Supplementary Materials

A Novel 2-Methylimidazole Promoted Oxyacyloxylation of α-Hydroxy Ketones and Anhydrides: An Easy Access to α-Acyloxy Ketones

Shi-Wei Yu [1,2], Zong-Hao Li [1], Miao-Xin Li [1], Yu Zeng [1], Wan-Xin Ye [1], Jia-Yu Xie [1] and Zhao-Yang Wang [1,*]

[1] School of Chemistry, South China Normal University, Guangzhou Key Laboratory of Analytical Chemistry for Biomedicine, GDMPA Key Laboratory for Process Control and Quality Evaluation of Chiral Pharmaceuticals, Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, Guangzhou 510006, China; 2021022671@m.scnu.edu.cn (S.-W.Y.); 2023022532@m.scnu.edu.cn (Z.-H.L.); limiaoxin1215@163.com (M.-X.L.); 2023022534@m.scnu.edu.cn (Y.Z.); 13286436564@163.com (W-X.Y.); 18689340784@163.com (J.-Y.X.)

[2] Key Laboratory for Biobased Materials and Energy of Ministry of Education, College of Materials and Energy, South China Agricultural University, 483 Wushan Road, Guangzhou 510642, China

* Correspondence: wangzy@scnu.edu.cn; Tel.: +86-020-3931-0258; Fax: +86-020-3931-0187

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General Information

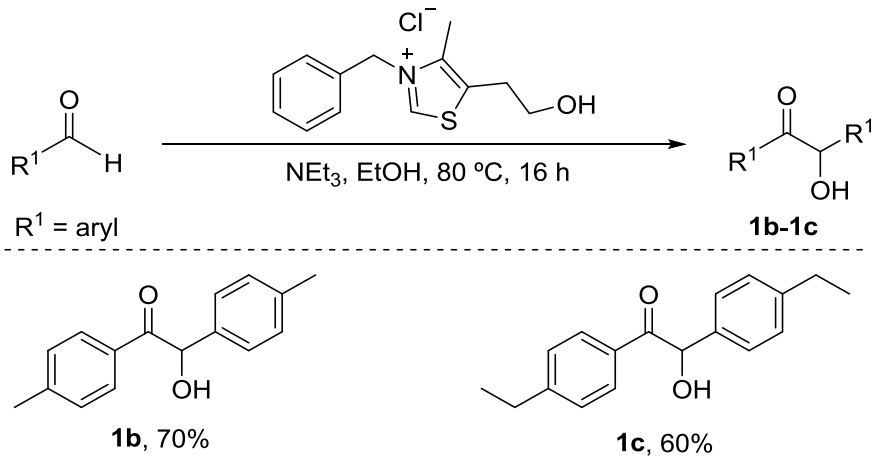
^{1}H and ^{13}C NMR spectra were collected on an AVANCE NEO-600 in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. High-resolution mass spectra (HR-MS) were obtained with a MAT 95XP mass spectrometer. Melting point (m.p.) was measured with WRS-1B melting point instrument. Single-crystal X-ray analysis was obtained using Agilent Gemini E. Reactions were monitored using thin-layer chromatography (TLC) and visualized with UV light at 254 nm.

All reagents and solvents were purchased from commercial sources and used without further purification. Different α-hydroxy ketones **1** were synthesized according to the literature procedure [1, 2], except for 2-hydroxy-2-phenylacetophenone (**1a**), and 2-hydroxy-1,2-bis(4-methoxyphenyl)ethan-1-one (**1d**).

Experimental Procedure for α-Hydroxy Ketones 1

Method A

As **Scheme S1** [1], α-hydroxy ketones **1b**-**1c** were synthesized.



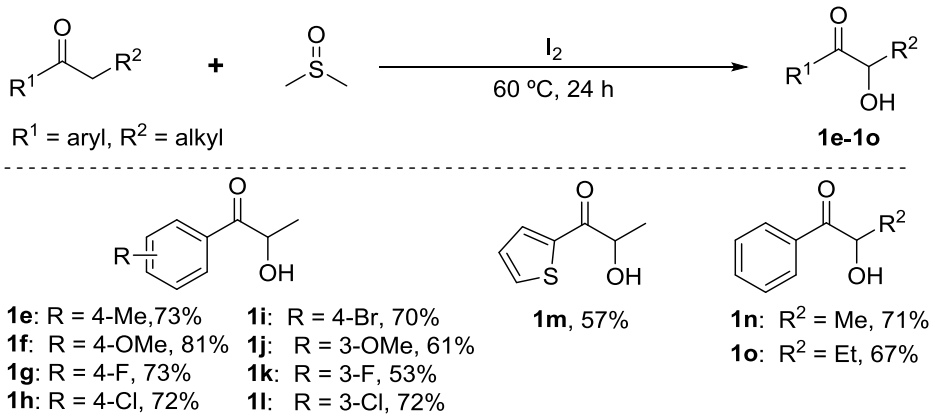
Scheme S1

According to the literature [1], the mixture of aldehyde (1.0 mmol), triethylamine (0.3 mmol), 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride (0.05 mmol) and EtOH (10 mL) was stirred at 80 °C for 16 h. After completion, the solvent was removed under reduced pressure. Then, ethyl acetate (15 mL) was poured into the reaction mixture. The organic layers were extracted with brine (3 × 15 mL) and dried with anhydrous Na_2SO_4.

Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude products were purified by column chromatography on silica gel to afford the desired products **1b**-**1c**.

Method B

As **Scheme S1** [2], α-hydroxy ketones **1e**-**1o** were synthesized.



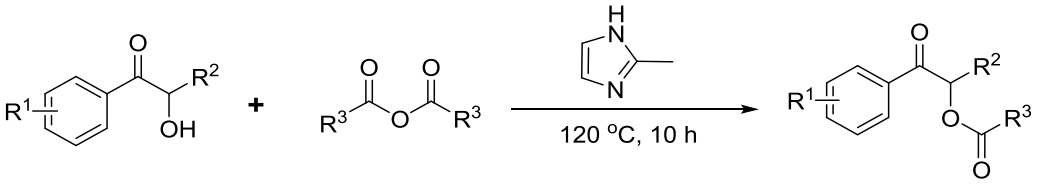
Scheme S2

According to the literature [2], the mixture of propiophenone compounds (1.0 mmol), I_2 (40 mol%), and DMSO (2 mL) was stirred at 60 °C for 24 h. After cooling down to room temperature, the solution was diluted with ethyl acetate (10 mL) and washed with 0.1 mol/L $Na_2S_2O_3$ (5 mL) aqueous solution, extracted with ethyl acetate (3×5 mL). Then, the organic layers were dried over anhydrous Na_2SO_4.

Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude products were purified by column chromatography on silica gel to afford the desired products **1e**-**1o**.

Experimental Procedure for Compounds 3a-3t

As **Scheme S3**, α-acyloxy ketones **3a**-**3t** were synthesized.



Scheme S3

The mixture of α-hydroxy ketones **1** (0.30 mmol, 1.0 equiv.), 2-methylimidazole (0.60 mmol, 2.0 equiv.) and anhydrides **2** (3 mL) under air atmosphere was stirred at 100 ℃ for 10 h. After the completion of reaction, the solvent was removed under reduced pressure and the resulting mixture was diluted with water (15 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (25 mL) and dried with anhydrous Na_2SO_4.

Finally, after the filtration and the evaporation of the solvents under reduced pressure, the crude products were purified by column chromatography on silica gel to afford the desired products **3a**-**3t**.

The HR-MS spectrum of compound 3b

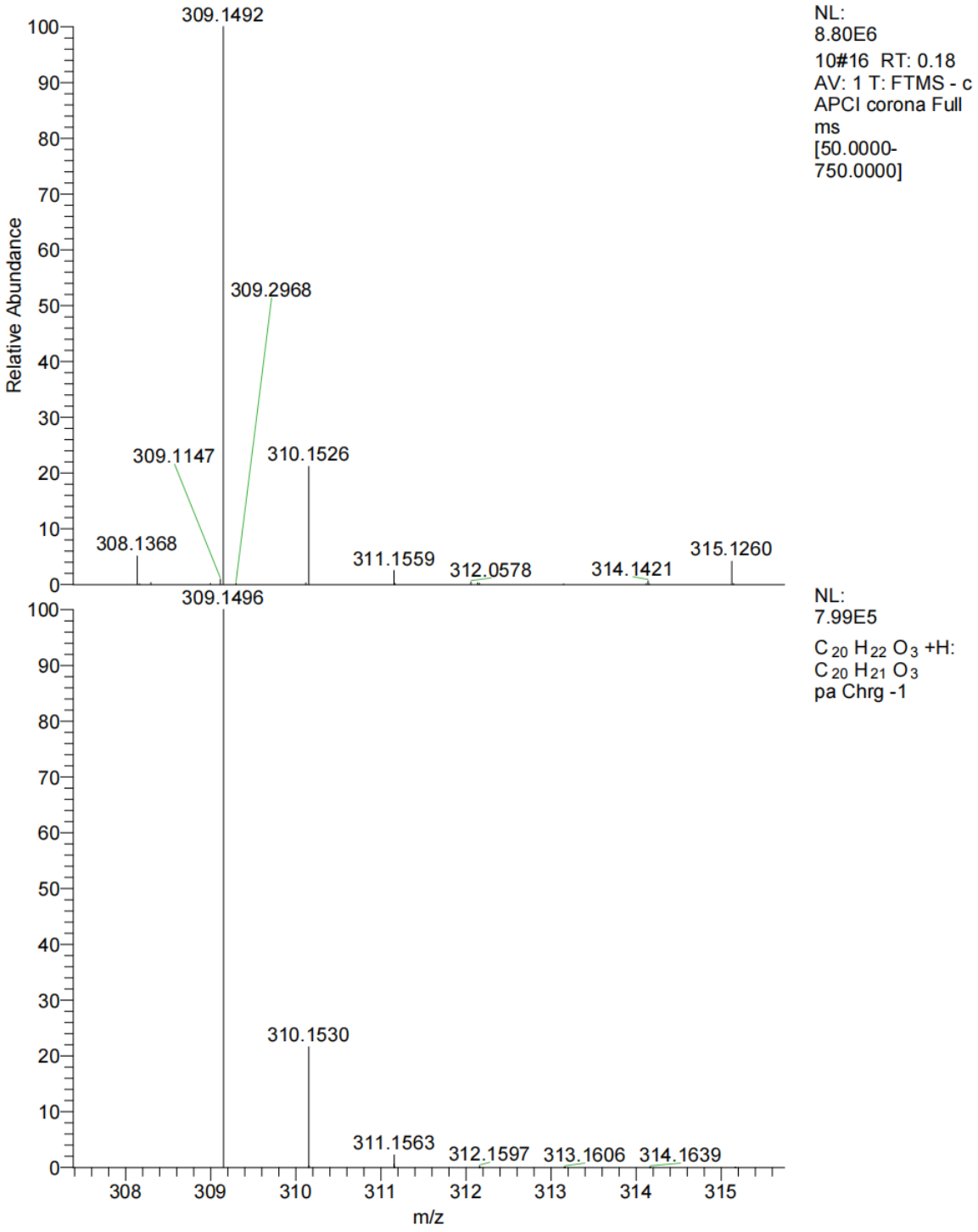


Figure S1. The HR-MS spectrum of compound **3b**.

Data of Single-crystal X-ray Analysis

Table S1. Crystal data and structure refinement for **3q**.

Compound	3q
Empirical formula	$C_{18}H_{18}O_3$
Formula weight	282.32
Temperature (K)	297
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	a = 9.1236(7), b = 10.8750(12), c = 15.9052(13) α = 90, β = 95.205(8), γ = 90
Volume (Å^3)	1571.6(2)
Z	4
Density (calculated) (g/cm^3)	1.193
Absorption coefficient (mm^{-1})	0.080
F(000)	600.0
Theta range for data collection	2.272 to 24.998
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -18 ≤ l ≤ 18
Reflections collected	6641
Independent reflections	2757 [R(int) = 0.0382, R(sigma) = 0.0560]
Completeness to theta = 24.998°	100 %
Absorption correction	Multi-Scan
Max. and min. transmission	1.000 and 0.874
Refinement method	Least Squares minimisation
Data / restraints / parameters	2757 / 0 / 192
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R_1 = 0.0567, wR_2 = 0.1141
R indices (all data)	R_1 = 0.0925, wR_2 = 0.1327
Largest diff. peak and hole	0.15 and -0.14 e.Å^{-3}

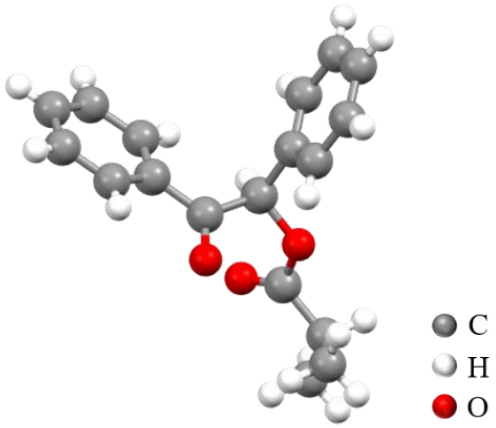
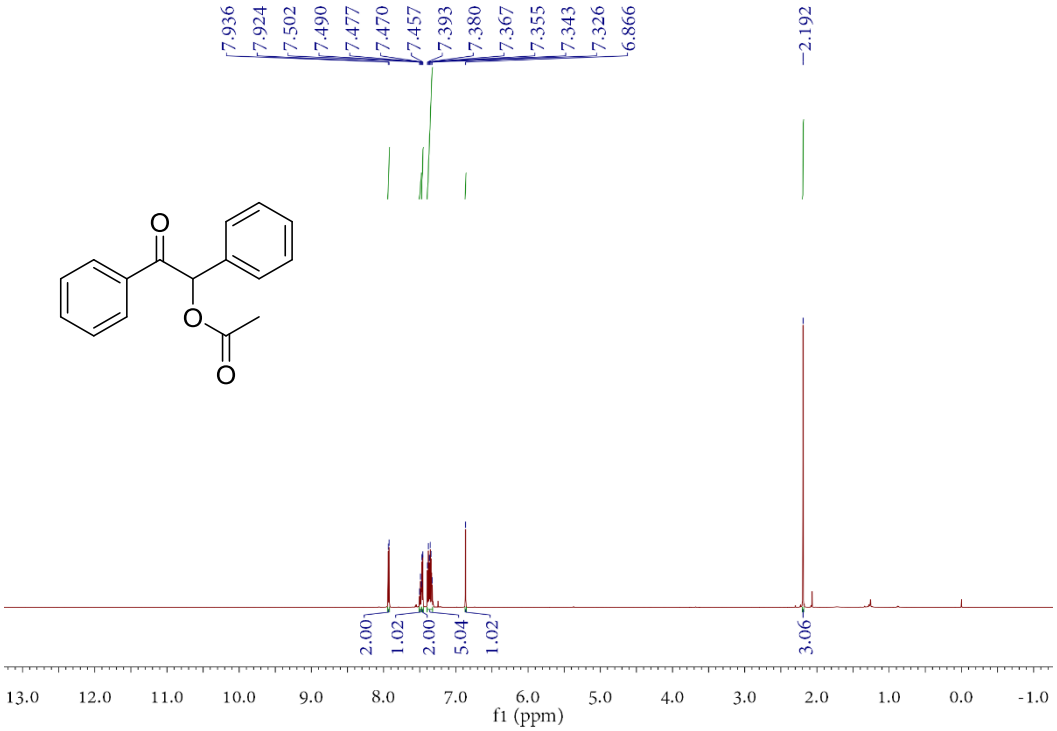
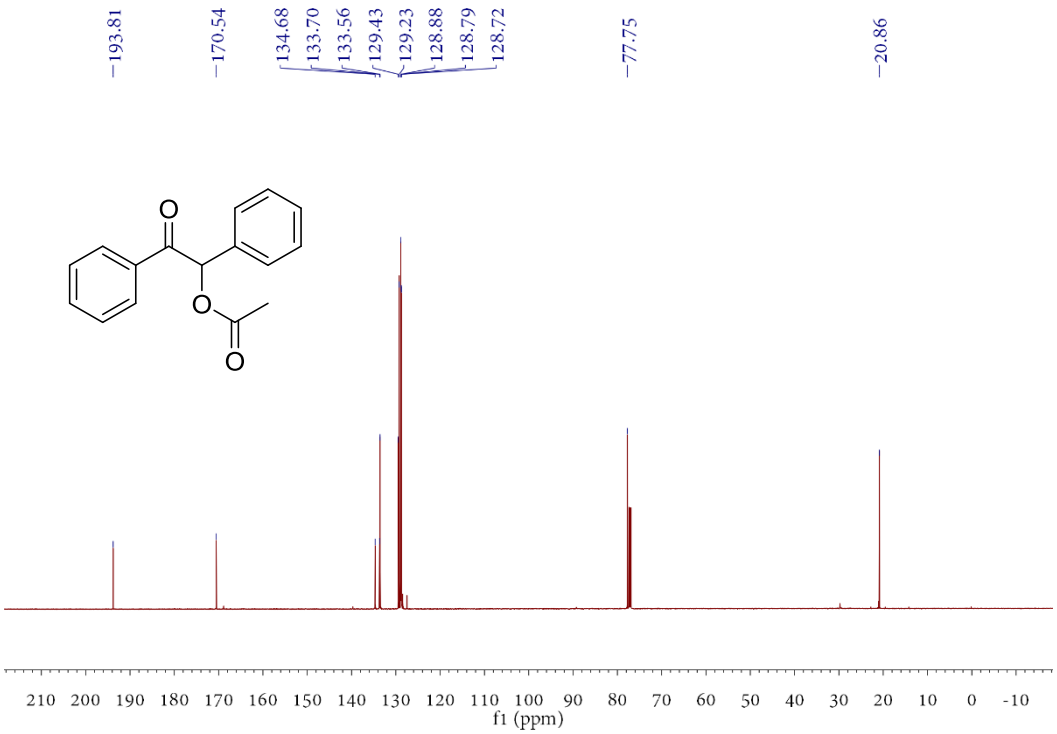


Figure S2. The molecular structure of **3q**.

