Supplementary Information

The Formal [3+2] Reaction of α,α-Diaryl Allylic Alcohols with *Sec*-Alcohols: Proceeding with Sequential Radical Addition/Migration toward 2,3-Dihydrofurans Bearing Quaternary Carbon Centers

Weiming Hu, Song Sun and Jiang Cheng *

School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, Jiangsu Province Key Laboratory of Fine Petrochemical Engineering, Changzhou University, Changzhou 213164, P. R. China.

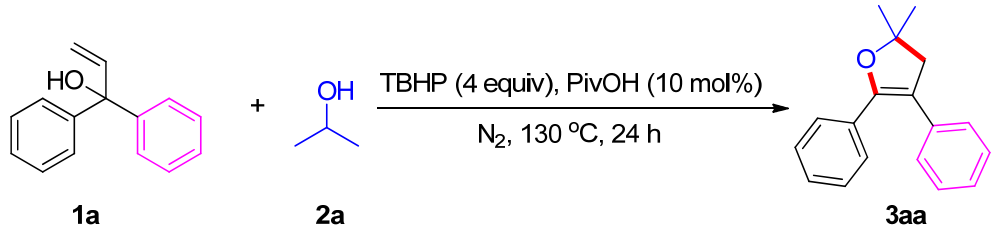
Email: jiangcheng@cczu.edu.cn

Table of Contents

1. Research of Mechanism

1.1 Free radical capture experiments

General procedure:



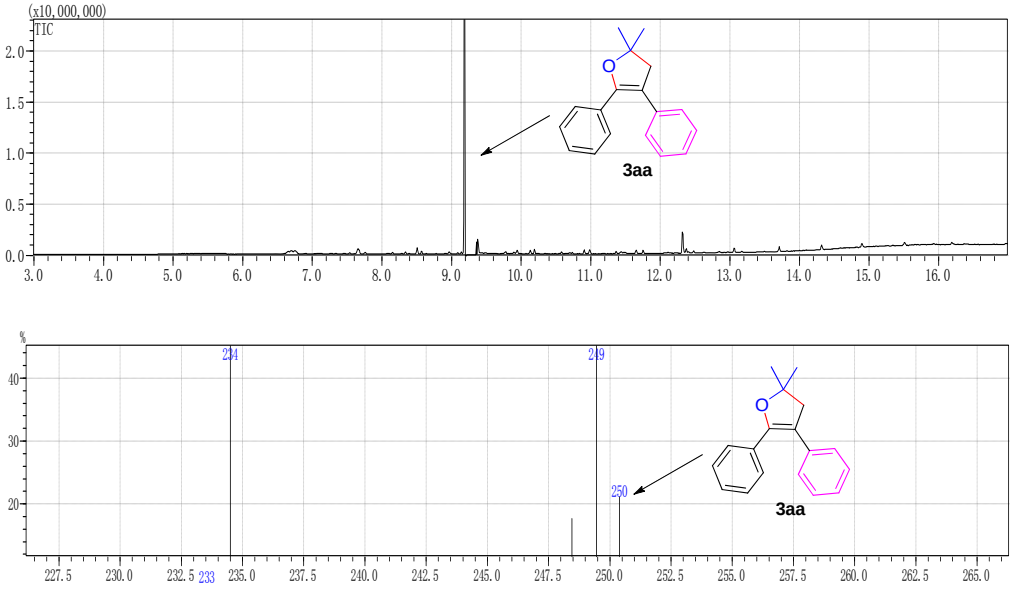
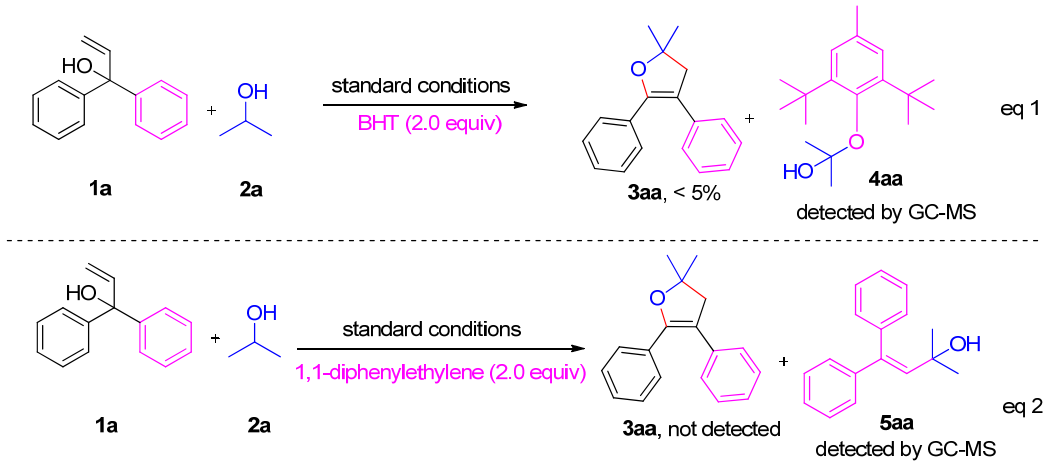


Fig S1 Detection of 3aa by GC-MS

Add 2.0 equiv of radical-trapping reagents to the reaction mixture

Under N_2, a 20 mL of Schlenk tube equipped with a stir bar was charged with **1a** (0.2 mmol), *tert*-butyl hydroperoxide (0.8 mmol), pivalic acid (2.04 mg, 10 mol%), 2,6-di-*tert*-butyl-4-methylphenol (BHT) or 1,1-diphenylethylene (2.0 equiv), isopropanol **2a** (2.0 mL). The tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at 130 °C for 24 h in oil bath. The reaction mixture was analyzed using GC-MS spectrometer, as shown in Figure S2 and Figure S3.

Scheme S1 Free radical capture experiments



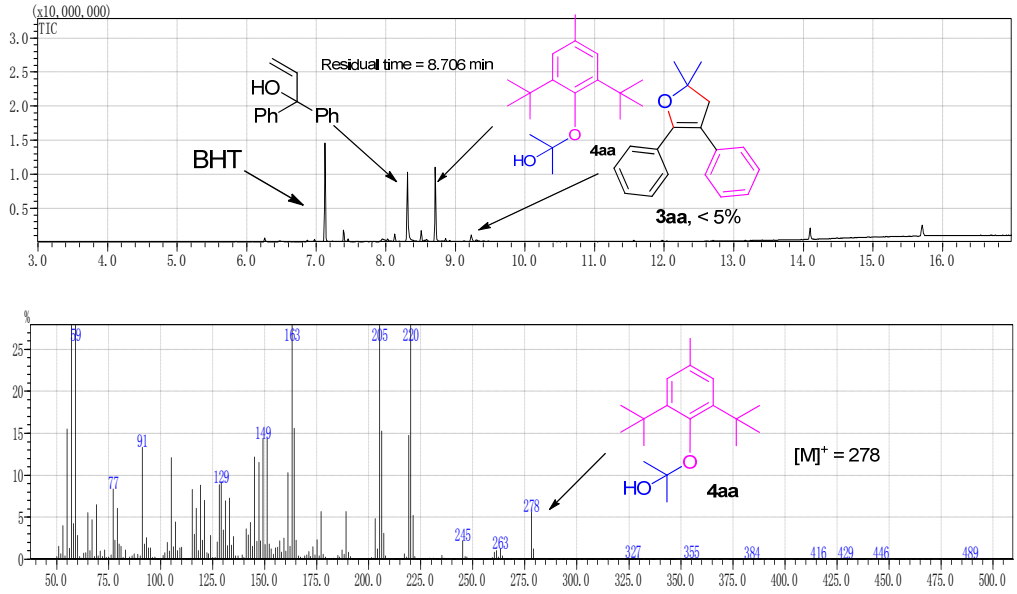
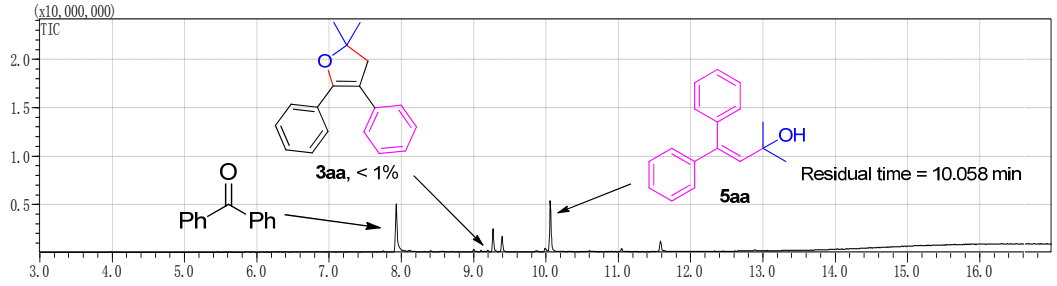


Fig S2 Detection of the adduct 4aa by GC-MS.



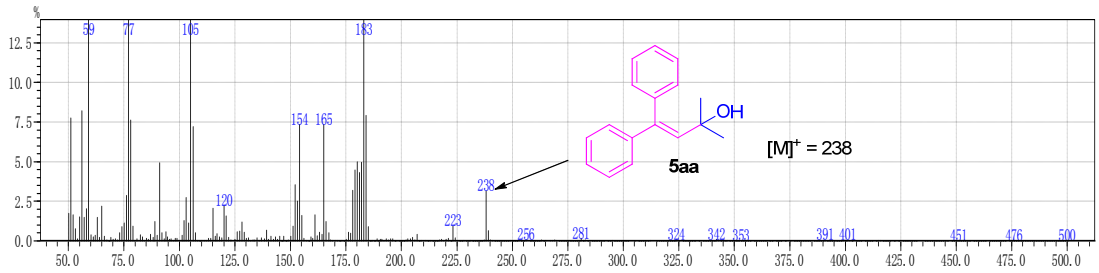
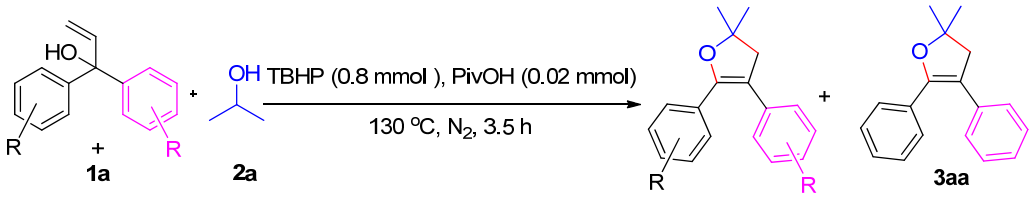


Fig S3 Detection of the adduct 5aa by GC-MS.

1.2 Competitive Experiments

In order to investigate deeply mechanism of the electronic effect, the competition experiments were conducted by using substrates of **3aa** and substituted **R-3aa** (1:1 molar ratio) under standard conditions with low conversion for 3.5 h. The ratios of **3aa** and **R-3aa** were analyzed by ^{1}H NMR (Figure S4). The results were listed (Scheme S2).

Scheme S2 Competitive Experiments



R = *p*-Me : **3aa** + **3ba** = 21 % yield
3ba : **3aa** = 0.4 : 1

R = *m*-CF_3 : **3aa** + **3fa** = 19 % yield
3fa : **3aa** = 1.4 : 1

The result indicated that the substrate with electron-withdrawing group was prone to promote this transformation.

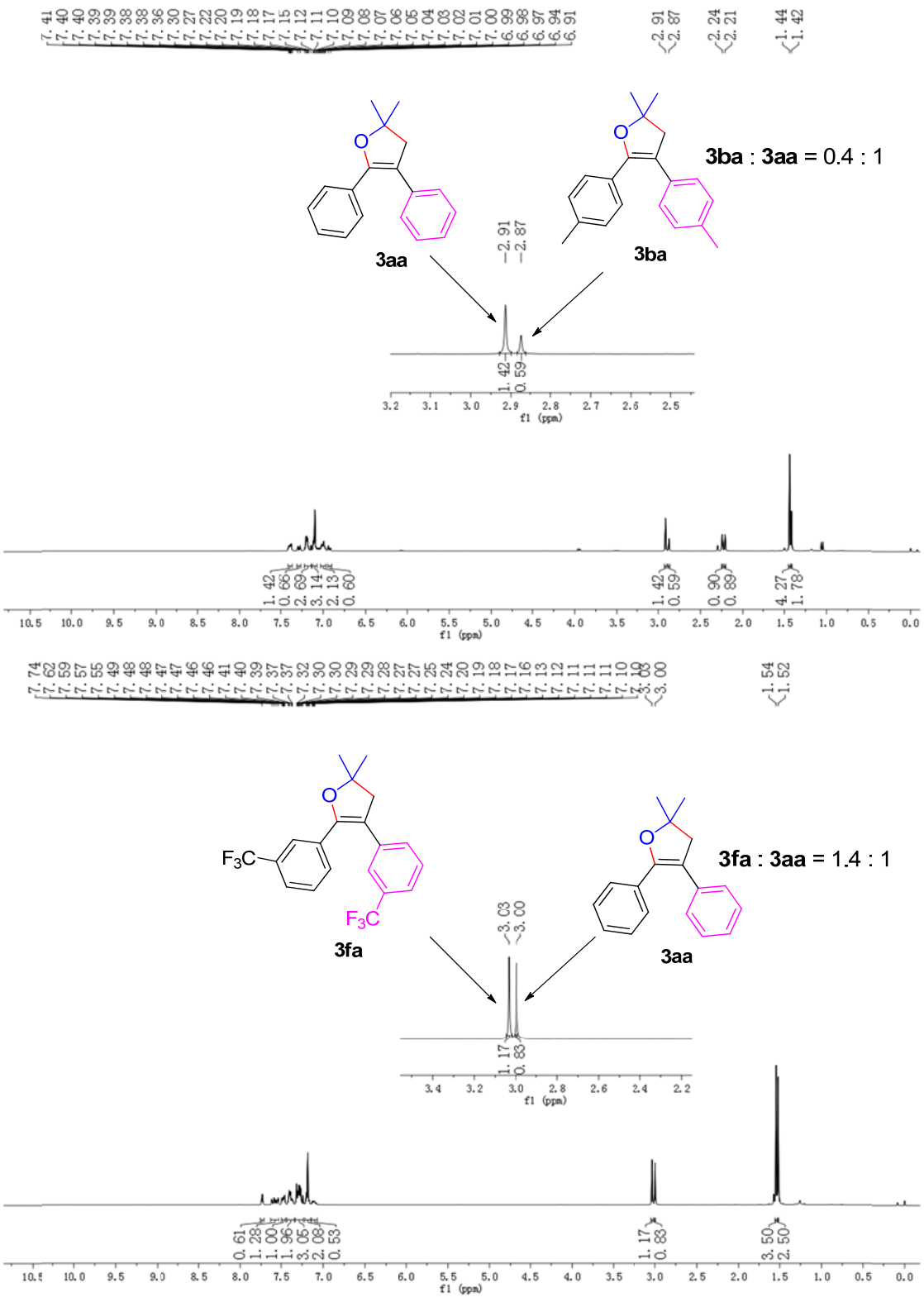


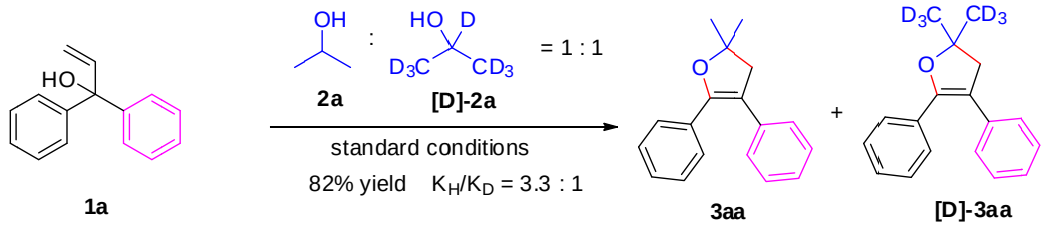
Figure S4 ^{1}H NMR spectra of 3aa and R-3aa

1.3 The KIE Experiment

Under N_2, a 20 mL of Schlenk tube equipped with a stir bar was charged with **1a** (0.2 mmol), *tert*-butyl hydroperoxide (0.8 mmol), pivalic acid (2.04 mg, 10 mol%),

isopropanol **2a** (1.0 mL), isopropanol-d7 **[D]-2a** (1.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 130 °C for 24 h in oil bath. After the completion of the reaction, the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc(100 : 1) as the eluent to give the desired product.

