Metal-free and regiospecific synthesis of 3-arylindoles

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Electronic Supplementary Information

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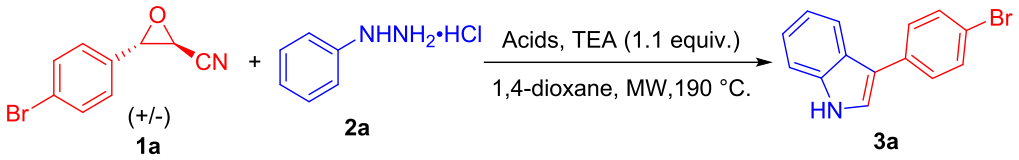
1. Optimization of the reaction conditions with different acids and bases.

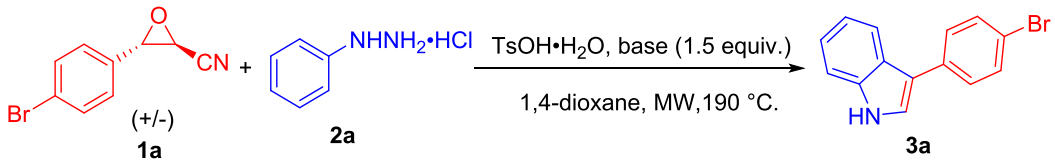
Table S1. Optimization of the reaction conditions with different acids[a]



entry	acid/equiv.	**2a**/equiv.	**3a** yield/%
1	$BF_3 \cdot OEt_2$/1.0	1.1	23[b]
2	$FeCl_2$/1.0	1.1	--
3	$FeCl_3$/1.0	1.1	--
4	$ZnCl_2$/1.0	1.1	21
5	$AlCl_3$/1.0	1.1	13
6	$MgCl_2$/1.0	1.1	22
7	$Zn(OTf)_2$/1.0	1.1	12
8	$Mg(OTf)_2$/1.0	1.1	17
9	AcOH/1.0	1.1	11
10	TFA/1.0	1.1	17
11	$TsOH \cdot H_2O$/1.0	1.1	27
12[c]	--	1.1	13

[a]Reacions were conducted on a 0.3 mmol scale of *trans*-**1a** in 3 mL of anhydrous 1,4-dioxane at 190 °C for 30 min under microwave irradiation in a sealed vessel. Yields of isolated product **3a** were illustrated. [b]2-(4-Bromophenyl)-*N*-phenylacetohydrazonoyl cyanide (**4**) was obtained in a small amount as a byproduct. [c]Reaction was conducted without TEA.

Table S2. Optimization of the reaction conditions with different bases[a]

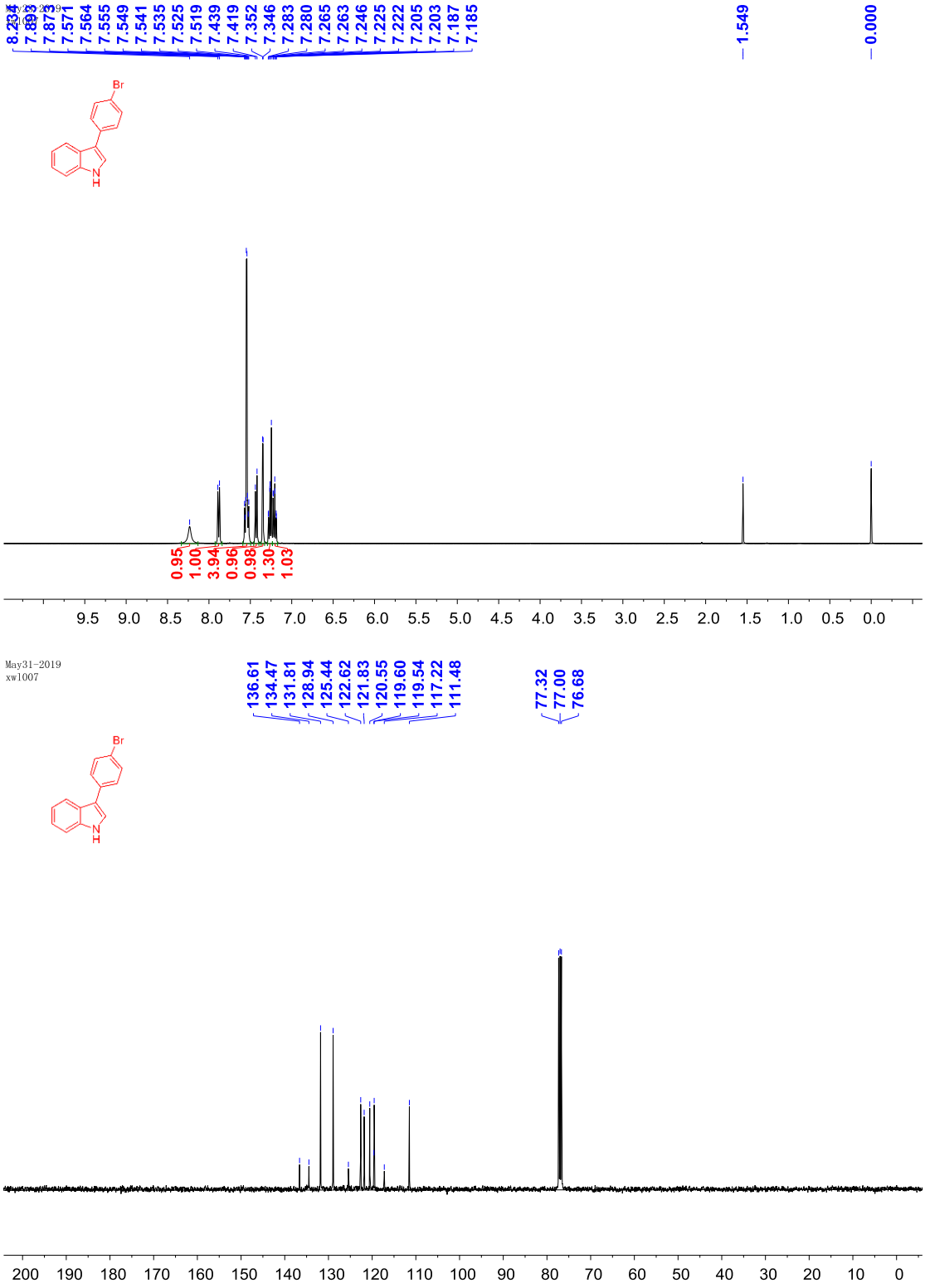


entry	$TsOH \cdot H_2O$/equiv.	**2a**/equiv.	base/equiv.	**3a** yield/%
1	0.5	2.5	pyridine/1.5	42
2	0.5	2.5	2,6-lutidine/1.5	34
3	0.5	2.5	2,6-dichloropyridine/1.5	25
4	0.5	2.5	DBU/1.5	51
5	0.5	2.5	DIPEA/1.5	55
6	0.5	2.5	quinuclidine/1.5	54
7	0.5	2.5	DABCO/1.5	49
8	0.5	2.5	$HNEt_2$/1.5	57
9	0.5	2.5	KOH/1.5	39
10	0.5	2.5	K_2CO_3/1.5	47
11	0.5	2.5	NaH/1.5	49
12	0.5	2.5	NaOH/1.5	40

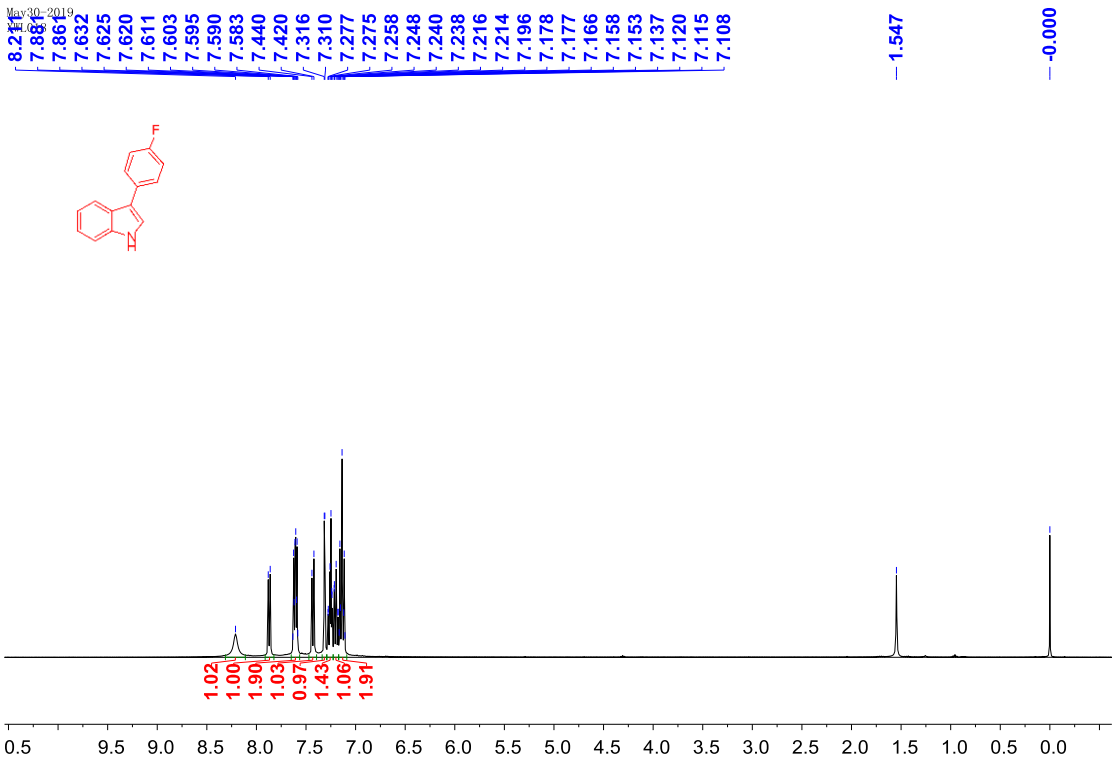
[a]Reacions were conducted on a 0.3 mmol scale of *trans*-**1a** in 3 mL of anhydrous 1,4-dioxane at 190 °C for 30 min under microwave irradiation in a sealed vessel. Yields of the isolated product **3a** were illustrated.

2. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of compounds 2-6.

^{1}H and ^{13}C NMR spectra of **3a**.



^{1}H, ^{13}C NMR and ^{19}F spectra of **3b**.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8.5
8.0
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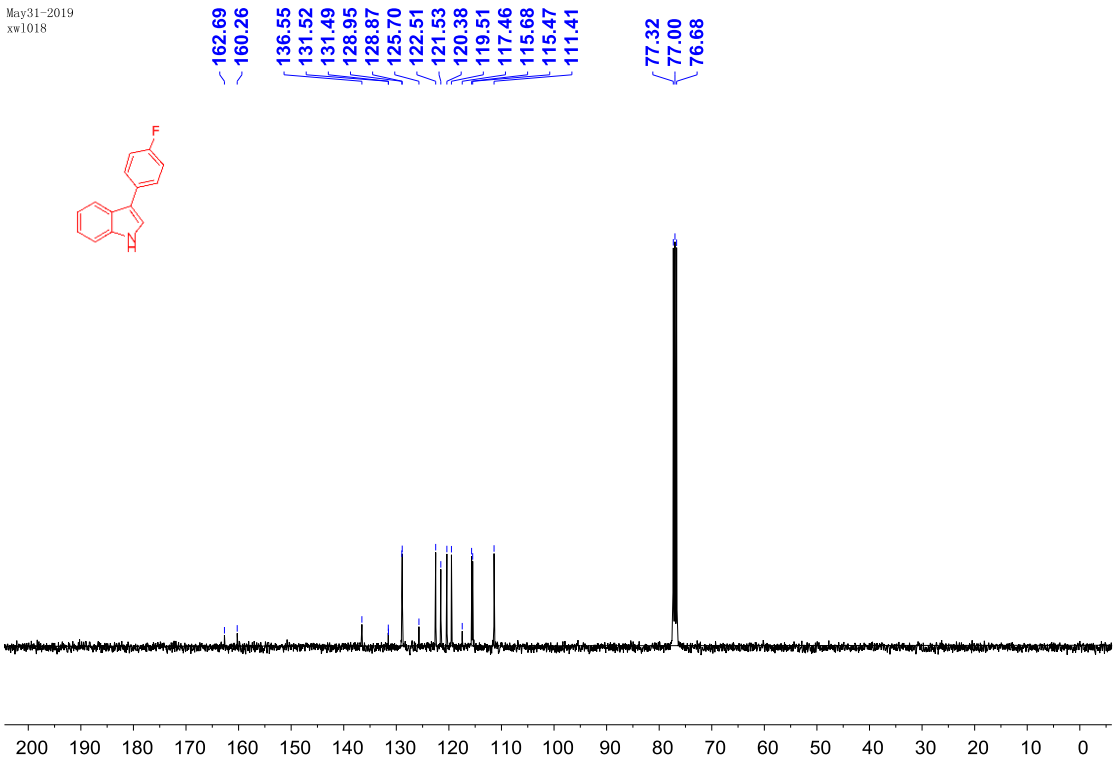
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115.47
111.41
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77.00
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F
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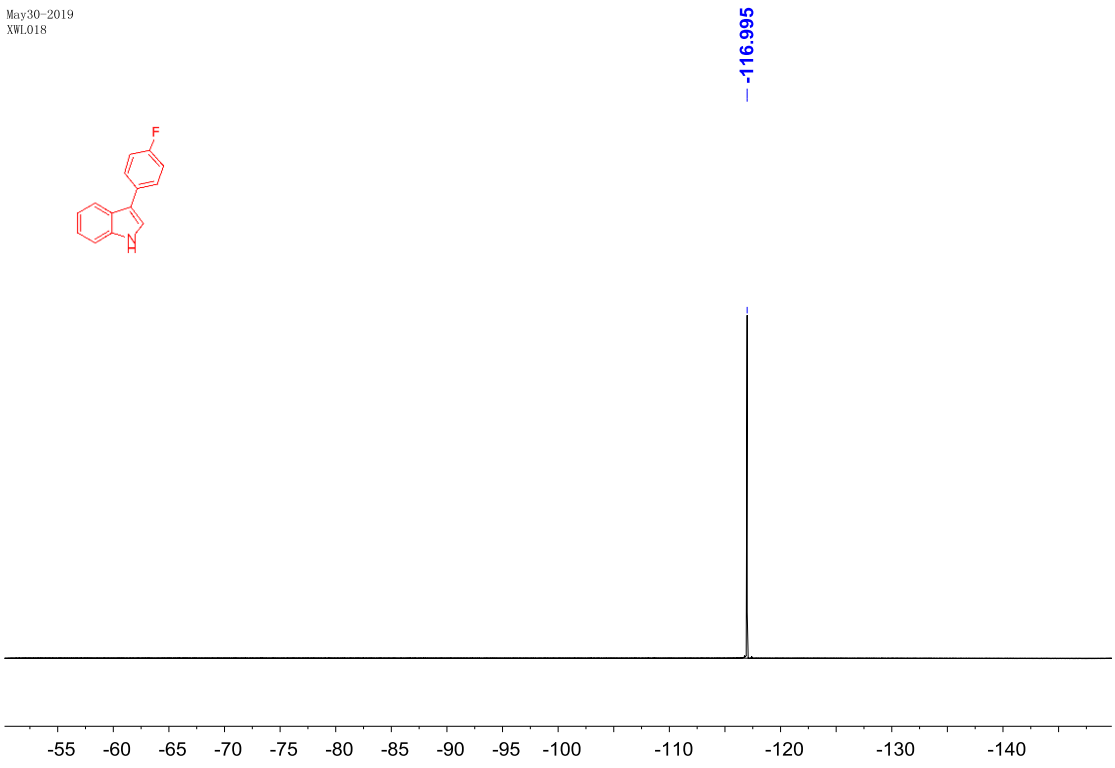
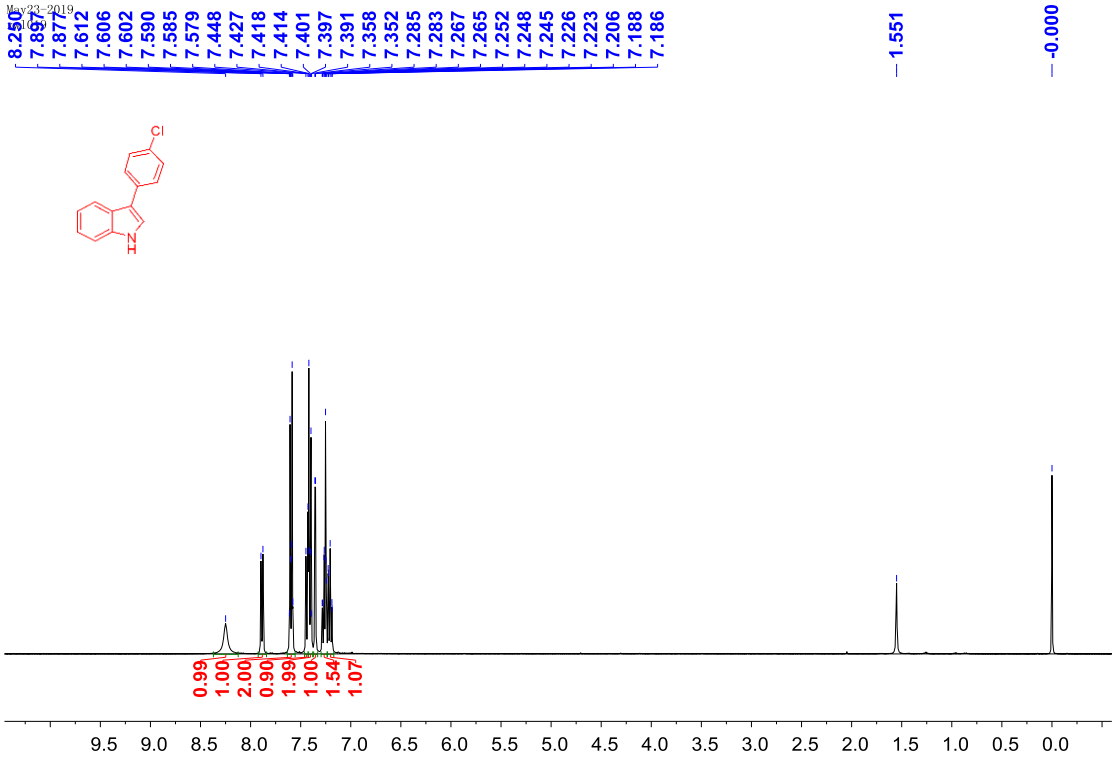
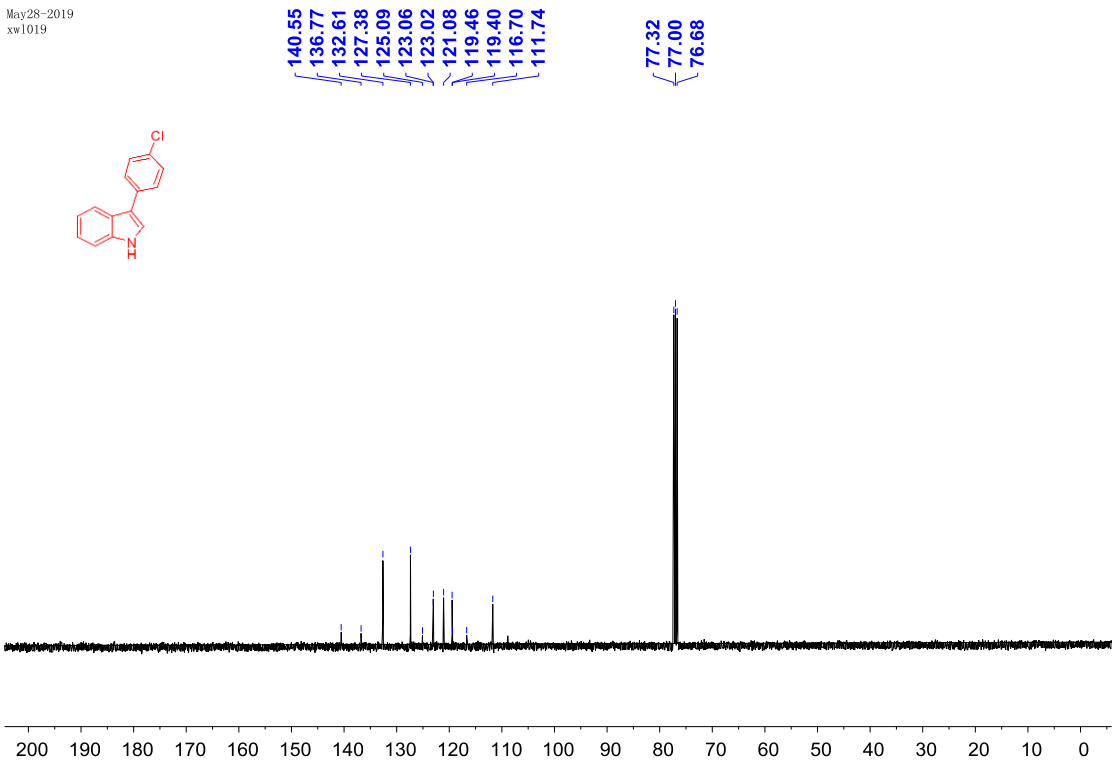
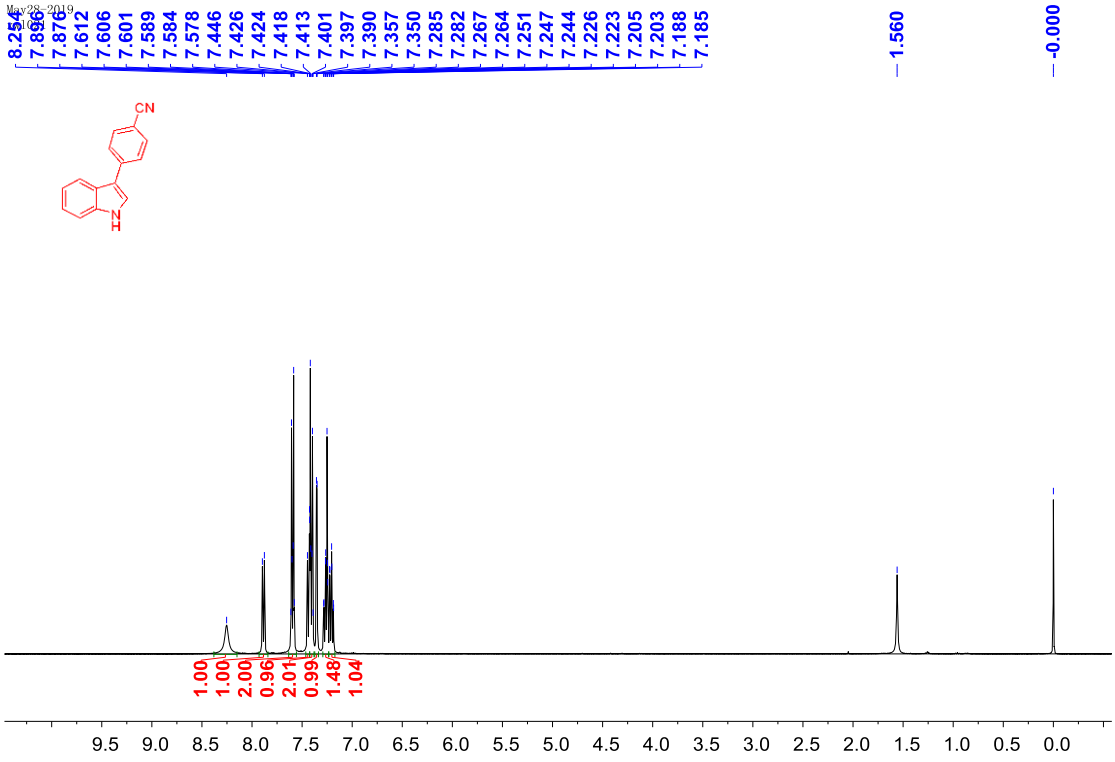


