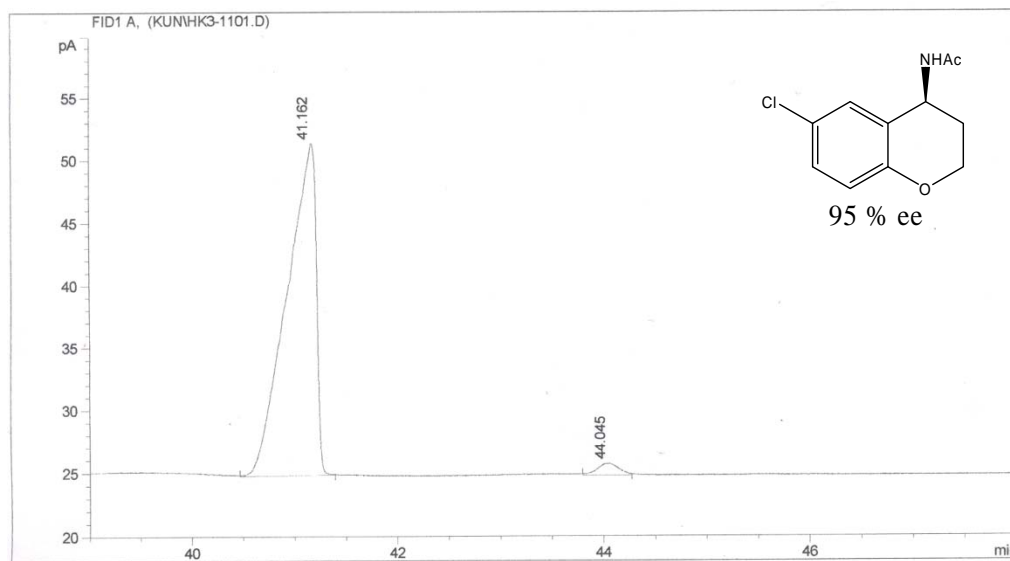
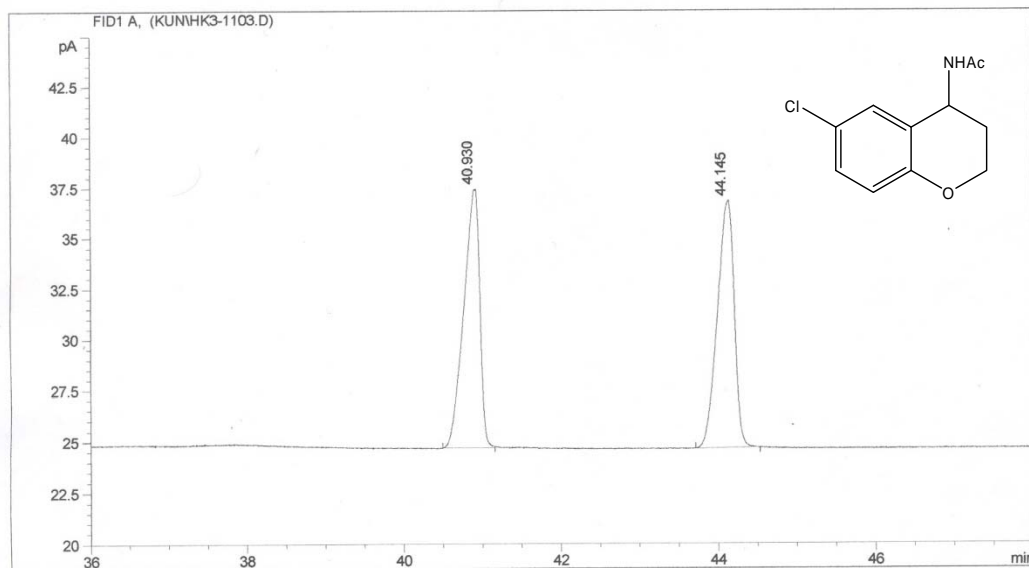
N-(6-chlorochroman-4-yl)acetamide (20d)



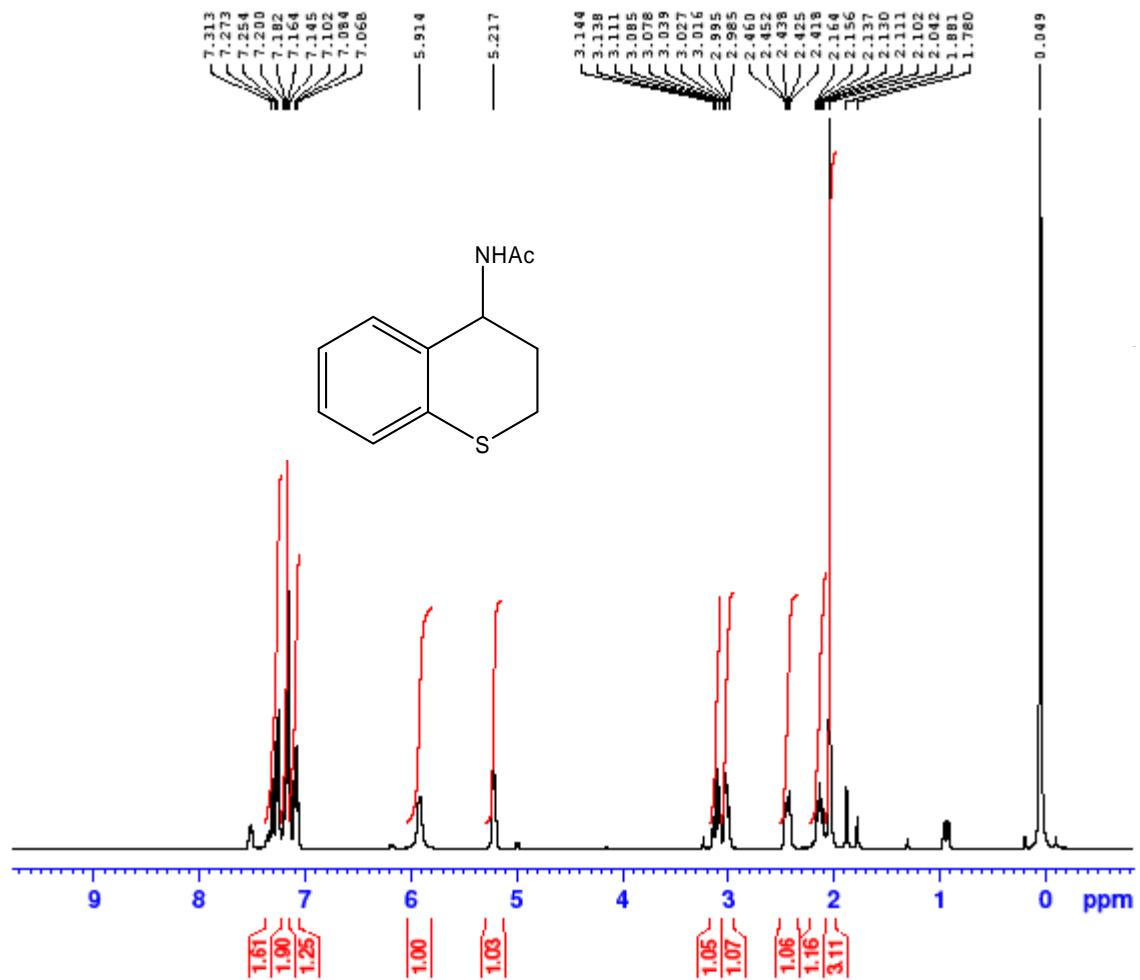
N-(6-chlorochroman-4-yl)acetamide (20d)



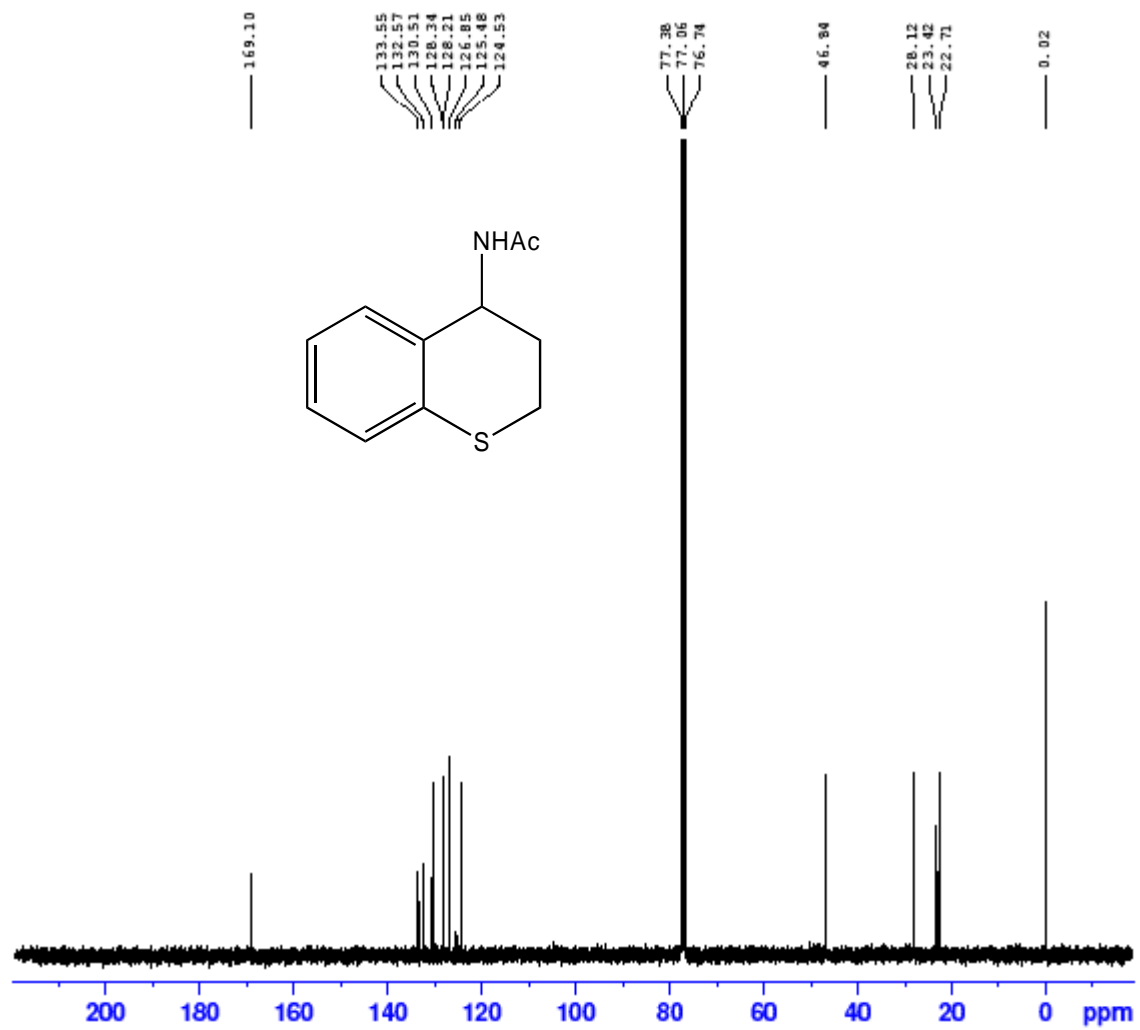
***N*-(6-chlorochroman-4-yl)acetamide (20d)**



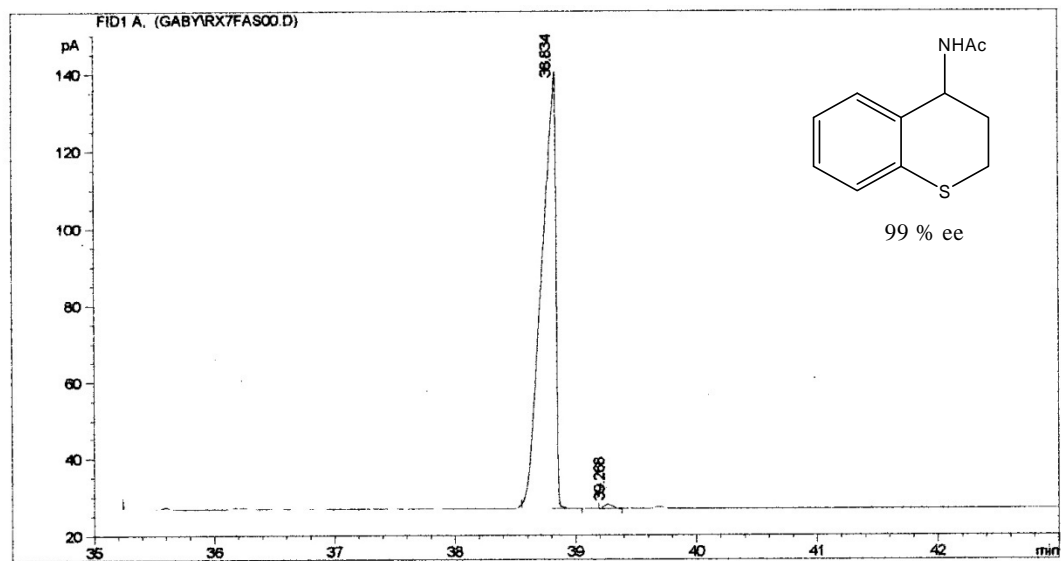
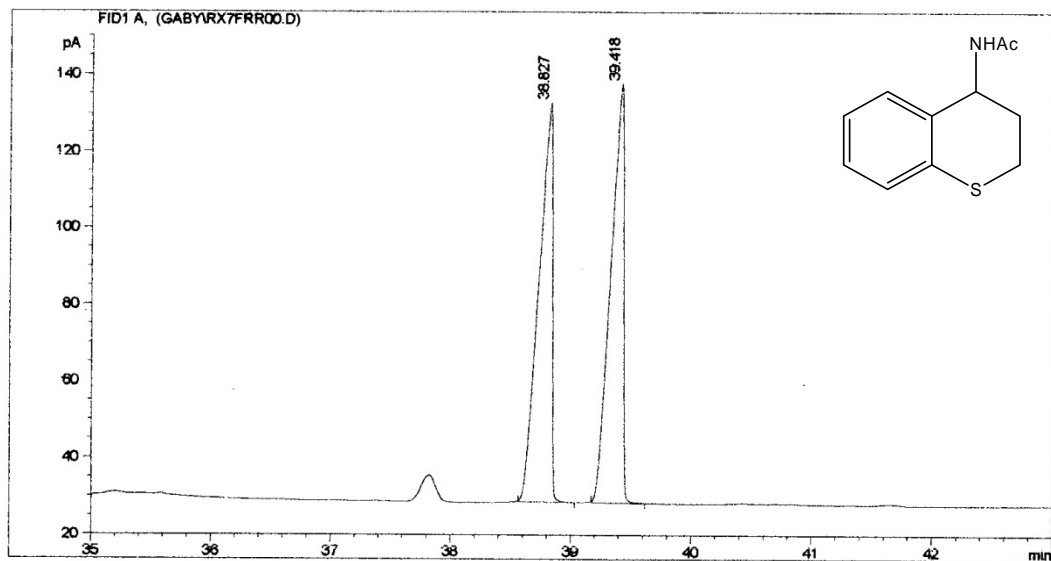
N-(thiochroman-4-yl)acetamide (20e)



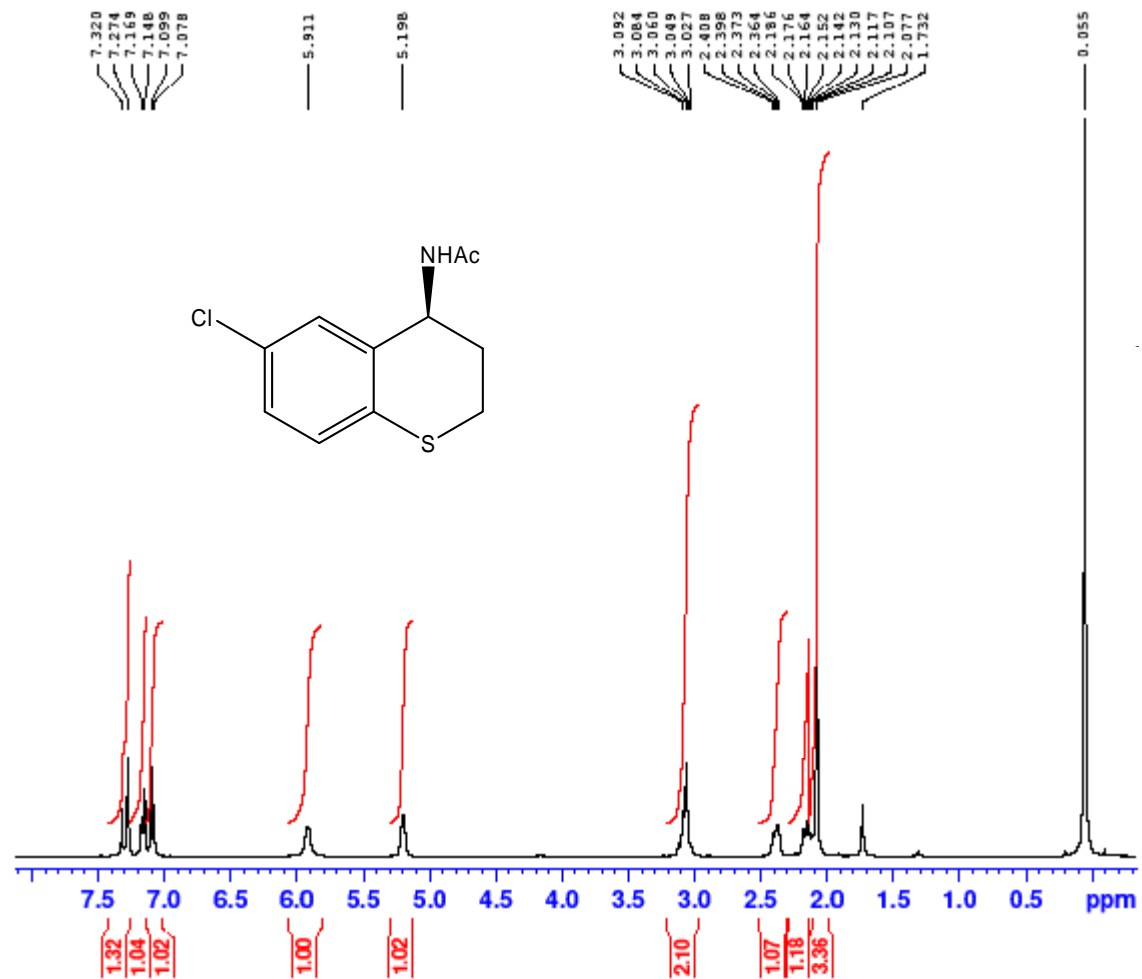
N-(thiochroman-4-yl)acetamide (20e)



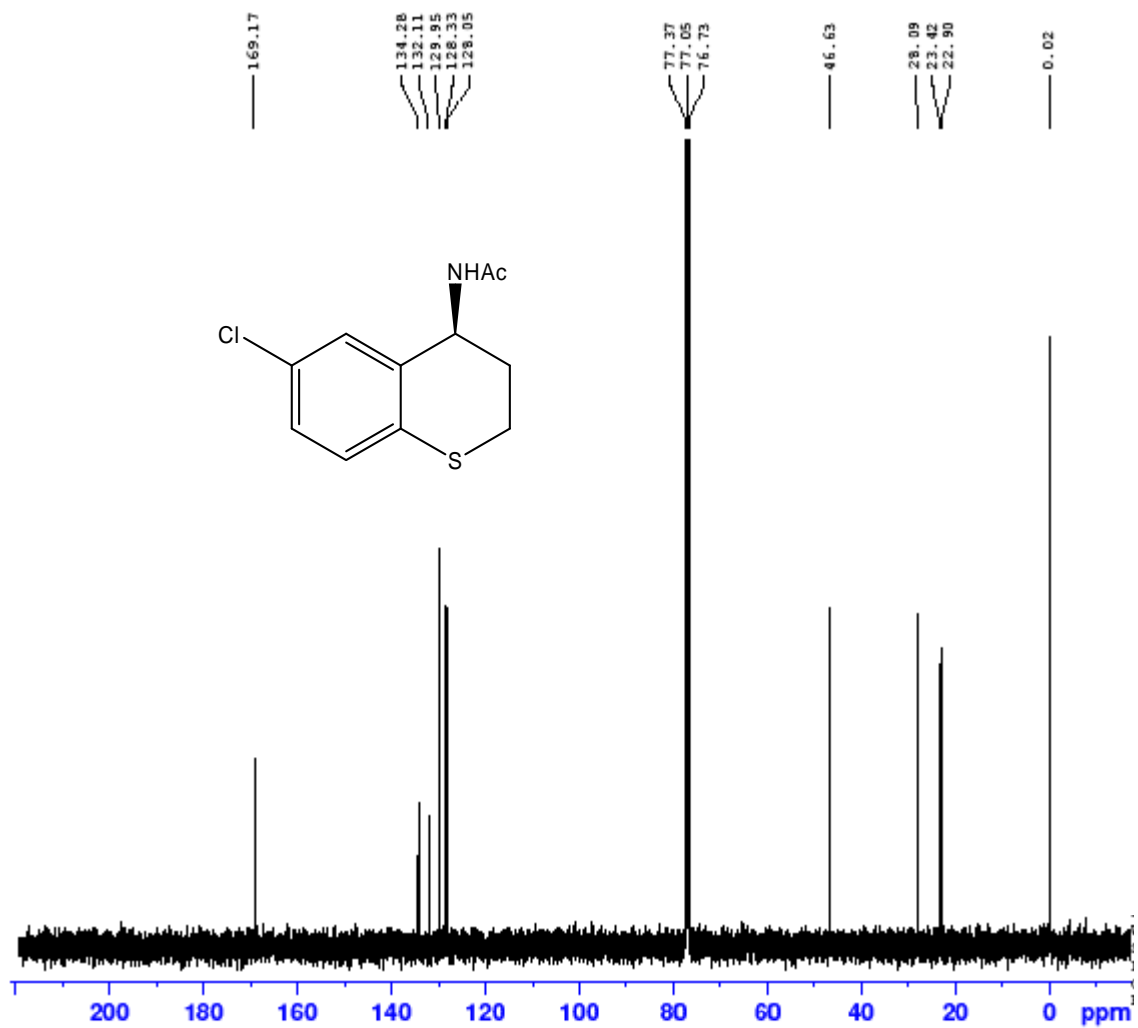
N-(thiochroman-4-yl)acetamide (20e)