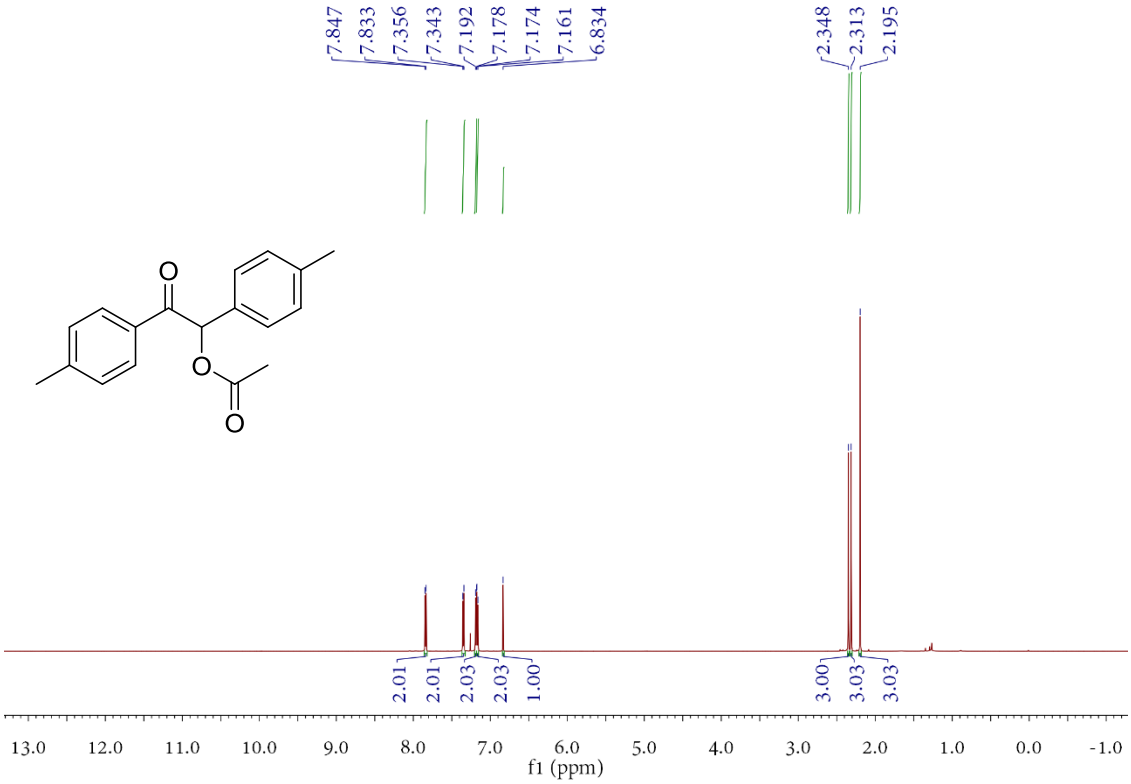
NMR Spectra for All Compounds 3a-3t



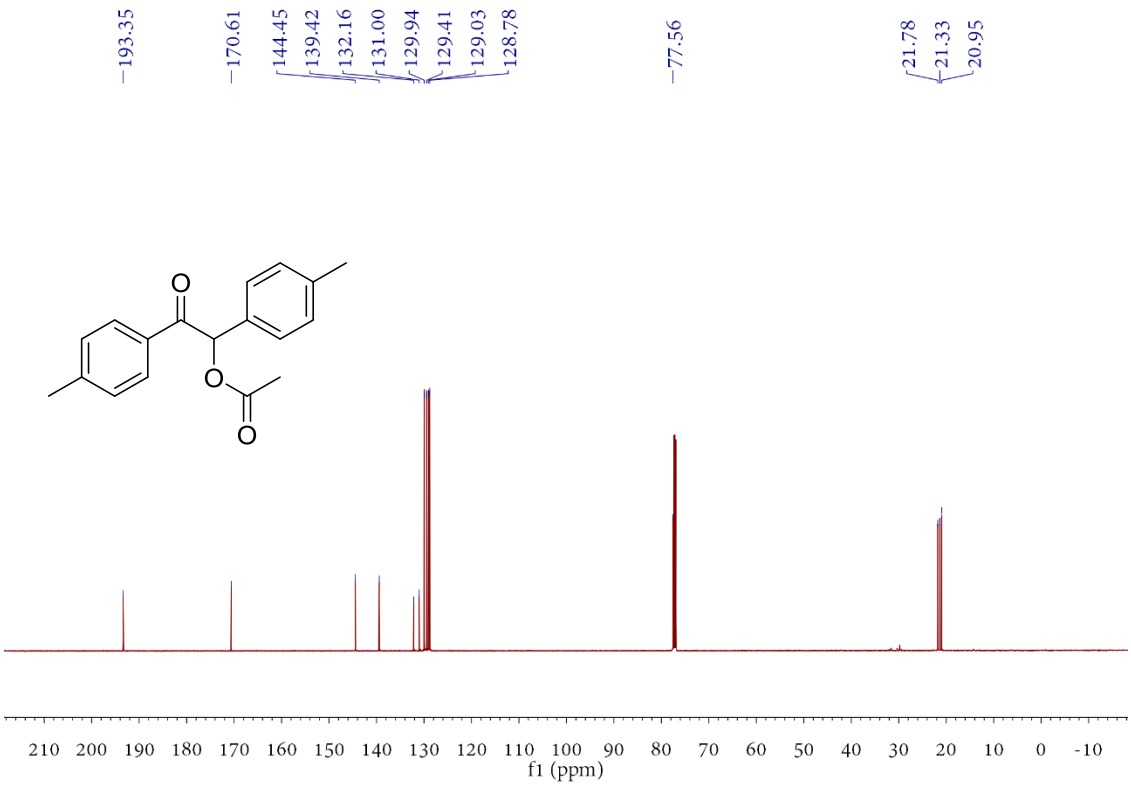
^{1}H NMR spectrum of compound **3a**



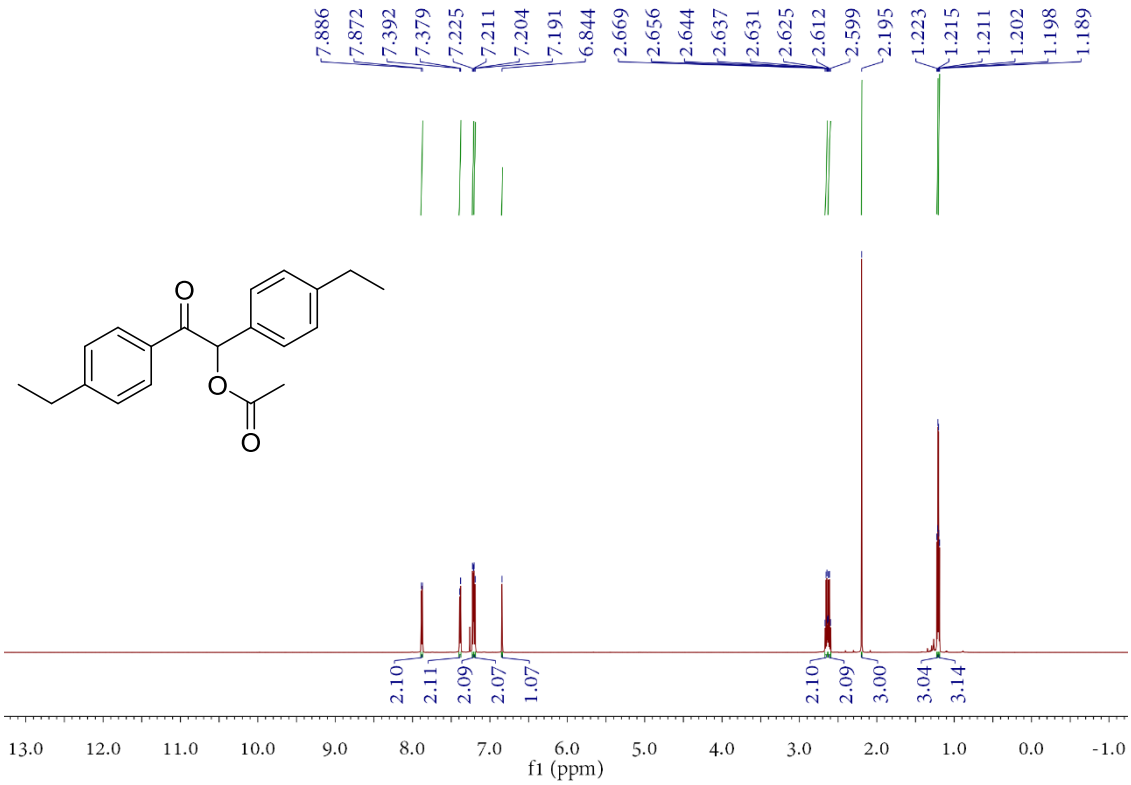
^{13}C NMR spectrum of compound **3a**



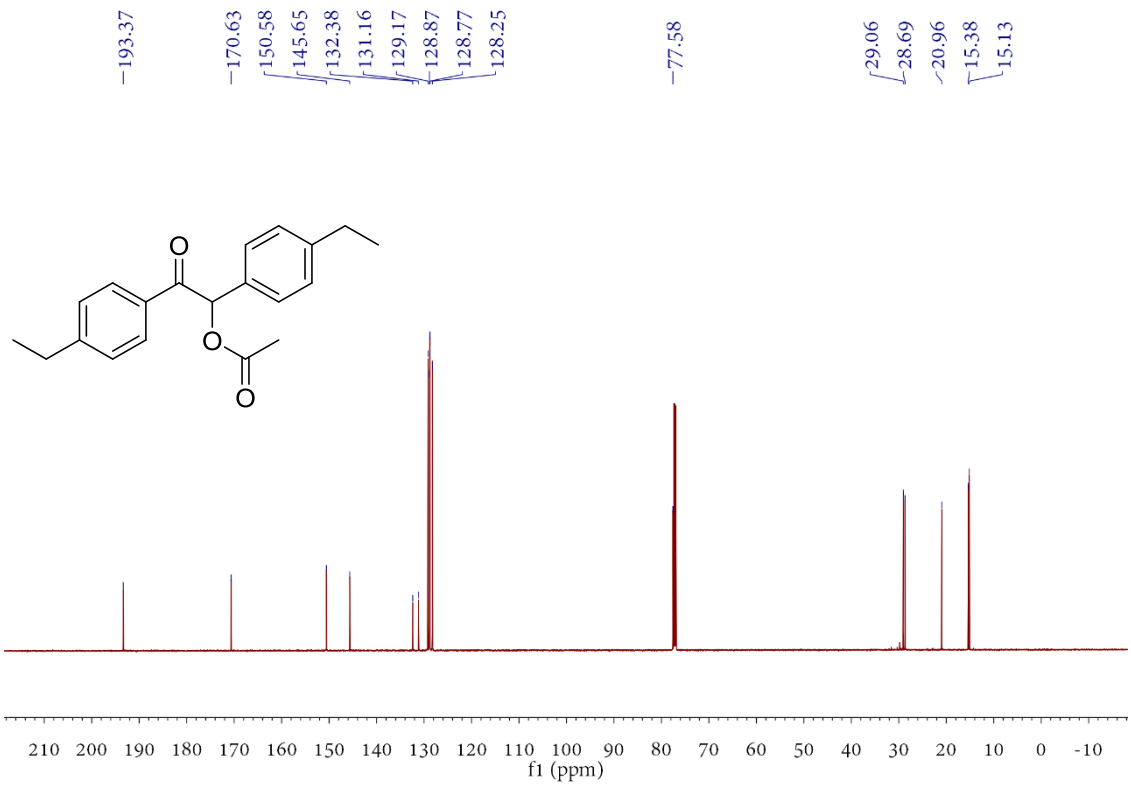
^{1}H NMR spectrum of compound **3b**



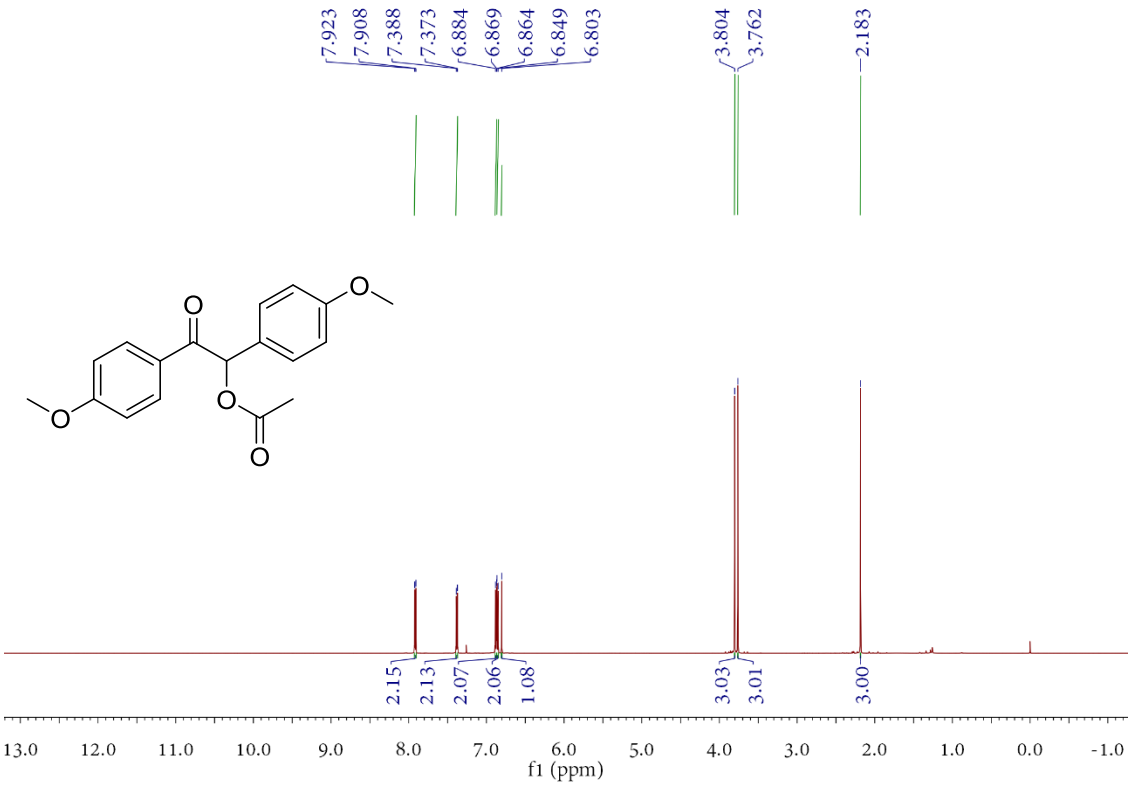
^{13}C NMR spectrum of compound **3b**



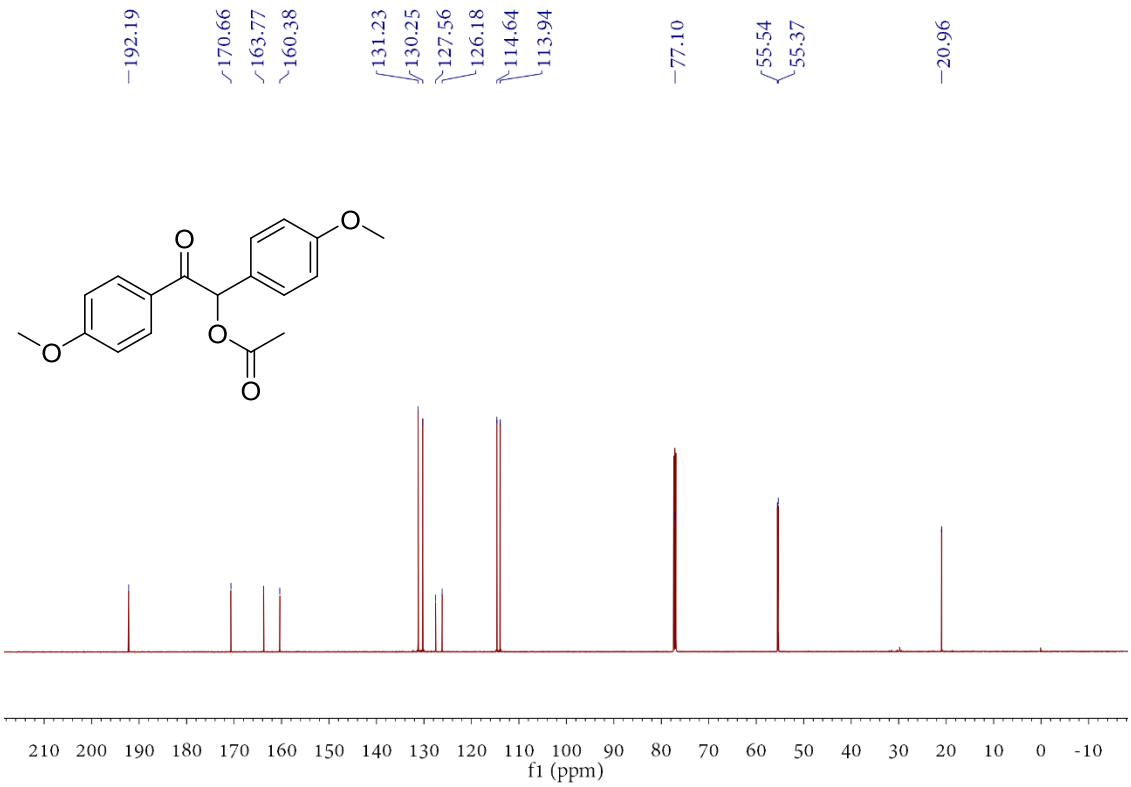
^{1}H NMR spectrum of compound **3c**



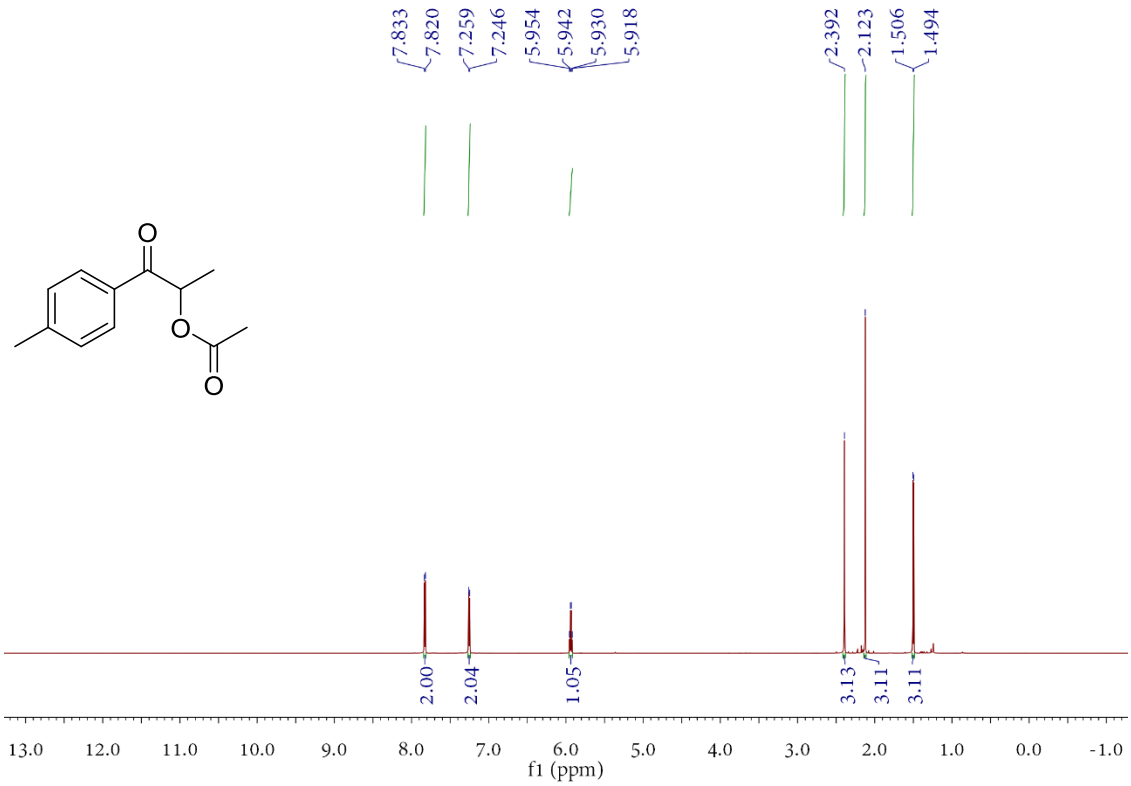
