Catalyst-Free Annulation of 2-Pyridylacetates and Ynals with Molecular Oxygen: an Access to 3-Acylated Indolizines

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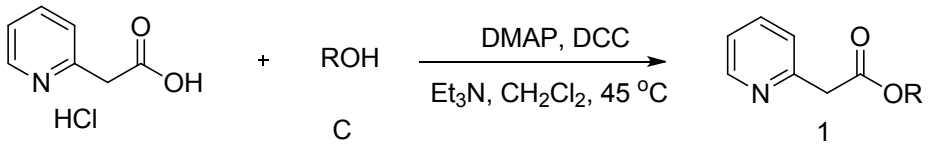
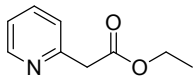
Preparation of starting materials:

The Route toward Substituted 2-Pyridylacetates:





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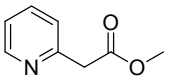

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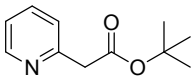

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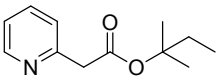

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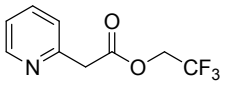

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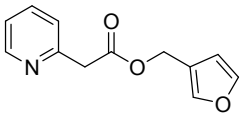

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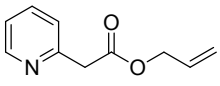

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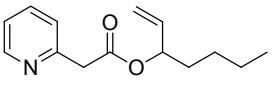

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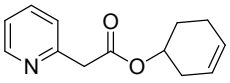

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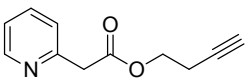

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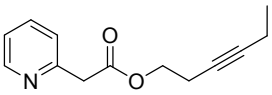

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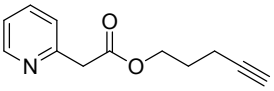

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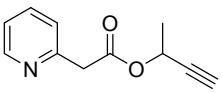

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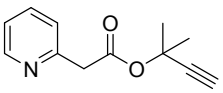

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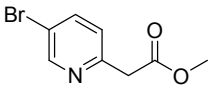

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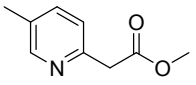

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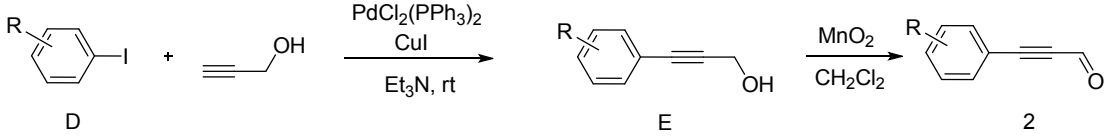

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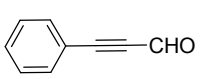

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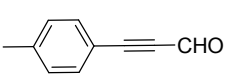

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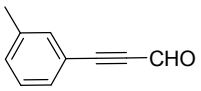

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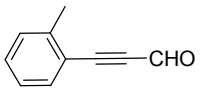

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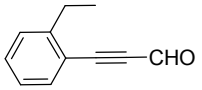

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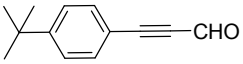

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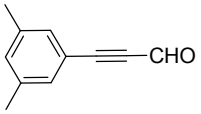

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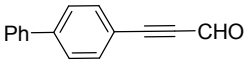

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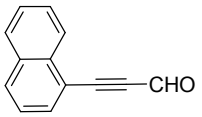

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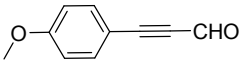

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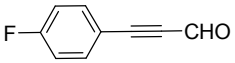

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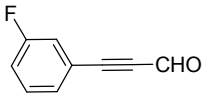

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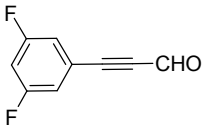

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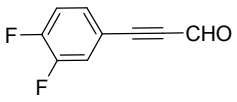

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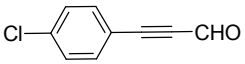

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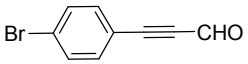

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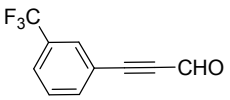

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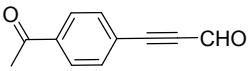

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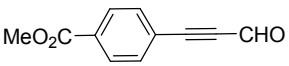

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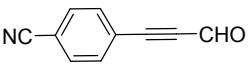

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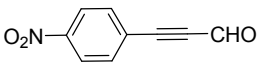

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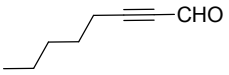

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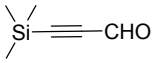

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GC-MS spectra of 3a and 3a-O[18]

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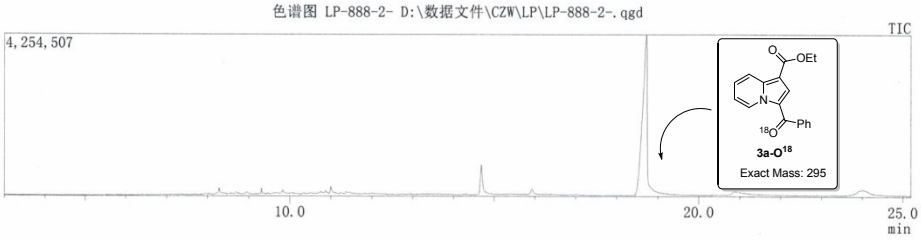

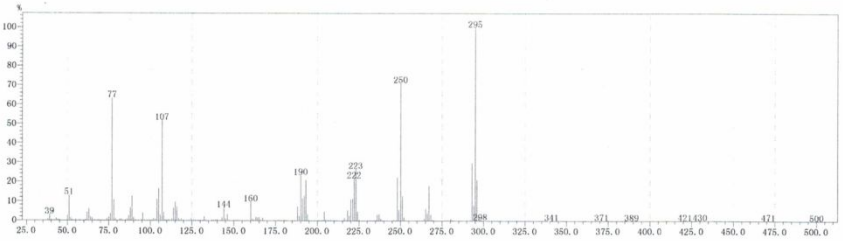

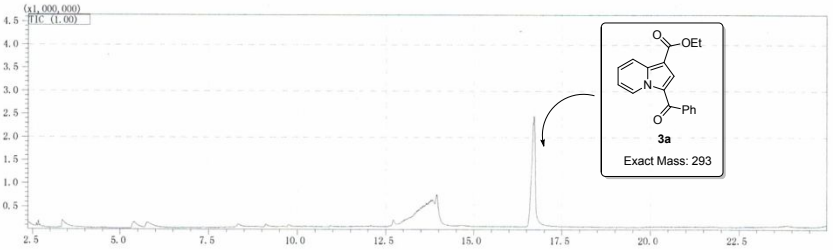

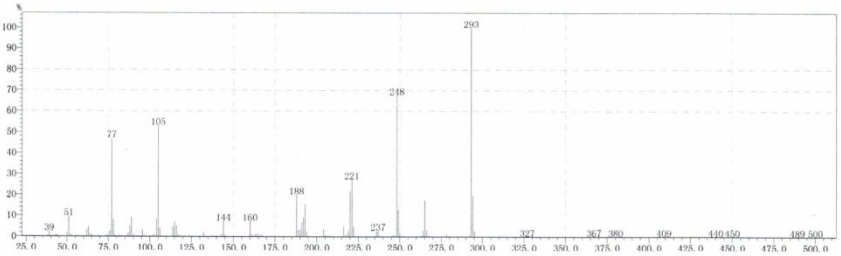

Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra

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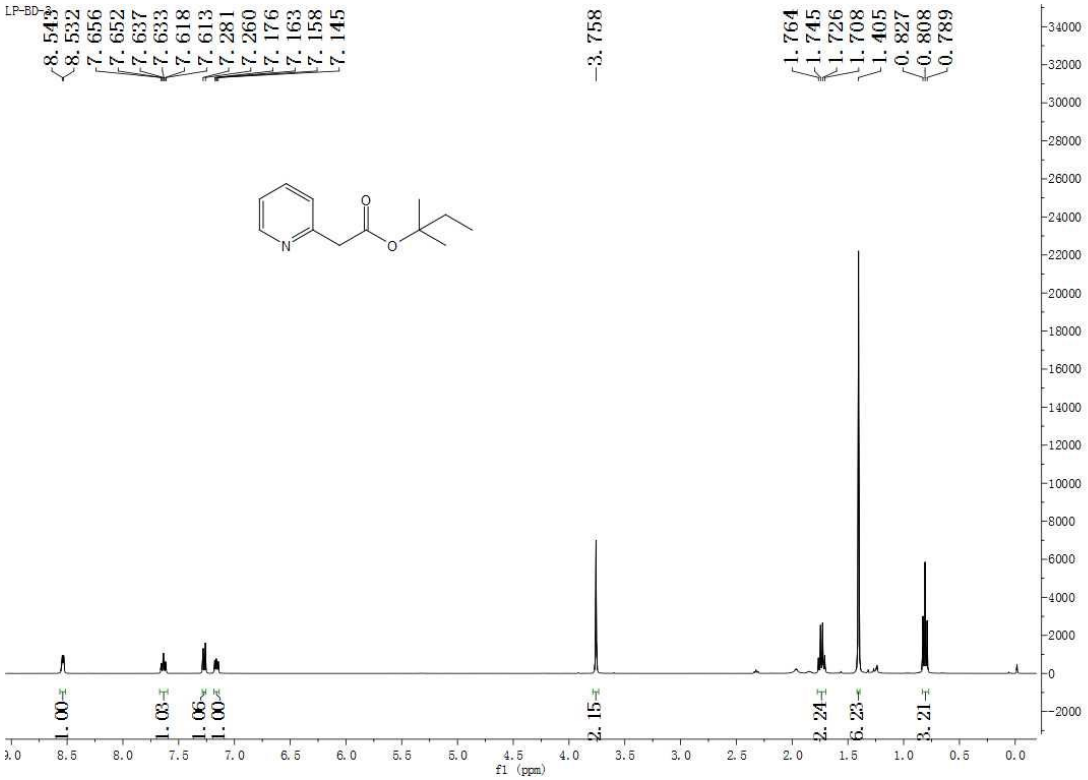
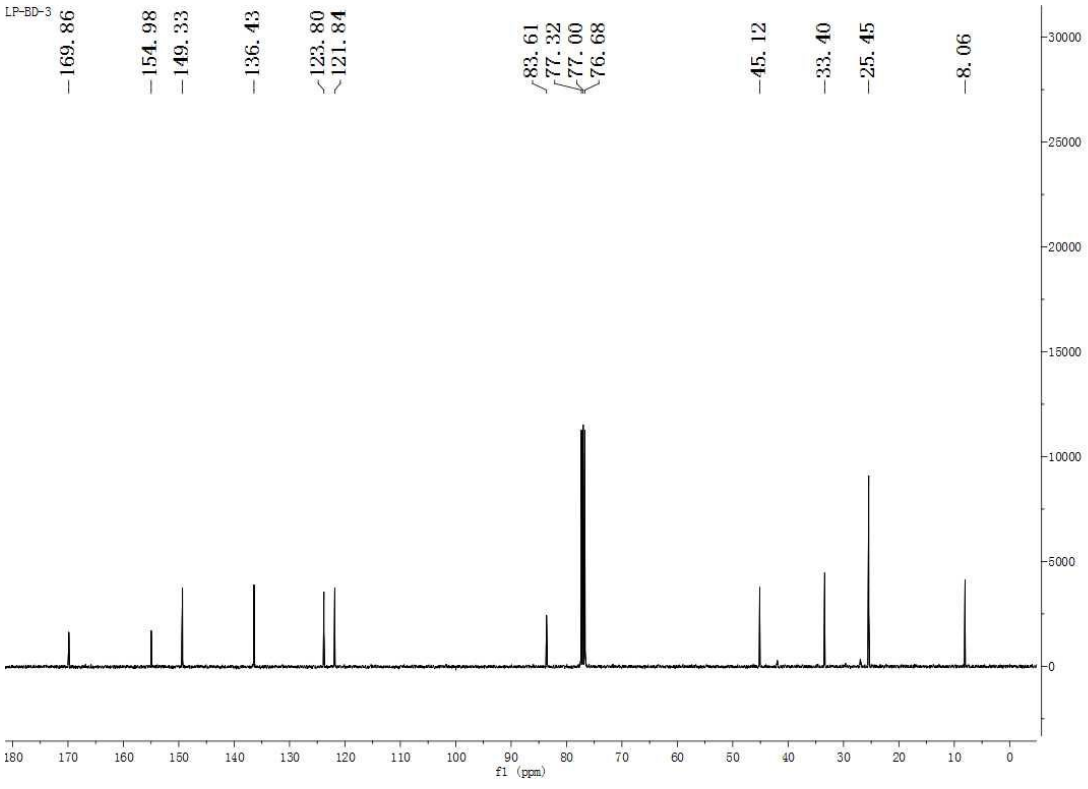
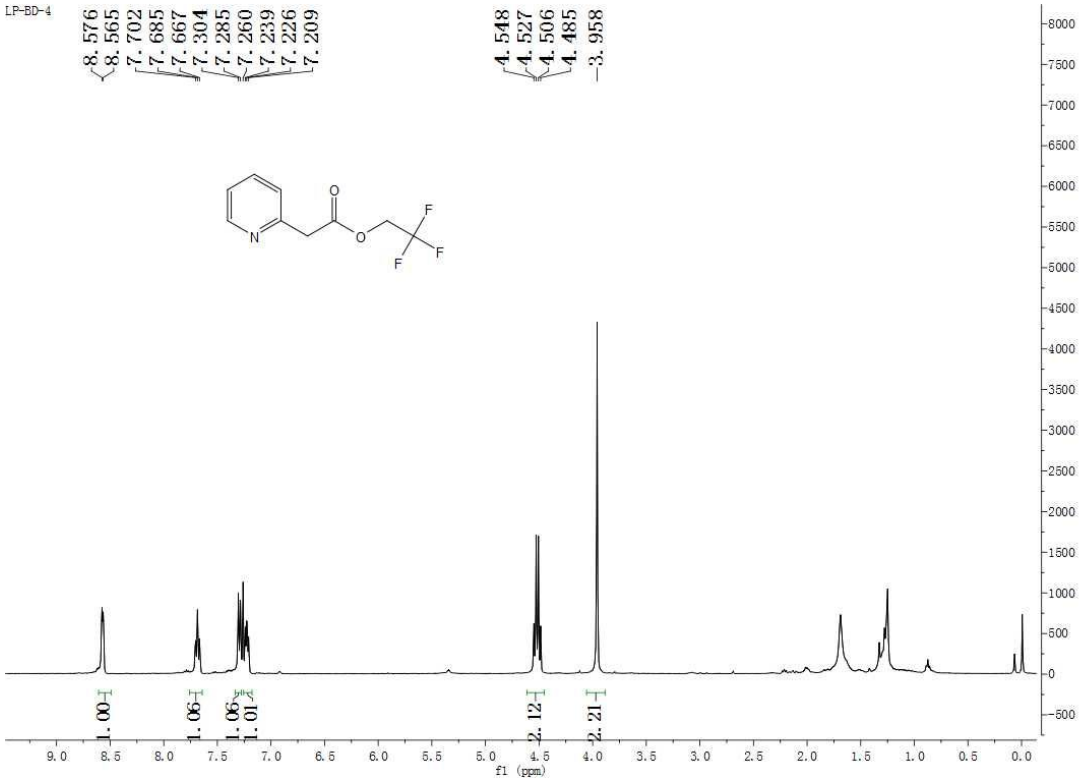
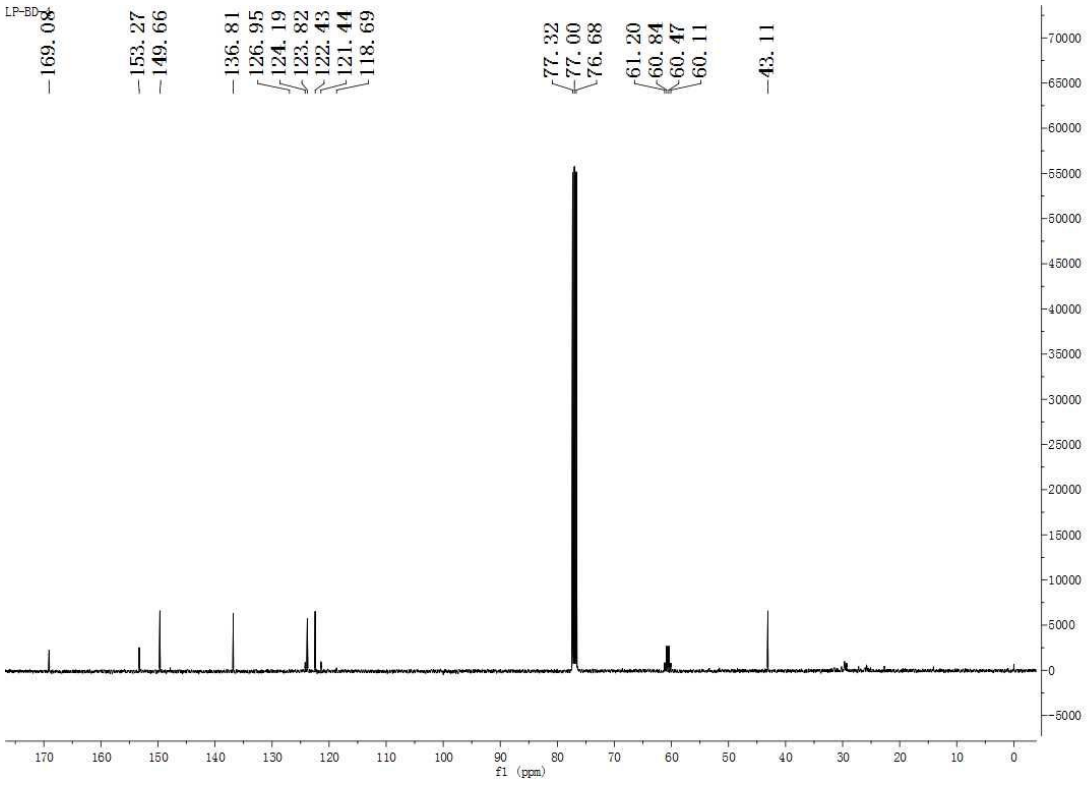


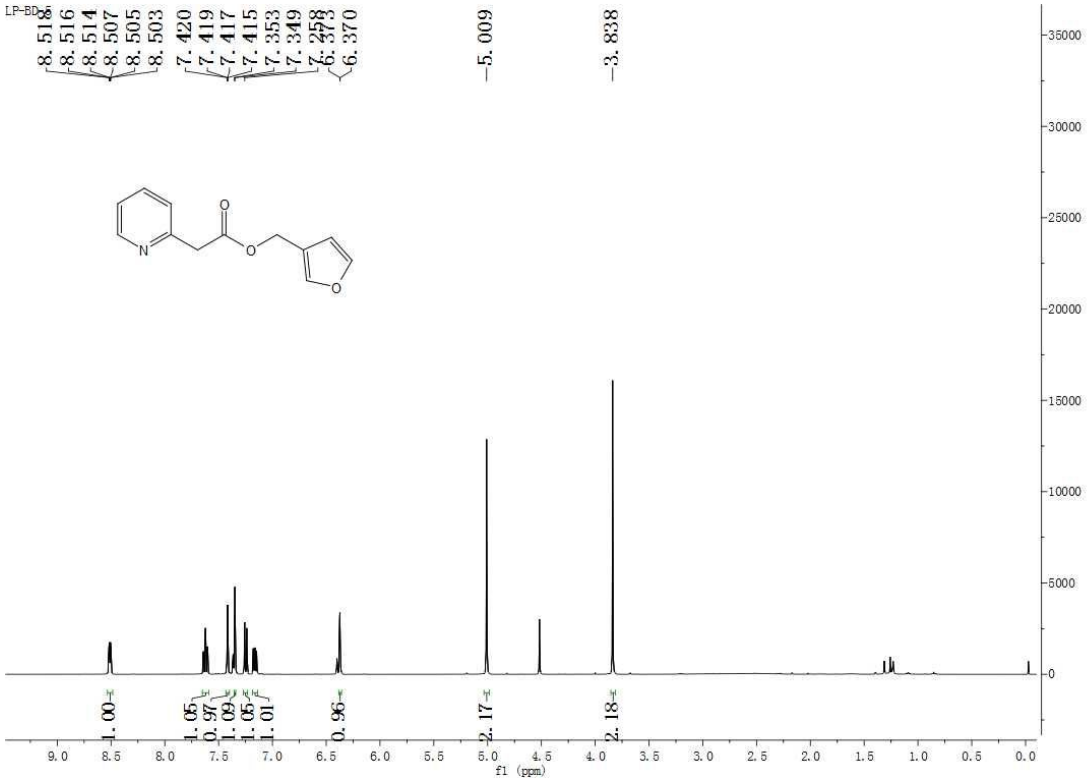


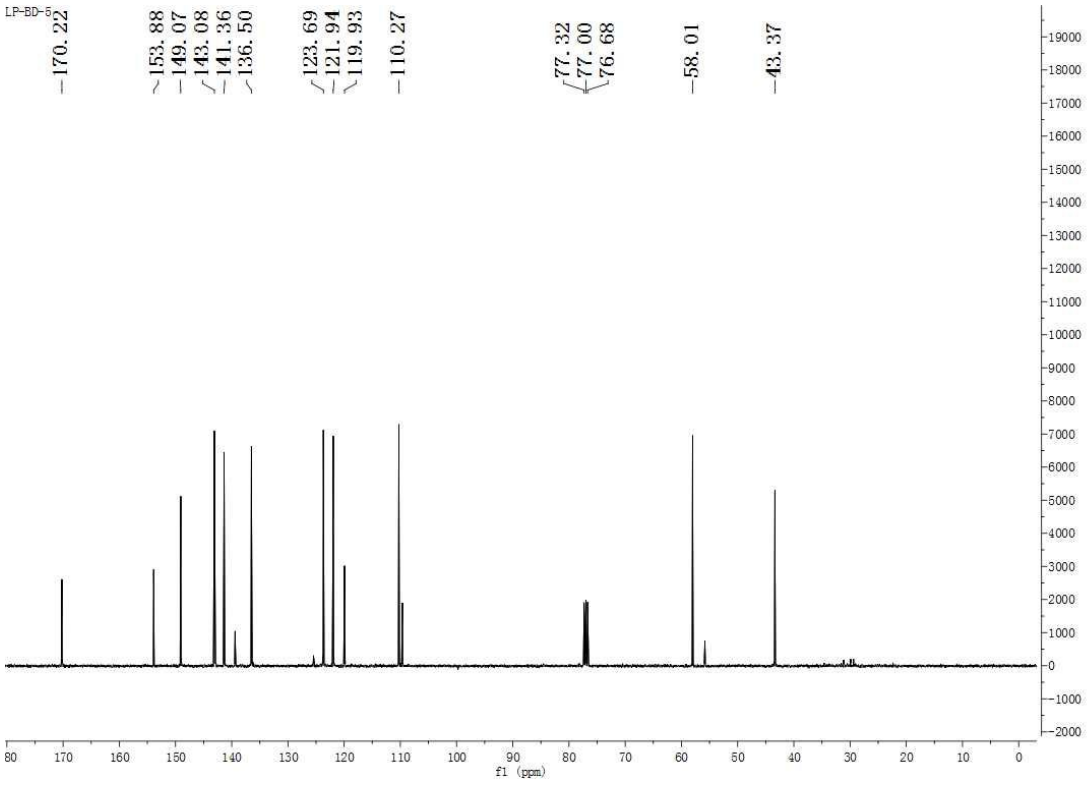
^{1}H NMR and ^{13}C NMR of 2,2,2-trifluoroethyl 2-(pyridin-2-yl)acetate (1e)





^{1}H NMR and ^{13}C NMR of furan-3-ylmethyl 2-(pyridin-2-yl)acetate (1f)





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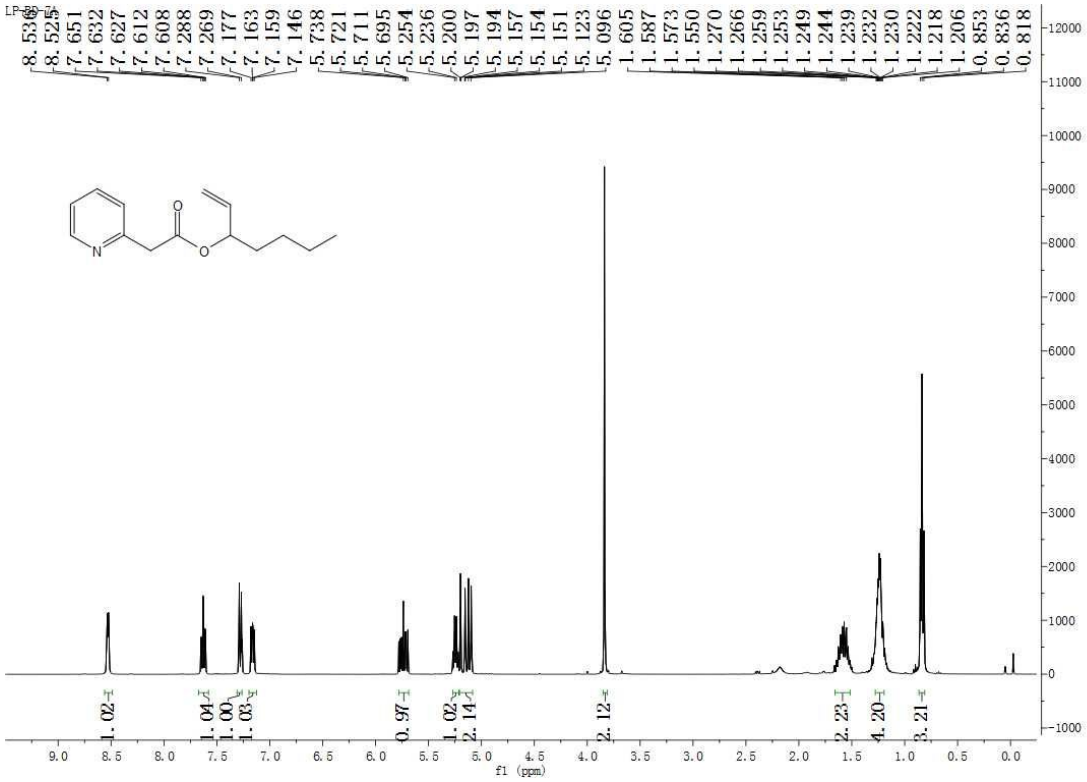
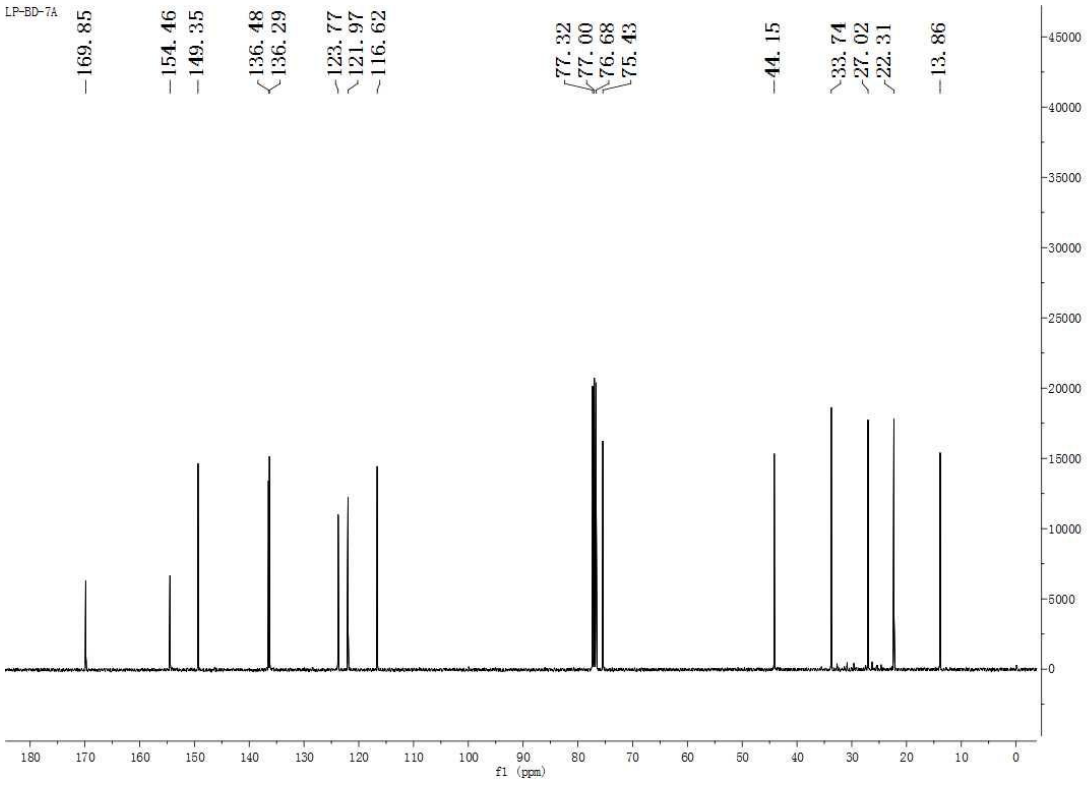
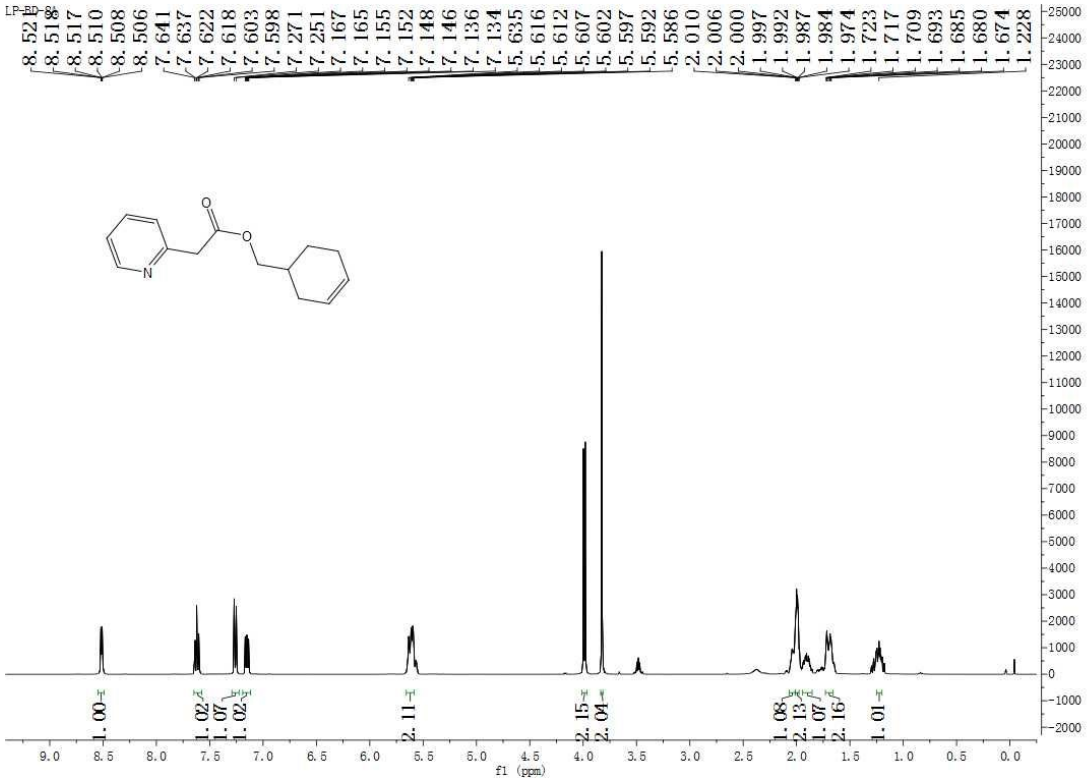
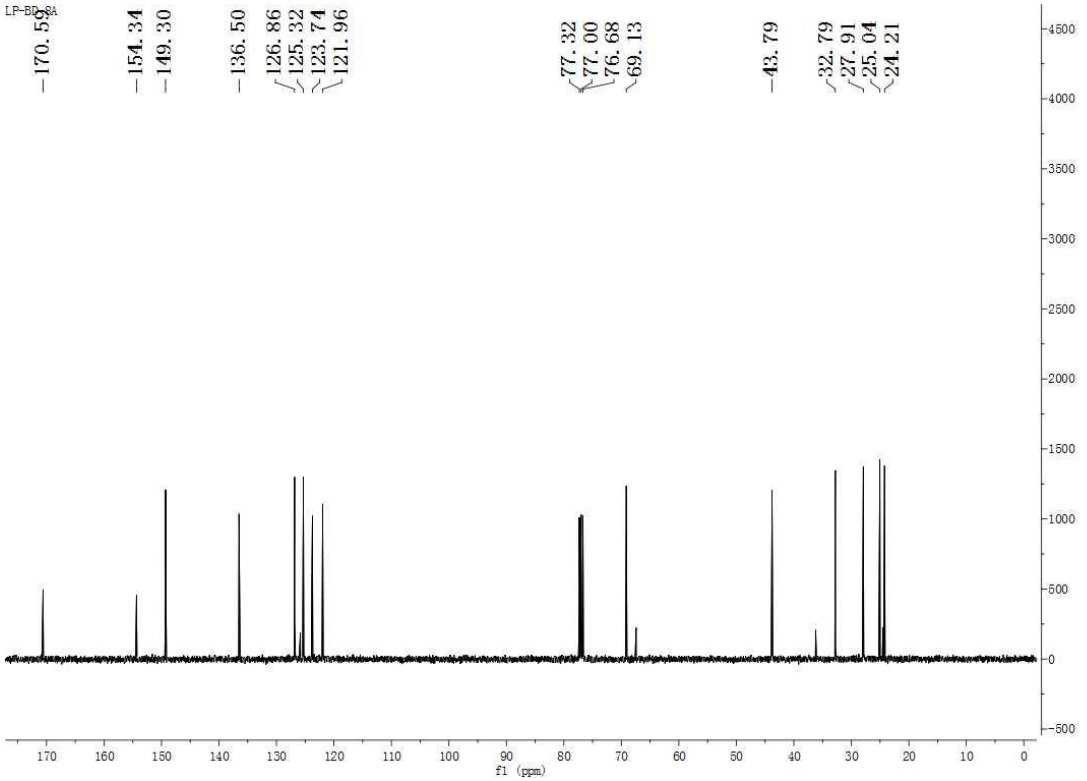