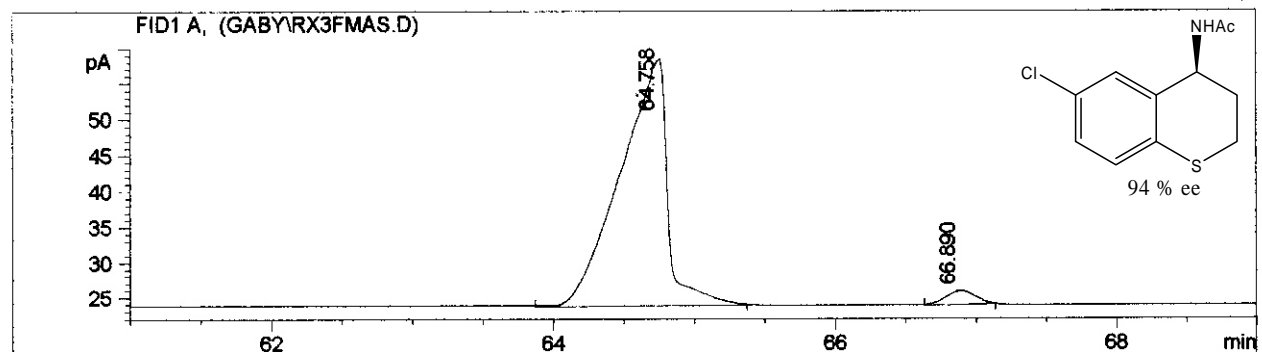
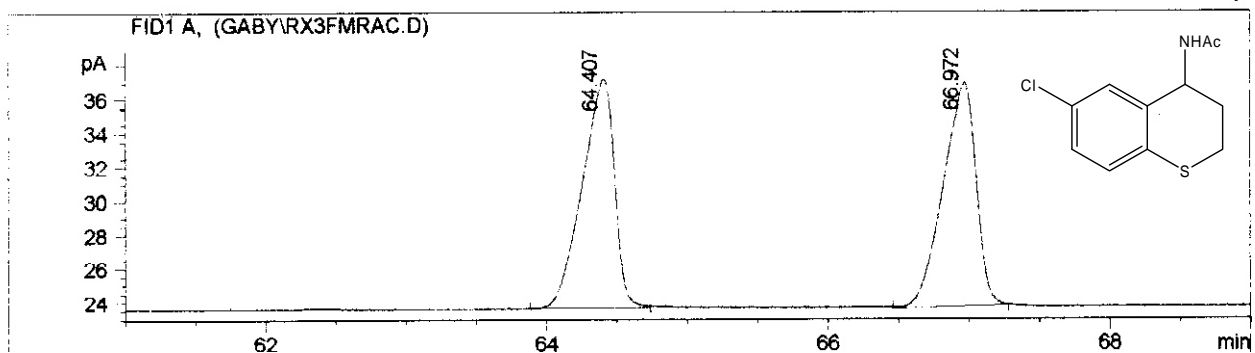
N-(6-chlorothiochroman-4-yl)acetamide (20f)



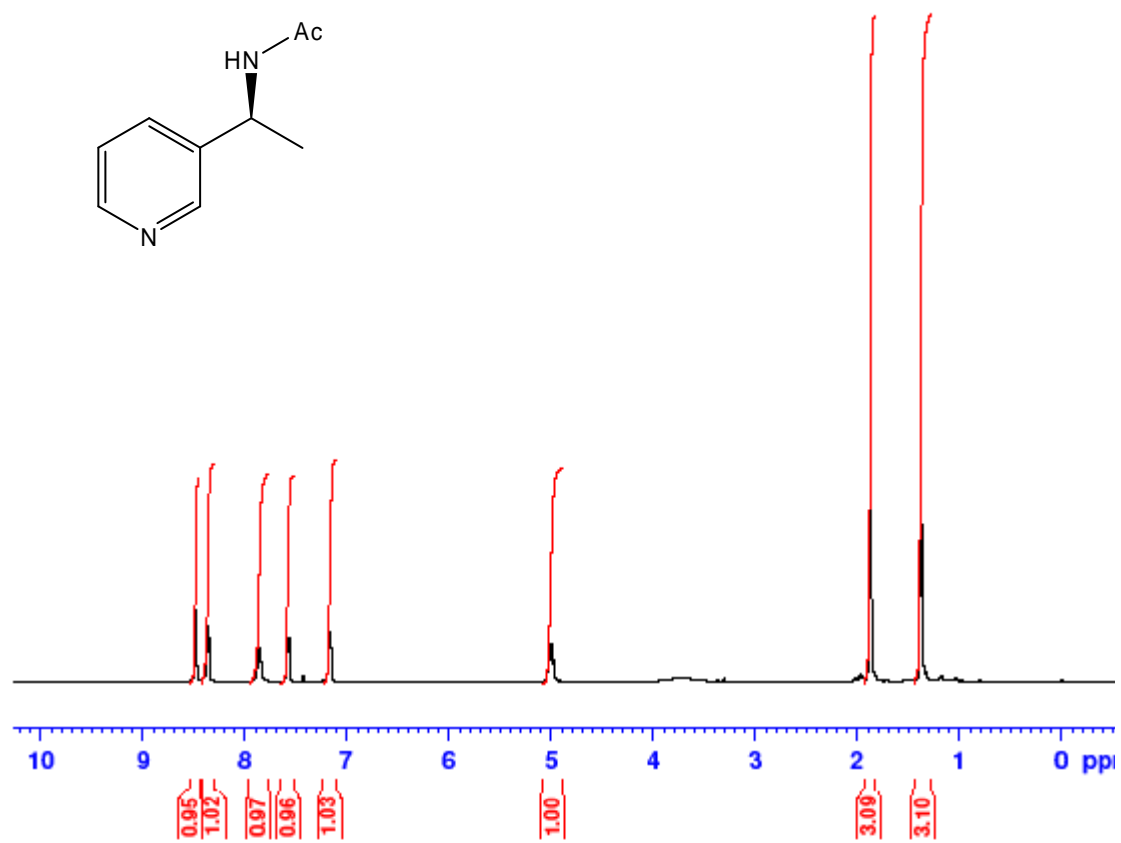
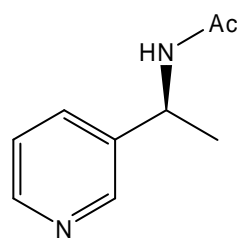
N-(6-chlorothiochroman-4-yl)acetamide (20f)



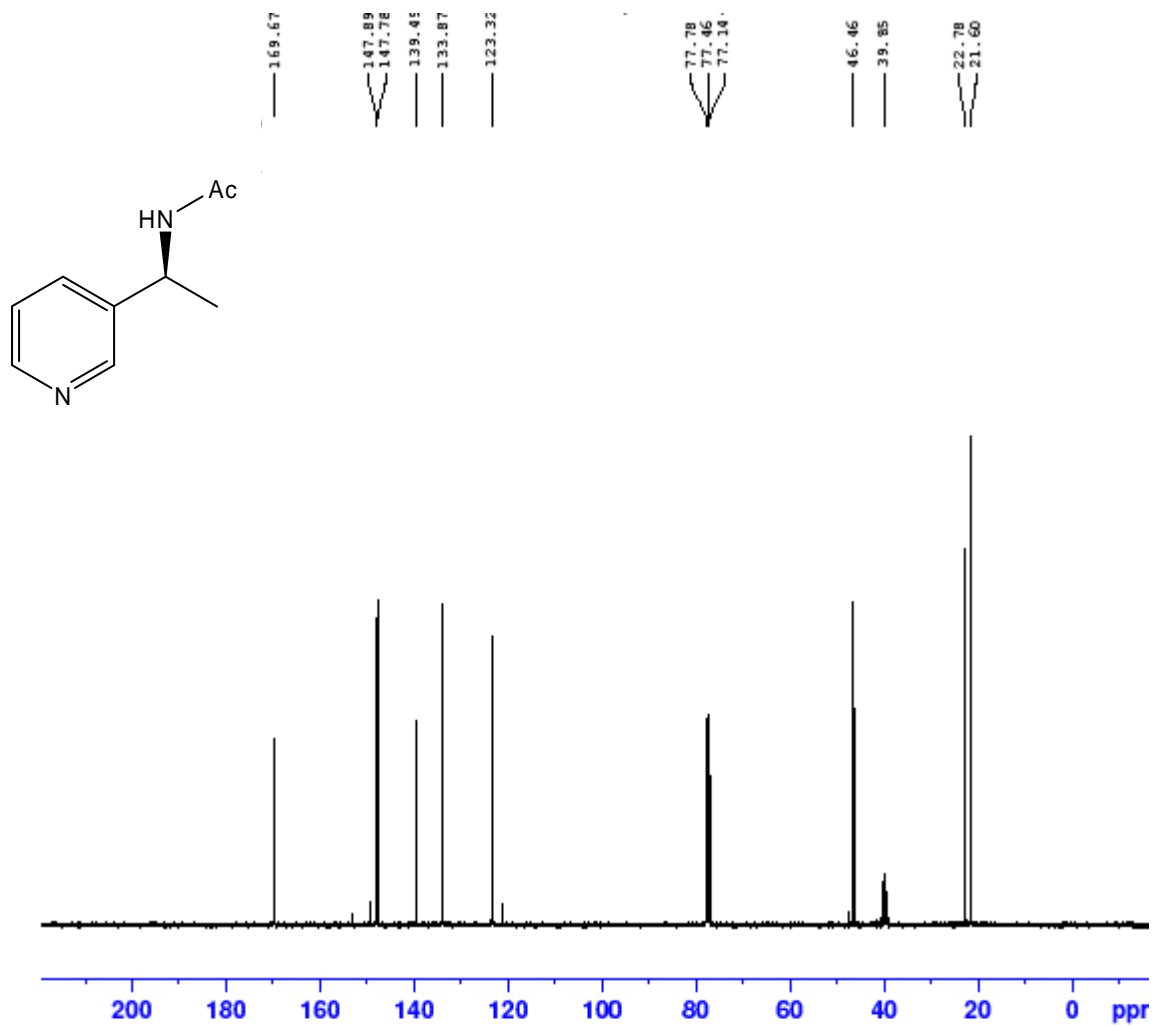
N-(6-chlorothiochroman-4-yl)acetamide (20f)



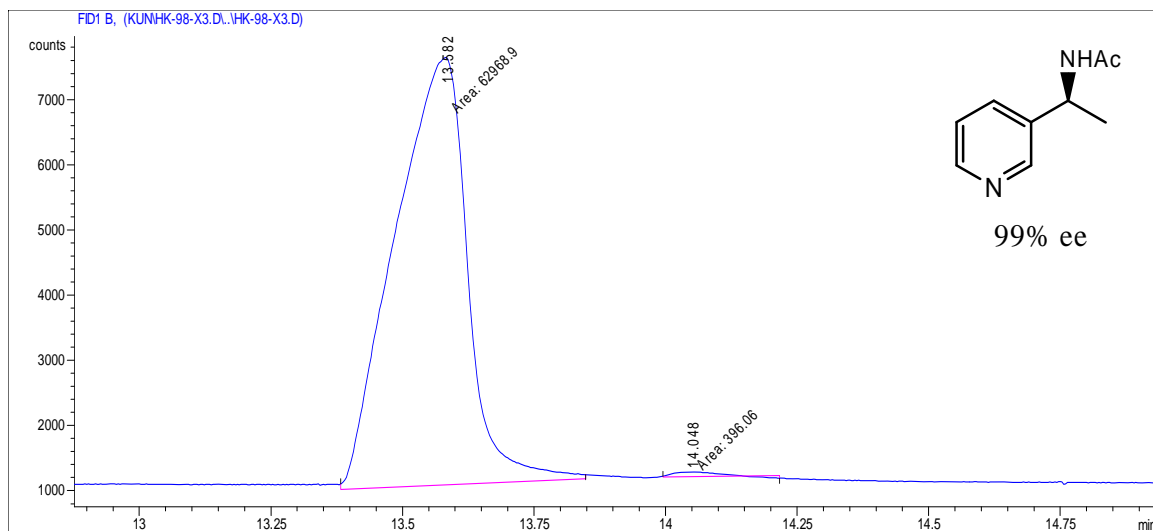
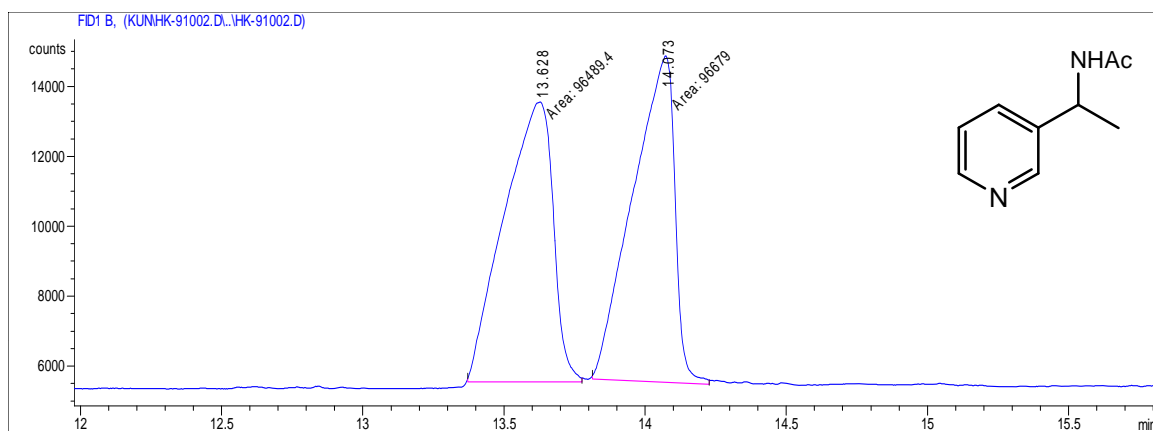
***N*--(1-(Pyridin-3-yl)ethyl)acetamide (22a)**



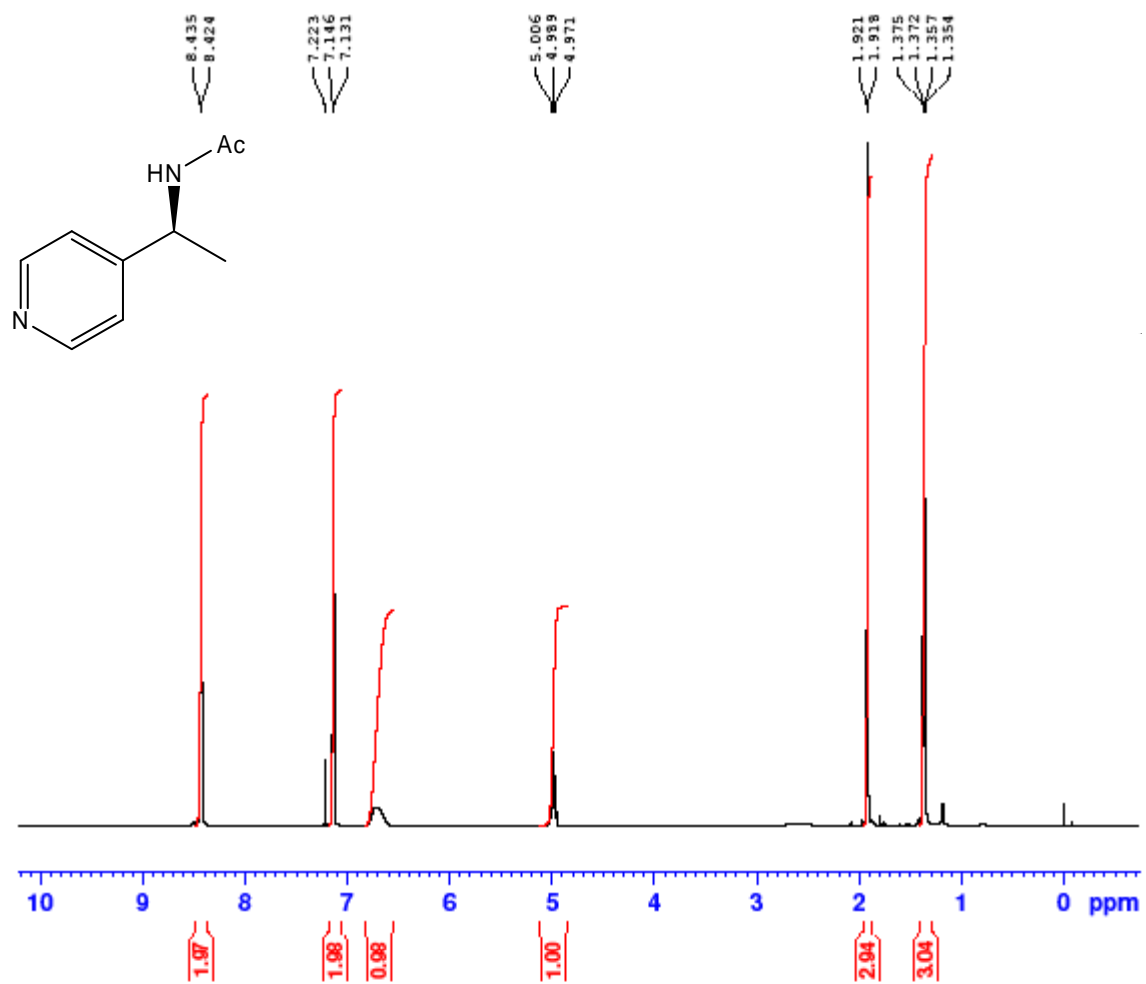
***N*-(1-(Pyridin-3-yl)-ethyl)acetamide (22a)**



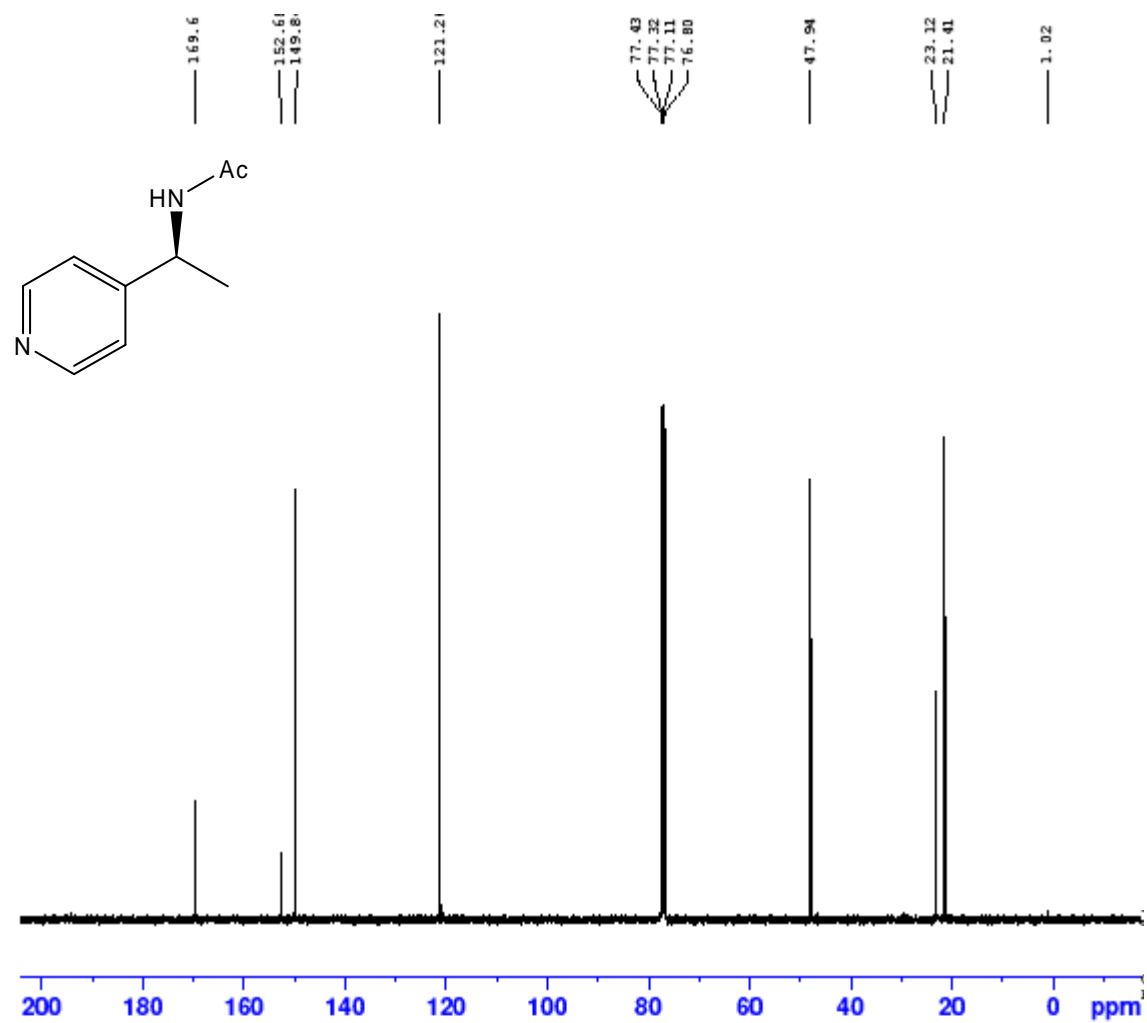
N-(1-(Pyridin-3-yl)-ethyl)acetamide (22a)



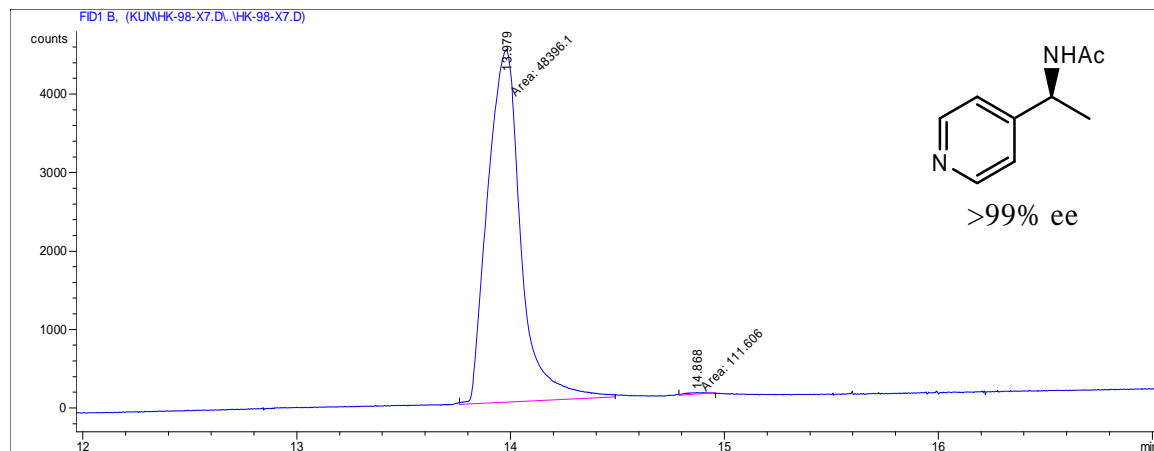
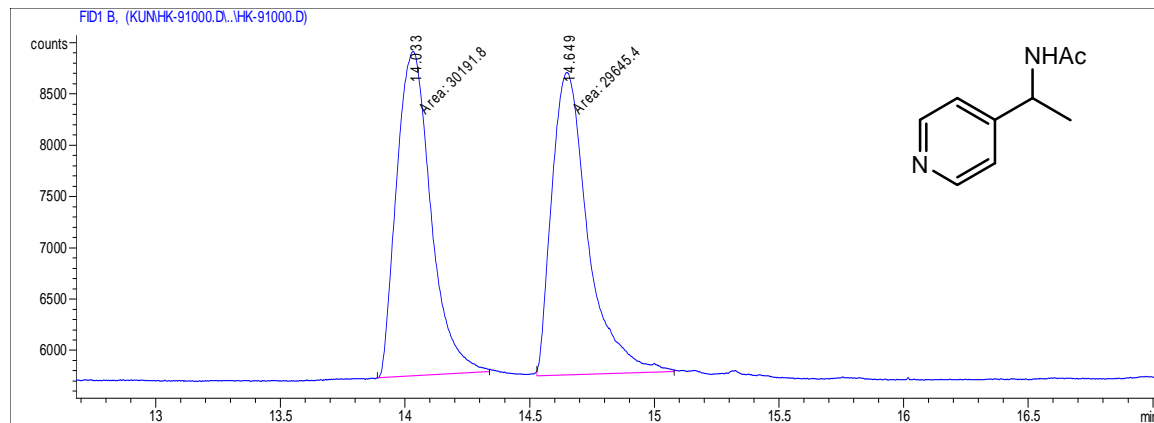
***N*-(1-(Pyridin-4-yl)-ethyl)acetamide (24a)**