^{13}C NMR spectrum of compound **3c**



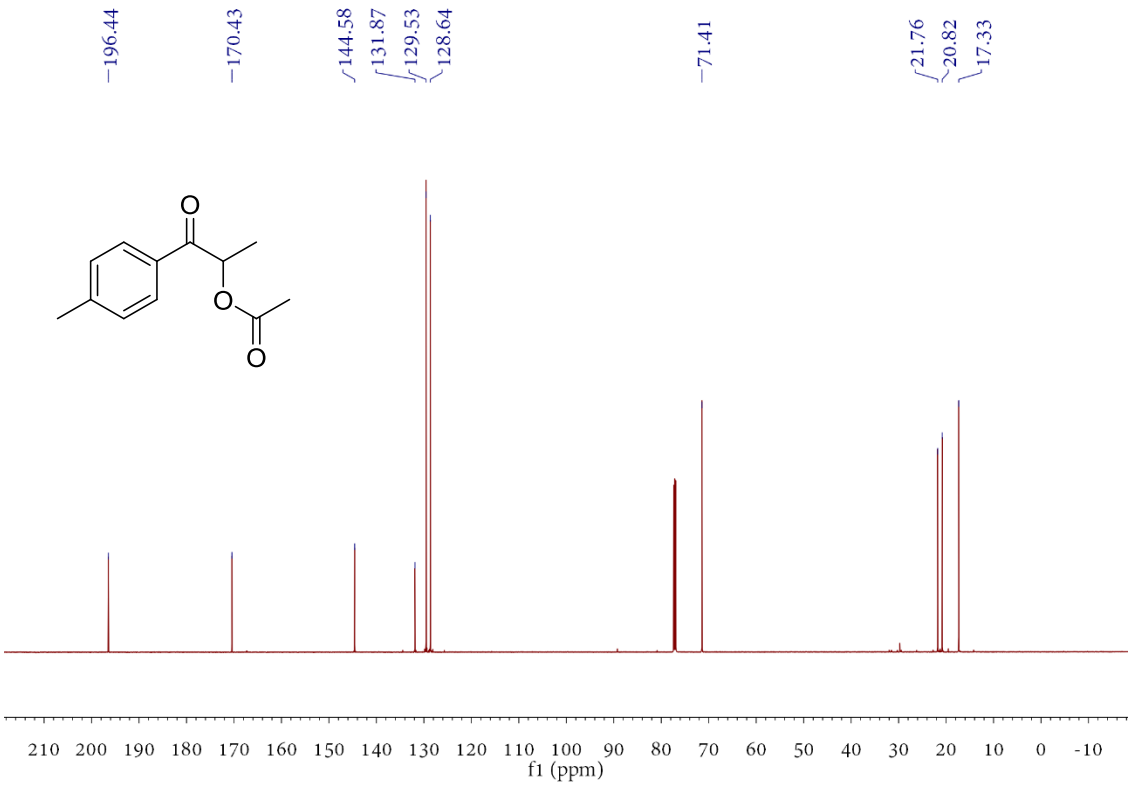
^{1}H NMR spectrum of compound **3d**



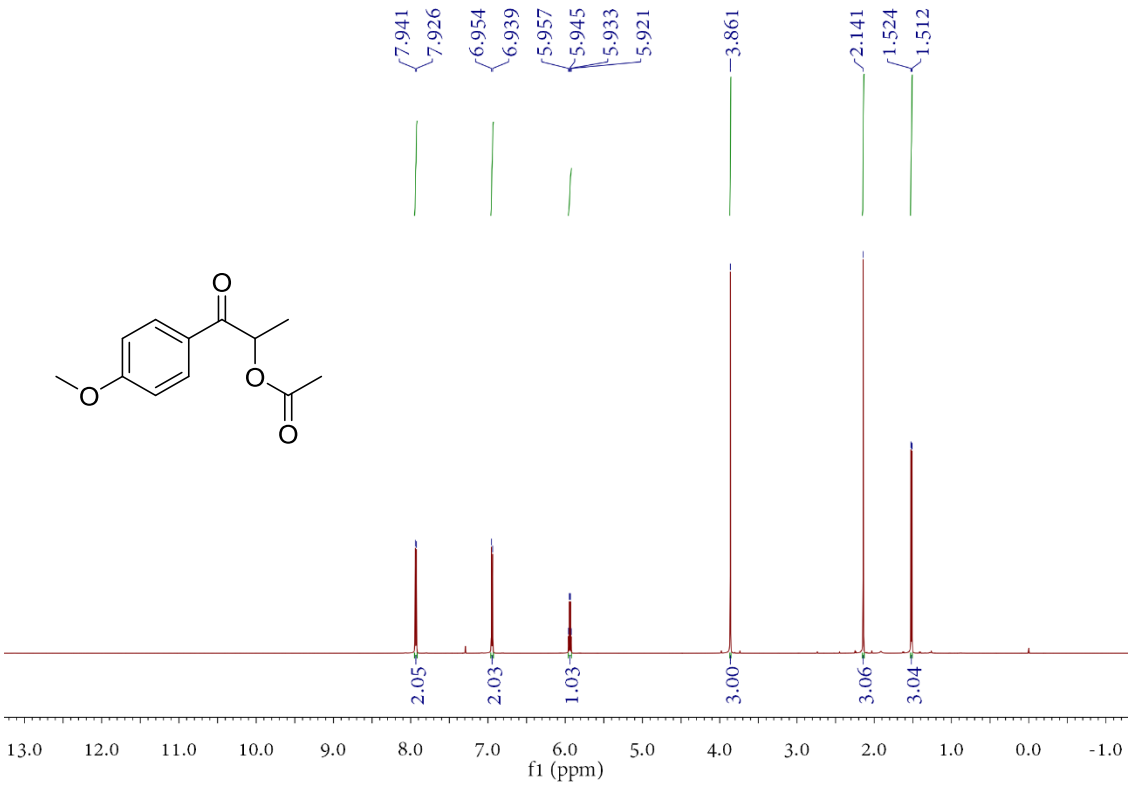
^{13}C NMR spectrum of compound **3d**



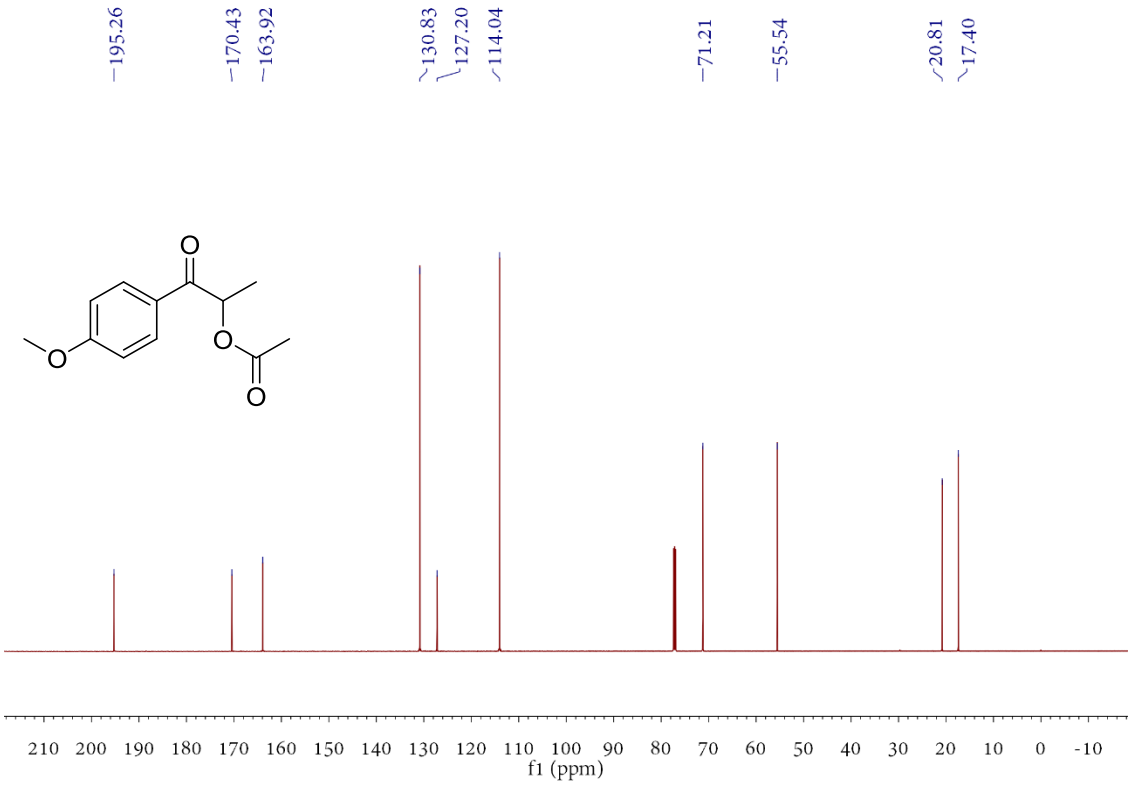
^{1}H NMR spectrum of compound **3e**



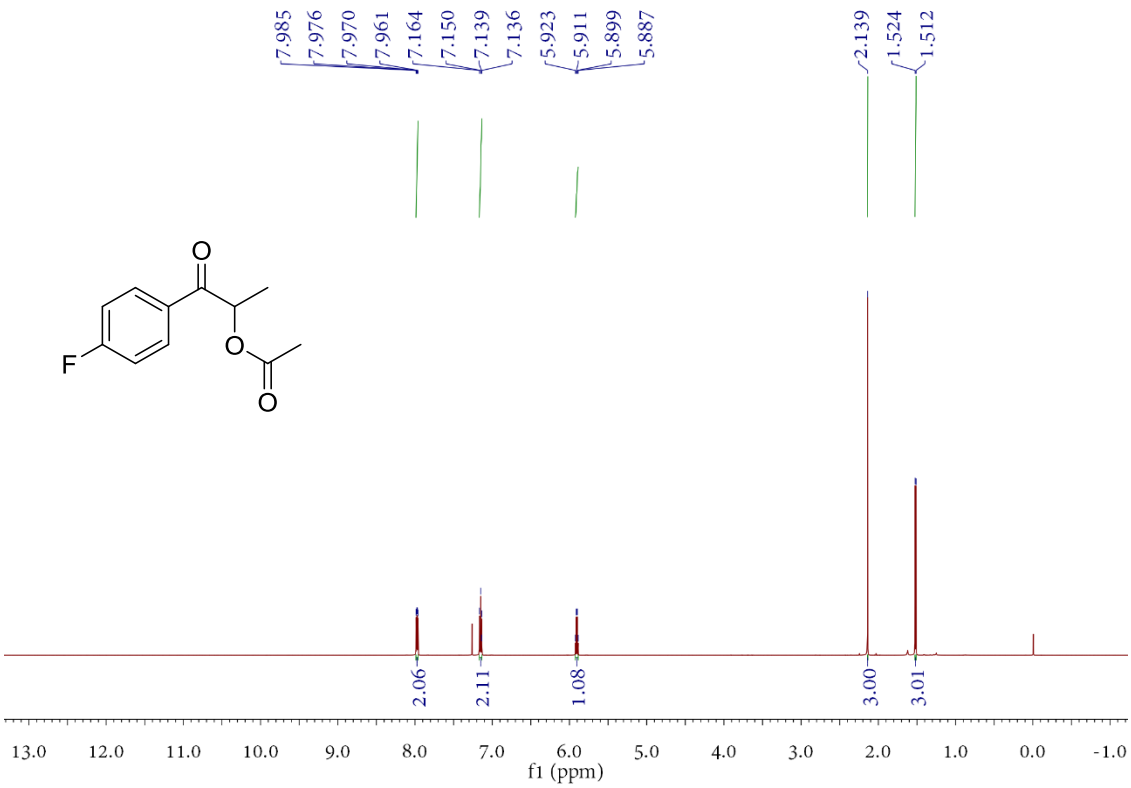
^{13}C NMR spectrum of compound **3e**



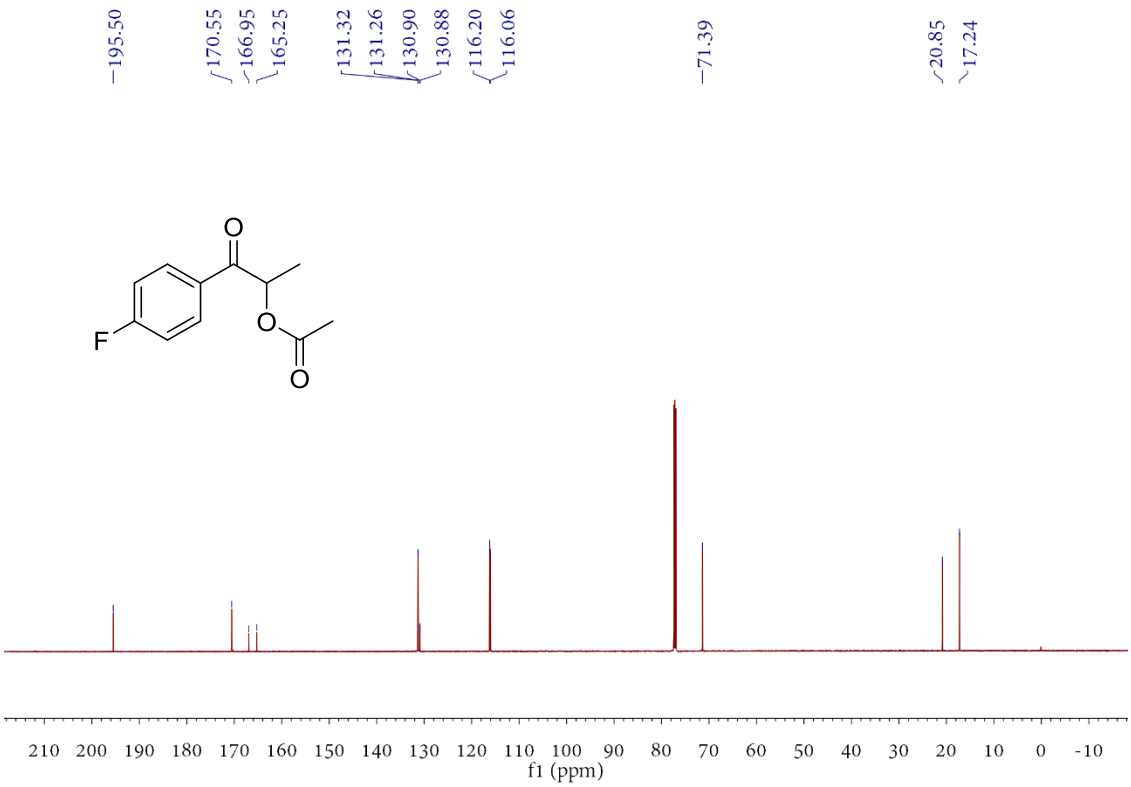
^{1}H NMR spectrum of compound **3f**



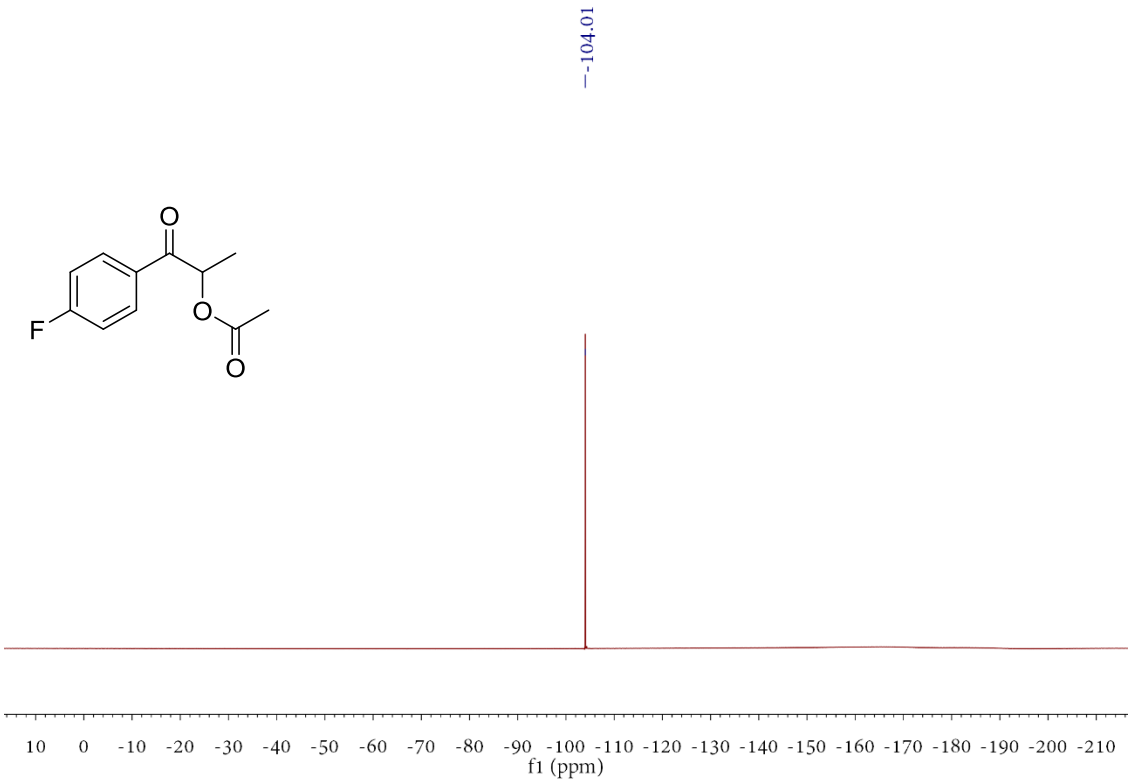
^{13}C NMR spectrum of compound **3f**