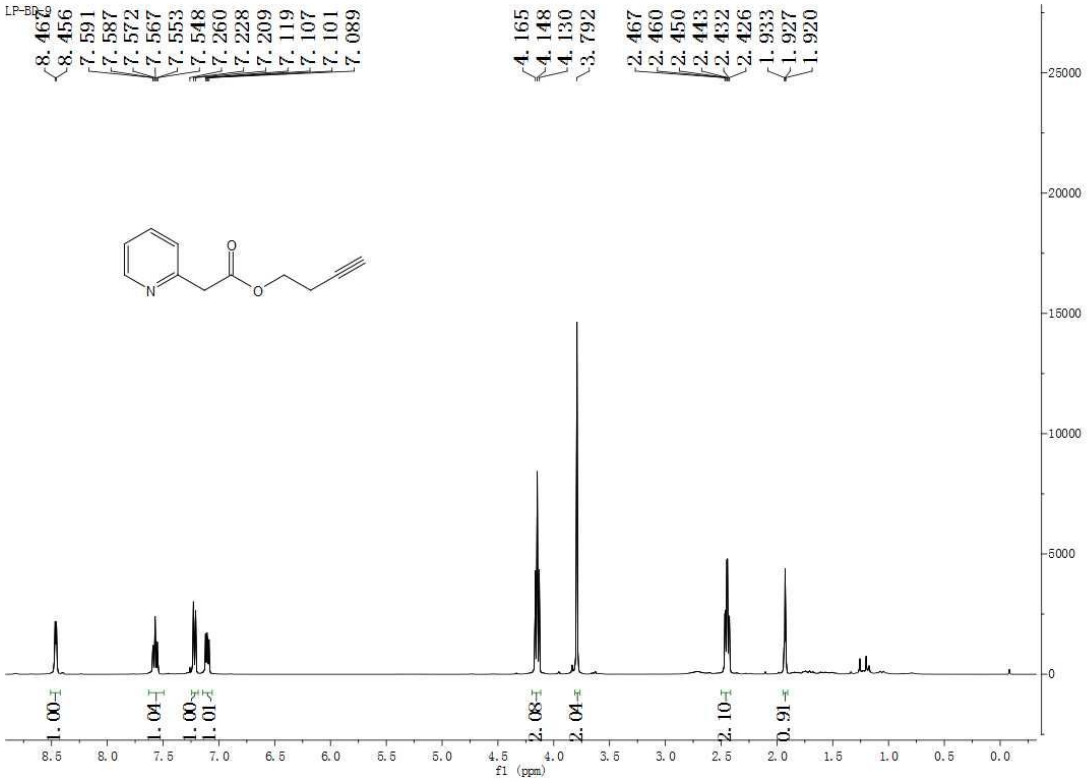


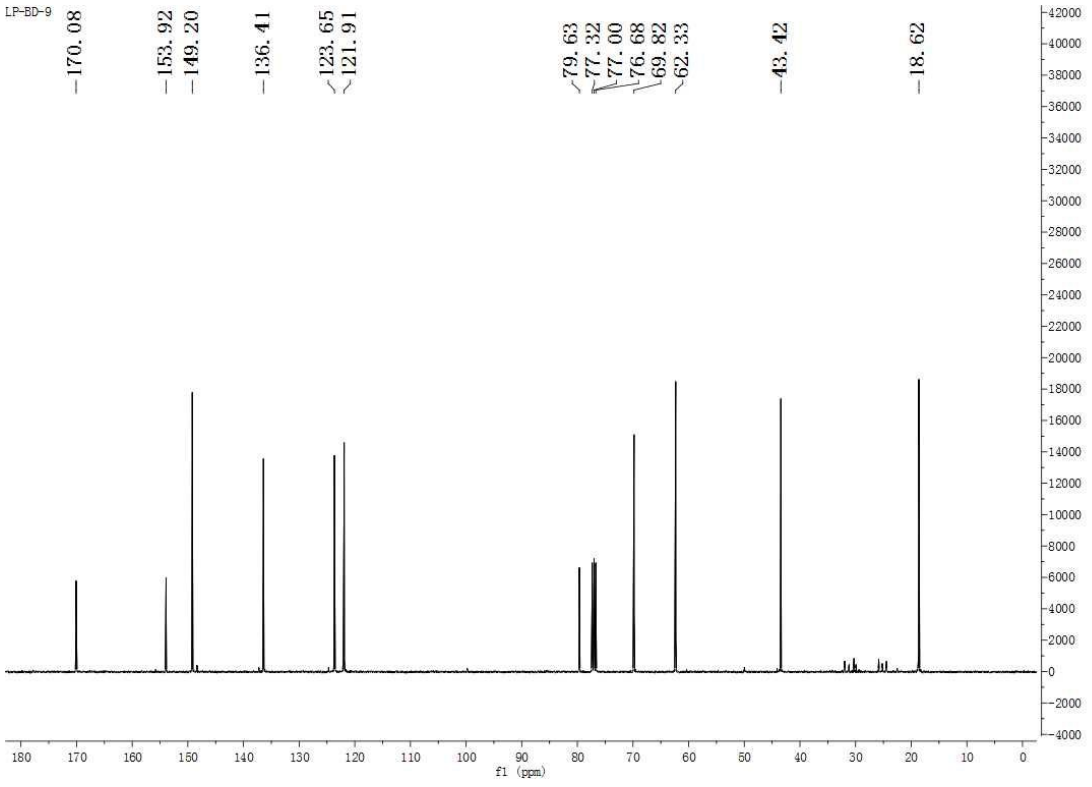
^{1}H NMR and ^{13}C NMR of cyclohex-3-en-1-yl 2-(pyridin-2-yl)acetate (1i)



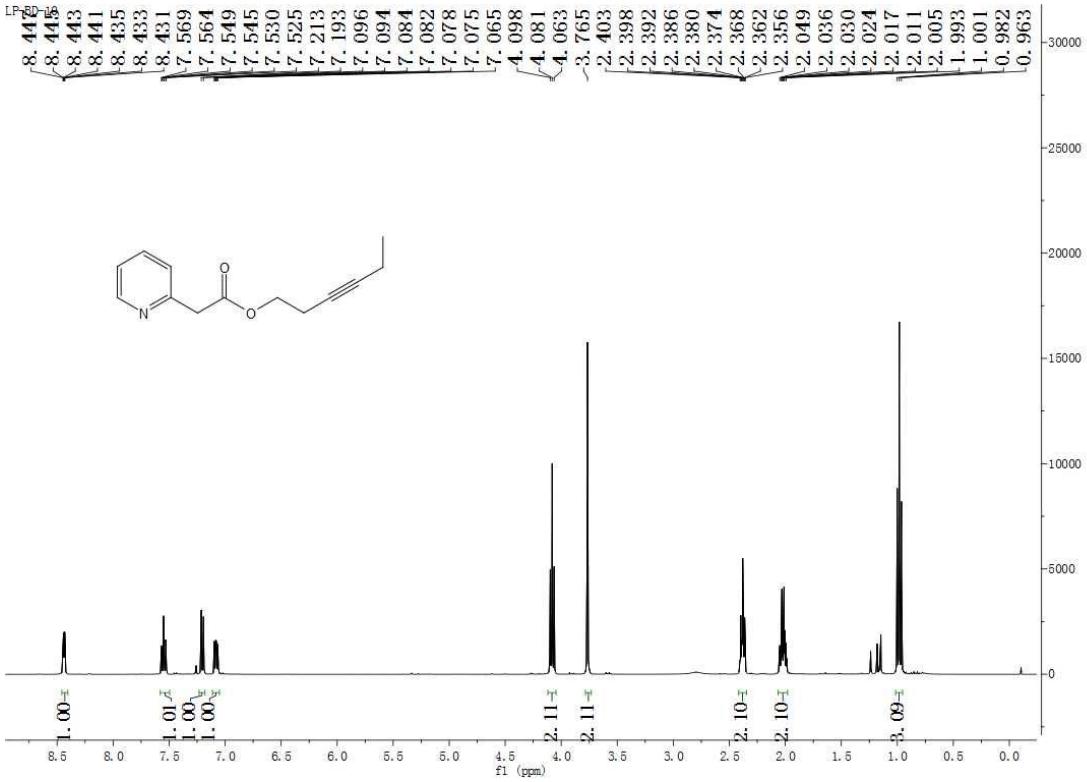


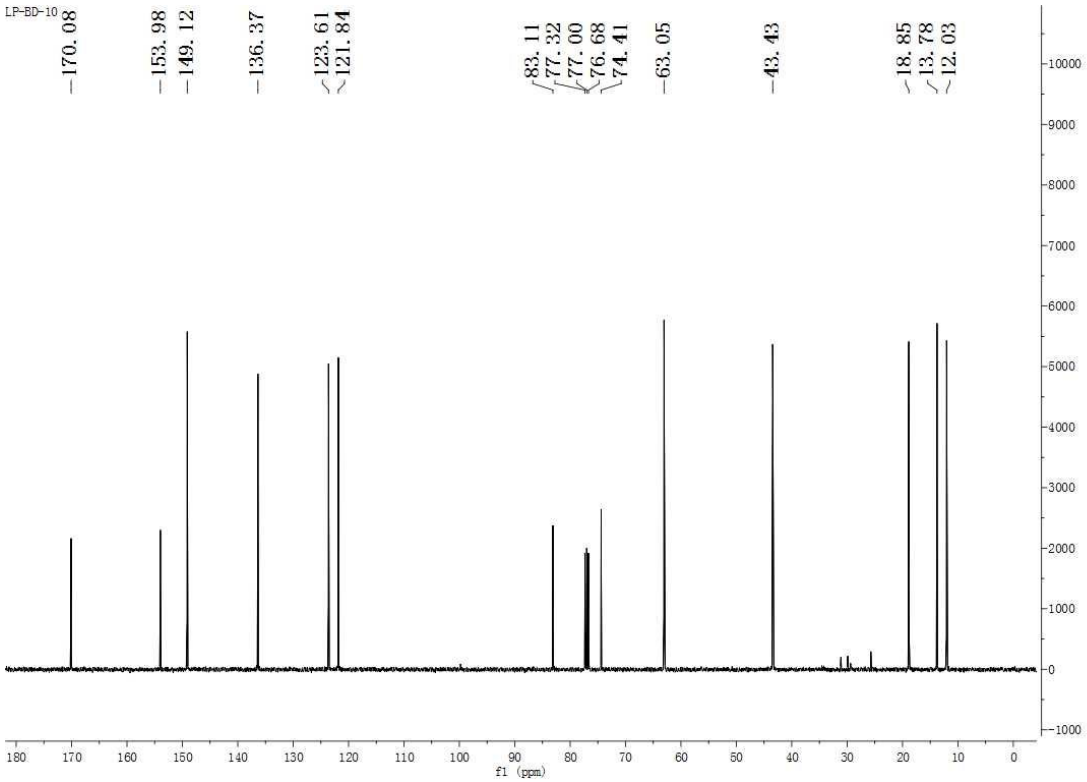
^{1}H NMR and ^{13}C NMR of but-3-yn-1-yl 2-(pyridin-2-yl)acetate (1j)



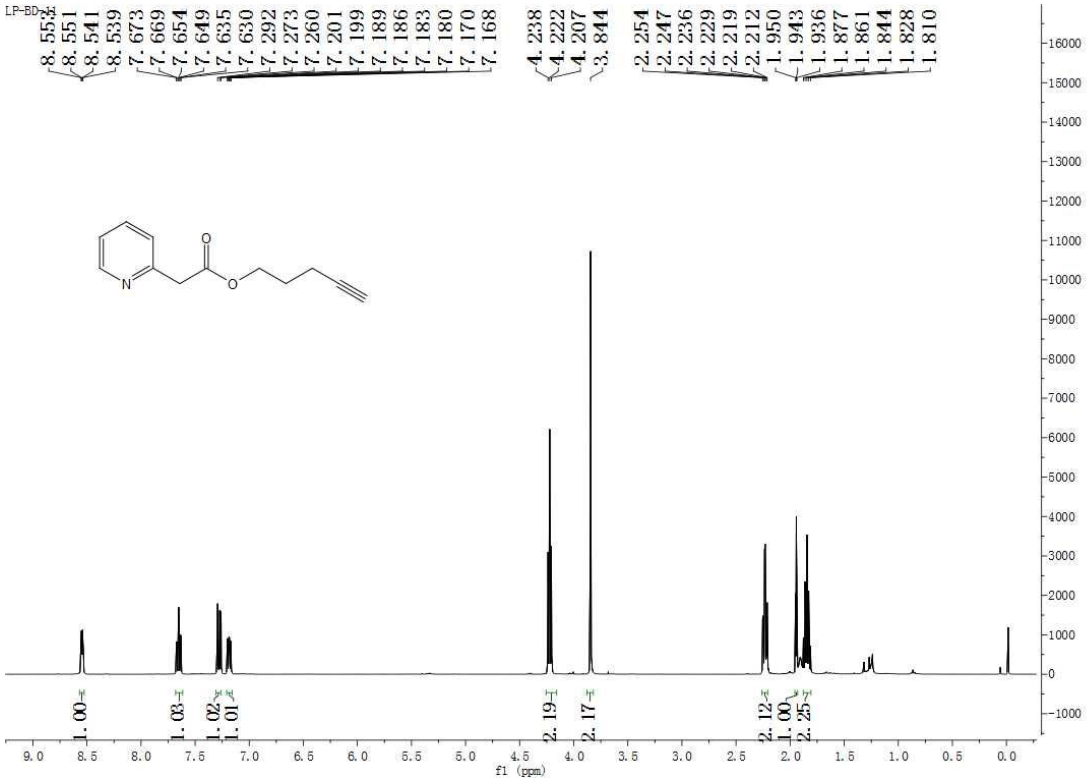


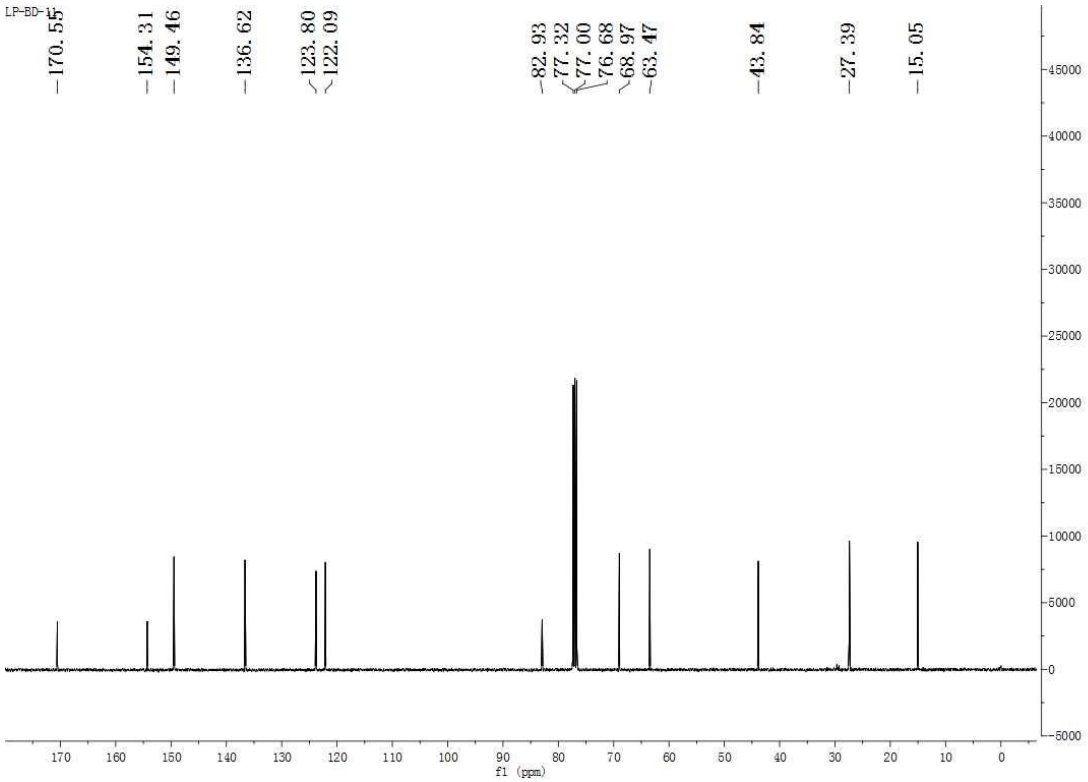
^{1}H NMR and ^{13}C NMR of hex-3-yn-1-yl 2-(pyridin-2-yl)acetate (1k)



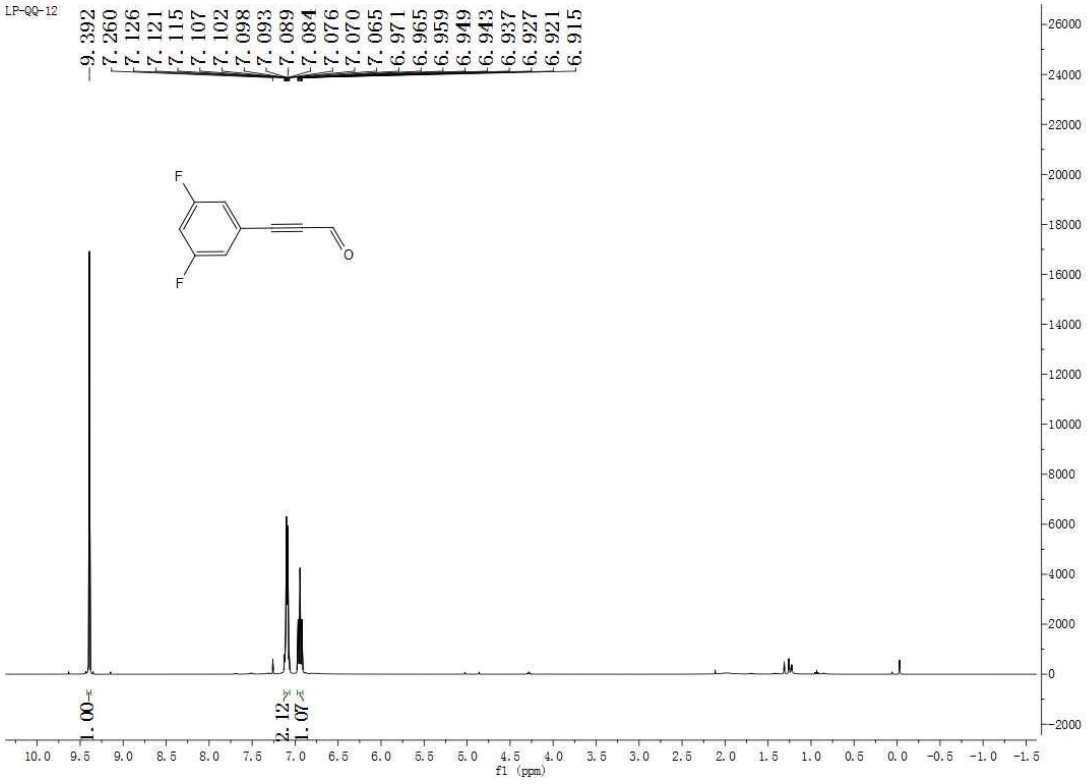


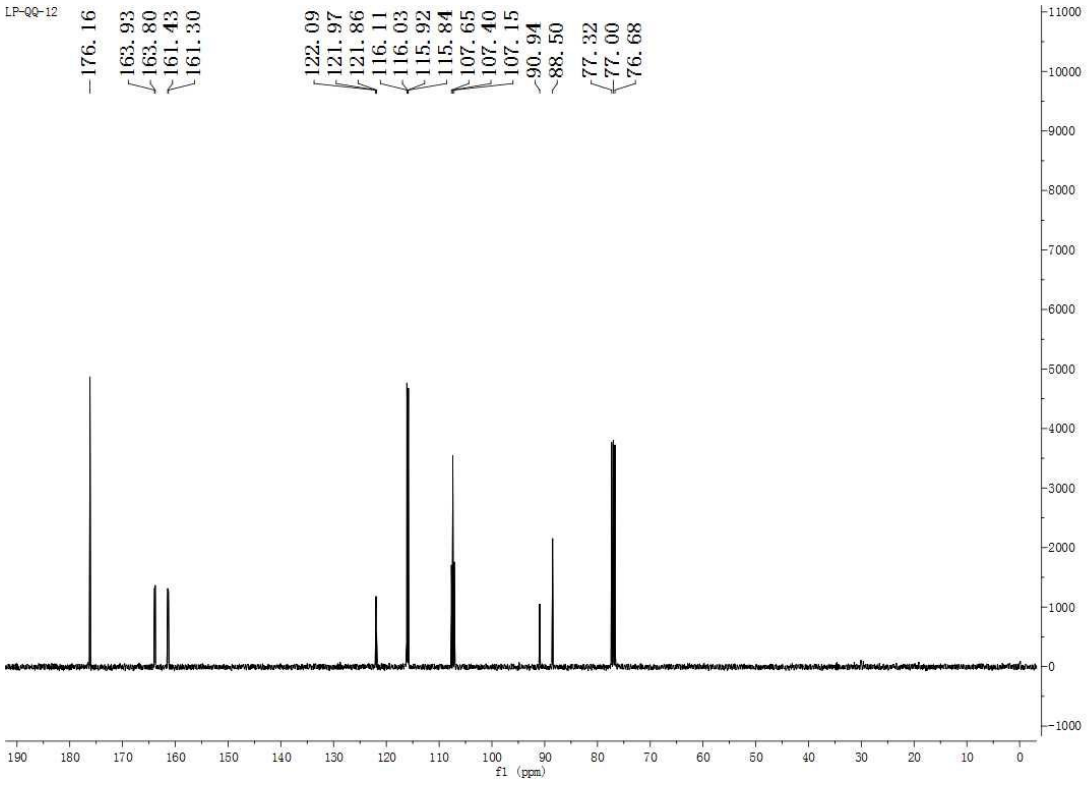
^{1}H NMR and ^{13}C NMR of pent-4-yn-1-yl 2-(pyridin-2-yl)acetate (1l)



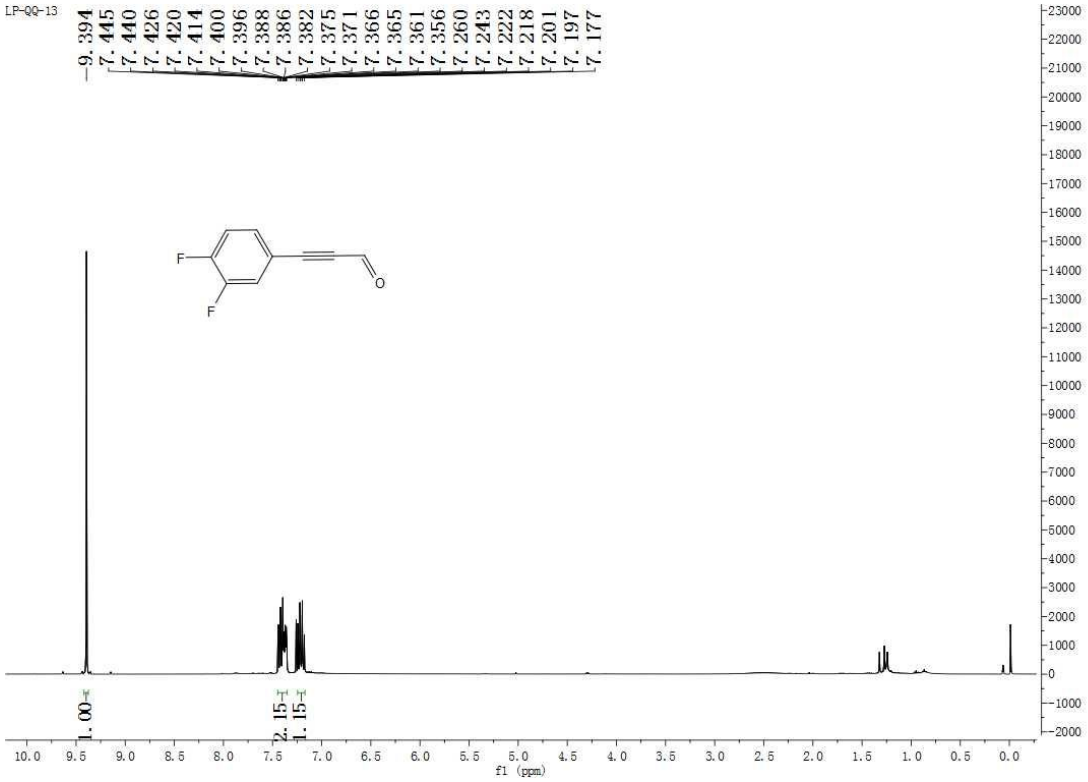


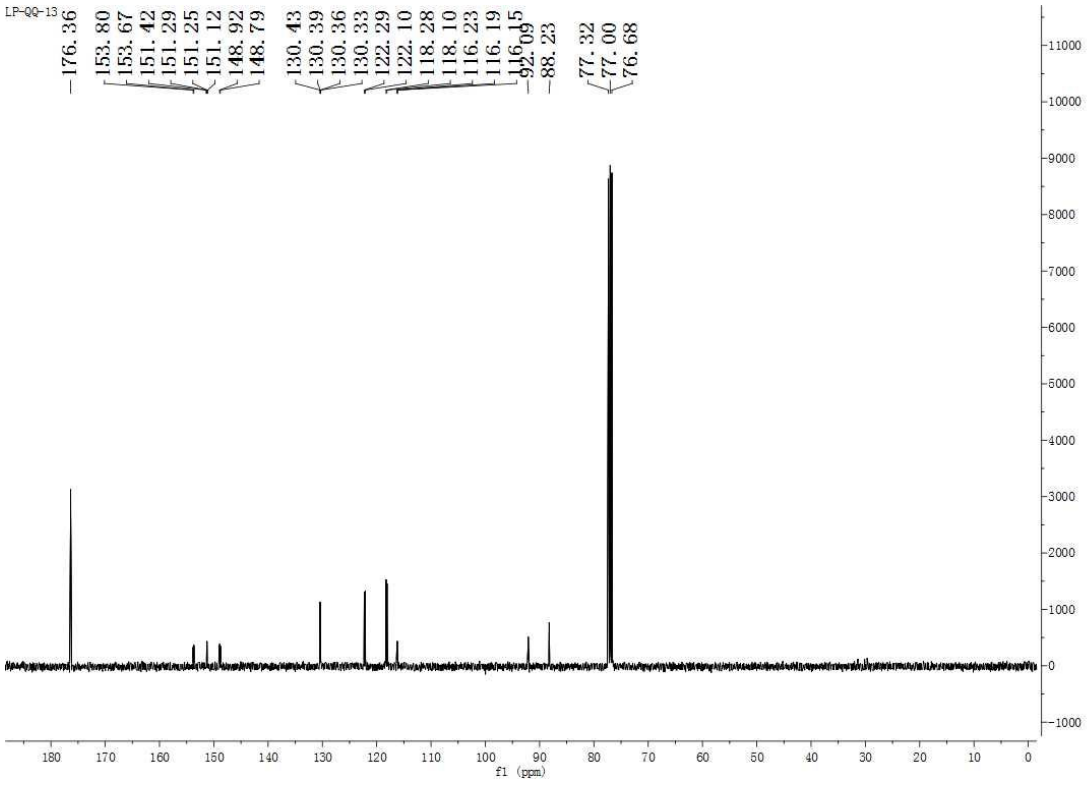
^{1}H NMR and ^{13}C NMR of 3-(3,5-difluorophenyl)propiolaldehyde (2m)



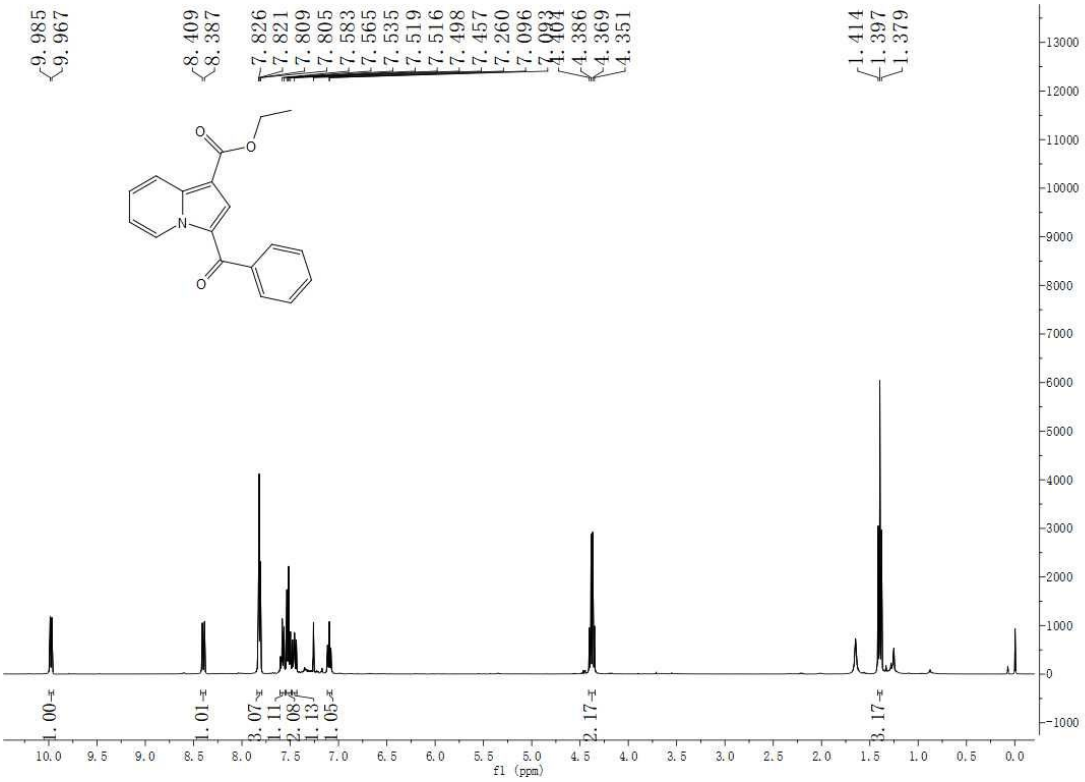


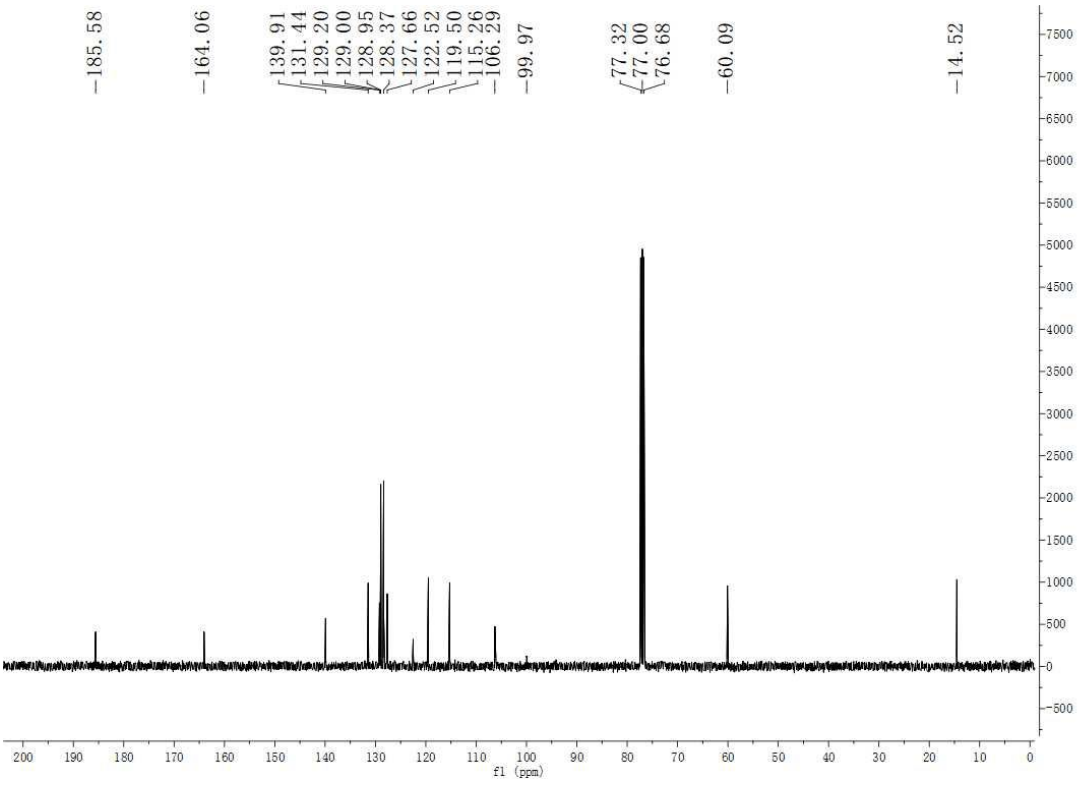
^{1}H NMR and ^{13}C NMR of 3-(3,4-difluorophenyl)propiolaldehyde (2n)