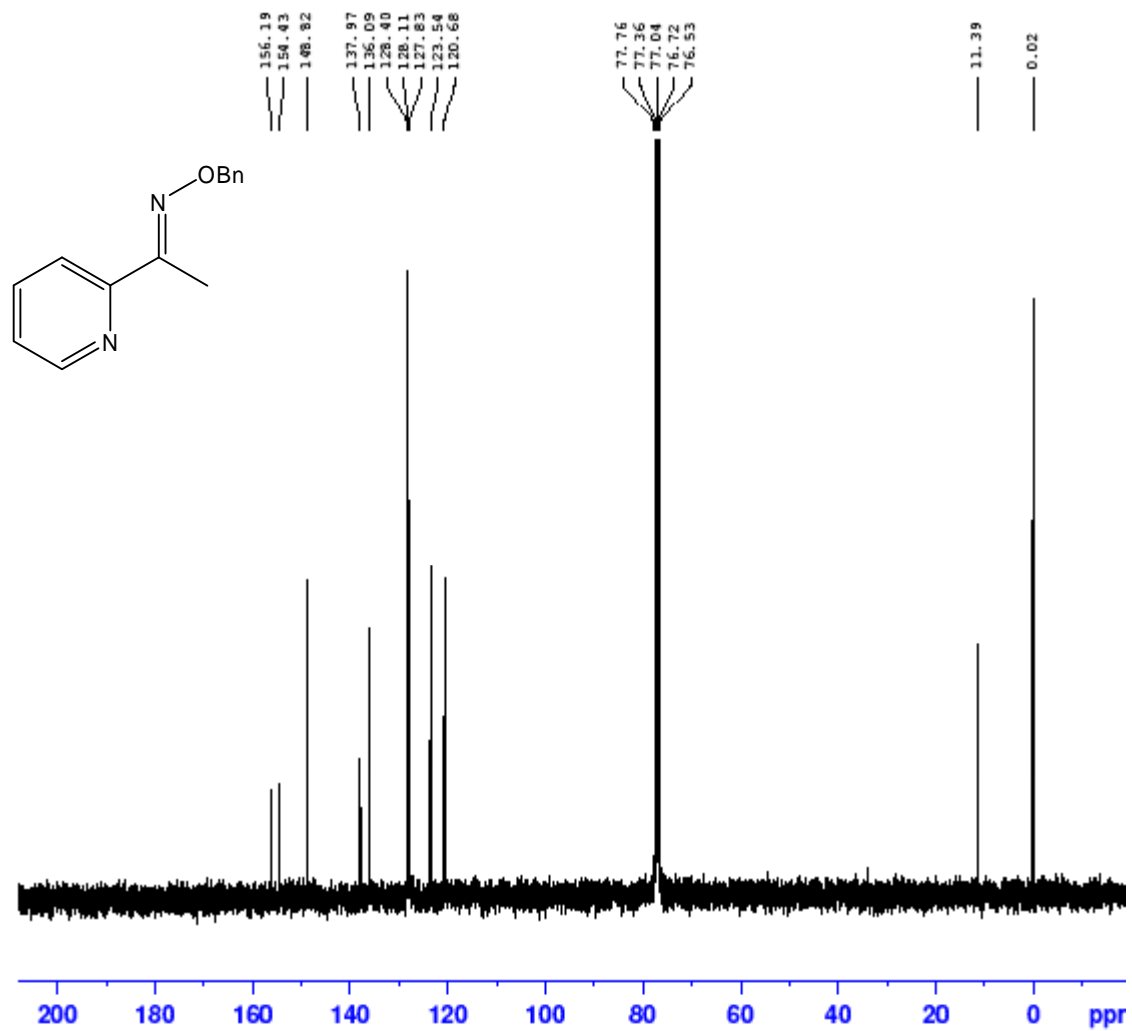
N-(1-(Pyridin-4-yl)-ethyl)acetamide (24a)



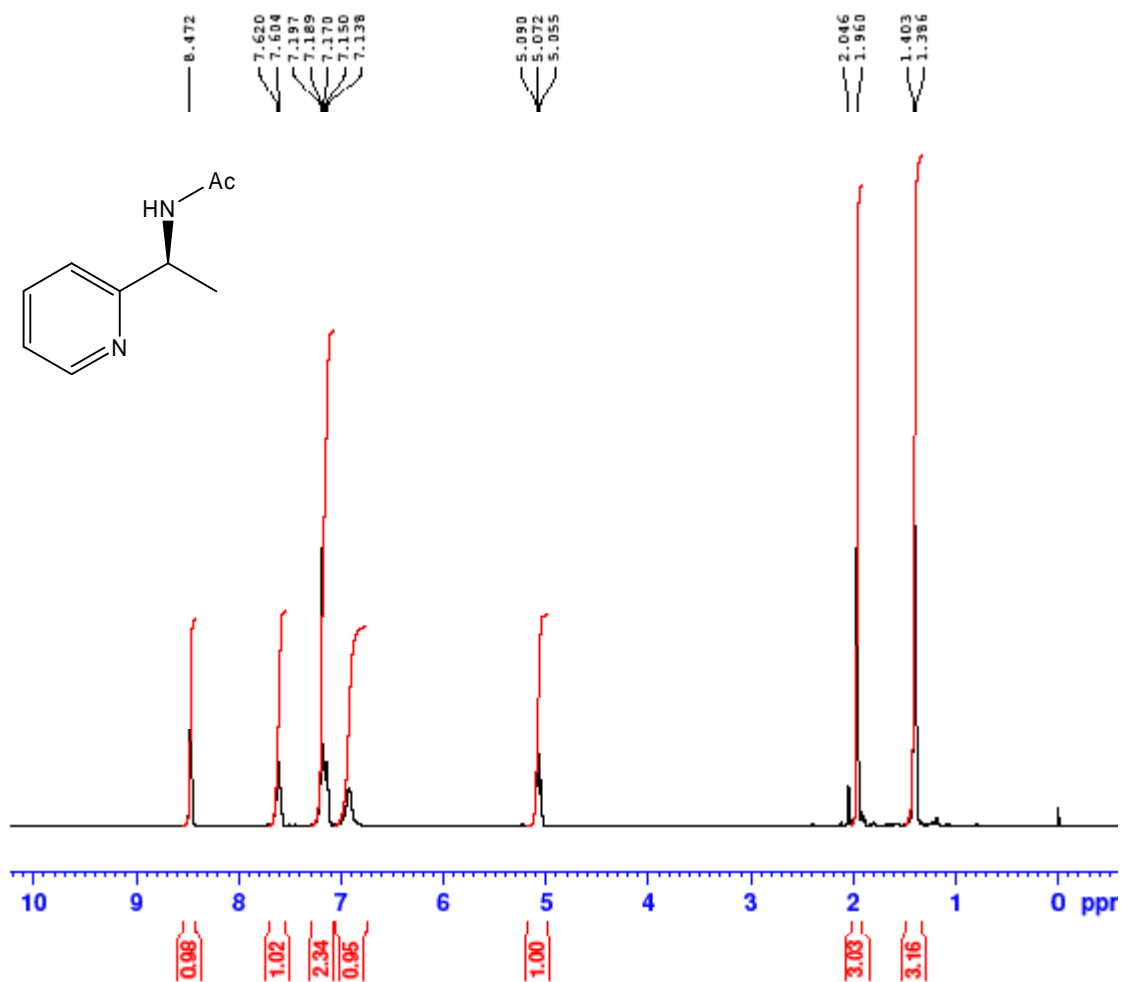
N-(1-(Pyridin-4-yl)-ethyl)acetamide (24a)



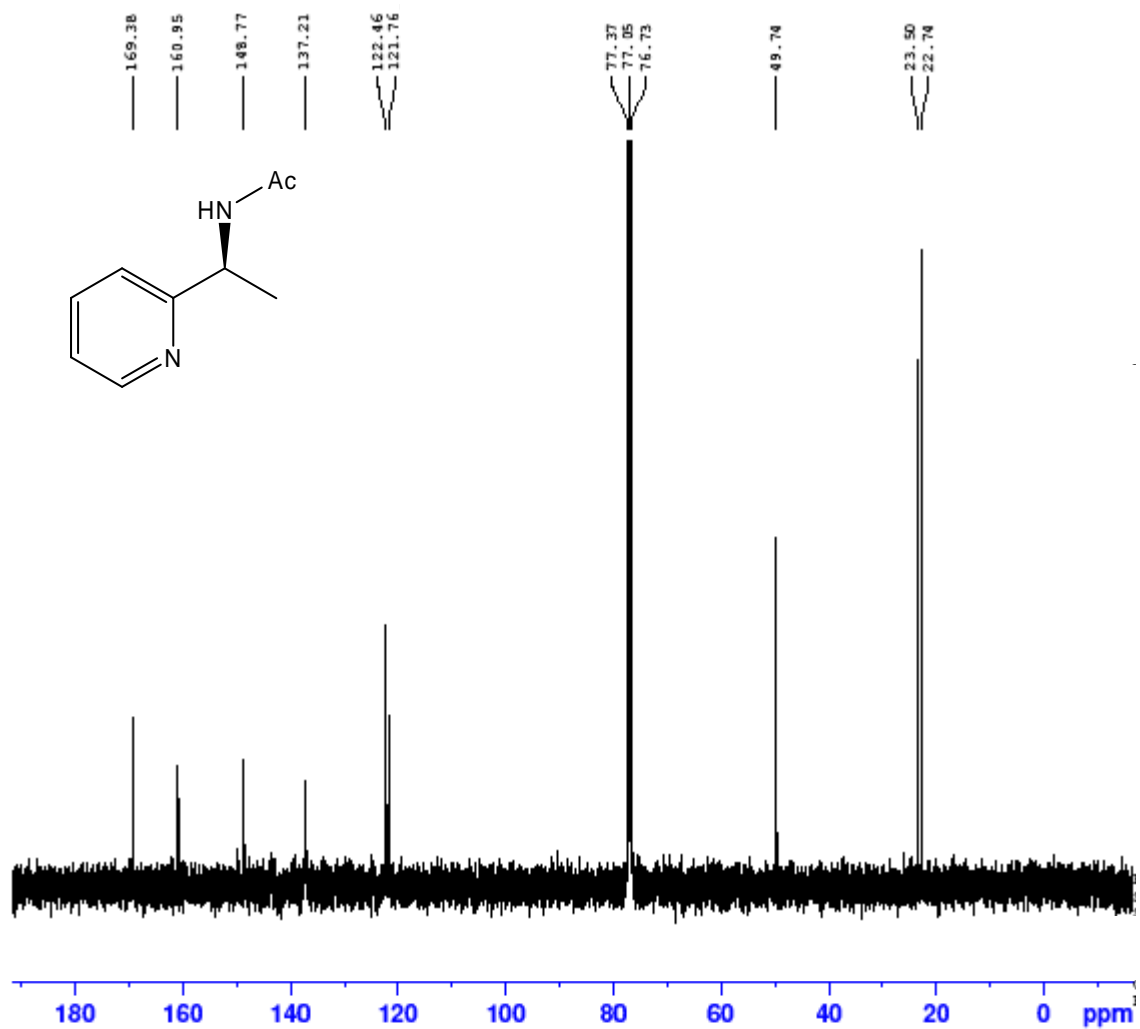
(E)-1-(Pyridine-2-yl)ethanone O-benzyl oxime (25)



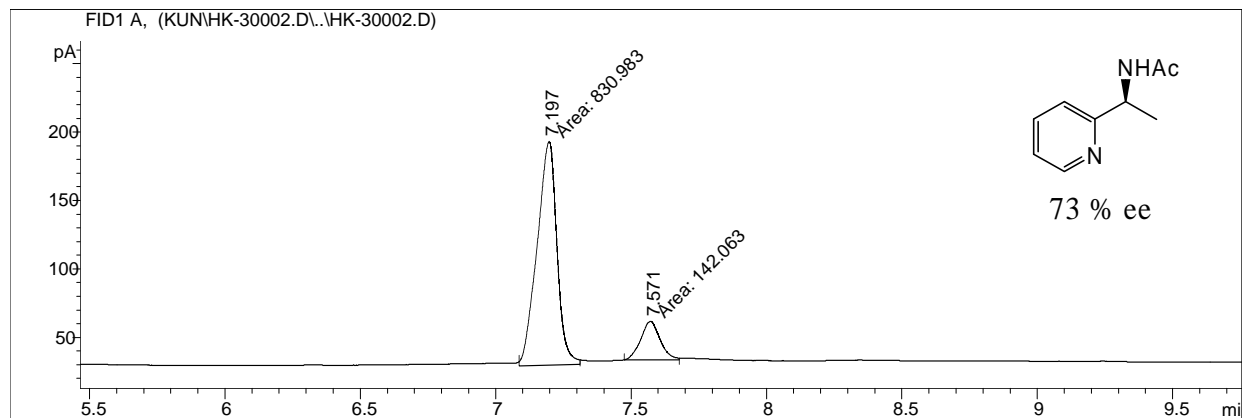
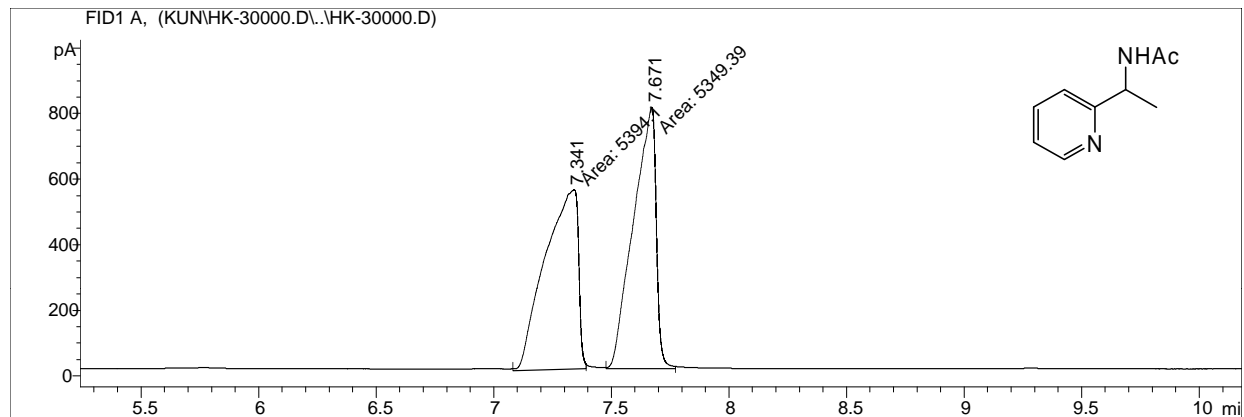
N-(1-(Pyridin-2-yl)-ethyl)acetamide (27)



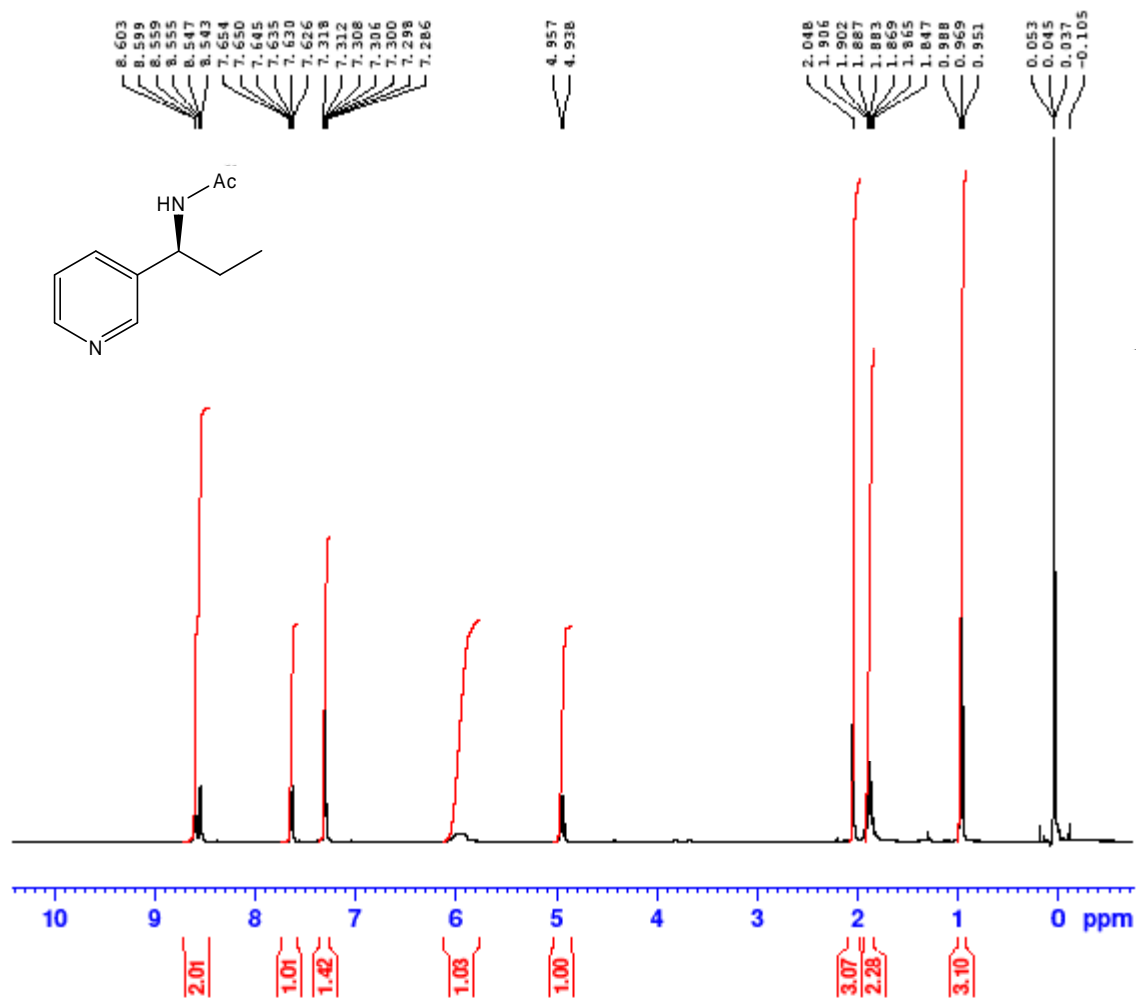
N-(1-(Pyridin-2-yl)-ethyl)acetamide (27)



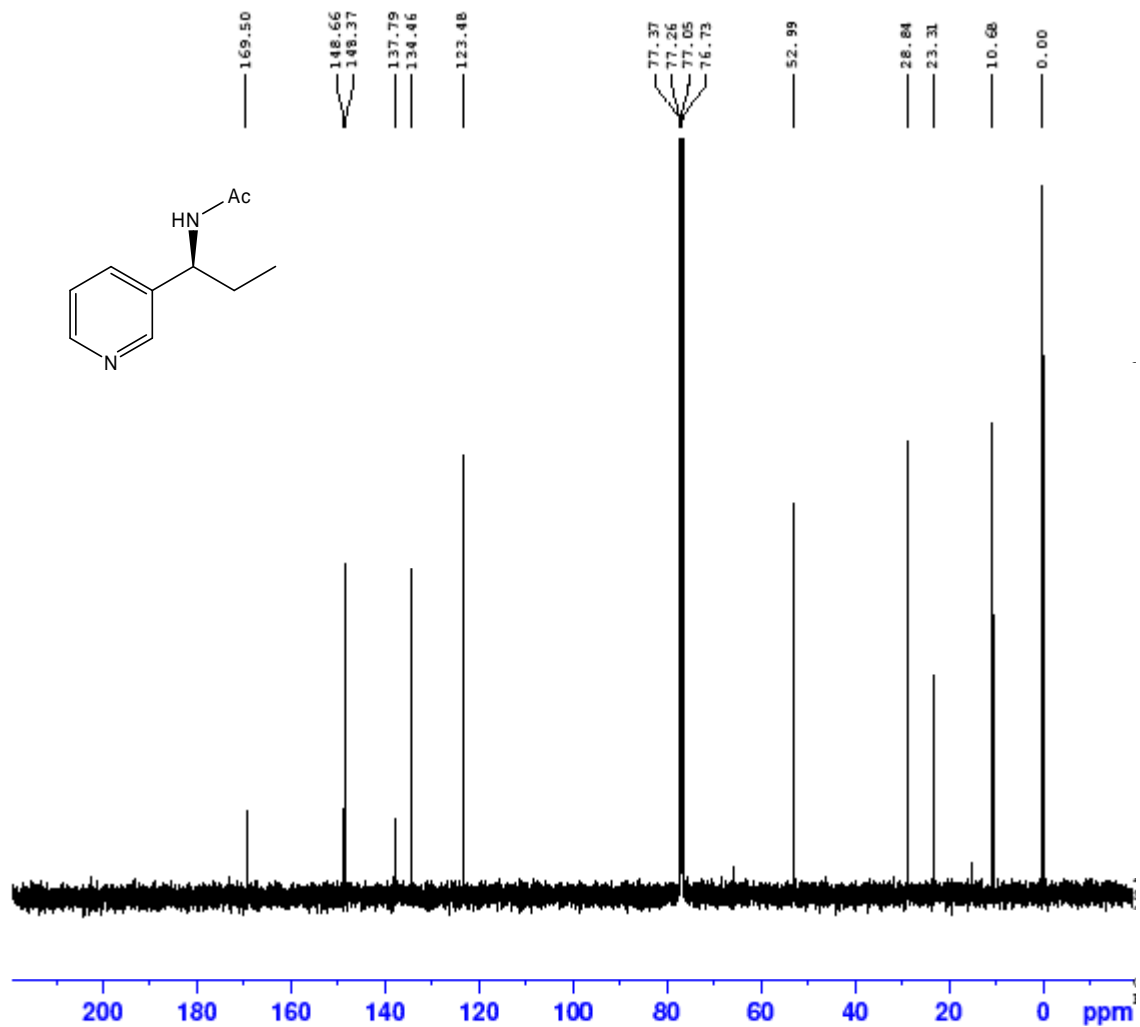
N-(1-(Pyridin-2-yl)-ethyl)acetamide (27)