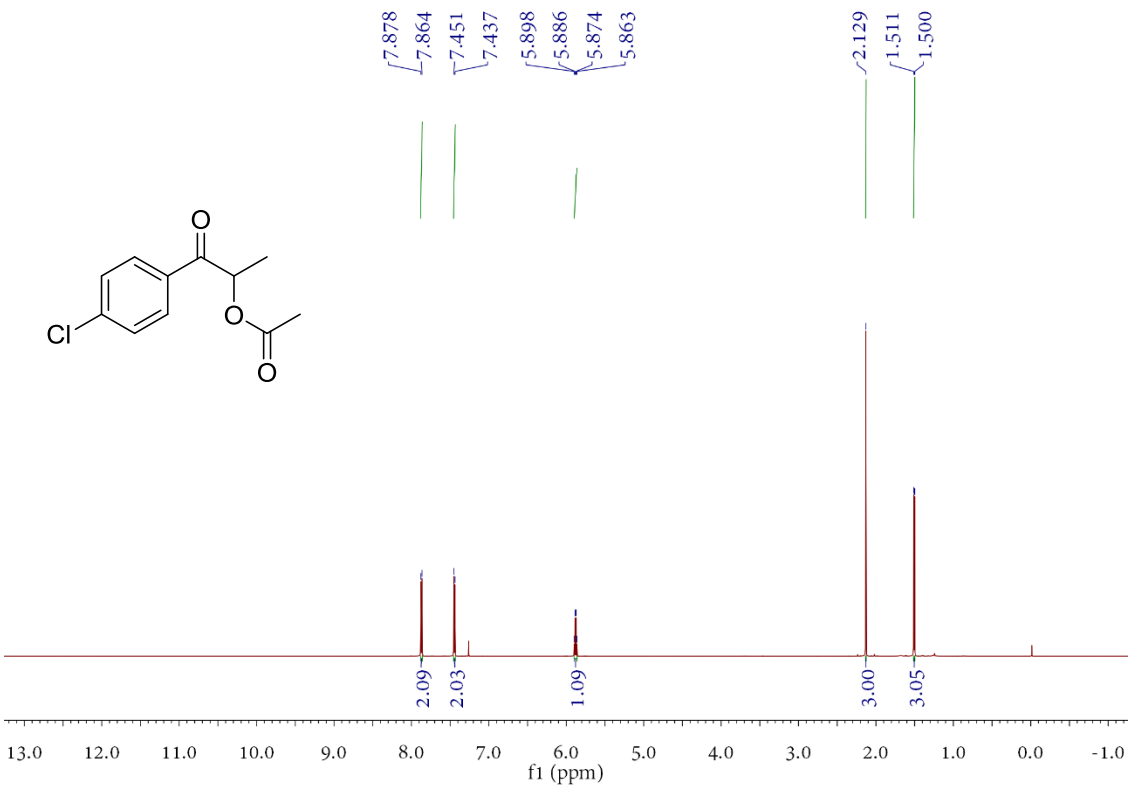
^{1}H NMR spectrum of compound **3g**



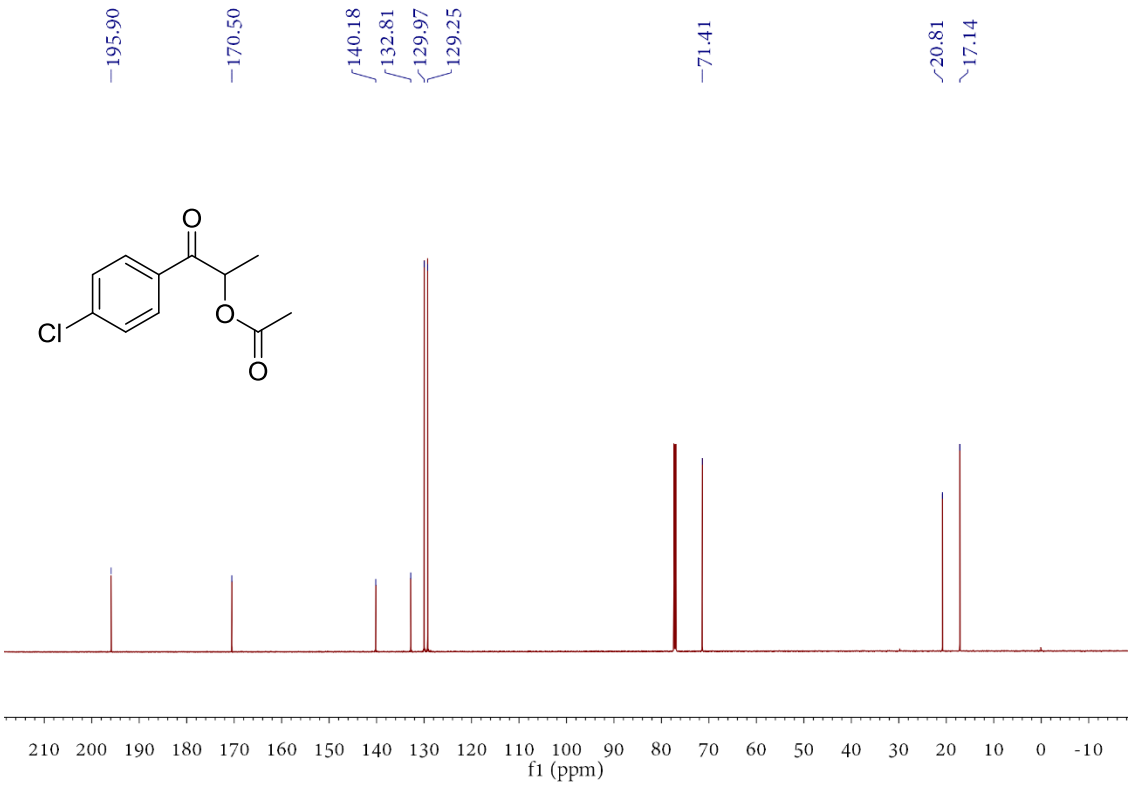
^{13}C NMR spectrum of compound **3g**



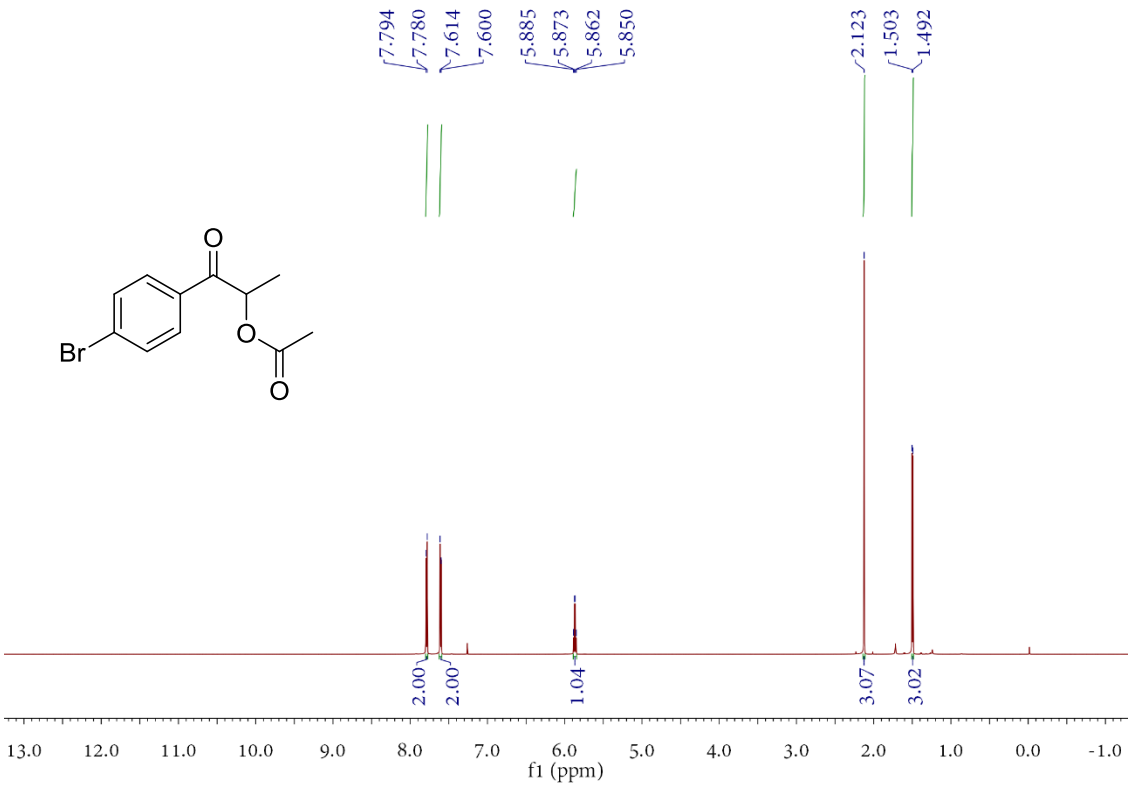
^{19}F NMR spectrum of compound **3g**



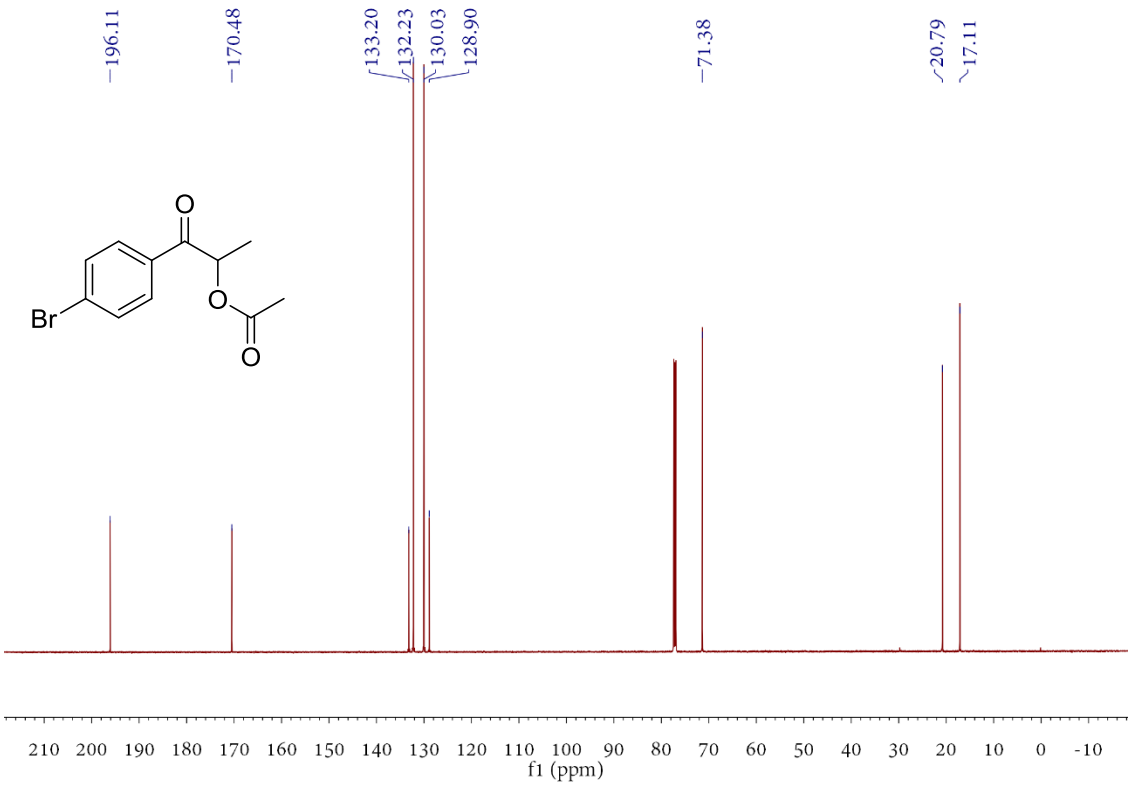
^{1}H NMR spectrum of compound **3h**



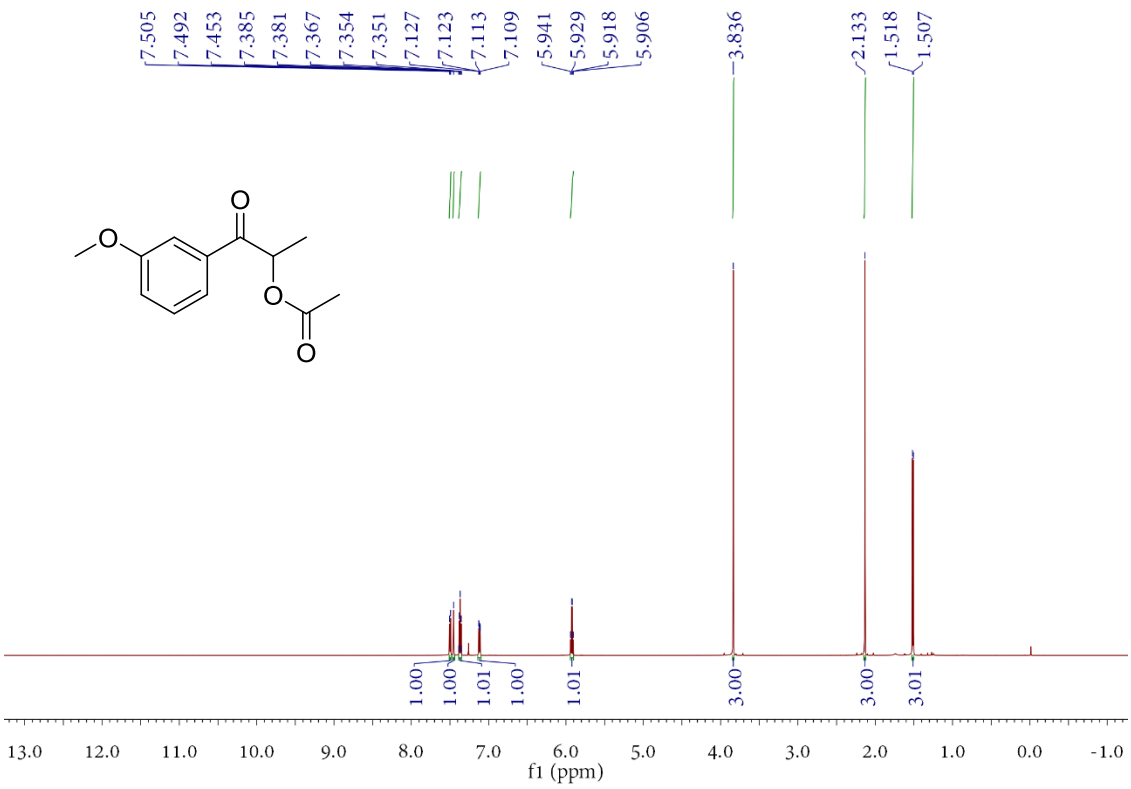
^{13}C NMR spectrum of compound **3h**



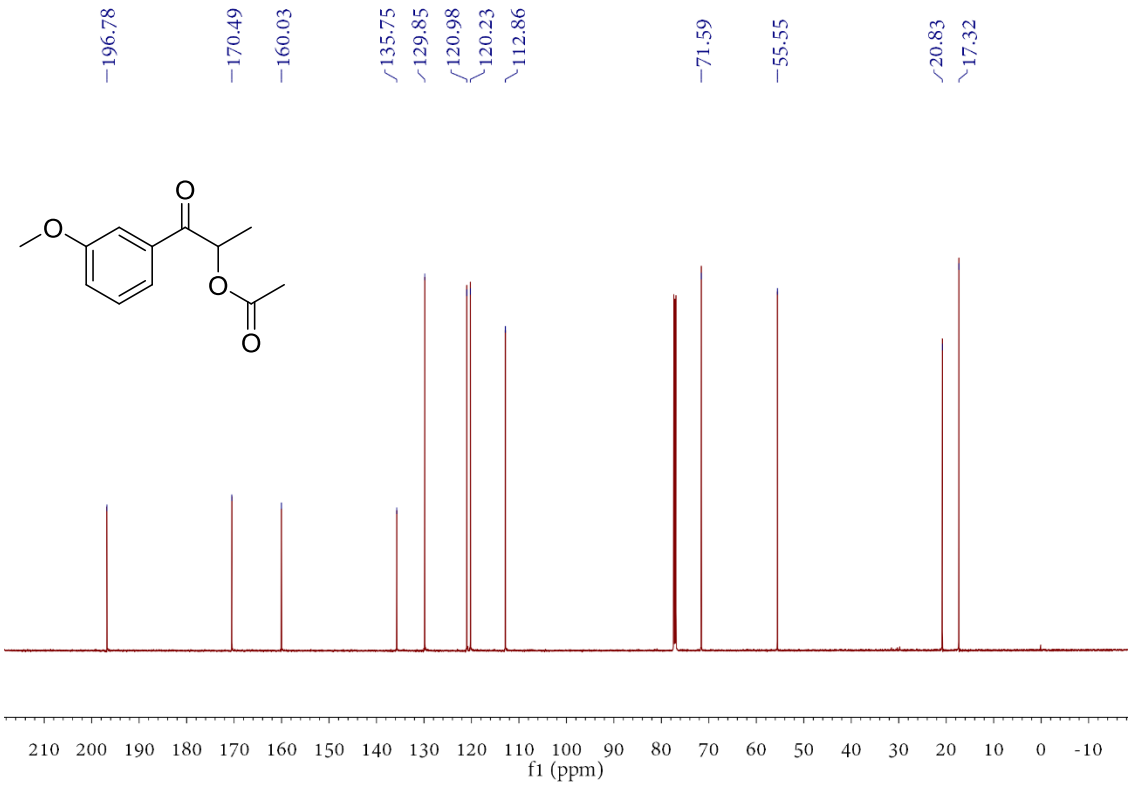
^{1}H NMR spectrum of compound **3i**



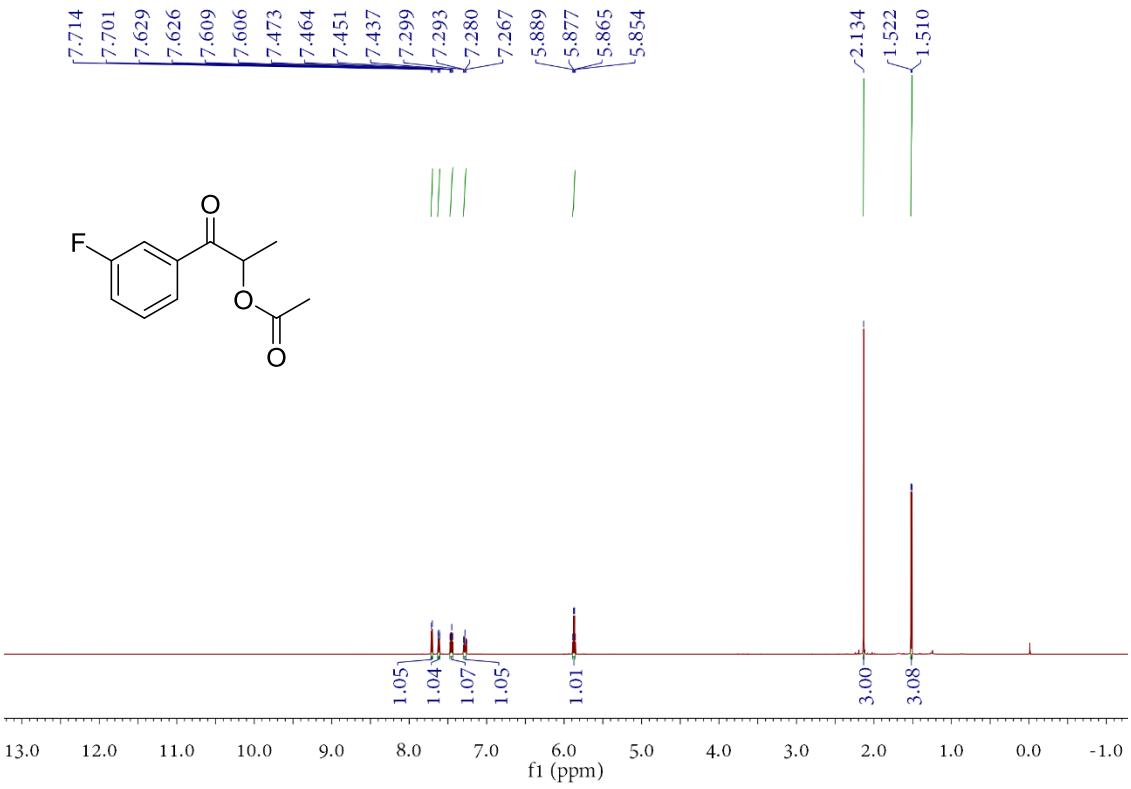