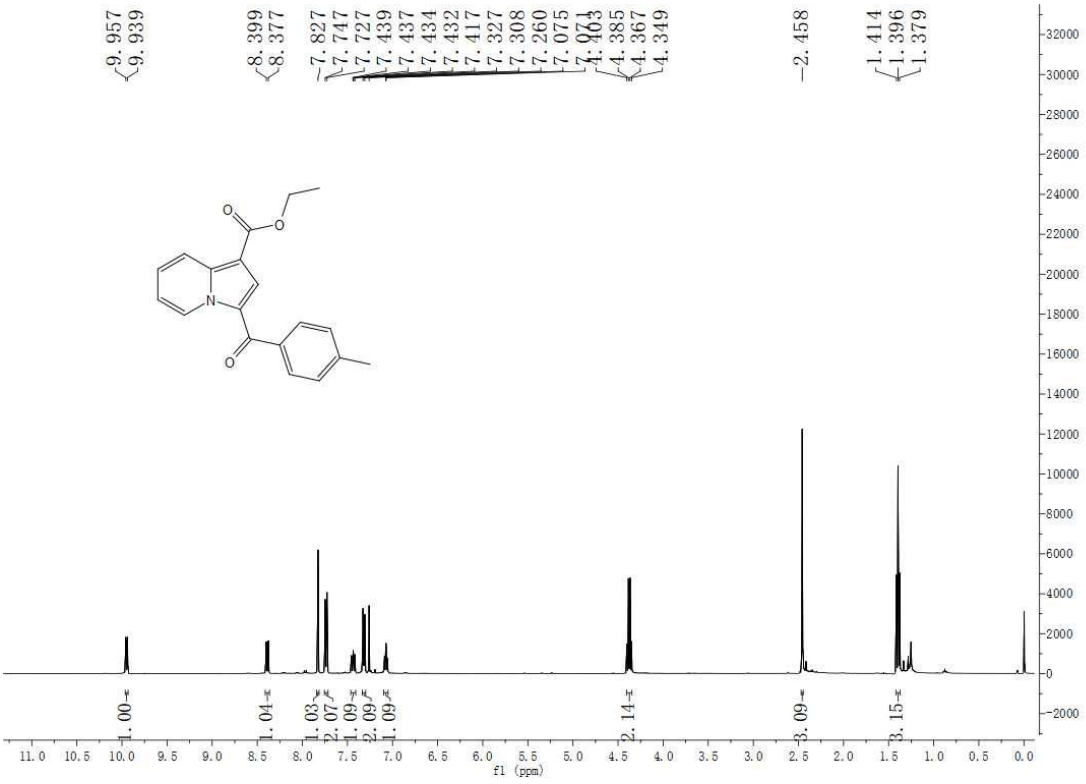


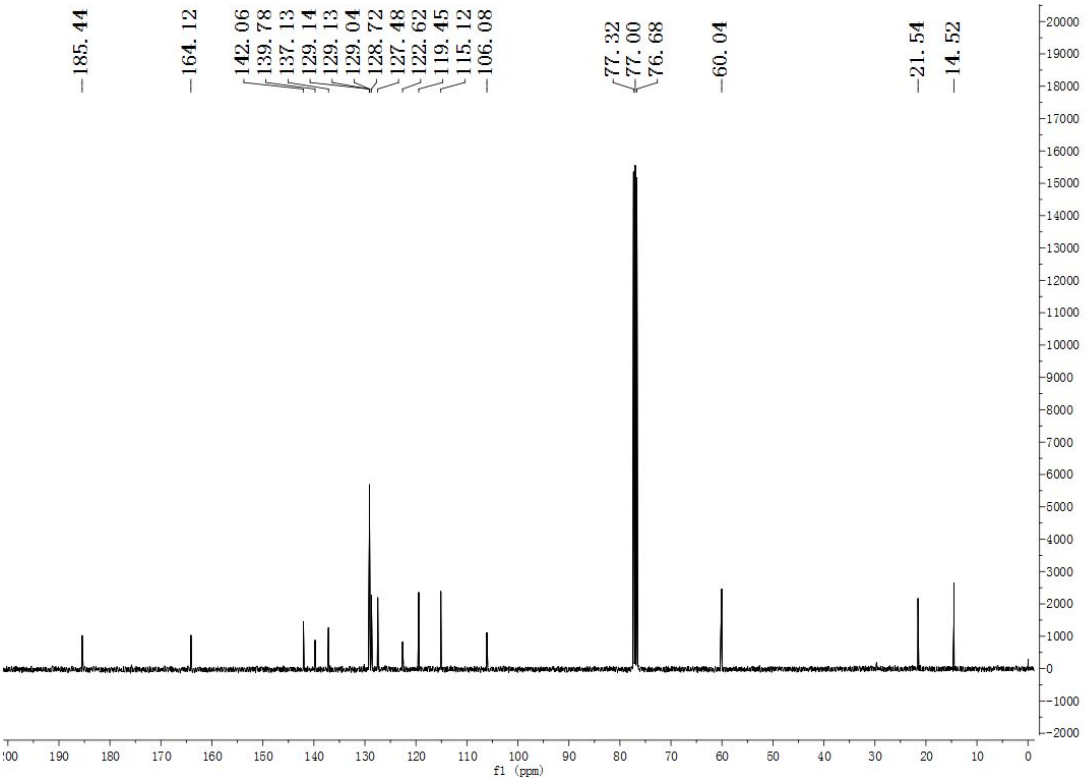
^{1}H NMR and ^{13}C NMR of ethyl 3-benzoylindolizine-1-carboxylate (3a)



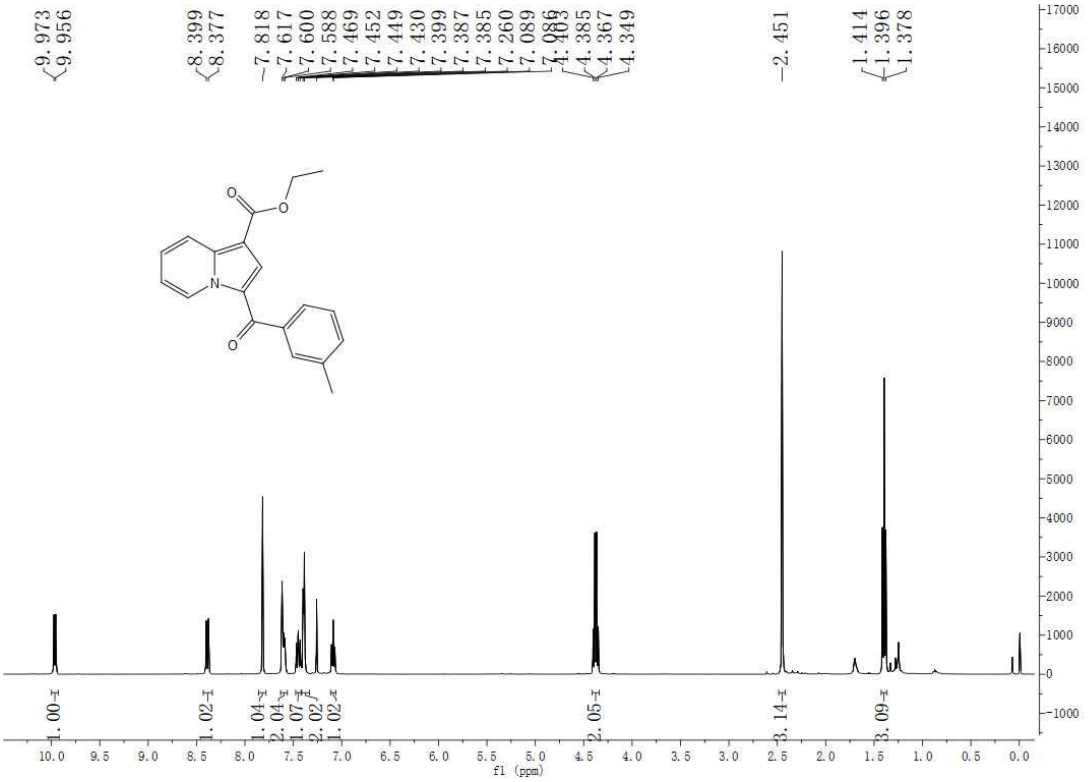


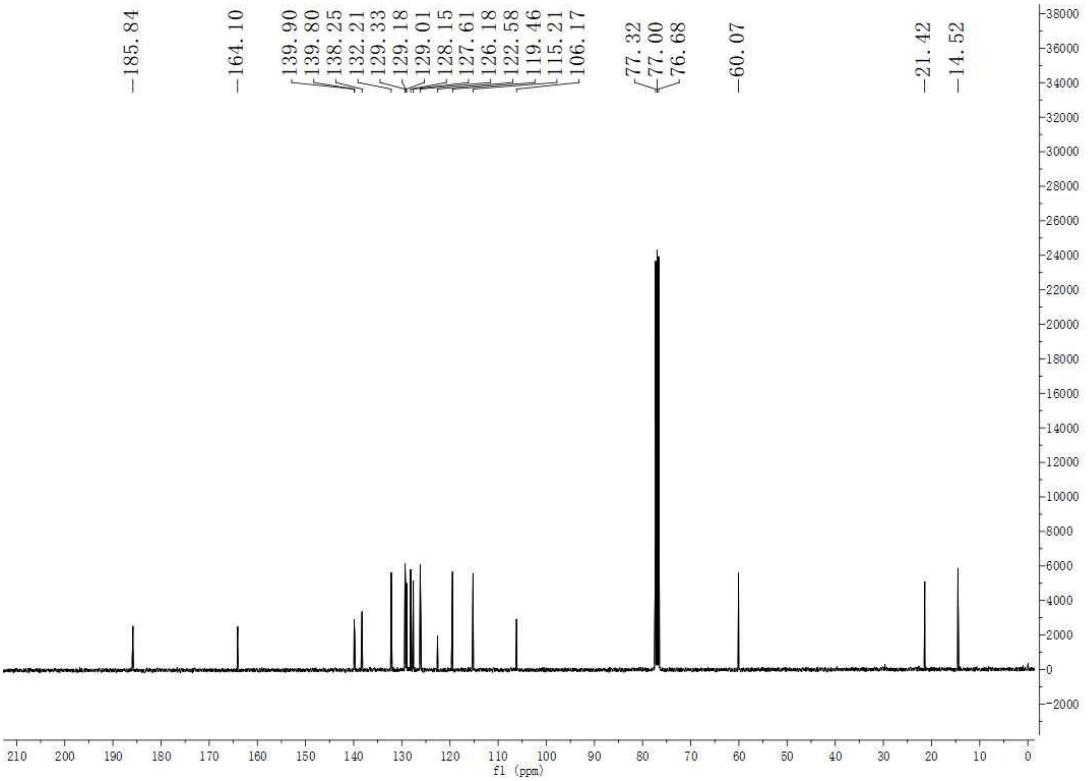
^{1}H NMR and ^{13}C NMR of ethyl 3-(4-methylbenzoyl)indolizine-1-carboxylate (3b)



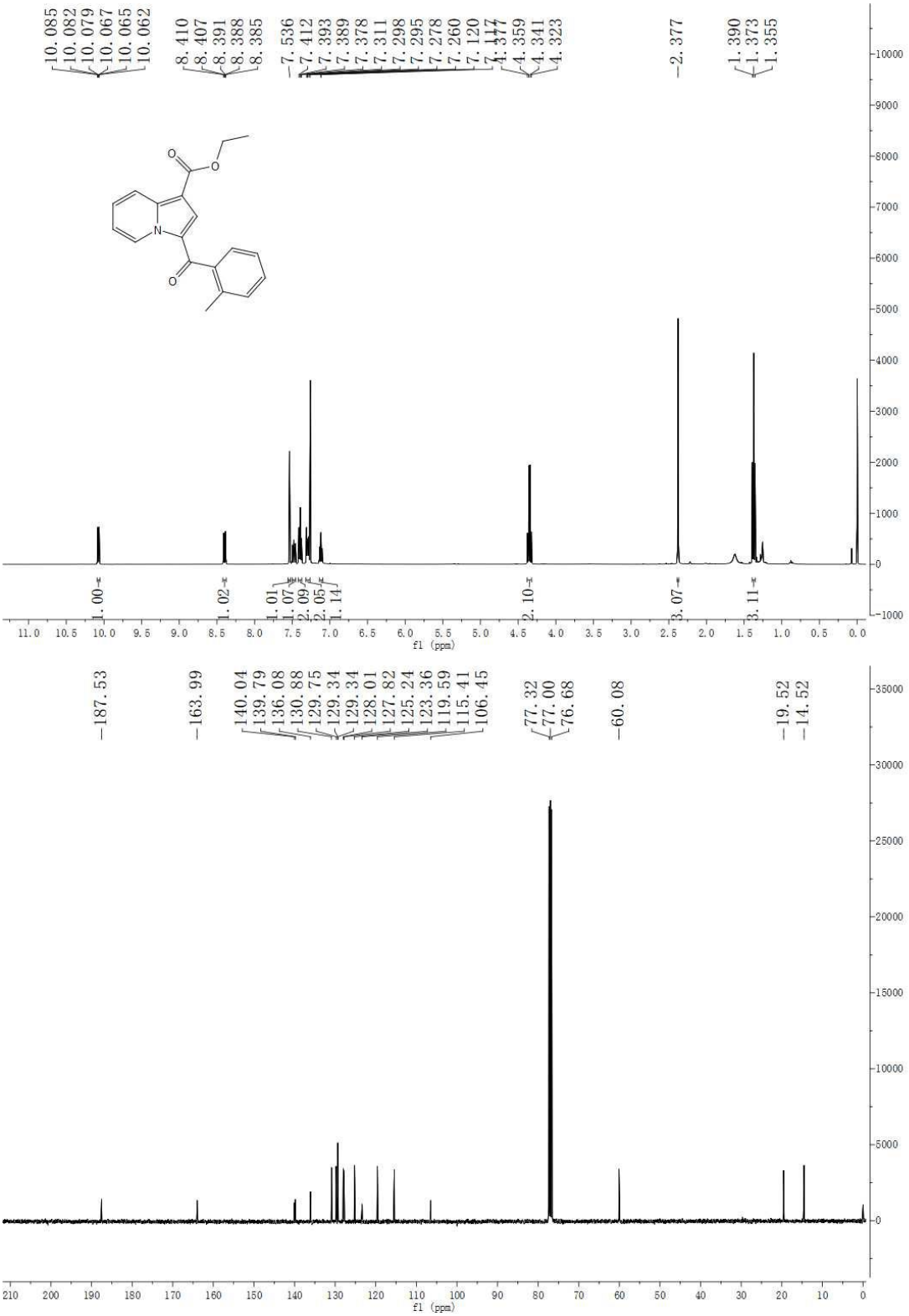


^{1}H NMR and ^{13}C NMR of ethyl 3-(3-methylbenzoyl)indolizine-1-carboxylate (3c)

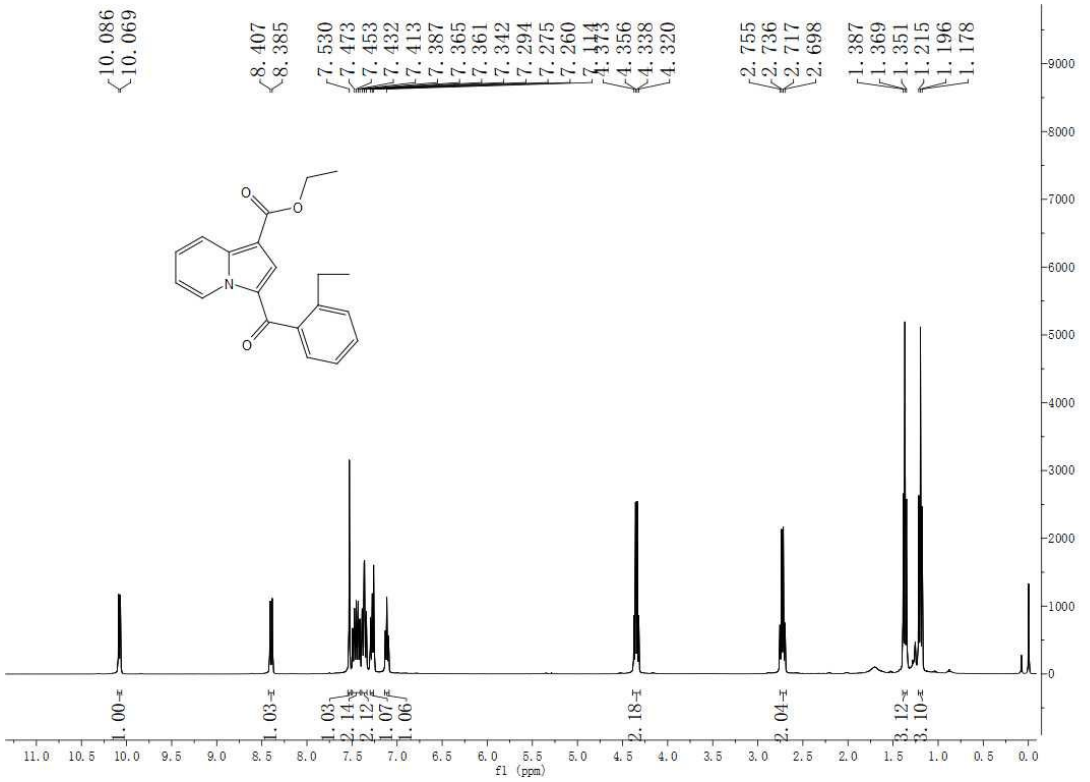


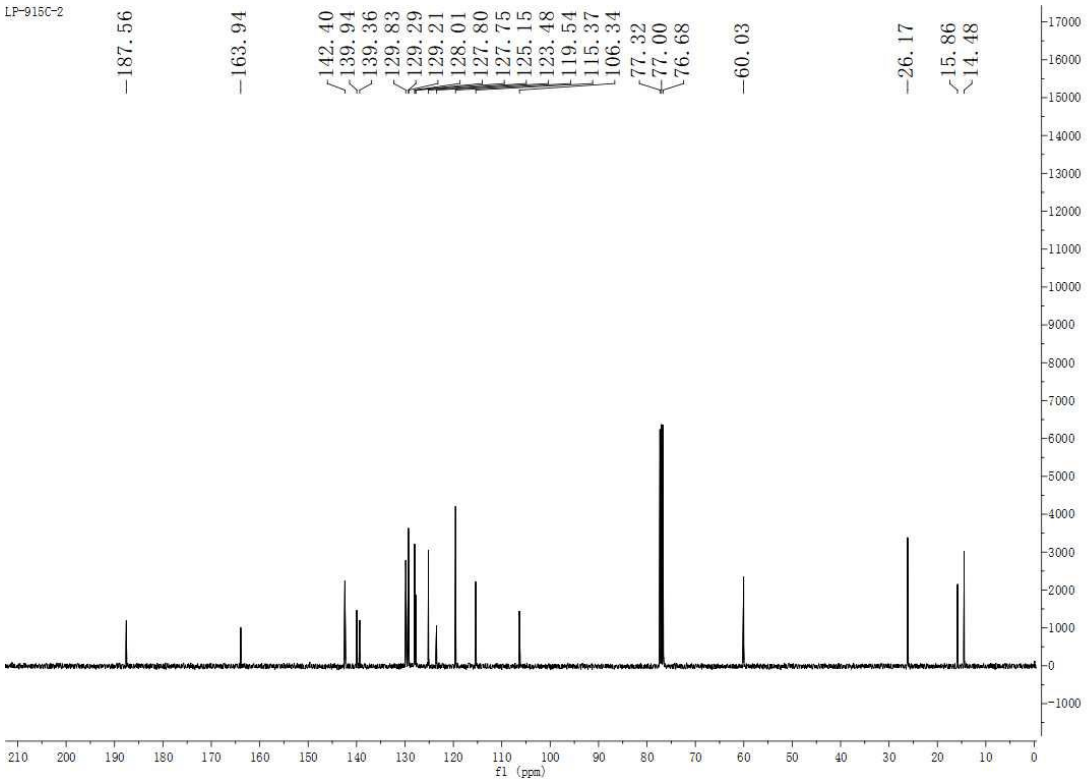


^{1}H NMR and ^{13}C NMR of ethyl 3-(2-methylbenzoyl)indolizine-1-carboxylate (3d)

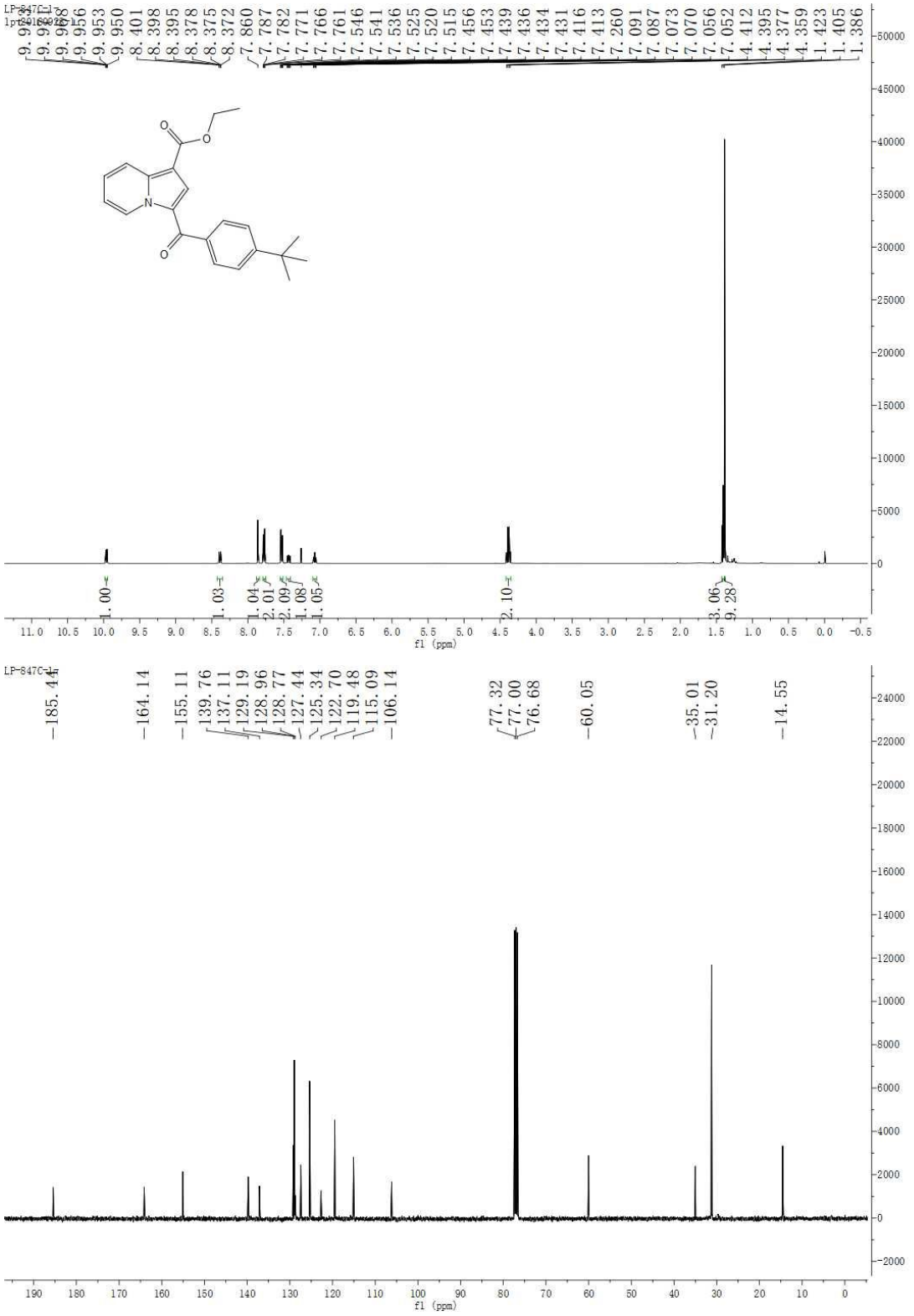


^{1}H NMR and ^{13}C NMR of ethyl 3-(2-ethylbenzoyl)indolizine-1-carboxylate (3e)

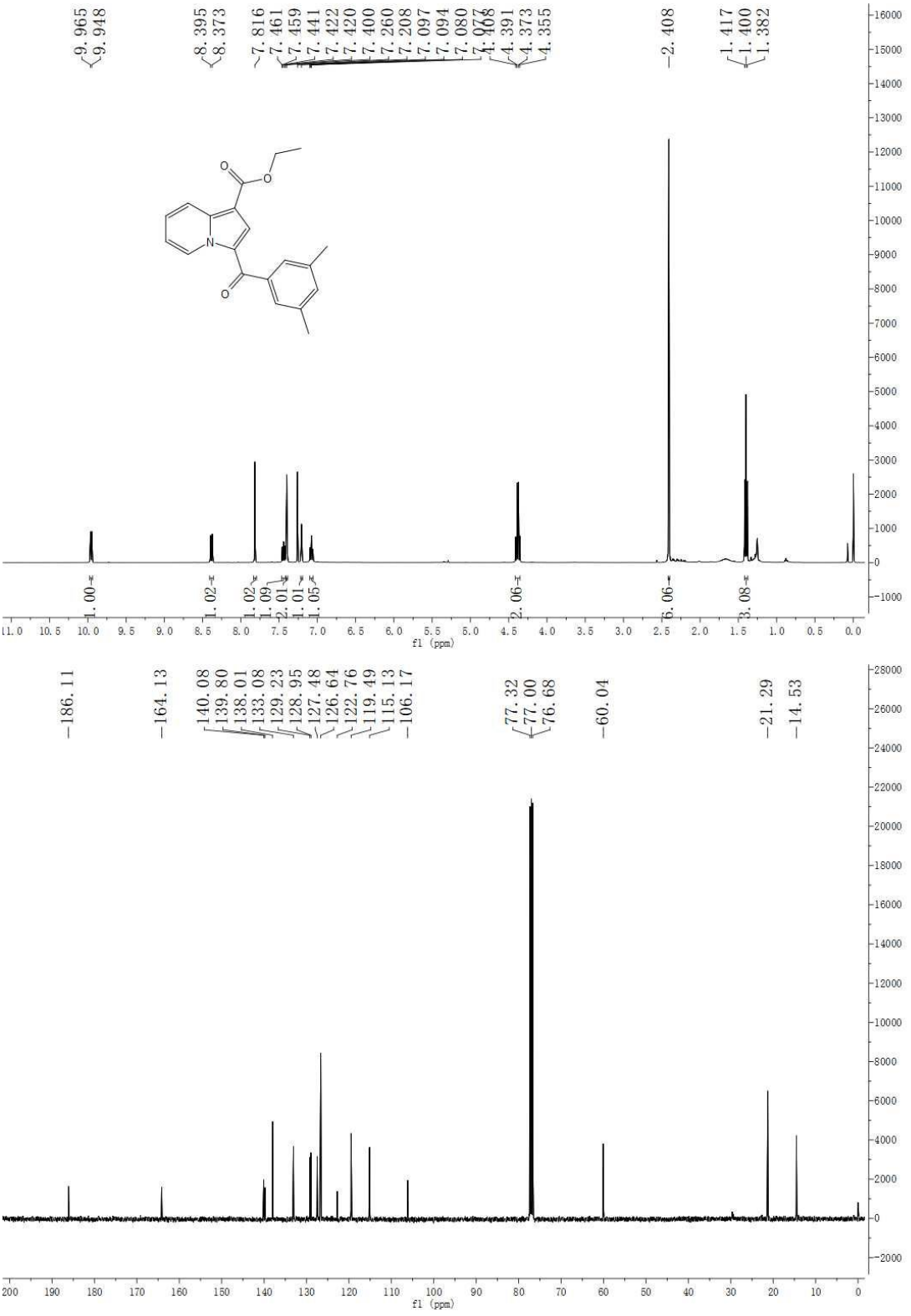




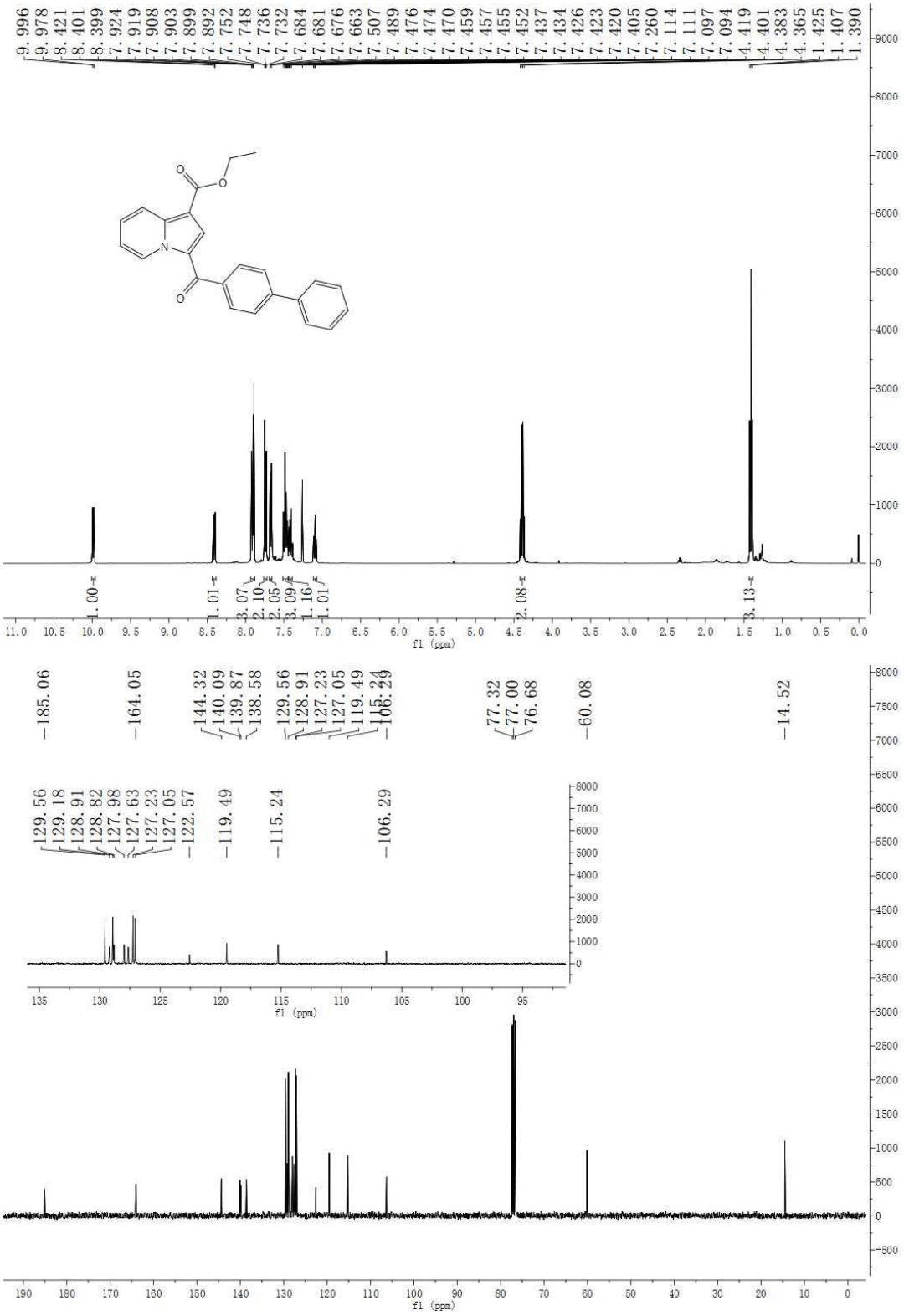
^{1}H NMR and ^{13}C NMR of ethyl 3-(4-(*tert*-butyl)benzoyl)indolizine-1-carboxylate (3f)



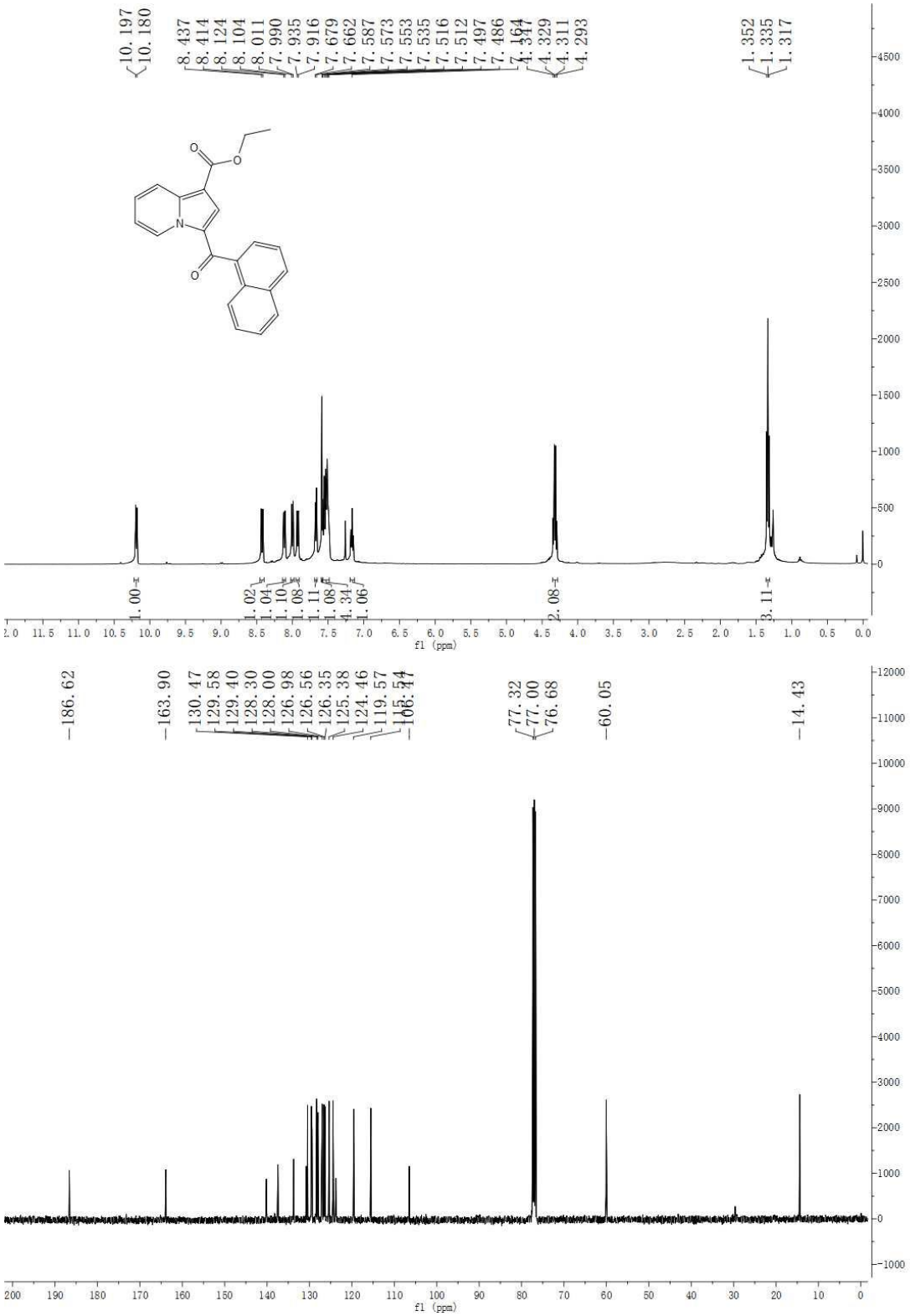
^{1}H NMR and ^{13}C NMR of ethyl 3-(3,5-dimethylbenzoyl)indolizine-1-carboxylate (3g)