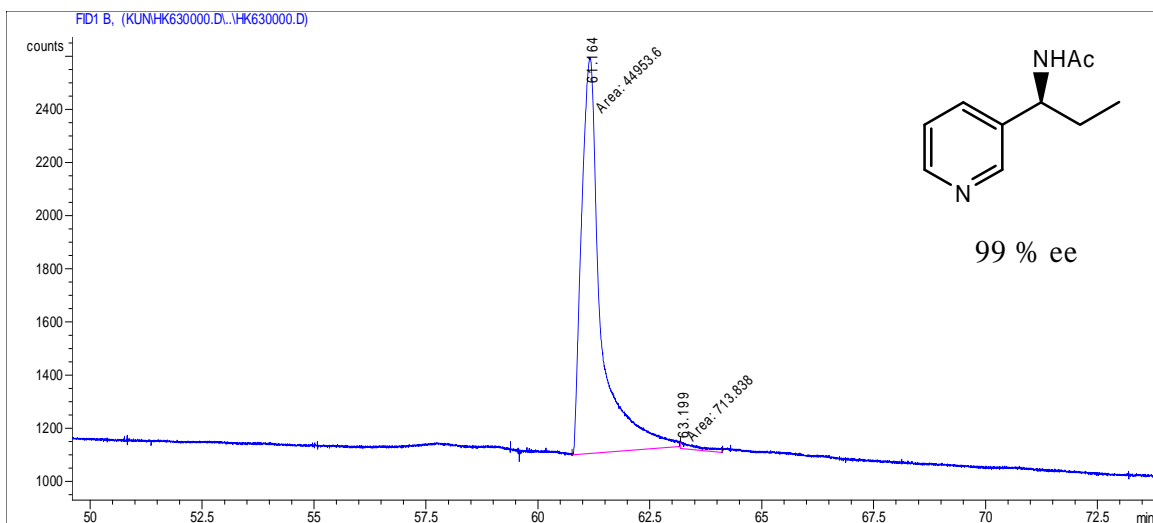
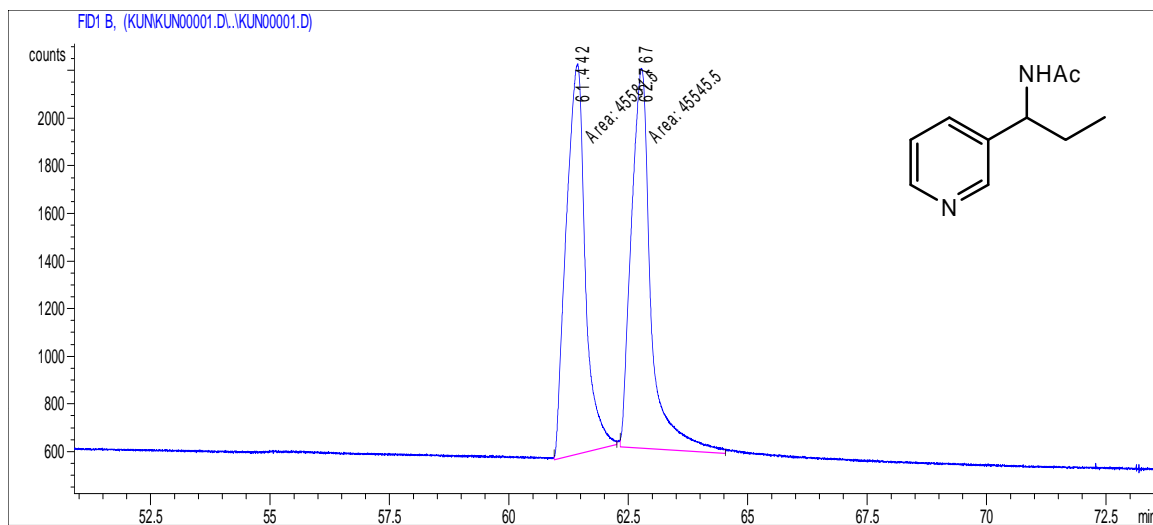
N-(1-(Pyridine-3-yl)-propyl)acetamide (28)



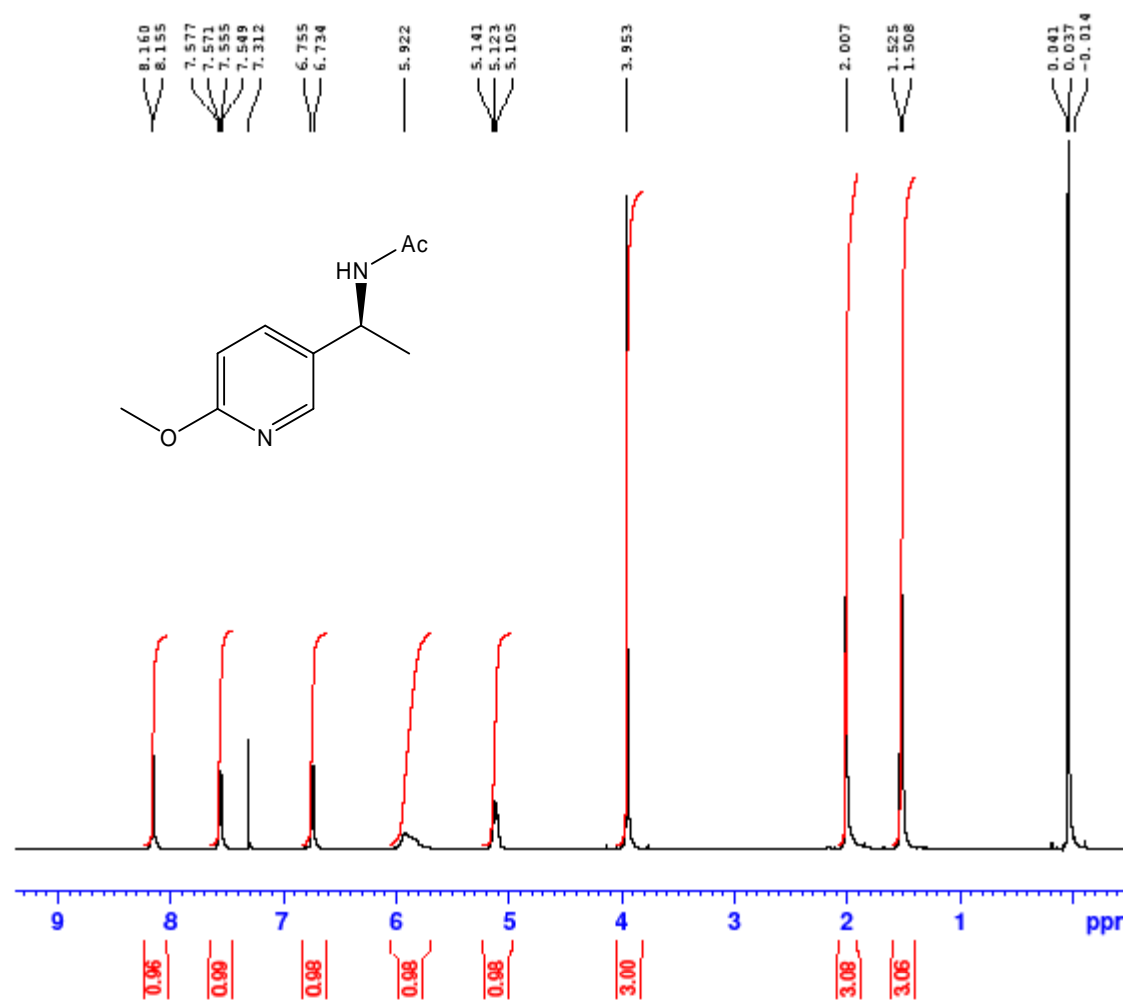
***N*-(1-(Pyridine-3-yl)-propyl)acetamide (28)**



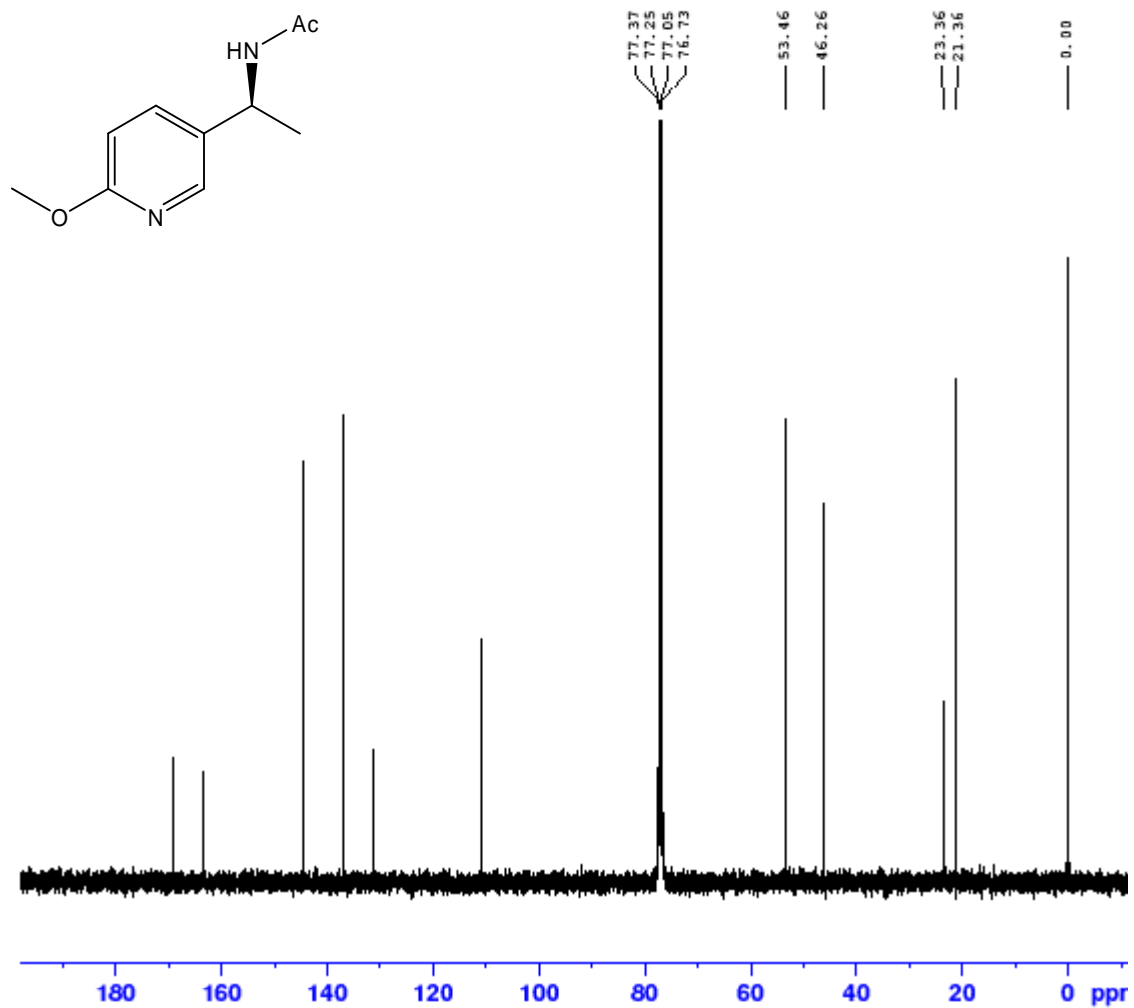
N-(1-(Pyridine-3-yl)-propyl)acetamide (28)



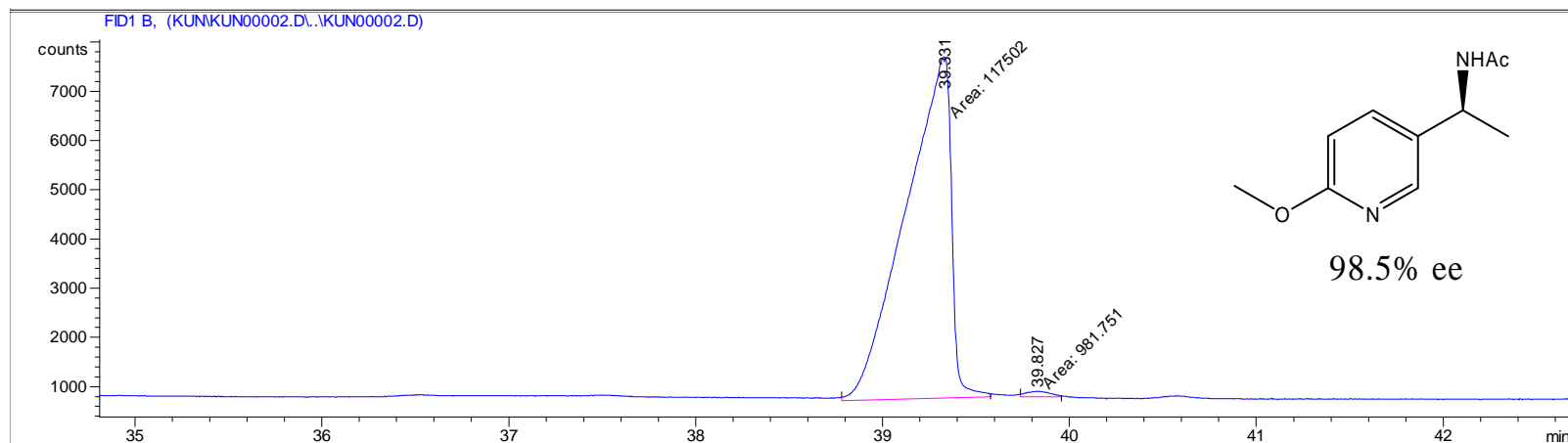
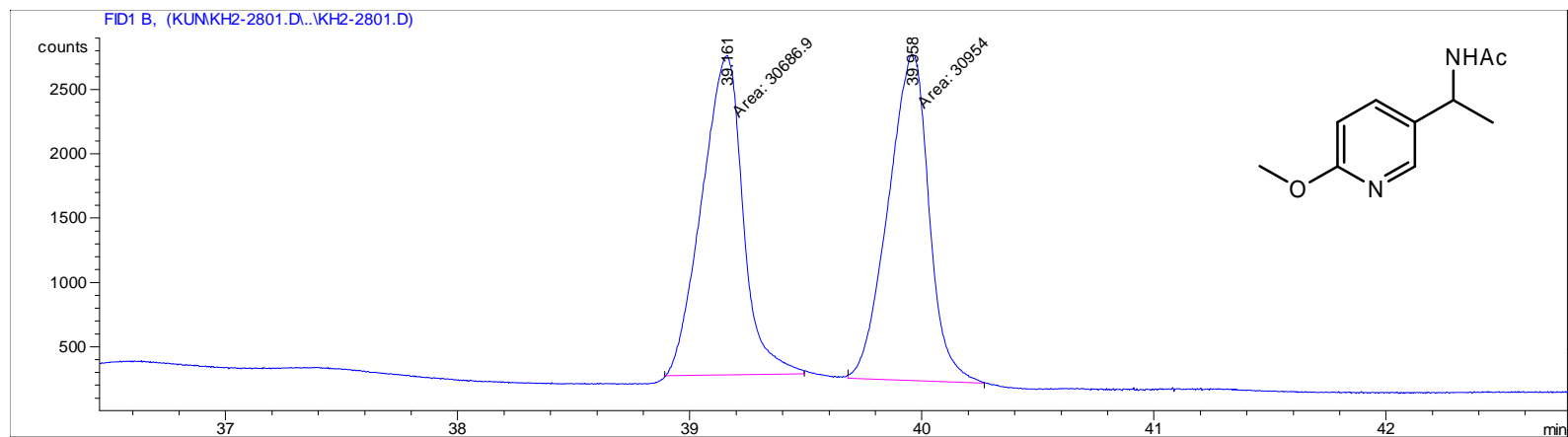
(S)-N-(1-(6-methoxypyridine-3-yl)ethyl)acetamide (29)



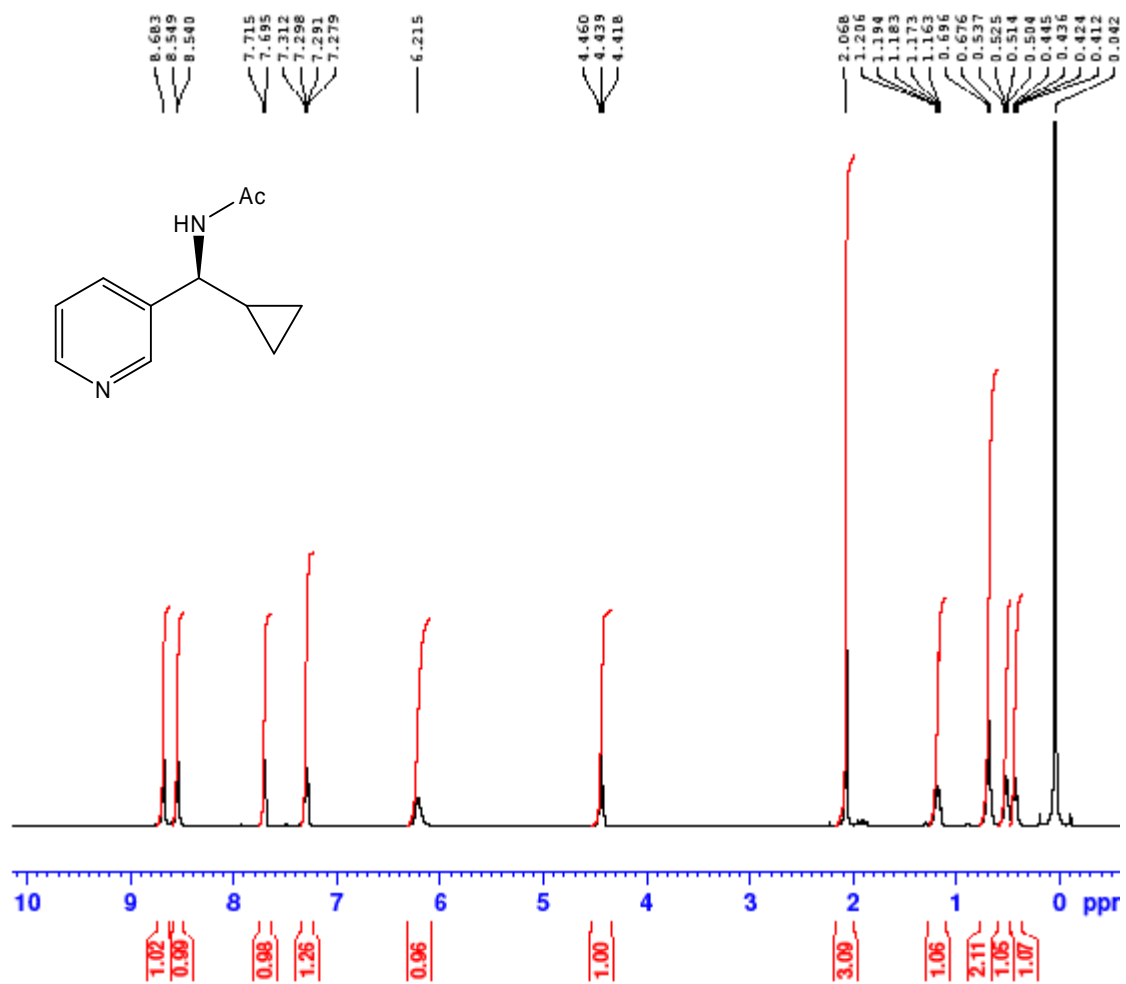
(S)-N-(1-(6-methoxypyridine-3-yl)ethyl)acetamide (29)



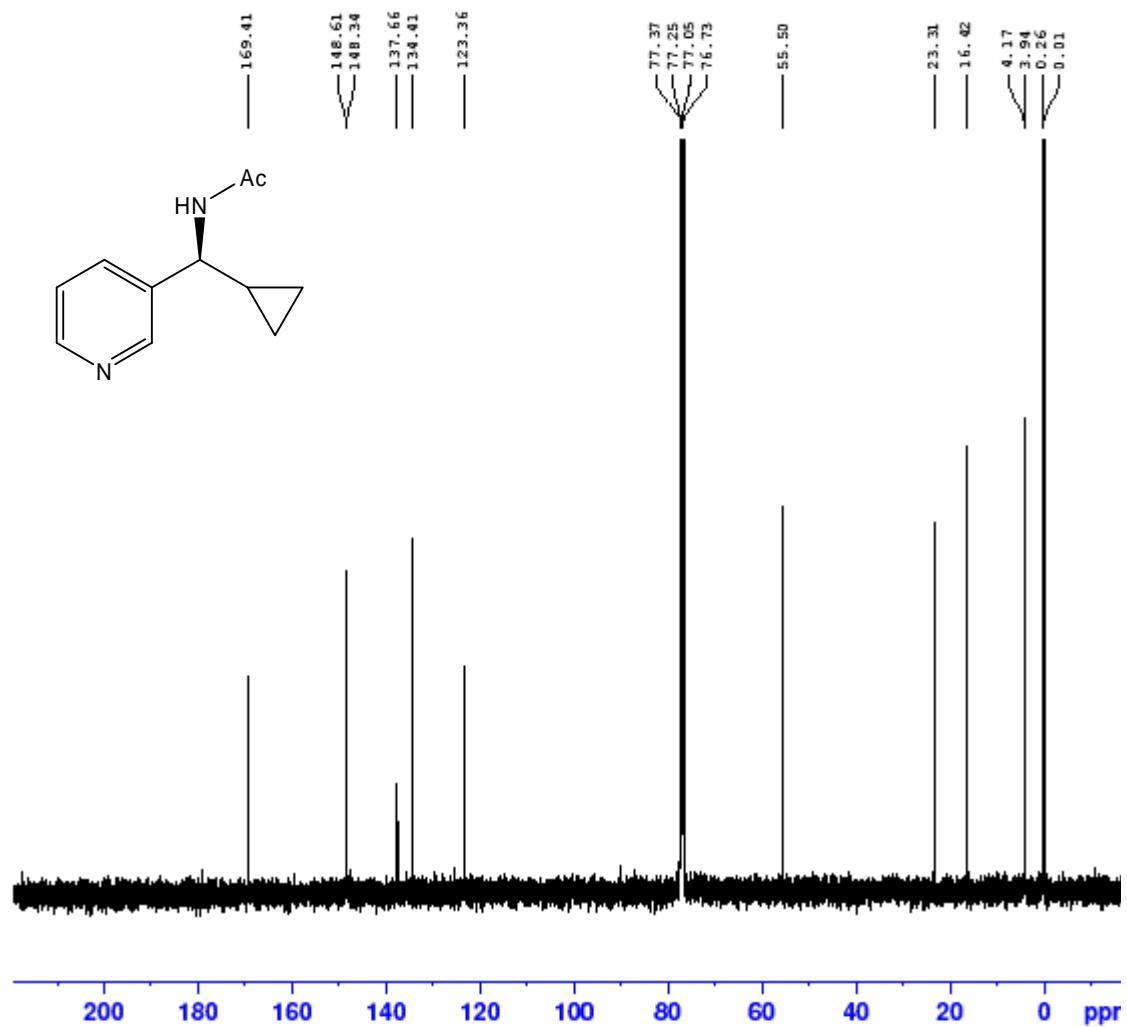
(S)-N-(1-(6-methoxypyridine-3-yl)ethyl)acetamide (29)