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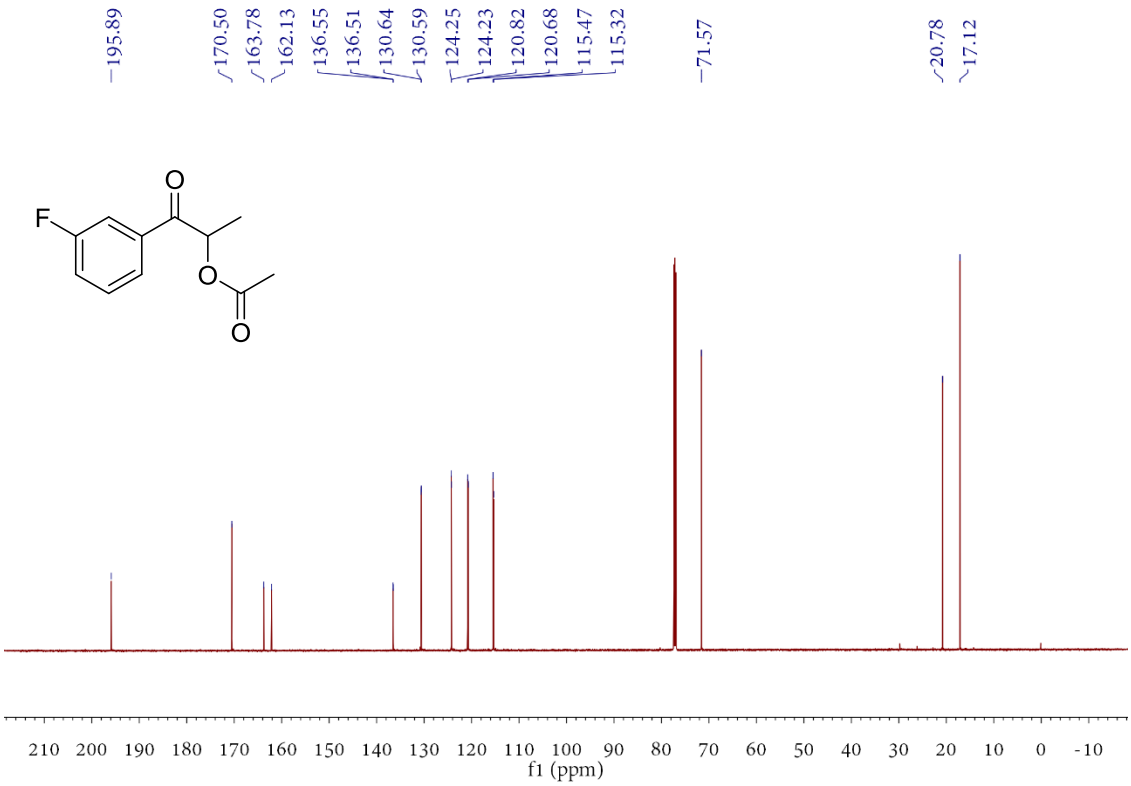
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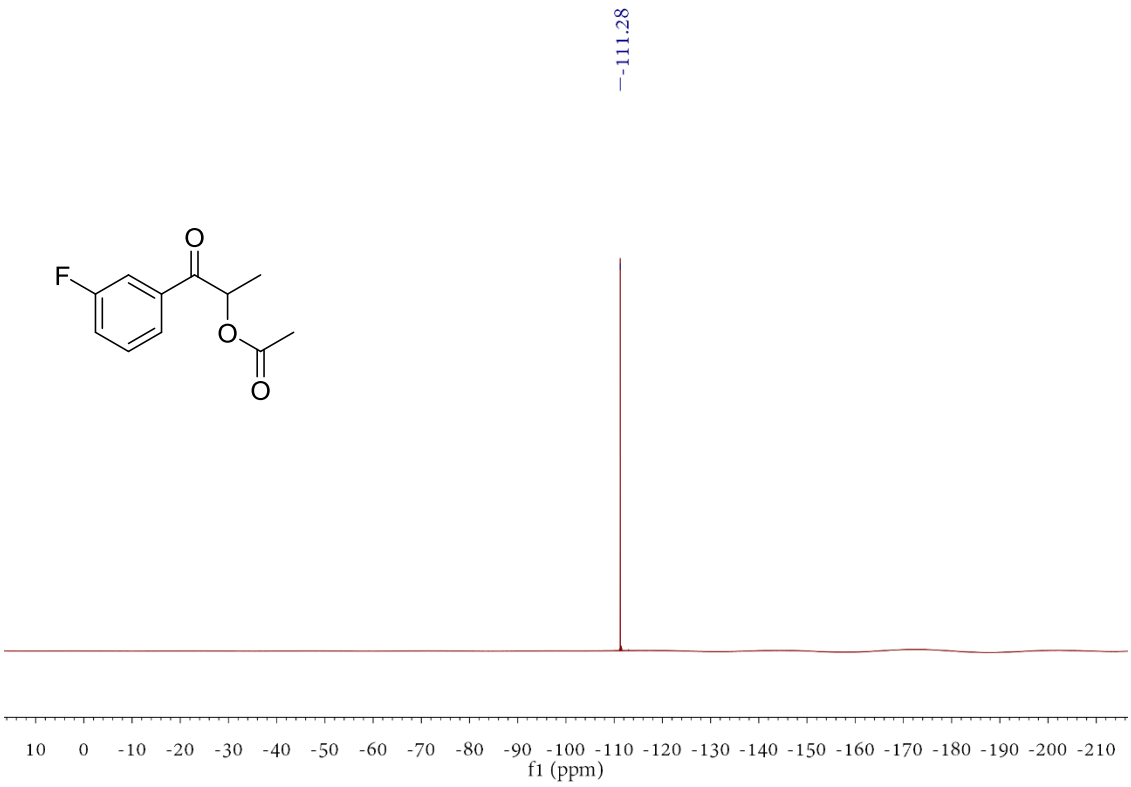
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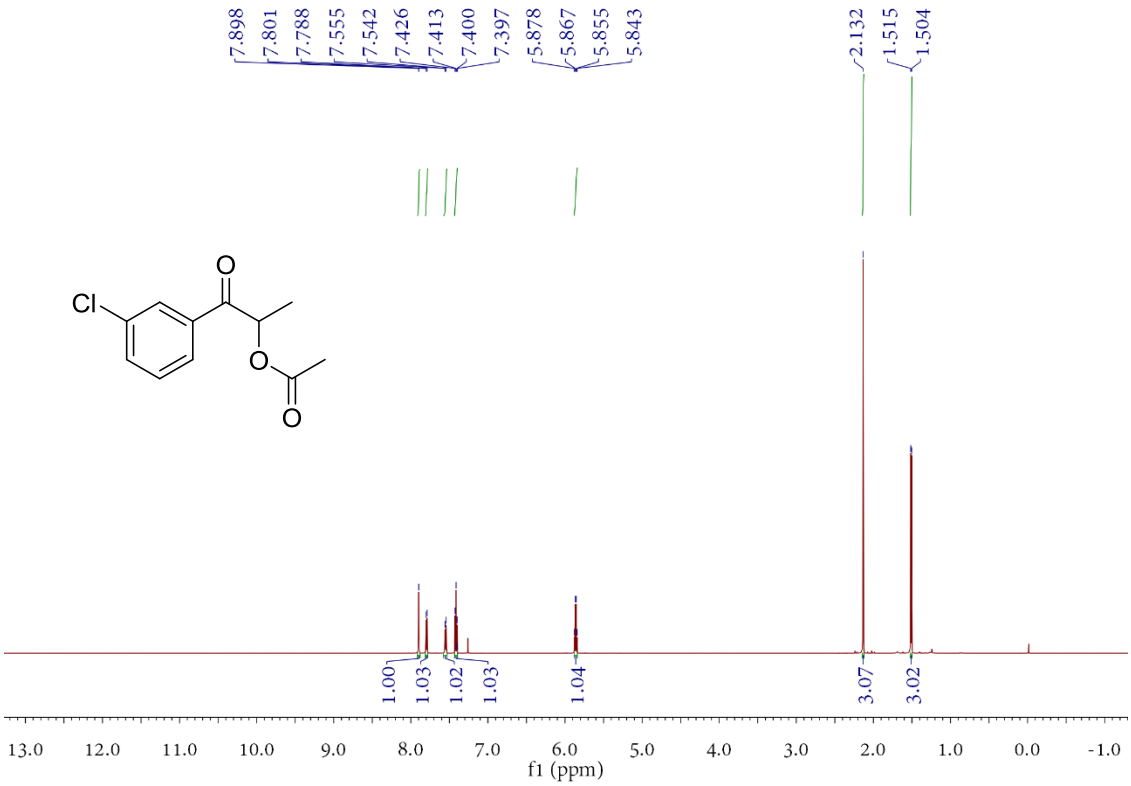
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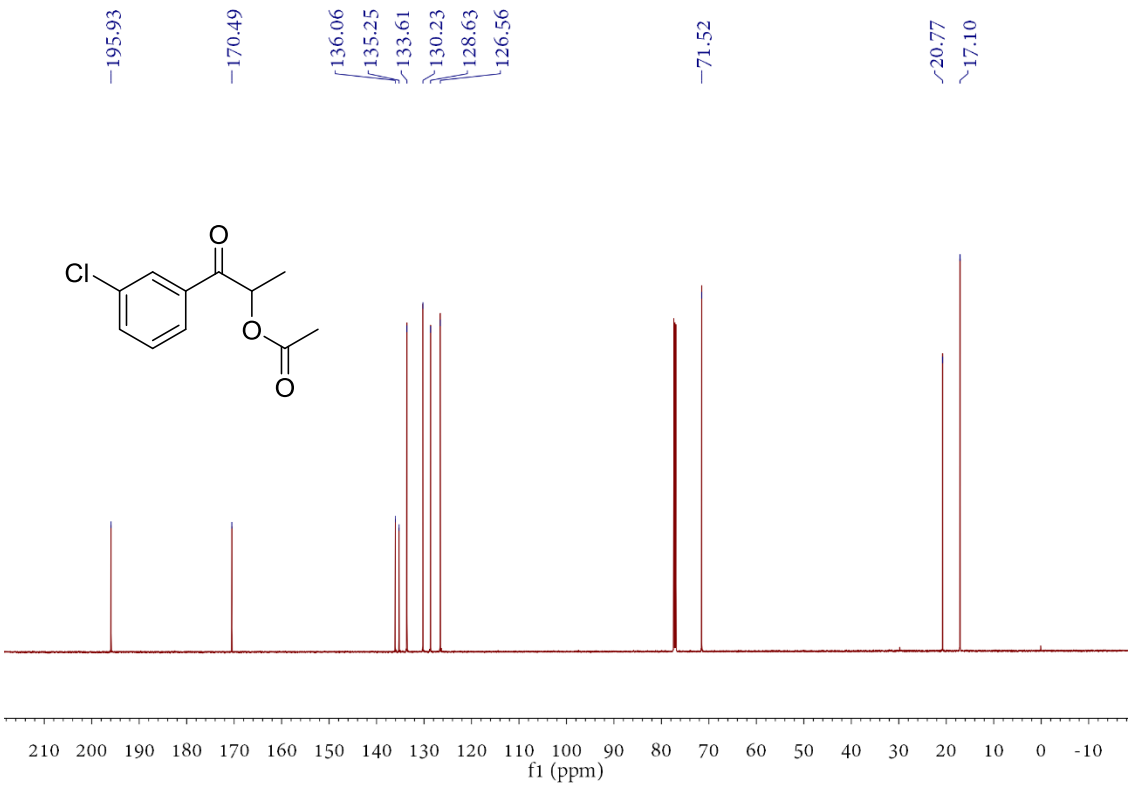
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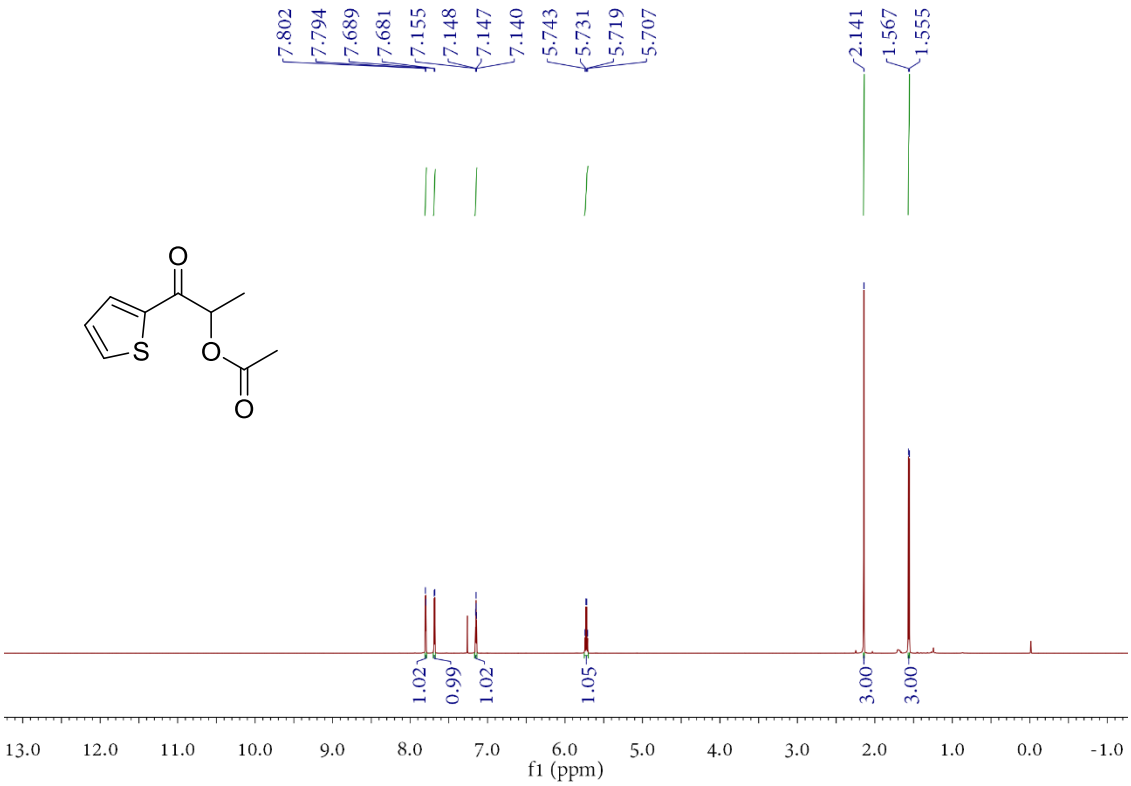
^{19}F NMR spectrum of compound **3k**