Scheme S3 The KIE Experiment



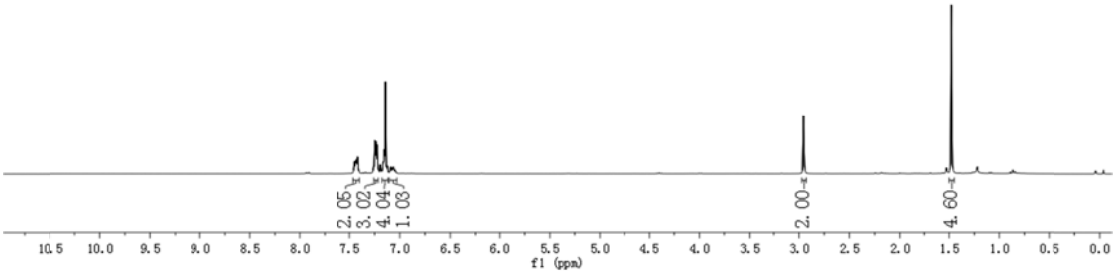
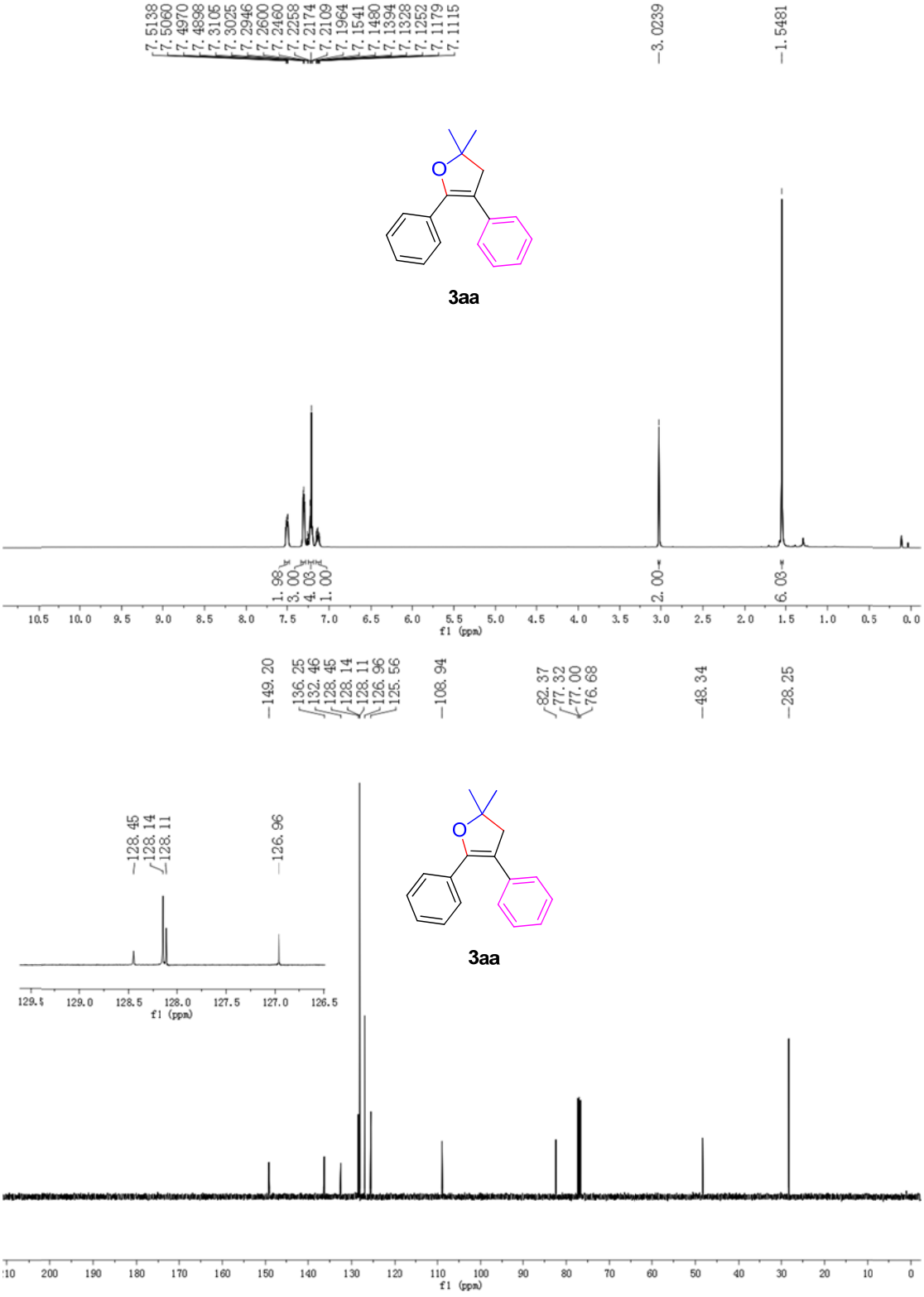


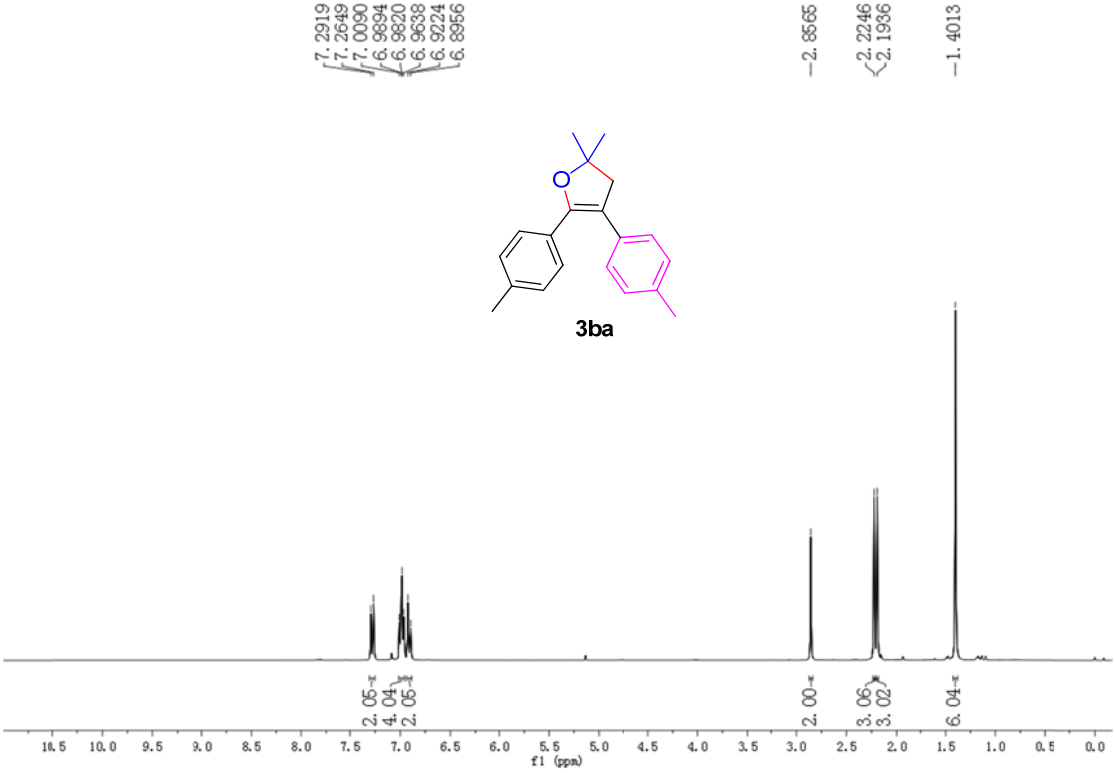
Figure S5 ^{1}H NMR spectrum of the mixture of 3aa and [D]-3aa

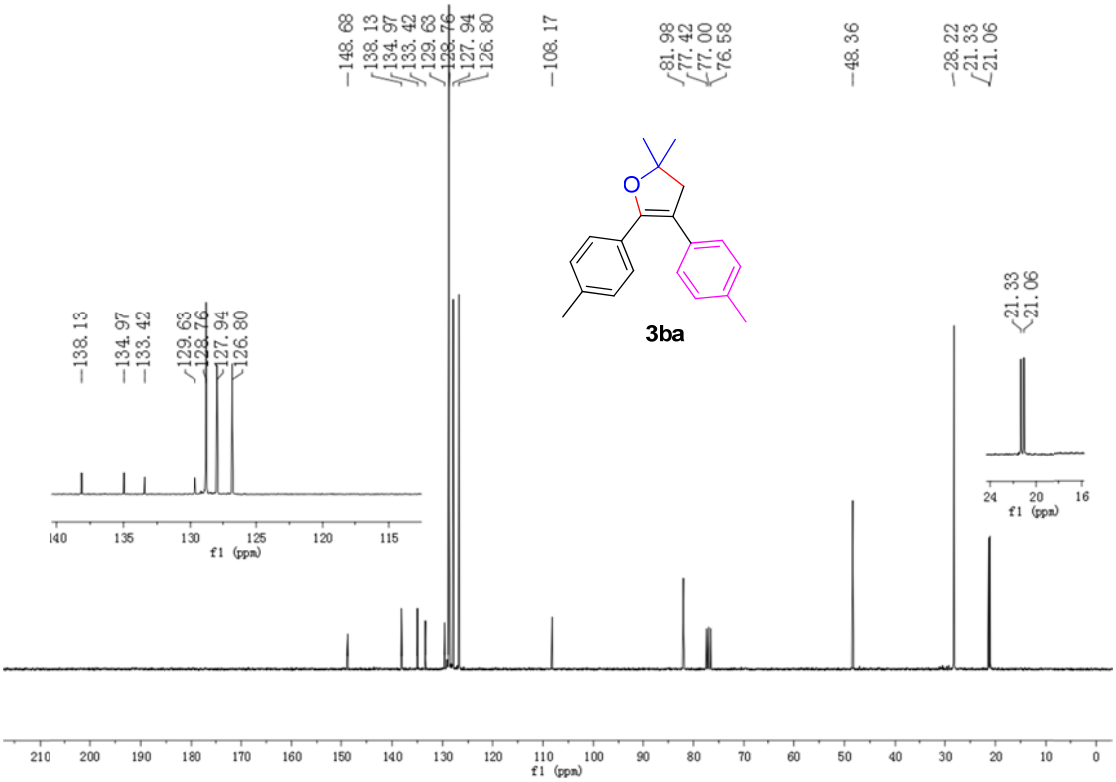
2. Copies of the ^{1}H NMR, ^{13}C NMR (DEPT) and ^{19}F NMR Spectra

2,2-dimethyl-4,5-diphenyl-2,3-dihydrofuran (3aa)

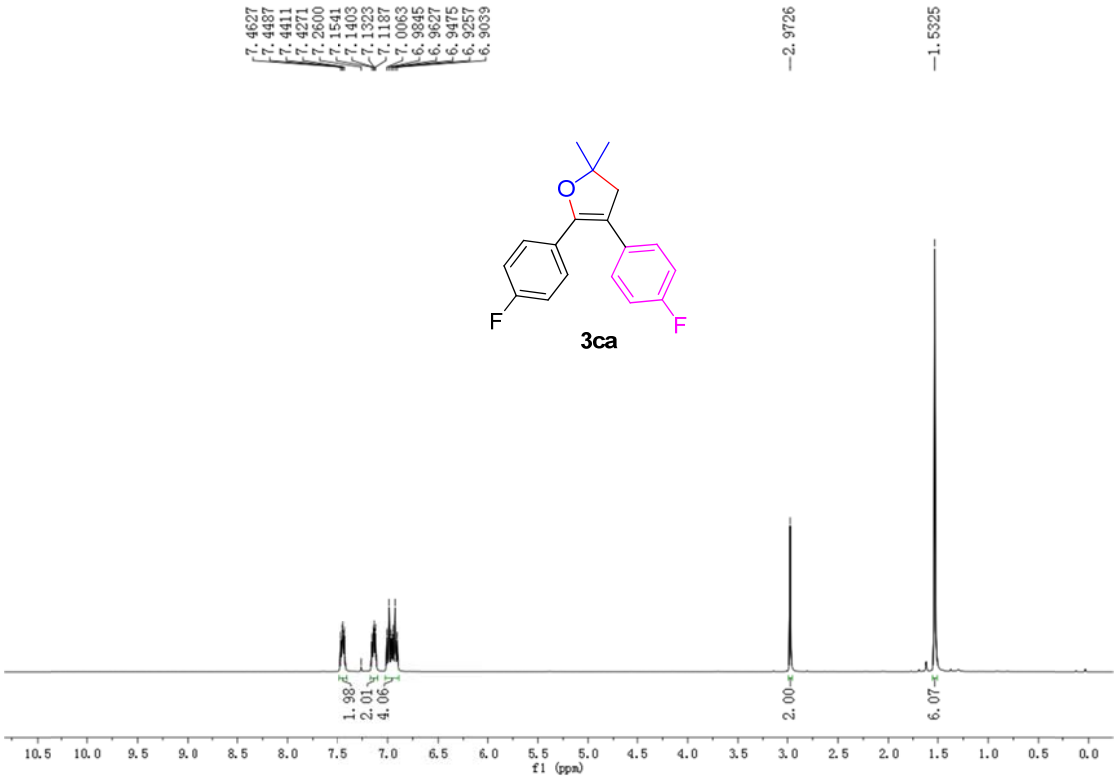


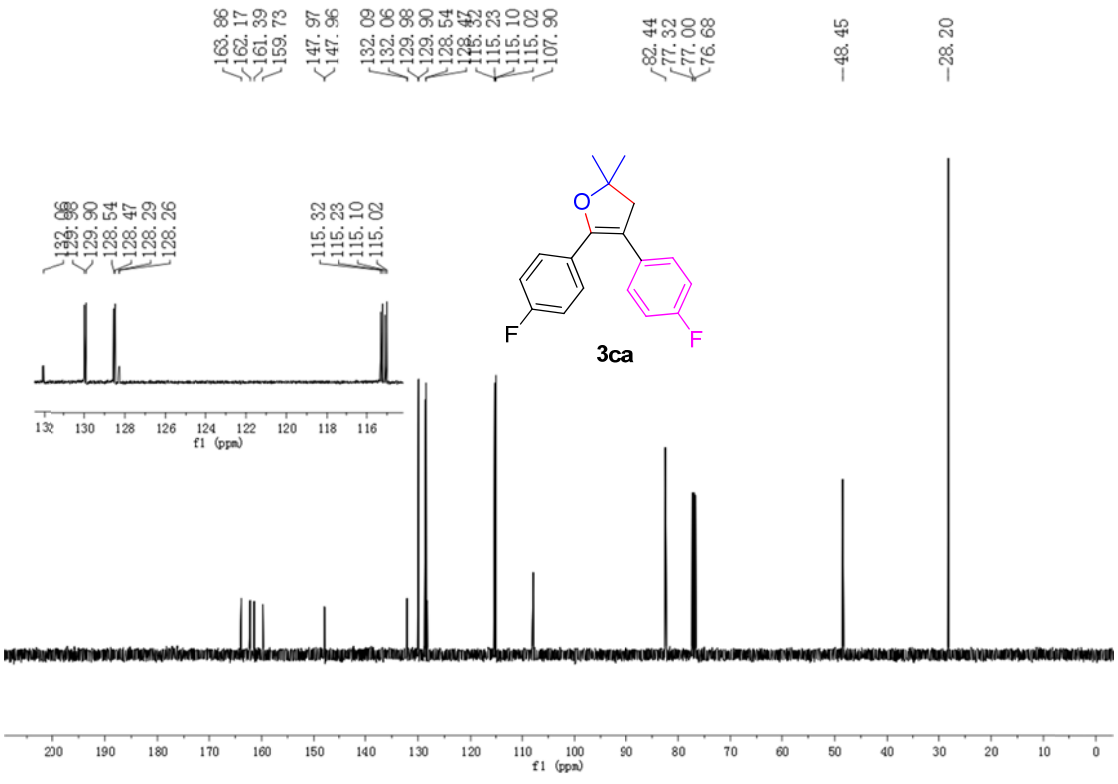
2,2-dimethyl-4,5-di-p-tolyl-2,3-dihydrofuran (3ba)