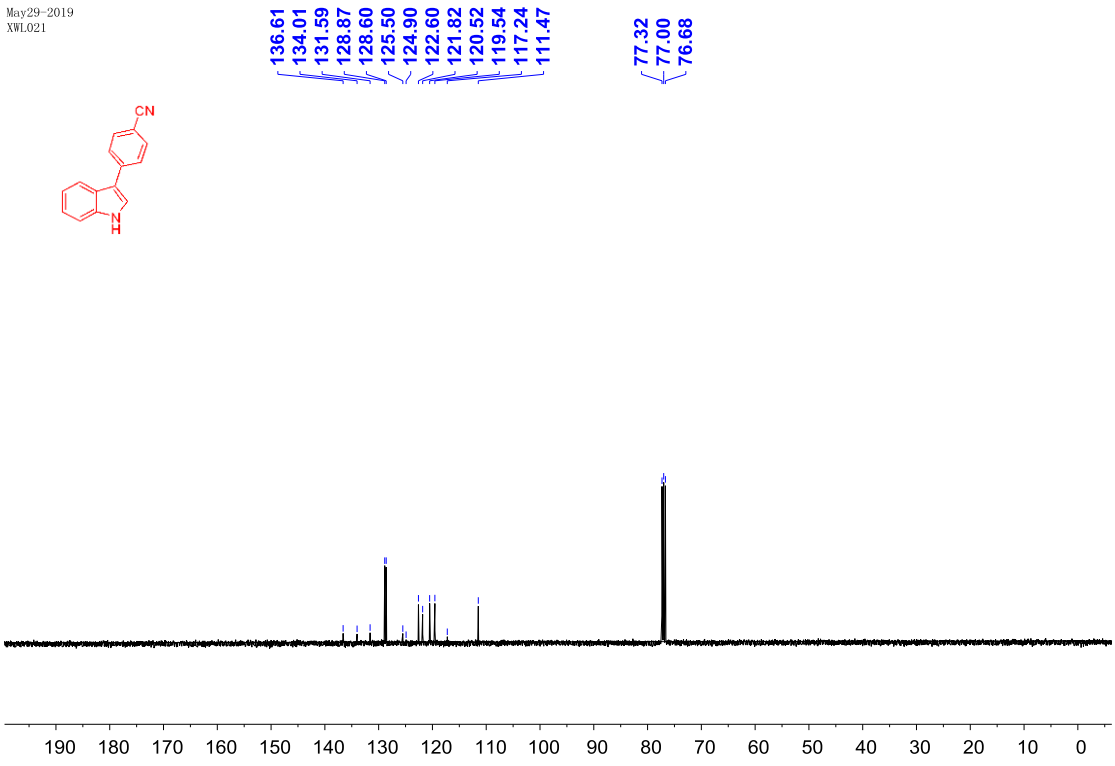
^{1}H and ^{13}C NMR spectra of **3c**.



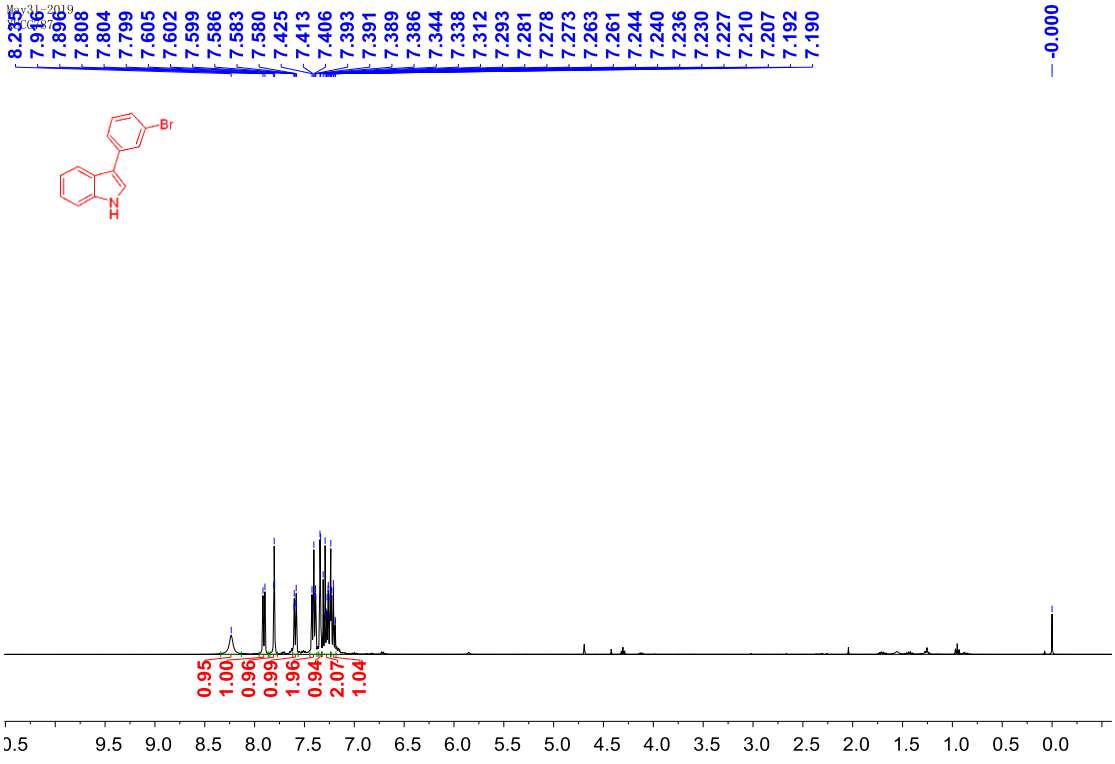


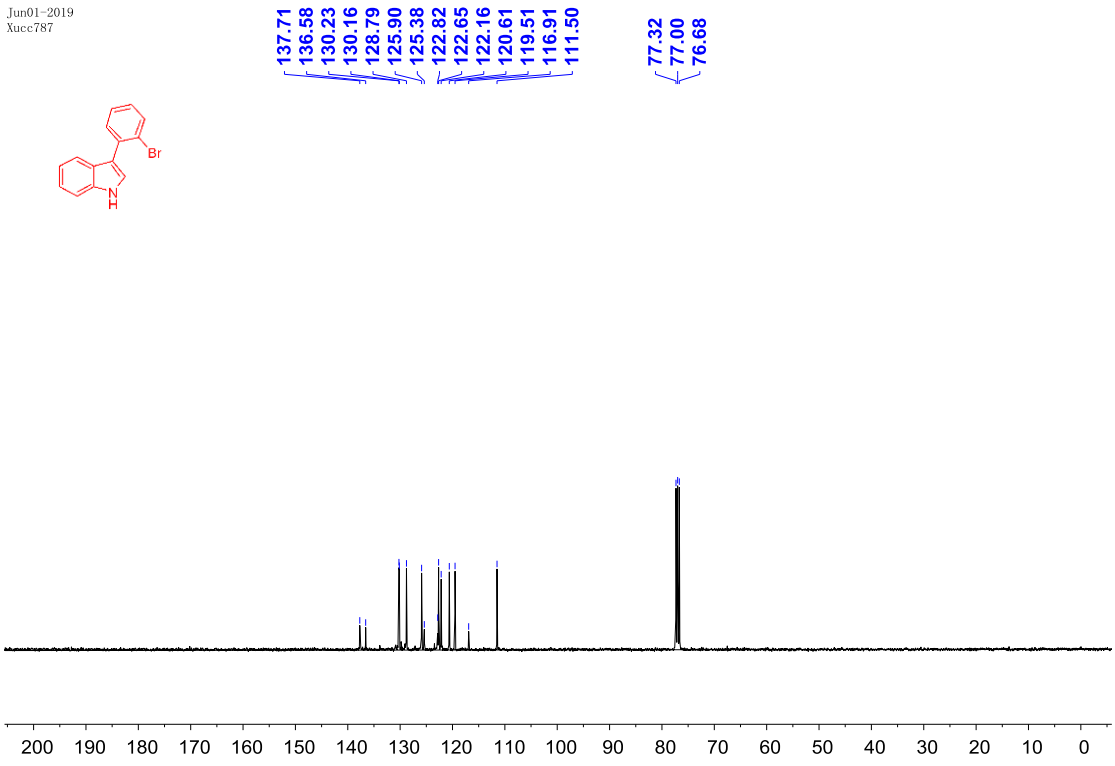
^{1}H and ^{13}C NMR spectra of **3d**.



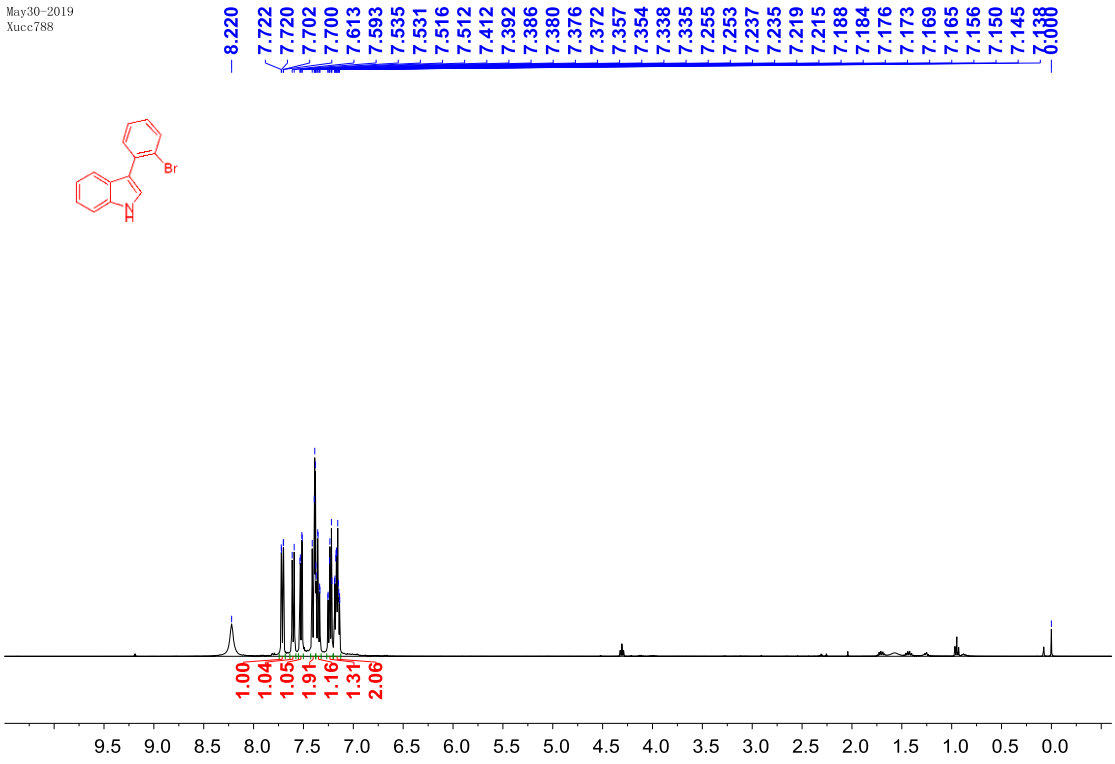


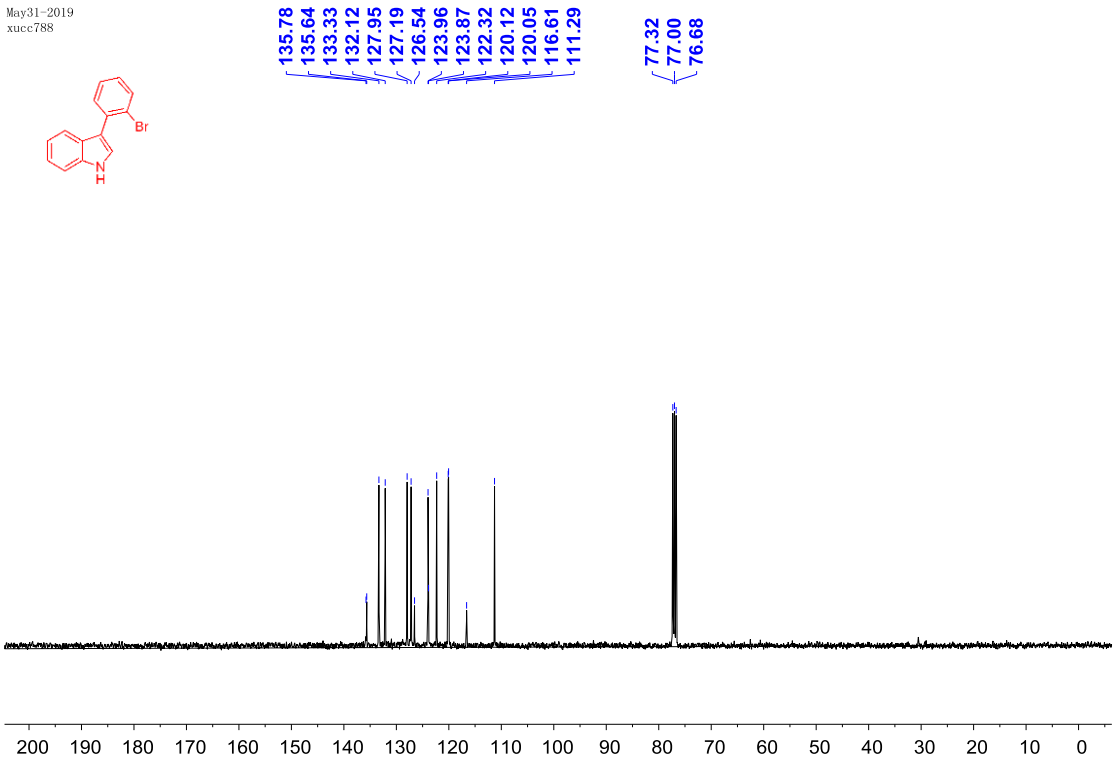
^{1}H and ^{13}C NMR spectra of **3e**.