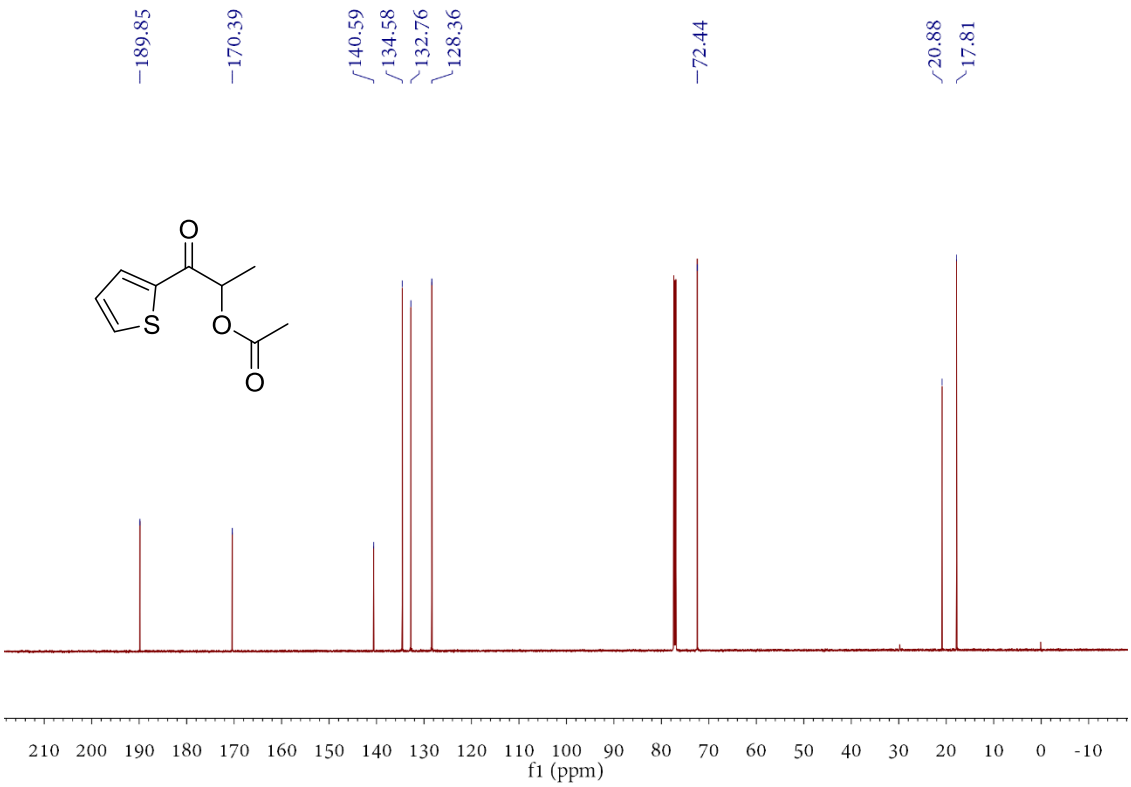
^{1}H NMR spectrum of compound **3l**



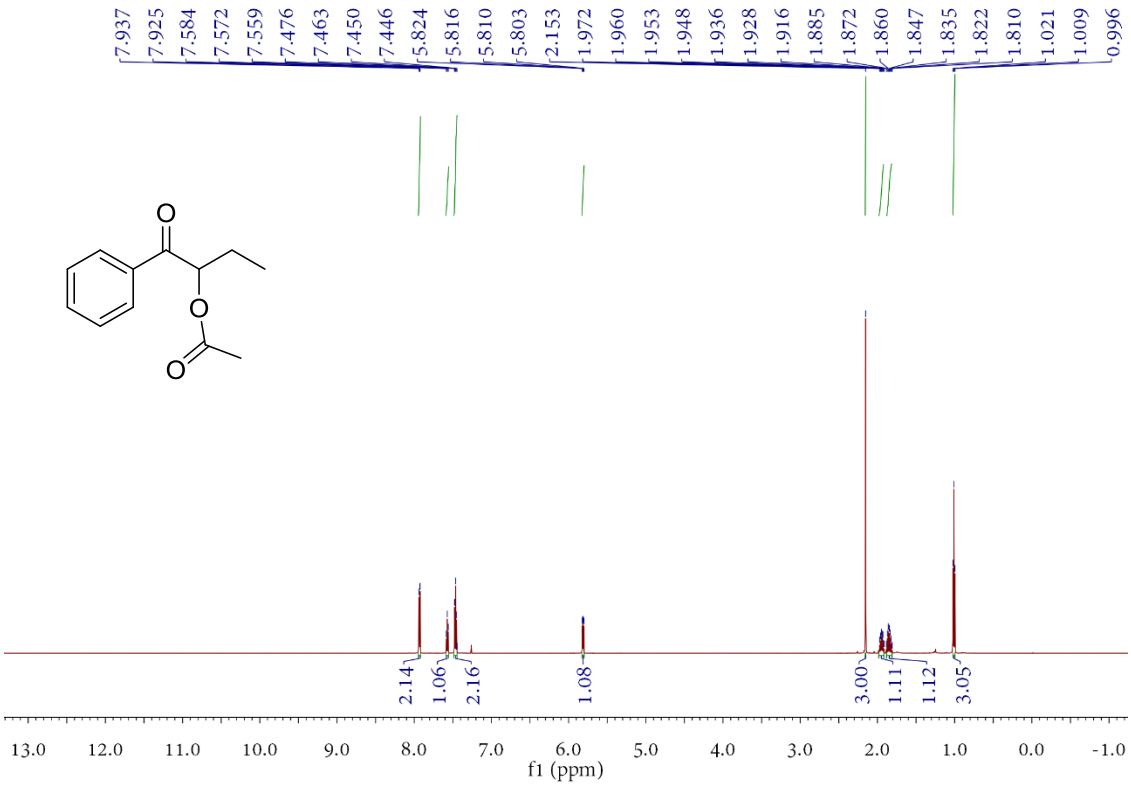
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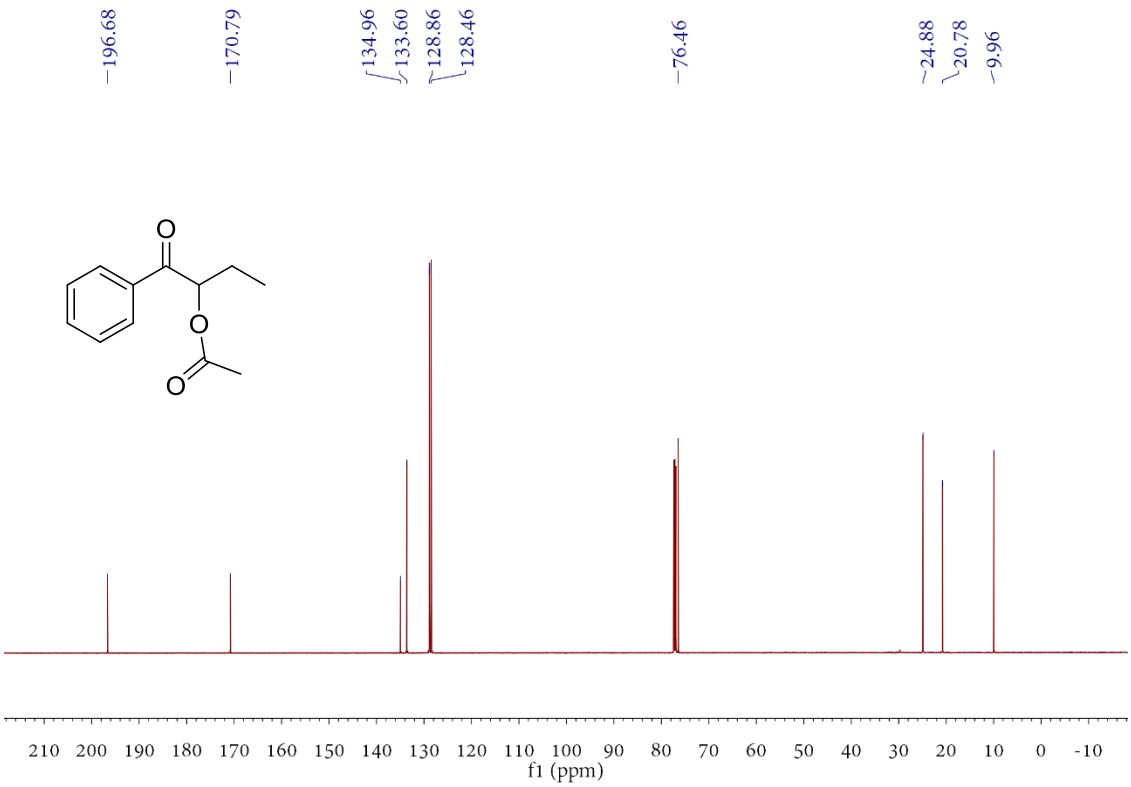
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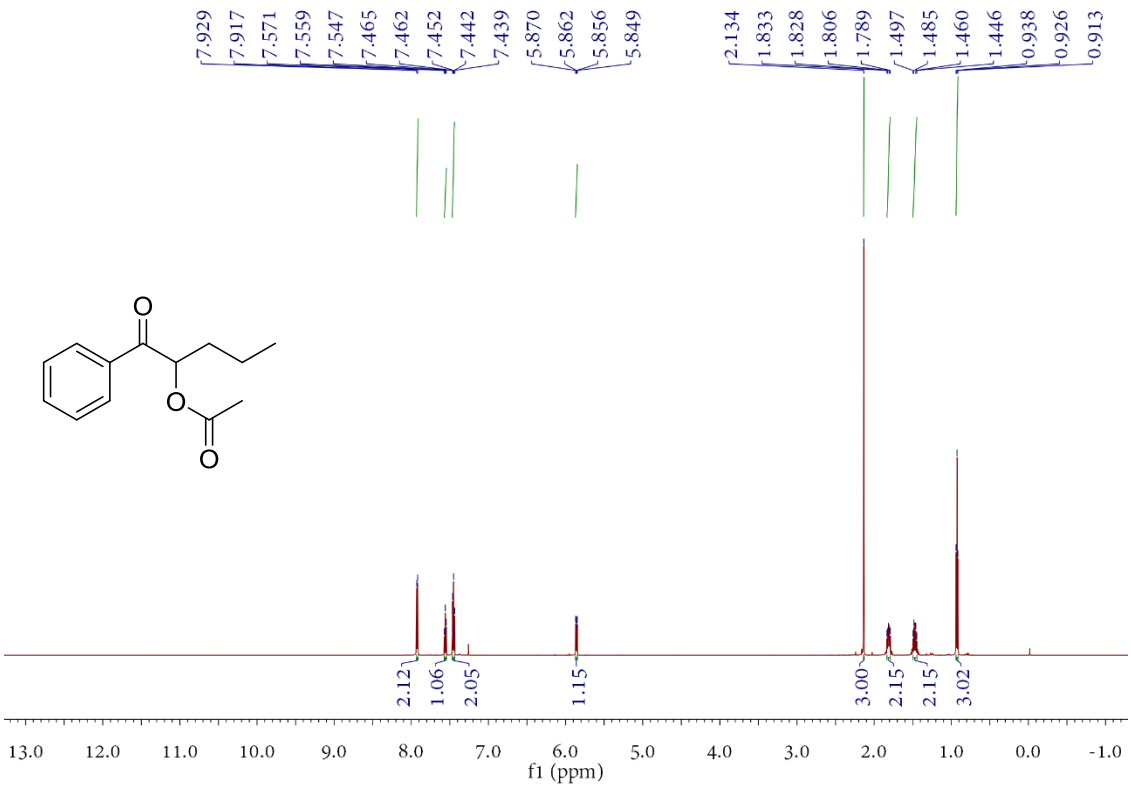
^{13}C NMR spectrum of compound **3m**