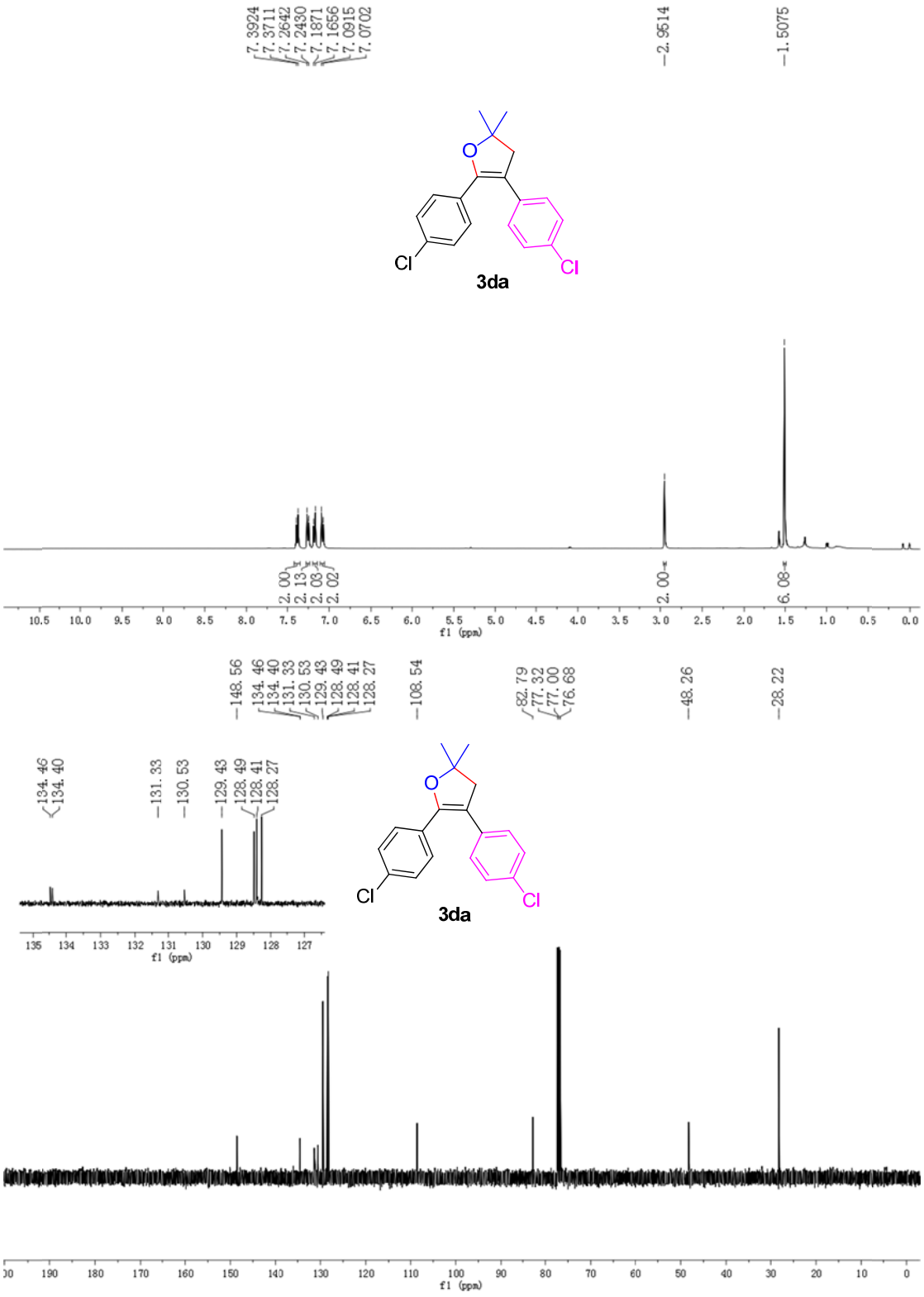


4,5-bis(4-fluorophenyl)-2,2-dimethyl-2,3-dihydrofuran (3ca)

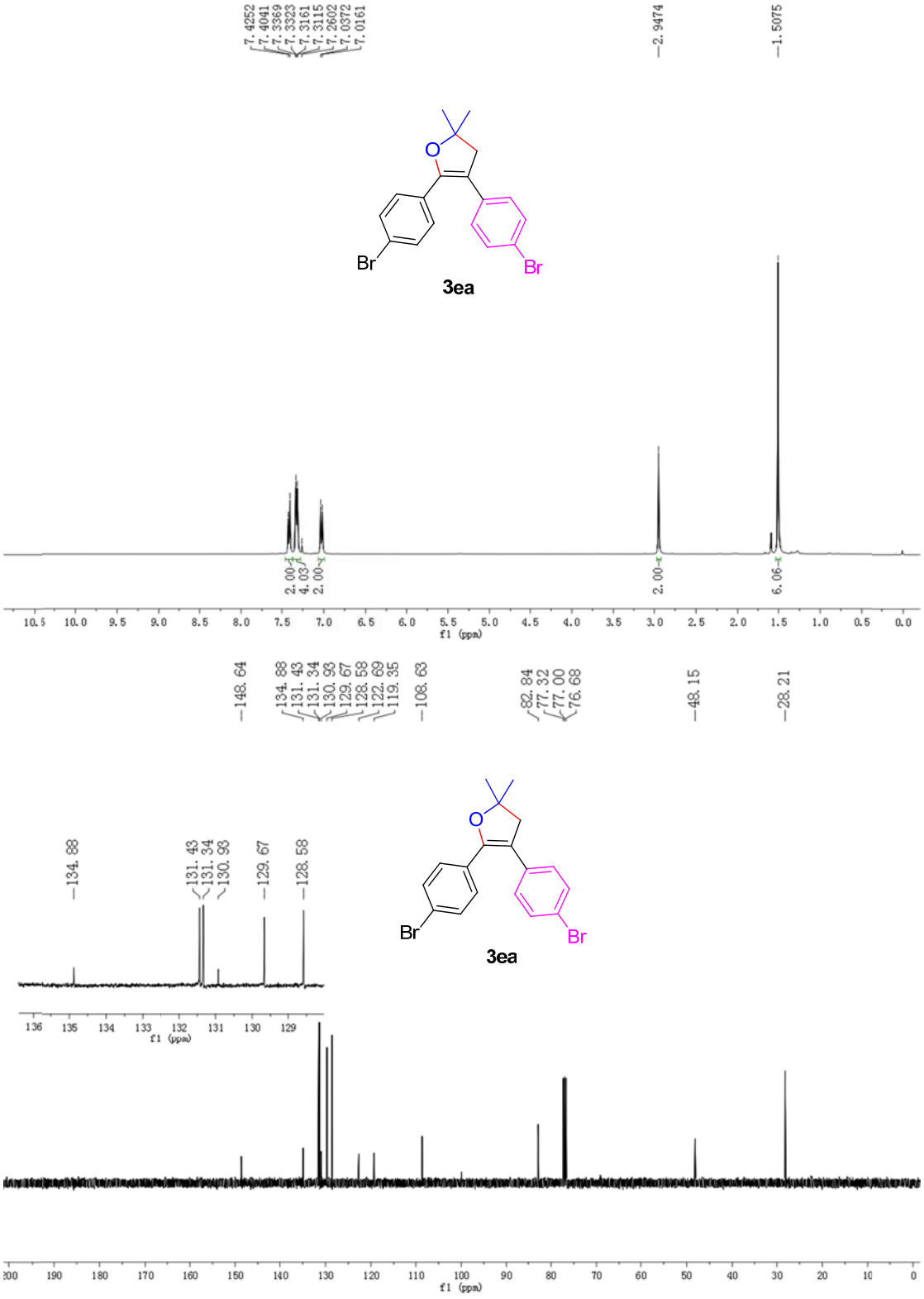


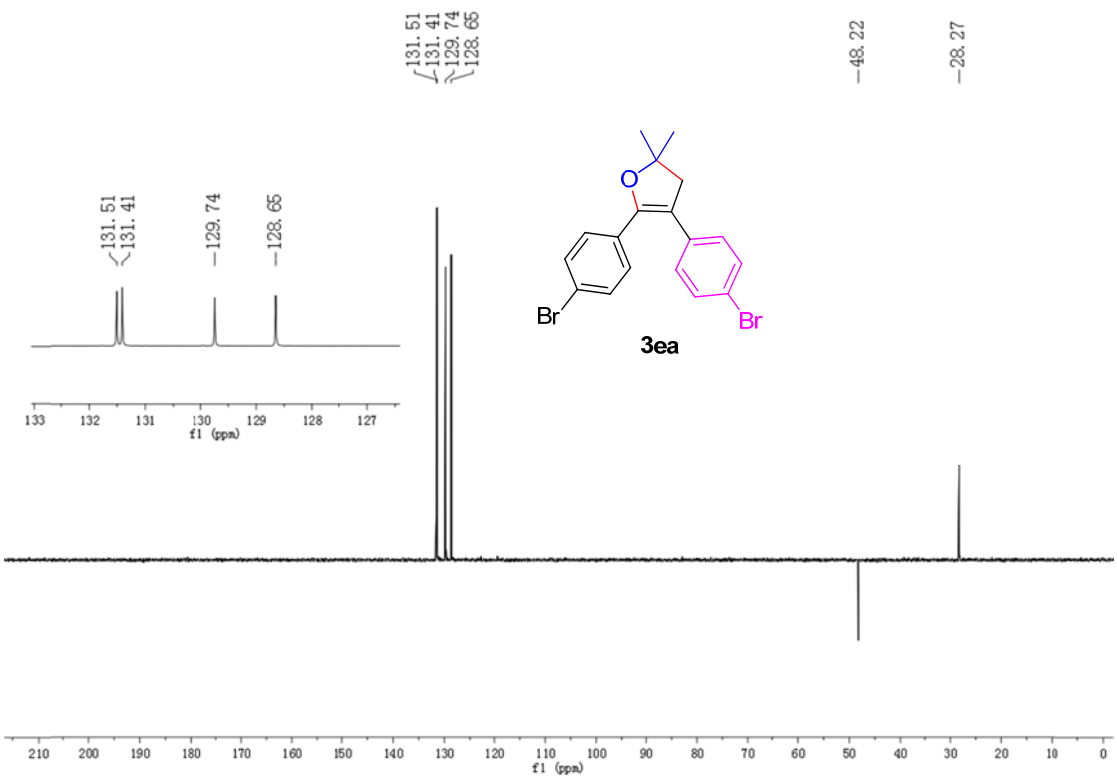


4,5-bis(4-chlorophenyl)-2,2-dimethyl-2,3-dihydrofuran (3da)

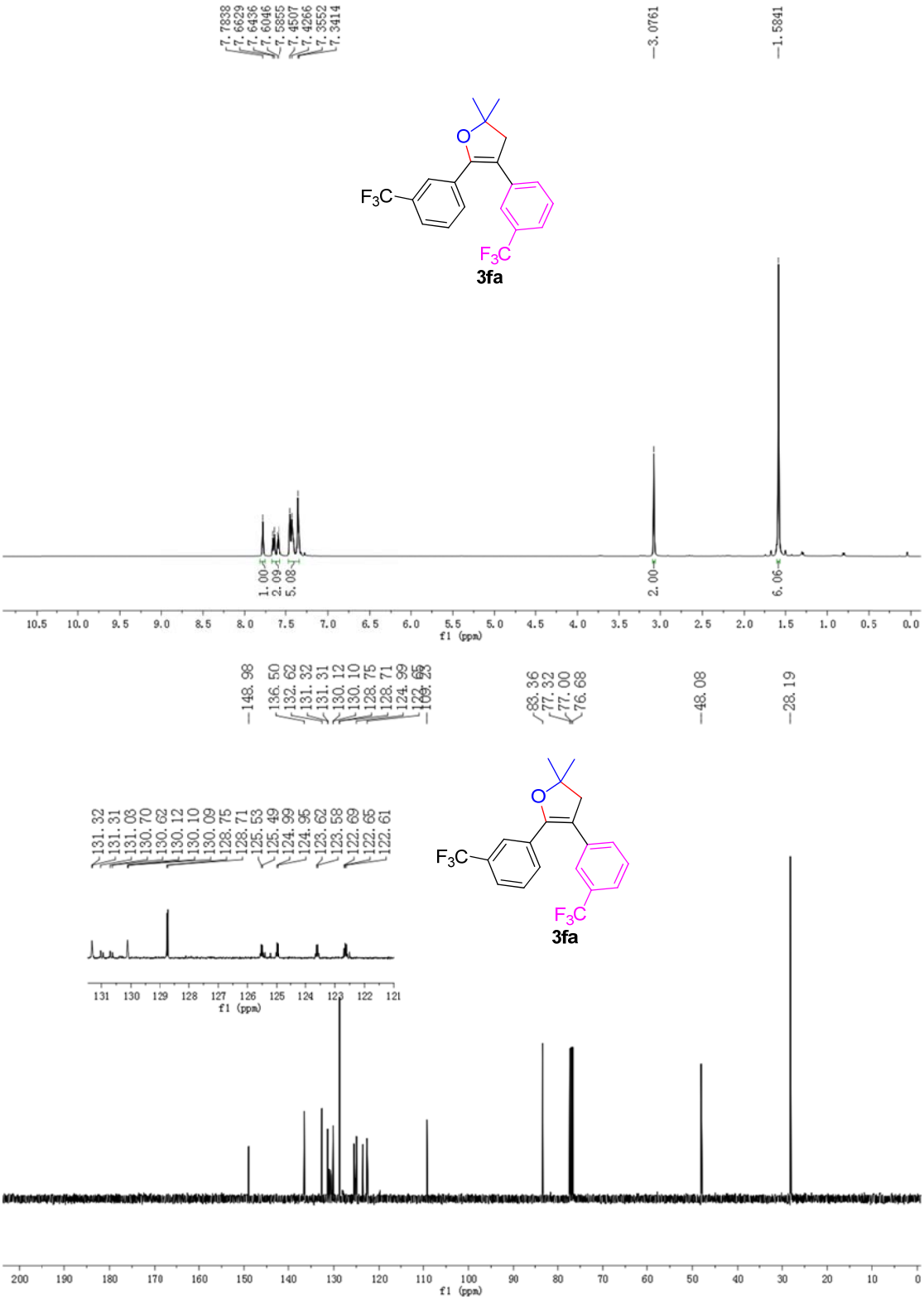


4,5-bis(4-bromophenyl)-2,2-dimethyl-2,3-dihydrofuran (3ea)