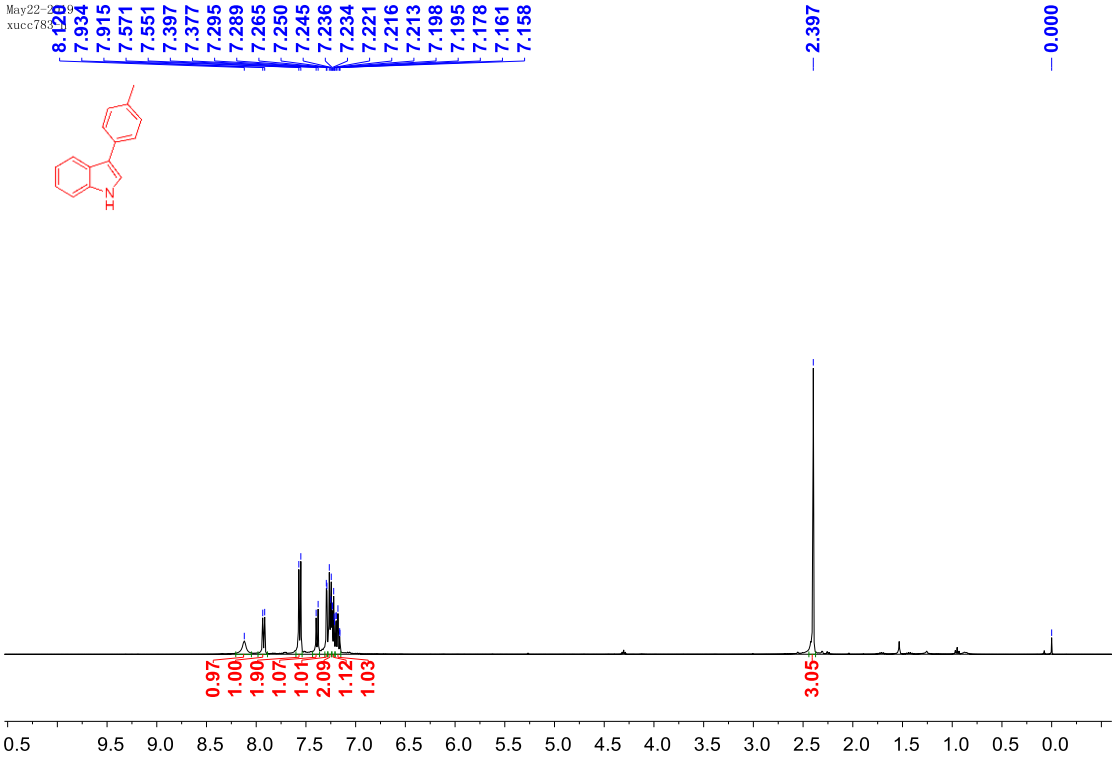


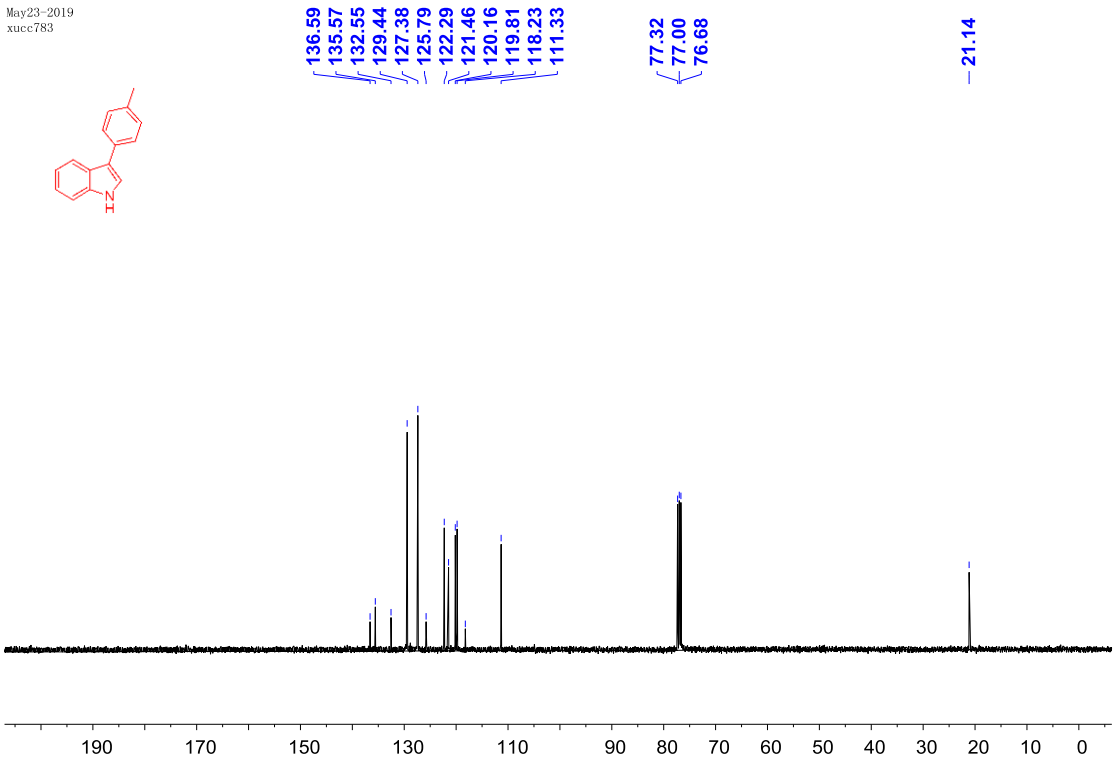
^{1}H and ^{13}C NMR spectra of **3f**.



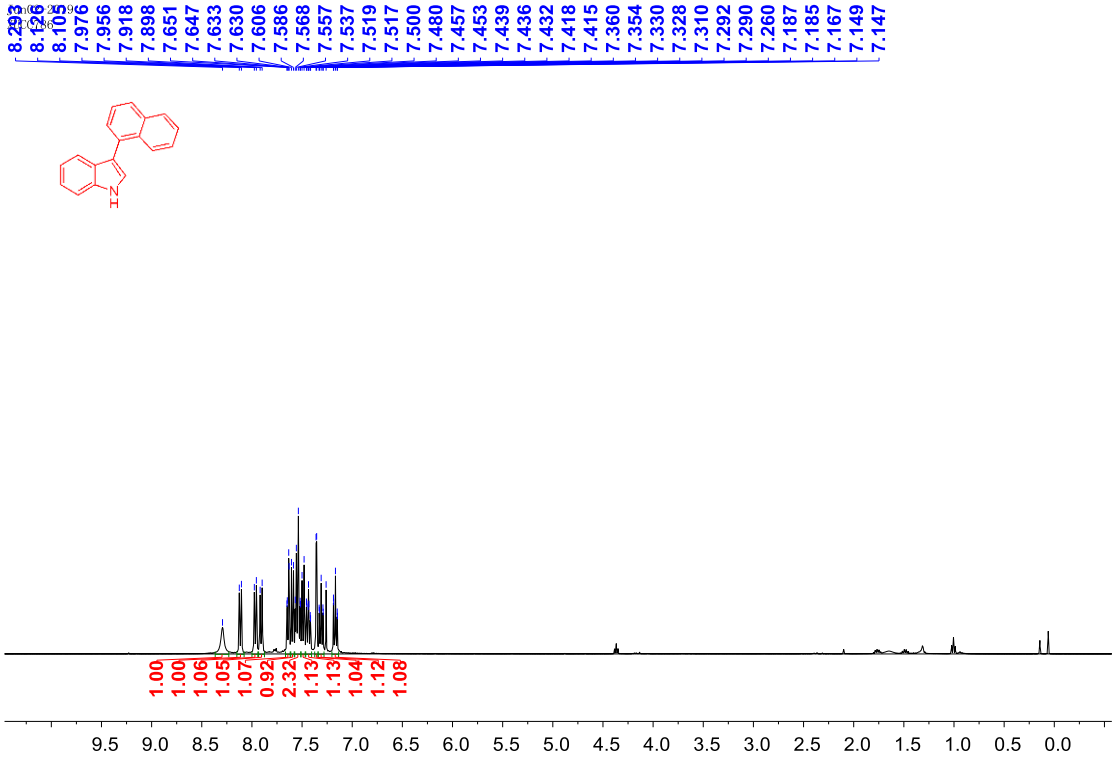


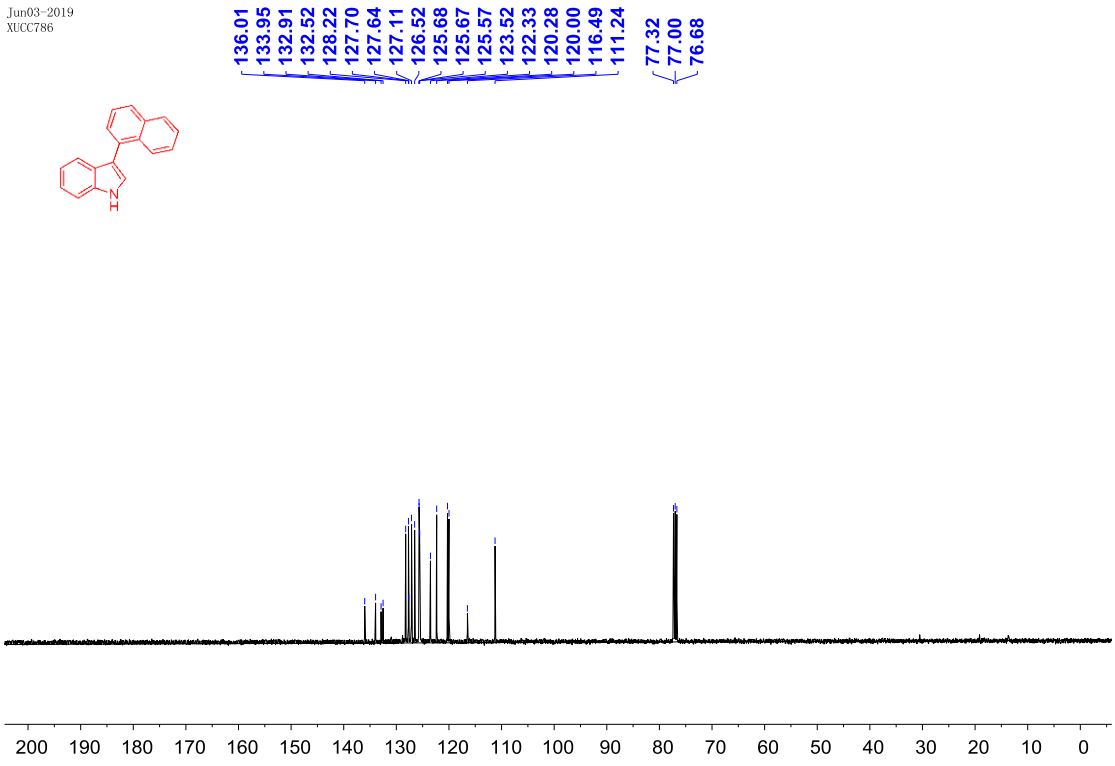
^{1}H and ^{13}C NMR spectra of **3g**.



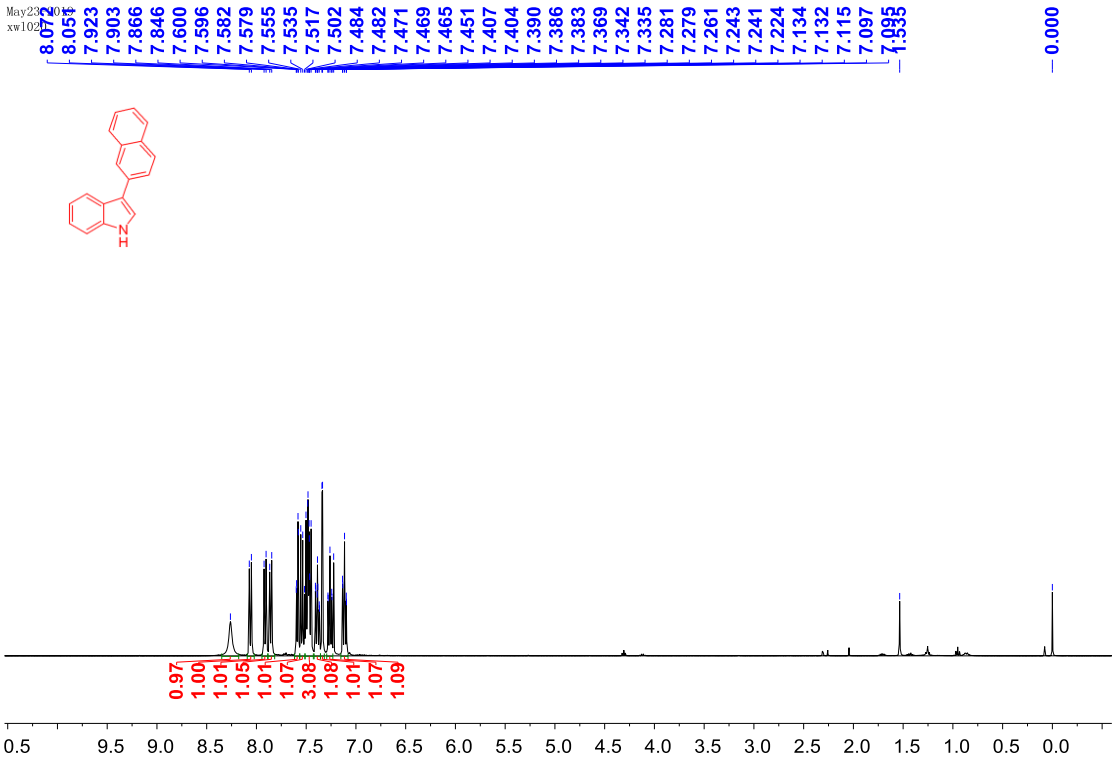


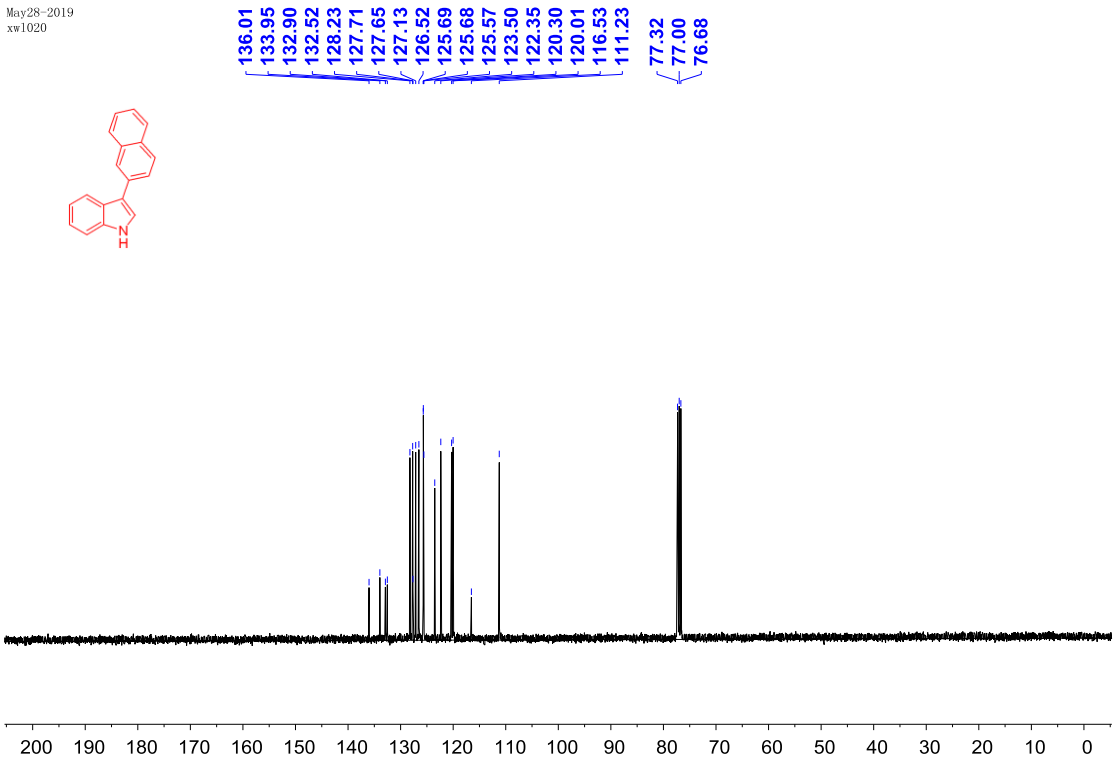
^{1}H and ^{13}C NMR spectra of **3h**.