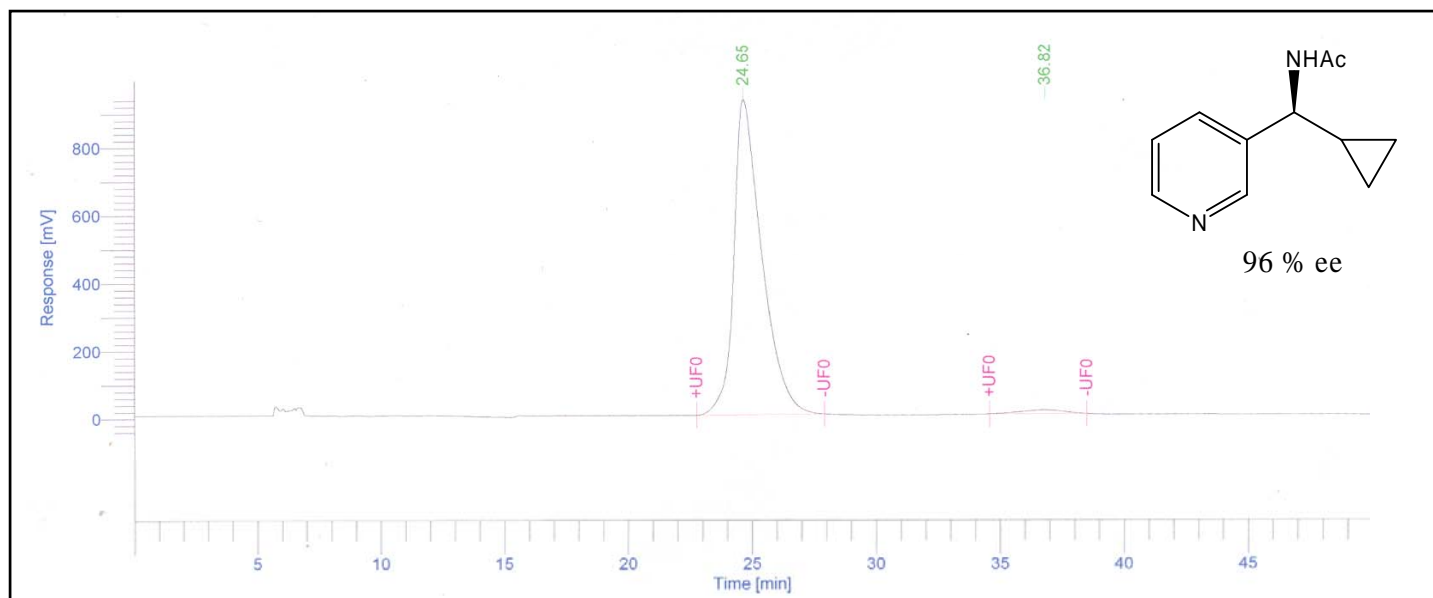
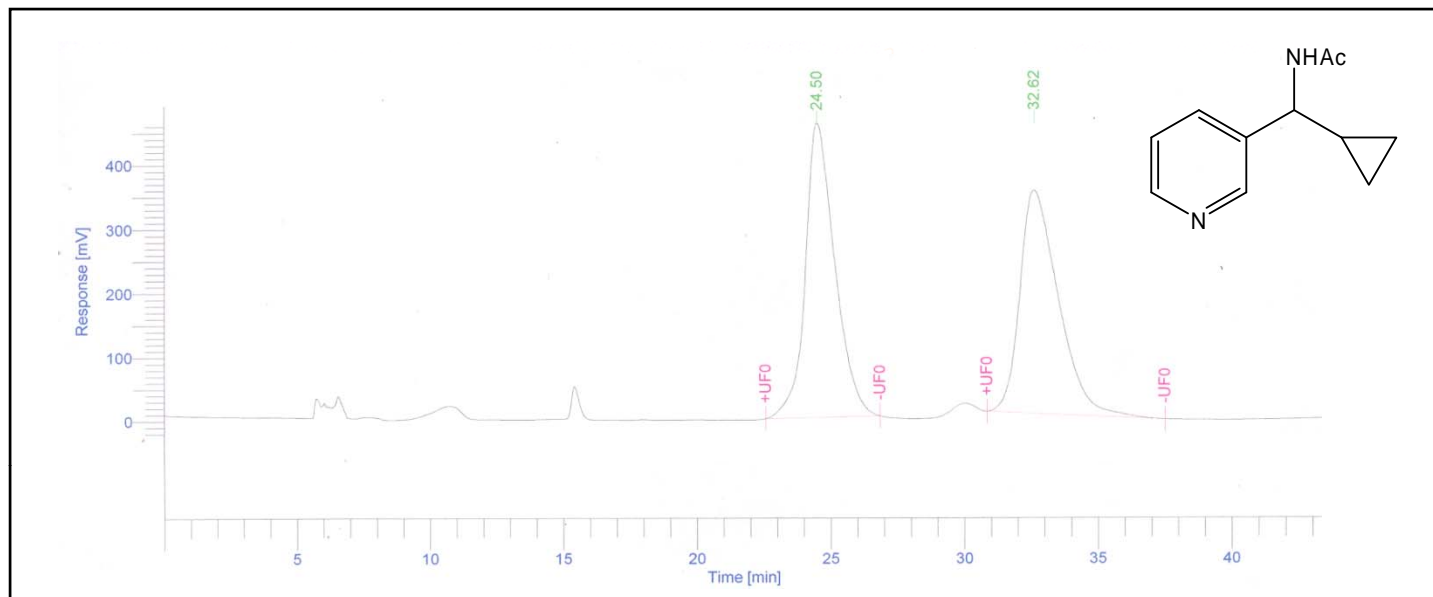
N-Cyclopropyl-(pyridine-3-yl)-methyl-acetamide (30)



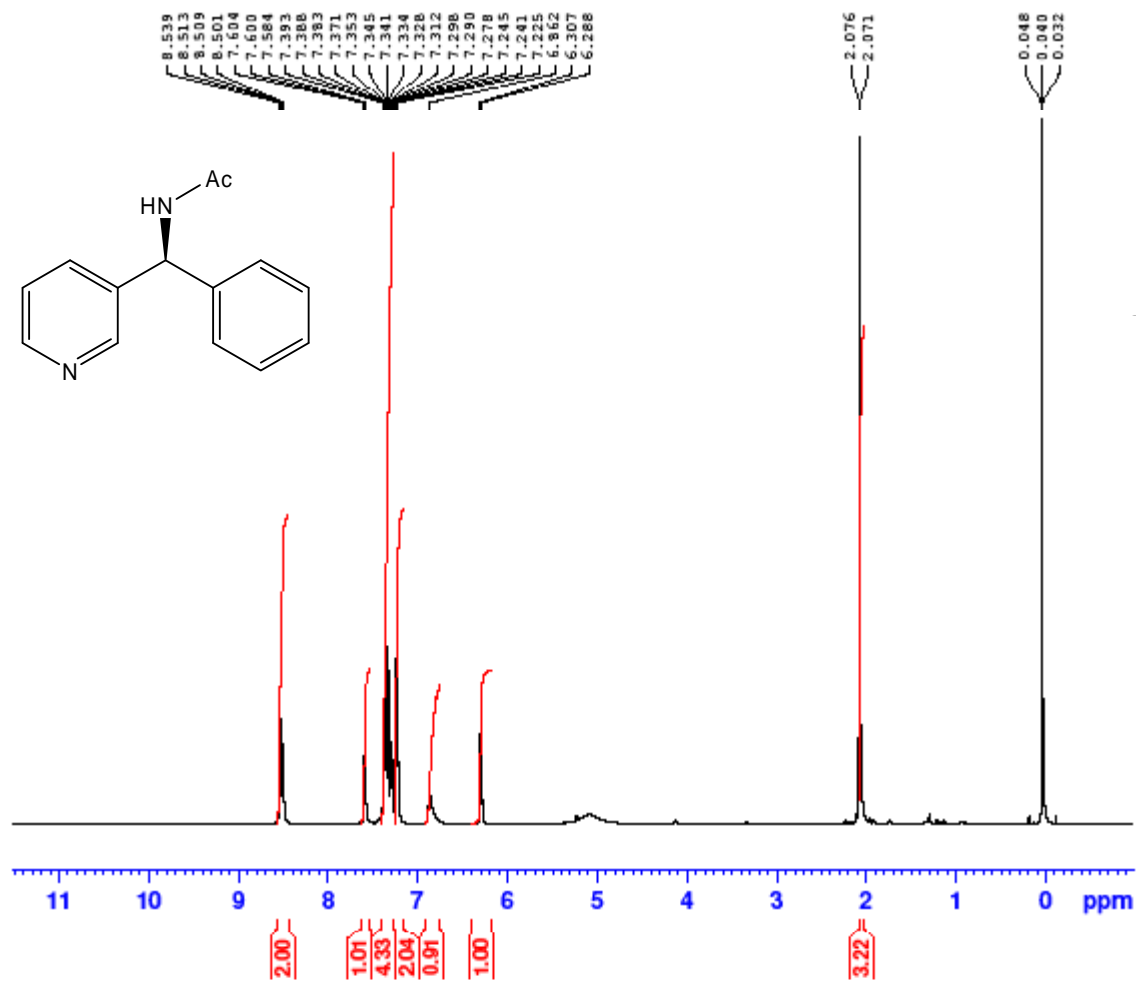
N-Cyclopropyl-(pyridine-3-yl)-methyl)-acetamide (30)



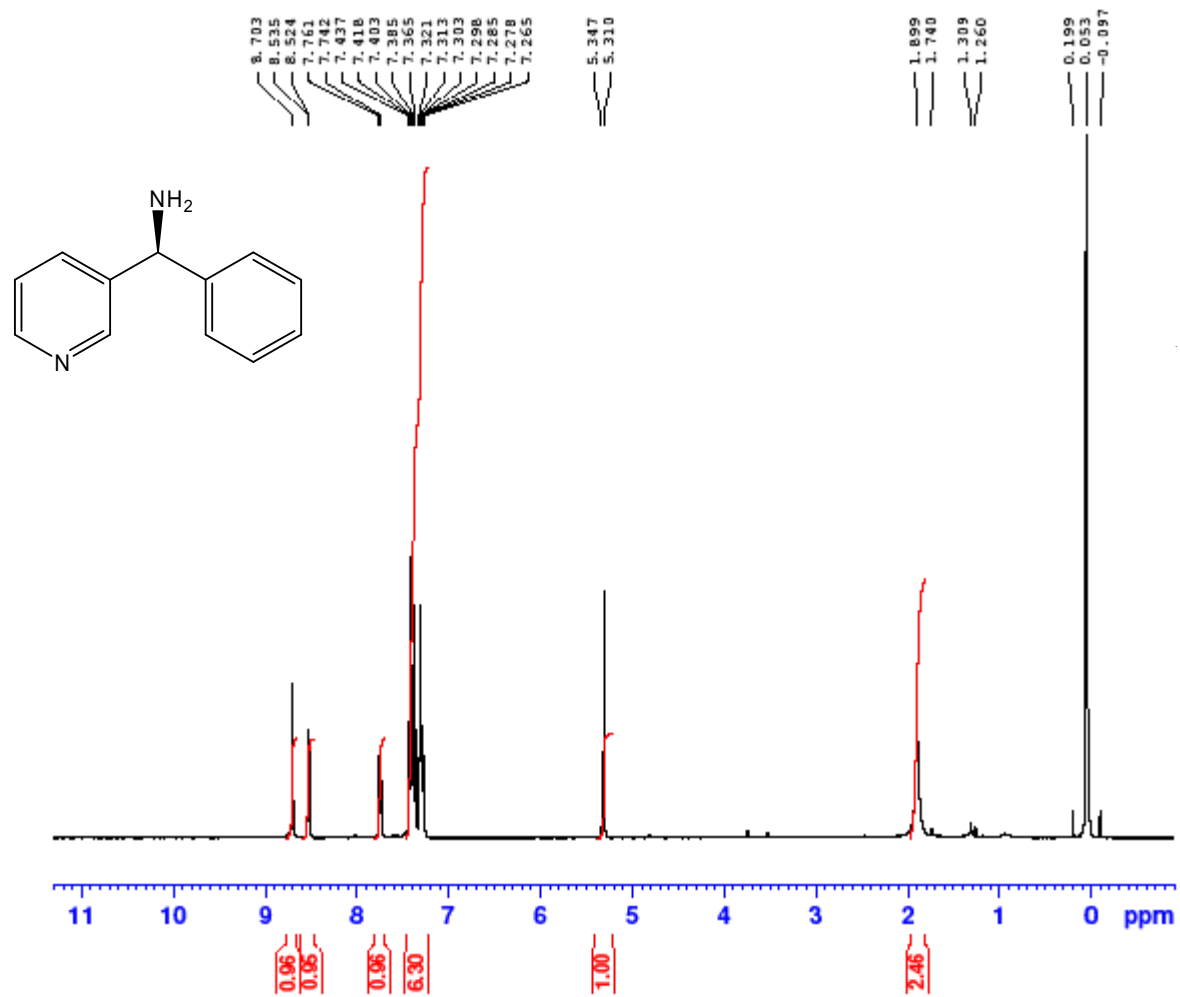
N-Cyclopropyl-(pyridine-3-yl)-methyl-acetamide (30)



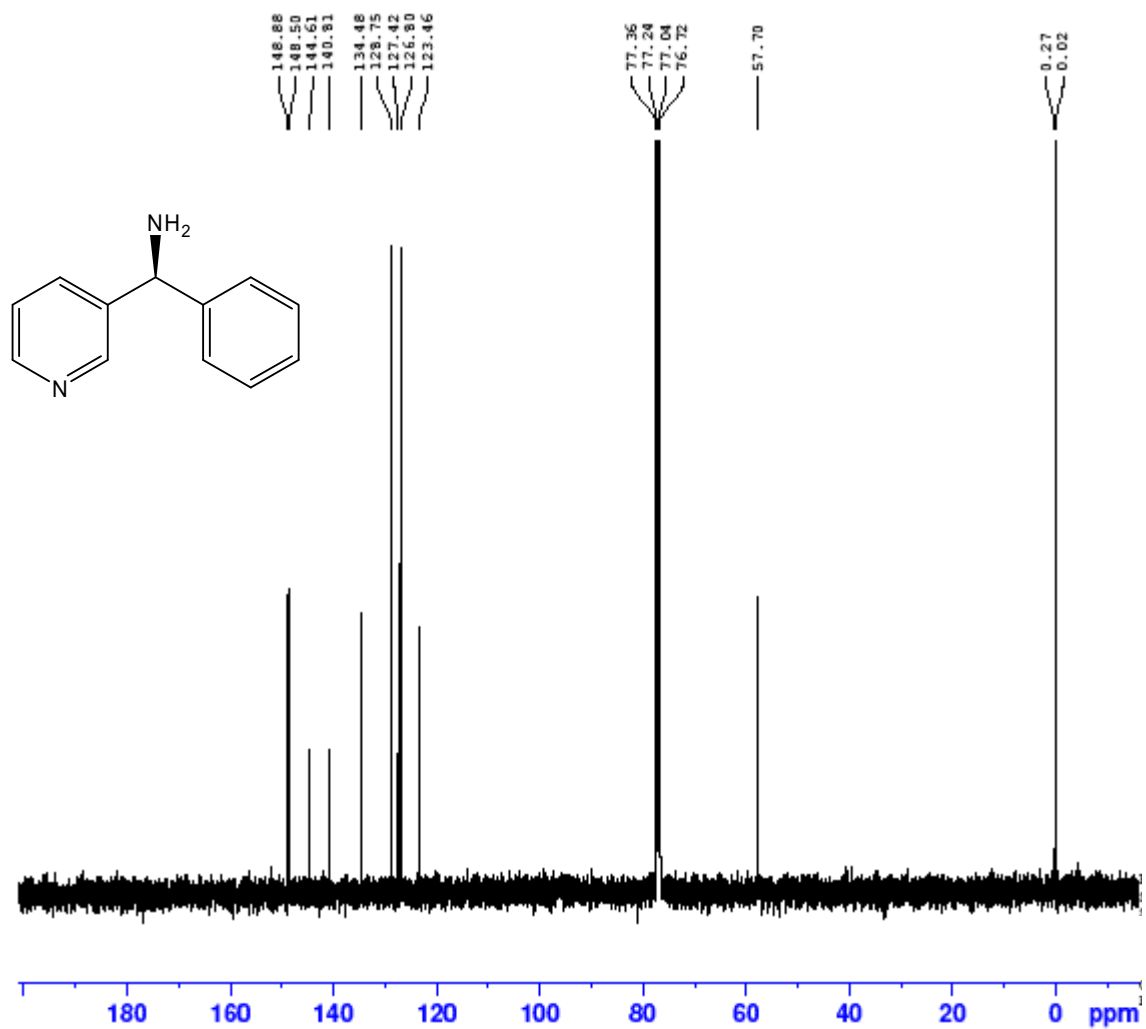
(S)-N-(phenyl(pyridin-3-yl)methyl)acetamide



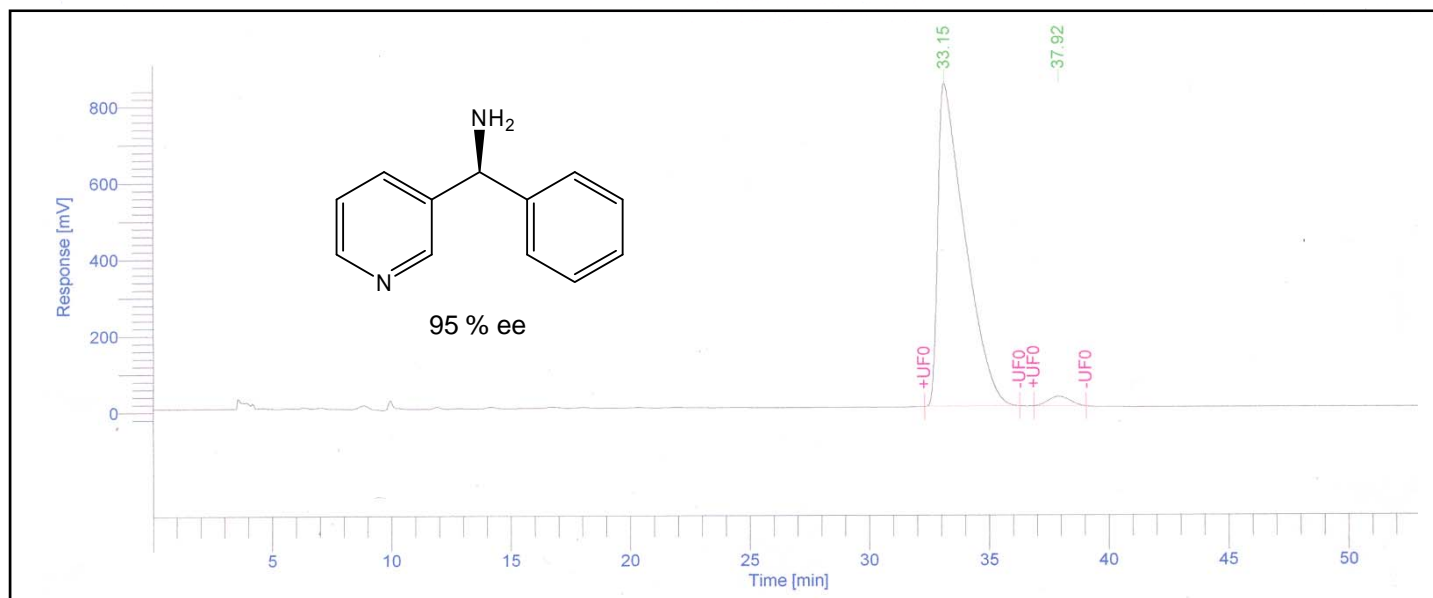
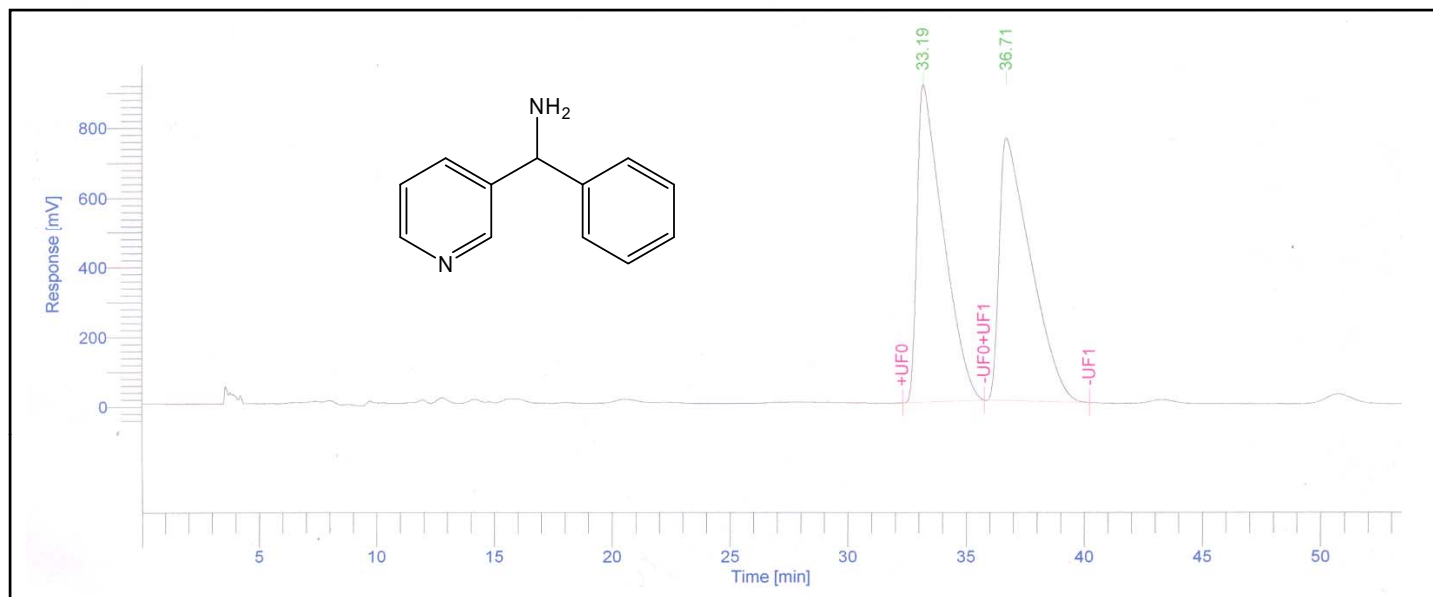
(S)-phenyl(pyridin-3-yl)methanamine (31)