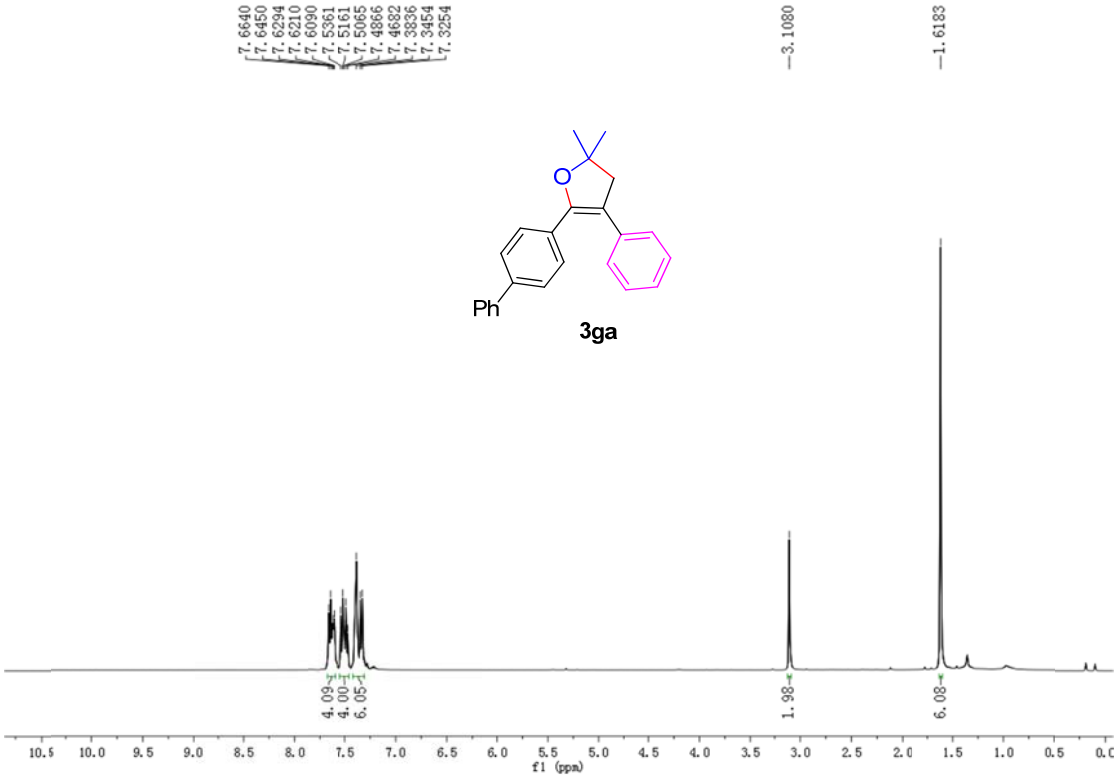


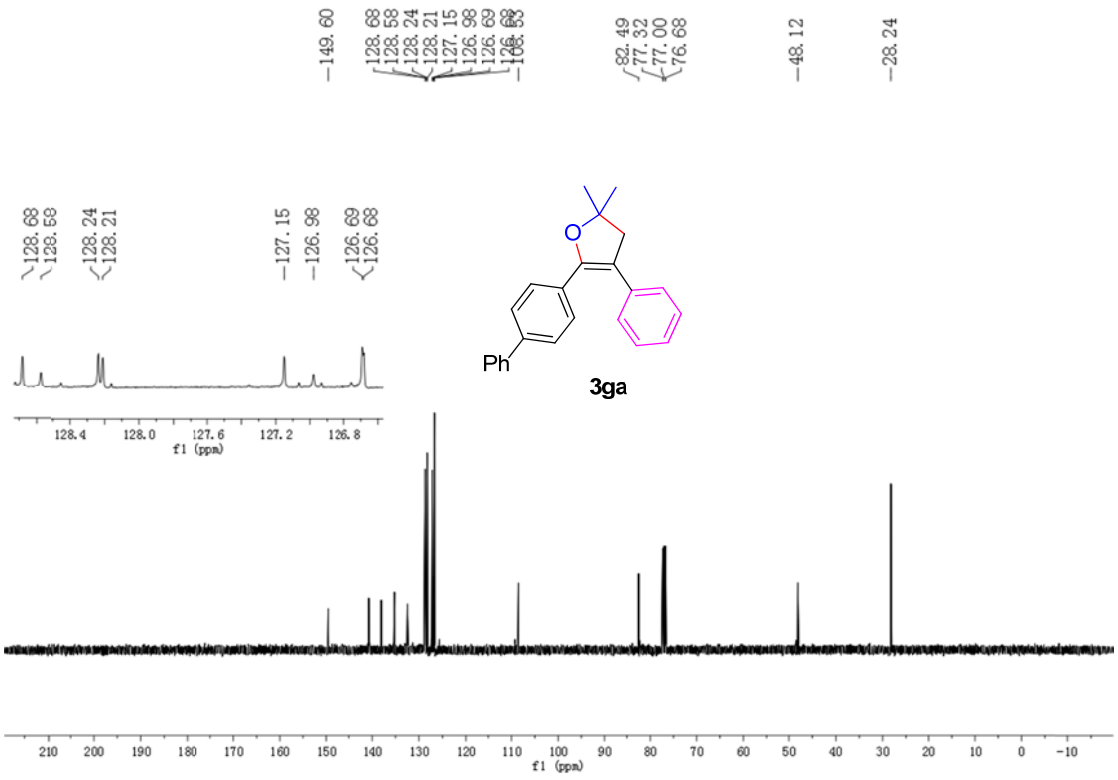

131.51
131.41
129.74
128.65
48.22
28.27
O
Br
Br
3ea
f1 (ppm)

2,2-dimethyl-4,5-bis(3-(trifluoromethyl)phenyl)-2,3-dihydrof-uran (3fa)

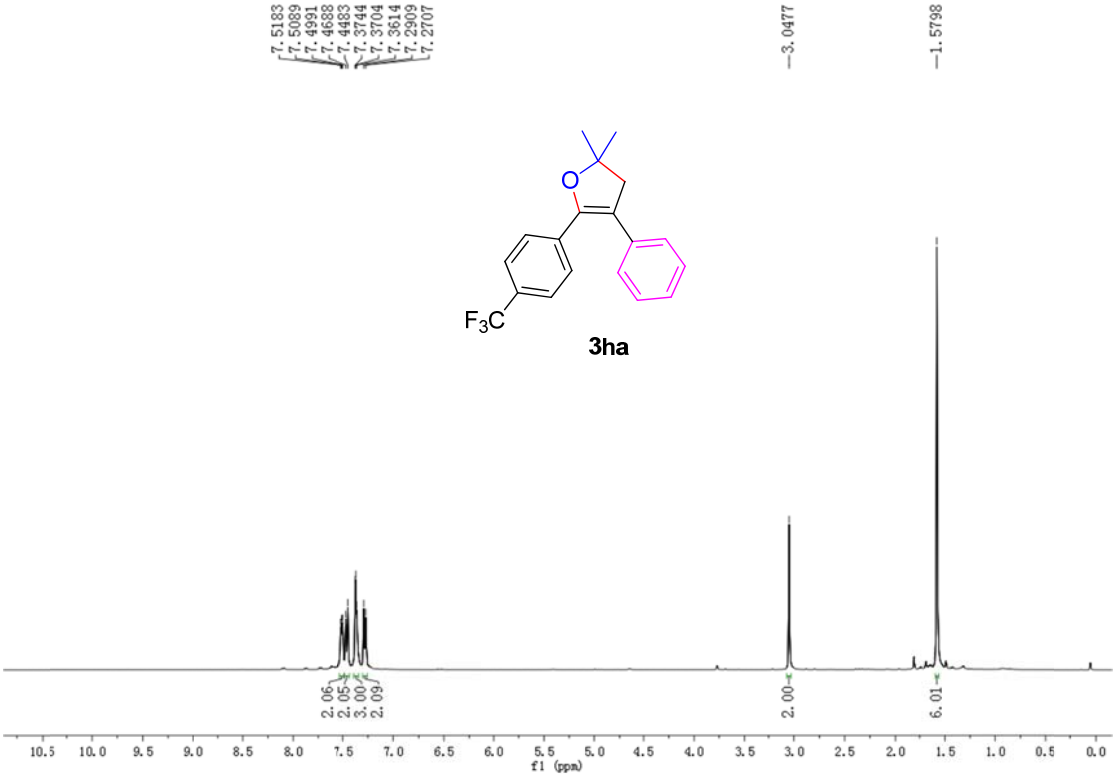


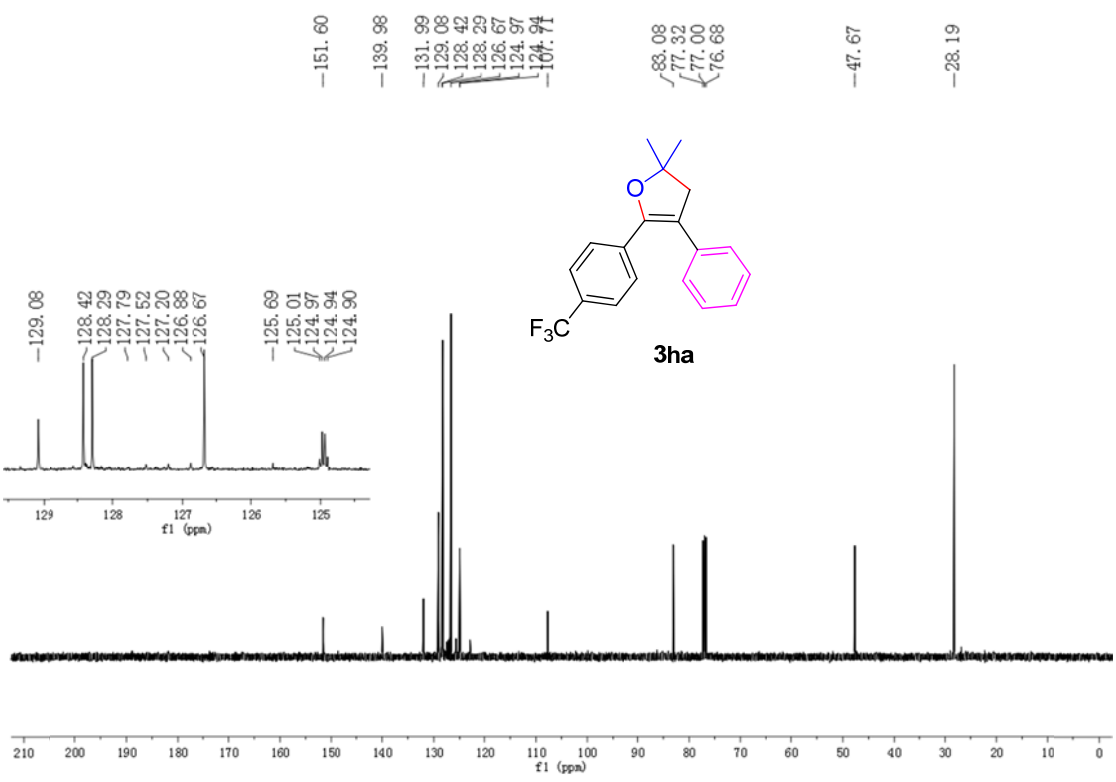
5-([1,1'-biphenyl]-4-yl)-2,2-dimethyl-4-phenyl-2,3-dihydrofuran (3ga)



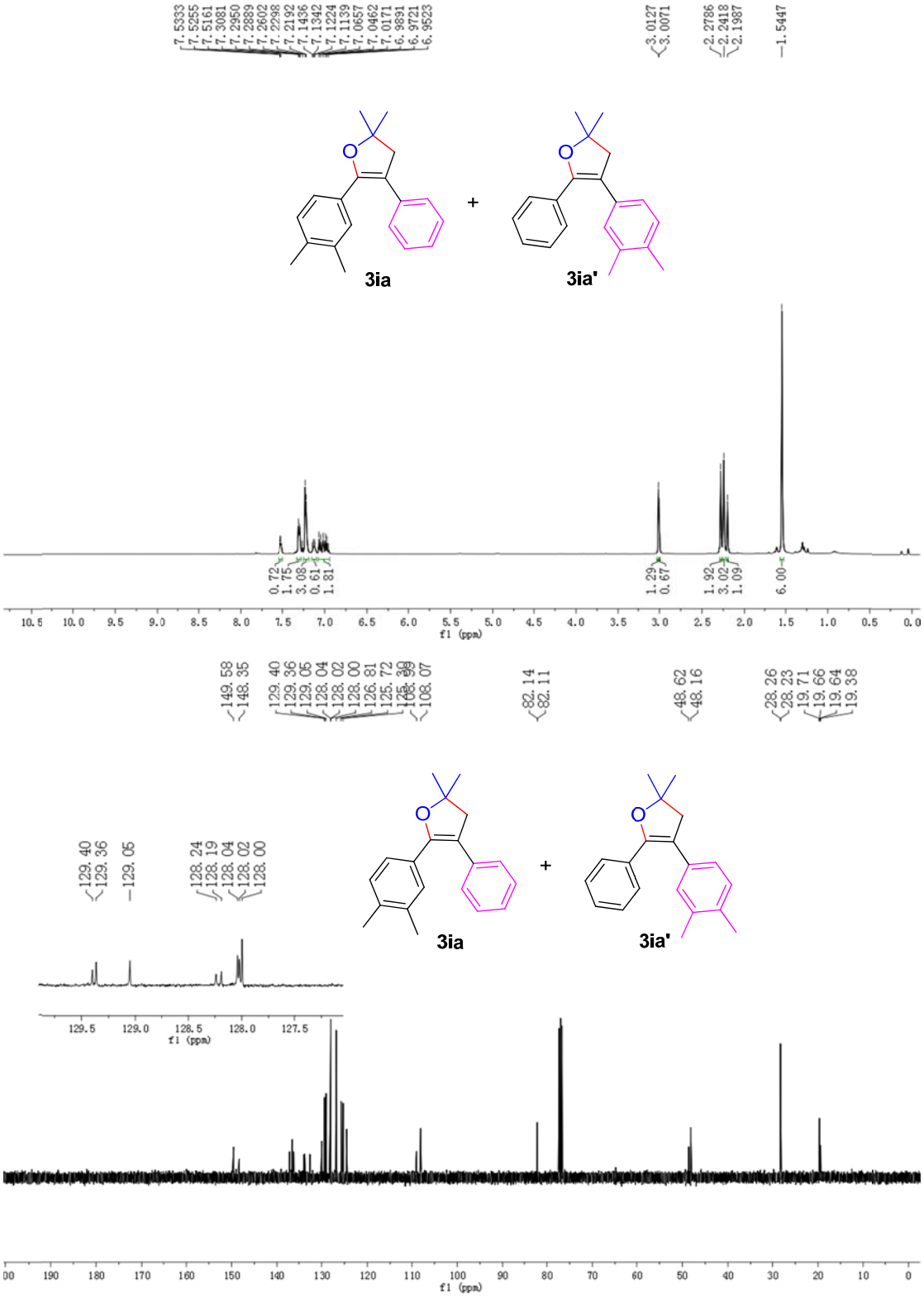


2,2-dimethyl-4-phenyl-5-(4-(trifluoromethyl)phenyl)-2,3-dihydrofuran (3ha)