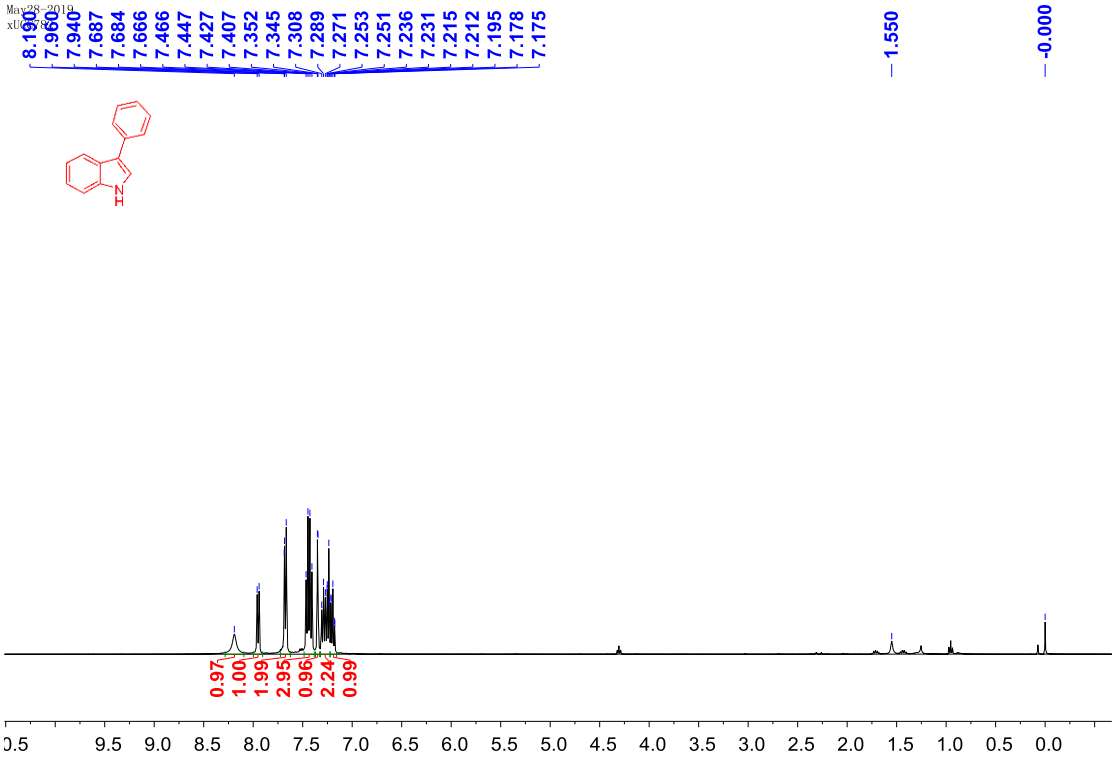


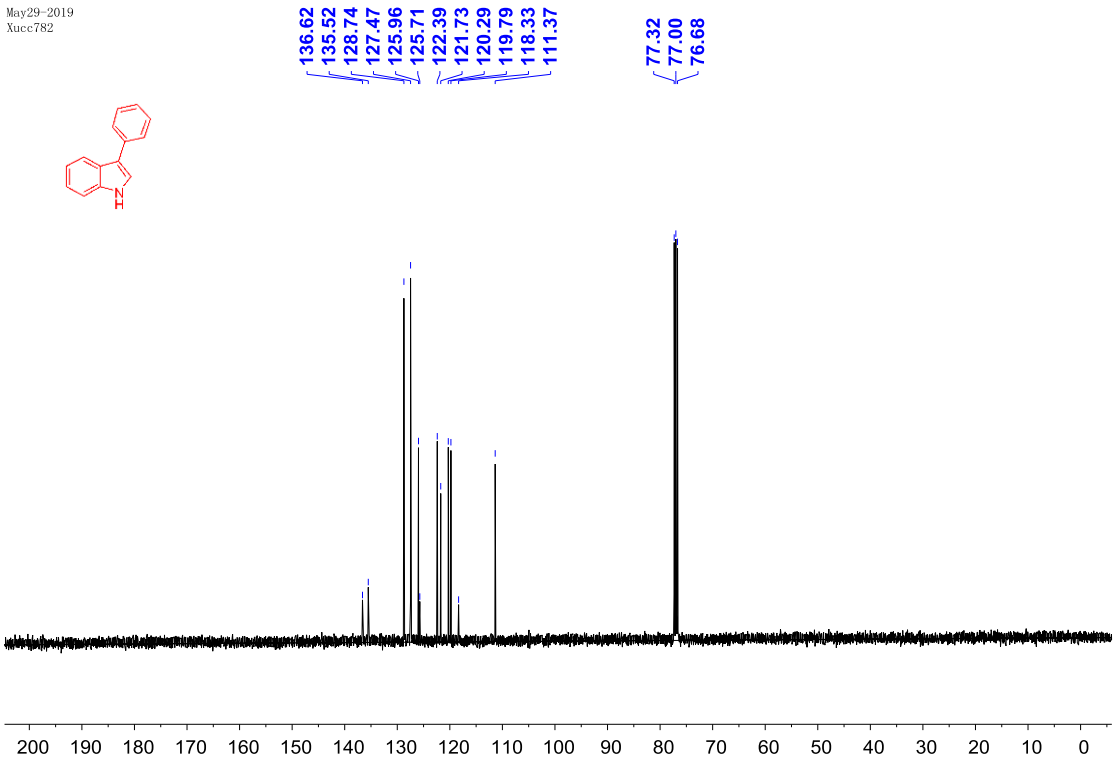
^{1}H and ^{13}C NMR spectra of **3i**.



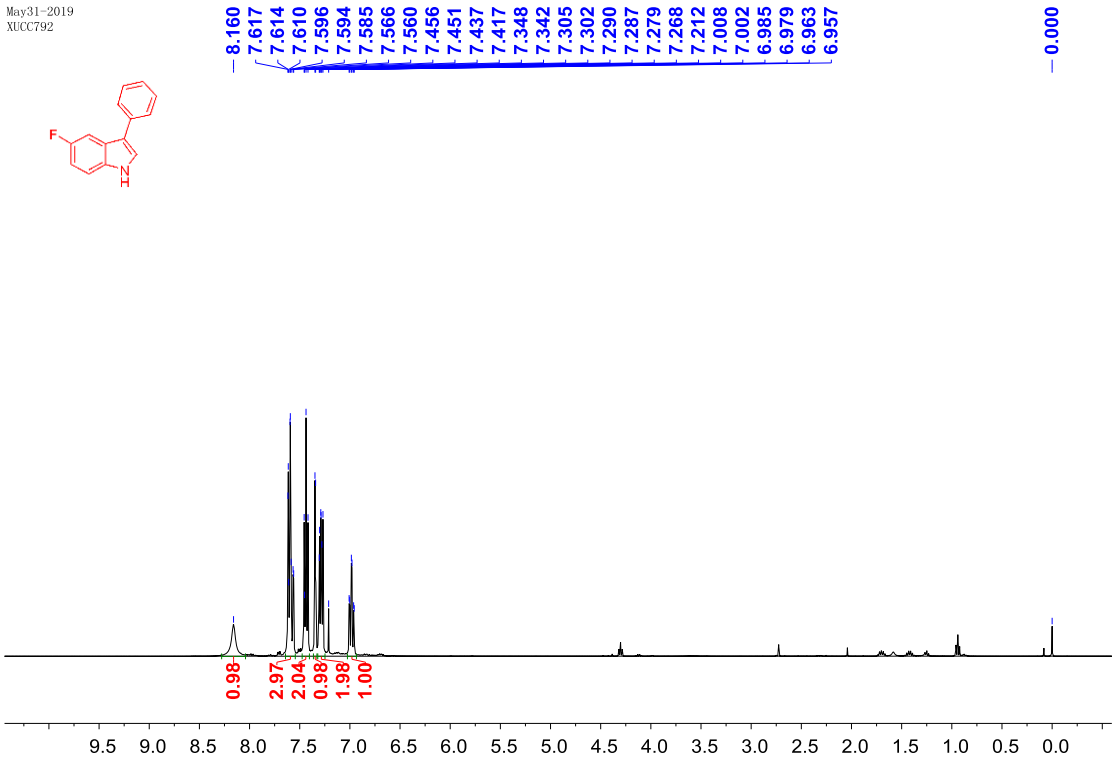


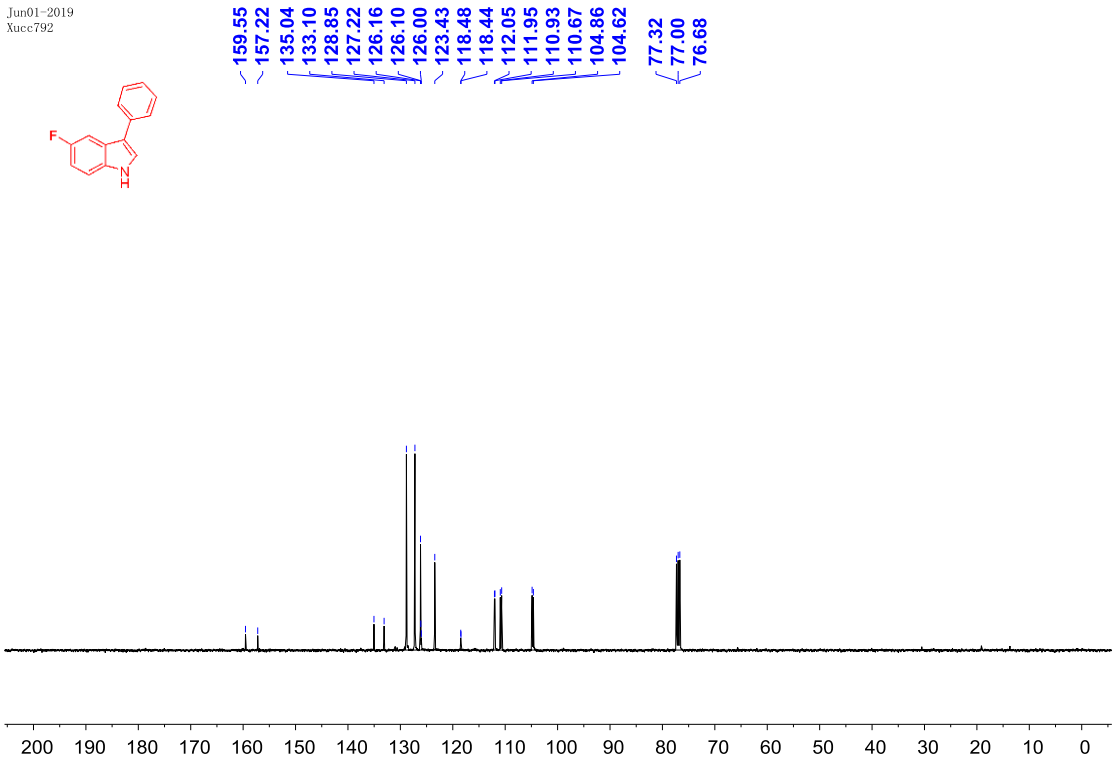
^{1}H and ^{13}C NMR spectra of **3j**.

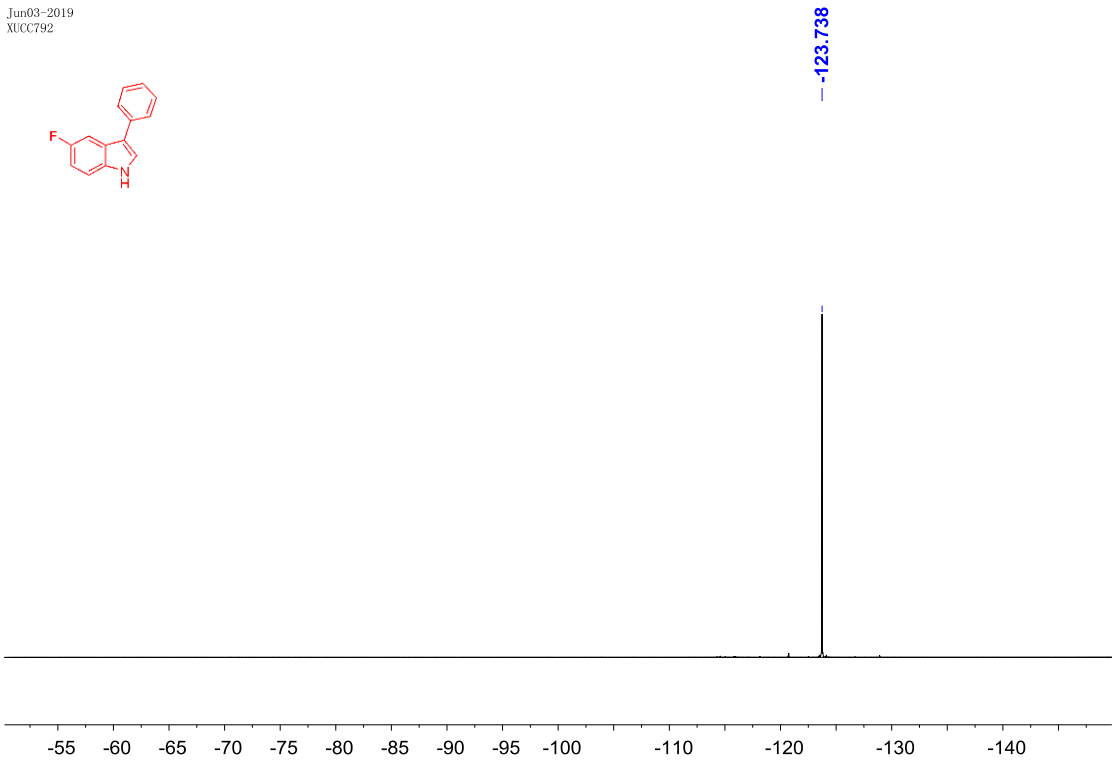




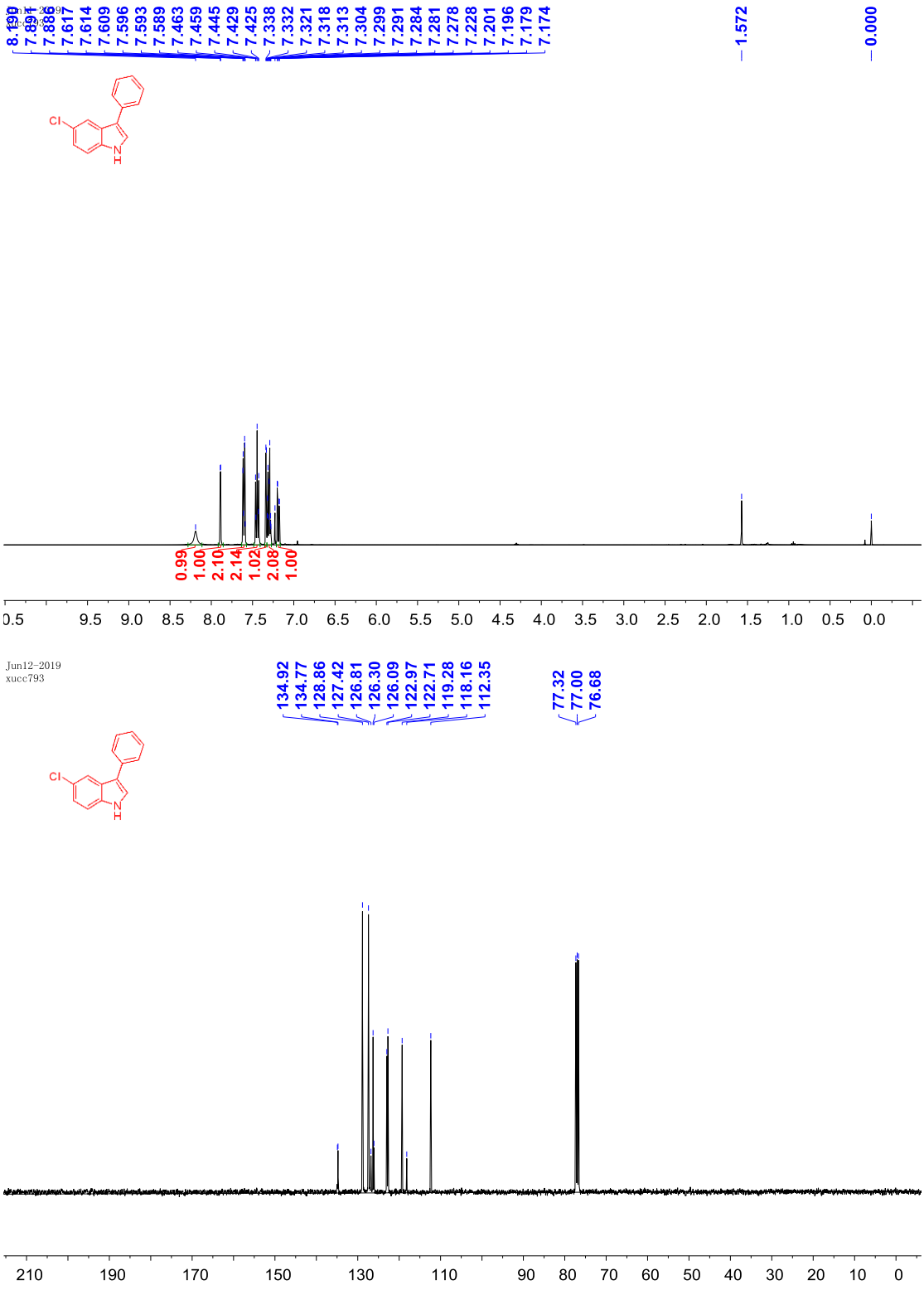
^{1}H, ^{13}C NMR and ^{19}F spectra of **3k**.