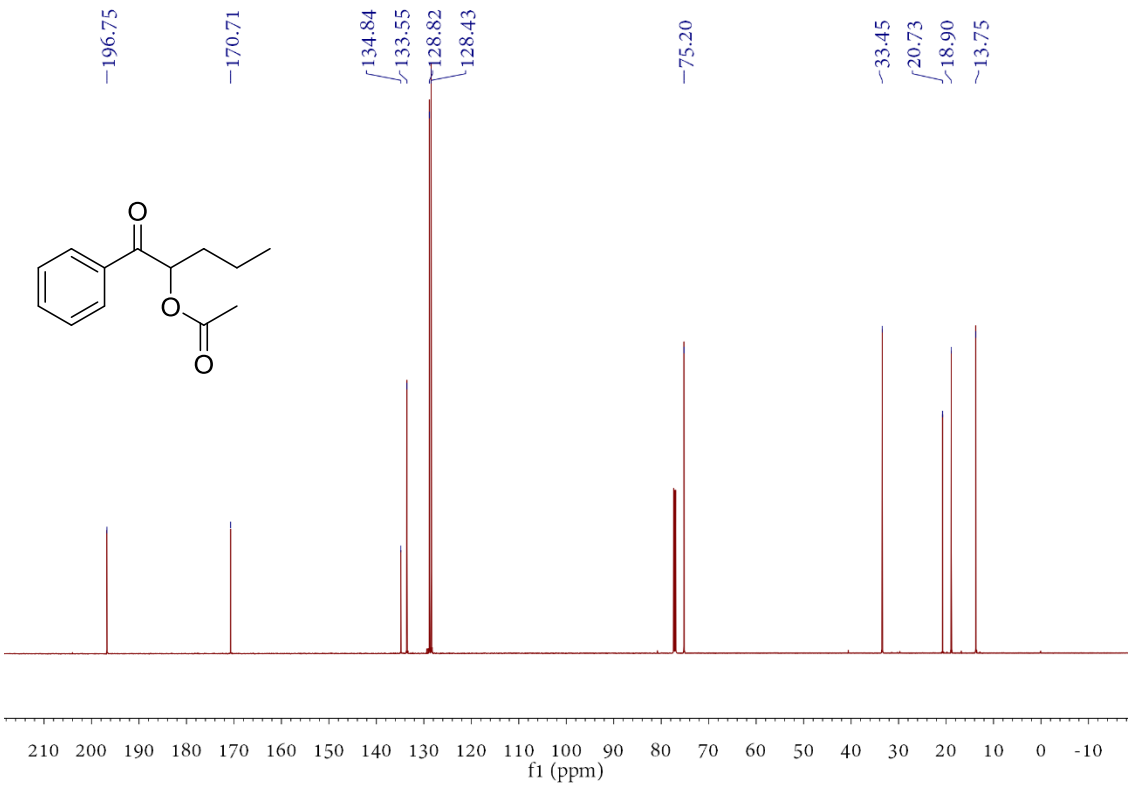
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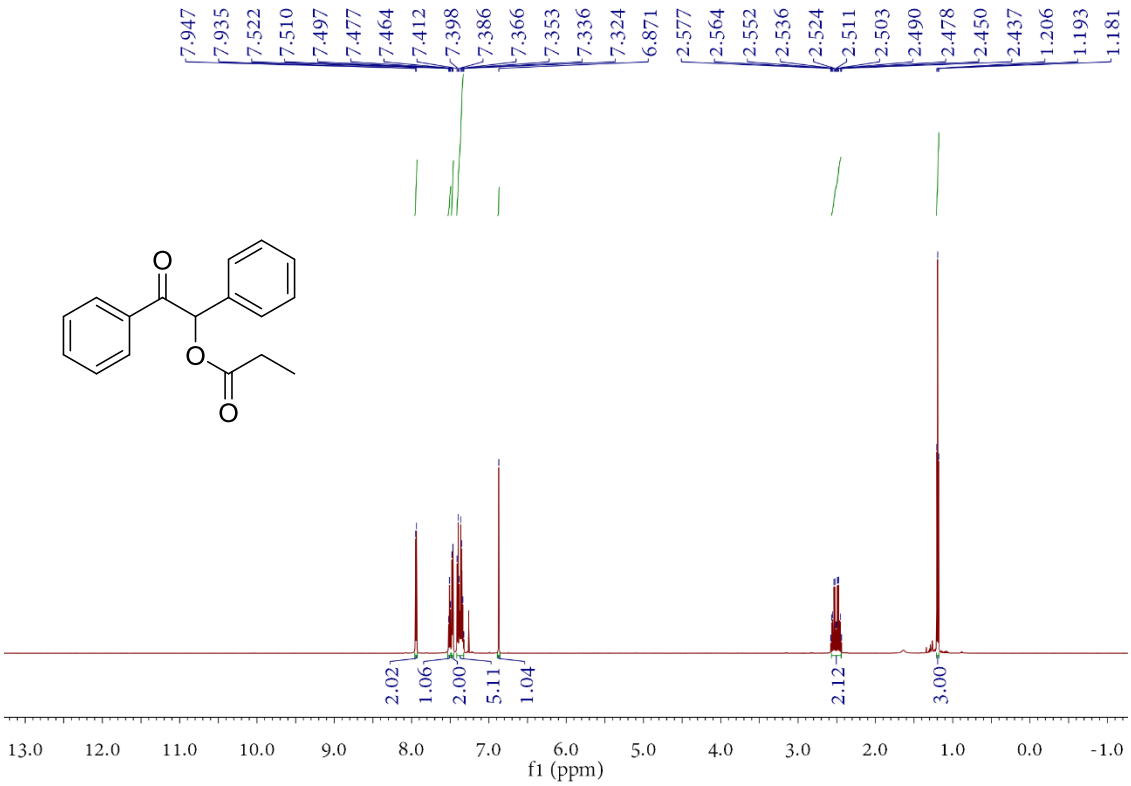
^{13}C NMR spectrum of compound **3n**