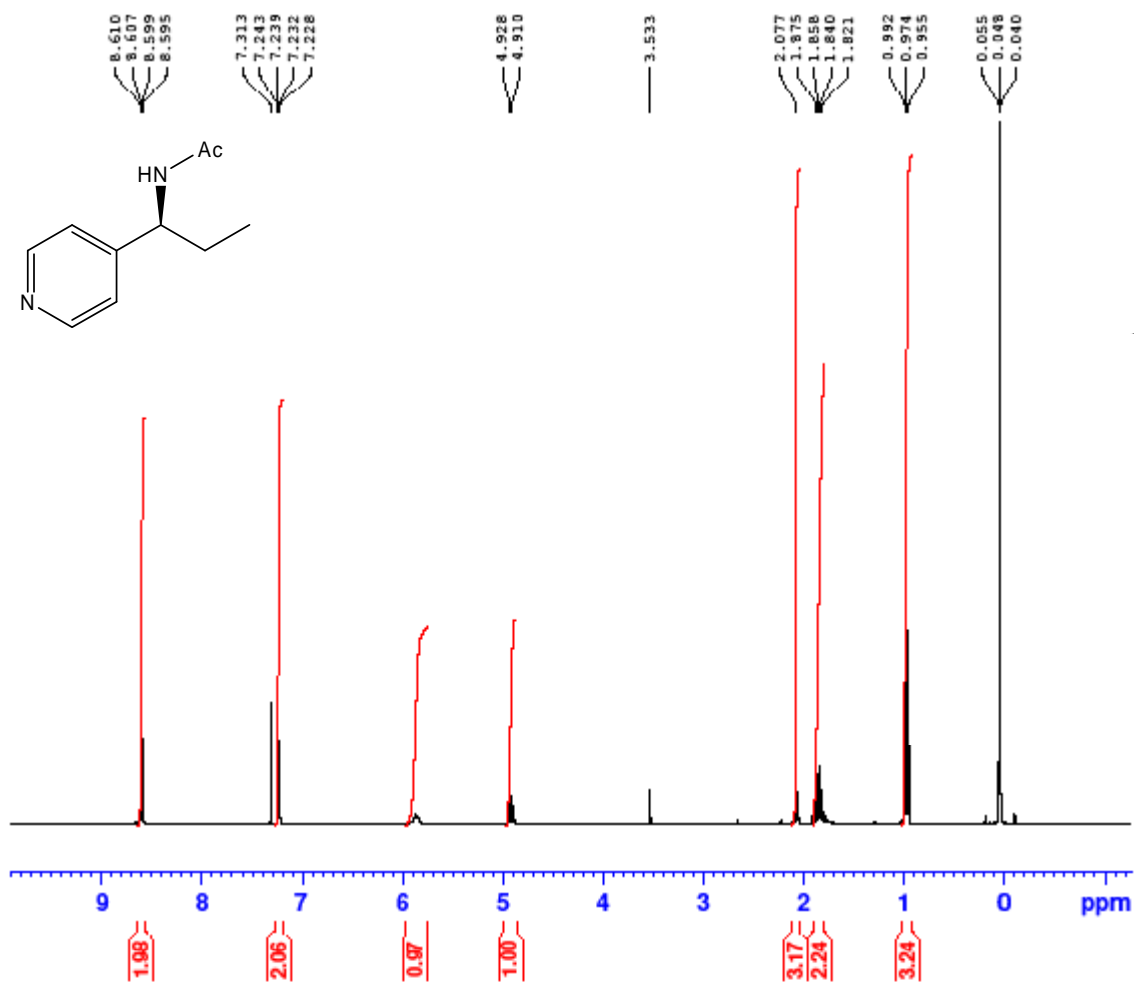
(S)-phenyl(pyridin-3-yl)methanamine (31)



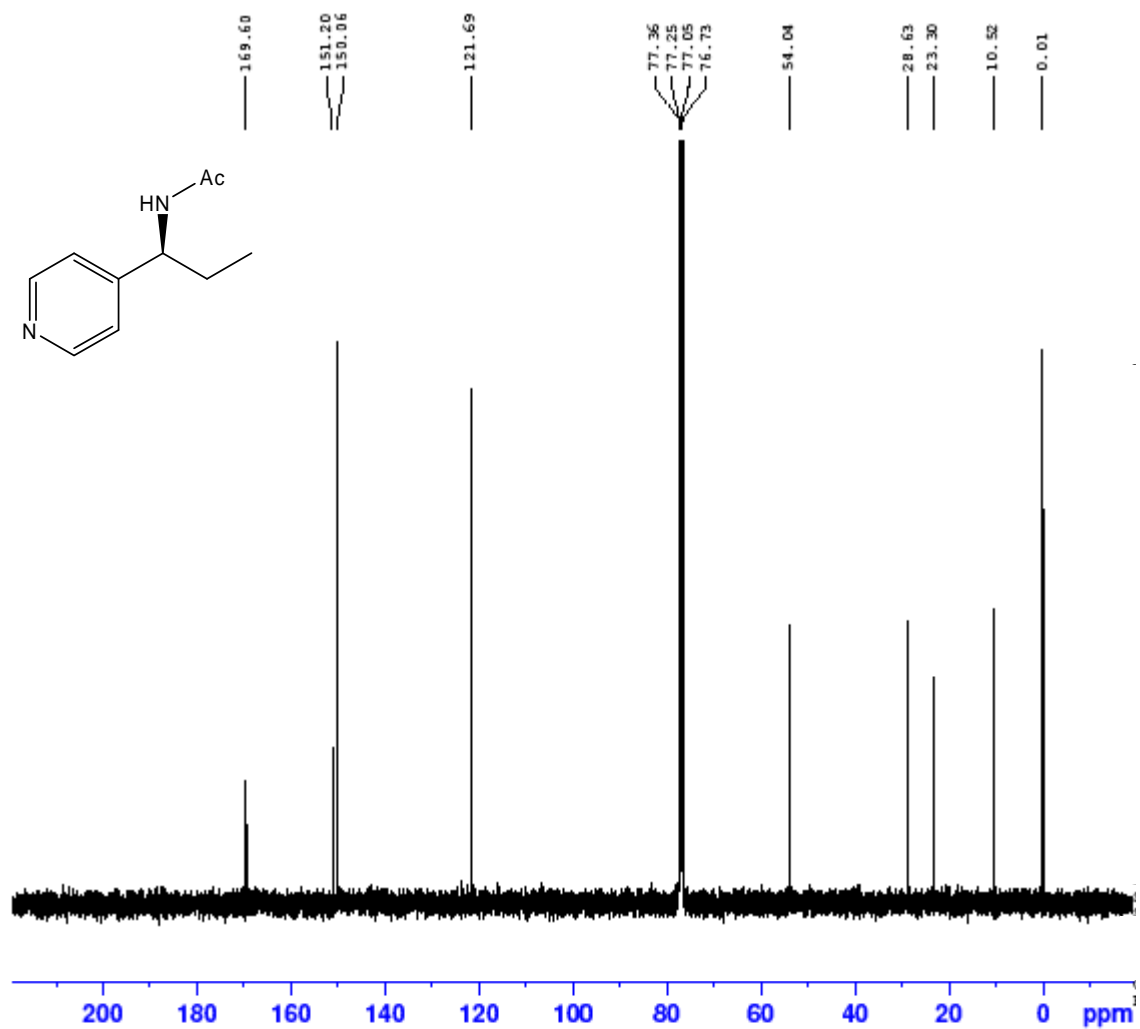
(S)-phenyl(pyridin-3-yl)methanamine (31)



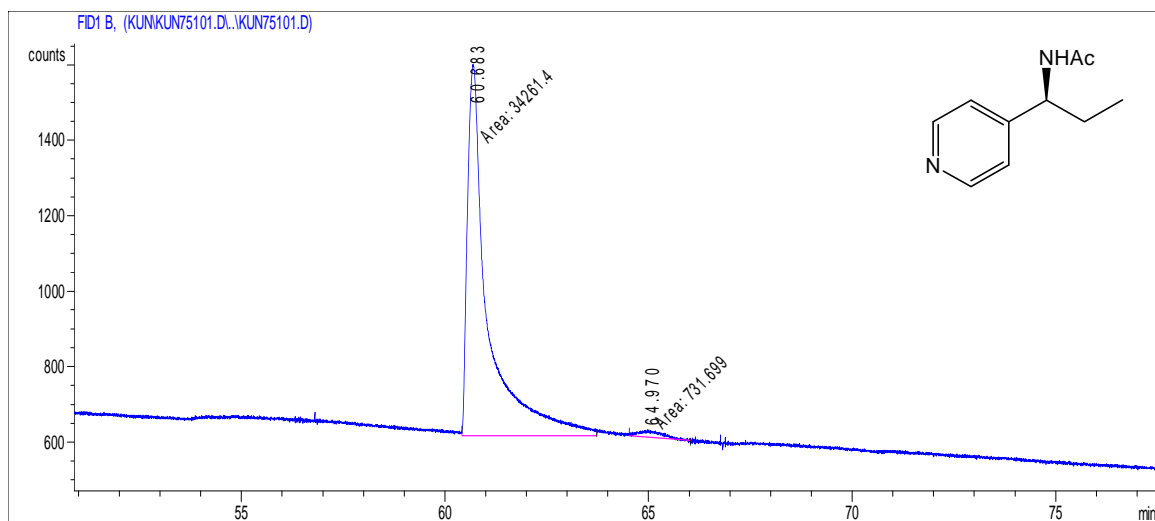
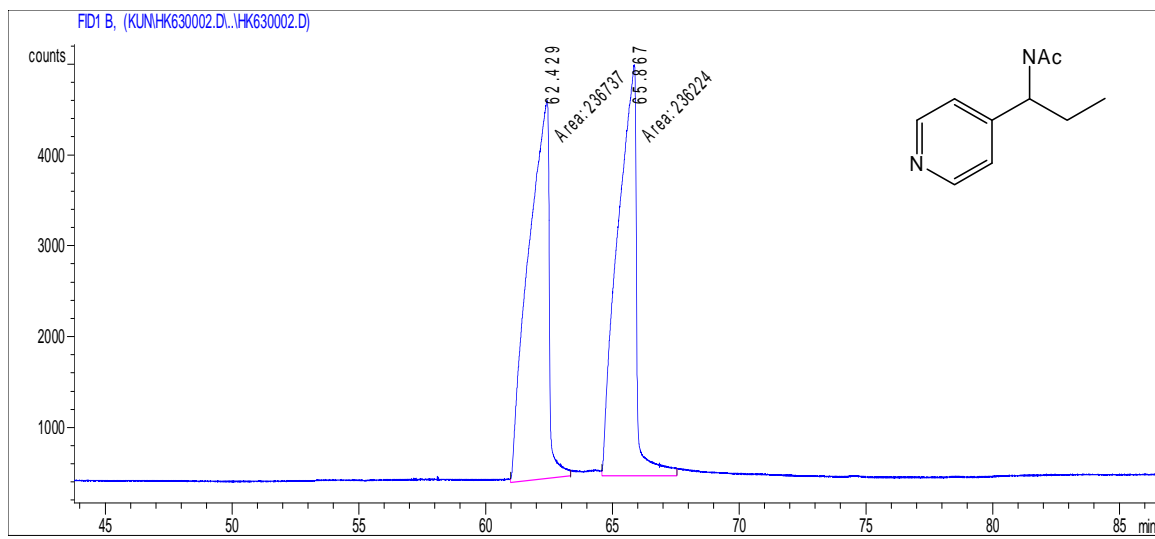
N-1-(Pyridine-4-yl)-propyl-acetamide (32)



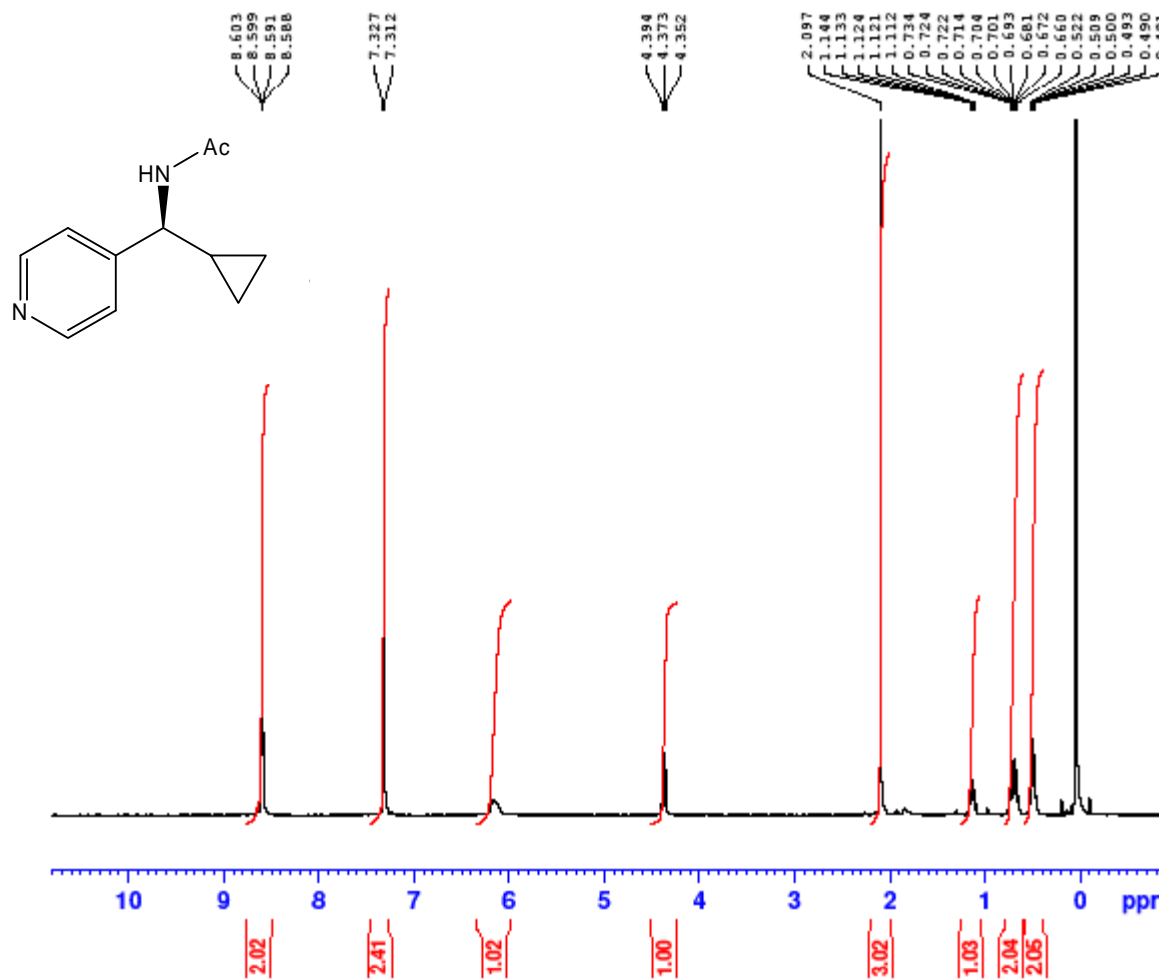
***N*-1-(Pyridine-4-yl)-propyl)-acetamide (32)**



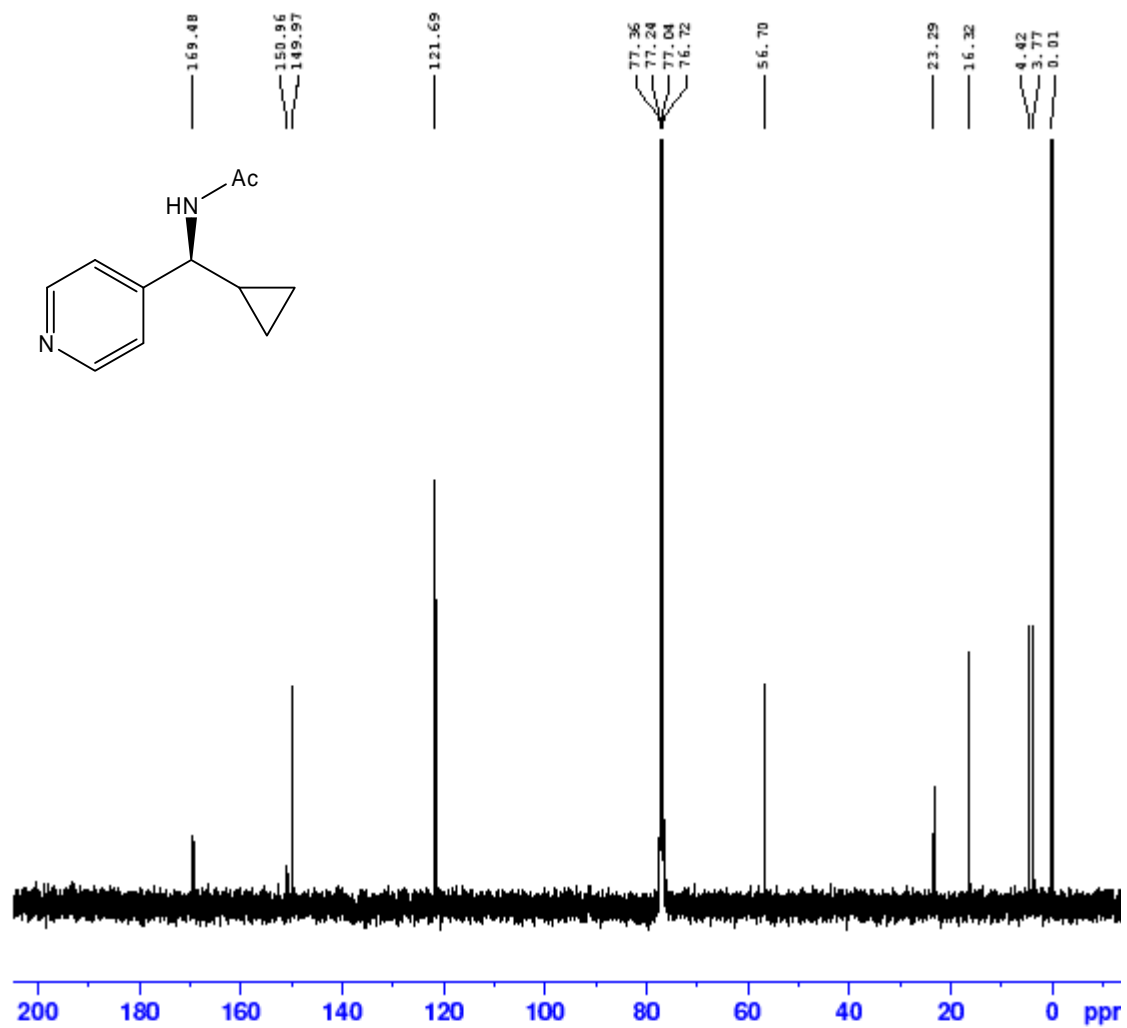
N-1-(Pyridine-4-yl)-propyl-acetamide (32)



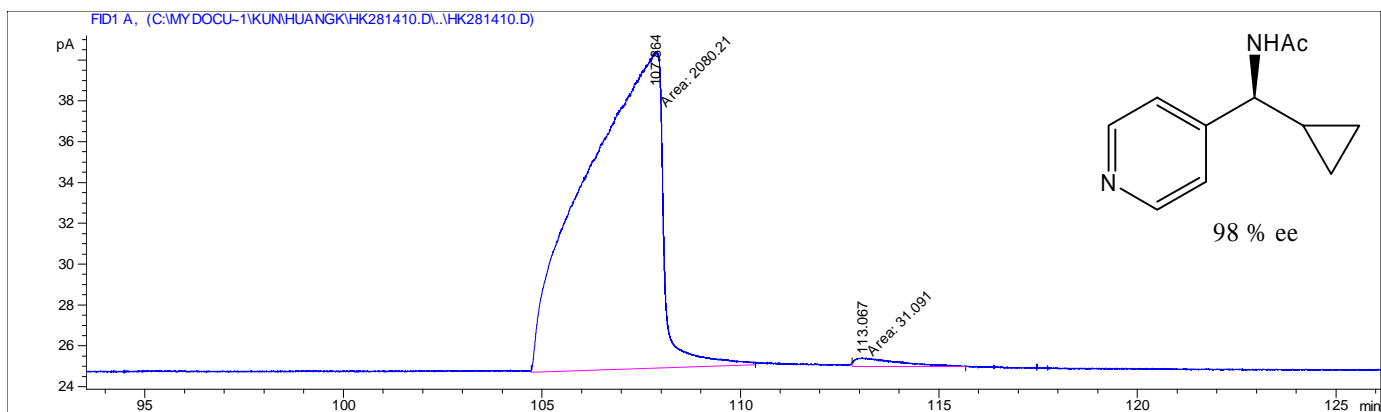
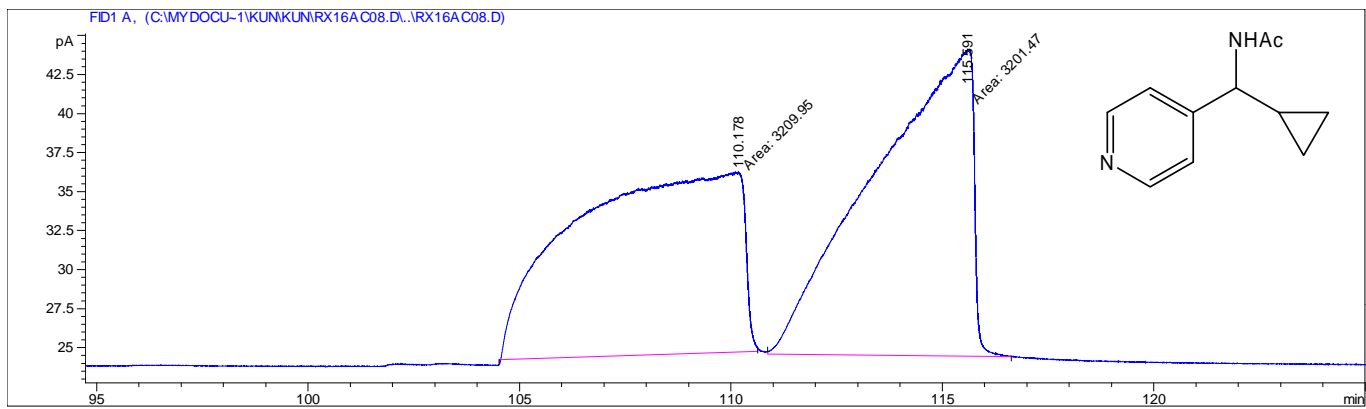
N-Cyclopropyl-(pyridine-4-yl)-methyl-acetamide (33)