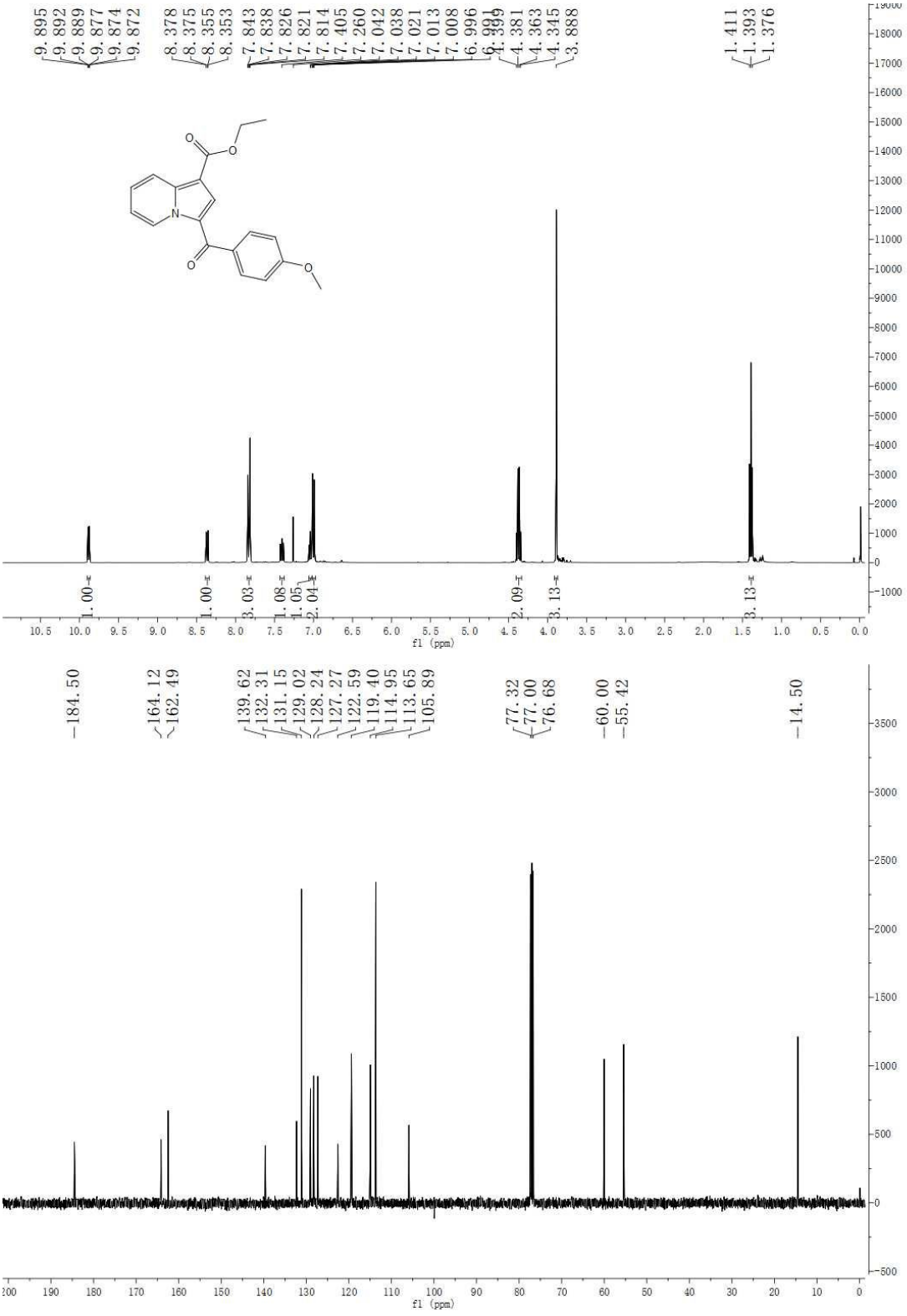
^{1}H NMR and ^{13}C NMR of ethyl 3-([1,1'-biphenyl]-4-carbonyl)indolizine-1-carboxylate (3h)



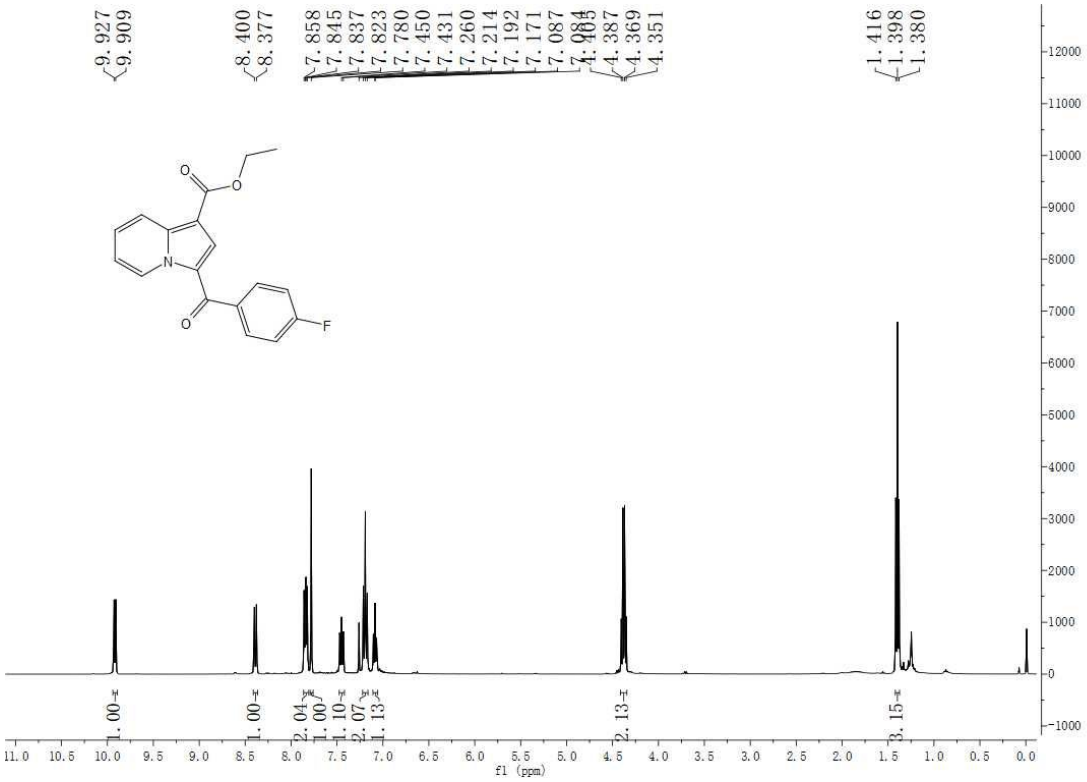
^{1}H NMR and ^{13}C NMR of ethyl 3-(1-naphthoyl)indolizine-1-carboxylate (3i)

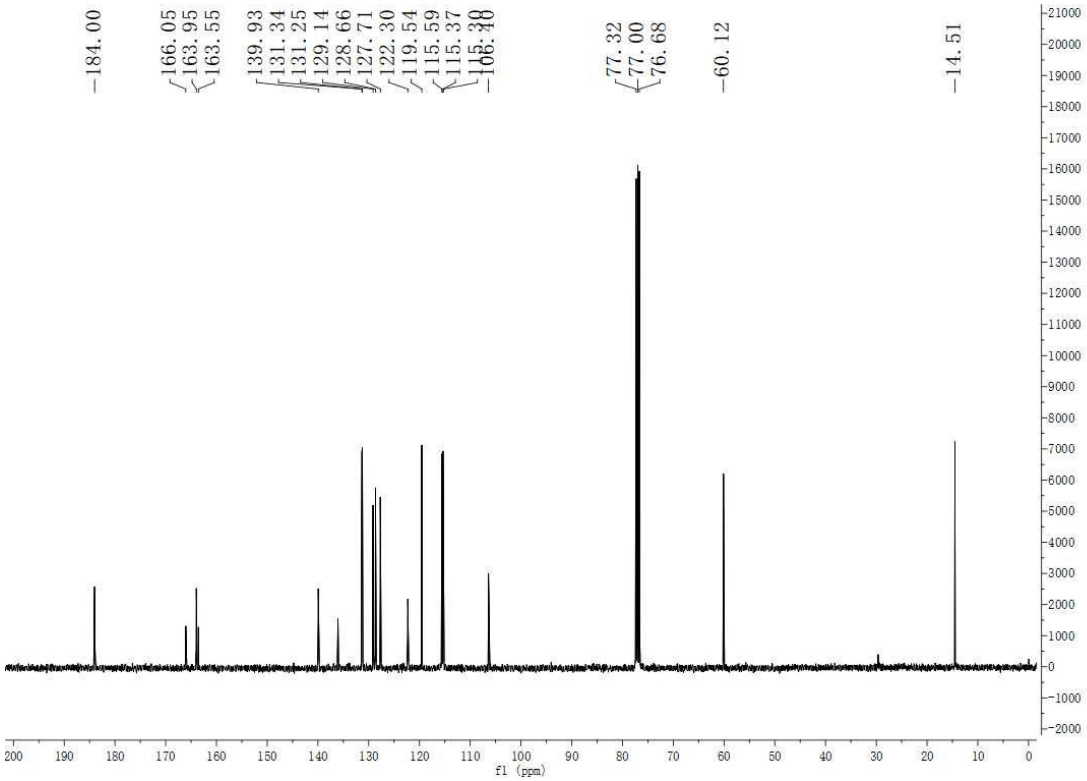


^{1}H NMR and ^{13}C NMR of ethyl 3-(4-methoxybenzoyl)indolizine-1-carboxylate (3j)

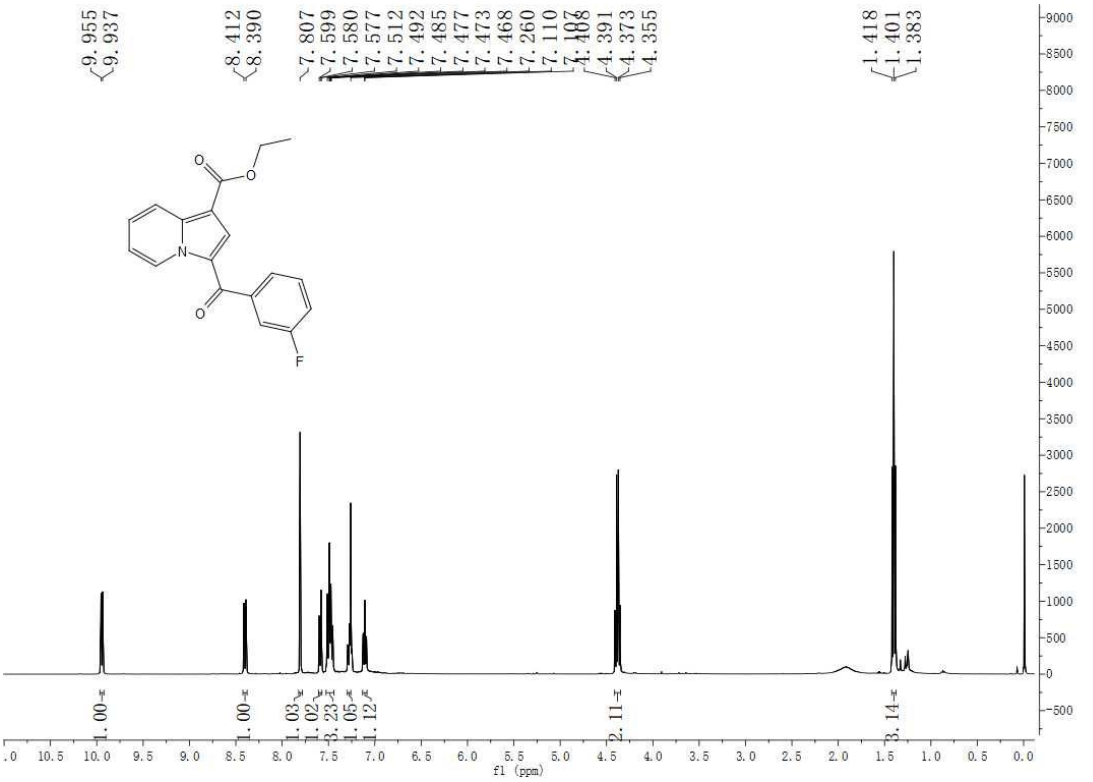


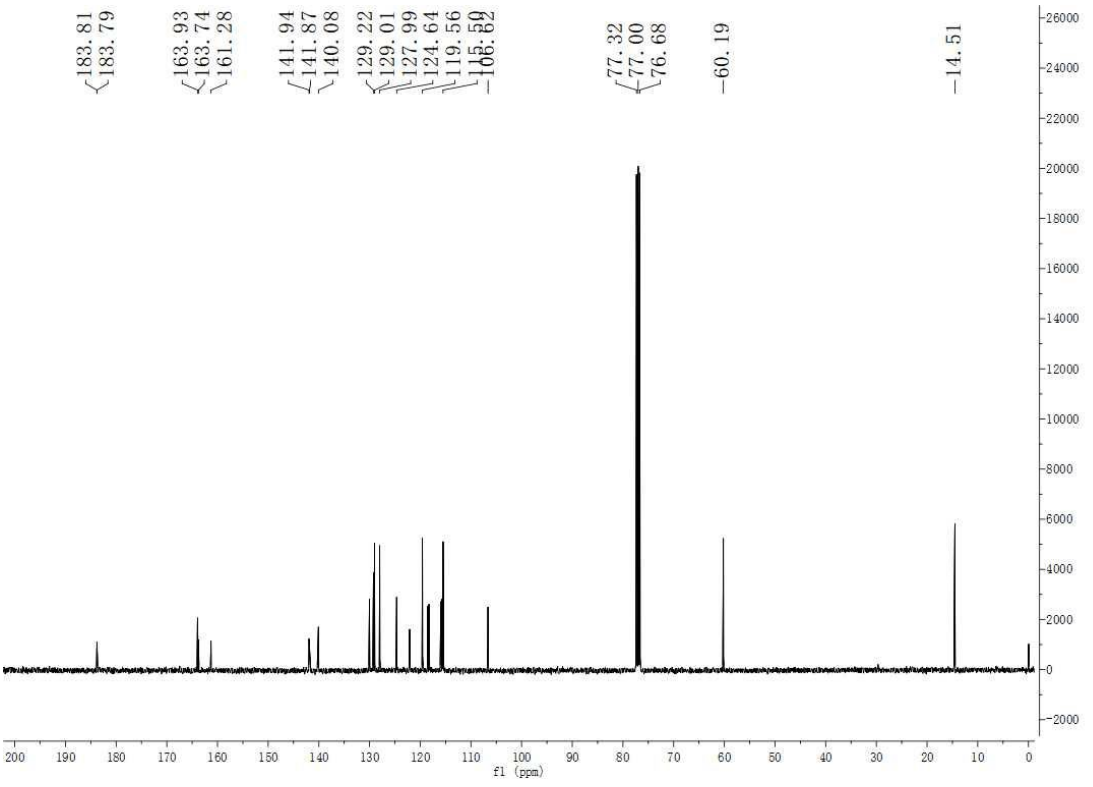
^{1}H NMR and ^{13}C NMR of ethyl 3-(4-fluorobenzoyl)indolizine-1-carboxylate (3k)



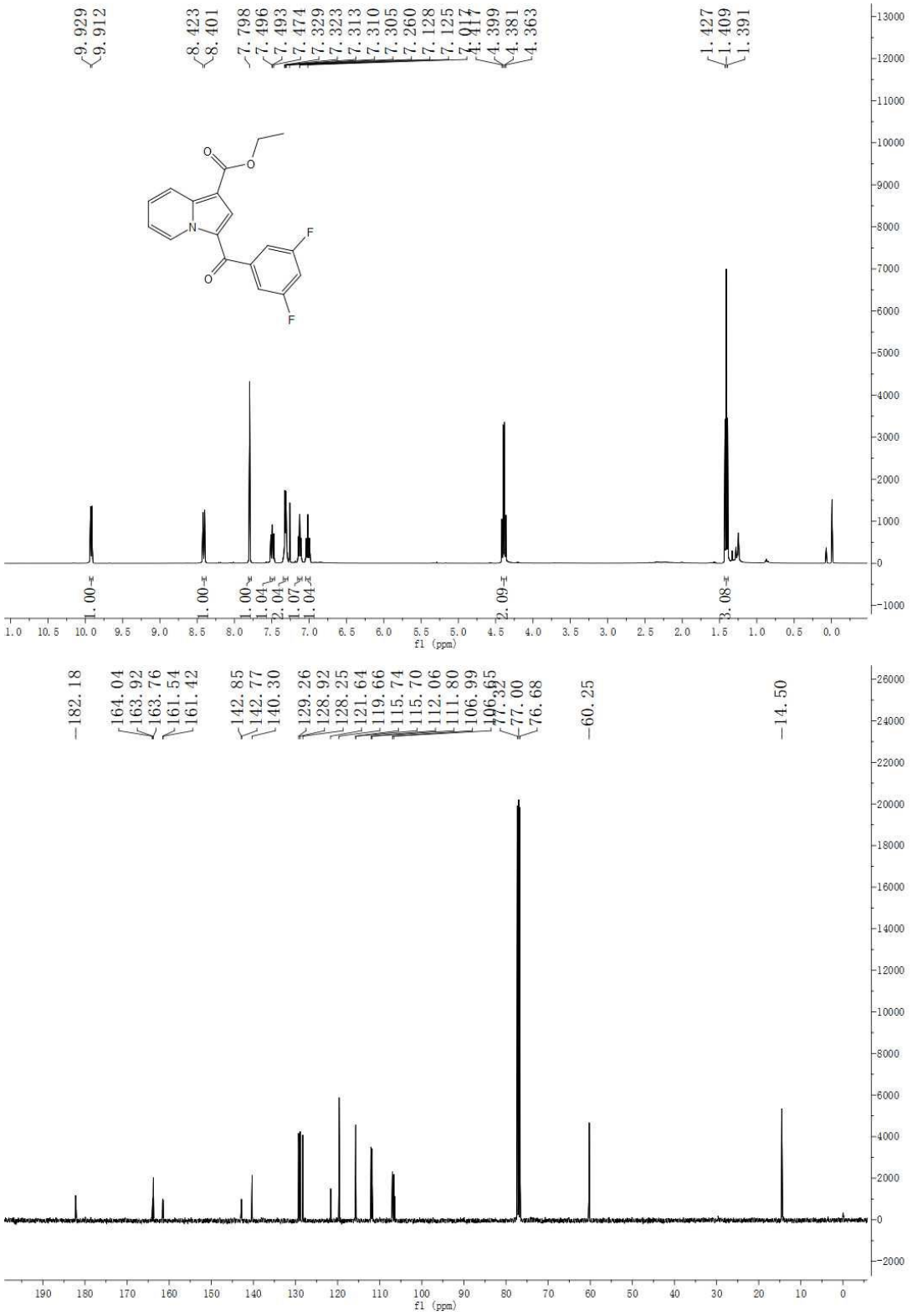


^{1}H NMR and ^{13}C NMR of ethyl 3-(3-fluorobenzoyl)indolizine-1-carboxylate (3l)

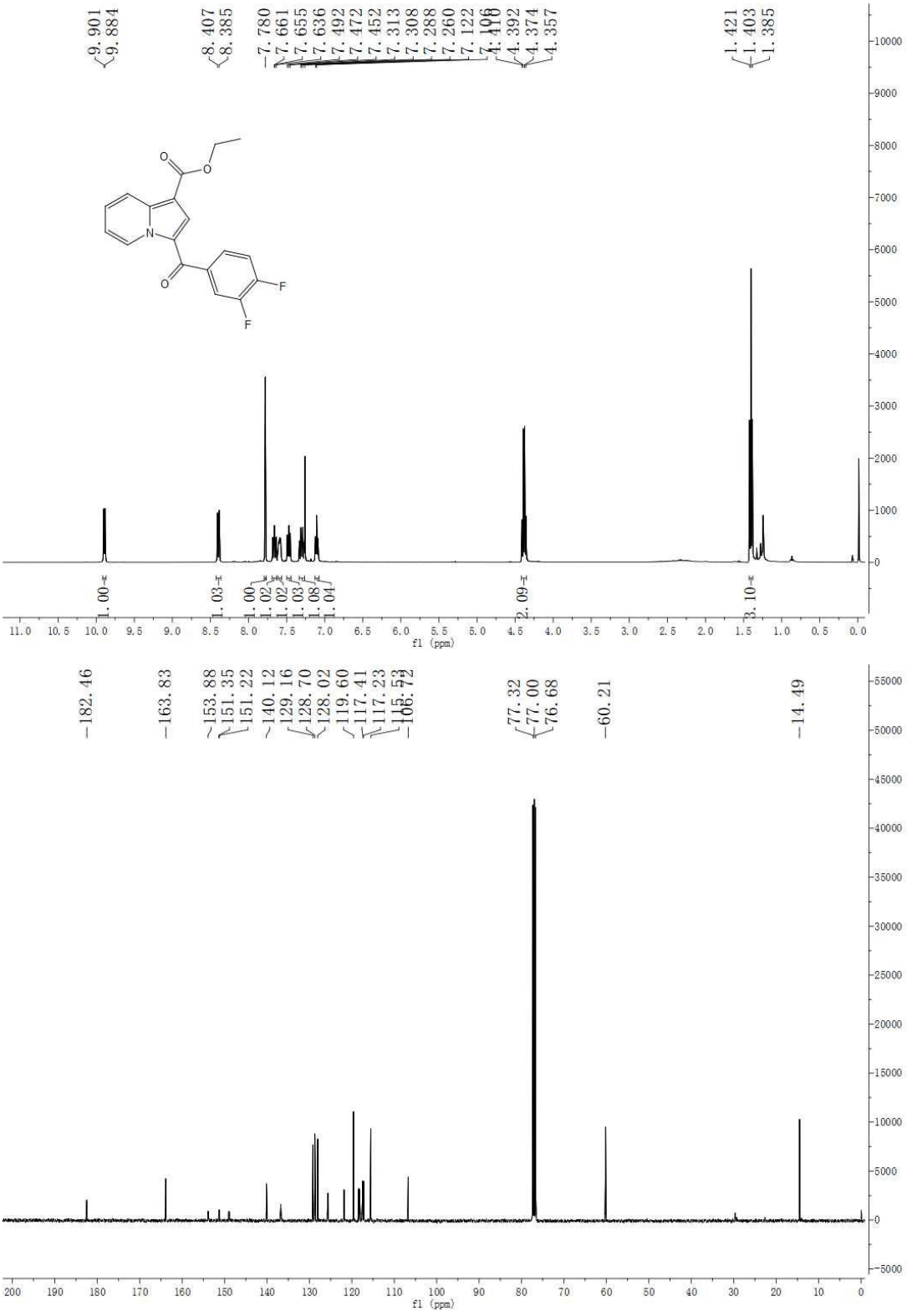




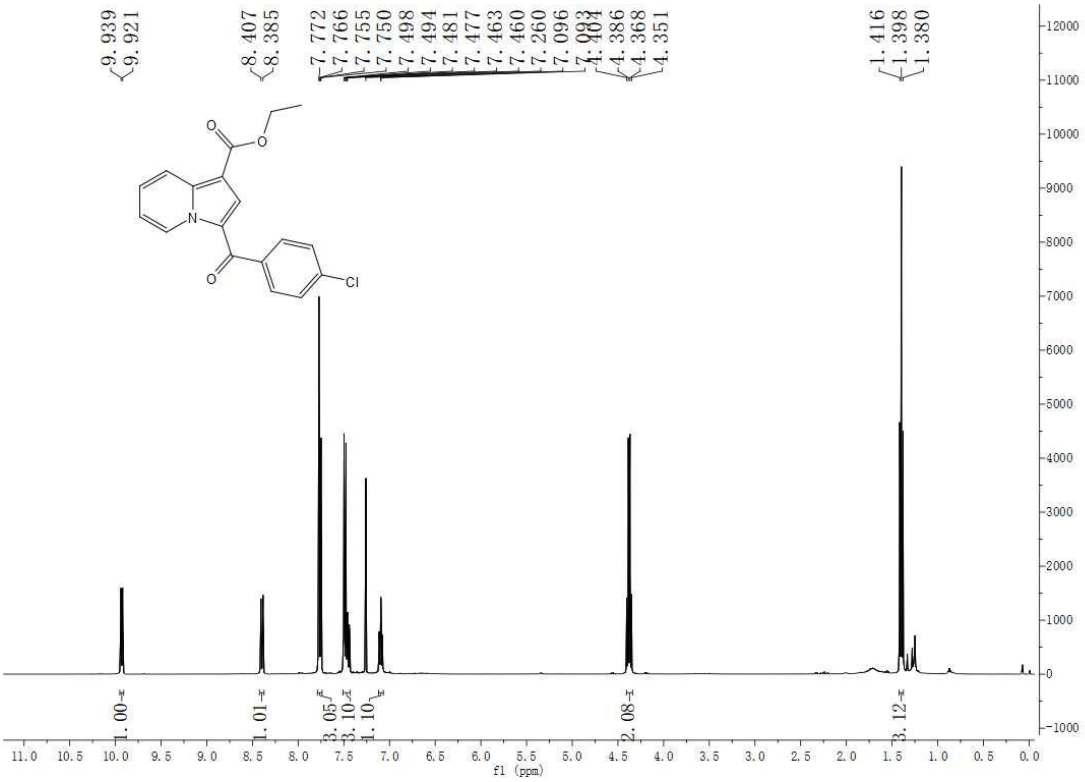
^{1}H NMR and ^{13}C NMR of ethyl 3-(3,5-difluorobenzoyl)indolizine-1-carboxylate (3m)

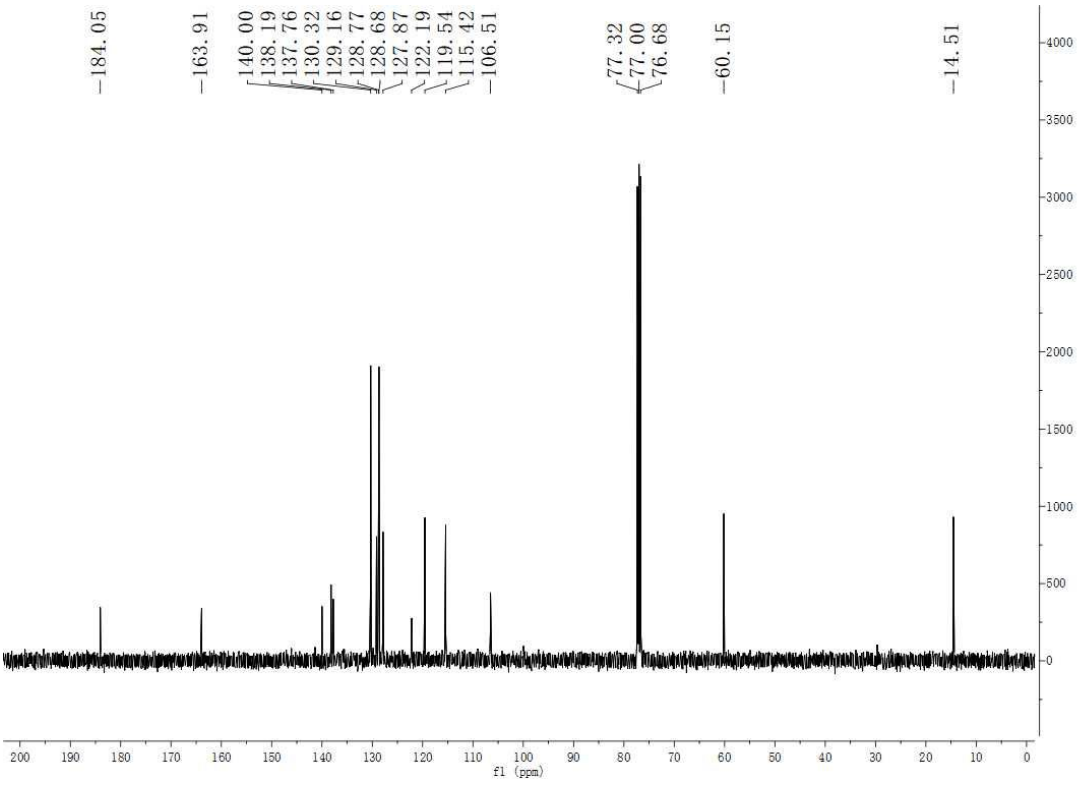


^{1}H NMR and ^{13}C NMR of ethyl 3-(3,4-difluorobenzoyl)indolizine-1-carboxylate (3n)

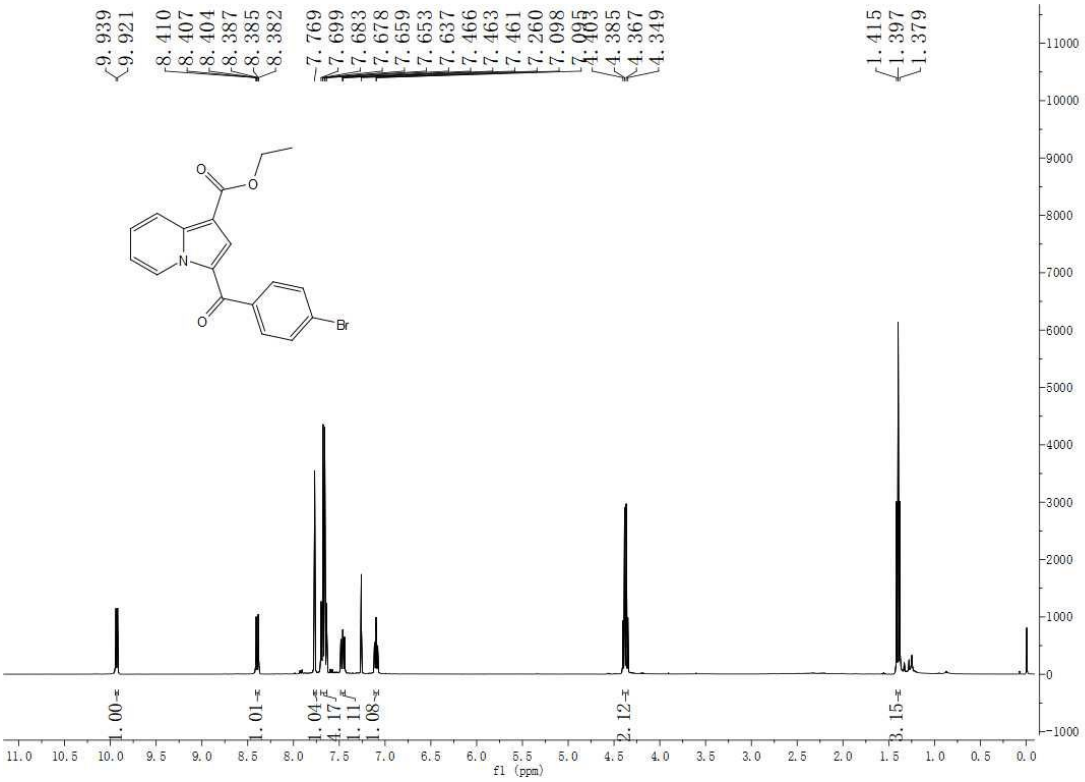


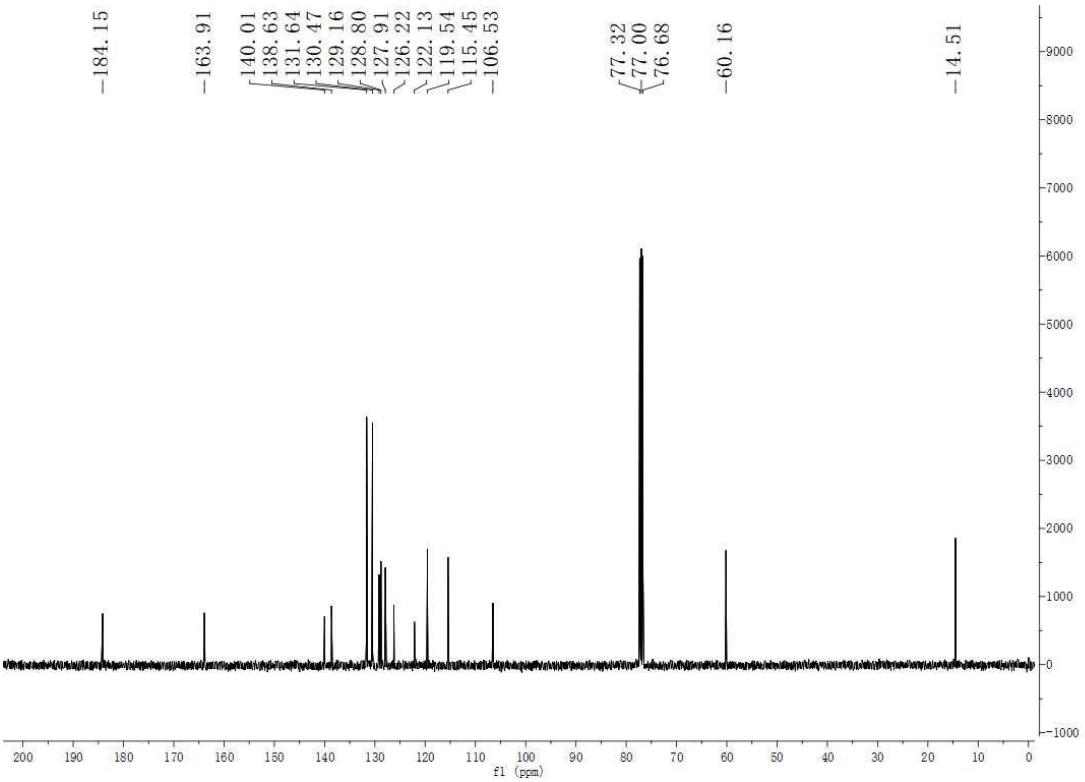
^{1}H NMR and ^{13}C NMR of ethyl 3-(4-chlorobenzoyl)indolizine-1-carboxylate (3o)