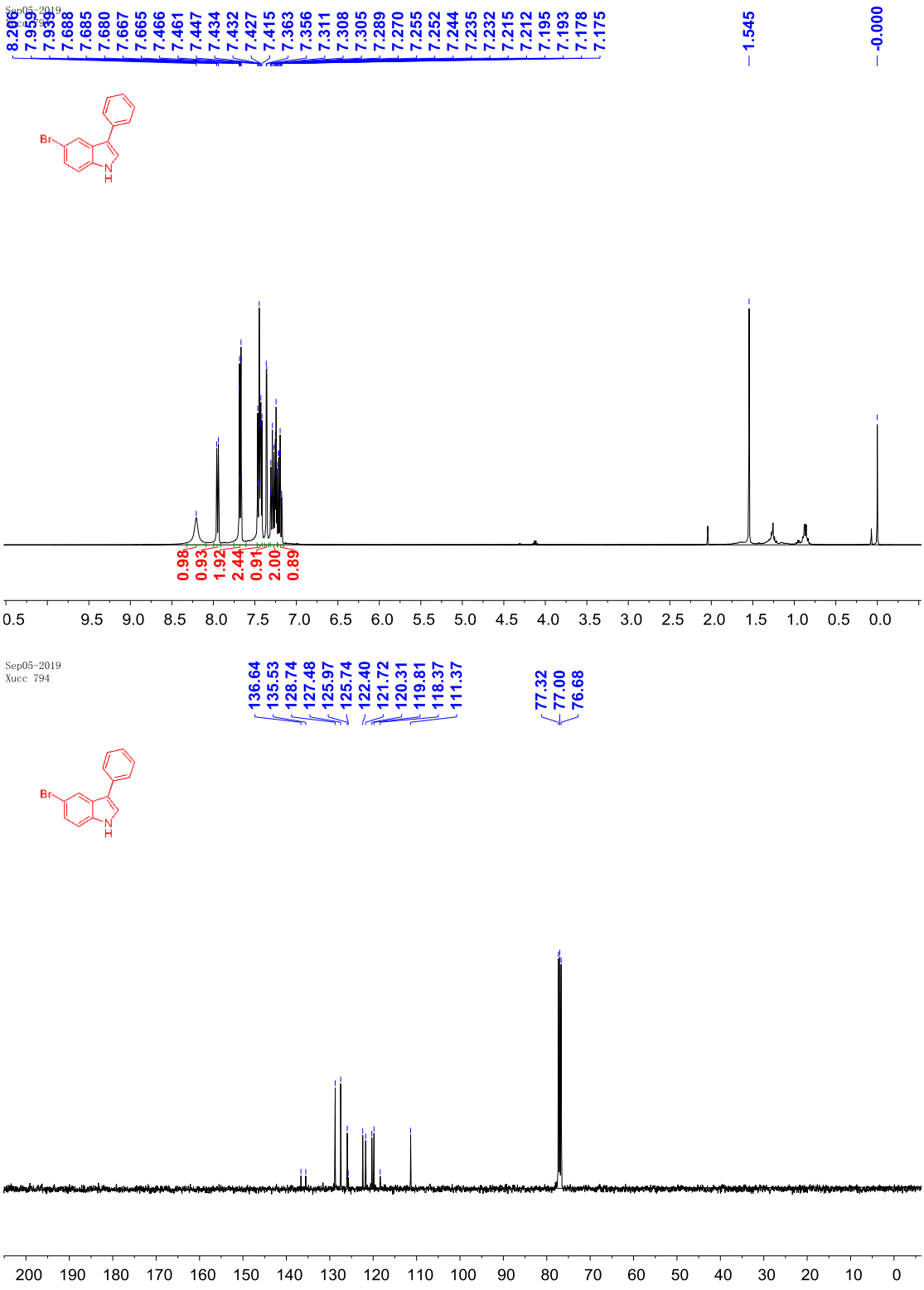




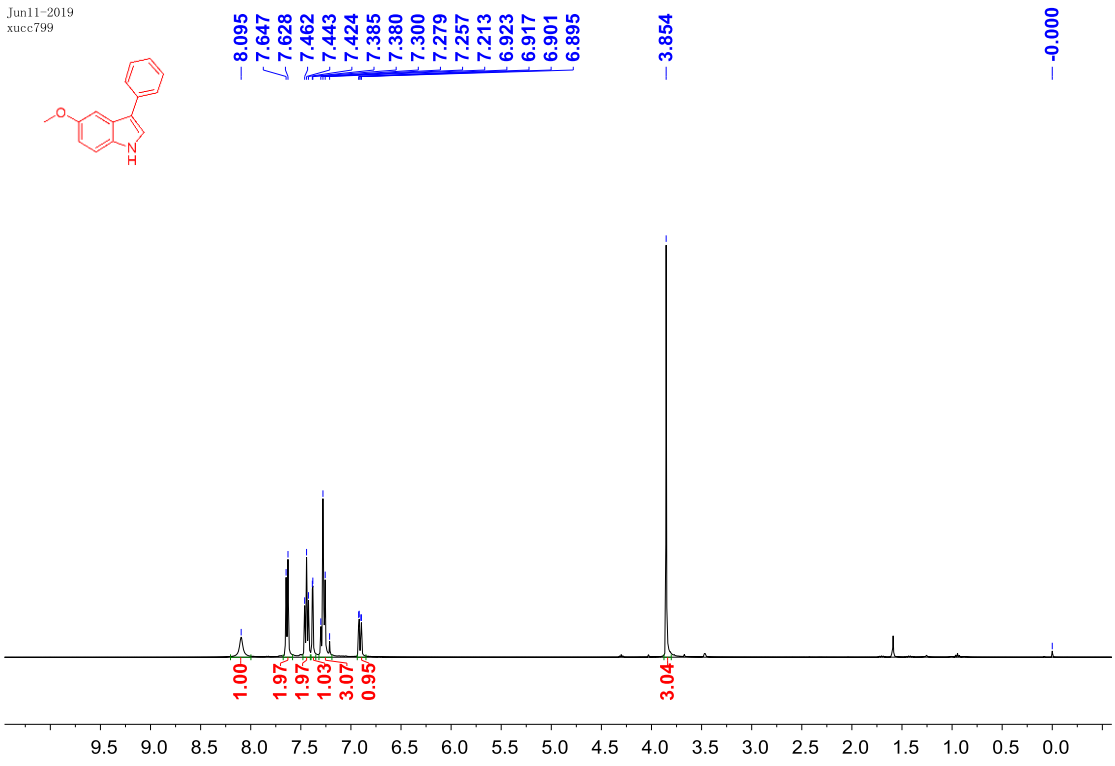
^{1}H and ^{13}C NMR spectra of **3l**.



^{1}H and ^{13}C NMR spectra of **3m**.



^{1}H and ^{13}C NMR spectra of **3n**.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1.03
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3.04
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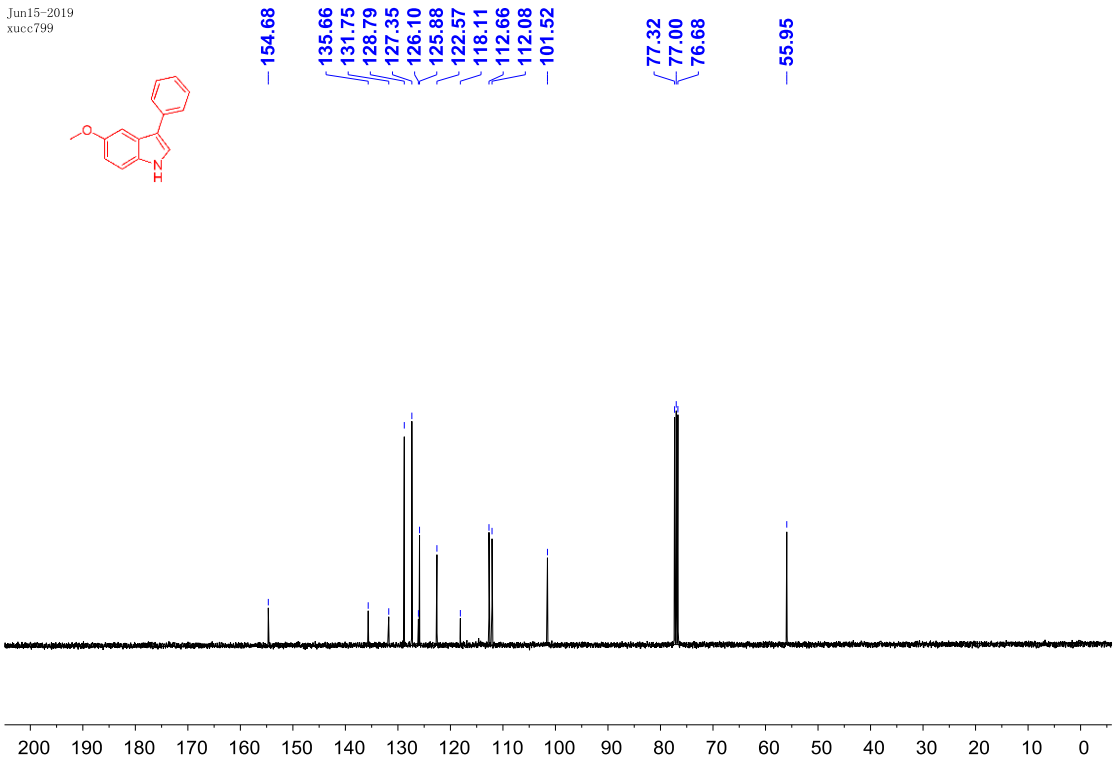
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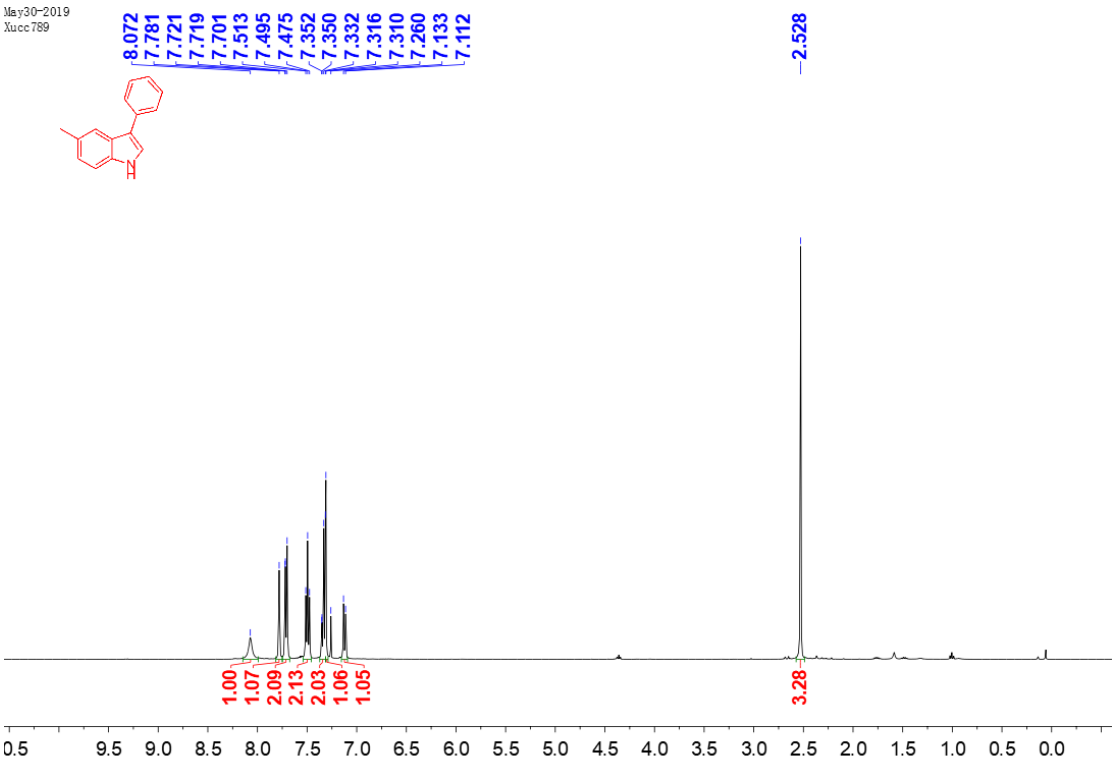
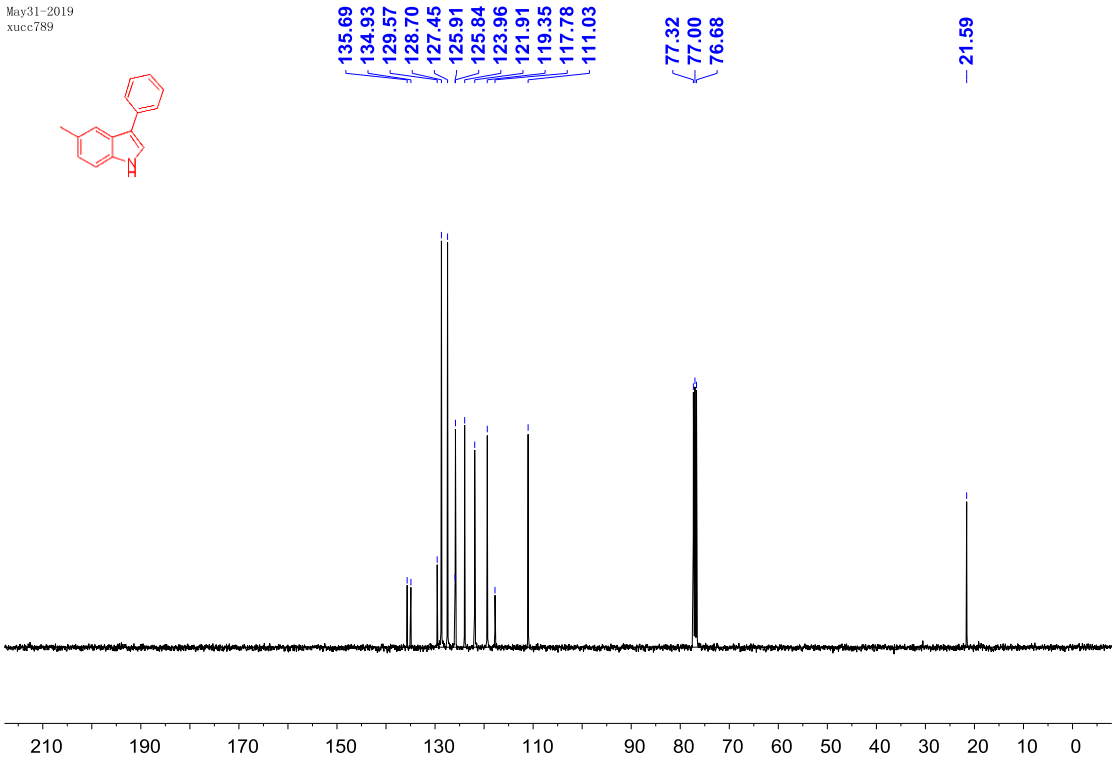
^{1}H and ^{13}C NMR spectra of **3o**.