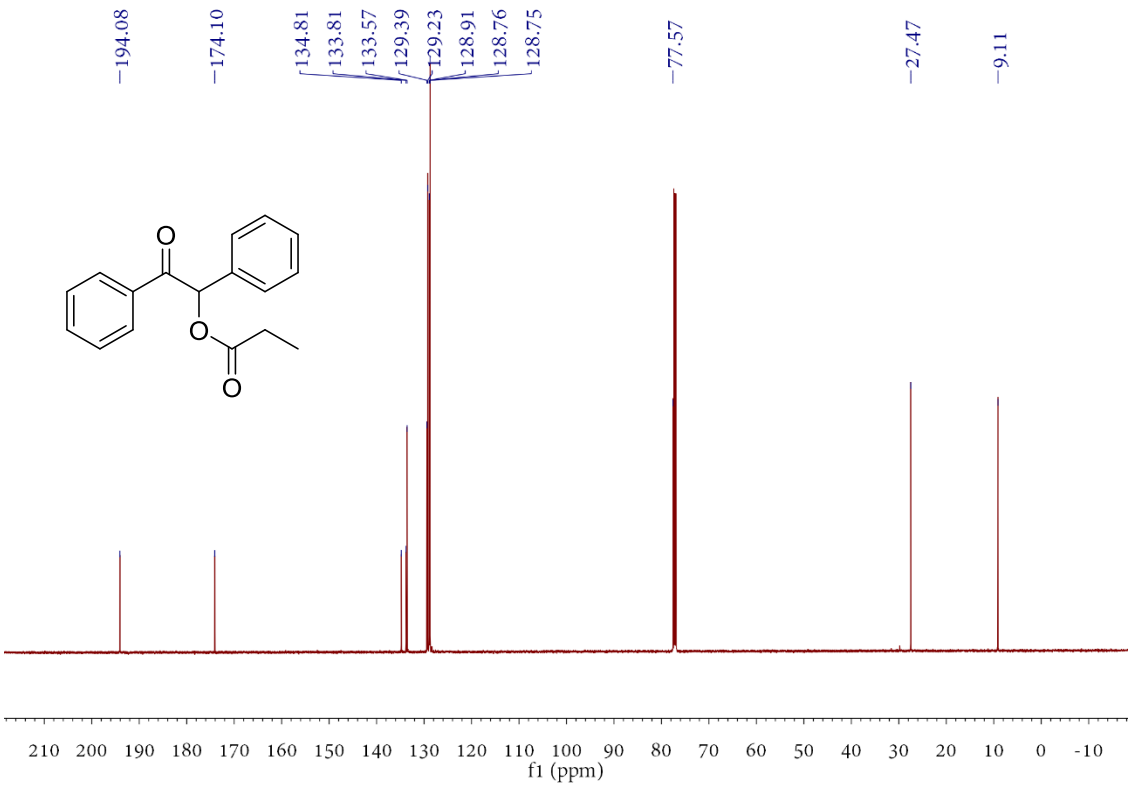
^{1}H NMR spectrum of compound **3o**



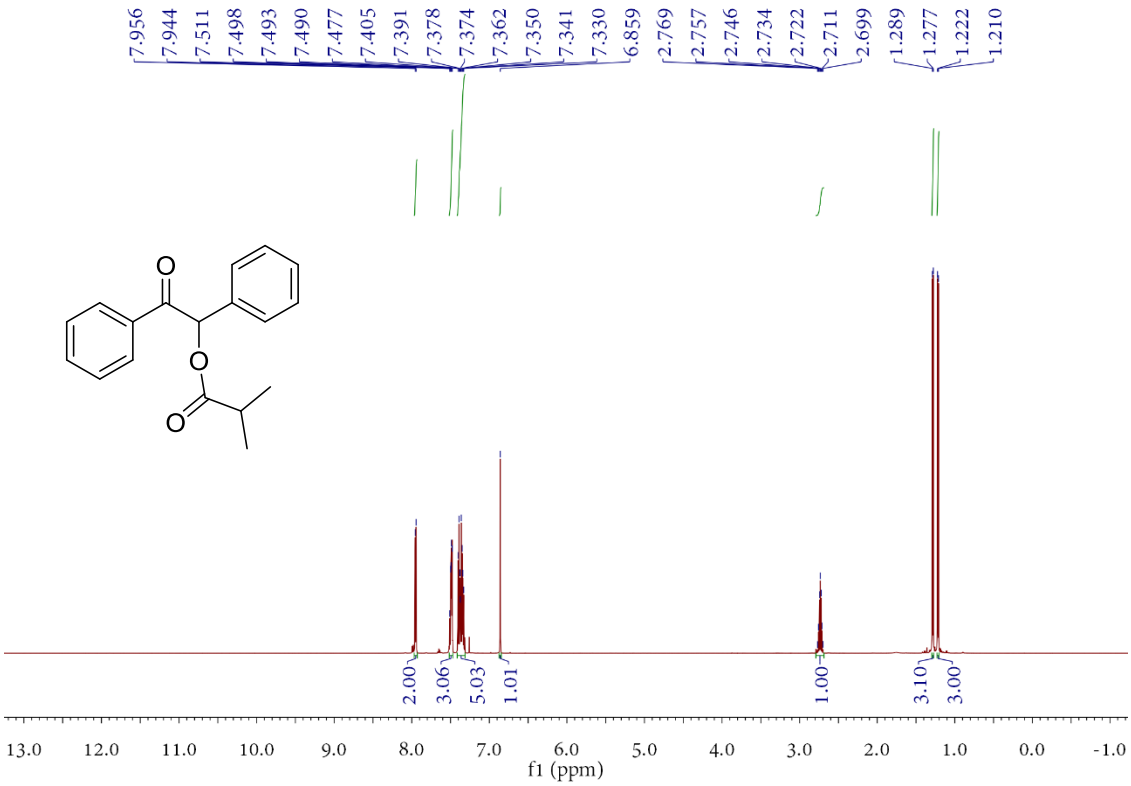
^{13}C NMR spectrum of compound **3o**



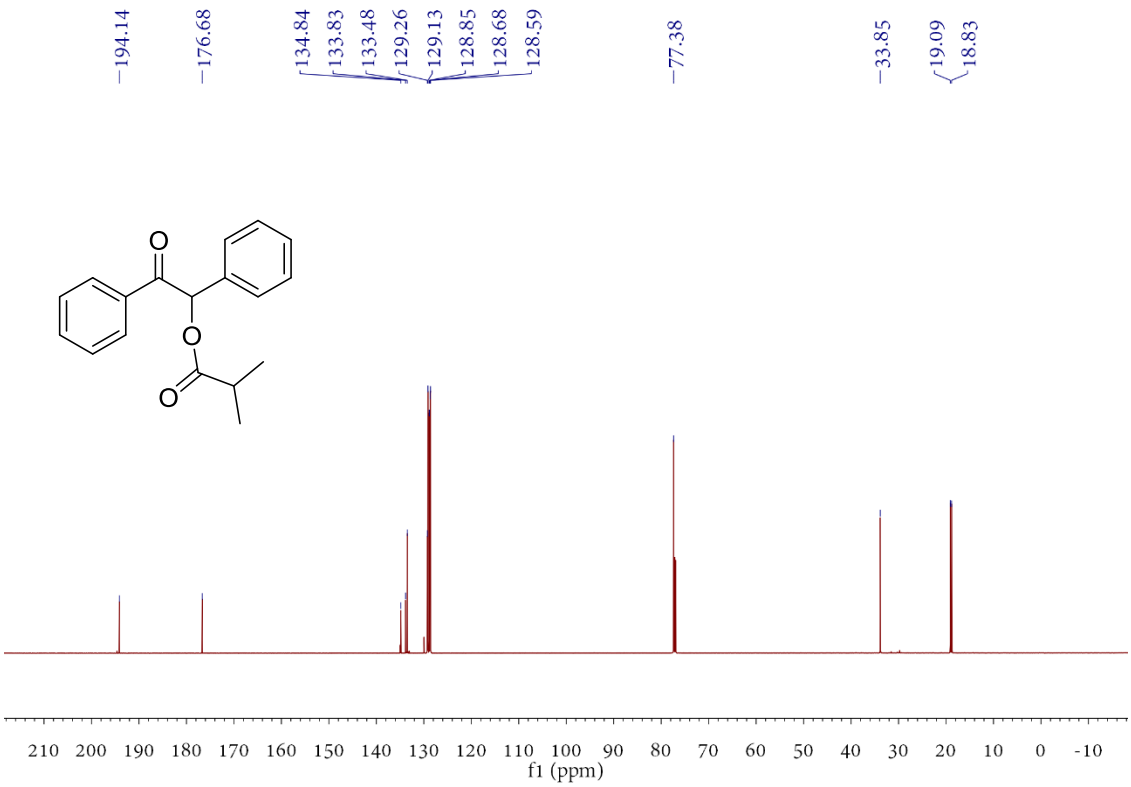
^{1}H NMR spectrum of compound **3p**



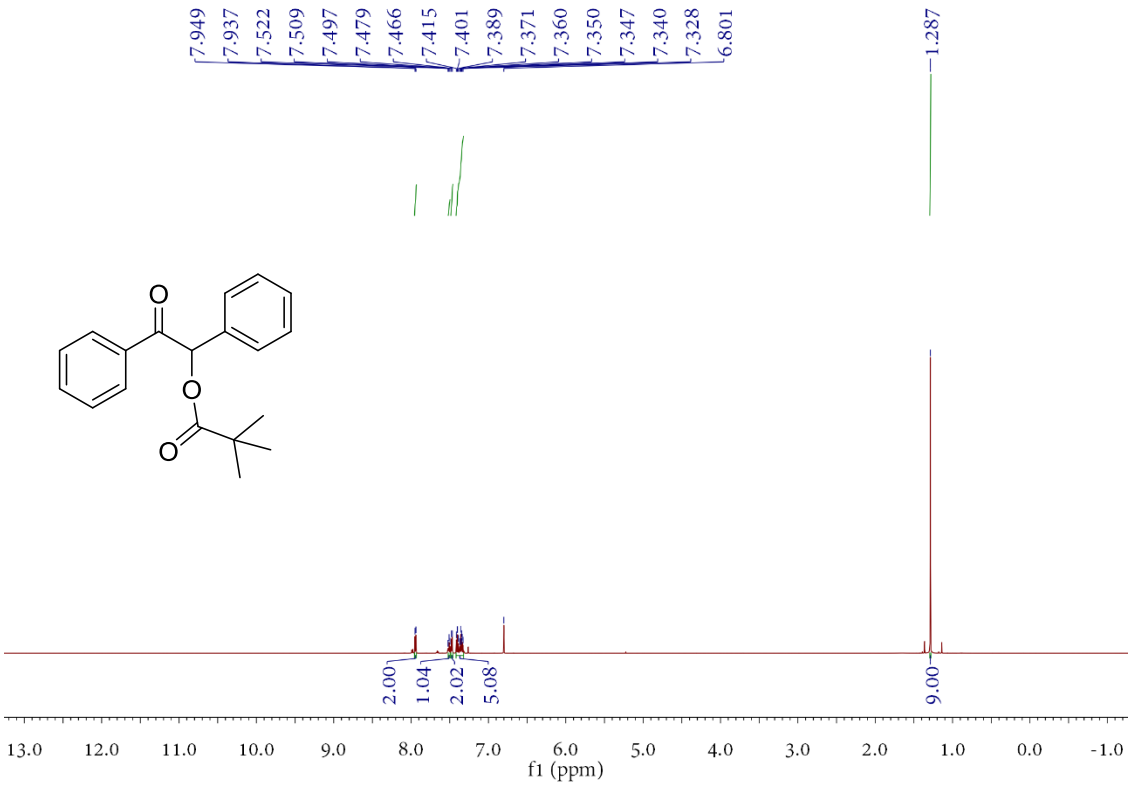
^{13}C NMR spectrum of compound **3p**



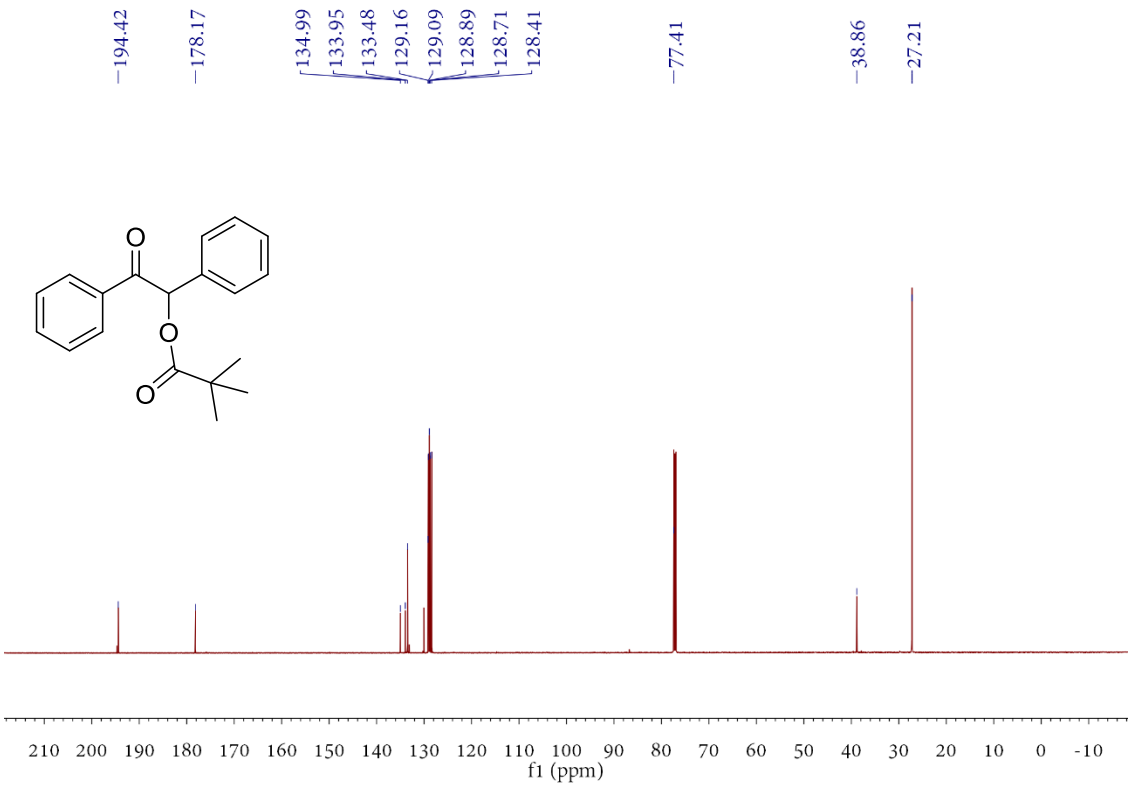
^{1}H NMR spectrum of compound **3q**



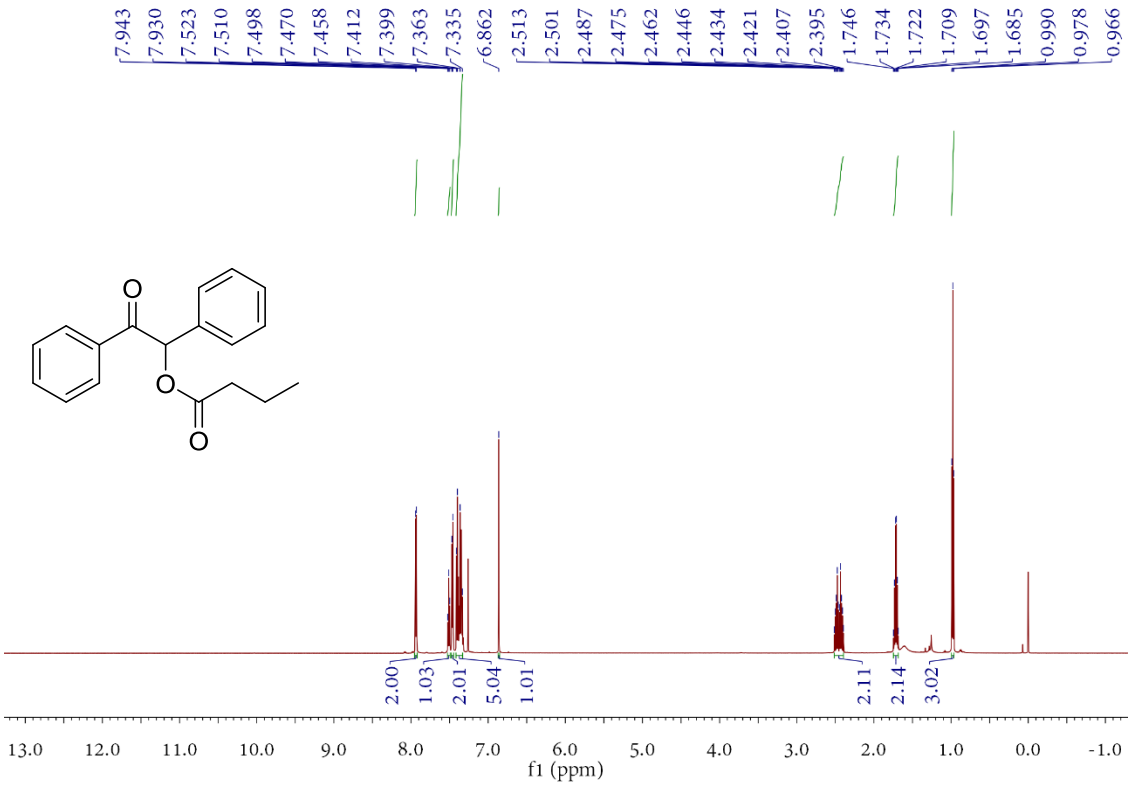
^{13}C NMR spectrum of compound **3q**



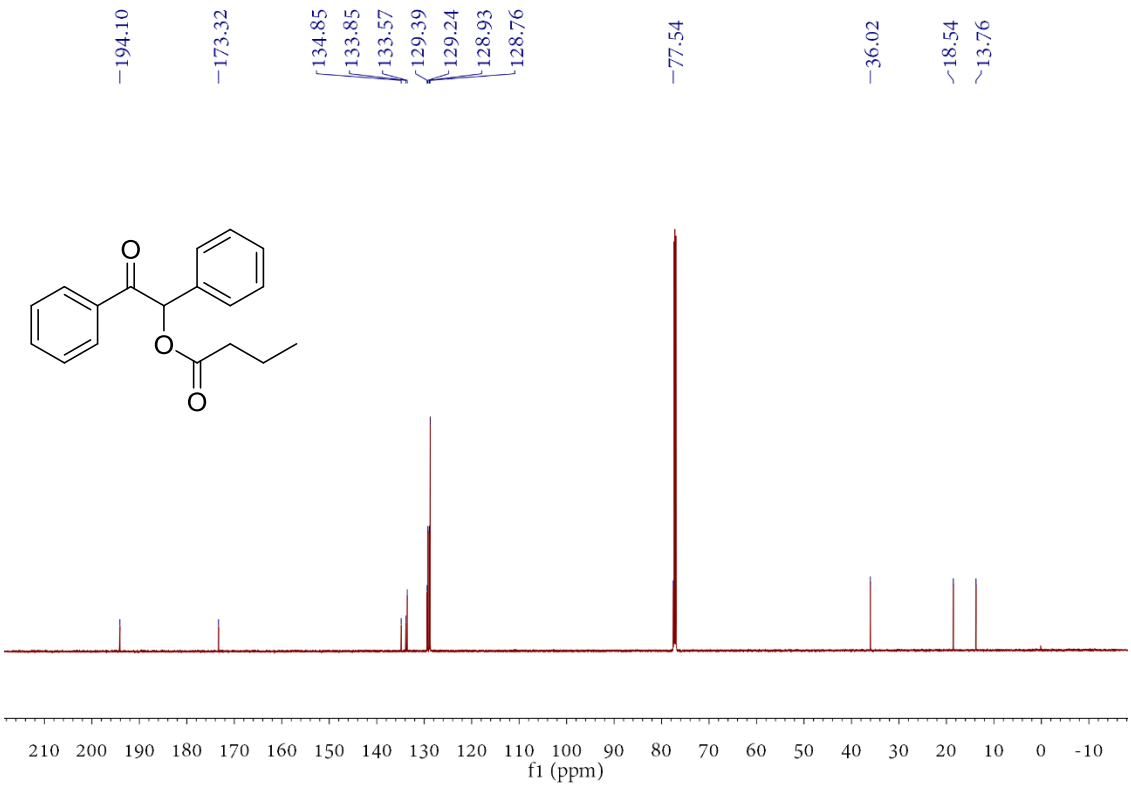
^{1}H NMR spectrum of compound **3r**



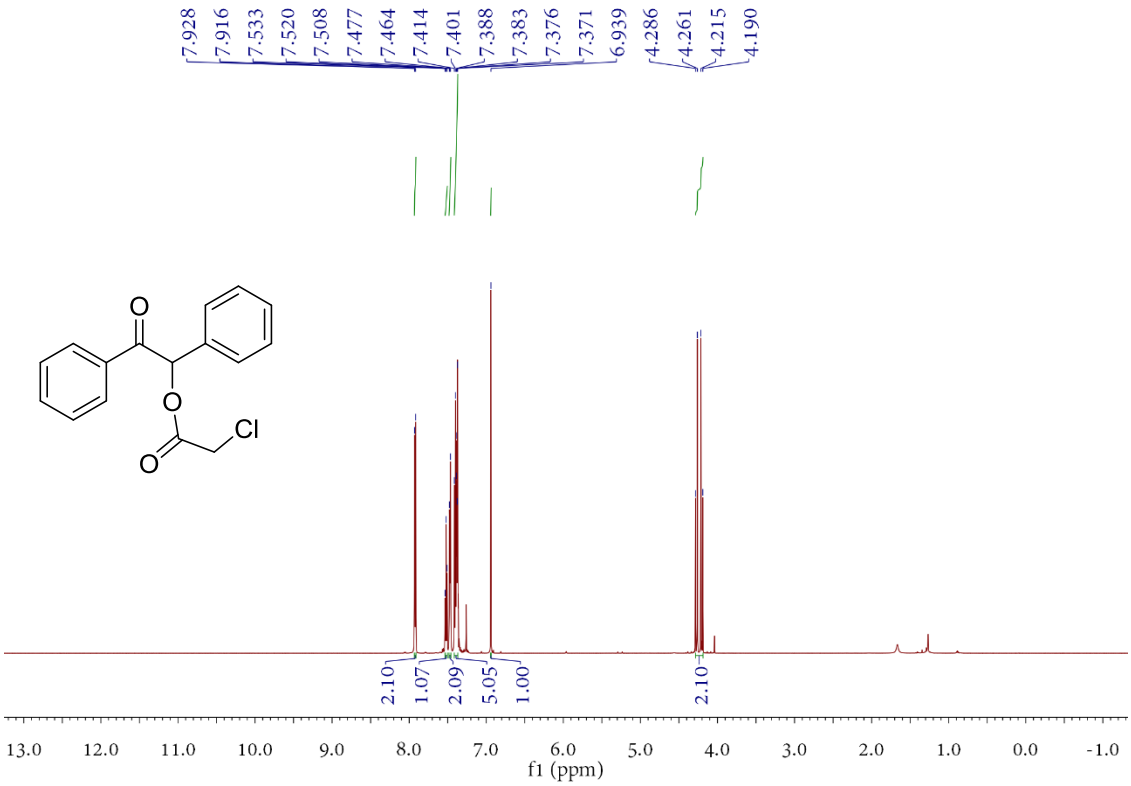
^{13}C NMR spectrum of compound **3r**



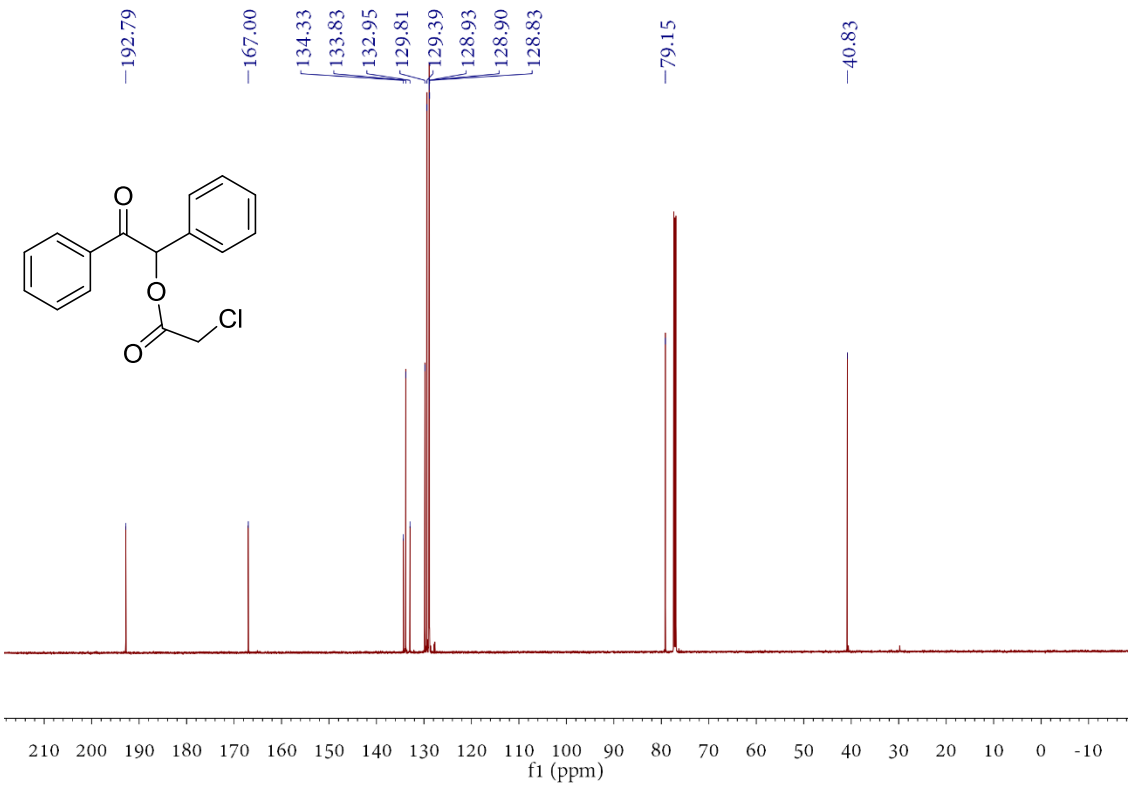
^{1}H NMR spectrum of compound **3s**



^{13}C NMR spectrum of compound **3s**



^{1}H NMR spectrum of compound **3t**



^{13}C NMR spectrum of compound **3t**

References

[1] Onida, K.; Haddleton, A. J.; Norsic, S.; Boisson, C.; D'Agosto, F.; Duguet, N. Organocatalytic synthesis of substituted vinylene carbonates. *Adv. Synth. Catal.,* **2021**, *363*, 5129-5137.

[2] Liang, Y. F.; Wu, K.; Song, S.; Li, X. Y.; Huang, X. Q.; Jiao, N. I_2- or NBS-catalyzed highly efficient α-hydroxylation of ketones with dimethyl sulfoxide. *Org. Lett.,* **2015**, *17*, 876-879.