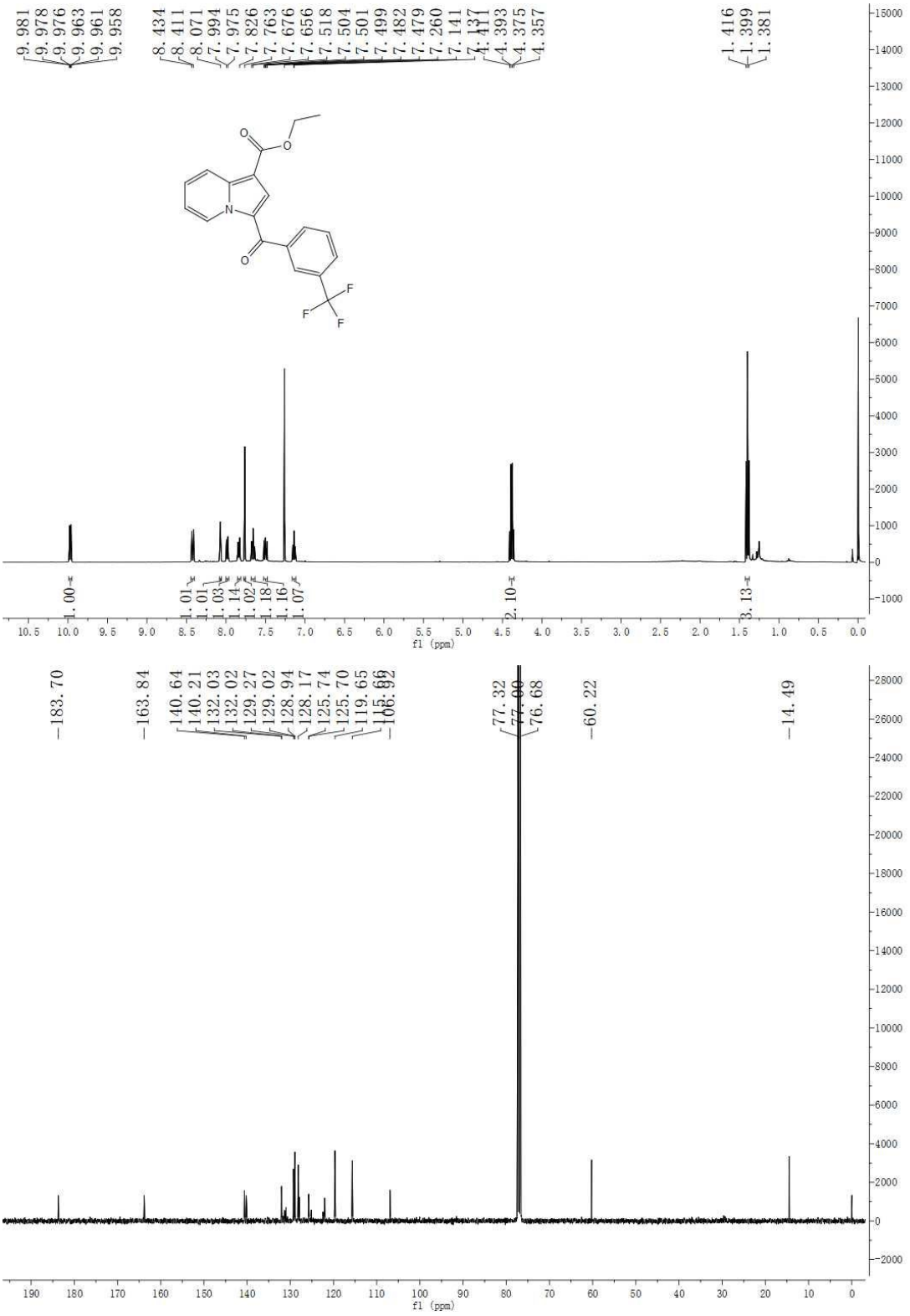


^{1}H NMR and ^{13}C NMR of ethyl 3-(4-bromobenzoyl)indolizine-1-carboxylate (3p)

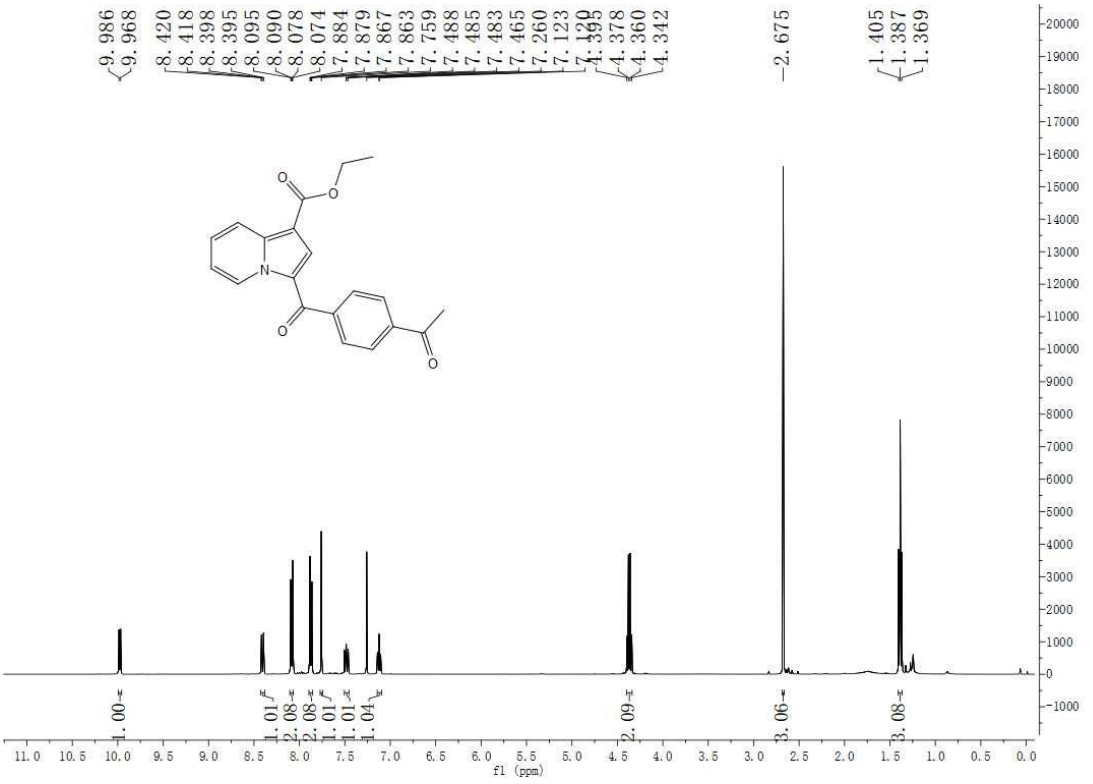


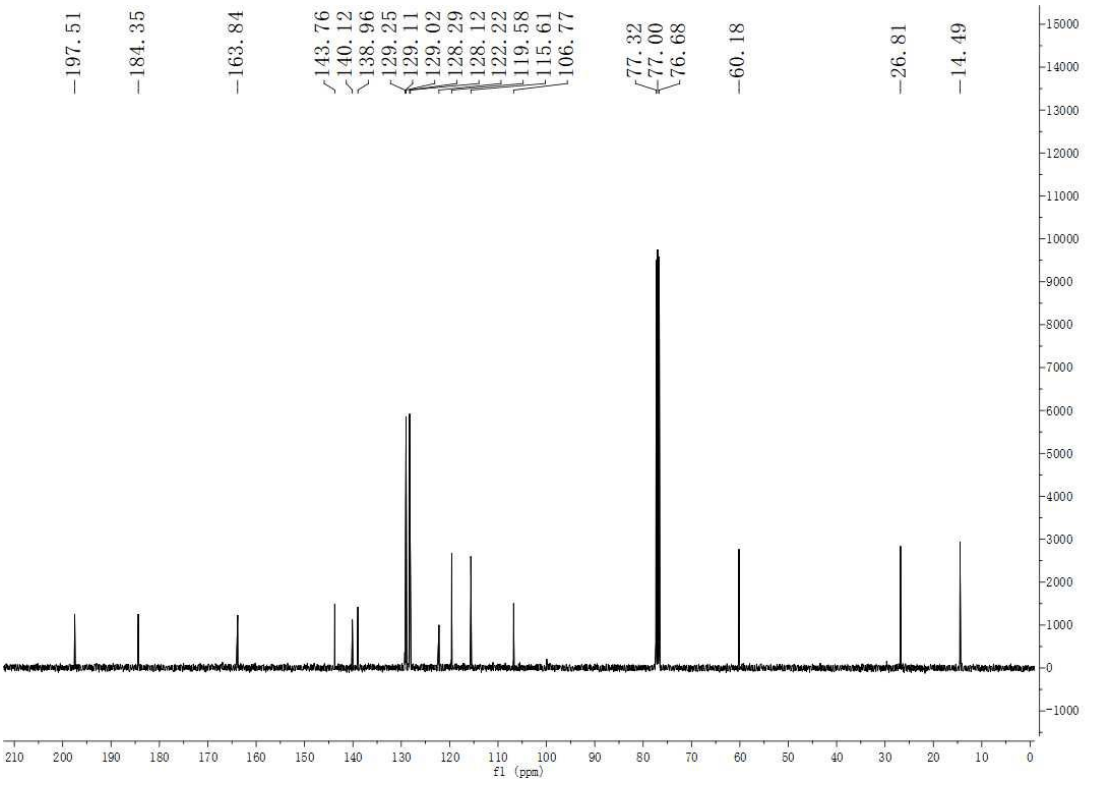


^{1}H NMR and ^{13}C NMR of ethyl 3-(3-(trifluoromethyl)benzoyl)indolizine-1-carboxylate (3q)

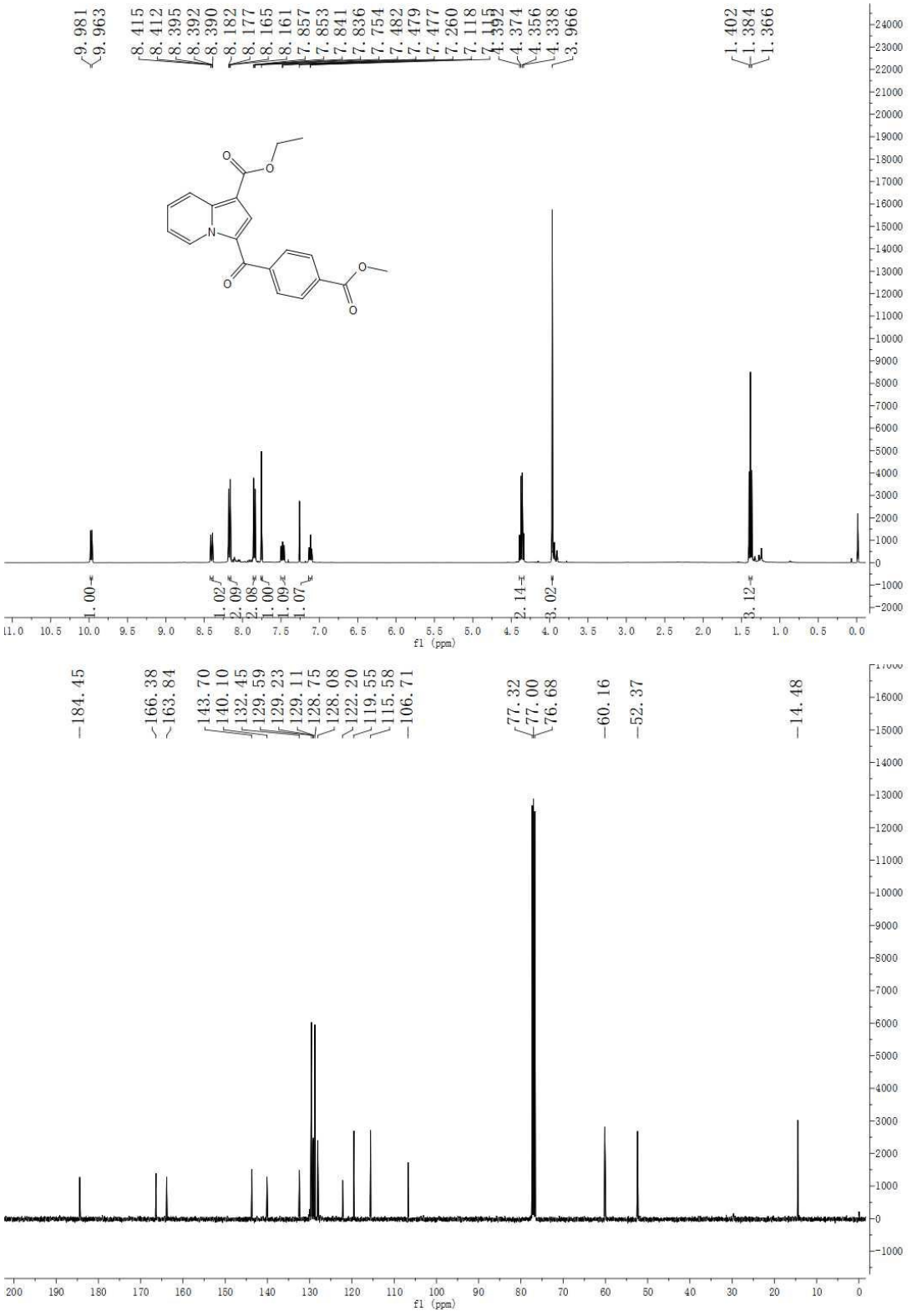


^{1}H NMR and ^{13}C NMR of ethyl 3-(4-acetylbenzoyl)indolizine-1-carboxylate (3r)

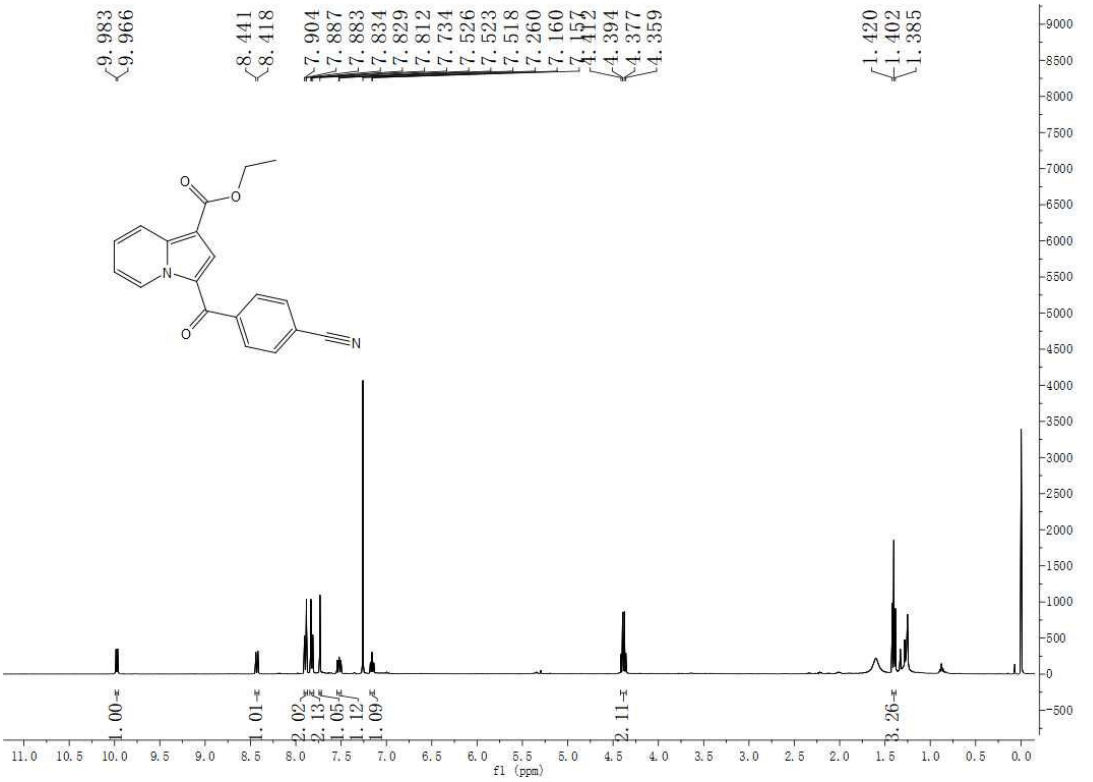


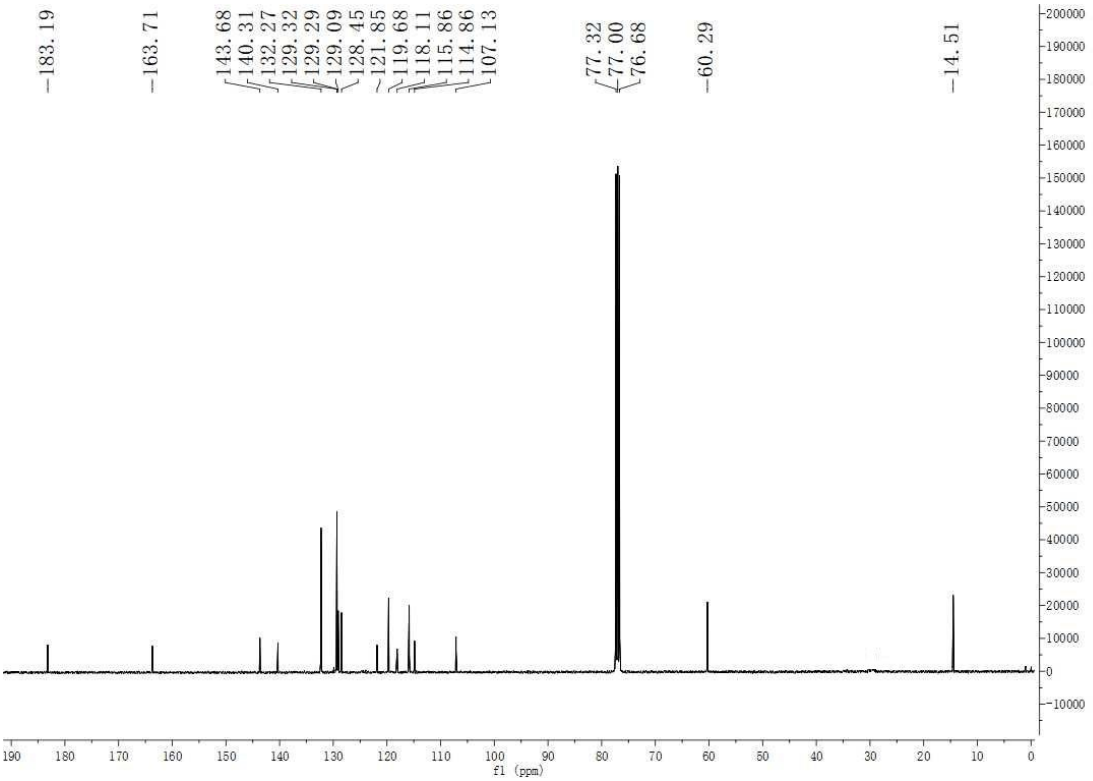


^{1}H NMR and ^{13}C NMR of ethyl 3-(4-(methoxycarbonyl)benzoyl)indolizine-1-carboxylate (3s)

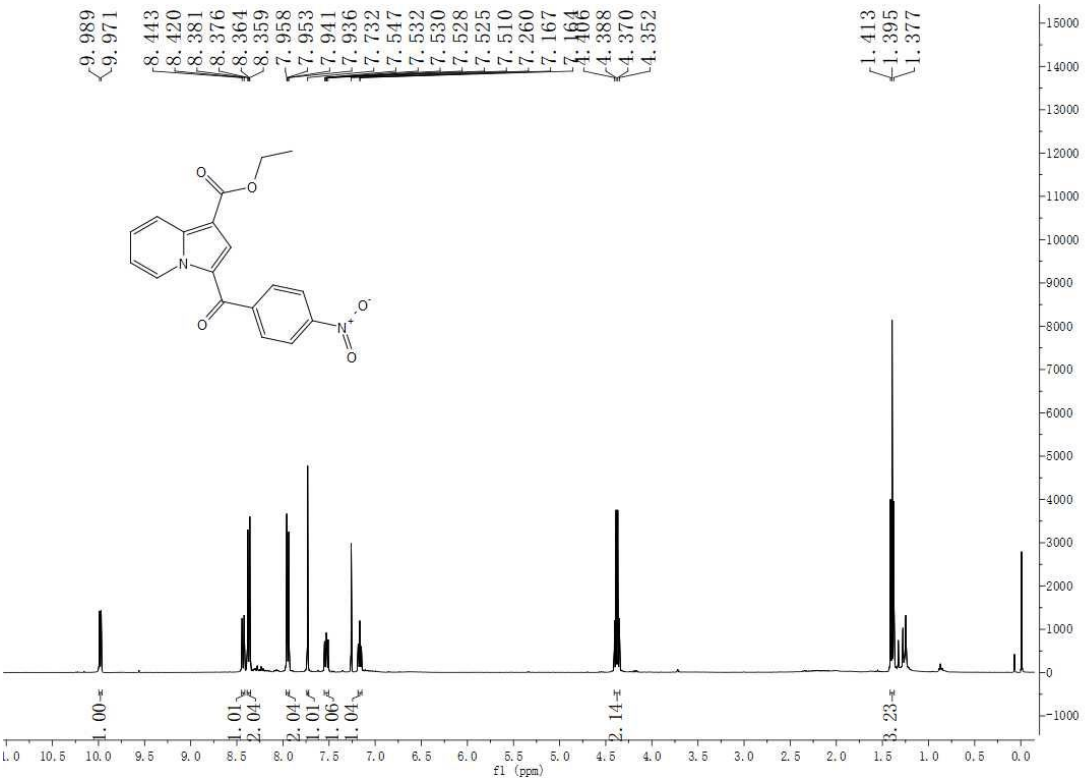


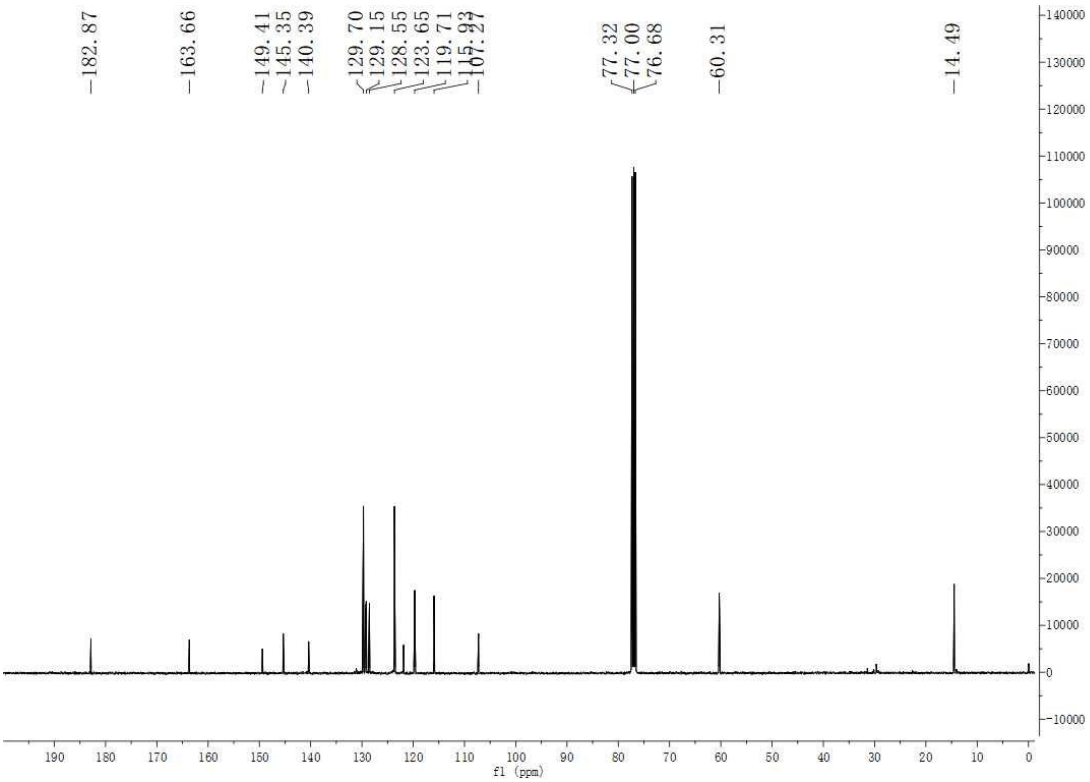
^{1}H NMR and ^{13}C NMR of ethyl 3-(4-cyanobenzoyl)indolizine-1-carboxylate (3t)



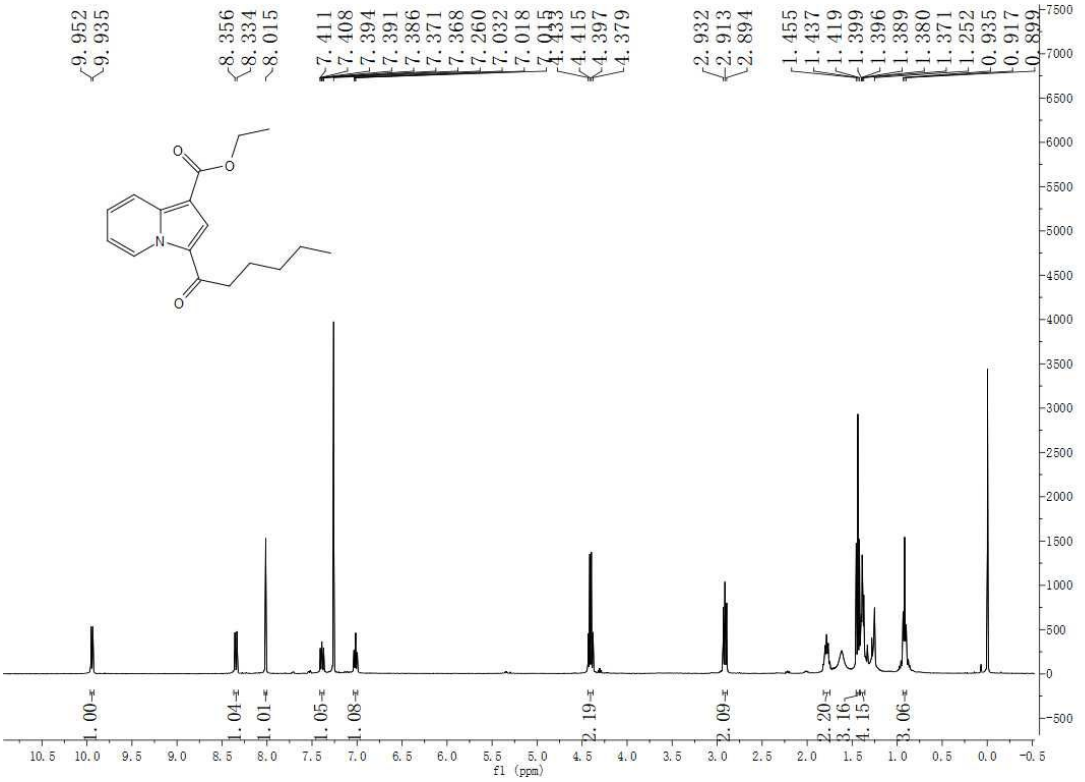


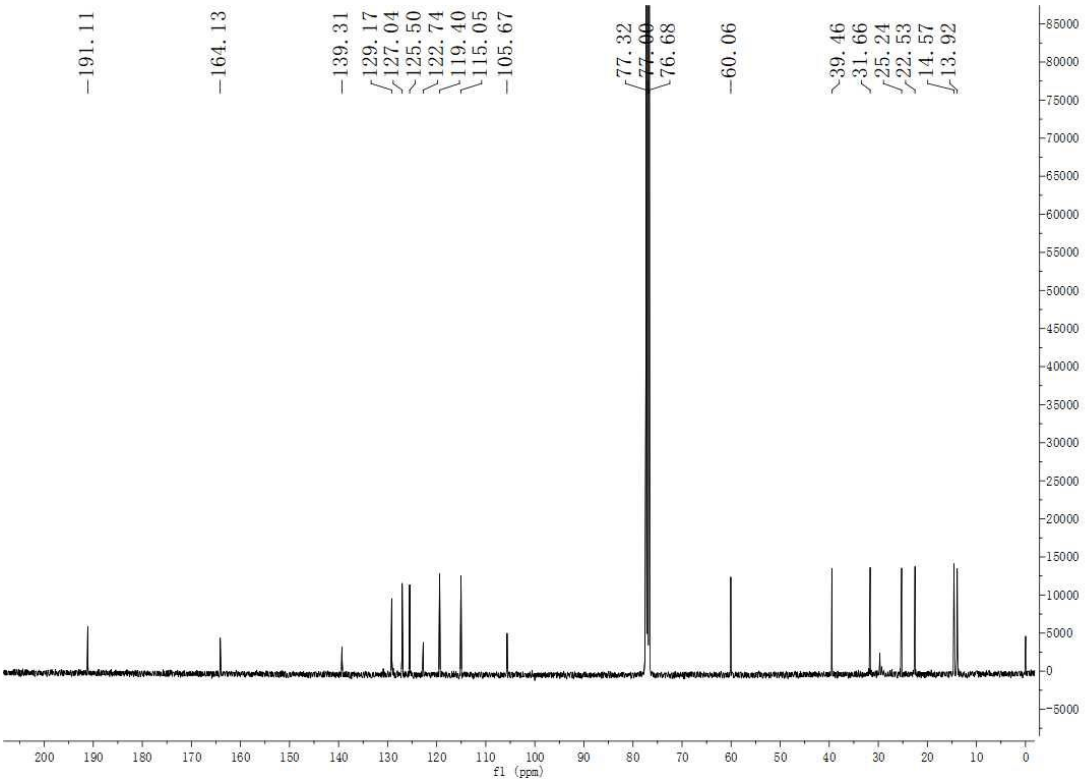
^{1}H NMR and ^{13}C NMR of ethyl 3-(4-nitrobenzoyl)indolizine-1-carboxylate (3u)



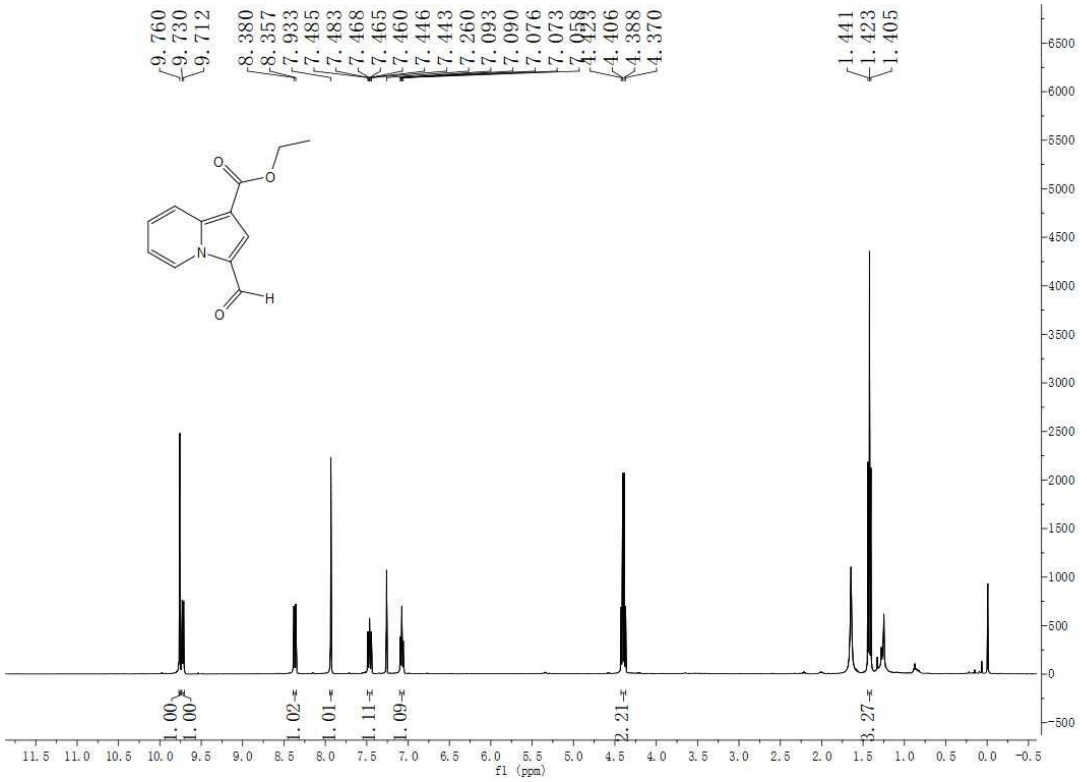


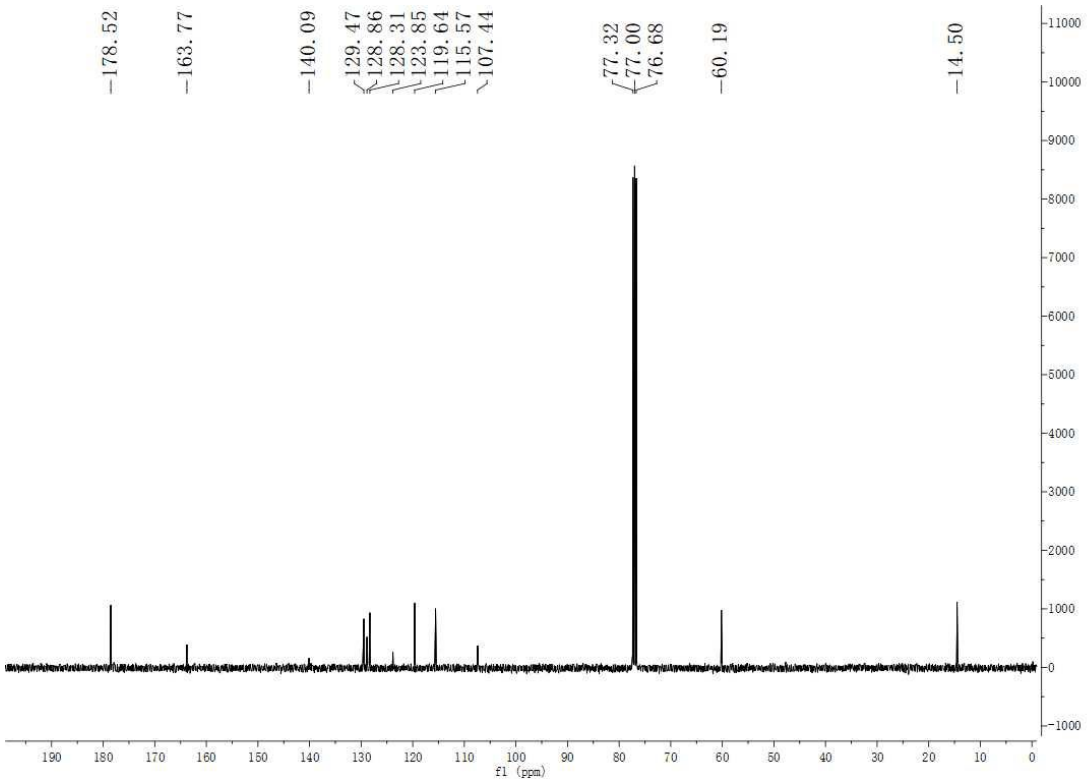
^{1}H NMR and ^{13}C NMR of ethyl 3-hexanoylindolizine-1-carboxylate (3v)