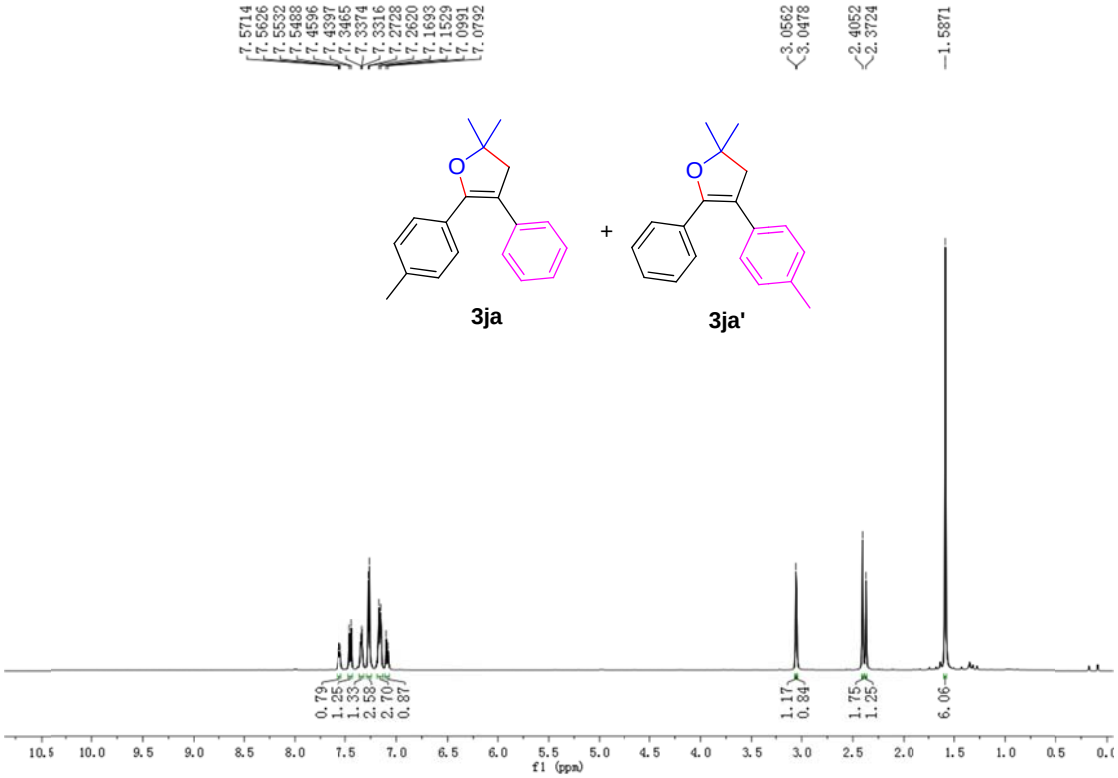


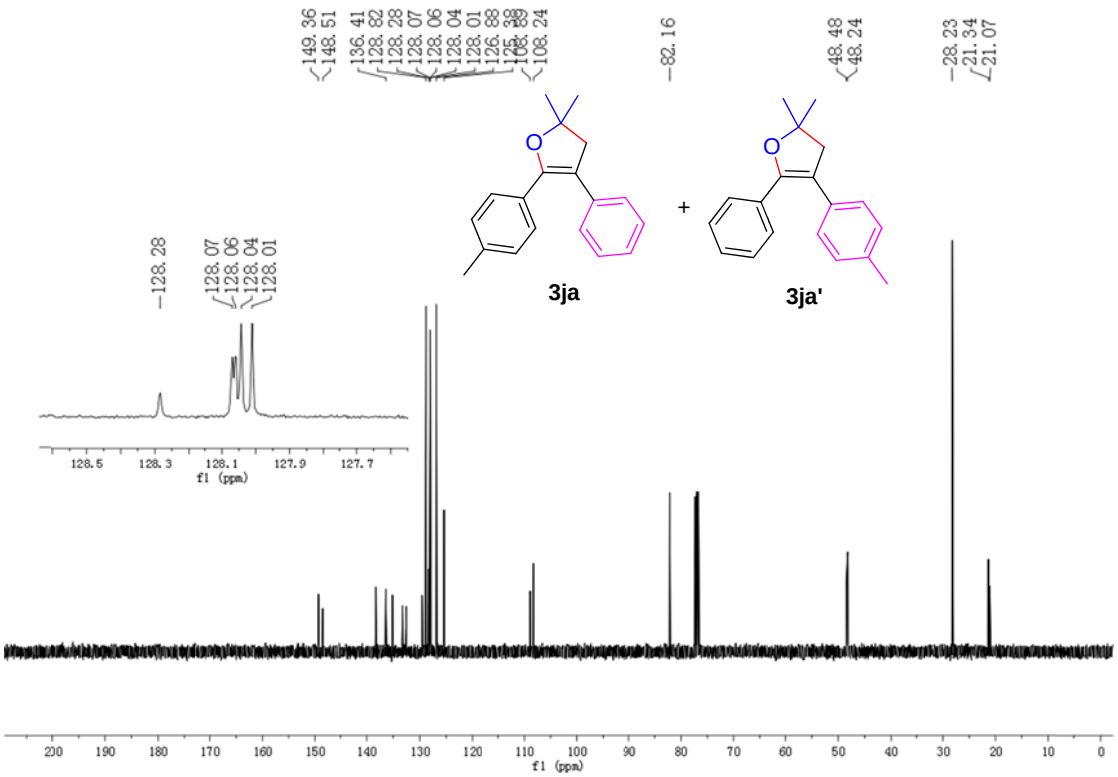


5-(3,4-dimethylphenyl)-2,2-dimethyl-4-phenyl-2,3-dihydrofuran (3ia and 3ia')

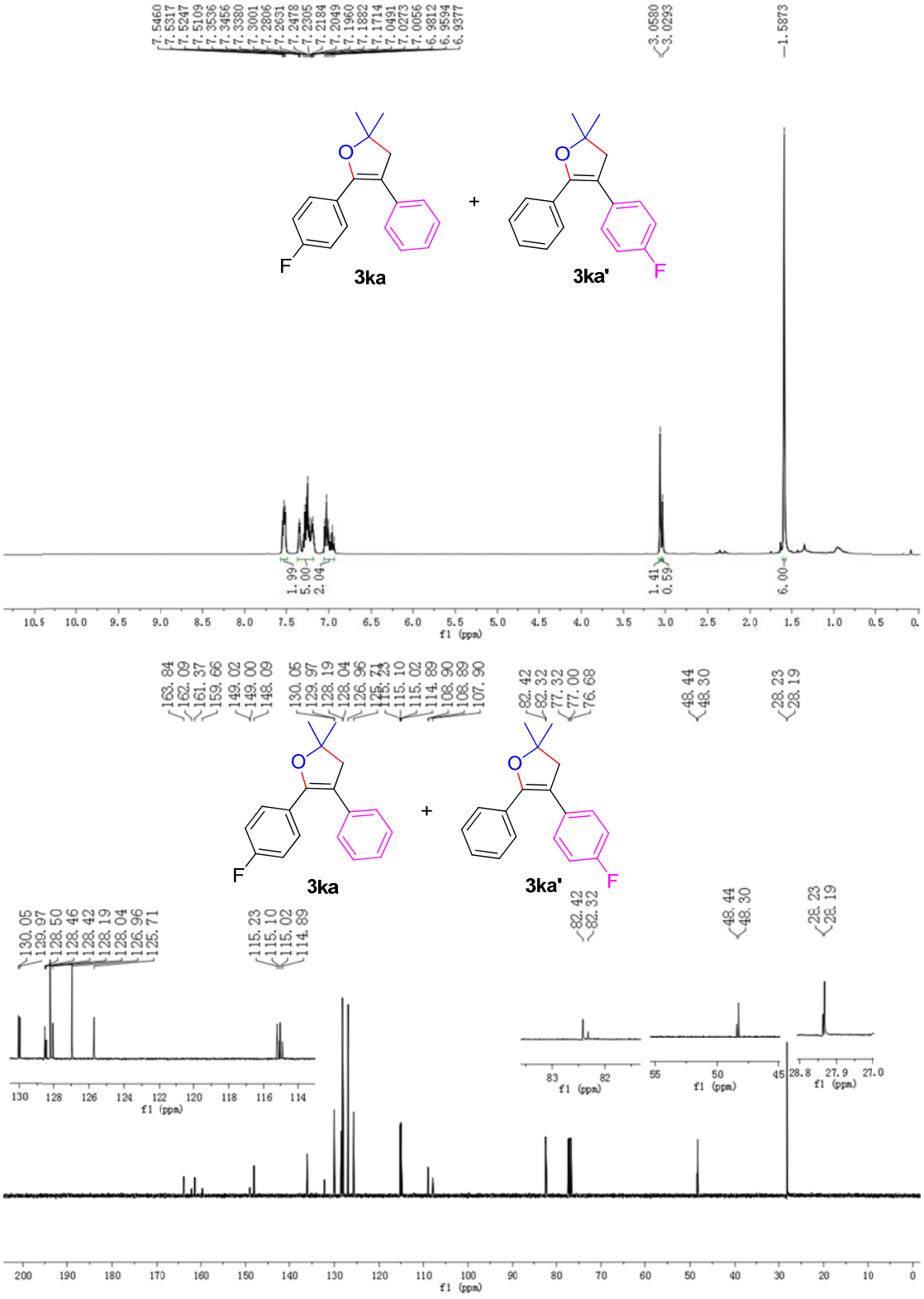


2,2-dimethyl-4-phenyl-5-(p-tolyl)-2,3-dihydrofuran (3ja and 3ja')

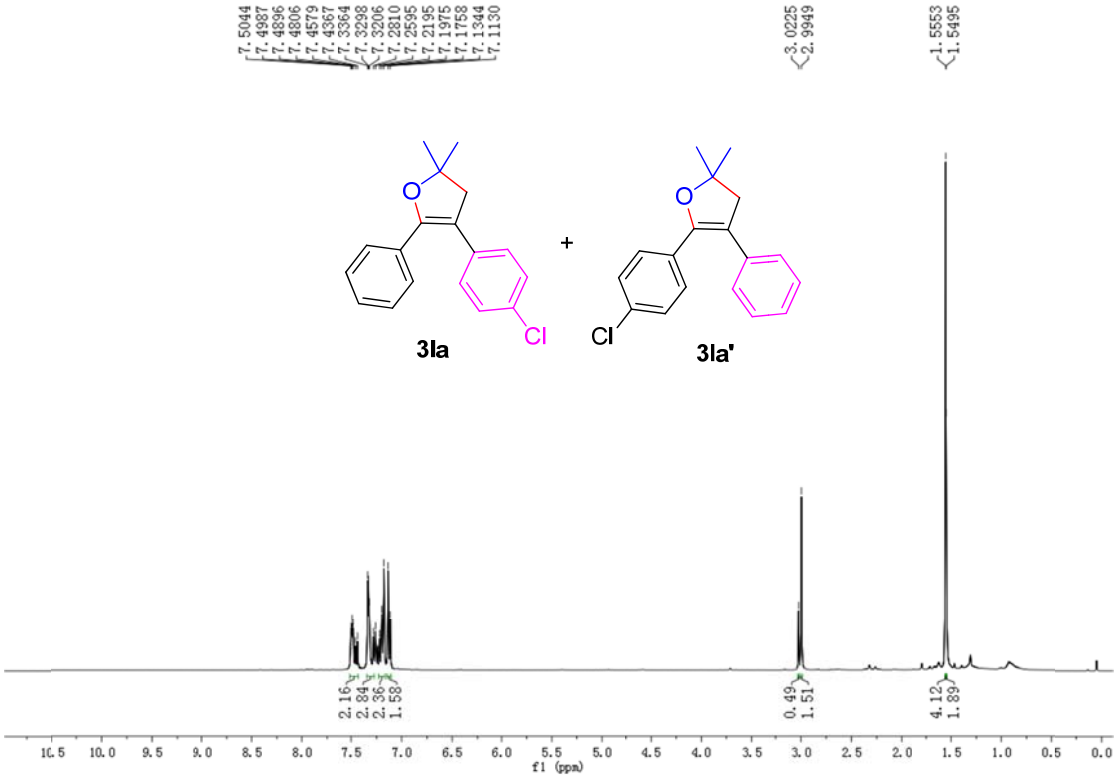


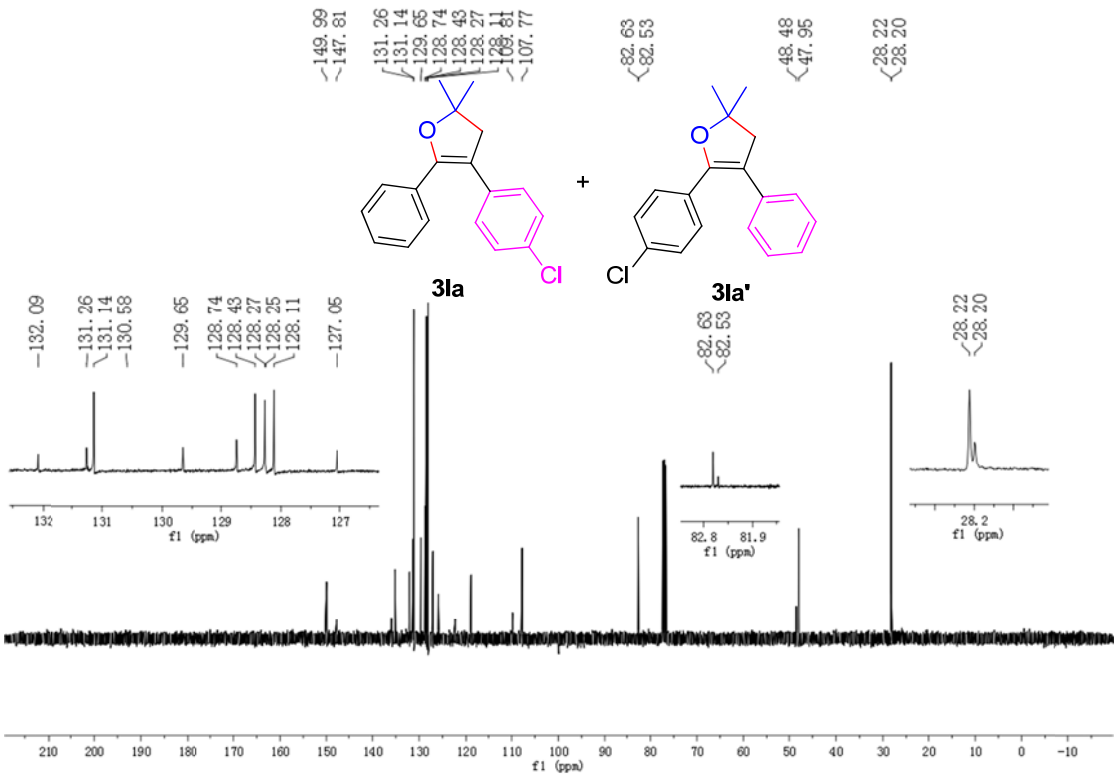


5-(4-fluorophenyl)-2,2-dimethyl-4-phenyl-2,3-dihydrofuran (3ka and 3ka')

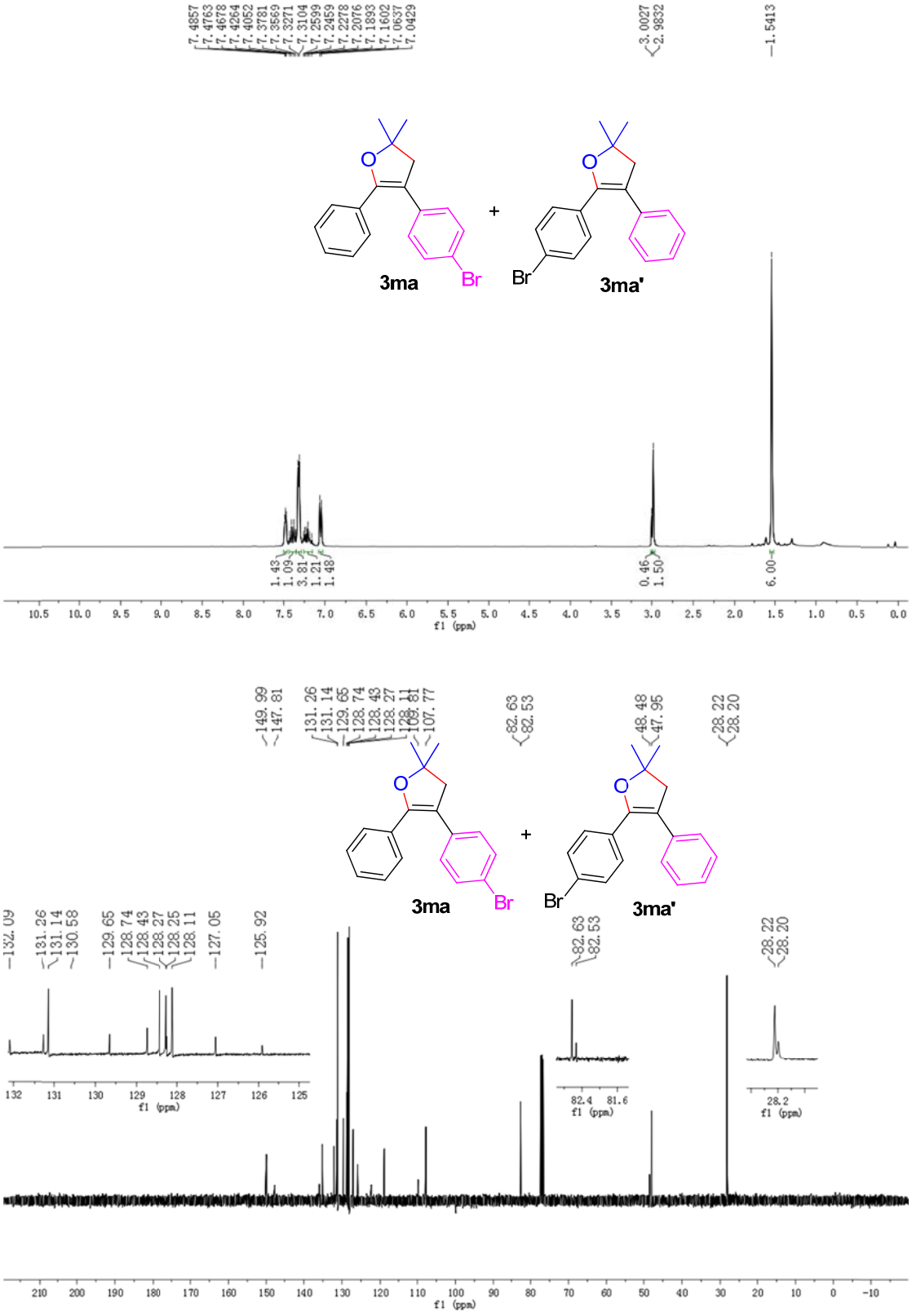


4-(4-chlorophenyl)-2,2-dimethyl-5-phenyl-2,3-dihydrofuran (3la and 3la')