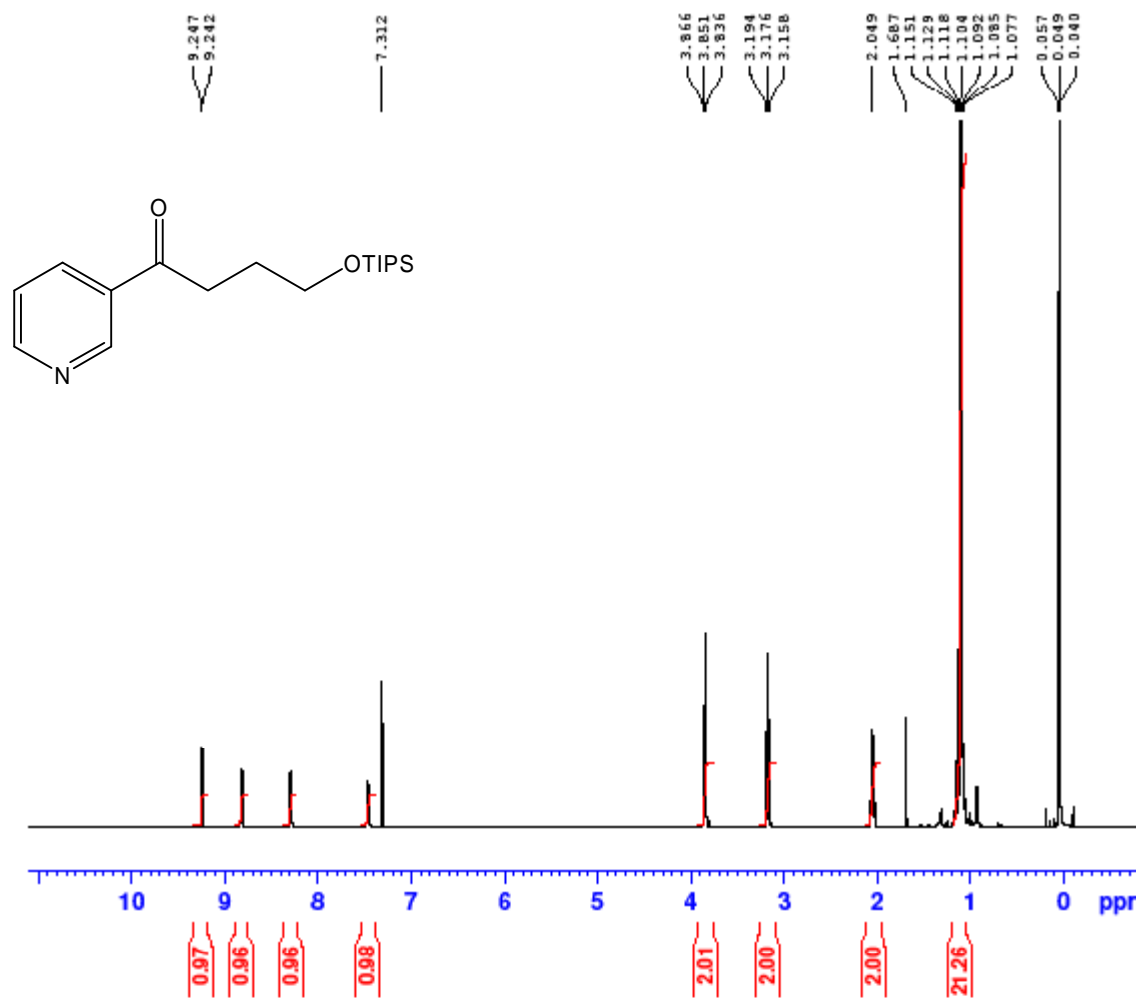
N-Cyclopropyl-(pyridine-4-yl)-methyl-acetamide (33)



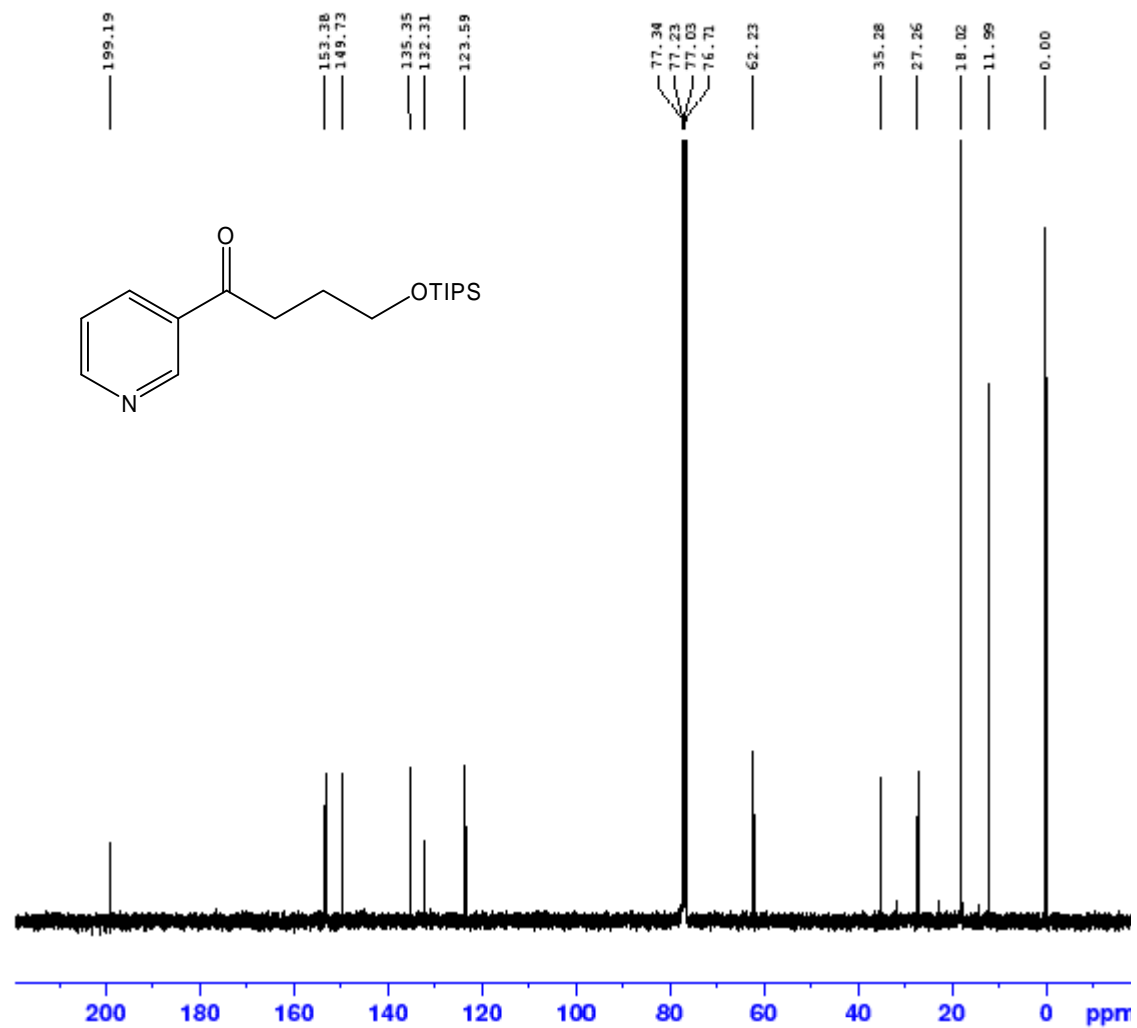
N-Cyclopropyl-(pyridine-4-yl)-methyl-acetamide (33)



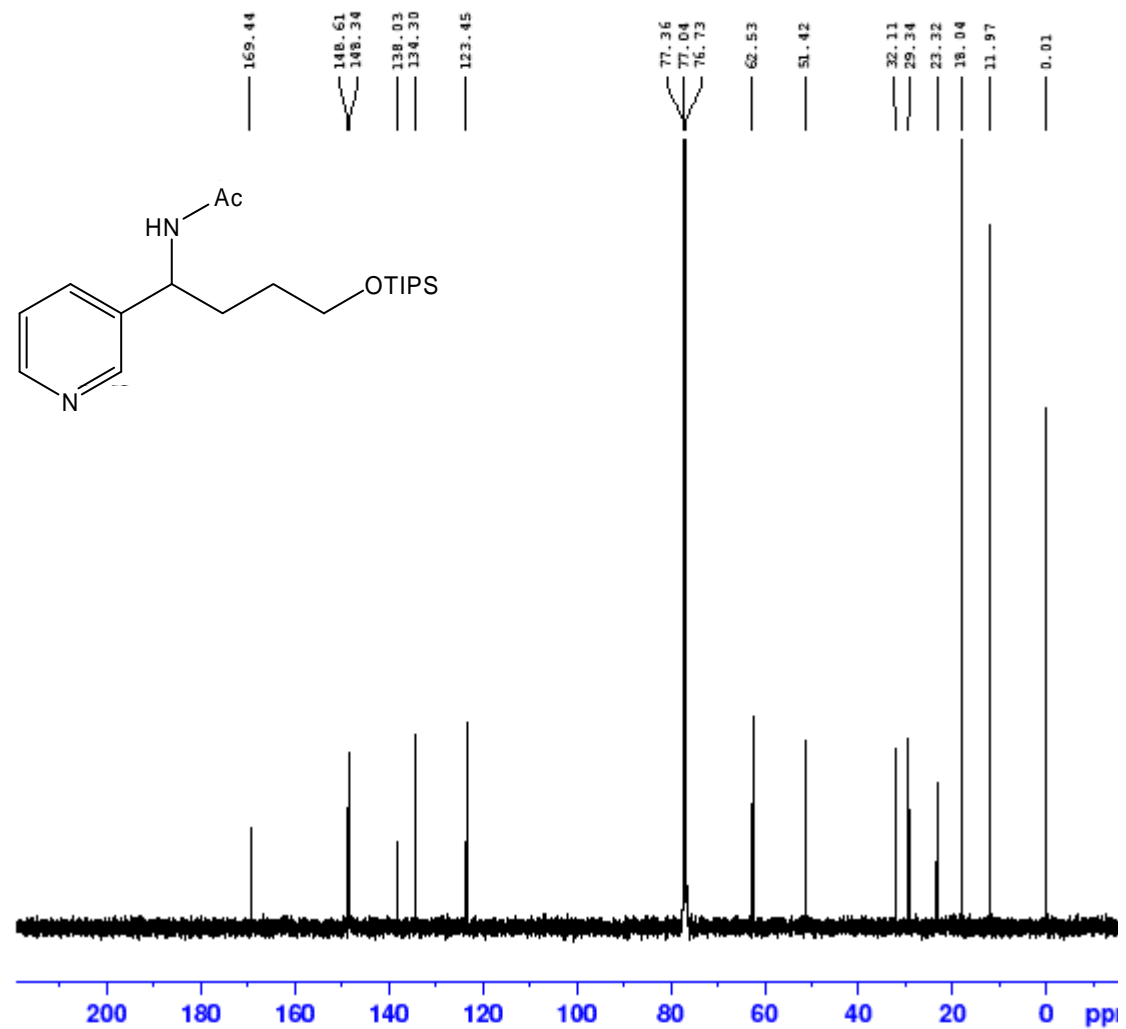
1-(pyridine-3-yl)-4-(triisopropylsilyloxy)butan-1-one



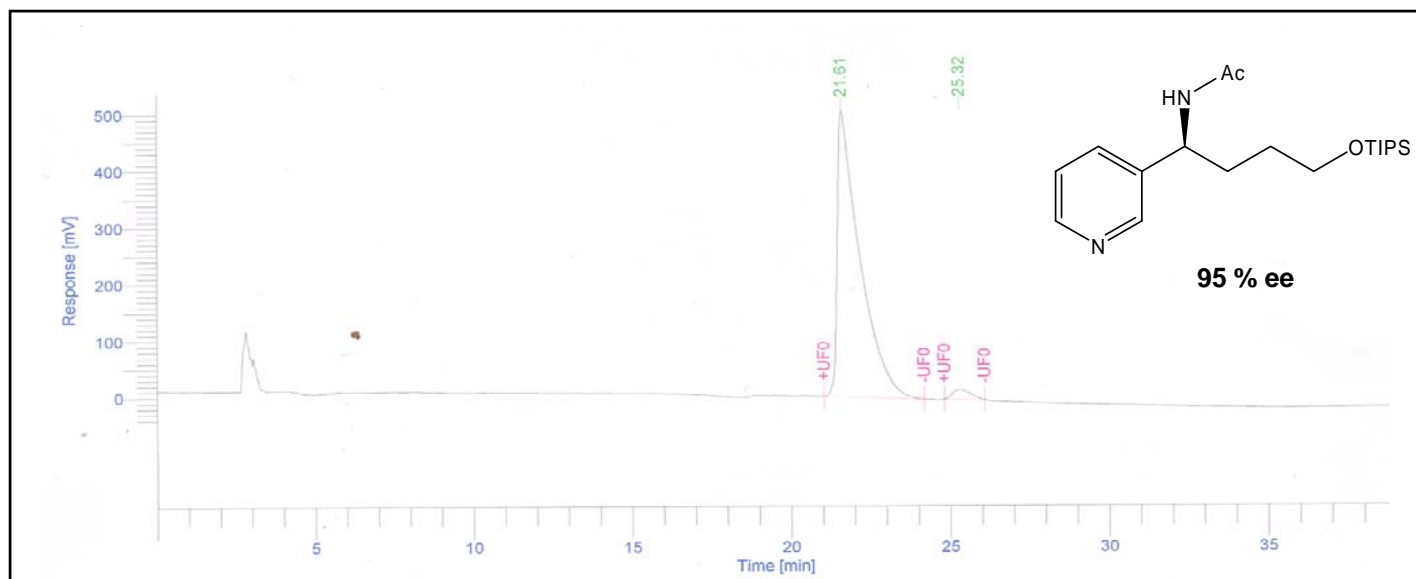
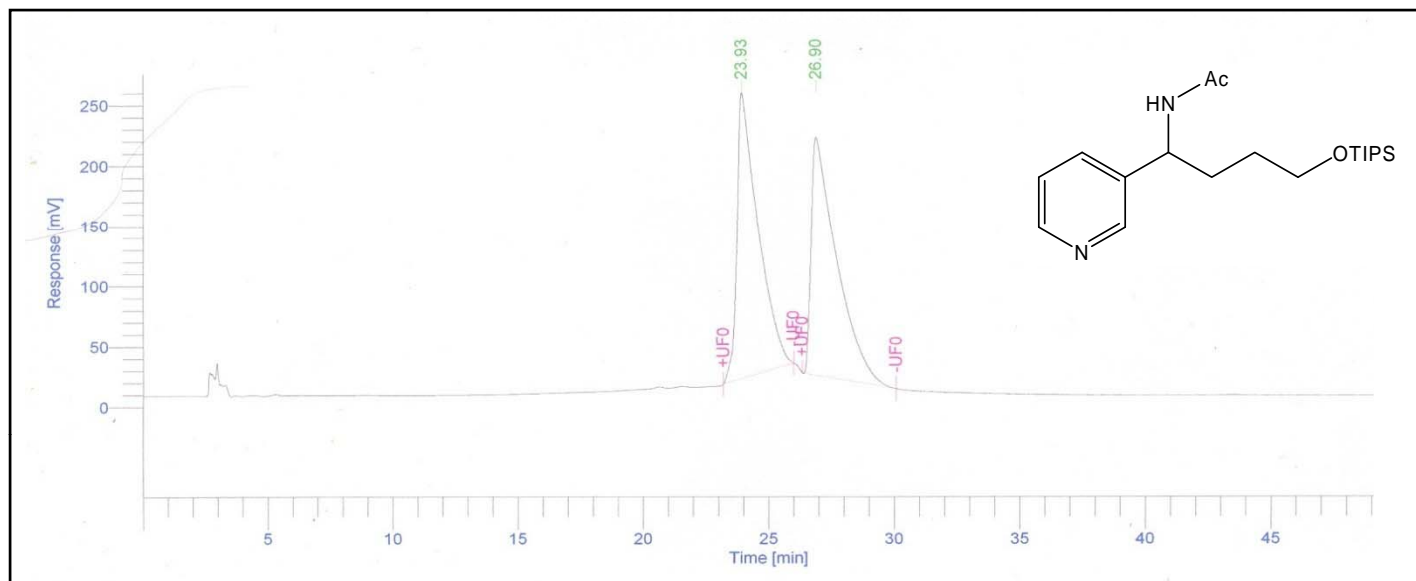
1-(pyridine-3-yl)-4-(triisopropylsilyloxy)butan-1-one



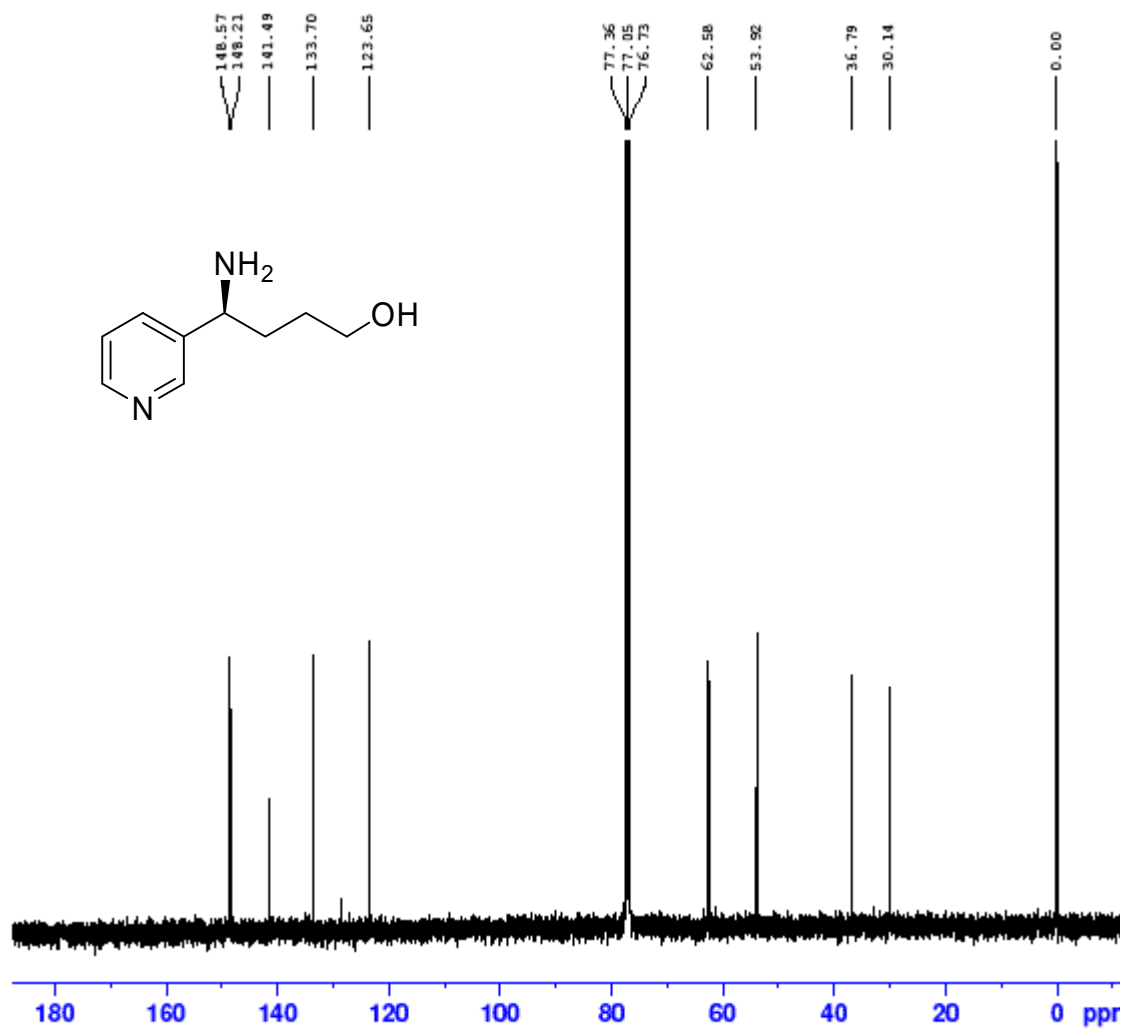
N-(1-(Pyridine-3-yl)-4-(triisopropylsilyloxy)butyl)acetamide (34)



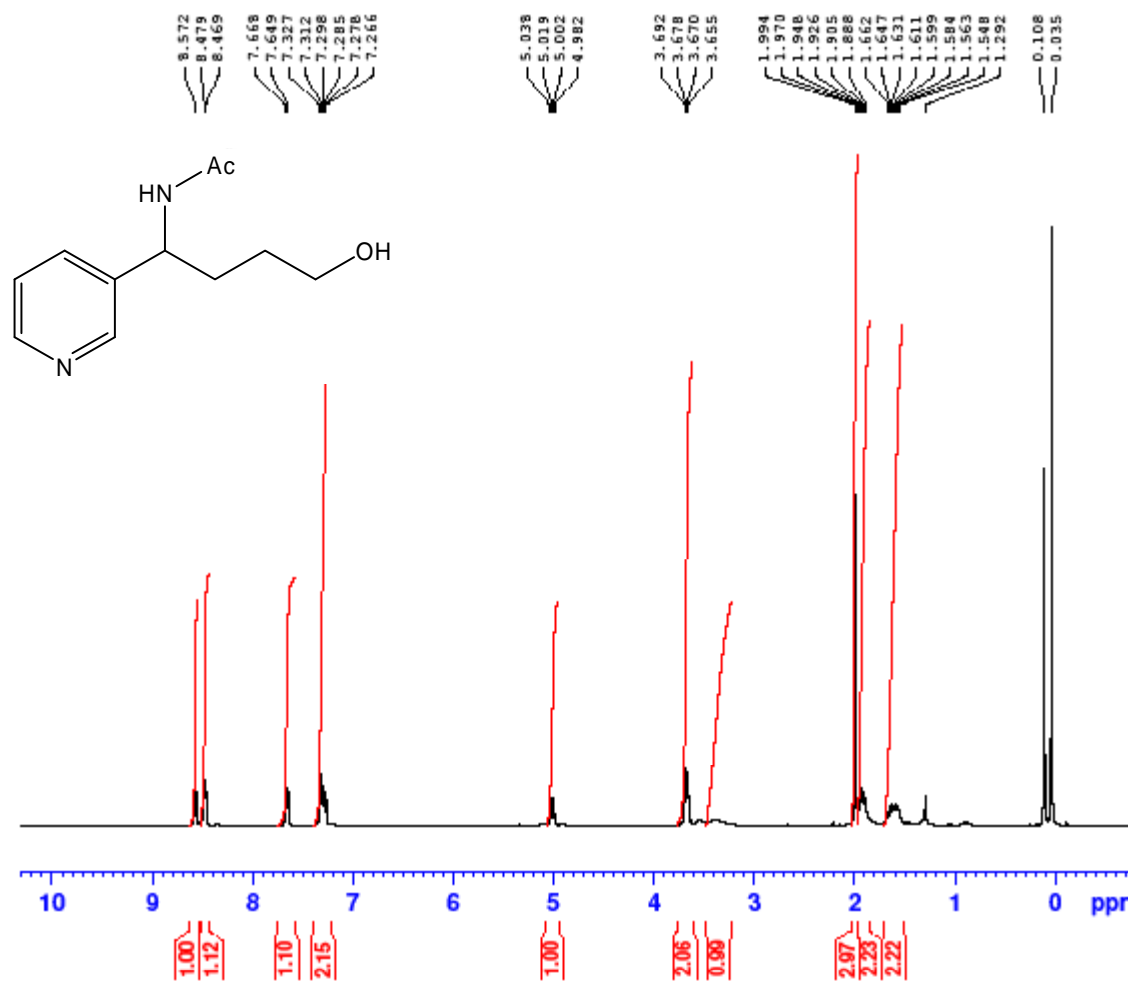
***N*-1-(Pyridine-3-yl)-4-(triisopropylsilyloxy)butyl)acetamide (34)**