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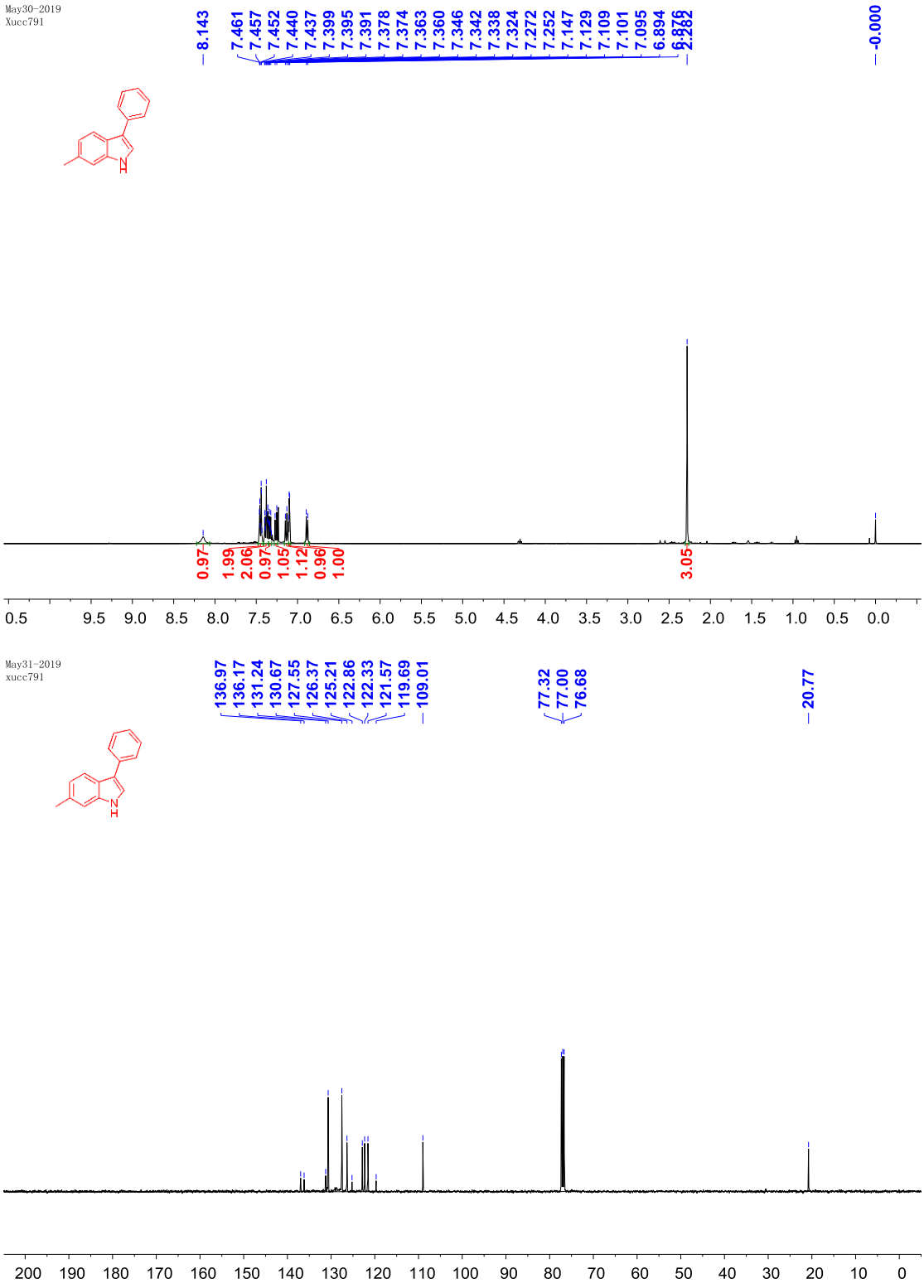
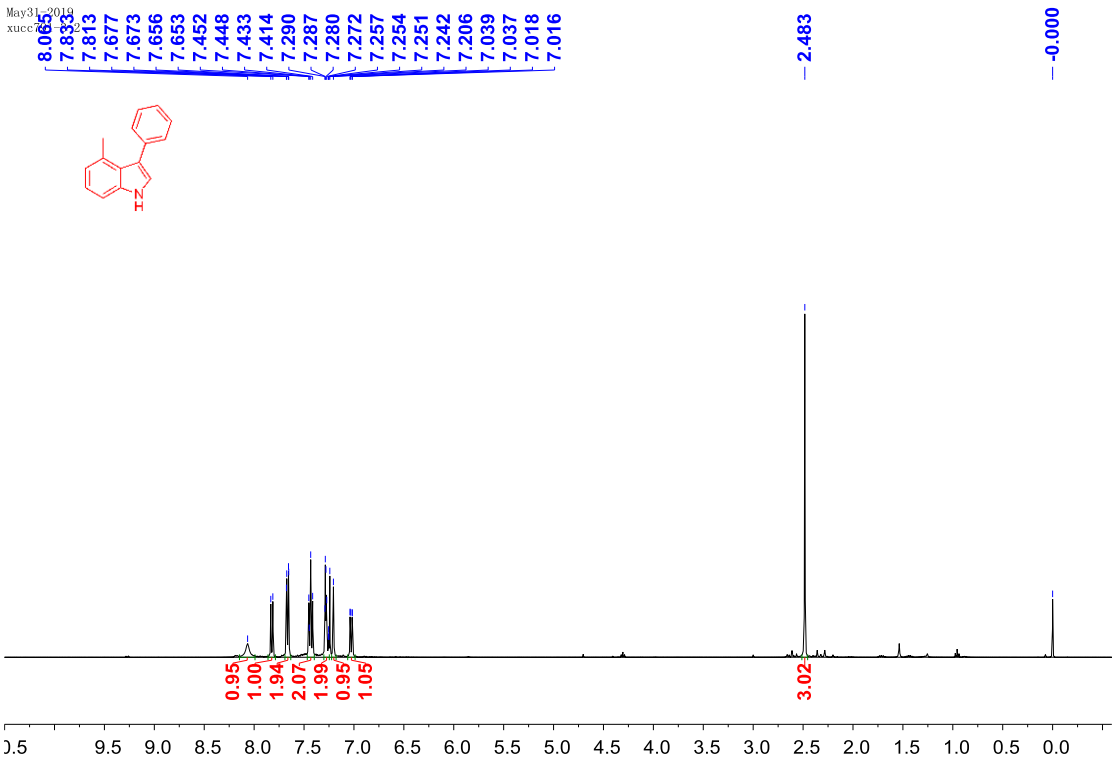


^{1}H and ^{13}C NMR spectra of **3q**.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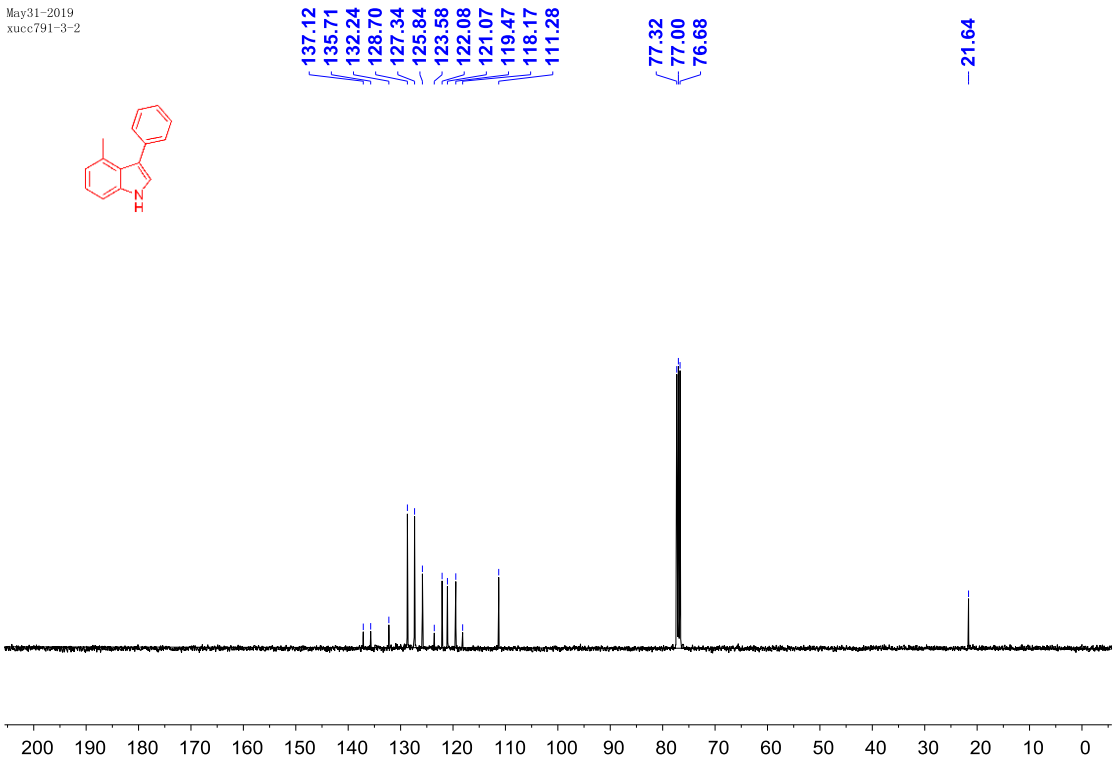
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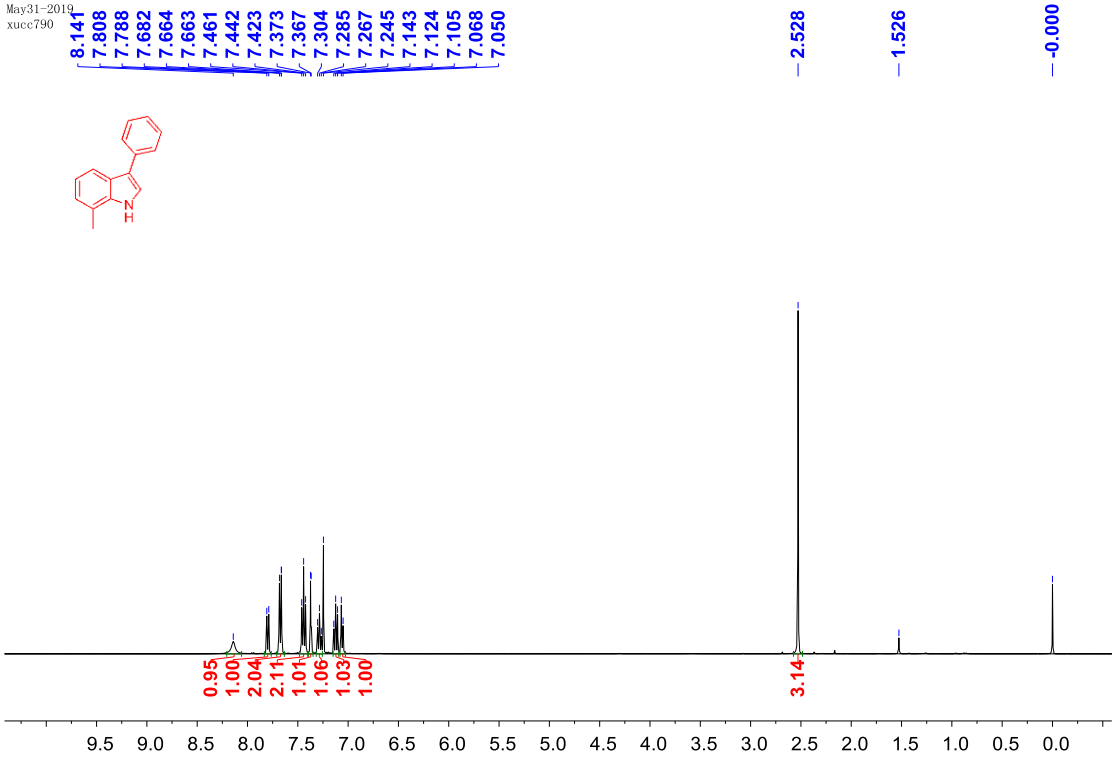
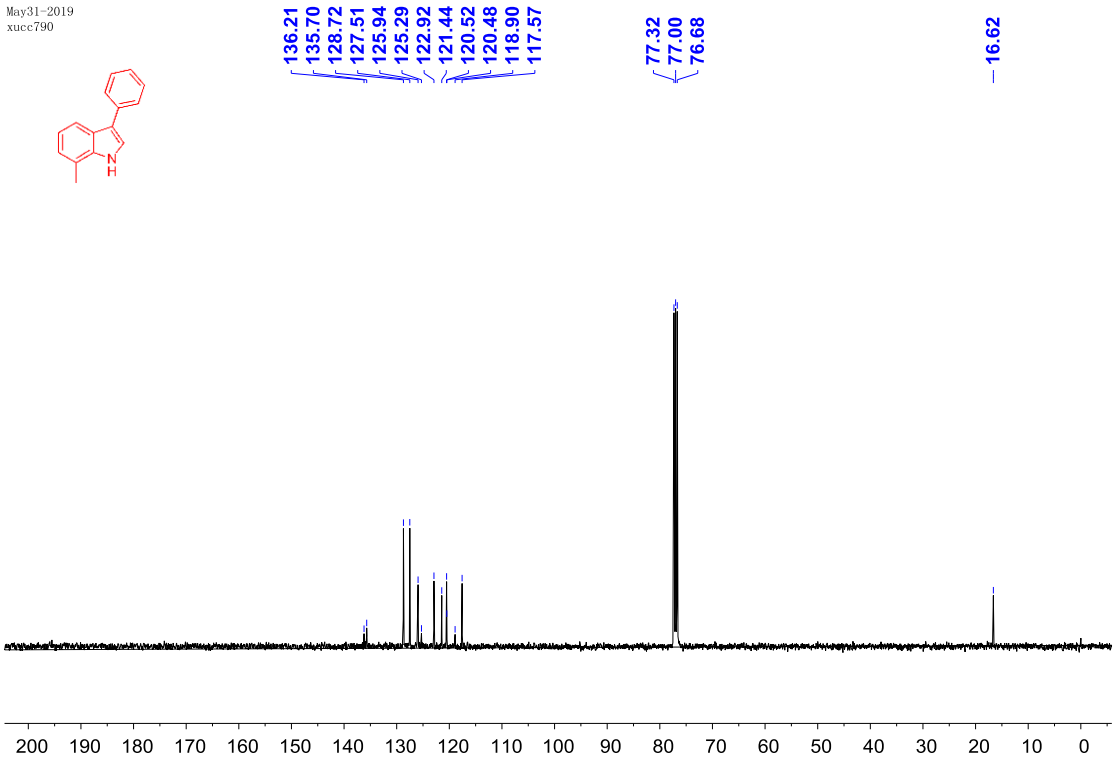
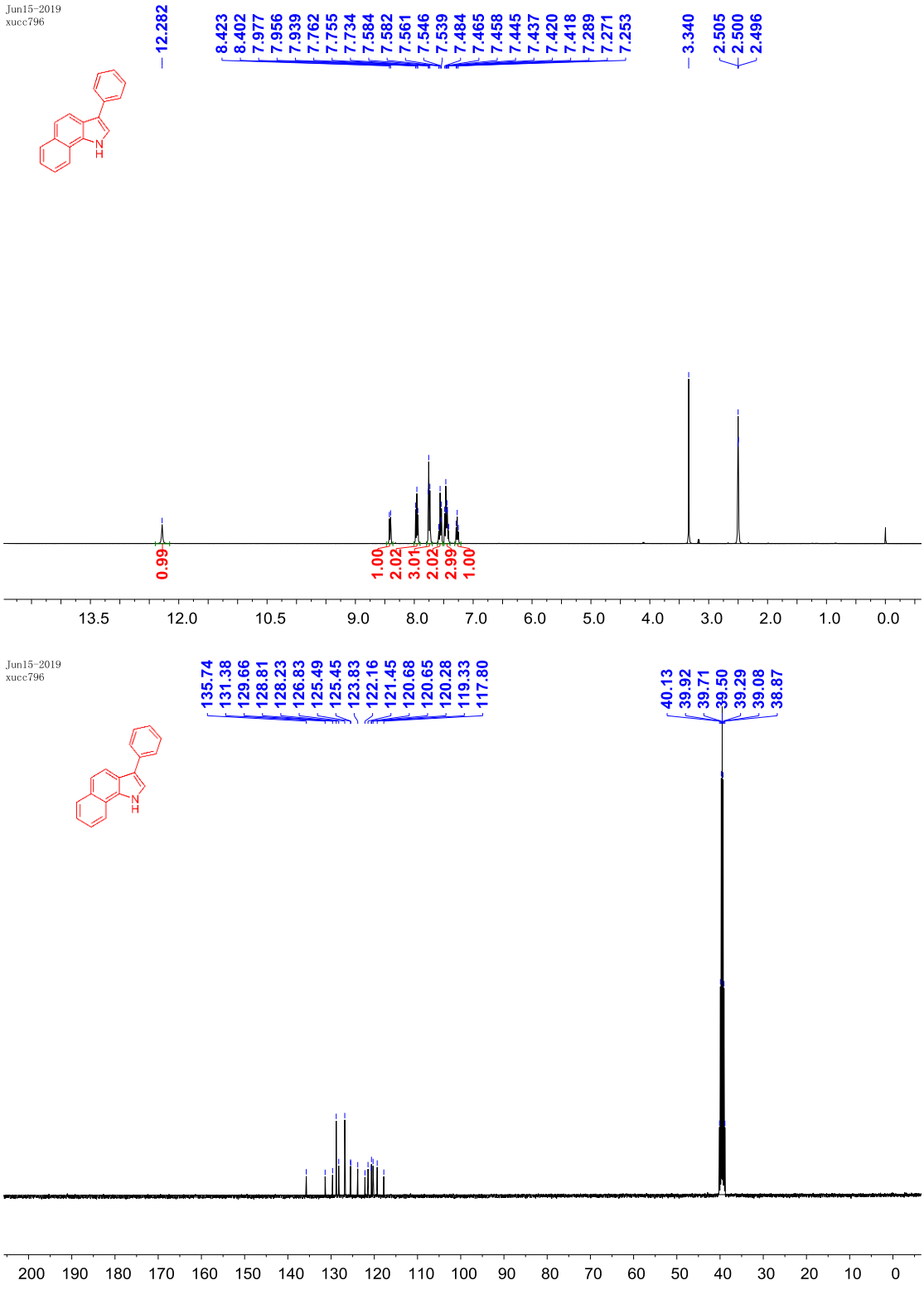
^{1}H and ^{13}C NMR spectra of **3r**.