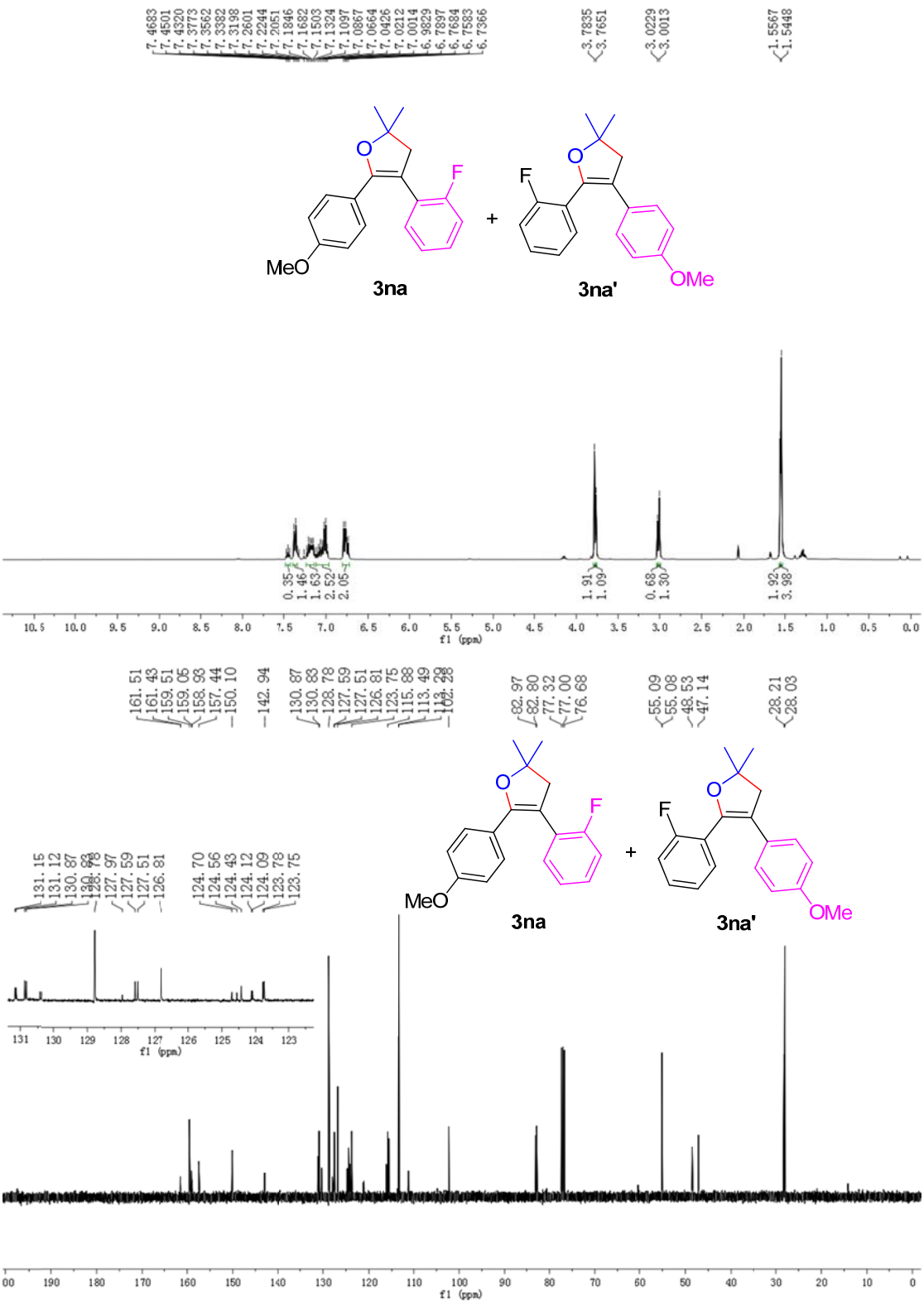




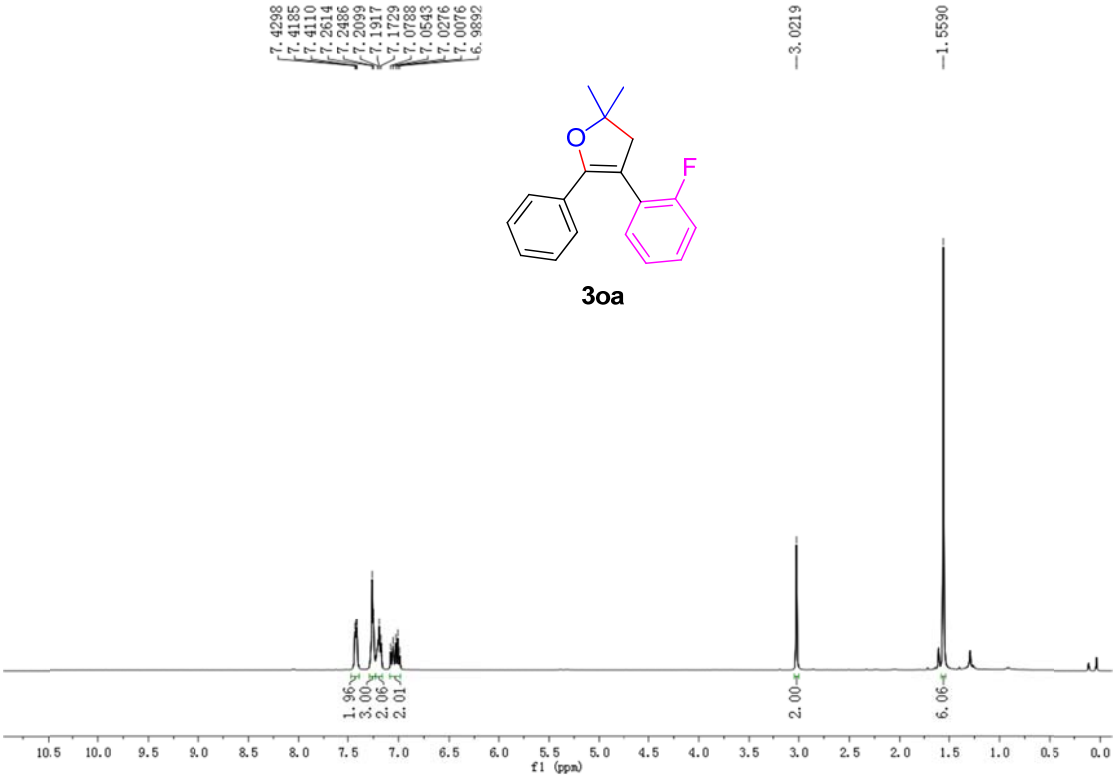
4-(4-bromophenyl)-2,2-dimethyl-5-phenyl-2,3-dihydrofuran (3ma + 3ma')

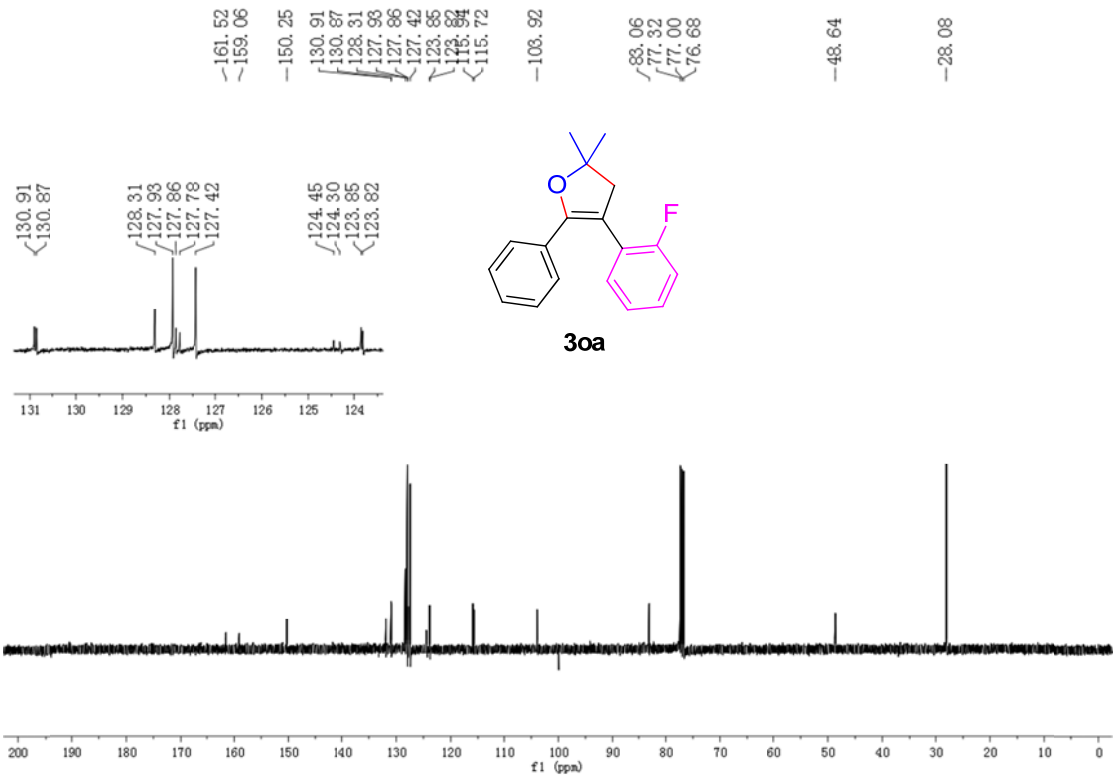


4-(2-fluorophenyl)-5-(4-methoxyphenyl)-2,2-dimethyl-2,3-dihydrofuran (3na and 3na')

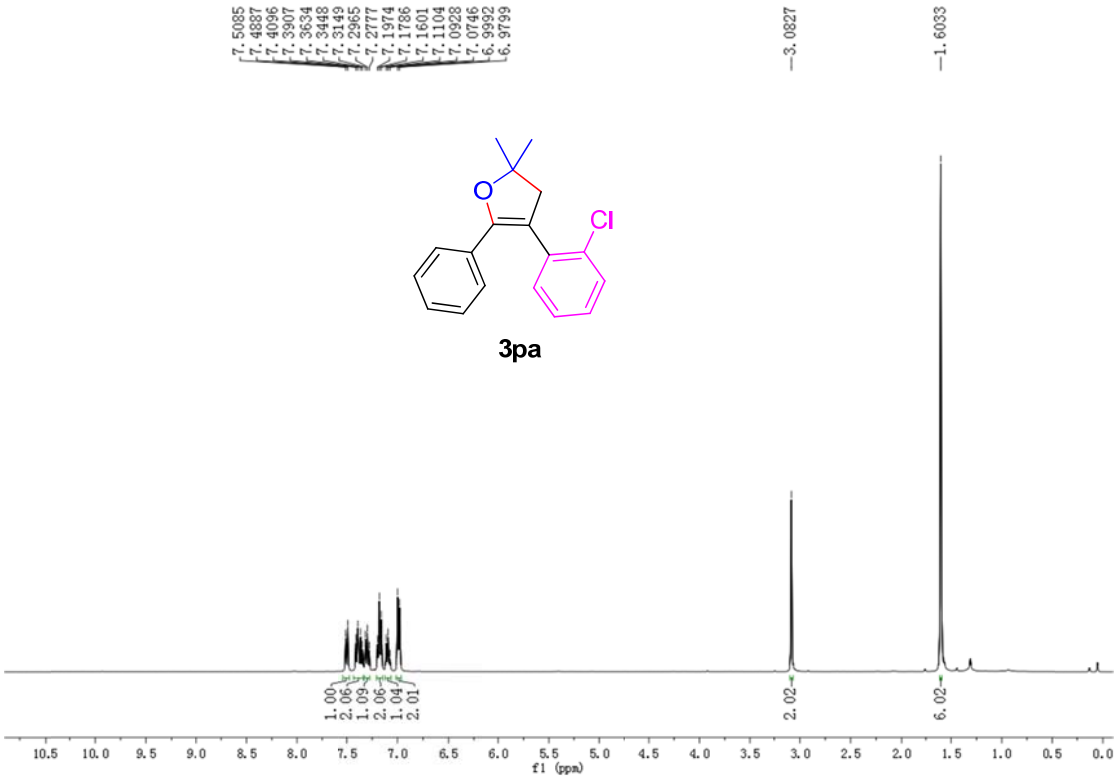


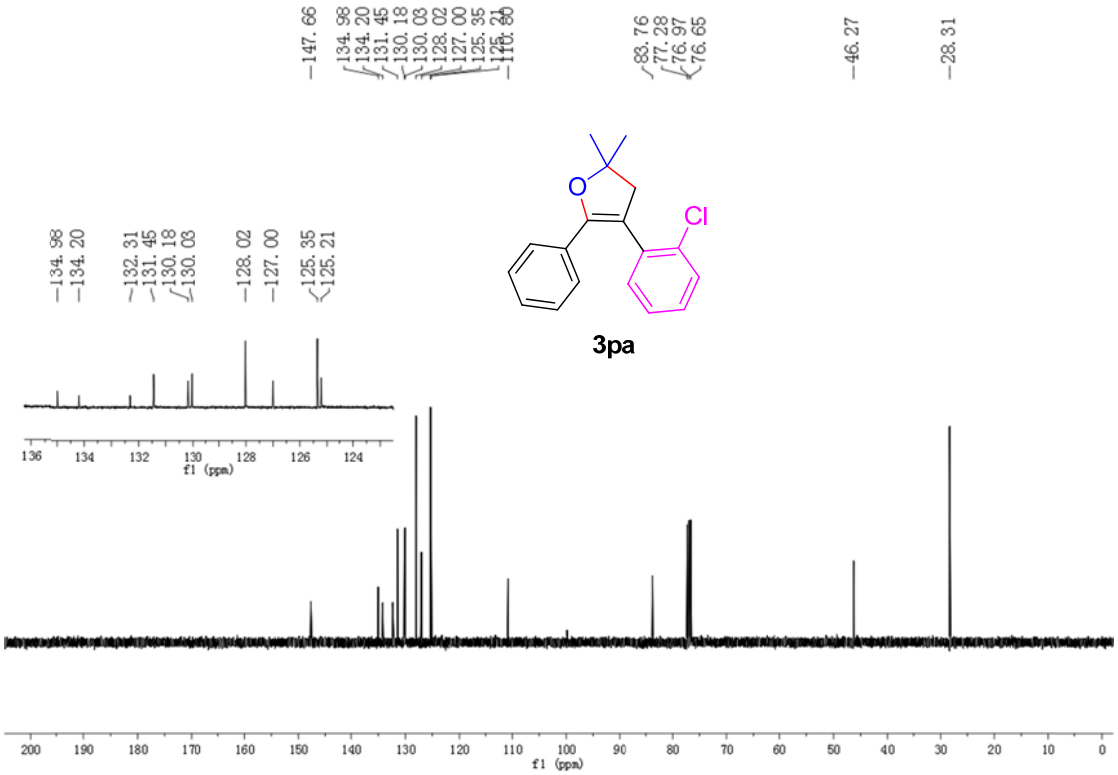
4-(2-fluorophenyl)-2,2-dimethyl-5-phenyl-2,3-dihydrofuran (3oa)