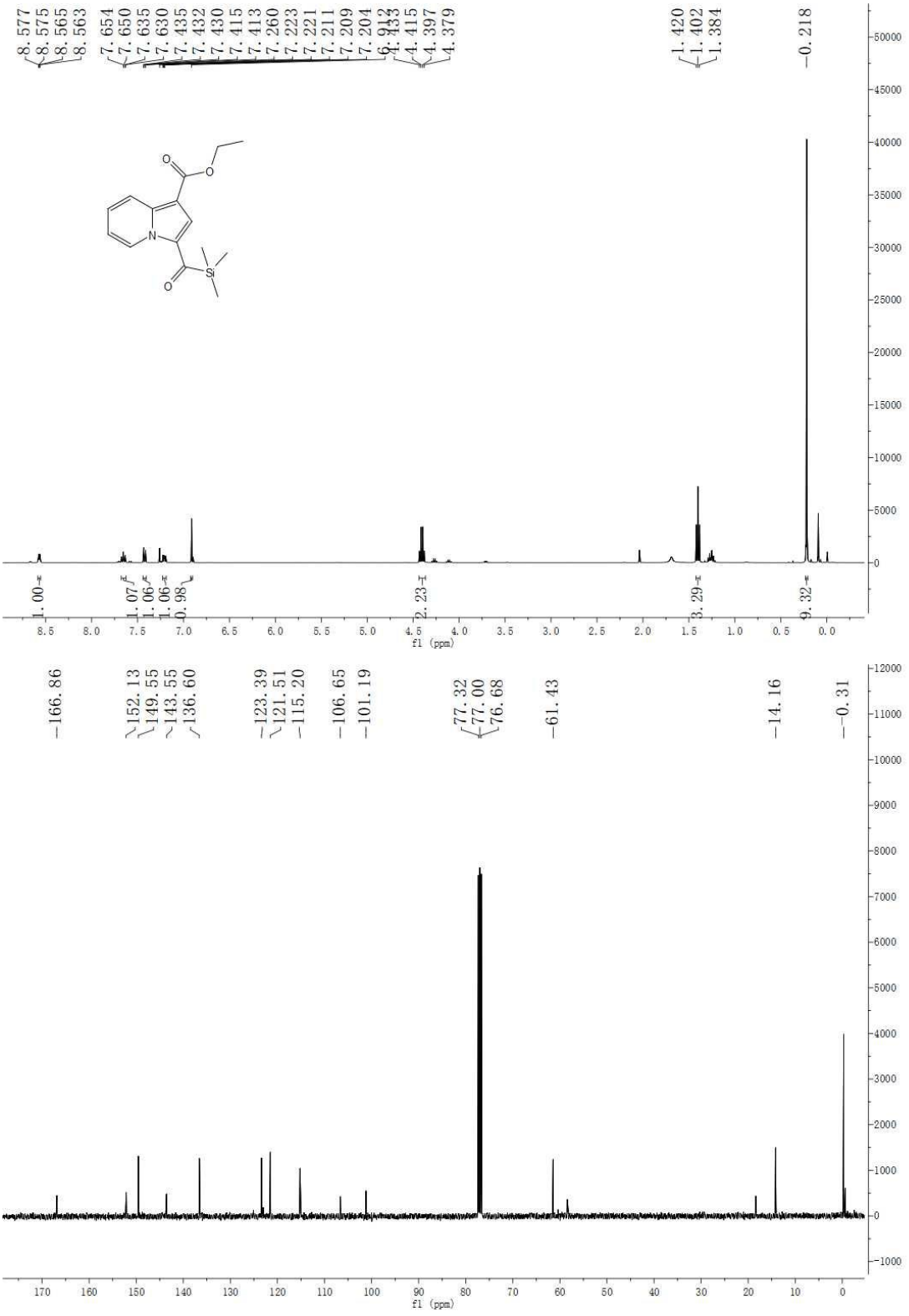


^{1}H NMR and ^{13}C NMR of ethyl 3-formylindolizine-1-carboxylate (3w)

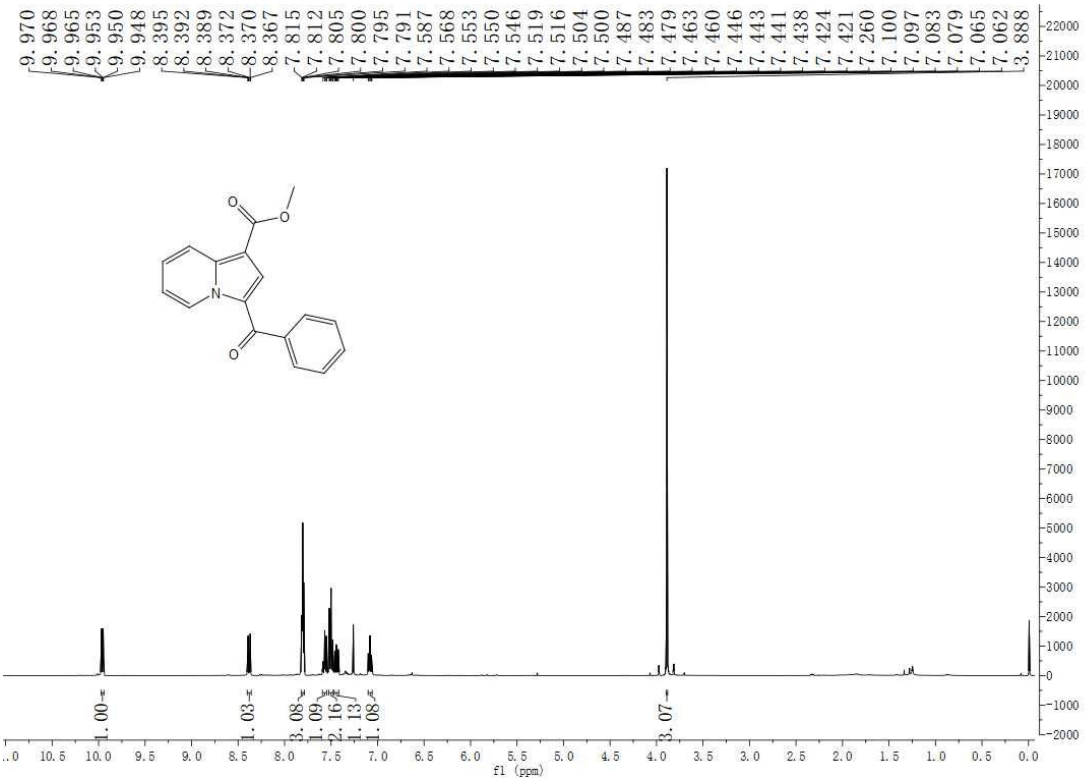


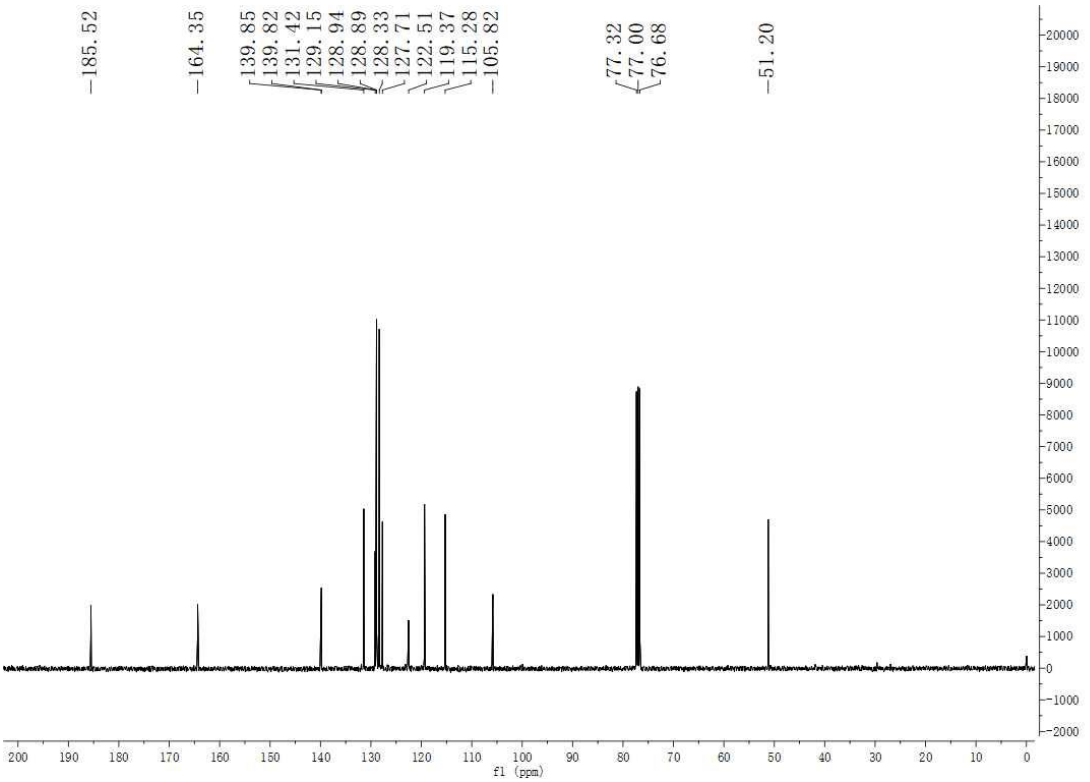


^{1}H NMR and ^{13}C NMR of ethyl 3-((trimethylsilyl)carbonyl)indolizine-1-carboxylate (3x)

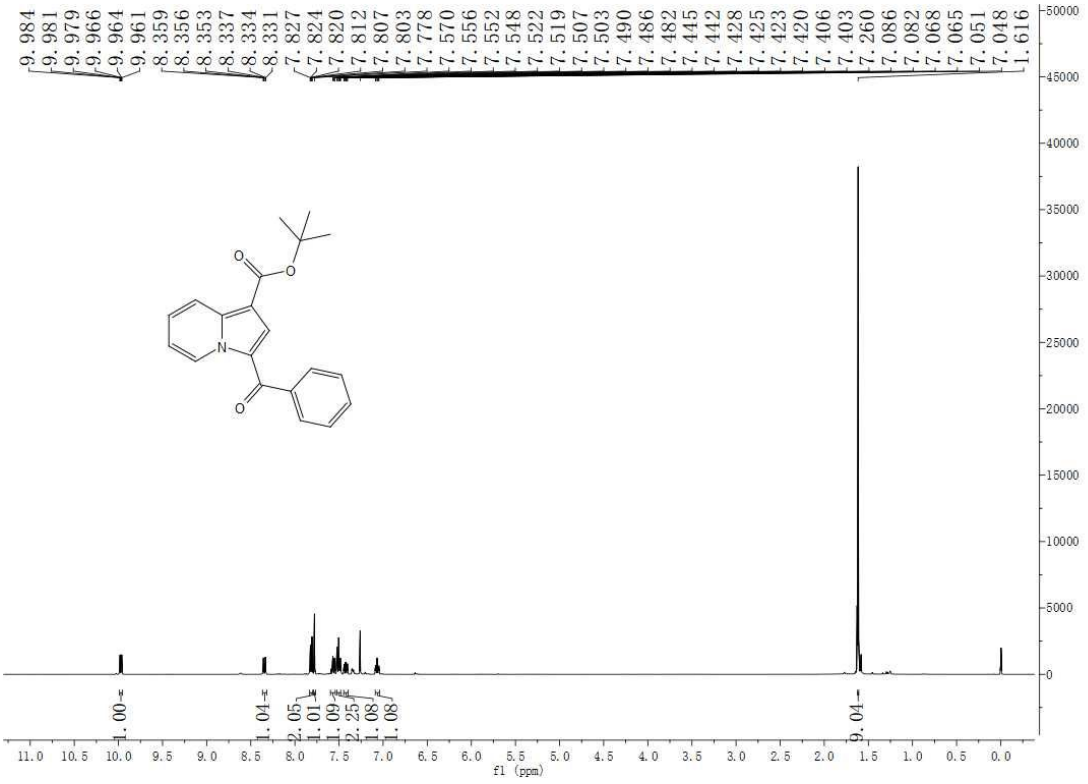


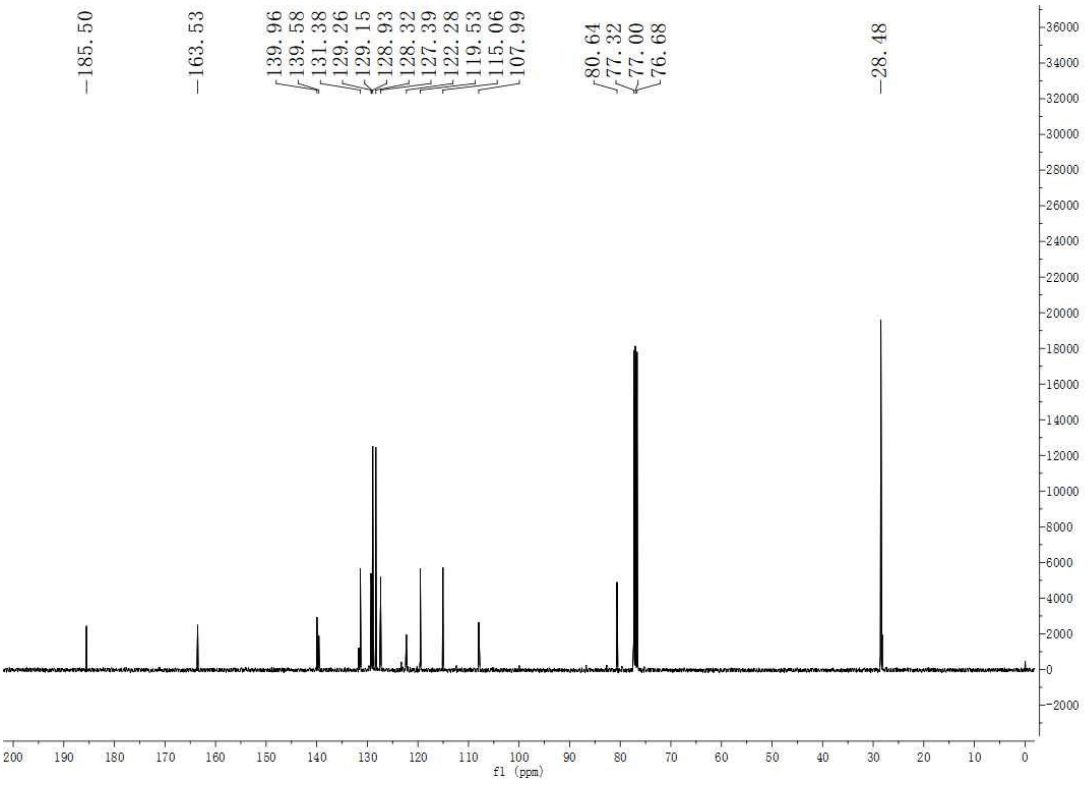
^{1}H NMR and ^{13}C NMR of methyl 3-benzoylindolizine-1-carboxylate (4a)



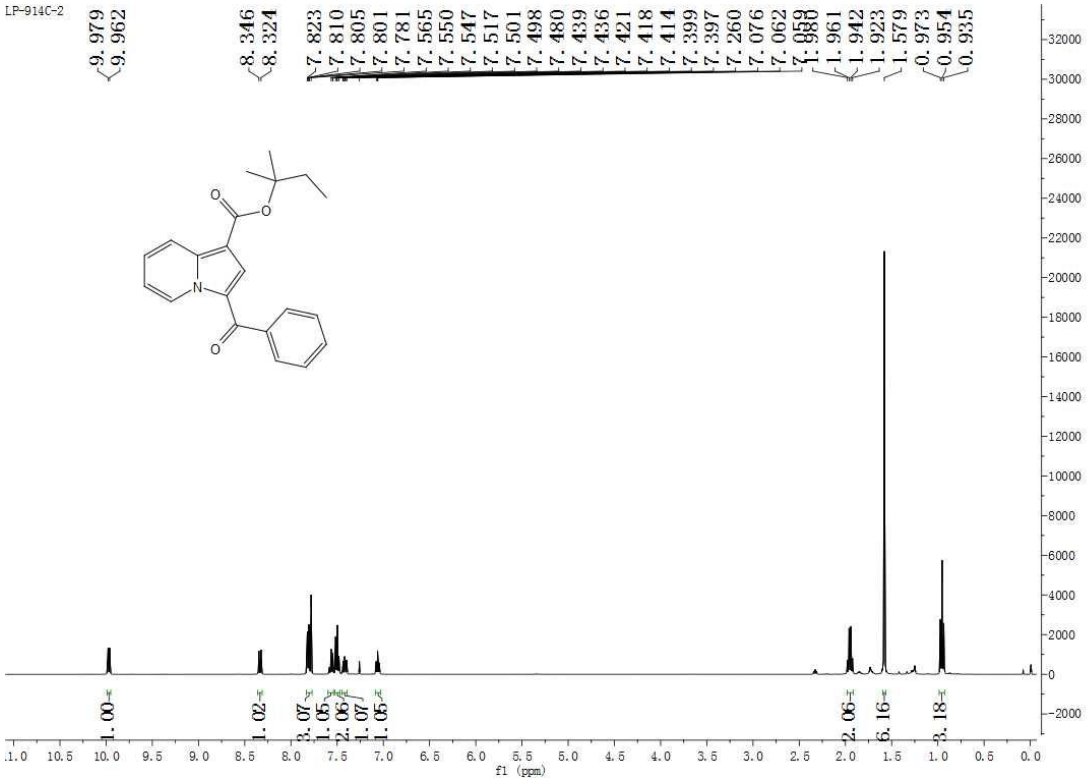


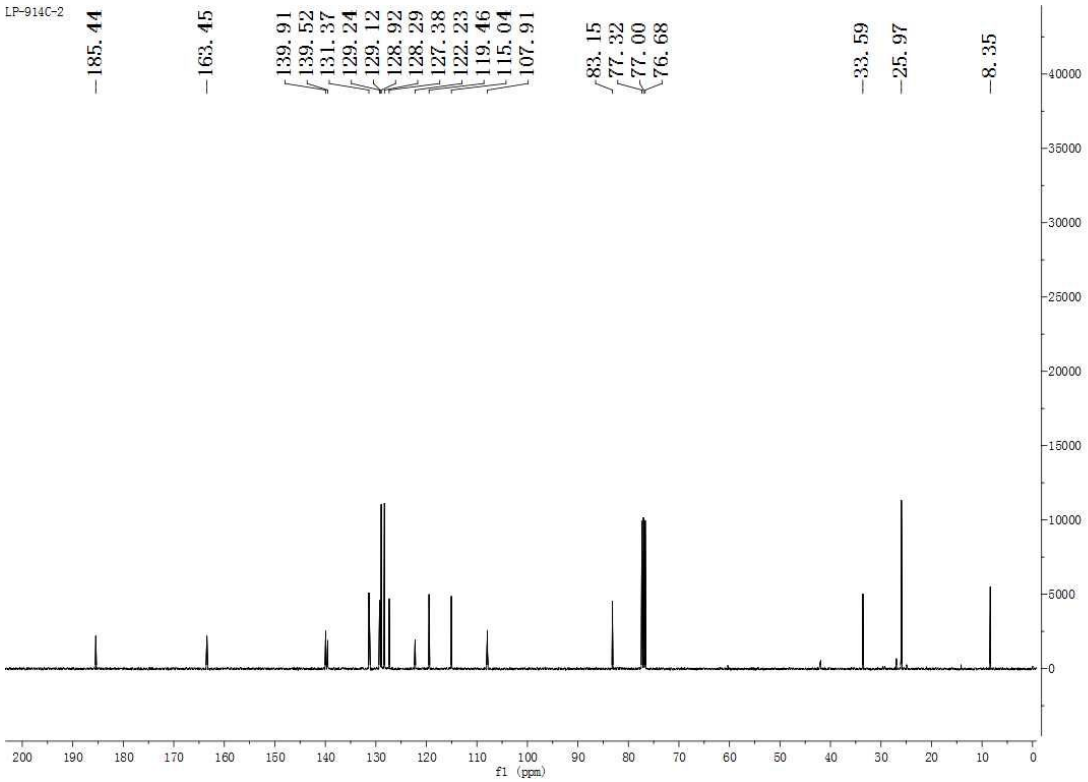
^{1}H NMR and ^{13}C NMR of *tert*-butyl 3-benzoylindolizine-1-carboxylate (4b)



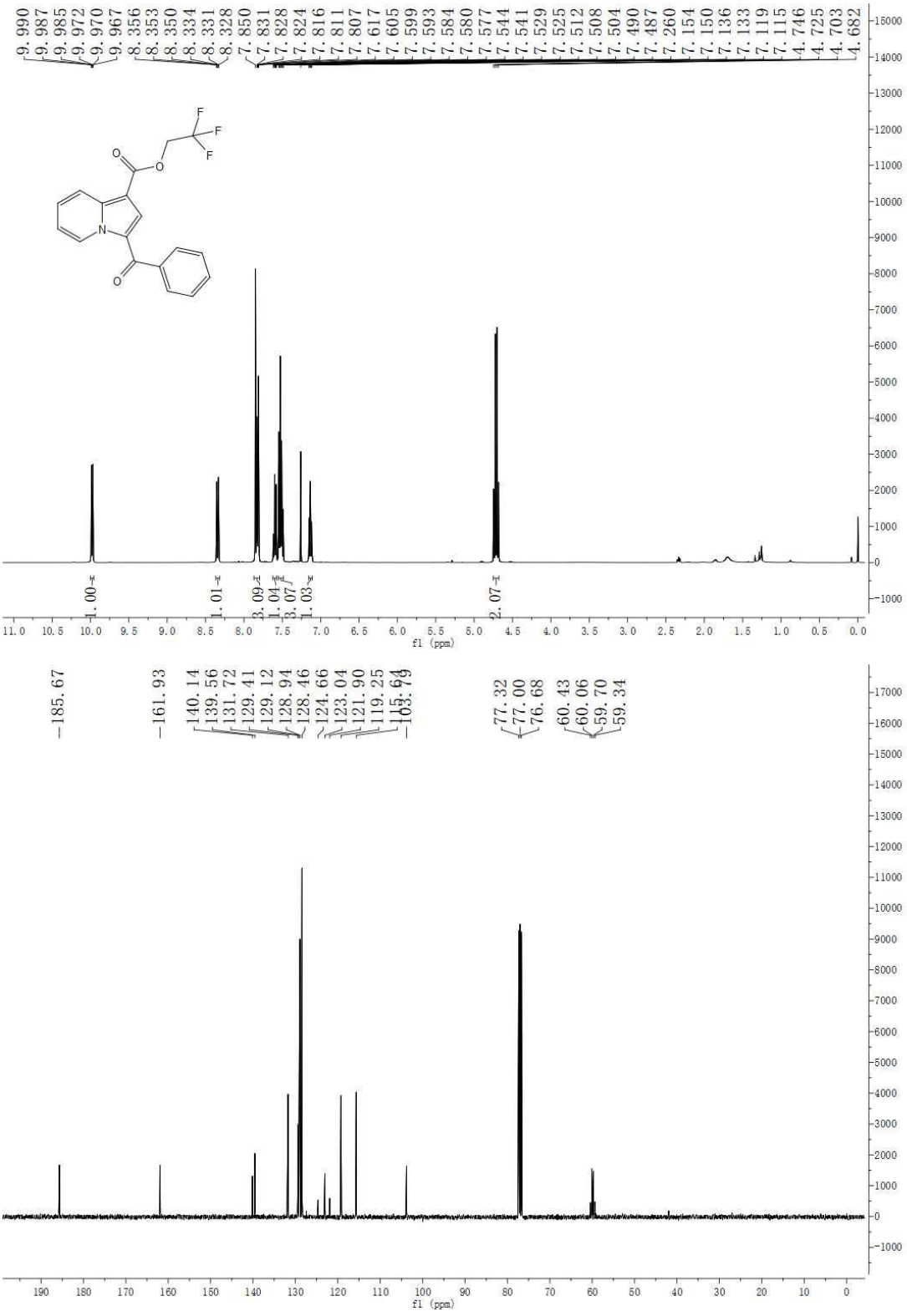


^{1}H NMR and ^{13}C NMR of tert-pentyl 3-benzoylindolizine-1-carboxylate (4c)

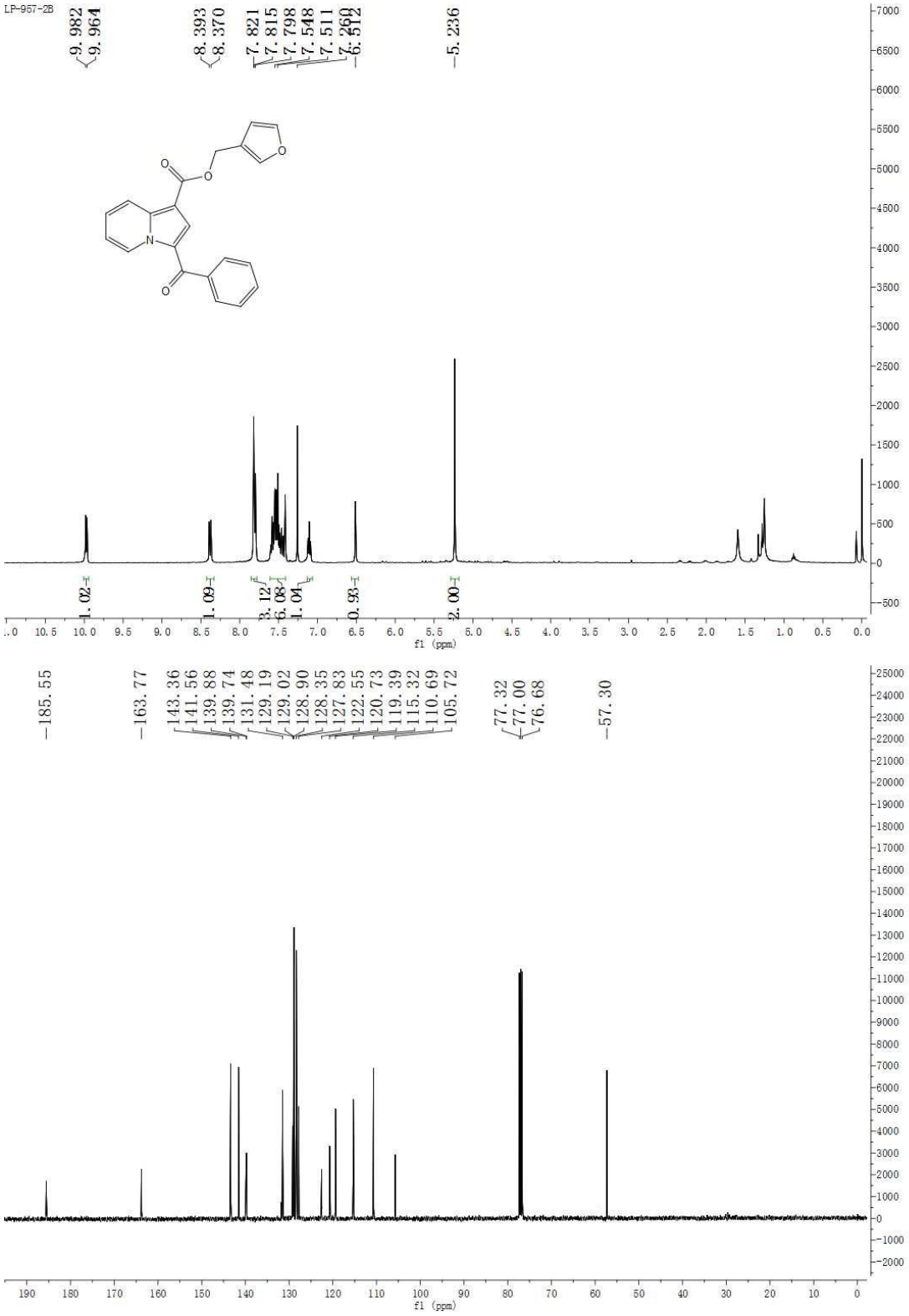




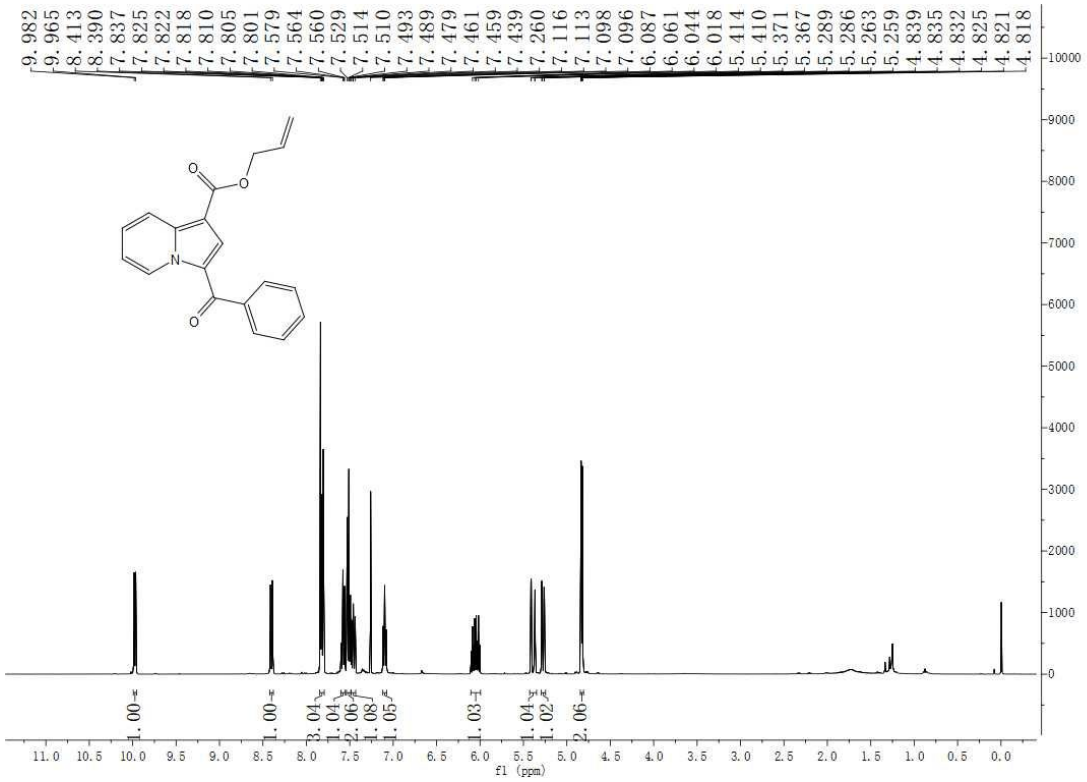
^{1}H NMR and ^{13}C NMR of 2,2,2-trifluoroethyl 3-benzoylindolizine-1-carboxylate (4d)

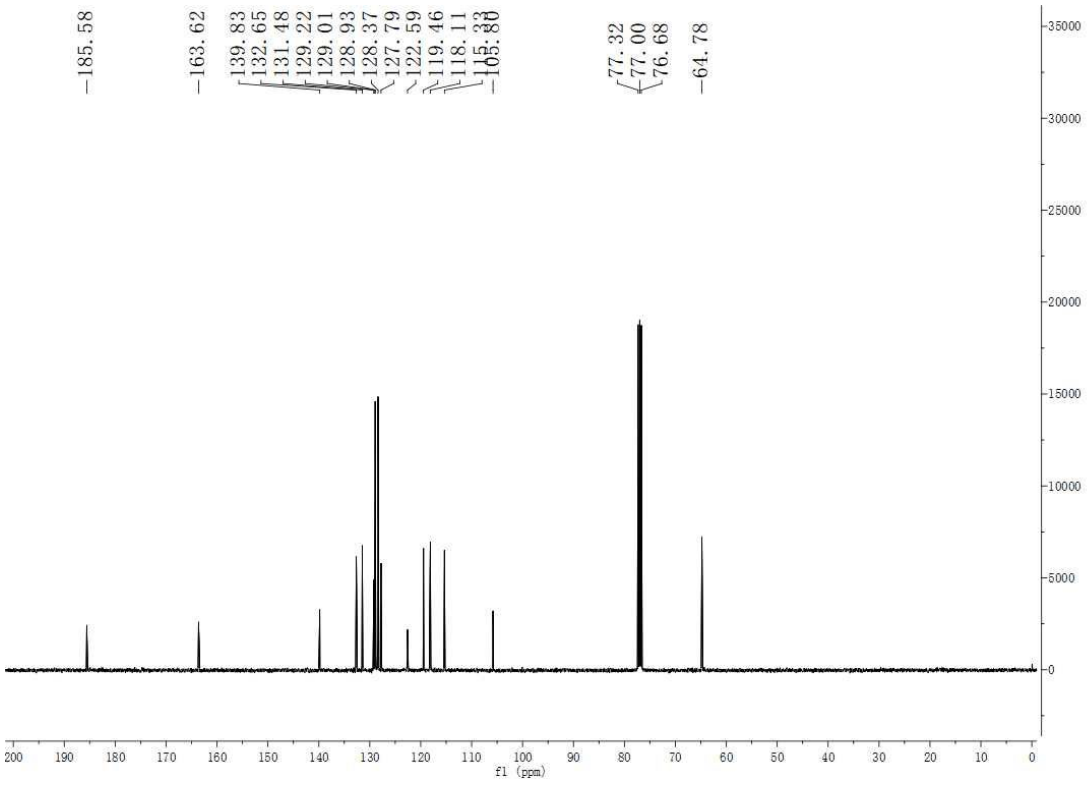


^{1}H NMR and ^{13}C NMR of furan-3-ylmethyl 3-benzoylindolizine-1-carboxylate (4e)