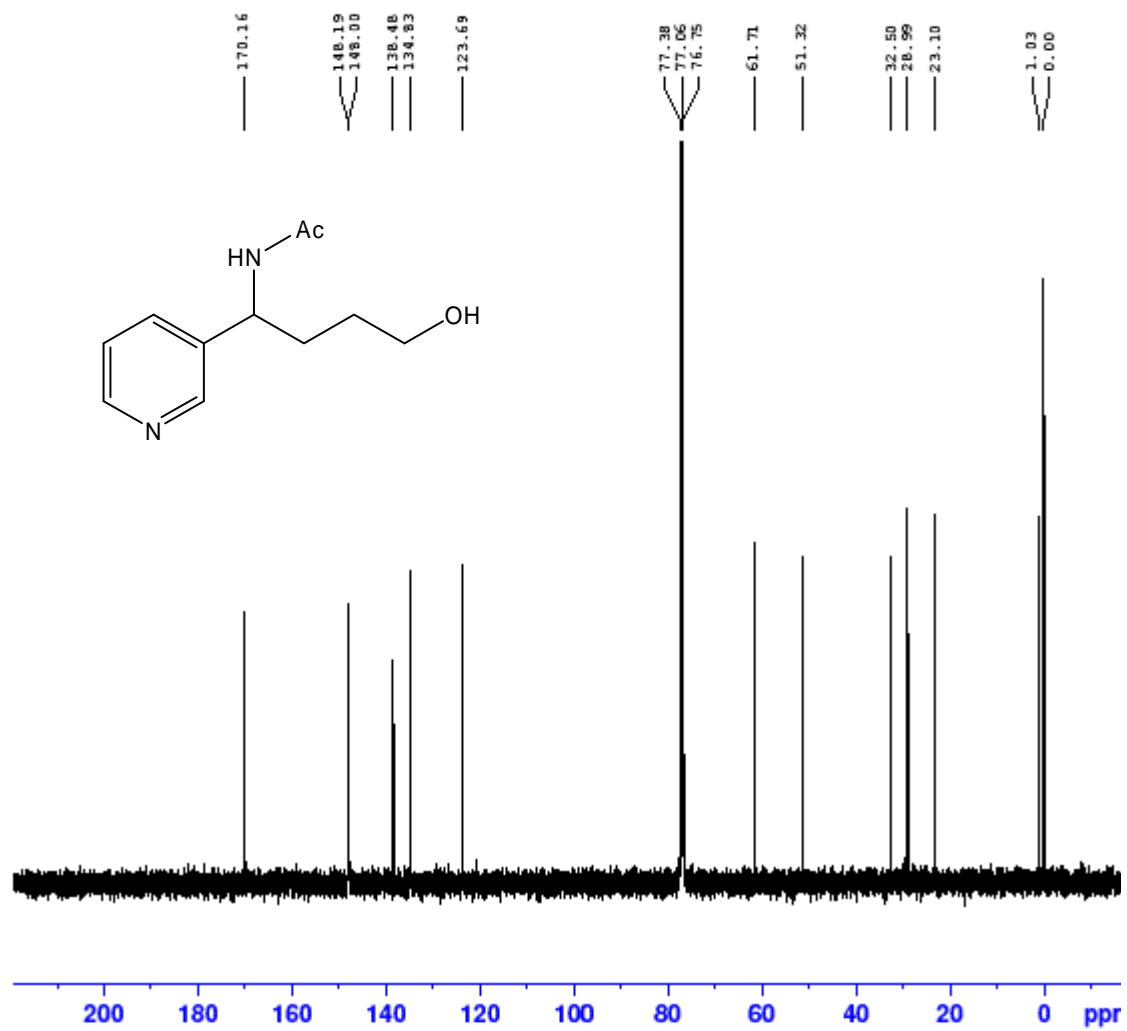
(S)-4-amino-4-(pyridin-3-yl)butan-1-ol (36)



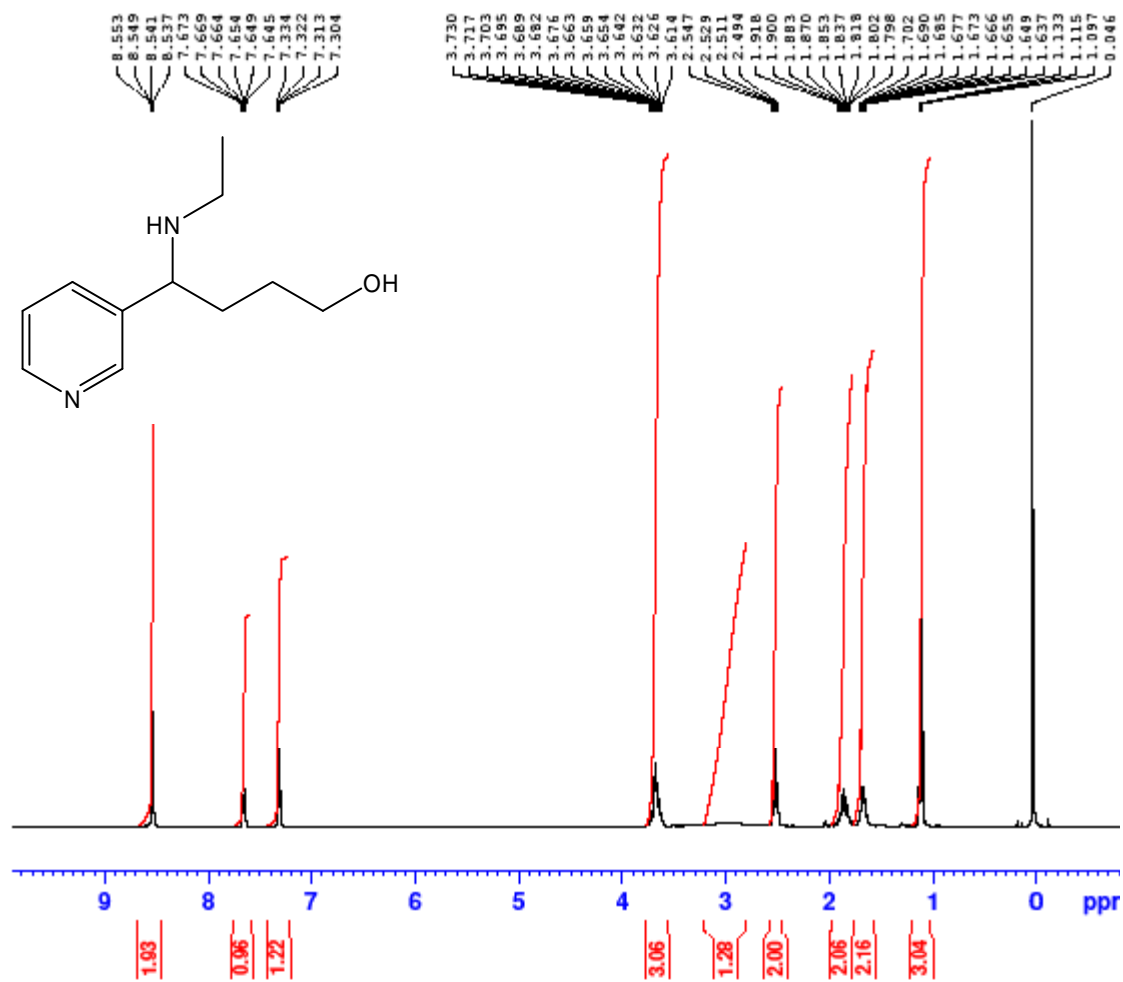
(S)-N-(4-hydroxy-1-(pyridin-3-yl)butyl)acetamide (37)



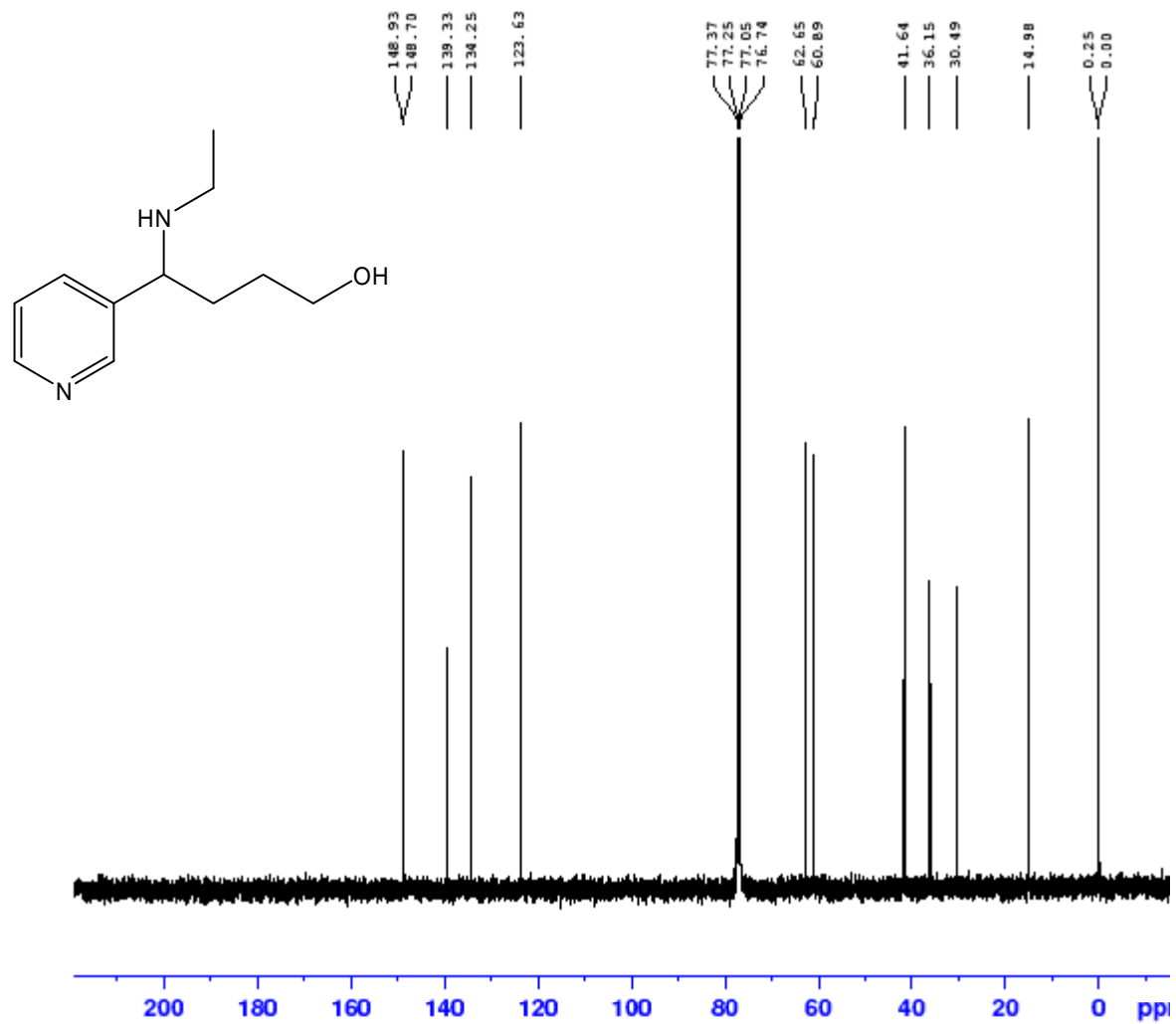
(S)-N-(4-hydroxy-1-(pyridin-3-yl)butyl)acetamide (37)



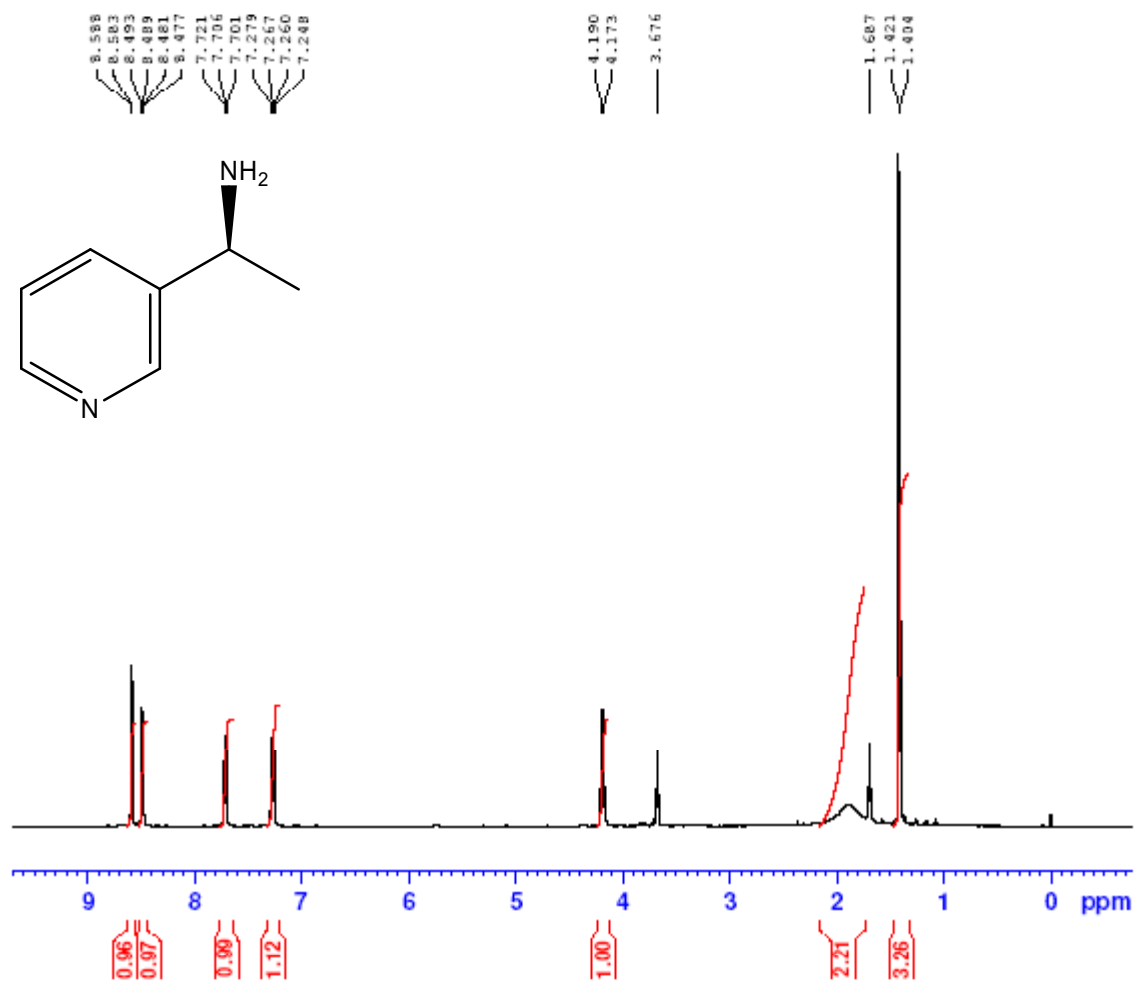
(S)-4-(N-Ethylamino)-4-(pyridin-3-yl)butan-1-ol (38)



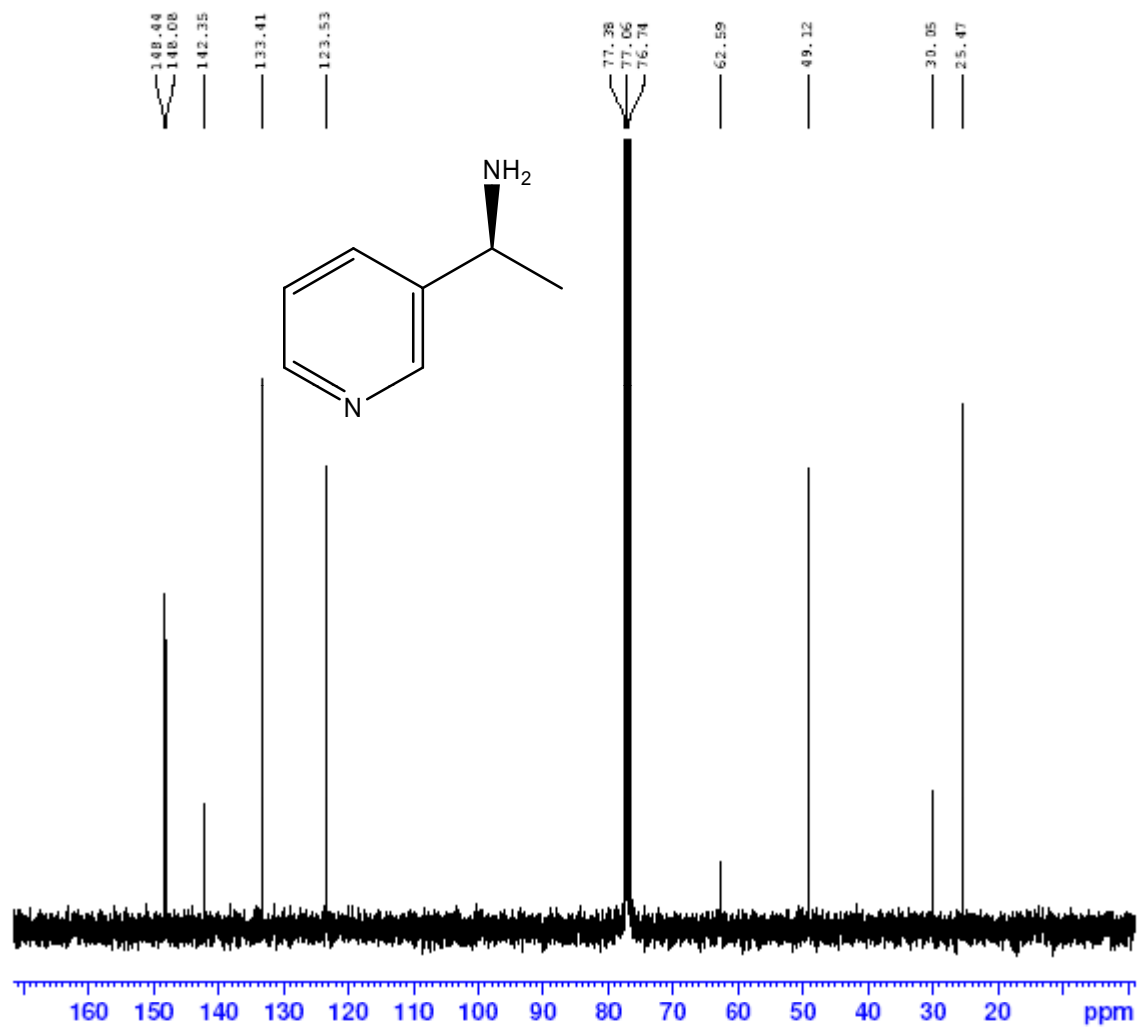
(S)-4-(N-Ethylamino)-4-(pyridin-3-yl)butan-1-ol (38)



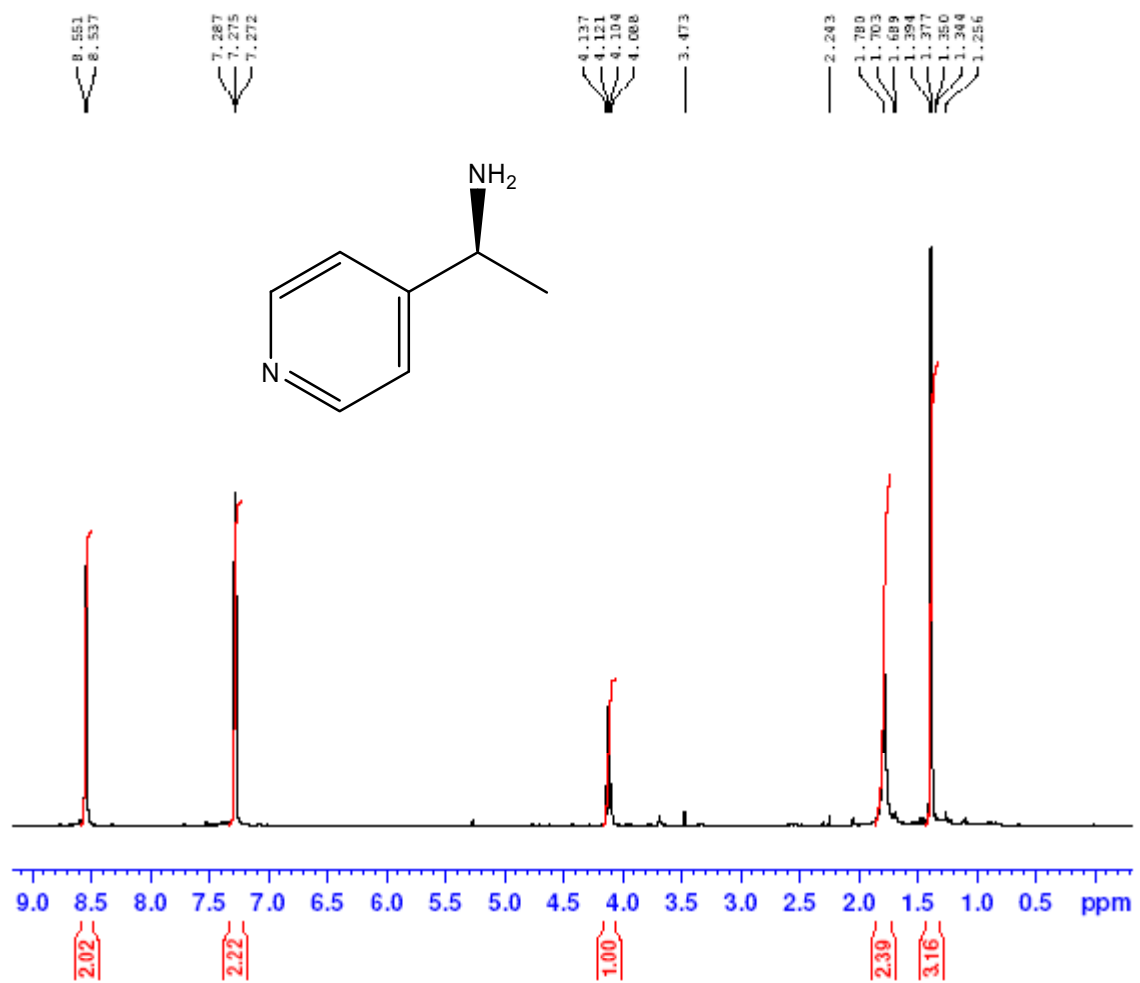
(S)-1-(3-pyridyl)ethylamine (21a)



(S)-1-(3-pyridyl)ethylamine (21a)



(S)-1-(4-pyridyl)ethylamine (23a)



(S)-1-(4-pyridyl)ethanamine (23a)