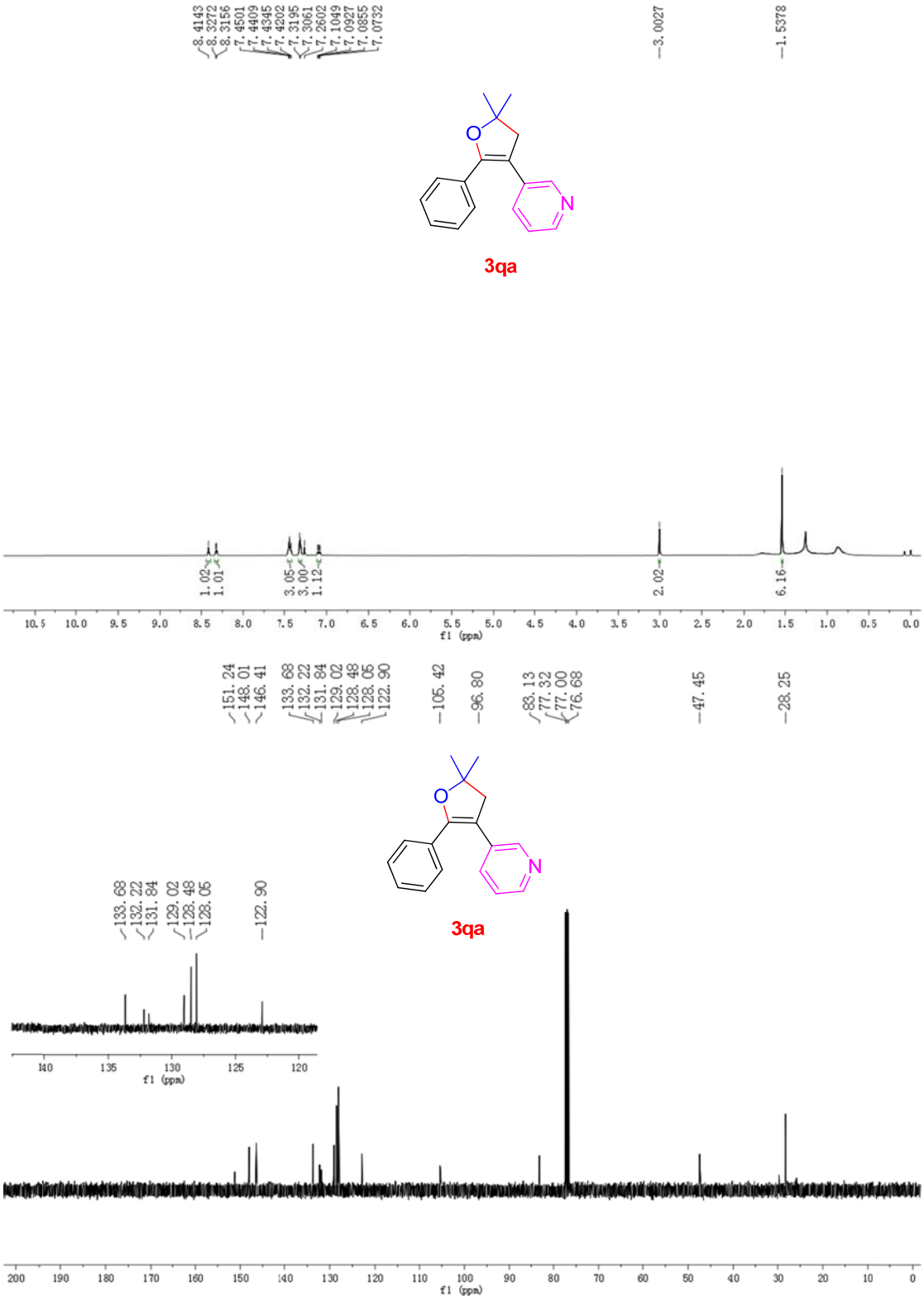


4-(2-chlorophenyl)-2,2-dimethyl-5-phenyl-2,3-dihydrofuran (3pa)

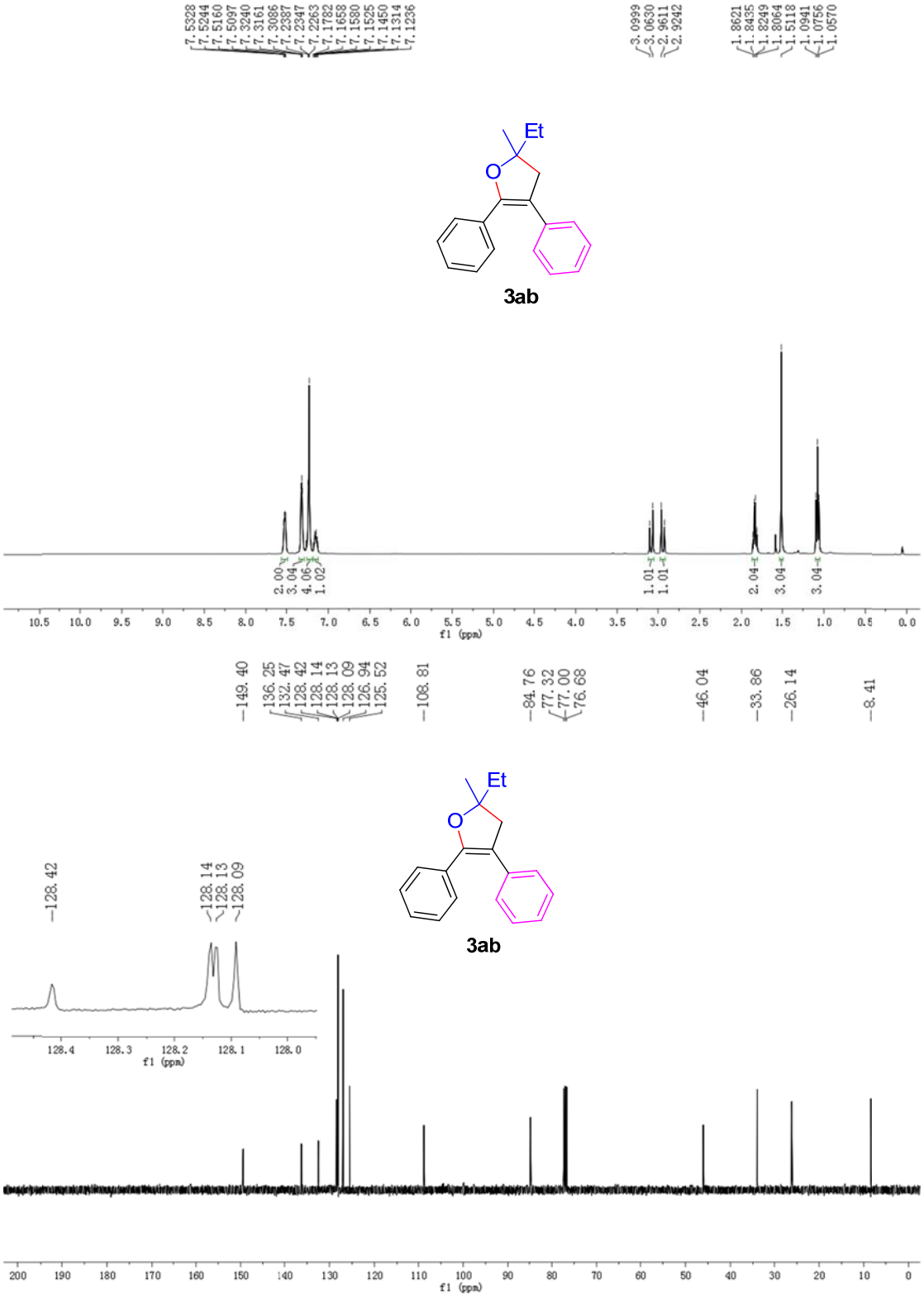




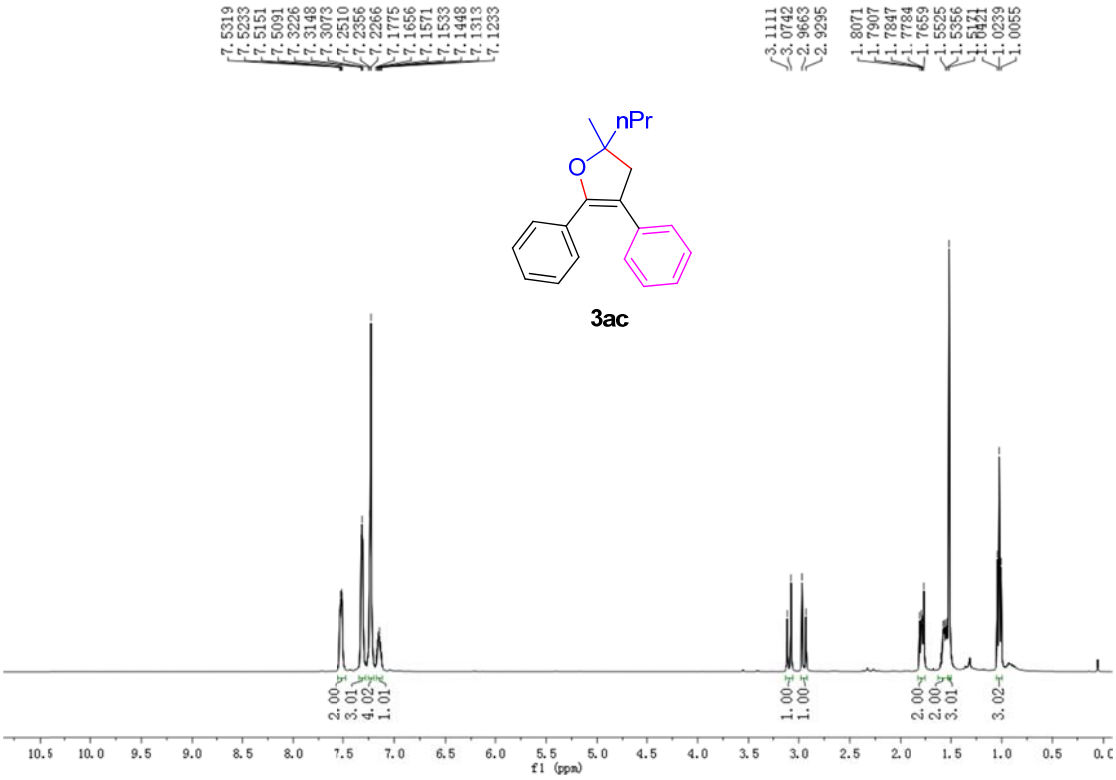
3-(5,5-dimethyl-2-phenyl-4,5-dihydrofuran-3-yl)pyridine (3qa)

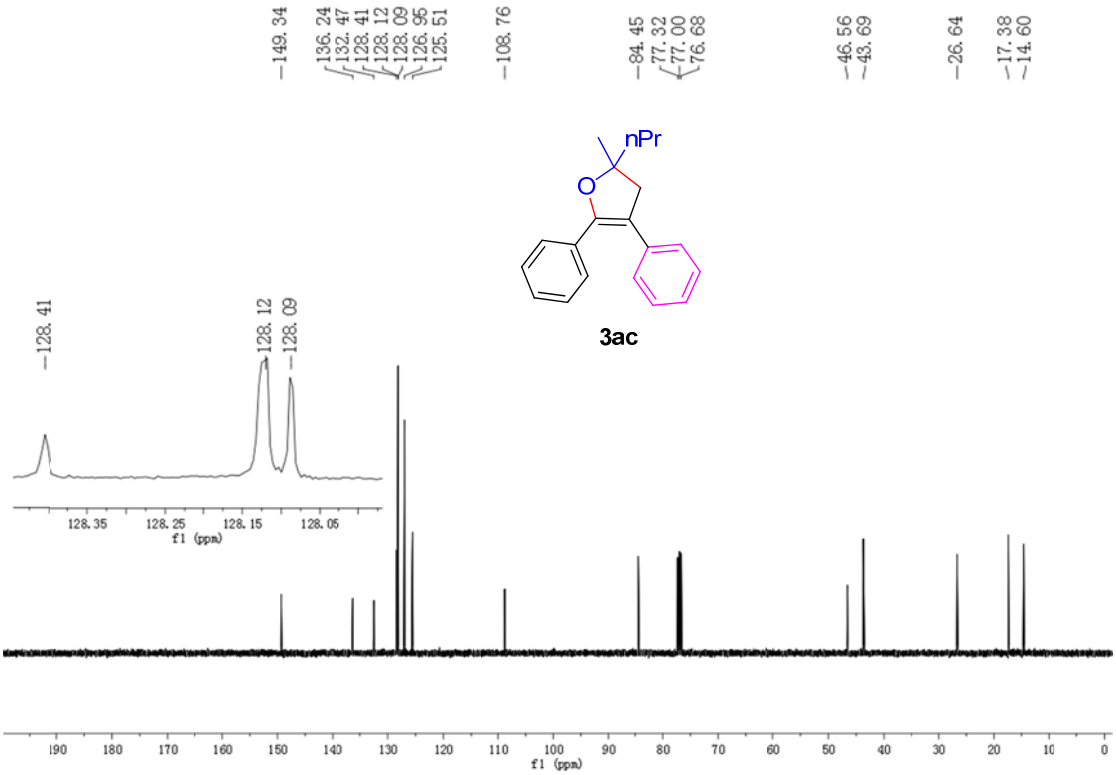


2-ethyl-2-methyl-4,5-diphenyl-2,3-dihydrofuran (3ab)

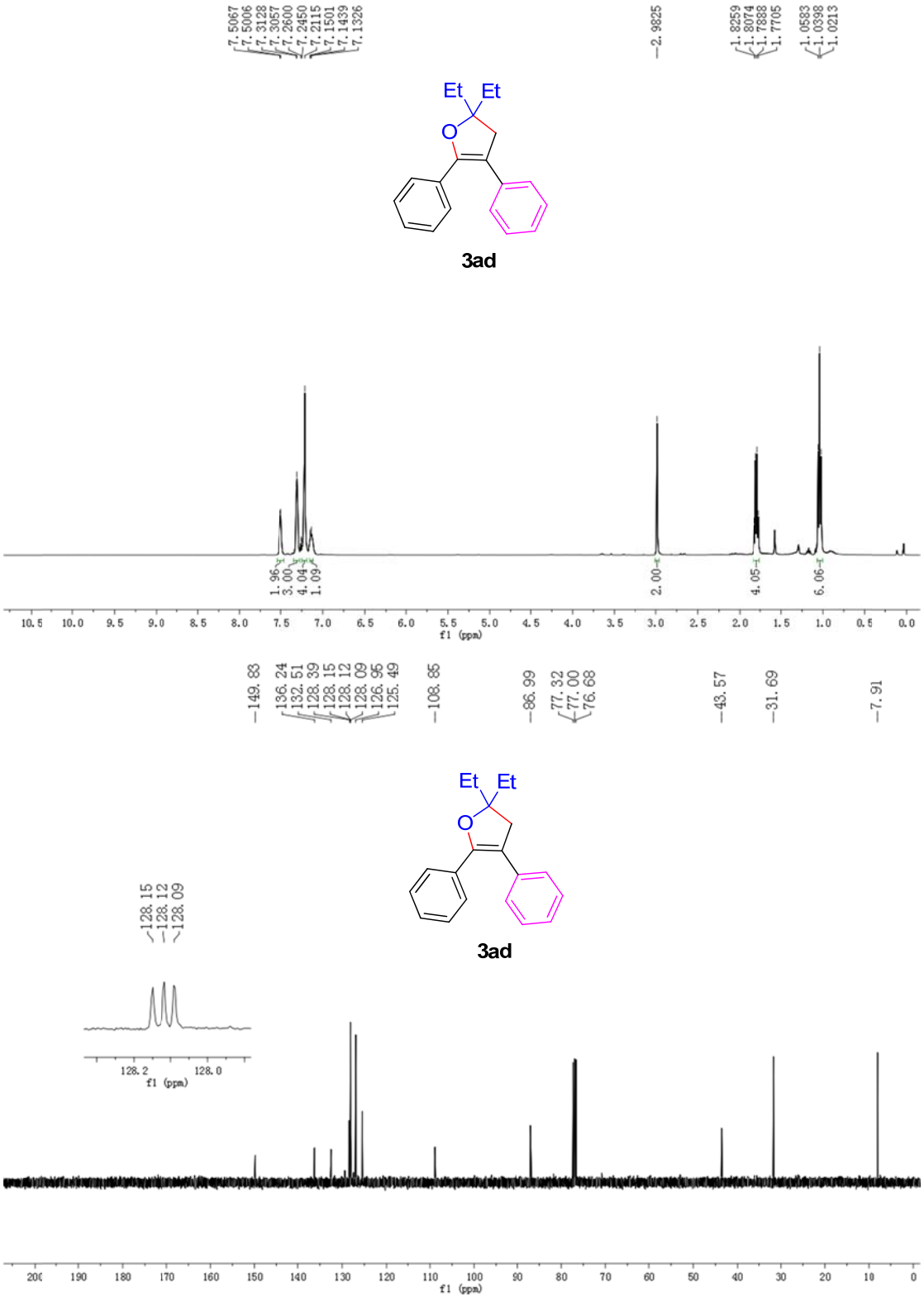


2-methyl-4,5-diphenyl-2-propyl-2,3-dihydrofuran (3ac)