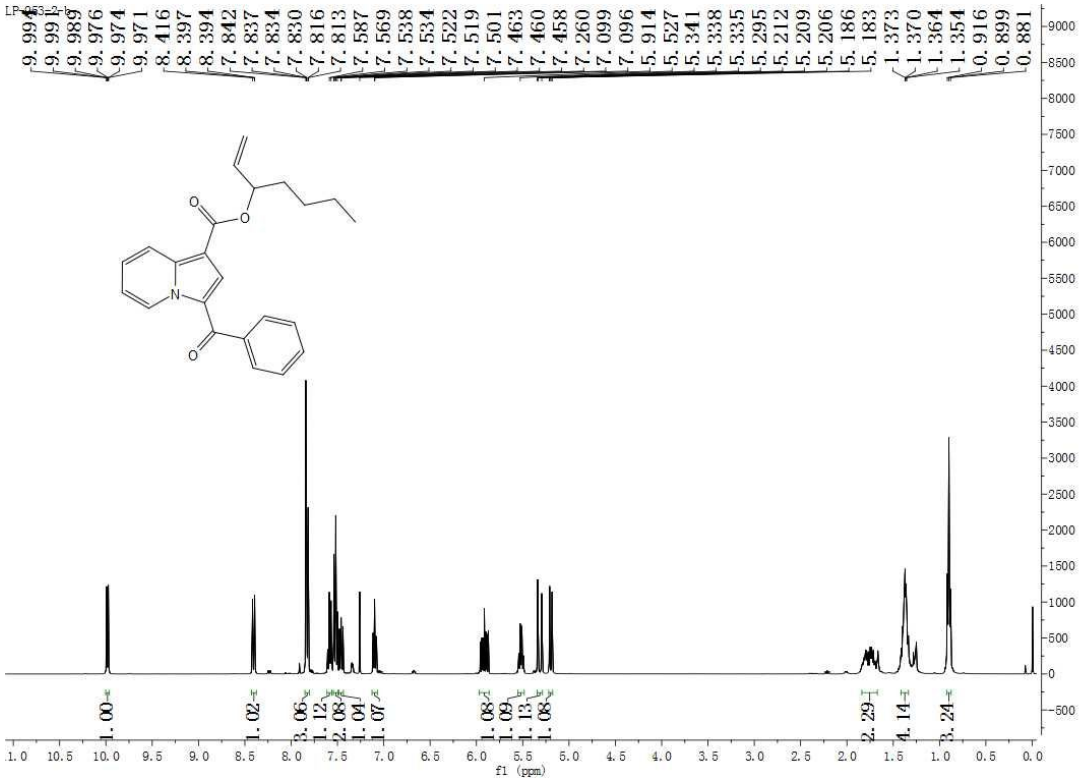


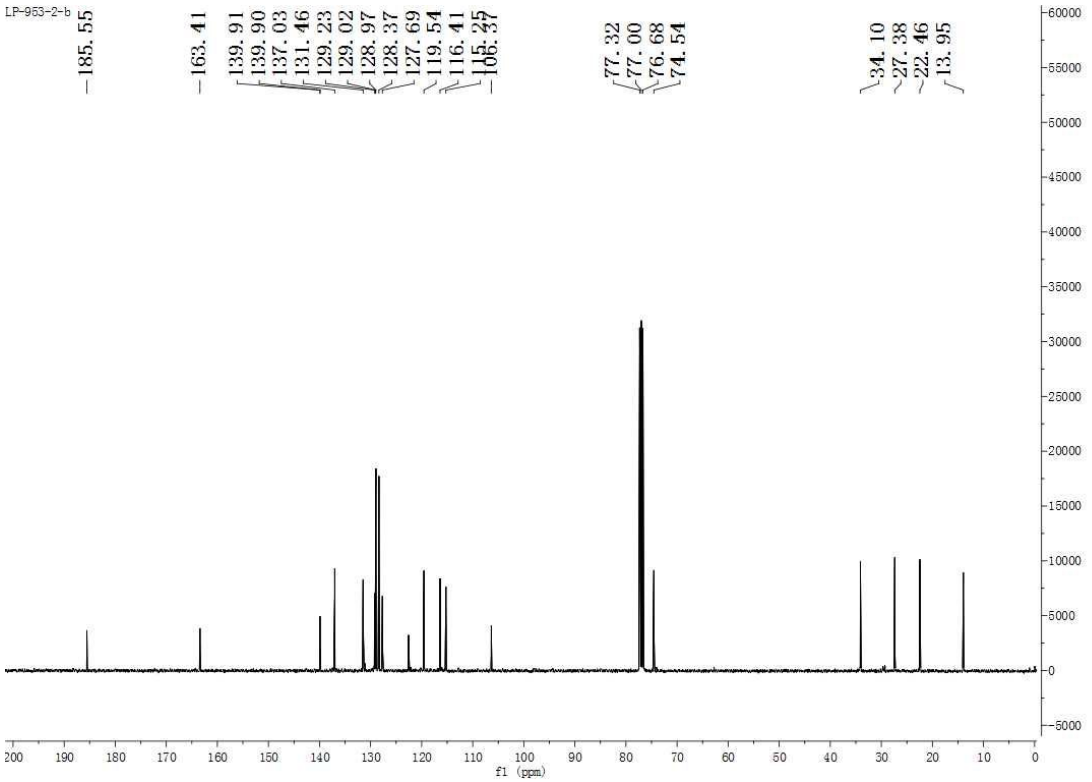
^{1}H NMR and ^{13}C NMR of allyl 3-benzoylindolizine-1-carboxylate (4f)



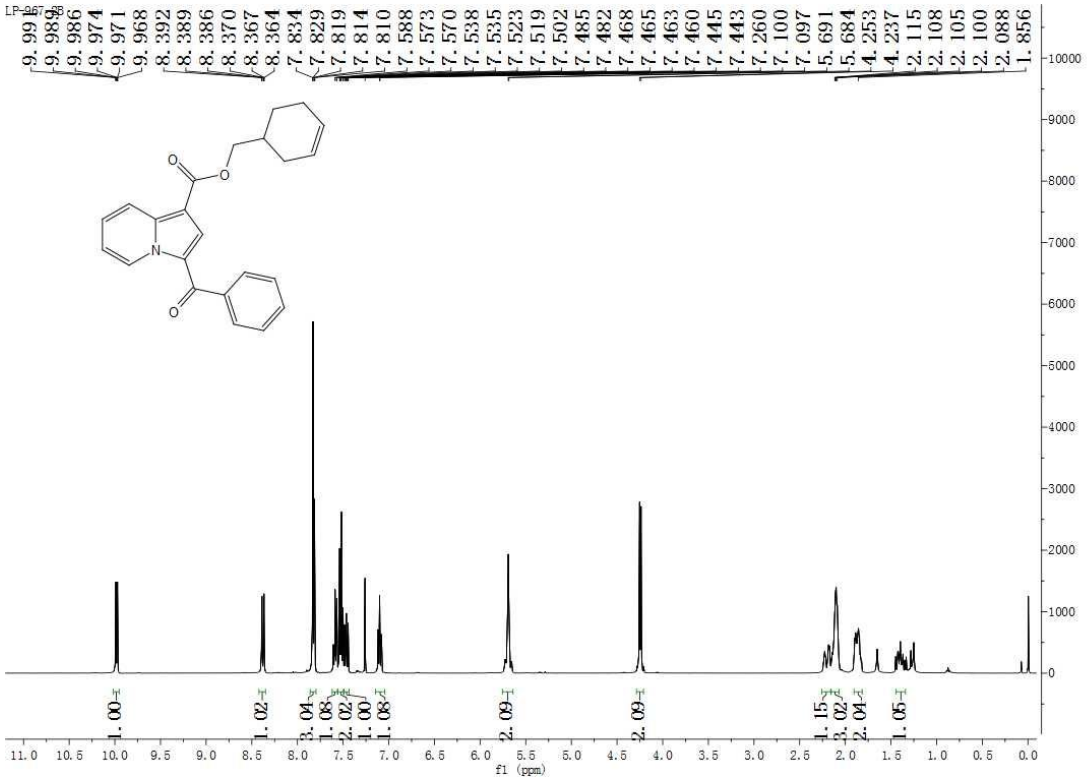


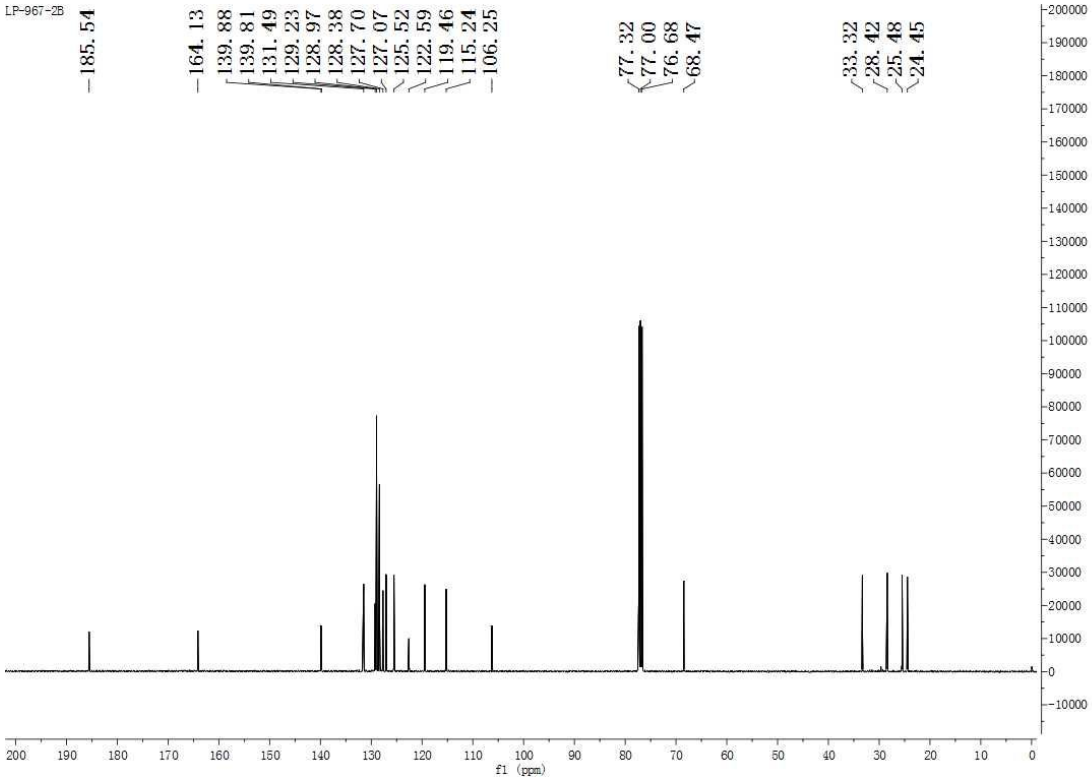
^{1}H NMR and ^{13}C NMR of hept-1-en-3-yl 3-benzoylindolizine-1-carboxylate (4g)



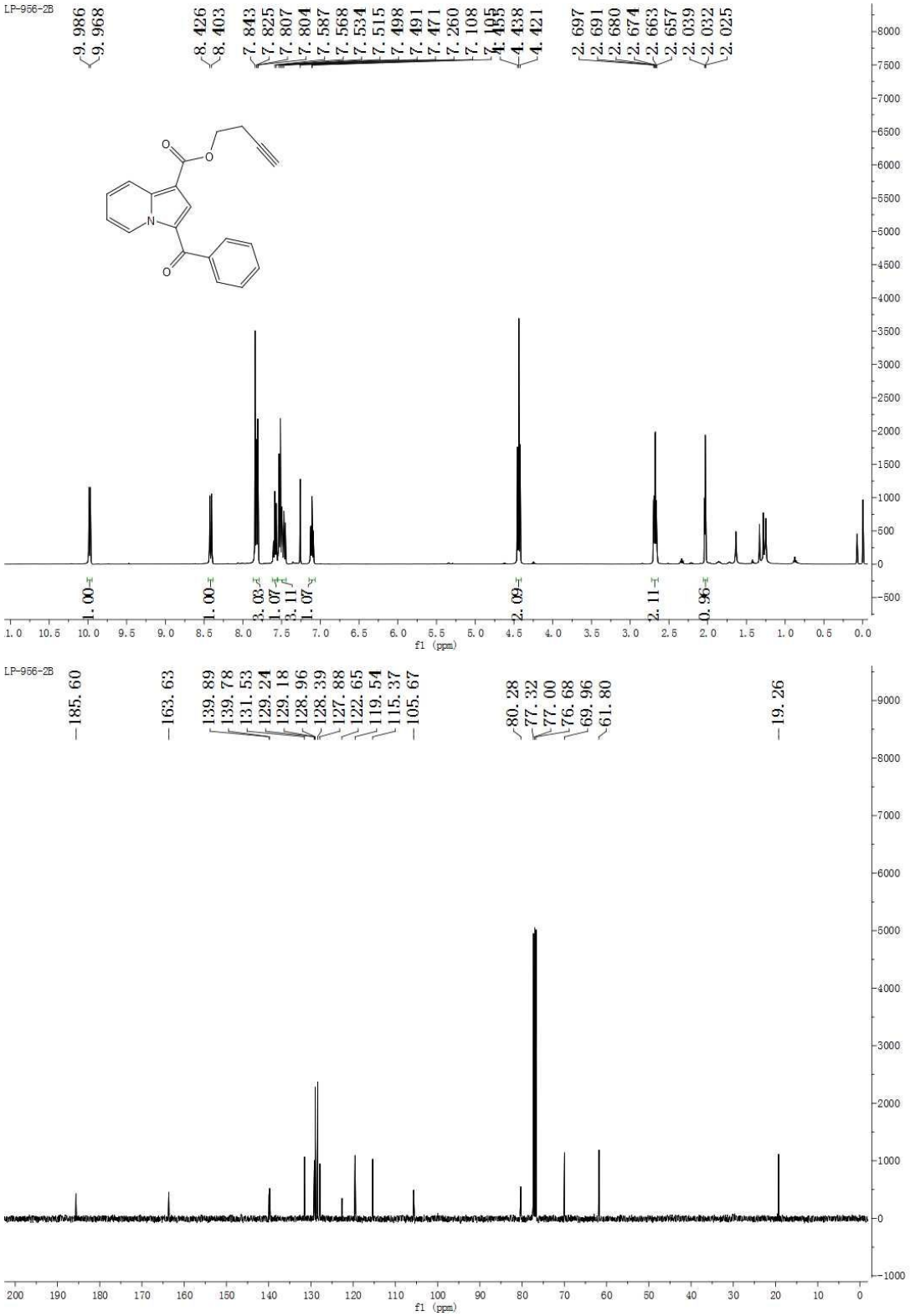


^{1}H NMR and ^{13}C NMR of cyclohex-3-en-1-ylmethyl 3-benzoylindolizine-1-carboxylate (4h)

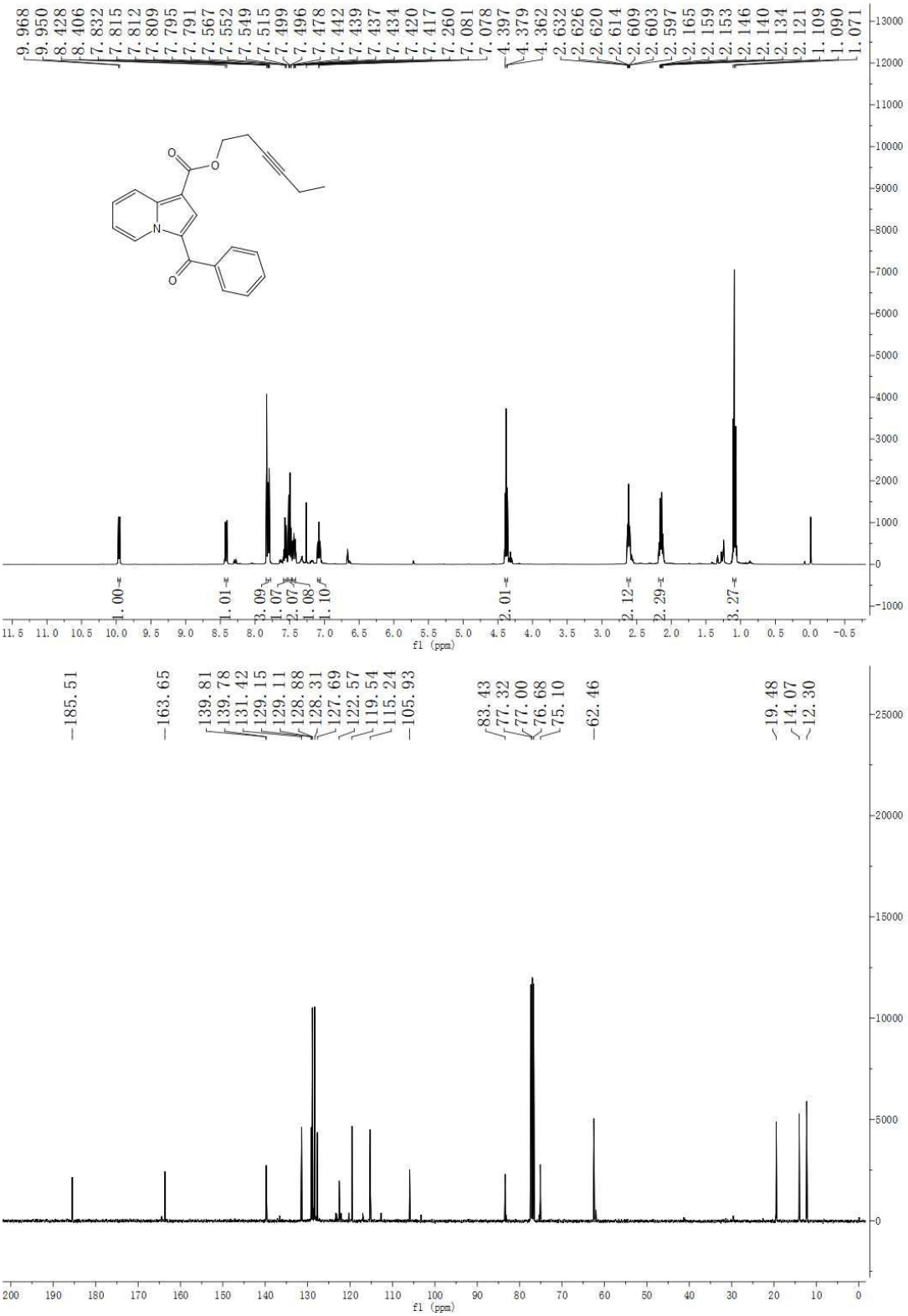




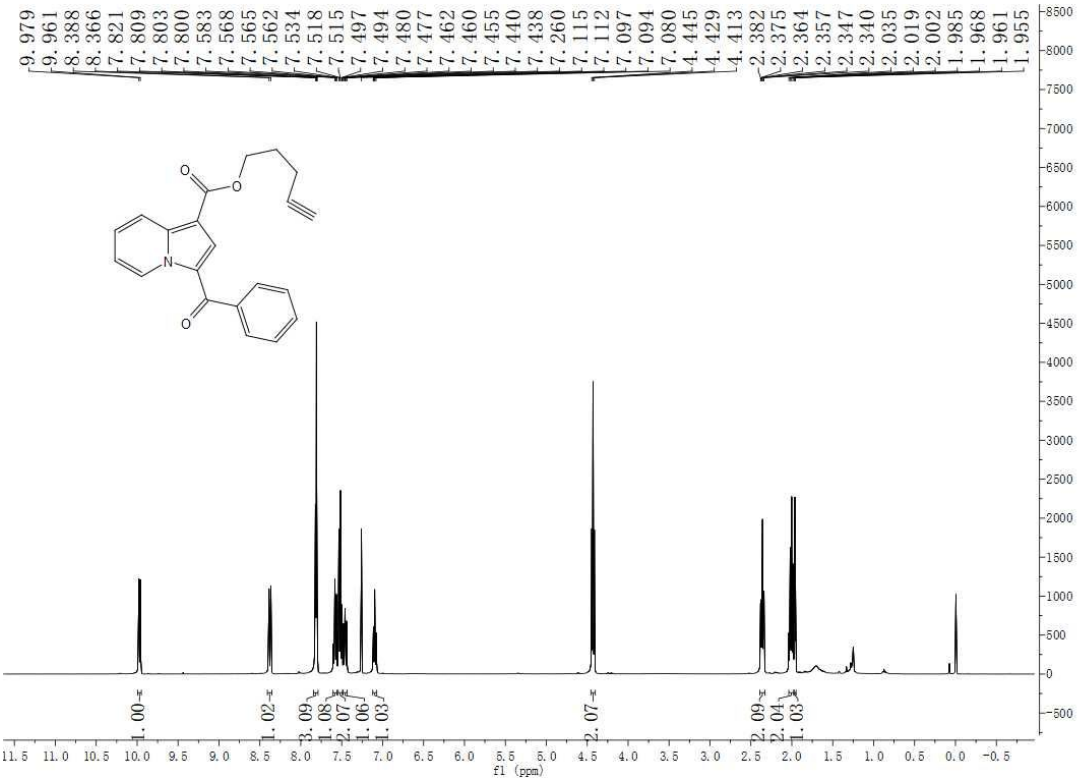
^{1}H NMR and ^{13}C NMR of but-3-yn-1-yl 3-benzoylindolizine-1-carboxylate (4i)

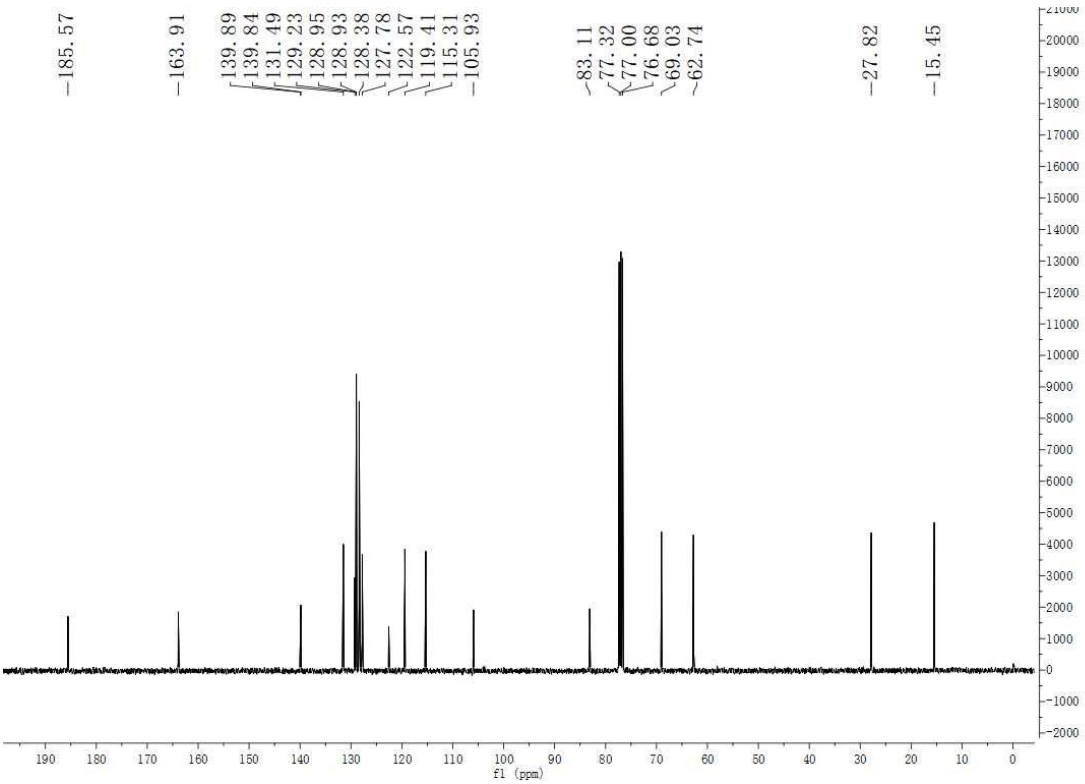


^{1}H NMR and ^{13}C NMR of hex-3-yn-1-yl 3-benzoylindolizine-1-carboxylate (4j)

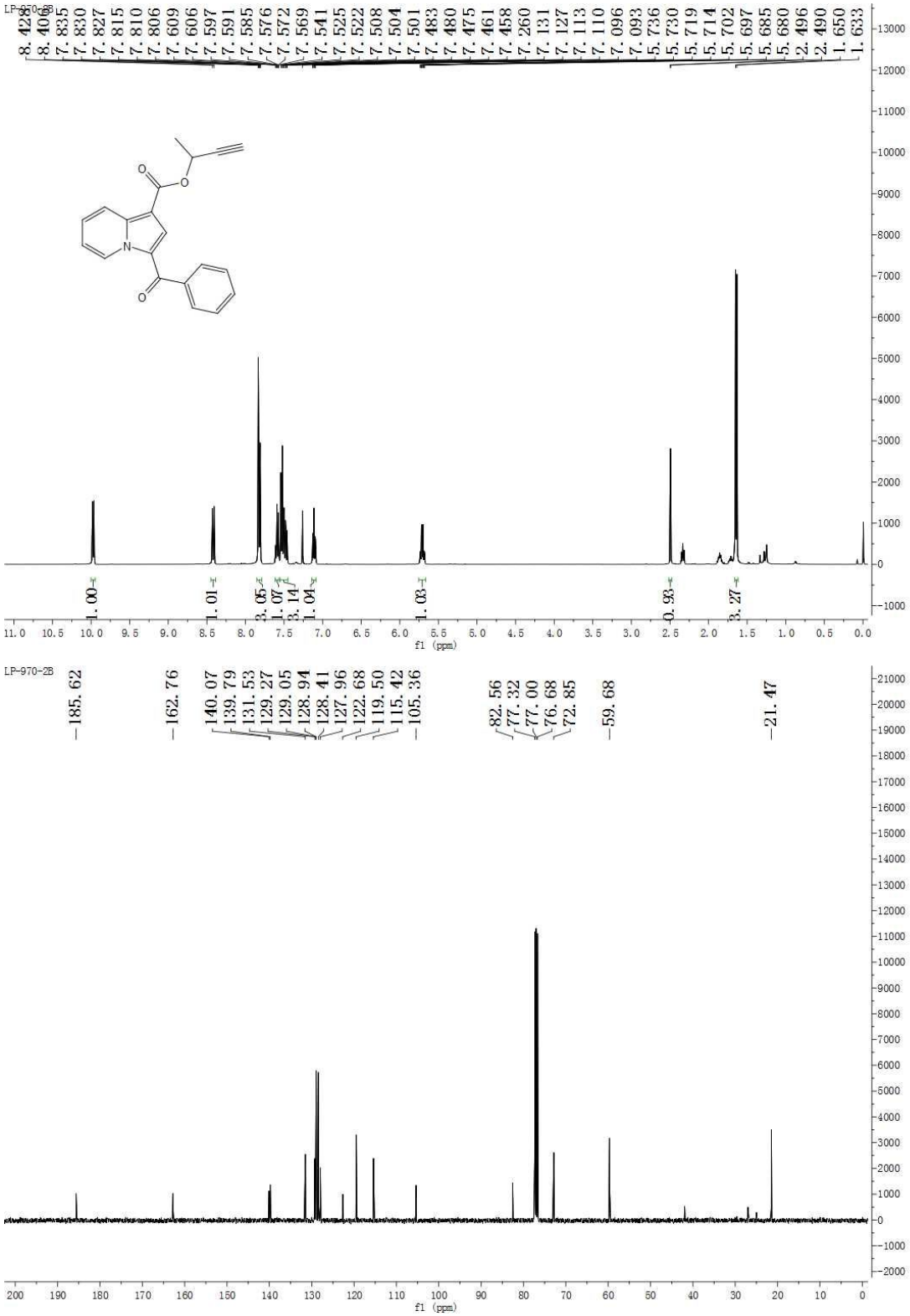


^{1}H NMR and ^{13}C NMR of pent-4-yn-1-yl 3-benzoylindolizine-1-carboxylate (4k)

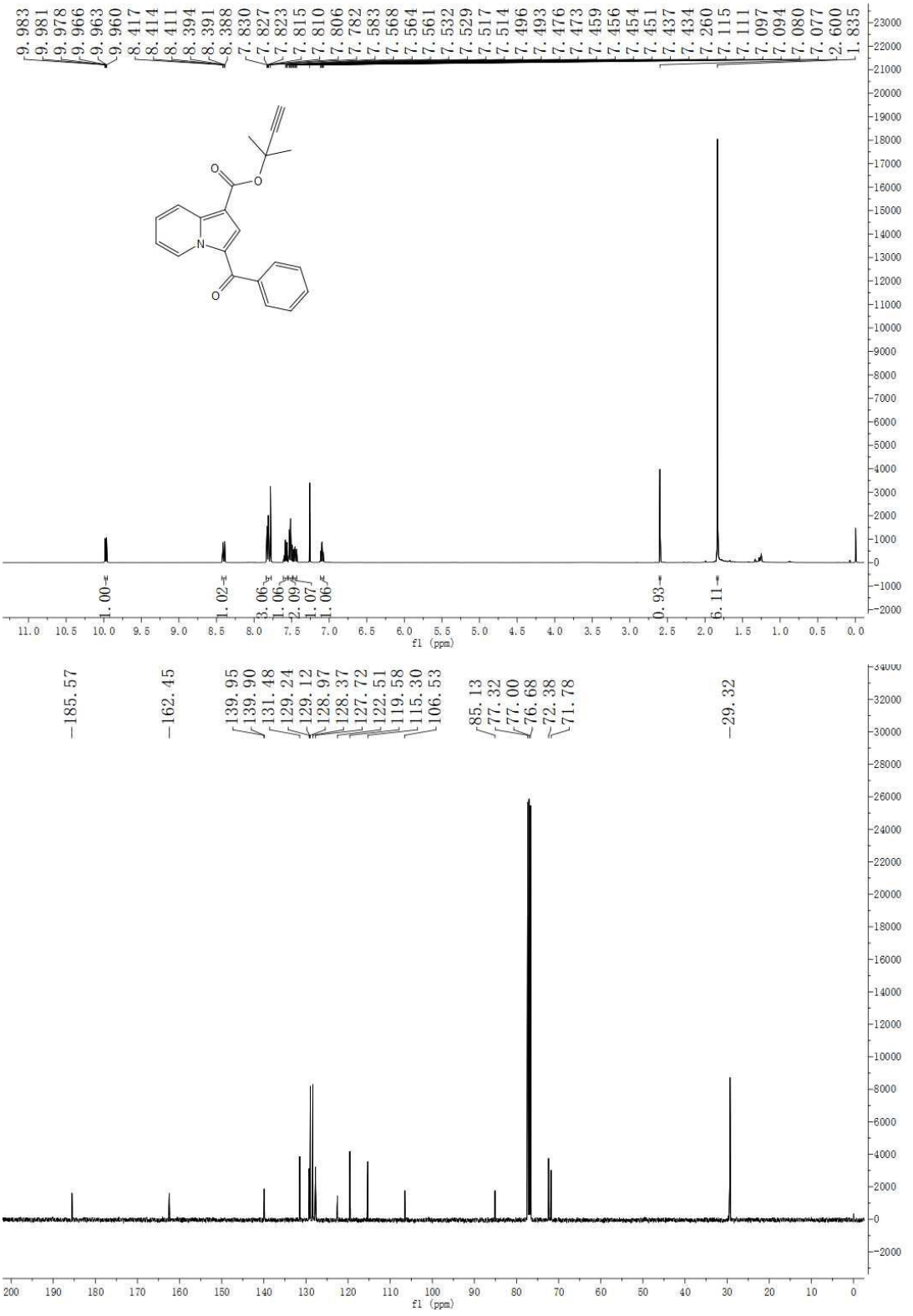




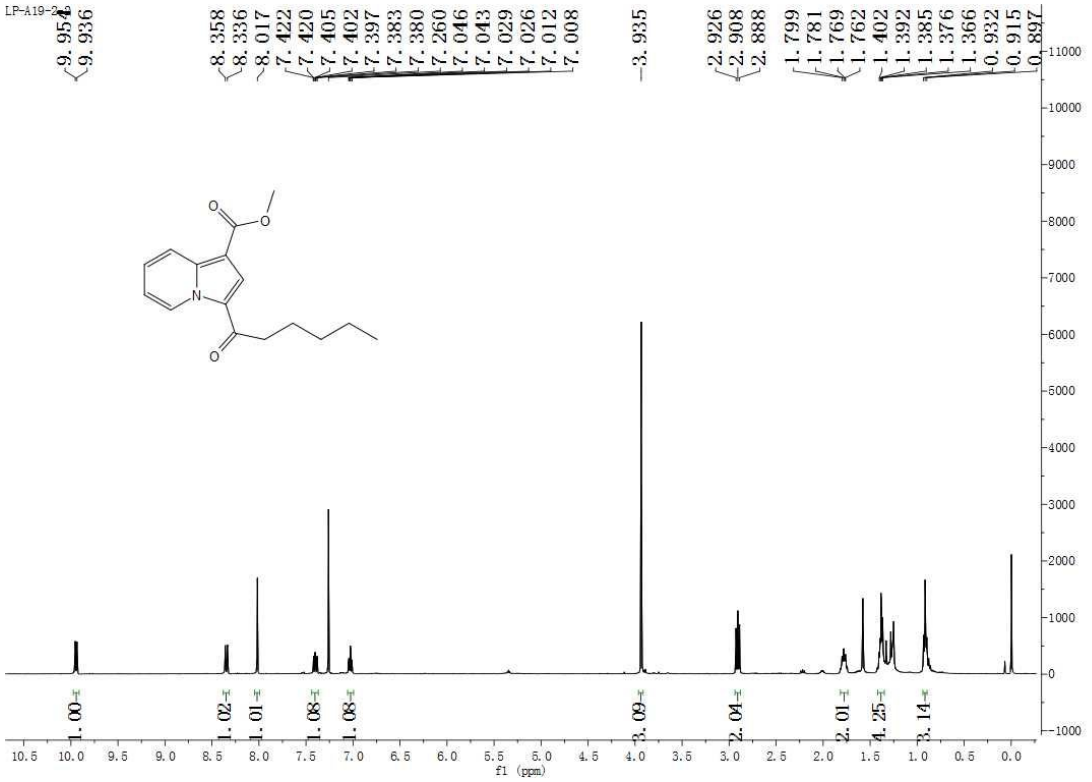
^{1}H NMR and ^{13}C NMR of but-3-yn-2-yl 3-benzoylindolizine-1-carboxylate (4l)