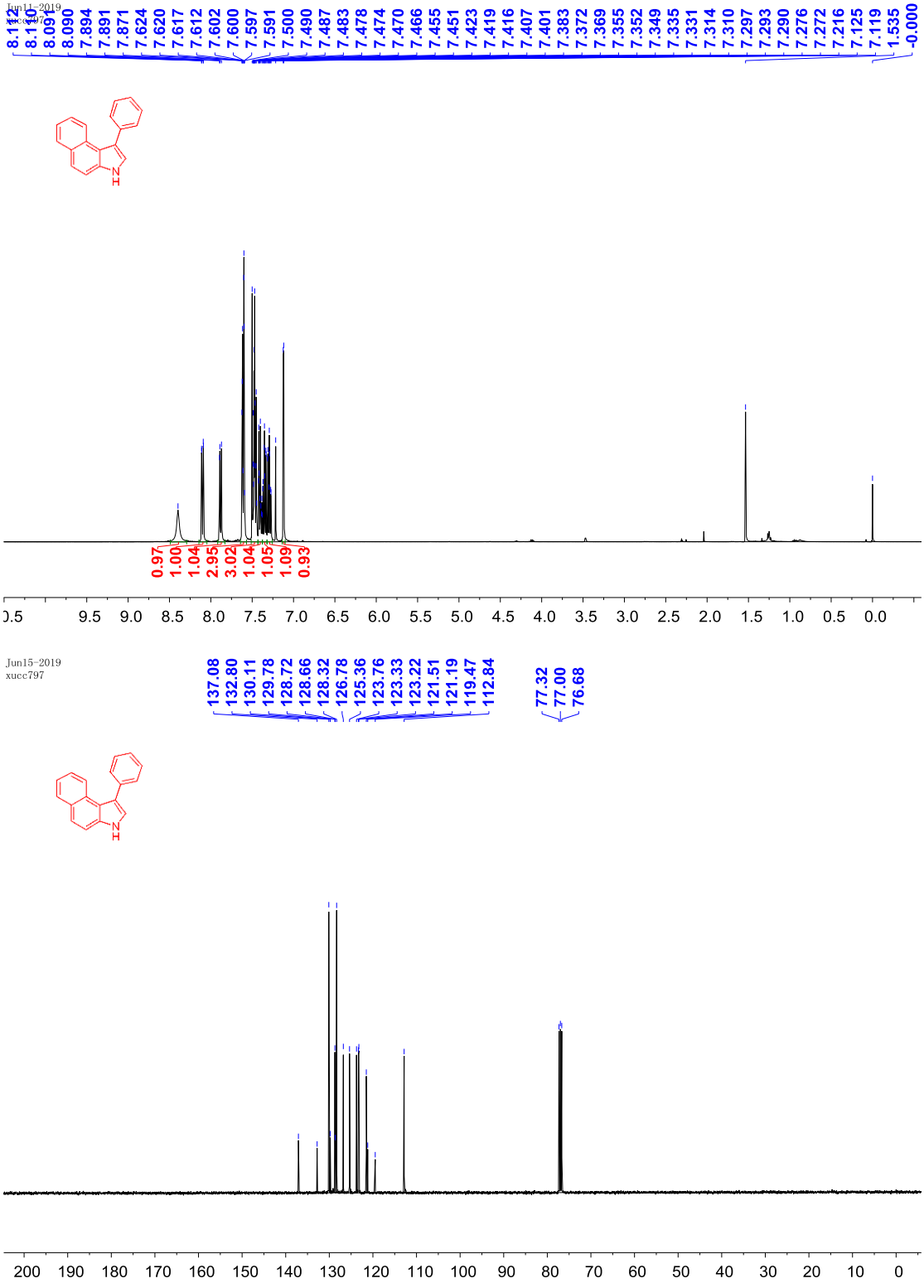




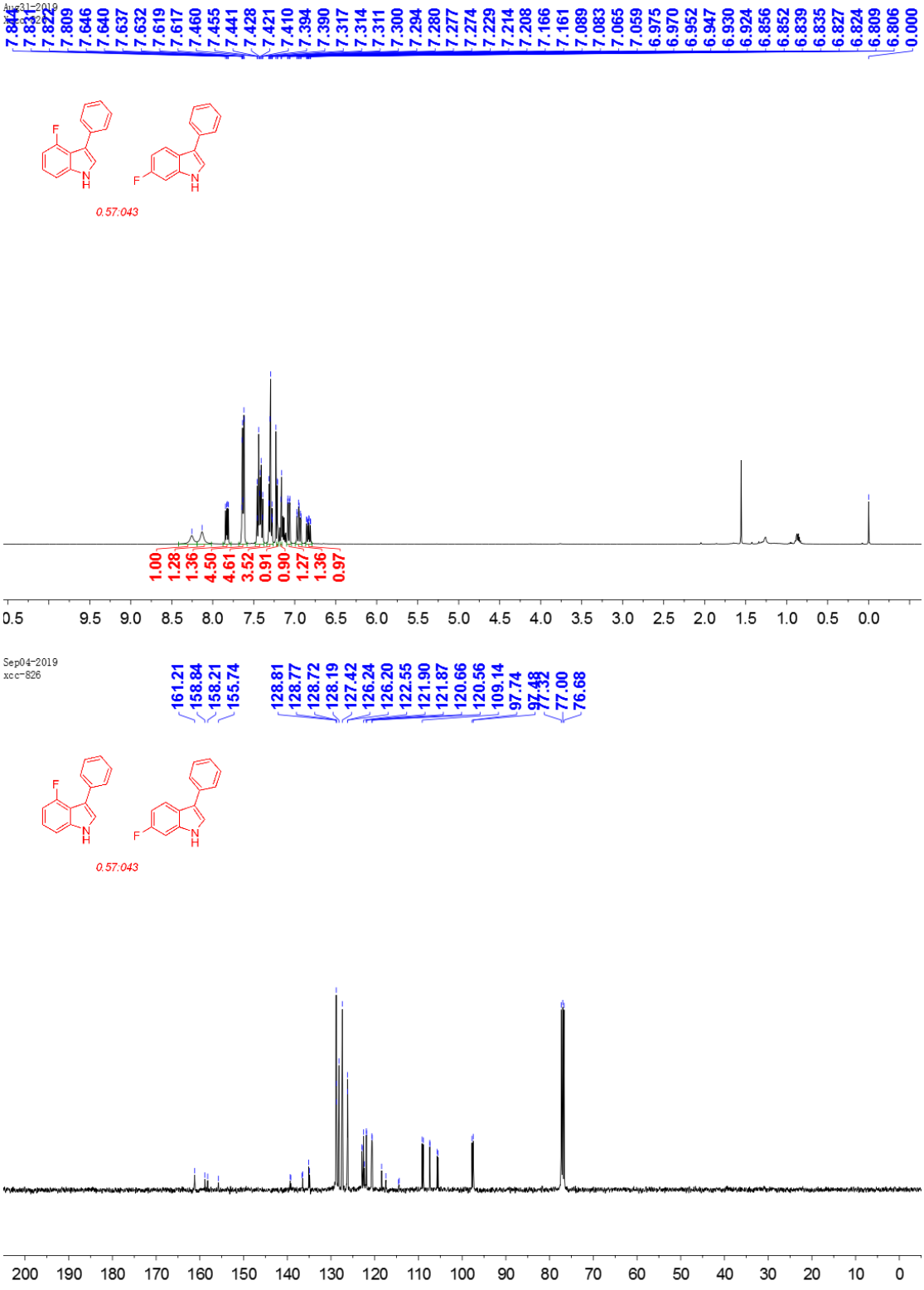
^{1}H and ^{13}C NMR spectra of **3s**.

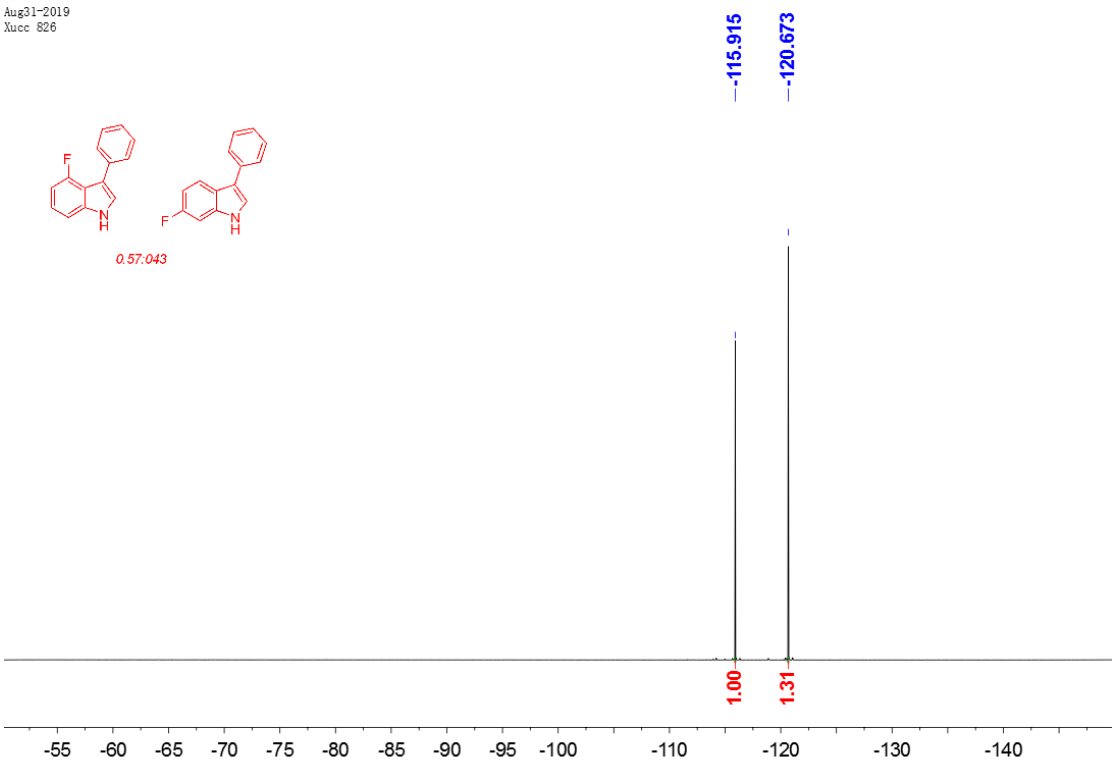


^{1}H and ^{13}C NMR spectra of **3t**.

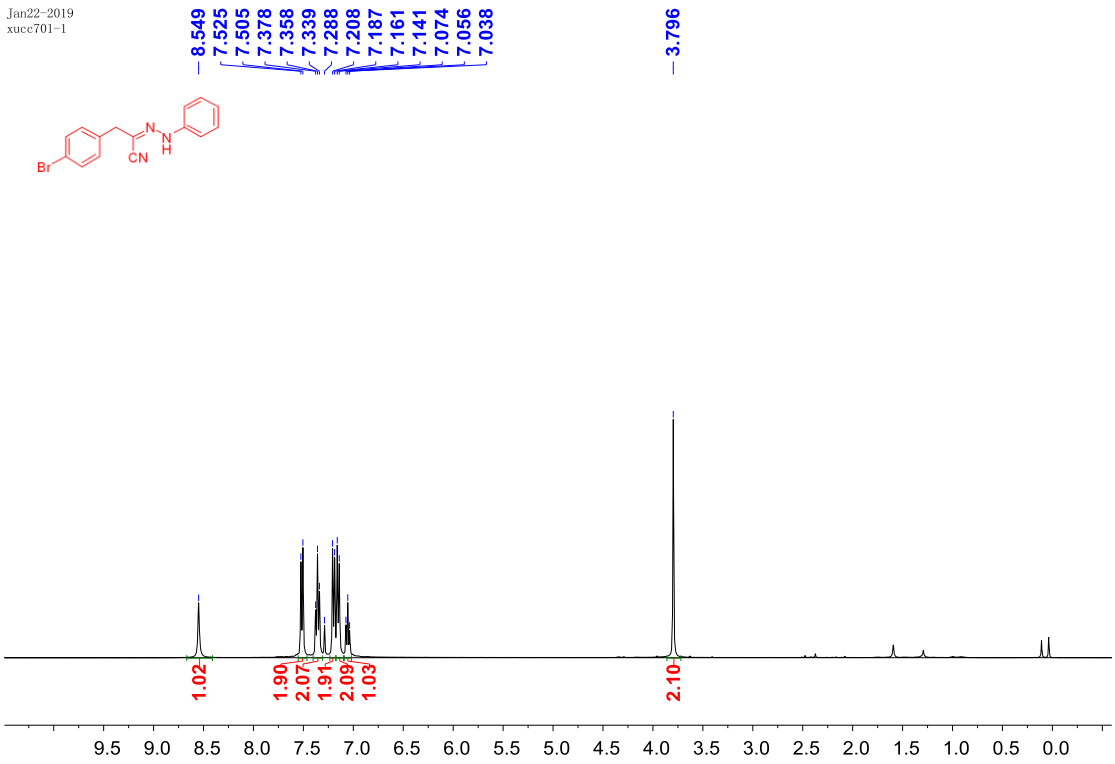


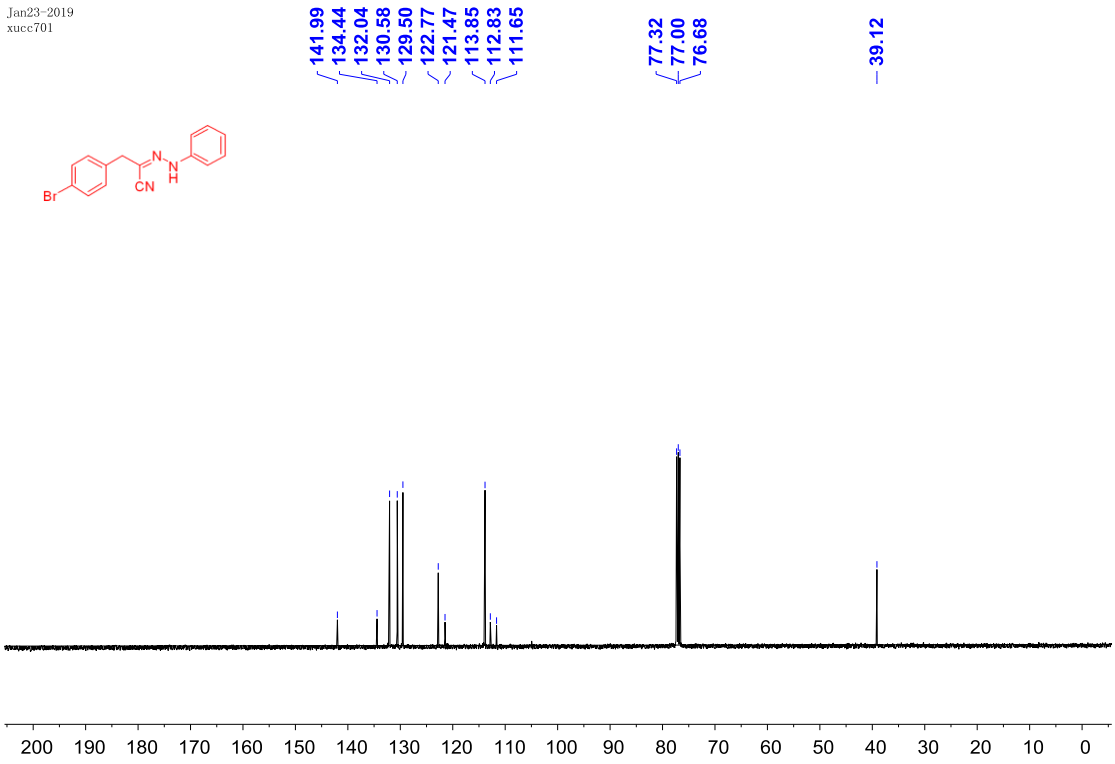
^{1}H, ^{13}C and $^{19}FNMR$ spectra of **3u** and **3v**.



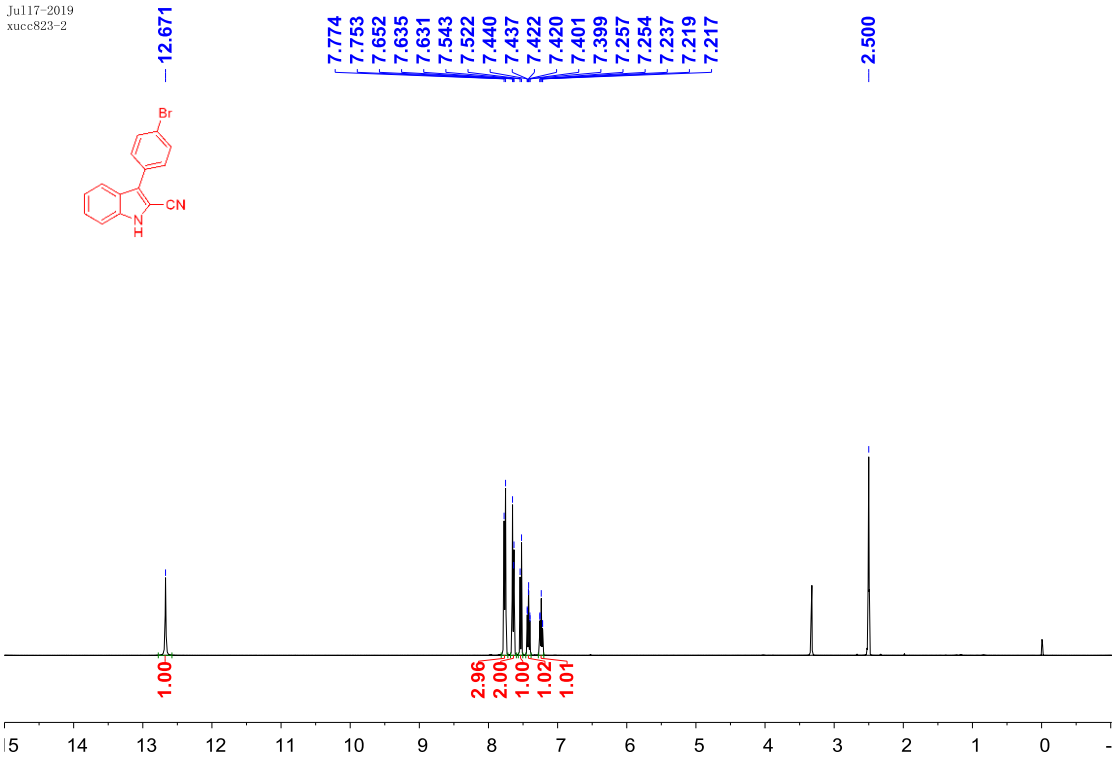


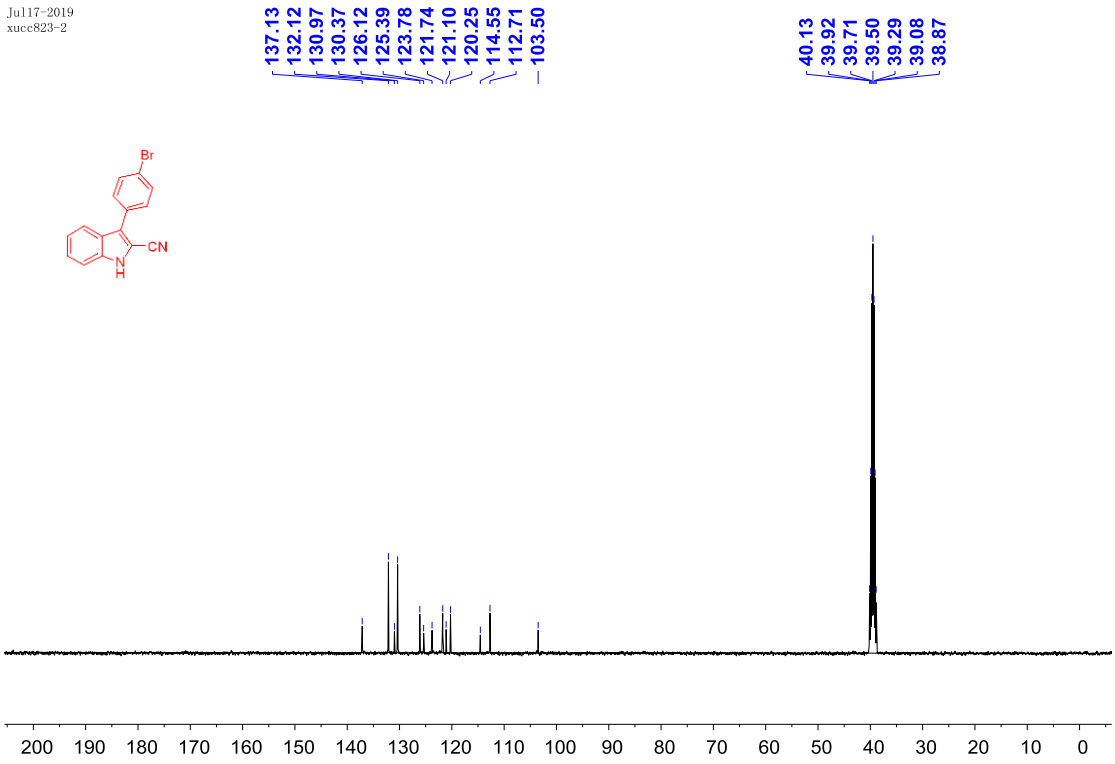
^{1}H and ^{13}C NMR spectra of **4**.