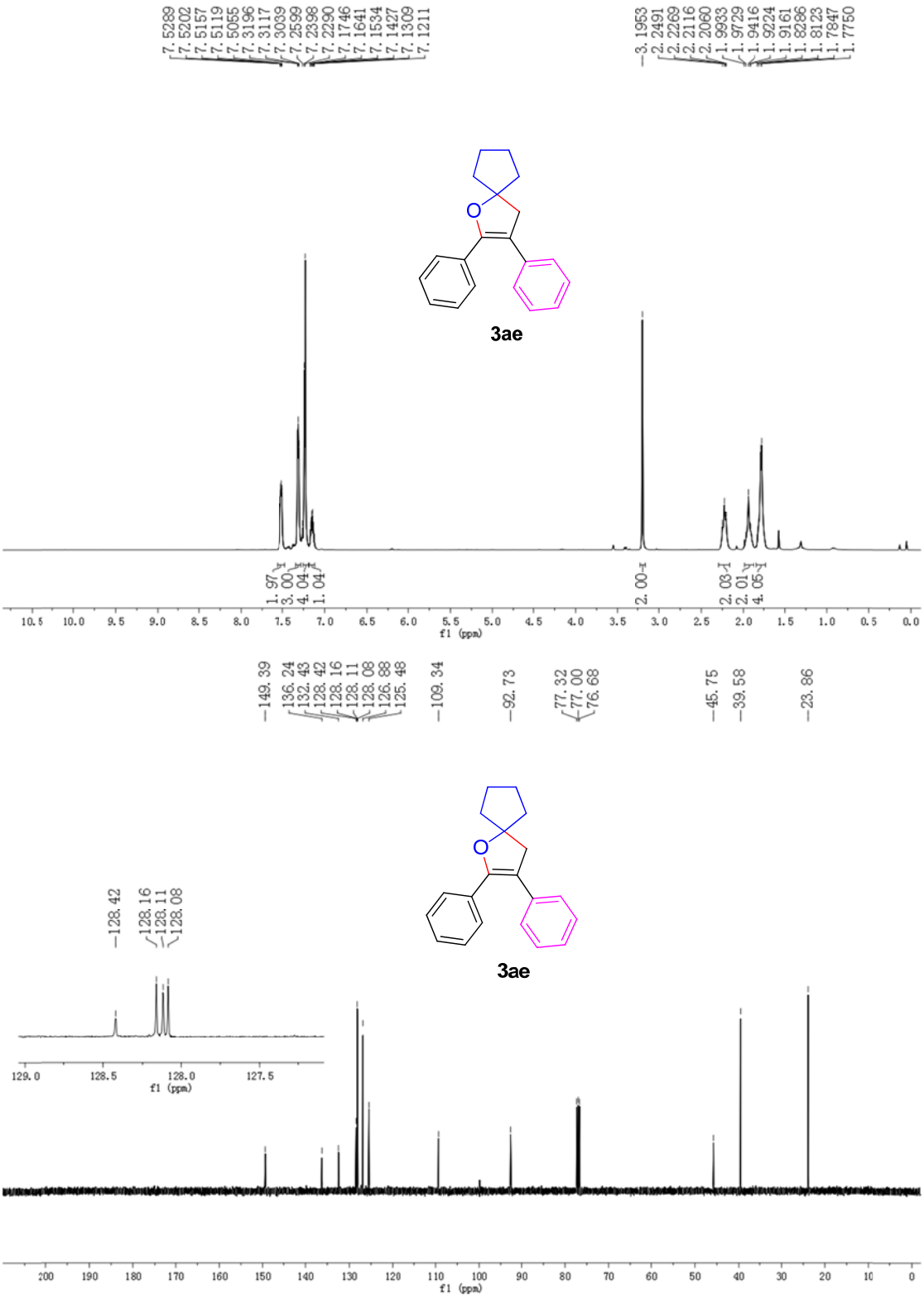




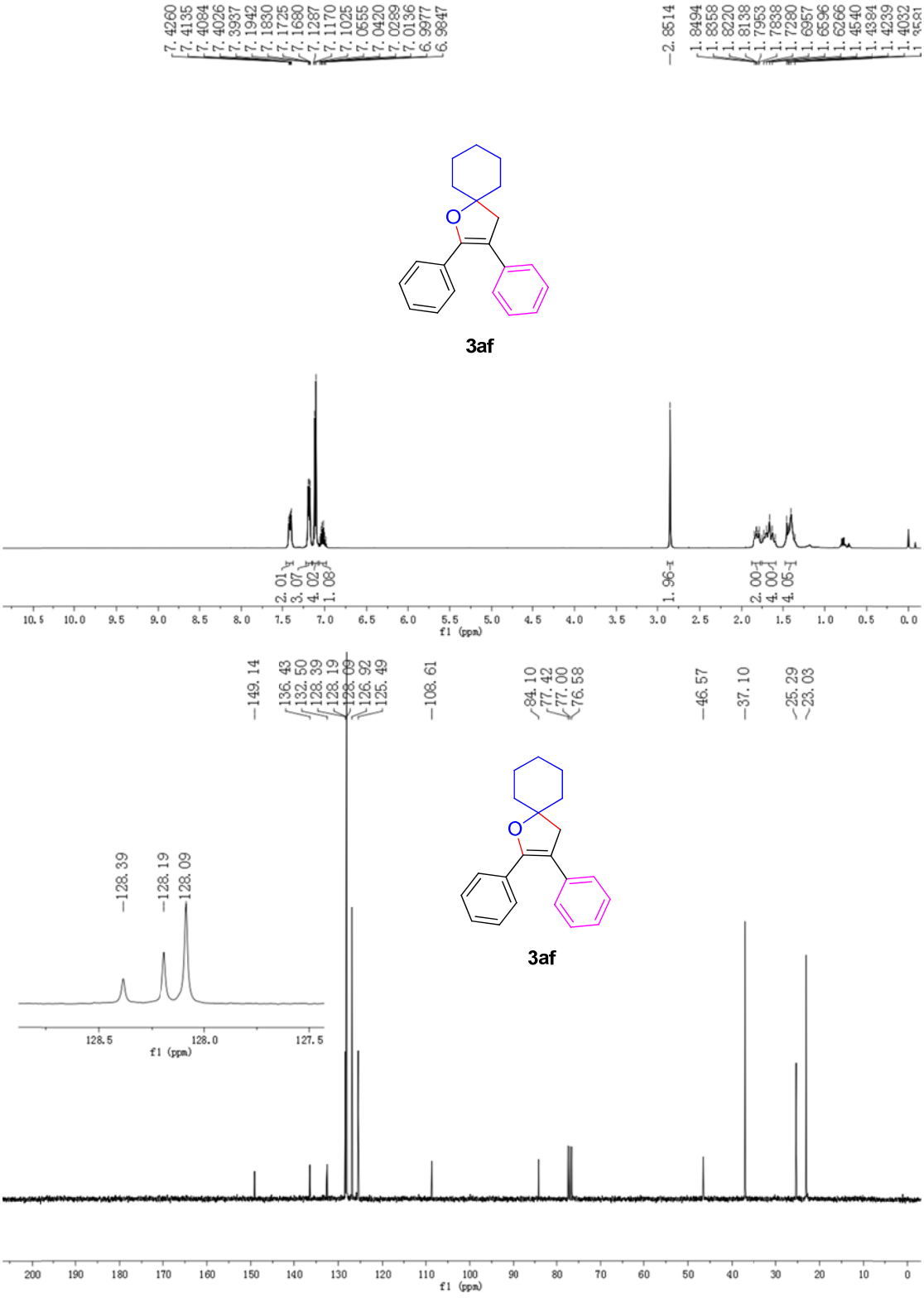
2,2-diethyl-4,5-diphenyl-2,3-dihydrofuran (3ad)



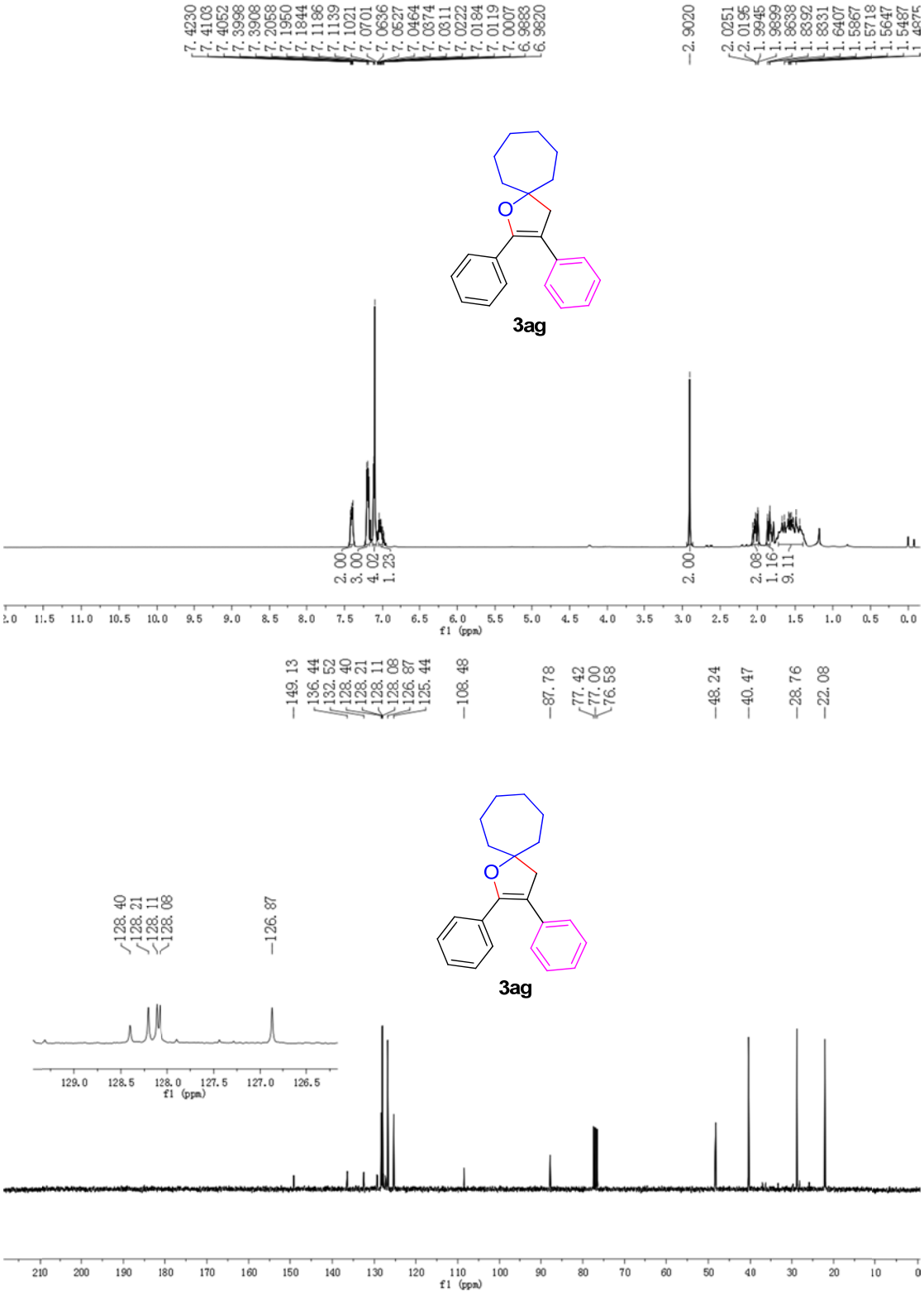
2,3-diphenyl-1-oxaspiro[4.4]non-2-ene (3ae)



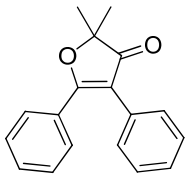
2,3-diphenyl-1-oxaspiro[4.5]dec-2-ene (3af)



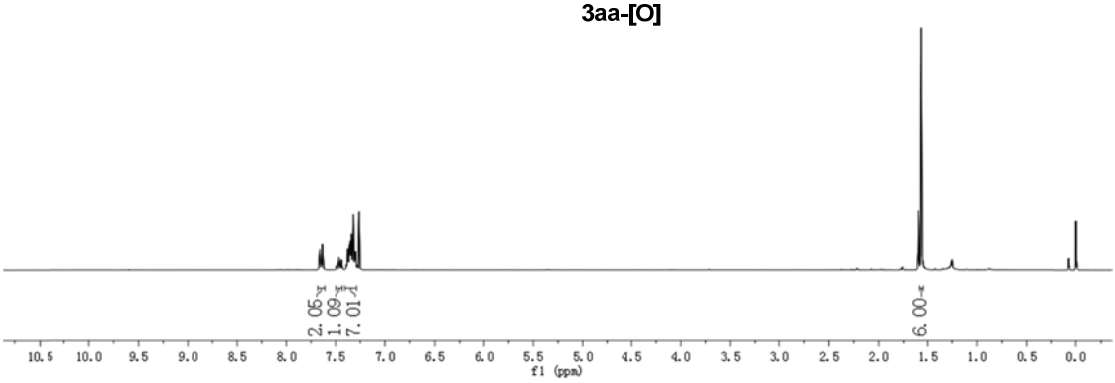
2,3-diphenyl-1-oxaspiro[4.6]undec-2-ene (3ag)

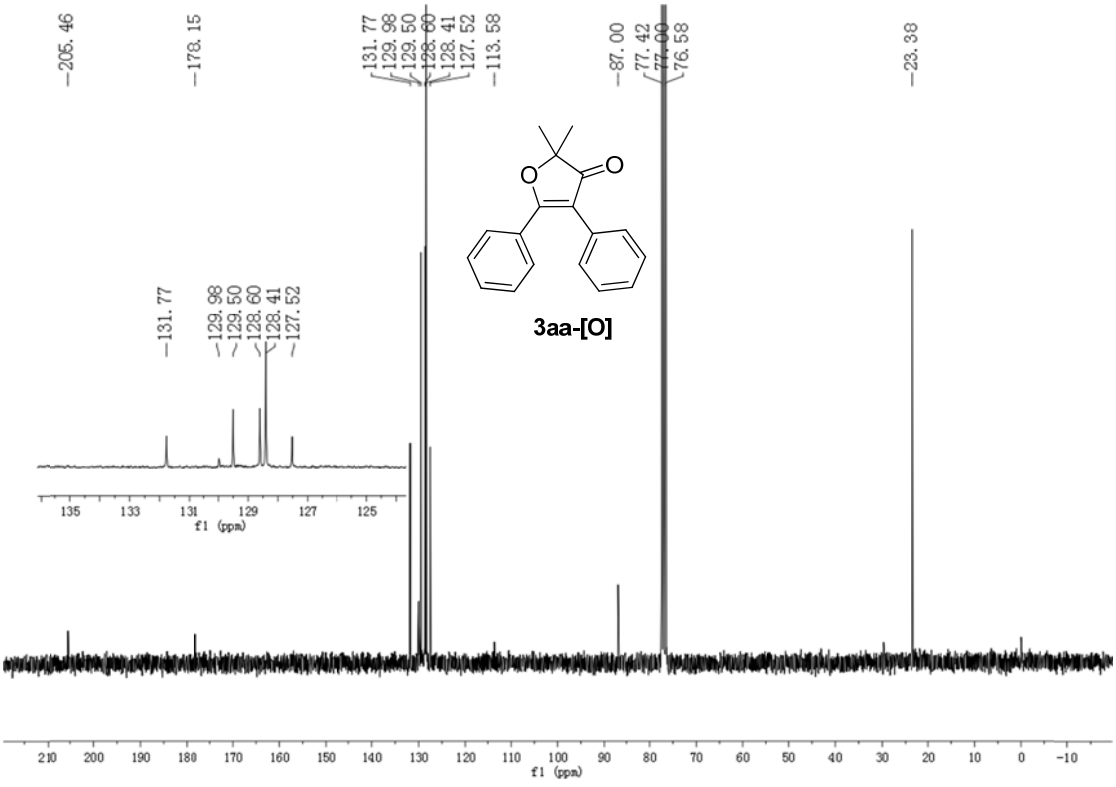


2,2-dimethyl-4,5-diphenylfuran-3(2H)-one (3aa-[O])



3aa-[O]





3aa-[O]