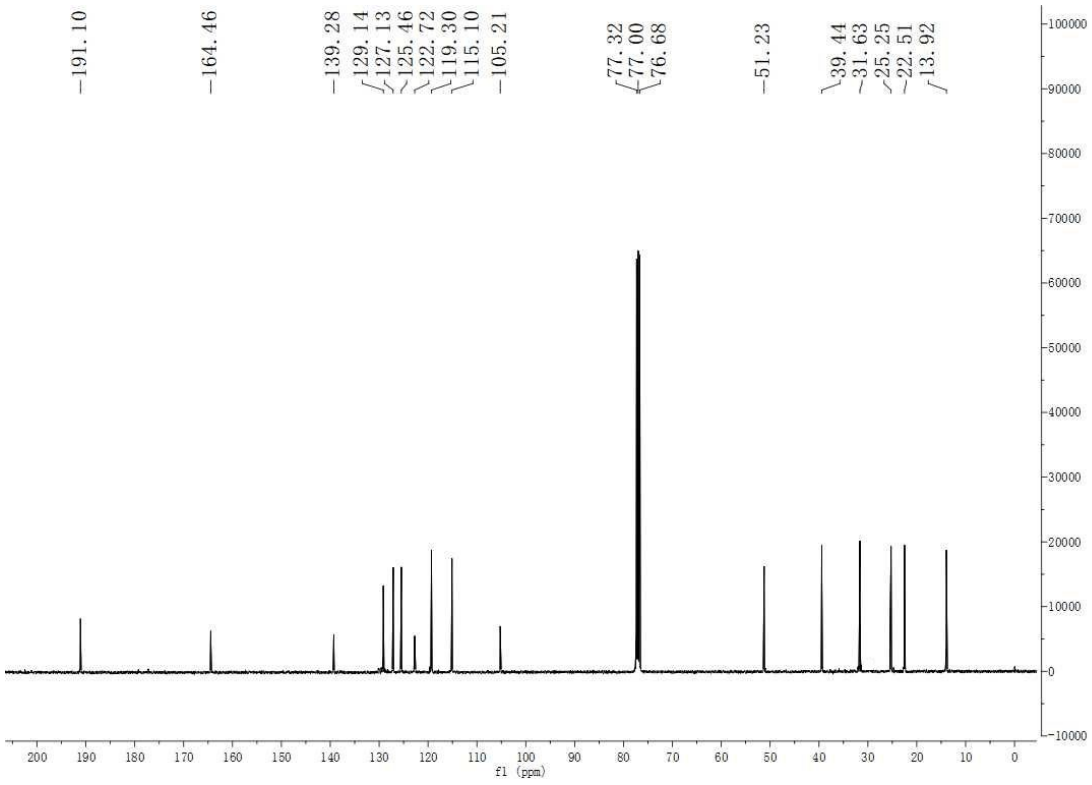


^{1}H NMR and ^{13}C NMR of 2-methylbut-3-yn-2-yl 3-benzoylindolizine-1-carboxylate (4m)

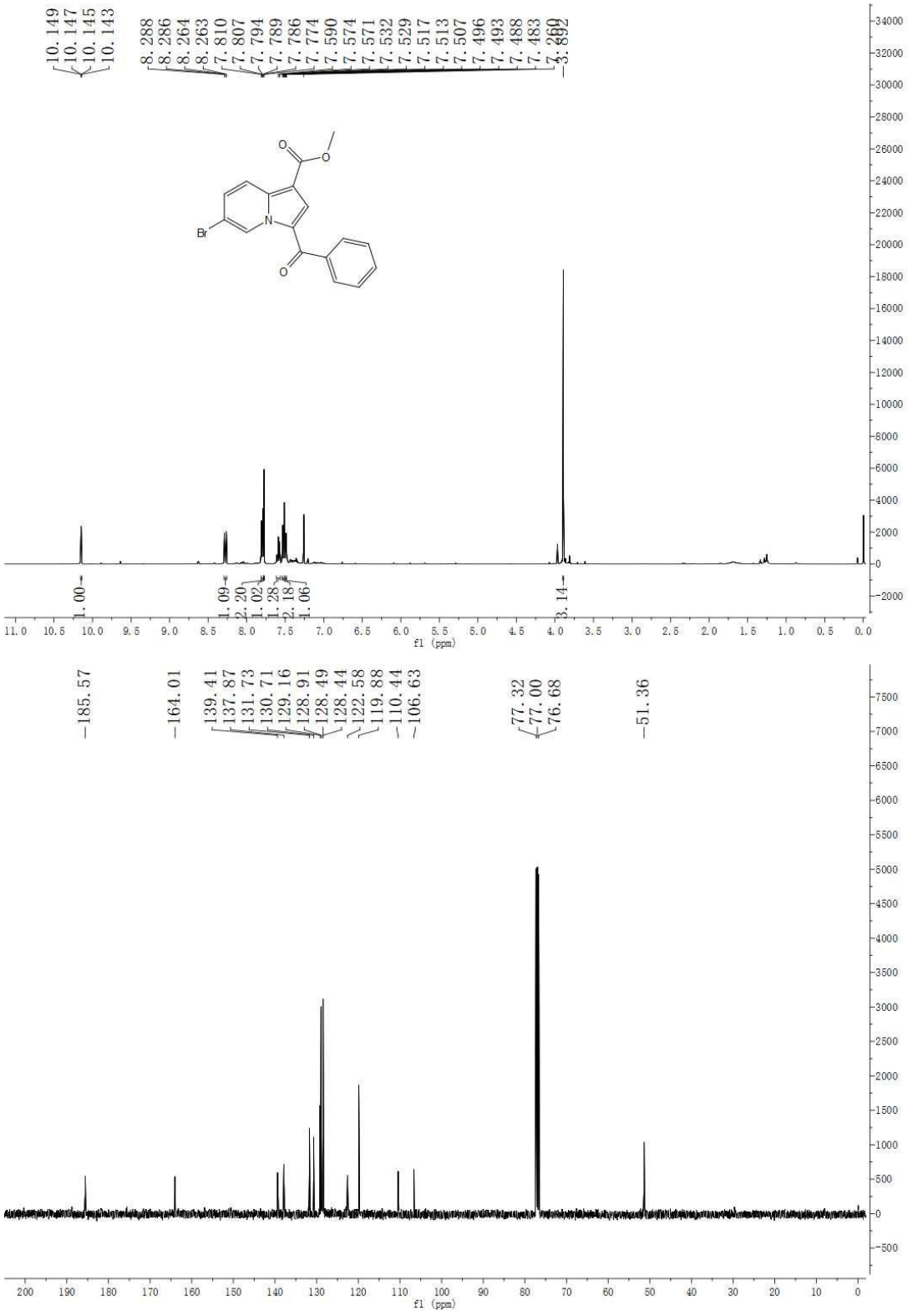


^{1}H NMR and ^{13}C NMR of methyl 3-hexanoylindolizine-1-carboxylate (4n)

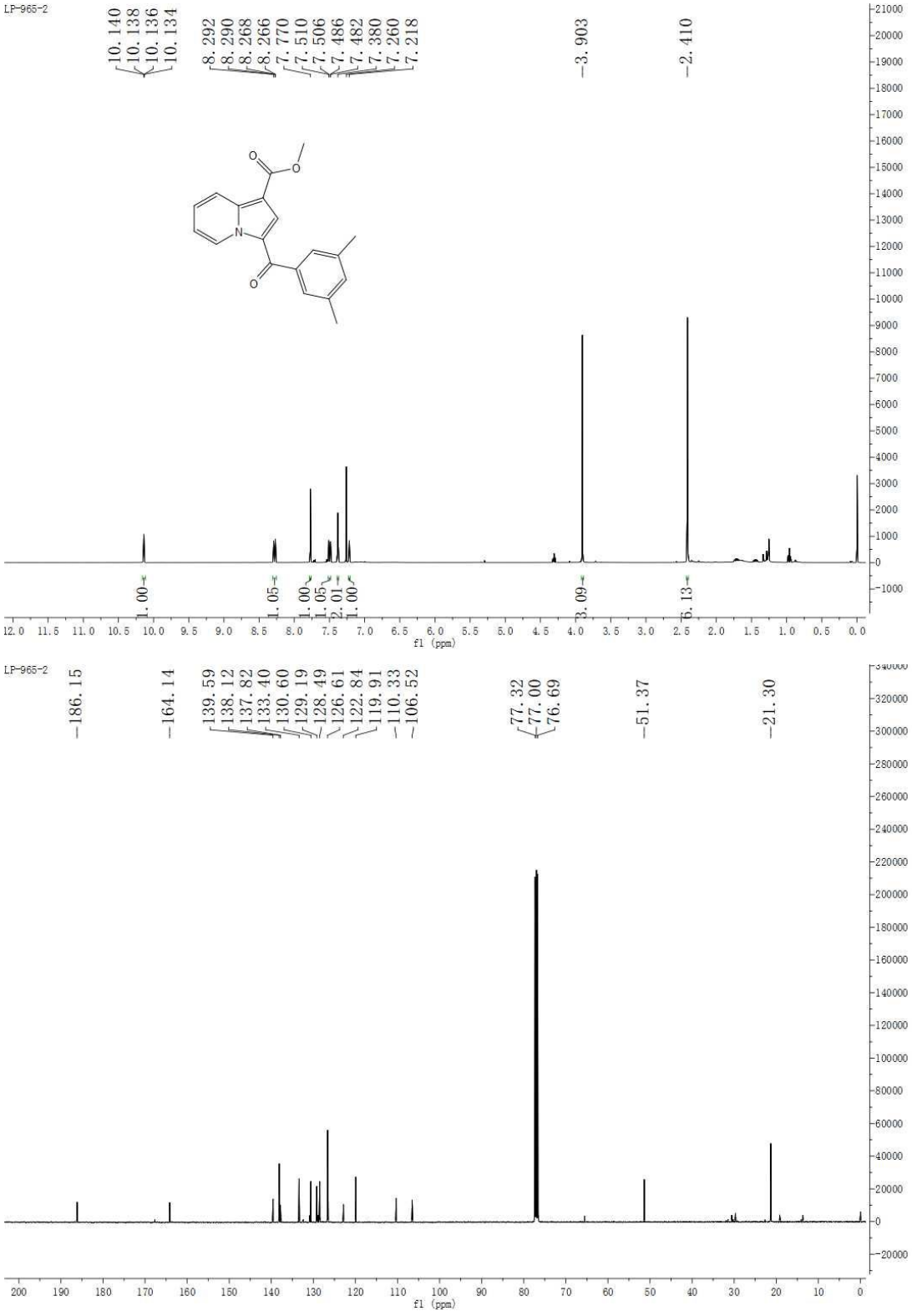




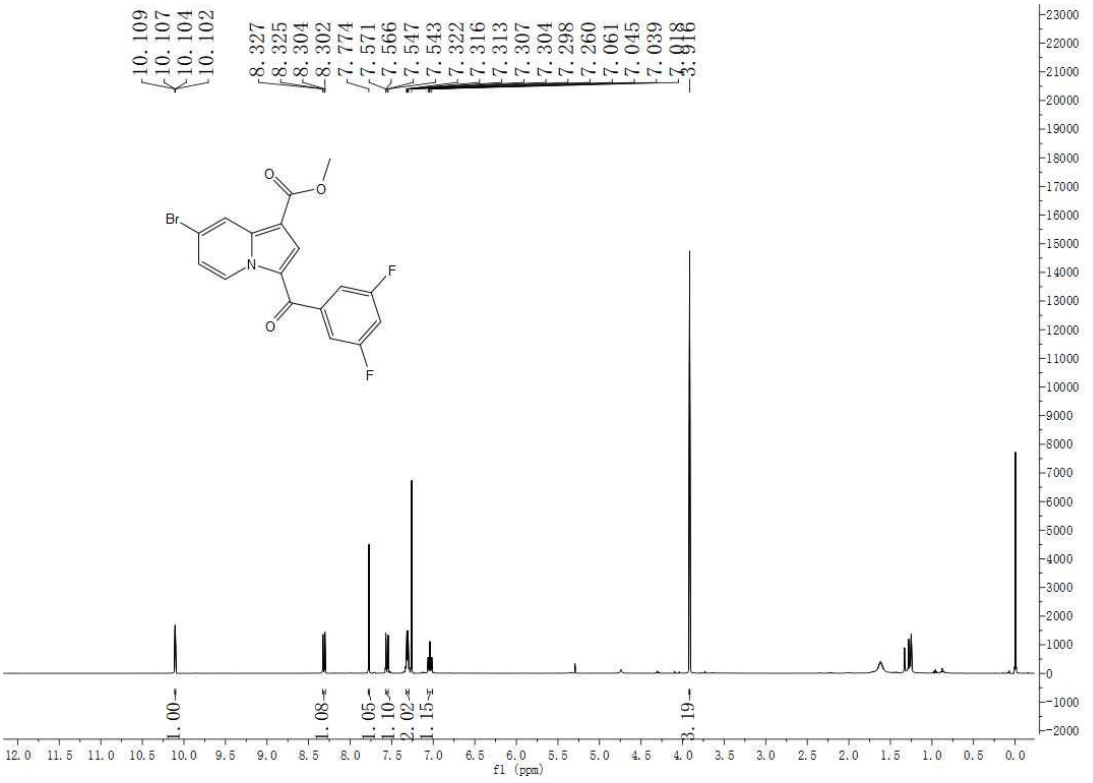
^{1}H NMR and ^{13}C NMR of methyl 3-benzoyl-6-bromoindolizine-1-carboxylate (4o)

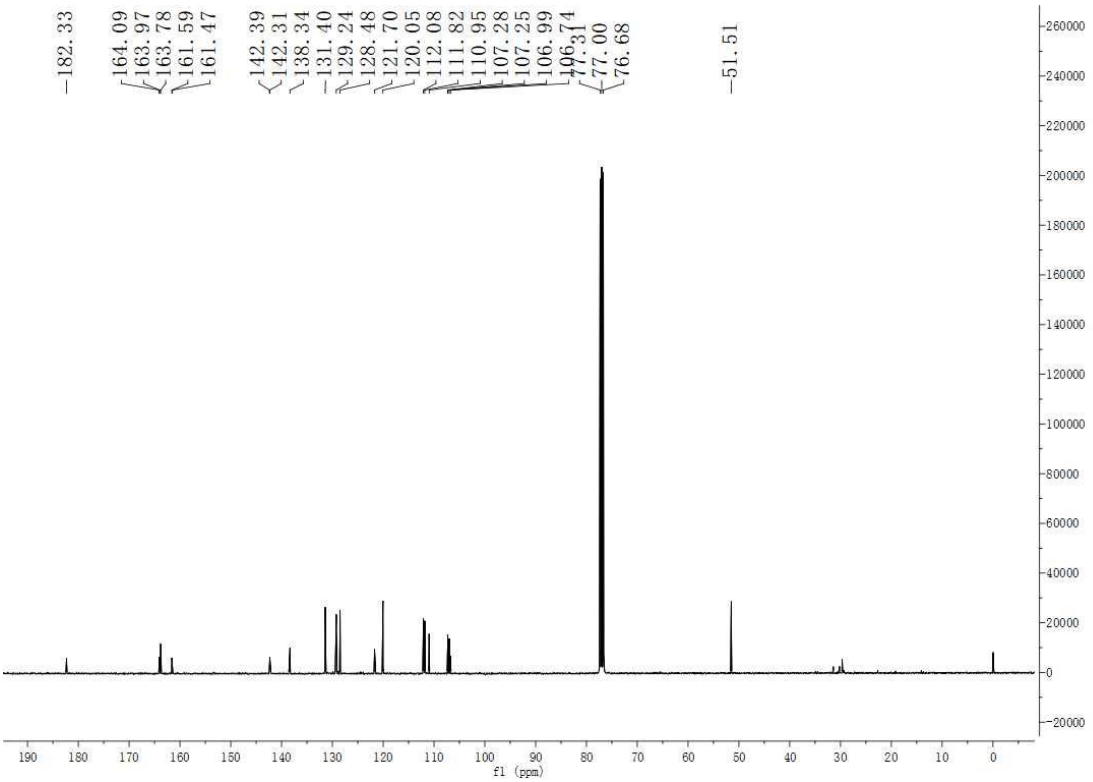


^{1}H NMR and ^{13}C NMR of methyl 6-bromo-3-(3,5-dimethylbenzoyl)indolizine-1-carboxylate (4p)

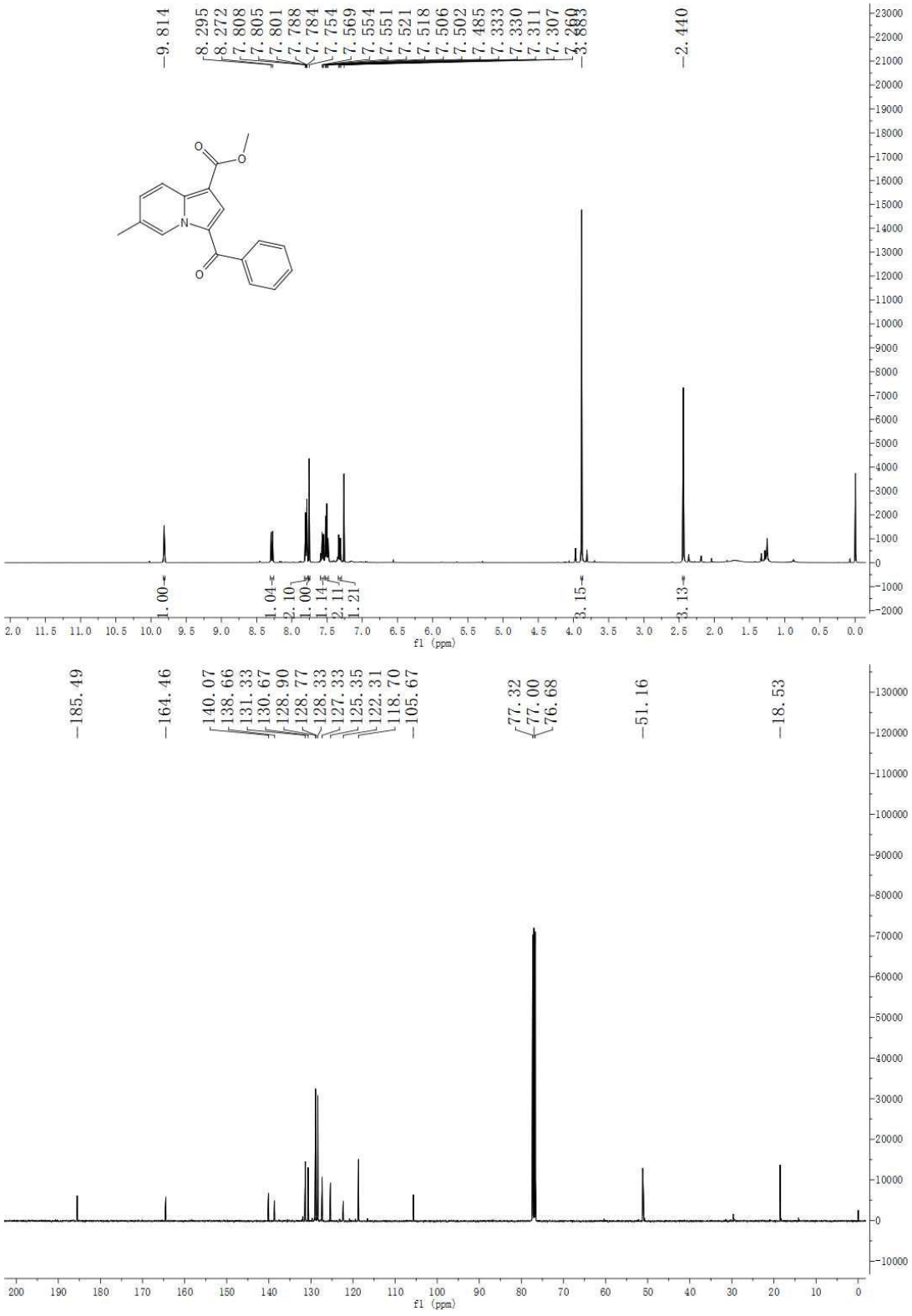


^{1}H NMR and ^{13}C NMR of methyl 6-bromo-3-(3,5-difluorobenzoyl)indolizine-1-carboxylate (4q)

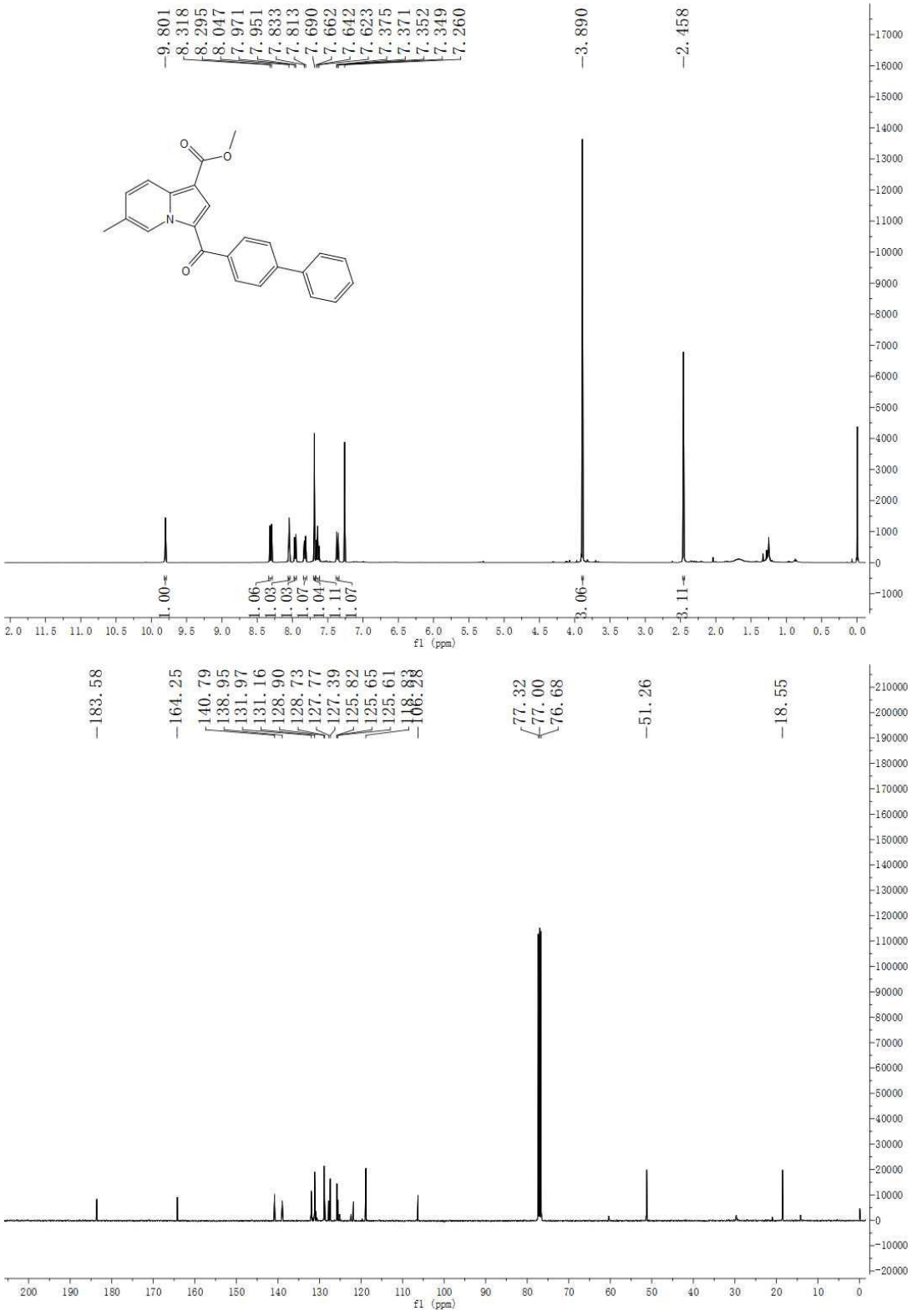




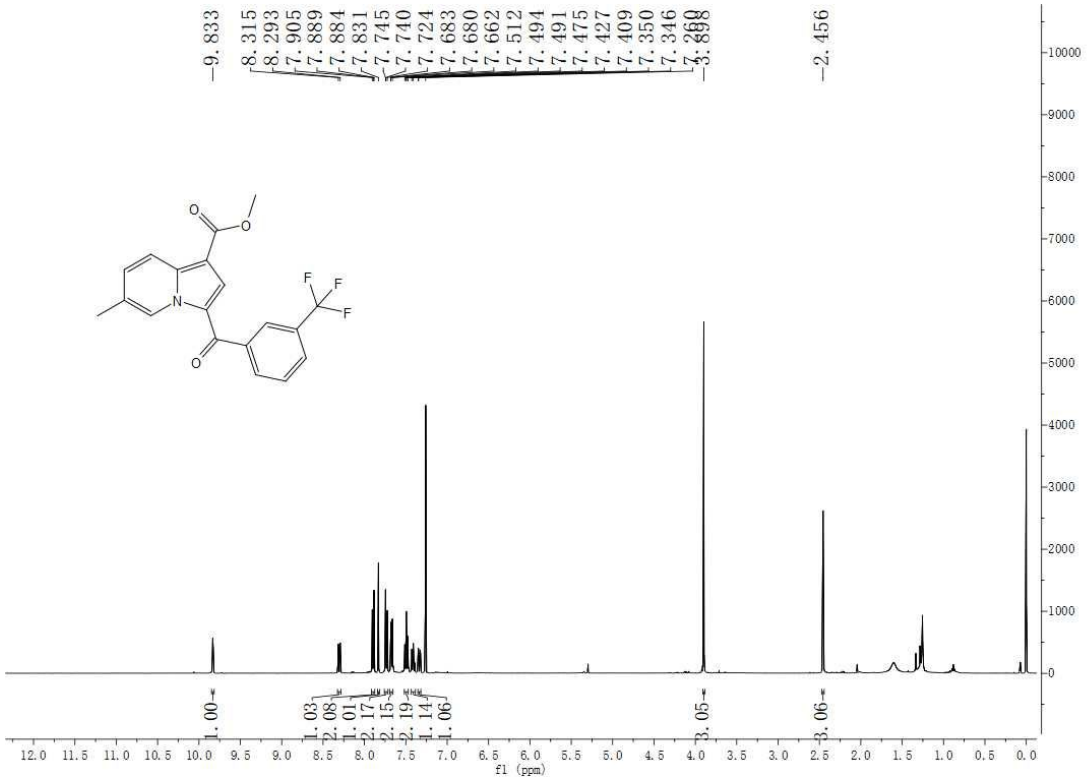
^{1}H NMR and ^{13}C NMR of methyl 3-benzoyl-6-methylindolizine-1-carboxylate (4r)

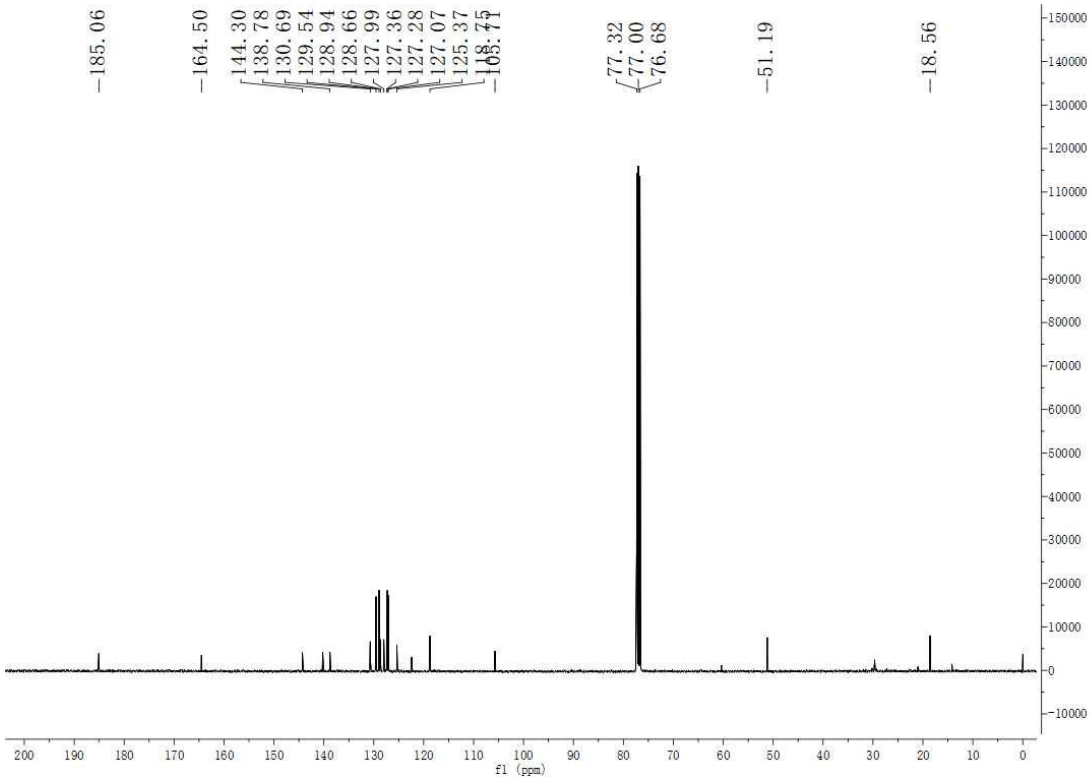


^{1}H NMR and ^{13}C NMR of methyl 3-([1,1'-biphenyl]-4-carbonyl)-6-methylindolizine-1-carboxylate (4s)

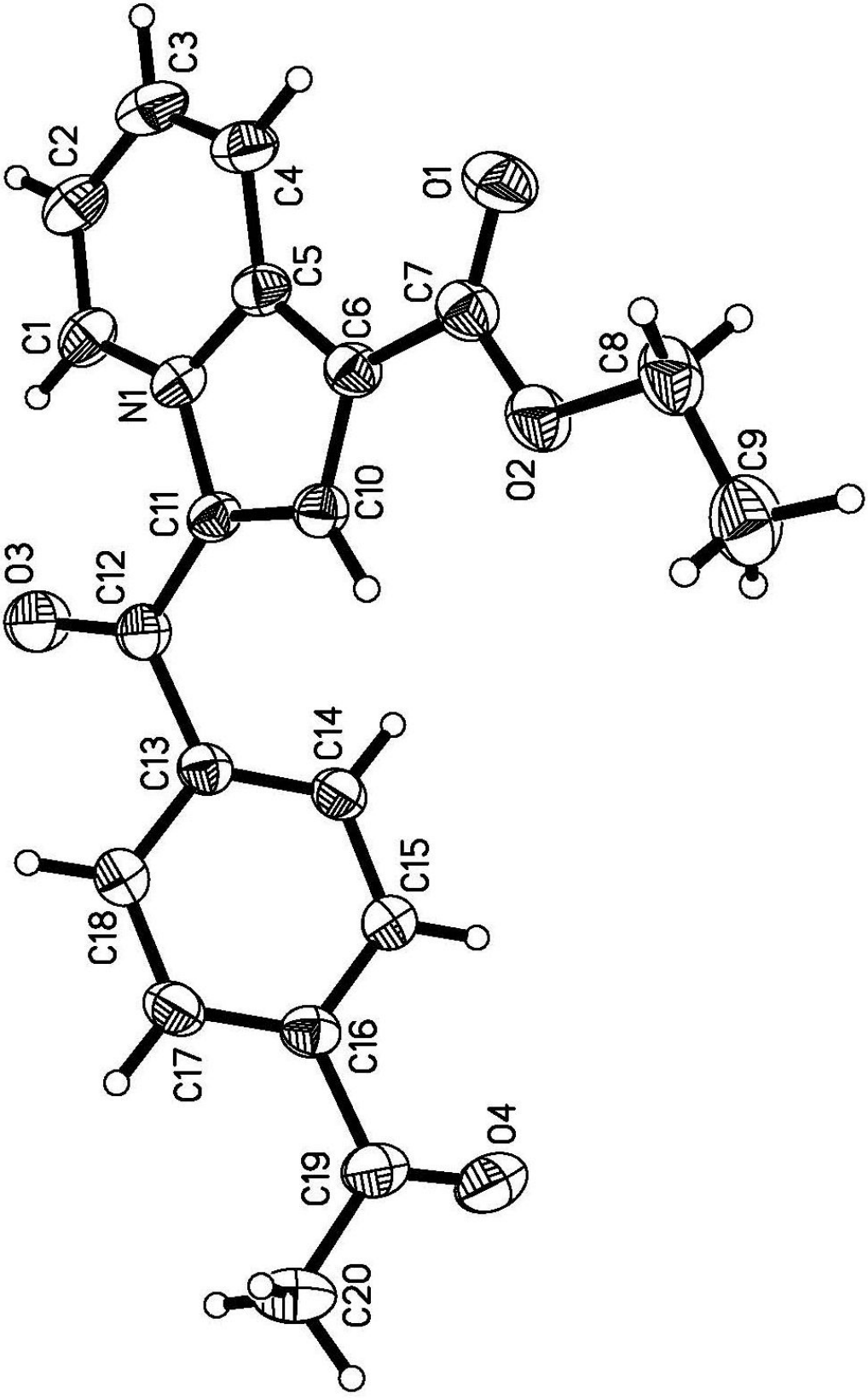


^{1}H NMR and ^{13}C NMR of methyl 6-methyl-3-(3-(trifluoromethyl)benzoyl)indolizine-1-carboxylate (4t)





X-Ray Crystallographic Data



The ORTEP diagram of **3r** (thermal ellipsoids are shown at 30% probability)

Sample Preparation: A crystalline solid was obtained via slow evaporation of compound **3r** in EA: hexane= 1: 4 at room temperature.

Crystal data and structure refinement for compound **3r** (CCDC: 1874168)

Table 1 Crystal data and structure refinement for 3r.

Identification code	3r
Empirical formula	$C_{20}H_{17}NO_4$
Formula weight	335.35
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.5751(6)
b/Å	15.3923(12)
c/Å	14.2928(13)
α/°	90
β/°	90.148(8)
γ/°	90
Volume/Å^3	1666.5(2)
Z	4
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	0.094
F(000)	704.0
Crystal size/mm^3	0.22 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.548 to 52.744
Index ranges	$-9 \le h \le 9$, $-19 \le k \le 19$, $-17 \le l \le 17$
Reflections collected	13541
Independent reflections	3407 [R_{int} = 0.0293, R_{sigma} = 0.0275]
Data/restraints/parameters	3407/0/228
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0549, wR_2 = 0.1247
Final R indexes [all data]	R_1 = 0.0733, wR_2 = 0.1368
Largest diff. peak/hole / e Å^{-3}	0.17/-0.24