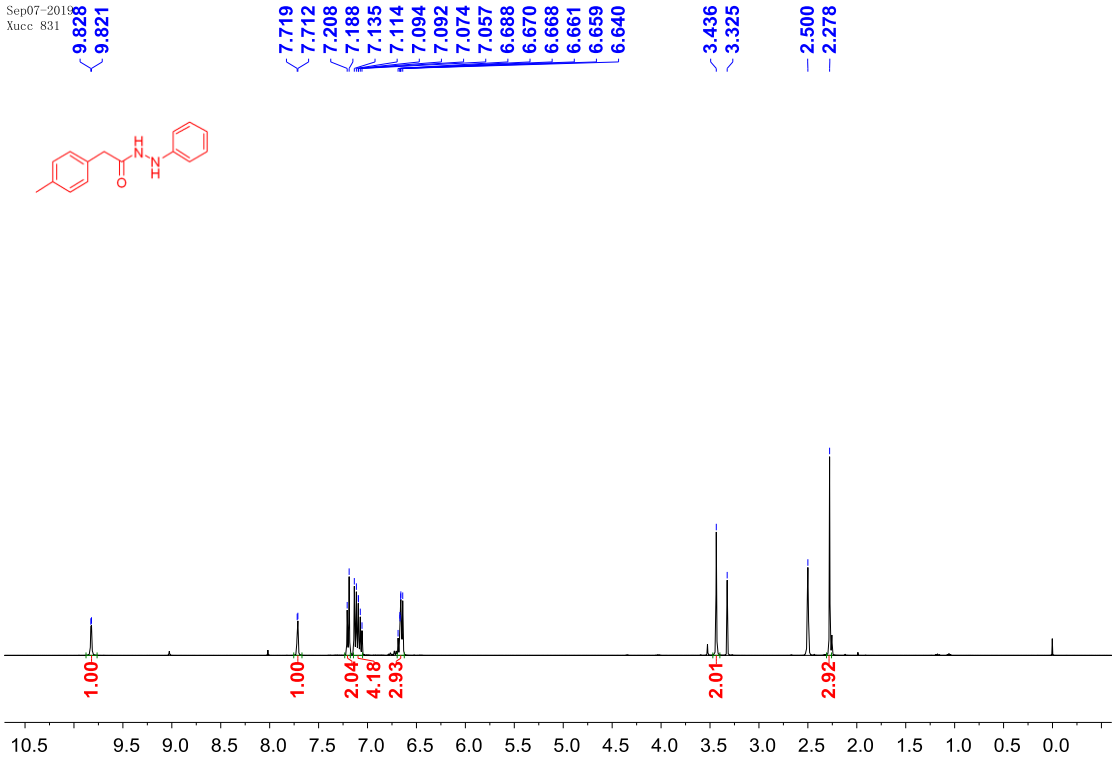


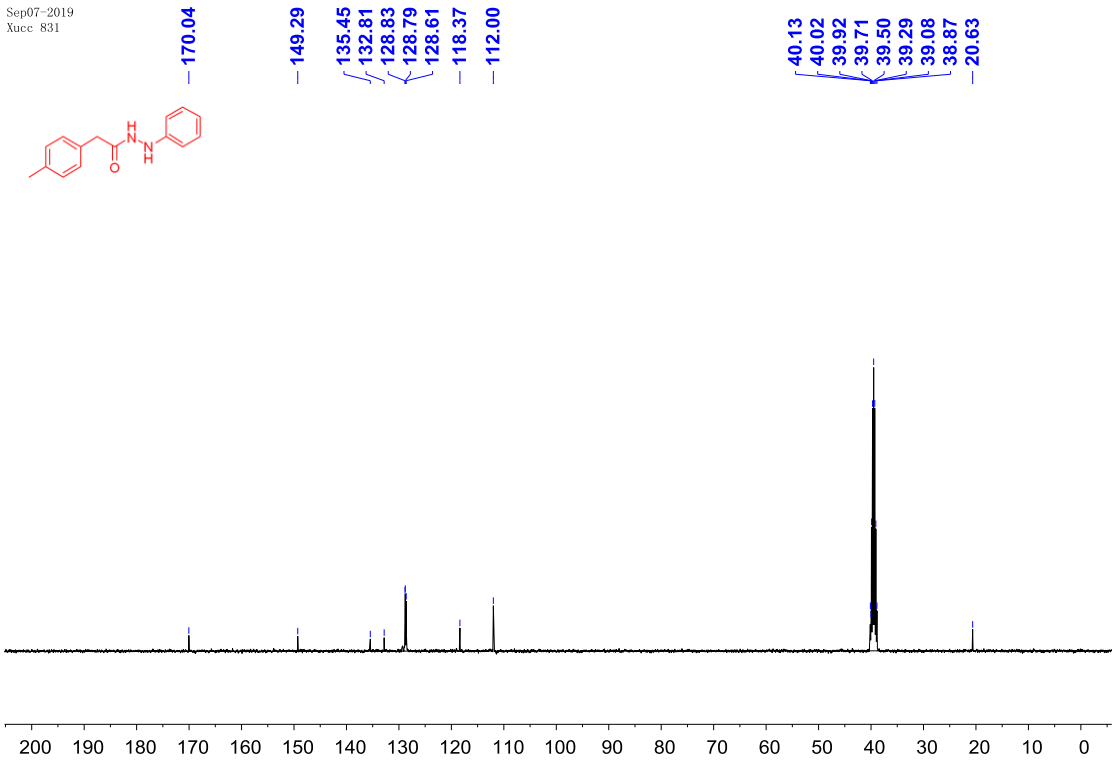
^{1}H and ^{13}C NMR spectra of **5**.



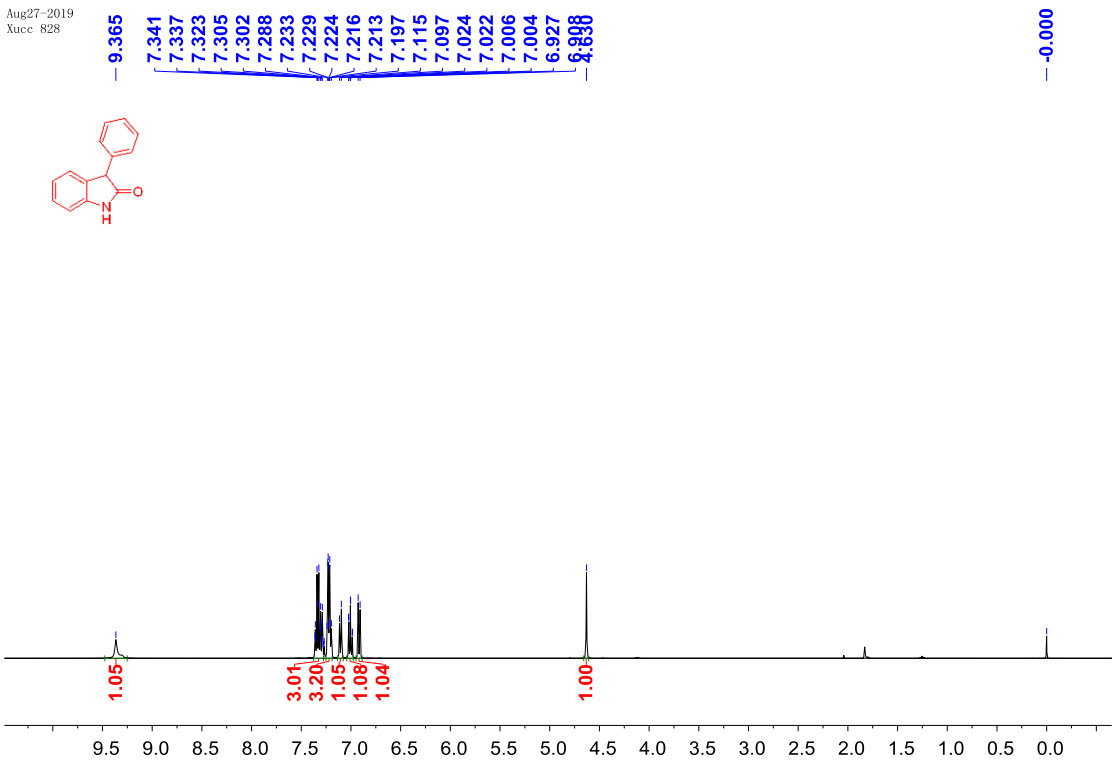


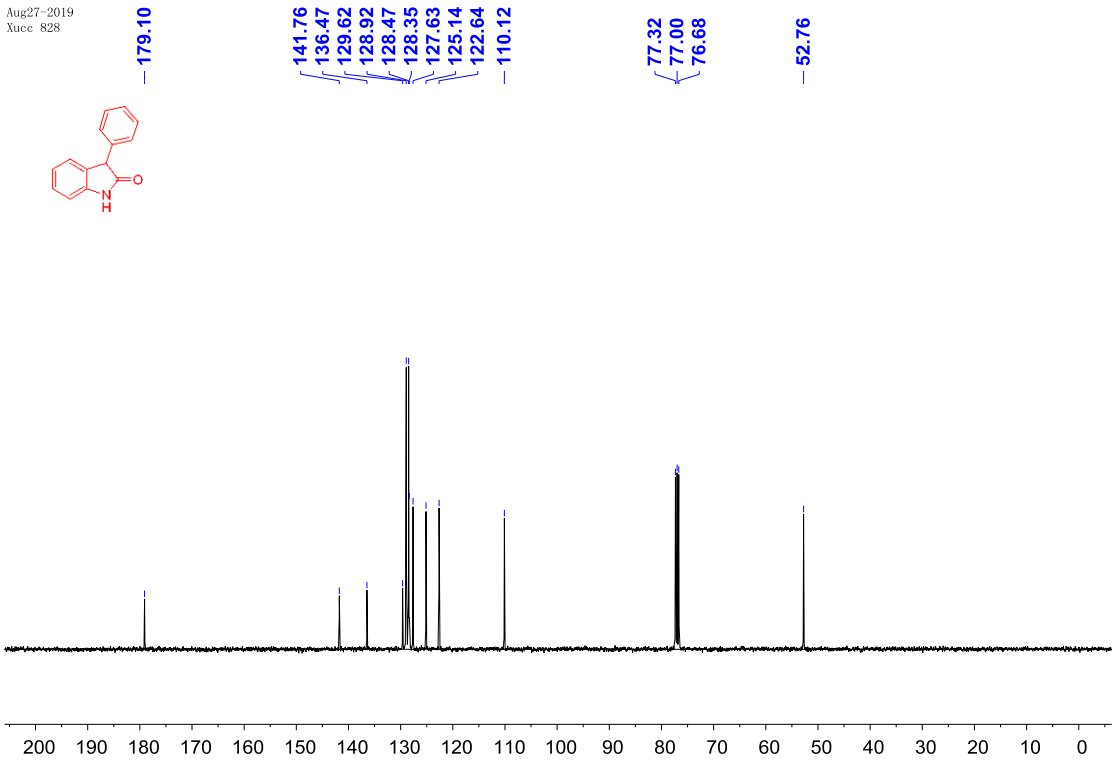
^{1}H and ^{13}C NMR spectra of **6**.



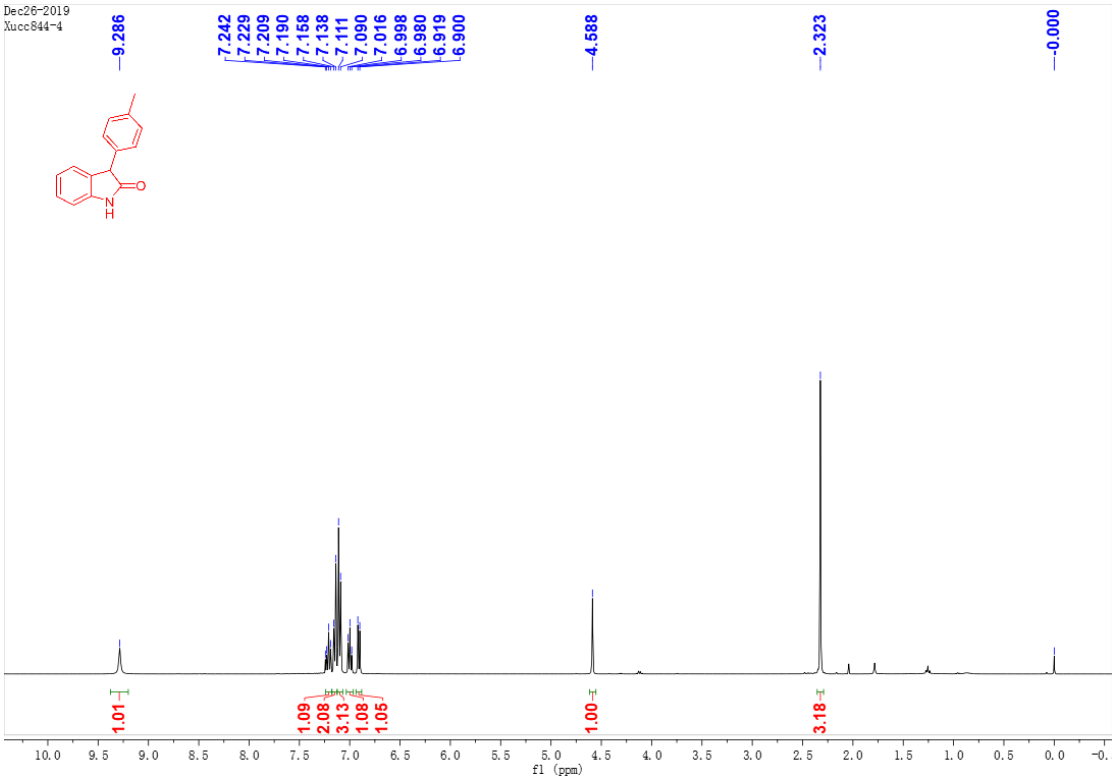


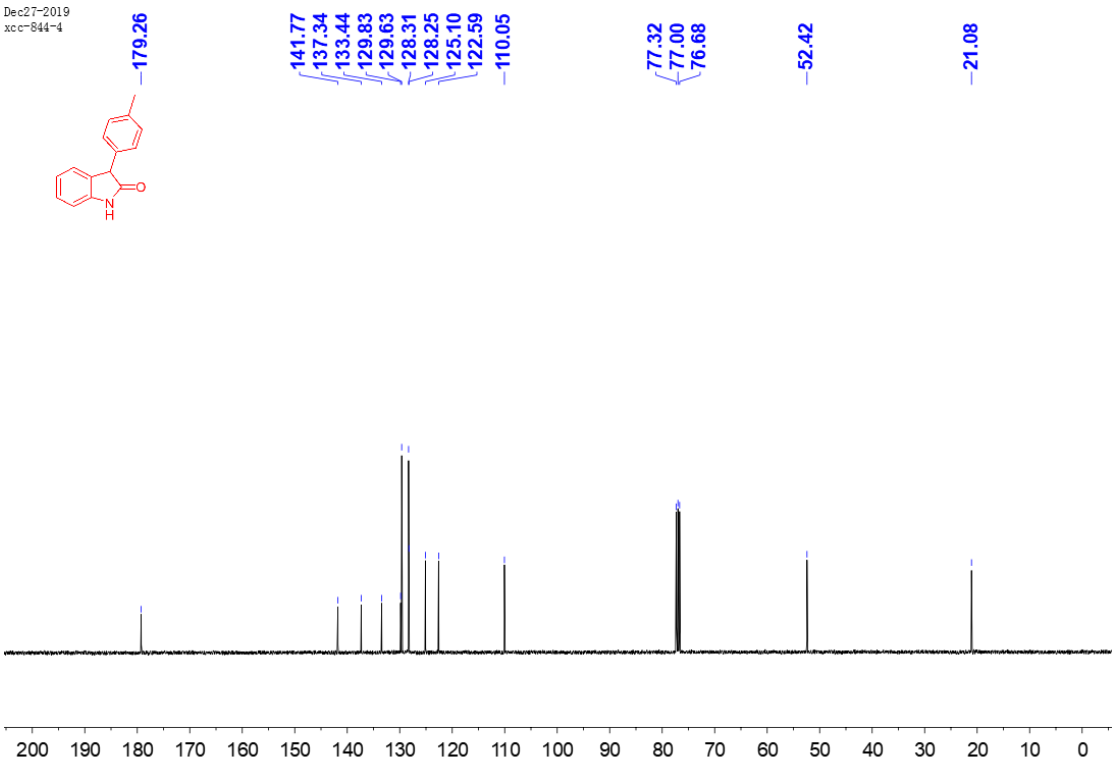
^{1}H and ^{13}C NMR spectra of **7a**.





^{1}H and ^{13}C NMR spectra of **7b**.

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